Supplementary Information

In Situ-Generated Halogen-Bonding Complex Enables Atom-Transfer Radical Addition (ATRA) Reactions of Olefins

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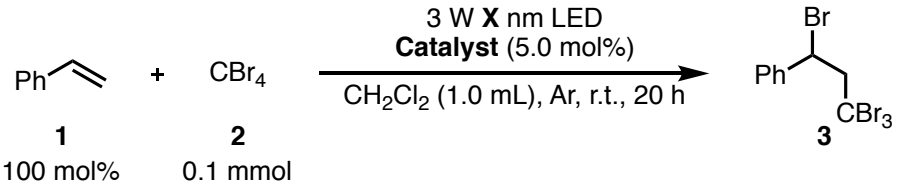
Table S1. Screening of catalysts

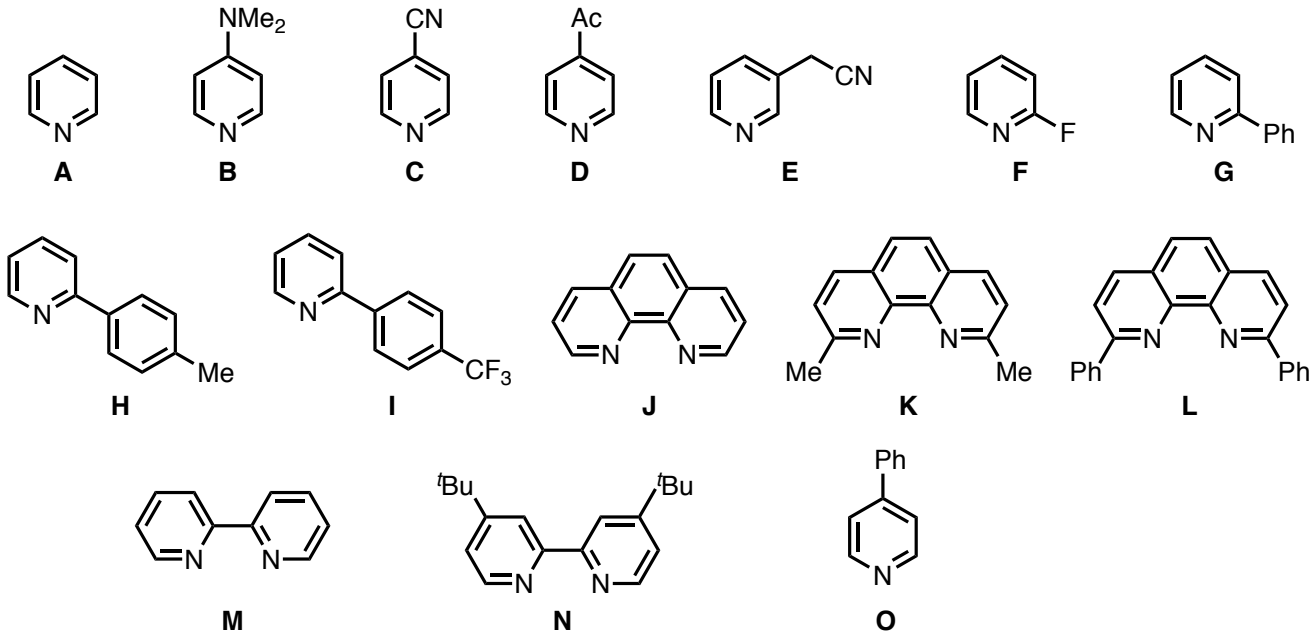


1 100 mol% + **2** 0.1 mmol → **3**

3W LED (**X** nm) \ Catalyst	A	B	C	D	E	F	G	H	I	J	K	L	M	N	O
370	29	40	18	28	32	27	30	29	23	44	20	17	16	25	27
380	41	14	17	34	34	24	34	25	24	38	32	17	38	26	6
390	43	41	20	35	38	30	31	29	30	39	16	21	24	20	27
400	49	43	28	42	42	37	35	42	34	56	26	23	53	37	47
410	52	34	30	40	47	37	45	45	38	56	34	26	44	46	51
420	51	27	37	46	43	37	44	45	43	52	49	29	44	40	53
450	42	23	48	49	49	0	25	15	12	42	56	42	1	10	57
470	5	10	36	49	2	0	0	1	3	34	5	41	0	5	20
500	0	0	0	0	0	0	0	0	0	0	3	39	0	0	2

[1]H NMR yields.

Catalyst

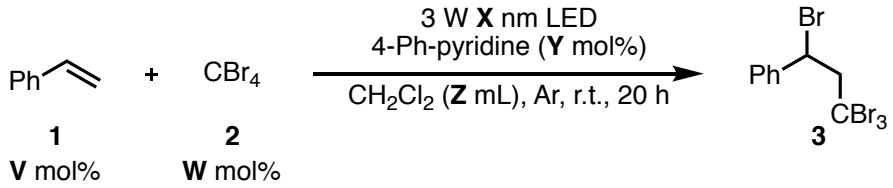


A **B** **C** **D** **E** **F** **G**

H **I** **J** **K** **L**

M **N** **O**

Table S2. Optimization of reaction conditions



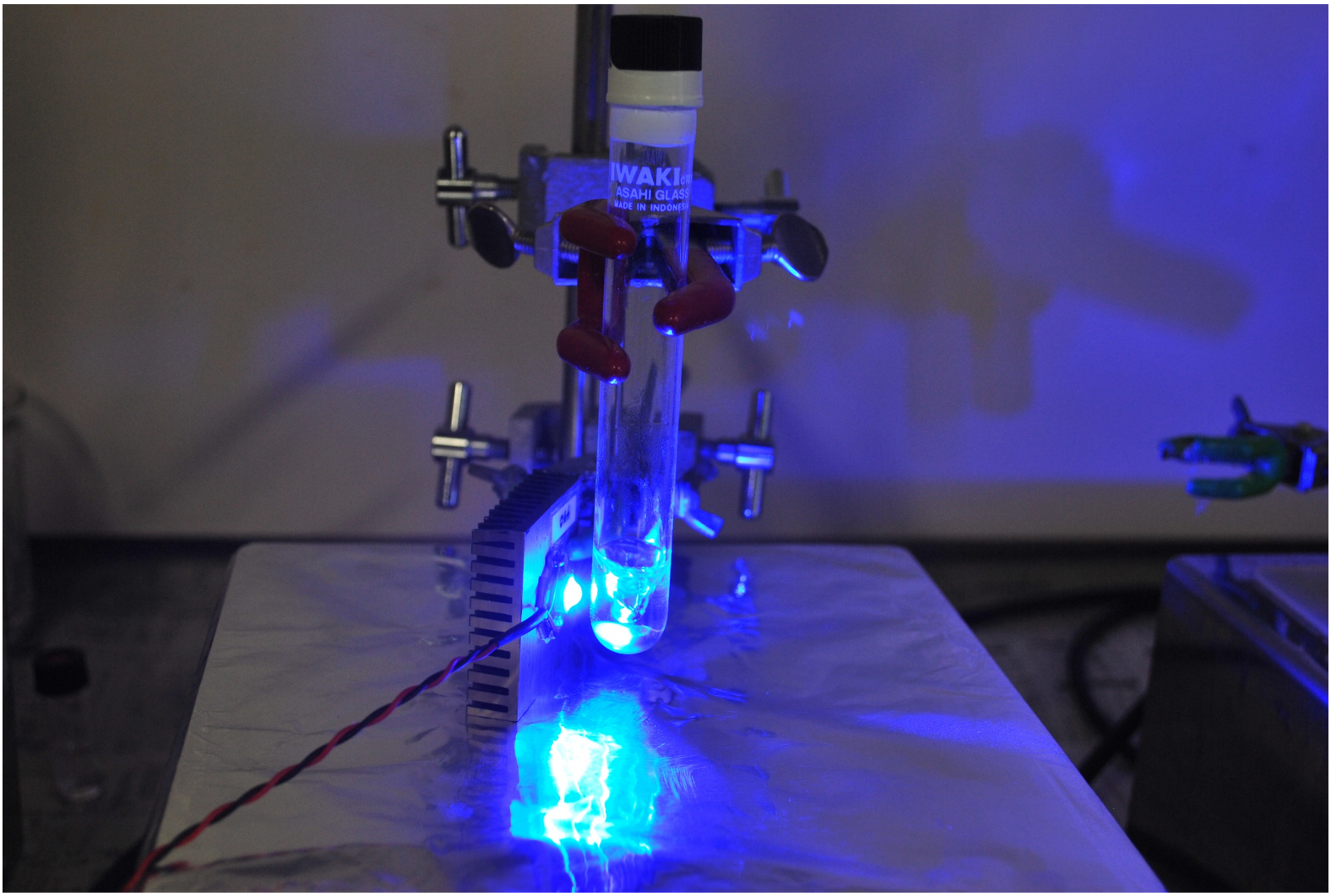
1 **V** mol% **2** **W** mol% **3**

1 (**V** mol%)	**2** (**W** mol%)	3 W LED (**X** nm)	4-Ph-pyridine (**Y** mol%)	CH_2Cl_2 (**Z** mL)	Yields (%)[a]
100	100	450	5.0	1.0	57
110	100	450	5.0	1.0	69(61)
120	100	450	5.0	1.0	76(65)
130	100	450	5.0	1.0	58(57)
140	100	450	5.0	1.0	45(44)
150	100	450	5.0	1.0	70(62)
160	100	450	5.0	1.0	71(71)
170	100	450	5.0	1.0	56
180	100	450	5.0	1.0	53
190	100	450	5.0	1.0	44
200	100	450	5.0	1.0	55
100	110	450	5.0	1.0	41
100	120	450	5.0	1.0	60
100	130	450	5.0	1.0	57
100	140	450	5.0	1.0	66(61)
100	150	450	5.0	1.0	66(61)
100	160	450	5.0	1.0	66
100	170	450	5.0	1.0	65
100	180	450	5.0	1.0	70(68)
100	190	450	5.0	1.0	62
100	200	450	5.0	1.0	63
100	100	400	5.0	1.0	47
100	100	410	5.0	1.0	51
100	100	420	5.0	1.0	53
100	100	470	5.0	1.0	20
100	100	500	5.0	1.0	2
100	100	450	1.0	1.0	16
100	100	450	2.5	1.0	42
100	100	450	7.5	1.0	26

100	100	450	10.0	1.0	59
100	100	450	20.0	1.0	60
100	100	450	5.0	0.5	67
100	100	450	5.0	1.5	41
100	100	450	5.0	2.0	18
100	100	450	5.0	2.5	11
100	100	450	5.0	3.0	18

[a] ^{1}H NMR yields. Numbers in parentheses are isolated yields.

Figure S3. General Reaction Set Up



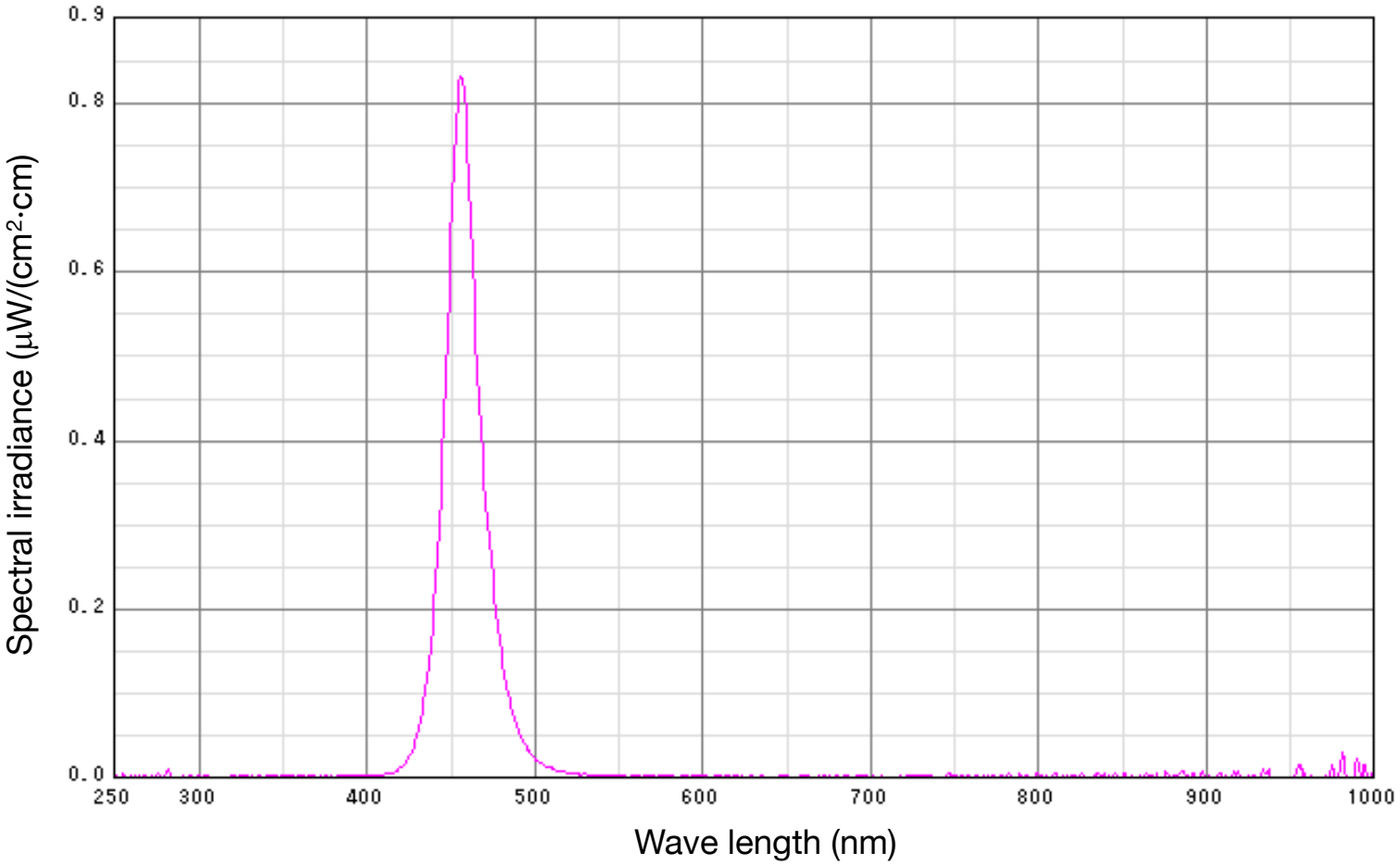
The light source (450 nm LED) was assembled using parts purchased below.

3W LED (https://store.shopping.yahoo.co.jp/ledg/3whhrb.html)

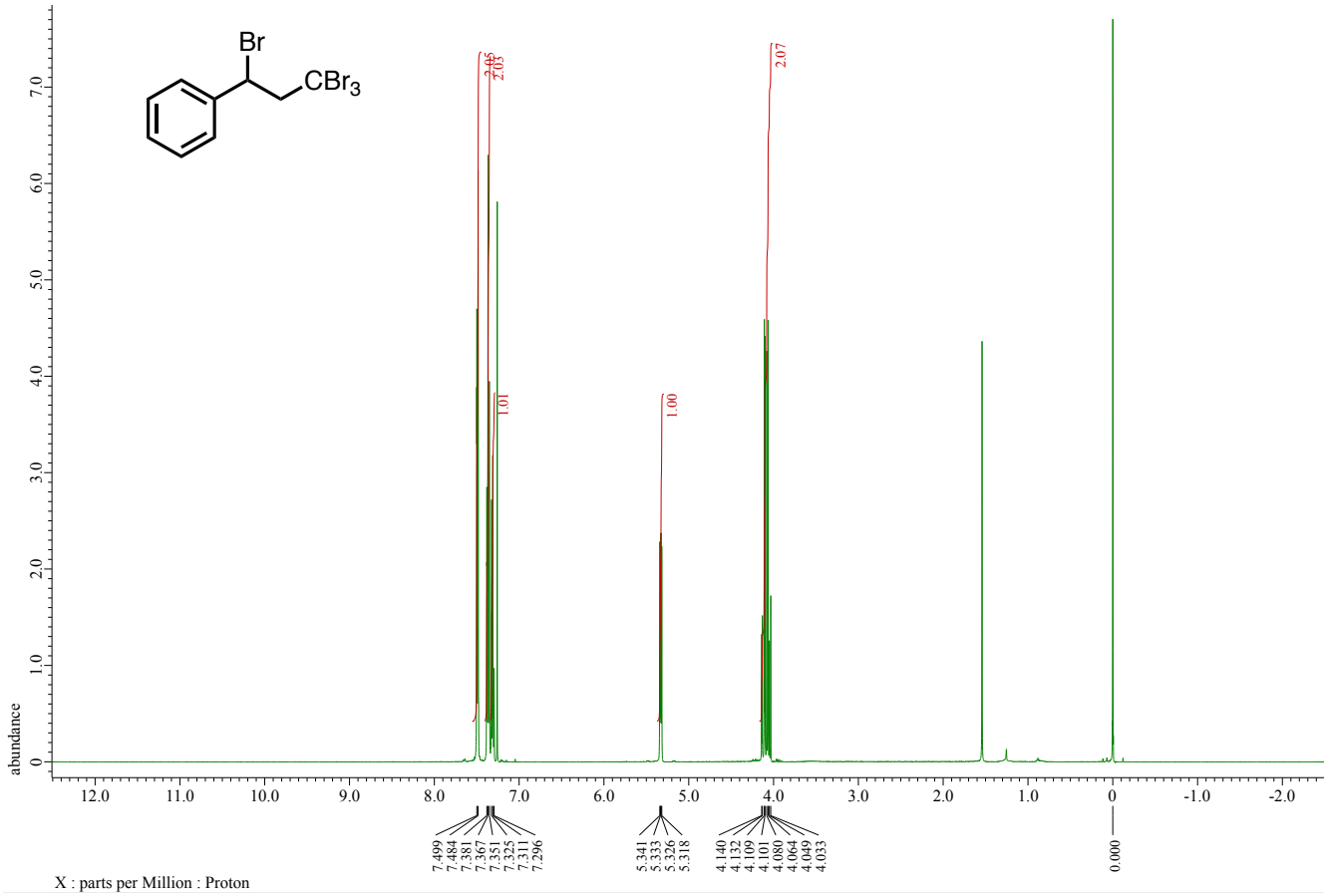
3W LED driver (https://store.shopping.yahoo.co.jp/ledg/dc-12v-14v-constant-current-high-power-led-driver-600ma-3w-9w.html)

Heatsink (https://store.shopping.yahoo.co.jp/ledg/aluminum-heat-sink-plate-radiator-40mm.html)

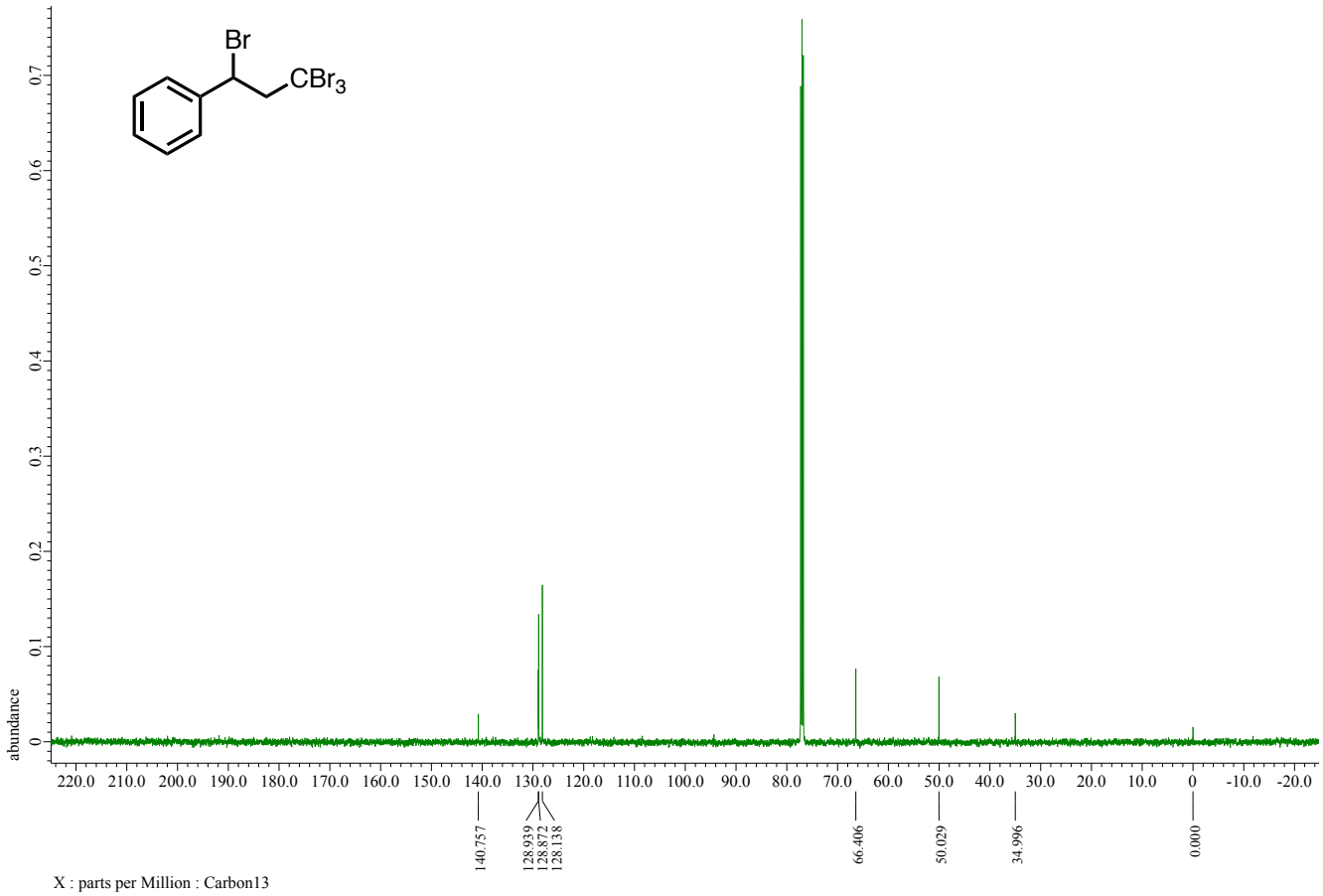
Figure S4. The wave length and spectral irradiance of 3W LED



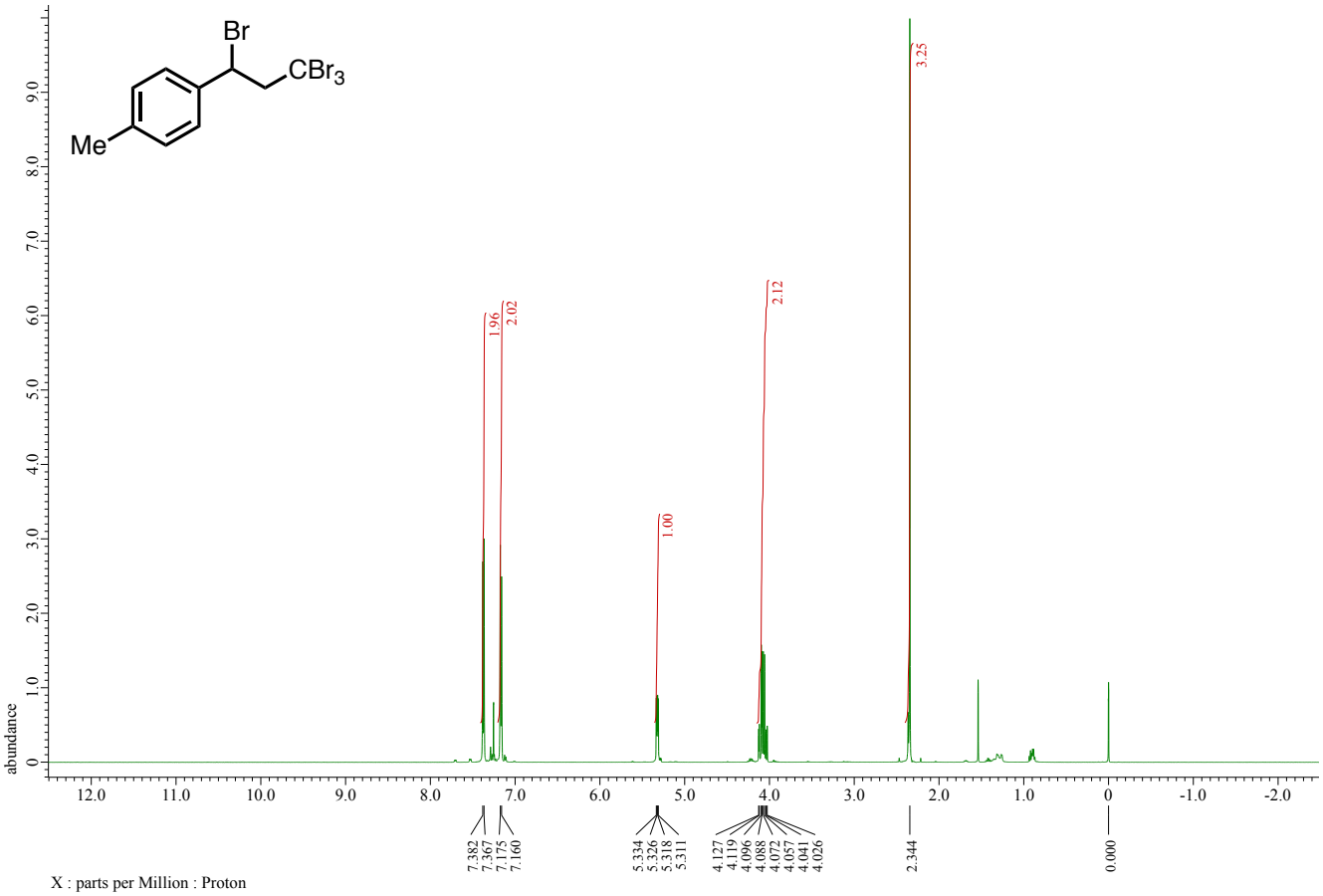
^{1}H NMR (500 MHz, $CDCl_3$) spectra of 3a



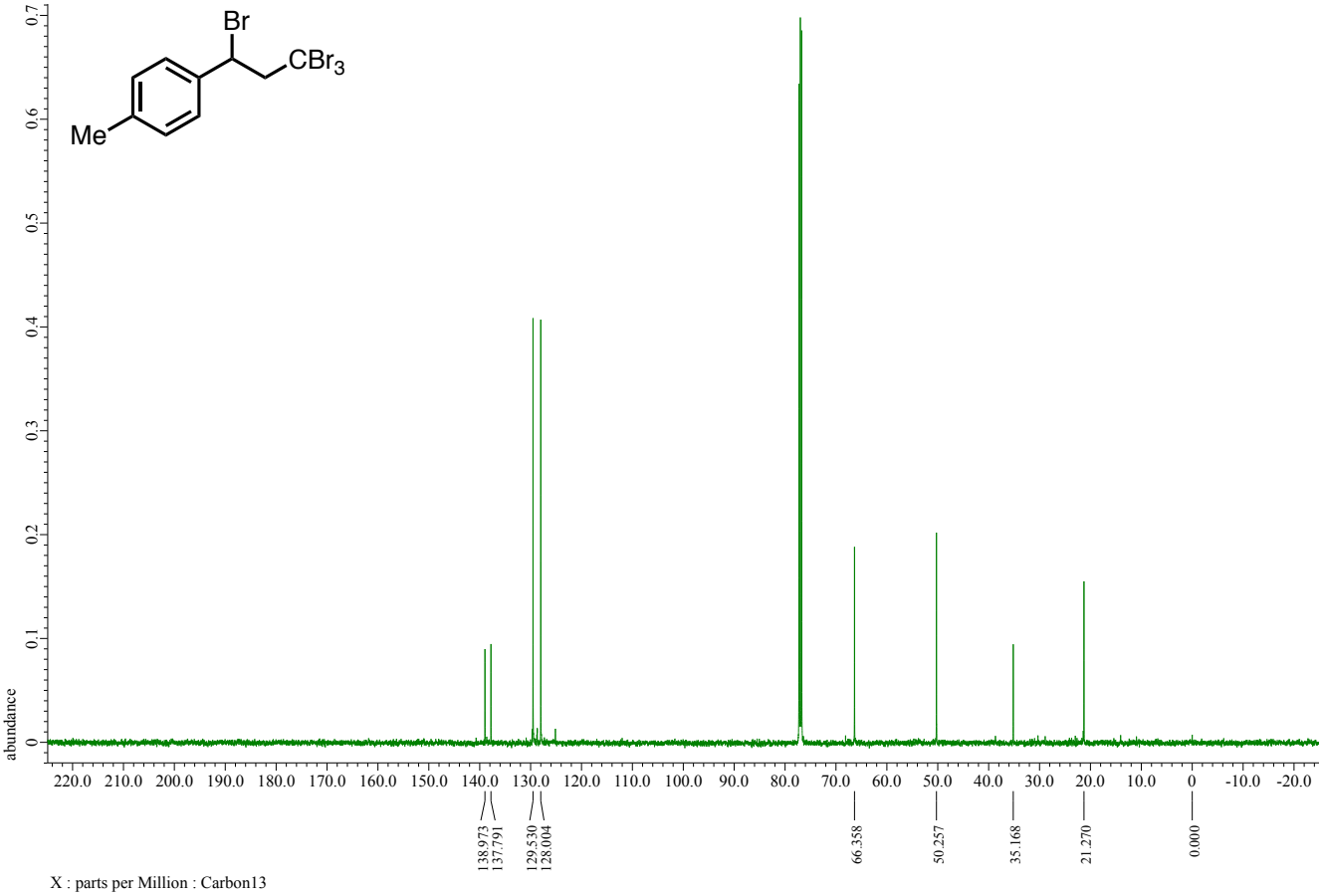
^{13}C{^{1}H} NMR (125 MHz, $CDCl_3$) spectra of 3a



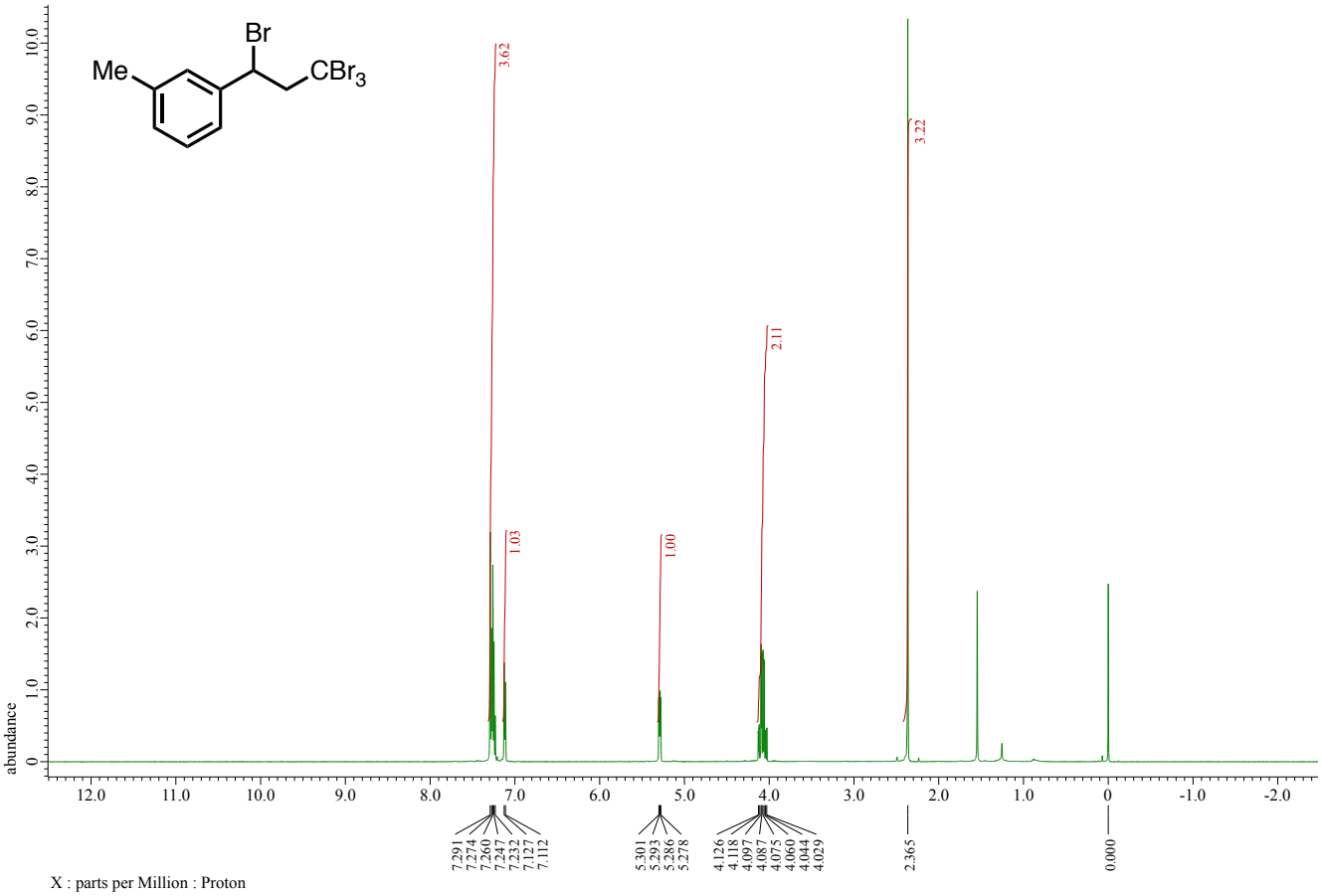
^{1}H NMR (500 MHz, $CDCl_3$) spectra 3b



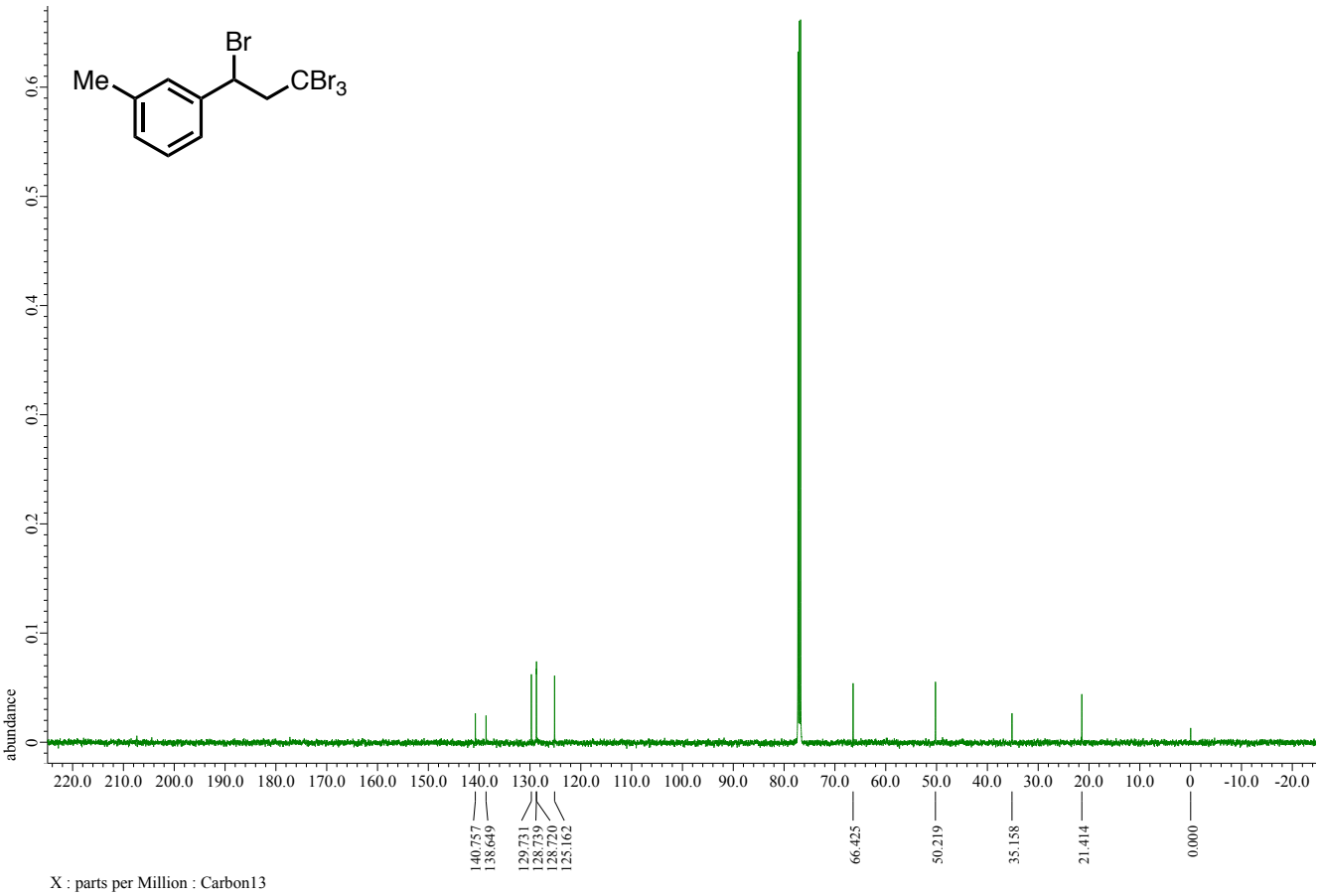
$^{13}C\{^{1}H\}$ NMR (125 MHz, $CDCl_3$) spectra 3b



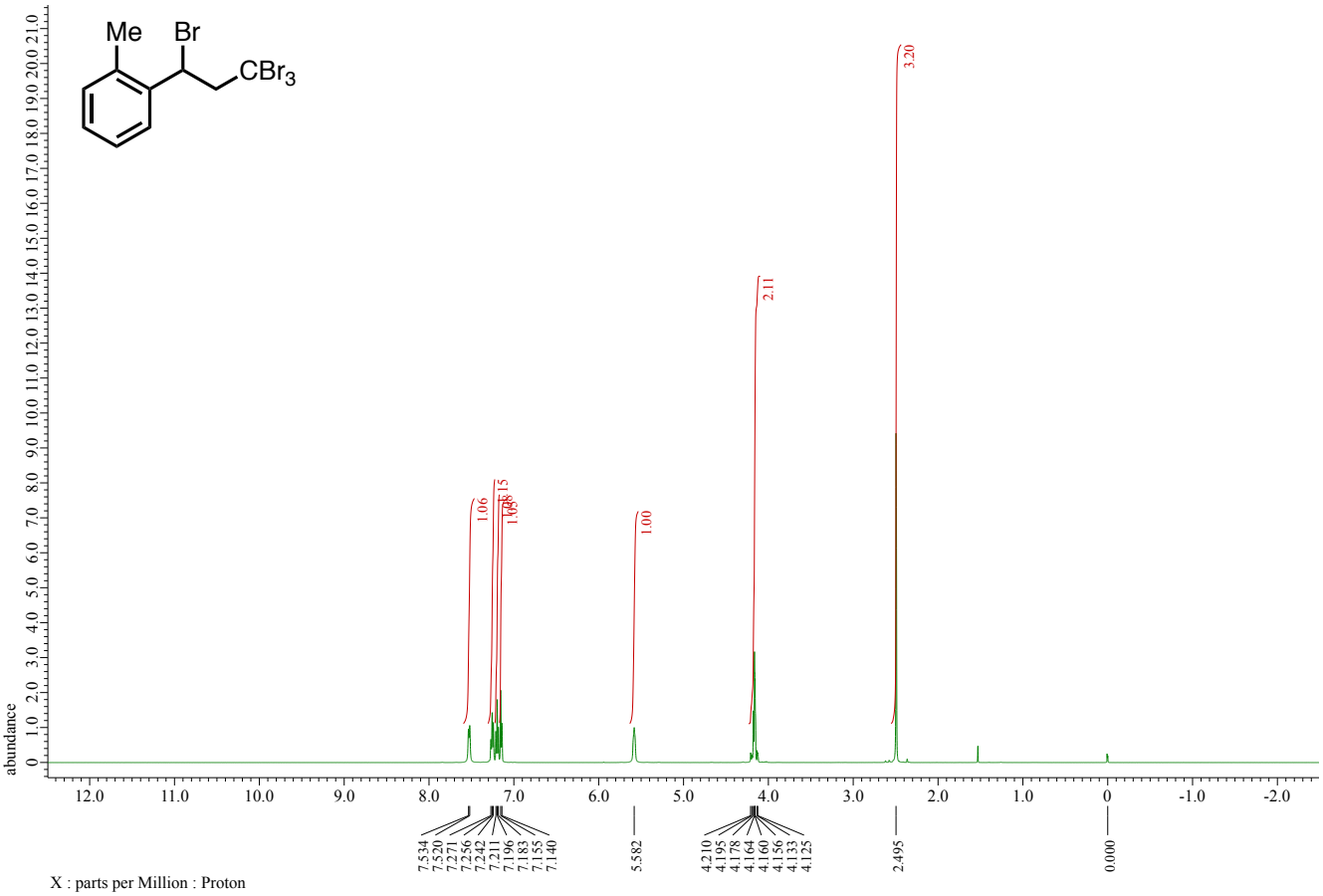
^{1}H NMR (500 MHz, $CDCl_3$) spectra 3c



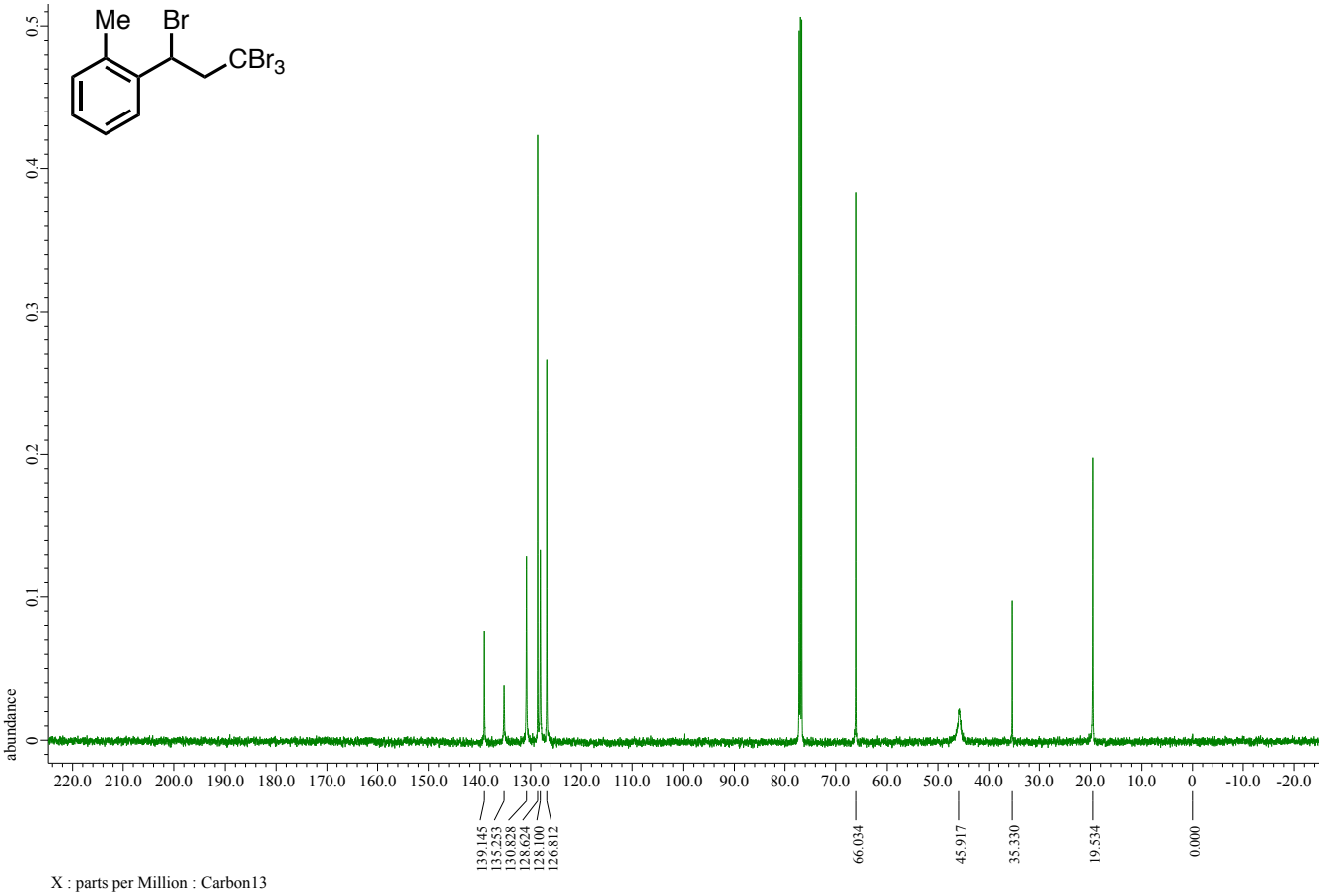
$^{13}C\{^{1}H\}$ NMR (125 MHz, $CDCl_3$) spectra 3c



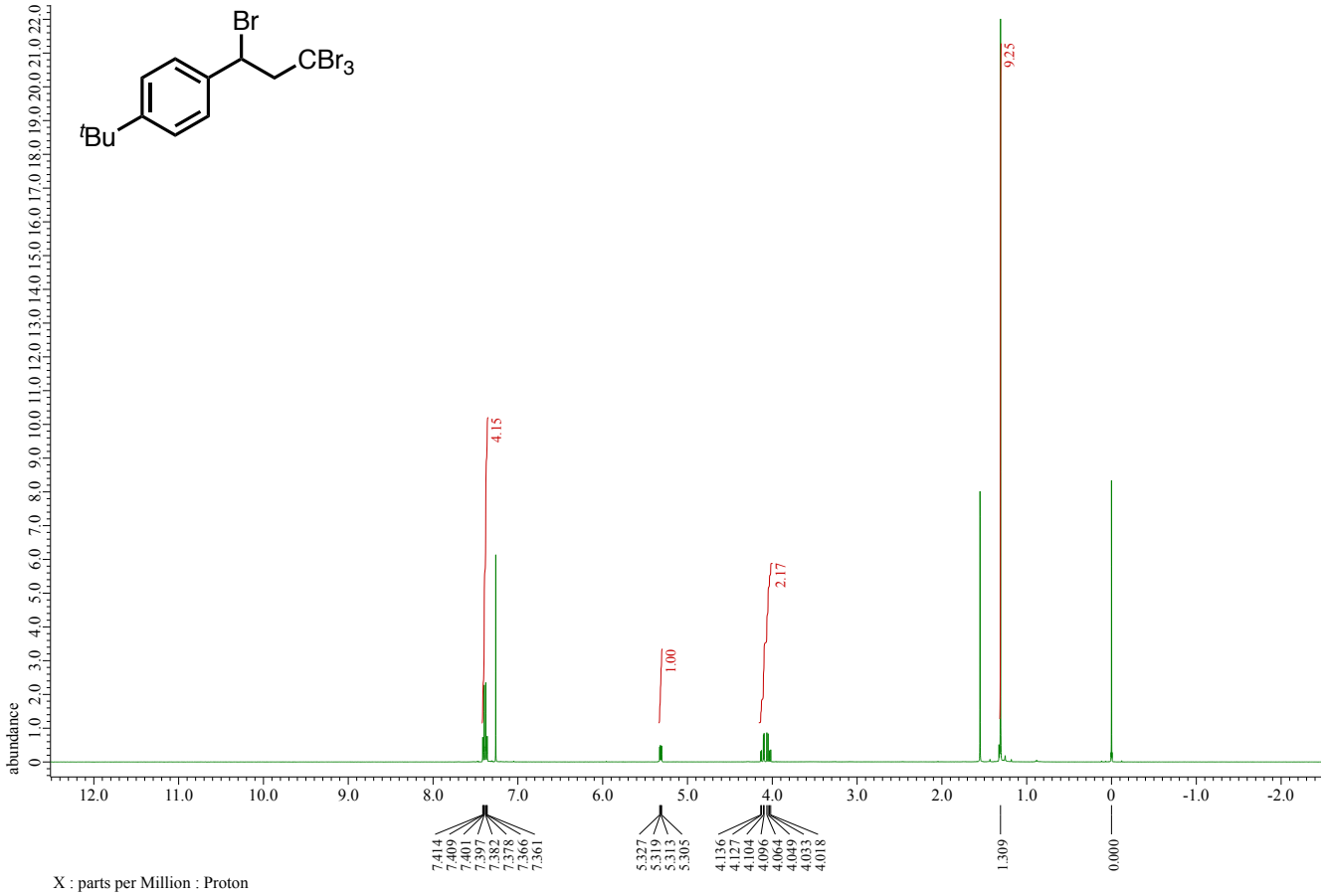
^{1}H NMR (500 MHz, $CDCl_3$) spectra of 3d



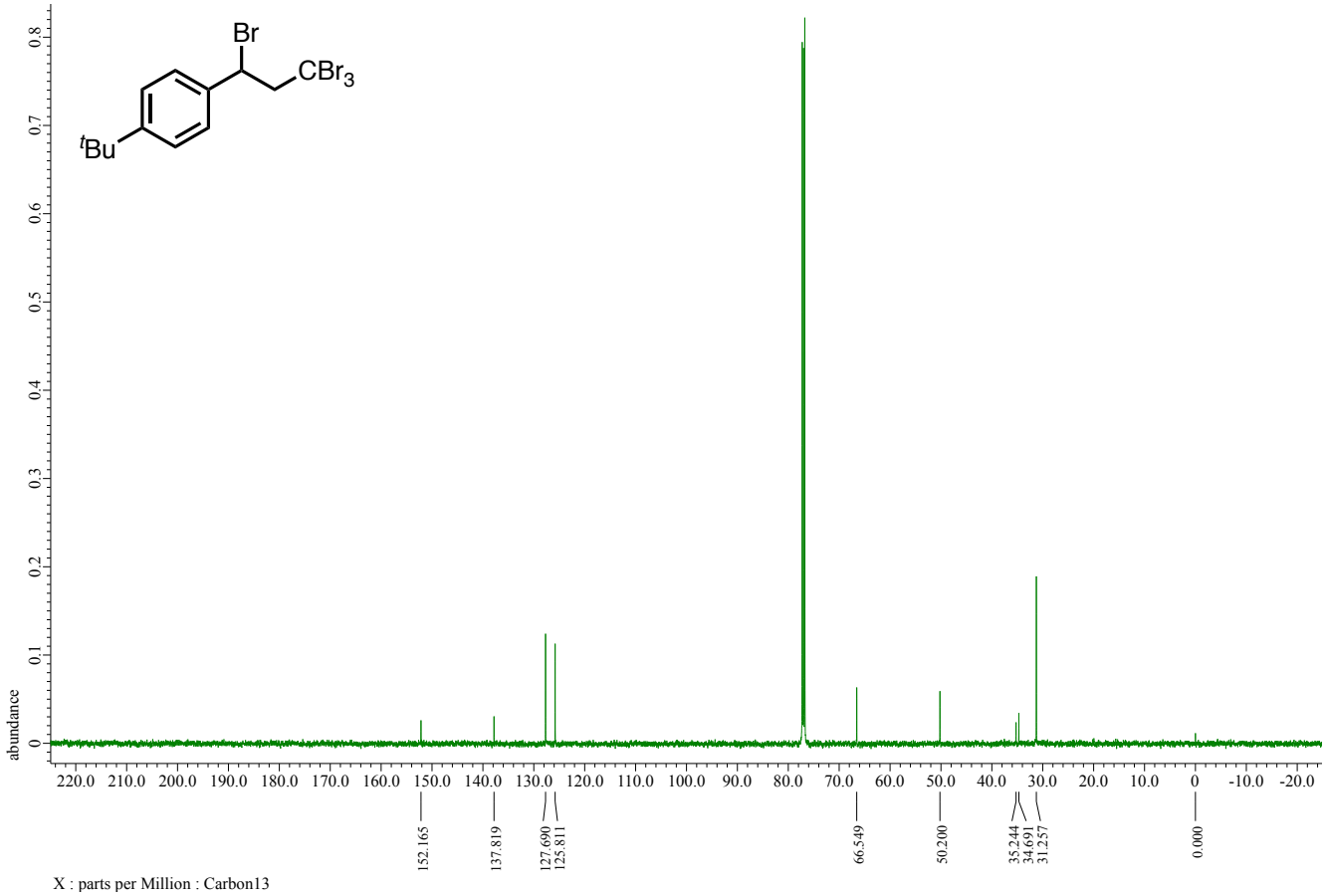
^{13}C NMR (125 MHz, $CDCl_3$) spectra of 3d



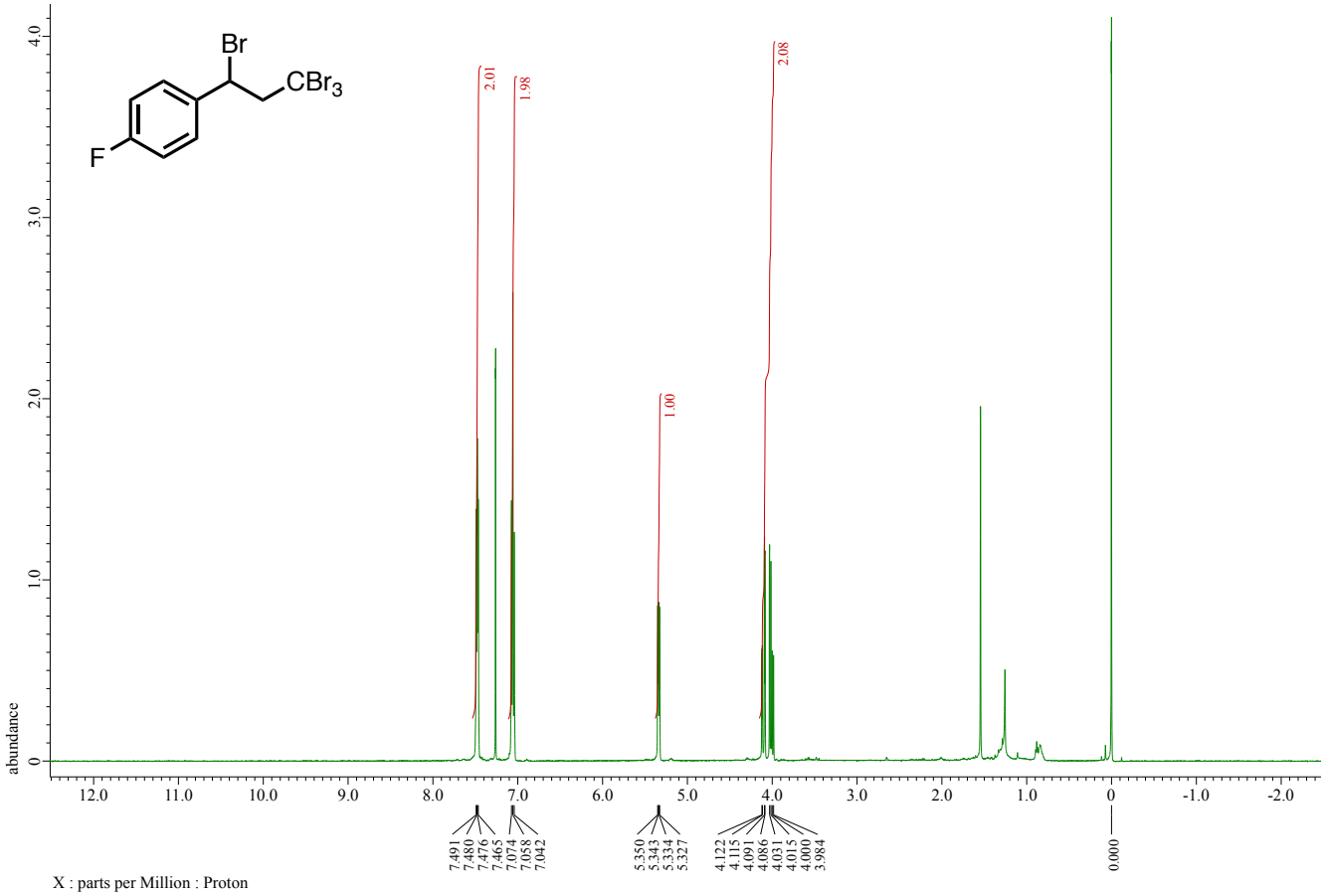
^{1}H NMR (500 MHz, $CDCl_3$) spectra of 3e



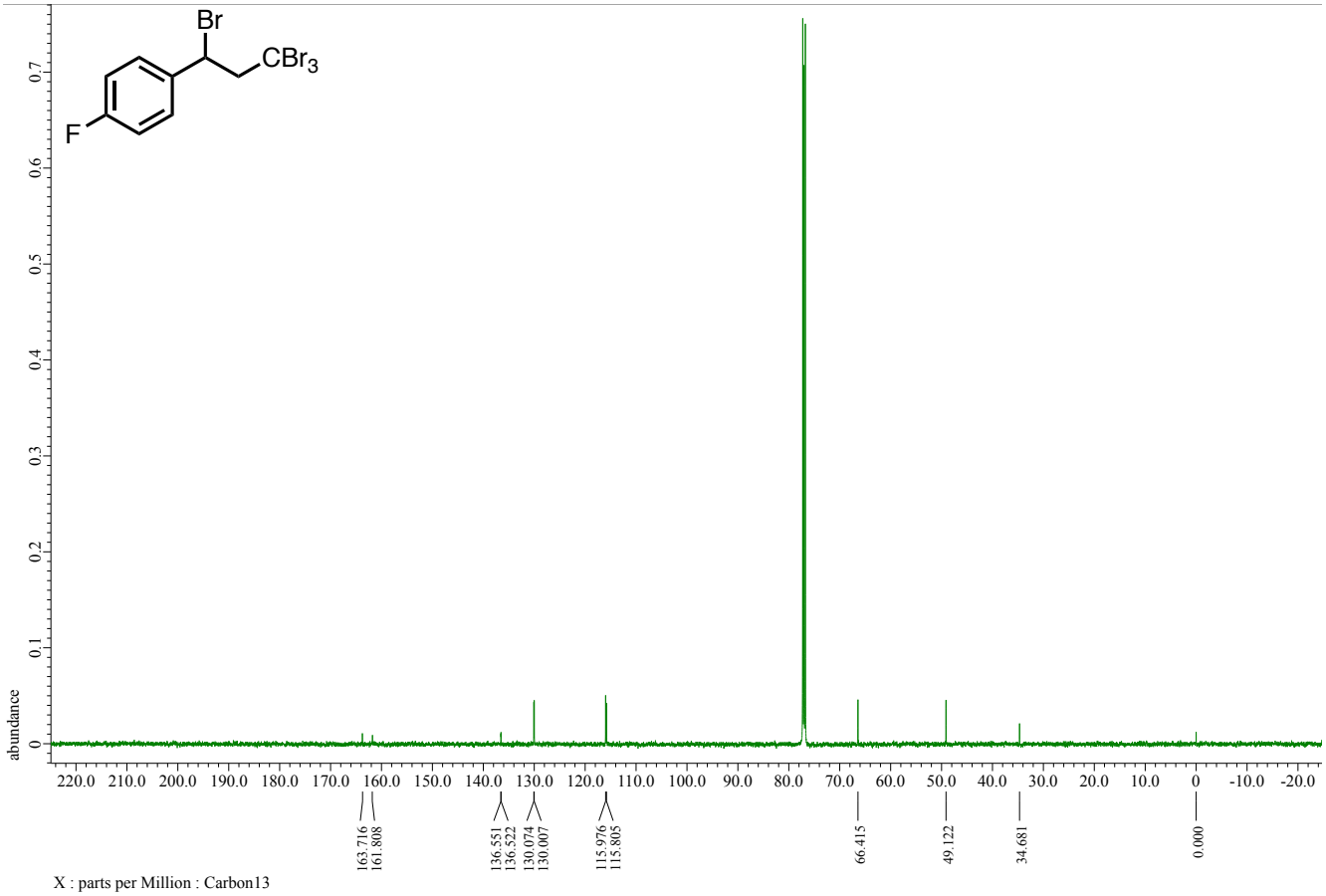
^{13}C NMR (125 MHz, $CDCl_3$) spectra of 3e



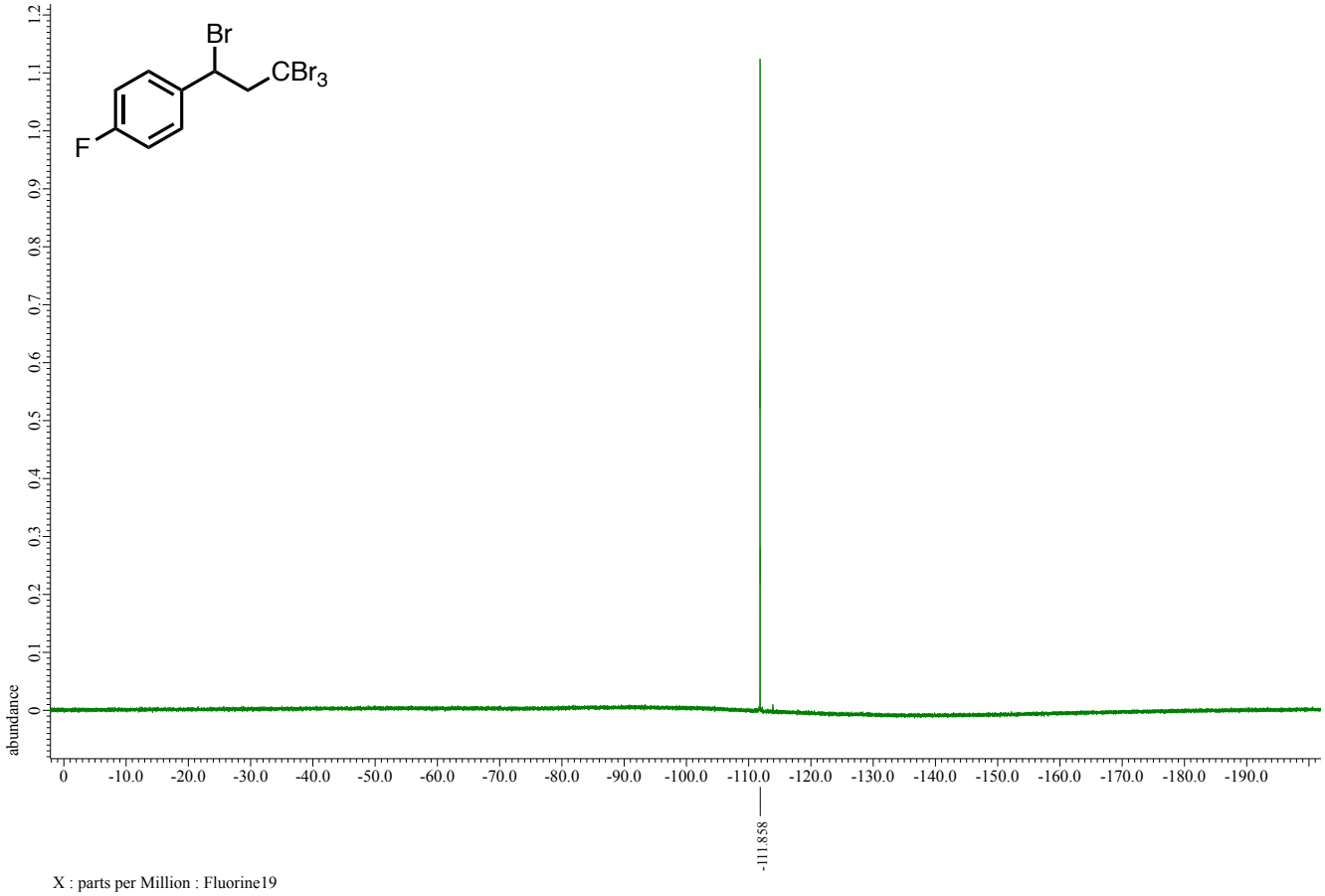
^{1}H NMR (500 MHz, $CDCl_3$) spectra of 3f



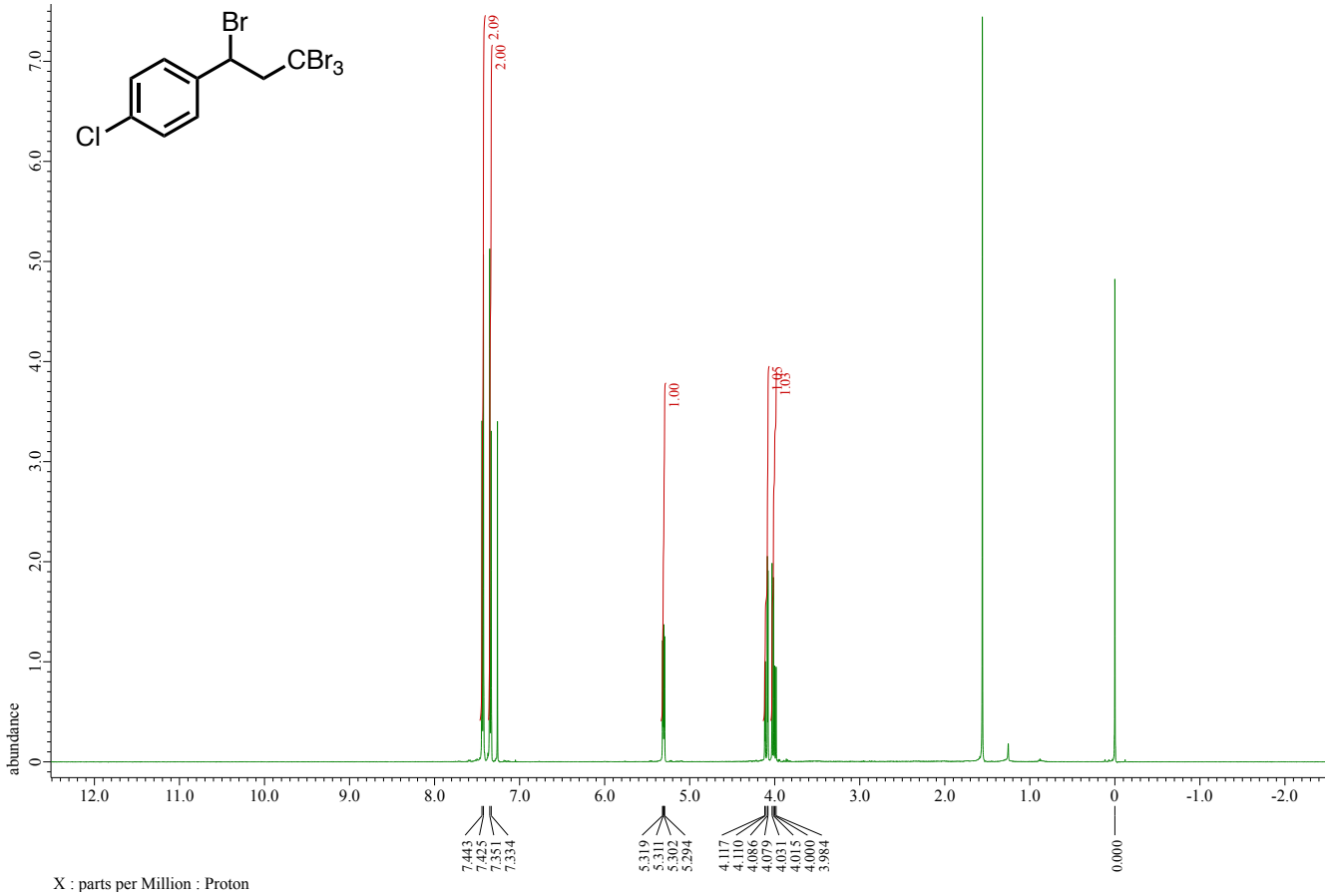
^{13}C NMR (125 MHz, $CDCl_3$) spectra of 3f



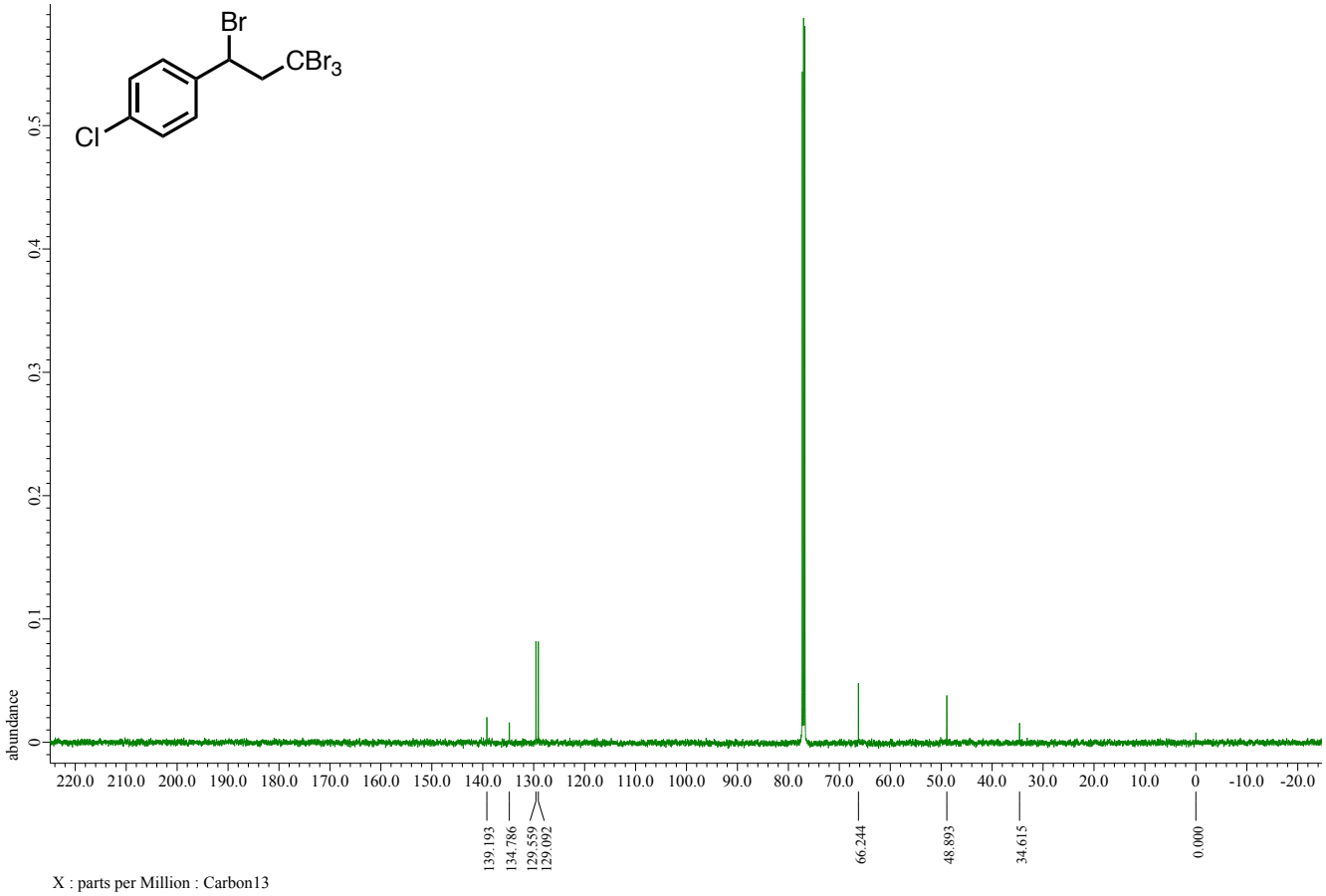
^{19}F NMR (475 MHz, $CDCl_3$) spectra of 3f



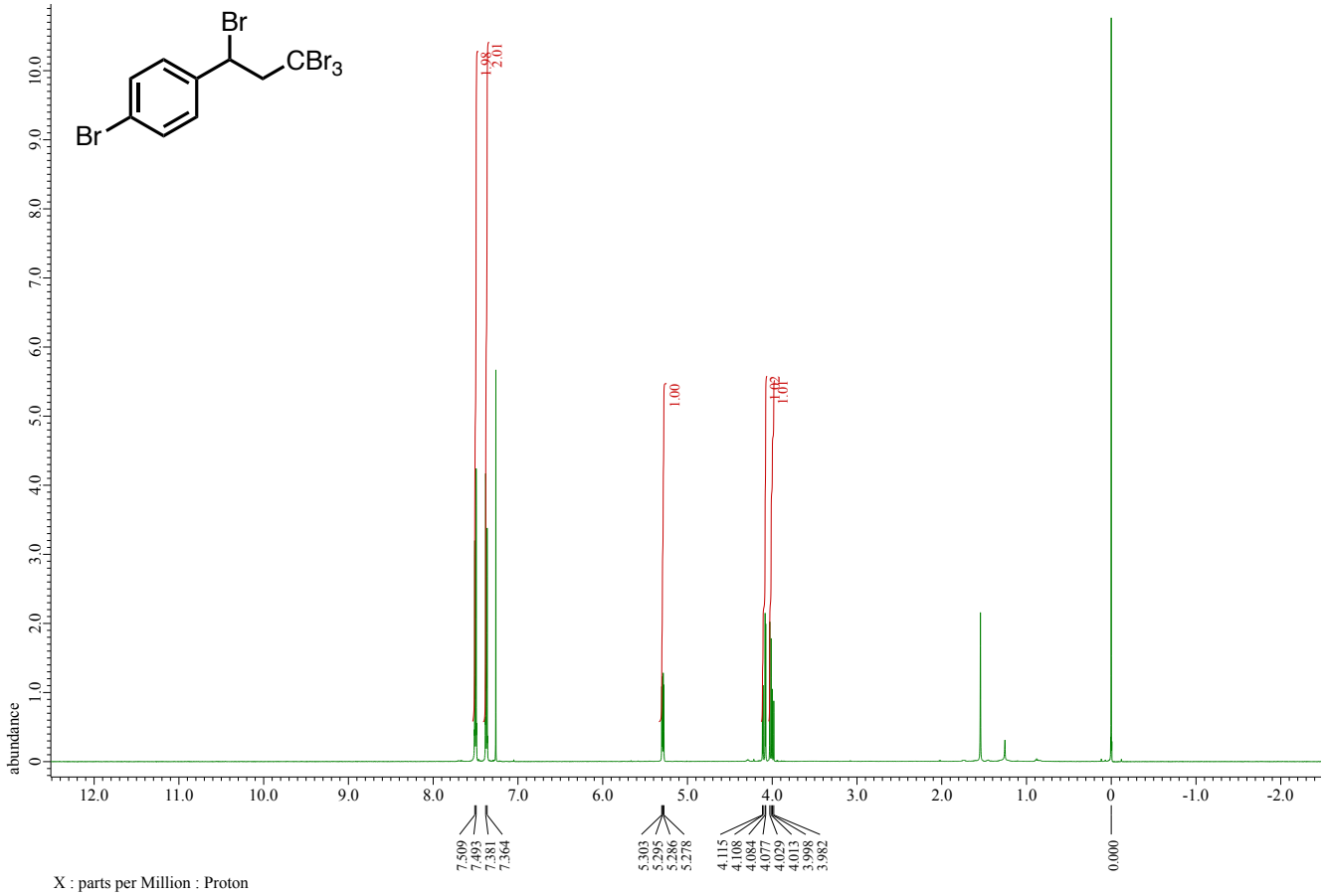
^{1}H NMR (500 MHz, $CDCl_3$) spectra of 3g



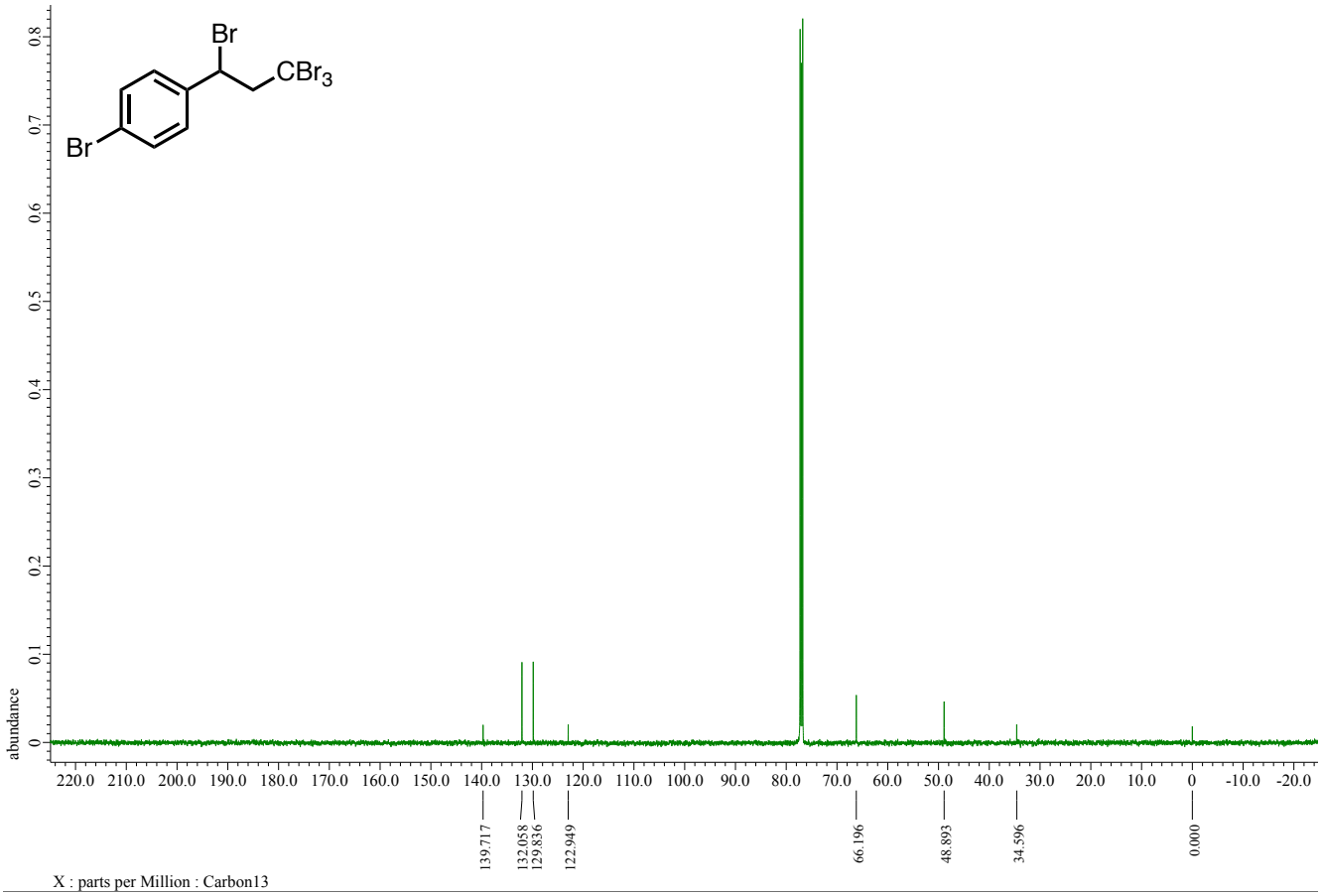
^{13}C NMR (125 MHz, $CDCl_3$) spectra of 3g



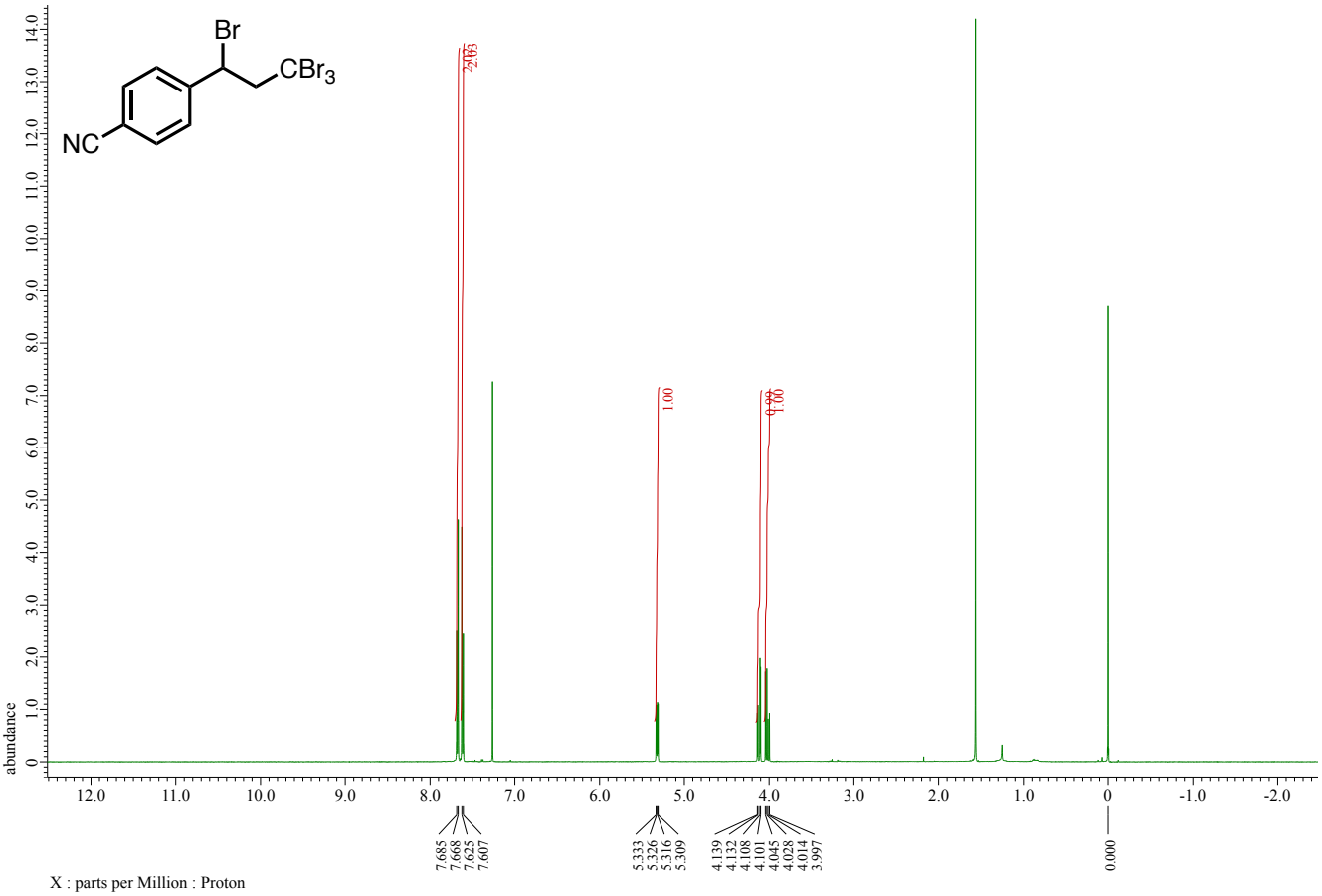
^{1}H NMR (500 MHz, $CDCl_3$) spectra of 3h



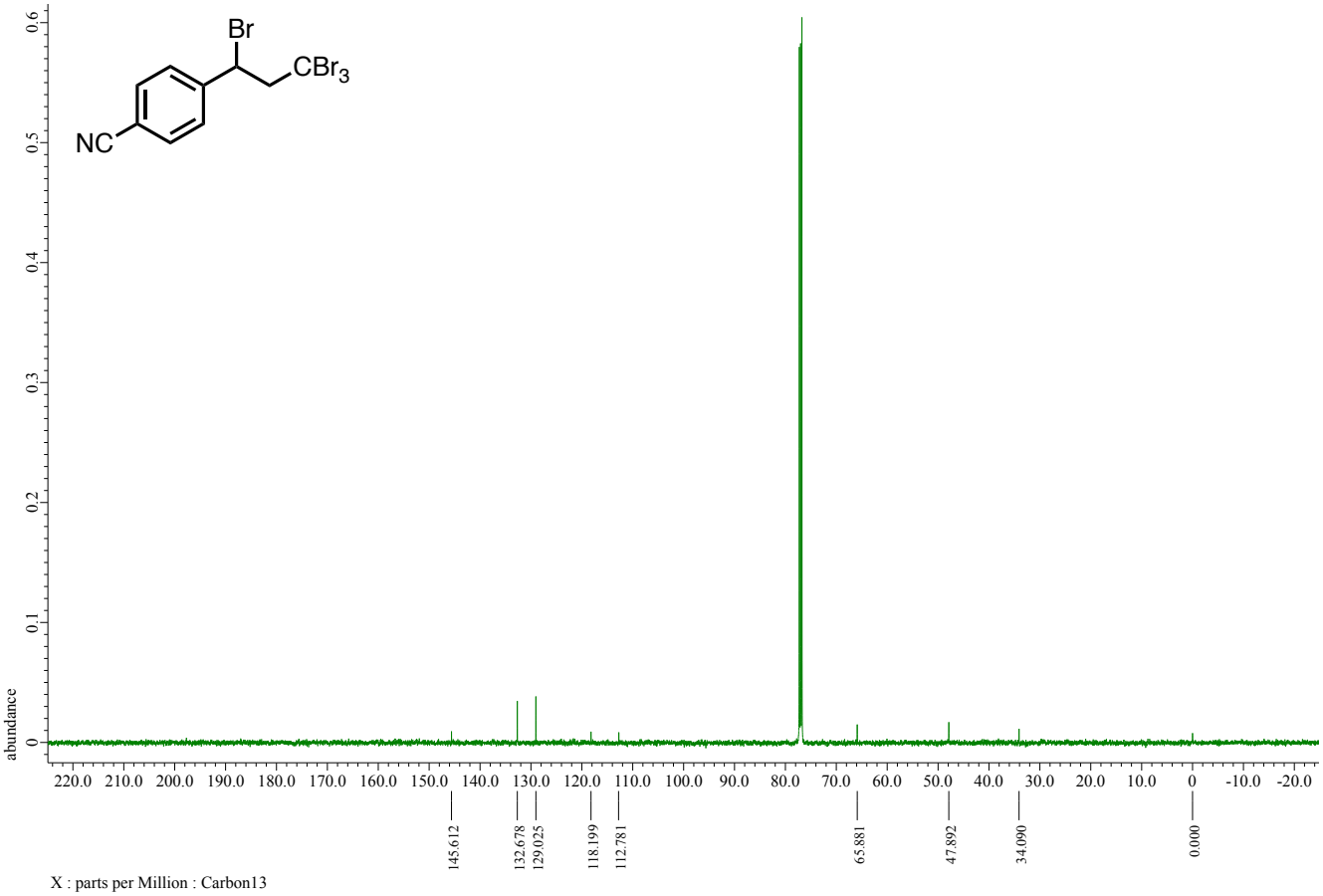
^{13}C NMR (125 MHz, $CDCl_3$) spectra of 3h



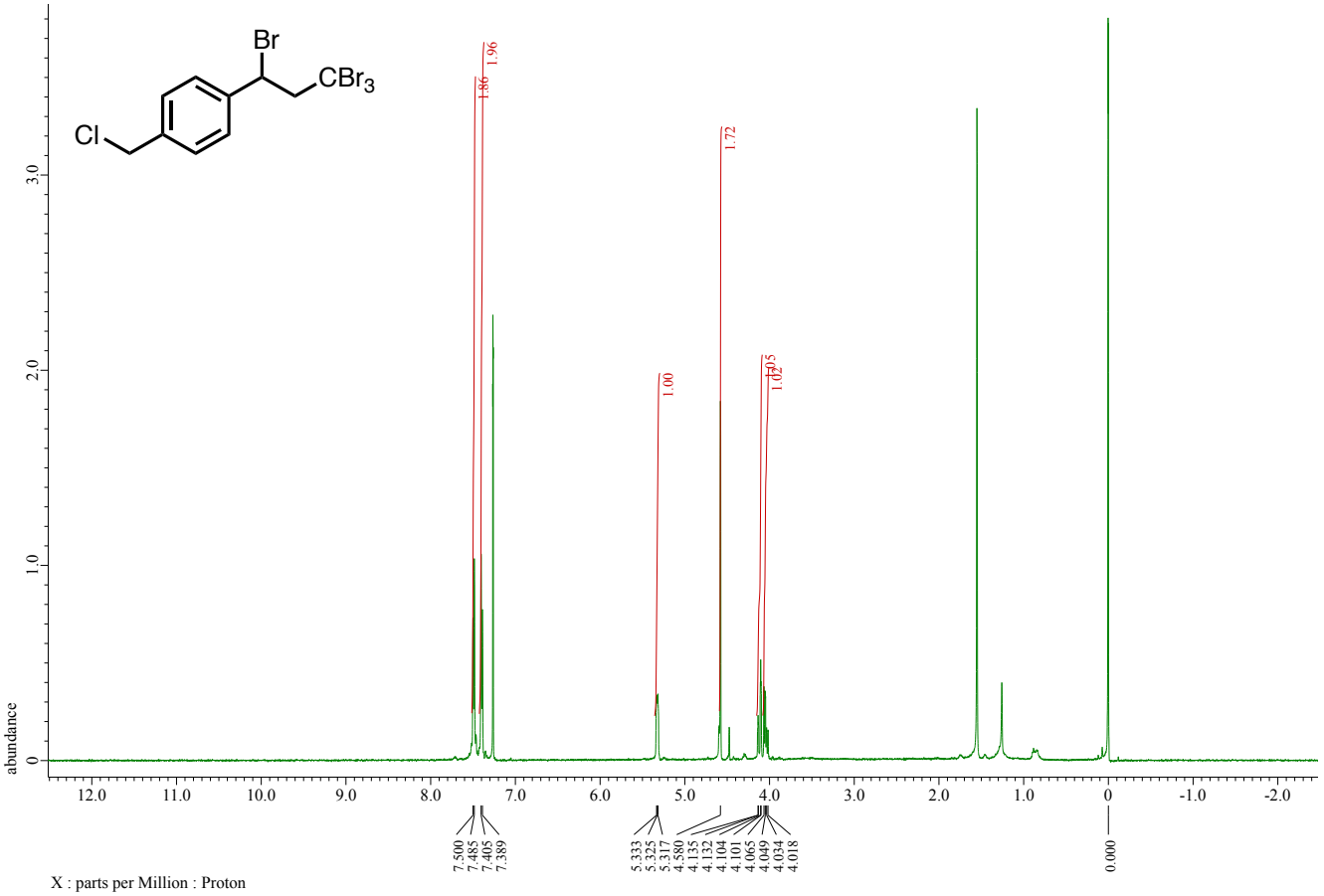
^{1}H NMR (500 MHz, $CDCl_3$) spectra of 3k



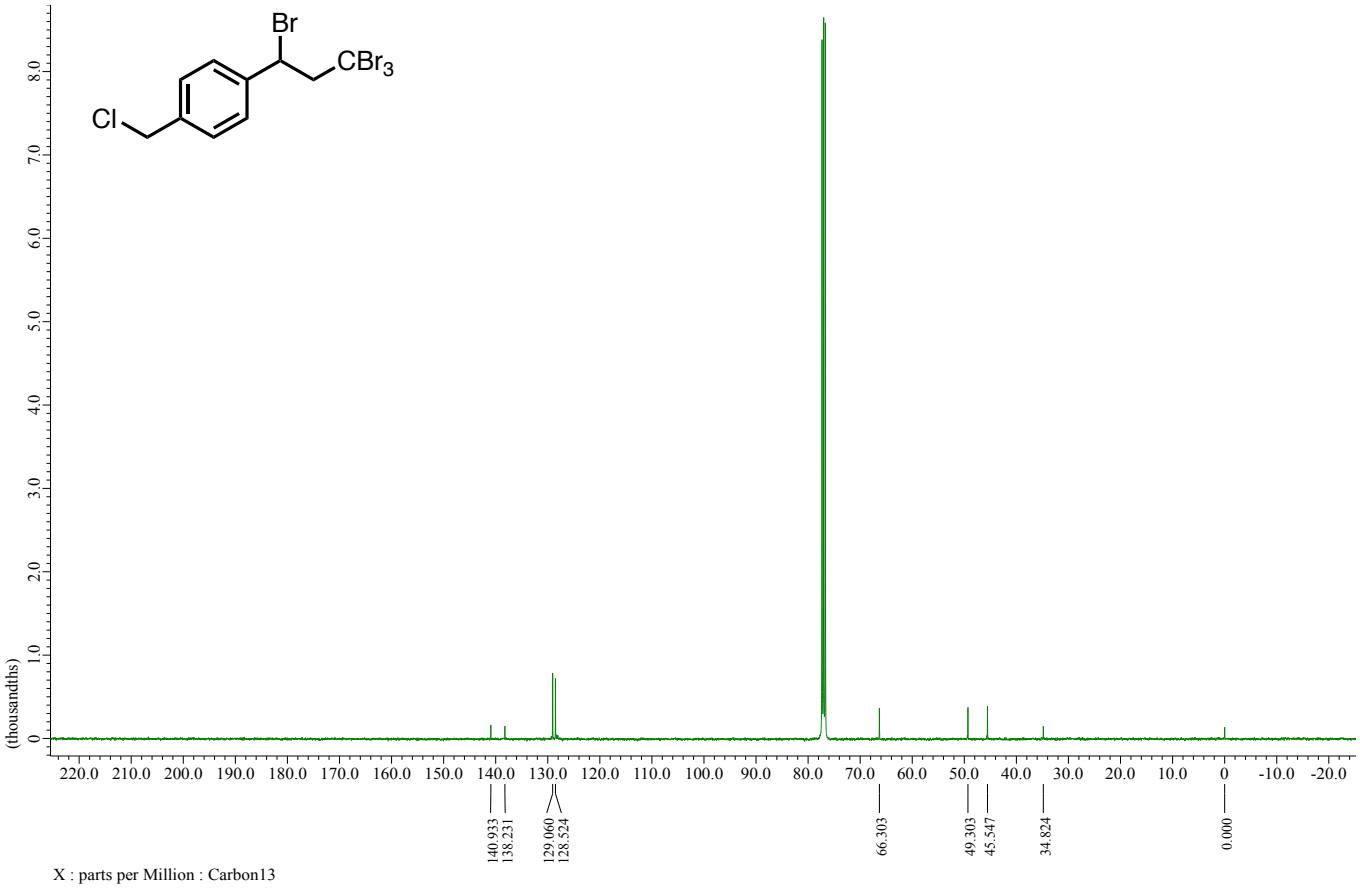
^{13}C NMR (125 MHz, $CDCl_3$) spectra of 3k



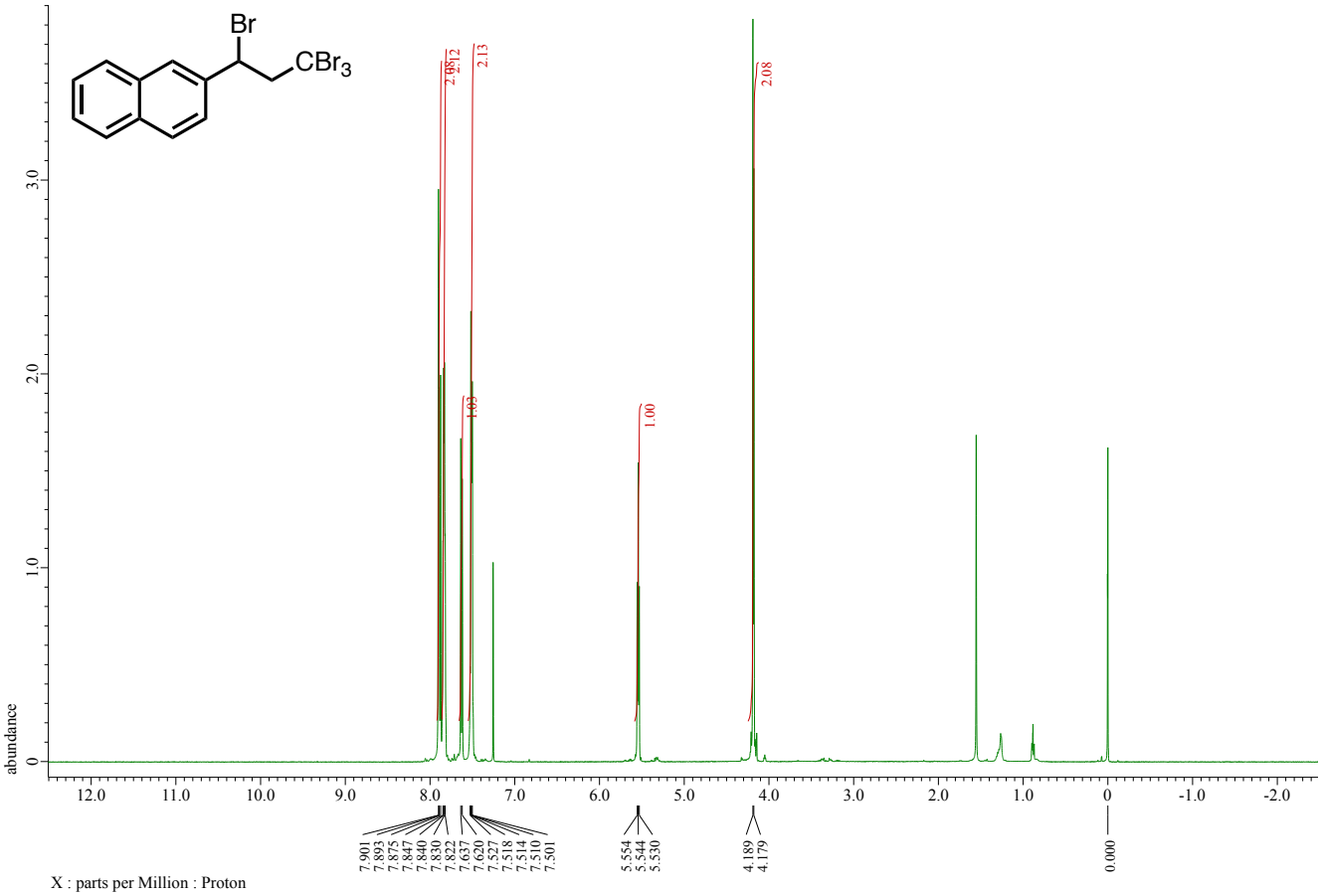
^{1}H NMR (500 MHz, $CDCl_3$) spectra of 3l



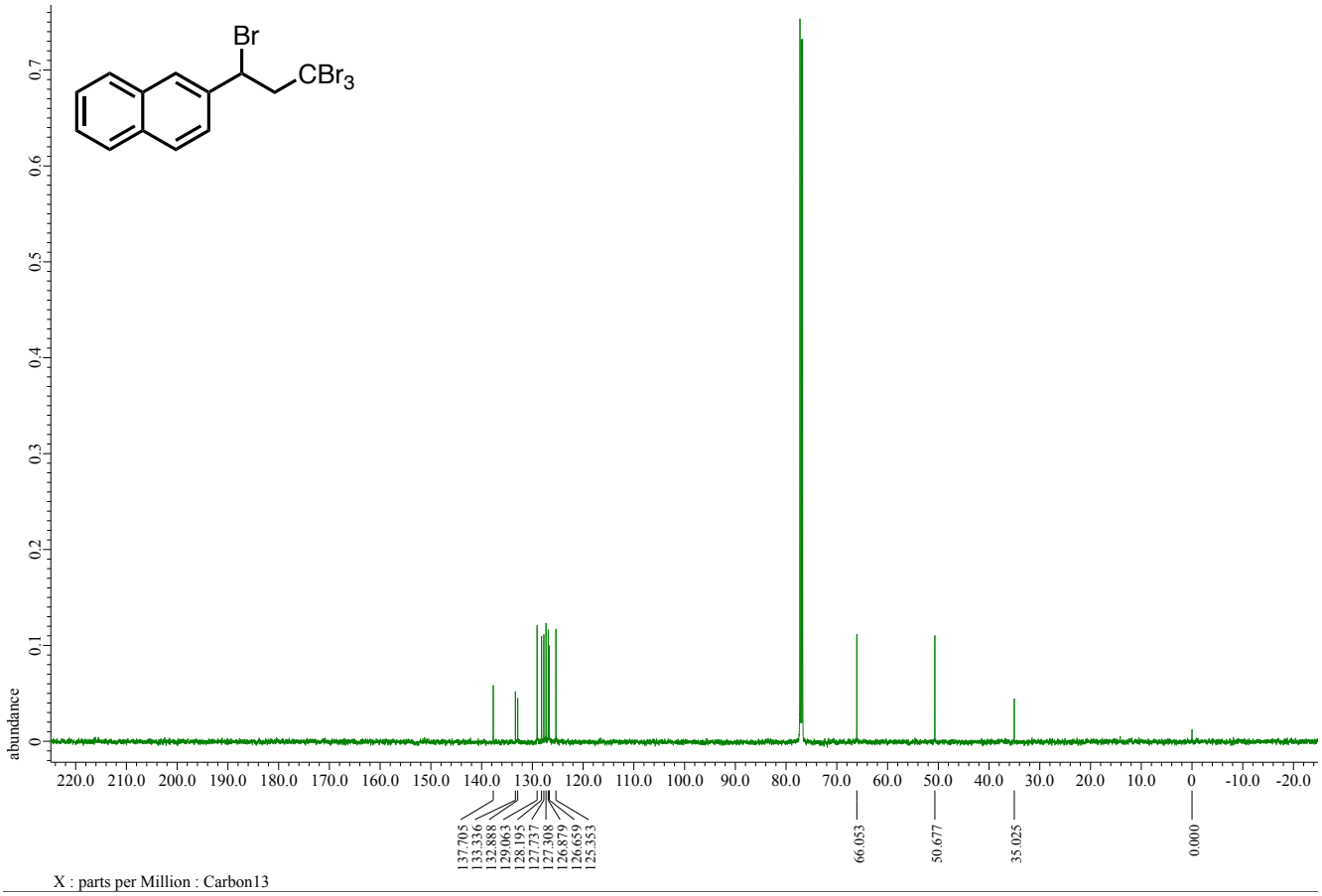
^{13}C NMR (125 MHz, $CDCl_3$) spectra of 3l



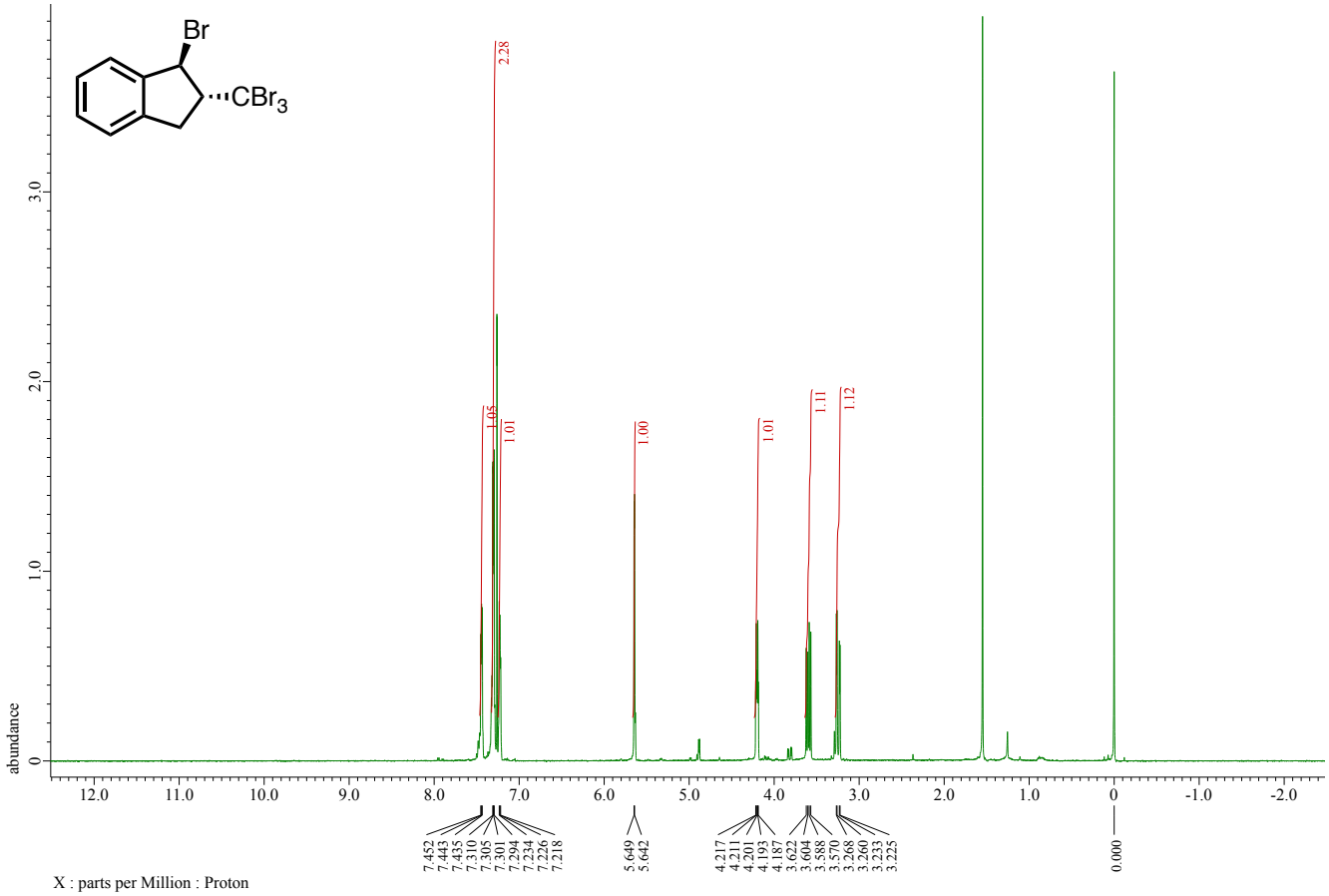
^{1}H NMR (500 MHz, $CDCl_3$) spectra of 3m



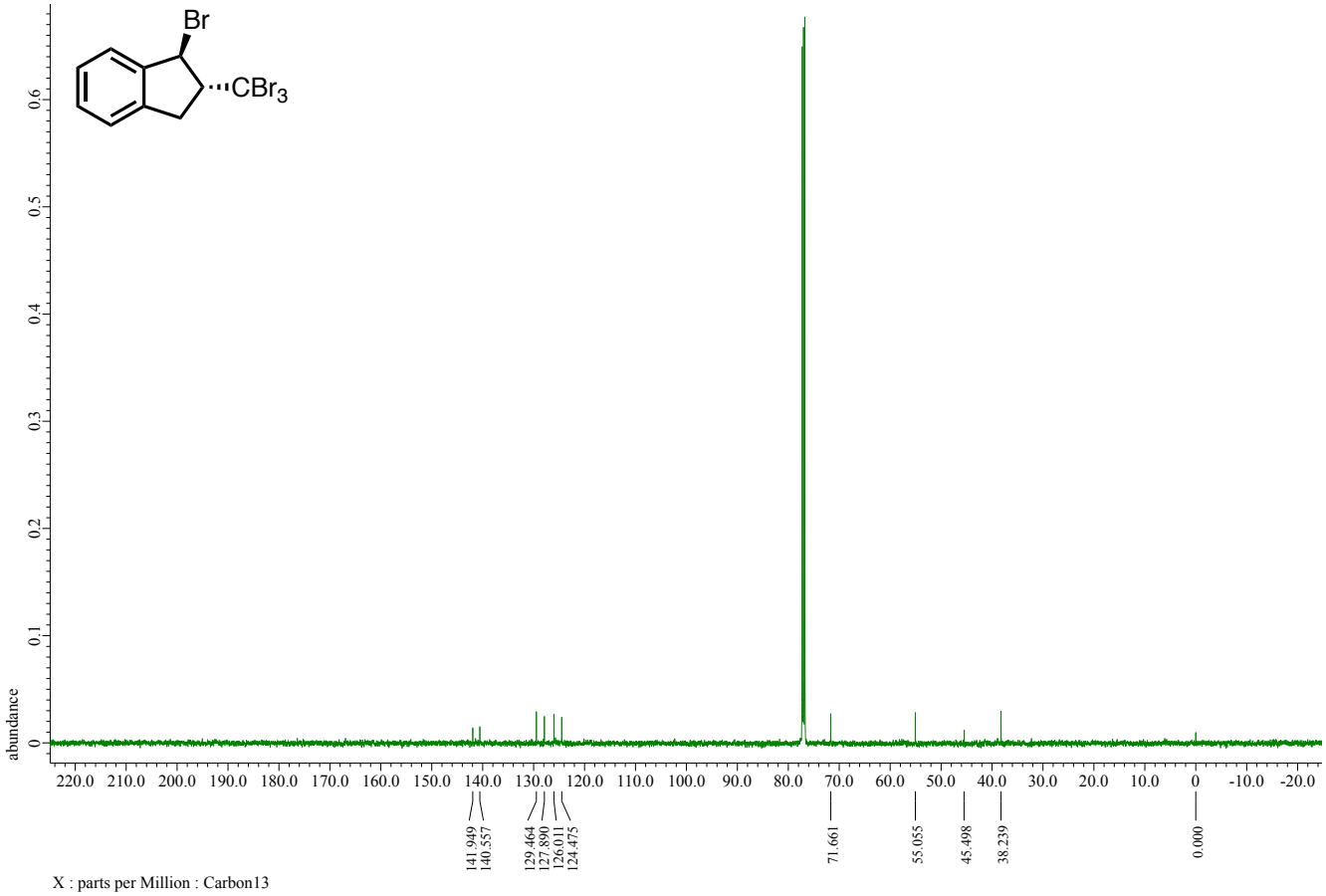
^{13}C NMR (125 MHz, $CDCl_3$) spectra of 3m



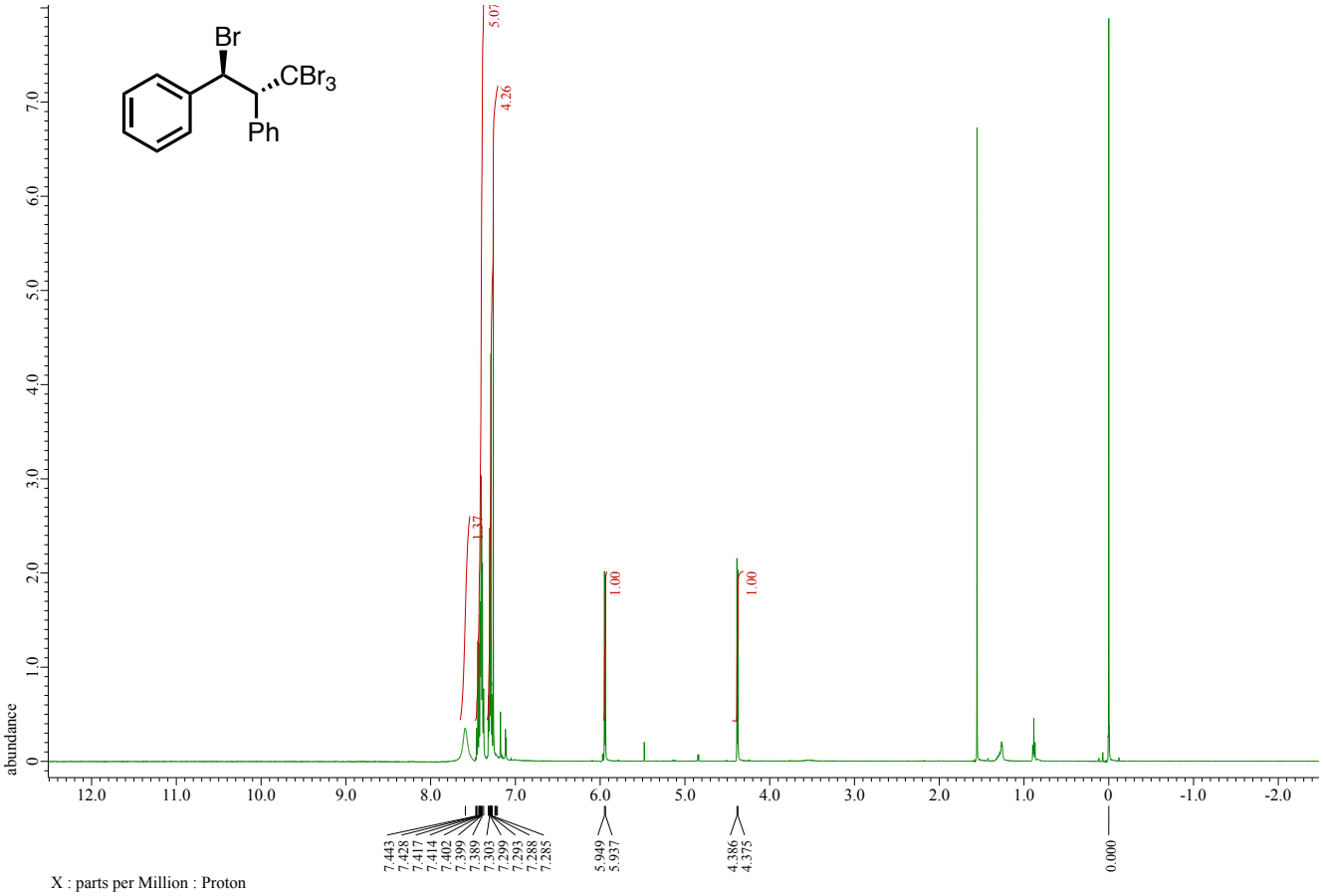
^{1}H NMR (500 MHz, $CDCl_3$) spectra of 3n



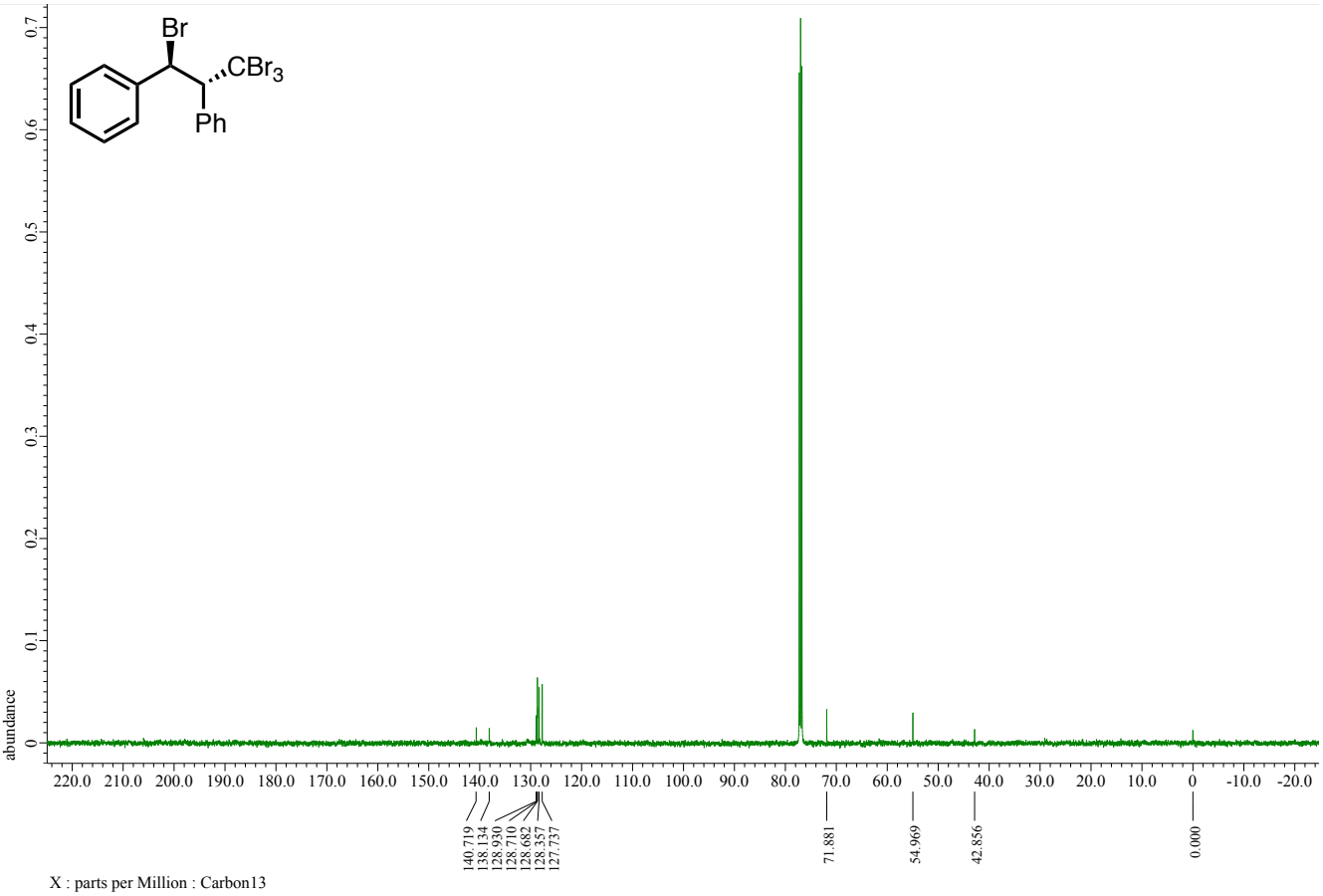
^{13}C NMR (125 MHz, $CDCl_3$) spectra of 3n



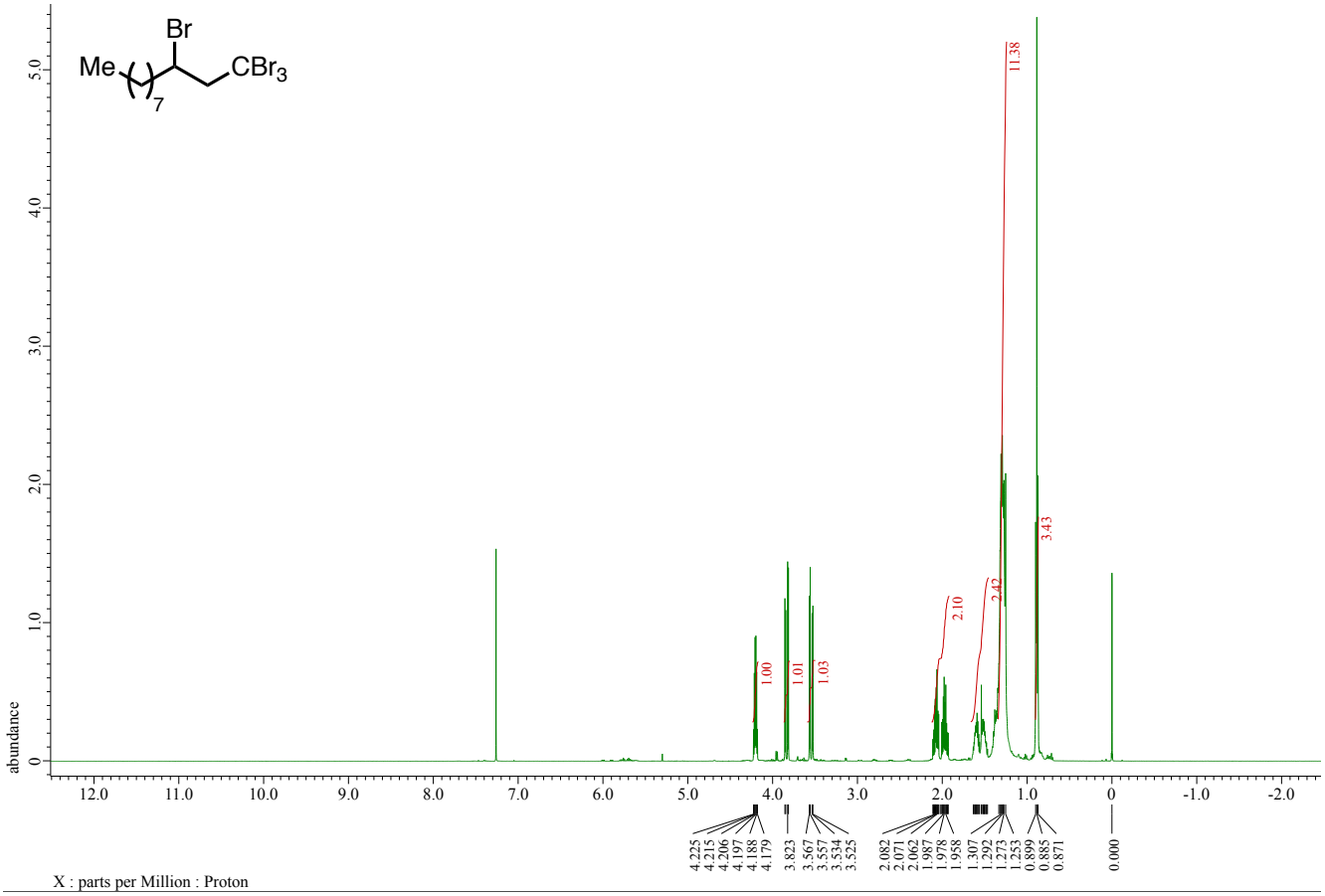
^{1}H NMR (500 MHz, $CDCl_3$) spectra of 3p



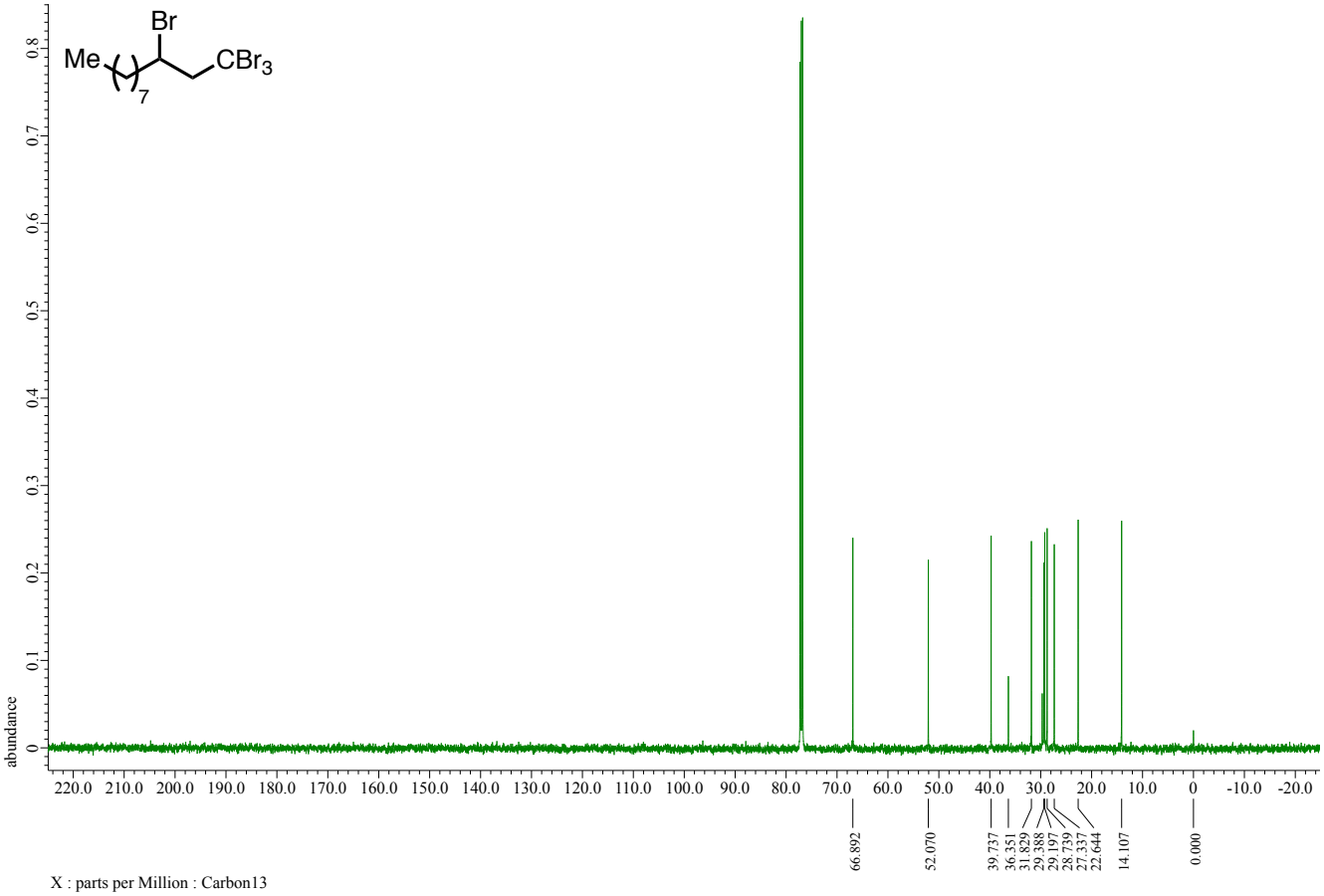
^{13}C NMR (125 MHz, $CDCl_3$) spectra of 3p



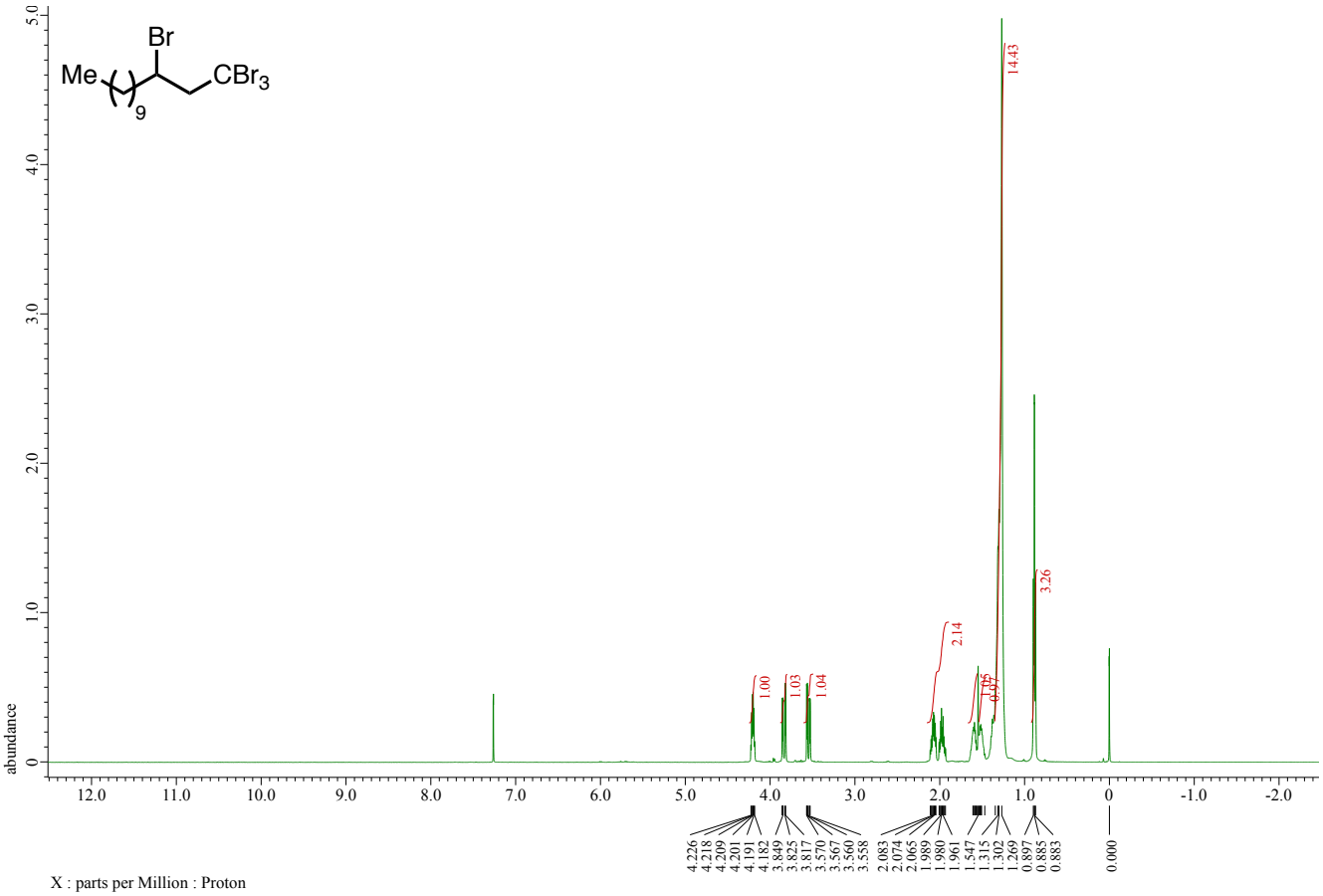
^{1}H NMR (500 MHz, $CDCl_3$) spectra of 3q



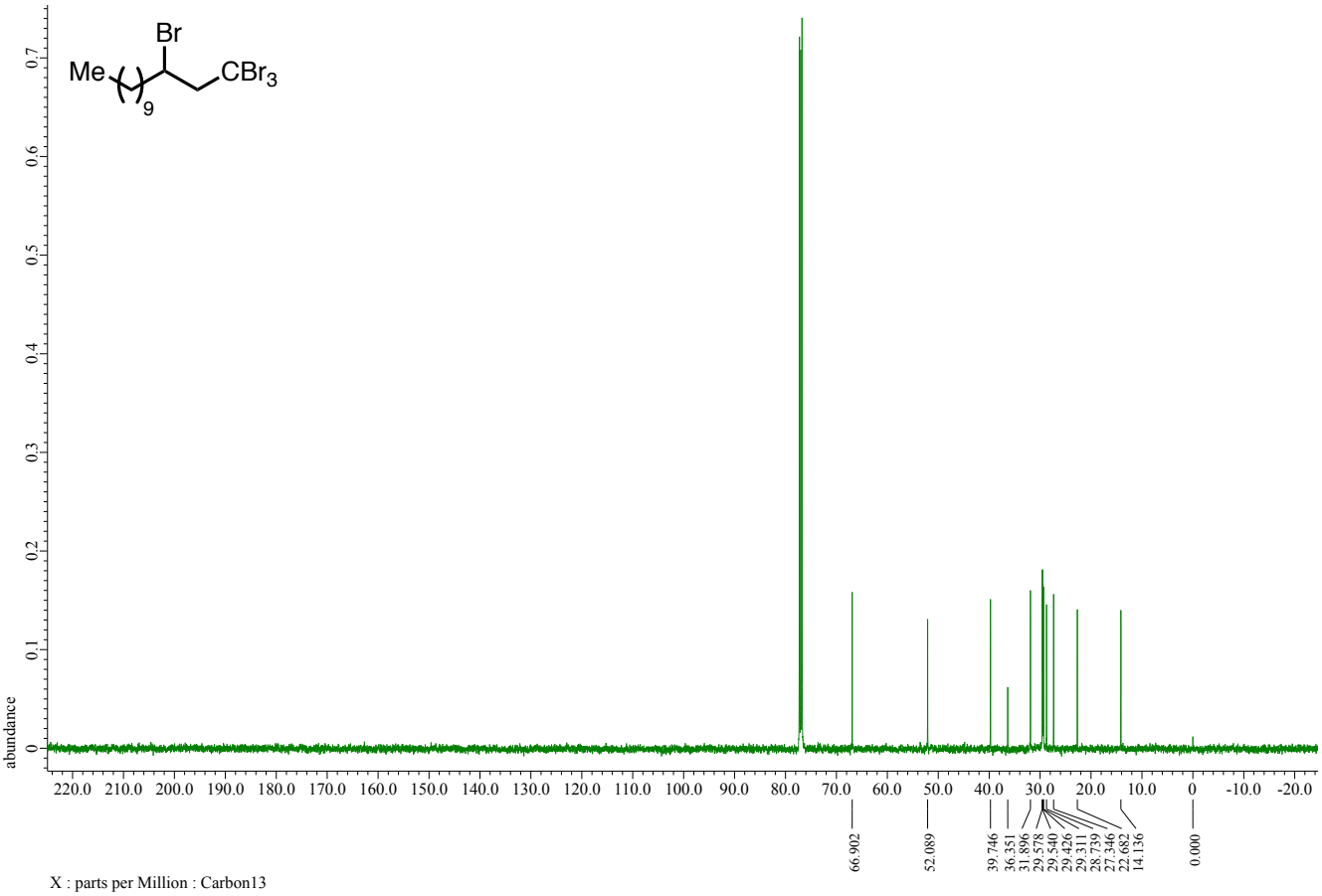
^{13}C NMR (125 MHz, $CDCl_3$) spectra of 3q



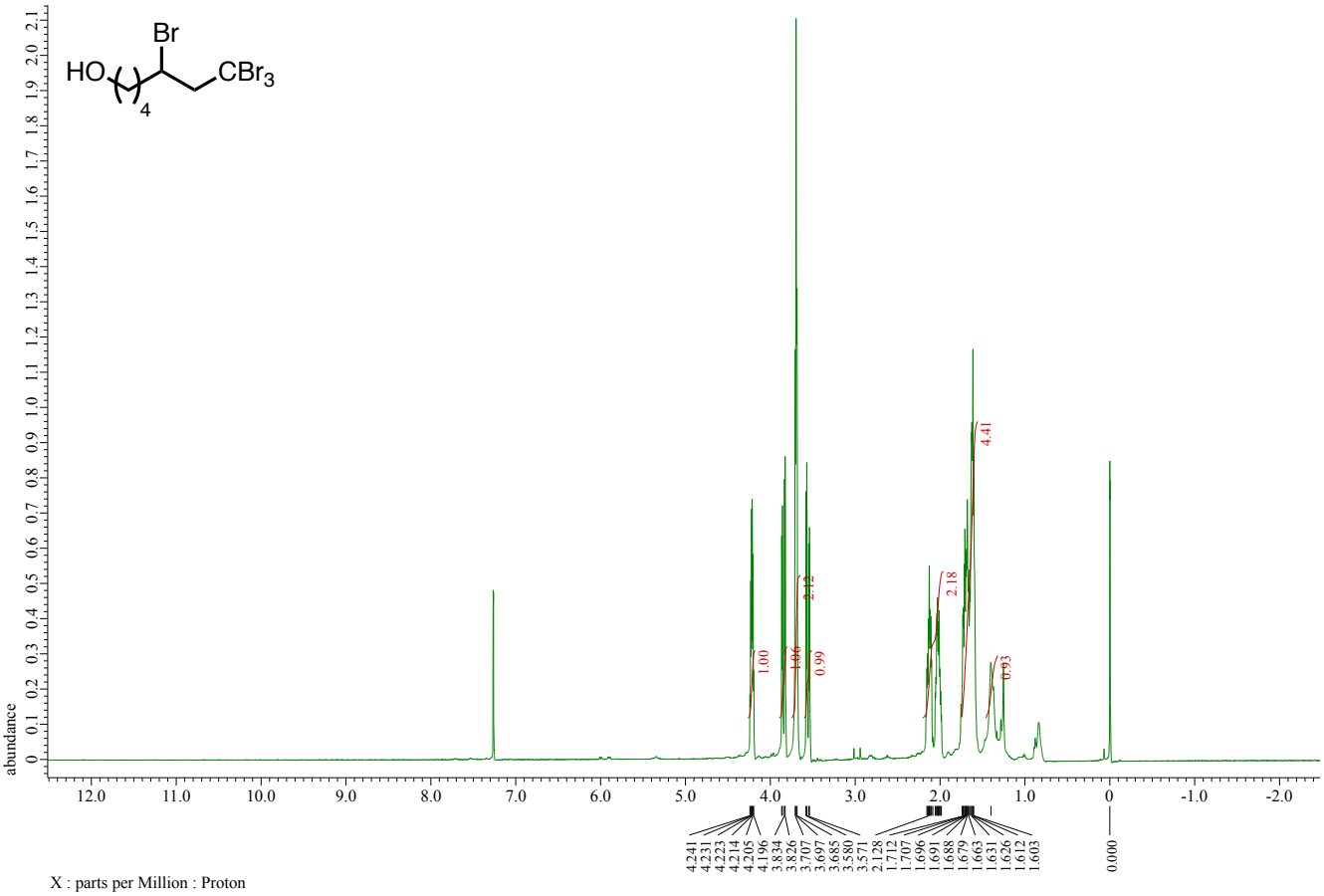
^{1}H NMR (500 MHz, $CDCl_3$) spectra of 3r



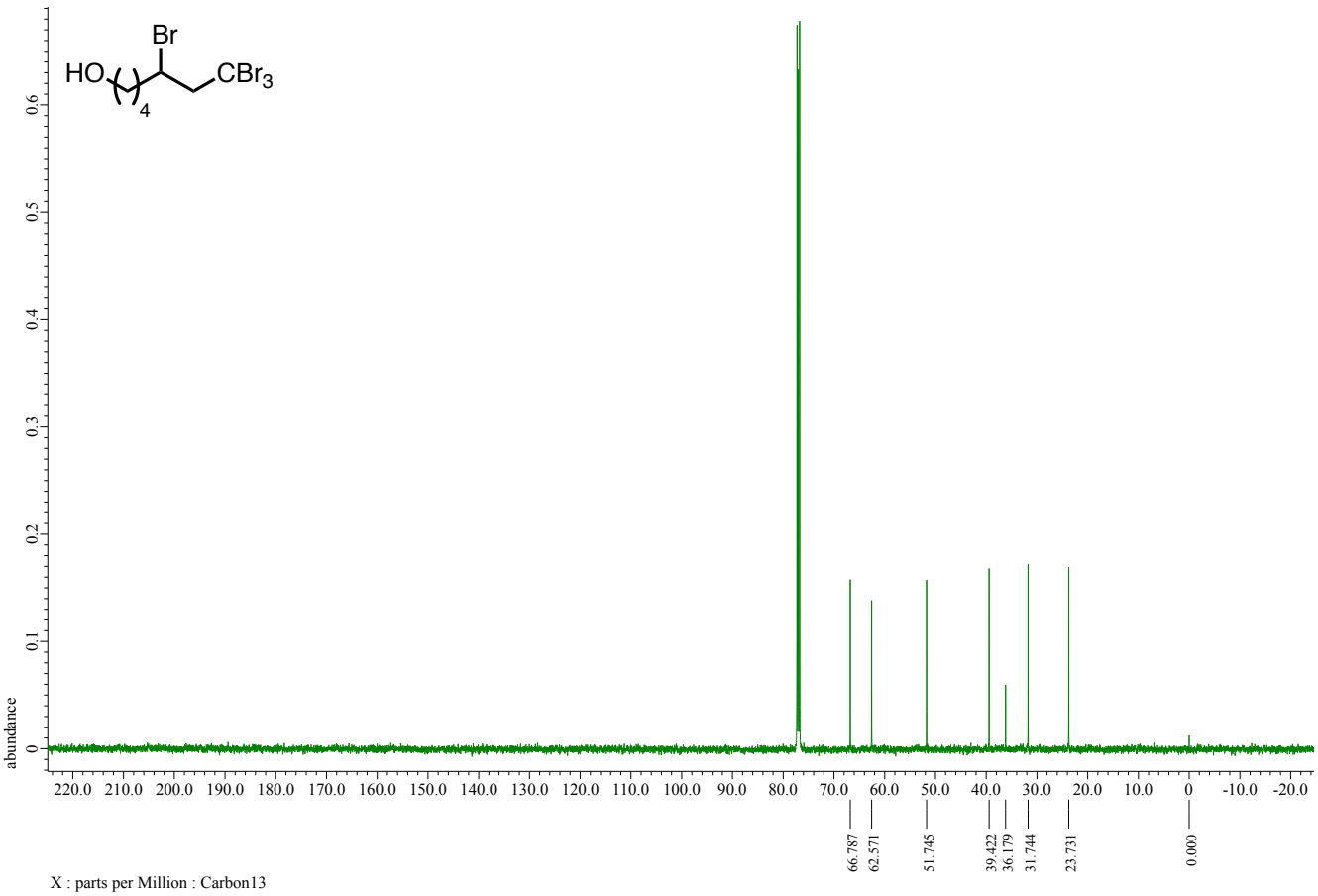
^{13}C NMR (125 MHz, $CDCl_3$) spectra of 3r



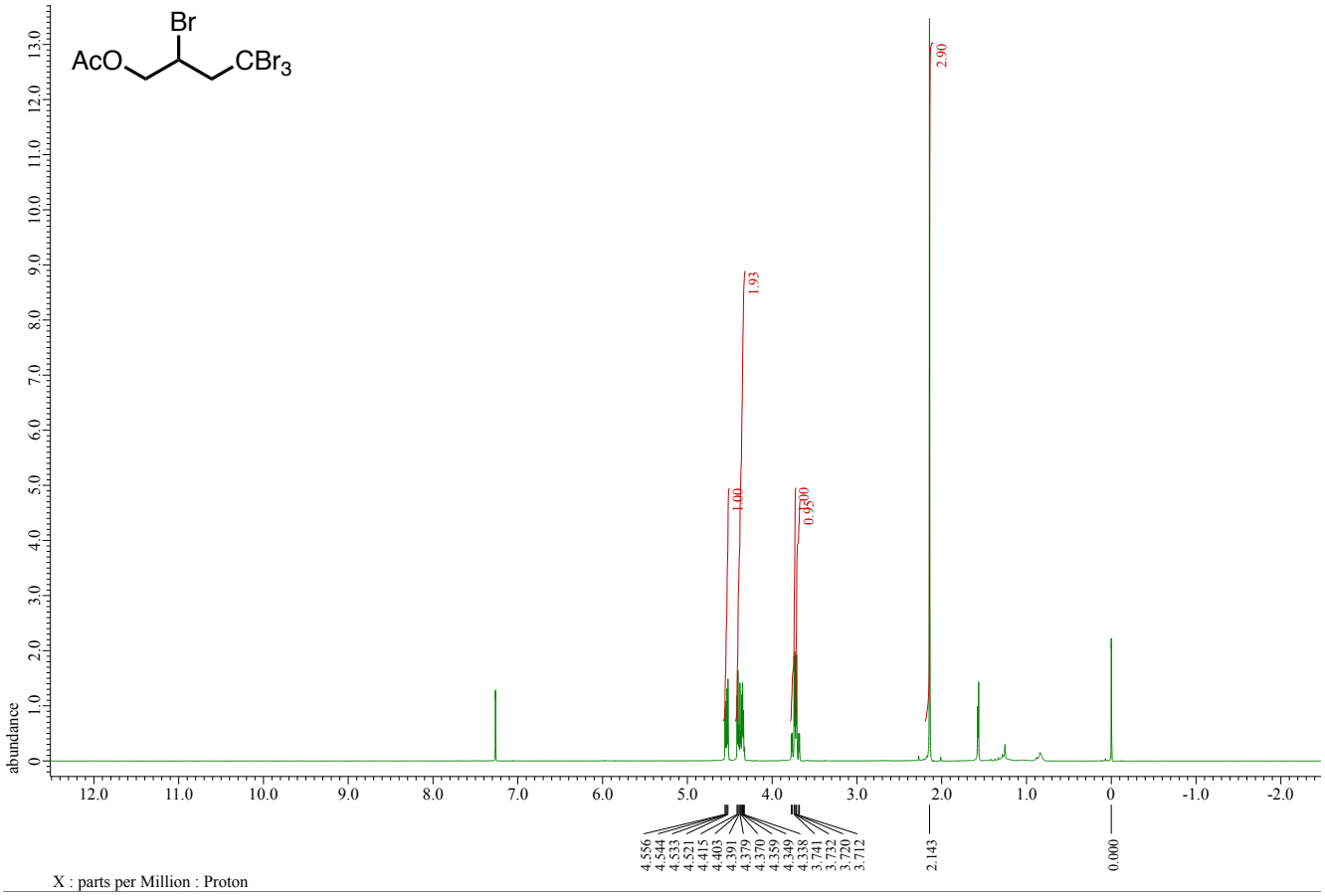
^{1}H NMR (500 MHz, $CDCl_3$) spectra of 3s



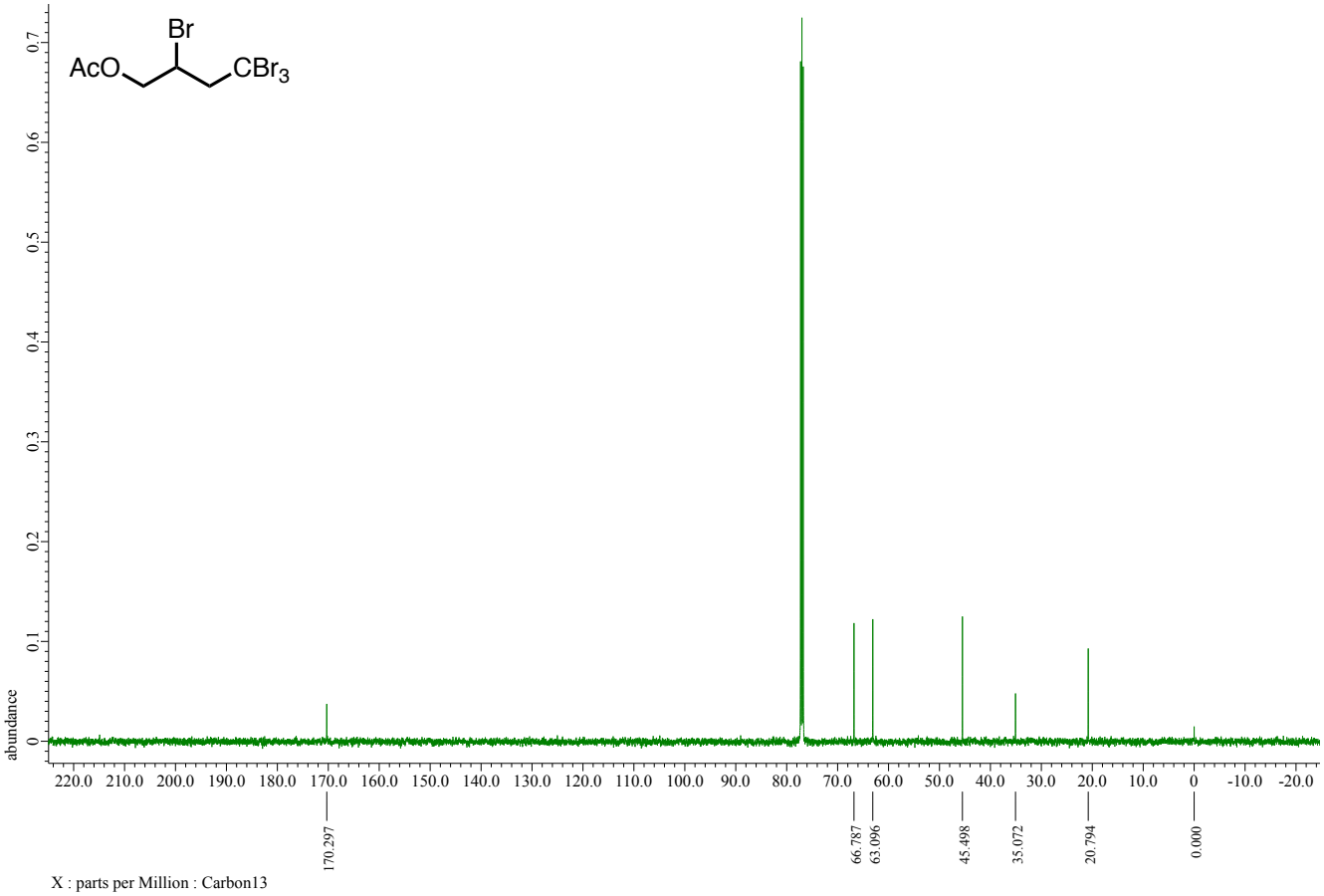
^{13}C NMR (125 MHz, $CDCl_3$) spectra of 3s



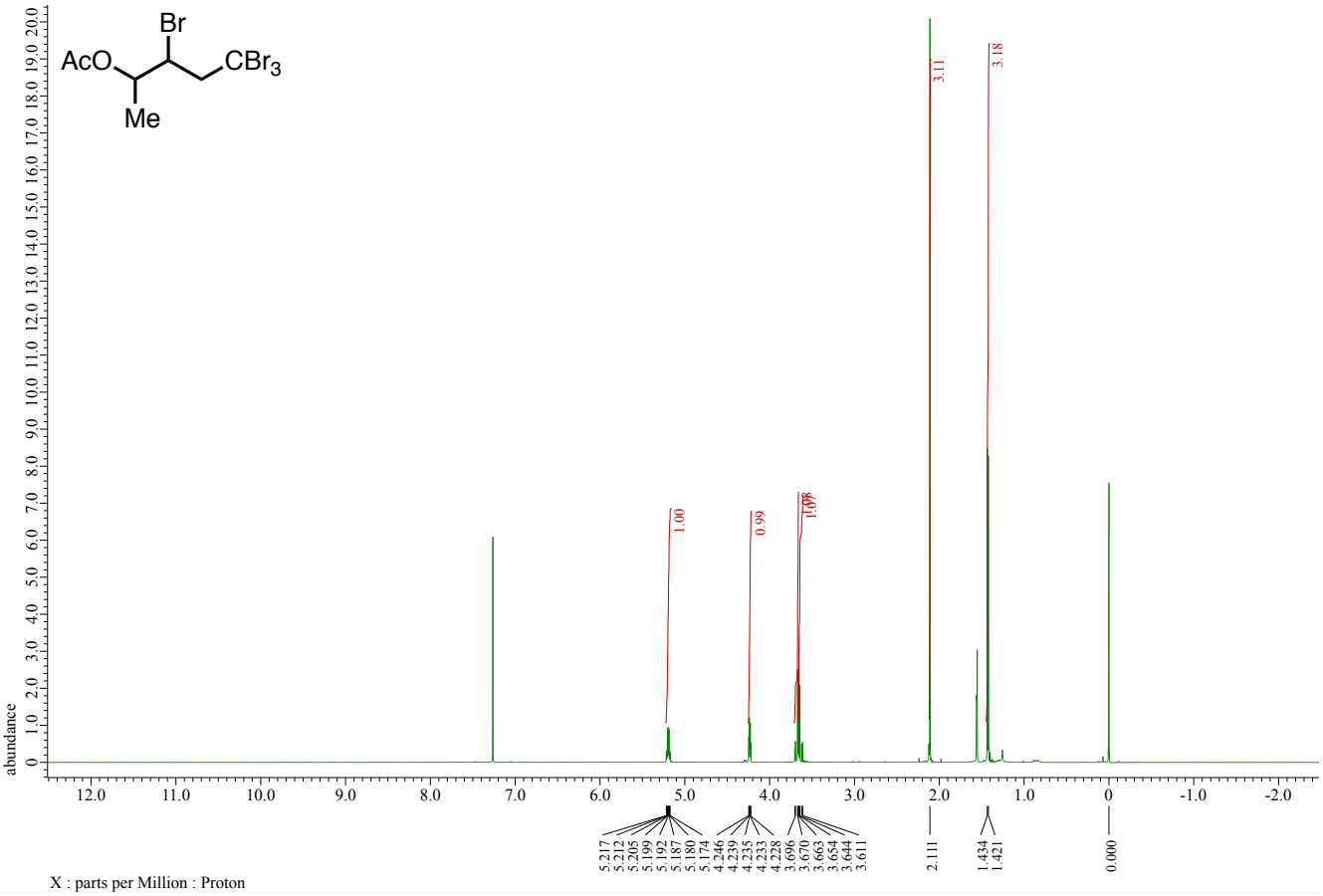
^{1}H NMR (500 MHz, $CDCl_3$) spectra of 3t



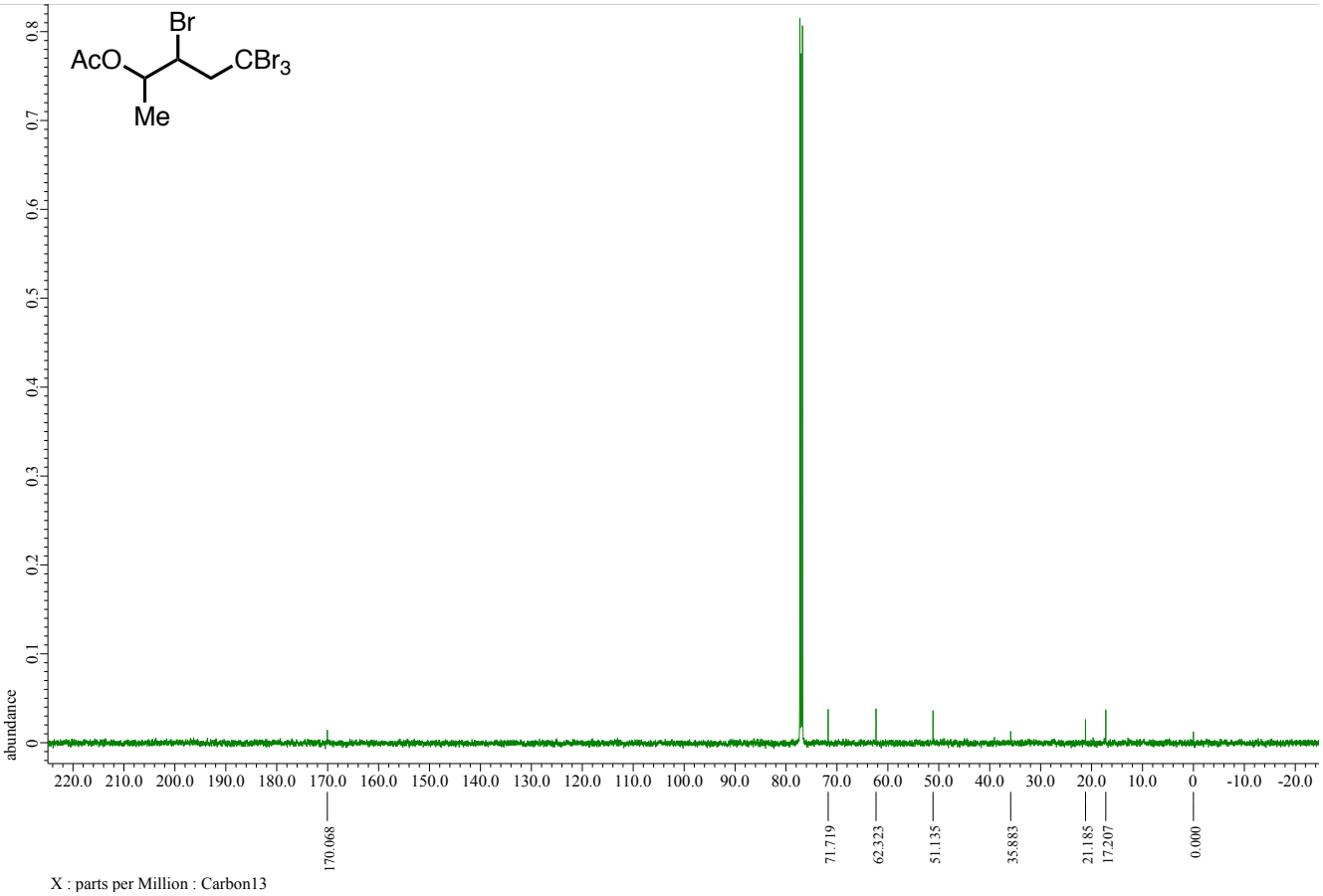
^{13}C NMR (125 MHz, $CDCl_3$) NMR spectra of 3t



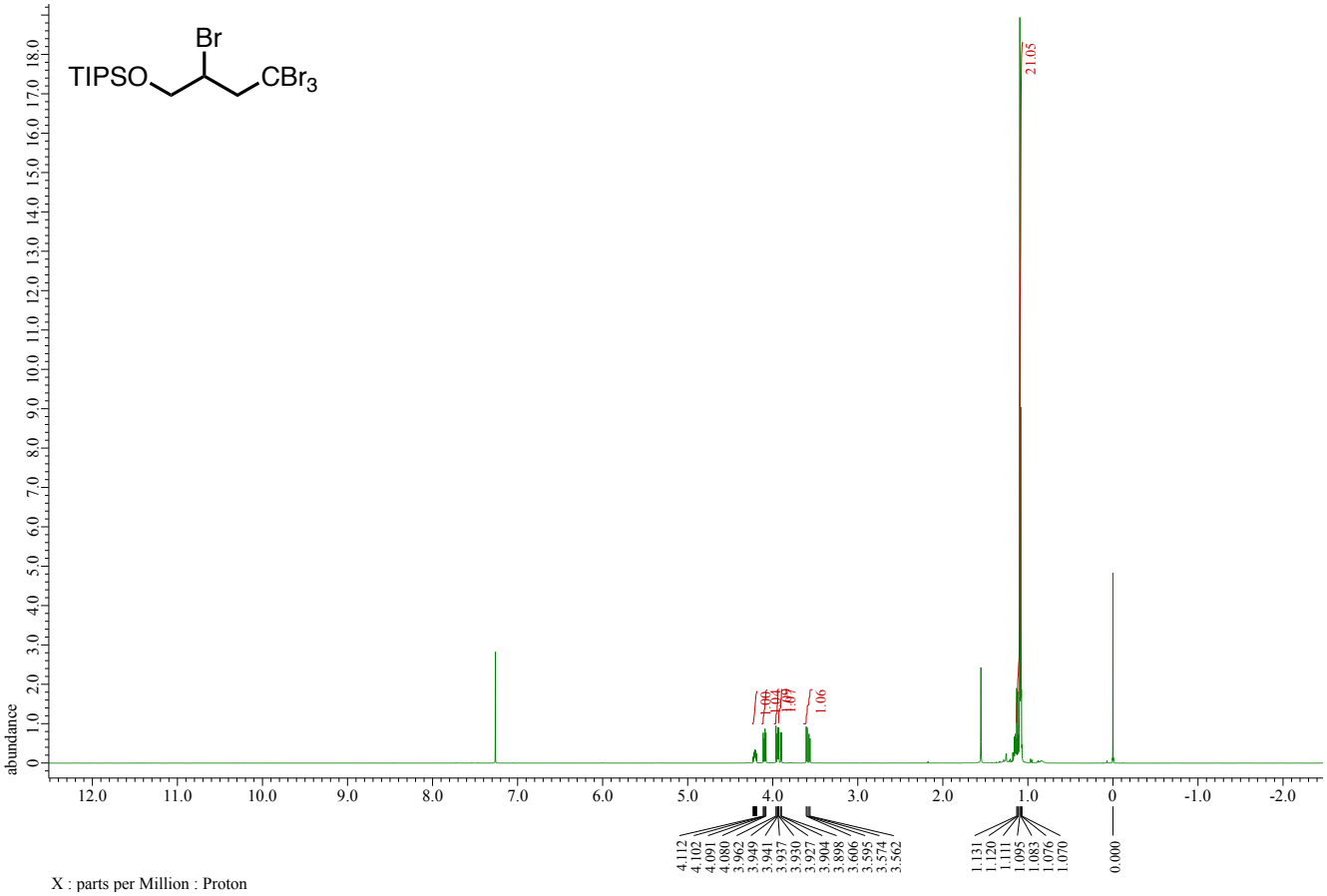
^{1}H NMR (500 MHz, $CDCl_3$) spectra of 3u



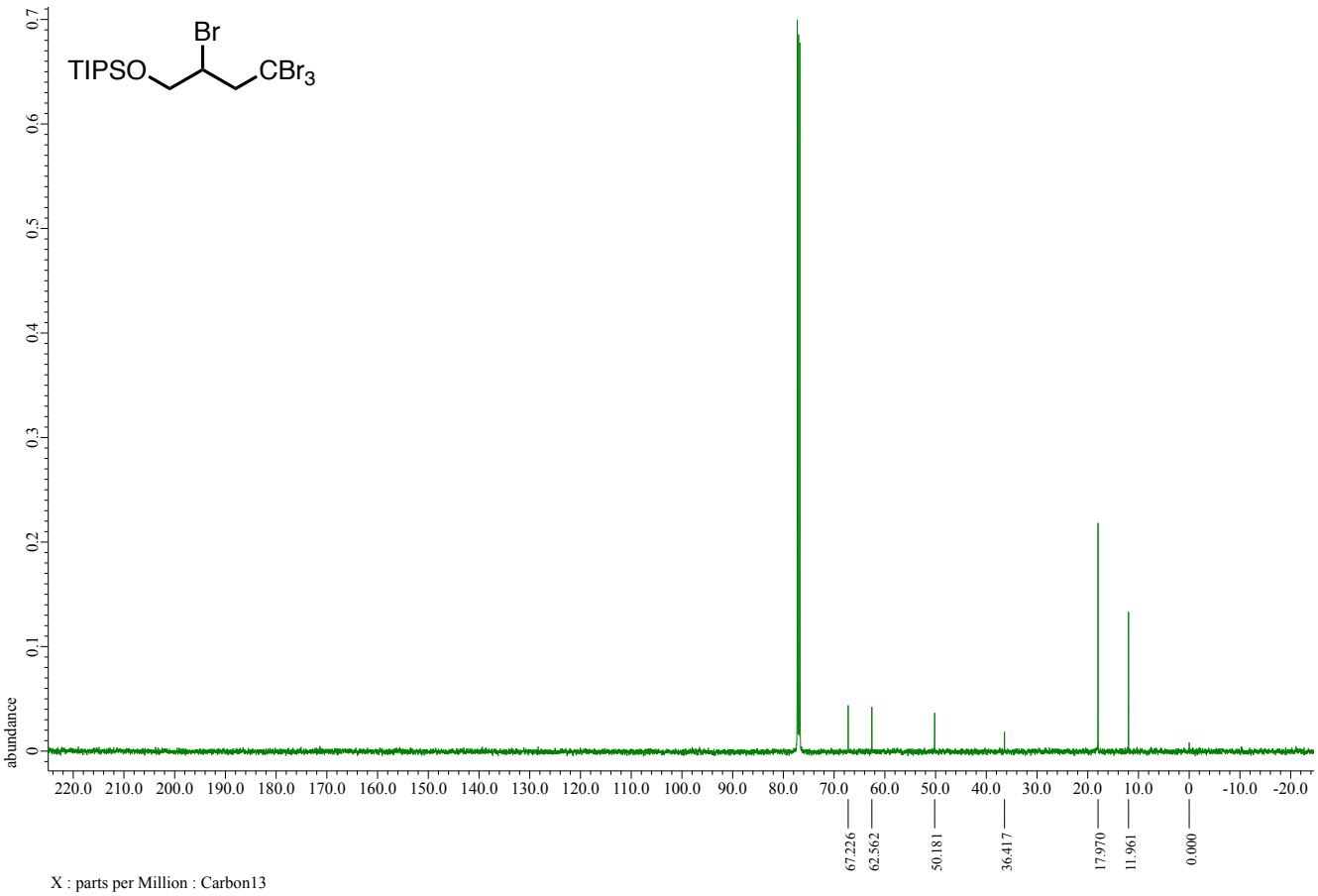
^{13}C NMR (125 MHz, $CDCl_3$) spectra of 3u



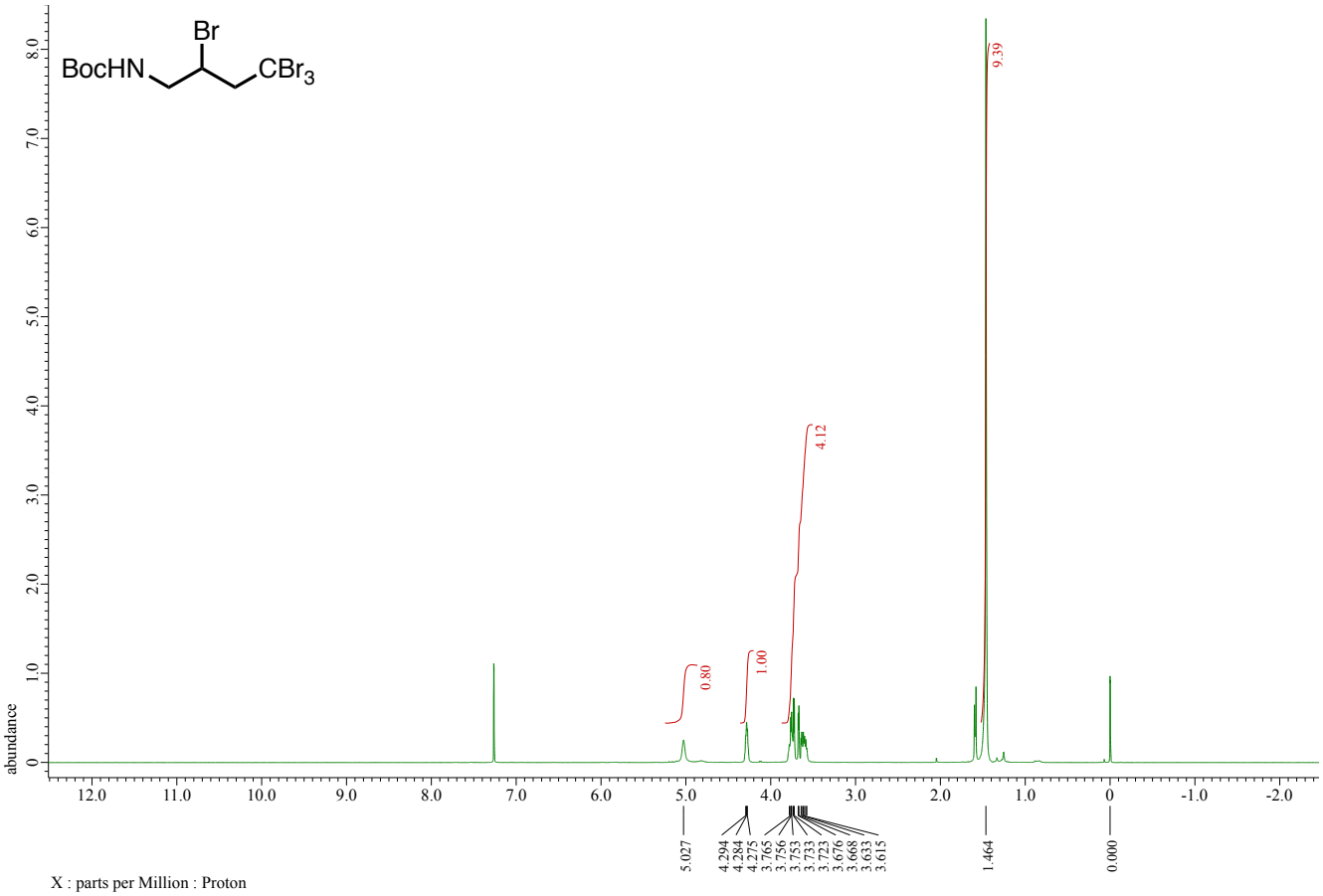
^{1}H NMR (500 MHz, $CDCl_3$) spectra of 3v



^{13}C NMR (125 MHz, $CDCl_3$) spectra of 3v

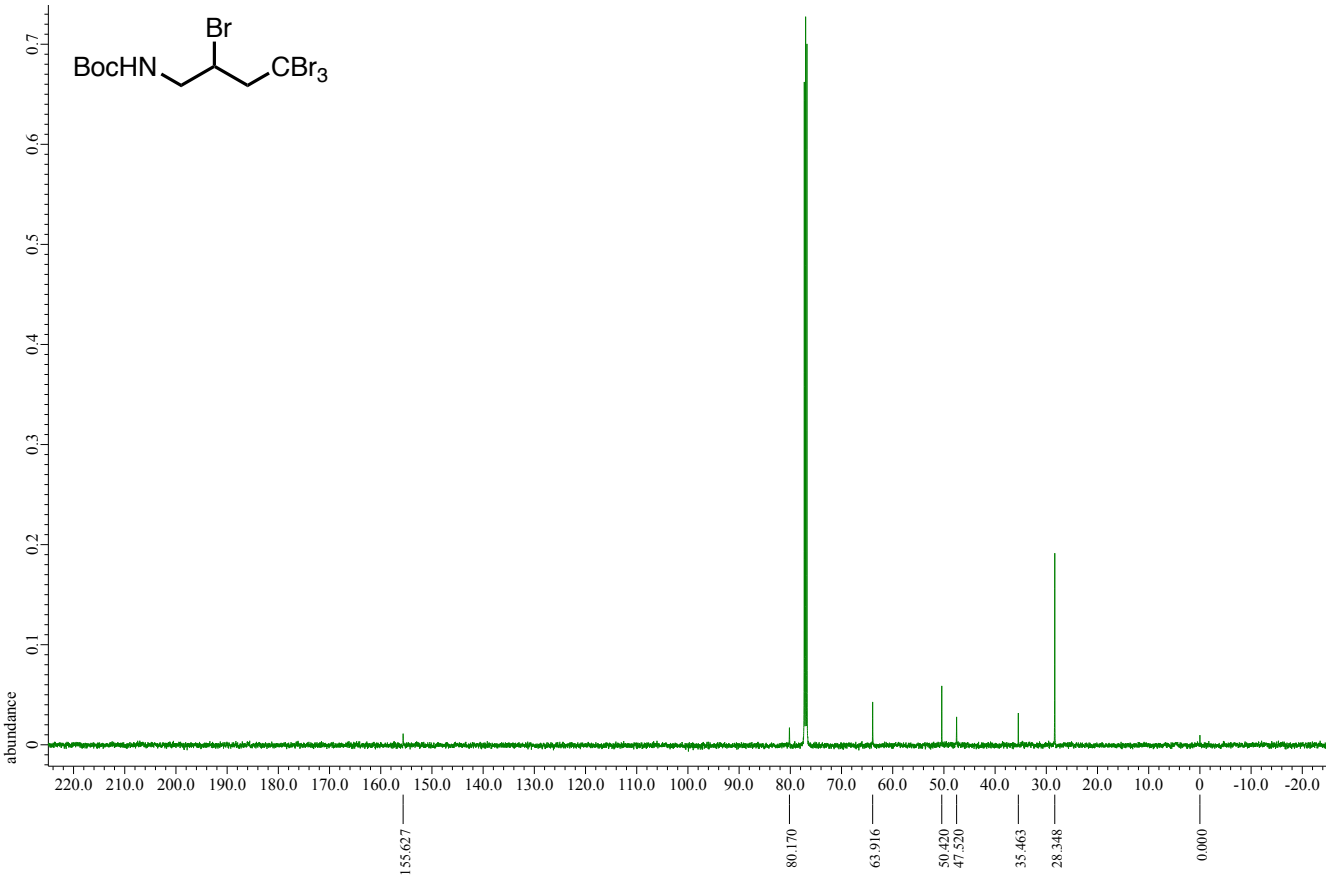


^{1}H NMR (500 MHz, $CDCl_3$) spectra of 3w



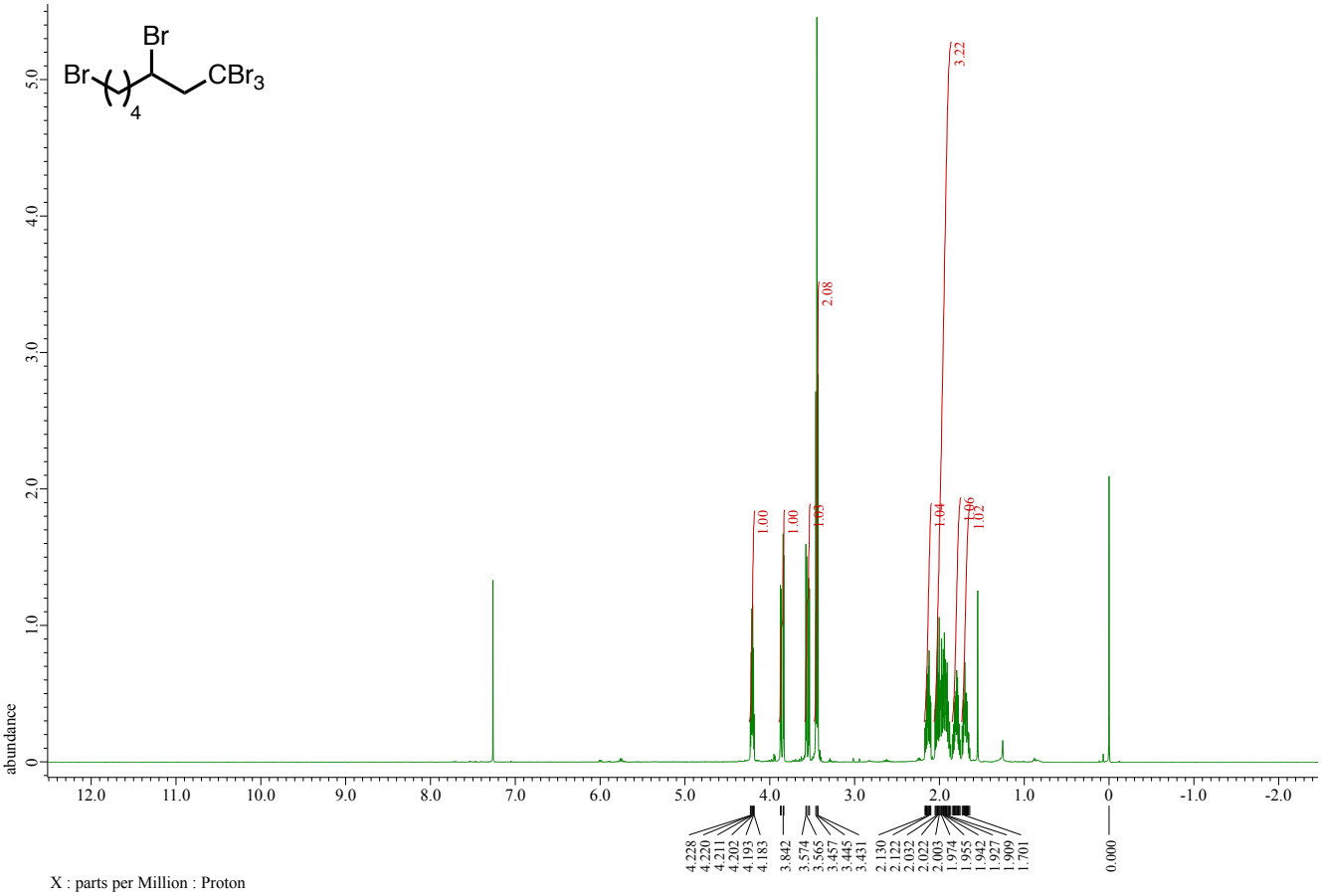
X : parts per Million : Proton

^{13}C NMR (125 MHz, $CDCl_3$) spectra of 3w

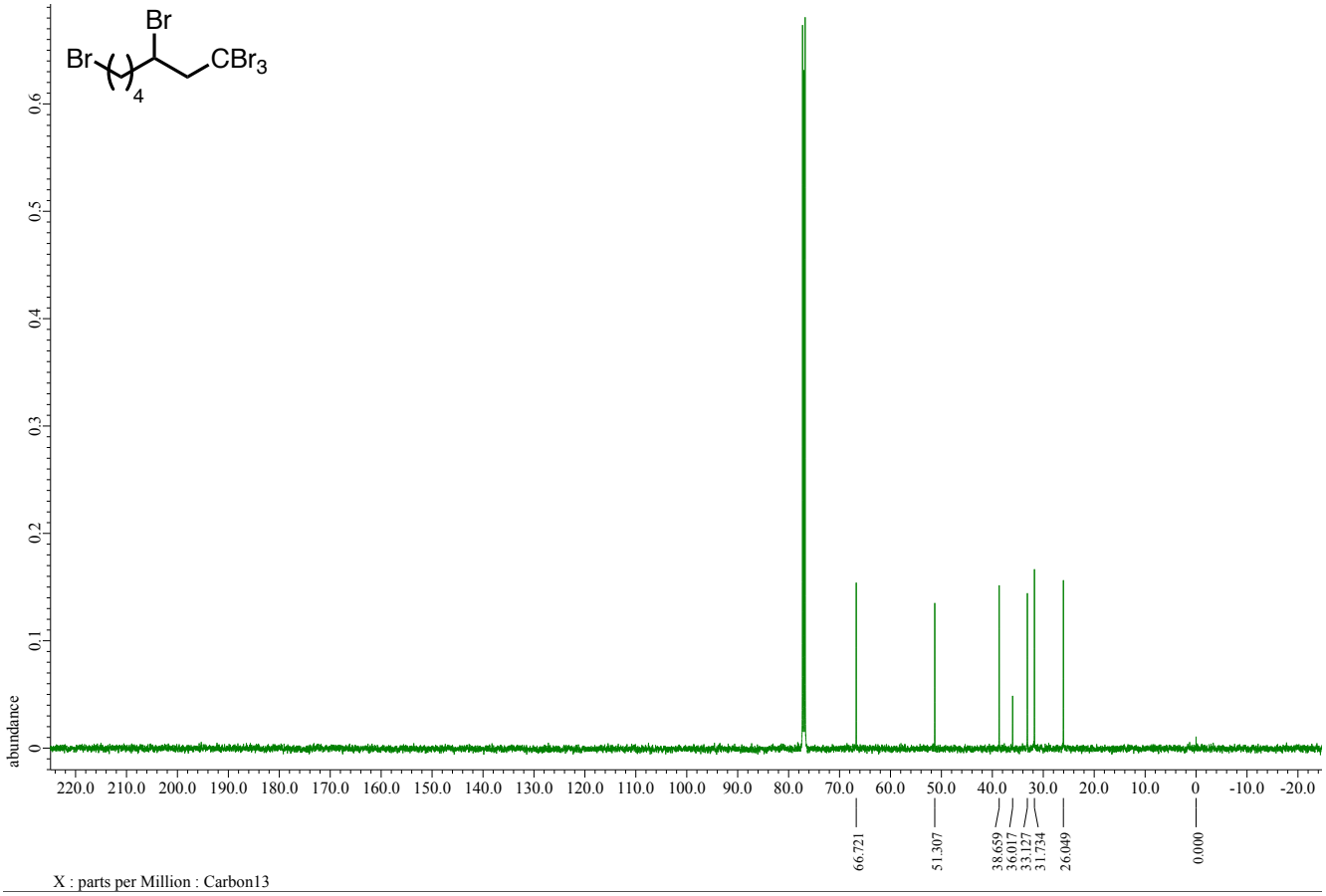


X : parts per Million : Carbon13

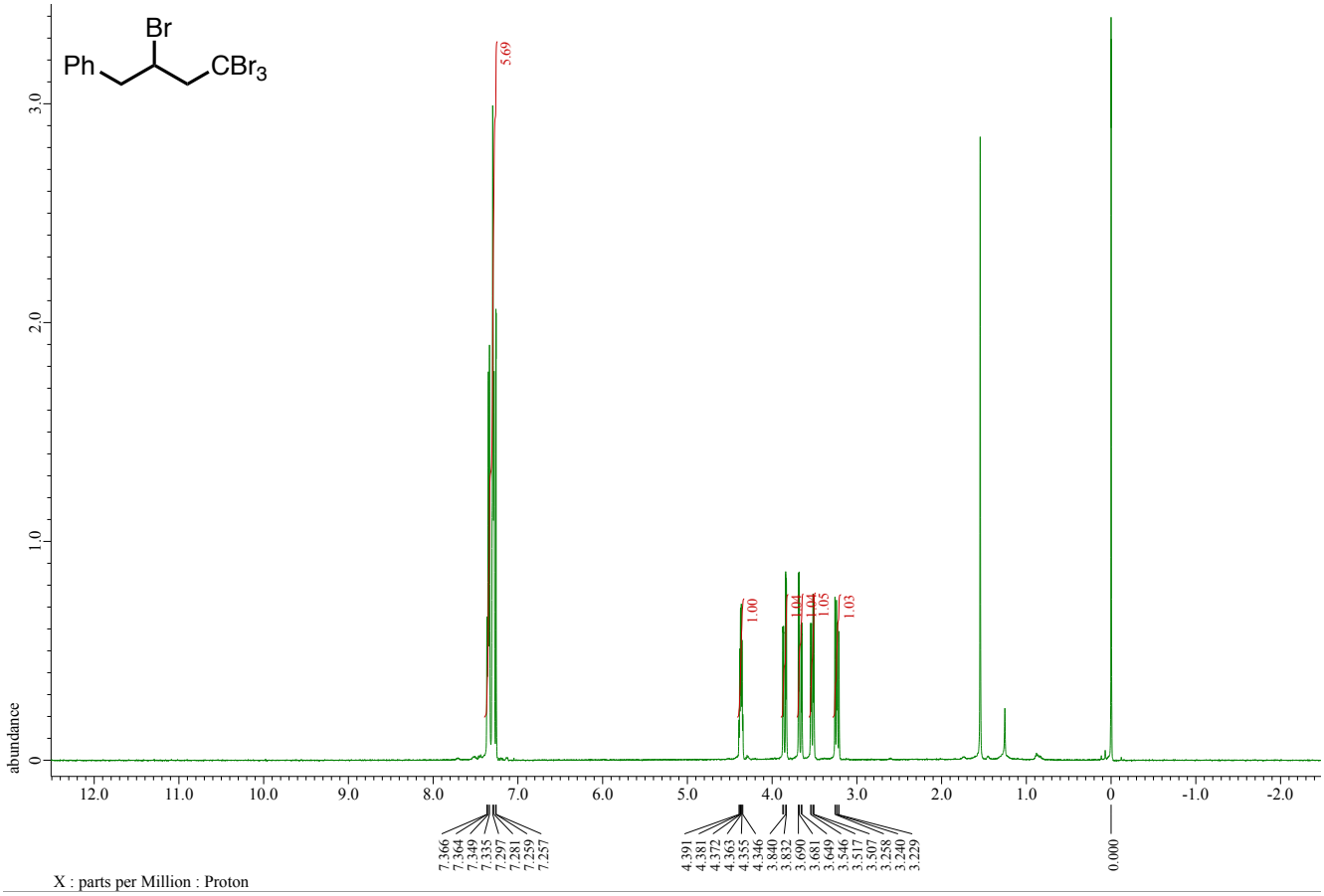
^{1}H NMR (500 MHz, $CDCl_3$) spectra of 3x



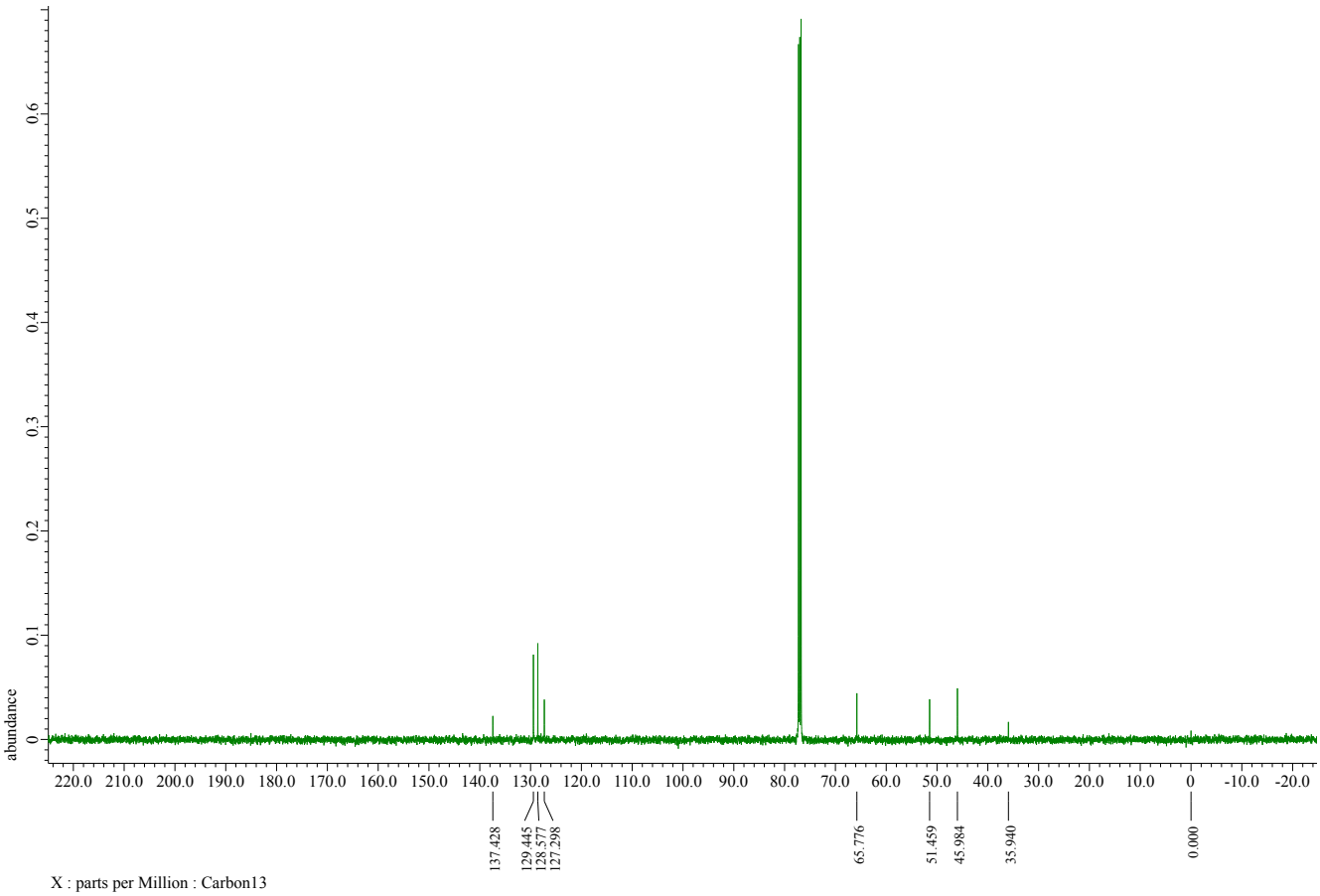
^{13}C NMR (125 MHz, $CDCl_3$) spectra of 3x



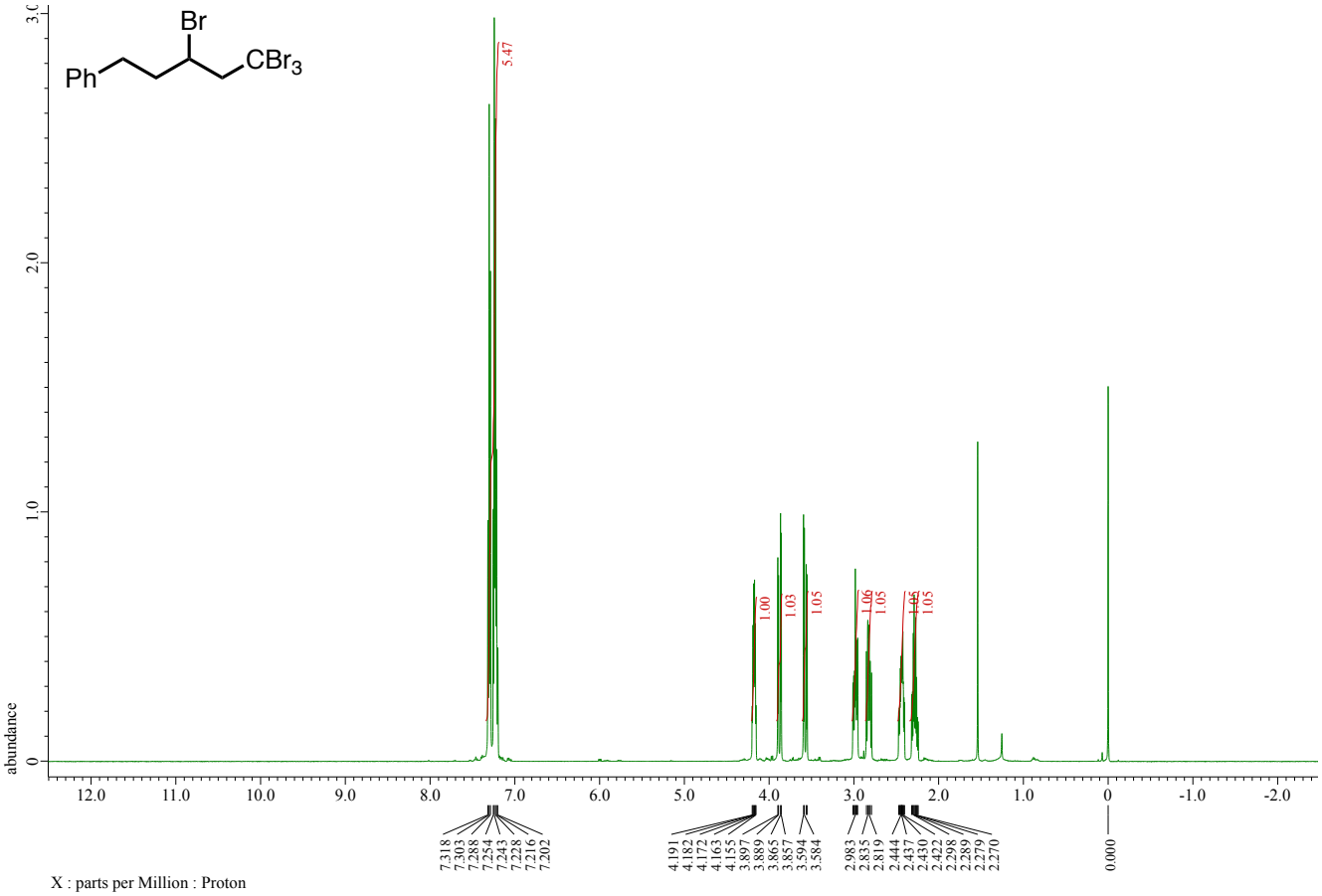
^{1}H NMR (500 MHz, $CDCl_3$) spectra of 3y



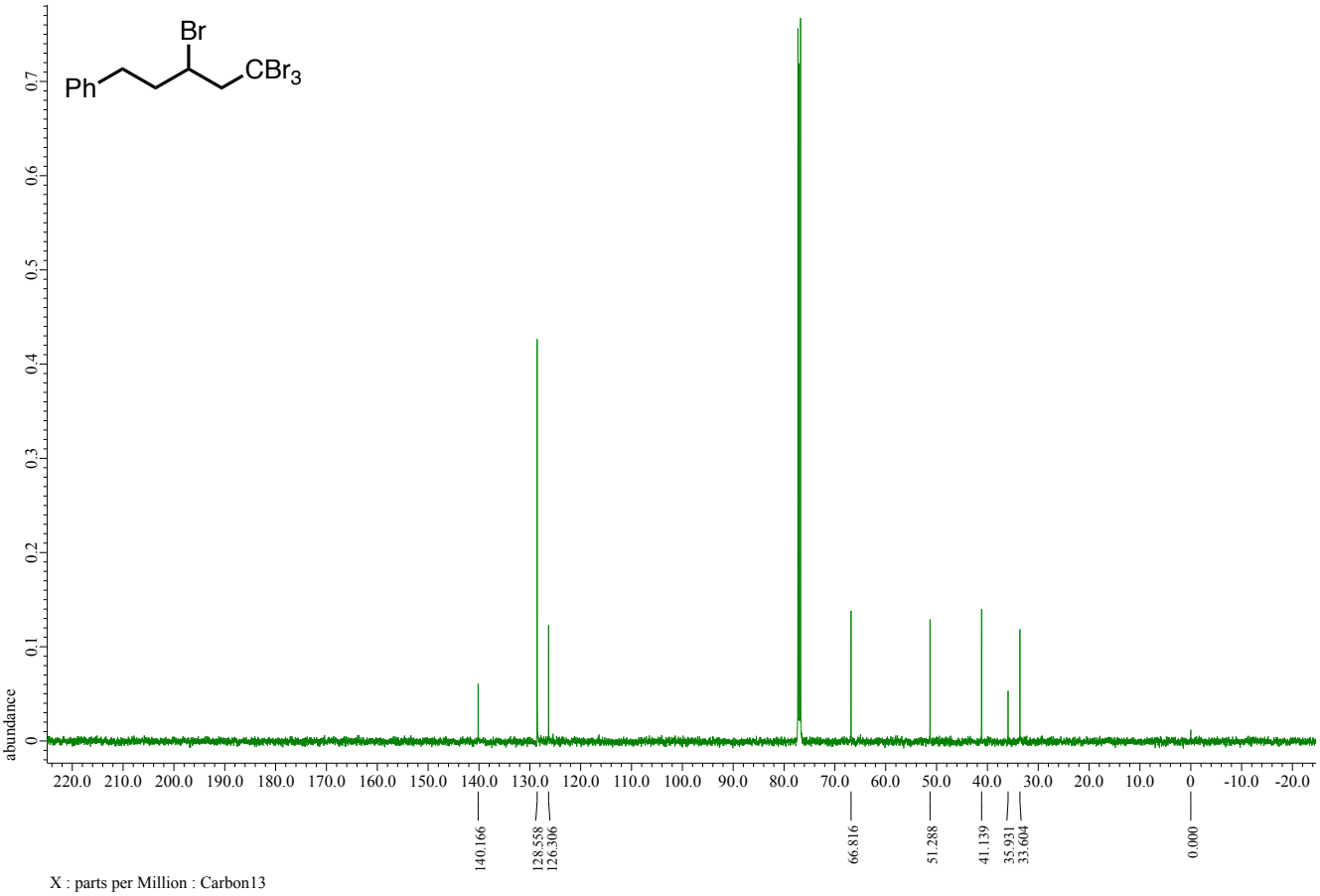
^{13}C NMR (125 MHz, $CDCl_3$) spectra of 3y



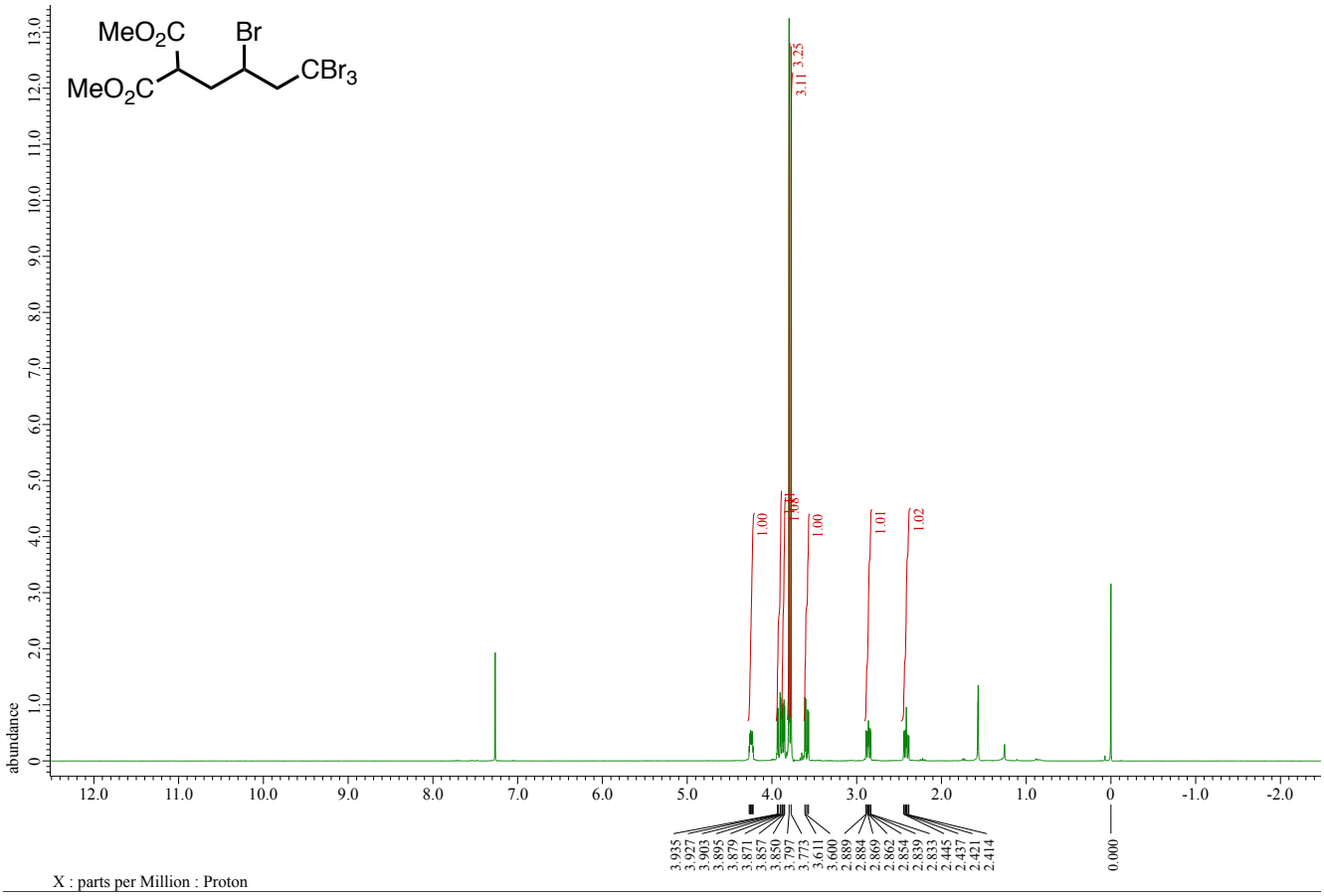
^{1}H NMR (500 MHz, $CDCl_3$) spectra of 3z



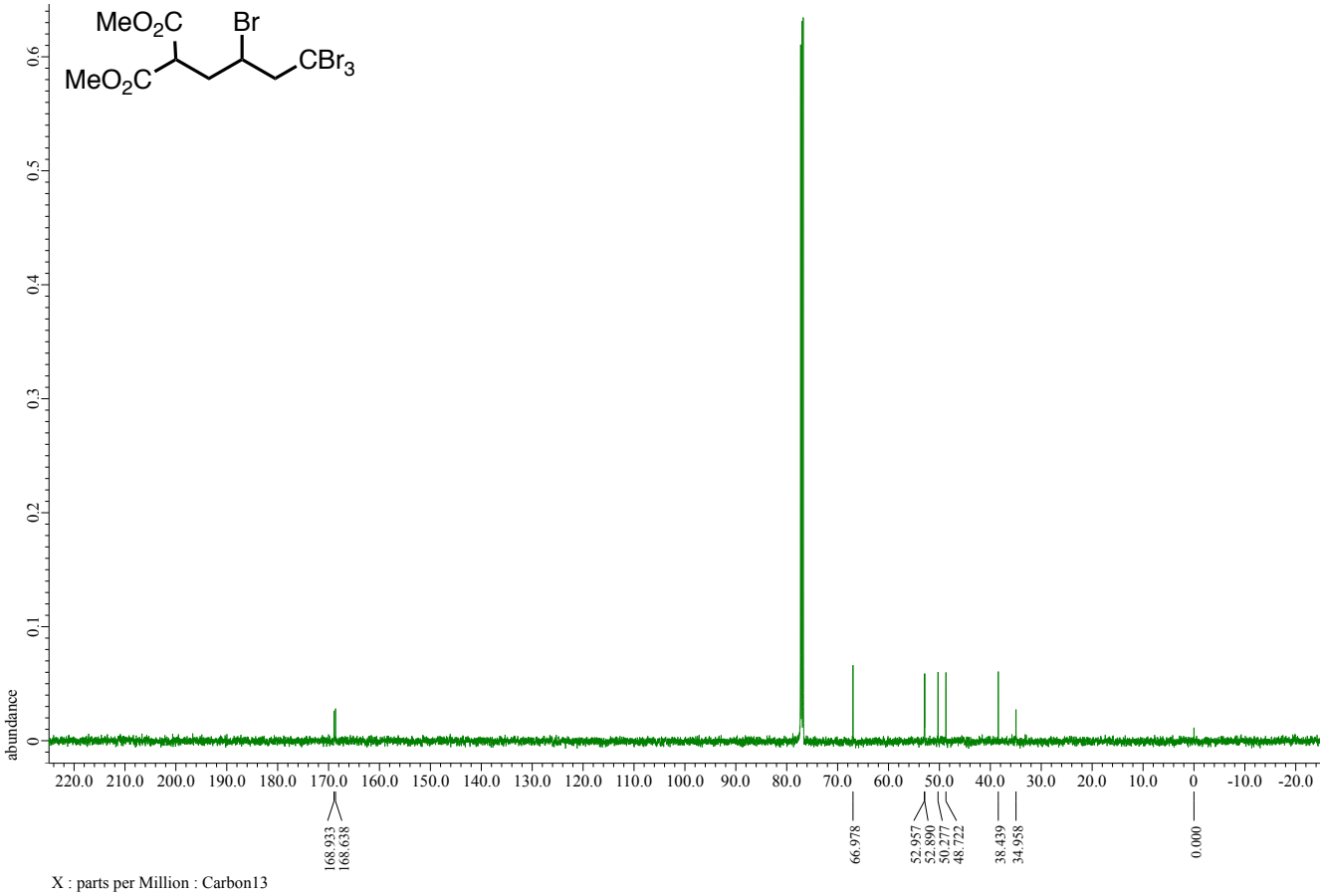
^{13}C NMR (125 MHz, $CDCl_3$) spectra of 3z



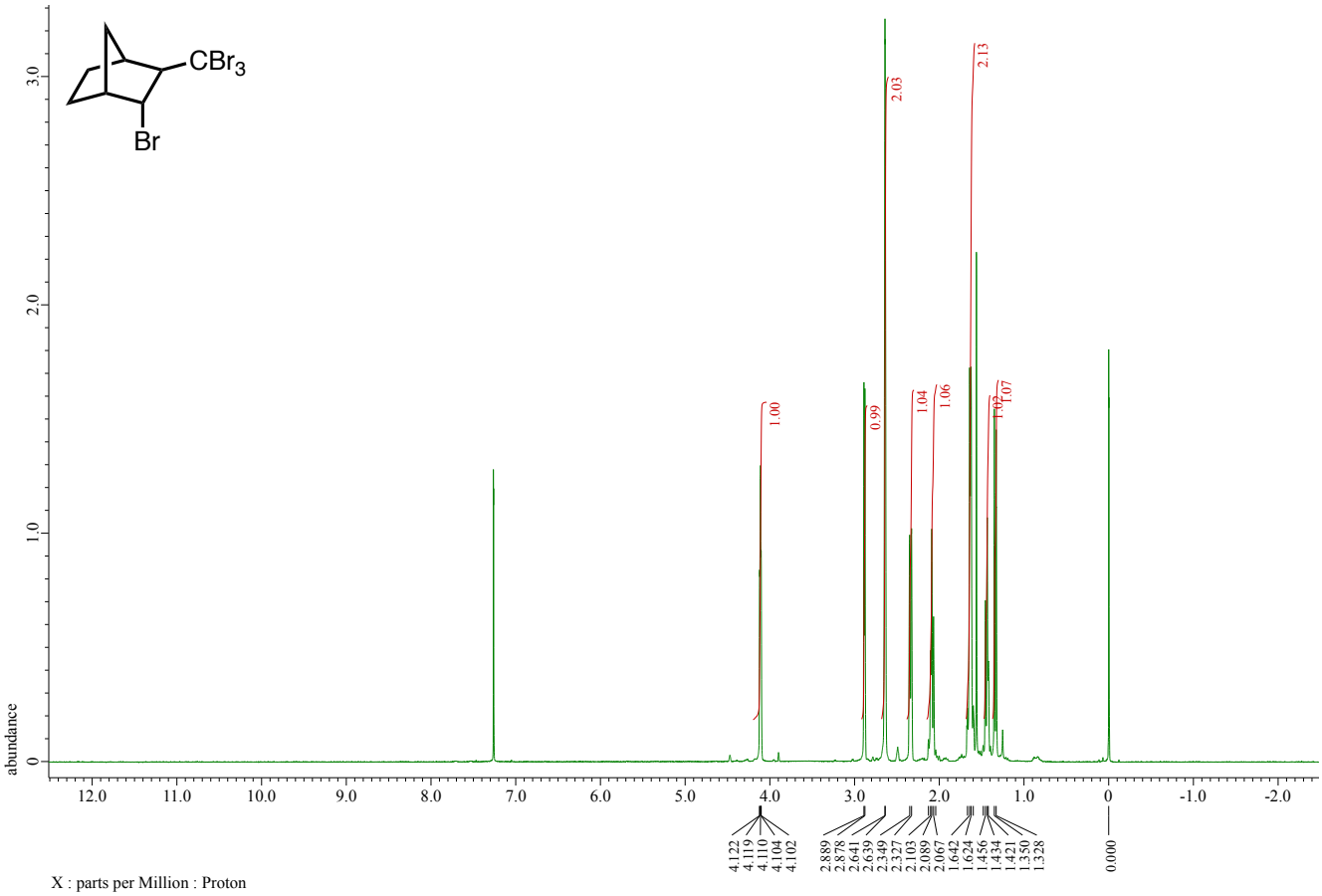
^{1}H NMR (500 MHz, $CDCl_3$) spectra of 3aa



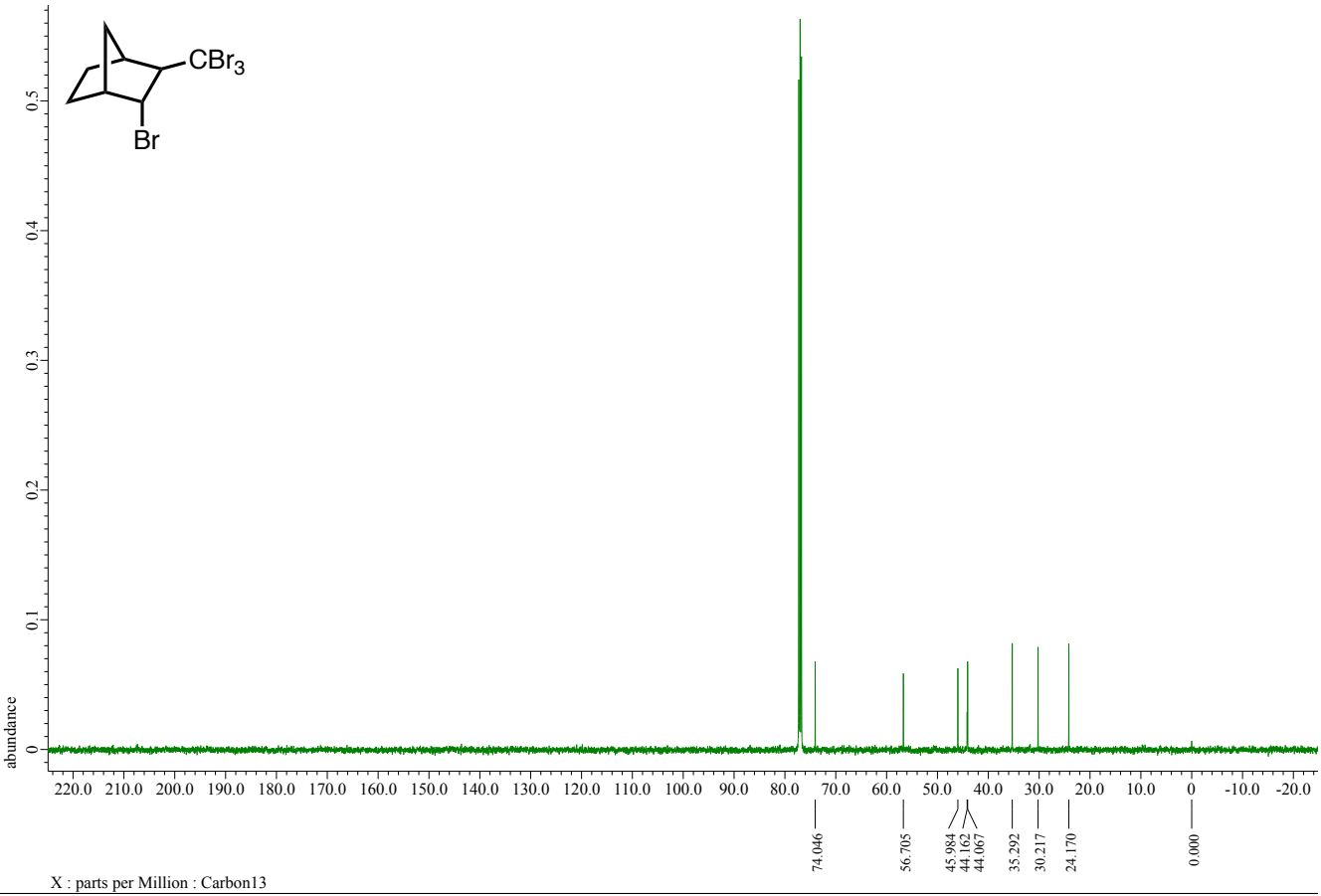
^{13}C NMR (125 MHz, $CDCl_3$) spectra of 3aa



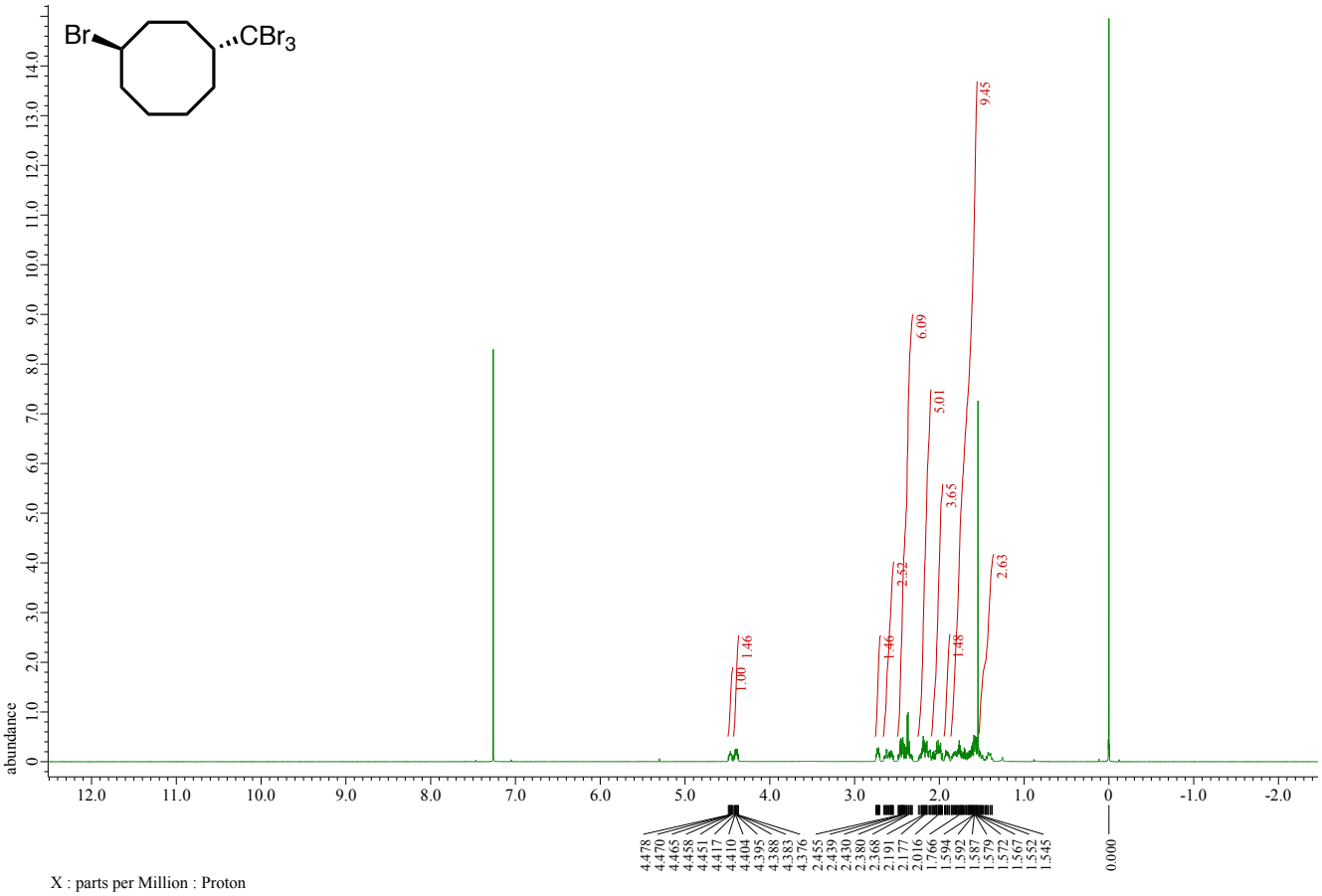
^{1}H NMR (500 MHz, $CDCl_3$) spectra of 3ab



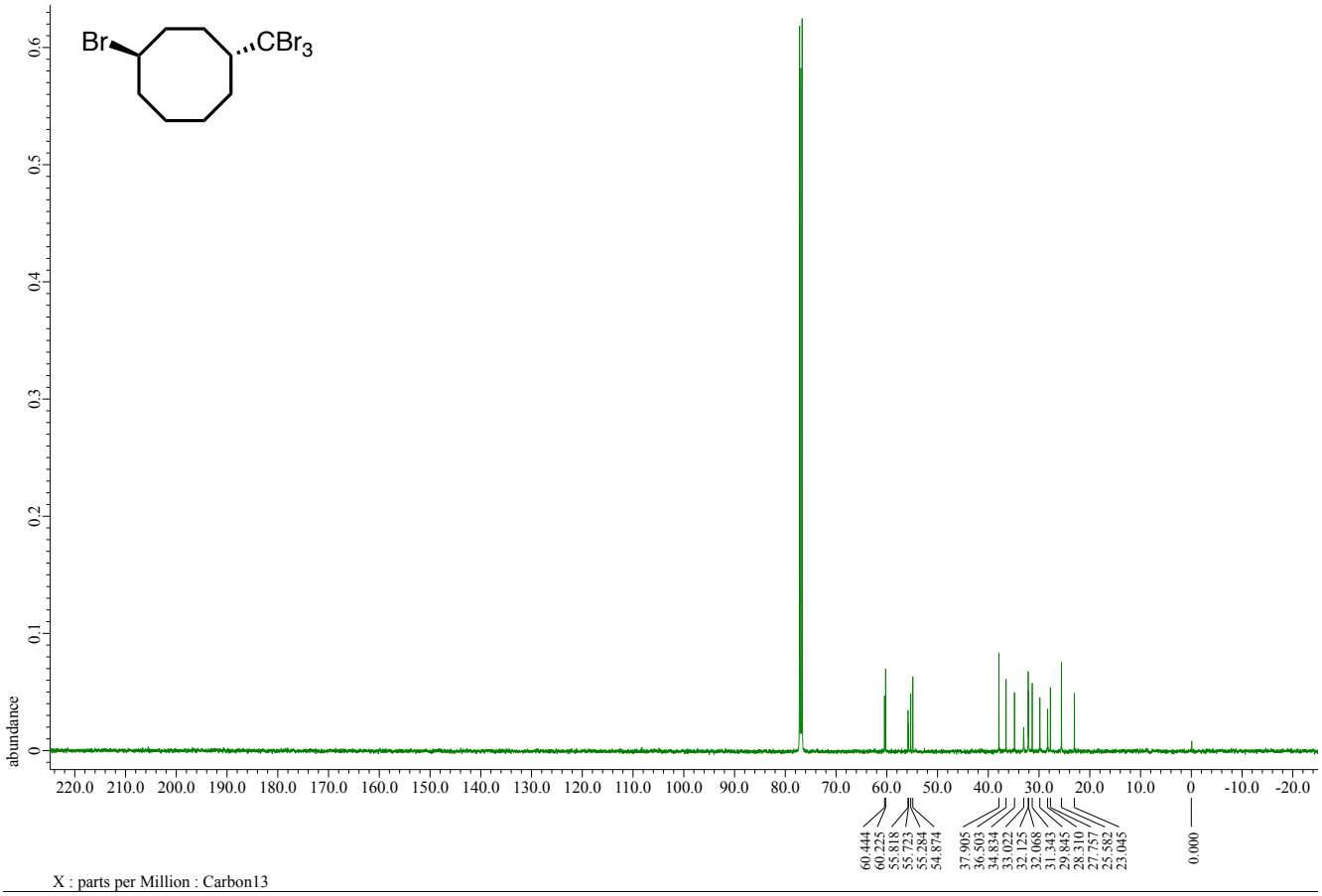
^{13}C NMR (125 MHz, $CDCl_3$) spectra of 3ab



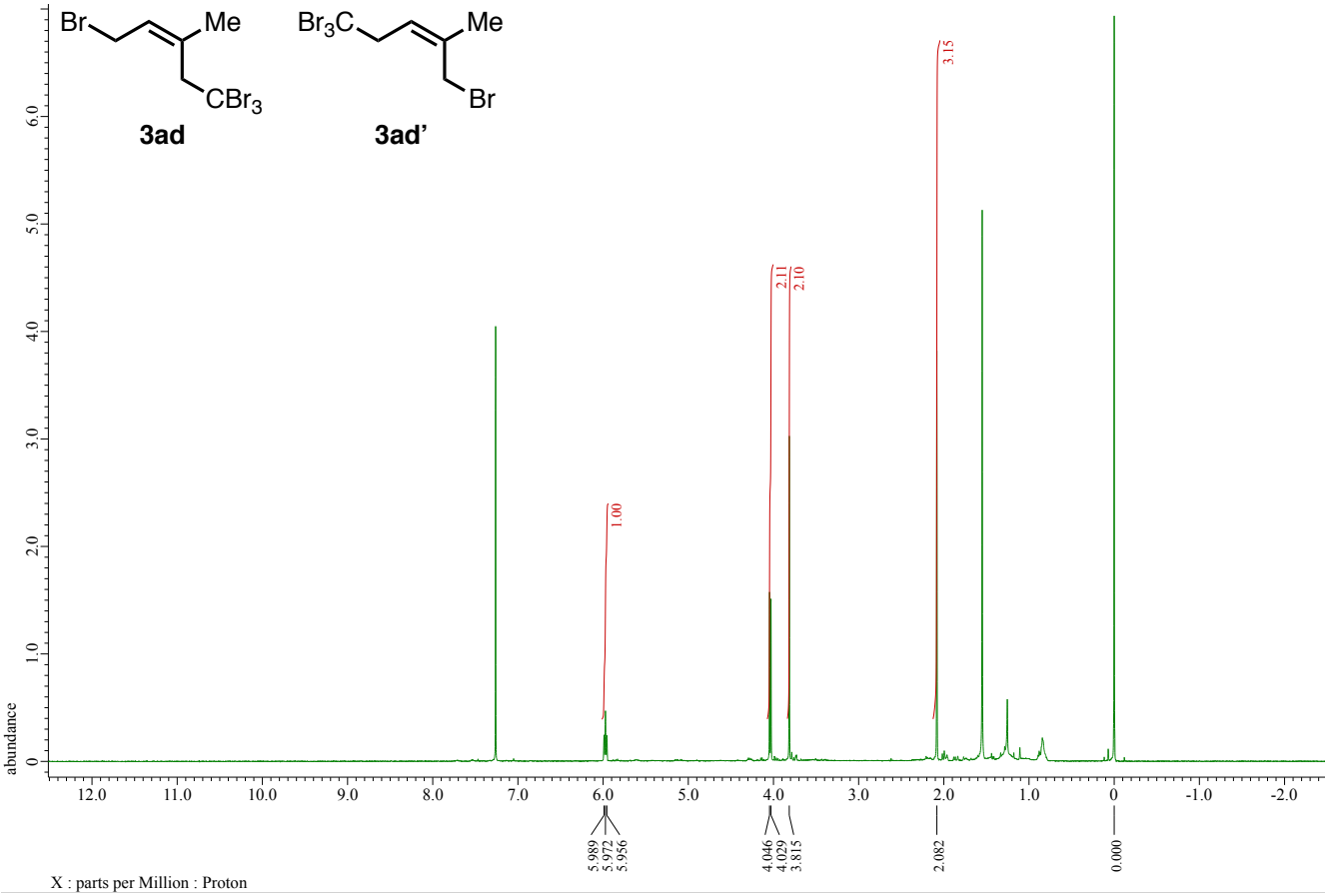
^{1}H NMR (500 MHz, $CDCl_3$) spectra of 3ac



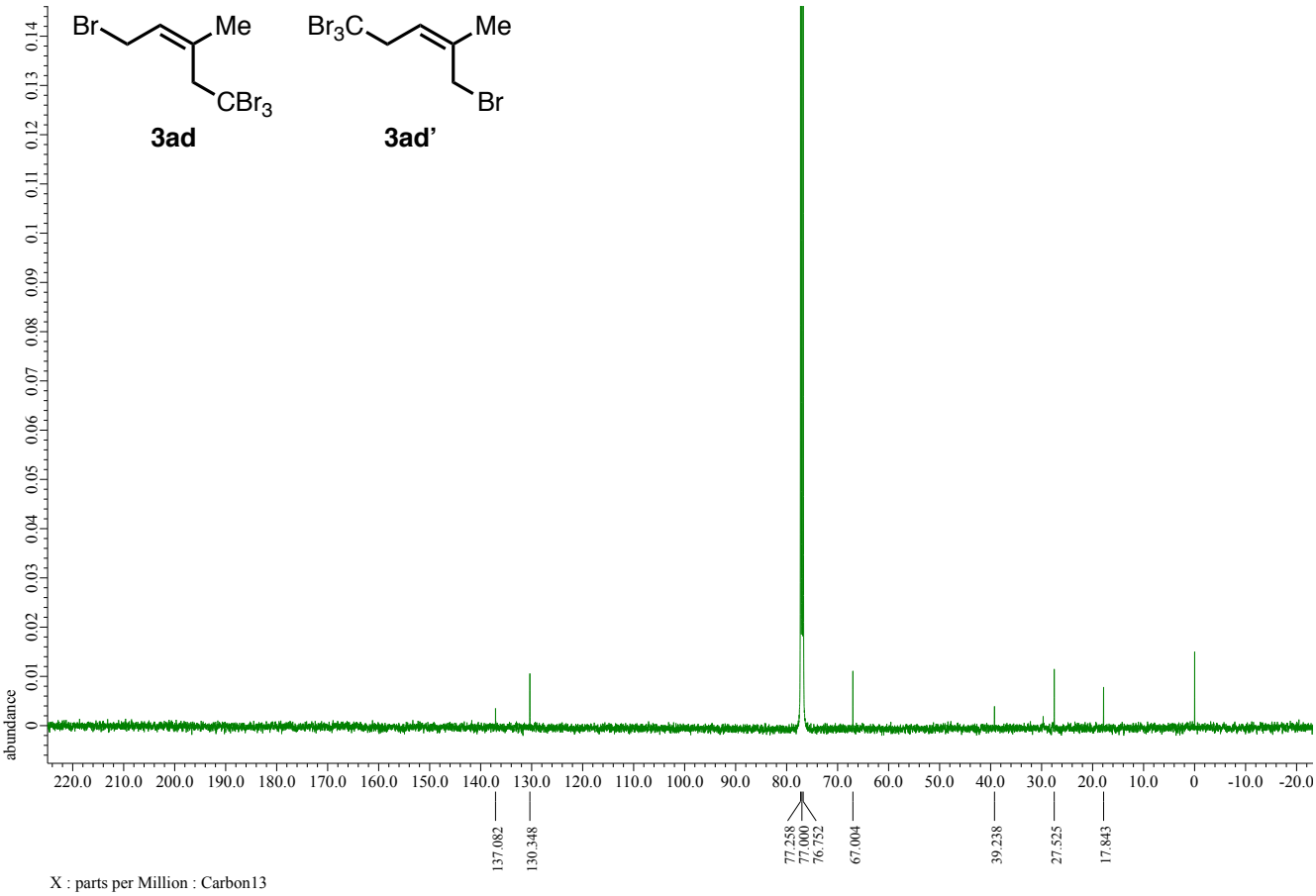
^{13}C NMR (125 MHz, $CDCl_3$) spectra of 3ac



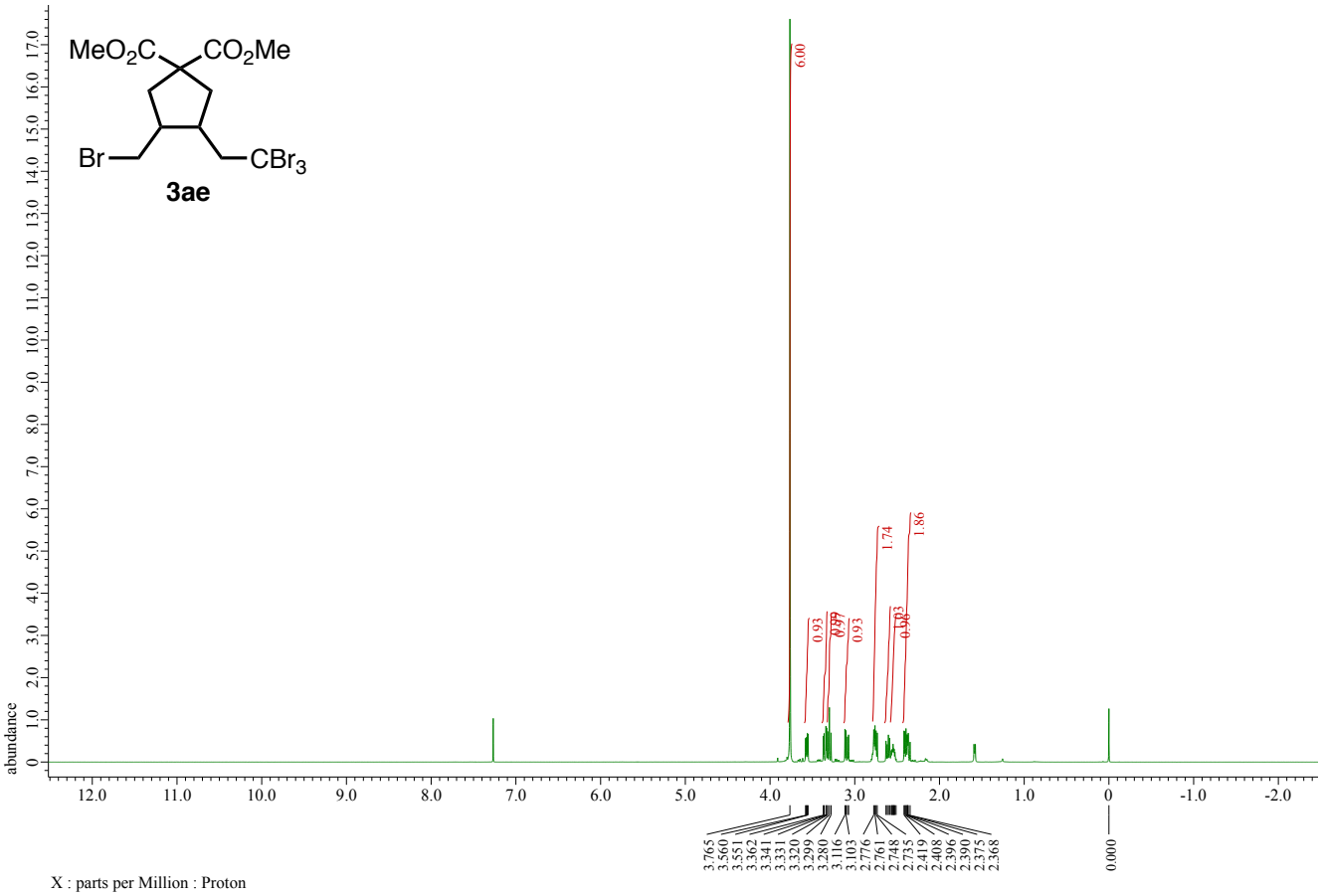
^{1}H NMR (500 MHz, $CDCl_3$) spectra of 3ad



^{13}C NMR (125 MHz, $CDCl_3$) spectra of 3ad



^{1}H NMR (500 MHz, $CDCl_3$) spectra of 3ae



^{13}C NMR (125 MHz, $CDCl_3$) spectra of 3ae