Supporting Information

A new approach to 10-arylated 5*H*-dibenzo[*b*,*f*]azepines using *syn*-selective hydrohalogenation of ethynylaniline

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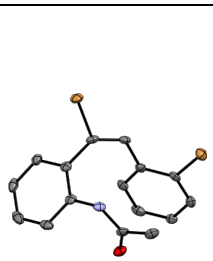
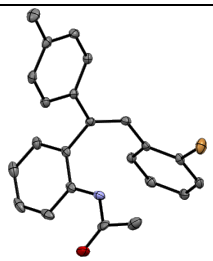
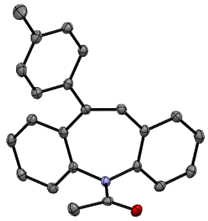
Crystallographic data for compounds **5**, **9a**, and **10**

	 **5**	 **9a**	 **10**
Empirical formula	$C_{16}H_{13}Br_2NO$	$C_{23}H_{20}BrNO$	$C_{23}H_{19}NO$
Formula weight	395.07	406.31	325.39
Temperature (K)	93(2)	93(2)	93(2)
Crystal system	triclinic	monoclinic	monoclinic
Space group	*P*-1 (#2)	$P2_1/c$ (#14)	$P2_1/c$ (#14)
Unit cell Dimensions	a = 9.9894(2) Å, b = 11.4609(3) Å c = 14.7673(4) Å, α = 106.052(2)°, β = 102.529(2)°, γ = 106.772(2)°	a = 8.3390(3) Å, b = 10.6181(3) Å c = 21.0722(6) Å, β = 92.485(3)°	a = 15.5398(5) Å, b = 8.6572(2) Å c = 13.0504(4) Å, β = 99.779(3)°
Volume (Å)	1472.53(7)	1864.07(10)	1730.18(9)
Z	4	4	4
ρ_{calc} (g•cm^{-3})	1.782	1.448	1.249
Absorption coefficient (mm^{-1})	5.499	2.216	0.076
θ range (°)	2.02 to 29.44	2.445 to 25.500	2.642 to 30.134
Reflections collected	5481	3460	3219
Independent reflections	4651	3085	2766
Completeness to θ	100	99.9	100
Goodness-of-fit	1.033	1.063	1.049
Final R indices [$I > 2\sigma(I)$]	R_1 = 0.0320, wR_2 = 0.0754	R_1 = 0.0294, wR_2 = 0.0642	R_1 = 0.0375, wR_2 = 0.0867
R indices (all data)	R_1 = 0.0421, wR_2 = 0.0784	R_1 = 0.0359, wR_2 = 0.0660	R_1 = 0.0452, wR_2 = 0.0909
Largest diff. peak (e•Å)	0.983	0.350	0.189
Largest diff. hole (e•Å)	–0.501	–0.418	–0.218
CCDC number	2150669	2150670	2150671

Single crystal was obtained from dichloromethane/hexane. Color labels: gray, carbon; white, hydrogen; orange, bromine; blue, nitrogen; red, oxygen. The thermal ellipsoids are represented at 50% probability level. All hydrogen atoms were omitted for clarity.

Temperature-variable NMR spectra of **10a** (DMSO-d_6)

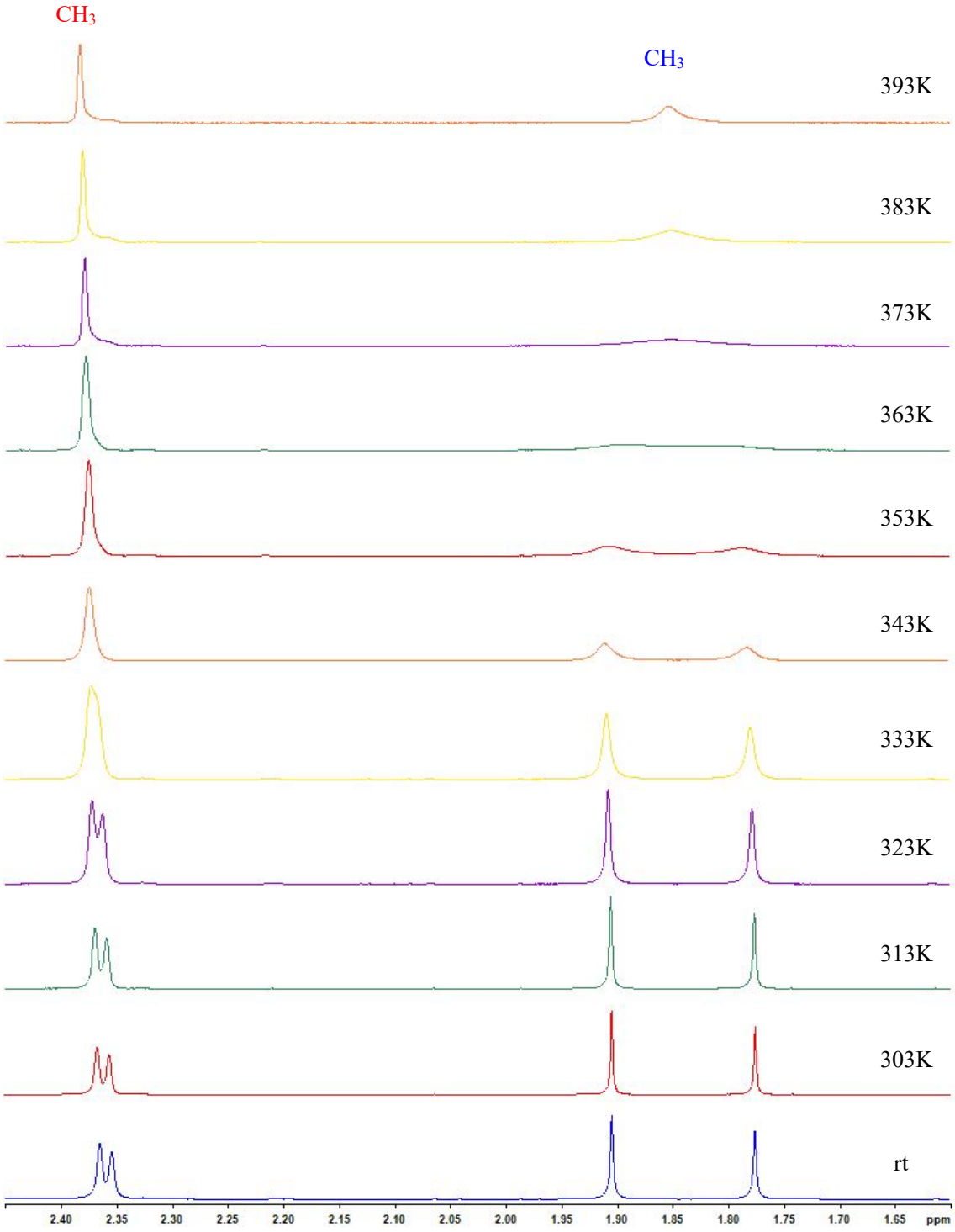
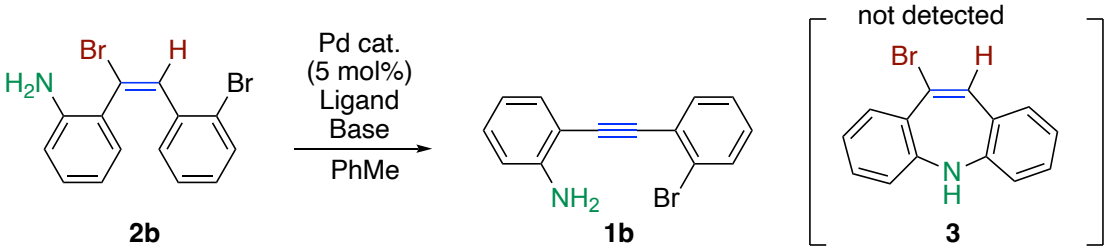


Table S1. Pd-catalyzed intramolecular cyclization of **2b**



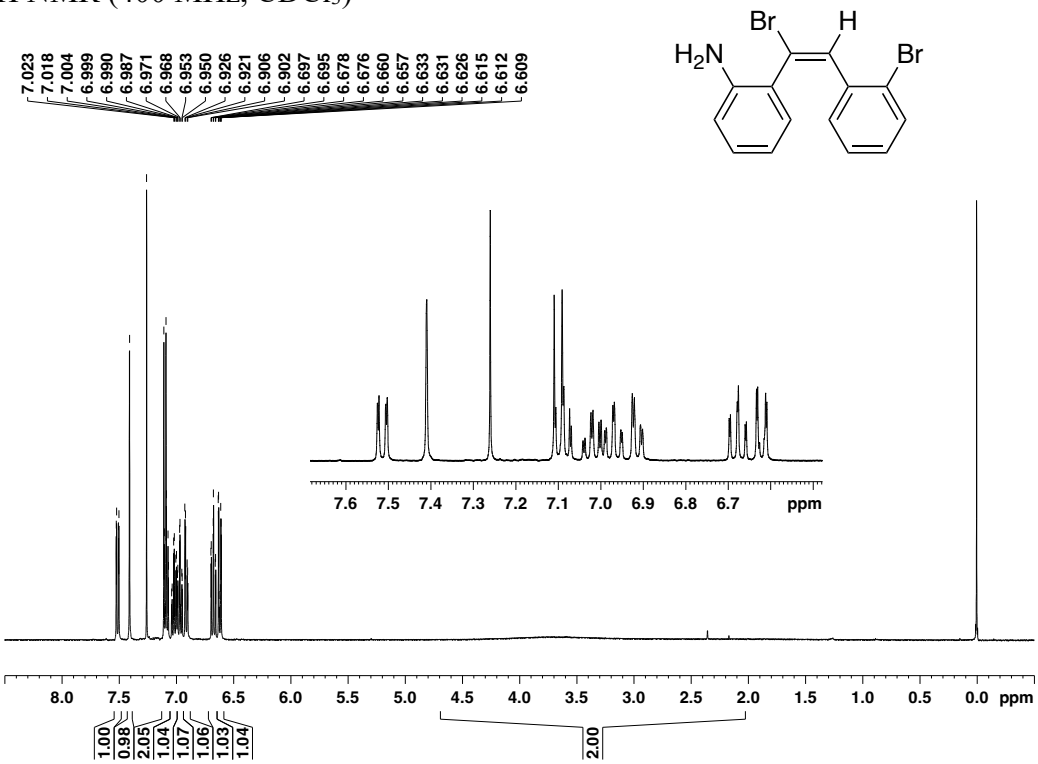
Entry	Cat.	Ligand (mol%)	Base (equiv.)	Temp./ °C	Time/ h	Yield of **1b**/%[a]	Recovery of **2b**/%[a]
1	$Pd(OAc)_2$	PPh_3 (15)	Cs_2CO_3 (2)	rt	17	0	75
2	$Pd(OAc)_2$	PPh_3 (15)	Cs_2CO_3 (2)	90	24	38	0
3	$Pd_2(dba)_3$	*t*-Bu_3P (5)	Cs_2CO_3 (1)	rt	3	0	91
4	$Pd_2(dba)_3$	*t*-Bu_3P (5)	$NaOBu^t$ (2)	rt	3	90	0
5	$Pd_2(dba)_3$	*t*-Bu_3P (5)	—	rt	3	0	93
6	—	—	$NaOBu^t$ (2)	rt	3	0	94

[a] Determined by ^1H NMR.

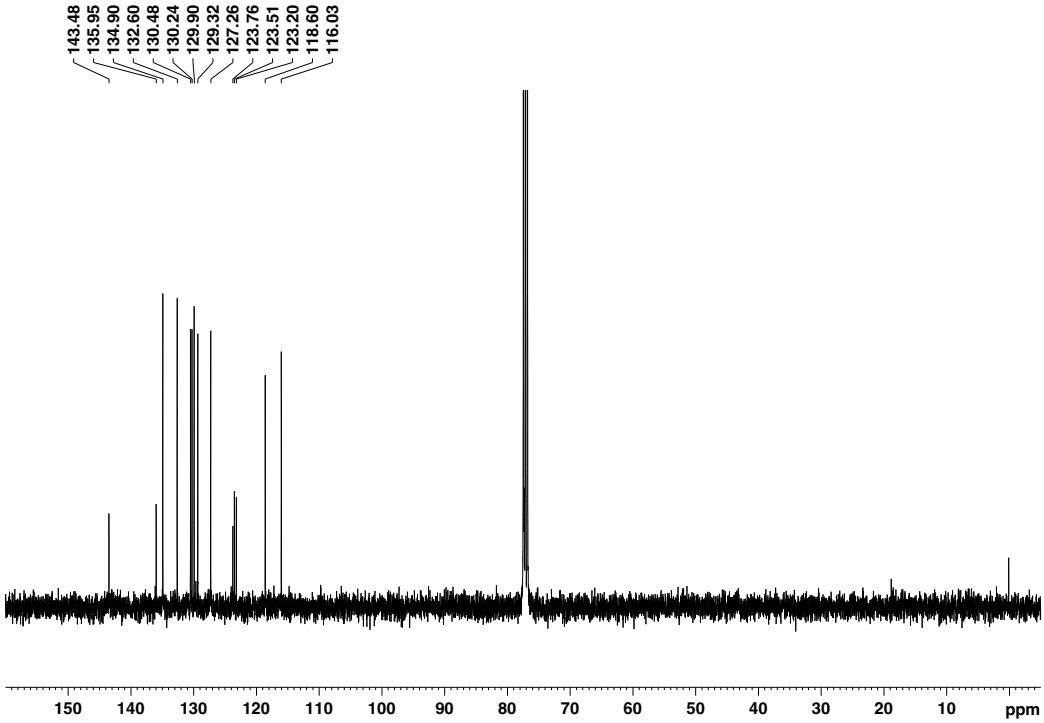
Copies of NMR spectra

E-2-[(2-bromophenyl)-1-bromoethenyl]aniline (2b)

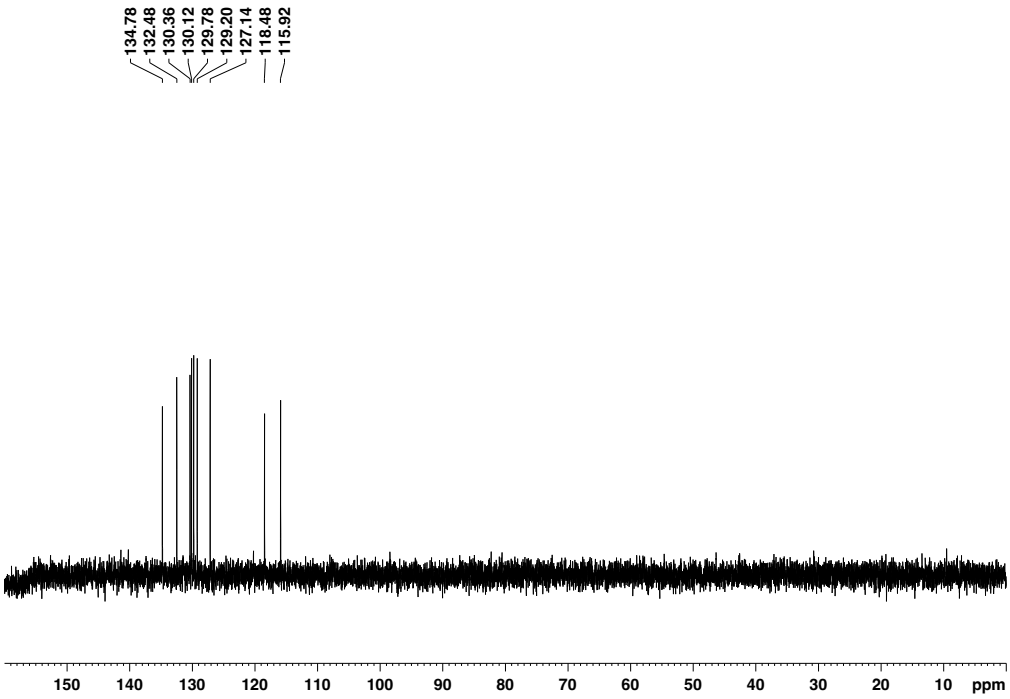
^{1}H NMR (400 MHz, $CDCl_3$)



^{13}C{^{1}H} NMR (100 MHz, $CDCl_3$)

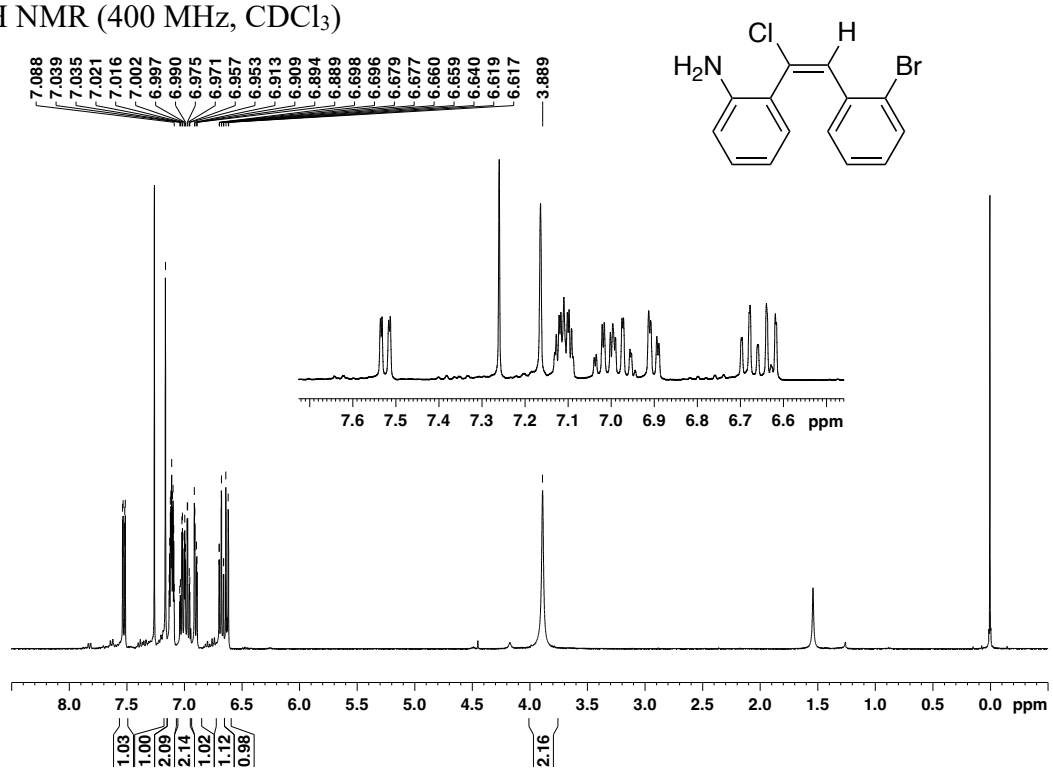


DEPT NMR (100 MHz, $CDCl_3$)

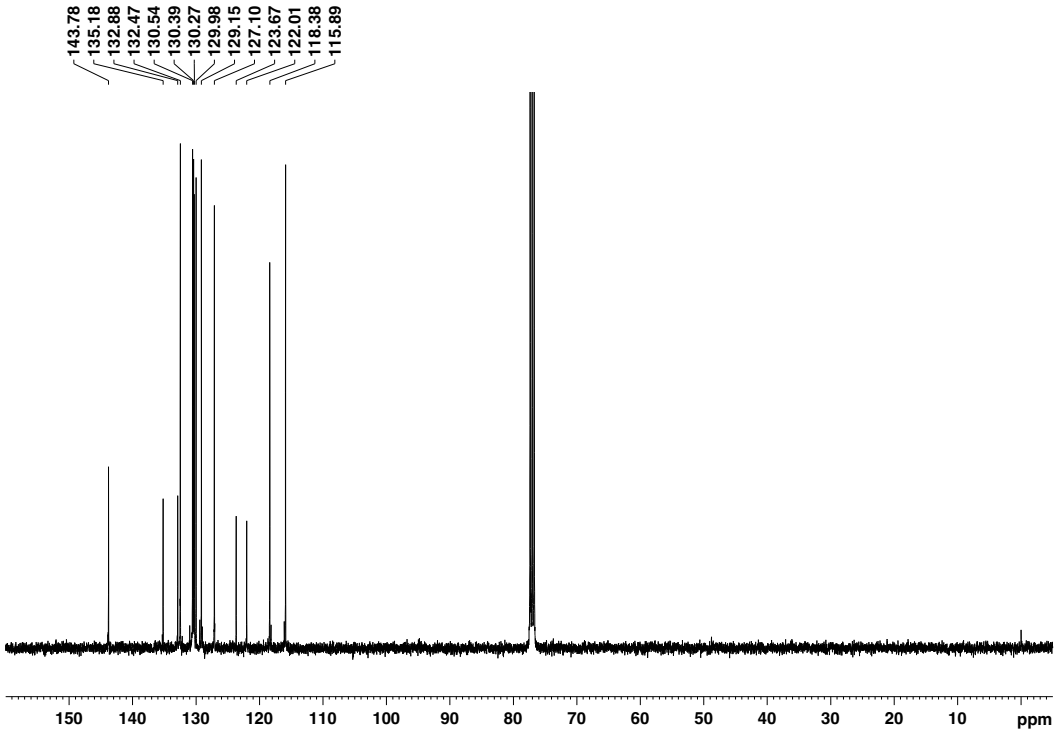


E-2-[2-(2-Bromophenyl)-1-chloroethenyl]aniline (2c)

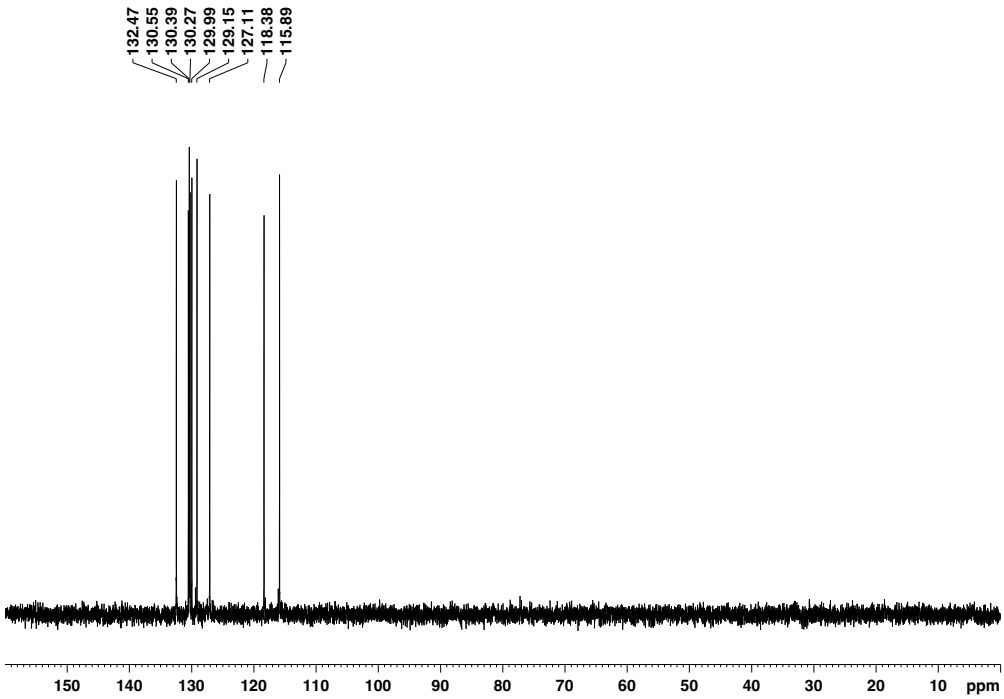
^{1}H NMR (400 MHz, $CDCl_3$)



$^{13}C\{^{1}H\}$ NMR (100 MHz, $CDCl_3$)

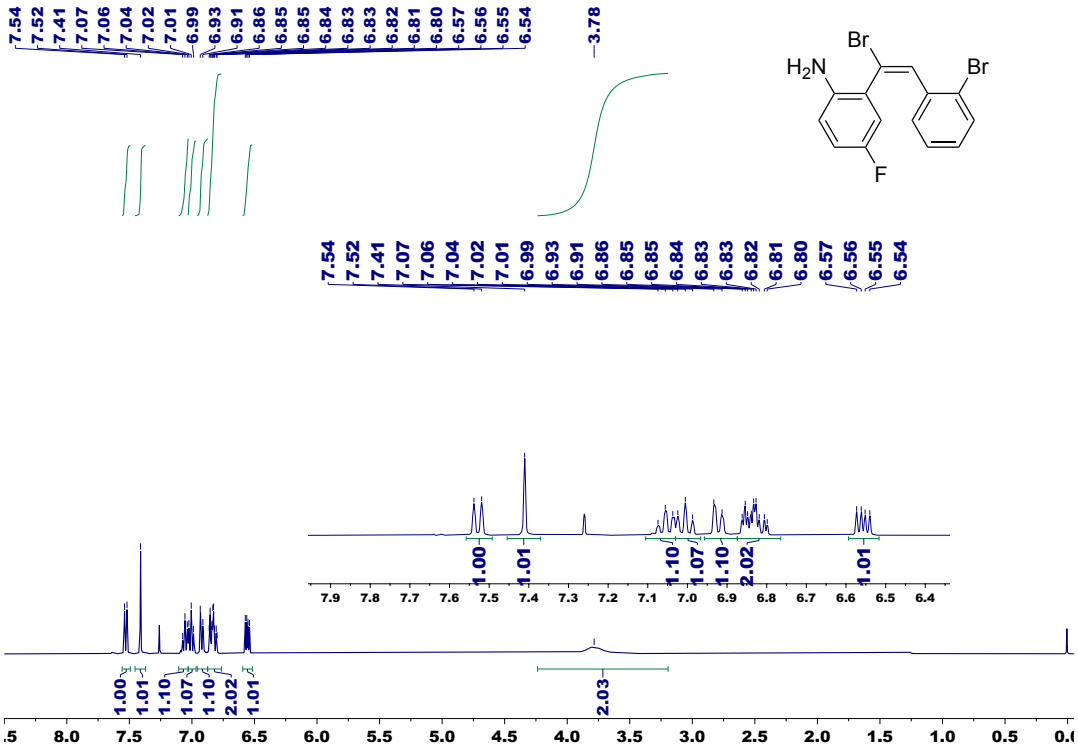


DEPT NMR (100 MHz, $CDCl_3$)

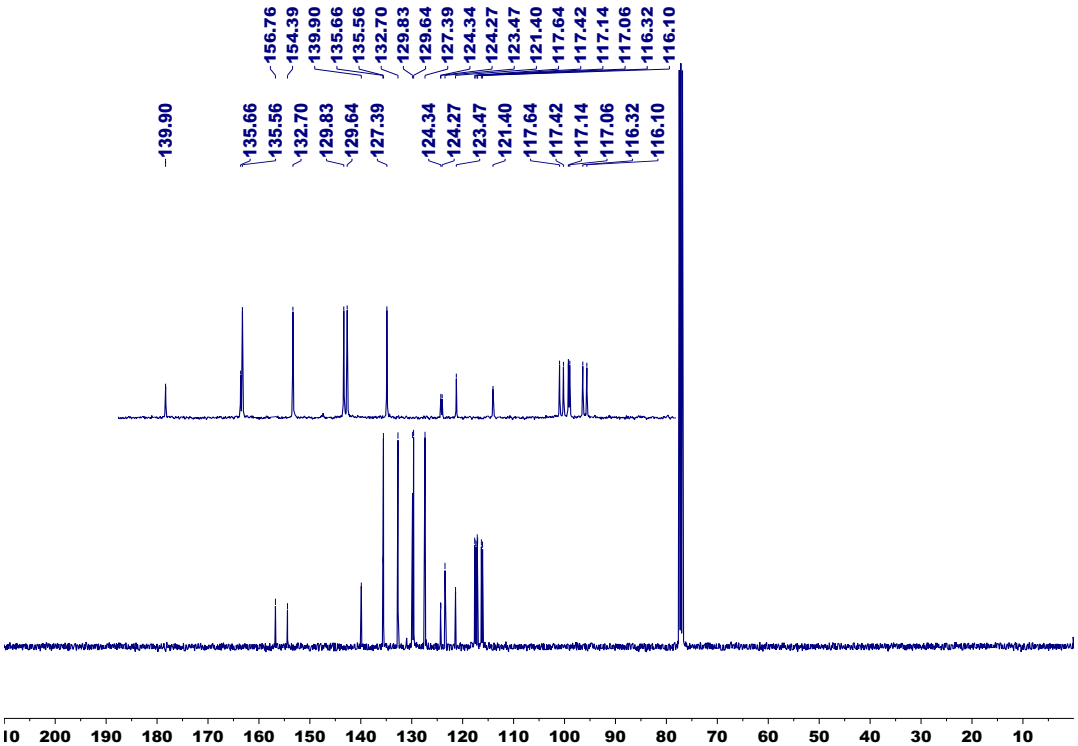


***E*-2-[2-(2-Bromophenyl)-1-bromoethenyl]-4-fluoroaniline (2d)**

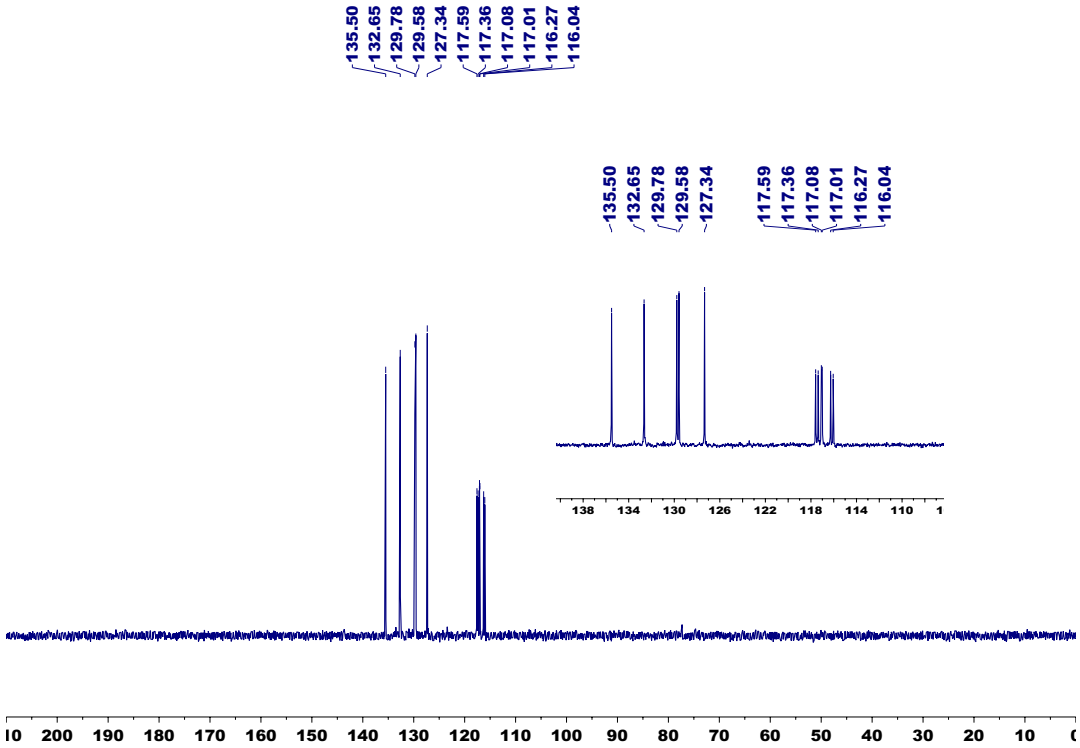
^{1}H NMR (400 MHz, $CDCl_3$)



^{13}C{^{1}H} NMR (100 MHz, $CDCl_3$)

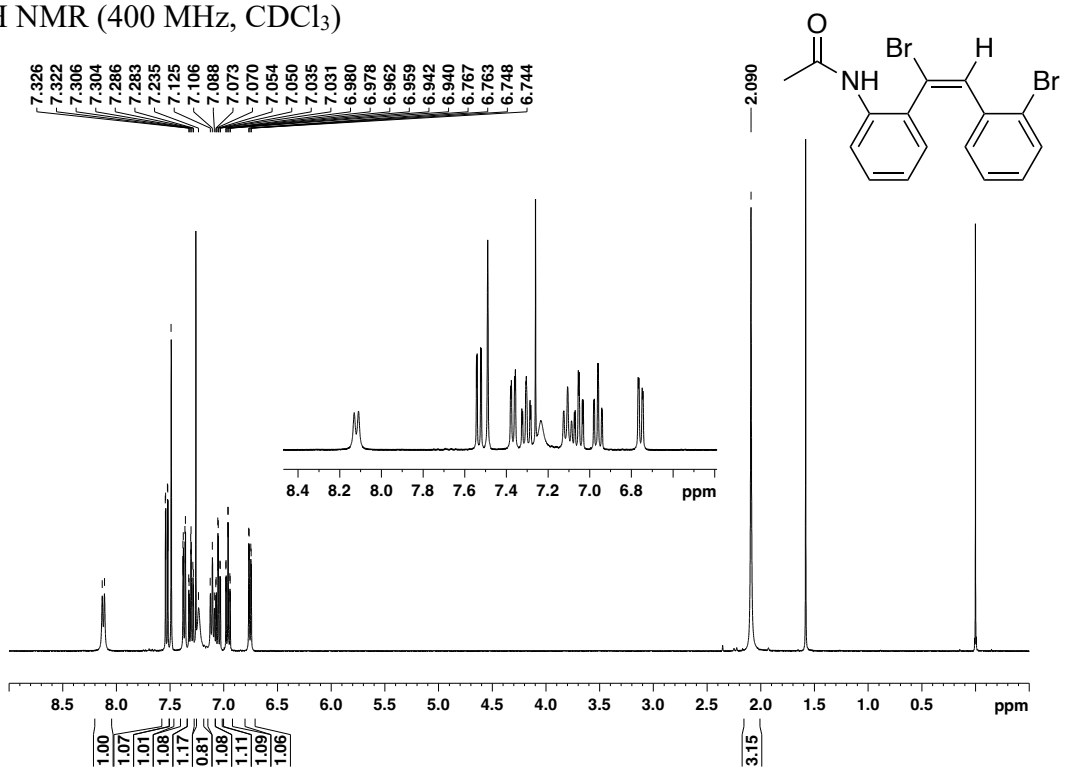


DEPT NMR (100 MHz, $CDCl_3$)

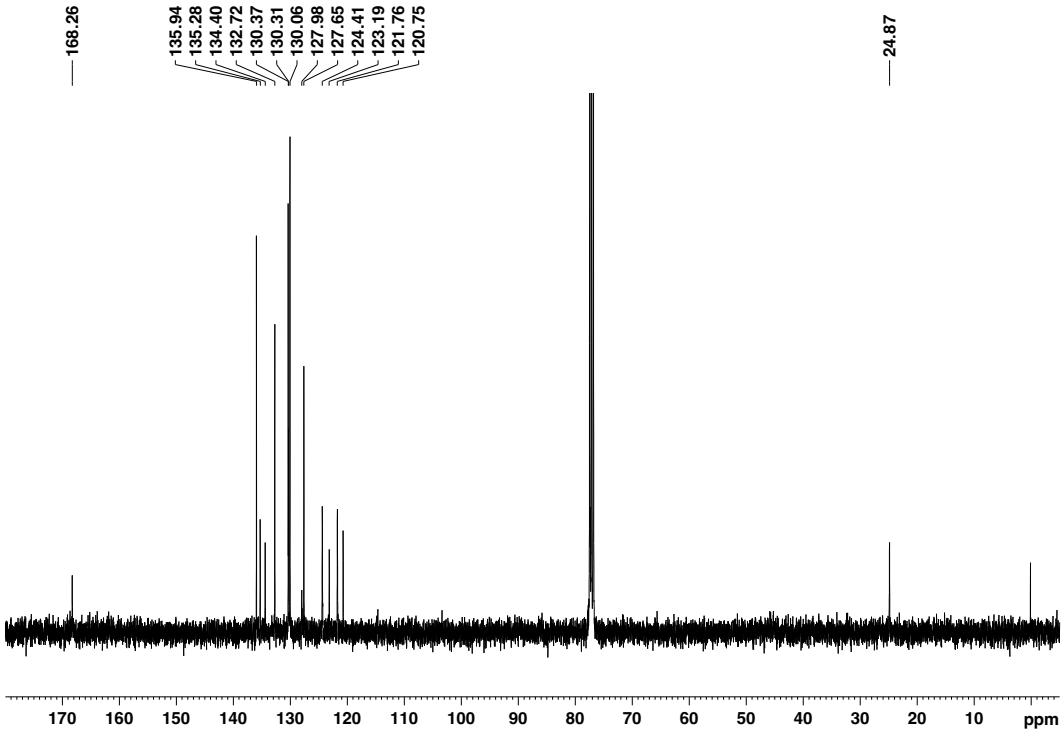


E-1-(2-Acetylamino)phenyl-1-bromo-2-(2-bromophenyl)ethene (5a)

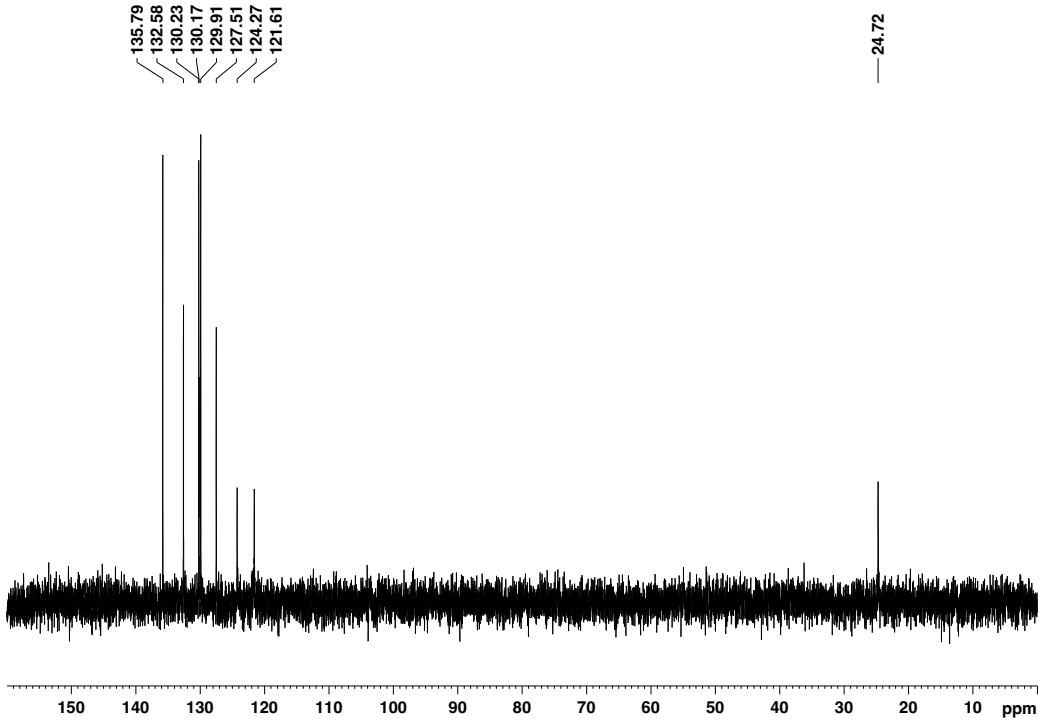
^{1}H NMR (400 MHz, $CDCl_3$)



^{13}C{^{1}H} NMR (100 MHz, $CDCl_3$)

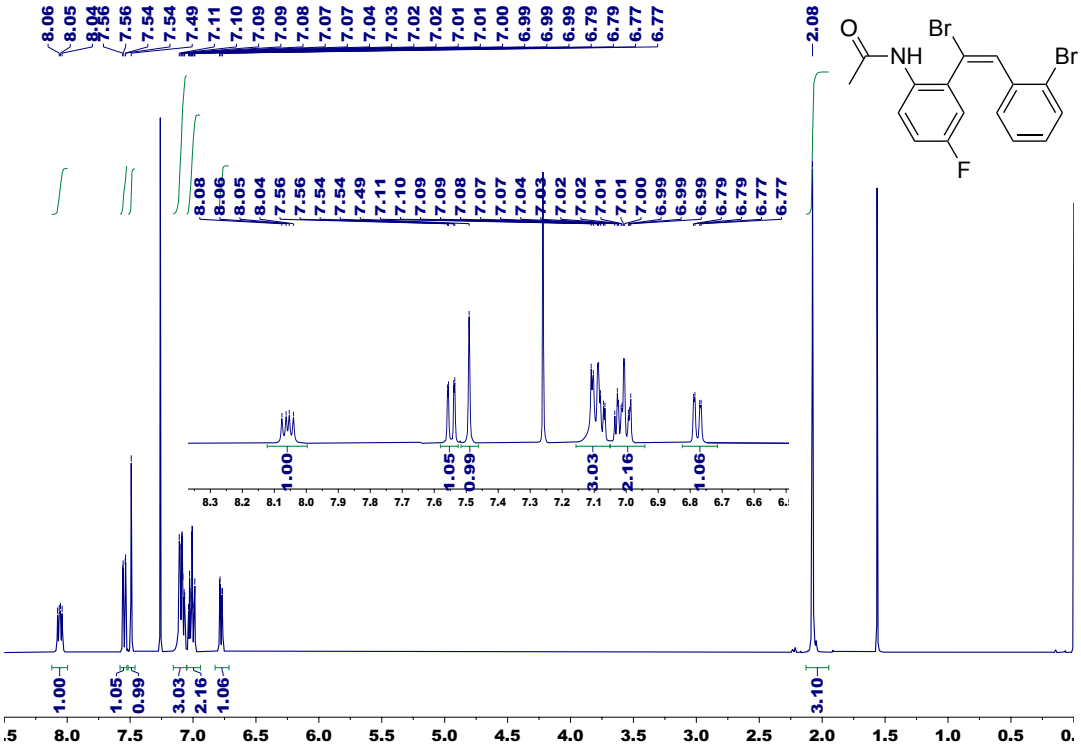


DEPT NMR (100 MHz, $CDCl_3$)

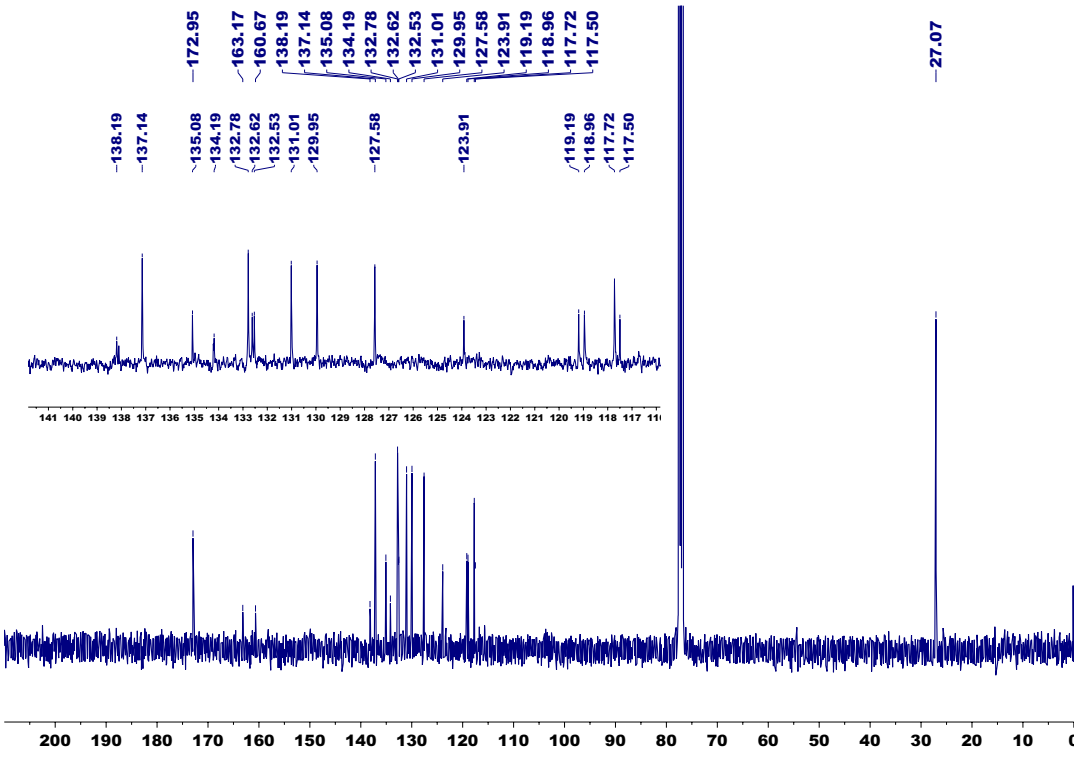


***E*-1-(2-Acetylamino-4-fluoro)phenyl-1-bromo-2-(2-bromophenyl)ethene (5b)**

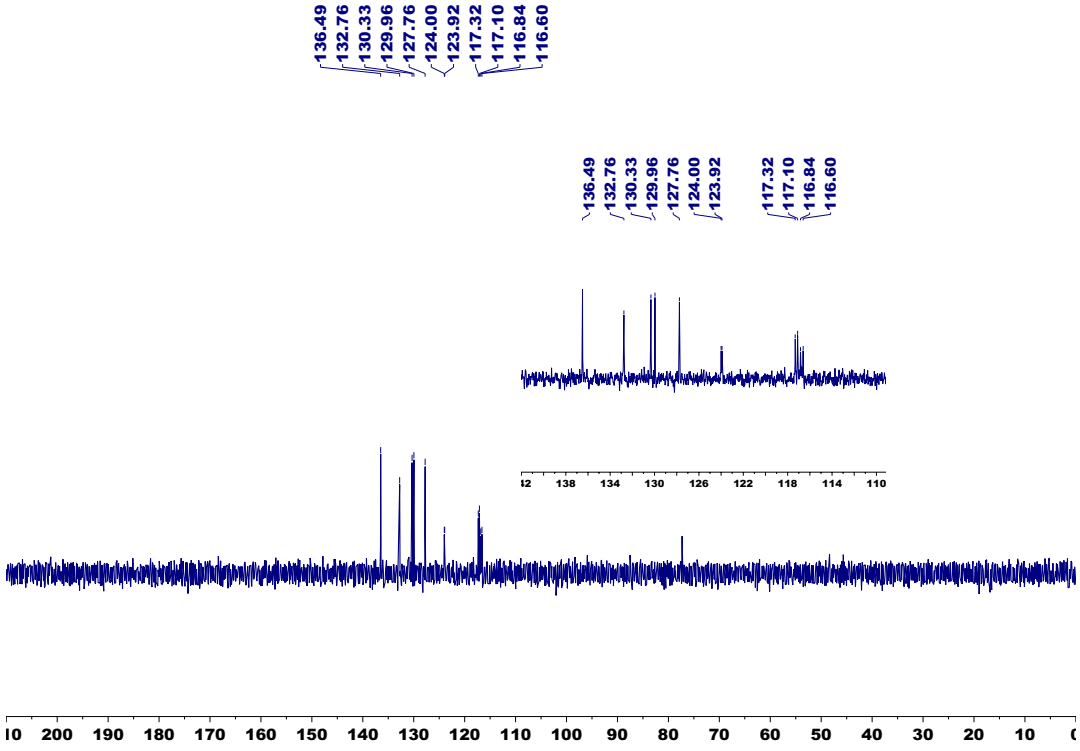
^{1}H NMR (400 MHz, $CDCl_3$)



^{13}C{^{1}H} NMR (100 MHz, $CDCl_3$)

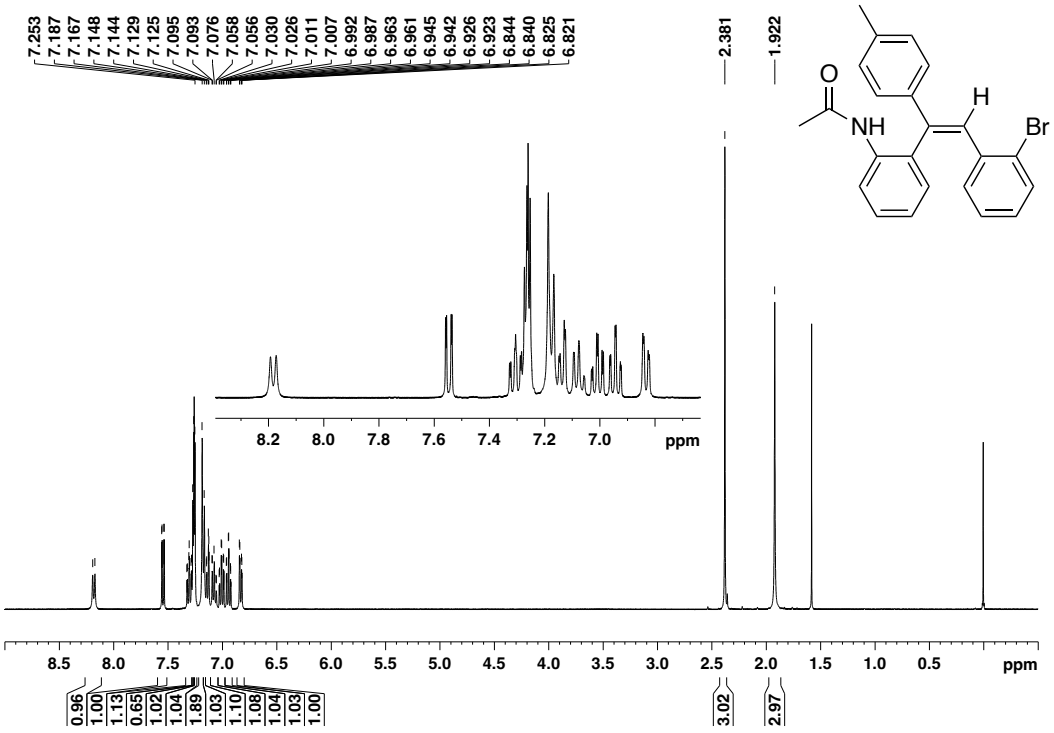


DEPT NMR (100 MHz, $CDCl_3$)

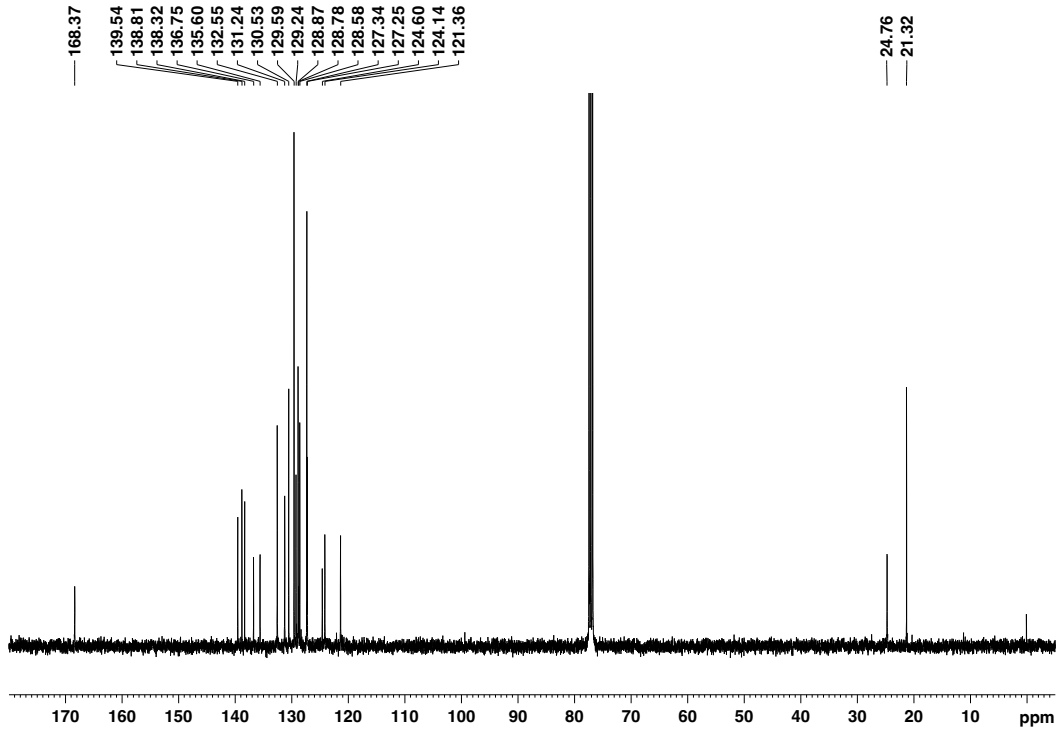


_Z_-2-(2-Bromophenyl)-1-(2-ethanoylamino)phenyl-1-(4-methylphenyl)ethene (9a)

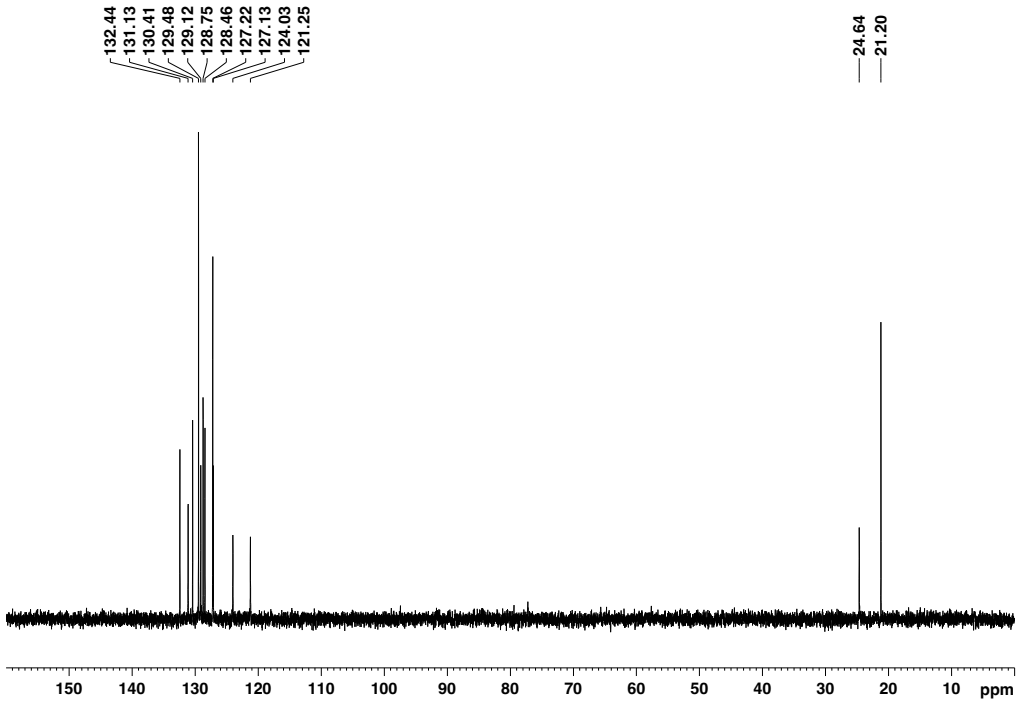
^{1}H NMR (400 MHz, $CDCl_3$)



^{13}C{^{1}H} NMR (100 MHz, $CDCl_3$)

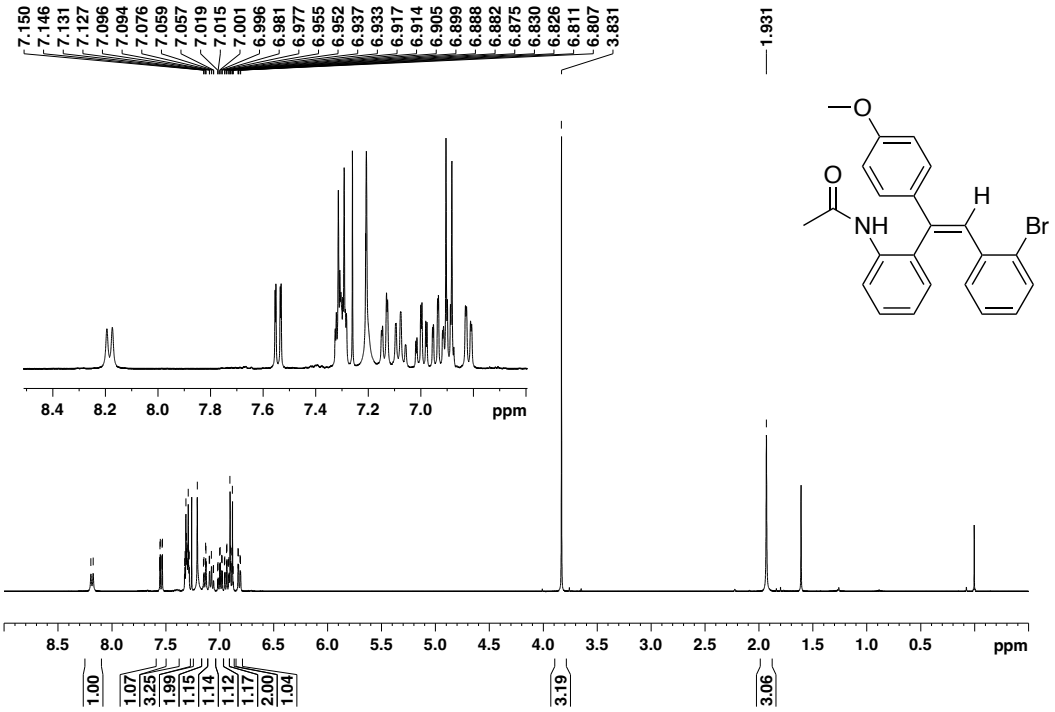


DEPT NMR (100 MHz, $CDCl_3$)

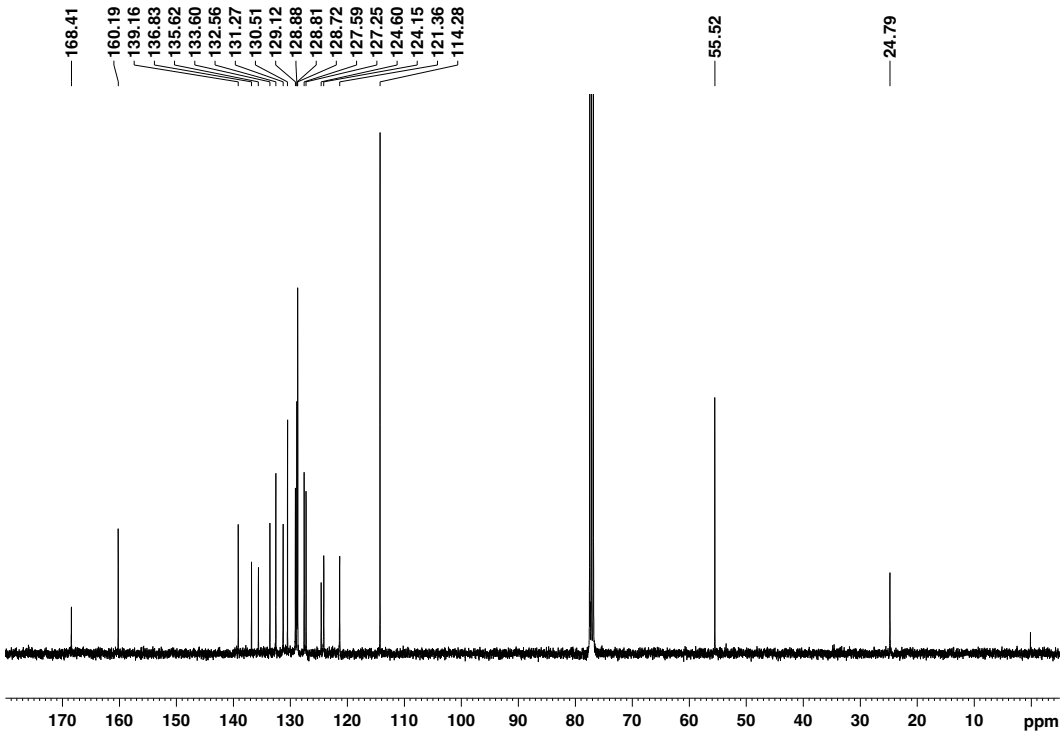


Z-2-(2-Bromophenyl)-1-(2-acetylamino)phenyl-1-(4-methoxyphenyl)ethene (9b)

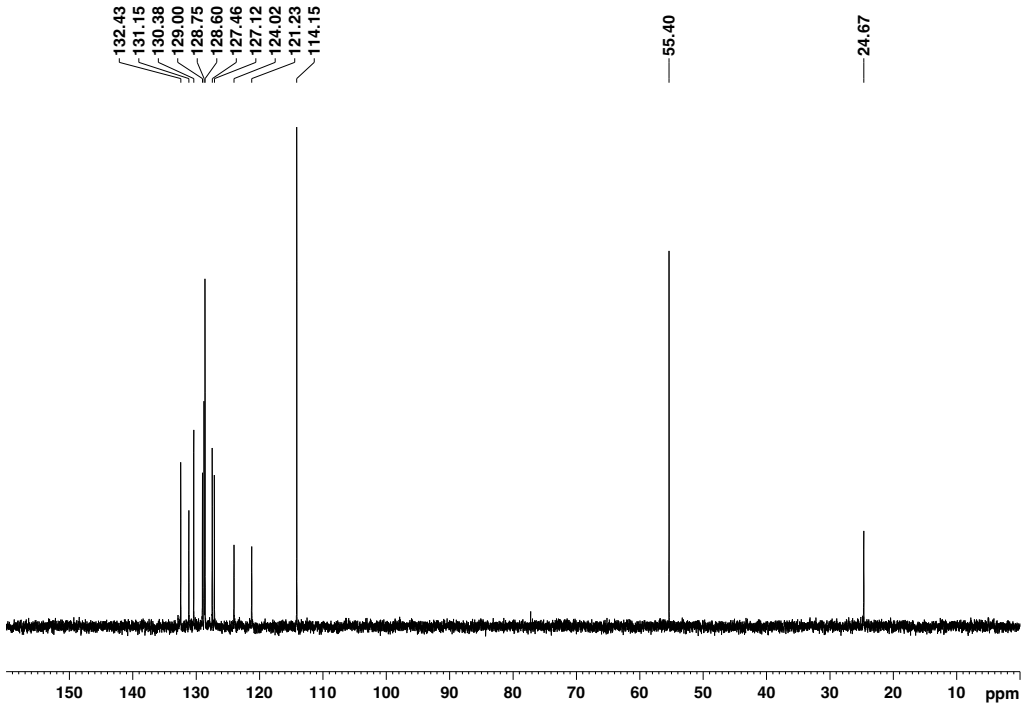
^{1}H NMR (400 MHz, $CDCl_3$)



^{13}C{^{1}H} NMR (100 MHz, $CDCl_3$)

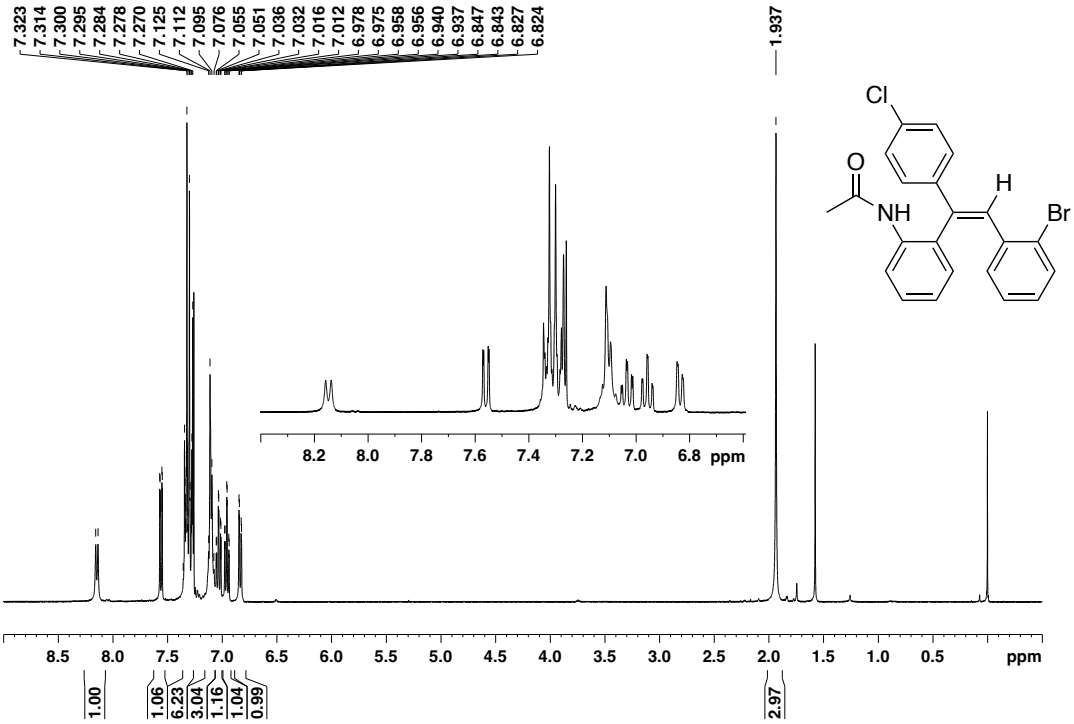


DEPT NMR (100 MHz, $CDCl_3$)

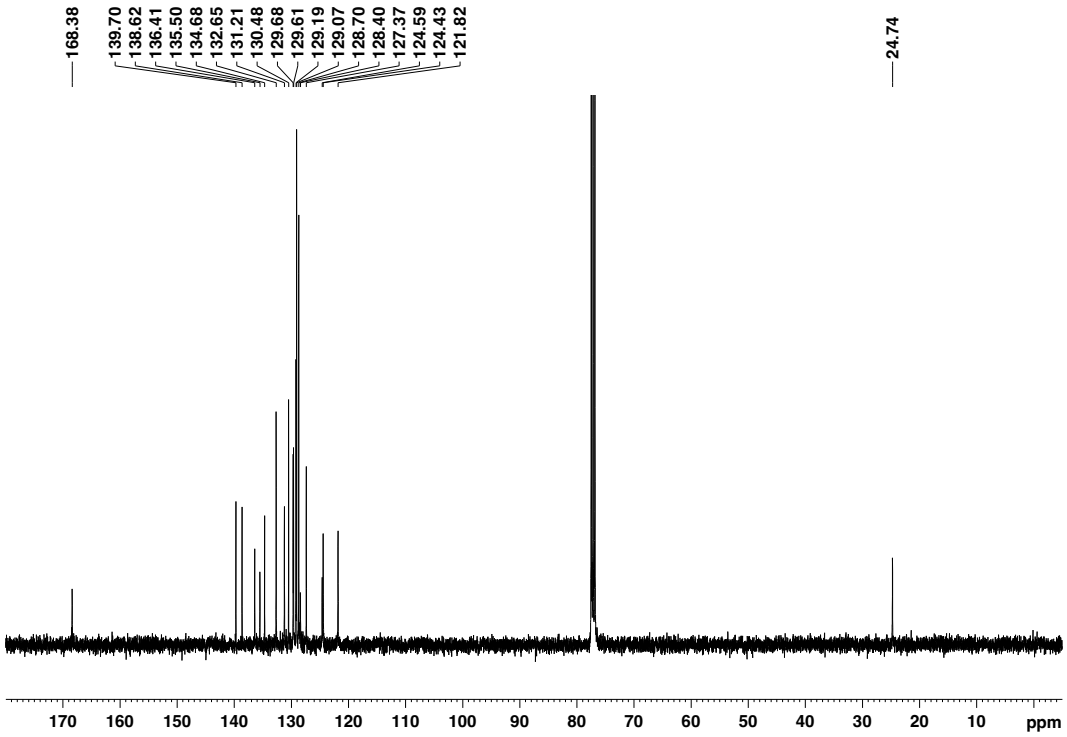


***Z*-2-(2-Bromophenyl)-1-(2-acetylamino)phenyl-1-(4-chlorophenyl)ethene (9c)**

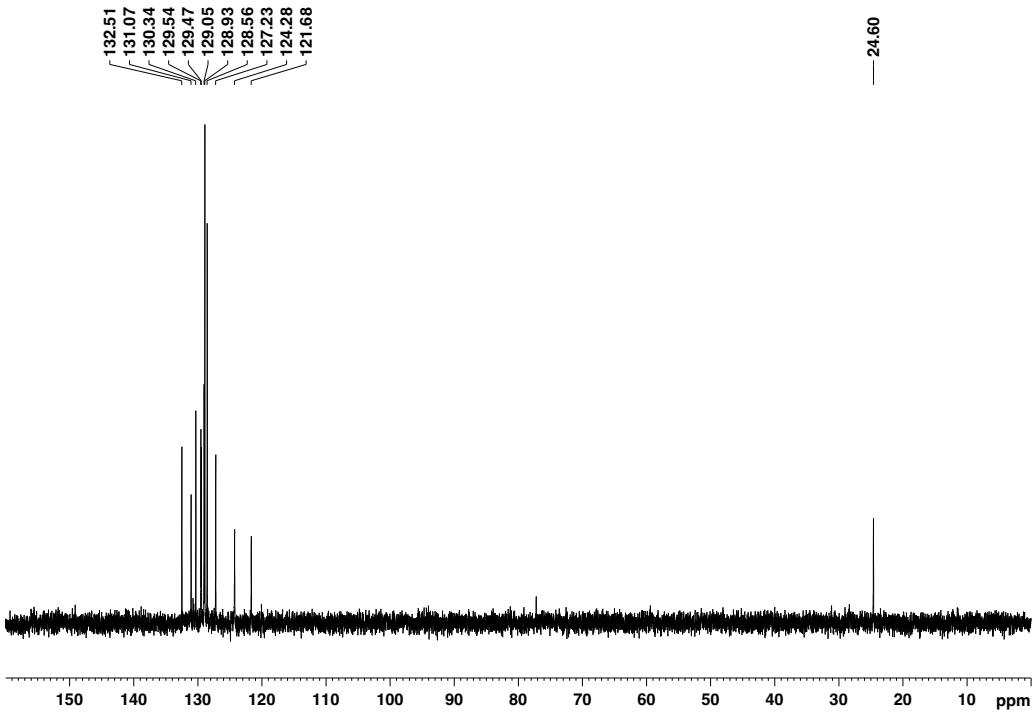
^{1}H NMR (400 MHz, $CDCl_3$)



^{13}C{^{1}H} NMR (100 MHz, $CDCl_3$)

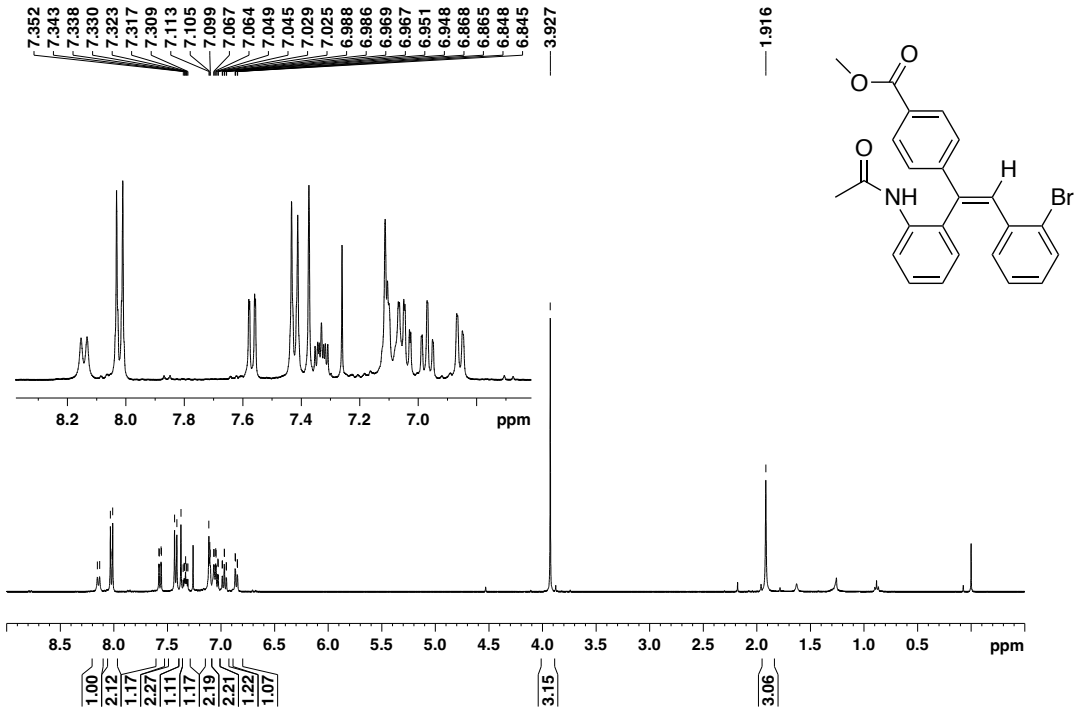


DEPT NMR (100 MHz, $CDCl_3$)

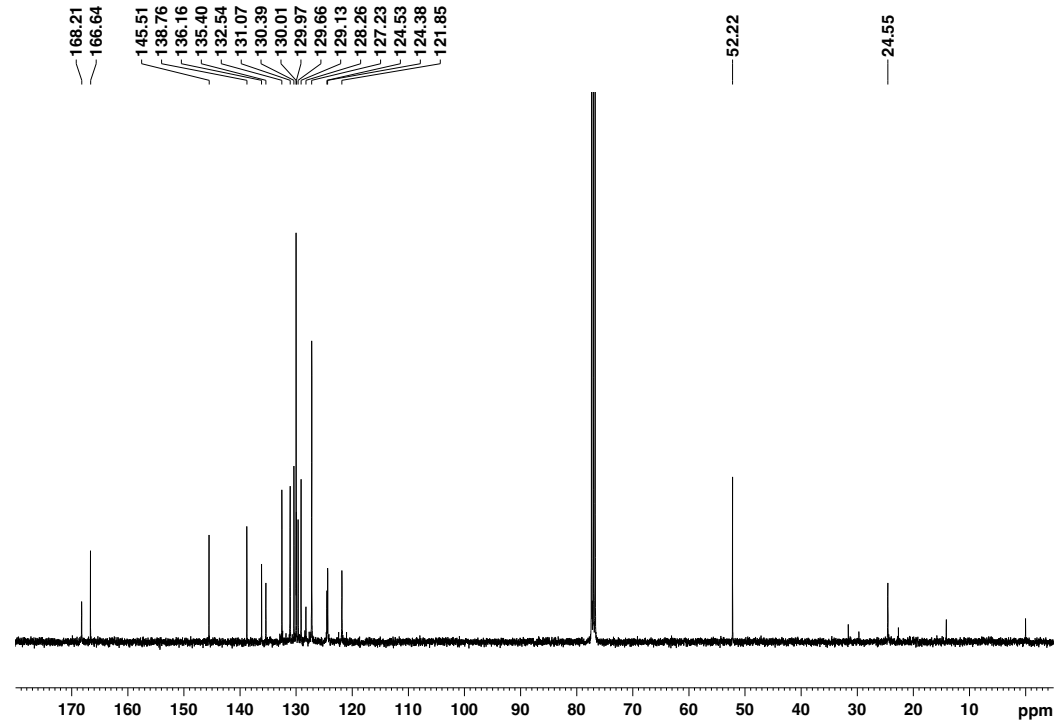


_Z_-2-(2-Bromophenyl)-1-(2-acetylamino)phenyl-1-(4-methoxycarbonylphenyl)ethene (9d)

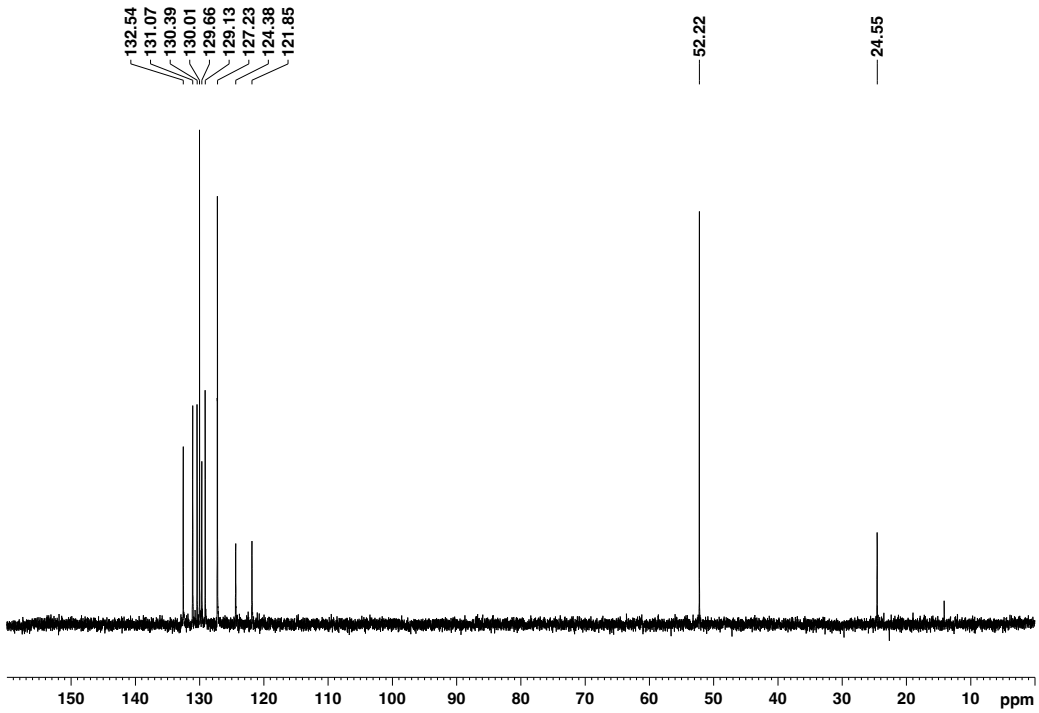
^{1}H NMR (400 MHz, $CDCl_3$)



^{13}C{^{1}H} NMR (100 MHz, $CDCl_3$)

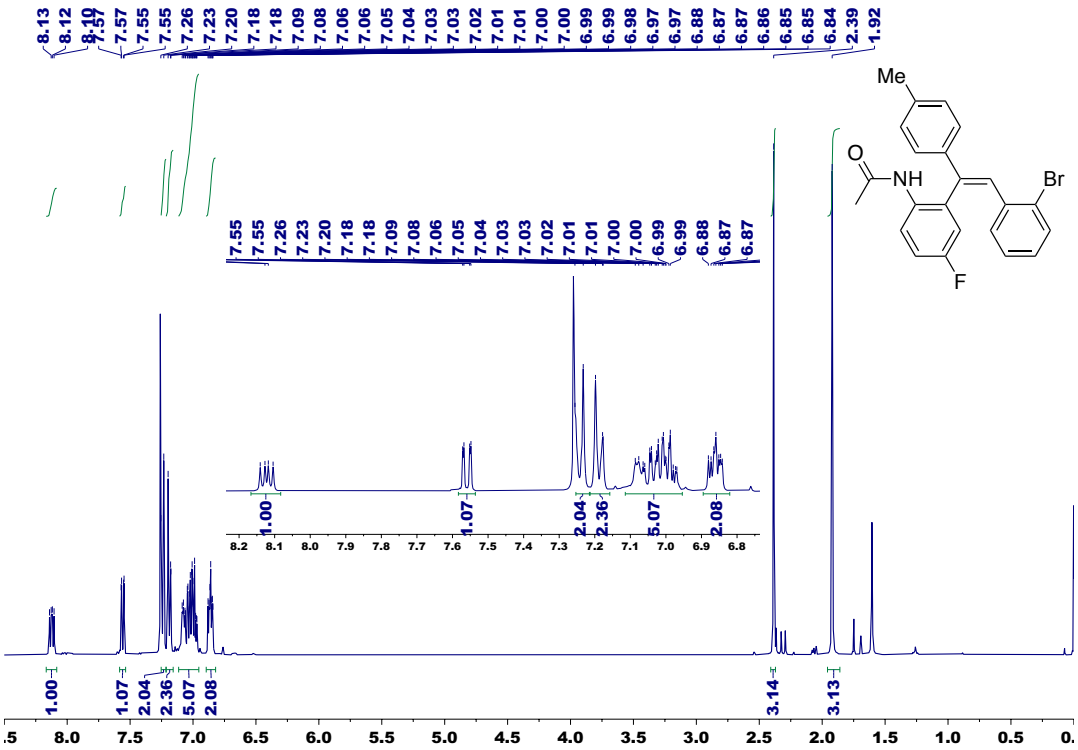


DEPT NMR (100 MHz, $CDCl_3$)

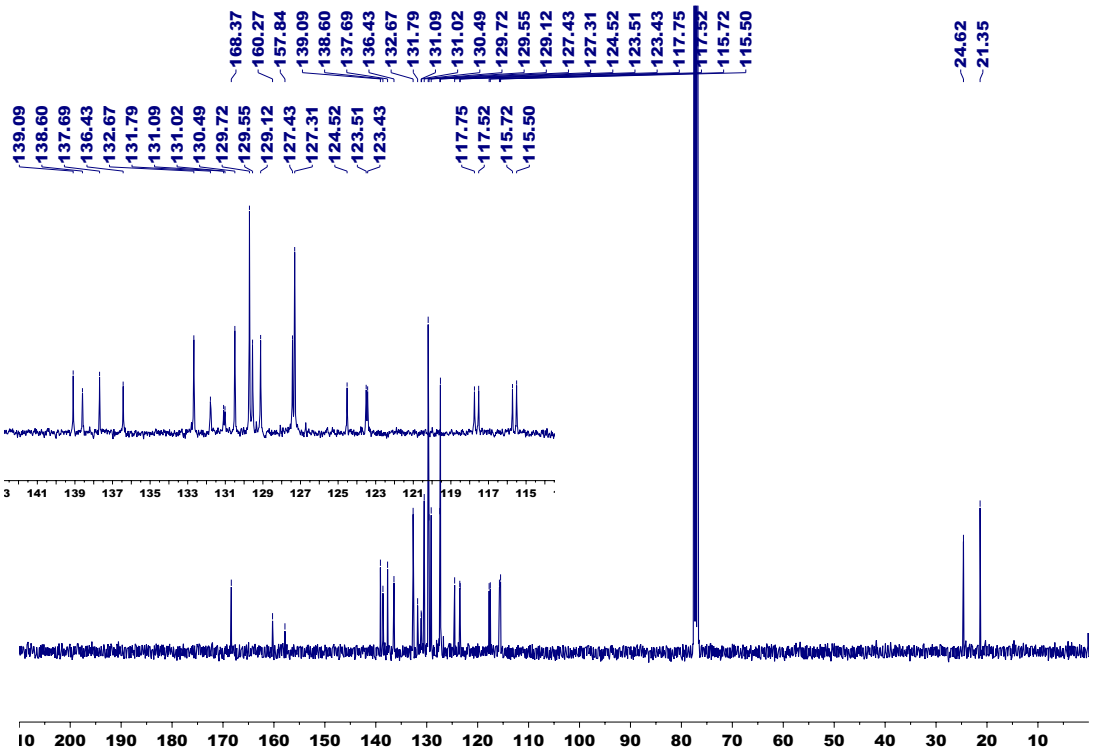


***Z*-2-(2-Bromophenyl)-1-(2-ethanoylamino-4-fluoro)phenyl-1-(4-methylphenyl)ethene (9e)**

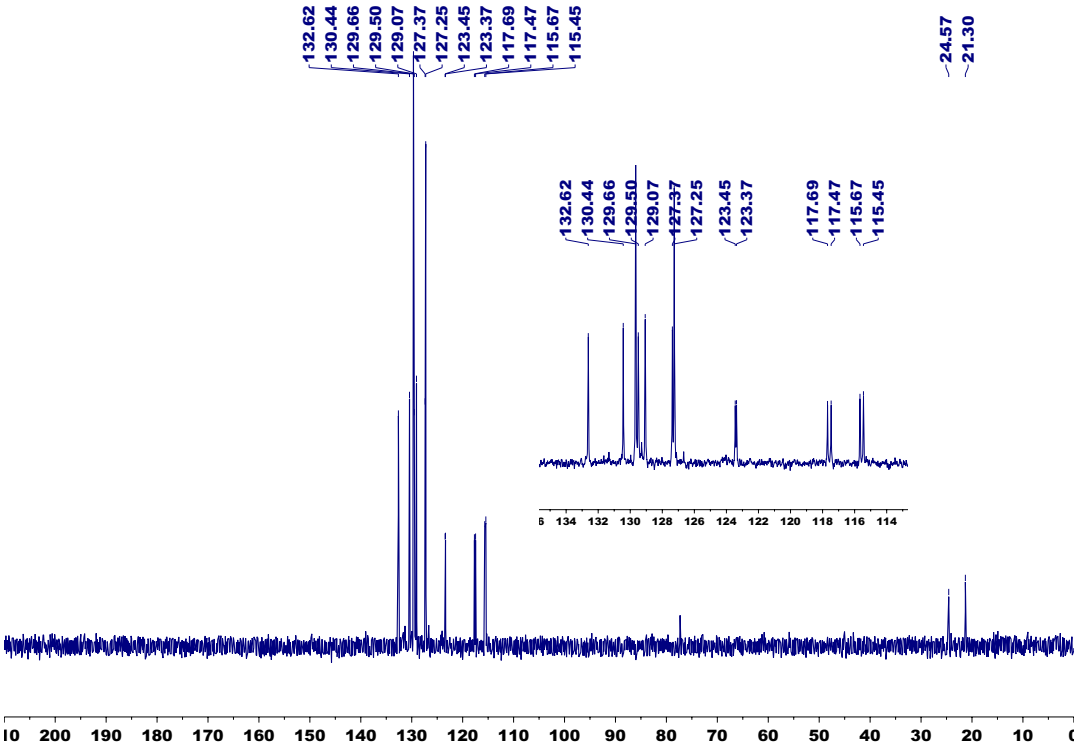
^{1}H NMR (400 MHz, $CDCl_3$)



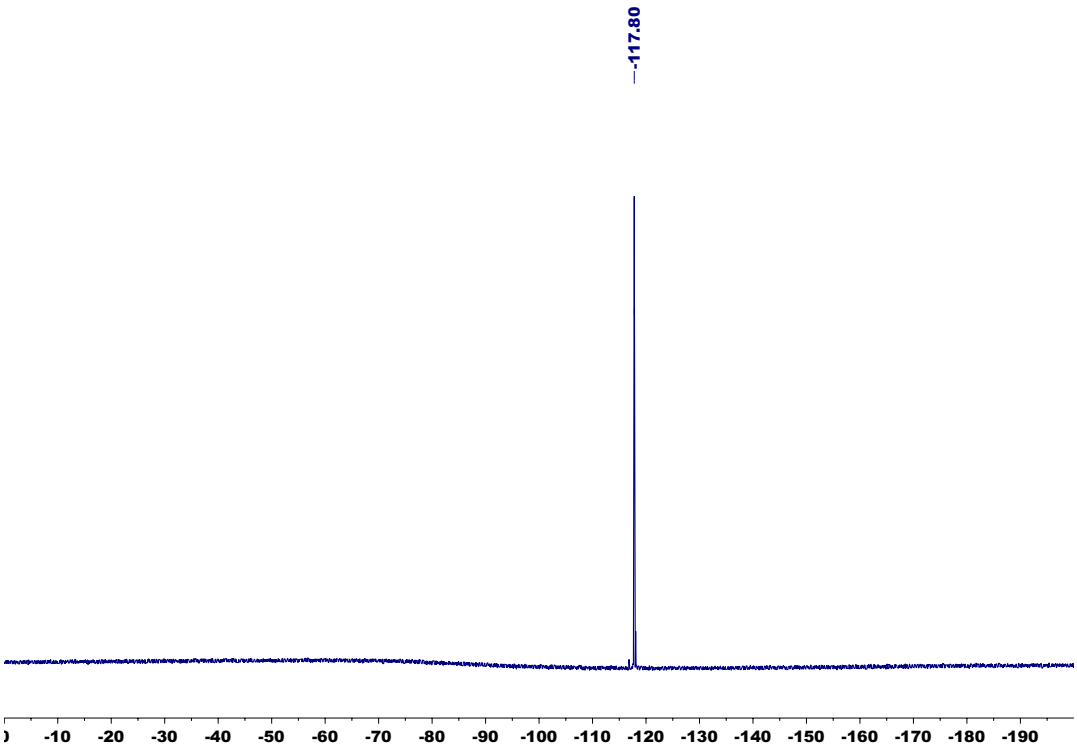
$^{13}C\{^{1}H\}$ NMR (100 MHz, $CDCl_3$)



DEPT NMR (100 MHz, $CDCl_3$)



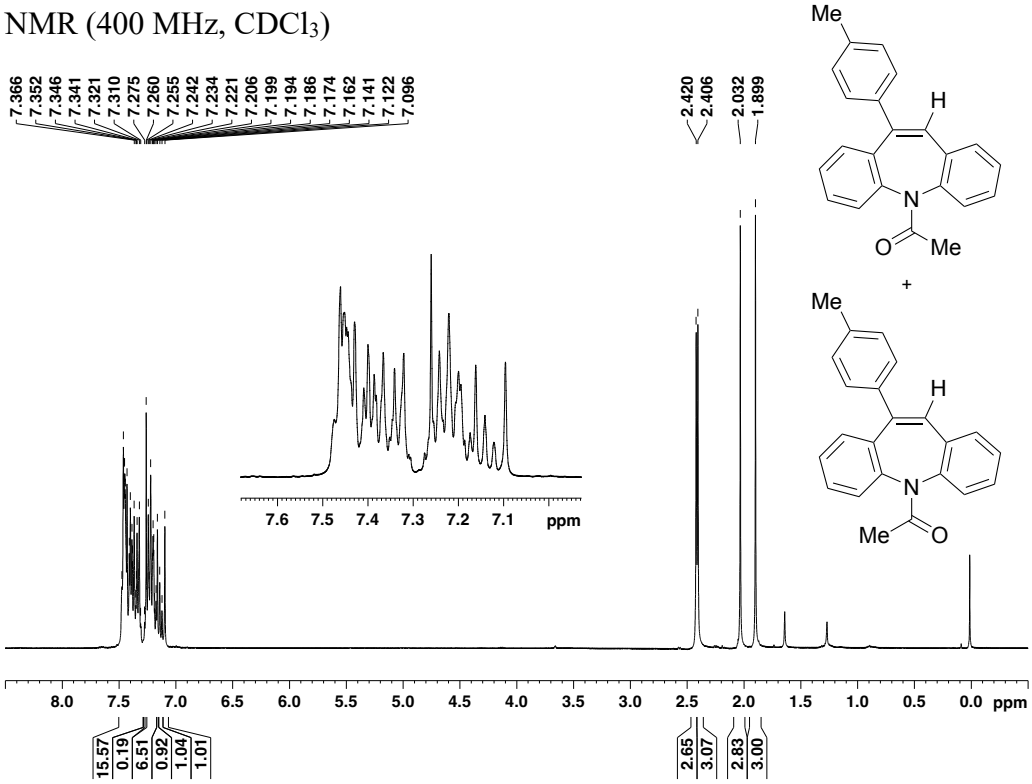
^{19}F NMR (376.5 MHz, $CDCl_3$)



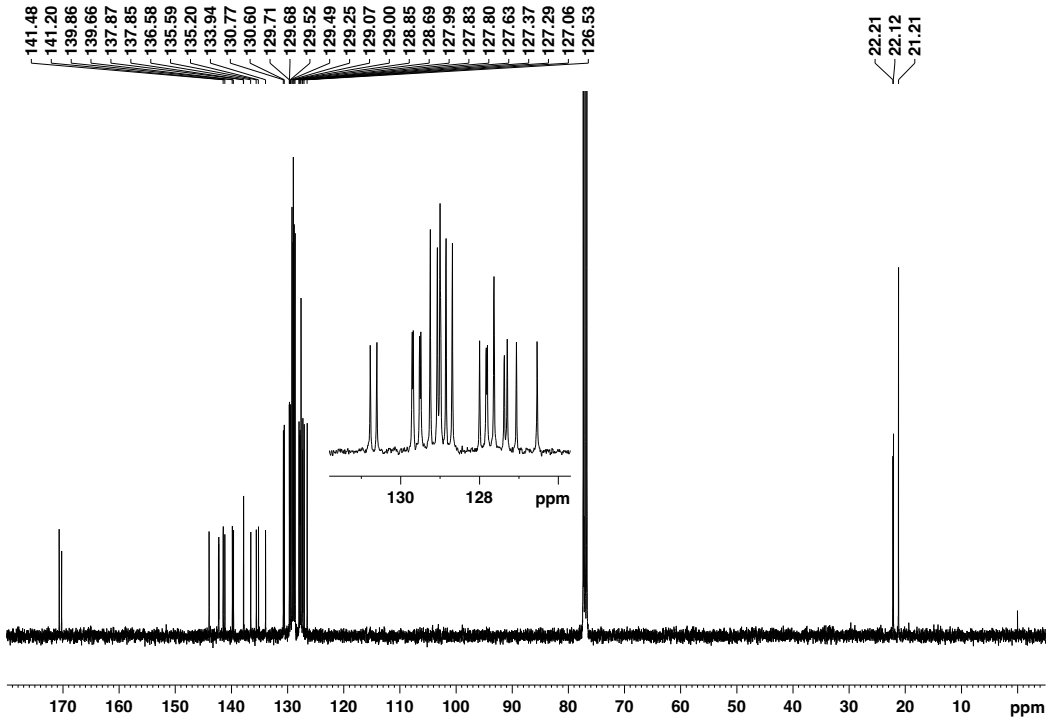
5-Ethanoyl-10-(4-methylphenyl)-*5H*-dibenzo[*b*,*f*]azepine (10a)

Isomeric ratio = 51/49

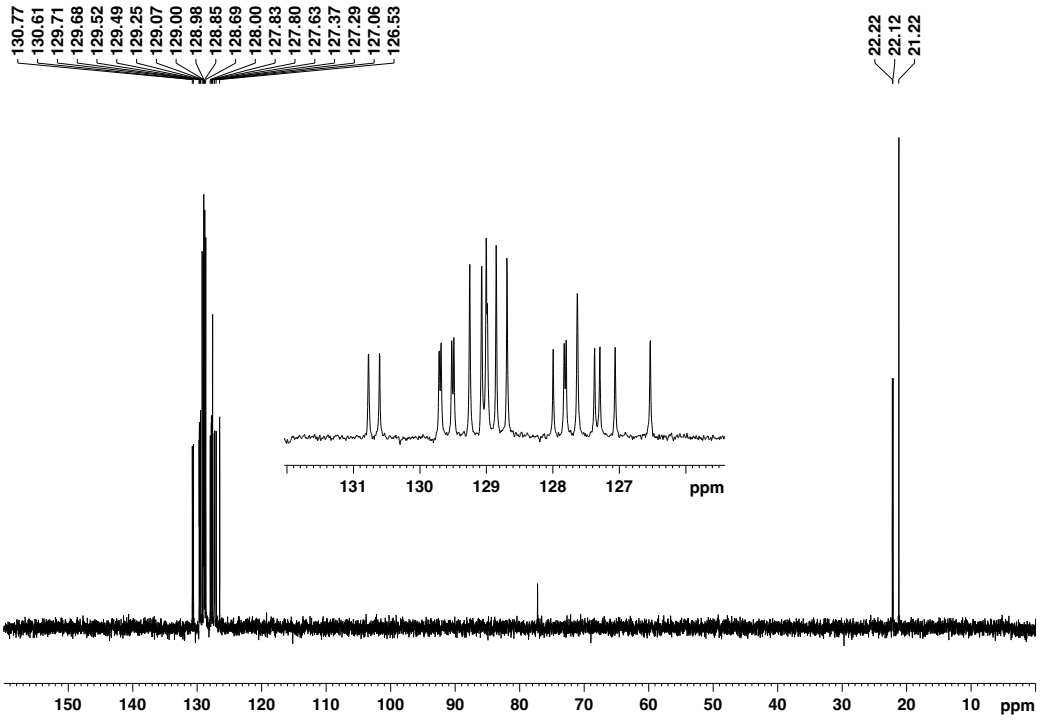
^{1}H NMR (400 MHz, $CDCl_3$)



^{13}C{^{1}H} NMR (100 MHz, $CDCl_3$)



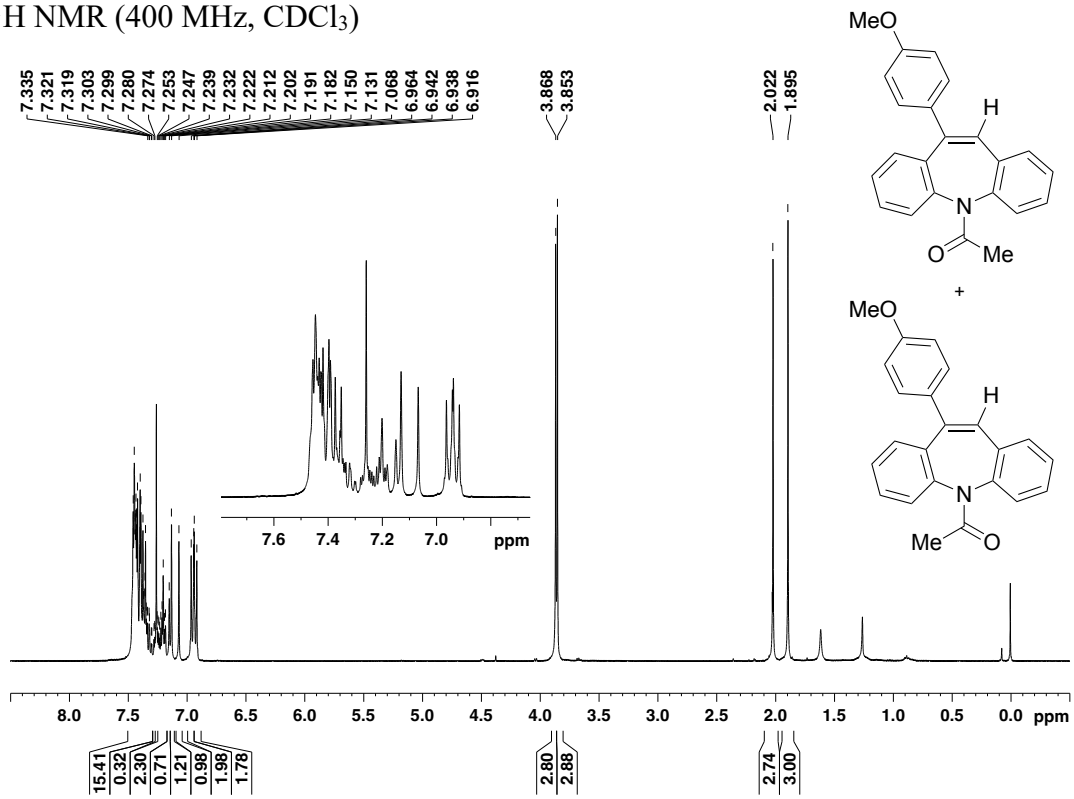
DEPT NMR (100 MHz, $CDCl_3$)



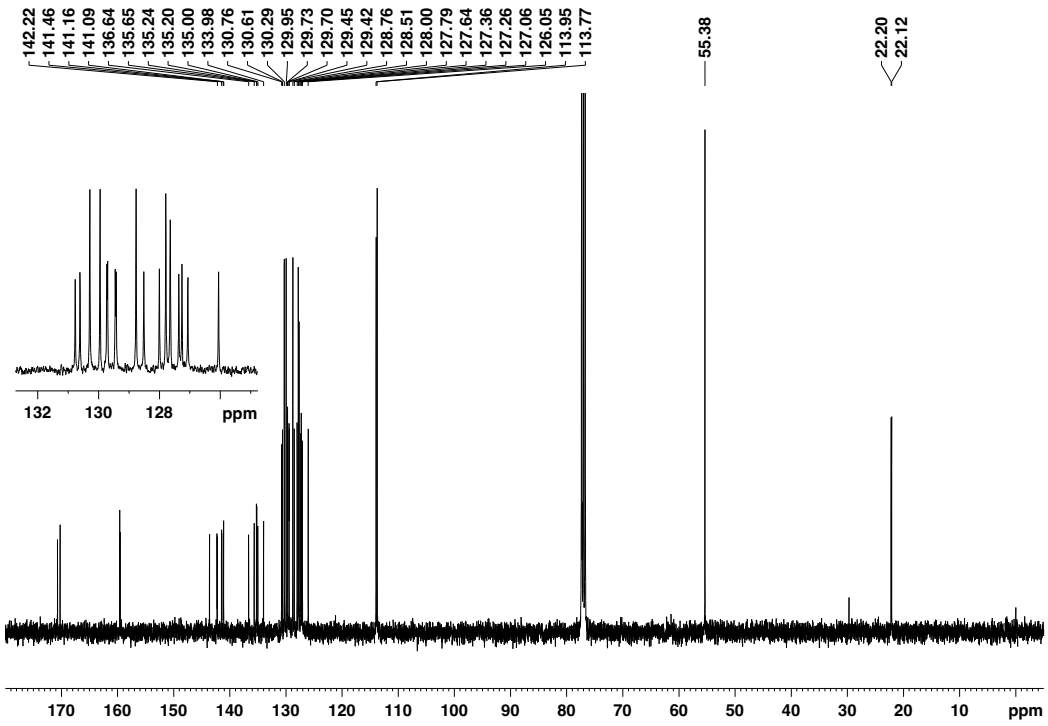
5-Ethanoyl-10-(4-methoxyphenyl)-*5H*-dibenzo[*b*,*f*]azepine (10b)

Isomeric ratio = 54/46

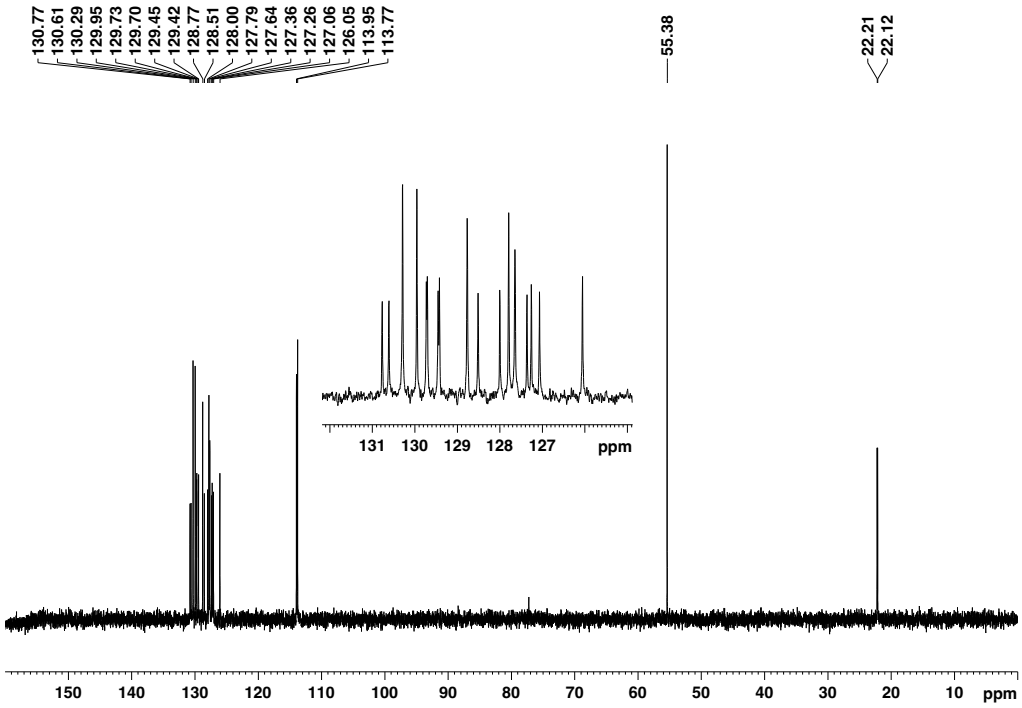
^{1}H NMR (400 MHz, $CDCl_3$)



^{13}C{^{1}H} NMR (100 MHz, $CDCl_3$)



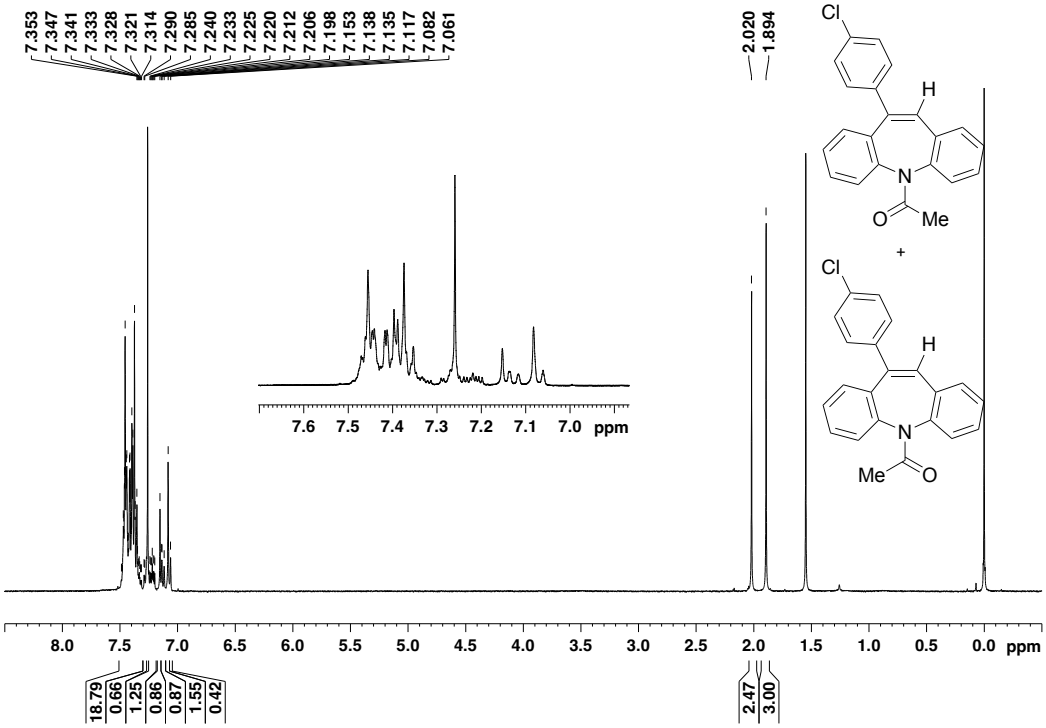
DEPT NMR (100 MHz, $CDCl_3$)



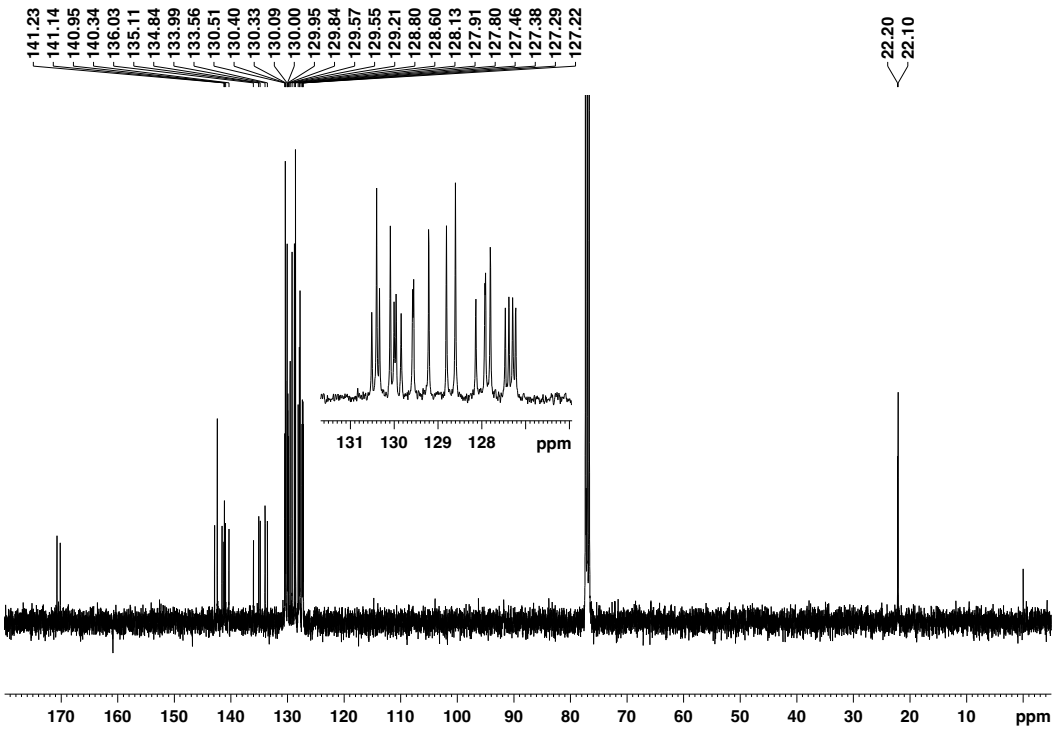
5-Ethanoyl-10-(4-chlorophenyl)-*5H*-dibenzo[*b*,*f*]azepine (10c)

Isomeric ratio = 56/44

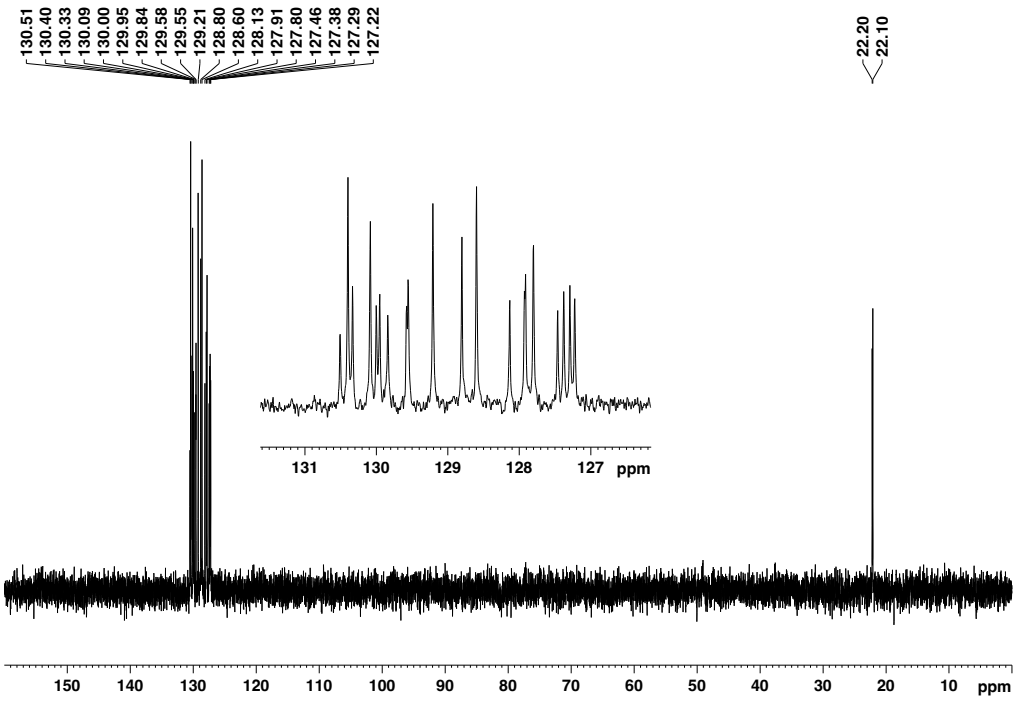
^{1}H NMR (400 MHz, $CDCl_3$)



^{13}C{^{1}H} NMR (100 MHz, $CDCl_3$)



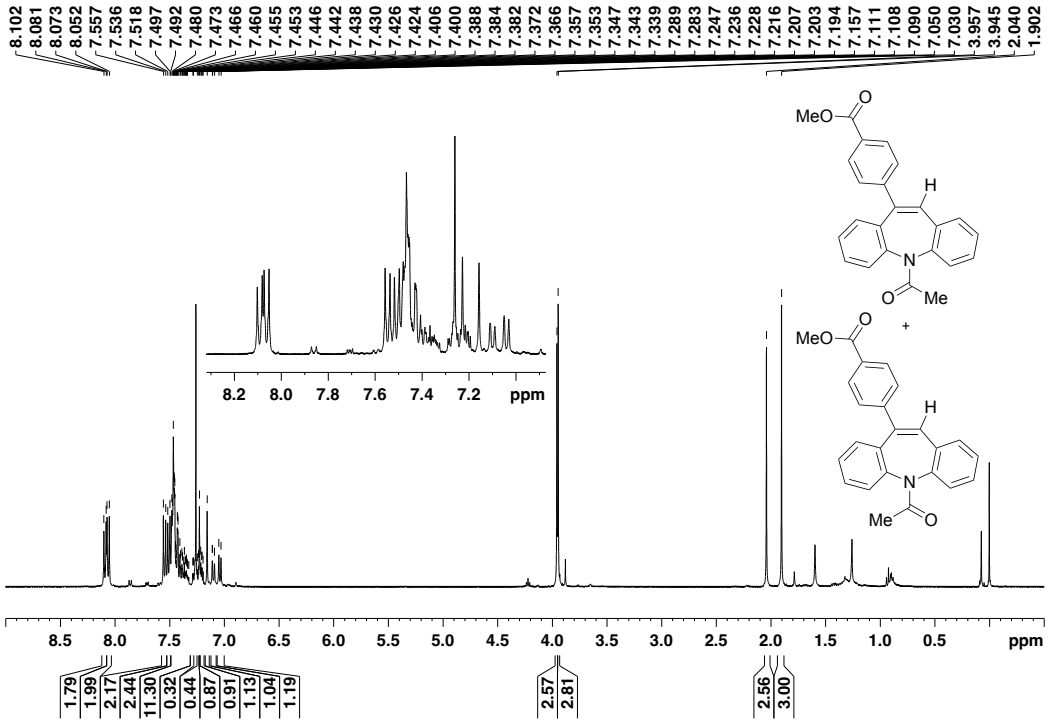
DEPT NMR (100 MHz, $CDCl_3$)



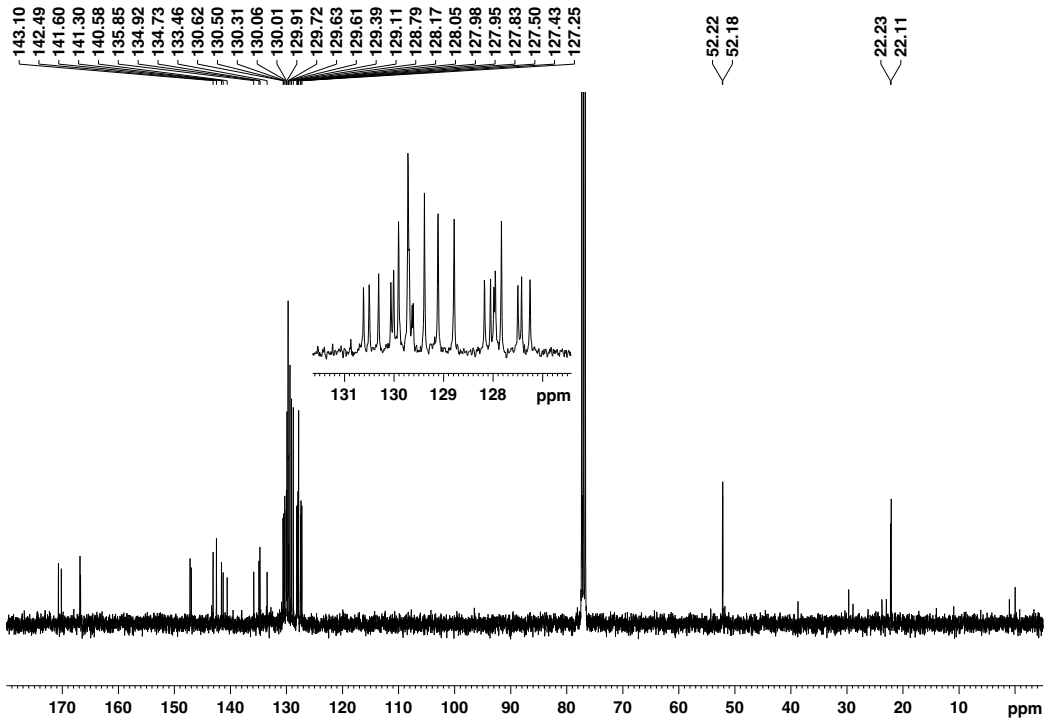
5-Ethanoyl-10-(4-methoxycarbonylphenyl)-*5H*-dibenzo[*b*,*f*]azepine (10d)

Isomeric ratio = 52/48

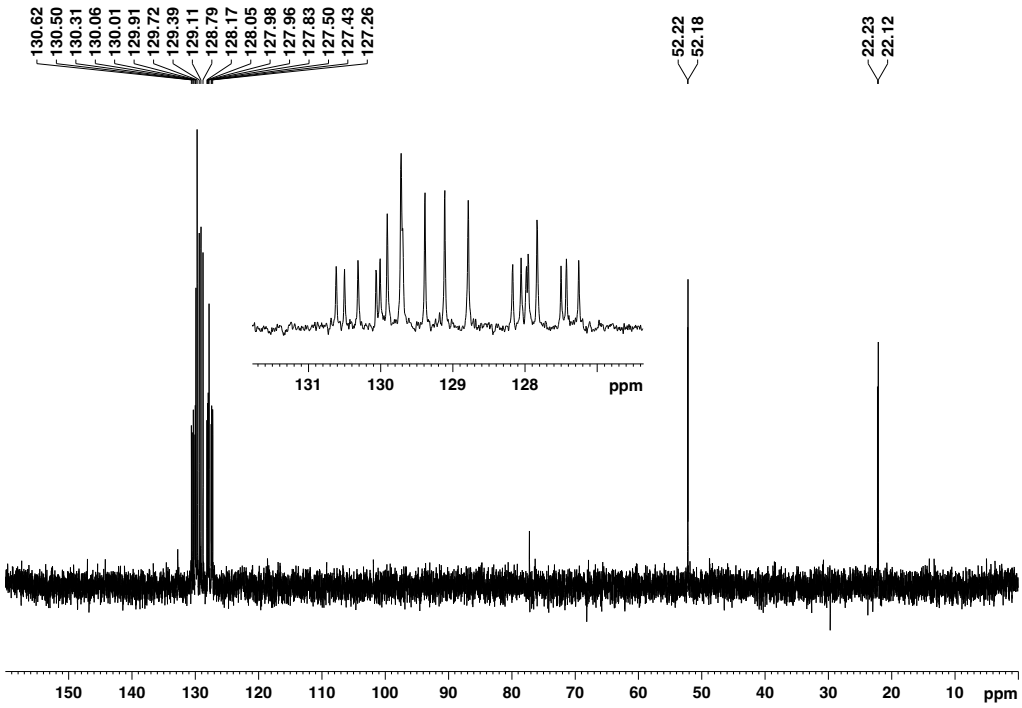
^{1}H NMR (400 MHz, $CDCl_3$)



^{13}C{^{1}H} NMR (100 MHz, $CDCl_3$)



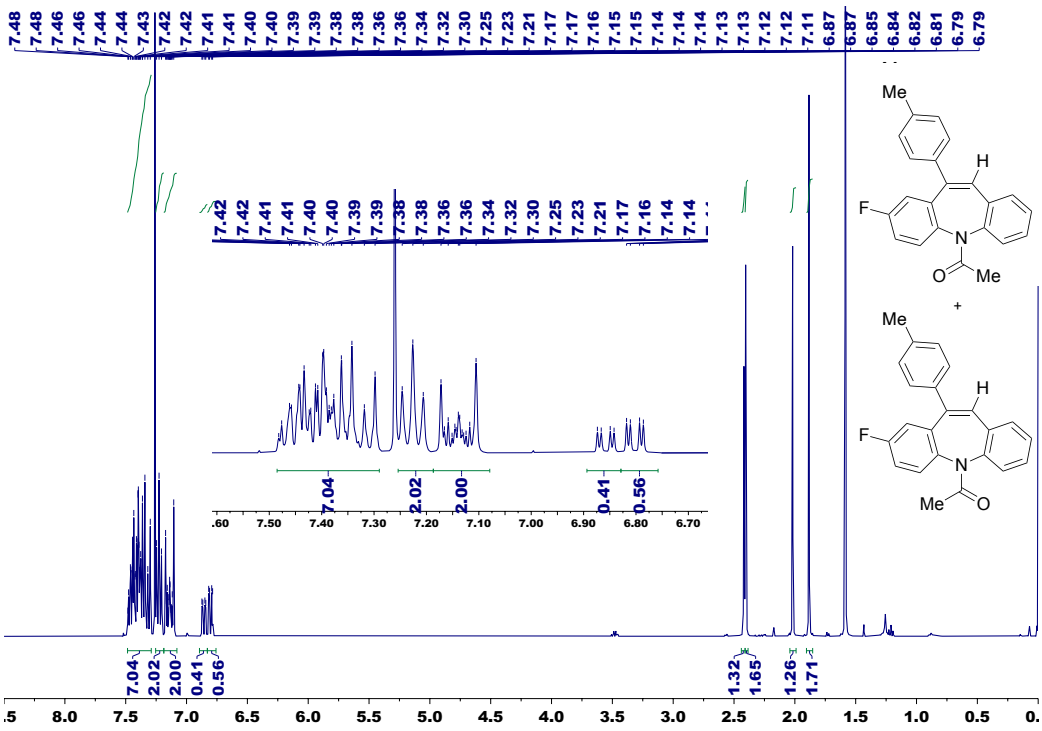
DEPT NMR (100 MHz, $CDCl_3$)



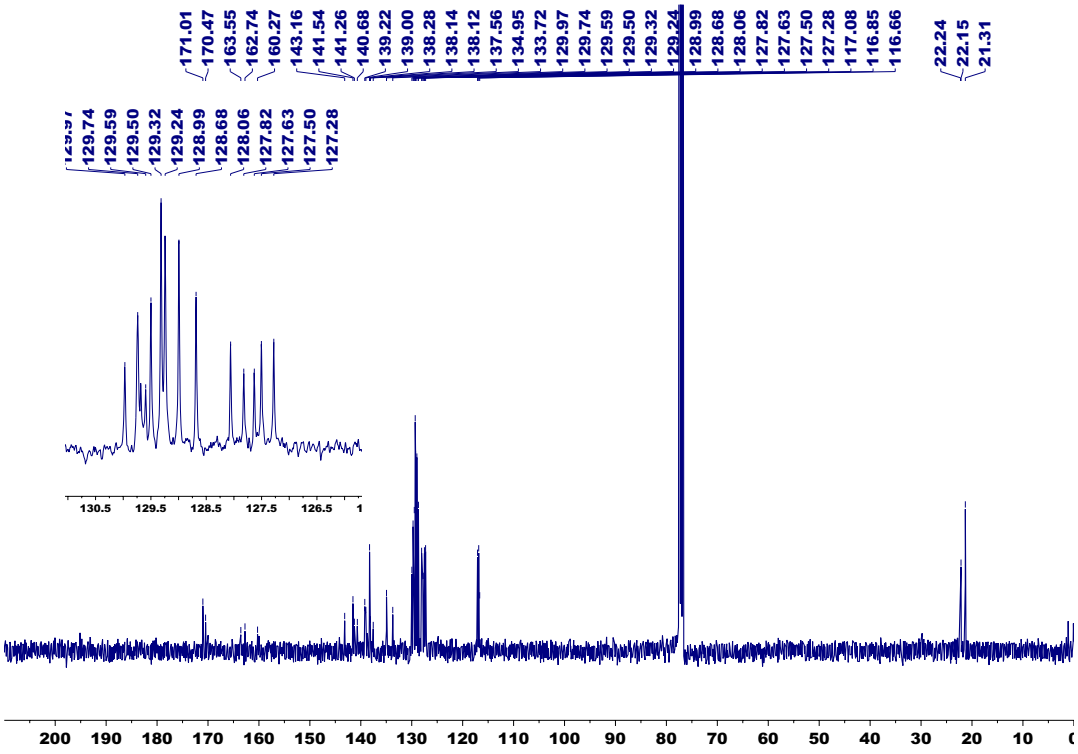
5-Ethanoyl-2-fluoro-11-(4-methylphenyl)-5*H*-dibenzo[*b*,*f*]azepine (10e)

Isomeric ratio = 56/44

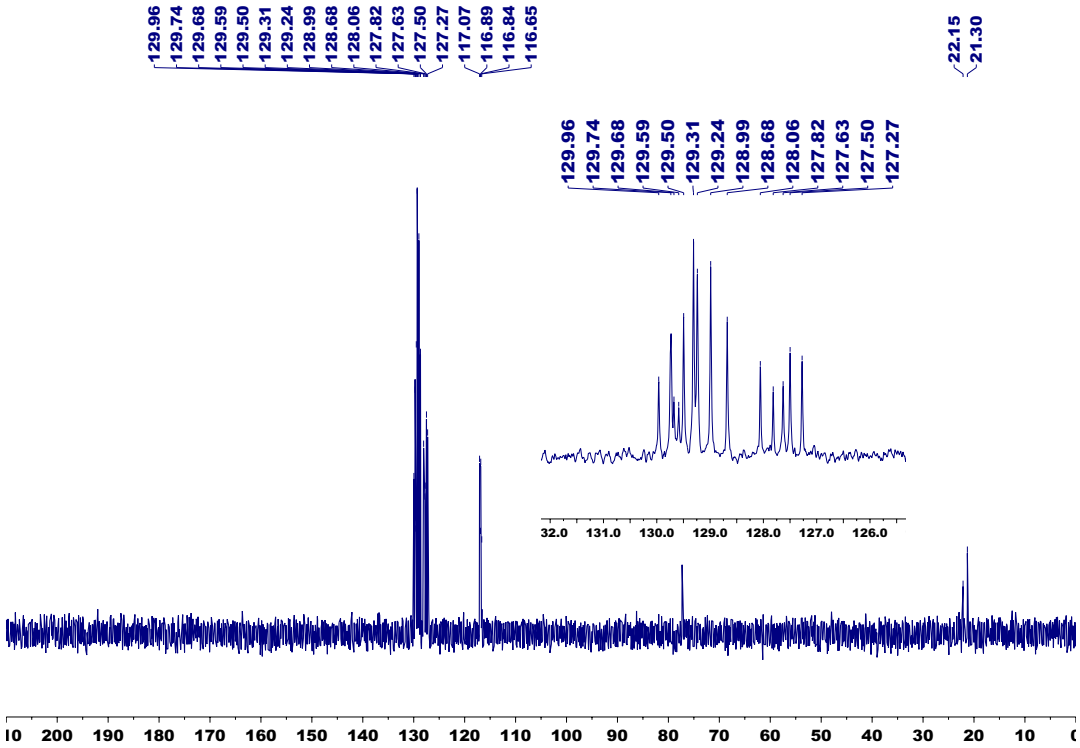
^{1}H NMR (400 MHz, $CDCl_3$)



^{13}C{^{1}H} NMR (100 MHz, $CDCl_3$)



DEPT NMR (100 MHz, $CDCl_3$)



^{19}F NMR (376.5 MHz, $CDCl_3$)