

Supporting Information
for

Isomerization of 5-(2*H*-Azirin-2-yl)oxazoles: an Atom-Economic Approach to 4*H*-Pyrrolo[2,3-*d*]oxazoles

Timur O. Zanakhov, Ekaterina E. Galenko, Mariya A. Kryukova, Mikhail S. Novikov,
Alexander A. Khlebnikov*

St. Petersburg State University, Institute of Chemistry, 7/9 Universitetskaya nab., St. Petersburg,
199034, Russia

E-mail: a.khlebnikov@spbu.ru

Table of Contents:

X-Ray Diffraction Experiments	S2
NMR Spectra of Compounds 2	S6
NMR Spectra of Compounds 3	S59
NMR Spectra of Compounds 4	S110
Computational Details	S116

X-RAY DIFFRACTION EXPERIMENTS

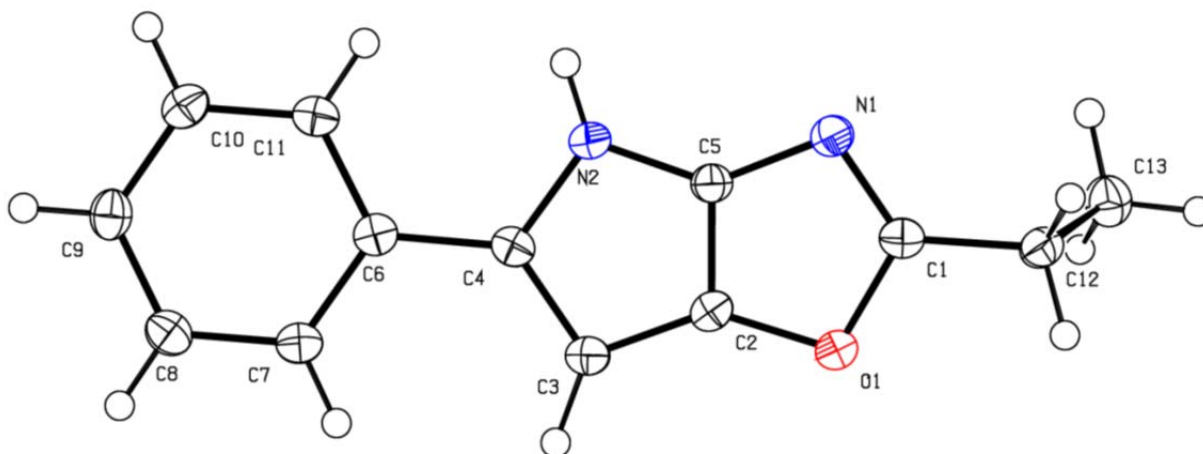
Crystal structure of **3d** was determined by single crystal X-ray diffraction analysis. Suitable crystals were selected and fixed on micro-mounts and the diffraction data were collected on a HyPix diffractometer. The crystal of **3d** was measured at a temperature of 100(2) K, using monochromated CuK α radiation. The unit cell parameters and refinement characteristics of the crystal structure of **3d** is given below. Using Olex2 [1], the structures were solved with the ShelXT [2] structure solution program using Intrinsic Phasing and refined with the ShelXL [3] refinement package using Least Squares minimization.

References

1. Dolomanov, O.V.; Bourhis, L.J.; Gildea, R.J.; Howard, J.A.K.; Puschmann, H. J. Appl. Cryst. 2009, 42, 339.
2. Sheldrick, G.M. Acta Cryst. 2015, A71, 3.
3. Sheldrick, G.M. Acta Cryst. 2015, C71, 3.

2-Ethyl-5-phenyl-4H-pyrrolo[2,3-d]oxazole

Single crystal of **3d** was obtained by slow evaporation of toluene solution at room temperature. (CCDC 2064882).



Molecular structure of compound **3d**, displacement parameters are drawn at 50% probability level.

Table S1. Crystal data and structure refinement for 3d.

Identification code	3d (17505 TZ-19)
Empirical formula	C ₁₃ H ₁₂ N ₂ O
Formula weight	212.25
Temperature/K	100.00(10)
Crystal system	monoclinic
Space group	P2 ₁ /c
a/Å	13.1494(3)
b/Å	14.4153(3)
c/Å	5.49770(10)
α/°	90
β/°	90.628(2)
γ/°	90
Volume/Å ³	1042.04(4)
Z	4
ρ _{calc} /g/cm ³	1.353
μ/mm ⁻¹	0.701
F(000)	448.0
Crystal size/mm ³	0.15 × 0.13 × 0.1
Radiation	CuKα (λ = 1.54184)
2Θ range for data collection/°	6.722 to 139.978
Index ranges	-16 ≤ h ≤ 16, -17 ≤ k ≤ 17, -6 ≤ l ≤ 6
Reflections collected	10049
Independent reflections	1920 [R _{int} = 0.0454, R _{sigma} = 0.0364]
Data/restraints/parameters	1920/0/150
Goodness-of-fit on F ²	1.059
Final R indexes [I ≥ 2σ (I)]	R ₁ = 0.0392, wR ₂ = 0.1004
Final R indexes [all data]	R ₁ = 0.0478, wR ₂ = 0.1053
Largest diff. peak/hole / e Å ⁻³	0.14/-0.22

Table S2. Fractional Atomic Coordinates (×10⁴) and Equivalent Isotropic Displacement Parameters (Å²×10³) for 3d. U_{eq} is defined as 1/3 of the trace of the orthogonalised U_{ij} tensor.

Atom	x	y	z	U(eq)
O ₁	3380.4(7)	3510.6(6)	5323.8(16)	21.7(2)
N ₂	5667.9(8)	4266.0(7)	7570.2(19)	20.5(3)
N ₁	3772.9(8)	4400.5(7)	8615(2)	21.5(3)
C ₄	6091.1(10)	3807.2(8)	5595(2)	18.8(3)
C ₅	4641.1(10)	4137.9(9)	7412(2)	19.5(3)
C ₂	4427.9(10)	3607.2(9)	5434(2)	20.1(3)
C ₁	3053.3(10)	4011.7(8)	7310(2)	20.2(3)
C ₁₁	7865.4(10)	4218.7(9)	6870(2)	21.6(3)
C ₈	8636.4(10)	3378.9(9)	2752(2)	23.5(3)
C ₆	7188.6(10)	3810.0(8)	5205(2)	19.1(3)
C ₁₂	1941.3(10)	4029.3(9)	7739(2)	21.5(3)
C ₃	5323.5(10)	3381.4(9)	4217(2)	20.8(3)
C ₉	9298.6(10)	3787.0(9)	4427(3)	23.7(3)
C ₇	7594.8(10)	3393.7(8)	3121(2)	20.9(3)
C ₁₀	8904.9(10)	4207.6(9)	6486(2)	24.0(3)
C ₁₃	1629.4(11)	3416.9(10)	9864(3)	27.8(3)

Table S3. Anisotropic Displacement Parameters ($\text{\AA}^2 \times 10^3$) for 3d. The Anisotropic displacement factor exponent takes the form: $-2\pi^2[h^2a^{*2}U_{11}+2hka^*b^*U_{12}+\dots]$.

Atom	U_{11}	U_{22}	U_{33}	U_{23}	U_{13}	U_{12}
O ₁	20.2(5)	24.0(5)	20.7(5)	-3.1(4)	-1.3(4)	-1.9(3)
N ₂	19.9(5)	22.2(5)	19.4(5)	-4.5(4)	-1.3(4)	-1.3(4)
N ₁	20.8(6)	22.2(5)	21.6(5)	-1.8(4)	-1.3(4)	-0.3(4)
C ₄	23.0(7)	15.4(6)	18.0(6)	0.7(5)	1.2(5)	0.6(5)
C ₅	20.3(6)	19.6(6)	18.5(6)	-1.4(5)	-0.7(5)	-0.1(5)
C ₂	19.8(6)	20.2(6)	20.2(6)	0.3(5)	-2.5(5)	-1.9(5)
C ₁	23.7(7)	18.3(6)	18.7(6)	0.6(5)	-1.3(5)	0.6(5)
C ₁₁	25.9(7)	20.4(6)	18.6(6)	-0.7(5)	0.0(5)	-0.2(5)
C ₈	26.8(7)	21.1(6)	22.6(6)	0.5(5)	1.9(5)	2.5(5)
C ₆	22.7(7)	15.3(6)	19.3(6)	3.2(5)	-0.9(5)	-0.4(5)
C ₁₂	20.8(6)	21.1(6)	22.4(6)	-1.5(5)	-3.1(5)	0.2(5)
C ₃	23.2(6)	20.9(6)	18.3(6)	-1.5(5)	-0.7(5)	-0.9(5)
C ₉	20.3(6)	23.6(6)	27.1(7)	4.7(5)	0.5(5)	1.5(5)
C ₇	24.9(7)	18.1(6)	19.8(6)	0.2(5)	-1.7(5)	0.0(5)
C ₁₀	24.1(7)	24.5(6)	23.3(7)	1.4(5)	-4.0(5)	-2.4(5)
C ₁₃	26.5(7)	28.9(7)	27.9(7)	2.4(6)	1.5(6)	1.0(6)

Table S4. Bond Lengths for 3d.

Atom	Atom	Length/ $\text{\AA}$	Atom	Atom	Length/ $\text{\AA}$
O ₁	C ₂	1.3852(15)	C ₂	C ₃	1.3990(19)
O ₁	C ₁	1.3816(16)	C ₁	C ₁₂	1.4839(19)
N ₂	C ₄	1.3926(17)	C ₁₁	C ₆	1.3995(17)
N ₂	C ₅	1.3647(16)	C ₁₁	C ₁₀	1.3855(19)
N ₁	C ₅	1.3787(18)	C ₈	C ₉	1.3910(18)
N ₁	C ₁	1.3074(16)	C ₈	C ₇	1.3870(19)
C ₄	C ₆	1.4614(18)	C ₆	C ₇	1.4041(19)
C ₄	C ₃	1.3973(17)	C ₁₂	C ₁₃	1.5243(19)
C ₅	C ₂	1.3562(18)	C ₉	C ₁₀	1.389(2)

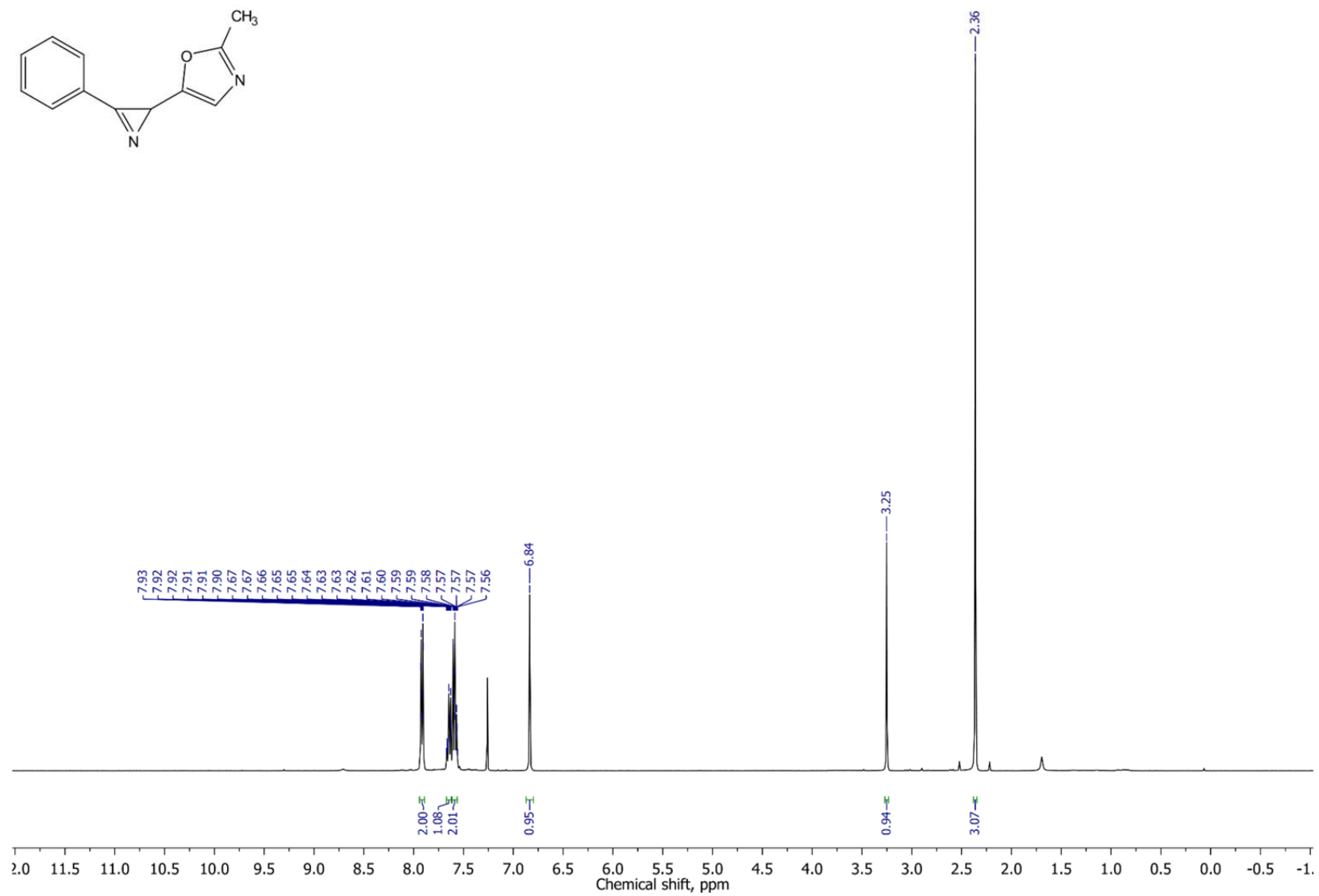
Table S5. Bond Angles for 3d.

Atom	Atom	Atom	Angle/°	Atom	Atom	Atom	Angle/°
C ₁	O ₁	C ₂	103.35(9)	N ₁	C ₁	O ₁	115.35(12)
C ₅	N ₂	C ₄	106.82(10)	N ₁	C ₁	C ₁₂	127.87(12)
C ₁	N ₁	C ₅	102.53(11)	C ₁₀	C ₁₁	C ₆	121.13(13)
N ₂	C ₄	C ₆	121.11(11)	C ₇	C ₈	C ₉	120.58(13)
N ₂	C ₄	C ₃	109.81(11)	C ₁₁	C ₆	C ₄	121.81(12)
C ₃	C ₄	C ₆	129.07(12)	C ₁₁	C ₆	C ₇	117.95(12)
N ₂	C ₅	N ₁	139.12(11)	C ₇	C ₆	C ₄	120.24(11)
C ₂	C ₅	N ₂	108.85(12)	C ₁	C ₁₂	C ₁₃	112.70(10)
C ₂	C ₅	N ₁	112.00(11)	C ₄	C ₃	C ₂	104.20(11)
O ₁	C ₂	C ₃	142.90(11)	C ₁₀	C ₉	C ₈	119.20(12)
C ₅	C ₂	O ₁	106.76(12)	C ₈	C ₇	C ₆	120.73(12)
C ₅	C ₂	C ₃	110.30(11)	C ₁₁	C ₁₀	C ₉	120.41(12)
O ₁	C ₁	C ₁₂	116.76(10)				

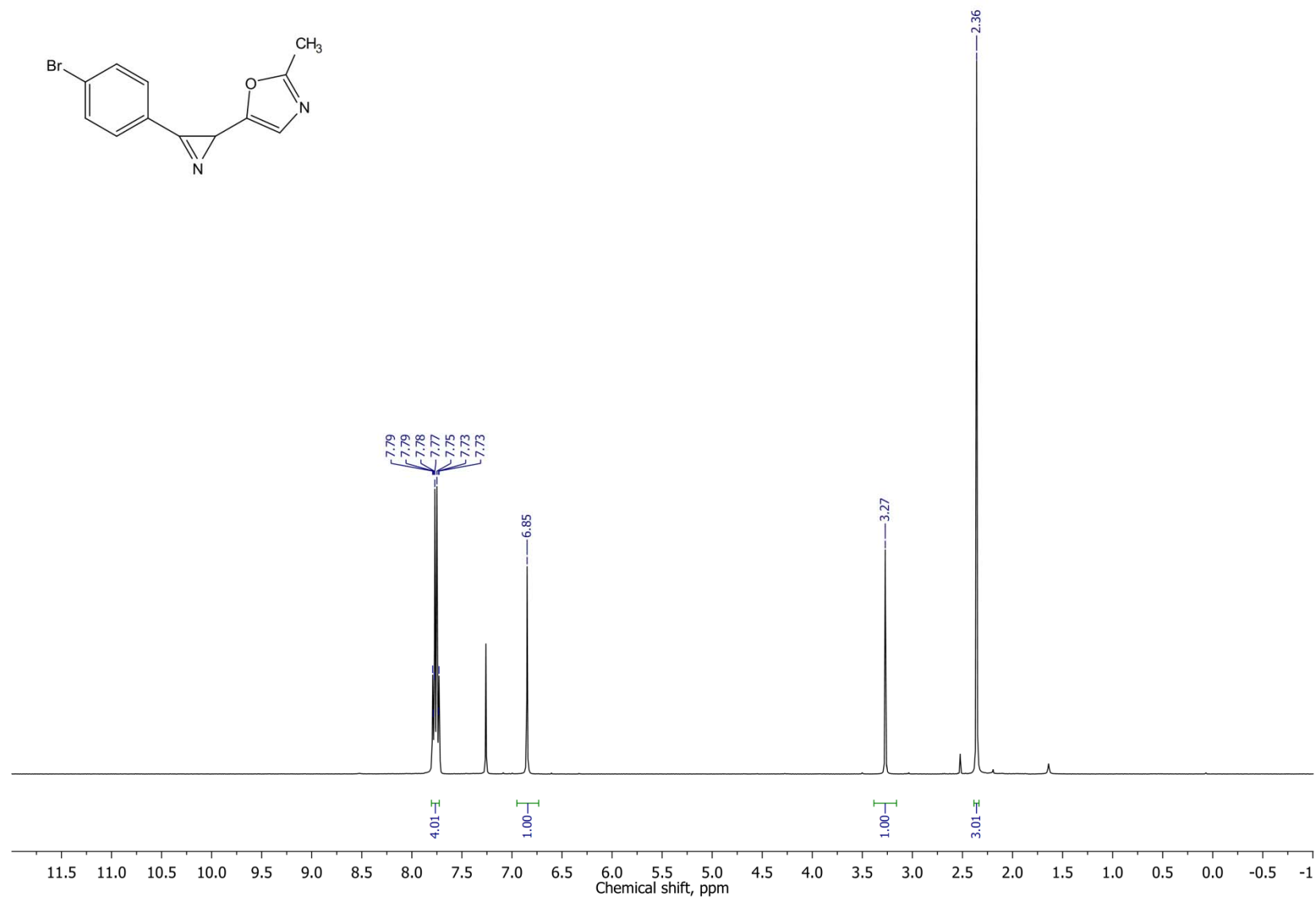
Table S6. Hydrogen Atom Coordinates ($\text{\AA} \times 10^4$) and Isotropic Displacement Parameters ($\text{\AA}^2 \times 10^3$) for 3d.

Atom	<i>x</i>	<i>y</i>	<i>z</i>	U(eq)
H ₂	5992	4571	8677	25
H ₁₁	7613	4503	8257	26
H ₈	8894	3094	1373	28
H _{12A}	1588	3822	6278	26
H _{12B}	1732	4663	8060	26
H ₉	9997	3778	4172	28
H ₇	7161	3125	1975	25
H ₁₀	9342	4484	7614	29
H _{13A}	1838	2790	9563	42
H _{13B}	904	3438	10036	42
H _{13C}	1949	3638	11332	42
H ₃	5427(12)	3017(12)	2730(30)	31(4)

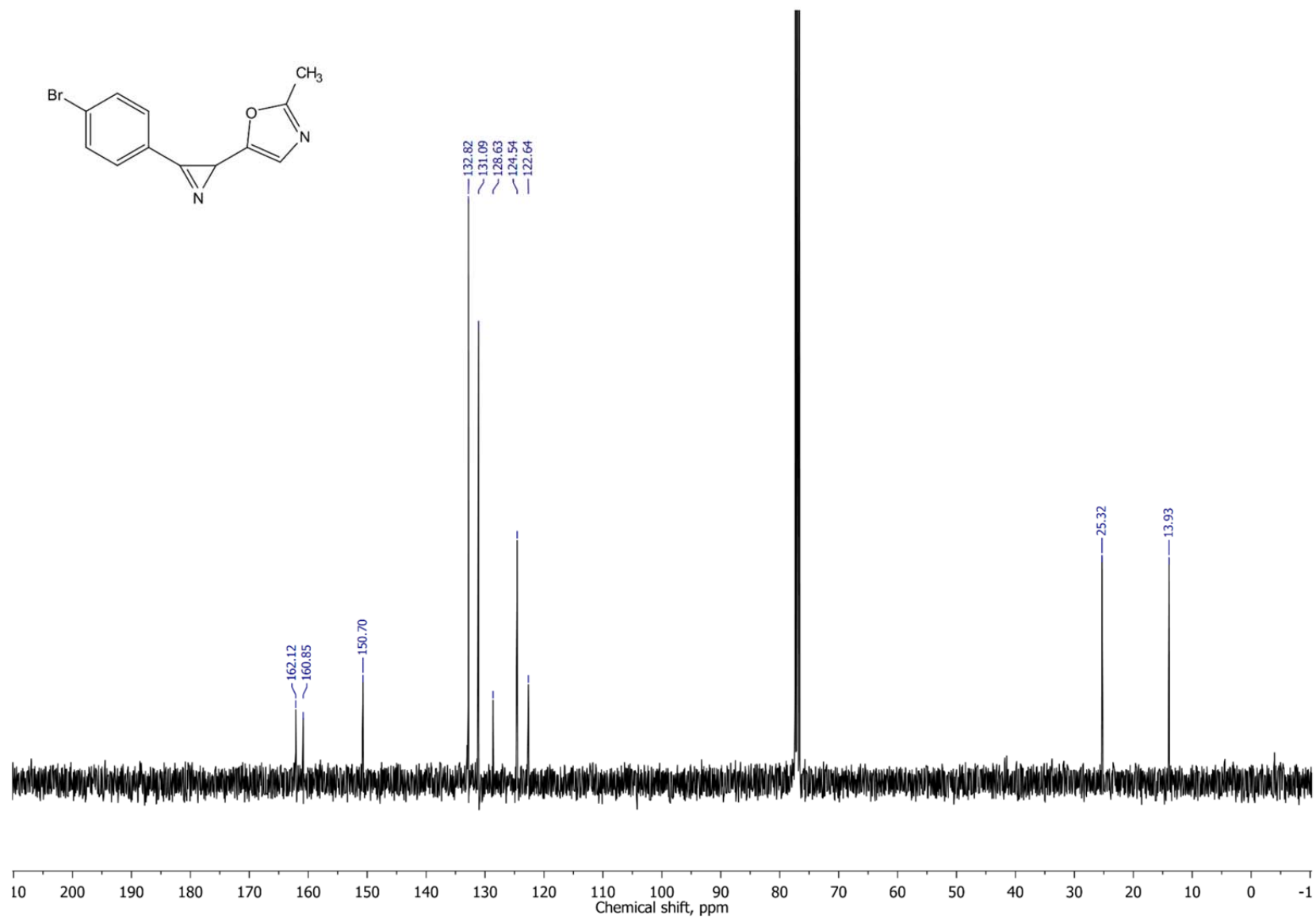
2-Methyl-5-(3-phenyl-2H-azirin-2-yl)oxazole 2a, ^1H NMR, 400 MHz, CDCl_3



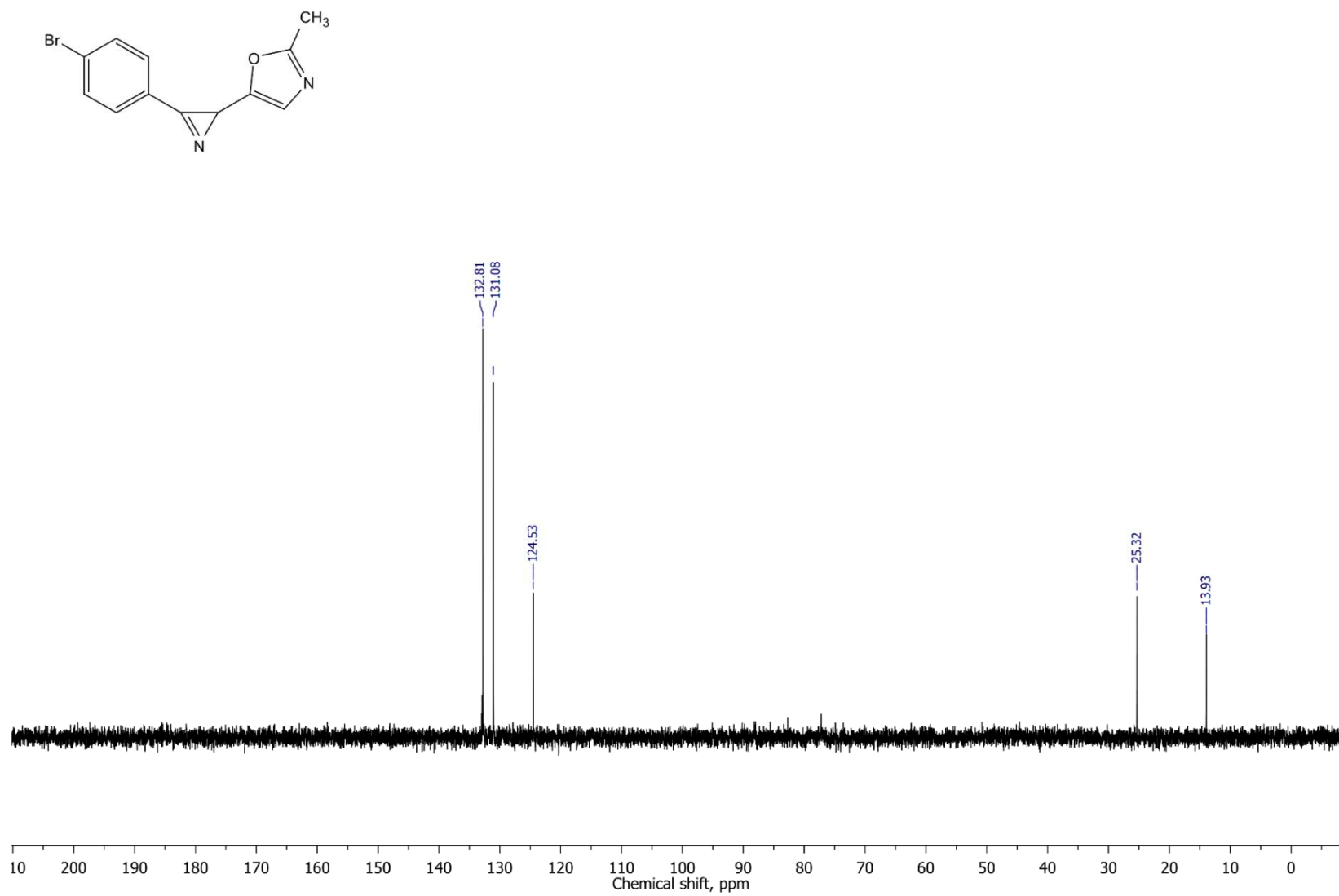
2-Methyl-5-(3-(4-bromophenyl)-2H-azirin-2-yl)oxazole 2b, ^1H NMR, 400 MHz, CDCl_3



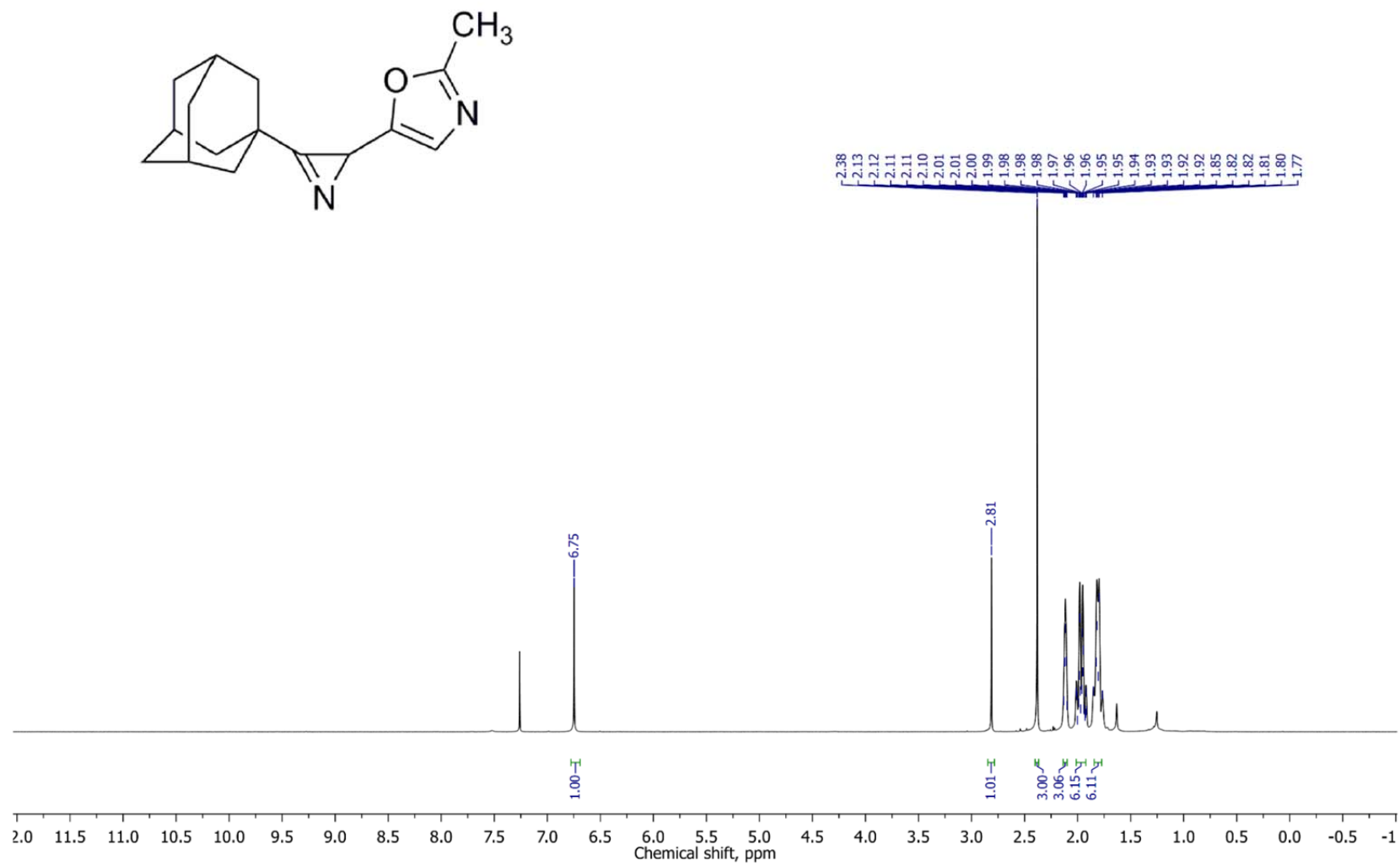
2-Methyl-5-(3-(4-bromophenyl)-2H-azirin-2-yl)oxazole 2b, $^{13}\text{C}\{^1\text{H}\}$ NMR, 100 MHz, CDCl_3



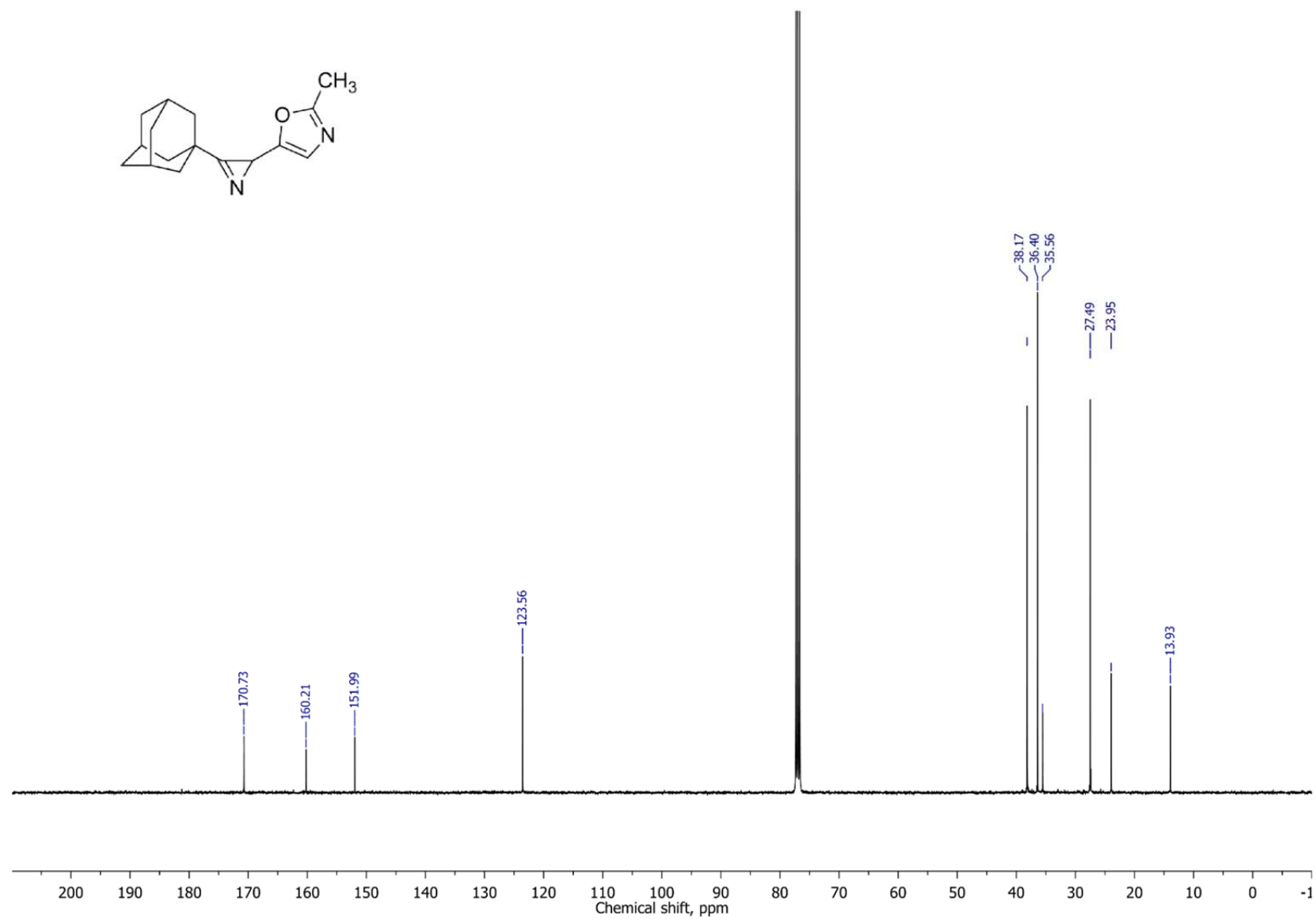
2-Methyl-5-(3-(4-bromophenyl)-2H-azirin-2-yl)oxazole 2b, DEPT, 100 MHz, CDCl₃



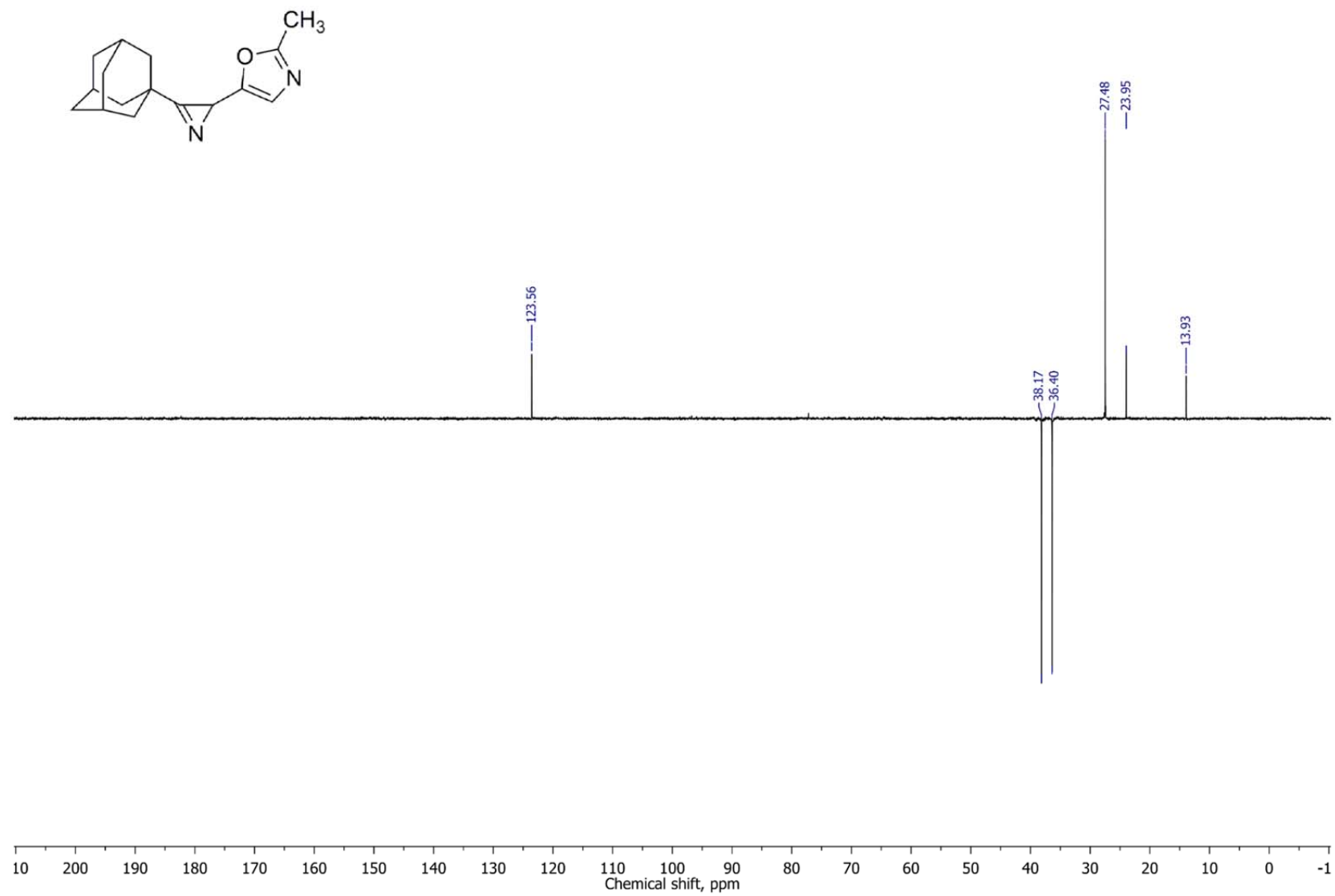
5-(3-(Adamantan-1-yl)-2*H*-azirin-2-yl)-2-methyloxazole 2c, ¹H NMR, 400 MHz, CDCl₃



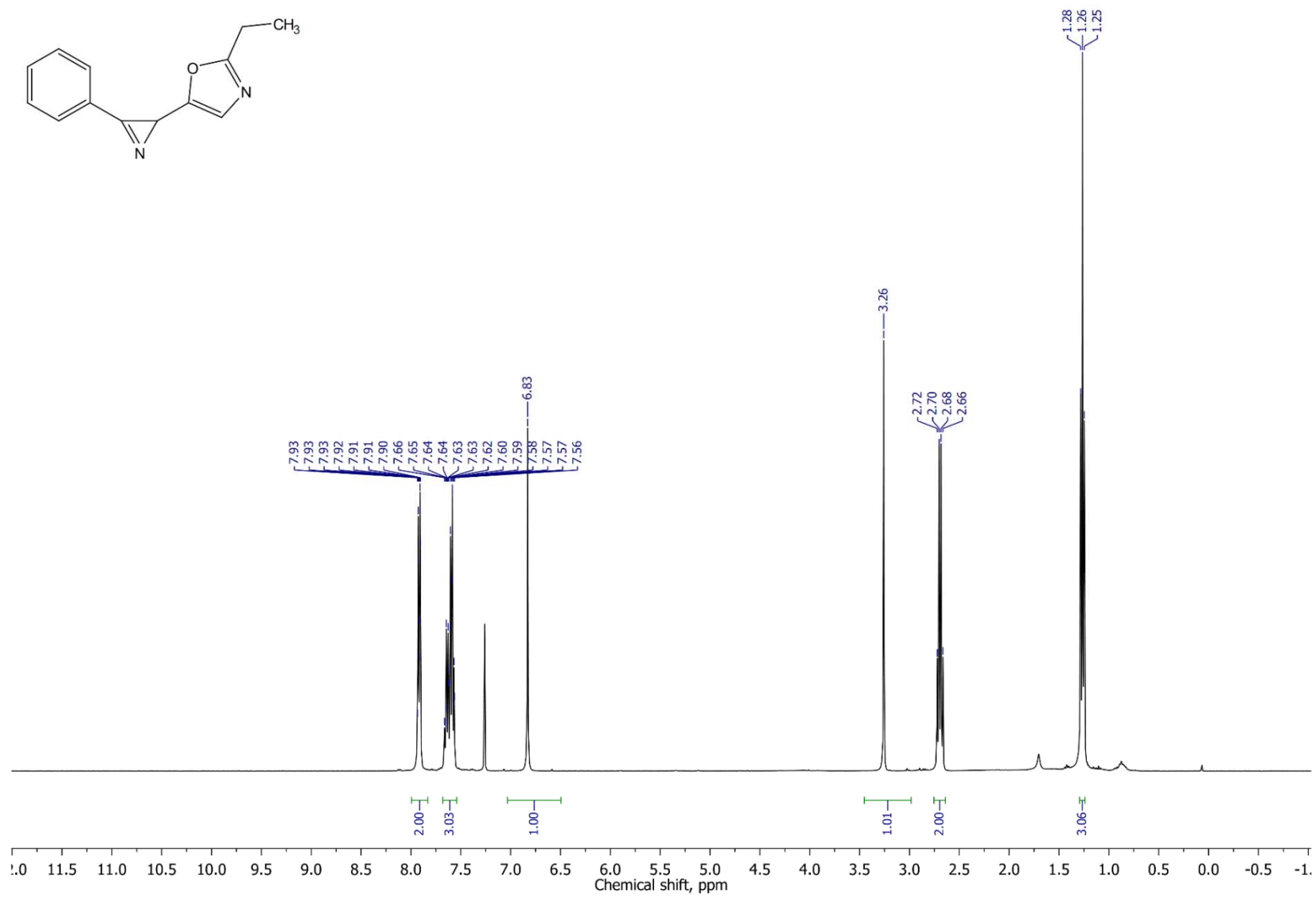
5-(3-(Adamantan-1-yl)-2*H*-azirin-2-yl)-2-methyloxazole 2c, $^{13}\text{C}\{^1\text{H}\}$ NMR, 100 MHz, CDCl_3



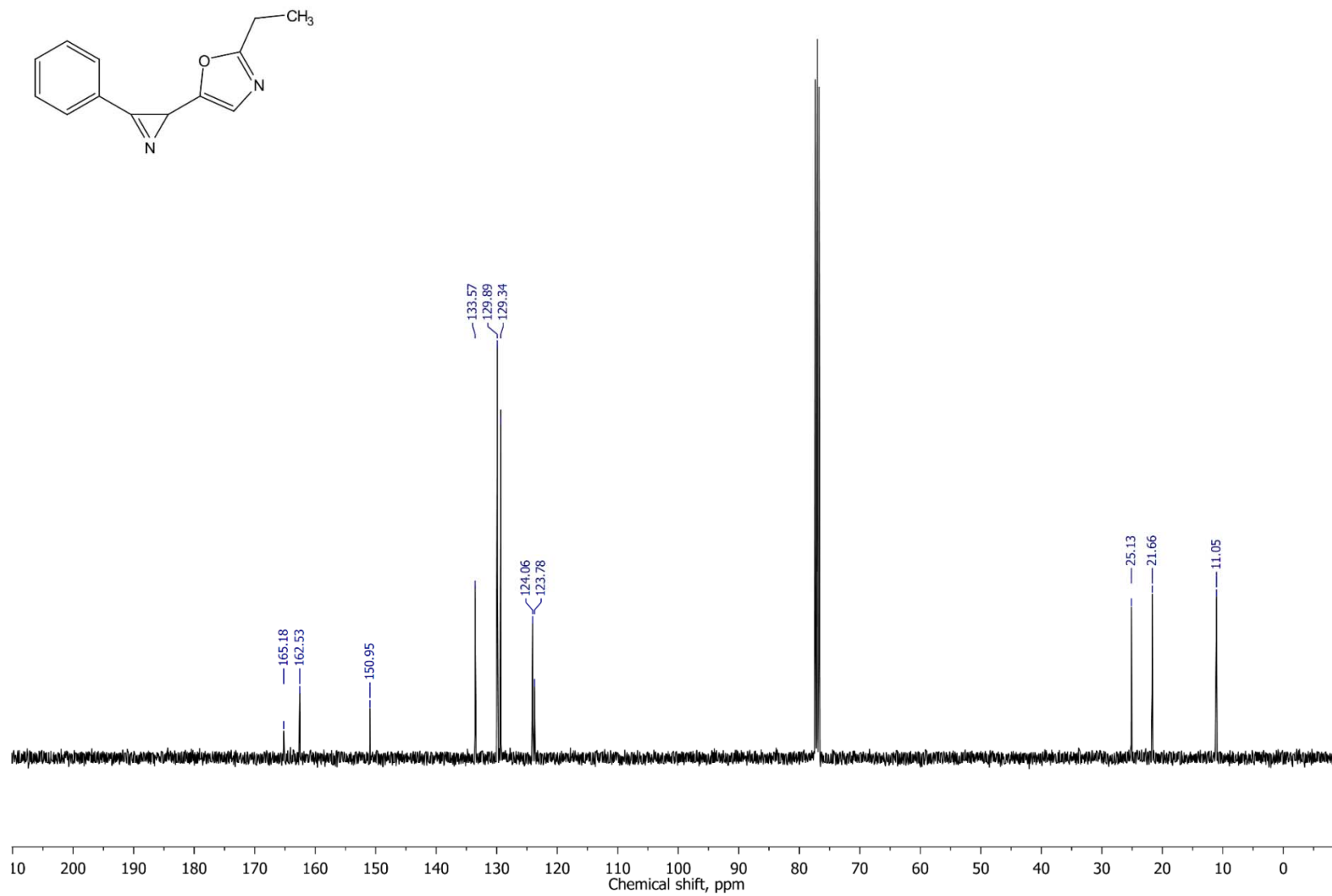
5-(3-(Adamantan-1-yl)-2*H*-azirin-2-yl)-2-methyloxazole 2c, DEPT, 100 MHz, CDCl₃



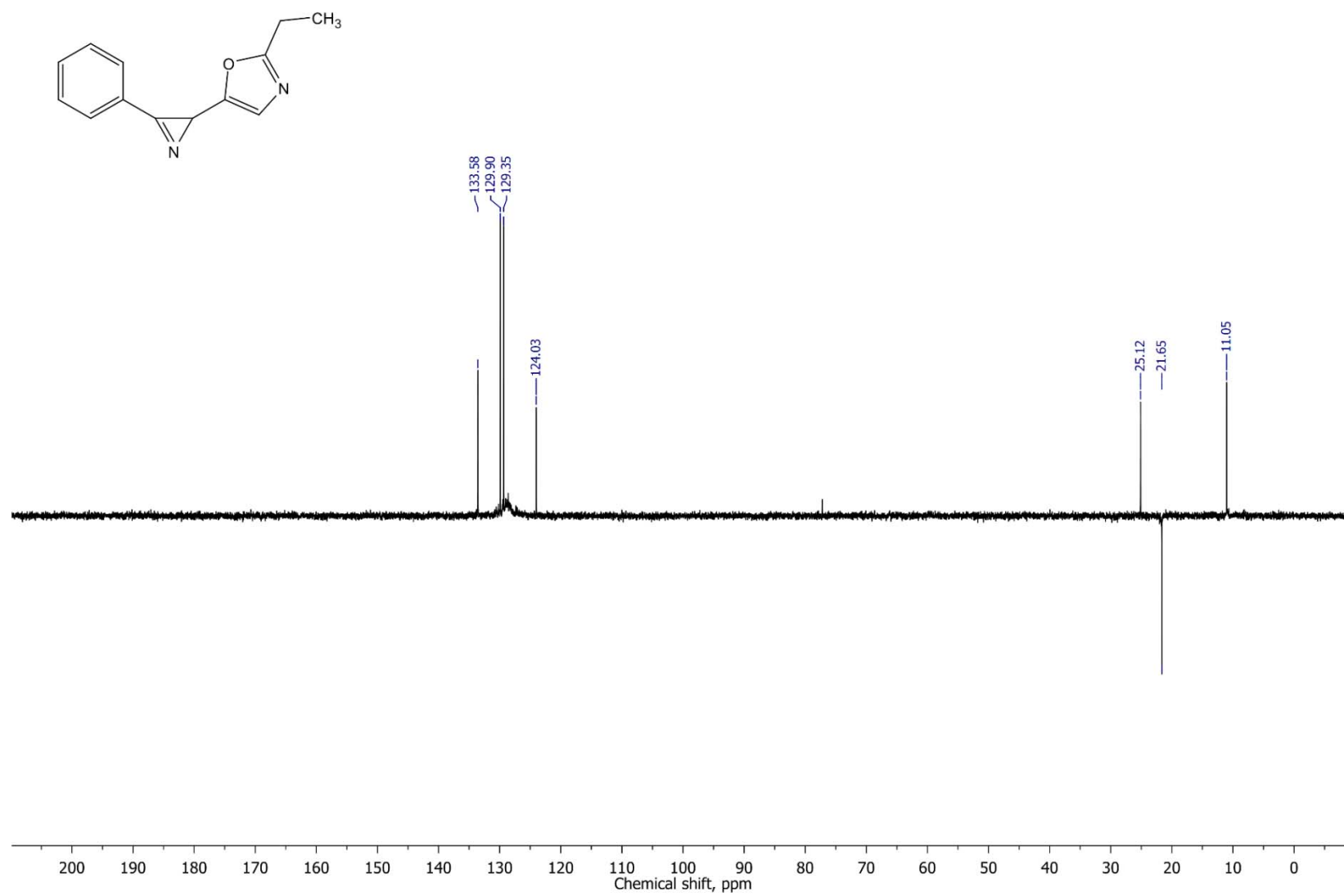
2-Ethyl-5-(3-phenyl-2H-azirin-2-yl)oxazole 2d, ^1H NMR, 400 MHz, CDCl_3



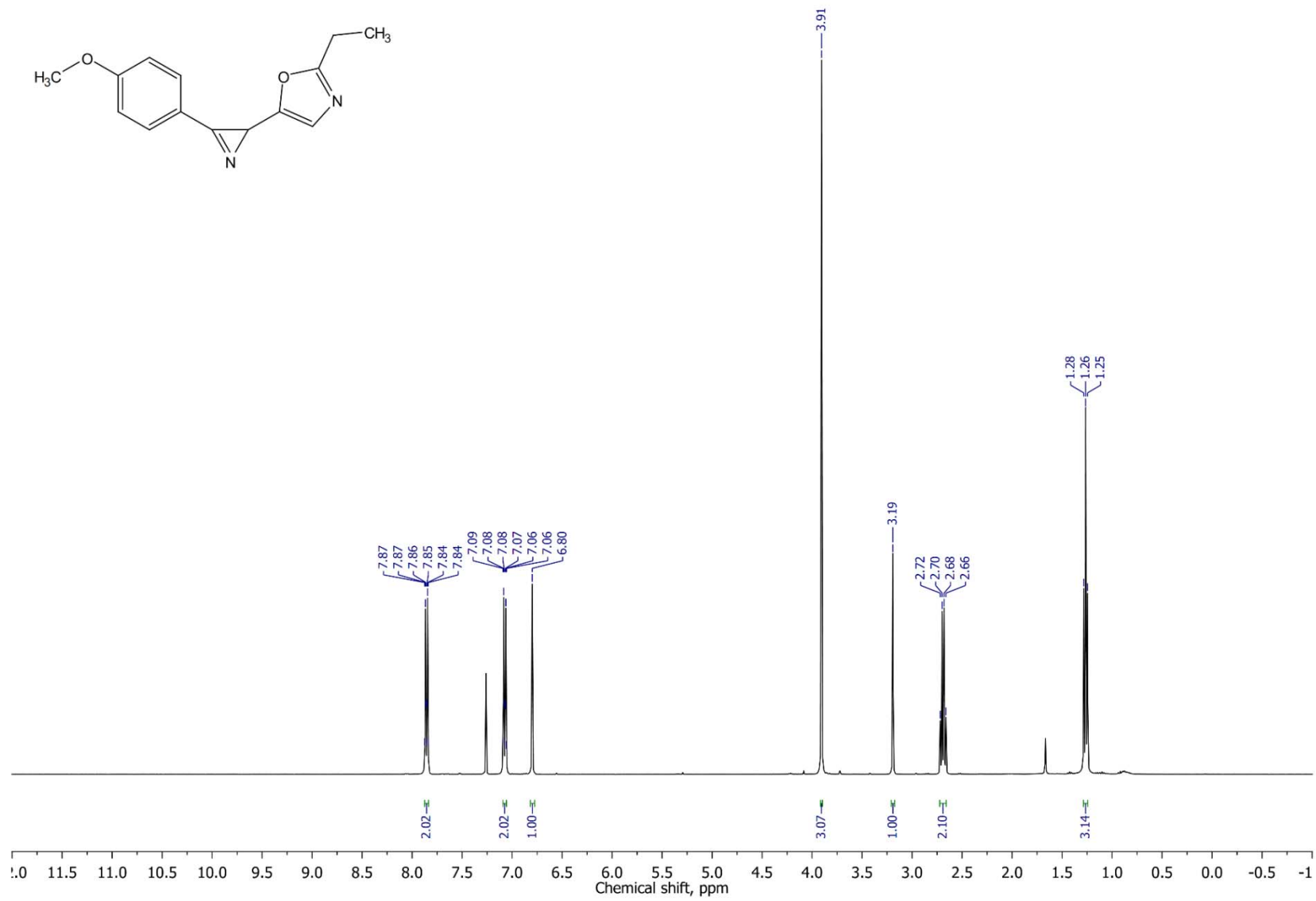
2-Ethyl-5-(3-phenyl-2H-azirin-2-yl)oxazole 2d, $^{13}\text{C}\{^1\text{H}\}$ NMR, 100 MHz, CDCl_3



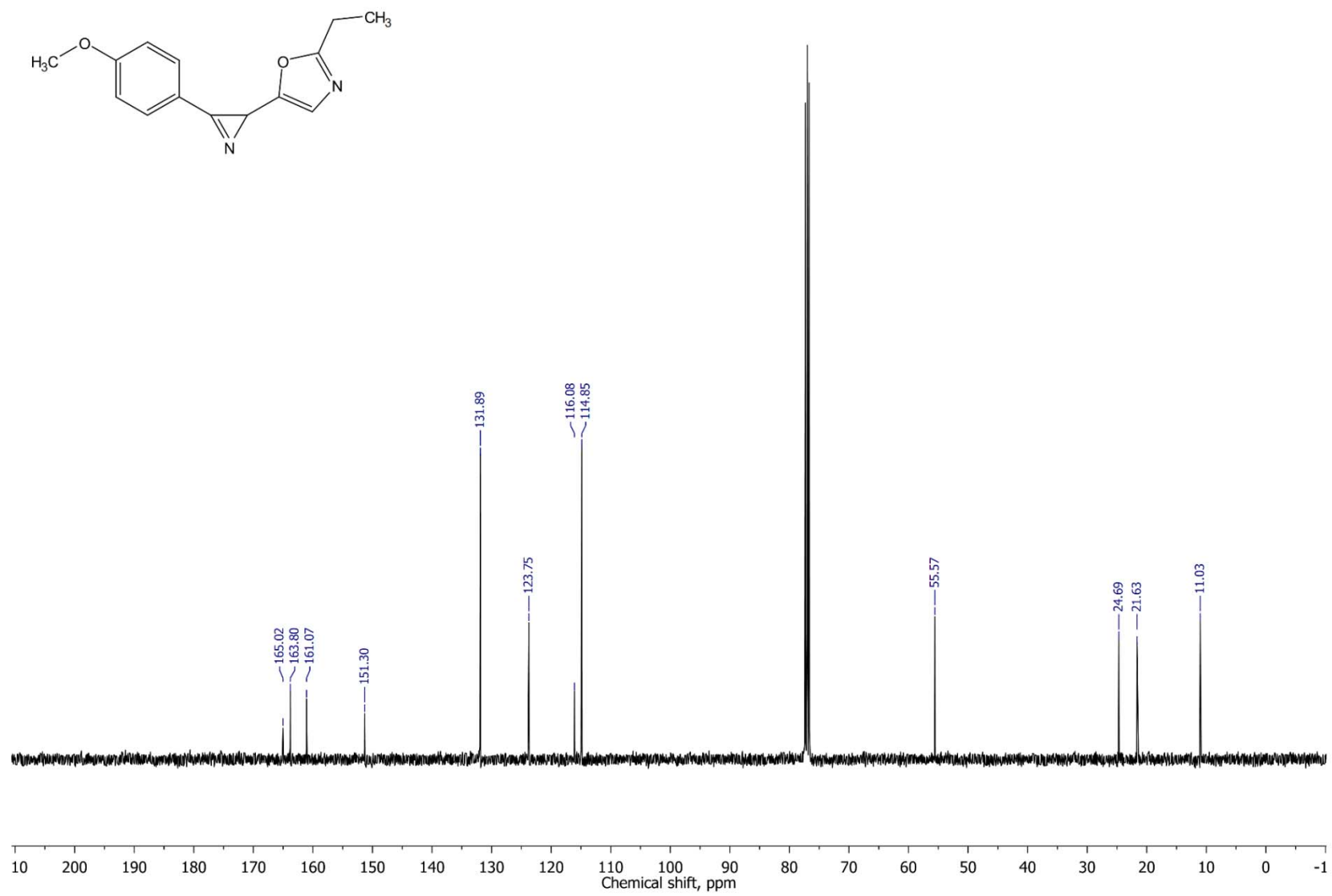
2-Ethyl-5-(3-phenyl-2H-azirin-2-yl)oxazole 2d, DEPT, 100 MHz, CDCl₃



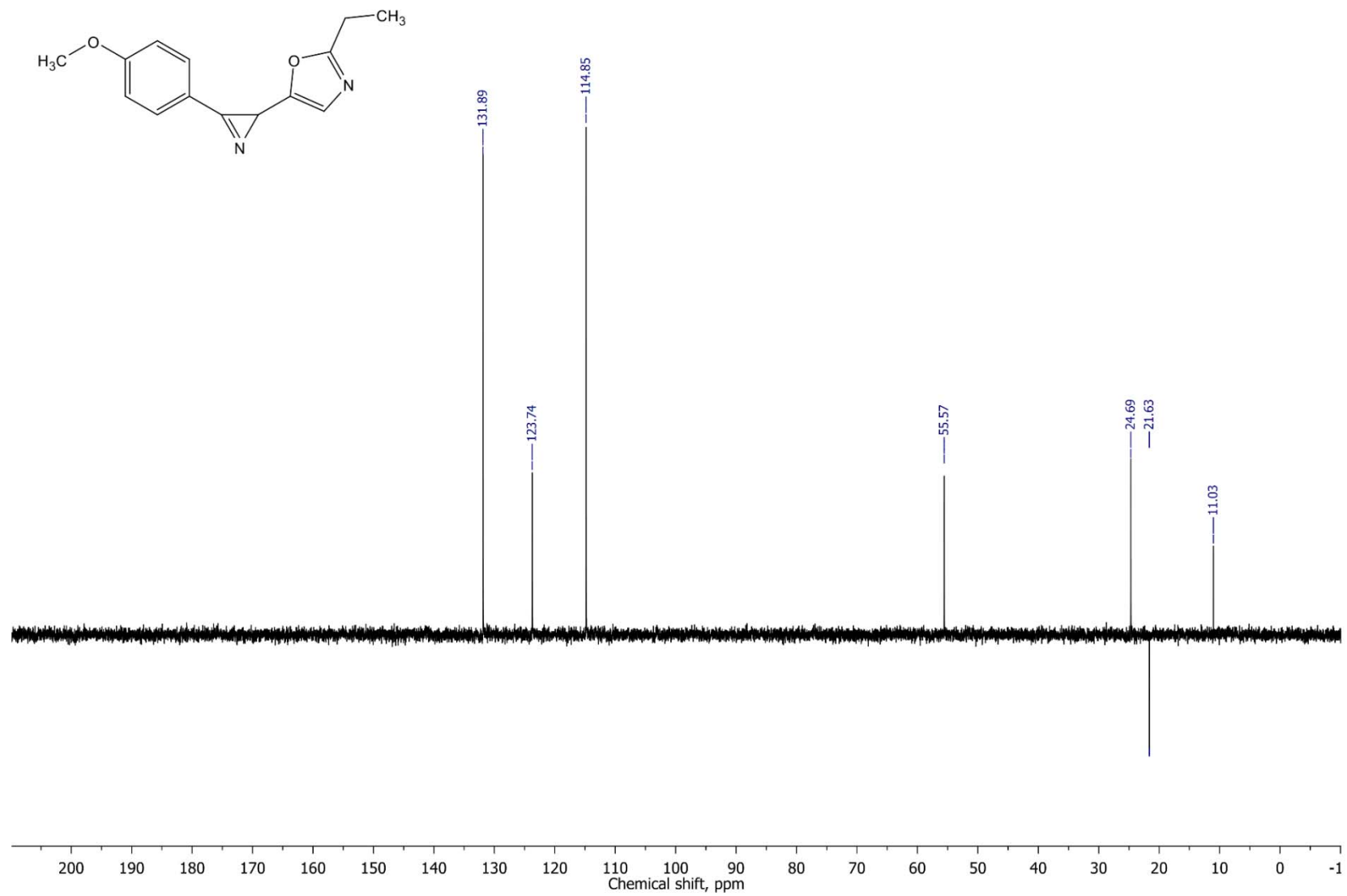
2-Ethyl-5-(3-(4-methoxyphenyl)-2H-azirin-2-yl)oxazole 2e, ^1H NMR, 400 MHz, CDCl_3



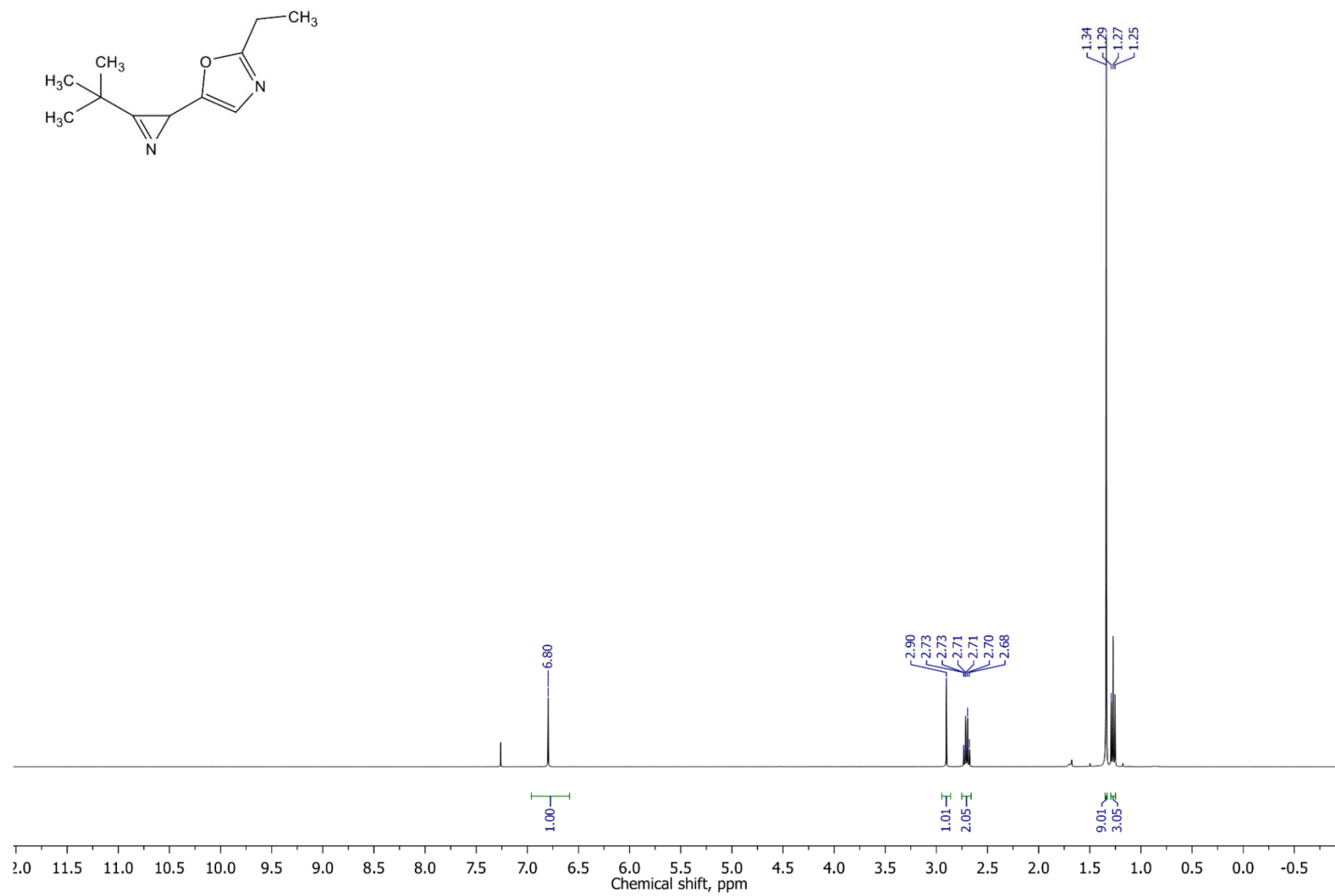
2-Ethyl-5-(3-(4-methoxyphenyl)-2H-azirin-2-yl)oxazole 2e, $^{13}\text{C}\{^1\text{H}\}$ NMR, 100 MHz, CDCl_3



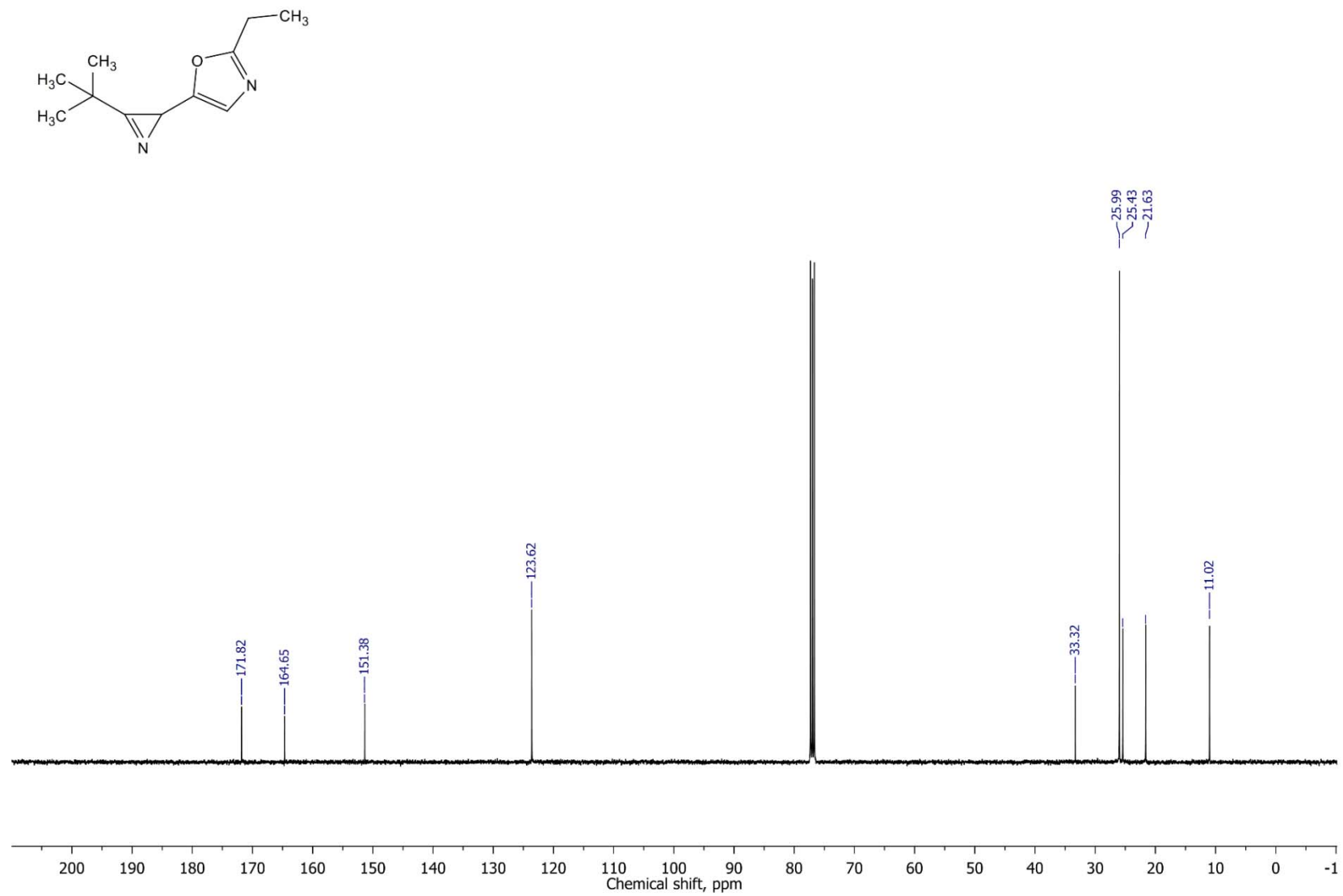
2-Ethyl-5-(3-(4-methoxyphenyl)-2H-azirin-2-yl)oxazole 2e, DEPT, 100 MHz, CDCl₃



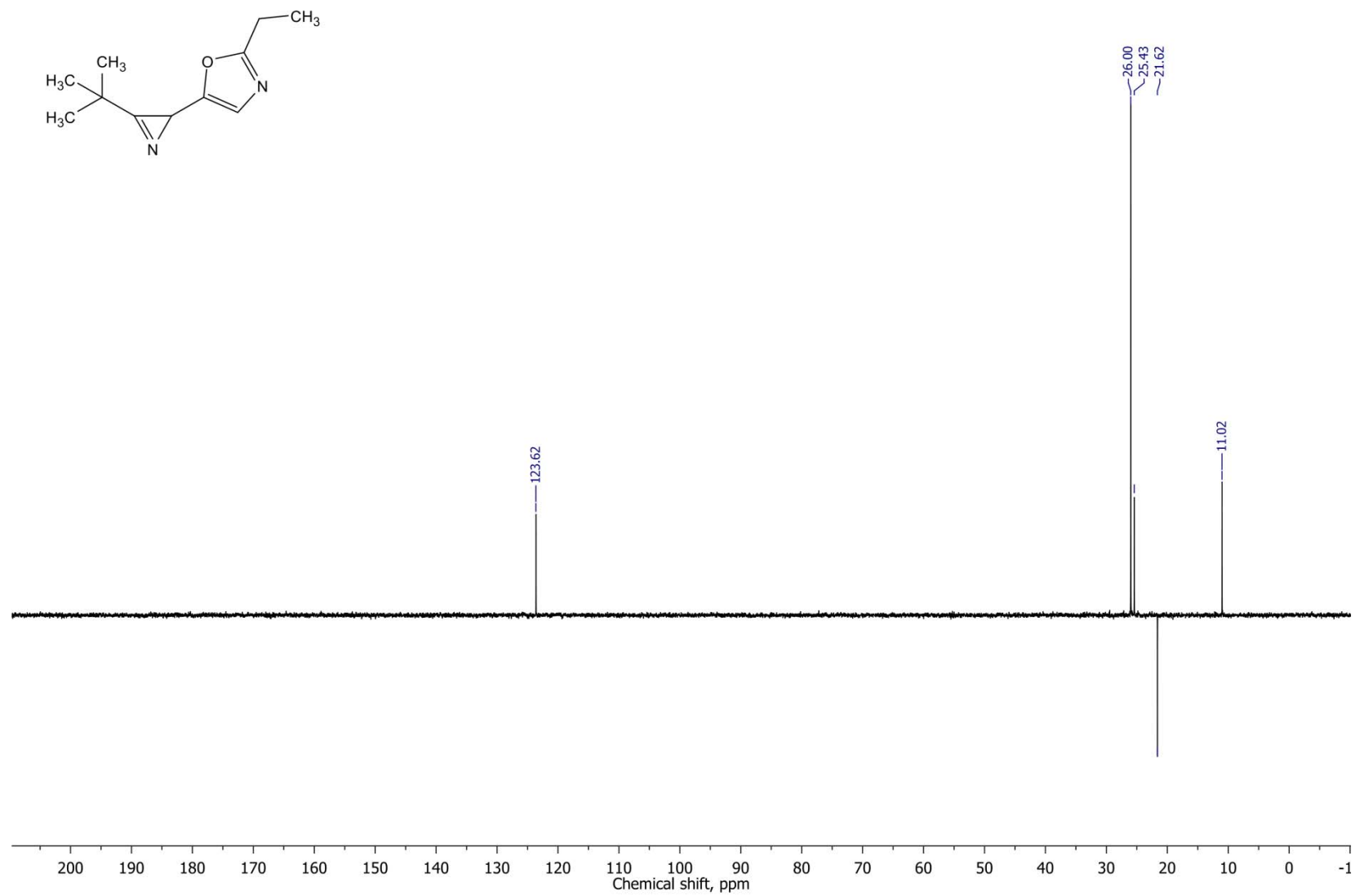
5-(3-(*tert*-Butyl)-2*H*-azirin-2-yl)-2-ethyloxazole 2f, ^1H NMR, 400 MHz, CDCl_3



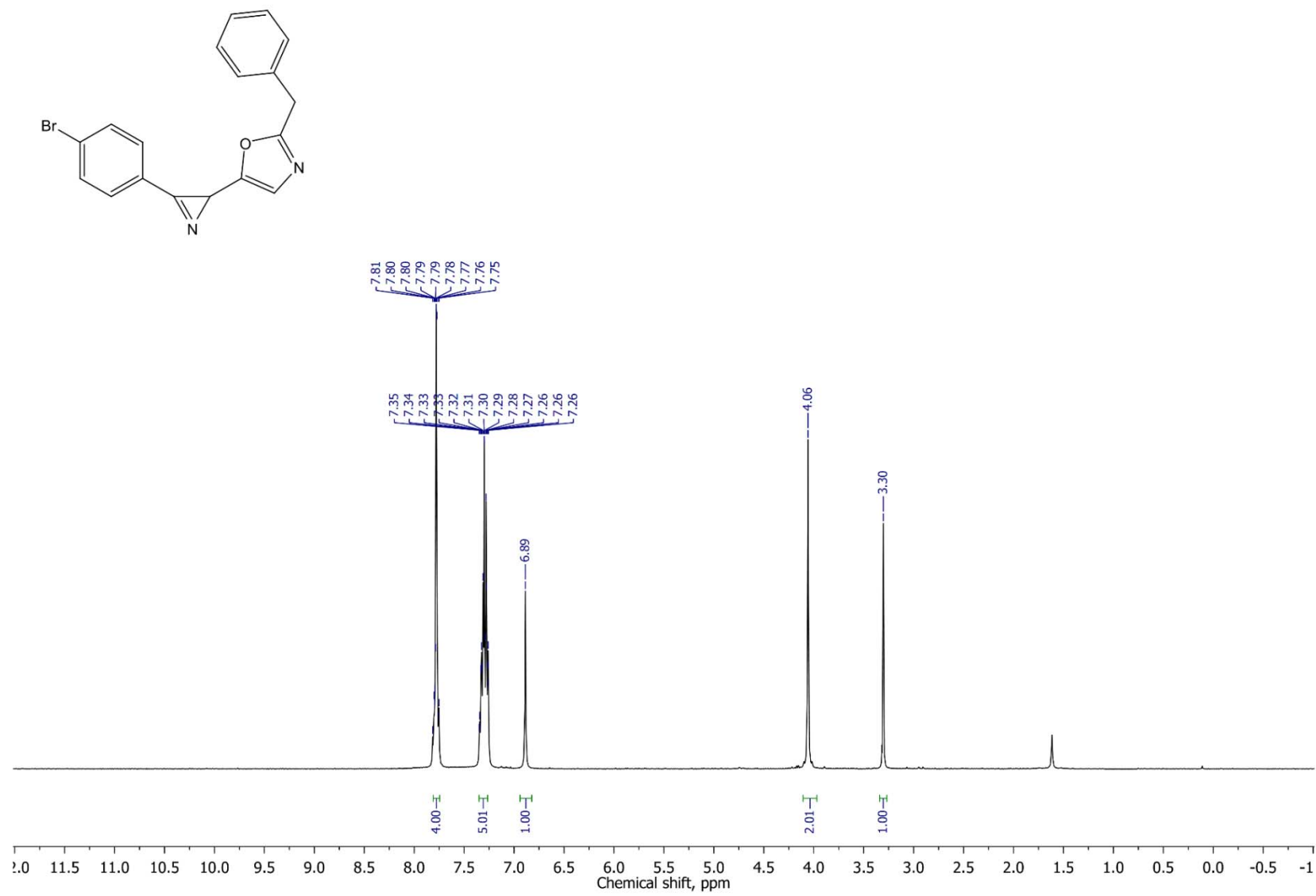
5-(3-(*tert*-Butyl)-2*H*-azirin-2-yl)-2-ethyloxazole 2f, $^{13}\text{C}\{^1\text{H}\}$ NMR, 100 MHz, CDCl_3



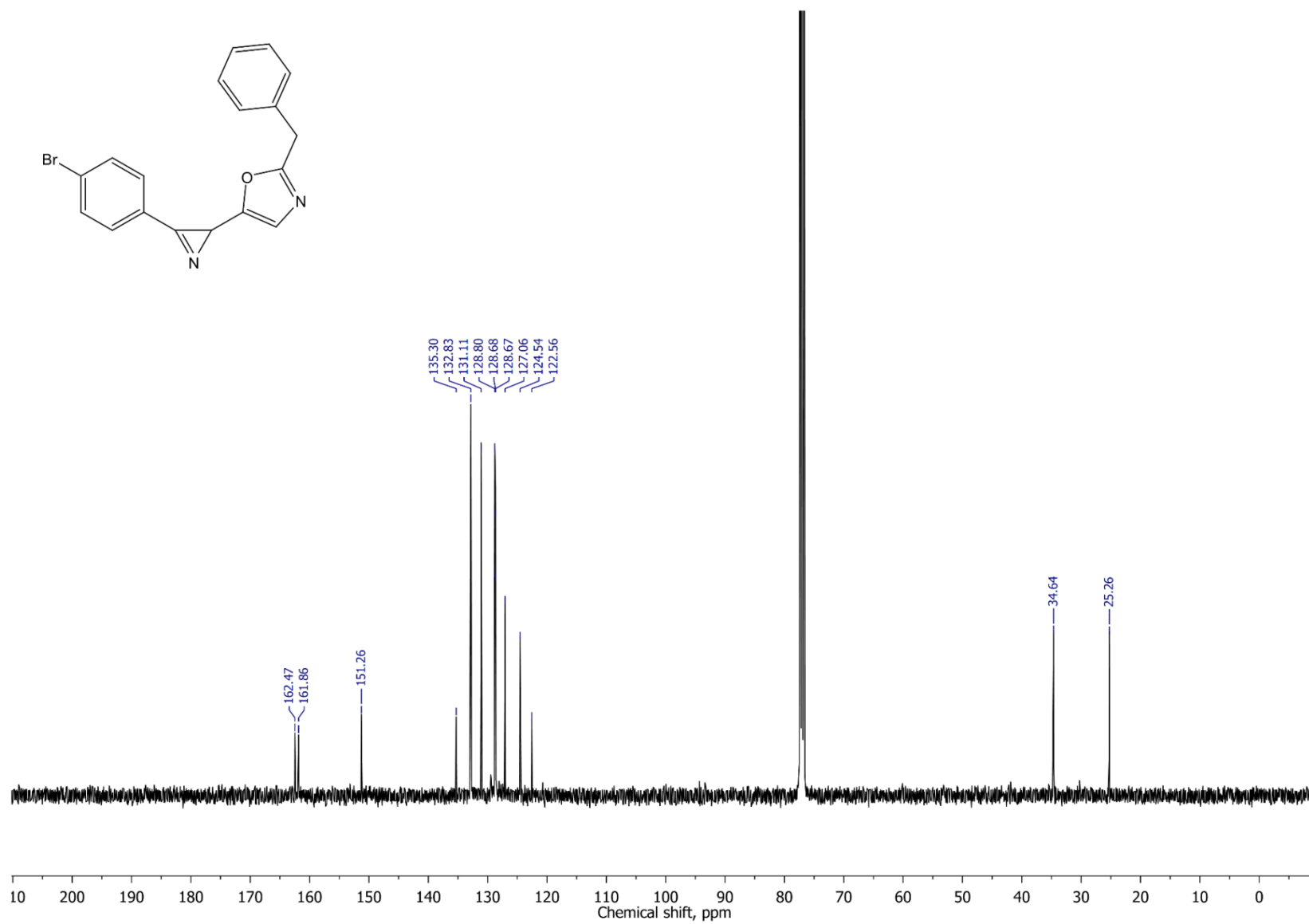
5-(3-(*tert*-Butyl)-2*H*-azirin-2-yl)-2-ethyloxazole 2f, DEPT, 100 MHz, CDCl₃



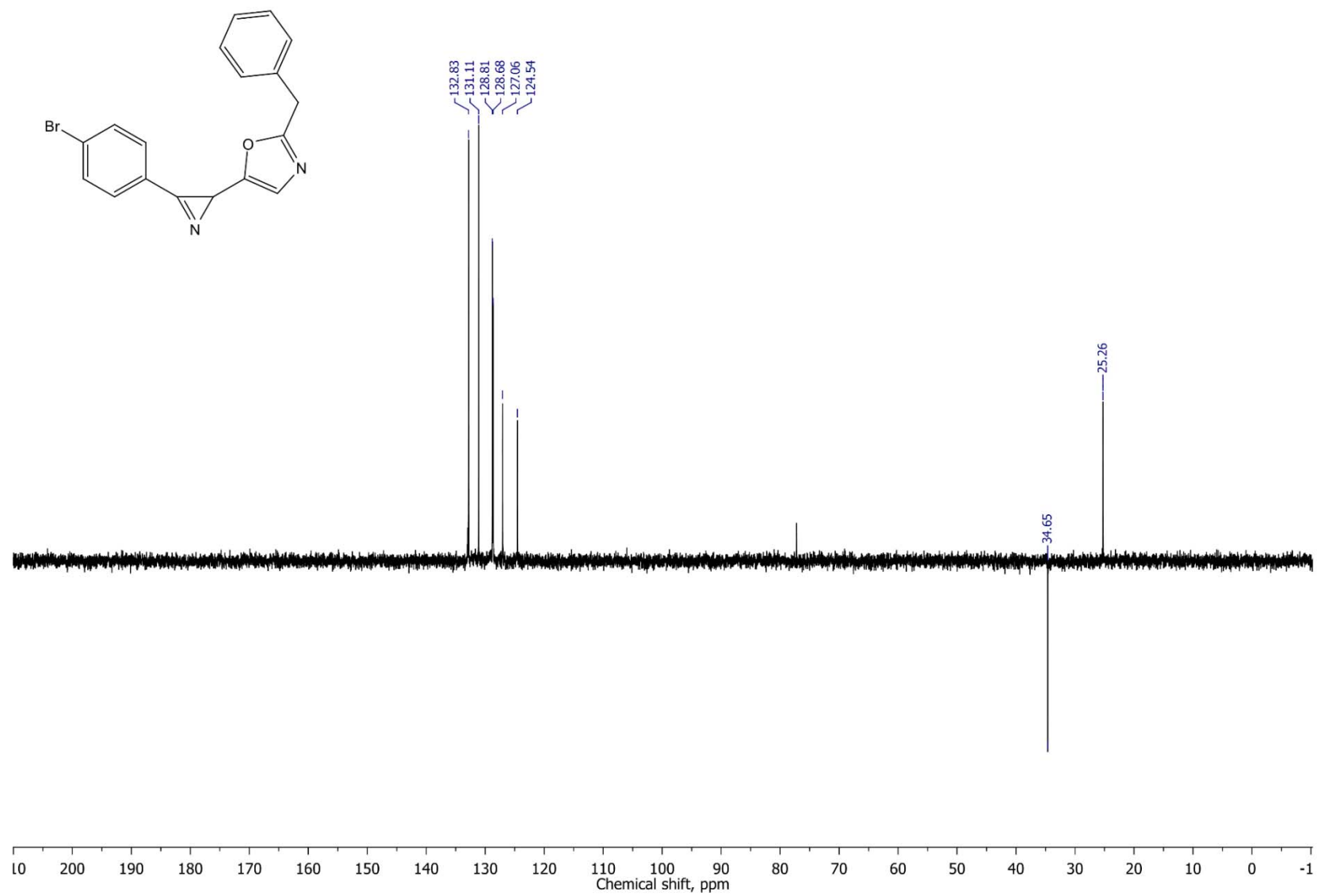
2-Benzyl-5-(3-(4-bromophenyl)-2H-azirin-2-yl)oxazole 2g, ^1H NMR, 400 MHz, CDCl_3



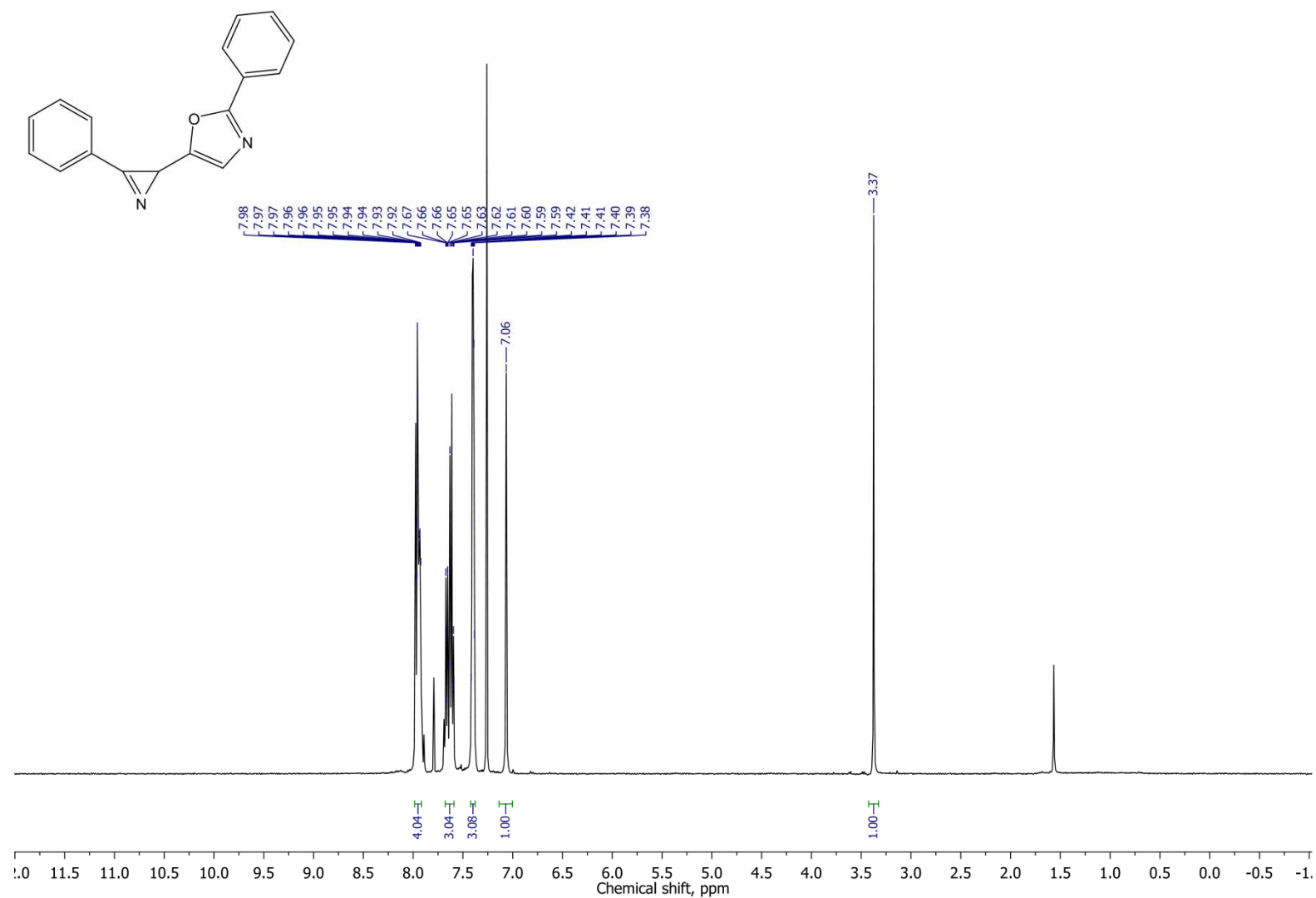
2-Benzyl-5-(3-(4-bromophenyl)-2H-azirin-2-yl)oxazole 2g, $^{13}\text{C}\{^1\text{H}\}$ NMR, 100 MHz, CDCl_3



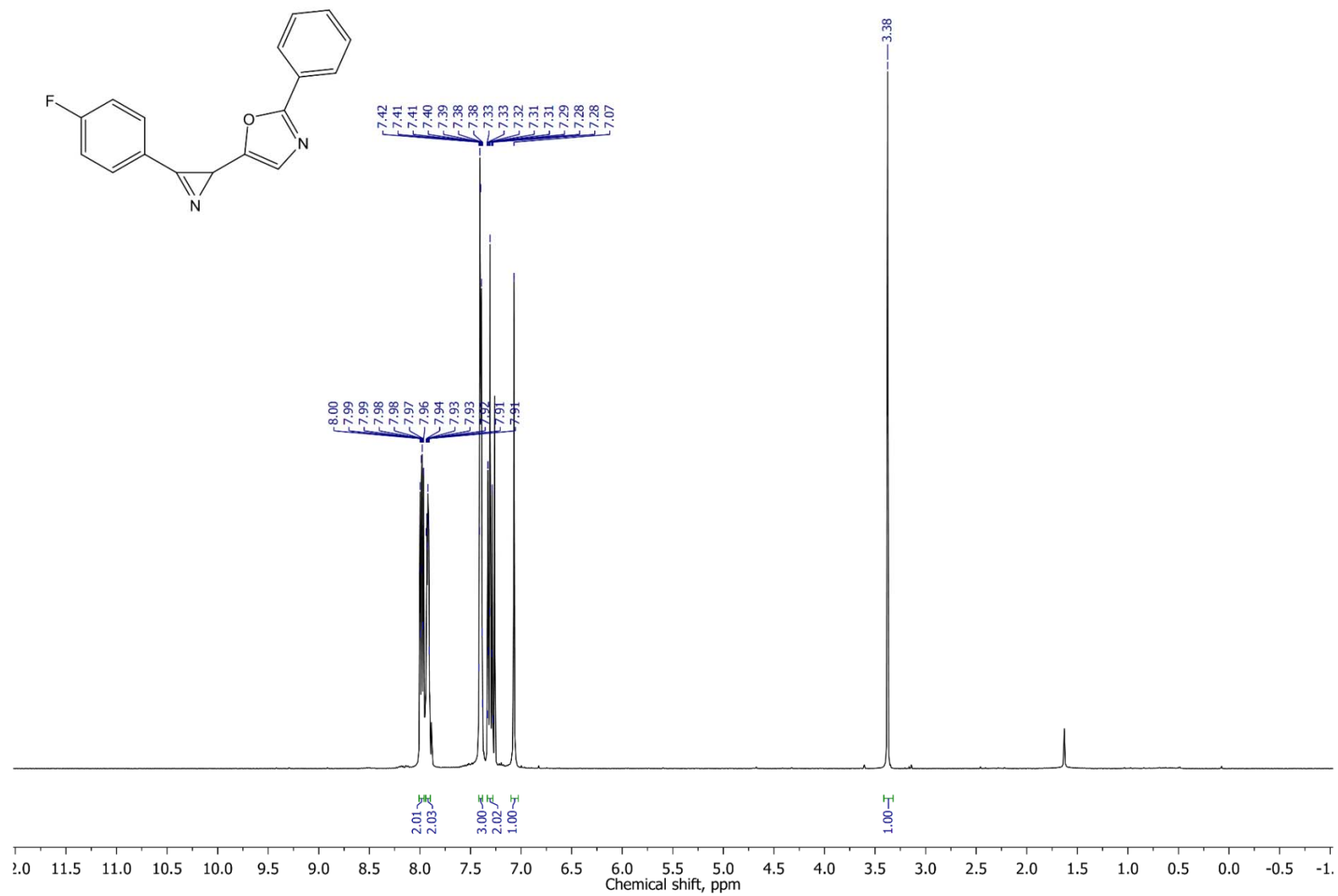
2-Benzyl-5-(3-(4-bromophenyl)-2H-azirin-2-yl)oxazole 2g, DEPT, 100 MHz, CDCl₃



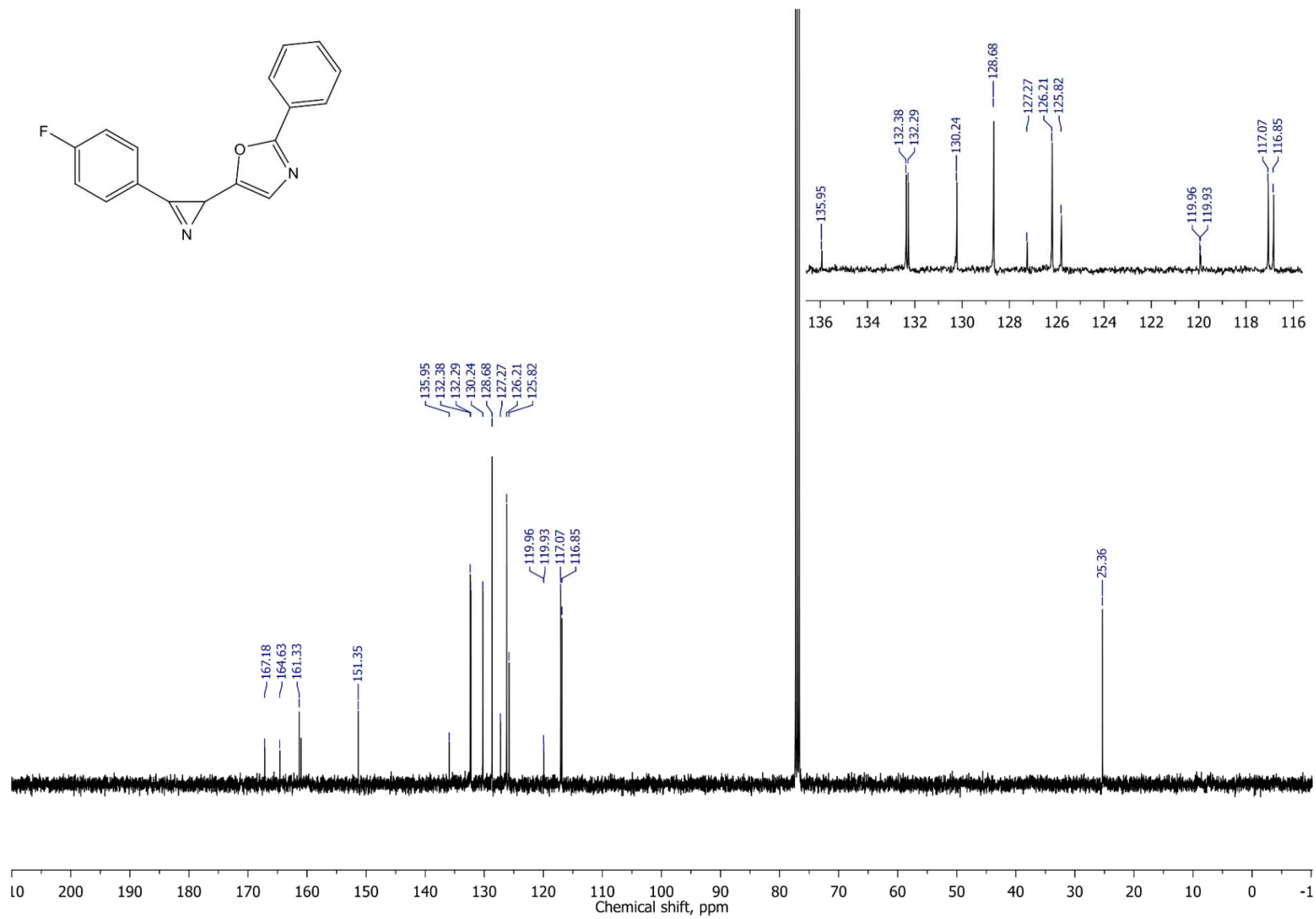
2-Phenyl-5-(3-phenyl-2H-azirin-2-yl)oxazole 2h, ^1H NMR, 400 MHz, CDCl_3



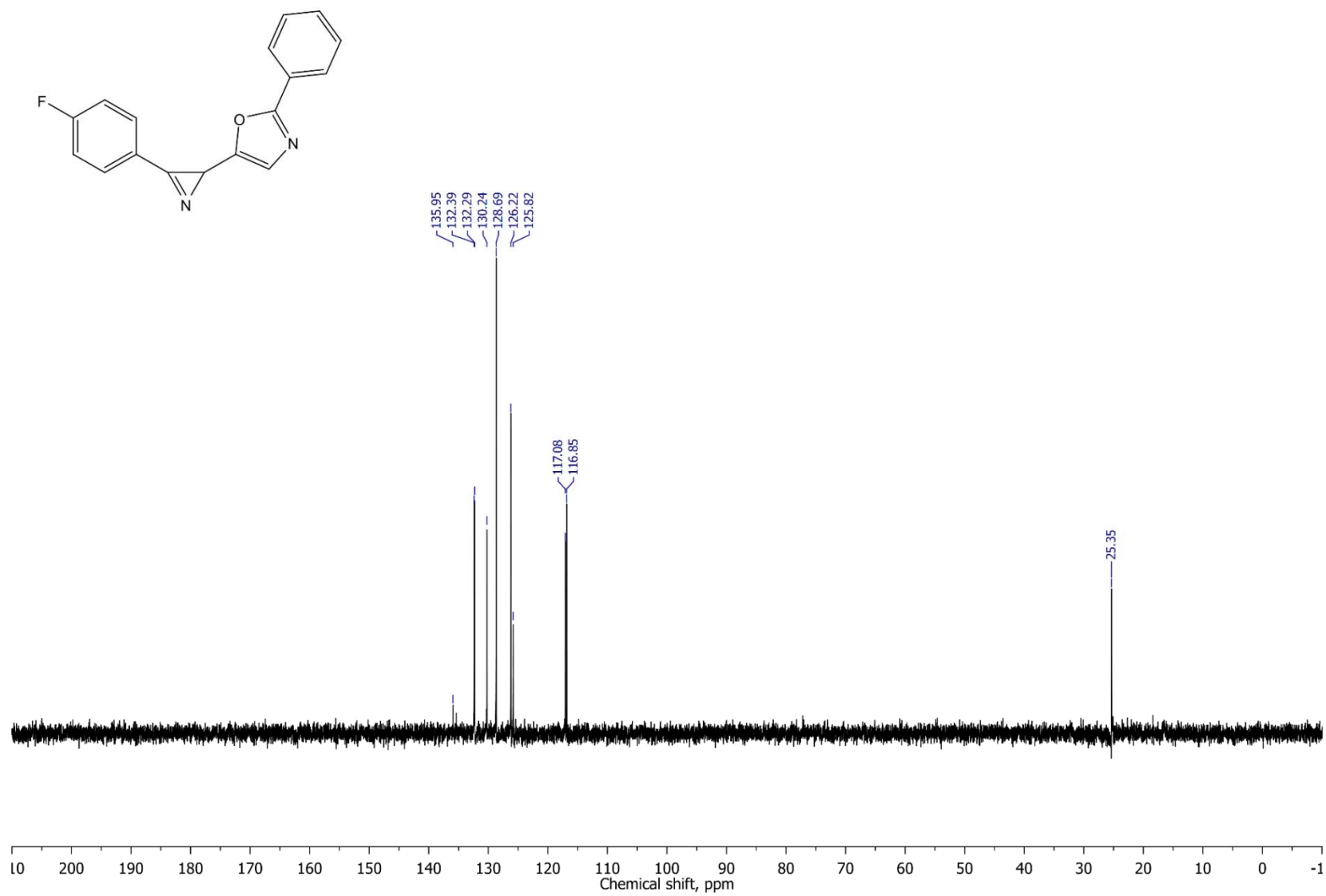
5-(3-(4-Fluorophenyl)-2H-azirin-2-yl)-2-phenyloxazole 2i, ^1H NMR, 400 MHz, CDCl_3



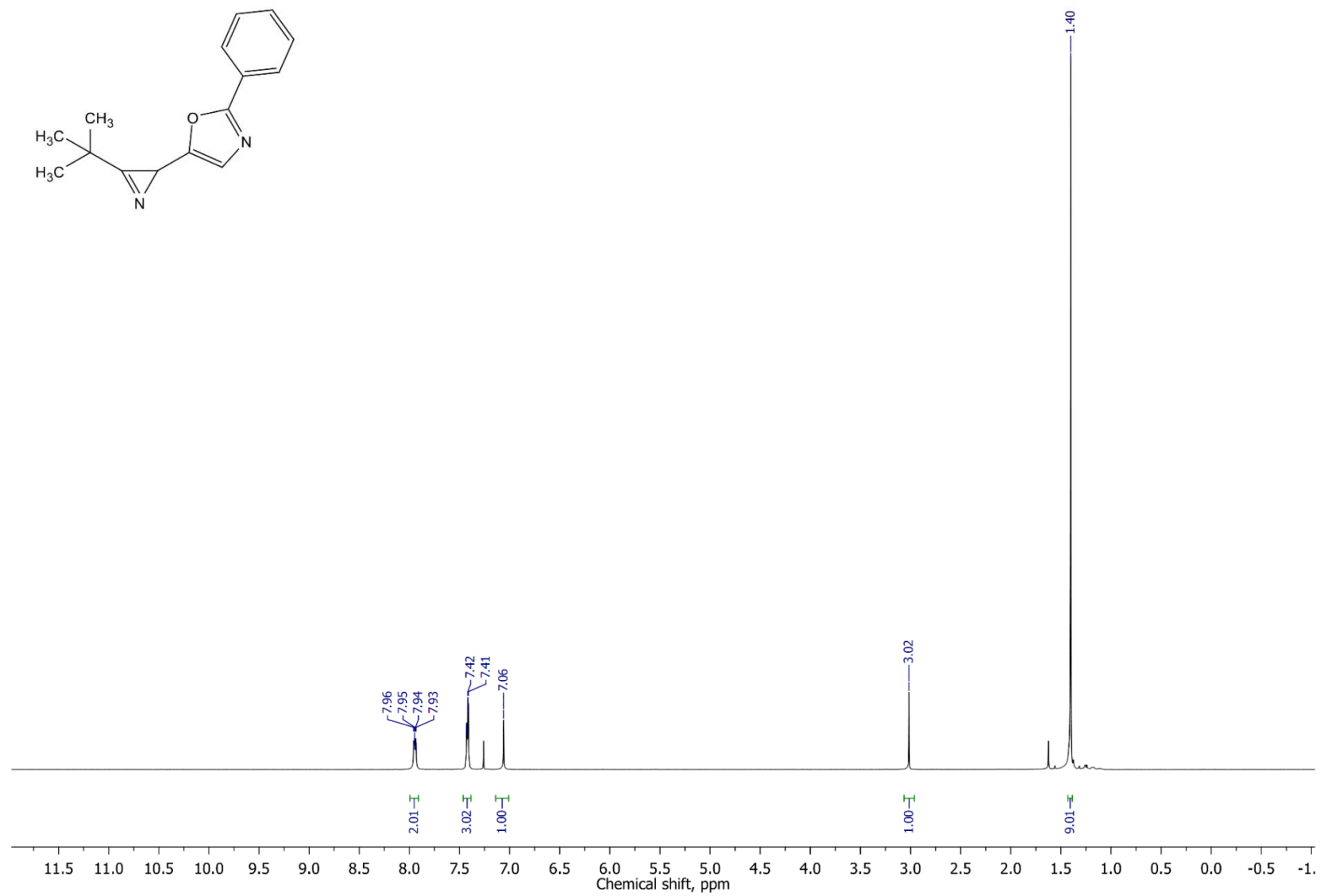
5-(3-(4-Fluorophenyl)-2H-azirin-2-yl)-2-phenyloxazole 2i, $^{13}\text{C}\{^1\text{H}\}$ NMR, 100 MHz, CDCl_3



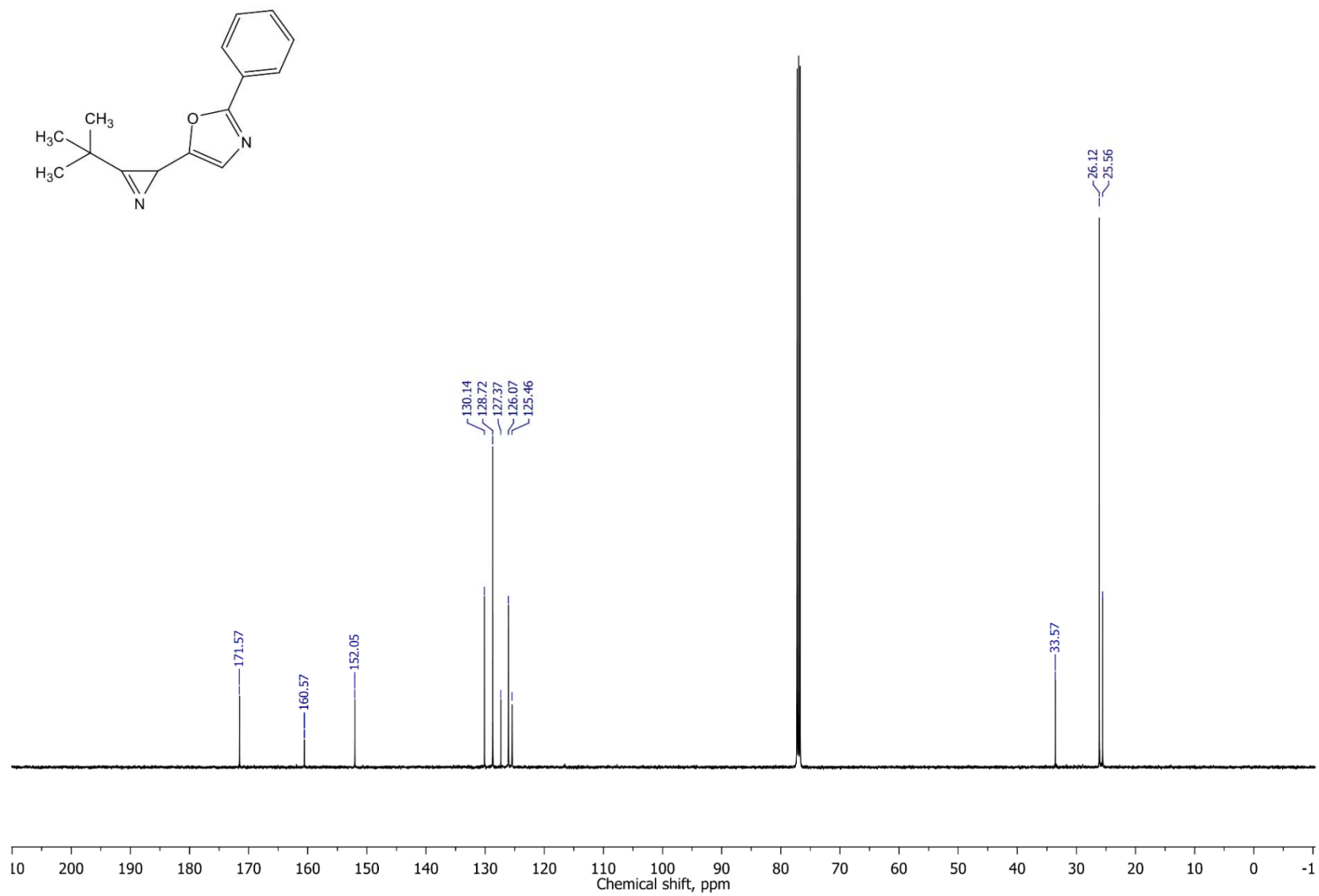
5-(3-(4-Fluorophenyl)-2H-azirin-2-yl)-2-phenyloxazole 2i, DEPT, 100 MHz, CDCl₃



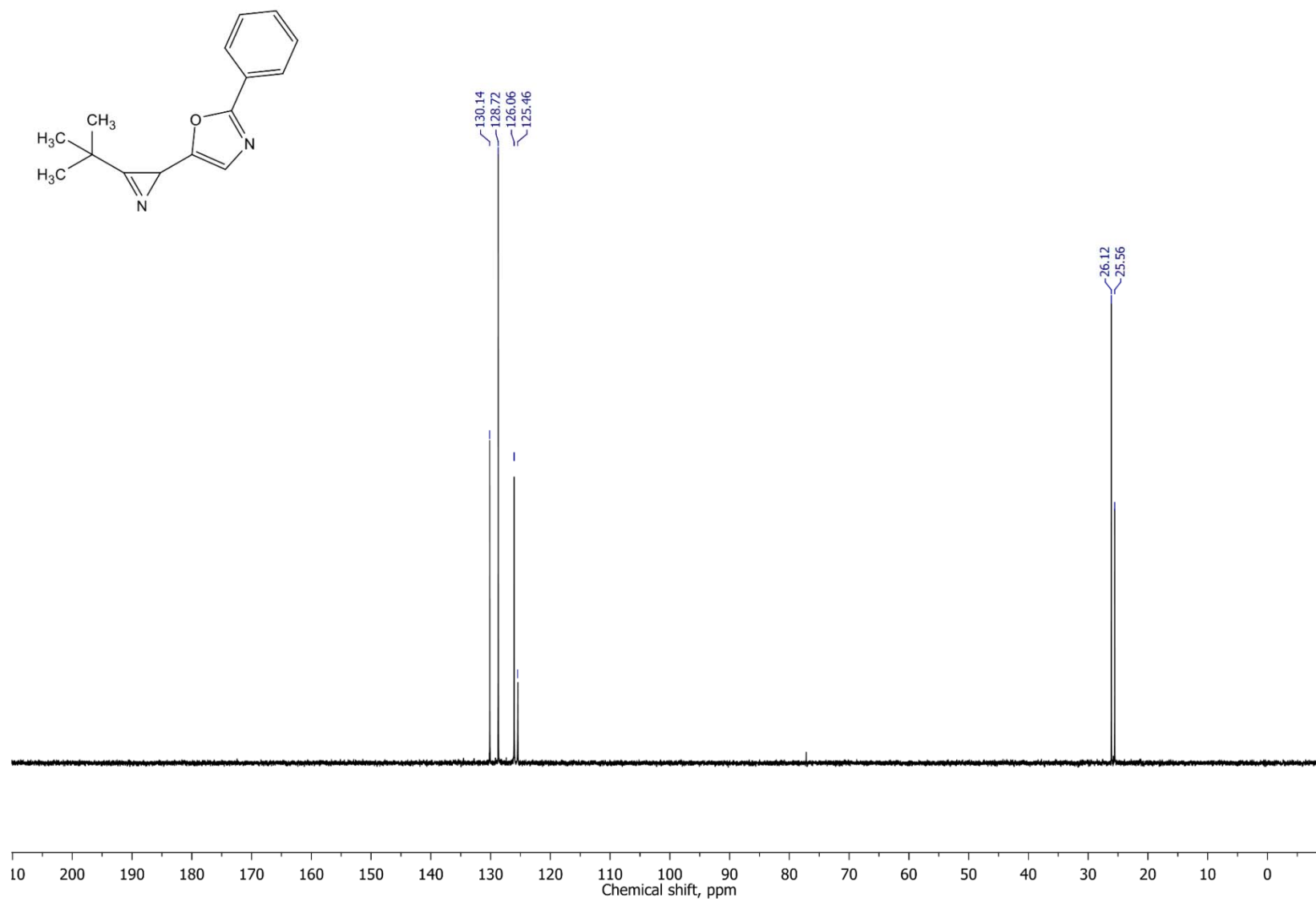
5-(3-(*tert*-Butyl)-2*H*-azirin-2-yl)-2-phenyloxazole 2j, ^1H NMR, 400 MHz, CDCl_3



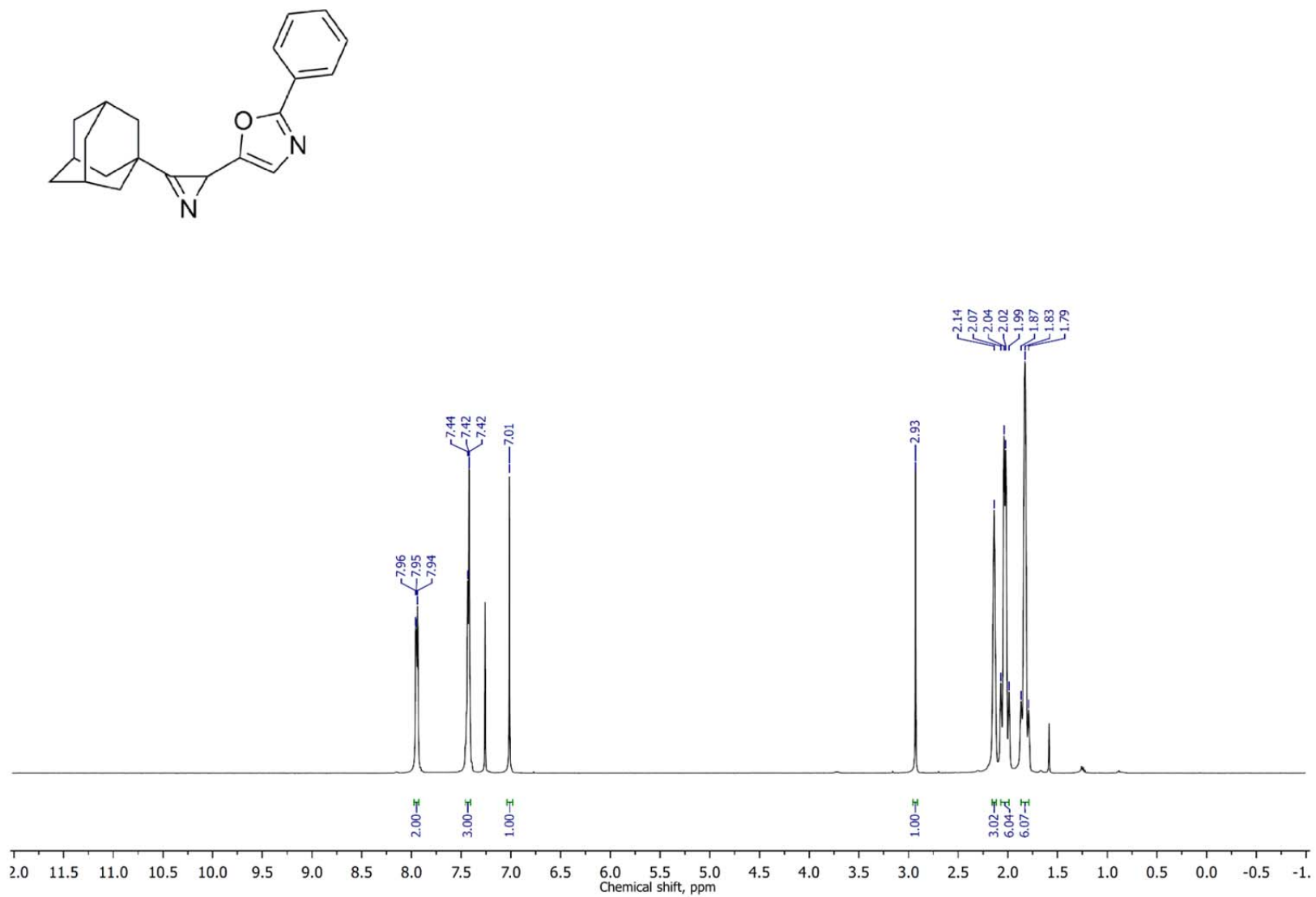
5-(3-(*tert*-Butyl)-2*H*-azirin-2-yl)-2-phenyloxazole 2j, $^{13}\text{C}\{^1\text{H}\}$ NMR, 100 MHz, CDCl_3



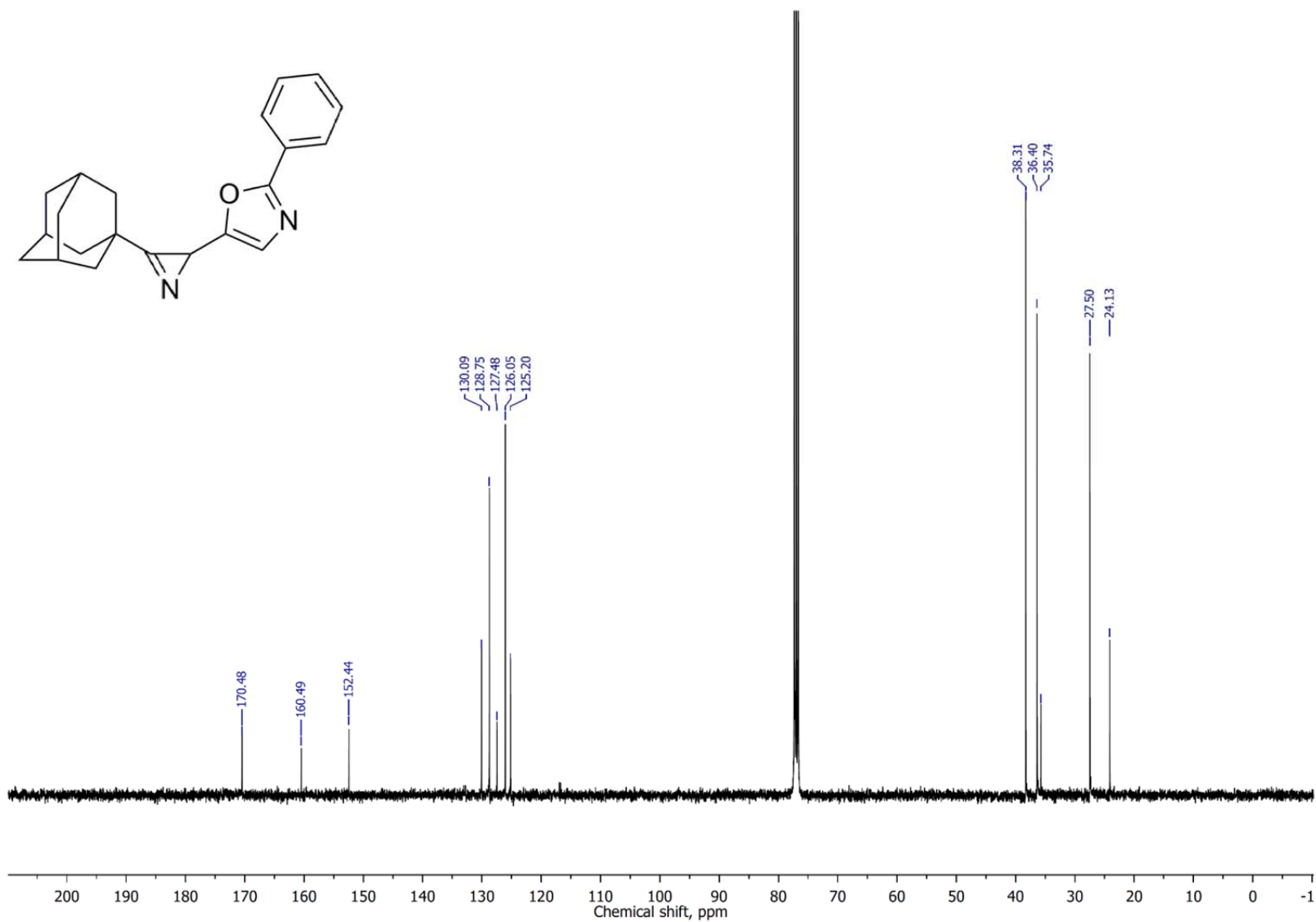
5-(3-(*tert*-Butyl)-2*H*-azirin-2-yl)-2-phenyloxazole 2j, DEPT, 100 MHz, CDCl₃



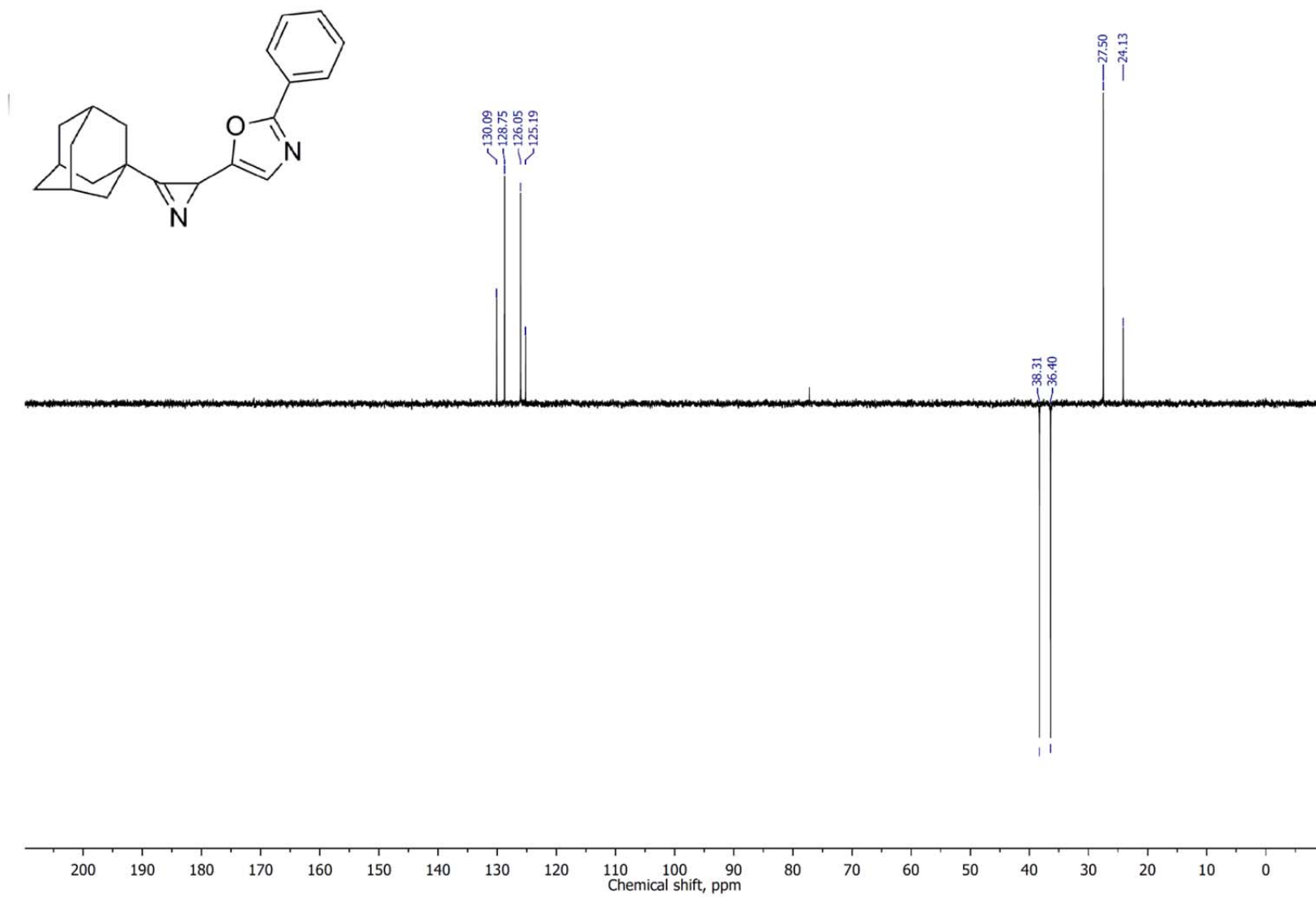
5-(3-(Adamantan-1-yl)-2*H*-azirin-2-yl)-2-phenyloxazole 2k, ¹H NMR, 400 MHz, CDCl₃



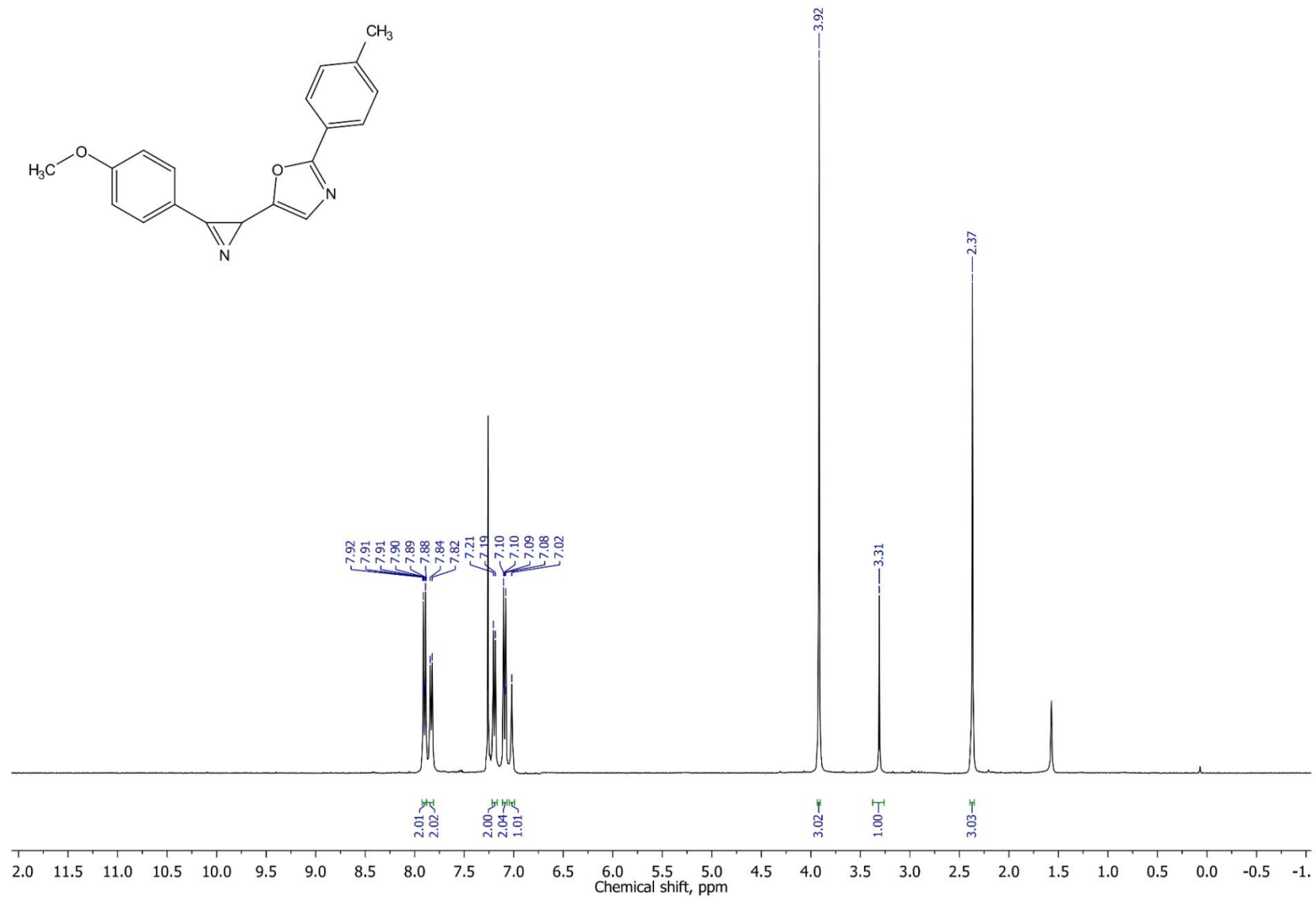
5-(3-(Adamantan-1-yl)-2H-azirin-2-yl)-2-phenyloxazole 2k, $^{13}\text{C}\{^1\text{H}\}$ NMR, 100 MHz, CDCl_3



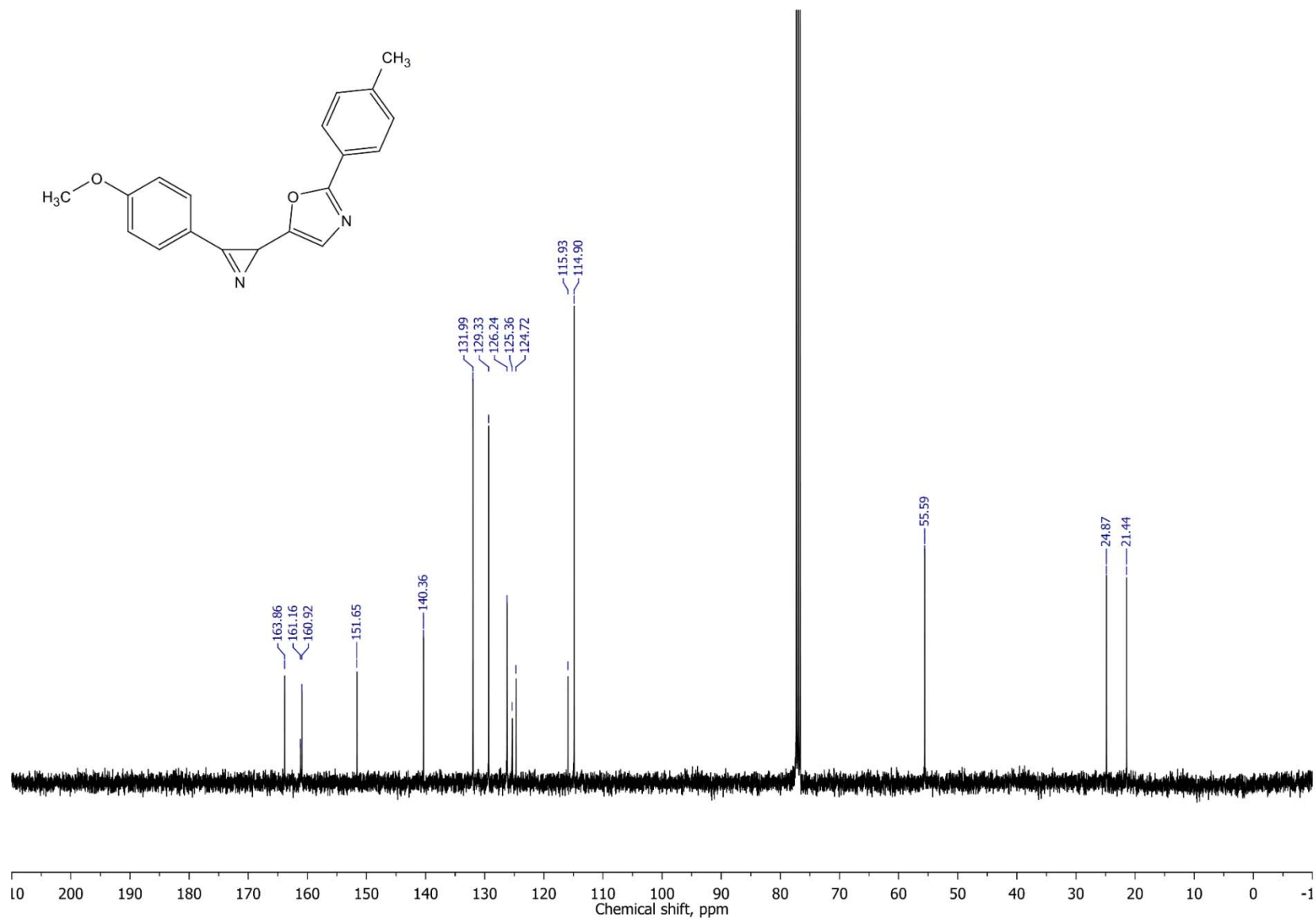
5-(3-(Adamantan-1-yl)-2*H*-azirin-2-yl)-2-phenyloxazole 2k, DEPT, 100 MHz, CDCl₃



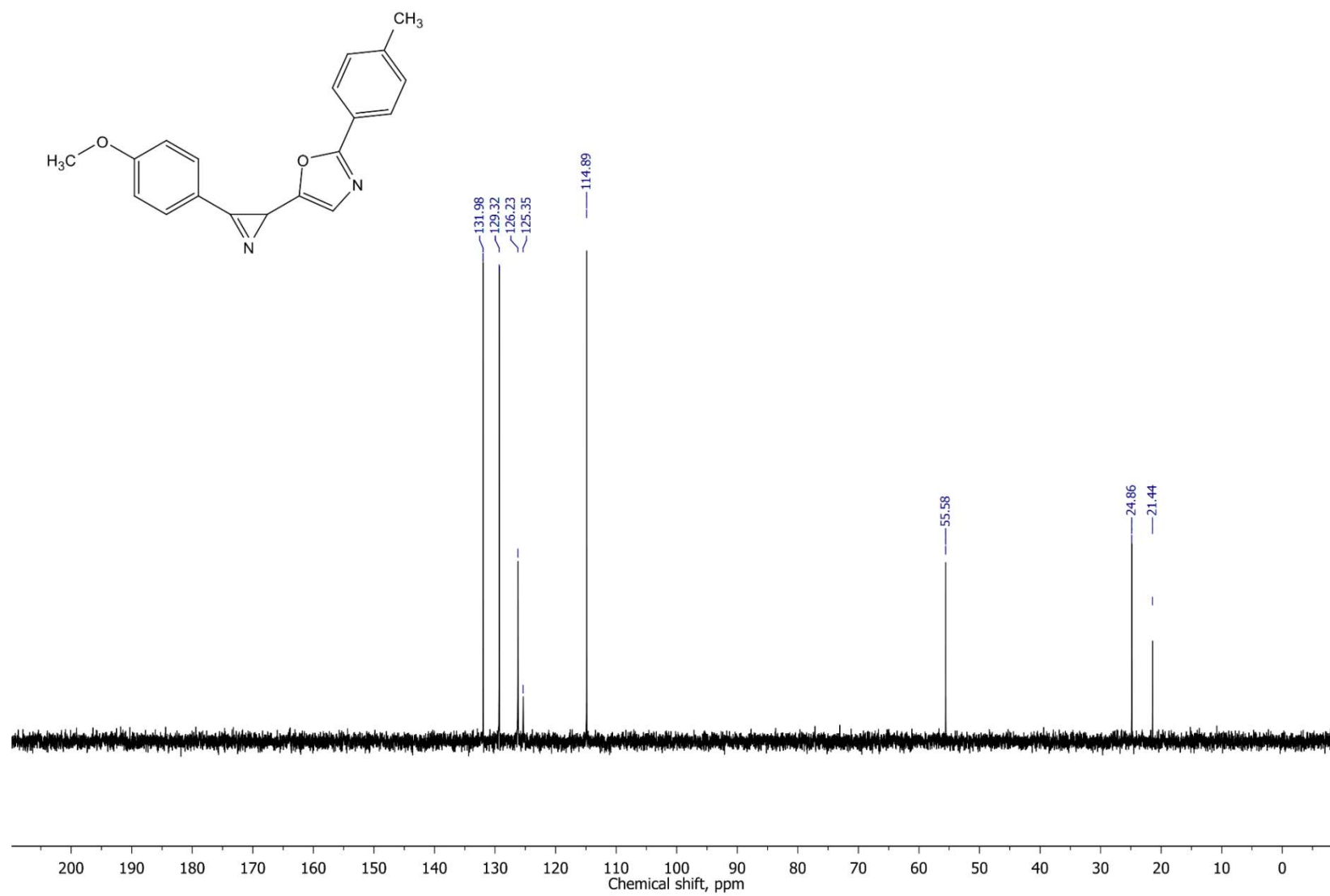
5-(3-(4-Methoxyphenyl)-2H-azirin-2-yl)-2-(*p*-tolyl)oxazole 2l, ^1H NMR, 400 MHz, CDCl_3



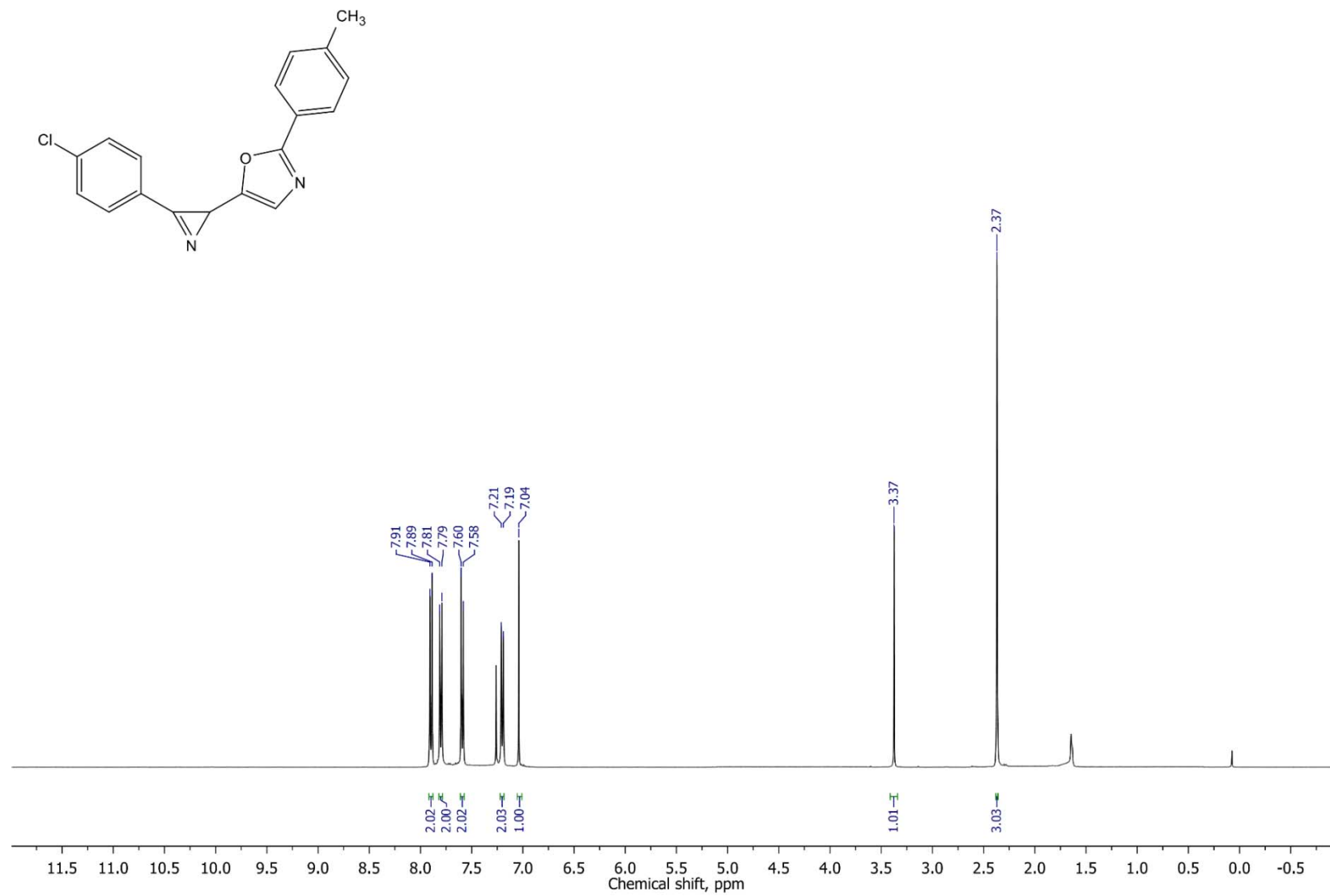
5-(3-(4-Methoxyphenyl)-2*H*-azirin-2-yl)-2-(*p*-tolyl)oxazole 2l, $^{13}\text{C}\{^1\text{H}\}$ NMR, 100 MHz, CDCl_3



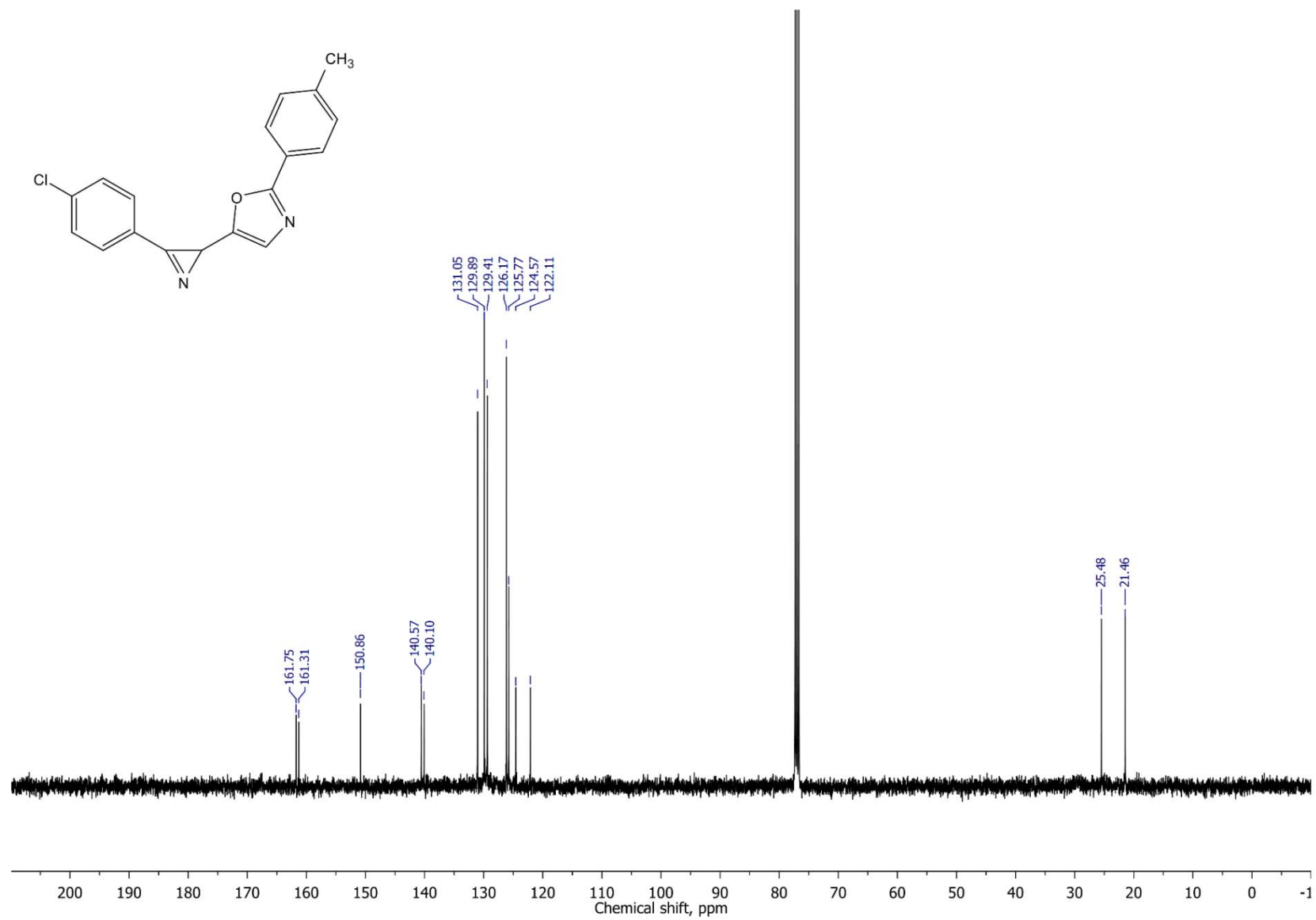
5-(3-(4-Methoxyphenyl)-2*H*-azirin-2-yl)-2-(*p*-tolyl)oxazole 2l, DEPT, 100 MHz, CDCl₃



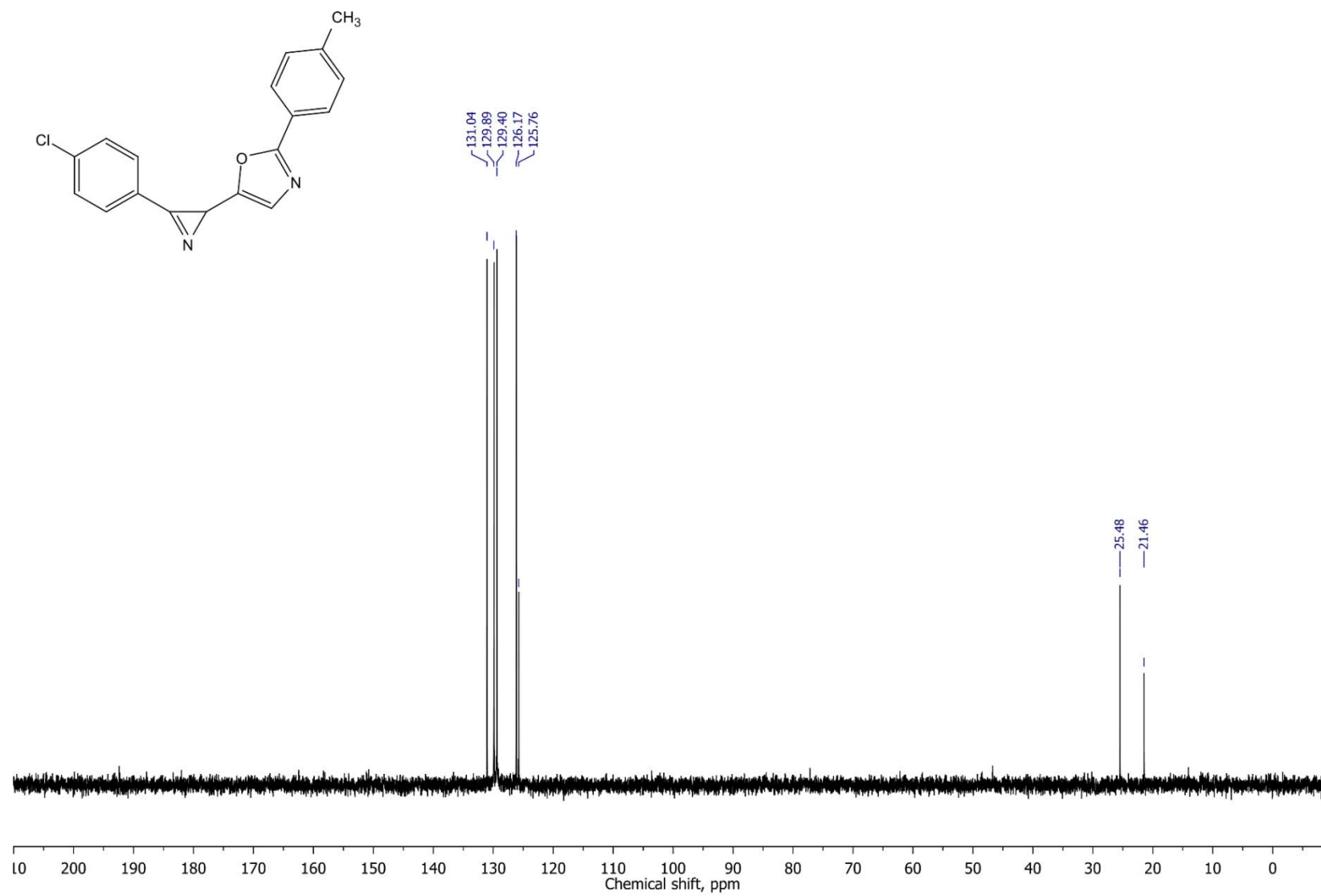
5-(3-(4-Chlorophenyl)-2H-azirin-2-yl)-2-(*p*-tolyl)oxazole 2m, ^1H NMR, 400 MHz, CDCl_3



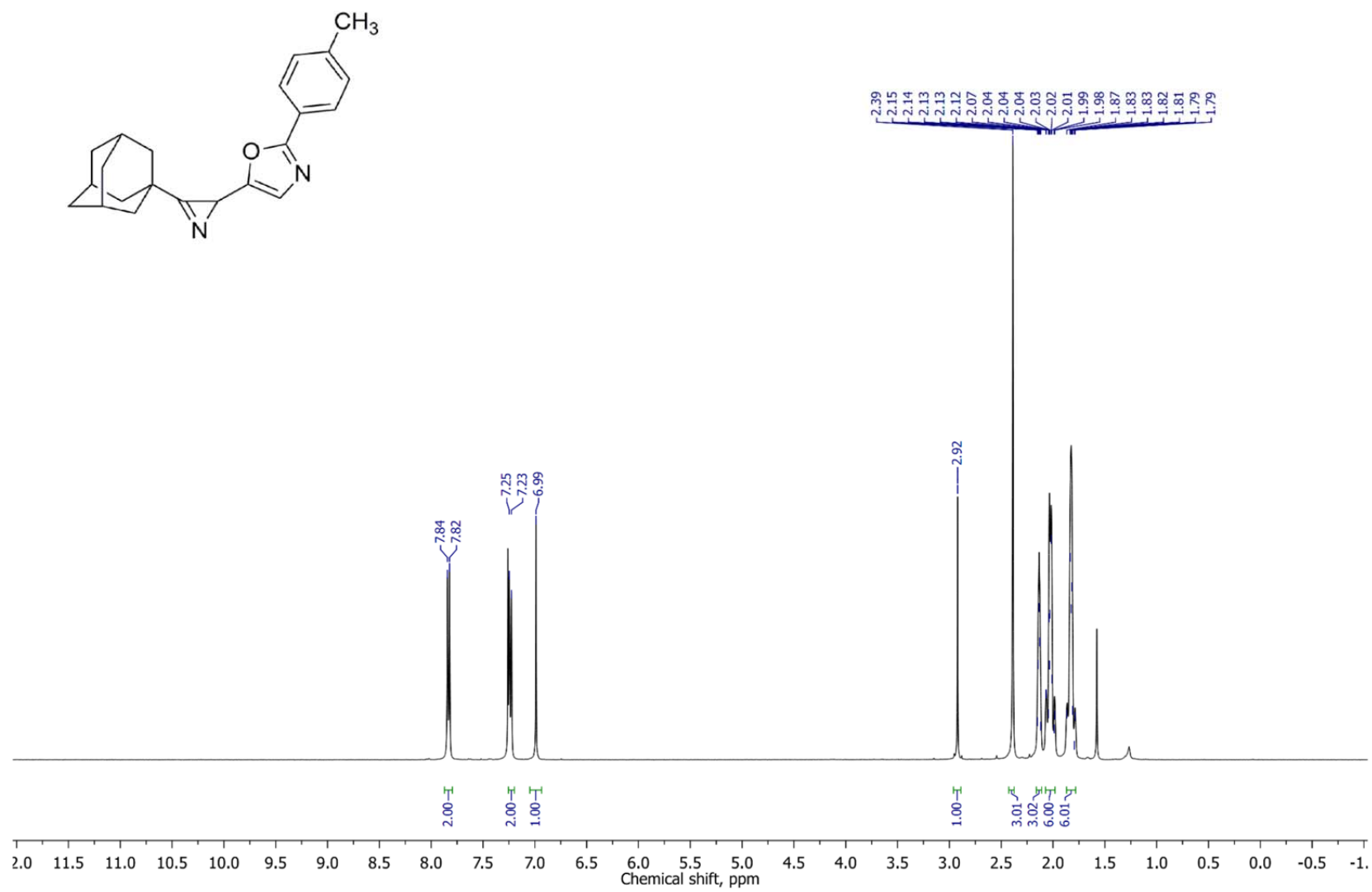
5-(3-(4-Chlorophenyl)-2H-azirin-2-yl)-2-(*p*-tolyl)oxazole 2m, $^{13}\text{C}\{^1\text{H}\}$ NMR, 100 MHz, CDCl_3



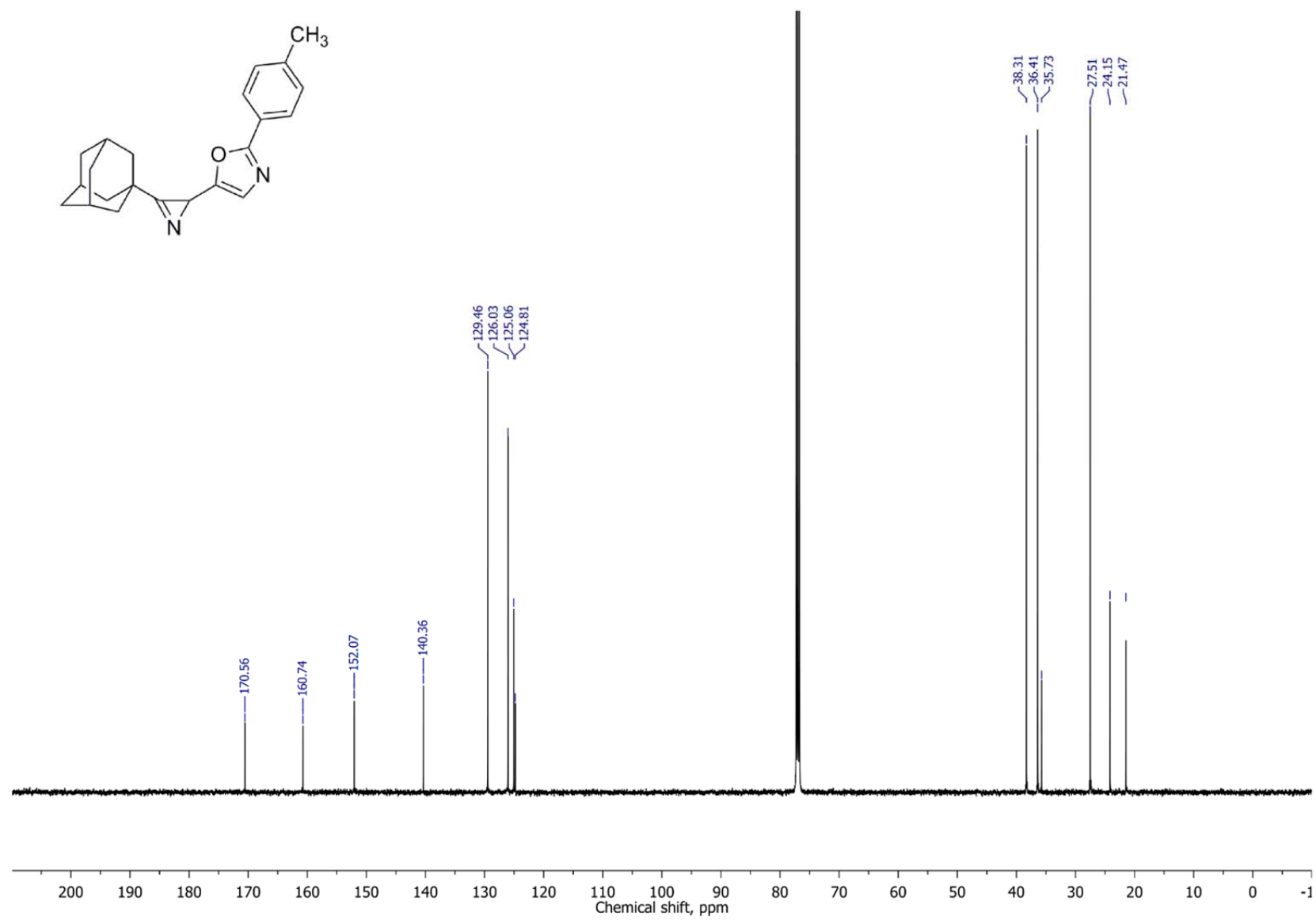
5-(3-(4-Chlorophenyl)-2H-azirin-2-yl)-2-(*p*-tolyl)oxazole 2m, DEPT, 100 MHz, CDCl₃



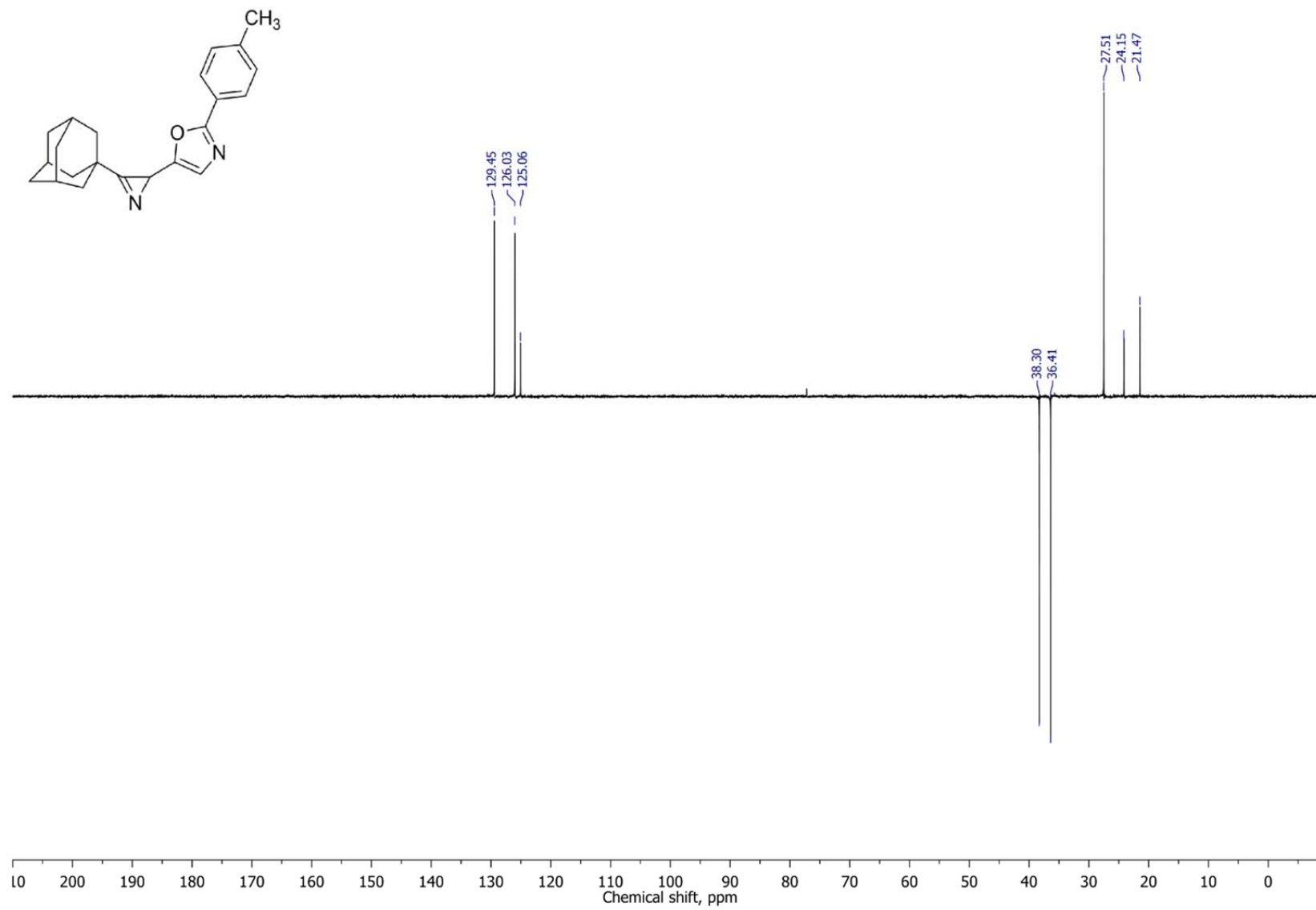
5-(3-(Adamantan-1-yl)-2*H*-azirin-2-yl)-2-(*p*-tolyl)oxazole 2n, ¹H NMR, 400 MHz, CDCl₃



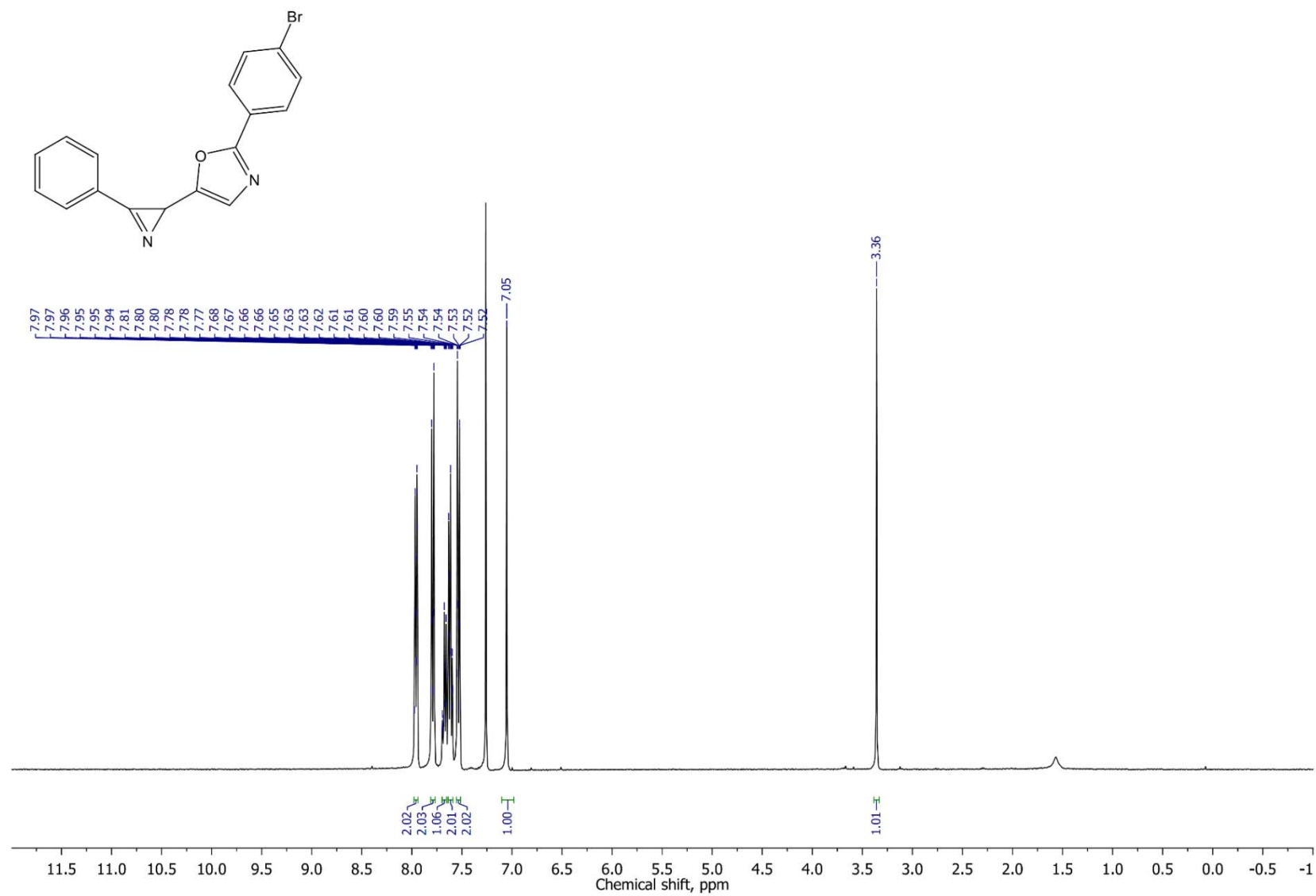
5-(3-(Adamantan-1-yl)-2*H*-azirin-2-yl)-2-(*p*-tolyl)oxazole 2n, $^{13}\text{C}\{^1\text{H}\}$ NMR, 100 MHz, CDCl_3



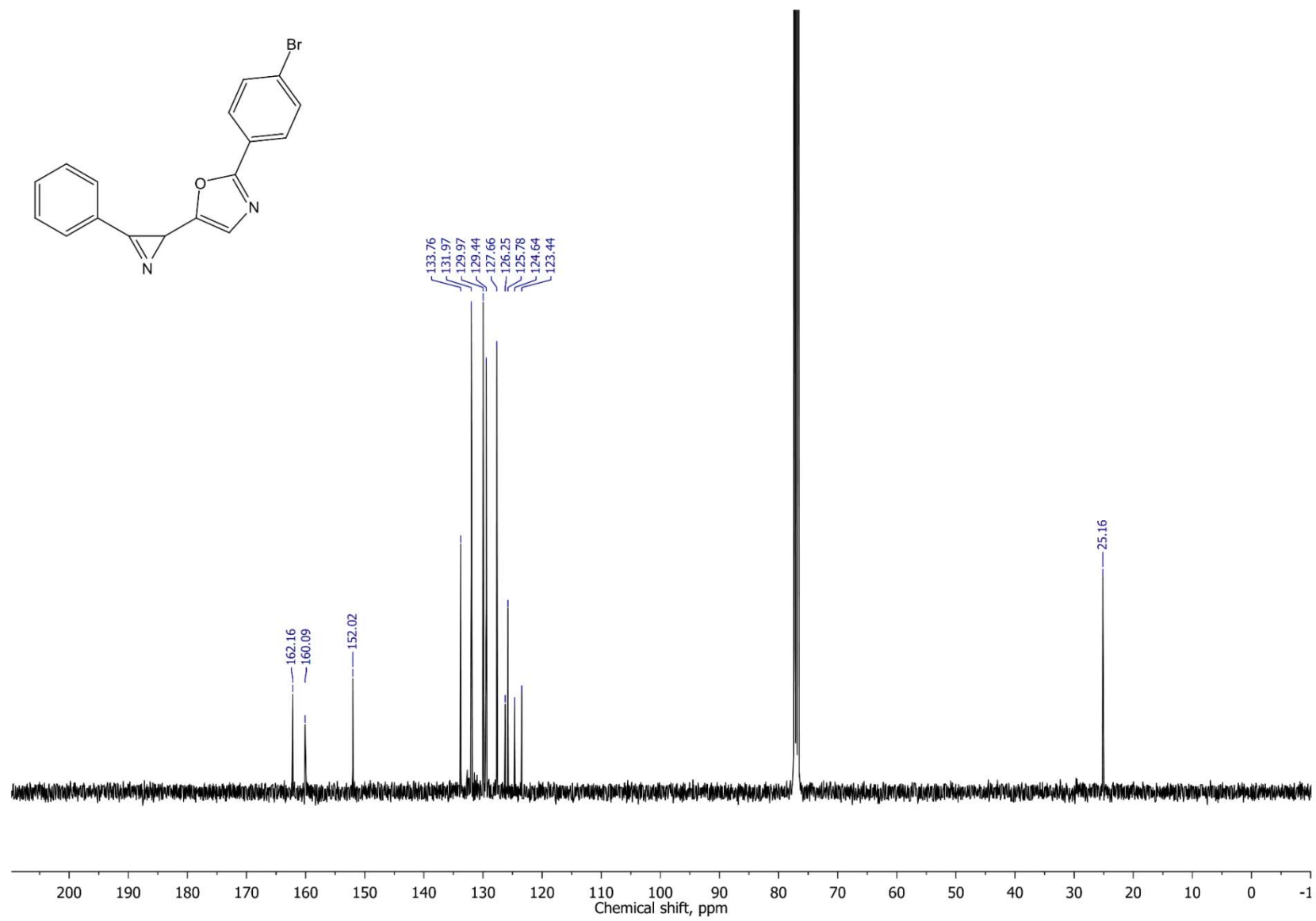
5-(3-(Adamantan-1-yl)-2*H*-azirin-2-yl)-2-(*p*-tolyl)oxazole 2n, DEPT NMR, 100 MHz, CDCl₃



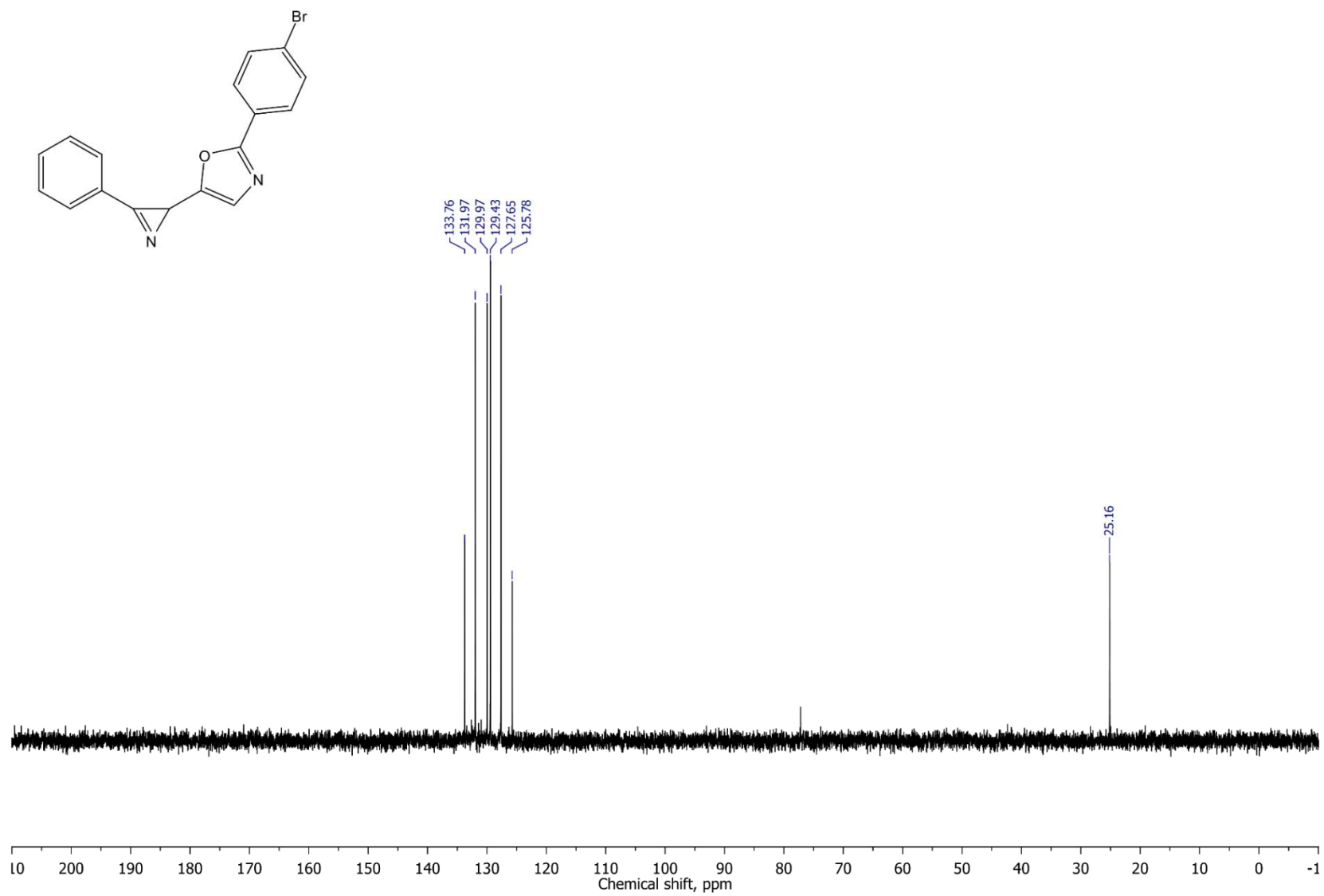
2-(4-Bromophenyl)-5-(3-phenyl-2H-azirin-2-yl)oxazole 2o, ^1H NMR, 400 MHz, CDCl_3



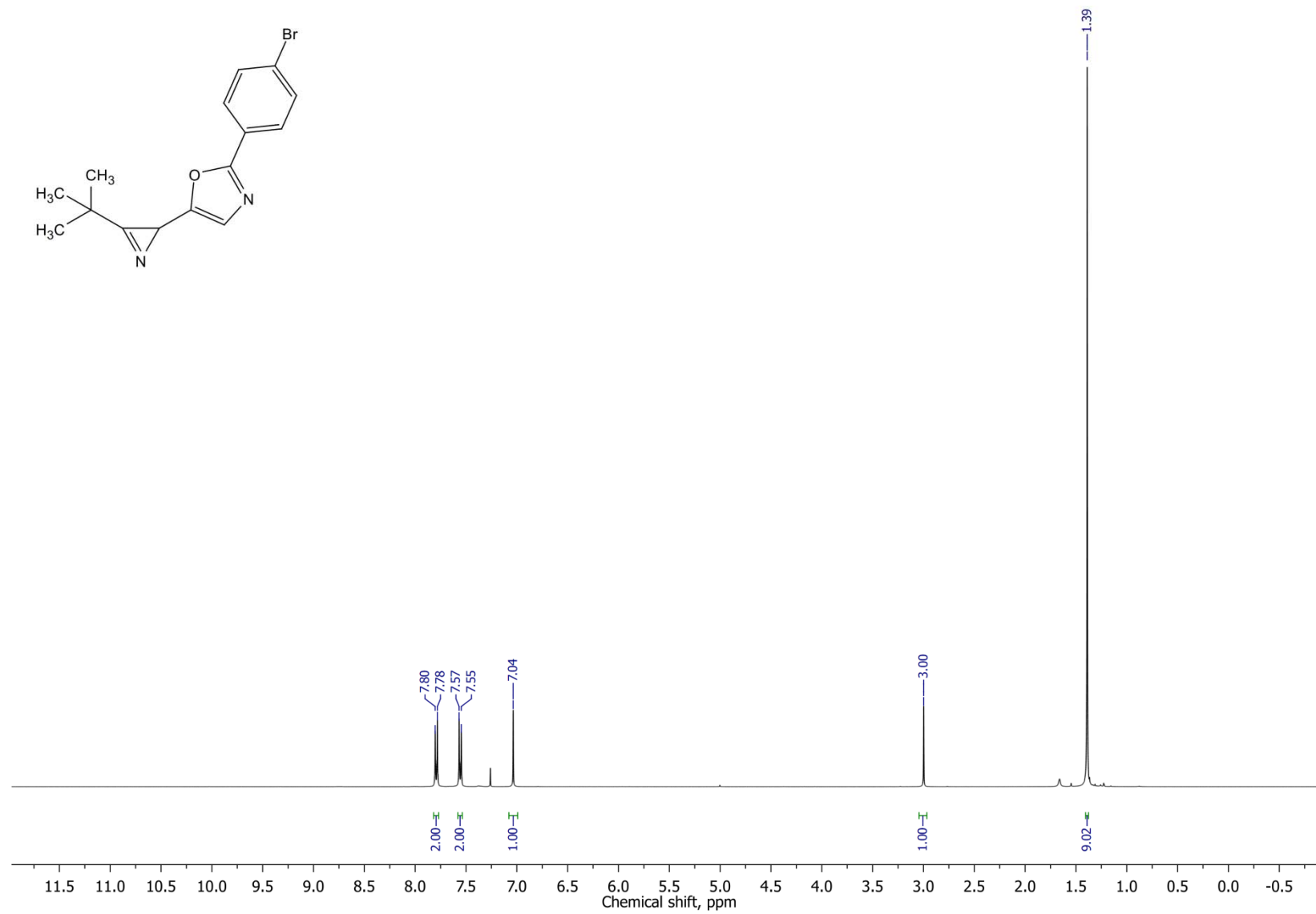
2-(4-Bromophenyl)-5-(3-phenyl-2H-azirin-2-yl)oxazole 2o, $^{13}\text{C}\{^1\text{H}\}$ NMR, 100 MHz, CDCl_3



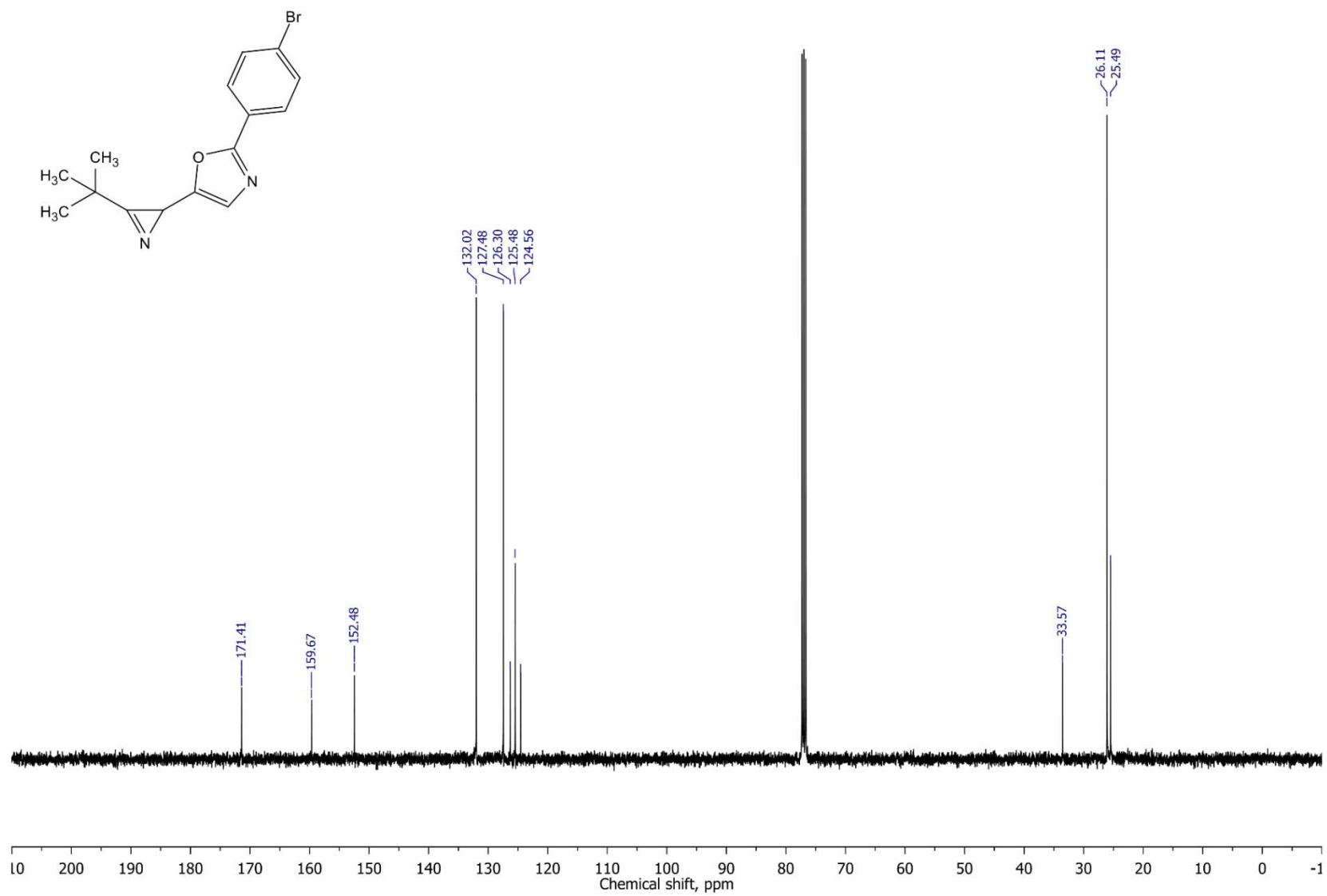
2-(4-Bromophenyl)-5-(3-phenyl-2H-azirin-2-yl)oxazole 2o, DEPT, 100 MHz, CDCl₃



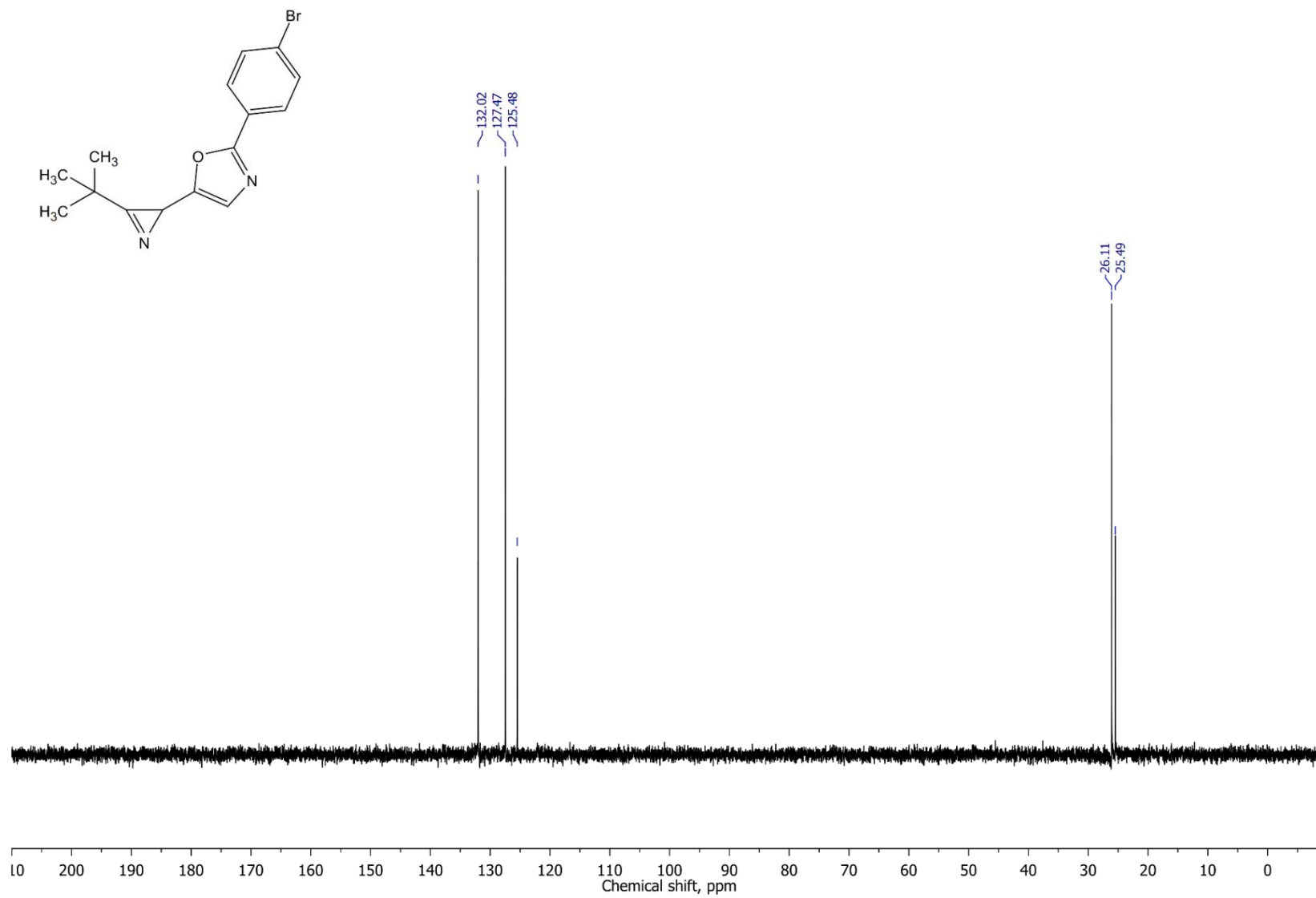
2-(4-Bromophenyl)-5-(3-(*tert*-butyl)-2*H*-azirin-2-yl)oxazole 2p, ^1H NMR, 400 MHz, CDCl_3



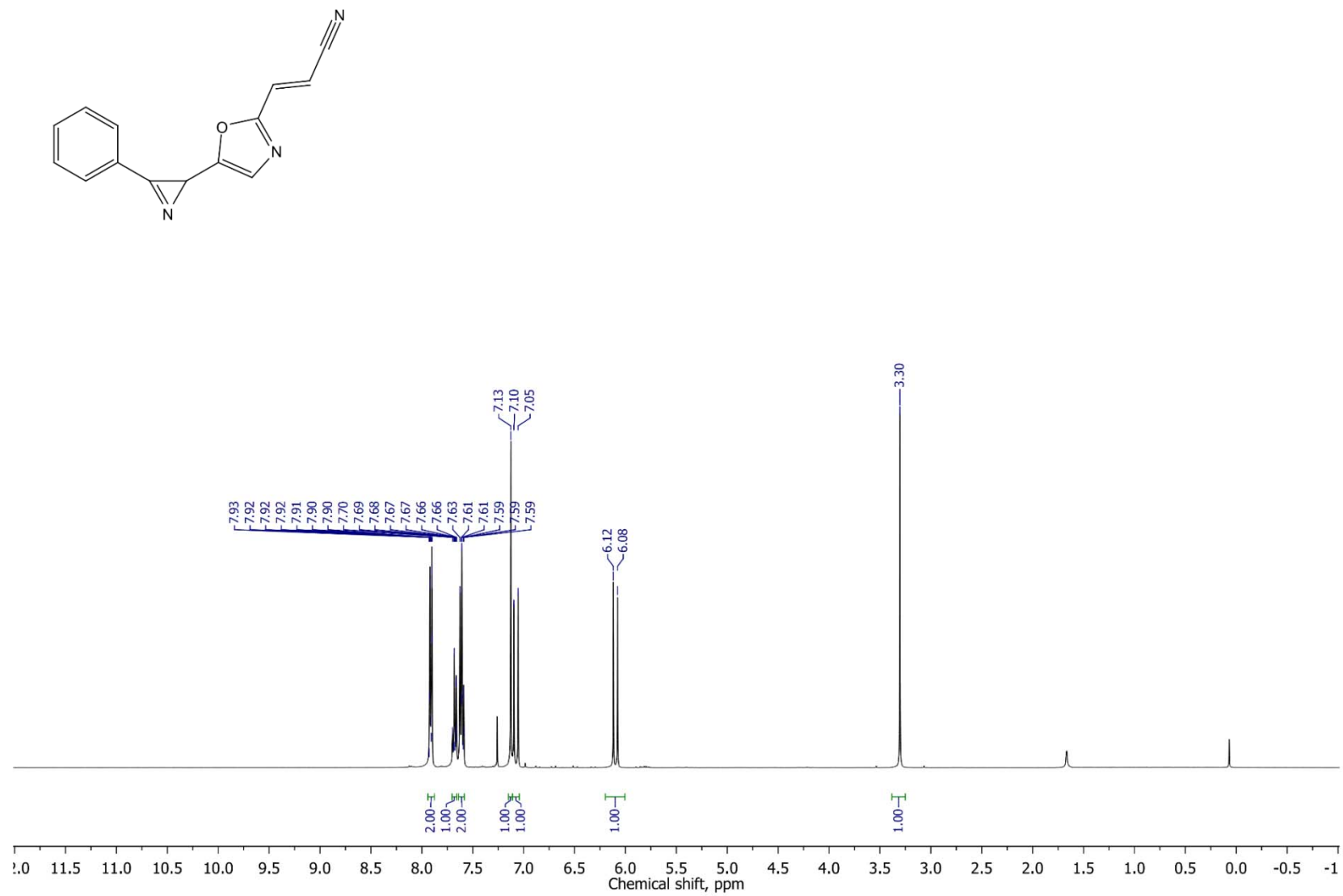
2-(4-Bromophenyl)-5-(3-(*tert*-butyl)-2*H*-azirin-2-yl)oxazole 2p, $^{13}\text{C}\{^1\text{H}\}$ NMR, 100 MHz, CDCl_3



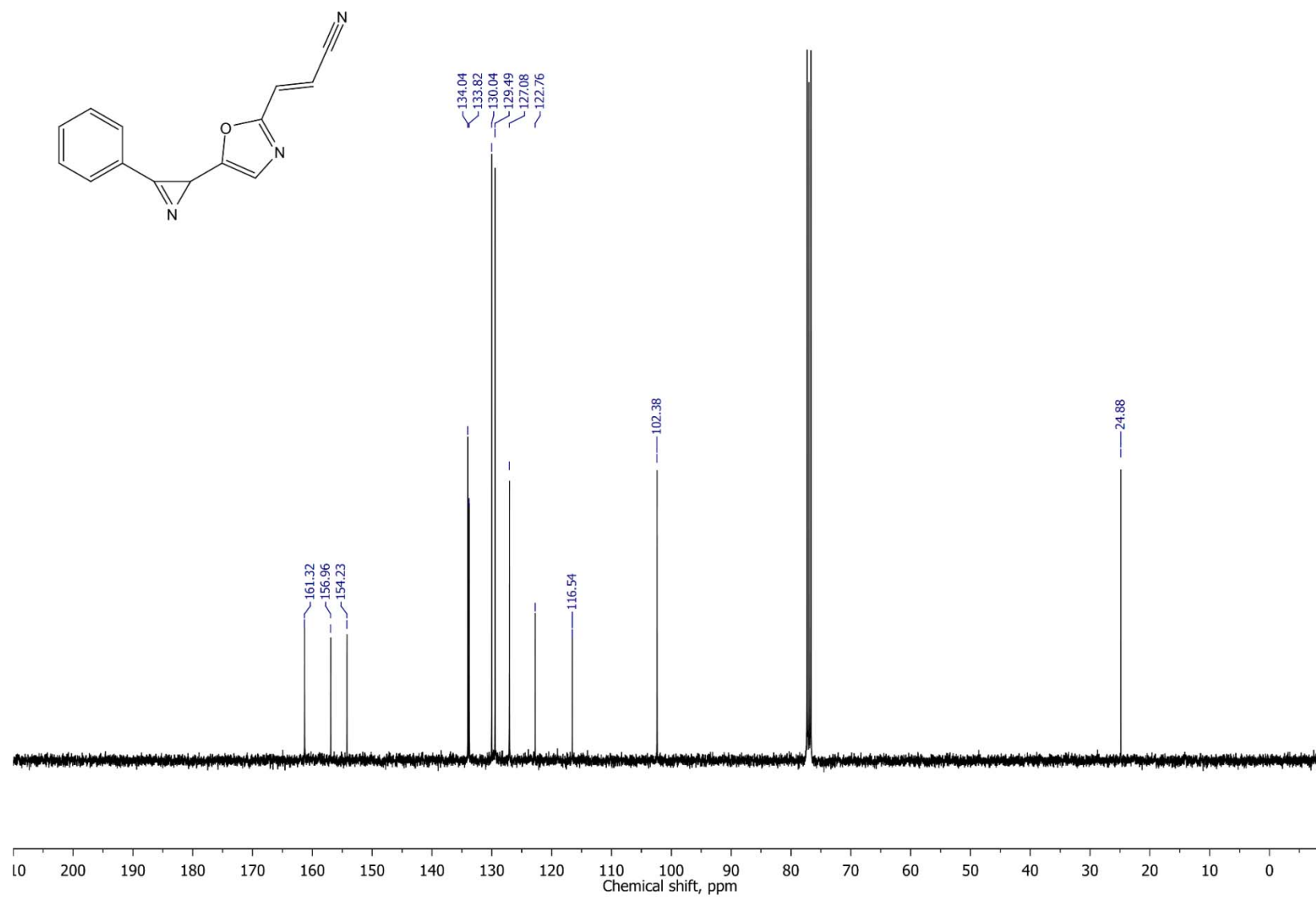
2-(4-Bromophenyl)-5-(3-(*tert*-butyl)-2*H*-azirin-2-yl)oxazole 2p, DEPT, 100 MHz, CDCl₃



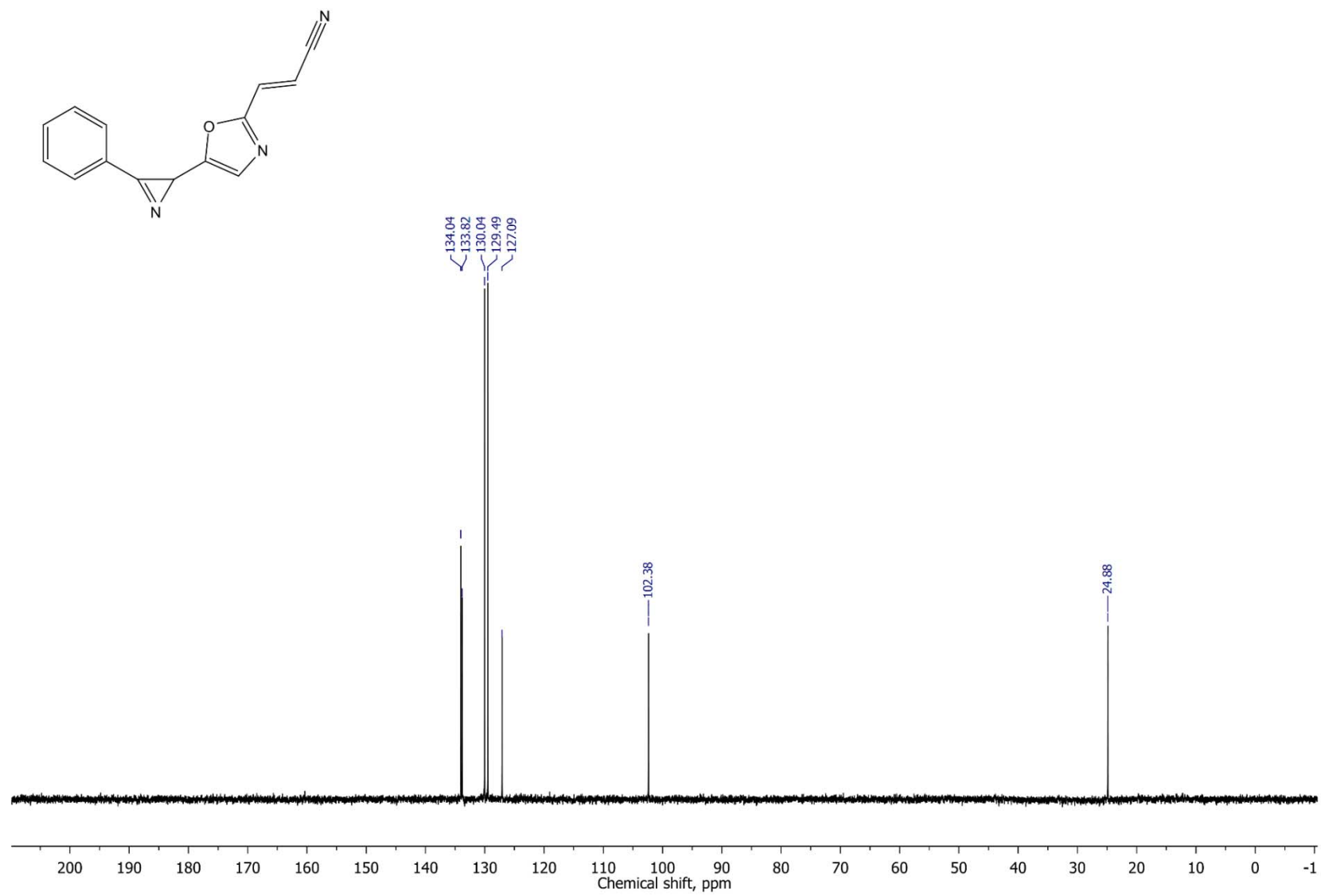
(*E*)-3-(5-(3-phenyl-2*H*-azirin-2-yl)oxazol-2-yl)acrylonitrile 2q, ^1H NMR, 400 MHz, CDCl_3



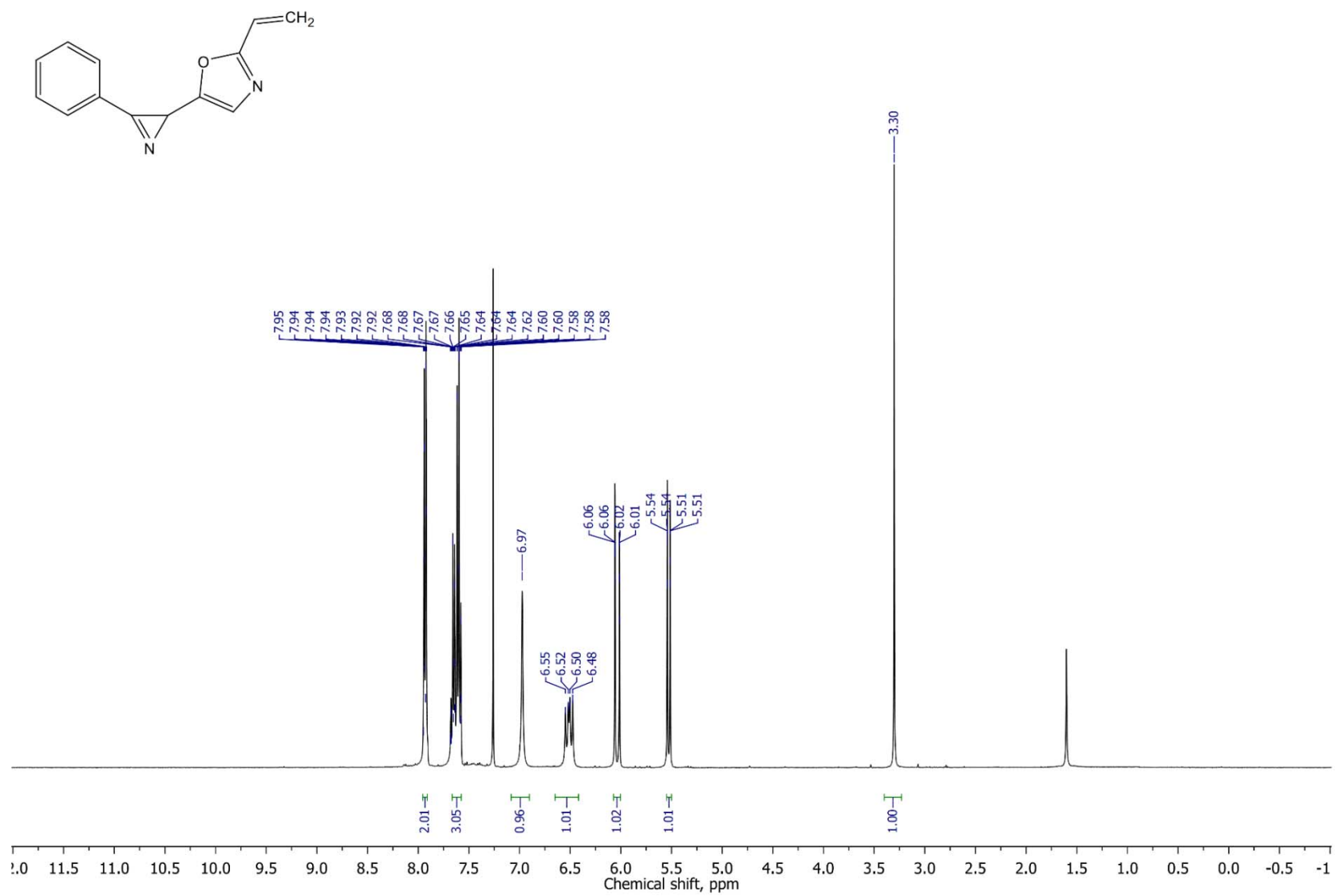
(*E*)-3-(5-(3-phenyl-2*H*-azirin-2-yl)oxazol-2-yl)acrylonitrile **2q**, $^{13}\text{C}\{^1\text{H}\}$ NMR, 100 MHz, CDCl_3



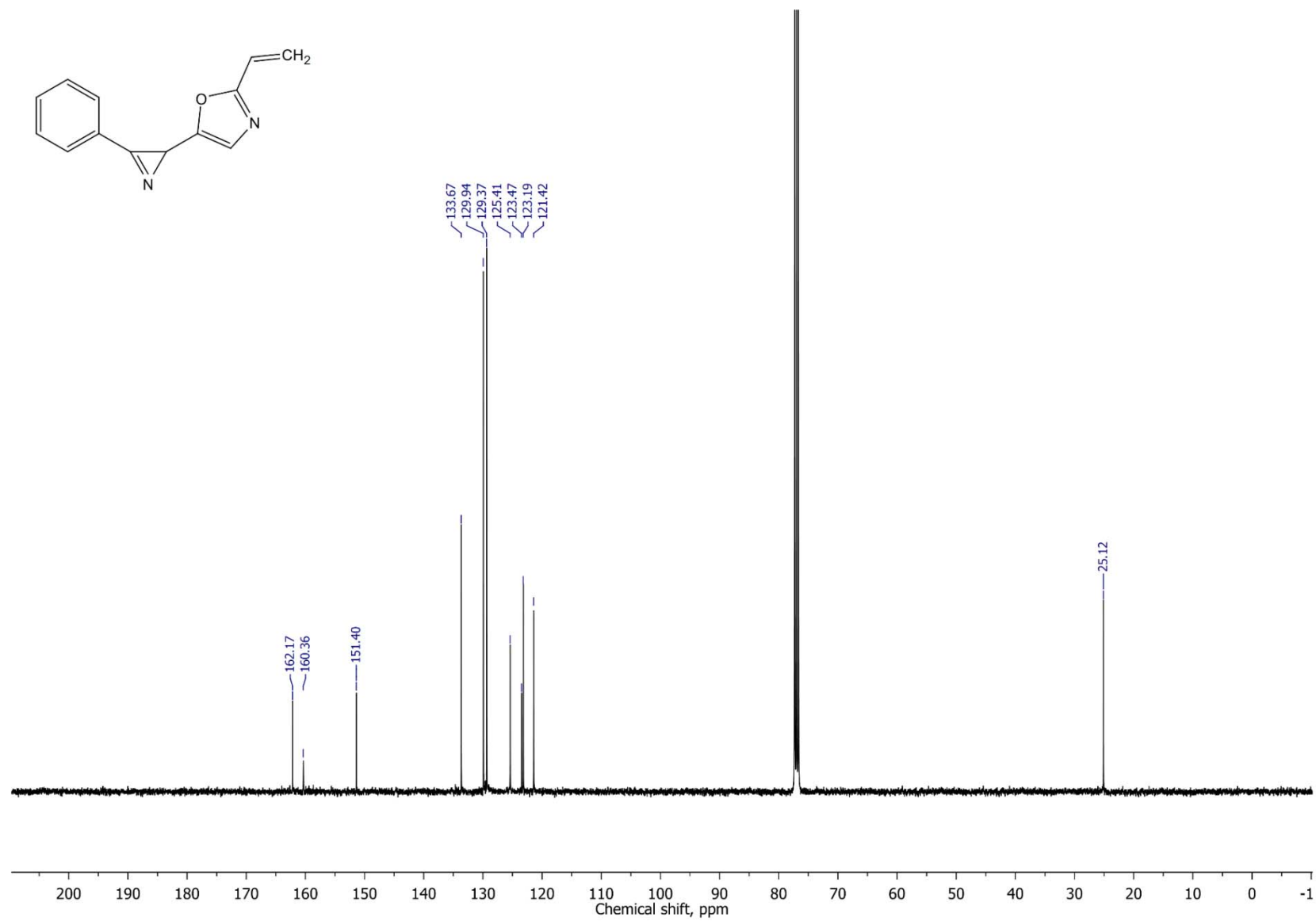
(E)-3-(5-(3-phenyl-2H-azirin-2-yl)oxazol-2-yl)acrylonitrile 2q, DEPT, 100 MHz, CDCl₃



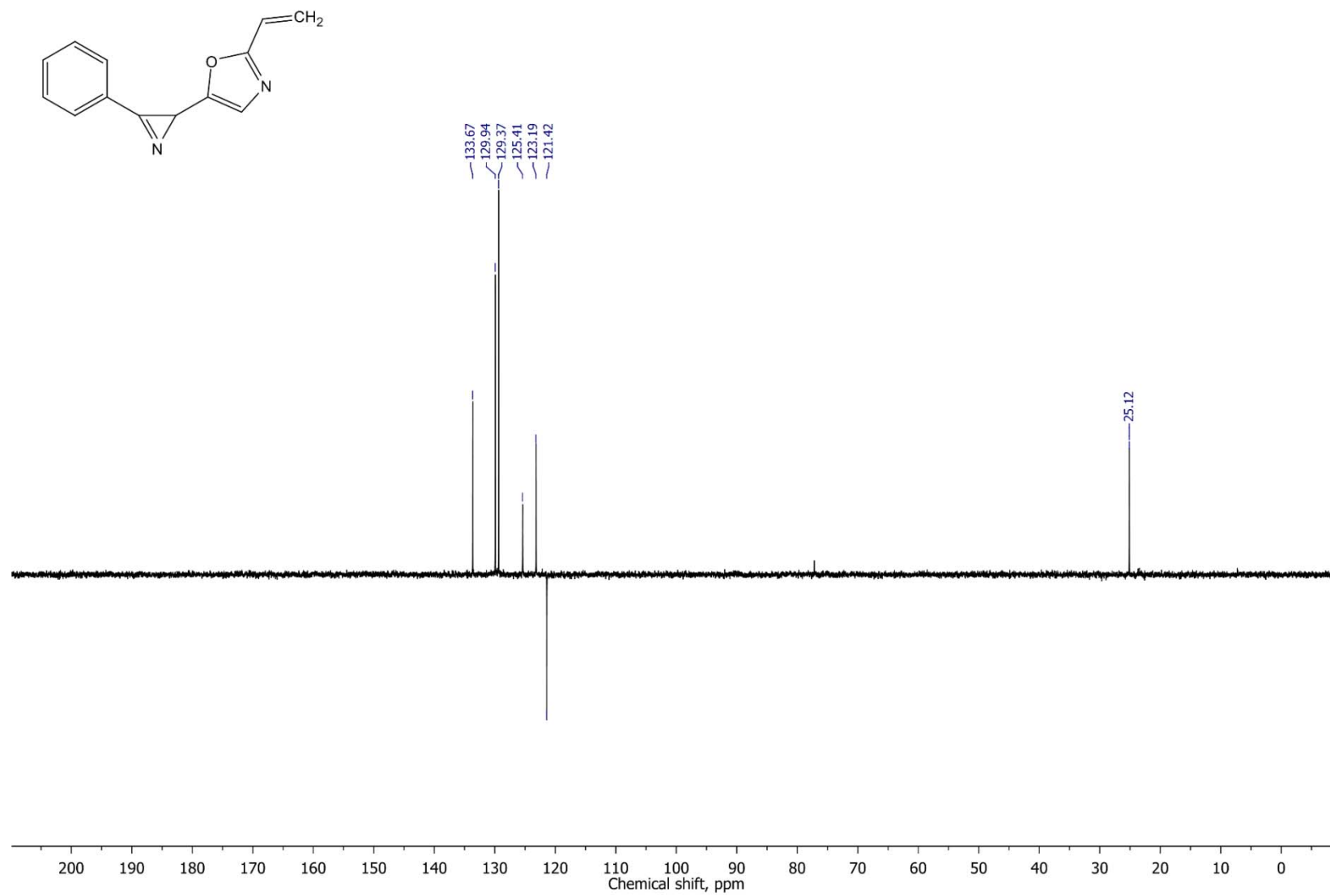
5-(3-Phenyl-2H-azirin-2-yl)-2-vinyloxazole 2r, ^1H NMR, 400 MHz, CDCl_3



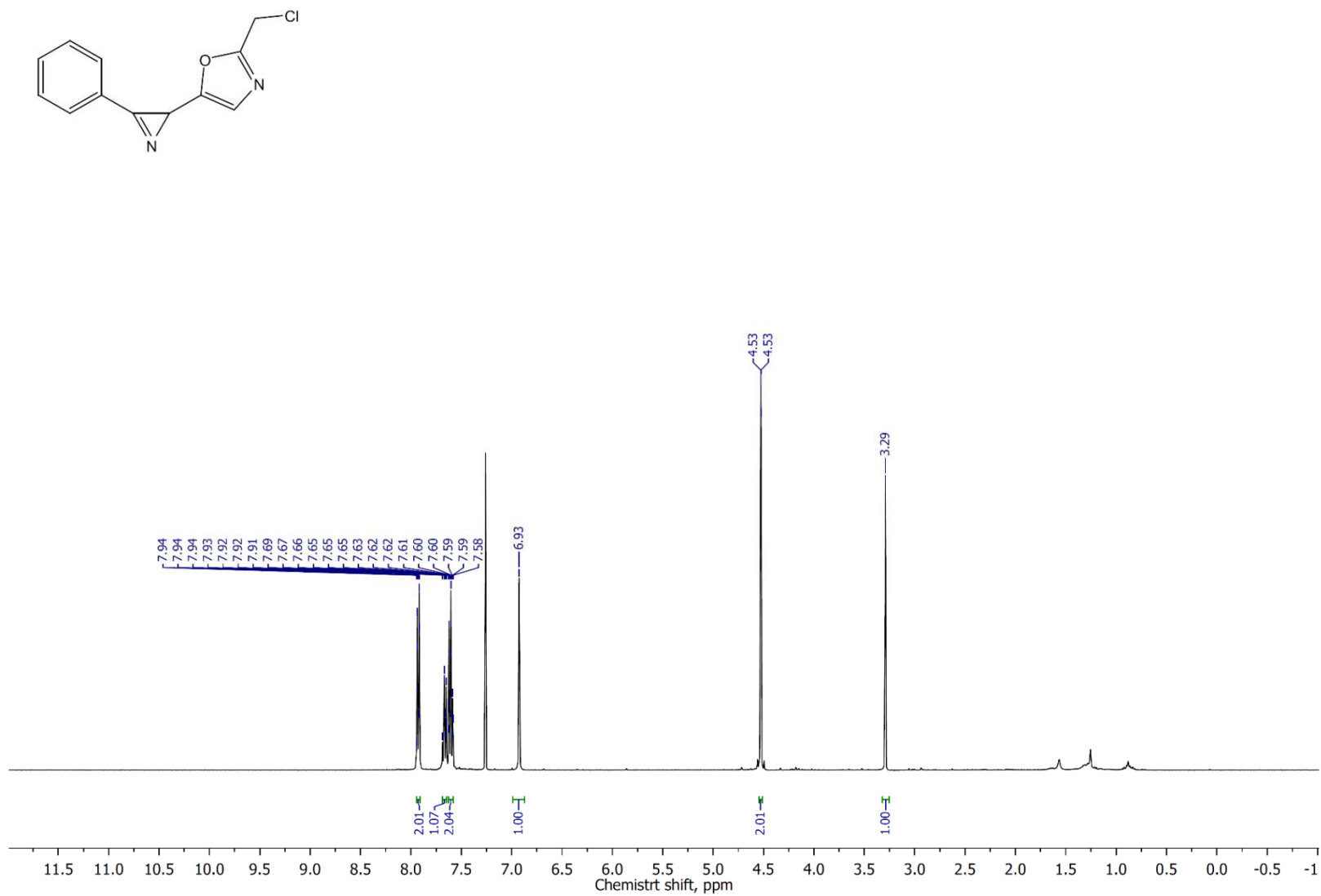
5-(3-Phenyl-2H-azirin-2-yl)-2-vinyloxazole 2r, $^{13}\text{C}\{^1\text{H}\}$ NMR, 100 MHz, CDCl_3



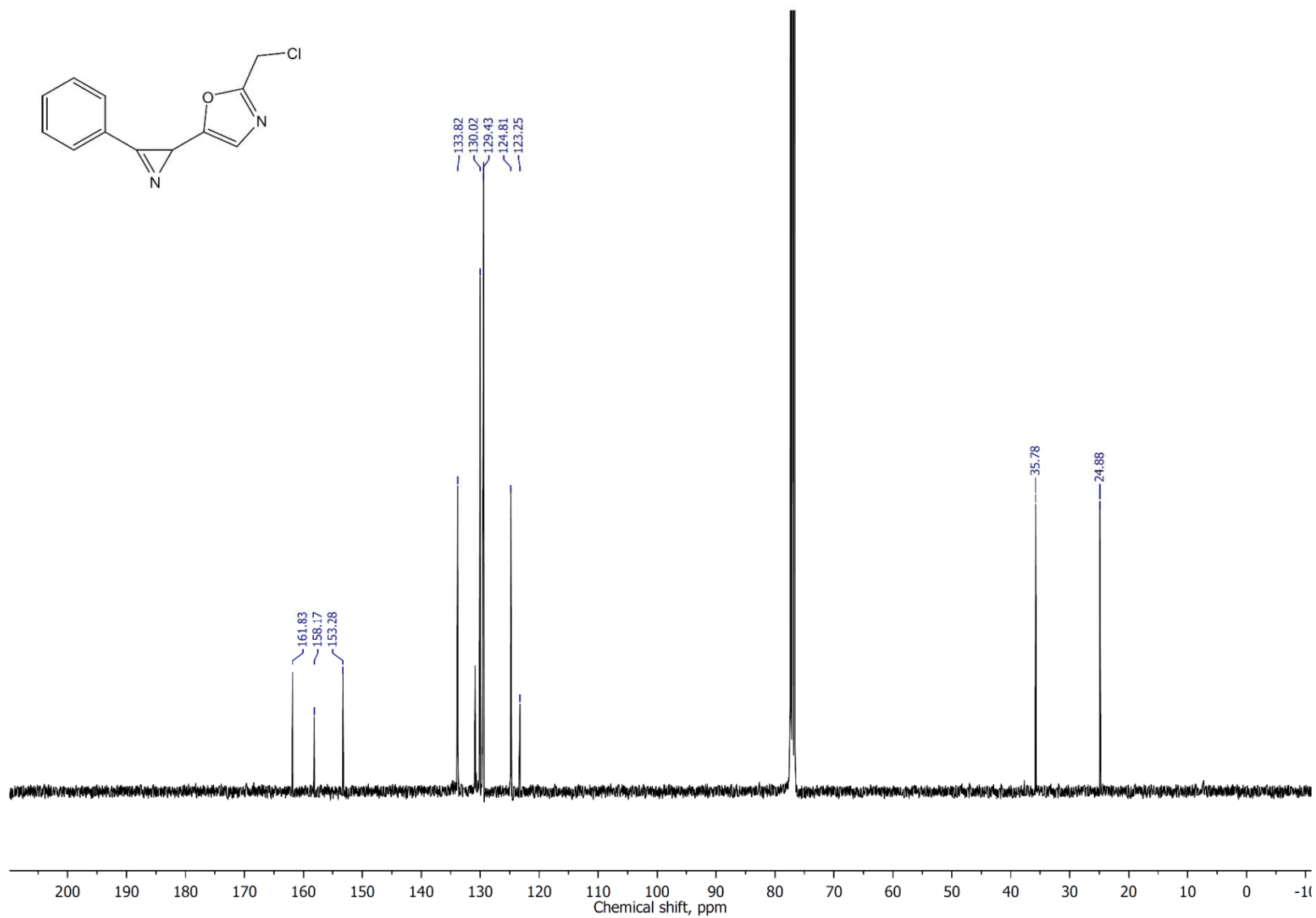
5-(3-Phenyl-2H-azirin-2-yl)-2-vinyloxazole 2r, DEPT, 100 MHz, CDCl₃



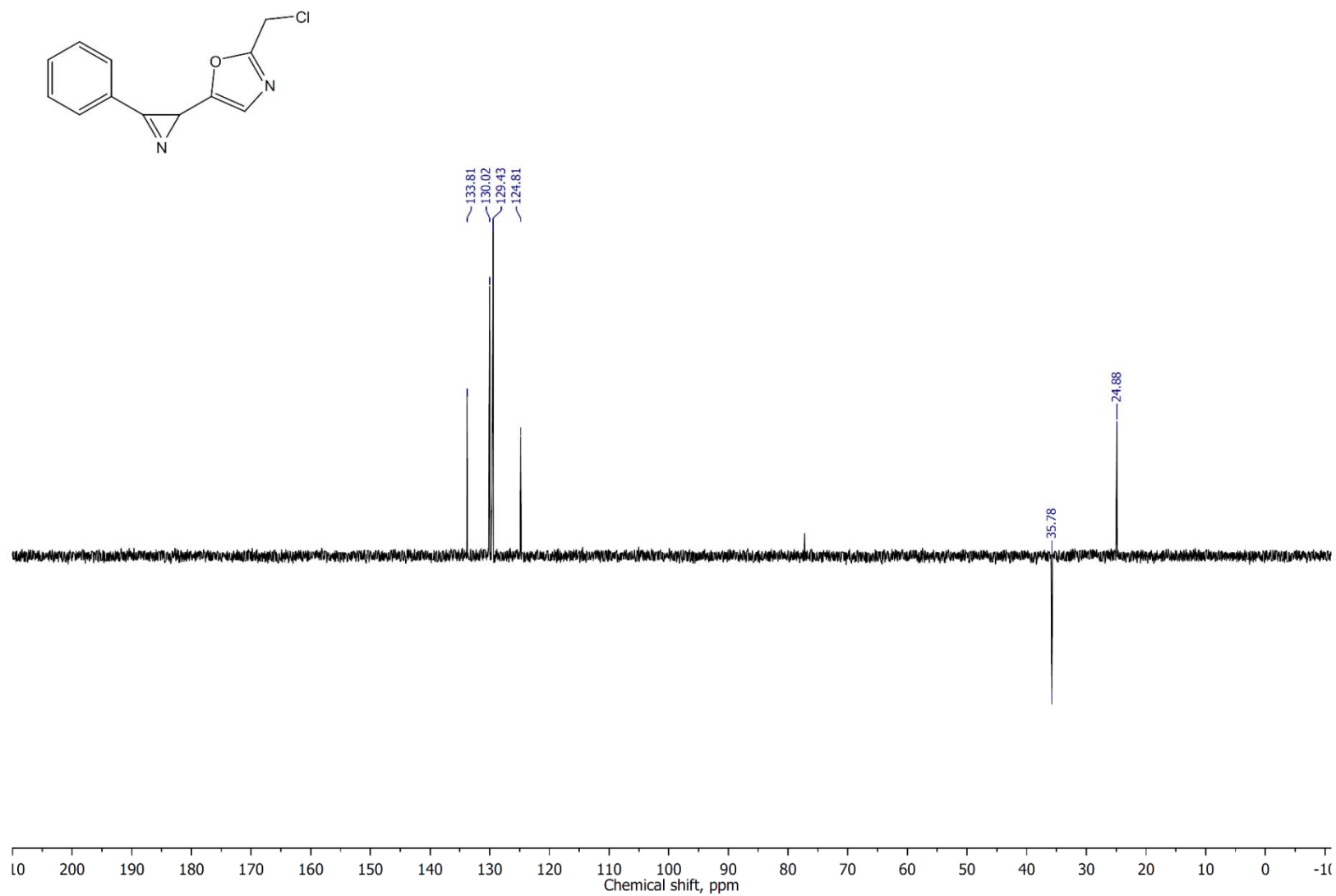
2-(Chloromethyl)-5-(3-phenyl-2H-azirin-2-yl)oxazole 2s, ^1H NMR, 400 MHz, CDCl_3



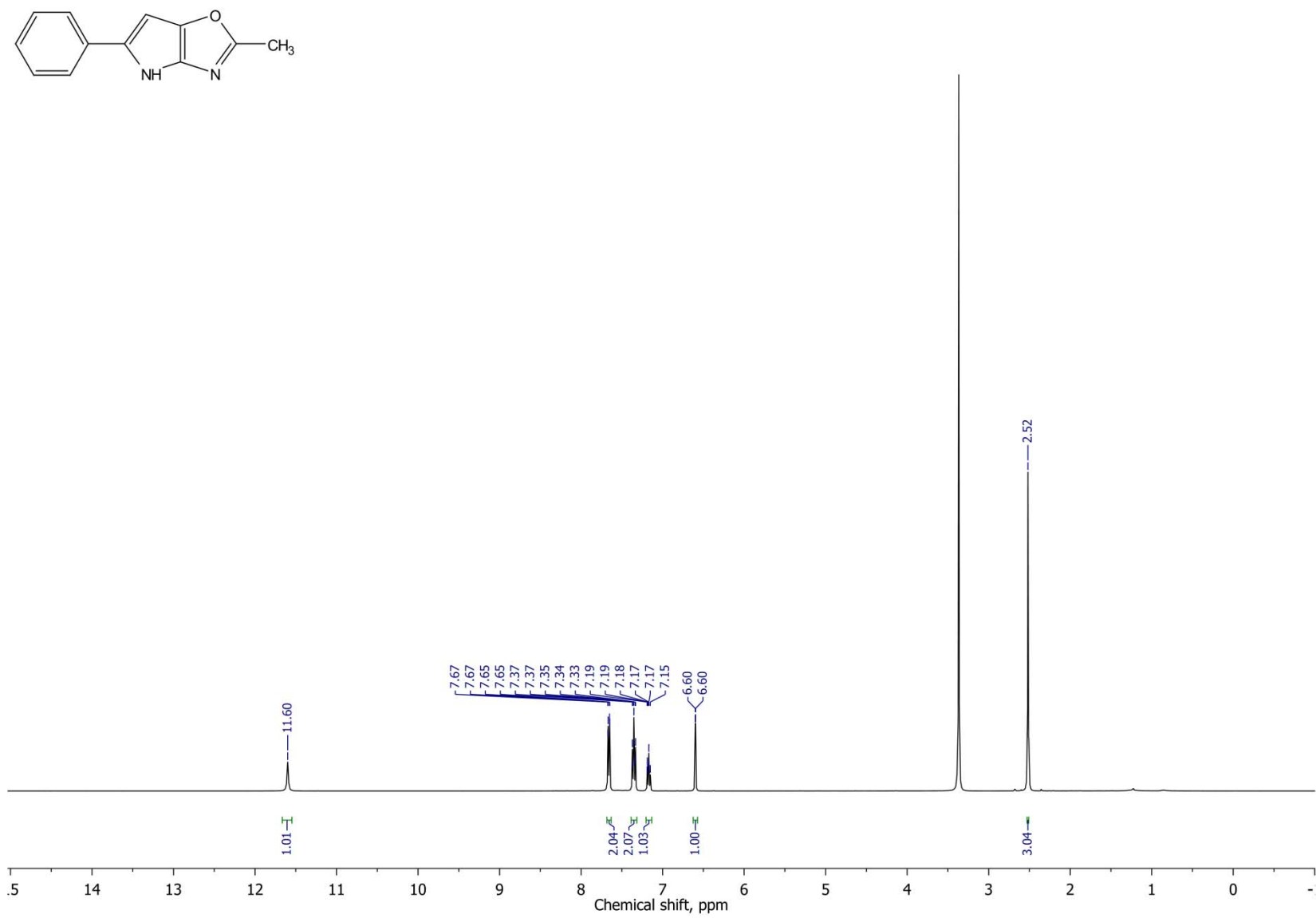
2-(Chloromethyl)-5-(3-phenyl-2*H*-azirin-2-yl)oxazole 2s, $^{13}\text{C}\{^1\text{H}\}$ NMR, 100 MHz, CDCl_3



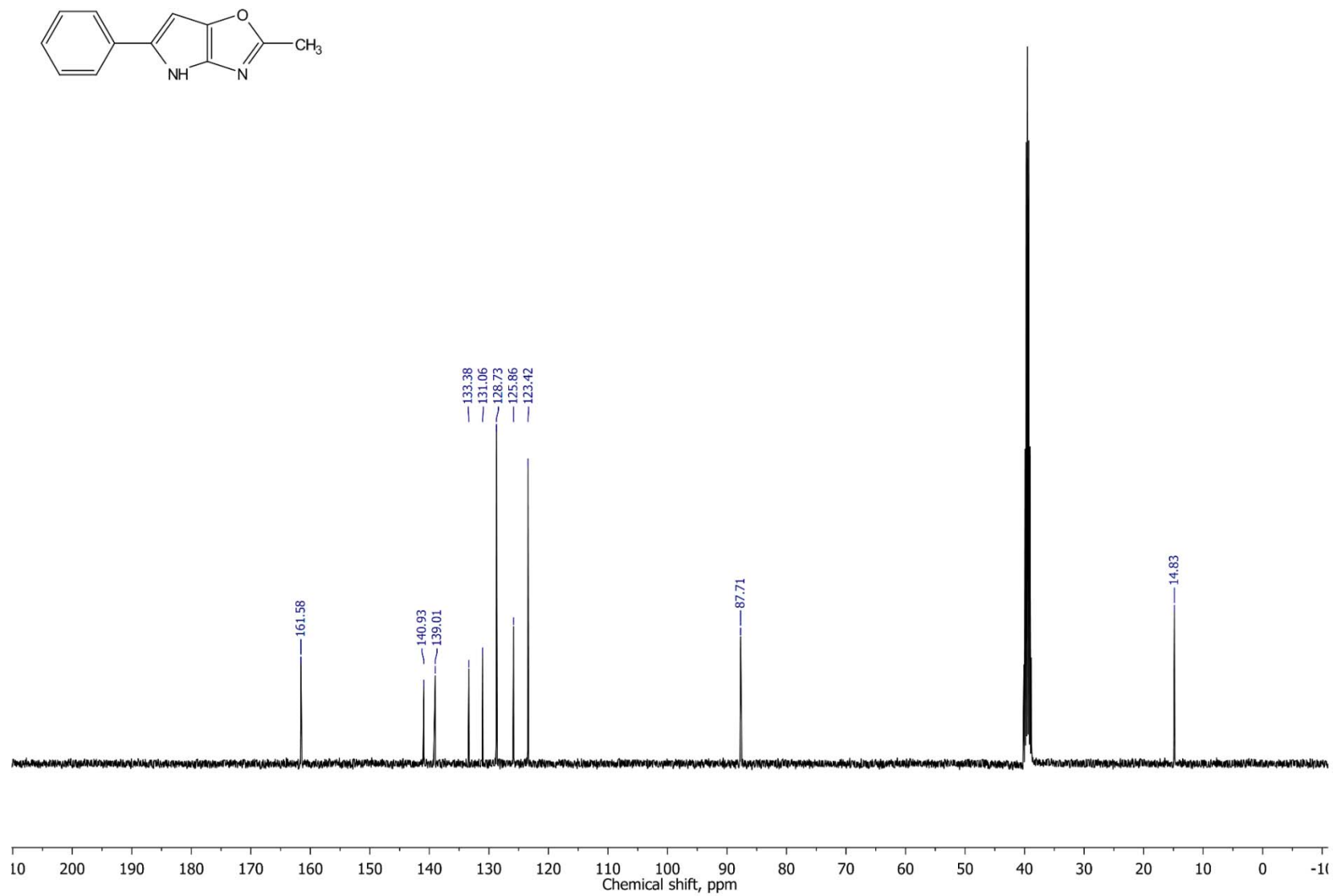
2-(Chloromethyl)-5-(3-phenyl-2*H*-azirin-2-yl)oxazole 2s, DEPT, 100 MHz, CDCl₃



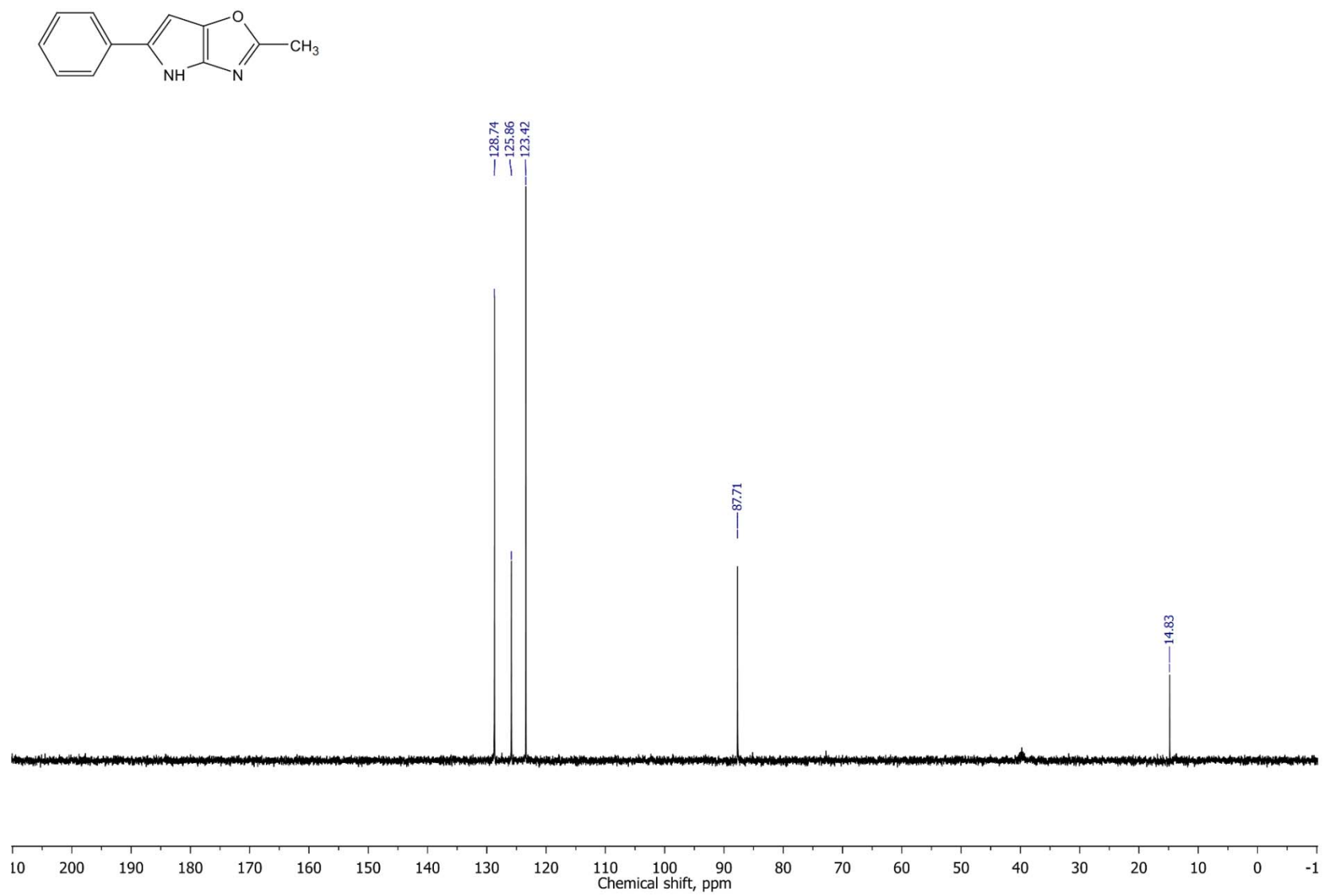
2-Methyl-5-phenyl-4*H*-pyrrolo[2,3-*d*]oxazole 3a, ¹H NMR, 400 MHz, DMSO-*d*₆



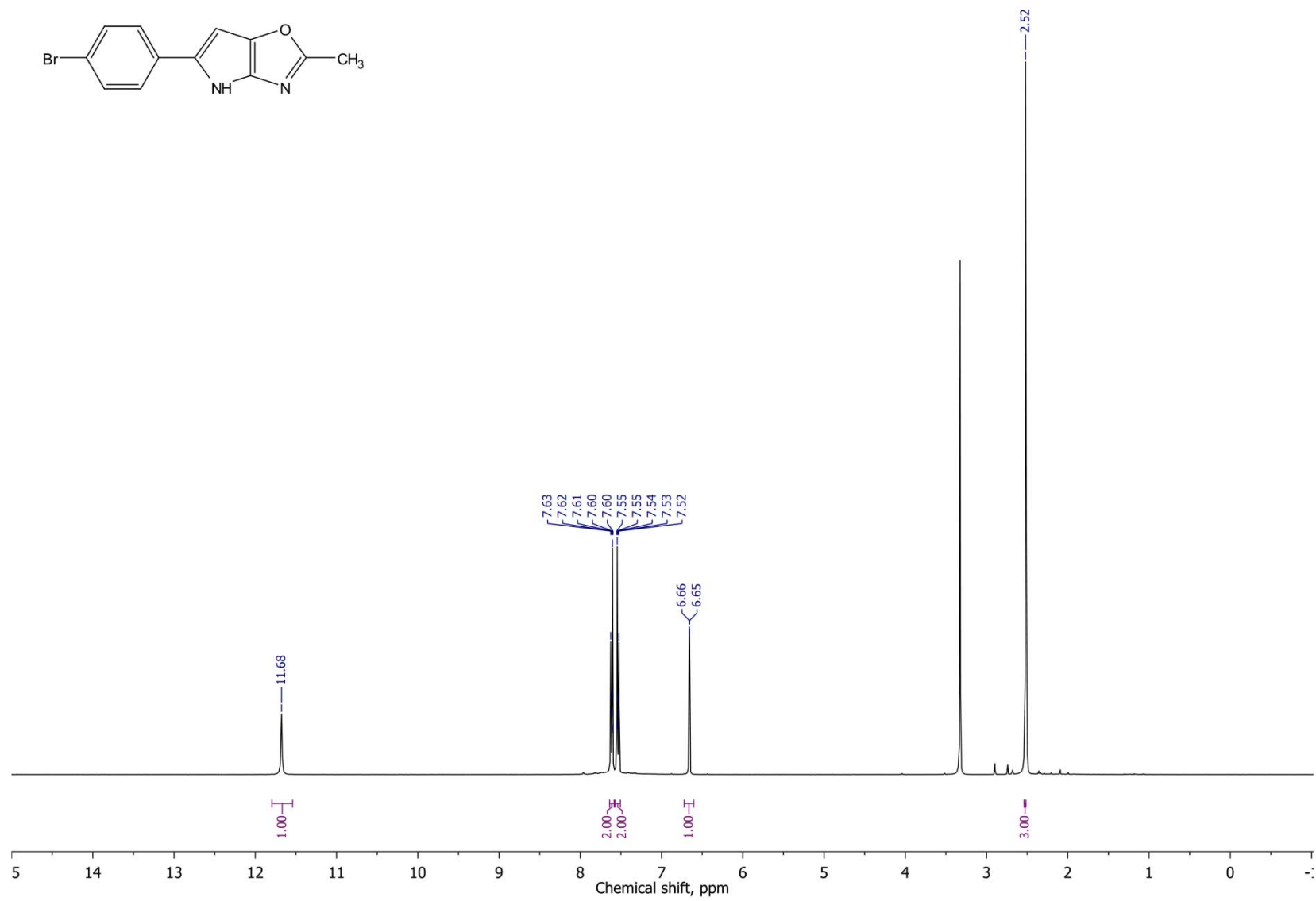
2-Methyl-5-phenyl-4*H*-pyrrolo[2,3-*d*]oxazole 3a, $^{13}\text{C}\{^1\text{H}\}$ NMR, 100 MHz, DMSO- d_6



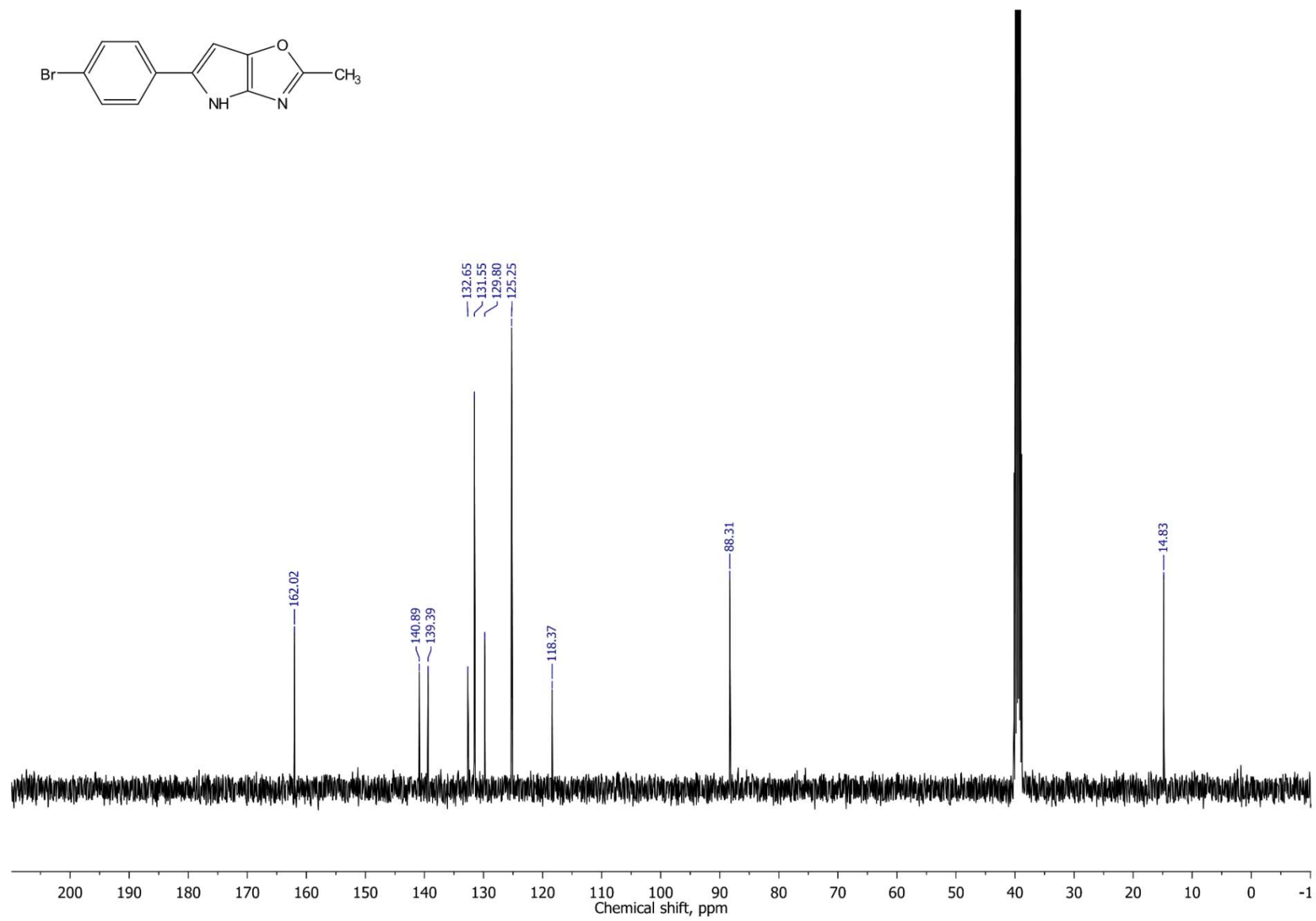
2-Methyl-5-phenyl-4*H*-pyrrolo[2,3-*d*]oxazole 3a, $^{13}\text{C}\{^1\text{H}\}$ NMR, 100 MHz, DMSO- d_6



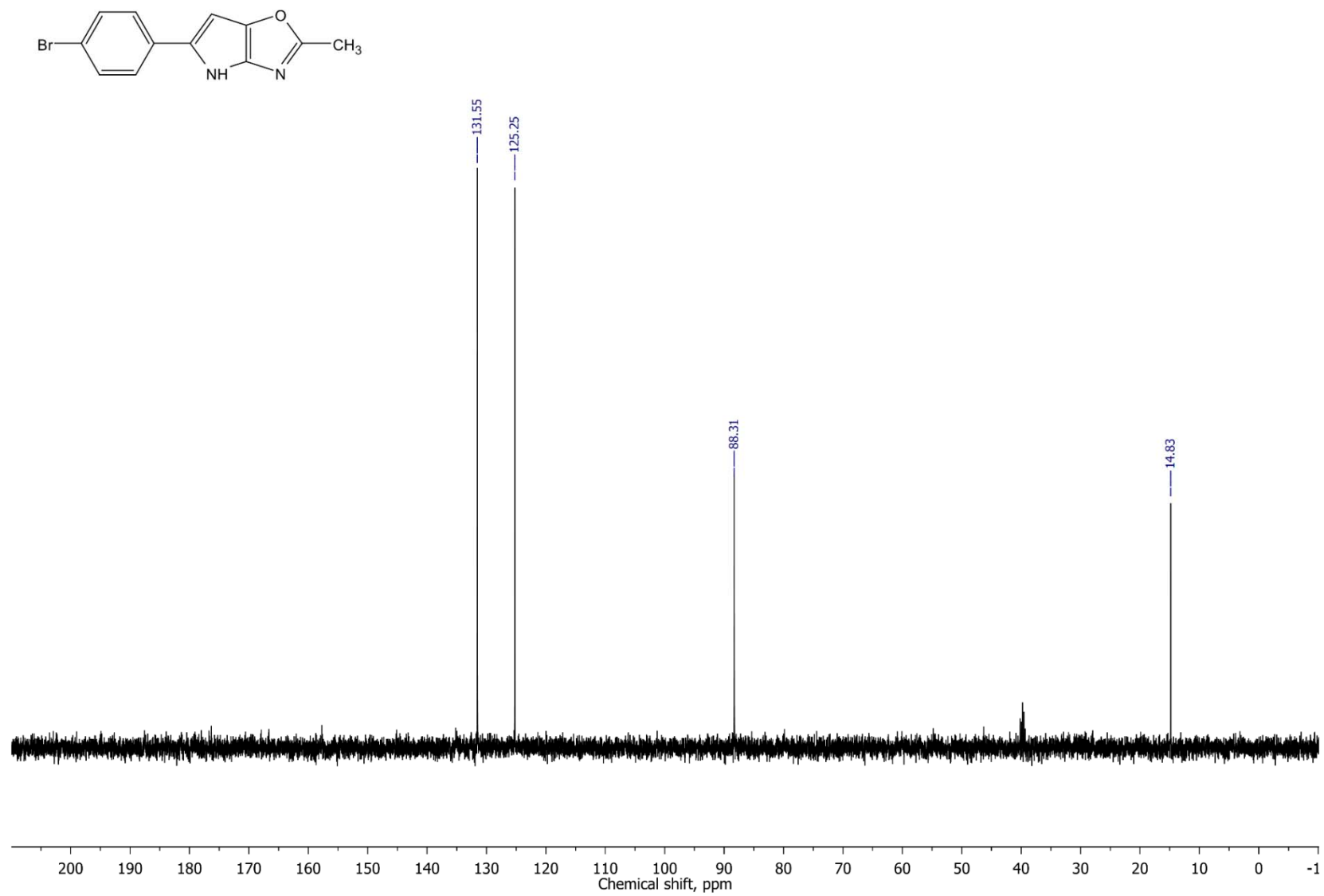
2-Methyl-5-(4-bromophenyl)-4*H*-pyrrolo[2,3-*d*]oxazole 3b, ¹H NMR, 400 MHz, DMSO-*d*₆



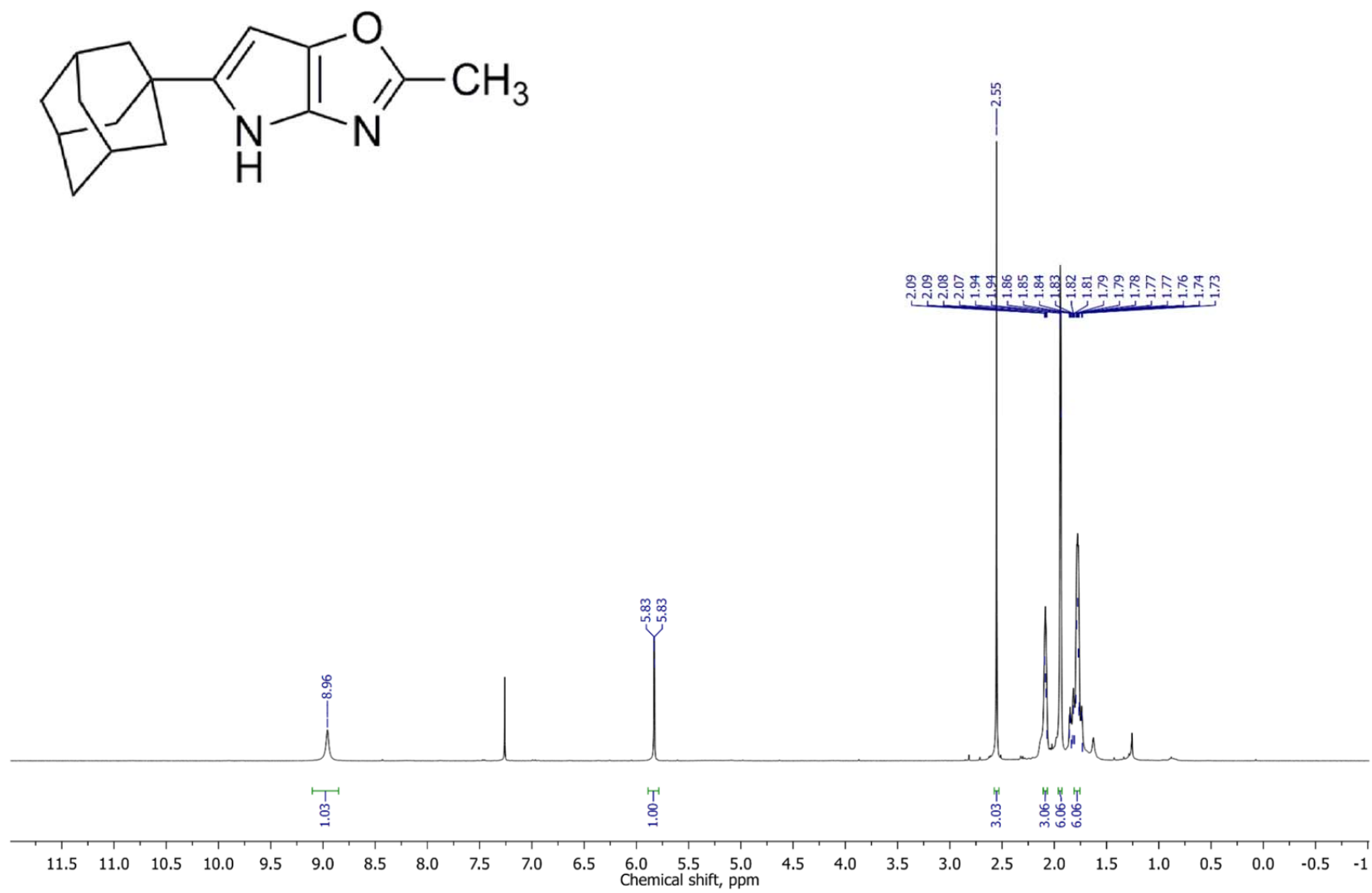
2-Methyl-5-(4-bromophenyl)-4*H*-pyrrolo[2,3-*d*]oxazole 3b, $^{13}\text{C}\{^1\text{H}\}$ NMR, 100 MHz, DMSO- d_6



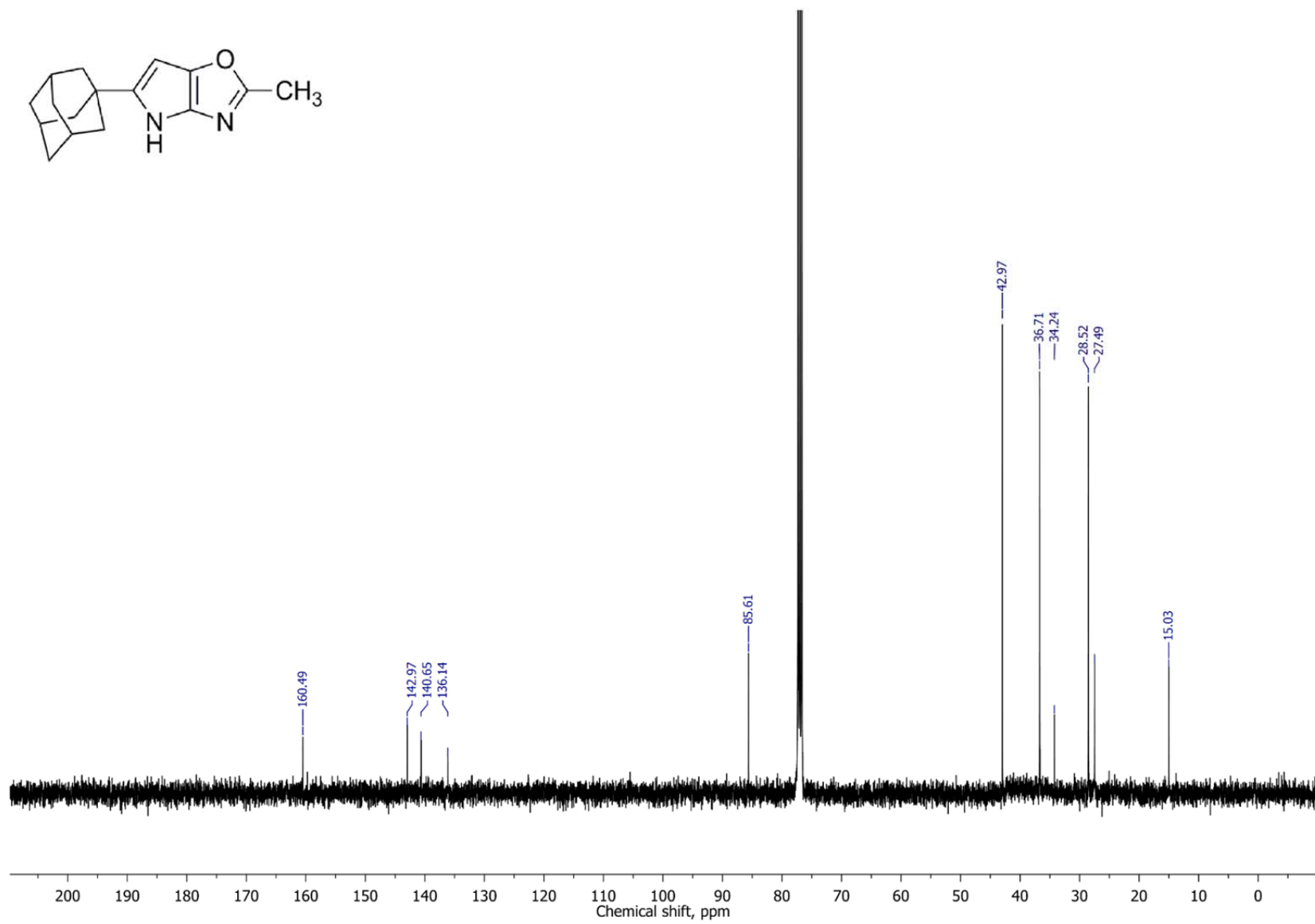
2-Methyl-5-(4-bromophenyl)-4*H*-pyrrolo[2,3-*d*]oxazole 3b, DEPT, 100 MHz, DMSO-*d*₆



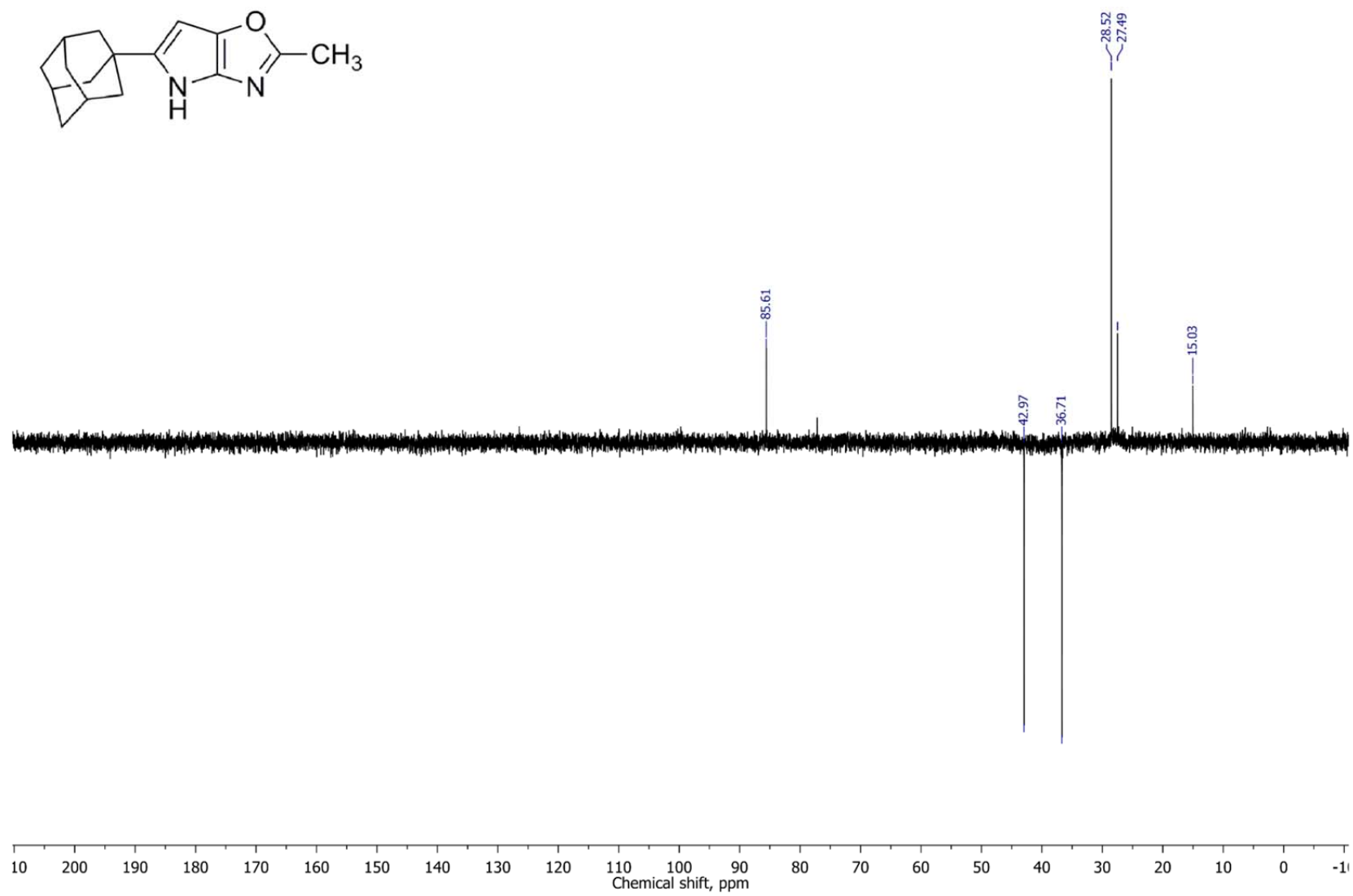
5-(Amantan-1-yl)-2-methyl-4*H*-pyrrolo[2,3-*d*]oxazole 3c, ¹H NMR, 400 MHz, CDCl₃



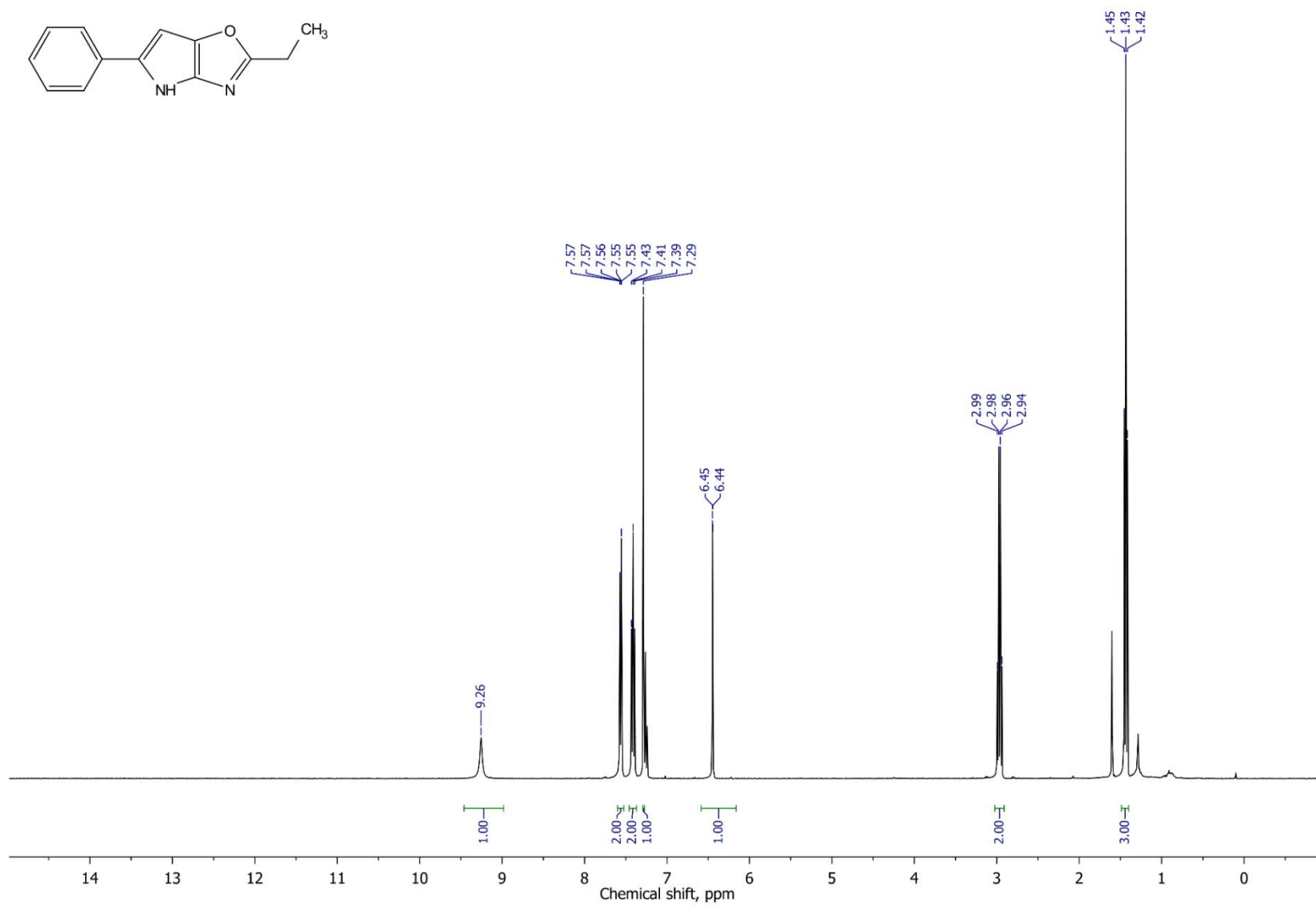
5-(Amantan-1-yl)-2-methyl-4*H*-pyrrolo[2,3-*d*]oxazole 3c, $^{13}\text{C}\{^1\text{H}\}$ NMR, 100 MHz, CDCl_3



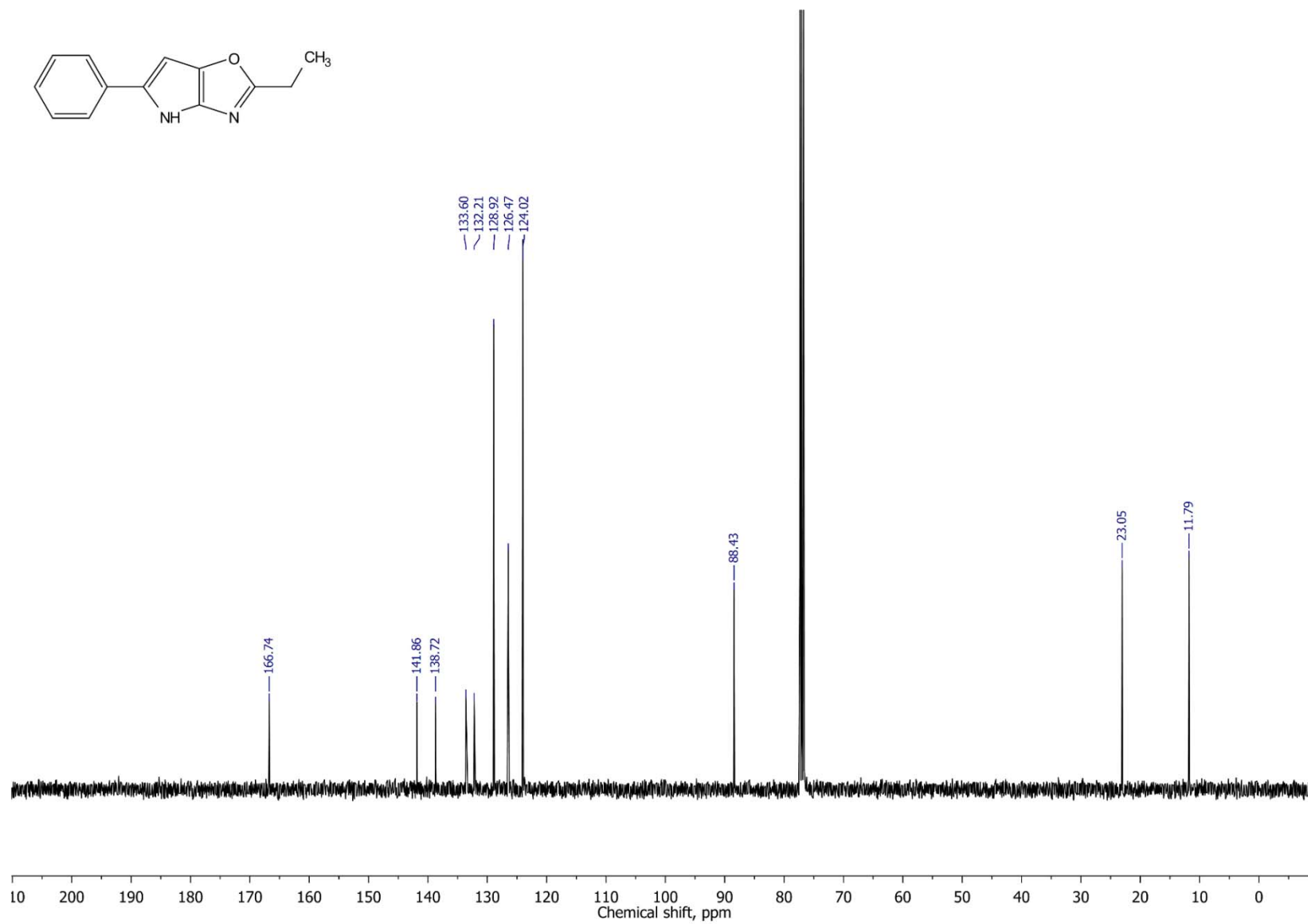
5-(Amantan-1-yl)-2-methyl-4*H*-pyrrolo[2,3-*d*]oxazole 3c, DEPT, 100 MHz, CDCl₃



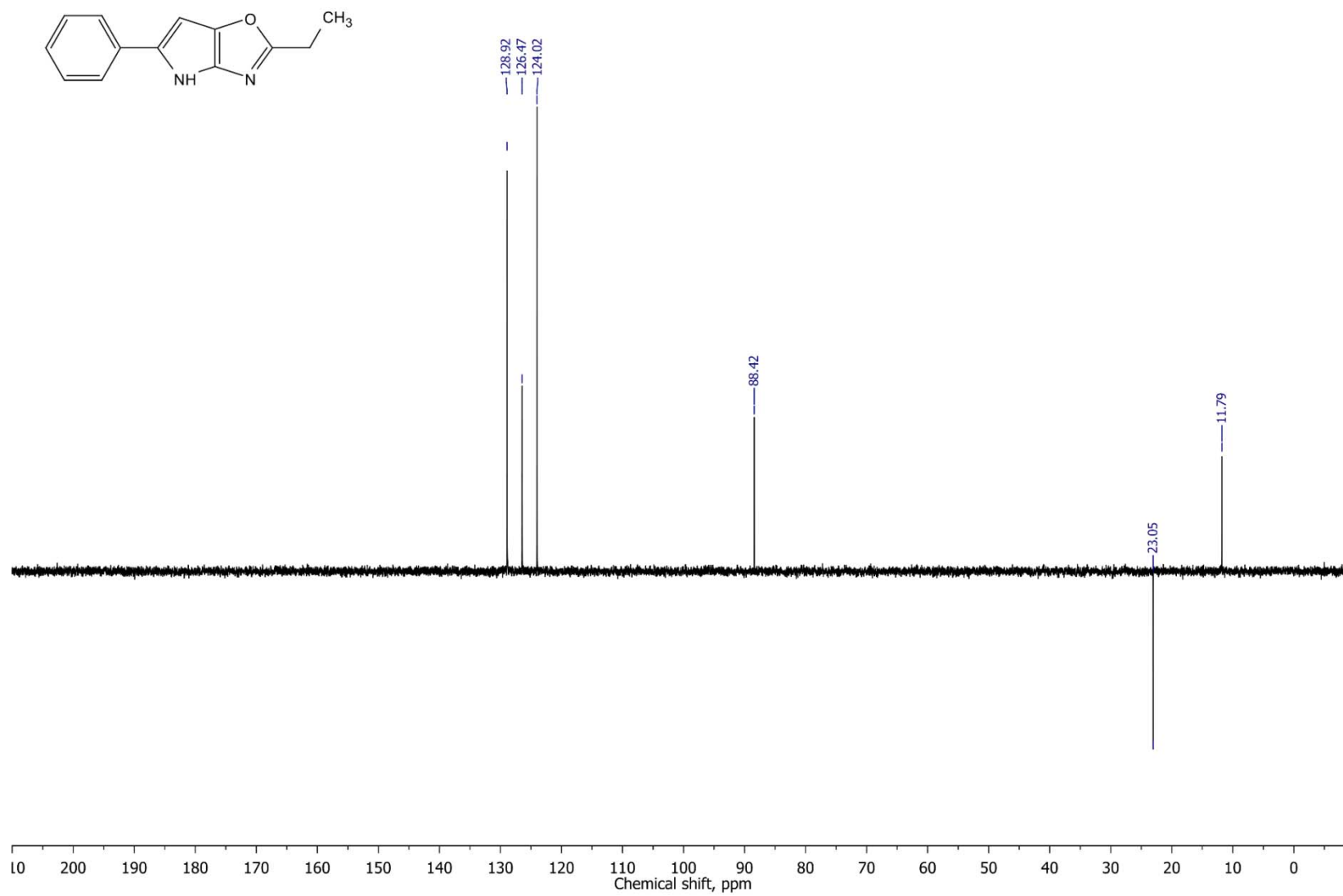
2-Ethyl-5-phenyl-4*H*-pyrrolo[2,3-*d*]oxazole 3d, ^1H NMR, 400 MHz, CDCl_3



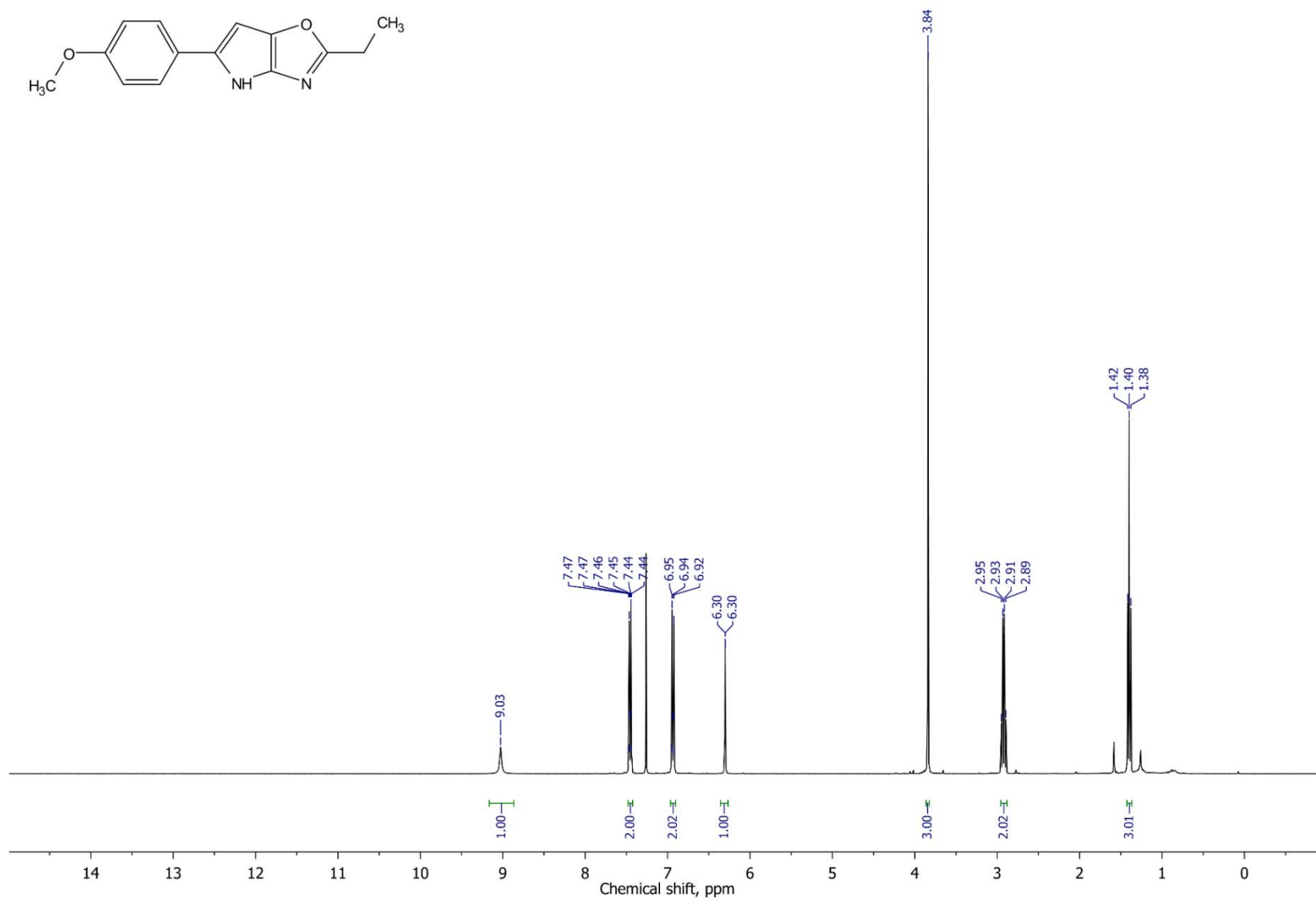
2-Ethyl-5-phenyl-4*H*-pyrrolo[2,3-*d*]oxazole 3d, $^{13}\text{C}\{^1\text{H}\}$ NMR, 100 MHz, CDCl_3



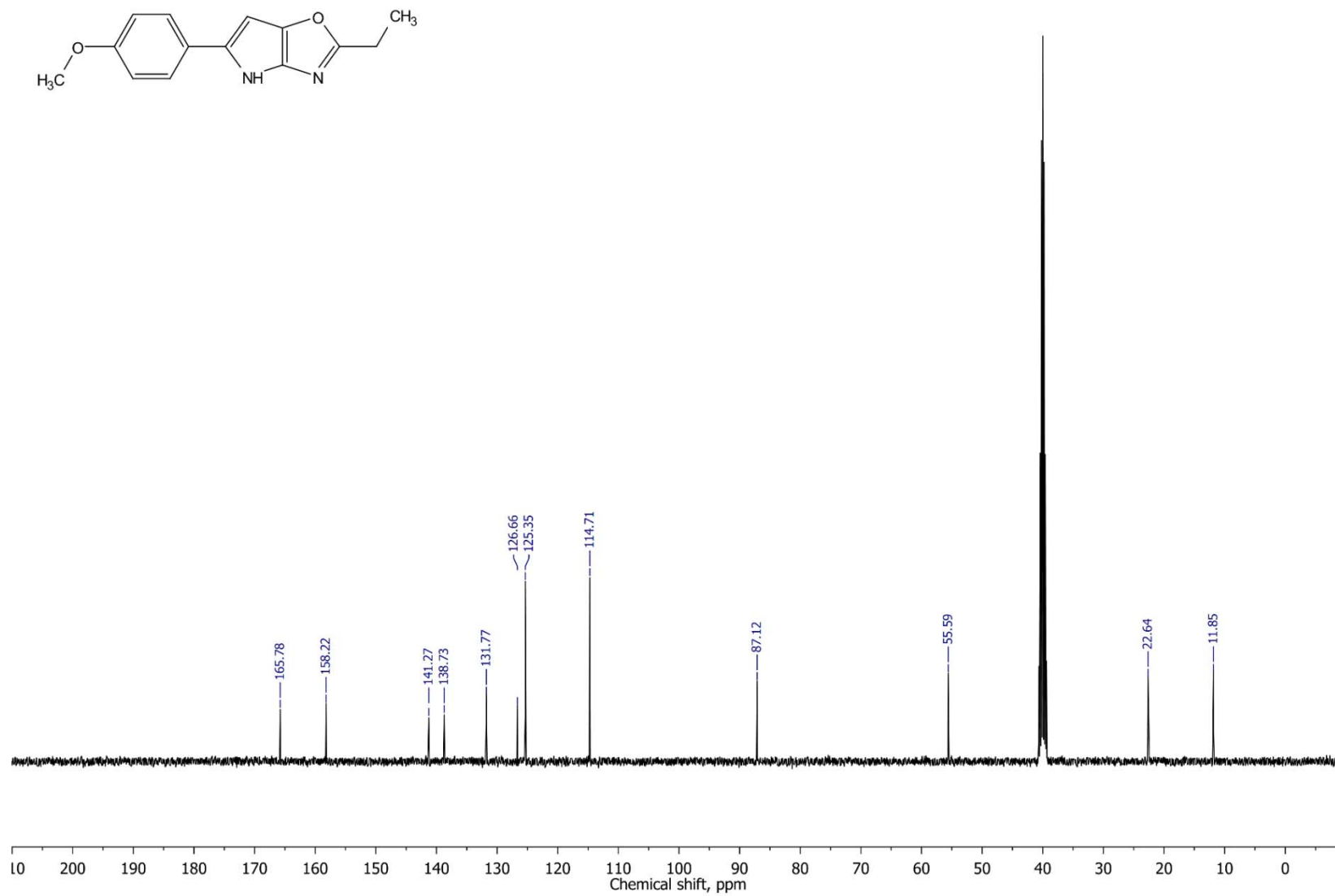
2-Ethyl-5-phenyl-4*H*-pyrrolo[2,3-*d*]oxazole 3d, DEPT, 100 MHz, CDCl₃



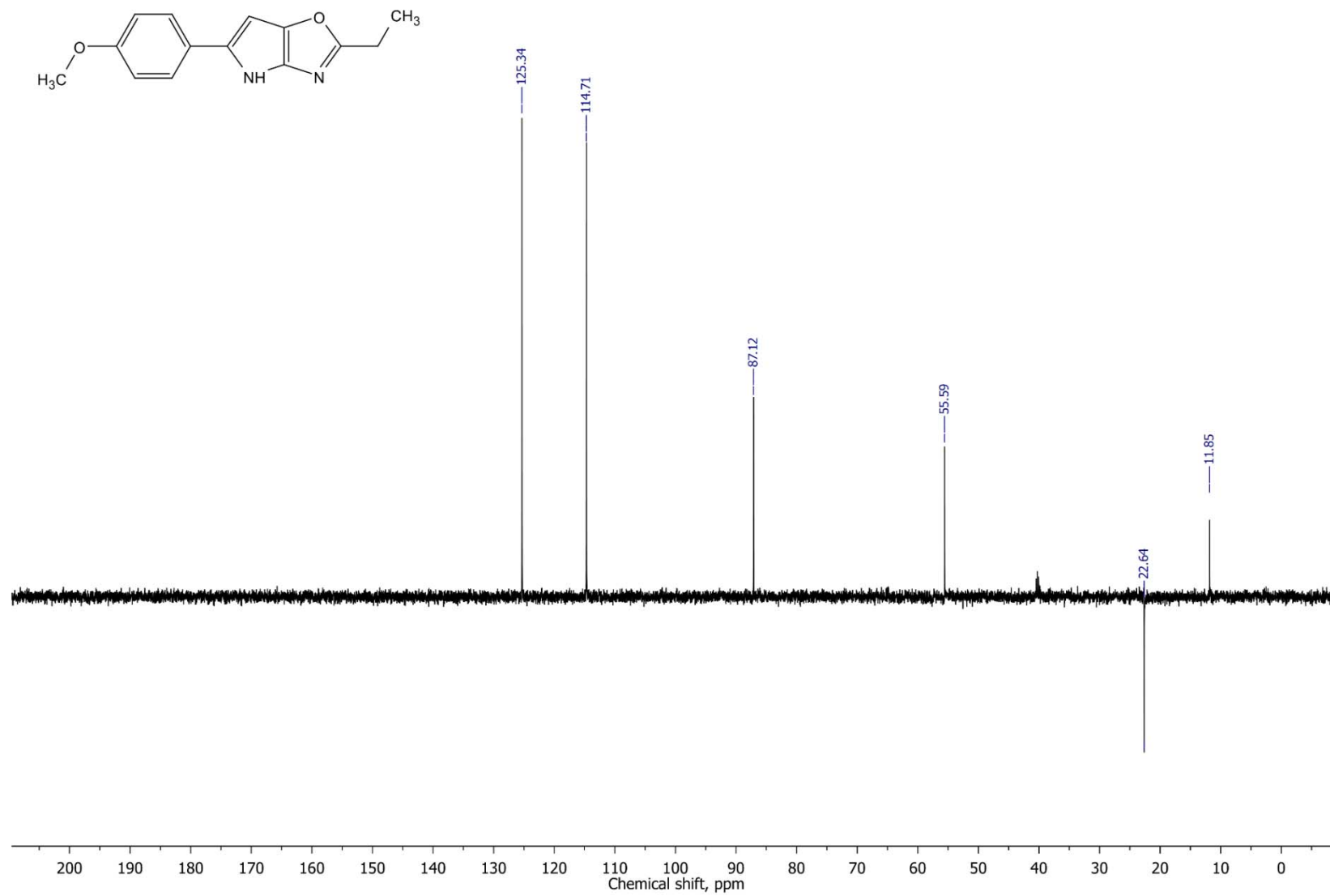
2-Ethyl-5-(4-methoxyphenyl)-4*H*-pyrrolo[2,3-*d*]oxazole 3e, ¹H NMR, 400 MHz, DMSO-*d*₆



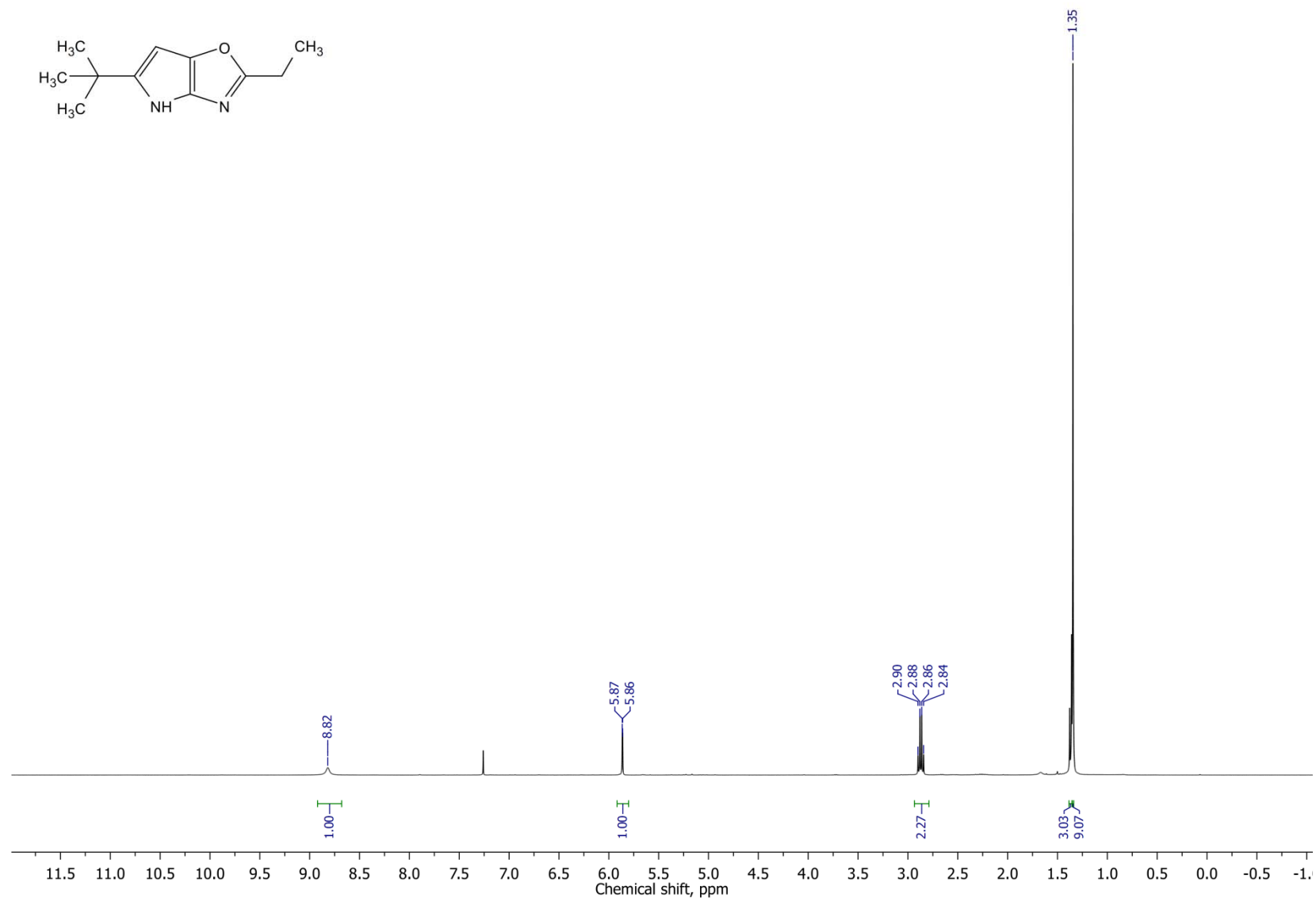
2-Ethyl-5-(4-methoxyphenyl)-4*H*-pyrrolo[2,3-*d*]oxazole 3e, $^{13}\text{C}\{^1\text{H}\}$ NMR, 100 MHz, DMSO- d_6



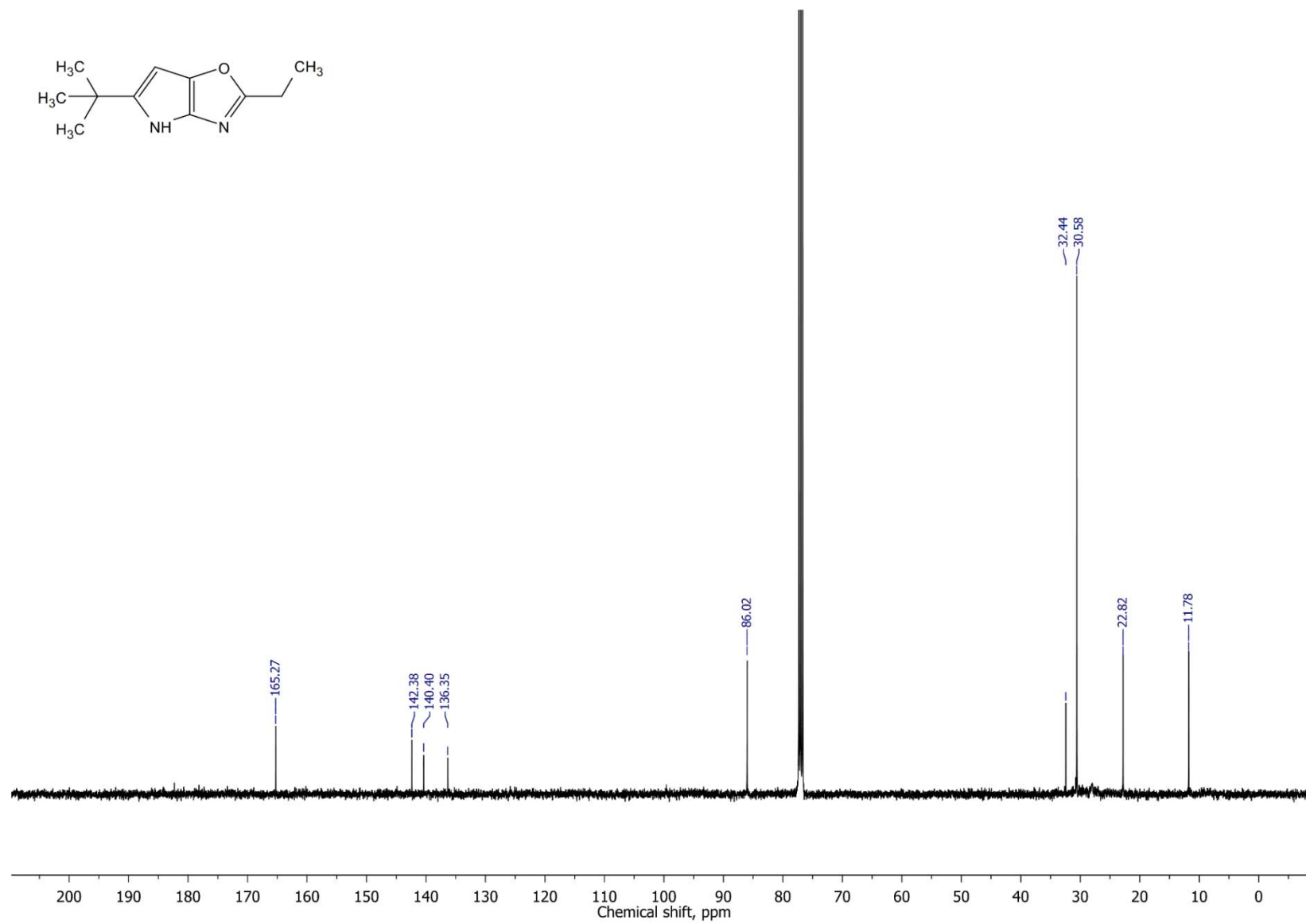
2-Ethyl-5-(4-methoxyphenyl)-4*H*-pyrrolo[2,3-*d*]oxazole 3e, DEPT NMR, 100 MHz, DMSO-*d*₆



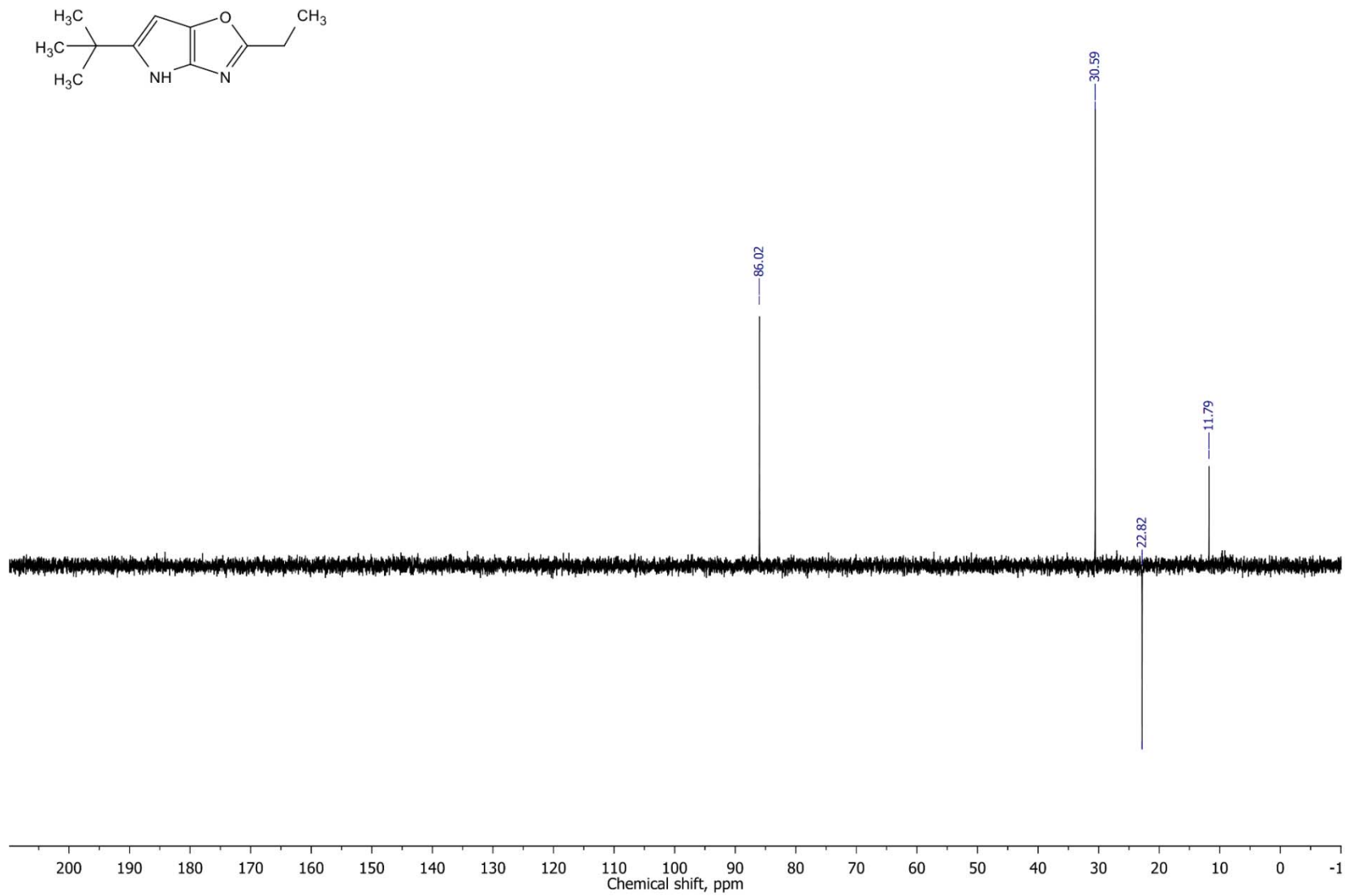
5-(*tert*-Butyl)-2-ethyl-4*H*-pyrrolo[2,3-*d*]oxazole 3f, ^1H NMR, 400 MHz, CDCl_3



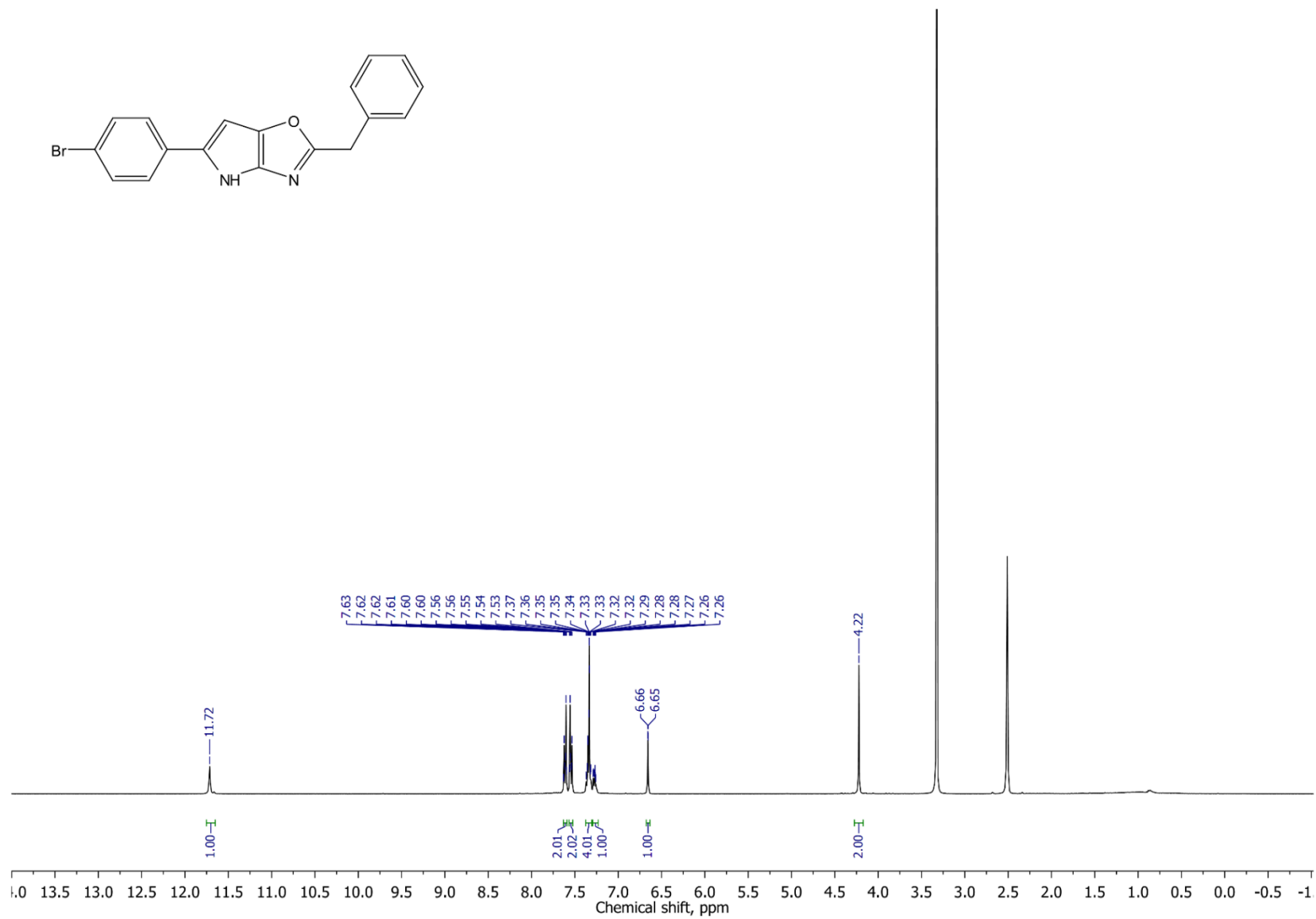
5-(*tert*-Butyl)-2-ethyl-4*H*-pyrrolo[2,3-*d*]oxazole 3f, $^{13}\text{C}\{^1\text{H}\}$ NMR, 100 MHz, CDCl_3



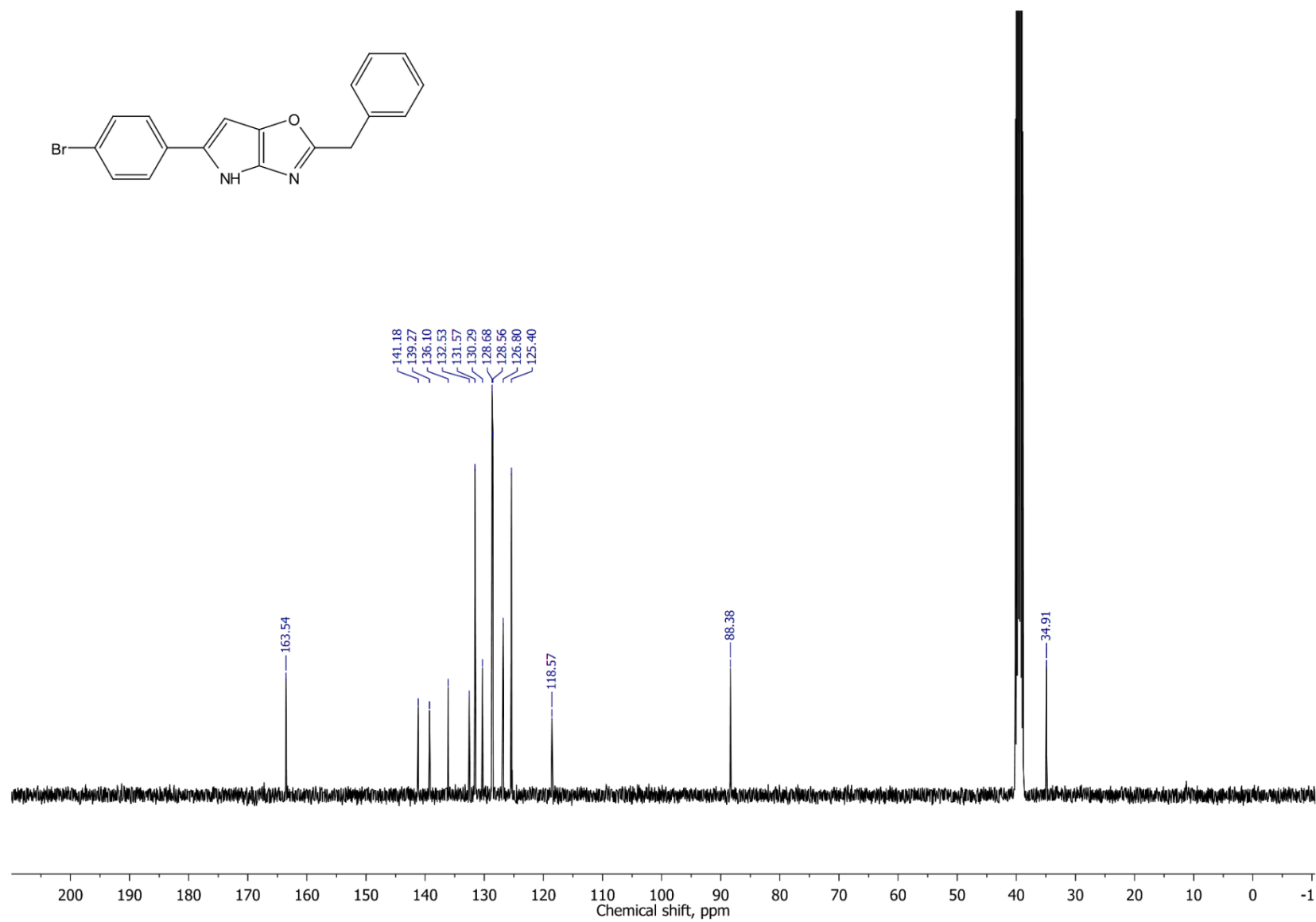
5-(*tert*-Butyl)-2-ethyl-4*H*-pyrrolo[2,3-*d*]oxazole 3f, DEPT, 100 MHz, CDCl₃



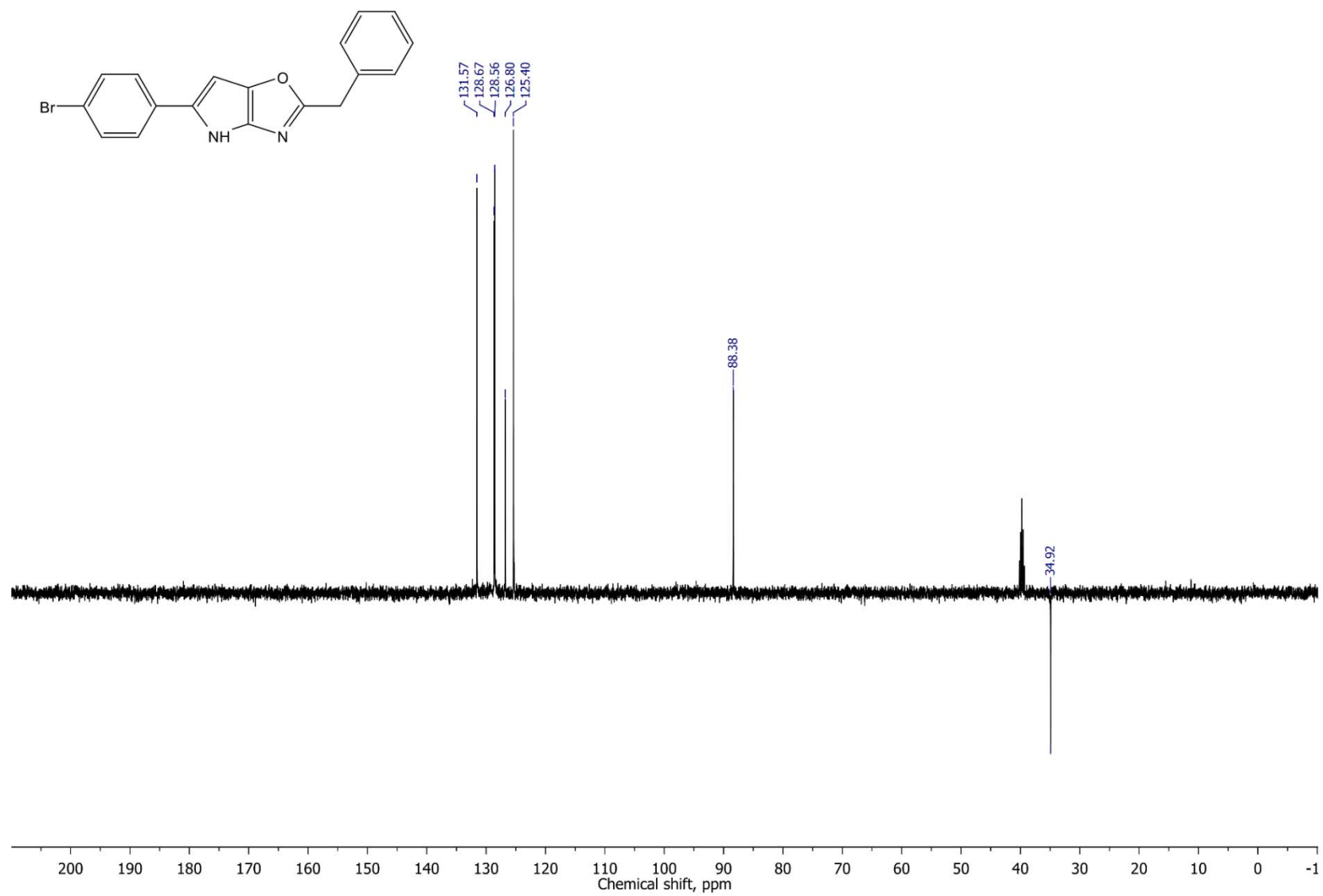
2-Benzyl-5-(4-bromophenyl)-4*H*-pyrrolo[2,3-*d*]oxazole 3g, ^1H NMR, 400 MHz, DMSO- d_6



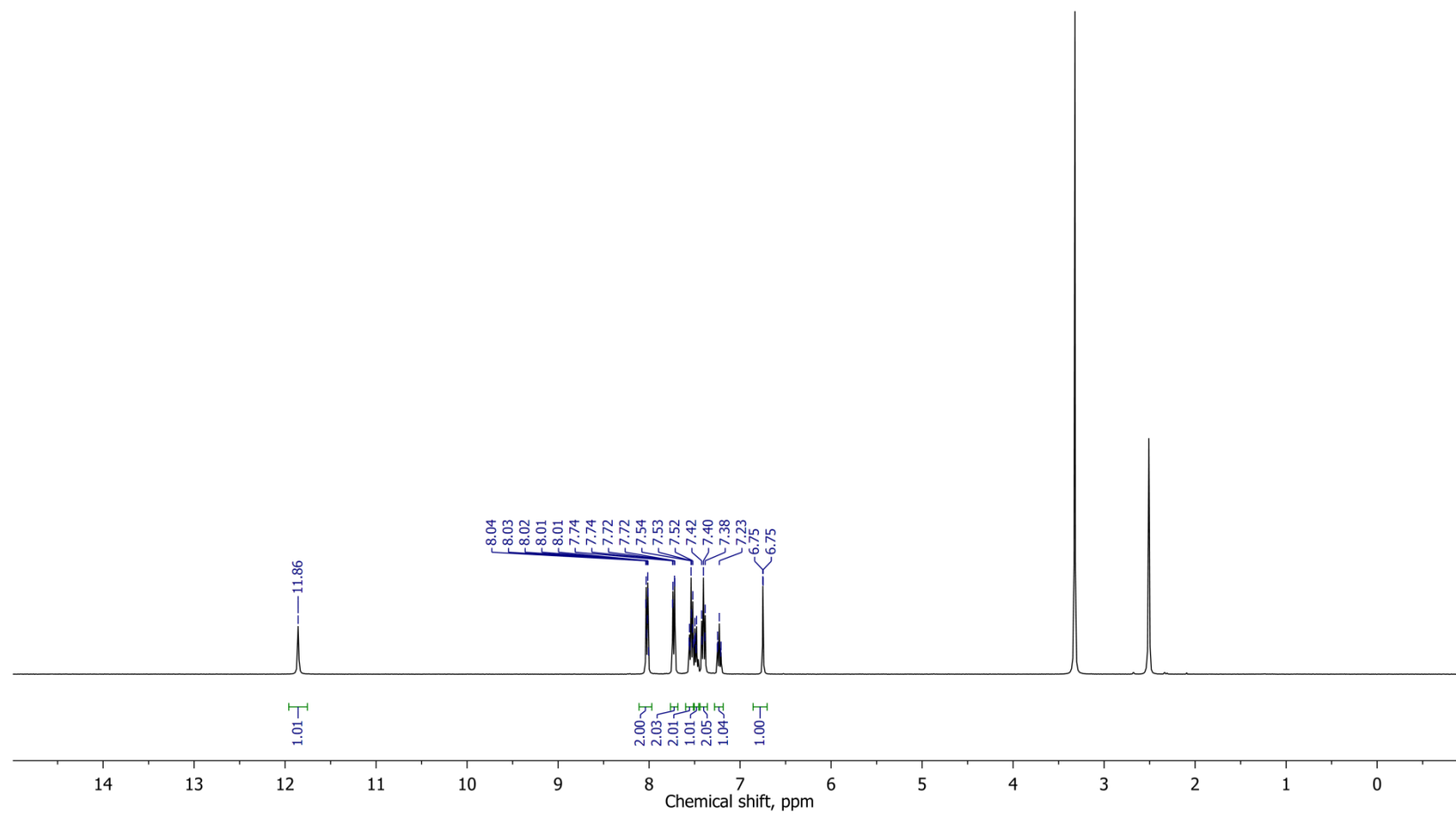
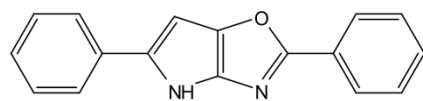
2-Benzyl-5-(4-bromophenyl)-4*H*-pyrrolo[2,3-*d*]oxazole 3g, $^{13}\text{C}\{^1\text{H}\}$ NMR, 100 MHz, DMSO- d_6



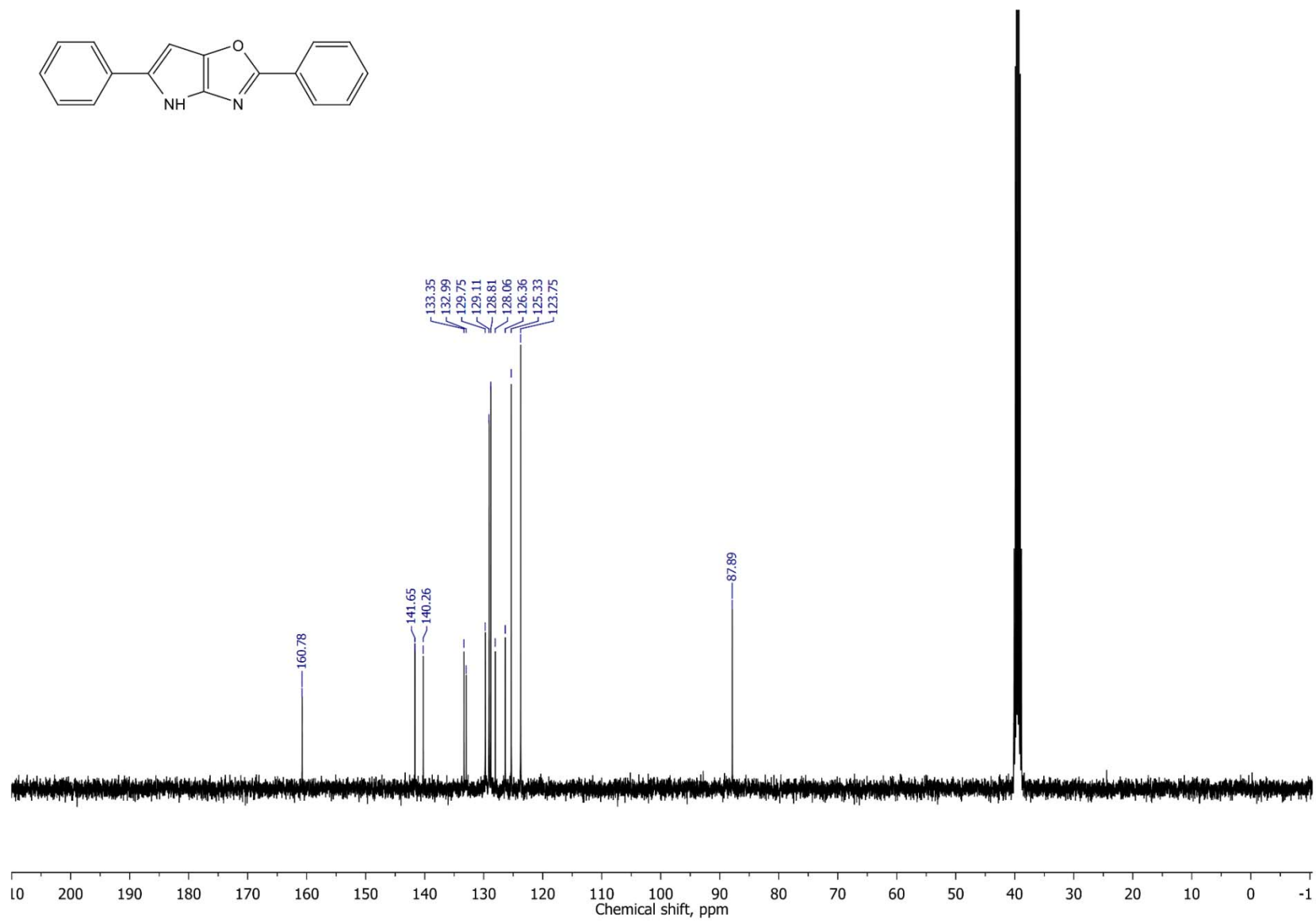
2-Benzyl-5-(4-bromophenyl)-4*H*-pyrrolo[2,3-*d*]oxazole 3g, DEPT, 100 MHz, DMSO-*d*₆



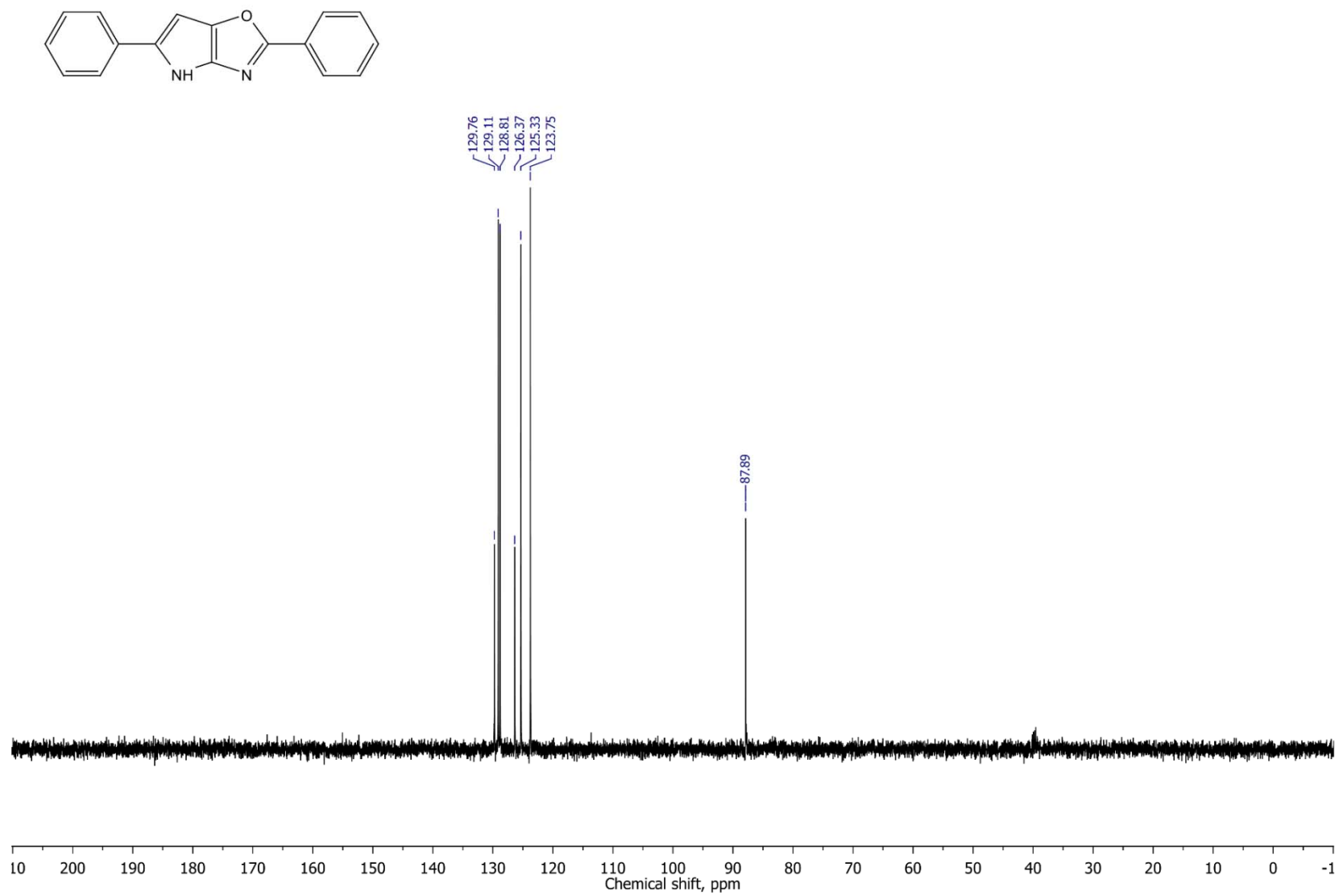
2,5-Diphenyl-4*H*-pyrrolo[2,3-*d*]oxazole 3h, ¹H NMR, 400 MHz, DMSO-*d*₆



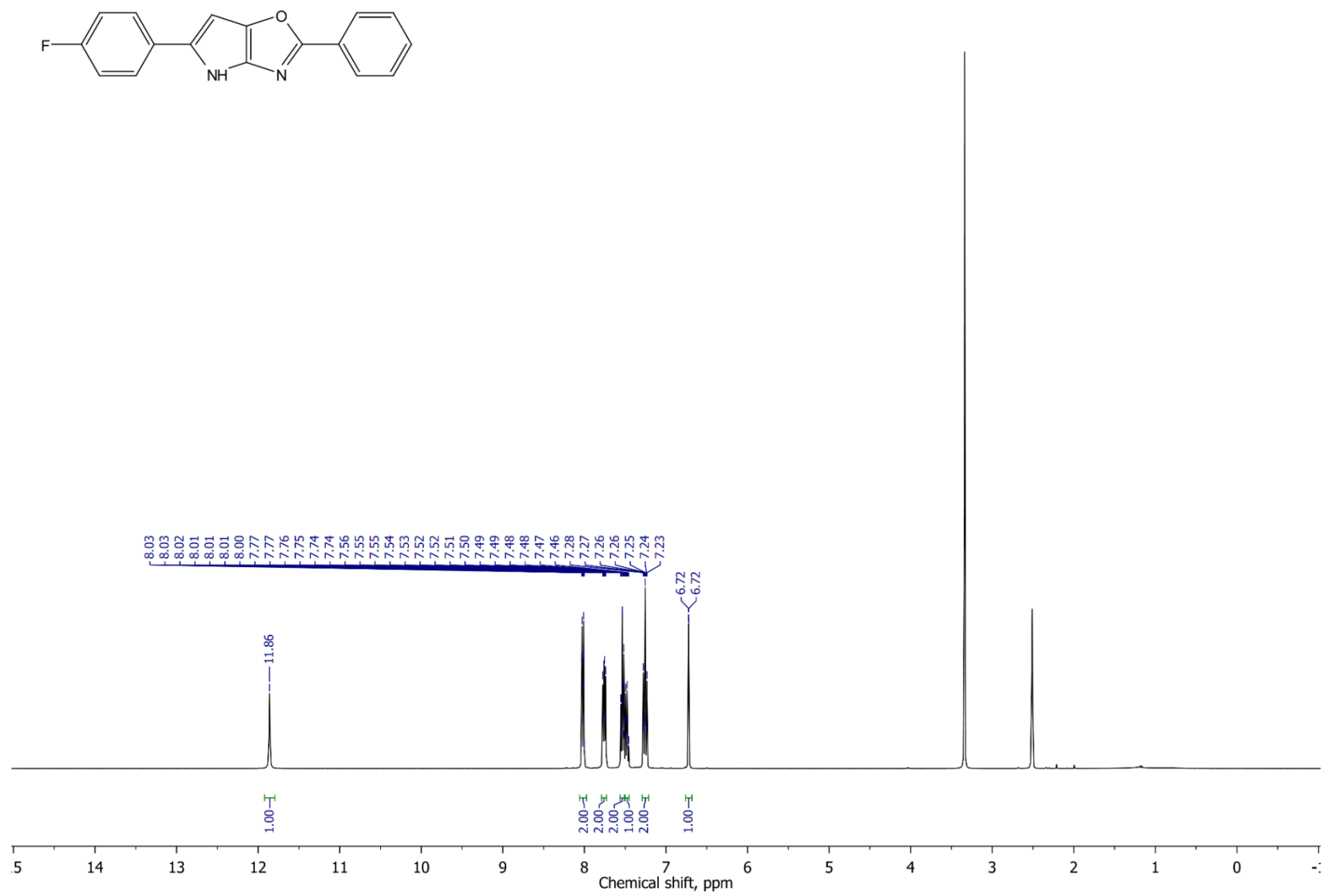
2,5-Diphenyl-4*H*-pyrrolo[2,3-*d*]oxazole 3h, $^{13}\text{C}\{^1\text{H}\}$ NMR, 100 MHz, DMSO- d_6



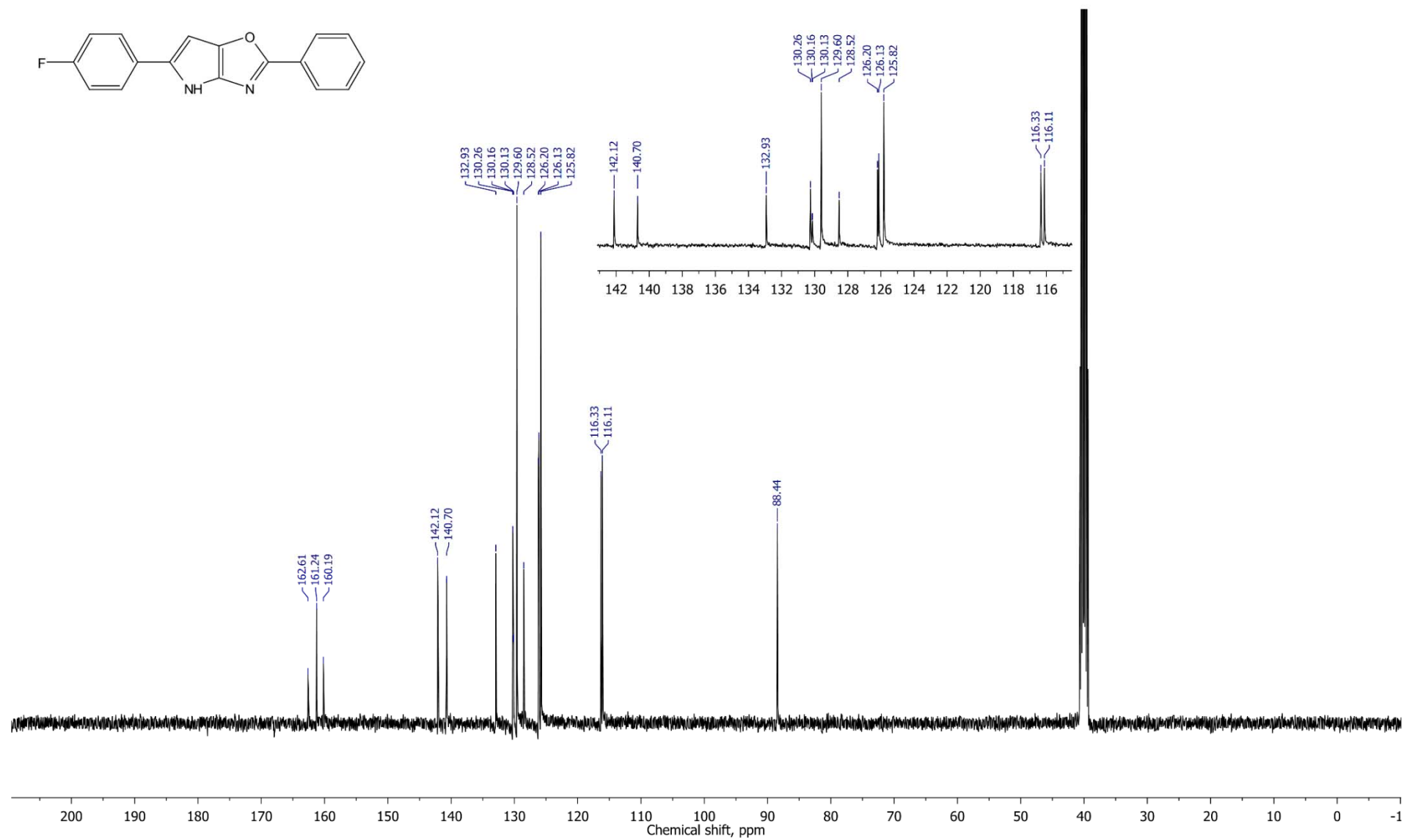
2,5-Diphenyl-4*H*-pyrrolo[2,3-*d*]oxazole 3h, DEPT, 100 MHz, DMSO-*d*₆



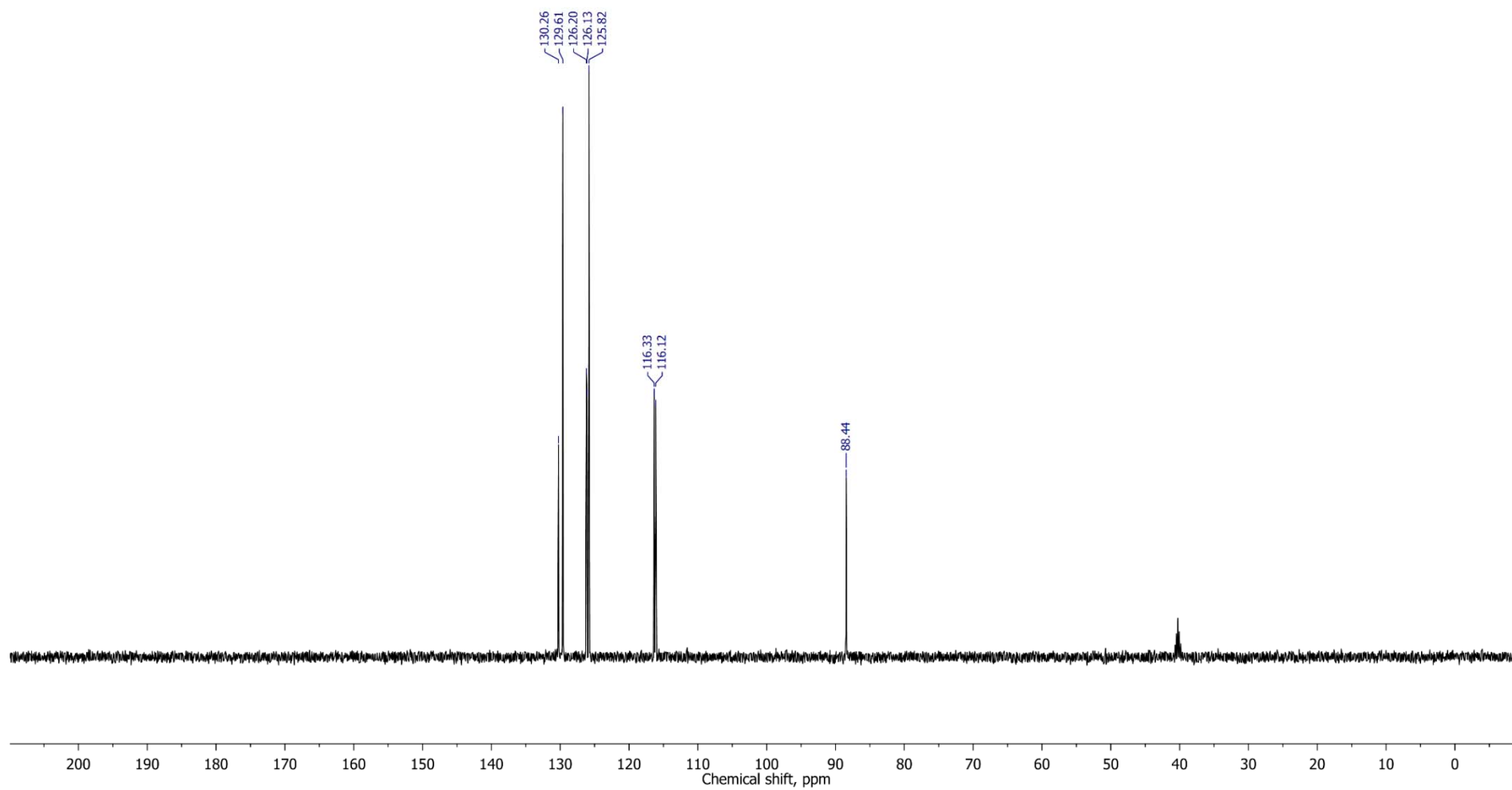
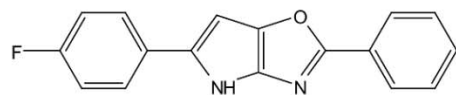
5-(4-Fluorophenyl)-2-phenyl-4*H*-pyrrolo[2,3-*d*]oxazole 3i, ¹H NMR, 400 MHz, DMSO-*d*₆



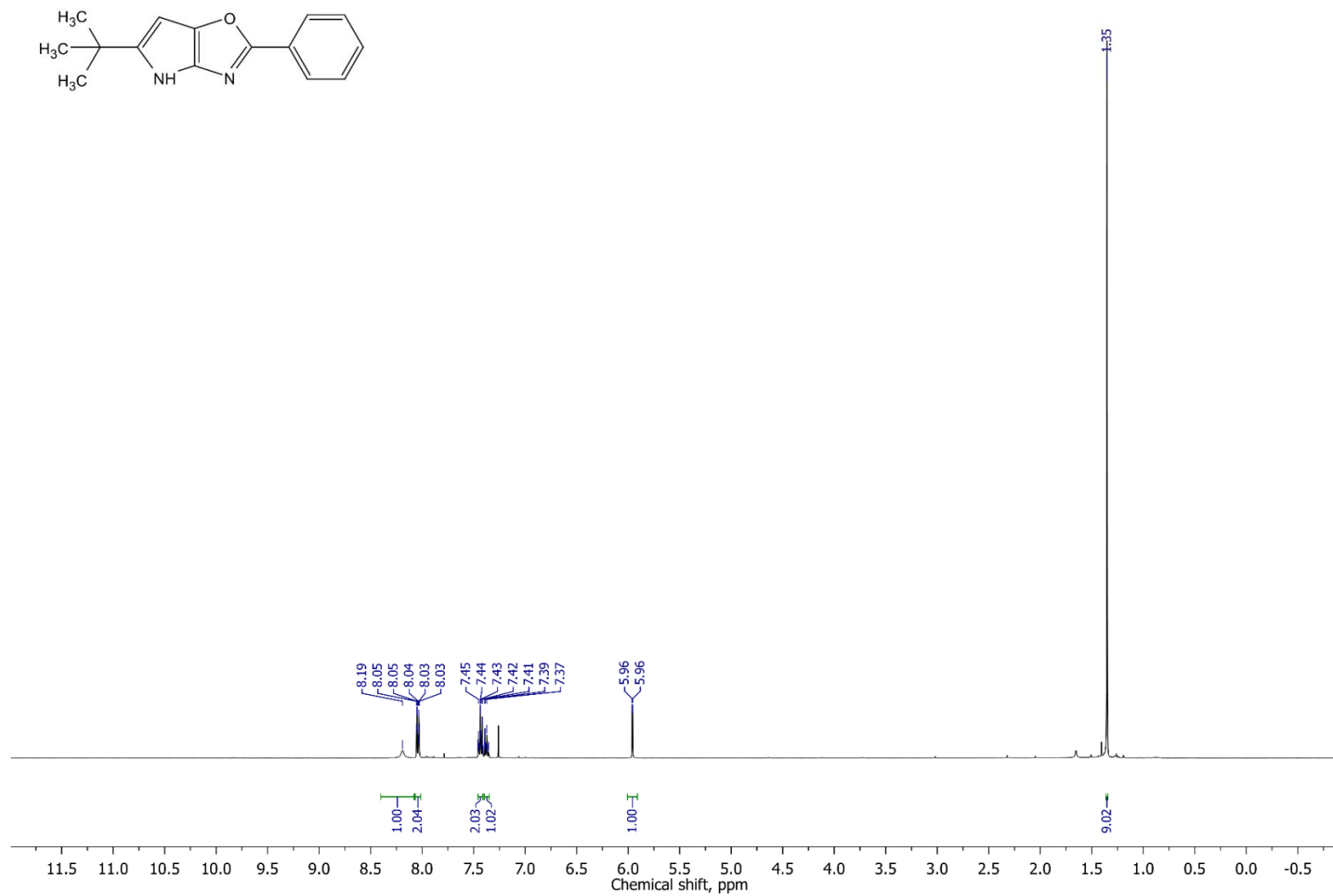
5-(4-Fluorophenyl)-2-phenyl-4*H*-pyrrolo[2,3-*d*]oxazole 3i, $^{13}\text{C}\{^1\text{H}\}$ NMR, 100 MHz, DMSO- d_6



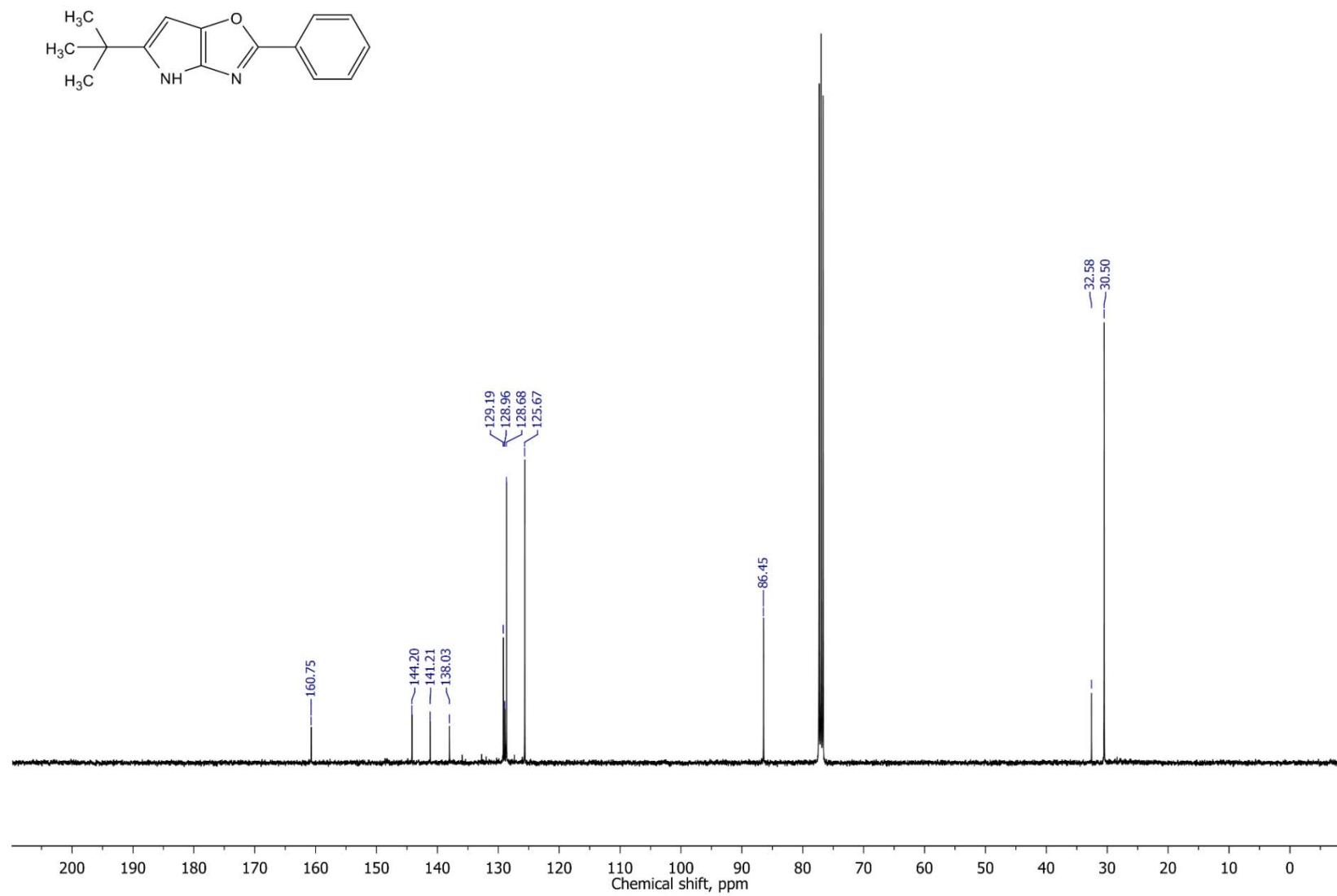
5-(4-Fluorophenyl)-2-phenyl-4*H*-pyrrolo[2,3-*d*]oxazole 3i, DEPT, 100 MHz, DMSO-*d*₆



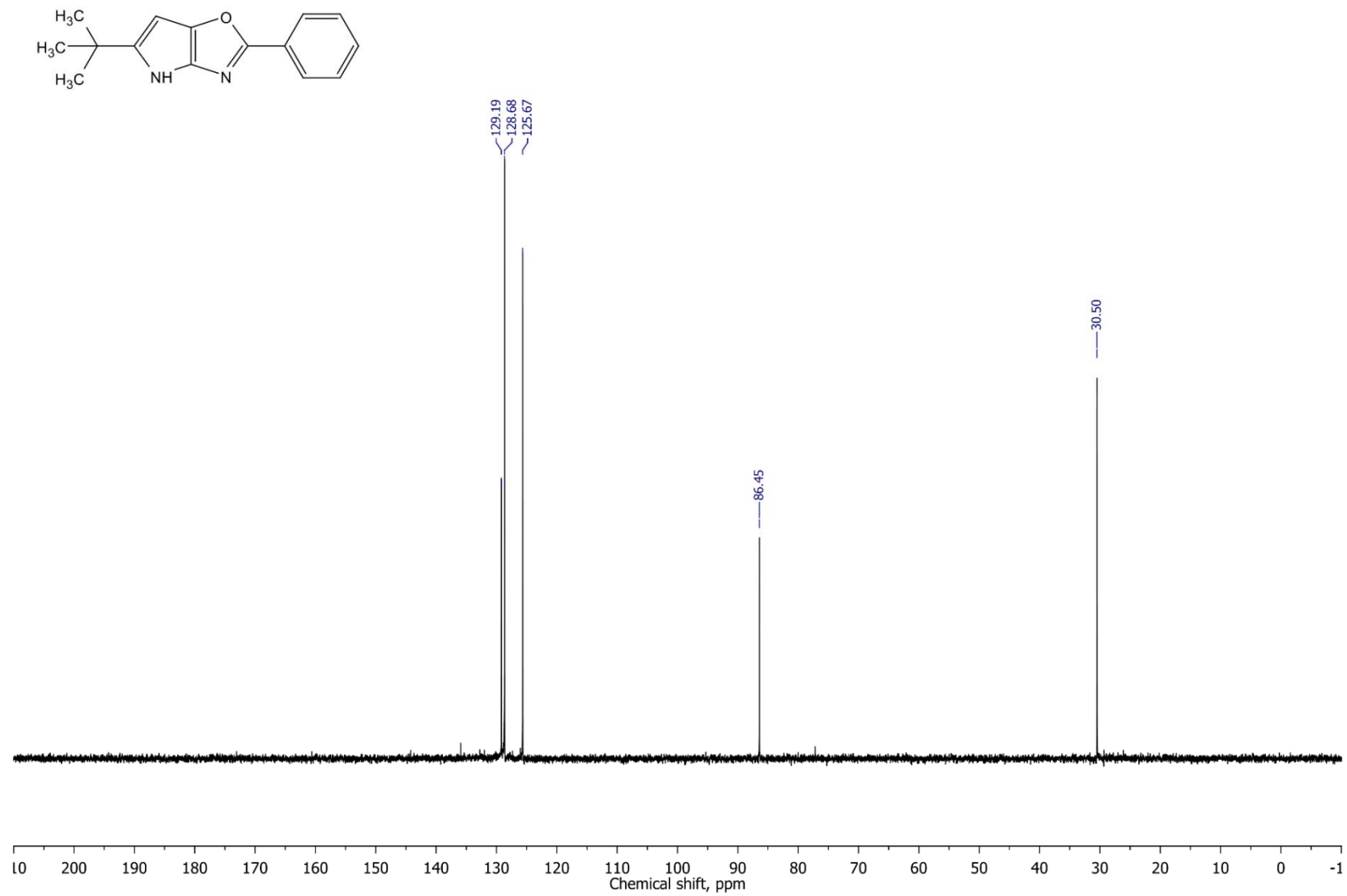
5-(*tert*-Butyl)-2-phenyl-4*H*-pyrrolo[2,3-*d*]oxazole 3j, ¹H NMR, 400 MHz, CDCl₃



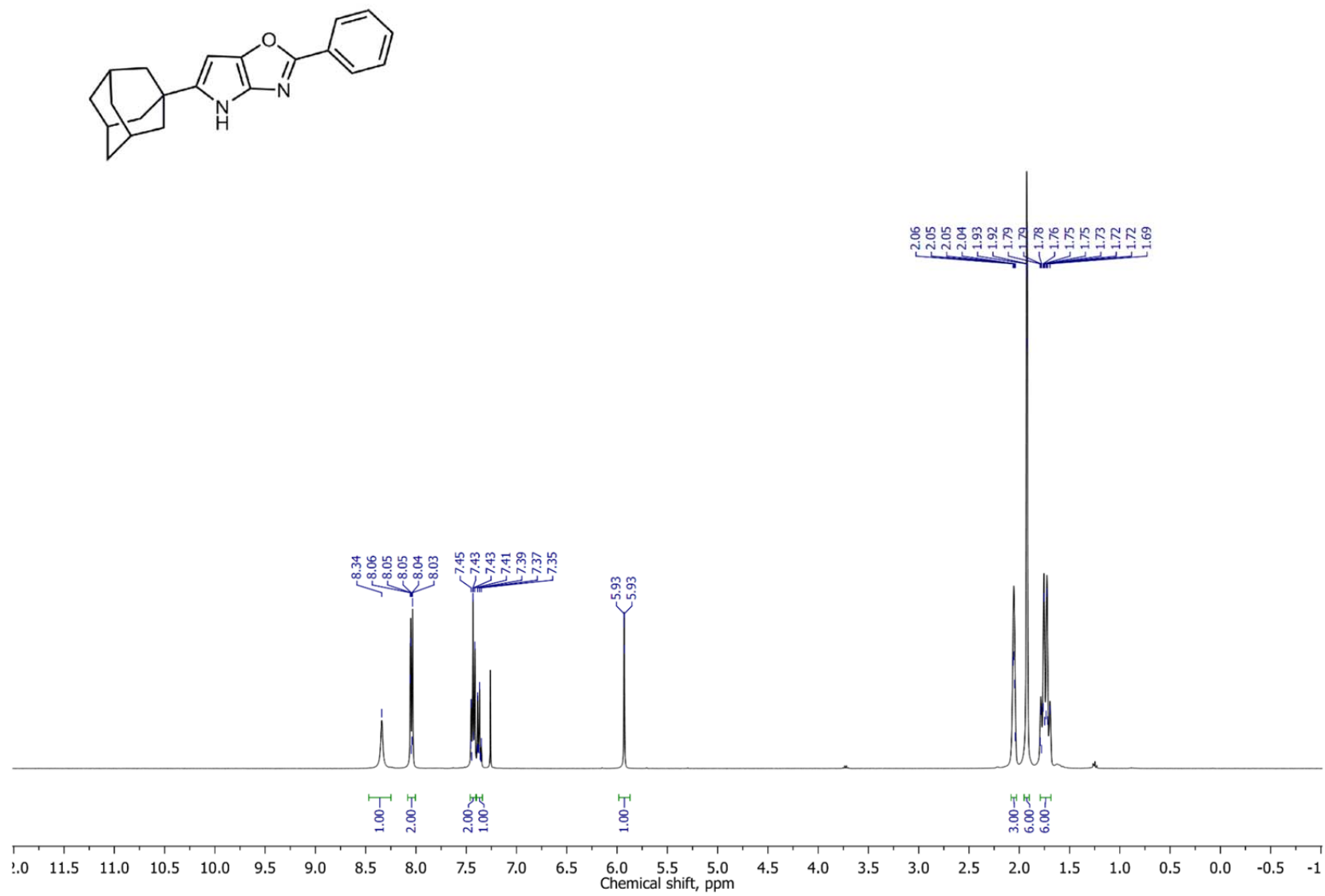
5-(*tert*-Butyl)-2-phenyl-4*H*-pyrrolo[2,3-*d*]oxazole 3j, $^{13}\text{C}\{^1\text{H}\}$ NMR, 100 MHz, CDCl_3



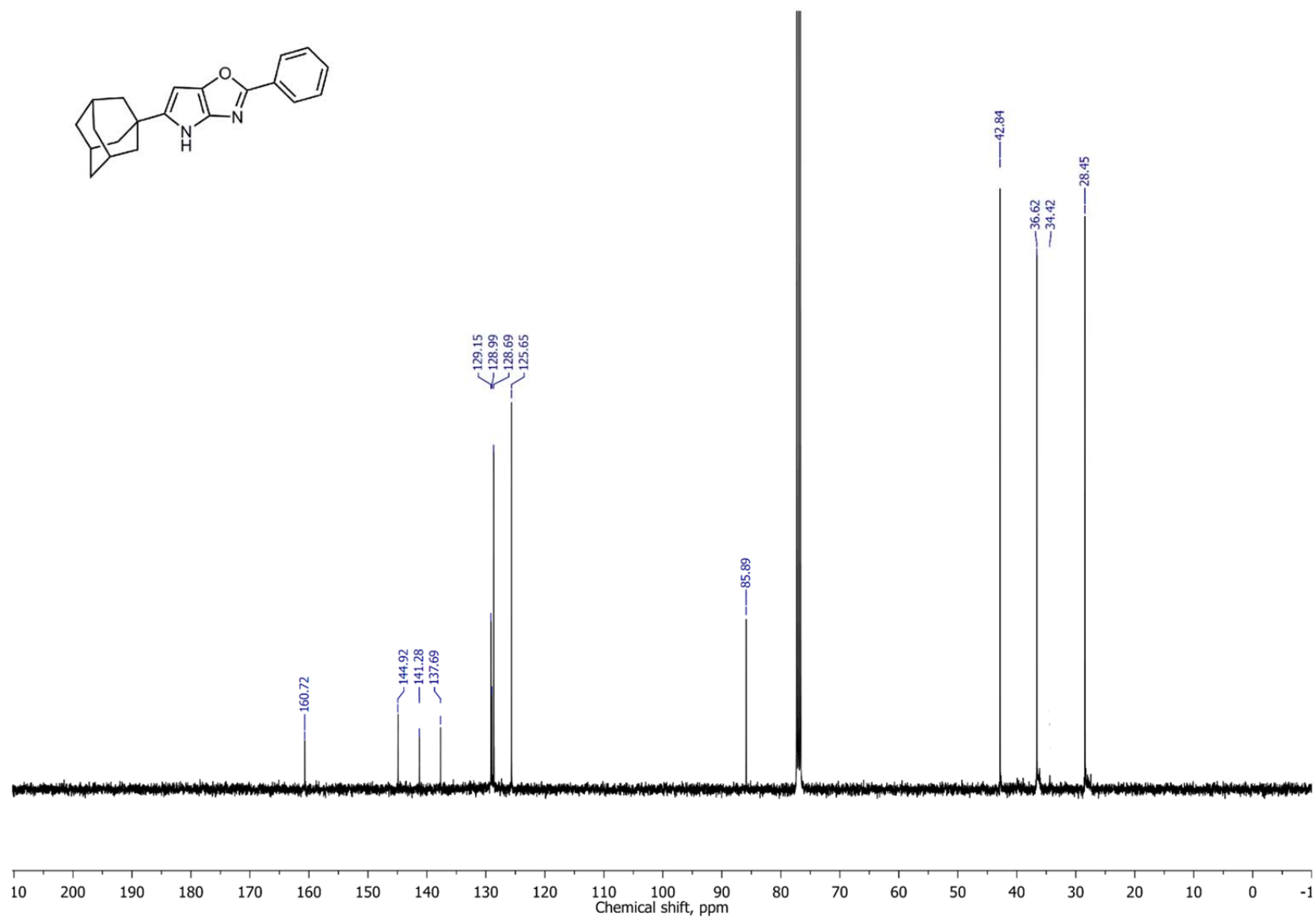
5-(*tert*-Butyl)-2-phenyl-4*H*-pyrrolo[2,3-*d*]oxazole 3j, DEPT, 100 MHz, CDCl₃



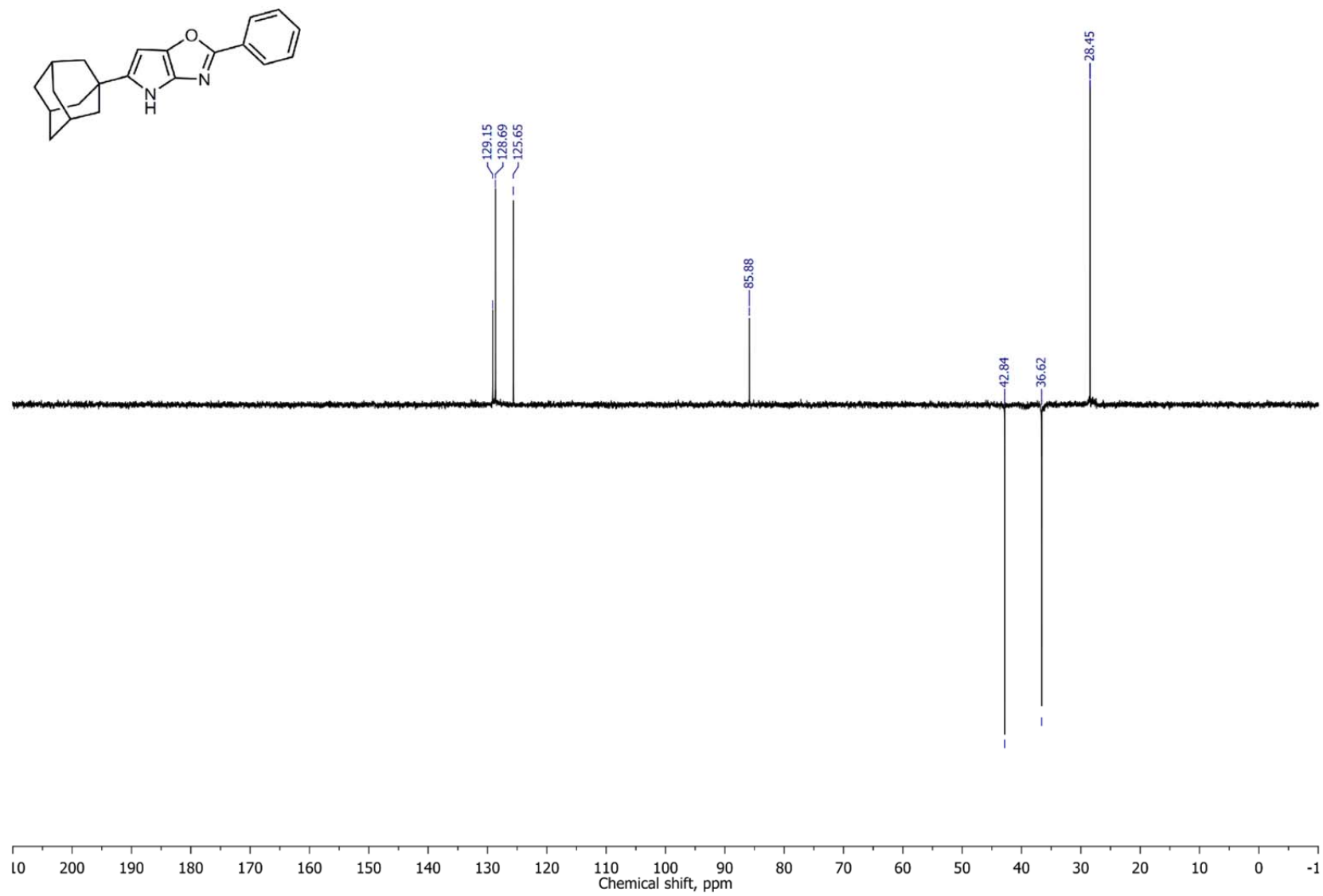
5-(Adamantan-1-yl)-2-phenyl-4*H*-pyrrolo[2,3-*d*]oxazole 3k, ¹H NMR, 400 MHz, CDCl₃



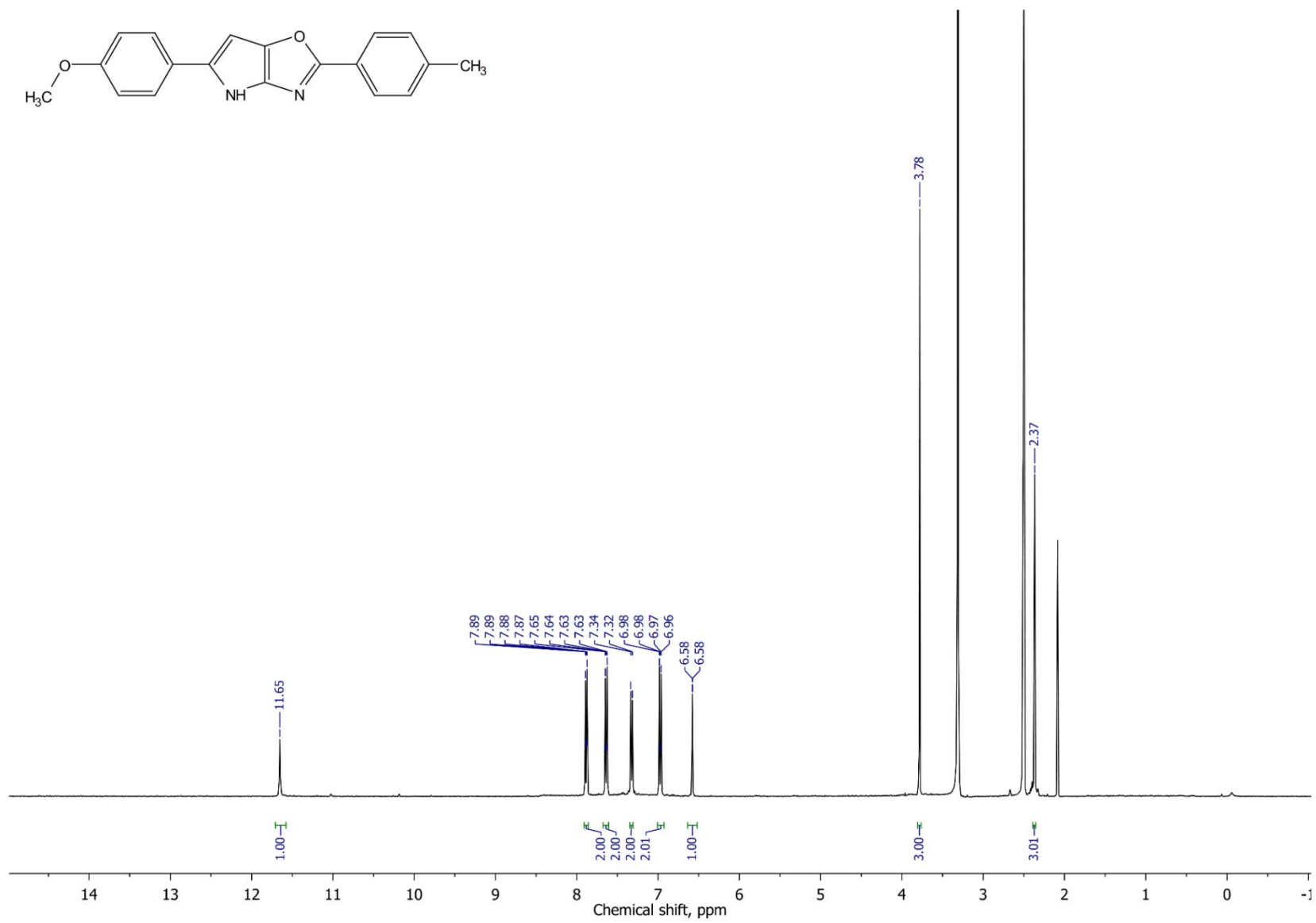
5-(Adamantan-1-yl)-2-phenyl-4*H*-pyrrolo[2,3-*d*]oxazole 3k, $^{13}\text{C}\{^1\text{H}\}$ NMR, 100 MHz, CDCl_3



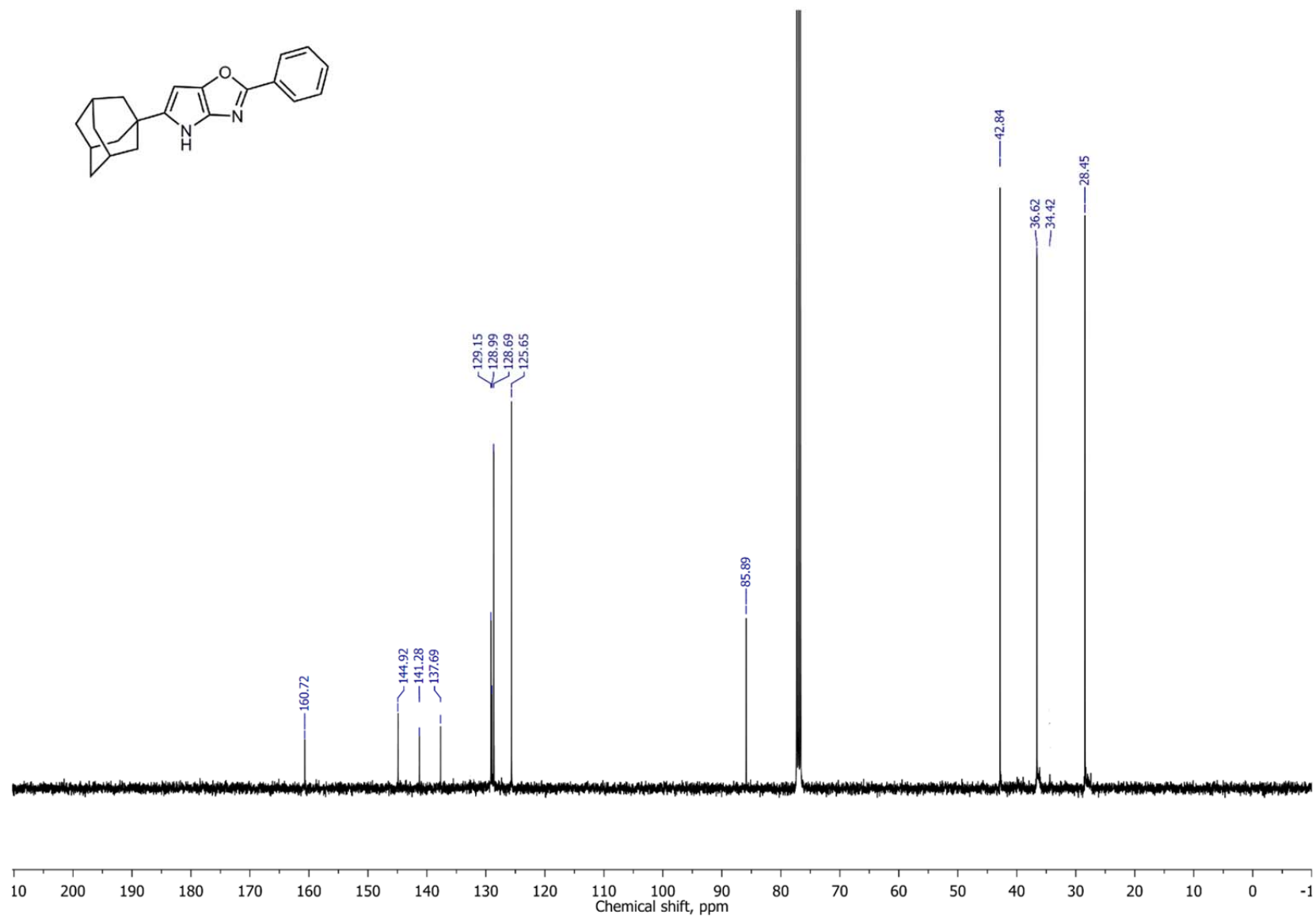
5-(Adamantan-1-yl)-2-phenyl-4H-pyrrolo[2,3-d]oxazole 3k, DEPT, 100 MHz, CDCl₃



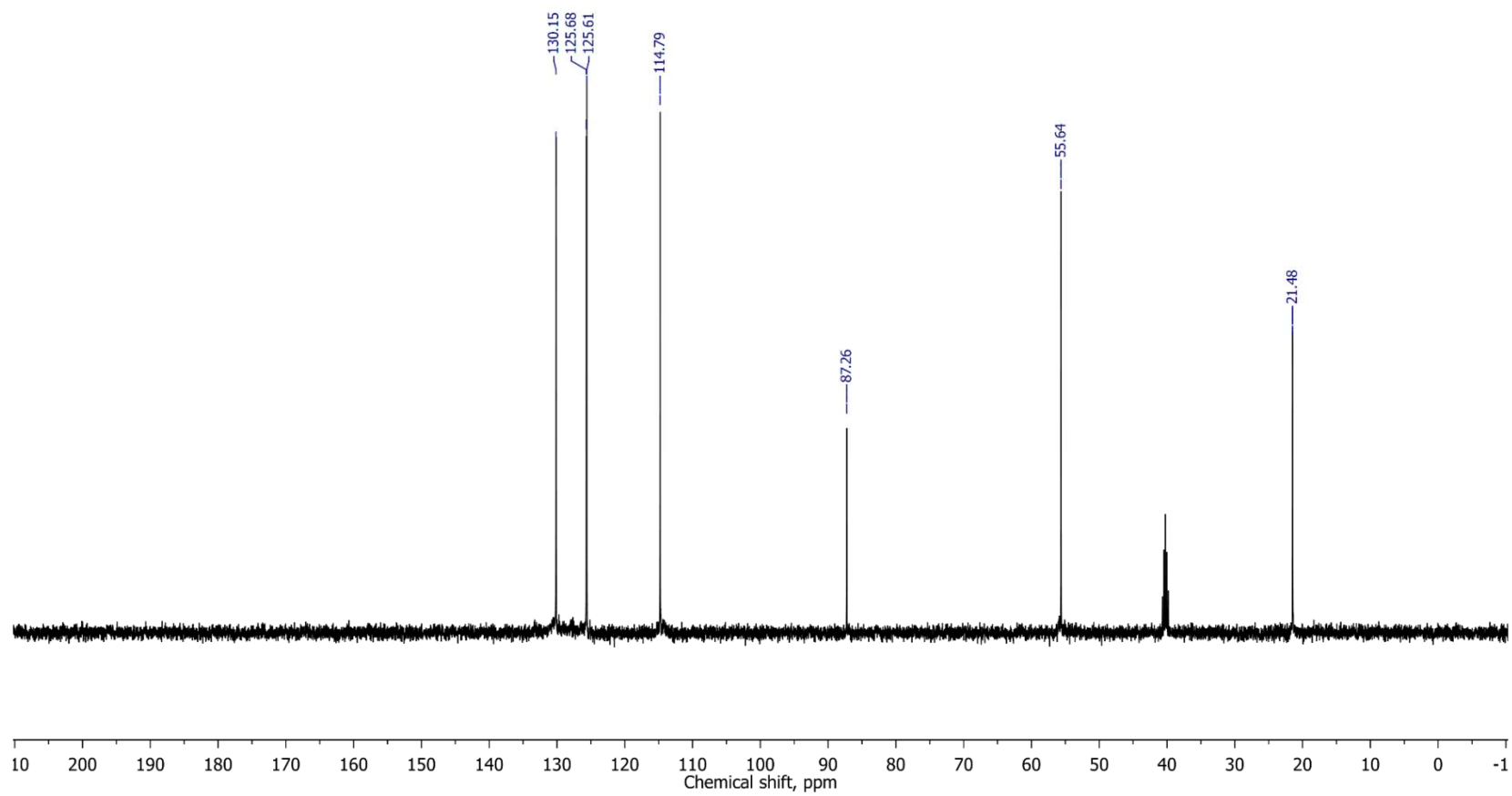
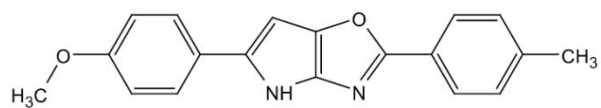
5-(4-Methoxyphenyl)-2-(*p*-tolyl)-4*H*-pyrrolo[2,3-*d*]oxazole 3l, ^1H NMR, 400 MHz, $\text{DMSO-}d_6$



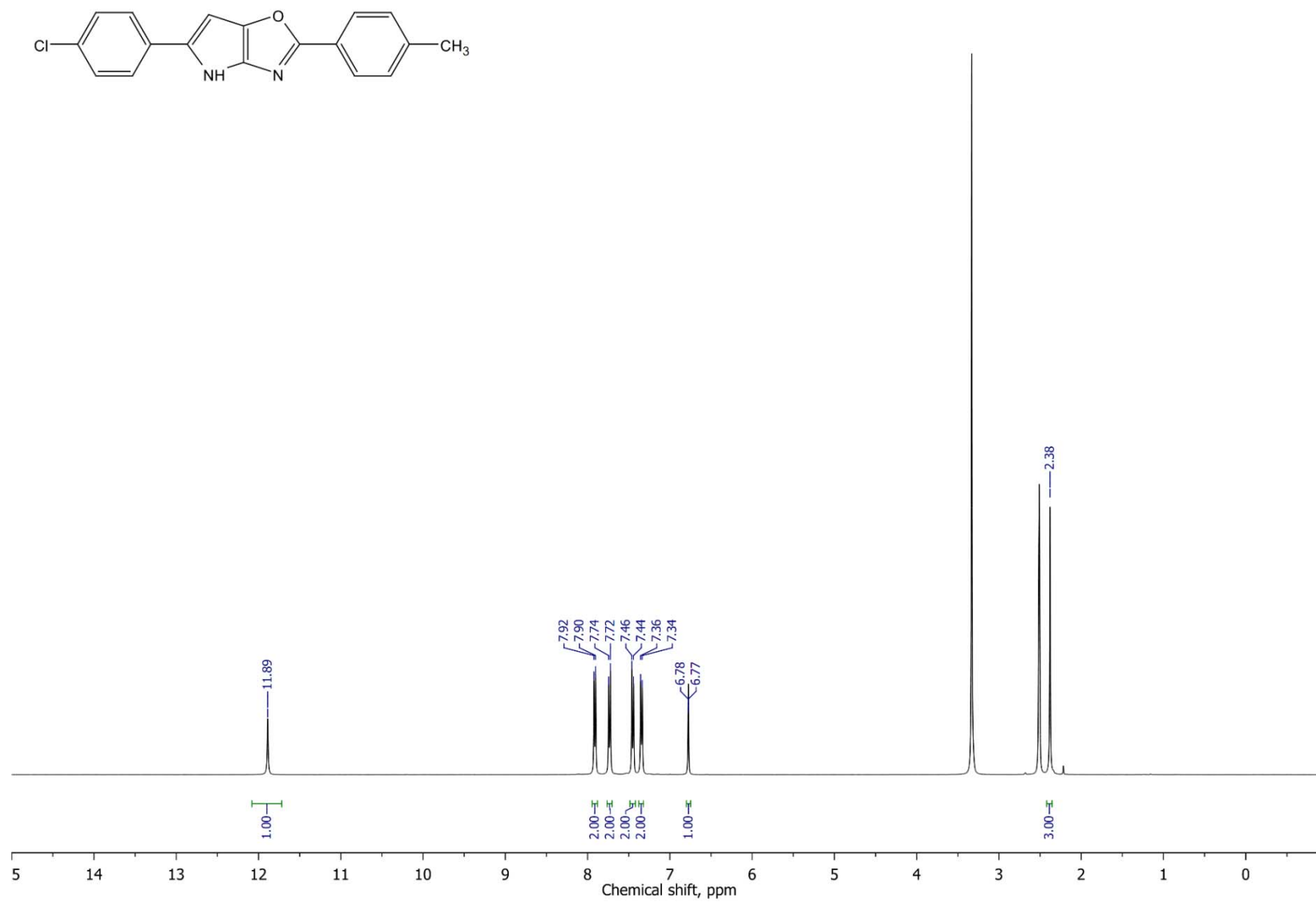
5-(4-Methoxyphenyl)-2-(*p*-tolyl)-4*H*-pyrrolo[2,3-*d*]oxazole 3l, $^{13}\text{C}\{^1\text{H}\}$ NMR, 100 MHz, DMSO- d_6



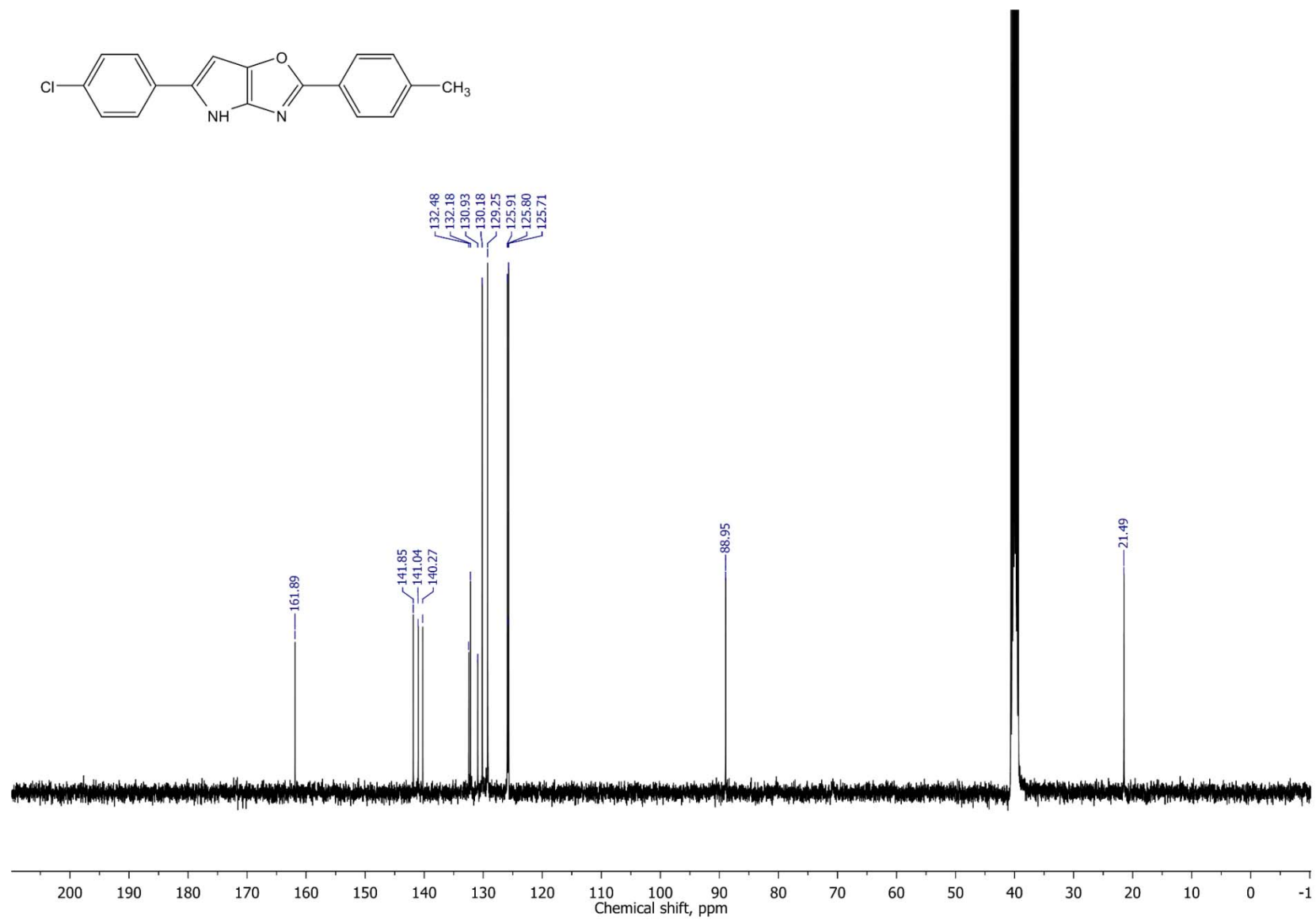
5-(4-Methoxyphenyl)-2-(*p*-tolyl)-4*H*-pyrrolo[2,3-*d*]oxazole 3l, DEPT, 100 MHz, DMSO-*d*₆



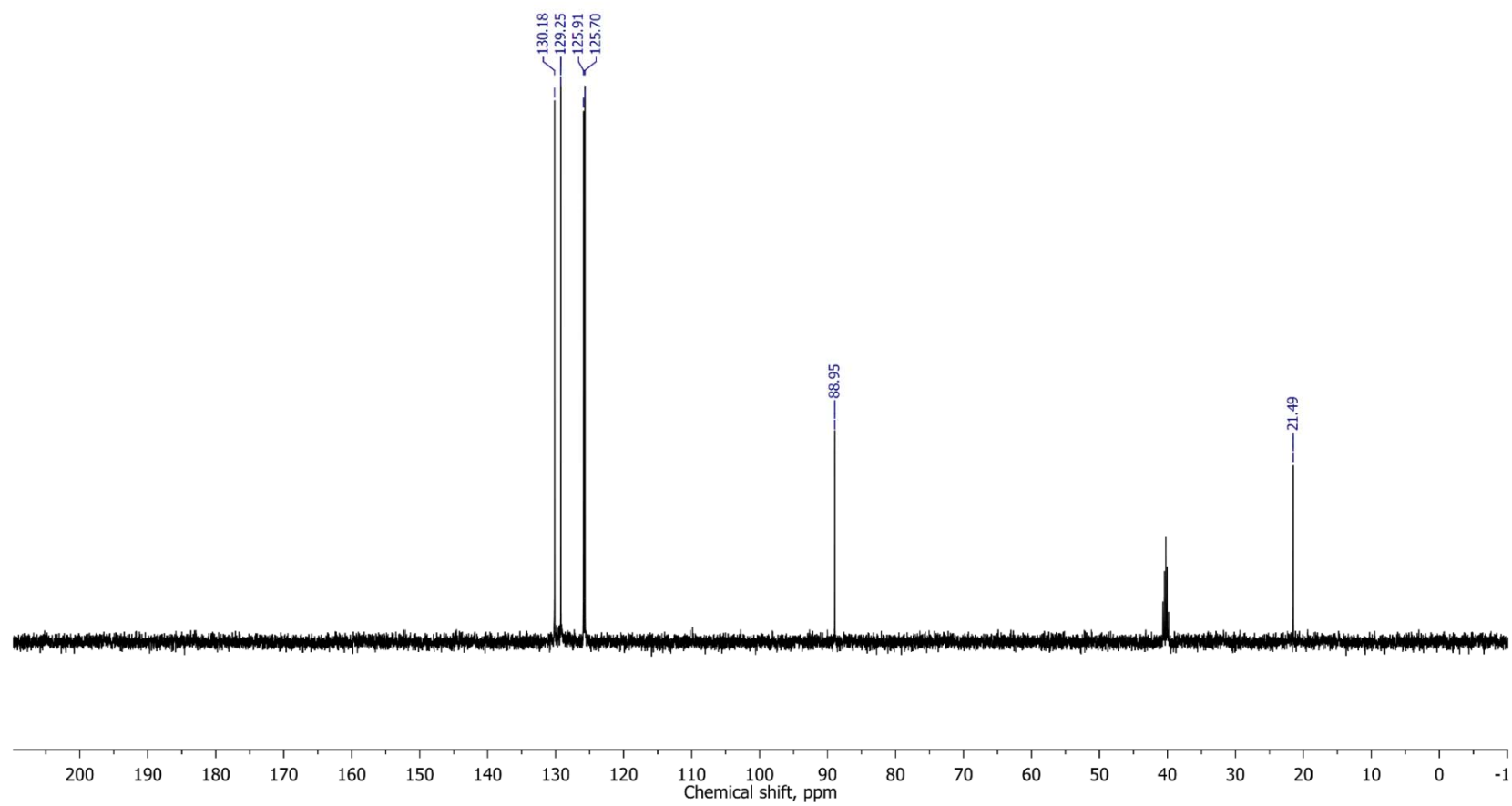
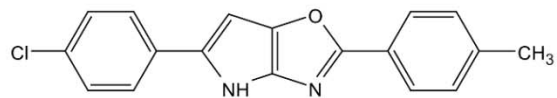
5-(4-Chlorophenyl)-2-(*p*-tolyl)-4*H*-pyrrolo[2,3-*d*]oxazole 3m, ^1H NMR, 400 MHz, $\text{DMSO-}d_6$



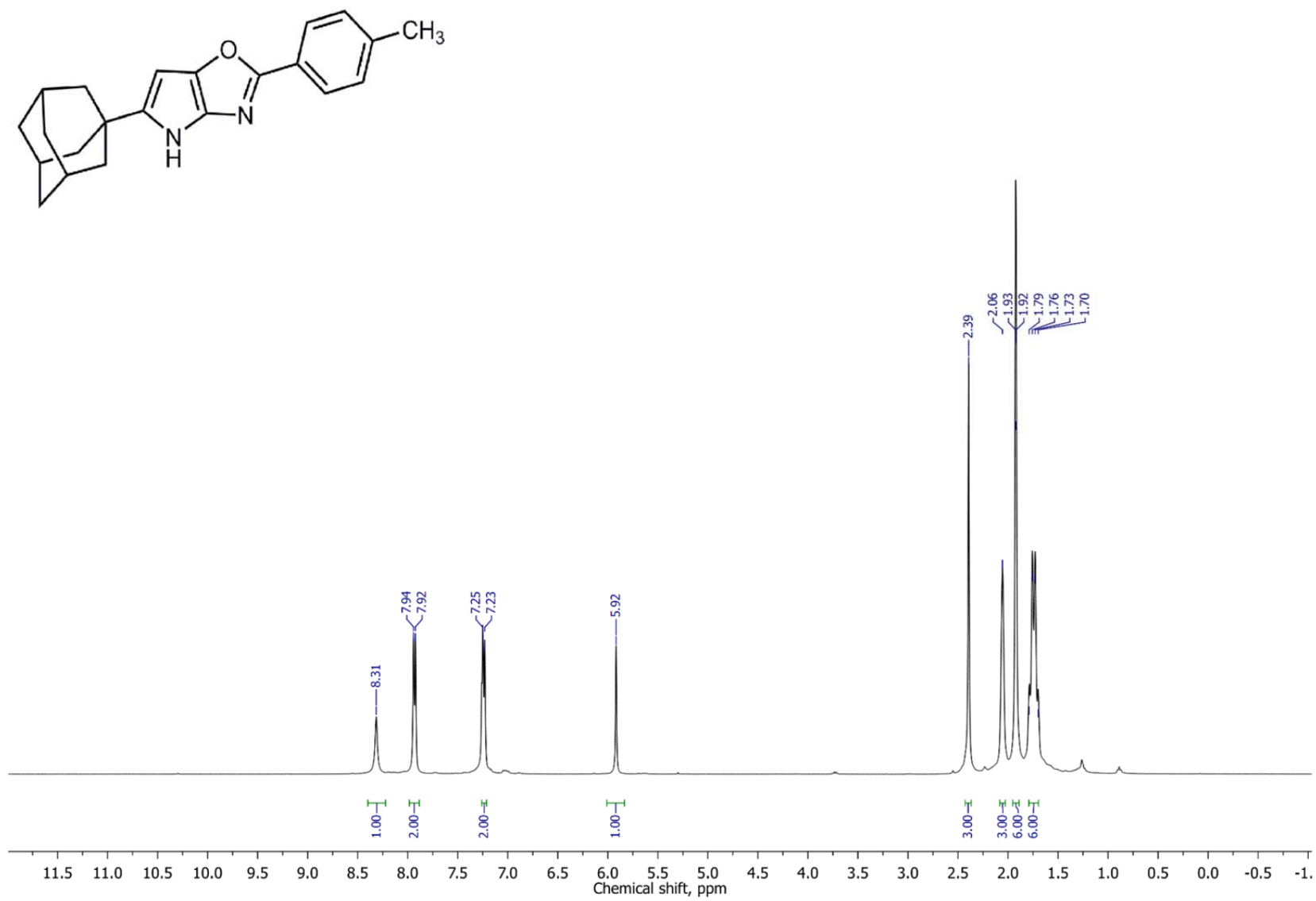
5-(4-Chlorophenyl)-2-(*p*-tolyl)-4*H*-pyrrolo[2,3-*d*]oxazole 3m, $^{13}\text{C}\{^1\text{H}\}$ NMR, 100 MHz, DMSO- d_6



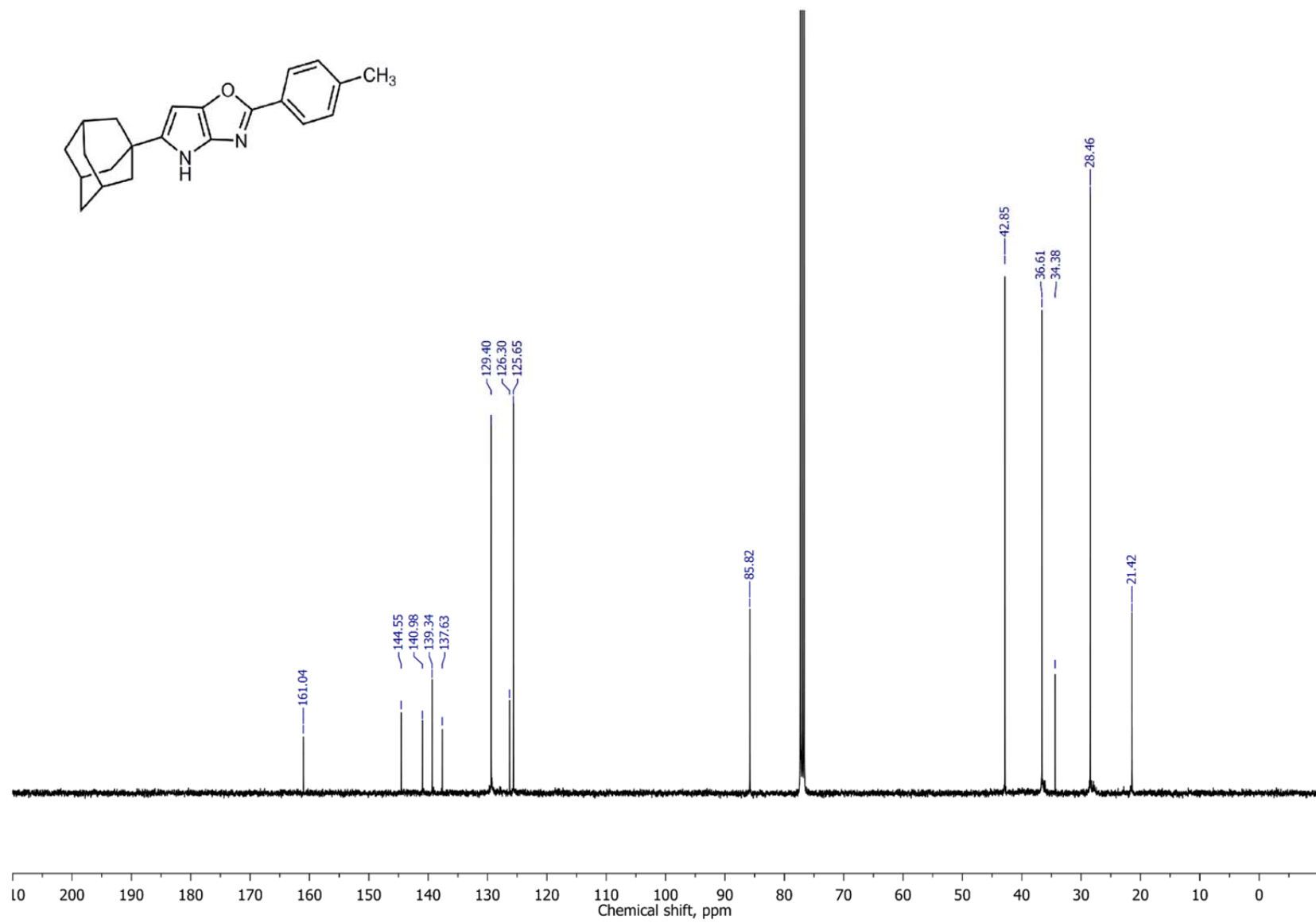
5-(4-Chlorophenyl)-2-(*p*-tolyl)-4*H*-pyrrolo[2,3-*d*]oxazole 3m, DEPT, 100 MHz, DMSO-*d*₆



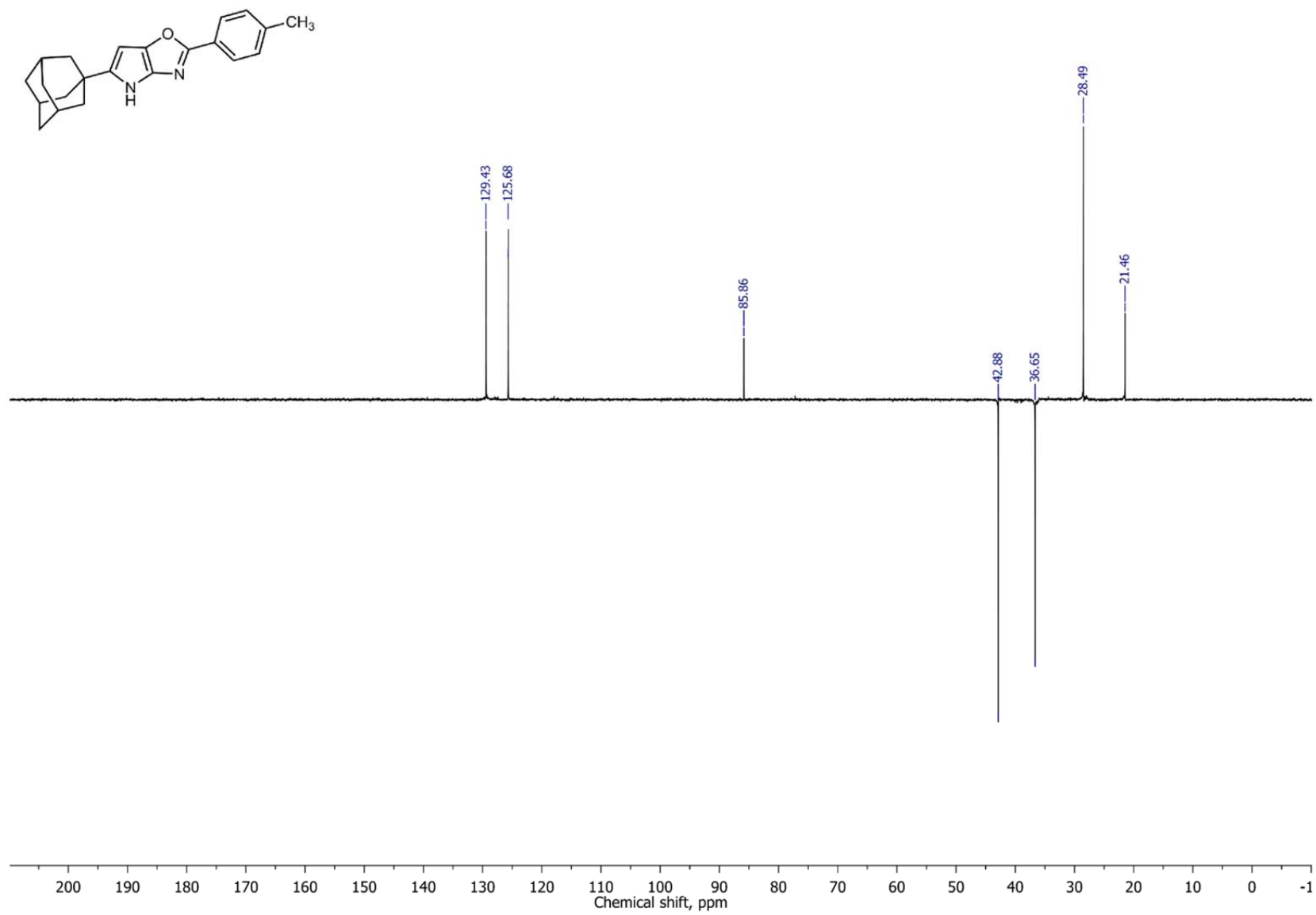
5-(Adamantan-1-yl)-2-(*p*-tolyl)-4*H*-pyrrolo[2,3-*d*]oxazole 3n, ^1H NMR, 400 MHz, CDCl_3



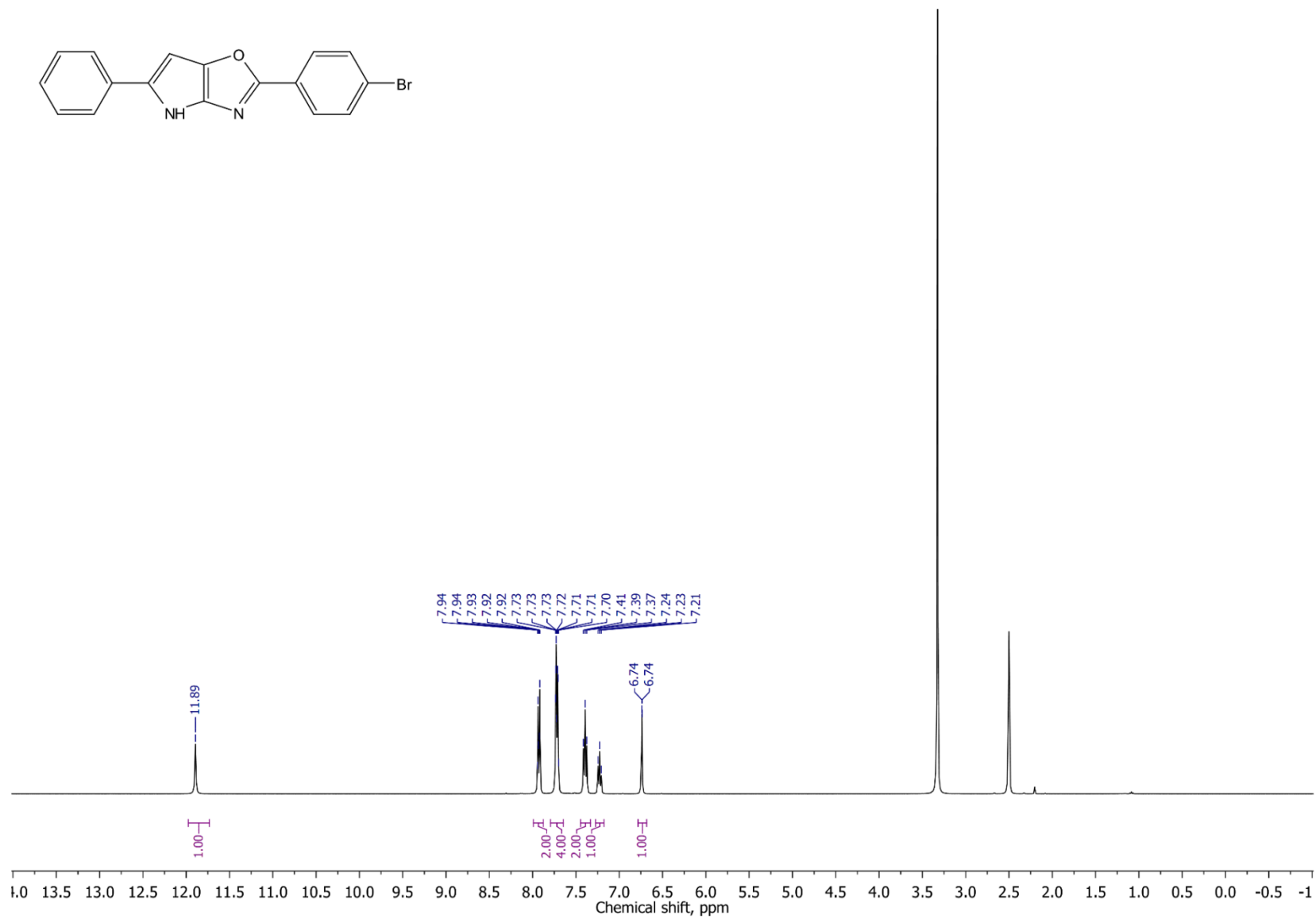
5-(Adamantan-1-yl)-2-(*p*-tolyl)-4*H*-pyrrolo[2,3-*d*]oxazole 3n, $^{13}\text{C}\{^1\text{H}\}$ NMR, 100 MHz, CDCl_3



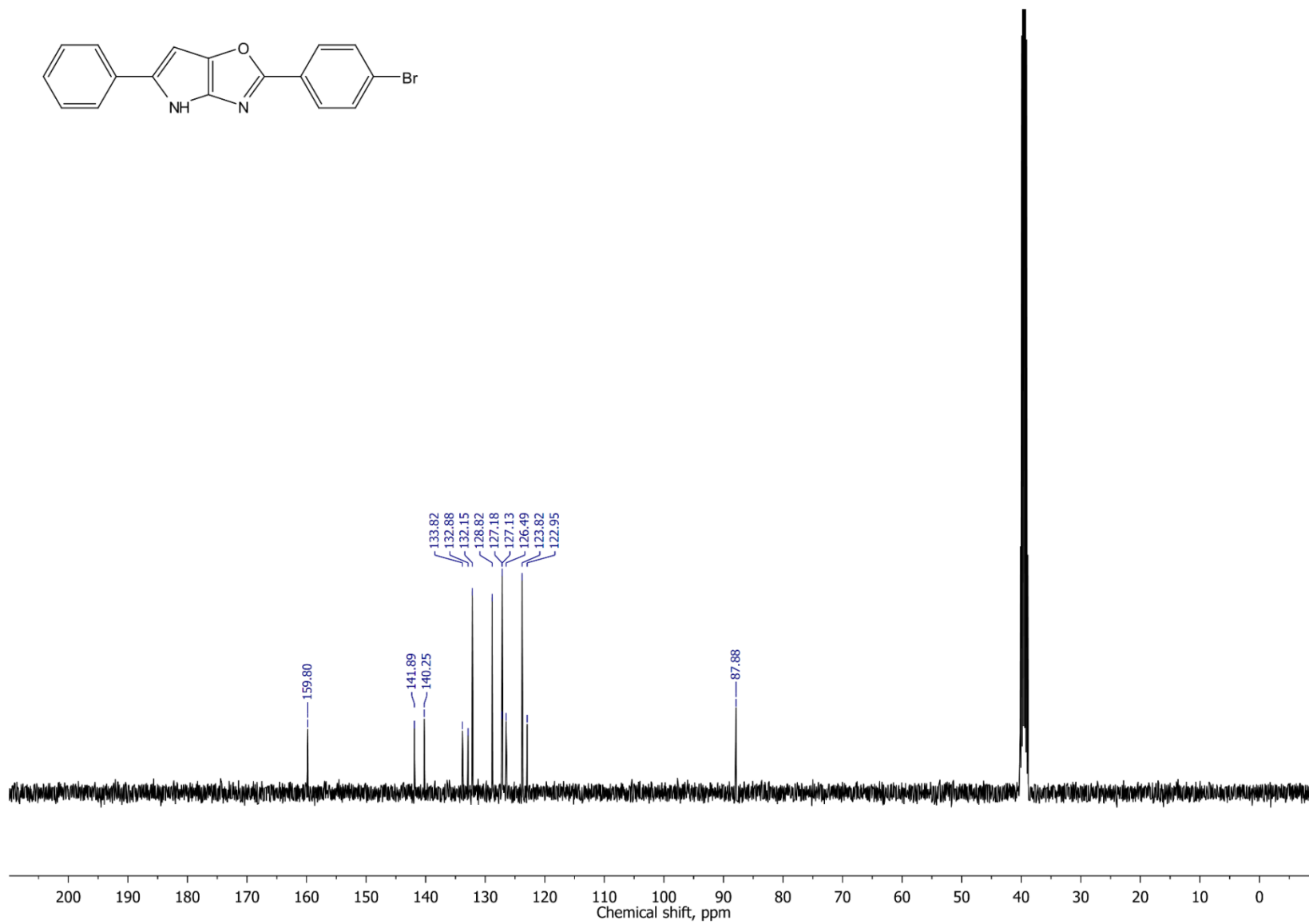
5-(Adamantan-1-yl)-2-(*p*-tolyl)-4*H*-pyrrolo[2,3-*d*]oxazole 3n, DEPT, 100 MHz, CDCl₃



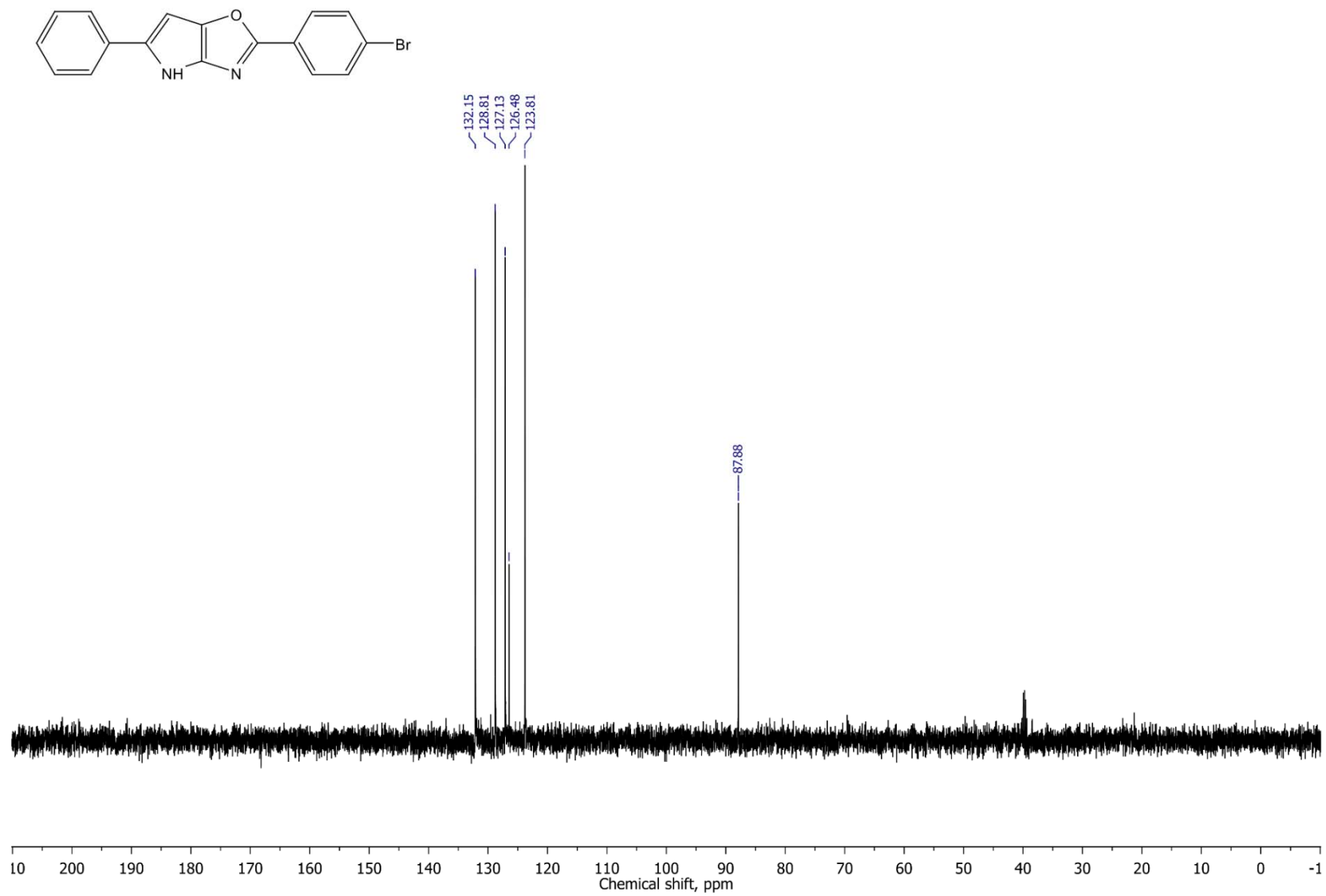
2-(4-Bromophenyl)-5-phenyl-4*H*-pyrrolo[2,3-*d*]oxazole 3o, ¹H NMR, 400 MHz, DMSO-*d*₆



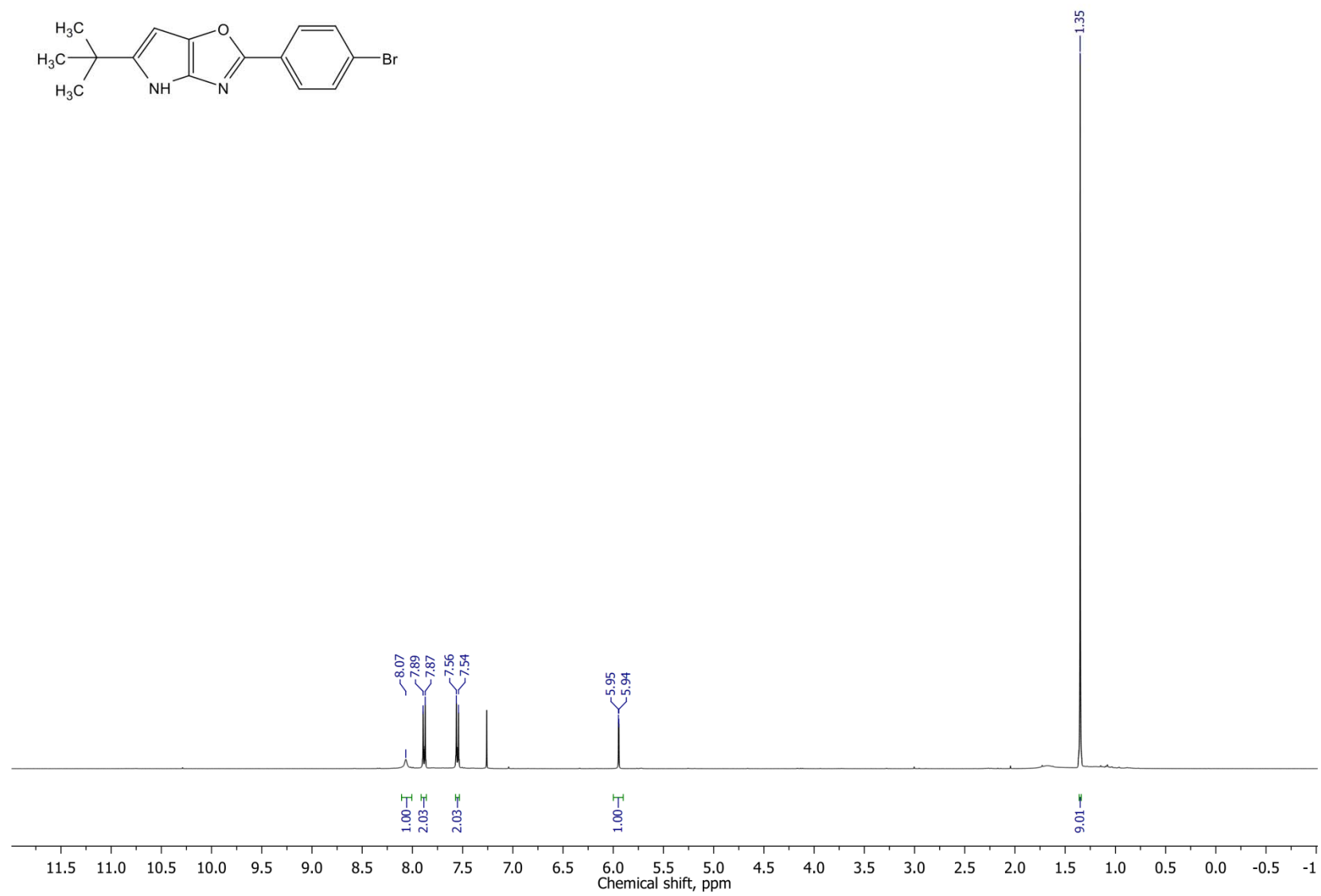
2-(4-Bromophenyl)-5-phenyl-4*H*-pyrrolo[2,3-*d*]oxazole 3o, $^{13}\text{C}\{^1\text{H}\}$ NMR, 100 MHz, DMSO- d_6



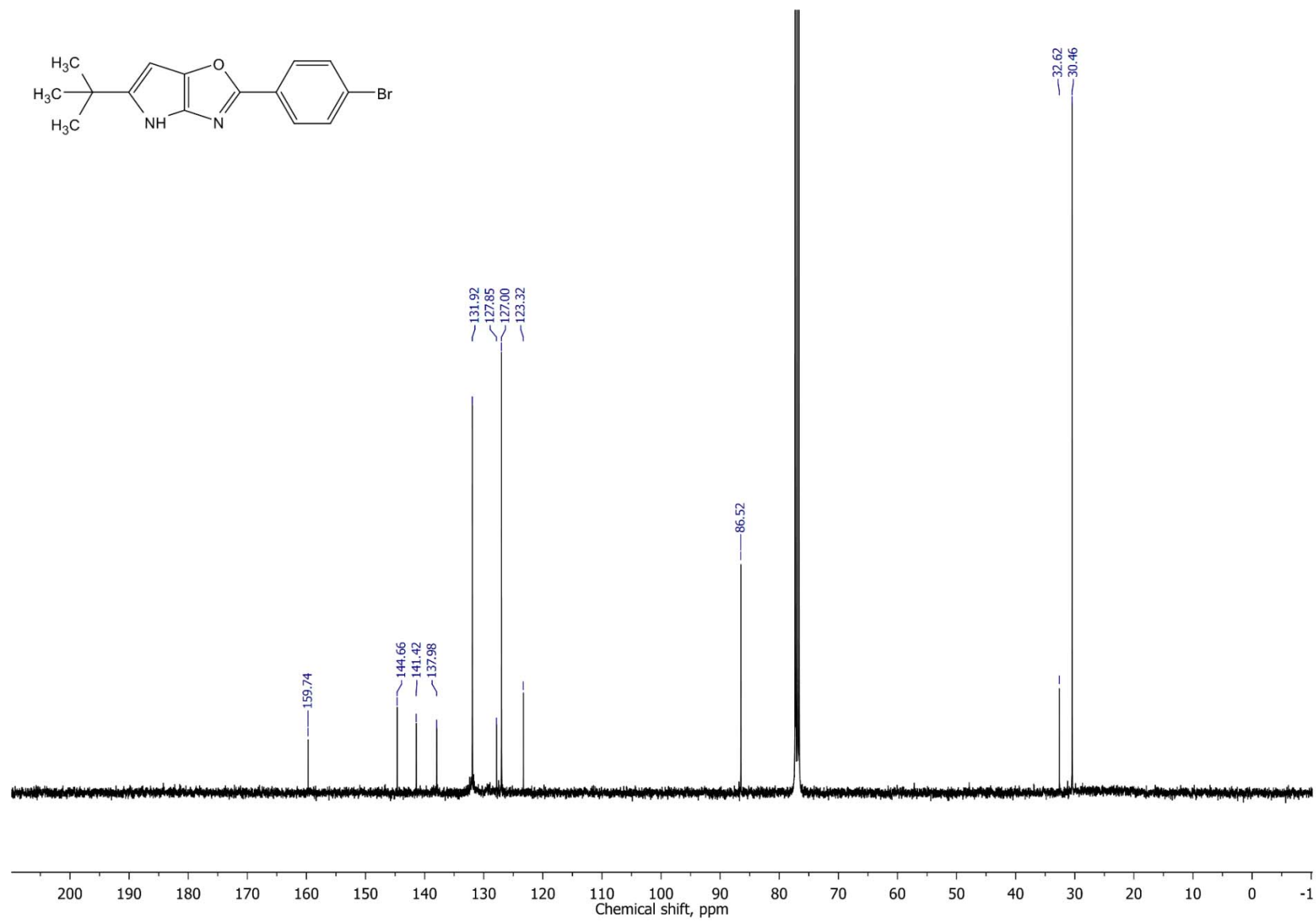
2-(4-Bromophenyl)-5-phenyl-4*H*-pyrrolo[2,3-*d*]oxazole 3o, DEPT, 100 MHz, DMSO-*d*₆



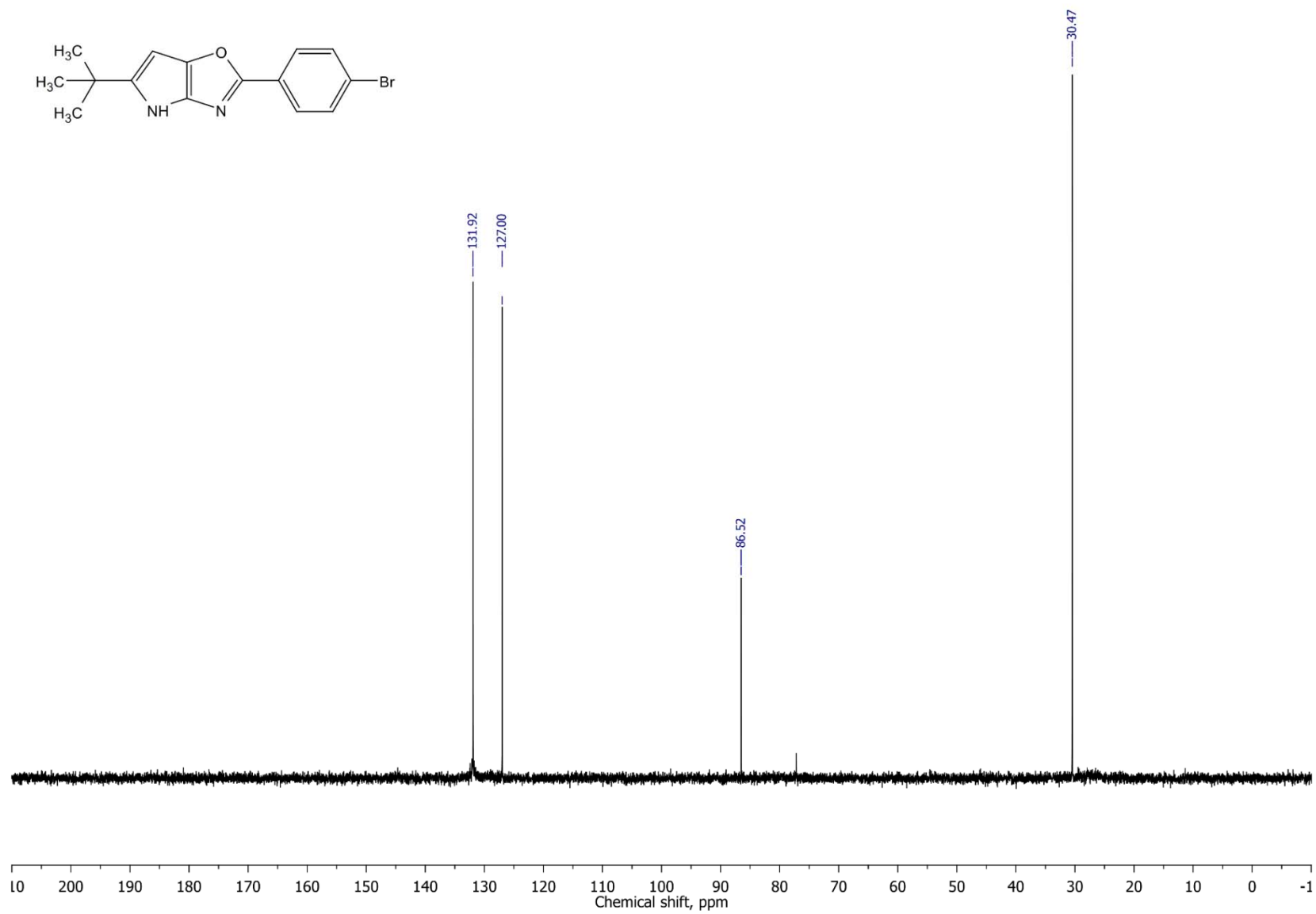
2-(4-Bromophenyl)-5-(*tert*-butyl)-4*H*-pyrrolo[2,3-*d*]oxazole 3p, ^1H NMR, 400 MHz, CDCl_3



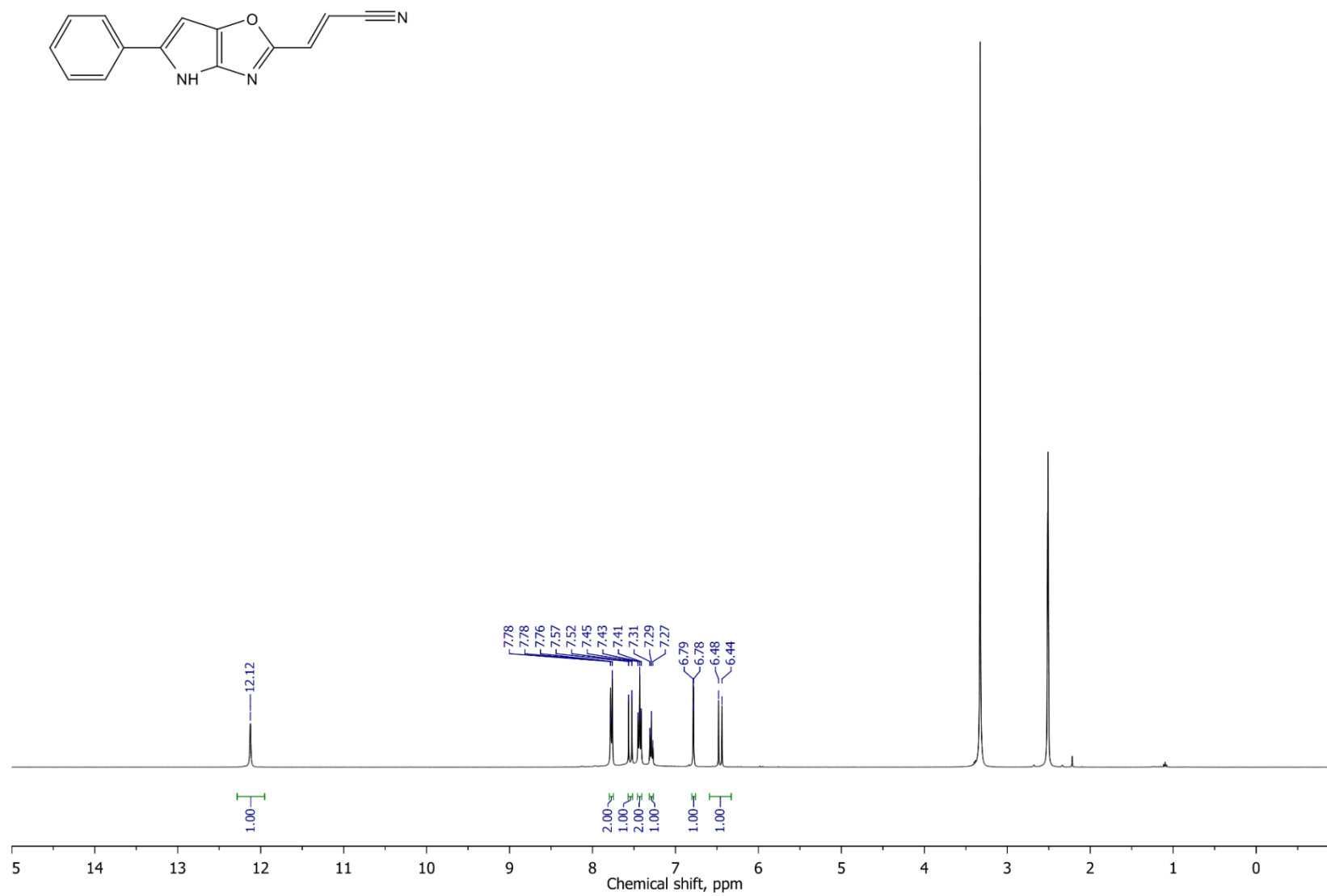
2-(4-Bromophenyl)-5-(*tert*-butyl)-4*H*-pyrrolo[2,3-*d*]oxazole 3p, $^{13}\text{C}\{^1\text{H}\}$ NMR, 100 MHz, CDCl_3



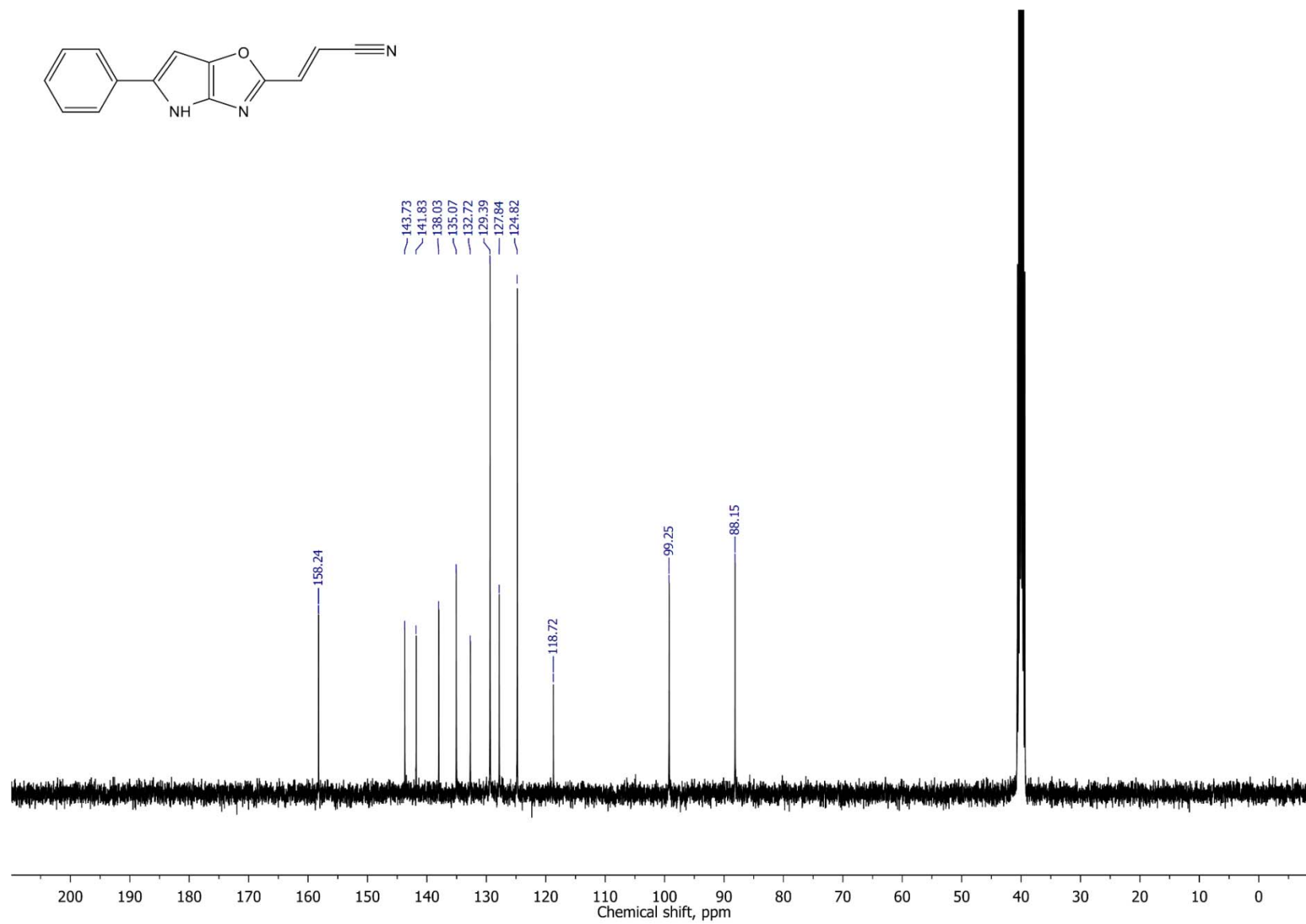
2-(4-Bromophenyl)-5-(*tert*-butyl)-4*H*-pyrrolo[2,3-*d*]oxazole 3p, DEPT, 100 MHz, CDCl₃



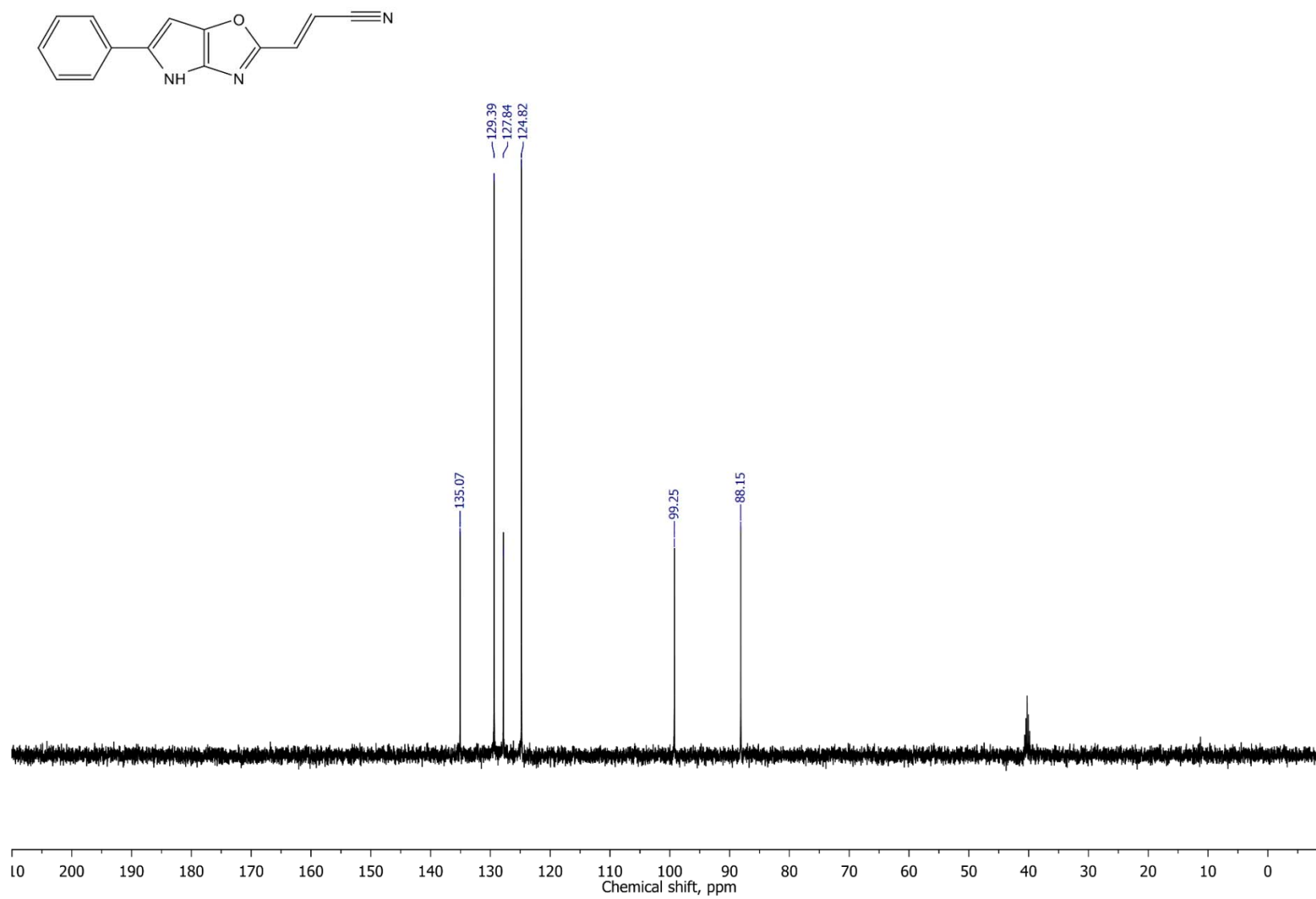
(*E*)-3-(5-phenyl-4*H*-pyrrolo[2,3-*d*]oxazol-2-yl)acrylonitrile 3q, ^1H NMR, 400 MHz, DMSO- d_6



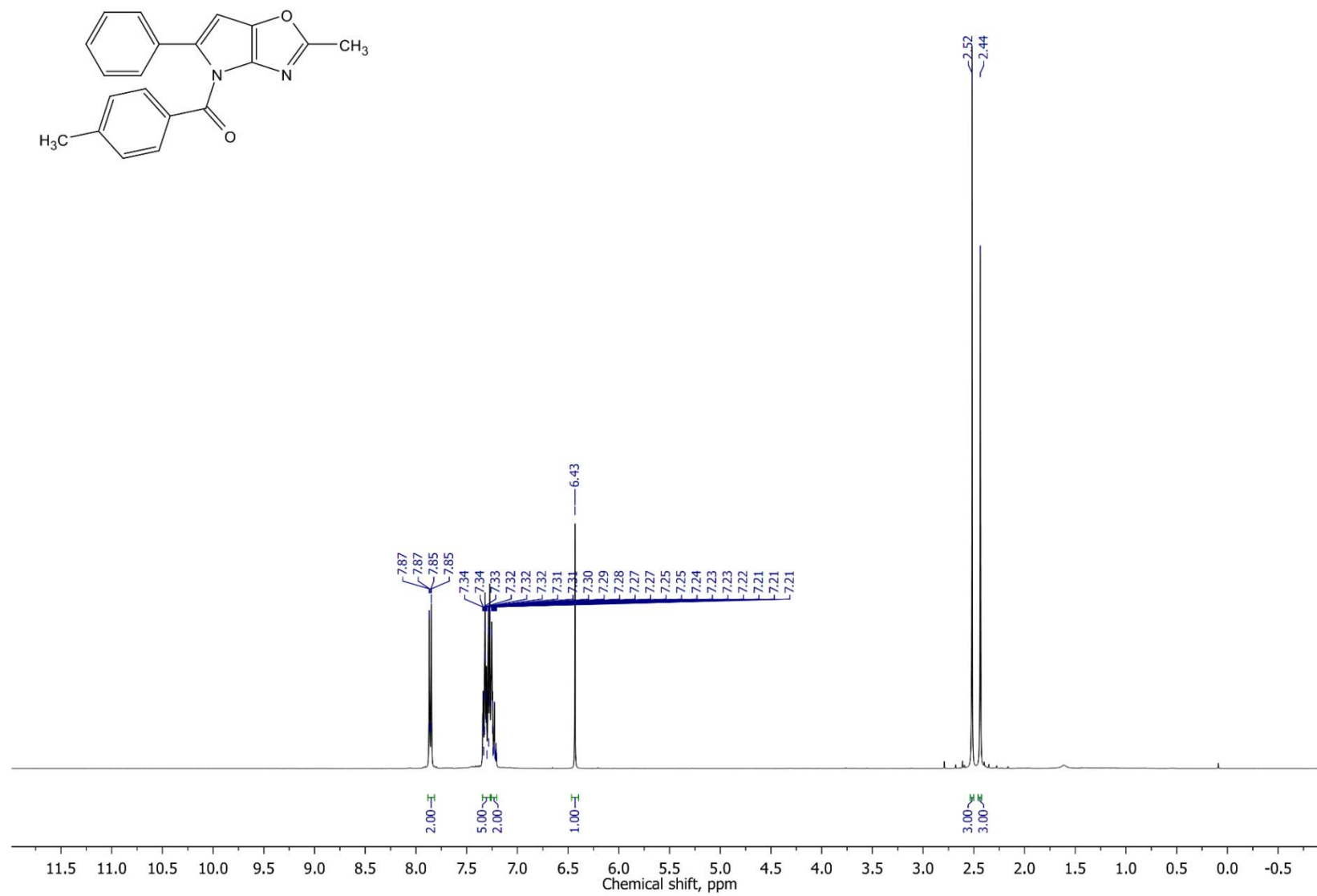
(*E*)-3-(5-phenyl-4*H*-pyrrolo[2,3-*d*]oxazol-2-yl)acrylonitrile 3q, $^{13}\text{C}\{^1\text{H}\}$ NMR, 100 MHz, DMSO- d_6



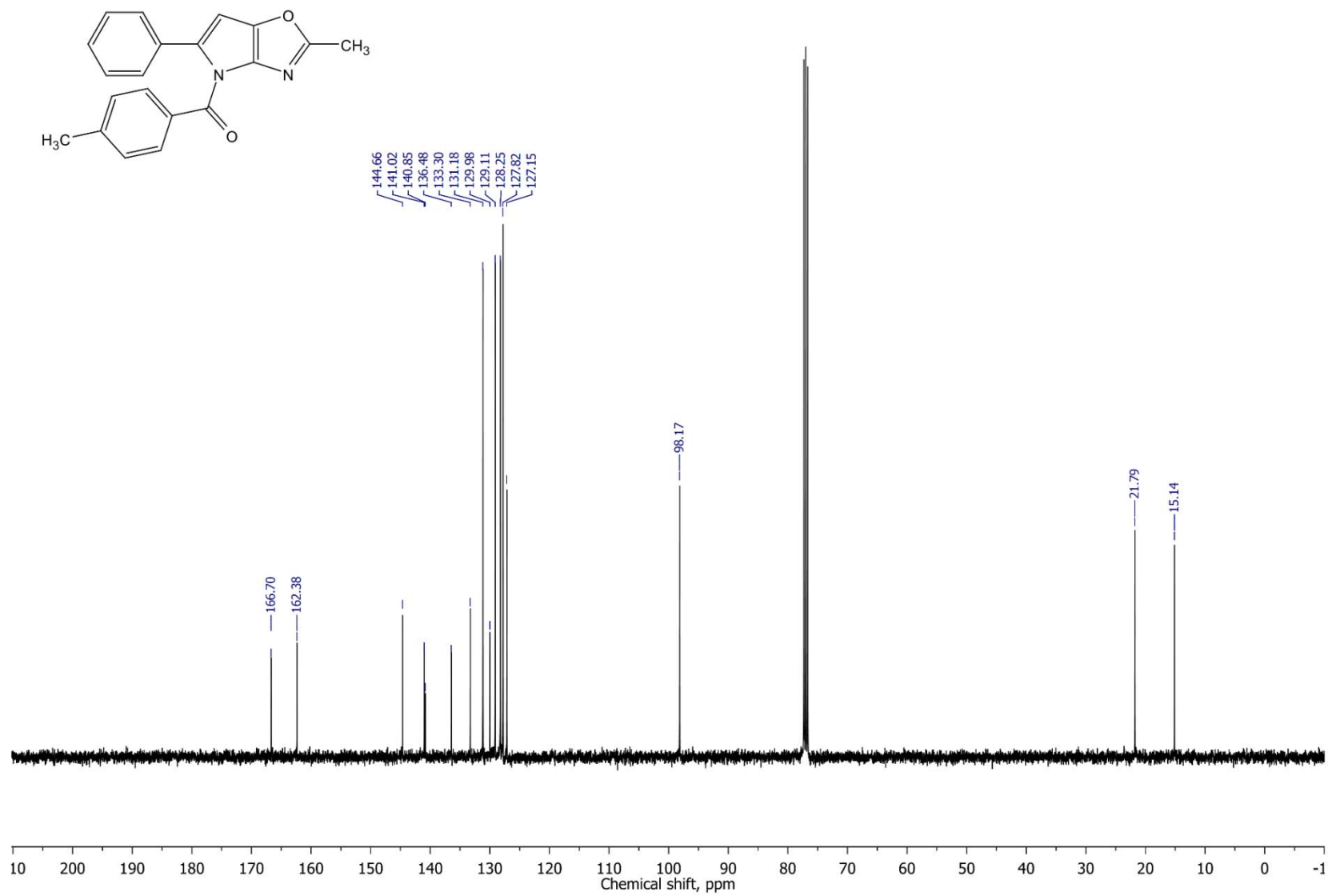
(E)-3-(5-phenyl-4H-pyrrolo[2,3-d]oxazol-2-yl)acrylonitrile 3q, DEPT, 100 MHz, DMSO-d₆



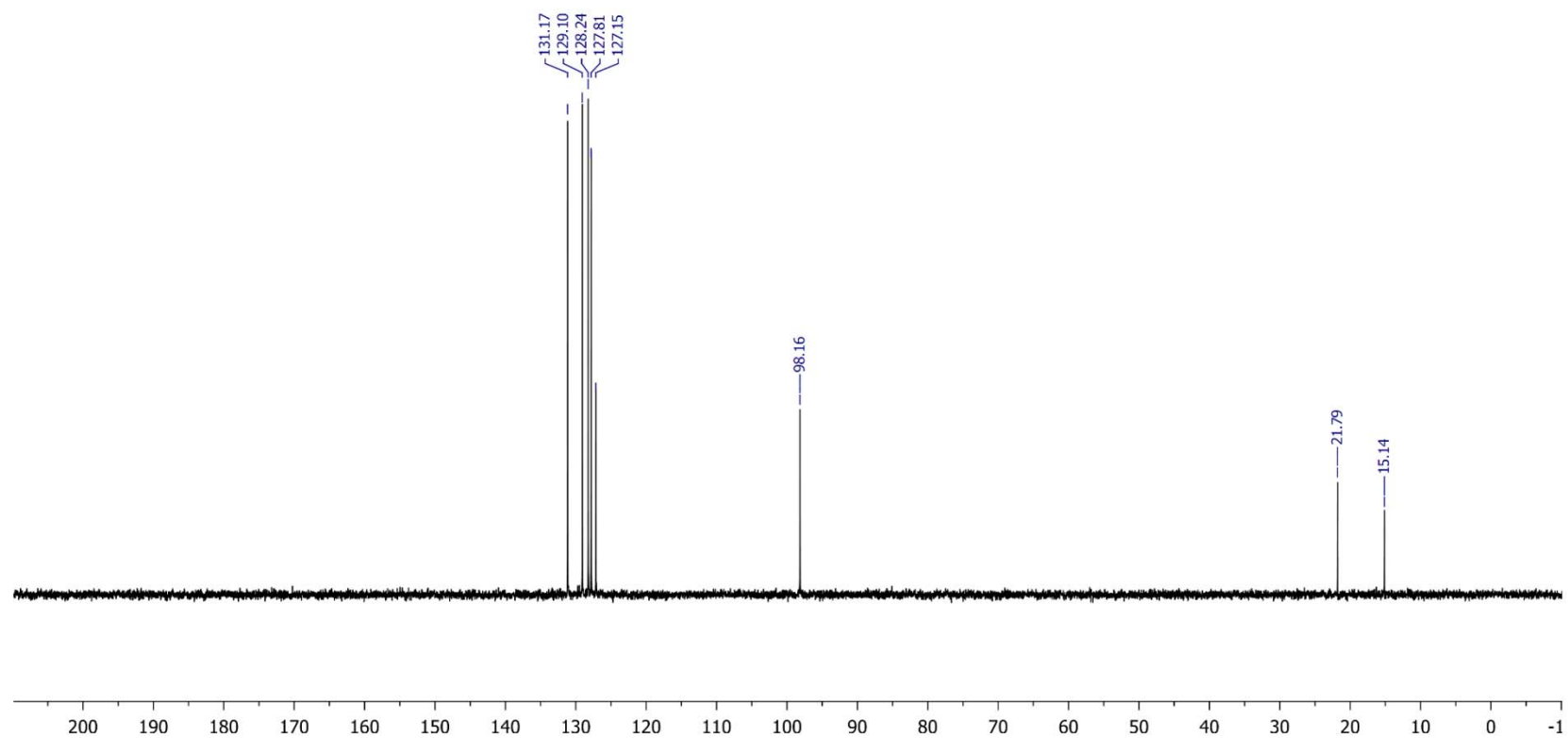
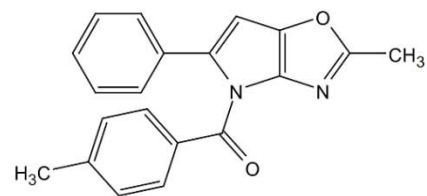
(2-Methyl-5-phenyl-4*H*-pyrrolo[2,3-*d*]oxazol-4-yl)(*p*-tolyl)methanone 4a, ¹H NMR, 400 MHz, CDCl₃



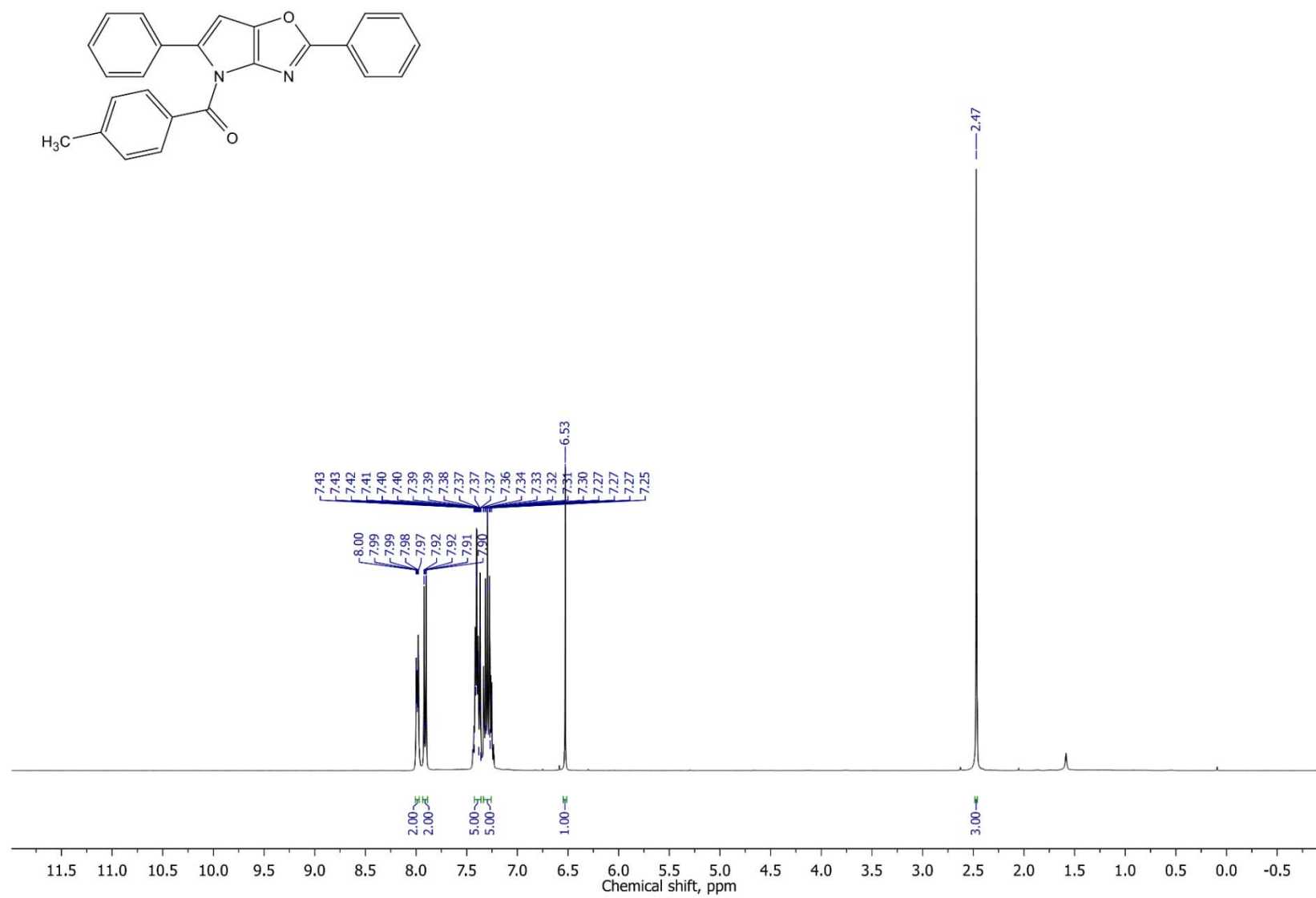
(2-Methyl-5-phenyl-4*H*-pyrrolo[2,3-*d*]oxazol-4-yl)(*p*-tolyl)methanone 4a, $^{13}\text{C}\{^1\text{H}\}$ NMR, 100 MHz, CDCl_3



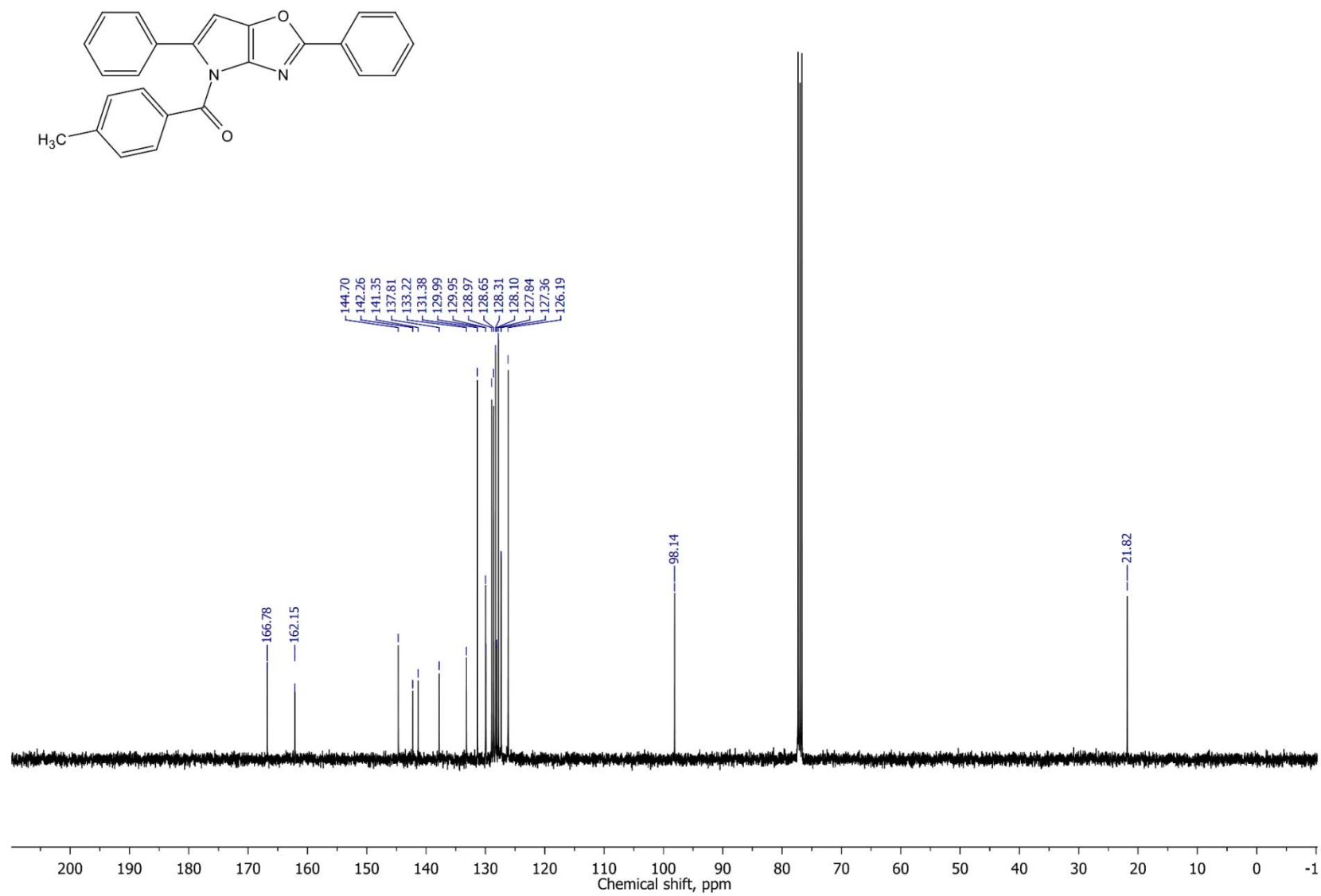
(2-Methyl-5-phenyl-4*H*-pyrrolo[2,3-*d*]oxazol-4-yl)(*p*-tolyl)methanone 4a, DEPT, 100 MHz, CDCl₃



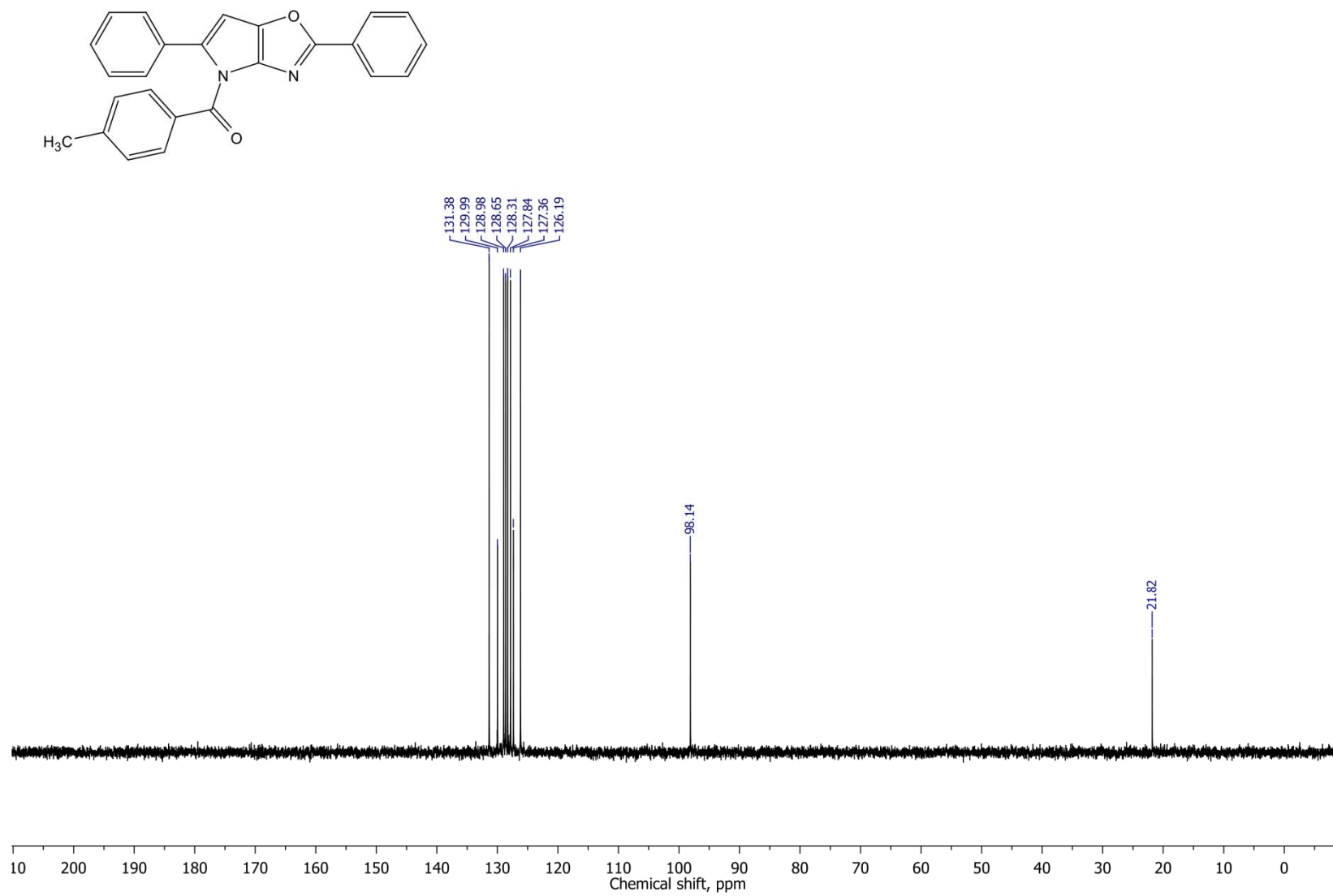
(2,5-Diphenyl-4*H*-pyrrolo[2,3-*d*]oxazol-4-yl)(*p*-tolyl)methanone 4b, ¹H NMR, 400 MHz, CDCl₃



(2,5-Diphenyl-4*H*-pyrrolo[2,3-*d*]oxazol-4-yl)(*p*-tolyl)methanone 4b, $^{13}\text{C}\{^1\text{H}\}$ NMR, 100 MHz, CDCl_3



(2,5-Diphenyl-4*H*-pyrrolo[2,3-*d*]oxazol-4-yl)(*p*-tolyl)methanone 4b, DEPT, 100 MHz, CDCl₃

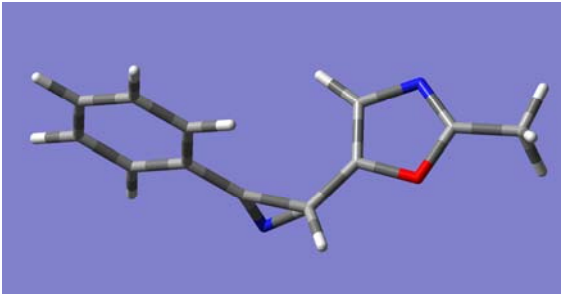
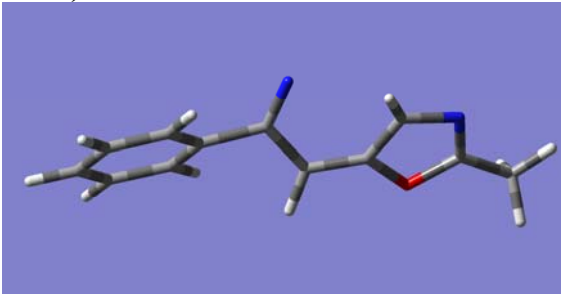


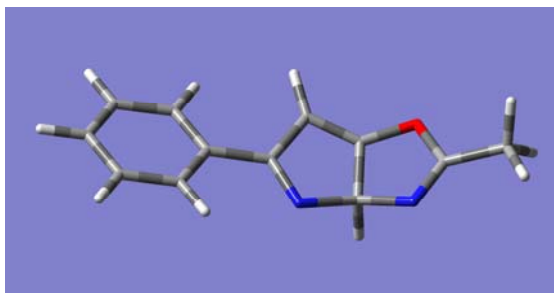
Computational Details

All calculations were performed by using the Gaussian 16 suite of quantum chemical programs¹ at Resource center "Computer center of Saint Petersburg State University". Geometry optimizations of molecules were performed with the B3LYP²-D3³ density functional method and 6-311+G(d,p) basis set using SMD⁴ solvent model. Stationary points on the respective potential-energy surfaces were characterized at the same level of theory by evaluating the corresponding Hessian indices. Careful verification of the unique imaginary frequency for the transition state was carried out to check whether the frequency indeed pertains to the desired reaction coordinate.

Table S7. B3LYP-D3/6-311+G(d,p), SMD solvent model for mesitylene.

Absolute Energies (au), Cartesian Coordinates of stationary points

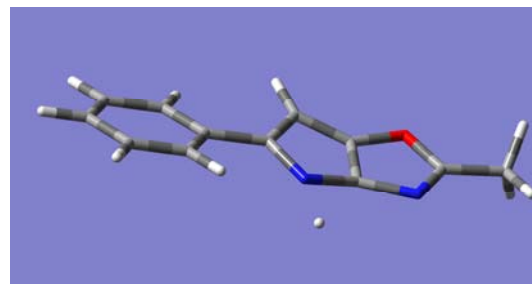
Molecule 2a				TS (2a-3'a)			
							
E = -648.157600, H (0K) = -647.964700, H (298K) = -647.950975, G (298K) = -648.007342 au. Imaginary frequency = 0.				E = -648.098093, H (0K) = -647.907189, H (298K) = -647.894304, G (298K) = -647.946297 au. Imaginary frequency = 1.			
N	-0.1844340	-2.1156980	-0.0904160	N	0.2497300	1.6546120	0.7006630
C	-0.7627840	-1.0587490	0.2753100	C	0.5960960	0.5193720	0.2622410
C	-2.0143230	-0.3428910	0.1550020	C	2.0527760	0.1369910	0.0920110
C	-4.2835410	-0.2224190	-0.6614600	C	4.3317010	0.7431380	-0.4359960
H	-5.1126700	-0.6611060	-1.2046020	H	5.0526080	1.4862030	-0.7587380
C	-2.1541080	0.9205340	0.7433660	C	2.4732320	-1.1614140	0.3900210
H	-1.3195260	1.3538860	1.2826410	H	1.7549710	-1.9006980	0.7293660
C	-4.4209750	1.0383240	-0.0738580	C	4.7504770	-0.5559140	-0.1436270
C	-3.0844680	-0.9145570	-0.5506480	C	2.9897260	1.0923190	-0.3110410
H	-2.9632780	-1.8926500	-1.0022920	H	2.6556480	2.1011900	-0.5218720
C	-3.3581690	1.6087090	0.6267700	C	3.8197320	-1.5058100	0.2744160
H	-3.4680830	2.5872810	1.0795240	H	4.1398670	-2.5136900	0.5147400
H	-5.3585440	1.5754130	-0.1637450	H	5.7970780	-0.8241310	-0.2355580
C	0.6080140	-1.0764520	0.7602730	C	-0.4067780	-0.4493840	-0.1885790
H	0.8234210	-1.3749460	1.7820450	H	-0.1221530	-1.3630500	-0.6993090
C	1.6622730	-0.3068050	0.0977450	C	-1.7210070	-0.0382690	-0.2077040
C	1.7478980	0.4559100	-1.0227330	C	-2.3175580	1.2167410	-0.0229020
O	2.9165040	-0.3274170	0.6663130	O	-2.7626460	-0.9474570	-0.3055850
H	0.9708640	0.7016630	-1.7284700	H	-1.8593820	2.1813770	-0.1552950
C	3.6974360	0.4316310	-0.1524690	C	-3.8841690	-0.2270790	-0.0518360
C	5.1232210	0.6007310	0.2183170	C	-5.1699460	-0.9535590	-0.0154440
H	5.6155430	1.2247970	-0.5265500	H	-5.9796610	-0.2508830	0.1733810
H	5.2160890	1.0747180	1.1999280	H	-5.3445270	-1.4690740	-0.9643860
H	5.6296190	-0.3676730	0.2650930	H	-5.1532730	-1.7107710	0.7747020
N	3.0518180	0.9148640	-1.1678360	N	-3.6676860	1.0511570	0.1190920
Molecule 3'a				TS (3'a-3a)			



E = -648.169593, H (0K) = -647.975062,
H (298K) = -647.962480,
G (298K) = -648.013872 au.

Imaginary frequency = 0.

N	-0.2914840	-1.0836640	0.4759810
C	0.3791840	0.0078040	0.2309730
C	1.8428700	-0.0028290	0.0454990
C	3.8919270	-1.2374910	-0.3473810
H	4.3981240	-2.1803800	-0.5219870
C	2.5868620	1.1842250	0.0915790
H	2.0925190	2.1308580	0.2743980
C	4.6254890	-0.0494060	-0.2977790
C	2.5135830	-1.2165800	-0.1754530
H	1.9380680	-2.1332230	-0.2113540
C	3.9701770	1.1597560	-0.0757280
H	4.5340860	2.0847190	-0.0313230
H	5.7013100	-0.0683840	-0.4323080
C	-0.4575000	1.2360940	0.0911430
H	-0.1371060	2.1929690	-0.2891870
C	-1.6937770	0.7889880	0.3386580
C	-1.6542970	-0.6429110	0.7357800
O	-2.9646120	1.1198860	-0.0088700
H	-1.7948810	-0.7684980	1.8214340
C	-3.5675900	-0.1599350	-0.2057490
C	-4.9434050	-0.0968410	-0.7468900
H	-5.3178000	-1.1054650	-0.9144820
H	-5.5977270	0.4233940	-0.0413730
H	-4.9527890	0.4636940	-1.6855200
N	-2.8668090	-1.1769100	0.0946960

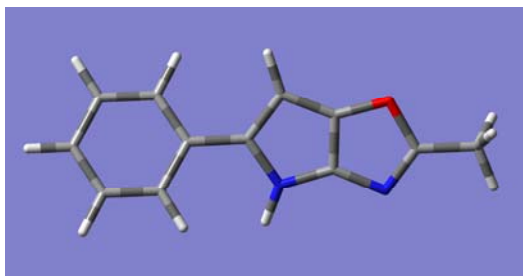


E = -648.123341, H (0K) = -647.933226,
H (298K) = -647.920753,
G (298K) = -647.971817 au.

Imaginary frequency = 1.

N	-0.2952580	-1.1145400	0.1474860
C	0.4099750	0.0496000	-0.0269190
C	1.8807810	0.0201340	-0.0199990
C	3.9581900	-1.2280980	-0.1879130
H	4.4702700	-2.1758150	-0.3136000
C	2.6312110	1.1968530	0.1317590
H	2.1286830	2.1456220	0.2792020
C	4.6937970	-0.0506780	-0.0437520
C	2.5679810	-1.1950710	-0.1790210
H	2.0008820	-2.1097120	-0.3009140
C	4.0231880	1.1611000	0.1154690
H	4.5841060	2.0812970	0.2368030
H	5.7776640	-0.0782460	-0.0534570
C	-0.4188370	1.2008080	-0.1517120
H	-0.0927080	2.2039050	-0.3765950
C	-1.6970970	0.7359090	0.0775680
C	-1.6573140	-0.6473780	0.2906280
O	-3.0023240	1.0914180	-0.0905710
H	-0.9476490	-1.0396630	1.2835430
C	-3.6814810	-0.1311700	-0.0505340
C	-5.1545570	-0.0510450	-0.1698540
H	-5.5691120	-1.0568500	-0.2203790
H	-5.5780500	0.4687120	0.6951730
H	-5.4356340	0.5074990	-1.0664400
N	-2.9411540	-1.1774420	0.1163600

Molecule 3a



E = -648.208497, H (0K) = -648.013163,
H (298K) = -648.000266,
G (298K) = -648.051998 au.

Imaginary frequency = 0.

C	-0.4244540	0.1155300	0.0108450
C	-1.8836370	0.0426000	0.0055190
C	-3.9493230	-1.2226920	0.2450950
H	-4.4469600	-2.1655800	0.4440120
C	-2.6545680	1.1911730	-0.2483700
H	-2.1587660	2.1297110	-0.4671960
C	-4.7008990	-0.0749660	-0.0030520
C	-2.5584030	-1.1653680	0.2566790
H	-1.9964310	-2.0626440	0.4923210
C	-4.0436920	1.1326000	-0.2446250
H	-4.6166660	2.0314090	-0.4449040
H	-5.7839800	-0.1197240	-0.0078290
C	0.4051540	1.2163530	0.2559180
H	0.0719740	2.2095380	0.5071160
C	1.7131450	0.7066290	0.1498410
C	1.6724820	-0.6310830	-0.1470230
O	3.0352420	1.0574390	0.2371400
C	3.7069750	-0.1224070	-0.0268540
C	5.1870940	-0.0652620	-0.0064980
H	5.5878930	-1.0523160	-0.2343350
H	5.5591420	0.6515930	-0.7447390
H	5.5501610	0.2500740	0.9764790
N	2.9385320	-1.1522520	-0.2610660
N	0.3638890	-1.0136320	-0.2212920
H	0.0155070	-1.9090250	-0.5263950

References

- (1) Gaussian 16, Revision A.03, Frisch, M. J.; Trucks, G. W.; Schlegel, H. B.; Scuseria, G. E.; Robb, M. A.; Cheeseman, J. R.; Scalmani, G.; Barone, V.; Petersson, G. A.; Nakatsuji, H.; Li, X.; Caricato, M.; Marenich, A. V.; Bloino, J.; Janesko, B. G.; Gomperts, R.; Mennucci, B.; Hratchian, H. P.; Ortiz, J. V.; Izmaylov, A. F.; Sonnenberg, J. L.; Williams-Young, D.; Ding, F.; Lipparini, F.; Egidi, F.; Goings, J.; Peng, B.; Petrone, A.; Henderson, T.; Ranasinghe, D.; Zakrzewski, V. G.; Gao, J.; Rega, N.; Zheng, G.; Liang, W.; Hada, M.; Ehara, M.; Toyota, K.; Fukuda, R.; Hasegawa, J.; Ishida, M.; Nakajima, T.; Honda, Y.; Kitao, O.; Nakai, H.; Vreven, T.; Throssell, K.; Montgomery, J. A., Jr.; Peralta, J. E.; Ogliaro, F.; Bearpark, M. J.; Heyd, J. J.; Brothers, E. N.; Kudin, K. N.; Staroverov, V. N.; Keith, T. A.; Kobayashi, R.; Normand, J.; Raghavachari, K.; Rendell, A. P.; Burant, J. C.; Iyengar, S. S.; Tomasi, J.; Cossi, M.; Millam, J. M.; Klene, M.; Adamo, C.; Cammi, R.; Ochterski, J. W.; Martin, R. L.; Morokuma, K.; Farkas, O.; Foresman, J. B.; Fox, D. J. Gaussian, Inc., Wallingford CT, 2016.
- (2) (a) Becke, A. D. *J. Chem. Phys.* **1993**, *98*, 5648–5652. (b) Becke, A. D. *Phys. Rev. A* **1988**, *38*, 3098–3100. (c) Lee, C.; Yang, W.; Parr, R. G. *Phys. Rev. B* **1988**, *37*, 785–789.
- (3) (a) Grimme, S.; Antony, J.; Ehrlich, S.; Krieg, H. *J. Chem. Phys.* **2010**, *132*, 1054104. (b) Grimme, S.; Ehrlich, S.; Goerigk, L. *J. Comput. Chem.* **2011**, *32*, 1456–1465.
- (4) Marenich, A. V.; Cramer, C. J.; Truhlar, D. G. *J. Phys. Chem. B*, **2009**, *11*, 6378-6396.