Supporting Information

Experimental Studies on the Selective β-C-H Halogenation of Enones

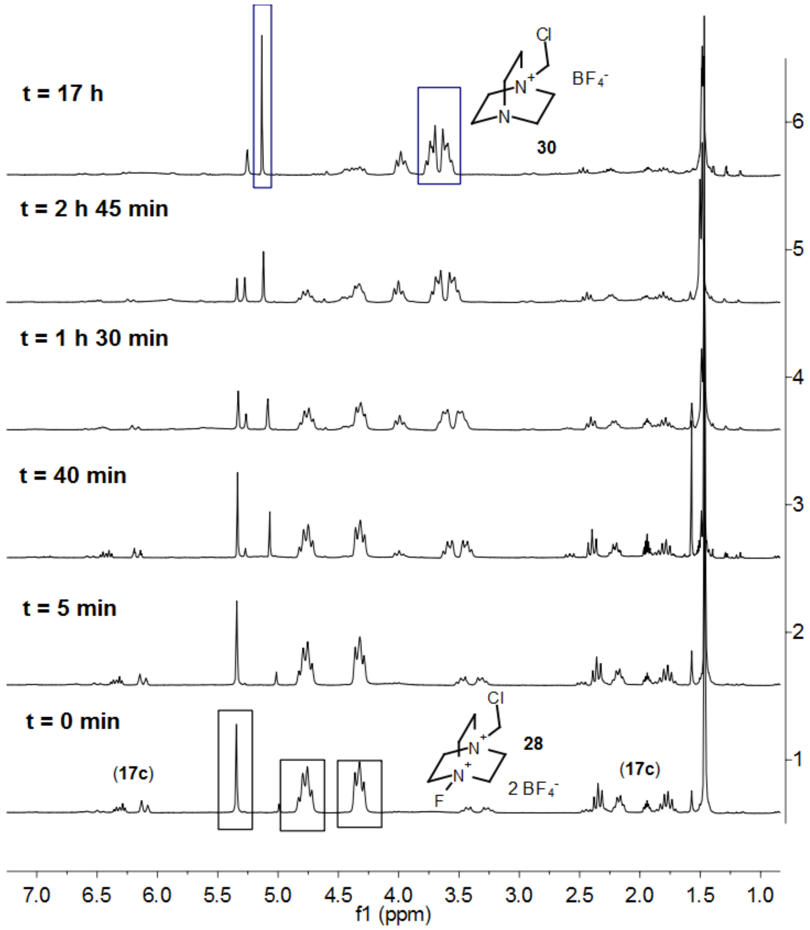
Tatjana Huber, Daniel Kaiser, Jens Rickmeier, and Thomas Magauer*

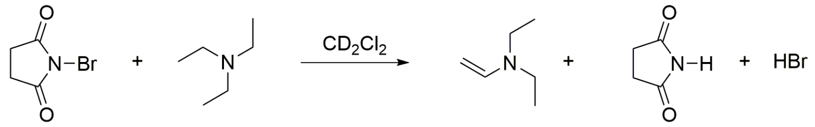
Department of Chemistry, Ludwig–Maximilians-Universität, Butenandtstrasse 5–13,

81377 Munich, Germany

I. ^{1}H NMR experiments

Monitoring of the reaction of Selectfluor™ with 17c via ^{1}H NMR spectroscopy. Selectfluor™ (**28**) (39.0 mg, 0.11 mmol, 1.10 equiv) was suspended in d_3-acetonitrile (1 mL, c = 0.1 M) and stirring was continued until a suspension was obtained (no remaining precipitate). *tert*-Butyl 2-(cyclohex-2-en-1-ylidene)hydrazinecarboxylate (**17c**) (21.0 mg, 0.10 mmol, 1 equiv, dr = 4:1) then was added and the reaction was monitored via ^{1}H NMR.



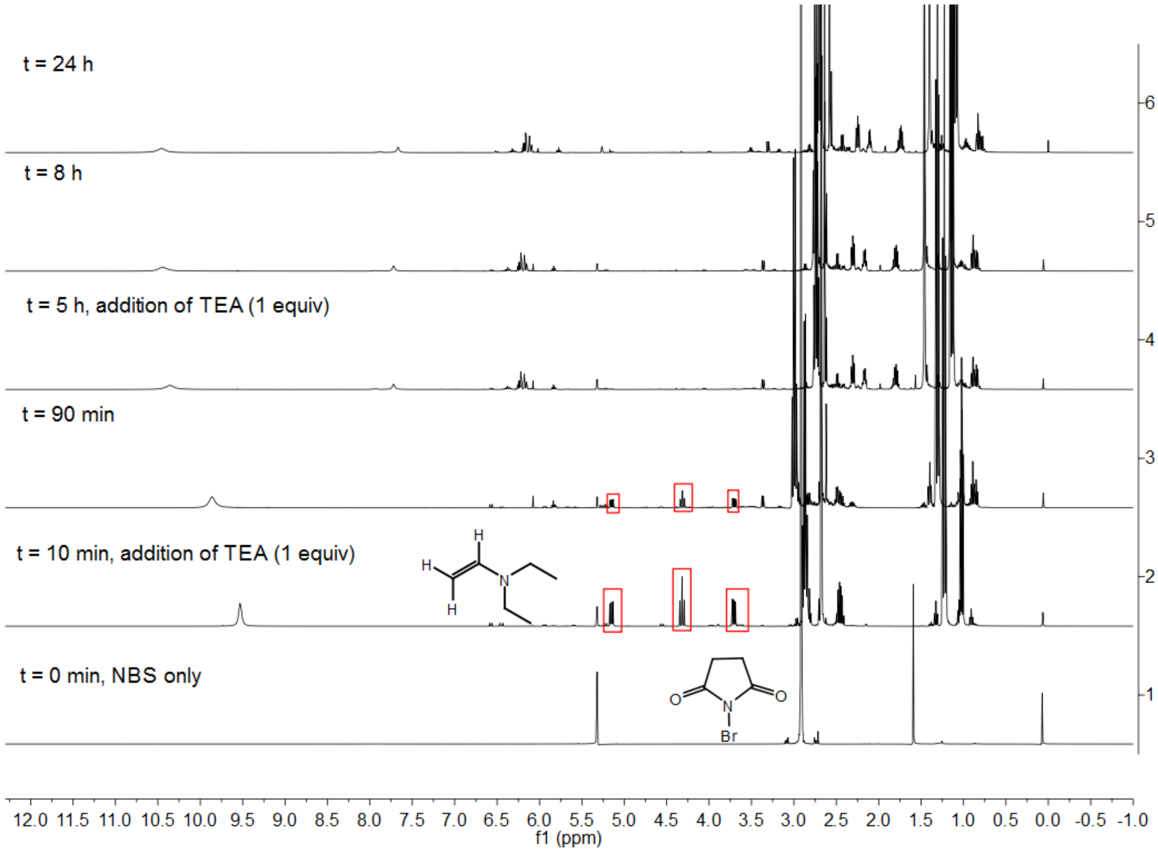


23

Monitoring the reaction between *N*-bromosuccinimide and triethylamine. *N*-Bromosuccinimide (14.2 mg, 0.08 mmol, 1 equiv) was dissolved in d_2-dichloromethane (0.8 mL) and the resulting solution was transferred to a NMR tube. Triethylamine (11.1 µL, 0.08 mmol, 1 equiv) was added and the progress of the reaction was monitored by ^{1}H NMR.

23:

^{1}H NMR (400 MHz, $CDCl_3$) δ 5.15 (dd, J = 10.0, 5.3 Hz, 1H), 4.32 (t, J = 10.1 Hz, 1H), 3.71 (dd, J = 10.2, 5.3 Hz, 1H). (Ethyl signals for triethylamine and triethylammonium salt overlap and could therefore not be determined).



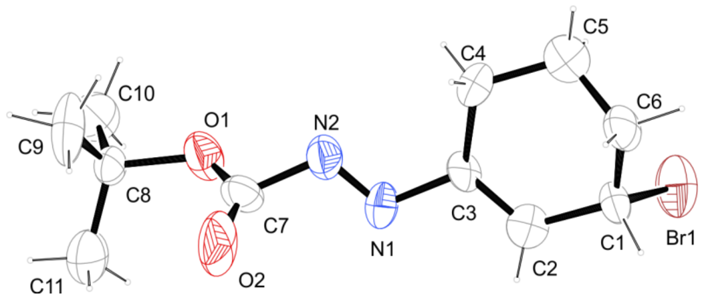
II. X-Ray Crystallographic Data

CCDC 1034038 contains the supplementary crystallographic data for allylic bromide **22**. These data can be obtained free of charge from The Cambridge Crystallographic Data Centre (CCDC) *via* www.ccdc.cam.ac.uk/data_request/cif.

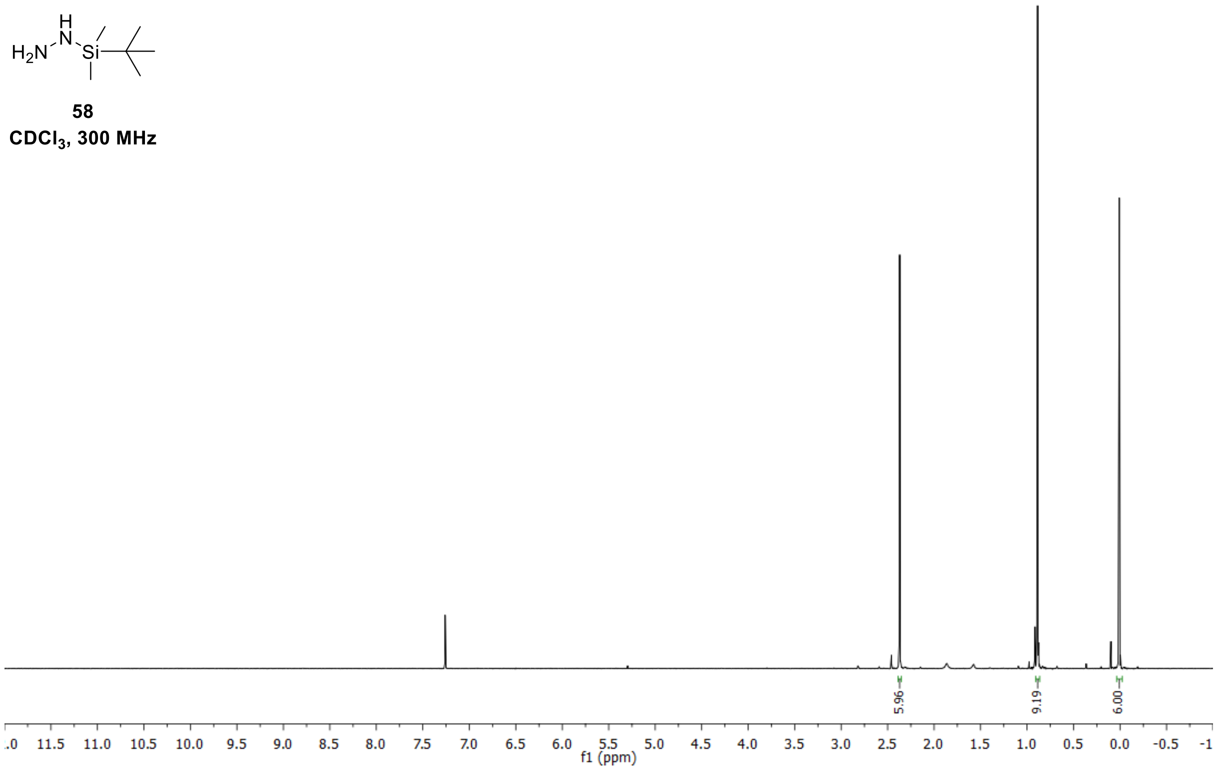
Table 1. Crystallographic data for allylic bromide **22**.

net formula	$C_{11}H_{17}BrN_2O_2$
M_r/g·mol^{-1}	289.169
crystal size/mm	0.117×0.029×0.027
T/K	173(2)
radiation	Mo Kα
diffractometer	Bruker D8Venture
crystal system	triclinic
space group	*P*1bar
a/Å	5.909(2)
b/Å	9.420(3)
c/Å	12.251(4)
α/°	97.002(10)
β/°	92.212(9)
γ/°	103.538(10)
V/Å^3	656.4(4)
Z	2
calc. density/g cm^{-3}	1.4631(9)
μ/mm^{-1}	3.121
absorption correction	multi-scan
transmission factor range	0.5932–0.9579
refls. measured	2416
R_{int}	0.0000
mean σ(*I*)/*I*	0.1845
θ range	3.36–25.13
observed refls.	1438

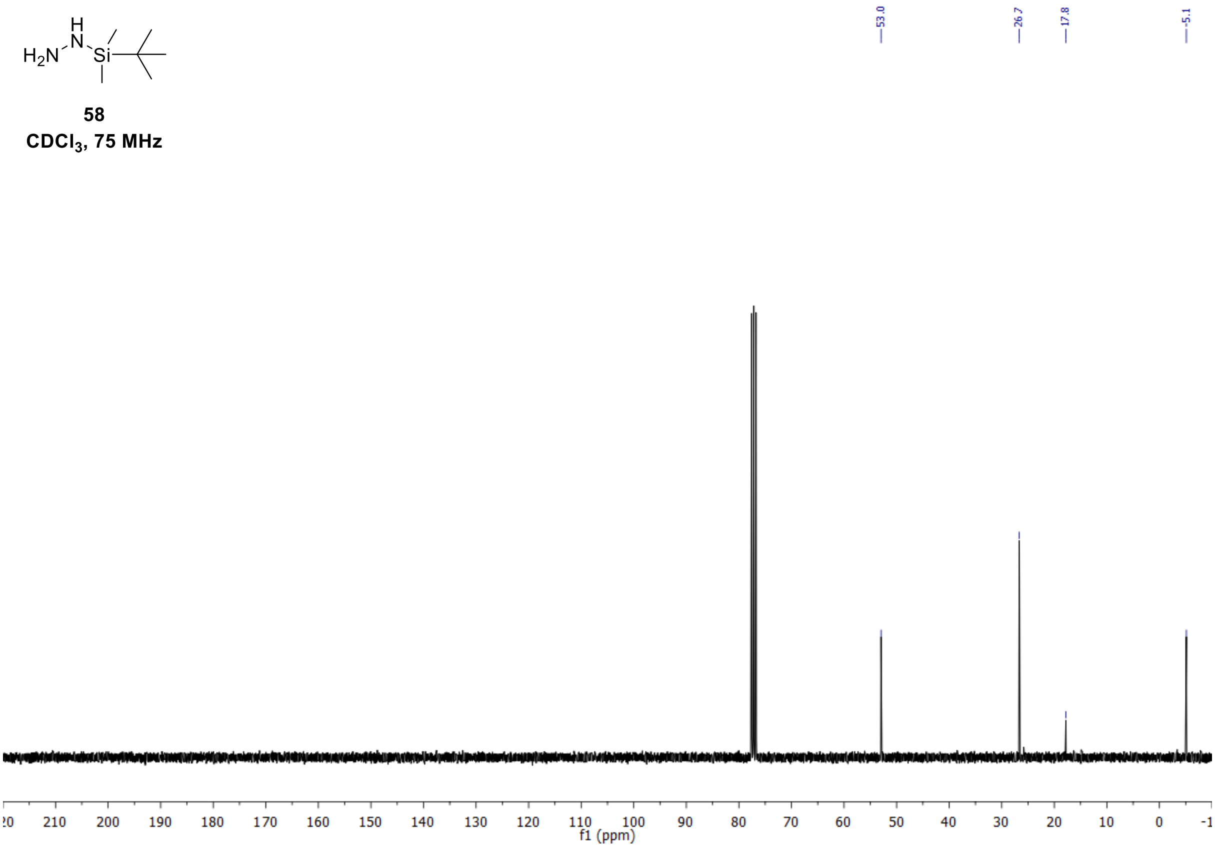
x, y (weighting scheme)	0.1577, 1.6742
hydrogen refinement	constr
refls in refinement	2454
parameters	149
restraints	0
$R(F_{obs})$	0.1051
$R_w(F^2)$	0.3029
S	1.091
shift/error$_{max}$	0.001
max electron density/e Å^{-3}	1.496
min electron density/e Å^{-3}	−0.729



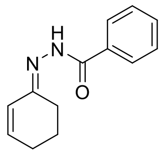
III. ^{1}H NMR and ^{13}C NMR spectra



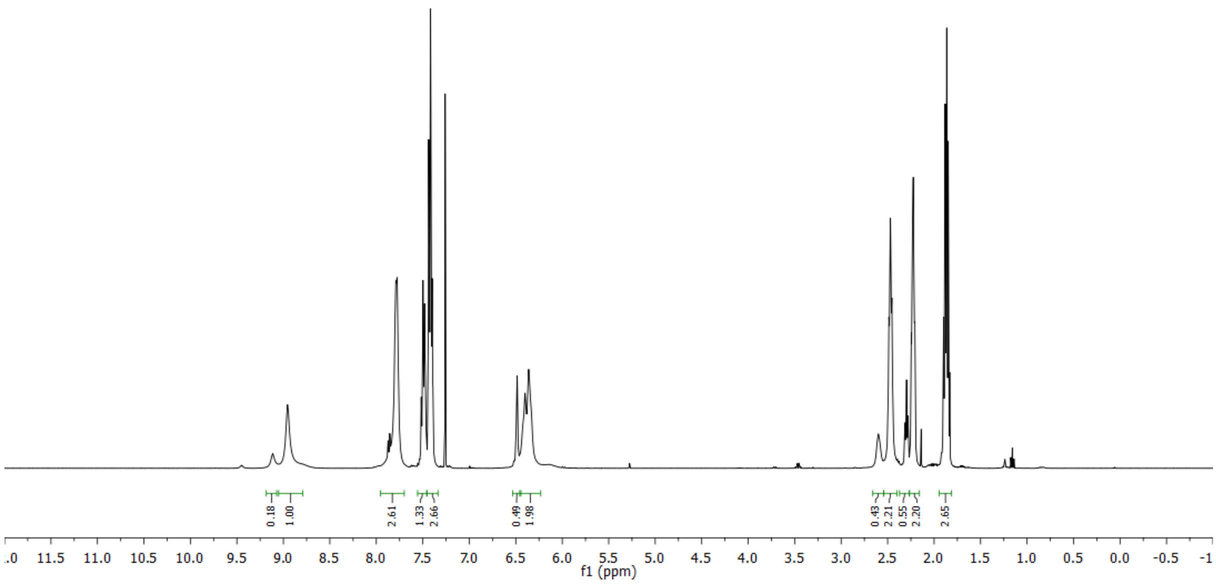
58
$CDCl_3$, 300 MHz

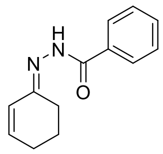


58
$CDCl_3$, 75 MHz

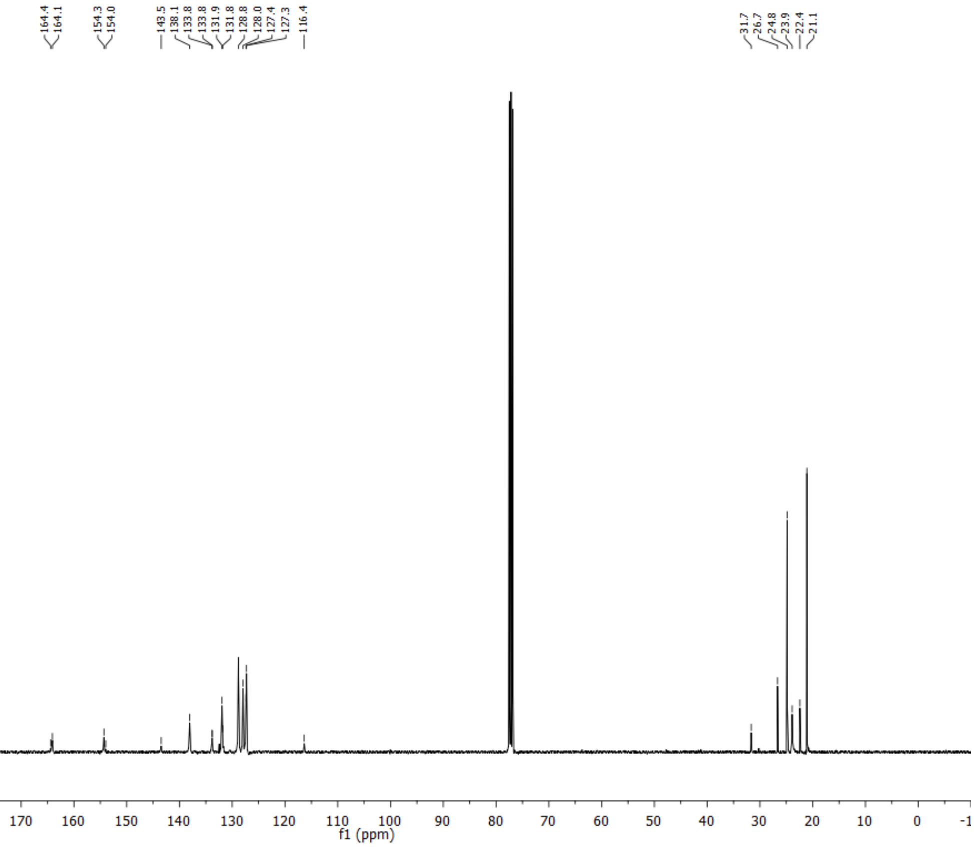


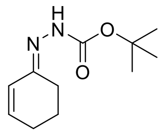
17b
$CDCl_3$, 400 MHz



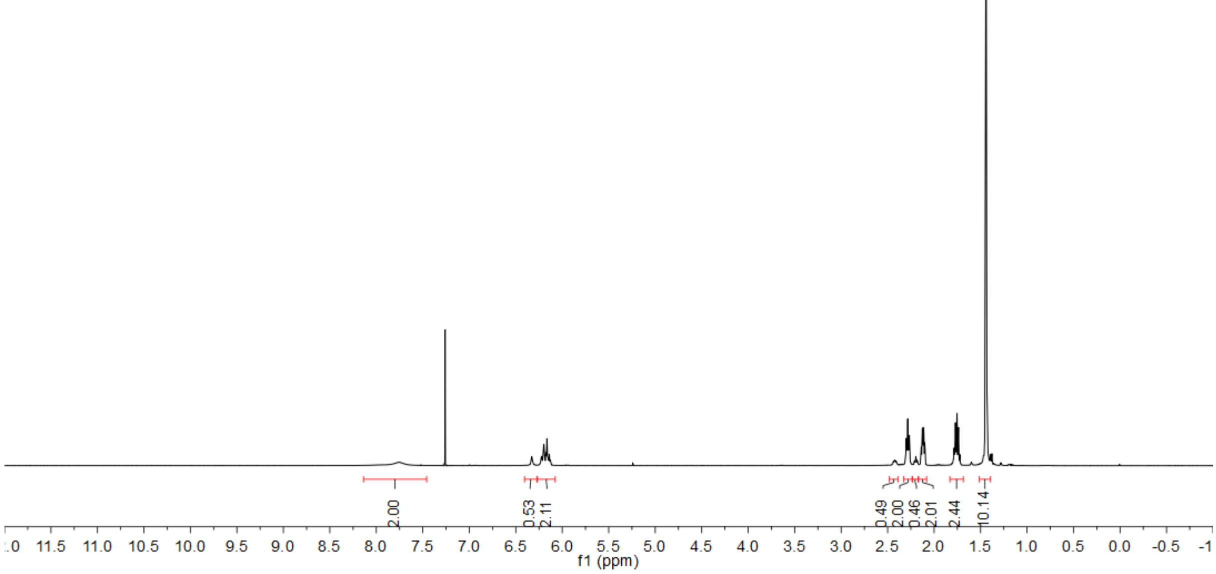


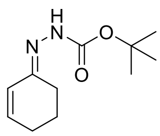
17b
$CDCl_3$, 100 MHz



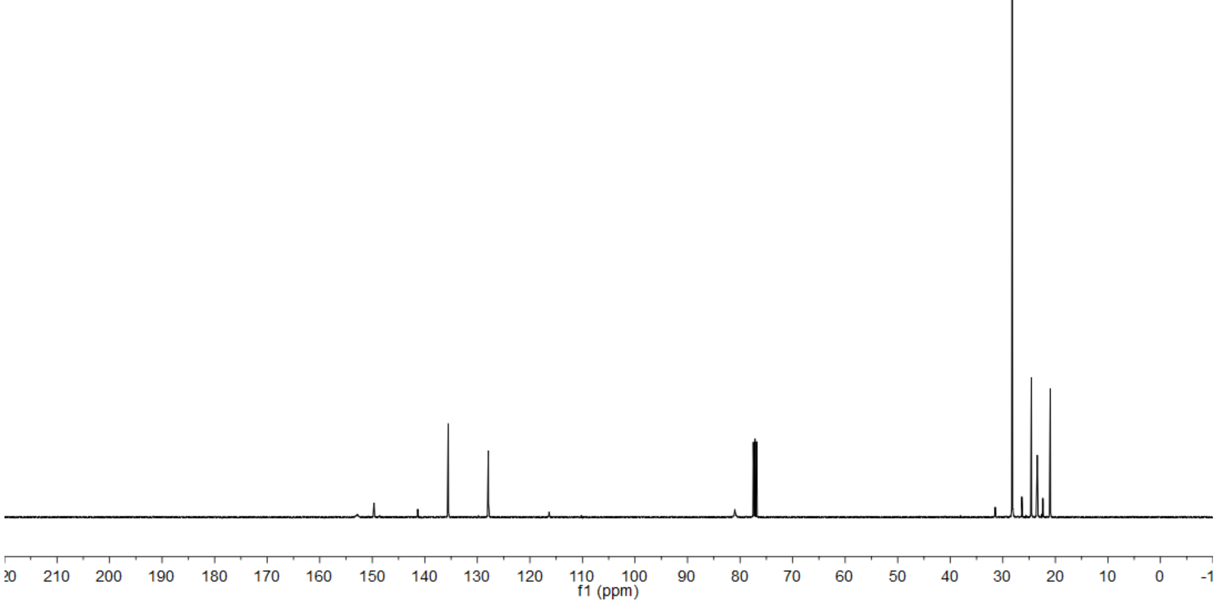


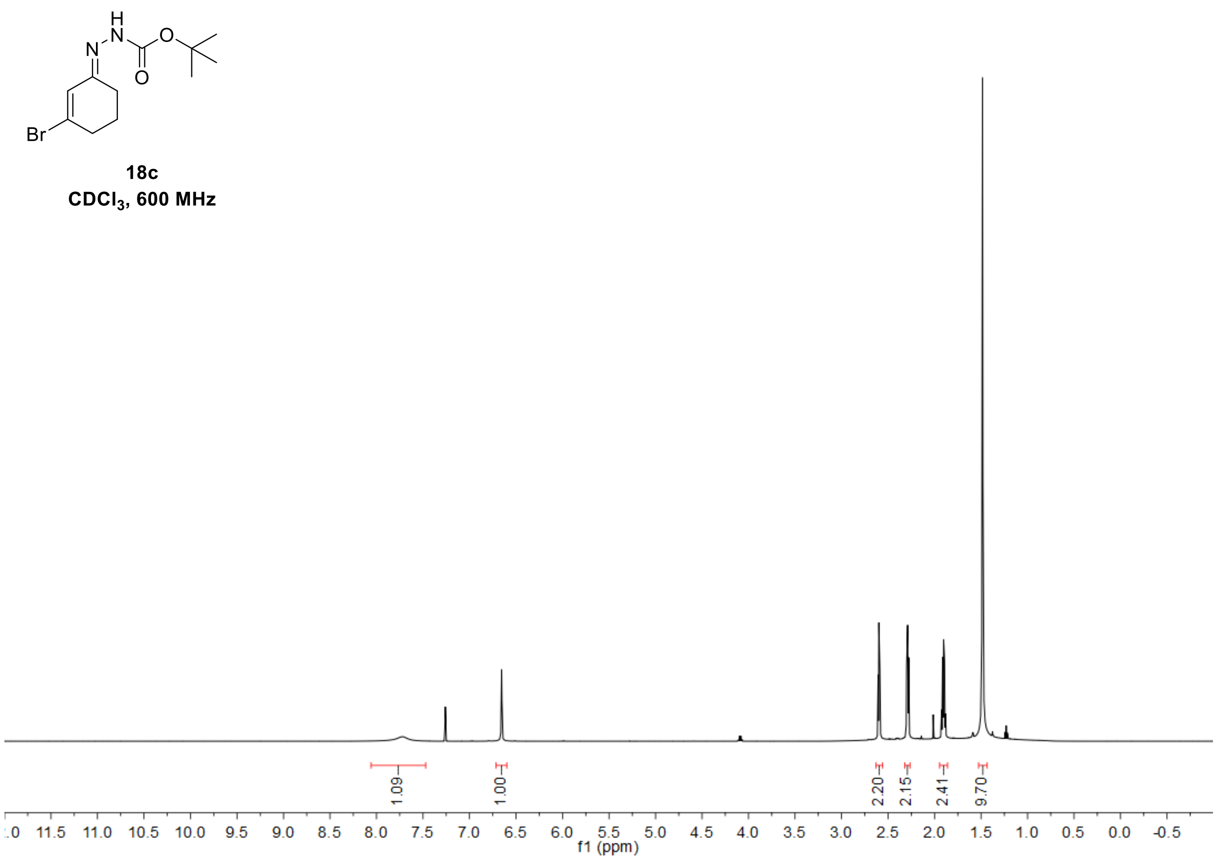
17c
$CDCl_3$, 400 MHz



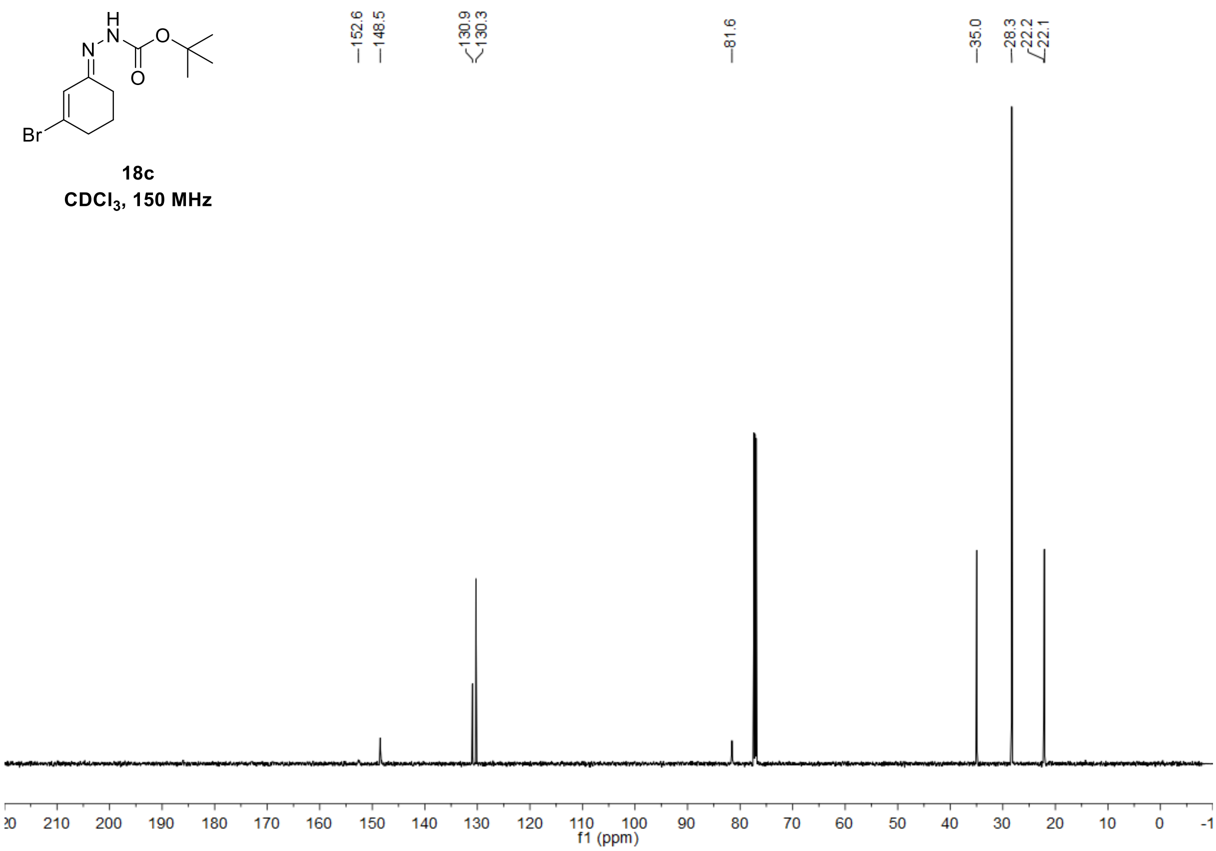


17c
$CDCl_3$, 100 MHz

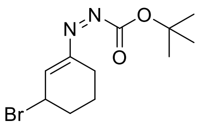




18c
CDCl3, 600 MHz
1.09
1.00
2.20
2.15
2.41
9.70
f1 (ppm)

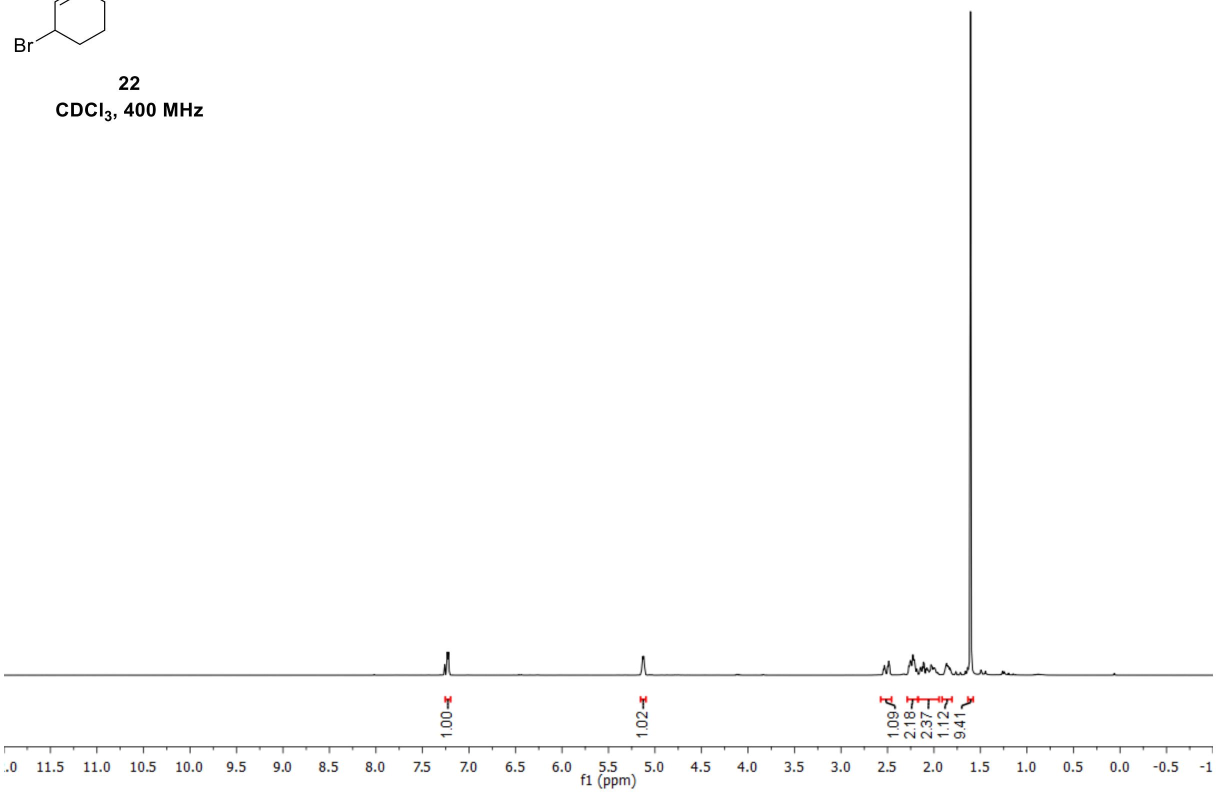


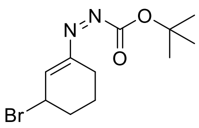
18c
CDCl3, 150 MHz
152.6
148.5
130.9
130.3
81.6
35.0
28.3
22.2
22.1
f1 (ppm)



22

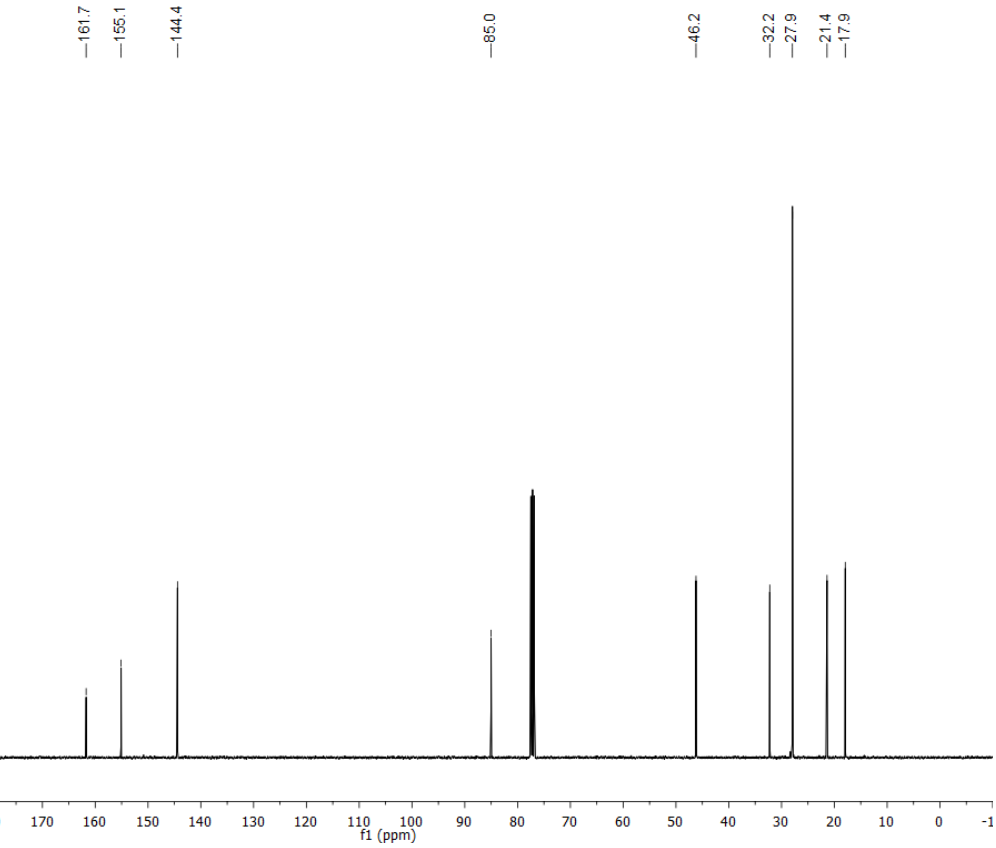
$CDCl_3$, 400 MHz

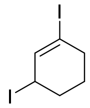




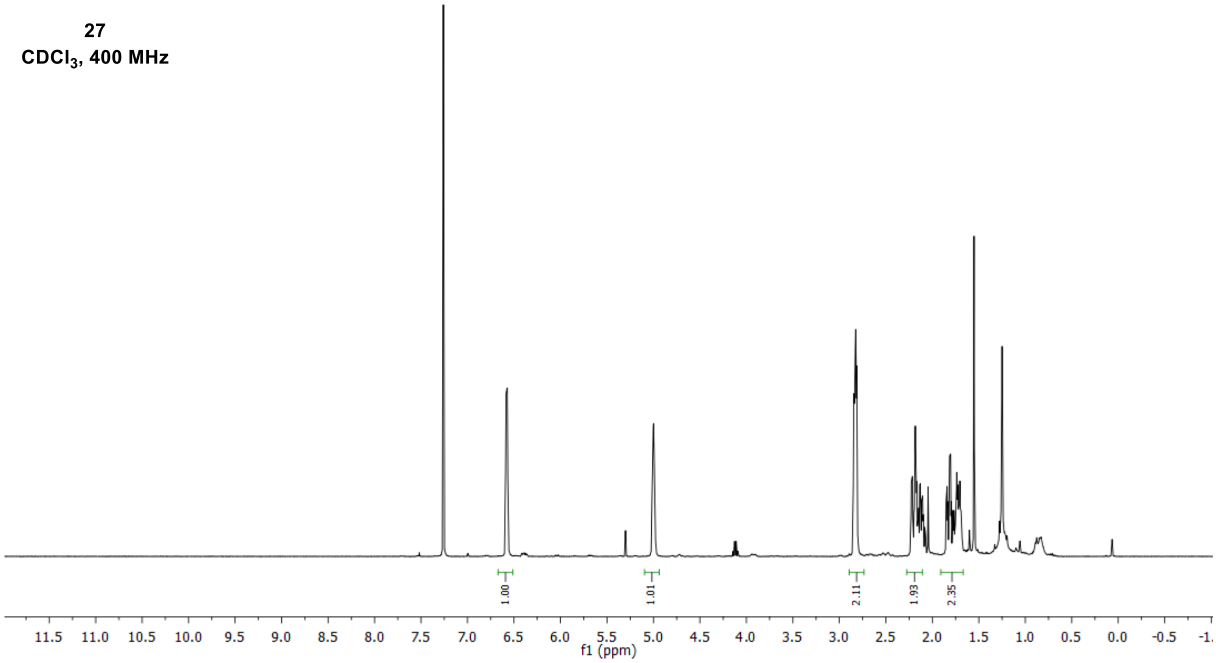
22

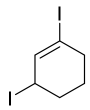
$CDCl_3$, 100 MHz



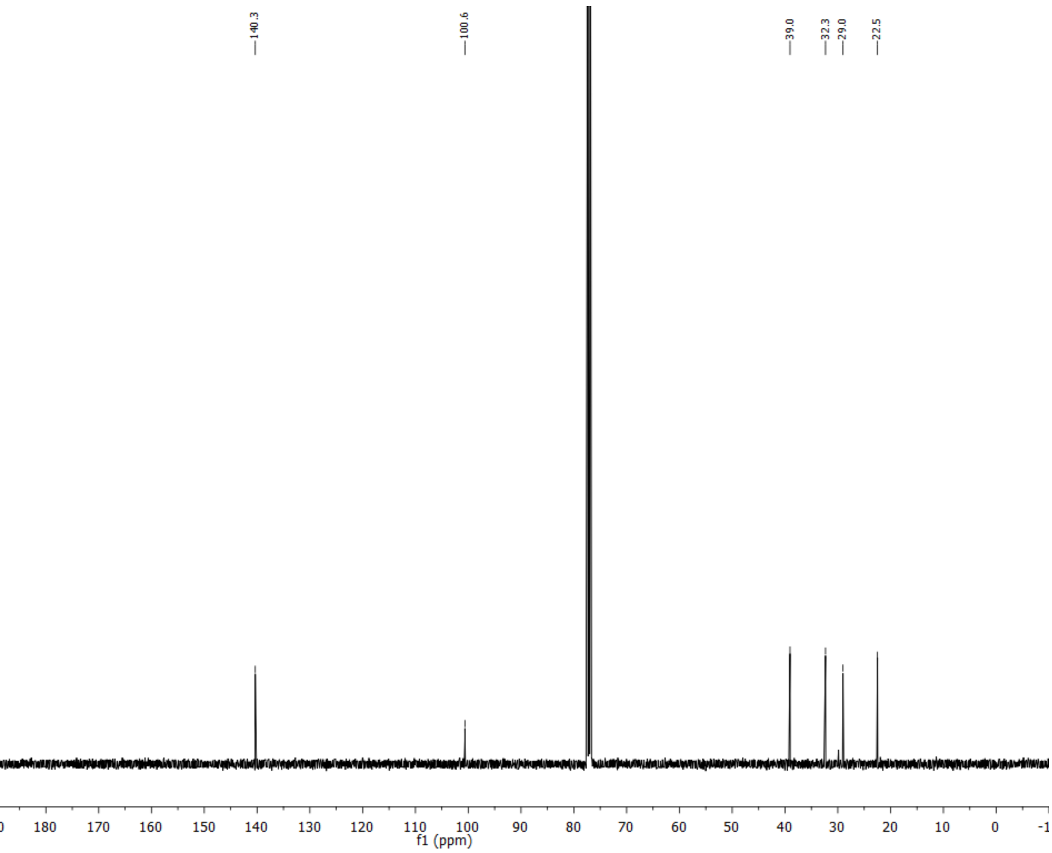


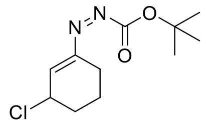
27
$CDCl_3$, 400 MHz



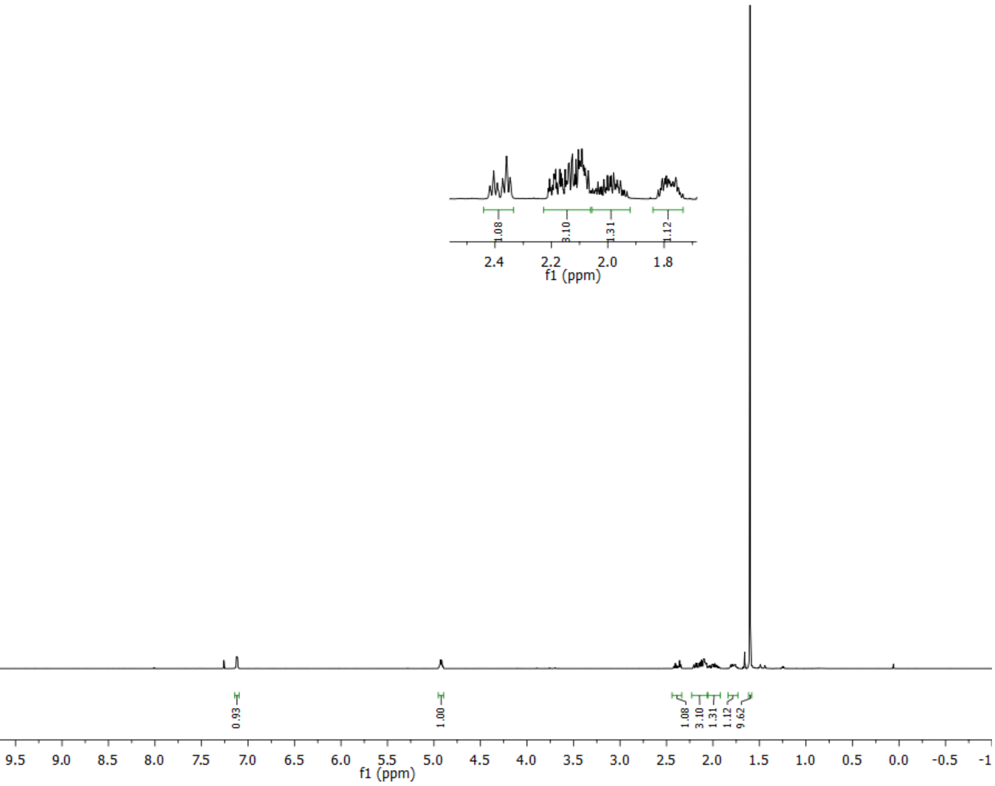


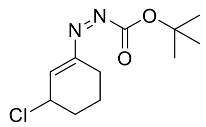
27
$CDCl_3$, 100 MHz



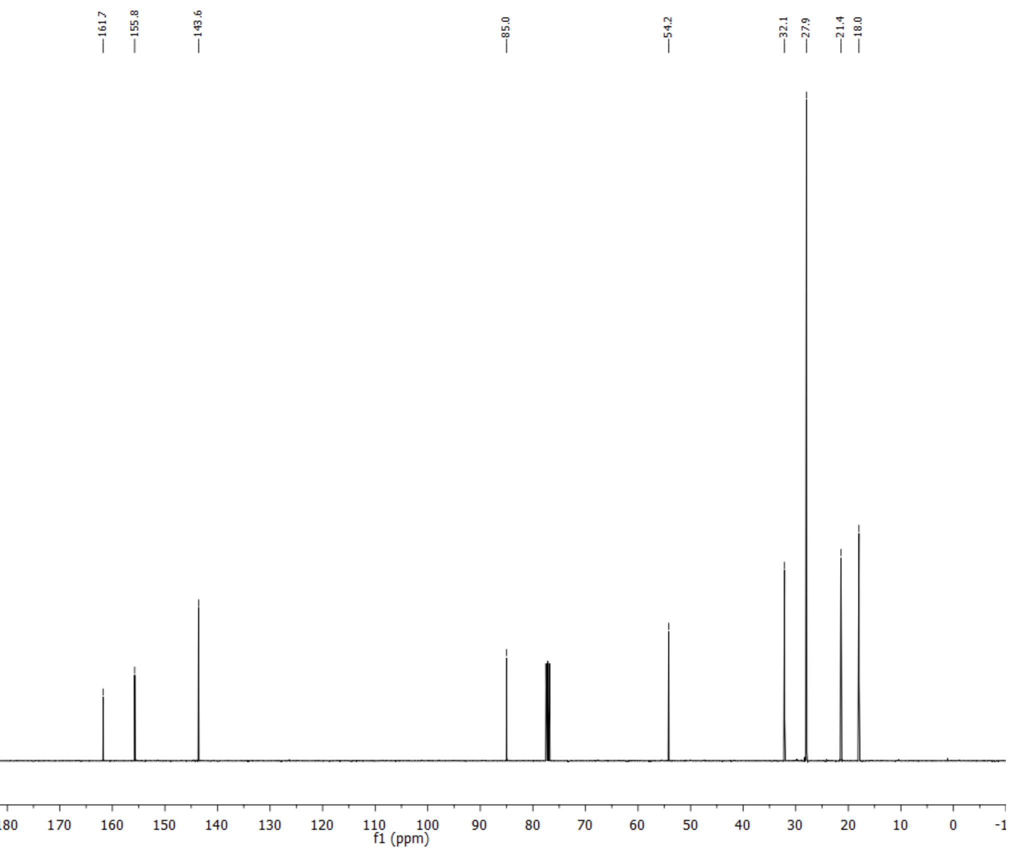


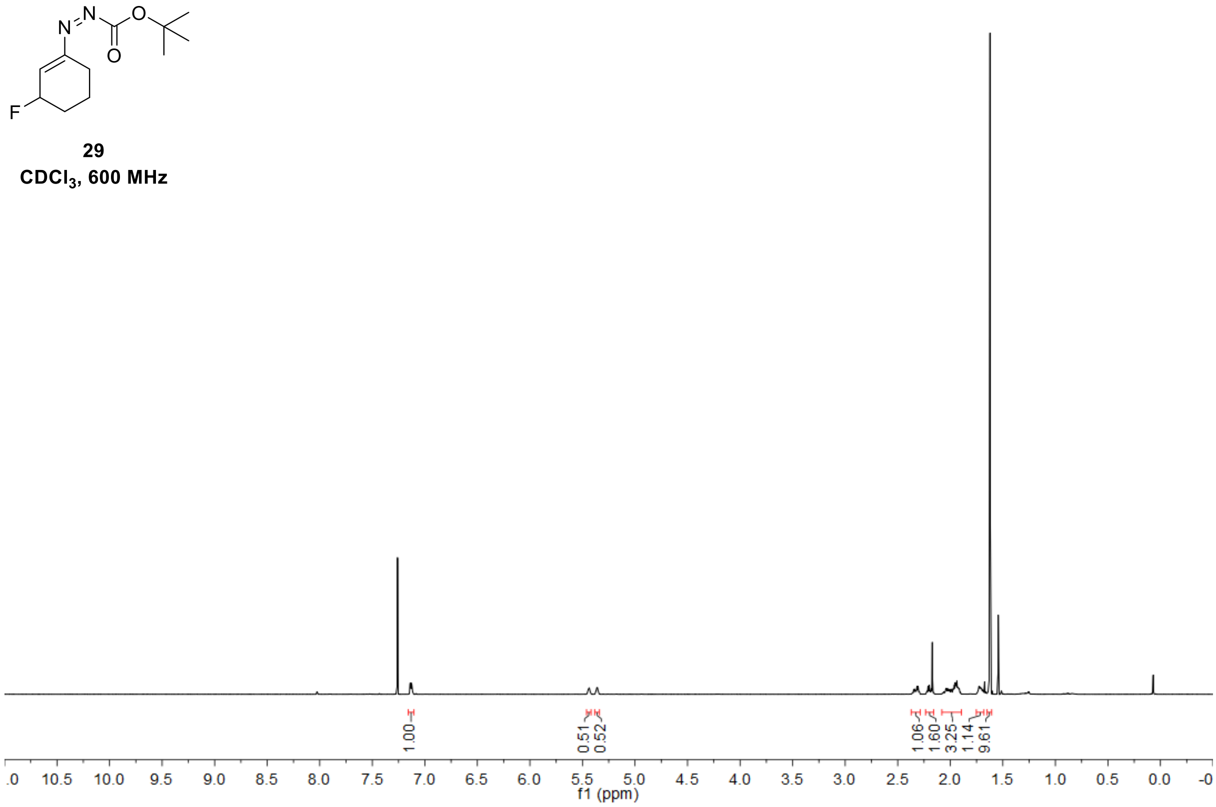
24
$CDCl_3$, 400 MHz



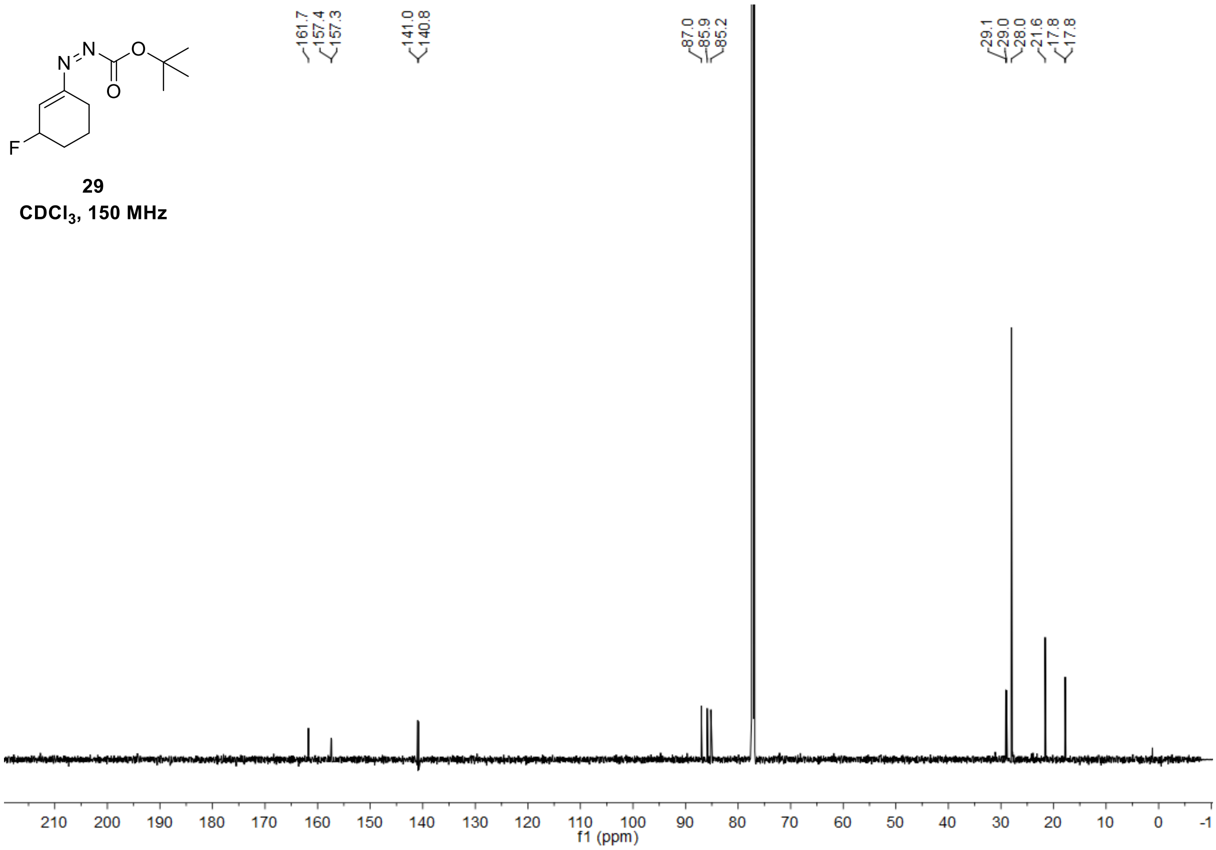


24
$CDCl_3$, 100 MHz

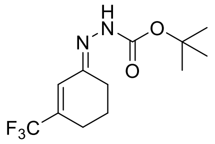




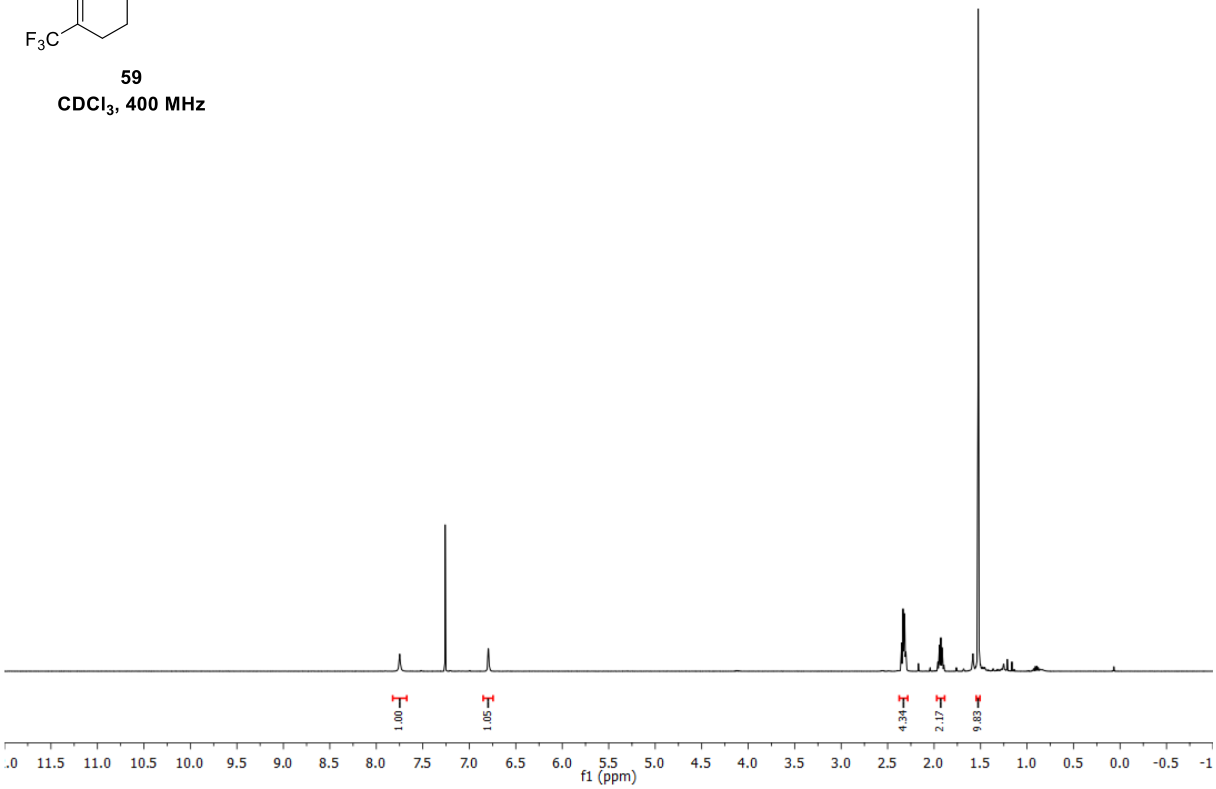
29
$CDCl_3$, 600 MHz

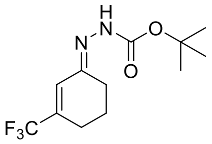


29
$CDCl_3$, 150 MHz

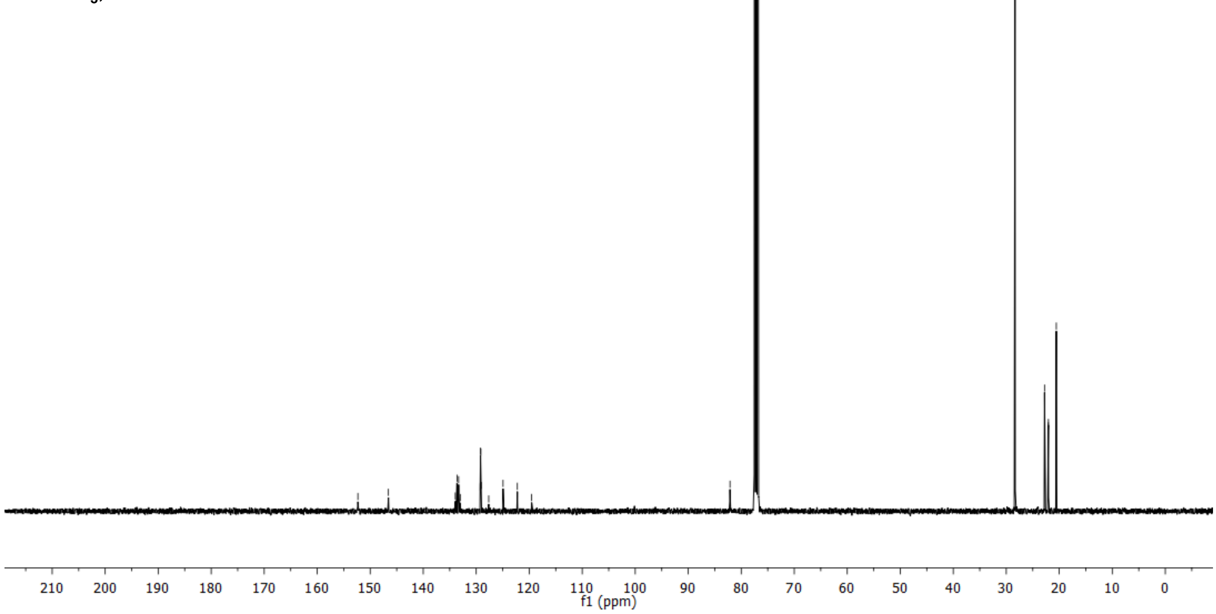


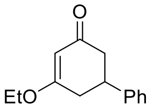
59
CDCl$_3$, 400 MHz



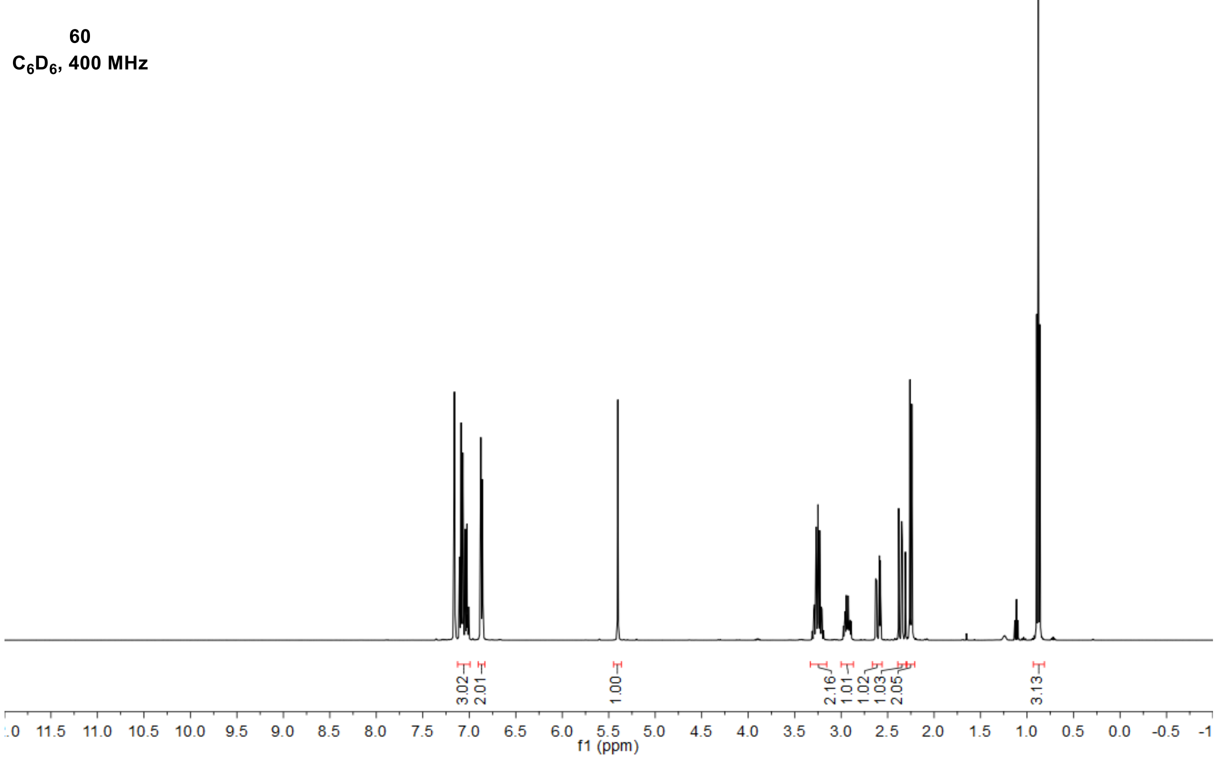


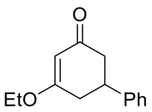
59
CDCl$_3$, 100 MHz



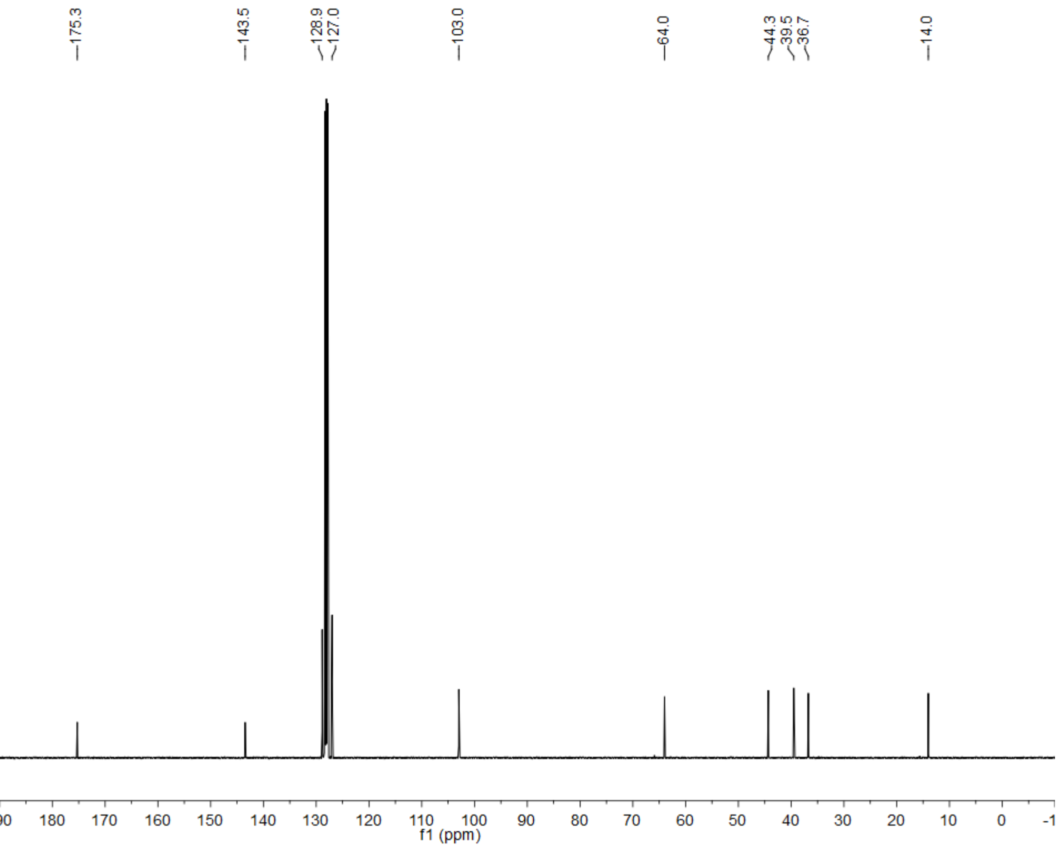


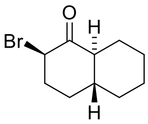
60
C_6D_6, 400 MHz



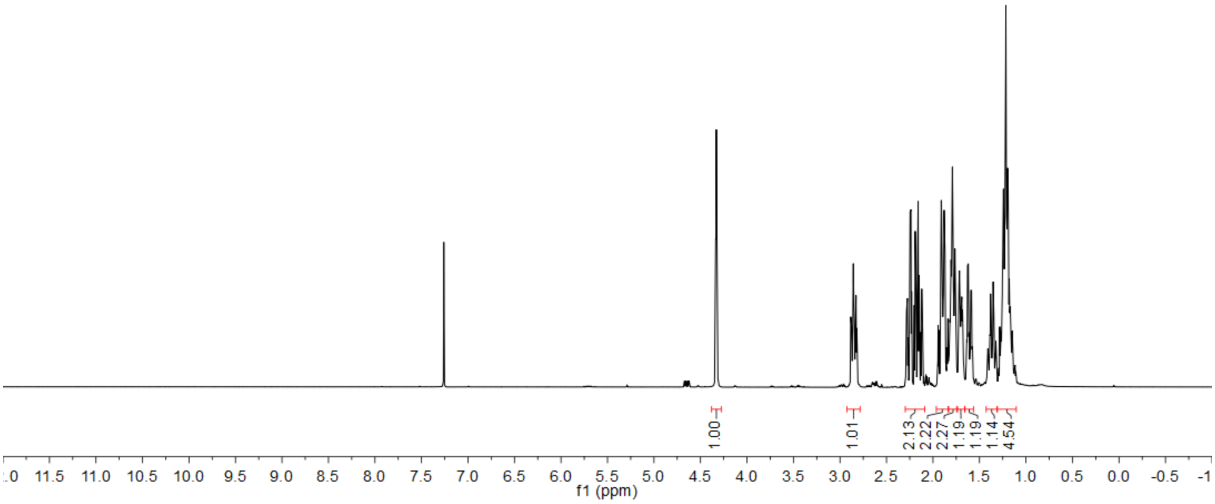


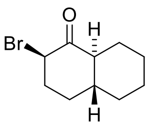
60
C_6D_6, 100 MHz



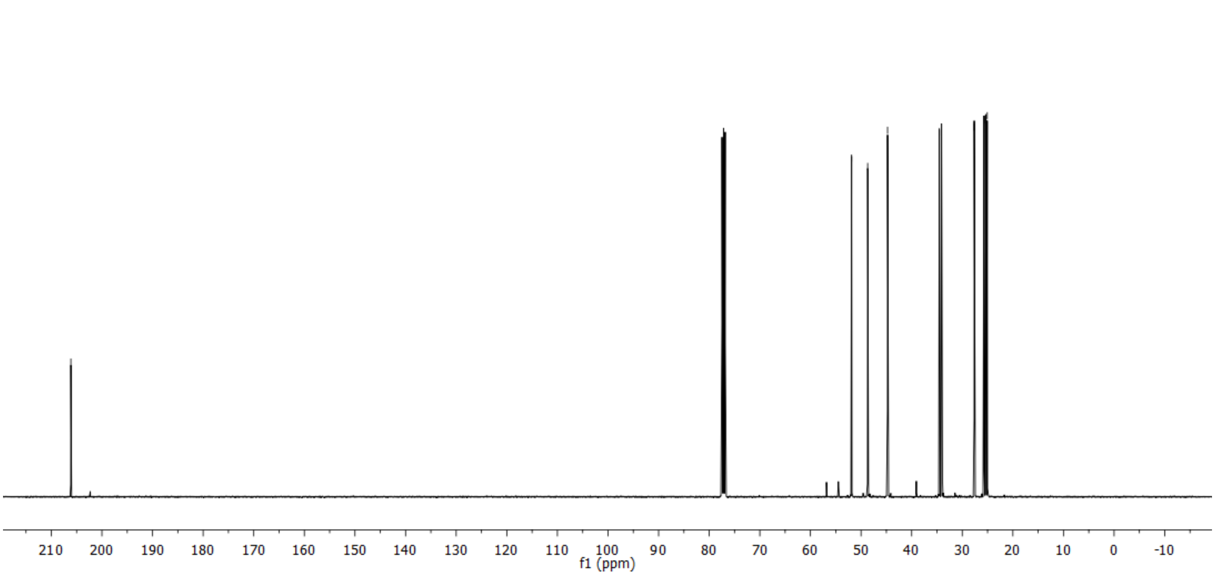


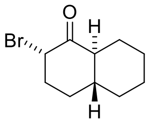
62
$CDCl_3$, 400 MHz



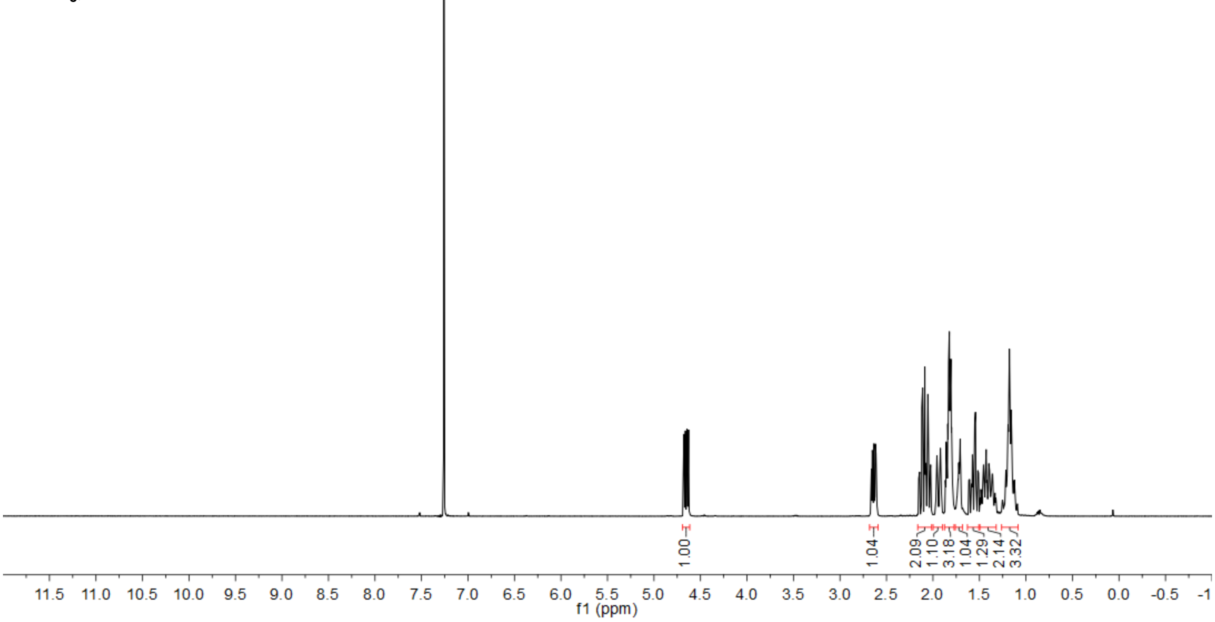


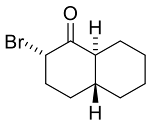
62
$CDCl_3$, 100 MHz



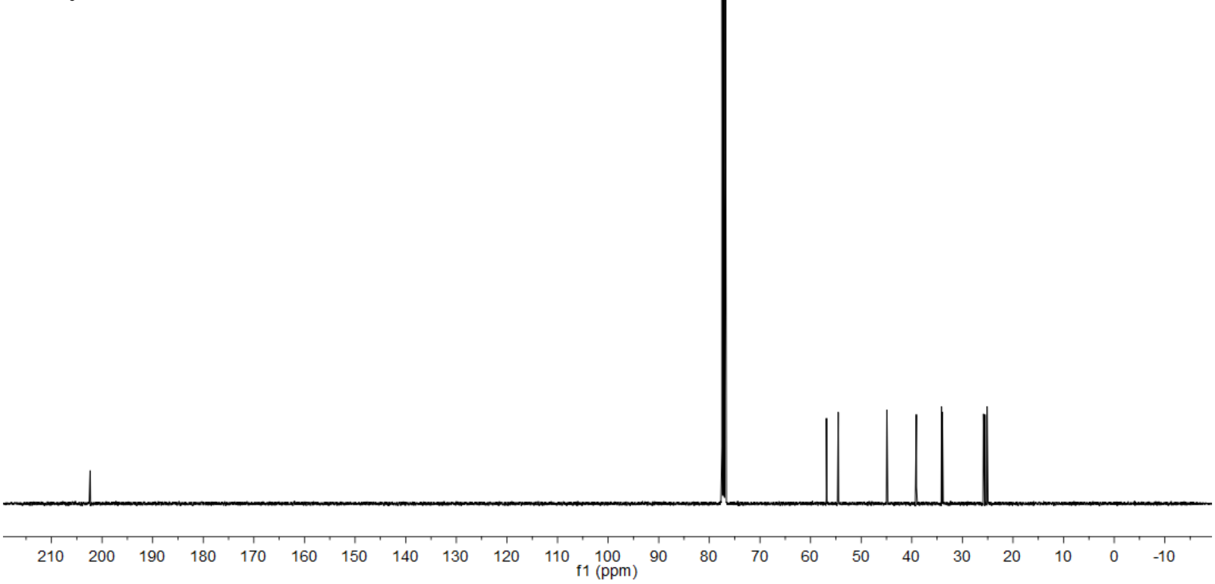


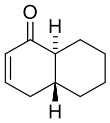
62
$CDCl_3$, 400 MHz



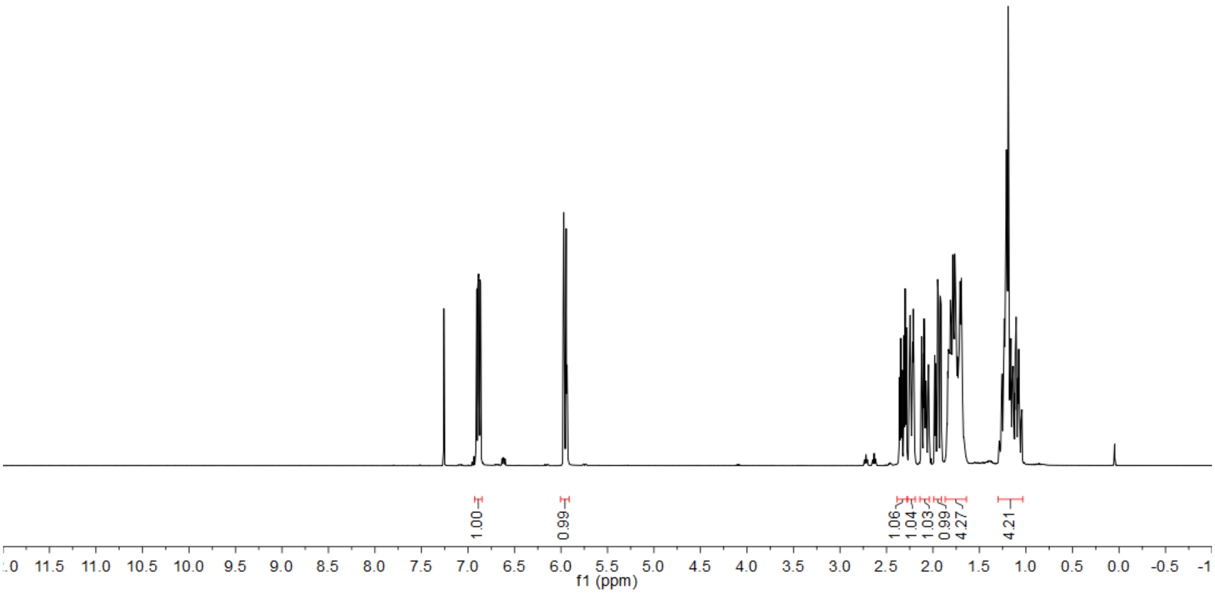


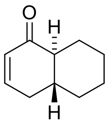
62
$CDCl_3$, 100 MHz



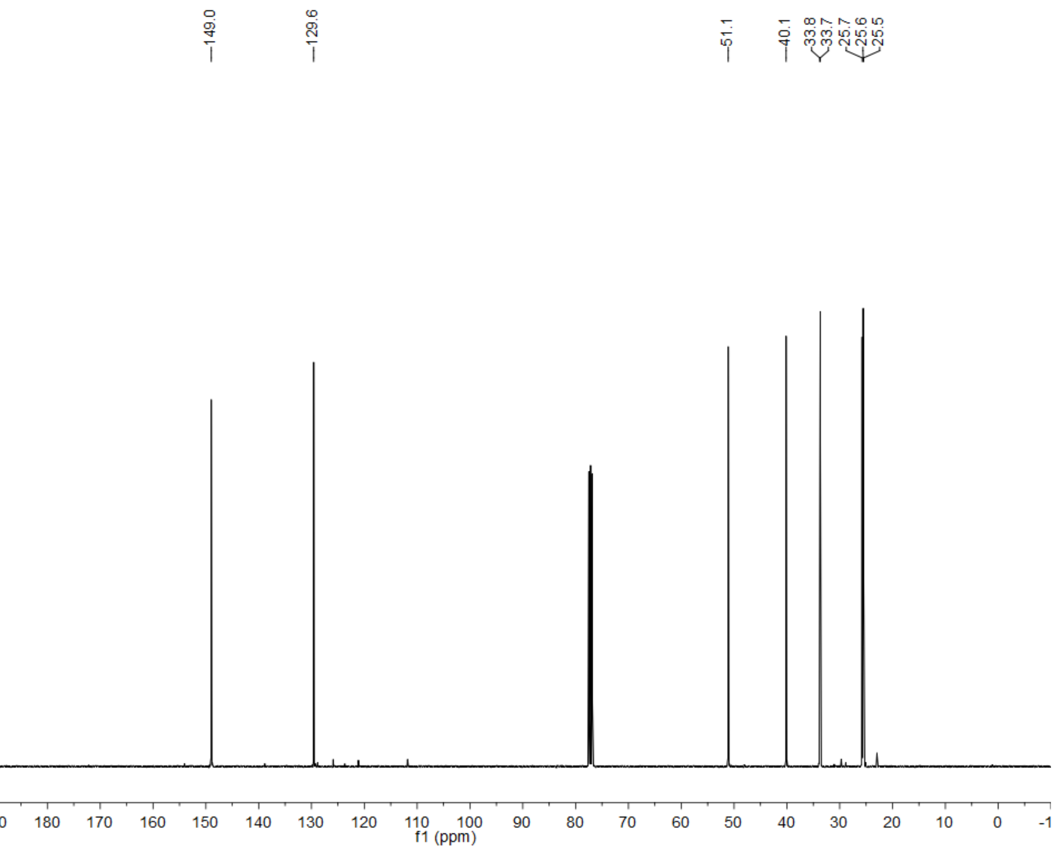


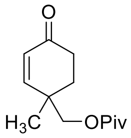
63
$CDCl_3$, 400 MHz





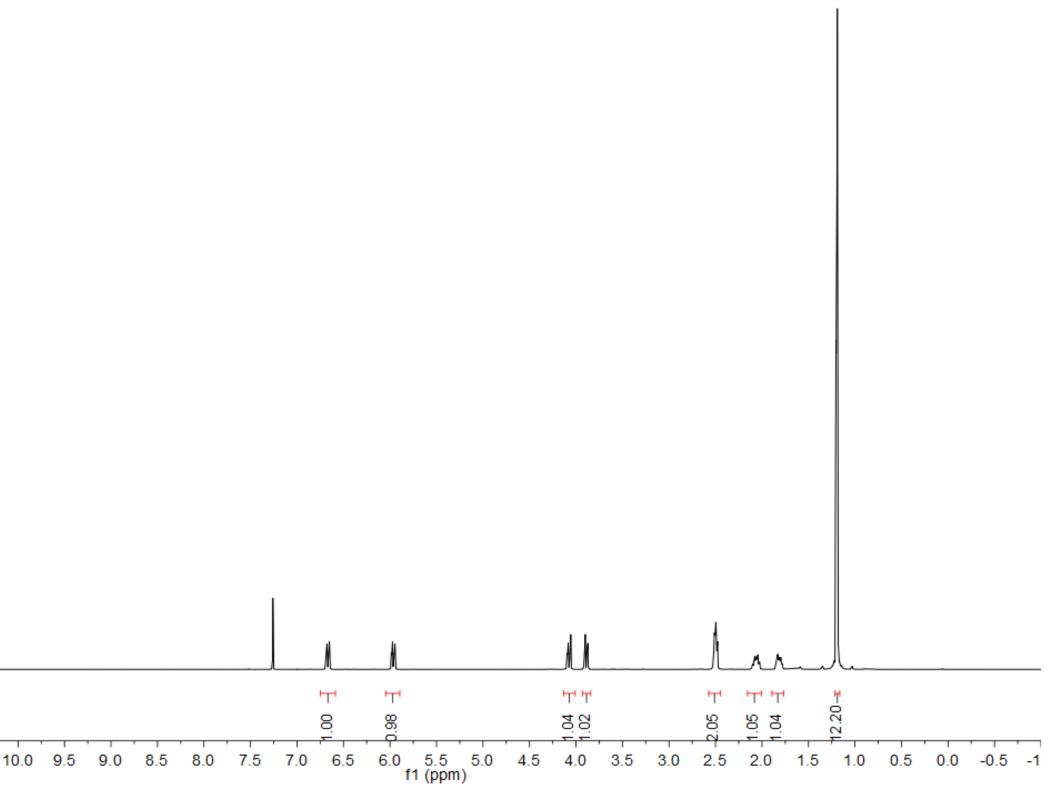
63
$CDCl_3$, 100 MHz

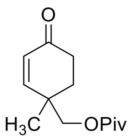




66

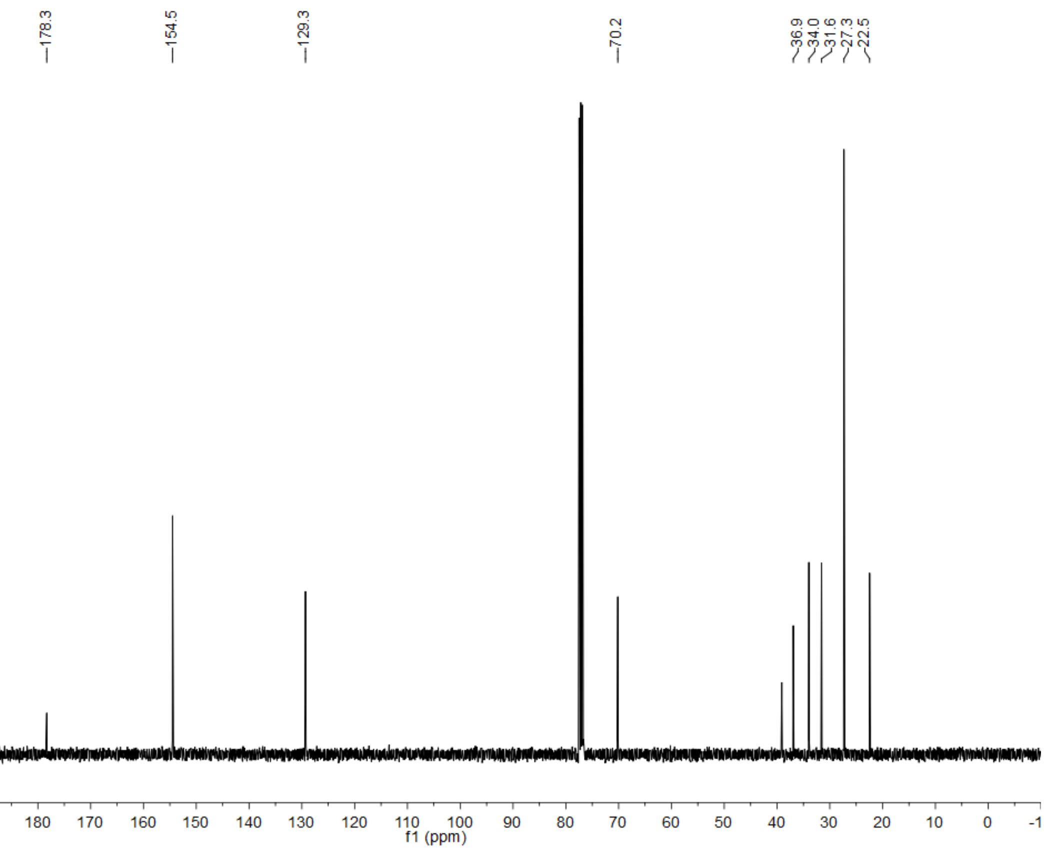
$CDCl_3$, 400 MHz

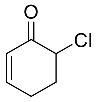




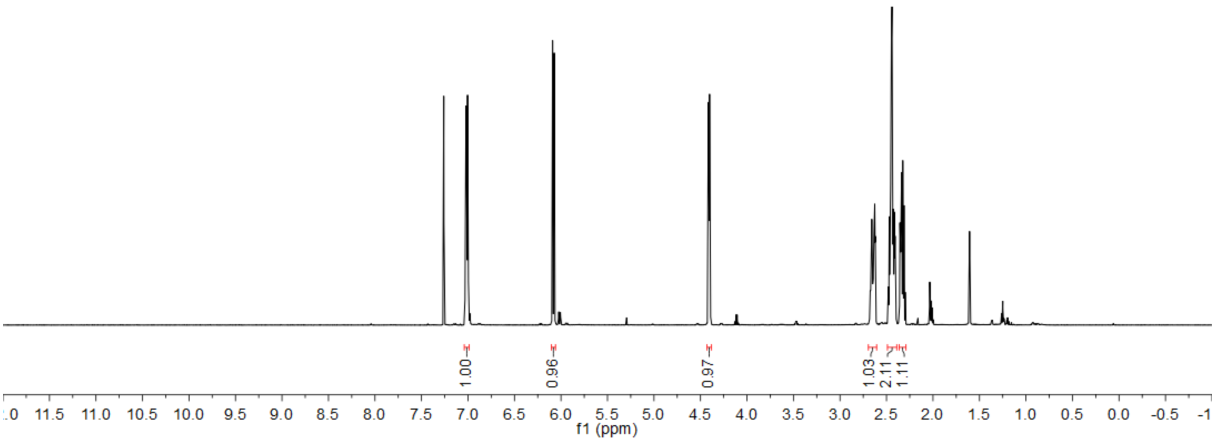
66

$CDCl_3$, 100 MHz

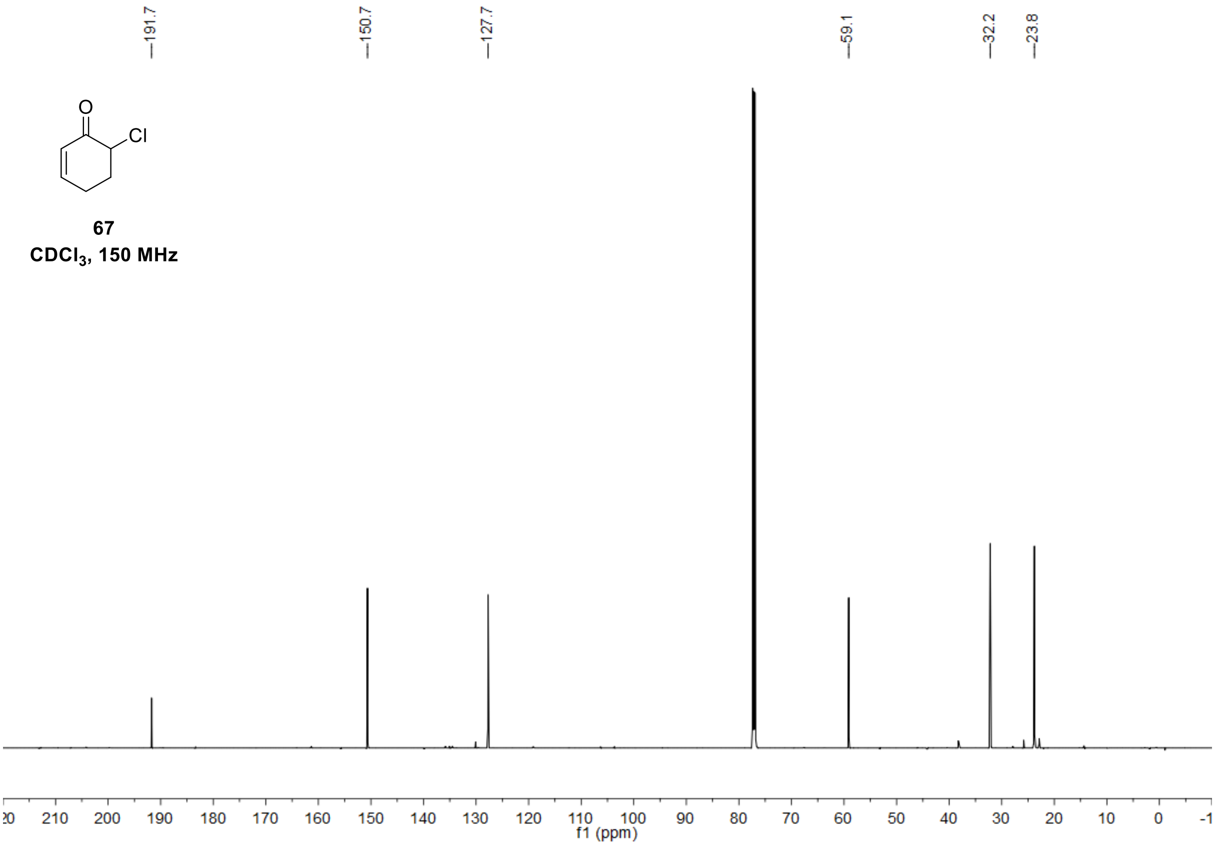


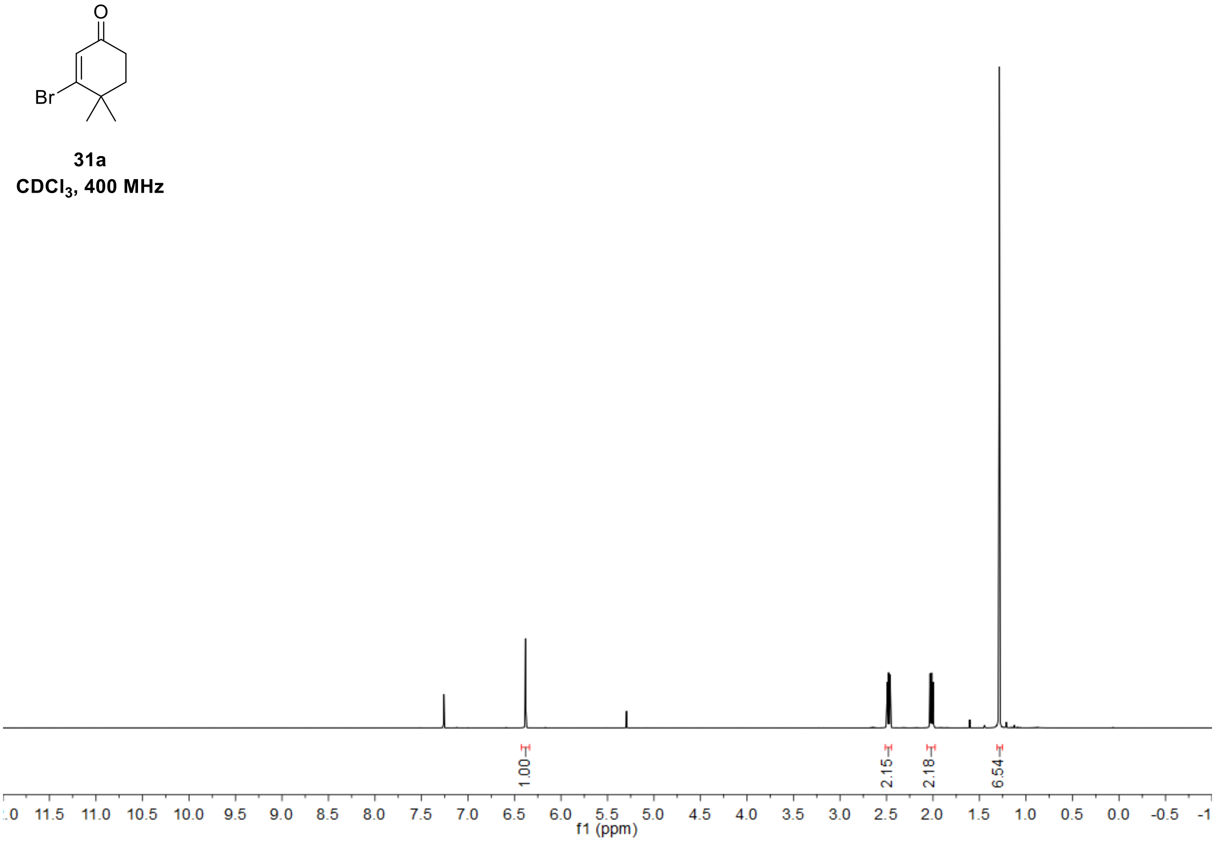


67
CDCl$_3$, 600 MHz

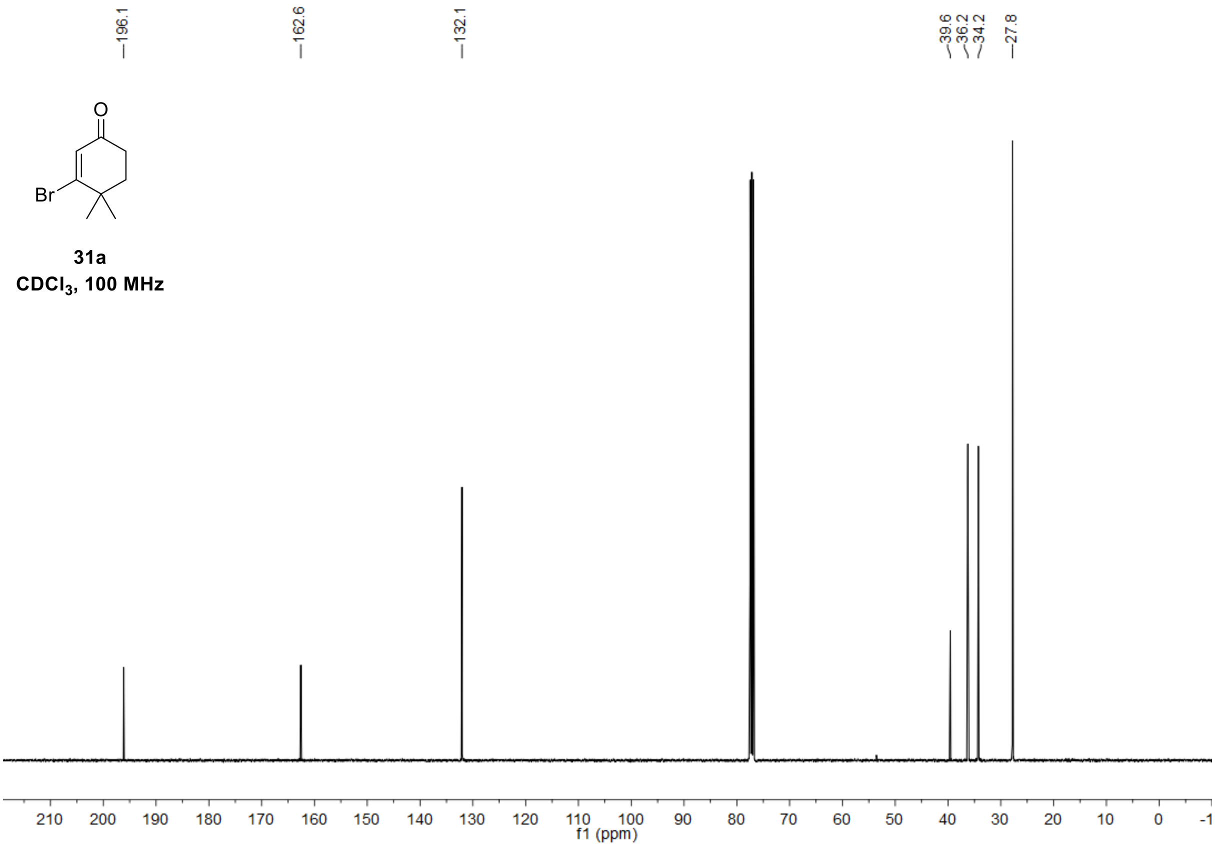


67
CDCl$_3$, 150 MHz

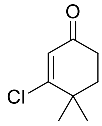




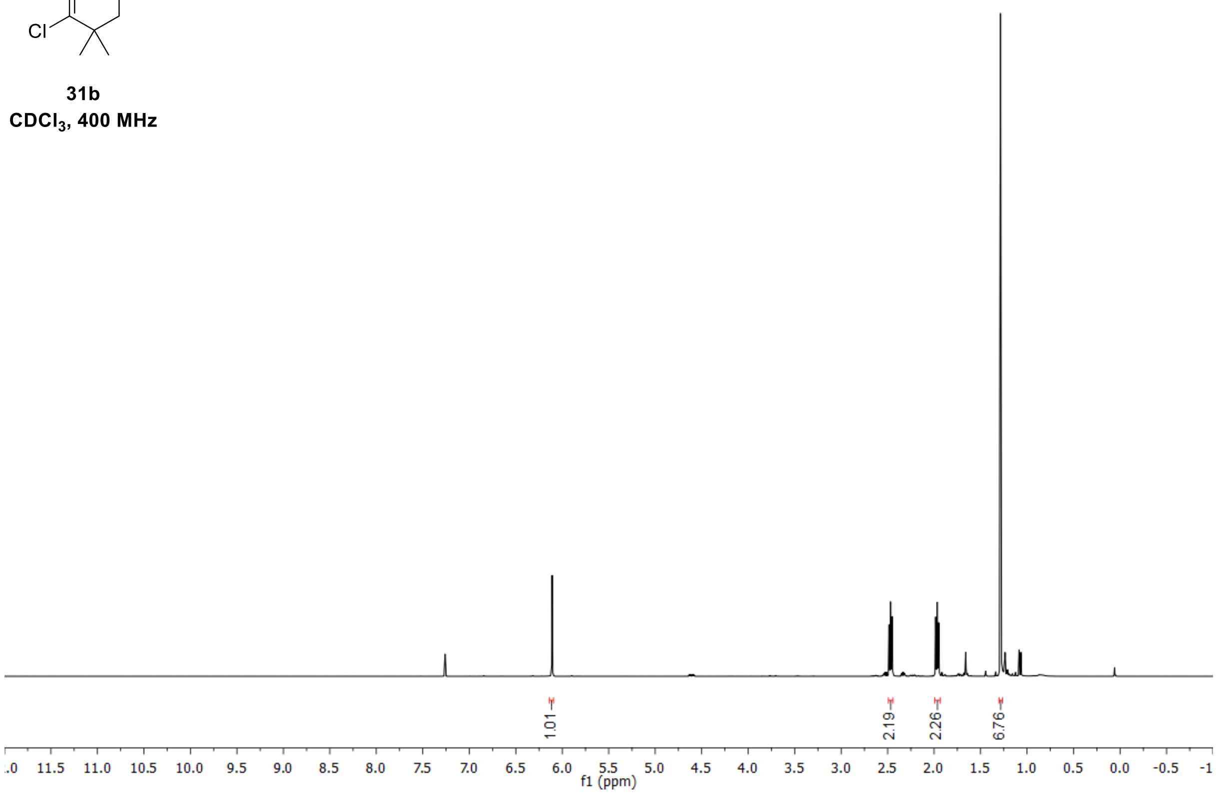
31a
$CDCl_3$, 400 MHz

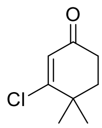


31a
$CDCl_3$, 100 MHz

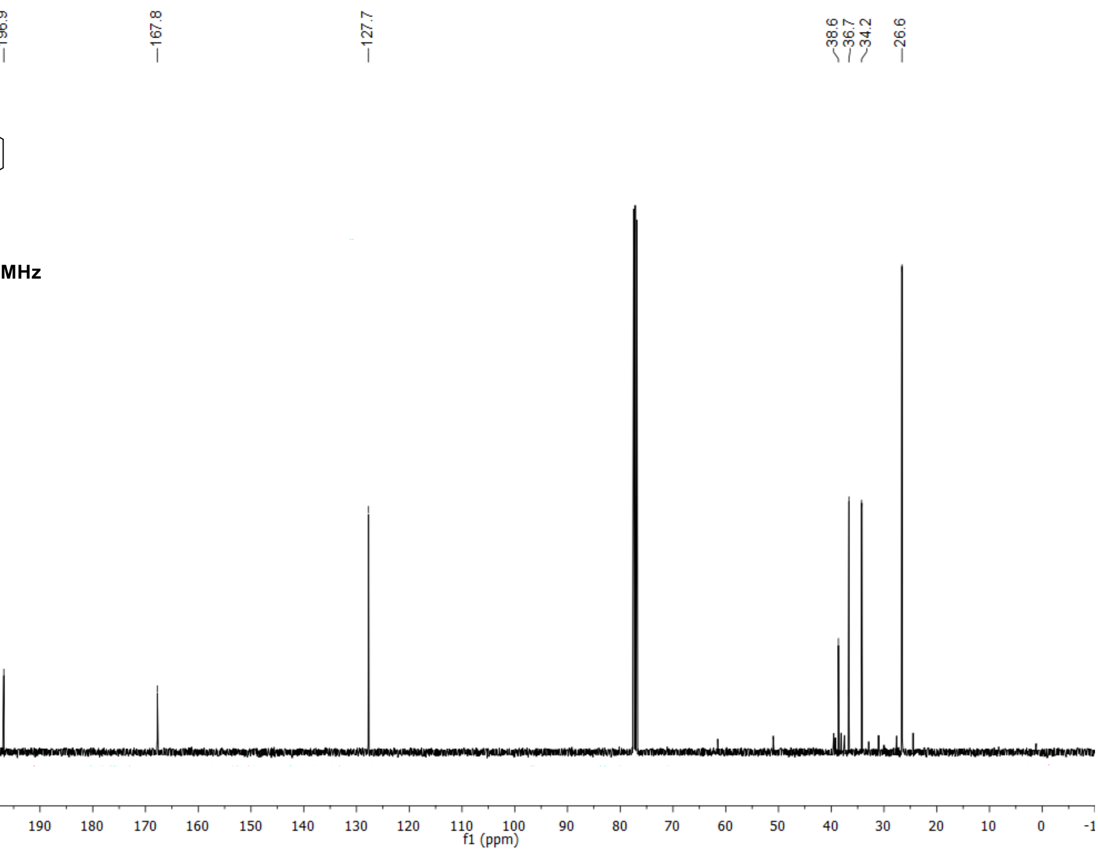


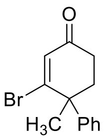
31b
$CDCl_3$, 400 MHz



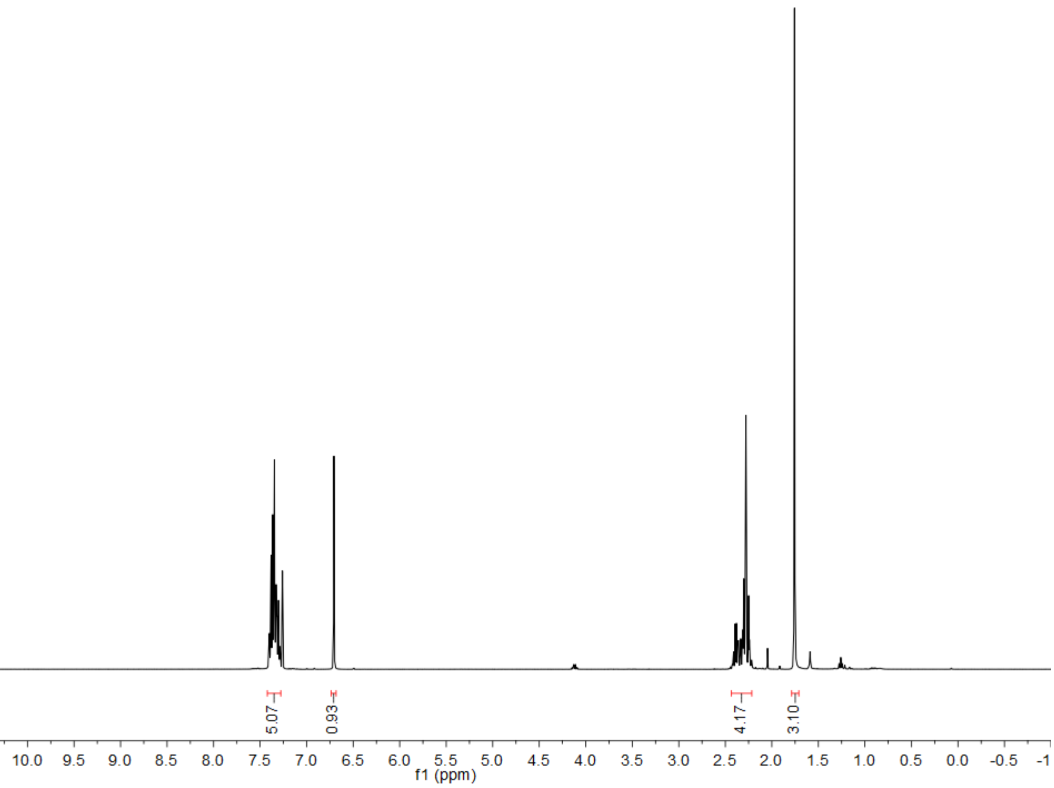


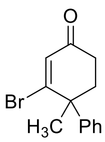
31b
$CDCl_3$, 100 MHz



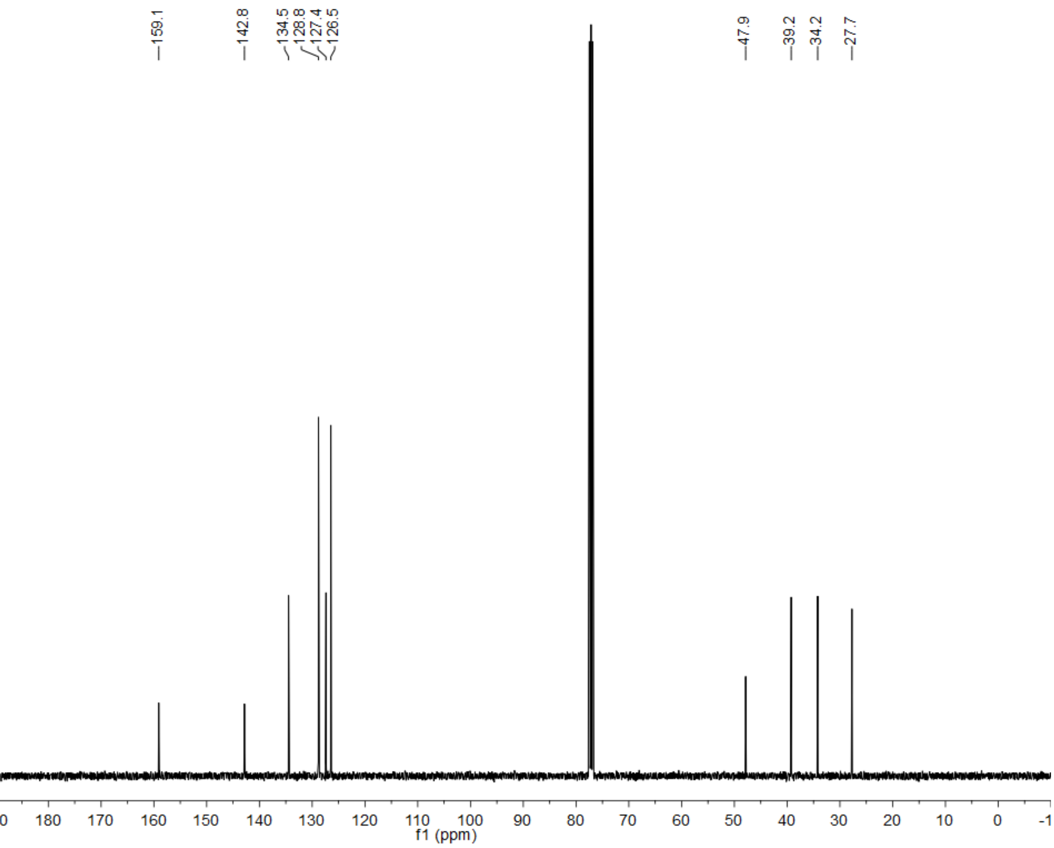


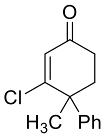
32a
$CDCl_3$, 400 MHz



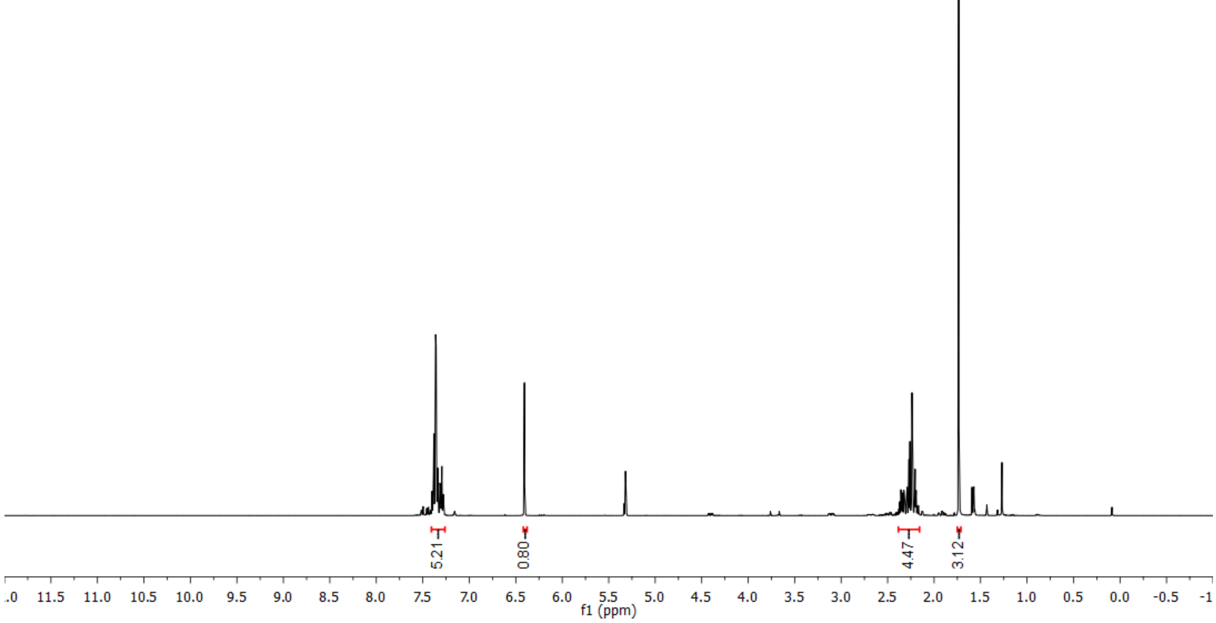


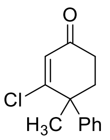
32a
$CDCl_3$, 100 MHz



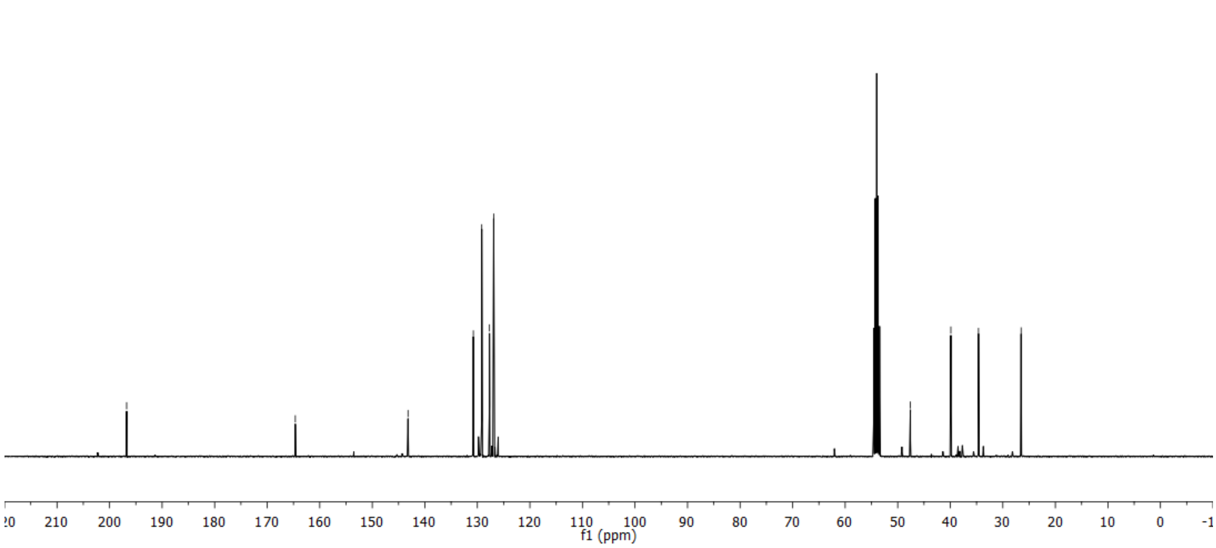


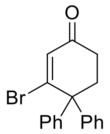
32b
CD_2Cl_2, 400 MHz



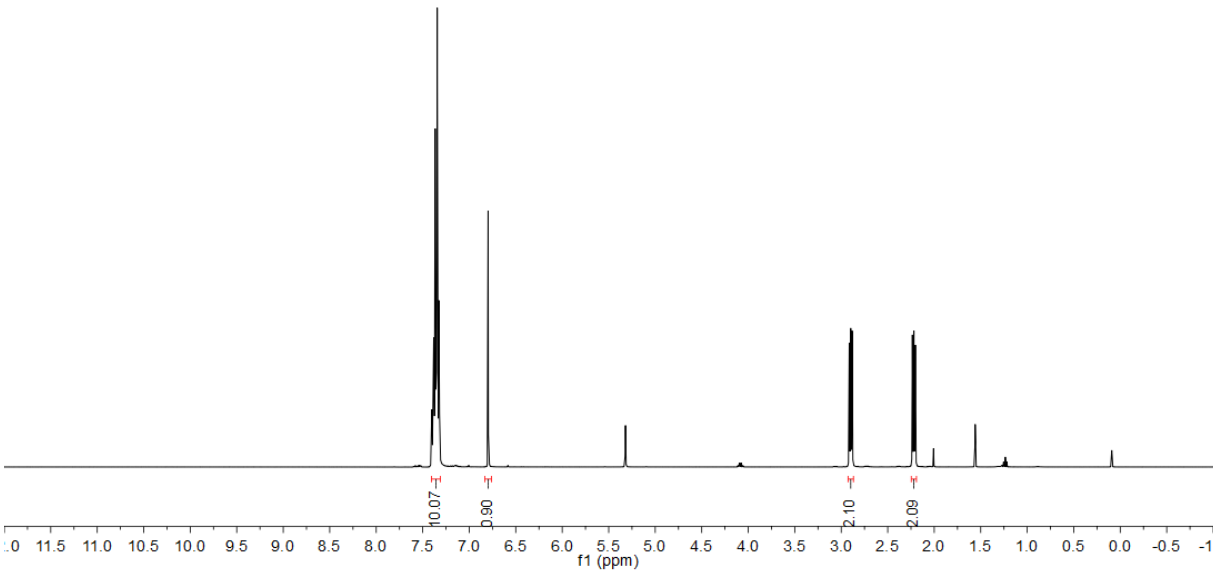


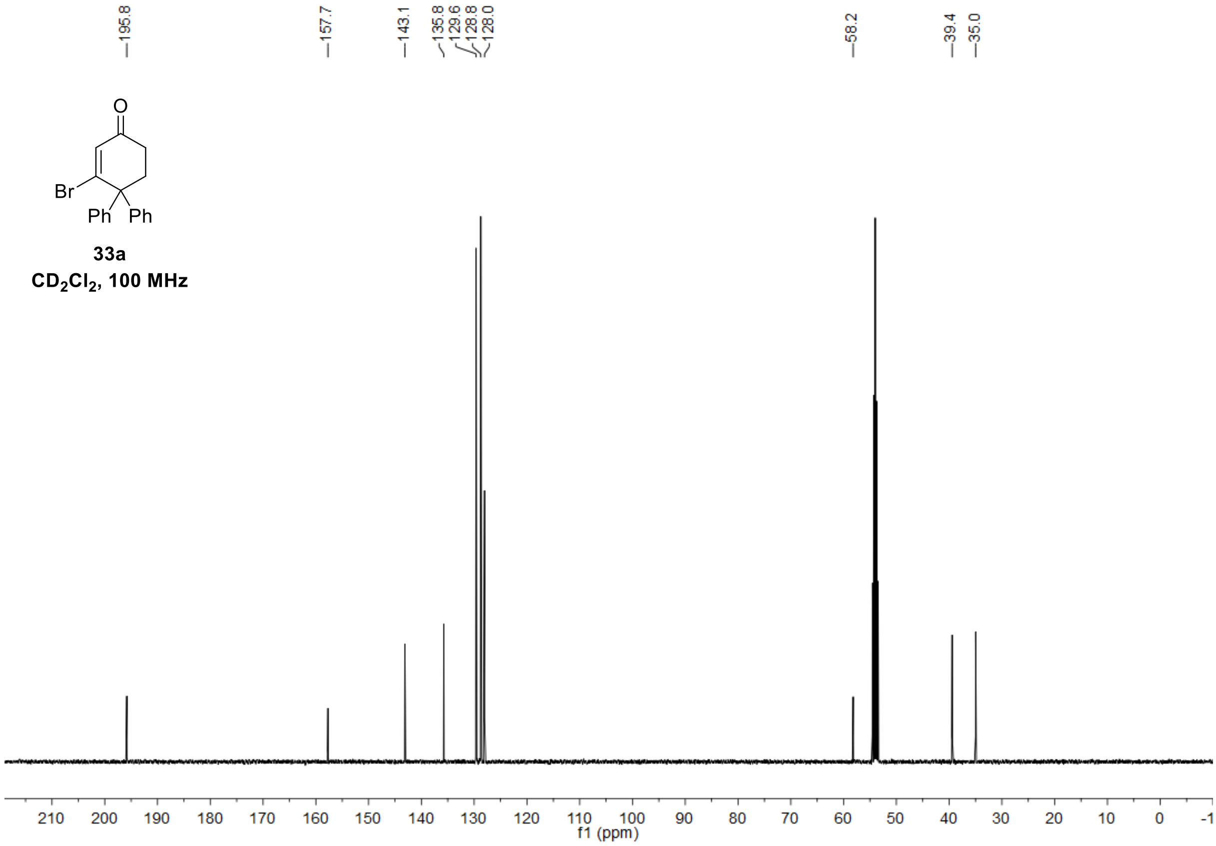
32b
CD_2Cl_2, 100 MHz



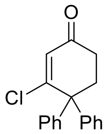


33a
CD_2Cl_2, 400 MHz

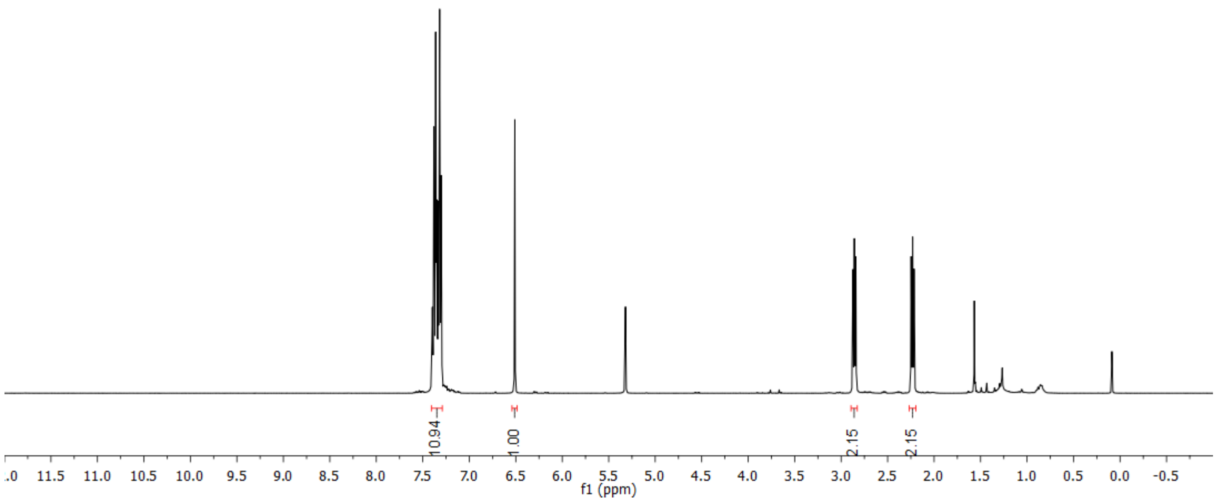


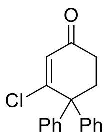


33a
CD_2Cl_2, 100 MHz

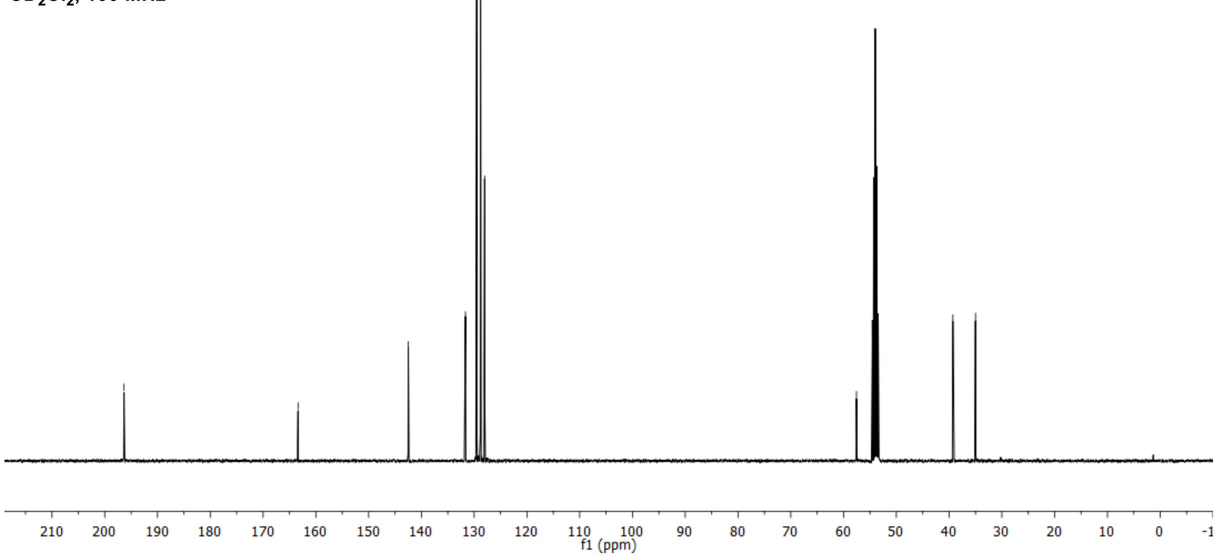


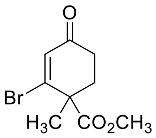
33b
CD_2Cl_2, 400 MHz



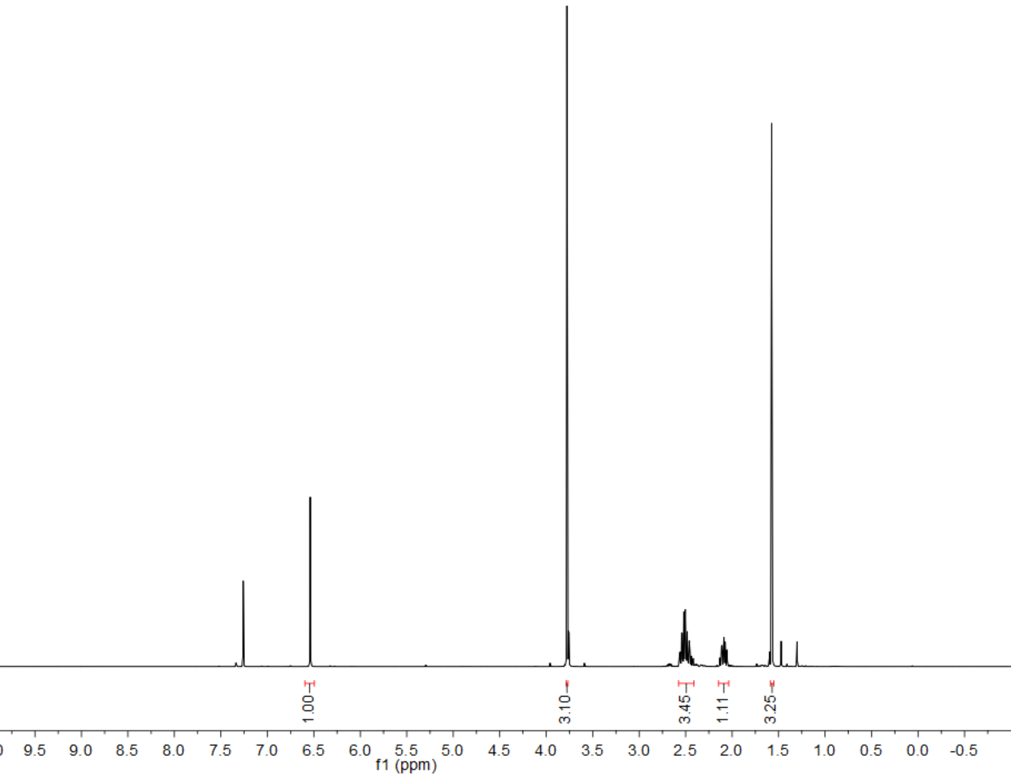


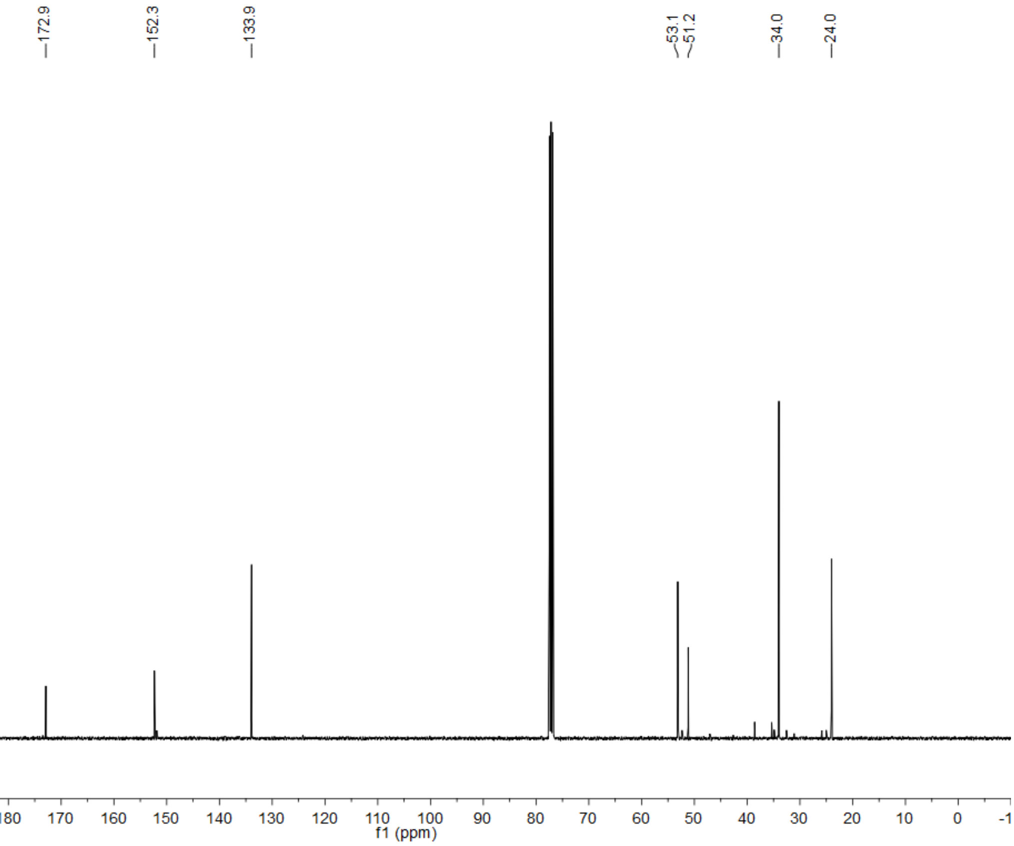
33b
CD_2Cl_2, 100 MHz

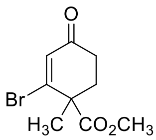




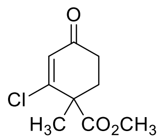
34a
$CDCl_3$, 400 MHz



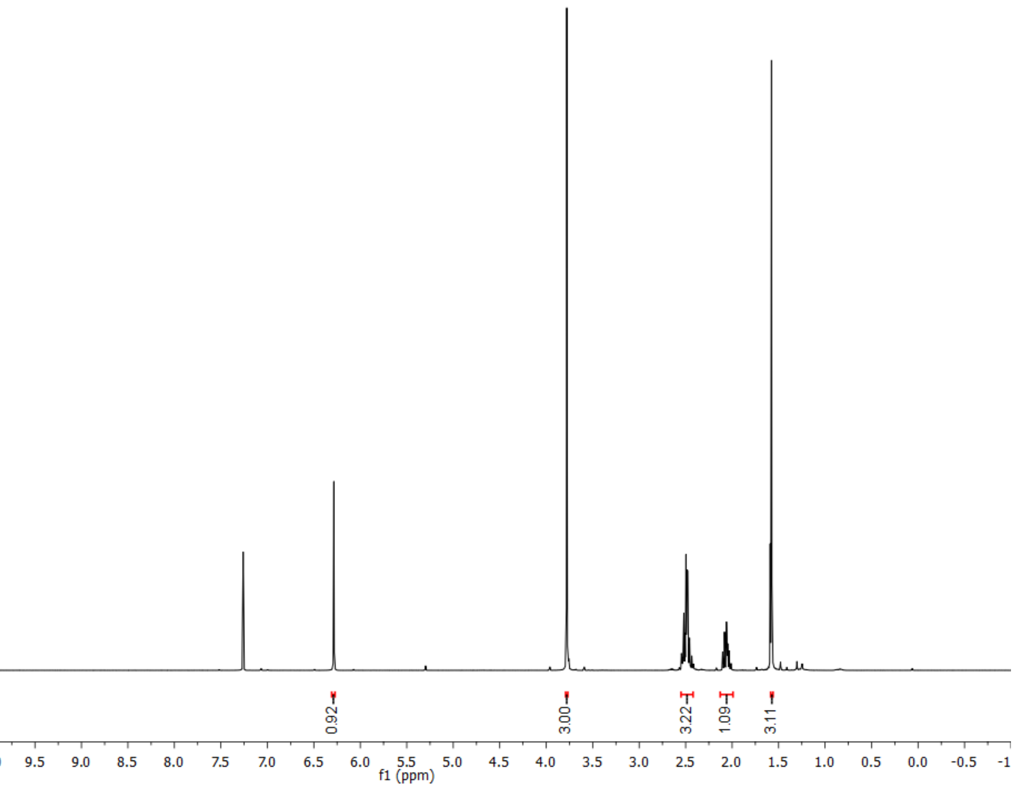


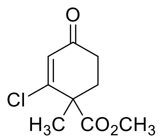


34a
$CDCl_3$, 100 MHz

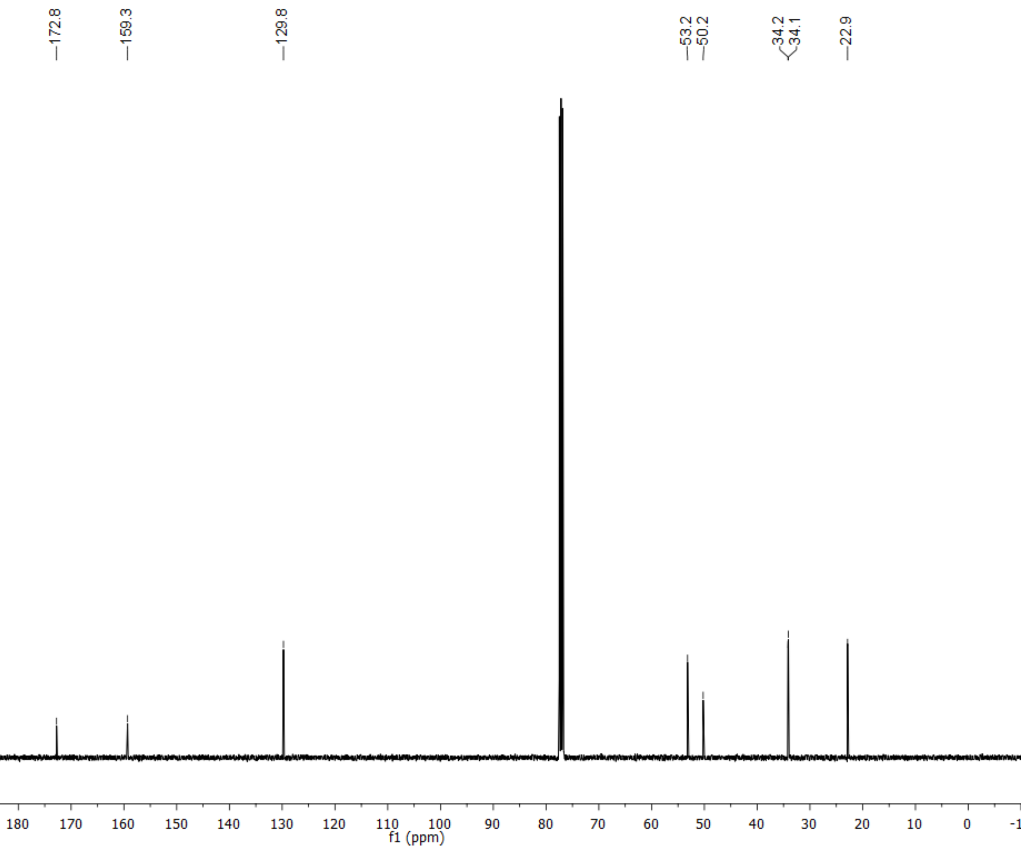


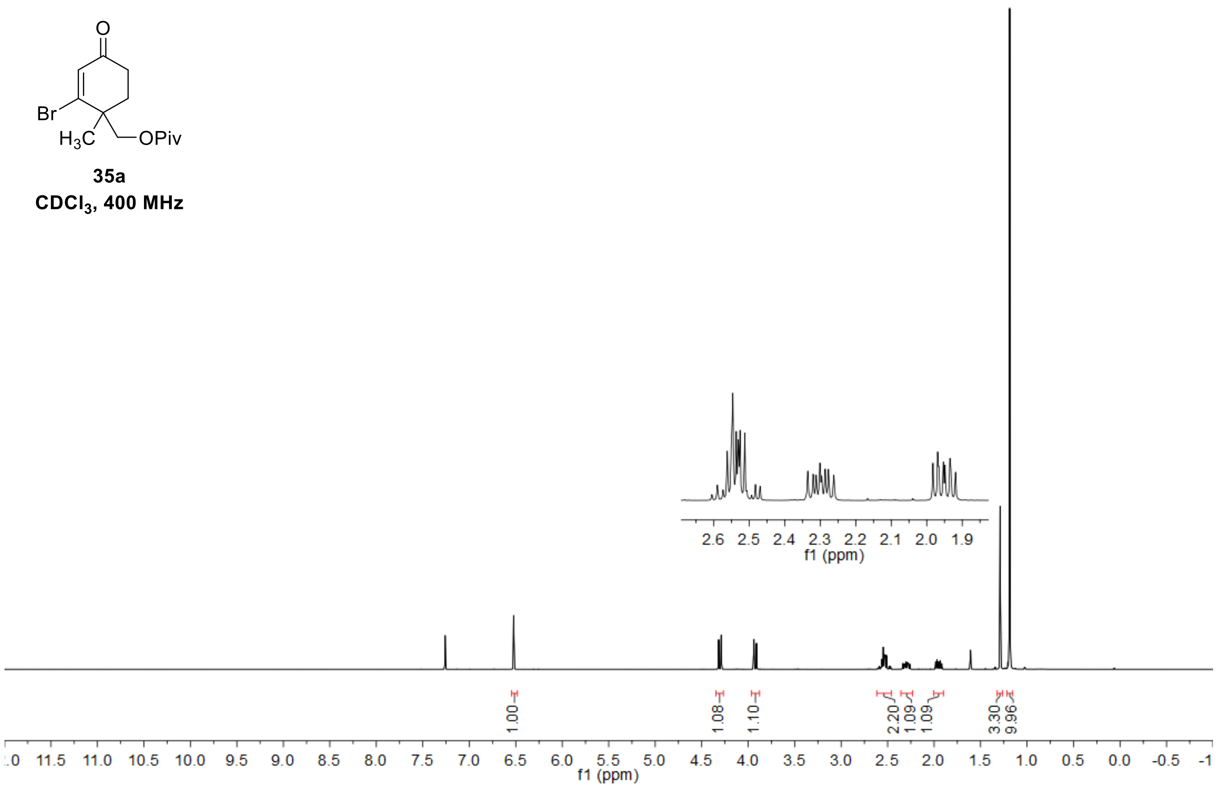
34b
$CDCl_3$, 400 MHz

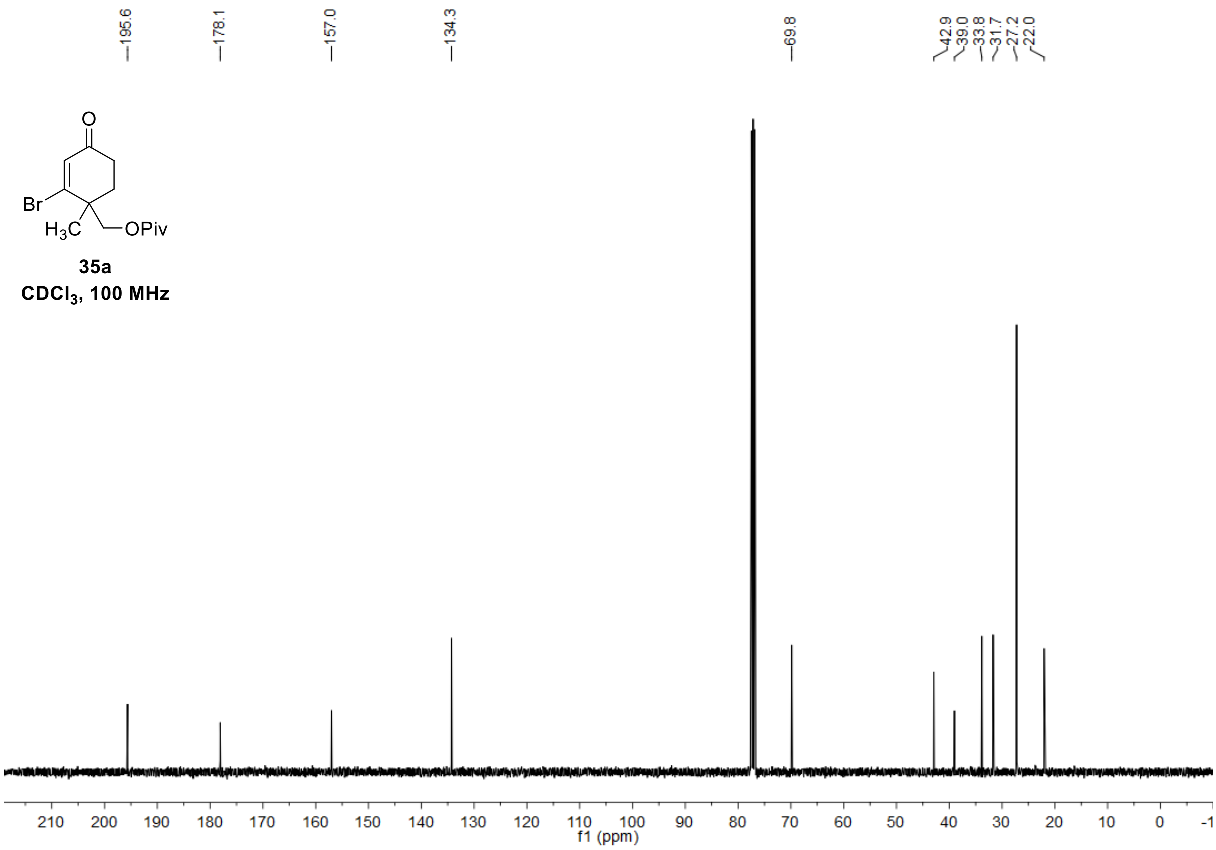


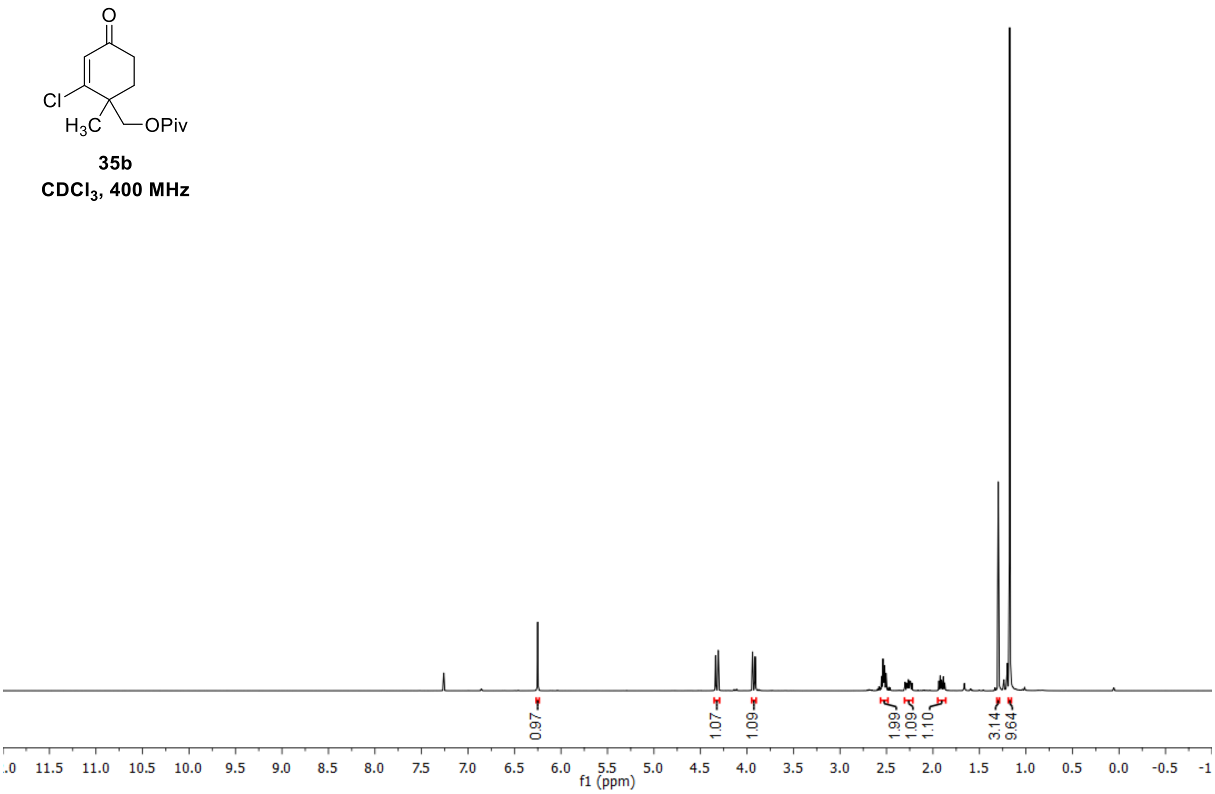


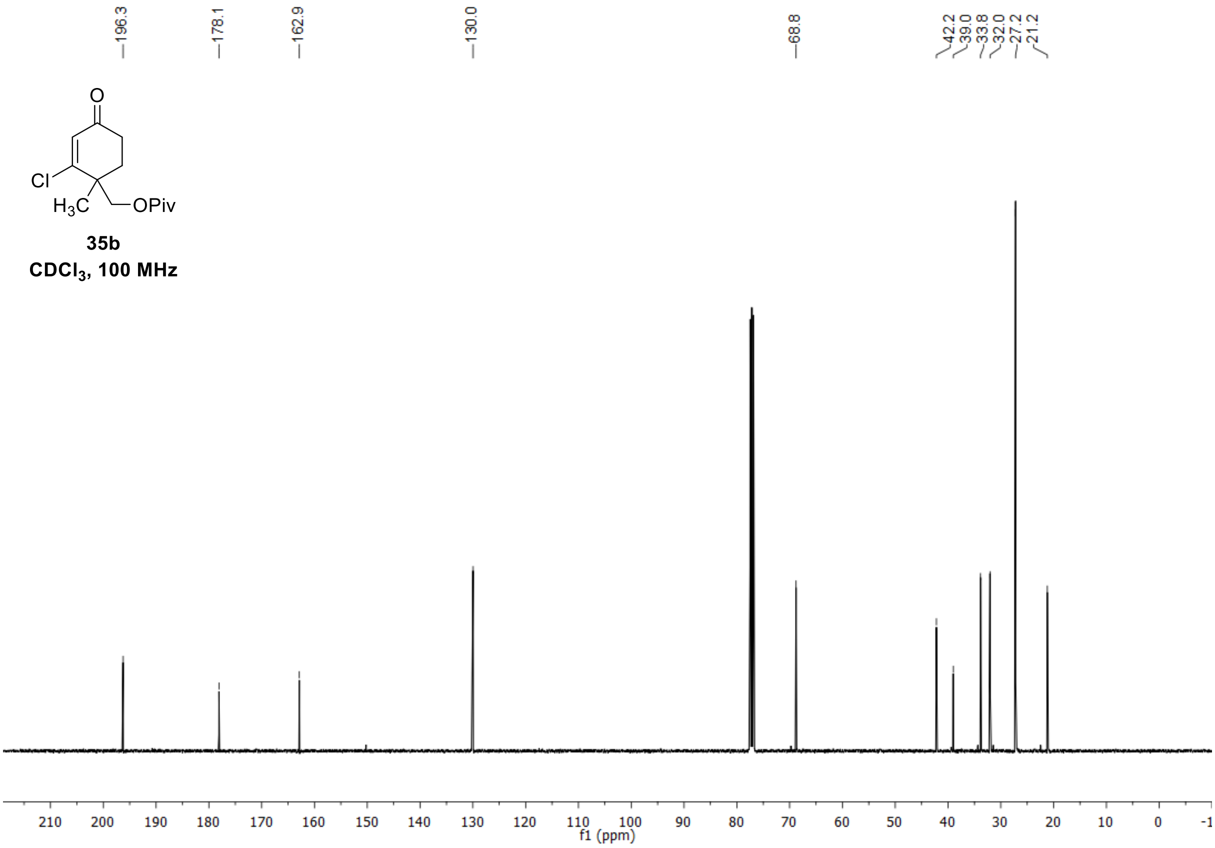
34b
$CDCl_3$, 100 MHz

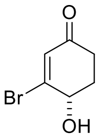



O
Br
H_3C
OPiv
35a
$CDCl_3$, 400 MHz
1.00
1.08
1.10
2.20
1.09
1.09
3.30
9.96
2.6 2.5 2.4 2.3 2.2 2.1 2.0 1.9
f1 (ppm)
f1 (ppm)


195.6
178.1
157.0
134.3
69.8
42.9
39.0
33.8
31.7
27.2
22.0
O
Br
H_3C
OPiv
35a
$CDCl_3$, 100 MHz
f1 (ppm)

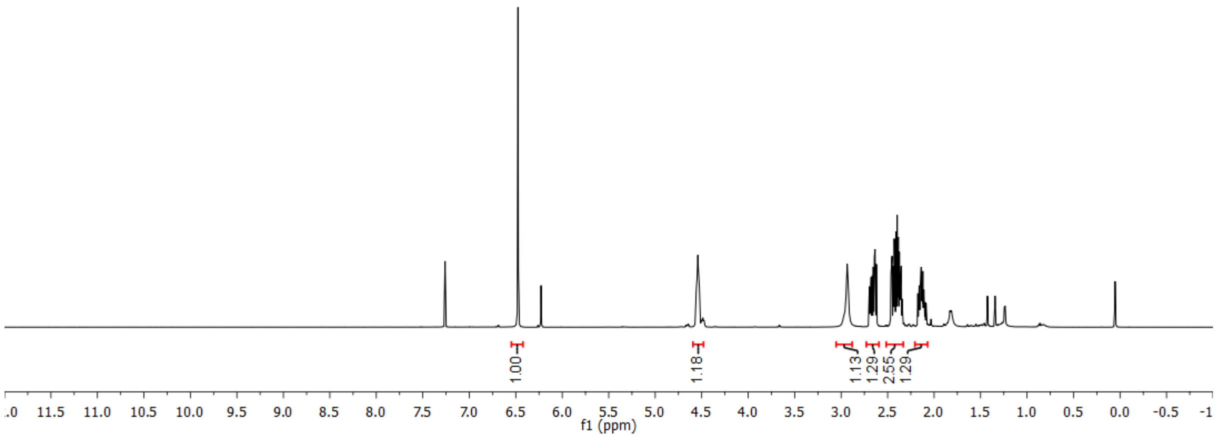

O
Cl
H_3C
OPiv
35b
$CDCl_3$, 400 MHz
0.97
1.07
1.09
1.99
1.09
1.10
3.14
9.64
f1 (ppm)

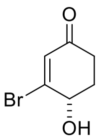

196.3
178.1
162.9
130.0
68.8
42.2
39.0
33.8
32.0
27.2
21.2
O
Cl
H_3C
OPiv
35b
$CDCl_3$, 100 MHz
f1 (ppm)



36

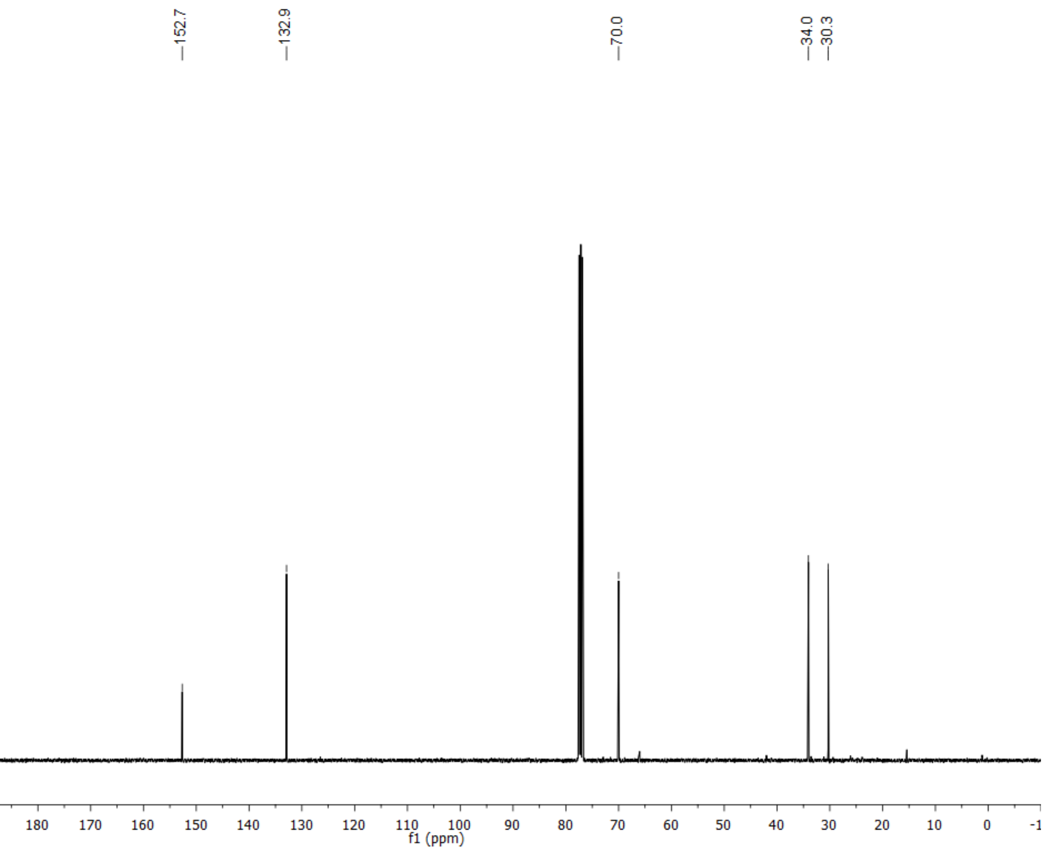
$CDCl_3$, 400 MHz

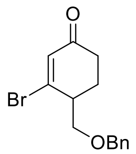




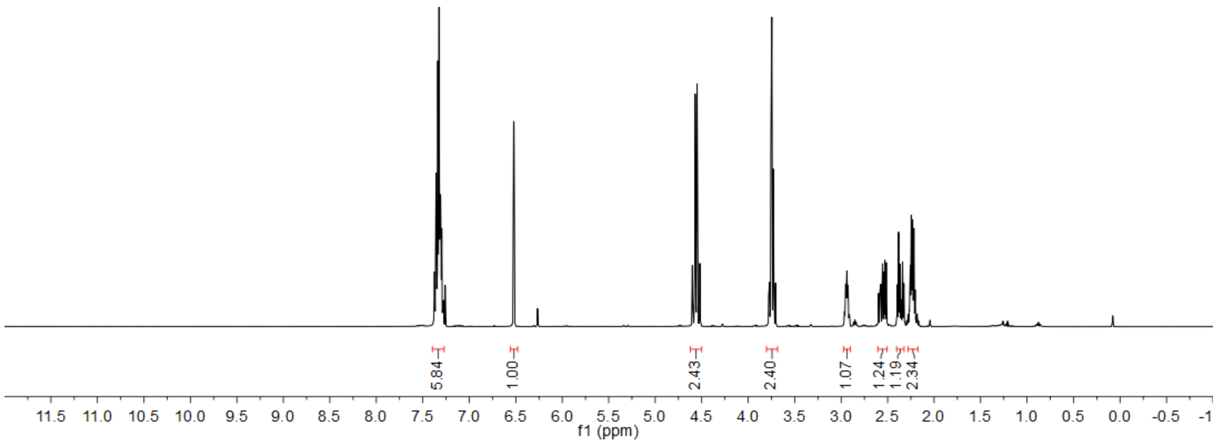
36

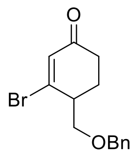
$CDCl_3$, 100 MHz



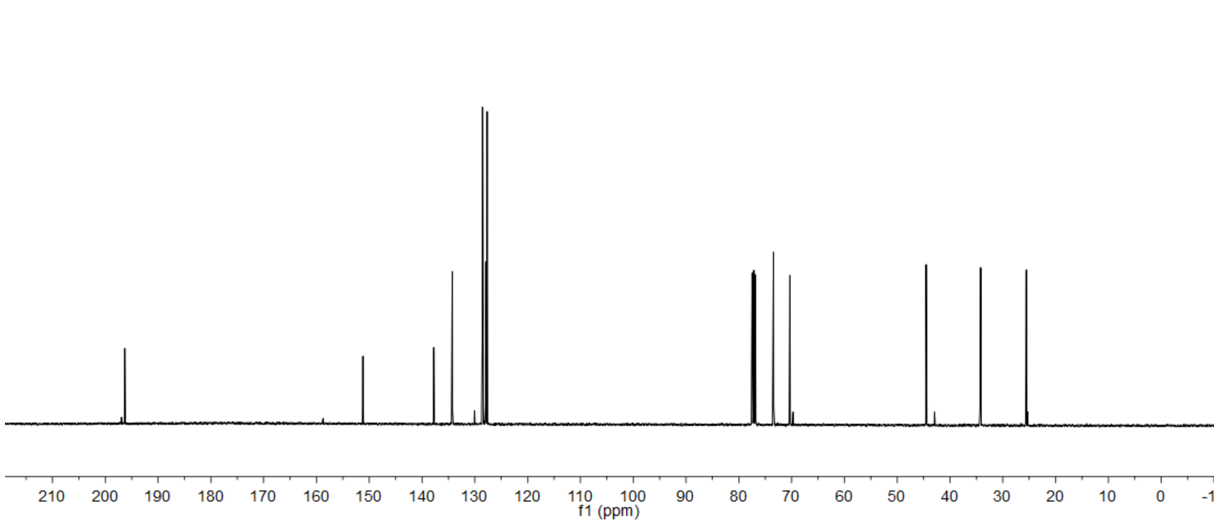


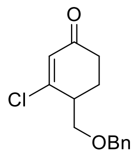
37a
$CDCl_3$, 400 MHz



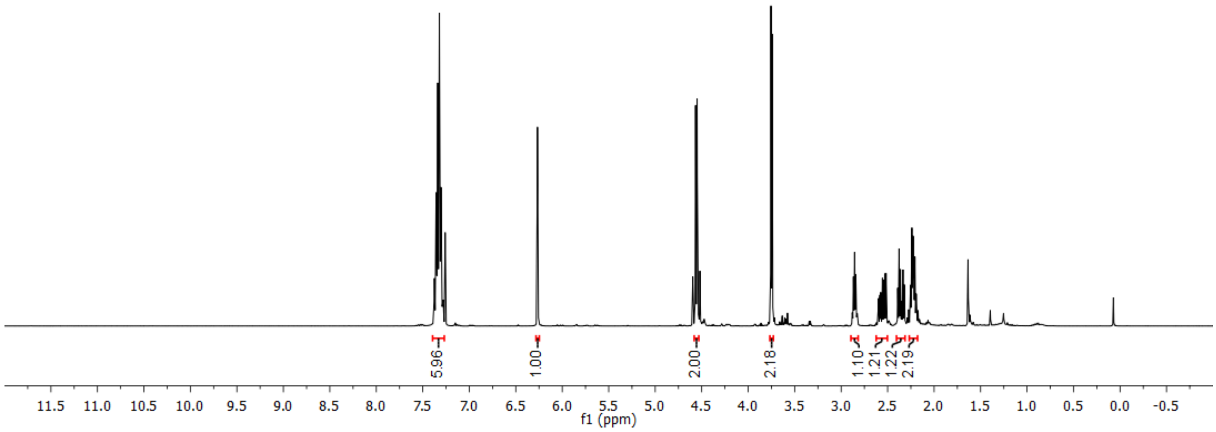


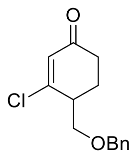
37a
$CDCl_3$, 100 MHz



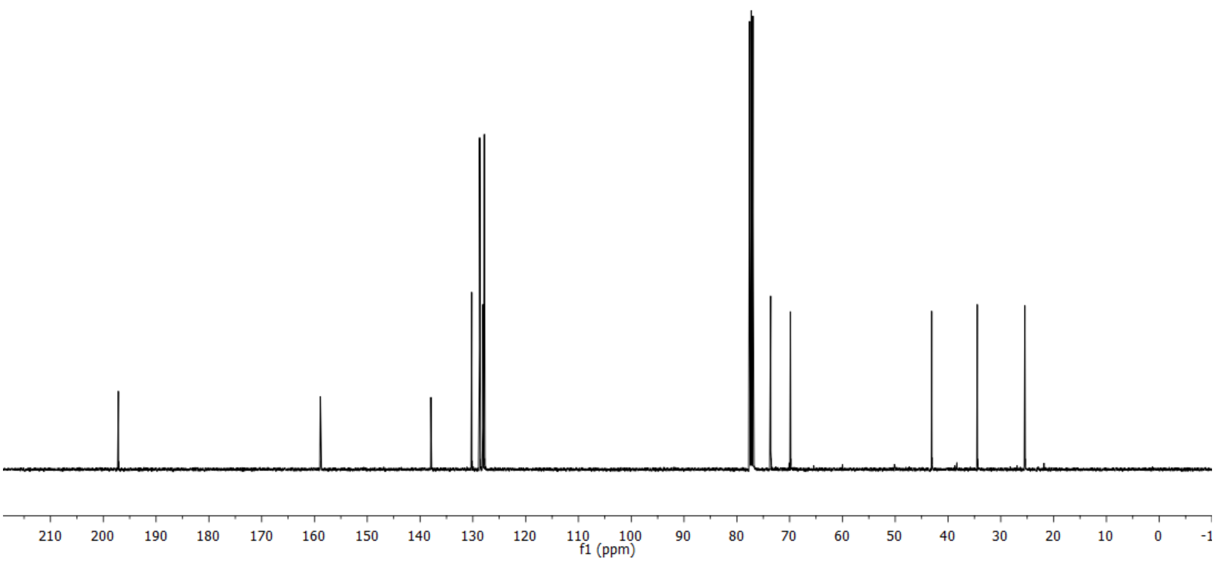


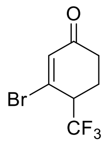
37b
$CDCl_3$, 400 MHz



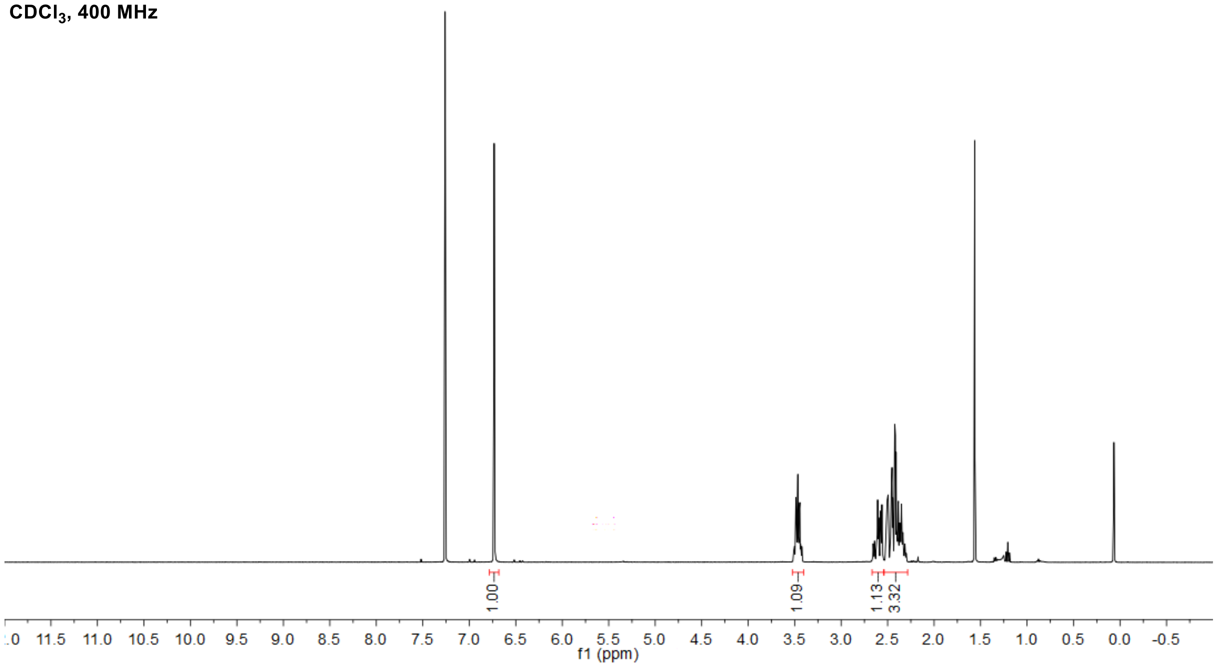


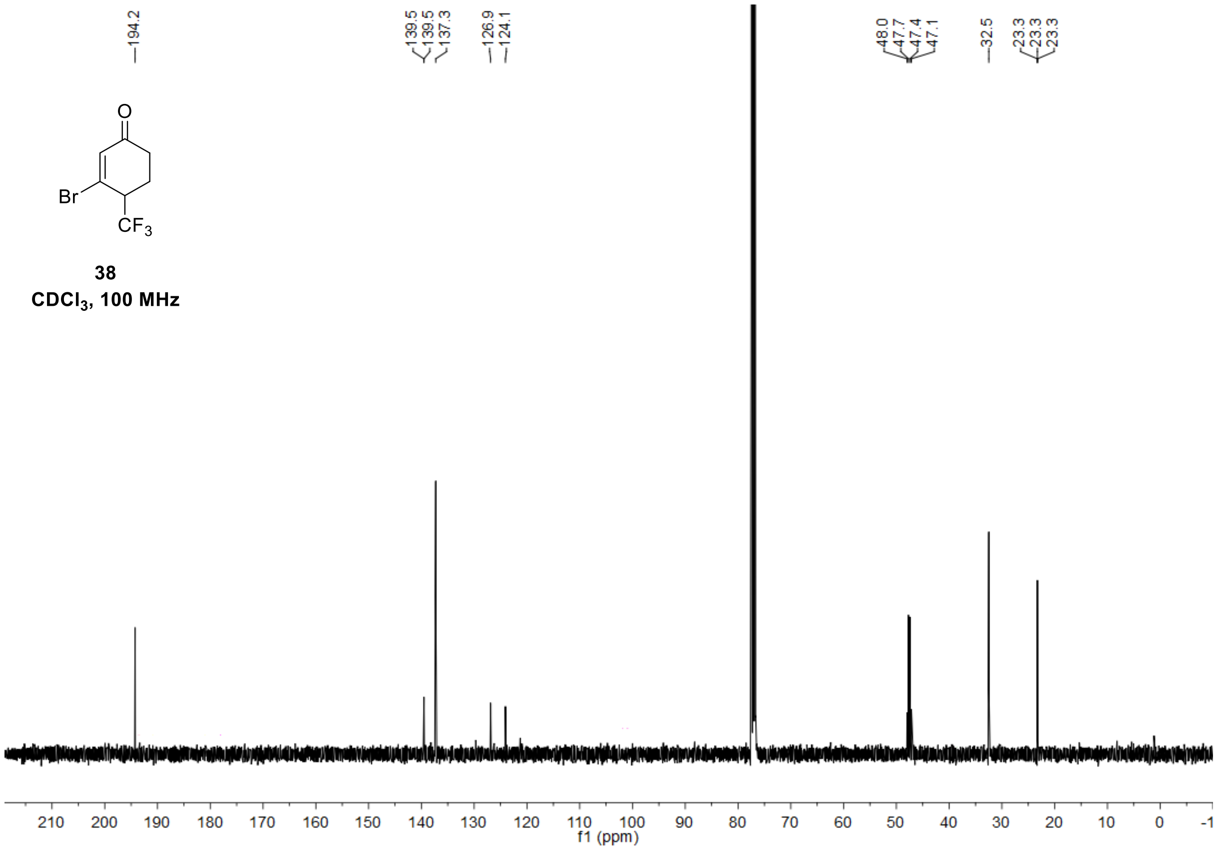
37b
$CDCl_3$, 100 MHz



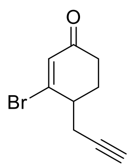


38
CDCl$_3$, 400 MHz

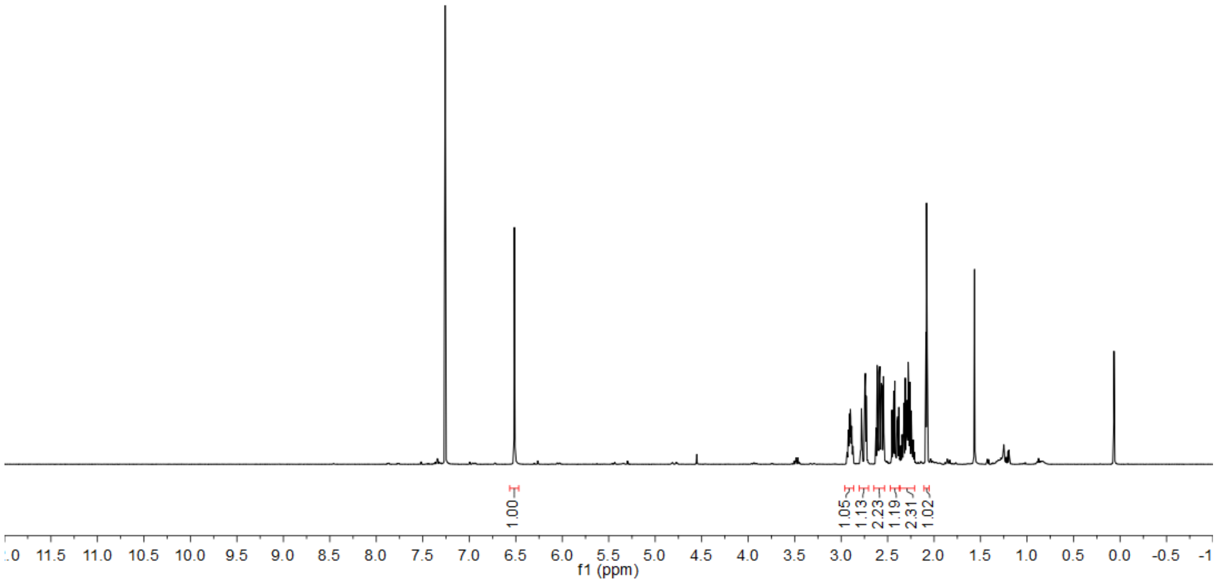


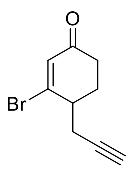


38
CDCl$_3$, 100 MHz

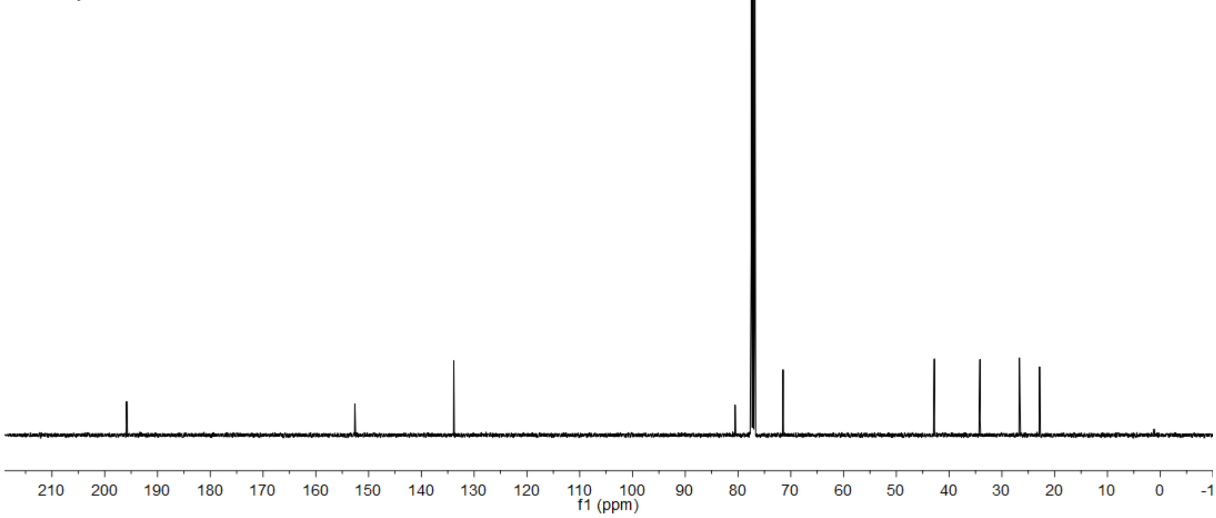


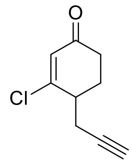
39a
$CDCl_3$, 400 MHz



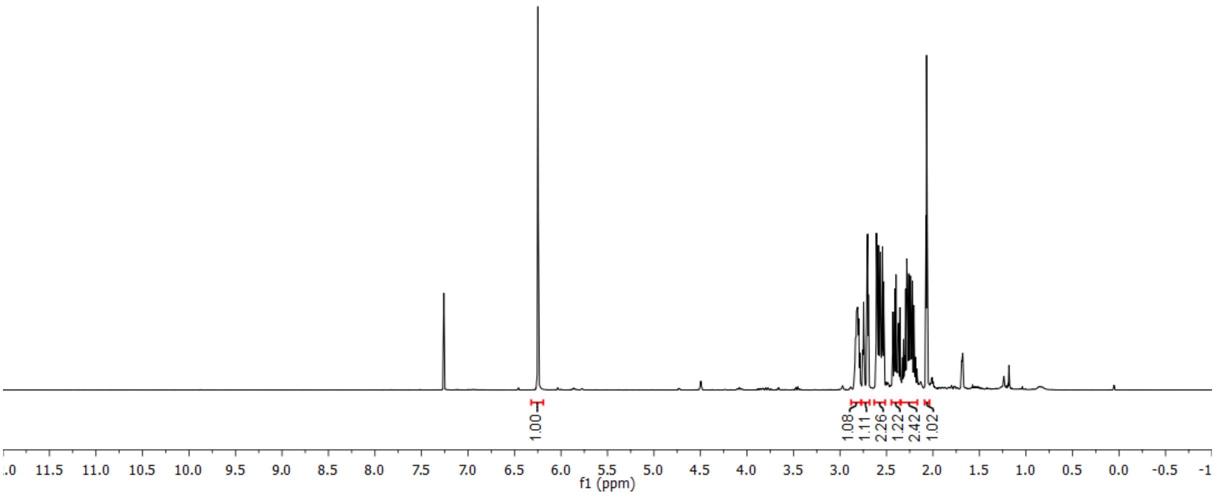


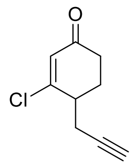
39a
$CDCl_3$, 100 MHz



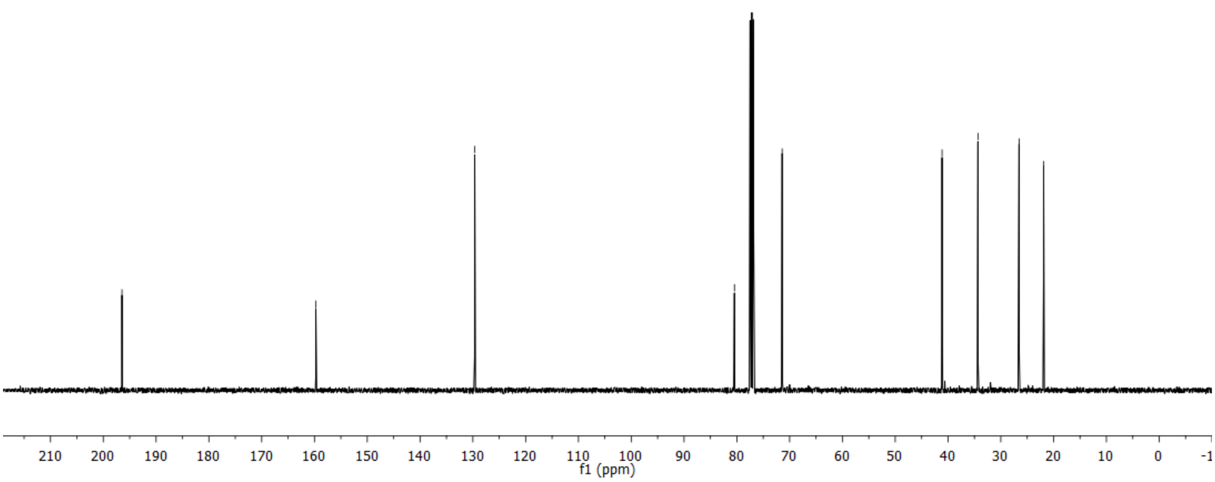


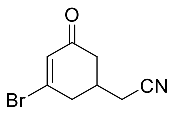
39b
$CDCl_3$, 400 MHz



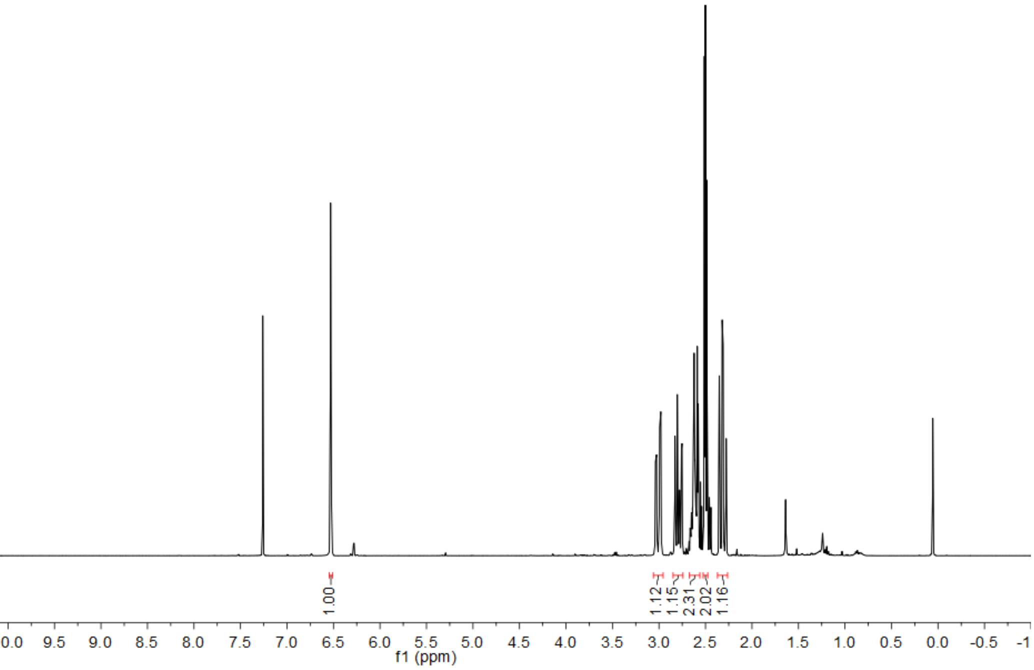


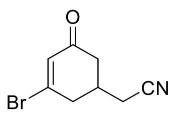
39b
$CDCl_3$, 100 MHz



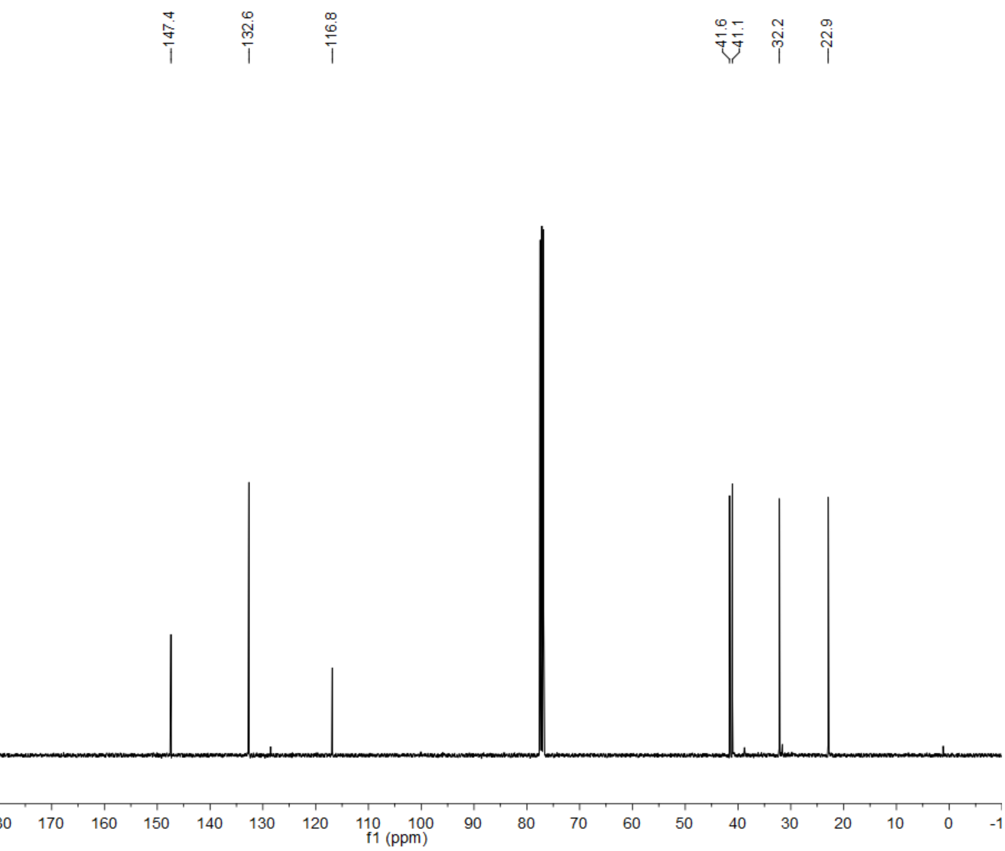


41
$CDCl_3$, 400 MHz

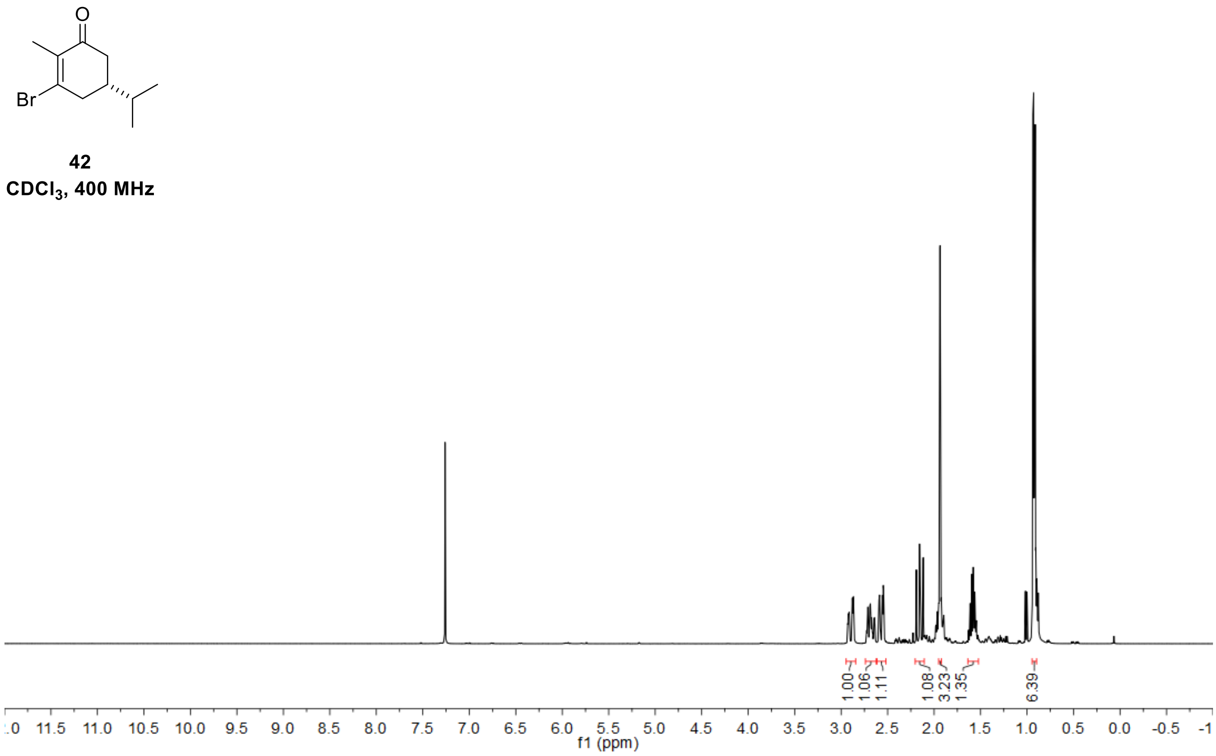




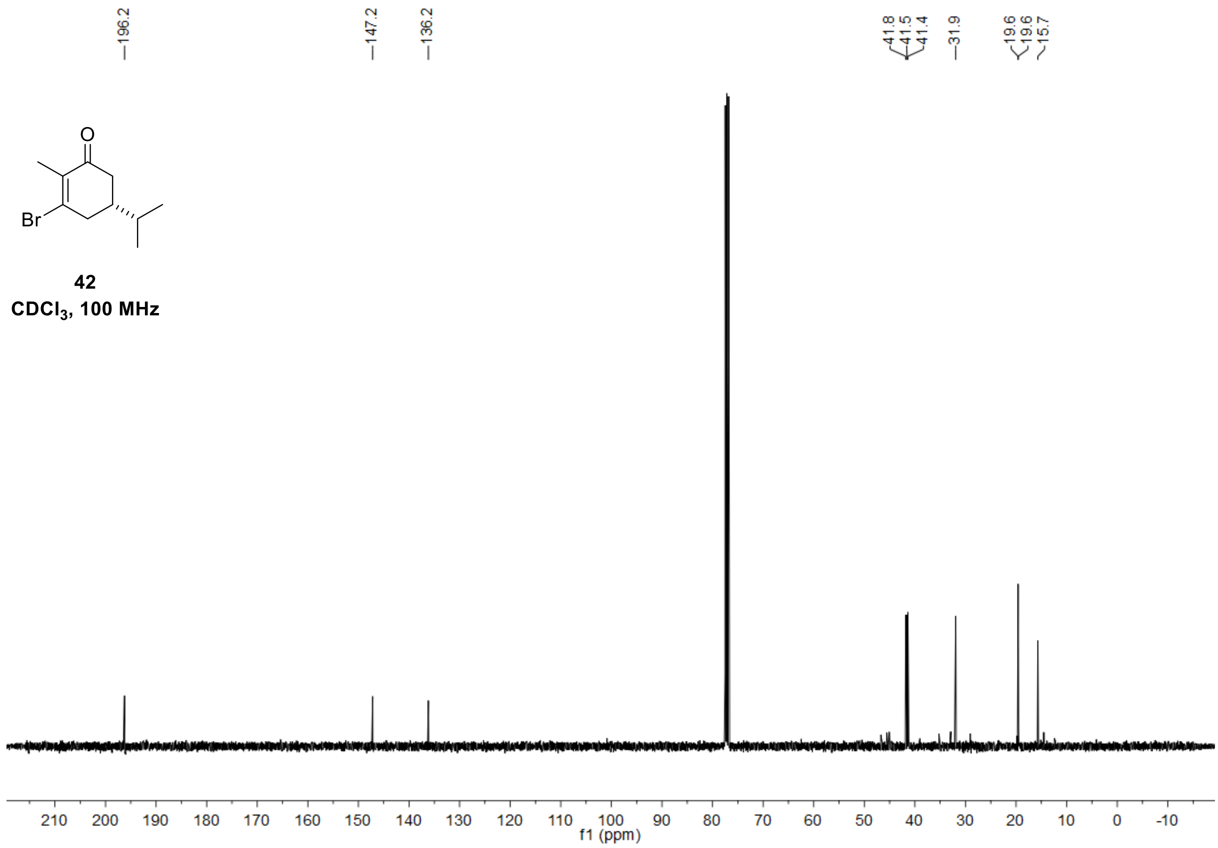
41
$CDCl_3$, 100 MHz

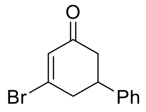


42
$CDCl_3$, 400 MHz

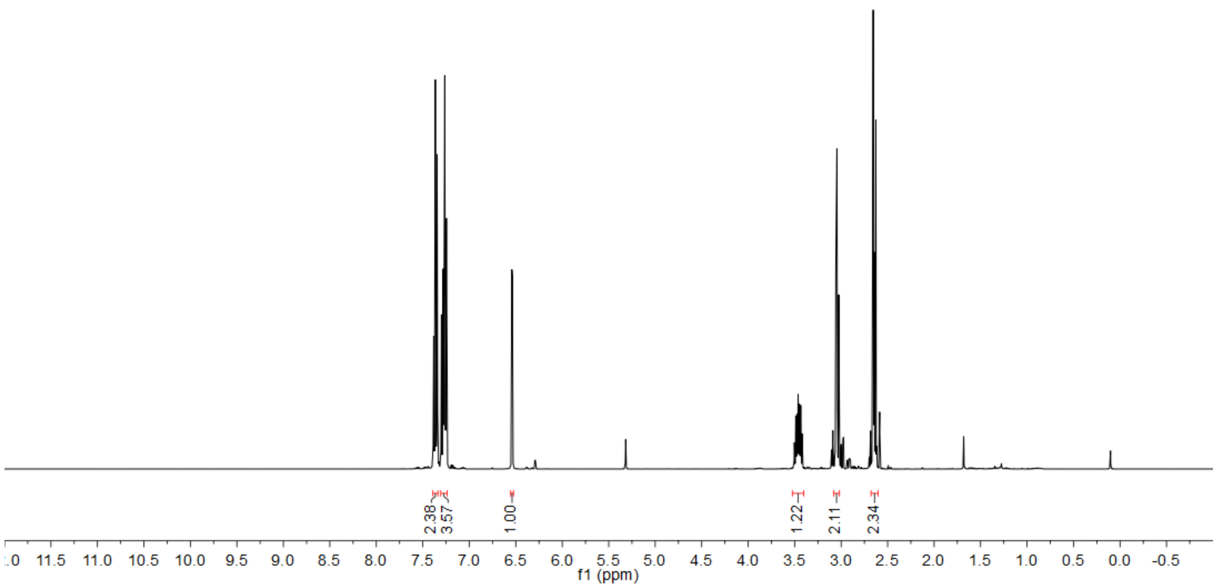


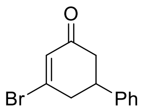
42
$CDCl_3$, 100 MHz



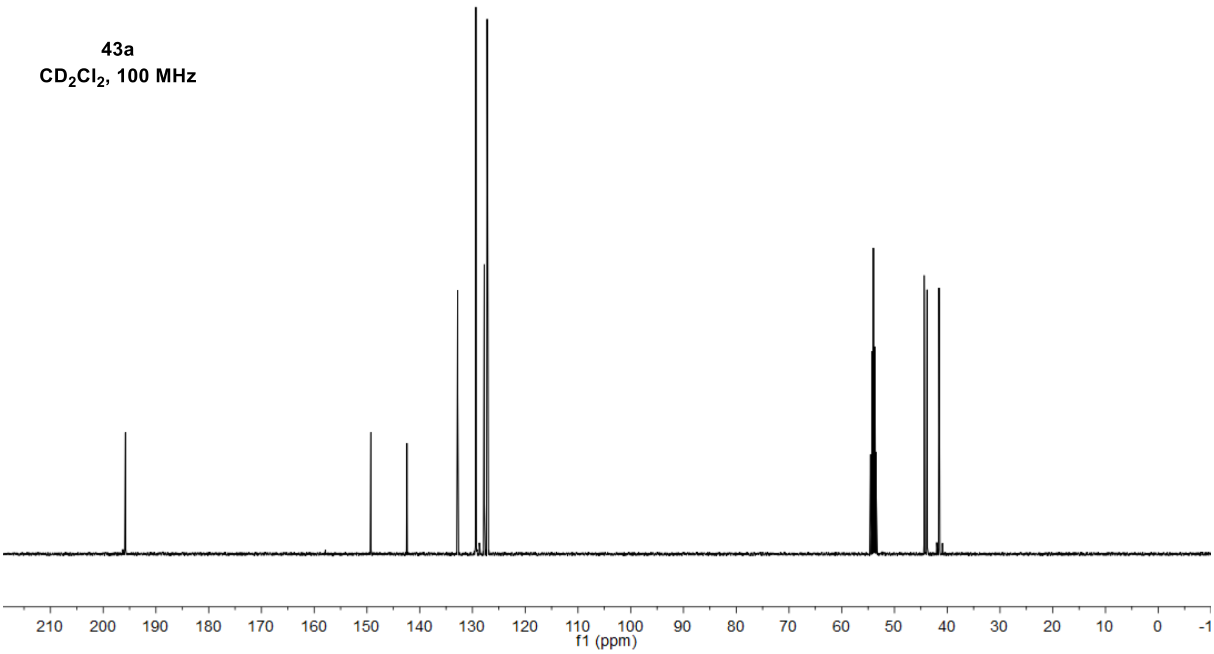


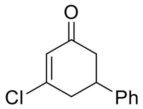
43a
CD_2Cl_2, 400 MHz



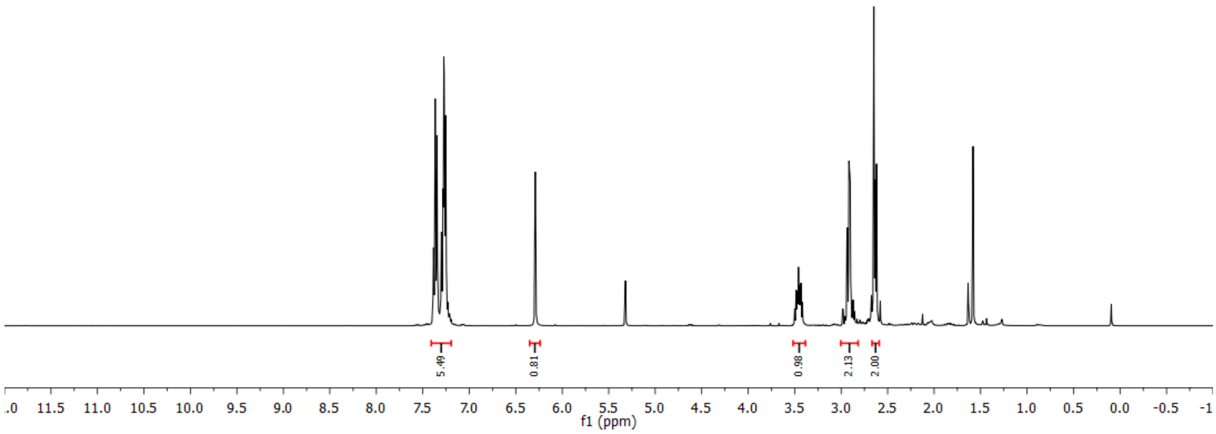


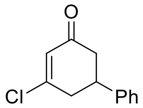
43a
CD_2Cl_2, 100 MHz



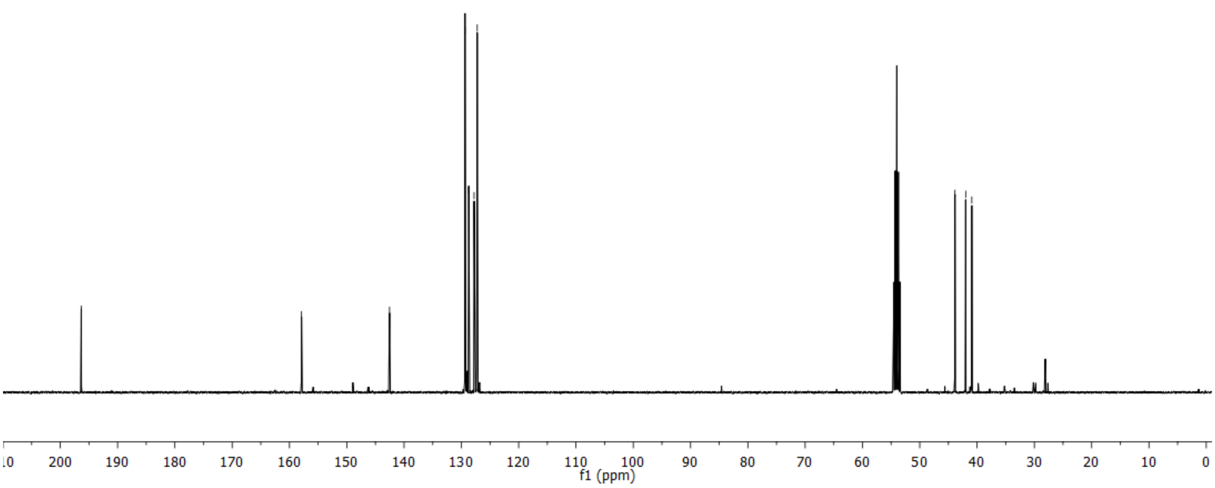


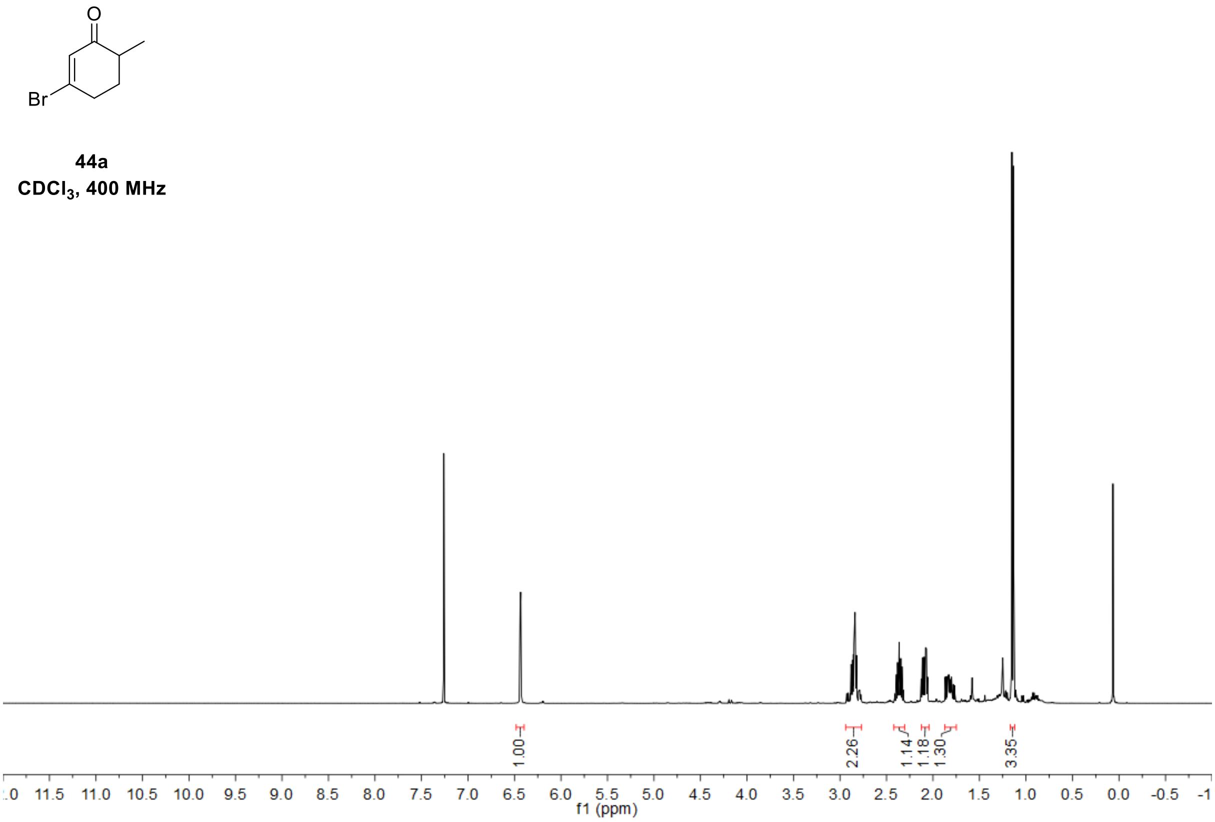
43b
CD_2Cl_2, 400 MHz

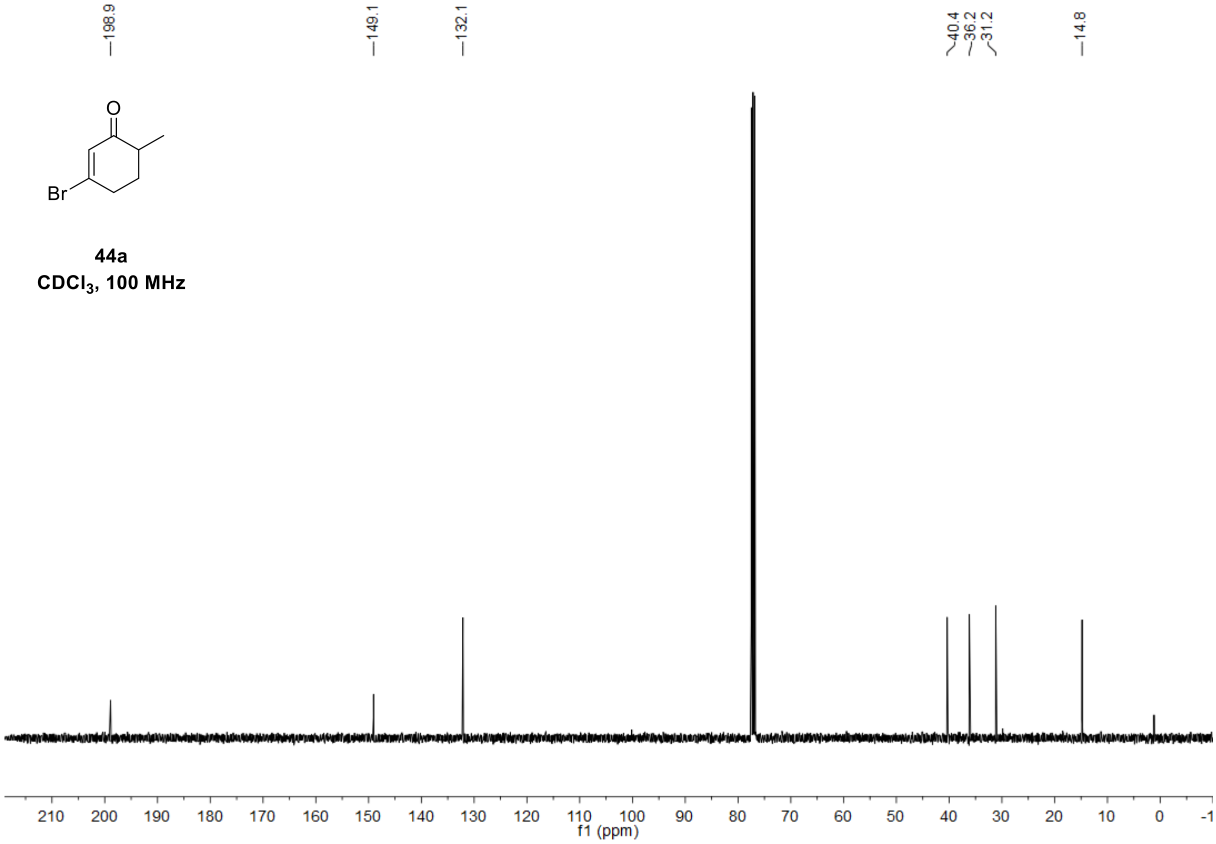


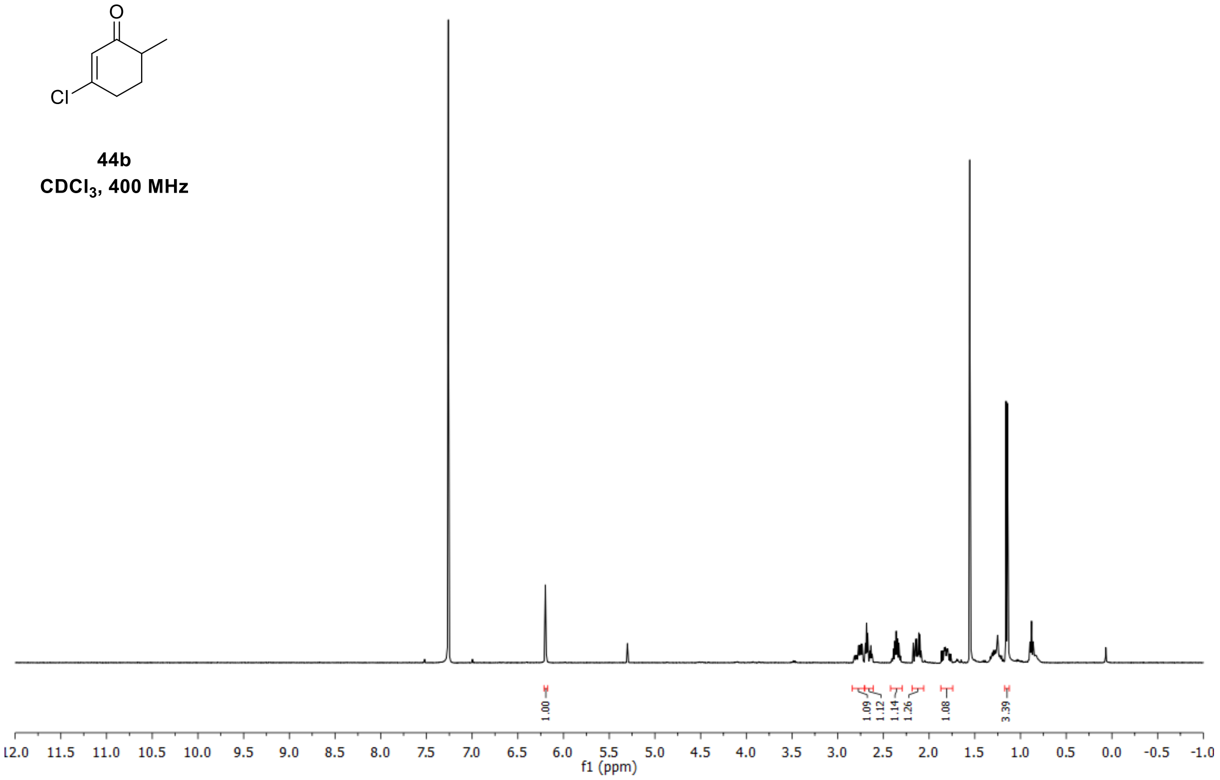


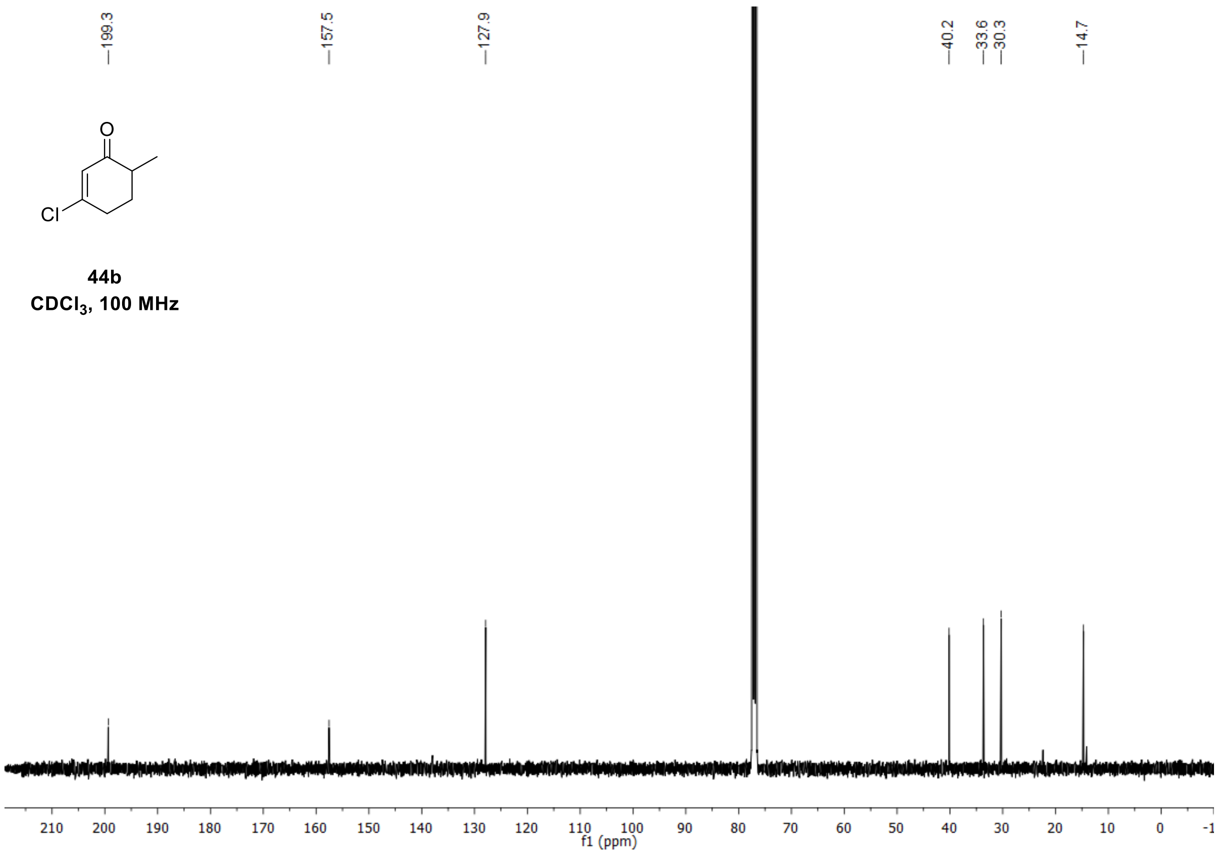
43b
CD_2Cl_2, 100 MHz

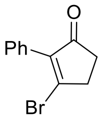



44a
CDCl3, 400 MHz
1.00
2.26
1.14
1.18
1.30
3.35
f1 (ppm)

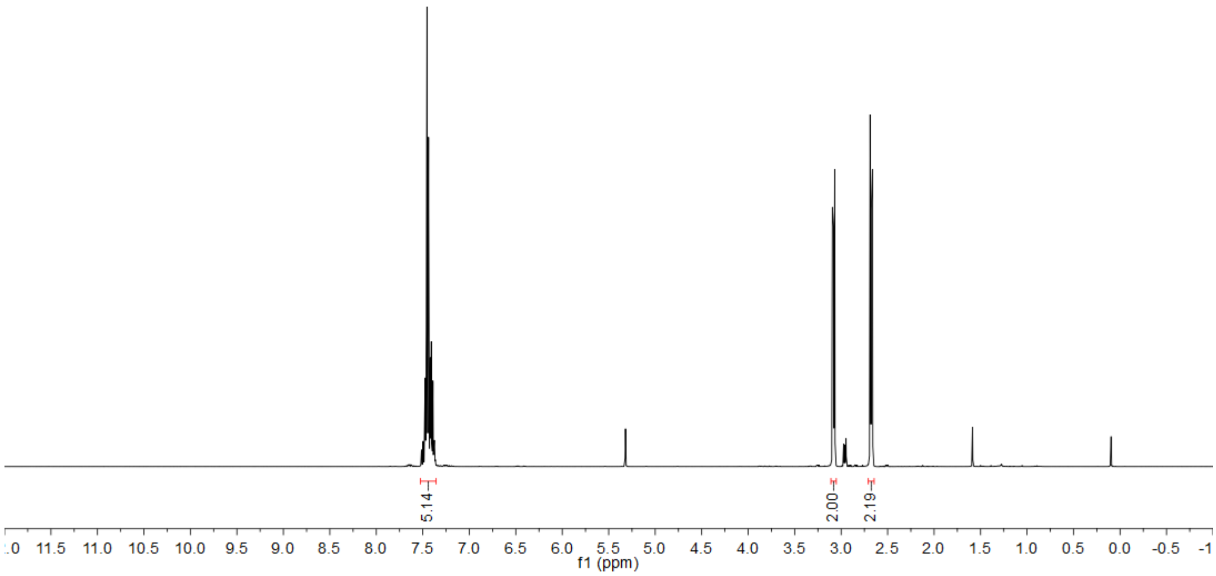

198.9
149.1
132.1
40.4
36.2
31.2
14.8
44a
CDCl3, 100 MHz
f1 (ppm)

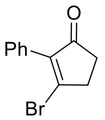

O
Cl
44b
$CDCl_3$, 400 MHz
1.00
1.09
1.12
1.14
1.26
1.08
3.39
12.0 11.5 11.0 10.5 10.0 9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0 -0.5 -1.0
f1 (ppm)


199.3
157.5
127.9
40.2
33.6
30.3
14.7
O
Cl
44b
$CDCl_3$, 100 MHz
210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 -1
f1 (ppm)

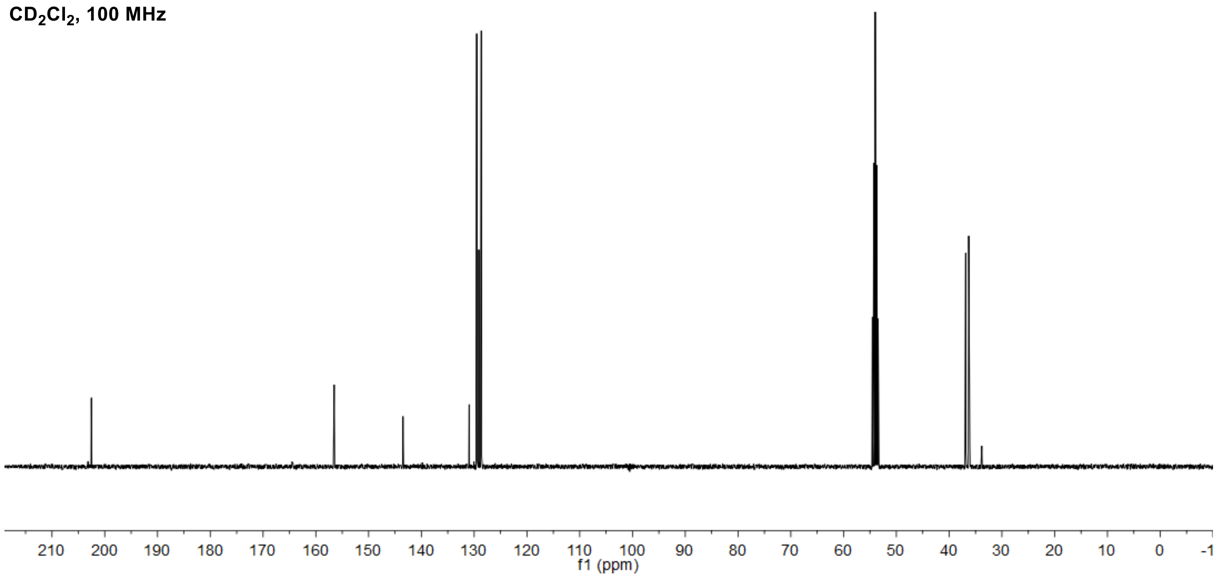


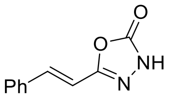
46
CD_2Cl_2, 400 MHz



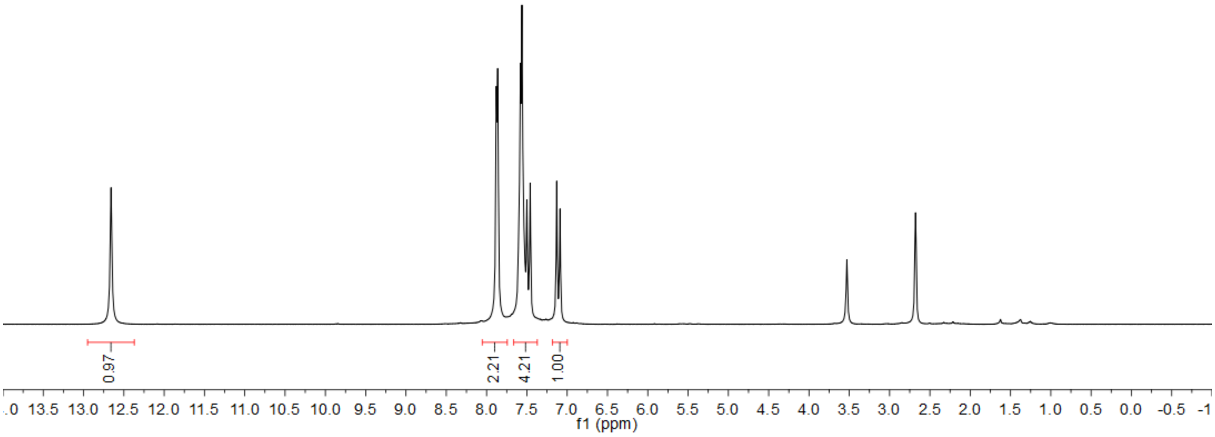


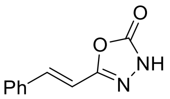
46
CD_2Cl_2, 100 MHz



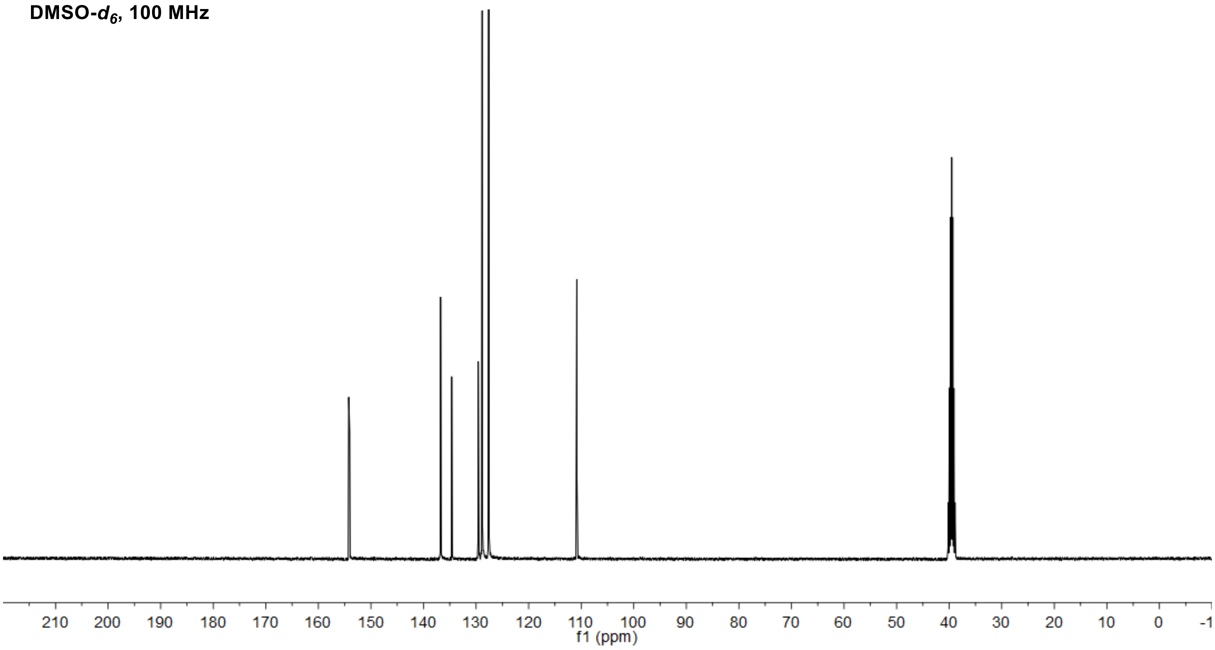


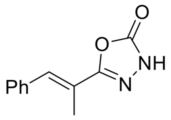
50
DMSO-d_6, 400 MHz



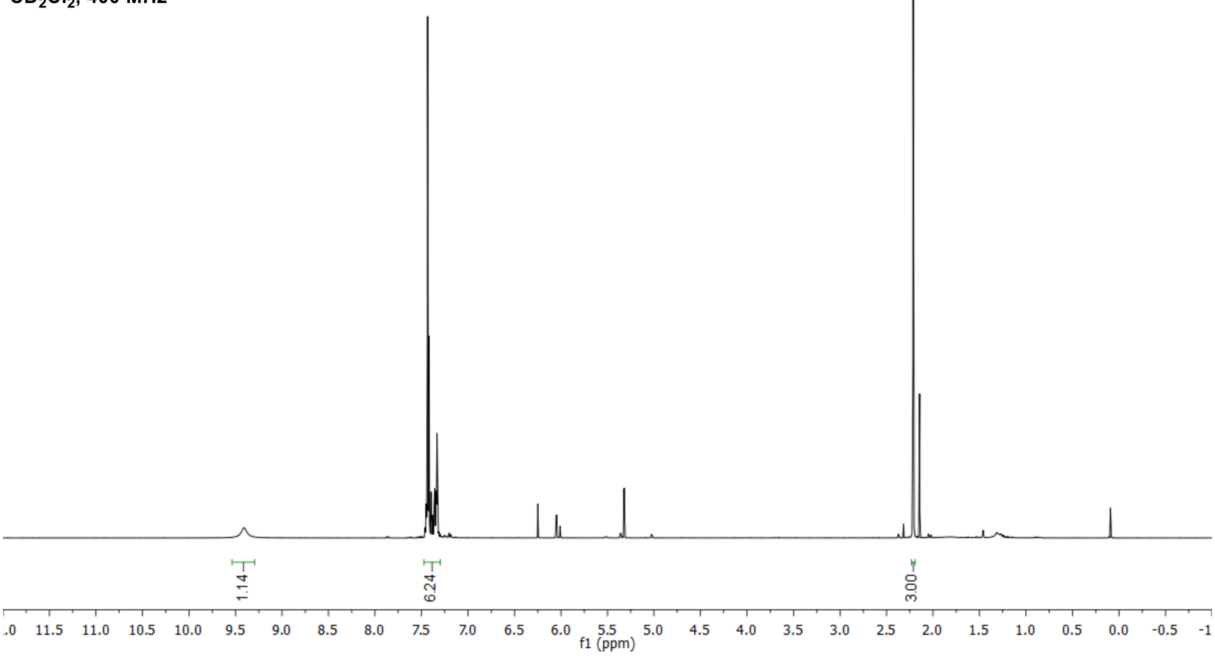


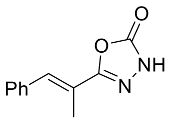
50
DMSO-d_6, 100 MHz



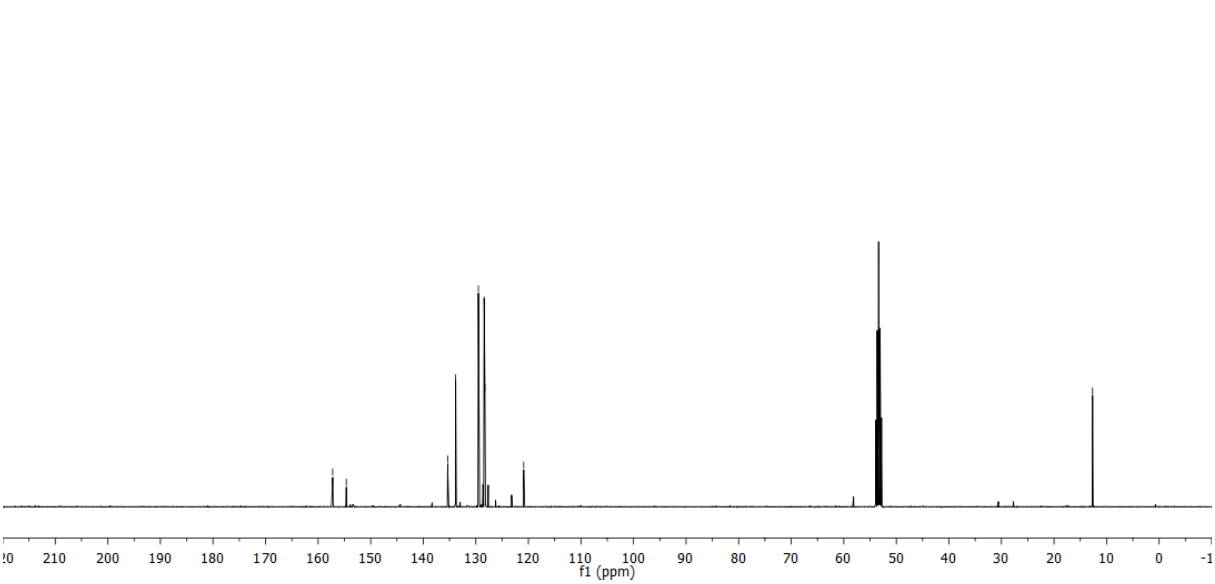


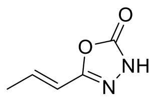
51
CD_2Cl_2, 400 MHz



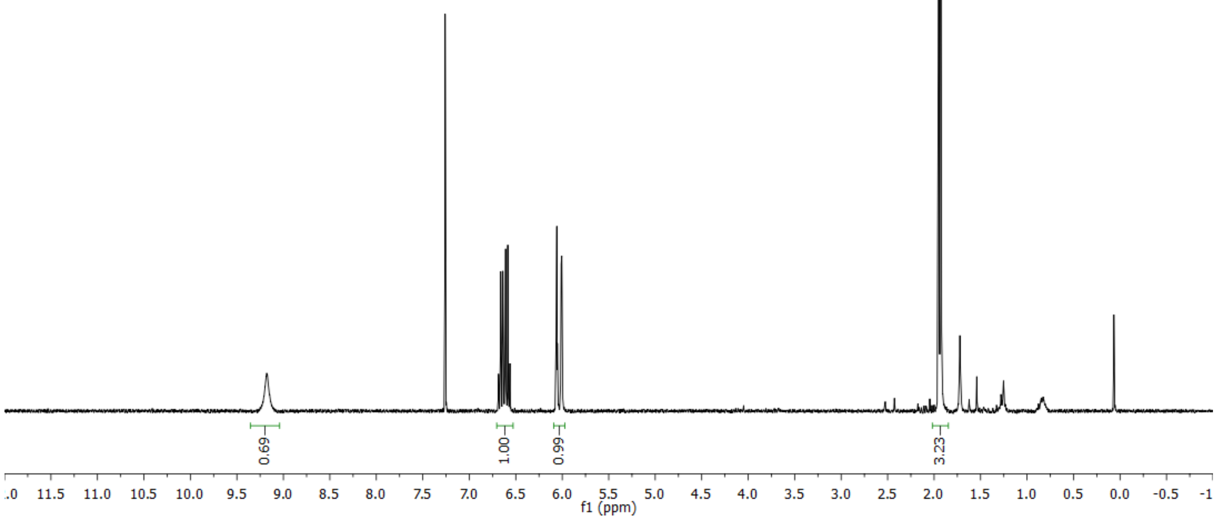


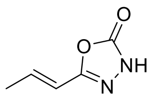
51
CD_2Cl_2, 100 MHz



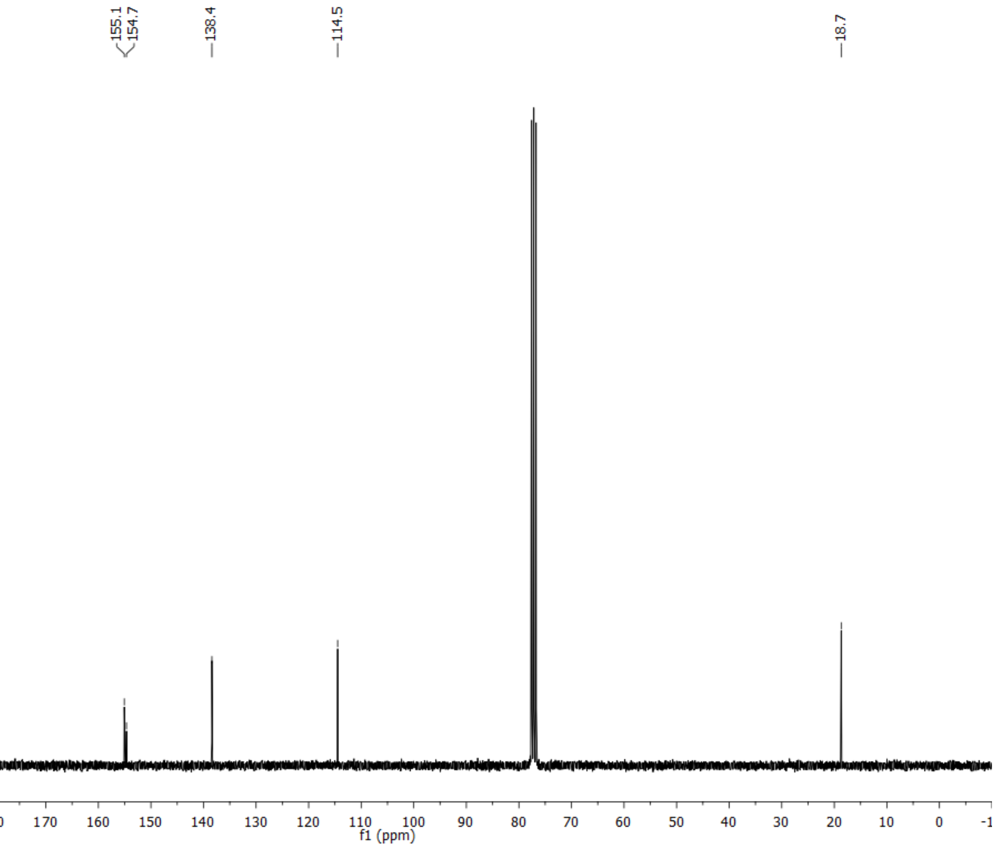


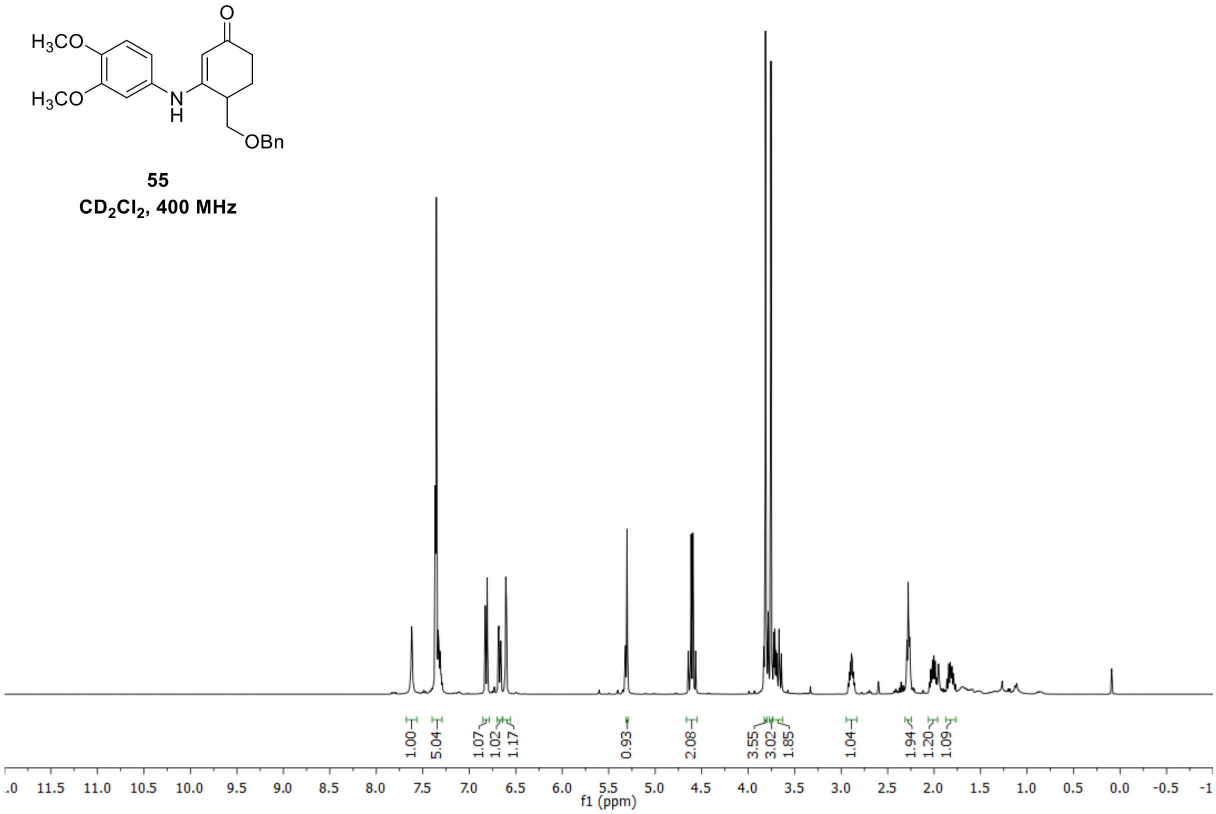
52
$CDCl_3$, 300 MHz



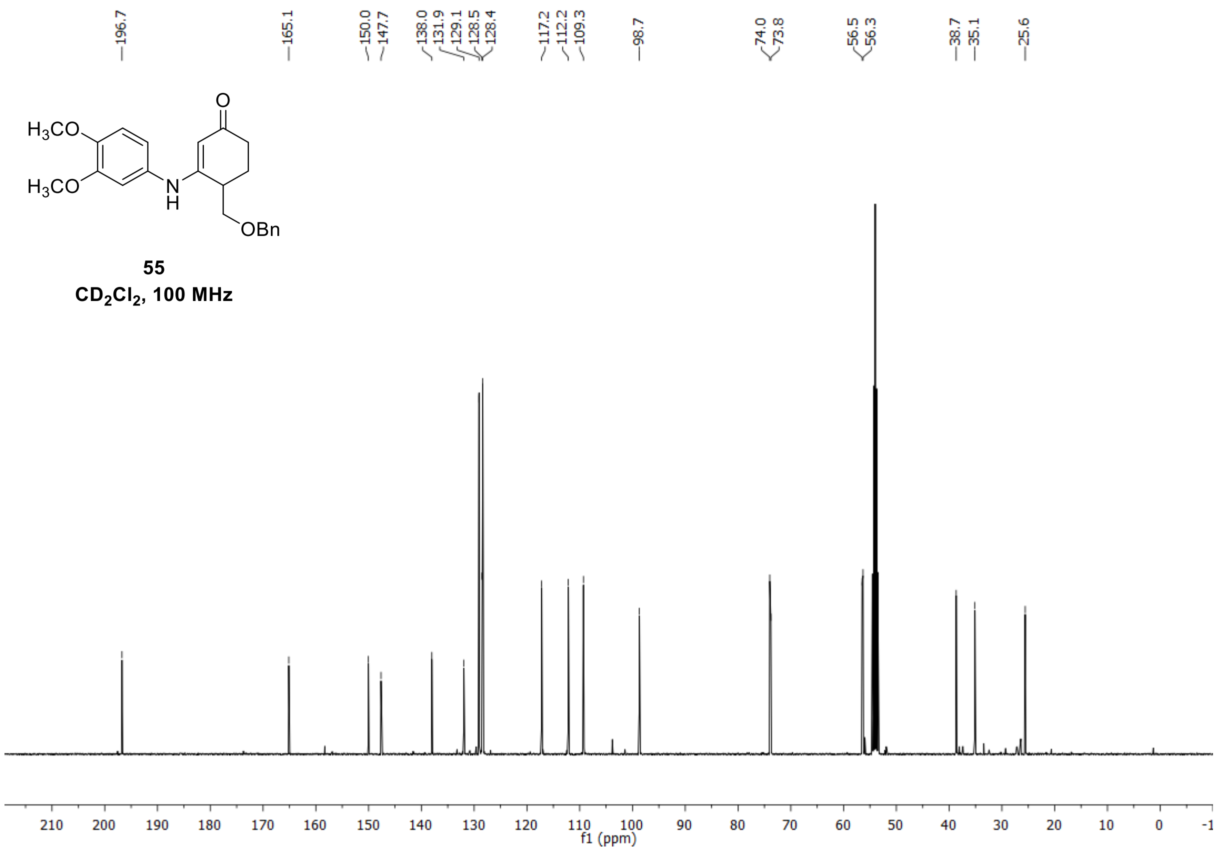


52
$CDCl_3$, 75 MHz

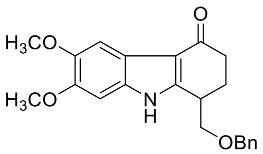




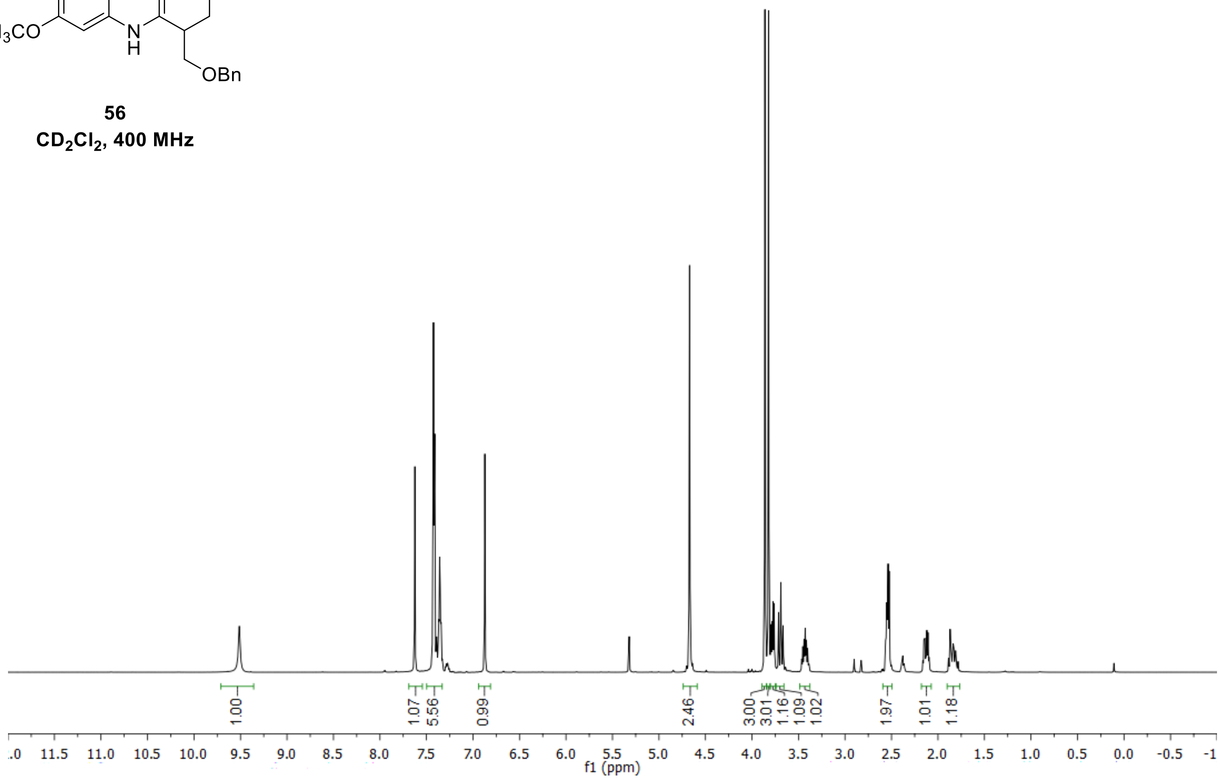
55
CD_2Cl_2, 400 MHz

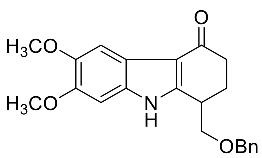


55
CD_2Cl_2, 100 MHz



56
CD_2Cl_2, 400 MHz





56
CD_2Cl_2, 100 MHz