Electrochemically Selective Double C(sp^2)-X(X=S/Se,N) Bonds Formation of One Carbon

Zhipeng Guan[a,1], Shuxiang Zhu[a,1], Yankai Yang[a], Yanlong Liu[a], Siyuan Wang[a], Faxiang Bu[a], Hengjiang Cong[a], Hesham Alhumade,[d,e] Heng Zhang,*[a] Aiwen Lei*[a,b,c]

a. Institute for Advanced Studies (IAS), College of Chemistry and Molecular Sciences, Engineering Research Center of Organosilicon Compounds & Materials (Ministry of Education), Wuhan University, Wuhan, Hubei 430072, People's Republic of China.

b. National Research Center for Carbohydrate Synthesis Jiangxi Normal University, Nanchang 330022, Jiangxi, P. R. China.

c. King Abdulaziz University, Jeddah, Saudi Arabia.

d. Department of Chemical and Materials Engineering, Faculty of Engineering, King Abdulaziz University, Jeddah, Saudi Arabia.

e. Center of Research Excellence in Renewable Energy and Power Systems, King Abdulaziz University, Jeddah, Saudi Arabia.

1. These authors contributed equally to this work.

*corresponding author: aiwenlei@whu.edu.cn; hengzhang@whu.edu.cn

Supporting Information

Table of Contents

General information……………………………………………………………S3

Experimental section…………………………………………………………...S3

1) **the optimization parameters of electrochemical oxidative difunctionalization of isocyanides**……………………………………………………………...S3
2) **General procedure for preparation electrochemical oxidative difunctionalization of isocyanides**………………………………………..S4
3) **Gram-scale experiments**…………………………………………………...S5
4) **Control experiment**…………………………………………………………S5
5) **General procedure for the electron paramagnetic resonance (EPR) experiment**……………………………………………………………...S6
6) **Crystallography data of 16**…………………………………………………..S7
7) **DFT calculations of *Z*-conformer (16) and *E*-conformer**…………………..S17

Detail descriptions for products………………………………………S22

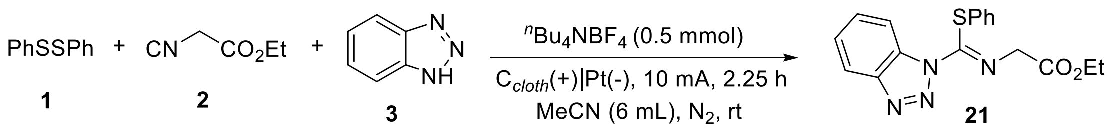
General information

All glassware was oven dried at 110 °C for hours and cooled down under vacuum. Unless otherwise noted, all reagents were purchased from commercial suppliers and used without further purification. The instrument for electrolysis was dual display potentiostat (DJS-292B) (made in China). Cyclic voltammograms were obtained on a CHI 605E potentiostat. The anodic electrode was carbon cloth (1.5 cm×1.5 cm) and cathodic electrode was platinum sheet (1.5 cm×1.5 cm×0.3 mm). These electrodes were commercially available from GaossUnion and Huanqiujinxin, China. Thin layer chromatography (TLC) employed glass 0.25 mm silica gel plates. Flash chromatography columns were packed with 200-300 mesh silica gel in petroleum (bp. 60-90 °C). GC-MS spectra were recorded on a Varian GC-MS 3900-2100T. The known compounds were characterized by ^{1}H NMR, ^{13}C NMR and ^{19}F NMR. ^{1}H, ^{19}F and ^{13}C NMR data were recorded with ADVANCE III 400 MHz with tetramethylsilane as an internal standard. High resolution mass spectra (HRMS) were measured with a Waters Micromass GCT instrument. All chemical shifts (δ) were reported in ppm and coupling constants (J) in Hz. All chemical shifts were reported relative to tetramethylsilane (0 ppm for ^{1}H), Chloroform-*d* (77.16 ppm for ^{13}C), respectively.

Experimental Section

1) the optimization parameters of electrochemical oxidative difunctionalization of isocyanides

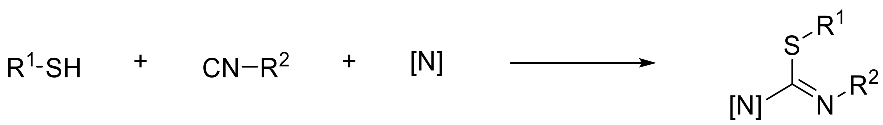
After reaction optimization, utilizing phenyl disulfide (**1**, 0.15 mmol), ethyl 2-isocyanoacetate (**2**, 0.6 mmol), 1*H*-benzo[*d*][1,2,3]triazole (**3**, 0.5 mmol) as coupling partners, isothiourea **21** could been obtained with 90% isolated yield successfully (entry 1). Adding HOAc showed a similar reactivity. (entry 2) Adding NaOAc to the system was found to be detrimental to the reaction process (entry 3). The presence of co-solvent, especially DMF, resulted in a sharp drop in yield (entry 5). With an alternative electrode material such as carbon felt or nickel plate, lower yields were observed in undivided cell (entries 6-7). As to the electric current, 15 mA and 5 mA showed a similar reactivity (entries 8-9). The reaction was sensitive to air, and 64% yield was only obtained (entry 10). Control experiments indicated that was completely abolished without electricity (entry 12).



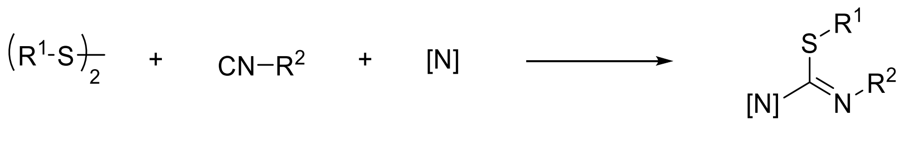
Entry	variation from standard conditions	Yield/%[a]
1	no	90[b]
2	HOAc (0.5 mmol)	85
3	NaOAc (0.5 mmol)	71
4	MeCN/HFIP = 5 mL/1 mL	82
5	MeCN/DMF = 5 mL/1 mL	34
6	C_{felt}(+)|Pt(-)	79
7	C_{cloth}(+)|Ni(-)	68
8	15 mA, 1.5 h	86
9	5 mA, 4.5 h	83
10	Air	64
11	no electric current	0

[a] **1** (0.15 mmol), **2** (0.6 mmol), **3** (0.5 mmol), $^nBu_4NBF_4$ (0.5 mmol), MeCN (6 mL), Cloth anode, Pt cathode, undivided cell, constant current = 10 mA, 2.25 h, room temperature, N_2, ^{1}HNMR yield, dibromomethane as an internal standard. [b] isolated yield.

2) General procedure for preparation electrochemical oxidative difunctionalization of isocyanides

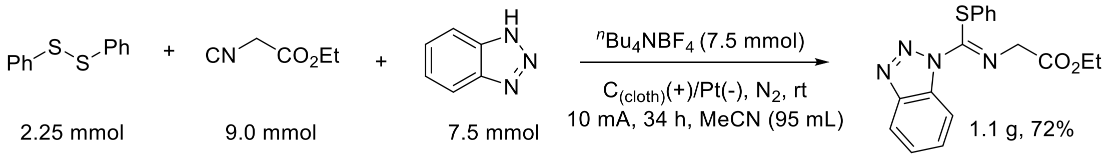


In an oven-dried undivided three-necked bottle (25 mL) equipped with a stir bar, thiol (0.3 mmol), azoles (0.5 mmol) and $^nBu_4NBF_4$ (0.5 mmol) were combined and added. The bottle was equipped with carbon cloth (1.5 cm×1.5 cm) as the anode and platinum plate (1.5 cm × 1.5 cm × 1 mm) as the cathode and was then charged with nitrogen. Under the protection of N_2, isocyanide (0.6 mmol) and MeCN (6.0 mL) were injected respectively into the tubes via syringes. The reaction mixture was stirred and electrolyzed at a constant current of 10 mA for 2 h 15 min at room temperature. When the reaction was finished, the pure product was purified by flash column chromatography (PE/EA) on silica gel.



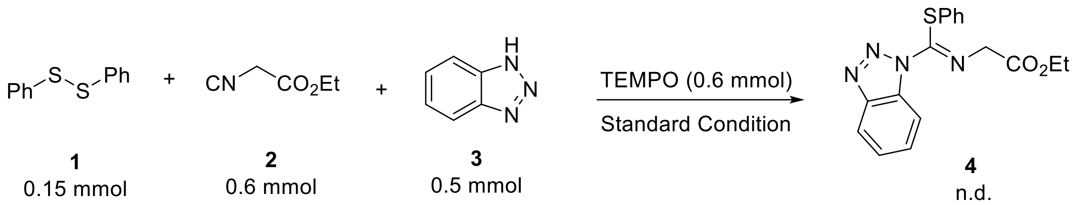
In an oven-dried undivided three-necked bottle (25 mL) equipped with a stir bar, disulfidel (0.15 mmol), azoles (0.5 mmol) and $^{n}Bu_4NBF_4$ (0.5 mmol) were combined and added. The bottle was equipped with carbon cloth (1.5 cm×1.5 cm) as the anode and platinum plate (1.5 cm × 1.5 cm × 1 mm) as the cathode and was then charged with nitrogen. Under the protection of N_2, isocyanide (0.6 mmol), MeCN (6.0 mL) were injected respectively into the tubes via syringes. The reaction mixture was stirred and electrolyzed at a constant current of 10 mA for 2 h 15 min at room temperature. When the reaction was finished, the pure product was purified by flash column chromatography (PE/EA) on silica gel.

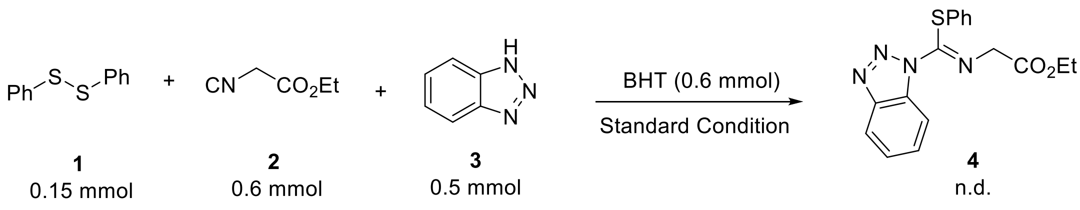
3) Gram-scale experiments

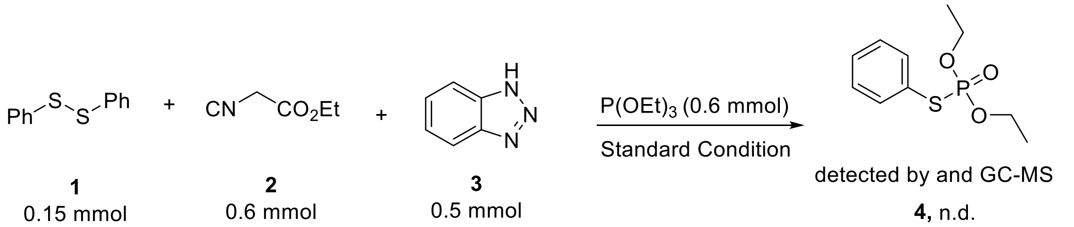


In an oven-dried undivided two-necked bottle (100 mL) equipped with a stir bar, phenyl disulfide (2.25 mmol), 1*H*-Benzotriazole (7.5 mmol) and $^{n}Bu_4NBF_4$ (7.5 mmol) were combined and added. The bottle was equipped with carbon cloth (1.5 cm×1.5 cm) as the anode and platinum plate (1.5 cm × 1.5 cm × 1 mm) as the cathode and was then charged with nitrogen. Under the protection of N_2, isocyanide (10.0 mmol) and MeCN (95 mL) were injected respectively into the tubes via syringes. The reaction mixture was stirred and electrolyzed at a constant current of 10 mA for 34 h at room temperature. When the reaction was finished, the pure product was purified by flash column chromatography (PE/EA) on silica gel.

4) Control experiment



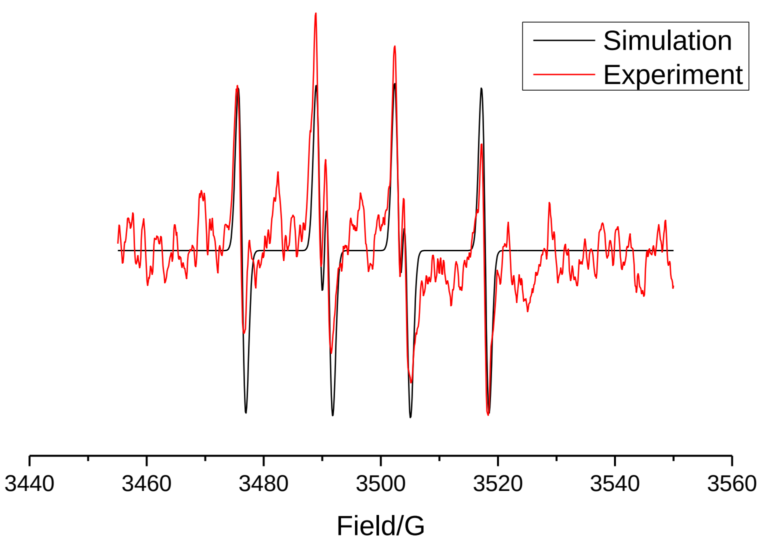




In an oven-dried undivided three-necked bottle (25 mL) equipped with a stir bar, phenyl disulfide (0.15 mmol), 1*H*-Benzotriazole (0.5 mmol) and $^{n}Bu_4NBF_4$ (0.5 mmol) were combined and added. The bottle was equipped with carbon cloth (1.5 cm×1.5 cm) as the anode and platinum plate (1.5 cm × 1.5 cm × 1 mm) as the cathode and was then charged with nitrogen. Under the protection of N_2, isocyanide (0.6 mmol) and MeCN (6 mL) were injected respectively into the tubes via syringes. The reaction mixture was stirred and electrolyzed at a constant current of 10 mA for 2 h 15 min at room temperature. When the reaction was finished, the pure product was purified by flash column chromatography (PE/EA) on silica gel.

5) General procedure for the electron paramagnetic resonance (EPR) experiment

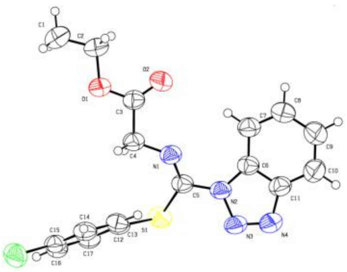
In an oven-dried undivided three-necked bottle (25 mL) equipped with a stir bar, thiol (0.3 mmol), and $^{n}Bu_4NBF_4$ (0.5 mmol) were combined and added. The bottle was equipped with graphite rod (ϕ 6 mm, about 18 mm immersion depth in solution) as the anode and platinum plate (1.5 cm × 1.5 cm × 1 mm) as the cathode and was then charged with nitrogen. Under the protection of N_2, DMPO (30 μL) and MeCN (6.0 mL) were injected respectively into the tubes via syringes. After 5 minutes, the solution sample was taken out into a small tube and analyzed by EPR. EPR spectra was recorded at room temperature on EPR spectrometer operated at 9.823307 GHz. Typical spectrometer parameters are shown as follows, scan range: 100 G; center field set: 3505.202 G; time constant: 163.84 ms; scan time: 30.72 s; modulation amplitude: 1.0 G; modulation frequency: 100 kHz; receiver gain: 1.00×10^{4}; microwave power: 21.49 mW.

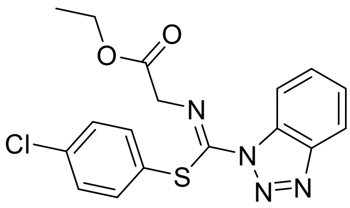


5）Crystallography Data of 16

Single crystal of the compounds were selected, mounted onto a cryoloop, and transferred in a cold nitrogen gasstream. Intensity data were collected with a BRUKER Kappa-APEXII diffractometer with graphite-monochromated Cu-Kα radiation (λ = 0.71073 Å). Data collection were performed with APEX2 suite (BRUKER). Unitcell parameters refinement, integration and data reduction were carried out with SAINT program (BRUKER). SADABS (BRUKER) was used for scaling and multi-scan absorption corrections. In the WinGX suite of programs, the structure were solved with Sir2014 program and refined by fullmatrix least-squares methods using SHELXL-14.

CCDC 2077984 contain the supplementary crystallographic data for this paper





16

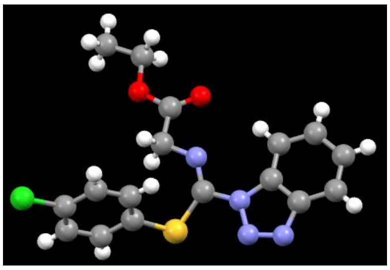


Table 1. Crystal data and structure refinement.

Empirical formula	C17 H15 Cl N4 O2 S	
Formula weight	374.84	
Temperature	297.46(12) K	
Wavelength	1.54184 Å	
Crystal system	Triclinic	
Space group	P-1	
Unit cell dimensions	a = 7.7386(2) Å	α= 102.235(2)°.
	b = 11.0939(2) Å	β= 107.273(2)°.
	c = 11.2012(3) Å	γ = 99.656(2)°.
Volume	869.57(4) Å^3	
Z	2	

Density (calculated)	1.432 Mg/m^3
Absorption coefficient	3.231 mm^{-1}
F(000)	388
Crystal size	0.08 x 0.06 x 0.04 mm^3
Theta range for data collection	4.208 to 65.646°.
Index ranges	-9<=h<=9, -13<=k<=13, -13<=l<=13
Reflections collected	27579
Independent reflections	2949 [R(int) = 0.0361]
Completeness to theta = 65.646°	98.0 %
Absorption correction	Semi-empirical from equivalents
Max. and min. transmission	1.00000 and 0.82449
Refinement method	Full-matrix least-squares on F^2
Data / restraints / parameters	2949 / 0 / 227
Goodness-of-fit on F^2	1.096
Final R indices [I>2sigma(I)]	R1 = 0.0312, wR2 = 0.0877
R indices (all data)	R1 = 0.0384, wR2 = 0.0917
Extinction coefficient	n/a
Largest diff. peak and hole	0.116 and -0.248 e.Å^{-3}

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

	x	y	z	U(eq)
S(1)	749(1)	1803(1)	5061(1)	65(1)
Cl(1)	8348(1)	644(1)	7783(1)	83(1)

O(1)	5558(2)	6368(1)	7796(1)	67(1)
O(2)	3463(2)	6602(1)	6046(1)	72(1)
N(2)	81(2)	2854(1)	3093(1)	57(1)
N(1)	2563(2)	4082(1)	4839(2)	59(1)
N(3)	-954(2)	1656(1)	2313(2)	69(1)
N(4)	-1967(2)	1753(1)	1212(2)	75(1)
C(12)	2958(2)	1558(1)	5841(2)	53(1)
C(13)	4440(2)	1758(2)	5384(2)	56(1)
C(15)	6268(2)	1000(1)	7042(2)	58(1)
C(3)	4218(2)	5943(2)	6641(2)	56(1)
C(5)	1319(2)	3051(2)	4370(2)	56(1)
C(6)	-319(2)	3744(2)	2430(2)	56(1)
C(14)	6099(2)	1494(2)	5997(2)	58(1)
C(4)	3776(2)	4506(1)	6183(2)	60(1)
C(16)	4800(3)	766(2)	7492(2)	64(1)
C(11)	-1630(3)	3036(2)	1236(2)	64(1)
C(17)	3146(2)	1055(2)	6891(2)	60(1)
C(7)	267(3)	5071(2)	2752(2)	66(1)
C(2)	6160(3)	7748(2)	8332(2)	75(1)
C(10)	-2419(3)	3606(2)	292(2)	77(1)
C(8)	-537(3)	5615(2)	1812(2)	78(1)
C(1)	7396(4)	8060(2)	9687(2)	96(1)
C(9)	-1858(3)	4909(2)	601(2)	82(1)

Table 3. Bond lengths [Å] and angles [°].

S(1)-C(12)	1.7688(17)
S(1)-C(5)	1.7777(17)
Cl(1)-C(15)	1.7304(17)
O(1)-C(3)	1.323(2)
O(1)-C(2)	1.459(2)
O(2)-C(3)	1.200(2)
N(2)-N(3)	1.3817(18)
N(2)-C(5)	1.413(2)
N(2)-C(6)	1.378(2)
N(1)-C(5)	1.260(2)
N(1)-C(4)	1.443(2)
N(3)-N(4)	1.287(2)
N(4)-C(11)	1.397(2)
C(12)-C(13)	1.392(2)
C(12)-C(17)	1.385(2)
C(13)-H(13)	0.9300
C(13)-C(14)	1.376(2)
C(15)-C(14)	1.376(3)
C(15)-C(16)	1.381(2)
C(3)-C(4)	1.513(2)
C(6)-C(11)	1.385(3)
C(6)-C(7)	1.399(2)
C(14)-H(14)	0.9300

C(4)-H(4A)	0.9700
C(4)-H(4B)	0.9700
C(16)-H(16)	0.9300
C(16)-C(17)	1.383(2)
C(11)-C(10)	1.385(3)
C(17)-H(17)	0.9300
C(7)-H(7)	0.9300
C(7)-C(8)	1.366(3)
C(2)-H(2A)	0.9700
C(2)-H(2B)	0.9700
C(2)-C(1)	1.463(3)
C(10)-H(10)	0.9300
C(10)-C(9)	1.373(3)
C(8)-H(8)	0.9300
C(8)-C(9)	1.398(3)
C(1)-H(1A)	0.9600
C(1)-H(1B)	0.9600
C(1)-H(1C)	0.9600
C(9)-H(9)	0.9300

C(12)-S(1)-C(5)	102.85(7)
C(3)-O(1)-C(2)	115.61(14)
N(3)-N(2)-C(5)	121.93(13)
C(6)-N(2)-N(3)	109.51(14)
C(6)-N(2)-C(5)	128.56(13)

C(5)-N(1)-C(4)	122.68(15)
N(4)-N(3)-N(2)	108.96(14)
N(3)-N(4)-C(11)	108.52(15)
C(13)-C(12)-S(1)	122.75(13)
C(17)-C(12)-S(1)	117.51(12)
C(17)-C(12)-C(13)	119.56(16)
C(12)-C(13)-H(13)	119.9
C(14)-C(13)-C(12)	120.14(16)
C(14)-C(13)-H(13)	119.9
C(14)-C(15)-Cl(1)	119.07(13)
C(14)-C(15)-C(16)	121.16(17)
C(16)-C(15)-Cl(1)	119.75(14)
O(1)-C(3)-C(4)	110.08(15)
O(2)-C(3)-O(1)	124.95(16)
O(2)-C(3)-C(4)	124.97(17)
N(2)-C(5)-S(1)	112.78(11)
N(1)-C(5)-S(1)	131.37(15)
N(1)-C(5)-N(2)	115.78(15)
N(2)-C(6)-C(11)	104.23(14)
N(2)-C(6)-C(7)	133.90(17)
C(11)-C(6)-C(7)	121.83(17)
C(13)-C(14)-C(15)	119.61(15)
C(13)-C(14)-H(14)	120.2
C(15)-C(14)-H(14)	120.2
N(1)-C(4)-C(3)	108.98(14)

N(1)-C(4)-H(4A)	109.9
N(1)-C(4)-H(4B)	109.9
C(3)-C(4)-H(4A)	109.9
C(3)-C(4)-H(4B)	109.9
H(4A)-C(4)-H(4B)	108.3
C(15)-C(16)-H(16)	120.4
C(15)-C(16)-C(17)	119.14(17)
C(17)-C(16)-H(16)	120.4
C(6)-C(11)-N(4)	108.77(17)
C(6)-C(11)-C(10)	121.67(17)
C(10)-C(11)-N(4)	129.54(18)
C(12)-C(17)-H(17)	119.8
C(16)-C(17)-C(12)	120.35(16)
C(16)-C(17)-H(17)	119.8
C(6)-C(7)-H(7)	122.2
C(8)-C(7)-C(6)	115.60(19)
C(8)-C(7)-H(7)	122.2
O(1)-C(2)-H(2A)	109.9
O(1)-C(2)-H(2B)	109.9
O(1)-C(2)-C(1)	109.04(17)
H(2A)-C(2)-H(2B)	108.3
C(1)-C(2)-H(2A)	109.9
C(1)-C(2)-H(2B)	109.9
C(11)-C(10)-H(10)	121.6
C(9)-C(10)-C(11)	116.89(19)

C(9)-C(10)-H(10)	121.6
C(7)-C(8)-H(8)	118.5
C(7)-C(8)-C(9)	123.02(19)
C(9)-C(8)-H(8)	118.5
C(2)-C(1)-H(1A)	109.5
C(2)-C(1)-H(1B)	109.5
C(2)-C(1)-H(1C)	109.5
H(1A)-C(1)-H(1B)	109.5
H(1A)-C(1)-H(1C)	109.5
H(1B)-C(1)-H(1C)	109.5
C(10)-C(9)-C(8)	121.0(2)
C(10)-C(9)-H(9)	119.5
C(8)-C(9)-H(9)	119.5

Symmetry transformations used to generate equivalent atoms:

Table 4. Anisotropic displacement parameters ($Å^2$x 10^3). 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)	48(1)	59(1)	90(1)	29(1)	24(1)	5(1)
Cl(1)	61(1)	76(1)	106(1)	35(1)	14(1)	16(1)
O(1)	69(1)	47(1)	71(1)	10(1)	14(1)	7(1)
O(2)	78(1)	54(1)	81(1)	25(1)	20(1)	12(1)
N(2)	50(1)	43(1)	72(1)	12(1)	16(1)	6(1)
N(1)	52(1)	48(1)	70(1)	14(1)	17(1)	6(1)
N(3)	62(1)	45(1)	81(1)	9(1)	11(1)	3(1)
N(4)	70(1)	56(1)	81(1)	9(1)	11(1)	4(1)
C(12)	51(1)	38(1)	64(1)	10(1)	21(1)	3(1)
C(13)	59(1)	47(1)	67(1)	19(1)	27(1)	10(1)
C(15)	54(1)	41(1)	71(1)	11(1)	14(1)	6(1)
C(3)	52(1)	50(1)	65(1)	15(1)	22(1)	5(1)
C(5)	47(1)	46(1)	72(1)	14(1)	21(1)	9(1)
C(6)	50(1)	50(1)	68(1)	15(1)	23(1)	10(1)
C(14)	53(1)	47(1)	76(1)	14(1)	28(1)	7(1)
C(4)	57(1)	45(1)	70(1)	15(1)	17(1)	4(1)
C(16)	70(1)	52(1)	68(1)	20(1)	23(1)	9(1)
C(11)	59(1)	53(1)	72(1)	12(1)	20(1)	8(1)
C(17)	60(1)	51(1)	72(1)	18(1)	30(1)	6(1)
C(7)	68(1)	51(1)	74(1)	15(1)	22(1)	8(1)

C(2)	81(1)	47(1)	80(1)	7(1)	20(1)	2(1)
C(10)	74(1)	74(1)	69(1)	17(1)	13(1)	7(1)
C(8)	89(1)	56(1)	86(2)	25(1)	26(1)	12(1)
C(1)	106(2)	68(1)	81(2)	3(1)	10(1)	2(1)
C(9)	89(1)	73(1)	83(2)	33(1)	24(1)	17(1)

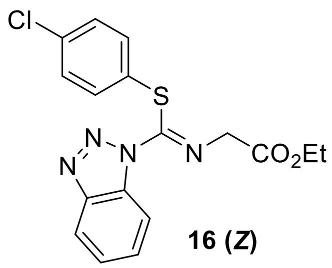
Table 5. Hydrogen coordinates (x 10^4) and isotropic displacement parameters ($Å^2$x 10^3).

	x	y	z	U(eq)
H(13)	4309	2072	4664	68
H(14)	7100	1648	5705	70
H(4A)	4922	4230	6269	72
H(4B)	3168	4140	6712	72
H(16)	4923	419	8191	76
H(17)	2154	910	7192	72
H(7)	1145	5552	3553	79
H(2A)	5082	8097	8290	90
H(2B)	6816	8118	7829	90
H(10)	-3289	3128	-513	92
H(8)	-190	6496	1985	93
H(1A)	8469	7723	9721	143
H(1B)	6739	7693	10180	143
H(1C)	7791	8967	10047	143
H(9)	-2363	5328	-4	98

6) DFT calculations of *Z*-conformer (16) and *E*-conformer

DFT calculations were performed using the Gaussian09 program[1]. M06-2x method[2] with the 6-31G(d) basis set was used for the geometry optimization in the acetonitrile. For the integration grid in the calculations, the parameter int = ultrafine was used. Frequency calculations at the same level of theory have been performed to identify all of the stationary points as minima (zero imaginary frequencies) and to provide free energies at 298.15 K. The solvent effects were considered during the geometry optimization with SMD model[3]. For the single point energy calculations, 6-311+G(d,p) basis set was used for all the elements. Grimme's dispersion correction[4] was used during the calculations.

The free energy of *Z*-conformer is 2.3 kcal/mol smaller than that of *E*-conformer.



16 (*Z*)

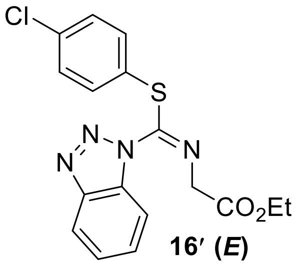
Thermal correction to Gibbs Free Energy= 0.247174

Sum of electronic and thermal Free Energies= -1884.253618

S	-0.01849400	-1.74677400	1.53743600
Cl	5.58418500	-1.68443000	-1.32252300
O	1.55398200	3.24704300	0.26508200
O	-0.62807200	3.16411200	-0.23488400
N	-2.30263900	-1.07607700	0.27971000
N	-0.64471600	0.44679000	-0.03819300
N	-2.70723800	-2.34617200	0.53635800
N	-3.94957600	-2.45619700	0.28390300
C	1.55881600	-1.69477100	0.70080700
C	1.65259800	-2.00756400	-0.65428600
C	4.02303600	-1.69417700	-0.53577000
C	0.40181500	2.61500800	0.05113500

C	-0.96822600	-0.64613400	0.48413200
C	-3.36521400	-0.32616900	-0.17090200
C	2.89036800	-1.99116700	-1.28377600
C	0.59131300	1.12176600	0.23784400
C	3.94735900	-1.40737900	0.81983400
C	-4.42526200	-1.23776600	-0.15992300
C	2.70233500	-1.39969000	1.43838300
C	-3.53316600	1.00948500	-0.56078300
C	1.52285200	4.68551100	0.15067100
C	-5.71580000	-0.85932200	-0.55078500
C	-4.81309900	1.36779500	-0.93911500
C	2.91494000	5.18968600	0.43887600
C	-5.89041500	0.45193200	-0.93960200
H	0.76496400	-2.25384400	-1.22645200
H	2.97126300	-2.22017200	-2.33928100
H	1.38087400	0.79470200	-0.44773600
H	0.96102900	0.95126400	1.25549300
H	4.84207200	-1.17870200	1.38574300
H	2.62903300	-1.15024800	2.49081600
H	-2.70797700	1.70917900	-0.56535100
H	0.79242500	5.07386100	0.86265900
H	1.19347300	4.94679300	-0.85651600
H	-6.52986700	-1.57422900	-0.54111500
H	-4.99861300	2.38979700	-1.24965100
H	3.63105500	4.78595100	-0.27920200

H	3.22943800	4.90677900	1.44515300
H	2.93209200	6.27873700	0.36664700
H	-6.87008900	0.79390200	-1.25177900



16′ (*E*)

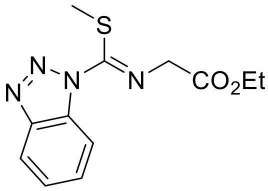
Thermal correction to Gibbs Free Energy= 0.247402

Sum of electronic and thermal Free Energies= -1884.248454

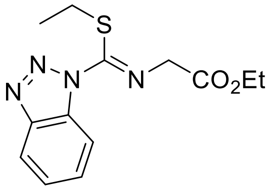
S	0.41702800	-2.40412600	-0.57840000
Cl	6.18789000	-0.22793300	0.63253000
O	-0.66601600	3.65787000	0.05981700
O	1.04806900	2.46777200	-0.75945400
N	-1.91202700	-1.14195900	-0.55766700
N	-0.03961000	0.13445300	0.17680900
N	-2.30714300	-1.62637600	-1.76392600
N	-3.57433500	-1.76325900	-1.76870800
C	2.05061800	-1.78031700	-0.23407200
C	2.74525100	-1.07687700	-1.21616100
C	4.58111400	-0.83118500	0.29705000
C	-0.01114200	2.52609800	-0.19832200
C	-0.53189400	-0.92747800	-0.26651200
C	-2.99757900	-0.98756600	0.26445600
C	4.01976700	-0.59335500	-0.95132800
C	-0.82048500	1.34351900	0.29971400

C	3.90373700	-1.53268000	1.28474000
C	-4.07052100	-1.38563900	-0.53839400
C	2.62487000	-2.00628600	1.01388700
C	-3.15853700	-0.57874000	1.59350300
C	-0.03520600	4.87584300	-0.38853500
C	-5.38240900	-1.37191300	-0.04361600
C	-4.45532400	-0.57338000	2.06544100
C	-0.96362000	6.01482000	-0.04607900
C	-5.55411900	-0.95847500	1.25981400
H	2.29203600	-0.89751100	-2.18405100
H	4.56717100	-0.04160500	-1.70544100
H	-1.06371700	1.52105200	1.35089600
H	-1.76328600	1.33102100	-0.25830000
H	4.36129400	-1.70445300	2.25118000
H	2.07930300	-2.54697800	1.77814200
H	-2.31730500	-0.29857700	2.21555000
H	0.14179200	4.80174100	-1.46287500
H	0.92977800	4.97050600	0.11279100
H	-6.21384300	-1.67924500	-0.66637700
H	-4.64063400	-0.26764300	3.08859300
H	-1.13656700	6.06492900	1.03049100
H	-1.92449800	5.89671200	-0.55022500
H	-0.52044500	6.95896700	-0.36799300
H	-6.54940000	-0.93153500	1.68703200

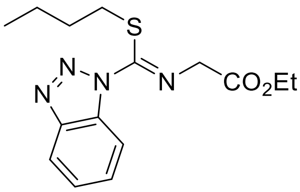
Detail descriptions for products



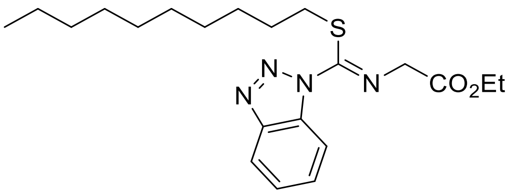
Ethyl (*Z*)-2-(((1*H*-benzo[*d*][1,2,3]triazol-1-yl)(methylthio)methylene)amino)acetate (4). 72.6 mg colorless oil was obtained in 87% isolated yield. ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.33 (dd, *J* = 8.3, 0.9 Hz, 1H), 8.10 (dd, *J* = 8.4, 0.9 Hz, 1H), 7.62 (m, 1H), 7.47 (m, 1H), 4.65 (s, 2H), 4.32 (q, *J* = 7.1 Hz, 2H), 2.54 (d, *J* = 0.7 Hz, 3H), 1.37 (t, *J* = 7.1, 3H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 169.55, 152.56, 146.09, 132.08, 129.65, 125.56, 119.84, 114.34, 61.52, 53.97, 16.94, 14.36. HRMS (ESI) calculated for $C_{12}H_{15}N_4O_2S^+$ $[M+H]^+$ 279.0910 found 279.0912.



Ethyl (*Z*)-2-(((1*H*-benzo[*d*][1,2,3]triazol-1-yl)(ethylthio)methylene)amino)acetate (5). 67.5 mg colorless oil was obtained in 77% isolated yield. ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.36 (d, *J* = 8.3 Hz, 1H), 8.10 (d, *J* = 8.3 Hz, 1H), 7.62 (m, 1H), 7.47 (m, 1H), 4.67 (s, 2H), 4.32 (q, *J* = 7.1 Hz, 2H), 3.10 (q, *J* = 7.4 Hz, 2H), 1.37 (t, *J* = 7.1 Hz, 3H), 1.18 (t, *J* = 7.4 Hz, 3H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 169.56, 151.89, 146.09, 131.93, 129.62, 125.56, 119.82, 114.39, 61.47, 54.15, 28.86, 15.43, 14.34. HRMS (ESI) calculated for $C_{13}H_{17}N_4O_2S^+$ $[M+H]^+$ 293.1067 found 293.1064.

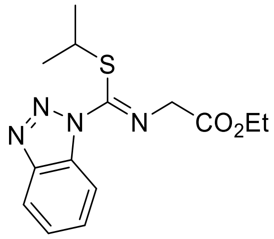


Ethyl (*Z*)-2-(((1*H*-benzo[*d*][1,2,3]triazol-1-yl)(butylthio)methylene)amino)acetate (6). 77.8 mg colorless oil was obtained in 81% isolated yield. ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.35 (d, *J* = 8.4 Hz, 1H), 8.10 (d, *J* = 8.4 Hz, 1H), 7.62 (m, 1H), 7.47 (m, 1H), 4.67 (s, 2H), 4.32 (q, *J* = 7.2 Hz, 2H), 3.06 (t, *J* = 7.4 Hz, 2H), 1.55 – 1.43 (m, 2H), 1.40 – 1.24 (m, 5H), 0.79 (t, *J* = 7.3 Hz, 3H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 169.59, 152.20, 146.10, 131.98, 129.61, 125.54, 119.83, 114.38, 61.48, 54.17, 34.10, 32.17, 21.62, 14.35, 13.48. HRMS (ESI) calculated for $C_{15}H_{21}N_4O_2S^+$ $[M+H]^+$ 321.1380 found 321.1376.

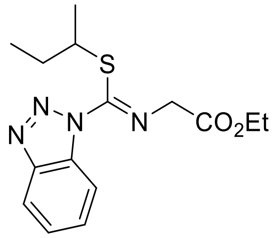


Ethyl (*Z*)-2-(((1*H*-benzo[*d*][1,2,3]triazol-1-yl)(decylthio)methylene)amino)acetate (7). 81.2 mg colorless oil was obtained in 67% isolated yield. ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.35 (d, *J* = 8.4 Hz, 1H), 8.10 (d, *J* = 8.3 Hz, 1H), 7.61 (m, 1H), 7.46 (m, 1H), 4.67 (s, 2H), 4.32 (q, *J* = 7.1 Hz, 2H), 3.08 – 3.03 (m, 2H), 1.48 (m, 2H), 1.37 (t, *J* = 7.1 Hz, 3H), 1.31 – 1.10 (m, 14H), 0.87 (t, *J* = 7.0 Hz, 3H). ^{13}C NMR

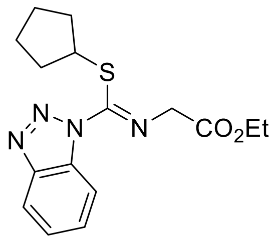
(101 MHz, $CDCl_3$) δ 169.57, 152.21, 146.09, 131.97, 129.59, 125.51, 119.81, 114.36, 61.45, 54.15, 34.37, 31.91, 30.16, 29.47, 29.36, 29.30, 28.91, 28.41, 22.73, 14.34, 14.20. HRMS (ESI) calculated for $C_{21}H_{33}N_4O_2S^+$ $[M+H]^+$ 405.2319 found 405.2312.



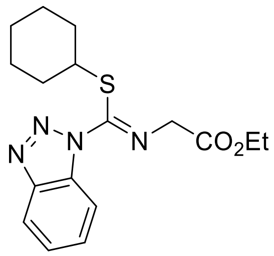
Ethyl (Z)-2-(((1*H*-benzo[*d*][1,2,3]triazol-1-yl)(isopropylthio)methylene)amino)acetate (8). 76.2 mg colorless oil was obtained in 83% isolated yield. ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.39 (d, *J* = 8.3 Hz, 1H), 8.10 (d, *J* = 8.4 Hz, 1H), 7.62 (m, 1H), 7.47 (m, 1H), 4.69 (s, 2H), 4.31 (q, *J* = 7.1 Hz, 2H), 3.90 (p, *J* = 6.7 Hz, 1H), 1.36 (t, *J* = 7.2 Hz, 3H), 1.22 (d, *J* = 6.7 Hz, 6H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 169.58, 151.97, 146.16, 131.91, 129.63, 125.59, 119.84, 114.52, 61.45, 54.28, 40.06, 23.67, 14.35. HRMS (ESI) calculated for $C_{14}H_{19}N_4O_2S^+$ $[M+H]^+$ 307.1223 found 307.1224.



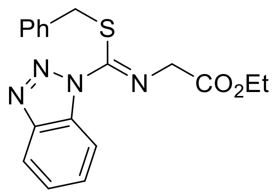
Ethyl (*Z*)-2-(((1*H*-benzo[*d*][1,2,3]triazol-1-yl)(sec-butylthio)methylene)amino)acetate (9). 67.2 mg colorless oil was obtained in 70% isolated yield. ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.39 (d, *J* = 8.4 Hz, 1H), 8.11 (d, *J* = 8.4 Hz, 1H), 7.62 (m, 1H), 7.48 (m, 1H), 4.70 (d, *J* = 2.1 Hz, 2H), 4.33 (q, *J* = 7.1 Hz, 2H), 3.71 (h, *J* = 6.7 Hz, 1H), 1.66 – 1.49 (m, 2H), 1.38 (t, *J* = 7.2 Hz, 3H), 1.21 (d, *J* = 6.7 Hz, 3H), 0.93 (t, *J* = 7.4 Hz, 3H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 169.59, 152.22, 146.20, 131.99, 129.59, 125.54, 119.84, 114.52, 61.44, 54.33, 46.46, 30.35, 21.14, 14.35, 11.21. HRMS (ESI) calculated for $C_{15}H_{21}N_4O_2S^+$ $[M+H]^+$ 321.1380 found 321.1374.



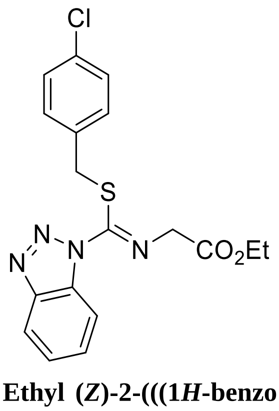
Ethyl (*Z*)-2-(((1*H*-benzo[*d*][1,2,3]triazol-1-yl)(cyclopentylthio)methylene)amino)acetate (10). 86.6 mg colorless oil was obtained in 87% isolated yield. ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.36 (d, *J* = 8.2 Hz, 1H), 8.10 (d, *J* = 8.2 Hz, 1H), 7.61 (ddd, *J* = 8.2, 7.0, 1.0 Hz, 1H), 7.46 (ddd, *J* = 8.1, 7.0, 1.0 Hz, 1H), 4.66 (s, 2H), 4.31 (q, *J* = 7.1 Hz, 2H), 4.01 (dd, *J* = 8.6, 4.2 Hz, 1H), 1.87 – 1.68 (m, 5H), 1.51 (tt, *J* = 5.8, 3.0 Hz, 4H), 1.36 (t, *J* = 7.1 Hz, 3H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 169.58, 152.58, 146.10, 131.96, 129.55, 125.51, 119.79, 114.38, 61.43, 54.14, 47.15, 34.01, 24.64, 14.34. HRMS (ESI) calculated for $C_{16}H_{21}N_4O_2S^+$ $[M+H]^+$ 333.1380 found 333.1374.



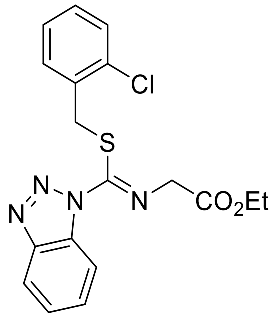
Ethyl (*Z*)-2-(((1*H*-benzo[*d*][1,2,3]triazol-1-yl)(cyclohexylthio)methylene)amino)acetate (11). 93.4 mg colorless oil was obtained in 90% isolated yield. ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.40 (d, *J* = 8.4 Hz, 1H), 8.10 (d, *J* = 8.3 Hz, 1H), 7.61 (m, 1H), 7.47 (m, 1H), 4.69 (s, 2H), 4.31 (q, *J* = 7.1 Hz, 2H), 3.67 (m, 1H), 1.84 – 1.74 (m, 2H), 1.72 – 1.62 (m, 2H), 1.56 – 1.50 (m, 1H), 1.37 (m, 5H), 1.24 – 1.12 (m, 3H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 169.60, 151.60, 146.14, 131.85, 129.54, 125.51, 119.78, 114.64, 61.38, 54.32, 47.69, 33.61, 25.61, 25.27, 14.31. HRMS (ESI) calculated for $C_{17}H_{23}N_4O_2S^+$ [M+H]$^+$ 347.1535 found 347.1536.



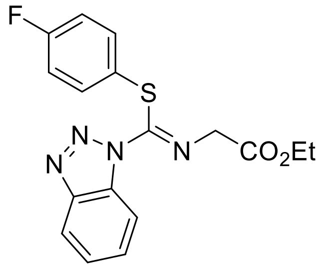
Ethyl (*Z*)-2-(((1*H*-benzo[*d*][1,2,3]triazol-1-yl)(benzylthio)methylene)amino)acetate (12). 75.4 mg white solid was obtained in 71% isolated yield. ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.15 – 8.07 (m, 2H), 7.57 – 7.50 (m, 1H), 7.44 (m, 1H), 7.13 – 7.05 (m, 3H), 6.97 – 6.89 (m, 2H), 4.54 (s, 2H), 4.29 – 4.22 (m, 4H), 1.33 (t, *J* = 7.1 Hz, 3H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 169.33, 150.98, 146.16, 136.00, 131.90, 129.56, 128.71, 128.50, 127.83, 125.54, 119.69, 114.36, 61.43, 54.18, 38.64, 14.31. HRMS (ESI) calculated for $C_{18}H_{19}N_4O_2S^+$ [M+H]$^+$ 355.1223 found 355.1221.



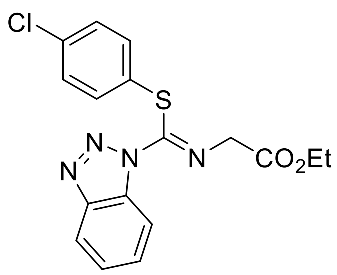
Ethyl (*Z*)-2-(((1*H*-benzo[*d*][1,2,3]triazol-1-yl)((4-chlorobenzyl)thio)methylene)amino)acetate (13). 79.2 mg colorless oil was obtained in 68% isolated yield. ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.16 – 8.01 (m, 2H), 7.56 (m, 1H), 7.46 (m, 1H), 7.08 – 7.00 (m, 2H), 6.89 – 6.82 (m, 2H), 4.55 (s, 2H), 4.27 (dd, *J* = 14.4, 7.2 Hz, 4H), 1.34 (t, *J* = 7.1 Hz, 3H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 169.20, 150.51, 146.13, 134.59, 133.69, 131.83, 129.83, 129.70, 128.88, 125.68, 119.72, 114.30, 61.54, 54.21, 37.90, 14.31. HRMS (ESI) calculated for $C_{18}H_{18}ClN_4O_2S^+$ [M+H]$^+$ 389.0834 found 389.0835.



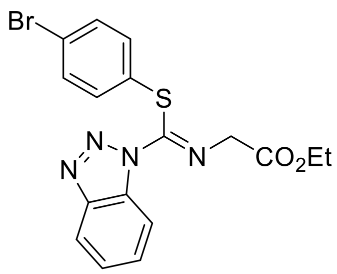
Ethyl (*Z*)-2-(((1*H*-benzo[*d*][1,2,3]triazol-1-yl)((2-chlorobenzyl)thio)methylene)amino)acetate (14). 81.5 mg white solid was obtained in 70% isolated yield. ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.25 (d, *J* = 8.3 Hz, 1H), 8.13 (d, *J* = 8.3 Hz, 1H), 7.59 (m, 1H), 7.51 – 7.43 (m, 1H), 7.34 – 7.24 (m, 1H), 7.14 (td, *J* = 7.7, 1.7 Hz, 1H), 6.94 (td, *J* = 7.5, 1.2 Hz, 1H), 6.73 (dd, *J* = 7.6, 1.6 Hz, 1H), 4.55 (s, 2H), 4.37 (s, 2H), 4.25 (q, *J* = 7.1 Hz, 2H), 1.32 (t, *J* = 7.1 Hz, 3H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 169.32, 150.81, 146.34, 134.14, 133.92, 131.95, 130.61, 130.01, 129.70, 129.49, 127.08, 125.67, 119.83, 114.60, 61.42, 54.21, 36.70, 14.30. HRMS (ESI) calculated for $C_{18}H_{18}ClN_4O_2S^+$ [M+H]$^+$ 389.0834 found 389.0831.



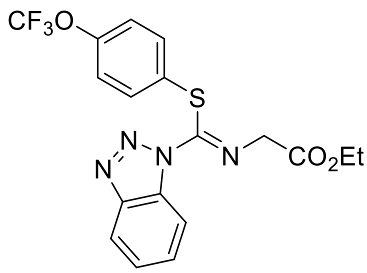
Ethyl (*Z*)-2-(((1*H*-benzo[*d*][1,2,3]triazol-1-yl)((4-fluorophenyl)thio)methylene)amino)acetate (15). 89.1 mg white solid was obtained in 83% isolated yield.^{1}H NMR (400 MHz, $CDCl_3$) δ 8.32 (d, *J* = 8.3 Hz, 1H), 7.99 (d, *J* = 8.3 Hz, 1H), 7.58 (m, 1H), 7.51 – 7.37 (m, 3H), 6.92 (t, *J* = 8.6 Hz, 2H), 4.70 (s, 2H), 4.32 (q, *J* = 7.1 Hz, 2H), 1.37 (t, *J* = 7.1 Hz, 3H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 169.18, 164.32, 161.83, 149.75, 146.01, 135.43, 135.35, 132.12, 129.46, 125.45, 124.21, 124.18, 119.81, 116.88, 116.66, 113.95, 61.61, 54.17, 14.28. ^{19}F NMR (377 MHz, $CDCl_3$) δ -110.67. HRMS (ESI) calculated for$C_{17}H_{16}FN_4O_2S^+$ [M+H]$^+$ 359.0973 found 359.0965.



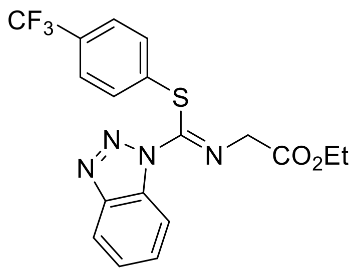
Ethyl (*Z*)-2-(((1*H*-benzo[*d*][1,2,3]triazol-1-yl)((4-chlorophenyl)thio)methylene)amino)acetate (16). 89.8 mg white solid was obtained in 80% isolated yield. 1H NMR (400 MHz, $CDCl_3$) δ 8.35 (d, J = 8.4 Hz, 1H), 8.01 (d, J = 8.3 Hz, 1H), 7.59 (m, 1H), 7.42 (m, 1H), 7.40 – 7.34 (m, 2H), 7.23 – 7.15 (m, 2H), 4.70 (s, 2H), 4.32 (q, J = 7.1 Hz, 2H), 1.37 (t, J = 7.1 Hz, 3H). 13C NMR (101 MHz, CDCl3) δ 169.20, 149.23, 146.16, 135.39, 134.00, 132.15, 129.81, 129.62, 127.85, 125.63, 119.93, 114.16, 61.70, 54.35, 14.35. HRMS (ESI) calculated for $C_{17}H_{16}ClN_4O_2S^+$ [M+H]$^+$ 375.0677 found 375.0669.



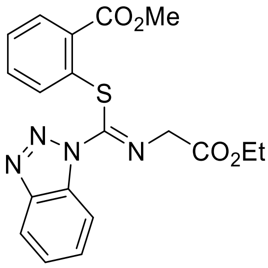
Ethyl (*Z*)-2-(((1*H*-benzo[*d*][1,2,3]triazol-1-yl)((4-bromophenyl)thio)methylene)amino)acetate (17). 106.6 mg white solid was obtained in 85% isolated yield. ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.35 (d, *J* = 8.3 Hz, 1H), 8.01 (d, *J* = 8.3 Hz, 1H), 7.59 (m, 1H), 7.43 (m, 1H), 7.36 – 7.27 (m, 4H), 4.70 (s, 2H), 4.32 (q, *J* = 7.1 Hz, 2H), 1.37 (t, *J* = 7.2 Hz, 3H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 169.19, 149.09, 146.21, 134.12, 132.78, 132.16, 129.64, 128.59, 125.66, 123.54, 119.97, 114.20, 61.71, 54.40, 14.37. HRMS (ESI) calculated for $C_{17}H_{16}BrN_4O_2^+$ $[M+H]^+$ 419.0172 found 419.0167.



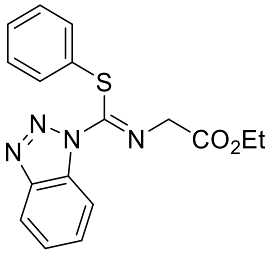
Ethyl (*Z*)-2-(((1*H*-benzo[*d*][1,2,3]triazol-1-yl)((4-(trifluoromethoxy)phenyl)thio)methylene)amino)acetate (18). 92.9 mg white solid was obtained in 73% isolated yield. ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.35 (m, 1H), 8.00 (m, 1H), 7.59 (m, 1H), 7.51 – 7.46 (m, 2H), 7.42 (m, 1H), 7.12 – 7.00 (m, 2H), 4.72 (s, 2H), 4.32 (q, *J* = 7.2 Hz, 2H), 1.37 (t, *J* = 7.1 Hz, 3H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 169.14, 149.60 (d, *J* = 2.0 Hz), 149.17, 146.20, 134.41, 132.17, 129.62, 127.89, 125.64, 121.78, 120.29 (q, *J* = 258.7 Hz), 119.94, 114.18, 61.71, 54.38, 14.33. ^{19}F NMR (377 MHz, $CDCl_3$) δ -58.07. HRMS (ESI) calculated for $C_{18}H_{16}F_3N4O_3S^+$ $[M+H]^+$ 425.0890 found 425.0883.



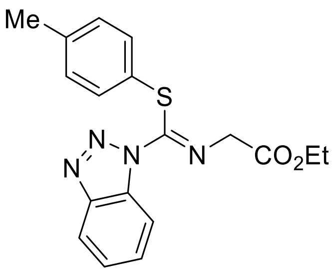
Ethyl (*Z*)-2-(((1*H*-benzo[*d*][1,2,3]triazol-1-yl)((4-(trifluoromethyl)phenyl)thio)methylene)amino)acetate (19). 49.0 mg white solid was obtained in 40% isolated yield. ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.40 (d, *J* = 8.3 Hz, 1H), 8.02 (d, *J* = 8.3 Hz, 1H), 7.62 (m, 1H), 7.54 – 7.41 (m, 4H), 4.73 (s, 2H), 4.32 (q, *J* = 7.2 Hz, 2H), 1.37 (t, *J* = 7.1 Hz, 3H). ^{19}F NMR (377 MHz, $CDCl_3$) δ -62.88. ^{13}C NMR (101 MHz, $CDCl_3$) δ 169.09, 148.35, 146.39, 132.16, 131.77, 130.63 (q, *J* = 33.0 Hz), 129.83, 126.52 (q, *J* = 3.7 Hz), 125.86, 123.65 (q, *J* = 272.2 Hz), 120.10, 114.41, 61.81, 54.61, 14.38. ^{19}F NMR (377 MHz, $CDCl_3$) δ -62.88. HRMS (ESI) calculated for $C_{18}H_{16}F_3N_4O_2S^+$ $[M+H]^+$ 409.0941 found 409.0936.



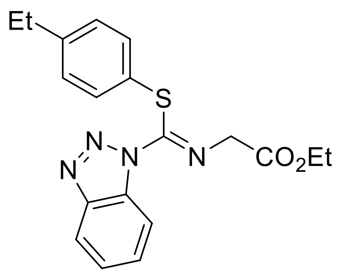
Methyl (*Z*)-2-(((1*H*-benzo[*d*][1,2,3]triazol-1-yl)((2-ethoxy-2-oxoethyl)imino)methyl)thio)benzoate (20). 77.6 mg white solid was obtained in 65% isolated yield. ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.48 (d, *J* = 8.3 Hz, 1H), 8.01 (d, *J* = 8.3 Hz, 1H), 7.96 – 7.90 (m, 1H), 7.61 (m, 1H), 7.44 (m, 1H), 7.27 – 7.16 (m, 3H), 4.75 (s, 2H), 4.31 (q, *J* = 7.1 Hz, 2H), 3.93 (s, 3H), 1.35 (t, *J* = 7.1 Hz, 3H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 169.43, 166.39, 150.09, 146.29, 133.68, 132.81, 132.06, 131.59, 131.09, 129.54, 129.51, 127.41, 125.59, 119.89, 114.57, 61.53, 54.44, 52.64, 14.32. HRMS (ESI) calculated for $C_{19}H_{19}N_4O_4S^+$ $[M+H]^+$ 399.1122 found 399.1119.



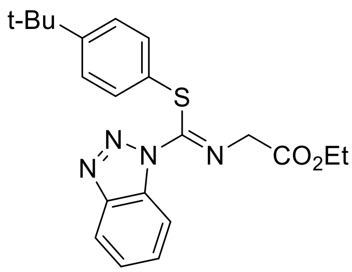
Ethyl (*Z*)-2-(((1*H*-benzo[*d*][1,2,3]triazol-1-yl)(phenylthio)methylene)amino)acetate (21). 91.8 mg white solid was obtained in 90% isolated yield. ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.38 (d, *J* = 8.4 Hz, 1H), 7.99 (d, *J* = 8.3 Hz, 1H), 7.58 (m, 1H), 7.46 – 7.37 (m, 3H), 7.25 – 7.16 (m, 3H), 4.66 (s, 2H), 4.31 (q, *J* = 7.1 Hz, 2H), 1.36 (t, *J* = 7.1 Hz, 3H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 169.36, 149.68, 146.16, 132.56, 132.21, 129.61, 129.46, 129.34, 128.94, 125.47, 119.84, 114.17, 61.59, 54.31, 14.33. HRMS (ESI) calculated for $C_{17}H_{17}N_4O_2S^+$ $[M+H]^+$ 341.1067 found 341.1063.9



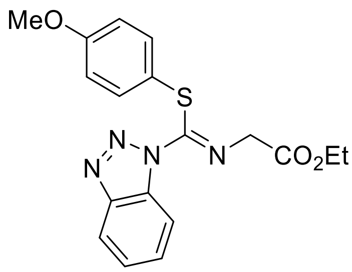
Ethyl (*Z*)-2-(((1*H*-benzo[*d*][1,2,3]triazol-1-yl)(p-tolylthio)methylene)amino)acetate (22). 79.6 mg white solid was obtained in 75% isolated yield. ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.36 (d, *J* = 8.3 Hz, 1H), 7.99 (d, *J* = 8.3 Hz, 1H), 7.57 (m, 1H), 7.40 (m, 1H), 7.32 (d, *J* = 8.2 Hz, 2H), 7.01 (d, *J* = 8.0 Hz, 2H), 4.65 (s, 2H), 4.31 (q, *J* = 7.1 Hz, 2H), 2.23 (s, 3H), 1.36 (t, *J* = 7.1 Hz, 3H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 169.42, 150.07, 146.09, 139.35, 132.90, 132.19, 130.34, 129.35, 125.47, 125.36, 119.76, 114.13, 61.53, 54.20, 21.21, 14.32. HRMS (ESI) calculated for $C_{18}H_{19}N_4O_2S^+$ $[M+H]^+$ 355.1223 found 355.1218.



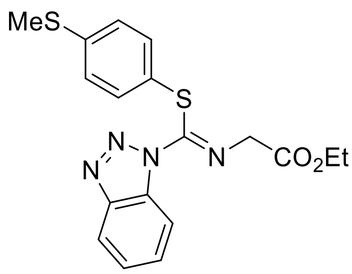
Ethyl (*Z*)-2-(((1*H*-benzo[d][1,2,3]triazol-1-yl)((4-ethylphenyl)thio)methylene)amino)acetate (23). 88.3 mg colorless oil was obtained in 80% isolated yield. ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.44 – 8.35 (m, 1H), 8.05 – 7.98 (m, 1H), 7.63 – 7.55 (m, 1H), 7.43 (m, 1H), 7.39 – 7.35 (m, 1H), 7.34 – 7.30 (m, 0.5H), 7.25 – 7.17 (m, 1H), 7.07 (d, *J* = 8.2 Hz, 1H), 6.99 (m, 0.5H), 4.65 (d, *J* = 18.3 Hz, 2H), 4.34 (q, *J* = 7.1 Hz, 2H), 2.95 (q, *J* = 7.6 Hz, 1H), 2.56 (q, *J* = 7.6 Hz, 1H), 1.39 (t, *J* = 7.1 Hz, 3H), 1.29 (t, *J* = 7.5 Hz, 1.5H), 1.16 (t, *J* = 7.6 Hz, 1.5H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 169.47, 150.11, 150.07, 146.18, 146.16, 146.13, 145.60, 133.75, 133.03, 132.25, 132.23, 129.63, 129.45, 129.41, 129.37, 129.18, 128.32, 126.93, 125.72, 125.40, 125.38, 119.81, 114.21, 114.15, 61.56, 54.26, 54.08, 28.50, 27.56, 15.20, 14.96, 14.36. HRMS (ESI) calculated for $C_{19}H_{21}N_4O_2S^+$ $[M+H]^+$ 369.1380 found 369.1375.



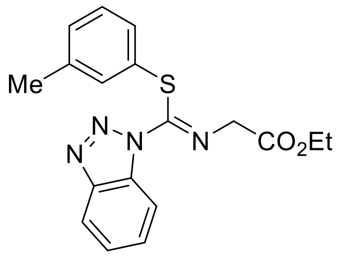
Ethyl (*Z*)-2-(((1*H*-benzo[*d*][1,2,3]triazol-1-yl)((4-(tert-butyl)phenyl)thio)methylene)amino)acetate (24). 102.2 mg white solid was obtained in 86% isolated yield. ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.37 (d, *J* = 8.4 Hz, 1H), 7.99 (d, *J* = 8.3 Hz, 1H), 7.57 (m, 1H), 7.43 – 7.33 (m, 3H), 7.26 – 7.19 (m, 2H), 4.65 (s, 2H), 4.31 (q, *J* = 7.1 Hz, 2H), 1.36 (t, *J* = 7.1 Hz, 3H), 1.21 (s, 9H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 169.44, 152.39, 149.94, 146.16, 132.60, 132.19, 129.32, 126.64, 125.52, 125.36, 119.75, 114.25, 61.52, 54.23, 34.69, 31.12, 14.33. HRMS (ESI) calculated for $C_{21}H_{25}N_4O_2S^+$ $[M+H]^+$ 397.1693 found 397.1683.



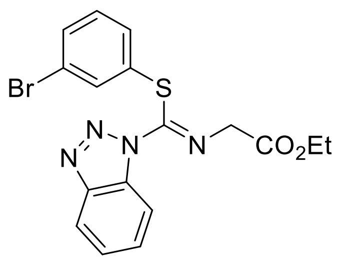
Ethyl (*Z*)-2-(((1*H*-benzo[*d*][1,2,3]triazol-1-yl)((4-methoxyphenyl)thio)methylene)amino)acetate (25). 82.1 mg colorless oil was obtained in 74% isolated yield. ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.32 (d, *J* = 8.3 Hz, 1H), 7.99 (d, *J* = 8.3 Hz, 1H), 7.56 (m, 1H), 7.46 – 7.37 (m, 3H), 6.78 – 6.67 (m, 2H), 4.66 (s, 2H), 4.32 (q, *J* = 7.2 Hz, 2H), 3.72 (s, 3H), 1.37 (t, *J* = 7.1 Hz, 3H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 169.50, 160.50, 150.64, 146.03, 135.50, 132.23, 129.35, 125.34, 119.78, 119.00, 115.07, 114.00, 61.59, 55.40, 54.08, 14.37. HRMS (ESI) calculated for $C_{18}H_{19}N_4O_3S^+$ $[M+H]^+$ 371.1172 found 371.1163.



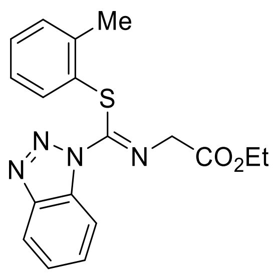
Ethyl (*Z*)-2-(((1*H*-benzo[*d*][1,2,3]triazol-1-yl)((4-(methylthio)phenyl)thio)methylene)amino)acetate (26). 46.3 mg white solid was obtained in 40% isolated yield. ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.34 (d, *J* = 8.4 Hz, 0H), 8.00 (d, *J* = 8.3 Hz, 1H), 7.58 (m 1H), 7.41 (m, 1H), 7.38 – 7.32 (m, 2H), 7.09 – 7.02 (m, 2H), 4.67 (s, 2H), 4.32 (q, *J* = 7.2 Hz, 2H), 2.40 (s, 3H), 1.37 (t, *J* = 7.1 Hz, 3H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 169.42, 149.91, 146.19, 140.95, 133.48, 132.24, 129.50, 126.67, 125.51, 124.63, 119.92, 114.18, 61.66, 54.31, 15.20, 14.39. HRMS (ESI) calculated for $C_{18}H_{19}N_4O_2S_2^+$ $[M+H]^+$ 387.0944 found 387.0947.



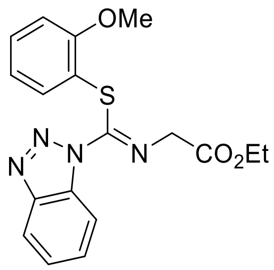
Ethyl (*Z*)-2-(((1*H*-benzo[*d*][1,2,3]triazol-1-yl)(m-tolylthio)methylene)amino)acetate (27). 79.6 mg colorless oil was obtained in 75% isolated yield. ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.40 (d, *J* = 8.4 Hz, 1H), 8.01 (d, *J* = 8.4 Hz, 1H), 7.59 (m, 1H), 7.41 (m, 1H), 7.24 (s, 1H), 7.21 – 7.17 (m, 1H), 7.09 (t, *J* = 7.6 Hz, 1H), 7.05 – 7.00 (m, 1H), 4.63 (s, 2H), 4.31 (q, *J* = 7.1 Hz, 2H), 2.22 (s, 3H), 1.36 (t, *J* = 7.2 Hz, 3H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 169.43, 149.75, 146.20, 139.62, 132.89, 132.26, 129.77, 129.43, 129.41, 129.00, 125.45, 119.84, 114.19, 61.56, 54.31, 21.26, 14.34. HRMS (ESI) calculated for $C_{18}H_{19}N_4O_2S^+$ $[M+H]^+$ 355.1223 found 355.1216.



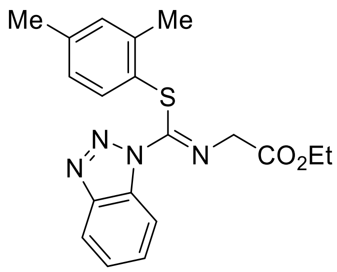
Ethyl (*Z*)-2-(((1*H*-benzo[*d*][1,2,3]triazol-1-yl)((3-bromophenyl)thio)methylene)amino)acetate (28). 66.5 mg colorless oil was obtained in 53% isolated yield. ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.38 (m, 1H), 8.02 (m, 1H), 7.65 – 7.55 (m, 2H), 7.44 (m, 1H), 7.39 – 7.32 (m, 2H), 7.09 (t, *J* = 8.0 Hz, 1H), 4.69 (s, 2H), 4.32 (q, *J* = 7.2 Hz, 2H), 1.37 (t, *J* = 7.2 Hz, 3H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 169.17, 148.72, 146.31, 134.68, 132.21, 132.05, 131.62, 130.90, 130.87, 129.72, 125.73, 123.16, 120.00, 114.29, 61.76, 54.49, 14.38. HRMS (ESI) calculated for $C_{17}H_{16}BrN_4O_2S^+$ $[M+H]^+$ 419.0172 found 419.0170.



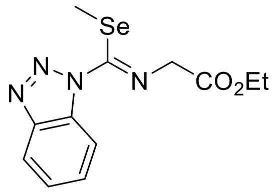
Ethyl (*Z*)-2-(((1*H*-benzo[*d*][1,2,3]triazol-1-yl)(o-tolylthio)methylene)amino)acetate (29). 82.8 mg white solid was obtained in 78% isolated yield. ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.38 (d, *J* = 8.3 Hz, 1H), 7.98 (d, *J* = 8.3 Hz, 1H), 7.58 (m, 1H), 7.44 – 7.34 (m, 2H), 7.17 – 7.11 (m, 2H), 7.05 – 6.95 (m, 1H), 4.59 (s, 2H), 4.31 (q, *J* = 7.1 Hz, 2H), 2.48 (s, 3H), 1.36 (t, *J* = 7.1 Hz, 3H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 169.45, 149.77, 146.07, 140.67, 133.93, 132.11, 131.05, 129.56, 129.41, 128.65, 127.02, 125.40, 119.81, 114.09, 61.55, 54.00, 21.07, 14.34. HRMS (ESI) calculated for $C_{18}H_{19}N_4O_2S^+$ $[M+H]^+$ 355.1223 found 355.1216.



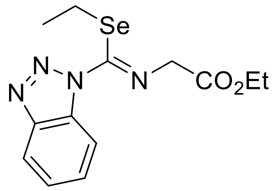
Ethyl (*Z*)-2-(((1*H*-benzo[*d*][1,2,3]triazol-1-yl)((2-methoxyphenyl)thio)methylene)amino)acetate (30). 85.5 mg colorless oil was obtained in 77% isolated yield. ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.37 (d, *J* = 8.3 Hz, 1H), 7.96 (d, *J* = 8.2 Hz, 1H), 7.60 – 7.47 (m, 2H), 7.38 (t, *J* = 7.7 Hz, 1H), 7.24 – 7.13 (m, 1H), 6.86 (t, *J* = 7.6 Hz, 1H), 6.62 (d, *J* = 8.3 Hz, 1H), 4.73 (s, 2H), 4.32 (q, *J* = 7.1 Hz, 2H), 3.57 (s, 3H), 1.37 (t, *J* = 7.1 Hz, 3H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 169.69, 157.89, 150.13, 145.79, 134.84, 132.15, 131.10, 129.15, 125.17, 121.48, 119.72, 117.13, 113.92, 110.96, 61.46, 55.79, 54.29, 14.38. HRMS (ESI) calculated for $C_{18}H_{19}N_4O_3S^+$ $[M+H]^+$ 371.1172 found 371.1164.



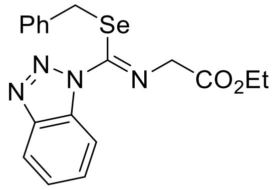
Ethyl (*Z*)-2-(((1*H*-benzo[*d*][1,2,3]triazol-1-yl)((2,4-dimethylphenyl)thio)methylene)amino)acetate (31). 88.3 mg white solid was obtained in 80% isolated yield. ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.37 (d, *J* = 8.4 Hz, 1H), 7.98 (d, *J* = 8.3 Hz, 1H), 7.57 (m, 1H), 7.39 (m, 1H), 7.31 – 7.25 (m, 1H), 6.97 – 6.94 (m, 1H), 6.82 (m, 1H), 4.58 (s, 2H), 4.30 (q, *J* = 7.2 Hz, 2H), 2.43 (s, 3H), 2.21 (s, 3H), 1.36 (t, *J* = 7.2 Hz, 3H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 169.53, 150.12, 146.03, 140.72, 139.94, 134.34, 132.12, 131.86, 129.33, 127.85, 125.31, 124.88, 119.76, 114.07, 61.51, 53.89, 21.15, 20.99, 14.33. HRMS (ESI) calculated for$C_{19}H_{21}N_4O_2S^+$ $[M+H]^+$ 369.1380 found 369.1370.



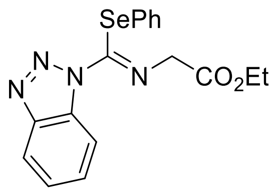
Ethyl (*Z*)-2-(((1*H*-benzo[*d*][1,2,3]triazol-1-yl)(methylselanyl)methylene)amino)acetate (32). 84.1 mg colorless oil was obtained in 86% isolated yield. ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.39 (d, *J* = 8.3 Hz, 1H), 8.09 (d, *J* = 8.3 Hz, 1H), 7.61 (m, 1H), 7.47 (m, 1H), 4.64 (s, 2H), 4.31 (q, *J* = 7.1 Hz, 2H), 2.44 (s, 3H), 1.37 (t, *J* = 7.2 Hz, 3H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 169.33, 148.37, 146.36, 131.66, 129.58, 125.61, 119.80, 114.62, 61.54, 56.09, 14.32, 9.81. HRMS (ESI) calculated for $C_{12}H_{15}N_4O_2Se^+$ [M+H]$^+$ 327.0355 found 327.0351.



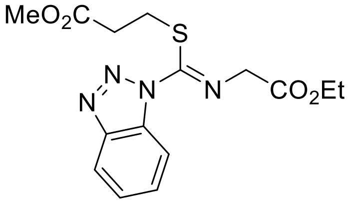
Ethyl (*Z*)-2-(((1*H*-benzo[*d*][1,2,3]triazol-1-yl)(ethylselanyl)methylene)amino)acetate (33). 82.6 mg colorless oil was obtained in 81% isolated yield. ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.42 (d, *J* = 8.4 Hz, 1H), 8.09 (d, *J* = 8.3 Hz, 1H), 7.62 (m, 1H), 7.47 (m, 1H), 4.65 (s, 2H), 4.32 (q, *J* = 7.1 Hz, 2H), 3.15 (q, *J* = 7.5 Hz, 2H), 1.36 (m, 6H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 169.36, 148.04, 146.41, 131.61, 129.56, 125.62, 119.82, 114.73, 61.49, 56.32, 24.39, 16.10, 14.33. HRMS (ESI) calculated for $C_{13}H_{17}N_4O_2Se^+$ [M+H]$^+$ 341.0511 found 341.0507.



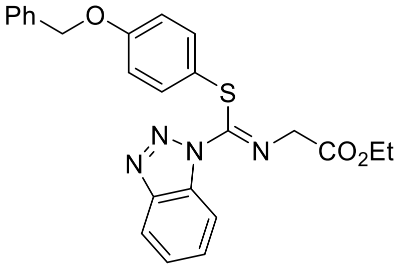
Ethyl (*Z*)-2-(((1*H*-benzo[*d*][1,2,3]triazol-1-yl)(benzylthio)methylene)amino)acetate (34). 88.0 mg white solid was obtained in 73% isolated yield. ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.26 (d, *J* = 8.3 Hz, 1H), 8.10 (d, *J* = 8.3 Hz, 1H), 7.57 (m, 1H), 7.46 (m, 1H), 7.11 (m, 3H), 7.04 – 6.97 (m, 2H), 4.51 (s, 2H), 4.35 (s, 2H), 4.26 (q, *J* = 7.1 Hz, 2H), 1.33 (t, *J* = 7.1 Hz, 3H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 169.23, 147.71, 146.53, 136.98, 131.65, 129.58, 128.77, 128.71, 127.61, 125.68, 119.79, 114.75, 61.51, 56.32, 33.76, 14.33. HRMS (ESI) calculated for $C_{18}H_{19}N_4O_2Se^+$ [M+H]$^+$ 403.0668 found 403.0662.



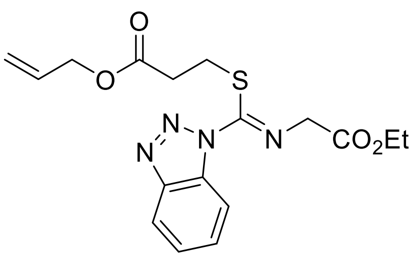
Ethyl (*Z*)-2-(((1*H*-benzo[*d*][1,2,3]triazol-1-yl)(phenylselanyl)methylene)amino)acetate (35). 94.3 mg white solid was obtained in 81% isolated yield. ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.45 (d, *J* = 8.4 Hz, 1H), 8.02 (d, *J* = 8.3 Hz, 1H), 7.65 – 7.54 (m, 3H), 7.43 (m, 1H), 7.32 – 7.17 (m, 3H), 4.48 (s, 2H), 4.27 (q, *J* = 7.2 Hz, 2H), 1.33 (t, *J* = 7.1 Hz, 3H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 169.34, 146.62, 145.84, 134.71, 131.72, 129.82, 129.50, 129.05, 126.84, 125.64, 119.89, 114.64, 61.54, 55.95, 14.32. HRMS (ESI) calculated for $C_{17}H_{17}N_4O_2Se^+$ [M+H]$^+$ 389.0511 found 389.0508.



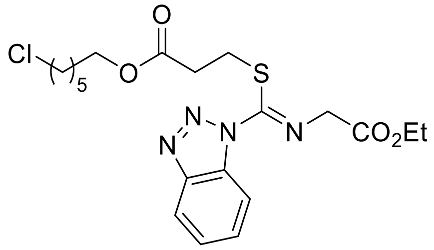
Methyl (*Z*)-3-(((1*H*-benzo[*d*][1,2,3]triazol-1-yl)((2-ethoxy-2-oxoethyl)imino)methyl)thio)propanoate (36). 84.0 mg colorless oil was obtained in 80% isolated yield. ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.38 (d, *J* = 8.3 Hz, 1H), 8.10 (d, *J* = 8.3 Hz, 1H), 7.63 (m, 1H), 7.48 (m, 1H), 4.65 (s, 2H), 4.31 (q, *J* = 7.2 Hz, 2H), 3.64 (s, 3H), 3.32 (t, *J* = 6.8 Hz, 2H), 2.63 (t, *J* = 6.8 Hz, 2H), 1.36 (t, *J* = 7.2 Hz, 3H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 171.39, 169.43, 151.05, 146.23, 131.98, 129.78, 125.72, 119.88, 114.65, 61.53, 54.19, 52.12, 34.96, 29.37, 14.35. HRMS (ESI) calculated for $C_{15}H_{19}N_4O_4S^+$ $[M+H]^+$ 351.1122 found 351.1124.



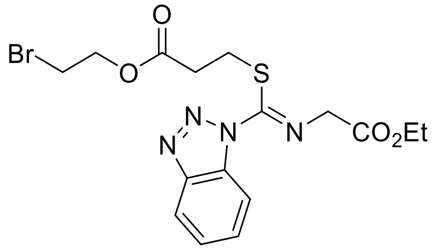
Ethyl (*Z*)-2-(((1*H*-benzo[*d*][1,2,3]triazol-1-yl)((4-(benzyloxy)phenyl)thio)methylene)amino)acetate (37). 81.6 mg white solid was obtained in 61% isolated yield. ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.32 (d, *J* = 8.3 Hz, 1H), 7.99 (d, *J* = 8.2 Hz, 1H), 7.60 – 7.52 (m, 1H), 7.43 – 7.29 (m, 8H), 6.80 (d, *J* = 8.8 Hz, 2H), 4.95 (s, 2H), 4.66 (s, 2H), 4.31 (q, *J* = 7.1 Hz, 2H), 1.37 (t, *J* = 7.1 Hz, 3H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 169.46, 159.70, 150.58, 146.06, 136.25, 135.48, 132.26, 129.34, 128.72, 128.27, 127.60, 125.34, 119.79, 119.42, 115.95, 114.05, 70.14, 61.58, 54.12, 14.38. HRMS (ESI) calculated for $C_{24}H_{23}N_4O_3S^+$ $[M+H]^+$ 447.1485 found 447.1476.



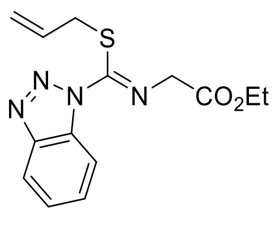
Allyl (*Z*)-3-(((1*H*-benzo[*d*][1,2,3]triazol-1-yl)((2-ethoxy-2-oxoethyl)imino)methyl)thio)propanoate (38). 71.1 mg colorless oil was obtained in 63% isolated yield. ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.37 (d, *J* = 8.4 Hz, 1H), 8.10 (d, *J* = 8.3 Hz, 1H), 7.62 (m, 2H), 7.48 (m, 2H), 5.86 (m, 1H), 5.33 – 5.09 (m, 2H), 4.65 (s, 2H), 4.55 (d, *J* = 5.8 Hz, 2H), 4.31 (q, *J* = 7.1 Hz, 2H), 3.33 (t, *J* = 6.8 Hz, 2H), 2.66 (t, *J* = 6.8 Hz, 2H), 1.36 (t, *J* = 7.2 Hz, 3H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 170.65, 169.43, 151.05, 146.27, 132.02, 131.76, 129.79, 125.73, 119.91, 118.89, 114.69, 77.48, 61.53, 54.23, 35.12, 29.40, 14.37. HRMS (ESI) calculated for $C_{17}H_{21}N_4O_4S^+$ $[M+H]^+$ 377.1278 found 377.1276.



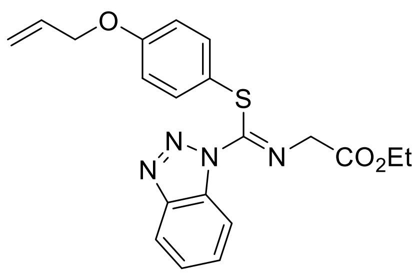
6-Chlorohexyl (*Z*)-3-(((1*H*-benzo[*d*][1,2,3]triazol-1-yl)((2-ethoxy-2-oxoethyl)imino)methyl)thio)propanoate (39). 102.2 mg colorless oil was obtained in 75% isolated yield. ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.38 (d, J = 8.2 Hz, 1H), 8.10 (d, J = 8.4 Hz, 1H), 7.63 (m, 1H), 7.48 (m, 1H), 4.65 (s, 2H), 4.31 (q, J = 7.1 Hz, 2H), 4.05 (t, J = 6.7 Hz, 2H), 3.53 (t, J = 6.6 Hz, 2H), 3.32 (t, J = 6.8 Hz, 2H), 2.63 (t, J = 6.8 Hz, 2H), 1.76 (m, 2H), 1.59 (m, 2H), 1.51 – 1.40 (m, 2H), 1.35 (m, 5H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 170.96, 169.38, 151.06, 146.21, 131.97, 129.74, 125.69, 119.85, 114.65, 64.98, 61.49, 54.17, 45.00, 35.14, 32.44, 29.40, 28.39, 26.50, 25.25, 14.33. HRMS (ESI) calculated for $C_{20}H_{28}ClN_4O_4S^+$ [M+H]$^+$ 455.1514 found 455.1508.



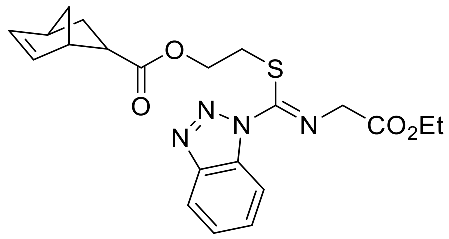
2-Bromoethyl (*Z*)-3-(((1*H*-benzo[*d*][1,2,3]triazol-1-yl)((2-ethoxy-2-oxoethyl)imino)methyl)thio)propanoate (40). 96.8 mg colorless oil was obtained in 73% isolated yield. ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.37 (d, J = 8.4 Hz, 1H), 8.10 (d, J = 8.3 Hz, 1H), 7.63 (m, 1H), 7.48 (m, 1H), 4.66 (s, 2H), 4.36 (t, J = 6.1 Hz, 2H), 4.31 (q, J = 7.1 Hz, 2H), 3.46 (t, J = 6.1 Hz, 2H), 3.34 (t, J = 6.8 Hz, 2H), 2.68 (t, J = 6.8 Hz, 2H), 1.36 (t, J = 7.1 Hz, 3H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 170.46, 169.35, 150.85, 146.20, 131.95, 129.77, 125.71, 119.85, 114.63, 64.25, 61.51, 54.18, 34.95, 29.21, 28.47, 14.33. HRMS (ESI) calculated for $C_{16}H_{20}BrN_4O_4S^+$ [M+H]$^+$ 443.0383 found 443.0376.



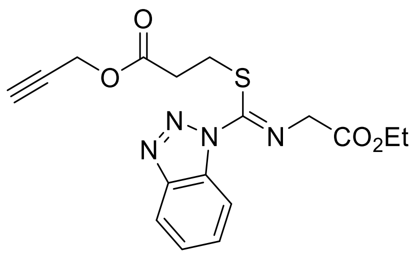
Ethyl (*Z*)-2-(((allylthio)(1*H*-benzo[*d*][1,2,3]triazol-1-yl)methylene)amino)acetate (41). 65.6 mg colorless oil was obtained in 72% isolated yield. ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.32 (d, J = 8.4 Hz, 1H), 8.09 (d, J = 8.2 Hz, 1H), 7.60 (m, 2H), 7.46 (m, 2H), 5.70 (m, 2H), 4.80 (dd, J = 9.9, 1.2 Hz, 2H), 4.67 (s, 4H), 4.60 (dd, J = 16.9, 1.4 Hz, 2H), 4.31 (q, J = 7.1 Hz, 4H), 3.73 (d, J = 7.3 Hz, 2H), 1.36 (t, J = 7.1 Hz, 3H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 169.48, 151.14, 146.10, 132.40, 131.93, 129.62, 125.55, 119.75, 118.86, 114.47, 61.49, 54.19, 37.27, 14.34. HRMS (ESI) calculated for $C_{14}H_{17}N4O_2S^+$ [M+H]$^+$ 305.1067 found 305.1064.



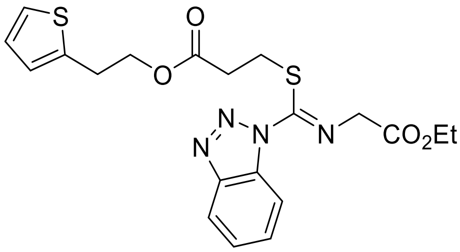
Ethyl (*Z*)-2-((((4-(allyloxy)phenyl)thio)(1*H*-benzo[*d*][1,2,3]triazol-1-yl)methylene)amino)acetate (42). 67.7 mg colorless oil was obtained in 57% isolated yield. ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.31 (d, *J* = 8.4 Hz, 1H), 7.98 (d, *J* = 8.3 Hz, 1H), 7.56 (m, 1H), 7.43 – 7.35 (m, 3H), 6.74 (d, *J* = 8.8 Hz, 2H), 5.97 (m, 1H), 5.39 – 5.21 (m, 2H), 4.66 (s, 2H), 4.43 (dt, *J* = 5.4, 1.5 Hz, 2H), 4.32 (q, *J* = 7.1 Hz, 2H), 1.37 (t, *J* = 7.1 Hz, 3H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 169.48, 159.55, 150.63, 146.07, 135.49, 132.61, 132.27, 129.34, 125.34, 119.80, 119.25, 118.20, 115.82, 114.03, 68.90, 61.59, 54.12, 14.38. HRMS (ESI) calculated for $C_{20}H_{21}N_4O_3S^+$ $[M+H]^+$ 397.1329 found 397.1323.



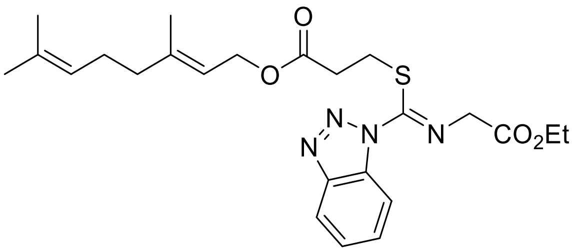
(*Z*)-2-(((1*H*-benzo[*d*][1,2,3]triazol-1-yl)((2-ethoxy-2-oxoethyl)imino)methyl)thio)ethyl bicyclo[2.2.1]hept-5-ene-2-carboxylate (43). 80.9 mg colorless oil was obtained in 63% isolated yield. ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.42 (d, *J* = 8.3 Hz, 1H), 8.11 (d, *J* = 8.4 Hz, 1H), 7.62 (m, 1H), 7.48 (m, 2H), 6.14 (dd, *J* = 5.7, 3.1 Hz, 1H), 5.82 (dd, *J* = 5.7, 2.8 Hz, 1H), 4.68 (s, 2H), 4.31 (q, *J* = 7.1 Hz, 2H), 4.18 – 4.08 (m, 2H), 3.49 – 3.34 (m, 2H), 2.96 – 2.82 (m, 2H), 2.72 (m, 1H), 1.84 – 1.69 (m, 1H), 1.43 – 1.11 (m, 6H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 174.31, 169.40, 150.72, 146.28, 138.03, 132.11, 131.95, 129.79, 125.75, 119.93, 114.78, 63.22, 61.54, 54.25, 49.71, 45.74, 42.99, 42.55, 33.36, 29.20, 14.37. HRMS (ESI) calculated for $C_{21}H_{24}N_4NaO_4S^+$ $[M+Na]^+$ 451.1410 found 451.1409.



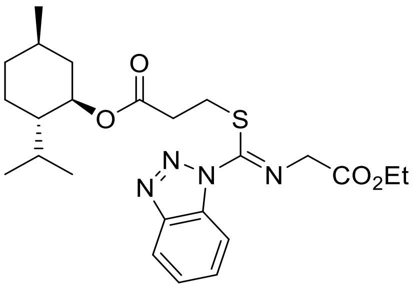
Prop-2-yn-1-yl (*Z*)-3-(((1*H*-benzo[*d*][1,2,3]triazol-1-yl)((2-ethoxy-2-oxoethyl)imino)methyl)thio)propanoate (44). 72.9 mg colorless oil was obtained in 65% isolated yield. ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.37 (dd, *J* = 8.5, 1.1 Hz, 1H), 8.10 (dd, *J* = 8.3, 1.0 Hz, 1H), 7.63 (ddd, *J* = 8.2, 7.0, 1.0 Hz, 1H), 7.48 (ddd, *J* = 8.2, 7.0, 1.0 Hz, 1H), 4.66 (d, *J* = 2.2 Hz, 4H), 4.31 (q, *J* = 7.1 Hz, 2H), 3.34 (t, *J* = 6.8 Hz, 2H), 2.68 (t, *J* = 6.8 Hz, 2H), 2.48 (t, *J* = 2.5 Hz, 1H), 1.36 (t, *J* = 7.1 Hz, 3H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 170.18, 169.36, 150.82, 146.24, 131.97, 129.78, 125.72, 119.88, 114.69, 77.48, 77.23, 77.16, 76.84, 75.37, 61.51, 54.21, 52.48, 34.90, 29.19, 14.34. HRMS (ESI) calculated for $C_{17}H_{18}N_4NaO_4S^+$ $[M+Na]^+$ 397.0941 found 397.0940.



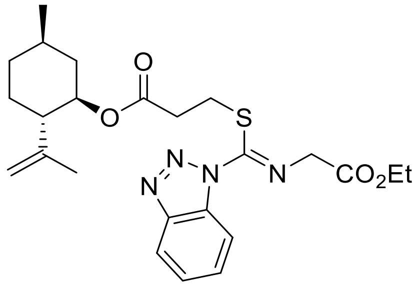
2-(thiophen-2-yl)Ethyl (*Z*)-3-(((1*H*-benzo[*d*][1,2,3]triazol-1-yl)((2-ethoxy-2-oxoethyl)imino)methyl)thio)propanoate (45). 69.6 mg colorless oil was obtained in 52% isolated yield. ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.37 (d, J = 8.4 Hz, 1H), 8.10 (d, J = 8.3 Hz, 1H), 7.62 (m, 1H), 7.47 (m, 1H), 7.13 (dd, J = 5.1, 1.2 Hz, 1H), 6.91 (dd, J = 5.1, 3.4 Hz, 1H), 6.84 – 6.79 (m, 1H), 4.63 (s, 2H), 4.34 – 4.22 (m, 4H), 3.31 (t, J = 6.9 Hz, 2H), 3.14 – 3.07 (m, 2H), 2.63 (t, J = 6.8 Hz, 2H), 1.35 (t, J = 7.1 Hz, 3H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 170.72, 169.39, 151.03, 146.23, 139.58, 131.99, 129.77, 126.96, 125.71, 125.67, 124.21, 119.88, 114.65, 65.19, 61.51, 54.18, 35.14, 29.31, 29.21, 14.34. HRMS (ESI) calculated for $C_{20}H_{23}N_4O_4S_2^+$ $[M+H]^+$ 447.1155 found 447.1147.



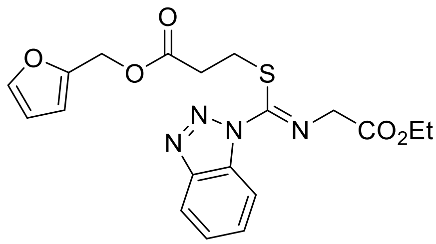
(*E*)-3,7-Dimethylocta-2,6-dien-1-yl 3-(((*Z*)-(1*H*-benzo[*d*][1,2,3]triazol-1-yl)((2-ethoxy-2-oxoethyl)imino)methyl)thio)propanoate (46). 70.8 mg colorless oil was obtained in 50% isolated yield. ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.37 (d, J = 8.3 Hz, 1H), 8.10 (d, J = 8.3 Hz, 1H), 7.62 (m, 1H), 7.47 (m, 1H), 5.33 – 5.22 (m, 1H), 5.13 – 5.01 (m, 1H), 4.65 (s, 2H), 4.57 (d, J = 7.2 Hz, 2H), 4.31 (q, J = 7.1 Hz, 2H), 3.32 (t, J = 6.8 Hz, 2H), 2.62 (t, J = 6.8 Hz, 2H), 2.13 – 1.97 (m, 4H), 1.67 (d, J = 1.4 Hz, 6H), 1.61 – 1.56 (m, 3H), 1.36 (t, J = 7.1 Hz, 3H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 170.98, 169.45, 151.18, 146.28, 142.97, 132.02, 129.77, 125.71, 123.76, 119.92, 117.86, 114.70, 62.03, 61.54, 54.23, 39.63, 35.22, 29.47, 26.37, 25.82, 17.83, 16.60, 14.38. HRMS (ESI) calculated for $C_{24}H_{32}N_4NaO_4S^+$ $[M+Na]^+$ 495.2036 found 495.2031.



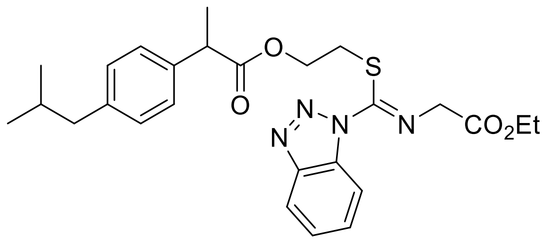
(1*R*,2*S*,5*R*)-2-Isopropyl-5-methylcyclohexyl 3-(((*Z*)-(1*H*-benzo[*d*][1,2,3]triazol-1-yl)((2-ethoxy-2-oxoethyl)imino)methyl)thio)propanoate (47). 96.7 mg colorless oil was obtained in 68% isolated yield. ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.37 (d, J = 8.4 Hz, 1H), 8.10 (d, J = 8.4 Hz, 1H), 7.63 (m, 1H), 7.48 (m, 1H), 4.65 (s, 2H), 4.31 (q, J = 7.1 Hz, 2H), 3.32 (t, J = 6.8 Hz, 2H), 2.58 (m, 2H), 1.98 – 1.89 (m, 1H), 1.83 – 1.73 (m, 1H), 1.66 (m, 2H), 1.47 (m, 1H), 1.36 (m, 4H), 1.08 – 0.79 (m, 10H), 0.73 (d, J = 7.0 Hz, 3H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 170.49, 169.42, 151.16, 146.21, 131.98, 129.75, 125.68, 119.87, 114.63, 75.12, 61.50, 54.14, 46.92, 40.87, 35.34, 34.19, 31.44, 29.54, 26.33, 23.37, 22.08, 20.81, 16.32, 14.35. HRMS (ESI) calculated for $C_{24}H_{34}N_4NaO_4S^+$ $[M+Na]^+$ 497.2193 found 497.2196.



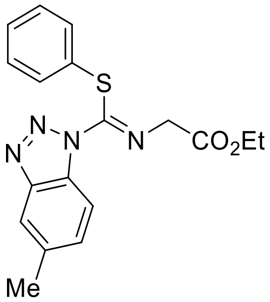
(1*R*,2*S*,5*R*)-5-Methyl-2-(prop-1-en-2-yl)cyclohexyl 3-(((*Z*)-(1*H*-benzo[*d*][1,2,3]triazol-1-yl)((2-ethoxy-2-oxoethyl)imino)methyl)thio)propanoate (48). 86.4 mg colorless oil was obtained in 61% isolated yield. ^1H NMR (400 MHz, $CDCl_3$) δ 8.37 (d, J = 8.3 Hz, 1H), 8.10 (d, J = 8.2 Hz, 1H), 7.62 (m, 1H), 7.47 (m, 1H), 4.78 (m, 1H), 4.70 – 4.58 (m, 4H), 4.32 (p, J = 6.8 Hz, 2H), 3.28 (m, 2H), 2.57 – 2.42 (m, 2H), 2.04 (m, 1H), 1.98 – 1.89 (m, 1H), 1.68 (m, 3H), 1.61 (s, 3H), 1.52 (m, 1H), 1.36 (t, J = 7.1 Hz, 3H), 0.92 (d, J = 6.6 Hz, 5H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 170.22, 169.46, 151.25, 146.23, 146.06, 132.01, 129.75, 125.68, 119.89, 114.63, 112.05, 74.28, 61.51, 54.20, 50.78, 40.38, 35.33, 34.06, 31.46, 30.31, 29.56, 22.10, 19.48, 14.38. HRMS (ESI) calculated for $C_{24}H_{33}N_4O_4S^+$ $[M+H]^+$ 473.2217 found 473.2211.



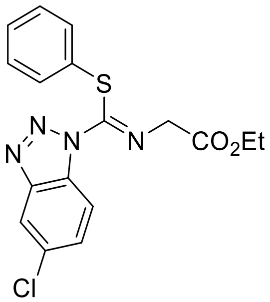
Furan-2-ylmethyl (*Z*)-3-(((1*H*-benzo[*d*][1,2,3]triazol-1-yl)((2-ethoxy-2 oxoethyl)imino)methyl)thio)propanoate (49). 82.4 mg colorless oil was obtained in 66% isolated yield. ^1H NMR (400 MHz, $CDCl_3$) δ 8.36 (d, J = 8.4 Hz, 1H), 8.09 (d, J = 8.3 Hz, 1H), 7.61 (m, 1H), 7.47 (m, 1H), 7.43 – 7.38 (m, 1H), 6.46 – 6.22 (m, 2H), 5.04 (s, 2H), 4.62 (s, 2H), 4.30 (q, J = 7.2 Hz, 2H), 3.33 (t, J = 6.8 Hz, 2H), 2.64 (t, J = 6.8 Hz, 2H), 1.36 (t, J = 7.1 Hz, 3H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 170.59, 169.37, 150.95, 149.00, 146.23, 143.47, 131.97, 129.72, 125.67, 119.86, 114.67, 111.07, 110.68, 77.48, 77.16, 76.84, 61.48, 58.50, 54.18, 34.99, 29.30, 14.33. HRMS (ESI) calculated for $C_{19}H_{20}N_4NaO_5S^+$ $[M+Na]^+$ 439.1047 found 439.1045.



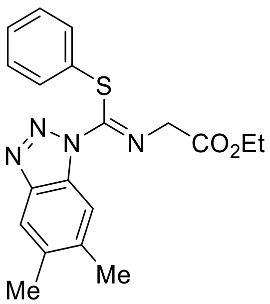
(*Z*)-2-(((1*H*-benzo[*d*][1,2,3]triazol-1-yl)((2-ethoxy-2-oxoethyl)imino)methyl)thio)ethyl 2-(4-isobutylphenyl)propanoate (50). 115.8 mg colorless oil was obtained in 78% isolated yield. ^1H NMR (400 MHz, $CDCl_3$) δ 8.40 (dt, J = 8.3, 1.0 Hz, 1H), 8.11 (dd, J = 8.3, 1.1 Hz, 1H), 7.63 (m, 1H), 7.48 (m, 1H), 7.09 – 7.01 (m, 4H), 4.59 (d, J = 1.1 Hz, 2H), 4.31 (q, J = 7.1 Hz, 2H), 4.20 (m, 1H), 4.14 – 4.05 (m, 1H), 3.50 (q, J = 7.2 Hz, 1H), 3.40 – 3.29 (m, 2H), 2.42 (d, J = 7.2 Hz, 2H), 1.82 (dt, J = 13.5, 6.8 Hz, 1H), 1.44 – 1.29 (m, 6H), 0.88 (d, J = 6.6 Hz, 6H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 174.32, 169.36, 150.63, 146.30, 140.79, 137.26, 131.97, 129.84, 129.44, 127.16, 125.77, 119.95, 114.81, 63.48, 61.54, 54.21, 45.11, 44.85, 33.18, 30.28, 22.50, 18.48, 14.38. HRMS (ESI) calculated for $C_{26}H_{32}N_4NaO_4S^+$ $[M+Na]^+$ 519.2036 found 519.2033.



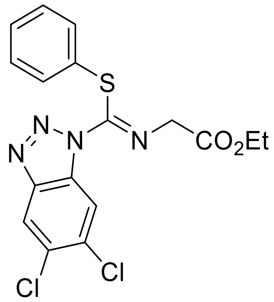
Ethyl (*Z*)-2-(((5-methyl-1*H*-benzo[*d*][1,2,3]triazol-1-yl)(phenylthio)methylene)amino)acetate (51). 79.6 mg white solid was obtained in 75% isolated yield. ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.24 (d, J = 8.5 Hz, 0.58H), 8.17 – 8.11 (m, 0.46H), 7.85 (d, J = 8.4 Hz, 0.46H), 7.77 – 7.72 (m, 0.54H), 7.41 (m, 2.60H), 7.22 (m, 3.37H), 4.67 (s, 0.88H), 4.64 (s, 1.09H), 4.31 (m, 2H), 2.55 (s, 1.49H), 2.50 (s, 1.63H), 1.36 (m, 3H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 169.44, 169.37, 149.97, 149.59, 146.78, 144.82, 140.36, 135.64, 132.62, 132.50, 132.47, 131.43, 130.64, 129.62, 129.59, 129.52, 129.50, 128.88, 128.87, 127.54, 119.29, 118.93, 113.67, 113.40, 61.60, 61.57, 54.41, 54.33, 22.30, 21.59, 14.40, 14.35. HRMS (ESI) calculated for $C_{18}H_{19}N_4O_2S^+$ $[M+H]^+$ 355.1223 found 355.1212.



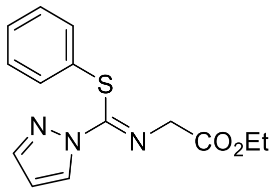
Ethyl (*Z*)-2-(((5-chloro-1*H*-benzo[*d*][1,2,3]triazol-1-yl)(phenylthio)methylene)amino)acetate (52). 79.7 mg white solid was obtained in 71% isolated yield. ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.45 – 8.42 (m, 0.49H), 8.36 (dd, J = 8.8, 0.7 Hz, 0.51H), 8.01 – 7.97 (m, 0.48H), 7.92 (dd, J = 8.8, 0.7 Hz, 0.51H), 7.55 (dd, J = 8.9, 1.9 Hz, 0.53H), 7.47 – 7.42 (m, 2.01H), 7.40 (dd, J = 8.8, 1.9 Hz, 0.54H), 7.28 – 7.22 (m, 2.96H), 4.66 (m, 2H), 4.34 (m, 2H), 1.39 (m, 3H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 169.24, 169.11, 149.46, 146.68, 144.67, 135.93, 132.65, 131.12, 130.87, 130.19, 129.68, 129.12, 129.10, 129.08, 129.03, 126.61, 120.66, 119.24, 115.25, 114.26, 77.48, 77.16, 76.84, 61.75, 61.64, 54.33, 54.20, 14.36, 14.33. HRMS (ESI) calculated for $C_{17}H_{16}ClN_4O_2S^+$ $[M+H]^+$ 375.0677 found 375.0677.



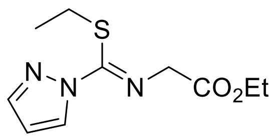
Ethyl (*Z*)-2-(((5,6-dimethyl-1*H*-benzo[*d*][1,2,3]triazol-1-yl)(phenylthio)methylene)amino)acetate (53). 77.3 mg white solid was obtained in 70% isolated yield. ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.12 (s, 1H), 7.72 (s, 1H), 7.44 – 7.38 (m, 2H), 7.24 – 7.18 (m, 3H), 4.66 (s, 2H), 4.31 (q, *J* = 7.1 Hz, 2H), 2.41 (d, *J* = 22.9 Hz, 6H), 1.37 (t, *J* = 7.1 Hz, 3H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 169.45, 149.86, 145.38, 139.95, 135.24, 132.40, 131.13, 129.69, 129.60, 128.80, 119.07, 113.64, 61.58, 54.42, 21.21, 20.56, 14.42. HRMS (ESI) calculated for $C_{19}H_{21}N_4O_2S^+$ $[M+H]^+$ 369.1380 found 369.1375.



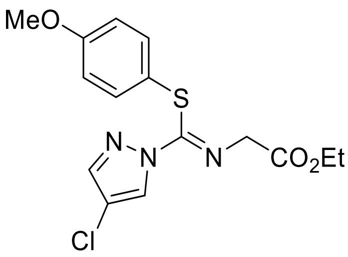
Ethyl (*Z*)-2-(((5,6-dichloro-1*H*-benzo[*d*][1,2,3]triazol-1-yl)(phenylthio)methylene)amino)acetate (54). 67.3 mg white solid was obtained in 55% isolated yield. ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.60 (s, 1H), 8.13 (s, 1H), 7.48 – 7.42 (m, 2H), 7.32 – 7.24 (m, 4H), 4.67 (s, 2H), 4.36 (q, *J* = 7.2 Hz, 2H), 1.41 (t, *J* = 7.2 Hz, 3H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 169.08, 149.36, 144.92, 134.65, 132.79, 131.05, 130.19, 129.80, 129.29, 128.94, 120.72, 115.83, 61.83, 54.30, 14.41. HRMS (ESI) calculated for $C_{17}H_{15}Cl_2N_4O_2S^+$ $[M+H]^+$ 409.0287 found 409.0289.



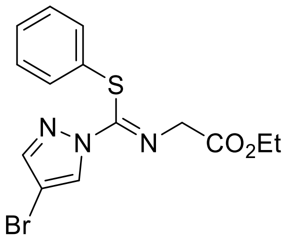
Ethyl (*Z*)-2-(((phenylthio)(1*H*-pyrazol-1-yl)methylene)amino)acetate (55). 73.7 mg colorless oil was obtained in 85% isolated yield. ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.18 (d, *J* = 2.0 Hz, 1H), 7.58 – 7.56 (m, 1H), 7.35 (dd, *J* = 7.5, 2.3 Hz, 2H), 7.30 – 7.18 (m, 3H), 6.31 (dd, *J* = 2.7, 1.6 Hz, 1H), 4.49 (s, 2H), 4.21 (q, *J* = 7.1 Hz, 2H) , 1.29 (t, *J* = 7.2 Hz, 3H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 169.39, 150.72, 142.40, 131.40, 130.52, 129.57, 129.52, 128.23, 108.19, 61.42, 54.53, 14.29. HRMS (ESI) calculated for $C_{14}H_{16}N_3O_2S^+$ $[M+H]^+$ 290.0958 found 290.0951.



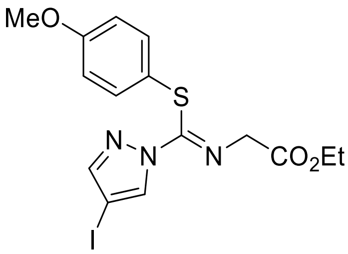
Ethyl (*Z*)-2-(((ethylthio)(1*H*-pyrazol-1-yl)methylene)amino)acetate (56). 38.9 mg white solid was obtained in 55% isolated yield. ^{1}H NMR (400 MHz, Chloroform-*d*) δ 8.18 (d, *J* = 2.7 Hz, 1H), 7.72 (d, *J* = 1.6 Hz, 1H), 6.48 – 6.28 (m, 1H), 4.53 (s, 2H), 4.25 (q, *J* = 7.1 Hz, 2H), 3.03 (q, *J* = 7.4 Hz, 2H), 1.31 (t, *J* = 7.1 Hz, 3H), 1.17 (t, *J* = 7.4 Hz, 3H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 169.60, 153.92, 142.35, 128.94, 107.66, 61.27, 54.38, 28.66, 15.50, 14.28. HRMS (ESI) calculated for $C_{10}H_{15}N_3NaO_2S^+$ $[M+Na]^+$ 264.0778 found 264.0779.



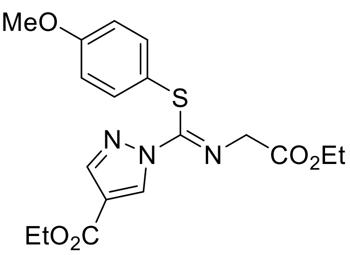
Ethyl (*Z*)-2-(((4-chloro-1*H*-pyrazol-1-yl)((4-methoxyphenyl)thio)methylene)amino)acetate (57). 78.4 mg colorless oil was obtained in 74% isolated yield. ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.16 (s, 1H), 7.50 (s, 1H), 7.37 (d, *J* = 8.8 Hz, 2H), 6.82 (d, *J* = 8.8 Hz, 2H), 4.46 (s, 2H), 4.23 (q, *J* = 7.2 Hz, 2H), 3.80 (s, 3H), 1.31 (t, *J* = 7.2 Hz, 3H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 169.29, 160.25, 151.01, 140.62, 134.68, 127.07, 119.69, 115.10, 113.26, 61.45, 55.44, 54.11, 14.29. HRMS (ESI) calculated for $C_{15}H_{17}ClN_3O_3S^+$ $[M+H]^+$ 354.0674 found 354.0673.



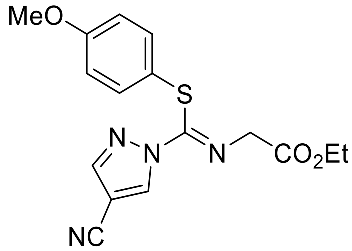
Ethyl (*Z*)-2-(((4-bromo-1*H*-pyrazol-1-yl)(phenylthio)methylene)amino)acetate (58). 71.6 mg colorless oil was obtained in 65% isolated yield. ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.28 (d, *J* = 0.7 Hz, 1H), 7.54 (d, *J* = 0.8 Hz, 1H), 7.38 – 7.32 (m, 2H), 7.27 (dt, *J* = 4.6, 1.4 Hz, 3H), 4.47 (s, 2H), 4.22 (q, *J* = 7.1 Hz, 2H), 1.29 (t, *J* = 7.1 Hz, 3H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 169.19, 149.79, 146.83, 133.76, 131.63, 129.98, 129.64, 128.52, 61.52, 61.03, 54.44, 14.31. HRMS (ESI) calculated for $C_{14}H_{15}BrN_3O_2S^+$ $[M+H]^+$ 368.0063 found 368.0053.



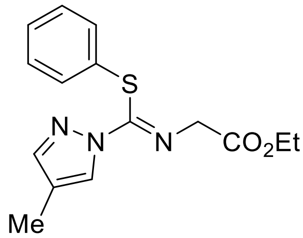
Ethyl (*Z*)-2-(((4-iodo-1*H*-pyrazol-1-yl)((4-methoxyphenyl)thio)methylene)amino)acetate (59). 84.1 mg colorless oil was obtained in 63% isolated yield. ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.24 (d, *J* = 0.7 Hz, 1H), 7.57 – 7.56 (m, 1H), 7.38 (d, *J* = 8.8 Hz, 2H), 6.83 (d, *J* = 8.8 Hz, 2H), 4.47 (s, 2H), 4.24 (q, *J* = 7.1 Hz, 2H), 3.80 (s, 3H), 1.32 (t, *J* = 7.1 Hz, 3H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 169.33, 160.28, 150.65, 146.63, 134.73, 133.74, 119.65, 115.12, 61.48, 60.72, 55.48, 54.11, 14.32. HRMS (ESI) calculated for $C_{15}H_{17}IN_3O_3S^+$ $[M+H]^+$ 446.0030 found 446.0023.



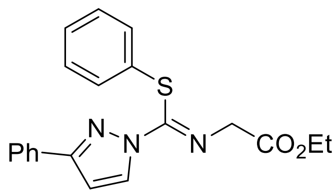
Ethyl (Z)-1-(((2-ethoxy-2-oxoethyl)imino)((4-methoxyphenyl)thio)methyl)-1*H*-pyrazole-4-carboxylate (60). 91.5 mg colorless oil was obtained in 78% isolated yield. ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.56 (d, *J* = 0.8 Hz, 1H), 7.93 – 7.83 (m, 1H), 7.35 (d, *J* = 8.9 Hz, 2H), 6.79 (d, *J* = 8.9 Hz, 2H), 4.50 (s, 2H), 4.26 (m, 4H), 3.78 (s, 3H), 1.32 (m, 6H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 169.16, 162.56, 160.43, 151.74, 142.47, 134.96, 132.70, 119.27, 116.78, 115.13, 61.58, 60.68, 55.47, 54.25, 14.42, 14.33. HRMS (ESI) calculated for $C_{18}H_{22}N_3O_5S^+$ $[M+H]^+$ 392.1275 found 392.1272.



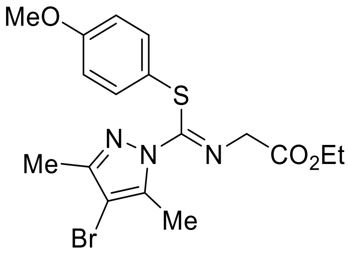
Ethyl (*Z*)-2-(((4-cyano-1*H*-pyrazol-1-yl)((4-methoxyphenyl)thio)methylene)amino)acetate (61). 82.6 mg colorless oil was obtained in 80% isolated yield. ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.47 (s, 1H), 7.75 (s, 1H), 7.34 (d, *J* = 8.8 Hz, 2H), 6.80 (d, *J* = 8.8 Hz, 2H), 4.50 (s, 2H), 4.25 (q, *J* = 7.2 Hz, 2H), 3.79 (s, 3H), 1.31 (t, *J* = 7.1 Hz, 3H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 168.81, 160.74, 151.34, 142.93, 135.24, 134.63, 118.54, 115.25, 112.59, 94.63, 61.70, 55.52, 54.13, 14.33. HRMS (ESI) calculated for $C_{16}H_{17}N_4O_3S^+$ $[M+H]^+$ 345.1016 found 345.1012.



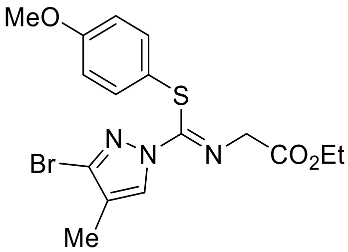
Ethyl (*Z*)-2-(((4-methyl-1*H*-pyrazol-1-yl)(phenylthio)methylene)amino)acetate (62). 36.4 mg colorless oil was obtained in 40% isolated yield. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.99 (s, 1H), 7.41 (s, 1H), 7.38 – 7.32 (m, 2H), 7.26 (d, *J* = 5.2 Hz, 3H), 4.44 (s, 2H), 4.20 (d, *J* = 7.2 Hz, 2H), 2.04 (d, *J* = 1.0 Hz, 3H), 1.28 (t, *J* = 7.2 Hz, 3H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 169.65, 143.76, 131.19, 130.91, 129.55, 128.08, 127.71, 119.10, 61.40, 54.52, 14.33, 9.06. HRMS (ESI) calculated for $C_{15}H_{18}N_3O_2S^+$ $[M+H]^+$ 304.1114 found 304.1114.



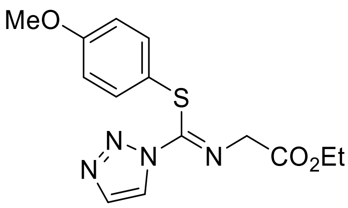
Ethyl (*Z*)-2-(((3-phenyl-1*H*-pyrazol-1-yl)(phenylthio)methylene)amino)acetate (63). 76.7 mg white solid was obtained in 70% isolated yield. ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.19 (d, *J* = 2.8 Hz, 1H), 7.72 – 7.67 (m, 2H), 7.45 – 7.39 (m, 2H), 7.39 – 7.29 (m, 3H), 7.27 – 7.19 (m, 3H), 6.59 (d, *J* = 2.7 Hz, 1H), 4.56 (s, 2H), 4.24 (q, *J* = 7.1 Hz, 2H), 1.30 (t, *J* = 7.1 Hz, 3H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 169.53, 153.75, 151.22, 132.41, 131.93, 130.85, 130.72, 129.39, 128.59, 128.53, 128.36, 126.15, 105.63, 61.44, 54.54, 14.32. HRMS (ESI) calculated for $C_{20}H_{20}N_3O_2S^+$ $[M+H]^+$ 366.1271 found 366.1270.



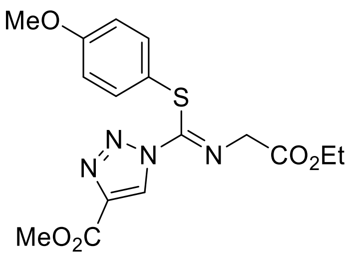
Ethyl (*Z*)-2-(((4-bromo-3,5-dimethyl-1*H*-pyrazol-1-yl)(phenylthio)methylene)amino)acetate (64). 102.0 mg colorless oil was obtained in 80% isolated yield. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.29 (d, *J* = 8.8 Hz, 1H), 6.75 (d, *J* = 8.9 Hz, 1H), 4.49 (s, 1H), 4.26 (q, *J* = 7.2 Hz, 1H), 3.77 (s, 2H), 2.37 (s, 2H), 2.08 (s, 2H), 1.32 (t, *J* = 7.2 Hz, 2H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 169.29, 160.41, 153.66, 148.10, 139.82, 135.55, 119.10, 114.56, 97.95, 61.42, 55.46, 54.18, 14.33, 12.35, 11.89. HRMS (ESI) calculated for $C_{17}H_{21}BrN_3O_3S^+$ $[M+H]^+$ 426.0482 found 426.0482.



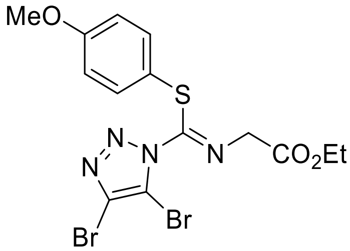
Ethyl (*Z*)-2-(((3-bromo-4-methyl-1*H*-pyrazol-1-yl)((4-methoxyphenyl)thio)methylene)amino)acetate (65). 80.1 mg colorless oil was obtained in 65% isolated yield. ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.11 (s, 1H), 7.40 – 7.33 (m, 2H), 6.84 – 6.78 (m, 2H), 4.42 (s, 2H), 4.20 (q, *J* = 7.1 Hz, 2H), 3.79 (s, 3H), 2.22 (s, 3H), 1.28 (t, *J* = 7.1 Hz, 3H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 169.44, 160.26, 150.71, 150.42, 134.60, 129.93, 120.02, 115.15, 98.40, 61.42, 55.50, 54.19, 14.33, 12.39. HRMS (ESI) calculated for $C_{16}H_{19}BrN_3O_3S^+$ $[M+H]^+$ 412.0325 found 412.0323.



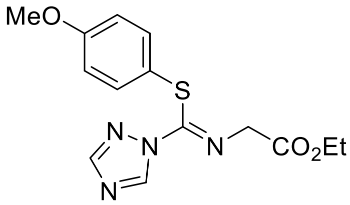
Ethyl (*Z*)-2-((((4-methoxyphenyl)thio)(1*H*-1,2,3-triazol-1-yl)methylene)amino)acetate (66). 59.5 mg white solid was obtained in 62% isolated yield. ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.05 (d, *J* = 1.3 Hz, 1H), 7.55 (d, *J* = 1.3 Hz, 1H), 7.41 – 7.33 (m, 2H), 6.81 – 6.74 (m, 2H), 4.57 (s, 2H), 4.27 (q, *J* = 7.1 Hz, 2H), 3.75 (s, 3H), 1.33 (t, *J* = 7.1 Hz, 3H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 168.77, 160.78, 150.82, 135.75, 133.20, 123.27, 118.17, 115.13, 61.65, 55.43, 54.11, 14.29. HRMS (ESI) calculated for $C_{14}H_{17}N_4O_3S^+$ $[M+H]^+$ 321.1016 found 321.1008.



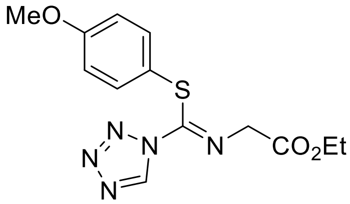
Methyl (*Z*)-1-(((2-ethoxy-2-oxoethyl)imino)((4-methoxyphenyl)thio)methyl)-1*H*-1,2,3-triazole-4-carboxylate (67). 94.1 mg colorless oil was obtained in 83% isolated yield. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.72 (s, 1H), 7.19 (d, *J* = 8.8 Hz, 2H), 6.67 (d, *J* = 8.8 Hz, 2H), 4.51 (s, 2H), 4.31 (q, *J* = 7.1 Hz, 2H), 3.88 (s, 3H), 3.73 (s, 3H), 1.34 (t, *J* = 7.1 Hz, 3H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 168.42, 161.46, 157.56, 152.66, 137.23, 135.73, 129.17, 115.64, 114.77, 61.66, 55.46, 53.92, 52.80, 14.33. HRMS (ESI) calculated for $C_{16}H_{19}N_4O_5S^+$ $[M+H]^+$ 379.1071 found 379.1065.



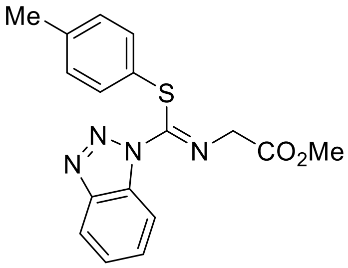
Ethyl (*Z*)-2-(((4,5-dibromo-1*H*-1,2,3-triazol-1-yl)((4-methoxyphenyl)thio)methylene)amino)acetate (68). 91.4 mg colorless oil was obtained in 64% isolated yield. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.37 (d, *J* = 8.8 Hz, 2H), 6.80 (d, *J* = 8.8 Hz, 2H), 4.64 (s, 2H), 4.26 (q, *J* = 7.2 Hz, 2H), 3.78 (s, 3H), 1.32 (t, *J* = 7.2 Hz, 3H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 168.31, 160.94, 151.64, 136.06, 128.36, 117.90, 115.02, 114.46, 61.80, 55.54, 54.66, 14.32. HRMS (ESI) calculated for $C_{14}H_{15}Br_2N_4O_3S^+$ $[M+H]^+$ 476.9226 found 476.9222.



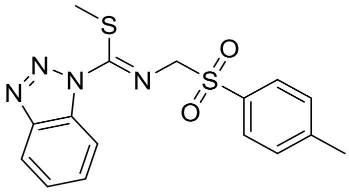
Ethyl (*Z*)-2-((((4-methoxyphenyl)thio)(1*H*-1,2,4-triazol-1-yl)methylene)amino)acetate (69). 40.3 mg white solid was obtained in 42% isolated yield. ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.62 (s, 1H), 7.84 (s, 1H), 7.37 – 7.31 (m, 2H), 6.84 – 6.76 (m, 2H), 4.55 (s, 2H), 4.26 (q, *J* = 7.1 Hz, 2H), 3.77 (s, 3H), 1.32 (t, *J* = 7.1 Hz, 3H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 168.81, 160.74, 152.08, 150.35, 143.55, 135.28, 118.39, 115.23, 61.66, 55.47, 54.15, 14.30. HRMS (ESI) calculated for $C_{14}H_{17}N_4O_3S^+$ $[M+H]^+$ 321.1016 found 321.1007.



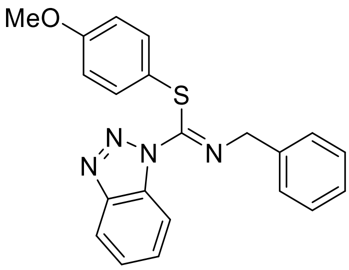
Ethyl (*Z*)-2-((((4-methoxyphenyl)thio)(1*H*-tetrazol-1-yl)methylene)amino)acetate (70). 41.4 mg colorless oil was obtained in 43% isolated yield. ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.94 (s, 1H), 7.37 (d, *J* = 8.8 Hz, 2H), 6.79 (d, *J* = 8.8 Hz, 2H), 4.61 (s, 2H), 4.29 (q, *J* = 7.0 Hz, 2H), 3.76 (s, 3H), 1.34 (t, *J* = 7.1 Hz, 3H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 168.25, 161.42, 149.01, 141.53, 136.34, 116.46, 115.50, 61.95, 55.53, 54.10, 14.33. HRMS (ESI) calculated for $C_{13}H_{16}N_5O_3S^+$ $[M+H]^+$ 322.0968 found 322.0959.



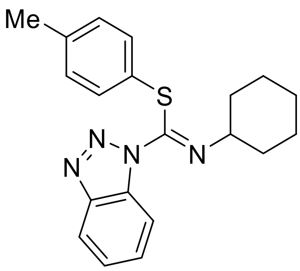
Methyl (*Z*)-2-(((1*H*-benzo[*d*][1,2,3]triazol-1-yl)(*p*-tolylthio)methylene)amino)acetate (71). 79.6 mg white solid was obtained in 78% isolated yield. ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.34 (d, *J* = 8.3 Hz, 1H), 7.99 (d, *J* = 8.3 Hz, 1H), 7.58 (m, 1H), 7.40 (m, 1H), 7.35 – 7.29 (m, 2H), 7.05 – 6.95 (m, 2H), 4.65 (s, 2H), 3.84 (s, 3H), 2.23 (s, 3H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 169.88, 150.20, 146.08, 139.38, 132.92, 132.14, 130.33, 129.40, 125.38, 125.37, 119.75, 114.09, 53.94, 52.44, 21.20. HRMS (ESI) calculated for $C_{17}H_{17}N_4O_2S^+$ $[M+H]^+$ 341.1067 found341.1069.



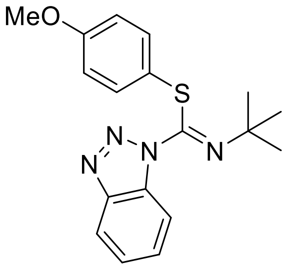
Methyl (*Z*)-*N*-(tosylmethyl)-1*H*-benzo[*d*][1,2,3]triazole-1-carbimidothioate (72). 84.2 mg white solid was obtained in 78% isolated yield. ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.13 – 8.06 (m, 2H), 7.87 (d, *J* = 8.3 Hz, 2H), 7.60 (m, 1H), 7.49 (m, 1H), 7.33 (d, *J* = 8.2 Hz, 2H), 5.19 (s, 2H), 2.52 (s, 3H), 2.42 (s, 3H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 155.69, 146.09, 145.34, 134.76, 131.72, 129.93, 129.87, 129.06, 125.86, 119.98, 114.40, 73.16, 21.77, 17.44. HRMS (ESI) calculated for $C_{16}H_{17}N_4O_2S_2^+$ $[M+H]^+$ 361.0787 found 361.0784.



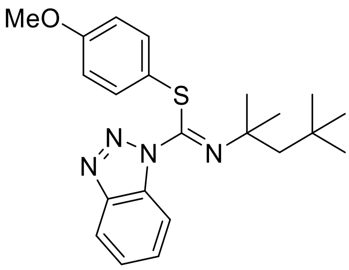
4-Methoxyphenyl (*Z*)-*N*-benzyl-1*H*-benzo[*d*][1,2,3]triazole-1-carbimidothioate (73). 90.9 mg white solid was obtained in 81% isolated yield. ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.01 (d, *J* = 8.3 Hz, 1H), 7.95 (d, *J* = 8.2 Hz, 1H), 7.47 (dd, *J* = 9.1, 7.4 Hz, 3H), 7.43 – 7.28 (m, 6H), 6.67 (d, *J* = 8.8 Hz, 1H), 5.09 (s, 2H), 3.67 (s, 3H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 160.34, 148.06, 145.87, 138.79, 135.48, 132.09, 128.95, 128.76, 127.84, 127.31, 125.02, 119.79, 119.41, 114.88, 113.35, 56.91, 55.32. HRMS (ESI) calculated for $C_{21}H_{19}N_4OS^+$ $[M+H]^+$ 375.1274found 375.1271.



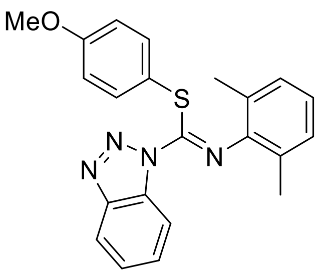
***p*-Tolyl (*Z*)-*N*-cyclohexyl-1*H*-benzo[*d*][1,2,3]triazole-1-carbimidothioate (74).** 81.9 mg colorless oil was obtained in 78% isolated yield. ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.03 (d, *J* = 8.4 Hz, 1H), 7.93 (d, *J* = 8.3 Hz, 1H), 7.51 (m, 1H), 7.34 (m, 1H), 7.24 (d, *J* = 8.2 Hz, 2H), 6.92 (d, *J* = 8.0 Hz, 2H), 4.14 (m, 1H), 2.17 (s, 3H), 1.89 (m, 4H), 1.76 – 1.29 (m, 6H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 145.85, 144.49, 138.84, 132.77, 132.21, 130.02, 128.74, 126.25, 124.88, 119.74, 113.31, 61.86, 33.73, 25.65, 24.48, 21.16. HRMS (ESI) calculated for $C_{20}H_{23}N_4S^+$ $[M+H]^+$ 351.1638 found 351.1636.



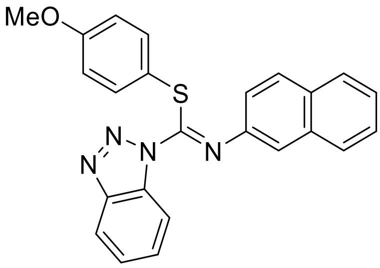
4-Methoxyphenyl (*Z*)-*N*-(tert-butyl)-1*H*-benzo[*d*][1,2,3]triazole-1-carbimidothioate (75). 82.6 mg colorless oil was obtained in 81% isolated yield. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.88 (d, *J* = 8.4 Hz, 2H), 7.48 (m, 1H), 7.34 – 7.28 (m, 1H), 7.26 – 7.20 (m, 2H), 6.58 (d, *J* = 8.8 Hz, 2H), 3.64 (s, 3H), 1.66 (s, 9H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 160.12, 145.53, 142.61, 135.01, 132.23, 128.49, 124.61, 120.19, 119.68, 114.59, 112.58, 57.06, 55.27, 29.89. HRMS (ESI) calculated for $C_{18}H_{21}N_4OS^+$ $[M+H]^+$ 341.1431 found 341.1429.



4-Methoxyphenyl (*Z*)-*N*-(2,4,4-trimethylpentan-2-yl)-1*H*-benzo[d][1,2,3]triazole-1-carbimidothioate (76). 79.6 mg colorless oil was obtained in 67% isolated yield. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.93 – 7.87 (m, 2H), 7.50 (m, 1H), 7.33 (m, 1H), 7.28 – 7.21 (m, 2H), 6.62 – 6.56 (m, 2H), 3.67 (s, 3H), 2.01 (s, 2H), 1.82 – 1.64 (m, 6H), 1.07 (s, 9H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 160.14, 145.43, 140.79, 135.12, 132.24, 128.32, 124.49, 120.34, 119.68, 114.53, 112.48, 55.77, 55.30, 32.17, 31.94, 31.91, 29.92. HRMS (ESI) calculated for $C_{22}H_{29}N_4OS^+$ $[M+H]^+$ 397.2051 found 397.2042.

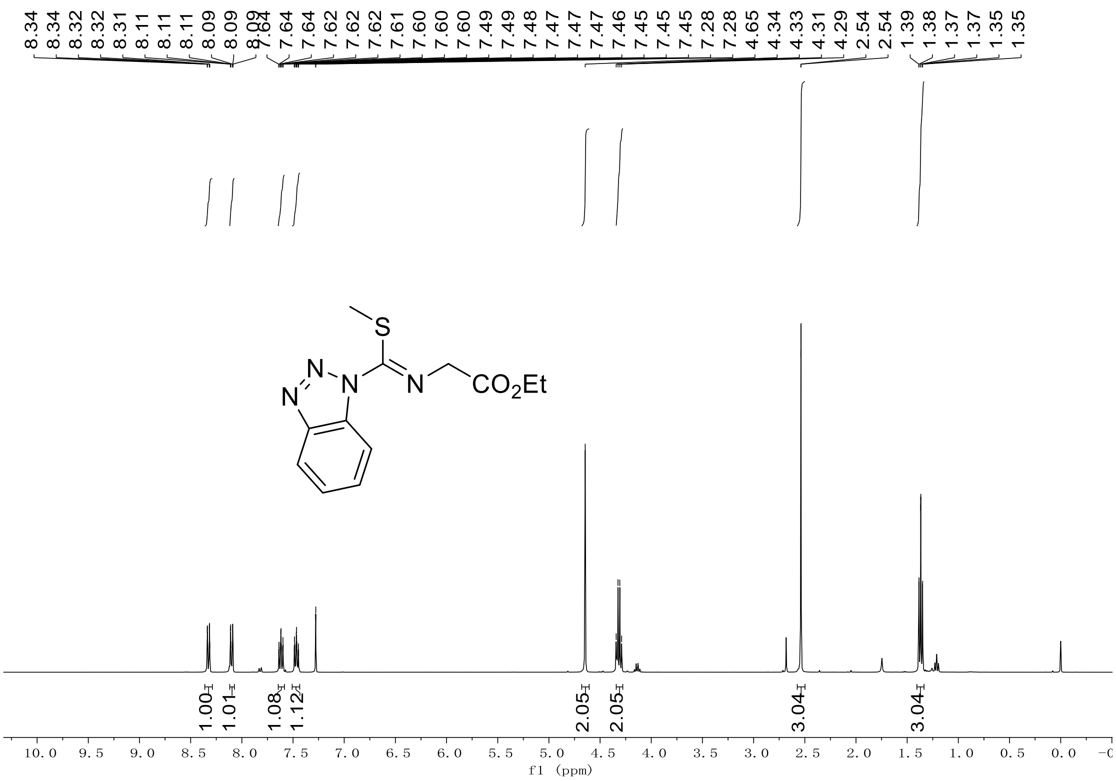


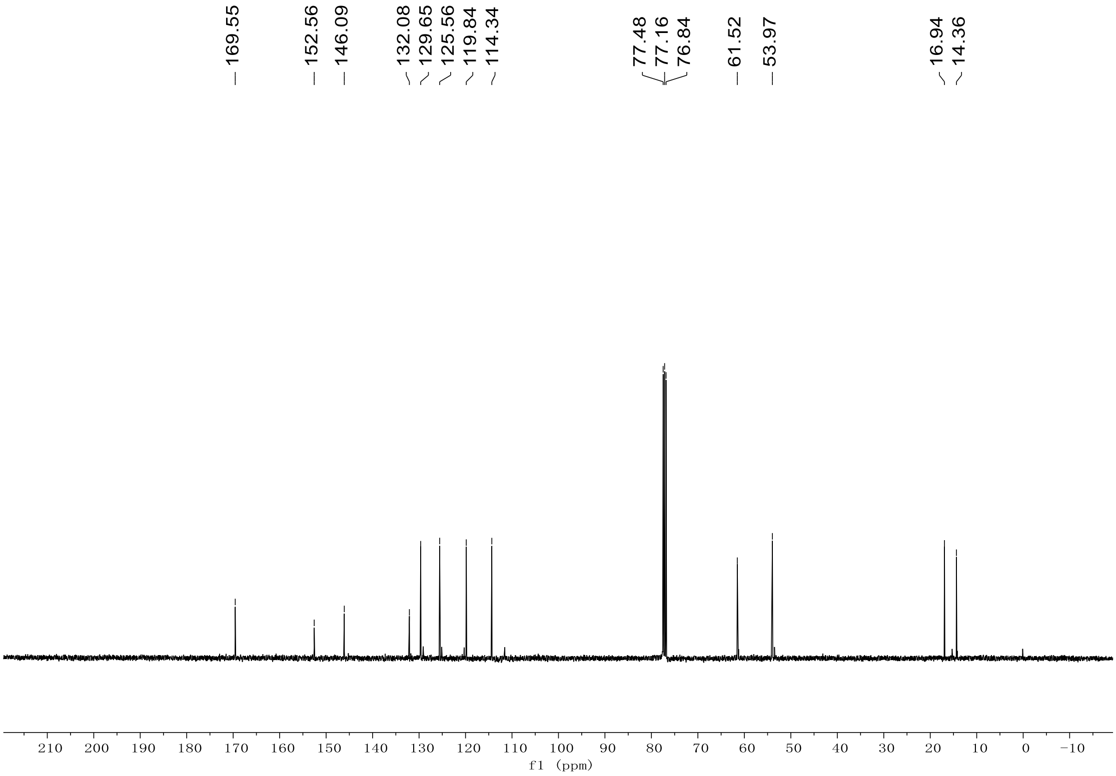
4-Methoxyphenyl (*Z*)-*N*-(2,6-dimethylphenyl)-1*H*-benzo[*d*][1,2,3]triazole-1-carbimidothioate (77). 47.7 mg white solid was obtained in 41% isolated yield. ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.27 (d, *J* = 8.4 Hz, 1H), 8.08 (d, *J* = 8.3 Hz, 1H), 7.57 (m, 1H), 7.45 (m, 1H), 7.30 – 7.22 (m, 2H), 6.99 – 6.93 (m, 2H), 6.89 (dd, *J* = 8.4, 6.4 Hz, 1H), 6.59 – 6.51 (m, 2H), 3.70 (s, 3H), 2.20 (s, 6H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 160.68, 147.13, 146.26, 143.75, 136.41, 132.04, 129.41, 128.02, 126.41, 125.44, 124.30, 120.13, 117.54, 114.47, 114.06, 55.40, 18.69. HRMS (ESI) calculated for $C_{22}H_{21}N_4OS^+$ [M+H]$^+$ 389.1434 found 389.1432.



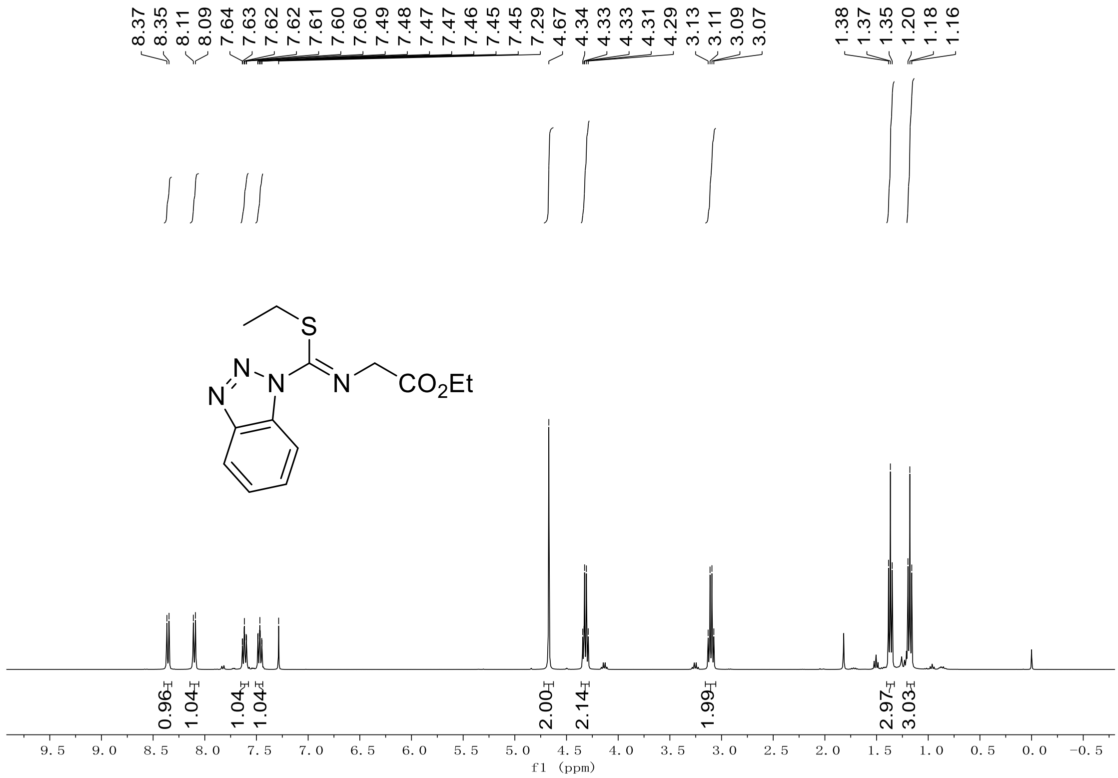
4-Methoxyphenyl (*Z*)-N-(naphthalen-2-yl)-1*H*-benzo[*d*][1,2,3]triazole-1-carbimidothioate (78). 36.9 mg white solid was obtained in 30% isolated yield. ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.30 (d, *J* = 8.3 Hz, 1H), 8.09 (d, *J* = 8.3 Hz, 1H), 7.79 (d, *J* = 8.0 Hz, 1H), 7.73 (d, *J* = 8.6 Hz, 2H), 7.60 (m, 1H), 7.51 – 7.40 (m, 3H), 7.26 (s, 1H), 7.21 – 7.15 (m, 2H), 7.12 (m, 1H), 6.42 – 6.35 (m, 2H), 3.51 (s, 3H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 160.31, 148.52, 146.40, 143.61, 136.42, 133.71, 131.96, 130.98, 129.50, 128.78, 127.76, 127.59, 126.52, 125.61, 125.17, 120.86, 120.17, 118.47, 117.04, 114.47, 114.21, 55.25. HRMS (ESI) calculated for $C_{24}H_{19}N_4OS^+$ [M+H]$^+$ 411.1274 found 411.1277.

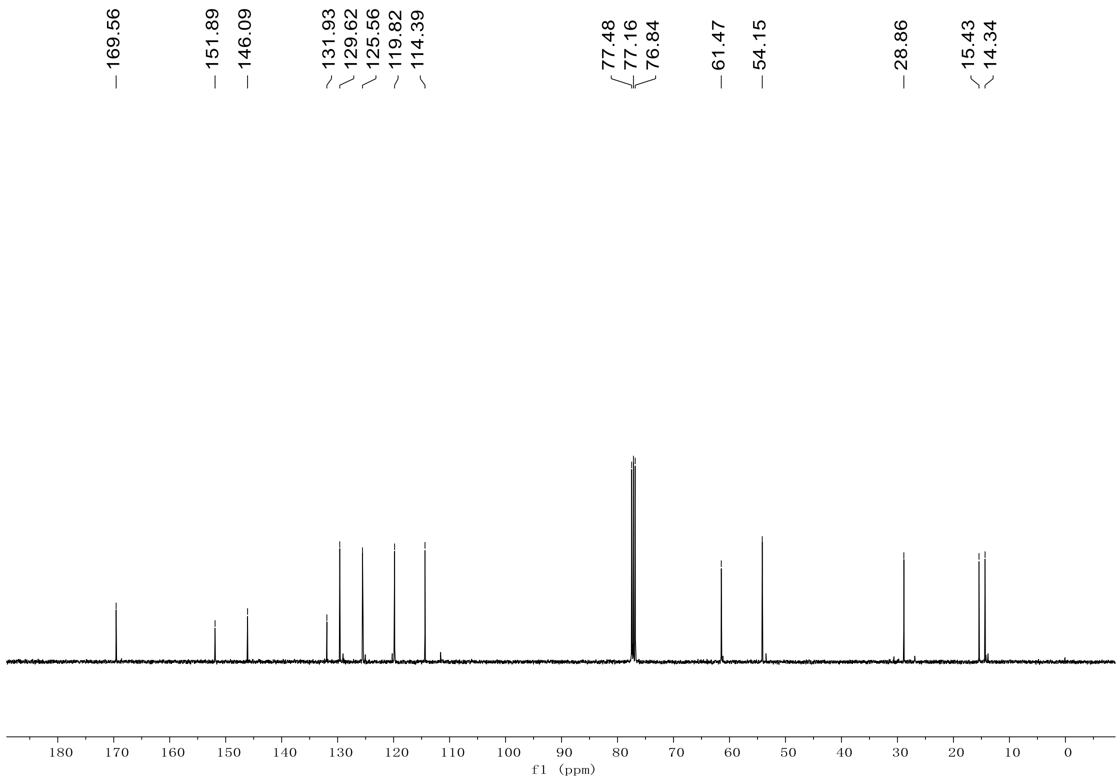
4


8.34 8.34 8.32 8.32 8.31 8.11 8.11 8.11 8.09 8.09 7.64 7.64 7.64 7.62 7.62 7.61 7.60 7.60 7.49 7.49 7.48 7.47 7.47 7.47 7.46 7.45 7.45 7.45 7.28 7.28 4.65 4.34 4.33 4.31 4.29 2.54 2.54 1.39 1.38 1.37 1.37 1.35 1.35
S
N
N
N
N
CO2Et
1.00
1.01
1.08
1.12
2.05
2.05
3.04
3.04
f1 (ppm)

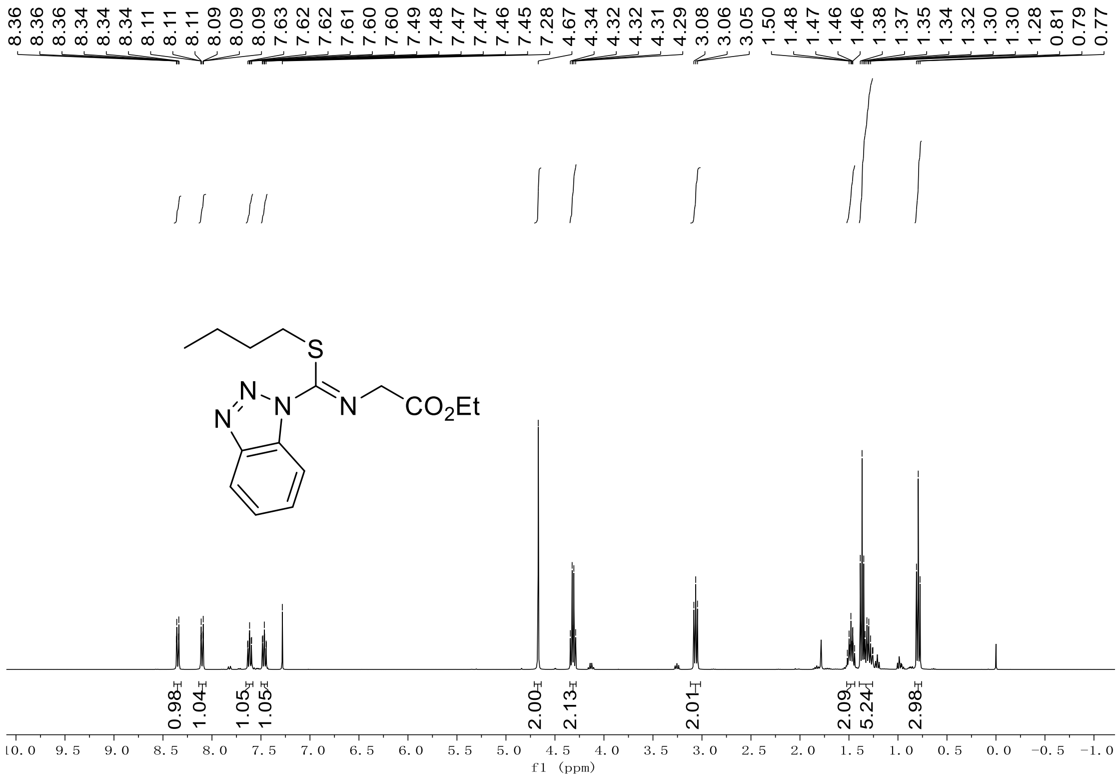

169.55 152.56 146.09 132.08 129.65 125.56 119.84 114.34 77.48 77.16 76.84 61.52 53.97 16.94 14.36
f1 (ppm)

5

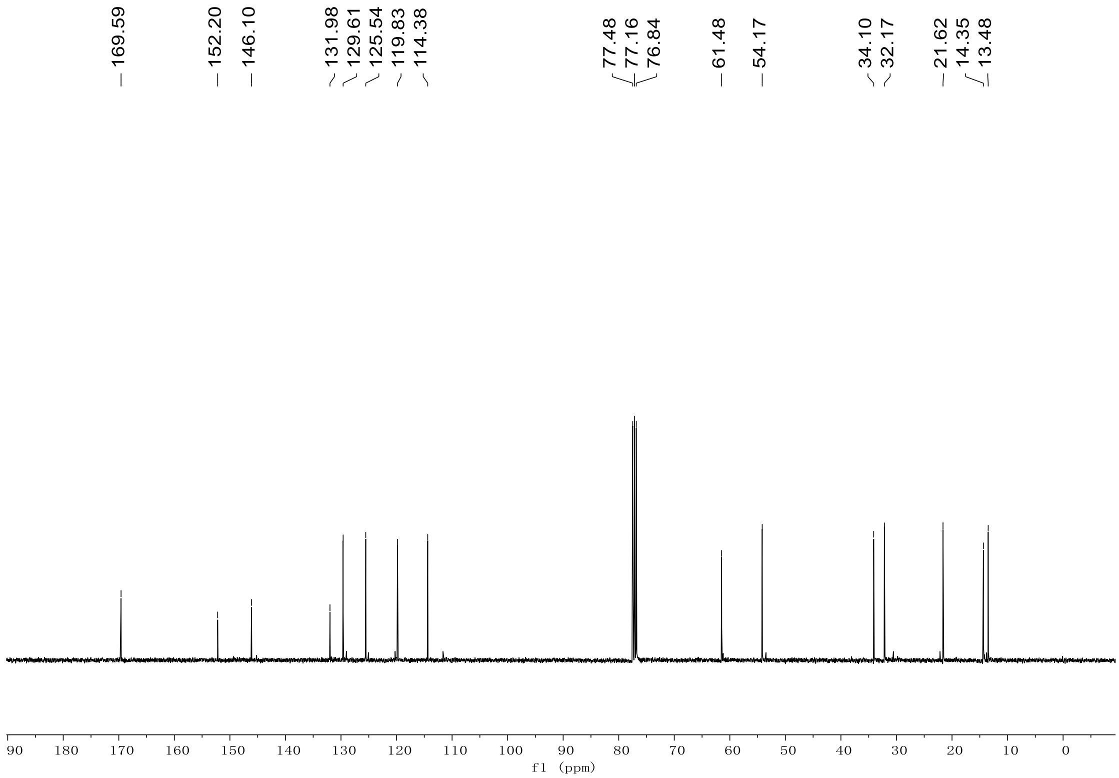

8.37 8.35 8.11 8.09 7.64 7.63 7.62 7.62 7.61 7.60 7.60 7.49 7.48 7.47 7.47 7.46 7.45 7.45 7.29 4.67 4.34 4.33 4.33 4.31 4.29 3.13 3.11 3.09 3.07 1.38 1.37 1.35 1.20 1.18 1.16
S
N
N
N
N
CO_2Et
0.96 1.04 1.04 1.04 2.00 2.14 1.99 2.97 3.03
9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0 -0.5
f1 (ppm)


169.56 151.89 146.09 131.93 129.62 125.56 119.82 114.39 77.48 77.16 76.84 61.47 54.15 28.86 15.43 14.34
180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0
f1 (ppm)

6

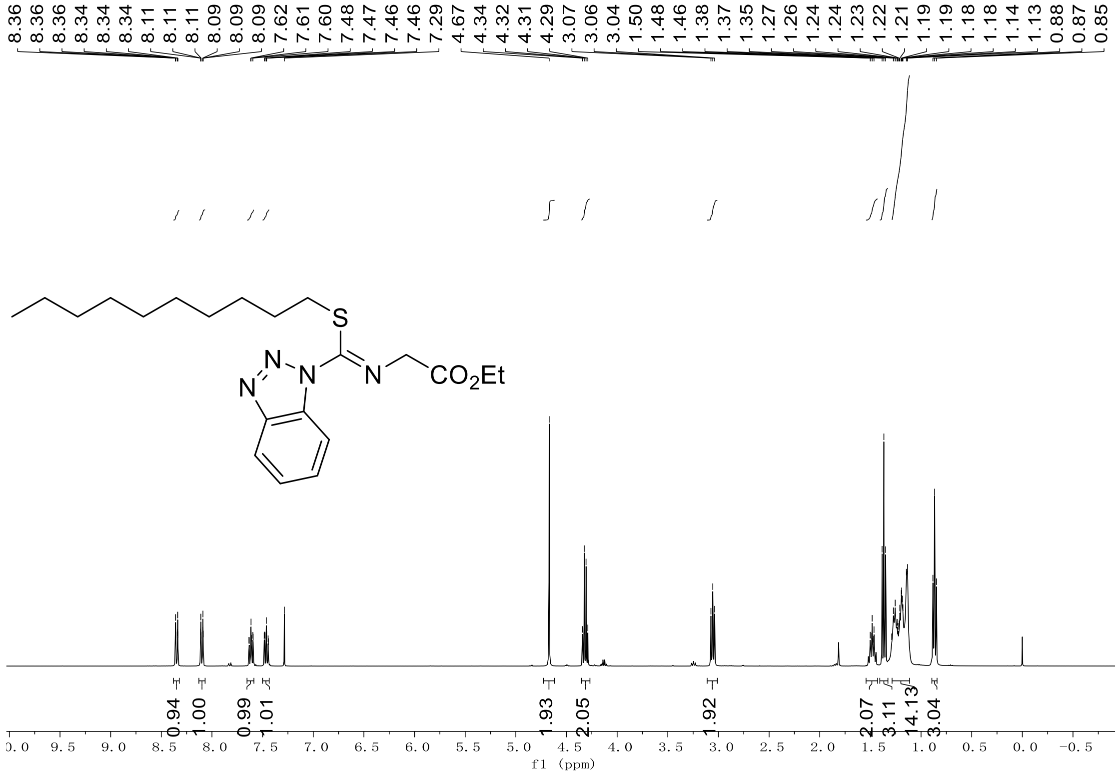


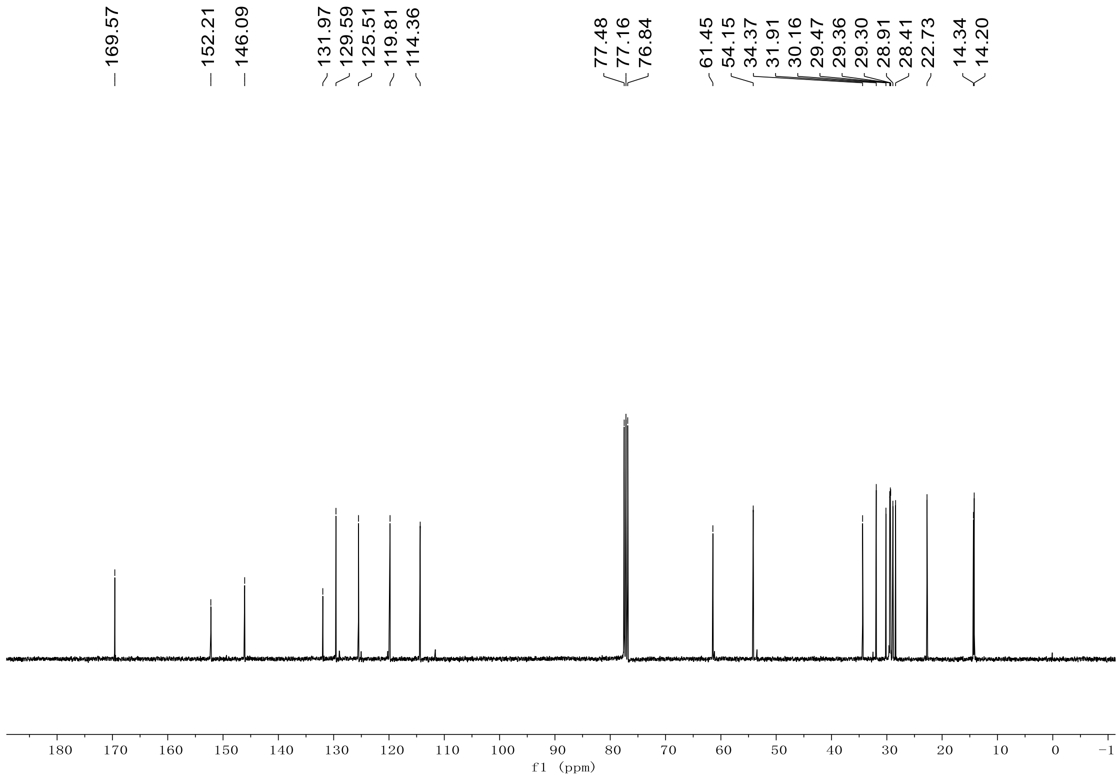
8.36 8.36 8.34 8.34 8.34 8.11 8.11 8.09 8.09 8.09 7.63 7.62 7.62 7.61 7.60 7.60 7.49 7.48 7.47 7.47 7.46 7.45 7.28 4.67 4.34 4.32 4.32 4.31 4.29 3.08 3.06 3.05 1.50 1.48 1.47 1.46 1.46 1.38 1.37 1.35 1.34 1.32 1.30 1.28 0.81 0.79 0.77
S
N
N
N
N
CO2Et
0.98
1.04
1.05
1.05
2.00
2.13
2.01
2.09
5.24
2.98
f1 (ppm)



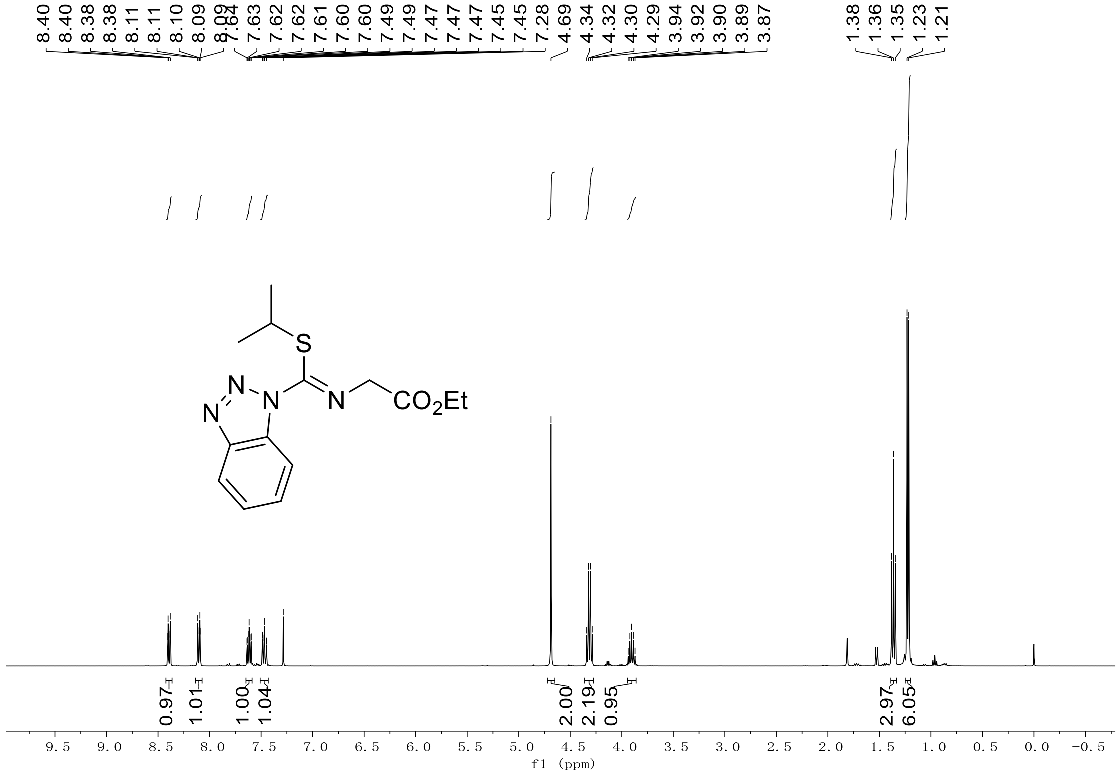
169.59
152.20
146.10
131.98
129.61
125.54
119.83
114.38
77.48
77.16
76.84
61.48
54.17
34.10
32.17
21.62
14.35
13.48
f1 (ppm)

7

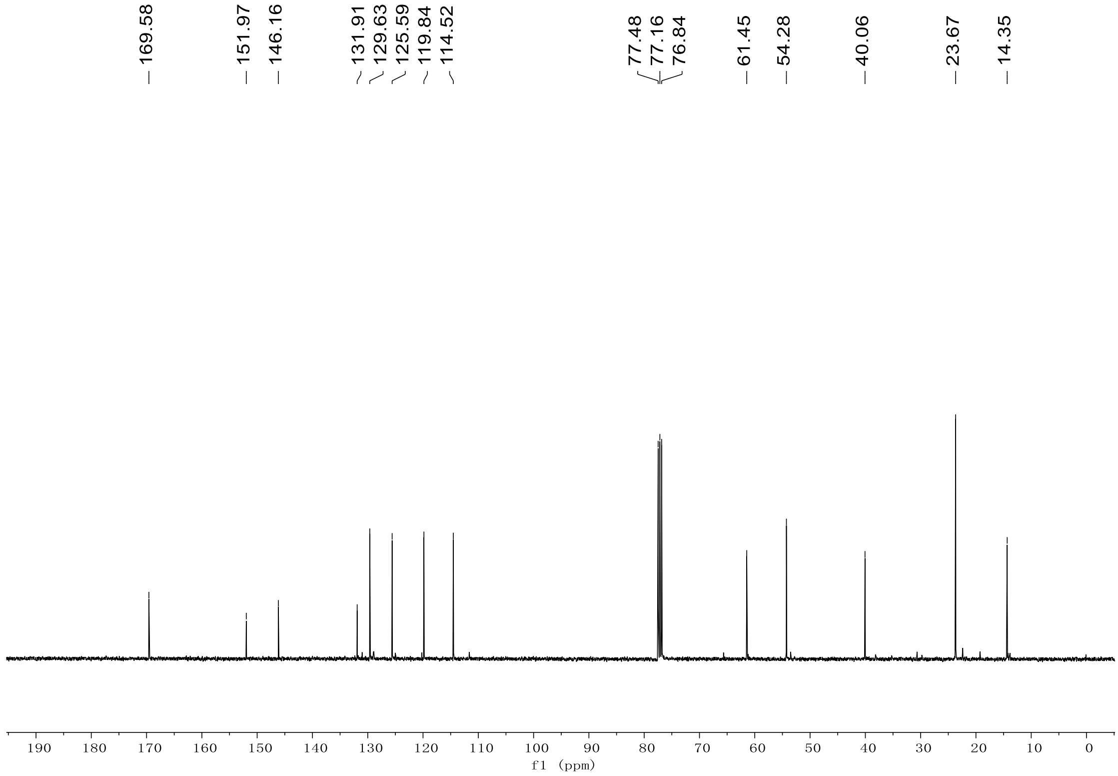




8

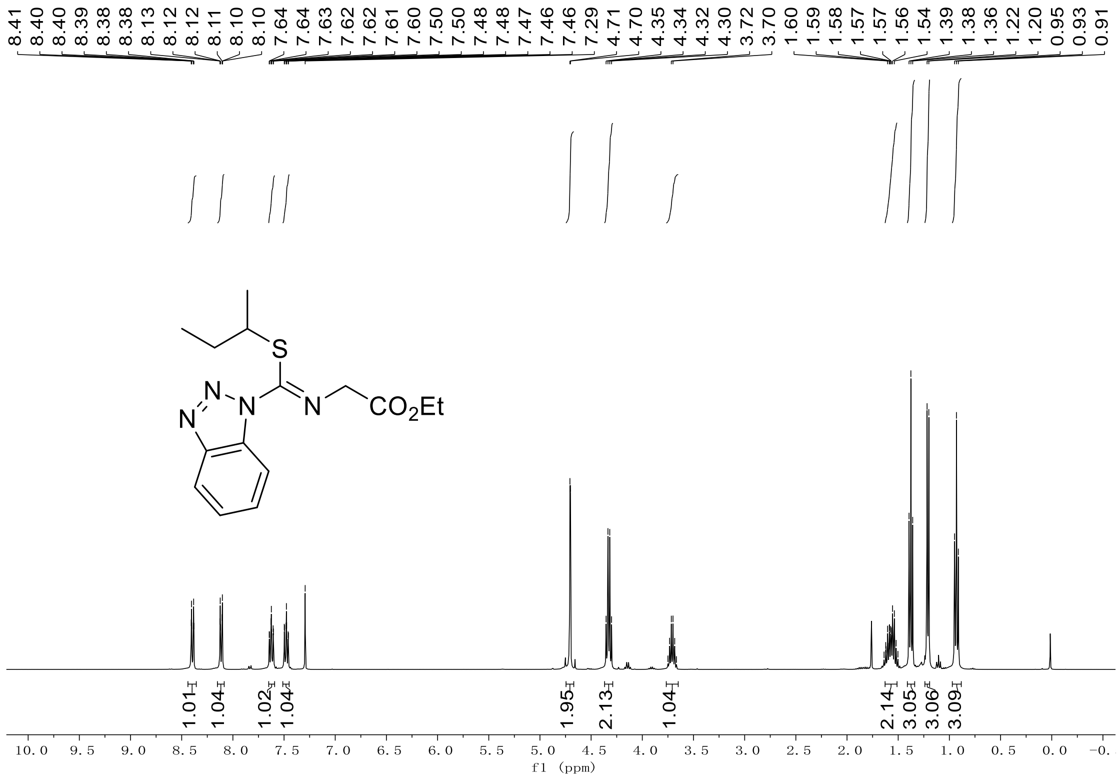


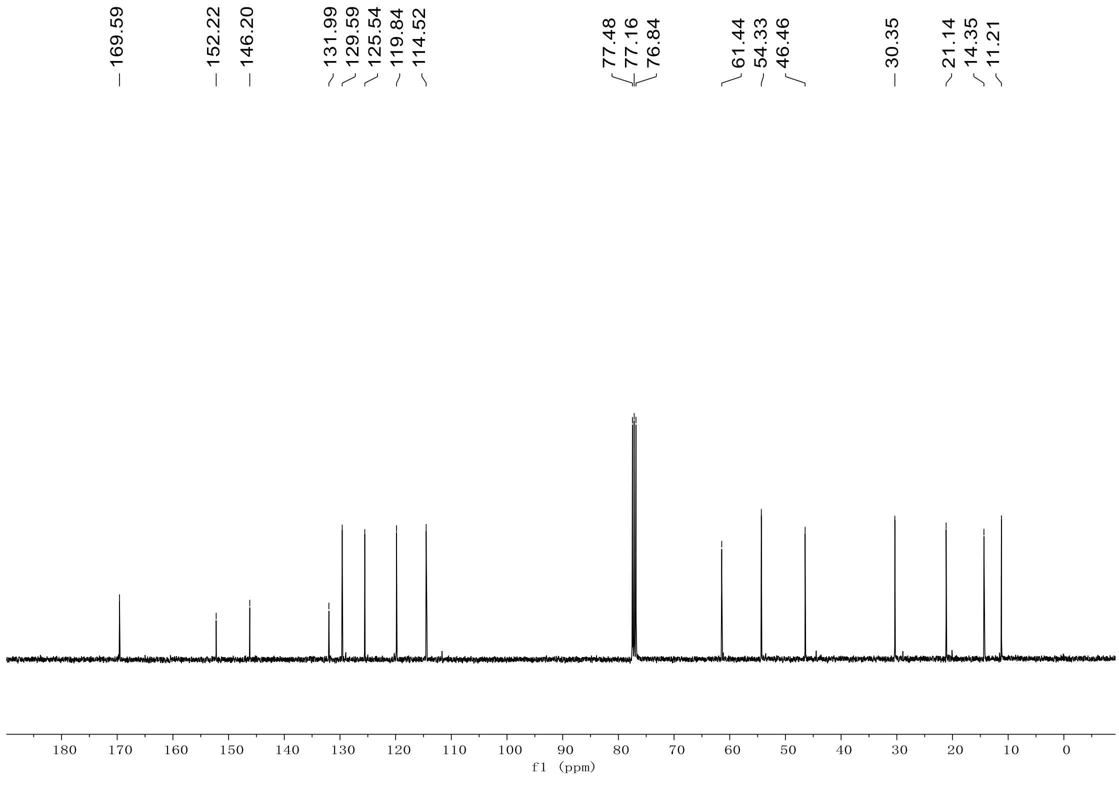
8.40 8.40 8.38 8.38 8.11 8.11 8.10 8.09 8.09 7.64 7.63 7.62 7.62 7.61 7.60 7.60 7.49 7.49 7.47 7.47 7.47 7.45 7.45 7.28 4.69 4.34 4.32 4.30 4.29 3.94 3.92 3.90 3.89 3.87
1.38 1.36 1.35 1.23 1.21
S
N
N
N
N
N
CO2Et
0.97
1.01
1.00
1.04
2.00
2.19
0.95
2.97
6.05
9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0 -0.5
f1 (ppm)



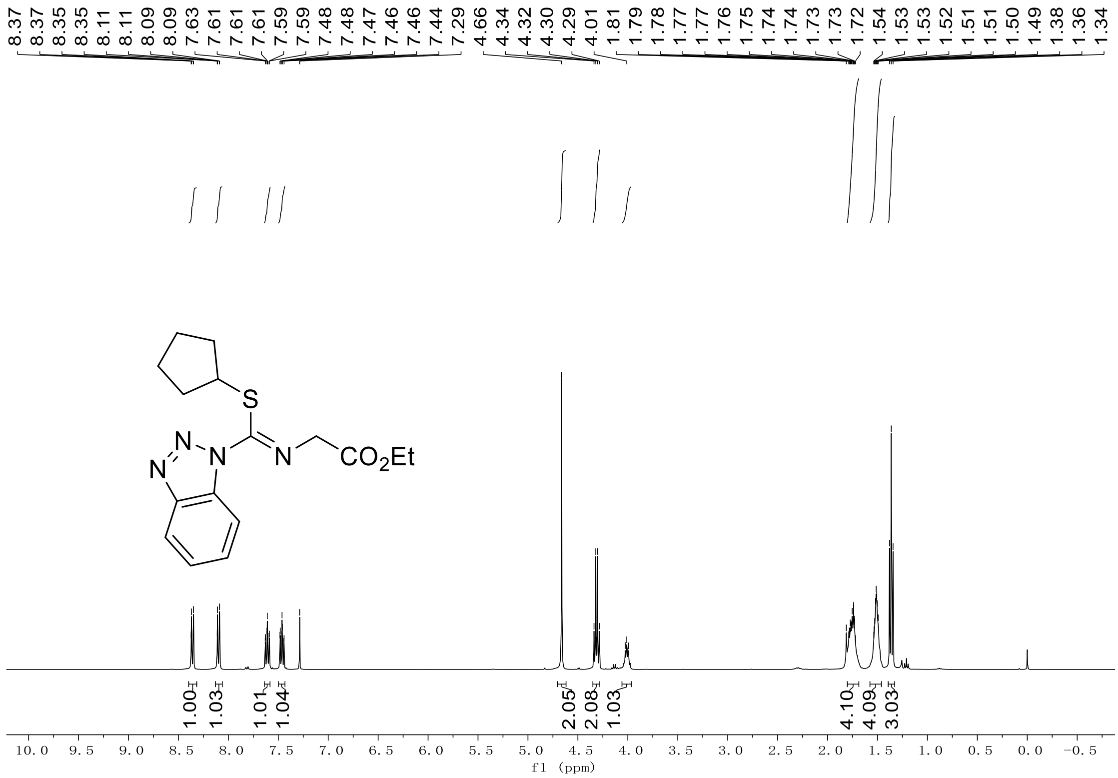
169.58
151.97
146.16
131.91 129.63 125.59 119.84 114.52
77.48 77.16 76.84
61.45
54.28
40.06
23.67
14.35
190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0
f1 (ppm)

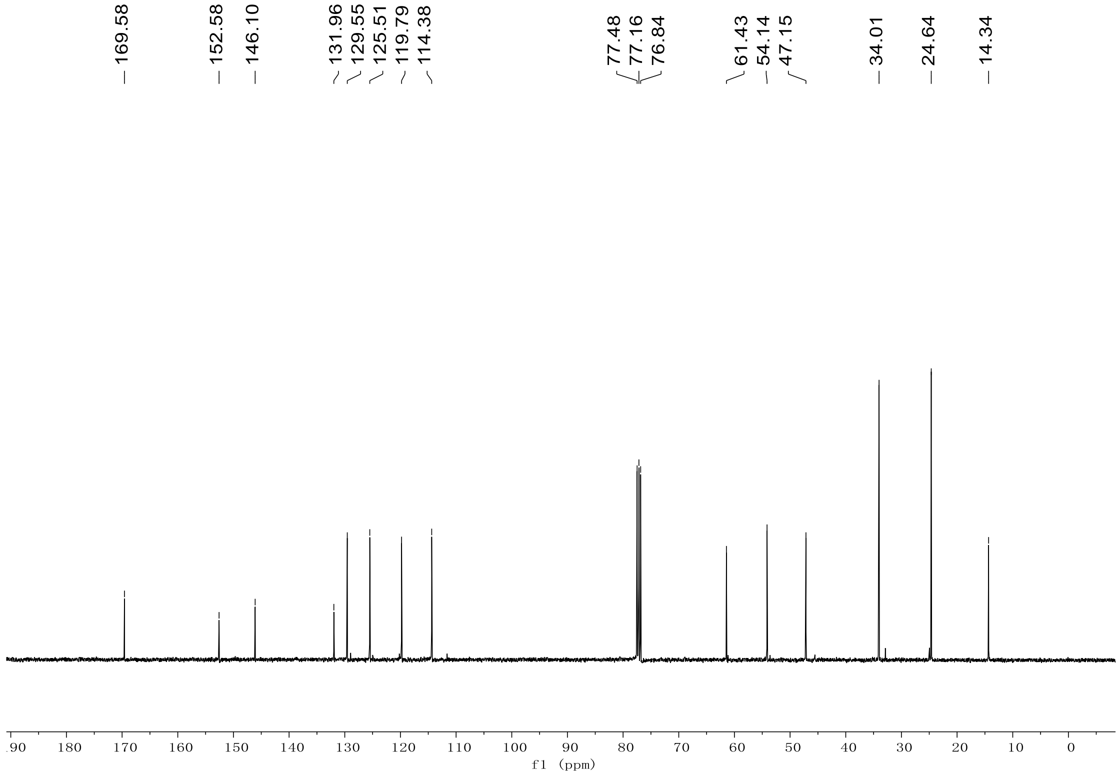
9


8.41 8.40 8.39 8.38 8.38 8.13 8.12 8.11 8.10 8.10 7.64 7.63 7.62 7.62 7.61 7.60 7.50 7.50 7.48 7.48 7.47 7.46 7.46 7.29 4.71 4.70 4.35 4.34 4.32 4.30 3.72 3.70 1.60 1.59 1.58 1.57 1.57 1.56 1.54 1.39 1.38 1.36 1.22 1.20 0.95 0.93 0.91
S
N
N
N
N
CO2Et
1.01 1.04 1.02 1.04 1.95 2.13 1.04 2.14 3.05 3.06 3.09
10.0 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 0.0 -0.
f1 (ppm)

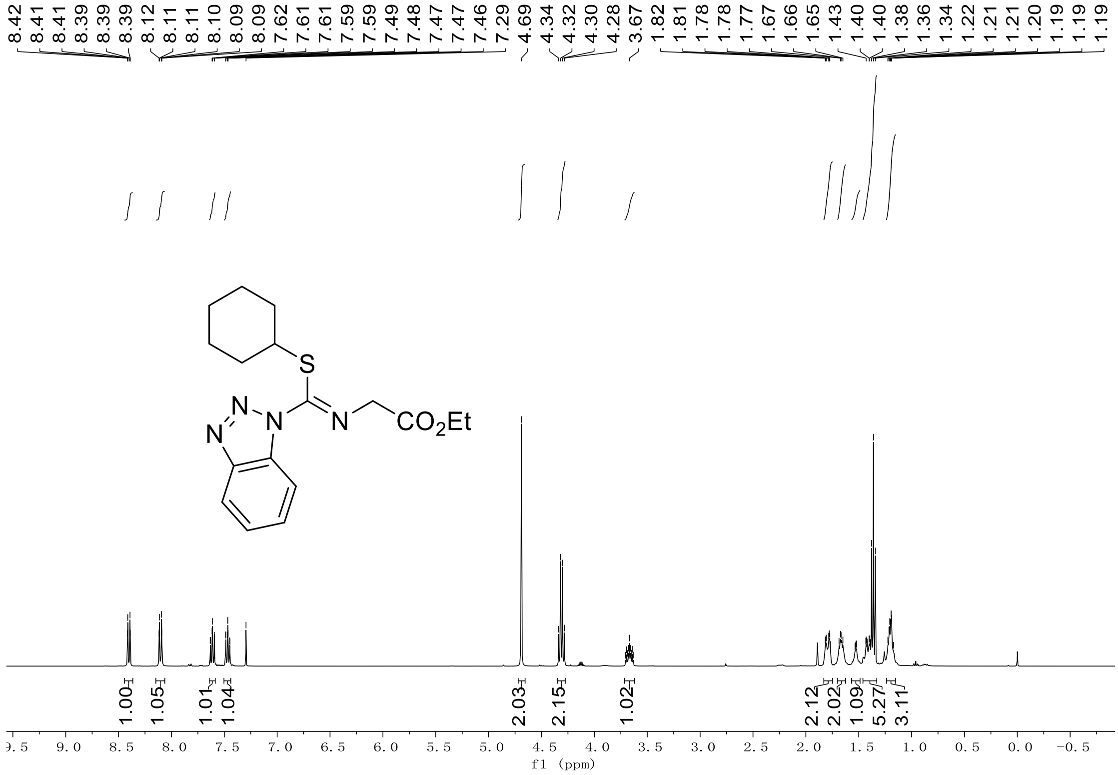

169.59
152.22
146.20
131.99 129.59 125.54 119.84 114.52
77.48 77.16 76.84
61.44 54.33 46.46
30.35
21.14 14.35 11.21
180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0
f1 (ppm)

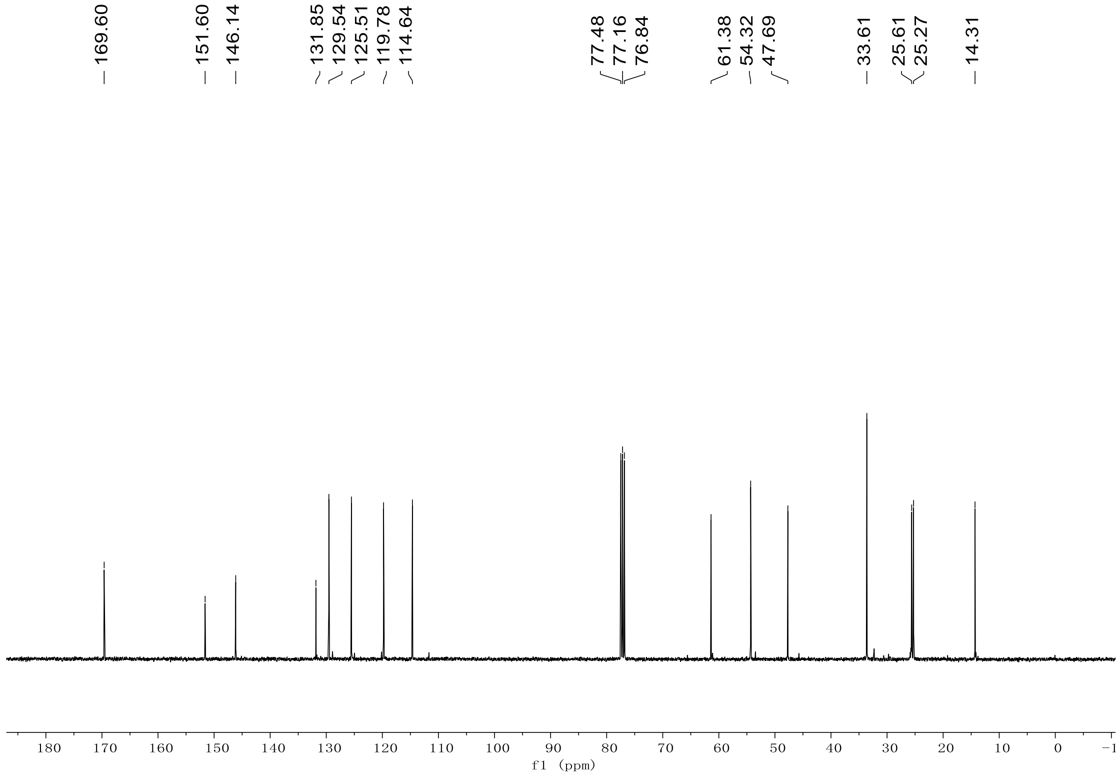
10


8.37 8.37 8.35 8.35 8.11 8.11 8.09 8.09 7.63 7.61 7.61 7.61 7.59 7.59 7.48 7.48 7.47 7.46 7.46 7.44 7.29 4.66 4.34 4.32 4.30 4.29 4.01 1.81 1.79 1.78 1.77 1.77 1.76 1.75 1.74 1.74 1.73 1.73 1.72 1.54 1.53 1.53 1.52 1.51 1.51 1.50 1.49 1.38 1.36 1.34
S
N
N
N
N
CO2Et
1.00
1.03
1.01
1.04
2.05
2.08
1.03
4.10
4.09
3.03
10.0 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 0.0 -0.5
f1 (ppm)

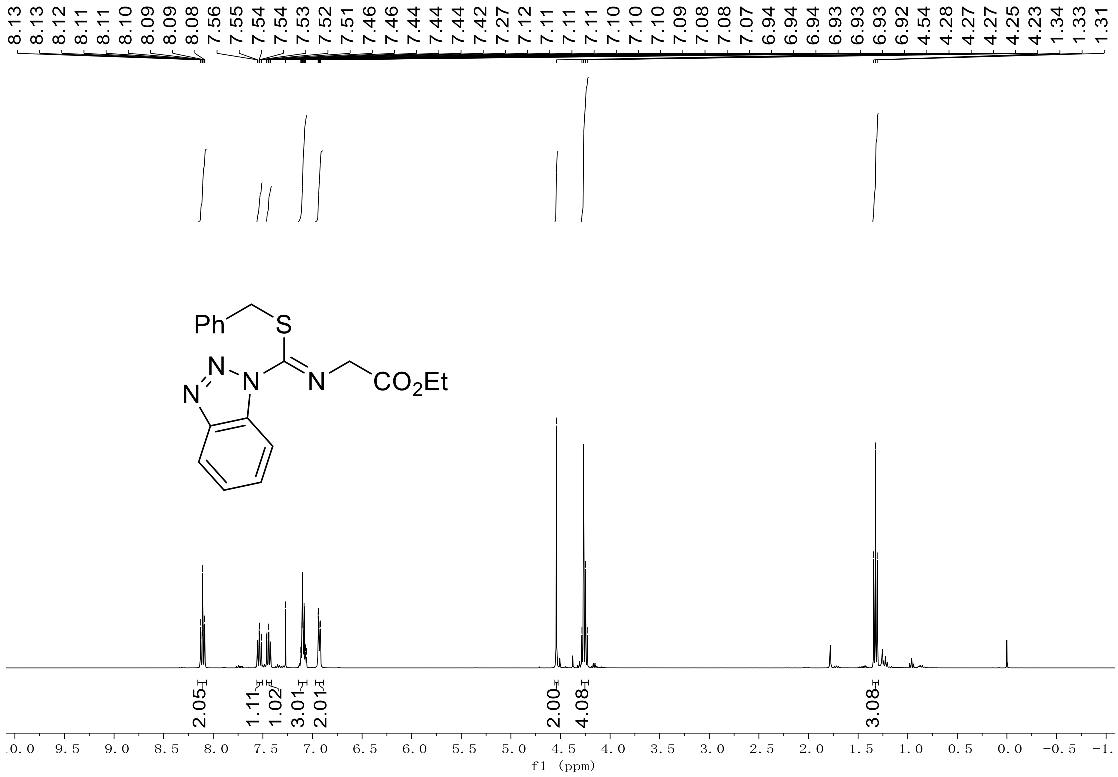

169.58
152.58
146.10
131.96 129.55 125.51 119.79 114.38
77.48 77.16 76.84
61.43 54.14 47.15
34.01
24.64
14.34
190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0
f1 (ppm)

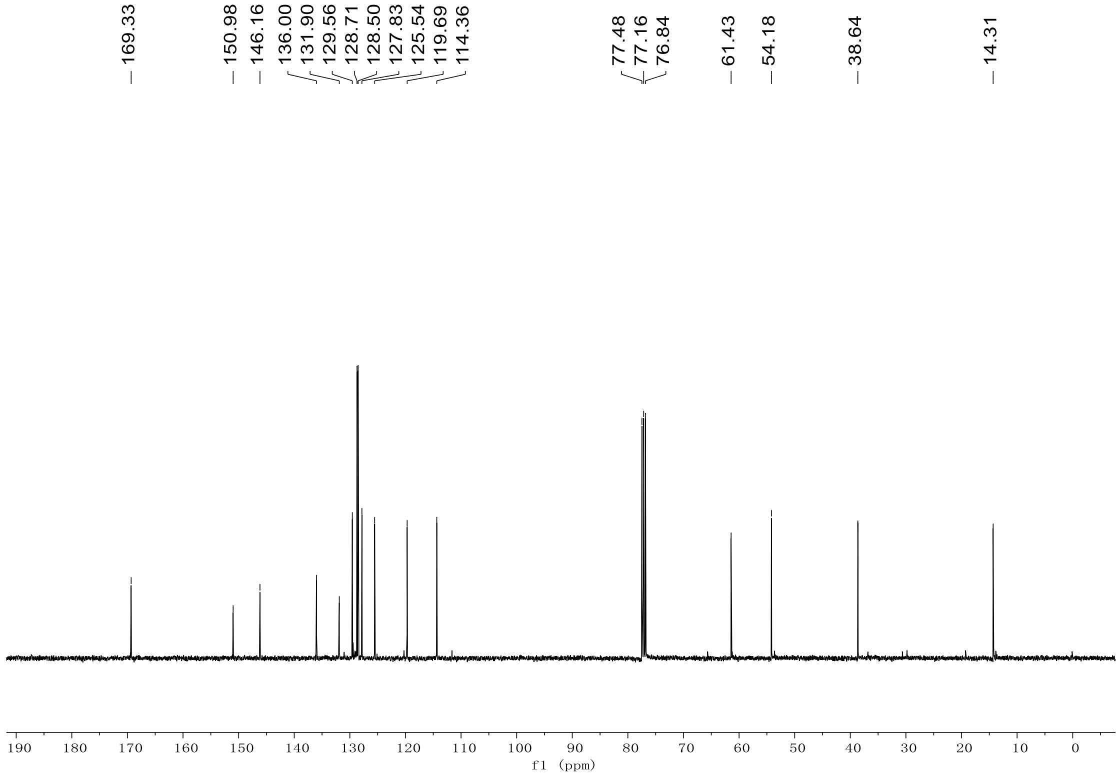
11


8.42 8.41 8.41 8.39 8.39 8.39 8.12 8.11 8.11 8.10 8.09 8.09 7.62 7.61 7.61 7.59 7.59 7.49 7.48 7.47 7.47 7.46 7.29 4.69 4.34 4.32 4.30 4.28 3.67 1.82 1.81 1.78 1.78 1.77 1.67 1.66 1.65 1.43 1.40 1.40 1.38 1.36 1.34 1.22 1.21 1.20 1.19 1.19 1.19
S
N
N
N
N
CO2Et
1.00
1.05
1.01
1.04
2.03
2.15
1.02
2.12
2.02
1.09
5.27
3.11
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 0.0 -0.5
f1 (ppm)

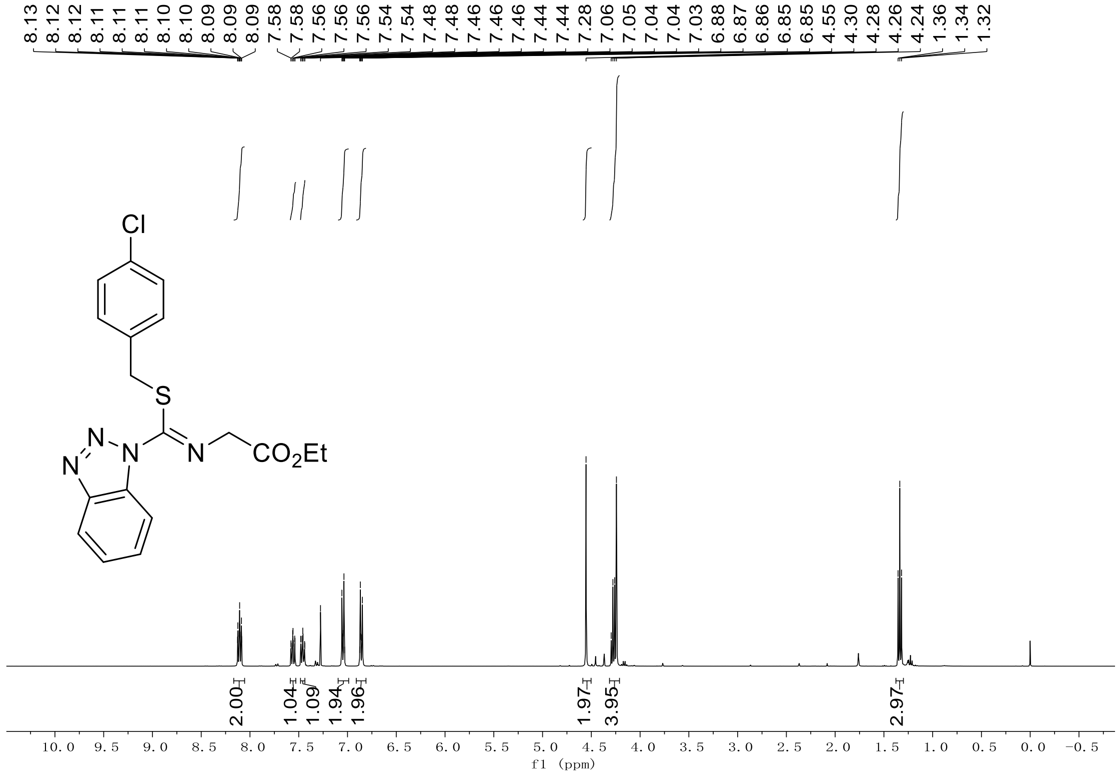

169.60
151.60
146.14
131.85 129.54 125.51 119.78 114.64
77.48 77.16 76.84
61.38 54.32 47.69
33.61
25.61 25.27
14.31
180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 -1
f1 (ppm)

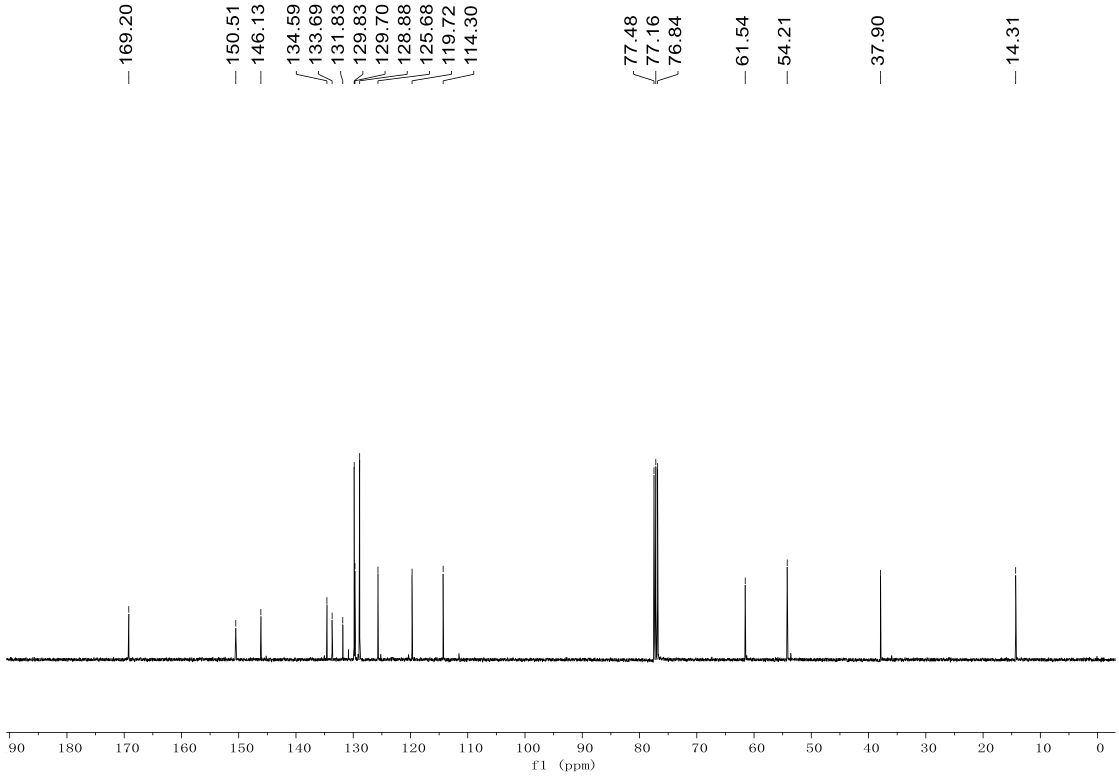
12


8.13 8.13 8.12 8.11 8.11 8.10 8.09 8.09 8.08 7.56 7.55 7.54 7.54 7.53 7.52 7.51 7.46 7.44 7.44 7.44 7.42 7.27 7.12 7.11 7.11 7.11 7.10 7.10 7.09 7.08 7.08 7.07 6.94 6.94 6.94 6.93 6.93 6.92 4.54 4.28 4.27 4.27 4.25 4.23 1.34 1.33 1.31
Ph
S
N
N
N
N
CO_2Et
2.05
1.11
1.02
3.01
2.01
2.00
4.08
3.08
10.0 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 0.0 −0.5 −1.
f1 (ppm)

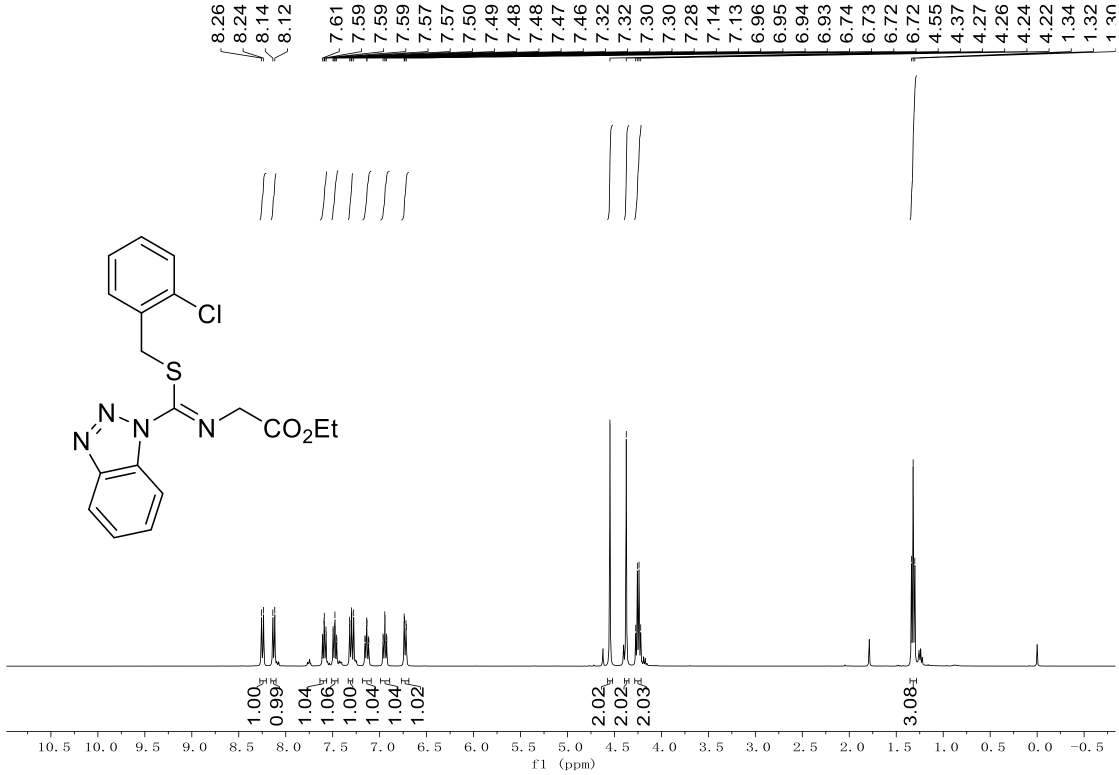

169.33
150.98 146.16 136.00 131.90 129.56 128.71 128.50 127.83 125.54 119.69 114.36
77.48 77.16 76.84
61.43
54.18
38.64
14.31
190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0
f1 (ppm)

13

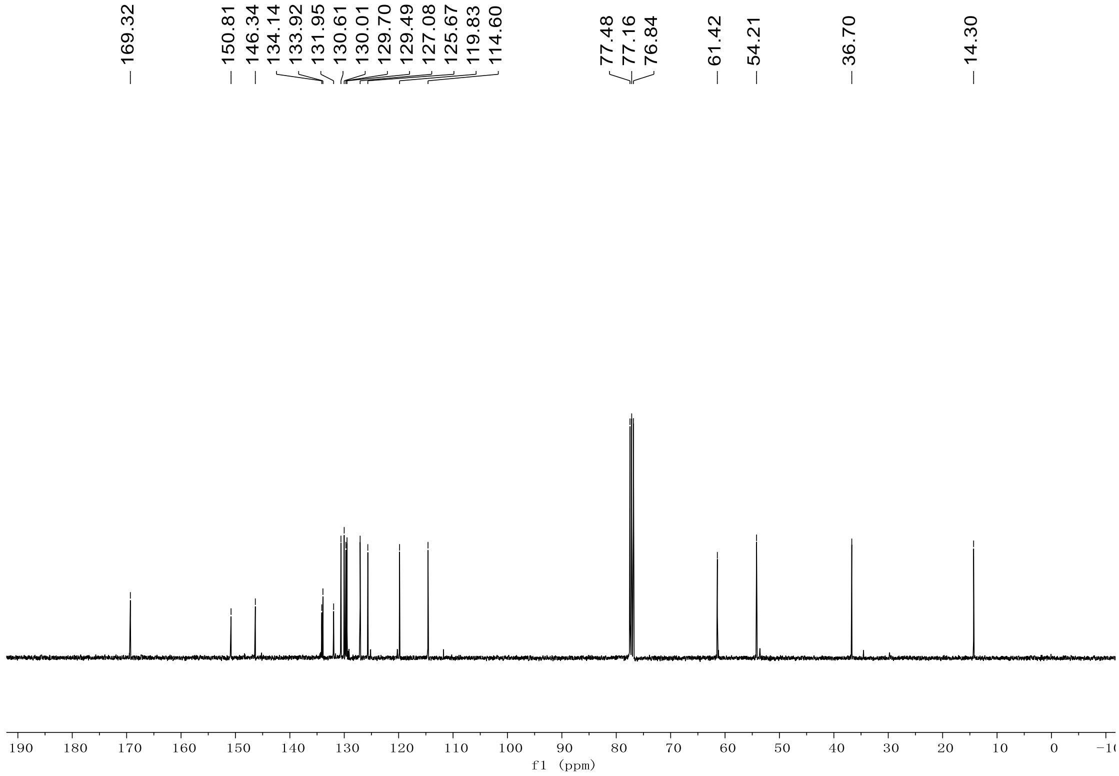

8.13 8.12 8.12 8.11 8.11 8.10 8.10 8.09 8.09 7.58 7.58 7.56 7.56 7.54 7.54 7.48 7.48 7.46 7.46 7.44 7.44 7.28 7.06 7.05 7.04 7.04 7.03 6.88 6.87 6.86 6.85 6.85 4.55 4.30 4.28 4.26 4.24 1.36 1.34 1.32
Cl
S
N
N
N
N
CO2Et
2.00
1.04
1.09
1.94
1.96
1.97
3.95
2.97
10.0 9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0 -0.5
f1 (ppm)


169.20
150.51 146.13
134.59 133.69 131.83 129.83 129.70 128.88 125.68 119.72 114.30
77.48 77.16 76.84
61.54 54.21
37.90
14.31
190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0
f1 (ppm)

14

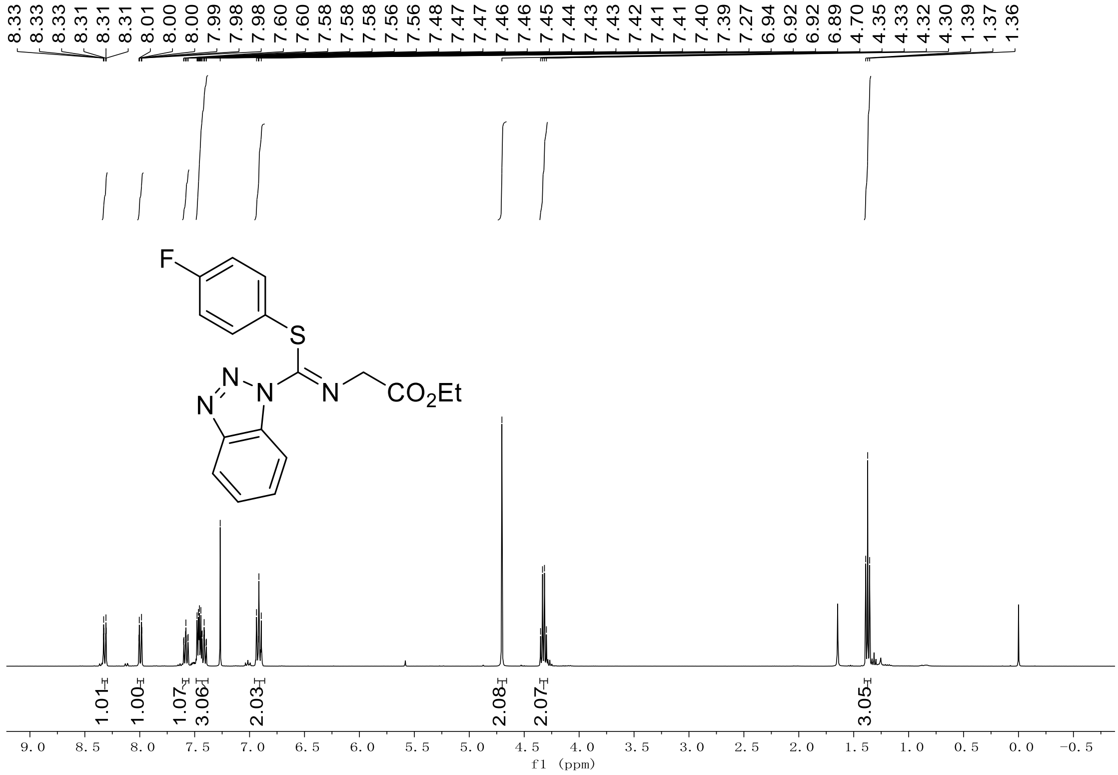


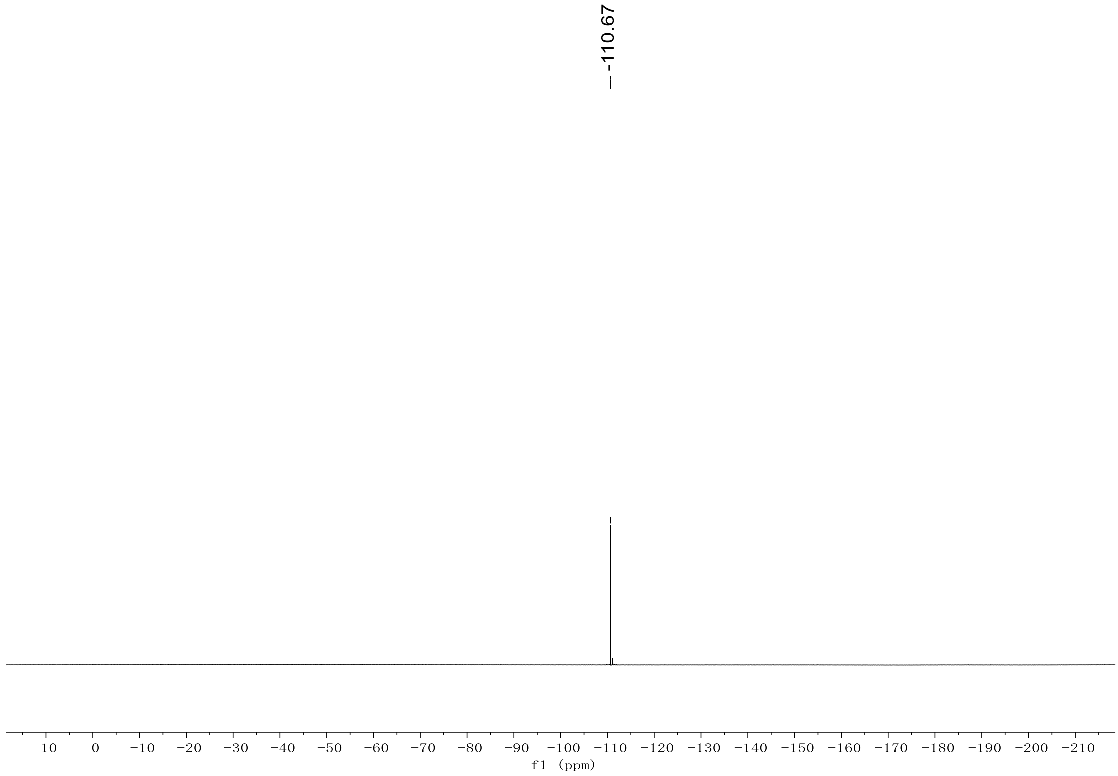
8.26 8.24 8.14 8.12 7.61 7.59 7.59 7.59 7.57 7.57 7.50 7.49 7.48 7.48 7.47 7.46 7.32 7.32 7.30 7.30 7.28 7.14 7.13 6.96 6.95 6.94 6.93 6.74 6.73 6.72 6.72 4.55 4.37 4.27 4.26 4.24 4.22 1.34 1.32
Cl
S
N
N
N
N
CO2Et
1.00 0.99 1.04 1.06 1.00 1.04 1.04 1.02 2.02 2.02 2.03 3.08
f1 (ppm)

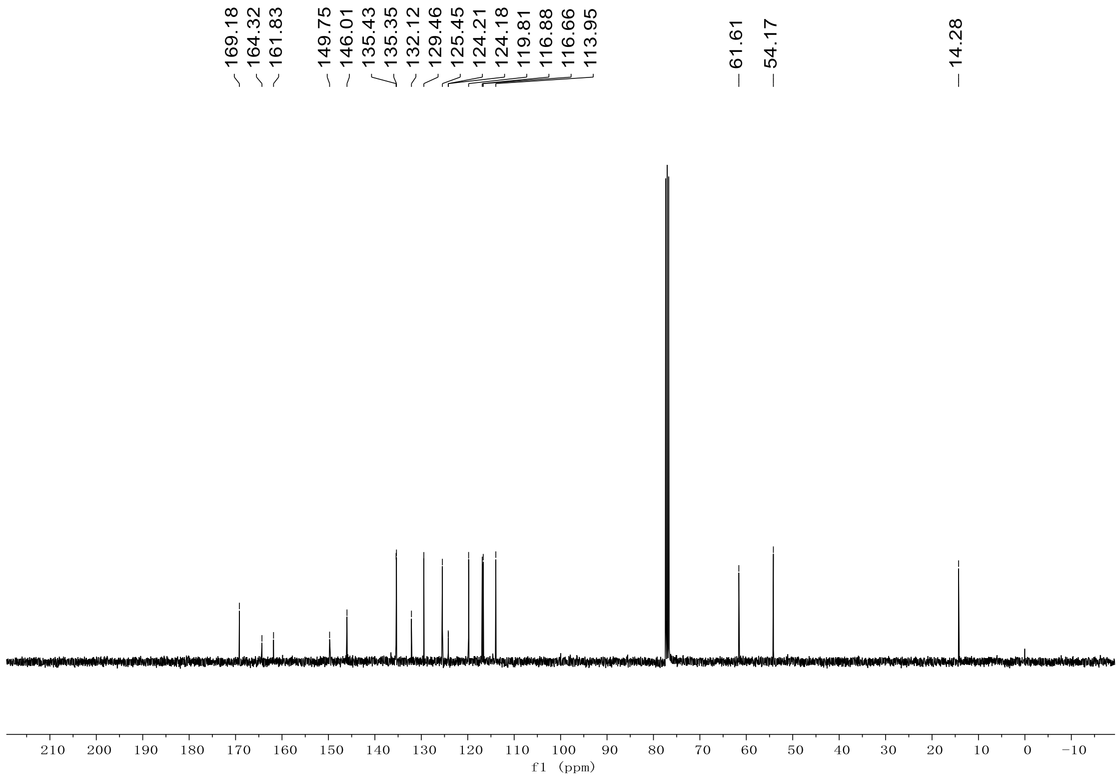


169.32 150.81 146.34 134.14 133.92 131.95 130.61 130.01 129.70 129.49 127.08 125.67 119.83 114.60 77.48 77.16 76.84 61.42 54.21 36.70 14.30
f1 (ppm)

15

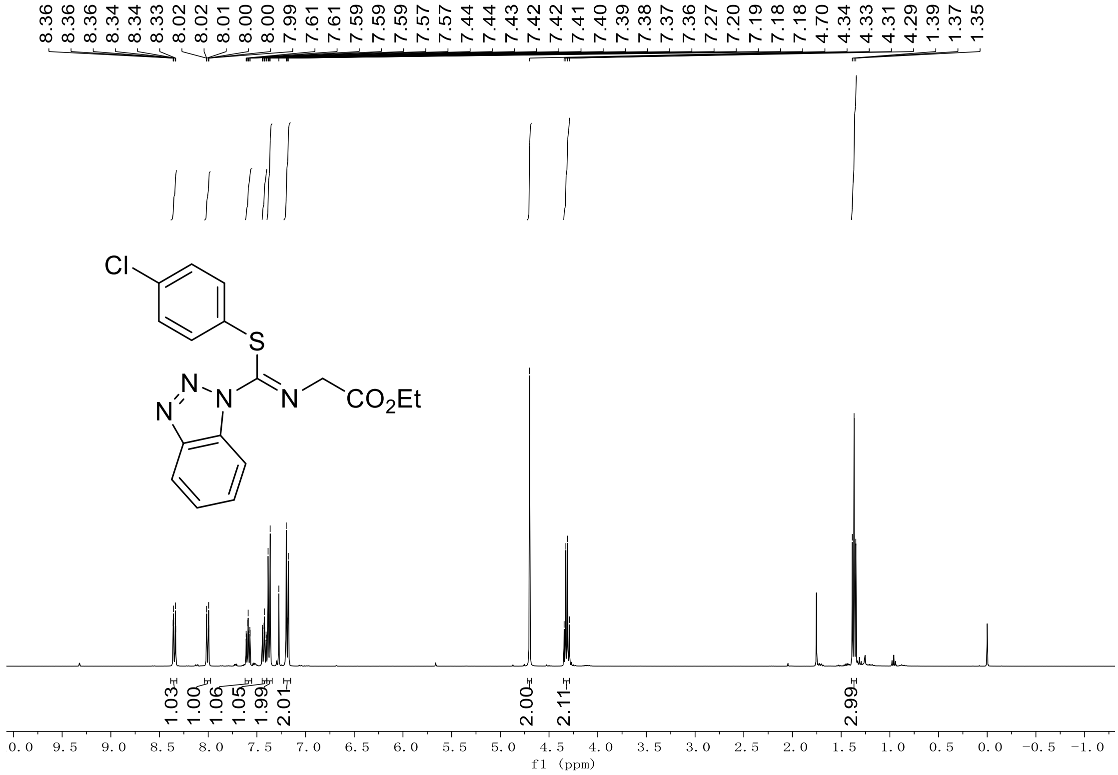

8.33
8.33
8.31
8.31
8.01
8.00
8.00
7.99
7.98
7.98
7.60
7.58
7.58
7.58
7.56
7.56
7.48
7.47
7.47
7.46
7.46
7.45
7.44
7.43
7.43
7.42
7.41
7.41
7.40
7.39
7.27
6.94
6.92
6.92
6.89
4.70
4.35
4.33
4.32
4.30
1.39
1.37
1.36
F
S
N
N
N
N
CO2Et
1.01
1.00
1.07
3.06
2.03
2.08
2.07
3.05
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
-0.5
f1 (ppm)


-110.67
10
0
-10
-20
-30
-40
-50
-60
-70
-80
-90
-100
-110
-120
-130
-140
-150
-160
-170
-180
-190
-200
-210
f1 (ppm)

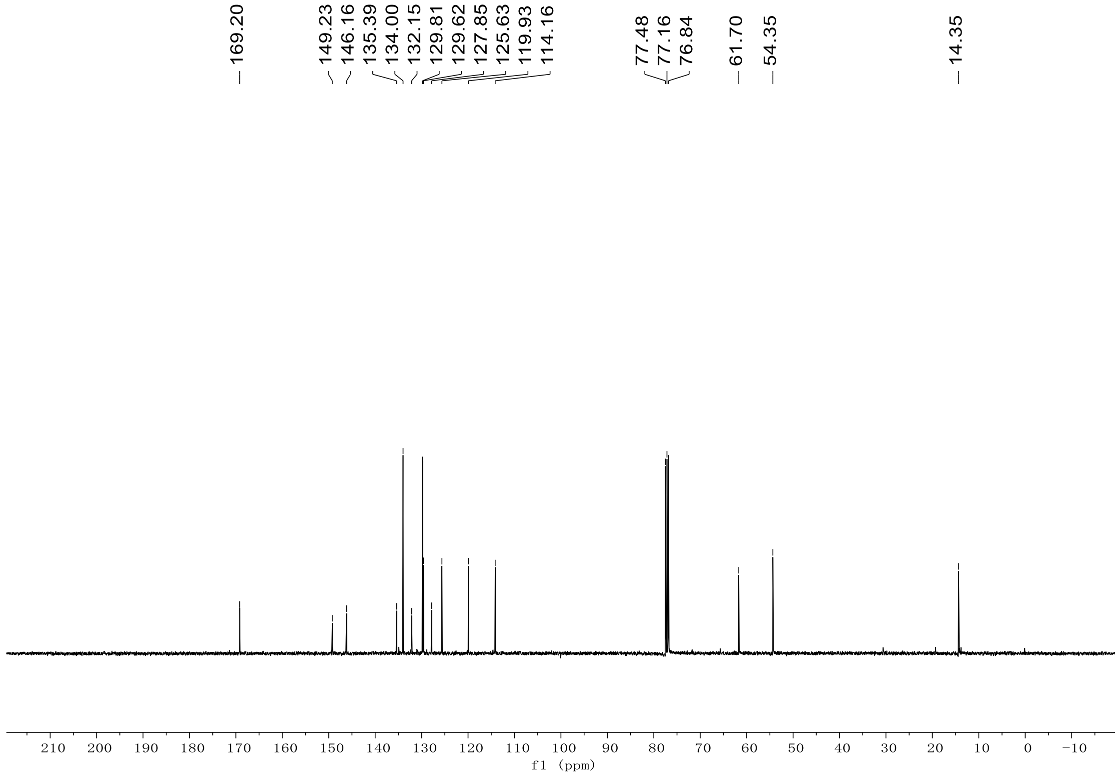


169.18
164.32
161.83
149.75
146.01
135.43
135.35
132.12
129.46
125.45
124.21
124.18
119.81
116.88
116.66
113.95
61.61
54.17
14.28
210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 -10
f1 (ppm)

16

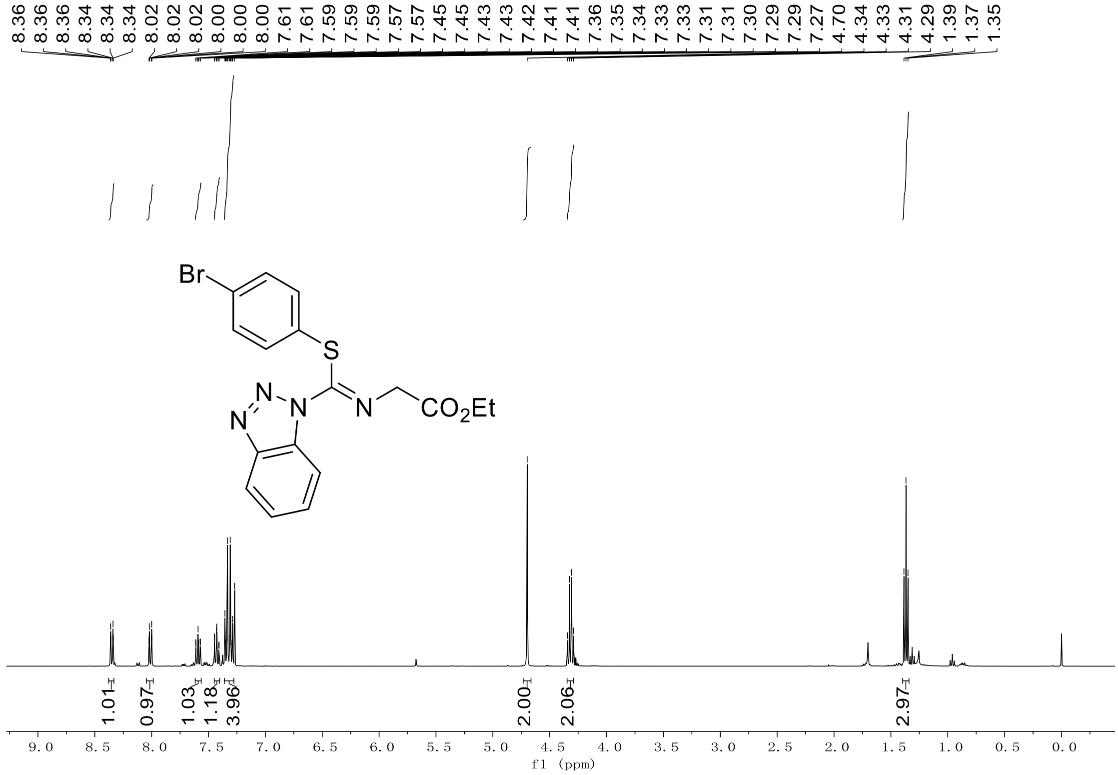


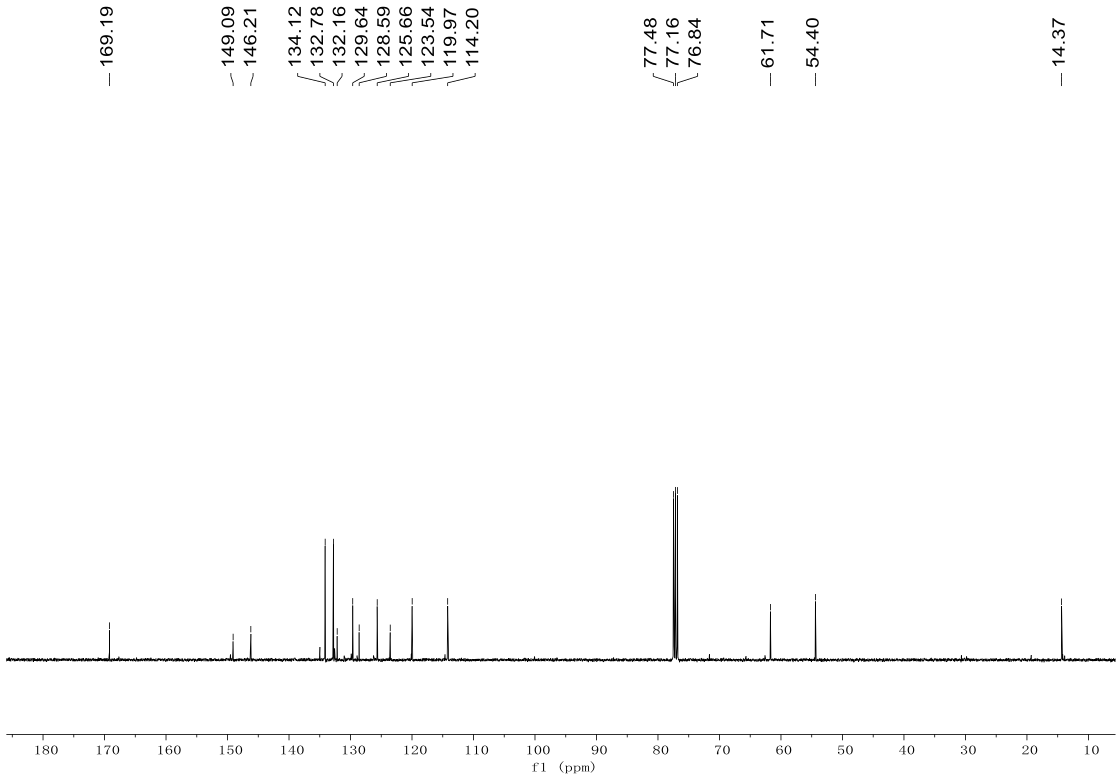
Cl
S
N
N
N
N
CO2Et
f1 (ppm)



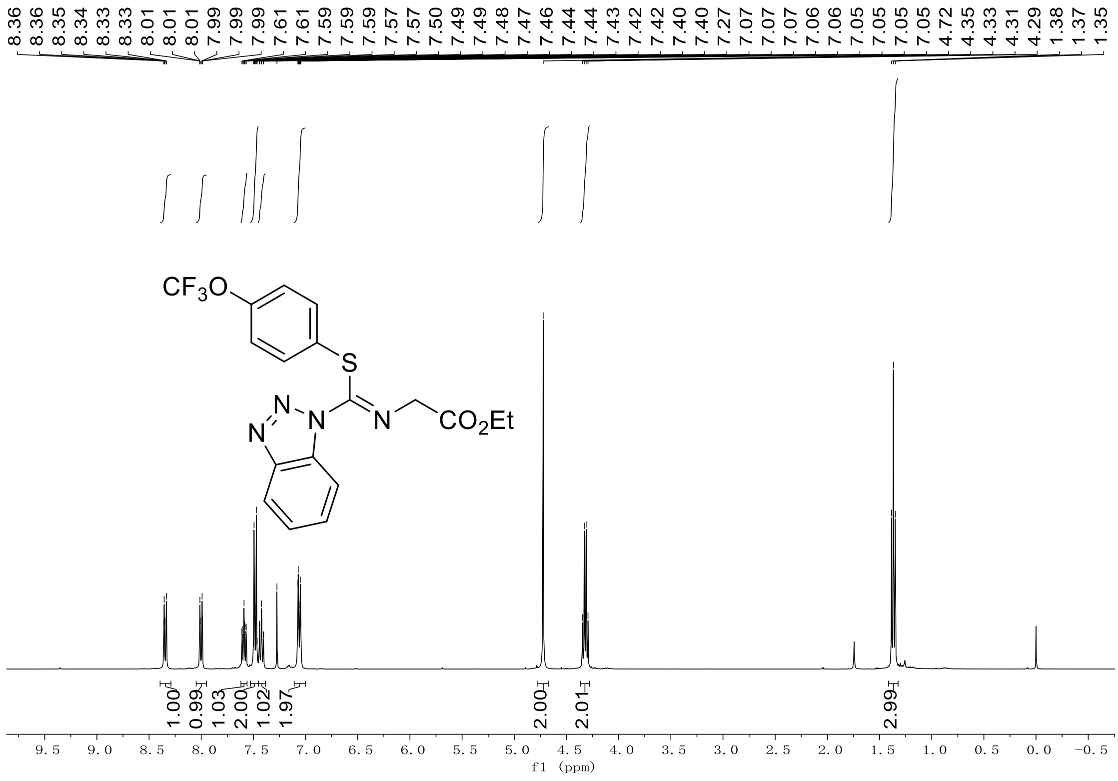
169.20
149.23
146.16
135.39
134.00
132.15
129.81
129.62
127.85
125.63
119.93
114.16
77.48
77.16
76.84
61.70
54.35
14.35
f1 (ppm)

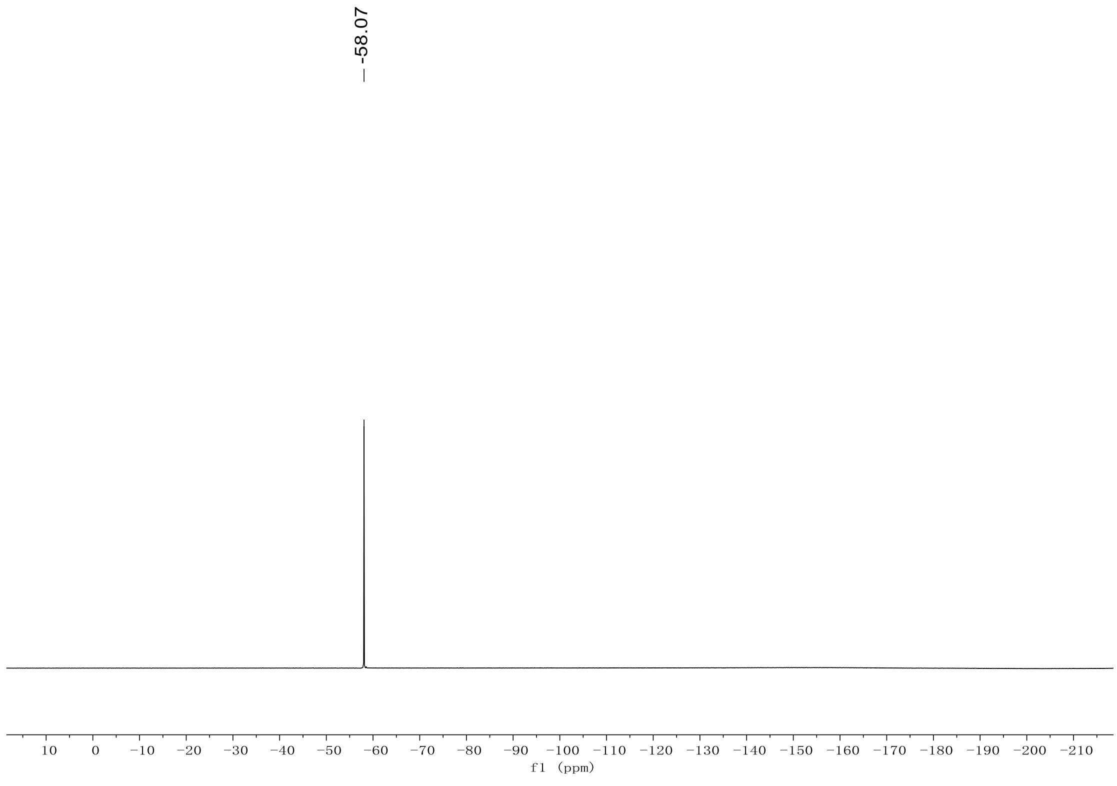
17

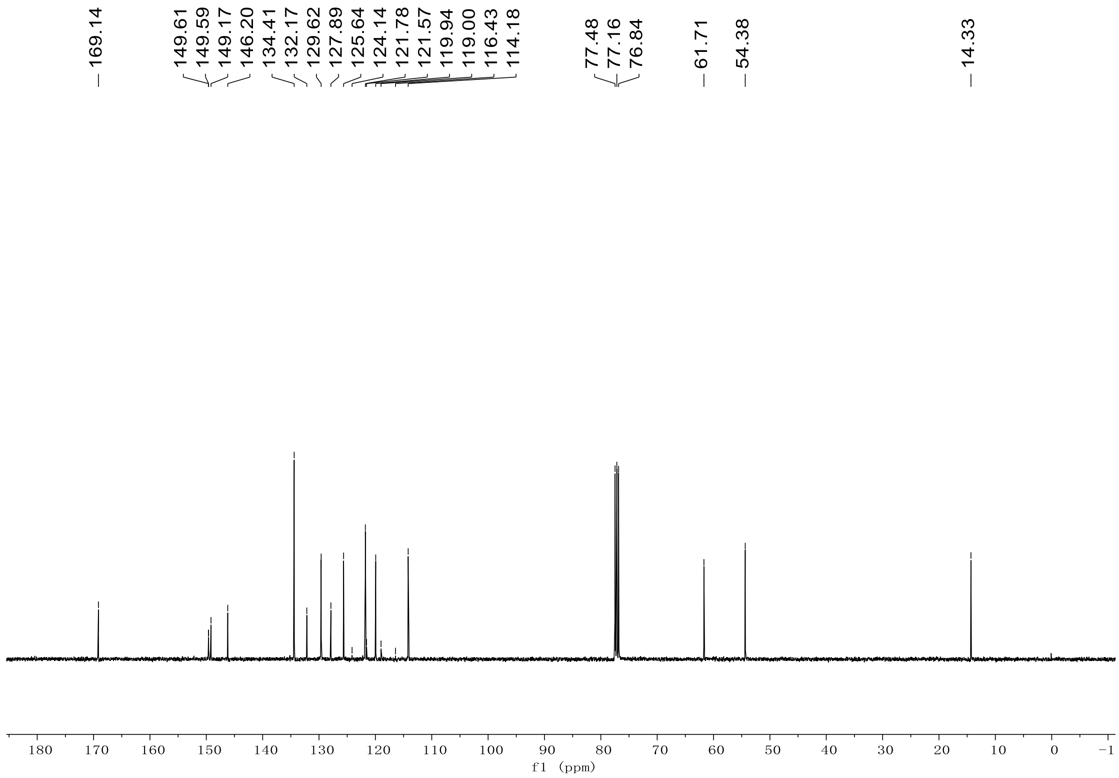

8.36 8.36 8.34 8.34 8.34 8.02 8.02 8.02 8.00 8.00 8.00 7.61 7.61 7.59 7.59 7.59 7.57 7.57 7.45 7.45 7.43 7.43 7.42 7.41 7.41 7.36 7.35 7.34 7.33 7.33 7.31 7.31 7.30 7.29 7.29 7.27 4.70 4.34 4.33 4.31 4.29 1.39 1.37 1.35
Br
S
N
N
N
N
CO_2Et
1.01 0.97 1.03 1.18 3.96 2.00 2.06 2.97
9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0
f1 (ppm)


169.19 149.09 146.21 134.12 132.78 132.16 129.64 128.59 125.66 123.54 119.97 114.20 77.48 77.16 76.84 61.71 54.40 14.37
180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10
f1 (ppm)

18

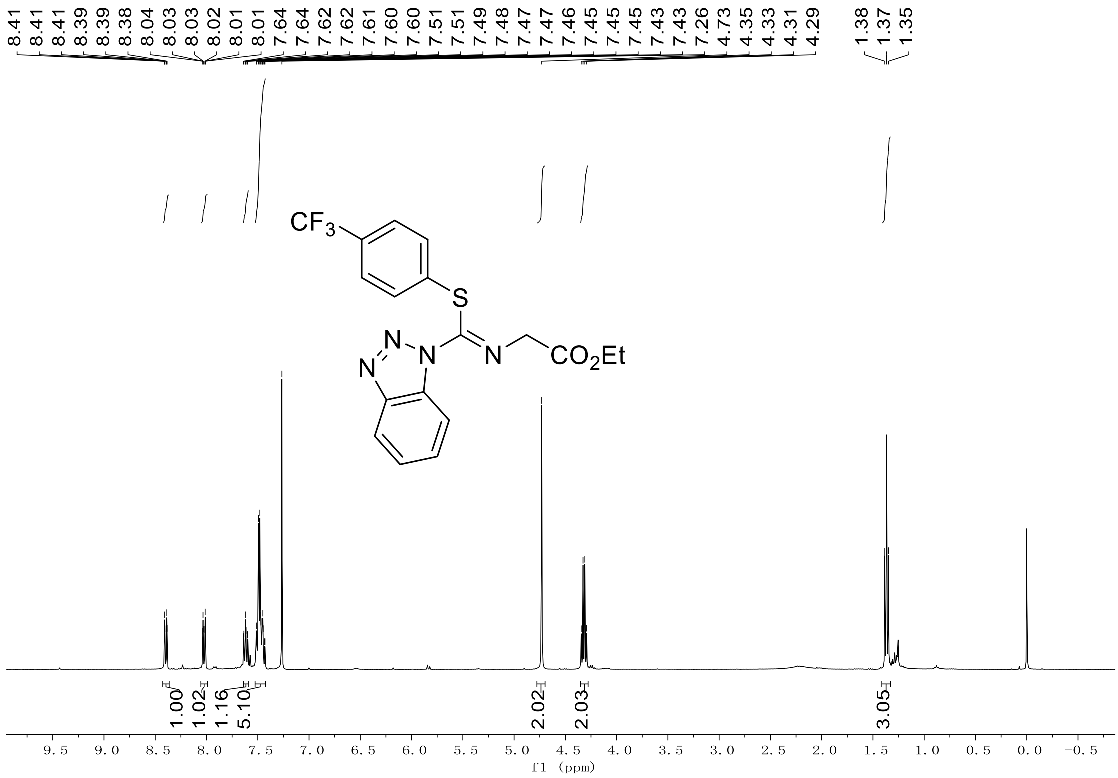




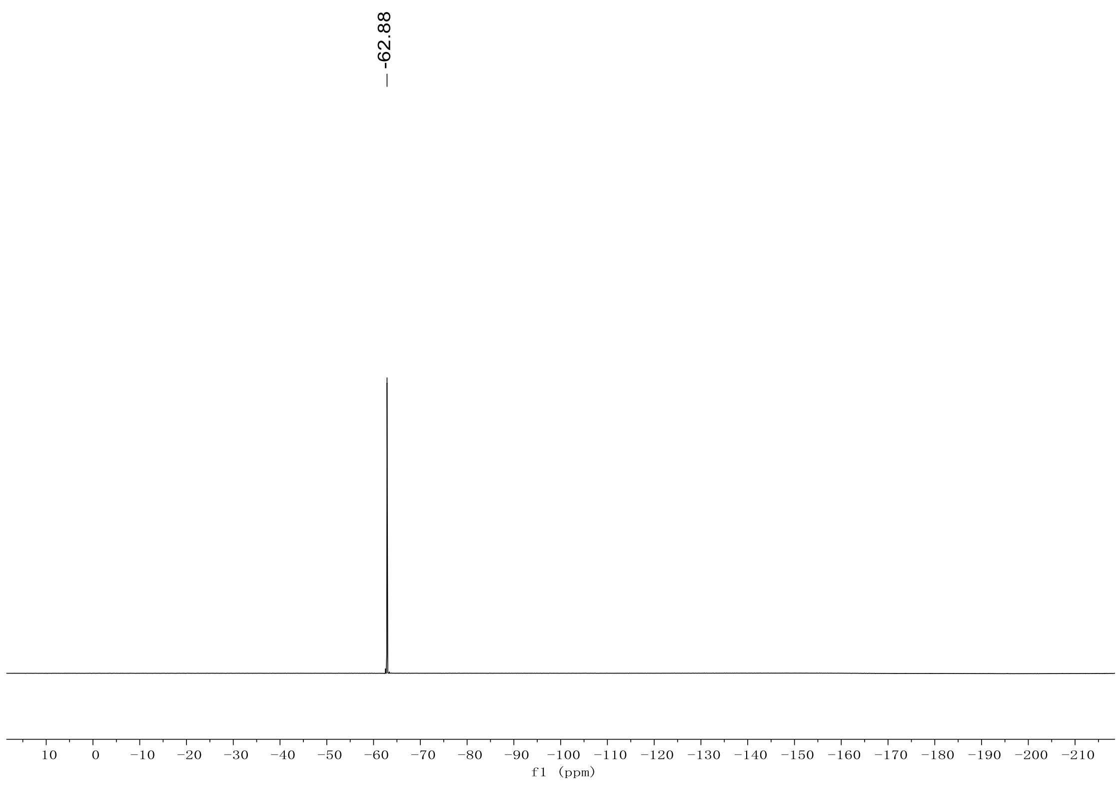


169.14
149.61
149.59
149.17
146.20
134.41
132.17
129.62
127.89
125.64
124.14
121.78
121.57
119.94
119.00
116.43
114.18
77.48
77.16
76.84
61.71
54.38
14.33
180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 -1
f1 (ppm)

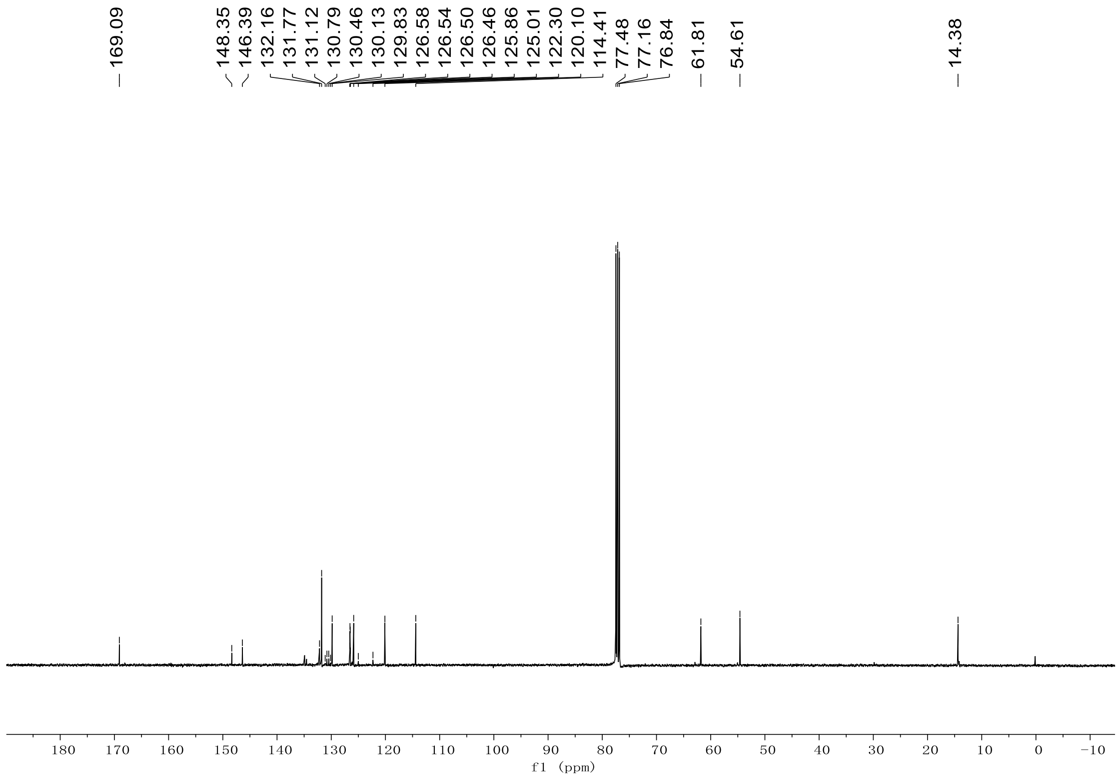
19



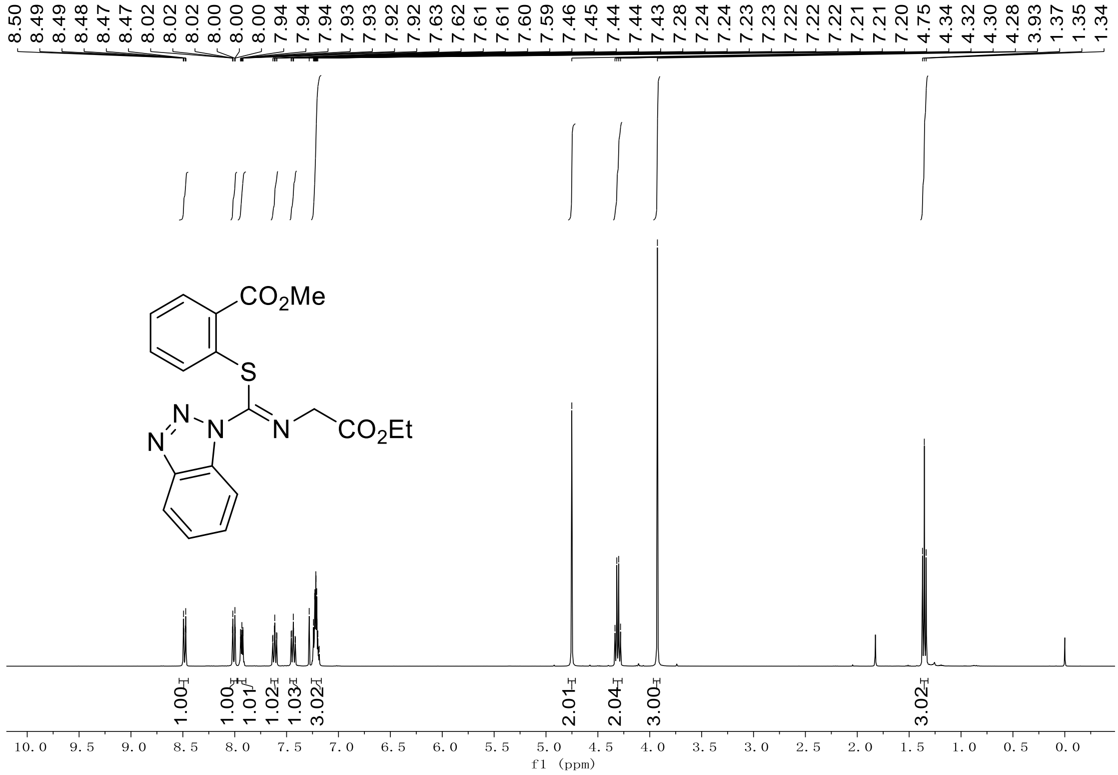
8.41
8.41
8.41
8.39
8.39
8.38
8.04
8.03
8.03
8.02
8.01
8.01
7.64
7.64
7.62
7.62
7.61
7.60
7.60
7.51
7.51
7.49
7.48
7.47
7.47
7.46
7.45
7.45
7.45
7.43
7.43
7.26
4.73
4.35
4.33
4.31
4.29
1.38
1.37
1.35
CF3
S
N
N
N
N
CO2Et
1.00
1.02
1.16
5.10
2.02
2.03
3.05
9.5
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
-0.5
f1 (ppm)

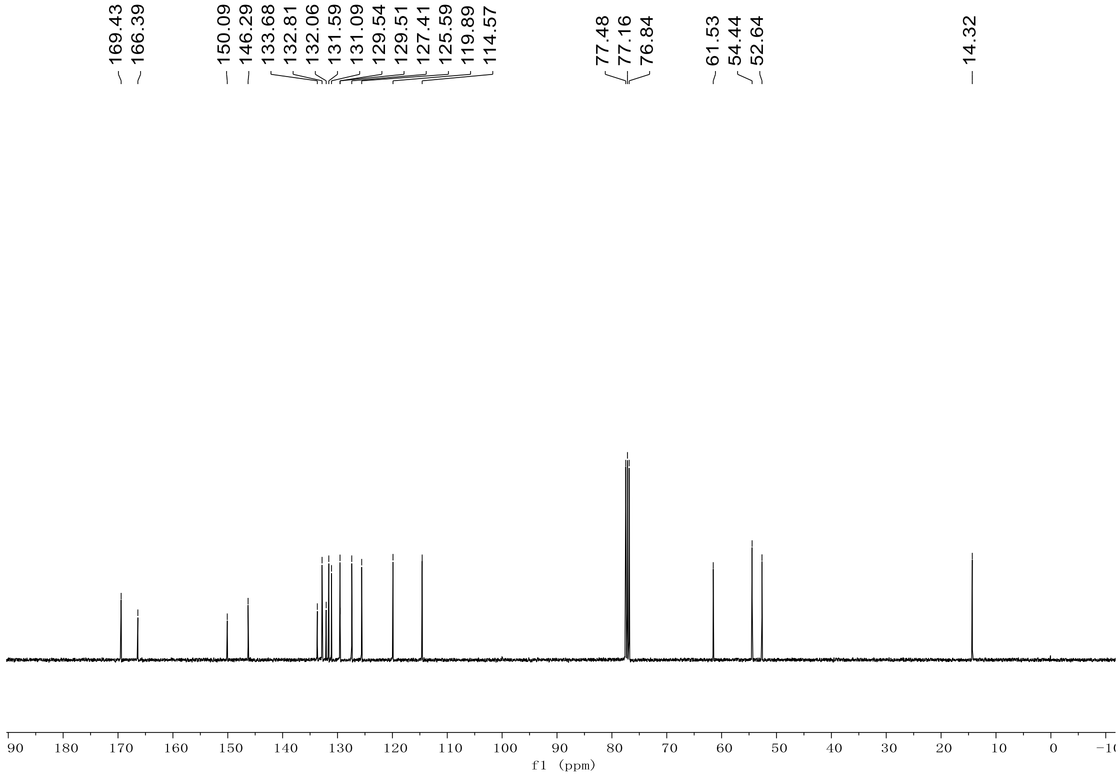


-62.88
10
0
-10
-20
-30
-40
-50
-60
-70
-80
-90
-100
-110
-120
-130
-140
-150
-160
-170
-180
-190
-200
-210
f1 (ppm)

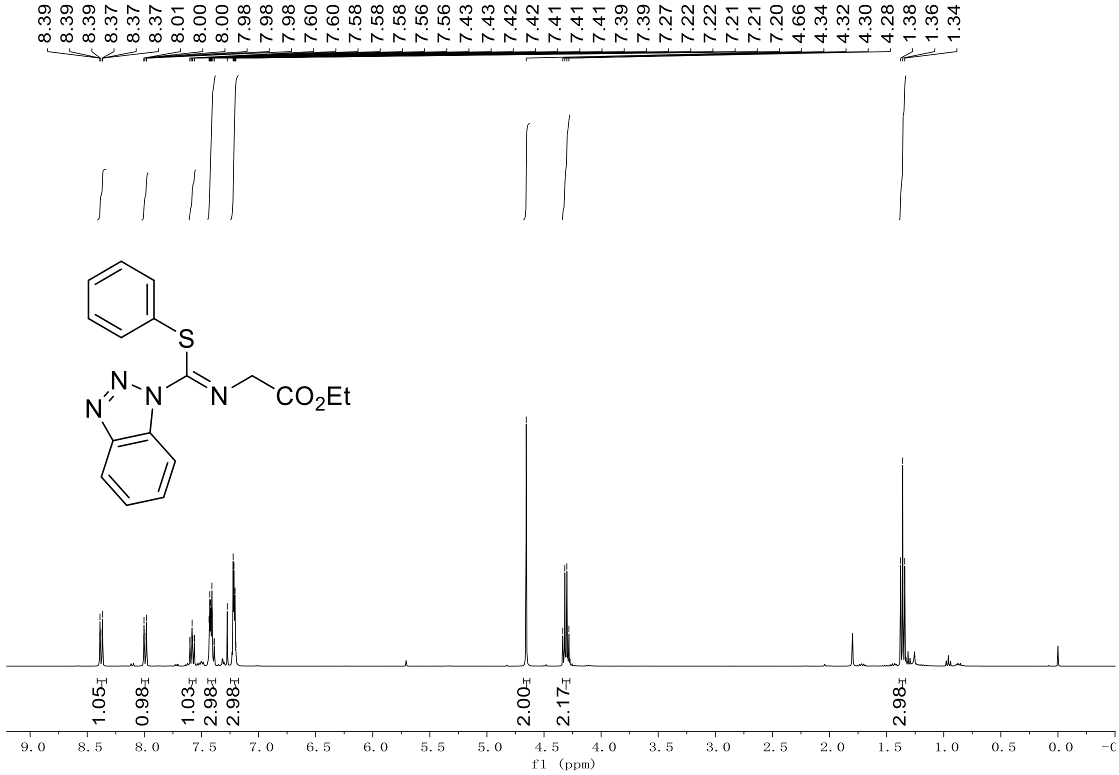

169.09
148.35
146.39
132.16
131.77
131.12
130.79
130.46
130.13
129.83
126.58
126.54
126.50
126.46
125.86
125.01
122.30
120.10
114.41
77.48
77.16
76.84
61.81
54.61
14.38
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
-10
f1 (ppm)

20

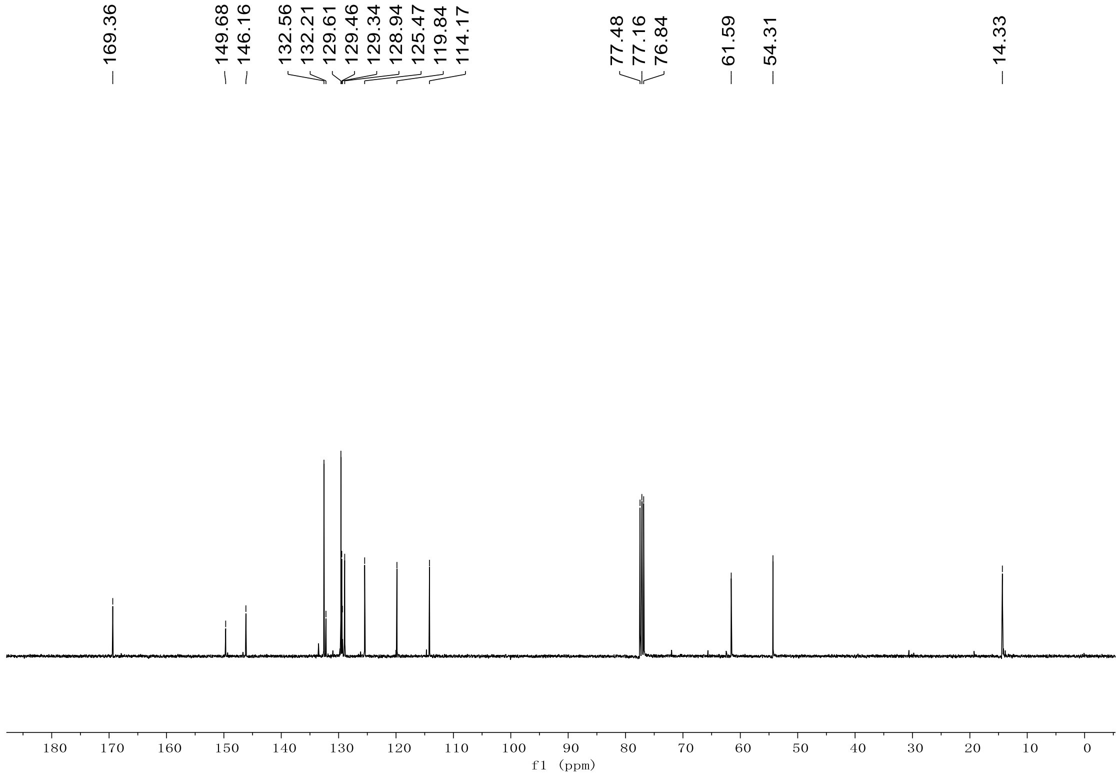

8.50 8.49 8.48 8.47 8.47 8.02 8.02 8.00 8.00 8.00 7.94 7.94 7.94 7.93 7.93 7.92 7.92 7.63 7.62 7.61 7.61 7.60 7.59 7.46 7.45 7.44 7.44 7.43 7.28 7.24 7.24 7.23 7.23 7.22 7.22 7.22 7.21 7.21 7.20 4.75 4.34 4.32 4.30 4.28 3.93 1.37 1.35 1.34
CO2Me
S
N
N
N
N
CO2Et
1.00
1.00
1.01
1.02
1.03
3.02
2.01
2.04
3.00
3.02
10.0 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 0.0
f1 (ppm)


169.43 166.39
150.09 146.29 133.68 132.81 132.06 131.59 131.09 129.54 129.51 127.41 125.59 119.89 114.57
77.48 77.16 76.84
61.53 54.44 52.64
14.32
190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 -10
f1 (ppm)

21

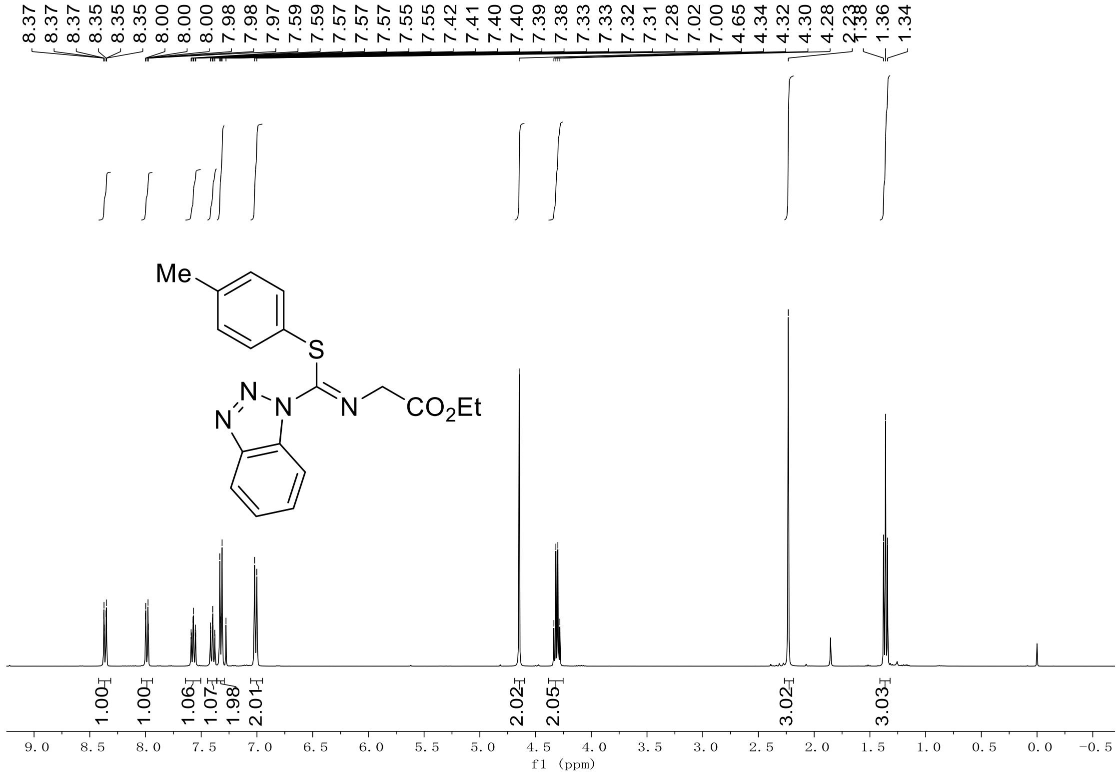


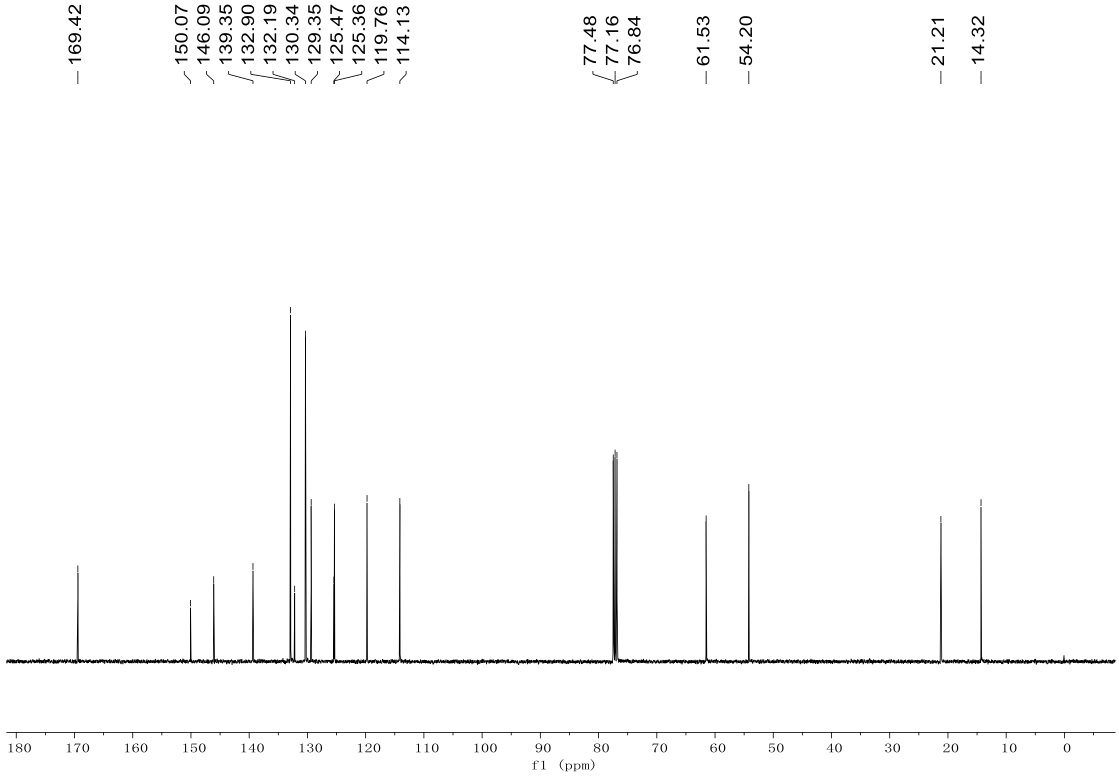
8.39 8.39 8.39 8.37 8.37 8.37 8.01 8.00 8.00 7.98 7.98 7.98 7.60 7.58 7.58 7.58 7.56 7.43 7.43 7.42 7.42 7.41 7.41 7.41 7.39 7.39 7.27 7.22 7.22 7.21 7.21 7.20 4.66 4.34 4.32 4.30 4.28 1.38 1.36 1.34
S
N
N
N
N
CO_2Et
1.05
0.98
1.03
2.98
2.98
2.00
2.17
2.98
9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0
f1 (ppm)



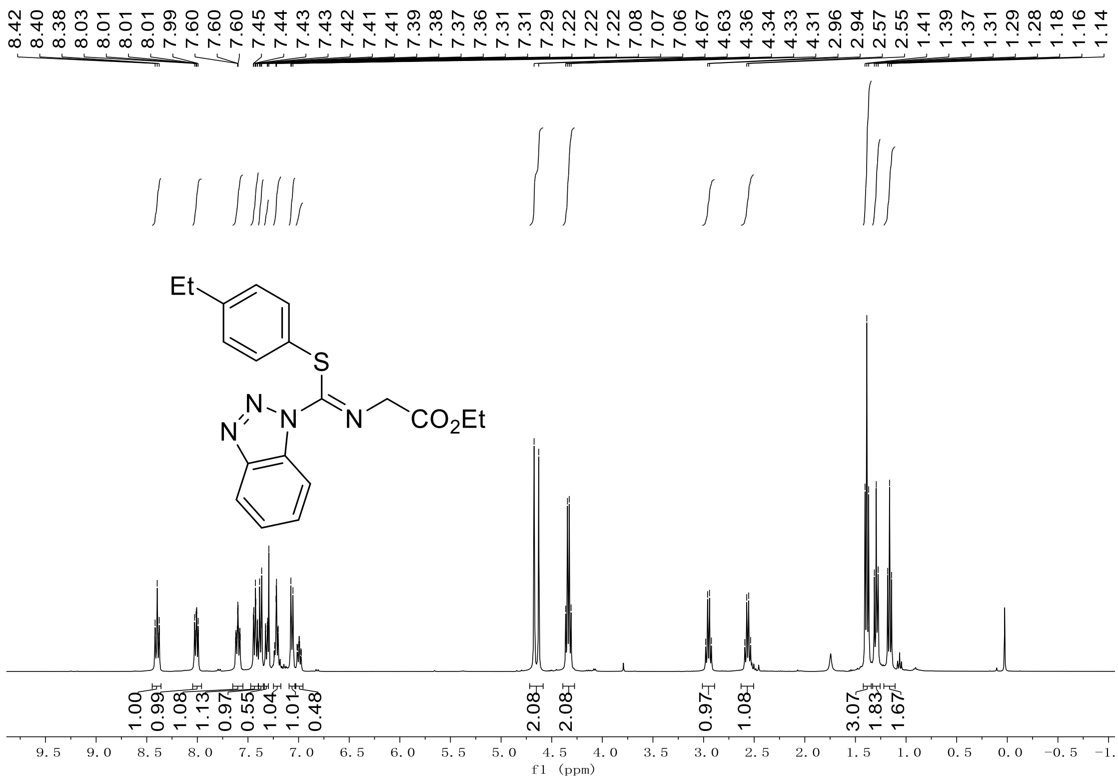
169.36
149.68 146.16
132.56 132.21 129.61 129.46 129.34 128.94 125.47 119.84 114.17
77.48 77.16 76.84
61.59
54.31
14.33
180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0
f1 (ppm)

22

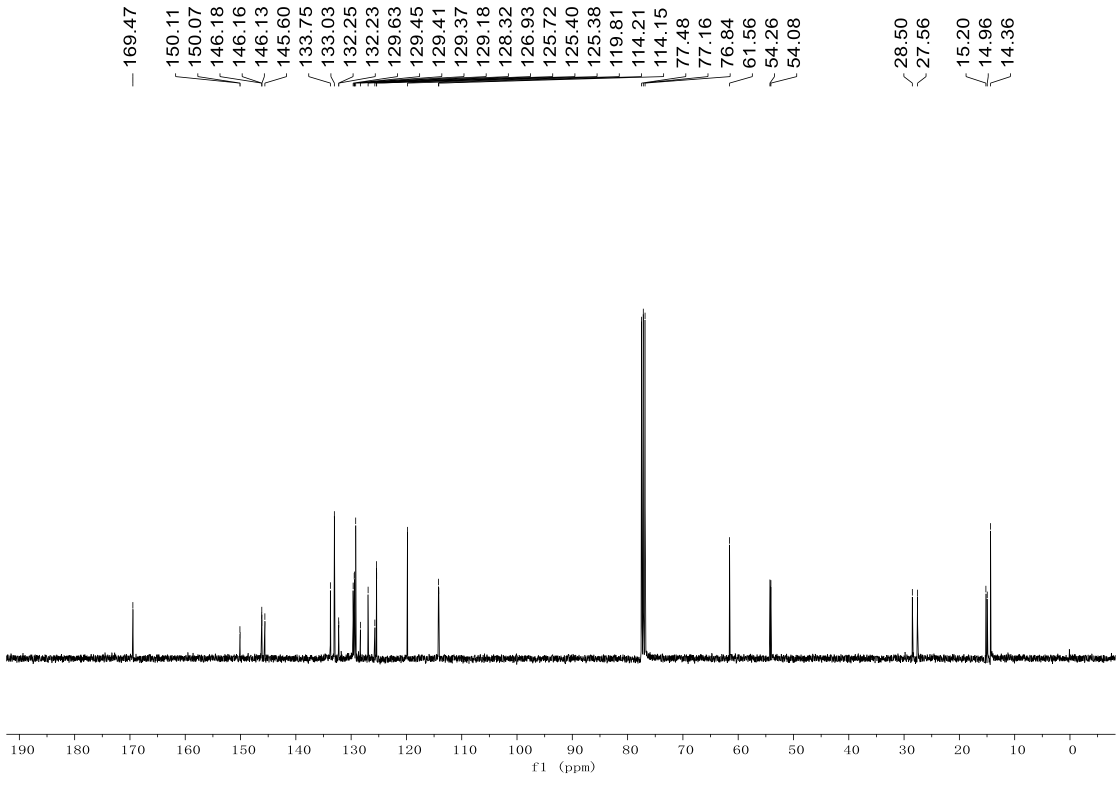

8.37 8.37 8.37 8.35 8.35 8.35 8.00 8.00 8.00 7.98 7.97 7.59 7.59 7.57 7.57 7.57 7.55 7.55 7.42 7.41 7.40 7.40 7.39 7.38 7.33 7.33 7.32 7.31 7.28 7.02 7.00 4.65 4.34 4.32 4.30 4.28 2.23 1.38 1.36 1.34
Me
S
N
N
N
N
CO2Et
1.00 1.00 1.06 1.07 1.98 2.01 2.02 2.05 3.02 3.03
9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0 -0.5
f1 (ppm)


169.42
150.07 146.09 139.35 132.90 132.19 130.34 129.35 125.47 125.36 119.76 114.13
77.48 77.16 76.84
61.53 54.20
21.21 14.32
180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0
f1 (ppm)

23

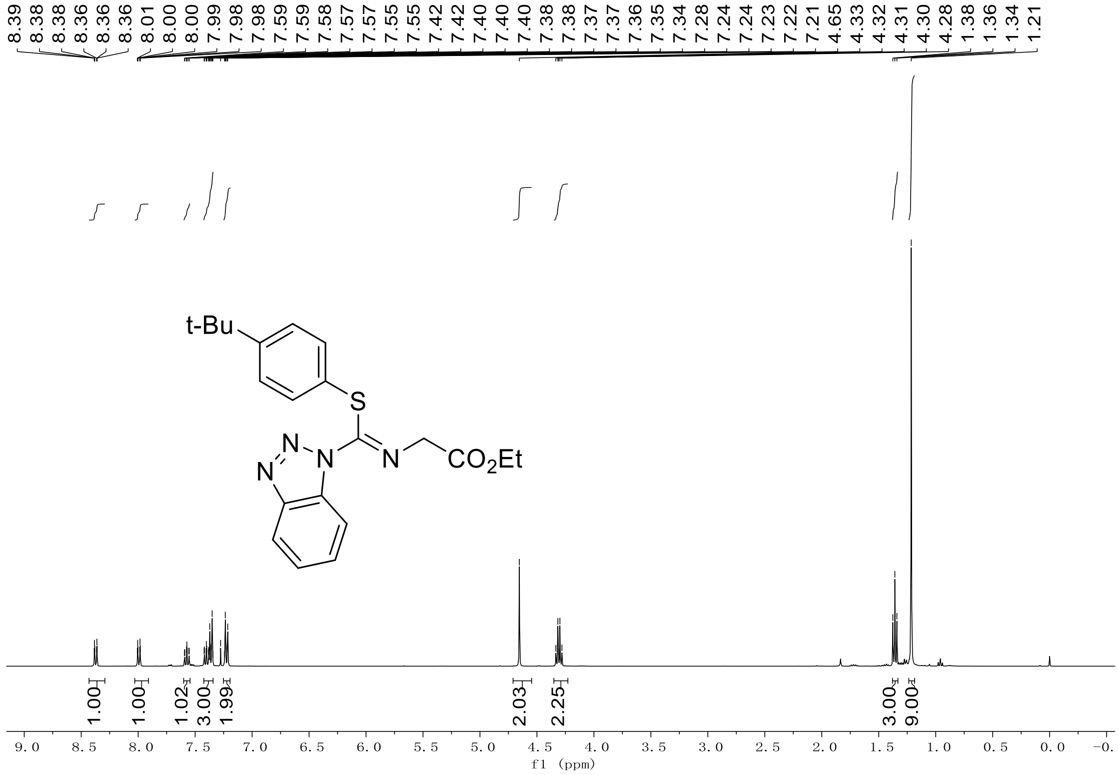


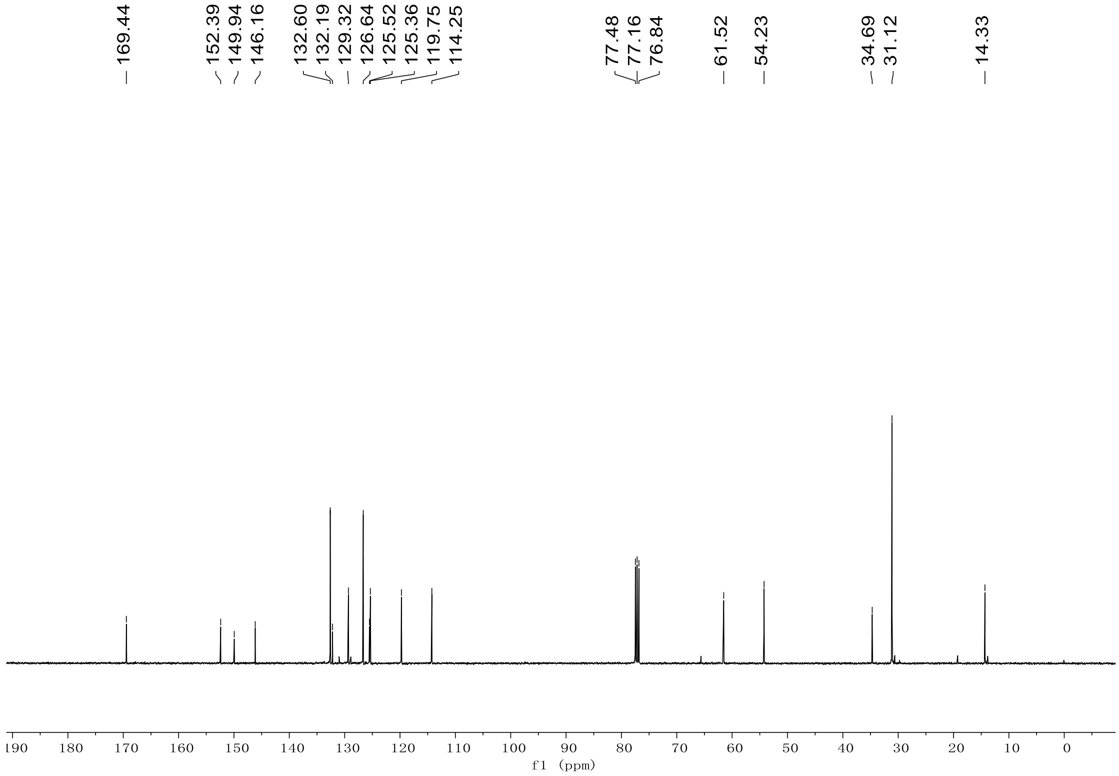
8.42 8.40 8.38 8.03 8.01 8.01 7.99 7.60 7.60 7.60 7.45 7.44 7.43 7.43 7.42 7.41 7.41 7.39 7.38 7.37 7.36 7.31 7.31 7.29 7.22 7.22 7.22 7.08 7.07 7.06 4.67 4.63 4.36 4.34 4.33 4.31 2.96 2.94 2.57 2.55 1.41 1.39 1.37 1.31 1.29 1.28 1.18 1.16 1.14
Et
S
N
N
N
N
CO_2Et
1.00 0.99 1.08 1.13 0.97 0.55 1.04 1.01 0.48
2.08 2.08
0.97 1.08
3.07 1.83 1.67
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 0.0 −0.5 −1.
f1 (ppm)



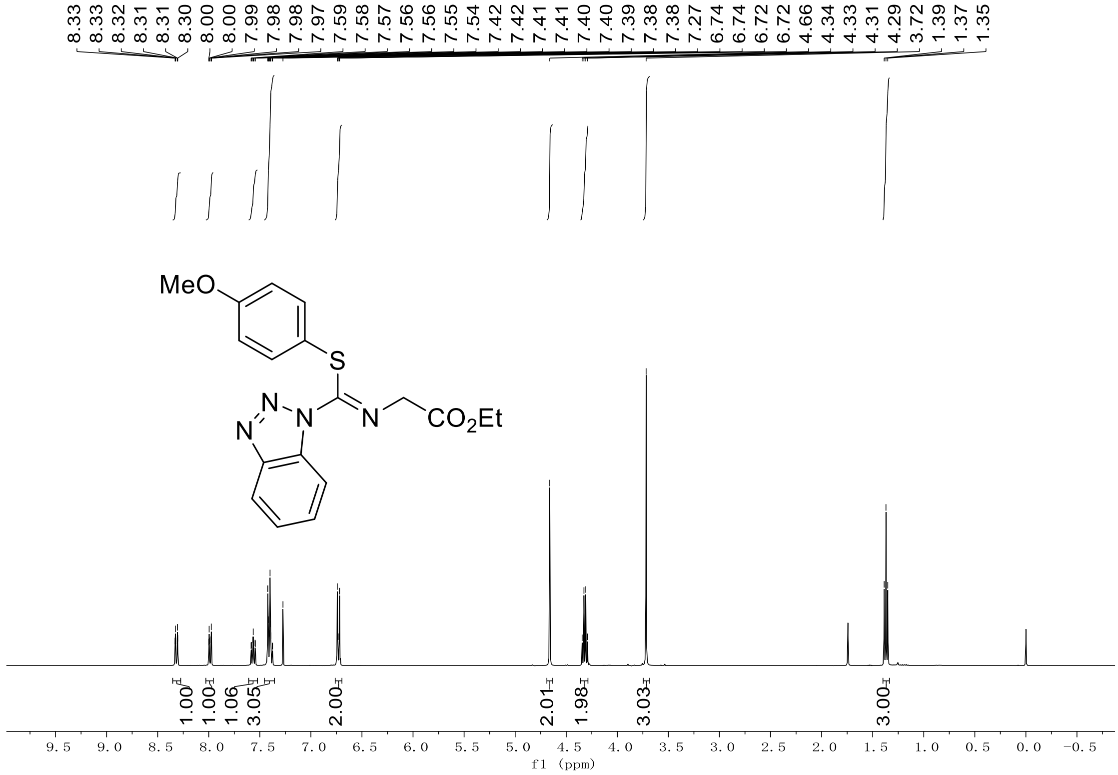
169.47
150.11 150.07 146.18 146.16 146.13 145.60 133.75 133.03 132.25 132.23 129.63 129.45 129.41 129.37 129.18 128.32 126.93 125.72 125.40 125.38 119.81 114.21 114.15 77.48 77.16 76.84 61.56 54.26 54.08
28.50 27.56
15.20 14.96 14.36
190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0
f1 (ppm)

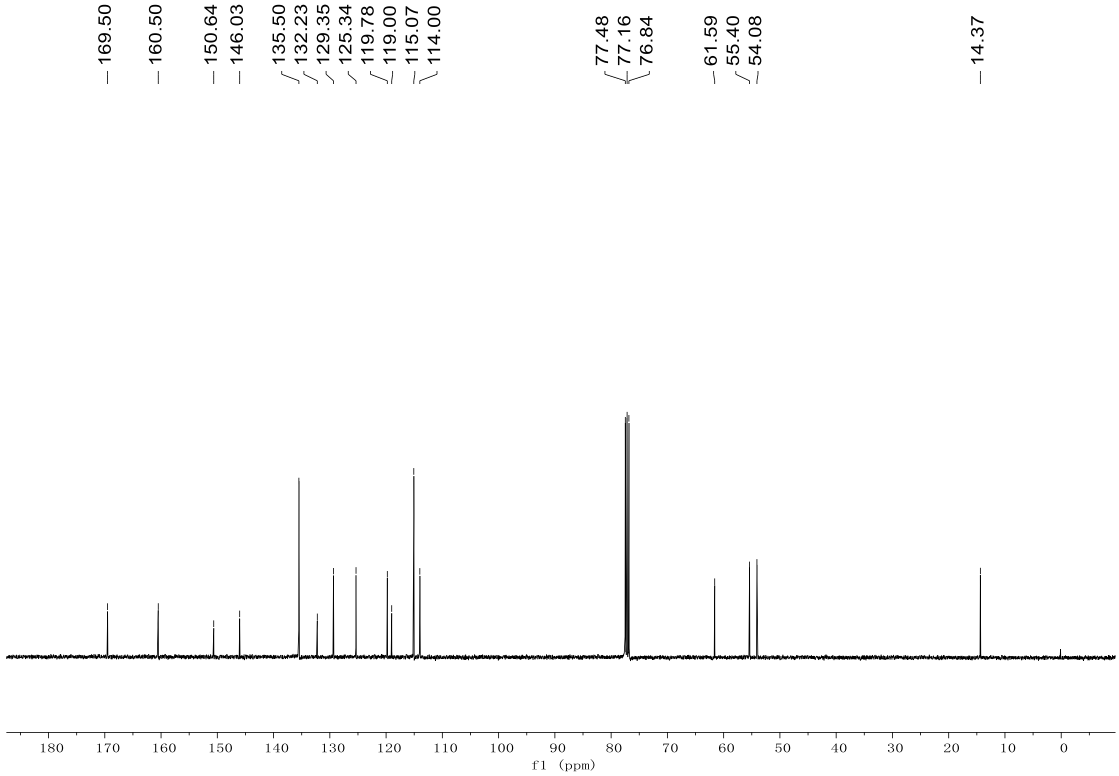
24


8.39 8.38 8.38 8.36 8.36 8.36 8.01 8.00 8.00 7.99 7.98 7.98 7.59 7.58 7.57 7.57 7.55 7.55 7.42 7.42 7.40 7.40 7.38 7.38 7.37 7.37 7.36 7.35 7.34 7.28 7.24 7.24 7.23 7.22 7.21 4.65 4.33 4.32 4.31 4.30 4.28 1.38 1.36 1.34 1.21
t-Bu
S
N
N
N
N
CO2Et
1.00
1.00
1.02
3.00
1.99
2.03
2.25
3.00
9.00
f1 (ppm)

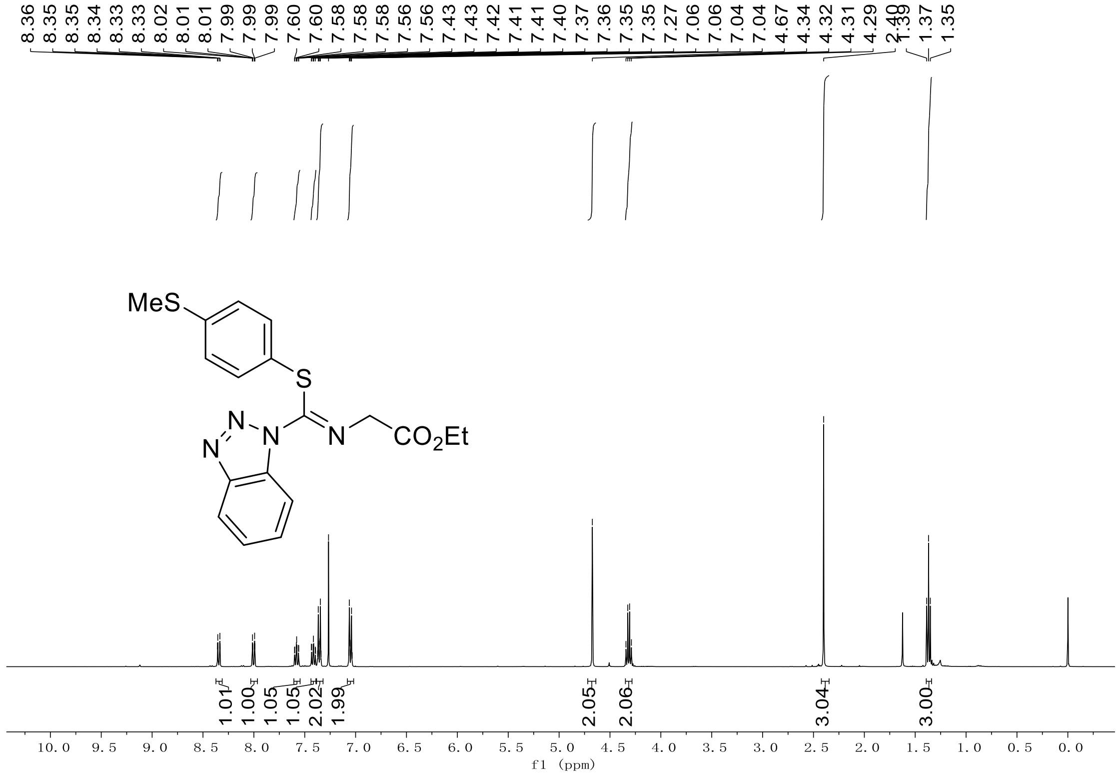

169.44
152.39 149.94 146.16
132.60 132.19 129.32 126.64 125.52 125.36 119.75 114.25
77.48 77.16 76.84
61.52
54.23
34.69 31.12
14.33
f1 (ppm)

25

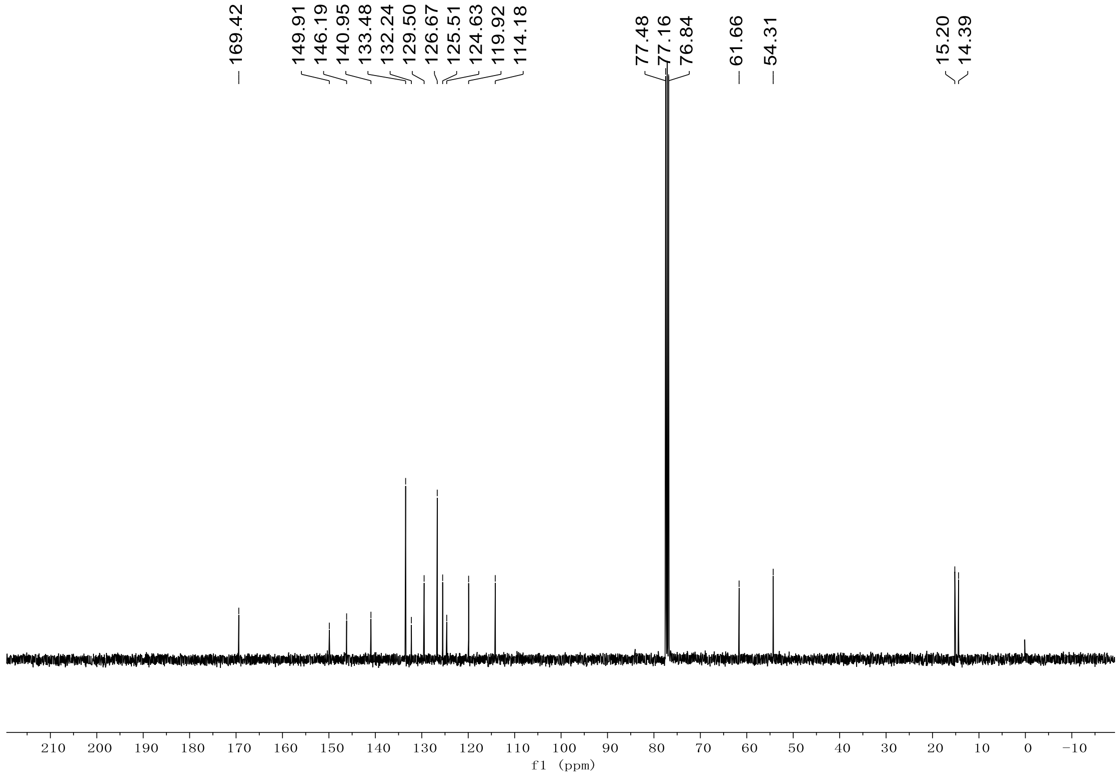

8.33 8.33 8.32 8.31 8.31 8.30 8.00 8.00 7.99 7.98 7.98 7.97 7.59 7.58 7.57 7.56 7.56 7.55 7.54 7.42 7.42 7.41 7.41 7.40 7.40 7.39 7.38 7.38 7.27 6.74 6.74 6.72 6.72 4.66 4.34 4.33 4.31 4.29 3.72 1.39 1.37 1.35
MeO
S
N
N
N
N
CO2Et
1.00
1.00
1.06
3.05
2.00
2.01
1.98
3.03
3.00
f1 (ppm)


169.50 160.50 150.64 146.03 135.50 132.23 129.35 125.34 119.78 119.00 115.07 114.00 77.48 77.16 76.84 61.59 55.40 54.08 14.37
f1 (ppm)

26

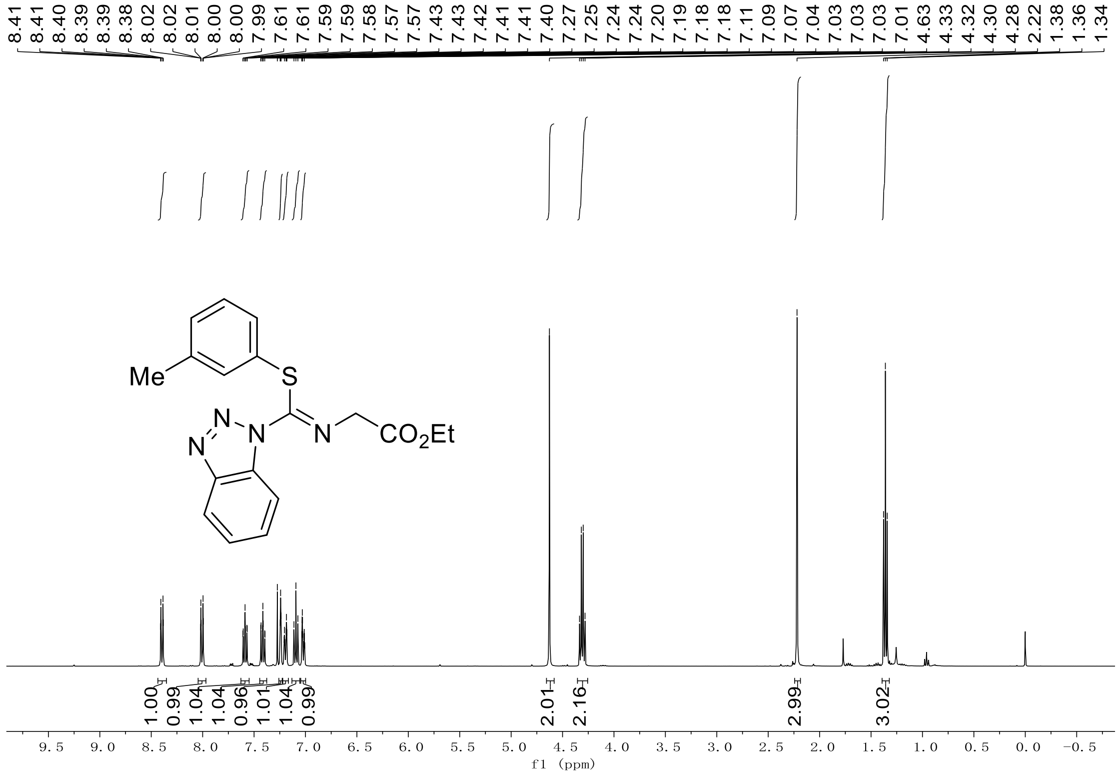


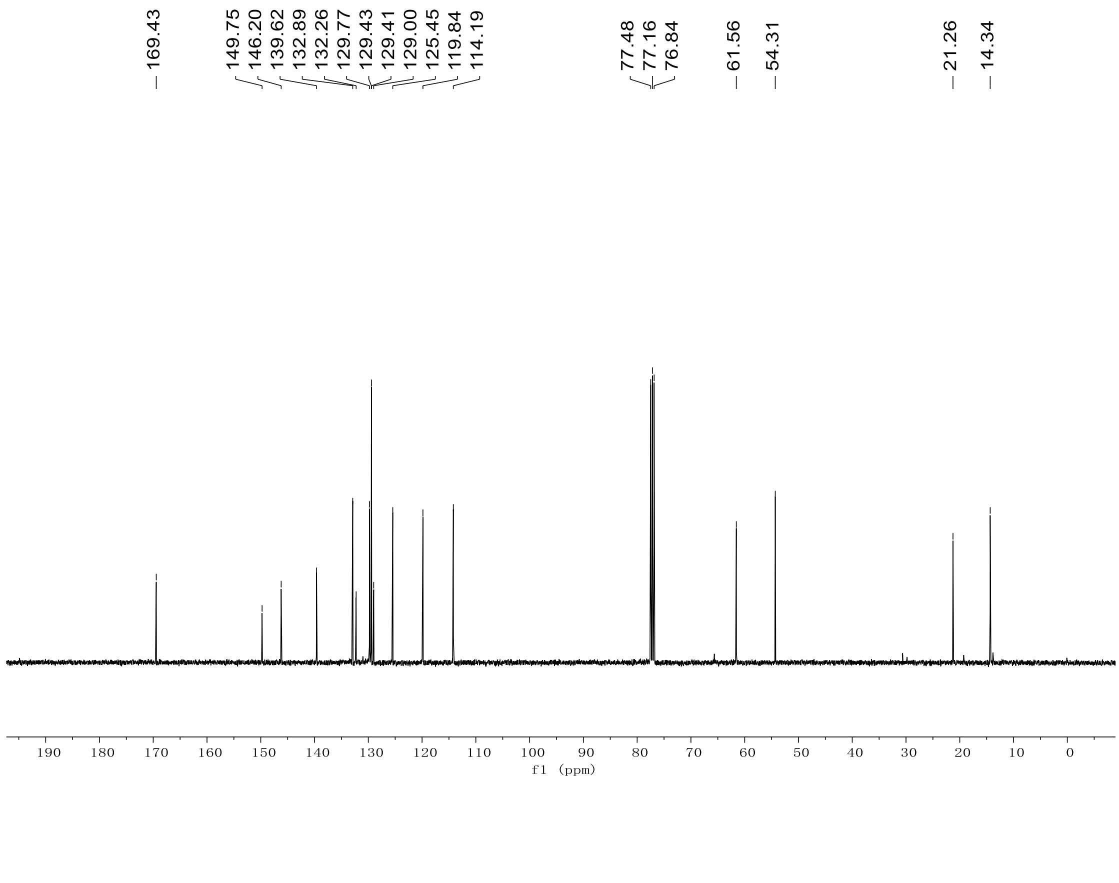
MeS
S
N
CO2Et
1.01
1.00
1.05
1.05
2.02
1.99
2.05
2.06
3.04
3.00
f1 (ppm)



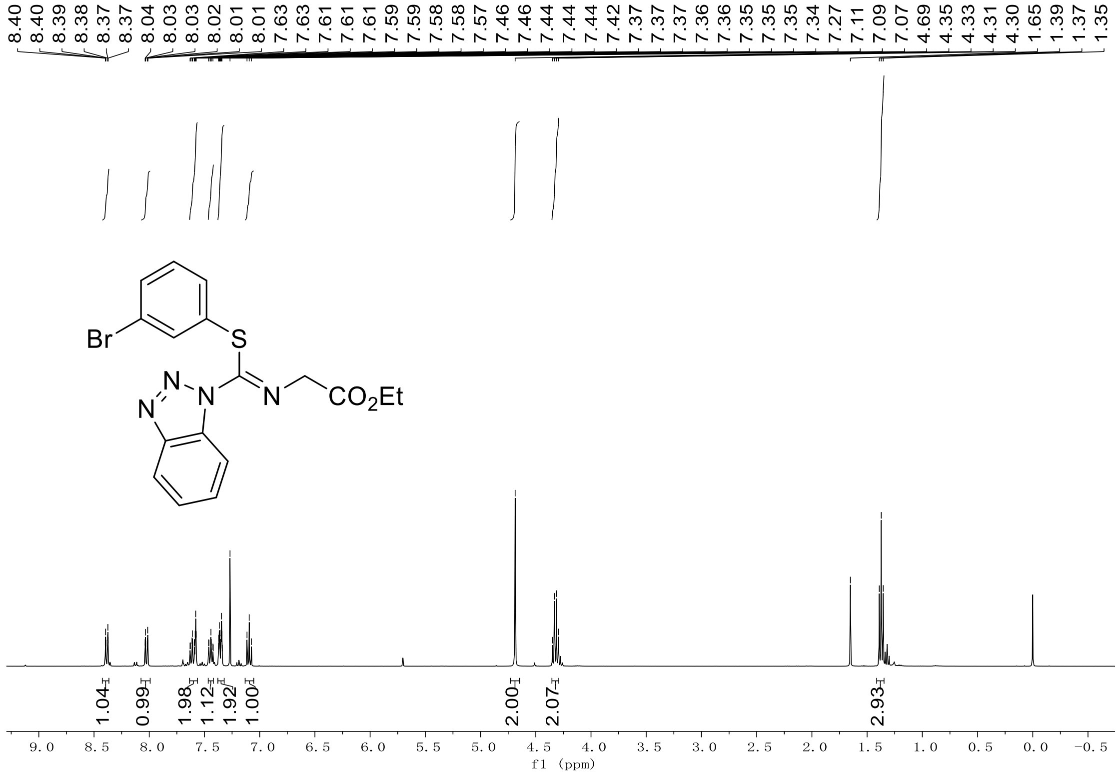
169.42
149.91
146.19
140.95
133.48
132.24
129.50
126.67
125.51
124.63
119.92
114.18
77.48
77.16
76.84
61.66
54.31
15.20
14.39
f1 (ppm)

27

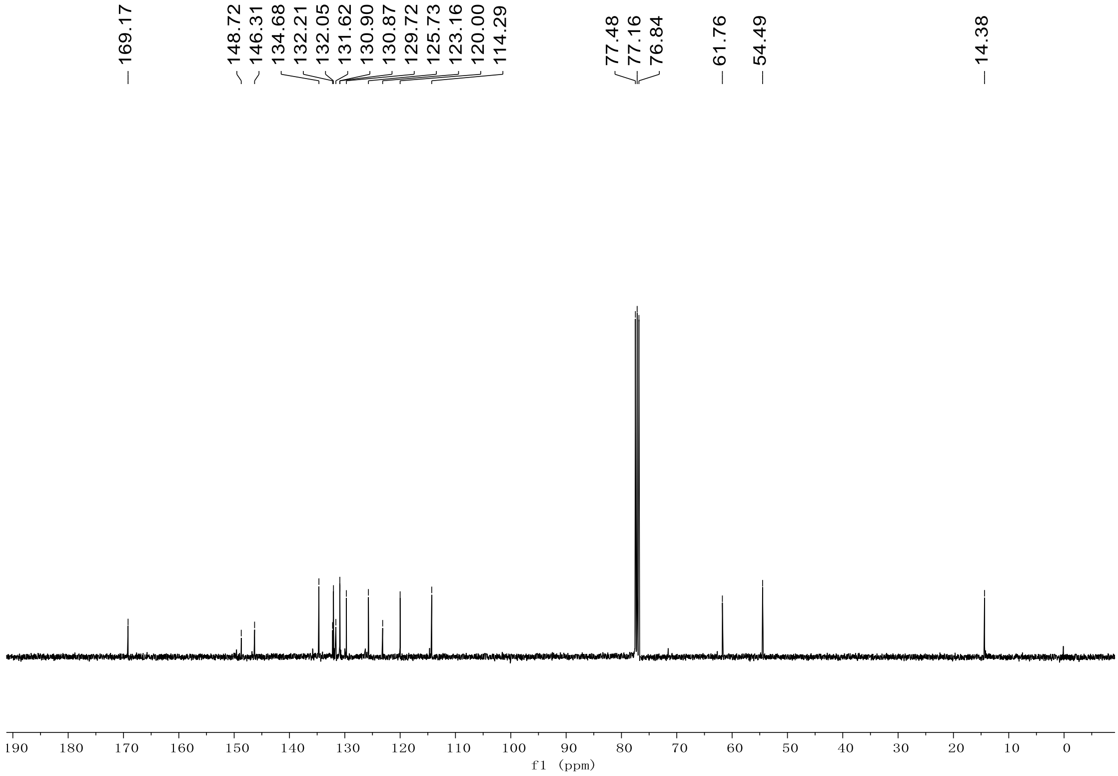

8.41 8.41 8.40 8.39 8.39 8.38 8.02 8.02 8.01 8.00 8.00 7.99 7.61 7.61 7.59 7.59 7.58 7.57 7.57 7.43 7.43 7.42 7.41 7.41 7.40 7.27 7.25 7.24 7.24 7.20 7.19 7.18 7.18 7.11 7.09 7.07 7.04 7.03 7.03 7.03 7.01 4.63 4.33 4.32 4.30 4.28 2.22 1.38 1.36 1.34
Me
S
N
N
N
N
CO_2Et
1.00 0.99 1.04 1.04 0.96 1.01 1.04 0.99
2.01 2.16
2.99
3.02
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 0.0 -0.5
f1 (ppm)


169.43
149.75 146.20 139.62 132.89 132.26 129.77 129.43 129.41 129.00 125.45 119.84 114.19
77.48 77.16 76.84
61.56
54.31
21.26
14.34
190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0
f1 (ppm)

28

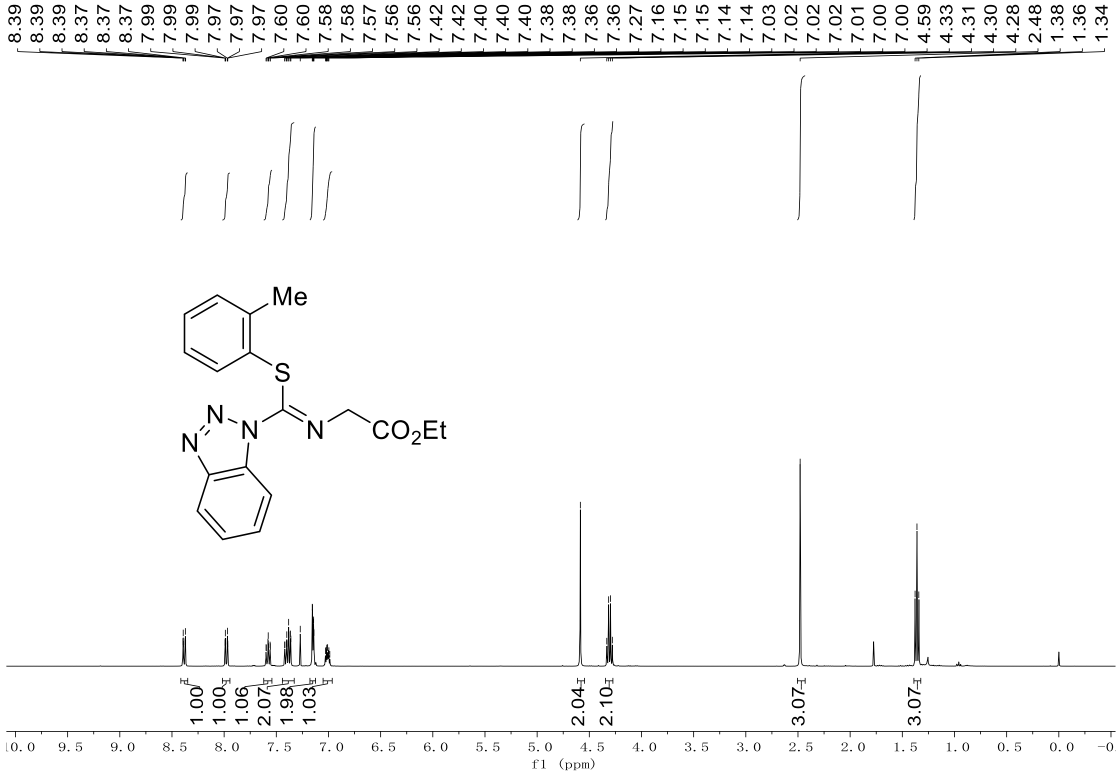


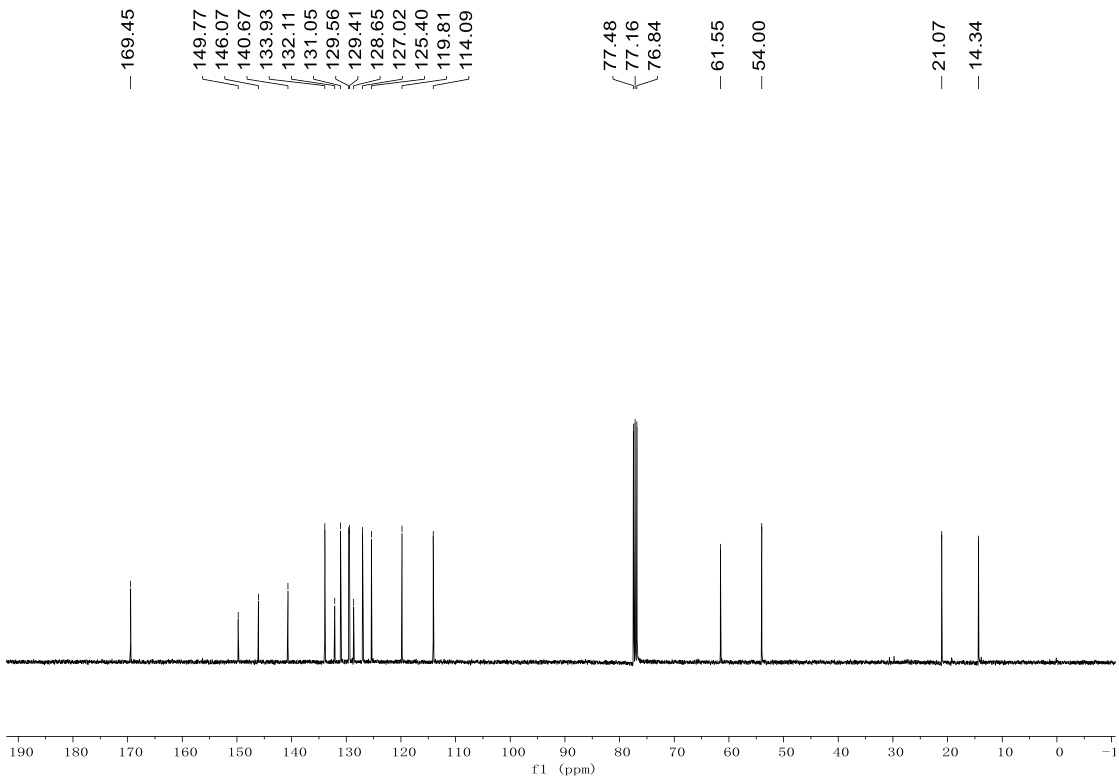
8.40 8.40 8.39 8.38 8.37 8.37 8.04 8.03 8.02 8.01 8.01 7.63 7.63 7.61 7.61 7.61 7.59 7.59 7.58 7.58 7.57 7.46 7.46 7.44 7.44 7.44 7.42 7.37 7.37 7.37 7.36 7.36 7.35 7.35 7.35 7.34 7.27 7.11 7.09 7.07 4.69 4.35 4.33 4.31 4.30 1.65 1.39 1.37 1.35
Br
S
N
N
N
N
CO2Et
1.04 0.99 1.98 1.12 1.92 1.00 2.00 2.07 2.93
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 0.0 -0.5
f1 (ppm)



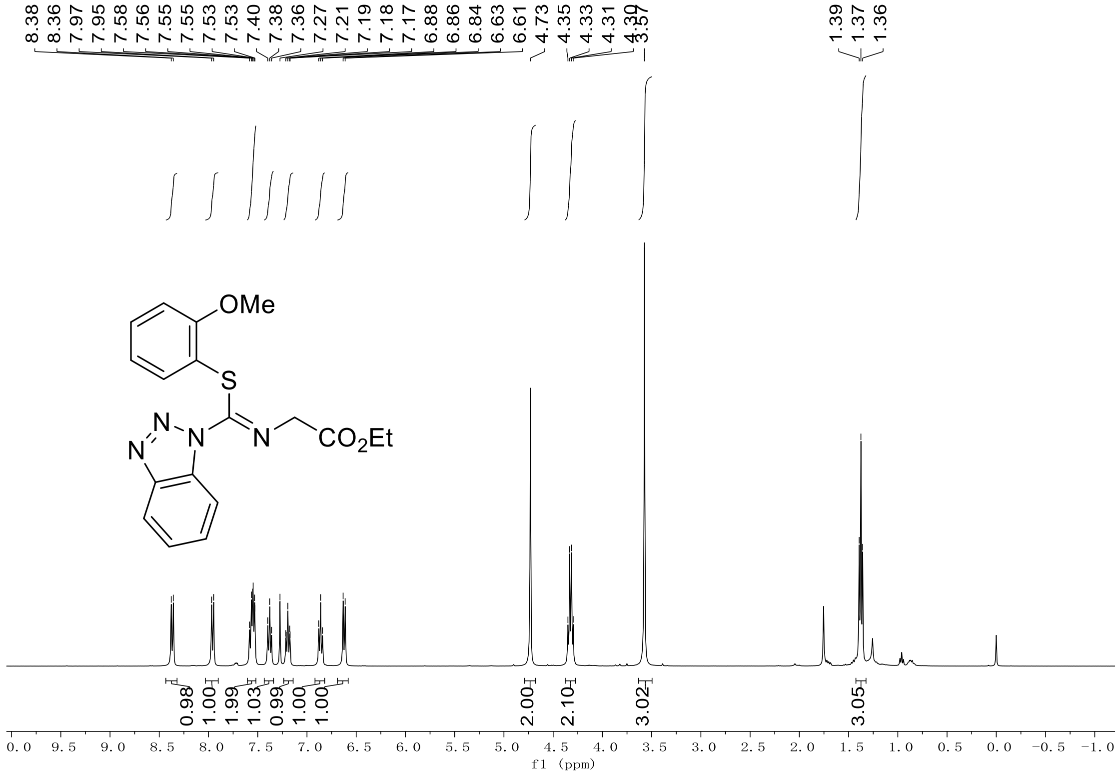
169.17 148.72 146.31 134.68 132.21 132.05 131.62 130.90 130.87 129.72 125.73 123.16 120.00 114.29 77.48 77.16 76.84 61.76 54.49 14.38
190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0
f1 (ppm)

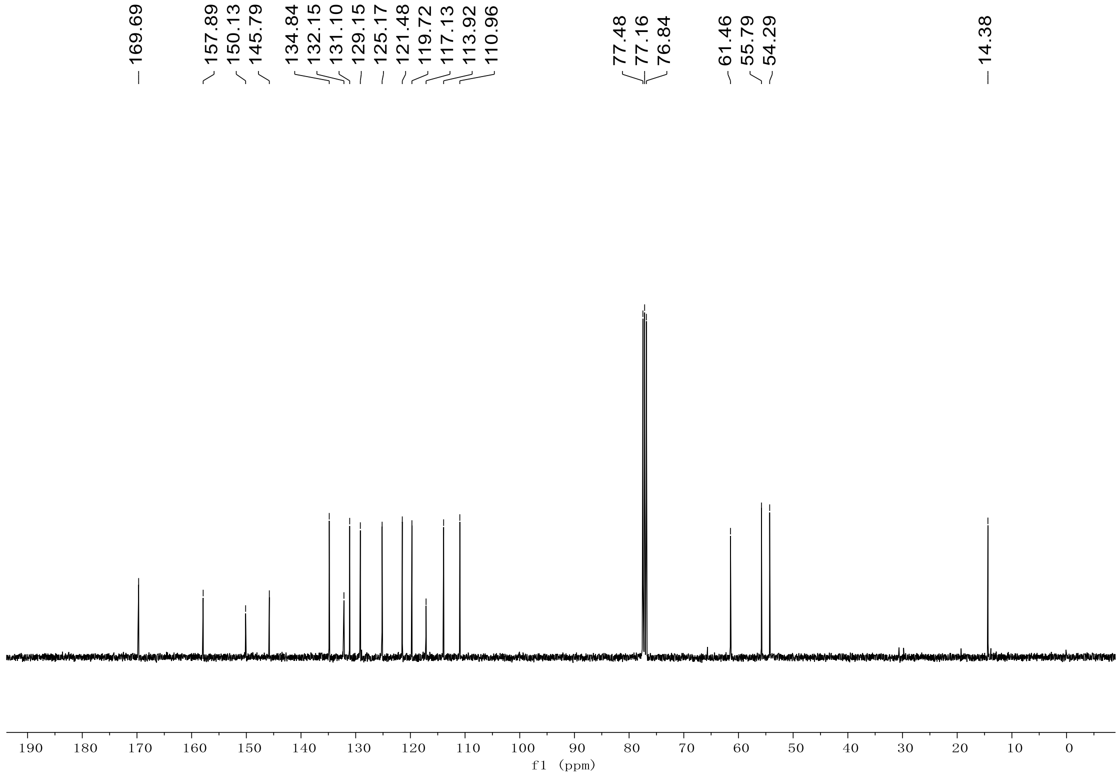
29



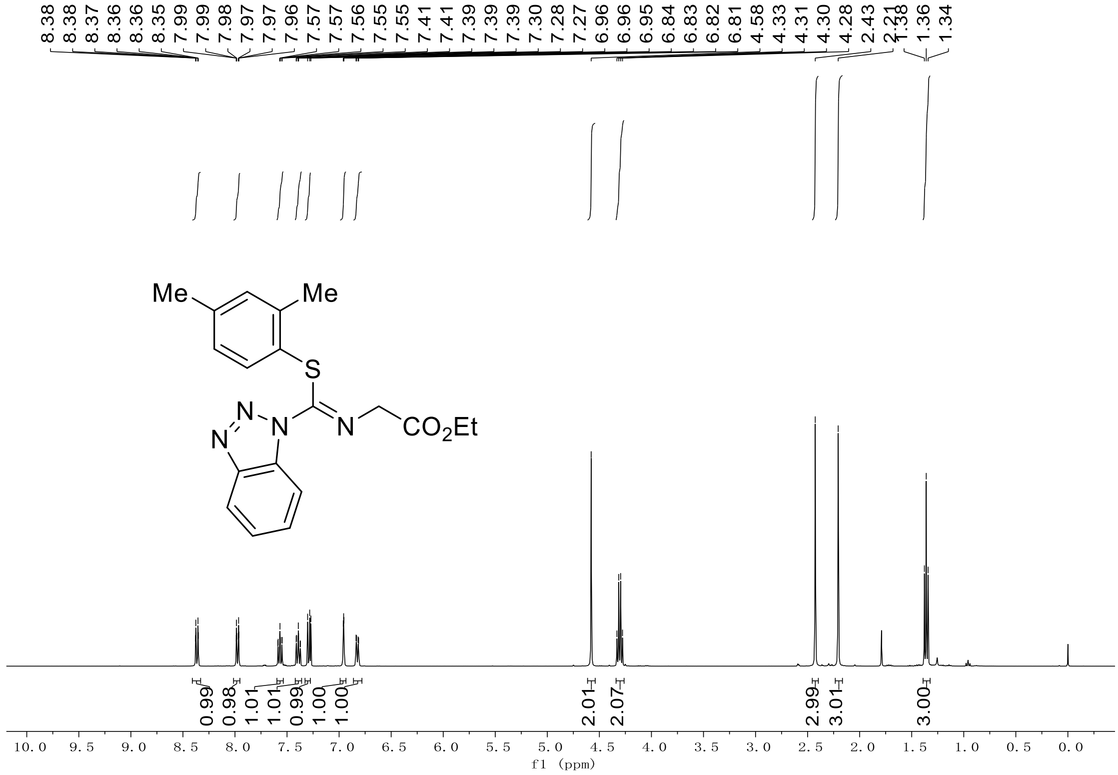


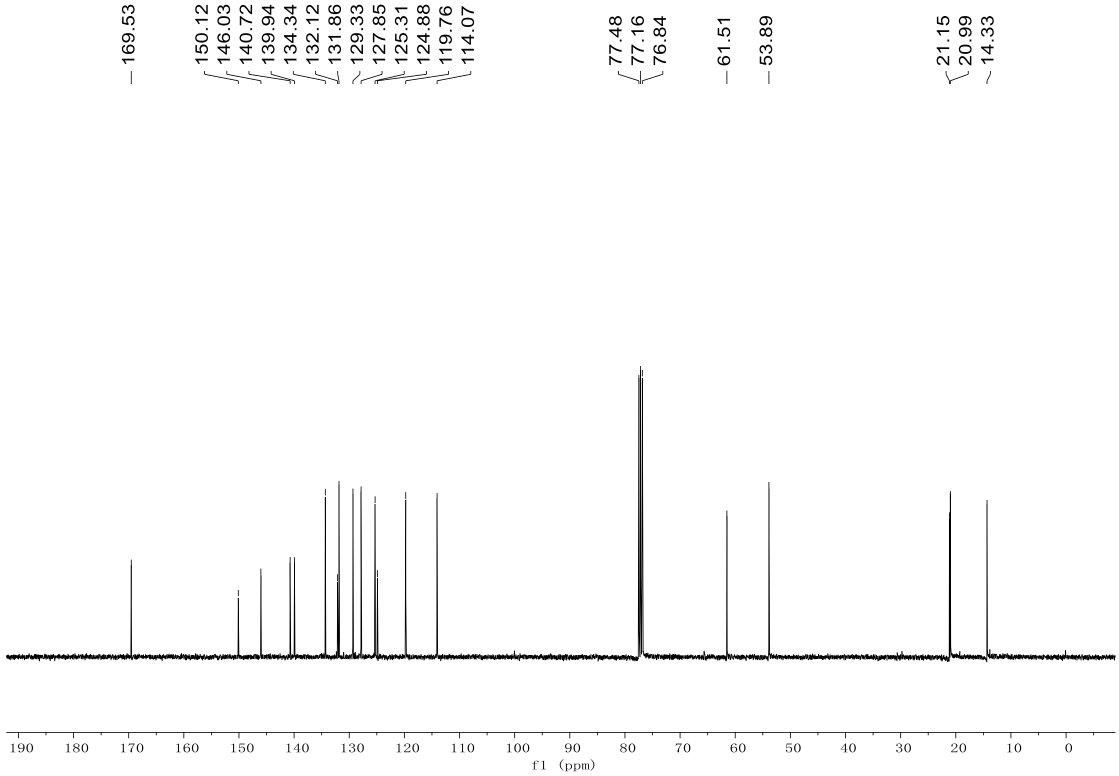
30


8.38
8.36
7.97
7.95
7.58
7.56
7.55
7.55
7.53
7.53
7.40
7.38
7.36
7.27
7.21
7.19
7.18
7.17
6.88
6.86
6.84
6.63
6.61
4.73
4.35
4.33
4.31
4.30
3.57
1.39
1.37
1.36
OMe
S
N
N
N
N
CO2Et
0.98
1.00
1.99
1.03
0.99
1.00
1.00
2.00
2.10
3.02
3.05
f1 (ppm)

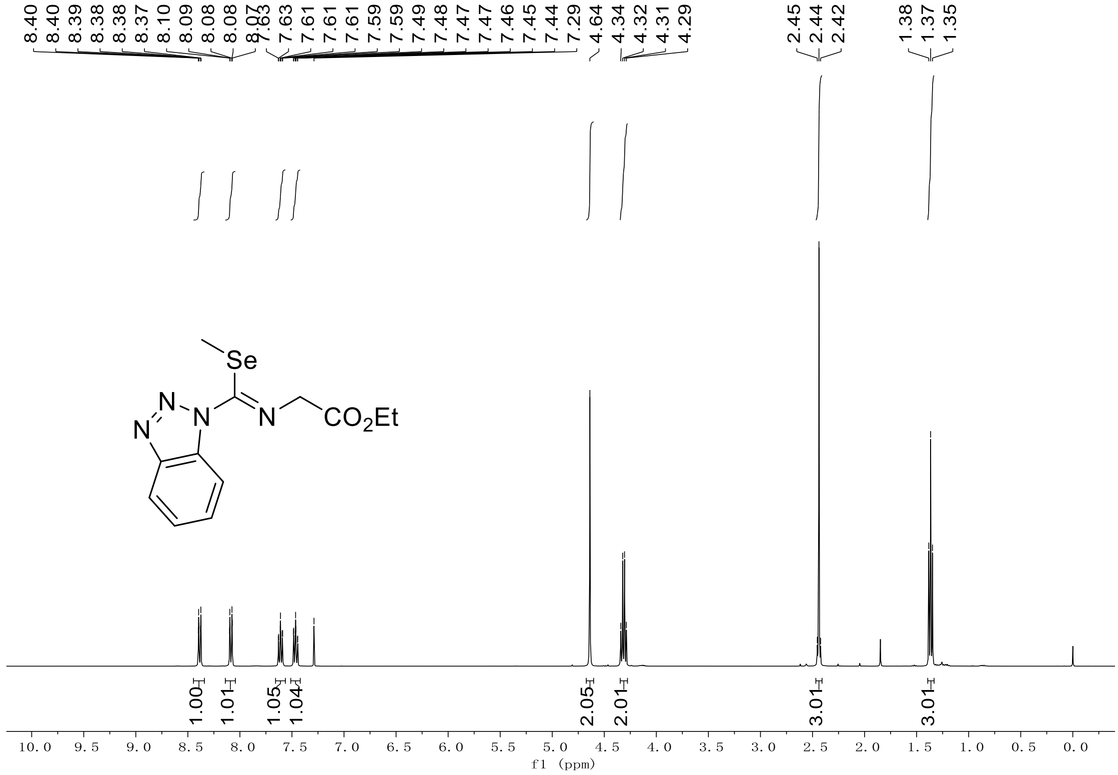

169.69
157.89
150.13
145.79
134.84
132.15
131.10
129.15
125.17
121.48
119.72
117.13
113.92
110.96
77.48
77.16
76.84
61.46
55.79
54.29
14.38
f1 (ppm)

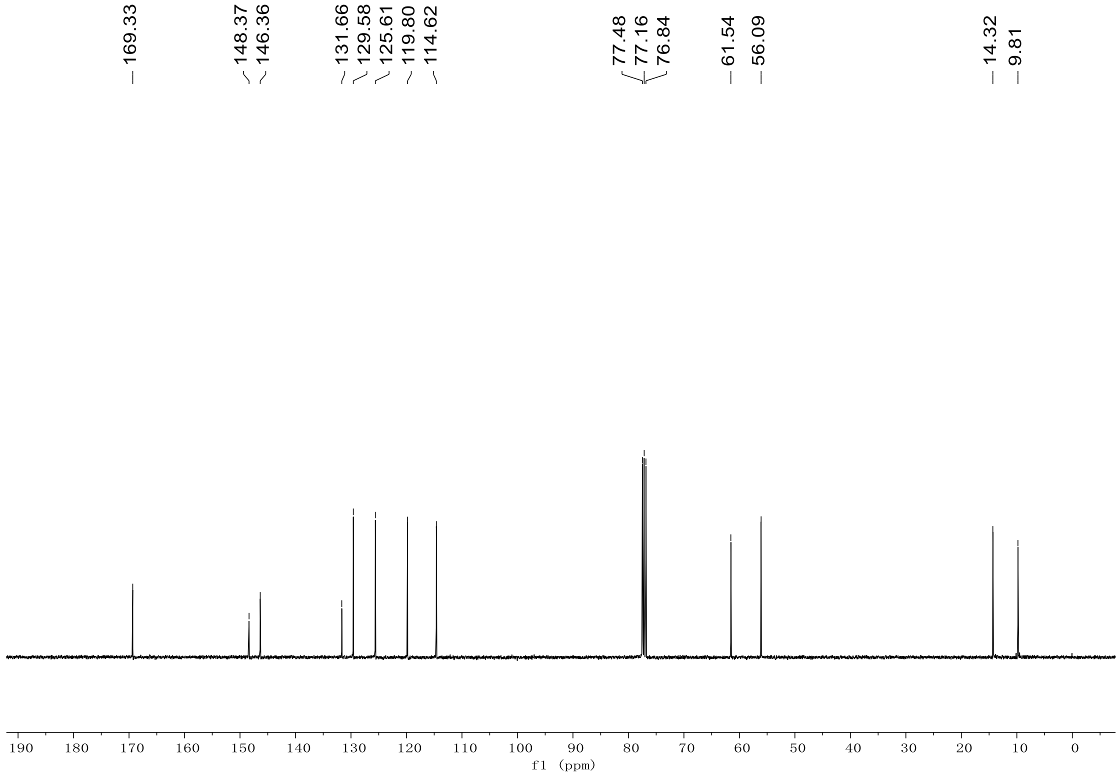
31


8.38 8.38 8.37 8.36 8.36 8.35 7.99 7.98 7.97 7.97 7.96 7.57 7.57 7.56 7.55 7.55 7.41 7.41 7.39 7.39 7.39 7.30 7.28 7.27 6.96 6.96 6.95 6.84 6.83 6.82 6.81 4.58 4.33 4.31 4.30 4.28 2.43 2.21 1.38 1.36 1.34
Me
Me
S
N
N
N
N
CO2Et
0.99 0.98 1.01 1.01 0.99 1.00 1.00 2.01 2.07 2.99 3.01 3.00
10.0 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 0.0
f1 (ppm)

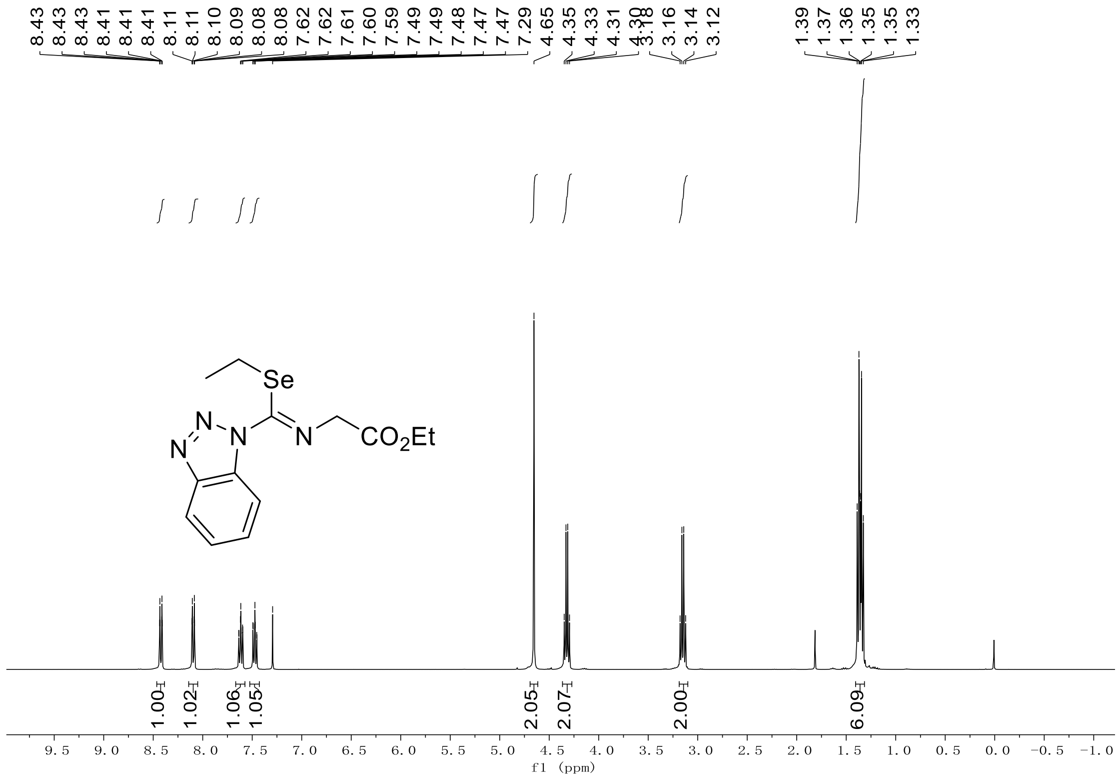

169.53 150.12 146.03 140.72 139.94 134.34 132.12 131.86 129.33 127.85 125.31 124.88 119.76 114.07 77.48 77.16 76.84 61.51 53.89 21.15 20.99 14.33
190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0
f1 (ppm)

32

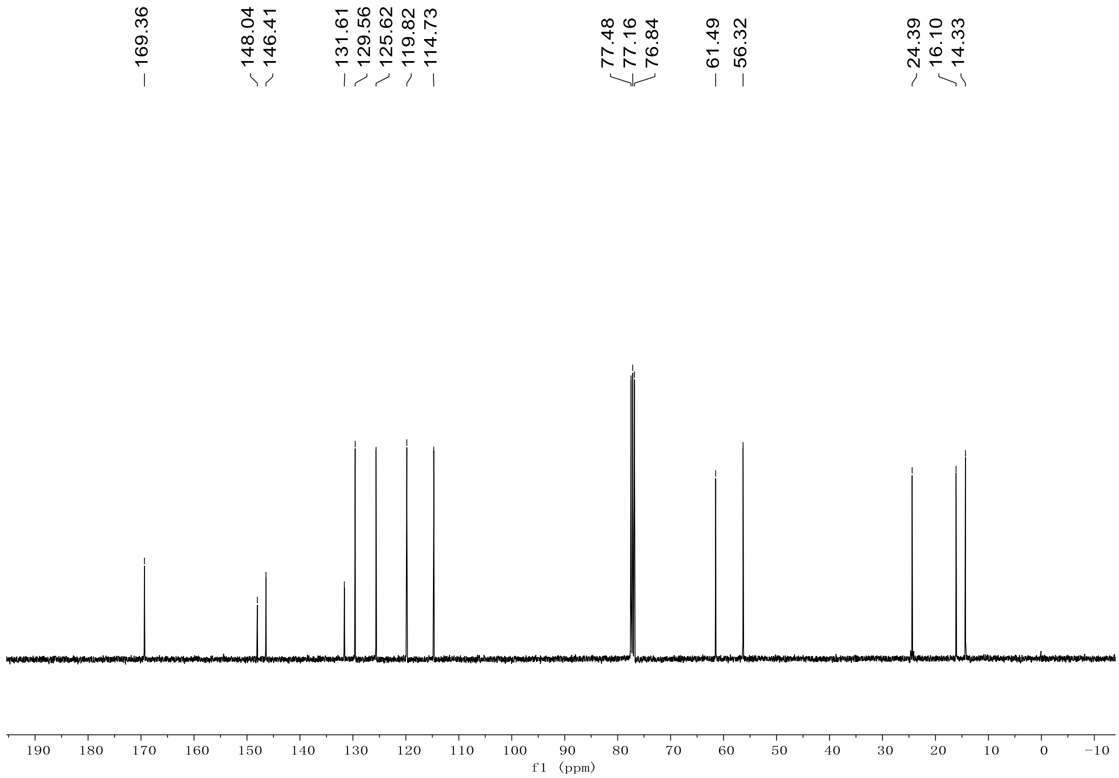

8.40 8.40 8.39 8.38 8.38 8.37 8.10 8.09 8.08 8.08 8.07 7.63 7.63 7.61 7.61 7.61 7.59 7.59 7.49 7.48 7.47 7.47 7.46 7.45 7.44 7.29 4.64 4.34 4.32 4.31 4.29
2.45 2.44 2.42
1.38 1.37 1.35
Se
N
N
N
N
CO2Et
1.00
1.01
1.05
1.04
2.05
2.01
3.01
3.01
10.0 9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0
f1 (ppm)


169.33
148.37 146.36
131.66 129.58 125.61 119.80 114.62
77.48 77.16 76.84
61.54 56.09
14.32 9.81
190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0
f1 (ppm)

33

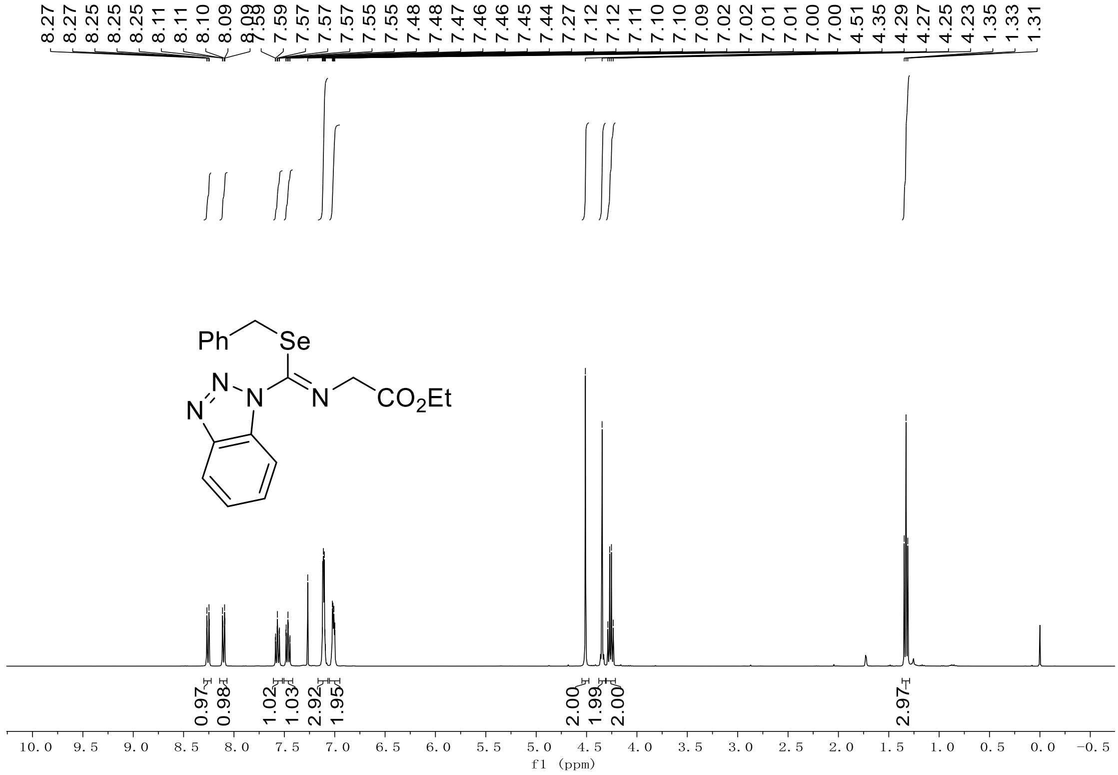


8.43 8.43 8.43 8.41 8.41 8.41 8.11 8.11 8.10 8.09 8.08 8.08 7.62 7.62 7.61 7.60 7.59 7.49 7.49 7.48 7.47 7.47 7.29 4.65 4.35 4.33 4.31 4.30 3.18 3.16 3.14 3.12
1.39 1.37 1.36 1.35 1.35 1.33
Se
N
N
N
N
CO2Et
1.00
1.02
1.06
1.05
2.05
2.07
2.00
6.09
f1 (ppm)

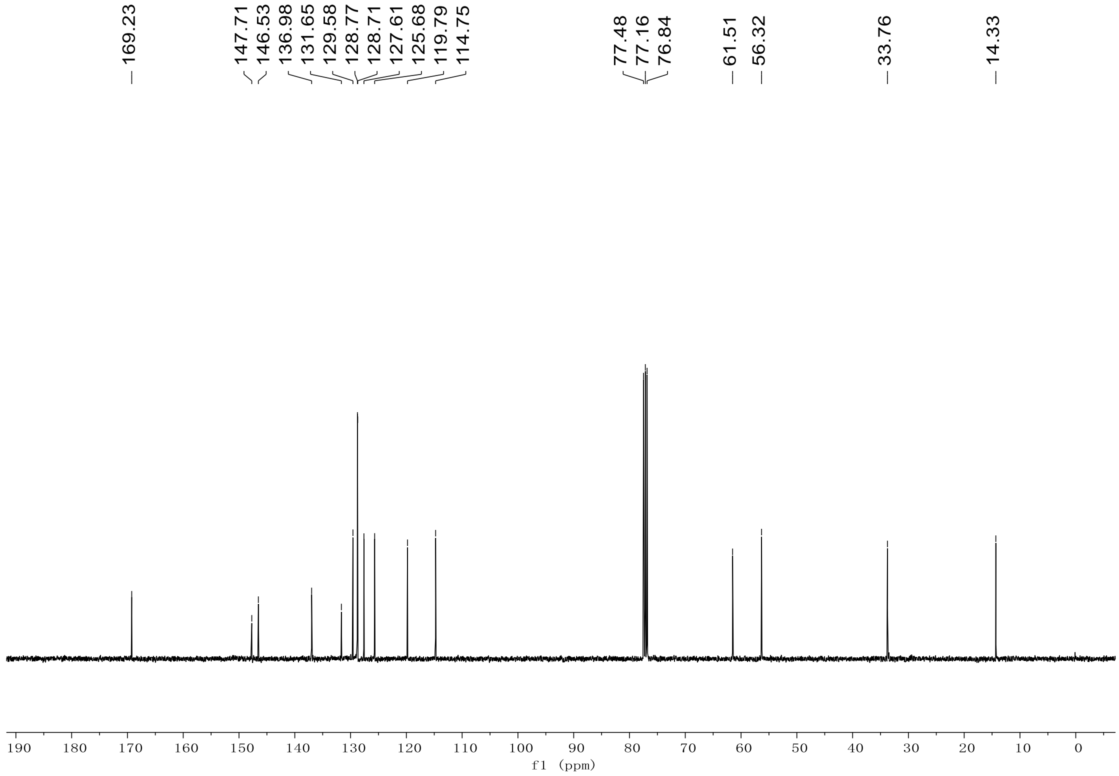


169.36
148.04 146.41
131.61 129.56 125.62 119.82 114.73
77.48 77.16 76.84
61.49 56.32
24.39 16.10 14.33
f1 (ppm)

34

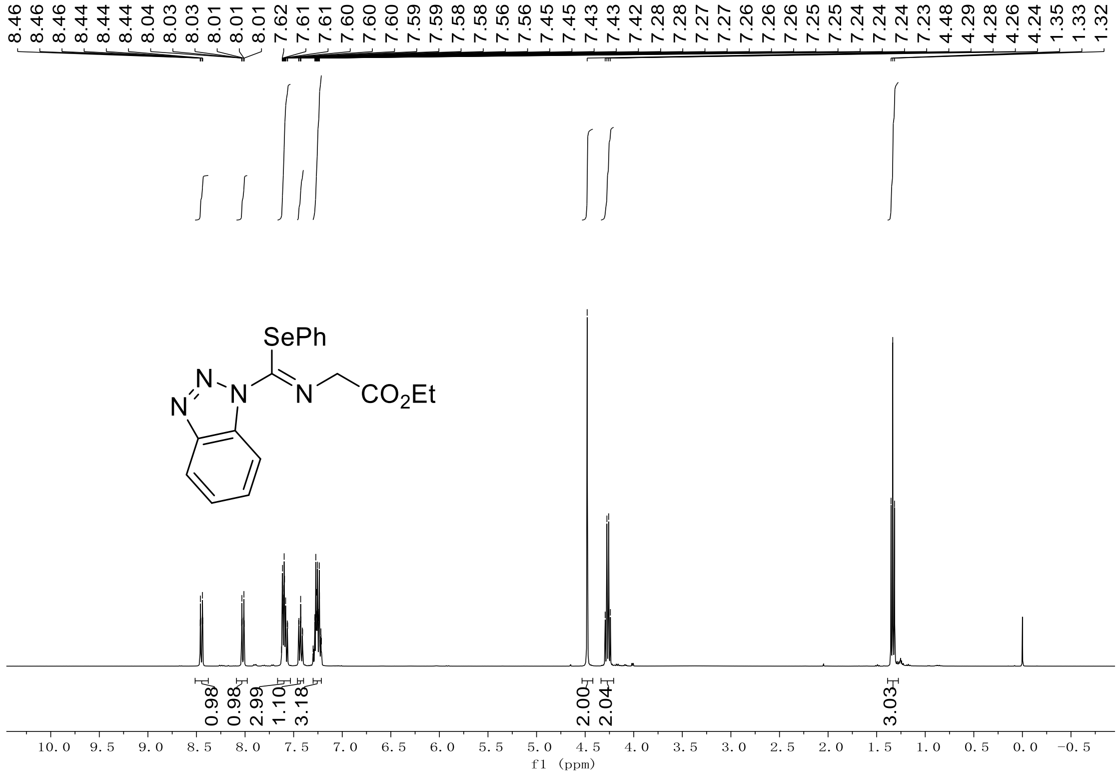


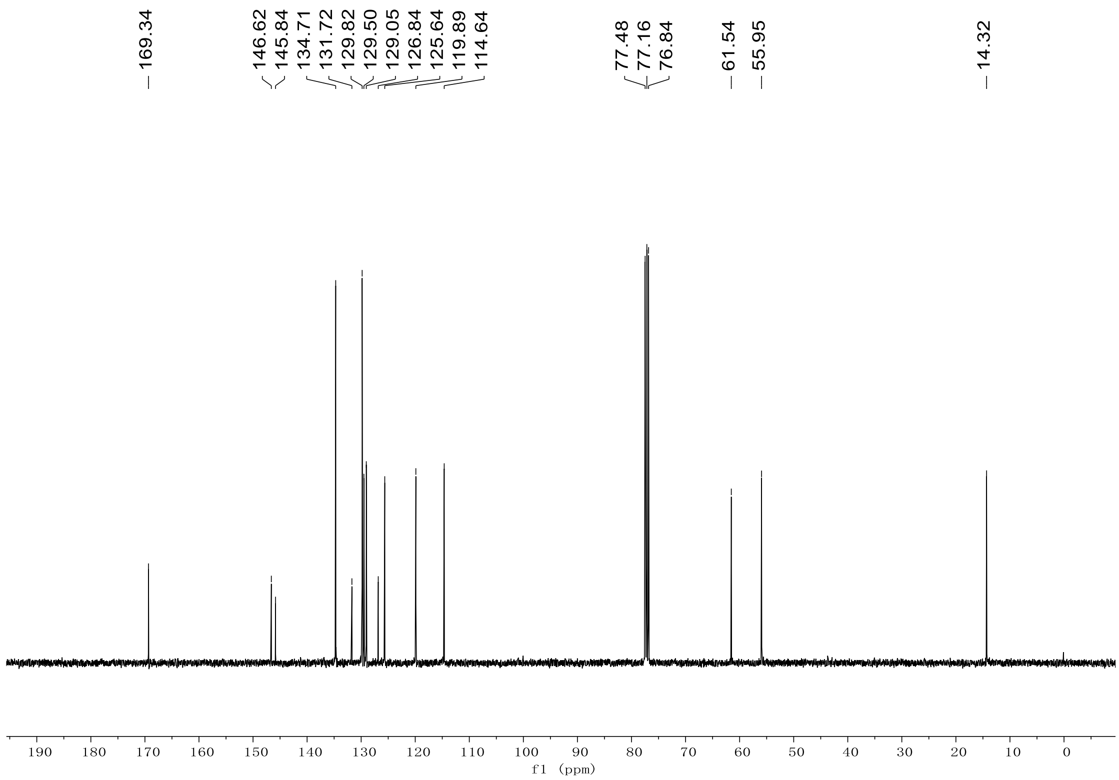
8.27 8.27 8.25 8.25 8.11 8.11 8.10 8.09 8.09 7.59 7.59 7.57 7.57 7.57 7.55 7.55 7.48 7.48 7.47 7.46 7.46 7.45 7.44 7.27 7.12 7.12 7.11 7.10 7.10 7.09 7.02 7.02 7.01 7.01 7.00 7.00 4.51 4.35 4.29 4.27 4.25 4.23 1.35 1.33 1.31
Ph
Se
N
N
N
N
CO2Et
0.97
0.98
1.02
1.03
2.92
1.95
2.00
1.99
2.00
2.97
f1 (ppm)



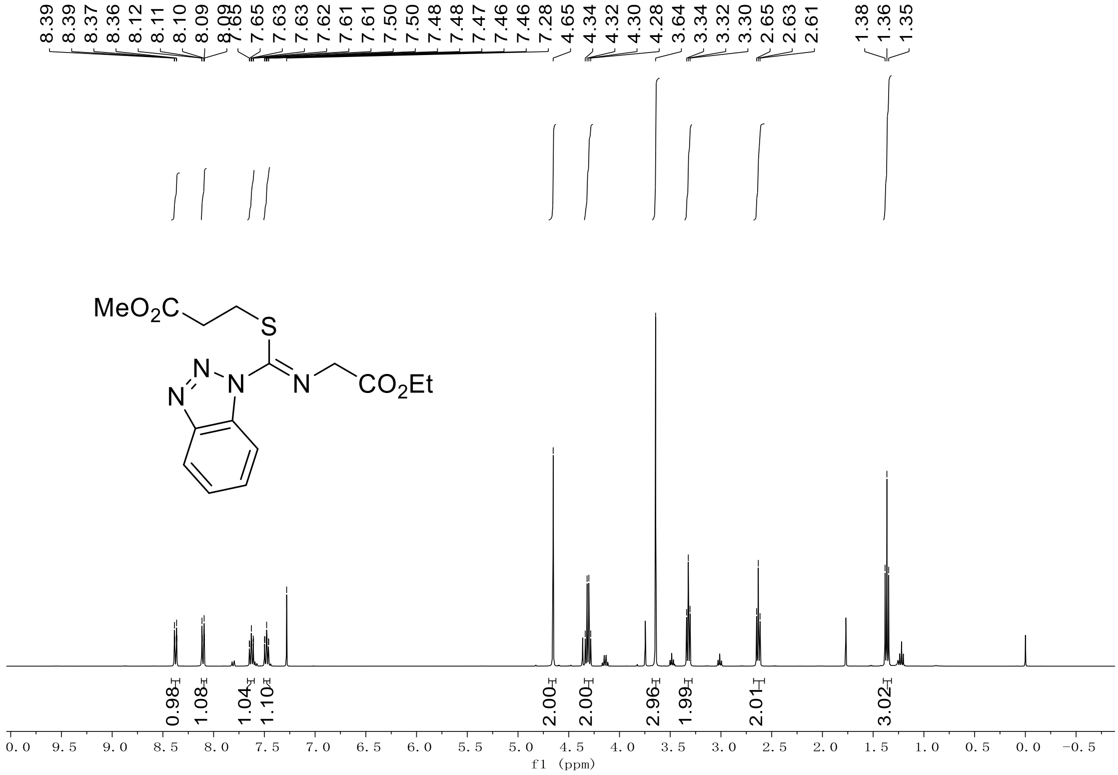
169.23
147.71 146.53 136.98 131.65 129.58 128.77 128.71 127.61 125.68 119.79 114.75
77.48 77.16 76.84
61.51
56.32
33.76
14.33
f1 (ppm)

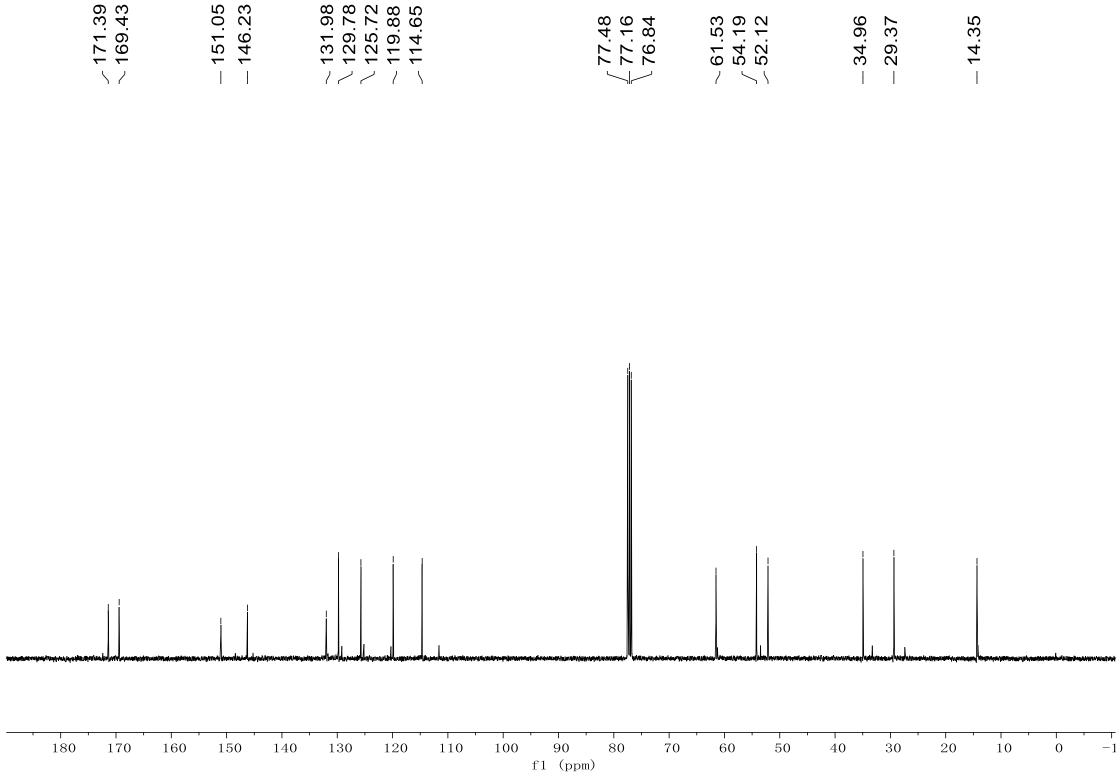
35



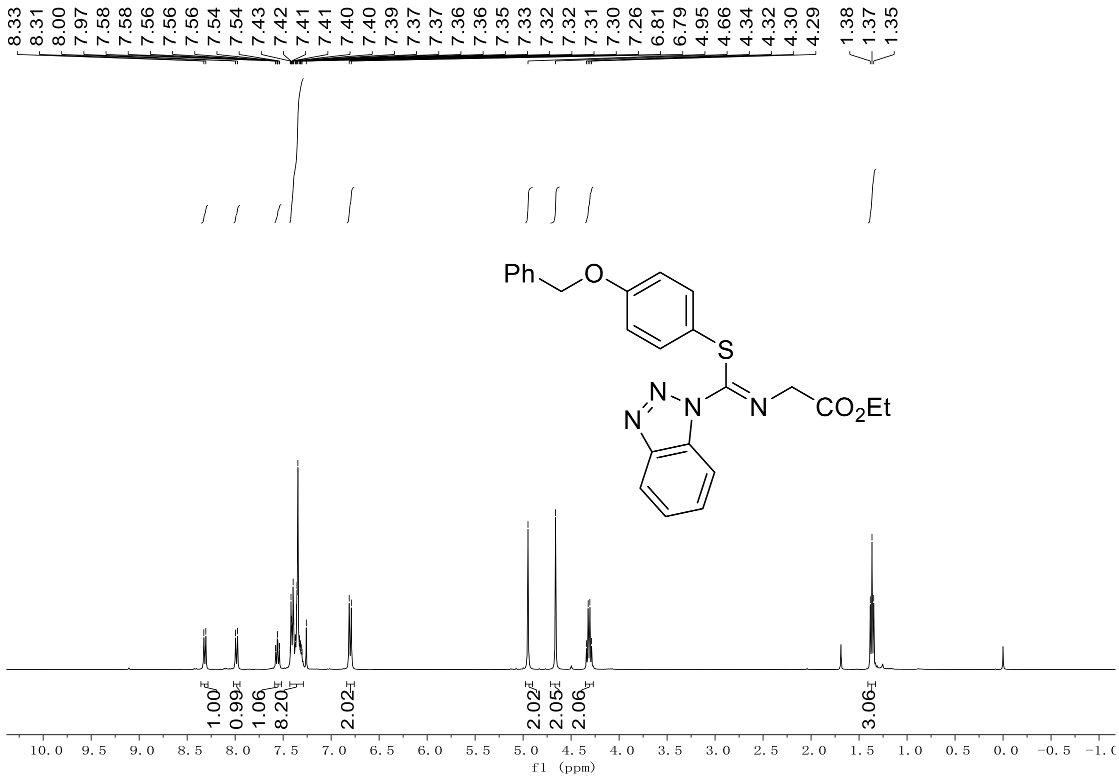


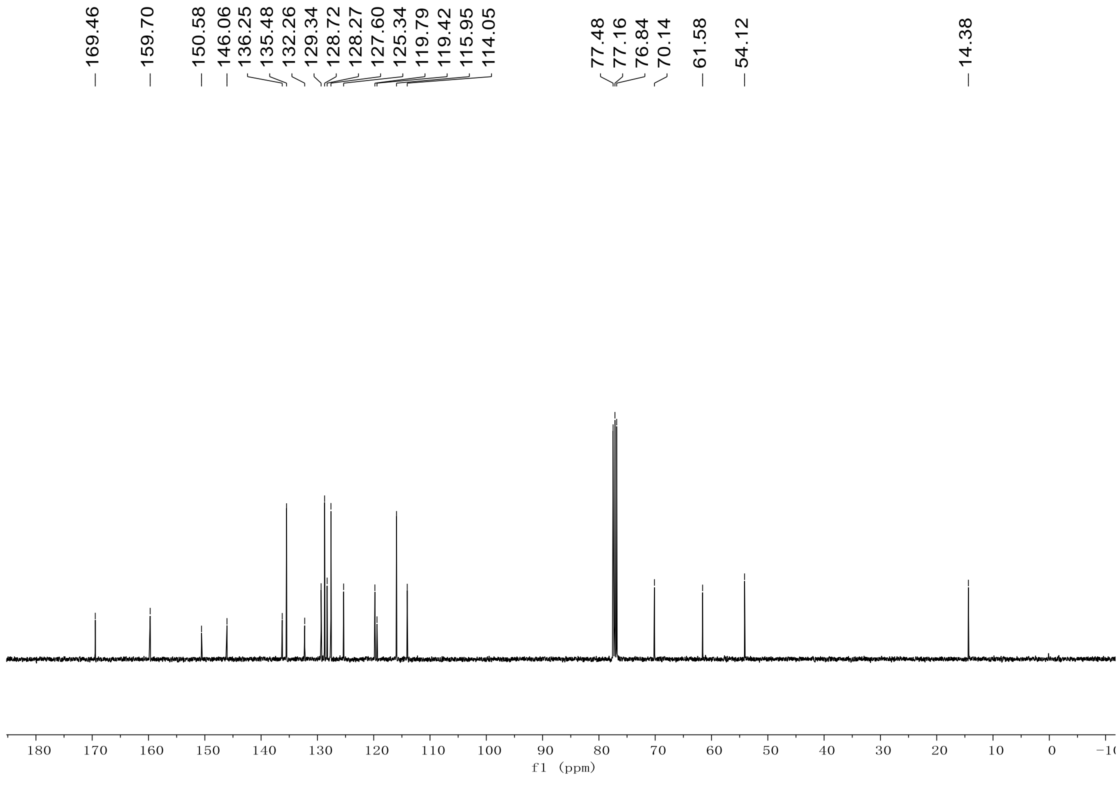
36


8.39 8.39 8.37 8.36 8.12 8.11 8.10 8.09 7.65 7.65 7.63 7.63 7.62 7.61 7.61 7.50 7.48 7.48 7.47 7.46 7.46 7.28 4.65 4.34 4.32 4.30 4.28 3.64 3.34 3.32 3.30 2.65 2.63 2.61 1.38 1.36 1.35
MeO2C
S
N
N
N
N
CO2Et
0.98 1.08 1.04 1.10 2.00 2.00 2.96 1.99 2.01 3.02
f1 (ppm)

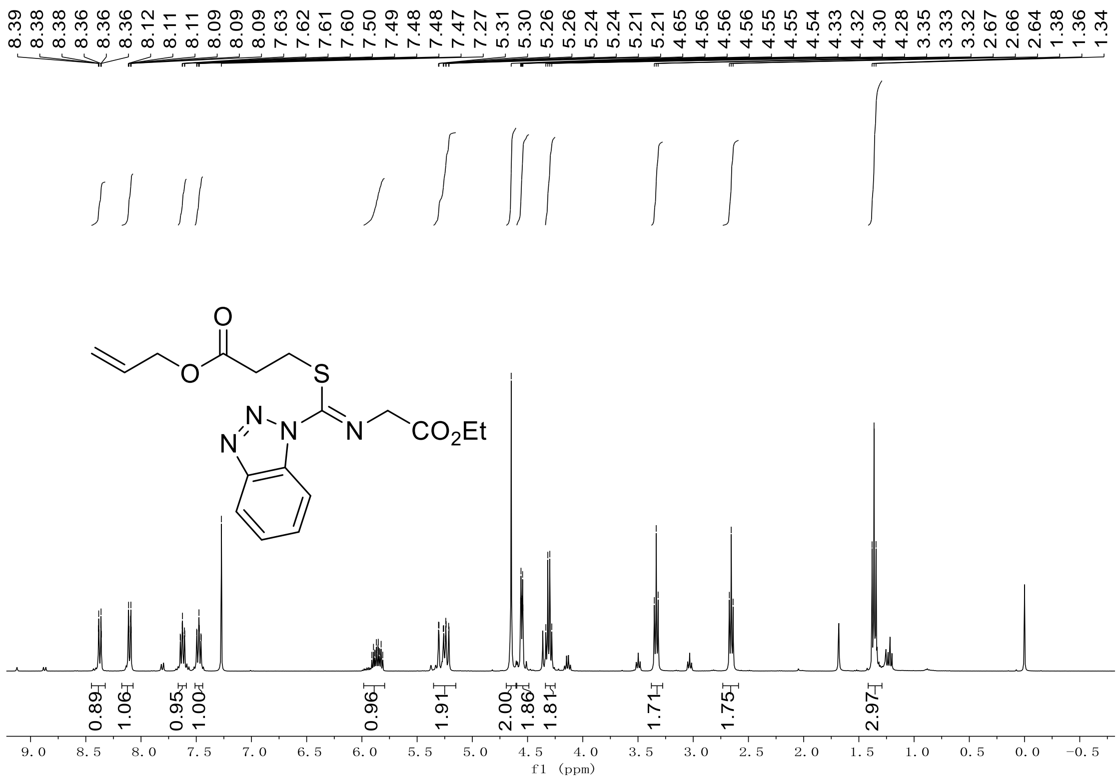

171.39 169.43 151.05 146.23 131.98 129.78 125.72 119.88 114.65 77.48 77.16 76.84 61.53 54.19 52.12 34.96 29.37 14.35
f1 (ppm)

37

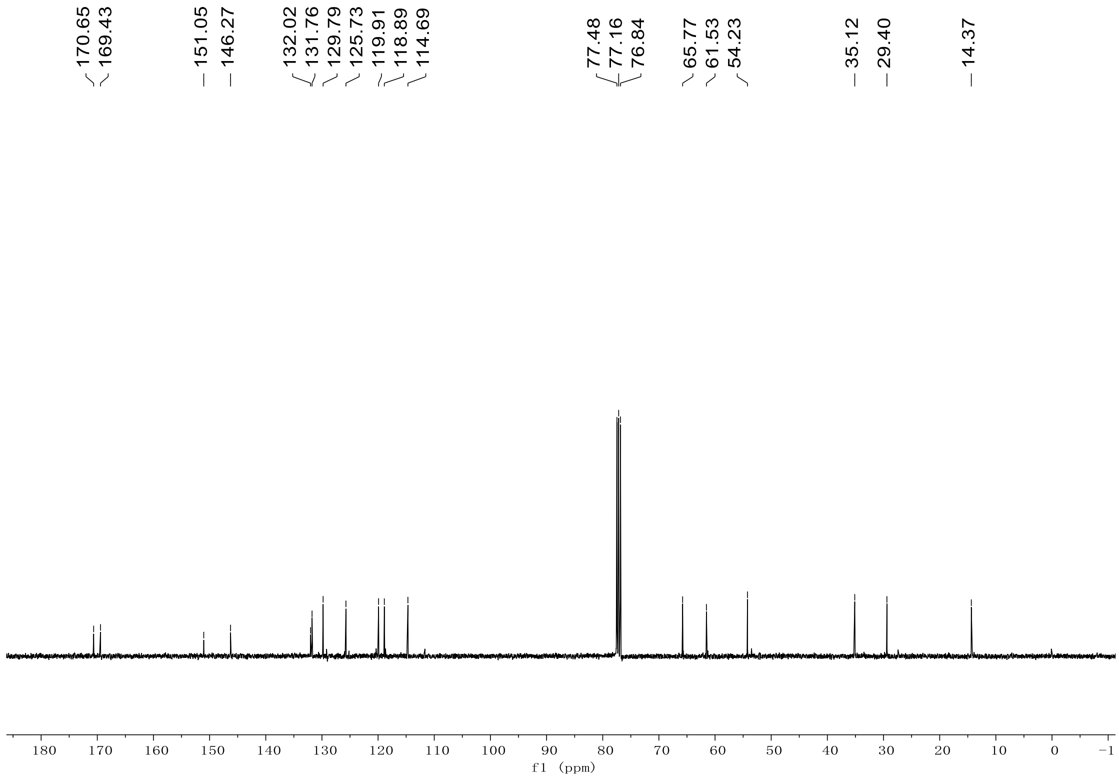

8.33 8.31 8.00 7.97 7.58 7.58 7.56 7.56 7.56 7.54 7.54 7.43 7.42 7.41 7.41 7.40 7.40 7.39 7.37 7.37 7.36 7.36 7.35 7.33 7.32 7.32 7.31 7.30 7.26 6.81 6.79 4.95 4.66 4.34 4.32 4.30 4.29
1.38 1.37 1.35
Ph
O
S
N
N
N
N
CO2Et
1.00 0.99 1.06 8.20 2.02 2.02 2.05 2.06 3.06
f1 (ppm)


169.46
159.70
150.58 146.06 136.25 135.48 132.26 129.34 128.72 128.27 127.60 125.34 119.79 119.42 115.95 114.05
77.48 77.16 76.84 70.14
61.58
54.12
14.38
f1 (ppm)

38

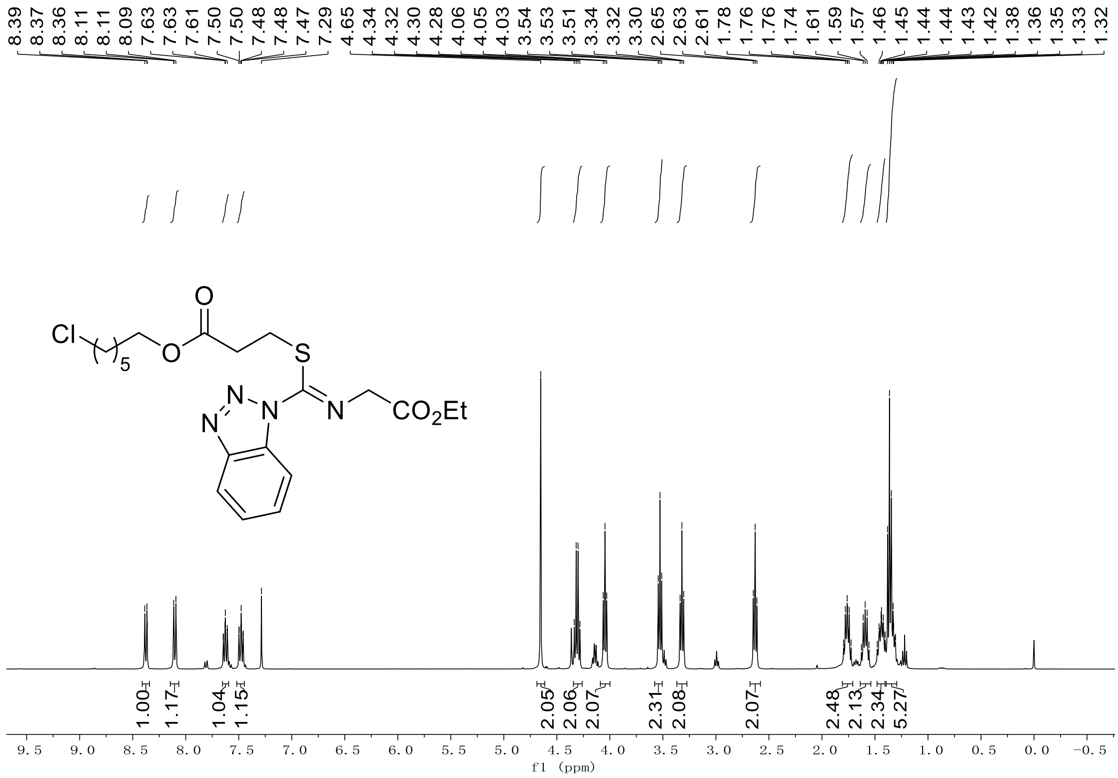


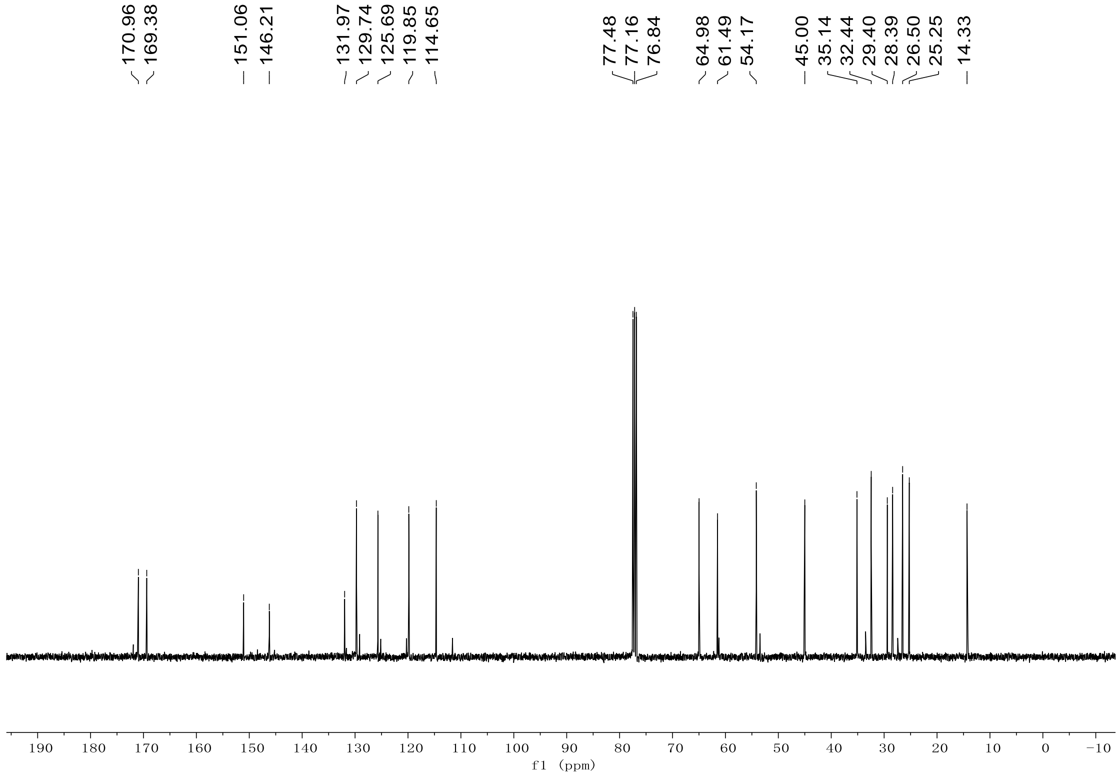
8.39
8.38
8.38
8.36
8.36
8.36
8.12
8.11
8.11
8.09
8.09
8.09
7.63
7.62
7.61
7.60
7.50
7.49
7.48
7.48
7.47
7.27
5.31
5.30
5.26
5.26
5.24
5.24
5.21
5.21
4.65
4.56
4.56
4.56
4.55
4.55
4.54
4.33
4.32
4.30
4.28
3.35
3.33
3.32
2.67
2.66
2.64
1.38
1.36
1.34
O
O
S
N
N
N
N
CO2Et
0.89
1.06
0.95
1.00
0.96
1.91
2.00
1.86
1.81
1.71
1.75
2.97
f1 (ppm)



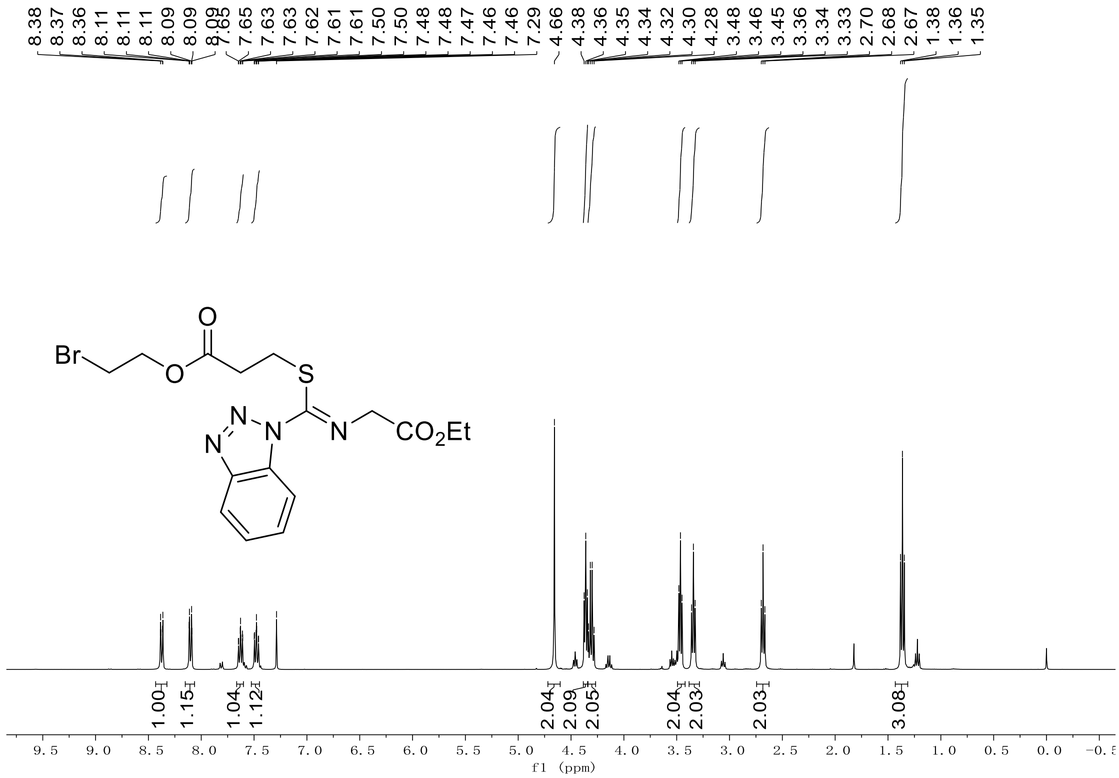
170.65
169.43
151.05
146.27
132.02
131.76
129.79
125.73
119.91
118.89
114.69
77.48
77.16
76.84
65.77
61.53
54.23
35.12
29.40
14.37
f1 (ppm)

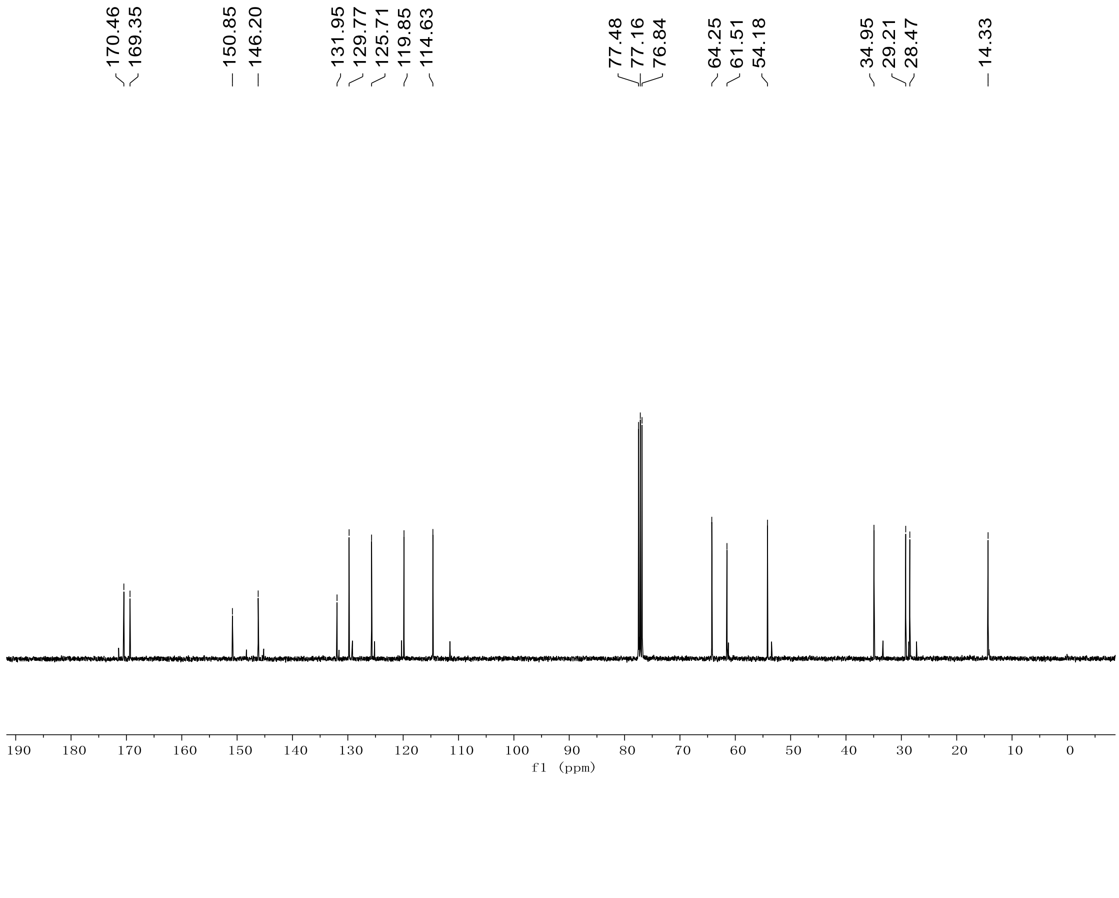
39


8.39 8.37 8.36 8.11 8.11 8.09 7.63 7.63 7.61 7.50 7.50 7.48 7.47 7.29 4.65 4.34 4.32 4.30 4.28 4.06 4.05 4.03 3.54 3.53 3.51 3.34 3.32 3.30 2.65 2.63 2.61 1.78 1.76 1.74 1.61 1.59 1.57 1.46 1.45 1.44 1.44 1.43 1.42 1.38 1.36 1.35 1.33 1.32
Cl
5
O
O
S
N
N
N
N
CO2Et
1.00 1.17 1.04 1.15 2.05 2.06 2.07 2.31 2.08 2.07 2.48 2.13 2.34 5.27
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 0.0 -0.5
f1 (ppm)

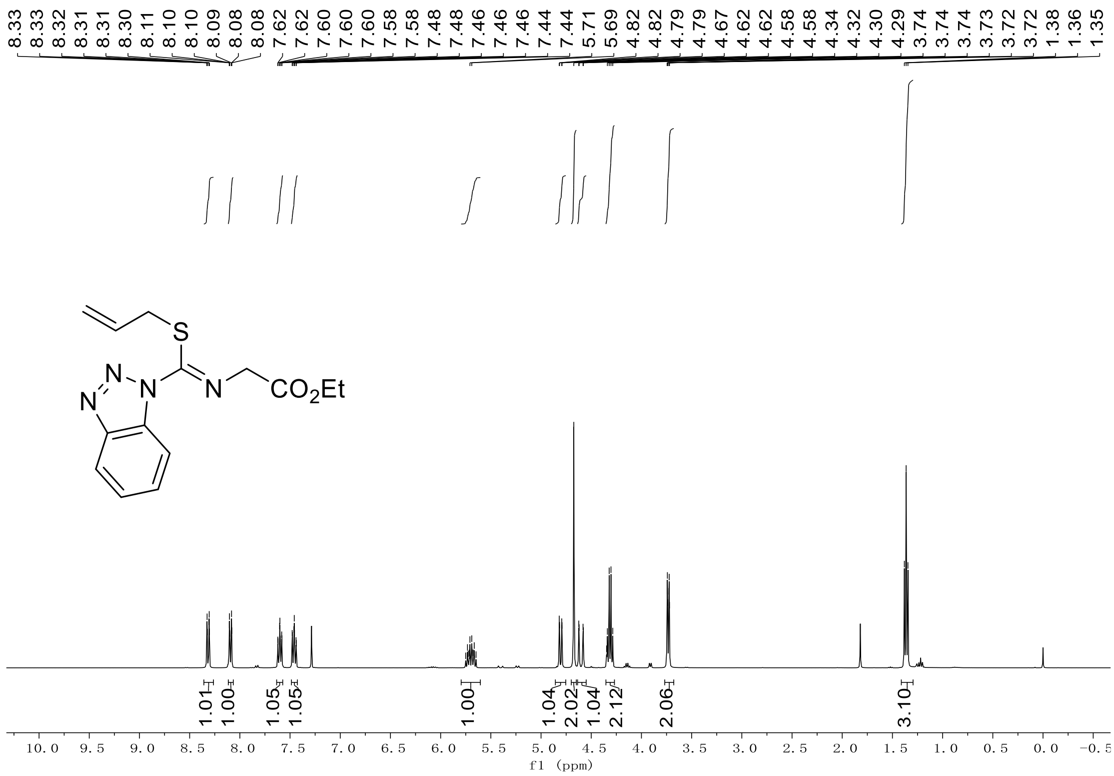

170.96 169.38 151.06 146.21 131.97 129.74 125.69 119.85 114.65 77.48 77.16 76.84 64.98 61.49 54.17 45.00 35.14 32.44 29.40 28.39 26.50 25.25 14.33
190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 -10
f1 (ppm)

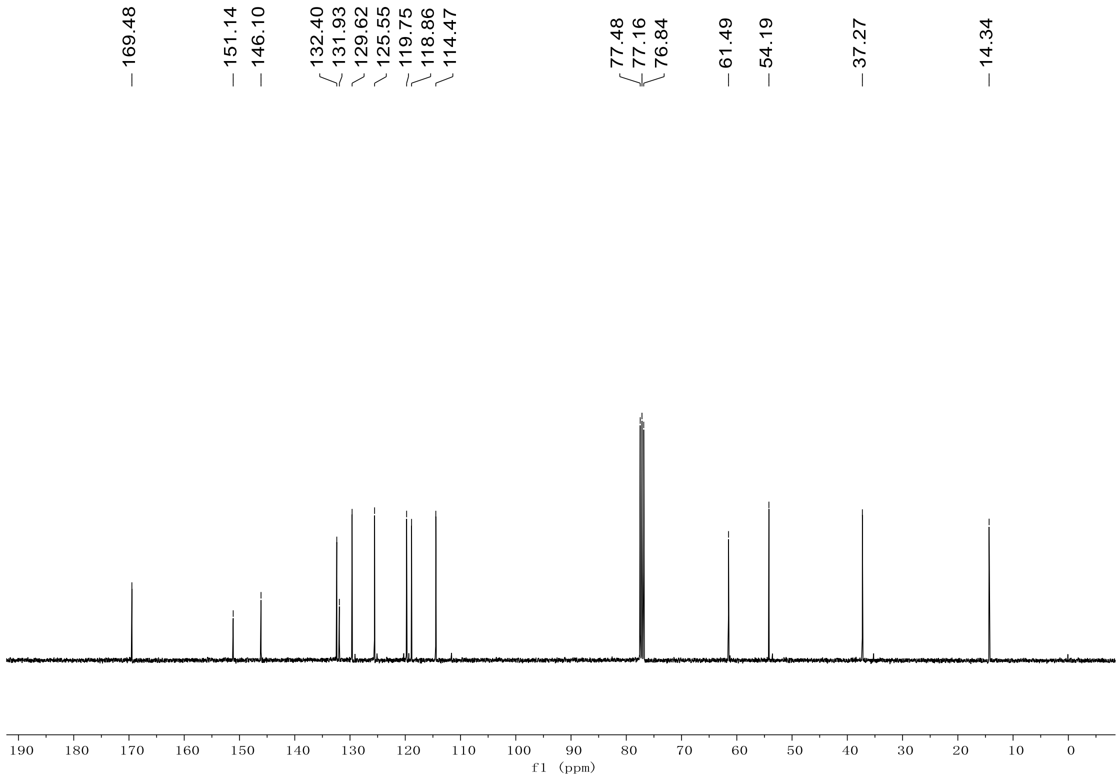
40


8.38 8.37 8.36 8.11 8.11 8.09 8.09 7.65 7.65 7.63 7.63 7.62 7.61 7.61 7.50 7.50 7.48 7.48 7.47 7.46 7.46 7.29 4.66 4.38 4.36 4.35 4.34 4.32 4.30 4.28 3.48 3.46 3.45 3.36 3.34 3.33 2.70 2.68 2.67 1.38 1.36 1.35
Br
O
O
S
N
N
N
N
CO2Et
1.00
1.15
1.04
1.12
2.04
2.09
2.05
2.04
2.03
2.03
3.08
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 0.0 -0.5
f1 (ppm)

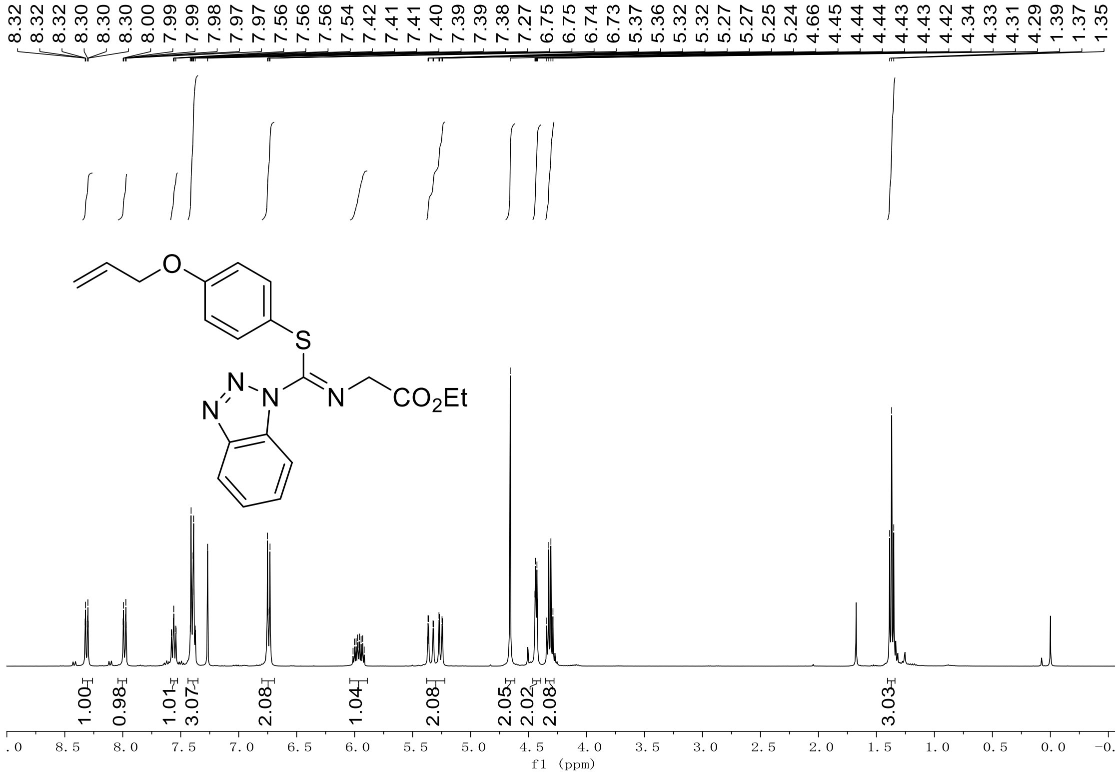

170.46 169.35 150.85 146.20 131.95 129.77 125.71 119.85 114.63 77.48 77.16 76.84 64.25 61.51 54.18 34.95 29.21 28.47 14.33
190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0
f1 (ppm)

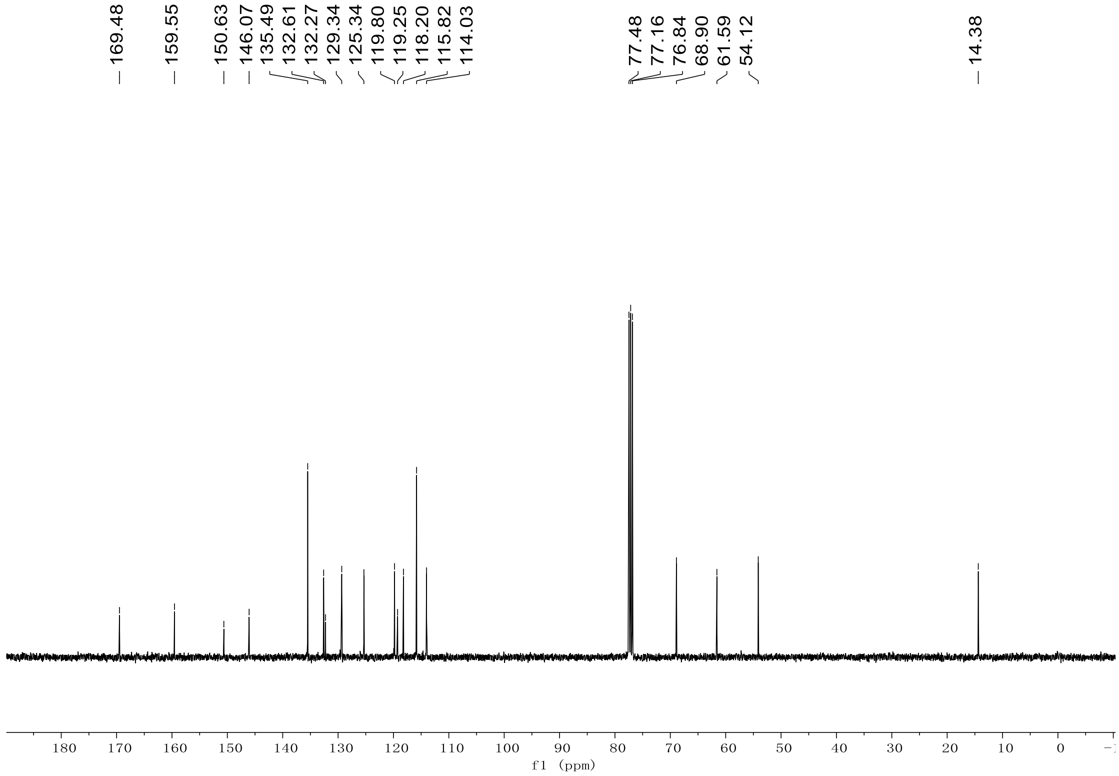
41


8.33 8.33 8.32 8.31 8.31 8.30 8.11 8.10 8.10 8.09 8.08 8.08 7.62 7.62 7.60 7.60 7.60 7.58 7.58 7.48 7.48 7.46 7.46 7.46 7.44 7.44 5.71 5.69 4.82 4.82 4.79 4.79 4.67 4.62 4.62 4.58 4.58 4.34 4.32 4.30 4.29 3.74 3.74 3.74 3.73 3.72 3.72 1.38 1.36 1.35
S
N
N
N
N
CO2Et
1.01 1.00 1.05 1.05 1.00 1.04 2.02 1.04 2.12 2.06 3.10
10.0 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 0.0 -0.5
f1 (ppm)

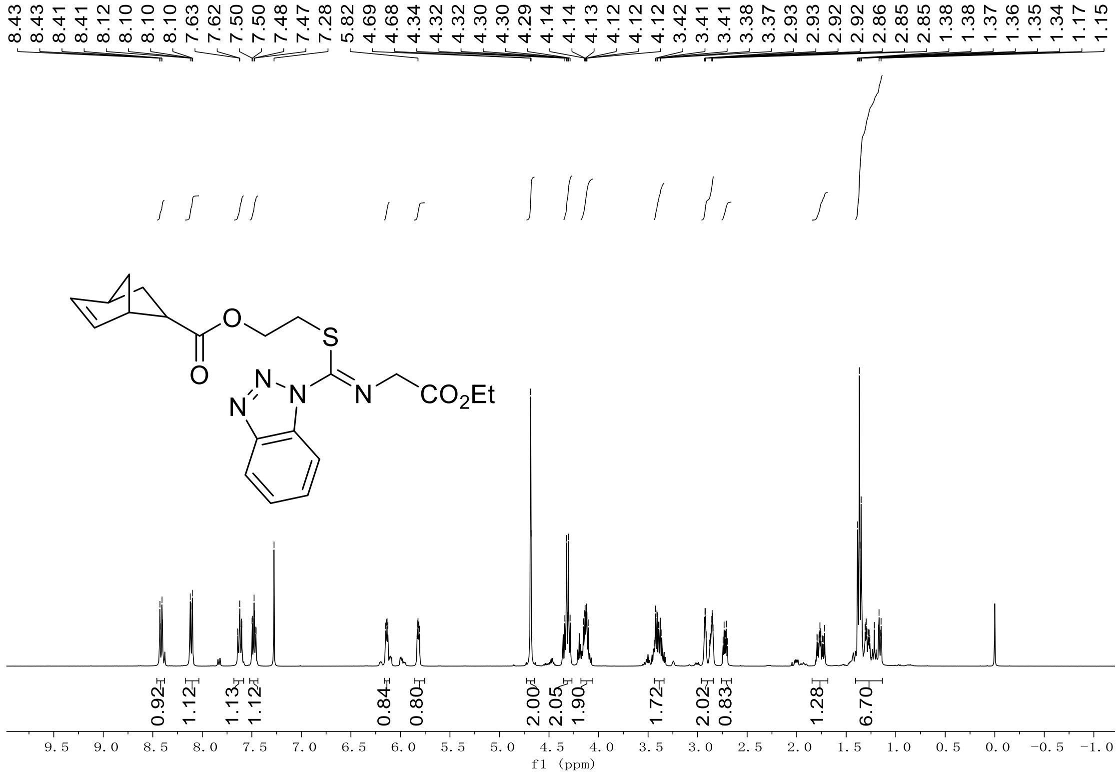

169.48
151.14 146.10
132.40 131.93 129.62 125.55 119.75 118.86 114.47
77.48 77.16 76.84
61.49 54.19
37.27
14.34
190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0
f1 (ppm)

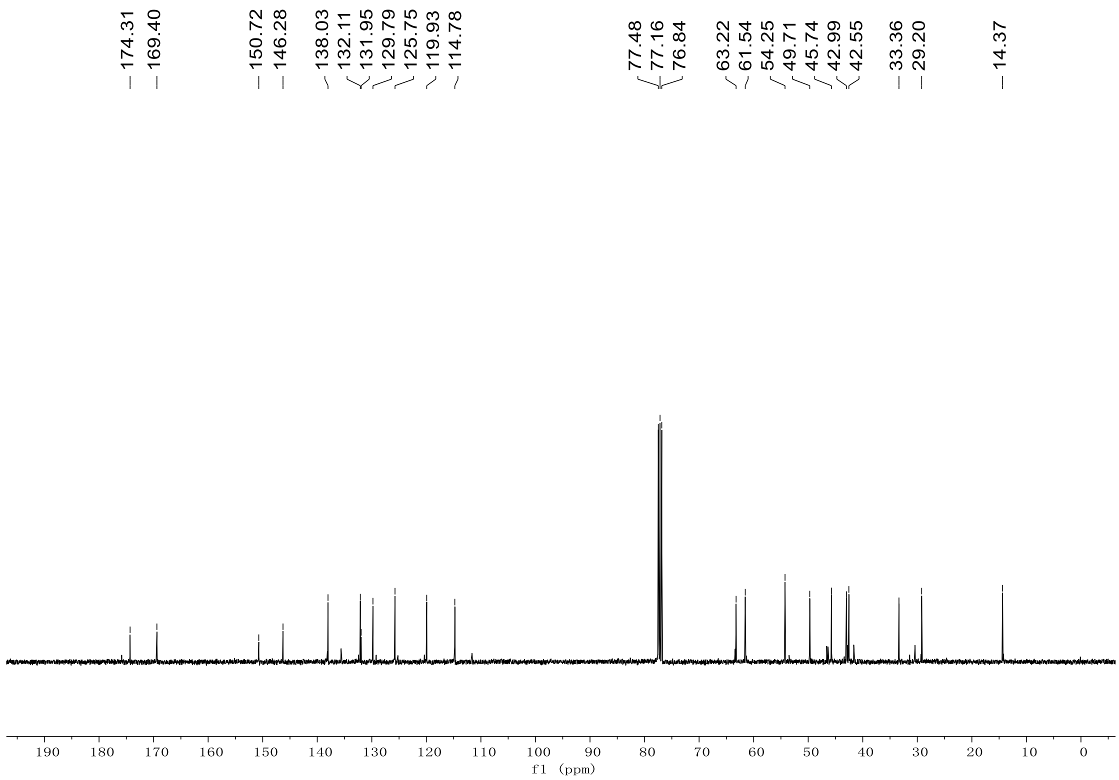
42


8.32 8.32 8.32 8.30 8.30 8.30 8.00 7.99 7.99 7.98 7.97 7.97 7.56 7.56 7.54 7.42 7.41 7.41 7.40 7.39 7.39 7.38 7.27 6.75 6.75 6.74 6.73 5.37 5.36 5.32 5.32 5.27 5.27 5.25 5.24 4.66 4.45 4.44 4.44 4.43 4.43 4.42 4.34 4.33 4.31 4.29 1.39 1.37 1.35
O
S
N
N
N
N
CO2Et
1.00 0.98 1.01 3.07 2.08 1.04 2.08 2.05 2.02 2.08 3.03
f1 (ppm)

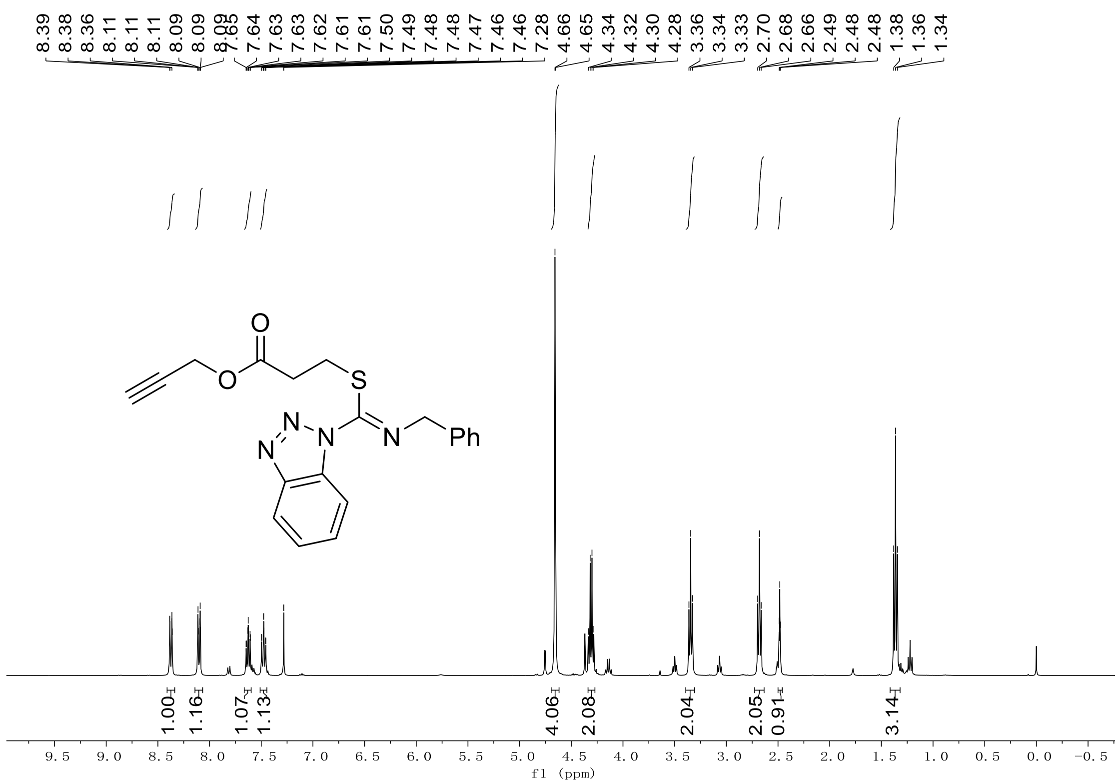

169.48 159.55 150.63 146.07 135.49 132.61 132.27 129.34 125.34 119.80 119.25 118.20 115.82 114.03 77.48 77.16 76.84 68.90 61.59 54.12 14.38
f1 (ppm)

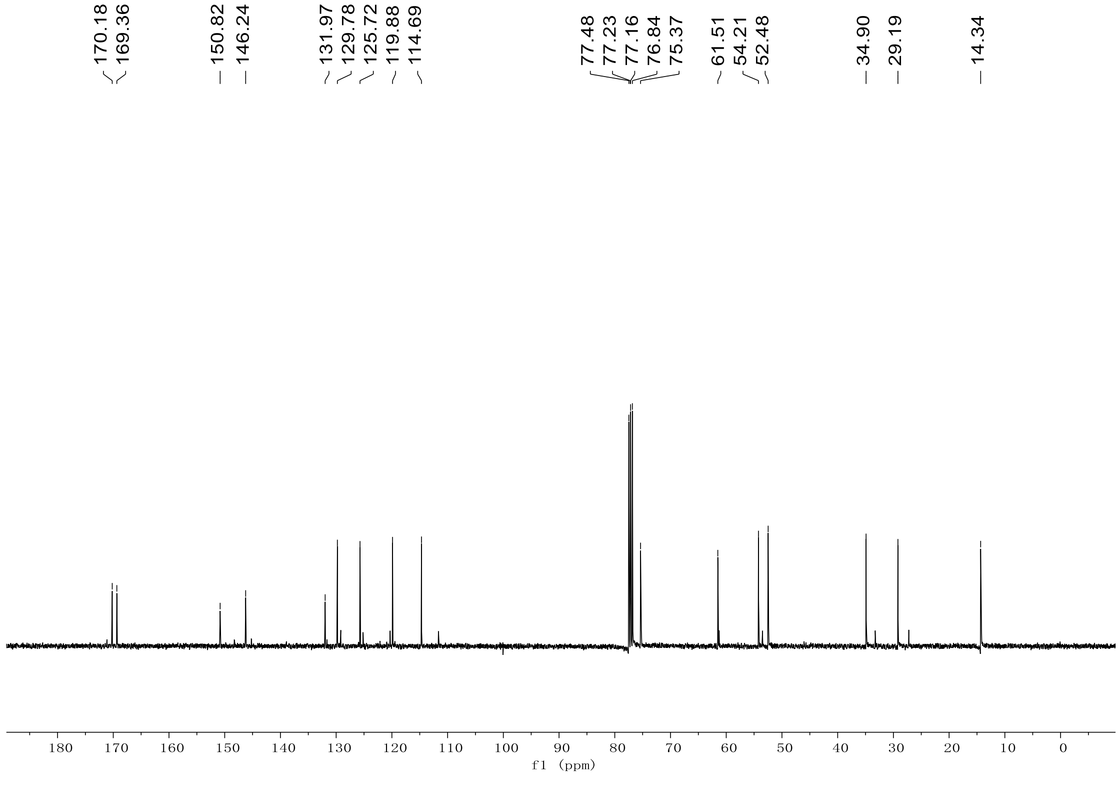
43


8.43 8.43 8.41 8.41 8.12 8.10 8.10 8.10 7.63 7.62 7.50 7.50 7.48 7.47 7.28 5.82 4.69 4.68 4.34 4.32 4.32 4.30 4.30 4.29 4.14 4.14 4.13 4.12 4.12 4.12 3.42 3.41 3.41 3.38 3.37 2.93 2.93 2.92 2.92 2.86 2.85 2.85 1.38 1.38 1.37 1.36 1.35 1.34 1.17 1.15
O
S
N
N
N
N
CO2Et
0.92
1.12
1.13
1.12
0.84
0.80
2.00
2.05
1.90
1.72
2.02
0.83
1.28
6.70
f1 (ppm)

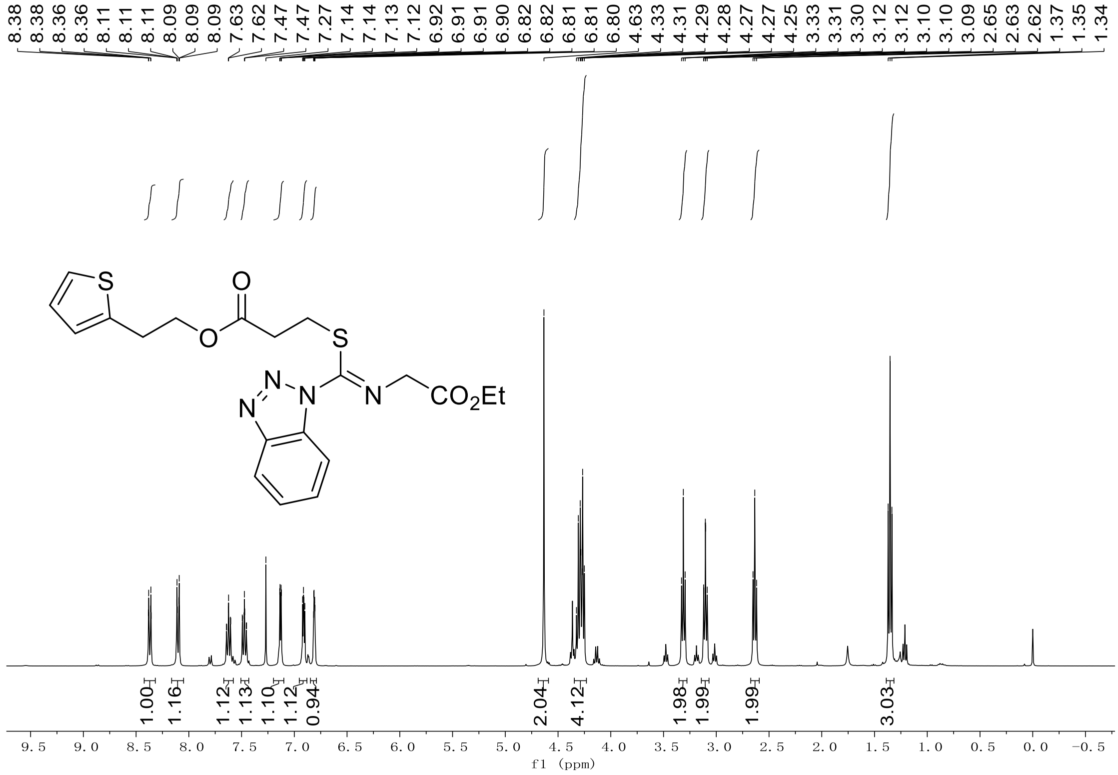

174.31
169.40
150.72
146.28
138.03
132.11
131.95
129.79
125.75
119.93
114.78
77.48
77.16
76.84
63.22
61.54
54.25
49.71
45.74
42.99
42.55
33.36
29.20
14.37
f1 (ppm)

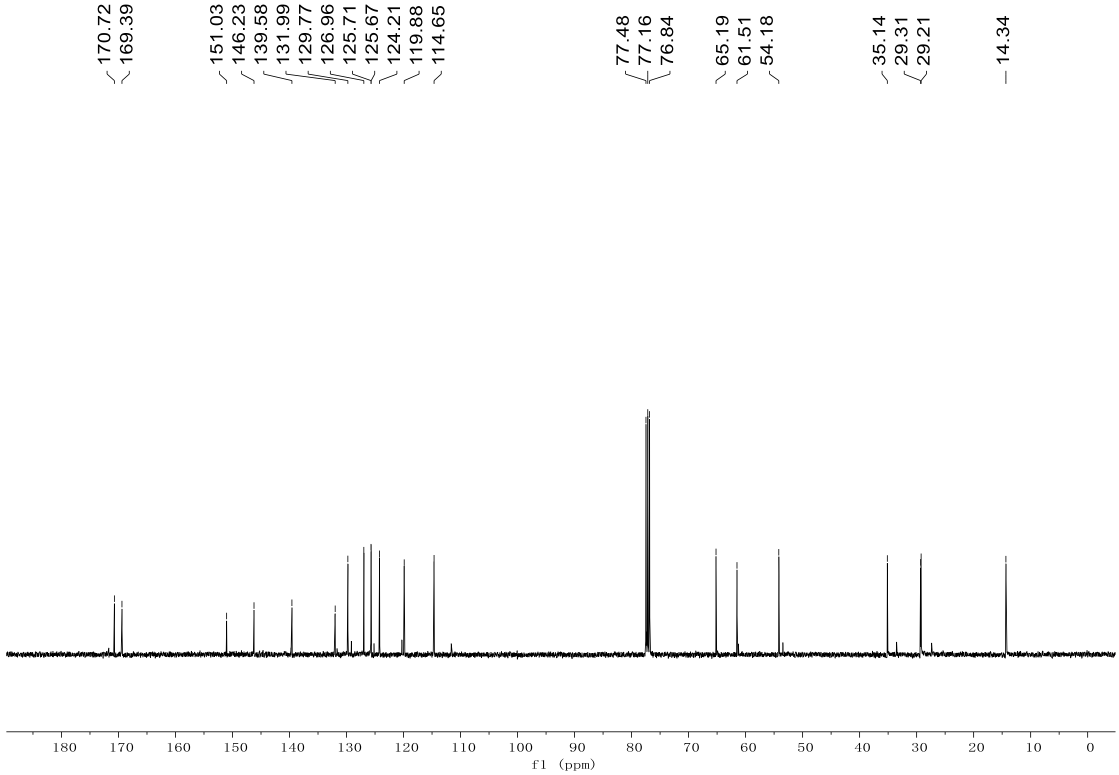
44


8.39
8.38
8.36
8.11
8.11
8.11
8.09
8.09
7.65
7.64
7.63
7.63
7.62
7.61
7.61
7.50
7.49
7.48
7.48
7.47
7.46
7.46
7.28
4.66
4.65
4.34
4.32
4.30
4.28
3.36
3.34
3.33
2.70
2.68
2.66
2.49
2.48
2.48
1.38
1.36
1.34
O
O
S
N
N
N
N
Ph
1.00
1.16
1.07
1.13
4.06
2.08
2.04
2.05
0.91
3.14
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
0.0
-0.5
f1 (ppm)

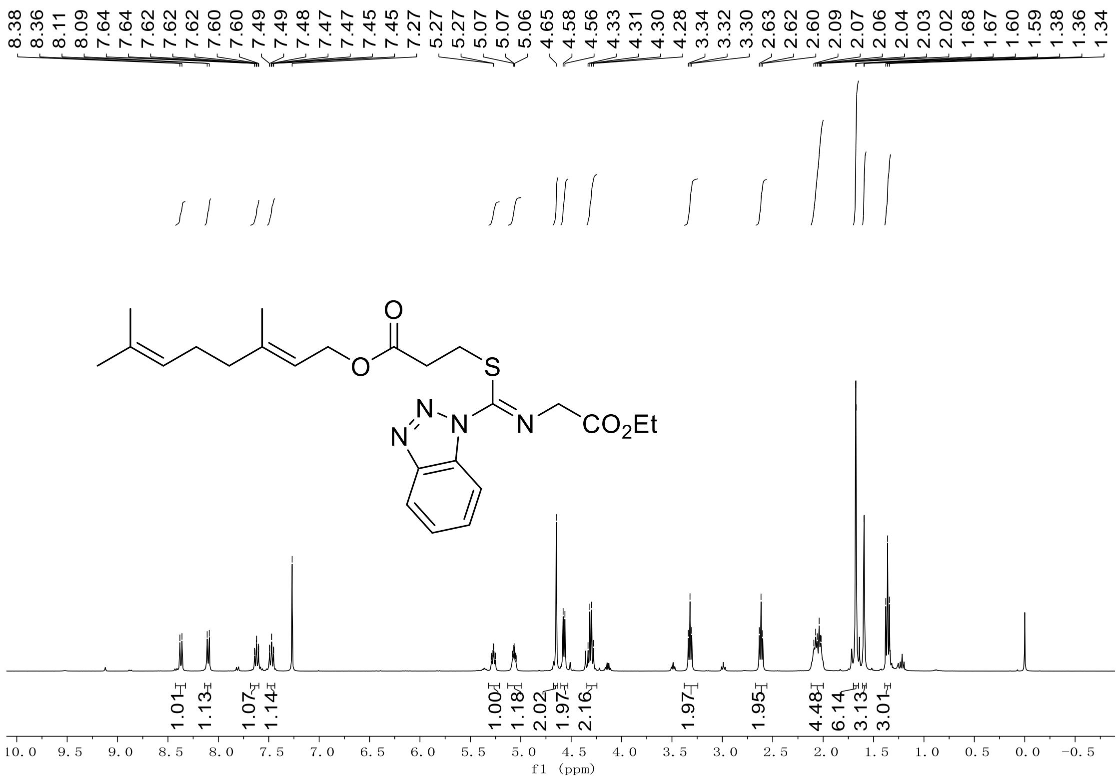

170.18
169.36
150.82
146.24
131.97
129.78
125.72
119.88
114.69
77.48
77.23
77.16
76.84
75.37
61.51
54.21
52.48
34.90
29.19
14.34
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
f1 (ppm)

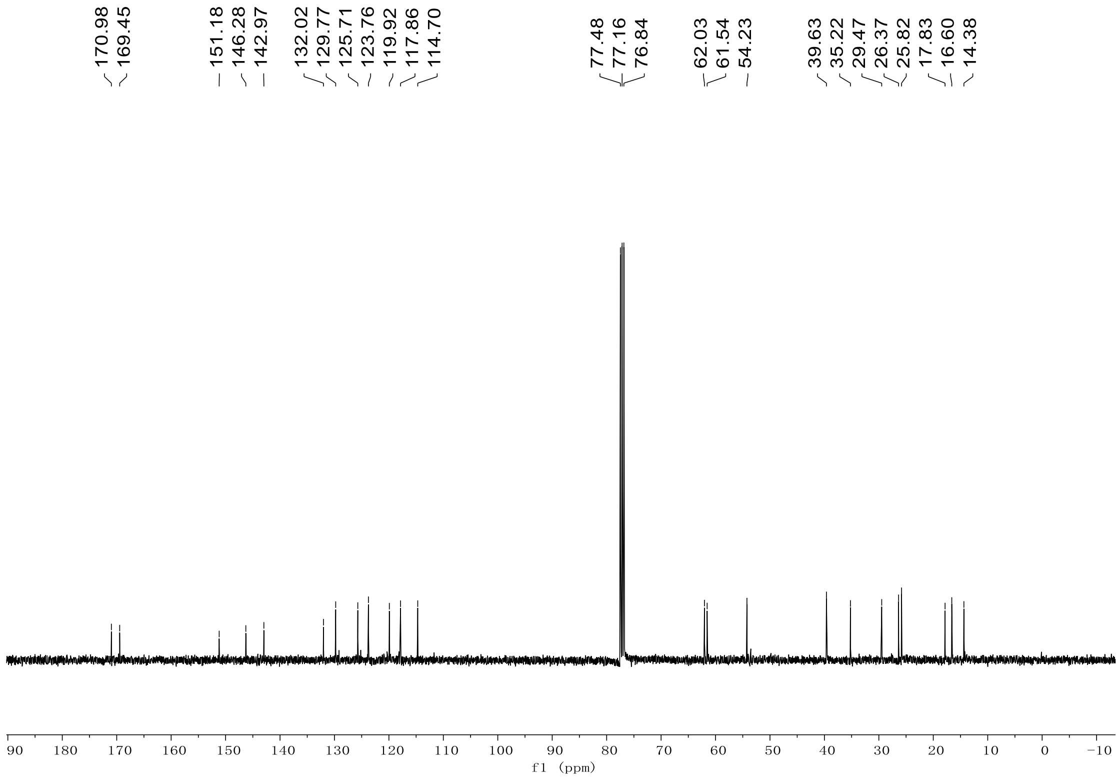
45


8.38 8.38 8.36 8.36 8.11 8.11 8.11 8.09 8.09 7.63 7.62 7.47 7.47 7.27 7.14 7.14 7.13 7.12 6.92 6.91 6.91 6.90 6.82 6.82 6.81 6.81 6.80 4.63 4.33 4.31 4.29 4.28 4.27 4.27 4.25 3.33 3.31 3.30 3.12 3.12 3.10 3.09 2.65 2.63 2.62 1.37 1.35 1.34
S
O
O
S
N
N
N
N
CO_2Et
1.00 1.16 1.12 1.13 1.10 1.12 0.94 2.04 4.12 1.98 1.99 1.99 3.03
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 0.0 -0.5
f1 (ppm)

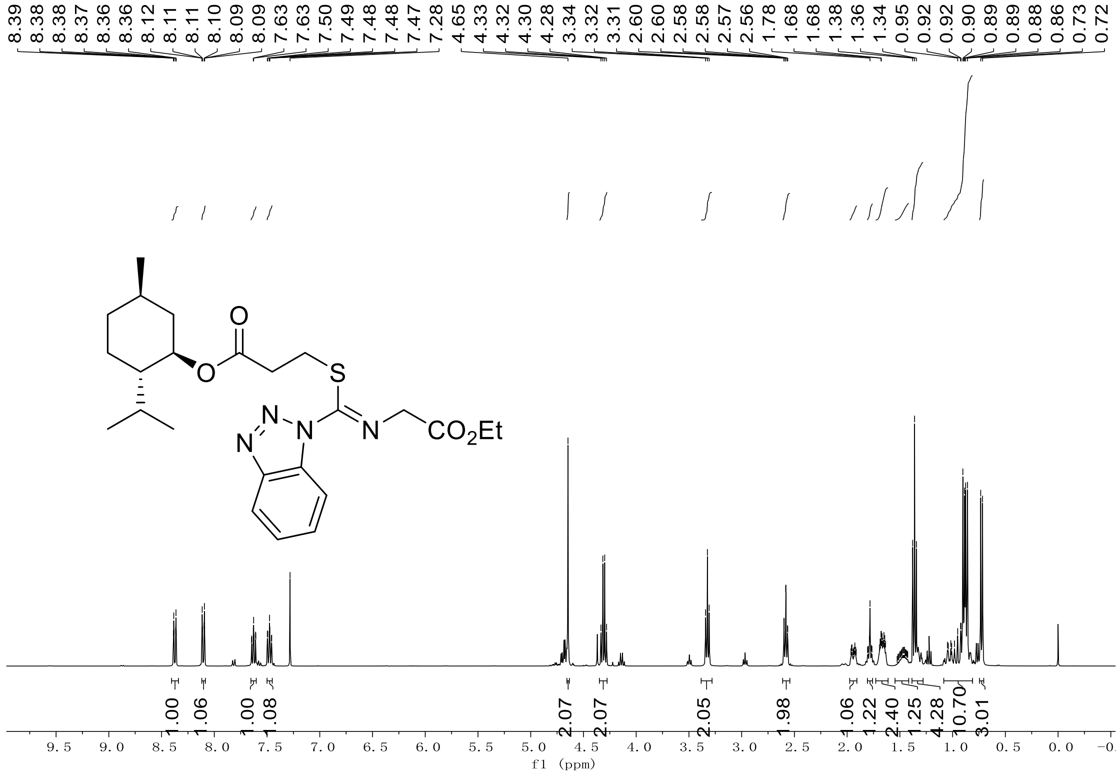

170.72 169.39 151.03 146.23 139.58 131.99 129.77 126.96 125.71 125.67 124.21 119.88 114.65 77.48 77.16 76.84 65.19 61.51 54.18 35.14 29.31 29.21 14.34
180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0
f1 (ppm)

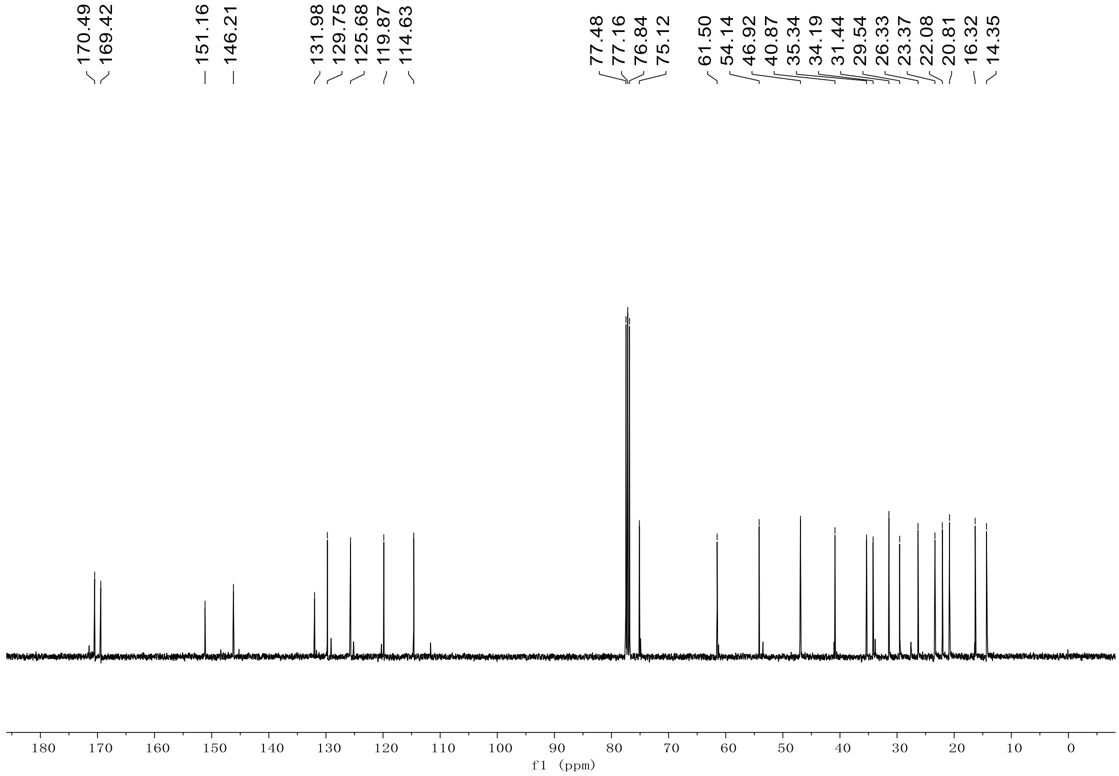
46

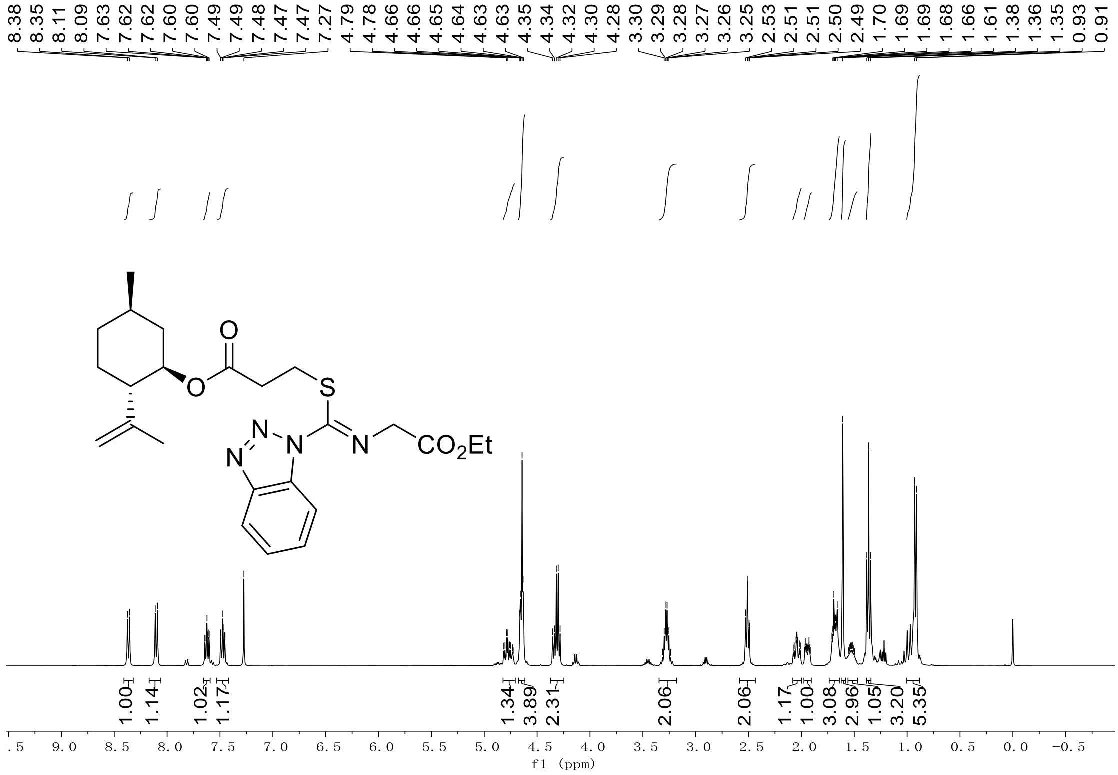

8.38 8.36 8.11 8.09 7.64 7.64 7.62 7.62 7.60 7.60 7.49 7.49 7.48 7.47 7.47 7.45 7.45 7.27 5.27 5.27 5.07 5.07 5.06 4.65 4.58 4.56 4.33 4.31 4.30 4.28 3.34 3.32 3.30 2.63 2.62 2.60 2.09 2.07 2.06 2.04 2.03 2.02 1.68 1.67 1.60 1.59 1.38 1.36 1.34
1.01 1.13 1.07 1.14 1.00 1.18 2.02 1.97 2.16 1.97 1.95 4.48 6.14 3.13 3.01
f1 (ppm)


170.98 169.45 151.18 146.28 142.97 132.02 129.77 125.71 123.76 119.92 117.86 114.70 77.48 77.16 76.84 62.03 61.54 54.23 39.63 35.22 29.47 26.37 25.82 17.83 16.60 14.38
f1 (ppm)

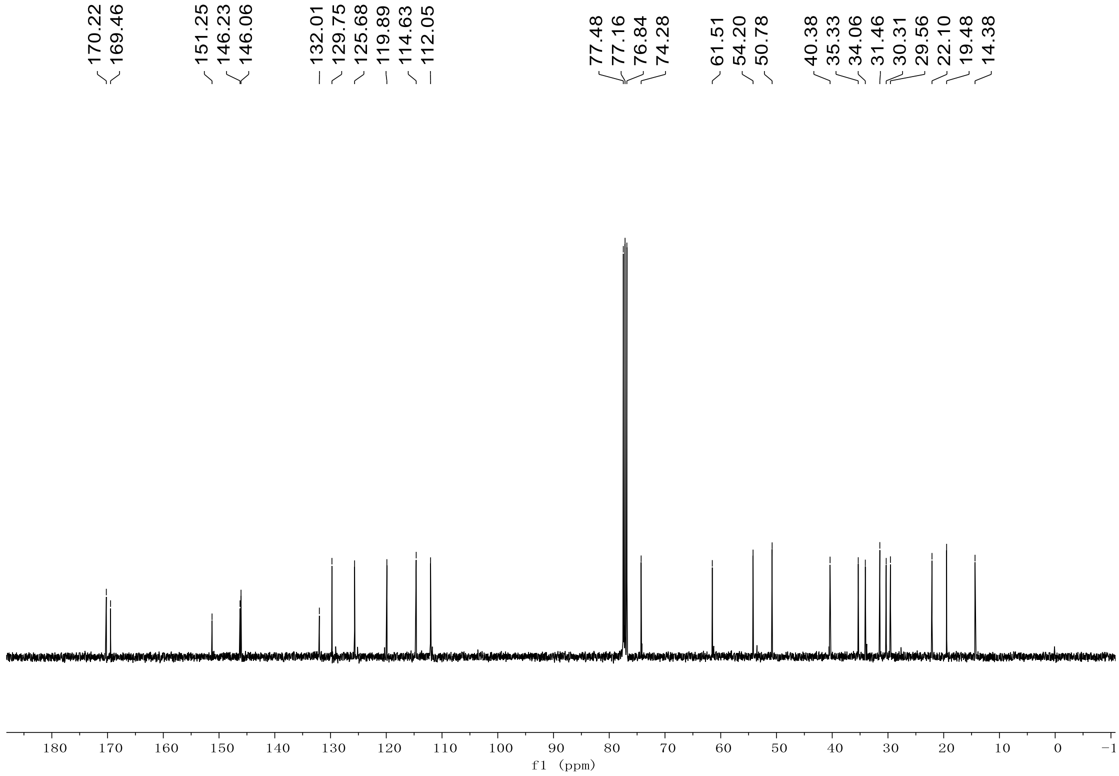
47


8.39 8.38 8.38 8.37 8.36 8.36 8.12 8.11 8.11 8.10 8.09 8.09 7.63 7.63 7.50 7.49 7.48 7.48 7.47 7.28 4.65 4.33 4.32 4.30 4.28 3.34 3.32 3.31 2.60 2.60 2.58 2.58 2.57 2.56 1.78 1.68 1.68 1.38 1.36 1.34 0.95 0.92 0.92 0.90 0.89 0.89 0.88 0.86 0.73 0.72
O
O
S
N
N
N
N
CO2Et
1.00 1.06 1.00 1.08 2.07 2.07 2.05 1.98 1.06 1.22 2.40 1.25 4.28 10.70 3.01
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 0.0
f1 (ppm)


170.49 169.42 151.16 146.21 131.98 129.75 125.68 119.87 114.63 77.48 77.16 76.84 75.12 61.50 54.14 46.92 40.87 35.34 34.19 31.44 29.54 26.33 23.37 22.08 20.81 16.32 14.35
180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0
f1 (ppm)

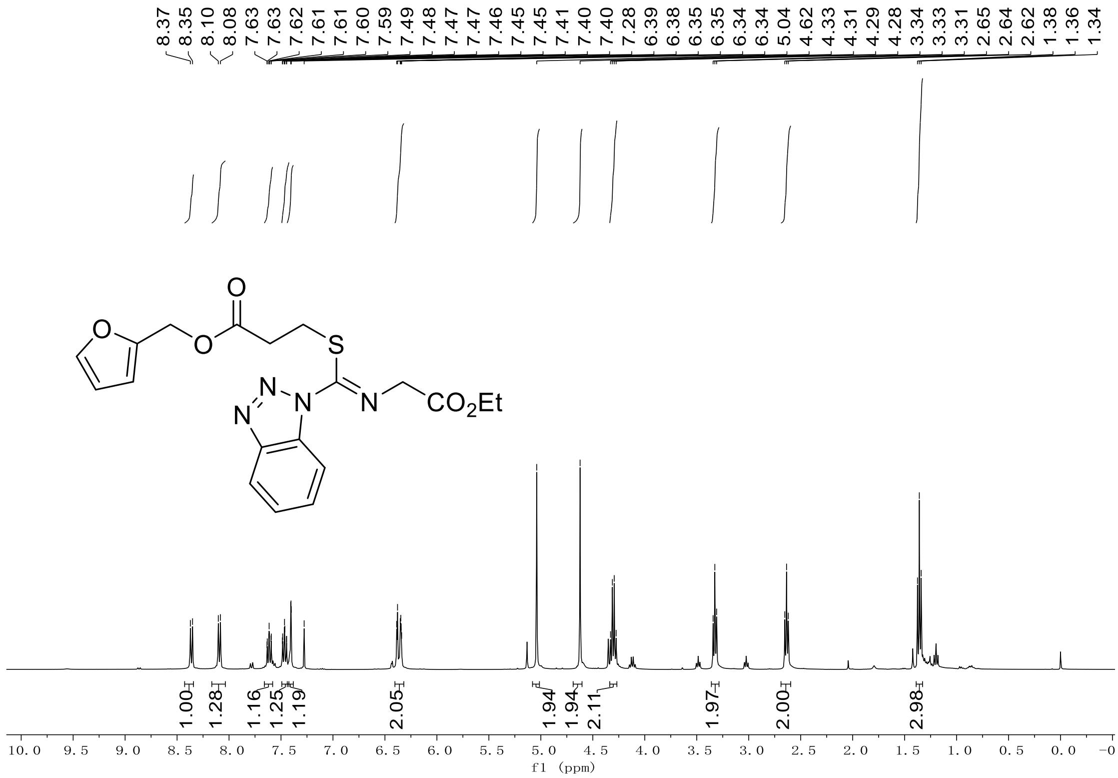


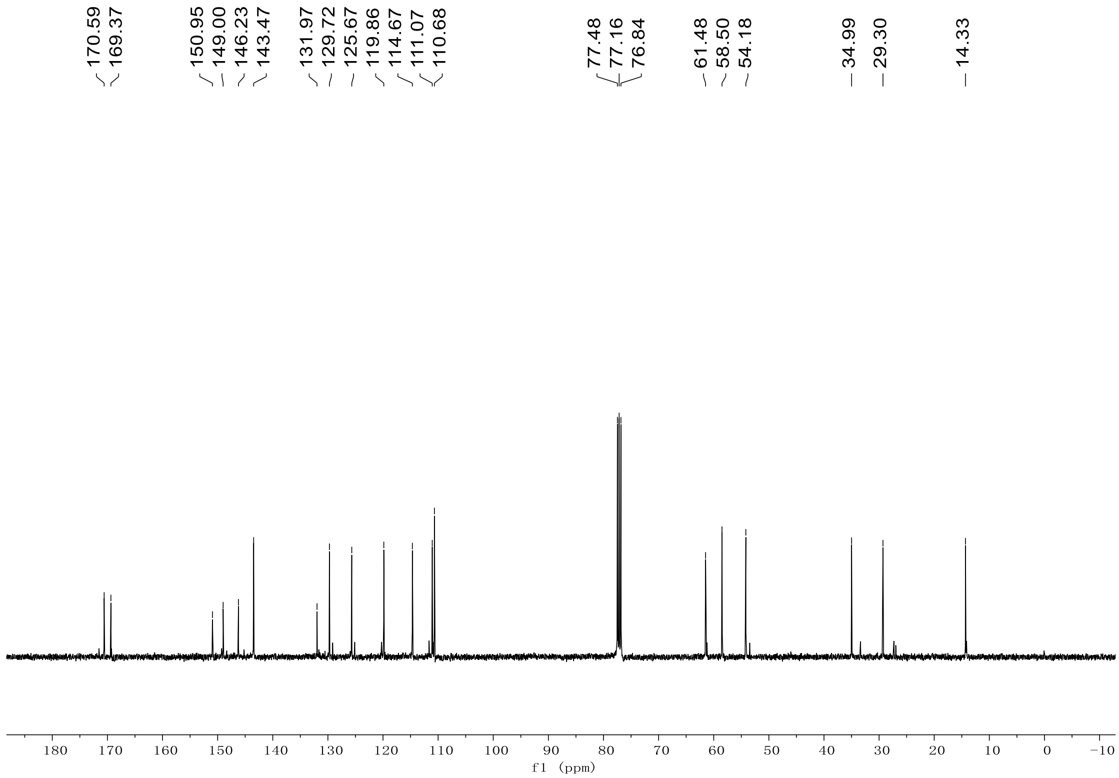
8.38 8.35 8.11 8.09 7.63 7.62 7.62 7.60 7.60 7.49 7.49 7.48 7.47 7.47 7.27 4.79 4.78 4.66 4.66 4.65 4.64 4.63 4.63 4.35 4.34 4.32 4.30 4.28 3.30 3.29 3.28 3.27 3.26 3.25 2.53 2.51 2.51 2.50 2.49 1.70 1.69 1.69 1.68 1.66 1.61 1.38 1.36 1.35 0.93 0.91
O
O
S
N
N
N
N
CO_2Et
1.00 1.14 1.02 1.17 1.34 3.89 2.31 2.06 2.06 1.17 1.00 3.08 2.96 1.05 3.20 5.35
f1 (ppm)



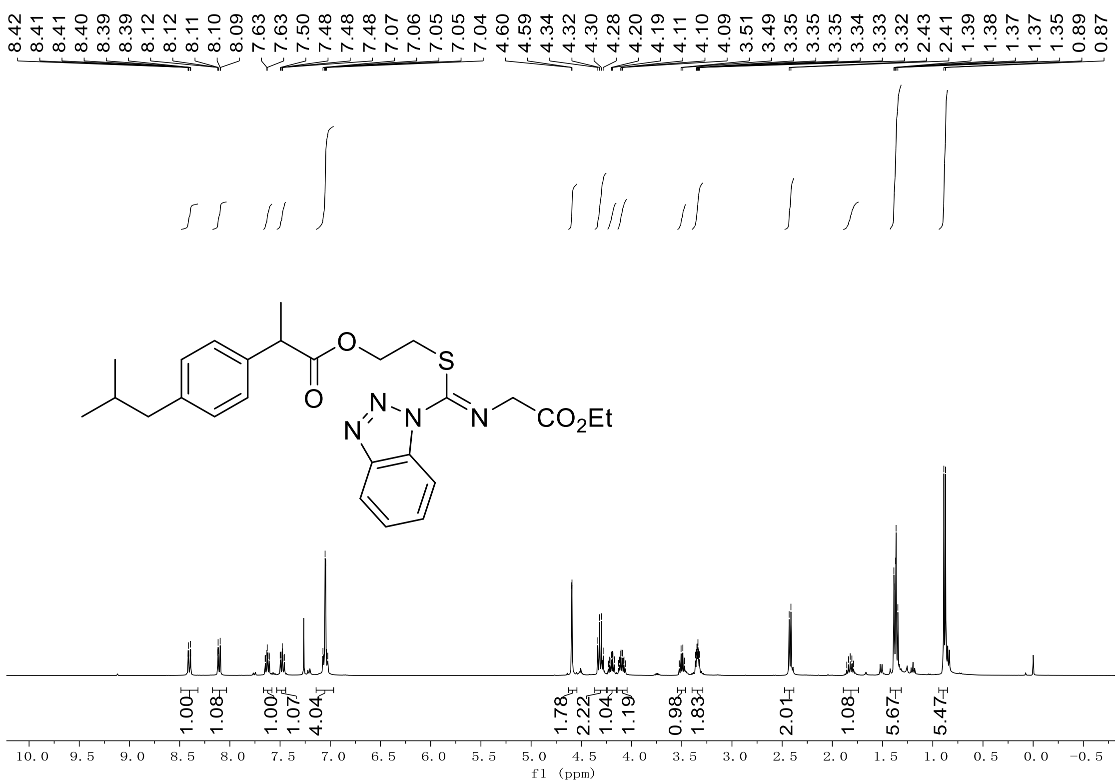
170.22 169.46 151.25 146.23 146.06 132.01 129.75 125.68 119.89 114.63 112.05 77.48 77.16 76.84 74.28 61.51 54.20 50.78 40.38 35.33 34.06 31.46 30.31 29.56 22.10 19.48 14.38
f1 (ppm)

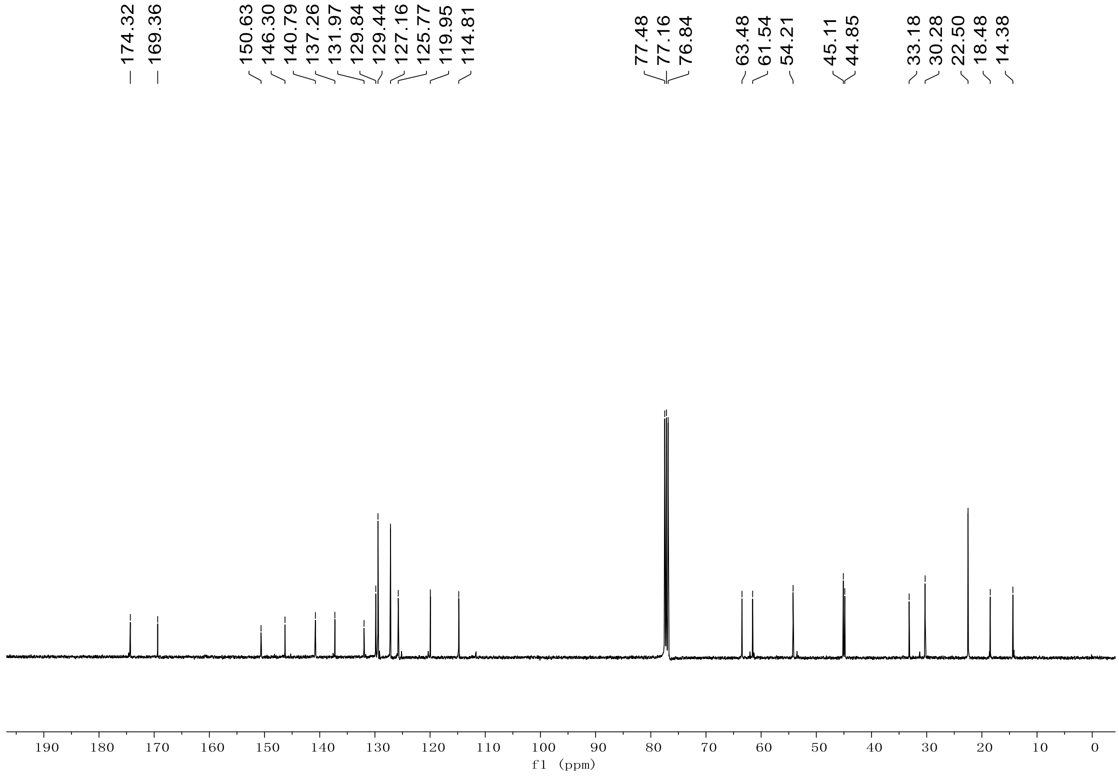
49


8.37 8.35 8.10 8.08 7.63 7.62 7.61 7.61 7.60 7.59 7.49 7.48 7.47 7.47 7.46 7.45 7.45 7.41 7.40 7.40 7.28 6.39 6.38 6.35 6.34 6.34 5.04 4.62 4.33 4.31 4.29 4.28 3.34 3.33 3.31 2.65 2.64 2.62 1.38 1.36 1.34
O
O
O
S
N
N
N
N
CO2Et
1.00 1.28 1.16 1.25 1.19 2.05 1.94 1.94 2.11 1.97 2.00 2.98
10.0 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 0.0 -0
f1 (ppm)

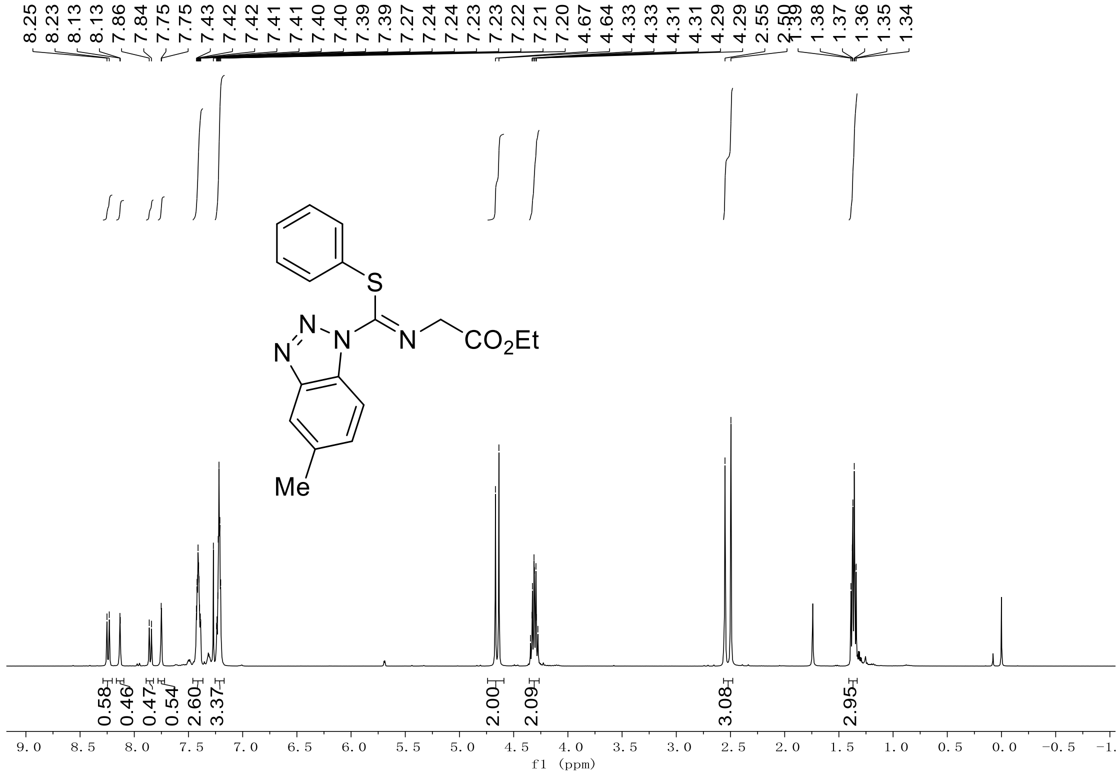

170.59 169.37 150.95 149.00 146.23 143.47 131.97 129.72 125.67 119.86 114.67 111.07 110.68 77.48 77.16 76.84 61.48 58.50 54.18 34.99 29.30 14.33
180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 -10
f1 (ppm)

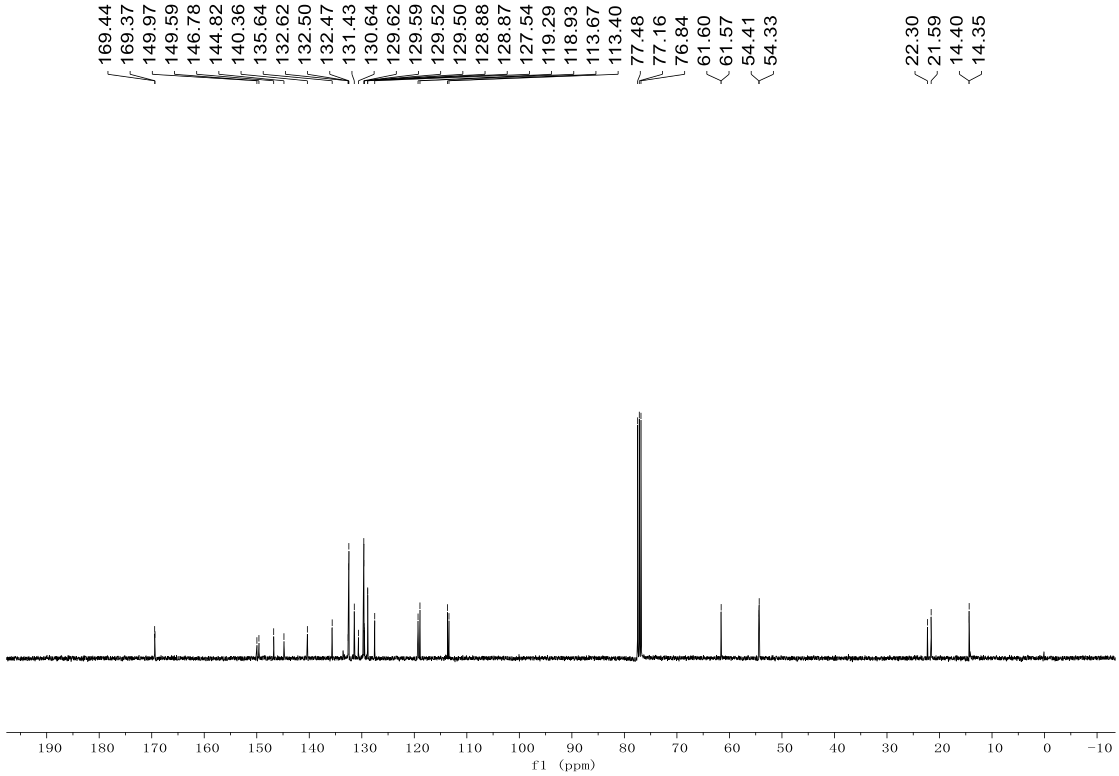
50


8.42 8.41 8.40 8.39 8.39 8.12 8.11 8.10 8.09 7.63 7.63 7.50 7.48 7.48 7.48 7.07 7.06 7.05 7.05 7.04 4.60 4.59 4.34 4.32 4.30 4.28 4.20 4.19 4.11 4.10 4.09 3.51 3.49 3.35 3.35 3.35 3.34 3.33 3.32 2.43 2.41 1.39 1.38 1.37 1.37 1.35 0.89 0.87
O
O
S
N
N
N
N
CO_2Et
1.00
1.08
1.00
1.07
4.04
1.78
2.22
1.04
1.19
0.98
1.83
2.01
1.08
5.67
5.47
10.0 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 0.0 -0.5
f1 (ppm)

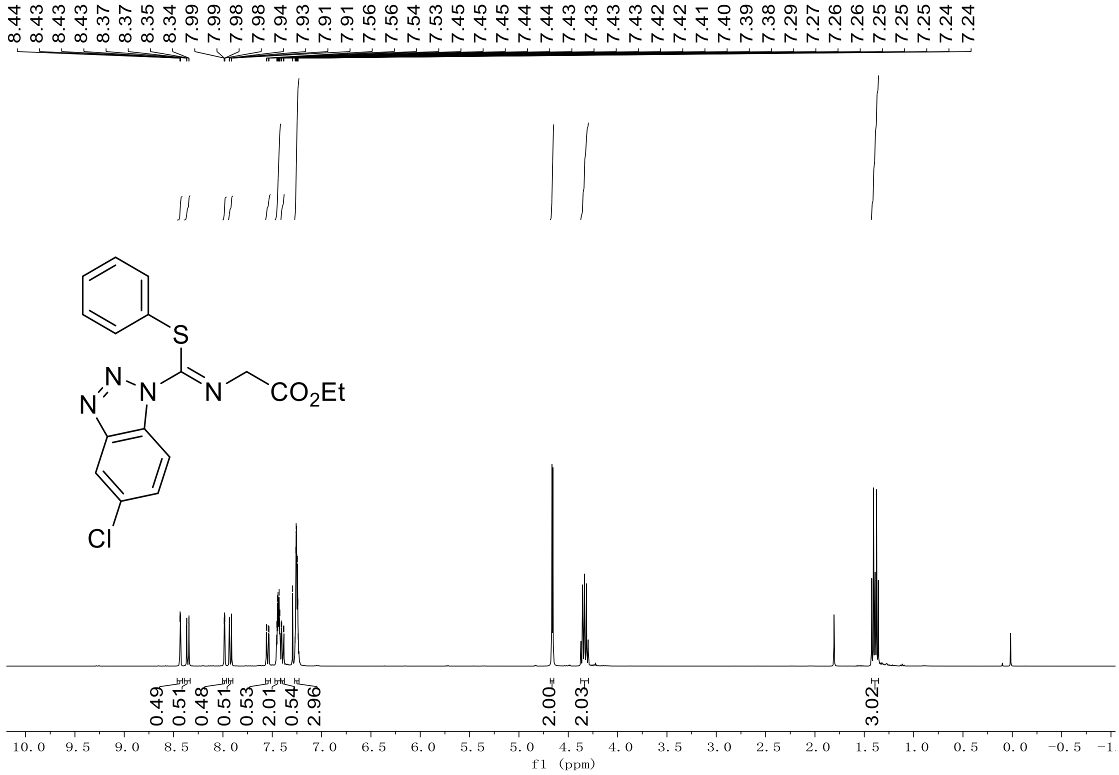

174.32 169.36 150.63 146.30 140.79 137.26 131.97 129.84 129.44 127.16 125.77 119.95 114.81 77.48 77.16 76.84 63.48 61.54 54.21 45.11 44.85 33.18 30.28 22.50 18.48 14.38
190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0
f1 (ppm)

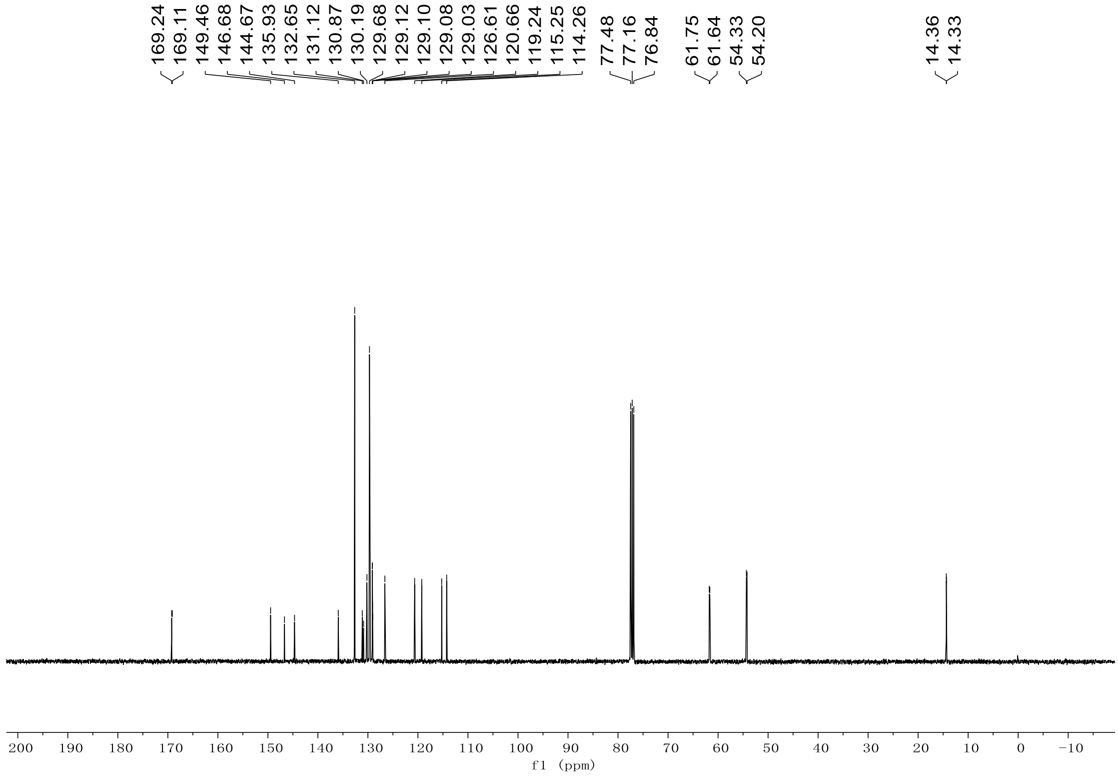
51


8.25 8.23 8.13 8.13 7.86 7.84 7.75 7.75 7.43 7.42 7.42 7.41 7.41 7.40 7.40 7.39 7.39 7.27 7.24 7.24 7.23 7.23 7.22 7.21 7.20 4.67 4.64 4.33 4.33 4.31 4.31 4.29 4.29 2.55 2.50 1.39 1.38 1.37 1.36 1.35 1.34
S
N
N
N
N
CO2Et
Me
0.58 0.46 0.47 0.54 2.60 3.37 2.00 2.09 3.08 2.95
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 0.0 −0.5 −1.
f1 (ppm)

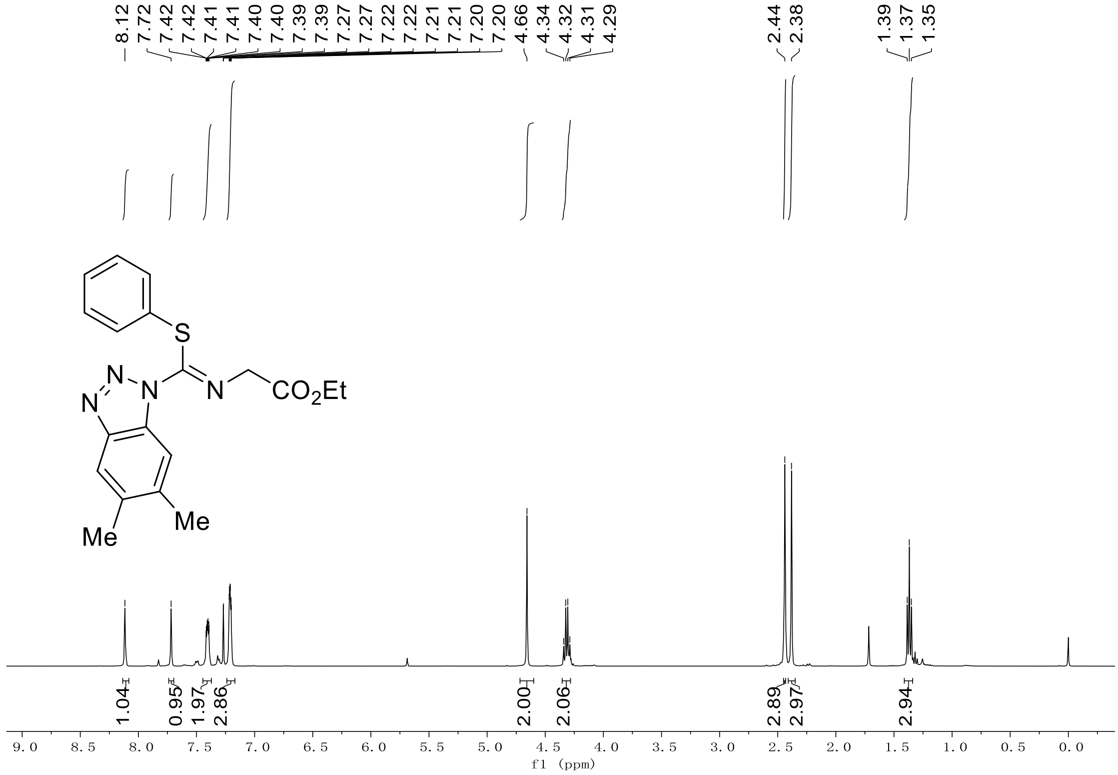

169.44 169.37 149.97 149.59 146.78 144.82 140.36 135.64 132.62 132.50 132.47 131.43 130.64 129.62 129.59 129.52 129.50 128.88 128.87 127.54 119.29 118.93 113.67 113.40 77.48 77.16 76.84 61.60 61.57 54.41 54.33 22.30 21.59 14.40 14.35
190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 −10
f1 (ppm)

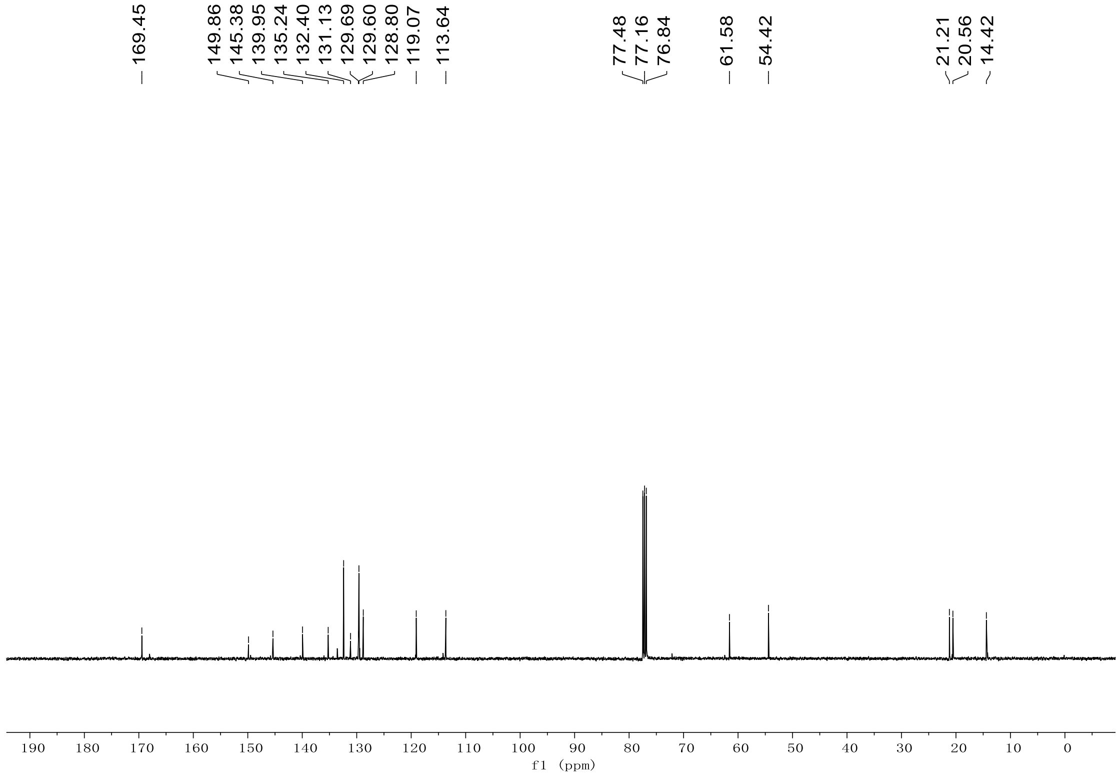
52


8.44 8.43 8.43 8.37 8.37 8.35 8.34 7.99 7.99 7.98 7.98 7.94 7.93 7.91 7.91 7.56 7.56 7.54 7.53 7.45 7.45 7.45 7.44 7.44 7.43 7.43 7.43 7.42 7.42 7.41 7.40 7.39 7.38 7.29 7.27 7.26 7.26 7.25 7.25 7.25 7.24 7.24
S
N
N
N
N
CO2Et
Cl
0.49 0.51 0.48 0.51 0.53 2.01 0.54 2.96
2.00
2.03
3.02
10.0 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 0.0 −0.5 −1
f1 (ppm)

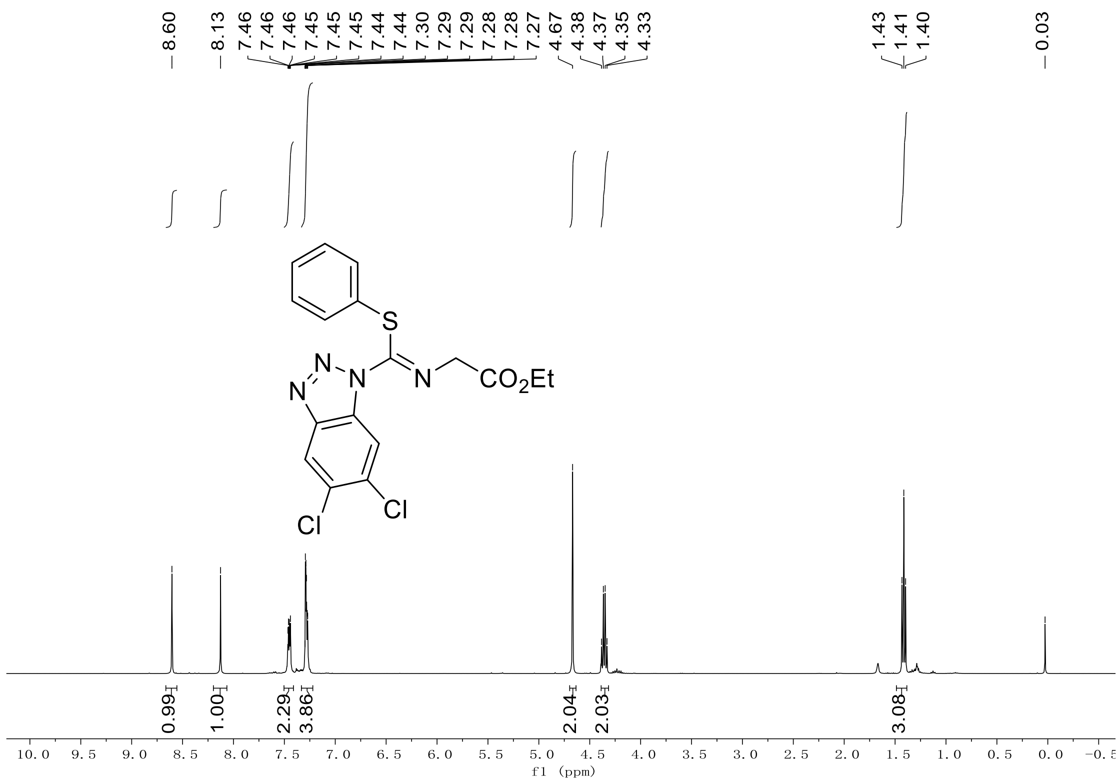

169.24 169.11 149.46 146.68 144.67 135.93 132.65 131.12 130.87 130.19 129.68 129.12 129.10 129.08 129.03 126.61 120.66 119.24 115.25 114.26
77.48 77.16 76.84
61.75 61.64 54.33 54.20
14.36 14.33
200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 −10
f1 (ppm)

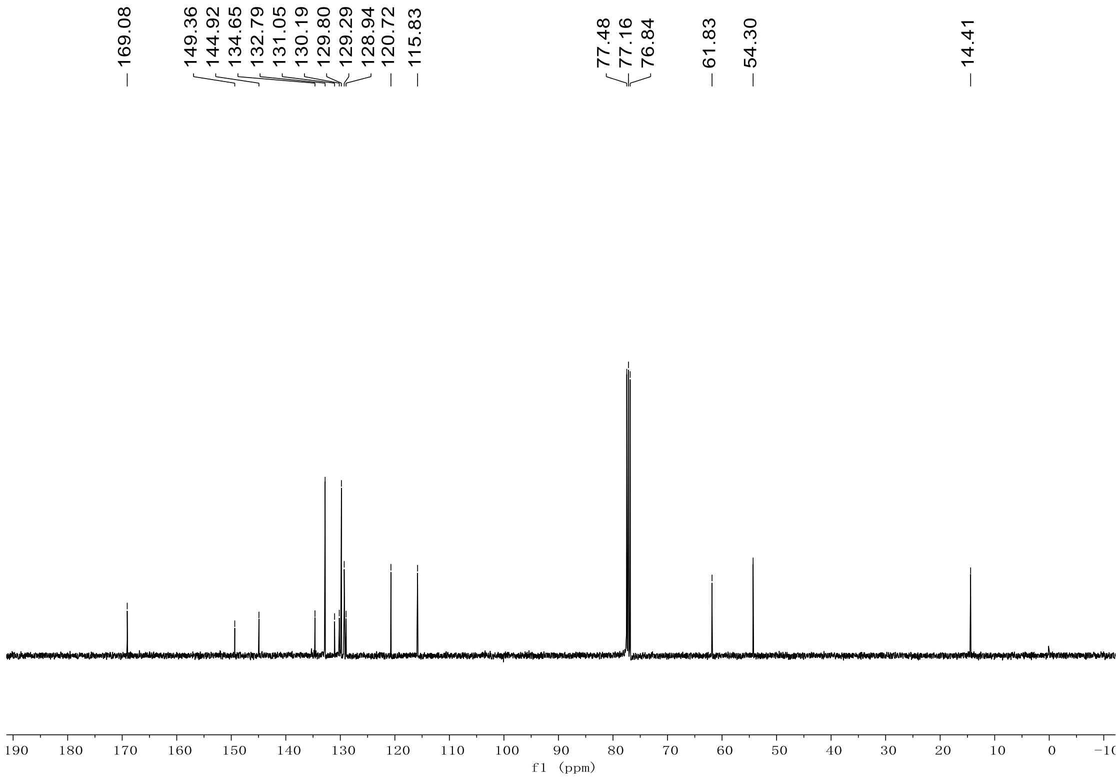
53


8.12
7.72
7.42
7.42
7.41
7.41
7.40
7.40
7.39
7.39
7.27
7.27
7.22
7.22
7.21
7.21
7.20
7.20
4.66
4.34
4.32
4.31
4.29
2.44
2.38
1.39
1.37
1.35
S
N
N
N
N
CO2Et
Me
Me
1.04
0.95
1.97
2.86
2.00
2.06
2.89
2.97
2.94
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
0.0
f1 (ppm)

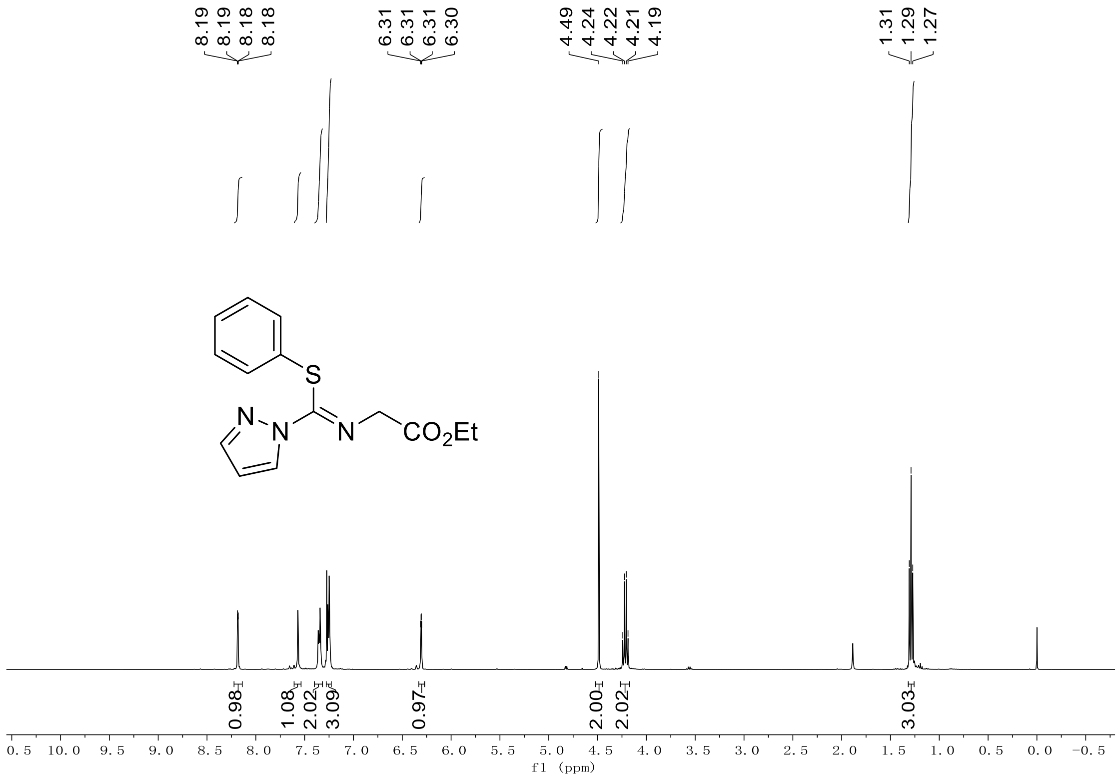

169.45
149.86
145.38
139.95
135.24
132.40
131.13
129.69
129.60
128.80
119.07
113.64
77.48
77.16
76.84
61.58
54.42
21.21
20.56
14.42
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
f1 (ppm)

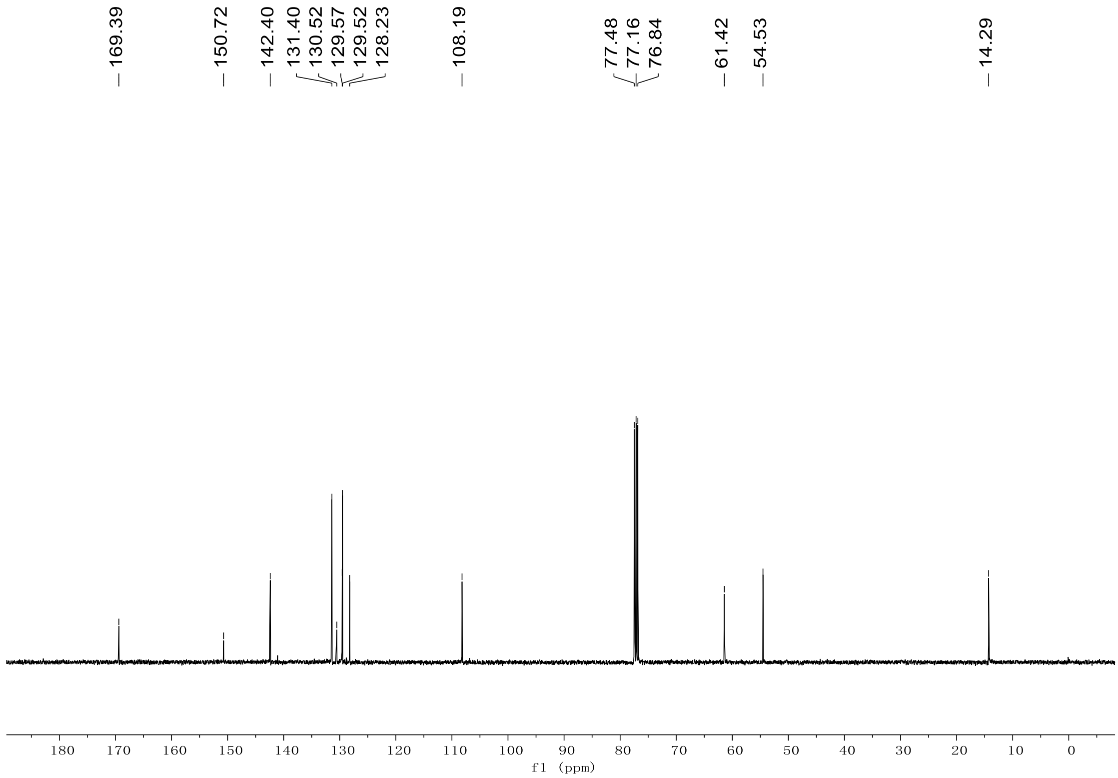
54


8.60
8.13
7.46
7.46
7.46
7.45
7.45
7.45
7.44
7.44
7.30
7.29
7.29
7.28
7.28
7.27
4.67
4.38
4.37
4.35
4.33
1.43
1.41
1.40
0.03
S
N
N
N
N
CO2Et
Cl
Cl
0.99
1.00
2.29
3.86
2.04
2.03
3.08
f1 (ppm)

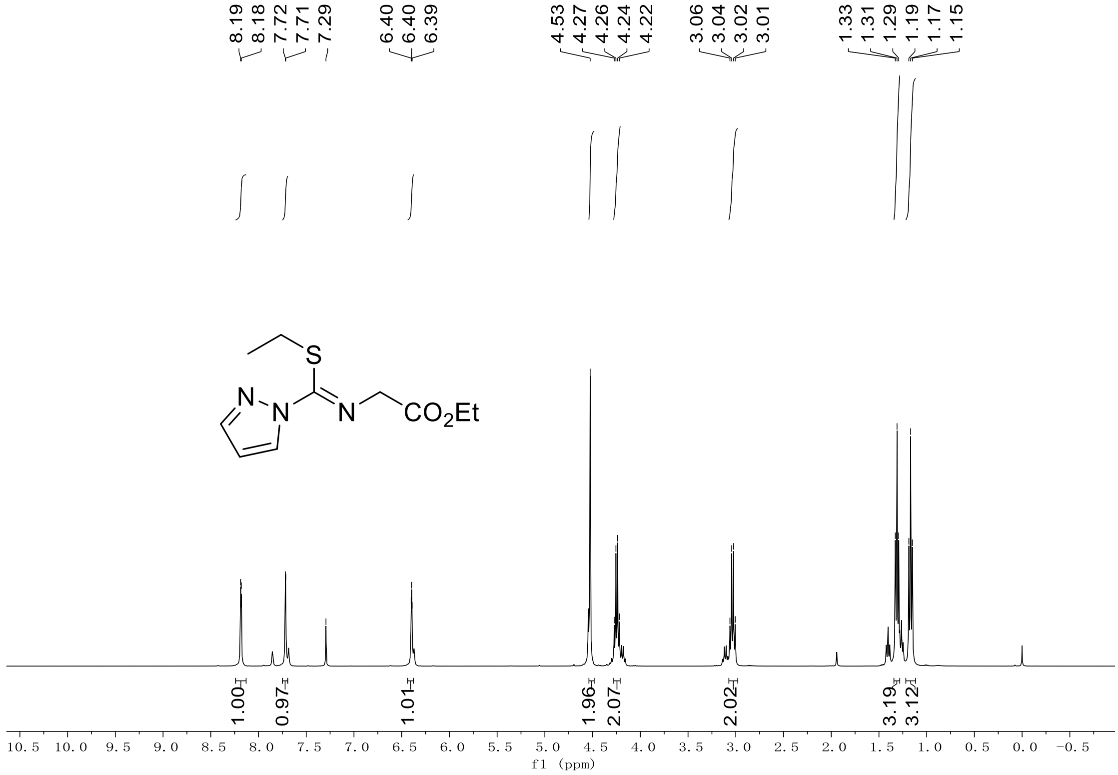

169.08
149.36
144.92
134.65
132.79
131.05
130.19
129.80
129.29
128.94
120.72
115.83
77.48
77.16
76.84
61.83
54.30
14.41
f1 (ppm)

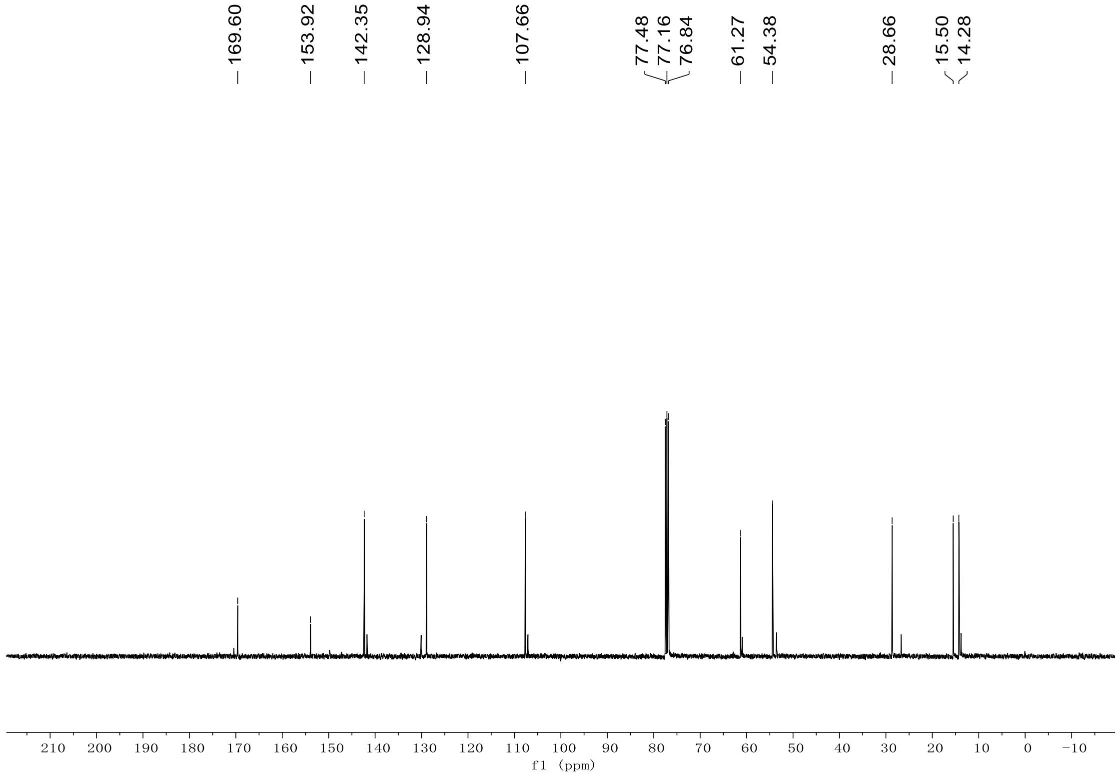
55


8.19
8.19
8.18
8.18
6.31
6.31
6.31
6.30
4.49
4.24
4.22
4.21
4.19
1.31
1.29
1.27
S
N
N
N
CO2Et
0.98
1.08
2.02
3.09
0.97
2.00
2.02
3.03
0.5 10.0 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 0.0 −0.5
f1 (ppm)

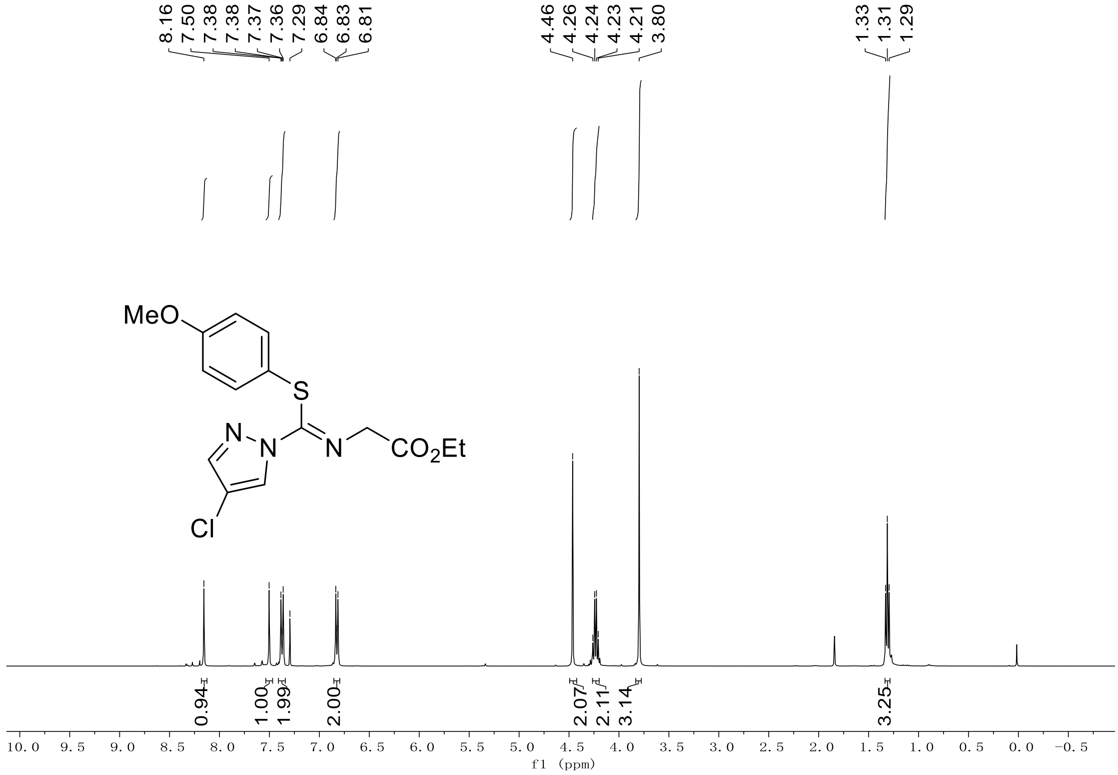

169.39
150.72
142.40
131.40
130.52
129.57
129.52
128.23
108.19
77.48
77.16
76.84
61.42
54.53
14.29
180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0
f1 (ppm)

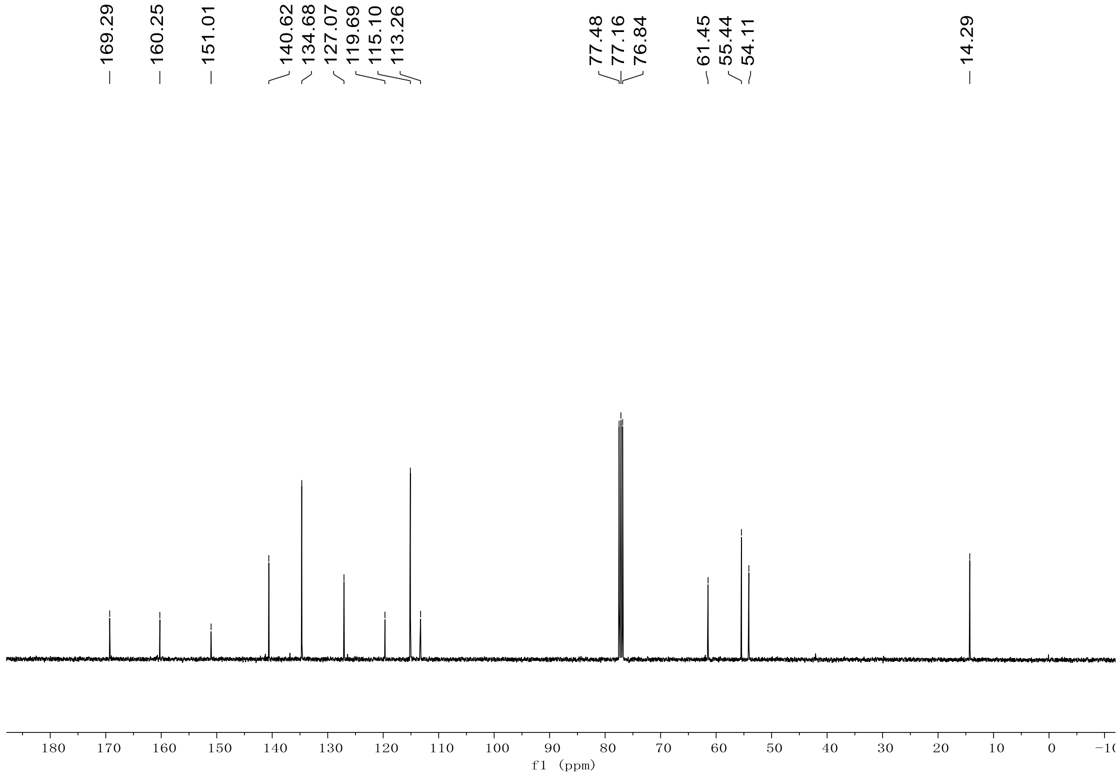
56


8.19
8.18
7.72
7.71
7.29
6.40
6.40
6.39
4.53
4.27
4.26
4.24
4.22
3.06
3.04
3.02
3.01
1.33
1.31
1.29
1.19
1.17
1.15
S
N
N
N
CO2Et
1.00
0.97
1.01
1.96
2.07
2.02
3.19
3.12
10.5 10.0 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 0.0 -0.5
f1 (ppm)

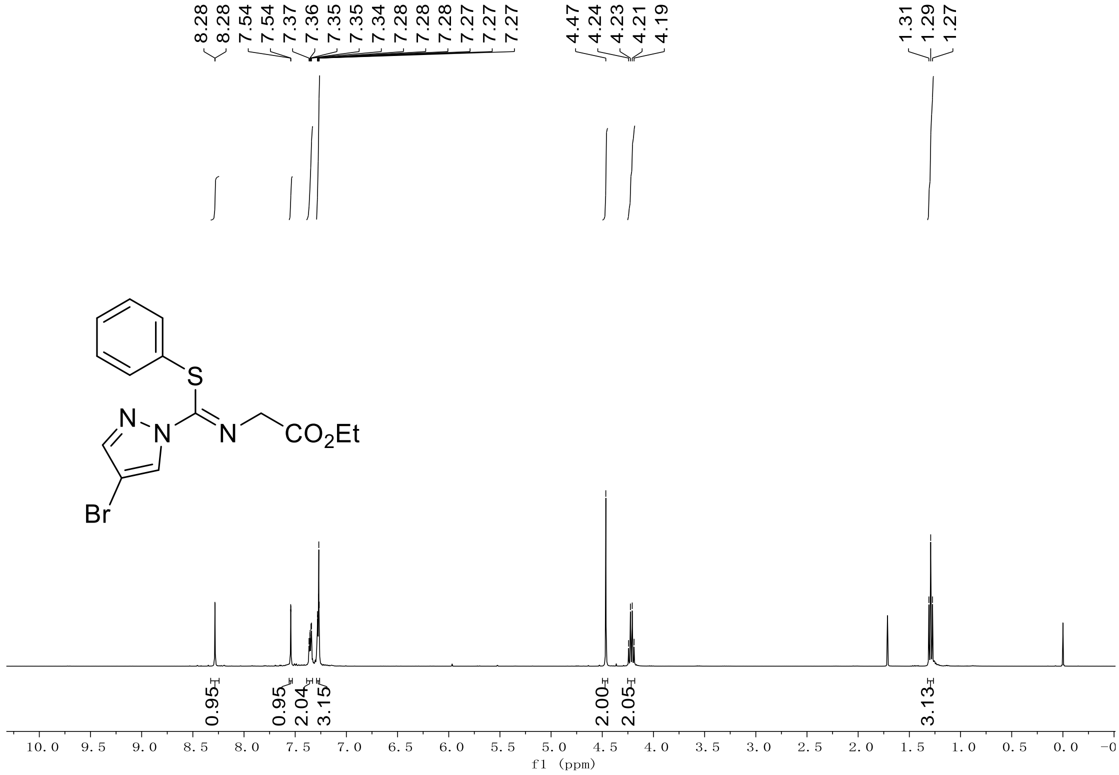

169.60
153.92
142.35
128.94
107.66
77.48
77.16
76.84
61.27
54.38
28.66
15.50
14.28
210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 -10
f1 (ppm)

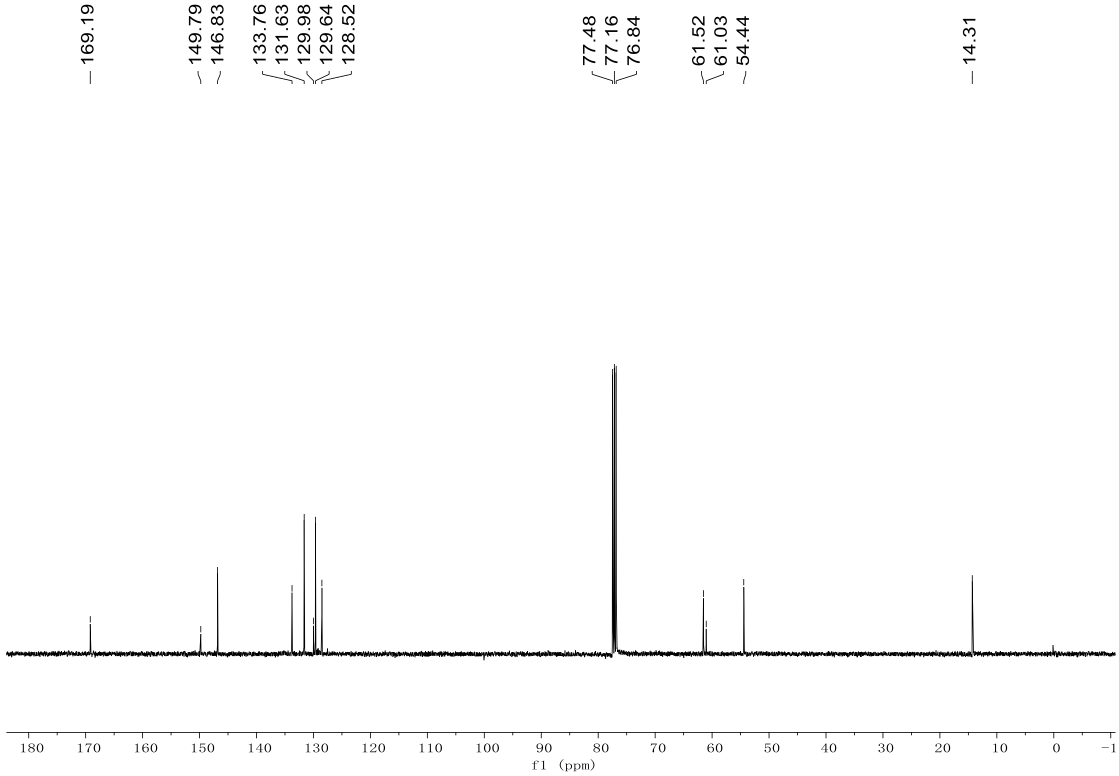
57


8.16
7.50
7.38
7.38
7.37
7.36
7.29
6.84
6.83
6.81
4.46
4.26
4.24
4.23
4.21
3.80
1.33
1.31
1.29
MeO
S
N
N
N
CO_2Et
Cl
0.94
1.00
1.99
2.00
2.07
2.11
3.14
3.25
f1 (ppm)

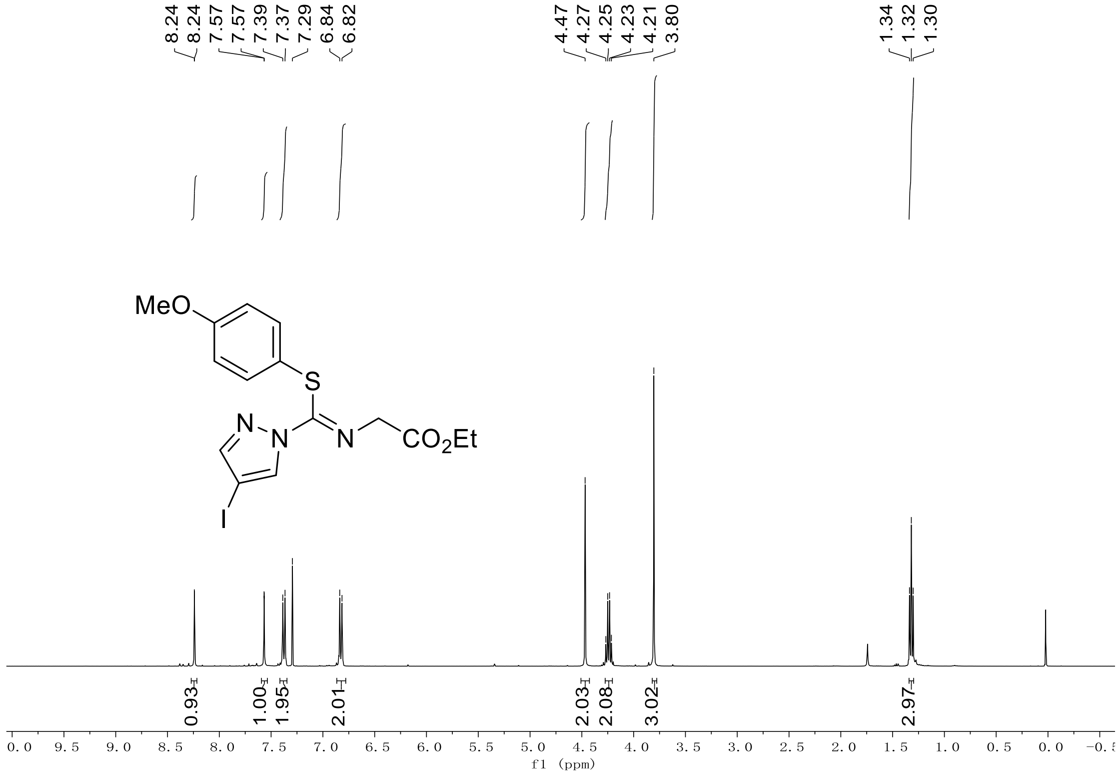

169.29
160.25
151.01
140.62
134.68
127.07
119.69
115.10
113.26
77.48
77.16
76.84
61.45
55.44
54.11
14.29
f1 (ppm)

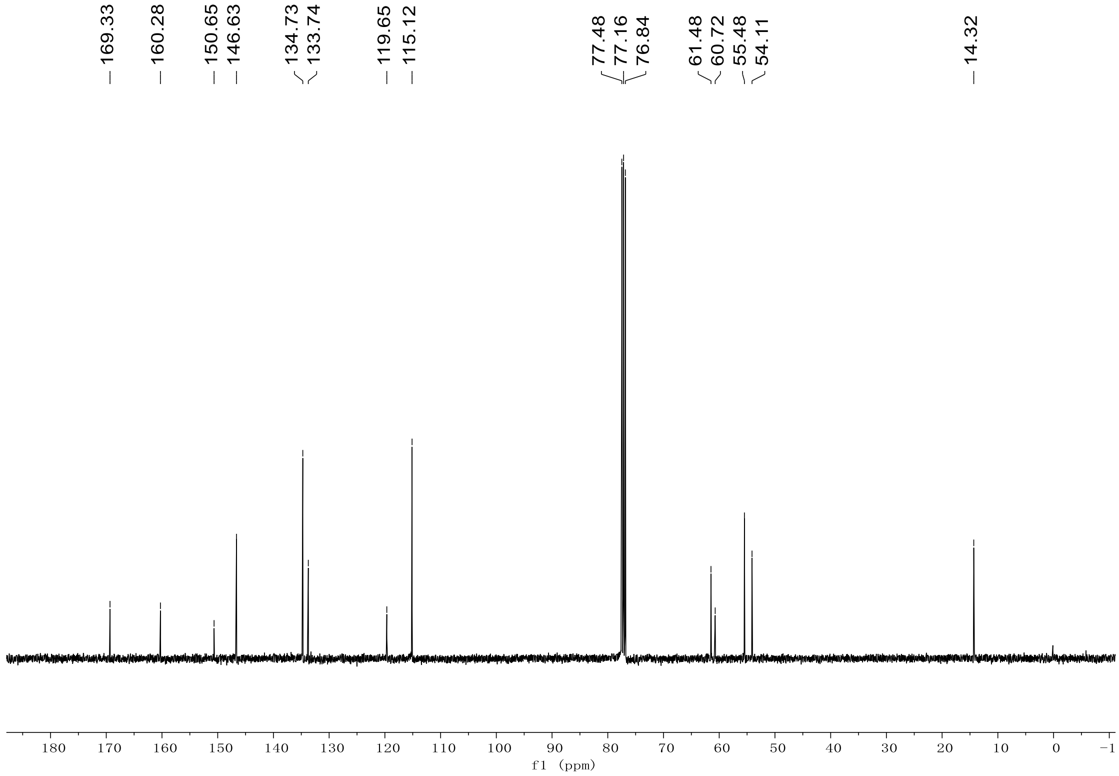
58


8.28
8.28
7.54
7.54
7.37
7.36
7.35
7.34
7.28
7.28
7.27
7.27
7.27
4.47
4.24
4.23
4.21
4.19
1.31
1.29
1.27
S
N
N
N
CO2Et
Br
0.95
0.95
2.04
3.15
2.00
2.05
3.13
10.0 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 0.0
f1 (ppm)

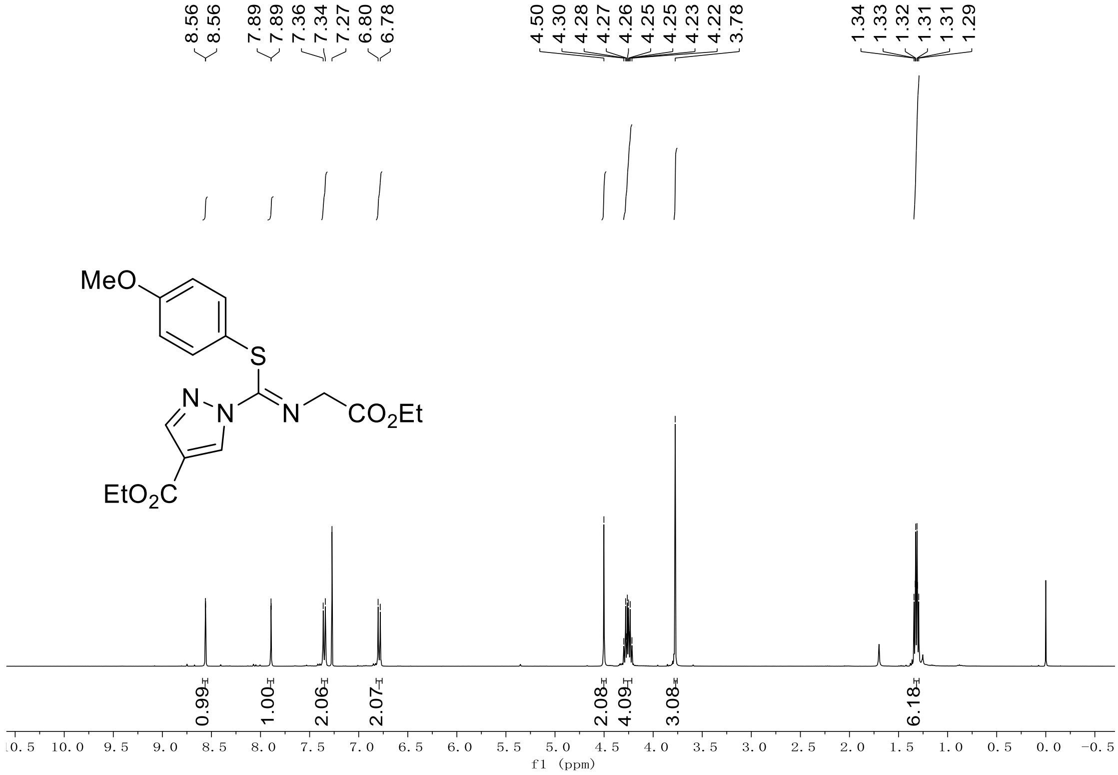

169.19
149.79
146.83
133.76
131.63
129.98
129.64
128.52
77.48
77.16
76.84
61.52
61.03
54.44
14.31
180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0
f1 (ppm)

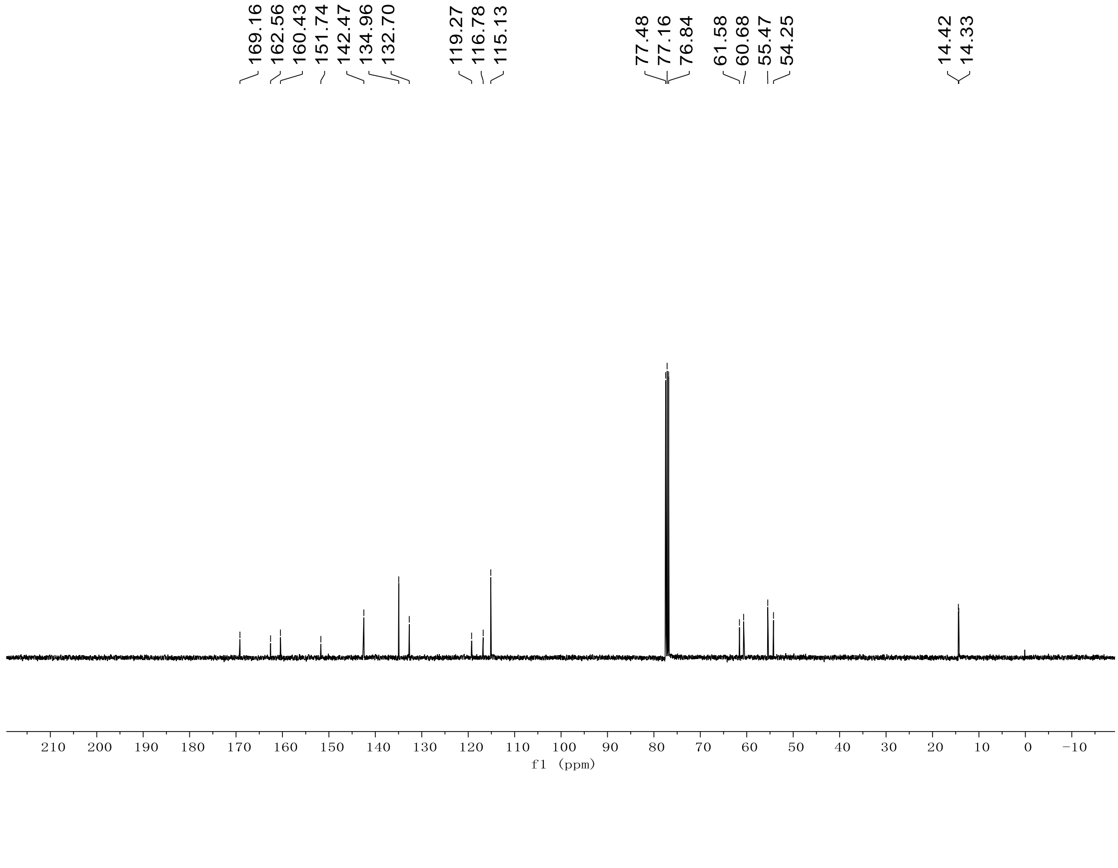
59


8.24
8.24
7.57
7.57
7.39
7.37
7.29
6.84
6.82
4.47
4.27
4.25
4.23
4.21
3.80
1.34
1.32
1.30
MeO
S
N
N
N
CO2Et
I
0.93
1.00
1.95
2.01
2.03
2.08
3.02
2.97
f1 (ppm)

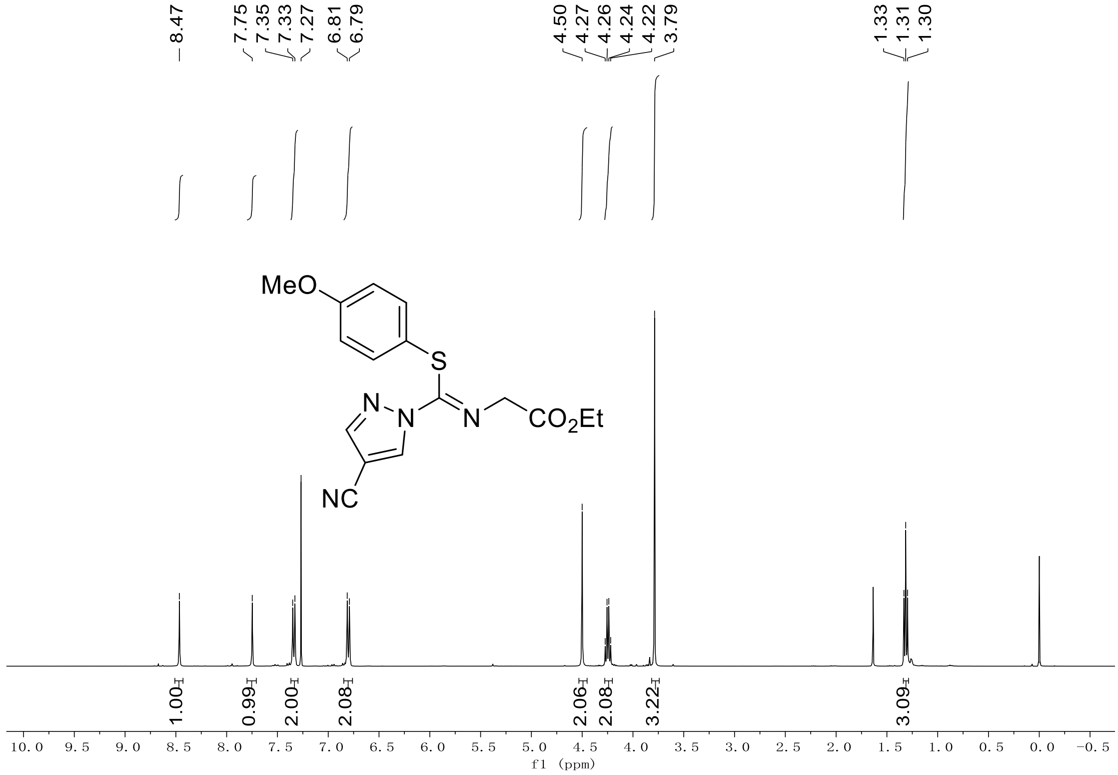

169.33
160.28
150.65
146.63
134.73
133.74
119.65
115.12
77.48
77.16
76.84
61.48
60.72
55.48
54.11
14.32
f1 (ppm)

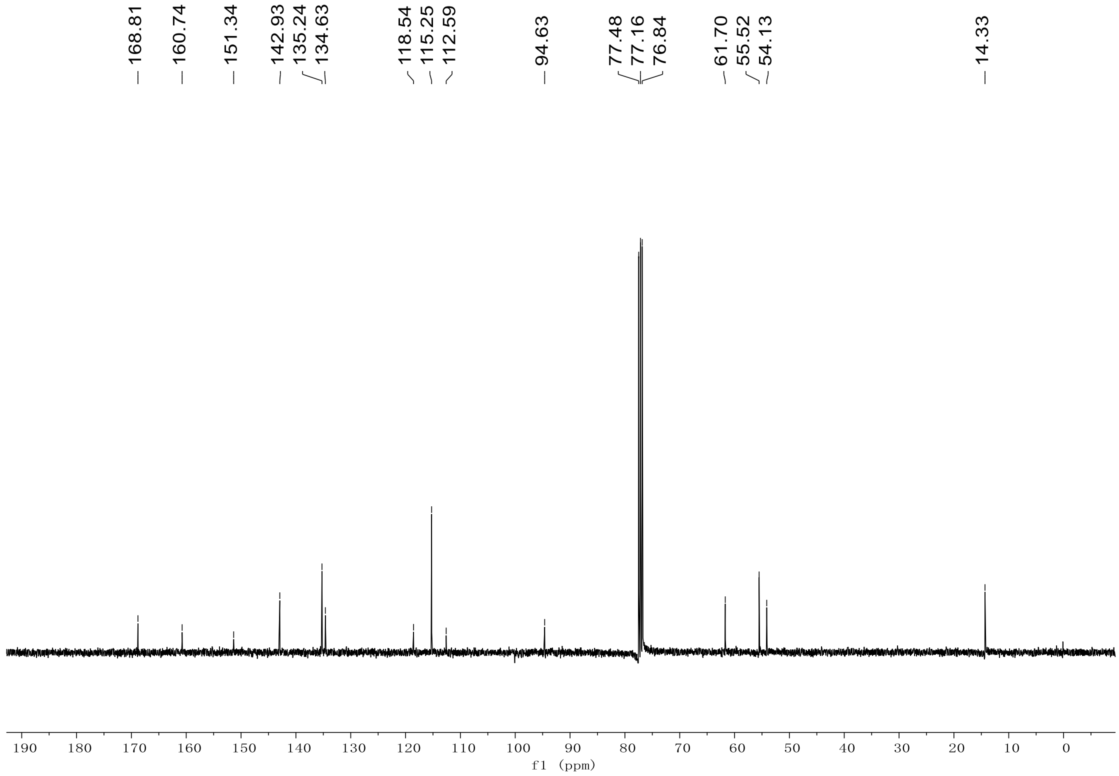
60


8.56
8.56
7.89
7.89
7.36
7.34
7.27
6.80
6.78
4.50
4.30
4.28
4.27
4.26
4.25
4.25
4.23
4.22
3.78
1.34
1.33
1.32
1.31
1.31
1.29
MeO
S
N
N
N
CO2Et
EtO2C
0.99
1.00
2.06
2.07
2.08
4.09
3.08
6.18
f1 (ppm)

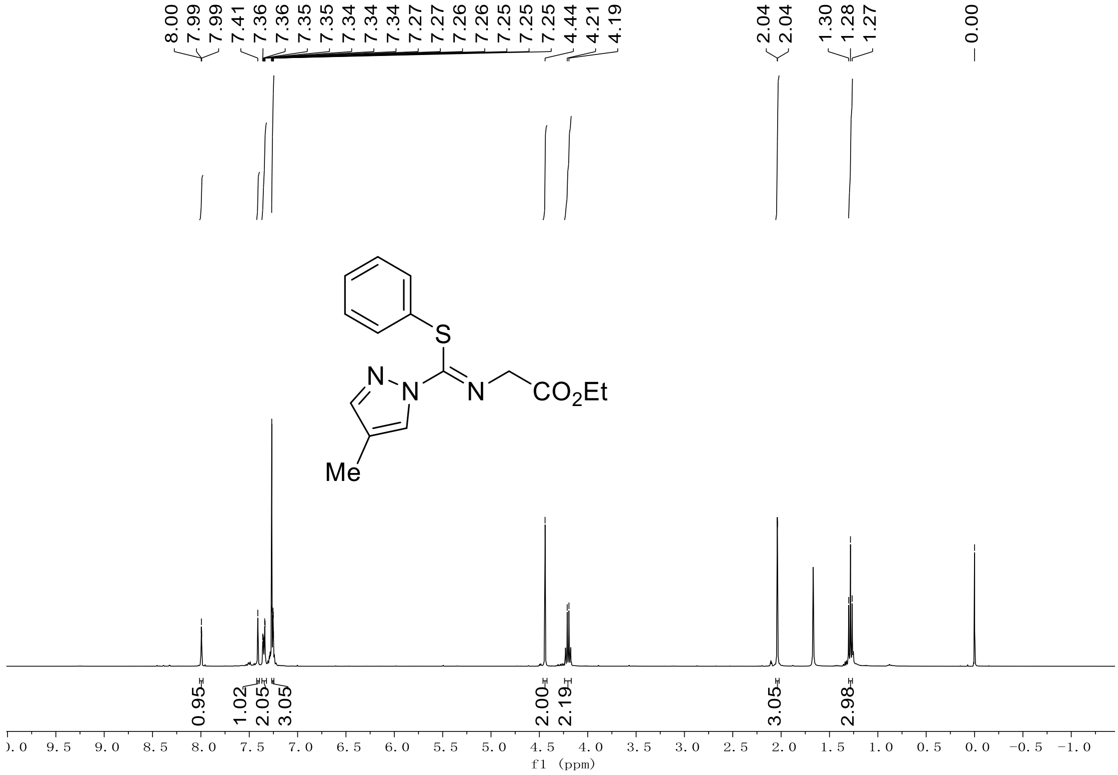

169.16
162.56
160.43
151.74
142.47
134.96
132.70
119.27
116.78
115.13
77.48
77.16
76.84
61.58
60.68
55.47
54.25
14.42
14.33
f1 (ppm)

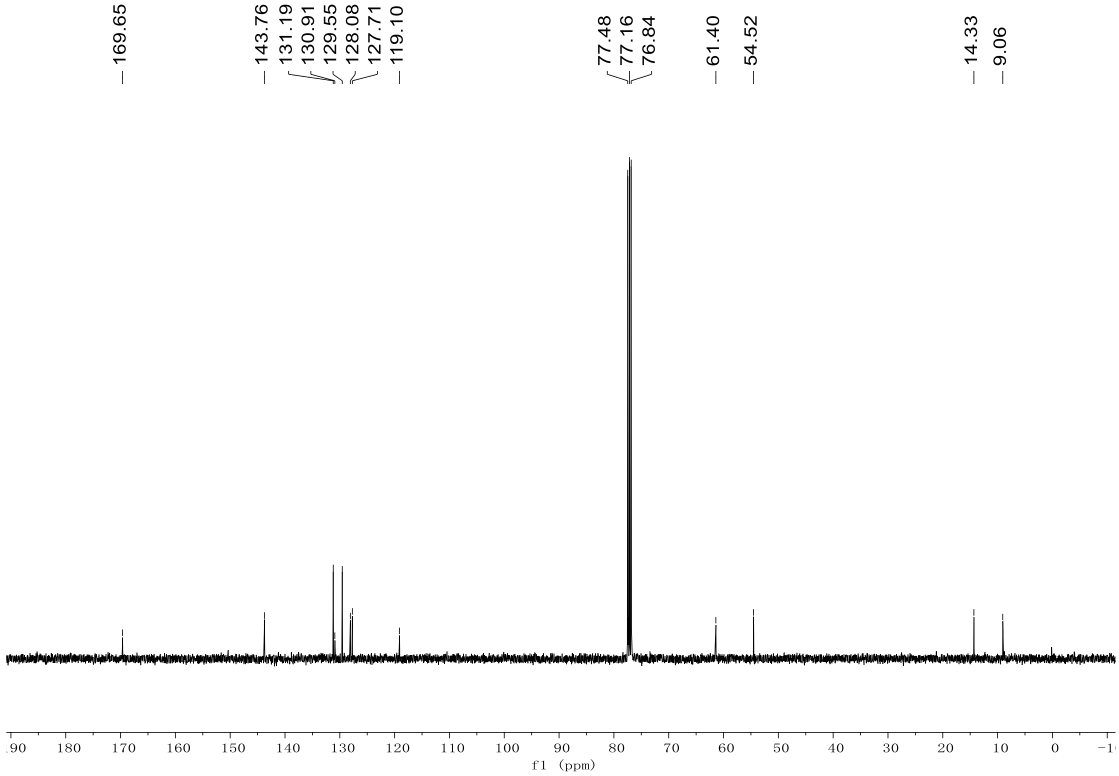
61


8.47
7.75
7.35
7.33
7.27
6.81
6.79
4.50
4.27
4.26
4.24
4.22
3.79
1.33
1.31
1.30
1.00
0.99
2.00
2.08
2.06
2.08
3.22
3.09
10.0 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 0.0 -0.5
f1 (ppm)
MeO
S
N
N
N
CO2Et
NC

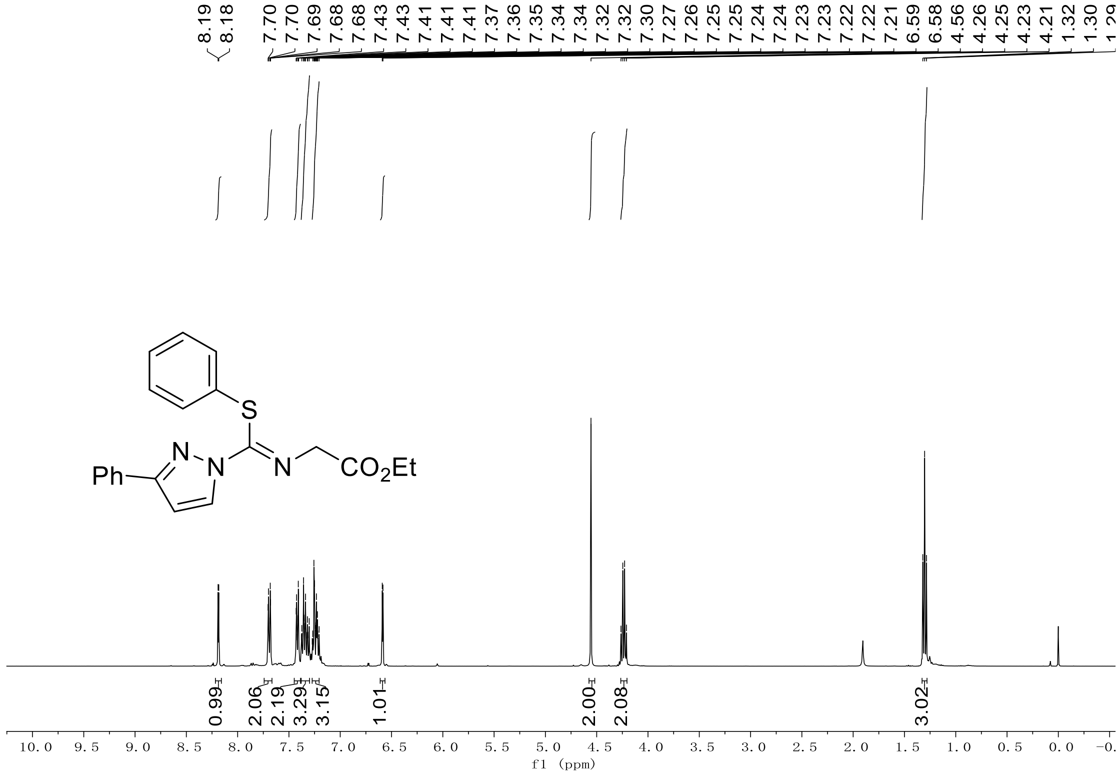

168.81
160.74
151.34
142.93
135.24
134.63
118.54
115.25
112.59
94.63
77.48
77.16
76.84
61.70
55.52
54.13
14.33
190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0
f1 (ppm)

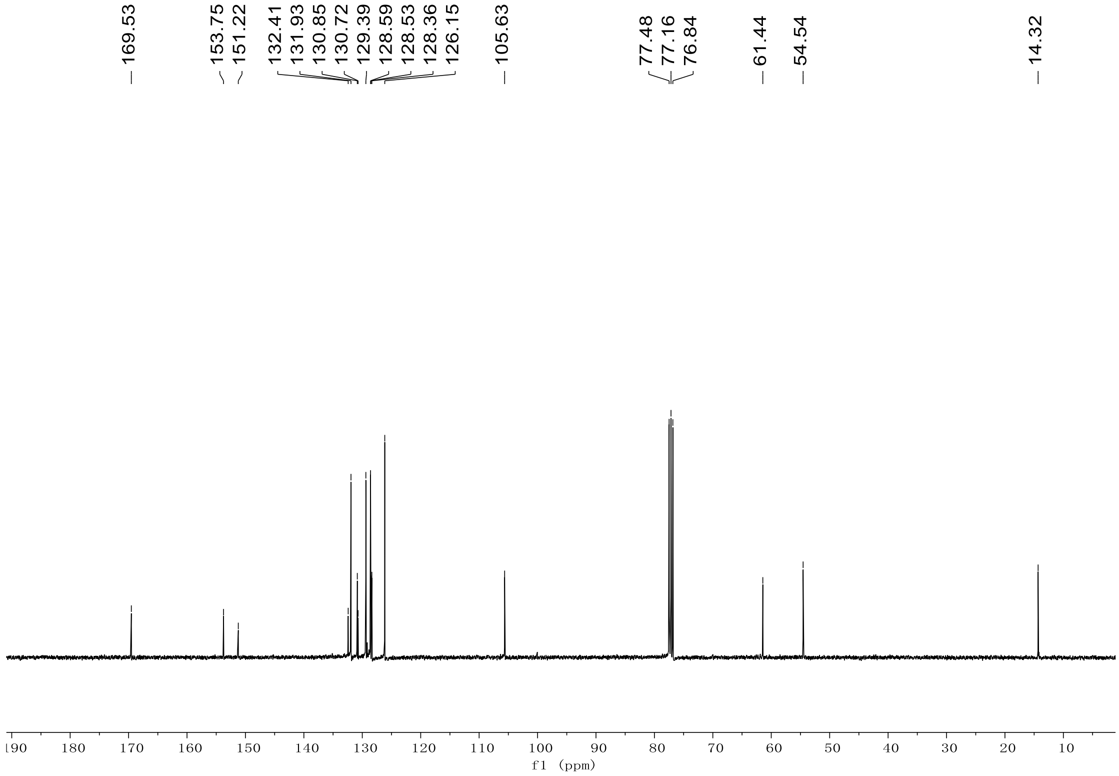
62


8.00
7.99
7.99
7.41
7.36
7.36
7.35
7.35
7.34
7.34
7.34
7.27
7.27
7.26
7.26
7.25
7.25
7.25
4.44
4.21
4.19
2.04
2.04
1.30
1.28
1.27
0.00
S
N
N
N
CO_2Et
Me
0.95
1.02
2.05
3.05
2.00
2.19
3.05
2.98
f1 (ppm)

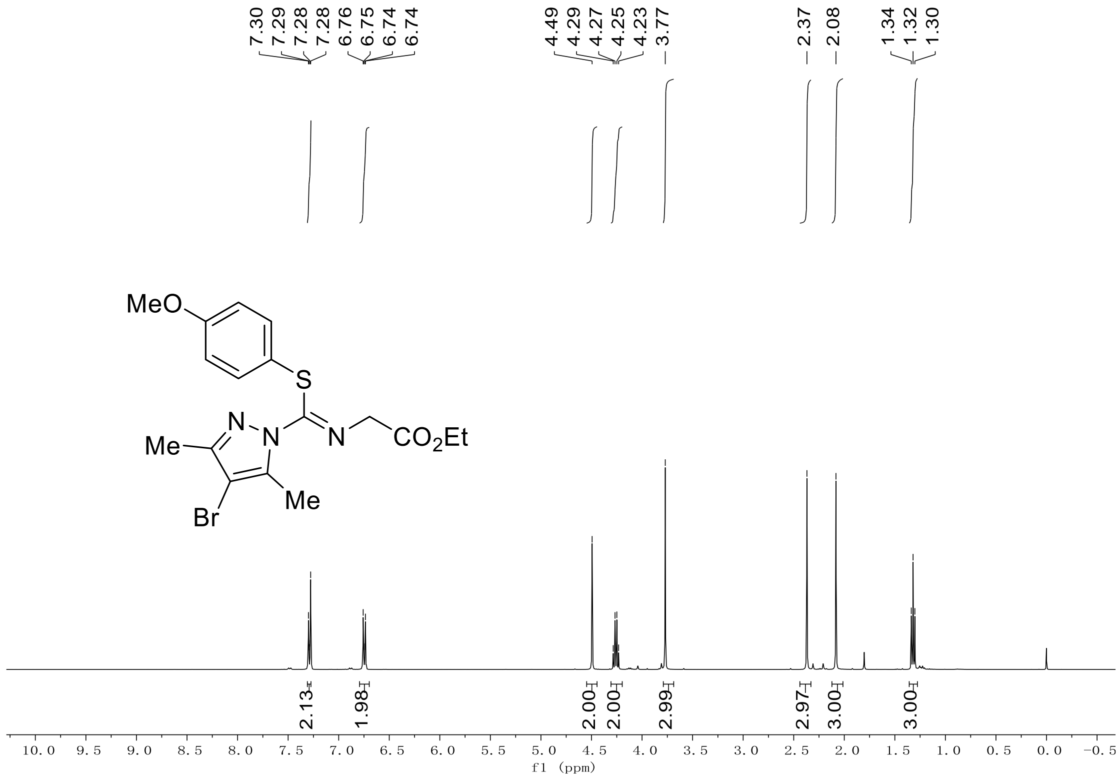

169.65
143.76
131.19
130.91
129.55
128.08
127.71
119.10
77.48
77.16
76.84
61.40
54.52
14.33
9.06
f1 (ppm)

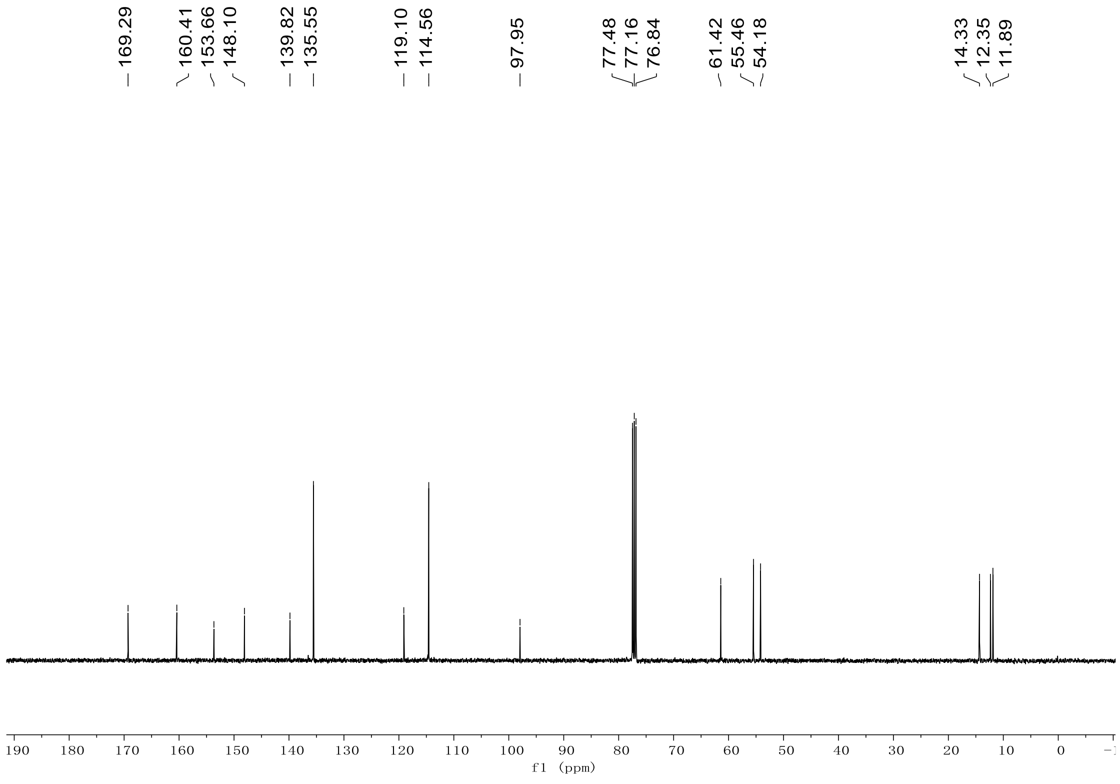
63



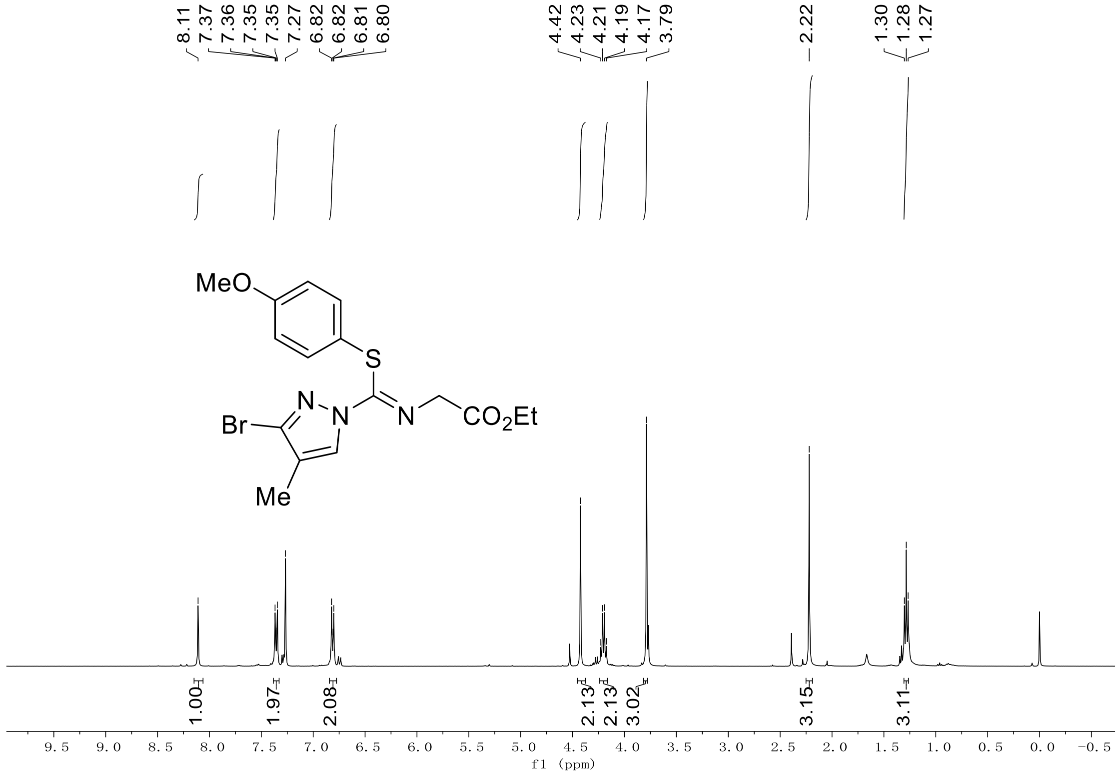


64

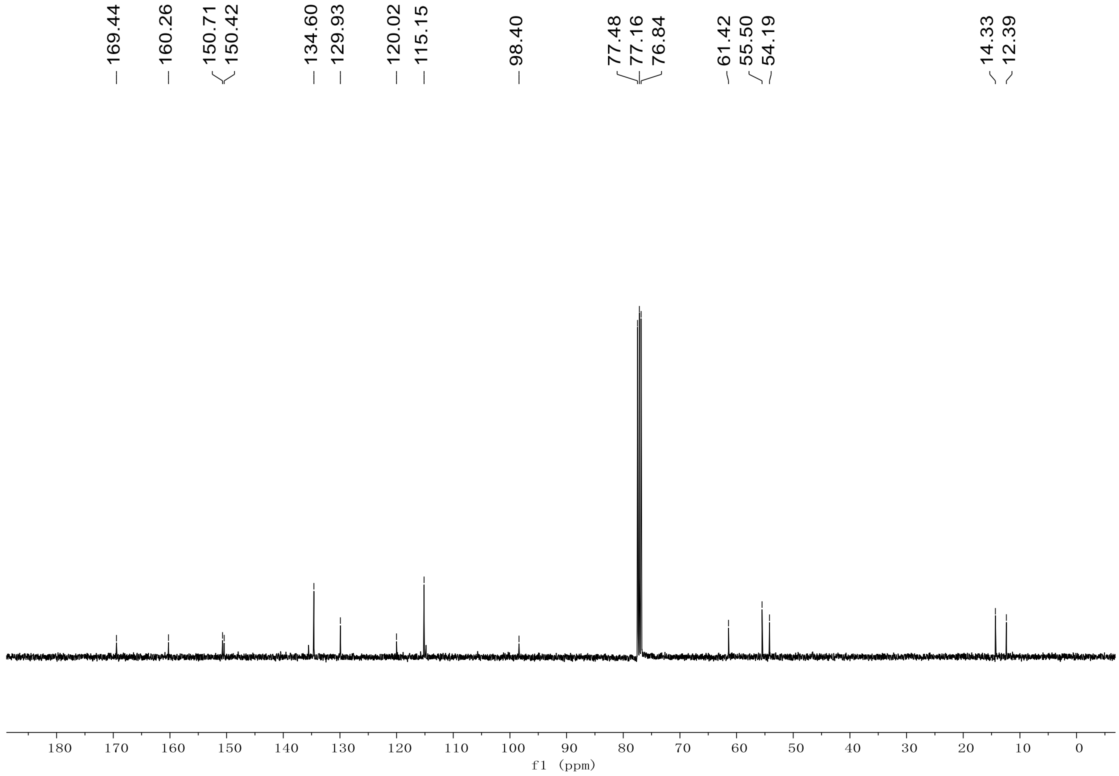

7.30 7.29 7.28 7.28 6.76 6.75 6.74 6.74
4.49 4.29 4.27 4.25 4.23 3.77
2.37 2.08
1.34 1.32 1.30
MeO
S
N
N
Me
N
CO2Et
Br
Me
2.13
1.98
2.00
2.00
2.99
2.97
3.00
3.00
10.0 9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0 −0.5
f1 (ppm)


169.29
160.41 153.66 148.10
139.82 135.55
119.10 114.56
97.95
77.48 77.16 76.84
61.42 55.46 54.18
14.33 12.35 11.89
190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0
f1 (ppm)

65

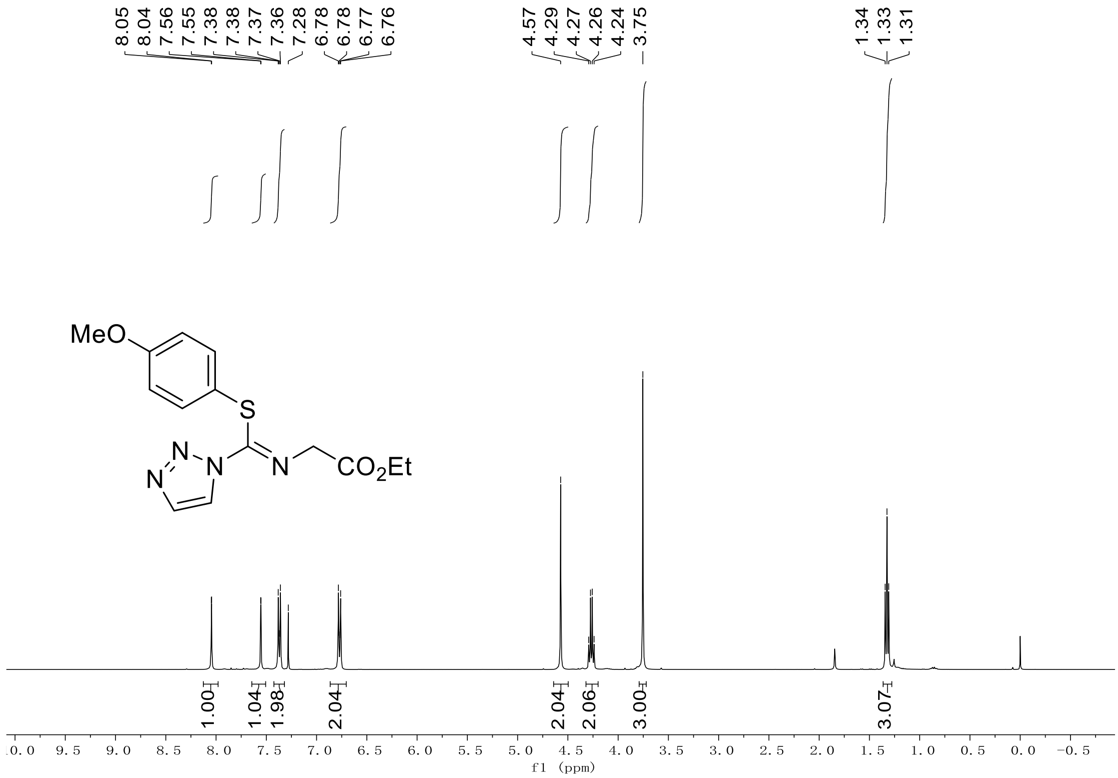


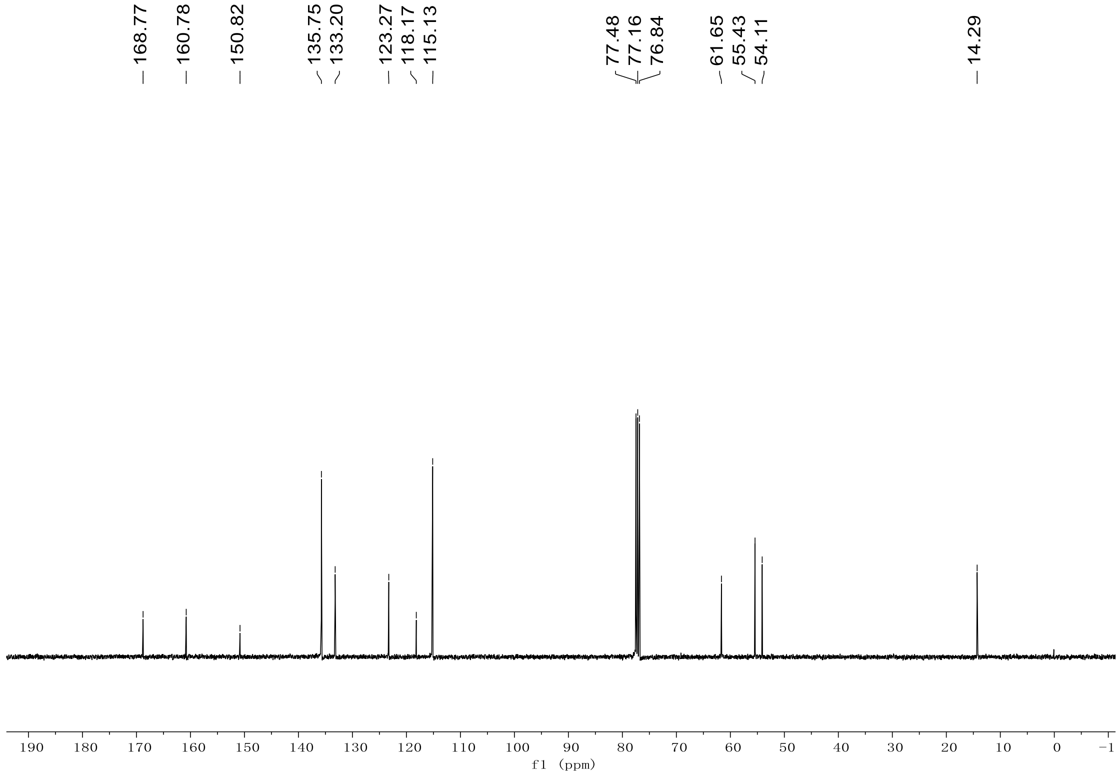
8.11
7.37
7.36
7.35
7.35
7.27
6.82
6.82
6.81
6.80
4.42
4.23
4.21
4.19
4.17
3.79
2.22
1.30
1.28
1.27
MeO
S
N
N
N
Br
Me
CO_2Et
1.00
1.97
2.08
2.13
2.13
3.02
3.15
3.11
f1 (ppm)



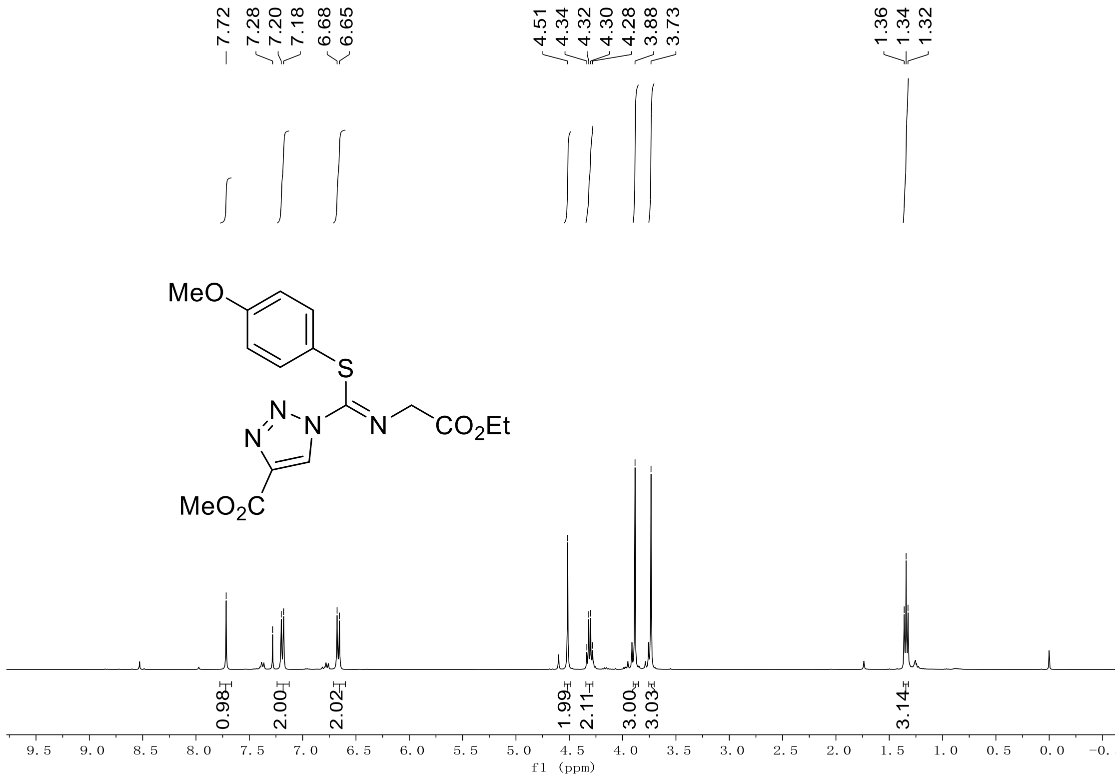
169.44
160.26
150.71
150.42
134.60
129.93
120.02
115.15
98.40
77.48
77.16
76.84
61.42
55.50
54.19
14.33
12.39
f1 (ppm)

66

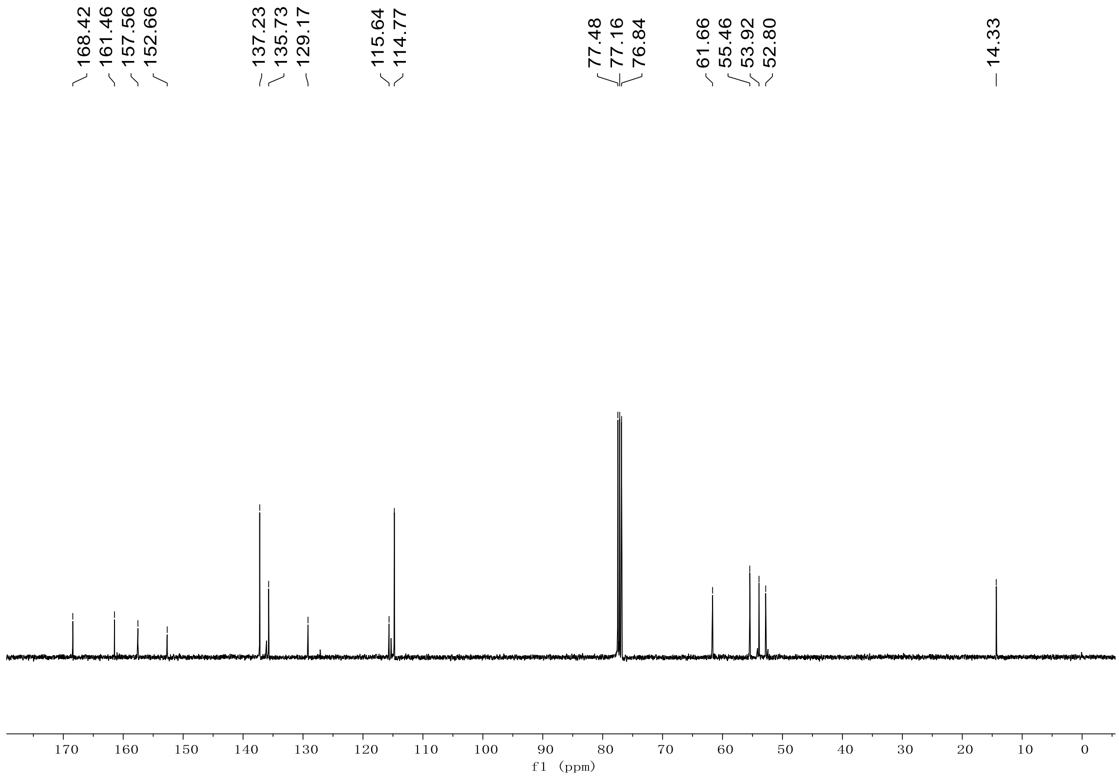

8.05
8.04
7.56
7.55
7.38
7.38
7.37
7.36
7.28
6.78
6.78
6.77
6.76
4.57
4.29
4.27
4.26
4.24
3.75
1.34
1.33
1.31
MeO
S
N
N
N
N
CO2Et
1.00
1.04
1.98
2.04
2.04
2.06
3.00
3.07
f1 (ppm)


168.77
160.78
150.82
135.75
133.20
123.27
118.17
115.13
77.48
77.16
76.84
61.65
55.43
54.11
14.29
f1 (ppm)

67

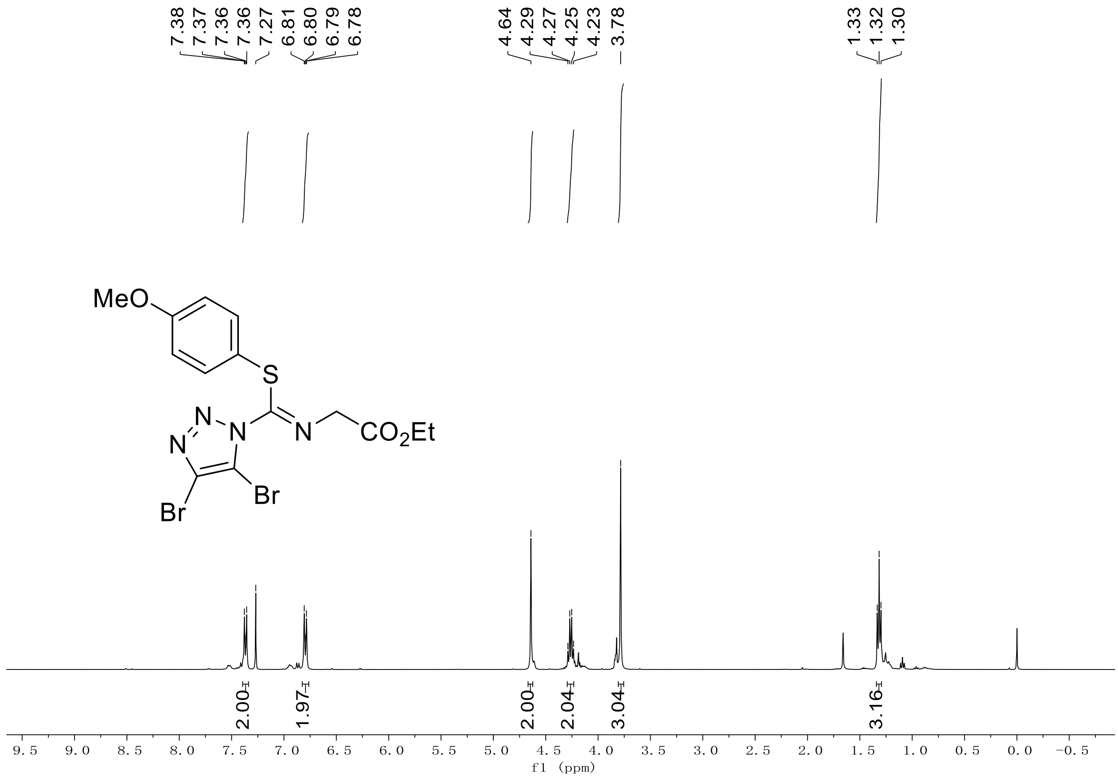


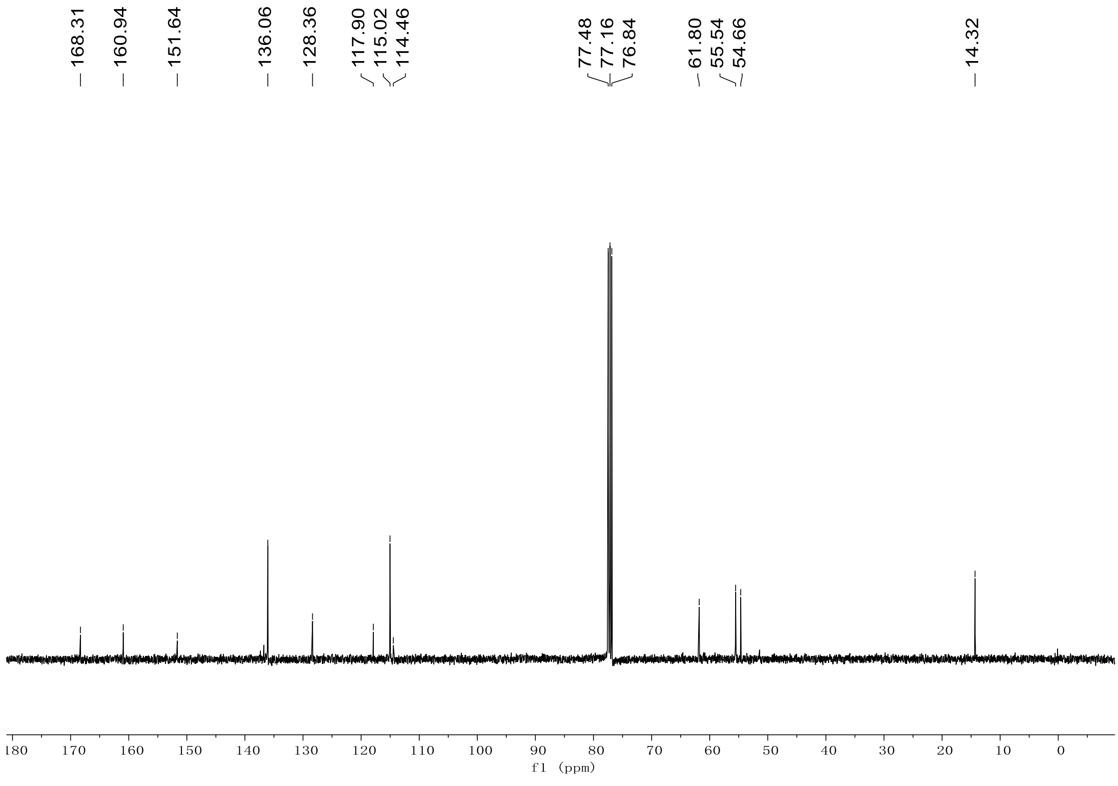
7.72
7.28
7.20
7.18
6.68
6.65
4.51
4.34
4.32
4.30
4.28
3.88
3.73
1.36
1.34
1.32
MeO
S
N
N
N
N
CO2Et
MeO2C
0.98
2.00
2.02
1.99
2.11
3.00
3.03
3.14
9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0 -0.
f1 (ppm)



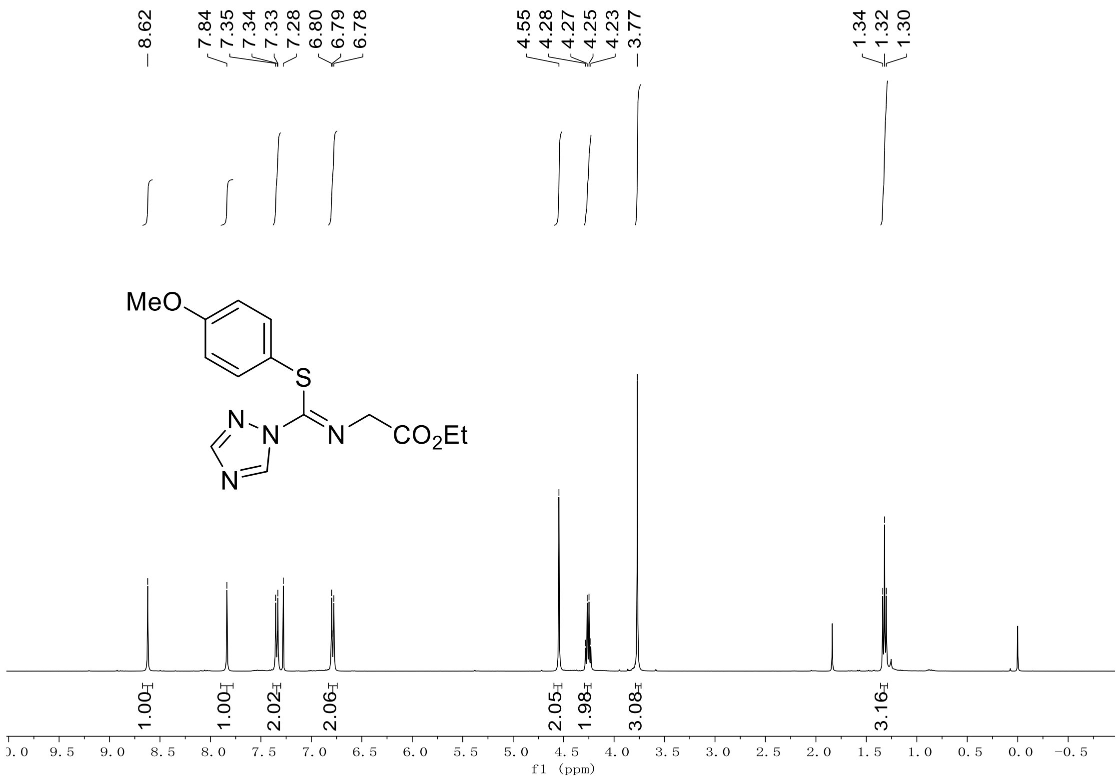
168.42
161.46
157.56
152.66
137.23
135.73
129.17
115.64
114.77
77.48
77.16
76.84
61.66
55.46
53.92
52.80
14.33
170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0
f1 (ppm)

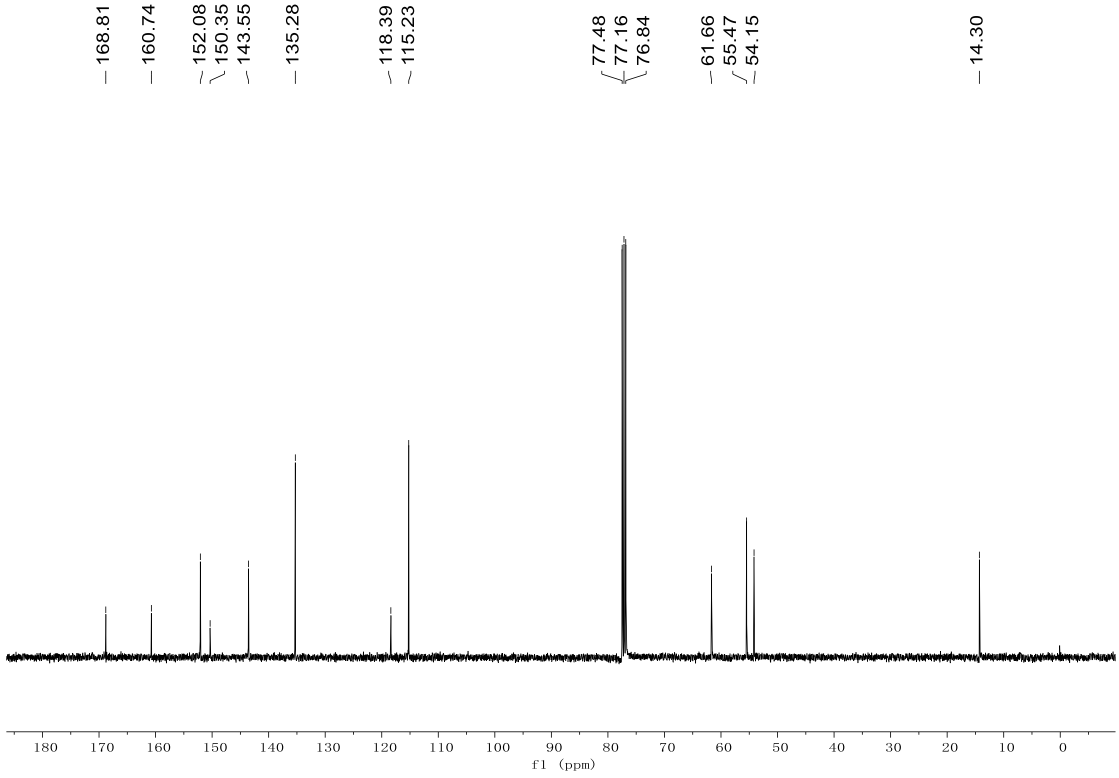
68


7.38 7.37 7.36 7.36 7.27 6.81 6.80 6.79 6.78
4.64 4.29 4.27 4.25 4.23 3.78
1.33 1.32 1.30
MeO
S
N
N
N
N
CO2Et
Br
Br
2.00 1.97 2.00 2.04 3.04 3.16
f1 (ppm)

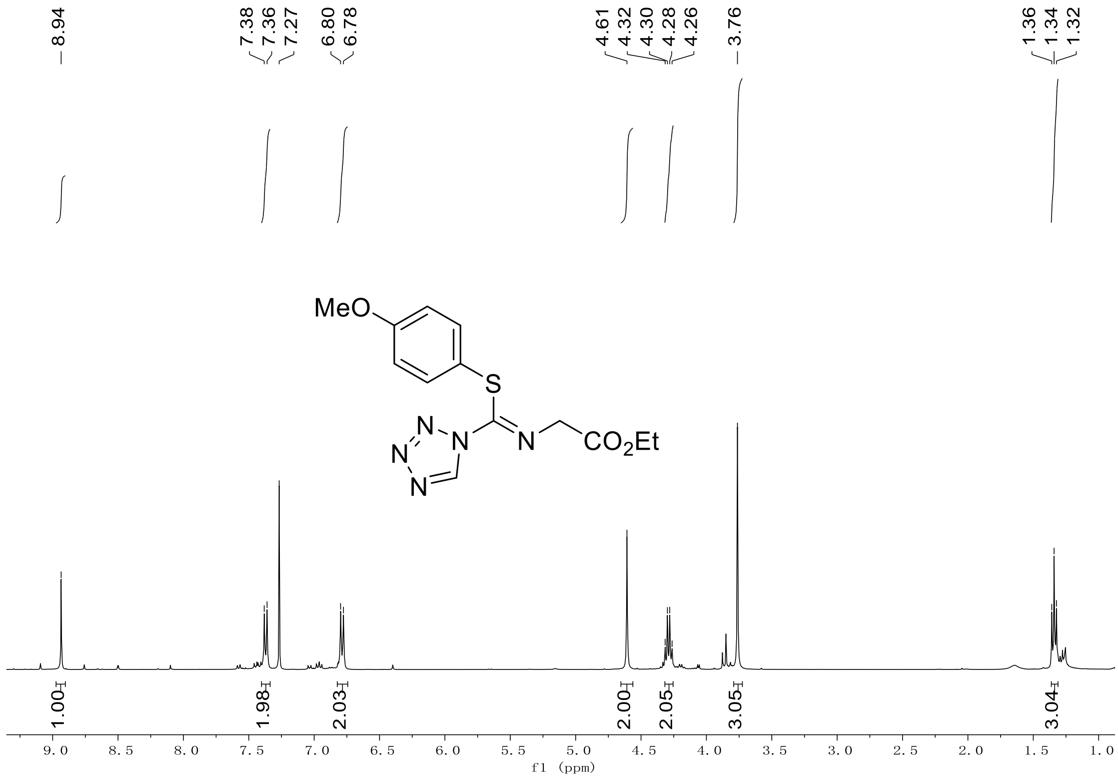

168.31 160.94 151.64 136.06 128.36 117.90 115.02 114.46
77.48 77.16 76.84 61.80 55.54 54.66
14.32
f1 (ppm)

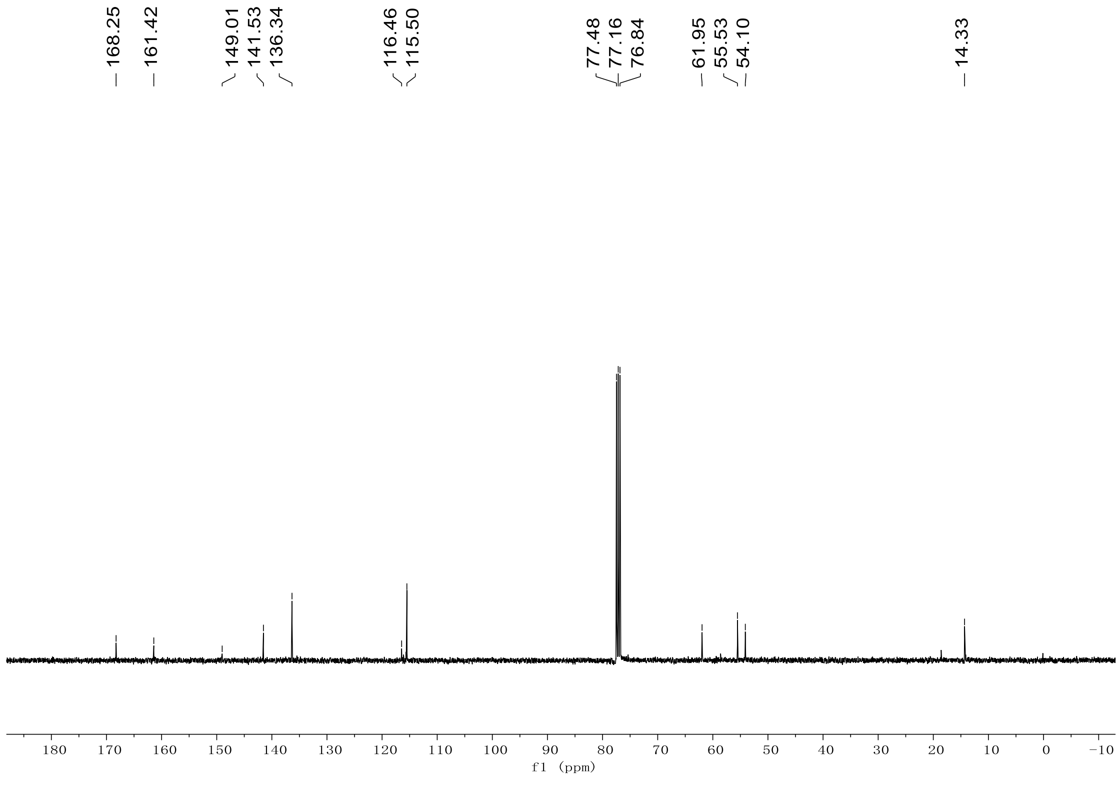
69


8.62
7.84
7.35
7.34
7.33
7.28
6.80
6.79
6.78
4.55
4.28
4.27
4.25
4.23
3.77
1.34
1.32
1.30
MeO
S
N
N
N
N
CO2Et
1.00
1.00
2.02
2.06
2.05
1.98
3.08
3.16
f1 (ppm)

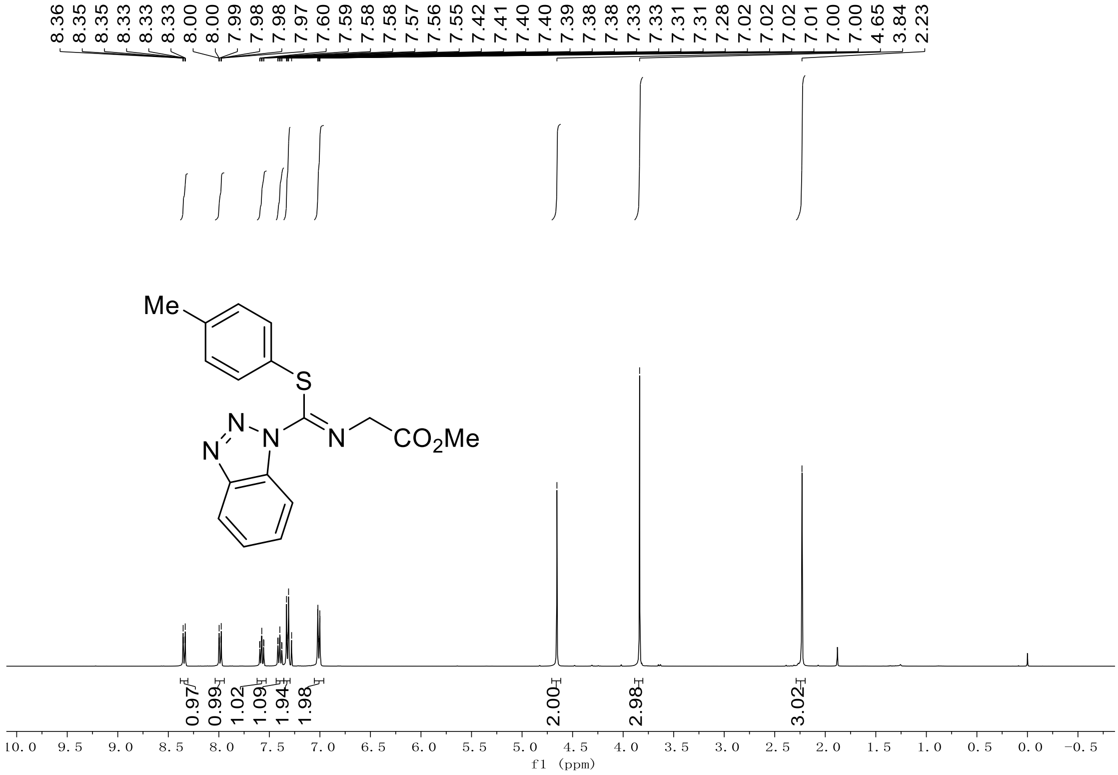

168.81
160.74
152.08
150.35
143.55
135.28
118.39
115.23
77.48
77.16
76.84
61.66
55.47
54.15
14.30
f1 (ppm)

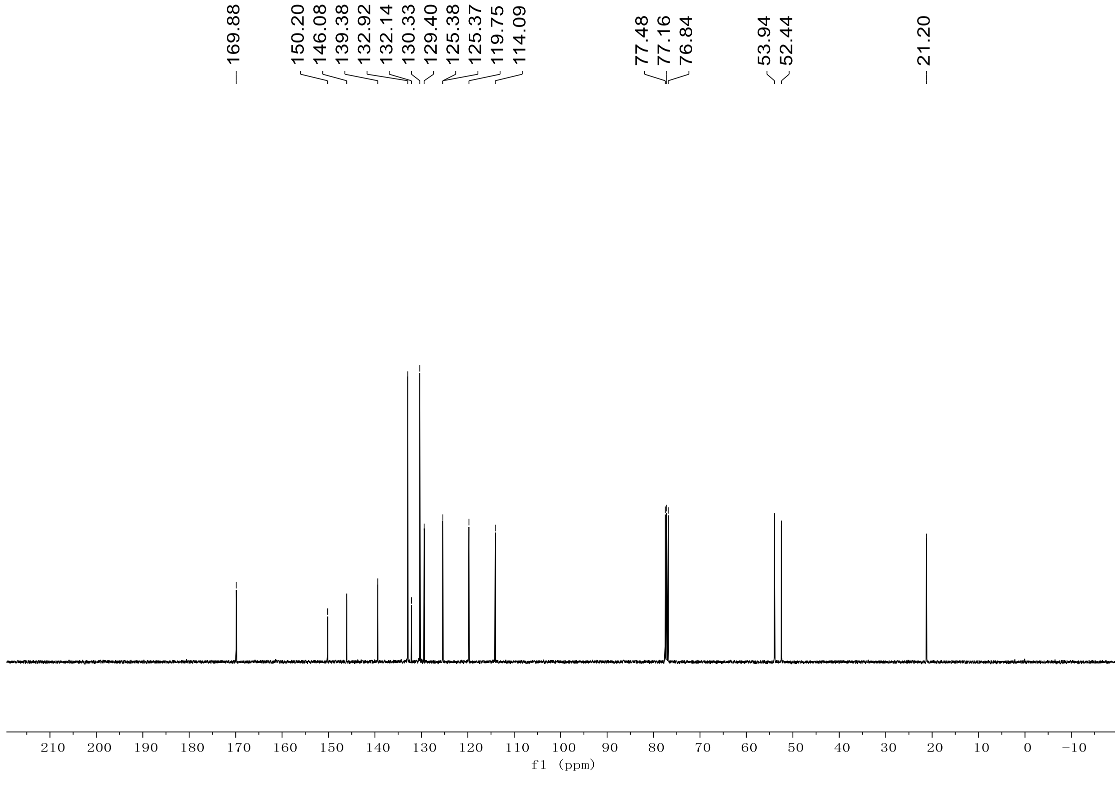
70


8.94
7.38
7.36
7.27
6.80
6.78
4.61
4.32
4.30
4.28
4.26
3.76
1.36
1.34
1.32
MeO
S
N
N
N
N
N
CO2Et
1.00
1.98
2.03
2.00
2.05
3.05
3.04
f1 (ppm)

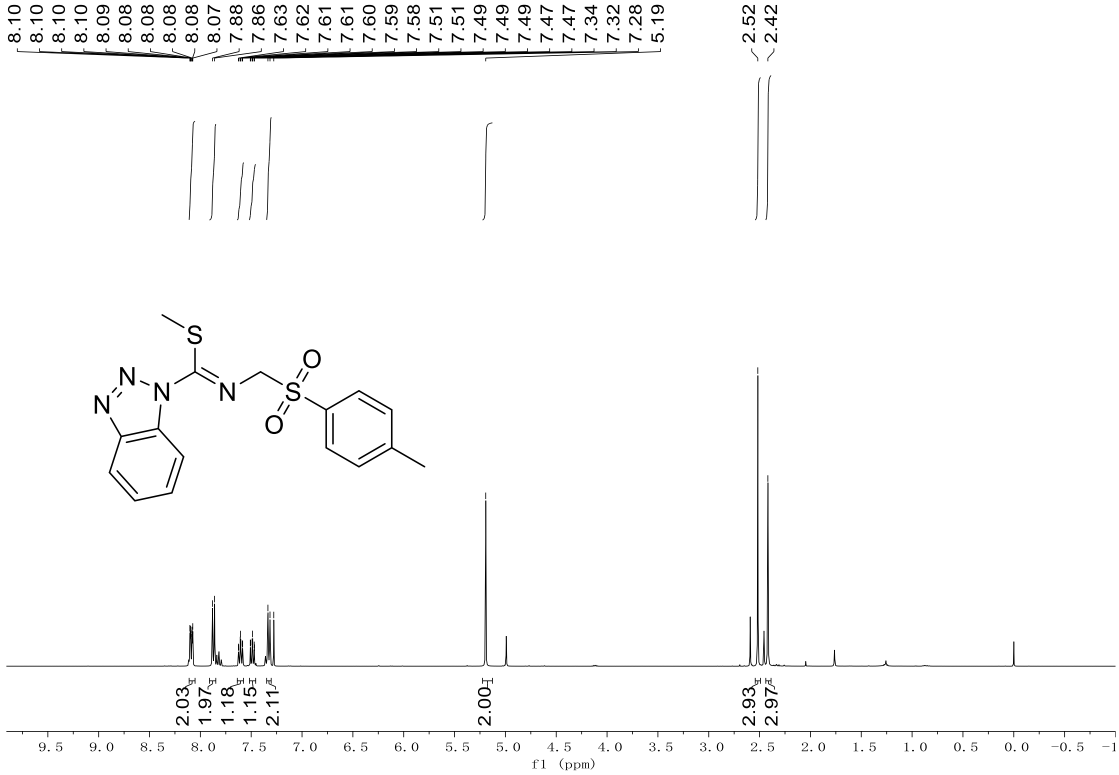

168.25
161.42
149.01
141.53
136.34
116.46
115.50
77.48
77.16
76.84
61.95
55.53
54.10
14.33
f1 (ppm)

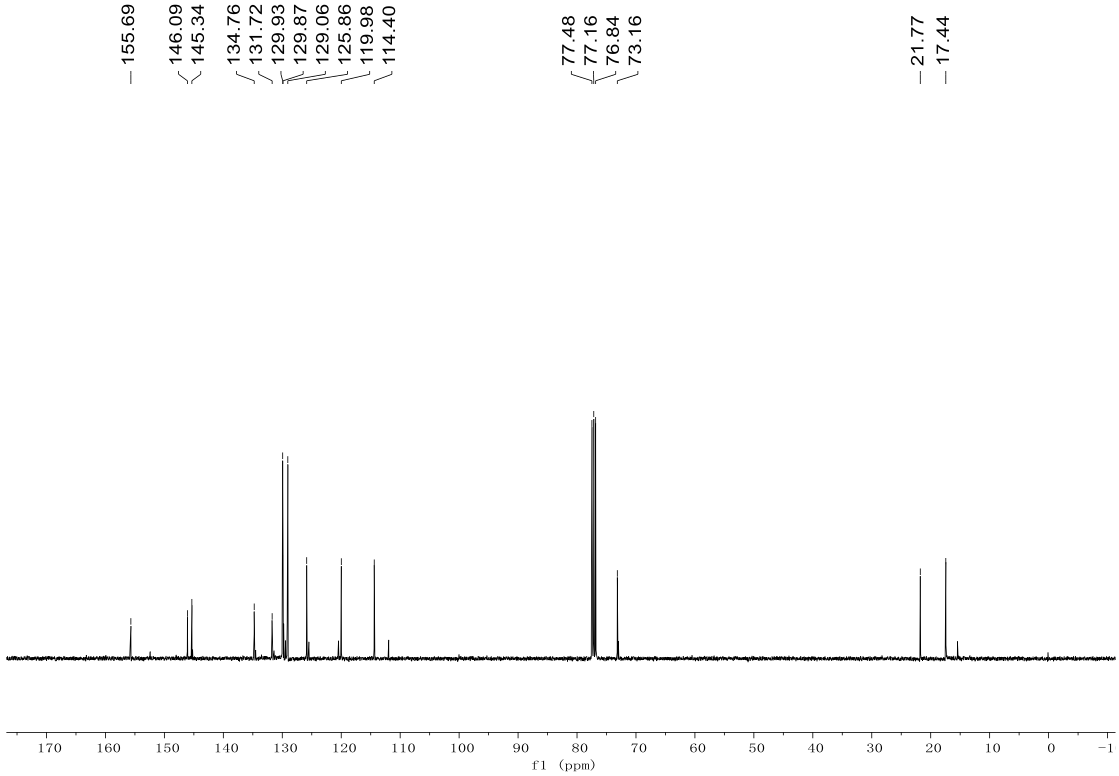
71


8.36
8.35
8.35
8.33
8.33
8.33
8.00
8.00
7.99
7.98
7.98
7.97
7.60
7.59
7.58
7.58
7.57
7.56
7.55
7.42
7.41
7.40
7.40
7.39
7.38
7.38
7.33
7.33
7.31
7.31
7.28
7.02
7.02
7.02
7.01
7.00
7.00
4.65
3.84
2.23
Me
S
N
N
N
N
CO2Me
0.97
0.99
1.02
1.09
1.94
1.98
2.00
2.98
3.02
f1 (ppm)

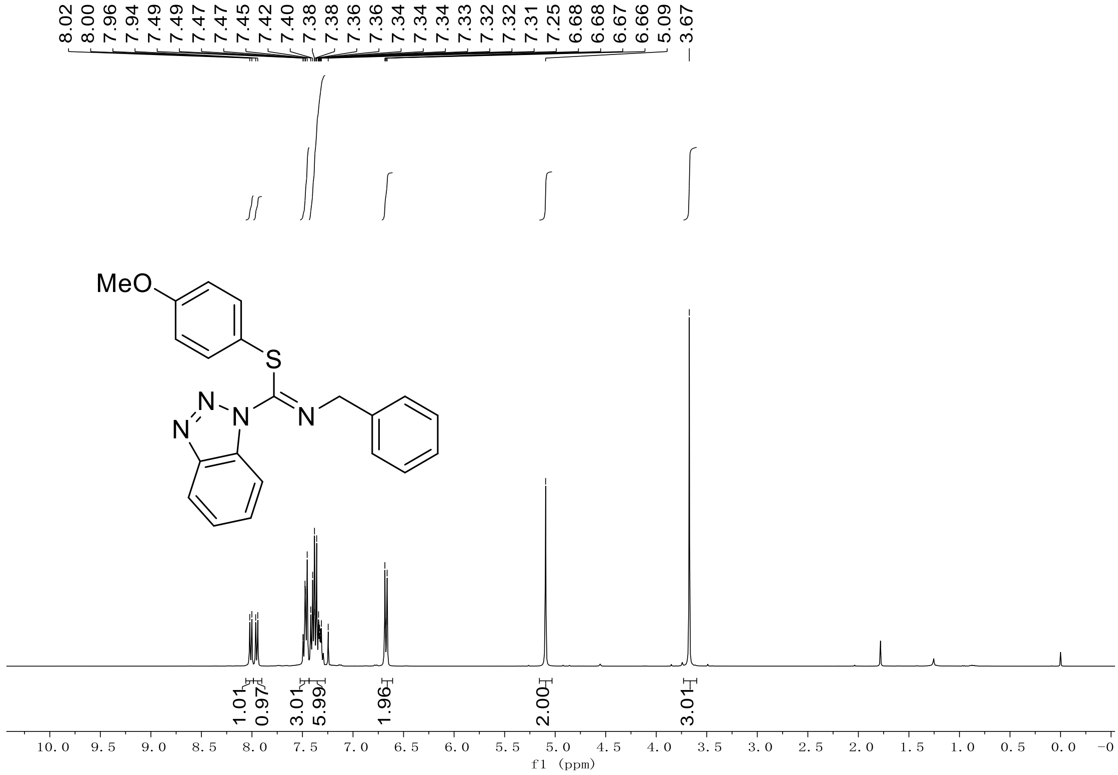

169.88
150.20
146.08
139.38
132.92
132.14
130.33
129.40
125.38
125.37
119.75
114.09
77.48
77.16
76.84
53.94
52.44
21.20
f1 (ppm)

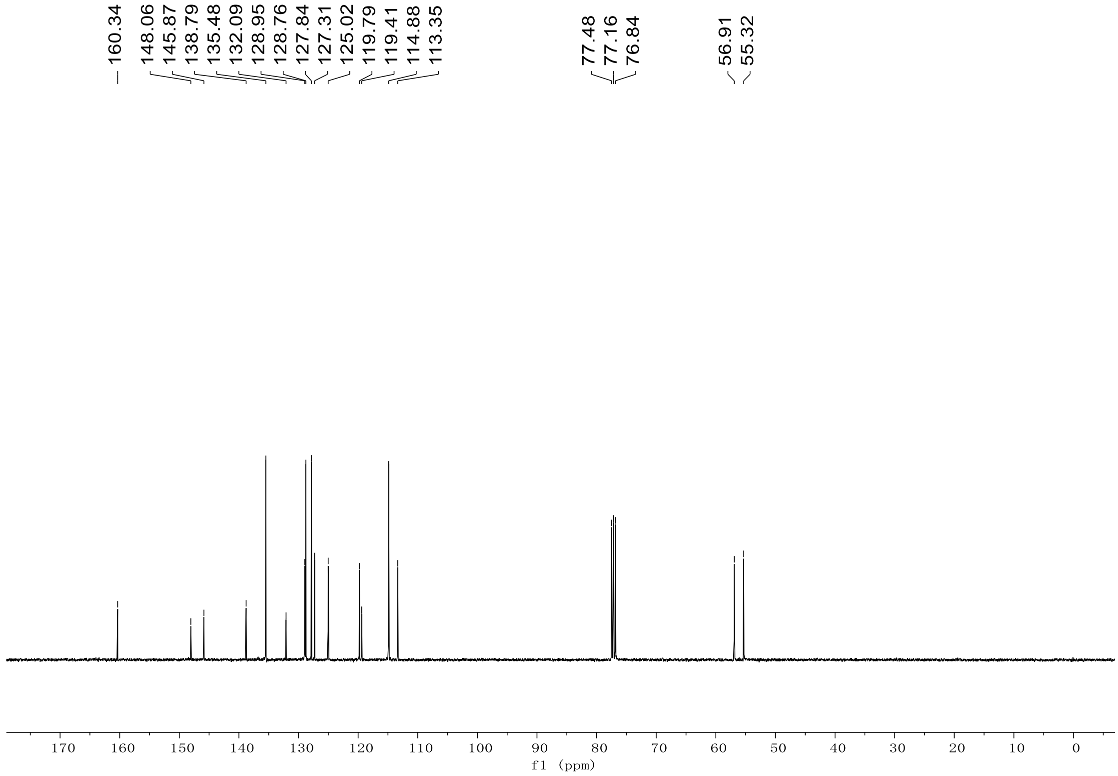
72


8.10 8.10 8.10 8.09 8.08 8.08 8.08 8.08 8.07 7.88 7.86 7.63 7.62 7.61 7.61 7.60 7.59 7.58 7.51 7.51 7.49 7.49 7.49 7.47 7.47 7.34 7.32 7.28 5.19
2.52 2.42
2.03 1.97 1.18 1.15 2.11
2.00
2.93 2.97
f1 (ppm)

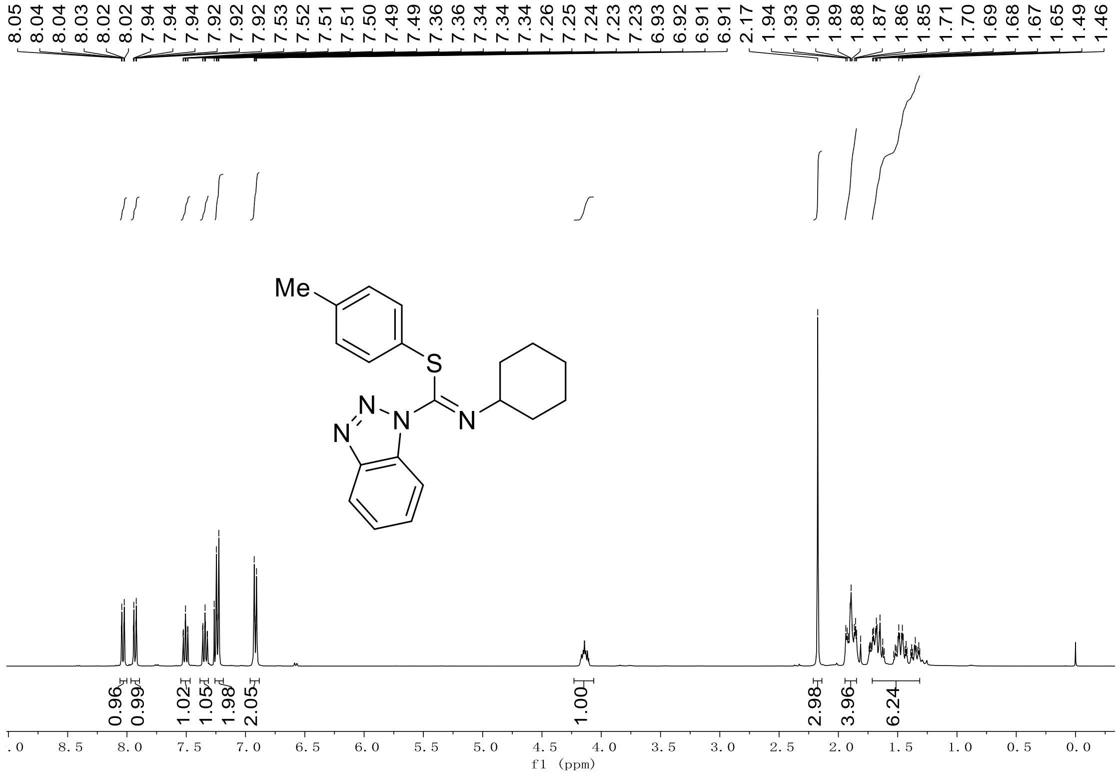

155.69
146.09 145.34
134.76 131.72 129.93 129.87 129.06 125.86 119.98 114.40
77.48 77.16 76.84 73.16
21.77 17.44
f1 (ppm)

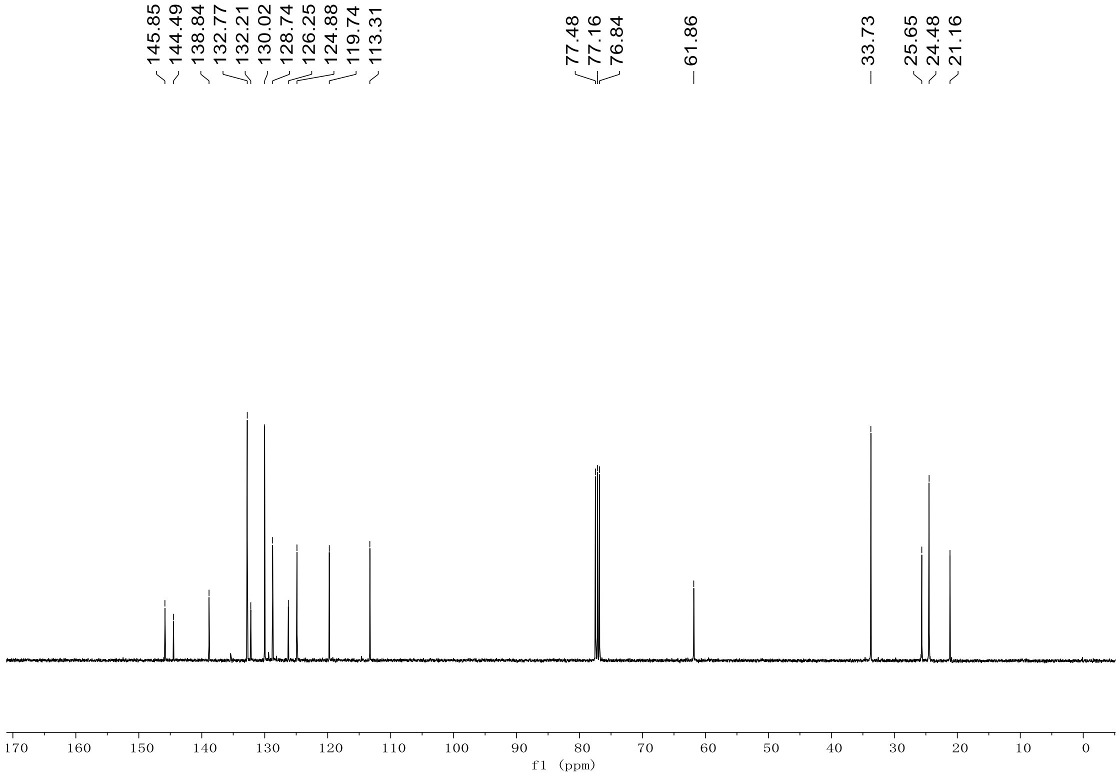
73


8.02
8.00
7.96
7.94
7.49
7.47
7.47
7.45
7.42
7.40
7.38
7.38
7.36
7.36
7.34
7.34
7.34
7.33
7.32
7.32
7.31
7.25
6.68
6.68
6.67
6.66
5.09
3.67
MeO
S
N
N
N
N
1.01
0.97
3.01
5.99
1.96
2.00
3.01
10.0 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 0.0
f1 (ppm)

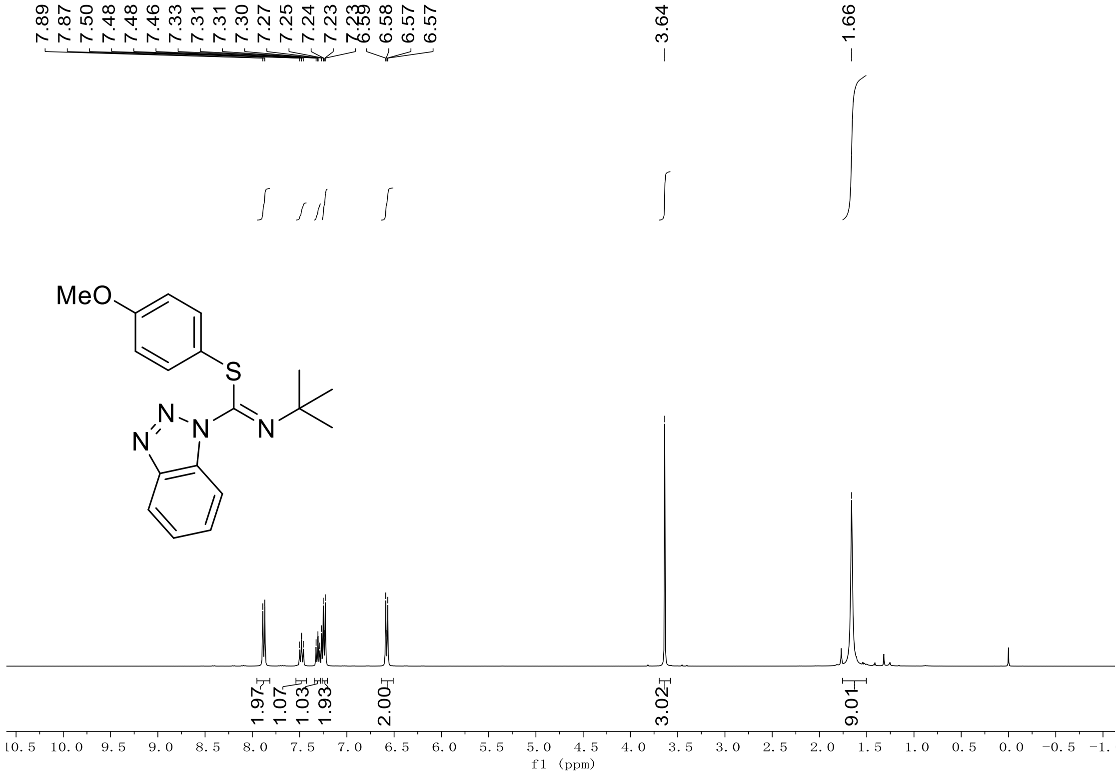

160.34
148.06
145.87
138.79
135.48
132.09
128.95
128.76
127.84
127.31
125.02
119.79
119.41
114.88
113.35
77.48
77.16
76.84
56.91
55.32
170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0
f1 (ppm)

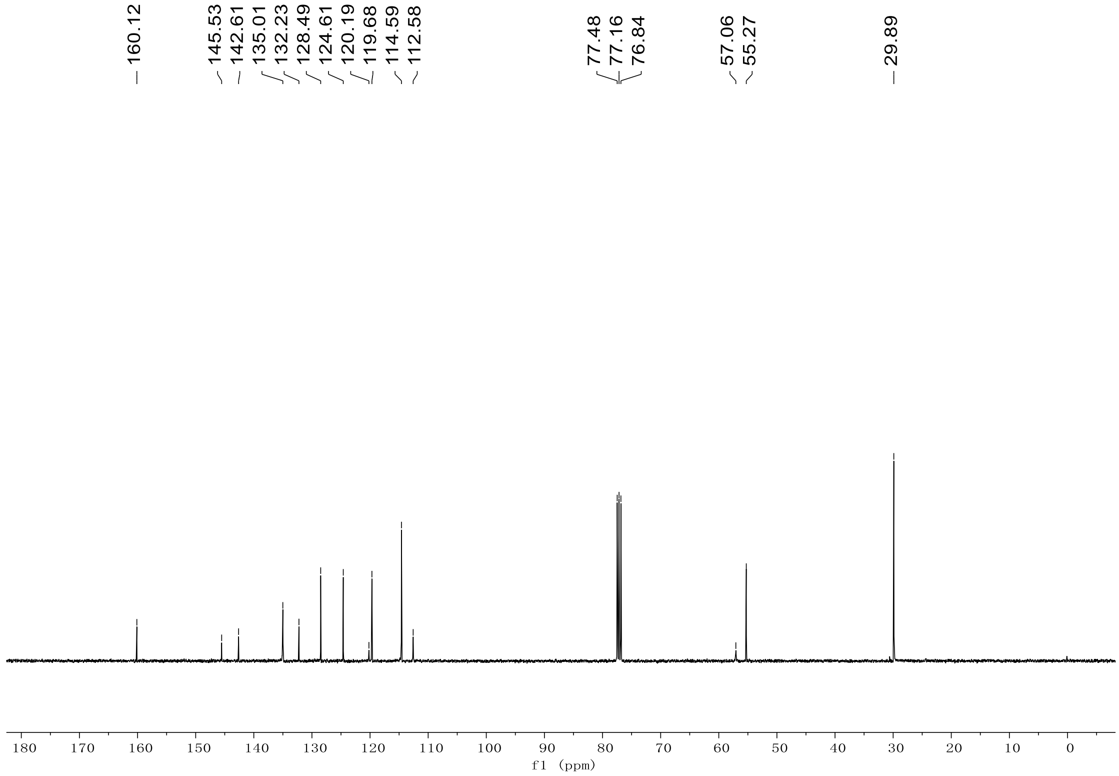
74


8.05
8.04
8.04
8.03
8.02
8.02
7.94
7.94
7.94
7.92
7.92
7.92
7.53
7.52
7.51
7.51
7.50
7.49
7.49
7.36
7.36
7.34
7.34
7.34
7.26
7.25
7.24
7.23
7.23
6.93
6.92
6.91
6.91
2.17
1.94
1.93
1.90
1.89
1.88
1.87
1.86
1.85
1.71
1.70
1.69
1.68
1.67
1.65
1.49
1.46
Me
S
N
N
N
N
N
0.96
0.99
1.02
1.05
1.98
2.05
1.00
2.98
3.96
6.24
f1 (ppm)

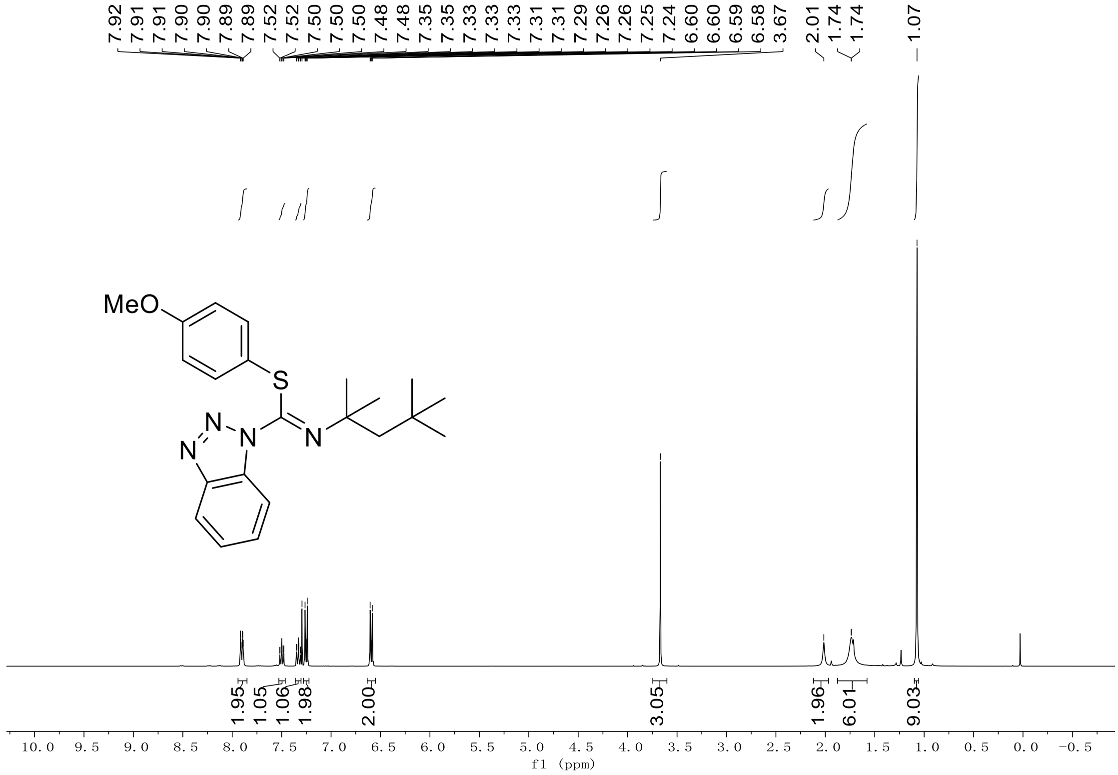

145.85
144.49
138.84
132.77
132.21
130.02
128.74
126.25
124.88
119.74
113.31
77.48
77.16
76.84
61.86
33.73
25.65
24.48
21.16
f1 (ppm)

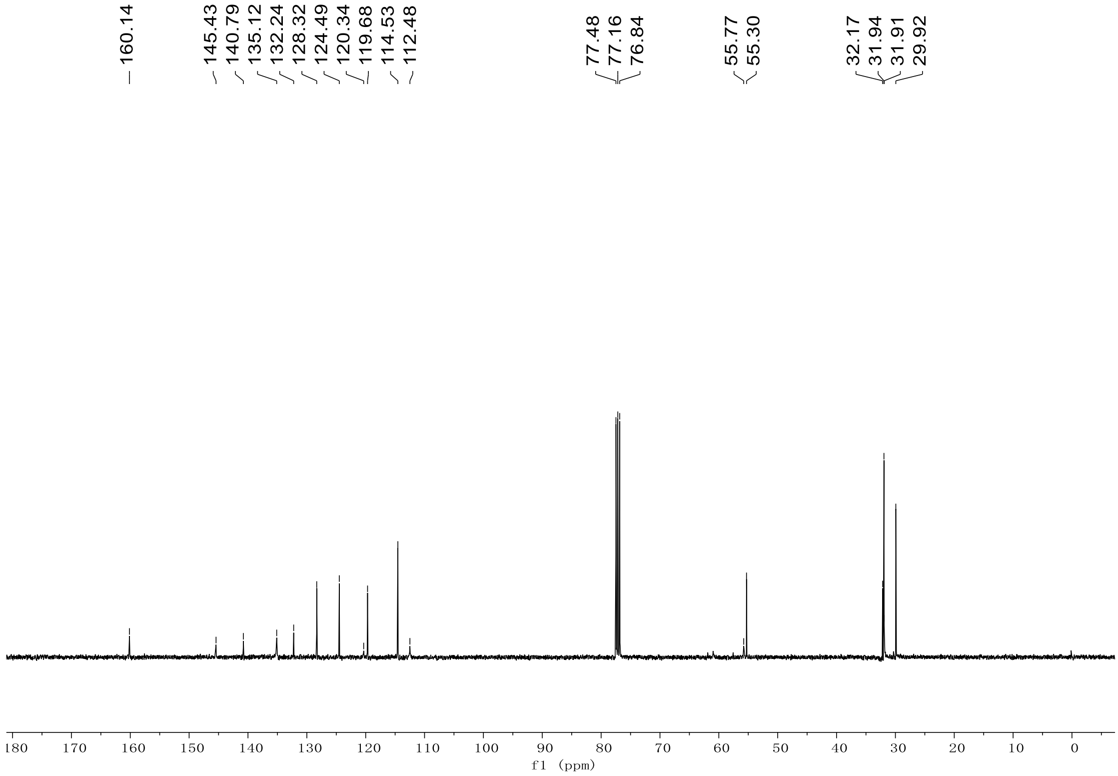
75


7.89
7.87
7.50
7.48
7.48
7.46
7.33
7.31
7.31
7.30
7.27
7.25
7.24
7.23
7.23
6.59
6.58
6.57
6.57
3.64
1.66
MeO
S
N
N
N
N
1.97
1.07
1.03
1.93
2.00
3.02
9.01
f1 (ppm)

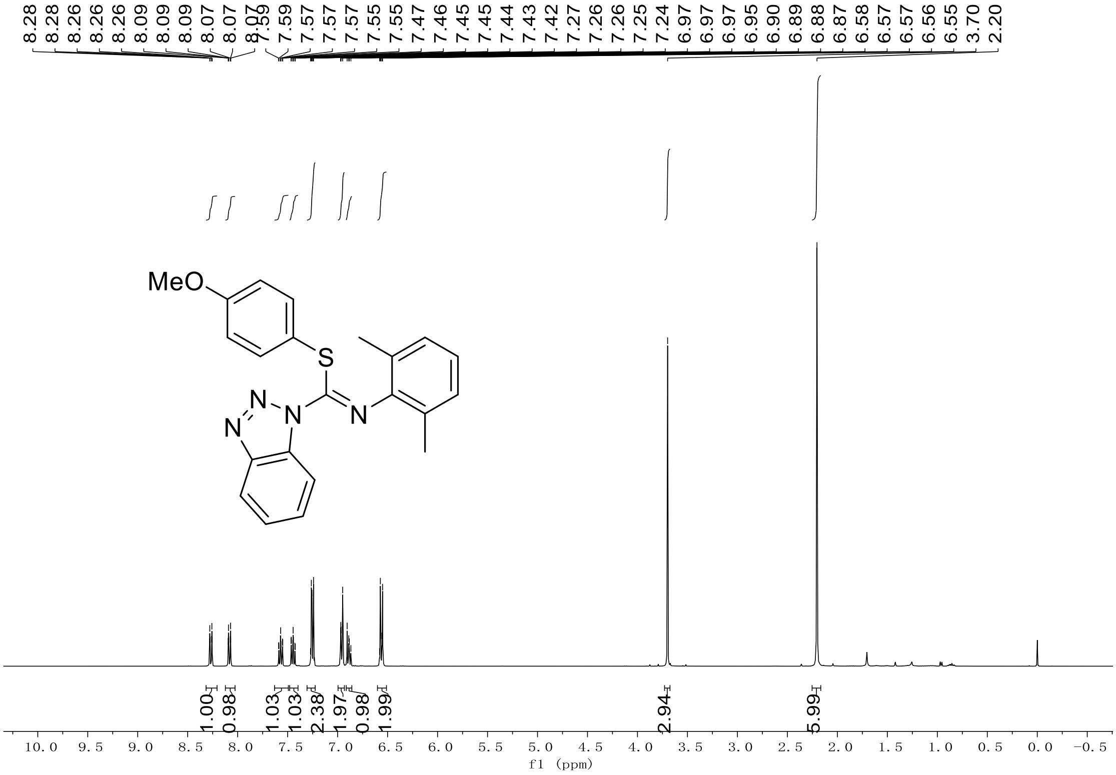

160.12
145.53
142.61
135.01
132.23
128.49
124.61
120.19
119.68
114.59
112.58
77.48
77.16
76.84
57.06
55.27
29.89
f1 (ppm)

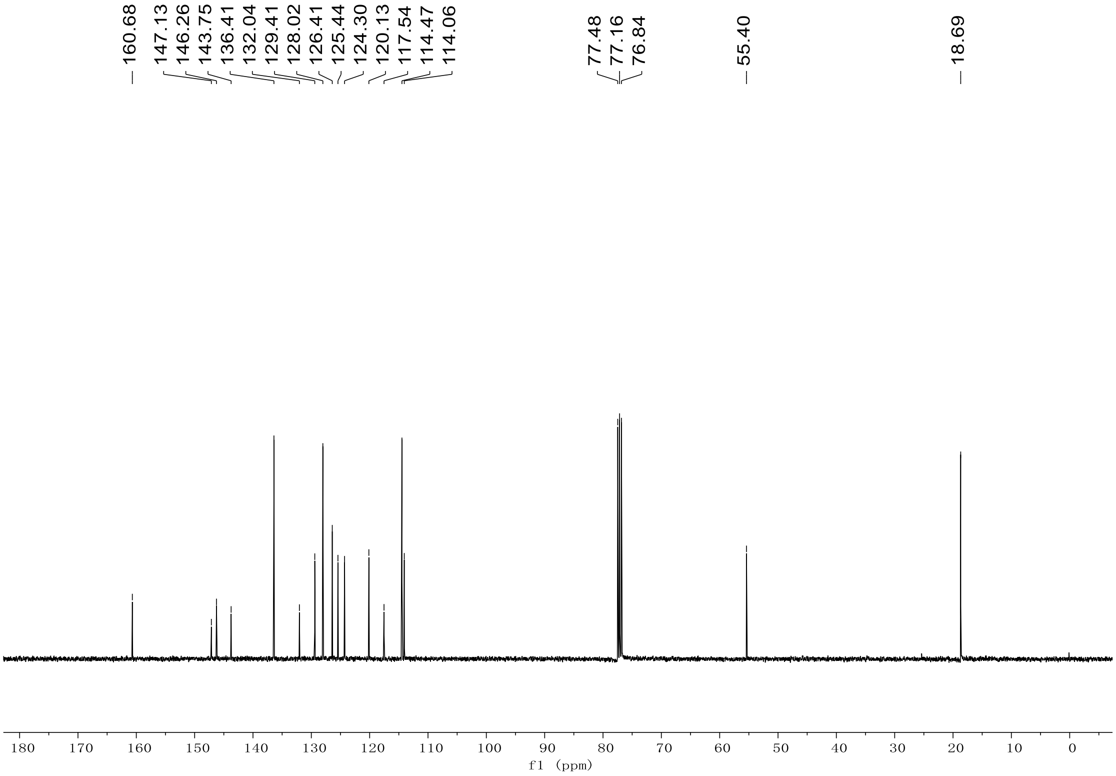
76


7.92 7.91 7.91 7.90 7.90 7.89 7.89 7.52 7.52 7.50 7.50 7.48 7.48 7.35 7.35 7.33 7.33 7.33 7.31 7.31 7.29 7.26 7.26 7.25 7.24 6.60 6.59 6.58 3.67 2.01 1.74 1.74 1.07
MeO
S
N
N
N
N
1.95 1.05 1.06 1.98 2.00 3.05 1.96 6.01 9.03
10.0 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 0.0 -0.5
f1 (ppm)

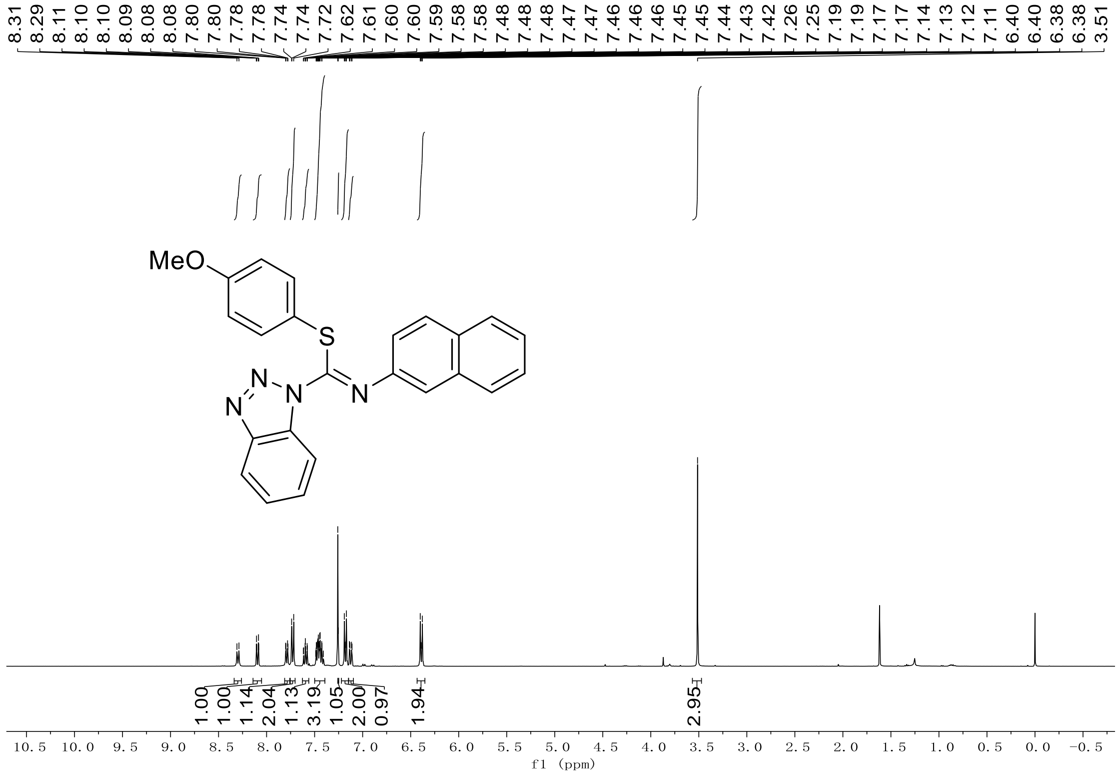

160.14 145.43 140.79 135.12 132.24 128.32 124.49 120.34 119.68 114.53 112.48 77.48 77.16 76.84 55.77 55.30 32.17 31.94 31.91 29.92
180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0
f1 (ppm)

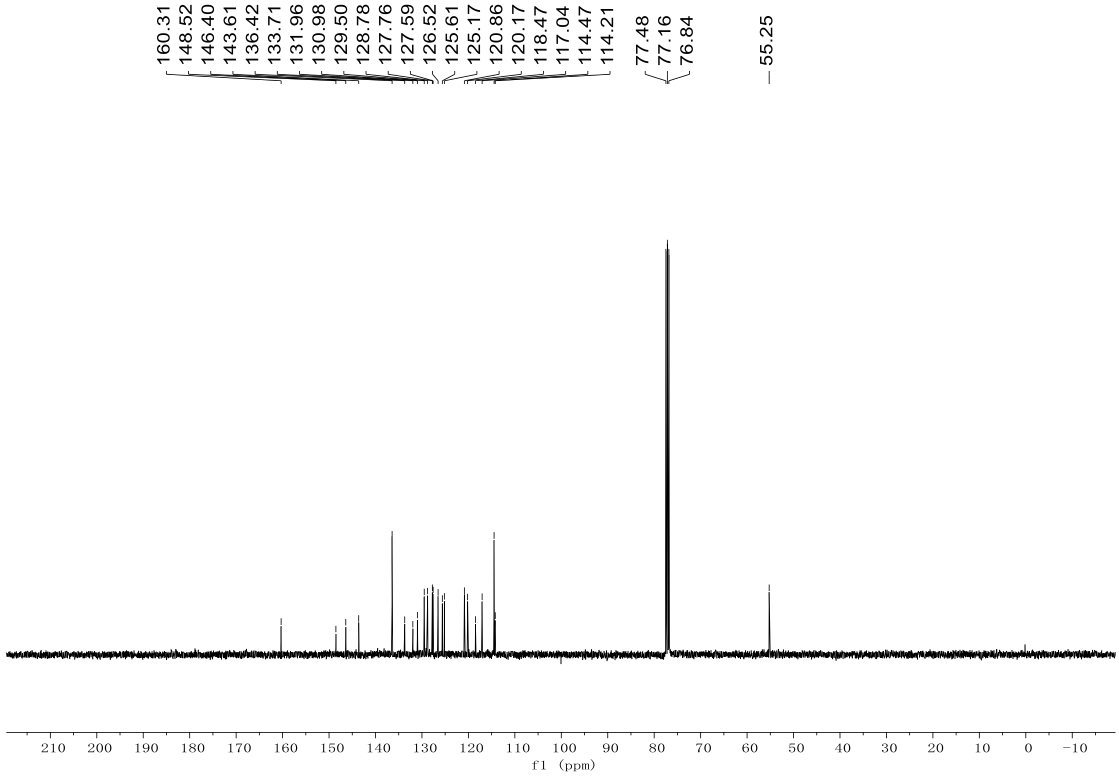
77


8.28 8.28 8.26 8.26 8.09 8.09 8.09 8.07 8.07 8.07 7.59 7.59 7.57 7.57 7.57 7.55 7.55 7.47 7.46 7.45 7.45 7.44 7.43 7.42 7.27 7.26 7.26 7.25 7.24 6.97 6.97 6.97 6.95 6.90 6.89 6.88 6.87 6.58 6.57 6.57 6.56 6.55 3.70 2.20
MeO
S
N
N
N
N
1.00 0.98 1.03 1.03 2.38 1.97 0.98 1.99 2.94 5.99
f1 (ppm)


160.68 147.13 146.26 143.75 136.41 132.04 129.41 128.02 126.41 125.44 124.30 120.13 117.54 114.47 114.06
77.48 77.16 76.84
55.40
18.69
f1 (ppm)

78


8.31
8.29
8.11
8.10
8.10
8.09
8.08
8.08
7.80
7.80
7.78
7.78
7.74
7.74
7.72
7.62
7.61
7.60
7.60
7.59
7.58
7.58
7.48
7.48
7.48
7.47
7.47
7.46
7.46
7.46
7.45
7.45
7.44
7.43
7.42
7.26
7.25
7.19
7.19
7.17
7.17
7.14
7.13
7.12
7.11
6.40
6.40
6.38
6.38
3.51
MeO
S
N
N
N
N
1.00
1.00
1.14
2.04
1.13
3.19
1.05
2.00
0.97
1.94
2.95
10.5
10.0
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
0.0
-0.5
f1 (ppm)


160.31
148.52
146.40
143.61
136.42
133.71
131.96
130.98
129.50
128.78
127.76
127.59
126.52
125.61
125.17
120.86
120.17
118.47
117.04
114.47
114.21
77.48
77.16
76.84
55.25
210
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
-10
f1 (ppm)