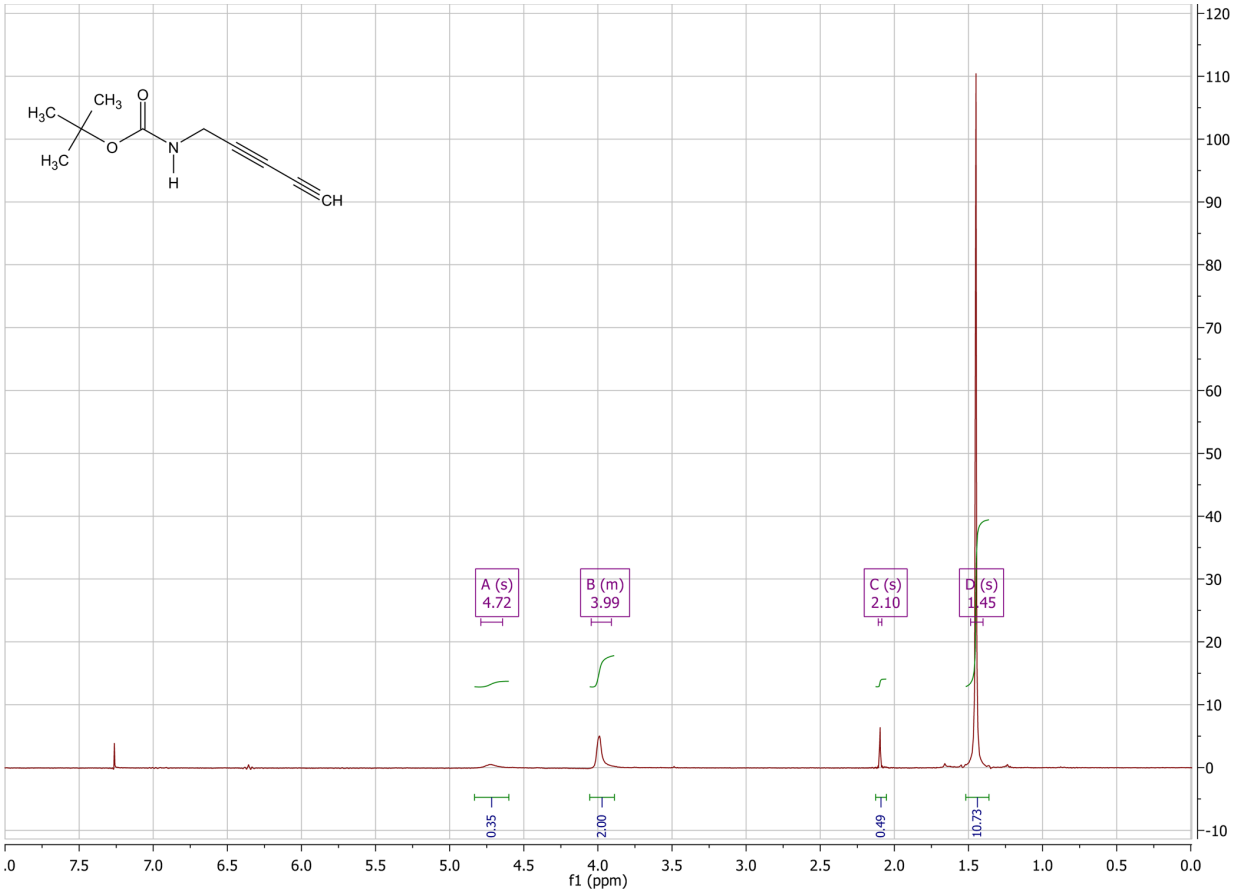
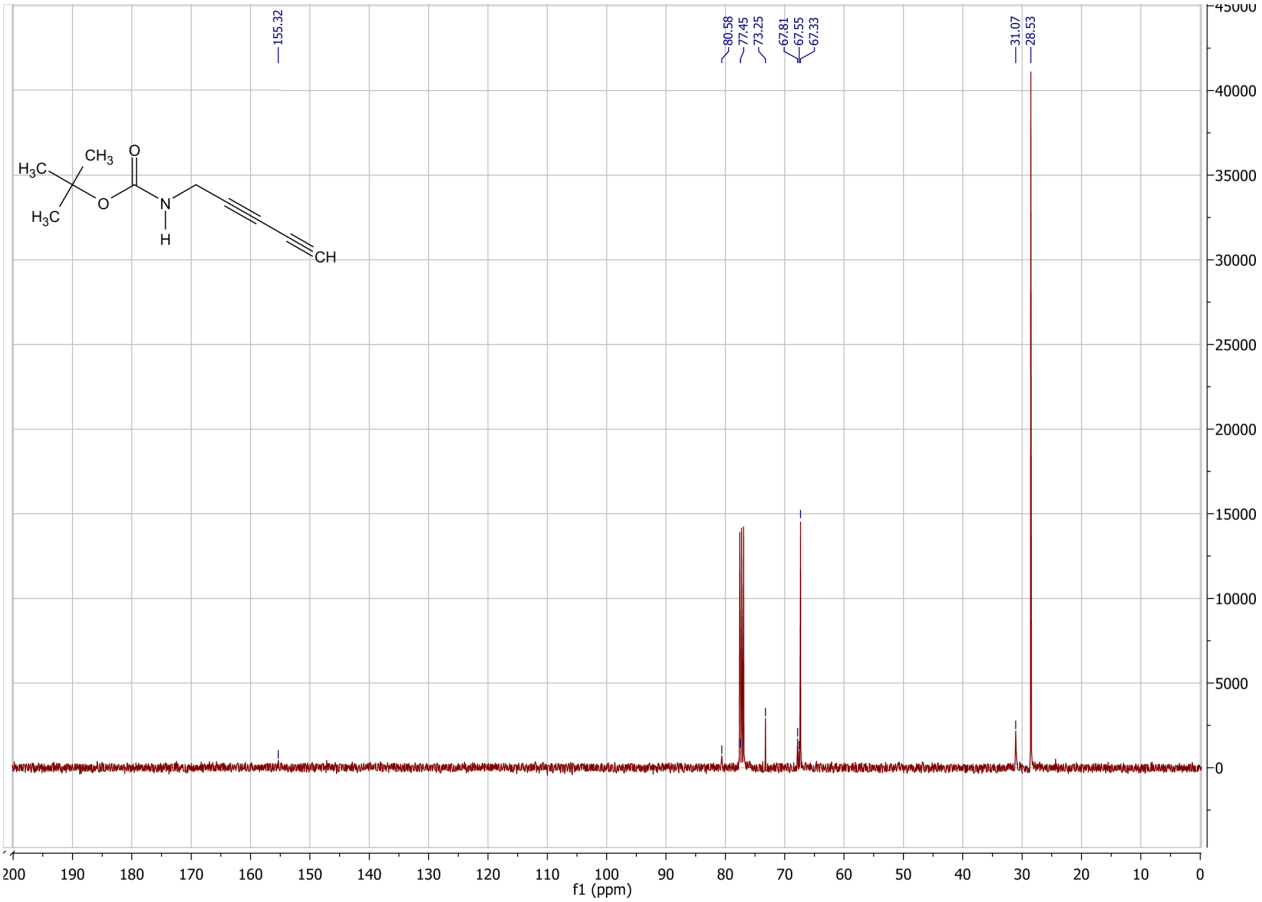
Supplementary Information

Isomorphous crystals from diynes and bromodiynes involved in hydrogen and halogen bonds

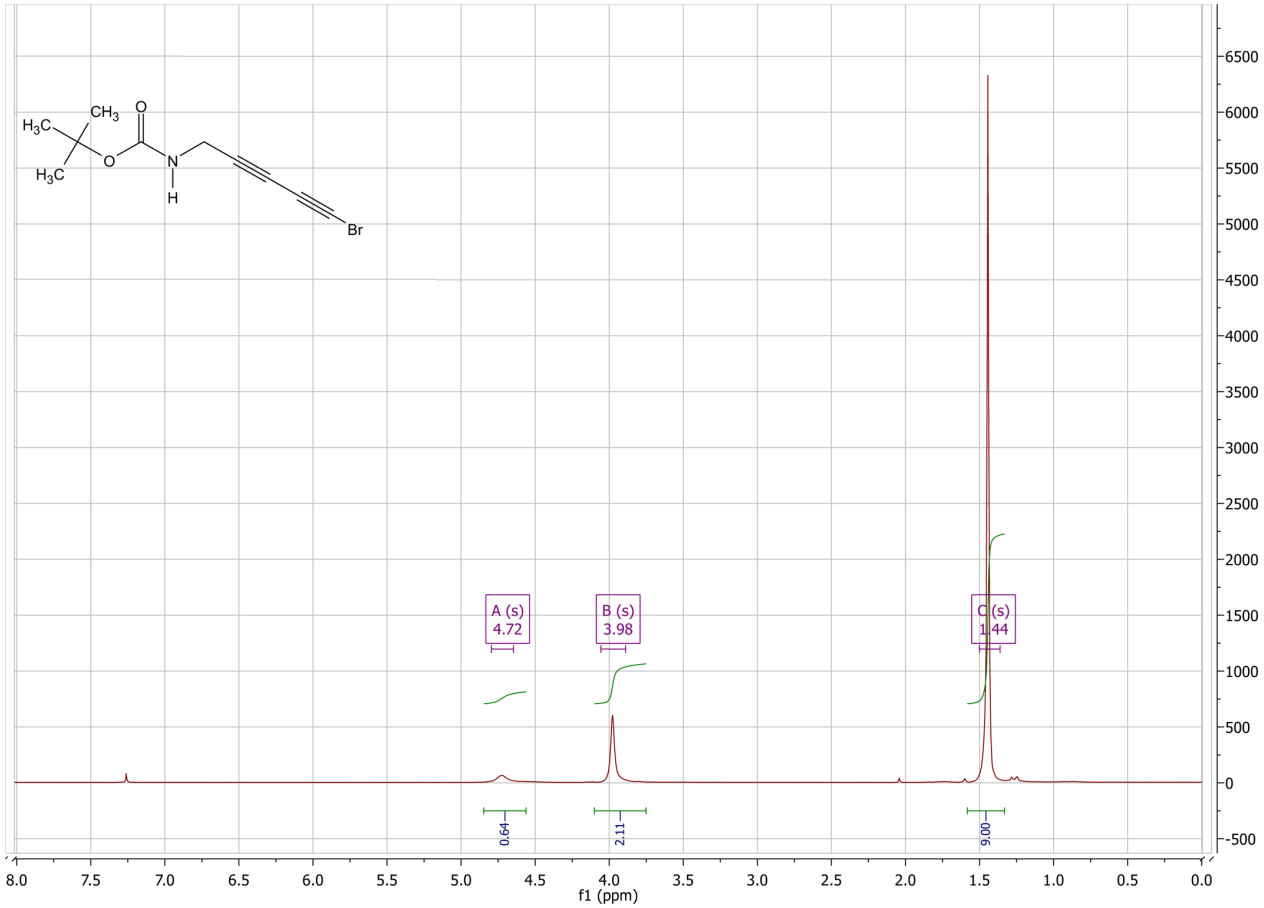
Baillargeon, Caron-Duval, Pellerin, Gagné, Dory



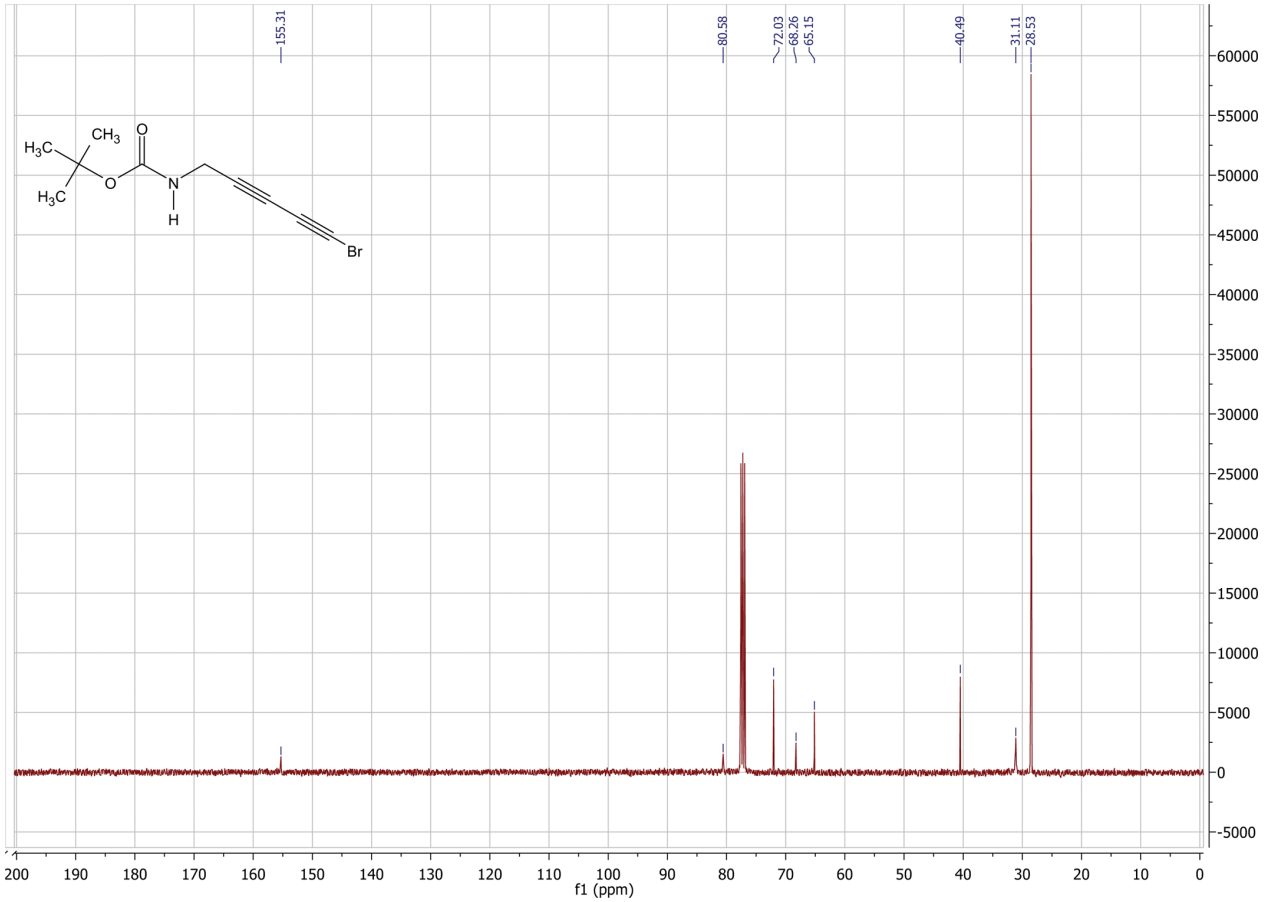
^{1}H NMR spectrum of compound **1** in $CDCl_3$, (400 MHz).



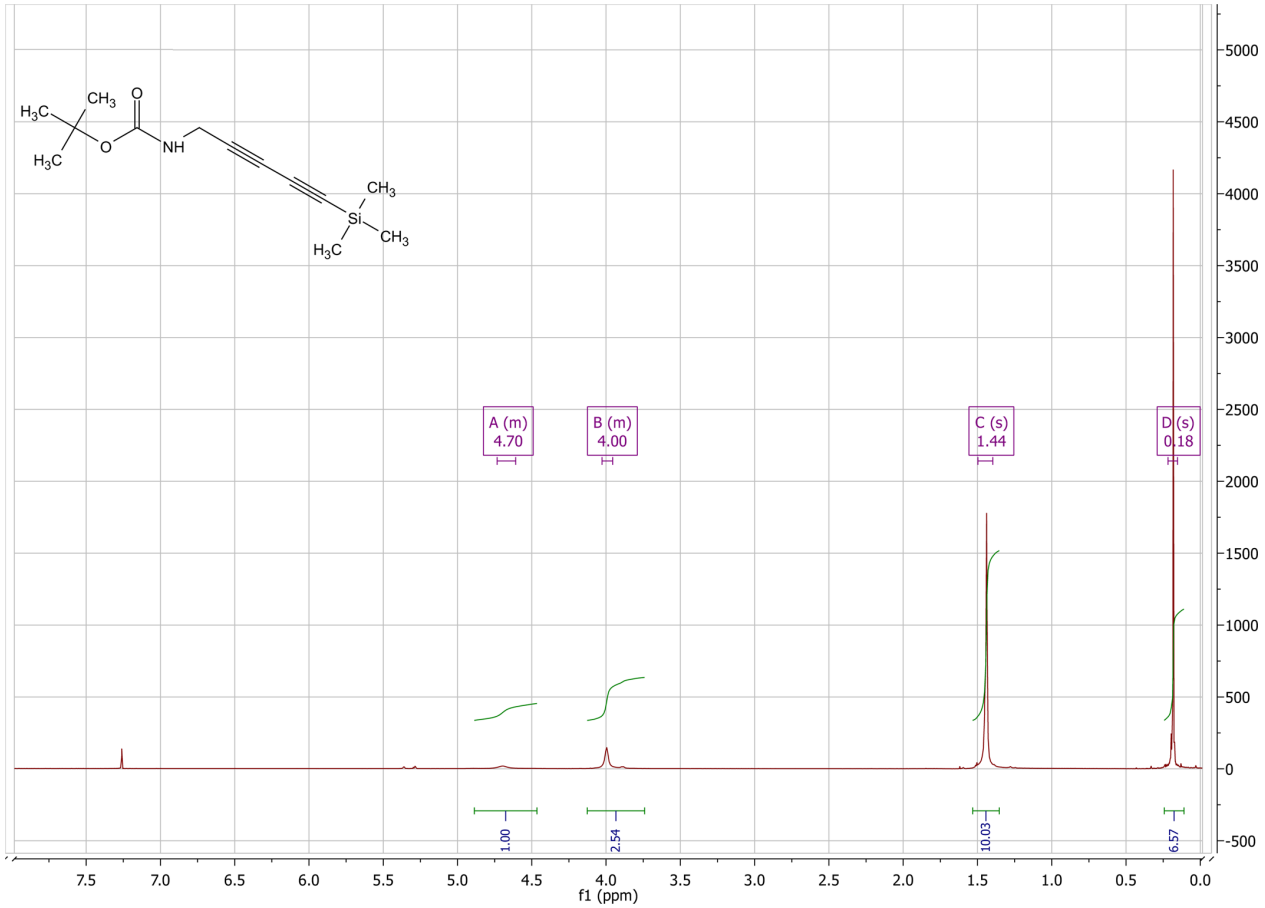
^{13}C NMR spectrum of compound **1** in $CDCl_3$, (100 MHz).



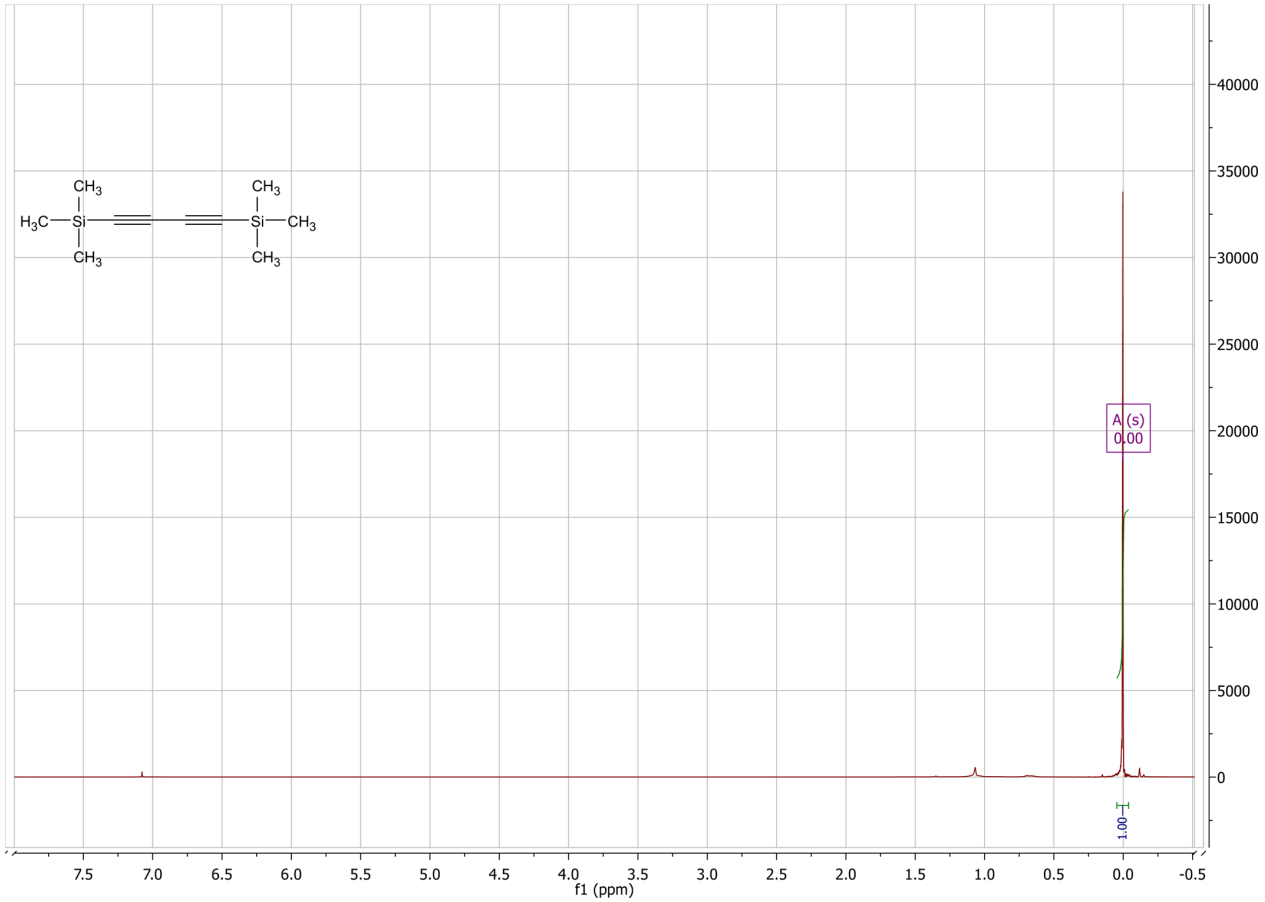
^{1}H NMR spectrum of compound **2** in $CDCl_3$, (400 MHz).



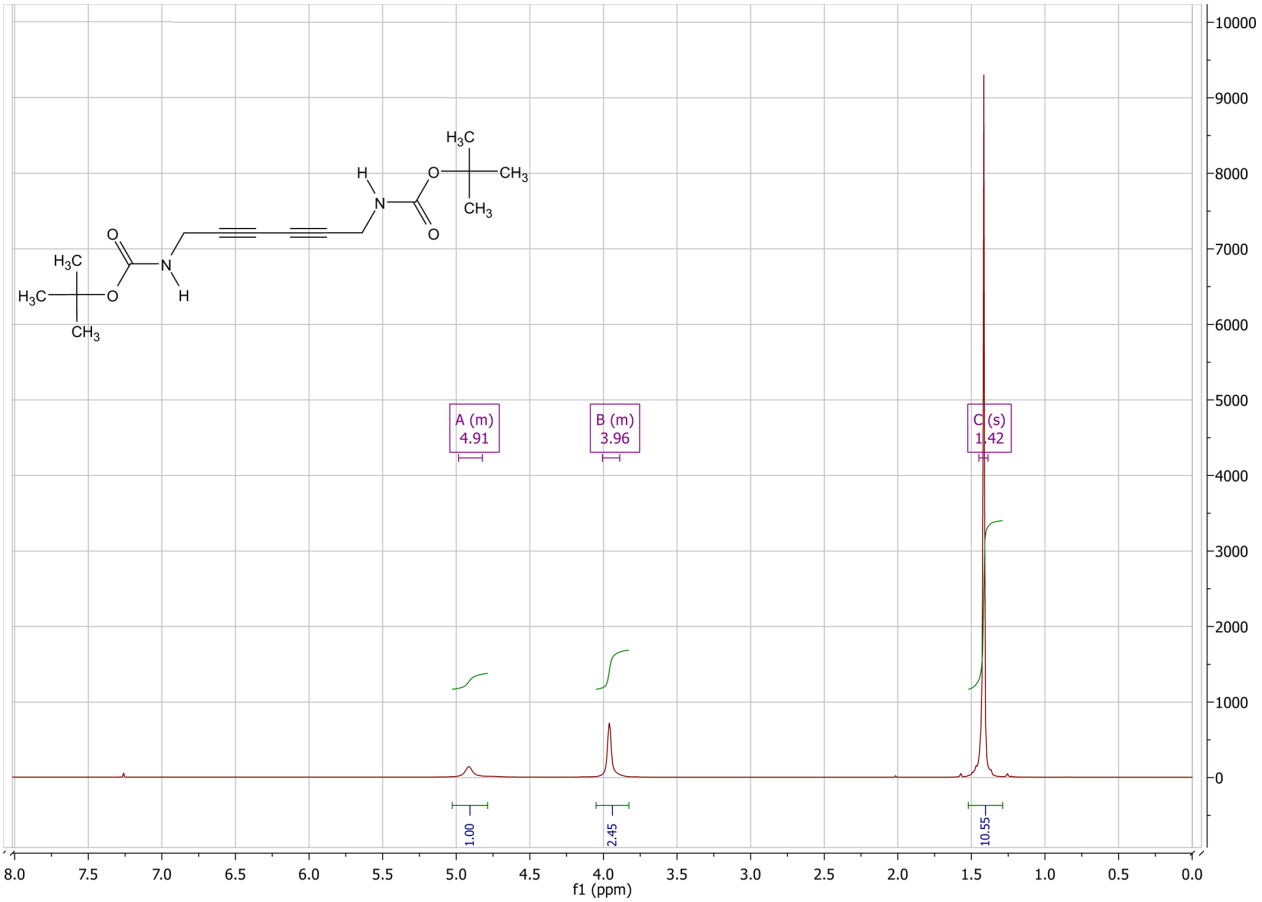
^{13}C NMR spectrum of compound **2** in $CDCl_3$, (100 MHz).



^{1}H NMR spectrum of compound **5** in $CDCl_3$, (400 MHz).



^{1}H NMR spectrum of compound **6** in $CDCl_3$, (400 MHz).



^{1}H NMR spectrum of compound **7** in $CDCl_3$, (400 MHz).

Crystal Structure Report for Dory_PBESNHdiyne

Compound **1**

A Needle-like specimen of $C_{10}H_{13}NO_2$, approximate dimensions 0.050 mm x 0.100 mm x 0.280 mm, was used for the X-ray crystallographic analysis. The X-ray intensity data were measured on a Bruker Apex DUO system equipped with a Cu Kα ImuS micro─focus source with MX optics (λ = 1.54178 Å).

Table 1: Data collection details for Dory_PBESNHdiyne.

Axis	dx/ mm	2θ/ °	ω/ °	ϕ/ °	χ/ °	Width/ °	Frames	Time/ s	Wave-length/Å	Voltage/ kV	Current/ mA	Temperature/ K
Phi	79.723	-76.00	180.66	-9.27	-21.74	6.00	61	10.00	1.54184	45	0.7	173.19
Phi	79.723	118.00	116.80	-350.39	22.49	6.00	61	10.00	1.54184	45	0.7	173.19
Phi	79.723	112.00	228.07	-18.32	-41.07	6.00	61	10.00	1.54184	45	0.7	173.19
Phi	79.723	-70.00	147.00	-335.97	51.78	6.00	61	10.00	1.54184	45	0.7	173.19
Phi	79.723	118.00	43.74	-321.81	72.77	6.00	61	10.00	1.54184	45	0.7	173.19
Phi	79.723	-24.00	204.61	-327.06	35.94	6.00	58	10.00	1.54184	45	0.7	173.19
Phi	79.723	122.00	93.61	-344.21	35.94	6.00	61	10.00	1.54184	45	0.7	173.19
Phi	79.723	-62.00	325.36	-8.61	-20.22	6.00	61	10.00	1.54184	45	0.7	173.19
Phi	79.723	88.00	212.94	-32.05	-64.62	6.00	61	10.00	1.54184	45	0.7	173.19
Phi	79.723	122.00	236.31	-40.72	-75.73	6.00	61	10.00	1.54184	45	0.7	173.19
Phi	79.723	120.00	149.15	-344.67	22.49	6.00	60	10.00	1.54184	45	0.7	173.19
Phi	79.723	120.00	214.34	-39.70	-74.56	6.00	61	10.00	1.54184	45	0.7	173.19
Phi	79.723	54.00	37.33	-69.16	-96.16	6.00	61	10.00	1.54184	45	0.7	173.19
Phi	79.723	90.00	14.44	-343.49	37.41	6.00	61	10.00	1.54184	45	0.7	173.19
Omega	79.723	-34.00	-207.90	28.98	88.60	6.00	13	10.00	1.54184	45	0.7	173.19
Omega	79.723	74.00	-201.07	-204.61	-96.69	6.00	12	10.00	1.54184	45	0.7	173.19
Phi	79.723	116.00	77.76	-339.07	46.12	6.00	61	10.00	1.54184	45	0.7	173.19
Phi	79.723	88.00	238.44	17.18	-79.13	6.00	50	10.00	1.54184	45	0.7	173.19
Omega	79.723	108.00	-200.59	38.39	-89.04	6.00	12	10.00	1.54184	45	0.7	173.19
Omega	79.723	120.00	-203.18	-13.70	-74.56	6.00	13	10.00	1.54184	45	0.7	173.19
Omega	79.723	122.00	-200.86	17.69	-95.00	6.00	13	10.00	1.54184	45	0.7	173.19
Omega	79.723	120.00	-208.96	69.95	-64.62	6.00	15	10.00	1.54184	45	0.7	173.19
Omega	79.723	-52.00	-179.66	-58.91	34.46	6.00	30	10.00	1.54184	45	0.7	173.19
Omega	79.723	120.00	15.56	-241.29	-26.26	6.00	39	10.00	1.54184	45	0.7	173.19
Omega	79.723	120.00	-10.81	-51.72	19.47	6.00	40	10.00	1.54184	45	0.7	173.19
Phi	79.723	108.00	57.47	-262.97	81.82	6.00	52	10.00	1.54184	45	0.7	173.19
Phi	79.723	-28.00	160.40	-66.31	-95.00	6.00	61	10.00	1.54184	45	0.7	173.19
Phi	79.723	76.00	100.36	-351.06	20.98	6.00	61	10.00	1.54184	45	0.7	173.19
Phi	79.723	58.00	27.40	-344.91	34.46	6.00	61	10.00	1.54184	45	0.7	173.19
Phi	79.723	120.00	175.91	-84.18	-99.71	6.00	61	10.00	1.54184	45	0.7	173.19
Phi	79.723	122.00	3.06	-302.47	90.31	6.00	61	10.00	1.54184	45	0.7	173.19
Phi	79.723	120.00	36.25	-281.19	98.91	6.00	61	10.00	1.54184	45	0.7	173.19
Phi	79.723	-68.00	177.05	-336.76	50.38	6.00	61	10.00	1.54184	45	0.7	173.19
Phi	79.723	-64.00	12.11	-10.61	-24.76	6.00	61	10.00	1.54184	45	0.7	173.19
Phi	79.723	62.00	191.34	-14.03	-32.24	6.00	61	10.00	1.54184	45	0.7	173.19
Phi	79.723	72.00	24.26	-337.54	48.96	6.00	61	10.00	1.54184	45	0.7	173.19
Phi	79.723	98.00	194.25	-348.37	27.01	6.00	61	10.00	1.54184	45	0.7	173.19

A total of 1871 frames were collected. The total exposure time was 5.20 hours. The frames were integrated with the Bruker SAINT software package using a wide-frame algorithm. The integration of the data using a monoclinic unit cell yielded a total of 5204 reflections to a maximum θ angle of 68.50° (0.83 Å resolution), of which 1848 were independent (average redundancy 2.816, completeness = 99.0%, R_{int} = 4.03%, R_{sig} = 4.14%) and 1409 (76.24%) were greater than 2σ(F^2). The final cell constants of a = 9.3613(15) Å, b = 9.3135(14) Å, c = 11.8981(19) Å, β = 102.497(5)°, volume = 1012.8(3) $Å^3$, are based upon the refinement of the XYZ-centroids of 7474 reflections above 20 σ(I) with 9.677° < 2θ < 136.9°. Data were corrected for absorption effects using the multi-scan method (SADABS). The ratio of minimum to maximum apparent transmission was 0.855. The calculated minimum and maximum transmission coefficients (based on crystal size) are 0.8353 and 0.9674.

The structure was solved and refined using the Bruker SHELXTL Software Package, using the space group P 1 21/c 1, with Z = 4 for the formula unit, $C_{10}H_{13}NO_2$. The final anisotropic full-matrix least-squares refinement on F^2 with 122 variables converged at R1 = 3.82%, for the observed data and wR2 = 9.15% for all data. The goodness-of-fit was 1.027. The largest peak in the final difference electron density synthesis was 0.170 $e^-/Å^3$ and the largest hole was -0.170 $e^-/Å^3$ with an RMS deviation of 0.038 $e^-/Å^3$. On the basis of the final model, the calculated density was 1.175 g/cm^3 and F(000), 384 e^-.

Table 2. Sample and crystal data for Dory_PBESNHdiyne.

Identification code	Dory_PBESNHdiyne	
Chemical formula	$C_{10}H_{13}NO_2$	
Formula weight	179.21	
Temperature	173(2) K	
Wavelength	1.54178 Å	
Crystal size	0.050 x 0.100 x 0.280 mm	
Crystal system	monoclinic	
Space group	P 1 21/c 1	
Unit cell dimensions	a = 9.3613(15) Å	α = 90°
	b = 9.3135(14) Å	β = 102.497(5)°
	c = 11.8981(19) Å	γ = 90°
Volume	1012.8(3) $Å^3$	
Z	4	
Density (calculated)	1.175 g/cm^3	
Absorption coefficient	0.667 mm^{-1}	
F(000)	384	

Table 3. Data collection and structure refinement for Dory_PBESNHdiyne.

Diffractometer	Bruker Apex DUO	
Radiation source	ImuS micro─focus source with MX optics, Cu Kα	
Theta range for data collection	4.84 to 68.50°	
Index ranges	-11<=h<=11, -11<=k<=9, -14<=l<=12	
Reflections collected	5204	
Independent reflections	1848 [R(int) = 0.0403]	
Coverage of independent reflections	99.0%	
Absorption correction	multi-scan	
Max. and min. transmission	0.9674 and 0.8353	
Structure solution technique	direct methods	
Structure solution program	SHELXS-97 (Sheldrick, 2008)	
Refinement method	Full-matrix least-squares on F^2	
Refinement program	SHELXL-97 (Sheldrick, 2008)	
Function minimized	$\Sigma w(F_o^2 - F_c^2)^2$	
Data / restraints / parameters	1848 / 0 / 122	
Goodness-of-fit on F^2	1.027	
Δ/σ_{max}	0.010	
Final R indices	1409 data; I>2σ(I)	R1 = 0.0382, wR2 = 0.0840
	all data	R1 = 0.0541, wR2 = 0.0915
Weighting scheme	$w=1/[\sigma^2(F_o^2)+(0.0356P)^2+0.1910P]$ where $P=(F_o^2+2F_c^2)/3$	
Extinction coefficient	0.0050(6)	
Largest diff. peak and hole	0.170 and -0.170 $eÅ^{-3}$	
R.M.S. deviation from mean	0.038 $eÅ^{-3}$	

Table 4. Atomic coordinates and equivalent isotropic atomic displacement parameters (Å²) for Dory_PBESNHdiyne.

U(eq) is defined as one third of the trace of the orthogonalized U_{ij} tensor.

	x/a	y/b	z/c	U(eq)
C1	0.22271(16)	0.87948(16)	0.97484(12)	0.0293(4)
C2	0.32477(17)	0.78169(18)	0.92805(15)	0.0368(4)
C3	0.29990(18)	0.01637(18)	0.02400(15)	0.0388(4)
C4	0.15163(19)	0.8066(2)	0.06278(14)	0.0410(4)
C5	0.01427(15)	0.84814(15)	0.80913(13)	0.0261(3)
C6	0.82339(16)	0.85516(17)	0.63405(14)	0.0348(4)
C7	0.67774(17)	0.90106(17)	0.64759(13)	0.0325(4)
C8	0.56255(17)	0.94867(17)	0.65721(13)	0.0331(4)
C9	0.43115(18)	0.00908(18)	0.66758(14)	0.0363(4)
C10	0.3191(2)	0.0629(2)	0.67699(15)	0.0463(5)
N1	0.94079(13)	0.92093(13)	0.71743(11)	0.0309(3)
O1	0.10993(10)	0.93585(10)	0.87716(9)	0.0287(3)
O2	0.99585(11)	0.72098(11)	0.82790(9)	0.0348(3)

Table 5. Bond lengths (Å) for Dory_PBESNHdiyne.

C1-O1	1.4866(17)	C1-C2	1.511(2)
C1-C4	1.517(2)	C1-C3	1.519(2)
C2-H9	0.98	C2-H10	0.98
C2-H11	0.98	C3-H1	0.98
C3-H7	0.98	C3-H8	0.98
C4-H3	0.98	C4-H12	0.98
C4-H13	0.98	C5-O2	1.2243(17)
C5-N1	1.3410(18)	C5-O1	1.3456(17)
C6-N1	1.4476(19)	C6-C7	1.471(2)
C6-H5	0.99	C6-H6	0.99
C7-C8	1.194(2)	C8-C9	1.382(2)
C9-C10	1.190(2)	C10-H2	0.95
N1-H4	0.88		

Table 6. Bond angles (°) for Dory_PBESNHdiyne.

O1-C1-C2	108.88(12)	O1-C1-C4	110.74(12)
C2-C1-C4	113.02(13)	O1-C1-C3	101.70(11)
C2-C1-C3	111.22(13)	C4-C1-C3	110.69(13)
C1-C2-H9	109.5	C1-C2-H10	109.5
H9-C2-H10	109.5	C1-C2-H11	109.5
H9-C2-H11	109.5	H10-C2-H11	109.5
C1-C3-H1	109.5	C1-C3-H7	109.5
H1-C3-H7	109.5	C1-C3-H8	109.5
H1-C3-H8	109.5	H7-C3-H8	109.5
C1-C4-H3	109.5	C1-C4-H12	109.5
H3-C4-H12	109.5	C1-C4-H13	109.5
H3-C4-H13	109.5	H12-C4-H13	109.5
O2-C5-N1	124.74(14)	O2-C5-O1	125.39(13)
N1-C5-O1	109.88(12)	N1-C6-C7	112.72(13)
N1-C6-H5	109.0	C7-C6-H5	109.0
N1-C6-H6	109.0	C7-C6-H6	109.0
H5-C6-H6	107.8	C8-C7-C6	175.07(17)
C7-C8-C9	177.76(17)	C10-C9-C8	179.06(19)
C9-C10-H2	180.0	C5-N1-C6	121.56(13)
C5-N1-H4	119.2	C6-N1-H4	119.2
C5-O1-C1	121.57(11)		

Table 7. Torsion angles (°) for Dory_PBESNHdiyne.

N1-C6-C7-C8	59.5(19)	C6-C7-C8-C9	0.(6)
C7-C8-C9-C10	-27.(15)	O2-C5-N1-C6	4.0(2)
O1-C5-N1-C6	-175.58(12)	C7-C6-N1-C5	103.25(17)
O2-C5-O1-C1	10.4(2)	N1-C5-O1-C1	-170.00(11)
C2-C1-O1-C5	63.05(16)	C4-C1-O1-C5	-61.80(17)
C3-C1-O1-C5	-179.47(12)		

Table 8. Anisotropic atomic displacement parameters (Å²) for Dory_PBESNHdiyne.

The anisotropic atomic 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}
C1	0.0255(8)	0.0321(8)	0.0277(8)	0.0035(7)	0.0001(6)	0.0048(7)
C2	0.0285(9)	0.0381(9)	0.0425(10)	0.0011(8)	0.0046(7)	0.0072(7)
C3	0.0351(9)	0.0384(9)	0.0372(9)	-0.0033(8)	-0.0050(8)	-0.0011(7)
C4	0.0412(10)	0.0462(10)	0.0364(10)	0.0056(8)	0.0099(8)	0.0049(8)
C5	0.0212(8)	0.0253(8)	0.0319(8)	-0.0036(6)	0.0056(6)	0.0002(6)
C6	0.0286(9)	0.0384(9)	0.0337(9)	-0.0074(7)	-0.0012(7)	-0.0009(7)
C7	0.0314(9)	0.0305(8)	0.0316(8)	-0.0030(7)	-0.0021(7)	-0.0041(7)
C8	0.0319(9)	0.0325(9)	0.0322(9)	-0.0006(7)	0.0011(7)	-0.0041(7)
C9	0.0336(9)	0.0419(10)	0.0314(9)	-0.0008(7)	0.0025(7)	-0.0022(8)
C10	0.0389(10)	0.0547(12)	0.0456(11)	-0.0007(9)	0.0096(8)	0.0034(9)
N1	0.0279(7)	0.0256(7)	0.0350(8)	-0.0017(6)	-0.0024(6)	-0.0031(5)
O1	0.0241(6)	0.0246(5)	0.0331(6)	0.0003(4)	-0.0033(4)	0.0007(4)
O2	0.0341(6)	0.0242(6)	0.0446(7)	-0.0002(5)	0.0052(5)	-0.0028(5)

Table 9. Hydrogen atomic coordinates and isotropic atomic displacement parameters (Å²) for Dory_PBESNHdiyne.

	x/a	y/b	z/c	U(eq)
H9	0.4059	0.7528	0.9907	0.055
H10	0.3634	0.8326	0.8690	0.055
H11	0.2712	0.6962	0.8941	0.055
H1	0.2300	1.0799	1.0498	0.058
H7	0.3399	1.0649	0.9645	0.058
H8	0.3797	0.9926	1.0894	0.058
H3	0.2255	0.7889	1.1334	0.062
H12	0.1088	0.7150	1.0316	0.062
H13	0.0747	0.8686	1.0801	0.062
H5	-0.1691	0.7495	0.6422	0.042
H6	-0.1653	0.8801	0.5556	0.042
H2	-0.7705	1.1058	0.6845	0.056
H4	-0.0355	1.0108	0.7077	0.037

Crystal Structure Report for Dory_PBBocNHdiyneBr5

Compound **2**

A prism-like specimen of $C_{10}H_{12}BrNO_2$, approximate dimensions 0.080 mm x 0.150 mm x 0.680 mm, was used for the X-ray crystallographic analysis. The X-ray intensity data were measured on a Bruker Apex DUO system equipped with a Cu Kα ImuS micro─focus source with MX optics (λ = 1.54178 Å).

Table 1: Data collection details for Dory_PBBocNHdiyneBr5.

Axis	dx/ mm	2θ/ °	ω/ °	ϕ/ °	χ/ °	Width/ °	Frames	Time/ s	Wave-length/Å	Voltage/ kV	Current/ mA	Temperature/ K
Omega	69.759	90.48	62.15	-152.33	-53.42	4.00	41	10.00	1.54184	45	0.7	173.19
Omega	69.759	98.61	49.54	-74.05	-30.89	4.00	44	10.00	1.54184	45	0.7	173.19
Omega	69.759	116.36	211.87	100.46	-80.80	4.00	8	10.00	1.54184	45	0.7	173.19
Omega	69.759	72.91	45.73	-232.83	-55.76	4.00	41	10.00	1.54184	45	0.7	173.19
Omega	69.759	88.45	59.84	23.63	-52.86	4.00	41	10.00	1.54184	45	0.7	173.19
Omega	69.759	118.94	91.72	87.96	-56.73	4.00	39	10.00	1.54184	45	0.7	173.19
Omega	69.759	114.72	87.37	165.09	-55.42	4.00	41	10.00	1.54184	45	0.7	173.19
Omega	69.759	50.90	23.29	-35.72	-54.88	4.00	41	10.00	1.54184	45	0.7	173.19
Omega	69.759	53.98	26.10	59.02	-54.33	4.00	41	10.00	1.54184	45	0.7	173.19
Omega	69.759	120.74	90.06	-43.21	-47.99	4.00	41	10.00	1.54184	45	0.7	173.19
Omega	69.759	47.91	-2.05	-148.20	-30.57	4.00	44	10.00	1.54184	45	0.7	173.19
Omega	69.759	118.79	89.06	-12.38	-49.76	4.00	29	10.00	1.54184	45	0.7	173.19
Omega	69.759	119.64	92.10	31.20	-55.03	4.00	41	10.00	1.54184	45	0.7	173.19
Omega	69.759	115.59	85.19	-130.66	-48.51	4.00	41	10.00	1.54184	45	0.7	173.19
Omega	69.759	83.55	56.49	88.94	-57.05	4.00	23	10.00	1.54184	45	0.7	173.19
Omega	69.759	120.17	81.35	-241.84	-37.80	4.00	42	10.00	1.54184	45	0.7	173.19
Omega	69.759	82.41	151.71	34.06	-80.70	4.00	22	10.00	1.54184	45	0.7	173.19
Omega	69.759	70.33	43.62	-87.87	-57.79	4.00	35	10.00	1.54184	45	0.7	173.19
Omega	69.759	118.92	191.84	-40.54	-70.05	4.00	15	10.00	1.54184	45	0.7	173.19
Omega	69.759	63.75	31.54	-185.73	-46.19	4.00	41	10.00	1.54184	45	0.7	173.19
Omega	69.759	118.79	89.06	-94.22	-49.76	4.00	36	10.00	1.54184	45	0.7	173.19
Omega	69.759	118.58	74.72	-162.27	-33.79	4.00	43	10.00	1.54184	45	0.7	173.19
Omega	69.759	28.69	-3.10	-234.56	-39.83	4.00	40	10.00	1.54184	45	0.7	173.19
Omega	69.759	79.02	51.91	-25.73	-55.90	4.00	40	10.00	1.54184	45	0.7	173.19
Omega	69.759	-39.08	-49.28	-146.40	-67.15	4.00	23	10.00	1.54184	45	0.7	173.19
Omega	69.759	116.67	88.79	69.08	-54.33	4.00	38	10.00	1.54184	45	0.7	173.19
Omega	69.759	-70.67	-96.09	-83.17	-61.60	4.00	42	10.00	1.54184	45	0.7	173.19
Omega	69.759	56.72	31.44	-137.30	-61.56	4.00	8	10.00	1.54184	45	0.7	173.19
Omega	69.759	112.19	82.28	-171.64	-50.33	4.00	18	10.00	1.54184	45	0.7	173.19
Omega	69.759	116.79	74.43	144.24	-34.82	4.00	41	10.00	1.54184	45	0.7	173.19
Omega	69.759	-23.94	-58.39	50.82	-42.53	4.00	38	10.00	1.54184	45	0.7	173.19
Omega	69.759	112.48	146.04	-86.82	-69.45	4.00	27	10.00	1.54184	45	0.7	173.19
Omega	69.759	87.89	52.88	94.74	-33.15	4.00	35	10.00	1.54184	45	0.7	173.19
Omega	69.759	16.10	2.23	-12.59	-43.44	4.00	28	10.00	1.54184	45	0.7	173.19
Omega	69.759	79.47	52.67	31.78	-56.54	4.00	30	10.00	1.54184	45	0.7	173.19
Omega	69.759	-53.00	-78.05	15.68	-62.22	4.00	27	10.00	1.54184	45	0.7	173.19
Omega	69.759	113.76	147.56	57.32	-71.11	4.00	26	10.00	1.54184	45	0.7	173.19
Omega	69.759	89.47	62.30	-189.62	-56.82	4.00	40	10.00	1.54184	45	0.7	173.19
Omega	69.759	104.30	75.65	-54.60	-52.79	4.00	8	10.00	1.54184	45	0.7	173.19
Omega	69.759	115.94	65.69	19.97	-30.36	4.00	44	10.00	1.54184	45	0.7	173.19
Omega	69.759	117.78	76.21	-90.70	-35.70	4.00	39	10.00	1.54184	45	0.7	173.19
Omega	69.759	85.45	123.23	-118.76	-32.02	4.00	8	10.00	1.54184	45	0.7	173.19
Omega	69.759	61.88	27.05	-13.14	-33.32	4.00	40	10.00	1.54184	45	0.7	173.19
Omega	69.759	118.52	90.15	-232.50	-53.36	4.00	8	10.00	1.54184	45	0.7	173.19
Omega	69.759	96.76	69.44	-134.01	-55.48	4.00	8	10.00	1.54184	45	0.7	173.19
Omega	69.759	117.66	149.05	168.03	-73.70	4.00	25	10.00	1.54184	45	0.7	173.19
Omega	69.759	86.41	56.10	-93.56	-48.66	4.00	41	10.00	1.54184	45	0.7	173.19
Omega	69.759	80.62	52.51	-49.78	-53.87	4.00	40	10.00	1.54184	45	0.7	173.19
Omega	69.759	82.55	205.97	-178.16	-77.18	4.00	8	10.00	1.54184	45	0.7	173.19
Omega	69.759	118.89	89.81	-136.53	-51.94	4.00	41	10.00	1.54184	45	0.7	173.19
Omega	69.759	93.61	46.20	47.88	-31.86	4.00	43	10.00	1.54184	45	0.7	173.19

Omega	69.759	118.37	76.83	85.40	-35.72	4.00	42	10.00	1.54184	45	0.7	173.19
Omega	69.759	116.82	150.43	-61.06	-32.31	4.00	11	10.00	1.54184	45	0.7	173.19
Omega	69.759	26.97	12.04	-112.94	-64.33	4.00	8	10.00	1.54184	45	0.7	173.19
Omega	69.759	115.54	129.35	-116.66	-30.02	4.00	9	10.00	1.54184	45	0.7	173.19
Omega	69.759	118.93	86.92	138.57	-46.51	4.00	41	10.00	1.54184	45	0.7	173.19
Omega	69.759	104.01	66.13	-7.93	-39.03	4.00	42	10.00	1.54184	45	0.7	173.19
Omega	69.759	118.84	154.66	165.99	-63.44	4.00	27	10.00	1.54184	45	0.7	173.19
Omega	69.759	89.47	38.26	-167.24	-30.00	4.00	44	10.00	1.54184	45	0.7	173.19
Omega	69.759	118.94	74.48	1.70	-33.68	4.00	34	10.00	1.54184	45	0.7	173.19
Omega	69.759	118.85	175.31	-143.28	-43.97	4.00	9	10.00	1.54184	45	0.7	173.19
Omega	69.759	28.58	27.97	80.28	-41.52	4.00	32	10.00	1.54184	45	0.7	173.19
Omega	69.759	53.02	175.99	71.68	-78.38	4.00	8	10.00	1.54184	45	0.7	173.19
Omega	69.759	115.77	154.68	64.60	-32.59	4.00	8	10.00	1.54184	45	0.7	173.19
Omega	69.759	103.29	66.45	-202.97	-39.76	4.00	42	10.00	1.54184	45	0.7	173.19
Omega	69.759	-56.88	-89.91	104.35	-34.64	4.00	20	10.00	1.54184	45	0.7	173.19
Omega	69.759	-47.66	-87.85	-78.88	-32.97	4.00	18	10.00	1.54184	45	0.7	173.19
Omega	69.759	116.84	71.45	-33.20	-30.25	4.00	43	10.00	1.54184	45	0.7	173.19

A total of 2082 frames were collected. The total exposure time was 5.78 hours. The frames were integrated with the Bruker SAINT software package using a wide-frame algorithm. The integration of the data using a monoclinic unit cell yielded a total of 16523 reflections to a maximum θ angle of 71.79° (0.81 Å resolution), of which 2175 were independent (average redundancy 7.597, completeness = 96.2%, R_{int} = 6.56%, R_{sig} = 4.11%) and 2066 (94.99%) were greater than 2σ(F^2). The final cell constants of a = 10.4435(16) Å, b = 9.2090(15) Å, c = 12.2744(19) Å, β = 102.599(4)°, volume = 1152.1(3) $Å^3$, are based upon the refinement of the XYZ-centroids of 9825 reflections above 20 σ(I) with 7.379° < 2θ < 143.5°. Data were corrected for absorption effects using the multi-scan method (SADABS). The ratio of minimum to maximum apparent transmission was 0.438. The calculated minimum and maximum transmission coefficients (based on crystal size) are 0.1429 and 0.7057.

The structure was solved and refined using the Bruker SHELXTL Software Package, using the space group P 1 21/c 1, with Z = 4 for the formula unit, $C_{10}H_{12}BrNO_2$. The final anisotropic full-matrix least-squares refinement on F^2 with 130 variables converged at R1 = 6.44%, for the observed data and wR2 = 16.79% for all data. The goodness-of-fit was 1.133. The largest peak in the final difference electron density synthesis was 1.034 $e^-/Å^3$ and the largest hole was -1.362 $e^-/Å^3$ with an RMS deviation of 0.156 $e^-/Å^3$. On the basis of the final model, the calculated density was 1.488 g/cm^3 and F(000), 520 e^-.

Table 2. Sample and crystal data for Dory_PBBocNHdiyneBr5.

Identification code	Dory_PBBocNHdiyneBr5	
Chemical formula	$C_{10}H_{12}BrNO_2$	
Formula weight	258.12	
Temperature	173(2) K	
Wavelength	1.54178 Å	
Crystal size	0.080 x 0.150 x 0.680 mm	
Crystal system	monoclinic	
Space group	P 1 21/c 1	
Unit cell dimensions	a = 10.4435(16) Å	α = 90°
	b = 9.2090(15) Å	β = 102.599(4)°
	c = 12.2744(19) Å	γ = 90°
Volume	1152.1(3) $Å^3$	
Z	4	
Density (calculated)	1.488 g/cm^3	
Absorption coefficient	4.683 mm^{-1}	
F(000)	520	

Table 3. Data collection and structure refinement for Dory_PBBocNHdiyneBr5.

Diffractometer	Bruker Apex DUO
Radiation source	ImuS micro─focus source with MX optics, Cu Kα
Theta range for data collection	4.34 to 71.79°
Index ranges	-12<=h<=12, -11<=k<=10, -15<=l<=15
Reflections collected	16523
Independent reflections	2175 [R(int) = 0.0656]
Coverage of independent reflections	96.2%
Absorption correction	multi-scan
Max. and min. transmission	0.7057 and 0.1429
Structure solution technique	direct methods
Structure solution program	SHELXS-97 (Sheldrick, 2008)
Refinement method	Full-matrix least-squares on F^2
Refinement program	SHELXL-97 (Sheldrick, 2008)
Function minimized	$\Sigma\, w(F_o^2 - F_c^2)^2$
Data / restraints / parameters	2175 / 0 / 130
Goodness-of-fit on F^2	1.133
Final R indices	2066 data; I>2σ(I) R1 = 0.0644, wR2 = 0.1662
	all data R1 = 0.0659, wR2 = 0.1679
Weighting scheme	$w=1/[\sigma^2(F_o^2)+(0.0869P)^2+2.9103P]$ where $P=(F_o^2+2F_c^2)/3$
Largest diff. peak and hole	1.034 and -1.362 eÅ^{-3}
R.M.S. deviation from mean	0.156 eÅ^{-3}

Table 4. Atomic coordinates and equivalent isotropic atomic displacement parameters (Å^2) for Dory_PBBocNHdiyneBr5.

U(eq) is defined as one third of the trace of the orthogonalized U_{ij} tensor.

	x/a	y/b	z/c	U(eq)
Br1	0.74220(5)	0.08875(5)	0.15967(4)	0.0447(3)
O1	0.6182(3)	0.9374(3)	0.3882(3)	0.0371(7)
N1	0.4688(4)	0.9112(4)	0.2336(4)	0.0405(9)
O2	0.5299(3)	0.7132(3)	0.3421(3)	0.0418(8)
C1	0.8183(5)	0.7927(6)	0.4350(5)	0.0538(13)
C2	0.7257(5)	0.8888(5)	0.4810(4)	0.0389(10)
C3	0.5388(4)	0.8424(4)	0.3233(4)	0.0332(9)
C4	0.3736(5)	0.8374(5)	0.1479(4)	0.0424(10)
C5	0.2380(5)	0.8816(6)	0.1490(4)	0.0419(11)
C6	0.1317(5)	0.9225(5)	0.1515(4)	0.0451(12)
C7	0.0094(5)	0.9739(5)	0.1550(4)	0.0412(10)
C8	0.9029(5)	0.0197(5)	0.1577(4)	0.0440(11)
C9	0.6688(6)	0.8141(6)	0.5709(4)	0.0541(13)
C10	0.7894(6)	0.0324(6)	0.5247(5)	0.0586(15)

Table 5. Bond lengths (Å) for Dory_PBBocNHdiyneBr5.

Br1-C8	1.800(5)	O1-C3	1.341(5)
O1-C2	1.483(5)	N1-C3	1.340(6)
N1-C4	1.449(6)	N1-H1	0.88
O2-C3	1.220(5)	C1-C2	1.508(7)
C1-H1A	0.98	C1-H1B	0.98
C1-H1C	0.98	C2-C10	1.525(6)
C2-C9	1.527(7)	C4-C5	1.476(7)
C4-H4A	0.99	C4-H4B	0.99
C5-C6	1.179(8)	C6-C7	1.372(7)
C7-C8	1.196(7)	C9-H9A	0.98
C9-H9B	0.98	C9-H9C	0.98
C10-H10A	0.98	C10-H10B	0.98
C10-H10C	0.98		

Table 6. Bond angles (°) for Dory_PBBocNHdiyneBr5.

C3-O1-C2	121.7(3)	C3-N1-C4	122.6(4)
C3-N1-H1	118.7	C4-N1-H1	118.7
C2-C1-H1A	109.5	C2-C1-H1B	109.5
H1A-C1-H1B	109.5	C2-C1-H1C	109.5
H1A-C1-H1C	109.5	H1B-C1-H1C	109.5
O1-C2-C1	109.2(4)	O1-C2-C10	102.0(3)
C1-C2-C10	112.0(5)	O1-C2-C9	110.0(4)
C1-C2-C9	112.9(4)	C10-C2-C9	110.2(5)
O2-C3-N1	124.5(4)	O2-C3-O1	125.9(4)
N1-C3-O1	109.6(4)	N1-C4-C5	111.9(4)
N1-C4-H4A	109.2	C5-C4-H4A	109.2
N1-C4-H4B	109.2	C5-C4-H4B	109.2
H4A-C4-H4B	107.9	C6-C5-C4	177.2(5)
C5-C6-C7	178.4(5)	C8-C7-C6	179.5(6)
C7-C8-Br1	179.2(5)	C2-C9-H9A	109.5
C2-C9-H9B	109.5	H9A-C9-H9B	109.5
C2-C9-H9C	109.5	H9A-C9-H9C	109.5
H9B-C9-H9C	109.5	C2-C10-H10A	109.5
C2-C10-H10B	109.5	H10A-C10-H10B	109.5
C2-C10-H10C	109.5	H10A-C10-H10C	109.5
H10B-C10-H10C	109.5		

Table 7. Torsion angles (°) for Dory_PBBocNHdiyneBr5.

C3-O1-C2-C1	59.0(5)	C3-O1-C2-C10	177.6(4)
C3-O1-C2-C9	-65.5(5)	C4-N1-C3-O2	-0.1(7)
C4-N1-C3-O1	-179.7(4)	C2-O1-C3-O2	12.7(7)
C2-O1-C3-N1	-167.6(4)	C3-N1-C4-C5	110.6(5)
N1-C4-C5-C6	30.(11)	C4-C5-C6-C7	10.(30)
C5-C6-C7-C8	30.(90)	C6-C7-C8-Br1	60.(100)

Table 8. Anisotropic atomic displacement parameters (Å²) for Dory_PBBocNHdiyneBr5.

The anisotropic atomic 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}
Br1	0.0452(4)	0.0366(4)	0.0529(4)	0.00006(19)	0.0122(2)	0.00353(19)
O1	0.0395(16)	0.0215(14)	0.0457(17)	-0.0028(12)	-0.0005(13)	-0.0017(12)
N1	0.041(2)	0.027(2)	0.049(2)	0.0030(15)	0.0005(17)	-0.0014(15)
O2	0.0488(18)	0.0183(15)	0.0545(19)	0.0007(13)	0.0028(15)	-0.0040(12)
C1	0.045(3)	0.044(3)	0.070(3)	0.000(3)	0.006(2)	0.010(2)
C2	0.042(2)	0.021(2)	0.048(2)	0.0005(18)	-0.002(2)	0.0005(17)
C3	0.031(2)	0.022(2)	0.048(2)	-0.0020(17)	0.0115(17)	-0.0002(16)
C4	0.043(2)	0.034(3)	0.047(2)	-0.0004(19)	0.0023(19)	0.0003(19)
C5	0.044(3)	0.029(2)	0.051(3)	0.0038(19)	0.006(2)	0.0003(18)
C6	0.051(3)	0.030(3)	0.048(3)	0.0015(19)	-0.001(2)	-0.004(2)
C7	0.037(2)	0.038(3)	0.046(2)	0.003(2)	0.0028(18)	0.0021(19)
C8	0.049(3)	0.035(3)	0.046(2)	0.004(2)	0.006(2)	-0.004(2)
C9	0.072(4)	0.041(3)	0.049(3)	0.005(2)	0.015(3)	-0.002(3)
C10	0.060(3)	0.034(3)	0.067(3)	-0.002(2)	-0.016(3)	-0.007(2)

Table 9. Hydrogen atomic coordinates and isotropic atomic displacement parameters (Å²) for Dory_PBBocNHdiyneBr5.

	x/a	y/b	z/c	U(eq)
H1	0.4812	1.0049	0.2265	0.049
H1A	0.7728	0.7033	0.4054	0.081
H1B	0.8942	0.7686	0.4946	0.081
H1C	0.8480	0.8439	0.3750	0.081
H4A	0.3824	0.7312	0.1598	0.051
H4B	0.3920	0.8596	0.0739	0.051
H9A	0.6022	0.8768	0.5918	0.081
H9B	0.7392	0.7959	0.6367	0.081
H9C	0.6287	0.7217	0.5421	0.081
H10A	0.8190	1.0831	0.4644	0.088
H10B	0.8647	1.0136	0.5862	0.088
H10C	0.7254	1.0928	0.5515	0.088

Variations of geometry during calculations of system **8-8-9**

Cartesian coordinates and RMSD values (heavy atoms)

	input (from crystal)			DFT/B3LYP				DFT/M06-2X			
atom	x	y	z	x	y	z	distance Å	x	y	z	distance Å
C	-4.255	2.128	-2.612	-4.1069	2.1968	-2.6259	*0.1639*	-4.0316	2.3873	-2.5687	*0.3450*
O	-3.451	2.653	-1.477	-3.5333	2.7294	-1.4184	*0.1266*	-3.3506	2.8286	-1.3930	*0.2190*
C	-2.730	1.836	-0.687	-2.7921	1.8641	-0.6821	*0.0684*	-2.7893	1.8517	-0.6563	*0.0686*
N	-2.279	2.514	0.378	-2.3529	2.4504	0.4543	*0.1238*	-2.1589	2.3508	0.4231	*0.2076*
C	-1.394	1.901	1.347	-1.4658	1.7841	1.3999	*0.1470*	-1.4135	1.5097	1.3444	*0.3918*
O	-2.510	0.652	-0.905	-2.5681	0.7022	-1.0215	*0.1395*	-2.8628	0.6645	-0.9517	*0.3560*
H	-2.526	3.351	0.492	-2.5628	3.4314	0.5696		-2.1249	3.3559	0.5054	
H	-4.651	2.975	-2.991	-4.5656	3.0501	-3.1252		-4.3972	3.2941	-3.0476	
H	-4.968	1.524	-2.252	-4.8640	1.4453	-2.3878		-4.8636	1.7316	-2.3033	
H	-3.663	1.677	-3.290	-3.3354	1.7500	-3.2561		-3.3446	1.8529	-3.2282	
H	-1.444	0.917	1.252	-1.6597	0.7105	1.3823		-1.8212	0.4982	1.3047	
H	-1.702	2.134	2.258	-1.6685	2.1646	2.4040		-1.5247	1.9005	2.3578	
H	-0.442	2.192	1.240	-0.4104	1.9567	1.1581		-0.3514	1.4703	1.0834	
C	-1.243	-2.529	2.612	-1.3327	-2.5375	2.6500	*0.0977*	-0.7757	-2.2851	2.0807	*0.7484*
O	-2.047	-2.004	1.477	-2.0250	-1.9270	1.5506	*0.1088*	-1.8406	-1.7970	1.2690	*0.3588*
C	-2.768	-2.821	0.687	-2.7728	-2.7878	0.7895	*0.1078*	-2.5145	-2.7566	0.5802	*0.2825*
N	-3.219	-2.143	-0.378	-3.3002	-2.1403	-0.2760	*0.1304*	-3.4066	-2.1870	-0.2612	*0.2253*
C	-4.104	-2.755	-1.347	-4.1339	-2.8220	-1.2493	*0.1222*	-4.1952	-2.9869	-1.1732	*0.3038*
O	-2.988	-4.005	0.905	-2.9227	-3.9706	1.0645	*0.1758*	-2.3235	-3.9472	0.7377	*0.6877*
H	-2.972	-1.306	-0.491	-3.0647	-1.1631	-0.4143		-3.3607	-1.1813	-0.3806	
H	-0.847	-1.682	2.991	-0.8380	-1.7175	3.1730		-0.3236	-1.4012	2.5320	
H	-0.530	-3.133	2.252	-0.5915	-3.2559	2.2878		-0.0413	-2.8121	1.4675	
H	-1.835	-2.980	3.290	-2.0333	-3.0497	3.3147		-1.1583	-2.9575	2.8511	
H	-4.054	-3.740	-1.252	-3.9822	-3.8975	-1.1466		-4.0975	-4.0314	-0.8765	
H	-3.796	-2.523	-2.258	-3.8520	-2.5146	-2.2610		-3.8439	-2.8802	-2.2044	
H	-5.055	-2.464	-1.240	-5.1994	-2.6062	-1.0980		-5.2485	-2.6991	-1.1212	
C	0.427	-0.821	-0.848	0.4629	-0.6920	-1.2151	*0.3908*	-0.0150	-0.8352	-0.9767	*0.4606*
C	1.500	-1.322	-0.957	1.5818	-1.1680	-1.2435	*0.3354*	1.1215	-1.2537	-0.9641	*0.3847*
C	2.757	-1.885	-1.078	2.8398	-1.7089	-1.2745	*0.2765*	2.4167	-1.7325	-0.9558	*0.3924*
C	3.860	-2.328	-1.189	3.9560	-2.1942	-1.3014	*0.1994*	3.5521	-2.1557	-0.9562	*0.4227*
C	5.259	-2.755	-1.347	5.2943	-2.7728	-1.3393	*0.0402*	4.9185	-2.6695	-0.9711	*0.5144*
H	-0.432	-0.421	-0.761	-0.5278	-0.2856	-1.1812		-1.0250	-0.4703	-0.9869	
H	5.308	-3.740	-1.252	5.2636	-3.8534	-1.1557		4.9518	-3.6866	-0.5716	
H	5.566	-2.523	-2.258	5.7634	-2.6090	-2.3170		5.3087	-2.6888	-1.9923	
H	5.868	-2.333	-0.679	5.9396	-2.3211	-0.5763		5.5750	-2.0403	-0.3642	
						RMSD (Å) →	***0.1643***			RMSD (Å) →	***0.3870***

Variations of geometry during calculations of system **8-8-10**

Cartesian coordinates and RMSD values (heavy atoms)

	input (from crystal)			DFT/B3LYP				DFT/M06-2X			
atom	x	y	z	x	y	z	distance Å	x	y	z	distance Å
C	-4.856	2.217	-2.767	-4.3213	2.0861	-2.8917	*0.5645*	-4.1700	2.1322	-2.8505	*0.6963*
O	-3.982	2.665	-1.656	-3.8948	2.6294	-1.6286	*0.0981*	-3.5569	2.6567	-1.6709	*0.4254*
C	-3.326	1.790	-0.878	-3.2671	1.7641	-0.7939	*0.1059*	-3.2514	1.7437	-0.7300	*0.1721*
N	-2.835	2.424	0.197	-2.9429	2.3684	0.3716	*0.2126*	-2.6585	2.3204	0.3325	*0.2454*
C	-2.070	1.744	1.224	-2.1915	1.7080	1.4318	*0.2434*	-2.2086	1.5727	1.4925	*0.3474*
O	-3.183	0.600	-1.104	-3.0416	0.5881	-1.0811	*0.1437*	-3.4934	0.5489	-0.8547	*0.4013*
H	-2.984	3.287	0.282	-3.1354	3.3576	0.4370		-2.4870	3.3130	0.2691	
H	-5.214	3.080	-3.109	-4.7464	2.9299	-3.4350		-4.3635	2.9961	-3.4837	
H	-5.577	1.631	-2.402	-5.0775	1.3111	-2.7395		-5.1016	1.6213	-2.6004	
H	-4.311	1.769	-3.470	-3.4730	1.6652	-3.4367		-3.4961	1.4330	-3.3498	
H	-2.130	0.766	1.081	-2.3663	0.6325	1.3844		-2.5843	0.5513	1.4172	
H	-2.461	1.949	2.110	-2.5375	2.0802	2.3995		-2.5959	2.0303	2.4061	
H	-1.103	2.021	1.215	-1.1147	1.8926	1.3403		-1.1155	1.5373	1.5363	
C	-1.378	-2.388	2.768	-1.7698	-2.4063	2.8818	*0.4083*	-1.3904	-2.0872	2.5918	*0.3488*
O	-2.253	-1.940	1.656	-2.4212	-1.8741	1.7188	*0.1913*	-2.4675	-1.7403	1.7266	*0.3015*
C	-2.908	-2.815	0.879	-3.1756	-2.7779	1.0138	*0.3019*	-2.8201	-2.7163	0.8470	*0.1360*
N	-3.399	-2.182	-0.197	-3.6783	-2.2026	-0.1043	*0.2950*	-3.7598	-2.2664	-0.0162	*0.4122*
C	-4.164	-2.861	-1.223	-4.5093	-2.9388	-1.0397	*0.3986*	-4.1166	-3.0941	-1.1523	*0.2482*
O	-3.051	-4.005	1.104	-3.3493	-3.9331	1.3787	*0.4118*	-2.3480	-3.8360	0.8679	*0.7606*
H	-3.251	-1.319	-0.282	-3.4255	-1.2414	-0.3143		-3.8572	-1.2603	-0.1001	
H	-1.021	-1.526	3.109	-1.2810	-1.5539	3.3569		-1.2164	-1.2076	3.2129	
H	-0.657	-2.974	2.403	-1.0266	-3.1565	2.5972		-0.4956	-2.3266	2.0102	
H	-1.923	-2.837	3.471	-2.4950	-2.8609	3.5606		-1.6560	-2.9464	3.2111	
H	-4.104	-3.839	-1.081	-4.5062	-3.9913	-0.7514		-4.4038	-4.0873	-0.8040	
H	-3.774	-2.657	-2.110	-4.1130	-2.8456	-2.0565		-3.2840	-3.2037	-1.8568	
H	-5.122	-2.586	-1.214	-5.5447	-2.5754	-1.0297		-4.9635	-2.6354	-1.6635	
C	1.339	-1.183	-1.106	1.5683	-0.9842	-1.4988	*0.4964*	0.9096	-1.1780	-1.1275	*0.4300*
C	2.458	-1.604	-1.138	2.7189	-1.3855	-1.4986	*0.4958*	2.0692	-1.5248	-1.1834	*0.3993*
C	3.745	-2.078	-1.180	4.0083	-1.8390	-1.4903	*0.4719*	3.3877	-1.9195	-1.2462	*0.3965*
C	4.862	-2.454	-1.210	5.1554	-2.2487	-1.4754	*0.4457*	4.5469	-2.2680	-1.3018	*0.3773*
C	6.281	-2.861	-1.223	6.5249	-2.7460	-1.4531	*0.3545*	5.9418	-2.6918	-1.3702	*0.4066*
Br	-0.346	-0.547	-1.082	-0.1375	-0.4172	-1.4613	*0.4519*	-0.8045	-0.6635	-1.0413	*0.4748*
H	6.341	-3.839	-1.081	6.5442	-3.8351	-1.3332		6.0235	-3.7693	-1.2051	
H	6.671	-2.657	-2.110	7.0493	-2.5002	-2.3835		6.3659	-2.4606	-2.3508	
H	6.802	-2.398	-0.523	7.0896	-2.3065	-0.6230		6.5372	-2.1809	-0.6089	
						RMSD (Å) →	***0.3393***			RMSD (Å) →	***0.3661***