

Stereospecific Isomerization of Allylic Halides via Ion Pairs with Induced NonCovalent Chirality

Samuel Martínez-Erro,[‡] Víctor García-Vázquez,[‡] Amparo Sanz-Marco, Belén Martín-Matute*

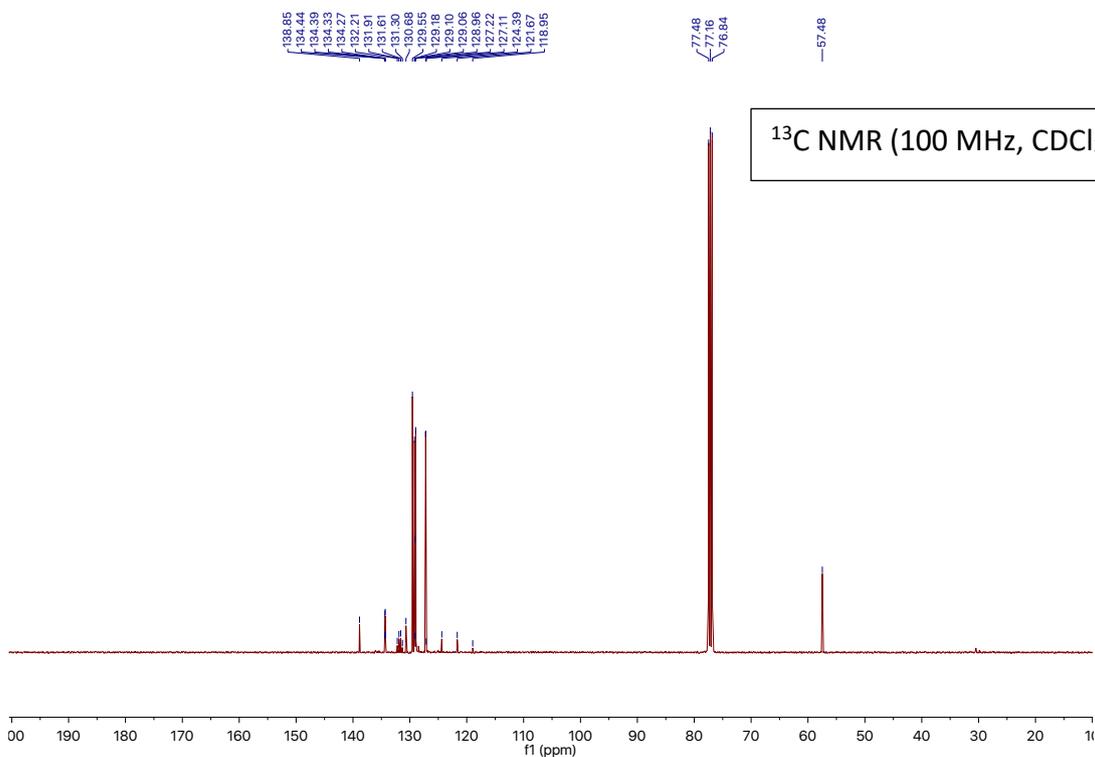
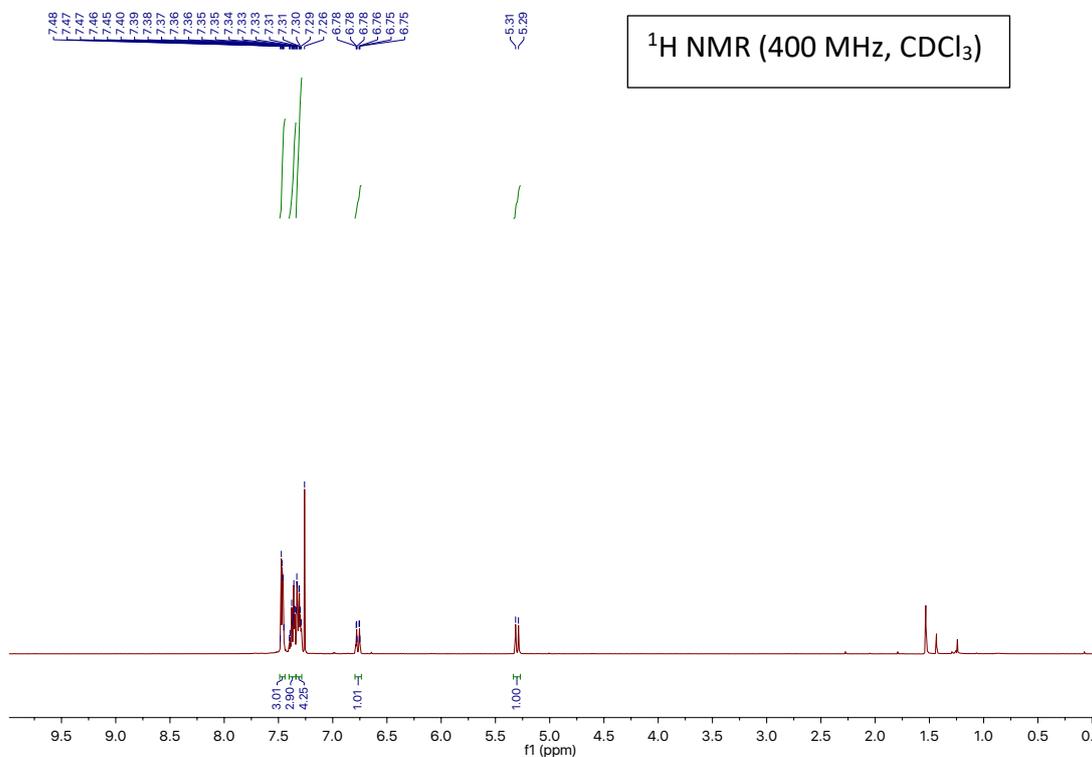
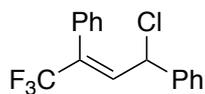
belen.martin.matute@su.se

Supporting Information – NMR Spectra

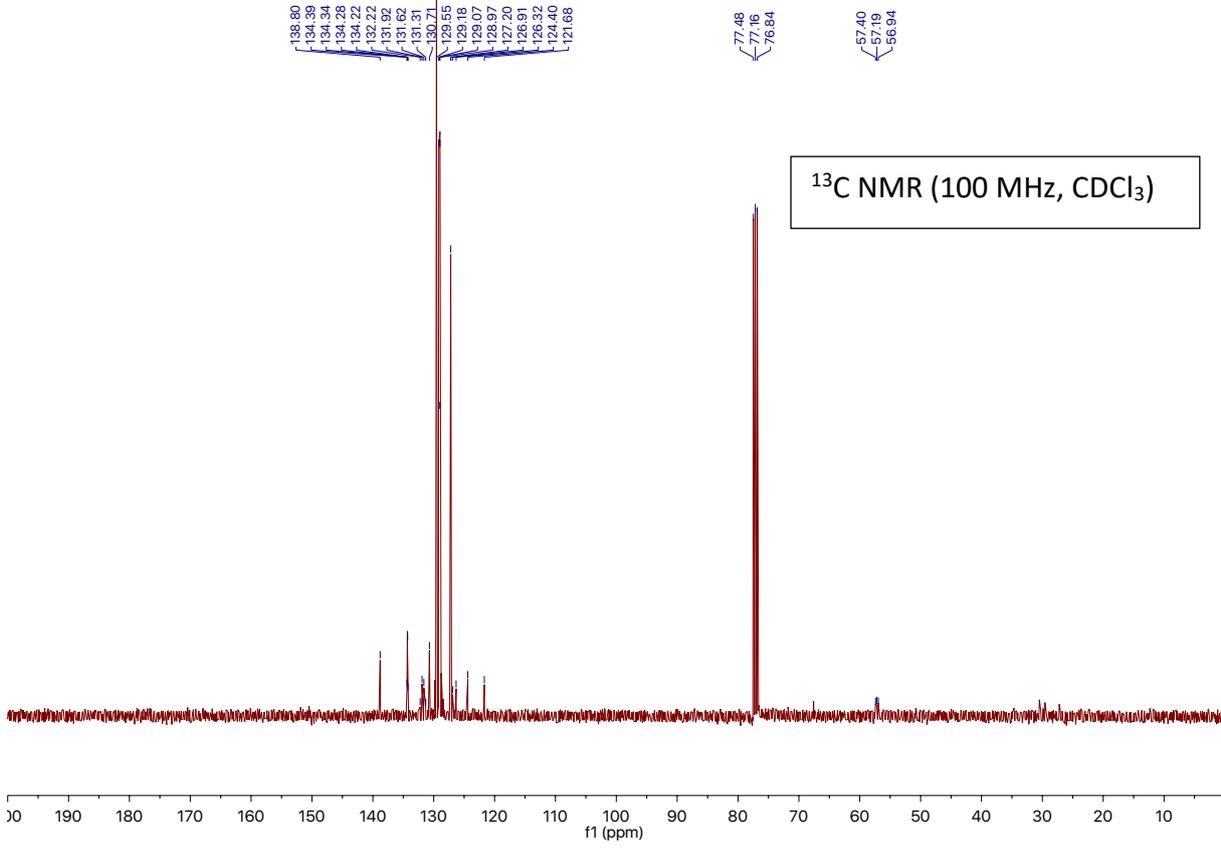
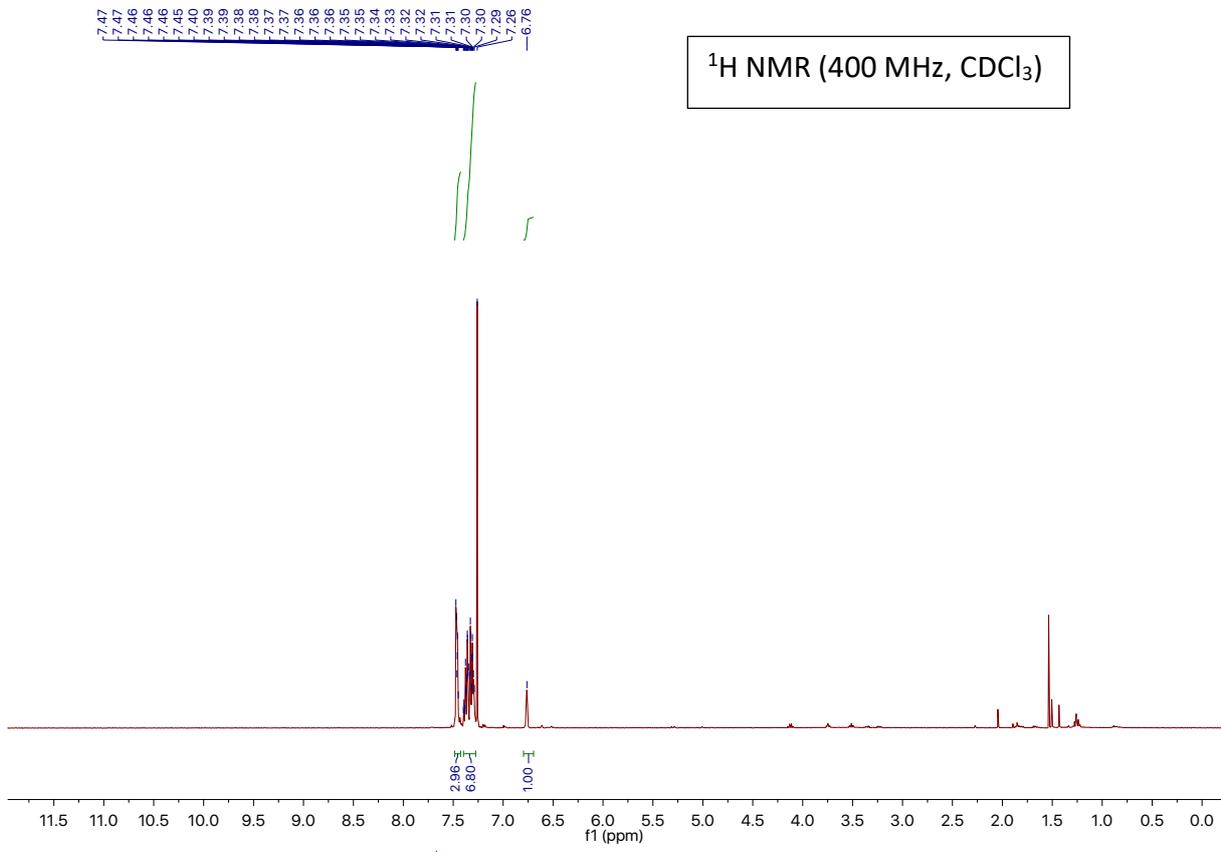
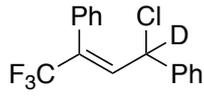
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S50 HPLC Chromatograms of vinyl chlorides **5a**, **5b**, **5c**, **5d**, **5e**, **5m** and **5g**

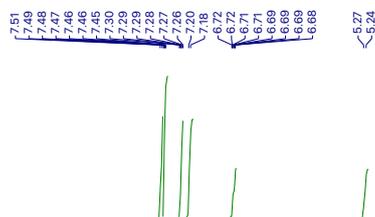
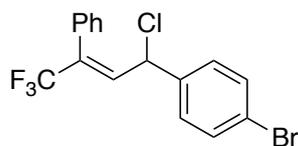
(E)-(1-chloro-4,4,4-trifluorobut-2-ene-1,3-diyl)dibenzene (2a)



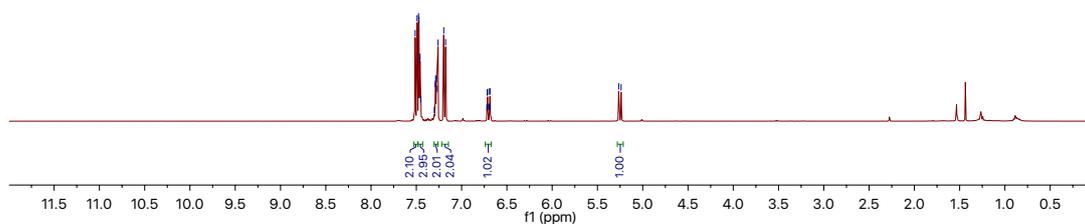
(E)-(1-chloro-4,4,4-trifluorobut-2-ene-1,3-diyl-1-d)dibenzene (2a-d)



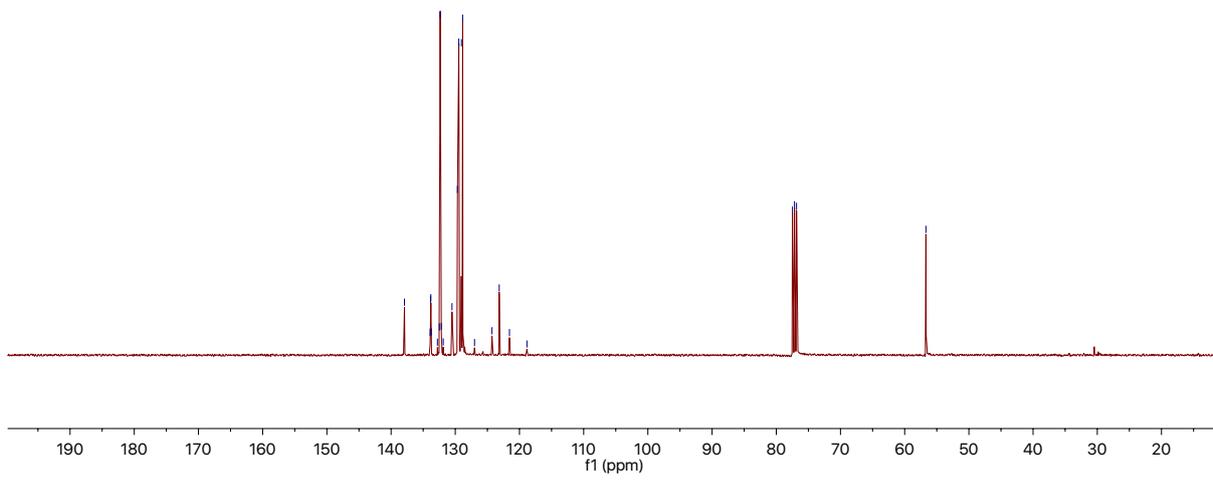
(E)-1-Bromo-4-(1-chloro-4,4,4-trifluoro-3-phenylbut-2-en-1-yl)benzene (2b)



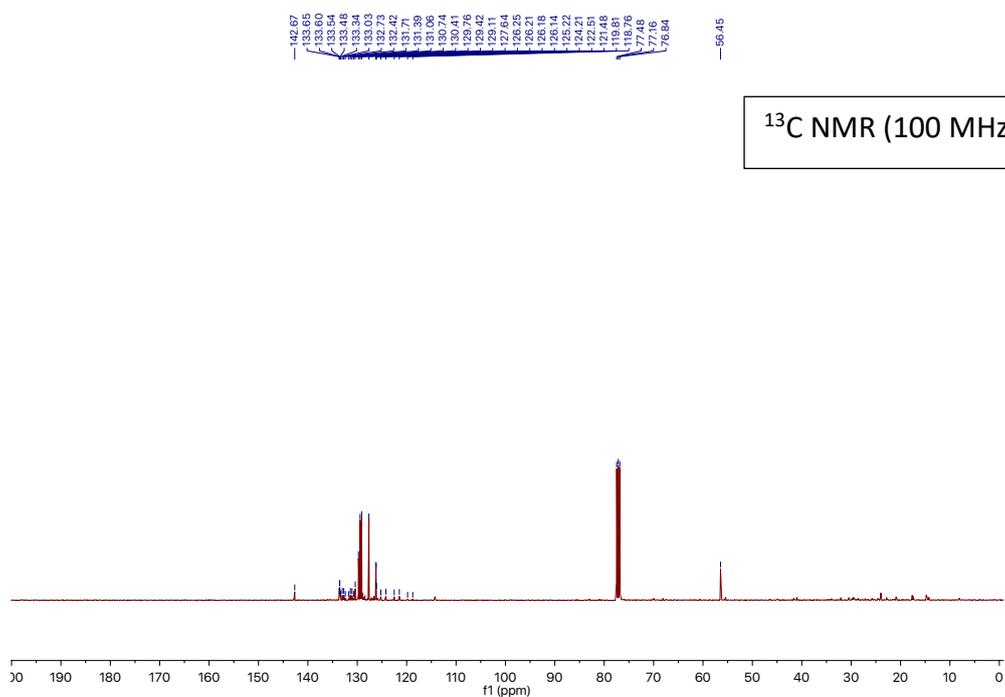
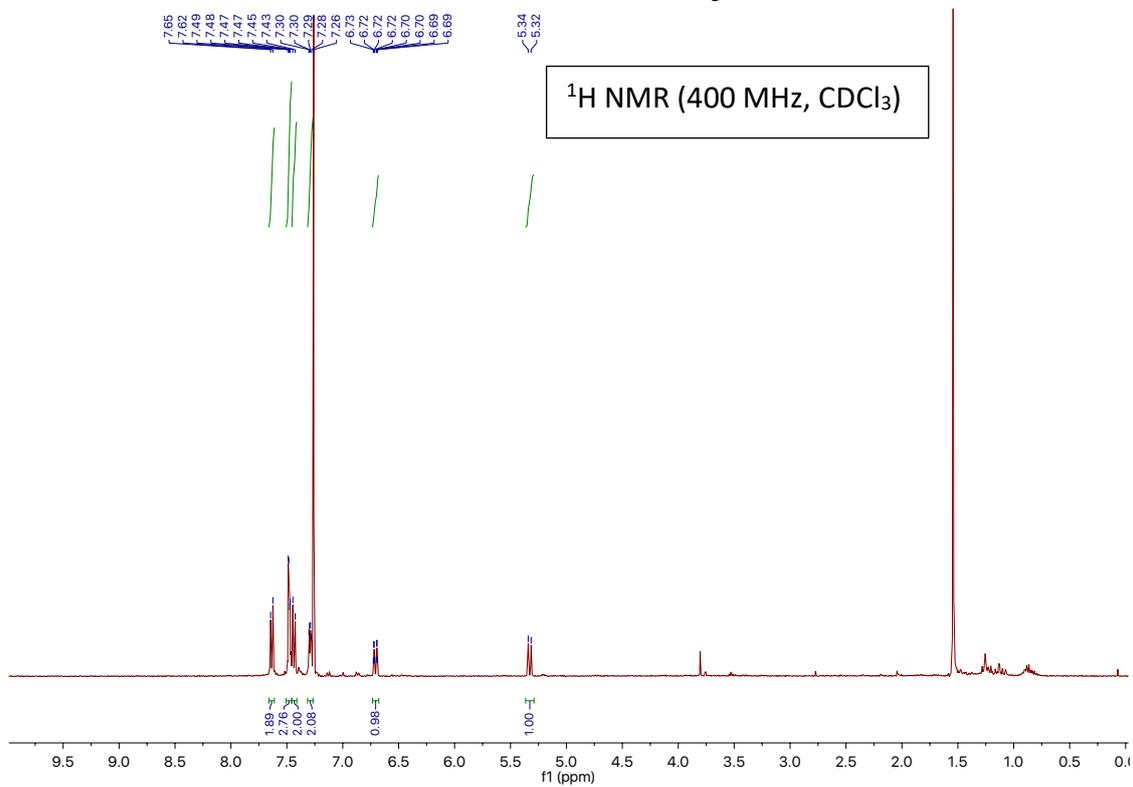
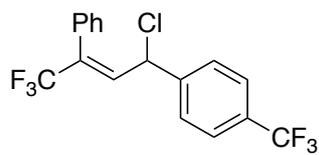
¹H NMR (400 MHz, CDCl₃)



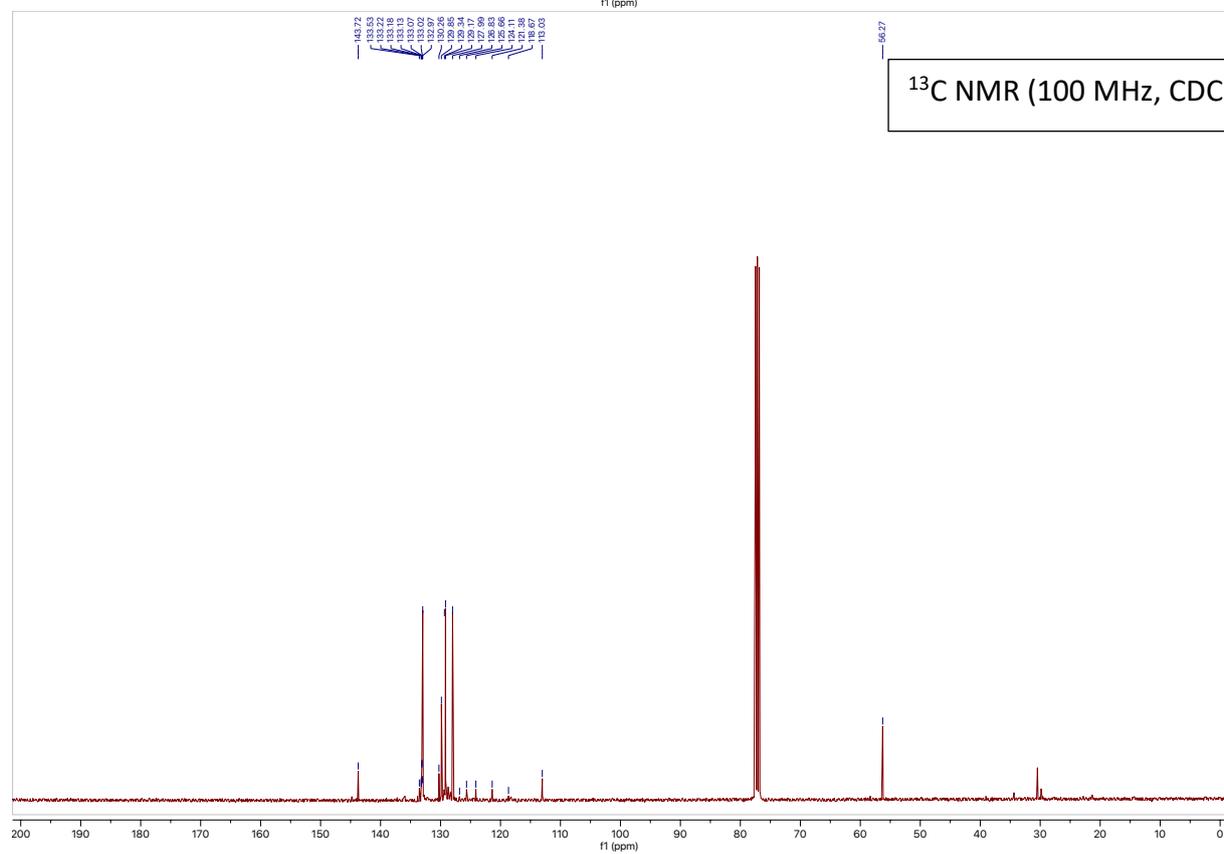
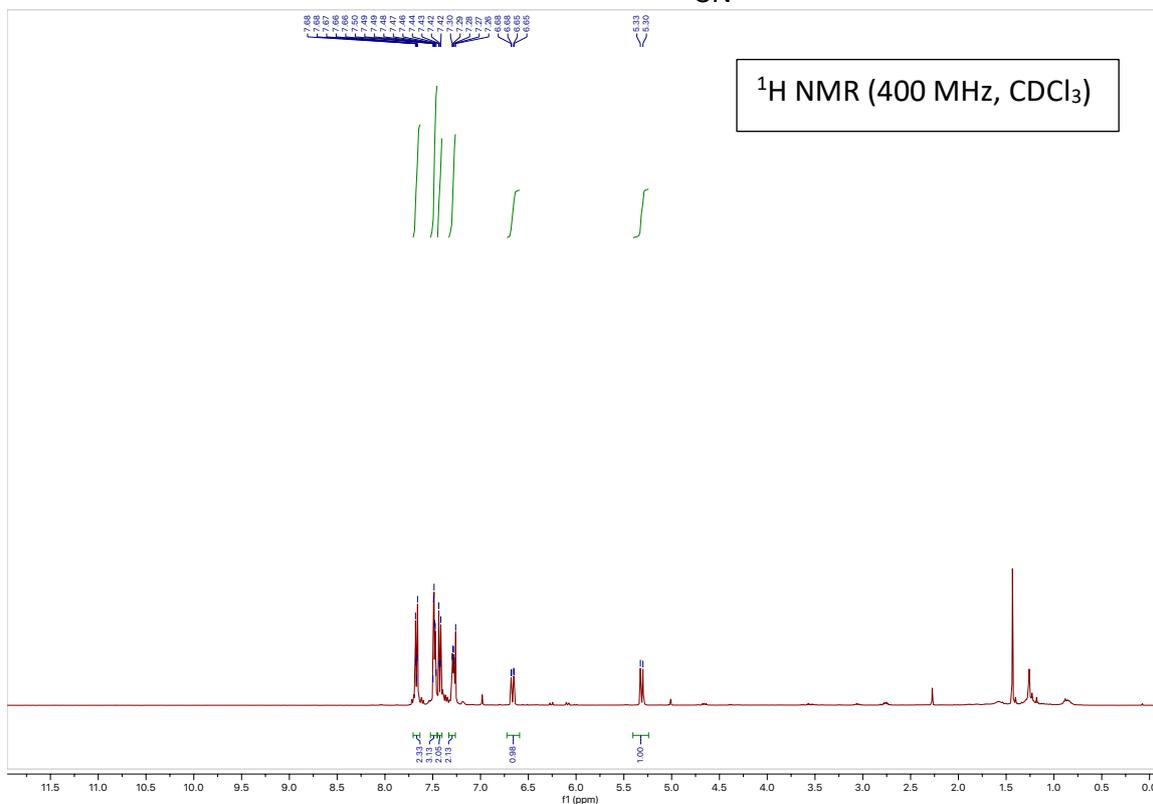
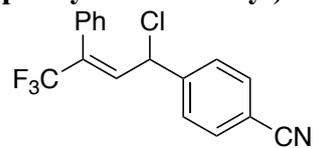
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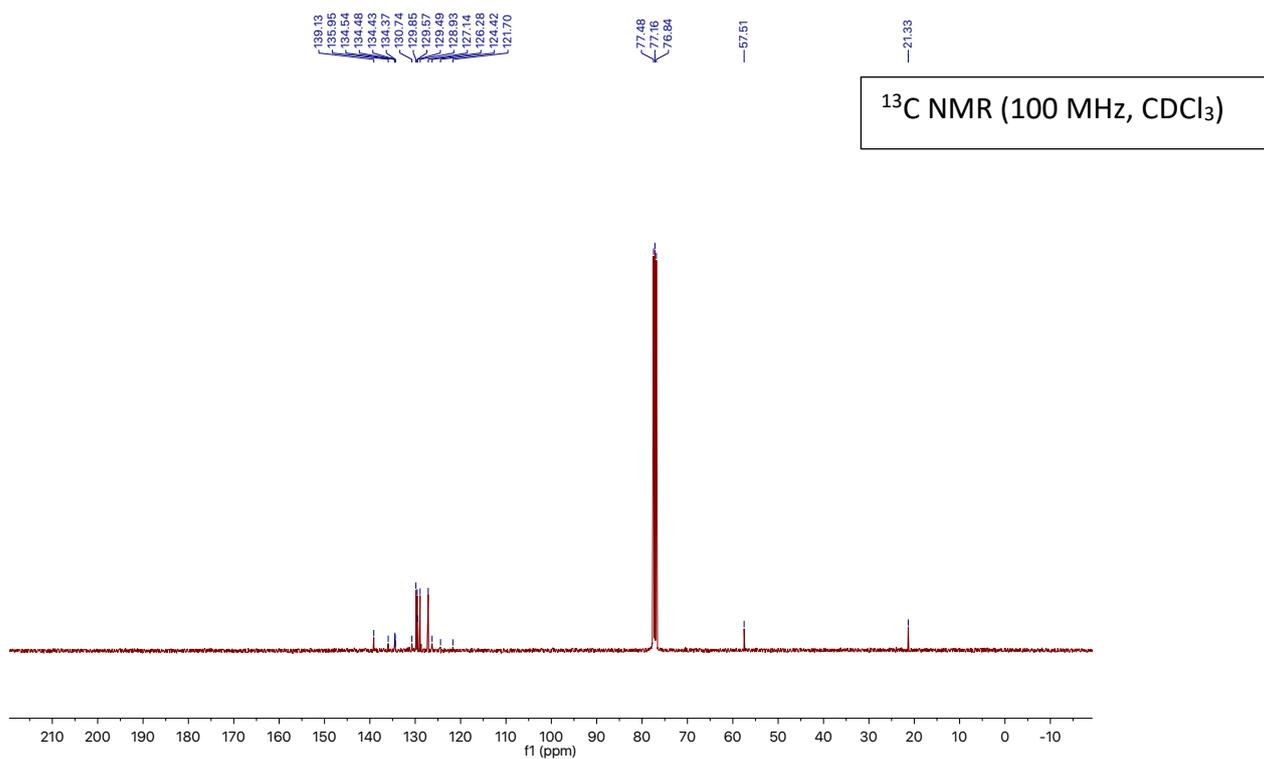
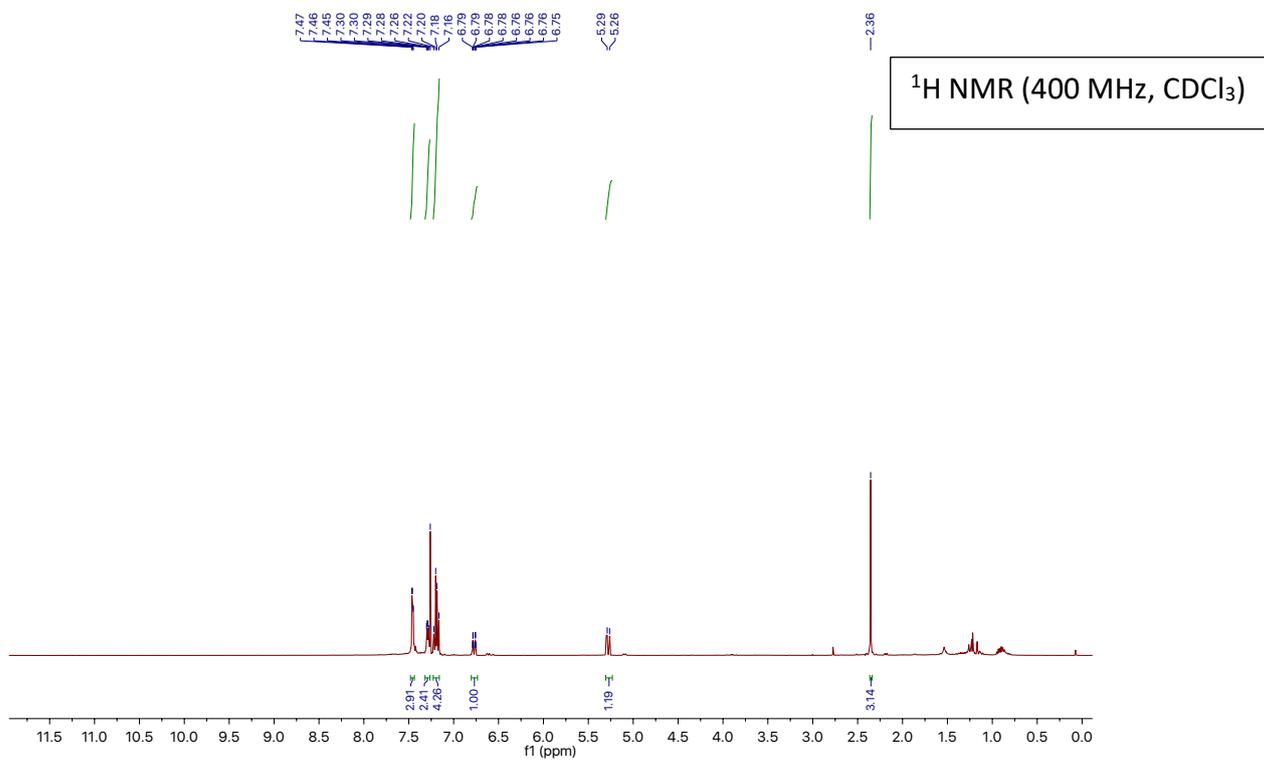
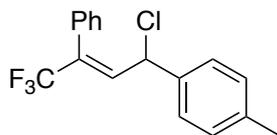
(E)-1-(1-chloro-4,4,4-trifluoro-3-phenylbut-2-en-1-yl)-4-(trifluoromethyl)benzene (2c)



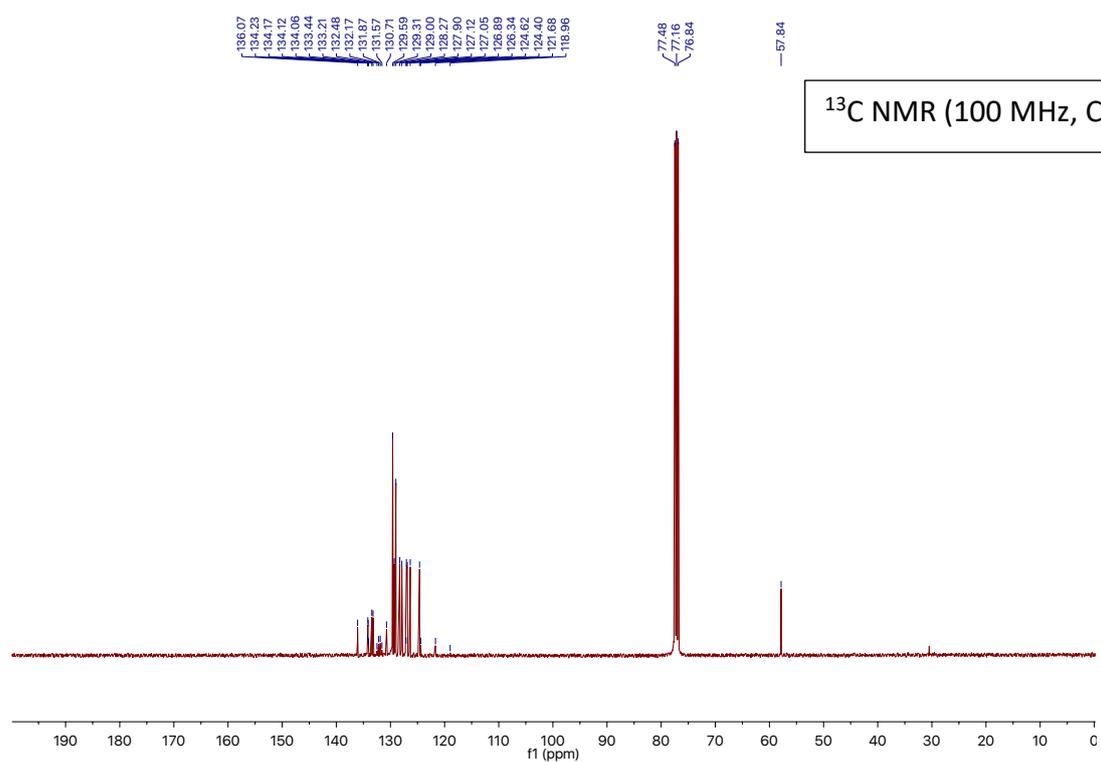
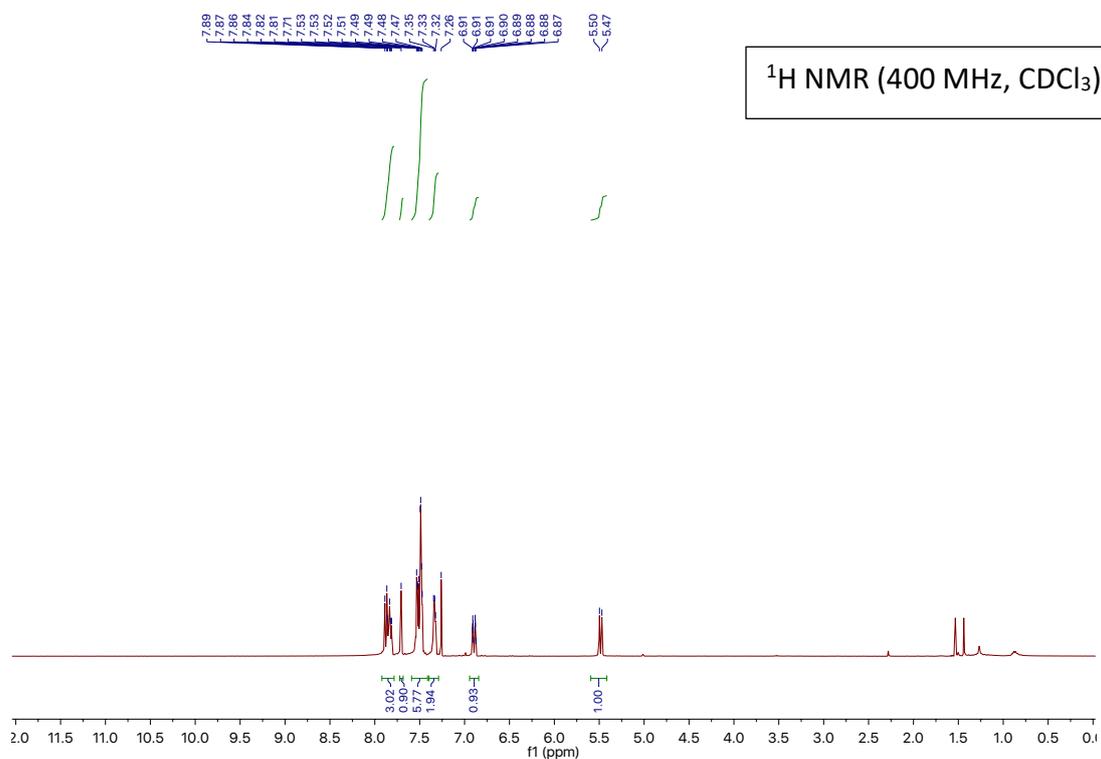
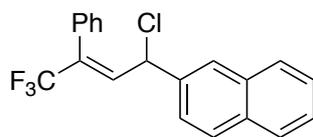
(E)-4-(1-chloro-4,4,4-trifluoro-3-phenylbut-2-en-1-yl)benzonitrile (2d)



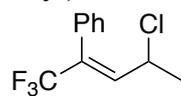
(E)-1-(1-chloro-4,4,4-trifluoro-3-phenylbut-2-en-1-yl)-4-methylbenzene (2f)



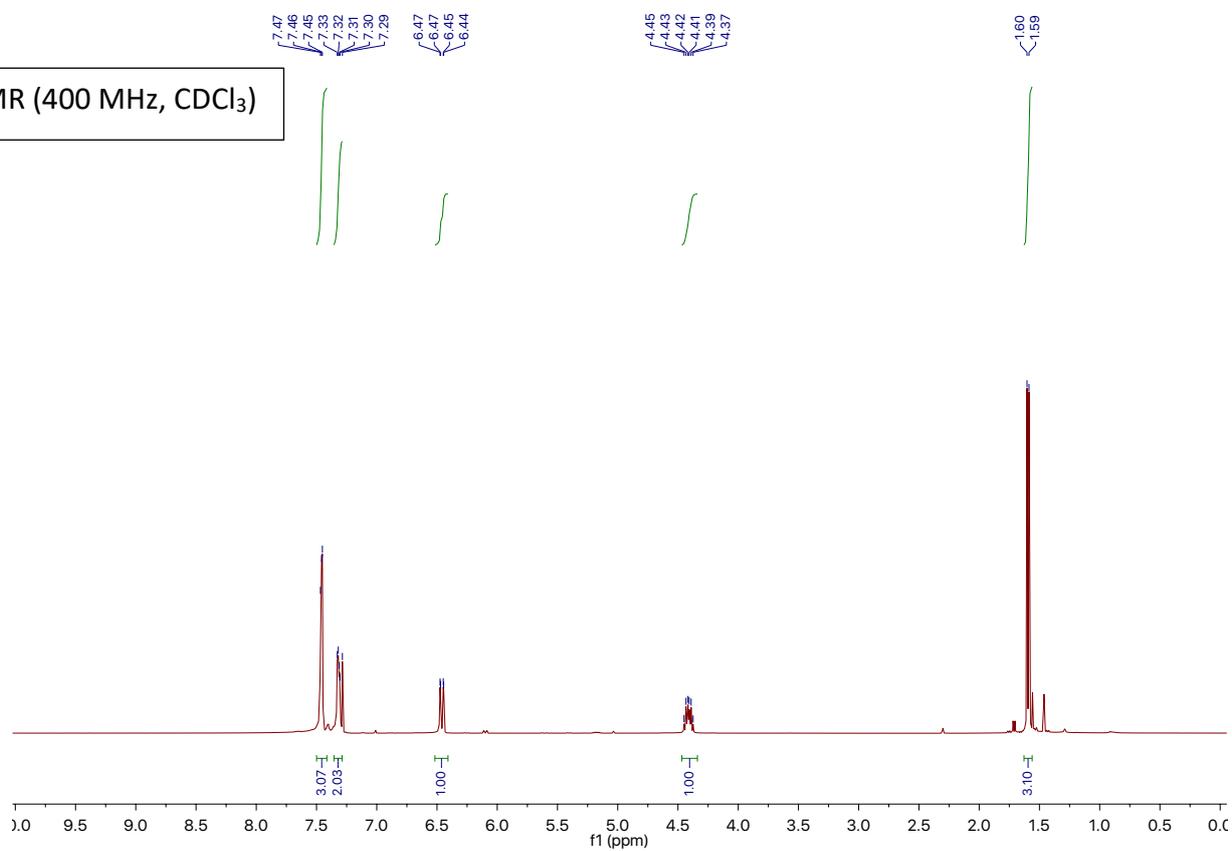
(E)-2-(1-chloro-4,4,4-trifluoro-3-phenylbut-2-en-1-yl)naphthalene (2g)



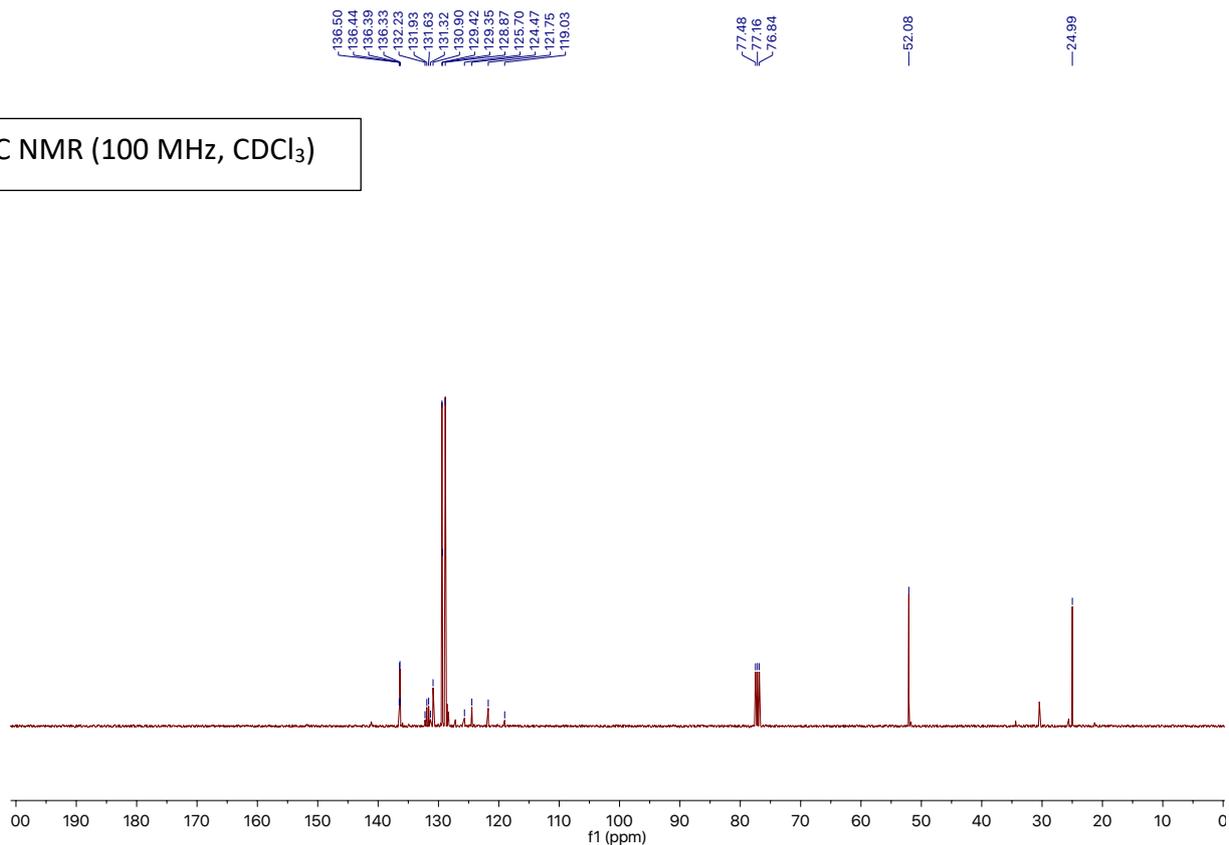
(E)-(4-chloro-1,1,1-trifluoropent-2-en-2-yl)benzene (2h)



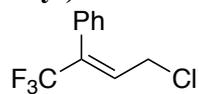
¹H NMR (400 MHz, CDCl₃)



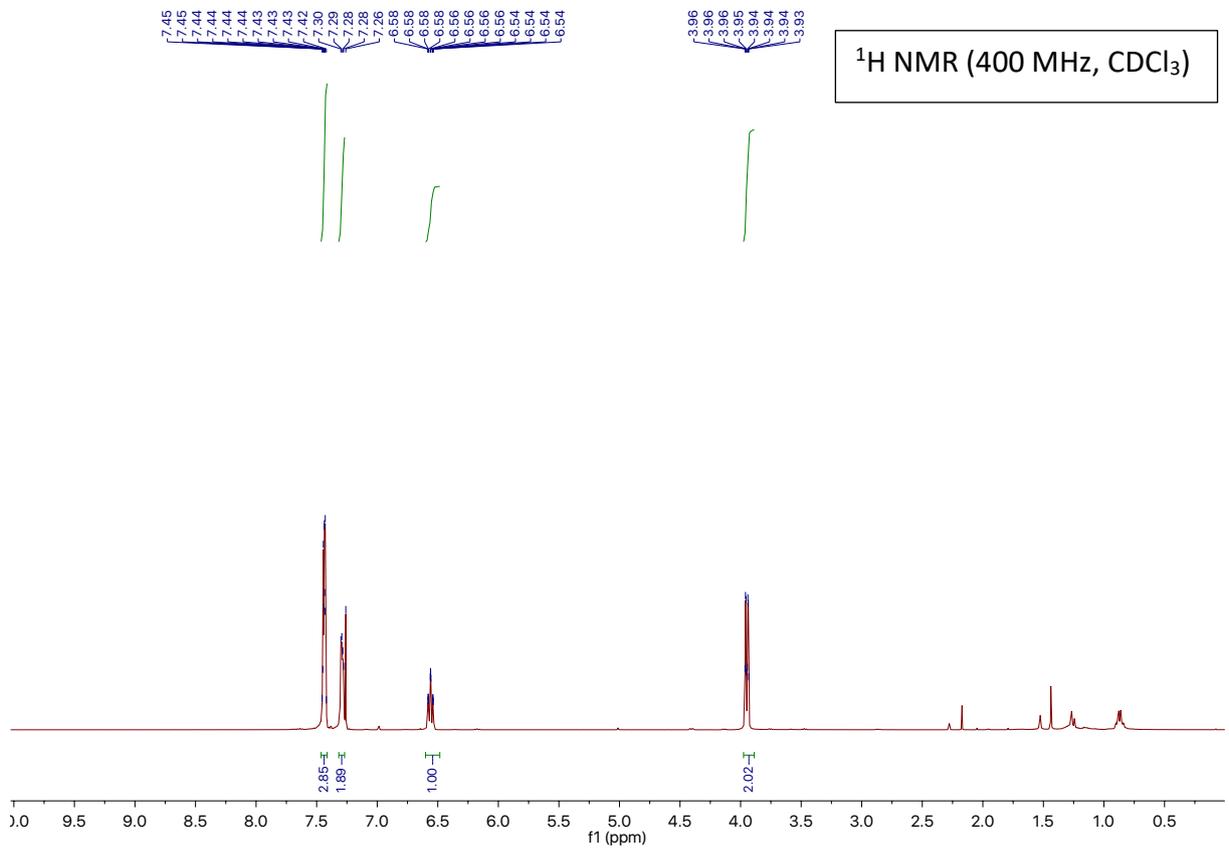
^{13}C NMR (100 MHz, CDCl_3)

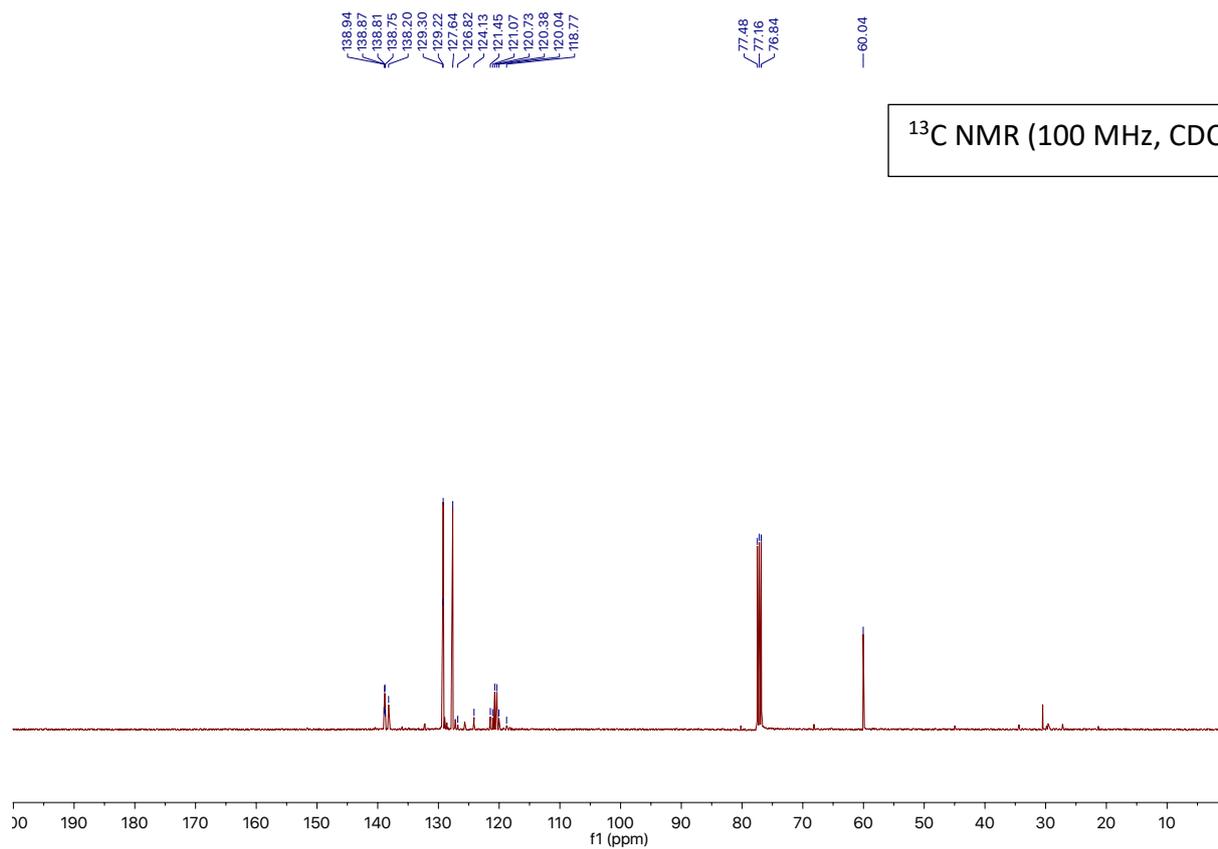


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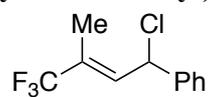


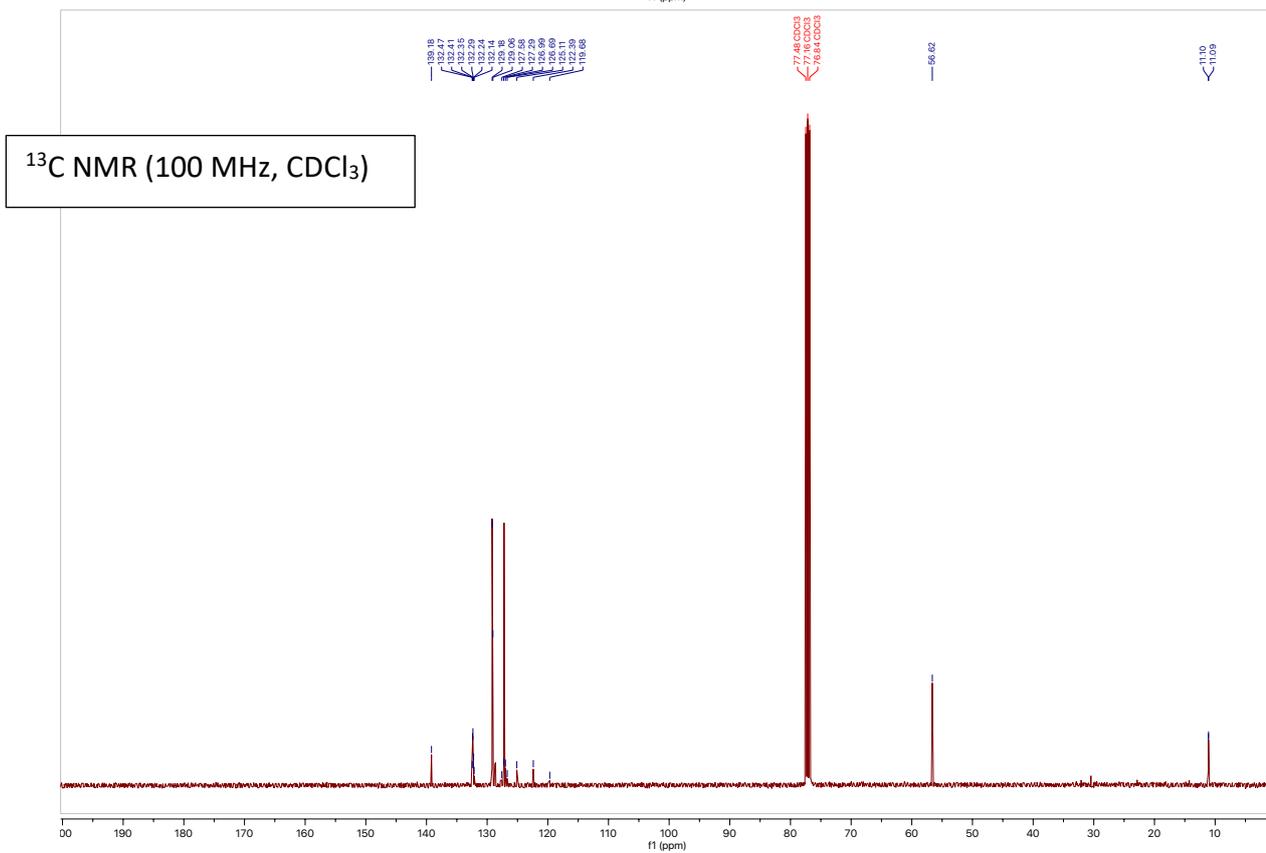
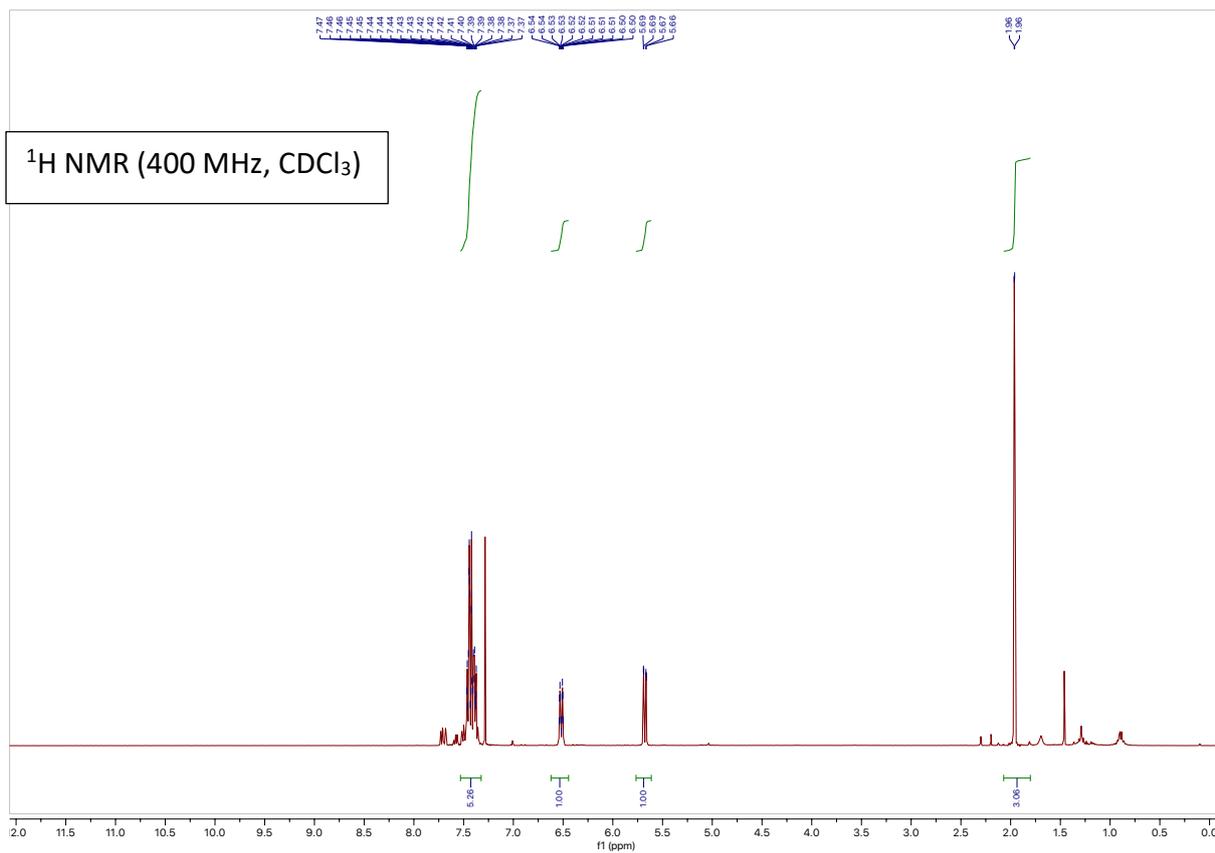
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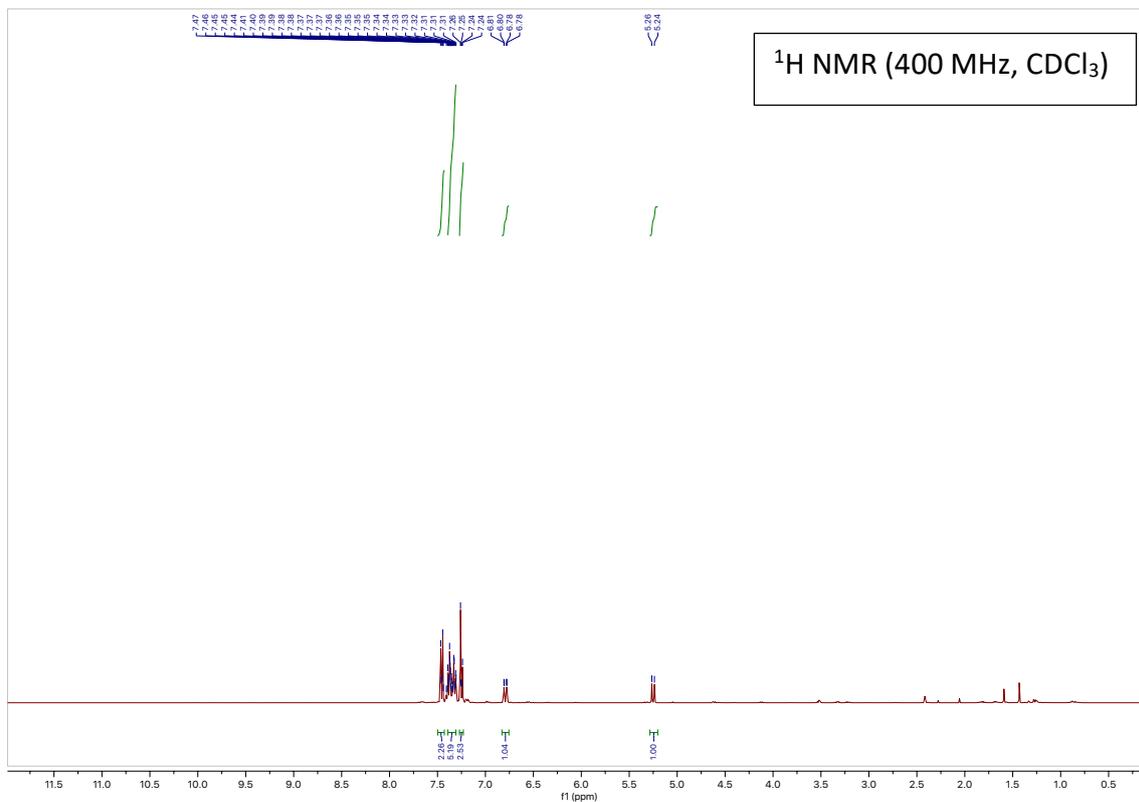
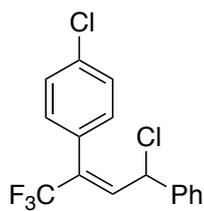


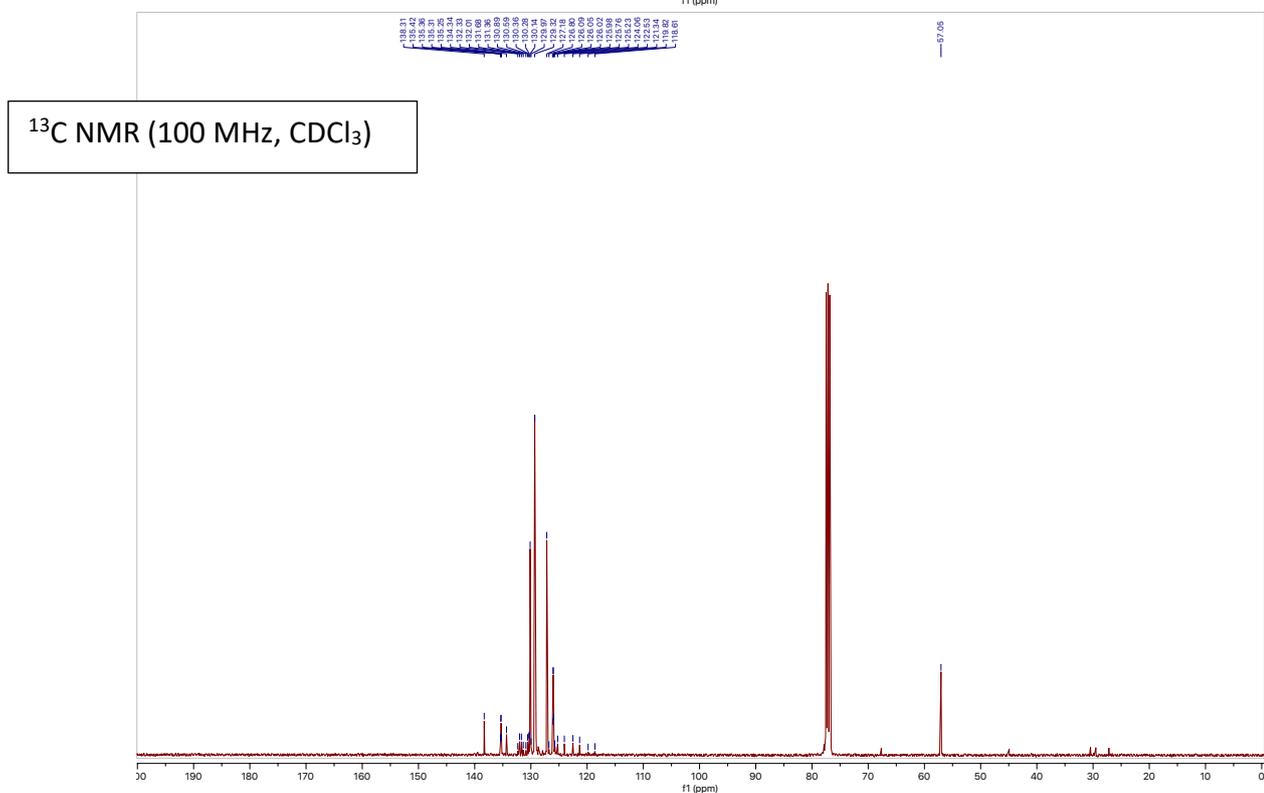
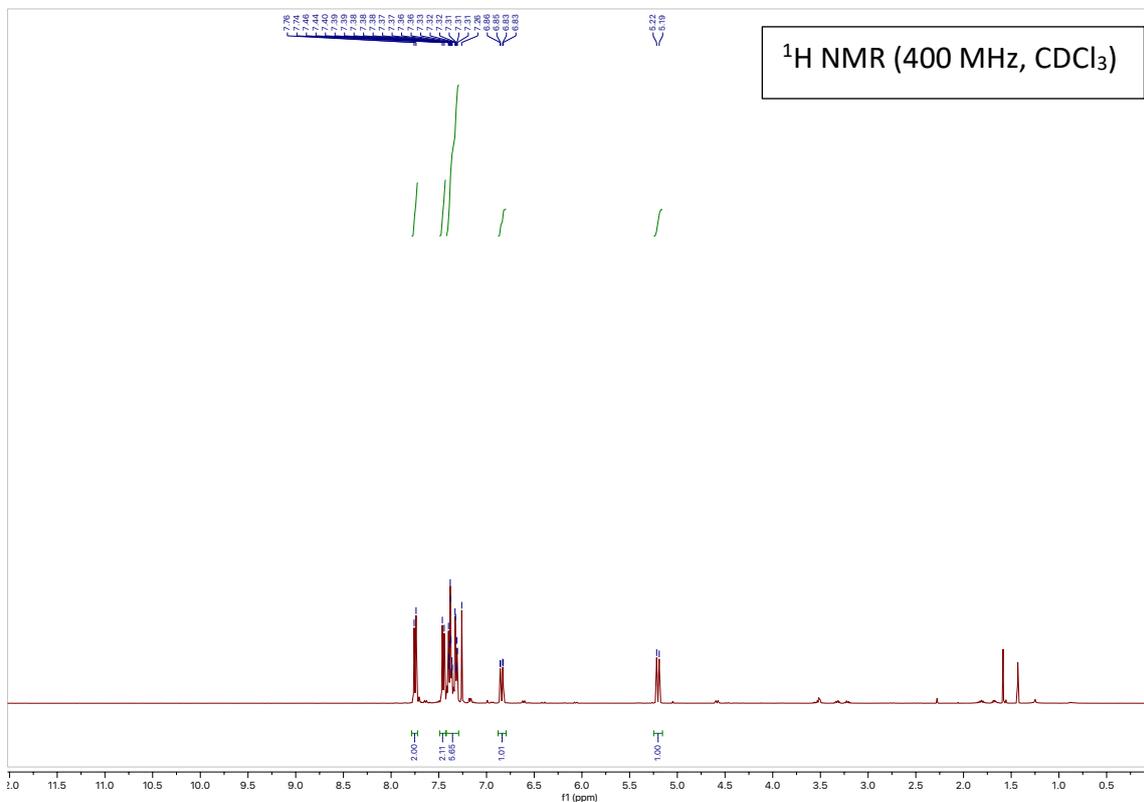
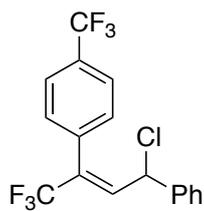
(E)-(1-chloro-4,4,4-trifluoro-3-methylbut-2-en-1-yl)benzene (2k)



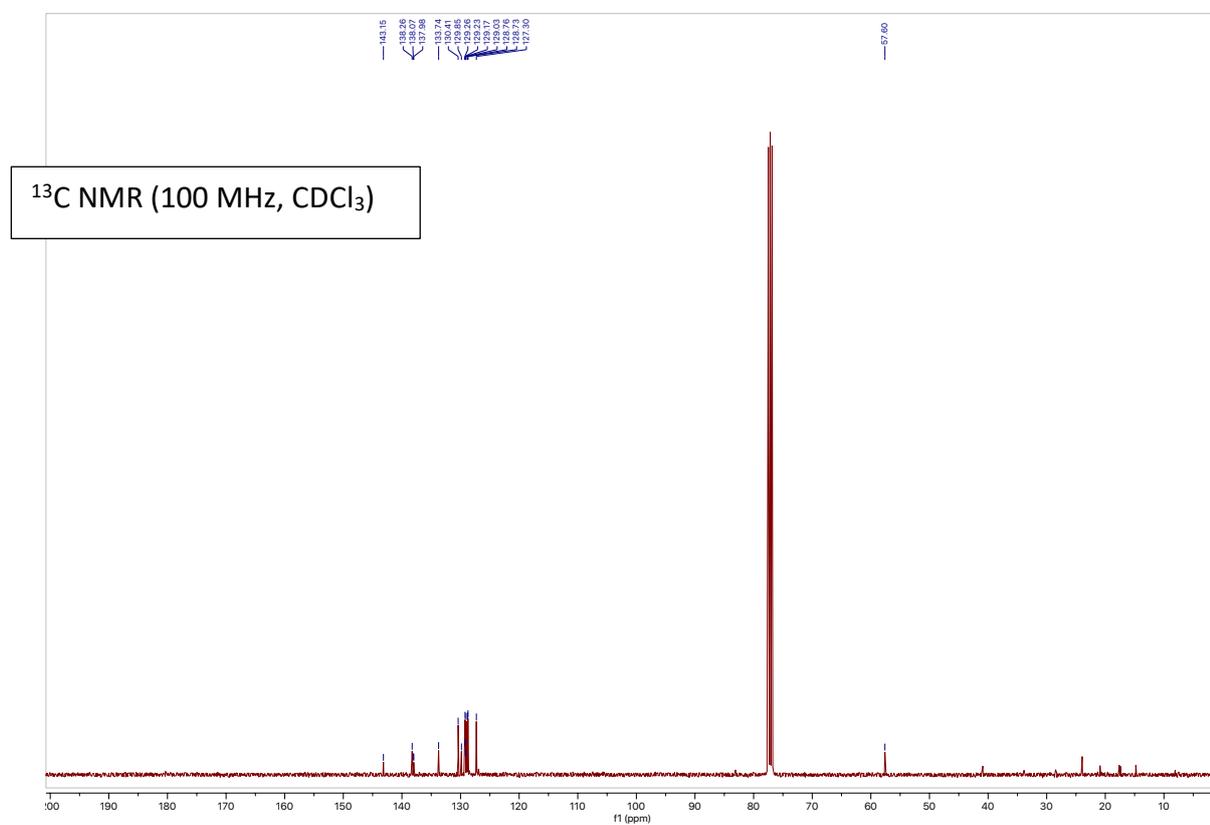
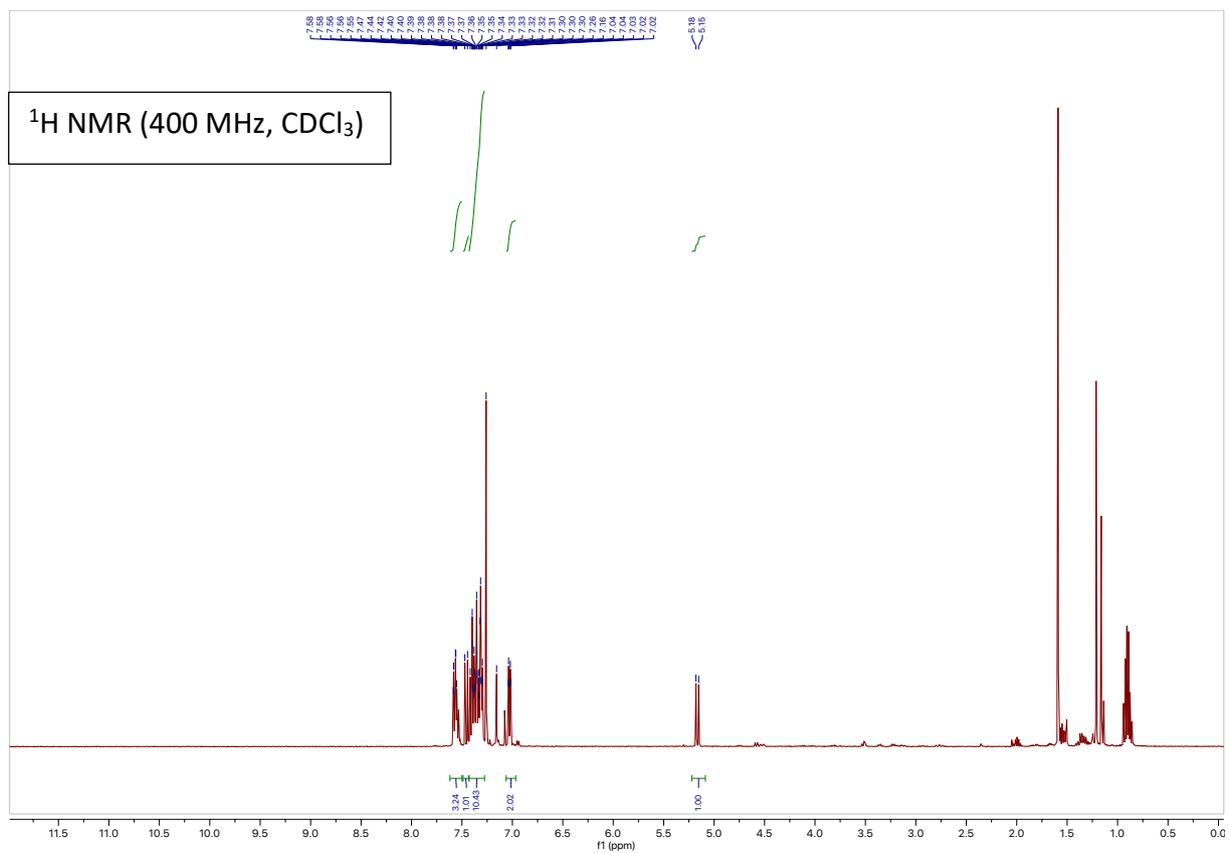
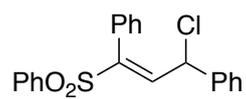


(E)-1-chloro-4-(4-chloro-1,1,1-trifluoro-4-phenylbut-2-en-2-yl)benzene (2l)

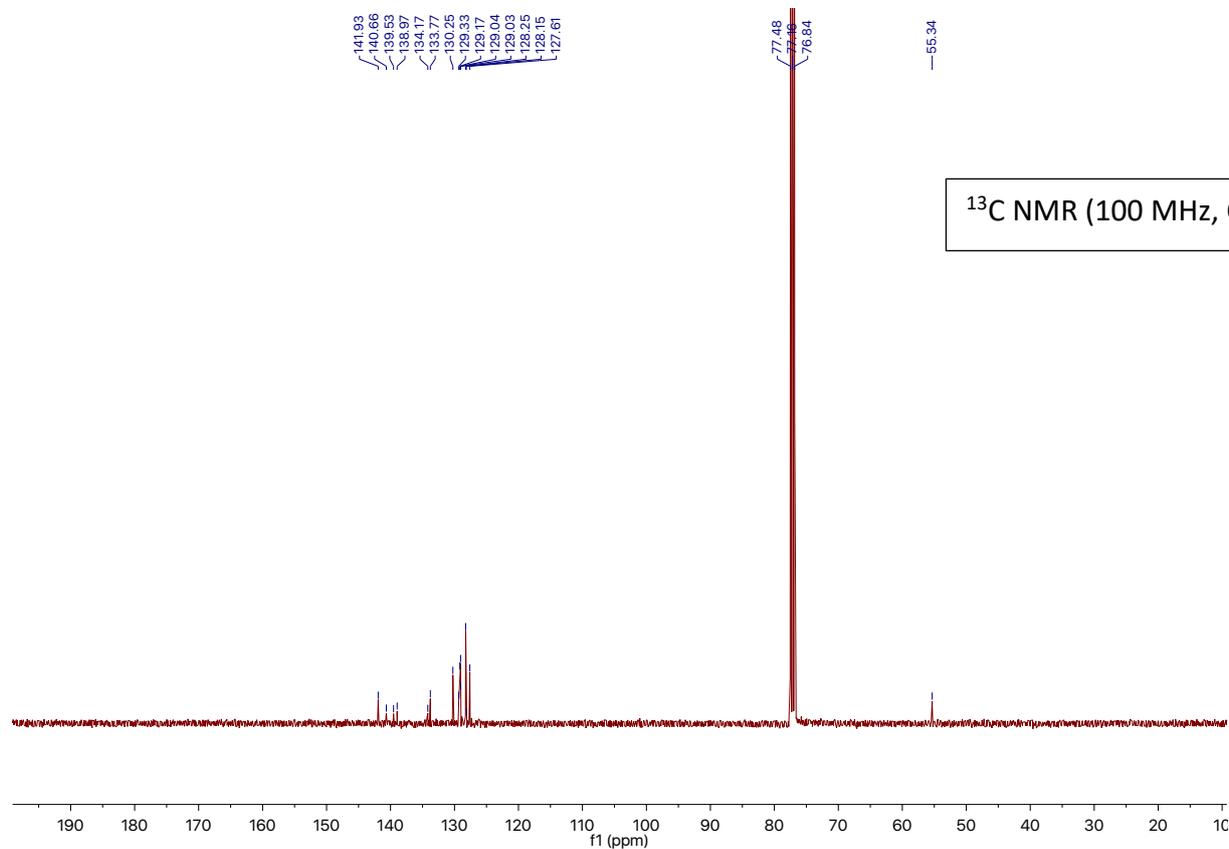
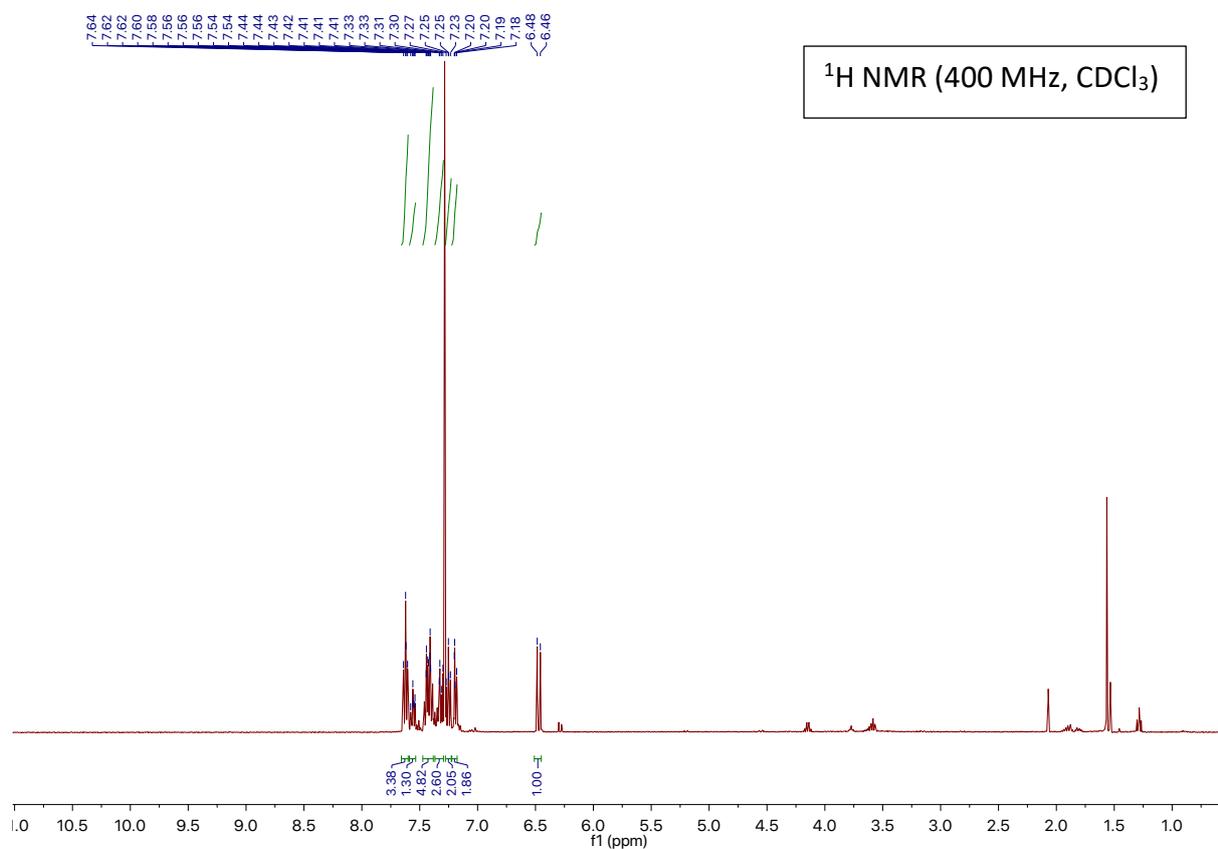
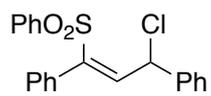




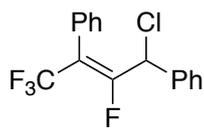
(E)-3-chloro-1-(phenylsulfonyl)prop-1-ene-1,3-diyl)dibenzene ((E)-2n)



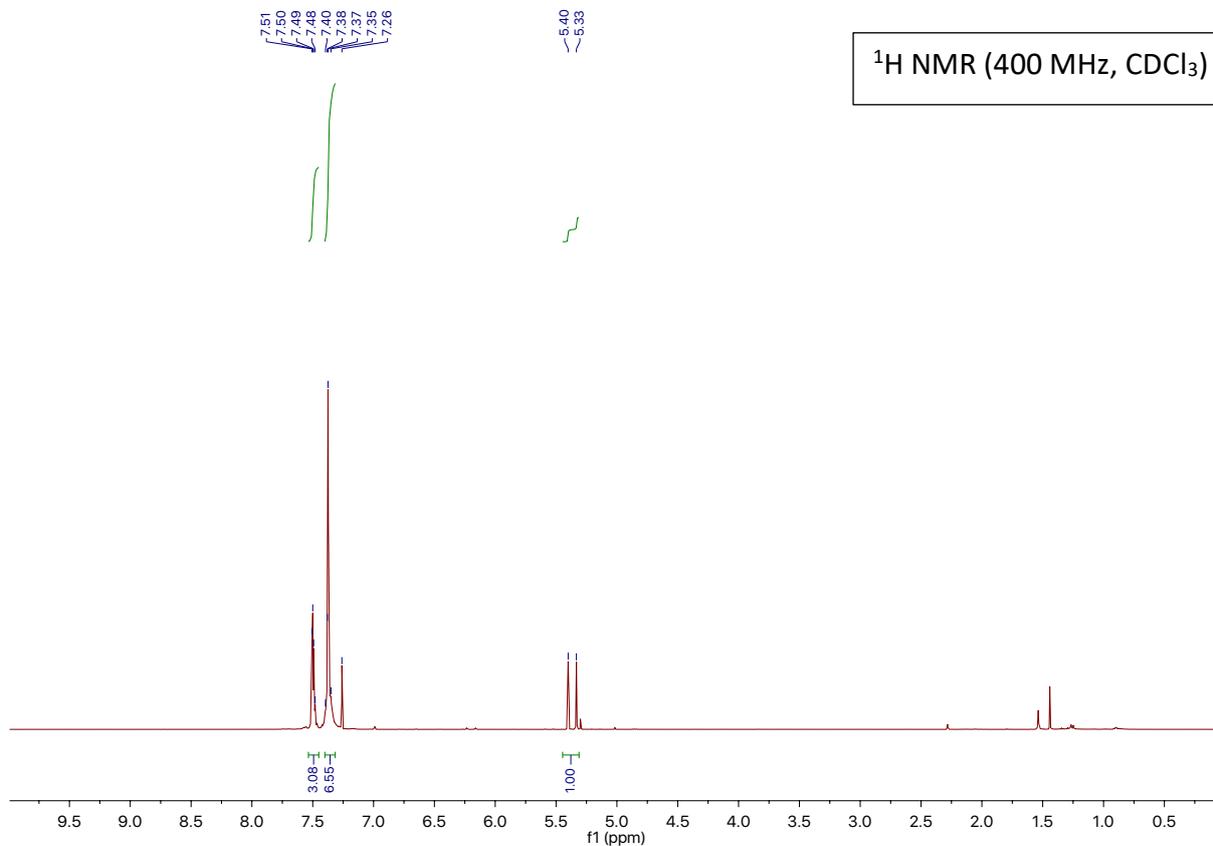
(Z)-3-chloro-1-(phenylsulfonyl)prop-1-ene-1,3-diyl dibenzene ((Z)-2n)



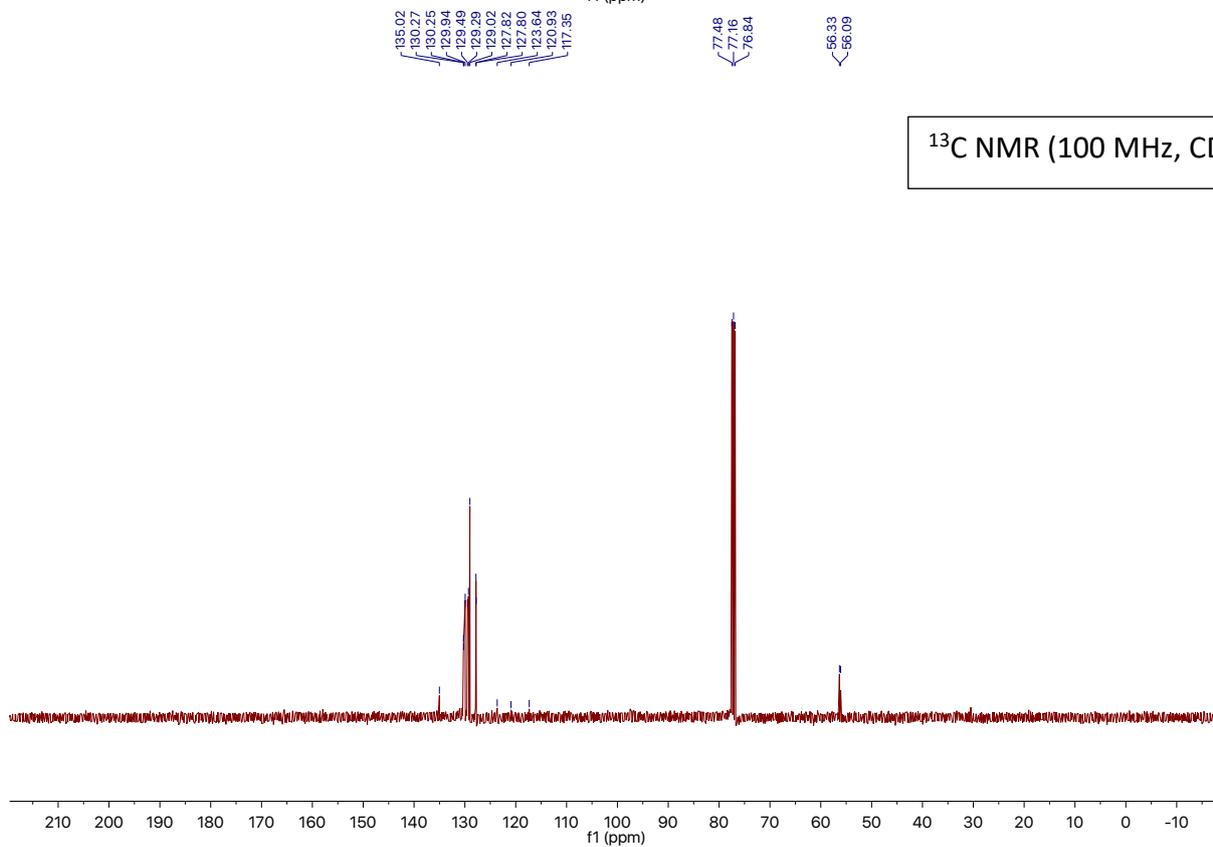
(Z)-(1-chloro-2,4,4,4-tetrafluorobut-2-ene-1,3-diyl)dibenzene (2o)



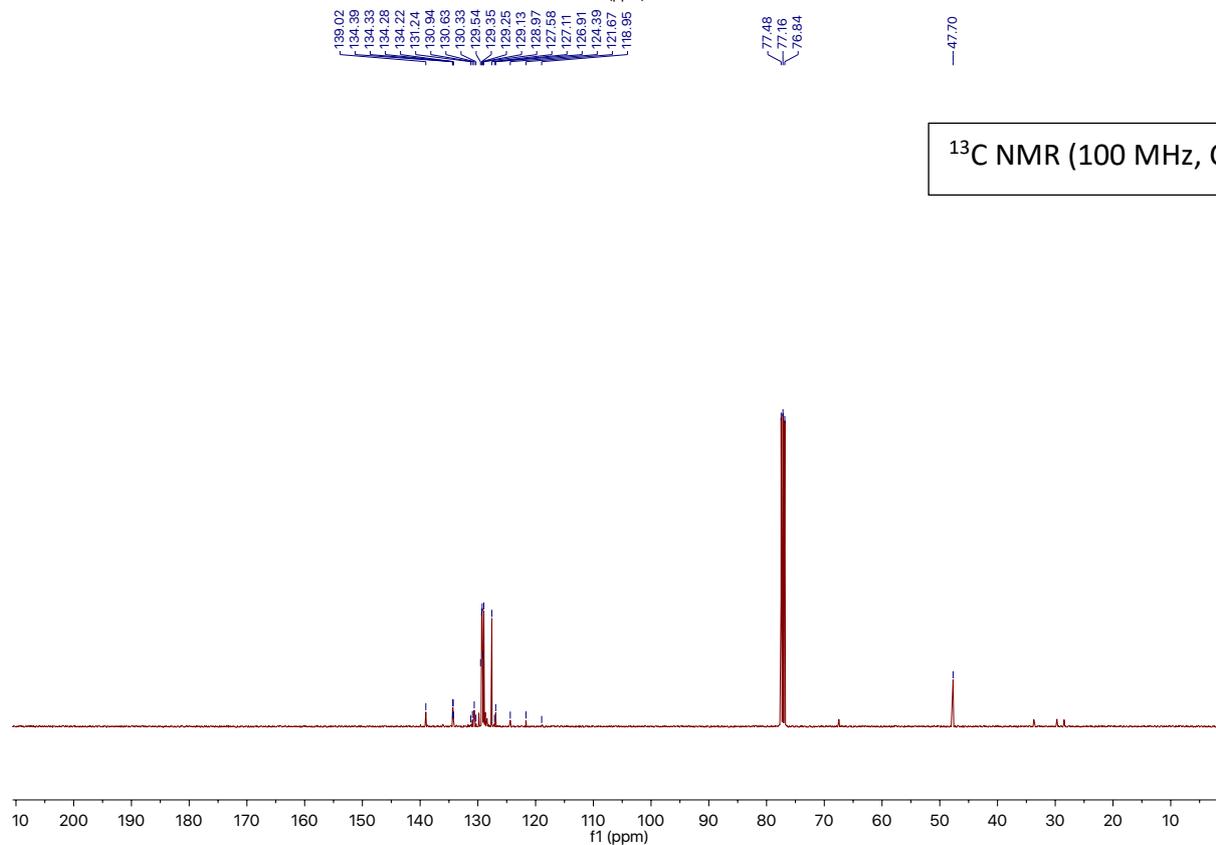
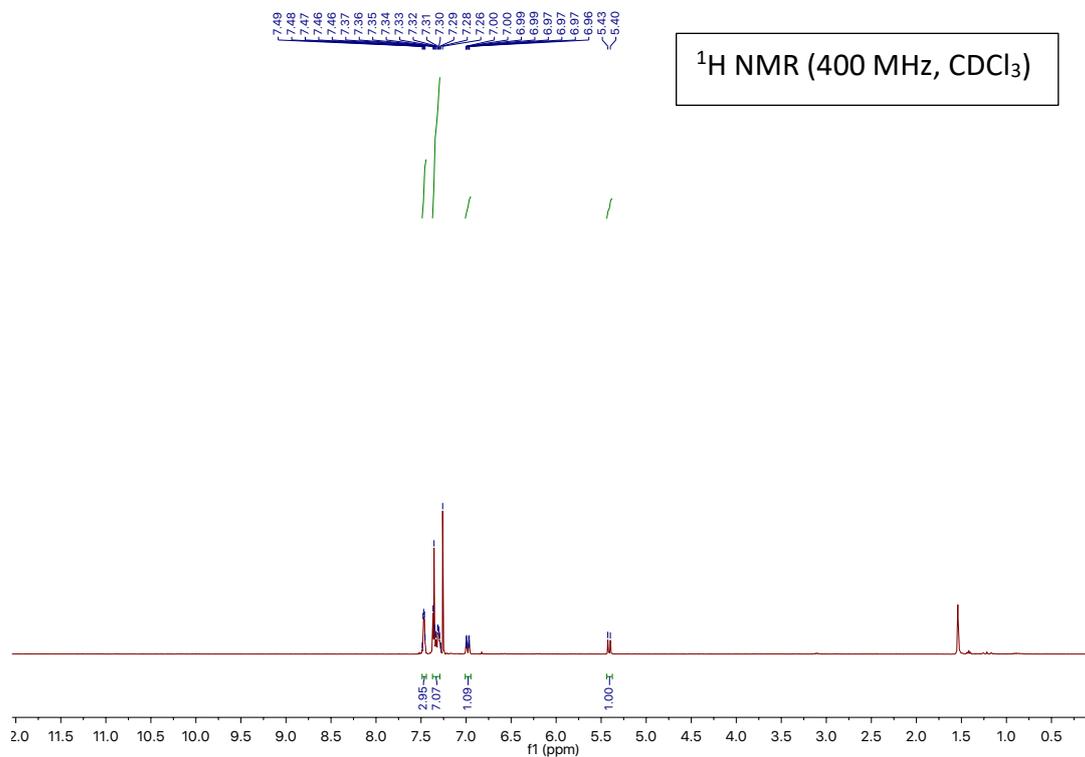
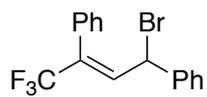
$^1\text{H NMR}$ (400 MHz, CDCl_3)



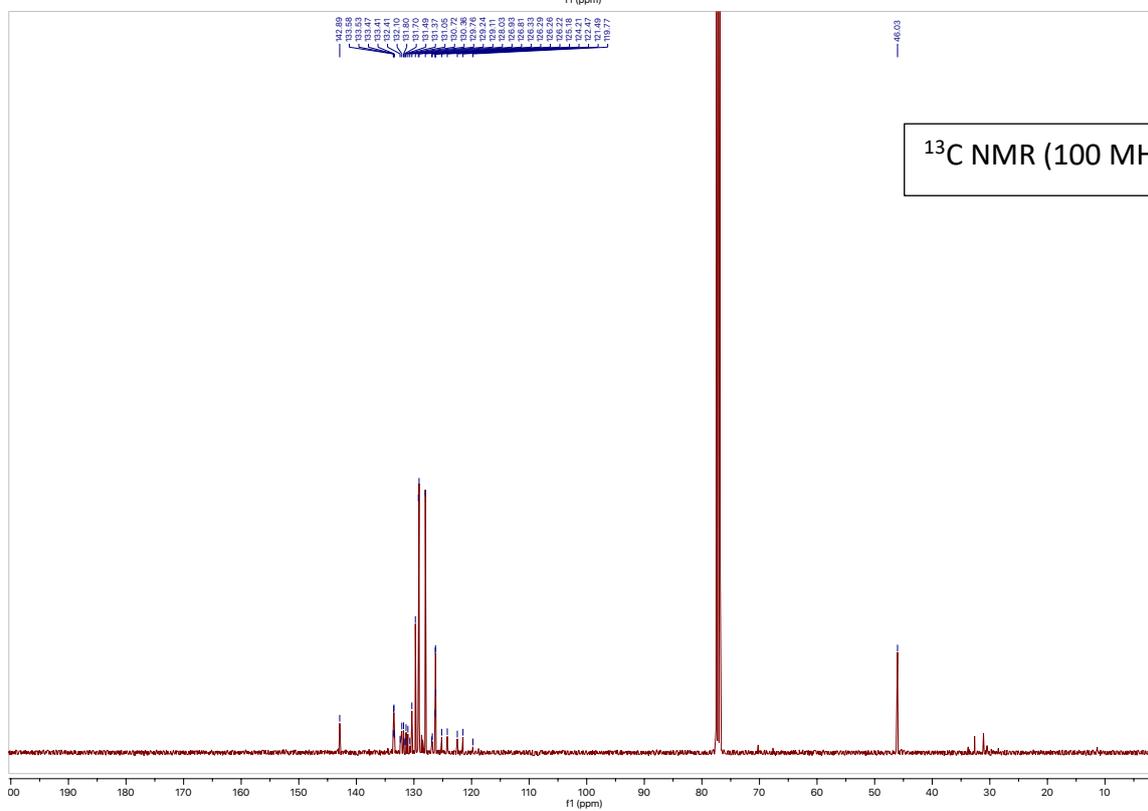
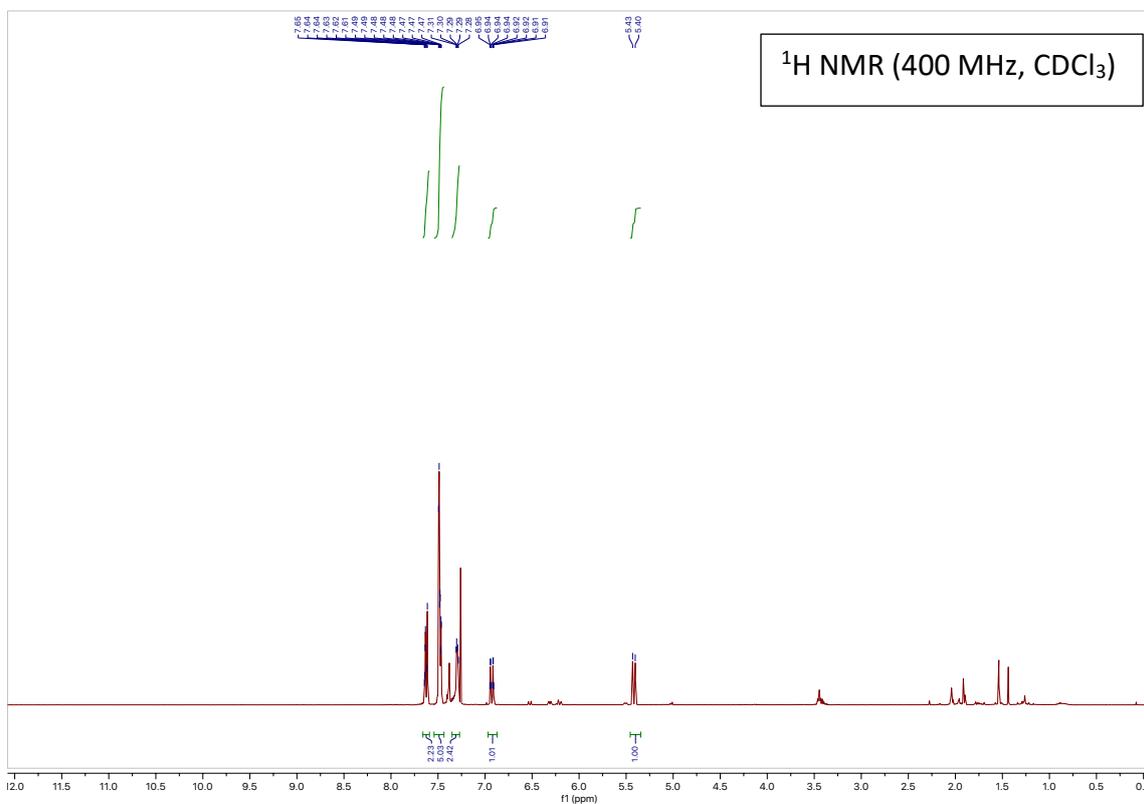
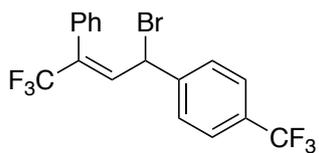
$^{13}\text{C NMR}$ (100 MHz, CDCl_3)



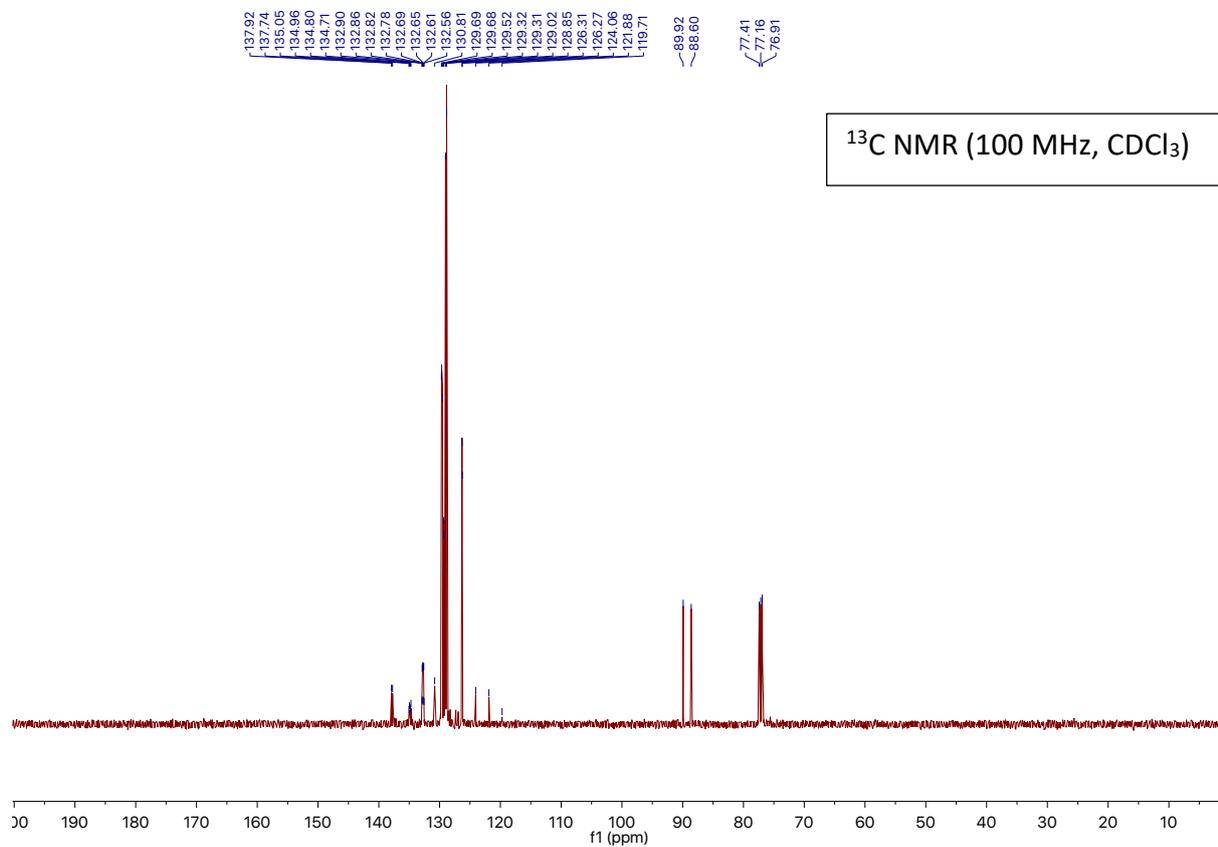
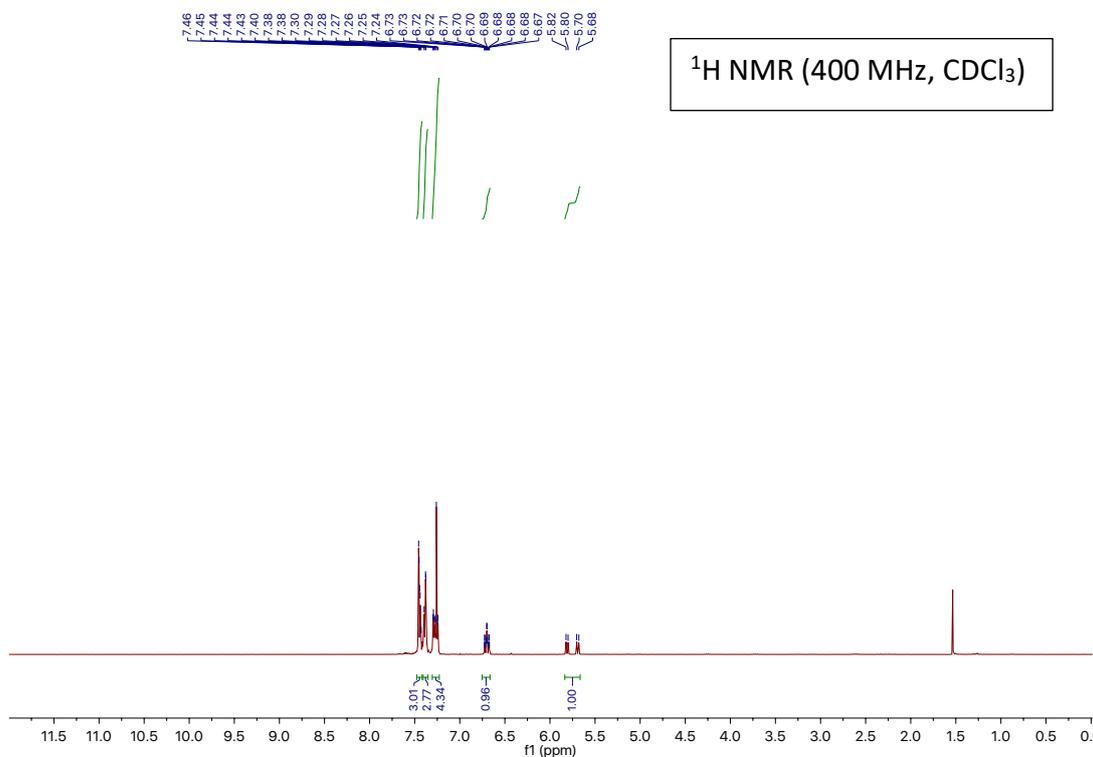
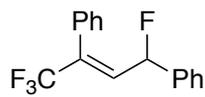
(*E*)-(1-bromo-4,4,4-trifluorobut-2-ene-1,3-diyl)dibenzene (3a)



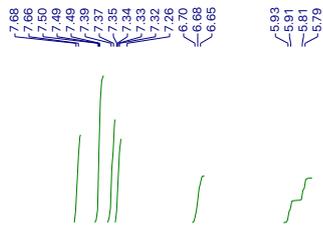
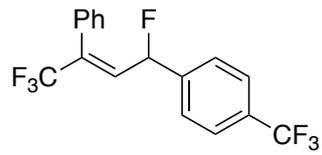
(E)-1-(1-bromo-4,4,4-trifluoro-3-phenylbut-2-en-1-yl)-4-(trifluoromethyl)benzene (3b)



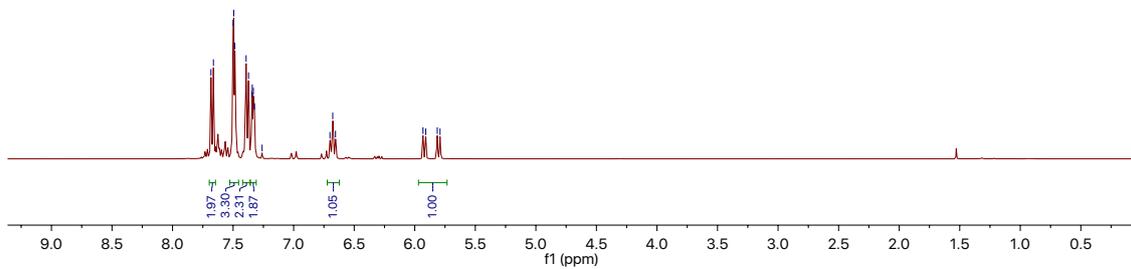
(E)-3-bromo-1-(phenylsulfonyl)prop-1-ene-1,3-diyl)dibenzene (3c)



(E)-1-(1,4,4-tetrafluoro-3-phenylbut-2-en-1-yl)-4-(trifluoromethyl)benzene (4b)

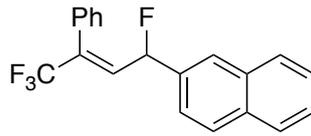


^1H NMR (400 MHz, CDCl_3)



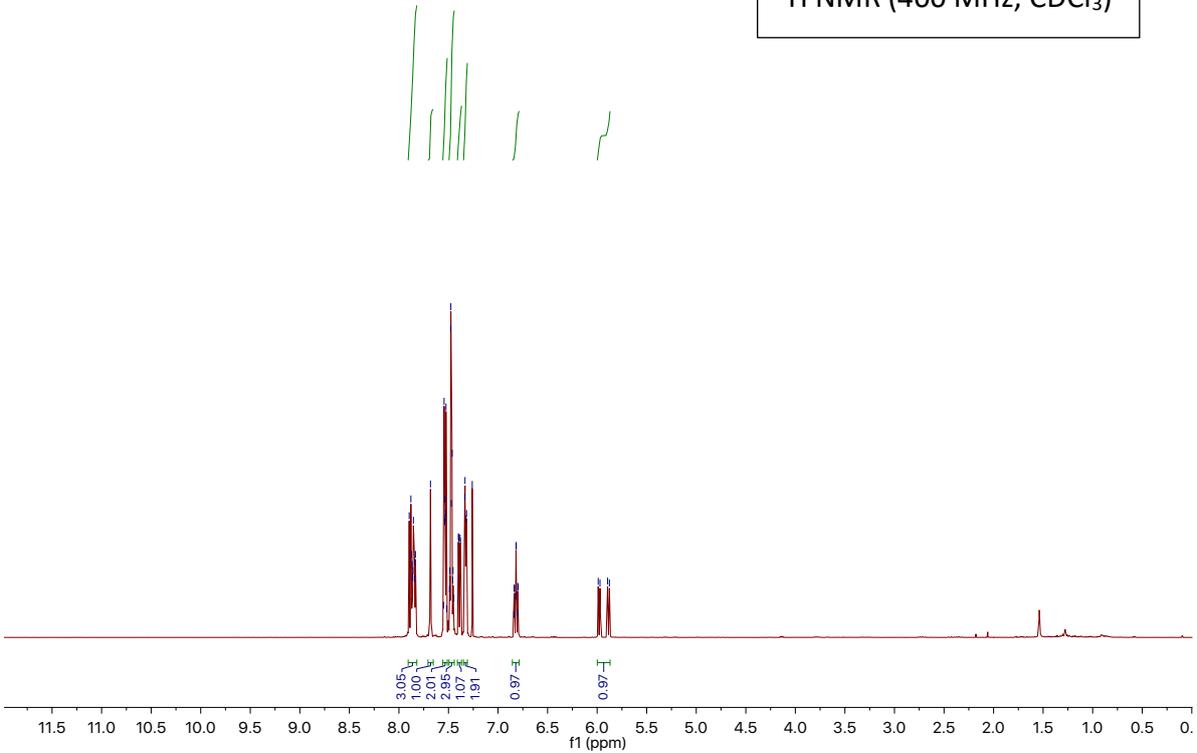
^{13}C NMR (100 MHz, CDCl_3)

(E)-2-(1,4,4,4-tetrafluoro-3-phenylbut-2-en-1-yl)naphthalene (4c)



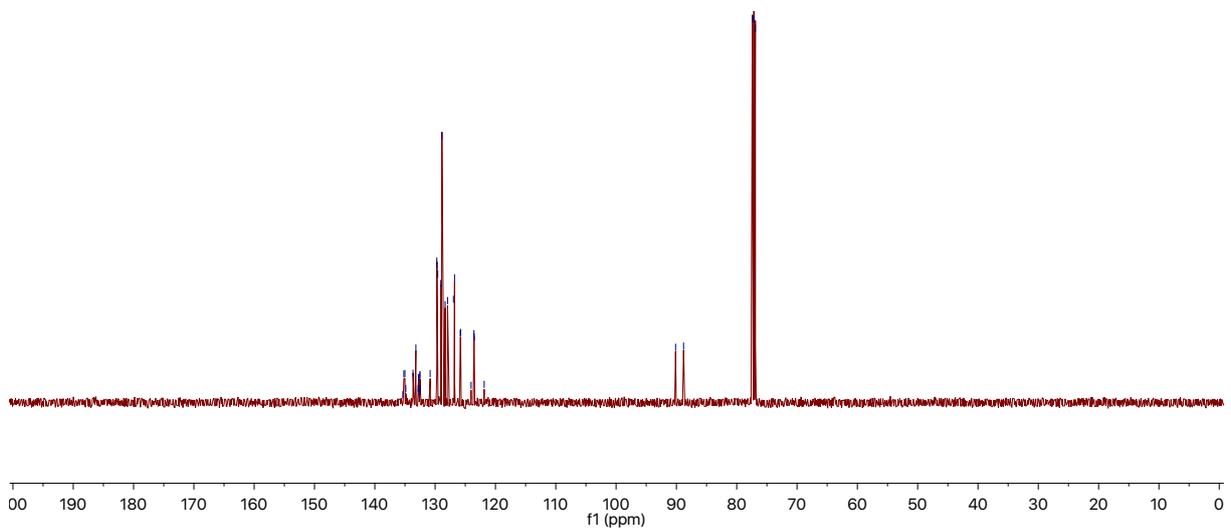
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7.88
7.87
7.87
7.86
7.86
7.85
7.84
7.84
7.83
7.83
7.82
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7.81
7.81
7.80
7.78
7.78
7.74
7.74
7.73
7.73
7.72
7.72
7.68
7.68
6.84
6.83
6.82
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5.99
5.96
5.96
5.93

¹H NMR (400 MHz, CDCl₃)



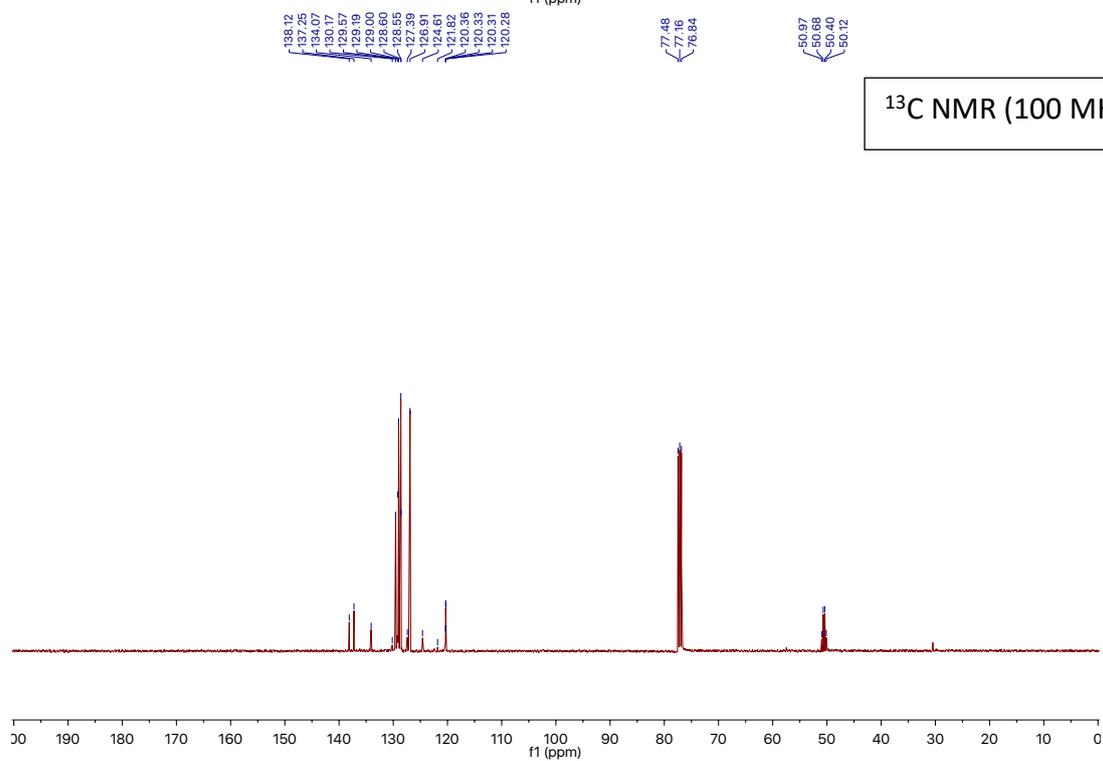
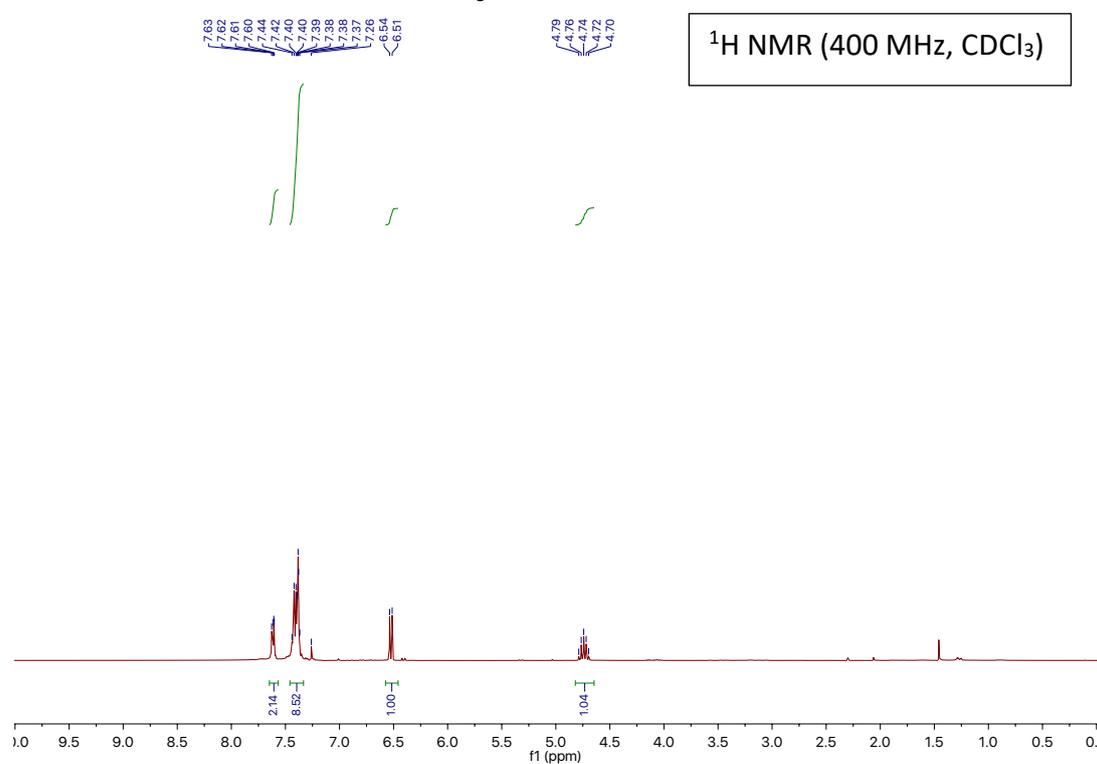
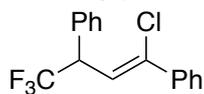
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135.19
135.01
134.87
133.67
133.19
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132.77
132.73
132.68
132.57
132.55
132.51
132.47
130.83
129.72
128.71
128.57
128.56
128.86
128.34
127.94
126.97
126.78
125.83
125.78
124.04
123.56
123.53
121.87
90.14
88.81
77.41
77.16
76.91

¹³C NMR (100 MHz, CDCl₃)

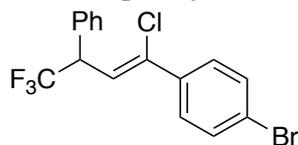


^1H NMR, ^{13}C NMR and ^{19}F NMR of vinyl halides 5a-5n, 6a-6c and 7a-7c

(Z)-(1-chloro-4,4,4-trifluorobut-1-ene-1,3-diyl)dibenzene (5a)



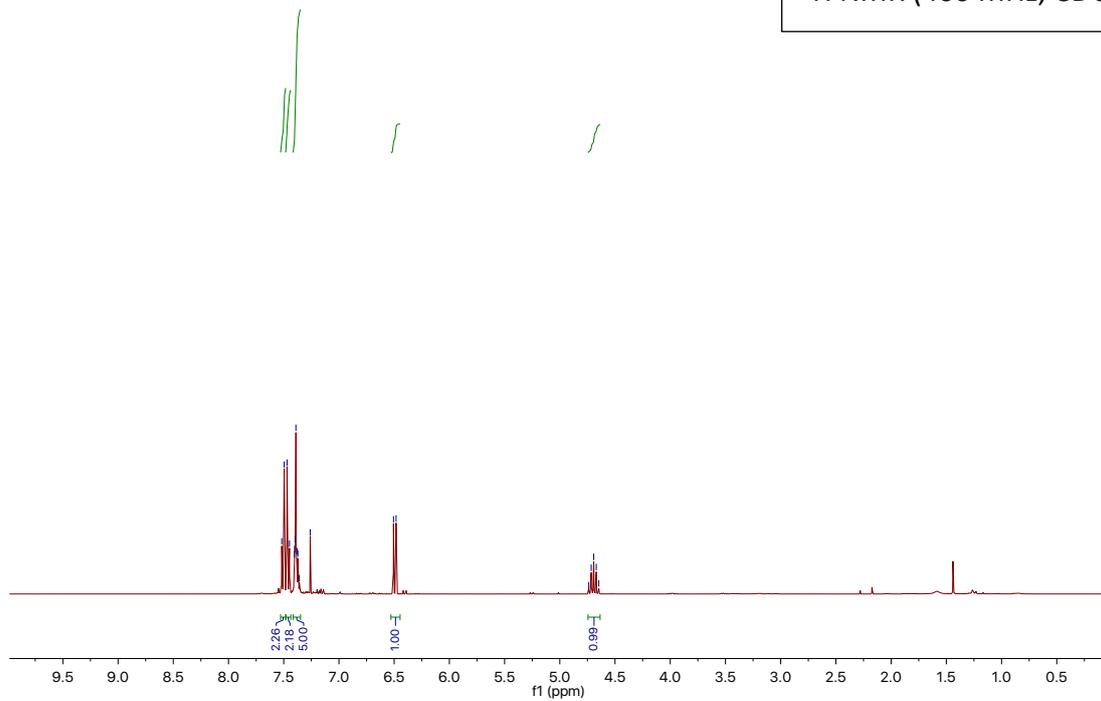
(Z)-1-bromo-4-(1-chloro-4,4,4-trifluoro-3-phenylbut-1-en-1-yl)benzene (5b)



7.52
7.50
7.47
7.45
7.40
7.40
7.39
7.38
7.37
7.36
7.26
6.51
6.48

4.74
4.72
4.69
4.65

¹H NMR (400 MHz, CDCl₃)

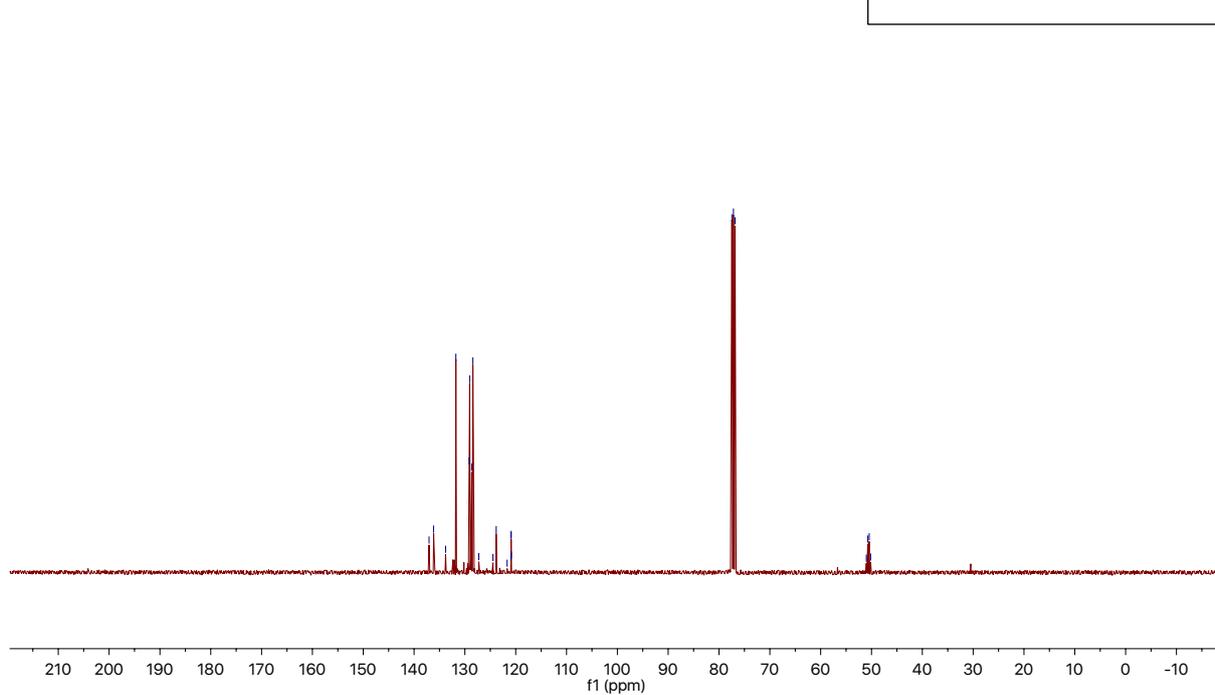


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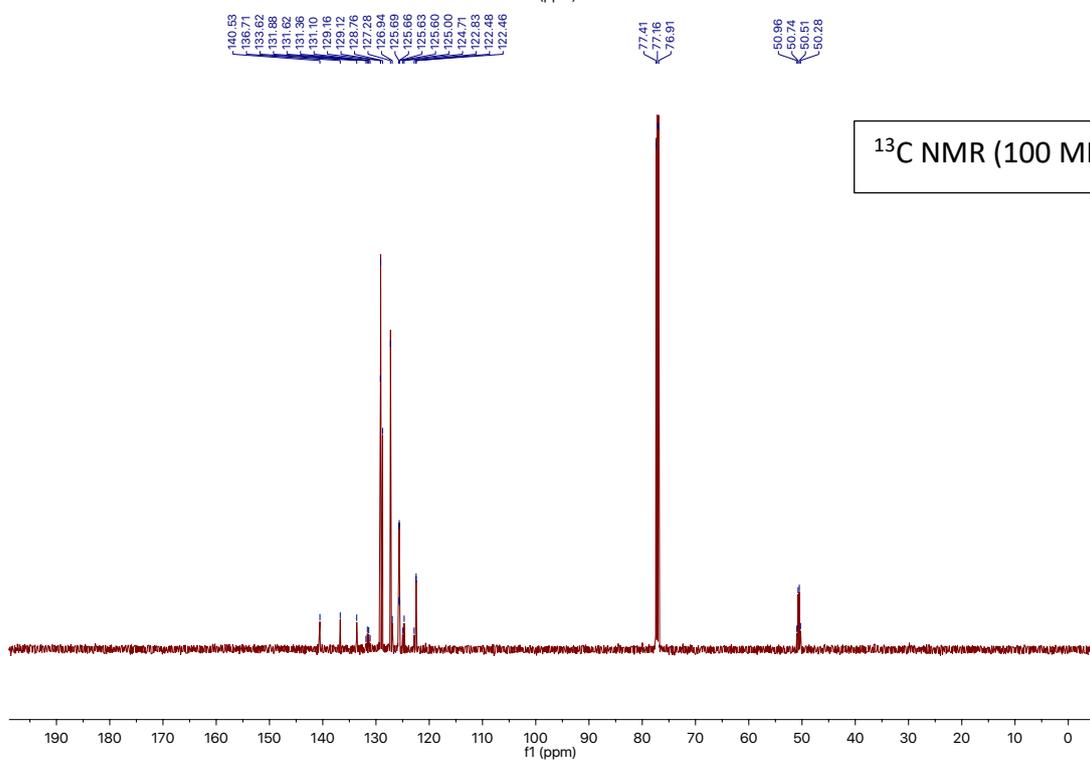
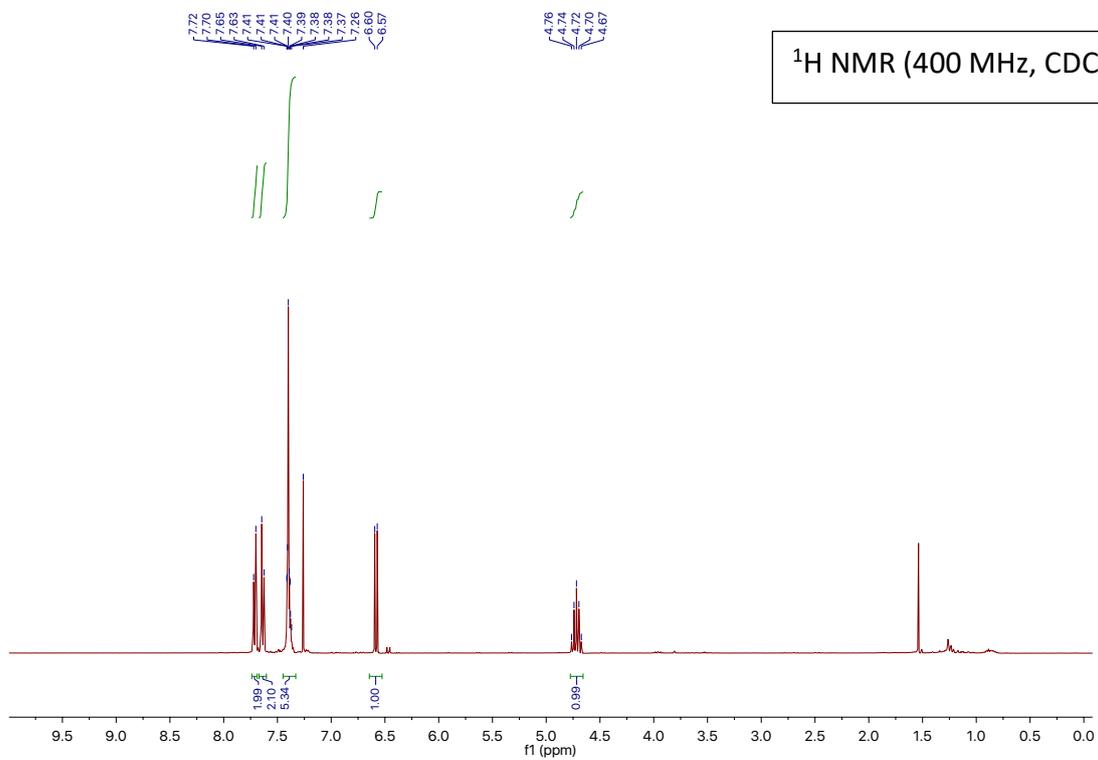
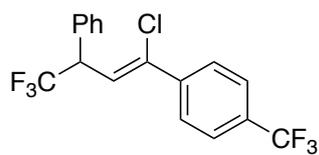
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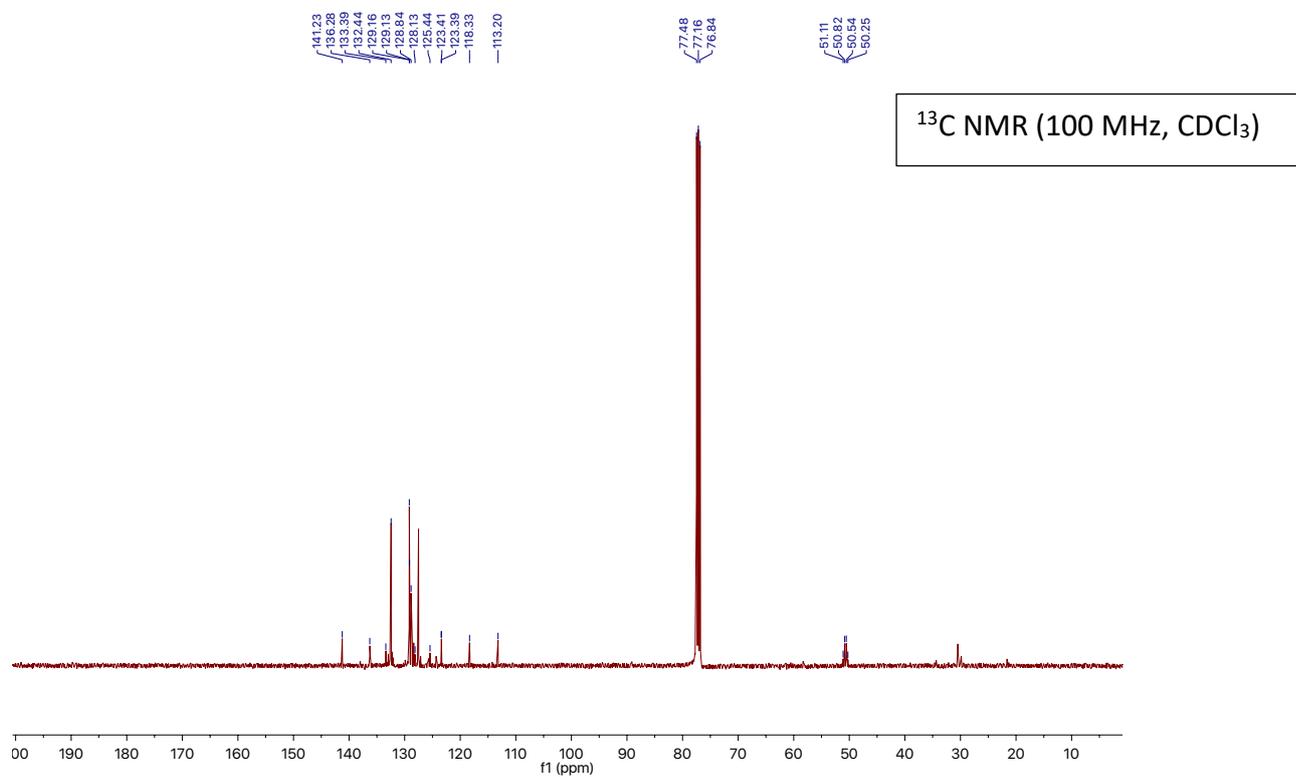
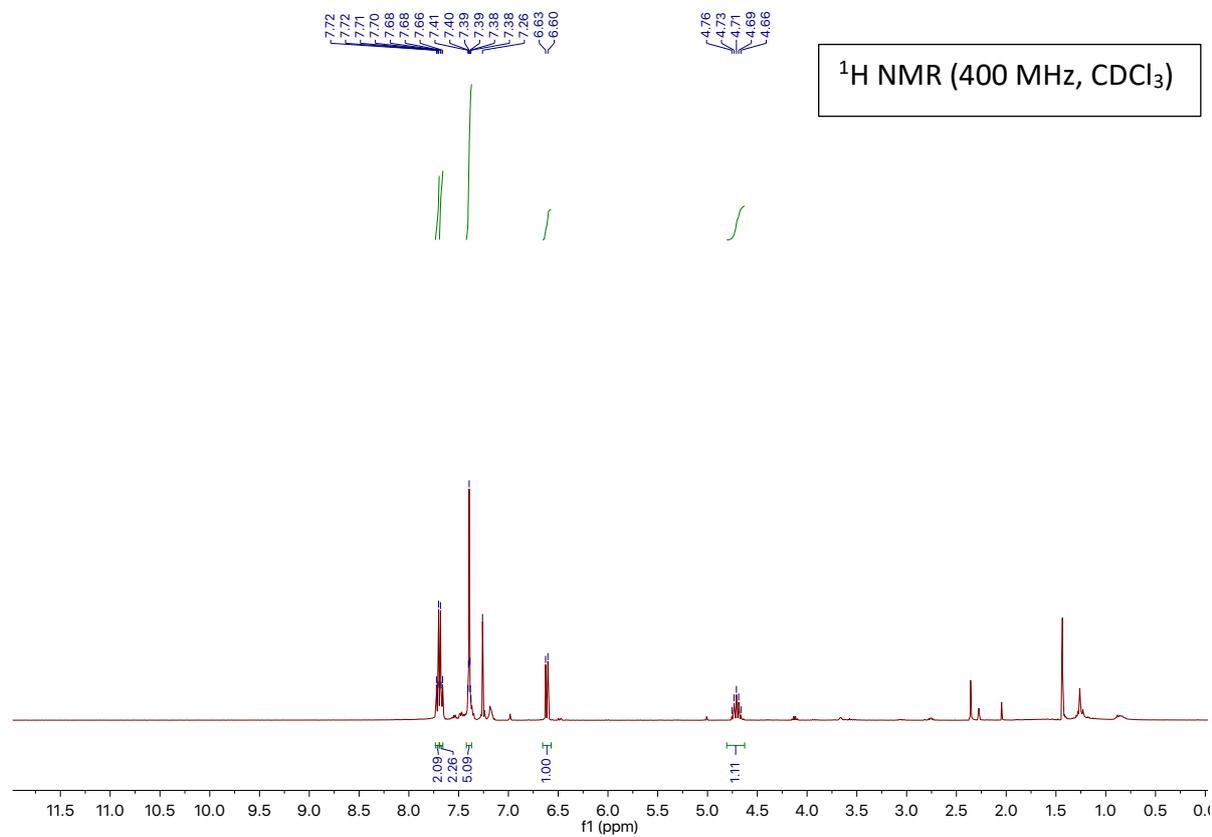
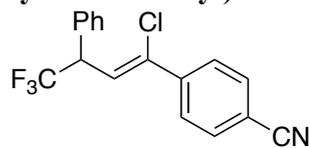
¹³C NMR (100 MHz, CDCl₃)



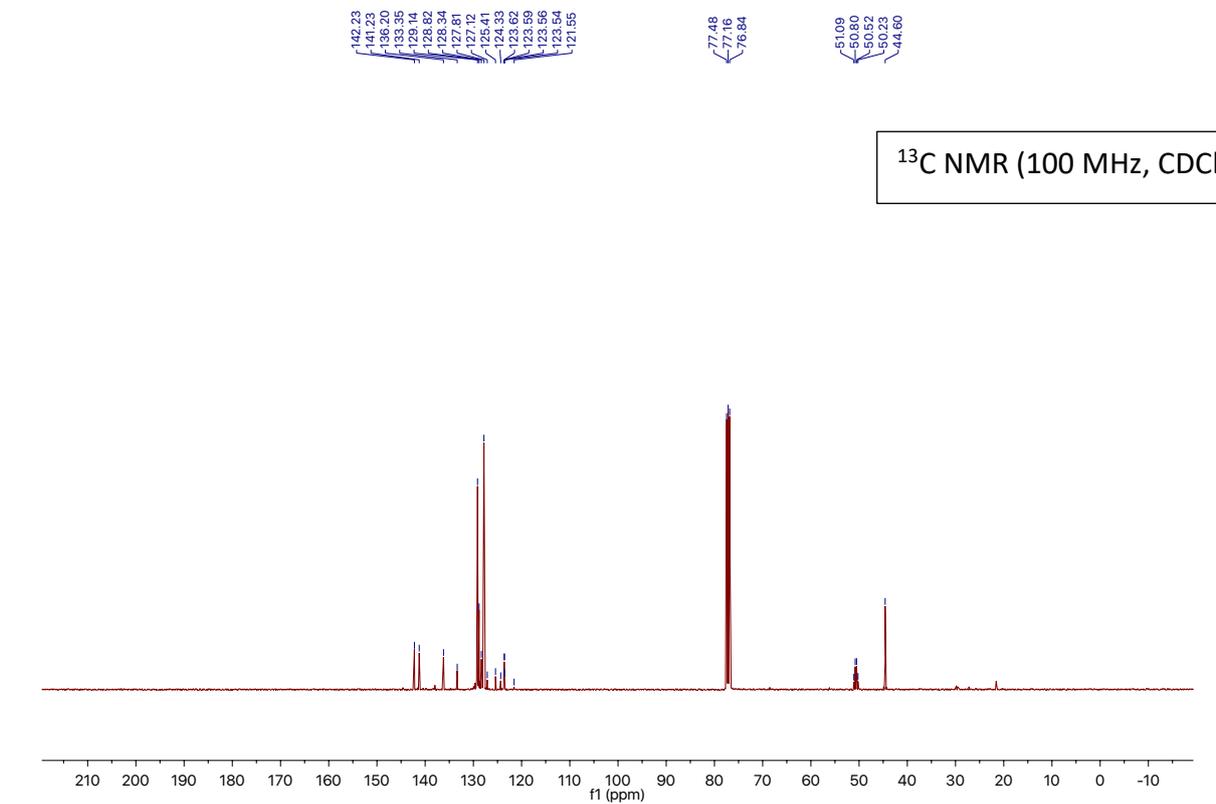
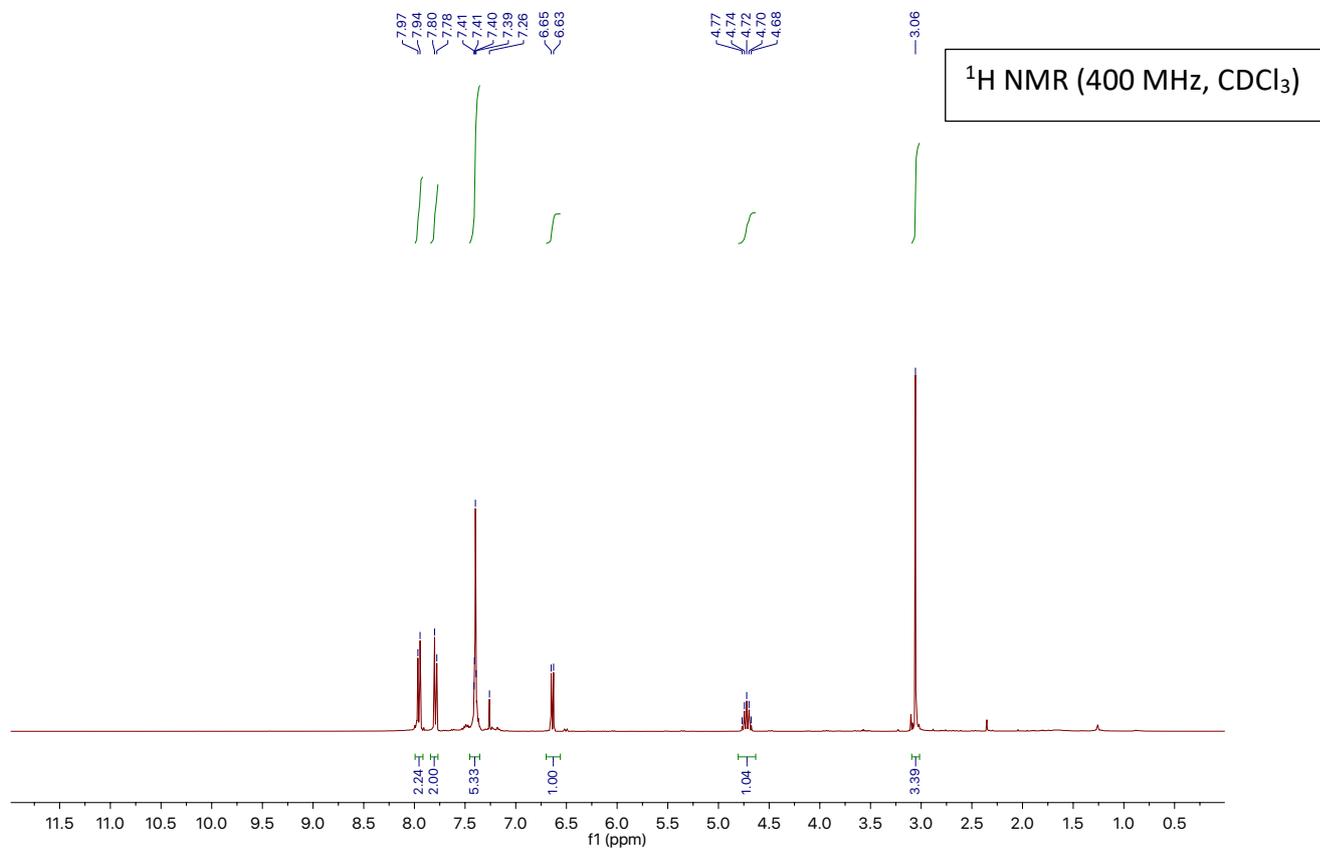
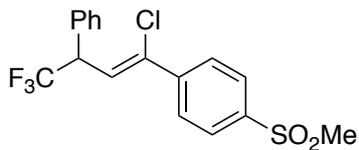
(Z)-1-(1-chloro-4,4,4-trifluoro-3-phenylbut-1-en-1-yl)-4-(trifluoromethyl)benzene (5c)



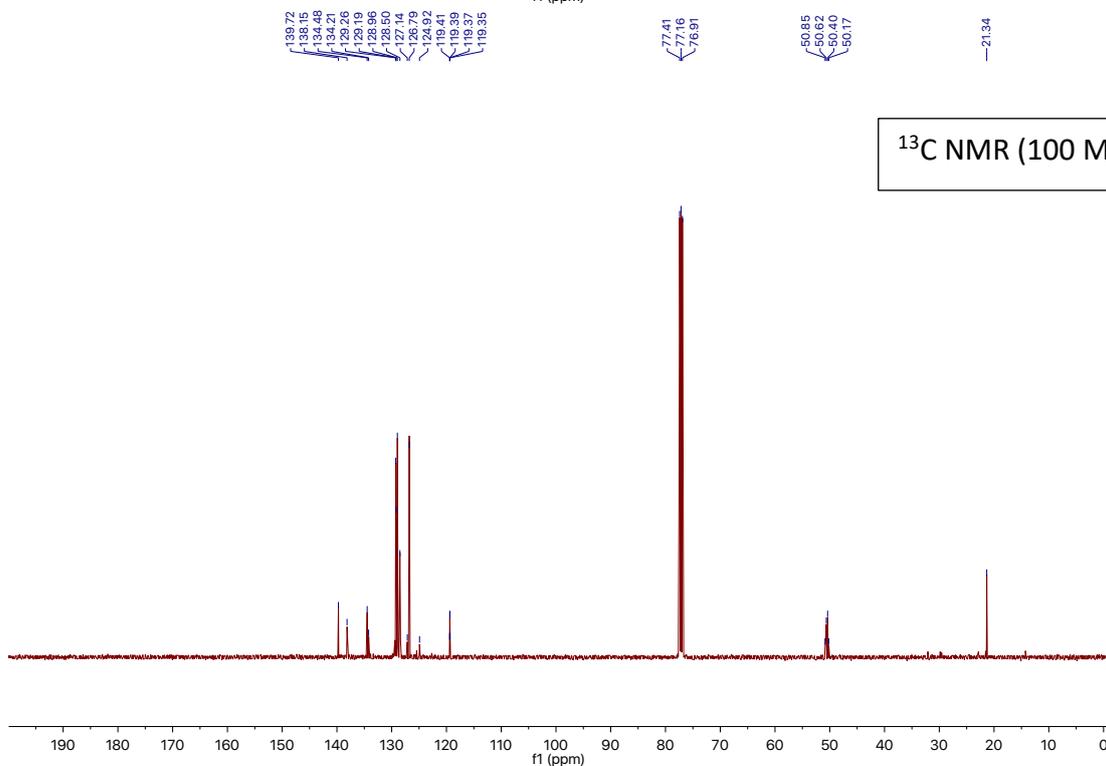
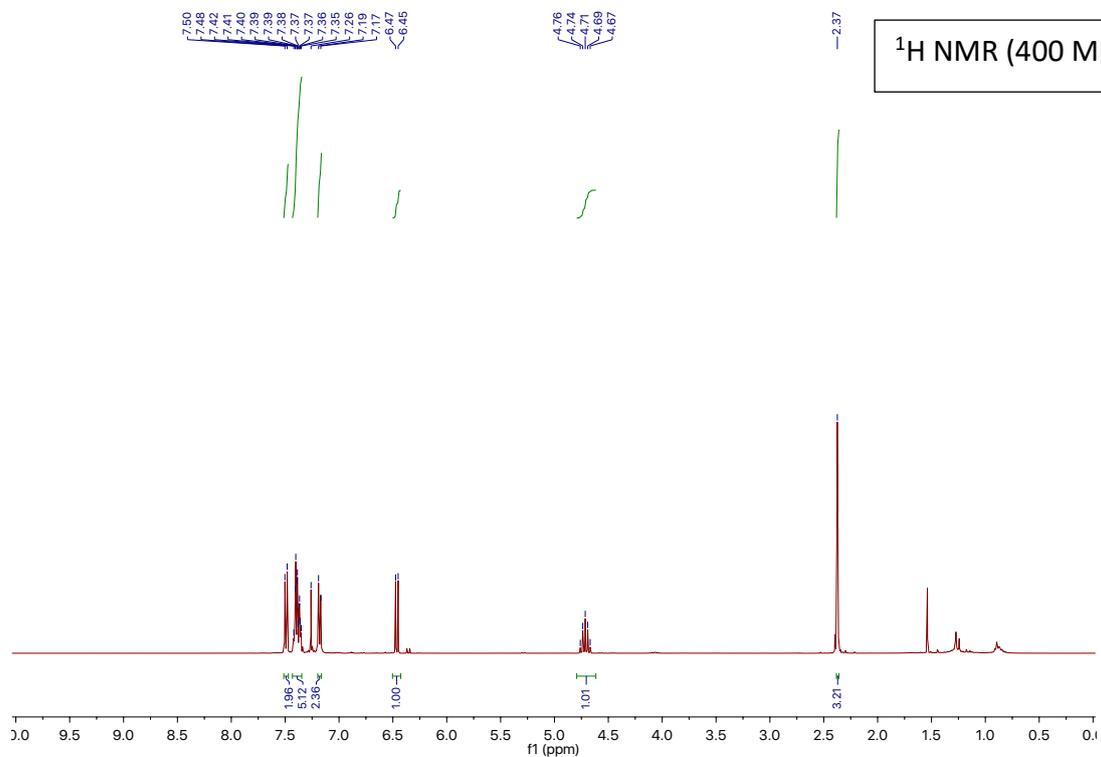
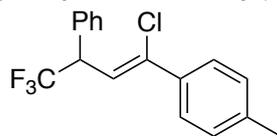
(Z)-4-(1-chloro-4,4,4-trifluoro-3-phenylbut-1-en-1-yl)benzonitrile (5d)



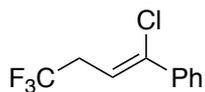
(Z)-1-(1-chloro-4,4,4-trifluoro-3-phenylbut-1-en-1-yl)-4-(methylsulfonyl)benzene (5e)



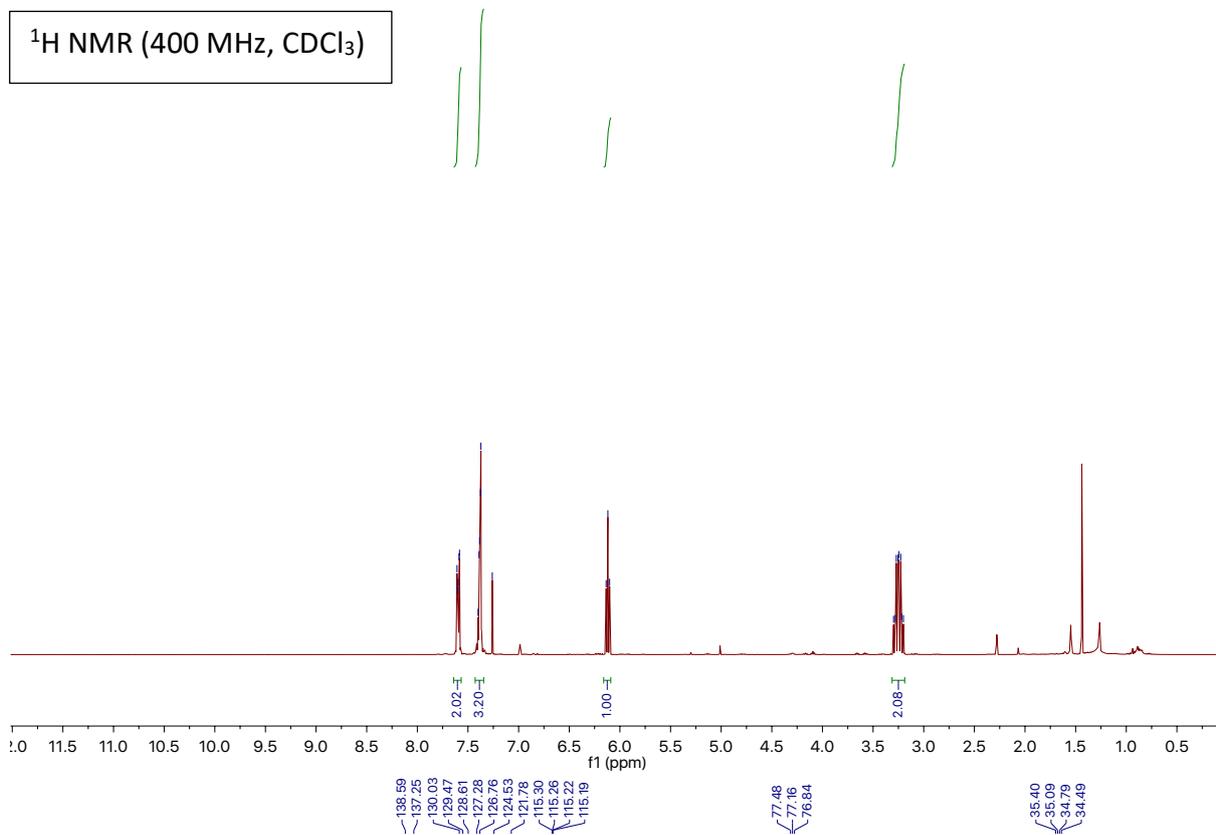
(Z)-1-(1-chloro-4,4,4-trifluoro-3-phenylbut-1-en-1-yl)-4-methylbenzene (5f)



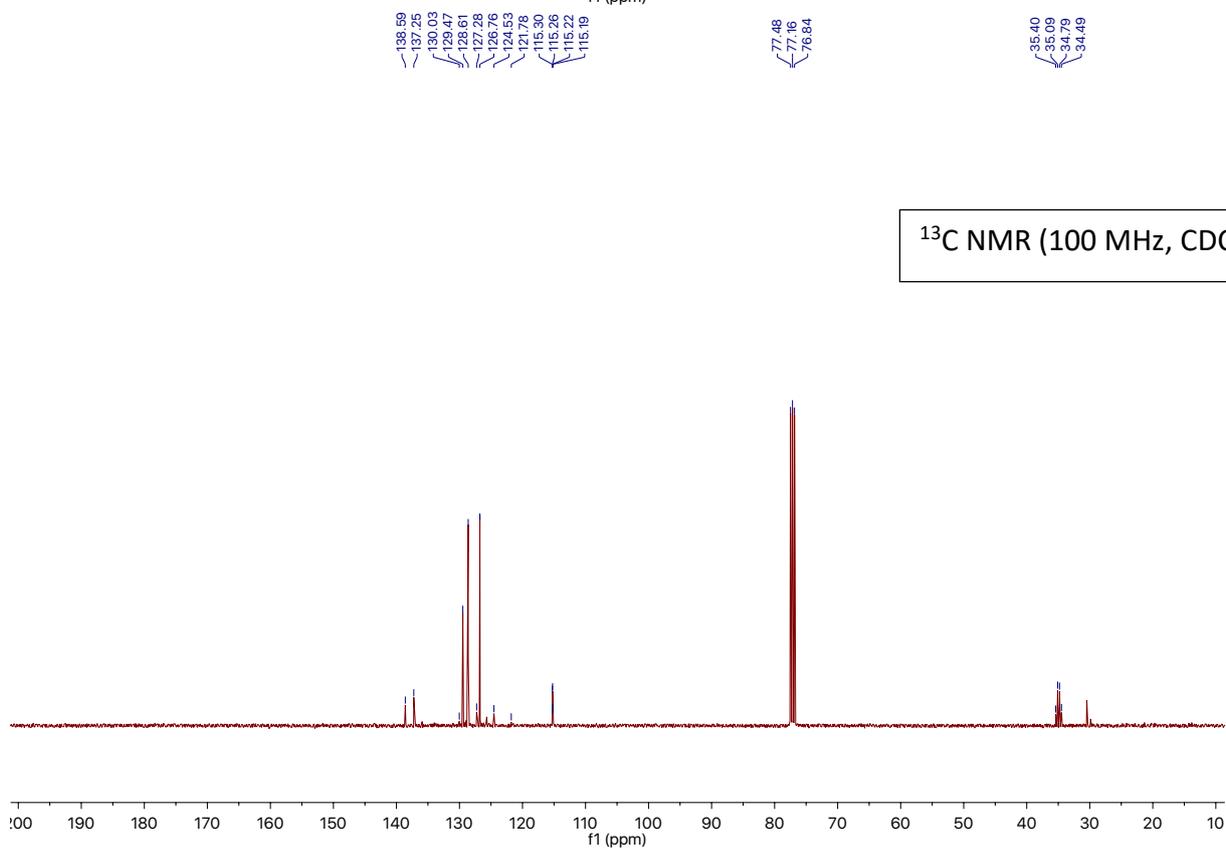
(Z)-(1-chloro-4,4,4-trifluorobut-1-en-1-yl)benzene (5j)



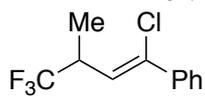
¹H NMR (400 MHz, CDCl₃)



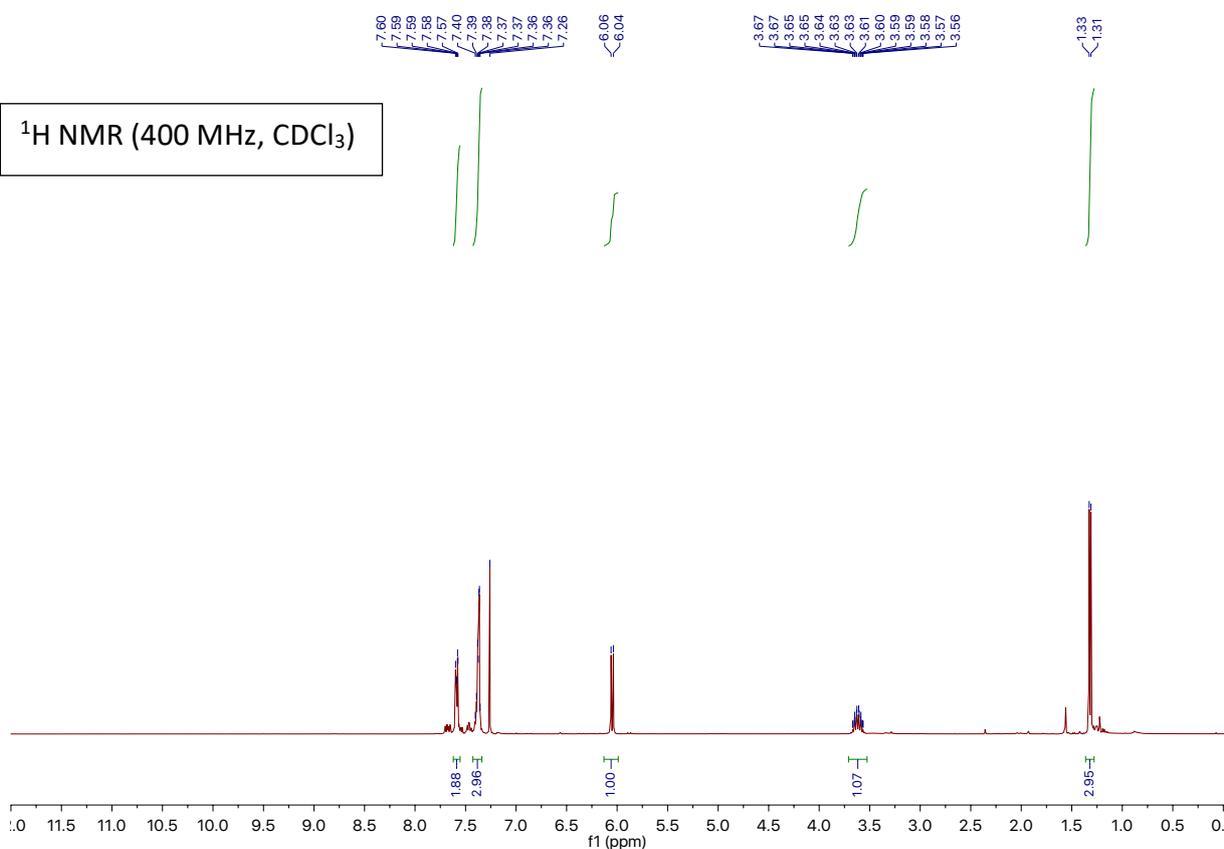
¹³C NMR (100 MHz, CDCl₃)



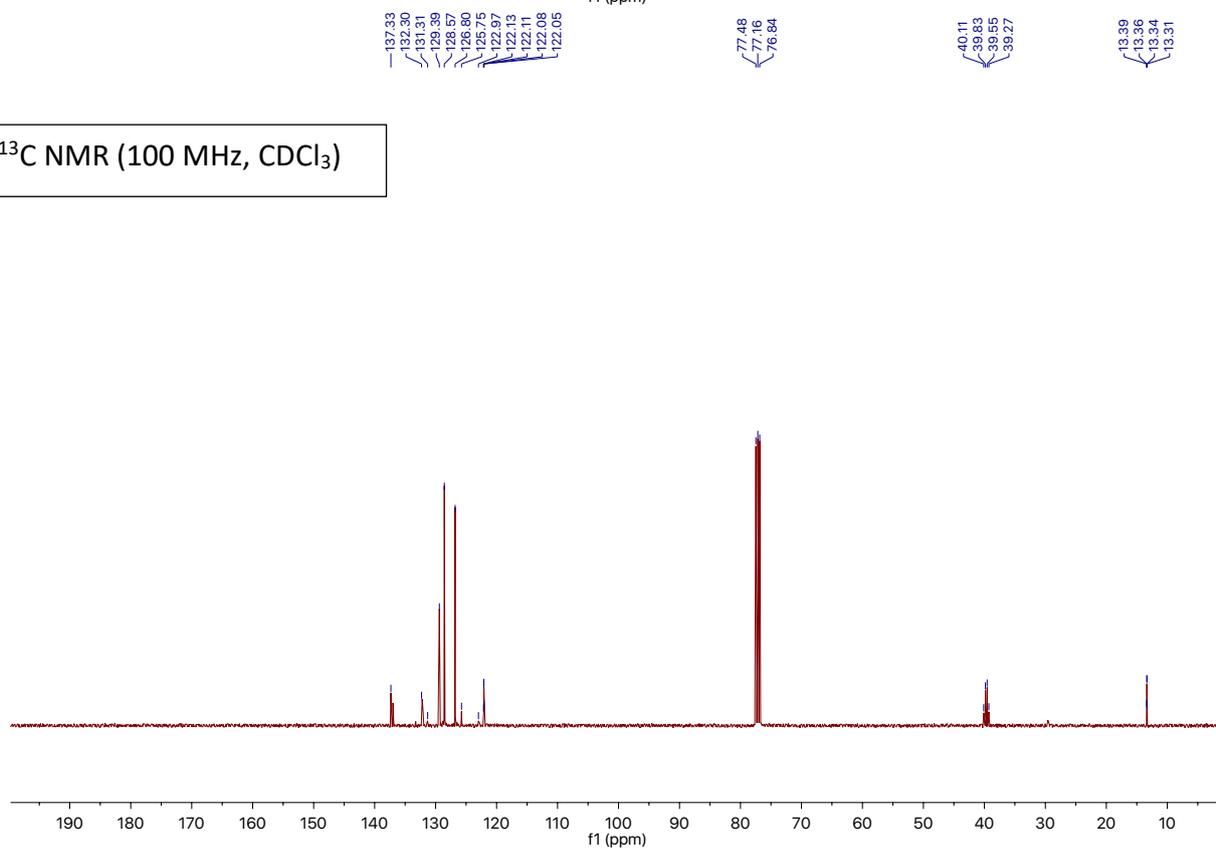
(Z)-(1-chloro-4,4,4-trifluoro-3-methylbut-1-en-1-yl)benzene (5k)



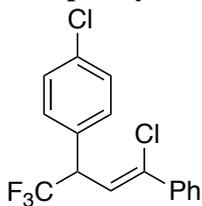
¹H NMR (400 MHz, CDCl₃)



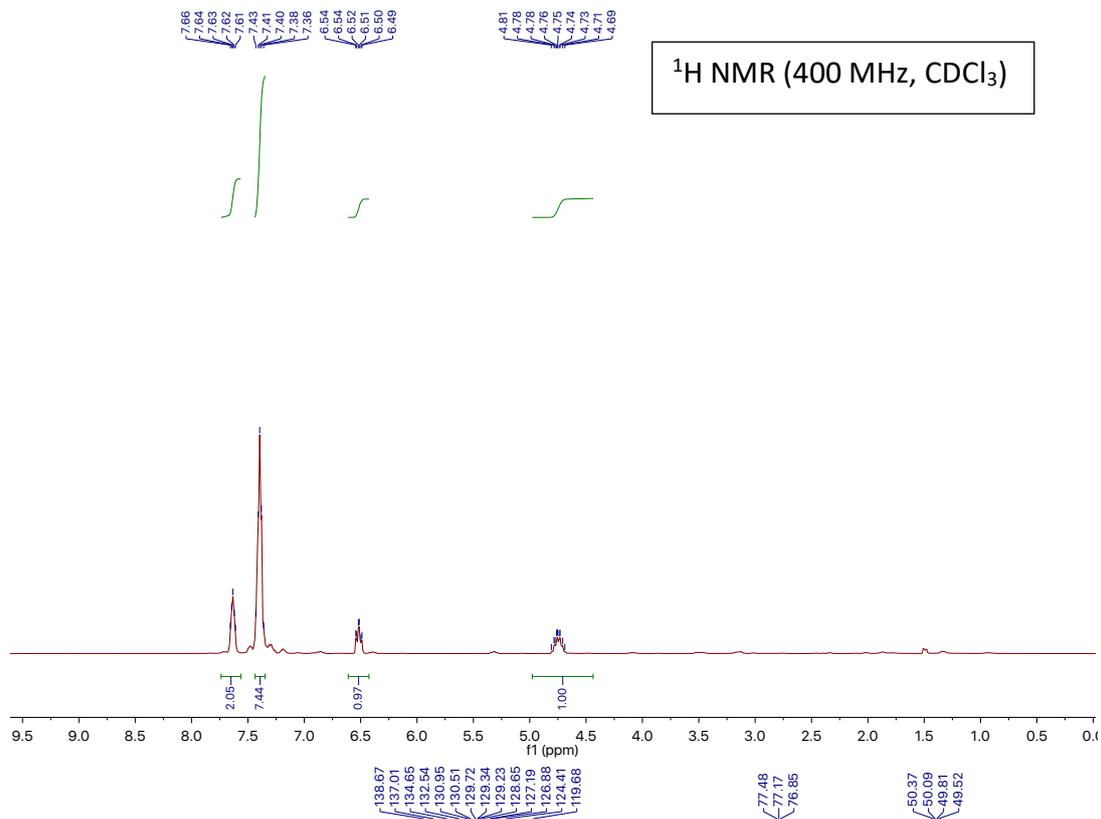
¹³C NMR (100 MHz, CDCl₃)



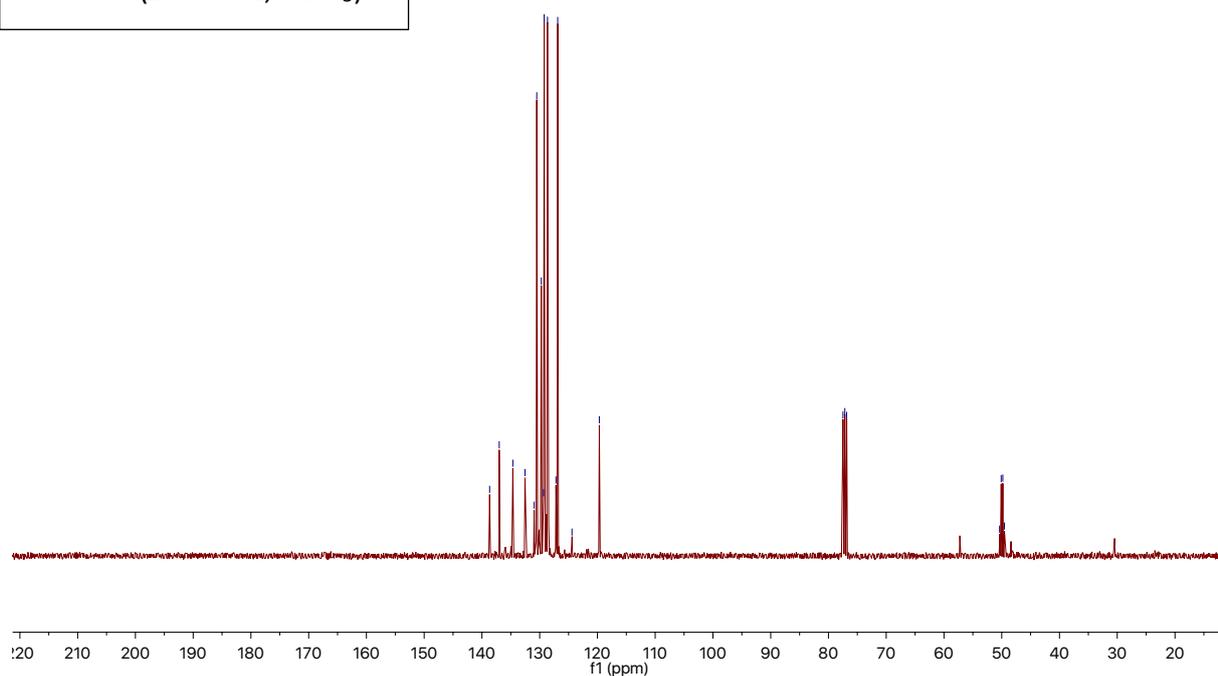
(Z)-1-chloro-4-(4-chloro-1,1,1-trifluoro-4-phenylbut-3-en-2-yl)benzene (5l)



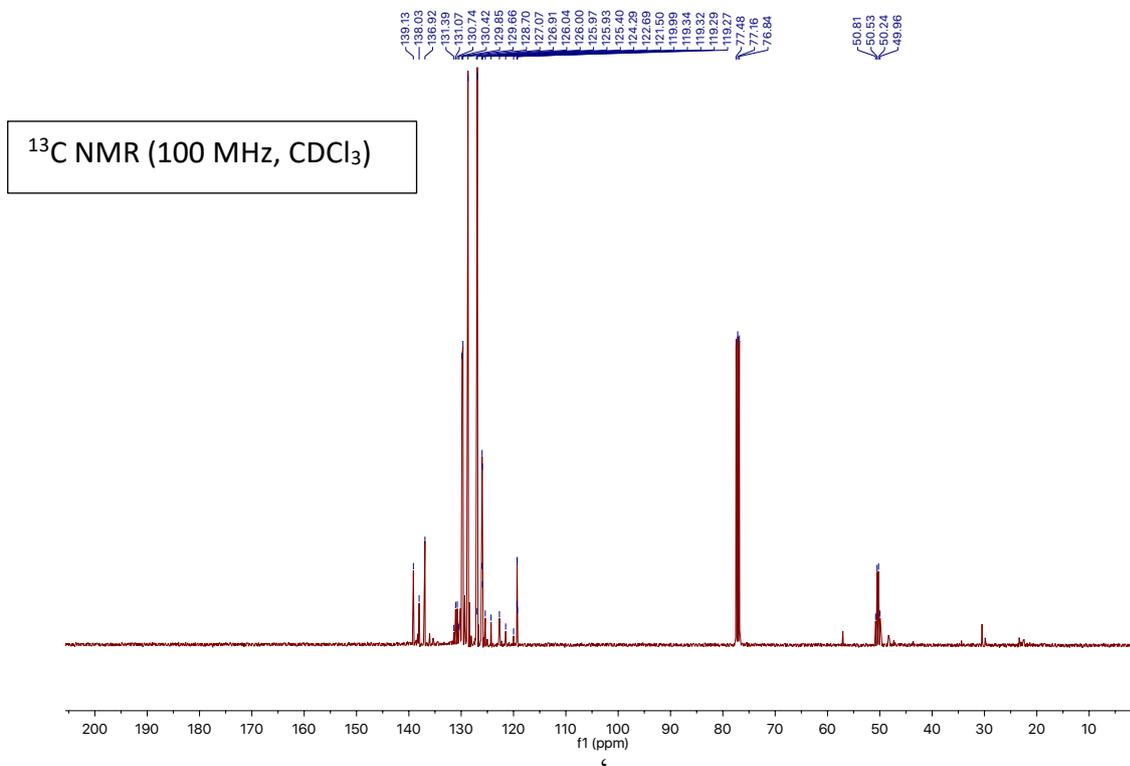
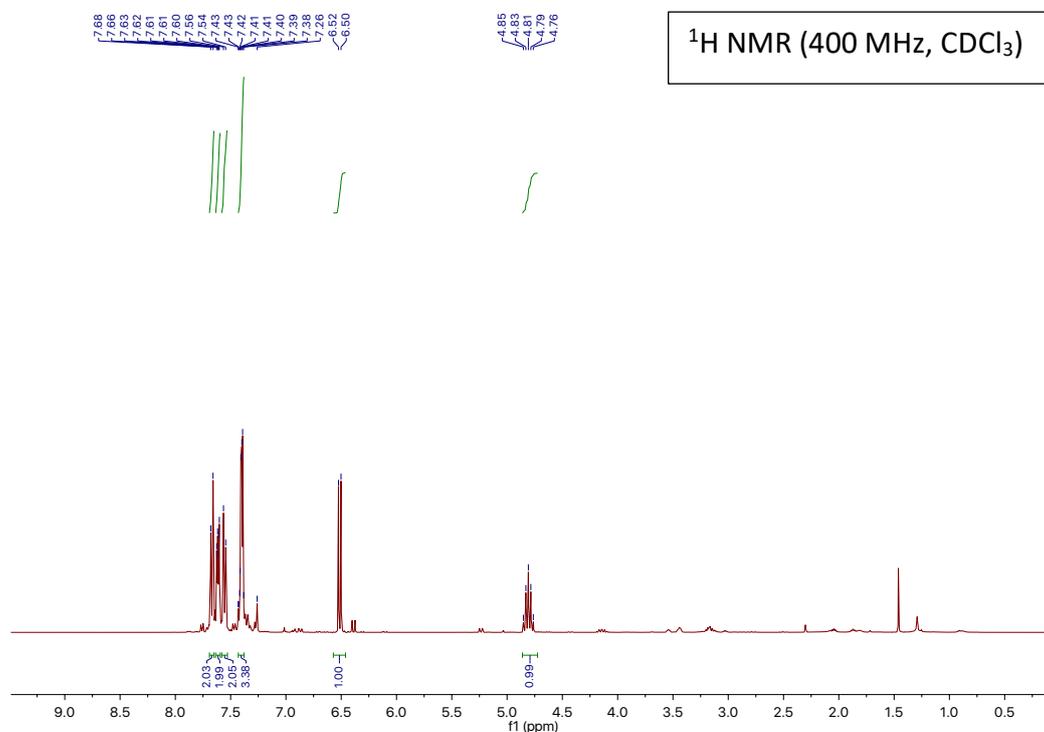
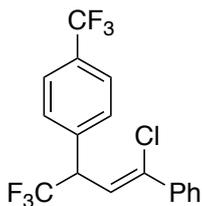
$^1\text{H NMR}$ (400 MHz, CDCl_3)



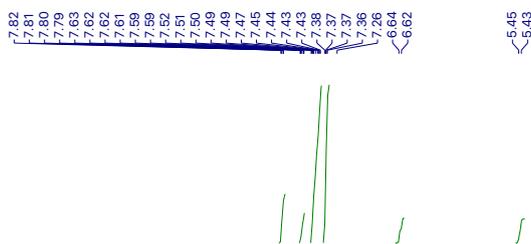
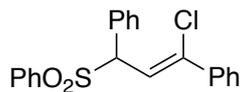
$^{13}\text{C NMR}$ (100 MHz, CDCl_3)



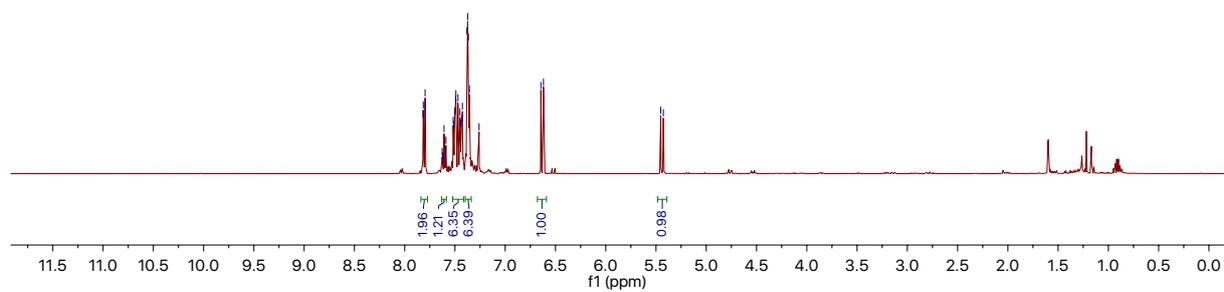
(Z)-1-(4-chloro-1,1,1-trifluoro-4-phenylbut-3-en-2-yl)-4-(trifluoromethyl)benzene (5m)



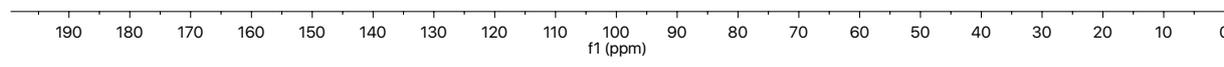
(Z)-(1-chloro-3-(phenylsulfonyl)prop-1-ene-1,3-diyl)dibenzene ((Z)-5n)



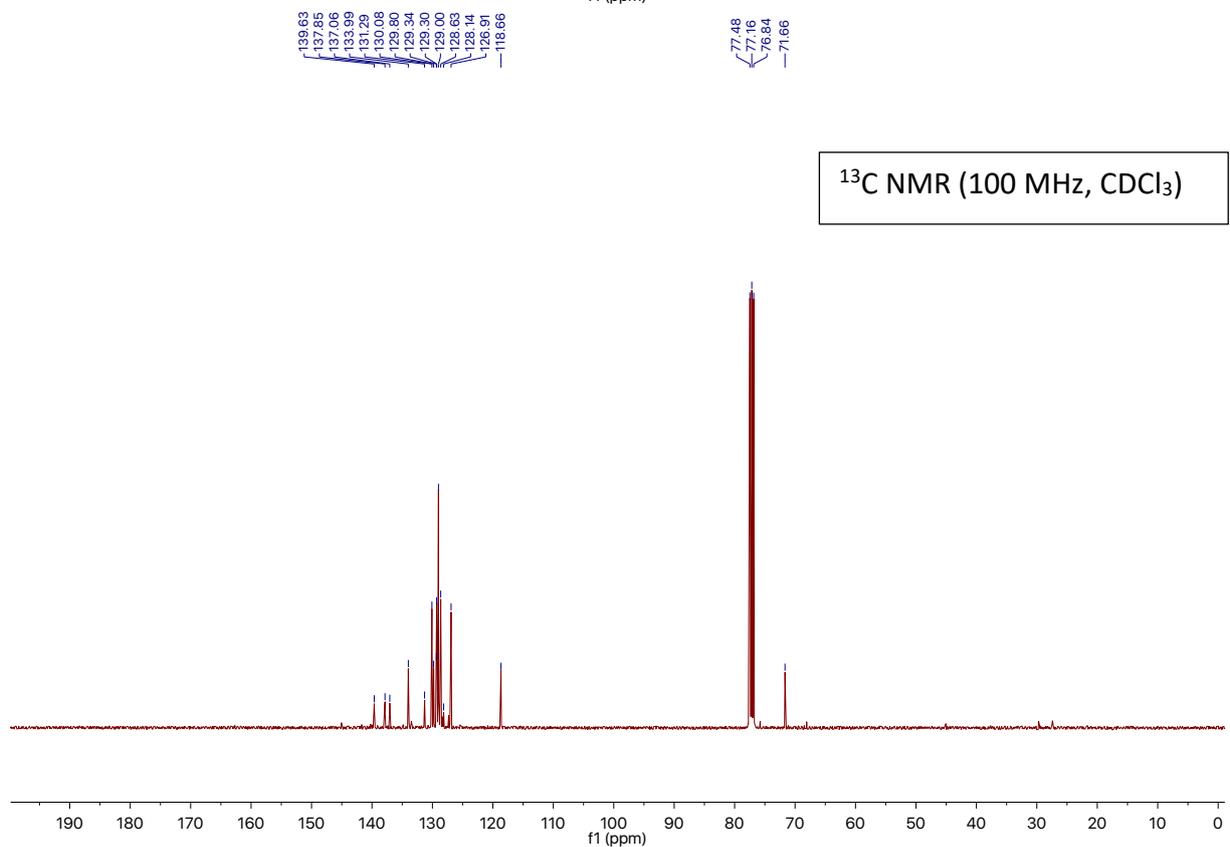
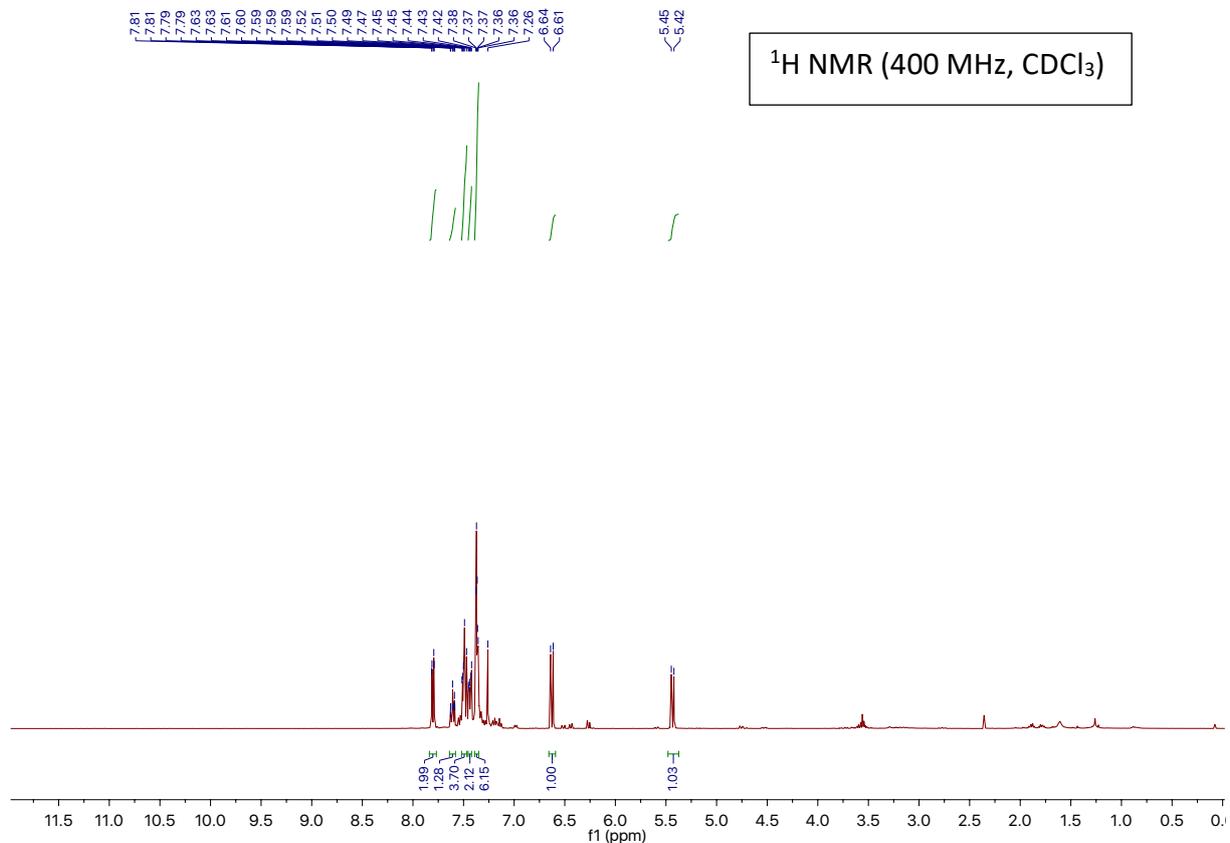
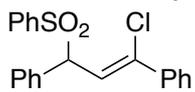
¹H NMR (400 MHz, CDCl₃)



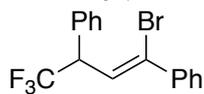
¹³C NMR (100 MHz, CDCl₃)



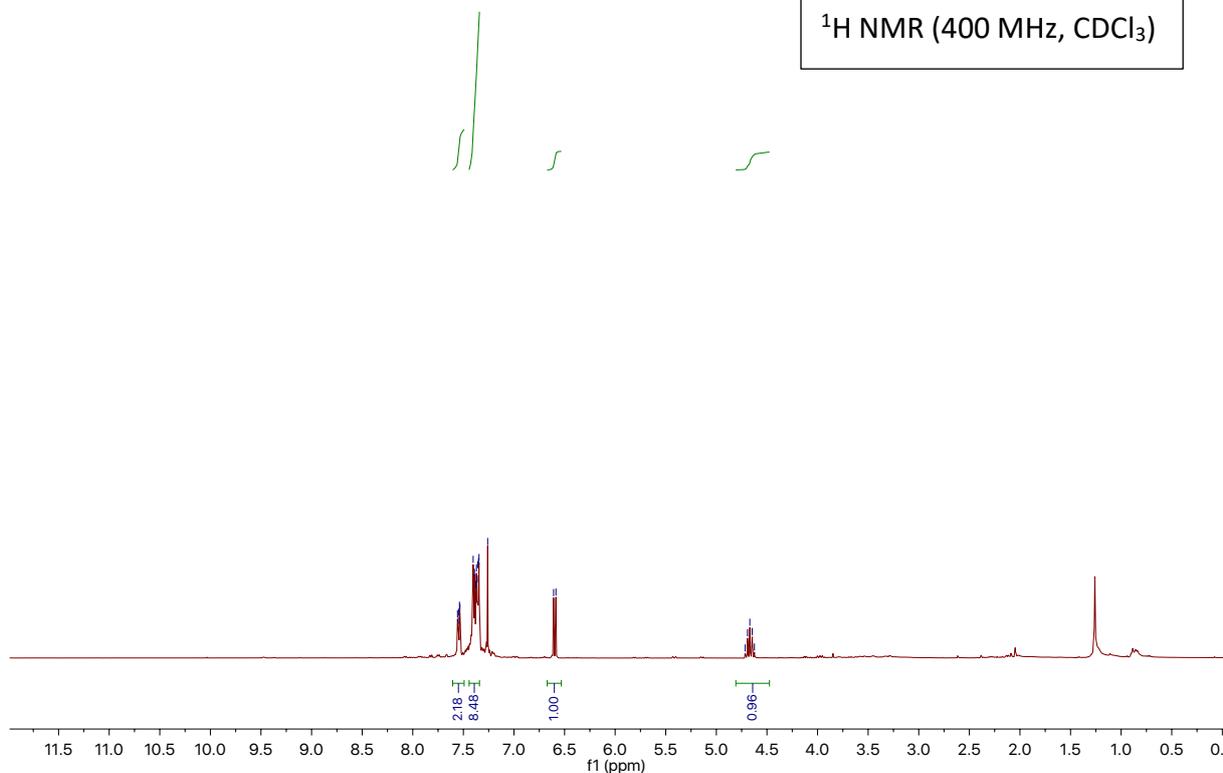
(E)-(1-chloro-3-(phenylsulfonyl)prop-1-ene-1,3-diyl)dibenzene ((E)-5n)



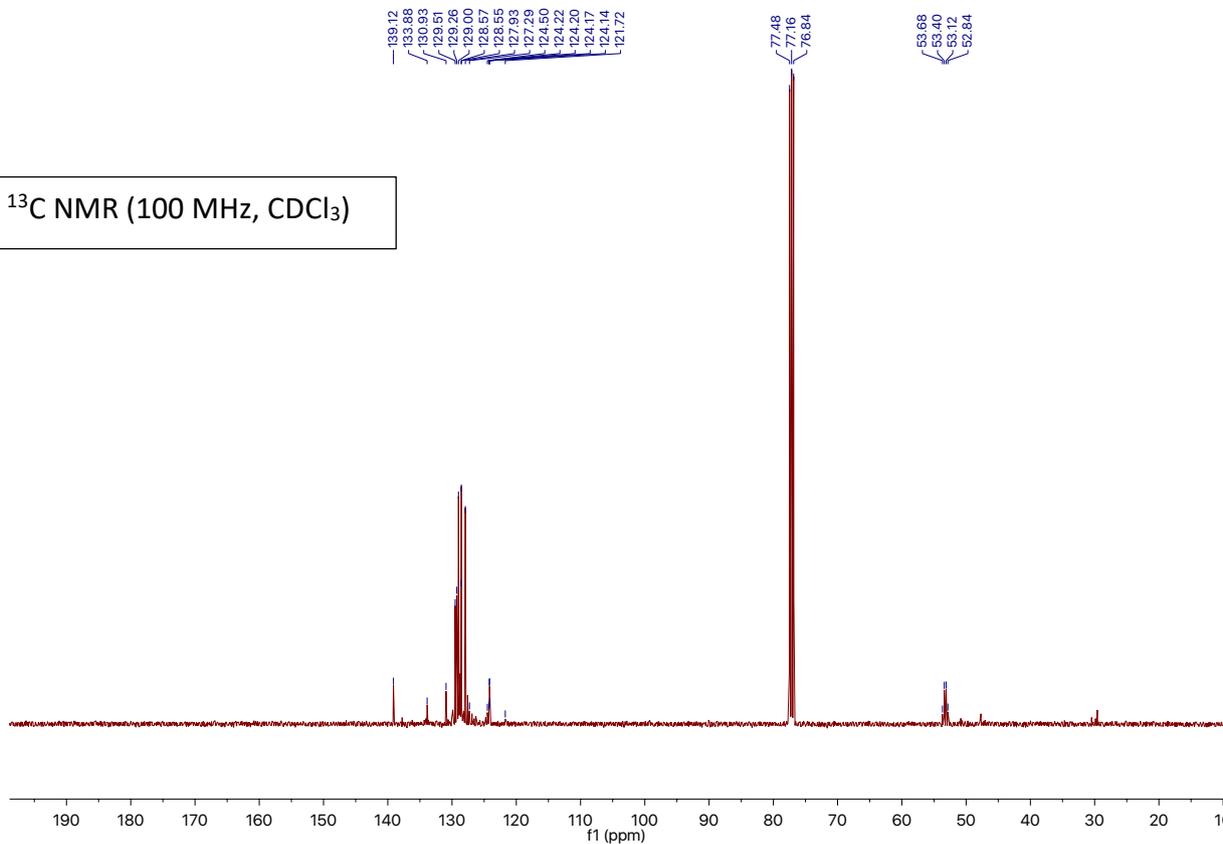
(Z)-(1-bromo-4,4,4-trifluorobut-1-ene-1,3-diyl)dibenzene (6a)



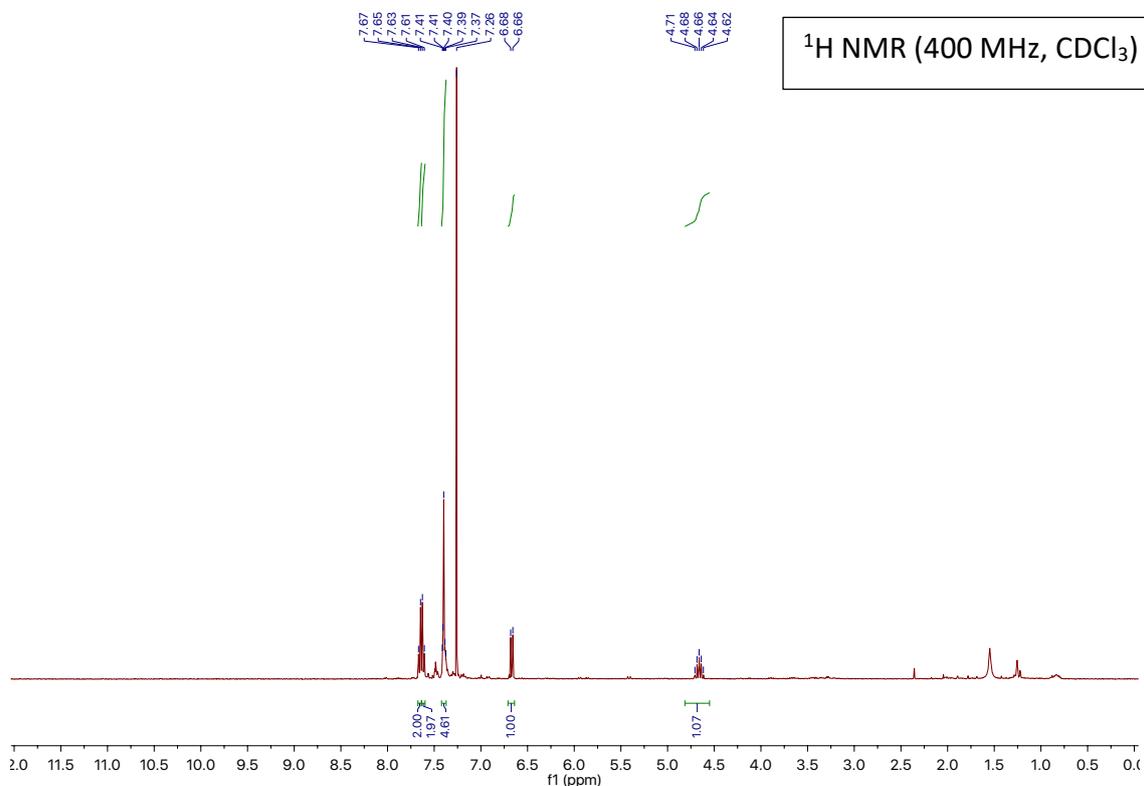
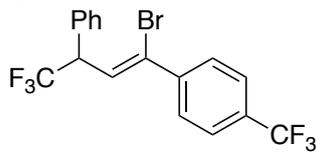
^1H NMR (400 MHz, CDCl_3)



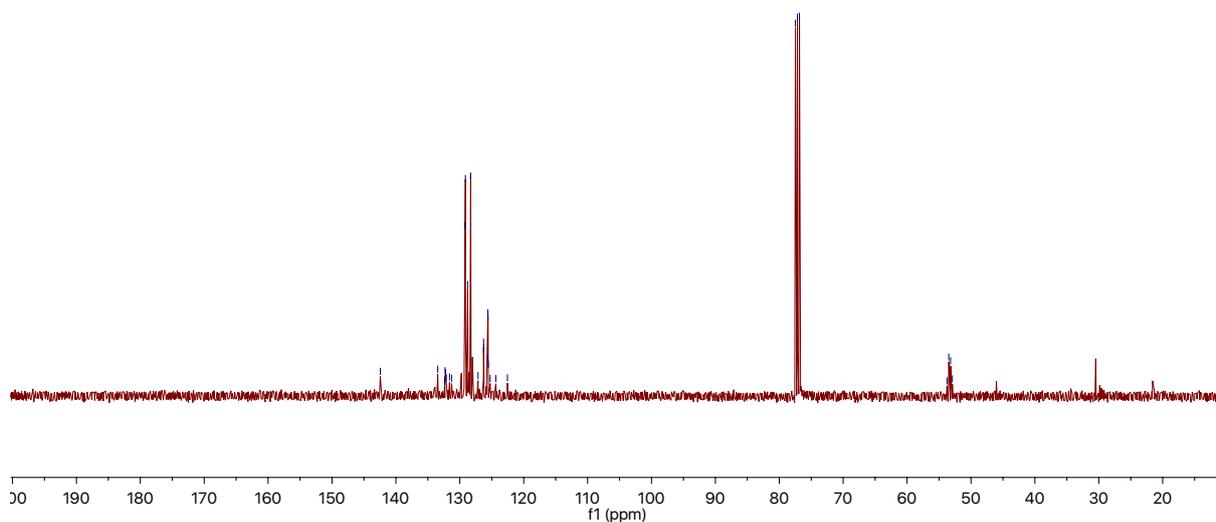
^{13}C NMR (100 MHz, CDCl_3)



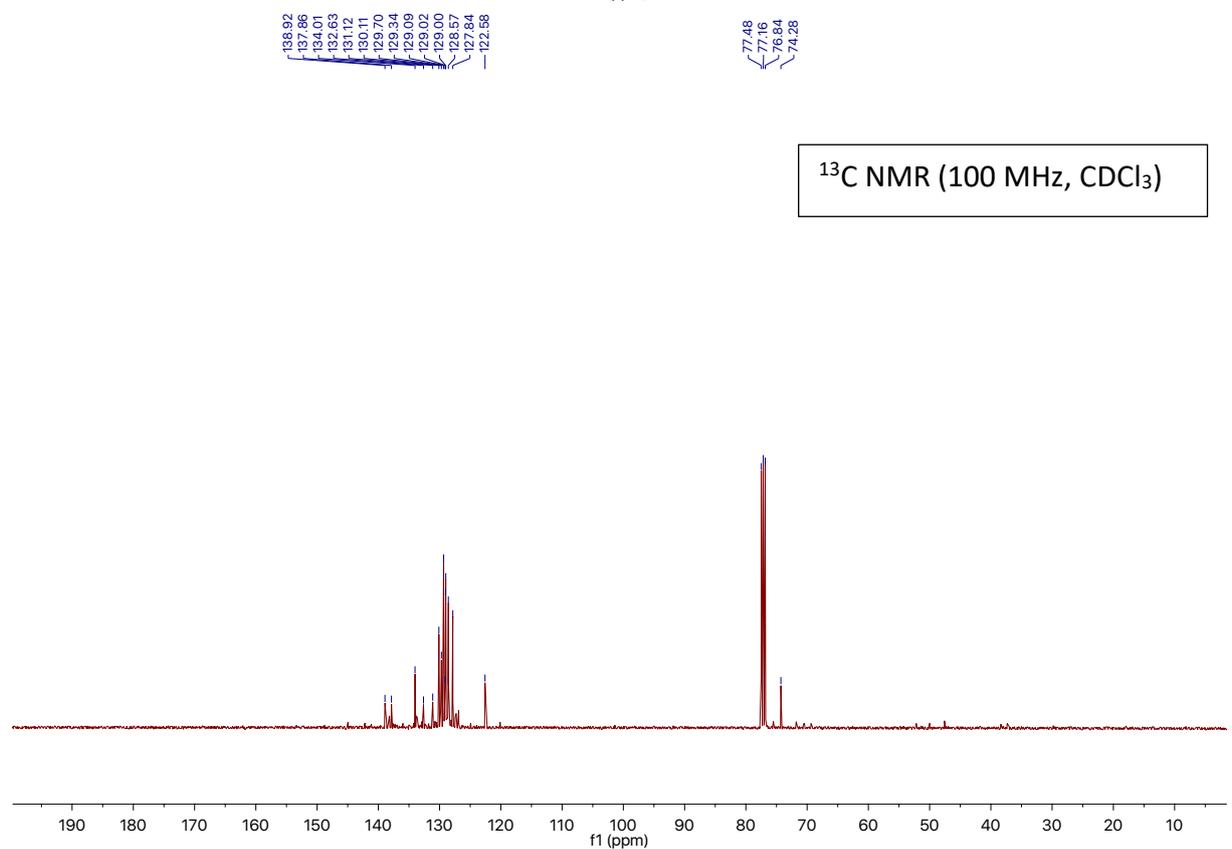
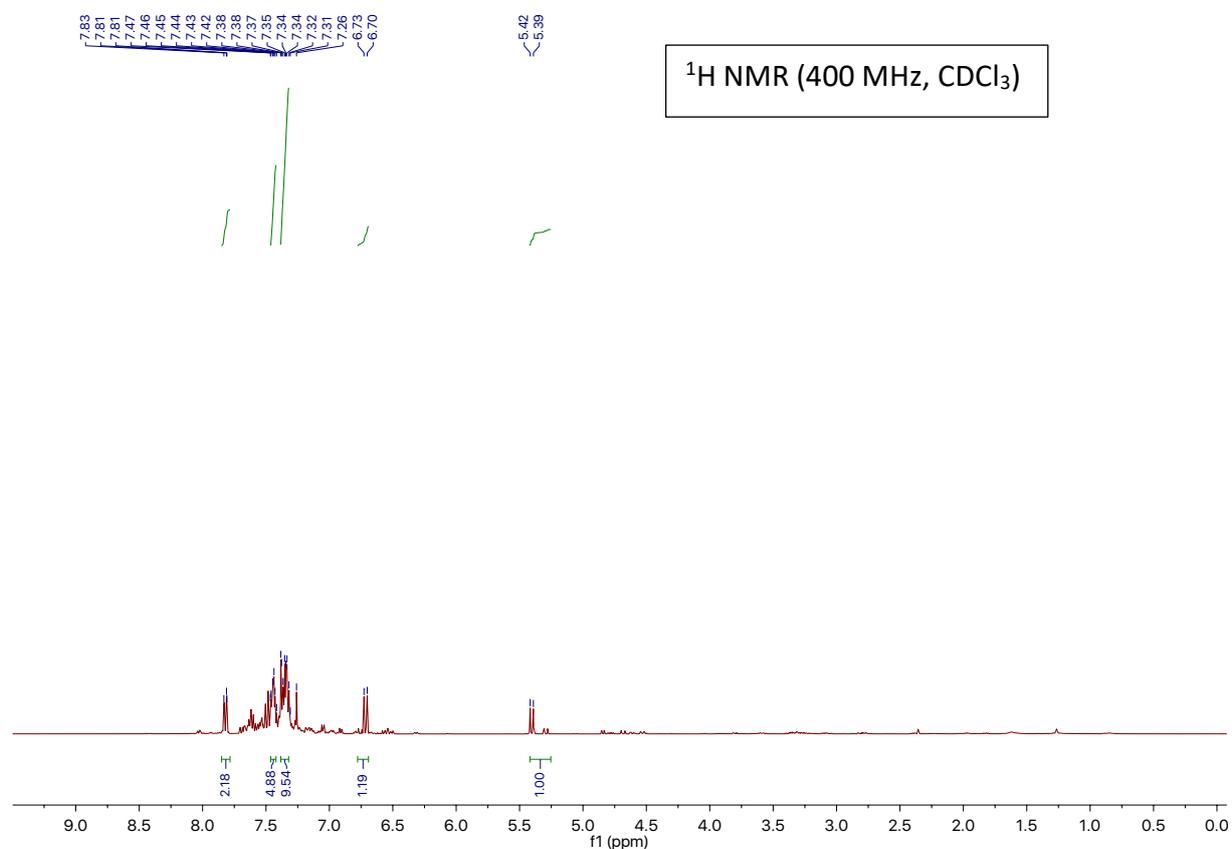
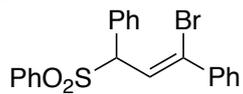
(Z)-1-(1-bromo-4,4,4-trifluoro-3-phenylbut-1-en-1-yl)-4-(trifluoromethyl)benzene (6b)



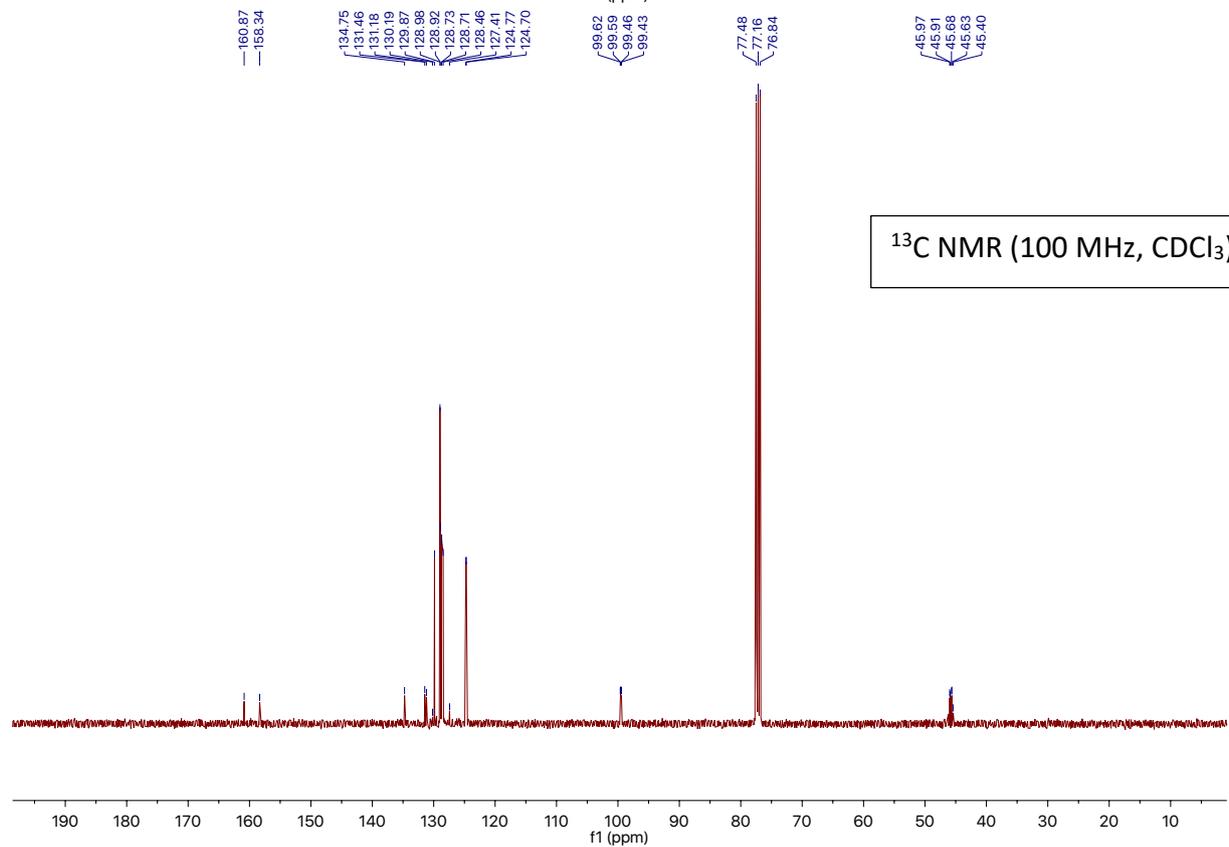
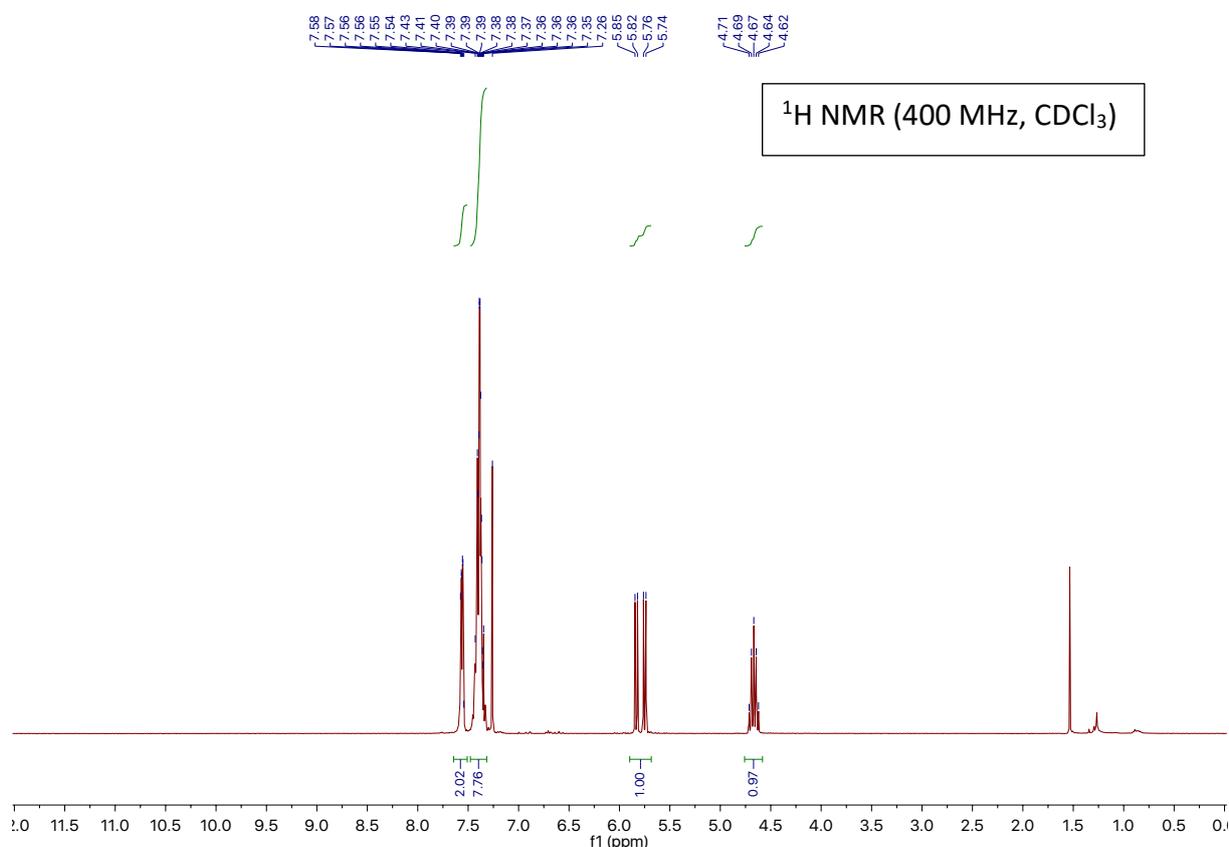
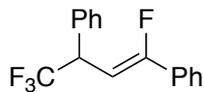
¹³C NMR (100 MHz, CDCl₃)



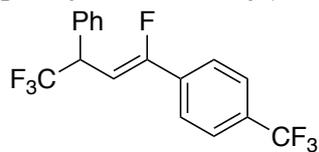
Z)-(1-bromo-3-(phenylsulfonyl)prop-1-ene-1,3-diyl)dibenzene (6c)



(Z)-(1-fluoro-4,4,4-trifluorobut-1-ene-1,3-diyl)dibenzene (7a)

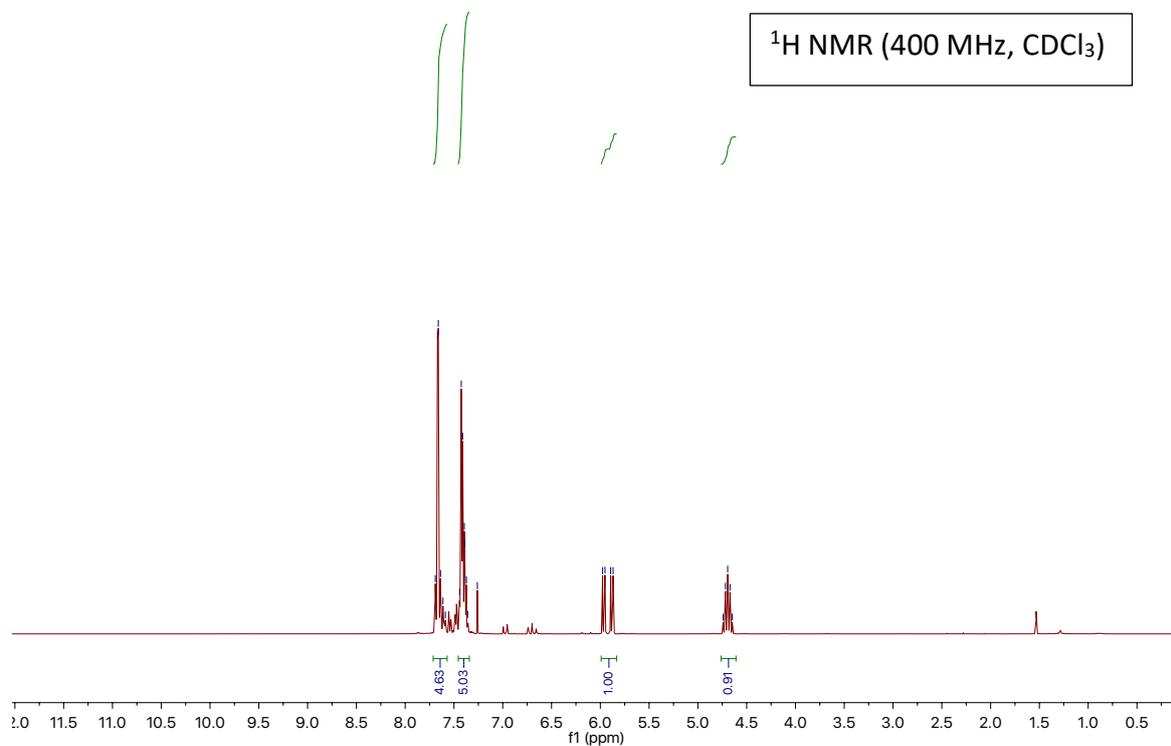


(Z)-1-(1-fluoro-4,4,4-trifluoro-3-phenylbut-1-en-1-yl)-4-(trifluoromethyl)benzene (7b)



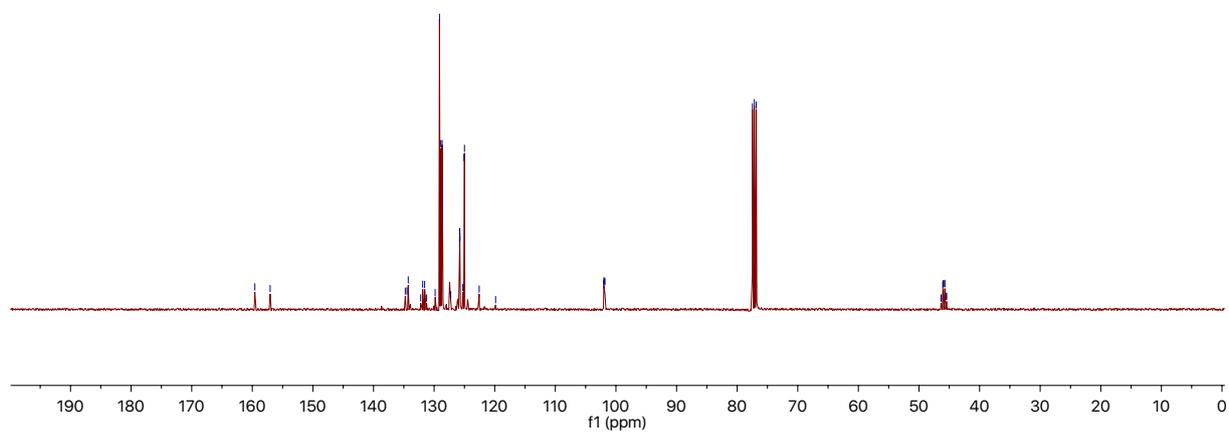
7.69
7.67
7.64
7.61
7.59
7.44
7.43
7.41
7.39
7.37
7.36
7.26
5.98
5.95
5.93
4.74
4.72
4.69
4.67
4.65

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

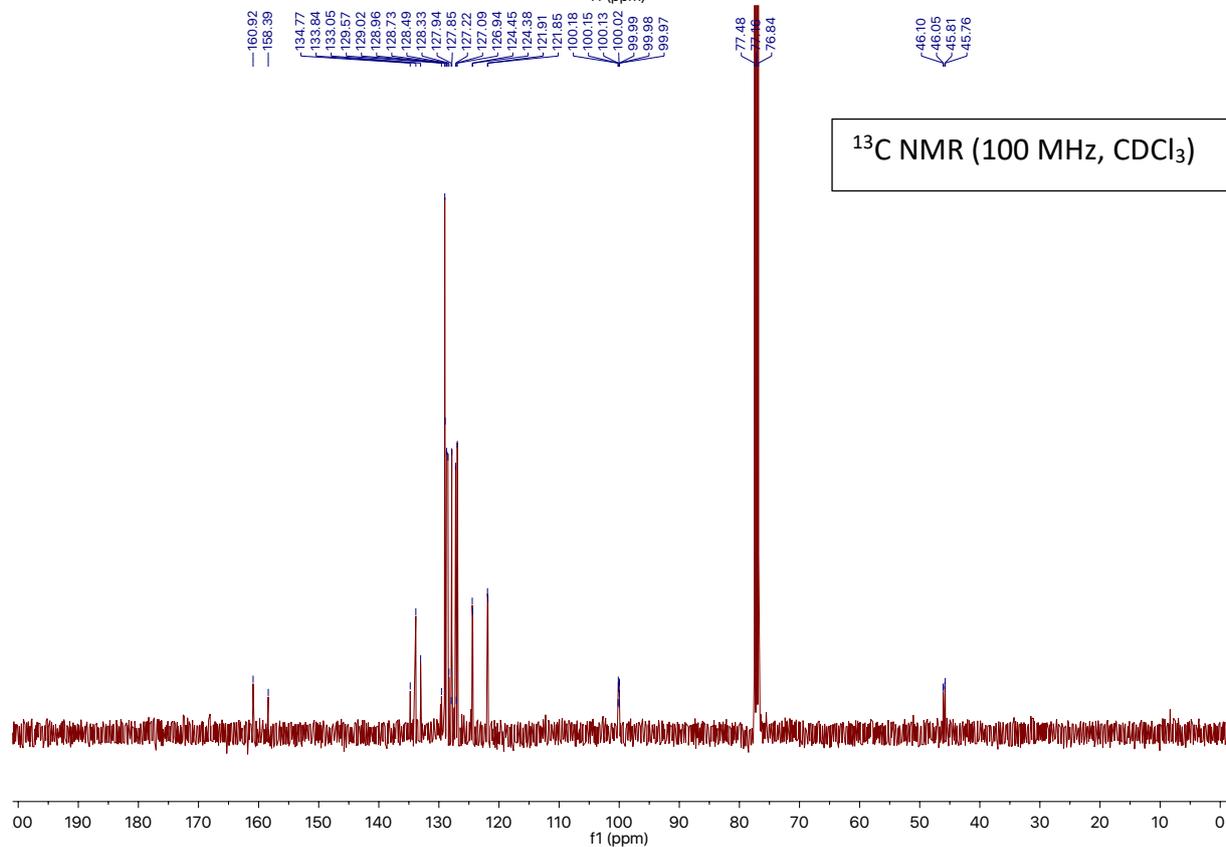
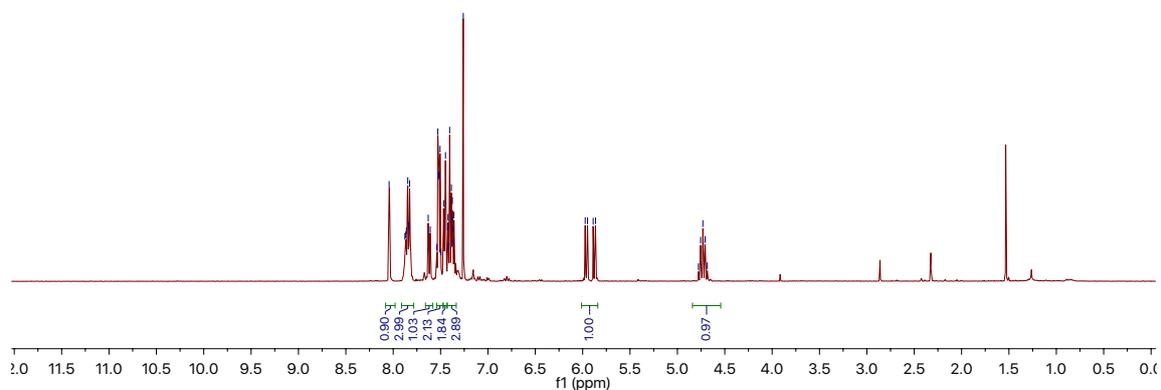
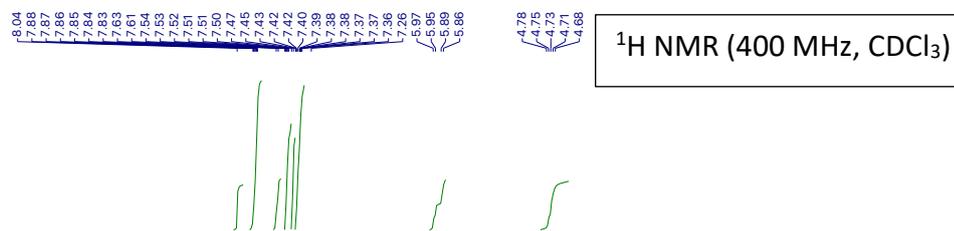
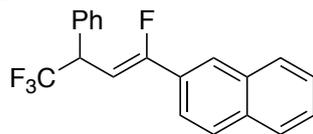


159.88
157.05
134.76
134.48
134.27
132.61
131.86
131.23
129.83
129.12
128.90
128.68
127.26
125.80
125.78
125.77
125.75
125.27
125.07
125.00
122.86
119.86
102.02
101.99
101.86
101.83
77.48
77.16
76.84
46.37
46.31
46.08
46.02
45.79
45.74
45.50
45.45

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

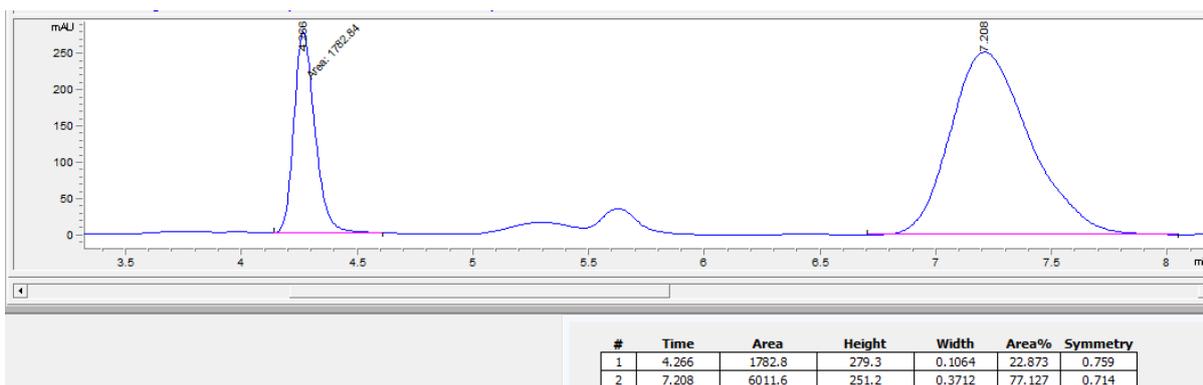
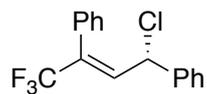
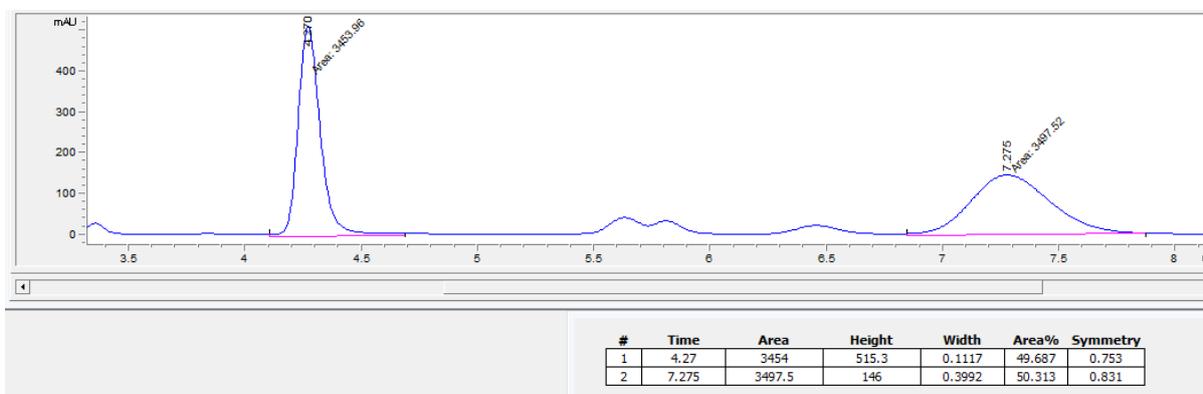
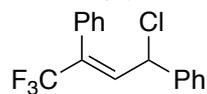


(Z)-2-(1-fluoro-4,4,4-trifluoro-3-phenylbut-1-en-1-yl)naphthalene (7c)

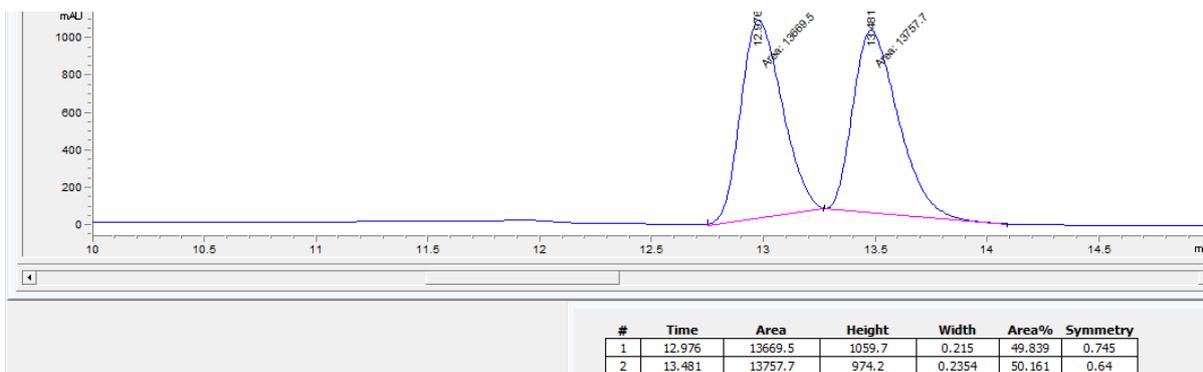
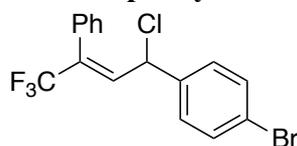


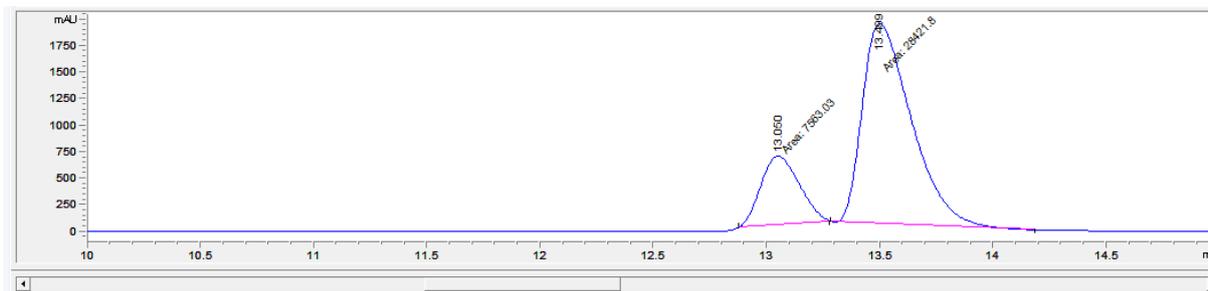
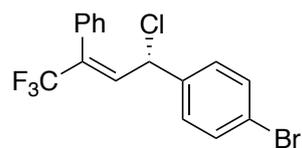
HPLC Chromatograms of allylic chlorides 2a, 2b, 2c, 2d, 2e, 2m and 2g

(E)-(1-chloro-4,4,4-trifluorobut-2-ene-1,3-diyl)dibenzene (2a)



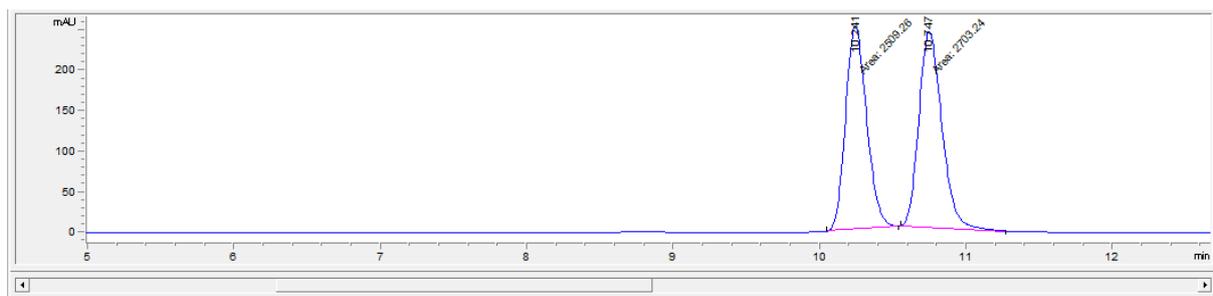
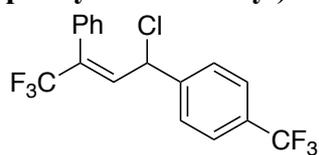
(E)-1-Bromo-4-(1-chloro-4,4,4-trifluoro-3-phenylbut-2-en-1-yl)benzene (2b)



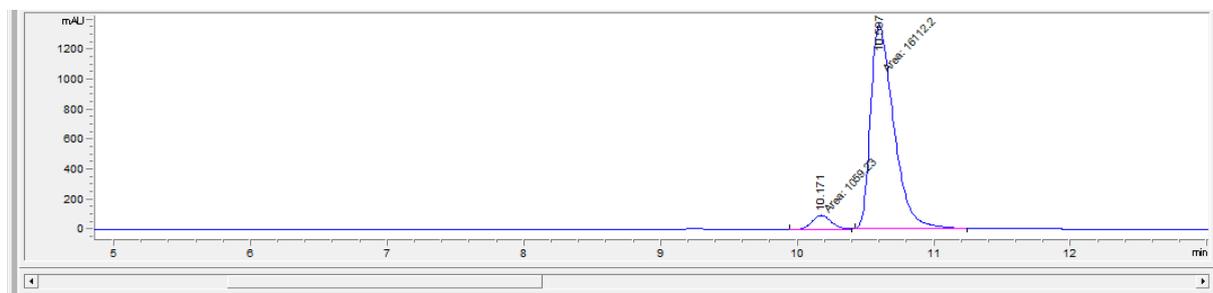
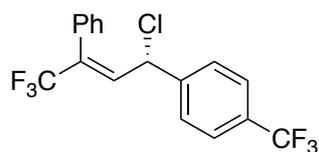


#	Time	Area	Height	Width	Area%	Symmetry
1	13.05	756.3	643.1	0.196	21.017	0.808
2	13.499	28421.8	1884.1	0.2514	78.983	0.538

(E)-1-(1-chloro-4,4,4-trifluoro-3-phenylbut-2-en-1-yl)-4-(trifluoromethyl)benzene (2c)

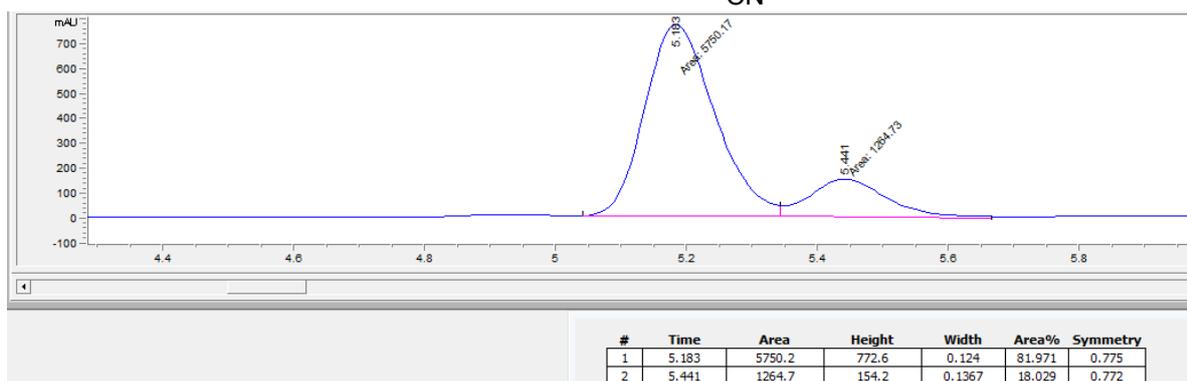
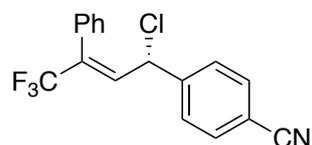
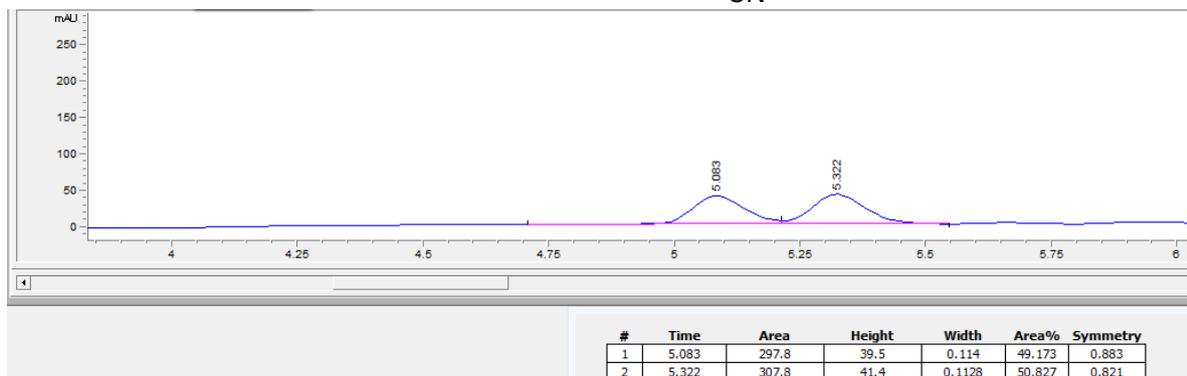
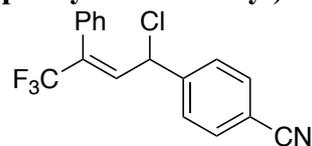


#	Time	Area	Height	Width	Area%	Symmetry
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2	10.747	2703.2	243.2	0.1853	51.861	0.717

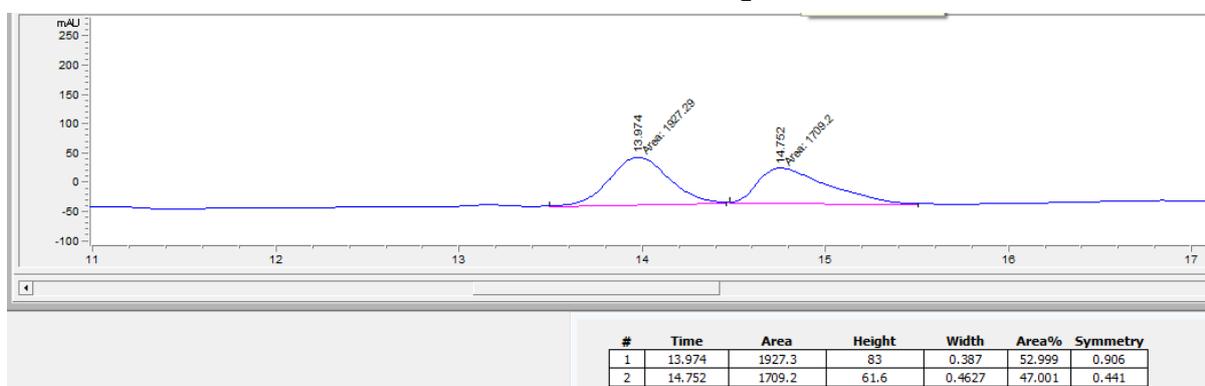
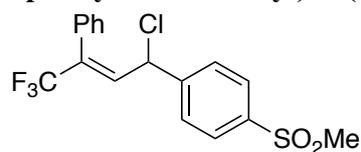


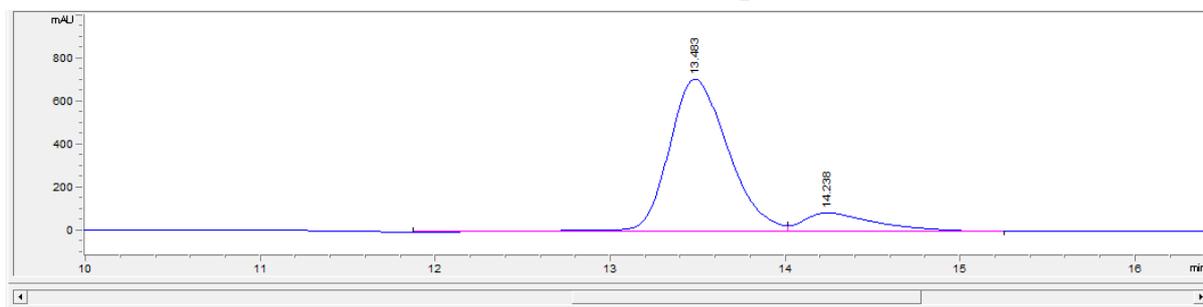
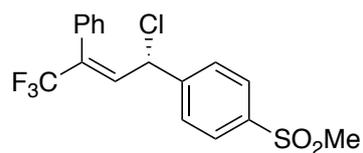
#	Time	Area	Height	Width	Area%	Symmetry
1	10.171	1059.2	98.4	0.1794	6.169	0.974
2	10.597	16112.2	1361.3	0.1973	93.831	0.606

(E)-4-(1-chloro-4,4,4-trifluoro-3-phenylbut-2-en-1-yl)benzonitrile (2d)



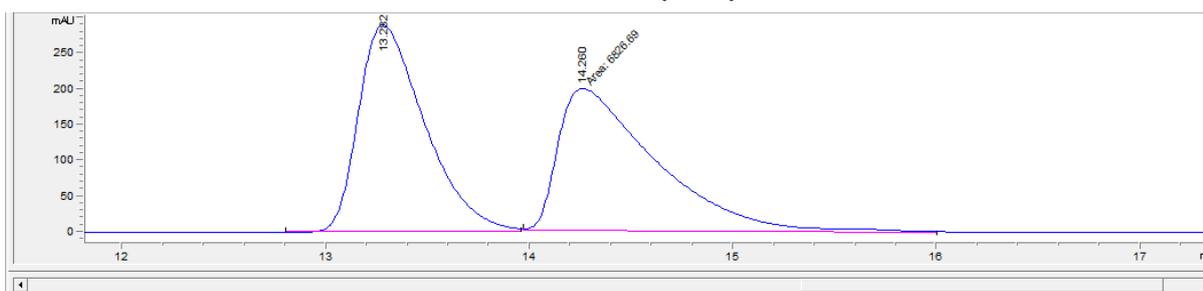
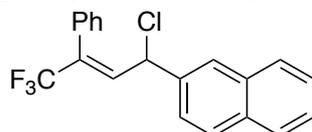
(E)-1-(1-chloro-4,4,4-trifluoro-3-phenylbut-2-en-1-yl)-4-(methylsulfonyl)benzene (2e)



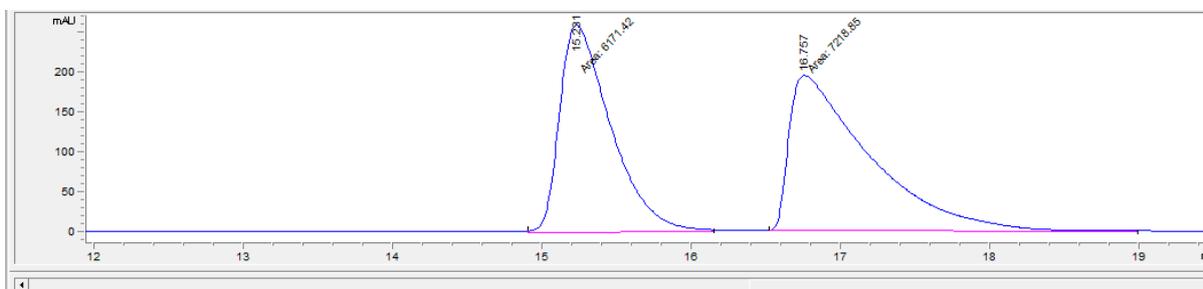
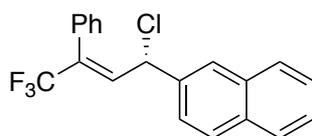


#	Time	Area	Height	Width	Area%	Symmetry
1	13.463	16741.7	708.6	0.3656	86.997	0.784
2	14.238	2502.4	87.2	0.4167	13.003	0.447

(E)-2-(1-chloro-4,4,4-trifluoro-3-phenylbut-2-en-1-yl)naphthalene (2g)

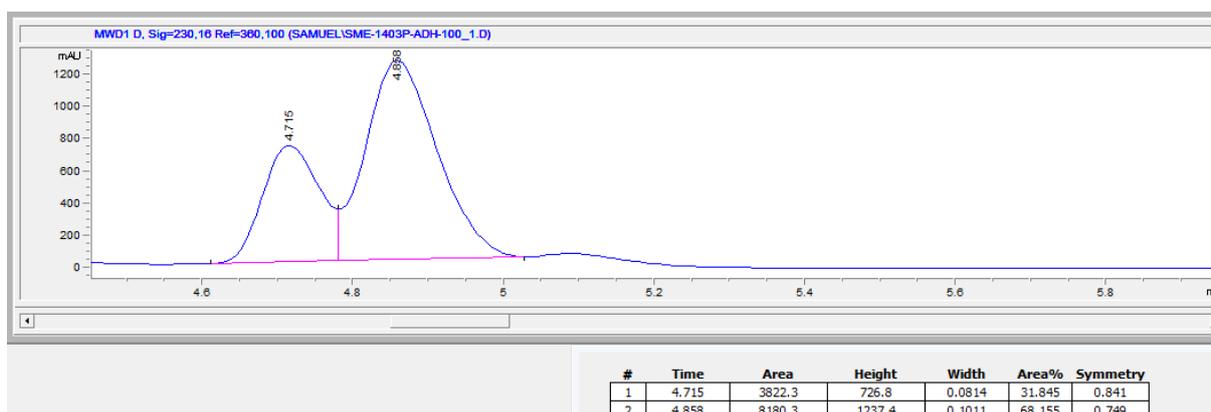
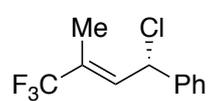
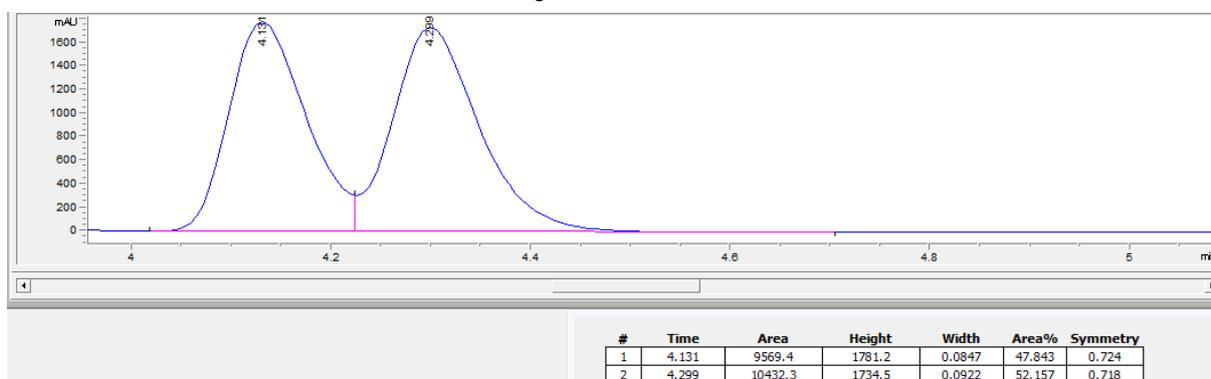
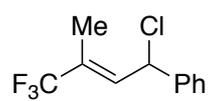


#	Time	Area	Height	Width	Area%	Symmetry
1	13.282	6605	290.6	0.3452	49.175	0.561
2	14.26	6826.7	200.6	0.5671	50.825	0.319



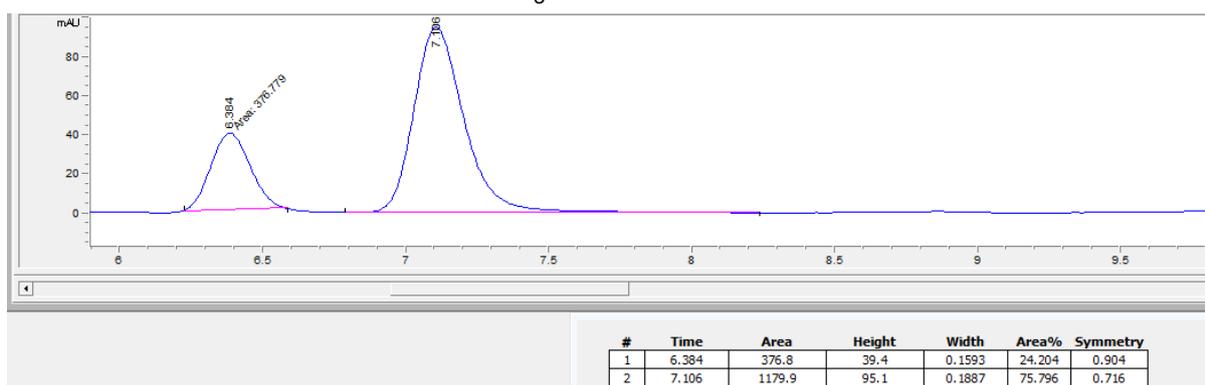
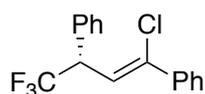
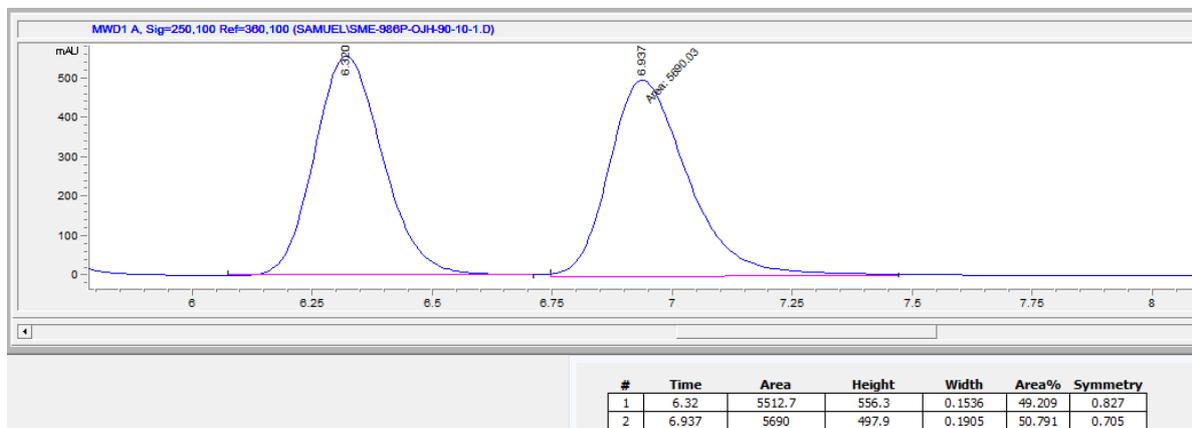
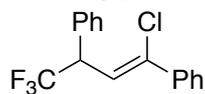
#	Time	Area	Height	Width	Area%	Symmetry
1	15.231	6171.4	258.6	0.3978	46.089	0.488
2	16.757	7218.8	193.2	0.6227	53.911	0.225

(E)-(1-chloro-4,4,4-trifluoro-3-methylbut-2-en-1-yl)benzene (2k)

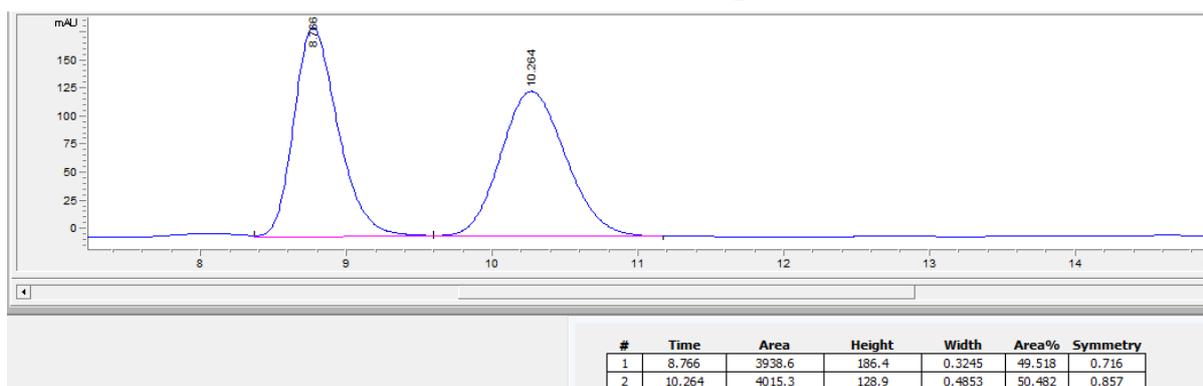
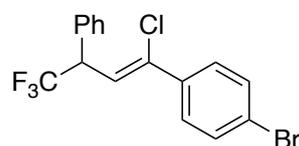


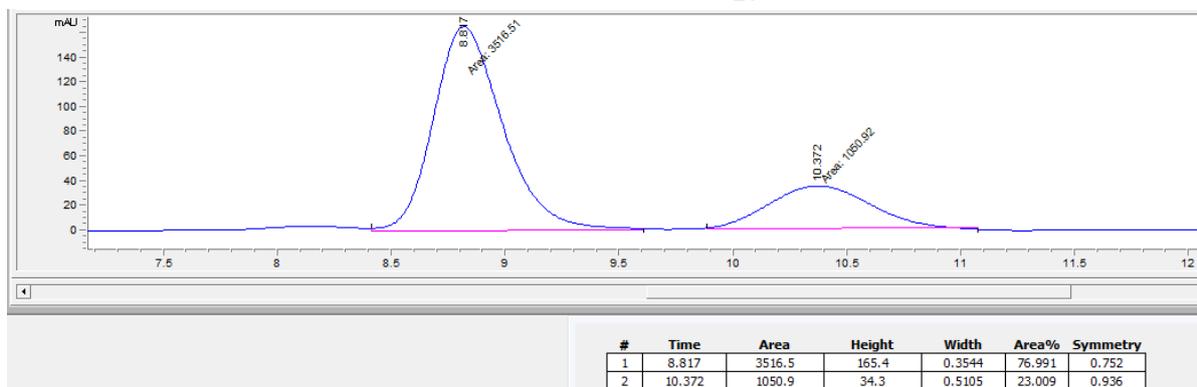
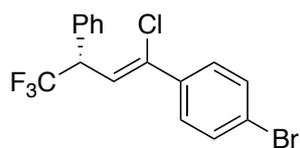
HPLC Chromatograms of vinyl chlorides 5a, 5b, 5c, 5d, 5e, 5m and 5g

(Z)-(1-chloro-4,4,4-trifluorobut-1-ene-1,3-diyl)dibenzene (5a)

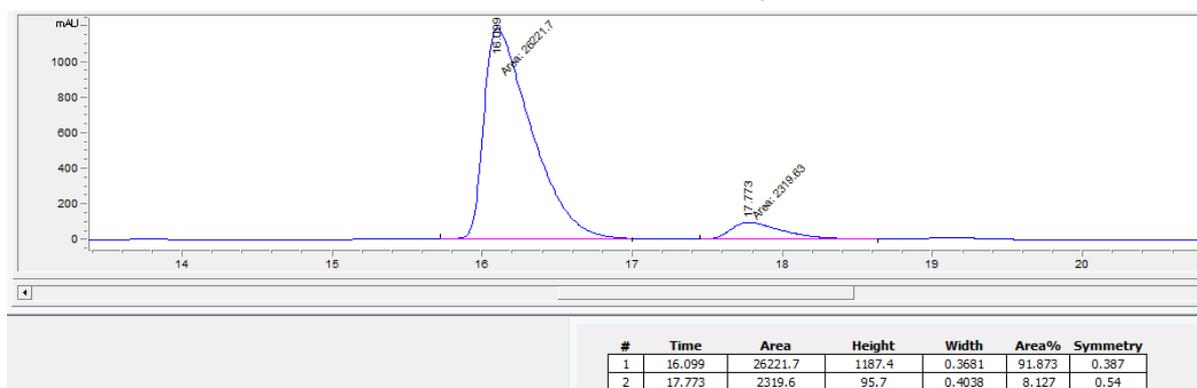
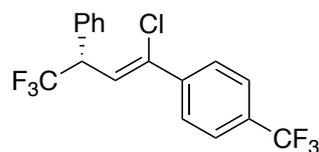
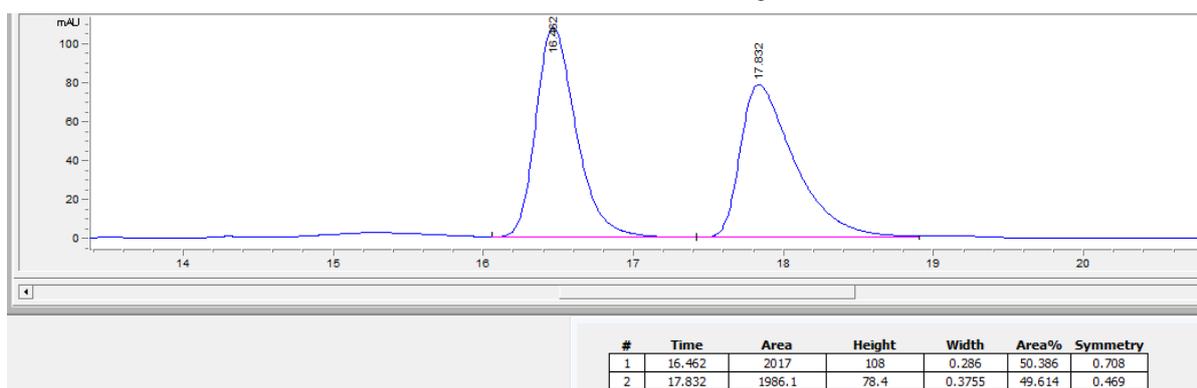
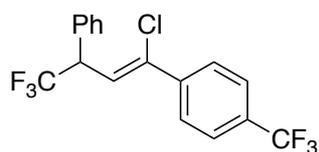


(Z)-1-bromo-4-(1-chloro-4,4,4-trifluoro-3-phenylbut-1-en-1-yl)benzene (5b)

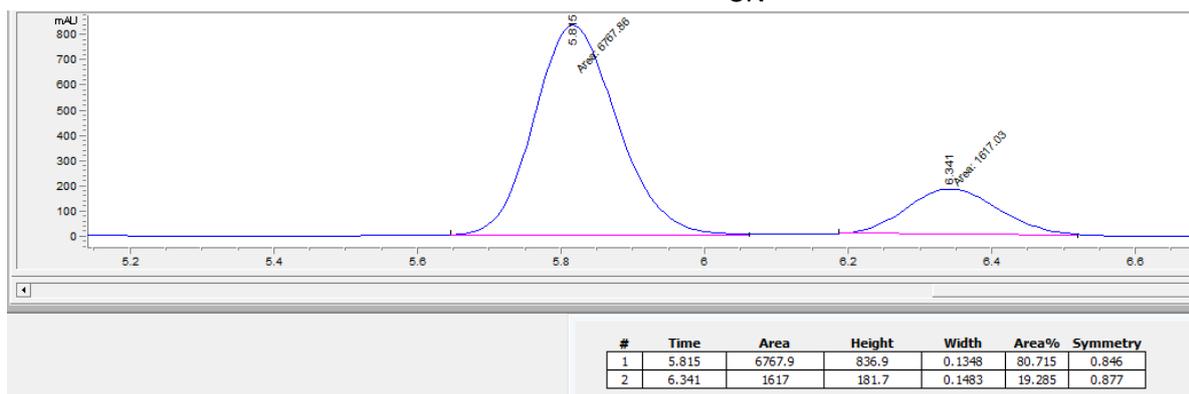
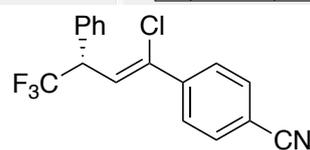
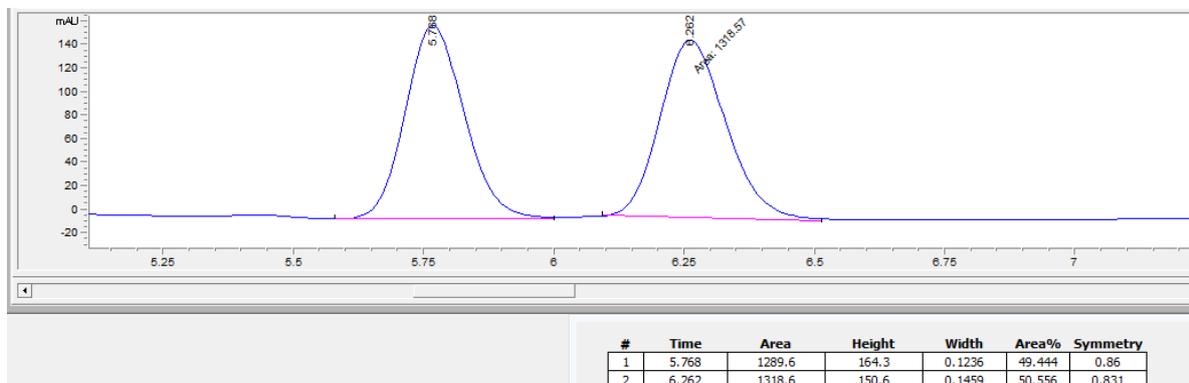
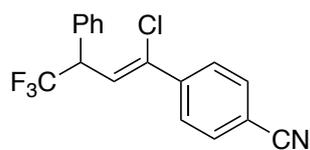




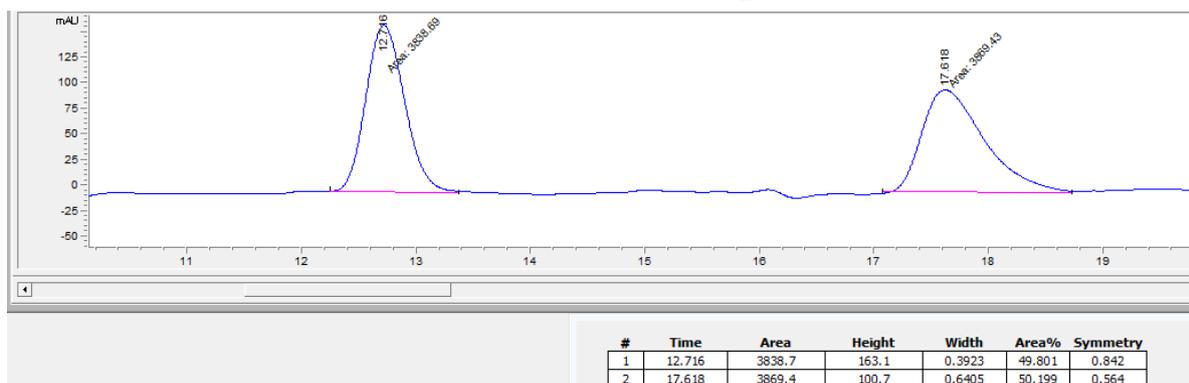
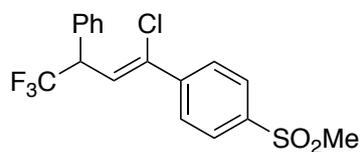
(Z)-1-(1-chloro-4,4,4-trifluoro-3-phenylbut-1-en-1-yl)-4-(trifluoromethyl)benzene (5c)

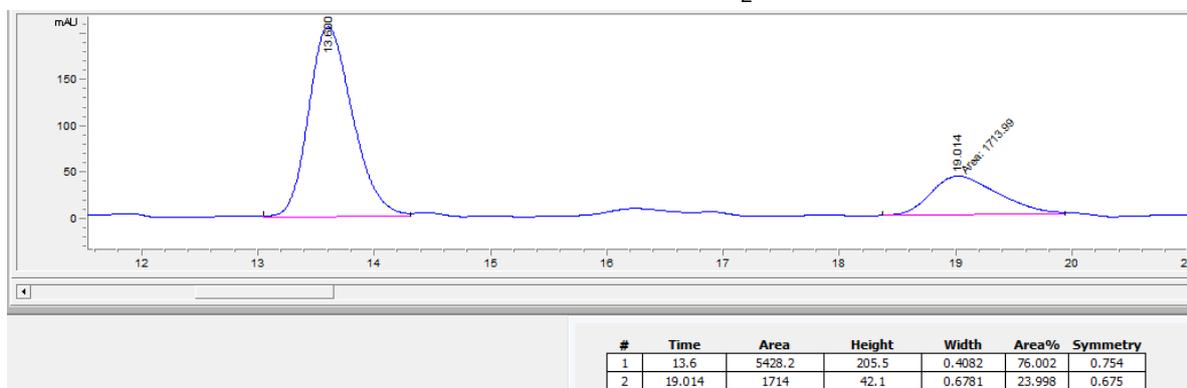
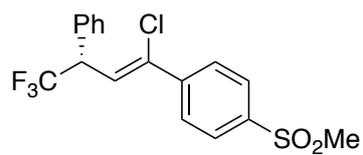


(Z)-4-(1-chloro-4,4,4-trifluoro-3-phenylbut-1-en-1-yl)benzonitrile (5d)

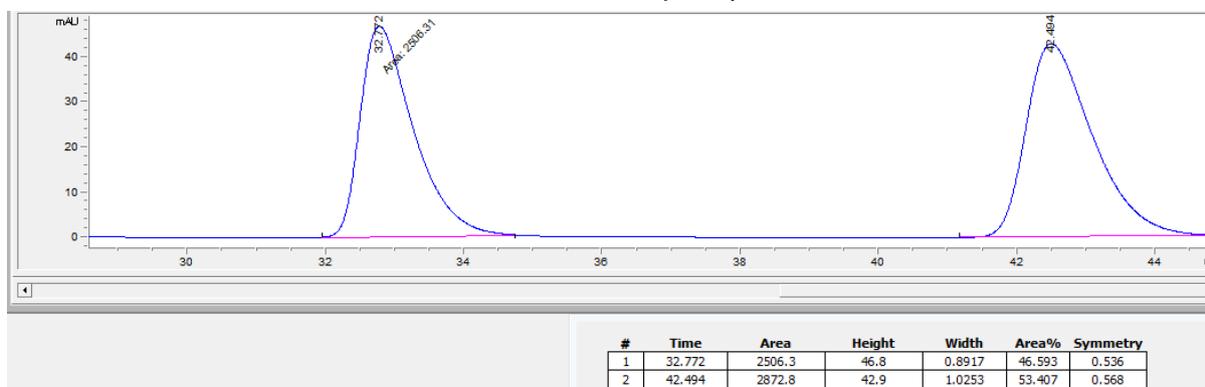
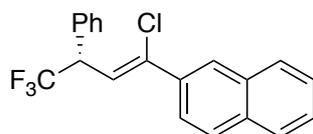
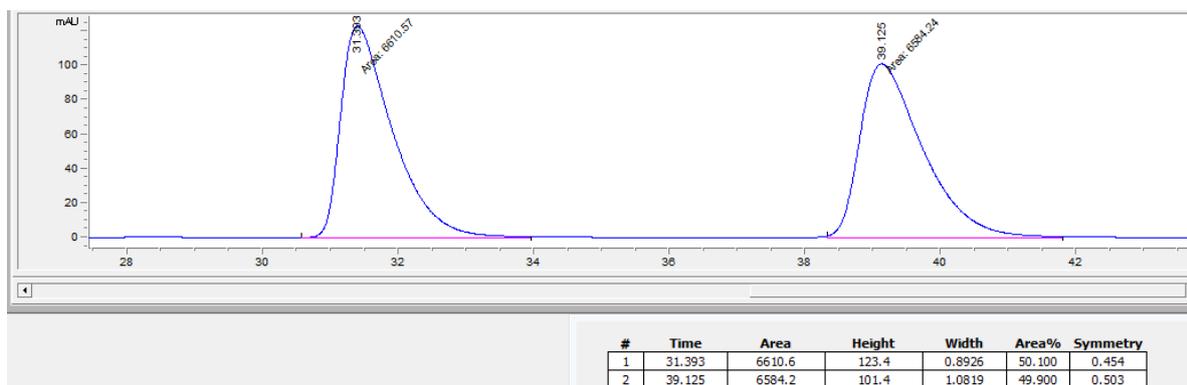
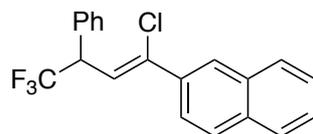


(Z)-1-(1-chloro-4,4,4-trifluoro-3-phenylbut-1-en-1-yl)-4-(methylsulfonyl)benzene (5e)





(Z)-2-(1-chloro-4,4,4-trifluoro-3-phenylbut-1-en-1-yl)naphthalene (5g)



(Z)-(1-chloro-4,4,4-trifluoro-3-methylbut-1-en-1-yl)benzene (5k)

