

Supplementary Material

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

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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 ₈ I ₂	C ₃₀ H ₂₁ Br ₃ O	C ₃₀ H ₂₀ Br ₂ O	C ₁₅ H ₁₀ Br ₂	C ₃₀ H ₁₉ Br ₃
<i>M_r</i>	442.01	637.20	556.28	350.05	619.18
Crystal system, space group	Triclinic, <i>P</i> -1	Monoclinic, <i>P</i> 2 ₁ / <i>n</i>	Monoclinic, <i>Cc</i>	Monoclinic, <i>P</i> 2 ₁ / <i>n</i>	Monoclinic, <i>P</i> 2 ₁ / <i>n</i>
Temperature (K)	100	95	100	100	120
<i>a</i> , <i>b</i> , <i>c</i> (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
<i>V</i> (Å ³)	1330.0 (8)	2486.3 (9)	2296.1 (15)	2613.1 (16)	4824 (3)
<i>Z</i>	4	4	4	8	8
Radiation type	Mo <i>K</i> α	Mo <i>K</i> α	Mo <i>K</i> α	Mo <i>K</i> α	Mo <i>K</i> 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 <i>CrysAlis RED</i>	Analytical <i>CrysAlis PRO.</i>	Analytical <i>CrysAlis PRO.</i>	Analytical <i>CrysAlis PRO</i>	Analytical <i>CrysAlis PRO</i>
<i>T</i> _{min} , <i>T</i> _{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>I</i> > 2σ(<i>I</i>)] reflections	13052, 6613, 3779	47603, 11911, 9533	7285, 4661, 4332	43189, 12049, 6471	20598, 9812, 7486
<i>R</i> _{int}	0.058	0.051	0.049	0.101	0.036
(sin θ/λ) _{max} (Å ⁻¹)	0.808	0.844	0.676	0.846	0.625
Refinement					
<i>R</i> [<i>F</i> ² > 2σ(<i>F</i> ²)], <i>wR</i> (<i>F</i> ²), <i>S</i>	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)

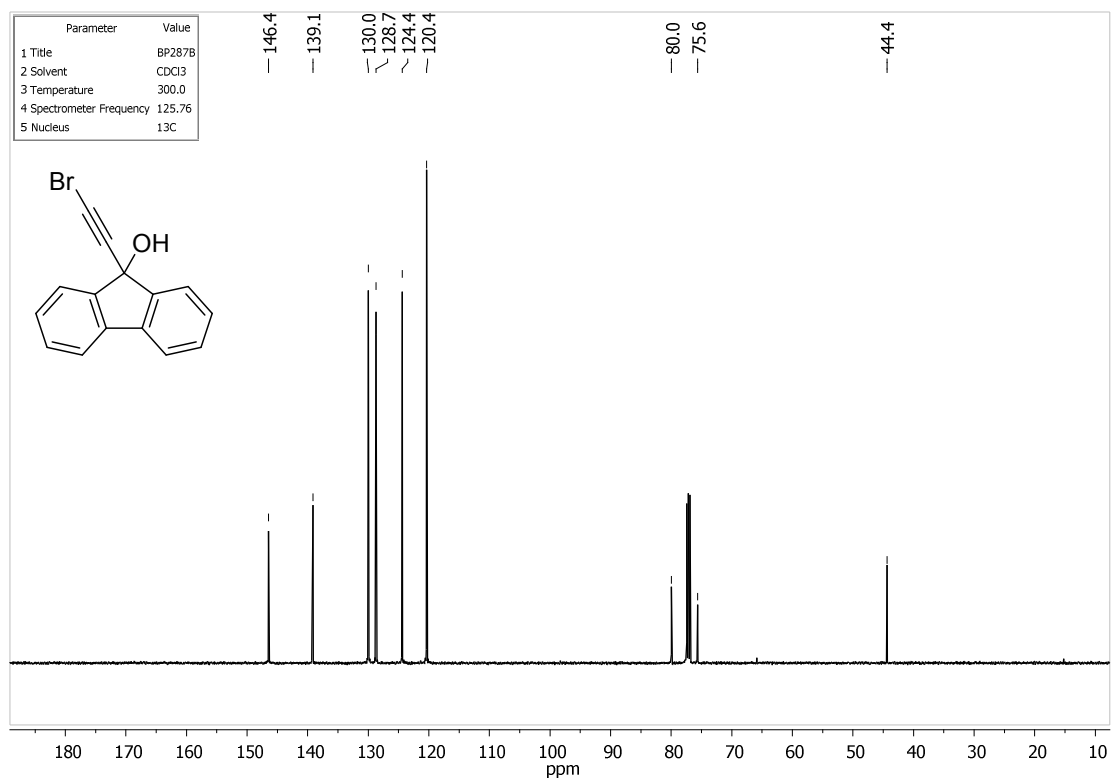
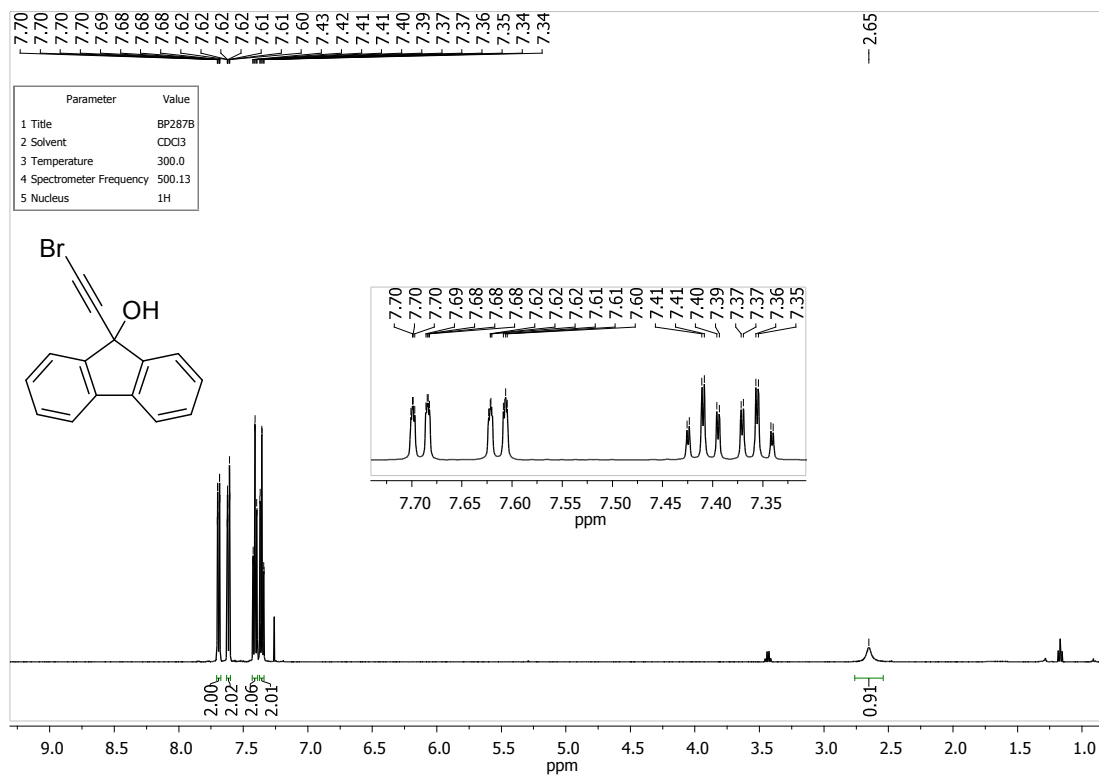
Table S3. Selected bond lengths and angles for **11**, **12** and **14**

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)

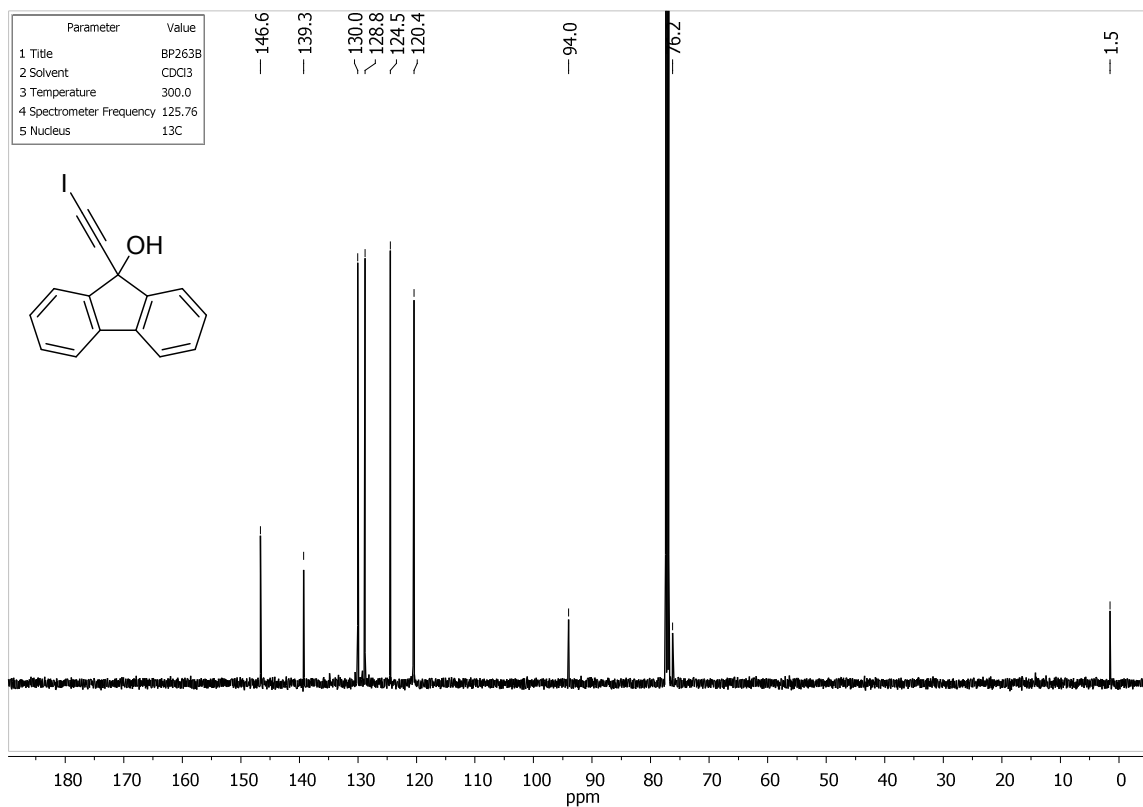
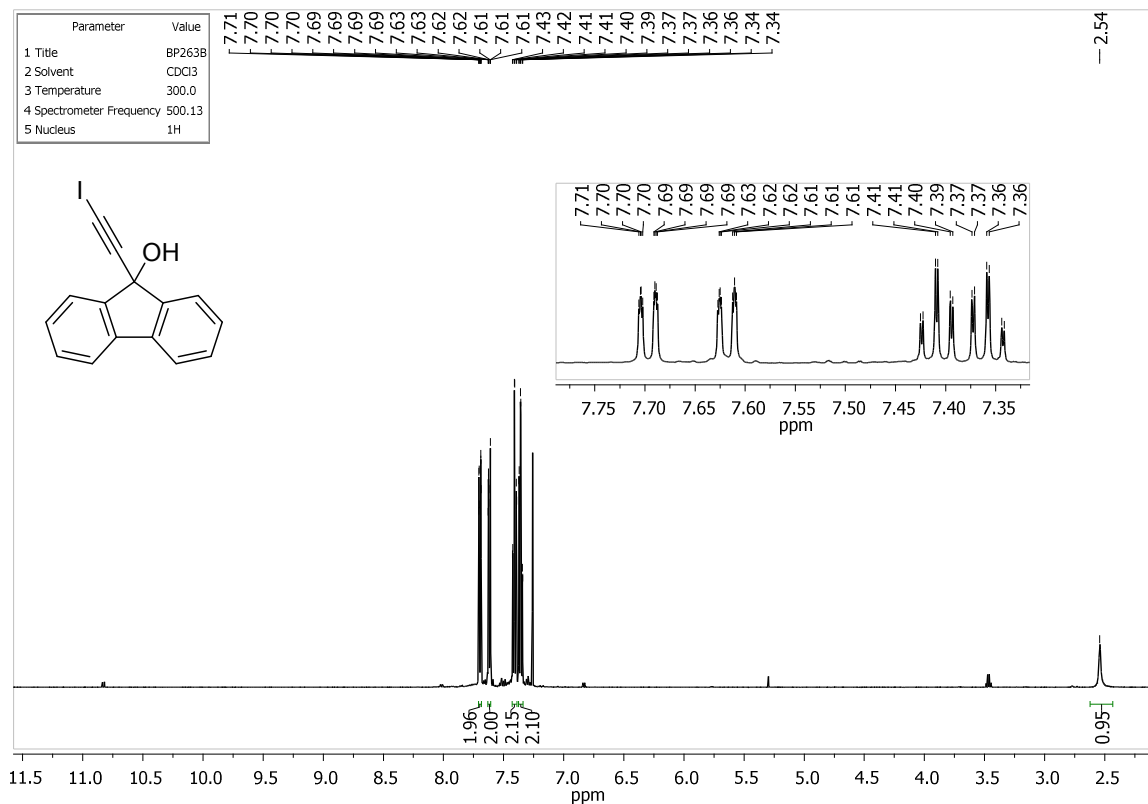
*Two molecules in the asymmetric unit

NMR spectra

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

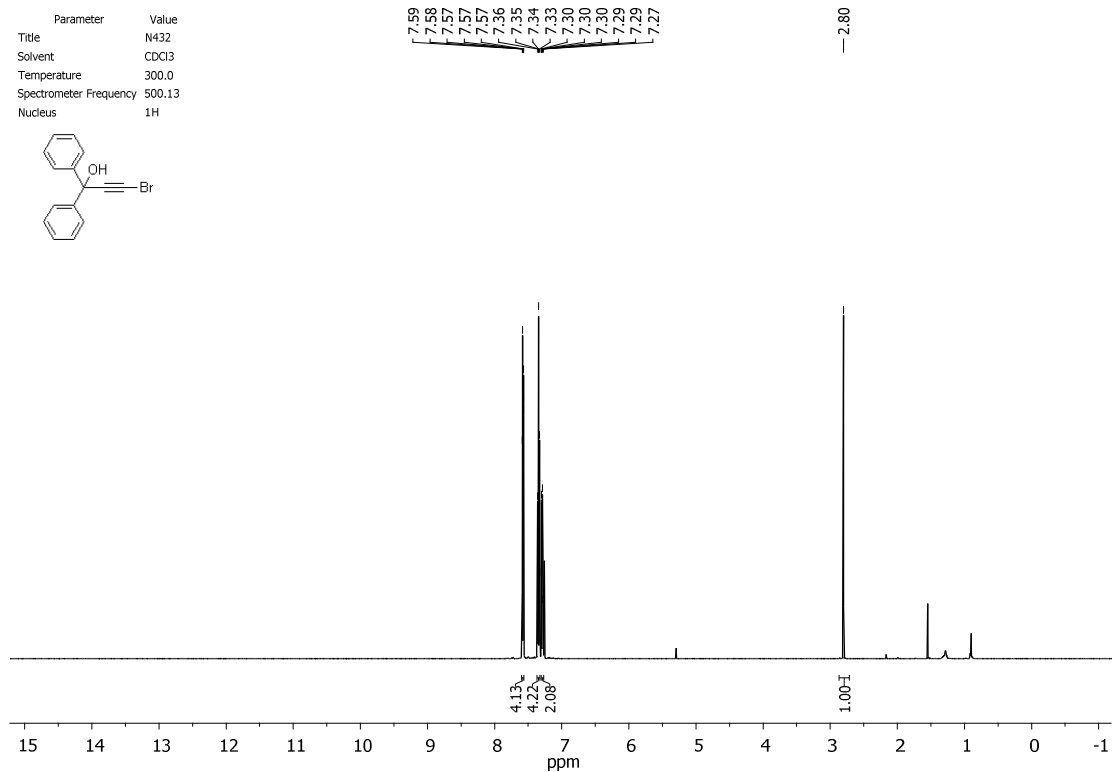
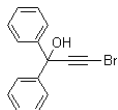


9-(Iodoethyl)-9H-fluoren-9-ol (4)

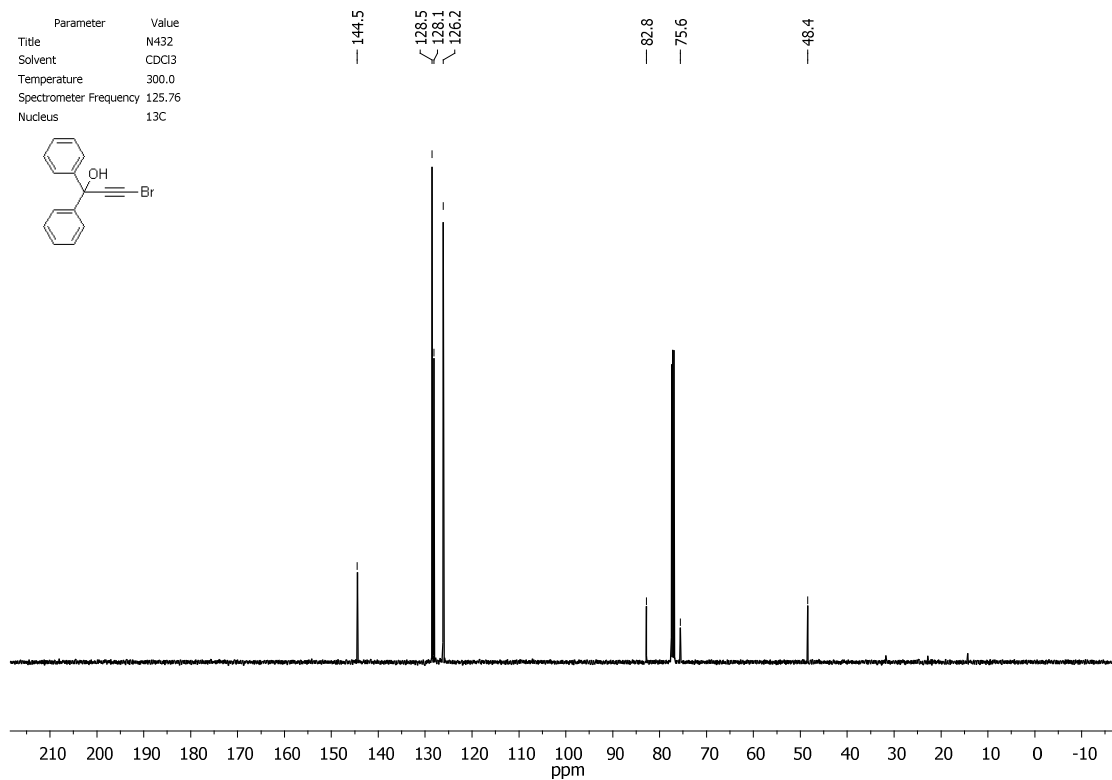
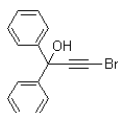


3-Bromo-1,1-diphenylprop-2-yn-1-ol (5)

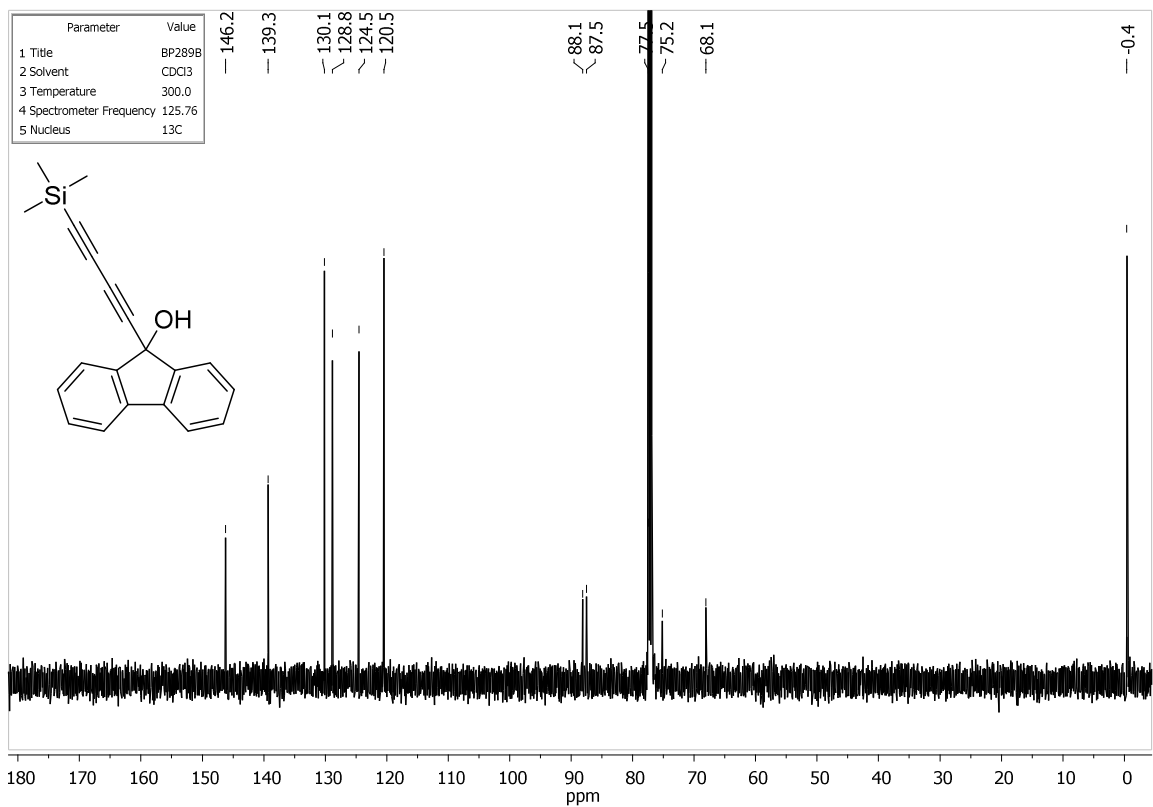
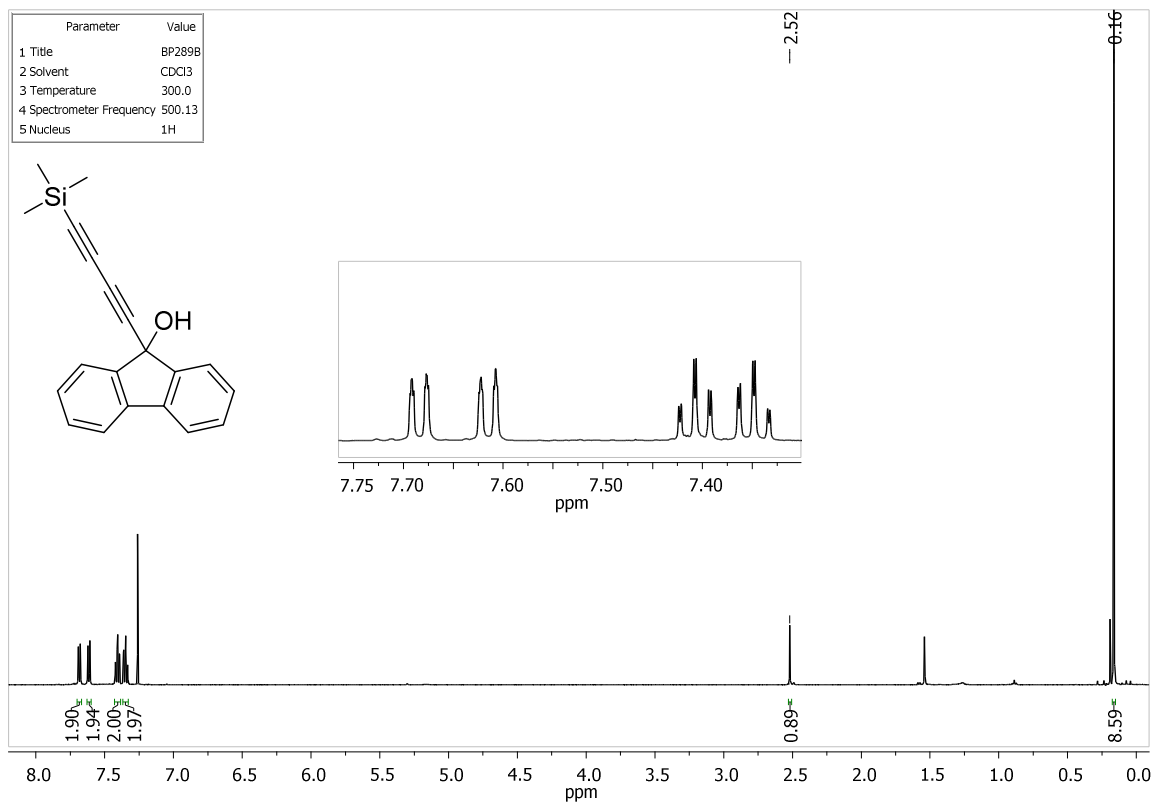
Parameter	Value
Title	N432
Solvent	CDCl ₃
Temperature	300.0
Spectrometer Frequency	500.13
Nucleus	¹ H

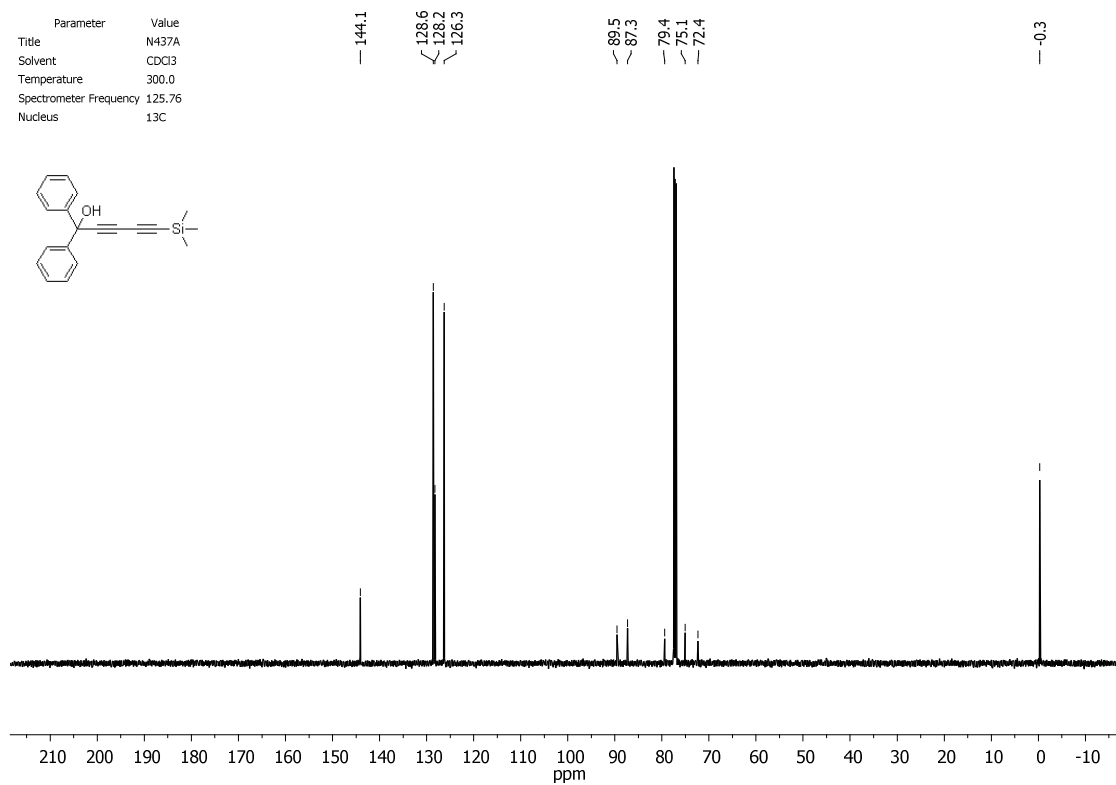
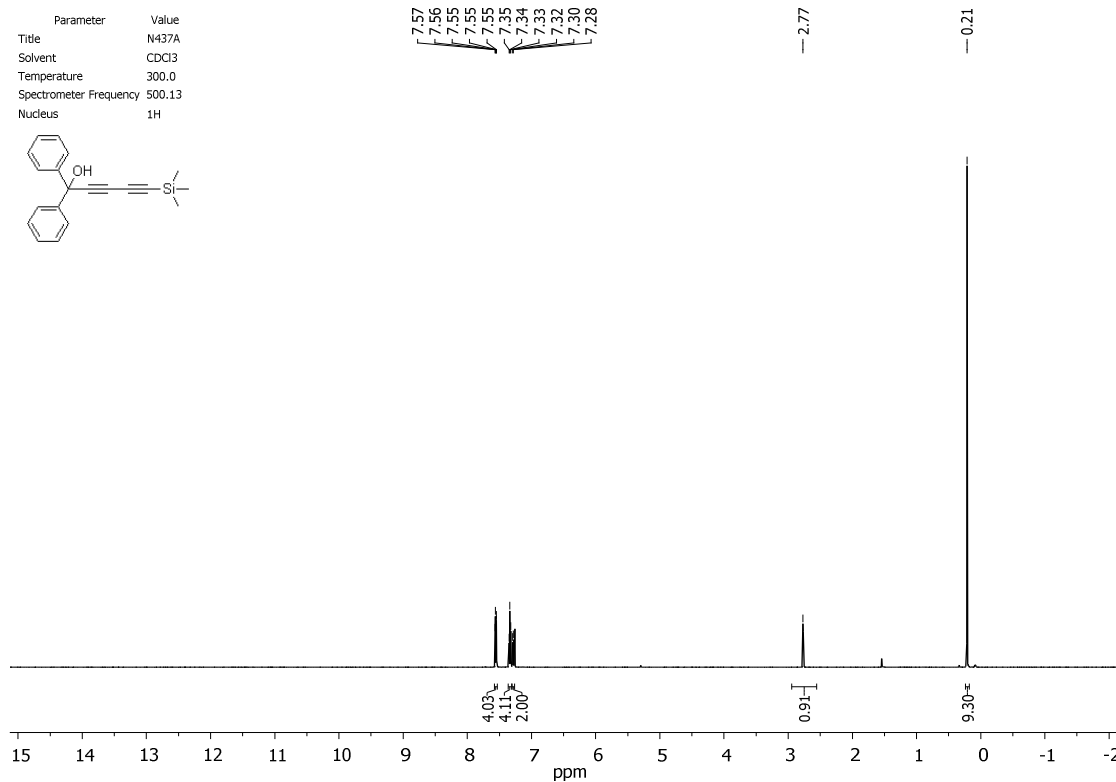


Parameter	Value
Title	N432
Solvent	CDCl ₃
Temperature	300.0
Spectrometer Frequency	125.76
Nucleus	¹³ C

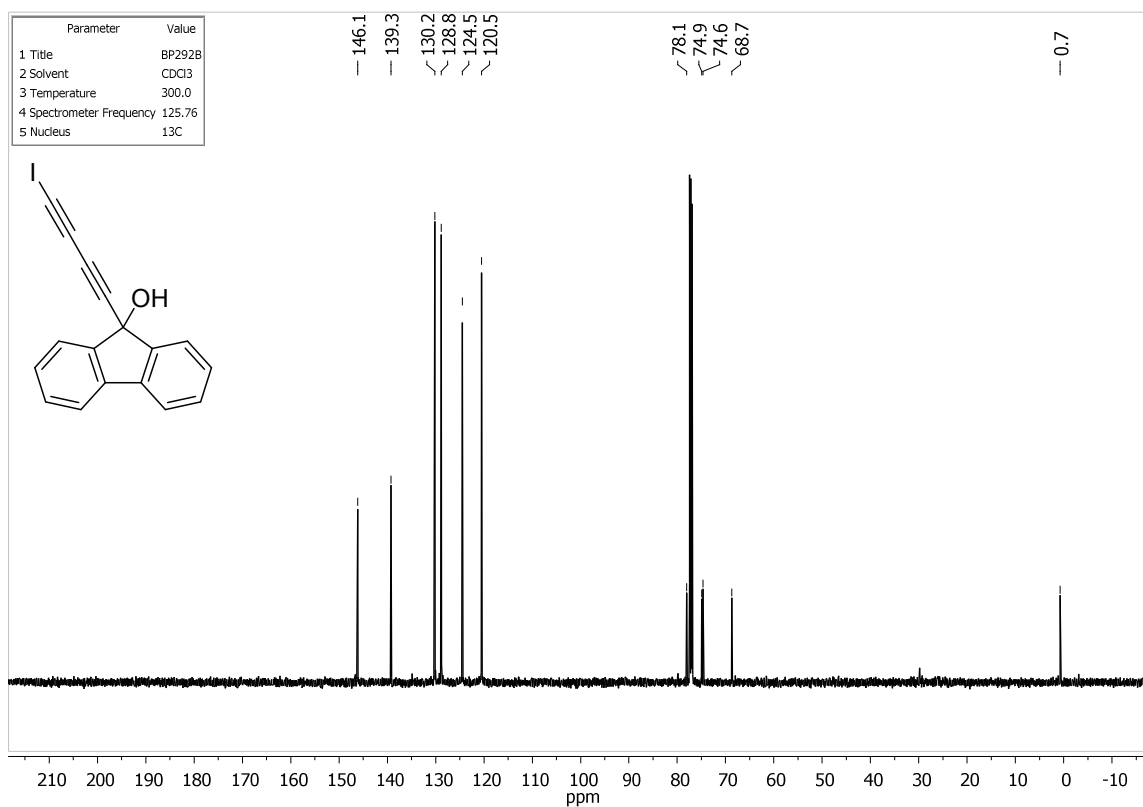
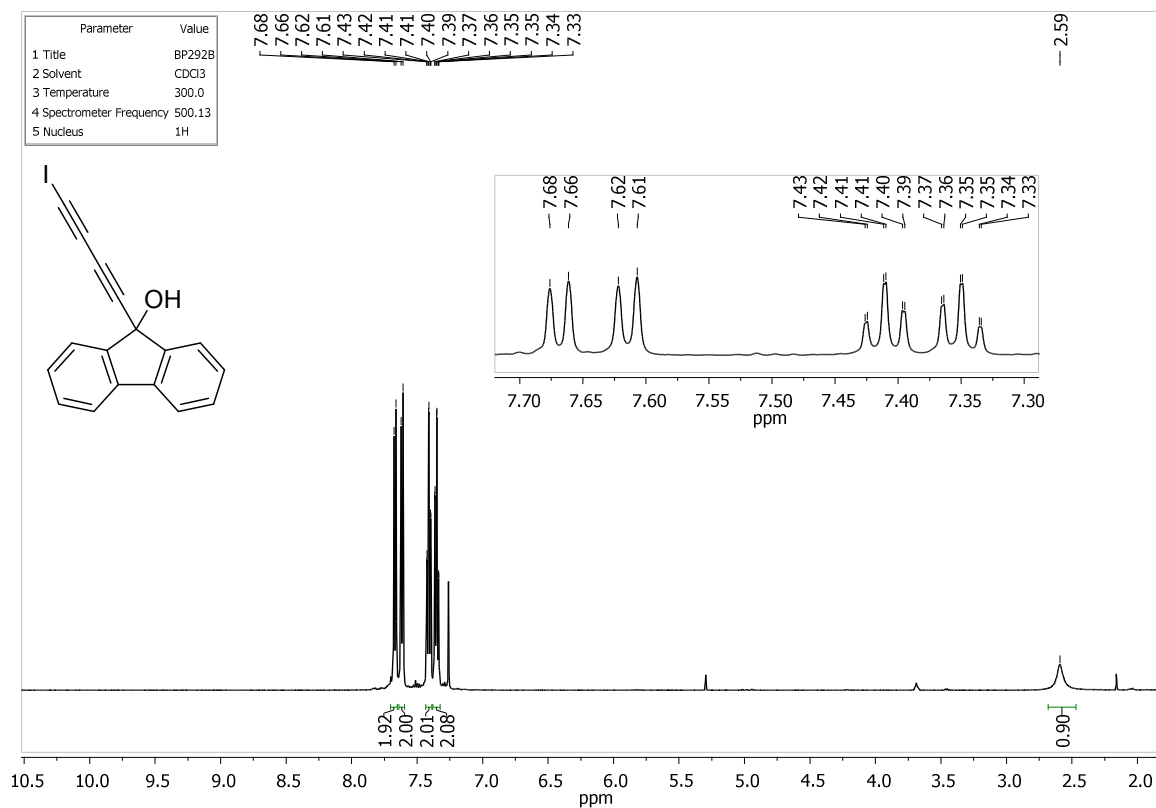


9-((Trimethylsilyl)buta-1,3-diy-1-yl)-9H-fluoren-9-ol (6)



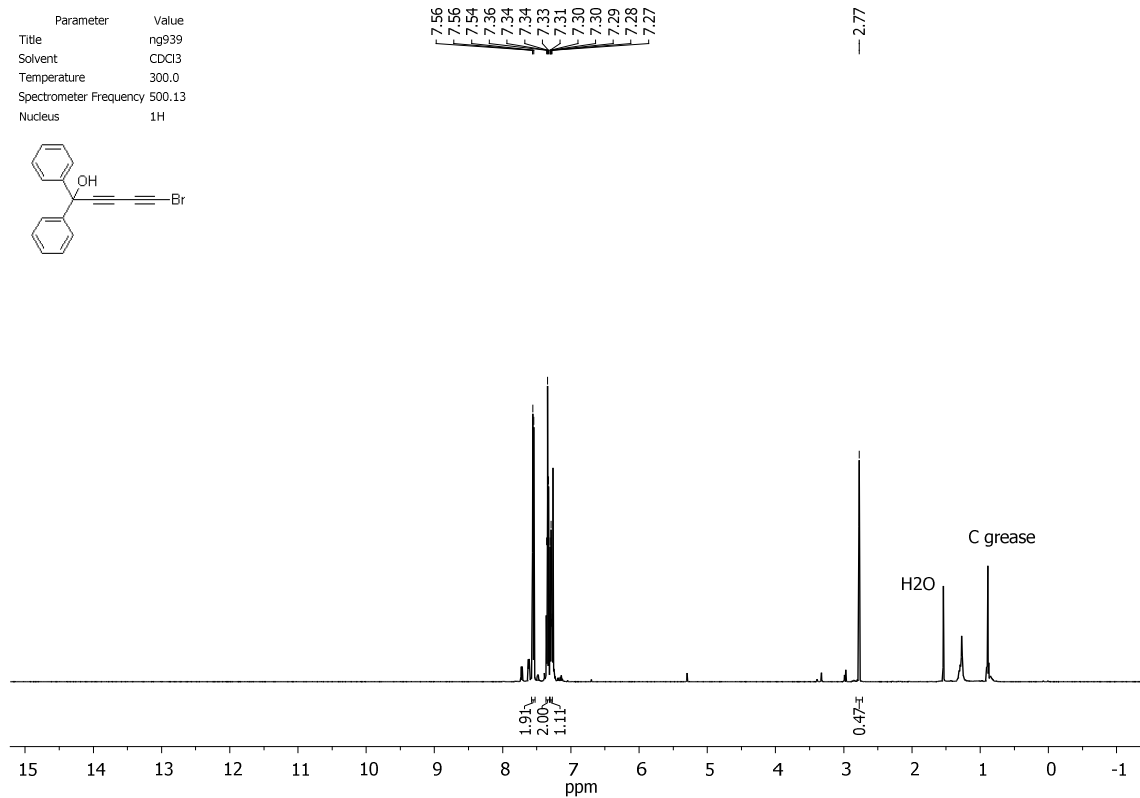
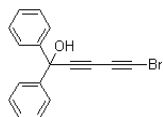
1,1-Diphenyl-5-(trimethylsilyl)penta-2,4-diyne-1-ol (7)

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

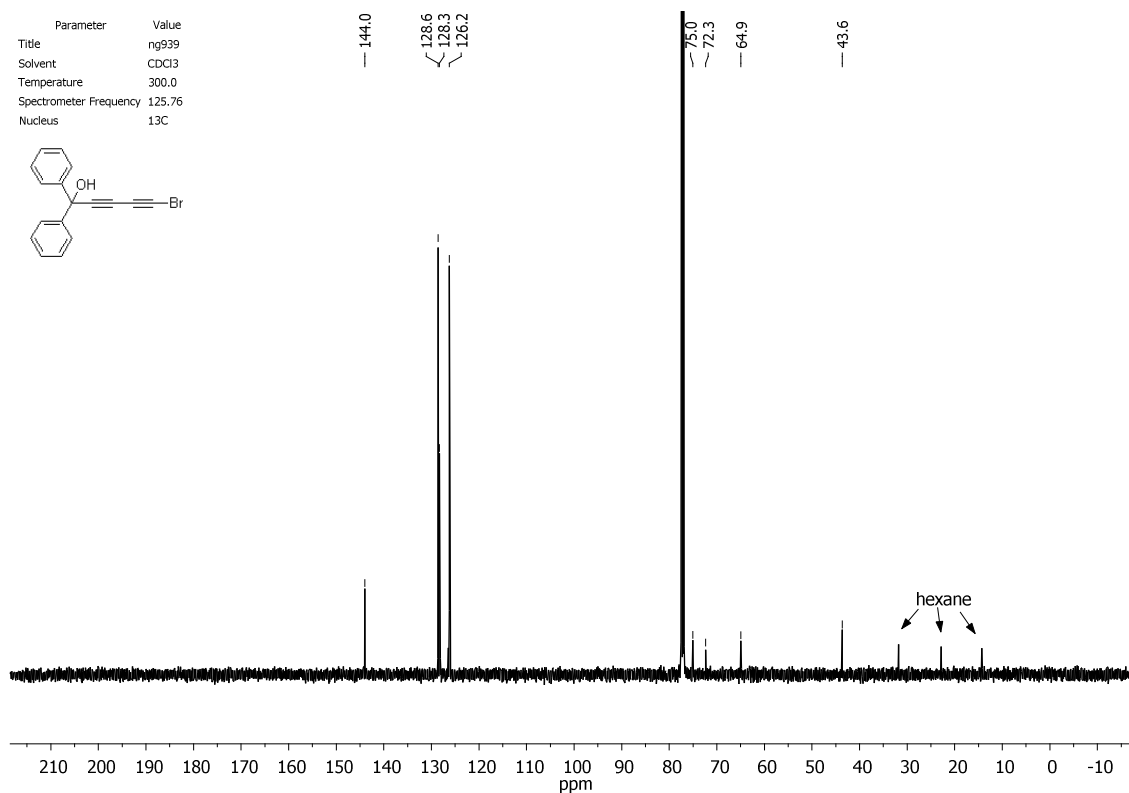
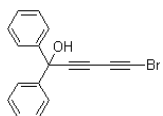


5-Bromo-1,1-diphenylpenta-2,4-diyne-1-ol (9)

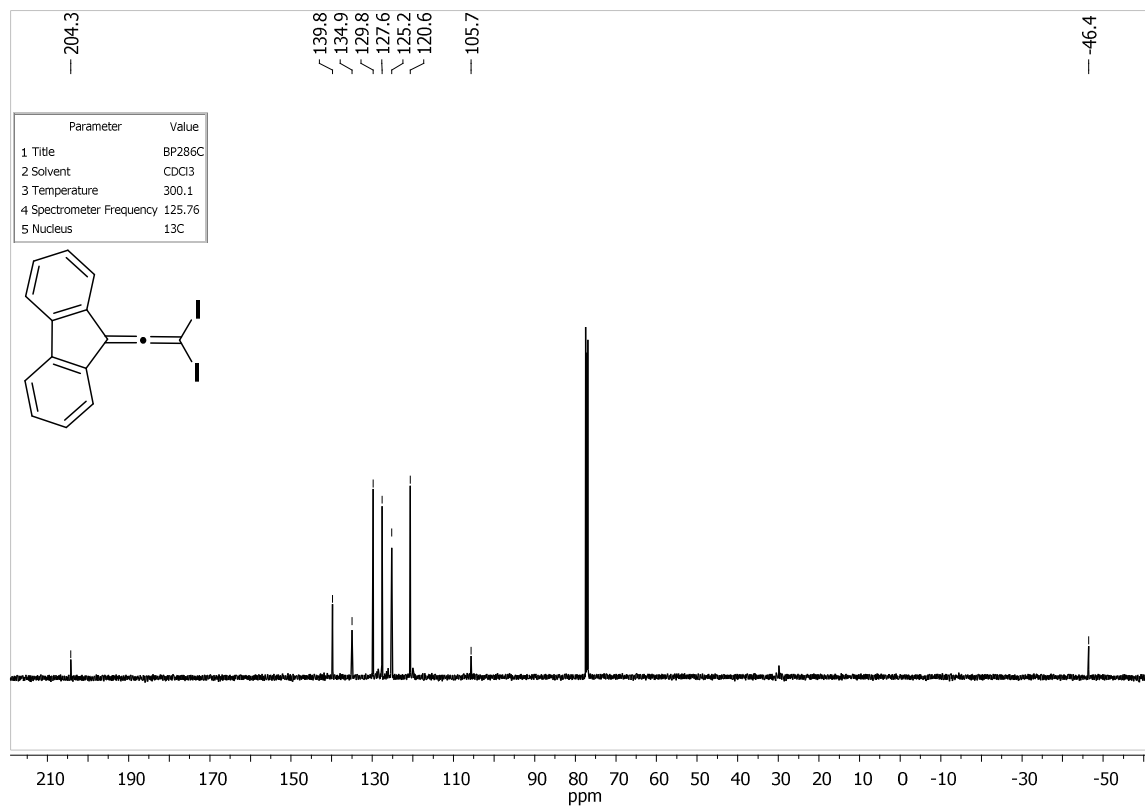
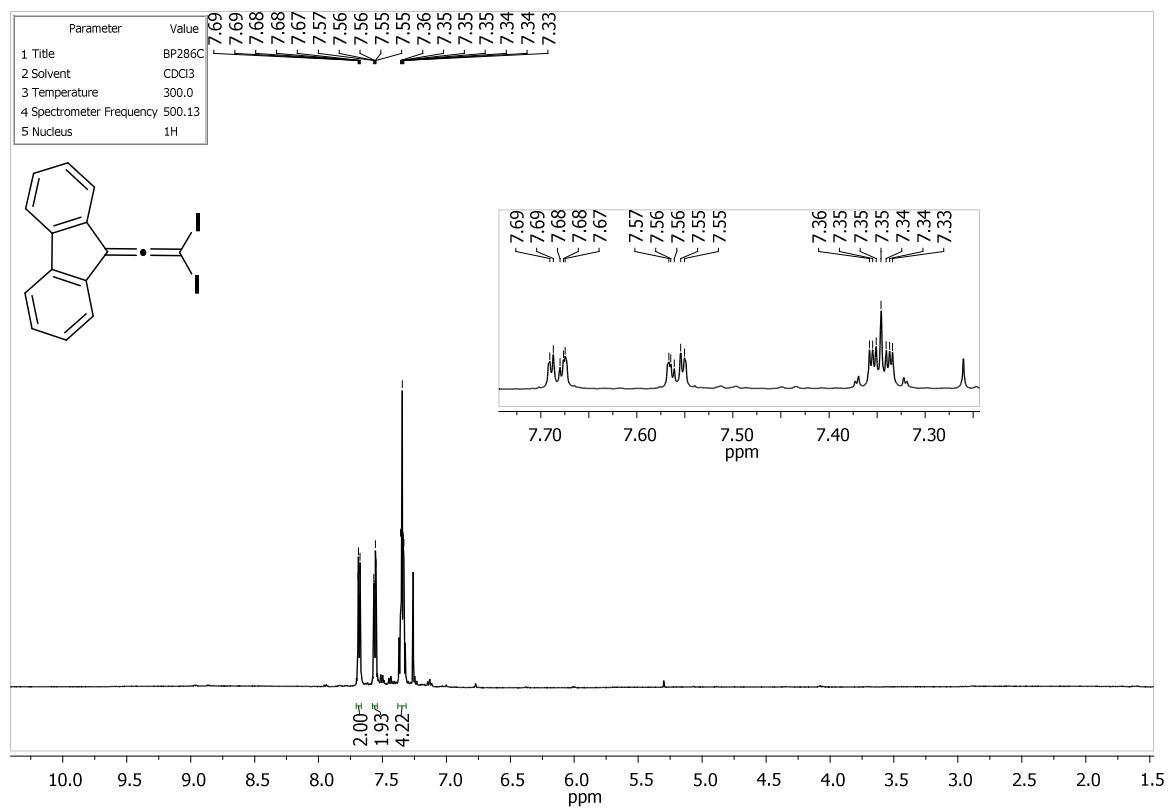
Parameter	Value
Title	ng939
Solvent	CDCl3
Temperature	300.0
Spectrometer Frequency	500.13
Nucleus	¹ H

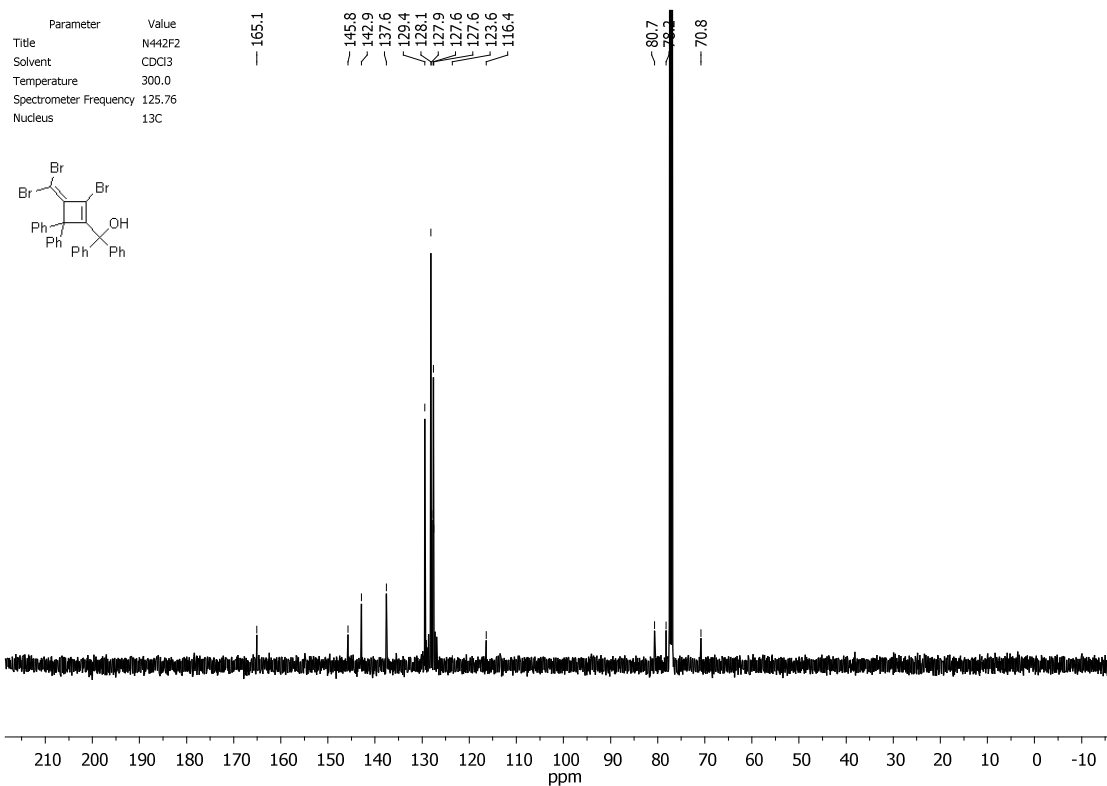
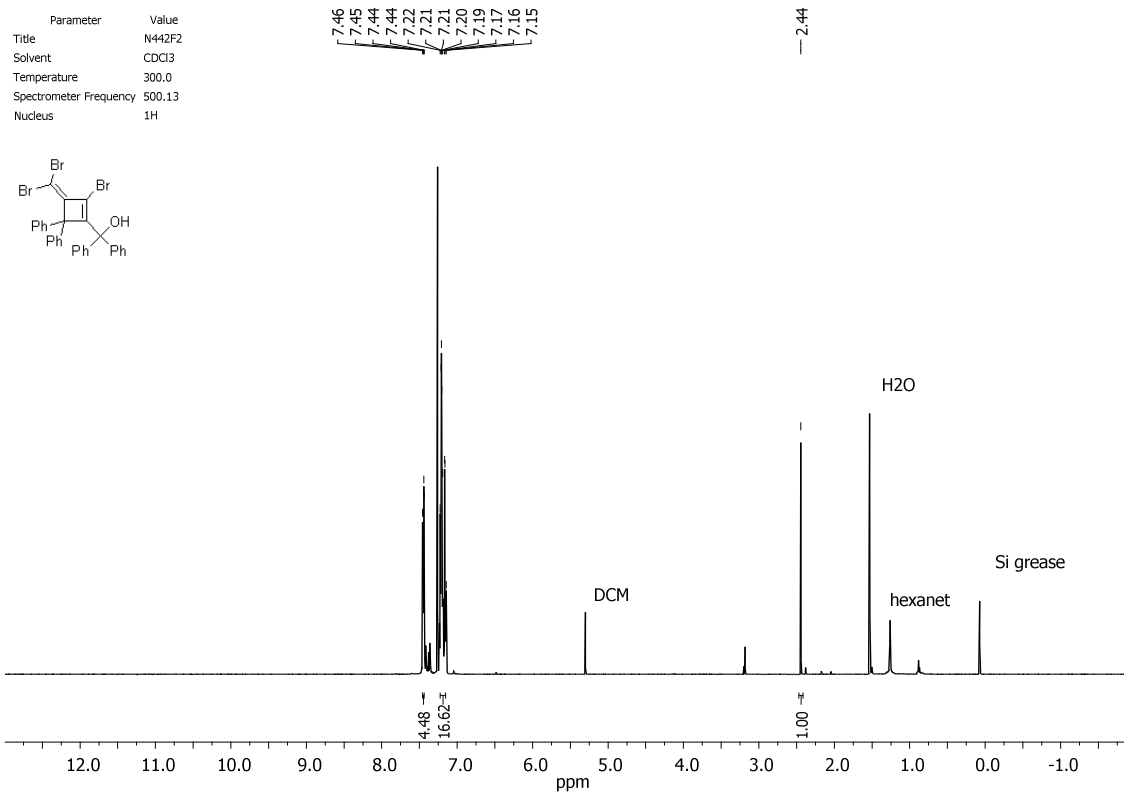


Parameter	Value
Title	ng939
Solvent	CDCl3
Temperature	300.0
Spectrometer Frequency	125.76
Nucleus	¹³ C

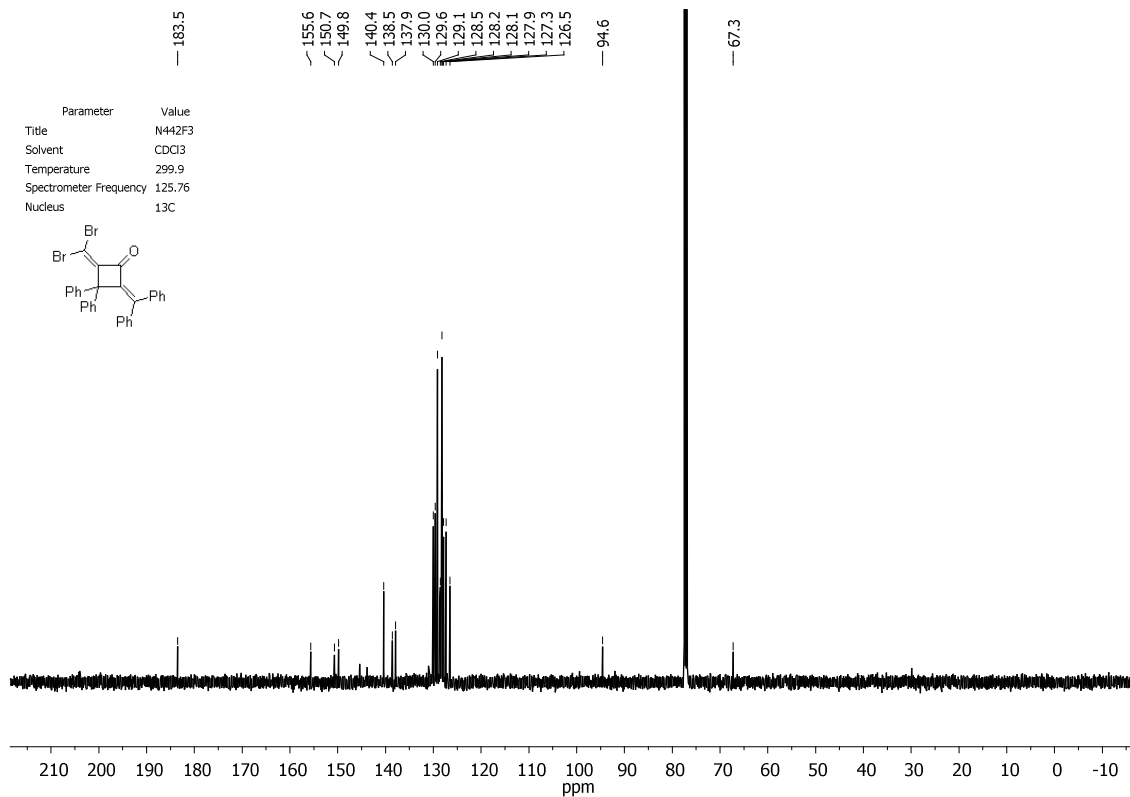
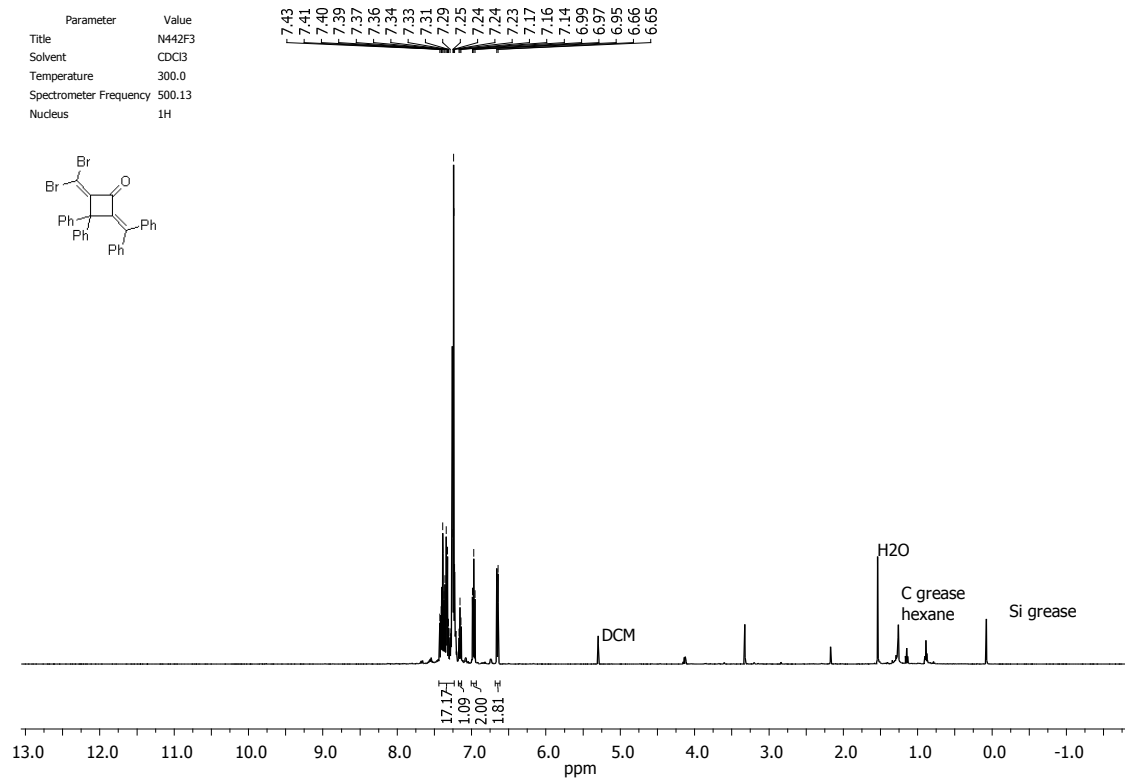


9-(2,2-Diodovinylidene)-9H-fluorene (10)



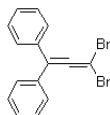
(2-Bromo-3-(dibromomethylene)-4,4-diphenylcyclobut-1-en-1-yl)diphenylmethanol (11)

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

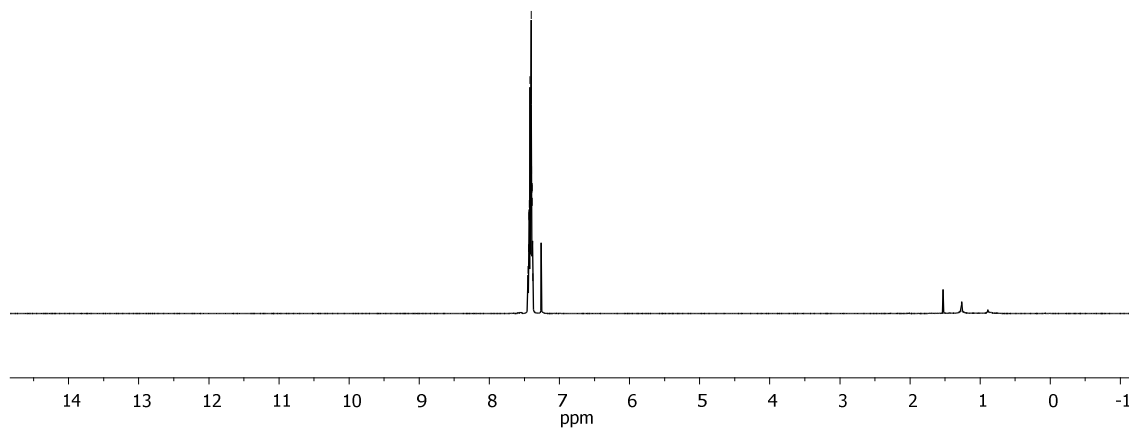


(3,3-Dibromopropa-1,2-diene-1,1-diyl)dibenzene (13)

Parameter	Value
Title	ng938
Solvent	CDCl ₃
Temperature	300.0
Spectrometer Frequency	500.13
Nucleus	¹ H



7.45
7.44
7.43
7.43
7.42
7.42
7.41
7.41
7.40
7.40
7.39
7.39
7.38



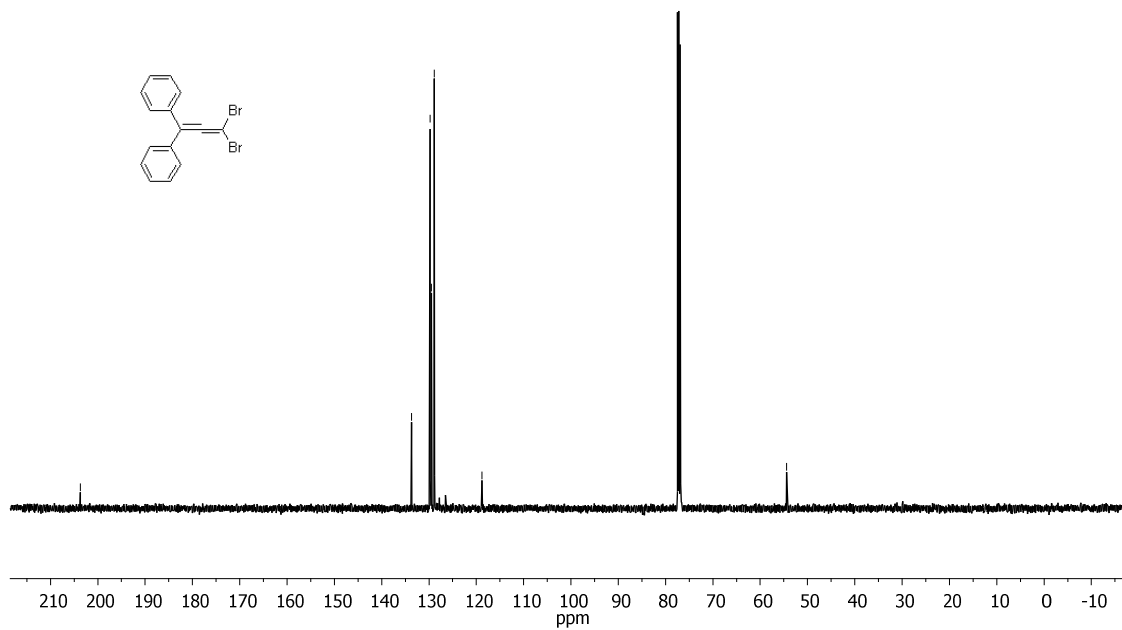
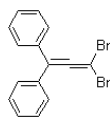
203.7

Parameter	Value
Title	ng938
Solvent	CDCl ₃
Temperature	300.0
Spectrometer Frequency	125.76
Nucleus	¹³ C

133.7
129.8
129.5
128.9

118.8

54.4



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