

Supporting Information

Binuclear molybdenum alkoxide as the versatile catalyst for the conversion of carbon dioxide

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Table S1. Synthesis of 3-phenylpropiolic acid from CO₂ and 1-ethynylbenzene with catalyst 1.^a

Entry	Catalyst (mol%)	Base (mmol)	Time (h)	Temp (°C)	Solvent	Yield ^f (%)
1	1.5	1.5	10	50	DMF	93.2
2	0.75	1.5	10	50	DMF	55.1
3	2.25	1.5	10	50	DMF	69.3
4	0	1.5	10	50	DMF	5.8
5	1.5	0.0	10	50	DMF	<5
6	1.5	0.5	10	50	DMF	22.3
7	1.5	1.0	10	50	DMF	46.8
8	1.5	1.5	5	50	DMF	44.6
9	1.5	1.5	20	50	DMF	78.9
10	1.5	1.5	10	25	DMF	<5
11	1.5	1.5	10	75	DMF	87.6
12	1.5	1.5	10	50	THF	<5
13	1.5	1.5	10	50	CH ₃ CN	<5
14	1.5	1.5	10	50	n-C ₆ H ₁₄	<5
15	1.5	3.0 ^b	10	50	DMF	65.8
16	1.5	3.0 ^c	10	50	DMF	34.4
17	1.5	1.5 ^d	10	50	DMF	21.5
18	1.5 ^e	1.5	10	50	DMF	98.2

^a Reaction conditions: 1-ethynylbenzene (1.0 mmol), catalyst 1, CO₂ (1.0 atm, using a balloon), solvent (5 mL). ^b K(O'Bu). ^c Li(O'Bu). ^d K₂CO₃. ^e 1·CO₂. ^f Yields of gas chromatography.

Single Crystal X-ray Diffraction Study

Crystallographic data of 3-(4-ethynylphenyl)propiolic acid and 3-(3-ethynylphenyl)propiolic acid were collected on an Agilent Technologies SuperNova Single Crystal Diffractometer at 120 K equipped with graphite-monochromatic Mo-Kα radiation ($\lambda = 0.71073 \text{ \AA}$). Absorption corrections were applied by using the multiscan program. All the structures were solved by direct methods with SHELXS and refined with the full-matrix least-squares technique using the SHELXL program¹ contained on Olex 2². All non-hydrogen atoms were refined anisotropically, while the hydrogen atoms were generated geometrically. Crystal data as well as details of data collection and refinement for the complexes are summarized in Table S1. CCDC: 1544088 and 1544089 for 3-(3-ethynylphenyl)propiolic and 3-(4-ethynylphenyl)propiolic, contains the supplementary crystallographic data for this paper, which can be obtained free of charge from the Cambridge Crystallographic Data Center.

Table S2. Crystallographic data and structure refinements.

	3-(4-ethynylphenyl)propiolic acid	3-(3-ethynylphenyl)propiolic acid	CsHCO₃
Formula	C ₁₁ H ₅ O ₂	C ₁₁ H ₆ O ₂	CHCsO ₃
Mol. wt.	169.15	170.16	193.93
Crystal system	Monoclinic	Triclinic	Monoclinic
Space group	<i>P</i> 2 ₁ /c	<i>P</i> -1	<i>P</i> 2 ₁ /n
a (Å)	3.8398(8)	3.7722(3)	4.5955(3)
b (Å)	6.201(3)	8.8640(7)	11.1835(7)
c (Å)	35.222(7)	25.643(2)	7.0836(4)
α (deg)		86.384(7)	
β (deg)	91.034(17)	89.405(7)	102.175(5)
γ (deg)		81.479(7)	
V (Å ³)	838.6(4)	846.26(12)	355.86(4)
Z	4	4	4
T (K)	120(10)	120(10)	120(10)
ρcalcd. (Mg/m ³)	1.340	1.336	3.620
μ (mm ⁻¹)	0.093	0.092	10.217
Reflns collected	3042	5086	1184
Reflns unique	1490 (R _{int} = 0.0413)	2978 (R _{int} = 0.0341)	620 (R _{int} = 0.0405)
Final R indices	R1 = 0.0890 wR2 = 0.1873	R1 = 0.0806 wR2 = 0.1831	R1 = 0.0298 wR2 = 0.0753
[I > 2σ(I)]			
S	1.168	1.110	1.064
Δρmax (eÅ ⁻³)	0.35	0.31	1.33
Δρmin (eÅ ⁻³)	-0.31	-0.29	-2.17

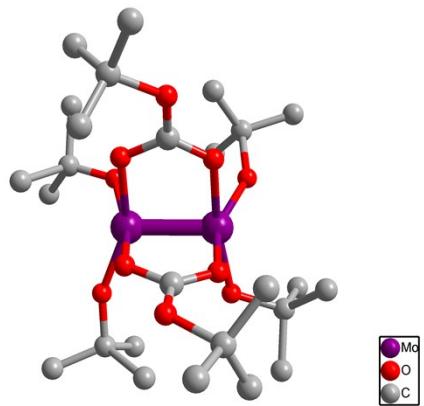


Figure S1. A ball-and-stick diagram of $\text{Mo}_2(\text{O}'\text{Bu})_4(\text{OOCO}'\text{Bu})_2(\mathbf{1}\cdot\text{CO}_2)$

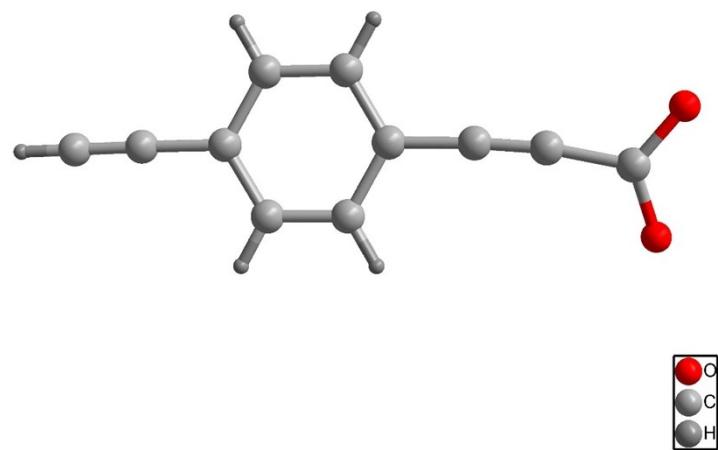


Figure S2. A ball-and-stick diagram of 3-(4-ethynylphenyl)propiolic acid

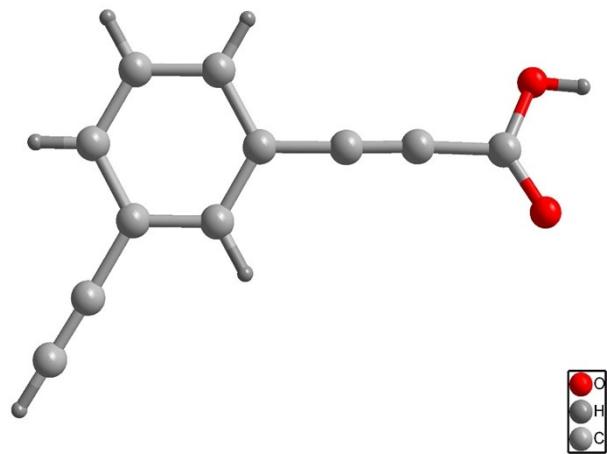


Figure S3. A ball-and-stick diagram of 3-(3-ethynylphenyl)propiolic acid

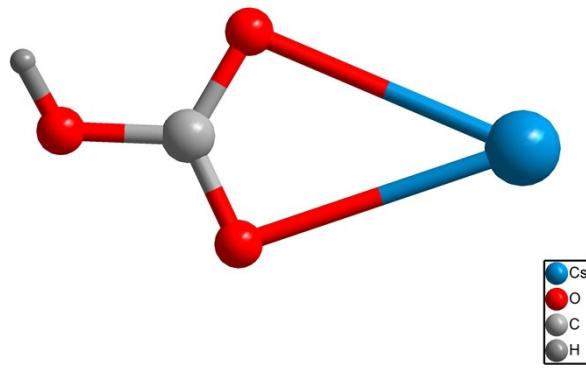
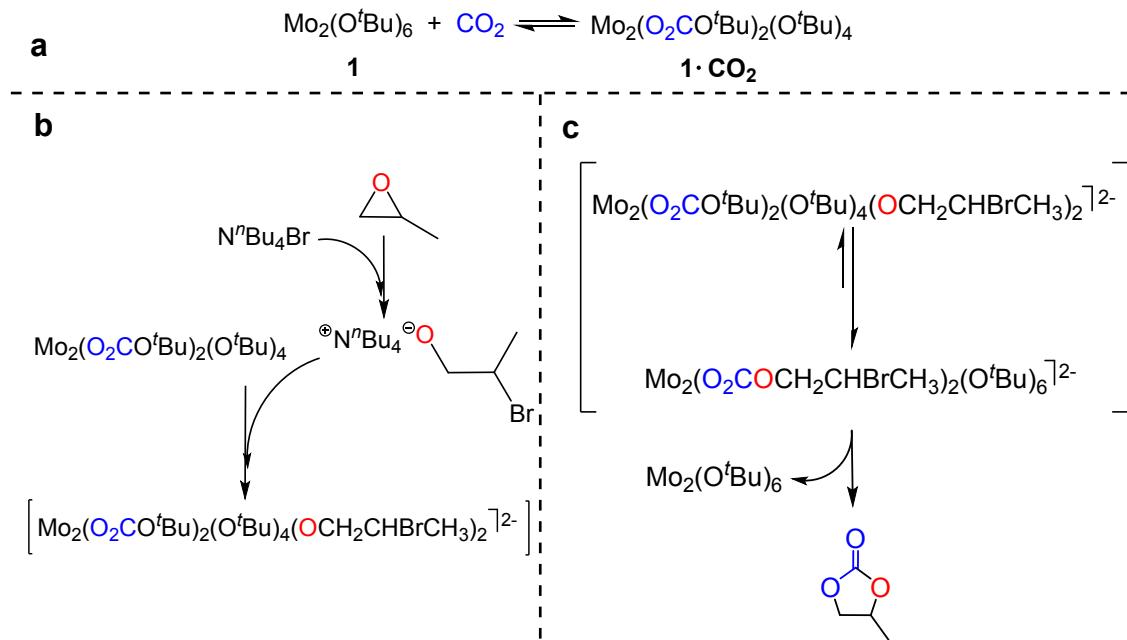


Figure S4. A ball-and-stick diagram of CsHCO_3 separated from the reaction of CO_2 with alkynes and heteroarenes catalyzed by **1**.



Scheme S1. Proposed catalytic process of CO_2 with epoxide by **1.** The first step is CO_2 insertion into Mo-O bonds of **1** to form $\mathbf{1}\cdot\text{CO}_2$ (**a**). The second step could be ring-open of epoxide anions by $\text{N}^n\text{Bu}_4\text{Br}$, which could react further with $\mathbf{1}\cdot\text{CO}_2$ via the “ionization reaction” leading to the “[$\text{Mo}_2(\text{O}_2\text{CO}^t\text{Bu})_2(\text{O}^t\text{Bu})_4(\text{anion})_2]^{2-}”$ intermediates(**c**). The third step could be an intramolecular rearrangement for the “[$\text{Mo}_2(\text{O}_2\text{CO}^t\text{Bu})_2(\text{O}^t\text{Bu})_4(\text{anion})_2]^{2-}”$ intermediate to form “[$\text{Mo}_2(\text{O}_2\text{C-anion})_2(\text{O}^t\text{Bu})_6]^{2-}”$ intermediate, which releases the carboxylated products to recover catalyst **1**.

Table S3. Comparison of the catalytic potentials of **1** with previously reported homogeneous catalysts in the carboxylation of CO₂ and terminal alkynes.

Entry	Catalyst	Time (h)	Base	Pressure	Temp	Yield for 3i or 3j (%)	Ref.
1	1 (1.5 mol%)	10	Cs ₂ CO ₃ , 1.5 equiv	1 atm	50 °C	82.7 for 3i 77.2 for 3j >99% selectivity for 3i and 3j	This paper
2	--	14-24	Cs ₂ CO ₃ , 1.2 equiv	2.5 atm	120 °C	0 for 3j	3
3	--	2-42	TBD, 2 equiv	12 bar	100 °C	44 for 3i	4
4	Ag-(NHC) ₂ (1 mol%)	16	Cs ₂ CO ₃ , 1.2 equiv	1 bar	R.T.	0 for 3i	5
5	Trimethylsilylacetylene (1.1 equiv) 18-crown-6 (0.2 equiv)	20	CsF, 1.5 equiv	1 atm	30 °C	0 for 3i	6
6	{LNd[N(SiMe ₃) ₂]·THF} ₂ (2.5 mol%)	24	Cs ₂ CO ₃ , 2.0 equiv	1 atm	40 °C	0 for 3i and 3j	7
7	Ag-NHC (0.5 mol%; 1 mol% Ag)	16	Cs ₂ CO ₃ , 1.5 equiv	1 atm	R.T.	0 for 3j	8
8	Ag ₂ WO ₄ (2.5 mol%)	24	Cs ₂ CO ₃ , 1.2 equiv	1 atm	25 °C	24 for 3i	9

Table S4. Comparison of the catalytic potentials of **1** with previously reported homogeneous catalysts in the cycloaddition of CO₂ with propylene oxide.

Entry	Catalyst	Co-catalyst	epoxide	Pressure	Temp	Time	Yield (%)	Ref.
1	1 (1 mol%)	"Bu ₄ NBr (7.2 mol%)	Propylene Oxide	1 atm	R.T.	24 2	97.5 86.0	This paper
2	[Cu ₆ (μ ₄ -O) ₂ (SO ₄) ₄ (DMA) ₆] (0.24 mol%)	"Bu ₄ NBr (7.2 mol%)	Propylene Oxide	1 atm	R.T.	24	98.2	10
3	[HTEA]I (1.9 mol%)	--	Propylene Oxide	20 atm	110 °C	6	91	11
4	Zn ₄ (OCOCF ₃) ₆ O (2.0 mol%)	"Bu ₄ NI 4.0 mol%	Propylene Oxide	1 atm	25 °C	6	99	12
5	DBU (10 mmol%)	cellulose (15 mg),	Propylene Oxide	20 atm	120 °C	2	90	13
6	UDIL-I (1.2 mol%)	--	Propylene Oxide	15 atm	130 °C	3	97	14
7	NBS/BPO (5 mol%/5 mol%)	--	2-hexyloxirane	100 psi	120 °C	0.5	96	15
8	1-(6-(1H-imidazol-1-yl)pyridin-2-yl)-3-propyl-1H-benzo[d]imidazol-3-ium iodide (1 mol%)	--	Propylene Oxide	10 atm	90 °C	5	90	16

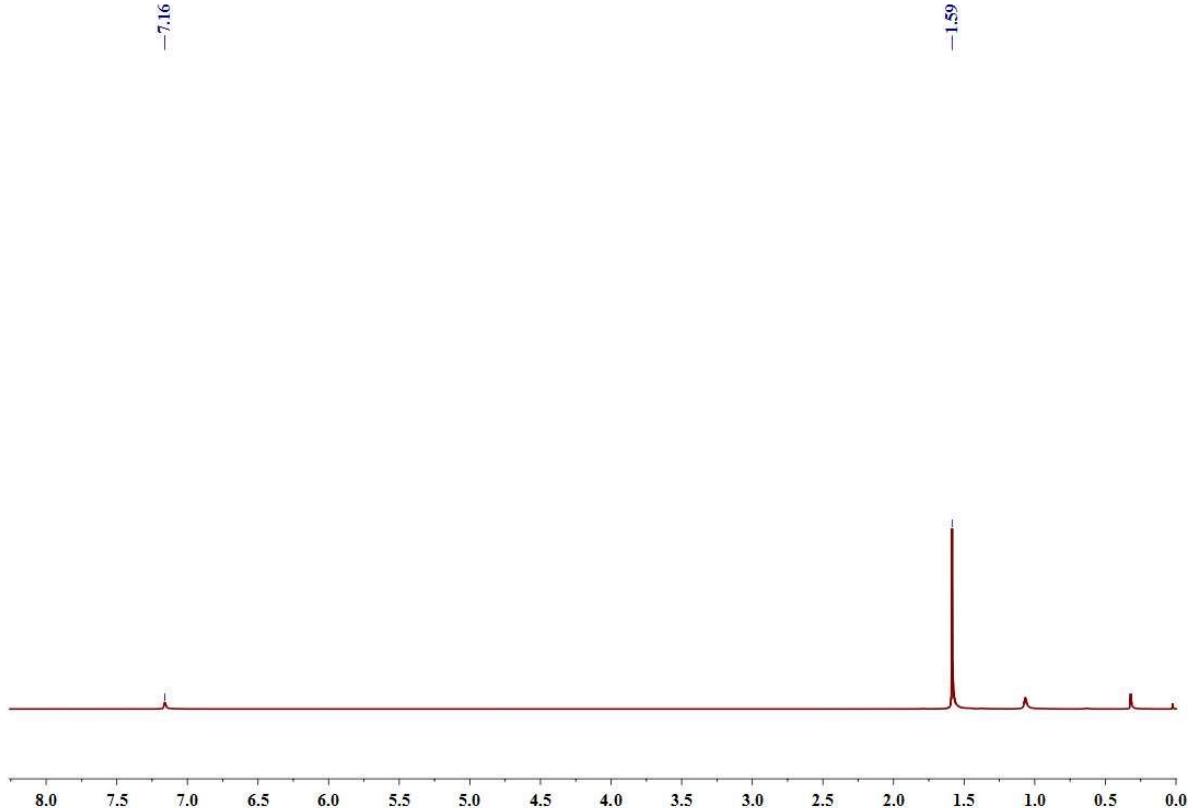
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¹H NMR and ¹³C NMR Spectra

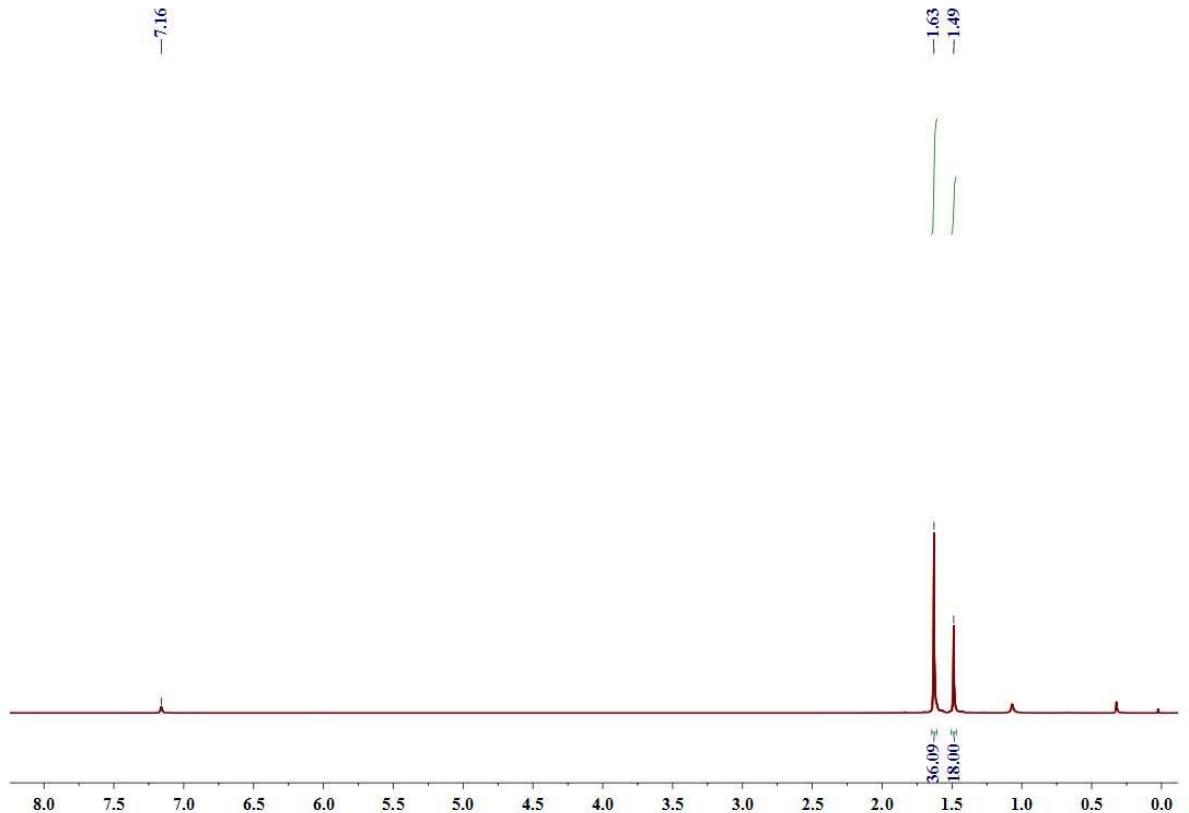
Mo₂(O'Bu)₆

¹H NMR (300 MHz, C₆D₆)



Mo₂(O'Bu)₄(OOCO'Bu)₂

¹H NMR (300 MHz, C₆D₆)

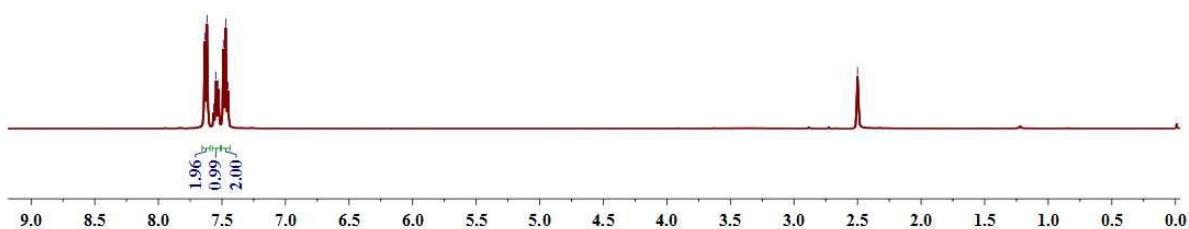
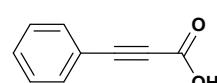


3-phenyl propionic acid (**3a**)

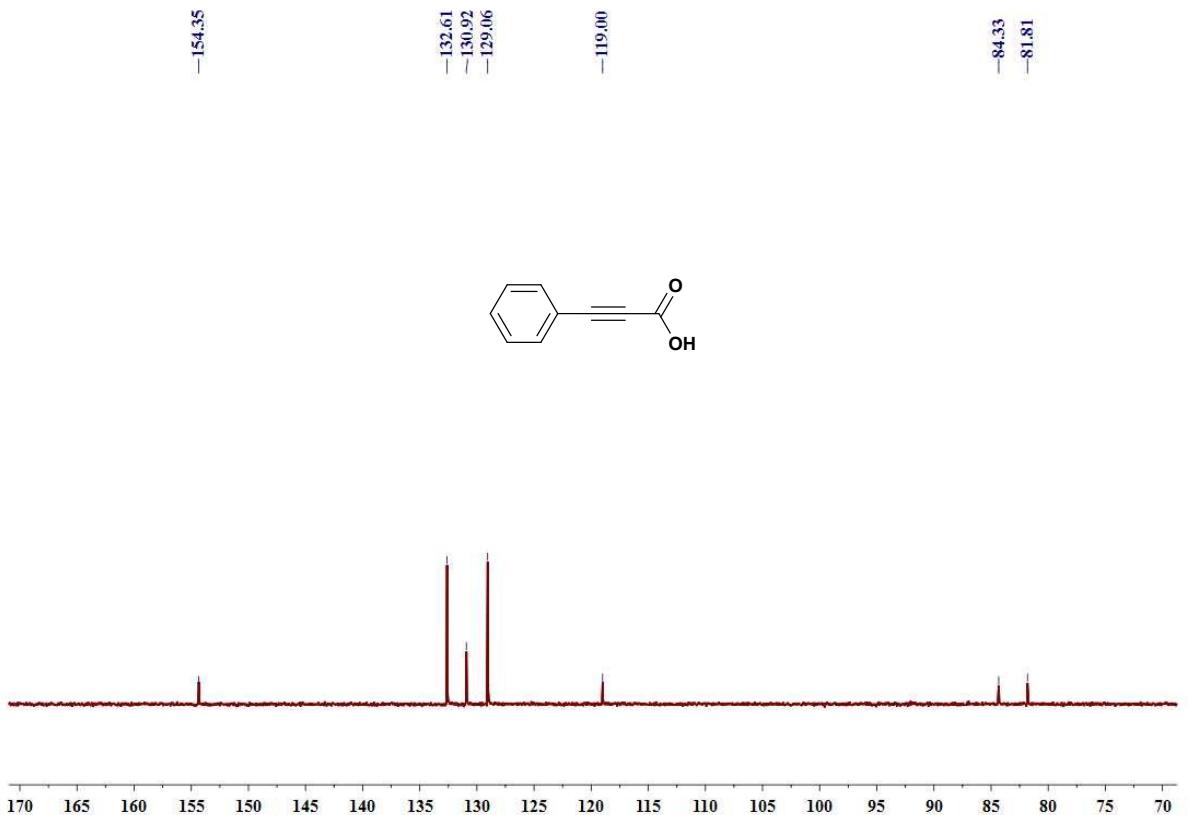
¹H NMR (300 MHz, DMSO-*d*₆)

7.64
7.62
7.55
7.53
7.49
7.47
7.45

-2.50

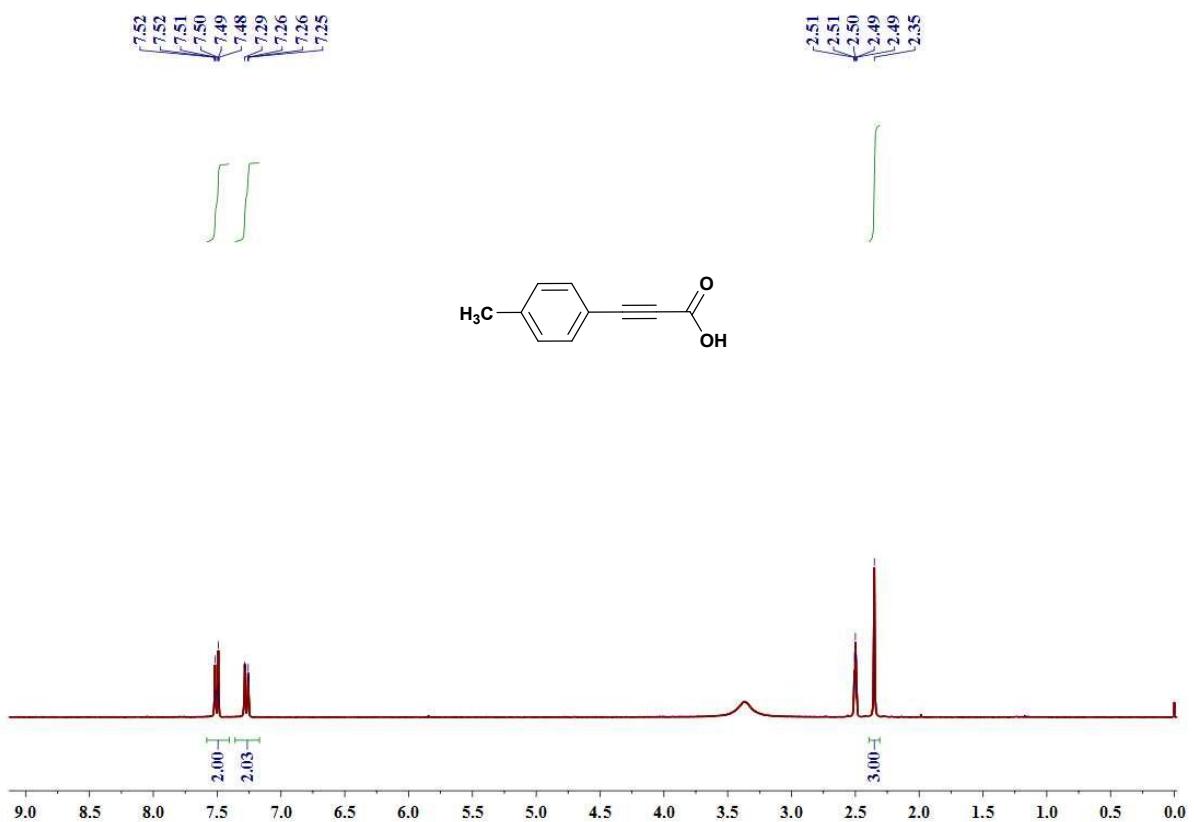


¹³C NMR (75 MHz, DMSO-*d*₆)

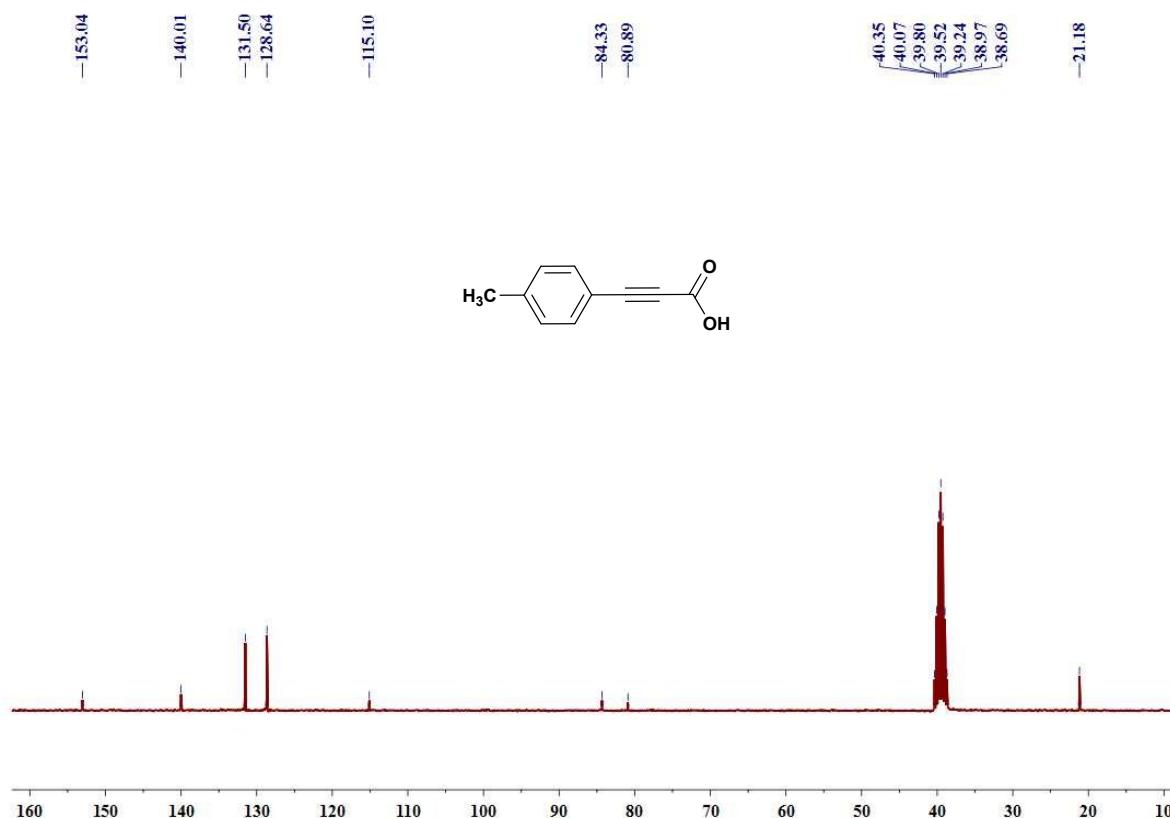


3-p-tolyl propiolic acid (**3b**)

¹H NMR (300 MHz, DMSO-*d*₆)

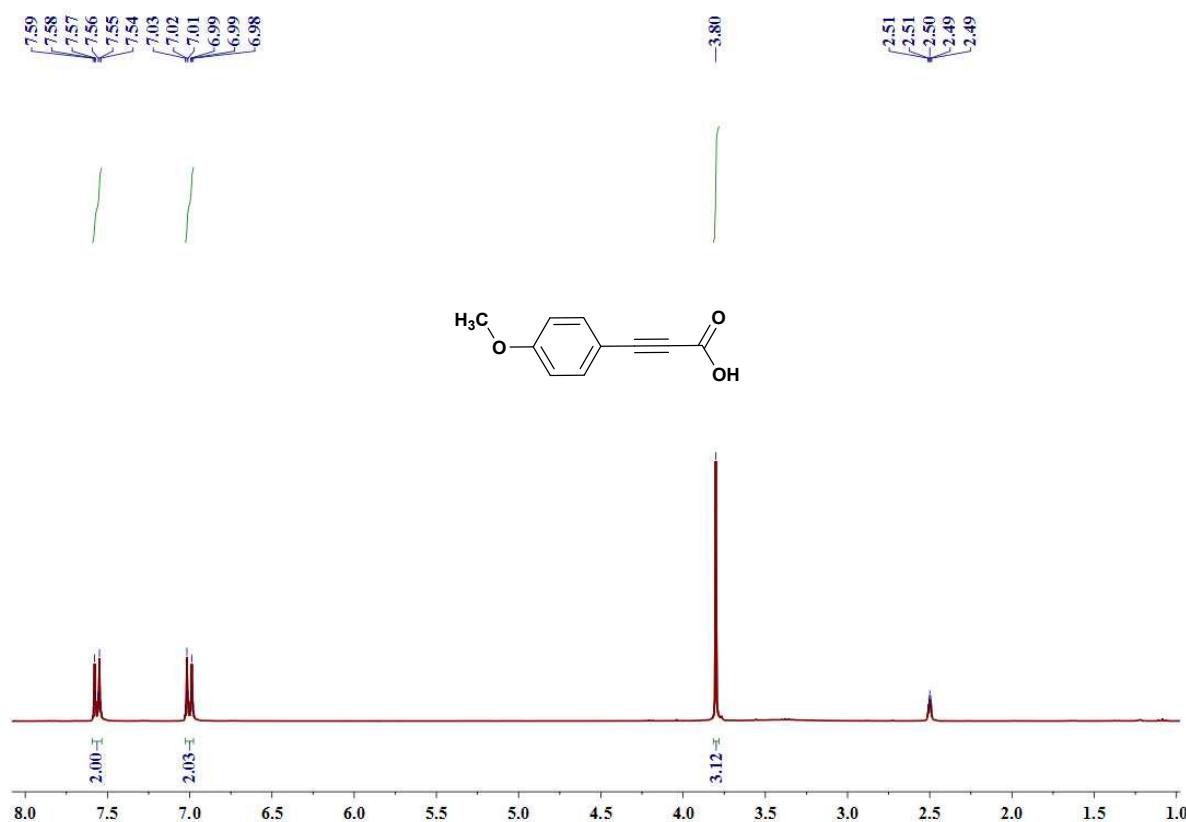


¹³C NMR (75 MHz, DMSO-*d*₆)

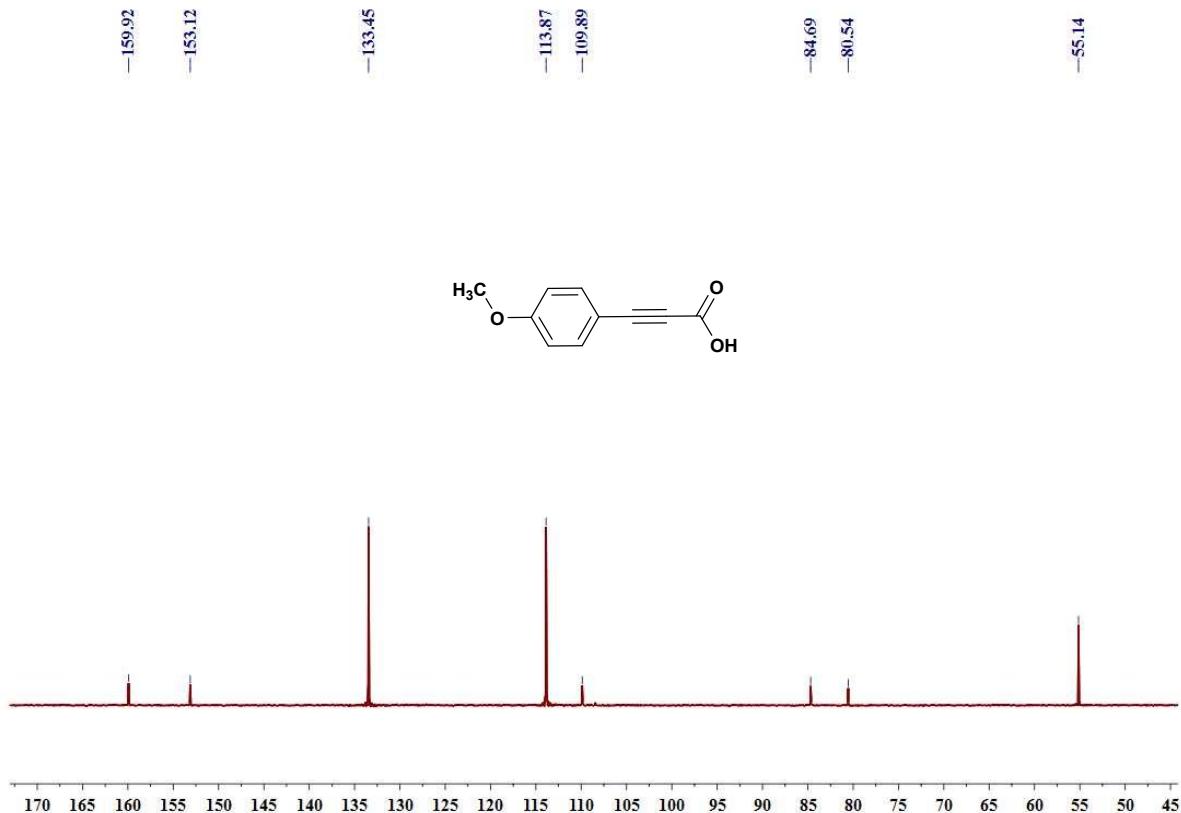


3-(4-methoxyphenyl)propiolic acid (**3c**)

¹H NMR (300 MHz, DMSO-*d*₆)

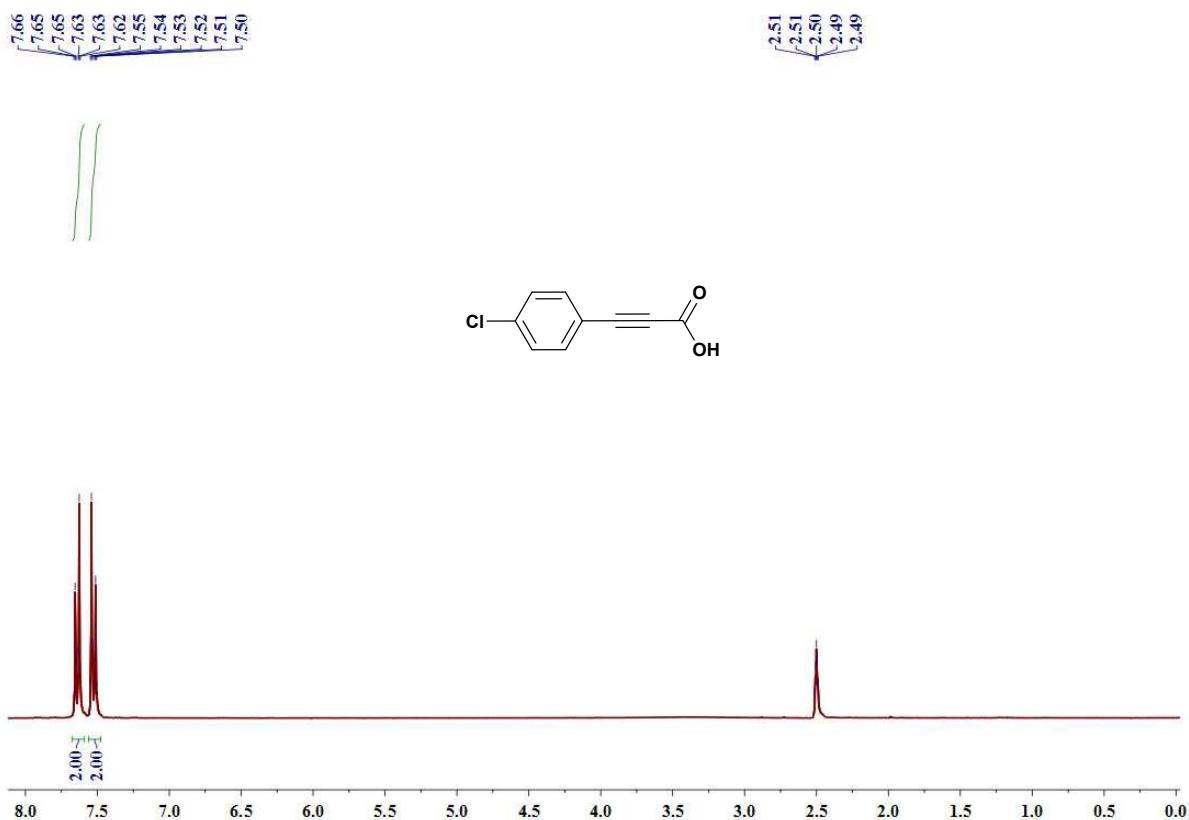


¹³C NMR (75 MHz, DMSO-*d*₆)

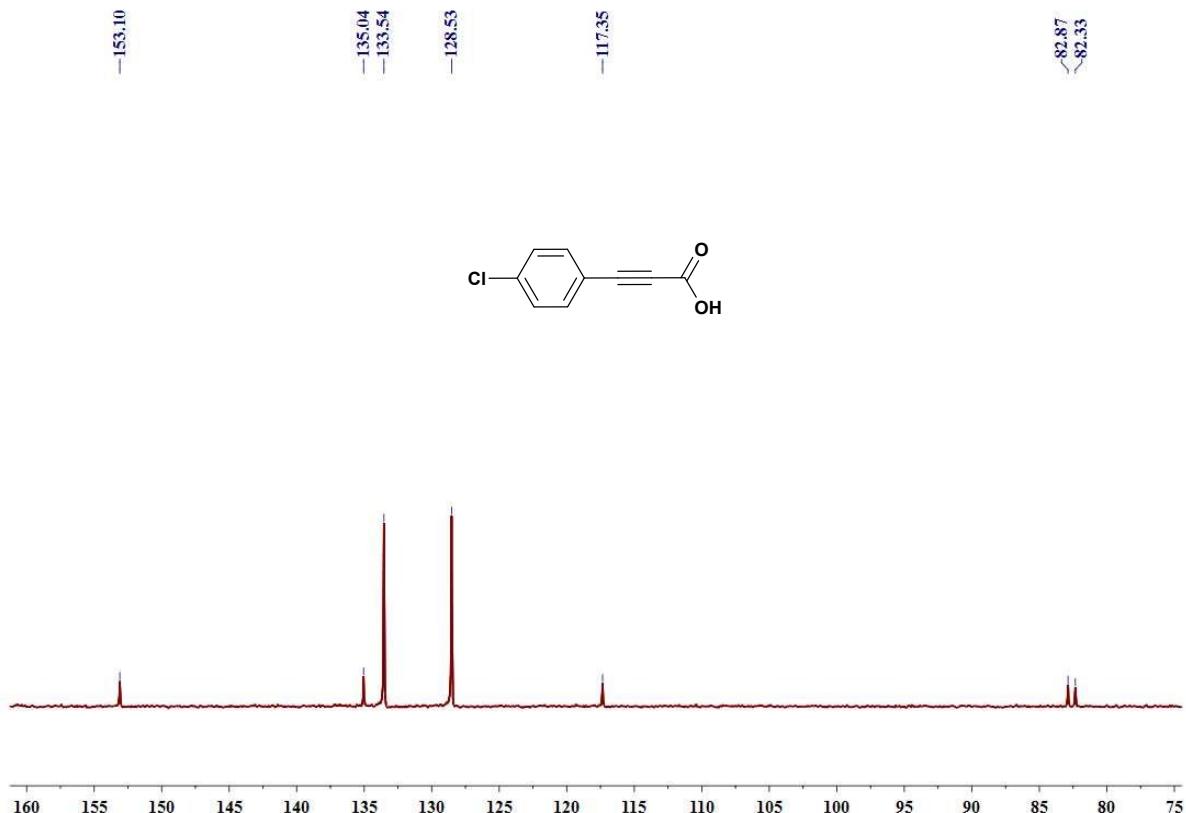


3-(4-chlorophenyl)propiolic acid (**3d**)

¹H NMR (300 MHz, DMSO-*d*₆)

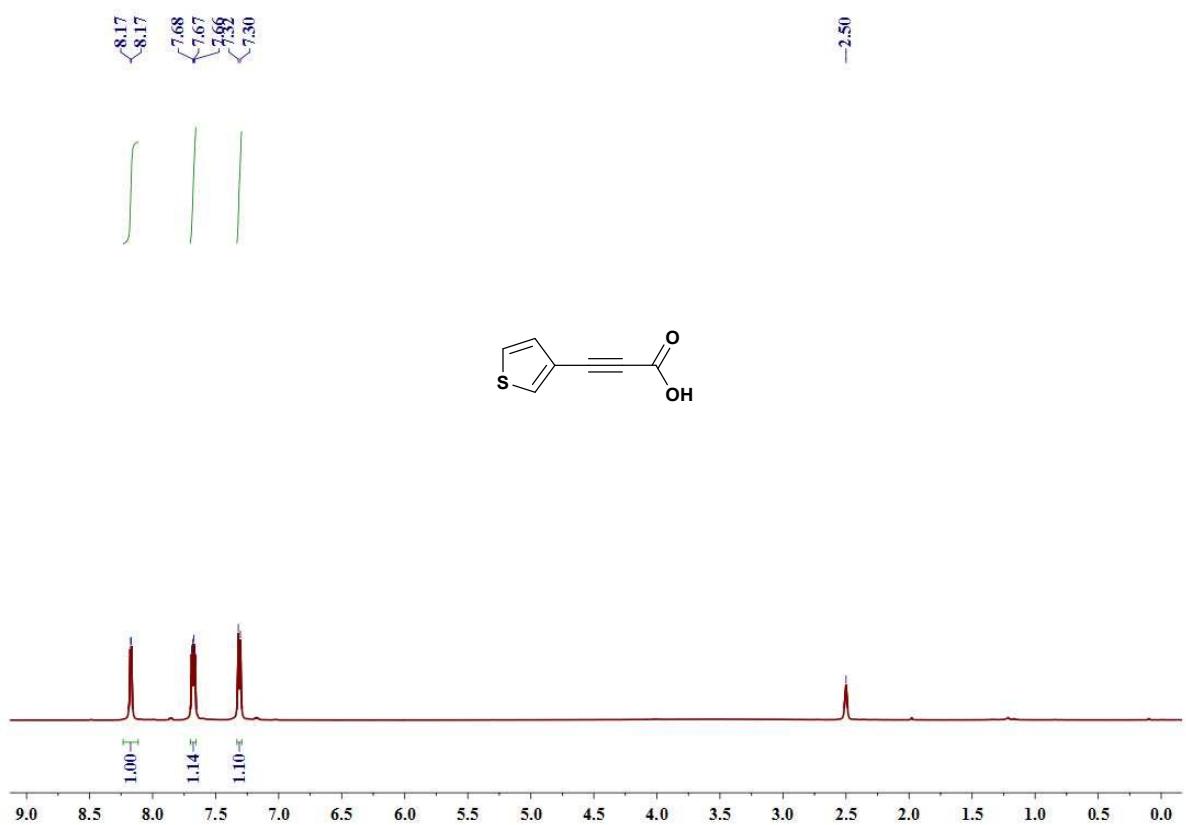


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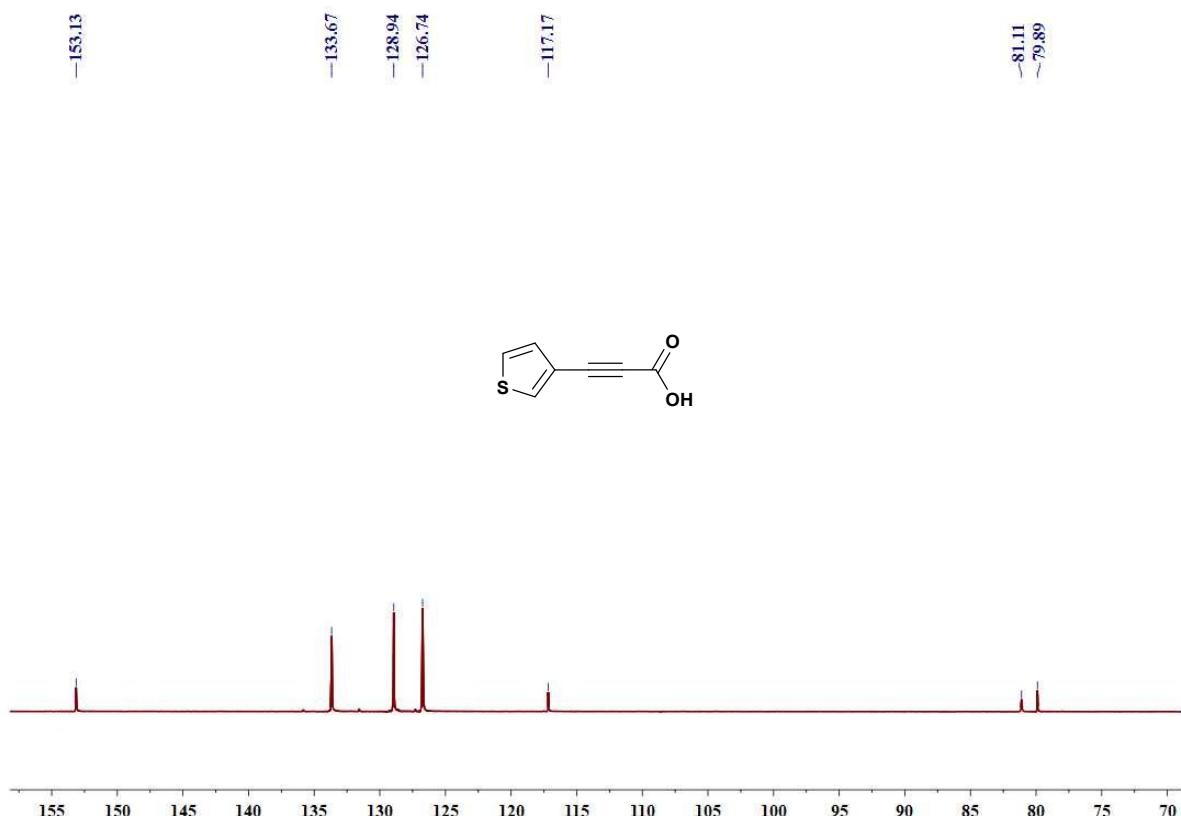


3-(thiophen-3-yl)propiolic acid (**3e**)

¹H NMR (300 MHz, DMSO-*d*₆)

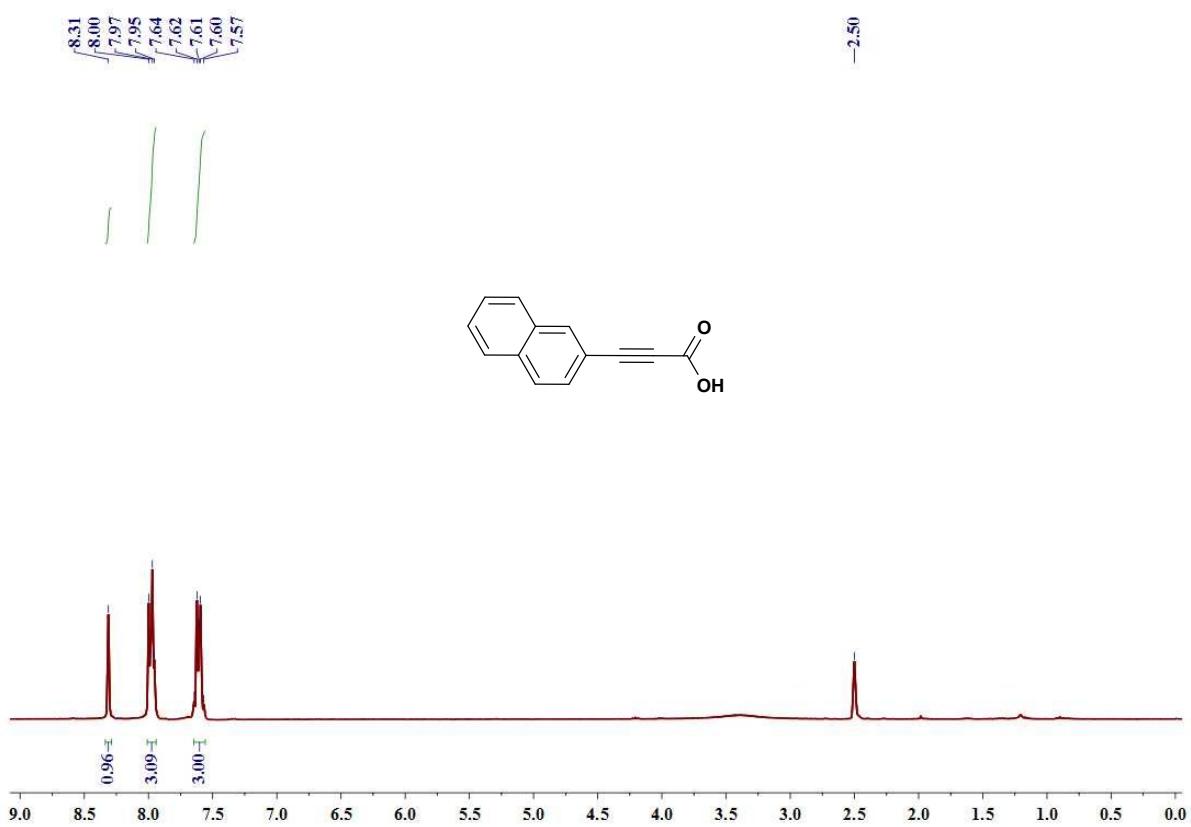


¹³C NMR (75 MHz, DMSO-*d*₆)

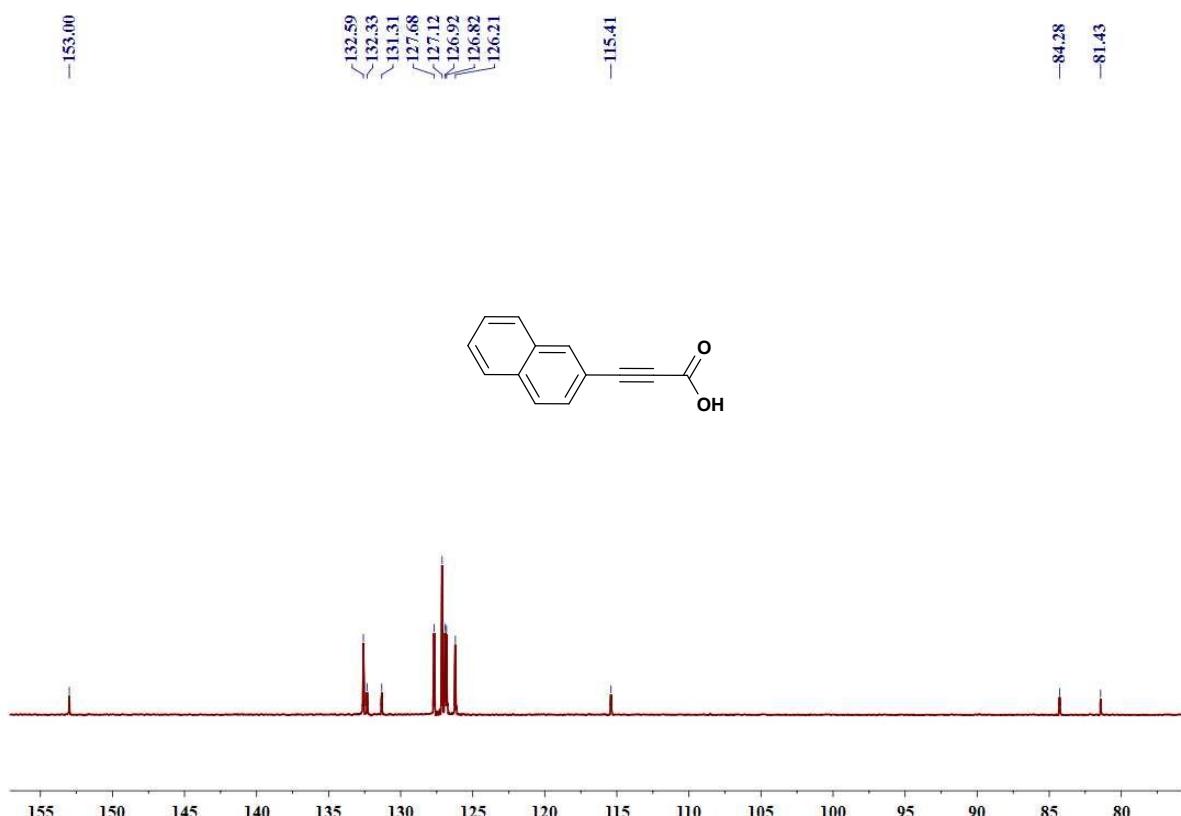


3-(naphthalen-2-yl)propionic acid (**3f**)

¹H NMR (300 MHz, DMSO-*d*₆)

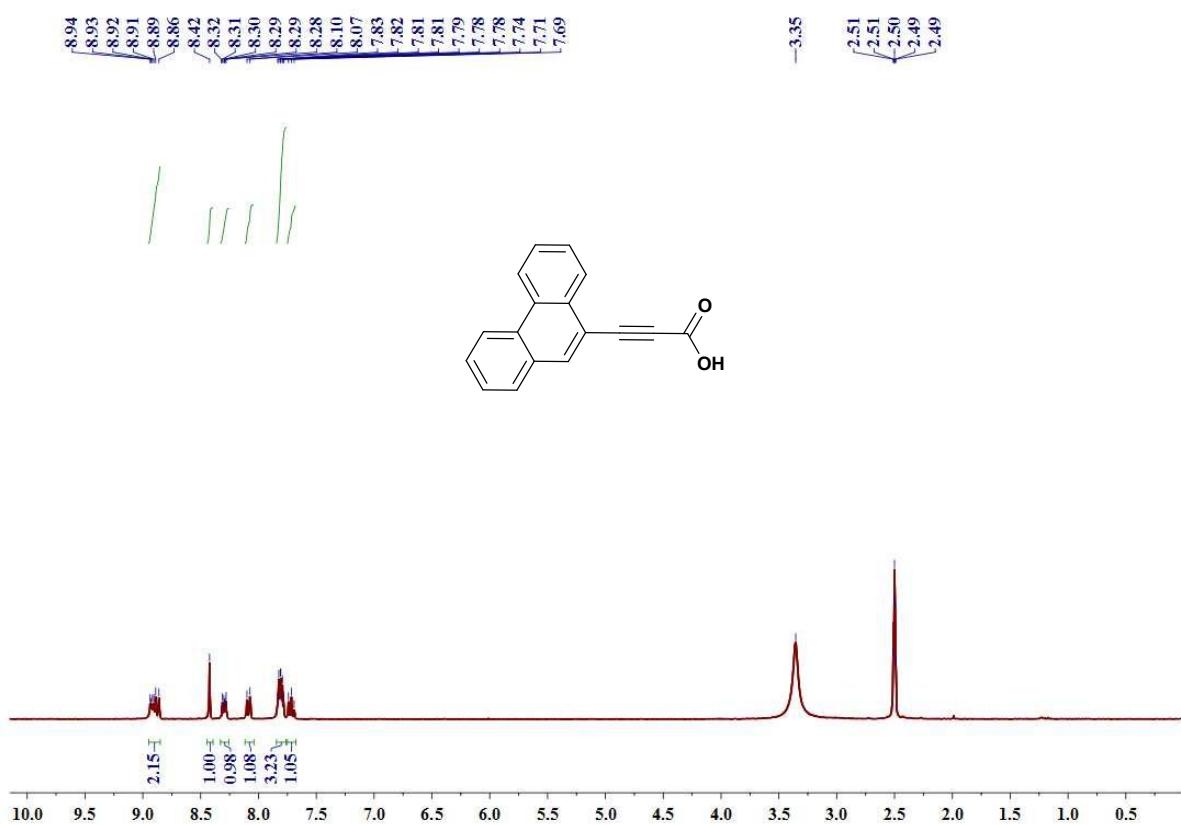


¹³C NMR (75 MHz, DMSO-*d*₆)

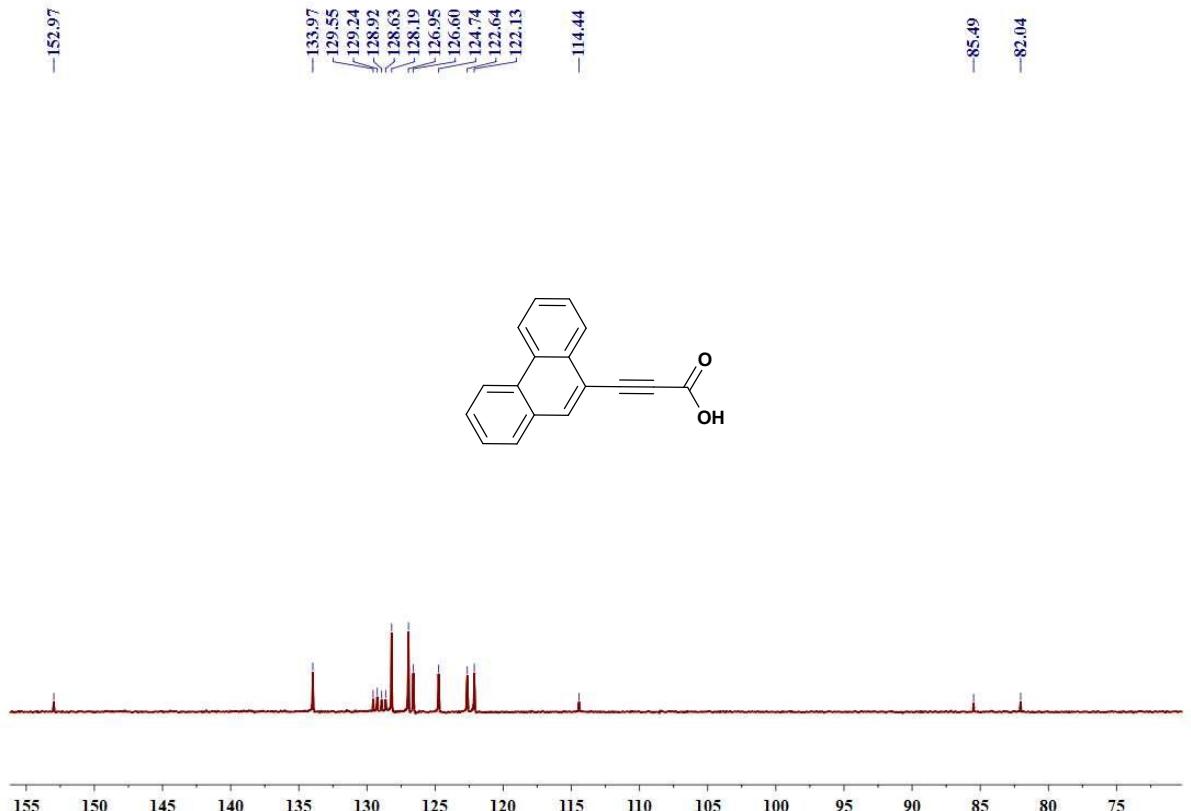


3-(phenanthren-9-yl)propiolic acid (**3g**)

¹H NMR (300 MHz, DMSO-*d*₆)

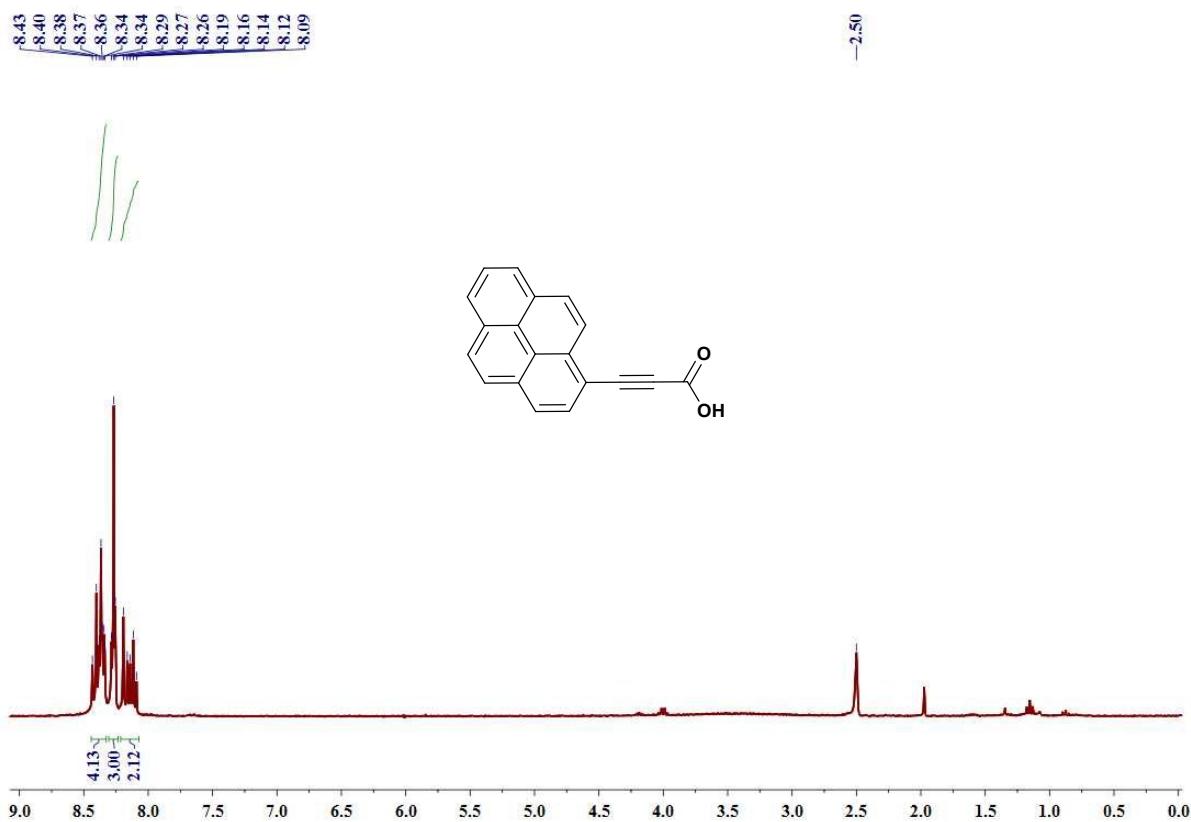


¹³C NMR (75 MHz, DMSO-*d*₆)

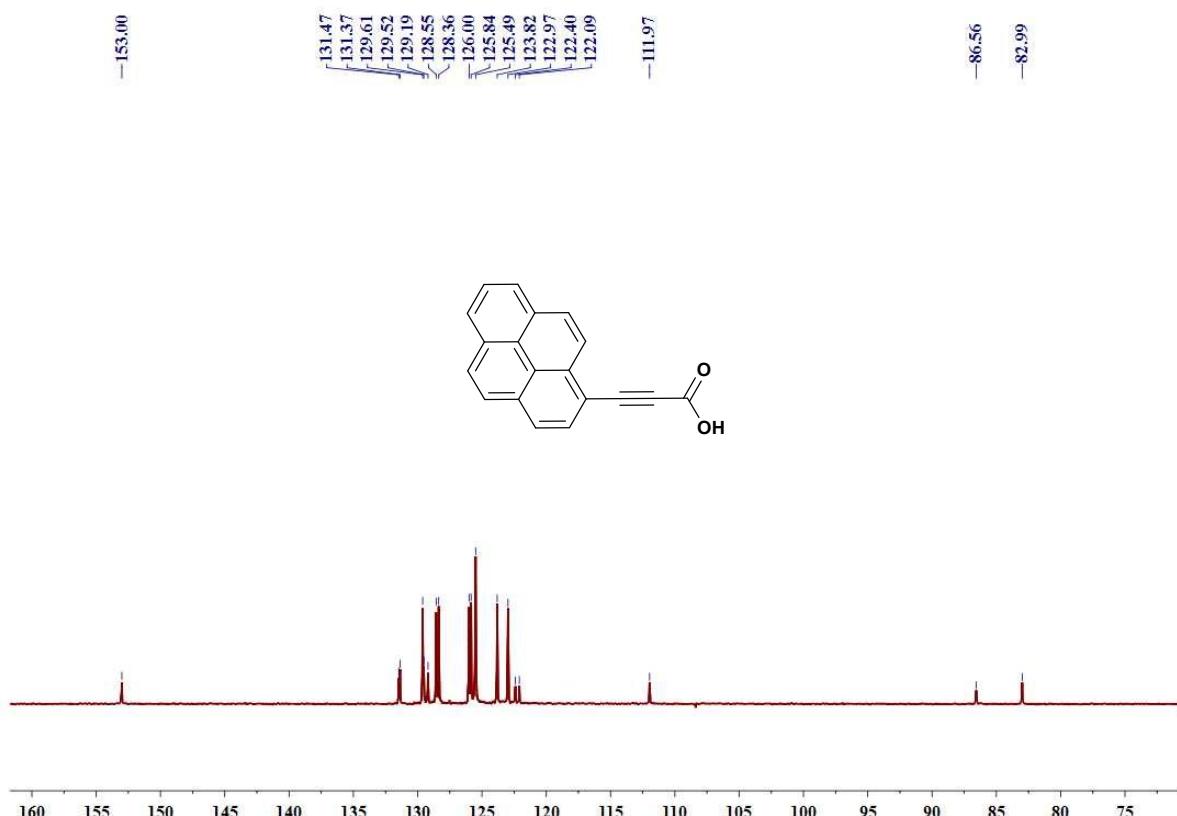


3-(pyren-1-yl)propiolic acid (3h**)**

¹H NMR (300 MHz, DMSO-*d*₆)

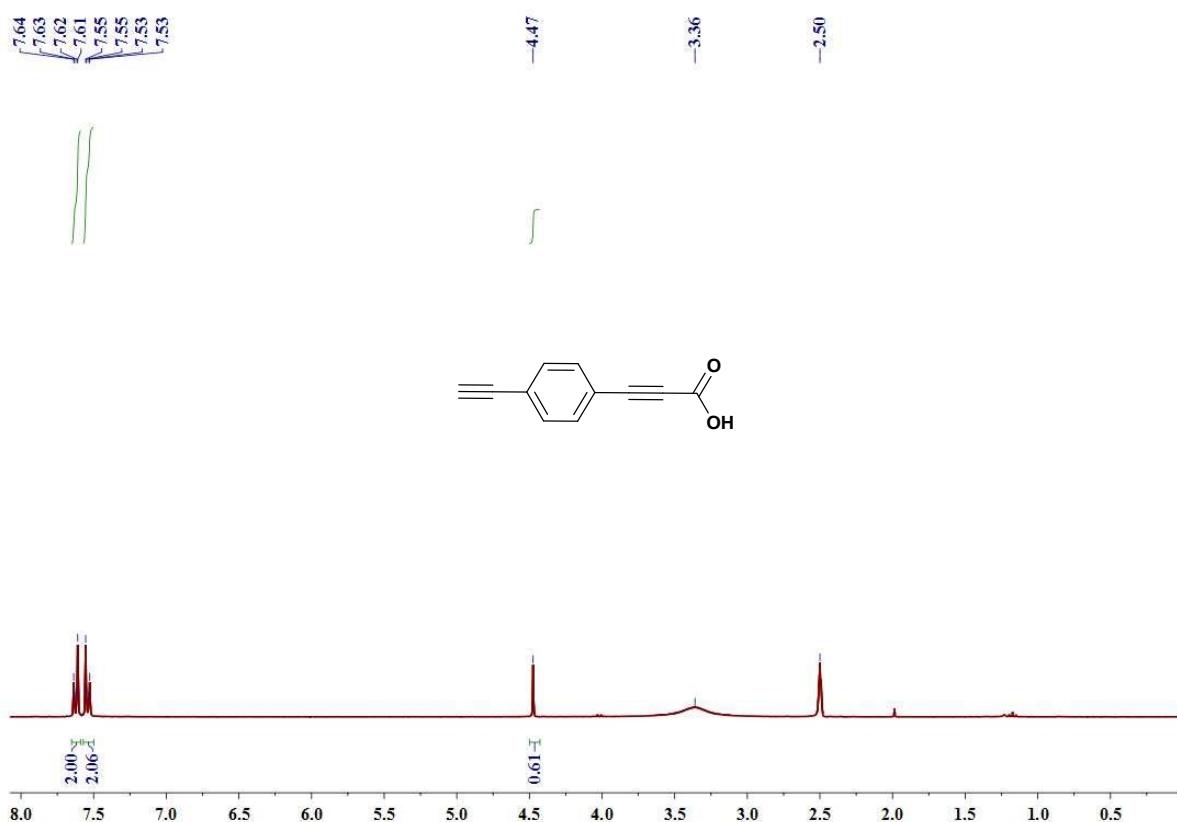


¹³C NMR (75 MHz, DMSO-*d*₆)

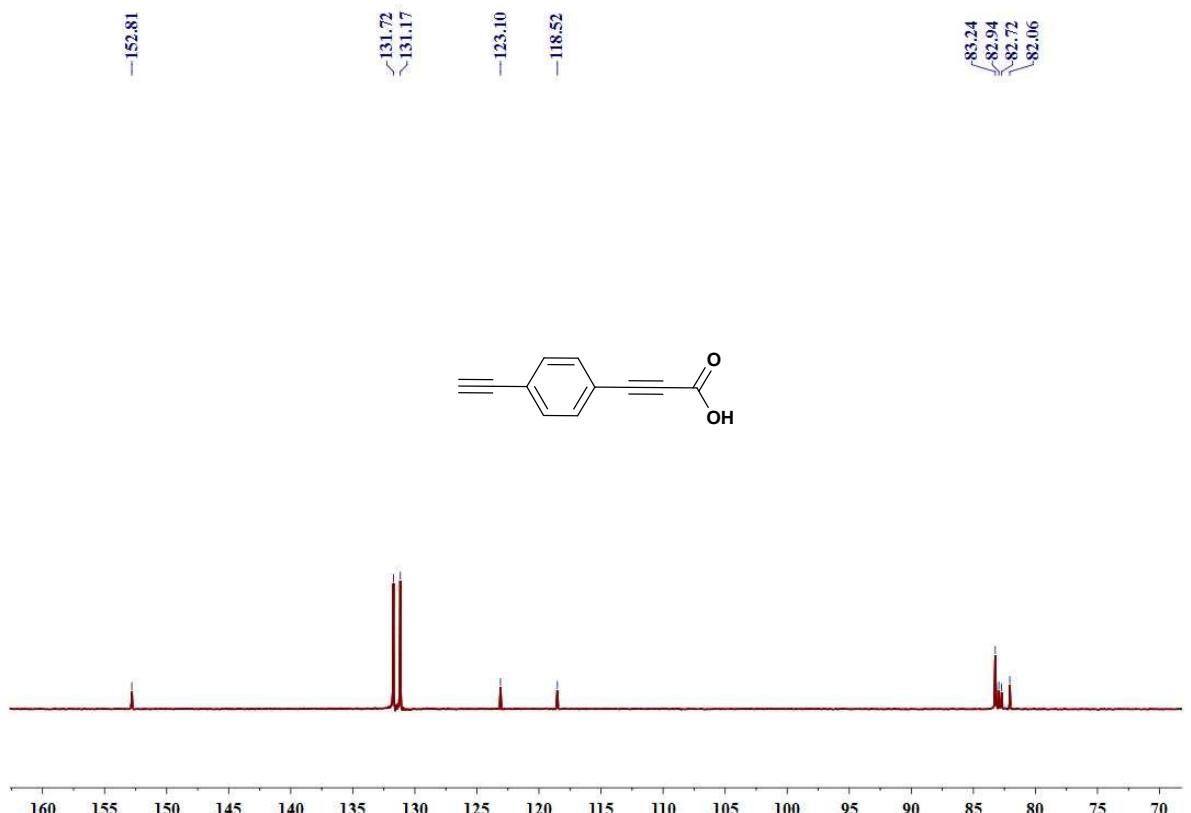


3-(4-ethynylphenyl)propiolic acid (**3i**)

¹H NMR (300 MHz, DMSO-*d*₆)

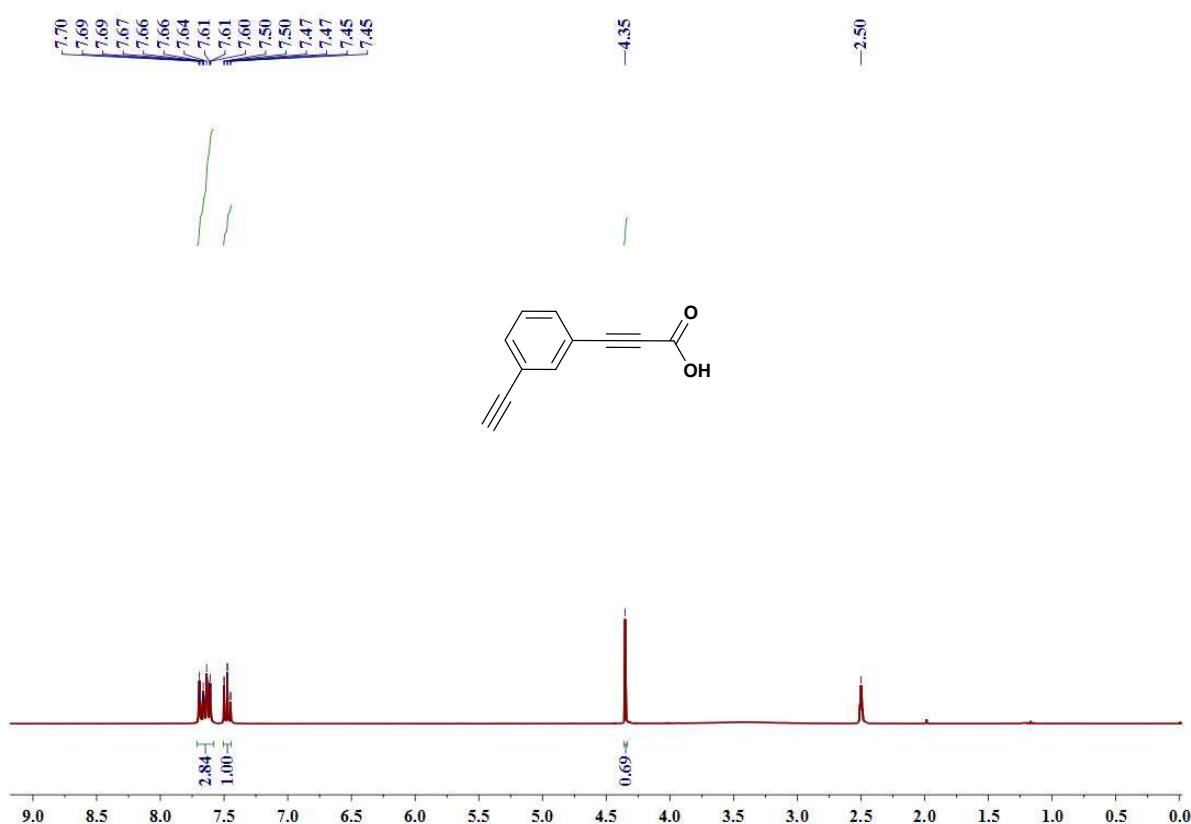


¹³C NMR (75 MHz, DMSO-*d*₆)

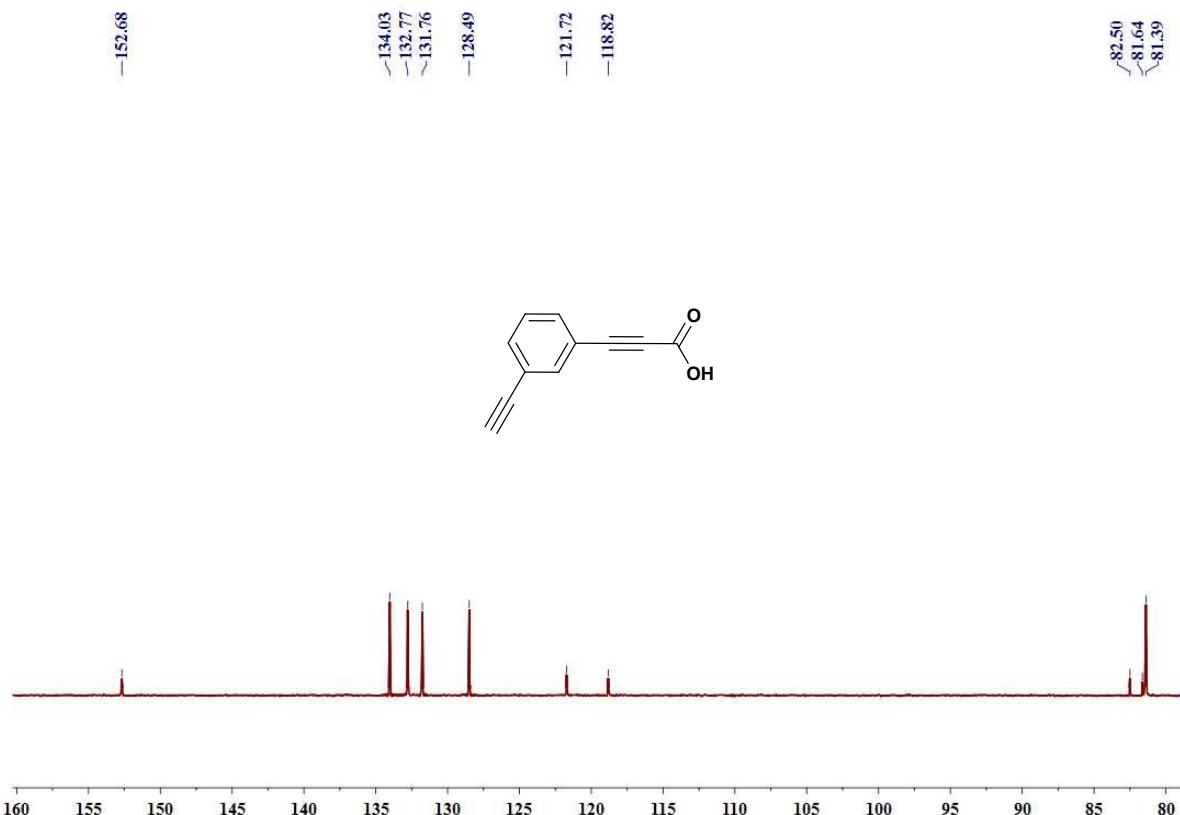


3-(3-ethynylphenyl)propiolic acid (**3j**)

¹H NMR (300 MHz, DMSO-*d*₆)

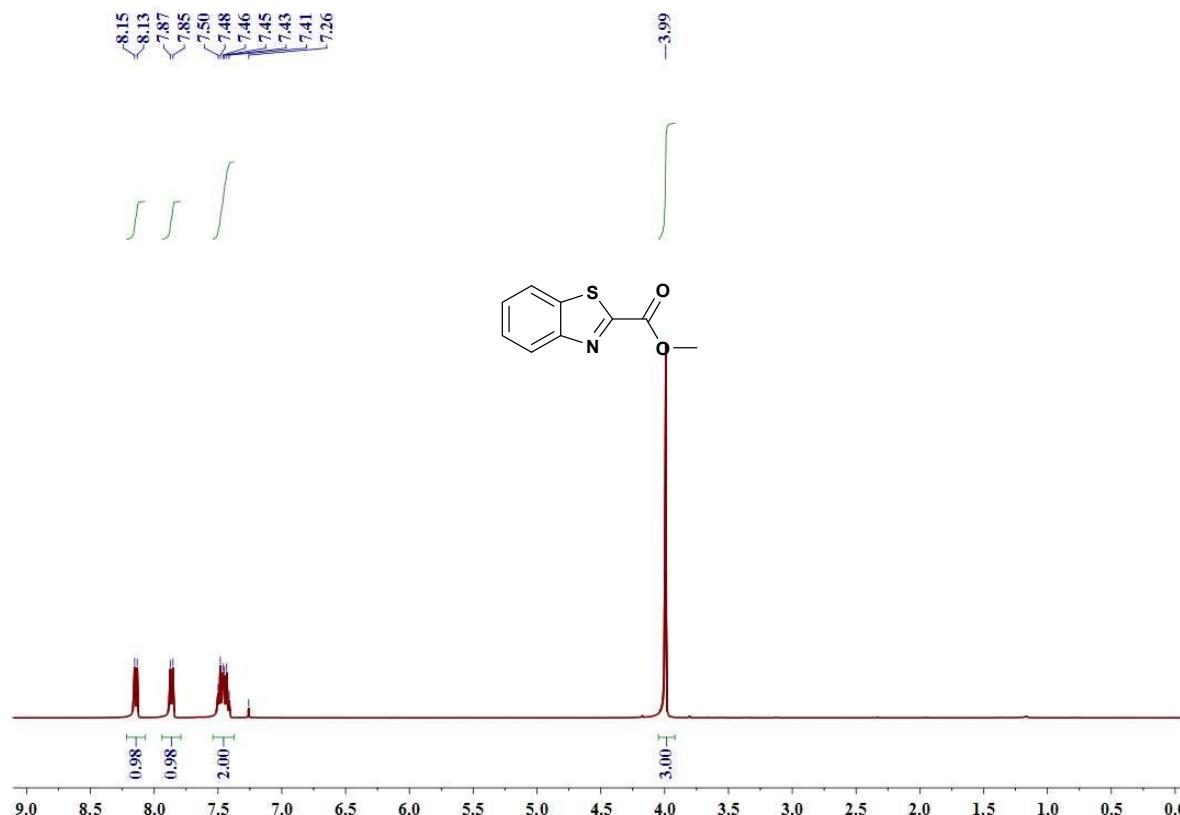


¹³C NMR (75 MHz, DMSO-*d*₆)

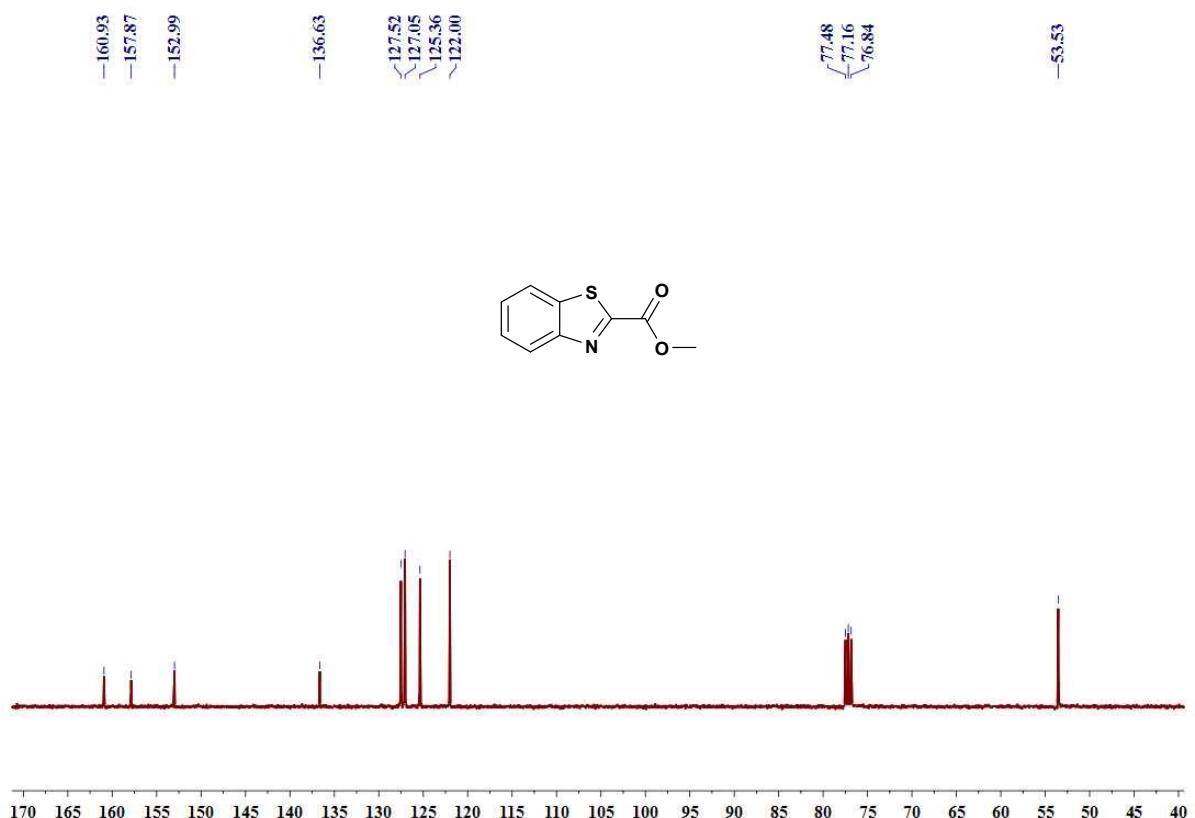


Methyl benzo[*d*]thiazole-2-carboxylate (**6a**)

¹H NMR (400 MHz, CDCl₃)

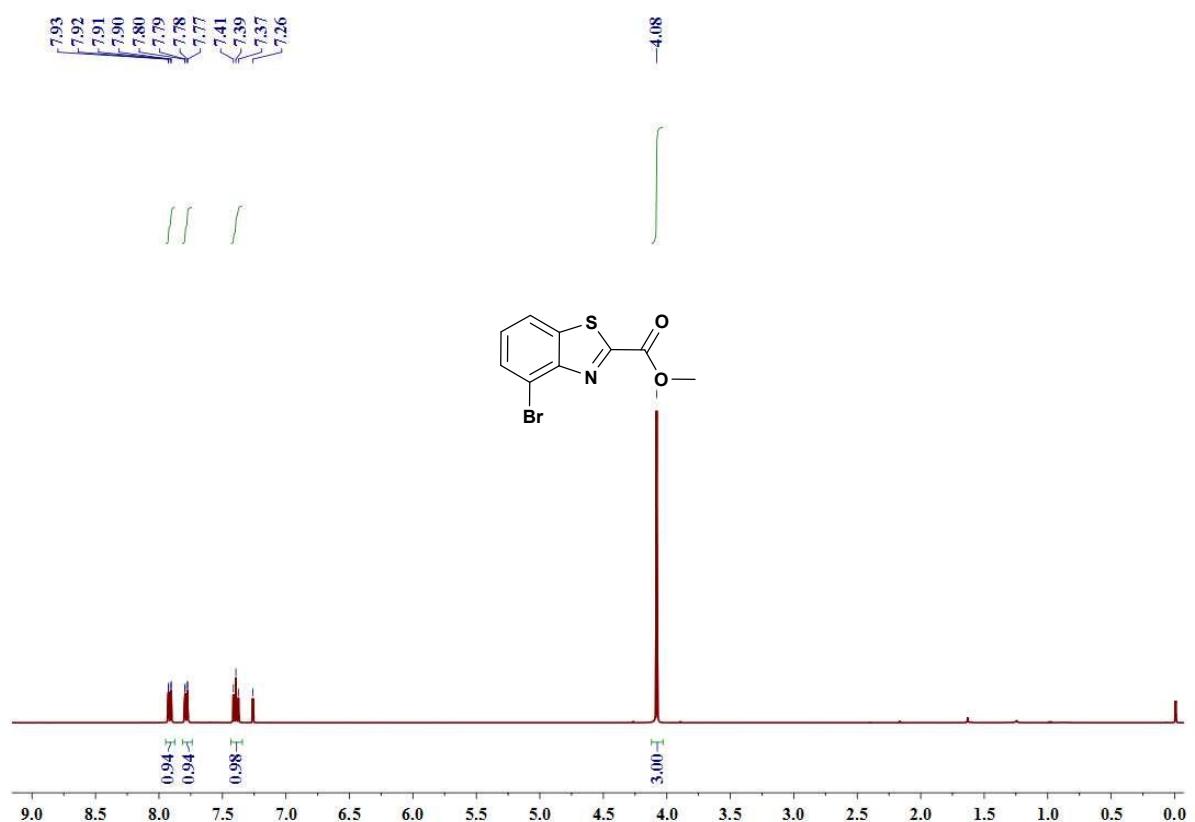


¹³C NMR (101 MHz, CDCl₃)

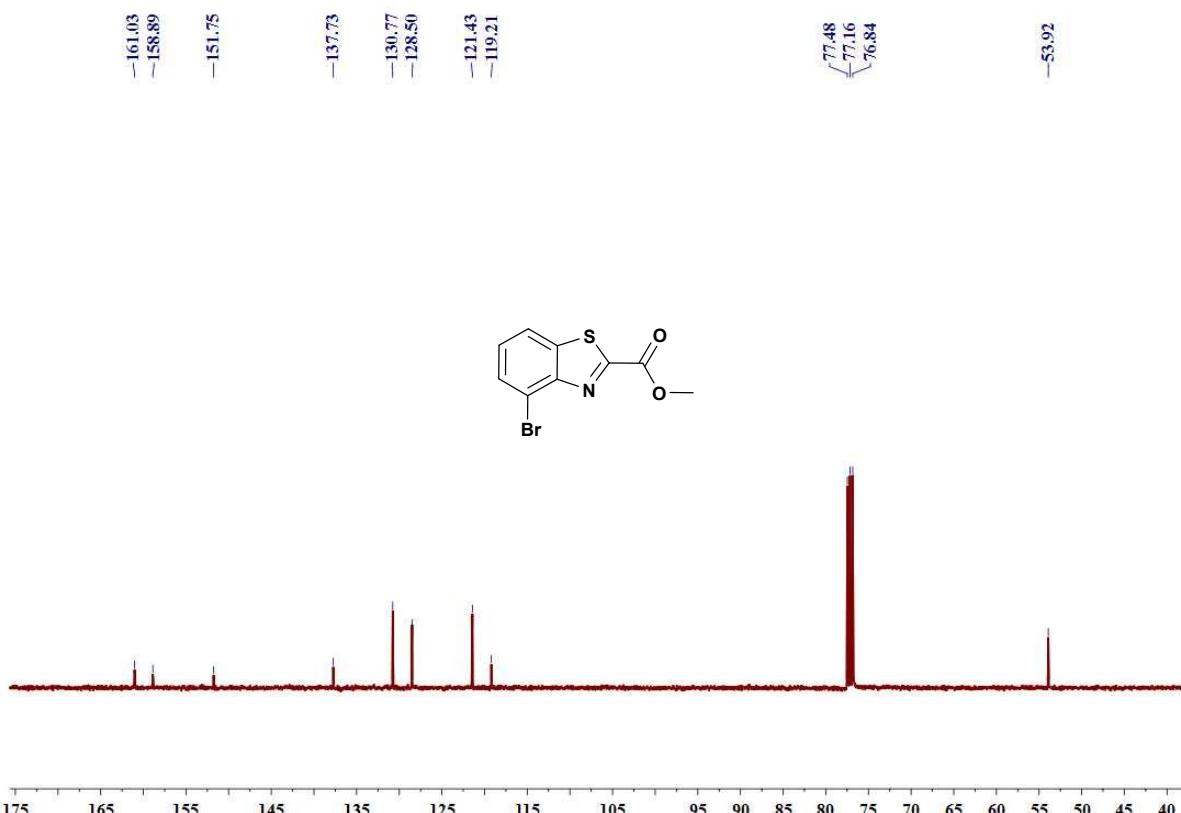


Methyl 4-bromobenzo[*d*]thiazole-2-carboxylate (**6b**)

¹H NMR (400 MHz, CDCl₃)

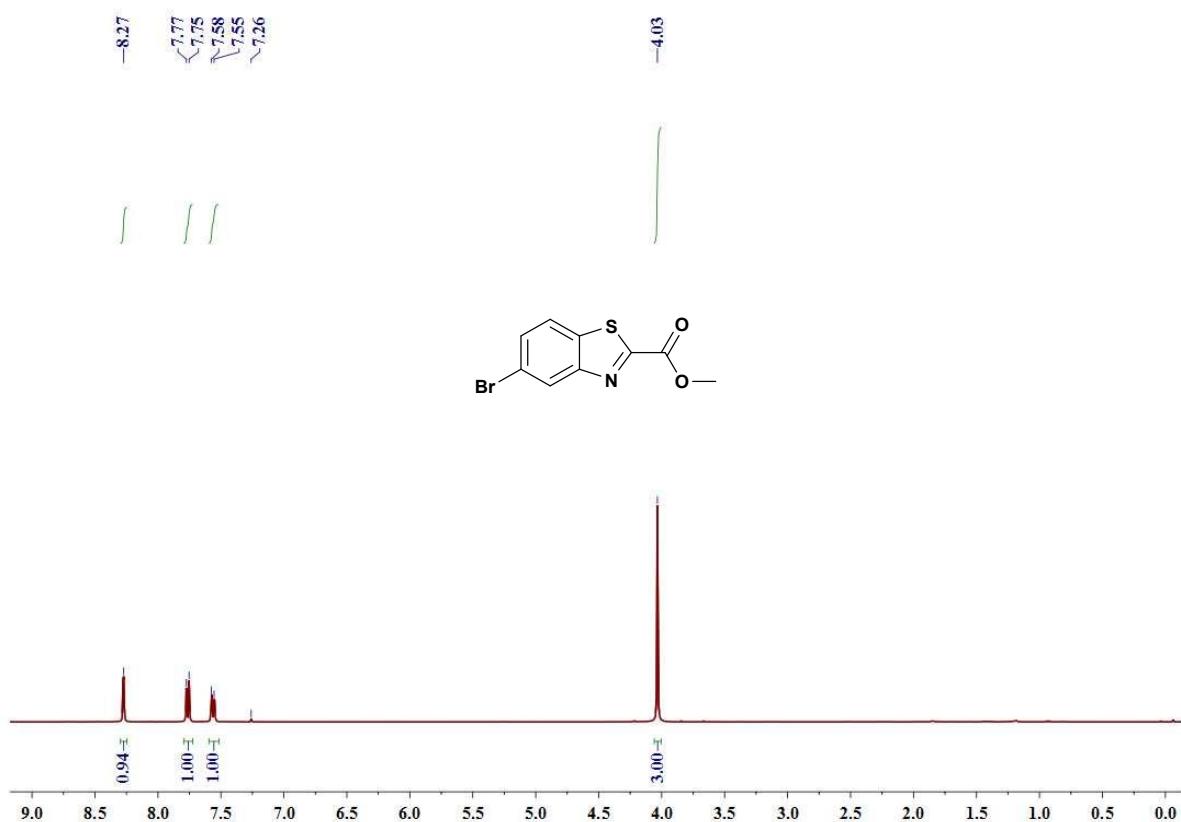


¹³C NMR (101 MHz, CDCl₃)

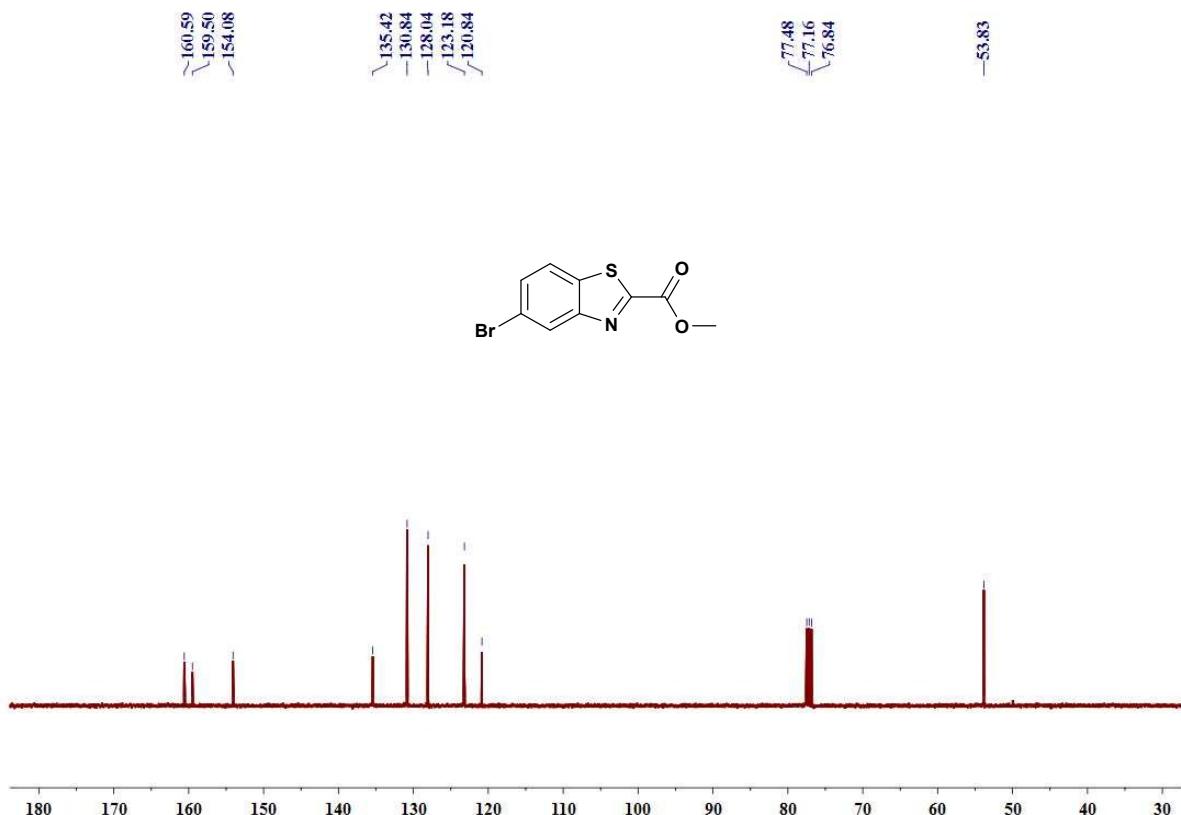


Methyl 5-bromobenzo[*d*]thiazole-2-carboxylate (**6c**)

¹H NMR (400 MHz, CDCl₃)

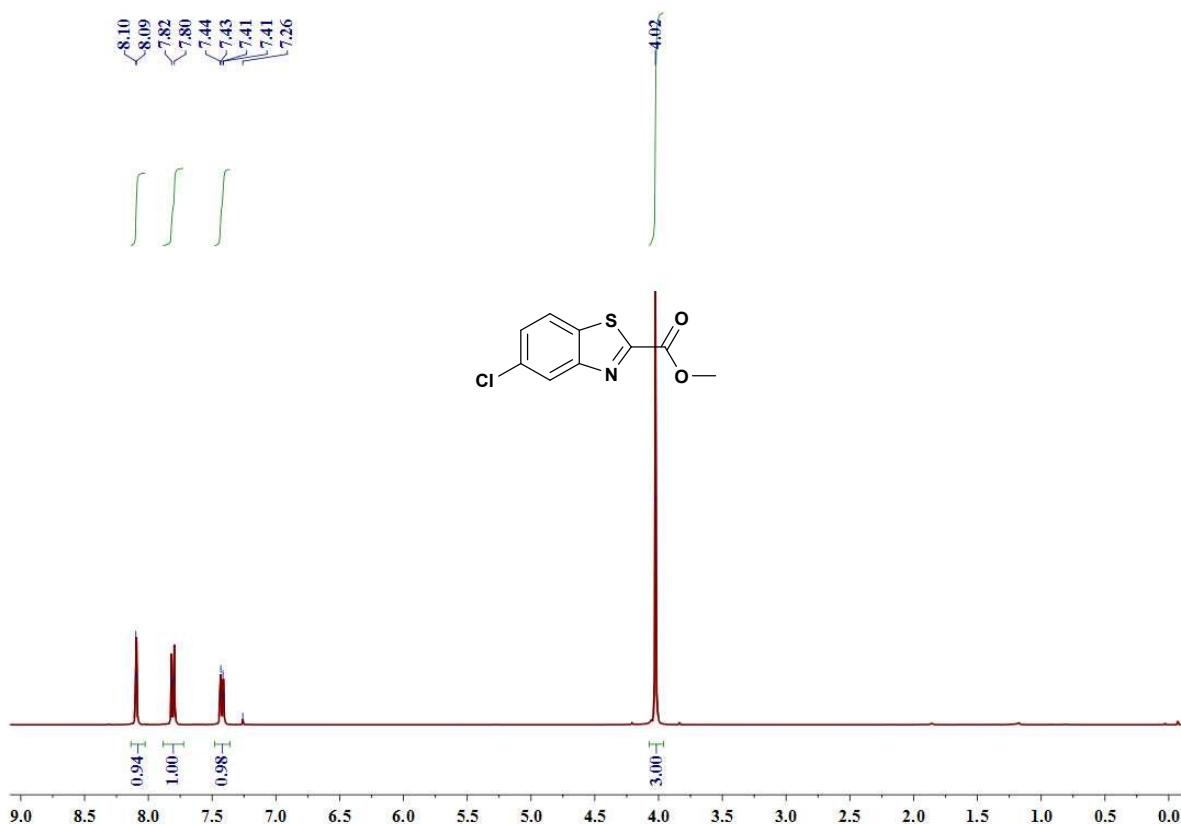


¹³C NMR (101 MHz, CDCl₃)

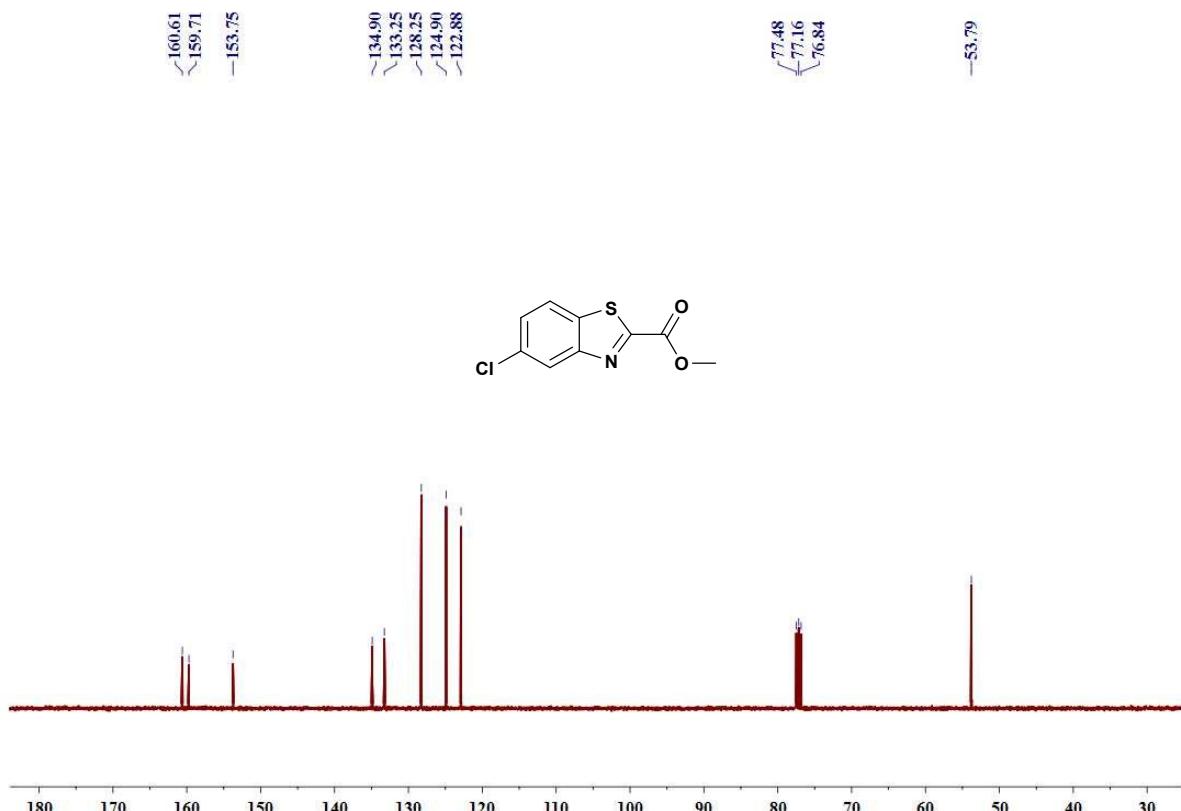


Methyl 5-chlorobenzo[*d*]thiazole-2-carboxylate (**6d**)

¹H NMR (400 MHz, CDCl₃)

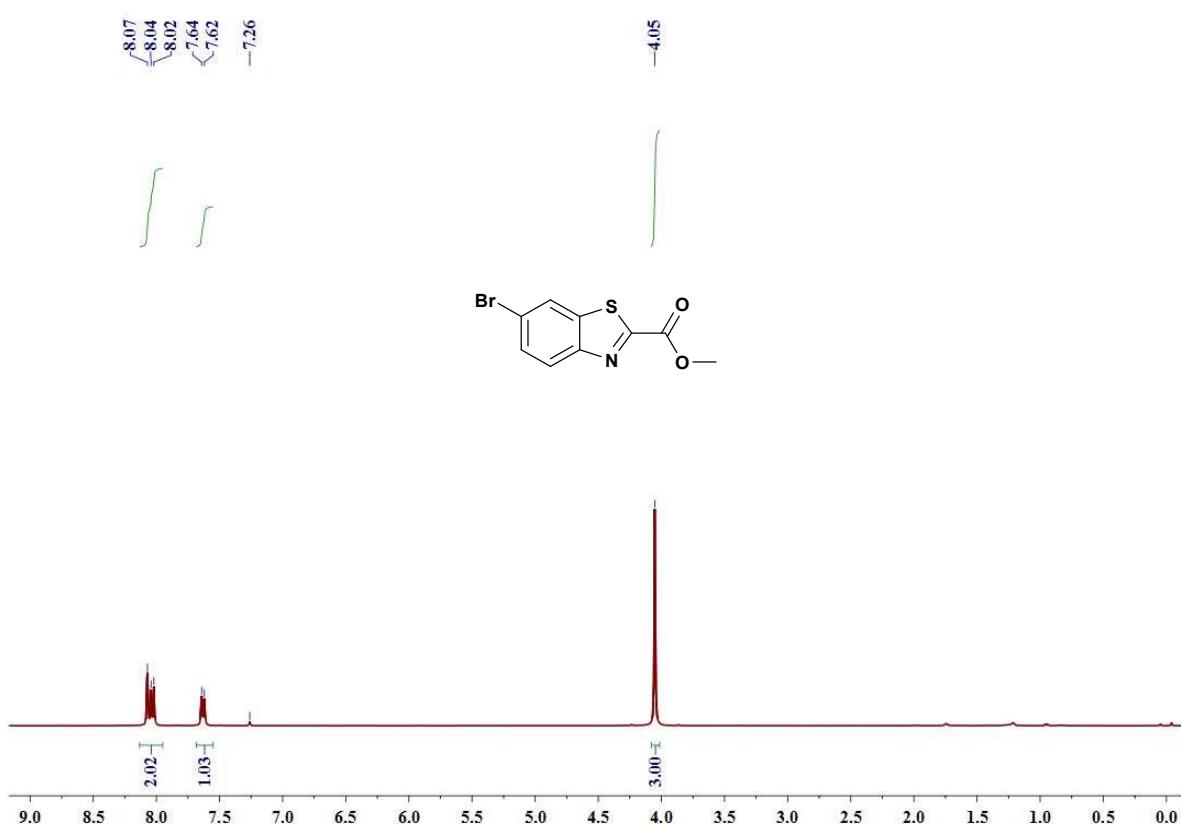


¹³C NMR (101 MHz, CDCl₃)

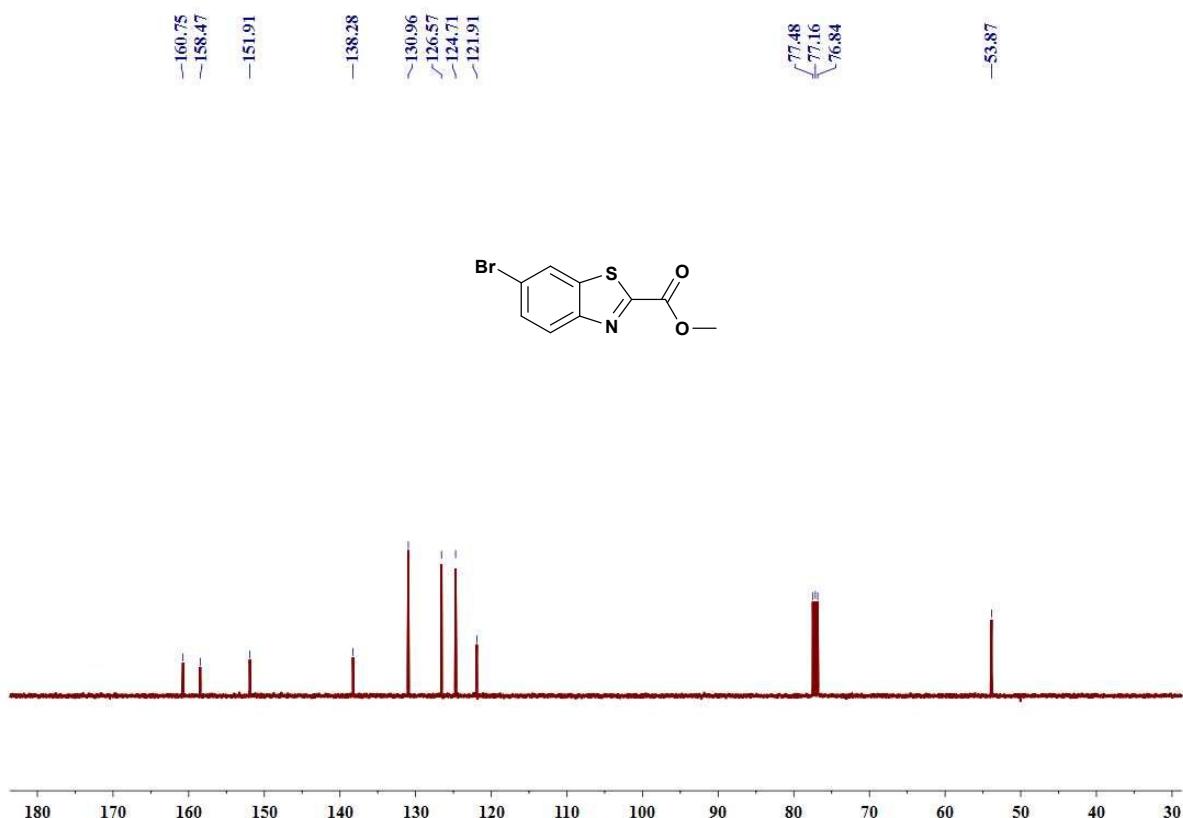


Methyl 6-bromobenzo[*d*]thiazole-2-carboxylate (**6e**)

¹H NMR (400 MHz, CDCl₃)

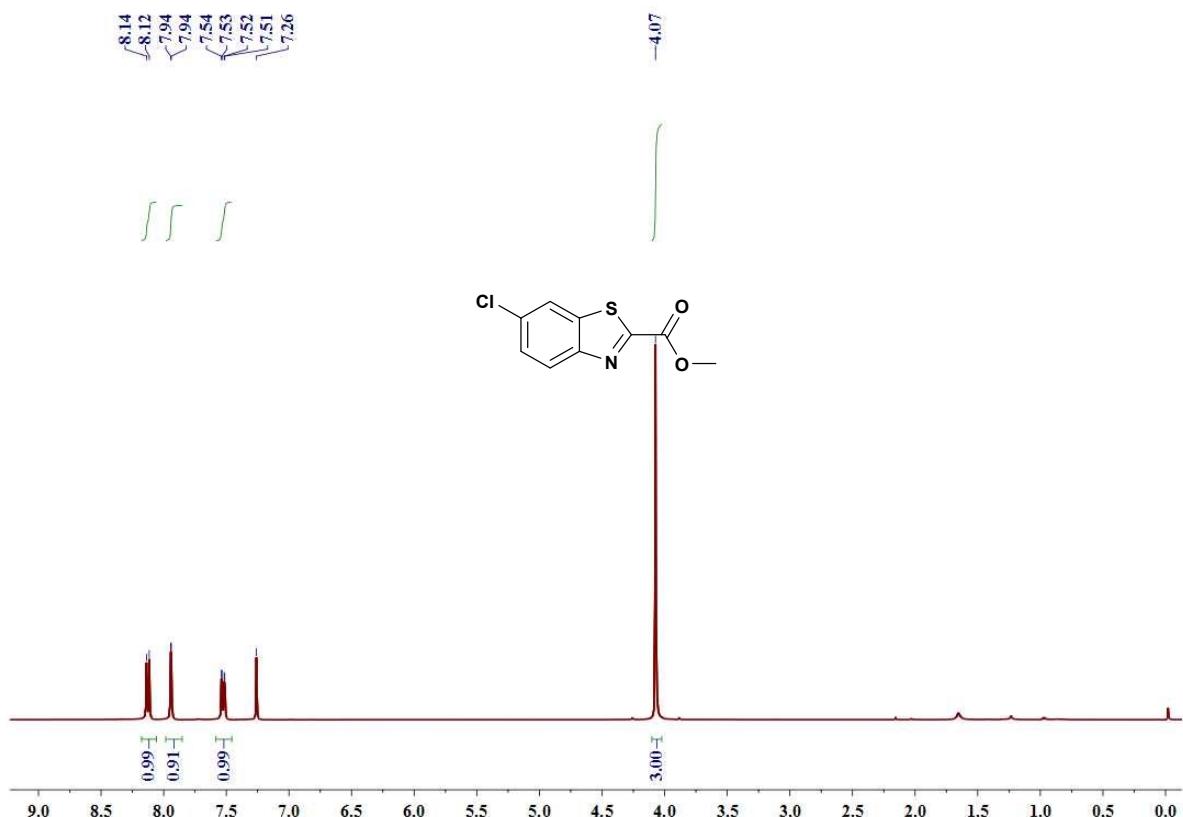


¹³C NMR (101 MHz, CDCl₃)

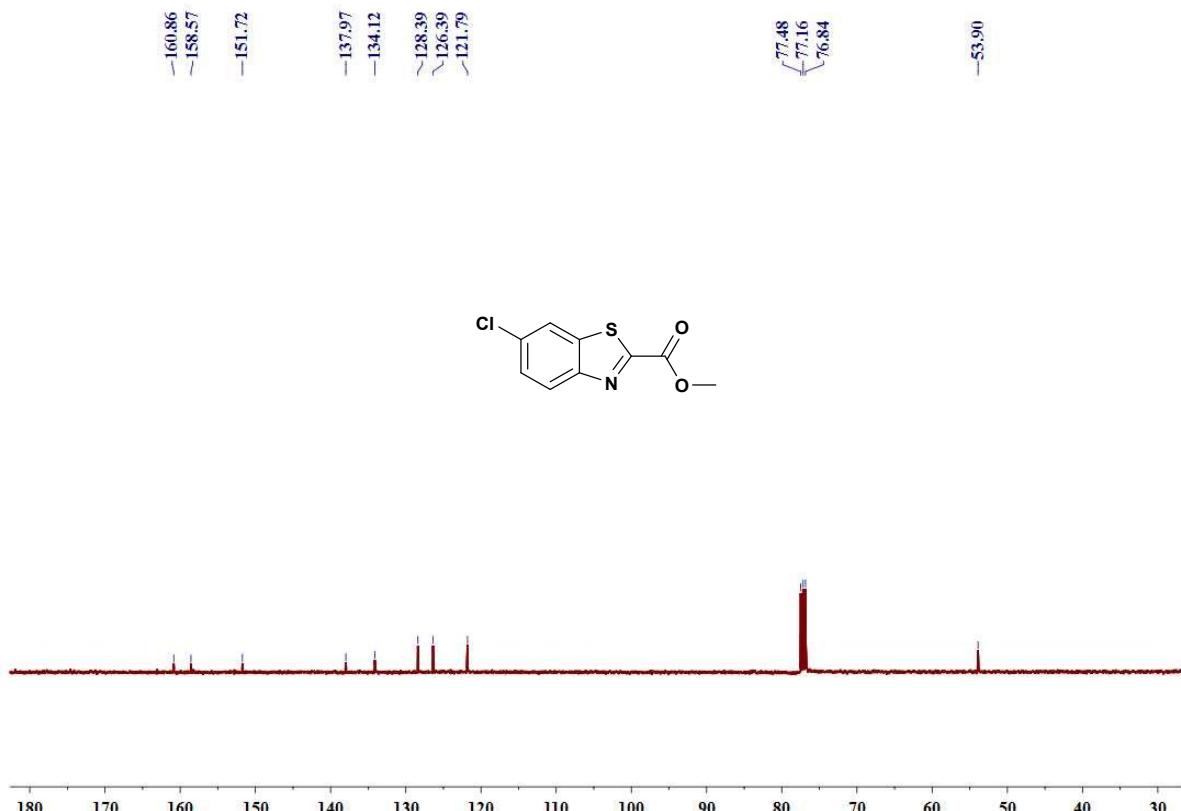


Methyl 6-chlorobenzo[*d*]thiazole-2-carboxylate (**6f**)

¹H NMR (400 MHz, CDCl₃)

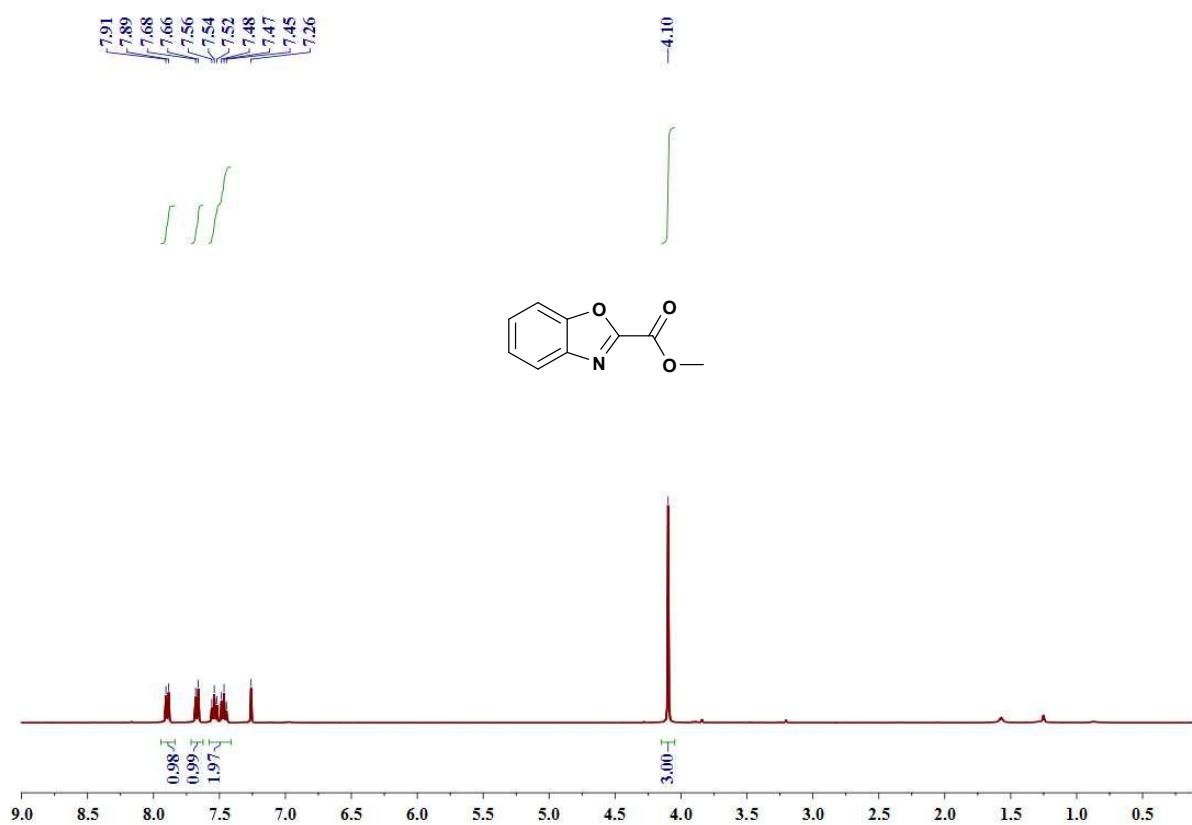


¹³C NMR (101 MHz, CDCl₃)

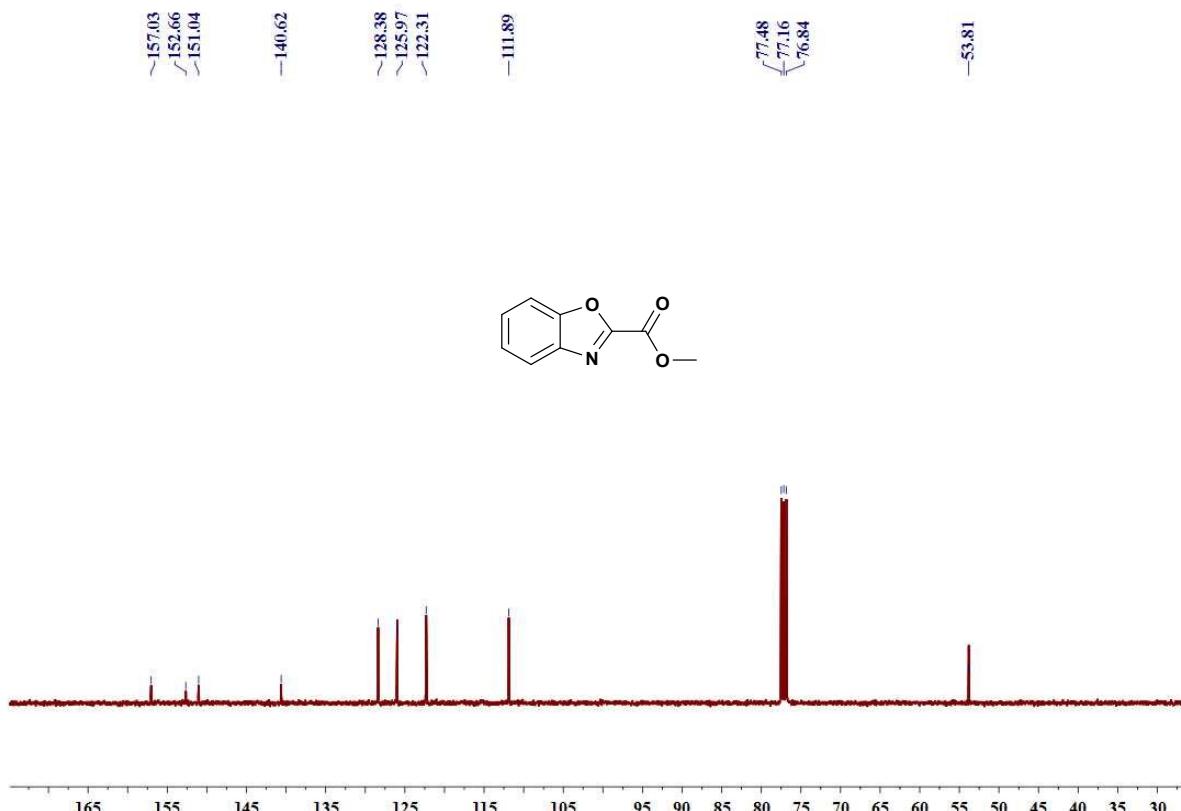


Methyl benzo[*d*]oxazole-2-carboxylate (**7a**)

¹H NMR (400 MHz, CDCl₃)

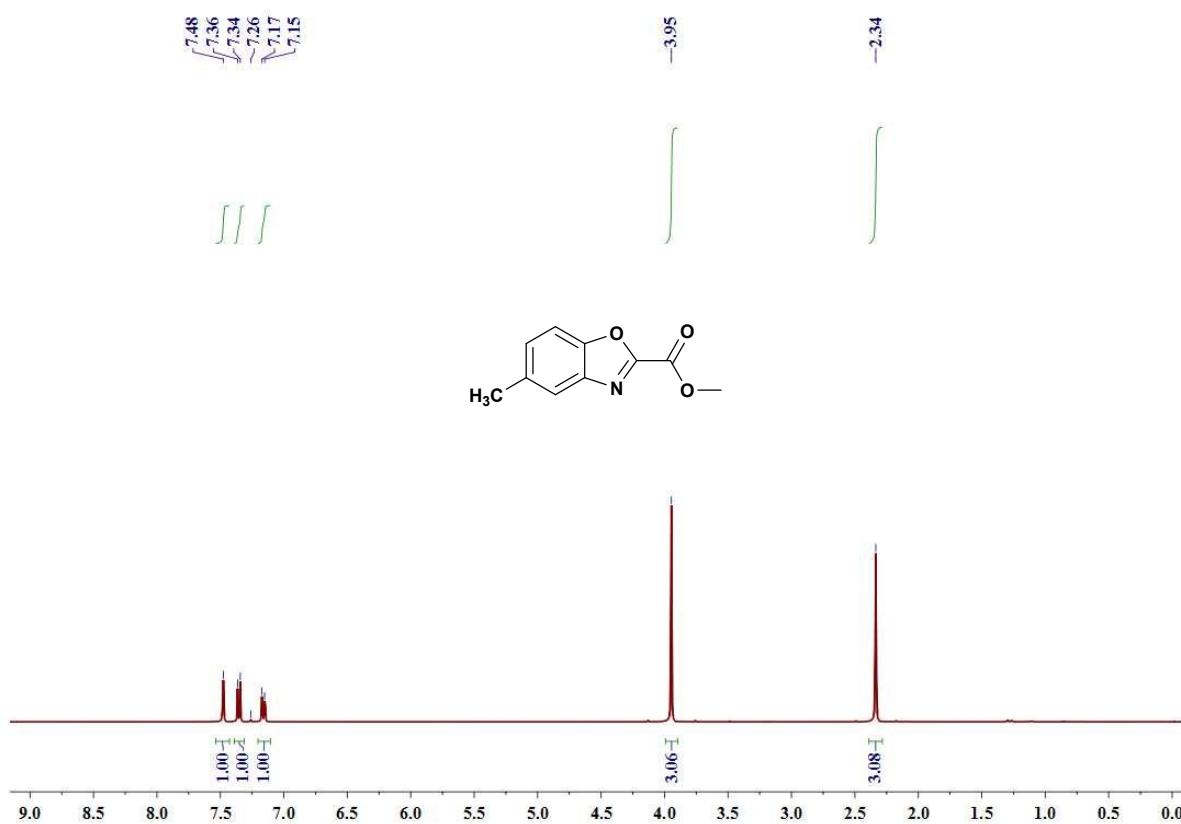


¹³C NMR (101 MHz, CDCl₃)

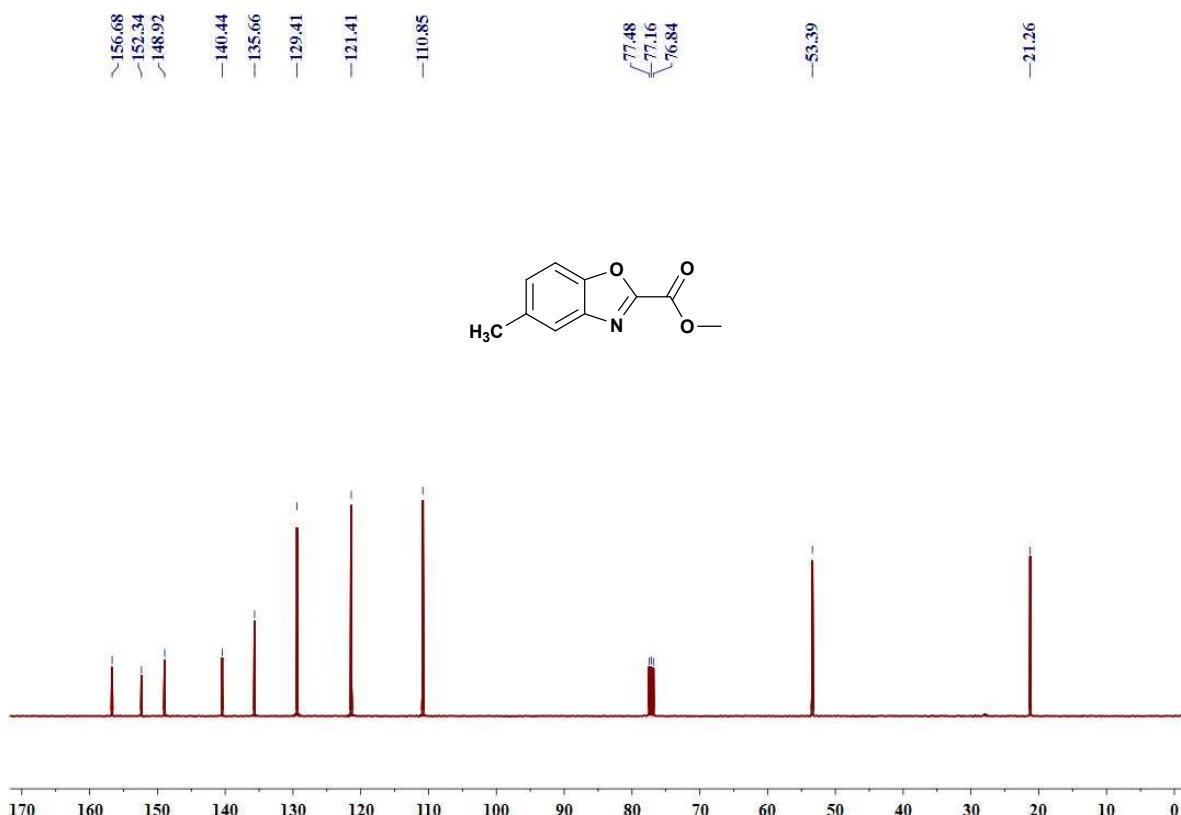


Methyl 5-methylbenzo[*d*]oxazole-2-carboxylate (**7b**)

¹H NMR (400 MHz, CDCl₃)

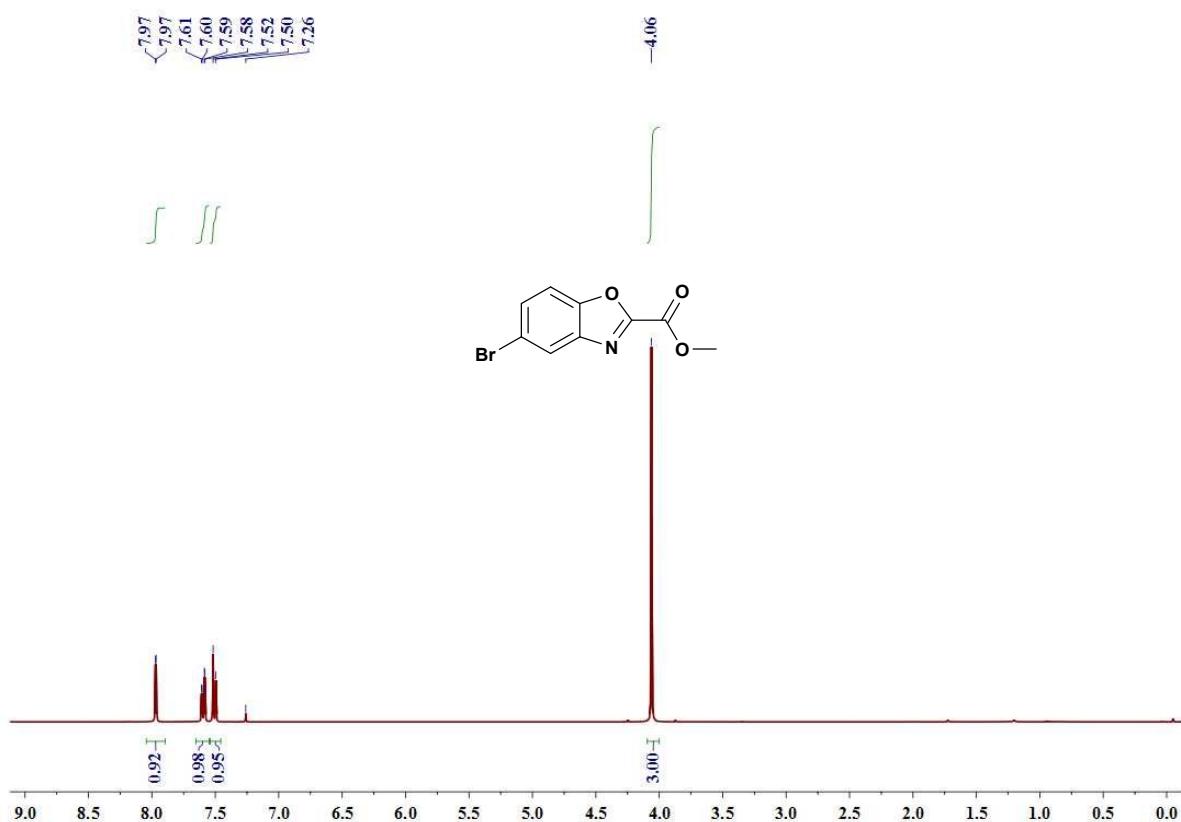


¹³C NMR (101 MHz, CDCl₃)

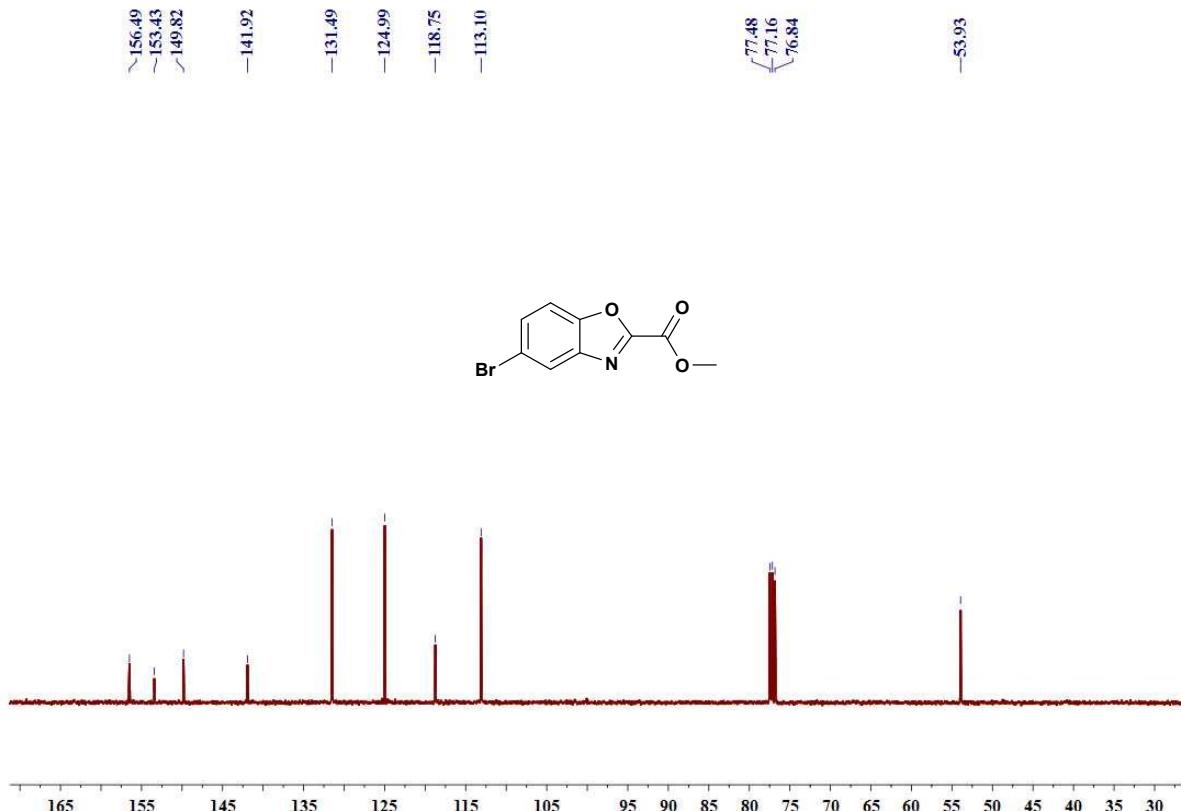


Methyl 5-bromobenzo[*d*]oxazole-2-carboxylate (**7c**)

¹H NMR (400 MHz, CDCl₃)

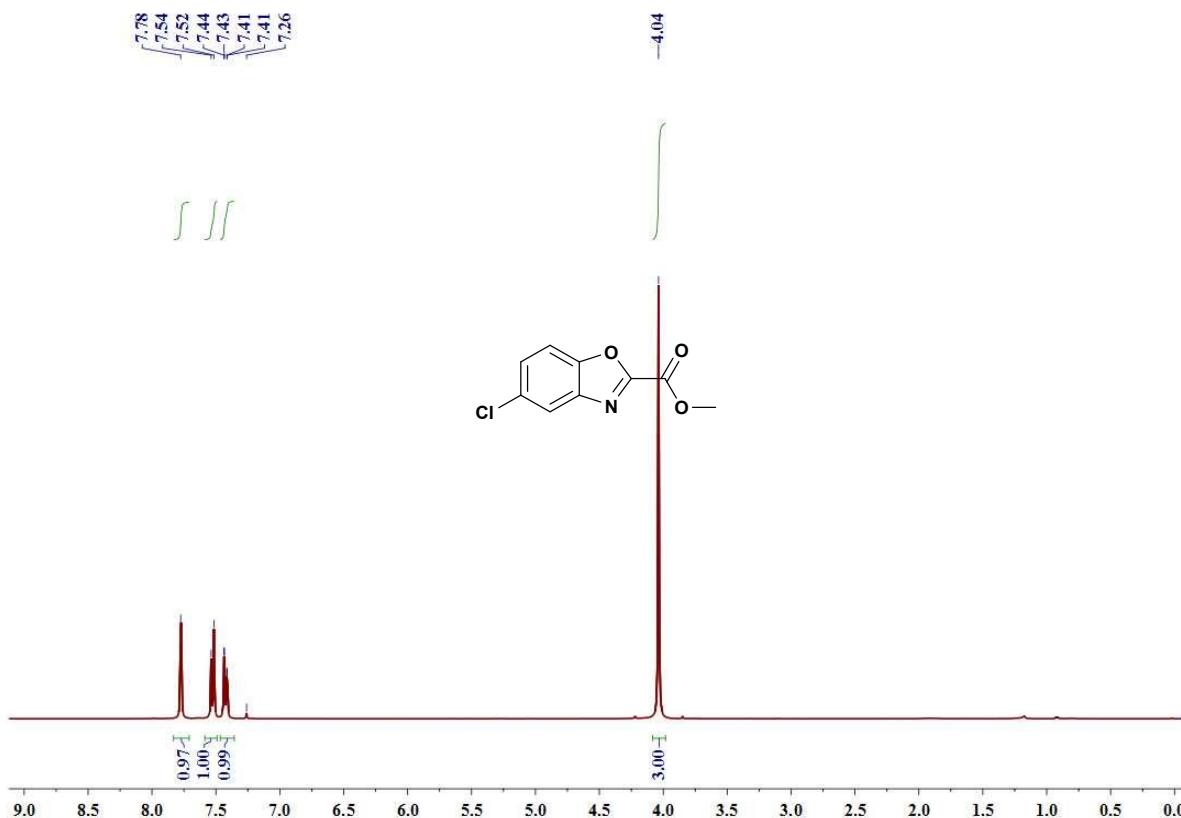


¹³C NMR (101 MHz, CDCl₃)

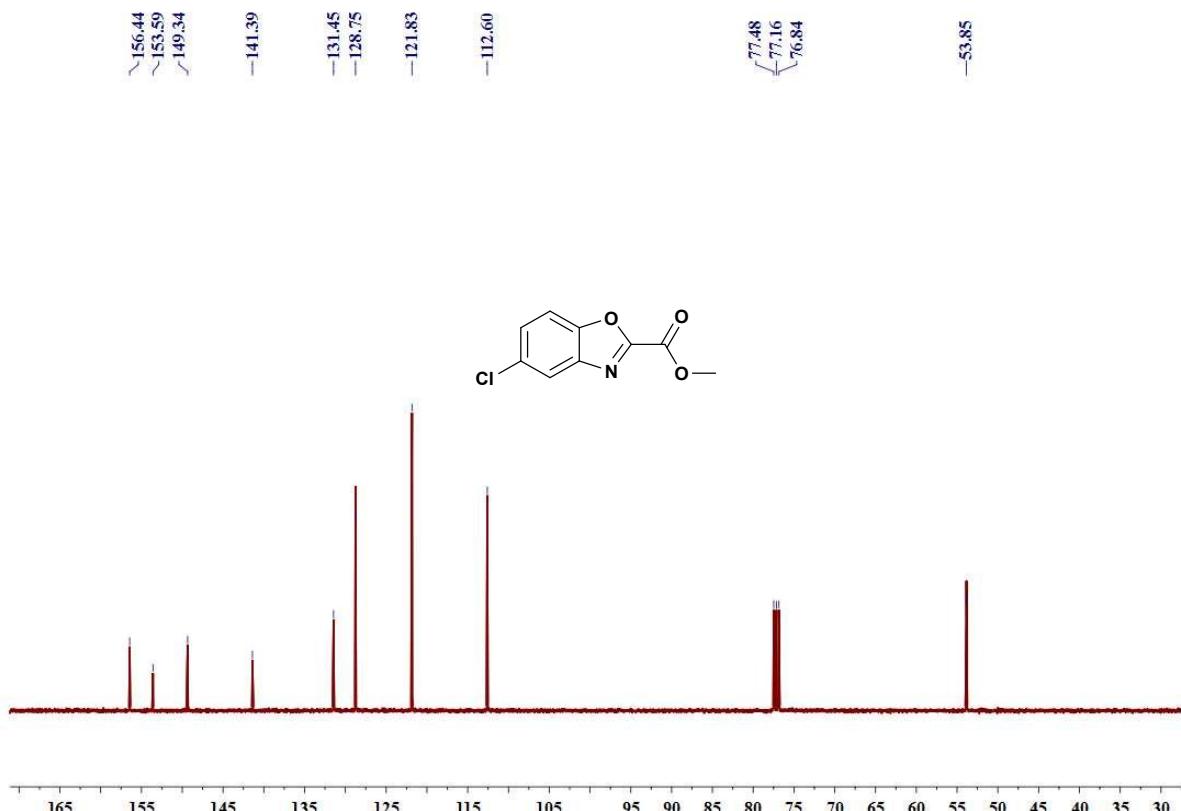


Methyl 5-chlorobenzo[*d*]oxazole-2-carboxylate (**7d**)

¹H NMR (400 MHz, CDCl₃)

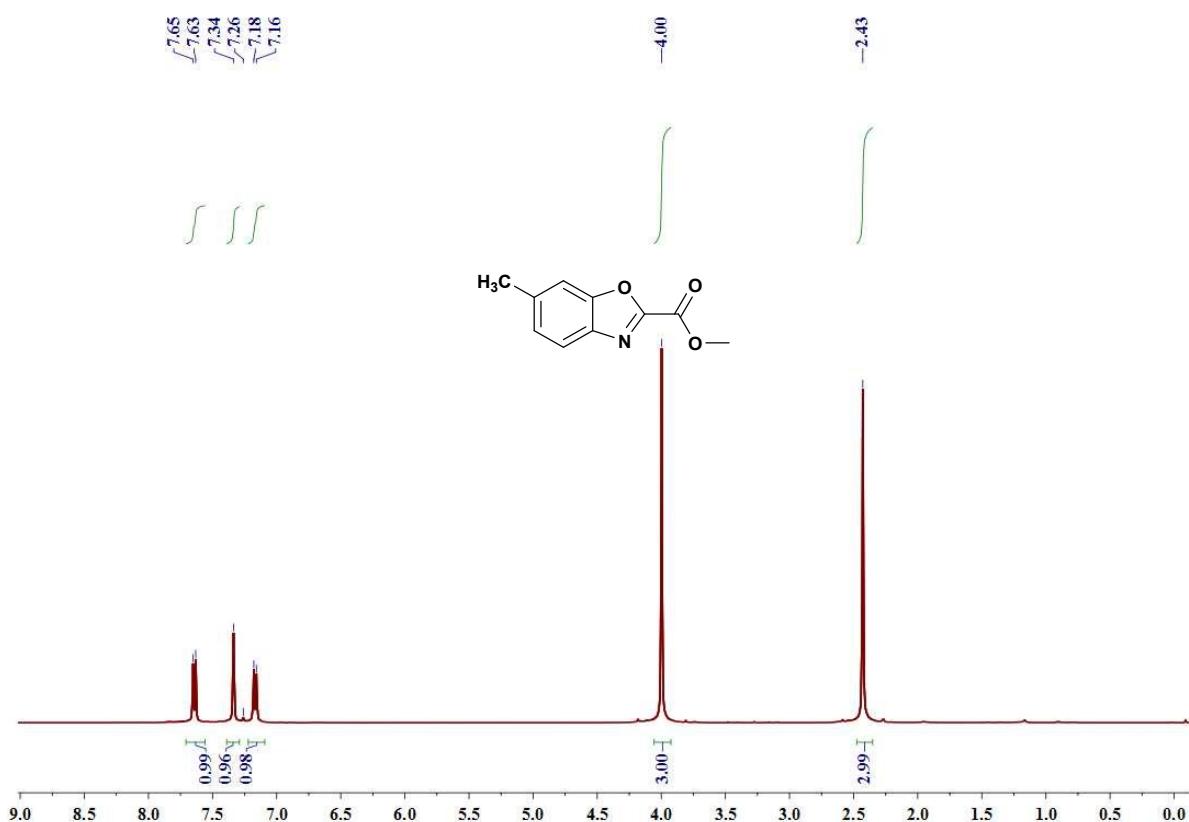


¹³C NMR (101 MHz, CDCl₃)

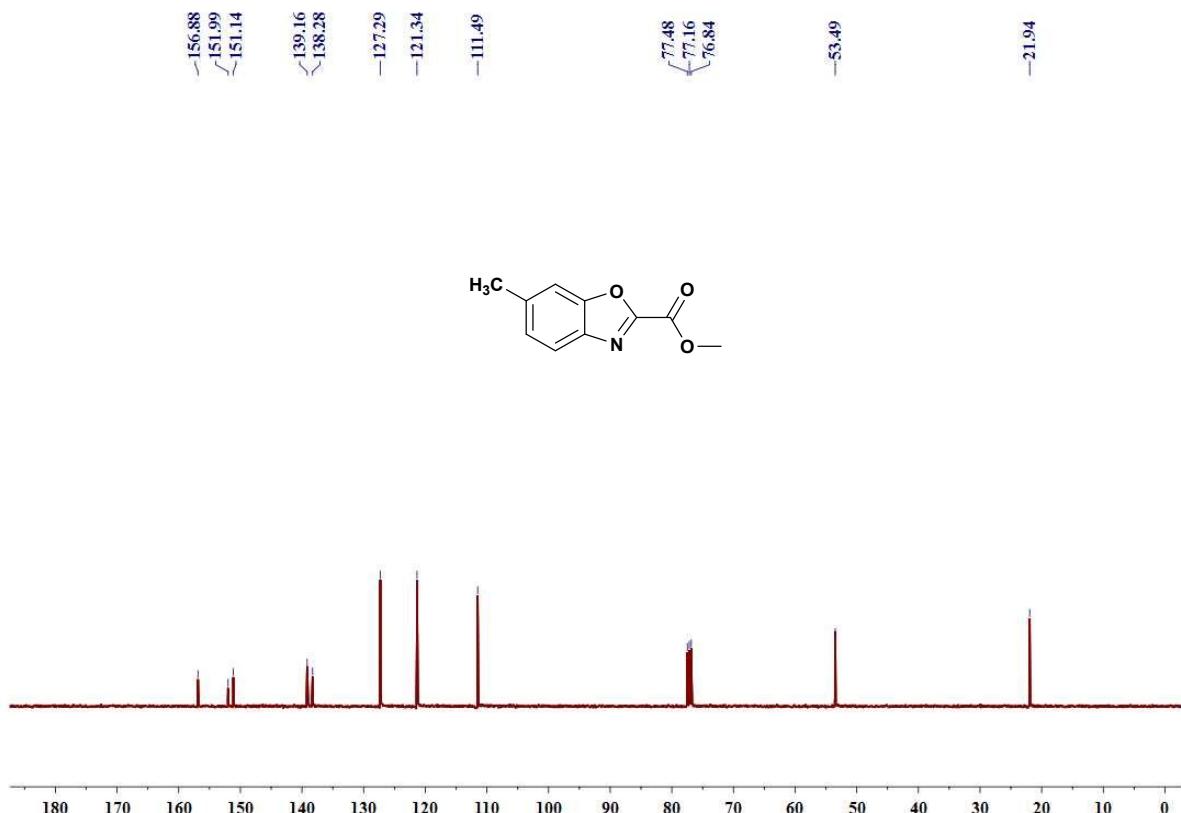


Methyl 6-methylbenzo[*d*]oxazole-2-carboxylate (**7e**)

¹H NMR (400 MHz, CDCl₃)

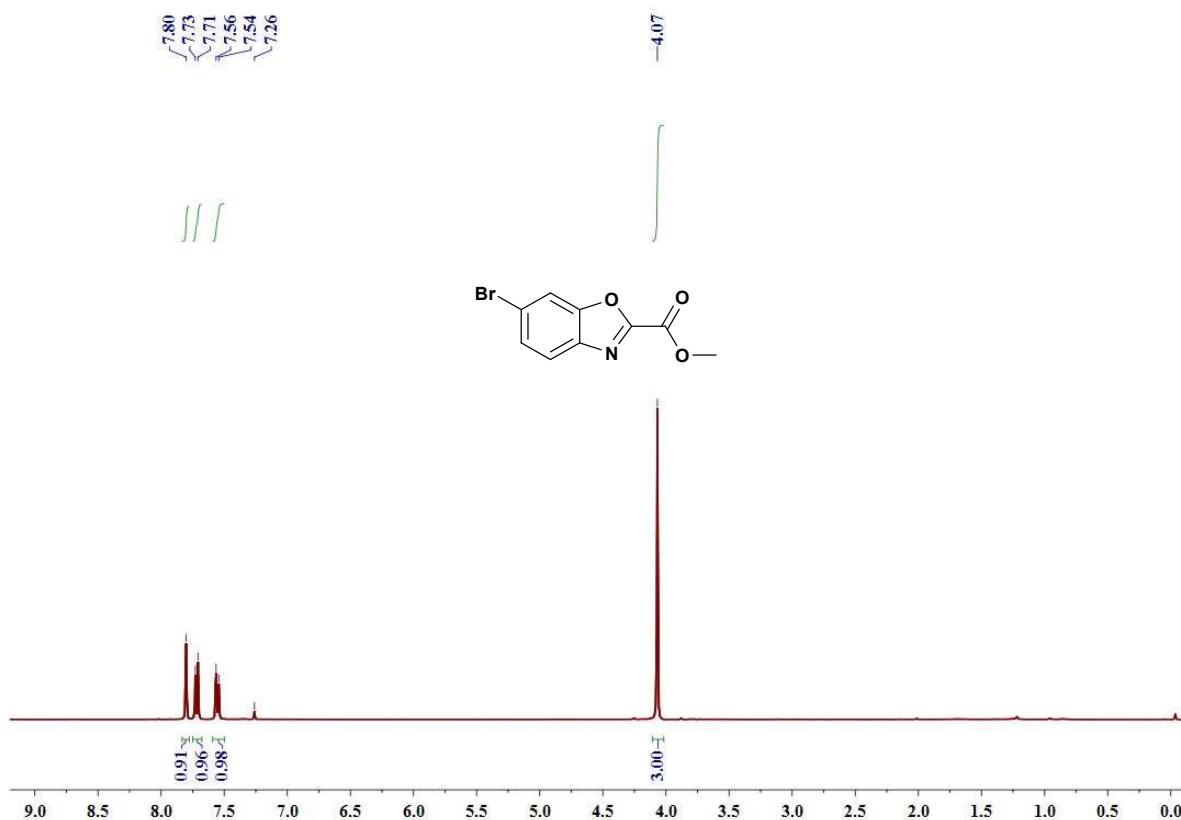


¹³C NMR (101 MHz, CDCl₃)

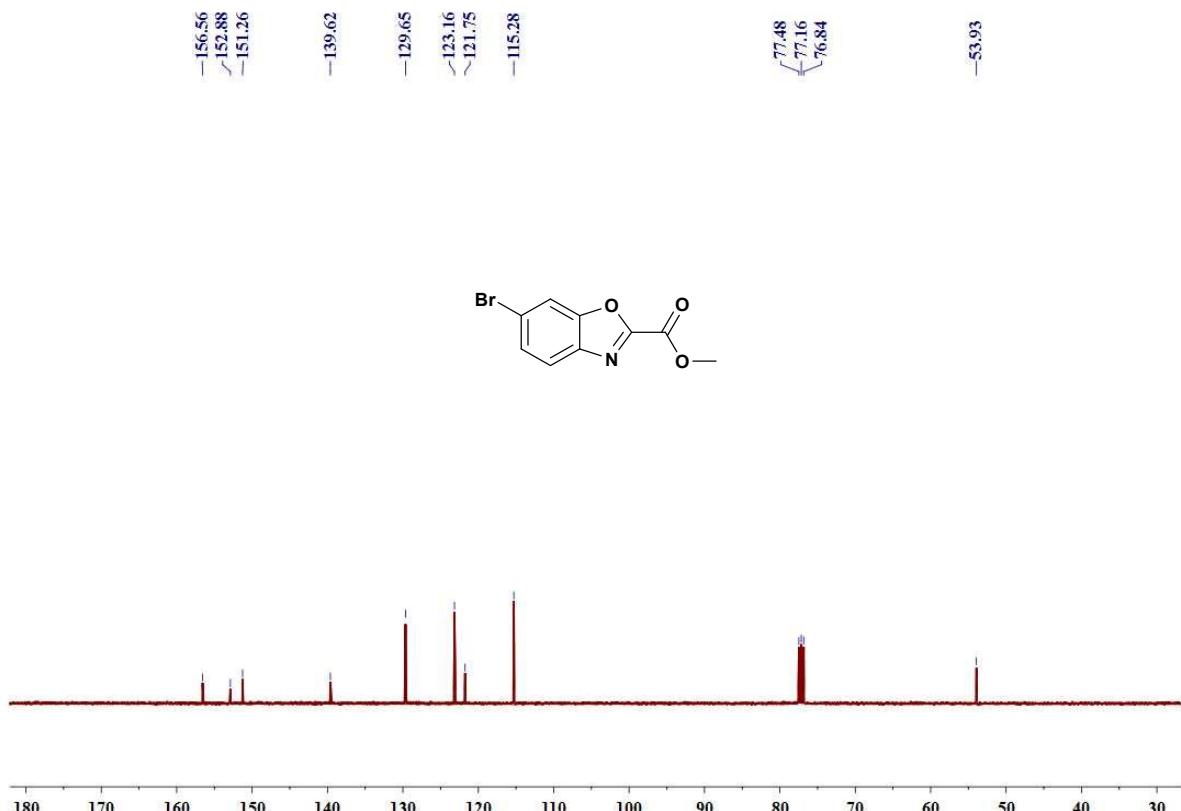


Methyl 6-bromobenzo[*d*]oxazole-2-carboxylate (**7f**)

¹H NMR (400 MHz, CDCl₃)

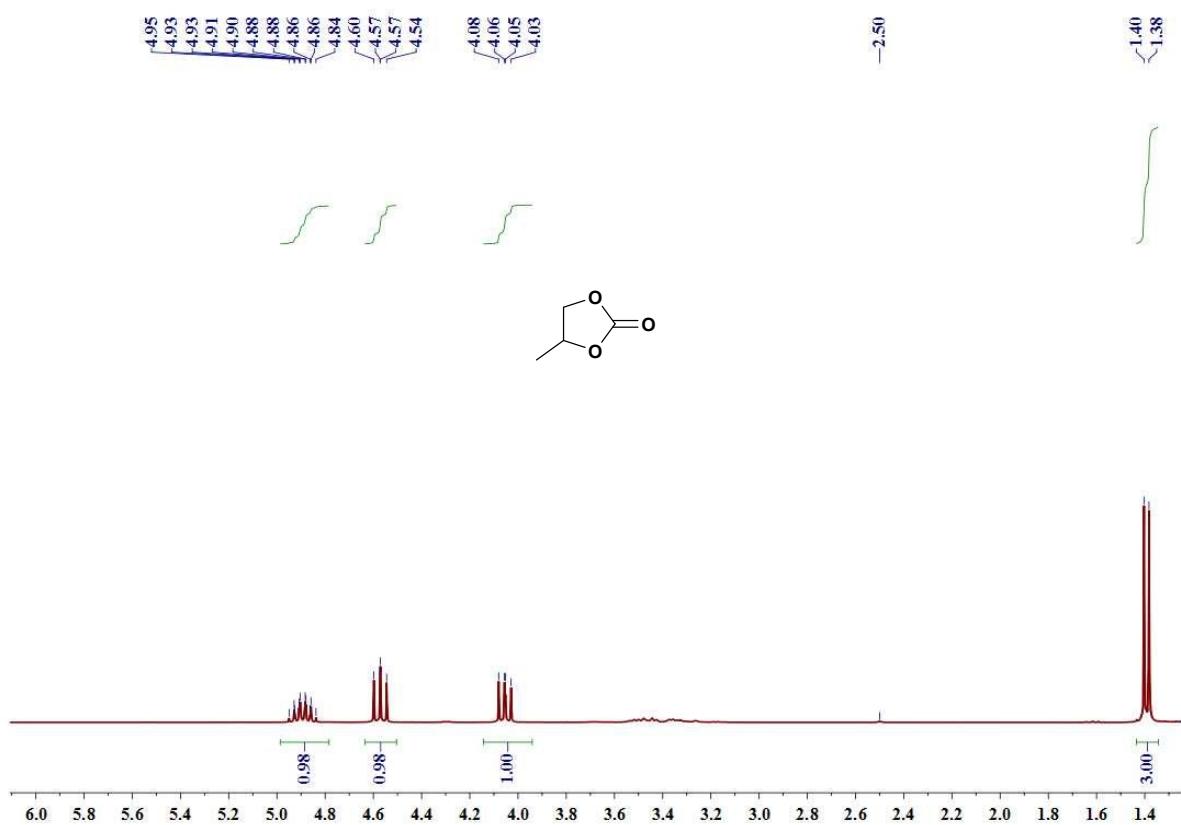


¹³C NMR (101 MHz, CDCl₃)

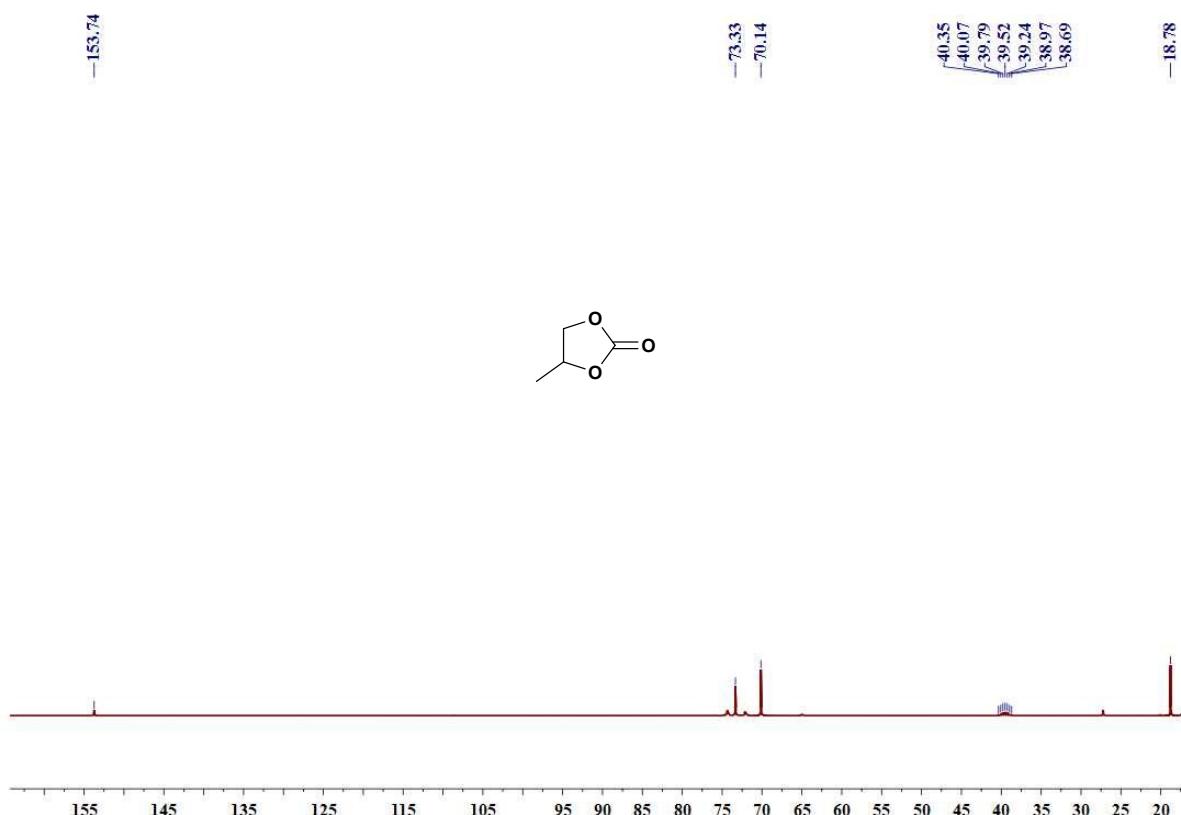


4-methyl-1,3-dioxolan-2-one (**9a**)

¹H NMR (300 MHz, DMSO-*d*₆)

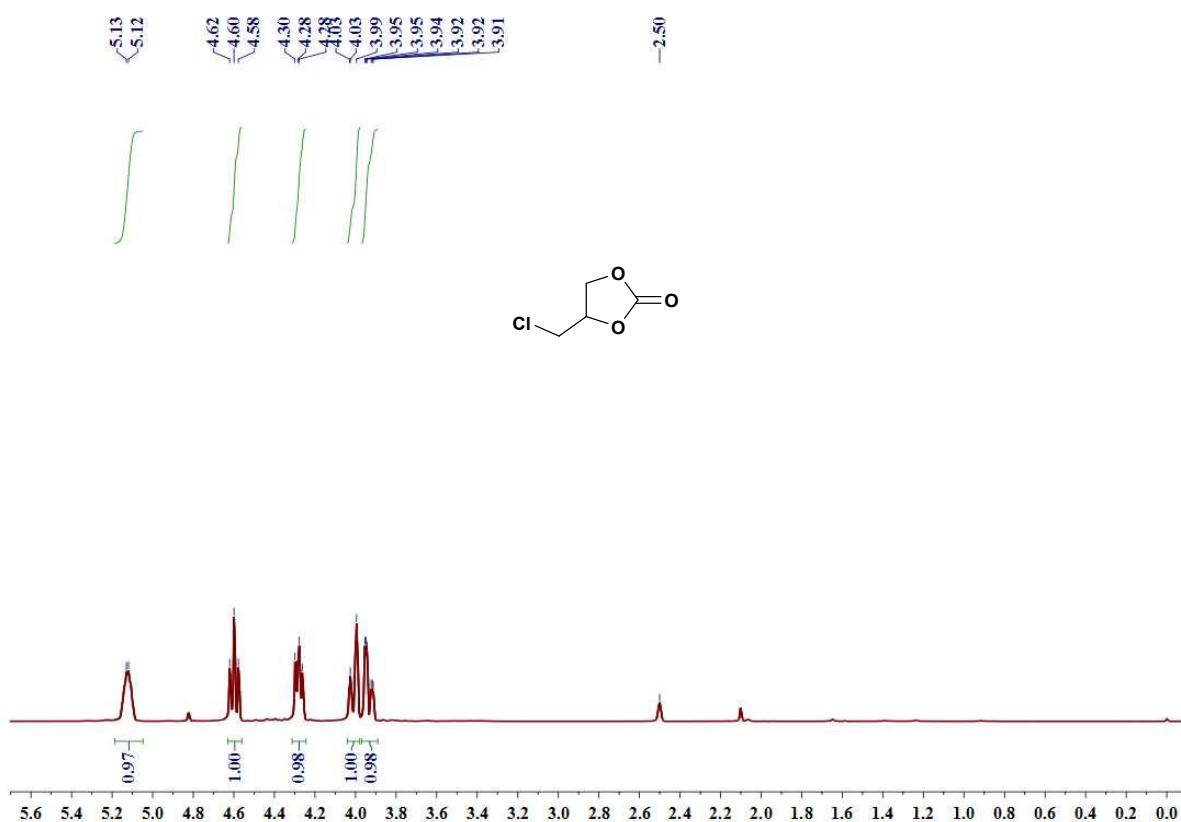


¹³C NMR (75 MHz, DMSO-*d*₆)

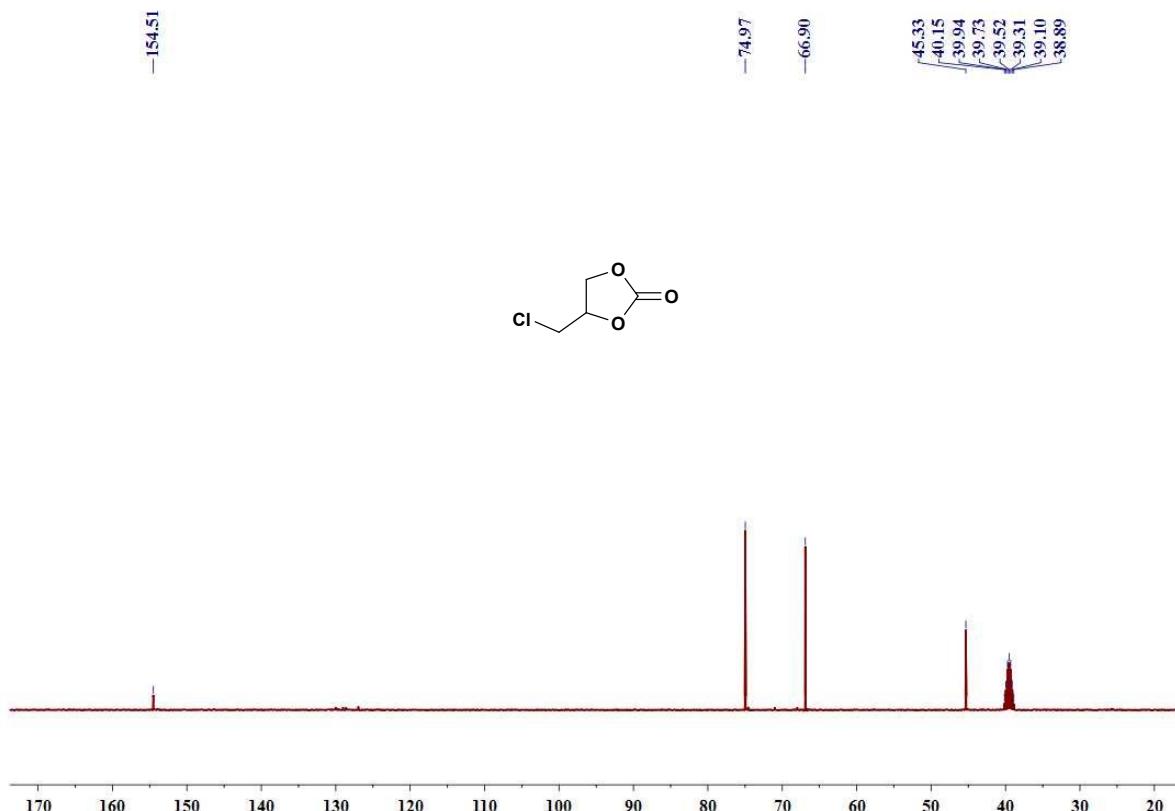


4-(chloromethyl)-1,3-dioxolan-2-one (**9b**)

¹H NMR (300 MHz, DMSO-*d*₆)

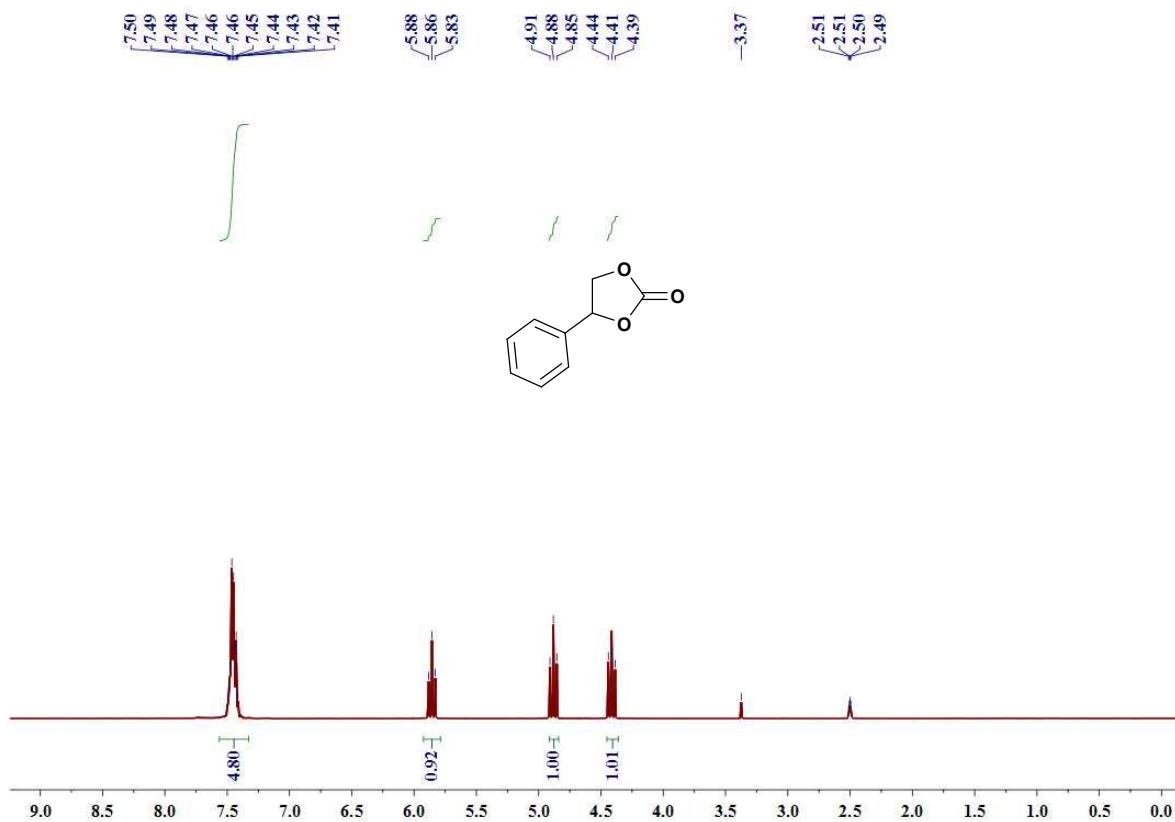


¹³C NMR (75 MHz, DMSO-*d*₆)

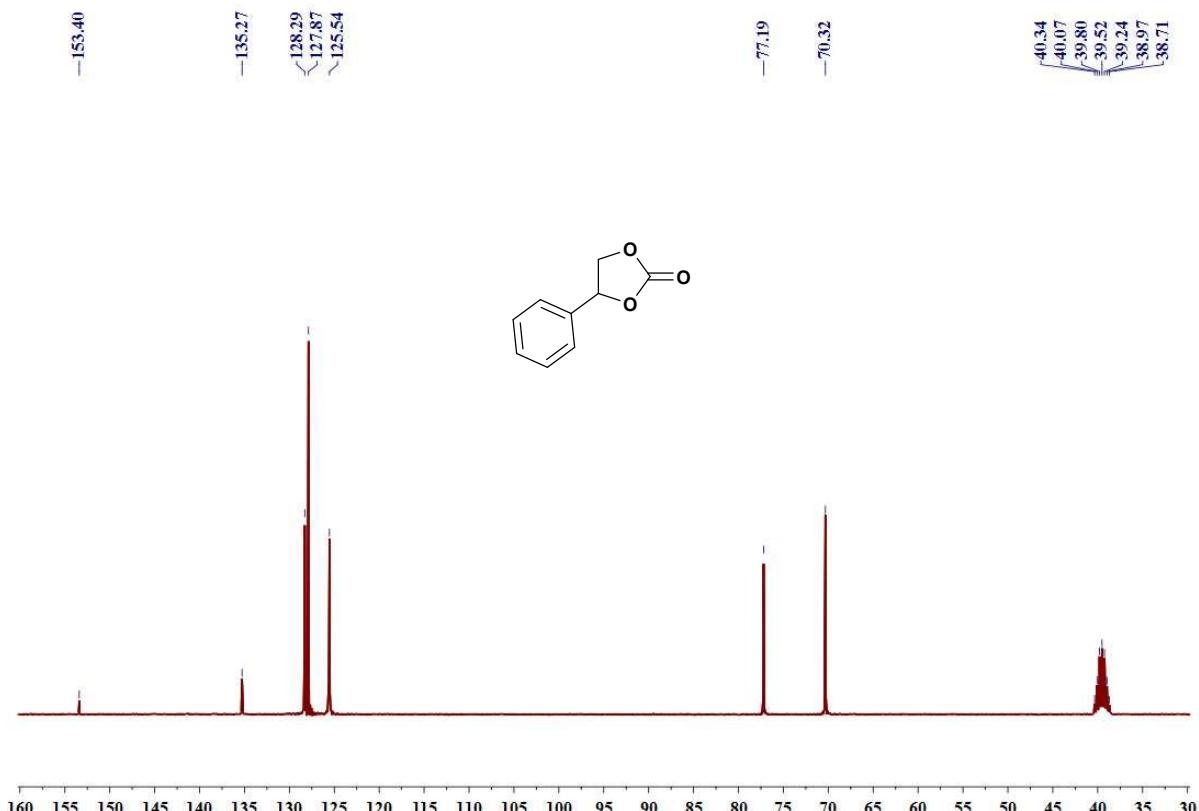


4-phenyl-1,3-dioxolan-2-one (**9c**)

¹H NMR (300 MHz, DMSO-*d*₆)

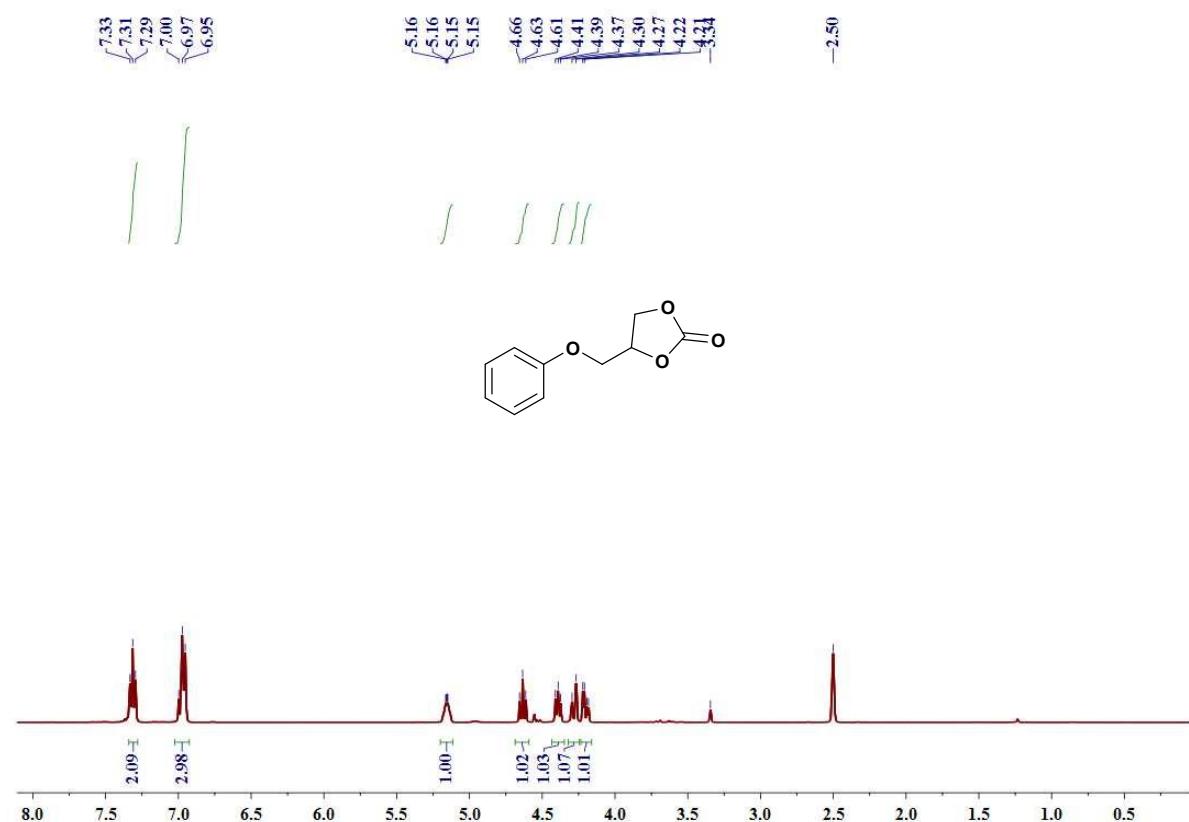


¹³C NMR (75 MHz, DMSO-*d*₆)

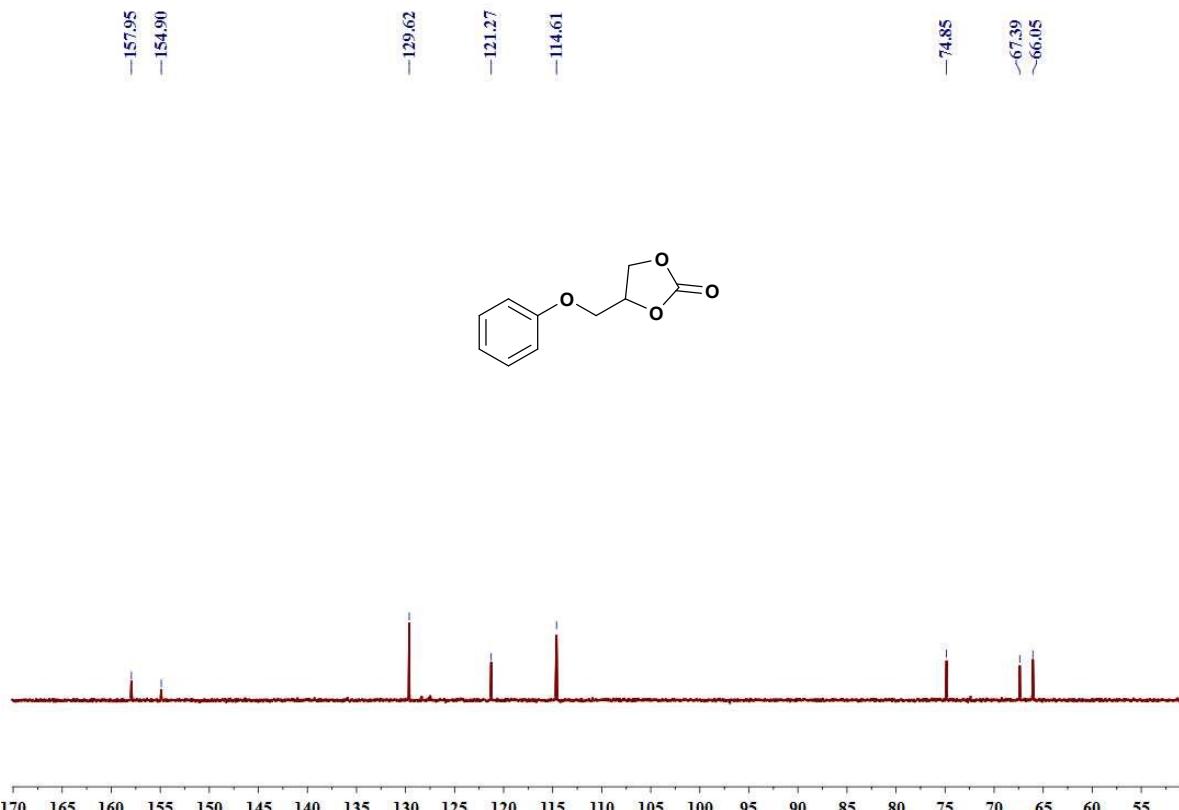


4-(phenoxy)methyl-1,3-dioxolan-2-one (**9d**)

¹H NMR (300 MHz, DMSO-*d*₆)

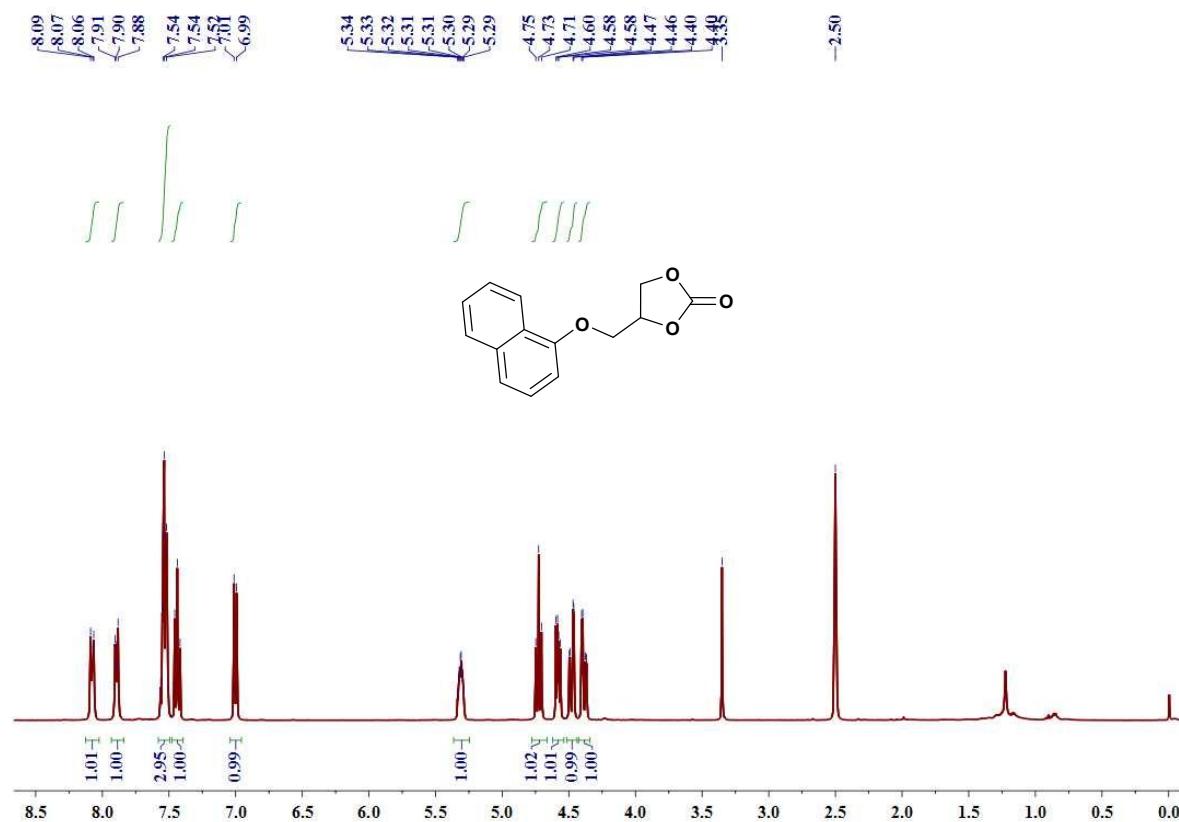


¹³C NMR (75 MHz, DMSO-*d*₆)

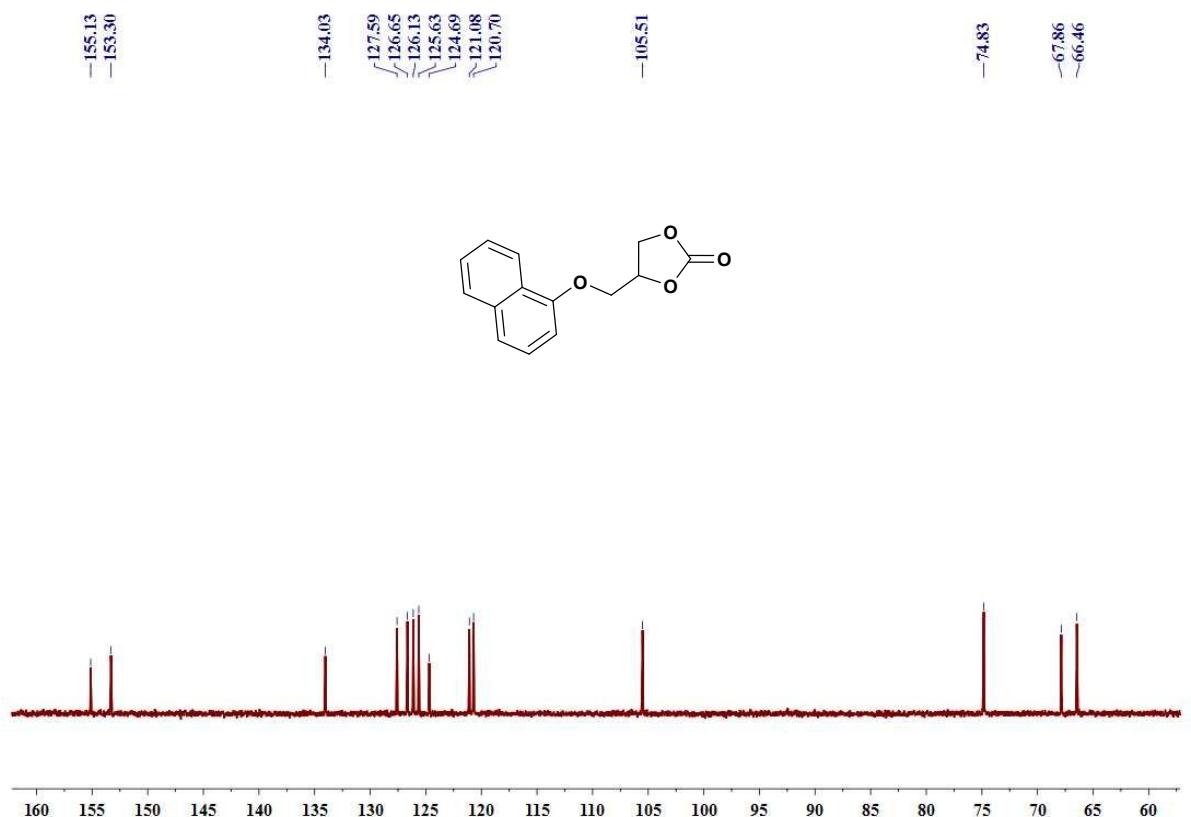


4-((naphthalen-1-yloxy)methyl)-1,3-dioxolan-2-one (**9e**)

¹H NMR (300 MHz, DMSO-*d*₆)

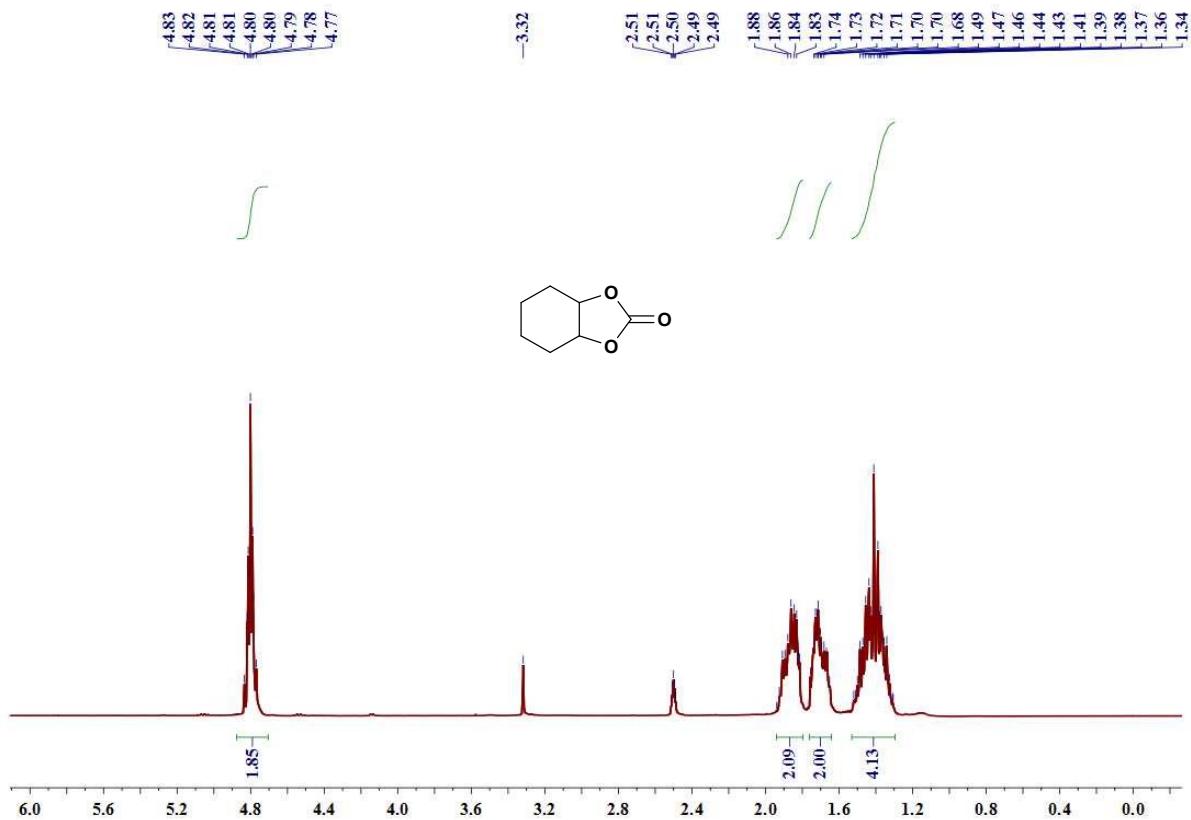


¹³C NMR (75 MHz, DMSO-*d*₆)



Hexahydrobenzo-1,3-dioxolan-2-one (9f)

¹H NMR (300 MHz, DMSO-*d*₆)



¹³C NMR (75 MHz, DMSO-*d*₆)

