Supplementary Material

Reactivity of 3-halopropynols: X-ray crystallographic analysis of 1,1-dihalocumulenes and 2+2 cycloaddition products

Nurbey Gulia, Bartłomiej Pigulski, and Sławomir Szafert*

Faculty of Chemistry, University of Wrocław, 14 F. Joliot-Curie, 50-383 Wrocław, Poland
Email: slawomir.szafert@chem.uni.wroc.pl

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X-ray crystallography

Table S1. Details of X-ray single crystal diffraction experiments

	Compound				
	10	**11**	**12**	**13**	**14**
Crystal data					
Chemical formula	$C_{15}H_8I_2$	$C_{30}H_{21}Br_3O$	$C_{30}H_{20}Br_2O$	$C_{15}H_{10}Br_2$	$C_{30}H_{19}Br_3$
M_r	442.01	637.20	556.28	350.05	619.18
Crystal system, space group	Triclinic, *P*-1	Monoclinic, $P2_1/n$	Monoclinic, *Cc*	Monoclinic, $P2_1/n$	Monoclinic, $P2_1/n$
Temperature (K)	100	95	100	100	120
a, *b*, *c* (Å)	8.753 (3), 10.919 (3), 14.015 (5)	11.085 (2), 14.238 (3), 15.788 (4)	9.230 (4), 17.047 (7), 14.793 (5)	18.664 (5), 8.019 (3), 19.190 (6)	15.410 (5), 17.303 (5), 19.224 (6)
α, β, γ (°)	94.94 (3), 92.68 (3), 93.61 (3)	90, 93.76 (2), 90	90, 99.45 (2), 90	90, 114.52 (3), 90	90, 109.75 (3), 90
V (Å^3)	1330.0 (8)	2486.3 (9)	2296.1 (15)	2613.1 (16)	4824 (3)
Z	4	4	4	8	8
Radiation type	Mo *K*α	Mo *K*α	Mo *K*α	Mo *K*α	Mo *K*α
μ (mm^{-1})	4.70	4.89	3.55	6.18	5.03
Crystal size (mm)	0.40 × 0.30 × 0.14	0.58 × 0.49 × 0.35	0.49 × 0.30 × 0.25	0.60 × 0.31 × 0.08	0.36 × 0.30 × 0.18
Data collection					
Absorption correction	Analytical *CrysAlis RED*	Analytical *CrysAlis PRO*.	Analytical *CrysAlis PRO*,.	Analytical *CrysAlis* PRO	Analytical *CrysAlis PRO*
T_{min}, T_{max}	0.619, 0.866	0.152, 0.276	0.299, 0.535	0.130, 0.658	0.342, 0.508
No. of measured, independent and observed [$I > 2\sigma(I)$] reflections	13052, 6613, 3779	47603, 11911, 9533	7285, 4661, 4332	43189, 12049, 6471	20598, 9812, 7486
R_{int}	0.058	0.051	0.049	0.101	0.036
$(\sin\theta/\lambda)_{max}$ (Å^{-1})	0.808	0.844	0.676	0.846	0.625
Refinement					
$R[F^2 > 2\sigma(F^2)]$, $wR(F^2)$, *S*	0.046, 0.081, 0.84	0.035, 0.092, 1.02	0.050, 0.127, 1.04	0.066, 0.186, 1.03	0.038, 0.077, 1.03
No. of reflections	6613	11911	4661	12049	9812
No. of parameters	307	308	298	307	595
No. of restraints	0	0	2	0	0
H-atom treatment	H-atom parameters constrained	H-atom parameters constrained	H-atom parameters constrained	H-atom parameters constrained	H-atom parameters constrained
$\Delta\rho_{max}$, $\Delta\rho_{min}$ (e Å^{-3})	1.59, −1.01	0.61, −0.66	0.96, −0.47	1.68, −1.21	0.53, −0.58

Table S2. Selected bond lengths and angles for **10** and **13**

Compound	Selected bond lengths [Å] and angles [°]						
	X1-C1	**X2-C1**	**C1-C2**	**C2-C3**	**<X1-C1-X2**	**<C2-C1-X1**	**<C2-C1-X2**
13A	1.907(4)	1.896(4)	1.284(6)	1.329(6)	114.5(2)	122.3(3)	123.3(3)
13B	1.899(4)	1.912(4)	1.281(6)	1.324(6)	113.7(2)	123.7(3)	122.6(3)
10A	2.105(7)	2.122(7)	1.276(9)	1.339(10)	116.8(3)	122.9(5)	120.3(5)
10B	2.107(7)	2.114(8)	1.295(9)	1.306(9)	116.1(3)	121.6(6)	122.2(6)

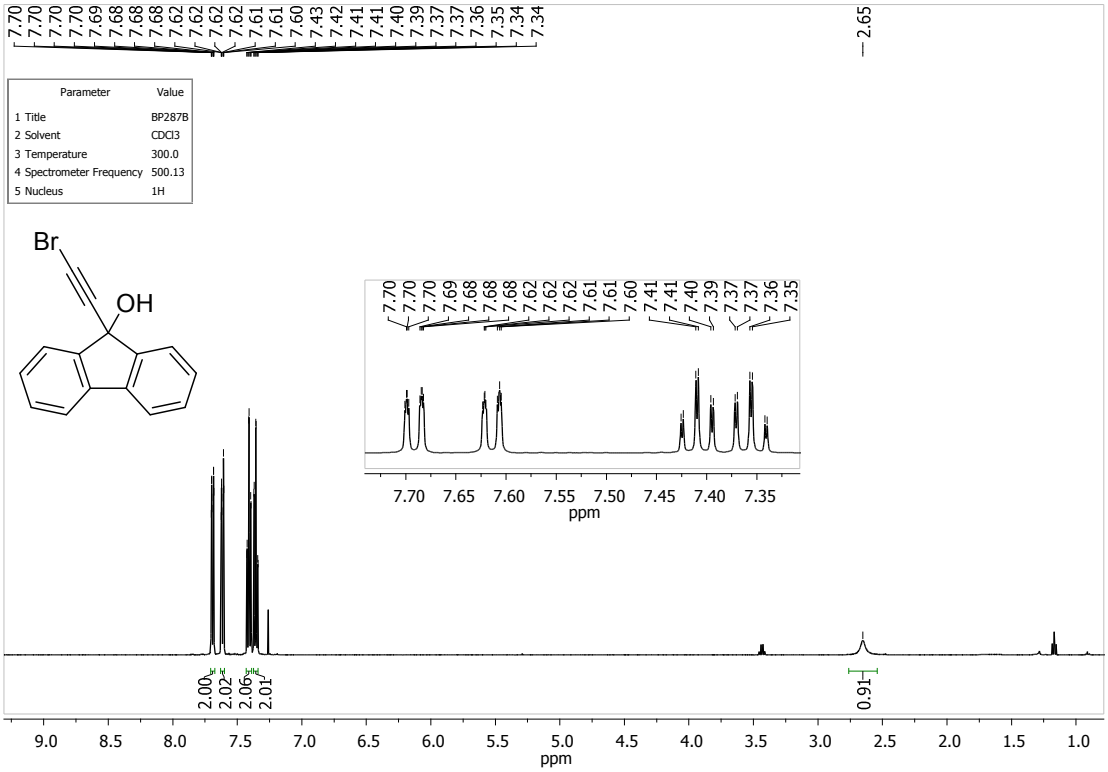
Table S3. Selected bond lengths and angles for **11**, **12** and **14**

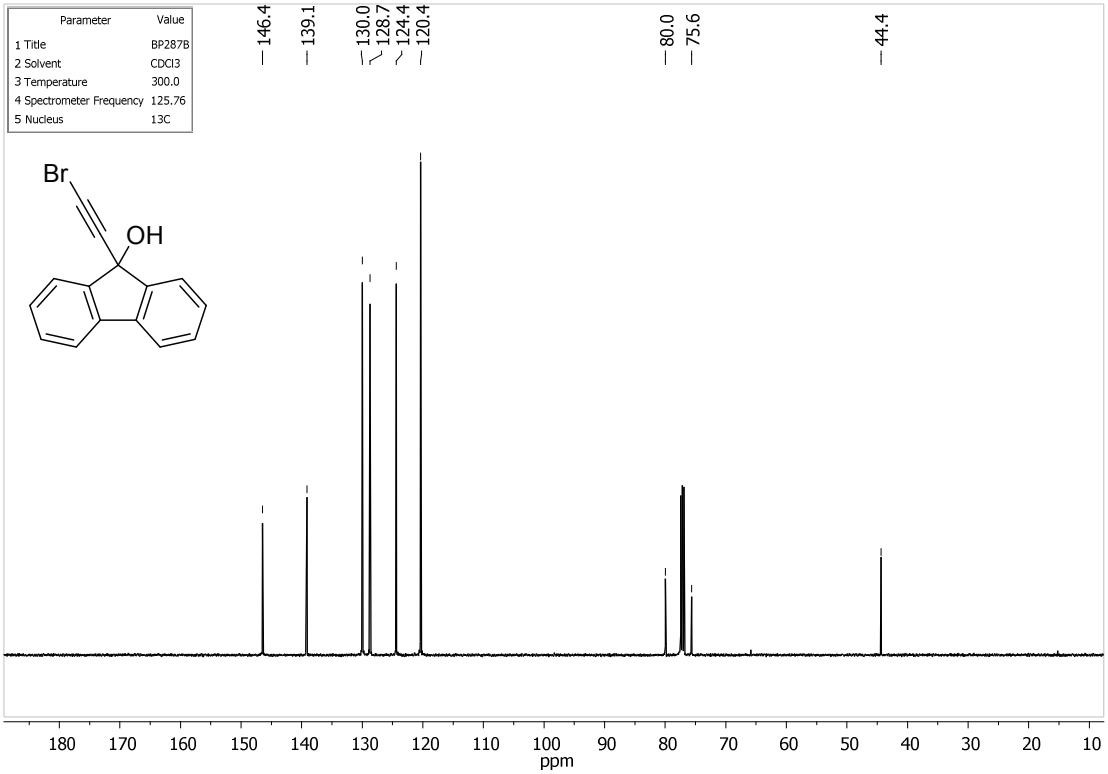
Compound	Selected bond lengths [Å] and angles [˚]							
	C2-C3	**C3-C4**	**C4-C5**	**C5-C2**	**<C5-C2-C3**	**<C2-C3-C4**	**<C3-C4-C5**	**<C4-C5-C2**
11	1.468(2)	1.354(2)	1.560(2)	1.557(2)	88.4(1)	95.1(1)	92.6(1)	83.9(1)
12	1.49(1)	1.50(1)	1.57(1)	1.55(1)	92.3(5)	90.4(6)	91.3(5)	85.8(5)
	C1-C2	**C2-C3**	**C3-C4**	**C4-C1**	**<C4-C1-C2**	**<C1-C2-C3**	**<C2-C3-C4**	**<C3-C4-C1**
14A*	1.644(5)	1.539(4)	1.399(5)	1.507(4)	88.0(2)	82.7(2)	96.3(3)	92.7(3)
14B*	1.662(5)	1.535(5)	1.410(5)	1.503(4)	88.2(2)	82.3(2)	96.3(3)	92.5(3)

*Two molecules in the asymmetric unit

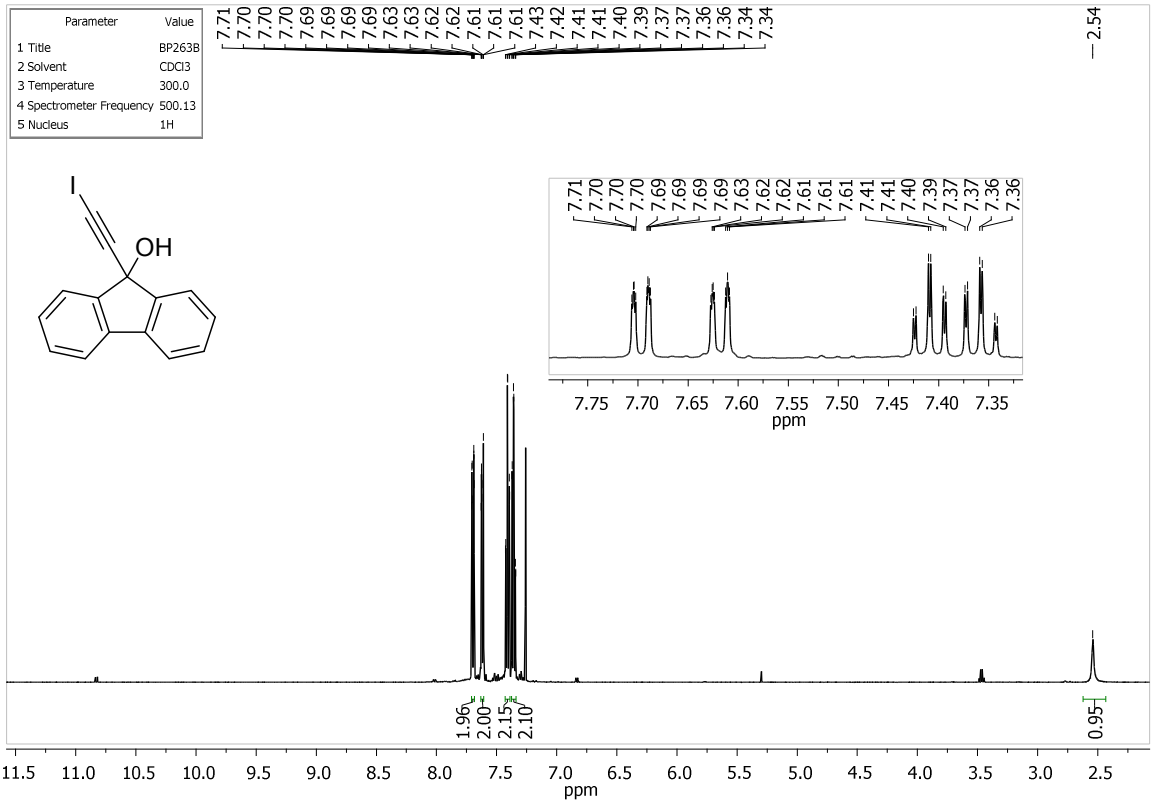
NMR spectra

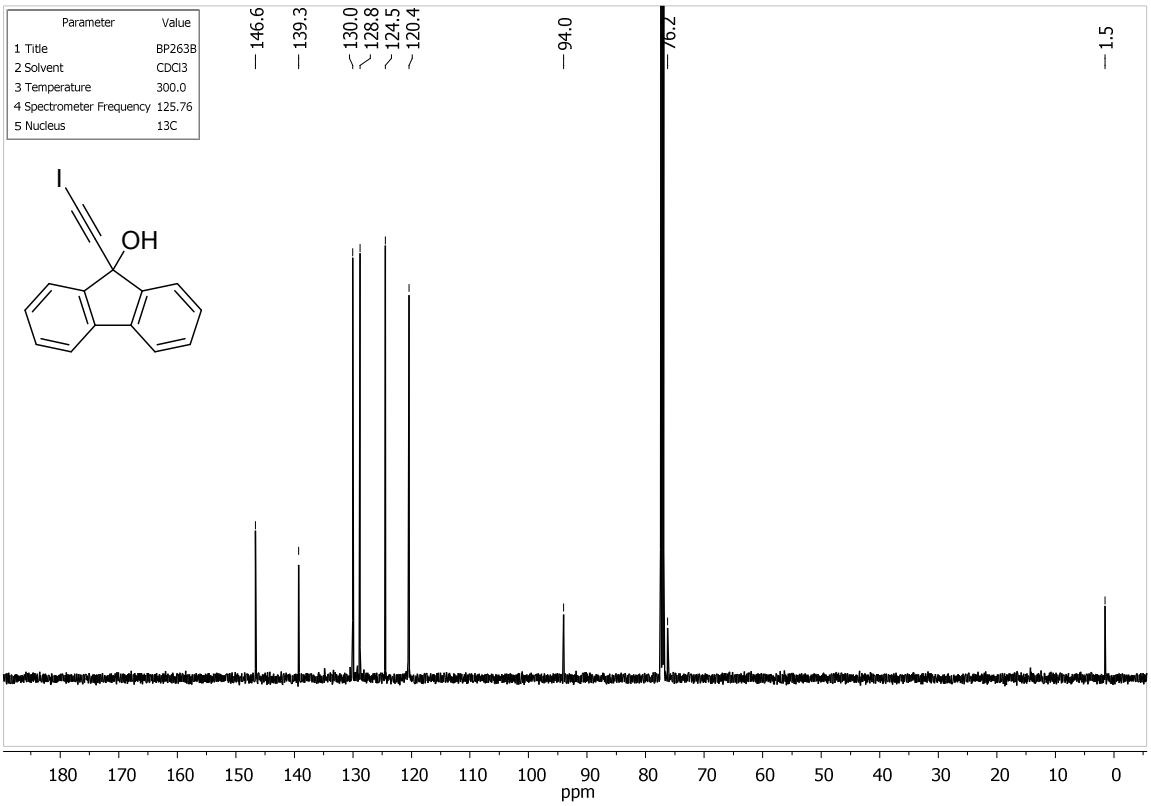
9-(Bromoethynyl)-9*H*-fluoren-9-ol (3)



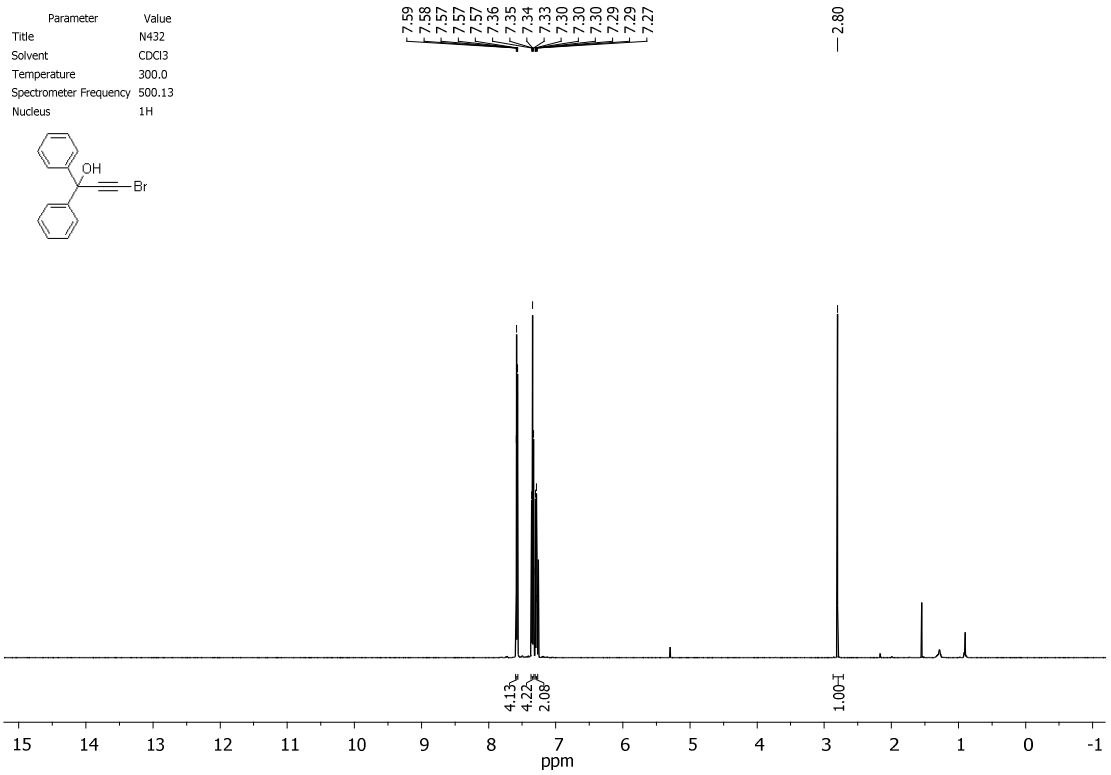


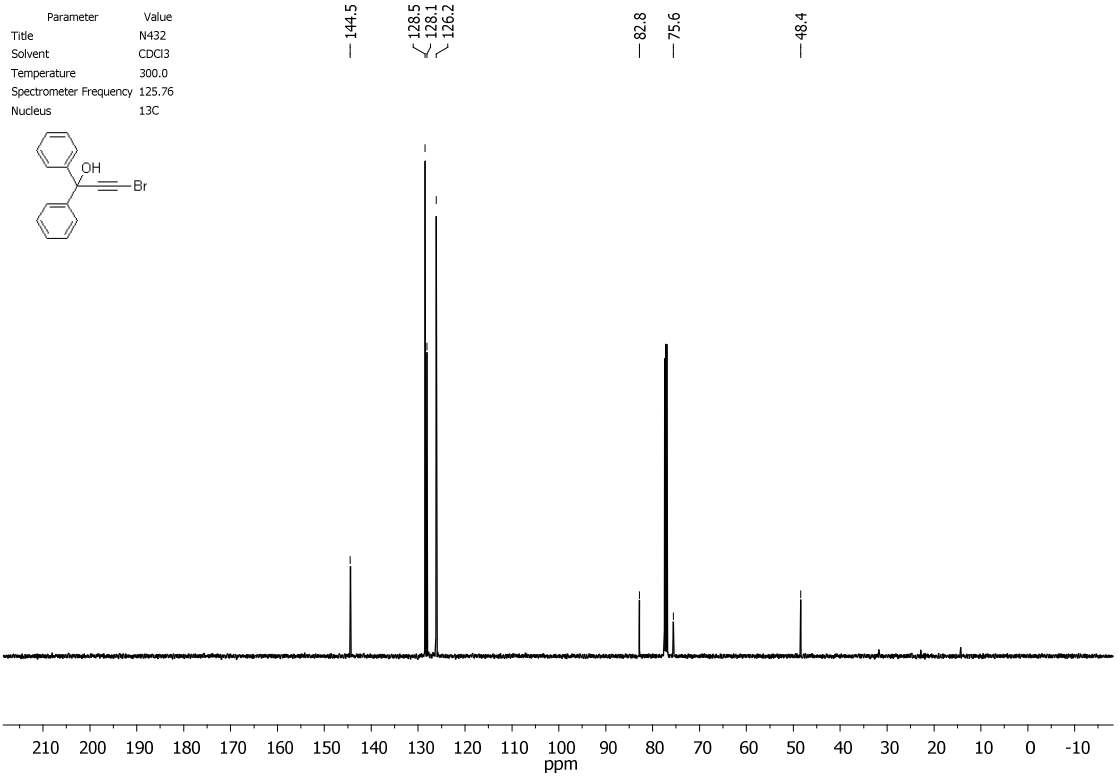
9-(Iodoethynyl)-9*H*-fluoren-9-ol (4)



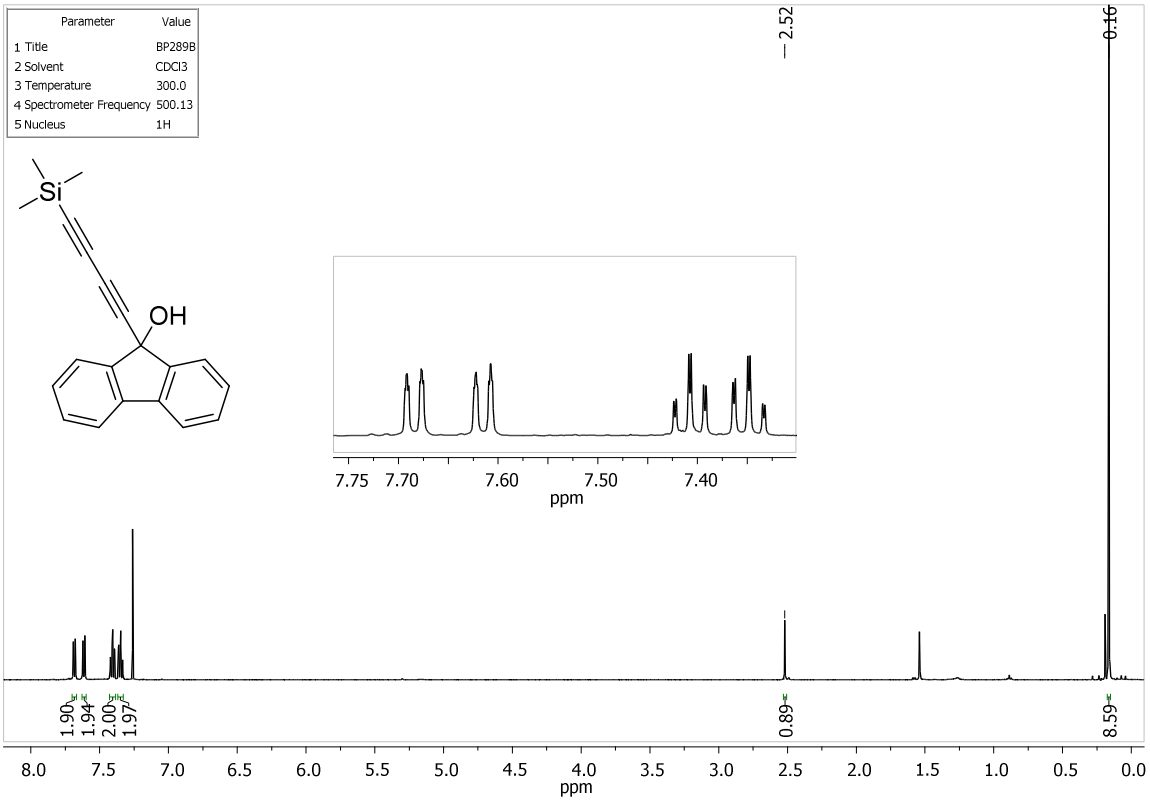


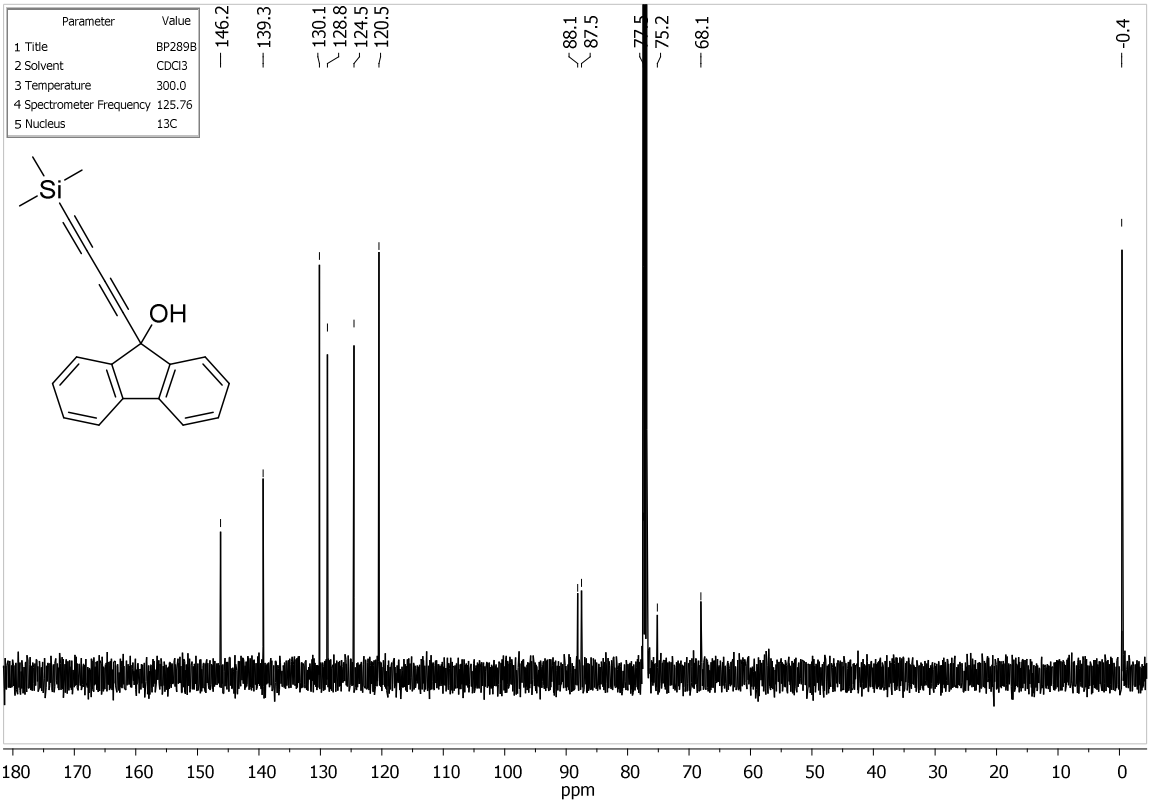
3-Bromo-1,1-diphenylprop-2-yn-1-ol (5)



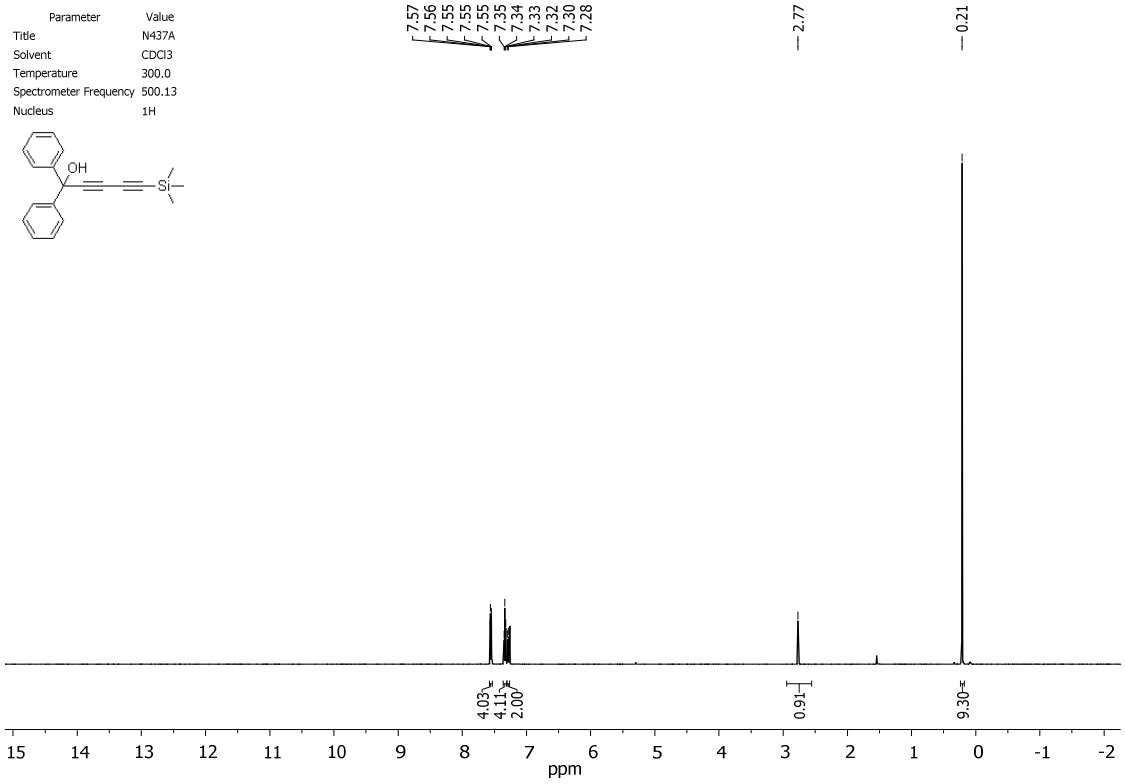


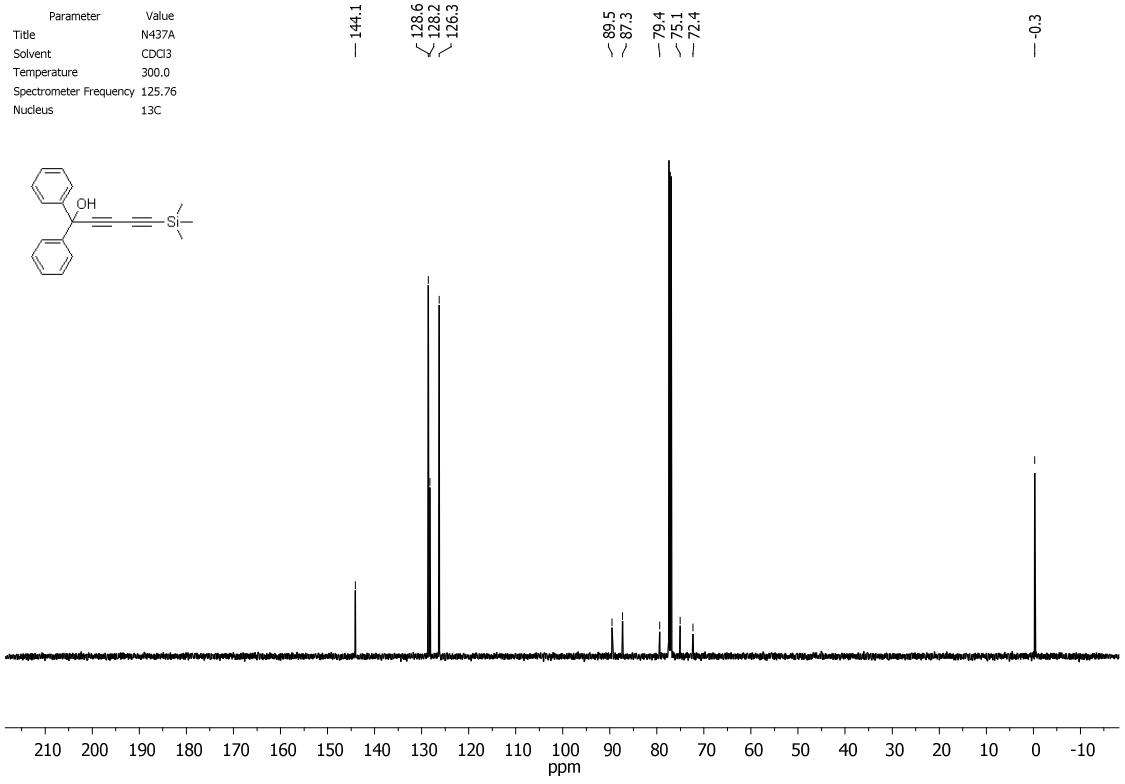
9-((Trimethylsilyl)buta-1,3-diyn-1-yl)-9*H*-fluoren-9-ol (6)



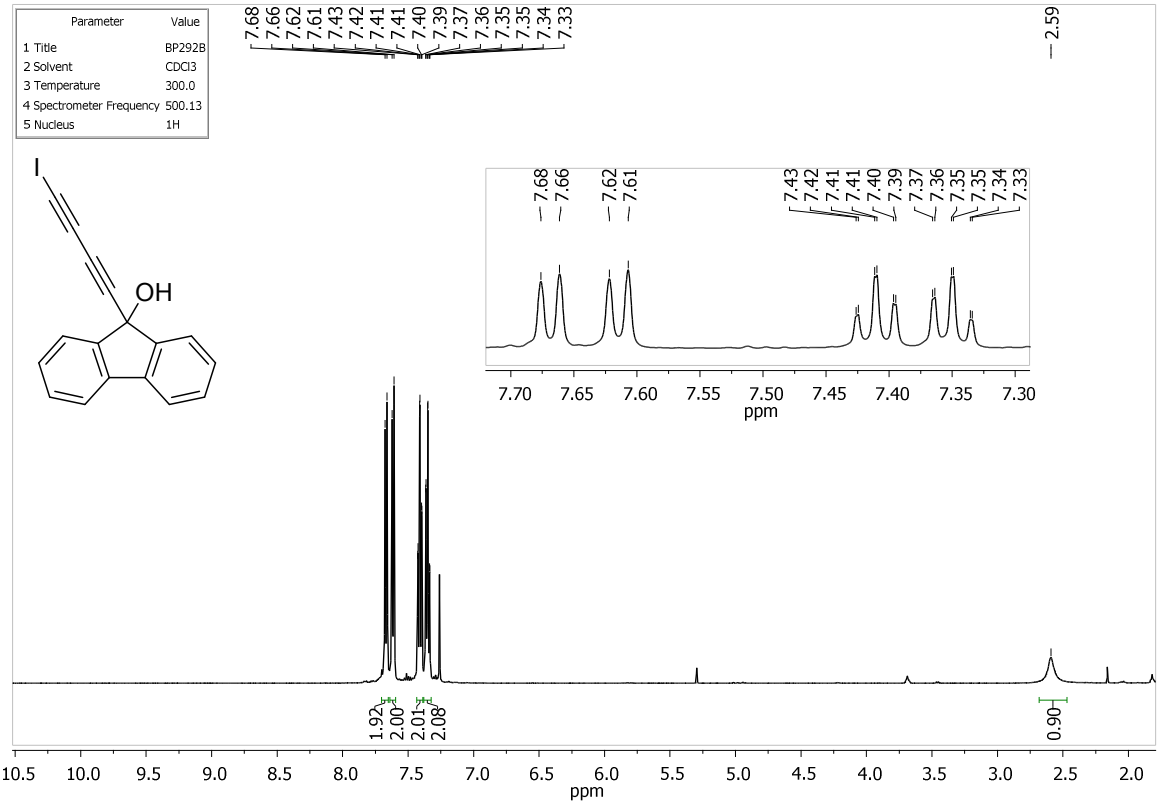


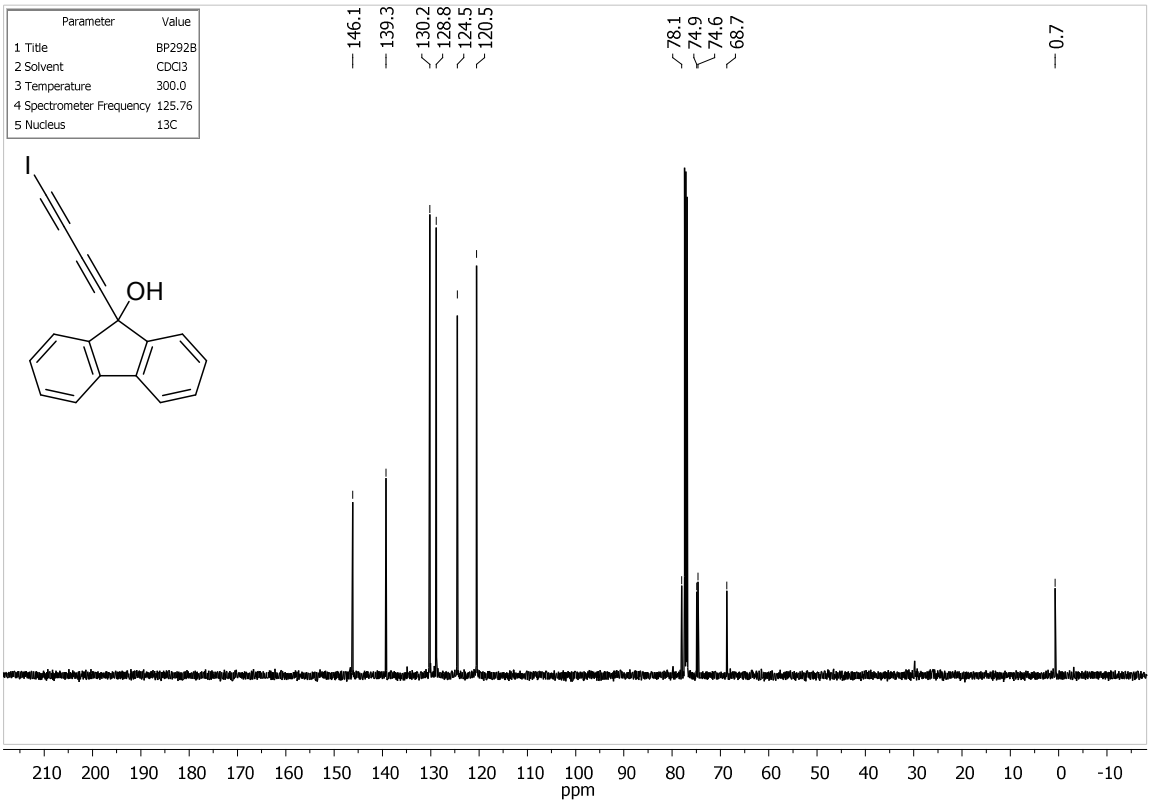
1,1-Diphenyl-5-(trimethylsilyl)penta-2,4-diyn-1-ol (7)



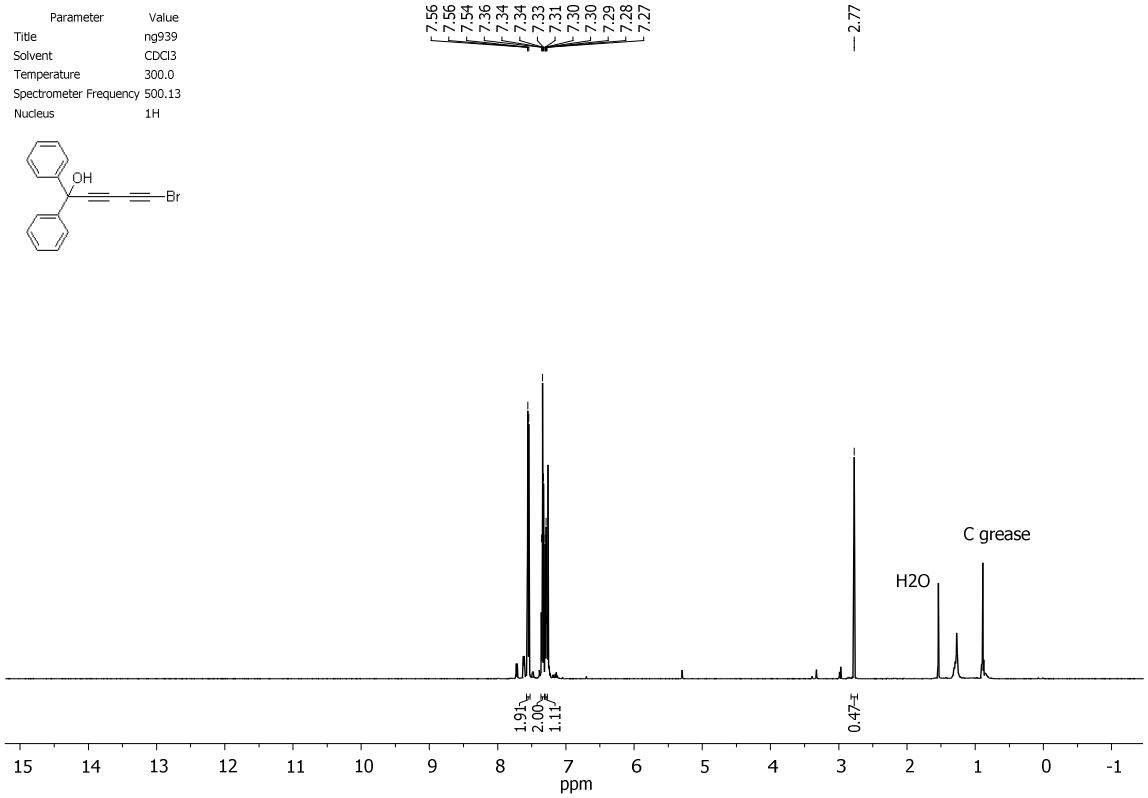


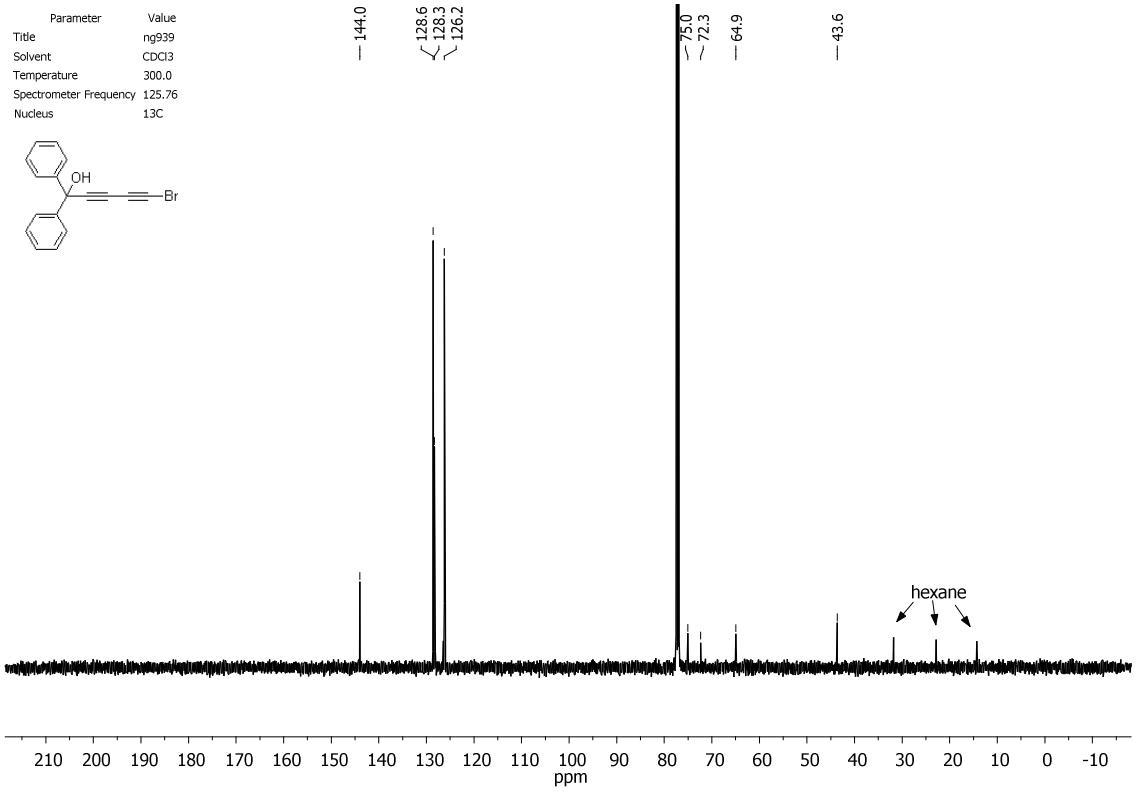
9-(Iodobuta-1,3-diyn-1-yl)-9*H*-fluoren-9-ol (8)



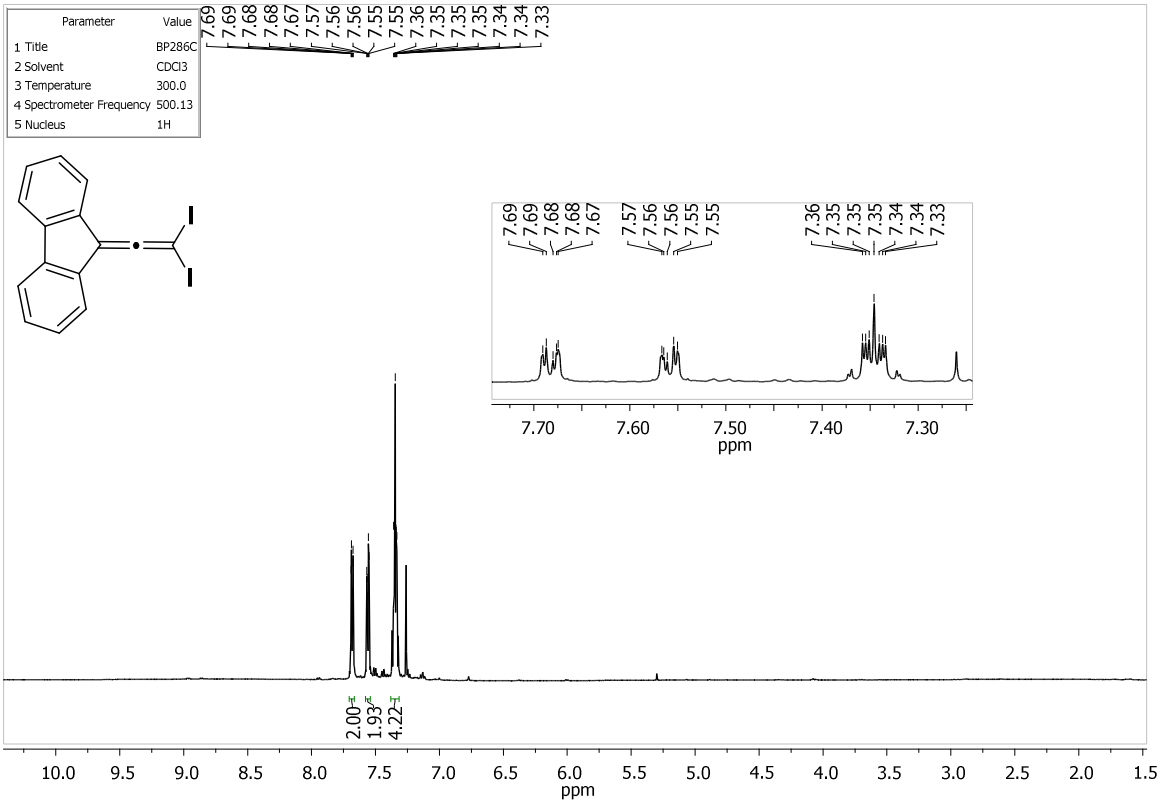


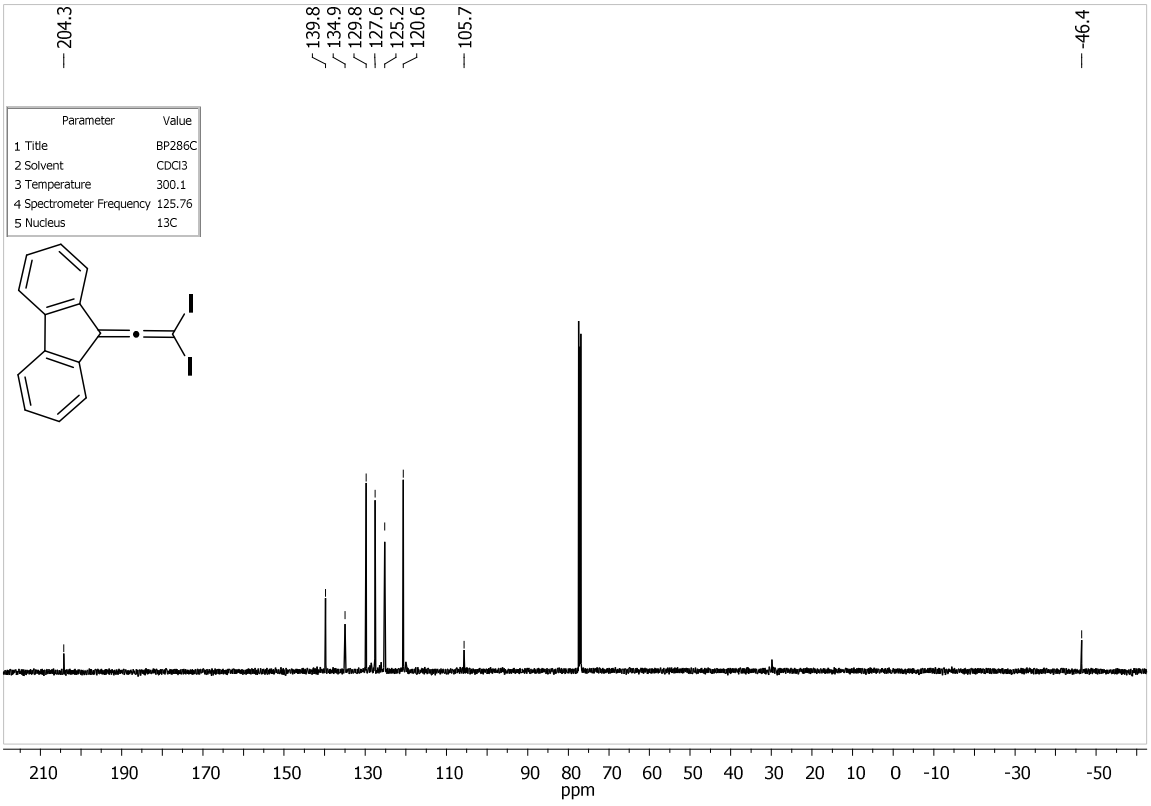
5-Bromo-1,1-diphenylpenta-2,4-diyn-1-ol (9)



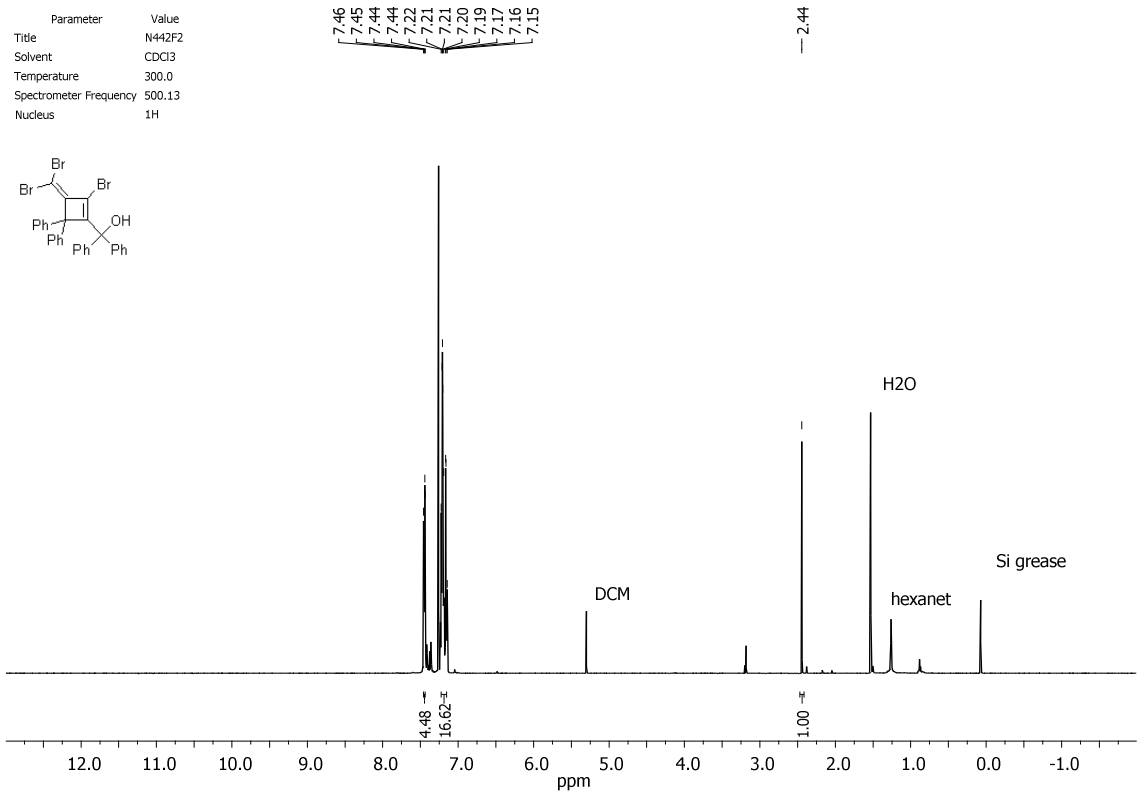


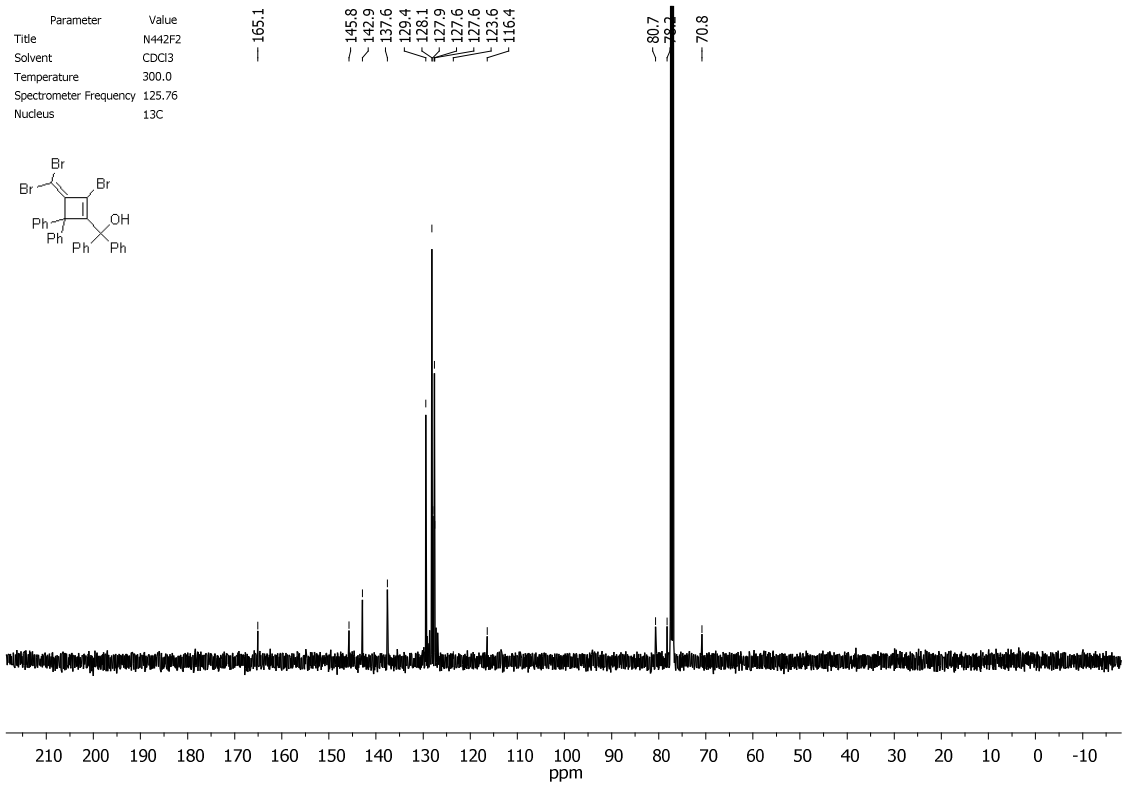
9-(2,2-Diiodovinylidene)-9*H*-fluorene (10)



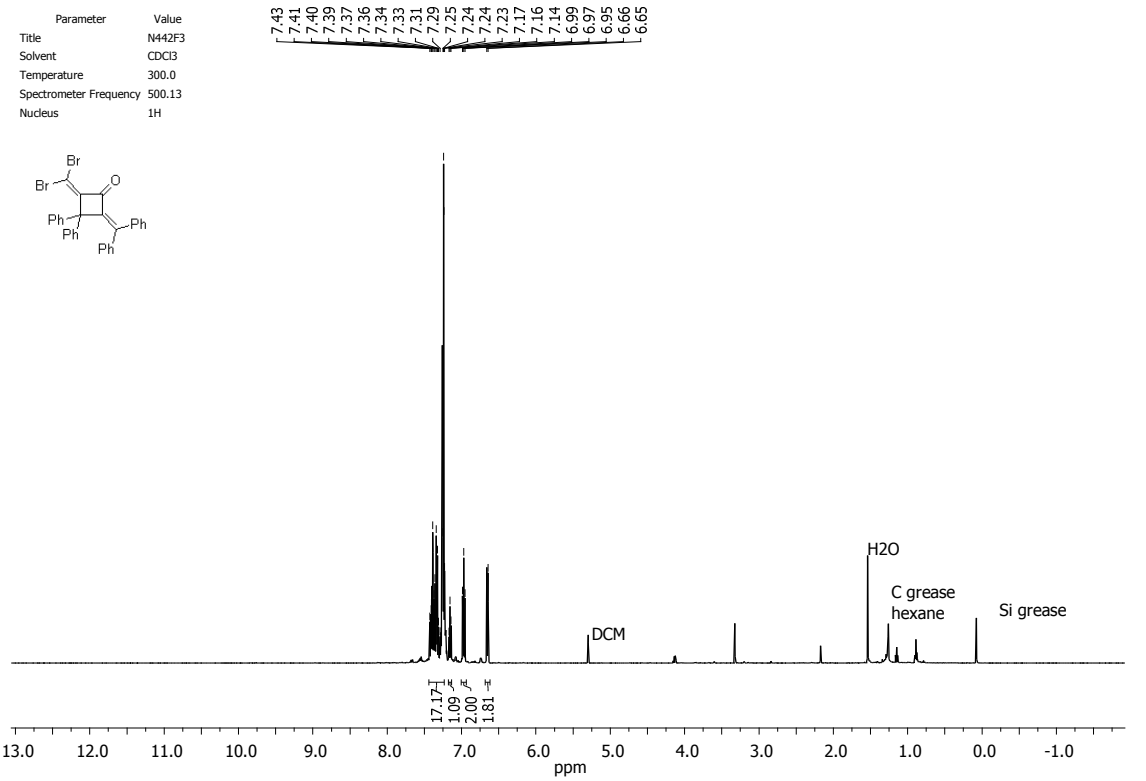


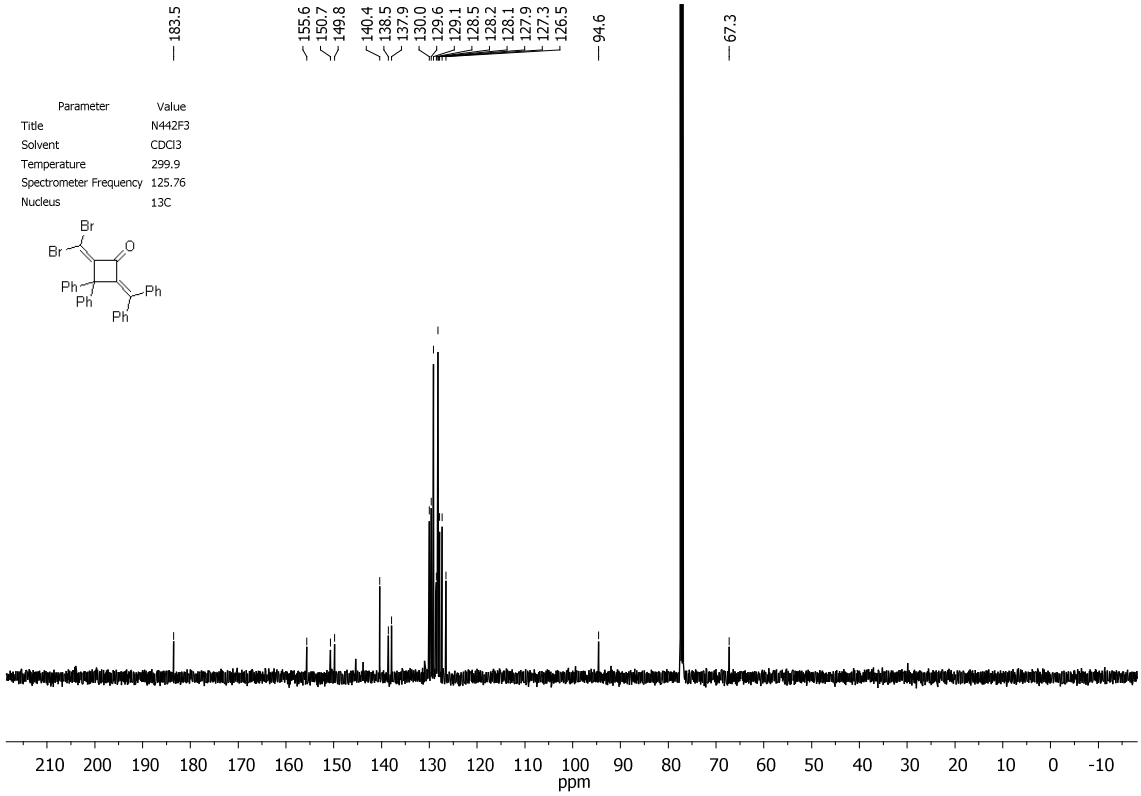
(2-Bromo-3-(dibromomethylene)-4,4-diphenylcyclobut-1-en-1-yl)diphenylmethanol (11)



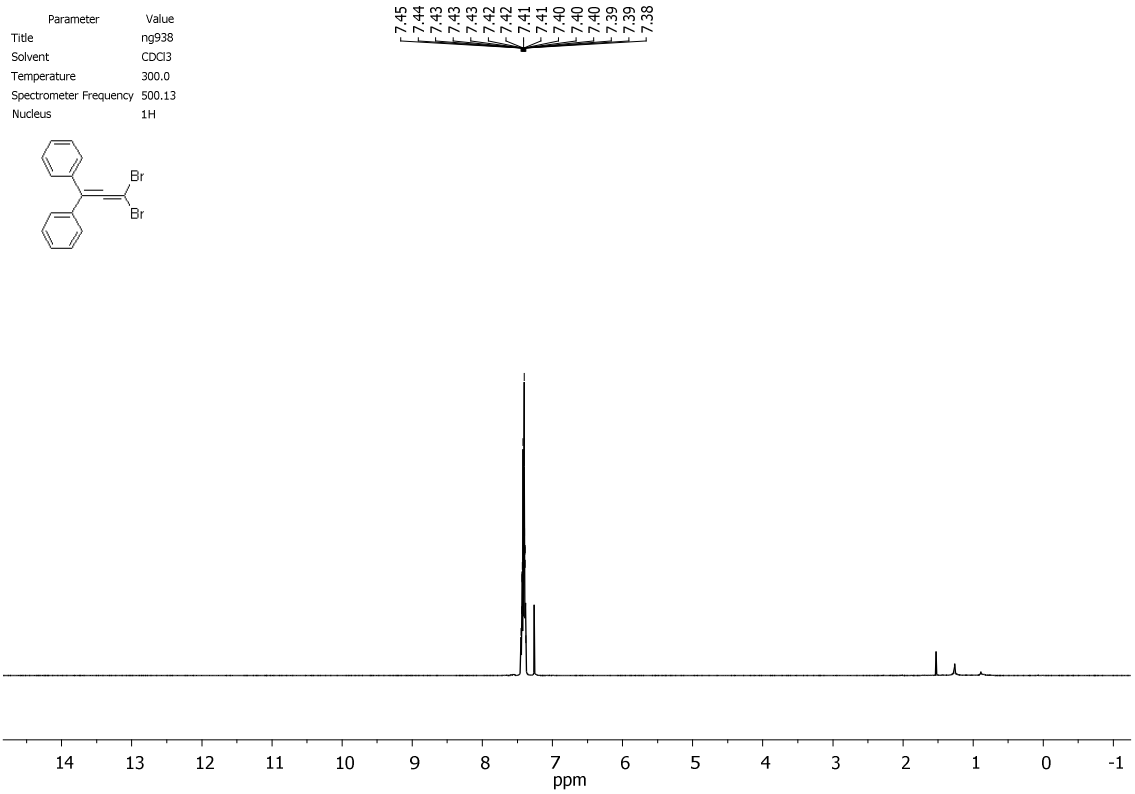


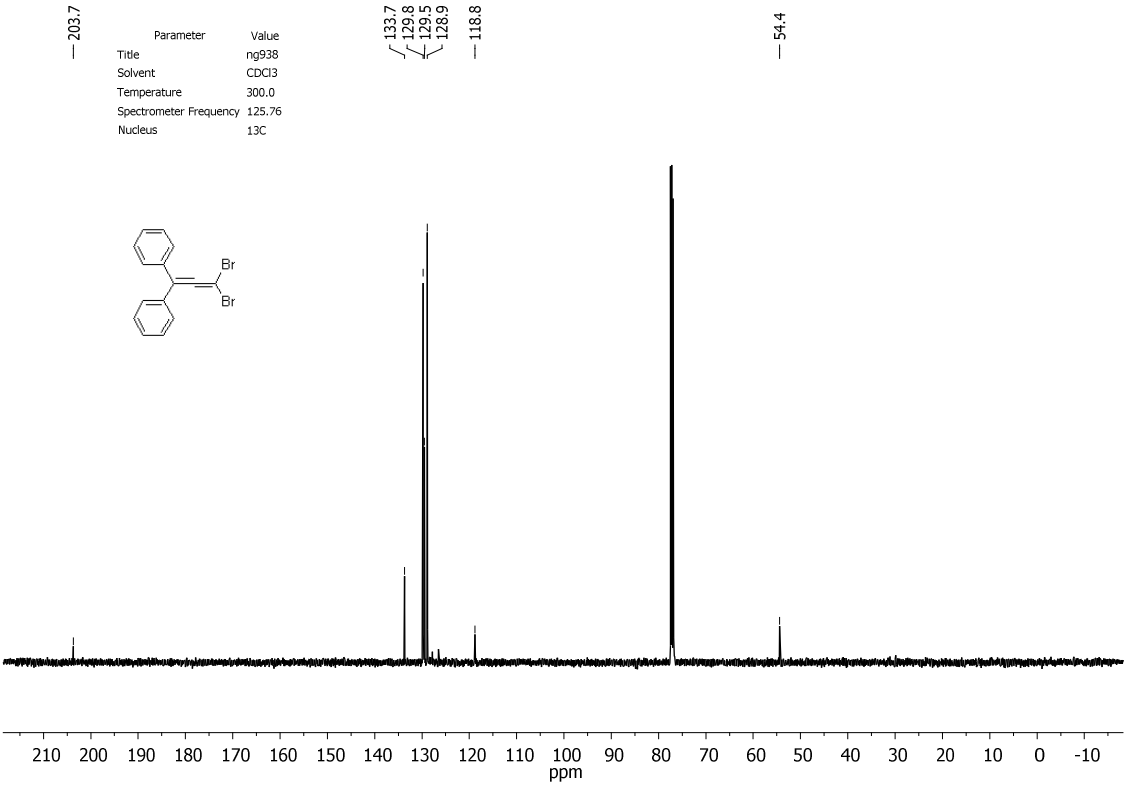
2-(Dibromomethylene)-4-(diphenylmethylene)-3,3-diphenylcyclobutan-1-one (12)





(3,3-Dibromopropa-1,2-diene-1,1-diyl)dibenzene (13)





1,1,3-Tribromo-2,2,8-triphenyl-1,2-dihydrocyclobuta[*b*]naphthalene (14)