Electronic Supplementary Material (ESI) for Organic Chemistry Frontiers.

Supporting Information

Photo-Hydroacylation: 1-Tetralones from ortho-Allylbenzaldehydes

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Table of Contents

1 Methods and Materials

All **non-aqueous reactions** were carried out under argon atmosphere using oven-dried glassware unless noted otherwise. All solvents were distilled by rotary evaporation prior to use. Solvents for non-aqueous reactions were dried as follows prior to use, unless noted otherwise: THF was dried and degassed with KOH and subsequently distilled from sodium/benzophenone or Solvona® under nitrogen atmosphere. CH_2Cl_2 and acetonitrile were dried and degassed by distillation from CaH_2 under nitrogen atmosphere. MeOH was dried and degassed by distillation from Mg-turnings (5 g/L) under nitrogen atmosphere. Toluene was dried and degassed with Solvona® und distilled from it under nitrogen atmosphere. All commercially available reagents and reactants were used without purification unless otherwise noted.

Certain sections of this paper were written with the assistance of an AI language model. Specifically, selected paragraphs were refined using the ChatGPT language model, developed by OpenAI. The AL model´s role was solely to provide language generation support and should not be considered as an author or contributor to the scientific work. The authors take full responsibility for the final content presented in this paper.

Thin layer chromatography (TLC) was performed to monitor reactions using MERCK silica gel 60 F_{245} plates. Visualization was performed by fluorescence quenching under UV-light (254, 365 nm) or using a cerium sulfate/phosphomolybdic acid stain. **Chromatographic purification** of products was performed using Merck silica gel 60 (230 – 400 mesh) by application of positive pressure. Concentration under reduced pressure was performed by rotary evaporation at 40 °C and by exposing to high vacuum at room temperature if necessary.

NMR spectra were recorded on a Bruker AV II 300 MHz, AV III 500 MHz or AV III HD 500 MHz spectrometer at room temperature. The signals were referenced to residual solvent and chemical shifts are reported in ppm. Signal patterns are reported based on appearance as follows: s = singlet, d = doublet, t = triplet, q = quartet, quint = quintet, m = multiplet.

Mass spectra were recorded by the mass service department of the Philipps-Universität Marburg. HR-ESI and APCI mass spectra were acquired with an LTQ-FT Ultra mass spectrometer (Thermo Fischer Scientific). The resolution was set to 100.000.

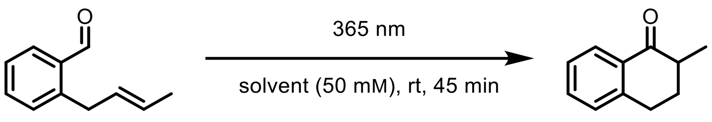
IR spectra were recorded on a Bruker IFS 200 spectrometer. Intensities are reported as follows: s = strong, m = medium, w = weak. Absorption bands are given in wave numbers (cm^{-1}).

Melting points were determined on a Mettler Toledo MP70 using one end closed capillary tubes.

Photochemical reactions were run in 25 mL round bottom flasks made of borosilicate glass (Duran®) unless noted otherwise, placed 6 – 7 cm away from the irradiation source. Irradiation was performed with a 365 nm LED lamp (7 LEDs, 200 mW each) over a stirring plate with two cooling fans.

2 Optimization & Effect of Reaction Conditions

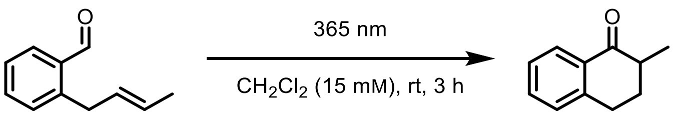
Table 1: Conversion of starting material in different solvents.



entry	solvent	Yield [%]	Recovered starting material [%]
1	MeCN	55	40
2	toluene	27	73
3	acetone	48	21
4	*i*-PrOH	28	n.d.
5	CH_2Cl_2	67	33
6	CH_2Cl_2 (55 mM)	68	32
7	CH_2Cl_2 (45 mM)	72	27
8	CH_2Cl_2 (200 mM), 150 min	78	22
9	CH_2Cl_2 (20 mM), 150 min	88	-
10	CH_2Cl_2 (15 mM), 180 min	93	-

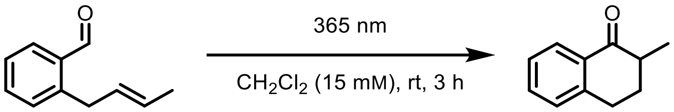
The reactions were carried out at 0.15 mmol scale. Product and starting material were isolated.

Table 2: Deviation from standard conditions in solvents and concentration.



entry	variation from conditions	Yield [%]	Recovered starting material [%]
1	none	93	-
2	10 mM instead of 15 mM	91	-
3	MeCN instead of CH_2Cl_2	88	-

Table 3: Control experiments.



4k **6k**

entry	variation from standard conditions	Yield [%]	Recovered starting material [%]
1	no light	0	100
2	2.5 h instead of 3 h	91	2

3 Emission Spectra of Employed Light Source

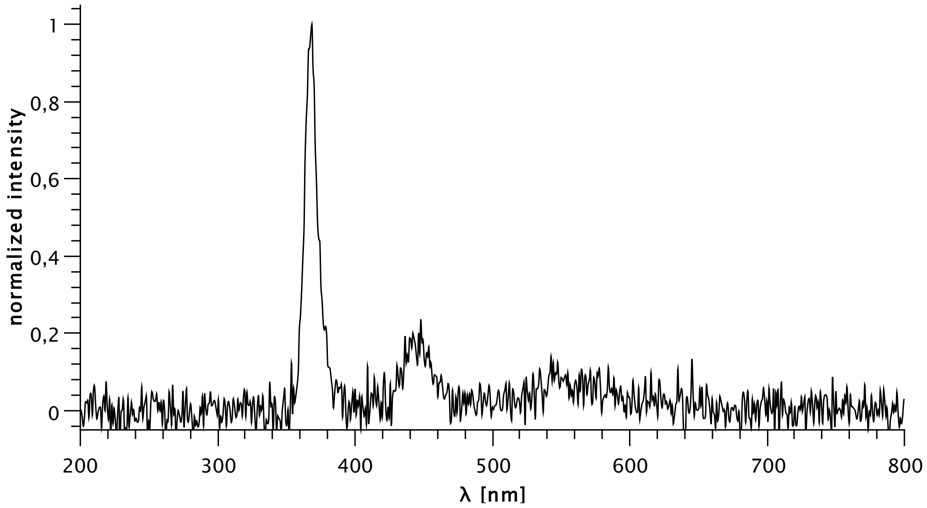
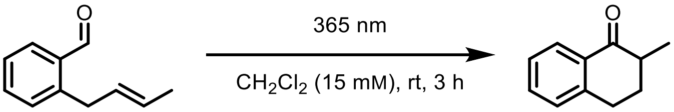


Figure S1: Emission spectra and plot of the 365 nm LED lamp.

The normalized overlay of the measured emission spectra of the lamp confirms an increased emission intensity at 365 nm (Figure S1).

4 Sensitivity Assessment



4k **6k**

The sensitivity assessment was conducted according to studies reported by GLORIUS *et al.*[1] The diagram shown in Figure S2 was made using the template provided by GLORIUS *et al*.[1]

Table 4: results of the sensitivity assessment.

entry	experiment	variation from standard conditions	yield [%]	recovered starting material (*)
1	High *c*	V_{rxn} – 10% V_{rxn}	-11	no
2	Low *c*	V_{rxn} + 10% V_{rxn}	-6	no
3	H_2O	+ H_2O; V_{H2O} = 1.00 equiv	-11	no
4	Low O_2	degassed, freeze-pump-thaw	-16	no
5	High O_2	+ air; V_{air} = 1.3 • V_{rxn}	-19	no
6	Low T	T – 10 °C	-13	no
7	High T	T + 10 °C	-22	no
8	Low I	distance / 2	-73	yes
9	High I	distance • 2	-14	no

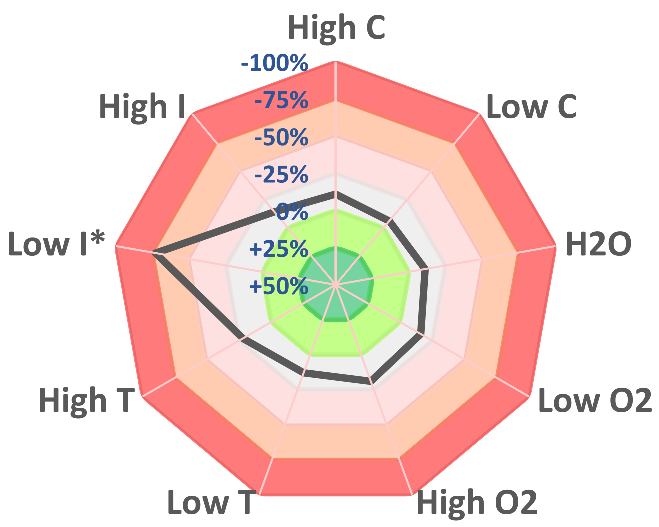
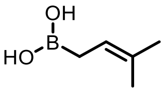


Figure S2: Radar diagram illustrating the results of the sensitivity assessment. C = concentration of starting material, T = temperature, I = light intensity, * = incomplete conversion.

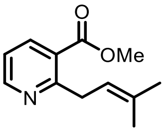
5 Substrate Synthesis

(3-methylbut-2-en-1-yl)boronic acid **S1**



was obtained according to a protocol reported by PARK *et al.*[2] The concentration was determined according to the protocol using naphthalene.

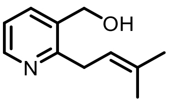
methyl 2-(3-methylbut-2-en-1-yl)nicotinate **S2**,



A solution of boronic acid **S1** (0.22 M in $CHCl_3$, 26.9 mL, 6.00 mmol, 2.00 equiv) was transferred into a SCHLENK-flask and the solvent was evaporated under stirring *in vacuo*. Methyl 2-bromonicatinate (648 mg, 3.00 mmol, 1.00 equiv), K_2CO_3 (1.66 mg, 12.0 mmol, 4.00 equiv), $Pd(PPh_3)_4$ (173 mg, 0.15 mmol, 0.05 equiv) and dioxane (9.0 mL) were added successively. The mixture was degassed and stirred at 100 °C for 12 h. The crude was diluted with CH_2Cl_2 5 mL and 10 mL sat. $NaHCO_3$ solution. The aqueous phase was extracted with CH_2Cl_2 (3 x 20 mL). The combined organic layer was washed with brine (20 mL) dried over Na_2SO_4, filtered and the solvent was removed under reduced pressure. The crude was purified by column chromatography (*n*-pentane/EtOAc 10:1 → 8:1 → 6:1) to give the product **S2** (288 mg, 1.41 mmol, 47%) as a yellow oil.

^{1}H NMR: (500 MHz, $CDCl_3$) δ = 8.65 (dd, *J* = 4.8, 1.8 Hz, 1H, CH_{arom}), 8.13 (dd, *J* = 7.9, 1.8 Hz, 1H, CH_{arom}), 7.19 (dd, *J* = 7.9, 4.8 Hz, 1H, CH_{arom}), 5.37 (tp, *J* = 6.9, 1.4 Hz, 1H, CH_{olef}), 3.92 (d, *J* = 7.4 Hz, 2H, CH_2), 3.91 (s, 3H, COOCH_3), 1.75 (d, *J* = 1.3 Hz, 3H, CH_3), 1.72 (q, *J* = 1.4 Hz, 3H, CH_3) ppm. **^{13}C NMR**: (126 MHz, $CDCl_3$) δ = 167.4, 162.5, 152.1, 138.6, 133.5, 125.6, 121.4, 121.0, 52.5, 36.2, 26.0, 18.4 ppm. **IR** (ATR) $\tilde{\nu}$ (cm^{-1}) = 2952 (w), 2915 (w), 2857 (w), 1727 (s), 1583 (w), 1568 (m), 1430 (s), 1376 (w), 1264 (s), 1189 (w), 1128 (s), 1101 (w), 1080 (s), 1060 (w), 964 (w), 923 (w), 875 (w), 838 (w), 78t6 (w), 758 (m), 608 (w), 551 (w), 449 (w). **HRMS** (ESI+) m/z: [M+H]+ Calcd for C12H15NO2H 206.1176, Found 206.1172.

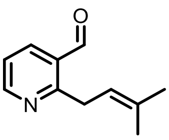
(2-(3-methylbut-2-en-1-yl)pyridin-3-yl)methanol **S3**,



Pyridine **S2** (287 mg, 1.40 mmol, 1.00 equiv) was dissolved in anhydrous MeOH (1.40 mL). NaOMe solution (25% in MeOH, 0.02 mL, 0.07 mmol, 0.05 equiv) and $NaBH_4$ (132 mg, 3.50 mmol, 2.50 equiv) was added successively and the mixture was stirred for 12 h at rt. The mixture was diluted with 5 mL sat. $NaHCO_3$-solution and 10 mL CH_2Cl_2. The layers were separated and the aqueous layer was extracted with CH_2Cl_2 (3 x 10 mL). The combined organic layer was washed with brine (20 mL) dried over Na_2SO_4, filtered and the solvent was removed under reduced pressure. The crude was purified by column chromatography (*n*-pentane/EtOAc 4:1→1:1→1:2→0:1) to give the product **S3** (95.2 mg, 0.54 mmol, 38%) as a colorless oil.

^{1}H NMR: (500 MHz, $CDCl_3$) δ = 8.46 (dd, J = 4.9, 1.8 Hz, 1H, CH_{arom}), 7.74 – 7.69 (m, 1H, CH_{arom}), 7.15 (dd, J = 7.6, 4.9 Hz, 1H, CH_{arom}), 5.32 (tp, J = 6.9, 1.4 Hz, 1H, CH_{olef}), 4.72 (s, 2H, CH_2OH), 3.58 (dt, J = 6.9, 1.2 Hz, 1H, CH_2), 1.97 (s, 1H, O*H*), 1.78 – 1.76 (m, 3H, CH_3), 1.73 (q, J = 1.5 Hz, 3H, CH_3) ppm. **^{13}C NMR**: (126 MHz, $CDCl_3$) δ = 159.2 (C_{arom}), 148.4 (C_{arom}), 135.6 (C_{arom}), 134.0 (C_{arom}), 133.5 (C_{olef}), 121.6 (C_{arom}), 121.4 (CH_{olef}), 62.2 (CH_2OH), 34.9 (CH_2), 25.9 (CH_3), 18.3 (CH_3) ppm. **IR** (ATR) $\tilde{\nu}$ (cm^{-1}) = 3225 (w), 3059 (w), 2967 (w), 2914 (m), 2856 (w), 1728 (m), 1671 (w), 1579 (m), 1434 (s), 1405 (w), 1376 (w), 1357 (w), 1266 (m), 1129 (w), 1100 (w), 1082 (w), 1043 (s), 922 (w), 874 (w), 836 (w), 790 (s), 760 (w), 687 (w), 616 (w), 554 (w), 450 (w). **HRMS** (ESI+) m/z: [M+H]+ Calcd for C11H16NOH 178.1223, Found 178.1226.

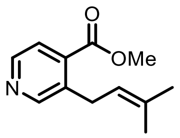
2-(3-methylbut-2-en-1-yl)nicotinaldehyde **4h**,



Pyridine **S3** (95.2 mg, 0.54 mmol, 1.00 equiv) was dissolved in anhydrous CH_2Cl_2 (2.6 mL) and the mixture was stirred for 12 h at rt. The mixture was diluted with 5 mL sat. $NaHCO_3$-solution and 10 mL CH_2Cl_2. The layers were separated and the aqueous layer was extracted with CH_2Cl_2 (3 x 10 mL). The combined organic layer was washed with brine (20 mL) dried over Na_2SO_4, filtered and the solvent was removed under reduced pressure. The crude was purified by column chromatography (*n*-pentane/EtOAc 5:1) to give the product **4h** (57.0 mg, 0.33 mmol, 61%) as a yellow oil.

^{1}H NMR: (500 MHz, $CDCl_3$) δ = 10.33 (s, 1H, C*H*O), 8.71 (dd, *J* = 4.8, 1.9 Hz, 1H, CH_{arom}), 8.12 (dd, *J* = 7.8, 1.9 Hz, 1H, CH_{arom}), 7.31 (dd, *J* = 7.8, 4.8 Hz, 1H, CH_{arom}), 5.35 (tp, *J* = 6.9, 1.4 Hz, 1H, CH_{olef}), 3.94 (dt, *J* = 6.8, 1.2 Hz, 2H, CH_2), 1.78 – 1.77 (m, 3H, CH_3), 1.72 (q, *J* = 1.5 Hz, 3H, CH_3) ppm. **^{13}C NMR**: (126 MHz, $CDCl_3$) δ = 191.3 (*C*HO), 163.7 (C_{arom}), 153.7 (C_{arom}), 137.6 (C_{arom}), 134.1 (C_{olef}), 129.4 (C_{arom}), 122.0 (C_{arom}), 121.2 (CH_{olef}), 34.7 (CH_2), 25.9 (CH_3), 18.4 (CH_3) ppm. **IR** (ATR) $\tilde{\nu}$ (cm^{-1}) = 3050 (w), 2969 (w), 2914 (w), 2859 (w), 2748 (w), 1965 (w), 1693 (s), 1581 (s), 1564 (w), 1439 (m), 1391 (m), 1377 (w), 1278 (w), 1254 (w), 1217 (m), 1196 (w), 1153 (w), 1101 (w), 1061 (w), 984 (w), 923 (w), 891 (w), 875 (w), 840 (w), 796 (m), 754 (w), 729 (w), 668 (w), 634 (w), 607 (w), 549 (w), 451 (w), 416 (w). **HRMS** (ESI+) m/z: [M+H]+ Calcd for C11H13NOH 176.1070, Found 176.1067.

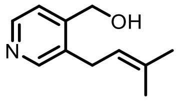
methyl 3-(3-methylbut-2-en-1-yl)isonicotinate **S4**,



A solution of boronic acid **S1** (0.47 M in $CHCl_3$, 4.00 mmol, 2.00 equiv) was transferred into a SCHLENK-flask and the solvent was evaporated under stirring *in vacuo*. Methyl 3-bromoisonicatinate (432 mg, 2.00 mmol, 1.00 equiv), K_2CO_3 (1.11 g, 8.00 mmol, 4.00 equiv) $Pd(PPh_3)_4$ (115 mg, 0.10 mmol, 0.05 equiv) and dioxane (6.0 mL) were added successively. The mixture was degassed and stirred at 100 °C for 12 h. The crude was diluted with CH_2Cl_2 5 mL and 10 mL sat. $NaHCO_3$ solution. The aqueous phase was extracted with CH_2Cl_2 (3 x 10 mL). The combined organic layer was washed with brine (20 mL) dried over Na_2SO_4, filtered and the solvent was removed under reduced pressure. The crude was purified by column chromatography (*n*-pentane/EtOAc 5:1) to give the product **S4** (365 mg, 1.78 mmol, 89%) as a yellow oil.

^{1}H NMR: (500 MHz, $CDCl_3$) δ = 8.58 (s, 1H, CH_{arom}), 8.55 (d, J = 5.0 Hz, 1H, CH_{arom}), 7.61 (d, J = 5.0 Hz, 1H, CH_{arom}), 5.23 (tp, J = 7.1, 1.5 Hz, 1H, CH_{olef}), 3.92 (s, 3H, $COOCH_3$), 3.66 (d, J = 7.1 Hz, 2H, CH_2), 1.73 (d, J = 1.2 Hz, 6H, 2 x CH_3) ppm. **^{13}C NMR**: (126 MHz, $CDCl_3$) δ = 167.0 ($COOCH_3$), 152.4 (C_{arom}), 147.9 (C_{arom}), 136.8 (C_{arom}), 136.7 (C_{olef}), 133.9 (C_{arom}), 123.2 (C_{arom}), 121.7 (CH_{olef}), 52.7 ($COOCH_3$), 30.1 (CH_2), 25.9 (CH_3), 18.1 (CH_3) ppm. **IR** (ATR) $\tilde{\nu}$ (cm^{-1}) = 3214 (m), 3052 (w), 2968 (w), 2915 (w), 1731 (s), 1589 (w), 1482 (w), 1435 (s), 1406 (w), 1274 (s), 1194 (w), 1145 (w), 1118 (w), 1100 (m), 1062 (w), 1027 (w), 965 (w), 883 (w), 848 (w), 834 (w), 786 (w), 748 (w), 720 (m), 696 (w), 673 (w), 643 (w), 542 (m), 513 (w), 478 (w), 450 (w). **HRMS** (ESI+) m/z: [M+Na]+ Calcd for C12H15NO2H 206.1176, Found 206.1171.

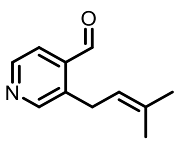
(3-(3-methylbut-2-en-1-yl)pyridin-4-yl)methanol **S5**,



Pyridine **S4** (363 mg, 1.77 mmol, 1.00 equiv) was dissolved in anhydrous MeOH (1.80 mL). NaOMe solution (25% in MeOH, 0.02 mL, 0.09 mmol, 0.05 equiv) and $NaBH_4$ (167 mg, 4.43 mmol, 2.50 equiv) was added successively and the mixture was stirred for 12 h at rt. The mixture was diluted with 5 mL sat. $NaHCO_3$-solution and 10 mL CH_2Cl_2. The layers were separated and the aqueous layer was extracted with CH_2Cl_2 (3 x 10 mL). The combined organic layer was washed with brine (20 mL) dried over Na_2SO_4, filtered and the solvent was removed under reduced pressure. The crude was purified by column chromatography (*n*-pentane/EtOAc 1:1→1:2) to give the product **S5** (89.9 mg, 0.51 mmol, 29%) as a yellow oil.

^{1}H NMR: (500 MHz, $CDCl_3$) δ 8.41 (d, J = 5.0 Hz, 1H, CH_{arom}), 8.32 (s, 1H, CH_{arom}), 7.42 (d, J = 5.0 Hz, 1H, CH_{arom}), 5.14 (tp, J = 7.1, 1.5 Hz, 1H, CH_{olef}), 4.72 (s, 2H, CH_2OH), 3.29 (d, J = 7.0 Hz, 2H, CH_2), 3.07 (br s, 1H, OH), 1.74 – 1.70 (m, 6H, 2 x CH_3) ppm. **^{13}C NMR**: (126 MHz, $CDCl_3$) δ = 149.7 (C_{arom}), 148.2 (C_{arom}), 147.9 (C_{arom}), 134.0 (C_{olef}), 133.8 (C_{arom}), 121.2 (C_{arom}), 121.0 (CH_{olef}), 61.2 (CH_2OH), 29.1 (CH_2), 25.8 (CH_3), 18.0 (CH_3) ppm. **IR** (ATR) $\tilde{\nu}$ (cm^{-1}) = 3476 (w), 2971 (w), 2914 (w), 2858 (w), 2360 (m), 2310 (w), 2276 (w), 1626 (m), 1493 (w), 1434 (s), 1377 (w), 1217 (w), 1160 (s), 1095 (m), 1058 (s), 984 (w), 924 (w), 901 (w), 833 (s), 774 (w), 718 (w), 678 (w), 537 (w), 491 (w), 448 (w). **HRMS** (ESI+) m/z: [M+Na]+ Calcd for C11H15NOH 178.1232, Found 178.1224.

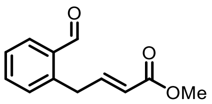
3-(3-methylbut-2-en-1-yl)isonicotinaldehyde **4i**,



Pyridine **S5** (89.9 mg, 0.51 mmol, 1.00 equiv) was dissolved in anhydrous CH_2Cl_2 (2.4 mL) and the mixture was stirred for 12 h at rt. The mixture was diluted with 5 mL sat. $NaHCO_3$-solution and 10 mL CH_2Cl_2. The layers were separated and the aqueous layer was extracted with CH_2Cl_2 (3 x 10 mL). The combined organic layer was washed with brine (20 mL) dried over Na_2SO_4, filtered and the solvent was removed under reduced pressure. The crude was purified by column chromatography (*n*-pentane/EtOAc 5:1) to give the product **4i** (34.0 mg, 0.19 mmol, 38%) as a yellow oil.

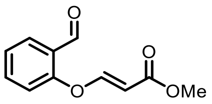
^{1}H NMR: (500 MHz, $CDCl_3$) δ = 10.33 (s, 1H, CHO), 8.69 (d, *J* = 5.0 Hz, 1H, CH_{arom}), 8.65 (s, 1H, CH_{arom}), 7.61 (d, *J* = 5.0 Hz, 1H, CH_{arom}), 5.24 (tp, *J* = 7.1, 1.5 Hz, 1H, CH_{olef}), 3.73 (d, *J* = 7.1 Hz, 2H, CH_2), 1.76 – 1.74 (m, 3H, CH_3), 1.73 (q, *J* = 1.4 Hz, 3H, CH_3) ppm. **^{13}C NMR**: (126 MHz, $CDCl_3$) δ = 191.9 (CHO), 152.8 (C_{arom}), 149.0 (C_{arom}), 139.0 (C_{arom}), 137.0 (C_{arom}), 134.3 (C_{olef}), 122.3 (C_{arom}), 121.7 (CH_{olef}), 28.9 (CH_2), 25.8 (CH_3), 18.2 (CH_3) ppm. **IR** (ATR) $\tilde{\nu}$ (cm^{-1}) = 3028 (w), 2971 (w), 2915 (w), 2858 (w), 2749 (w), 1705 (s), 1561 (w), 1482 (w), 1449 (w), 1409 (m), 1377 (w), 1310 (w), 1284 (w), 1220 (m), 1200 (w), 1133 (w), 1099 (w), 1054 (w), 984 (w), 829 (m), 800 (w), 773 (w), 738 (w), 658 (m), 438 (w). **HRMS** (ESI+) m/z: [M+H]+ Calcd for C11H13NOH 176.1070, Found 176.1068.

methyl (*E*)-4-(2-formylphenyl)but-2-enoate **S6**



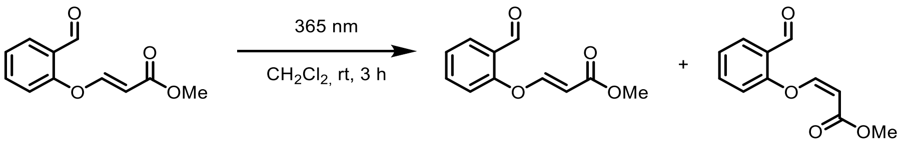
was obtained according to a protocol reported by DIXON *et al*.[3]

methyl (*E*)-3-(2-formylphenoxy)acrylate **S7**



was obtained according to a protocol reported by KOKETSU *et al*.[4]

5.1 Isomerisation Reaction of S7



S7 (64.3 mg, 0.29 mmol, 0.015 M) was irradiated in CH_2Cl_2 (19.5 mL) with 365 nm UV-Light for 3 h. The solvent was removed under reduced pressure. The isomer mixture was obtained in a 1:0.82 *E/Z*-ratio (see Figure 4).

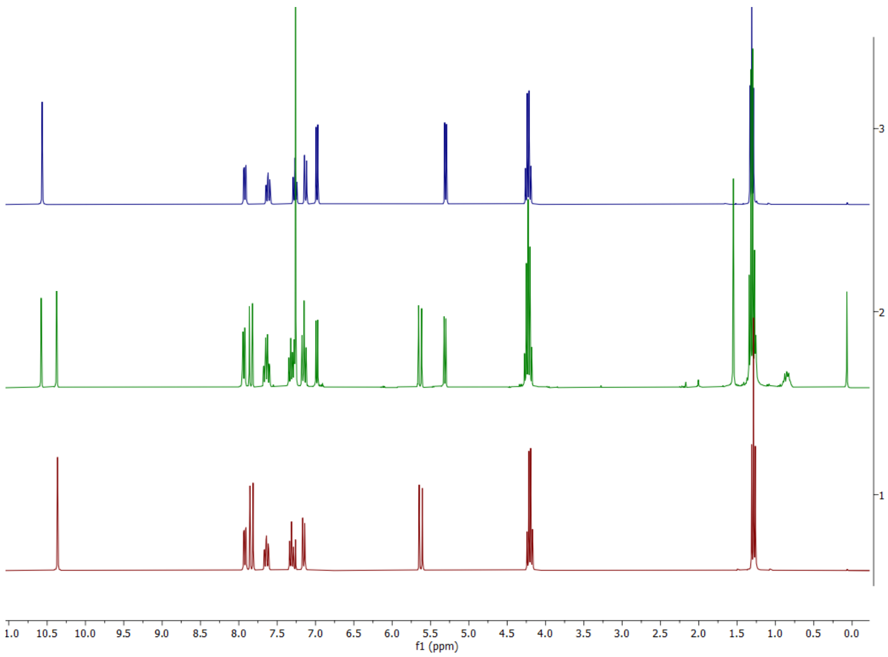


Figure 3: Stacked ^{1}H-NMR spectra of **S7**-(*E*)-isomer (blue), **S7**-isomer mixture after irradiation (green), **S7**-(*Z*)-isomer (red).

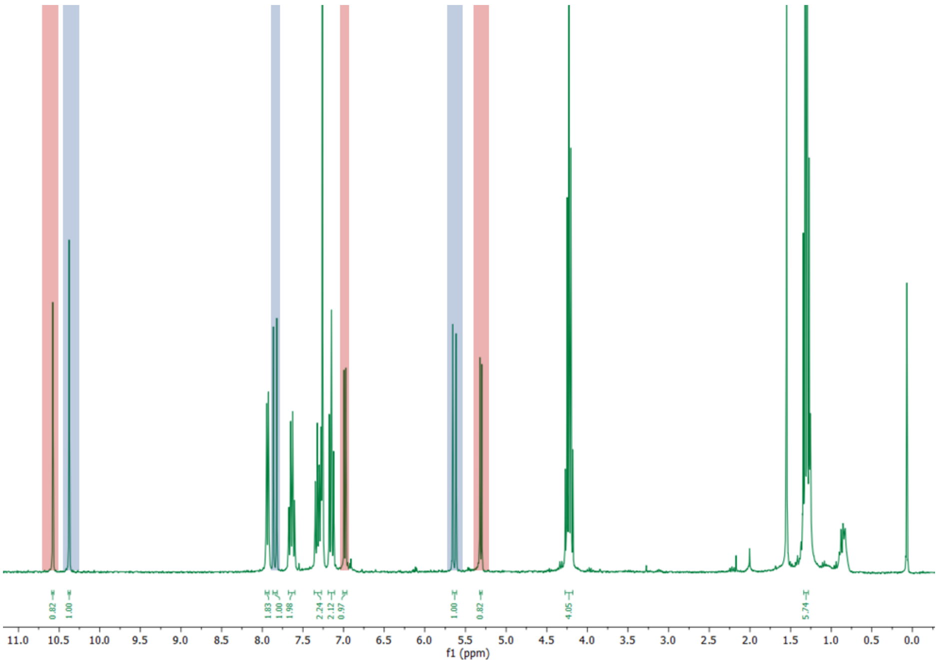
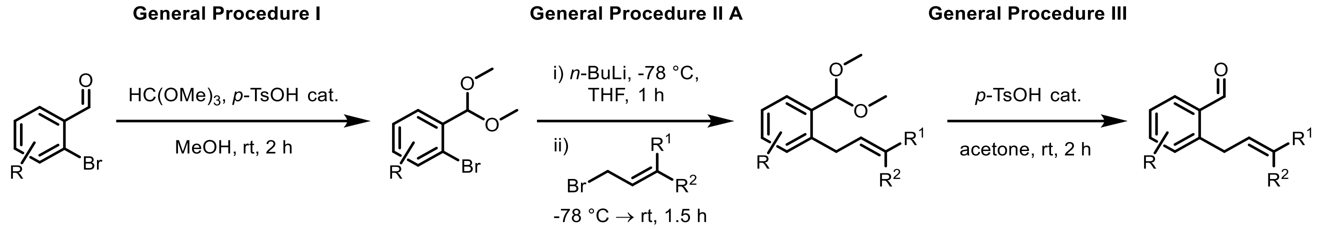
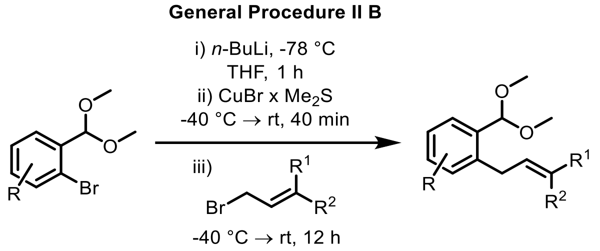


Figure 4: ^{1}H-NMR spectrum of irridation mixture of **S7.** *E*-isomer (blue) and *Z*-isomer (red) marked.

6 General Procedures I – III: Substrate Synthesis





General Procedure I: Acetylation

The acetylation was carried out according to a protocol reported by NISHIBAYASHI *et al.*[5]

2-Bromobenzaldeyde **3S** (1.00 equiv) and anhydrous MeOH (17 M) were placed in a SCHLENK-flask under inert atmosphere. Trimethyl orthomormate (4.00 equiv) and *p*TsOH x H_2O (0.01 equiv) were added and the reaction mixture was stirred for 2 h at rt. The mixture was concentrated under reduced pressure. Sat. $NaHCO_3$-solution was added and the mixture was extracted with Et_2O (3 x). The combined organic layers were washed with water (2 x) and brine, dried over Na_2SO_4. The product was purified as indicated.

General Procedure II A: Alkylation

Unless otherwise noted the alkylation was carried out with the following protocol.

To a solution of *ortho*-bromo acetal **3S** (1.00 equiv) in anhydrous THF (0.3 M) at -78 °C *n*-BuLi (1.10 equiv, 2.5 M) were added dropwise and the solution was stirred for 1 h. R^1,R^2-Allylbromide (1.30 equiv) was added to the solution and the mixture was allowed to warm to rt for 2 h. The reaction was quenched with sat. $NaHCO_3$-solution and extracted with Et_2O (3 x). The combined organic layers were washed with brine and dried over Na_2SO_4. The solvent was removed under reduced pressure. Unless otherwise noted, the obtained acetal was used in the next reaction without further purification and characterization due to instability on the column chromatography.

General Procedure II B: Alkylation

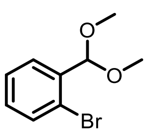
Unless otherwise noted the alkylation was carried out with the following protocol.

To a solution of *ortho*-bromo acetal **3S** (1.00 equiv) in anhydrous THF (0.3 M) at -78 °C *n*-BuLi (1.10 equiv, 2.5 M) were added dropwise and the solution was stirred for 1 h. CuBr x Me_2S (0.5 equiv) were added and the reaction was allowed to warm to -40 °C and stirred at -40 °C for 40 min. R^1,R^2-Allylbromide (1.30 equiv) was added to the solution and the mixture was allowed to warm to rt over night. The reaction was quenched with sat. $NaHCO_3$-solution and extracted with Et_2O (3 x). The combined organic layers were washed with brine and dried over Na_2SO_4. The solvent was removed under reduced pressure. Unless otherwise noted, the obtained acetal was used in the next reaction without further purification and characterization due to instability on the column chromatography.

General Procedure III: Acetal Cleavage

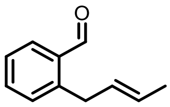
Acetal **3S** (1.00 equiv) was dissolved in acetone (0.075 M) and *p*TsOH x H_2O (0.05 equiv) was added. The solution was stirred for 2 h at rt. Et_2O and sat. $NaHCO_3$-solution were added and the mixture was extracted with Et_2O (3 x). The combined organic layers were washed with brine and dried over Na_2SO_4. The solvent was removed under reduced pressure. The residue was purified by column chromatography to give **4** as a colorless oil

1-bromo-2-(dimethoxymethyl)benzene **3S1**



was obtained according to general procedure I, a protocol reported by NISHIBAYASHI *et al.*[5]

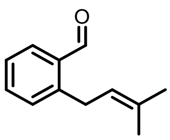
2-(but-2-en-1-yl)benzaldehyde **4k**



was obtained utilizing first the general procedure II A, using corresponding aryl bromide **3S1** (2.31 g, 10.0 mmol) and crotyl bromide (1.34 mL, 13.0 mmol). The crude was then used according to general procedure III. Purification by column chromatography using 100:1 (*n*-pentane/Et_2O) afforded **4k** (1.21 mg, 7.57 mmol, 76% over two steps, *E/Z* 86:14) as a colorless oil.

^{1}H NMR: (500 MHz, $CDCl_3$) δ = 10.29 (s, 1H, C*H*O), 7.86 – 7.82 (m, 1H, CH_{arom}), 7.53 (s, 1H, CH_{arom}), 7.37 (tdd, *J* = 7.7, 1.2, 0.4 Hz, 1H, CH_{arom}), 7.33 – 7.31 (m, 0.14H, $CH_{arom,minor}$), 7.29 (ddd, *J* = 7.6, 1.3, 0.7 Hz, 0.86H, $CH_{arom,major}$), 5.67 – 5.51 (m, 1.23H, CH_{olef}, $CH_{olef,minor}$), 5.48 – 5.40 (m, 0.86H, $CH_{olef,major}$), 3.84 (d, *J* = 6.9 Hz, 0.28H, $CH_{2,minor}$), 3.75 (dt, *J* = 6.3, 1.6 Hz, 1.75H, $CH_{2,major}$), 1.75 (ddt, *J* = 6.6, 1.6, 0.9 Hz, 0.41H, $CH_{3,minor}$), 1.66 (dq, *J* = 6.4, 1.5 Hz, 2.60H, $CH_{2,major}$) ppm. **^{13}C NMR**: (126 MHz, $CDCl_3$) δ = 192.6 (CHO_{minor}), 192.5 (CHO_{major}), 143.6 ($C_{arom,major}$), 134.1 ($C_{arom, major}$), 134.0 ($C_{arom,minor}$), 131.8 ($C_{arom,minor}$), 131.2 ($C_{arom,major}$), 131.1 ($C_{arom,major}$), 130.7 ($C_{arom,minor}$), 129.8 ($CH_{olef,major}$), 128.6 ($C_{arom,minor}$), 127.3 ($CH_{olef, major}$), 126.9 ($C_{arom,major}$), 126.8 ($C_{arom,minor}$), 125.5 ($C_{arom,minor}$), 35.5 ($CH_{2,major}$), 30.2 ($CH_{2,minor}$), 18.0 ($CH_{3,major}$), 13.1 ($CH_{3,minor}$) ppm. **IR** (ATR) $\tilde{\nu}$ (cm^{-1}) = 3024 (w), 2916 (w), 2855 (w), 2733 (w), 1692 (s), 1598 (m), 1573 (w), 1485 (w), 1451 (w), 1401 (w), 1377 (w), 1287 (w), 1264 (w), 1206 (m), 1159 (w), 1112 (w), 1088 (w), 1057 (w), 1044 (w), 1029 (w), 967 (m), 899 (w), 858 (w), 832 (w), 808 (w), 752 (s), 687 (w), 660 (w), 635 (w), 587 (w), 547 (w), 468 (w), 435 (w). **HRMS** (ESI+) m/z: [M+Na]+ Calcd for C11H12OH 161.0961, Found 161.0960.

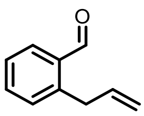
2-(3-methylbut-2-en-1-yl)benzaldehyde **4l**



was obtained utilizing first the general procedure II A, using corresponding aryl bromide **3S1** (1.16 g, 5.00 mmol) and prenyl bromide (0.75 mL, 6.50 mmol). The crude was then used according to general procedure III. Purification by column chromatography using 100:1 (*n*-pentane/Et_2O) afforded **4l** (418 mg, 2.40 mmol, 48% over two steps) as a colorless oil.

^{1}H NMR: (300 MHz, $CDCl_3$) δ = 10.29 (s, 1H, C*H*O), 7.84 (dd, *J* = 7.6, 1.7 Hz, 1H, CH_{arom}), 7.51 (td, *J* = 7.6, 1.6 Hz, 1H, CH_{arom}), 7.42 – 7.26 (m, 2H, 2 x CH_{arom}), 5.27 (ddp, *J* = 7.0, 5.7, 1.5 Hz, 1H, CH_{olef}), 3.76 (d, *J* = 7.1 Hz, 2H, CH_2), 1.74 (s, 2H, CH_3), 1.73 (s, 3H, CH_3) ppm. **^{13}C NMR**: (75 MHz, $CDCl_3$) δ = 192.7 (*C*HO), 144.7, 134.2, 134.0, 133.3, 131.4, 130.8, 126.7, 122.9, 31.5, 25.9, 18.2 ppm. **IR** (ATR) $\tilde{\nu}$ (cm^{-1}) = 3367 (w), 2978 (w), 2934 (w), 1694 (s), 1601 (w), 1464 (w), 1378 (w), 1328 (w), 1285 (w), 1206 (m), 1156 (w), 1093 (w), 1034 (w), 976 (w), 842 (w), 753 (s), 711 (w), 686 (w), 637 (w), 591 (w), 467 (w). **HRMS** (ESI+) m/z: [M+H]+ Calcd for C12H14OH 175.1117, Found 175.0750.

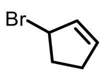
2-allylbenzaldehyde **4m**,



To a solution of *ortho*-bromo acetal **3S1** (466 mg, 1.90 mmol) in anhydrous THF (5.8 mL) at -78 °C *n*-BuLi (0.87 mL, 2.5 M) were added dropwise and the solution was stirred for 30 min. To the solution CuBr x Me_2S (195 mg, 0.95 mmol) was added and the mixture was warmed to -40 °C for 1 h. Allylbromide (0.22 mL, 2.47 mmol) was added dropwise and the reaction was stirred for 18 h at rt. To the mixture sat. ammonium chloride solution (10 mL) was added carefully. The mixture was extracted with Et_2O (3 x 15 mL). The combined organic phases were washed with brine, dried with Na_2SO_4, filtered and concentrated under reduced pressure. The crude was then treated according to general procedure III. Purification by column chromatography using 100:1 (*n*-pentane/Et_2O) afforded **4m** (166 mg, 1.14 mmol, 60% over two steps) as a colorless oil.

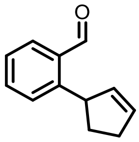
^{1}H NMR: (500 MHz, $CDCl_3$) δ = 10.26 (s, 1H, C*H*O), 7.85 (dd, *J* = 7.6, 1.6 Hz, 1H, CH_{arom}), 7.54 (td, *J* = 7.5, 1.5 Hz, 1H, CH_{arom}), 7.40 (td, *J* = 7.5, 1.3 Hz, 1H, CH_{arom}), 7.30 (dd, *J* = 7.6, 1.1 Hz, 1H, CH_{arom}), 6.04 (ddt, *J* = 17.1, 10.1, 6.2 Hz, 1H, CH_{olef}), 5.09 (dq, *J* = 10.1, 1.5 Hz, 1H, CHH_{olef}), 4.98 (dq, *J* = 17.1, 1.7 Hz, 1H, CHH_{olef}), 3.83 (dt, *J* = 6.3, 1.8 Hz, 2H, CH_2) ppm. **^{13}C NMR**: (126 MHz, $CDCl_3$) δ = 192.5 (*C*HO), 142.4 (C_{arom}), 137.1 (C_{arom}), 134.1 (C_{arom}), 134.0 (C_{arom}), 131.7 (C_{arom}), 131.2 (C_{arom}), 127.1 (C_{arom}), 116.6 (C_{arom}), 36.7 (CH_2)ppm. **IR** (ATR) $\tilde{\nu}$ (cm^{-1}) = 3076 (w), 3008 (w), 2979 (w), 2859 (w), 2735 (w), 1694 (s), 1637 (w), 1599 (m), 1574 (w), 1485 (w), 1452 (w), 1404 (w), 1287 (w), 1208 (m), 1190 (w), 1161 (w), 1093 (w), 995 (w), 916 (w), 856 (w), 835 (w), 803 (w), 780 (w), 753 (s), 661 (w), 635 (w), 555 (w), 512 (w), 441 (w). **HRMS** (ESI+) m/z: [M+H]+ Calcd for C10H10OH 147.0804, Found 147.0807.

3-bromocyclopent-1-ene **S8**



was obtained according to a protocol reported by TAN *et al*.[6]

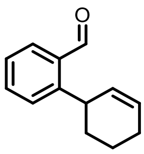
2-(cyclopent-2-en-1-yl)benzaldehyde **4o**



was obtained utilizing first the general procedure II B, using corresponding aryl bromide **3S1** (0.70 g, 3.00 mmol) and 3-bromocyclopent-1-ene **S8** (0.74 mL, 6.50 mmol). The crude was then used according to general procedure III. Purification by column chromatography using 100:1 (*n*-pentane/Et_2O) afforded **4o** (42.0 mg, 0.24 mmol, 16% over two steps) as a colorless oil.

^{1}H NMR: (500 MHz, $CDCl_3$) δ = 10.39 (s, 1H, C*H*O), 7.86 – 7.80 (m, 1H, CH_{arom}), 7.52 (td, *J* = 7.6, 1.5 Hz, 1H, CH_{arom}), 7.40 – 7.31 (m, 1H, CH_{arom}), 6.02 (dq, *J* = 5.8, 2.4 Hz, 1H, CH_{olef}), 5.79 (dq, *J* = 5.7, 2.1 Hz, 1H, CH_{olef}), 4.84 (ddt, *J* = 9.1, 4.5, 2.3 Hz, 1H, C$H_{benzylic}$), 2.61 – 2.52 (m, 1H, C*H*H), 2.52 – 2.41 (m, 2H, CH_2), 1.66 (ddt, *J* = 12.5, 8.6, 6.7 Hz, 1H, CH*H*) ppm. **^{13}C NMR**: (126 MHz, $CDCl_3$) δ = 192.7 (*C*HO), 149.0 (C_{arom}), 134.2 (C_{arom}), 133.5 (C_{arom}), 133.2 (CH_{olef}), 133.1 (CH_{olef}), 131.6 (C_{arom}), 127.9 (C_{arom}), 126.6 (C_{arom}), 46.1 (*C*H), 34.1 (CH_2), 32.5 (CH_2) ppm. **IR** (ATR) $\tilde{\nu}$ (cm^{-1}) = 3369 (w), 3056 (w), 2937 (w), 2850 (w), 2733 (w), 1691 (s), 1597 (m), 1572 (w), 1483 (w), 1453 (w), 1406 (w), 1353 (w), 1292 (w), 1207 (w), 1189 (w), 1162 (w), 1109 (w), 1012 (w), 952 (w), 915 (w), 849 (w), 823 (w), 758 (s), 657 (w), 575 (w), 535 (w), 441 (w). **HRMS** (APCI+) m/z: [M+H]+ Calcd for C12H12OH 173.0961, Found 173.0958.

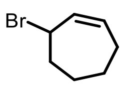
1',2',3',4'-tetrahydro-[1,1'-biphenyl]-2-carbaldehyde **4p**



was obtained utilizing first the general procedure II A, using corresponding aryl bromide **3S1** (577 mg, 2.50 mmol) and cyclohexenyl bromide (0.37 mL, 3.25 mmol). The crude was then used according to general procedure III. Purification by column chromatography using 50:1 (*n*-pentane/Et_2O) afforded **4p** (0.14 g, 0.72 mmol, 29% over two steps) as a colorless oil.

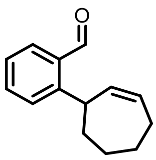
^{1}H NMR: (300 MHz, $CDCl_3$) δ = 10.36 (s, 1H, C*H*O), 7.84 (d, *J* = 7.6 Hz, 1H, CH_{arom}), 7.54 (t, *J* = 7.6 Hz, 1H, CH_{arom}), 7.44 – 7.34 (m, 2H, 2 x CH_{arom}), 5.98 (ddd, *J* = 10.1, 3.6, 2.5 Hz, 1H, CH_{olef}), 5.75 – 5.66 (m, 1H, CH_{olef}), 4.40 (dq, *J* = 5.5, 2.9 Hz, 1H, C$H_{benzylic}$), 2.19 – 2.08 (m, 3H, 1.5 x CH_2), 1.79 – 1.65 (m, 2H, CH_2), 1.58 – 1.48 (m, 1H, 0.5 x CH_2) ppm. **^{13}C NMR**: (75 MHz, $CDCl_3$) δ = 192.6 (*C*HO), 149.2 (C_{arom}), 133.9 (C_{arom}), 133.5 (C_{arom}), 131.9 (C_{arom}), 129.6 (C_{arom}), 129.4 (C_{olef}), 129.3 (C_{olef}), 126.6 (C_{arom}), 36.7 (*C*H), 32.9 (CH_2), 25.1 (CH_2), 21.3 (CH_2) ppm. **IR** (ATR) $\tilde{\nu}$ (cm^{-1}) 3020 (w), 2928 (m), 2858 (w), 2836 (w), 2732 (w), 1691 (s), 1598 (m), 1572 (w), 1483 (w), 1449 (w), 1407 (w), 1320 (w), 1291 (w), 1248 (w), 1191 (m), 1161 (w), 1135 (w), 1105 (w), 984 (w), 932 (w), 900 (w), 853 (w), 822 (w), 786 (w), 758 (s), 722 (w), 640 (w), 602 (w), 539 (w), 442 (w). **HRMS** (ESI+) m/z: [M+Na]+ Calcd for C13H14O1Na 187.1114, Found 187.1117.

3-bromocyclohept-1-ene **S9**



was obtained according to a protocol reported by TAN *et al*.[6]

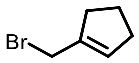
2-(cyclohept-2-en-1-yl)benzaldehyde **4q**



was obtained utilizing first the general procedure II B, using corresponding aryl bromide **3S1** (0.35 g, 1.50 mmol) and 3-bromocyclohept-1-ene **S9** (0.29 mL, 1.95 mmol). The crude was then used according to general procedure III. Purification by column chromatography using 100:1 (*n*-pentane/Et_2O) afforded **4q** (122 mg, 0.49 mmol, 33% over two steps) as a colorless oil.

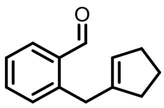
^{1}H NMR: (300 MHz, $CDCl_3$) δ = 10.38 (s, 1H, C*H*O), 7.84 (d, *J* = 7.7 Hz, 1H, CH_{arom}), 7.54 (d, *J* = 7.6 Hz, 1H, CH_{arom}), 7.43 (d, *J* = 6.7 Hz, 1H, CH_{arom}), 7.36 (d, *J* = 7.5 Hz, 1H, CH_{arom}), 5.94 – 5.84 (m, 1H, CH_{olef}), 5.79 – 5.71 (m, 1H, CH_{olef}), 4.53 – 4.44 (m, 1H, C$H_{benzylic}$), 2.34 – 2.22 (m, 2H, CH_2), 2.03 – 1.94 (m, 1H, 0.5 x CH_2), 1.89 – 1.71 (m, 4H, 2 x CH*H*, 2 x C*H*H), 1.53 – 1.43 (m, 1H, 0.5 x CH_2) ppm. **^{13}C NMR**: (126 MHz, $CDCl_3$) δ = 192.5 (*C*HO), 150.5 (C_{arom}), 136.3 (CH_{olef}), 134.1 (C_{arom}), 133.0 (C_{arom}), 132.3 (CH_{olef}), 131.2 (C_{arom}), 128.8 (C_{arom}), 126.5 (C_{arom}), 41.9 ($CH_{benzylic}$), 36.8 (CH_2), 30.5 (CH_2), 29.0 (CH_2), 27.1 (CH_2) ppm. **IR** (ATR) $\tilde{\nu}$ (cm^{-1}) = 3032 (w), 2927 (m), 2855 (w), 2739 (w), 1693 (s), 1599 (m), 1574 (w), 1482 (w), 1446 (w), 1401 (w), 1291 (w), 1262 (w), 1240 (w), 1185 (m), 1162 (w), 1080 (w), 1030 (w), 908 (w), 835 (w), 819 (w), 756 (s), 684 (w), 656 (w), 621 (w), 606 (w), 539 (w), 481 (w), 443 (w). **HRMS** (EI+) m/z: [M+H]+ Calcd for C14H16O 200.12011, Found 200.12066.

1-(bromomethyl)cyclopent-1-ene **S10**



was obtained according to a protocol reported by WERZ *et al.*[7]

2-(cyclopent-1-en-1-ylmethyl)benzaldehyde **4t**

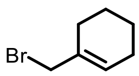


was prepared according to a protocol reported by DIXON *et al*.[3]

Magnesium turnings (120 mg, 4.93 mmol, 1.14 equiv) and iodine crystals were degassed and stirred in THF (2 mL) at rt until mixture did the color disappeared. A solution of aryl bromide **3S1** (1.00 g, 4.33 mmol, 1.00 equiv) in THF (5 mL) was added and stirred for 10 min before being cooled to – 78 °C and stirred for 1h. 8 mL THF were added, followed by CuBr x Me_2S (44.5 mg, 0.22 mmol, 0.05 equiv) and stirred for 10 min. Bromide **S10** (0.66 mL, 5.63 mmol, 1.30 equiv) was added and the mixture was allowed to warm to rt over 16 h. The reaction mixture was quenched by sat. NH_4Cl solution (15 mL) and extracted with CH_2Cl_2 (3 x 15 mL). The combined organic layer was washed with brine (20 mL), dried over Na_2SO_4 and the solvent was removed under reduced pressure. The crude was then used according to general procedure III. Purification by column chromatography using 100:1 (*n*-pentane/Et_2O) afforded **4t** (126 mg, 0.67 mmol, 16% over two steps) as a colorless oil.

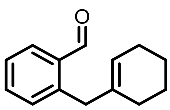
^{1}H NMR: (300 MHz, $CDCl_3$) δ 10.26 (s, 1H, C*H*O), 7.87 (d, J = 7.6 Hz, 1H, CH_{arom}), 7.51 (td, J = 7.5, 1.7 Hz, 1H, CH_{arom}), 7.37 (t, J = 7.5 Hz, 1H, CH_{arom}), 7.27 (d, J = 7.6 Hz, 1H, CH_{arom}), 5.12 (s, 1H, CH_{olef}), 3.77 (s, 2H, CH_2), 2.27 (t, J = 7.3 Hz, 4H, 2 x CH_2), 1.86 (p, J = 7.4 Hz, 2H, CH_2) ppm. **^{13}C NMR**: (75 MHz, $CDCl_3$) δ = 192.2 (*C*=O), 144.1 (C_{olef}), 142.9 (C_{arom}), 134.2 (C_{arom}), 133.9 (C_{arom}), 131.5 (C_{arom}), 130.1 (C_{arom}), 126.9 (C_{arom}), 126.5 (CH_{olef}), 35.5 (CH_2), 34.4 ($CH_{2,benzylic}$), 32.6 (CH_2), 23.5 (CH_2) ppm. **IR** (ATR) $\tilde{\nu}$ (cm^{-1}) = 3049 (w), 2923 (w), 2893 (w), 2845 (m), 2755 (w), 1693 (s), 1598 (m), 1573 (w), 1484 (w), 1450 (w), 1400 (w), 1286 (w), 1205 (m), 1160 (w), 1127 (w), 1088 (w), 1036 (w), 962 (w), 861 (w), 840 (w), 805 (w), 758 (s), 662 (w), 637 (w), 585 (w), 472 (w), 437 (w). **HRMS** (ESI+) m/z: [M]+ Calcd for C13H14OH 187.1117, Found 187.1113.

1-(bromomethyl)cyclohex-1-ene **S11**



was obtained according to a protocol reported by BOWER *et al.*[8]

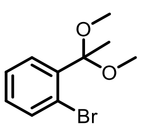
2-(cyclohex-1-en-1-ylmethyl)benzaldehyde **4u**



was obtained utilizing first the general procedure II A, using corresponding aryl bromide **3S1** (185 mg, 0.80 mmol) and 1-(bromomethyl)cyclohex-1-ene **S11** (0.14 mL, 1.04 mmol). The crude was then used according to general procedure III. Purification by column chromatography using 50:1 (*n*-pentane/Et_2O) afforded **4u** (106 mg, 0.53 mmol, 98% over two steps) as a colorless oil.

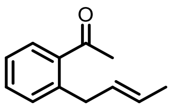
^{1}H NMR: (300 MHz, $CDCl_3$) δ = 10.28 (s, 1H, C*H*O), 7.87 (d, *J* = 7.6 Hz, 1H, CH_{arom}), 7.51 (t, *J* = 7.5 Hz, 1H, CH_{arom}), 7.36 (t, *J* = 7.5 Hz, 1H, CH_{arom}), 7.26 (d, *J* = 7.6 Hz, 1H, CH_{arom}), 5.25 – 5.17 (m, 1H, CH_{olef}), 3.65 (s, 2H, $CH_{2,benzyl}$), 2.02 – 1.89 (m, 4H, 2 x $CH_{2,cychex}$), 1.68 – 1.46 (m, 4H, 2 x $CH_{2,cychex}$) ppm. **^{13}C NMR**: (75 MHz, $CDCl_3$) δ = 192.2 (*C*HO), 142.9 (C_{arom}), 137.7 (C_{olef}), 134.6 (C_{arom}), 133.9 (C_{arom}), 131.7 (C_{arom}), 129.8 (C_{arom}), 126.9 (C_{arom}), 124.0 (CH_{olef}), 40.3 (CH_2), 29.0 ($CH_{2,cychex}$), 25.4 ($CH_{2,cychex}$), 23.0 ($CH_{2,cychex}$), 22.5 ($CH_{2,cychex}$) ppm. **IR** (ATR) $\tilde{\nu}$ (cm^{-1}) = 3000 (w), 2925 (m), 2855 (w), 2834 (w), 2755 (w), 1692 (s), 1598 (m), 1573 (w), 1484 (w), 1449 (w), 1399 (w), 1373 (w), 1342 (w), 1292 (w), 1242 (w), 1206 (m), 1159 (w), 1134 (w), 1077 (w), 1046 (w), 999 (w), 955 (w), 920 (w), 865 (w), 838 (w), 805 (w), 750 (s), 636 (m), 596 (w), 514 (w), 473 (w), 435 (w). **HRMS** (EI+) m/z: [M]+ Calcd for C14H16O 200.12011, Found 200.11818.

1-bromo-2-(1,1-dimethoxyethyl)benzene **S12**



was obtained according to a protocol reported by YANG *et al.*[9]

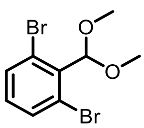
1-(2-(but-2-en-1-yl)phenyl)ethan-1-one **S13**



was obtained utilizing first the general procedure II A, using corresponding aryl bromide **S12** (2.50 g, 10.2 mmol) and crotyl bromide (1.36 mL, 13.3 mmol). The crude was then used according to general procedure III. Purification by column chromatography using 100:1 (*n*-pentane/Et_2O) afforded **S13** (1.13 mg, 6.47 mmol, *E/Z* 86:14, 56% over two steps) as a colorless oil.

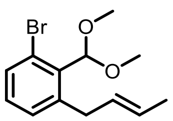
^{1}H NMR: (500 MHz, $CDCl_3$) δ = 7.61 (d, *J* = 1.2 Hz, 1H, CH_{arom}), 7.40 (td, *J* = 7.7, 1.4 Hz, 1H, CH_{arom}), 7.31 – 7.25 (m, 2H, 2 x CH_{arom}), 5.47 (s, 2H, 2 x CH_{olef}), 3.65 (d, *J* = 7.5 Hz, 0.29H, $CH_{2,minor}$), 3.56 (d, *J* = 8.0 Hz, 1.71H, $CH_{2,major}$), 2.58 (s, 0.44H, C=O$CH_{3,minor}$), 2.56 (s, 2.52H, C=O$CH_{3,major}$), 1.72 – 1.70 (m, 0.44H, $CH_{olef}CH_{3,minor}$), 1.66 (dq, *J* = 6.3, 1.3 Hz, 2.56H, $CH_{olef}CH_{3,major}$) ppm. **^{13}C NMR**: (126 MHz, $CDCl_3$) δ = 202.6 (C=O_{major}), 202.5 (C=O_{minor}), 141.0 ($C_{arom,minor}$), 140.8 ($C_{arom,major}$), 138.3 ($C_{arom,minor}$), 138.3 ($C_{arom,major}$), 131.6 ($C_{arom,ffminor}$), 131.5 ($C_{arom,major}$), 131.2 ($C_{arom,major}$), 130.8 ($C_{arom,minor}$), 130.0 ($CH_{olef,major}$), 129.0 ($C_{arom,minor}$), 129.0 ($CH_{olef,minor}$), 128.9 ($C_{arom,major}$), 126.6 ($CH_{olef,major}$), 126.0 ($C_{arom,major}$), 126.0 ($C_{arom,minor}$), 125.2 ($CH_{olef,minor}$), 36.9 ($CH_{2,major}$), 31.4 ($CH_{2,minor}$), 30.1 (CO$CH_{3,major}$), 30.0 (CO$CH_{3,minor}$), 18.1 ($CH_{3,major}$), 13.1 ($CH_{3,minor}$) ppm. **IR** (ATR) $\tilde{\nu}$ (cm^{-1}) = 3023 (w), 2963 (w), 2916 (w), 2855 (w), 1683 (s), 1599 (w), 1571 (w), 1484 (w), 1435 (w), 1354 (m), 1287 (w), 1249 (s), 1186 (w), 1165 (w), 1124 (w), 1071 (w), 1041 (w), 1014 (w), 967 (m), 938 (w), 757 (s), 718 (w), 685 (w), 600 (s), 543 (w), 458 (w). **HRMS** (ESI+) m/z: [M+H]+ Calcd for C12H14OH 175.1117, Found 175.1117.

1,3-dibromo-2-(dimethoxymethyl)benzene **3S2**



was obtained according to a protocol reported by HALL *et al.*[10]

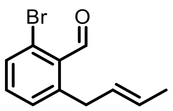
1-bromo-3-(but-2-en-1-yl)-2-(dimethoxymethyl)benzene **S14**



was obtained according to general procedure II A, using corresponding aryl bromide **3S2** (326 g, 1.05 mmol) and crotyl bromide (0.12 mL, 1.16 mmol). Purification by column chromatography using 100:1:5 (*n*-pentane/Et_2O/Et_3N) afforded **S14** (260 mg, 0.91 mmol, 87%, *E/Z* 83:17) as a colorless oil.

^{1}H NMR: (500 MHz, $CDCl_3$) δ = 7.38 (dd, *J* = 7.9, 1.3 Hz, 1H, CH_{arom}), 7.20 (ddd, *J* = 7.7, 1.3, 0.5 Hz, 1H, CH_{arom}), 7.08 (t, *J* = 7.8 Hz, 1H, CH_{arom}), 5.86 (s, 0.17H, $C(OCH_3)_2H_{minor}$), 5.83 (s, 0.83H, $C(OCH_3)_2H_{major}$), 5.60 – 5.47 (m, 2H, 2 x CH_{olef}), 3.76 – 3.74 (m, 0.34H, $CH_{2,minor}$), 3.66 – 3.64 (m, 1.66H $CH_{2,major}$), 3.46 (s, 1.01H, 2 x O$CH_{3,minor}$), 3.45 (s, 4.99H, 2 x O$CH_{3,major}$), 1.74 – 1.72 (m, 0.56H, $CH_{3,minor}$), 1.69 – 1.67 (m, 2.47H, $CH_{3,major}$) ppm. **^{13}C NMR**: (126 MHz, $CDCl_3$) δ = 143.8 ($C_{arom,minor}$), 143.6 ($C_{arom,major}$), 134.7 ($C_{arom,minor}$), 134.6 ($C_{arom,major}$), 130.8 ($C_{arom,major}$), 130.7 ($C_{arom,major}$), 130.7 ($C_{arom,major}$), 130.6 ($C_{arom,minor}$), 130.4 ($CH_{olef,major}$), 129.9 ($C_{arom,minor}$), 129.8 ($CH_{olef,minor}$), 129.8 ($C_{arom,major}$), 126.2 ($CH_{olef,major}$), 124.5 ($C_{arom,minor}$), 124.5 ($C_{arom,minor}$), 124.4 ($CH_{olef,minor}$), 107.9 ($CH(OCH_3)_{2,minor}$), 107.8 ($CH(OCH_3)_{2,major}$), 56.0 (2 x OCH_3), 35.8 ($CH_{2,major}$), 30.0 ($CH_{2,minor}$), 18.1 ($CH_{3,major}$), 13.1 ($CH_{3,minor}$)ppm. **IR** (ATR) $\tilde{\nu}$ (cm^{-1}) = 2989 (w), 2930 (w), 2855 (w), 2828 (w), 1591 (w), 1562 (w), 1450 (w), 1378 (w), 1213 (m), 1185 (w), 1125 (w), 1102 (w), 1067 (s), 993 (w), 964 (m), 910 (w), 890 (w), 817 (w), 777 (m), 743 (w), 706 (w), 689 (w), 601 (w), 567 (w), 545 (w). **HRMS** (ESI+) m/z: [M+Na]+ Calcd for C13H17BrO2Na 307.0304, 309.0285 Found 307.0301, 309.0279.

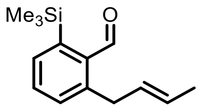
2-bromo-6-(but-2-en-1-yl)benzaldehyde **4j**



was obtained according to general procedure III using **S14** (85.6 mg, 0.30 mmol). Purification by column chromatography using 100:1 (*n*-pentane/Et_2O) afforded **4j** (65.7mg, 0.27 mmol, 92%) as a colorless oil.

^{1}H NMR: (300 MHz, $CDCl_3$) δ = 10.49 (s, 0.2H, CHO_{minor}), 10.47 (s, 0.8H, CHO_{major}), 7.51 (dd, *J* = 7.5, 1.7 Hz, 1H, CH_{arom}), 7.33 – 7.21 (m, 2H, 2 x CH_{arom}), 5.63 – 5.39 (m, 2H, 2 x CH_{olef}), 3.73 (d, *J* = 7.2 Hz, 0.4H, $CH_{2,minor}$), 3.63 (d, *J* = 6.2 Hz, 1.60H $CH_{2,major}$), 1.70 (ddt, *J* = 6.7, 1.9, 0.9 Hz, 0.6H, $CH_{3,minor}$), 1.70 – 1.61 (m, 2.42H, $CH_{3,major}$) ppm. **^{13}C NMR**: (75 MHz, $CDCl_3$) δ = 194.6 (CHO_{minor}), 194.4 (CHO_{major}), 145.4 ($C_{arom,minor}$), 145.3 ($C_{arom,major}$), 133.8 ($C_{arom,major}$), 133.8 ($C_{arom,major}$), 133.7 ($C_{arom,minor}$), 132.1 ($C_{arom,minor}$), 132.0 ($C_{arom,major}$), 131.9 ($C_{arom,minor}$), 131.8 ($C_{arom,minor}$), 130.6 ($C_{arom,major}$), 130.2 ($C_{arom,minor}$), 129.1 ($CH_{olef,major}$), 127.9 ($CH_{olef,minor}$), 127.7 ($C_{arom,major}$), 127.3 ($CH_{olef,major}$), 126.0 ($CH_{olef,minor}$), 36.4 ($CH_{2,major}$), 30.8 ($CH_{2,minor}$), 18.0 ($CH_{3,major}$), 13.1 ($CH_{3,minor}$) ppm. **IR** (ATR) $\tilde{\nu}$ (cm^{-1}) = 3024 (w), 2963 (w), 2917 (w), 2854 (w), 2764 (w), 1697 (s), 1587 (w), 1557 (w), 1449 (m), 1401 (w), 1377 (w), 1248 (w), 1185 (w), 1132 (w), 1102 (w), 1054 (w), 968 (w), 943 (w), 858 (w), 779 (m), 726 (w), 680 (w), 603 (w). **HRMS** (ESI+) m/z: [M+H]+ Calcd for C11H11BrOH 239.0066, 241.0046, Found 239.0064, 241.0044.

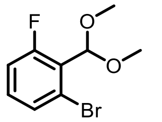
2-(but-2-en-1-yl)-6-(trimethylsilyl)benzaldehyde **4f**



Aryl bromide **S14** (150 mg, 0.53 mmol, 1.00 equiv) was dissolved in anhydrous THF (1.6 mL), cooled to -78 °C, *n*-BuLi (2.5 M, 0.23 mL, 0.58 mmol, 1.10 equiv) was added dropwise and stirred for 1 h. A solution of TMSCl (0.08 mL, 0.63 mmol, 1.20 equiv) in 1 mL THF was added dropwise to the reaction mixture. The reaction was allowed to warm to rt over 3 h. Water (10 mL) was added and the mixture was diluted with Et_2O (5 mL). The aqueous phase was extracted with Et_2O (3 x 10 mL) and the combined organic phases were washed with brine (15 mL), dried over Na_2SO_4, filtered and the solvent was removed under reduced pressure. The crude was used according to procedure III. Purification by column chromatography using 100:1 (*n*-pentane/Et_2O) afforded **4j** (25.3 mg, 0.28 mmol, 52%, *E/Z* 83:17) as a colorless oil.

^{1}H NMR: (500 MHz, $CDCl_3$) δ = 10.50 (s, 0.17H, CHO$_{minor}$), 10.49 (s, 0.83H, CHO$_{major}$), 7.61 – 7.58 (m, 1H, CH_{arom}), 7.48 – 7.44 (m, 1H, CH_{arom}), 7.33 – 7.31 (m, 0.17H, C$H_{arom,minor}$), 7.29 – 7.27 (m, 0.83H, C$H_{arom,major}$), 5.68 – 5.39 (m, 2H, 2xCH_{olef}), 3.80 – 3.78 (m, 0.34H, C$H_{2,minor}$), 3.71 (dt, J = 6.3, 1.6 Hz, 1.66H, C$H_{2,minor}$), 1.76 – 1.74 (m, 0.51H C$H_{3,minor}$), 1.67 (dq, J = 6.5, 1.5 Hz, 2.50H, C$H_{3,major}$), 0.32 (s, 9H, Si(CH_3)$_3$). ppm. **^{13}C NMR**: (126 MHz, $CDCl_3$) δ = 193.4 (CHO$_{minor}$), 193.3 (CHO$_{major}$), 144.3 ($C_{arom,major}$), 143.9 ($C_{arom,minor}$), 143.6 ($C_{arom,major}$), 138.6 ($C_{arom,major}$), 135.5 ($C_{arom,minor}$), 134.1 ($C_{arom,major}$), 134.0 ($C_{arom,minor}$), 132.7 ($C_{arom,major}$), 132.6 ($C_{arom,minor}$), 132.1 ($C_{arom,major}$), 131.8 ($C_{arom,minor}$), 130.1 (CH$_{olef,major}$), 129.0 (CH$_{olef,minor}$), 127.3 (CH$_{olef,major}$), 125.3 (CH$_{olef,minor}$), 36.4 (CH$_{2,major}$), 31.1 (CH$_{2,minor}$), 18.1 (CH$_{3,major}$), 13.2 (CH$_{3,minor}$), 0.7 (Si(CH$_3$)$_{3,minor}$), 0.6 (Si(CH$_3$)$_{3,major}$) ppm. One ^{13}C-signal of the minor isomer could not be found due to the noise to signal ratio. **^{60}Si NMR**: (60 MHz, $CDCl_3$) δ = -3.5 ppm. **IR** (ATR) $\tilde{\nu}$ (cm^{-1}) = 3023 (w), 2949 (w), 2764 (w), 1693 (s), 1573 (w), 1454 (w), 1395 (w), 1284 (w), 1247 (m), 1211 (w), 1172 (w), 1136 (w), 1079 (w), 968 (w), 867 (w), 839 (s), 795 (w), 763 (m), 676 (w), 625 (w), 488 (w). **HRMS** (ESI+) m/z: [M+H]+ Calcd for C14H21OSiH 233.1356, Found 233.1356.

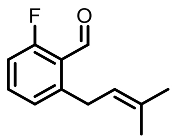
1-bromo-2-(dimethoxymethyl)-3-fluorobenzene **3S3**



was obtained according to general procedure I, aldehyde **S15** (1.00 g, 4.93 mmol). Purification by column chromatography using 2:1:0.01 (*n*-pentane/Et_2O/Et_3N) afforded **3S3** (1.11 mg, 4.46 mmol, 91%) as a colorless oil.

^{1}H NMR: (500 MHz, $CDCl_3$) δ = 7.37 (dt, *J* = 8.0, 1.1 Hz, 1H, CH_{arom}), 7.16 (td, *J* = 8.2, 5.6 Hz, 1H, CH_{arom}), 7.05 (ddd, *J* = 10.5, 8.3, 1.2 Hz, 1H, CH_{arom}), 5.71 (d, *J* = 1.3 Hz, 1H, CH), 3.49 (s, 6H, 2 x CH_3) ppm. **^{13}C NMR**: (126 MHz, $CDCl_3$) δ =161.52 (d, *J* = 256.5 Hz, FC_{arom}), 130.94 (d, *J* = 10.0 Hz, C_{arom}), 129.18 (d, *J* = 3.8 Hz, C_{arom}), 125.39 (d, *J* = 14.3 Hz, C_{arom}), 123.50 (d, *J* = 5.2 Hz, C_{arom}), 116.17 (d, *J* = 22.9 Hz, C_{arom}) 104.85 (CH), 55.70 (2 x OCH3) ppm. **^{19}F NMR**: (282 MHz, $CDCl_3$) δ = -111.12 ppm. **IR** (ATR) $\tilde{\nu}$ (cm^{-1}) = 2993 (w), 2932 (w), 2830 (w), 1601 (w), 1572 (m), 1454 (m), 1375 (w), 1276 (w), 1248 (m), 1201 (w), 1175 (w), 1137 (w), 1103 (w), 1059 (s), 968 (m), 892 (s), 846 (w), 816 (w), 782 (s), 730 (m), 689 (w), 571 (w), 535 (w), 501 (w), 471 (w). **HRMS** (ESI+) m/z: [M+Na]+ Calcd for C9H10BrFO2Na 270.9740, 272.9721, Found 270.9739, 272.9719.

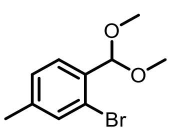
2-fluoro-6-(3-methylbut-2-en-1-yl)benzaldehyde **4d**



was obtained utilizing first the general procedure II A, using corresponding aryl bromide **3S3** (1.10 g, 4.42 mmol) and prenyl bromide (0.74 mL, 5.74 mmol). The crude was then used according to general procedure III. Purification by column chromatography using 20:1 (*n*-pentane/Et_2O) afforded **4d** (473 mg, 2.46 mmol, 56% over two steps) as a colorless oil.

^{1}H NMR: (500 MHz, $CDCl_3$) δ = 10.52 (s, 1H, CHO), 7.45 (td, *J* = 8.1, 5.8 Hz, 1H, CH_{arom}), 7.09 (d, *J* = 7.7 Hz, 1H, CH_{arom}), 7.00 (dd, *J* = 10.9, 8.3 Hz, 1H, CH_{arom}), 5.25 (ddq, *J* = 8.7, 5.8, 1.5 Hz, 1H, CH_{olef}), 3.74 (d, *J* = 7.2 Hz, 2H CH_2), 1.72 (d, *J* = 13.3 Hz, 6H, 2 x CH_3) ppm. **^{13}C NMR**: (126 MHz, $CDCl_3$) δ = 189.4 (d, *J* = 10.5 Hz, CHO), 166.2 (d, *J* = 257.5 Hz, FC_{arom}), 146.2 (C_{arom}) 135.3 (d, *J* = 10.5 Hz, C_{arom}), 133.9 (C_{olef}), 126.2 (d, *J* = 3.8 Hz, C_{arom}), 122.3 (d, *J* = 5.7 Hz, C_{arom}), 121.4 (CH$_{olef}$), 114.0 (d, *J* = 21.9 Hz, C_{arom}), 32.0 (CH$_2$), 25.9 (CH$_3$), 18.1 (CH$_3$). ppm. **^{19}F NMR**: (282 MHz, $CDCl_3$) δ = -120.80 ppm. **IR** (ATR) $\tilde{\nu}$ (cm^{-1}) = 2970 (w), 2915 (w), 2881 (w), 2780 (w), 1695 (s), 1610 (m), 1571 (m), 1469 (m), 1450 (w), 1414 (w), 1378 (w), 1285 (w), 1258 (w), 1240 (m), 1186 (w), 1159 (w), 1101 (w), 1070 (w), 986 (w), 922 (w), 888 (w), 850 (w), 826 (m), 792 (s), 771 (w), 729 (w), 709 (w), 625 (w), 595 (w), 511 (w), 449 (w). **HRMS** (ESI+) m/z: [M+Na]+ Calcd for C12H13FONa 215.0800, Found 215.0842.

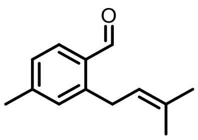
2-bromo-1-(dimethoxymethyl)-4-methylbenzene **3S4**



was obtained according to general procedure I using the corresponding aldehyde **S16** (0.80 g, 4.00 mmol). Purification by column chromatography using 2:1:0.01 (*n*-pentane/Et_2O/Et_3N) afforded **3S4** (873 mg, 3.56 mmol, 89%) as a colorless oil.

^{1}H NMR: (500 MHz, $CDCl_3$) δ =7.47 (d, *J* = 7.9 Hz, 1H, CH_{arom}), 7.41 – 7.37 (m, 1H, CH_{arom}), 7.13 (dtd, *J* = 7.9, 1.3, 0.6 Hz, 1H, CH_{arom}), 5.53 (s, 1H, C*H*), 3.37 (s, 6H, 2 x OCH_3), 2.32 (s, 3H, $C_{arom}CH_3$) ppm. **^{13}C NMR**: (126 MHz, $CDCl_3$) δ = 140.5, 133.9, 133.4, 128.2, 128.1, 122.8, 103.0, 53.9, 20.8 ($C_{arom}CH_3$) ppm. **IR** (ATR) $\tilde{\nu}$ (cm^{-1}) =2989 (w), 2930 (w), 2828 (w), 1607 (w), 1563 (w), 1488 (w), 1446 (w), 1389 (w), 1361 (m), 1279 (w), 1209 (m), 1189 (w), 1140 (w), 1104 (m), 1055 (s), 978 (m), 912 (w), 874 (w), 833 (w), 811 (m), 714 (w), 674 (w), 651 (w), 594 (w), 568 (w), 551 (w), 478 (w), 439 (w). **HRMS** (ESI+) m/z: [M+Na]+ Calcd for C10H13BrO2Na 266.9991, 268.9971, Found 266.9992, 268.9971.

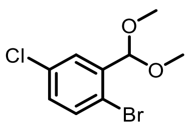
4-methyl-2-(3-methylbut-2-en-1-yl)benzaldehyde **4e**



was obtained utilizing first the general procedure II A, using corresponding aryl bromide **3S4** (613 mg, 2.50 mmol) and prenyl bromide (0.33 mL, 3.25 mmol). The crude was then used according to general procedure III. Purification by column chromatography using 100:1 (*n*-pentane/Et_2O) afforded **4e** (194 mg, 1.03 mmol, 41% over two steps) as a colorless oil.

^{1}H NMR: (500 MHz, $CDCl_3$) δ = 10.22 (s, 1H, C*H*O), 7.73 (d, *J* = 7.7 Hz, 1H, CH_{arom}), 7.16 (dd, *J* = 7.8, 1.9 Hz, 1H, CH_{arom}), 7.09 (d, *J* = 1.7 Hz, 1H, CH_{arom}), 5.26 (tp, *J* = 7.1, 1.4 Hz, 1H, CH_{olef}), 3.73 (d, *J* = 7.1 Hz, 2H, CH_2), 2.39 (s, 3H, CH_3), 1.74 (d, *J* = 1.3 Hz, 3H, $C_{olef}CH_3$), 1.73 (q, *J* = 1.4 Hz, 3H, $C_{olef}CH_3$) ppm. **^{13}C NMR**: (126 MHz, $CDCl_3$) δ = 192.2 (*C*HO), 145.0 (C_{arom}), 144.7 ($C_{olef,quart}$), 133.0 (C_{arom}), 131.7 (C_{arom}), 131.7 (C_{arom}), 131.4 (C_{arom}), 127.4 (C_{arom}), 122.9 (CH_{olef}), 31.3 (CH_2), 25.9 (CH_3), 22.0 ($C_{arom}CH_3$), 18.1 (CH_3)f ppm. **IR** (ATR) $\tilde{\nu}$ (cm^{-1}) = 2970 (w), 2916 (w), 2857 (w), 2730 (w), 1691 (s), 1606 (m), 1569 (w), 1494 (w), 1448 (w), 1398 (w), 1377 (w), 1293 (w), 1198 (w), 1101 (w), 1037 (w), 927 (w), 885 (w), 816 (w), 735 (w), 446 (w). **HRMS** (ESI+) m/z: [M+Na]+ Calcd for C13H16ONa 211.1093, Found 211.1095.

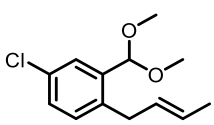
1-bromo-4-chloro-2-(dimethoxymethyl)benzene **3S5**



was obtained according to general procedure I using the corresponding aldehyde **S17** (0.50 g, 2.28 mmol). Purification by column chromatography using 20:1:0.02 (*n*-pentane/Et_2O/Et_3N) afforded **3S5** (519 mg, 1.96 mmol, 86%) as a colorless oil.

^{1}H NMR: (500 MHz, $CDCl_3$) δ = 7.60 (d, *J* = 2.7 Hz, 1H, CH_{arom}), 7.48 (d, *J* = 8.5 Hz, 1H, CH_{arom}), 7.18 (dd, *J* = 8.5, 2.7 Hz, 1H, CH_{arom}), 5.50 (s, 1H, C*H*), 3.38 (s, 6H, 2 x CH_3) ppm. **^{13}C NMR**: (126 MHz, $CDCl_3$) δ = 138.7 (CH_{arom}), 134.1 (CH_{arom}), 133.7 (CH_{arom}), 130.2 (CH_{arom}), 128.8 (CH_{arom}), 120.8 (CH_{arom}), 102.4 (*C*H), 54.0 (2 x OCH_3) ppm. **IR** (ATR) $\tilde{\nu}$ (cm^{-1}) =3089 (w), 2993 (w), 2933 (w), 2830 (w), 1562 (w), 1456 (m), 1390 (w), 1359 (m), 1254 (w), 1195 (m), 1155 (w), 1129 (w), 1105 (w), 1094 (w), 1054 (s), 1031 (w), 981 (m), 914 (w), 877 (m), 813 (m), 761 (w), 742 (w), 705 (w), 644 (w), 614 (w), 568 (w), 512 (m), 456 (w). **HRMS** (EI+) m/z: [M]+ Calcd for C9H10BrClO2 263.95527, 265.95322 , Found 263.95650, 265.95415.

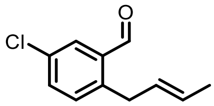
1-(but-2-en-1-yl)-4-chloro-2-(dimethoxymethyl)benzene **S18**



was obtained according to general procedure II A, using corresponding aryl bromide **3S5** (0.51 g, 1.92 mmol) and crotyl bromide (0.30 mL, 2.50 mmol). Purification by column chromatography using 100:1:1 (*n*-pentane/Et_2O/Et_3N) afforded **S18** (818 mg, 3.43 mmol, 78%, *E/Z* 79:21) as a yellow oil.

^{1}H NMR: (300 MHz, $CDCl_3$) δ = 7.56 (d, J = 2.3 Hz, 1H, CH_{arom}), 7.23 (dd, J = 8.2, 2.4 Hz, 1H, CH_{arom}), 7.12 (dd, J = 8.2, 5.3 Hz, 1H, CH_{arom}), 5.63 – 5.39 (m, 2H, 2 x CH_{olef}), 5.46 (s, 0.21H, $CH(OCH_3)_{2,minor}$), 5.46 (s, 0.79H, $CH(OCH_3)_{2,major}$), 3.45 (d, J = 7.1 Hz, 0.42H, $CH_{2,minor}$), 3.37 (dd, J = 7.3, 1.3 Hz, 1.60H, $CH_{2,major}$), 3.31 (s, 1.38H, $CH(OCH_3)_{2,minor}$), 3.31 (s, 4.64H, $CH(OCH_3)_{2,major}$), 1.72 (ddt, J = 6.8, 1.8, 0.9 Hz, 0.70H, $CH_{3,minor}$), 1.69 – 1.65 (m, 2.31H, $CH_{3,major}$) ppm. **^{13}C NMR**: (75 MHz, $CDCl_3$) δ = 137.8 ($C_{arom,minor}$), 137.4 ($C_{arom,major}$), 137.3 ($C_{arom,major}$), 131.8 ($C_{arom,minor}$), 131.7 ($C_{arom,minor}$), 131.2 ($C_{arom,major}$), 130.7 ($C_{arom,minor}$), 129.2 ($CH_{olef,major}$), 128.6 ($C_{arom,minor}$), 128.5 ($C_{arom,major}$), 128.3 ($CH_{olef,minor}$), 127.7 ($CH_{olef,major}$), 127.0 ($C_{arom,minor}$), 126.9 ($C_{arom,major}$), 126.8 ($C_{arom,major}$), 125.3 ($CH_{olef,minor}$), 100.6 ($CH(OCH_3)_{2,minor}$), 100.5 ($CH(OCH_3)_{2,major}$), 53.1 ($CH(OCH_3)_{2,major}$), 53.0 ($CH(OCH_3)_{2,minor}$), 34.6 ($CH_{2,major}$), 29.1($CH_{2,minor}$), 17.9 ($CH_{3,major}$), 12.9 ($CH_{3,minor}$) ppm. **IR** (ATR) $\tilde{\nu}$ (cm^{-1}) = 3024 (w), 2918 (w), 2856 (w), 2732 (w), 1692 (s), 1592 (w), 1563 (w), 1479 (m), 1451 (w), 1398 (w), 1298 (w), 1279 (w), 1259 (w), 1197 (s), 1109 (w), 1055 (w), 968 (m), 939 (w), 898 (m), 832 (w), 811 (w), 790 (w), 737 (w), 691 (w), 648 (w), 557 (w). **HRMS** (ESI+) m/z: [M+H]+ Calcd for C13H17ClO2H 241.0990, Found 241.0987.

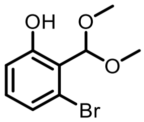
2-(but-2-en-1-yl)-5-chlorobenzaldehyde **4a**



was obtained according to general procedure III using **S18** (250 mg, 1.04 mmol). Purification by column chromatography using 100:1 (*n*-pentane/Et_2O) afforded **4a** (149 mg, 0.77 mmol, 74%, 77:23 *E/Z*) as a yellow oil.

^{1}H NMR: (500 MHz, $CDCl_3$) δ 10.23 (s, 1H, C*H*O), 7.81 (t, *J* = 2.8 Hz, 1H, CH_{arom}), 7.47 (dd, *J* = 8.2, 2.4 Hz, 1H, CH_{arom}), 7.25 (dd, *J* = 11.3, 8.1 Hz, 1H, CH_{arom}), 5.65 – 5.36 (m, 2H, 2 x CH_{olef}), 3.78 (d, *J* = 7.1 Hz, 0.66H, $CH_{2,minor}$), 3.69 (dt, *J* = 6.2, 1.6 Hz, 1.34H, $CH_{2,major}$), 1.75 – 1.71 (m, 0.99H, $CH_{3,minor}$), 1.66 (dq, *J* = 6.2, 1.5 Hz, 2.02H, $CH_{3,major}$) ppm. **^{13}C NMR**: (126 MHz, $CDCl_3$) δ = 191.0 (CHO_{minor}), 190.9 (CHO_{major}), 142.2 ($C_{arom,minor}$), 141.8 ($C_{arom,major}$), 135.1 ($C_{arom,minor}$), 135.1 ($C_{arom,major}$), 133.9 ($C_{arom,major}$), 133.1 ($C_{arom,major}$), 133.0 ($C_{arom,minor}$), 132.6 ($C_{arom,major}$), 132.2 ($C_{arom,minor}$), 130.9 ($C_{arom,minor}$), 130.3 ($C_{arom,major}$), 129.3 ($CH_{olef,major}$), 128.4 ($C_{arom, minor}$), 128.0 ($CH_{olef,minor}$), 127.8 ($CH_{olef,major}$), 126.1 ($CH_{olef,minor}$), 34.8 ($CH_{2,major}$), 29.6 ($CH_{2,minor}$), 18.0 ($CH_{3,major}$), 13.0 ($CH_{3,minor}$) ppm. **IR** (ATR) $\tilde{\nu}$ (cm^{-1}) = 3023 (w), 2918 (w), 2855 (w), 2732 (w), 1689 (s), 1604 (m), 1569 (w), 1495 (w), 1450 (w), 1398 (w), 1380 (w), 1290 (w), 1267 (w), 1232 (w), 1202 (m), 1125 (w), 1039 (w), 968 (m), 866 (w), 816 (m), 778 (w), 713 (w), 693 (w), 672 (w), 616 (w), 535 (w), 488 (w), 442 (w). **HRMS** (ESI+) m/z: [M+Na]+ Calcd for C12H14ONa 197.0937, Found 197.0936.

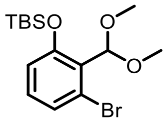
3-bromo-2-(dimethoxymethyl)phenol **3S6**



was obtained according to general procedure I using the corresponding aldehyde **S19** (5.03 g, 25.0 mmol). Aqueous workup afforded **3S6** (6.00 g, 24.3 mmol, 97%) as a brown oil.

^{1}H NMR: (500 MHz, $CDCl_3$) δ = 8.71 (s, 1H, CH_{arom}), 7.12 – 7.03 (m, 1H, CH_{arom}), 6.84 (dd, *J* = 7.6, 1.8 Hz, 1H, CH_{arom}), 5.83 (s, 1H, C*H*), 3.48 (s, 6H, 2 x CH_3) ppm. **^{13}C NMR**: (126 MHz, $CDCl_3$) δ = 157.8 (C_{arom}), 131.2 (C_{arom}), 124.5 (C_{arom}), 123.5 (C_{arom}), 120.1 (C_{arom}), 117.1 (C_{arom}), 106.8 (*C*H), 54.6 (2 x CH_3) ppm. **IR** (ATR) $\tilde{\nu}$ (cm^{-1}) =3316 (w), 2936 (w), 2833 (w), 1608 (w), 1571 (m), 1452 (s), 1356 (m), 1290 (w), 1244 (m), 1191 (w), 1163 (m), 1132 (w), 1096 (m), 1047 (s), 988 (w), 951 (m), 893 (s), 835 (w), 817 (w), 780 (m), 730 (m), 688 (w), 654 (w), 539 (w), 471 (w). **HRMS** (ESI+) m/z: [M+Na]+ Calcd for C9H11BrO3Na 268.9784, 270.9764, Found 268.9775, 270.9753.

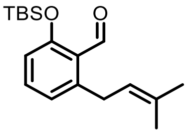
(3-bromo-2-(dimethoxymethyl)phenoxy)(tert-butyl)dimethylsilane **3S7**,



Alcohol **3S6** (6.00 g, 24.3 mmol), imidazole (3.14 g, 46.2 mmol, 1.90 equiv.) were dissolved in anhydrous THF (24 mL), TBSCl (4.38 g, 29.2 mmol, 1.20 equiv.) was added and stirred at rt for 18 h. 15 mL water and 15 mL Et_2O were added and the aqueous phase was extracted with Et_2O (3 x 20 mL). The combined organic phase was dried over Na_2SO_4, filtered and the solvent was removed under reduced pressure. Purification by column chromatography using 100:1 (*n*-pentane/Et_2O) afforded the silyl ether **3S7** (7.77 g, 21.5 mmol, 89%) as a colorless oil.

^{1}H NMR: (500 MHz, $CDCl_3$) δ = 7.60 (d, *J* = 2.7 Hz, 1H, CH_{arom}), 7.19 (dd, J = 8.0, 1.1 Hz, 1H, CH_{arom}), 7.00 (t, J = 8.1 Hz, 1H, CH_{arom}), 6.76 (dd, J = 8.2, 1.1 Hz, 1H, CH_{arom}), 5.76 (s, 1H, C*H*), 3.42 (s, 6H, 2 x OCH_3), 1.03 (s, 9H, $(CH_3)SiC(CH_3)_3$), 0.25 (s, 6H, $(CH_3)SiC(CH_3)_3$) ppm. **^{13}C NMR**: (126 MHz, $CDCl_3$) δ = 155.4 (C_{arom}), 130.0 (C_{arom}), 127.9 (C_{arom}), 127.2 (C_{arom}), 123.0 (C_{arom}), 118.6 (C_{arom}), 103.3 (*C*H), 55.6 (2 x OCH_3), 25.9 ($(CH_3)SiC(CH_3)_3$), 18.5 (C_{quart}), -4.1($(CH_3)SiC(CH_3)_3$) ppm. **^{29}Si NMR**: (60 MHz, $CDCl_3$) δ = 22.0. **IR** (ATR) $\tilde{\nu}$ (cm^{-1}) = 2955 (w), 2931 (m), 2886 (w), 2859 (w), 1703 (s), 1586 (s), 1562 (w), 1448 (s), 1402 (w), 1363 (w), 1291 (m), 1255 (m), 1210 (w), 1181 (w), 1165 (w), 1136 (w), 1103 (w), 1075 (w), 936 (s), 840 (s), 811 (w), 784 (m), 732 (w), 667 (w), 578 (w). **HRMS** (ESI+) m/z: [M+Na]+ Calcd for C15H25BrO3SiNe 383.0654, 385.0630, Found 383.0634, 385.0610.

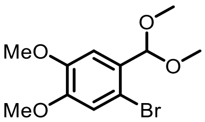
2-((tert-butyldimethylsilyl)oxy)-6-(3-methylbut-2-en-1-yl)benzaldehyde **4S1**



was obtained utilizing first the general procedure II A, using corresponding aryl bromide **3S7** (7.67 g, 21.2 mmol) and prenyl bromide (2.99 mL, 25.5 mmol). The crude was then used according to general procedure III. Purification by column chromatography using 100:1 (*n*-pentane/Et_2O) afforded **4S1** (4.98 g, 16.0 mmol, 75% over two steps) as a colorless oil.

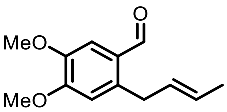
^{1}H NMR: (500 MHz, $CDCl_3$) δ = 10.63 (s, 1H, C*H*O), 7.31 (t, *J* = 8.0 Hz, 1H, CH_{arom}), 6.87 (dt, *J* = 7.7, 1.1 Hz, 1H, CH_{arom}), 5.27 (tp, *J* = 7.2, 1.4 Hz, 1H, CH_{olef}), 3.70 (d, 2H, C$H_{2,benzylic}$), 1.73 (q, *J* = 1.4 Hz, 3H, CH=CCH_3CH_3), 1.70 (s, 3H, CH=CCH_3CH_3), 1.01 (s, 9H, $(CH_3)_2$SiC(CH_3)$_3$), 0.27 (s, 6H, (CH_3)$_2$SiC(CH_3)$_3$) ppm. **^{13}C NMR**: (126 MHz, $CDCl_3$) δ = 193.0 (*C*HO), 160.2 (C_{arom}), 145.6 (C_{arom}), 134.5 (C_{arom}), 132.9 (C_{olef}), 125.5 (C_{arom}), 123.2 (C_{arom}), 122.7 (CH_{olef}), 117.7 (C_{arom}), 32.2 (CH_2), 25.9 (CH_3), 25.9 ((CH_3)SiC(CH_3)$_3$), 18.5 (C_{quart}), 18.1 (CH_3), -4.1 ((CH_3)SiC(CH_3)$_3$) ppm. **^{29}Si NMR**: (60 MHz, $CDCl_3$) δ = 23.0. **IR** (ATR) $\tilde{\nu}$ (cm^{-1}) =2956 (w), 2930 (m), 2859 (w), 2772 (w), 1688 (s), 1591 (m), 1574 (w), 1465 (s), 1443 (w), 1404 (m), 1293 (w), 1253 (s), 1182 (w), 1162 (w), 1102 (w), 1078 (w), 1031 (m), 1004 (w), 926 (w), 859 (w), 838 (w), 810 (w), 780 (s), 730 (w), 702 (w), 666 (w), 611 (w), 575 (w), 462 (w). **HRMS** (ESI+) m/z: [M+Na]+ Calcd for C18H28O2SiNa 327.1751, Found 327.1737.

1-bromo-2-(dimethoxymethyl)-4,5-dimethoxybenzene **3S8**



was obtained according to a protocol reported by GREETS *et al*.[11]

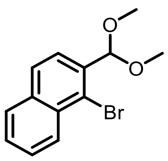
2-(but-2-en-1-yl)-4,5-dimethoxybenzaldehyde **4S2**



was obtained utilizing first the general procedure II A, using corresponding aryl bromide **3S8** (501 mg, 1.72 mmol) and crotyl bromide (0.27 mL, 2.24 mmol). The reaction mixture was quenched with sat. NH_4Cl solution (5 mL) and extracted with CH_2Cl_2 (3 x 15 mL). The combined organic layer was washed with brine (15 mL), dried over Na_2SO_4 and the solvent was removed under reduced pressure. Purification by column chromatography using 20:1→10:1 (*n*-pentane/EtOAc) afforded **4S2** (353 mg, 1.60 mmol, 93%, *E/Z* 75:25) as a colorless oil.

^{1}H NMR: (500 MHz, $CDCl_3$) δ = 10.20 (s, 0.25H, CHO_{minor}), 10.19 (s, 0.75H , CHO_{major}), 7.38 (s, 0.74H, C$H_{arom,major}$), 7.37 (s, 0.26H, C$H_{arom,minor}$), 6.73 (s, 0.24H, C$H_{arom,minor}$), 6.69 (s, 0.76H, C$H_{arom,major}$), 5.65 – 5.37 (m, 2H, 2xC$H_{olef,major+minor}$), 3.95 – 3.94 (m, 3H, OCH_3), 3.91 (s, 3H, OCH_3), 3.77 – 3.74 (m, 0.51H, C$H_{2,minor}$), 3.68 – 3.65 (m, 1.52H, C$H_{2,major}$), 1.76 – 1.73 (m, 0.75H, C$H_{3,minor}$), 1.67 – 1.64 (m, 2.25H, C$H_{3,major}$) ppm. **^{13}C NMR**: (126 MHz, $CDCl_3$) δ = 190.2 (*C*=O), 154.0 ($C_{arom,major}$), 154.0 ($C_{arom,minor}$), 147.9 ($C_{arom,major}$), 147.8 ($C_{arom,minor}$), 139.4 ($C_{arom,minor}$), 138.9 ($C_{arom,major}$), 130.1 (C$H_{olef,major}$), 128.9 (C$H_{olef,minor}$), 127.2 (C$H_{olef,major}$), 126.9 ($C_{arom,major}$), 126.8 ($C_{arom,minor}$), 125.3 (C$H_{olef,minor}$), 112.9 ($C_{arom,major}$), 112.5 ($C_{arom,minor}$), 111.1 ($C_{arom,minor}$), 110.6 ($C_{arom,major}$), 56.2 (OCH_3), 56.1 (OCH_3), 34.7 ($CH_{2,major}$), 29.3 ($CH_{2,minor}$), 18.0 ($CH_{3,major}$), 13.2 ($CH_{3,minor}$) ppm. **IR** (ATR) $\tilde{\nu}$ (cm^{-1}) = 3422 (w), 2936 (w), 2856 (w), 1672 (m), 1595 (s), 1510 (s), 1461 (m), 1406 (w), 1352 (w), 1312 (w), 1262 (s), 1226 (w), 1176 (w), 1104 (s), 1035 (w), 998 (w), 968 (w), 871 (m), 786 (w), 747 (m), 693 (w), 662 (w), 581 (m), 452 (w). **HRMS** (APCI+) m/z: [M+H]+ Calcd for C13H16O3H 221.1172, Found 221.1167.

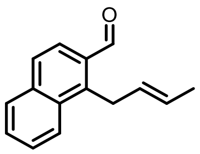
1-bromo-2-(dimethoxymethyl)naphthalene **3S9**



was obtained according to general procedure I using the corresponding aldehyde **S28** (156 mg,0.66 mmol). **3S9** was afforded (184 mg, 0.65 mmol, 99%) as a colorless solid.

^{1}H NMR: (500 MHz, $CDCl_3$) δ = 8.38 (d, J = 9.2 Hz, 1H, CH_{arom}), 7.83 (d, J = 8.4 Hz, 2H, 2xCH_{arom}), 7.72 (d, J = 8.5 Hz, 1H, CH_{arom}), 7.61 (ddd, J = 8.5, 6.8, 1.4 Hz, 1H, CH_{arom}), 7.55 (ddd, J = 8.1, 6.8, 1.3 Hz, 1H, CH_{arom}), 5.88 (s, 1H, C*H*), 3.45 (s, 6H, 2xOCH_3) ppm. **^{13}C NMR**: (126 MHz, $CDCl_3$) δ = 135.3 (C_{arom}), 134.8 (C_{arom}), 132.3 (C_{arom}), 128.3 (C_{arom}), 127.8 (C_{arom}), 127.7 (C_{arom}), 127.6 (C_{arom}), 127.2 (C_{arom}), 124.9 (C_{arom}), 123.7 (C_{arom}), 104.2 (*C*H), 54.4 (OCH_3) ppm. **IR** (ATR) $\tilde{\nu}$ (cm^{-1}) = 3063 (w), 2990 (w), 2931 (w), 2828 (w), 1557 (w), 1501 (w), 1461 (w), 1380 (w), 1324 (m), 1258 (w), 1221 (w), 1209 (w), 1189 (m), 1149 (w), 1133 (w), 1106 (m), 1054 (s), 1000 t(w), 967 (m), 917 (w), 890 (w), 864 (w), 823 (m), 801 (w), 769 (m), 746 (m), 657 (w), 532 (m), 414 (w). **HRMS** (ESI+) m/z: [M+Na]+ Calcd for C13H13BrO2Na 302.9991, 304.9972, Found 302.9993, 304.9972. **m.p**. 53.9– 54.9°C (CH_2Cl_2).

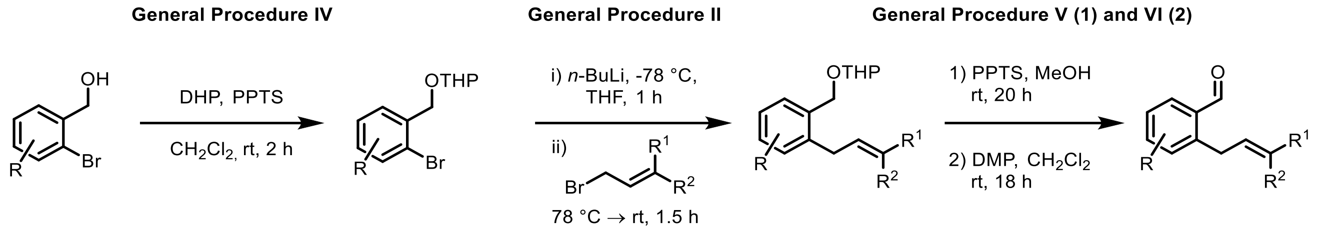
1-(but-2-en-1-yl)-2-naphthaldehyde **4g**



was obtained according to general procedure II A using **3S9** (178 mg, 0.63 mmol). The crude was then used according to general procedure III. Purification by column chromatography using 40:1 (*n*-pentane/Et_2O) afforded **4g** (64 mg, 0.34 mmol, 66% *E/Z* 80:20) as a pale yellow oil.

^{1}H NMR: (500 MHz, $CDCl_3$) δ = 10.61 (s, 0.2H, CHO_{minor}), 10.60 (s, 0.80H, CHO_{major}), 8.26 – 8.18 (m, 1H, CH_{arom}), 7.98 – 7.92 (m, 1H, CH_{arom}), 7.90 – 7.84 (m, 1H, CH_{arom}), 7.80 (d, J = 8.8 Hz, 1H, CH_{arom}), 7.65 – 7.55 (m, 2H, 2xCH_{arom}), 5.82 – 5.33 (m, 2H, 2xCH_{olef}), 4.33 – 4.29 (m, 0.39H, $CH_{2,minor}$), 4.24 (dt, J = 5.8, 1.8 Hz, 1.61H $CH_{2,major}$), 1.93 – 1.88 (m, 0.59H, $CH_{3,minor}$), 1.62 (dq, J = 6.5, 1.7 Hz, 2.41H, $CH_{3,major}$). ppm. **^{13}C NMR**: (126 MHz, $CDCl_3$) δ = 192.2 (CHO_{minor}), 192.1 (CHO_{major}), 143.6 ($C_{arom,minor}$), 142.7 ($C_{arom,major}$), 137.7 ($C_{arom,minor}$), 136.5 ($C_{arom,major}$), 132.2 ($C_{arom,major}$), 131.2 ($C_{arom,major}$), 131.1 ($C_{arom,minor}$), 129.2 ($CH_{olef,major}$), 129.1 ($C_{arom,minor}$), 129.0 ($C_{arom,major}$), 128.8 ($C_{arom,minor}$), 128.8 ($C_{arom,minor}$), 128.7 ($C_{arom,major}$), 127.7 ($CH_{olef,major}$), 127.6 ($C_{arom,major}$), 127.5 ($C_{arom,minor}$), 127.0 ($C_{arom,major}$), 125.6 ($C_{arom,major}$), 125.5 ($C_{arom,minor}$), 125.0 ($CH_{olef,minor}$), 124.3 ($C_{arom,minor}$), 124.1 ($C_{arom,major}$), 29.5 ($CH_{2,major}$), 24.9 ($CH_{2,minor}$), 18.1 ($CH_{3,major}$), 13.5 ($CH_{3,minor}$) ppm. Two ^{13}C-signals of the minor isomer could not be found due to the noise to signal ratio. **IR** (ATR) $\tilde{\nu}$ (cm^{-1}) = 3058 (w), 3022 (w), 2916 (w), 2856 (w), 2735 (w), 1678 (s), 1620 (w), 1597 (w), 1566 (w), 1511 (w), 1470 (w), 1451 (w), 1431 (w), 1378 (w), 1342 (w), 1261 (w), 1225 (m), 1190 (w), 1165 (w), 1145 (w), 1105 (w), 1067 (w), 1033 (w), 966 (w), 910 (w), 865 (w), 817 (m), 790 (w), 763 (w), 745 (m), 663 (w), 611 (w), 564 (w), 523 (w), 482 (w), 438 (w). **HRMS** (ESI+) m/z: [M+H]+ Calcd for C15H14OH 211.1117, Found 211.1117.

7 General Procedures IV – VI: Substrate Synthesis



General Procedure IV: Tetrahydropyran Protection

The reduction was carried out according to a protocol reported by KOERT *et al.*

To a solution of *ortho*-bromo benzyl alcohol (1.00 equiv) and PPTS (0.05 equiv) in anhydrous CH_2Cl_2 (0.2 M) DHP was added and stirred for 2 h at rt. The mixture was diluted with CH_2Cl_2, washed with water (2 x) and bine and dried over Na_2SO_4. The solvent was removed under reduced pressure. The product was afforded as an oil and used without further purification.

General Procedure II A: Alkylation

To a solution of acetal (1.00 equiv) in anhydrous THF (0.3 M) at -78 °C *n*-BuLi (1.10 equiv, 2.5 M) were added dropwise and the solution was stirred for 30 min. R^1,R^2-Allylbromide (1.30 equiv) was added to the solution and the mixture was allowed to warm to rt for 2 h. The reaction was quenched with sat. $NaHCO_3$-solution and extracted with Et_2O (3 x). The combined organic layers were washed with brine and dried over Na_2SO_4. The solvent was removed under reduced pressure. The residue was purified by column chromatography (*n*-pentane/Et_2O/Et_3N 40:1:0.5, unless otherwise noted) to give the product as a colorless oil.

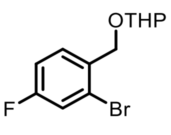
General Procedure V: Tetrahydropyran Deprotection

Alkylated acetal (1.00 equiv) and PPTS (0.05 equiv) were dissolved in MeOH (0.5 M) and stirred at rt overnight. The mixture was extracted with Et_2O (3x). The combined organic layers were washed with water (2 x), followed by brine and dried over Na_2SO_4. The solvent was removed under reduced pressure. The residue was purified by column chromatography (*n*-pentane/EtOAc 10:1, unless otherwise noted) to give the product as a colorless oil.

General Procedure VI: Oxitation to Benzaldehyde

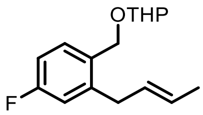
To a solution of alcohol (1.00 equiv) in CH_2Cl_2 (0.2 M) DMP (1.10 equiv) was added and stirred at rt overnight. The mixture was diluted with sat. $NaHCO_3$-solution and extracted with Et_2O (3 x). The combined organic layers were washed with water, followed by brine and dried over Na_2SO_4. The solvent was removed under reduced pressure. The residue was purified by column chromatography (*n*-pentane/Et_2O 100:1, unless otherwise noted) to give the product as a colorless oil.

2-((2-bromo-4-fluorobenzyl)oxy)tetrahydro-2H-pyran **S20**



was obtained according to general procedure IV, using the corresponding alcohol **S21** (1.00 g, 4.90 mmol). Purification by column chromatography afforded **S20** (1.41 mg, 4.90 mmol, 99%) as a colorless oil.
^{1}H NMR: (300 MHz, $CDCl_3$) δ = 7.48 (dd, *J* = 8.6, 6.1 Hz, 1H, CH_{arom}), 7.30 (dd, *J* = 8.2, 2.6 Hz, 1H, CH_{arom}), 7.03 (td, *J* = 8.4, 2.6 Hz, 1H, CH_{arom}), 4.82 – 4.74 (m, 2H, OC*H*O and C*H*$H_{benzylic}$), 4.53 (d, *J* = 13.0 Hz, 1H, CH$H_{benzylic}$), 3.91 (ddd, *J* = 11.4, 8.8, 3.5 Hz, 1H, OC*H*H_{THP}), 3.57 (dtd, *J* = 11.3, 4.3, 1.4 Hz, 1H, OCHH_{THP}), 1.92 – 1.52 (m, 6H, 3 x C$H_{2,THP}$) ppm. **^{13}C NMR**: (75 MHz, $CDCl_3$) δ = 161.8 (d, *J* = 250.1 Hz, CF_{arom}), 133.9 (d, *J* = 3.6 Hz, C_{arom}), 130.3 (d, *J* = 8.3 Hz, C_{arom}), 122.9 (d, *J* = 9.6 Hz, C_{arom}), 119.9 (d, *J* = 24.5 Hz, C_{arom}), 114.5 (d, *J* = 20.6 Hz, C_{arom}), 98.6 (O*C*HO), 68.2 ($CH_{2,benzylic}$), 62.4 ($CH_{2,THP}$), 30.7 ($CH_{2,THP}$), 25.6 ($CH_{2,THP}$), 19.5 ($CH_{2,THP}$)ppm. **^{19}F NMR**: (282 MHz, $CDCl_3$) δ = -113.44 ppm. **IR** (ATR) $\tilde{\nu}$ (cm^{-1}) = 2942 (m), 2870 (w), 1600 (m), 1589 (w), 1488 (s), 1455 (w), 1441 (w), 1386 (w), 1350 (w), 1323 (w), 1261 (w), 1230 (m), 1201 (w), 1183 (w), 1155 (w), 1126 (m), 1069 (m), 1037 (w), 1028 (s), 973 (m), 906 (w), 874 (m), 859 (w), 815 (m), 769 (w), 430 (w). **HRMS** (ESI+) m/z: [M+Na]+ Calcd for C12H14BrFO2Na 311.0053, 313.0034, Found 311.0051, 313.0029.

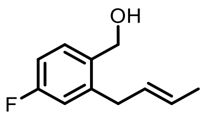
2-((2-(but-2-en-1-yl)-4-fluorobenzyl)oxy)tetrahydro-2H-pyran **S22**



was obtained according to general procedure IV, using the corresponding acetal **S20** (1.13 g, 3.92 mmol) and crotylbromide (0.66 mL, 6.37 mmol, 85:15 *E/Z*). Purification by column chromatography afforded **S22** (0.84 g, 3.17 mmol, 81%, 77:23 *E*/*Z*) as a colorless oil.

^{1}H NMR: (500 MHz, $CDCl_3$) δ = 7.33 (dd, *J* = 8.4, 6.0 Hz, 1H, CH_{arom}), 6.94 – 6.85 (m, 2H, 2 x CH_{arom}), 5.66 – 5.43 (m, 2H, $CH_{2,olef}$), 4.79 – 4.74 (m, 1H, $OCHH_{benzylic}$), 4.70 – 4.67 (m, 1H, OCHO), 4.49 – 4.44 (m, 1H, $OCHH_{benzylic}$), 3.90 (ddd, *J* = 11.7, 8.5, 3.4 Hz, 1H, $OCHH_{THP}$), 3.57 – 3.53 (m, 1H, $OCHH_{THP}$), 3.45 (d, *J* = 7.8 Hz, 0.46H, $CH_{2,benzylic,minor}$), 3.39 – 3.34 (m, 1.54H, $CH_{2,benzylic,major}$), 1.89 – 1.82 (m, 1H, CHH_{THP}), 1.69 (d, *J* = 9.1 Hz, 4H, $CHH_{THP,}$ CH_3), 1.66 – 1.53 (m, 4H, 2x$CH_{2,THP}$) ppm. **^{13}C NMR**: (126 MHz, $CDCl_3$) δ = 162.7 (d, *J* = 244.1 Hz, $CF_{arom,minor}$), 161.7 (d, *J* = 245.2 Hz, $CF_{arom,major}$), 142.4 (d, *J* = 7.7 Hz, $C_{arom,minor}$), 142.2 (d, *J* = 7.2 Hz, $C_{arom,major}$), 131.9 ($C_{arom,minor}$), 131.8 (d, *J* = 2.9 Hz, $C_{arom,major}$), 130.9 (d, *J* = 8.6 Hz, $C_{arom,major}$), 128.9 ($CH_{olef,major}$), 127.9 ($CH_{olef,minor}$), 127.3 ($CH_{olef,major}$), 125.9 ($CH_{olef,minor}$), 116.2 (d, *J* = 21.5 Hz, $C_{arom,major}$), 115.8 (d, *J* = 21.9 Hz, $C_{arom,minor}$), 112.8 (d, *J* = 20.9 Hz, $C_{arom,major}$), 112.7 (d, *J* = 21.0 Hz, $C_{arom,minor}$), 98.1 ($OCHO_{major}$), 98.1 ($OCHO_{minor}$), 66.6 ($OCH_{2,benzylic,minor}$), 66.5 ($OCH_{2,benzylic,major}$), 62.4 ($OCH_{2,THP}$), 35.5 ($CH_{2,benzylic,major}$), 30.8 ($CH_{2,THP}$), 29.9 ($CH_{2,benzylic,minor}$), 25.6 ($CH_{2,THP}$), 19.6 ($CH_{2,THP}$), 18.0 ($CH_{3,major}$), 13.0 ($CH_{3,minor}$) ppm. Due to the noise to signal ratio, the aromatic carbon atom of the minor isomer could not be detected. **^{19}F NMR**: (282 MHz, $CDCl_3$) δ = -115.15 ppm. **IR** (ATR) $\tilde{\nu}$ (cm^{-1}) = 3024 (w), 2941 (m), 2872 (w), 1612 (w), 1592 (m), 1498 (m), 1466 (w), 1453 (w), 1441 (w), 1385 (w), 1350 (w), 1323 (w), 1260 (m), 1201 (w), 1183 (w), 1150 (w), 1119 (m), 1078 (w), 1054 (w), 1035 (w), 1025 (s), 973 (m), 959 (w), 906 (w), 869 (m), 814 (m), 524 (w), 507 (w), 475 (w), 429 (w). **HRMS** (APCI+) m/z: [M+H]+ Calcd for C16H21FO2H 265.1598, Found 265.1599.

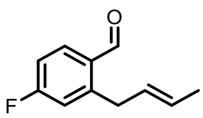
2-(but-2-en-1-yl)-4-fluorophenyl)methanol **S23**



was obtained according to general procedure VI, using the corresponding acetal **S22** (587 mg, 2.03 mmol) Purification by column chromatography afforded **S23** (354 mg, 1.34 mmol, 66%) as a colorless oil.

^{1}H NMR: (500 MHz, $CDCl_3$) δ = 7.34 – 7.30 (m, 1H, CH_{arom}), 6.95 – 6.87 (m, 2H, 2 x CH_{arom}), 5.67 – 5.44 (m, 2H, 2 x CH_{olef}), 4.69 – 4.64 (m, 2H, OCH_2), 3.46 (d, *J* = 7.2 Hz, 0.47H, $CH_{2,benzylic,minor}$), 3.38 (dt, *J* = 6.3, 1.5 Hz, 1.53H, $CH_{2,benzylic,major}$), 1.74 (ddt, *J* = 6.8, 1.9, 1.0 Hz, 0.72H, $CH_{3,minor}$), 1.68 (dq, *J* = 6.2, 1.5 Hz, 2.28H, $CH_{3,major}$) ppm. **^{13}C NMR**: (126 MHz, $CDCl_3$) δ = 162.7 (d, *J* = 246.0 Hz, $CF_{arom,minor}$), 162.6 (d, *J* = 245.6 Hz, $CF_{arom,major}$), 142.0 (d, *J* = 7.6 Hz, $C_{arom,minor}$), 141.6 (d, *J* = 7.6 Hz, $C_{arom,major}$), 134.4 ($C_{arom,major}$), 134.4 ($C_{arom,minor}$), 130.2 (d, *J* = 8.3 Hz, $C_{arom,major}$), 130.2 (d, *J* = 8.6 Hz, $C_{arom,minor}$), 129.2 ($CH_{olef,major}$), 128.1 ($CH_{olef,minor}$), 127.4 ($CH_{olef,major}$), 126.0 ($CH_{olef,minor}$), 116.6 (d, *J* = 21.9 Hz, $C_{arom,major}$), 116.2 (d, *J* = 21.0 Hz, $C_{arom,minor}$), 113.1 (d, *J* = 21.0 Hz, $C_{arom,major}$), 113.0 (d, *J* = 21.0 Hz, $C_{arom,minor}$), 62.8 ($OCH_{2,benzylic,minor}$), 62.8 ($OCH_{2,benzylic,major}$), 35.6 ($CH_{2,benzylic,major}$), 30.1 ($CH_{2,benzylic,minor}$), 18.1 ($CH_{3,benzylic,major}$), 13.1 ($CH_{3,benzylic,minor}$) ppm. **^{19}F NMR**: (282 MHz, $CDCl_3$) δ = -114.80 ppm. **IR** (ATR) $\tilde{\nu}$ (cm^{-1}) = 3365 (m), 3070 (w), 3024 (w), 2958 (w), 2920 (m), 2857 (w), 1612 (w), 1591 (s), 1495 (s), 1452 (w), 1419 (w), 1364 (w), 1243 (s), 1179 (w), 1148 (m), 1123 (w), 1084 (w), 1034 (w), 1010 (s), 969 (m), 959 (w), 865 (w), 816 (m), 753 (w), 684 (s), 609 (w), 568 (m), 528 (w), 517 (w), 467 (w), 449 (w), 433 (w), 419 (w). **HRMS** (APCI+) m/z: [M-H2O]+ Calcd for C11H12F 163.0923, Found 163.0918.

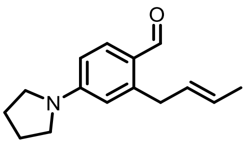
2-(but-2-en-1-yl)-4-fluorobenzaldehyde **4c**



was obtained according to general procedure VI, using the corresponding alcohol **S23** (254 mg, 1.41 mmol) Purification by column chromatography (*n*-pentane/Et_2O, 10:1) afforded **4c** (143 mg, 0.80 mmol, 57%) as a colorless oil.

^{1}H NMR: (500 MHz, $CDCl_3$) δ = 10.21 (s, 1H, CHO), 7.88 – 7.84 (m, 1H, CH_{arom}), 7.07 – 6.97 (m, 2H, 2 x CH_{arom}), 5.68 – 5.44 (m, 2H, $CH_{2,olef}$), 3.84 (dd, *J* = 7.2, 0.7 Hz, 0.48H, $CH_{2,benzylic,minor}$), 3.74 (dt, *J* = 6.3, 1.5 Hz, 1.62H, $CH_{2,benzylic,major}$), 1.73 (ddt, *J* = 6.8, 1.9, 0.9 Hz, 0.71H, $CH_{3,minor}$), 1.68 (dq, *J* = 6.3, 1.4 Hz, 2.29H, $CH_{3,major}$) ppm. **^{13}C NMR**: (126 MHz, $CDCl_3$) δ = 191.0 (CHO_{minor}), 190.8 (CHO_{major}), 166,1 (d, *J* = 256.5 Hz, $CF_{arom,major}$), 147.4 (d, *J* = 8.5 Hz, $C_{arom,minor}$), 147.1 (d, *J* = 8.6 Hz, $C_{arom,major}$), 134.8 (d, *J* = 9.5 Hz, $C_{arom,minor}$), 134.2 (d, *J* = 10.5 Hz, $C_{arom,major}$), 130.5 (d, *J* = 3.0 Hz, $C_{arom,minor}$), 130.5 (d, *J* = 2.9 Hz, $C_{arom,major}$), 128.7 ($CH_{olef,major}$), 128.2 ($CH_{olef,major}$), 127.4 ($CH_{olef,minor}$), 126.5 ($CH_{olef,minor}$), 117.8 (d, *J* = 21.9 Hz, $C_{arom,major}$), 117.4 (d, *J* = 21.9 Hz, $C_{arom,minor}$), 114.1 (d, *J* = 22.1 Hz, $C_{arom,major}$), 114.0 (d, *J* = 21.9 Hz, $C_{arom,minor}$), 35.3 ($CH_{2,benzylic,major}$), 30.0 ($CH_{2,benzylic,minor}$), 18.1 ($CH_{3,major}$), 13.1 ($CH_{3,minor}$) ppm. Due to the noise to signal ratio and ^{19}F-coupling, the quaternary aromatic carbon atom of the minor isomer $CF_{arom,major}$ could not be detected. **^{19}F NMR**: (282 MHz, $CDCl_3$) δ = -103.58 ppm. **IR** (ATR) $\tilde{\nu}$ (cm^{-1}) = 3026 (w), 2919 (w), 2858 (w), 2734 (w), 1693 (s), 1605 (m), 1582 (s), 1491 (w), 1432 (w), 1399 (w), 1310 (w), 1277 (w), 1243 (s), 1212 (w), 1200 (w), 1151 (w), 1109 (w), 1084 (w), 1026 (w), 965 (m), 869 (w), 818 (m), 616 (w), 466 (w). **HRMS** (ESI+) m/z: [M+H]+ Calcd for C11H11FOH 179.0867, Found 179.0865.

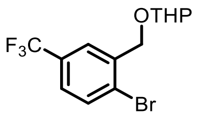
2-(but-2-en-1-yl)-4-(pyrrolidin-1-yl)benzaldehyde **4S3**



aldehyde **4c** (89.1 mg, 0.50 mmol), K_2CO_3 (138 mg ,1.00 mmol, 2.00 equiv) and pyrrolidine (0.08 mL, 1.00 mmol, 2.00 equiv) were added to a Schlenk-flask under inert atmosphere. 4 mL DMF were added and the reaction mixture was stirred for 16 h at 80 °C. Sat.5CF3 $NaHCO_3$ solution (5 mL) was added and the mixture was extracted with CH_2Cl_2 (3 x 10 mL). The combined organic layers were washed with water (3 x 15 mL) and brine (15 mL), dried over Na_2SO_4, filtered and the solvent was removed under reduced pressure. Purification by column chromatography 10:1 (*n*-pentane/EtOAc) afforded **4S3** (92.0 mg, 0.40 mmol, 80%) as a blue oil.

^{1}H NMR: (300 MHz, $CDCl_3$) δ = 10.00 (s, 1H, C*H*O), 7.78 – 7.68 (m, 1H, CH_{arom}), 6.48 (dd, *J* = 8.6, 2.5 Hz, 1H, CH_{arom}), 6.41 – 6.33 (m, 1H, CH_{arom}), 5.73 – 5.45 (m, 2H, 2 x CH_{olef}), 3.81 (d, *J* = 5.6 Hz, 0.29H, C$H_{2,benzylic,minor}$), 3.71 (d, *J* = 7.3 Hz, 1.71H, C$H_{2,benzylic,major}$), 3.45 – 3.37 (m, 4H, 2 x CH_2), 12.11 – 2.03 (m, 4H, 2 x CH_2), 1.77 (d, *J* = 4.7 Hz, 0.43H, C$H_{3,minor}$), 1.68 (d, *J* = 6.5 Hz, 2.57H, C$H_{3,major}$) ppm. **^{13}C NMR**: (75 MHz, $CDCl_3$) δ = 190.1 (*C*HO), 151.6 (C_{arom}), 146.0 (C_{arom}), 134.3 (C_{arom}), 130.2 (CH_{olef}), 126.6 (CH_{olef}), 122.6 (C_{arom}), 112.7 (C_{arom}), 109.6 (C_{arom}), 47.7 ($CH_{2,major}$), 36.3 ($CH_{2,minor}$), 25.6 ($CH_{3,major}$), 18.1 ($CH_{3,minor}$) ppm. **IR** (ATR) $\tilde{\nu}$ (cm^{-1}) = 2923 (m), 2852 (w), 1668 (w), 1590 (s), 1544 (w), 1516 (w), 1484 (w), 1449 (w), 1384 (m), 1351 (w), 1263 (m), 1214 (w), 1179 (w), 1106 (w), 1023 (w), 968 (w), 803 (m), 733 (s), 701 (w), 666 (w), 595 (w), 456 (w). **HRMS** (ESI+) m/z: [M+Na]+ Calcd for C15H19NONa 252.1359, Found 252.1362.

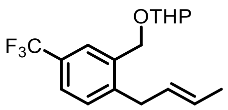
2-((2-bromo-5-(trifluoromethyl)benzyl)oxy)tetrahydro-2H-pyran **S24**



was obtained according to general procedure IV, using the corresponding alcohol **S25** (1.00 g, 3.93 mmol). Purification by column chromatography afforded **S24** (1.32 mg, 3.89 mmol, 99%) as a colorless oil.

^{1}H NMR: (300 MHz, $CDCl_3$) δ = 7.79 (d, *J* = 2.6 Hz, 1H, CH_{arom}), 7.66 (d, *J* = 8.3 Hz, 1H, CH_{arom}), 7.40 (dd, *J* = 8.3, 2.5 Hz, 1H, CH_{arom}), 4.86 (d, *J* = 14.0 Hz, 1H, C*H*$H_{benzylic}$), 4.80 (t, *J* = 3.4 Hz, 1H, OC*H*O), 4.58 (d, *J* = 14.0 Hz, 1H, CH$H_{benzylic}$), 3.90 (ddd, *J* = 11.5, 8.5, 3.5 Hz, 1H, OC*H*H_{THP}), 3.58 (dtd, *J* = 11.3, 4.5, 1.7 Hz, 1H, OCHH_{THP}), 2.01 – 1.50 (m, 6H. 3 x C$H_{2,THP}$) ppm. **^{13}C NMR**: (126 MHz, $CDCl_3$) δ = 139.4 (C_{arom}), 133.0 (C_{arom}), 130.08 (q, ^2J = 30.9 Hz, CF_3C_{arom}), 126.19 (q, ^1J = 276.0 Hz, CF_3), 125.58 (q, ^3J = 3.9 Hz, CH_{arom}), 125.42 (q, ^3J = 4.1 Hz, CF_3CCH_{arom}), 98.8 (O*C*HO), 68.2 ($CH_{2,benzylic}$), 62.4 (O$CH_{2,THP}$), 30.6 ($CH_{2,THP}$), 25.5 ($CH_{2,THP}$), 19.4 ($CH_{2,THP}$) ppm. **^{19}F NMR**: (282 MHz, $CDCl_3$) δ = - 62.73 ppm. **IR** (ATR) $\tilde{\nu}$ (cm^{-1}) = 2944 (w), 2872 (w), 1606 (w), 1583 (w), 1455 (w), 1442 (w), 1414 (w), 1387 (w), 1328 (s), 1258 (w), 1200 (w), 1168 (m), 1125 (s), 1081 (s), 1038 (m), 1025 (w), 972 (w), 907 (w), 871 (w), 824 (w), 750 (w), 438 (w), 423 (w). **HRMS** (ESI+) m/z: [M+Na]+ Calcd for C13H14BrF3O2Na 361.0021, 363.0002, Found 361.0019, 362.9999.

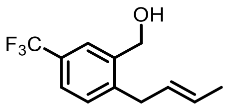
2-((2-(but-2-en-1-yl)-5-(trifluoromethyl)benzyl)oxy)tetrahydro-2H-pyran **S26**



was obtained according to general procedure IV, using the corresponding acetal **S24** (0.66 g, 1.94 mmol) and crotylbromide (0.26 mL, 2.52 mmol, 85:15 *E/Z*). Purification by column chromatography afforded **S26** (0.36 g, 1.15 mmol, 60%, 75:25 *E/Z*) as a colorless oil.

^{1}H NMR: (500 MHz, $CDCl_3$) δ = 7.68 (s, 1H, CH_{arom}), 7.48 (d, *J* = 8.1 Hz, 1H, CH_{arom}), 7.30 (t, *J* = 8.8 Hz, 1H, CH_{arom}), 5.69 – 5.39 (m, 2H, 2 x C$H_{,olef}$), 4.87 – 4.82 (m, 1H, OC*H*$H_{benzylic}$), 4.72 (d, *J* = 7.0 Hz, 1H, OC*H*O), 4.55 – 4.50 (m, 1H, OCH$H_{benzylic}$), 3.90 (ddd, *J* = 11.6, 8.6, 3.3 Hz, 1H, OC*H*H_{THP}), 3.60 – 3.54 (m, 1H, OCHH_{THP}), 3.47 (d, *J* = 7.1 Hz, 0.5H, C$H_{2,benzylic,minor}$), 3.40 (d, *J* = 7.5 Hz, 1.5H C$H_{2,benzylic,major}$), 1.91 – 1.84 (m, 1H, C*H*H_{THP}), 1.78 – 1.66 (m, 5H, CHH_{THP}, CH_3, C*H*H_{THP}), 1.65 – 1.55 (m, 3H, CH$H_{THP,}$ C$H_{2,THP}$) ppm. **^{13}C NMR**: (126 MHz, $CDCl_3$) δ = 143.4 ($C_{arom,minor}$), 143.2 ($C_{arom,major}$), 137.1 ($C_{arom,major}$), 129.9 ($C_{arom,major}$), 129.4 ($C_{arom,minor}$), 128.6 (q, ^2J = 31.9 Hz, CF_3C_{arom}), 128.5 ($CH_{olef,major}$), 127.6 ($CH_{olef,minor}$), 127.4 ($CH_{olef,major}$), 126.1 ($CH_{olef,minor}$), 125.3 (q, ^3J = 3.8 Hz, $C_{arom,major}$), 125.2 (q, ^1J = 271.4 Hz, CF_3), 124.6 – 124.5 (m, 2C, 2 x $C_{arom,major}$), 98.4 (OCHO_{major}), 98.4 (OCHO_{minor}), 66.4 (O$CH_{2,benzylic,minor}$), 66.3 (O$CH_{2,benzylic,major}$), 62.4 (O$CH_{2,THP}$), 35.5 ($CH_{2,benzylic,major}$), 30.7 ($CH_{2,THP}$), 30.0 ($CH_{2,benzylic,minor}$), 25.6 ($CH_{2,THP}$), 19.5 ($CH_{2,THP}$), 18.1 ($CH_{3,major}$), 13.1 ($CH_{3,minor}$) ppm. **^{19}F NMR**: (282 MHz, $CDZCl_3$) δ = -62.30 ppm. **IR** (ATR) $\tilde{\nu}$ (cm^{-1}) = 2943 (w), 2872 (w), 1620 (w), 1426 (w), 1384 (w), 1329 (s), 1268 (w), 1202 (w), 1161 (m), 1119 (s), 1080 (m), 1059 (w), 1031 (m), 971 (m), 945 (w), 907 (m), 871 (w), 835 (w), 816 (w). **HRMS** (ESI+) m/z: [M+Na]+ Calcd for C17H21F3O2Na 337,1397, Found 337.1386.

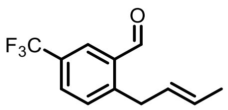
(2-(but-2-en-1-yl)-5-(trifluoromethyl)phenyl)methanol **S27**



was obtained according to general procedure VI, using the corresponding acetal **S26** (0.31 g, 0.97 mmol) and aqueous HCl solution (1 M, 0.1 mL) instead of PPTS. Purification by column chromatography (*n*-pentane/Et_2O, 20:1 → 10:1 → 4:1) afforded **S27** (0.20 g, 0.87 mmol, 89%) as a colorless oil.

^{1}H NMR: (500 MHz, $CDCl_3$) δ = 7.69 (s, 1H, CH_{arom}), 7.49 (d, *J* = 7.9 Hz, 1H, CH_{arom}), 7.34 – 7.28 (m, 1H, CH_{arom}), 5.55 (s, 2H, 2 x $CH_{2,olef}$), 4.77 (t, *J* = 5.2 Hz, 2H, OCH_2), 3.48 (d, *J* = 7.2 Hz, 0.5H, $CH_{2,benzylic,minor}$), 3.41 (d, *J* = 6.3 Hz, 1.5H, $CH_{2,benzylic,major}$), 1.75 – 1.74 (m, 0.73H, $CH_{3,minor}$), 1.68 (dq, *J* = 6.2, 1.4 Hz, 2.24H, $CH_{3,major}$) ppm. **^{13}C NMR**: (126 MHz, $CDCl_3$) δ = 143.0 ($C_{arom,minor}$), 142.6 ($C_{arom,major}$), 139.4 ($C_{arom,major}$), 139.4 ($C_{arom,minor}$), 130.1 ($C_{arom,major}$), 129.7 ($C_{arom,minor}$), 128.9 (q, ^2J = 32.4 Hz, CF_3C_{arom}), 128.7 ($CH_{olef,major}$), 127.7 ($CH_{olef,minor}$), 127.6 ($CH_{olef,major}$), 126.2 ($CH_{olef,minor}$), 125.0 (q, ^1J = 272.4 Hz, CF_3), 124.8 – 124.5 (m, 2 x C_{arom}), 123.3 ($C_{arom,minor}$), 62.7 ($OCH_{2,benzylic,minor}$), 62.6 ($OCH_{2,benzylic,major}$), 35.6 ($CH_{2,benzylic,major}$), 30.2 ($CH_{2,benzylic,minor}$), 18.0 ($CH_{3,major}$), 13.1 ($CH_{3,minor}$) ppm. Due to the noise to signal ratio and ^{19}F-coupling, some aromatic carbon atom of the minor isomer could not be detected.**^{19}F NMR**: (282 MHz, $CDCl_3$) δ = -62.37 ppm. **IR** (ATR) $\tilde{\nu}$ (cm^{-1}) = 3365 (m), 3070 (w), 3024 (w), 2958 (w), 2920 (m), 2857 (w), 1612 (w), 1591 (s), 1495 (s), 1452 (w), 1419 (w), 1364 (w), 1243 (s), 1179 (w), 1148 (m), 1123 (w), 1084 (w), 1034 (w), 1010 (s), 969 (m), 959 (w), 865 (w), 816 (m), 753 (w), 684 (s), 609 (w), 568 (m), 528 (w), 517 (w), 467 (w), 449 (w), 433 (w), 419 (w). **HRMS** (ESI-) m/z: [M]- Calcd for C12H12F3O 229.0846, Found 229.0830.

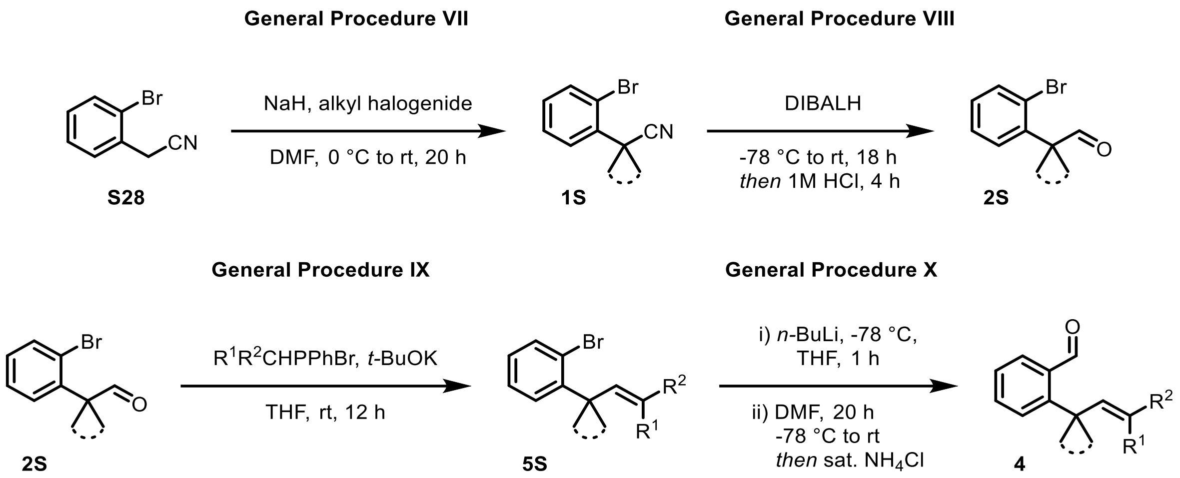
2-(but-2-en-1-yl)-5-(trifluoromethyl)benzaldehyde **4b**



was obtained according to general procedure VI, using the corresponding alcohol **S27** (191 mg, 1.06 mmol) Purification by column chromatography (*n*-pentane/Et_2O, 50:1) afforded **4b** (64 mg, 0.36 mmol, 34%) as a pale-yellow oil.

^{1}H NMR: (500 MHz, $CDCl_3$) δ = 10.31 (s, 1H, CHO), 8.12 – 8.09 (m, 1H, CH_{arom}), 7.77 – 7.74 (m, 1H, CH_{arom}), 7.48 – 7.42 (m, 1H, CH_{arom}), 5.68 – 5.41 (m, 2H, 2 x $CH_{2,olef}$), 3.88 (d, *J* = 7.1 Hz, 0.5H, $CH_{2,minor}$), 3.79 (d, *J* = 6.4 Hz, 1.5H, $CH_{2,major}$), 1.75 (ddt, *J* = 6.9, 1.9, 1.0 Hz, 0.75H, $CH_{3,minor}$), 1.67 (dq, *J* = 6.4, 1.5 Hz, 2.25H, $CH_{3,major}$) ppm. **^{13}C NMR**: (126 MHz, $CDCl_3$) δ = 191.1 (CHO_{minor}), 190.9 (CHO_{major}), 147.6 ($C_{arom,minor}$), 147.2 ($C_{arom,major}$), 134.1 ($C_{arom,minor}$), 134.1 ($C_{arom,major}$), 131.8 ($C_{arom,major}$), 131.4 ($C_{arom,minor}$), 130.3 (q, ^3J = 3.8 Hz, 2 x C_{arom}), 129.6 (p, ^2J = 33.3 Hz, $C_{arom,major}$), 129.1 (q, ^2J = 33.5 Hz, $C_{arom,minor}$), 128.7 ($CH_{olef,major}$), 128.3 ($CH_{olef,major}$), 128.3 (q, ^3J = 3.8 Hz $C_{arom,minor}$), 127.7 (q, ^3J = 3.8 Hz $C_{arom,major}$), 127.3 ($CH_{olef,minor}$), 126.6 ($CH_{olef,minor}$), 124.3 (q, ^1J = 271.8 Hz, CF_3), 35.4 ($CH_{2,benzylic,major}$), 30.1 ($CH_{2,benzylic,minor}$), 18.1 ($CH_{3,major}$), 13.2 ($CH_{3,minor}$) ppm. **^{19}F NMR**: (282 MHz, $CDCl_3$) δ = -62.79 ppm. **IR** (ATR) $\tilde{\nu}$ (cm^{-1}) = 3027 (w), 2921 (w), 2860 (w), 2737 (w), 1697 (m), 1617 (w), 1577 (w), 1502 (w), 1453 (w), 1396 (w), 1330 (s), 1270 (w), 1165 (m), 1125 (s), 1083 (w), 1054 (w), 968 (w), 942 (w), 914 (w), 842 (w), 816 (w), 766 (w), 735 (w), 693 (w), 644 (w), 580 (w), 557 (w), 441 (w), 416 (w). **HRMS** (APCI+) m/z: [M+H]+ Calcd for C12H11FOH 229.0835, Found 229.0832.

8 General Procedure VII-X: Substrate Synthesis



General Procedure VII: Alkylation of Benzyl Nitriles

Unless otherwise noted the alkylation was carried out with the following protocol.

NaH (2.30 equiv.) was placed in an oven dried flask and suspended in anhydrous DMF (0.5 M). To the suspension 2-brom-phenylacetonitrile **11** (1.00 equiv.) was added at 0 °C dropwise to control the gas formation and stirred for 20 min. When the gas formation resigned, the alkyl halogenide (1.30 equiv. for dihalogenides, 2.60 equiv. for gem-dimethyl product **1S1** using methyl iodide) was added carefully over a time span of 15 min at 0 °C. The reaction was allowed to warm to rt and stirred overnight. Sat. NH_4Cl-solution was added dropwise and the mixture was extracted with Et_2O (3 x). The combined organic layers were washed with brine and dried over Na_2SO_4. The solvent was removed under reduced pressure. The residue was purified by column chromatography (*n*-pentane/EtOAc 20:1→10:1, unless otherwise noted) to give the product as a colorless oil or solid.

General Procedure VIII: Nitrile Reduction to Aldehyde

The reduction was carried out according to a protocol reported by BACH *et al.*[12]

In an oven dried flask nitrile **1S** (1.00 equiv.) was dissolved in anhydrous CH_2Cl_2 (0.3 M) and cooled to -78 °C. DIBAL-H (1.20 equiv., 1.1 M in hexane) was added dropwise and the solution was stirred for 2 h at -78 °C. The solution was allowed to warm to rt and stirred at rt for 2 h. The solution was then cooled to 0 °C and 6 M HCl (6 mL/ 1 mmol starting material) was added dropwise. The mixture was allowed to warm to rt and stirred overnight. Afterwards the mixture was extracted by CH_2Cl_2 (3 x). The combined organic layers were washed with brine and dried over Na_2SO_4. The solvent was removed under reduced pressure. The residue was purified by column chromatography (*n*-pentane/Et_2O 50:1→20:1→10:1, unless otherwise noted) to give **2S** as a colorless oil.

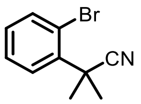
General Procedure IX: Wittig Reaction

In an oven dried flask, the phosphonium salt (1.30 equiv.) and *t*-BuOK (1.5 equiv.) were dissolved in anhydrous Et_2O (0.2 M) and stirred for 2 h at rt. The mixture was cooled to 0 °C and the corresponding aldehyde **2S** (1.00 equiv.) was added as a solution in anhydrous Et_2O (1 M) and the mixture was stirred overnight at rt. Afterwards, silica gel was added and the solvent was removed under reduced pressure. The residue was purified by column chromatography (*n*-pentane, unless otherwise noted) the resulting product was then stirred with CuCl (1.00 equiv.) in acetone for 2 h. The mixture was filtered over a silica plug and washed with acetone to give the olefin **5S** as a colorless oil.

General Procedure X: Benzaldehyde Formation

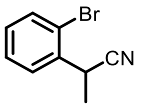
In an oven dried flask, the olefin **5S** (1.00 equiv.) was dissolved in anhydrous Et_2O (0.25 M) at 0 °C and *n*-BuLi (1.40 equiv., 2.5 M in hexane) was added dropwise. The solution was stirred for 3 h at 0 °C. DMF (1.30 equiv.) was added and the solution was stirred at rt overnight. Sat. NH_4Cl-solution was added to the reaction and the mixture was extracted with Et_2O (3 x). The combined organic layers were washed with brine and dried over Na_2SO_4. The solvent was removed under reduced pressure. The residue was purified by column chromatography (*n*-pentane/Et_2O 100:1, unless otherwise noted) to give **4** as a colorless oil.

2-(2-bromophenyl)-2-methylpropanenitrile **1S1**



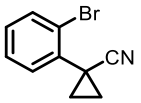
was obtained following the procedure reported by ZHANG *et al*. starting from 2-brom-phenylacetonitrile **11**.[13] Spectral data was in agreement with the literature.[14]

2-(2-bromophenyl)propanenitrile **1S2**



was obtained following the procedure reported by ZHANG *et al*. starting from 2-brom-phenylacetonitrile **11**.[13] Spectral data was in agreement with the literature.[14]

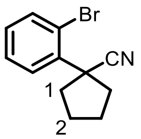
1-(2-bromophenyl)cyclopropane-1-carbonitrile **1S3**



was obtained according to general procedure VII, using 2-brom-phenylacetonitrile **11** (0.59 g, 3.00 mmol) and 1,2-dibromoethane (0.34 mL, 3.90 mmol). Purification by column chromatography afforded **1S3** (0.47 mg, 2.10 mmol, 70%) as a colorless solid.

^{1}H NMR: (500 MHz, $CDCl_3$) δ = 7.62 (ddd, *J* = 7.9, 1.3, 0.4 Hz, 1H, CH_{arom}), 7.34 (dd, *J* = 7.7, 1.8 Hz, 1H, CH_{arom}), 7.30 (td, *J* = 7.5, 1.3 Hz, 1H, CH_{arom}), 7.22 (ddd, *J* = 7.9, 7.3, 1.8 Hz, 1H, CH_{arom}), 1.80 – 1.74 (m, 2H. 2 x CH*H*), 1.38 – 1.32 (m, 2H, 2 x C*H*H).ppm. **^{13}C NMR**: (126 MHz, $CDCl_3$) δ = 135.5 (C_{arom}), 133.6 (C_{arom}), 131.7 (C_{arom}), 130.4 (C_{arom}), 127.9 (C_{arom}), 126.8 (C_{arom}), 121.8 (*C*N), 17.0 (2 x CH_2), 15.7 (C_{quart}CN) ppm. **IR** (ATR) $\tilde{\nu}$ (cm^{-1}) = 3060 (w), 3019 (w), 2234 (m), 1927 (w), 1590 (w), 1567 (w), 1472 (m), 1428 (m), 1319 (w), 1252 (w), 1163 (w), 1114 (w), 1075 (w), 1026 (s), 952 (w), 940 (w), 865 (w), 758 (s), 725 (m), 698 (w), 646 (w), 577 (m), 520 (w), 453 (w), 421 (w). **HRMS** (ESI+) m/z: [M+Na]+ Calcd for C10H8BrNNa 243.9732, 245.9711, Found 243.9733, 245.9712. **m.p**. 70.0 – 72.0 °C (ethyl acetate).

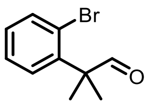
1-(2-bromophenyl)cyclopentane-1-carbonitrile **1S4**



was obtained according to general procedure VII, using 2-brom-phenylacetonitrile **11** (0.98 g, 5.00 mmol) and 1,4-dibromobutane (1.40 mL, 6.50 mmol). Purification by column chromatography (*n*-pentane/Et_2O 20:1) afforded **1S4** (1.33 g, 5.32 mmol, 83%) as a light brown oil.

^{1}H NMR: (500 MHz, $CDCl_3$) δ = 7.67 (dd, *J* = 7.9, 1.4 Hz, 1H, CH_{arom}), 7.42 (dd, *J* = 8.0, 1.7 Hz, 1H, CH_{arom}), 7.32 (ddd, *J* = 8.0, 7.3, 1.4 Hz, 1H, CH_{arom}), 7.19 (ddd, *J* = 8.0, 7.3, 1.7 Hz, 1H, CH_{arom}), 2.79 – 2.73 (m, 2H, 2 x ^{1}C*H*H), 2.24 – 2.17 (m, 2H, 2 x ^{1}CH*H*), 2.08 – 2.01 (m, 2H, 2 x ^{2}C*H*H), 1.94 – 1.87 (m, 2H, 2 x ^{2}CH*H*) ppm. **^{13}C NMR**: (126 MHz, $CDCl_3$) δ = 137.8 (C_{arom}), 135.4 (C_{arom}), 129.7 (C_{arom}), 127.9 (C_{arom}), 127.7 (C_{arom}), 123.9 (C_{arom}), 123.2 (*C*N), 47.8 (C_{quart}), 38.4 (2 x CH_2), 23.9 (2 x CH_2) ppm. **IR** (ATR) $\tilde{\nu}$ (cm^{-1}) = 3066 (w), 2958 (m), 2876 (w), 2231 (w), 1926 (w), 1684 (w), 1587 (w), 1566 (w), 1468 (m), 1454 (w), 1434 (w), 1319 (w), 1275 (w),1228 (w), 1167 (w), 1023 (m), 957 (w), 902 (w), 863 (w), 755 (s), 724 (w), 686 (w), 641 (w), 554 (w), 538 (w), 481 (w), 447 (w). **HRMS** (ESI+) m/z: [M+Na]+ Calcd for C12H12BrNNa 272.0056, Found 272.0039.

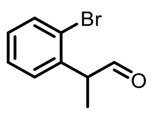
2-(2-bromophenyl)-2-methylpropanal **2S1**



was obtained according to general procedure VIII, using the corresponding nitrile **1S1** (2.94 g, 15.0 mmol). Purification by column chromatography afforded **2S1** (2.52 mg, 11.1 mmol, 74%) as a colorless oil.

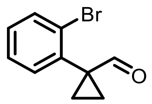
^{1}H NMR: (500 MHz, $CDCl_3$) δ = 9.80 (s, 1H, C*H*O), 7.61 (dd, *J* = 7.9, 1.4 Hz, 1H, CH_{arom}), 7.42 (dd, *J* = 7.9, 1.8 Hz, 1H, CH_{arom}), 7.37 (ddd, *J* = 7.8, 7.2, 1.3 Hz, 1H, CH_{arom}), 7.19 (ddd, *J* = 7.9, 7.2, 1.8 Hz, 1H, CH_{arom}), 1.52 (s, 6H, 2 x CH_3) ppm. **^{13}C NMR**: (126 MHz, $CDCl_3$) δ = 203.1 (*C*HO), 142.4 (C_{arom}), 134.5 (C_{arom}), 129.1 (C_{arom}), 128.6 (C_{arom}), 127.9 (C_{arom}), 123.5 (C_{arom}), 51.8 (C_{quart}), 23.2 (2 x CH_3) ppm. **IR** (ATR) $\tilde{\nu}$ (cm^{-1}) = 3067 (w), 2976 (w), 2935 (w), 2875 (w), 2803 (w), 2703 (w), 1721 (s), 1589 (w), 1565 (w), 1468 (m), 1426 (w), 1390 (w), 1361 (w), 1274 (w), 1239 (w), 1168 (w), 1112 (w), 1044 (w), 1023 (m), 983 (w), 948 (w), 907 (w), 886 (w), 839 (w), 756 (s), 733 (w), 722 (w), 670 (w), 653 (w), 637 (w), 617 (w), 550 (w), 452 (w), 422 (w). **HRMS** (ESI+) m/z: [M+H]+ Calcd for C10H11BrOH 227.0066, 229.0046, Found 227.0063, 229.0414.

2-(2-bromophenyl)propanal **2S2**



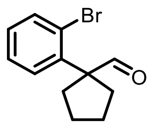
was obtained according to general procedure VIII, using the corresponding nitrile **1S2** (2.10 g, 10.0 mmol). Purification by column chromatography afforded **2S2** (1.22 g, 5.74 mmol, 57%) as a colorless oil.
^{1}H NMR: (500 MHz, $CDCl_3$) δ = 9.74 (s, 1H, C*H*O), 7.64 (dd, *J* = 8.1, 1.3 Hz, 1H, CH_{arom}), 7.34 (dd, *J* = 7.7, 1.3 Hz, 1H, CH_{arom}), 7.18 (ddd, *J* = 8.1, 7.4, 1.7 Hz, 1H, CH_{arom}), 7.12 (dd, *J* = 7.7, 1.7 Hz, 1H, CH_{arom}), 4.17 (q, *J* = 7.1 Hz, 1H, C*H*), 1.44 (d, *J* = 7.1 Hz, 3H, CH_3) ppm. **^{13}C NMR**: (126 MHz, $CDCl_3$) δ = 200.4 (*C*HO), 138.0 (C_{arom}), 133.5 (C_{arom}), 129.4 (C_{arom}), 129.2 (C_{arom}), 128.2 (C_{arom}), 125.3 (C_{arom}), 52.1 (*C*H), 14.2 (CH_3) ppm. **IR** (ATR) $\tilde{\nu}$ (cm^{-1}) = 3060 (w), 2979 (w), 2935 (w), 2874 (w), 2816 (w), 2722 (w), 1720 (s), 1589 (w), 1567 (w), 1471 (m), 1438 (w), 1389 (w), 1371 (w), 1278 (w), 1245 (w), 1194 (w), 1162 (w), 1126 (w), 1071 (w), 1047 (w), 1022 (s), 945 (w), 897 (w), 865 (w), 752 (s), 722 (w), 669 (w), 654 (w), 538 (w), 449 (m). **HRMS** (ESI-) m/z: [M]- Calcd for C9H8BrO 210.9764, 212.9744, Found 210.9759, 212.9738.

1-(2-bromophenyl)cyclopropane-1-carbaldehyde **2S3**



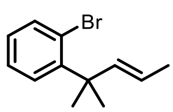
was obtained according to general procedure VIII, using the corresponding nitrile **1S3** (1.11 g, 5.00 mmol). Purification by column chromatography afforded **2S3** (1.07 g, 4.74 mmol, 95%) as a colorless oil.
^{1}H NMR: (500 MHz, $CDCl_3$) δ = 9.21 (s, 1H, C*H*O), 7.63 (ddd, *J* = 8.0, 1.3, 0.5 Hz, 1H, CH_{arom}), 7.31 (ddd, *J* = 7.7, 7.2, 1.3 Hz, 1H, CH_{arom}), 7.28 – 7.26 (m, 1H, CH_{arom}), 7.20 (ddd, *J* = 8.0, 7.2, 2.0 Hz, 1H, CH_{arom}), 1.75 – 1.72 (m, 1H, 2 x CH*H*), 1.42 – 1.39 (m, 1H, 2 x C*H*H). ppm. **^{13}C NMR**: (126 MHz, $CDCl_3$) δ =199.9 (*C*HO), 137.5 (C_{arom}), 133.2 (C_{arom}), 132.4 (C_{arom}), 129.6 (C_{arom}), 127.7 (C_{arom}), 127.4 (C_{arom}), 38.3 (C_{quart}), 17.8 (2 x CH_2). ppm. **IR** (ATR) $\tilde{\nu}$ (cm^{-1}) =3057 (w), 3006 (w), 2830 (w), 2749 (w), 2703 (w), 1712 (s), 1654 (w), 1590 (w), 1564 (w), 1473 (m), 1437 (w), 1395 (w), 1344 (w), 1246 (w), 1160 (w), 1111 (w), 1069 (w), 1039 (w), 1024 (m), 968 (w), 899 (w), 865 (w), 758 (m), 742 (w), 725 (w), 670 (w), 655 (w), 636 (w), 589 (w), 563 (w), 546 (w), 517 (w), 495 (w), 471 (w), 451 (w). **HRMS** (ESI+) m/z: [M+Na]+ Calcd for C10H9BrONa 246.9729, 248.9709, Found 246.9727, 248.9706.

1-(2-bromophenyl)cyclopentane-1-carbaldehyde **2S4**



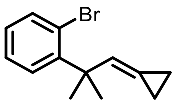
was obtained according to general procedure VIII, using the corresponding nitrile **1S4** (1.04 g, 4.14 mmol). Purification by column chromatography afforded **2S4** (0.45 g, 1.76 mmol, 43%) as a colorless oil.
^{1}H NMR: (500 MHz, $CDCl_3$) δ 9.67 (s, 1H, C*H*O), 7.62 (dd, J = 7.9, 1.4 Hz, 1H, CH_{arom}), 7.40 (dd, J = 7.9, 1.7 Hz, 1H, CH_{arom}), 7.34 (td, J = 7.5, 1.4 Hz, 1H, CH_{arom}), 7.17 (ddd, J = 7.9, 7.2, 1.7 Hz, 1H, CH_{arom}), 2.47 – 2.35 (m, 2H, 2 x C*H*H), 2.12 – 2.07 (m, 2H, 2 x CH*H*), 1.81 – 1.73 (m, 2H, 2 x CH_2) ppm. **^{13}C NMR**: (126 MHz, $CDCl_3$) δ =201.9 (*C*HO), 141.7 (C_{arom}), 134.6 (C_{arom}), 129.1 (C_{arom}), 128.9 (C_{arom}), 127.6 (C_{arom}), 124.7 (C_{arom}), 64.0 (C_{quart}), 34.2 (2 x CH_2), 25.1 (2 x CH_2) ppm. **IR** (ATR) $\tilde{\nu}$ (cm^{-1}) = 3063 (w), 2953 (m), 2871 (w), 2801 (w), 2717 (w), 1721 (s), 1587 (w), 1564 (w), 1467 (m), 1433 (w), 1385 (w), 1319 (w), 1268 (w), 1228 (w), 1102 (w), 1062 (w), 1042 (w), 1022 (m), 906 (w), 862 (w), 755 (m), 735 (w), 681 (w), 650 (w), 591 (w), 452 (w). **HRMS** (ESI+) m/z: [M+Na]+ Calcd for C12H13BrONa 275.0047, 277.0022, Found 275.0032, 277.0007.

(*E*)-1-bromo-2-(2-methylpent-3-en-2-yl)benzene **5S1**



was obtained according to general procedure IX, using the corresponding aldehyde **2S1** (0.50 g, 2.20 mmol). Purification by column chromatography afforded **5S1** (246 mg, 1.03 mmol, 47%) as a colorless oil.
^{1}H NMR: (500 MHz, $CDCl_3$) δ = 7.57 (dd, *J* = 7.9, 1.5 Hz, 1H, CH_{arom}), 7.52 (dd, *J* = 8.0, 1.7 Hz, 1H, CH_{arom}), 7.30 – 7.26 (m, 1H, CH_{arom}), 7.05 (ddd, *J* = 8.0, 7.3, 1.7 Hz, 1H, CH_{arom}), 5.75 (dq, *J* = 11.3, 1.8 Hz, 1H, CH_{olef}), 5.30 (dq, *J* = 11.3, 7.2 Hz, 1H, CH_{olef}), 1.54 (s, 6H, 2 x CH_3), 1.08 (dd, *J* = 7.2, 1.8 Hz, 3H, $CH_{olef}CH_3$).ppm. **^{13}C NMR**: (126 MHz, $CDCl_3$) δ = 148.1 (C_{arom}), 139.3 (C_{olef}), 135.2 (C_{arom}), 127.6 (C_{arom}), 127.5 (C_{arom}), 127.3 (C_{arom}), 123.4 (C_{arom}), 122.9 (C_{olef}), 41.1 (C_{quart}), 29.7 (2 x CH_3), 13.5 ($CH_{olef}CH_3$) ppm. **IR** (ATR) $\tilde{\nu}$ (cm^{-1}) = 3059 (w), 3013 (w), 2964 (w), 2870 (w), 1649 (w), 1588 (w), 1562 (w), 1466 (m), 1434 (w), 1423 (w), 1402 (w), 1381 (w), 1361 (w), 1289 (w), 1262 (w), 1227 (w), 1186 (w), 1167 (w), 1149 (w), 1105 (w), 1061 (w), 1045 (w), 1020 (s), 955 (w), 916 (w), 859 (w), 755 (s), 729 (m), 706 (s), 653 (m), 633 (m), 538 (w), 492 (w), 454 (m).**HRMS** (EI+) m/z: [M+Na]+ Calcd for C12H15Br 238.03571, Found 238.03690.

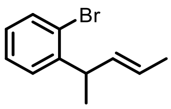
1-bromo-2-(1-cyclopropylidene-2-methylpropan-2-yl)benzene **5S2**



was obtained by the following procedure. A mixture of 1-bromopropyl-3-triphenylphosphonium bromide (369 mg, 0.79 mmol, 1.50 equiv.) and KO*t*Bu (178 mg, 1.59 mmol, 3.00 equiv.) in anhydrous THF (1.5 mL) under inert atmosphere was stirred at 60 °C for 90 min. Then aldehyde **2S1** (120 mg, 0.53 mmol, 1.00 equiv.) in 1.5 mL THF was added and the reaction was stirred for 2 h at 60 °C. The mixture was cooled to rt, quenched with water and diluted with Et_2O. The mixture was extracted with Et_2O (15 mL x 3), washed with brine (20 mL), dried over Na_2SO_4, filtered and the solvent was removed under reduced pressure. The crude was purified by column chromatography (*n*-pentane) and the product **5S2** (53.0 mg, 0.21 mmol, 40%) was obtained as a colorless oil.

^{1}H NMR: (300 MHz, $CDCl_3$) δ = 7.56 (dd, *J* = 7.9, 1.4 Hz, 1H, CH_{arom}), 7.49 (dd, *J* = 8.0, 1.7 Hz, 1H, CH_{arom}), 7.29 – 7.23 (m, 1H, CH_{arom}), 7.04 (ddd, *J* = 7.9, 7.3, 1.7 Hz, 1H, CH_{arom}), 6.05 (p, *J* = 2.1 Hz, 1H, CH_{olef}), 1.61 (s, 6H, 2 x CH_3), 0.95 – 0.84 (m, 4H, 2 x CH_2) ppm. **^{13}C NMR**: (76 MHz, $CDCl_3$) δ = 147.4 (C_{arom}), 135.4 (C_{arom}), 128.2 (C_{arom}), 127.6 (C_{arom}), 127.2 (C_{arom}), 126.6 (CH_{olef}), 123.7 (C_{arom}), 119.4 (C_{olef}), 43.0 (C_{quart}), 28.7 (2 x CH_3), 3.6 (CH_2), 0.5 (CH_2) ppm. **IR** (ATR) $\tilde{\nu}$ (cm^{-1}) = 3080 (w), 3003 (w), 2965 (w), 2871 (w), 1914 (w), 1797 (w), 1691 (w), 1646 (w), 1588 (w), 1563 (w), 1466 (m), 1425 (w), 1380 (w), 1361 (w), 1317 (w), 1264 (w), 1232 (w), 1189 (w), 1157 (w), 1096 (w), 1045 (w), 1019 (s), 949 (m), 878 (w), 813 (w), 754 (s), 729 (m), 655 (w), 645 (m), 547 (w), 505 (w), 454 (m). **HRMS** (EI+) m/z: [M+Na]+ Calcd for C12H14Br 249.02789, 251.02593, Found 249.02861, 251.02684.

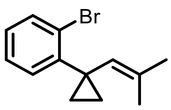
1-bromo-2-(pent-3-en-2-yl)benzene **5S3**



was obtained according to general procedure IX, using the corresponding aldehyde **2S2** (490 mg, 2.30 mmol). Purification by column chromatography afforded **5S3** (303 mg, 1.34 mmol, 58%, *E/Z* 84:16) as a colorless oil.

^{1}H NMR: (500 MHz, $CDCl_3$) δ = 7.56 – 7.49 (m, 1H, CH_{arom}), 7.32 – 7.20 (m, 2H, 2 x CH_{arom}), 7.07 – 7.00 (m, 1H, CH_{arom}), 5.63 – 5.44 (m, 2H, 2 x CH_{olef}), 4.25 – 4.16 (m, 0.84H, CH_{major}), 3.91 (ddt, *J* = 7.0, 5.8, 1.3 Hz, 0.16H, CH_{minor}), 1.71 – 1.68 (m, 0.45H, $CHCH_{3,minor}$), 1.67 – 1.63 (m, 2.53H, $CHCH_{3,major}$), 1.33 – 1.27 (m, 3H, $CH_{olef}CH_3$) ppm. **^{13}C NMR**: (126 MHz, $CDCl_3$) δ = 146.1 ($C{=}O_{major}$), 145.5 ($C{=}O_{minor}$), 134.6 ($CH_{olef,major}$), 134.5 ($CH_{olef,minor}$), 133.0 ($C_{arom,minor}$), 132.9 ($C_{arom,major}$), 128.3 ($C_{arom,minor}$), 128.1 ($C_{arom,major}$), 127.8 ($C_{arom,major}$), 127.7 ($C_{arom,minor}$), 127.6 ($C_{arom,minor}$), 127.5 ($C_{arom,major}$), 124.7 ($CH_{olef,minor}$), 124.5 ($CH_{olef,major}$), 124.4($C_{arom,minor}$), 124.0 ($C_{arom,major}$), 40.8 (CH_{minor}), 36.5 (CH_{major}), 22.2 ($CH_{3,major}$), 20.5 ($CH_{3,minor}$), 18.2 ($CH_{3,minor}$), 13.6 ($CH_{3,major}$) ppm. **IR** (ATR) $\tilde{\nu}$ (cm^{-1}) = 3060 (w), 3013 (w), 2967 (m), 2927 (w), 2870 (w), 1911 (w), 1795 (w), 1654 (w), 1590 (w), 1566 (w), 1469 (s), 1438 (w), 1401 (w), 1369 (w), 1319 (w), 1248 (w), 1194 (w), 1161 (w), 1110 (w), 1084 (w), 1022 (s), 999 (w), 971 (w), 938 (w), 859 (w), 789 (w), 752 (s), 731 (m), 712 (w), 660 (w), 618 (w), 583 (w), 551 (w), 517 (w), 448 (w). **HRMS** (EI+) m/z: [M]+ Calcd for C11H13Br 224.02006, 226.01808, Found 224.02018, 226.01819.

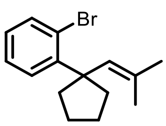
1-bromo-2-(1-(2-methylprop-1-en-1-yl)cyclopropyl)benzene **5S4**



was obtained according to general procedure IX, using the corresponding aldehyde **2S3** (563 mg, 2.50 mmol). Purification by column chromatography afforded **5S4** (537 mg, 2.14 mmol, 86%) as a colorless oil.

^{1}H NMR: (500 MHz, $CDCl_3$) δ = 7.54 (dd, *J* = 7.9, 1.3 Hz, 1H, CH_{arom}), 7.41 (dd, *J* = 7.7, 1.8 Hz, 1H, CH_{arom}), 7.23 (td, *J* = 7.5, 1.4 Hz, 1H, CH_{arom}), 7.06 (ddd, *J* = 7.9, 7.3, 1.7 Hz, 1H, CH_{arom}), 5.72 – 5.67 (m, 1H, CH_{olef}), 1.67 (d, *J* = 1.5 Hz, 3H, CH_3), 1.65 (d, *J* = 1.6 Hz, 3H, CH_3), 1.09 – 1.05 (m, 2H, 2 x CHH), 1.03 – 0.99 (m, 2H, 2 x CH*H*) ppm. **^{13}C NMR**: (126 MHz, $CDCl_3$) δ = 145.1 (C_{olef}), 135.7 (C_{arom}), 133.1(C_{arom}), 131.5(C_{arom}), 127.6(C_{arom}), 127.2(CH_{olef}), 127.0 (C_{arom}), 126.5 (C_{arom}), 26.1 (CH_3), 18.9 (CH_3), 16.0 (2 x $C_{cycprop}$).**IR** (ATR) $\tilde{\nu}$ (cm^{-1}) = 3078 (w), 3001 (w), 2968 (w), 2912 (w), 2854 (w), 1662 (w), 1588 (w), 1562 (w), 1469 (w), 1435 (m), 1422 (w), 1374 (w), 1337 (w), 1308 (w), 1250 (w), 1197 (w), 1160 (w), 1113 (w), 1064 (w), 1032 (w), 1021 (m), 981 (w), 951 (w), 911 (w), 890 (w), 861 (w), 825 (m), 808 (w), 754 (s), 734 (w), 723 (w), 655 (m), 604 (w), 547 (w), 515 (w), 474 (w), 448 (w). **HRMS** (EI+) m/z: [M]+ Calcd for C13H15Br 250.03571, 252.03375, Found 250.03762, 252.03710.

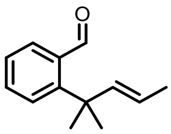
1-bromo-2-(1-(2-methylprop-1-en-1-yl)cyclopentyl)benzene **5S5**



was obtained according to general procedure IX, using the corresponding aldehyde **2S4** (157 mg, 0.62 mmol) and isopropyl triphenylphosphonium iodide (348 mg, 0.81 mmol). Purification by column chromatography afforded **5S5** (136 mg, 0.54 mmol, 87%) as a colorless oil.

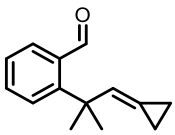
^{1}H NMR: (300 MHz, $CDCl_3$) δ = 7.54 (dd, *J* = 7.9, 1.5 Hz, 1H, CH_{arom}), 7.46 (dd, *J* = 7.9, 1.7 Hz, 1H, CH_{arom}), 7.25 – 7.18 (m, 1H, CH_{arom}), 7.05 – 6.97 (m, 1H, CH_{arom}), 5.66 (p, *J* = 1.4 Hz, 1H, CH_{olef}), 2.21 – 2.04 (m, 4H, 2 x CH_2), 1.76 – 1.62 (m, 4H, 2 x CH_2), 1.65 (d, *J* = 1.4 Hz, 3H, CH_3), 1.13 (d, *J* = 1.3 Hz, 3H, CH_3) ppm. **^{13}C NMR**: (75 MHz, $CDCl_3$) δ =147.9 (C_{arom}), 135.0 (C_{arom}), 133.4 (CH_{olef}), 130.6 (C_{olef}), 128.3 (C_{arom}), 127.1 (C_{arom}), 126.6 (C_{arom}), 124.0 (C_{arom}), 52.8 ($C_{benzylic}$), 39.3 (2 x CH_2), 26.8 (CH_3), 23.5 (2 x CH_2), 18.4 (CH_3) ppm. **IR** (ATR) $\tilde{\nu}$ (cm^{-1}) =3057 (w), 2958 (m), 2912 (w), 2871 (w), 1661 (w), 1586 (w), 1563 (w), 1452 (m), 1434 (w), 1376 (w), 1321 (w), 1262 (w), 1233 (w), 1187 (w), 1165 (w), 1080 (w), 1020 (s), 964 (w), 939 (w), 823 (w), 753 (s), 736 (w), 670 (w), 651 (w), 622 (w), 592 (w), 541 (w), 451 (w), 420 (w). **HRMS** (EI+) m/z: [M+Na]+ Calcd for C15H19Br 278.06701, 280.06508, Found 278.06873, 280.06672.

(*E*)-2-(2-methylpent-3-en-2-yl)benzaldehyde **4r**



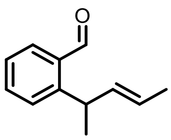
was obtained according to general procedure X, using the corresponding bromide **5S1** (244 mg, 1.02 mmol). Purification by column chromatography afforded **4r** (107 mg, 0.57 mmol, 56%) as a colorless oil.
^{1}H NMR: (500 MHz, $CDCl_3$) δ = 10.64 (s, 1H, C*H*O), 7.91 (dd, *J* = 7.7, 2.1 Hz, 1H, CH_{arom}), 7.56 – 7.50 (m, 2H, 2 x CH_{arom}), 7.33 (dddd, *J* = 7.6, 6.8, 1.7, 0.8 Hz, 1H, CH_{arom}), 5.95 (dq, *J* = 11.2, 1.8 Hz, 1H, CH_{olef}), 5.35 (dq, *J* = 11.2, 7.2 Hz, 1H, CH_{olef}), 1.56 (s, 6H, 2 x CH_3), 0.98 (dd, *J* = 7.3, 1.8 Hz, 3H, $CH_{olef}CH_3$) ppm. **^{13}C NMR**: (126 MHz, $CDCl_3$) δ = 192.5 (*C*HO), 152.2 (C_{arom}), 142.2 (CH_{olef}), 134.5 (C_{arom}), 133.6 (C_{arom}), 129.2 (C_{arom}), 126.6 (C_{arom}), 125.6 (C_{arom}), 125.2 (CH_{olef}), 39.6 (C_{quart}), 32.2 (2 x CH_3), 13.7 ($CH_{olef}CH_3$) ppm. **IR** (ATR) $\tilde{\nu}$ (cm^{-1}) = 3064 (w), 3008 (w), 2968 (w), 2933 (w), 2873 (w), 2771 (w), 1685 (s), 1645 (w), 1596 (m), 1469 (w), 1446 (w), 1399 (w), 1383 (w), 1363 (w), 1288 (w), 1270 (w), 1225 (w), 1195 (m), 1142 (w), 1120 (w), 1079 (w), 1064 (w), 1045 (w), 959 (w), 916 (w), 862 (w), 821 (m), 765 (s), 744 (w), 725 (w), 707 (m), 648 (w), 631 (m), 537 (w), 452 (w). **HRMS** (ESI+) m/z: [M+Na]+ Calcd for C13H16OH 189.1274, Found 189.1272.

2-(1-cyclopropylidene-2-methylpropan-2-yl)benzaldehyde **4x**



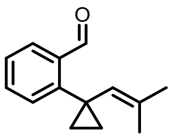
was obtained according to general procedure X, using the corresponding bromide **5S2** (37.7 mg, 0.15 mmol). Purification by column chromatography afforded **4x** (12.8 mg, 0.01 mmol, 43%) as a colorless oil.
^{1}H NMR: (500 MHz, $CDCl_3$) δ = 10.59 (s, 1H, C*H*O), 7.88 (dt, *J* = 7.7, 1.2 Hz, 1H, CH_{arom}), 7.57 – 7.47 (m, 2H, 2 x CH_{arom}), 7.38 – 7.29 (m, 1H, CH_{arom}), 6.22 (p, *J* = 2.0 Hz, 1H, CH_{olef}), 1.61 (s, 6H, 2 x CH_3), 0.95 – 0.86 (m, 2H, 2 x C*H*H), 0.85 – 0.76 (m, 2H, 2 x CH*H*)ppm. **^{13}C NMR**: (126 MHz, $CDCl_3$) δ = 192.9 (*C*HO), 151.2 (C_{arom}), 135.4 (C_{arom}), 133.3 (C_{arom}), 129.5 (CH_{olef}), 128.9 (C_{arom}), 126.7 (C_{arom}), 126.2 (C_{arom}), 120.9 (C_{olef}), 41.8 (C_{quart}), 31.5 (CH_3), 3.6 (CH_2), 0.7 (CH_2) ppm. **IR** (ATR) $\tilde{\nu}$ (cm^{-1}) = 3069 (w), 2963 (m), 2929 (w), 2869 (w), 2120 (w), 1796 (w), 1709 (s), 1602 (m), 1467 (m), 1387 (w), 1365 (w), 1323 (w), 1290 (w), 1274 (w), 1244 (m), 1221 (w), 1161 (w), 1109 (w), 1087 (w), 1066 (w), 1027 (m), 944 (w), 881 (w), 825 (w), 761 (s), 696 (w), 642 (w), 605 (w), 535 (w), 445 (w). **HRMS** (ESI+) m/z: [M+Na]+ Calcd for C14H16OH 201.1274, Found 201.1274.

2-(pent-3-en-2-yl)benzaldehyde **4n**



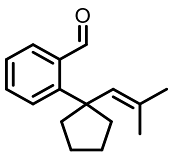
was obtained according to general procedure X, using the corresponding bromide **5S3** (293 mg, 1.30 mmol). Purification by column chromatography afforded **4n** (131 mg, 0.75 mmol, 58%, 86/14 *E/Z*) as a colorless oil.
^{1}H NMR: (500 MHz, $CDCl_3$) δ = 10.37 (s, 1H, C*H*O), 7.84 – 7.77 (m, 1H, CH_{arom}), 7.54 (td, *J* = 7.6, 1.6 Hz, 1H, CH_{arom}), 7.46 (dd, *J* = 7.8, 1.4 Hz, 0.86H, $CH_{arom,major}$), 7.40 (dd, *J* = 7.9, 1.3 Hz, 0.14H, $CH_{arom,minor}$), 7.37 – 7.31 (m, 1H, CH_{arom}), 5.68 (ddq, *J* = 15.4, 6.2, 1.7 Hz, 0.14H, $CH_{olef,minor}$), 5.62 (ddq, *J* = 10.5, 8.7, 1.7 Hz, 0.86H, $CH_{olef,major}$), 5.52 – 5.41 (m, 1H, CH_{olef}), 4.80 (p, *J* = 7.4 Hz, 0.86H, CH_{major}), 4.46 (p, *J* = 7.0 Hz, 0.14H, CH_{minor}), 1.68 (dd, *J* = 6.5, 1.5 Hz, 0.41H, $CH_{3,minor}$), 1.63 (dd, *J* = 6.8, 1.7 Hz, 2.55H, $CH_{3,major}$), 1.39 (d, *J* = 7.0 Hz, 0.42H, $CH_{3,minor}$), 1.37 (d, *J* = 7.0 Hz, 2.58H, $CH_{3,major}$) ppm. **^{13}C NMR**: (126 MHz, $CDCl_3$) δ = 192.6 (*C*HO), 149.8 ($C_{arom,major}$), 149.1 ($C_{arom,minor}$), 135.6 ($CH_{olef,minor}$), 135.3 ($CH_{olef,major}$), 134.2 ($C_{arom,major}$), 134.1 ($C_{arom,minor}$), 133.3 ($C_{arom,minor}$), 133.2 ($C_{arom,major}$), 131.5 ($C_{arom,major}$), 131.2 ($C_{arom,minor}$), 127.9 ($C_{arom,minor}$), 127.6 ($C_{arom,major}$), 126.5 ($CH_{olef,minor}$), 126.4 ($C_{arom,major}$), 125.0 ($CH_{olef,minor}$)f, 124.3 ($CH_{olef,major}$), 36.1 (CH_{minor}), 31.7 (CH_{major}), 23.1 ($CH_{3,major}$), 21.6 ($CH_{3,minor}$), 18.1 ($CH_{3,minor}$), 13.3 ($CH_{3,major}$) ppm. **IR** (ATR) $\tilde{\nu}$ (cm^{-1}) = 3067 (w), 3014 (w), 2966 (w), 2926 (w), 2869 (w), 2731 (w), 1688 (s), 1598 (m), 1572 (w), 1484 (w), 1450 (m), 1403 (w), 1374 (w), 1294 (w), 1204 (w), 1193 (w), 1182 (m), 1162 (w), 1141 (w), 1080 (w), 1040 (w), 999 (w), 971 (w), 938 (w), 884 (w), 844 (m), 827 (w), 758 (s), 739 (w), 712 (w), 658 (w), 621 (w), 544 (w), 440 (w). **HRMS** (ESI+) m/z: [M+H]+ Calcd for C12 H14 OH 175.1117, Found 175.1117.

2-(1-(2-methylprop-1-en-1-yl)cyclopropyl)benzaldehyde **4w**



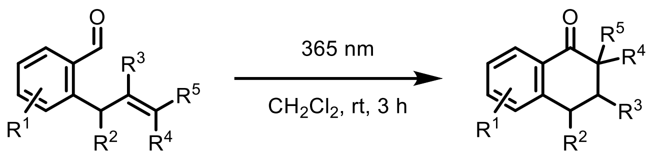
was obtained according to general procedure X, using the corresponding bromide **5S4** (535 mg, 2.13 mmol). Purification by column chromatography afforded **4w** (344 mg, 1.72 mmol, 81%) as a colorless oil.
^{1}H NMR: (500 MHz, $CDCl_3$) δ = 10.80 (s, 1H, C*H*O), 7.91 – 7.86 (m, 1H, CH_{arom}), 7.53 – 7.48 (m, 2H, 2 x CH_{arom}), 7.34 (dddd, *J* = 7.7, 6.2, 2.3, 0.8 Hz, 1H, CH_{arom}), 5.45 (p, *J* = 1.4 Hz, 1H, CH_{olef}), 1.63 (d, *J* = 1.5 Hz, 3H, CH_3), 1.54 (d, *J* = 1.4 Hz, 3H, CH_3), 1.20 – 1.18 (m, 2H, 2 x C*H*H), 1.10 – 1.07 (m, 2H, CH*H*) ppm. **^{13}C NMR**: (126 MHz, $CDCl_3$) δ = 193.0 (*C*HO), 148.7 (C_{arom}), 136.2 (C_{olef}), 135.0 (C_{arom}), 133.9 (C_{arom}), 130.0 (C_{arom}), 129.9 (CH_{olef}), 128.2 (C_{arom}), 126.8 (C_{arom}), 26.2 (CH_3), 22.9 (C_{quart}), 18.8 (CH_3), 15.8 (2 x CH_2) ppm. **IR** (ATR) $\tilde{\nu}$ (cm^{-1}) = 3066 (w), 2996 (w), 2965 (w), 2917 (w), 2853 (w), 2756 (w), 1689 (s), 1596 (m), 1569 (w), 1479 (w), 1450 (w), 1423 (w), 1394 (w), 1375 (w), 1341 (w), 1293 (w), 1261 (w), 1194 (m), 1161 (w), 1118 (w), 1086 (w), 1063 (w), 1029 (w), 982 (w), 960 (w), 913 (w), 891 (w), 825 (m), 763 (s), 743 (w), 723 (w), 642 (w), 593 (w), 543 (w), 447 (w), 420 (w). **HRMS** (ESI+) m/z: [M+Na]+ Calcd for C14H16ONa 223.1093, Found 223.1090.

2-(1-(2-methylprop-1-en-1-yl)cyclopentyl)benzaldehyde **4s**



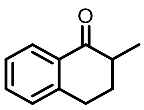
was obtained according to general procedure X, using the corresponding bromide **5S5** (531 mg, 1.90 mmol). Purification by column chromatography (*n*-pentane/toluene 5:1, 1% Et_3N) afforded **4s** (378 mg, 1.66 mmol, 87%) as a colorless oil.
^{1}H NMR: (300 MHz, $CDCl_3$) δ = 10.58 (s, 1H, C*H*O), 7.91 (d, *J* = 7.6 Hz, 1H, CH_{arom}), 7.58 – 7.43 (m, 1H, CH_{arom}), 7.36 – 7.30 (m, 1H, CH_{arom}), 5.80 (s, 1H, CH_{olef}), 2.25 – 2.13 (m, 2H, CH_2), 2.10 – 2.00 (m, 2H, CH_2), 1.88 – 1.73 (m, 4H, 2 x CH_2), 1.64 (s, 3H, CH_3), 1.07 (s, 3H, CH_3) ppm. **^{13}C NMR**: (126 MHz, $CDCl_3$) δ = 192.9 (*C*HO), 151.9 (C_{arom}), 136.6 (CH_{olef}), 133.9 (C_{arom}), 134.8 (C_{arom}), 133.0 (C_{olef}), 129.1 (C_{arom}), 126.3 (C_{arom}), 126.3 (C_{arom}), 51.2 (C_{quart}), 41.9 (2 x CH_2), 26.6 (CH_3), 23.8 (2 x CH_2), 18.6 (CH_3) ppm. **IR** (ATR) $\tilde{\nu}$ (cm^{-1}) =3463 (w), 3068 (w), 3024 (w), 2953 (s), 2869 (w), 1688 (s), 1639 (w), 1597 (w), 1473 (w), 1451 (m), 1377 (w), 1271 (w), 1232 (w), 1199 (w), 1159 (w), 1095 (w), 1071 (m), 1020 (w), 965 (w), 890 (w), 825 (w), 757 (s), 726 (w), 702 (w), 540 (w), 445 (w). **HRMS** (ESI+) m/z: [M+Na]+ Calcd for C16H20OH 229.1587, Found 229.1585.

9 General Procedure XI: Photocyclization to Tetralones



The *o*-allyl benzaldeyde **4** (0.20 mmol, 1.00 equiv) was placed in a 25 mL round bottom flask. The flask was put under argon atmosphere and dry, degassed CH_2Cl_2 (13.5 mL, 15 mM or 20.0 mL, 10 mM) was added (unless otherwise noted). The reaction was stirred and irradiated 6 cm away from a 365 nm LED for the noted time. After completion of the reaction, the solvent was removed under reduced pressure. The afforded crude was applied onto a silica gel chromatography column and eluted with 100:1 *n*-pentane/Et_2O, unless otherwise indicated. After removal of the solvents under reduced pressure, the analytically pure tetralone **6** was isolated as an oil or solid.

2-methyl-3,4-dihydronaphthalen-1(2H)-one **6k**



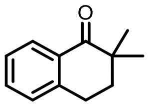
was obtained following general procedure XI using the corresponding aldehyde **4k** (33.7 mg, 0.20 mmol) and the reaction was carried out at a concentration of 15 mM for 3 h. The product **6k** (29.8 mg, 18.6 mmol, 93%) was afforded as a colorless oil.

Yield at 10 mM: 91%

Spectral data was in agreement with the literature.[15]

^{1}H NMR: (500 MHz, $CDCl_3$) δ = 8.04 (dd, *J* = 7.9, 1.7 Hz, 1H, CH_{arom}), 7.45 (td, *J* = 7.5, 1.5 Hz, 1H, CH_{arom}), 7.30 (t, *J* = 7.6 Hz, 1H, CH_{arom}), 7.23 (d, *J* = 7.7 Hz, 1H, CH_{arom}), 3.08 – 2.93 (m, 2H, $CH_{2,benzylic}$), 2.65 – 2.54 (m, 1H, C*H*), 2.20 (dq, *J* = 13.2, 4.5 Hz, 1H, CH*H*), 1.89 (dddd, *J* = 13.2, 11.9, 11.1, 4.8 Hz, 1H, C*H*H), 1.28 (d, *J* = 6.8 Hz, 3H, CH_3) ppm. **^{13}C NMR**: (126 MHz, $CDCl_3$) δ = 200.9 (*C*=O), 144.3 (C_{arom}), 133.2 (C_{arom}), 132.6 (C_{arom}), 128.8 (C_{arom}), 127.6 (C_{arom}), 126.7 (C_{arom}), 42.8 ($CH_{2,benzylic}$), 31.5 (*C*H), 29.0 (CH_2), 15.6 (CH_3) ppm. **IR** (ATR) $\tilde{\nu}$ (cm^{-1}) = 3067 (w), 2964 (w), 2931 (w), 2862 (w), 1716 (w), 1682 (s), 1601 (m), 1486 (w), 1455 (m), 1433 (w), 1375 (w), 1358 (w), 1323 (w), 1300 (w), 1267 (w), 1227 (s), 1157 (w), 1127 (w), 1077 (w), 1016 (w), 968 (m), 907 (w), 847 (w), 803 (w), 777 (w), 739 (s), 707 (w), 674 (w), 645 (w), 573 (w), 515 (w), 491 (w), 448 (w), 432 (w). **HRMS** (ESI+) m/z: [M+H]+ Calcd for C11H12OH 161.0961, Found 161.0959.

3,4-dihydronaphthalen-1(2H)-one **6l**



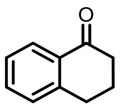
was obtained following general procedure XI using the corresponding aldehyde **4l** (36.7 mg, 0.2 mmol) and the reaction was carried out at a concentration of 15 mM for 3 h. The product **6l** (28.5 mg, 0.16 mmol, 82%) was afforded as a colorless oil.

Yield at 10 mM: 83%

Spectral data was in agreement with the literature.[16]

^{1}H NMR: (500 MHz, $CDCl_3$) δ = 8.04 (ddd, J = 7.9, 1.5, 0.5 Hz, 1H, CH_{arom}), 7.45 (td, J = 7.5, 1.5 Hz, 1H, CH_{arom}), 7.30 (dddt, J = 8.0, 7.3, 1.4, 0.7 Hz, 1H, CH_{arom}), 7.22 (dtd, J = 7.7, 1.5, 1.0 Hz, 1H, CH_{arom}), 2.99 (t, J = 6.4 Hz, 2H, $CH_{2,benzylic}$), 2.02 – 1.95 (m, 2H, CH_2), 1.22 (s, 6H, 2 x CH_3) ppm. **^{13}C NMR**: (126 MHz, $CDCl_3$) δ = 203.1 (*C*=O), 143.7 (C_{arom}), 133.3 (C_{arom}), 131.5 (C_{arom}), 128.8 (C_{arom}), 128.1 (C_{arom}), 126.7 (C_{arom}), 41.7 (C_{quart}), 36.7 (CH_2), 25.8 ($CH_{2,benzylic}$), 24.5 (2 x CH_3) ppm. **IR** (ATR) $\tilde{\nu}$ (cm^{-1}) = 2962 (w), 2925 (w), 2855 (w), 1681 (s), 1601 (m), 1474 (w), 1453 (m), 1383 (w), 1347 (w), 1308 (m), 1252 (w), 1218 (s), 1157 (w), 1128 (w), 1096 (w), 1016 (w), 994 (w), 968 (m), 897 (w), 798 (w), 775 (w), 740 (s), 697 (w), 676 (w), 625 (w), 573 (w), 524 (w), 489 (w), 455 (w), 431 (w). **HRMS** (ESI+) m/z: [M+H]+ Calcd for C12H14OH 175.1111, Found 175.1113.

2,2-dimethyl-3,4-dihydronaphthalen-1(2H)-one **6m**

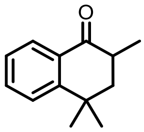


was obtained following general procedure XI using the corresponding aldehyde **4m** (29.6 mg, 0.19 mmol) and the reaction was carried out at a concentration of 15 mM for 24 h. The product **6m** (8.3 mg, 0.06 mmol, 30%) was afforded as a colorless oil.

Spectral data was in agreement with the literature.[17]

^{1}H NMR: (500 MHz, $CDCl_3$) δ = 8.04 (d, *J* = 7.7 Hz, 1H, CH_{arom}), 7.47 (t, *J* = 7.3 Hz, 1H, CH_{arom}), 7.35 – 7.21 (m, 2H, 2 x CH_{arom}), 2.97 (t, *J* = 6.2 Hz, 2H, CH_2), 2.66 (t, *J* = 6.6 Hz, 2H, CH_2), 2.15 (p, *J* = 6.2 Hz, 2H, CH_2) ppm. **^{13}C NMR**: (126 MHz, $CDCl_3$) δ = 198.5 (*C*=O), 144.6 (C_{arom}), 133.5 (C_{arom}), 132.8 (C_{arom}), 128.9 (C_{arom}), 127.3 (C_{arom}), 126.8 (C_{arom}), 39.3 (CH_2), 29.9 (CH_2), 23.4 (CH_2) ppm.

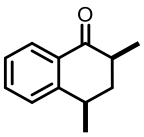
2,4,4-trimethyl-3,4-dihydronaphthalen-1(2H)-one **6r**



was obtained following general procedure XI using the corresponding aldehyde **4r** (43.6 mg, 0.25 mmol) and the reaction was carried out at a concentration of 15 mM for 3 h. The product **6r** (42.3 mg, 0.24 mmol, 97%) was afforded as a colorless oil.

^{1}H NMR: (500 MHz, $CDCl_3$) δ = 8.03 (ddd, *J* = 7.8, 1.5, 0.5 Hz, 1H, CH_{arom}), 7.53 (ddd, *J* = 8.0, 7.1, 1.6 Hz, 1H, CH_{arom}), 7.43 (ddd, *J* = 7.9, 1.2, 0.5 Hz, 1H, CH_{arom}), 7.31 (ddd, *J* = 7.8, 7.2, 1.2 Hz, 1H, CH_{arom}), 2.85 (ddq, *J* = 10.4, 8.3, 6.6 Hz, 1H, C*H*), 1.95 – 1.92 (m, 2H, CH_3CCH_2), 1.45 (s, 3H, CH_3CCH_3), 1.41 (s, 3H, $CHCH_3$), 1.28 (d, *J* = 6.6 Hz, 3H, CH_3) ppm. **^{13}C NMR**: (126 MHz, $CDCl_3$) δ = 201.0 (*C*=O), 152.2 (C_{arom}), 133.6 (C_{arom}), 131.4 (C_{arom}), 127.6 (C_{arom}), 126.4 (C_{arom}), 126.1 (C_{arom}), 46.4 (CH_2), 38.6 (*C*H), 34.4 (C_{quart}), 30.8 (CH_3CCH_3), 29.9 (CH_3CCH_3), 15.6 ($CHCH_3$) ppm. **IR** (ATR) $\tilde{\nu}$ (cm^{-1}) = 3064 (w), 3008 (w), 2967 (w), 2931 (w), 2872 (w), 2772 (w), 1686 (s), 1645 (w), 1596 (m), 1469 (w), 1446 (w), 1399 (w), 1383 (w), 1363 (w), 1288 (w), 1270 (w), 1225 (w), 1195 (m), 1142 (w), 1120 (w), 1079 (w), 1064 (w), 1045 (w), 959 (w), 916 (w), 862 (w), 821 (m), 765 (s), 744 (w), 725 (w), 707 (m), 648 (w), 631 (m), 537 (w), 452 (w). **HRMS** (ESI+) m/z: [M+H]+ Calcd for C13H16OH 189.1274, Found 189.1272.

2,4-dimethyl-3,4-dihydronaphthalen-1(2H)-one **6n**

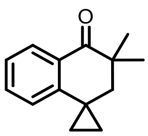


major diasteromer

was obtained following general procedure XI using the corresponding aldehyde **4n** (39.2 mg, 0.23 mmol) and the reaction was carried out at a concentration of 15 mM for 3 h. The product **6n** (39.1 mg, 0.22 mmol, 99%, d.r. 1:0.53) was afforded as a colorless oil.

^{1}H NMR: (500 MHz, $CDCl_3$) δ =8.07 (dd, *J* = 7.8, 1.6 Hz, 1H, C$H_{arom,major}$), 8.04 (dd, *J* = 7.8, 1.5 Hz, 0H), 7.54 (td, *J* = 7.5, 1.7 Hz, 1H), 7.50 (td, *J* = 7.5, 1.5 Hz, 0H), 7.42 (dtd, *J* = 7.9, 1.2, 0.5 Hz, 1H), 7.36 – 7.27 (m, 0H), 3.22 – 3.12 (m, 0H), 2.92 – 2.81 (m, 0H), 2.65 (dqd, *J* = 13.3, 6.7, 4.5 Hz, 1H), 2.20 – 2.10 (m, 1H), 2.02 (ddd, *J* = 13.4, 4.9, 3.8 Hz, 0H), 1.66 (td, *J* = 13.6, 12.0 Hz, 1H), 1.44 (d, *J* = 6.8 Hz, 3H), 1.44 (d, *J* = 7.2 Hz, 1H), 1.29 (d, *J* = 6.6 Hz, 3H), 1.28 (d, *J* = 6.8 Hz, 1H). ppm. **^{13}C NMR**: (126 MHz, $CDCl_3$) δ = 201.0 (*C*=O), 149.1 ($C_{arom,minor}$), 148.4 ($C_{arom,major}$), 133.5 ($C_{arom,minor}$), 133.4 ($C_{arom,major}$), 132.5 ($C_{arom,major}$),, 131.5 ($C_{arom,minor}$), 128.4 ($C_{arom,minor}$), 127.6 ($C_{arom,minor}$), 127.5 ($C_{arom,major}$), 126.6 ($C_{arom,minor}$), 126.5 ($C_{arom,major}$), 126.5 ($C_{arom,major}$), 43.1 (CH_{major}), 41.2 ($CH_{2,major}$), 38.0 ($CH_{2,minor}$), 37.5 (CH_{minor}), 33.2 ($COCH_{major}$), 31.9 ($COCH_{minor}$), 21.8 ($CH_{3,minor}$), 20.4 ($CH_{3,major}$), 15.8 ($CH_{3,minor}$), 15.5 ($CH_{3,major}$) ppm. **IR** (ATR) $\tilde{\nu}$ (cm^{-1}) = 3063 (w), 2963 (m), 2929 (w), 2869 (w), 1686 (s), 1600 (w), 1480 (w), 1457 (w), 1388 (w), 1365 (w), 1331 (w), 1301 (w), 1254 (w), 1235 (m), 1162 (w), 1130 (w), 1092 (w), 1033 (w), 987 (w), 955 (w), 891 (w), 849 (w), 781 (w), 763 (m), 710 (w), 681 (w), 632 (w), 555 (w). **HRMS** (ESI+) m/z: [M+H]+ Calcd for C13H16OH 189.1274, Found 189.1272.

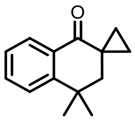
3',3'-dimethyl-2',3'-dihydro-4'H-spiro[cyclopropane-1,1'-naphthalen]-4'-one **6w**



was obtained following general procedure XI using the corresponding aldehyde **4w** (42.1 mg, 0.21 mmol) and the reaction was carried out at a concentration of 15 mM for 3 h. The product **6w** (25.3 mg, 0.13 mmol, 60%) was afforded as a colorless oil.

^{1}H NMR: (500 MHz, $CDCl_3$) δ = 8.03 (ddd, *J* = 7.9, 1.6, 0.6 Hz, 1H, CH_{arom}), 7.44 (ddd, *J* = 8.1, 7.2, 1.6 Hz, 1H, CH_{arom}), 7.24 (ddd, *J* = 8.2, 7.2, 1.2 Hz, 1H, CH_{arom}), 6.74 (dd, *J* = 8.1, 1.4 Hz, 1H, CH_{arom}), 1.87 (s, 2H, CH_2), 1.24 (s, 6H, 2 x CH_3), 1.15 – 1.10 (m, 2H, 2 x C*H*H), 1.01 – 0.97 (m, 2H, 2 x CH*H*) ppm. **^{13}C NMR**: (126 MHz, $CDCl_3$) δ = 203.30 (*C*=O), 147.82 (C_{arom}), 133.60 (C_{arom}), 131.50 (C_{arom}), 128.08 (C_{arom}), 125.69 (C_{arom}), 122.08 (C_{arom}), 46.59 (CH_2), 43.08 ($C_{quart}(CH_3)_2$), 24.93 (2 x CH_3), 18.40 (2 x $CH_{2,cycprop}$), 16.88 ($C_{quar,cycprop}$) ppm. **IR** (ATR) $\tilde{\nu}$ (cm^{-1}) = 3066 (w), 2963 (w), 2924 (w), 2867 (w), 2843 (w), 1679 (s), 1600 (m), 1571 (w), 1482 (m), 1469 (w), 1449 (w), 1383 (m), 1362 (w), 1298 (m), 1284 (w), 1246 (m), 1212 (m), 1170 (w), 1145 (w), 1110 (w), 1087 (m), 1053 (w), 1043 (w), 1021 (w), 994 (m), 979 (w), 956 (m), 938 (w), 905 (w), 876 (w), 846 (w), 807 (w), 796 (w), 756 (s), 706 (m), 688 (w), 628 (w), 566 (w), 552 (w), 459 (w), 409 (w).**HRMS** (ESI+) m/z: [M+H]+ Calcd for C14H16OH 201.1274, Found 201.1270.

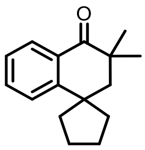
4',4'-dimethyl-3',4'-dihydro-1'H-spiro[cyclopropane-1,2'-naphthalen]-1'-one **6x**



was obtained following general procedure XI using the corresponding aldehyde **4x** (41.1 mg, 0.21 mmol) and the reaction was carried out at a concentration of 15 mᴍ for 12 h. The product **6x** (38.9 mg, 0.19 mmol, 95%) was afforded as a colorless oil.

^{1}H NMR: (300 MHz, $CDCl_3$) δ = 8.00 (dd, *J* = 7.8, 1.6 Hz, 1H, CH_{arom}), 7.52 (ddd, *J* = 7.9, 7.1, 1.6 Hz, 1H, CH_{arom}), 7.43 (dd, *J* = 7.9, 1.8 Hz, 1H, CH_{arom}), 7.31 (ddd, *J* = 7.8, 7.1, 1.4 Hz, 1H, CH_{arom}), 1.94 (s, 2H, CH_3), 1.53 (q, *J* = 3.3 Hz, 2H, 2 x C*H*H), 1.41 (s, 6H, 2 x CH_3), 0.83 (q, *J* = 3.4 Hz, 2H, 2 x CH*H*) ppm. **^{13}C NMR**: (75 MHz, $CDCl_3$) δ = 199.8 (*C*=O), 152.5 (C_{arom}), 133.6 (C_{arom}), 131.9 (C_{arom}), 127.4 (C_{arom}), 126.4 (C_{arom}), 125.1 (C_{arom}), 46.0 (CH_2), 35.3 ($C_{quart}(CH_3)_2$), 29.9 (2 x CH_3), 25.3 ($C_{quart}(CH_2)_{cycprop}$), 19.9 (2 x $CH_{2,cycprop}$) ppm. **IR** (ATR) $\tilde{\nu}$ (cm^{-1}) = 3064 (w), 2998 (w), 2963 (w), 2916 (w), 2865 (w), 1671 (s), 1599 (m), 1465 (w), 1448 (w), 1416 (w), 1387 (w), 1358 (s), 1336 (w), 1297 (w), 1228 (s), 1173 (w), 1148 (w), 1111 (w), 1088 (w), 1061 (w), 1044 (w), 1030 (w), 1001 (m), 968 (w), 910 (w), 875 (w), 808 (w), 782 (w), 764 (m), 707 (m), 636 (w), 552 (w), 520 (w), 477 (w), 435 (w). **HRMS** (ESI+) m/z: [M+H]+ Calcd for C14H16OH 201.1274, Found 201.1270.

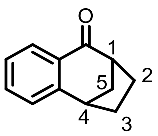
3',3'-dimethyl-2',3'-dihydro-4'H-spiro[cyclopentane-1,1'-naphthalen]-4'-one **6s**



was obtained following general procedure XI using the corresponding aldehyde **4s** (40.8 mg, 0.18 mmol) and the reaction was carried out at a concentration of 15 mᴍ for 3 h. The product **6s** (17.2 mg, 0.08 mmol, 42%) was afforded as a colorless oil.

^{1}H NMR: (500 MHz, $CDCl_3$) δ = 7.96 (dd, *J* = 7.8, 1.6 Hz, 1H, CH_{arom}), 7.51 (ddd, *J* = 8.0, 7.2, 1.6 Hz, 1H, CH_{arom}), 7.35 (dd, *J* = 8.0, 1.4 Hz, 1H, CH_{arom}), 7.30 – 7.26 (m, 1H, CH_{arom}), 2.01 – 1.82 (m, 10H, 5 x CH_2), 1.24 (s, 6H, 3 x CH_3) ppm. **^{13}C NMR**: (126 MHz, $CDCl_3$) δ = 204.3 (*C*=O), 152.5 (C_{arom}), 133.5 (C_{arom}), 130.9 (C_{arom}), 127.6 (C_{arom}), 126.9 (C_{arom}), 126.2 (C_{arom}), 49.5 (CH_2), 45.0 (C_{quart}), 44.4 (2 x $CH_{2,pent}$), 42.2 (C_{quart}), 27.1 (2 x CH_3), 25.9 (2 x $CH_{2,pent}$) ppm. **IR** (ATR) $\tilde{\nu}$ (cm^{-1}) = 3063 (w), 2954 (m), 2870 (w), 1682 (s), 1598 (m), 1474 (w), 1449 (m), 1383 (w), 1361 (w), 1308 (w), 1225 (m), 1167 (w), 1138 (w), 1104 (w), 996 (w), 963 (m), 909 (w), 878 (w), 800 (w), 759 (s), 712 (m), 543 (w), 457 (w). **HRMS** (ESI+) m/z: [M+H]+ Calcd for C16H20OH 229.1587, Found 229.1585.

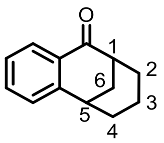
5,6,7,8-tetrahydro-9H-5,8-methanobenzo[7]annulen-9-one **6o**



was obtained following general procedure XI using the corresponding aldehyde **4o** (30.4 mg, 0.18 mmol) and the reaction was carried out at a concentration of 15 mᴍ for 3 h. The product **6o** (21.8 mg, 0.13 mmol, 72%) was afforded as a colorless oil.

^{1}H NMR: (300 MHz, $CDCl_3$) δ = 8.04 – 7.98 (m, 1H, CH_{arom}), 7.32 (td, *J* = 7.6, 1.3 Hz, 1H, CH_{arom}), 7.28 – 7.26 (m, 1H, CH_{arom}), 3.41 (t, *J* = 4.7 Hz, 1H, ^{4}C*H*), 3.19 – 3.14 (m, 1H, ^{1}C*H*), 2.27 – 2.14 (m, 3H, ^{2}C*H*H, ^{3}C*H*H, ^{5}C*H*H), 1.88 (dt, *J* = 11.7, 4.5 Hz, 1H, ^{5}CH*H*), 1.74 – 1.69 (m, 1H, ^{3}CH*H*), 1.68 – 1.61 (m, 1H, ^{2}CH*H*) ppm. **^{13}C NMR**: (126 MHz, $CDCl_3$) δ = 201.9 (*C*=O), 151.1 (C_{arom}), 133.8 (C_{arom}), 130.5 (C_{arom}), 127.7 (C_{arom}), 126.9 (C_{arom}), 126.7 (C_{arom}), 50.0 (C=O^1*C*H), 42.4 ($^4CH_{benz}$), 39.6 ($^5CH_2$), 31.9 ($^2CH_2$), 24.9 ($^3CH_2$) ppm. **IR** (ATR) $\tilde{\nu}$ (cm^{-1}) = 3067 (w), 2947 (m), 2870 (w), 1686 (s), 1602 (m), 1478 (w), 1457 (w), 1326 (w), 1302 (w), 1279 (m), 1243 (w), 1198 (w), 1152 (w), 1132 (w), 1099 (w), 1011 (w), 947 (w), 924 (w), 904 (w), 824 (w), 772 (w), 734 (w), 674 (w), 561 (w), 540 (w), 517 (w), 499 (w). **HRMS** (ESI+) m/z: [M+H]+ Calcd for C12H12OH 173.0961, Found 178.0960.

6,7,8,9-tetrahydro-5,9-methanobenzo[8]annulen-10(5H)-one **6p**

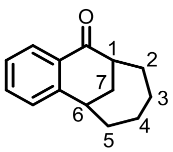


was obtained following general procedure XI using the corresponding aldehyde **4p** (39.2 mg, 0.2 mmol) and the reaction was carried out at a concentration of 10 mM for 3 h. The product **6p** (23.3 mg, 0.13 mmol, 63%) was afforded as a colorless oil.

Yield at 15 mM: 53%

^{1}H NMR: (300 MHz, $CDCl_3$) δ = 8.07 (dd, *J* = 7.8, 1.6 Hz, 1H, CH_{arom}), 7.54 (td, *J* = 7.4, 1.6 Hz, 1H, CH_{arom}), 7.36 (td, *J* = 7.5, 1.3 Hz, 1H, CH_{arom}), 7.27 (dd, *J* = 7.6, 1.4 Hz, 1H, CH_{arom}), 3.20 (p, *J* = 3.7 Hz, 1H, $^5CH_{benzylic}$), 2.78 (p, *J* = 4.0 Hz, 1H, ^1CH), 2.40 (dtd, *J* = 13.4, 3.9, 2.0 Hz, 1H, ^6CHH), 2.06 – 1.87 (m, 3H, ^2CHH, ^4CHH, ^6CHH), 1.84 – 1.68 (m, 2H, ^2CHH, ^4CHH), 1.55 – 1.46 (m, 1H, ^3CHH), 1.26 (qt, *J* = 13.9, 4.4 Hz, 1H, ^3CHH) ppm. **^{13}C NMR**: (75 MHz, $CDCl_3$) δ = 202.4 (*C*=O), 147.7 (C_{arom}), 134.4 (C_{arom}), 134.0 (C_{arom}), 128.3 (C_{arom}), 126.7 (C_{arom}), 126.3 (C_{arom}), 43.3 (C=O^{1}CH), 35.3 ($^5CH_{benz}$), 33.7 ($^6CH_2$), 31.1 ($^4CH_2$), 29.8 ($^2CH_2$), 18.1 ($^3CH_2$) ppm. **IR** (ATR) $\tilde{\nu}$ (cm^{-1}) = 927 (m), 2856 (w), 1714 (w), 1682 (s), 1600 (m), 1455 (w), 1365 (w), 1347 (w), 1316 (w), 1286 (m), 1228 (w), 1187 (w), 1147 (w), 1122 (w), 1081 (w), 1017 (w), 990 (w), 914 (w), 863 (w), 796 (w), 761 (m), 737 (w), 709 (w), 558 (w), 534 (w), 514 (w). **HRMS** (ESI+) m/z: [M+Na]+ Calcd for C13H14O1Na 187.1114, Found 187.1117.

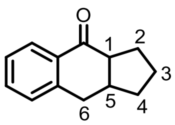
5,6,7,8,9,10-hexahydro-11H-5,10-methanobenzo[9]annulen-11-one **6q**



was obtained following general procedure XI using the corresponding aldehyde **4q** (40.0 mg, 0.20 mmol) and the reaction was carried out at a concentration of 15 mM for 3 h. The product **6q** (8.00 mg, 0.04 mmol, 20%) was afforded as a colorless oil.

^{1}H NMR: (300 MHz, $CDCl_3$) δ = δ 8.01 (d, J = 7.8 Hz, 1H, CH_{arom}), 7.50 (t, J = 7.7 Hz, 1H, CH_{arom}), 7.31 (t, J = 7.4 Hz, 1H, CH_{arom}), 7.26 – 7.22 (m, 1H, CH_{arom}), 3.38 – 3.27 (m, 1H, ^6CH), 2.93 – 2.81 (m, 1H, ^1CH), 2.45 (dt, J = 12.7, 6.1 Hz, 1H, ^7CHH), 2.16 – 2.09 (m, 1H, ^7CHH), 2.07 – 1.91 (m, 4H, $^3CH_2$, $^4CH_2$), 1.76 – 1.65 (m, 2H, ^2CHH), 1.64 – 1.46 (m, 2H, ^2CHH, ^5CHH), 1.13 – 1.00 (m, 1H, ^5CHH) ppm. **^{13}C NMR**: (126 MHz, $CDCl_3$) δ = 203.2 (*C*=O), 148.6 (C_{arom}), 133.7 (C_{arom}), 132.7 (C_{arom}), 128.7 (C_{arom}), 127.1 (C_{arom}), 126.7 (C_{arom}), 43.1 (^1CH), 39.1 ($^3CH_2$), 36.4 (^6CH), 32.6 ($^4CH_2$), 29.6 ($^7CH_2$), 26.3 ($^2CH_2$), 24.4 ($^5CH_2$) ppm. **IR** (ATR) $\tilde{\nu}$ (cm^{-1}) = 3065 (w), 3023 (w), 2917 (m), 2857 (w), 2686 (w), 1672 (s), 1599 (m), 1478 (w), 1452 (m), 1366 (w), 1323 (w), 1293 (m), 1234 (w), 1205 (w), 1158 (w), 1119 (w), 1062 (w), 1029 (w), 970 (m), 840 (w), 817 (w), 763 (s), 695 (w), 676 (w), 593 (w), 557 (w), 502 (w), 427 (w). **HRMS** (EI+) m/z: [M]+ Calcd for C14H16O 200.12011, Found 200.12066.

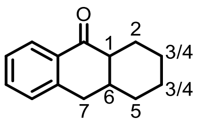
1,2,3,3a,9,9a-hexahydro-4H-cyclopenta[b]naphthalen-4-one **6t**



was obtained following general procedure XI using the corresponding aldehyde **4t** (38.7 mg, 0.21 mmol) and the reaction was carried out at a concentration of 15 mM for 3 h. The product **6t** (38.2 mg, 0.21 mmol, 99%, 2:1 *cis/trans*) was afforded as a colorless oil.

Major isomer (cis):[18] **^{1}H NMR**: (300 MHz, $CDCl_3$) δ =7.98 (d, J = 8.0 Hz, 1H, CH_{arom}), 7.47 (t, J = 7.2 Hz, 1H, CH_{arom}), 7.33 – 7.27 (m, 1H, CH_{arom}), 7.22 (d, J = 7.1 Hz, 1H, CH_{arom}), 3.00 (dd, J = 16.2, 5.6 Hz, 1H, ^6CHH), 2.92 – 2.76 (m, 2H, ^6CHH, ^1CH), 2.76 – 2.66 (m, 1H, ^5CH), 2.12 – 2.00 (m, 2H, $^2CH_2$), 1.90 – 1.79 (m, 1H, ^4CHH), 1.73 (d, J = 4.8 Hz, 2H, $^3CH_2$), 1.58 – 1.41 (m, 1H, ^4CHH) ppm. **^{13}C NMR**: (126 MHz, $CDCl_3$) δ = 201.2 (*C*=O), 142.8 (C_{aorm}), 133.6 (C_{aorm}), 132.3 (C_{aorm}), 129.1 (C_{aorm}), 127.4 (C_{aorm}), 126.8 (C_{aorm}), 50.7 (^1CH), 38.9 (^5CH), 31.3 ($^4CH_2$), 31.1 ($^6CH_2$), 28.7 ($^2CH_2$), 23.5 ($^3CH_2$) ppm. Minor isomer (trans):[18] **^{1}H NMR**: (300 MHz, $CDCl_3$) δ = 8.05 (d, J = 7.7 Hz, 1H, CH_{arom}), 7.46 (t, J = 7.7 Hz, 1H, CH_{arom}), 7.34 – 7.27 (m, 2H, 2 x CH_{arom}), 3.21 (dd, J = 16.1, 3.7 Hz, 1H, ^6CHH), 2.91 – 2.76 (m, 1H, ^6CHH), 2.49 – 2.34 (m, 1H, ^1CH), 2.12 – 1.99 (m, 3H, ^5CH, ^4CHH, ^2CHH), 1.93 – 1.73 (m, 3H, ^2CHH, ^3CHH, ^3CHH), 1.49 – 1.41 (m, 1H, ^4CHH) ppm. **^{13}C NMR**: 200.2 (*C*=O), 144.5 (C_{aorm}), 133.8 (C_{aorm}), 133.1 (C_{aorm}), 129.3 (C_{aorm}), 127.3 (C_{aorm}), 126.6 (C_{aorm}), 55.7 (^1CH), 44.6 (^5CH), 36.9 (^6CH), 32.3 ($^4CH_2$), 23.7 ($^2CH_2$), 22.4 ($^3CH_2$) ppm. **IR** (ATR) $\tilde{\nu}$ (cm^{-1}) = 1684 (s), 1597 (m), 1472 (w), 1450 (m), 1366 (w), 1349 (w), 1331 (w), 1293 (w), 1250 (m), 1199 (w), 1151 (w), 1132 (w), 1111 (w), 1020 (w), 977 (w), 957 (w), 869 (w), 823 (w), 802 (w), 759 (m), 725 (w), 674 (w), 633 (w), 592 (w), 505 (w), 460 (w). **HRMS** (ESI+) m/z: [M]+ Calcd for C13H14OH 187.1117, Found 187.1115.

1,3,4,4a,9a,10-hexahydroanthracen-9(2H)-one **6u**

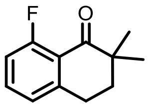


was obtained following general procedure XI using the corresponding aldehyde **4u** (40.0 mg, 0.20 mmol) and the reaction was carried out at a concentration of 15 mM for 3 h. The product **6u** (39.4 mg, 0.19 mmol, 98%, 73:27 *cis/trans*) was afforded as a colorless solid. The trans isomer could not be obtained separately.

^{1}H NMR: (300 MHz, $CDCl_3$) δ =8.05 (d, J = 7.7 Hz, 1H, CH_{arom}), 7.47 (t, J = 7.5 Hz, 1H, CH_{arom}), 7.30 (d, J = 7.4 Hz, 1H, CH_{arom}), 7.22 (d, J = 7.7 Hz, 1H, CH_{arom}), 3.00 (qd, J = 16.7, 5.9 Hz, 2H, ^{7}C$H_{2,benzylic}$), 2.74 – 2.67 (m, 1H, ^{1}C*H*), 2.47 – 2.37 (m, 1H, ^{6}C*H*), 2.26 – 2.14 (m, 1H, ^{5}C*H*H), 1.69 – 1.58 (m, 1H, ^{2}C*H*H), 1.52 – 1.36 (m, 6H, ^{5}CH*H*, ^{2}CH*H*, ^{3}CH_2, ^{4}CH_2) ppm.

^{13}C NMR: (126 MHz, $CDCl_3$) δ = 200.5 (*C*=O), 143.0 (C_{arom}), 133.5 (C_{arom}), 132.0 (C_{arom}), 129.4 (C_{arom}), 127.4 (C_{arom}), 126.6 (C_{arom}), 48.5 (^{1}*C*H), 36.0 (^{6}CH), 33.5 (^{7}*C*H_2), 29.1 ($^{3/4}$*C*H_2), 25.6 (^{5}*C*H_2), 24.0 (^{2}*C*H_2), 23.6 ($^{3/4}$*C*H_2) ppm. **IR** (ATR) $\tilde{\nu}$ (cm^{-1}) =3063 (w), 2922 (s), 2851 (w), 1676 (s), 1598 (m), 1480 (w), 1450 (m), 1366 (w), 1334 (w), 1307 (w), 1287 (w), 1265 (w), 1231 (m), 1209 (w), 1156 (w), 1138 (w), 1105 (w), 1024 (w), 1003 (w), 958 (w), 940 (w), 912 (w), 882 (w), 843 (w), 819 (w), 792 (w), 750 (m), 670 (w), 617 (w), 580 (w), 492 (w), 446 (w). **HRMS** (EI+) m/z: [M]+ Calcd for C14H16O 200.12011, Found 200.12027. **m.p.** 76.7 – 81.7 °C (Et_2O).

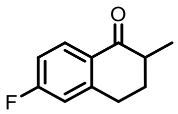
8-fluoro-2,2-dimethyl-3,4-dihydronaphthalen-1(2H)-one **6d**



was obtained following general procedure XI using the corresponding aldehyde **4d** (34.9 mg, 0.20 mmol) and the reaction was carried out at a concentration of 15 mM for 3 h. The product **6d** (28.8 mg, 0.16 mmol, 83%) was afforded as a colorless oil.

^{1}H NMR: (500 MHz, $CDCl_3$) δ = 7.39 (td, *J* = 8.0, 5.1 Hz, 1H, CH_{arom}), 7.01 (d, *J* = 7.6 Hz, 1H, CH_{arom}), 6.96 (ddd, *J* = 11.5, 8.2, 1.1 Hz, 1H, CH_{arom}), 3.01 – 2.97 (m, 2H, C$H_{2,benzylic}$), 1.99 – 1.92 (m, 2H, CH_2), 1.21 (s, 6H, 2 x CH_3). ppm. **^{13}C NMR**: (126 MHz, $CDCl_3$) δ = 201.18 (d, *J* = 1.2 Hz, *C*=O), 162.94 (d, *J* = 264.9 Hz, FC_{arom}), 146.0 (C_{arom}), 134.00 (d, *J* = 10.3 Hz, C_{arom}), 124.40 (d, *J* = 4.1 Hz, C_{arom}), 120.60 (d, *J* = 5.0 Hz, C_{arom}), 115.08 (d, *J* = 22.4 Hz, C_{arom}) 42.75 (C_{quart}), 36.30 (*C*H_2), 26.10 (*C*$H_{2,benzylic}$), 24.47 (2 x *C*H_3) ppm. **^{19}F NMR**: (282 MHz, $CDCl_3$) δ = -111.93 ppm. **IR** (ATR) $\tilde{\nu}$ (cm^{-1}) = 2964 (w), 2928 (w), 2867 (w), 1687 (s), 1609 (s), 1572 (w), 1454 (m), 1384 (w), 1350 (w), 1300 (w), 1256 (m), 1221 (w), 1203 (w), 1161 (w), 1072 (w), 1043 (w), 1024 (w), 1000 (m), 960 (w), 889 (w), 862 (w), 801 (m), 778 (w), 748 (w), 692 (w), 641 (w), 605 (w), 560 (w), 482 (w), 461 (w), 433 (w). **HRMS** (ESI+) m/z: [M+Na]+ Calcd for C12H13FONa 215.0800, Found 215.0847.

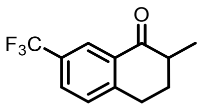
6-fluoro-2-methyl-3,4-dihydronaphthalen-1(2H)-one **6c**



was obtained following general procedure XI using the corresponding aldehyde **4c** (35.1 mg, 0.20 mmol) and the reaction was carried out at a concentration of 15 mM for 3 h. The product **6c** (29.8 mg, 0.17 mmol, 85%) was afforded as a colorless oil.

^{1}H NMR: (500 MHz, $CDCl_3$) δ = 8.06 (dd, *J* = 8.7, 6.0 Hz, 1H, CH_{arom}), 6.98 (td, *J* = 8.5, 2.6 Hz, 1H, CH_{arom}), 6.94 – 6.87 (m, 1H, CH_{arom}), 3.06 – 2.93 (m, 2H, C$H_{2,benzylic}$), 2.58 (dqd, *J* = 11.3, 6.8, 4.5 Hz, 1H, C*H*), 2.23 – 2.17 (m, 1H, C*H*H), 1.93 – 1.84 (m, 1H, CH*H*), 1.27 (d, *J* = 6.8 Hz, 3H, CH_3) ppm. **^{13}C NMR**: (126 MHz, $CDCl_3$) δ = 199.4 (*C*=O), 165.7 (d, *J* = 254.6 Hz, C_{arom}), 147.3 (d, *J* = 8.6 Hz, C_{arom}), 130.7 (d, *J* = 9.5 Hz, C_{arom}), 129.3 – 129.2 (m, C_{arom}), 115.1 (d, *J* = 21.0 Hz, C_{arom}), 114.4 (d, *J* = 21.9 Hz, C_{arom}), 42.6 (*C*H), 31.4 (*C*H_2), 29.1 (*C*$H_{2,benzylic}$), 15.5 (*C*H_3) ppm. **^{19}F NMR**: (282 MHz, $CDCl_3$) δ = -105.58 ppm. **IR** (ATR) $\tilde{\nu}$ (cm^{-1}) = 3063 (w), 2930 (m), 2861 (w), 1683 (s), 1607 (s), 1584 (m), 1487 (w), 1457 (w), 1432 (w), 1375 (w), 1358 (w), 1318 (w), 1243 (s), 1141 (w), 1115 (w), 1082 (w), 1023 (w), 973 (m), 902 (w), 869 (m), 829 (w), 801 (w), 757 (w), 727 (w), 662 (w), 601 (w), 574 (w), 522 (w), 449 (w), 424 (w). **HRMS** (ESI+) m/z: [M+H]+ Calcd for C11H12FOH 179.0867, Found 179.0867.

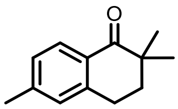
2-methyl-7-(trifluoromethyl)-3,4-dihydronaphthalen-1(2H)-one **6b**



was obtained following general procedure XI using the corresponding aldehyde **4b** (45.6 mg, 0.20 mmol) and the reaction was carried out at a concentration of 15 mM for 3 h. The product **6b** (23.9 mg, 0.13 mmol, 67%) was afforded as a colorless oil.

^{1}H NMR: (500 MHz, $CDCl_3$) δ = 8.33 (s, 1H, CH_{arom}), 7.71 (dd, *J* = 8.0, 2.7 Hz, 1H, CH_{arom}), 7.40 (d, *J* = 8.0 Hz, 1H, CH_{arom}), 3.17 – 3.02 (m, 2H, $CH_{2,benzylic}$), 2.71 – 2.60 (m, 1H, C*H*), 2.26 (dq, *J* = 13.4, 4.5 Hz, 1H, C*H*H), 1.93 (dddd, *J* = 13.5, 12.2, 10.8, 5.2 Hz, 1H, CH*H*), 1.31 (d, *J* = 6.8 Hz, 3H, CH_3) ppm. **^{13}C NMR**: (126 MHz, $CDCl_3$) δ = 199.6 (*C*=O), 147.8 (C_{arom}), 132.8 (C_{arom}), 129.8 – 128.9 (m, C_{arom}), 129.7 (C_{arom}), 129.3 (q, *J* = 3.3 Hz, C_{arom}), 124.8 (q, *J* = 3.8 Hz, C_{arom}), 124.0 (q, *J* = 272.1 Hz, CF_3), 42.7 (*C*H), 31.0 (CH_2), 28.9 ($CH_{2,benzylic}$), 15.4 (CH_3)ppm. **^{19}F NMR**: (282 MHz, $CDCl_3$) δ = -62.71 ppm. **IR** (ATR) $\tilde{\nu}$ (cm^{-1}) = 2936 (w), 2869 (w), 1692 (s), 1619 (m), 1457 (w), 1434 (w), 1377 (w), 1332 (s), 1318 (w), 1260 (m), 1242 (w), 1208 (m), 1165 (m), 1124 (s), 1091 (w), 1071 (m), 988 (w), 926 (w), 861 (w), 842 (w), 815 (w), 760 (w), 745 (w), 717 (w), 693 (w), 651 (w), 613 (w), 532 (w), 514 (w), 436 (w), 418 (w). **HRMS** (ESI-) m/z: [M]- Calcd for C12H10FO 227.0689, Found 227.0690.

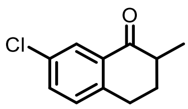
2,2,6-trimethyl-3,4-dihydronaphthalen-1(2H)-one **6e**



was obtained following general procedure XI using the corresponding aldehyde **4e** (37.7 mg, 0.2 mmol) and the reaction was carried out at a concentration of 15 mM for 3 h. The product **6e** (33.2 mg, 0.18 mmol, 88%) was afforded as a colorless oil.

^{1}H NMR: (500 MHz, $CDCl_3$) δ = 7.94 (d, *J* = 8.0 Hz, 1H, CH_{arom}), 7.13 – 7.08 (m, 1H , CH_{arom}), 7.02 (dp, *J* = 1.6, 0.8 Hz, 1H, CH_{arom}), 2.94 (t, *J* = 6.4 Hz, 2H, $CH_{2,benzylic}$), 2.37 (s, 3H, $C_{arom}CH_3$), 1.96 (dd, *J* = 6.8, 5.9 Hz, 2H, CH_2), 1.21 (s, 6H, 2 x CH_3). ppm. **^{13}C NMR**: (126 MHz, $CDCl_3$) δ = 202.8 (*C*=O), 143.9 (C_{arom}), 143.6 (C_{arom}), 129.3 (C_{arom}), 129.2 (C_{arom}), 128.3 (C_{arom}), 127.8 (C_{arom}), 41.7 (C_{quart}), 36.9 (CH_2), 25.8 (CH_2), 24.6 (2 x CH_3), 21.8 ($C_{arom}CH_3$) ppm. **IR** (ATR) $\tilde{\nu}$ (cm^{-1}) = 2962 (w), 2924 (m), 2855 (w), 1679 (s), 1609 (m), 1471 (w), 1452 (w), 1383 (w), 1362 (w), 1348 (w), 1306 (m), 1227 (s), 1110 (w), 1036 (w), 1022 (w), 994 (w), 967 (w), 903 (w), 835 (w), 772 (w), 724 (w), 698 (w), 665 (w), 569 (w), 518 (w), 460 (w), 437 (w). **HRMS** (ESI+) m/z: [M+Na]+ Calcd for C13H16ONa 211.1093, Found 211.1095.

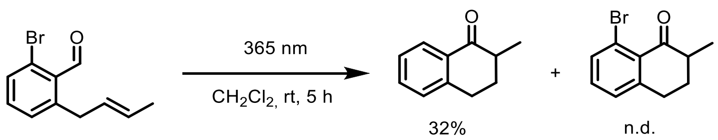
7-chloro-2-methyl-3,4-dihydronaphthalen-1(2H)-one **6a**



was obtained following general procedure XI using the corresponding aldehyde **4a** (40.4 mg, 0.21 mmol) and the reaction was carried out at a concentration of 15 mM for 8 h. The product **6a** (39.8 mg, 0.21 mmol, 99%) was afforded as a colorless solid.

^{1}H NMR: (500 MHz, $CDCl_3$) δ = 7.99 (d, *J* = 2.3 Hz, 1H, CH_{arom}), 7.41 (dd, *J* = 8.1, 2.3 Hz, 1H, CH_{arom}), 7.19 (d, *J* = 8.1 Hz, 1H, CH_{arom}), 3.05 – 2.90 (m, 2H, $CH_{2,benzylic}$), 2.63 – 2.52 (m, 1H, C*H*), 2.20 (dq, *J* = 13.3, 4.4 Hz, 1H, CH*H*), 1.87 (dddd, *J* = 13.4, 12.2, 10.9, 5.1 Hz, 1H, C*H*H), 1.27 (d, *J* = 6.8 Hz, 3H, CH_3) ppm. **^{13}C NMR**: (126 MHz, $CDCl_3$) δ = 199.7 (*C*=O), 142.5 (C_{arom}), 133.8 (C_{arom}), 133.1 (C_{arom}), 132.9 (C_{arom}), 130.4 (C_{arom}), 127.3 (C_{arom}), 42.6 (*C*H), 31.3 (CH_2), 28.4 ($CH_{2,benzylic}$), 15.5 (CH_3) ppm. **IR** (ATR) $\tilde{\nu}$ (cm^{-1}) = 3060 (w), 2964 (w), 2932 (w), 2863 (w), 1688 (s), 1595 (w), 1568 (w), 1476 (m), 1455 (w), 1433 (w), 1410 (w), 1375 (w), 1356 (w), 1318 (w), 1293 (w), 1257 (w), 1215 (s), 1136 (w), 1097 (w), 1020 (w), 985 (w), 905 (w), 855 (w), 830 (w), 804 (m), 758 (w), 707 (w), 685 (w), 651 (w), 527 (w), 468 (w), 436 (w). **HRMS** (EI+) m/z: [M]+ Calcd for C11H11ClO 194.04984,196.04713, Found 194.04851, 196.04624.

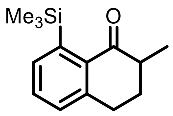
Irridiation of 4j



was obtained following general procedure XI for 5 h using the corresponding aldehyde **6j** (47.8 mg, 0.20 mmol) and the reaction was carried out at a concentration of 10 mM. The resulting product **6k** (15.5 mg, 0.06 mmol, 32%) was afforded as a colorless oil.

^{1}H NMR: (500 MHz, $CDCl_3$) δ =8.04 (dd, *J* = 7.9, 1.7 Hz, 1H, CH_{arom}), 7.46 (td, *J* = 7.5, 1.5 Hz, 1H , CH_{arom}), 7.30 (t, *J* = 7.6 Hz, 1H , CH_{arom}), 7.24 (d, *J* = 7.6 Hz, 1H), 3.10 – 2.93 (m, 2H), 2.65 – 2.54 (m, 1H), 2.20 (dq, *J* = 13.2, 4.4 Hz, 1H), 1.89 (dtd, *J* = 13.2, 11.5, 4.7 Hz, 1H), 1.28 (d, *J* = 6.7 Hz, 3H) ppm. **^{13}C NMR**: (126 MHz, $CDCl_3$) δ = 201.0 (*C*=O), 144.4 (C_{arom}), 133.2 (C_{arom}), 132.5 (C_{arom}), 128.9 (C_{arom}), 127.5 (C_{arom}), 126.7 (C_{arom}), 42.8 (*C*H), 31.5 (CH_2), 29.0 ($CH_{2,benzylic}$), 15.6 (CH_3) ppm.

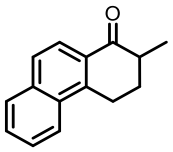
2-methyl-8-(trimethylsilyl)-3,4-dihydronaphthalen-1(2H)-one **6f**



was obtained following general procedure XI using the corresponding aldehyde **4f** (45.6 mg, 0.20 mmol) and the reaction was carried out at a concentration of 15 mM for 5 h. The product **6f** (38.0 mg, 0.16 mmol, 83%) was afforded as a colorless solid.

^{1}H NMR: (500 MHz, $CDCl_3$) δ = 7.60 (d, *J* = 7.3 Hz, 1H, CH_{arom}), 7.42 (t, *J* = 7.5 Hz, 1H, CH_{arom}), 7.26 – 7.24 (m, 1H, CH_{arom}), 3.11 – 2.94 (m, 2H, C$H_{2,benzylic}$), 2.66 – 2.57 (m, 1H, C*H*CH_3), 2.20 (dq, *J* = 13.3, 4.6 Hz, 1H, C*H*H), 1.88 (dtd, *J* = 13.2, 11.2, 4.7 Hz, 1H, CH*H*), 1.27 (d, *J* = 6.8 Hz, 3H, CH_3), 0.29 (s, 9H, Si$(CH_3)_3$) ppm. **^{13}C NMR**: (126 MHz, $CDCl_3$) δ = 202.0 (*C*=O), 144.7 (C_{arom}), 143.1 (C_{arom}), 137.1 (C_{arom}), 134.3 (C_{arom}), 131.9 (C_{arom}), 130.1 (C_{arom}), 42.9 (*C*HCH_3), 31.3 ($CH_{2,benzylic}$), 29.8 (CH_2), 15.9 (CH_3), 0.7 (Si$(CH_3)_3$) ppm. **^{29}Si NMR**: (60 MHz, $CDCl_3$) δ = 5.35. **IR** (ATR) $\tilde{\nu}$ (cm^{-1}) = 3043 (w), 2934 (w), 1680 (s), 1575 (w), 1458 (w), 1414 (w), 1375 (w), 1359 (w), 1319 (w), 1286 (w), 1245 (m), 1225 (w), 1198 (w), 1147 (w), 1106 (w), 1081 (w), 1022 (w), 967 (w), 939 (w), 859 (w), 838 (s), 783 (w), 760 (m), 690 (w), 674 (w), 625 (w), 581 (w), 529 (w), 481 (w), 452 (w), 429 (w). **HRMS** (ESI+) m/z: [M+Na]+ Calcd for C14H20OSiNa 255.1176, Found 255.1168.

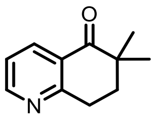
2-methyl-3,4-dihydrophenanthren-1(2H)-one **6g**



was obtained following general procedure XI using the corresponding aldehyde **4g** (45.2 mg, 0.19 mmol) and the reaction was carried out at a concentration of 15 mM for 8 h. The crude was purified by column chromatography (*n*-pentane/toluene 6:1). **6g** (11.8 mg, 0.05 mmol, 26%) was afforded as a colorless solid.

^{1}H NMR: (500 MHz, $CDCl_3$) δ = 8.19 – 8.11 (m, 2H, 2 x CH_{arom}), 7.91 – 7.88 (m, 1H, CH_{arom}), 7.78 (d, *J* = 8.6 Hz, 1H, CH_{arom}), 7.64 – 7.60 (m, 2H, 2 x CH_{arom}), 3.59 (dt, *J* = 17.3, 4.4 Hz, 1H, C*H*$H_{benzylic}$), 3.32 (ddd, *J* = 16.8, 10.9, 5.0 Hz, 1H, CH$H_{benzylic}$), 2.79 – 2.68 (m, 1H, C*H*), 2.47 – 2.38 (m, 1H, C*H*H), 2.09 – 2.00 (m, 1H, CH*H*), 1.35 (d, *J* = 6.8 Hz, 3H, CH_3) ppm. **^{13}C NMR**: (126 MHz, $CDCl_3$) δ = 201.2 (*C*=O), 142.5 (C_{arom}), 135.7 (C_{arom}), 131.6 (C_{arom}), 129.9 (C_{arom}), 128.9 (C_{arom}), 128.3 (C_{arom}), 127.1 (C_{arom}), 126.8 (C_{arom}), 124.9 (C_{arom}), 123.2 (C_{arom}), 41.8 (*C*H), 30.9 (CH_2), 25.2 ($CH_{2,benzylic}$), 15.5 (CH_3) ppm. **IR** (ATR) $\tilde{\nu}$ (cm^{-1}) = 3061 (w), 2961 (w), 2930 (w), 2862 (w), 1677 (s), 1621 (w), 1596 (w), 1458 (w), 1430 (w), 1374 (w), 1328 (w), 1265 (w), 1231 (m), 1177 (w), 1124 (w), 1072 (w), 1025 (w), 964 (w), 905 (w), 868 (w), 824 (w), 758 (m), 718 (w), 666 (w), 576 (w), 542 (w), 523 (w), 413 (w). **HRMS** (ESI+) m/z: [M+H]+ Calcd for C15H14OH 211.1117, Found 211.1120. **m.p.** 49.7 – 54.7 °C (Et_2O).

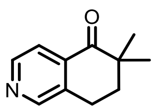
6,6-dimethyl-7,8-dihydroquinolin-5(6H)-one **6h**



was obtained following general procedure XI using the corresponding aldehyde **4h** (39.1 mg, 0.23 mmol) and the reaction was carried out at a concentration of 15 mM for 3 h. The crude was purified by column chromatography (*n*-pentane/EtOAc 2:1). The product **6h** (38.8 mg, 0.23 mmol, 99%) was afforded as a yellow oil.

^{1}H NMR: (500 MHz, $CDCl_3$) δ = 8.67 (dd, J = 4.8, 1.9 Hz, 1H, CH_{arom}), 8.29 (dd, J = 7.9, 1.9 Hz, 1H, CH_{arom}), 7.30 – 7.25 (m, 1H, CH_{arom}), 3.17 (t, J = 6.4 Hz, 2H, CH_2), 2.04 (t, J = 6.5 Hz, 2H, CH_2), 1.23 (s, 6H, 2 x CH_3) ppm. **^{13}C NMR**: (126 MHz, $CDCl_3$) δ = 202.5 (*C*=O), 162.7 (C_{arom}), 153.4 (C_{arom}), 136.1 (C_{arom}), 127.1 (C_{arom}), 122.3 (C_{arom}), 41.6 (C_{quart}), 35.4 (CH_2), 29.0 (CH_2), 24.2 (2 x CH_3) ppm. **IR** (ATR) $\tilde{\nu}$ (cm^{-1}) = 3367 (w), 3054 (w), 2963 (w), 2929 (w), 2867 (w), 1686 (s), 1582 (s), 1472 (w), 1457 (m), 1438 (w), 1423 (w), 1385 (m), 1364 (w), 1347 (w), 1310 (m), 1261 (w), 1247 (w), 1222 (m), 1159 (w), 1094 (m), 1058 (w), 1019 (w), 994 (w), 966 (m), 897 (w), 826 (w), 802 (w), 784 (w), 756 (m), 717 (w), 672 (w), 632 (w), 574 (w), 536 (w), 491 (w), 455 (w), 437 (w). **HRMS** (ESI+) m/z: [M+H]+ Calcd for C11H13NOH 176.1063, Found 176.1070.

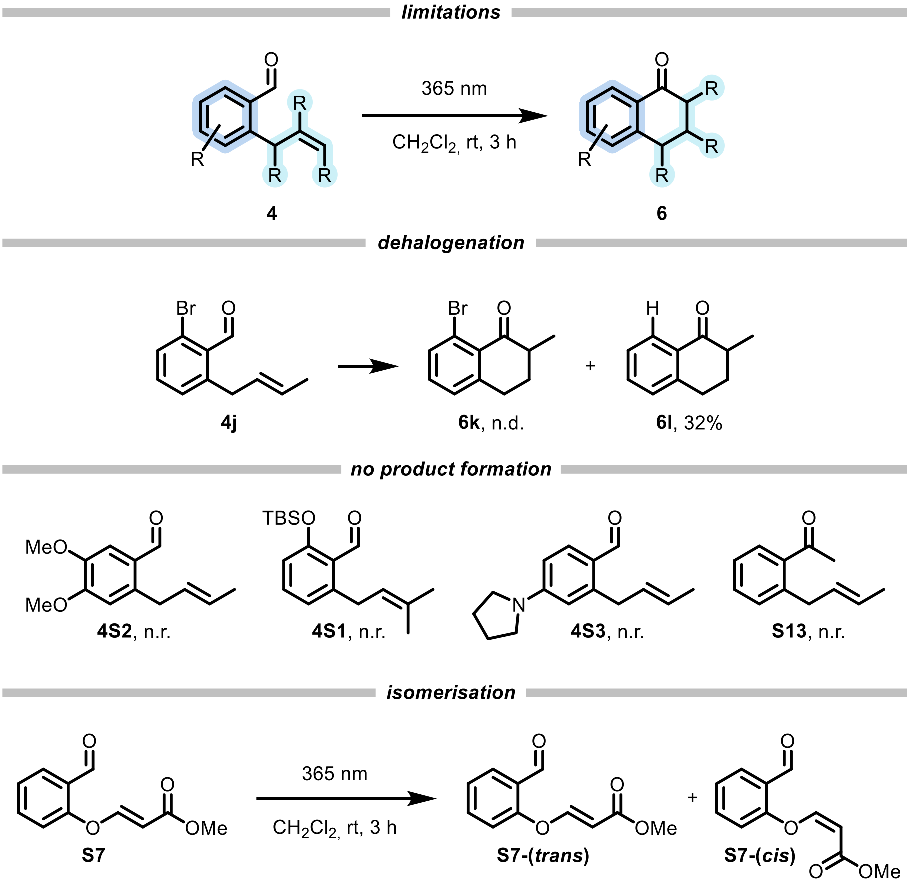
6,6-dimethyl-7,8-dihydroisoquinolin-5(6H)-one **6i**



was obtained following general procedure XI using the corresponding aldehyde **4i** (33.8 mg, 0.20 mmol) and the reaction was carried out at a concentration of 15 mM for 3 h. The crude was purified by column chromatography (*n*-pentane/EtOAc 2:1). The product **6i** (33.0 mg, 0.19 mmol, 98%) was afforded as a yellow oil.

^{1}H NMR: (300 MHz, $CDCl_3$) δ = 8.64 (s, 1H, CH_{arom}), 8.61 (d, J = 5.0 Hz, 1H, CH_{arom}), 7.78 (d, J = 5.1 Hz, 1H, CH_{arom}), 2.99 (t, J = 6.3 Hz, 2H, C$H_{2,benzylic}$), 2.03 (t, J = 6.4 Hz, 2H, CH_2), 1.23 (s, 9H, 3 x CH_3) ppm. **^{13}C NMR**: (126 MHz, $CDCl_3$) δ = 202.4 (*C*=O), 151.5 (C_{arom}), 148.6 (C_{arom}), 136.8 (C_{arom}), 136.7 (C_{arom}), 120.1 (C_{arom}), 42.2 (C_{quart}), 36.3 (CH_2), 24.1 (2 x CH_3), 22.6 ($CH_{2,benzylic}$) ppm. **IR** (ATR) $\tilde{\nu}$ (cm^{-1}) = 3026 (w), 2965 (w), 2929 (w), 2868 (w), 1695 (s), 1590 (w), 1563 (w), 1472 (w), 1452 (w), 1433 (w), 1412 (w), 1385 (w), 1364 (w), 1349 (w), 1314 (m), 1228 (m), 1172 (w), 1137 (w), 1050 (w), 1034 (w), 996 (w), 976 (w), 911 (w), 896 (w), 849 (w), 823 (w), 787 (w), 707 (w), 693 (w), 630 (w), 528 (w), 424 (w). **HRMS** (ESI+) m/z: [M+H]+ Calcd for C11H13NOH 176.1070, Found 176.1064.

9.1 Limitation of the Substrate Scope



scheme 1: Irradiation experiments that have not led to the corresponding cyclized photo-hydroacylation products.

The observed absence of conversion of substrates bearing electron donating substituents indicates the inhibition of required mechanistic steps. However, after irradiation isomerization of the olefine can be observed. It is reasonable to suggest that 1,5-HAT does not occur.

9.2 Isomerisation of Olefin in Substrates bearing EDG-substituents

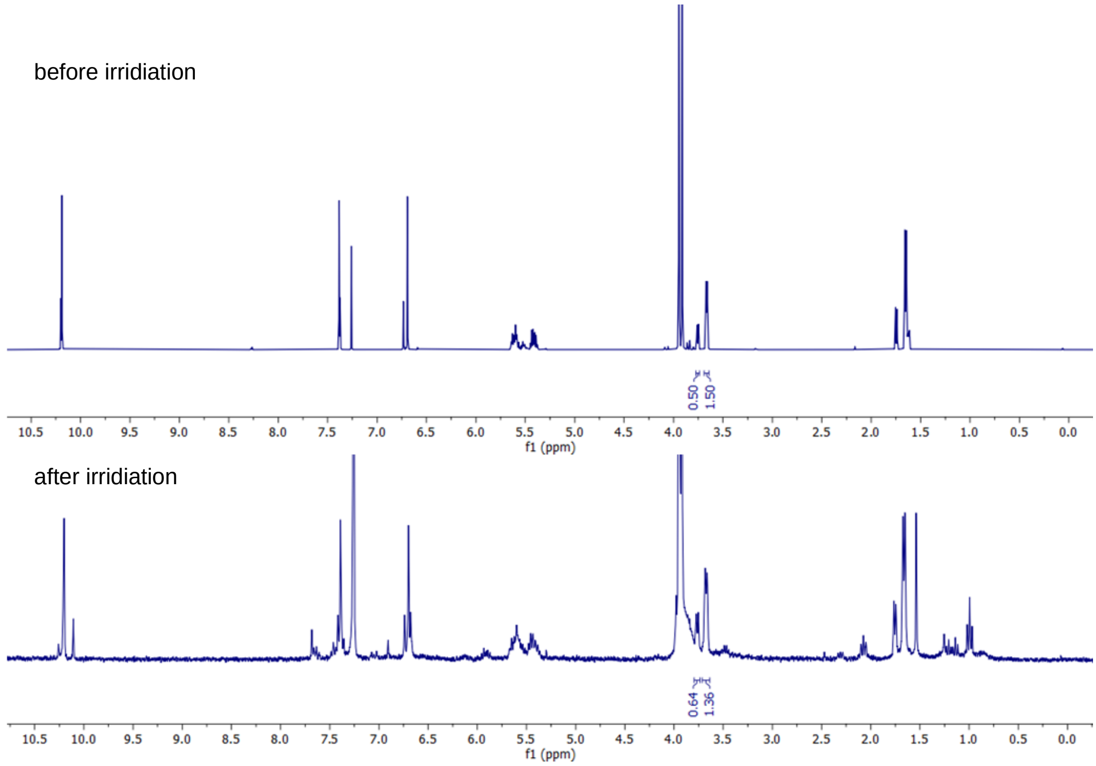


Figure 5: ^{1}H-NMR spectrum before and after irradiation of **4S2** showing isomerization of the olefin.

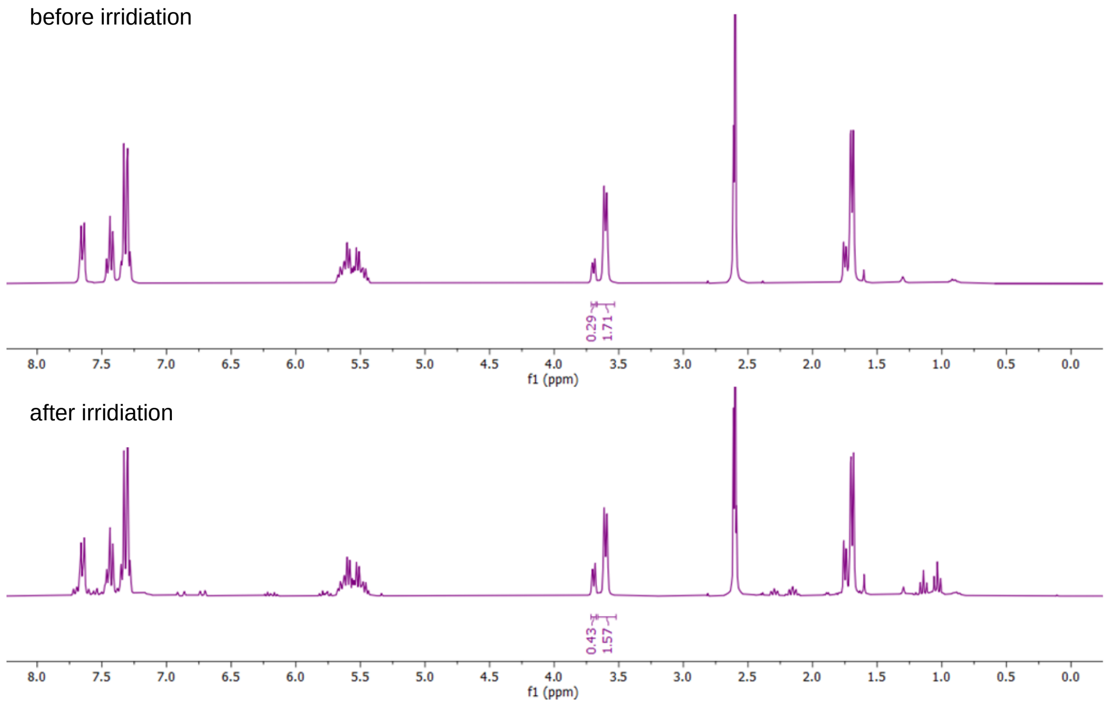
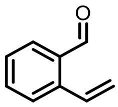


Figure 6: ^{1}H-NMR spectrum before and after irradiation of **S13** showing isomerization of the olefin.

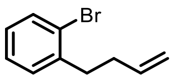
10 Synthesis of Prolonged Sidechain

2-vinylbenzaldehyde **4y**



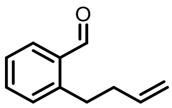
was obtained following the procedure reported by OH *et al*. starting from 2-bromo benzaldehyde.[19]

1-bromo-2-(but-3-en-1-yl)benzene **S29**,



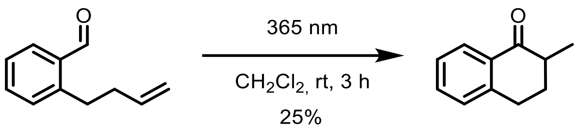
To a solution of 1-bromo-2-(bromomethyl)benzene (300 mg, 1.20 mmol) in anhydrous THF (0.87 mL) allyl magnesium bromide (1.83 mL, 0.79 M, 1.20 equiv) in anhydrous THF (1.45 mL) were added slowly at 0 °C and the mixture was stirred at rt overnight. HCl aq. (1 M, 5 mL) was added, the organic layer was extracted with CH_2Cl_2 (3 x 15 mL) and dried over Na_2SO_4. The solvent was removed under reduced pressure. Purification by column chromatography (*n*-pentane) afforded **S29** (113 mg, 0.54 mmol, 44%) as a pale yellow oil. Spectral data was in agreement with the literature.[20]
^{1}H NMR: (300 MHz, $CDCl_3$) δ = 7.56 – 7.51 (m, 1H, CH_{arom}), 7.25 – 7.18 (m, 2H, 2xCH_{arom}), 7.03 (d, J = 3.3 Hz, 1H, CH_{arom}), 5.89 (ddt, J = 16.9, 10.2, 6.6 Hz, 1H, CH=CH_2), 5.11 – 4.98 (m, 1H, CH=CH_2), 2.87 – 2.80 (m, 2H, $CH_{2,benzylic}$), 2.43 – 2.34 (m, 2H, CH_2) ppm. **^{13}C NMR:** (75 MHz, $CDCl_3$) δ = 141.2 (C_{arom}), 137.8 (CH_{olef}), 132.3 (C_{arom}), 130.5 (C_{arom}), 127.7 (C_{arom}), 127.5 (C_{arom}), 124.6 (C_{arom}), 114.8 ($CH_{2,olef}$), 35.8 ($CH_{2,benzylic}$), 34.0 (CH_2) ppm.

2-(but-3-en-1-yl)benzaldehyde **S30**,



was obtained according to general procedure X, using the corresponding bromide **S29** (113 mg, 0.54 mmol). Purification by column chromatography afforded **S30** (20.8 mg, 0.13 mmol, 24%) as a colorless oil.
^{1}H NMR: (300 MHz, $CDCl_3$) δ = 10.27 (s, 1H, CHO), 7.83 (dd, *J* = 7.6, 1.6 Hz, 1H, CH_{arom}), 7.51 (td, *J* = 7.5, 1.5 Hz, 1H, CH_{arom}), 7.38 (td, *J* = 7.5, 1.3 Hz, 1H, CH_{arom}), 7.28 (d, *J* = 7.6 Hz, 1H, CH_{arom}), 5.87 (ddt, *J* = 16.9, 10.2, 6.6 Hz, 1H, CH_{olef}), 5.04 (dq, *J* = 17.0, 1.5 Hz, 1H, CH_{olef}), 5.00 (ddt, *J* = 10.2, 2.0, 1.2 Hz, 1H, CH_{olef}), 3.16 – 3.12 (m, 2H, $CH_{2,benzylic}$), 2.41 – 2.35 (m, 2H, CH_2) ppm. **^{13}C NMR:** (126 MHz, $CDCl_3$) δ = 192.5 (CHO), 144.7 (C_{arom}), 137.6 (CH_{olef}), 134.0 (C_{arom}), 133.9 (C_{arom}), 132.2 (C_{arom}), 131.2 (C_{arom}), 126.8 (C_{arom}), 115.6 ($CH_{2,olef}$), 36.1 (CH_2), 32.2 ($CH_{2,benzylic}$). **IR** (ATR) $\tilde{\nu}$ (cm^{-1}) = 3074 (w), 2927 (w), 2860 (w), 2733 (w), 1695 (s), 1640 (w), 1600 (w), 1574 (w), 1486 (w), 1451 (w), 1403 (w), 1293 (w), 1206 (w), 1192 (w), 1161 (w), 1112 (w), 996 (w), 913 (w), 870 (w), 827 (w), 803 (w), 756 (m), 661 (w), 636 (w), 585 (w), 447 (w). **HRMS (ESI+)** m/z: [M+H]+ Calcd for C11H12OH 161.0961; Found 161.0953.

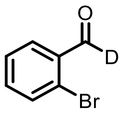
2-methyl-3,4-dihydronaphthalen-1(2H)-one **6k**,



was obtained via irradiation of homoallyl aldehyde **S30** (20 mg, 0.12 mmol, 0.015 M) in CH_2Cl_2 (9.5 mL) with 365 nm UV-Light for 3 h. Purification by column chromatography afforded 6k (5.0 mg, 0.03 mmol, 25%) as a colorless oil.

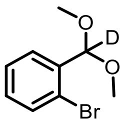
11 Synthesis of Deuterated Compounds

2-Bromobenzaldeyde-d **S31**



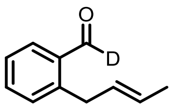
was obtained following the procedure reported by YOU *et al.* starting from 2-Bromobenzaldeyde.[21]

1-bromo-2-(dimethoxymethyl-d)benzene **S32**



was obtained according to general procedure I using the corresponding aldehyde **S31** (967 mg, 5.20 mmol). The crude was used in the following steps without further purification.

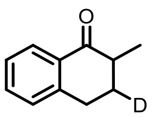
2-(but-2-en-1-yl)-benzaldehyde-d **4v**,



was obtained according to general procedure II A, using corresponding aryl bromide **S32** (74.3 mg, 0.32 mmol) and crotyl bromide (0.05 mL, 0.37 mmol, 85:15 *E/Z*). The crude was then used according to general procedure III. Purification by column chromatography using 100:1 (*n*-pentane/Et_2O) afforded **4v** (27.6 mg, 0.17 mmol, 67:33 *E/Z*, 53% over two steps) as a colorless oil.

^{1}H NMR: (300 MHz, $CDCl_3$) δ = 7.84 (dt, *J* = 7.6, 2.3 Hz, 1H, CH_{arom}), 7.52 (tt, *J* = 7.6, 1.4 Hz, 1H, CH_{arom}), 7.40 – 7.27 (m, 2H, 2 x CH_{arom}), 5.69 – 5.38 (m, 2H, 2 x CH_{olef}), 3.83 (d, *J* = 5.7 Hz, 0.68H, $CH_{2,minor}$), 3.74 (dt, *J* = 6.2, 1.6 Hz, 1.32H, $CH_{2,major}$), 1.74 (dt, *J* = 6.4, 1.2 Hz, 1H, $CH_{3,minor}$), 1.66 (dq, *J* = 6.3, 1.6 Hz, 2H, $CH_{3,major}$) ppm. **^{13}C NMR:** (75 MHz, $CDCl_3$) δ =192.0 (t, *J* = 26.7 Hz, *C*OD), 143.9 ($C_{arom,minor}$), 143.6 ($C_{arom,major}$), 134.1 (2C, $C_{arom,major,}$ $C_{arom,minor}$), 133.9 (d, *J* = 3.7 Hz, $C_{arom,major}$), 131.8 ($C_{arom,minor}$), 131.1 ($C_{arom,major}$), 131.0 ($C_{arom,major}$), 130.7 ($C_{arom,minor}$), 129.8 ($CH_{olef,major}$), 128.6 ($CH_{olef,minor}$), 127.3 ($CH_{olef,major}$), 126.9 ($C_{arom,major}$), 126.8 ($C_{arom,minor}$), 125.5 ($CH_{olef,minor}$), 35.5 ($CH_{2,major}$), 30.2 ($CH_{2,minor}$), 18.0 ($CH_{3,major}$), 13.1 ($CH_{3,minor}$) ppm. Due to the noise to signal ratio, the quaternary carbon atom C_{arom}COD could not be detected. **^{2}H-NMR:** (77 MHz, $CHCl_3$) δ = 10.13 (s, 1D, C=*D*) ppm. **IR** (ATR) $\tilde{\nu}$ (cm^{-1}) = 3402 (w), 3067 (w), 3024 (w), 2976 (w), 2932 (w), 1768 (w), 1715 (w), 1679 (s), 1598 (m), 1572 (w), 1481 (w), 1451 (w), 1368 (w), 1286 (w), 1217 (m), 1158 (w), 1121 (w), 1057 (w), 1022 (w), 969 (m), 859 (w), 753 (s), 656 (w), 632 (w), 549 (w), 526 (w), 492 (w), 462 (w), 427 (w). **HRMS (ESI+)** m/z: [M+NH]+ Calcd for C11H12D1O1 162.1024; Found 162.1018.

2-methyl-3,4-dihydronaphthalen-1(2H)-one-3-d **6v**,

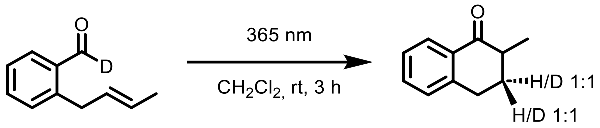


was obtained following general procedure XI using the corresponding aldehyde **4v** (31.4 mg, 0.20 mmol) and the reaction was carried out at a concentration of 15 mM for 3 h. The product **6v** (18.5 mg, 0.11 mmol, 59%) was afforded as a colorless oil.

^{1}H NMR: (500 MHz, $CDCl_3$) δ = 8.04 (dd, *J* = 7.8, 1.6 Hz, 1H, CH_{arom}), 7.45 (td, *J* = 7.5, 1.5 Hz, 1H, CH_{arom}), 7.33 – 7.27 (m, 1H, CH_{arom}), 7.25 – 7.21 (m, 1H, CH_{arom}), 3.02 (d, *J* = 11.2 Hz, 0.5H, CD*H*), 2.63 – 2.54 (m, 0.5H, C*H*D) ppm. **^{13}C NMR:** (126 MHz, $CDCl_3$) δ = 200.9 (*C*=O), 144.3 (C_{arom}), 133.2 (C_{arom}), 132.6 (C_{arom}), 128.9 (C_{arom}), 127.6 (C_{arom}), 126.7 (C_{arom}), 42.7 (*C*HCH3), 31.4 – 30.9 (m, *C*DH).28.9 (CH_2), 15.57 (CH_3) ppm. **^{2}H-NMR:** (77 MHz, $CHCl_3$) δ = 2.00 (s, 0.5 D, C*D*H), 1.69 (s, 0.5 D, CH*D*) ppm. **IR** (ATR) $\tilde{\nu}$ (cm^{-1}) = 3351 (w), 3068 (w), 2967 (w), 2931 (w), 1683 (s), 1600 (m), 1455 (m), 1434 (w), 1375 (w), 1292 (w), 1248 (m), 1221 (w), 1158 (w), 1125 (w), 1093 (w), 1032 (w), 969 (m), 914 (w), 897 (w), 848 (w), 792 (w), 782 (w), 732 (m), 708 (w), 697 (w), 673 (w), 561 (w), 517 (w), 489 (w), 448 (w). **HRMS (ESI+)** m/z: [M+NH]+ Calcd for C11H12D1O1 162.1024; Found 162.1019.

12 Mechanistic Studies

12.1 Deuteration Studies



4v **6v**, 59% yield, **100% D**

Deuterated benzaldehyde **4v** (31.4 mg, 0.20 mmol, 1.00 equiv) was placed in a 25 mL round bottom flask. The flask was put under argon atmosphere and dry, degassed CH_2Cl_2 (13 mL, 15 mM) was added. The reaction was irradiated 6-7 cm away from a 365 nm LED for 3 h at rt. The entire reaction mixture was filtered through a short pad of silica gel and washed with CH_2Cl_2 (100 mL). After removal of the solvents under reduced pressure, tetralone **6v** (18.5 mg, 0.11 mmol, 59%, 100% deuteration) was isolated as a colorless oil. The deuterium atom insertion occurred both in *cis* and *trans* position (1:1 H/D), in relation to the *α*-methyl group.

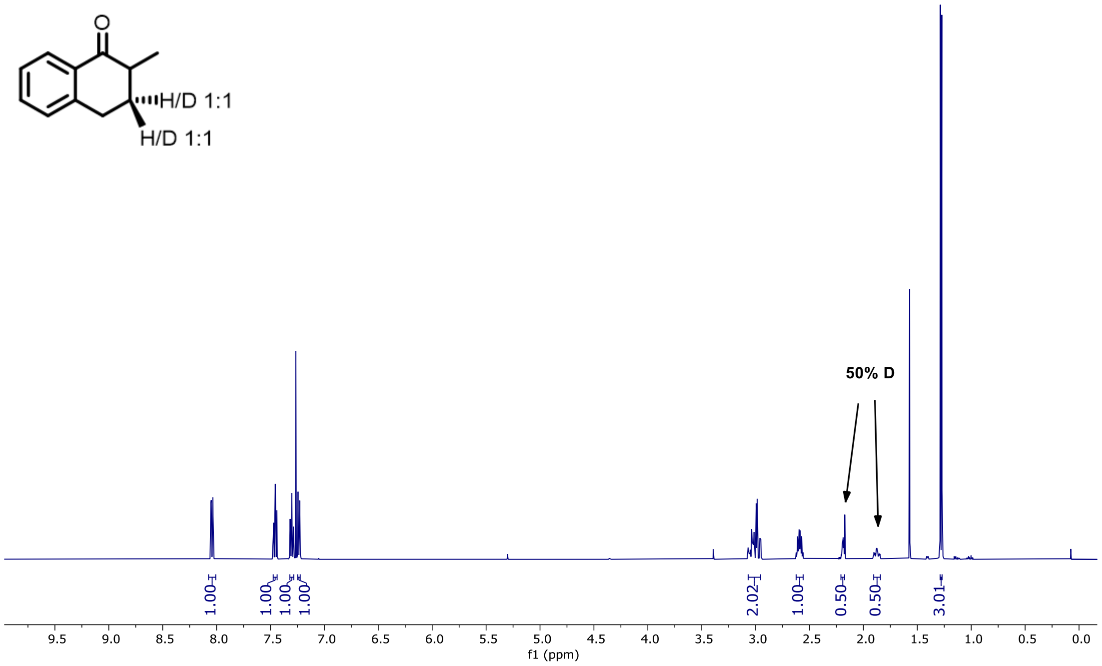
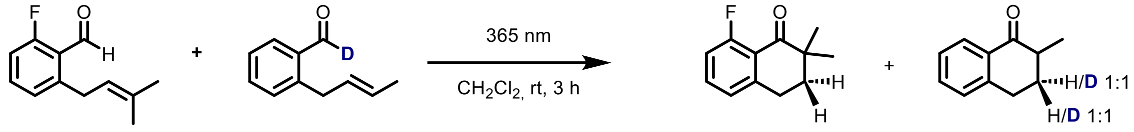


Figure S7: ^{1}H-NMR spectrum of **6v** in $CDCl_3$, 500 MHz.

12.2 Deuterium Scrambling Experiment



4d **4v** **6d**, 81% yield, **0% D** **6v**, 56% yield, **100% D**

Deuterated benzaldehyde **4v** (17.9 mg, 0.11 mmol, 0.50 equiv) and **4d** (19.8 mg, 0.11 mmol, 0.50 equiv) was placed in a 25 mL round bottom flask. The flask was put under argon atmosphere and dry, degassed CH_2Cl_2 (14.8 mL, 15 mM) was added. The reaction was irradiated 6-7 cm away from a 365 nm LED for 3 h at rt. The entire reaction mixture was filtered through a short pad of silica gel and washed with CH_2Cl_2 (100 mL) and concentrated under reduced pressure. The crude was purified by column chromatography (*n*--pentane/Et_2O 100:1→10:1

) to give tetralone **6v** (10.1 mg, 0.06 mmol, 56%, 100% deuteration) and tetralone **6d** (17.2 mg, 0.09 mmol, 81%, 0% deuteration). No deuterium scrambling was observed.

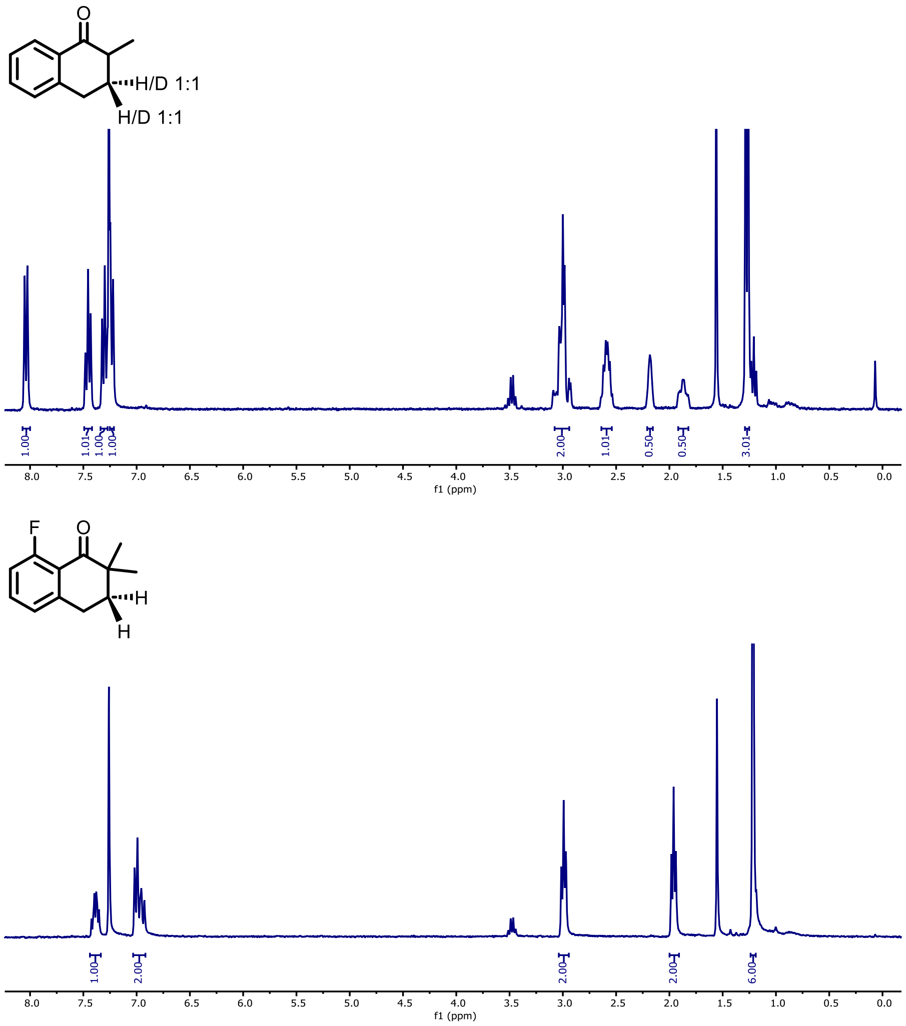


Figure S8: ^{1}H-NMR spectrum of **6v** and **6d** after deuterium scrambling experiment in $CDCl_3$, 300 MHz.

12.3 Quantum Yield Determination

The quantum yield measurement was carried out according to a procedure reported by MEGGERS *et al.*[22]

As a light source a 365 nm LED used. A Powermeter was employed as a detector. The measurement was carried out in a dark room with a 1.1 W red LED. The quantum yield was determined for the reaction **4k** → **6k**. The setup is explained in the following:

Step 1: To determine the radiant power of light transmitted, the cuvette was measured containing a blank solution (CH_2Cl_2). The measurement gave the value of $P_{blank} = 286\ mW$.

Step 2: The solution of **4k** (7.2 mg, 0.045 mmol) in CH_2Cl_2 (3 mL, 15 mM) was added into the fluorescence cuvette containing a stirring bar under a stream of nitrogen. The cuvette was irradiated in the set-up and irradiated with a 365 nm LED. The measured transmitted radiant power $P^0{}_{sample} = 270\ mW$ was observed at the beginning of the reaction.

Step 3: After irradiation of 300 s the transmitted radiant power of $P^1{}_{sample} = 220.2\ mW$ was measured.

Resulting in $P^{\varnothing}{}_{sample} = 245.1\ mW$

Using ^{1}H-NMR spectroscopy, the amount of formed product **6k** was determined to be $1.04\ x\ 10^{-5}\ mol$.

Step 4: Using the following formula, the quantum yield of the reaction was determined to be 0.28:

$$Quantum\ Yield = \frac{N_{product}}{N_{photon}} = \frac{N_A x\ n_{product}}{\frac{P_{absorbed}\ x\ t}{\frac{h\ x\ c}{\lambda}}} = \frac{h\ x\ c\ x\ N_A x\ n_{product}}{(P_{blank} - P^{\varnothing}{}_{sample})\ x\ t\ x\ \lambda}$$

$$= \frac{6.626\ x\ 10^{-34} Js\ x\ 2.998\ x\ 10^{8}\ ms^{-1}\ x\ 6.022\ x\ 10^{23}\ mol^{-1}\ x\ 1.04\ x\ 10^{-5}\ mol}{(286 - 245.1)\ x\ 10^{-3} Js^{-1}\ x\ 300\ s\ x\ 365\ x\ 10^{-9}} = 0.28$$

With the quantum yield being QY < 1, a chain reaction process for the reported photoreaction can be discarded.

12.4 UV-Vis Measurements

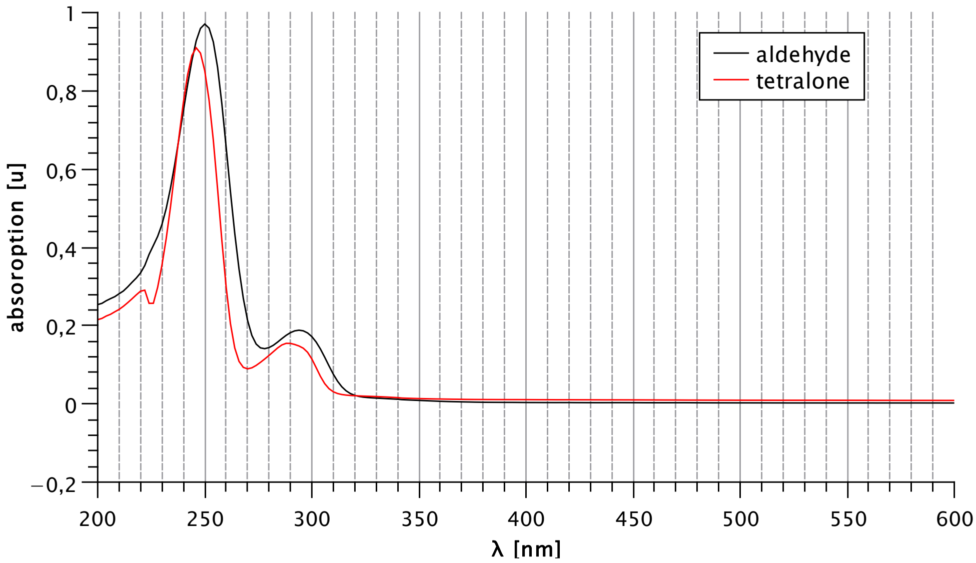
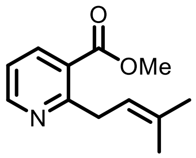
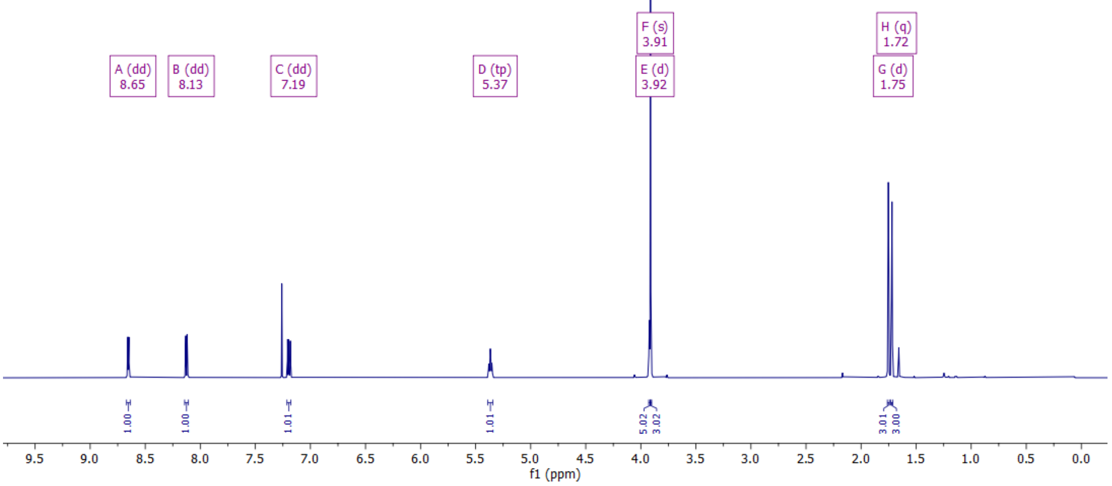


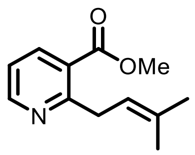
Figure S9: Absorption spectra of aldehyde **4k** and tetralone **6k** in CH_2Cl_2 (0.05 mM).



S2

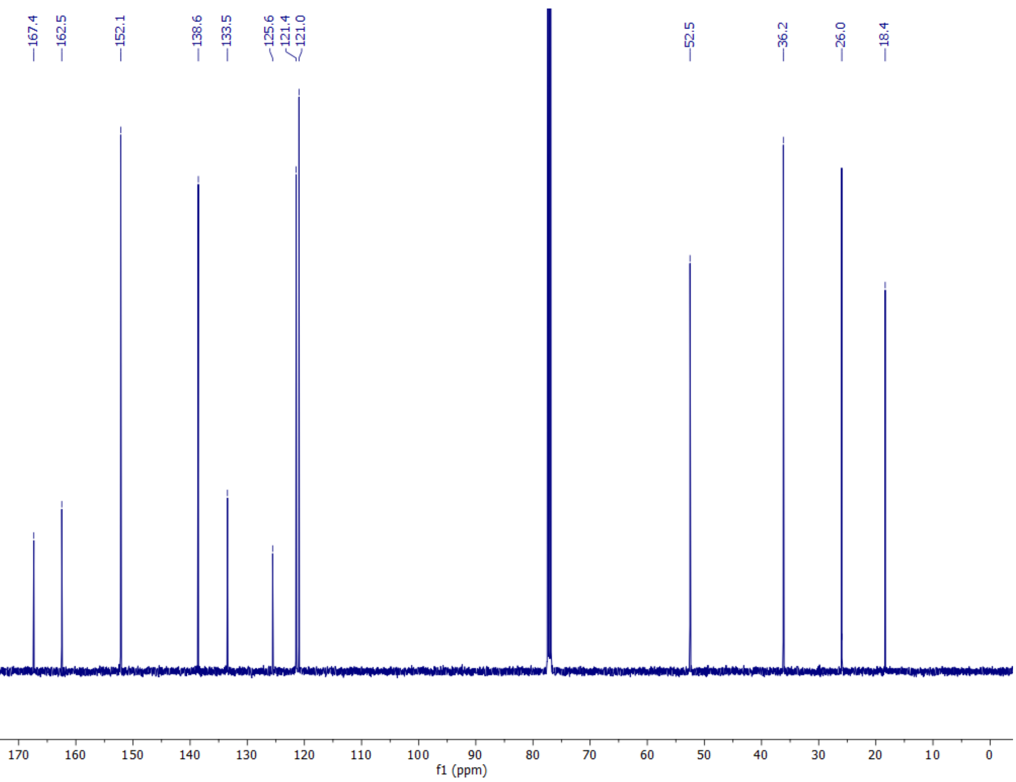
(500 MHz, $CDCl_3$)

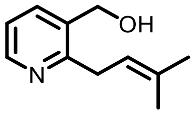




S2

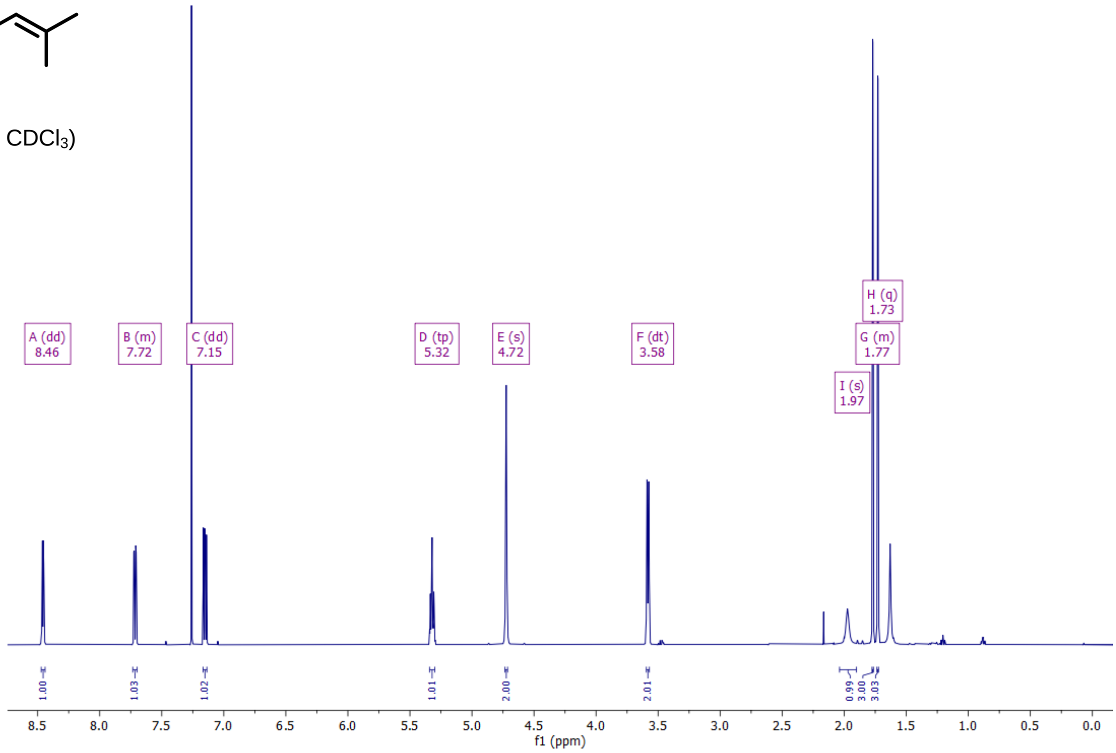
(126 MHz, $CDCl_3$)

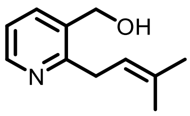




S3

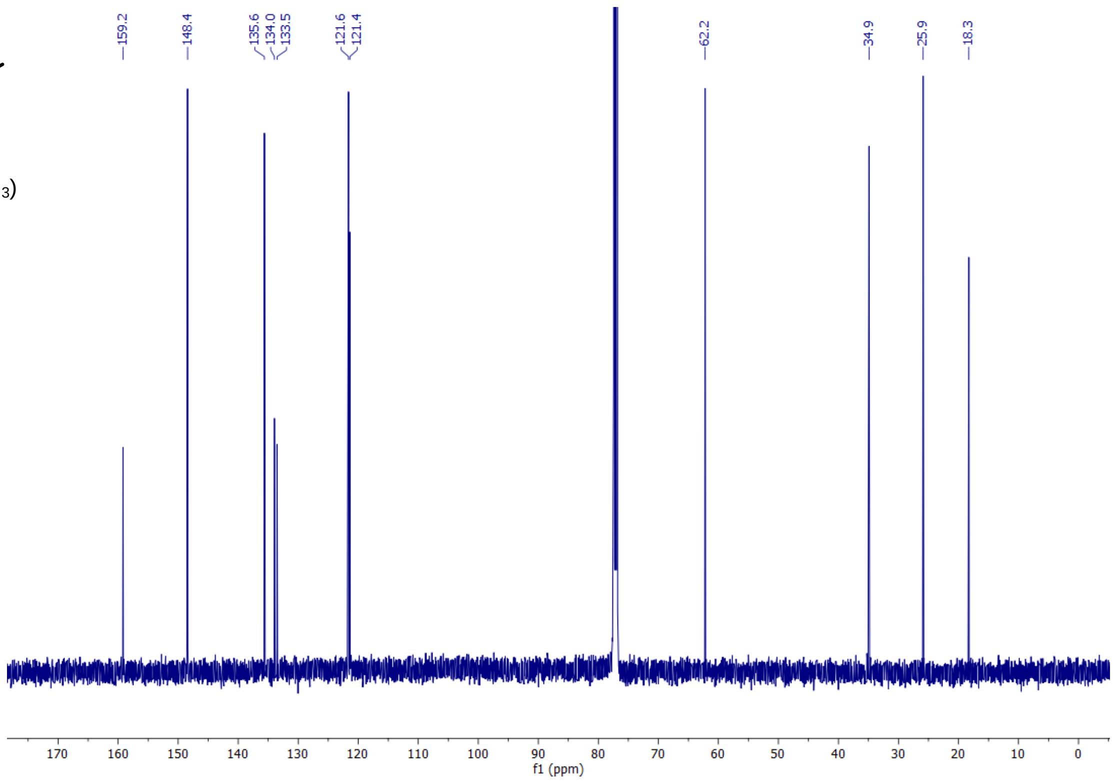
(500 MHz, $CDCl_3$)

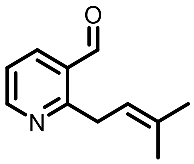




S3

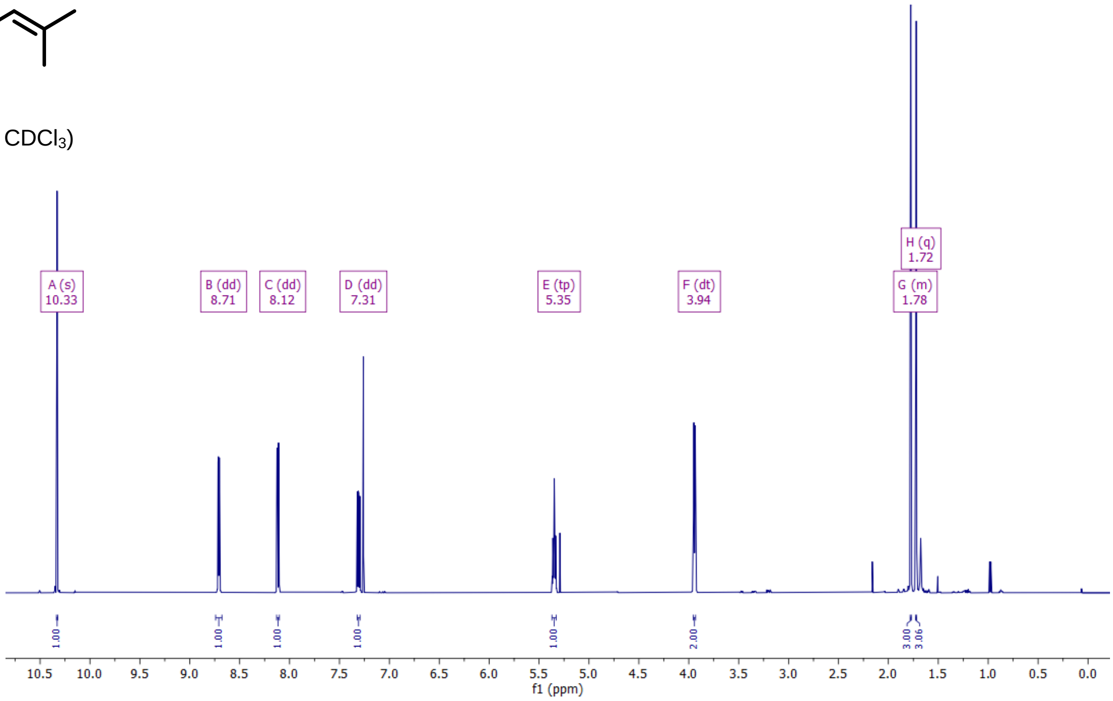
(126 MHz, $CDCl_3$)

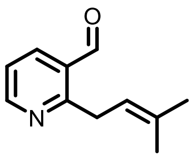




4h

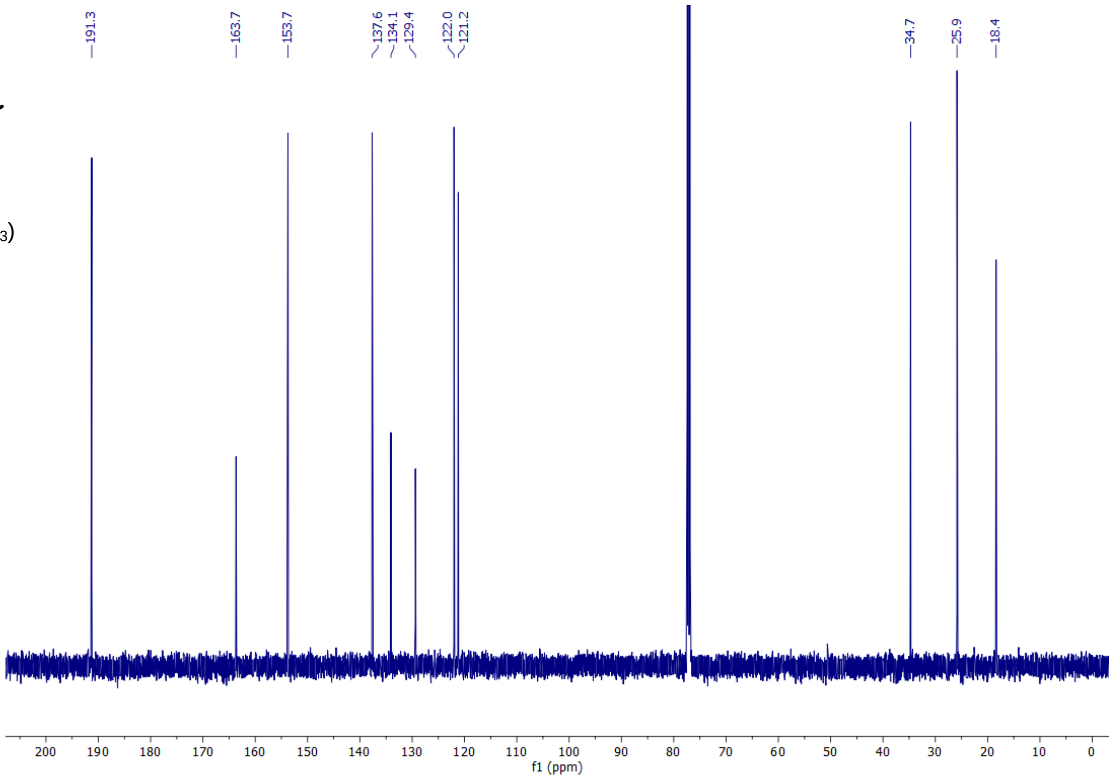
(500 MHz, $CDCl_3$)

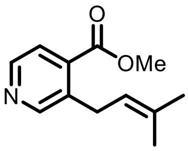




4h

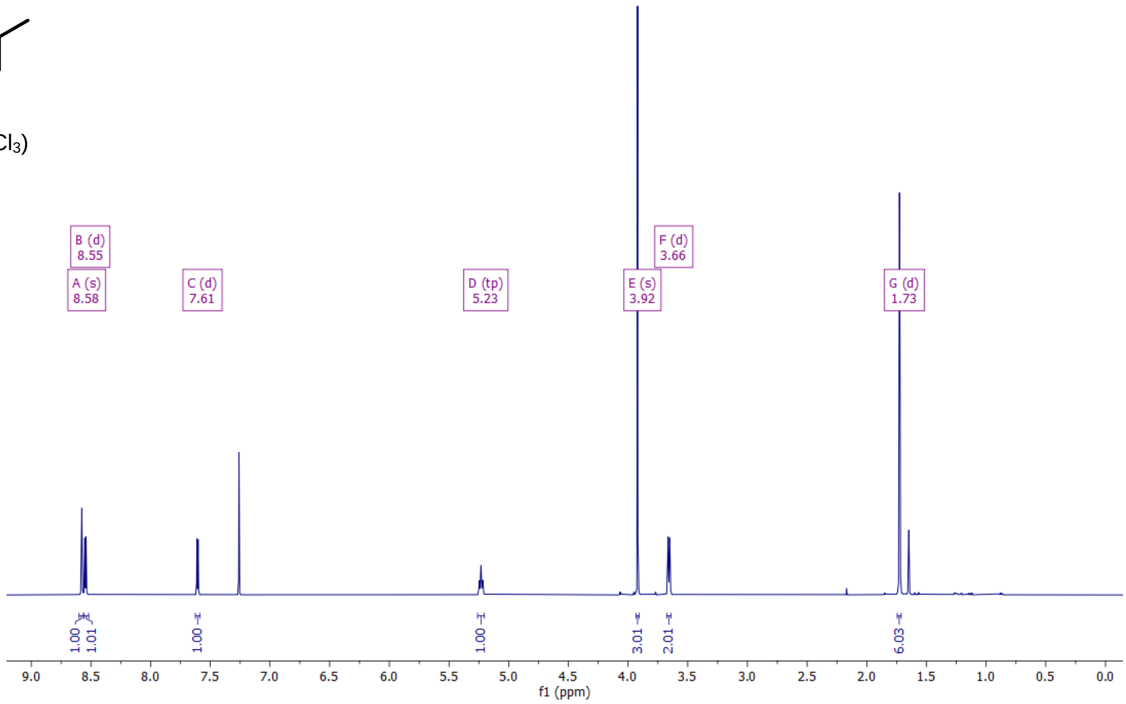
(126 MHz, $CDCl_3$)

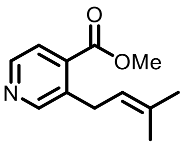




S4

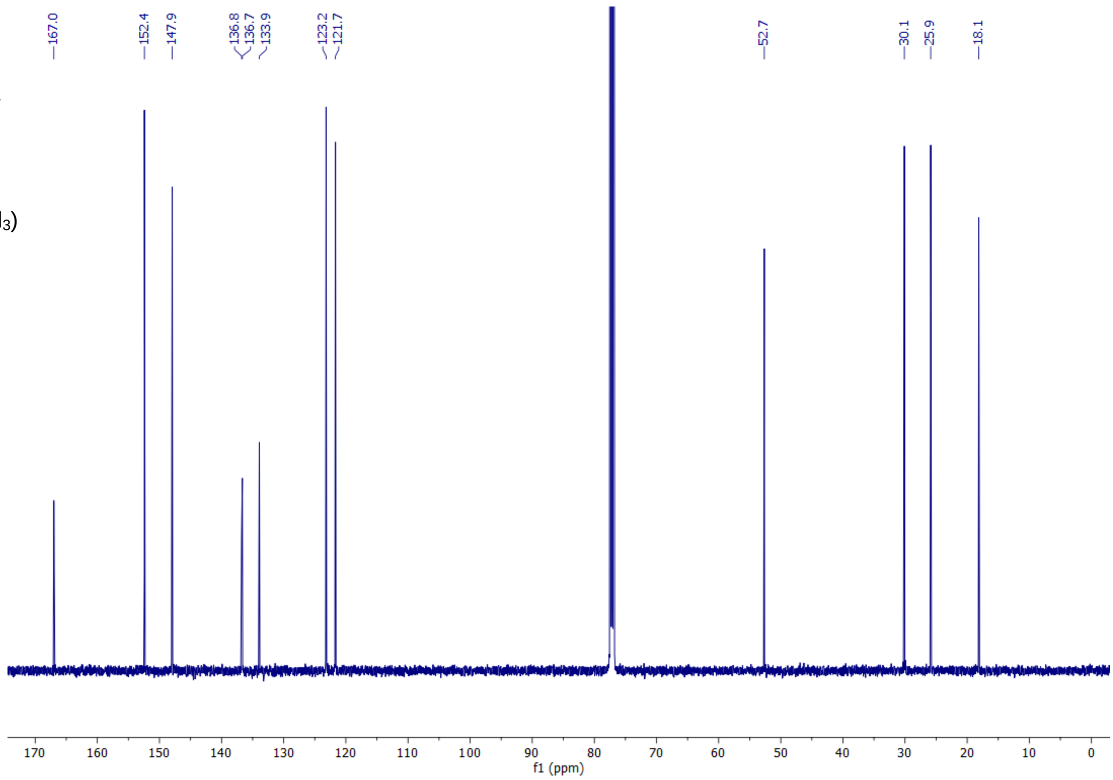
(500 MHz, $CDCl_3$)

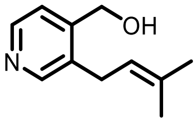




S4

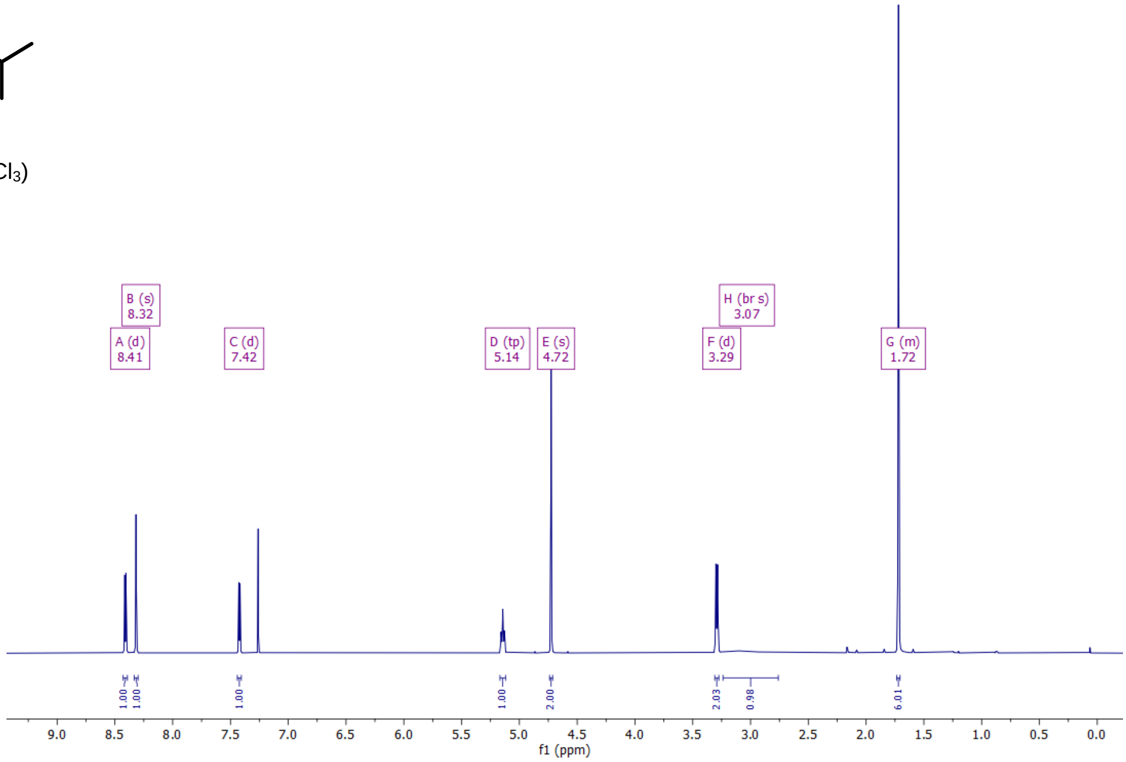
(126 MHz, $CDCl_3$)

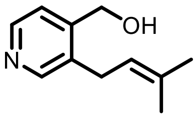




S5

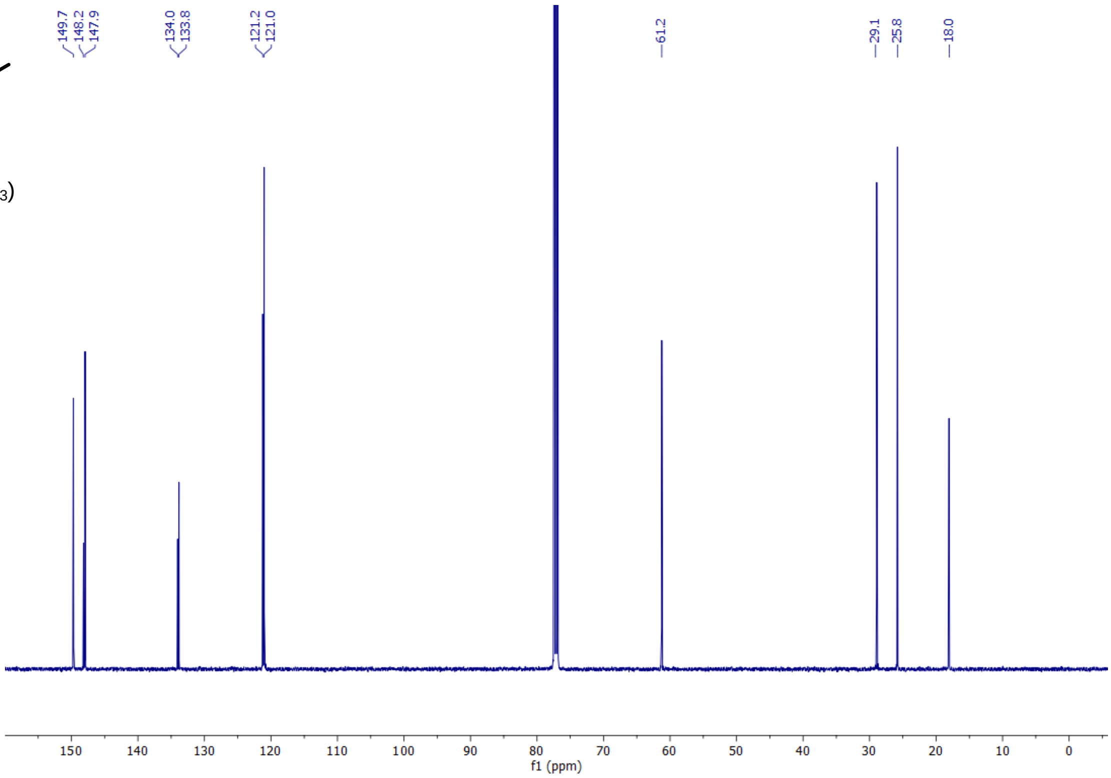
(500 MHz, $CDCl_3$)

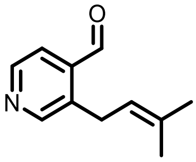




S5

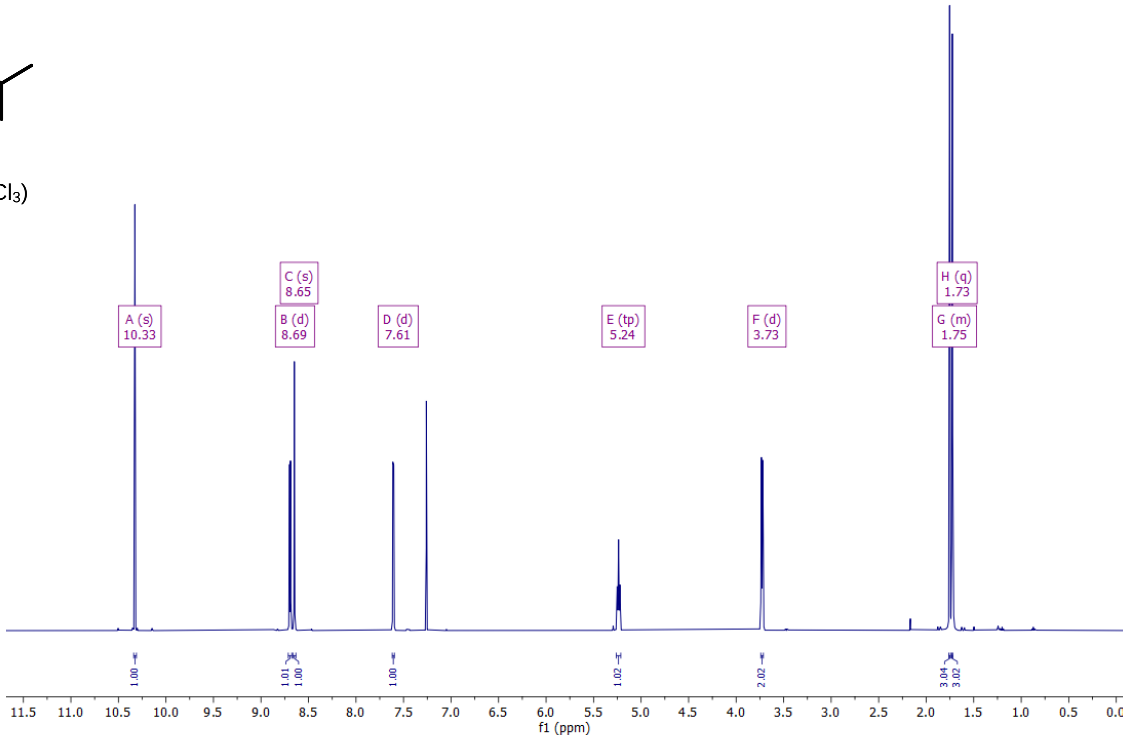
(126 MHz, $CDCl_3$)

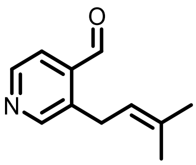




4i

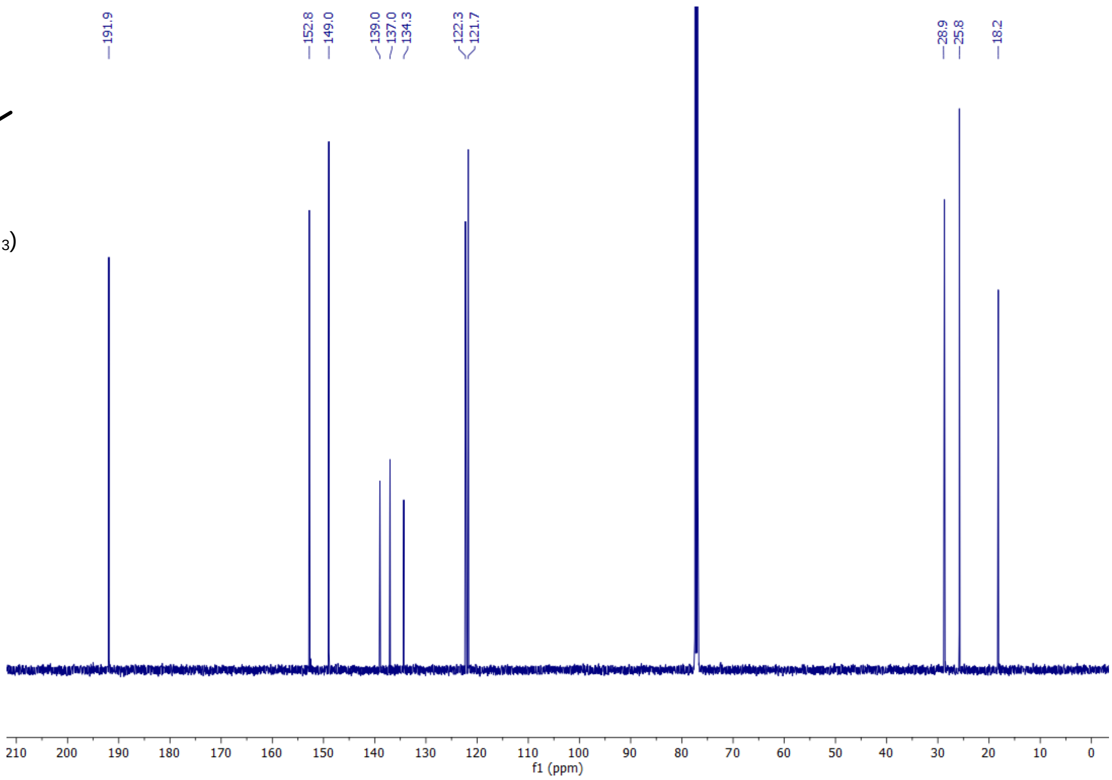
(500 MHz, $CDCl_3$)

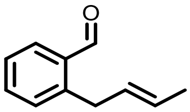




4i

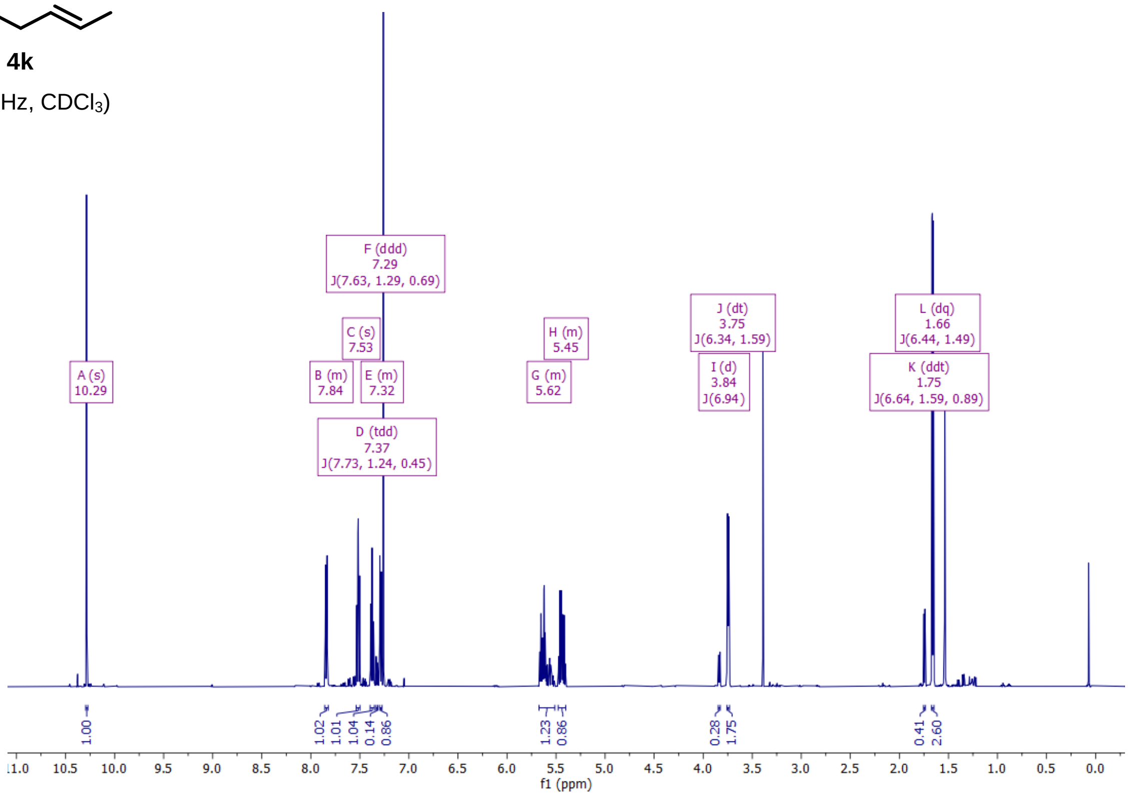
(126 MHz, $CDCl_3$)

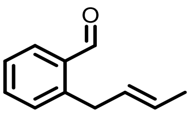




4k

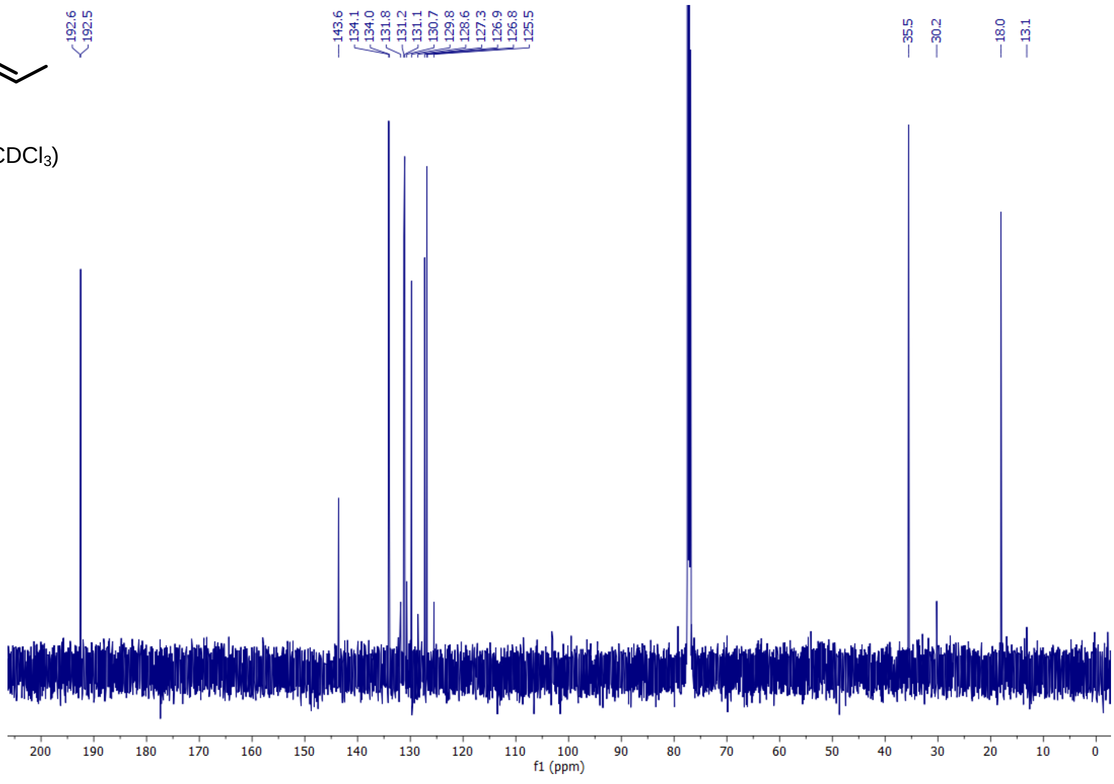
(500 MHz, $CDCl_3$)

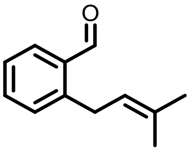




4k

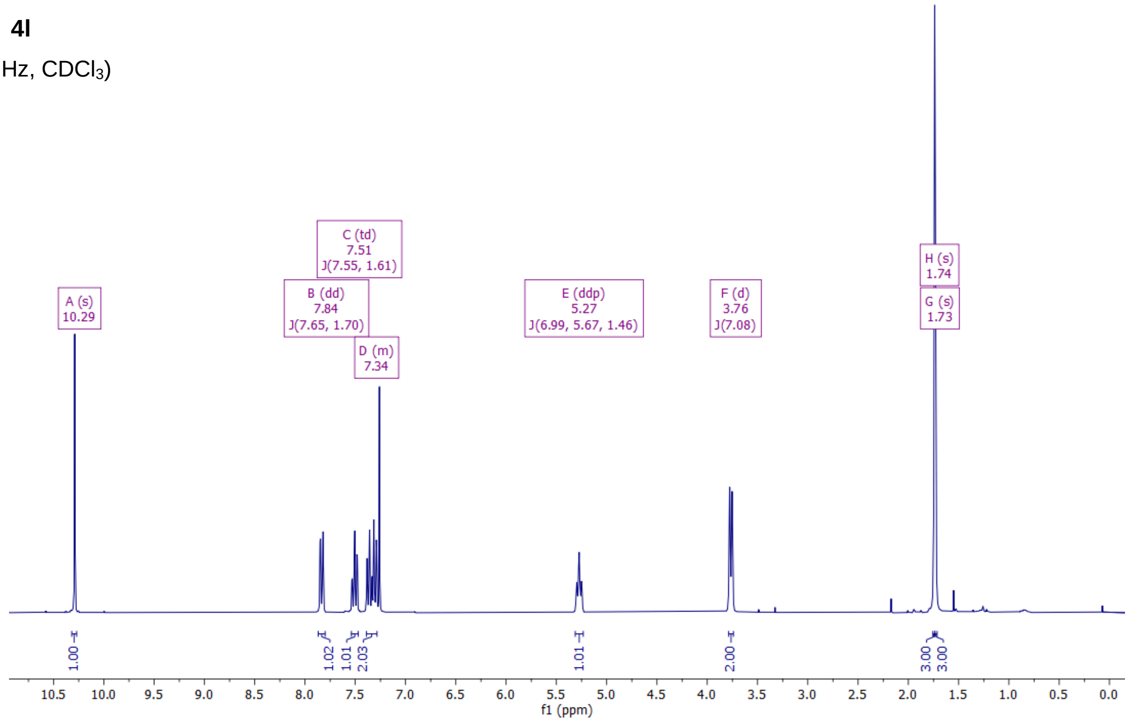
(126 MHz, $CDCl_3$)

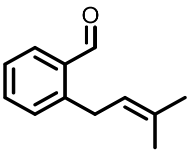




4l

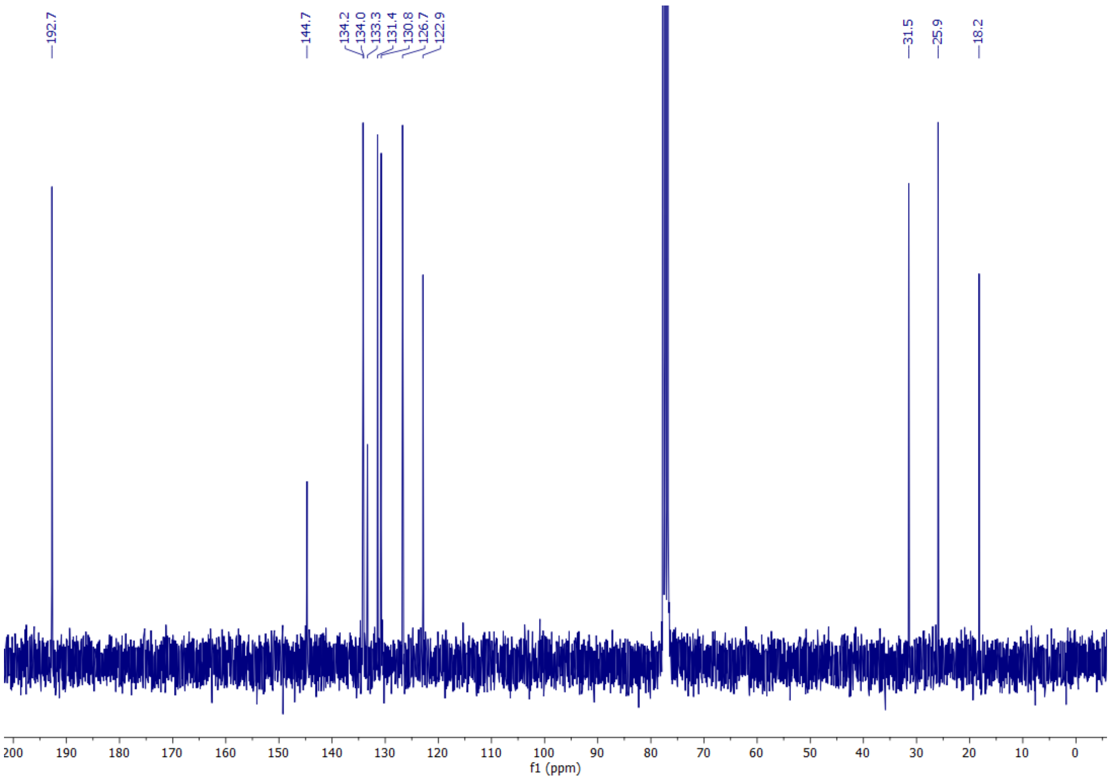
(300 MHz, $CDCl_3$)

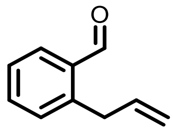




4l

(75 MHz, $CDCl_3$)





4m

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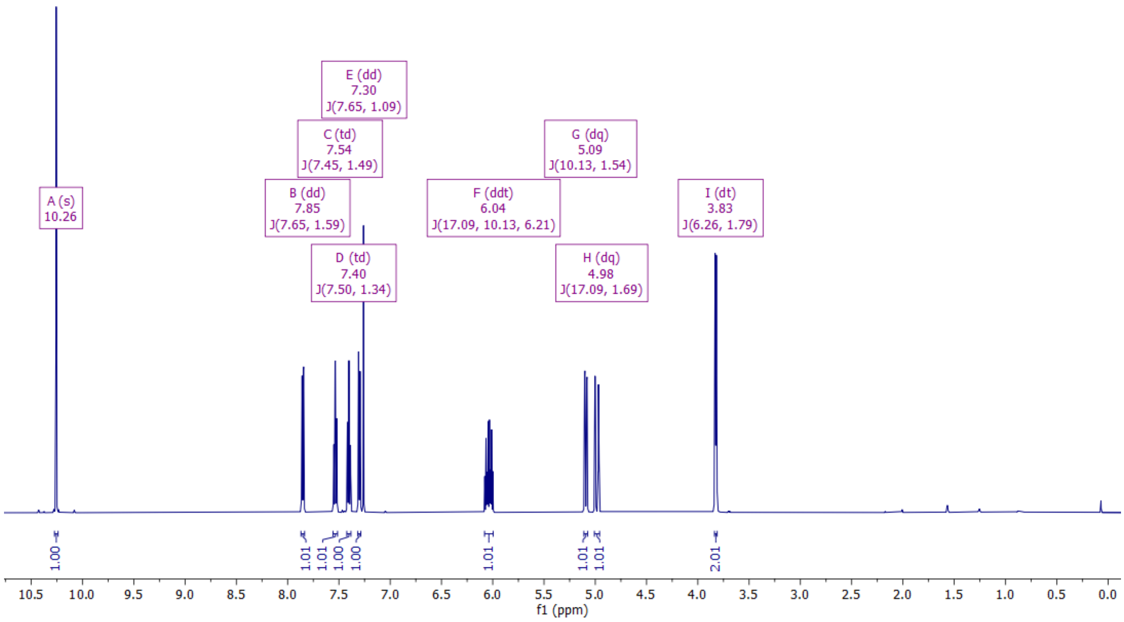
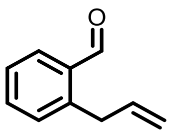
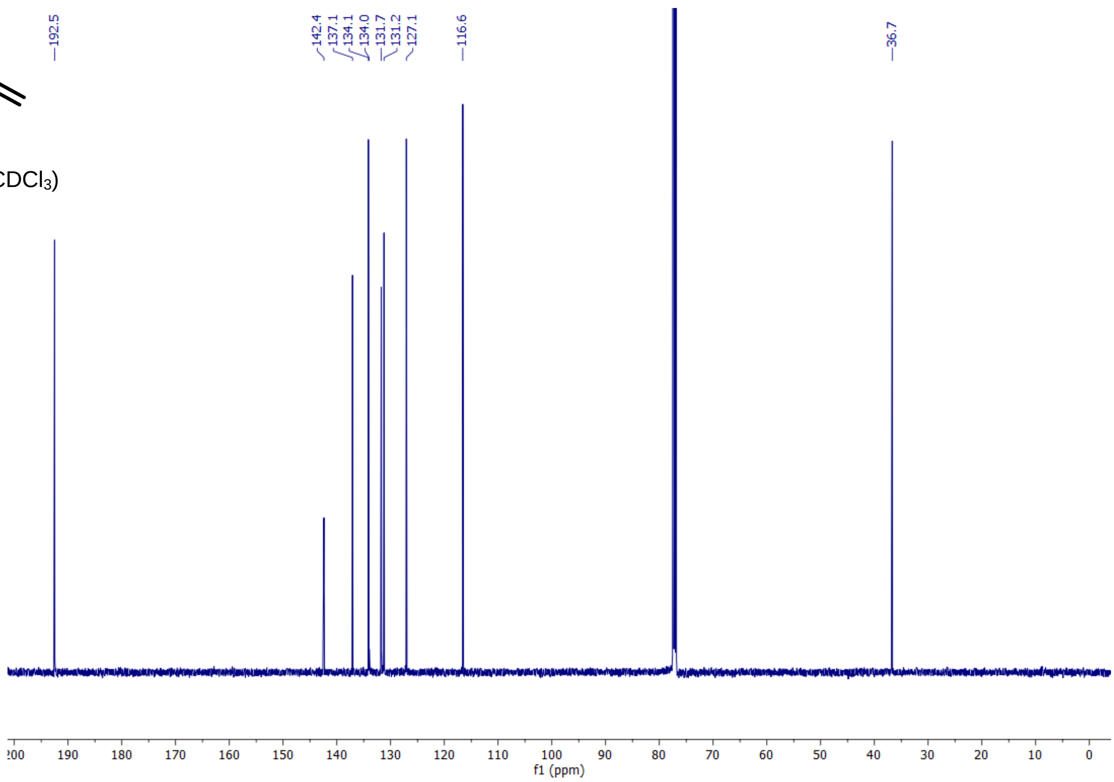
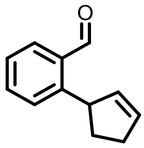




4m

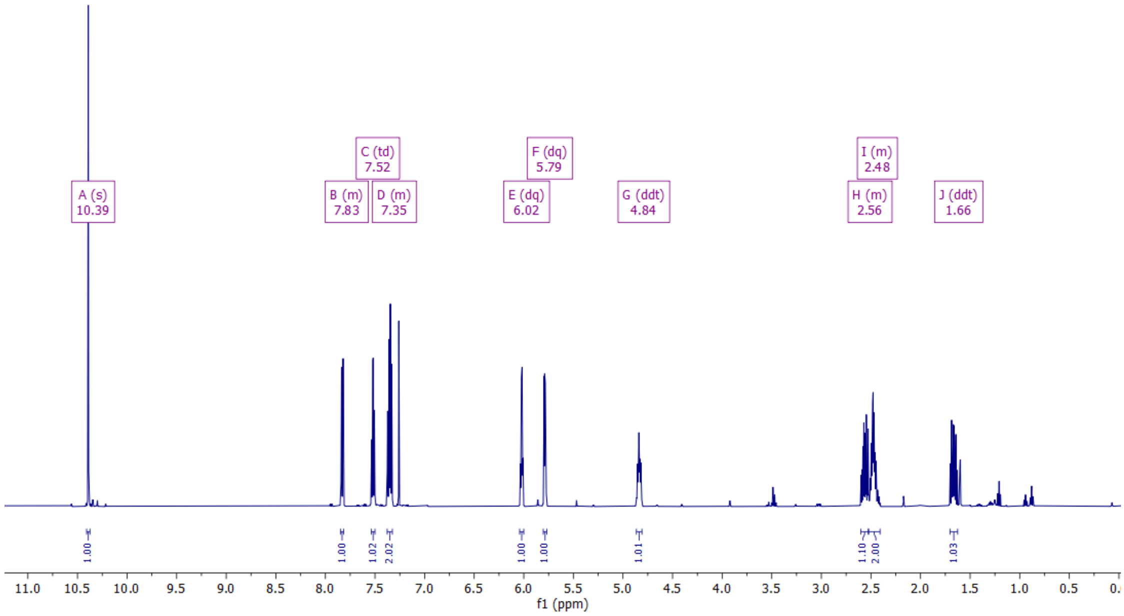
(126 MHz, $CDCl_3$)

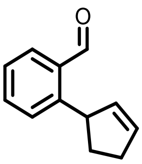




4o

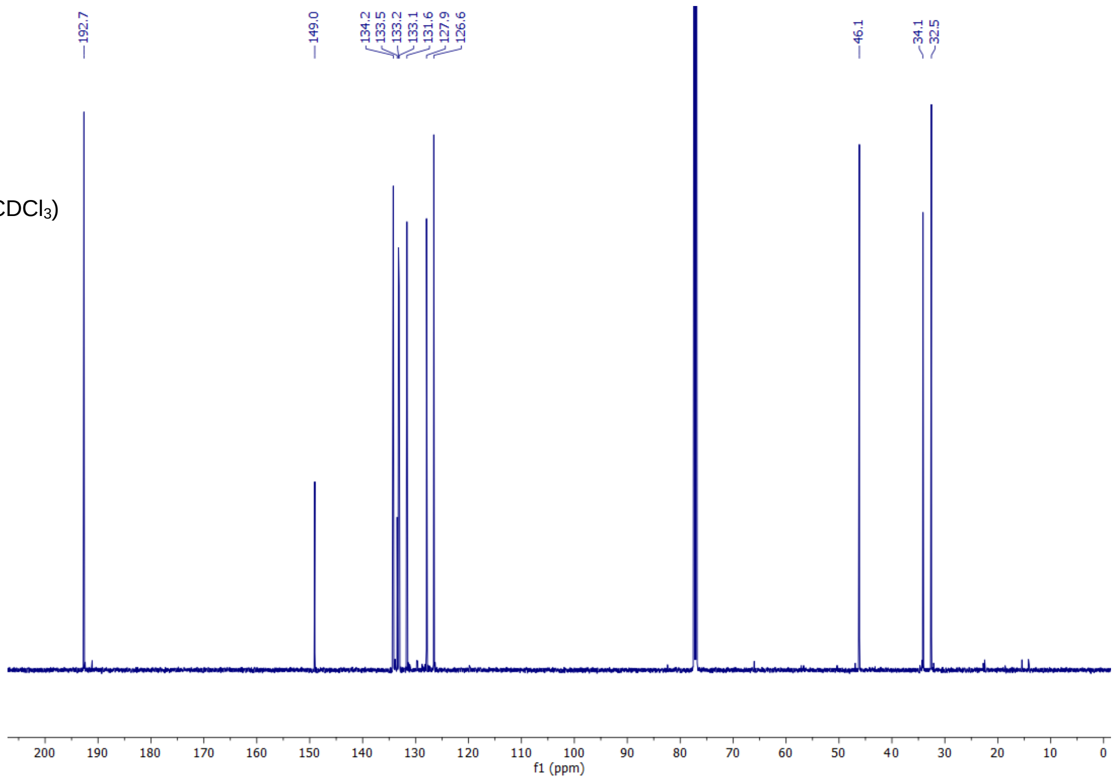
(500 MHz, $CDCl_3$)

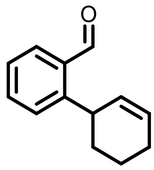




4o

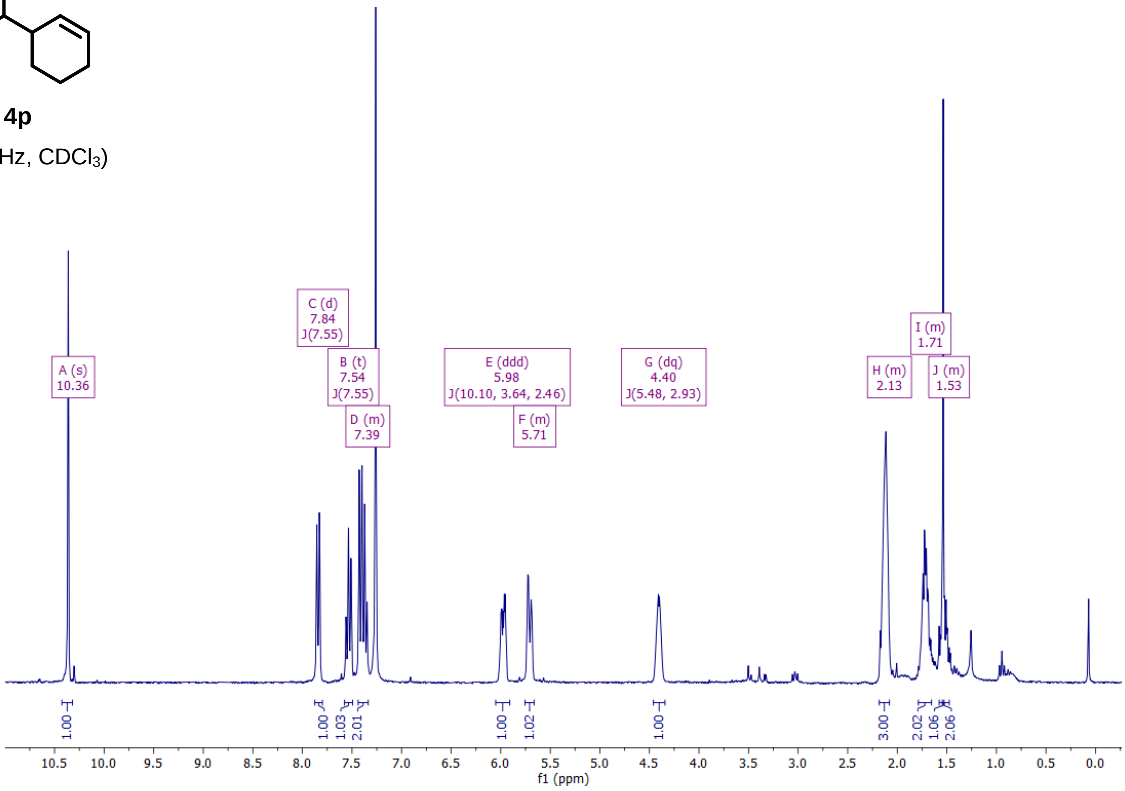
(126 MHz, $CDCl_3$)

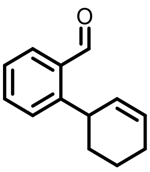




4p

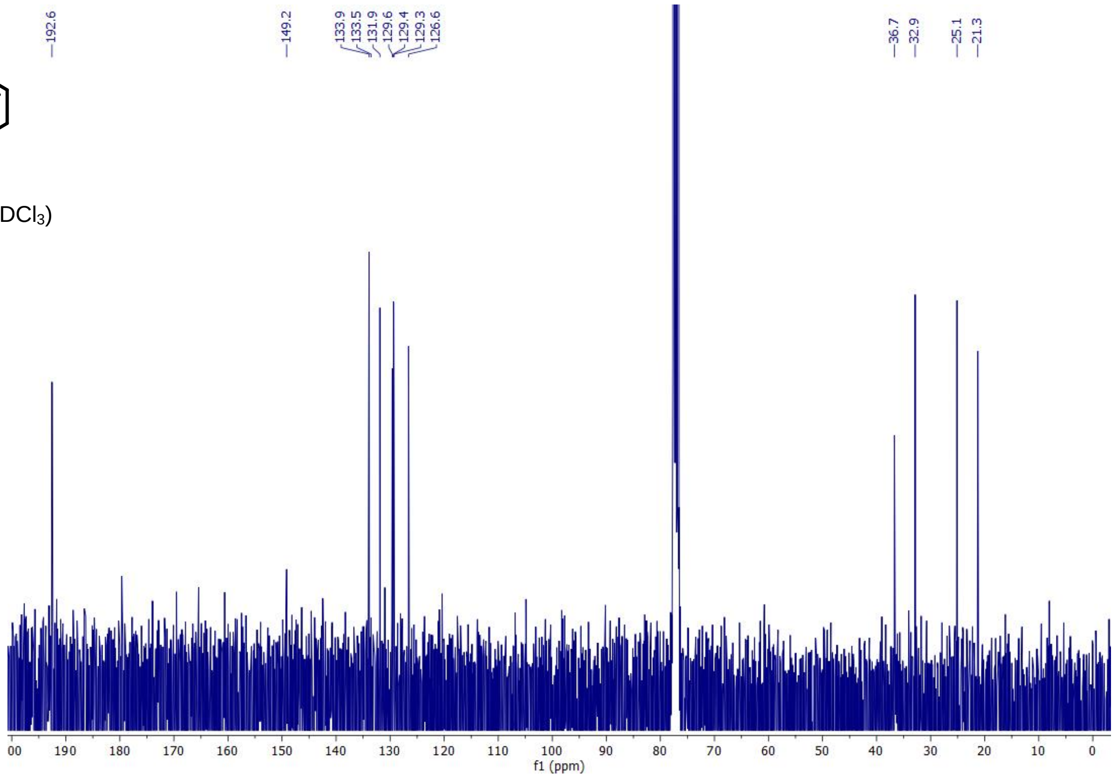
(300 MHz, $CDCl_3$)

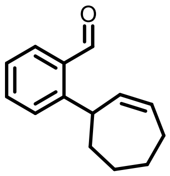




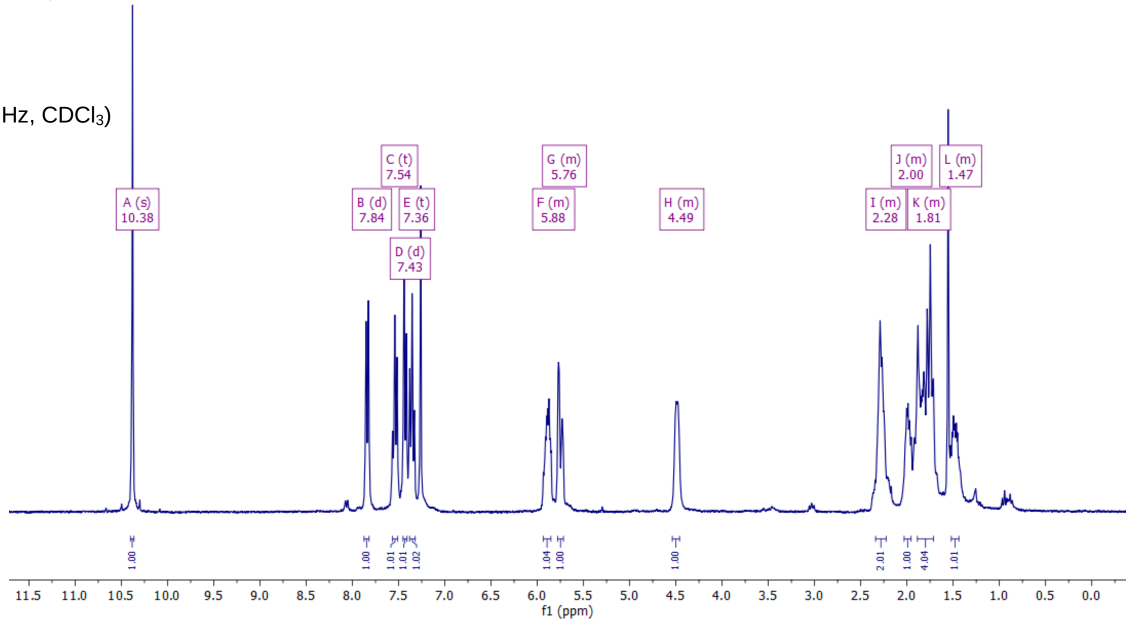
4p

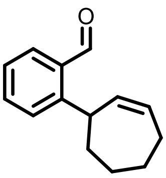
(75 MHz, $CDCl_3$)





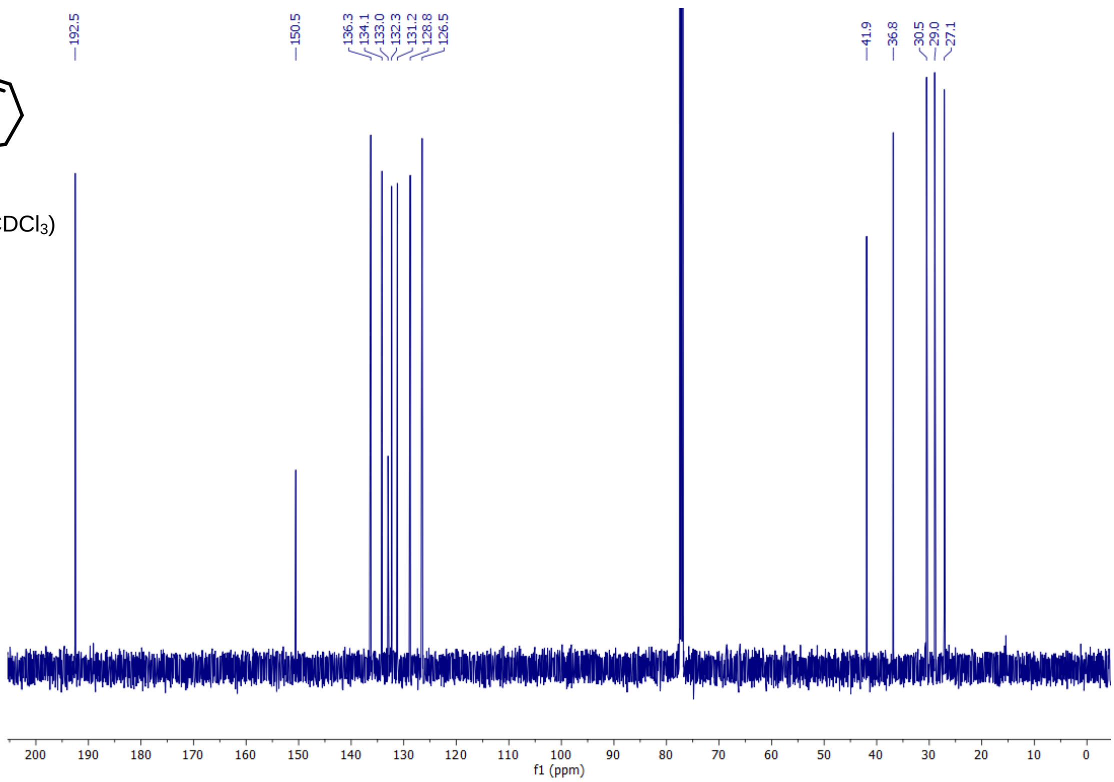
(500 MHz, $CDCl_3$)

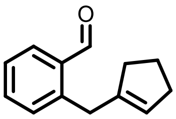




4q

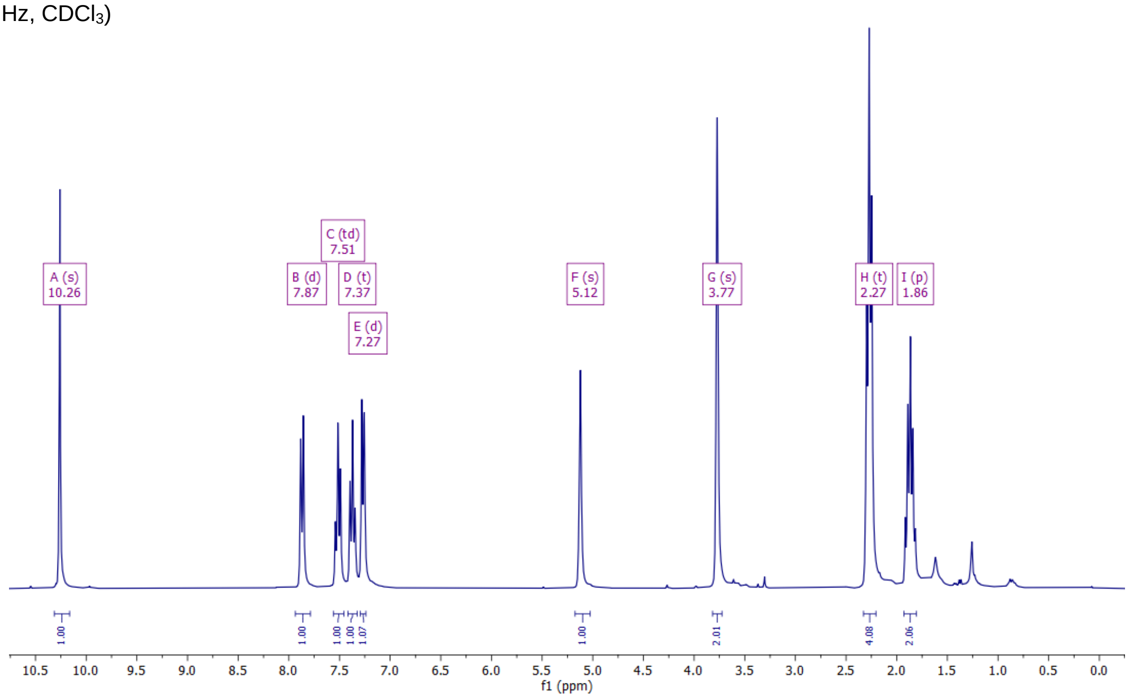
(126 MHz, $CDCl_3$)

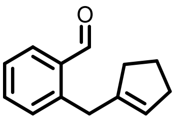




4t

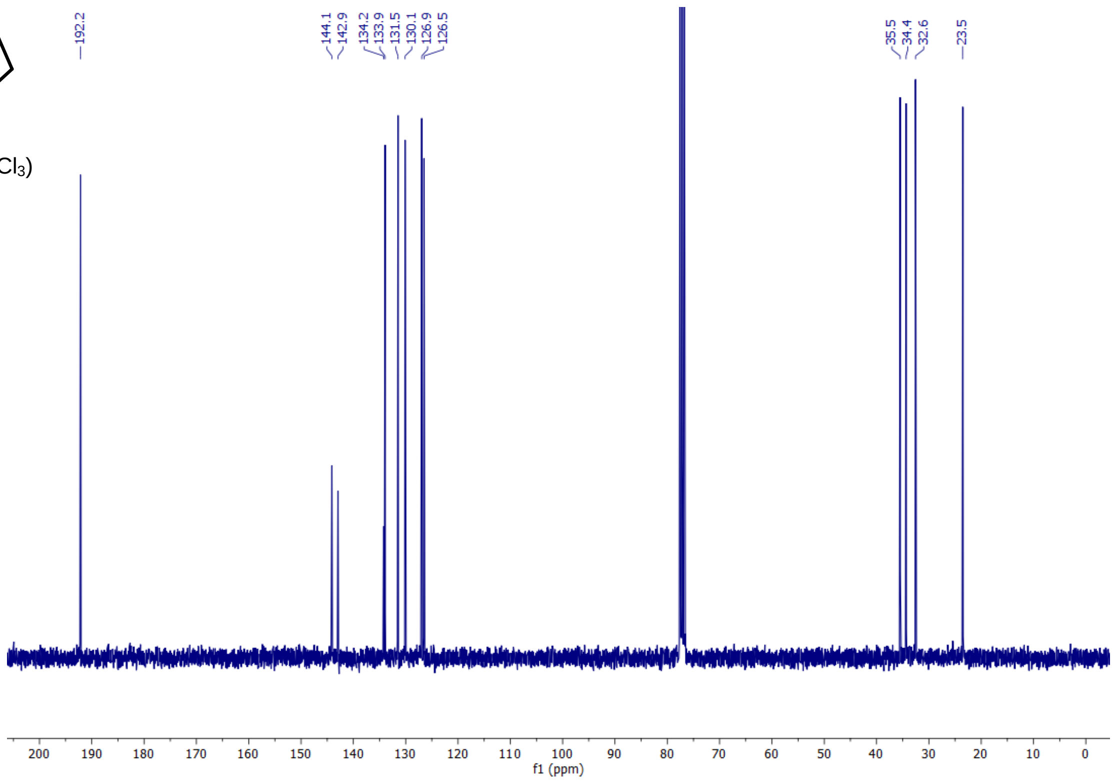
(300 MHz, $CDCl_3$)

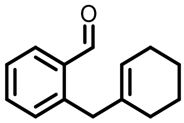




4t

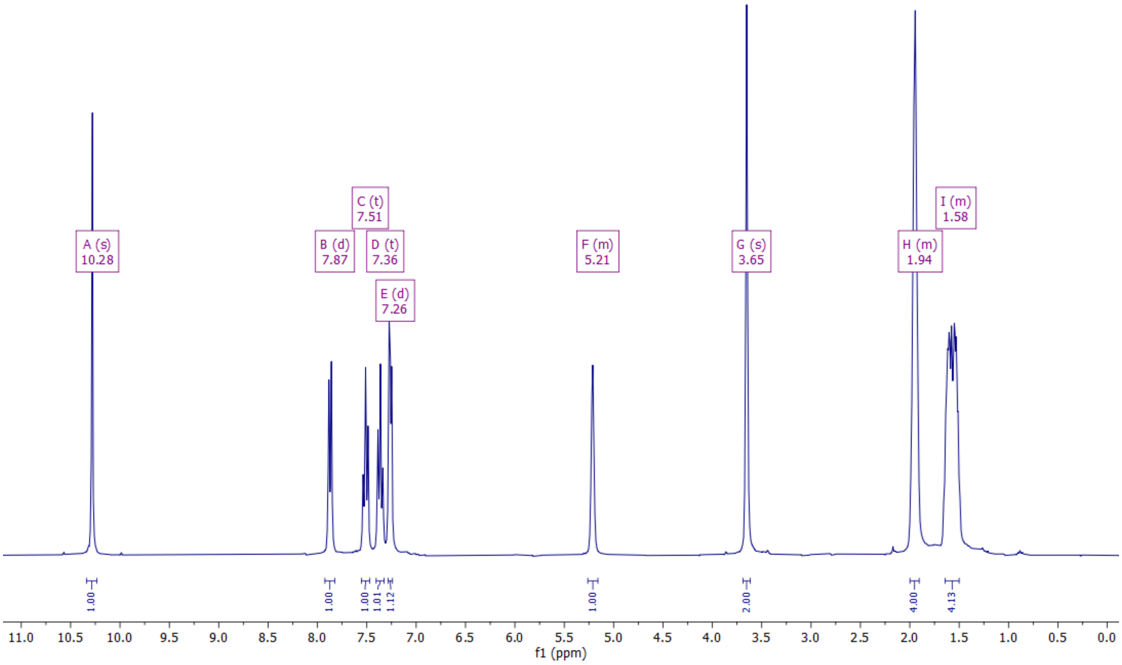
(75 MHz, $CDCl_3$)

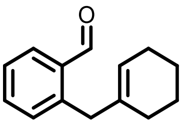




4u

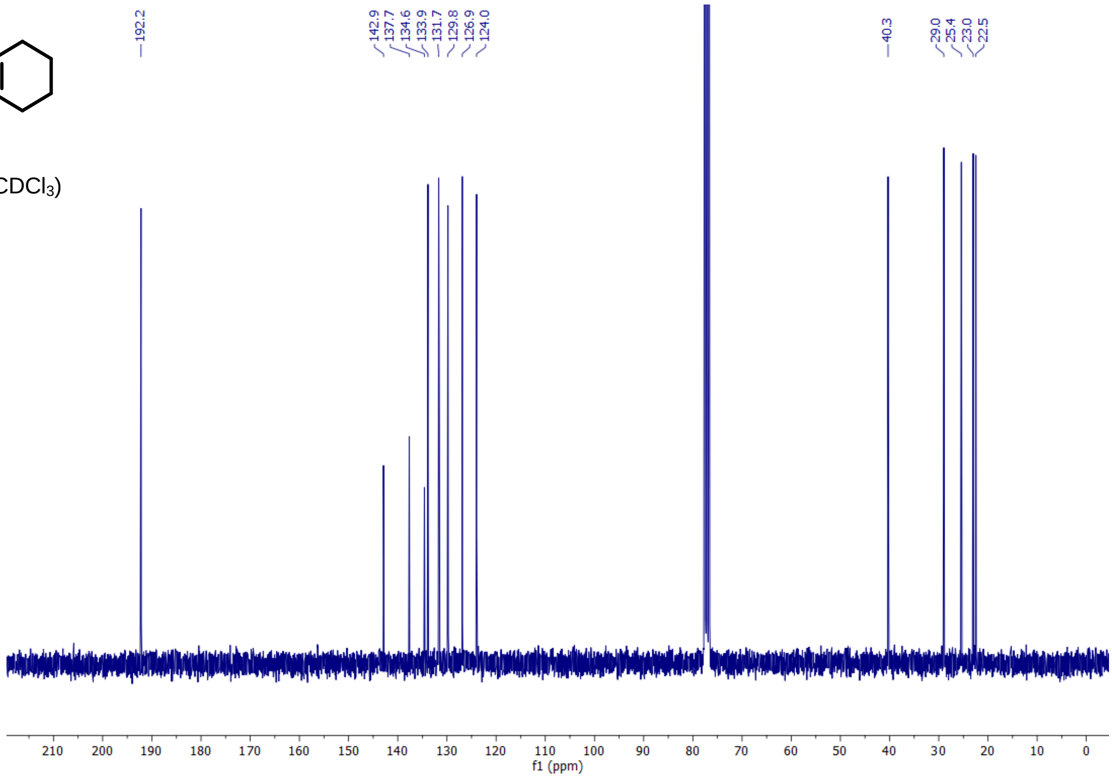
(300 MHz, $CDCl_3$)

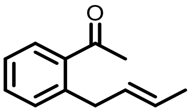




4u

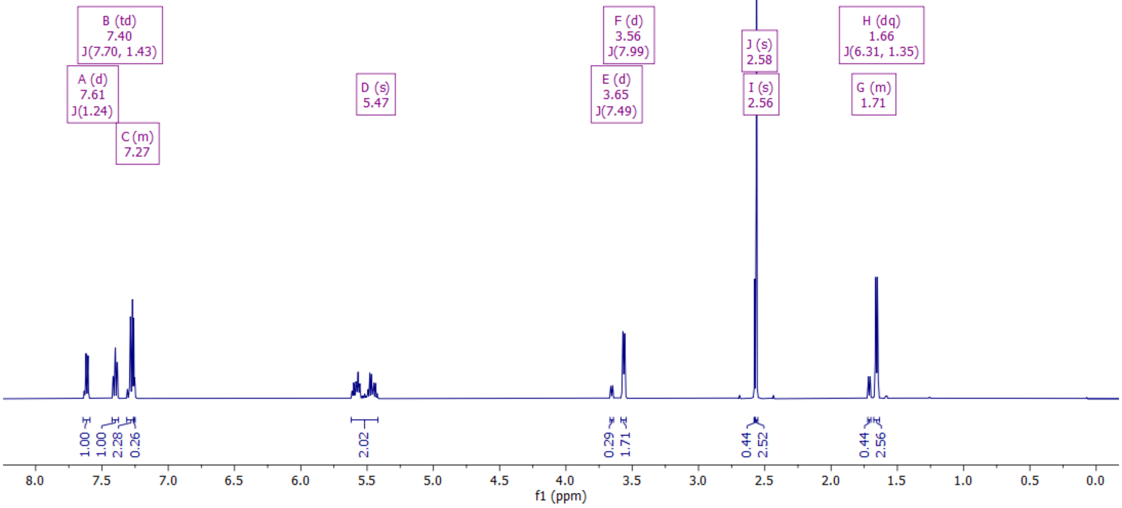
(75 MHz, $CDCl_3$)

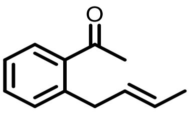




S13

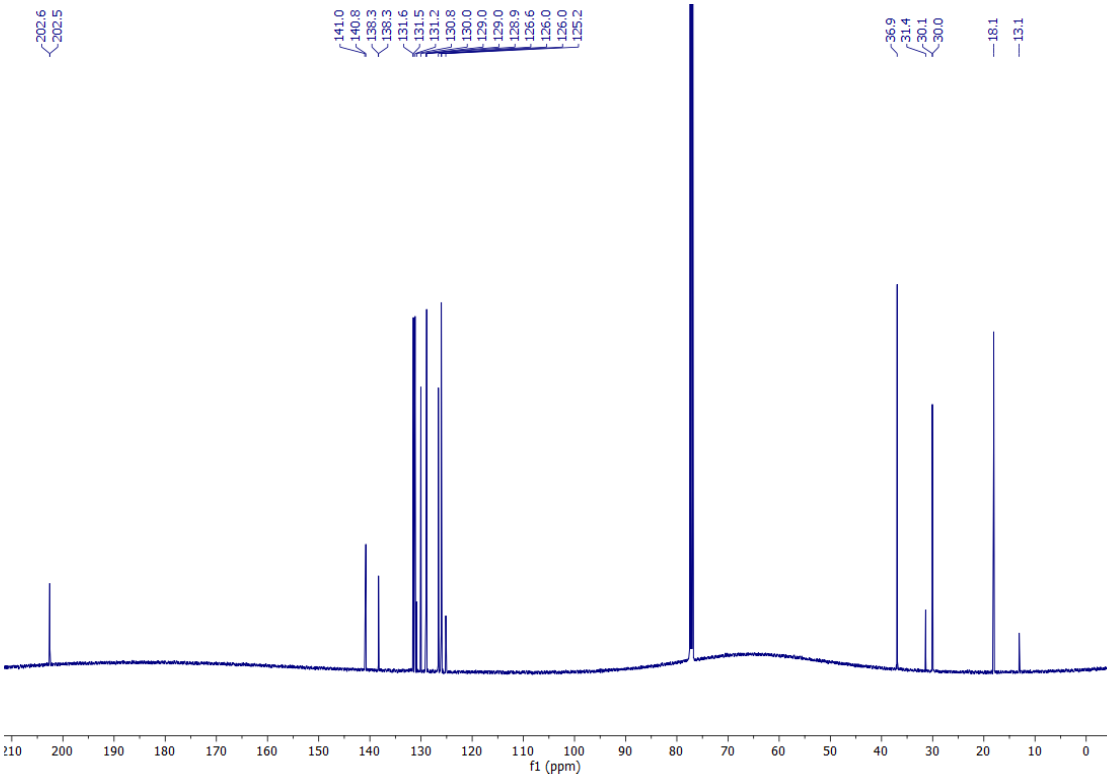
(500 MHz, $CDCl_3$)

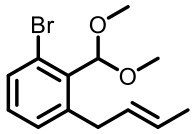




S13

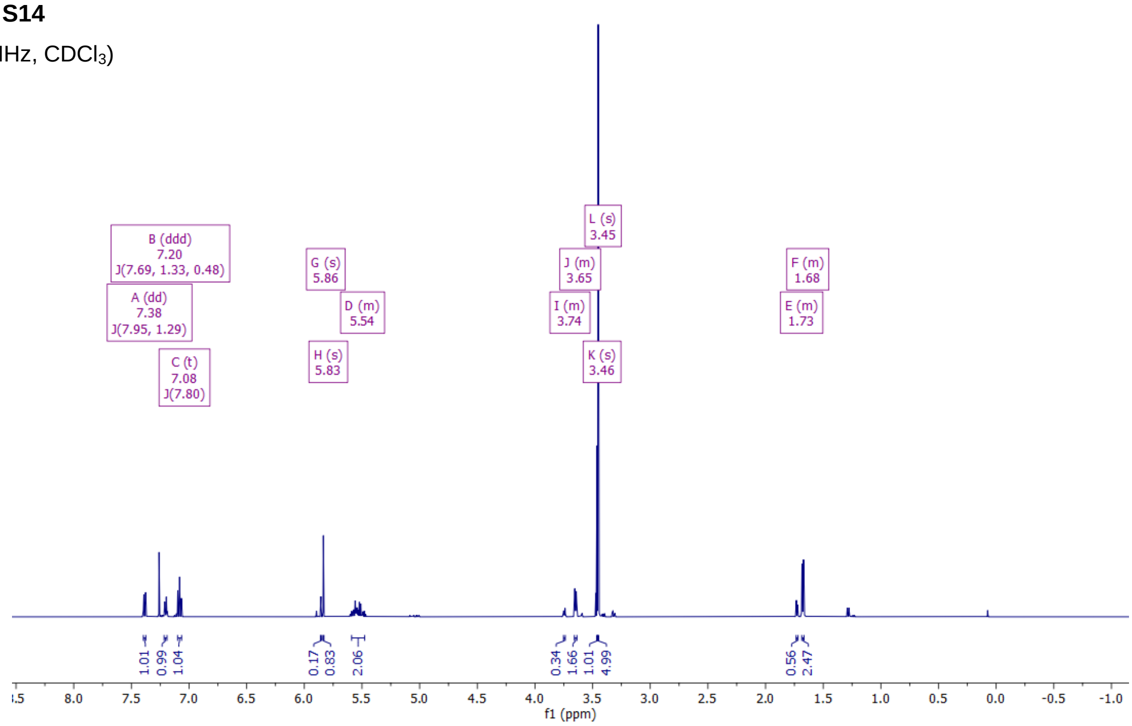
(126 MHz, $CDCl_3$)

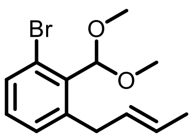




S14

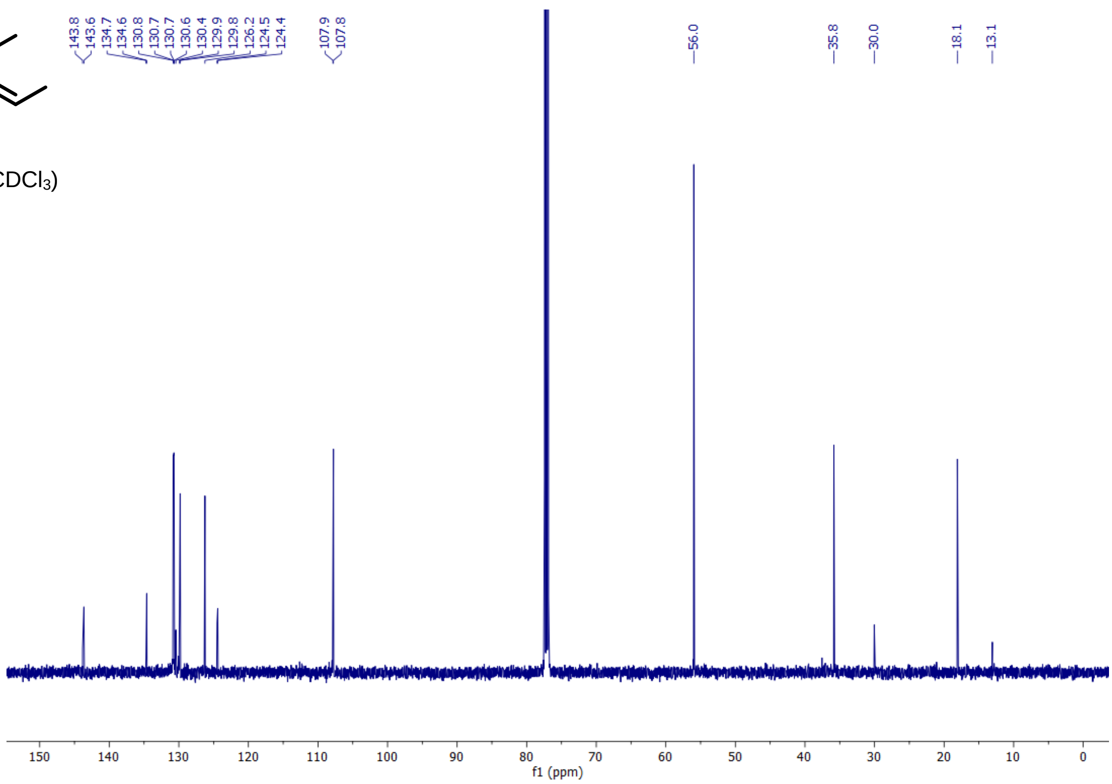
(500 MHz, $CDCl_3$)

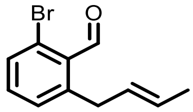




S14

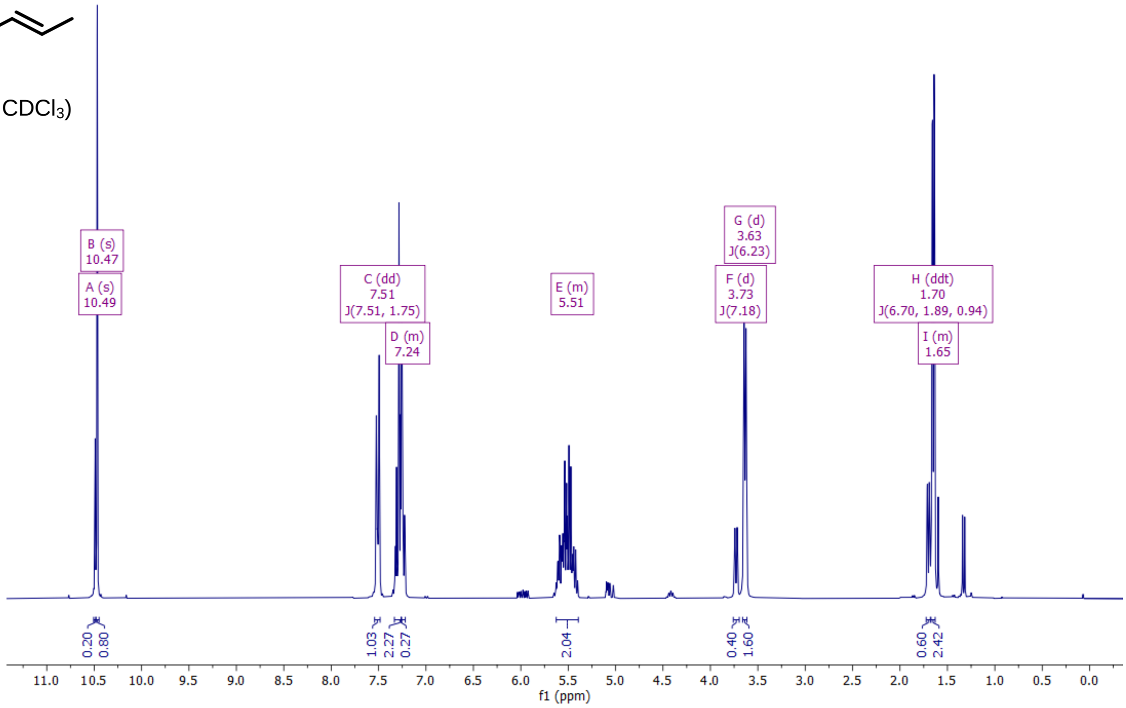
(126 MHz, $CDCl_3$)

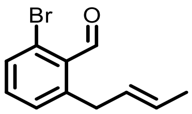




4j

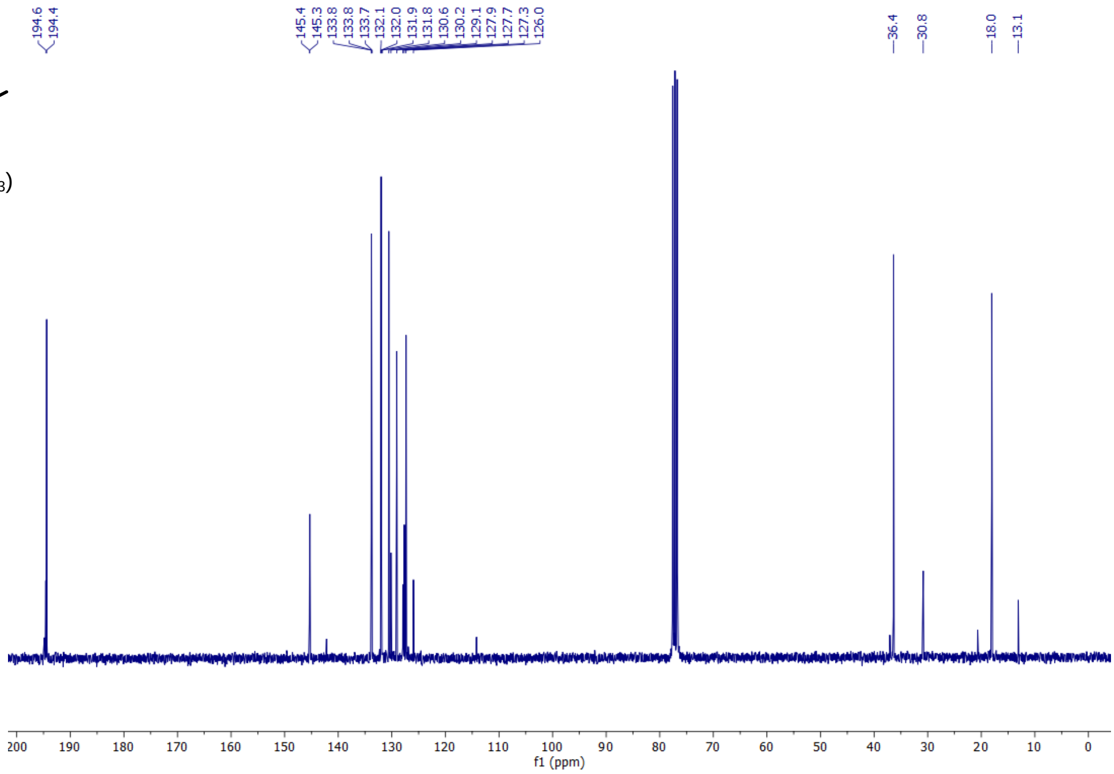
(500 MHz, $CDCl_3$)

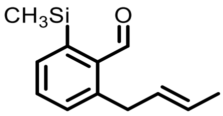




4j

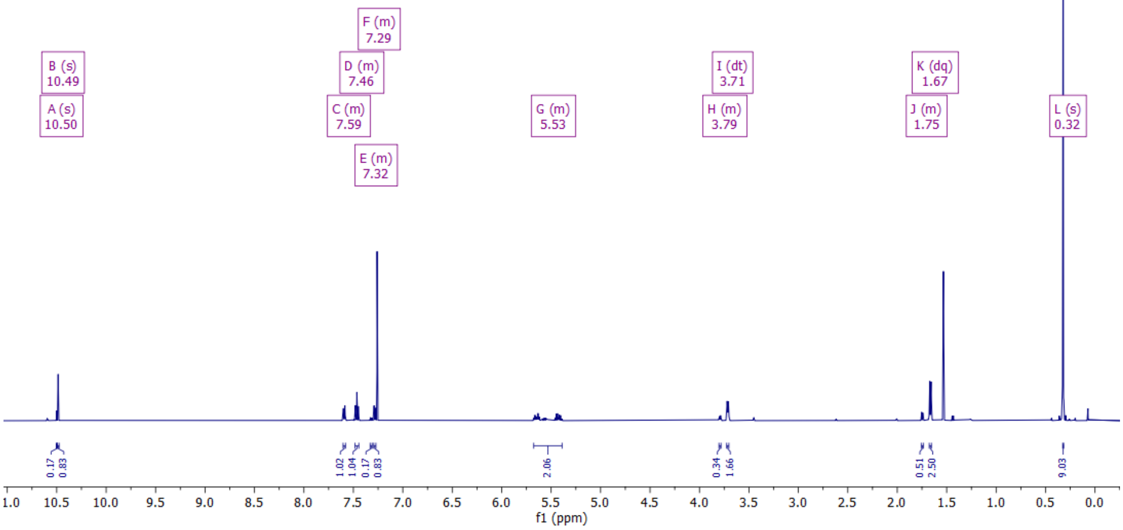
(75 MHz, $CDCl_3$)

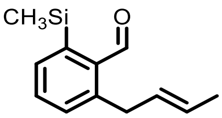




4f

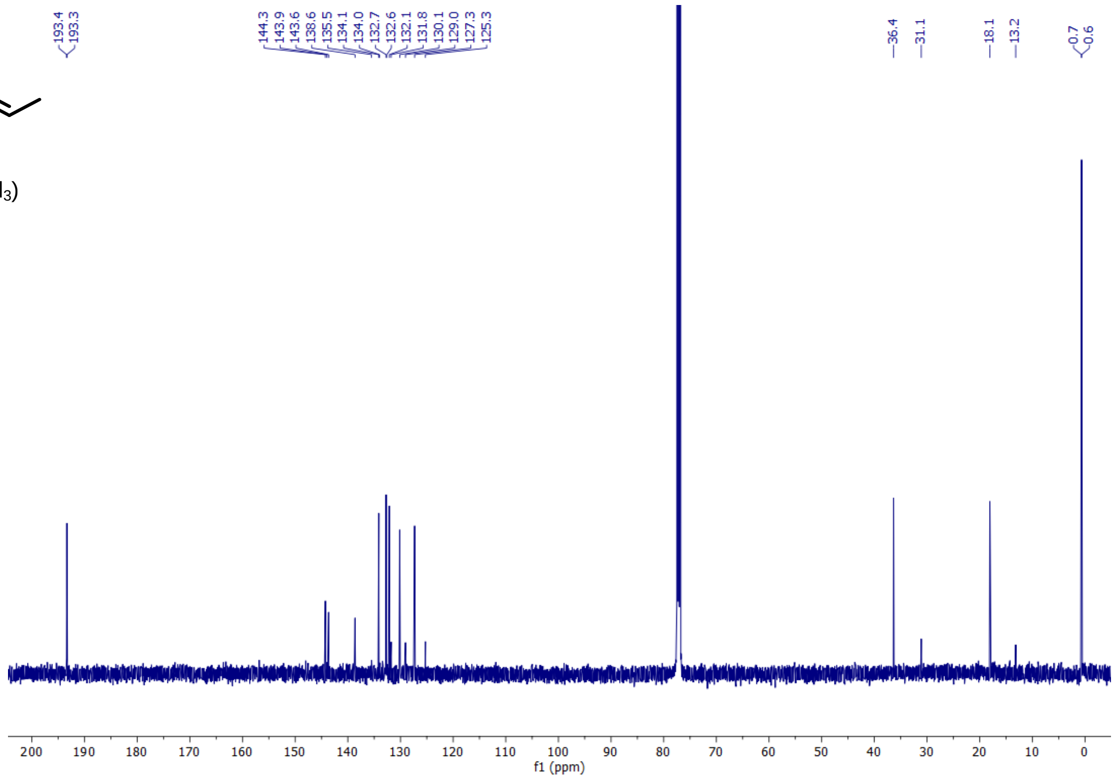
(500 MHz, $CDCl_3$)

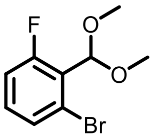




4f

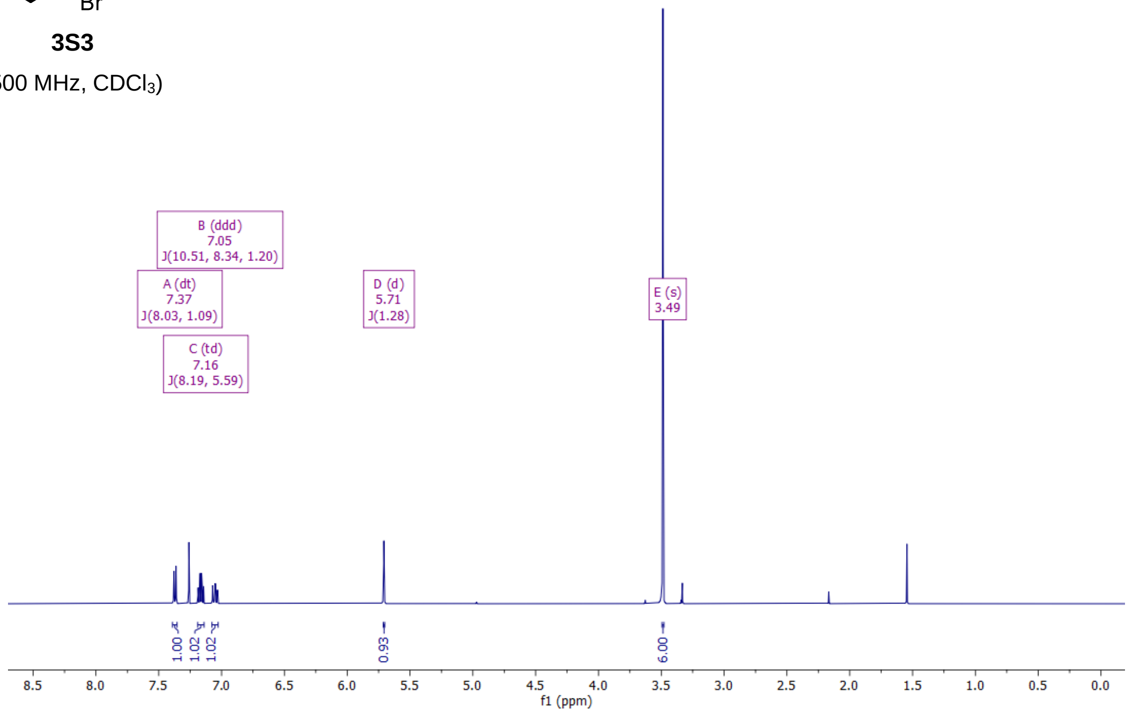
(126 MHz, $CDCl_3$)

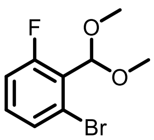




3S3

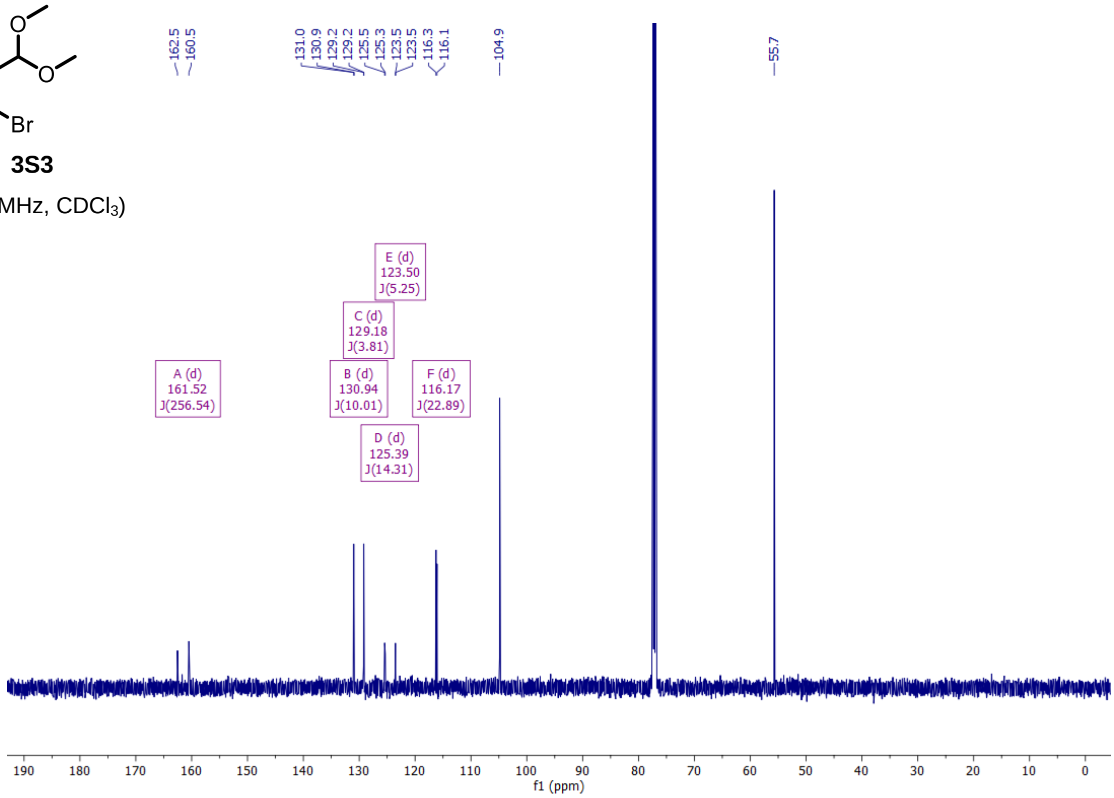
(500 MHz, $CDCl_3$)

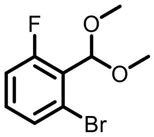




3S3

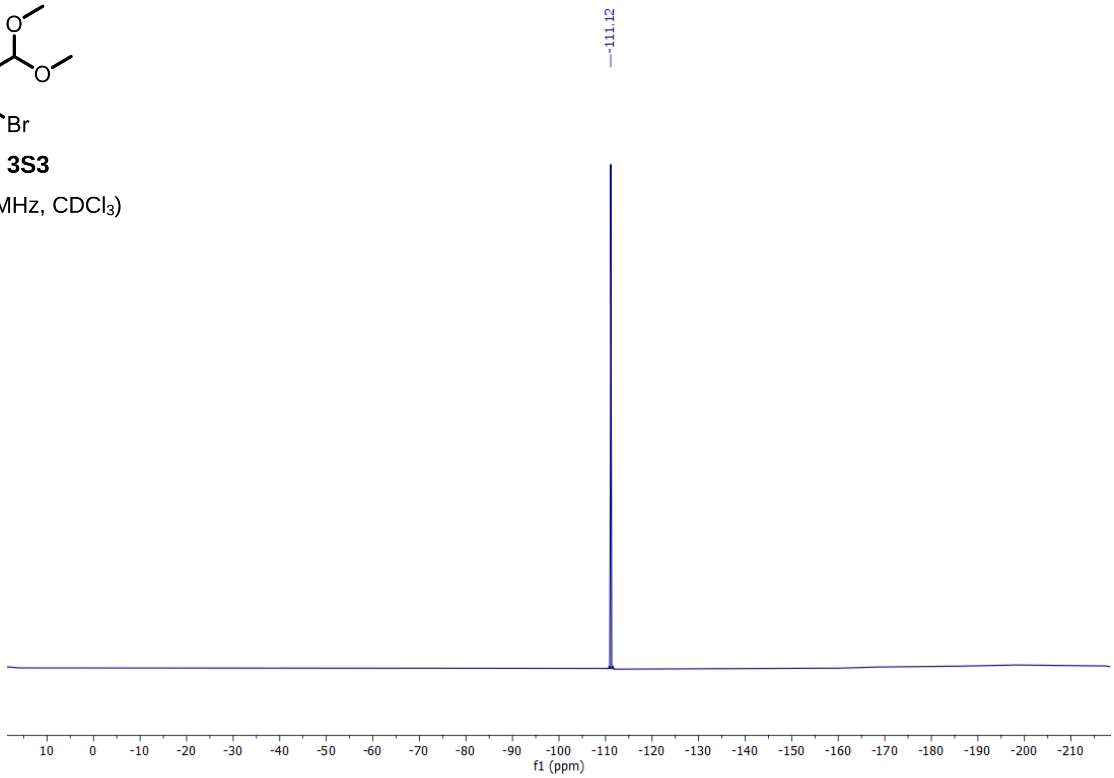
(126 MHz, $CDCl_3$)

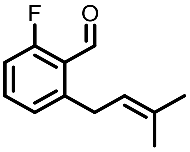




3S3

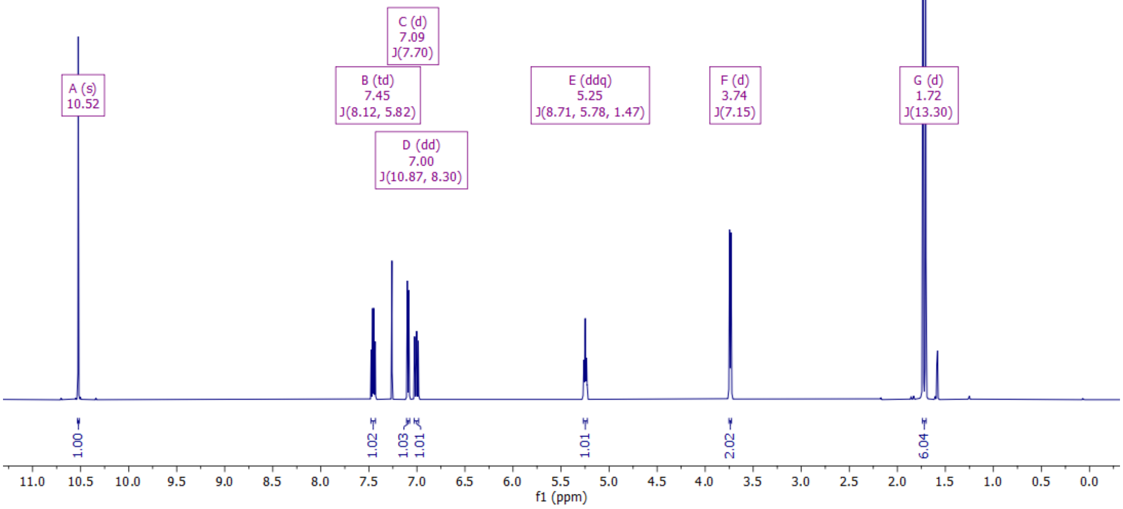
(282 MHz, $CDCl_3$)

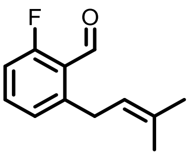




4d

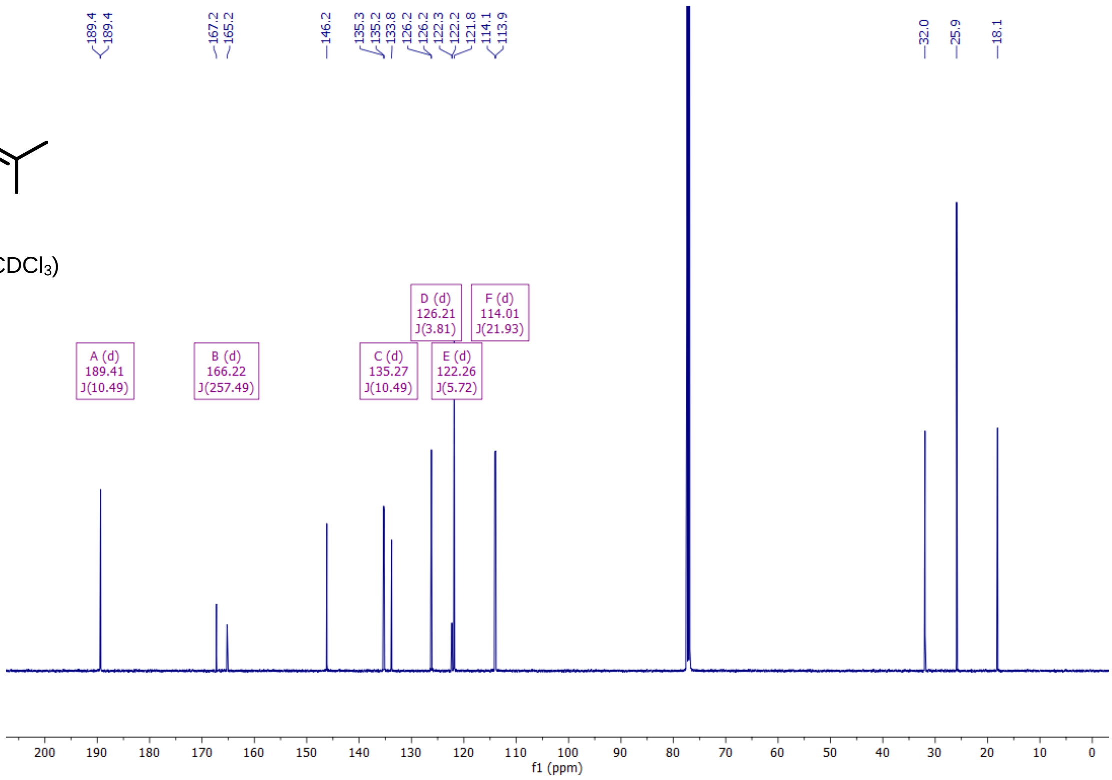
(500 MHz, $CDCl_3$)

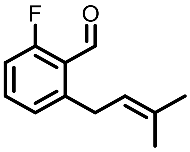




4d

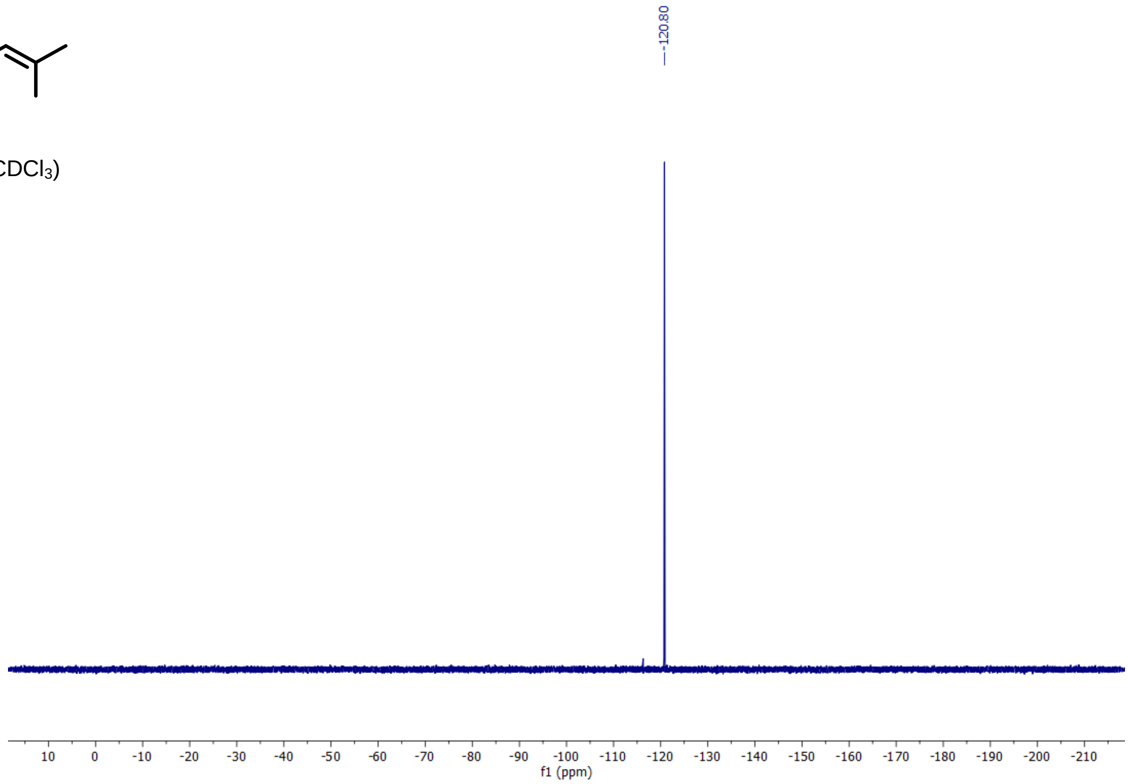
(126 MHz, $CDCl_3$)

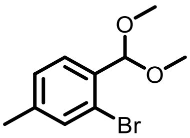




4d

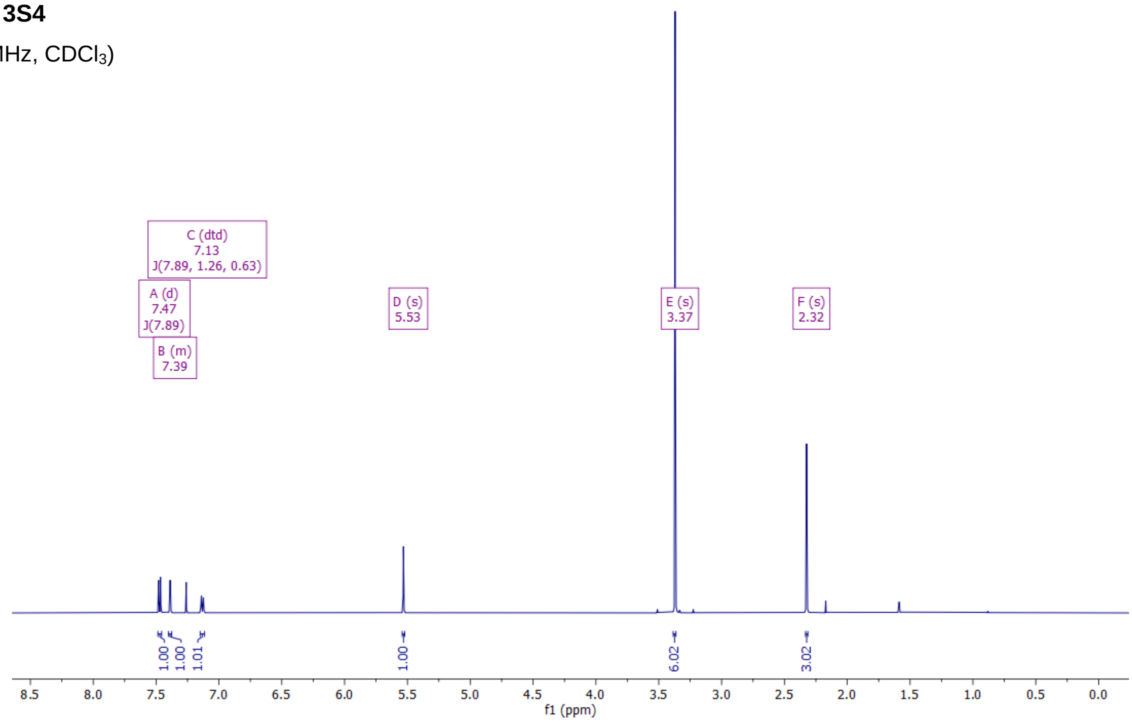
(282 MHz, $CDCl_3$)

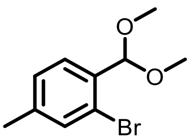




3S4

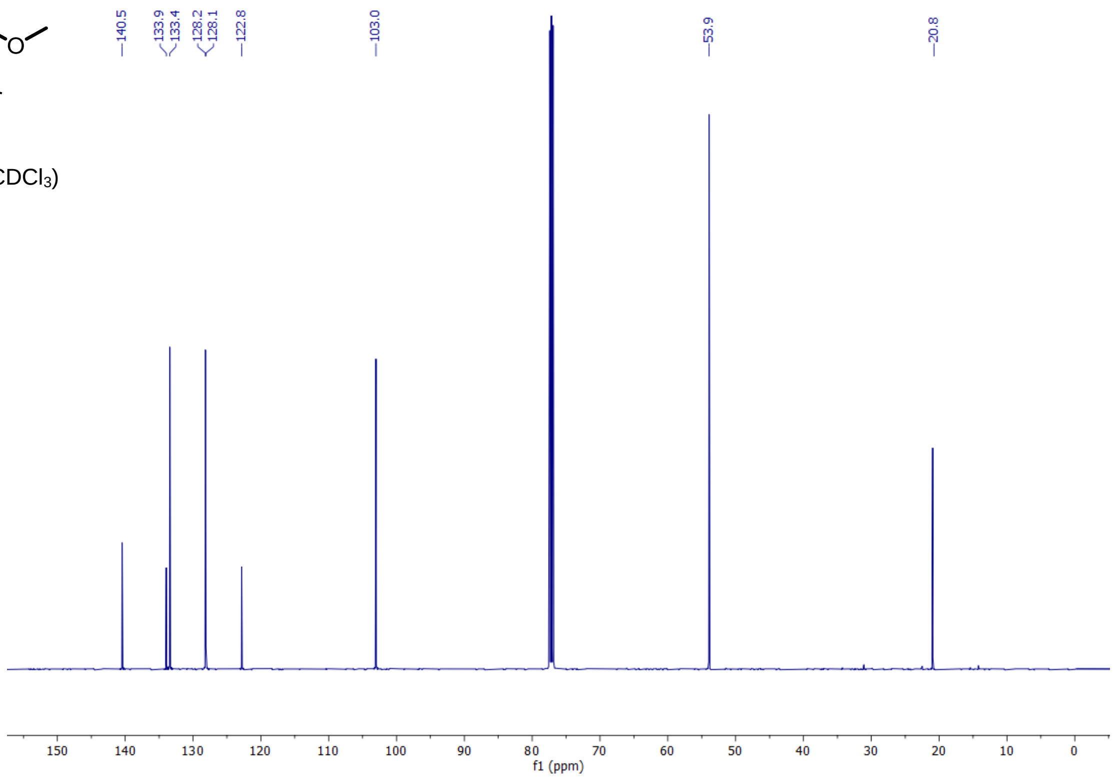
(500 MHz, $CDCl_3$)

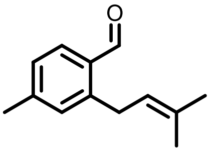




3S4

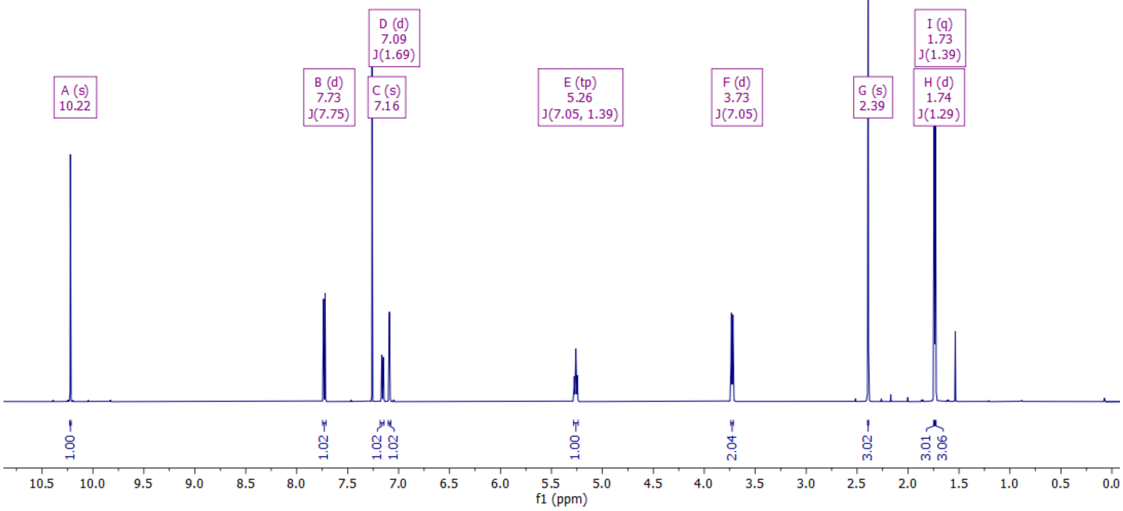
(126 MHz, $CDCl_3$)

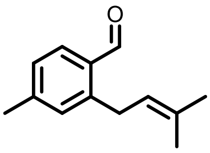




4e

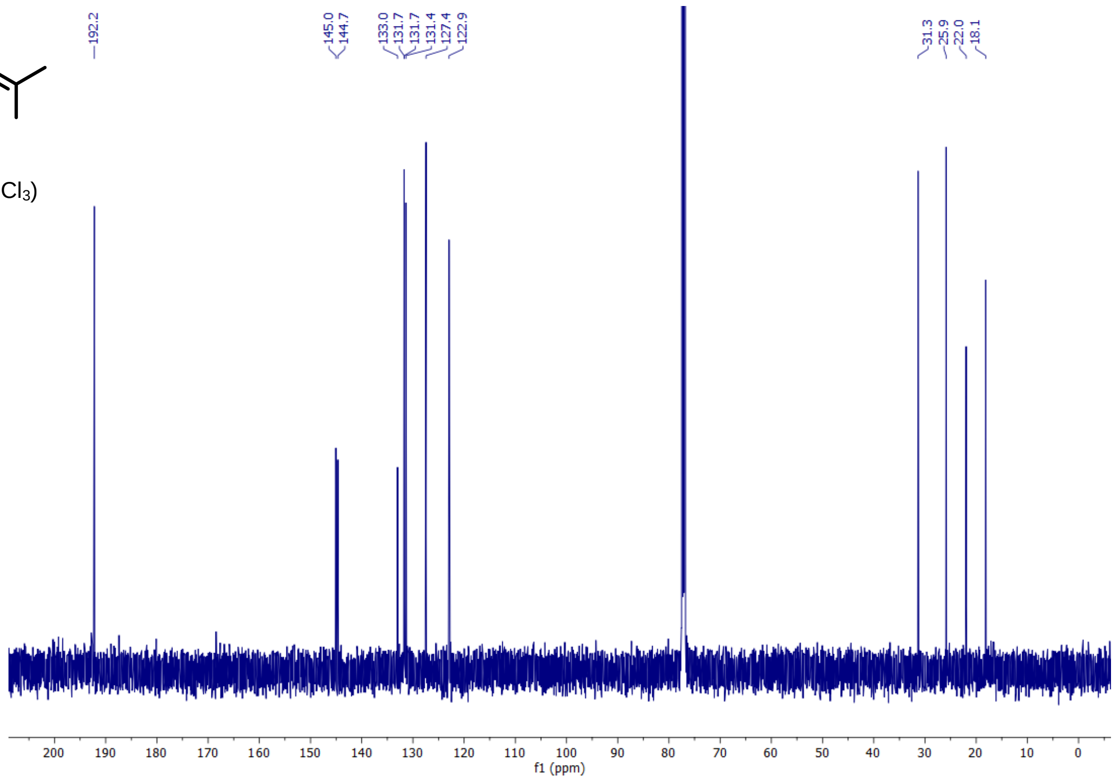
(500 MHz, $CDCl_3$)

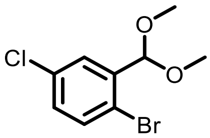




4e

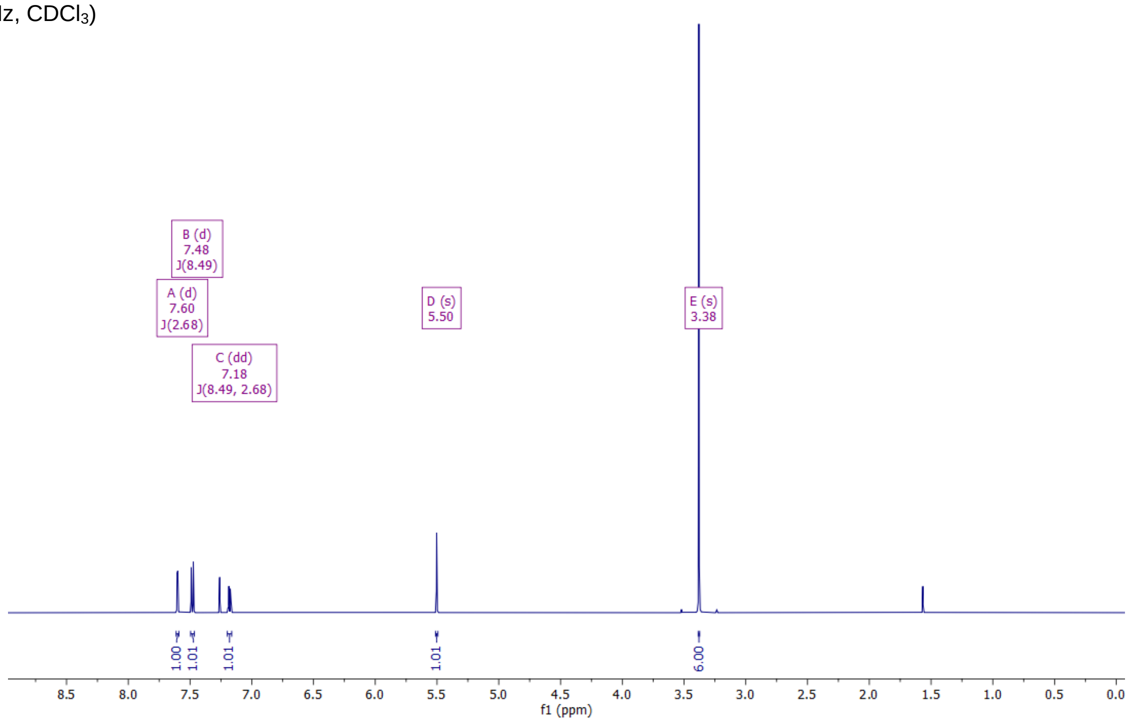
(126 MHz, $CDCl_3$)

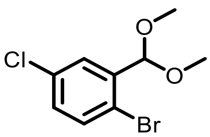




3S5

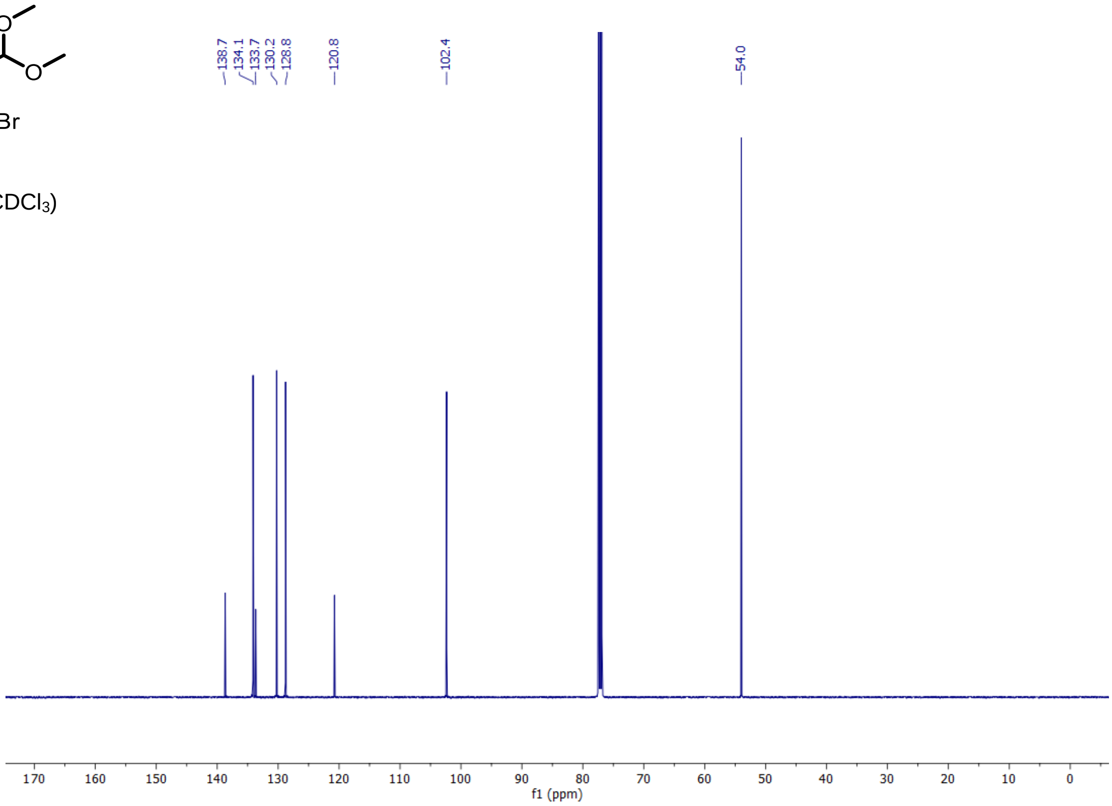
(500 MHz, $CDCl_3$)

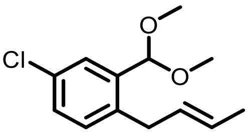




3S5

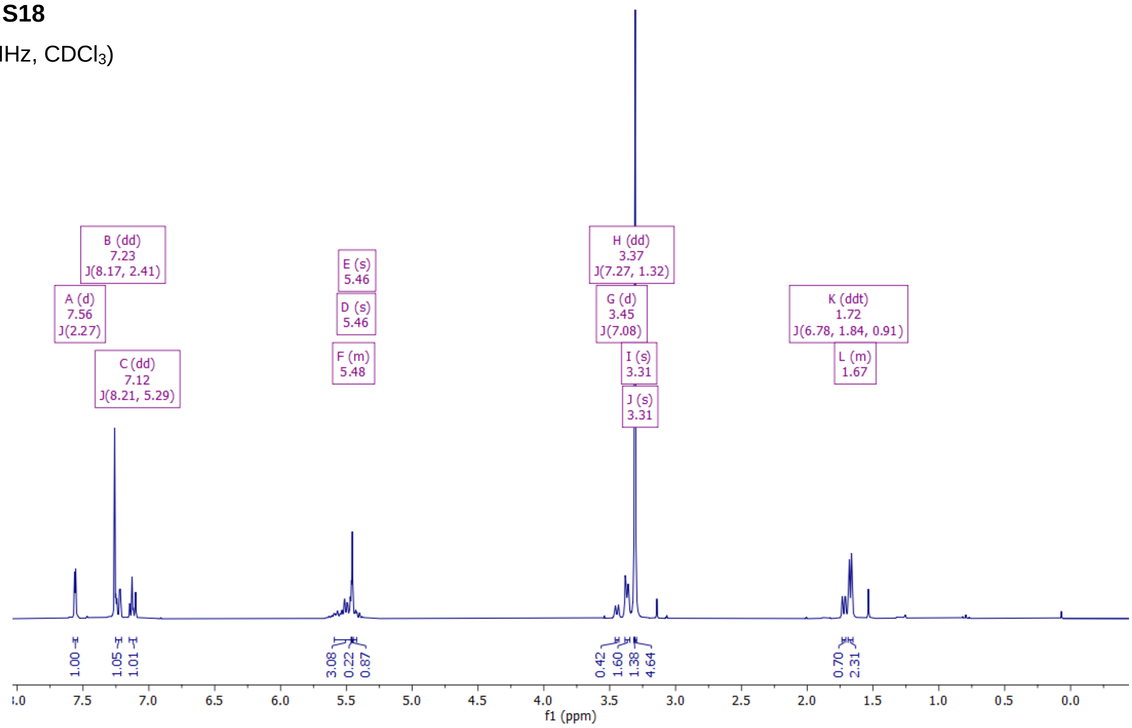
(126 MHz, $CDCl_3$)

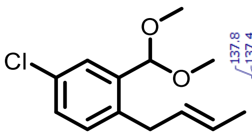




S18

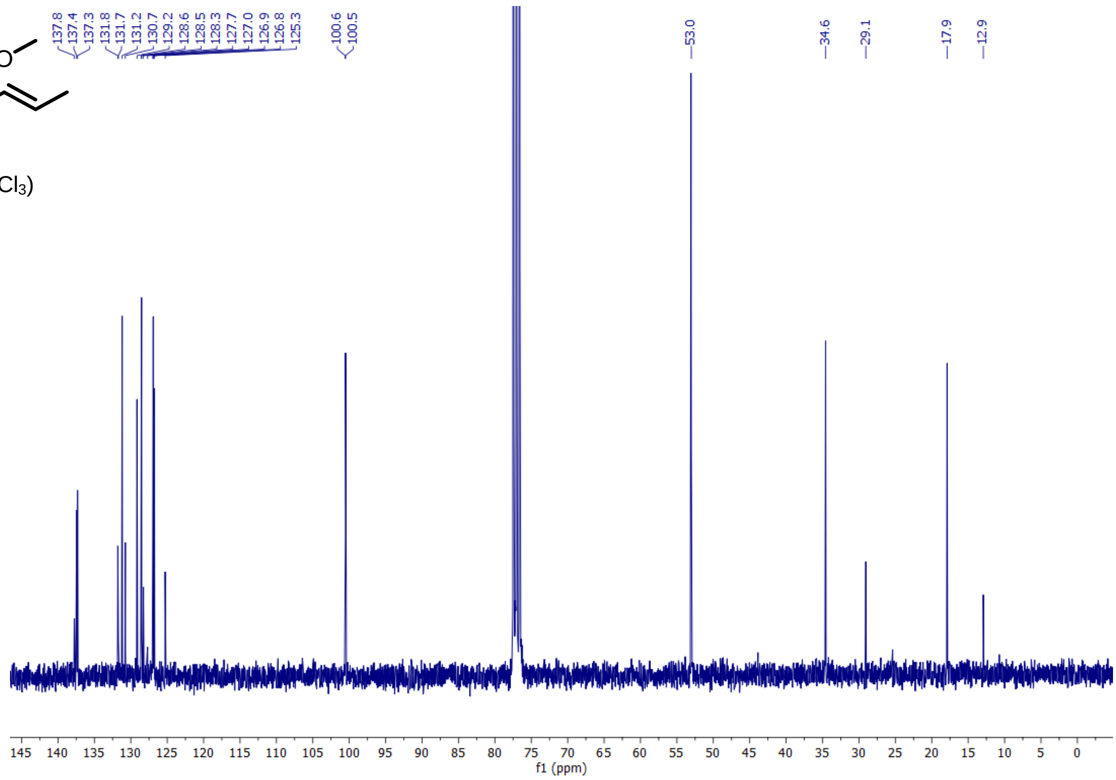
(300 MHz, $CDCl_3$)

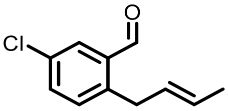




S18

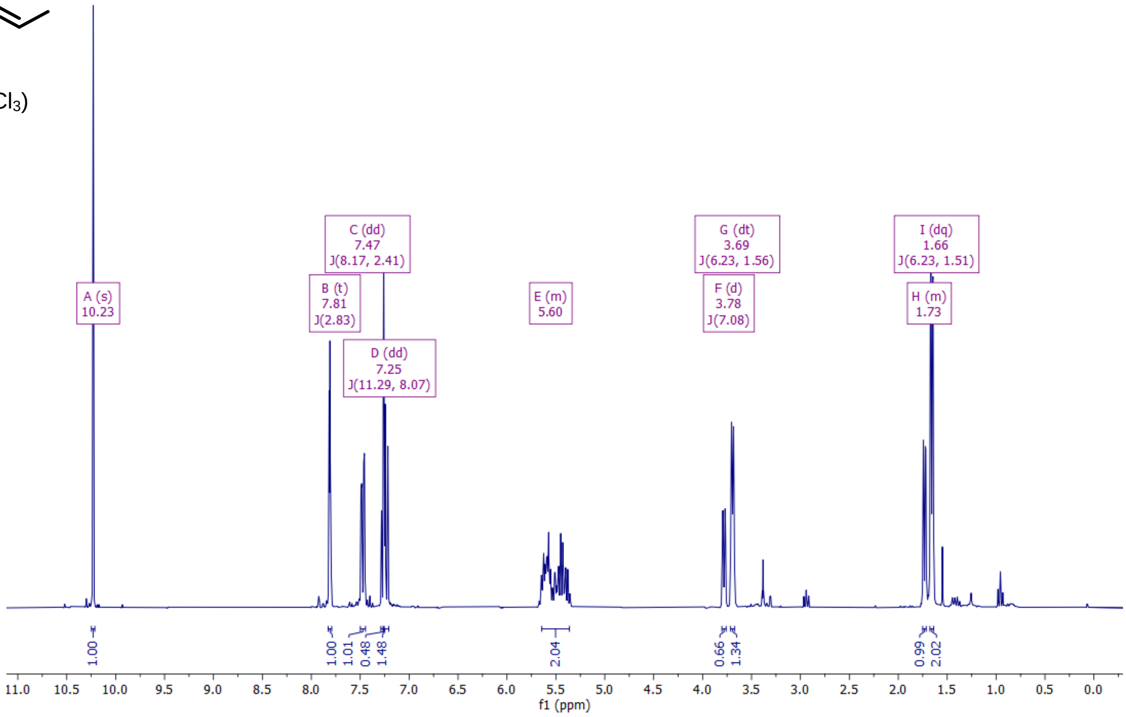
(75 MHz, $CDCl_3$)

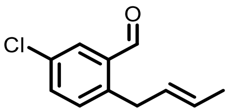




4a

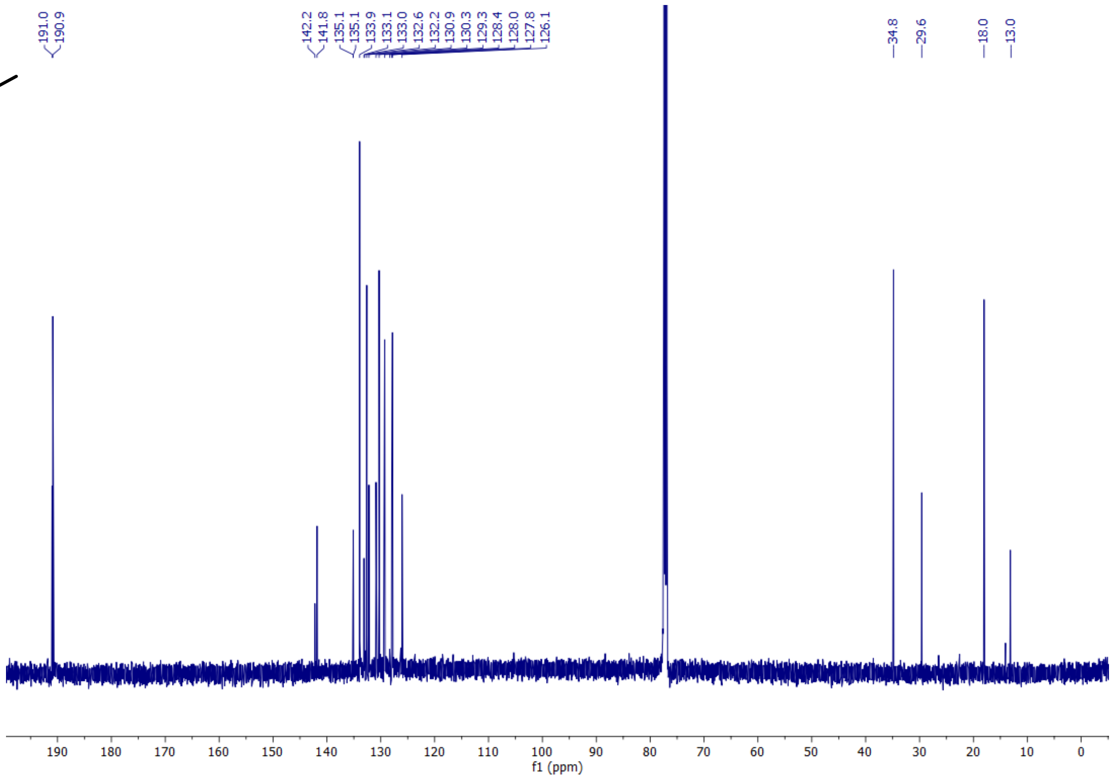
(500 MHz, $CDCl_3$)

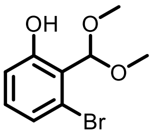




4a

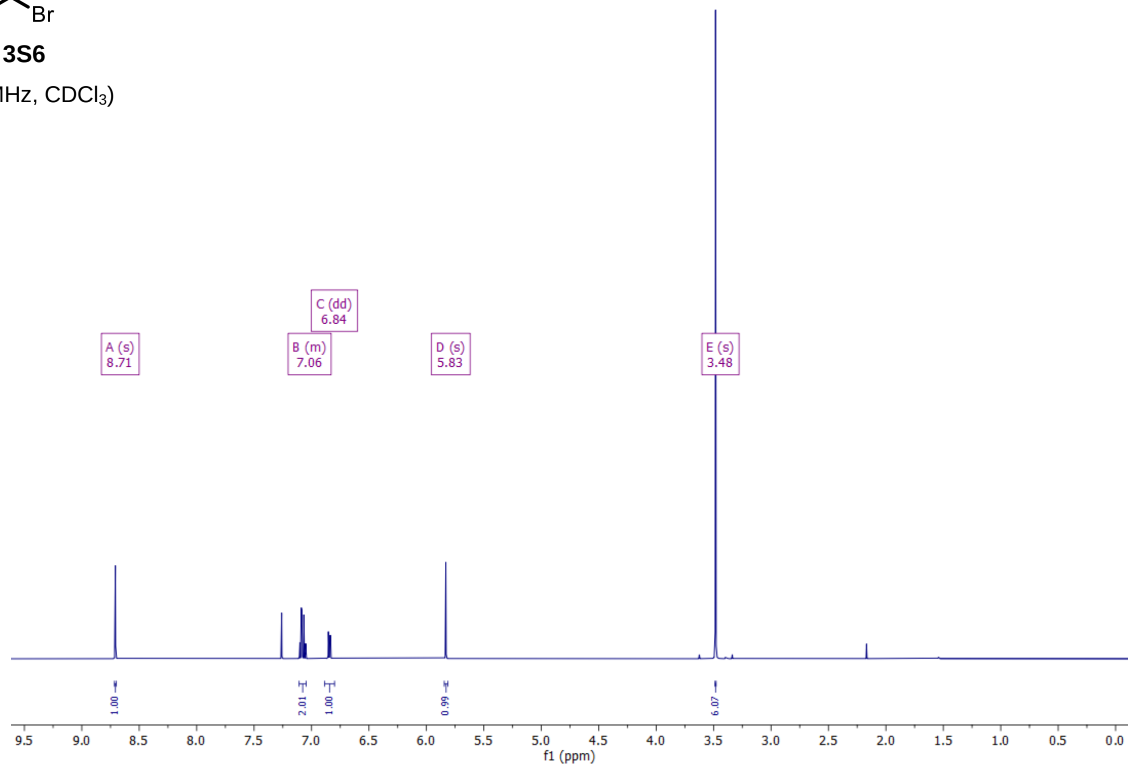
(126 MHz, $CDCl_3$)

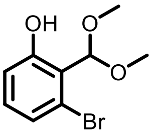




3S6

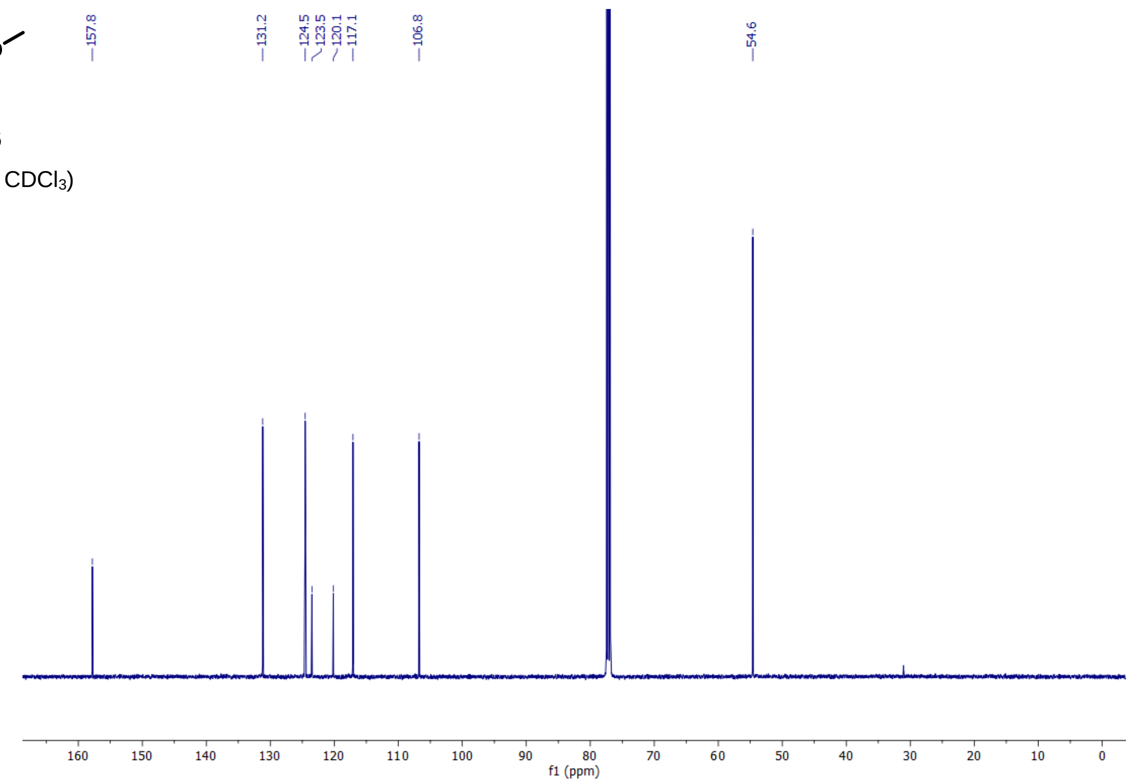
(500 MHz, $CDCl_3$)

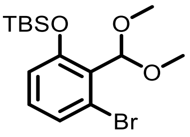




3S6

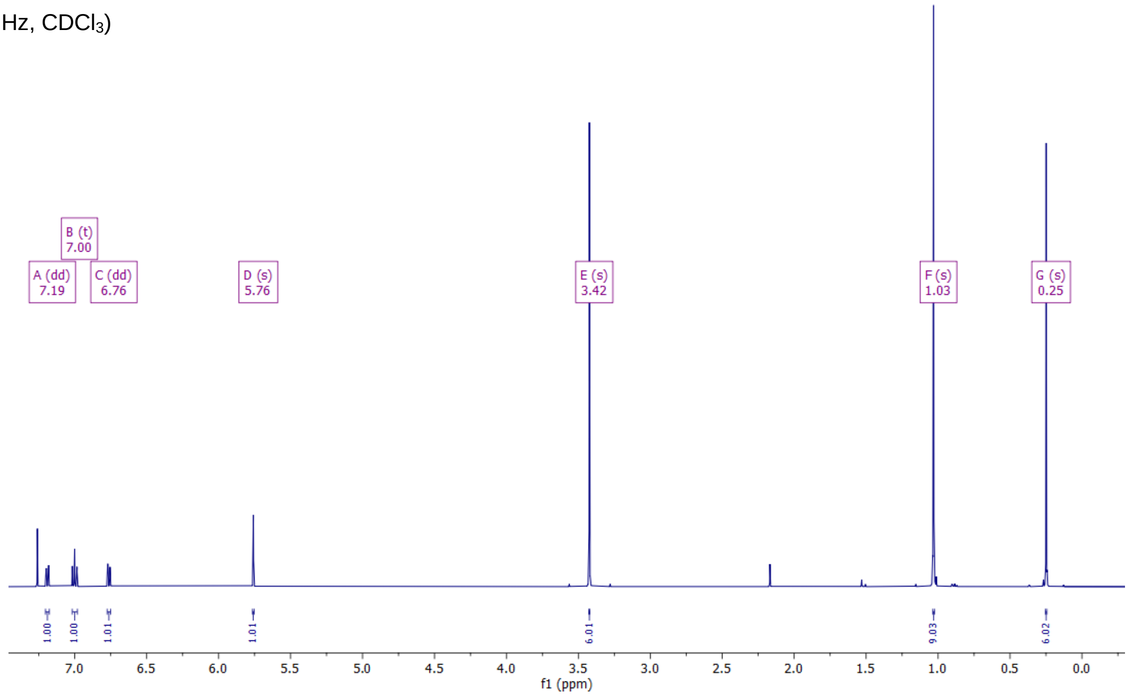
(126 MHz, $CDCl_3$)

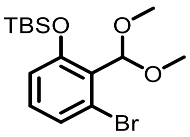




3S7

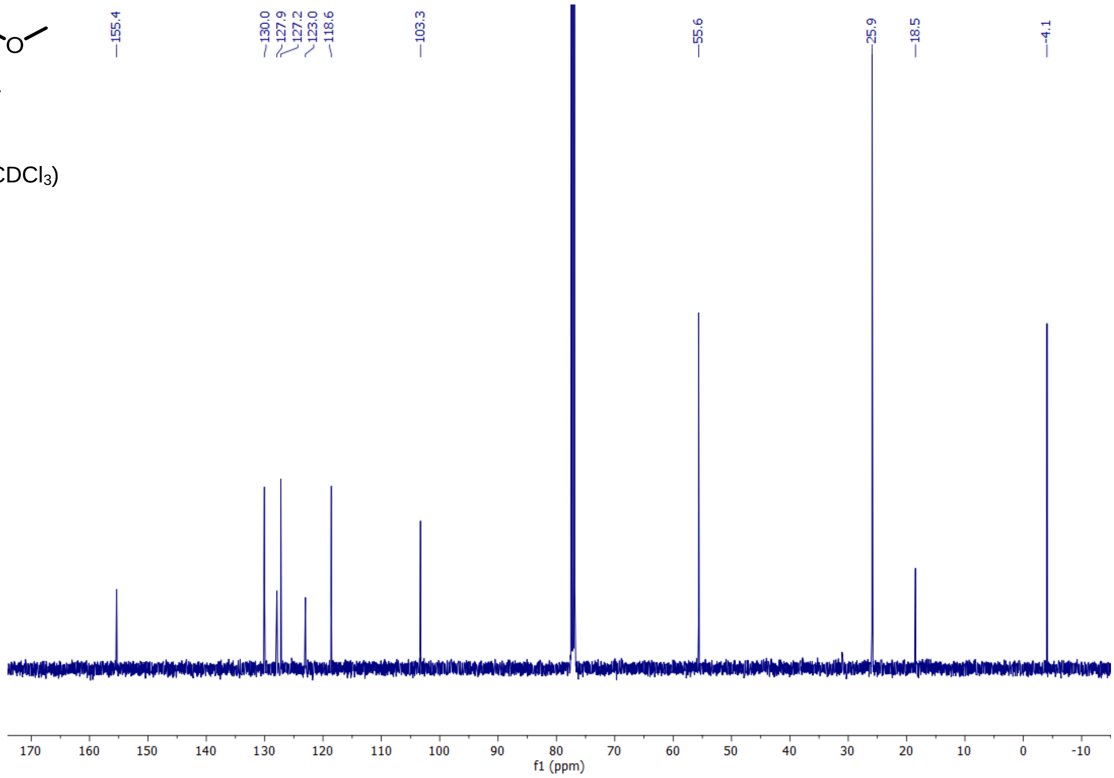
(500 MHz, $CDCl_3$)

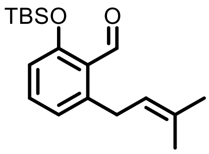




3S7

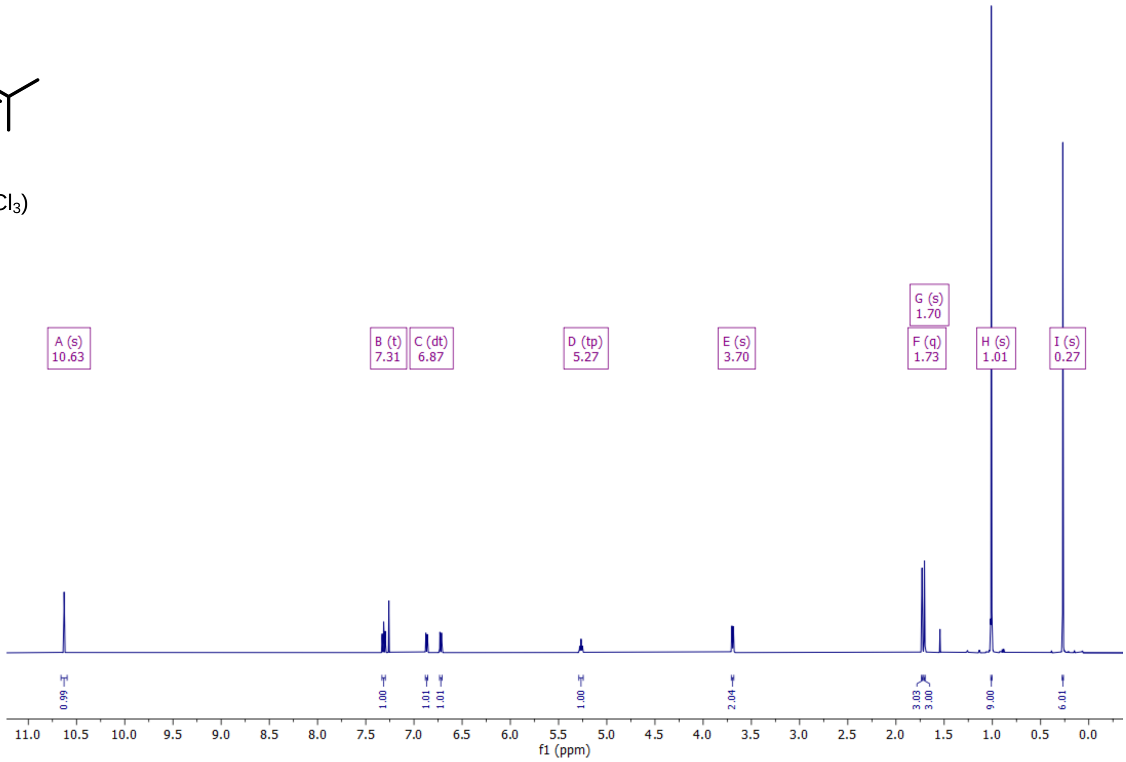
(126 MHz, $CDCl_3$)

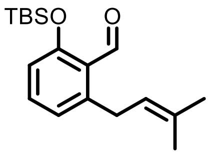




4S1

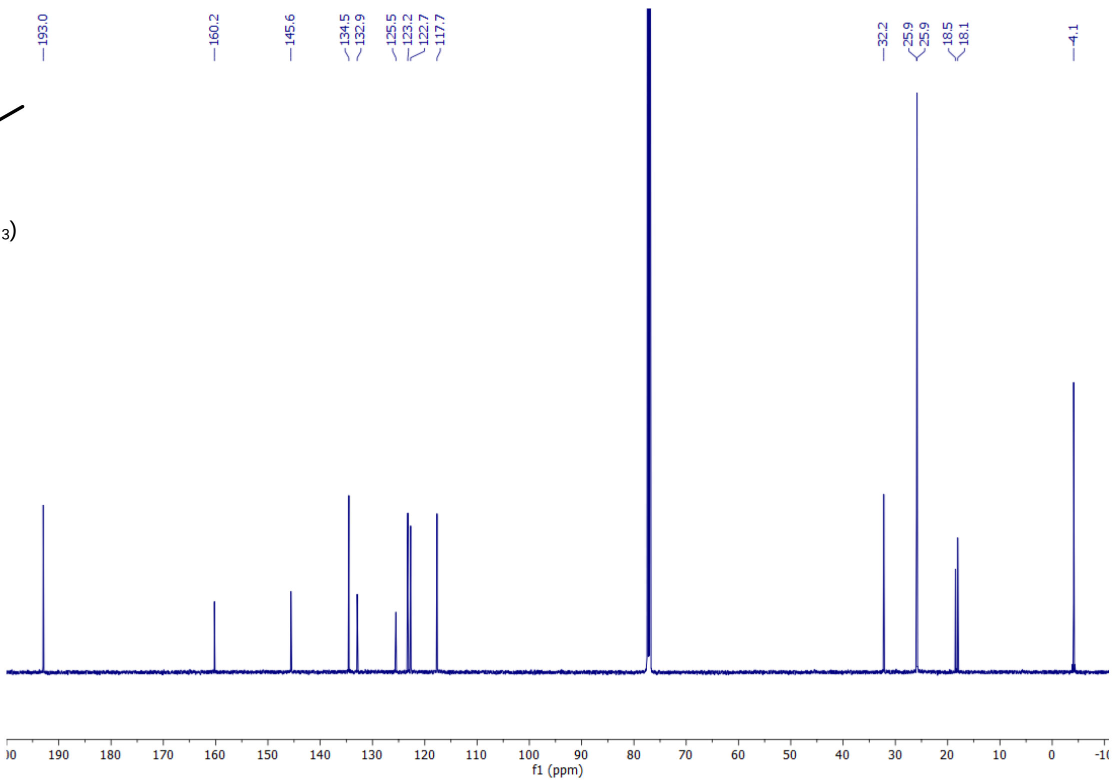
(500 MHz, $CDCl_3$)

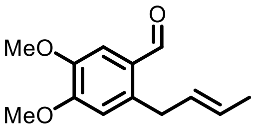




4S1

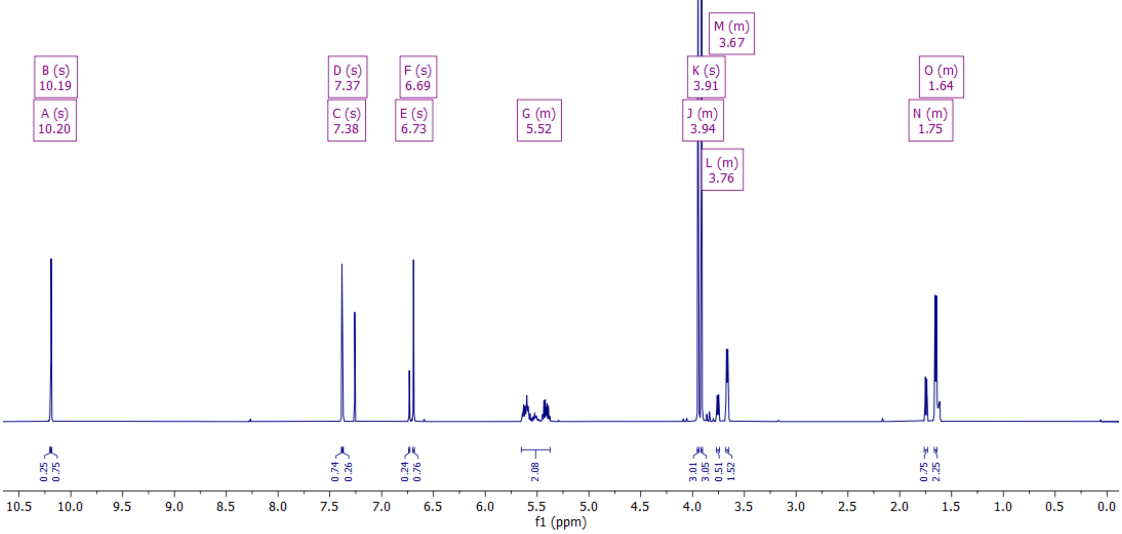
(126 MHz, $CDCl_3$)

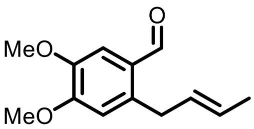




4S2

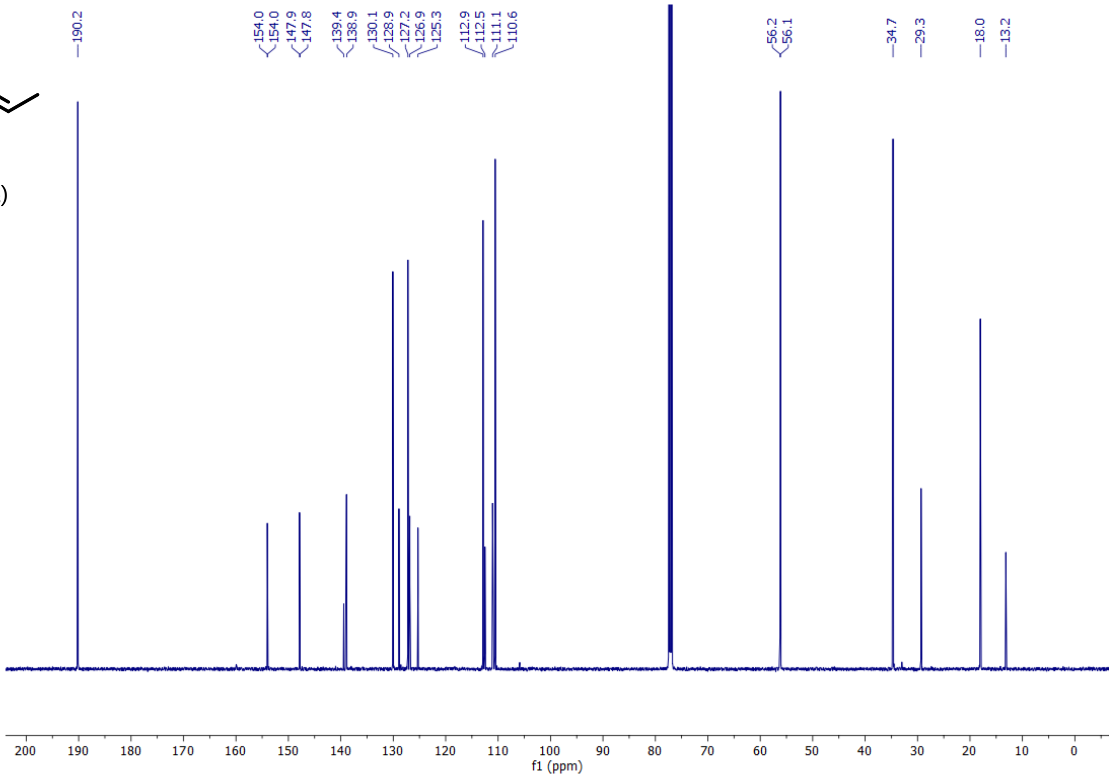
(500 MHz, $CDCl_3$)

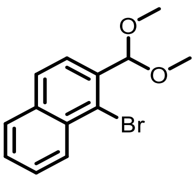




4S2

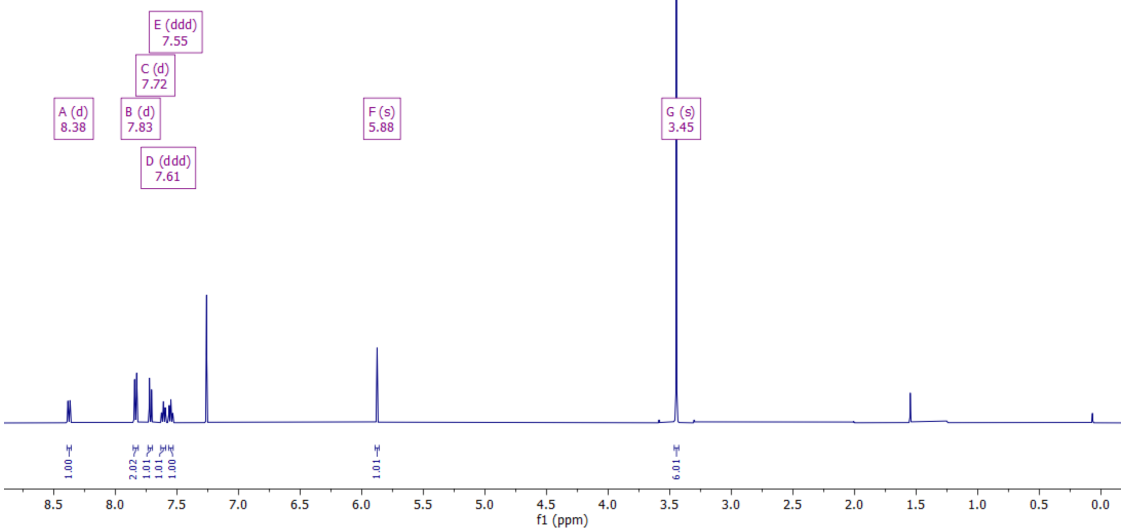
(126 MHz, $CDCl_3$)

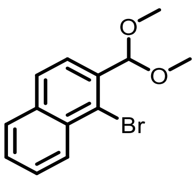




3S9

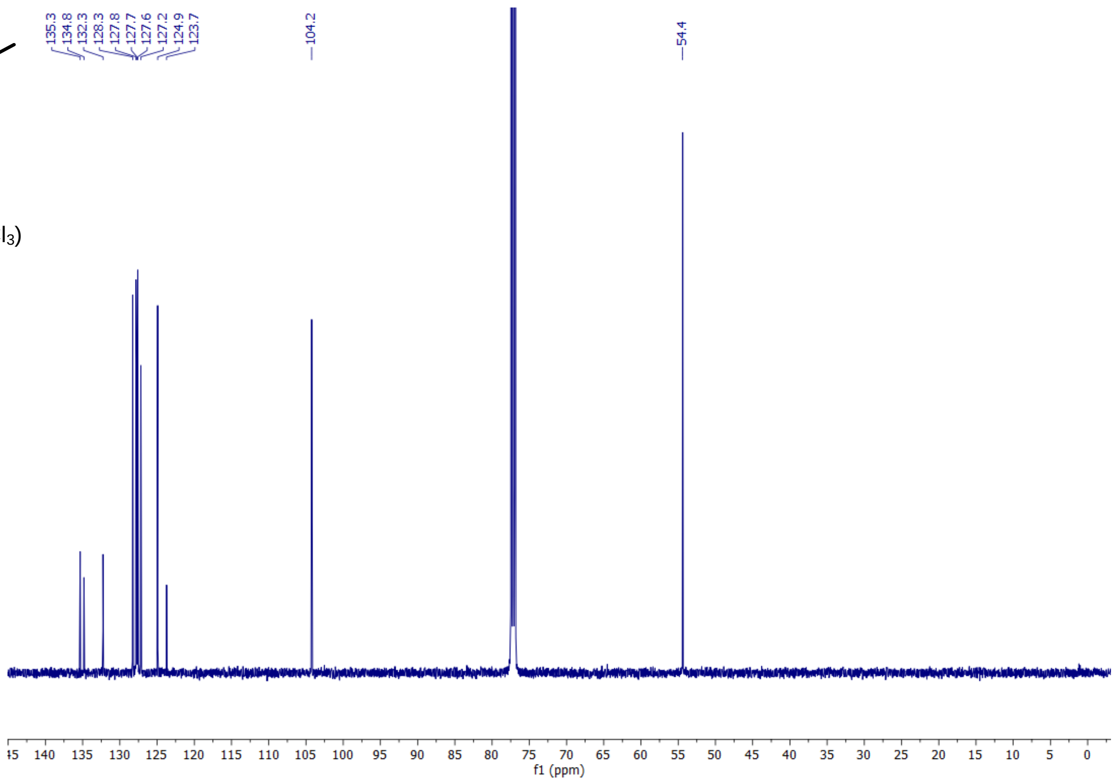
(500 MHz, $CDCl_3$)

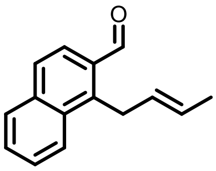




3S9

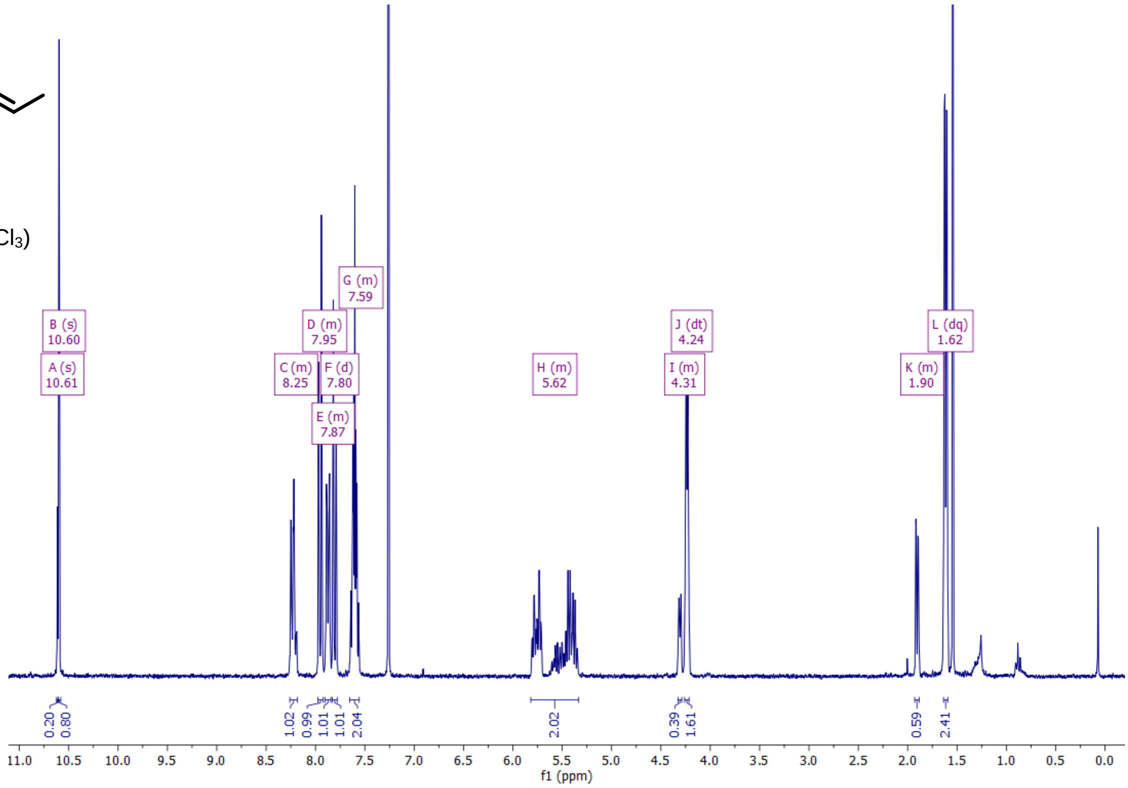
(126 MHz, $CDCl_3$)

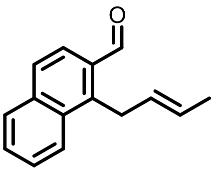




4g

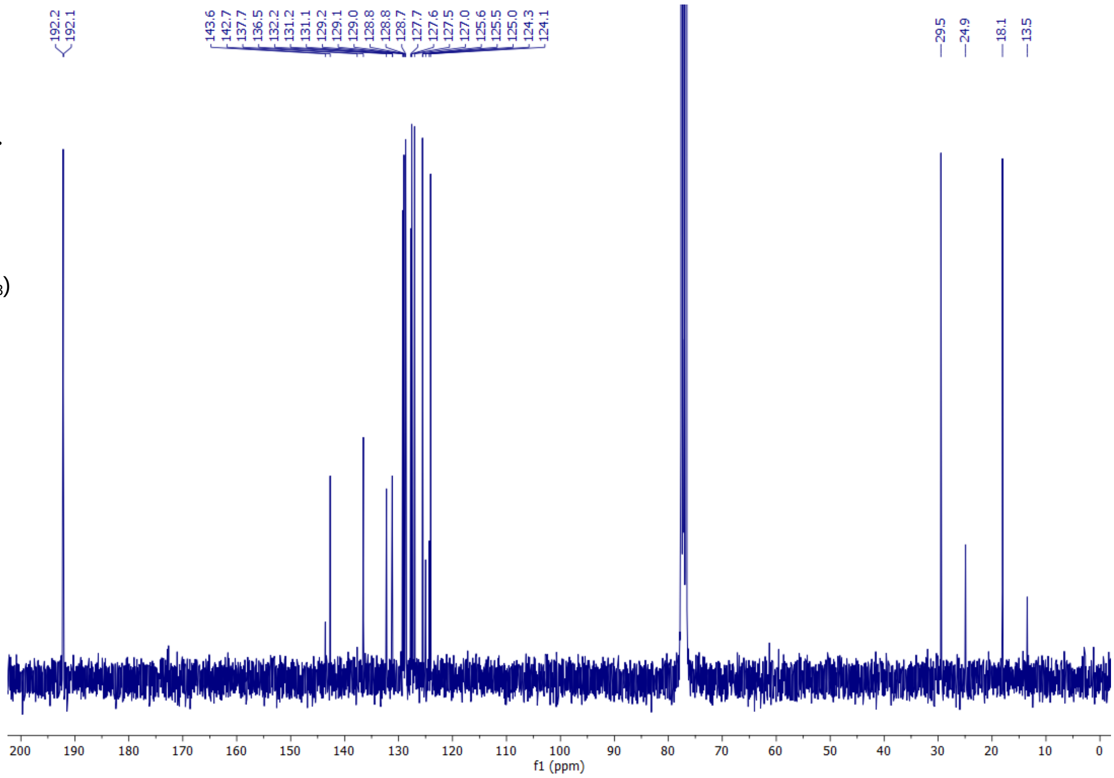
(500 MHz, $CDCl_3$)

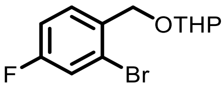




4g

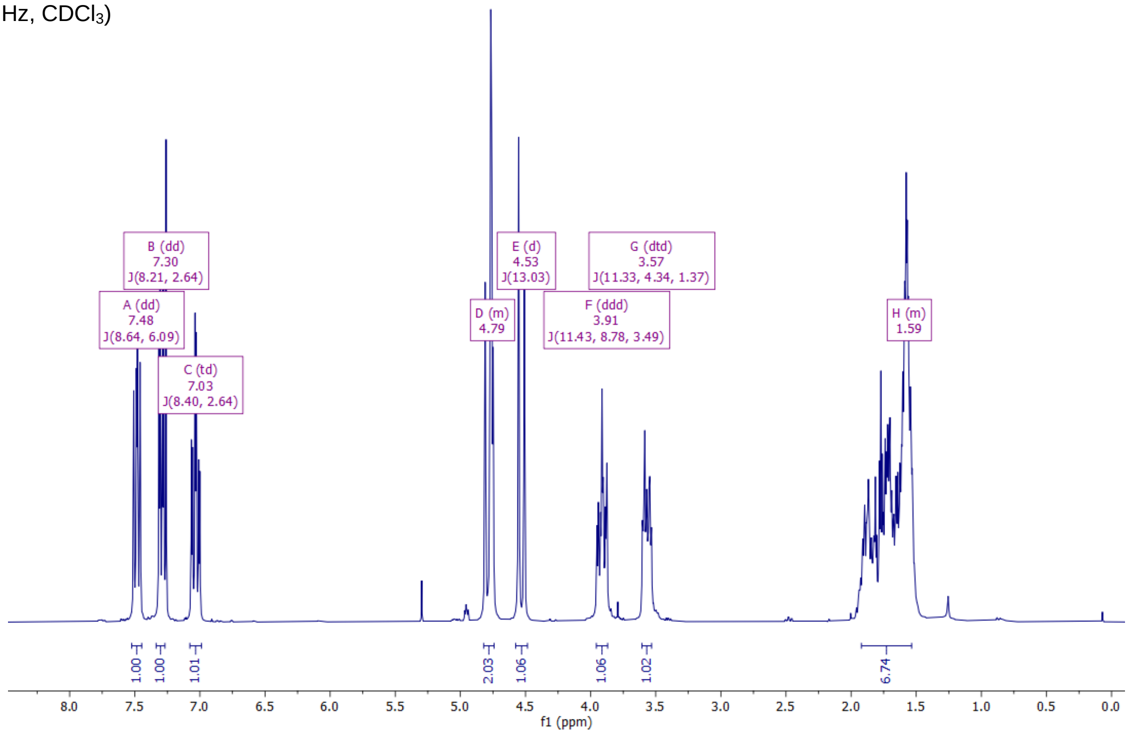
(126 MHz, $CDCl_3$)

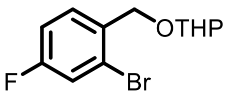




S20

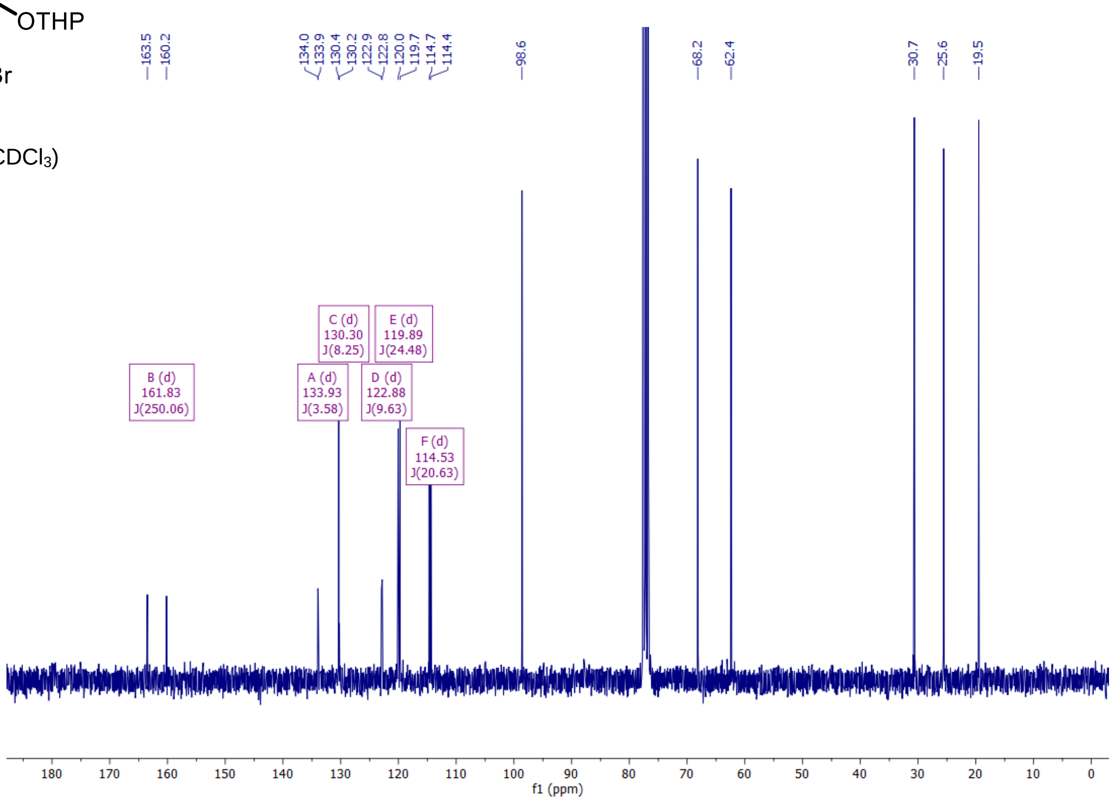
(300 MHz, $CDCl_3$)

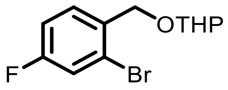




S20

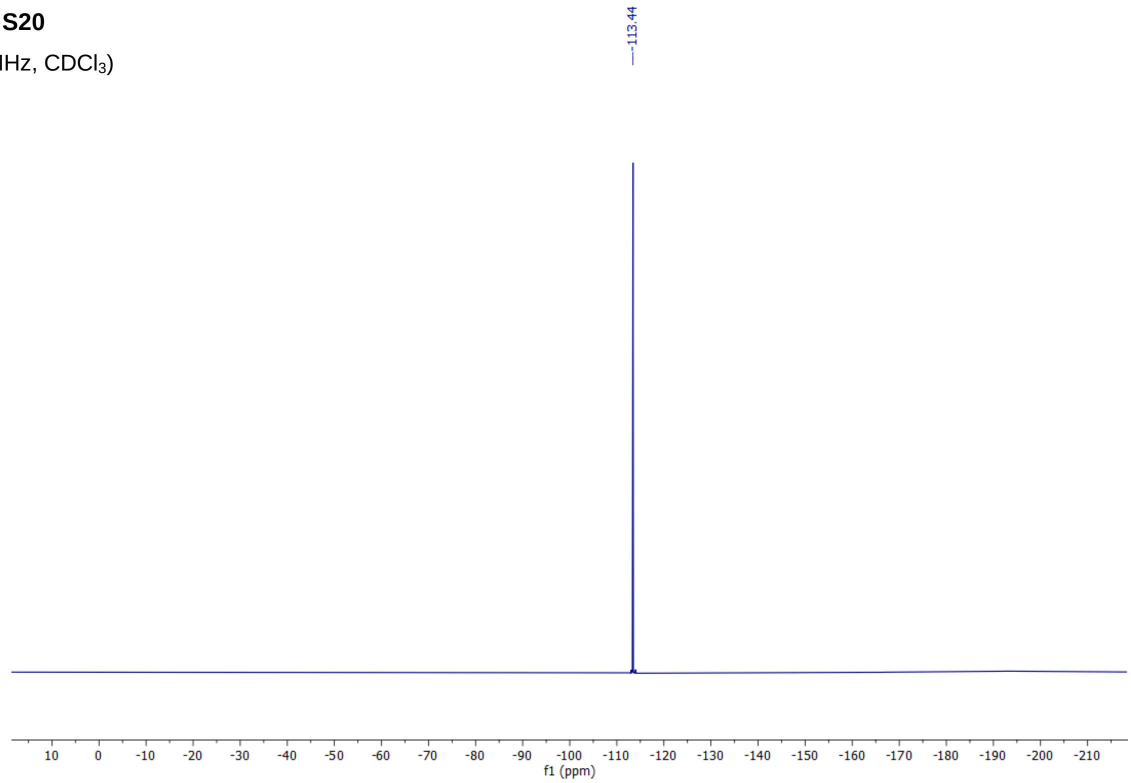
(75 MHz, $CDCl_3$)

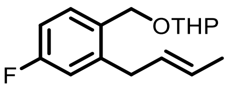




S20

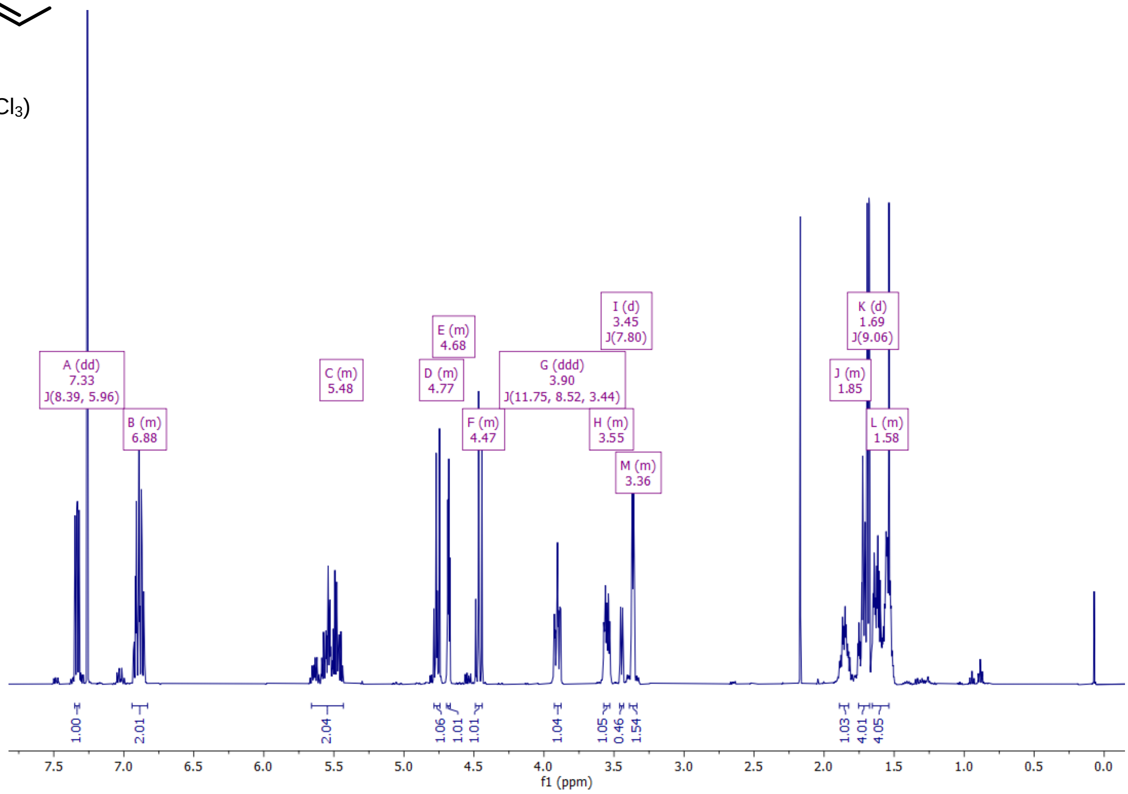
(282 MHz, $CDCl_3$)





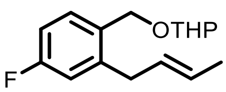
S22

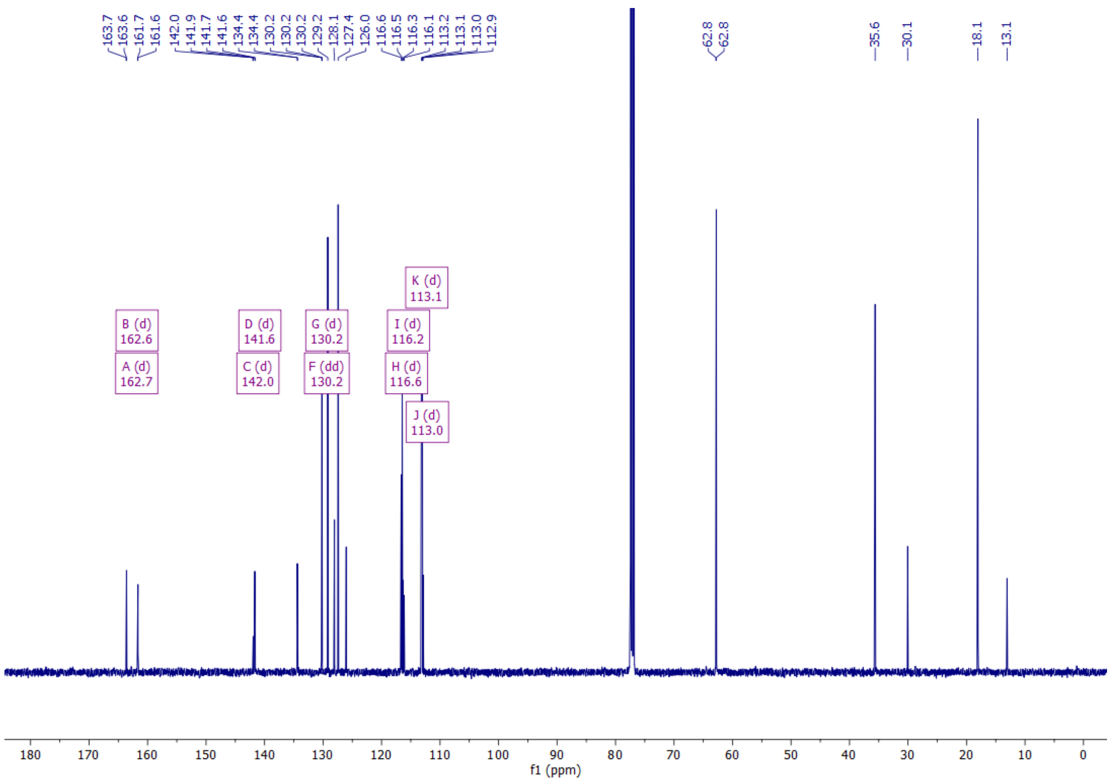
(500 MHz, $CDCl_3$)

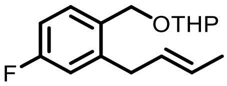


S22

(126 MHz, $CDCl_3$)

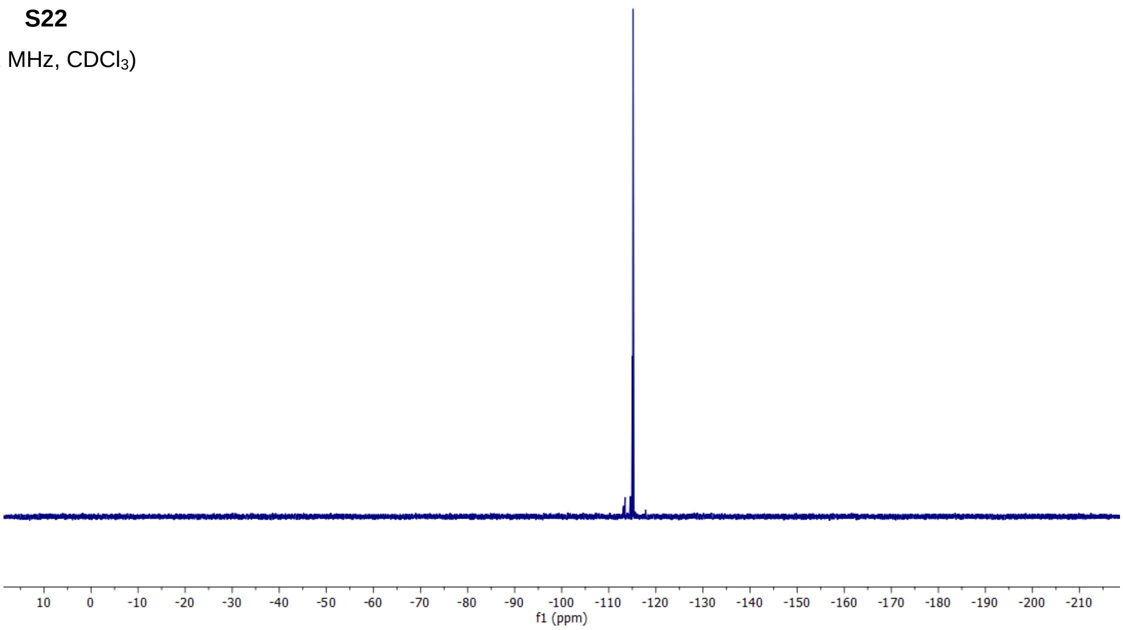


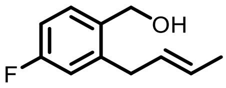




S22

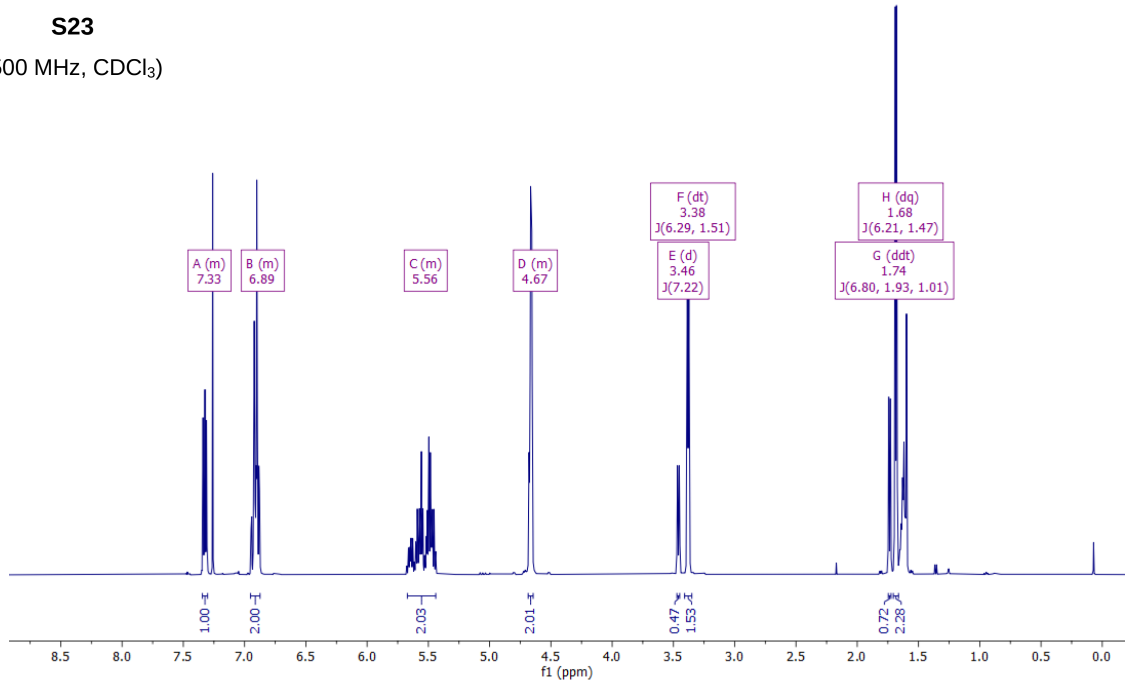
(282 MHz, $CDCl_3$)

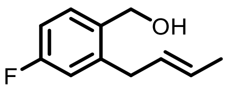




S23

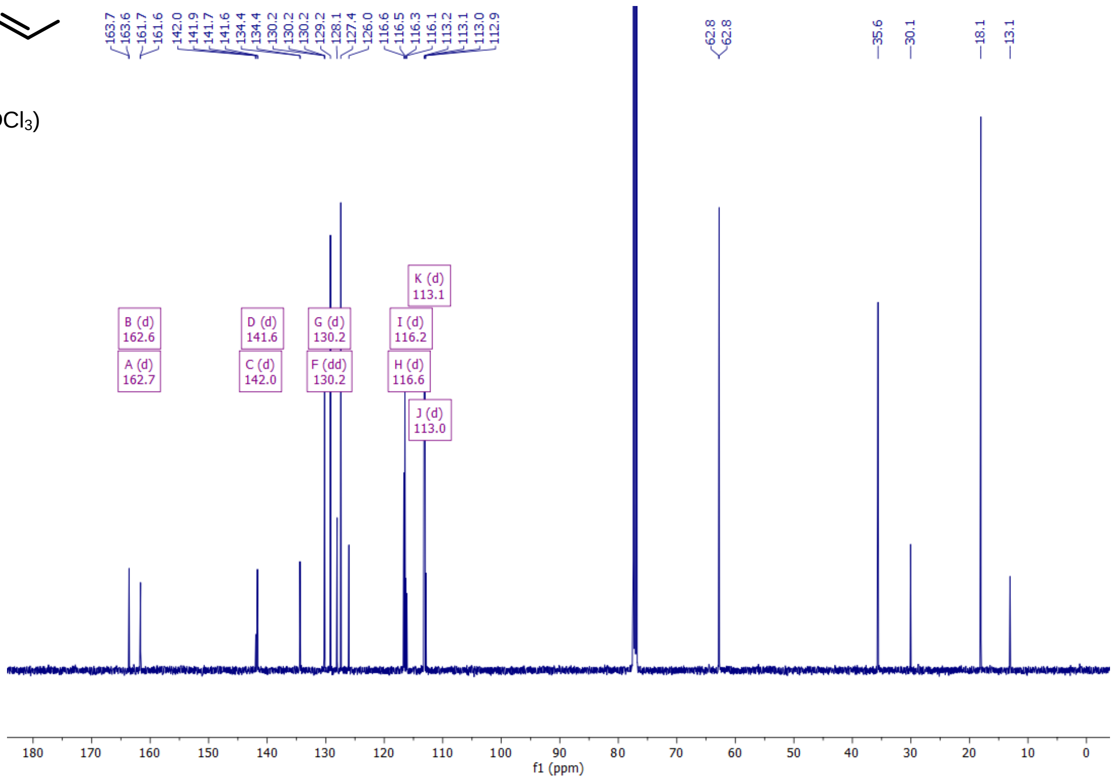
(500 MHz, $CDCl_3$)

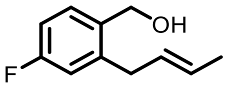




S23

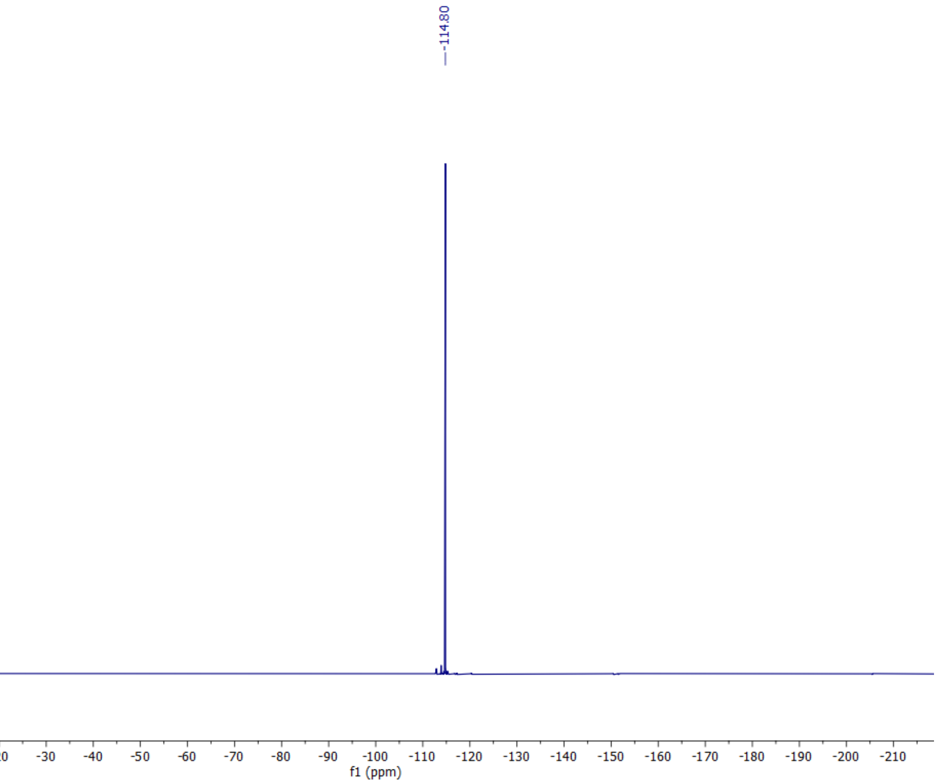
(126 MHz, $CDCl_3$)

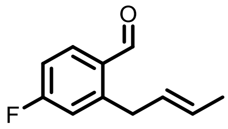




S23

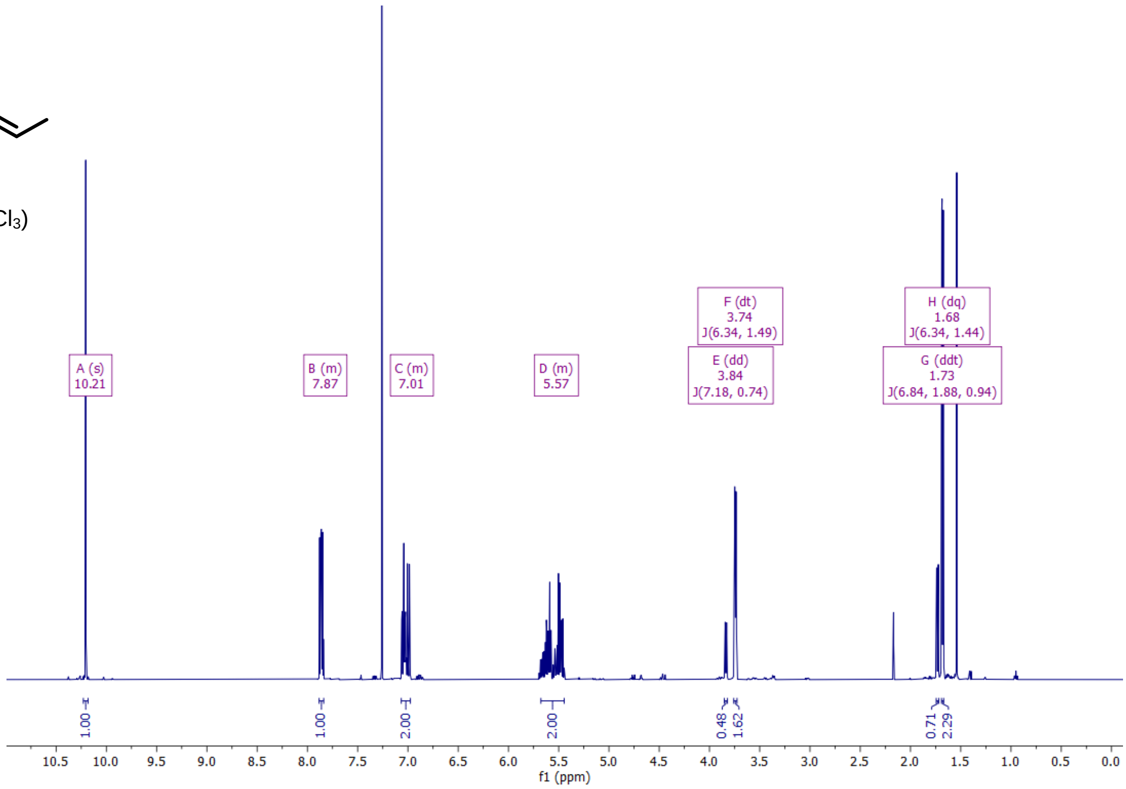
(500 MHz, $CDCl_3$)

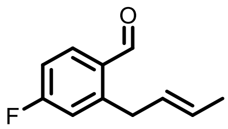




4c

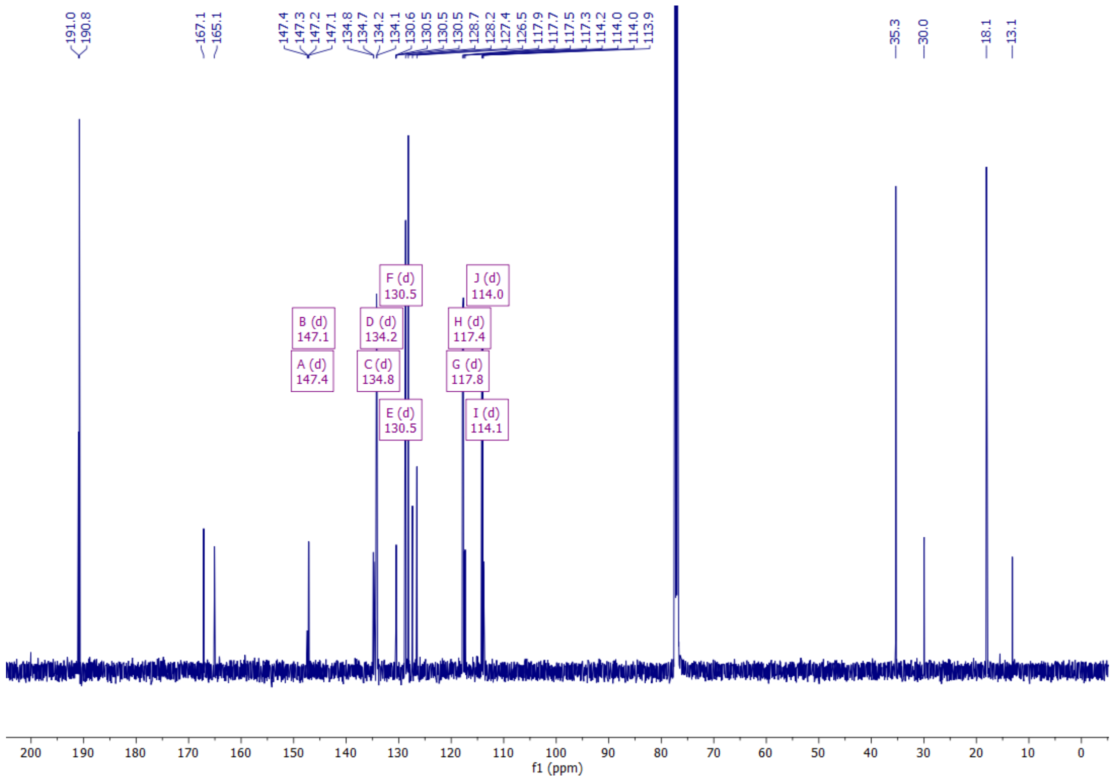
(500 MHz, $CDCl_3$)

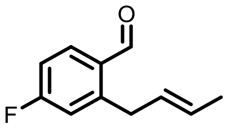




4c

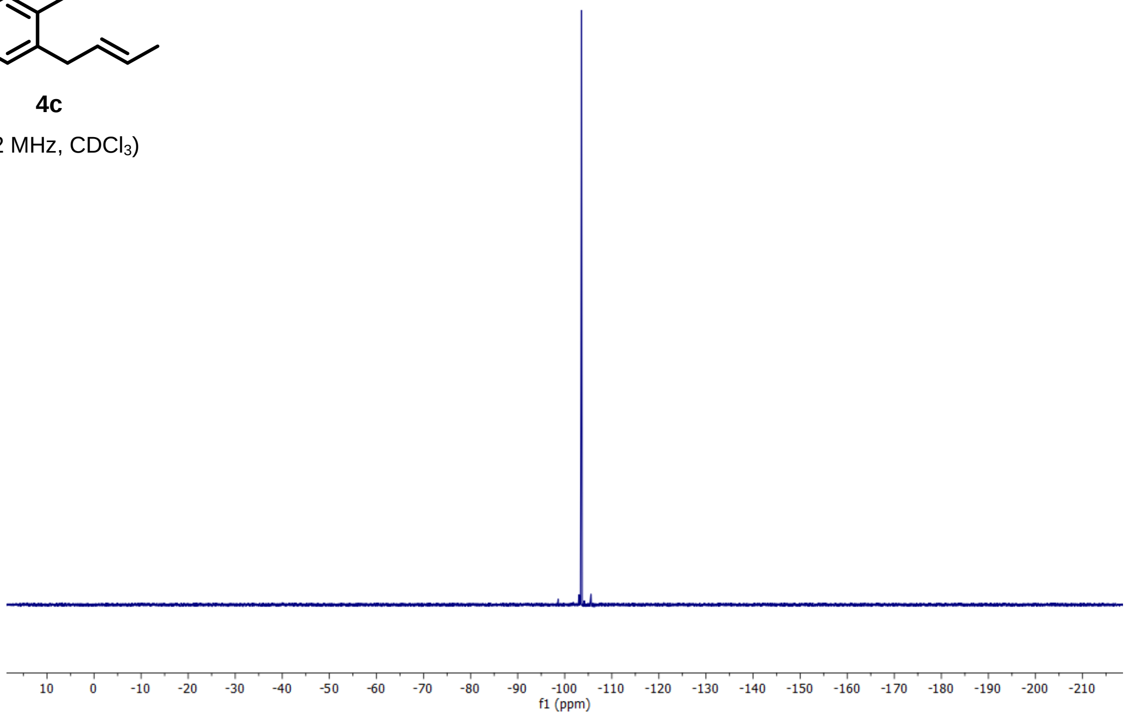
(126 MHz, $CDCl_3$)

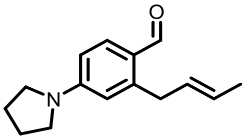




4c

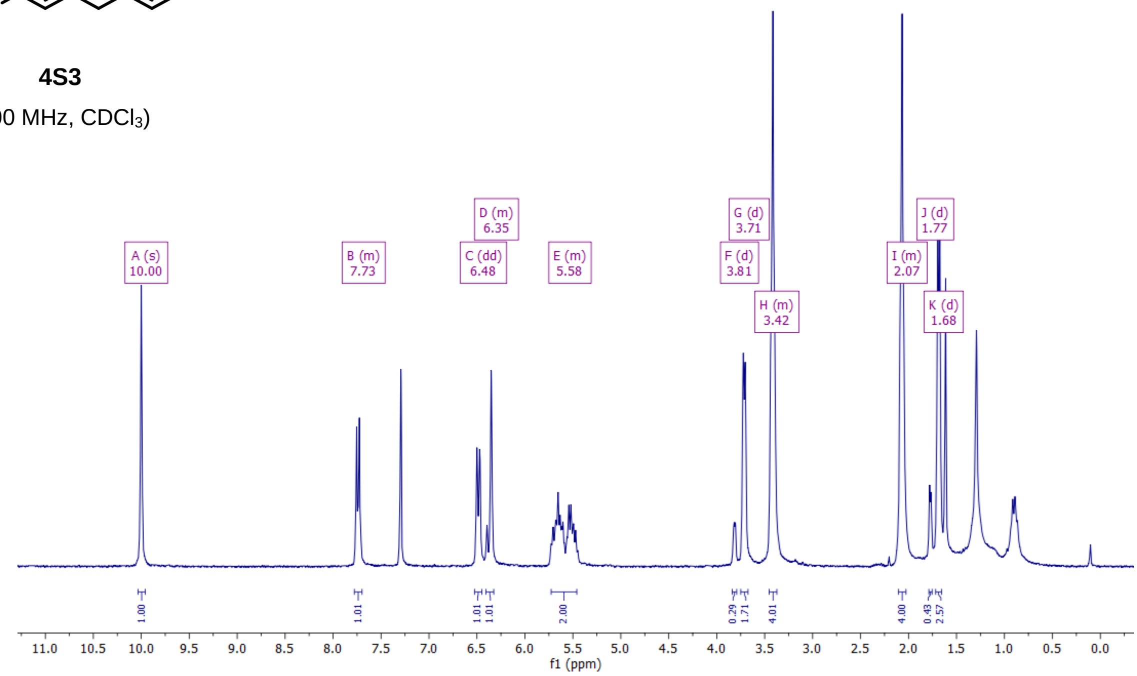
(282 MHz, $CDCl_3$)

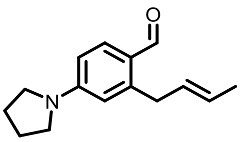




4S3

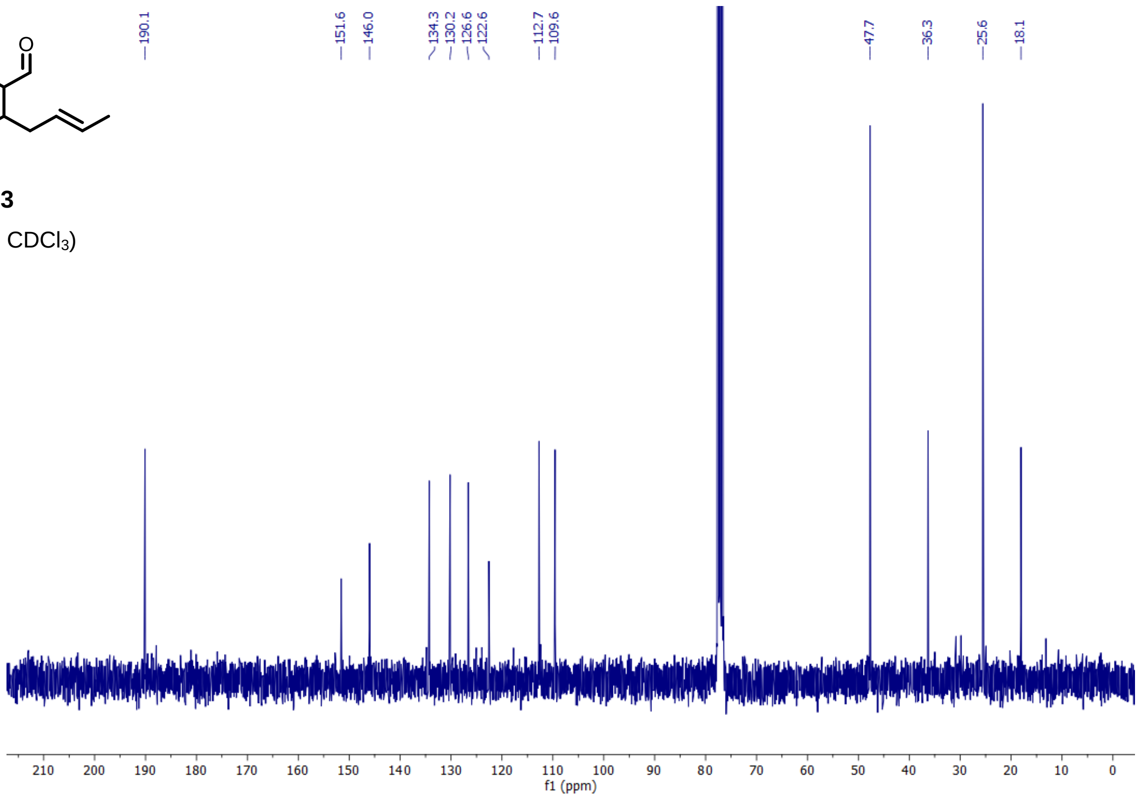
(300 MHz, $CDCl_3$)

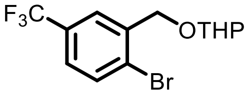




4S3

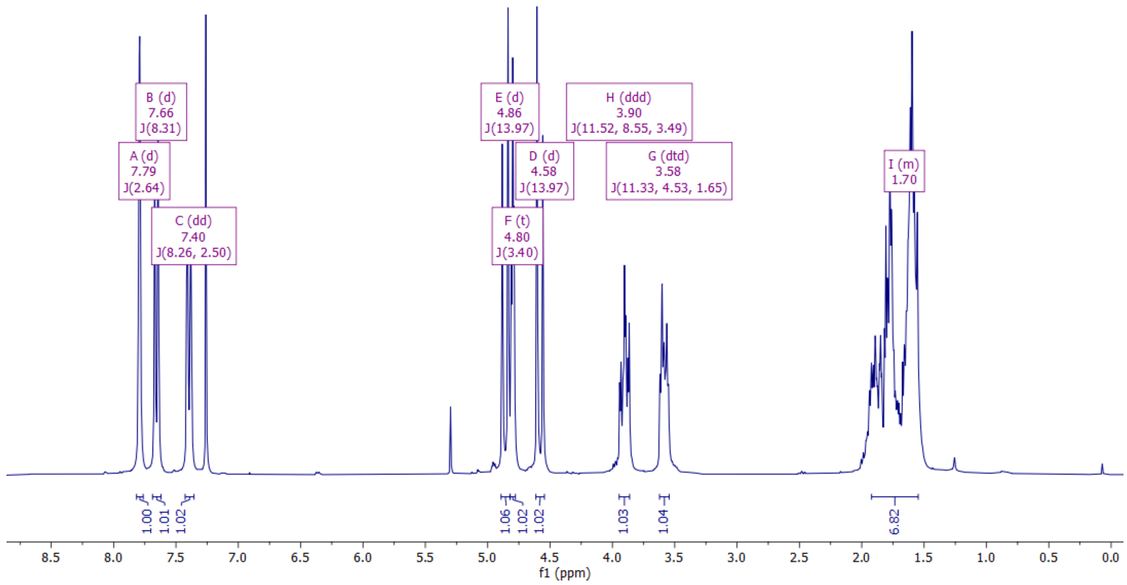
(75 MHz, $CDCl_3$)

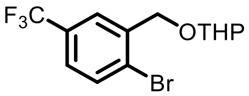




S24

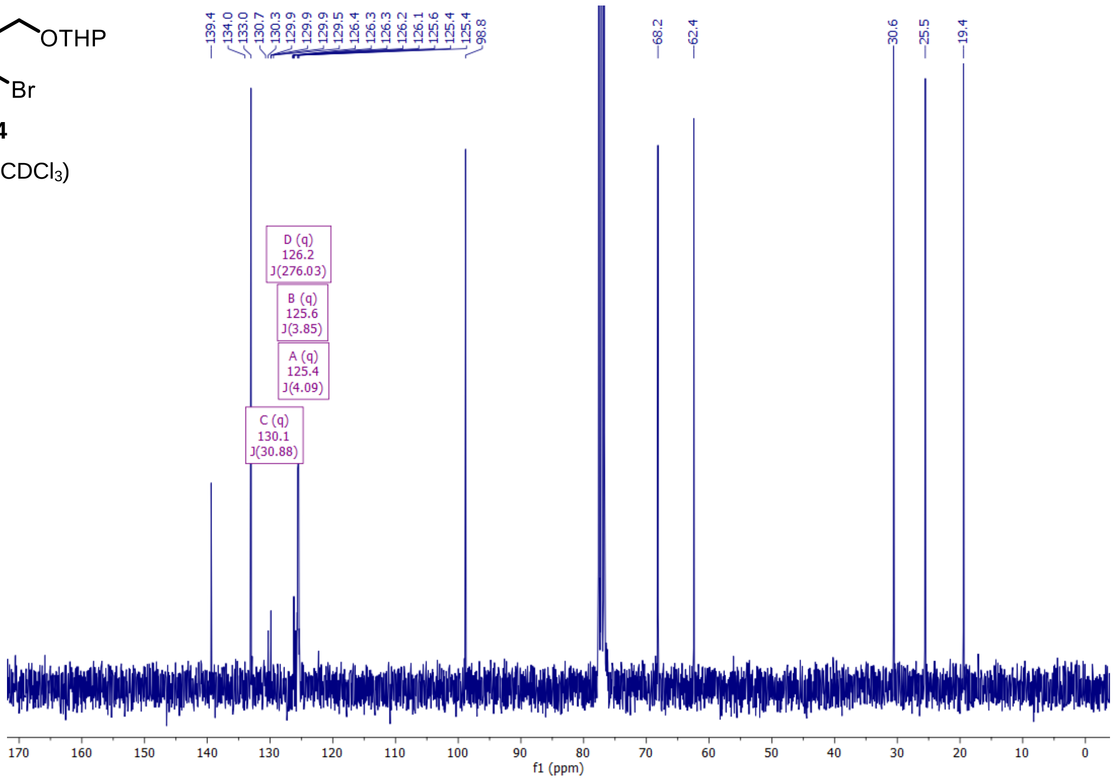
(300 MHz, $CDCl_3$)

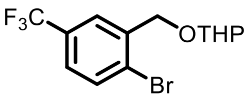




S24

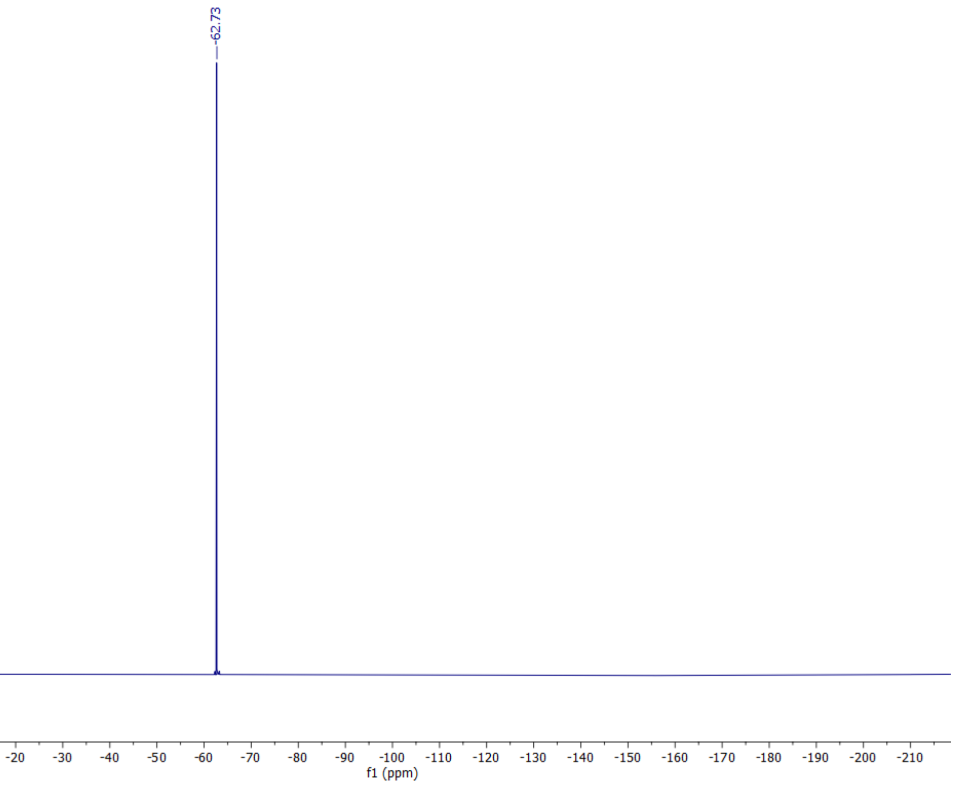
(75 MHz, $CDCl_3$)

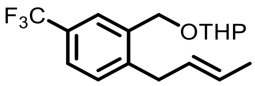




S24

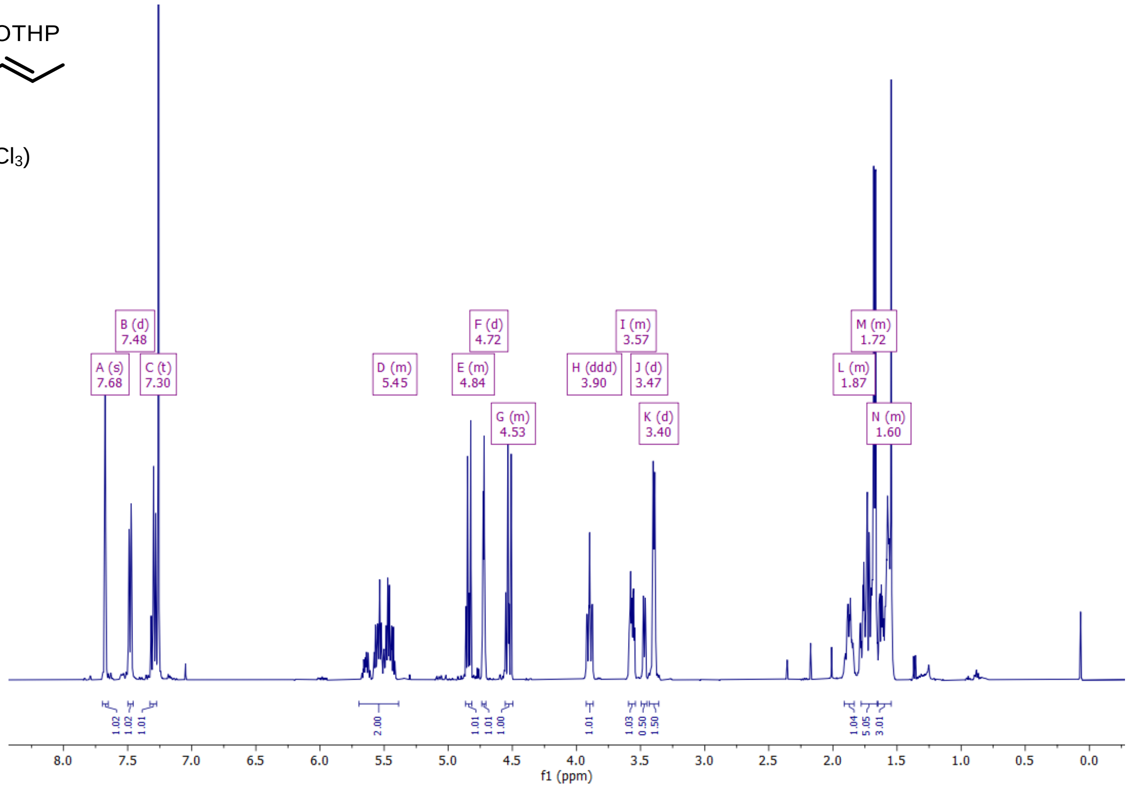
(282 MHz, $CDCl_3$)

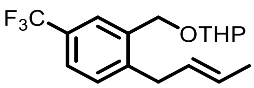




S26

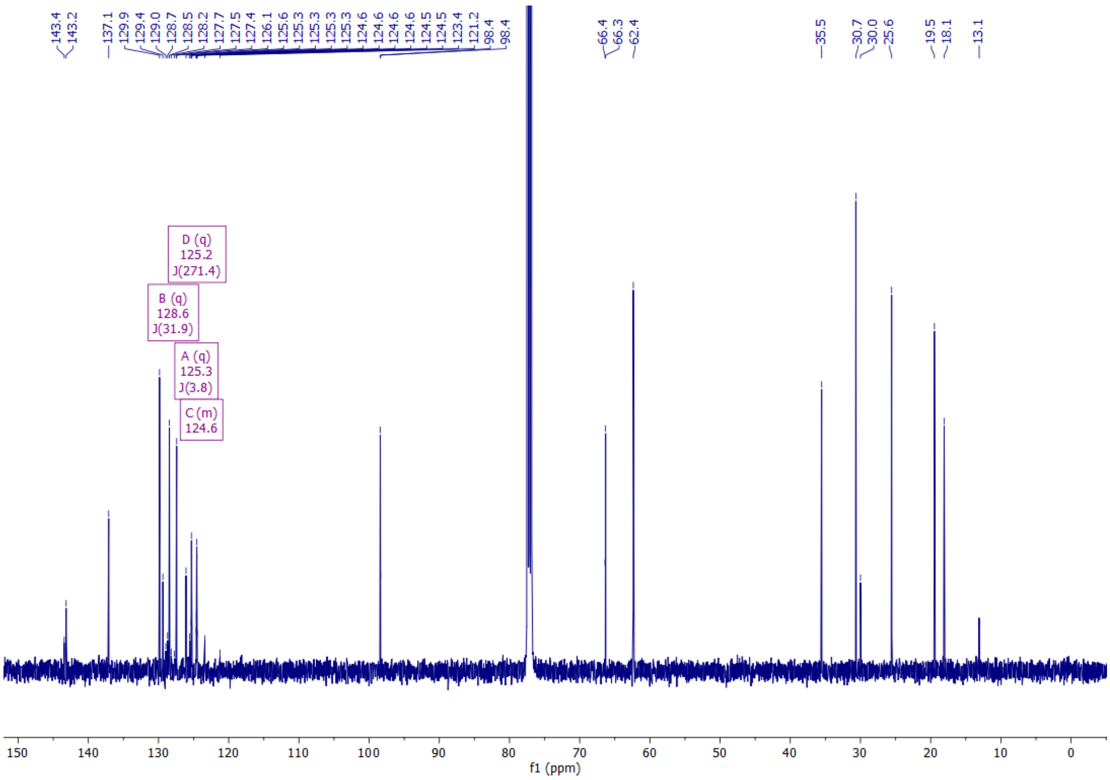
(500 MHz, $CDCl_3$)

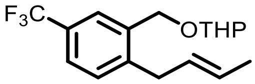




S26

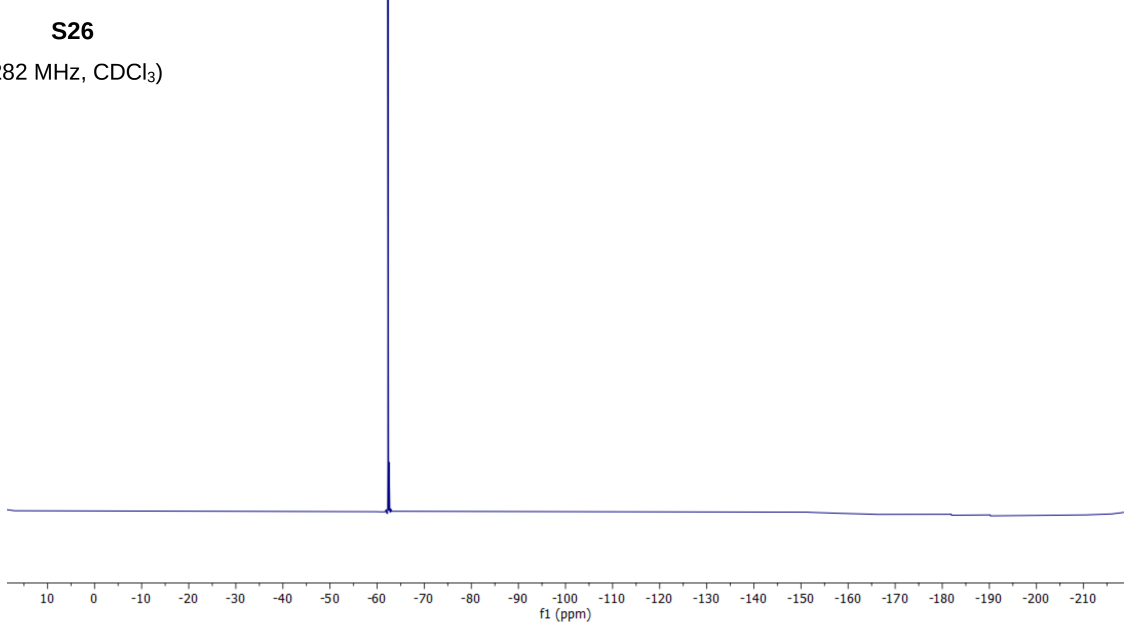
(126 MHz, $CDCl_3$)

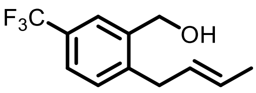




S26

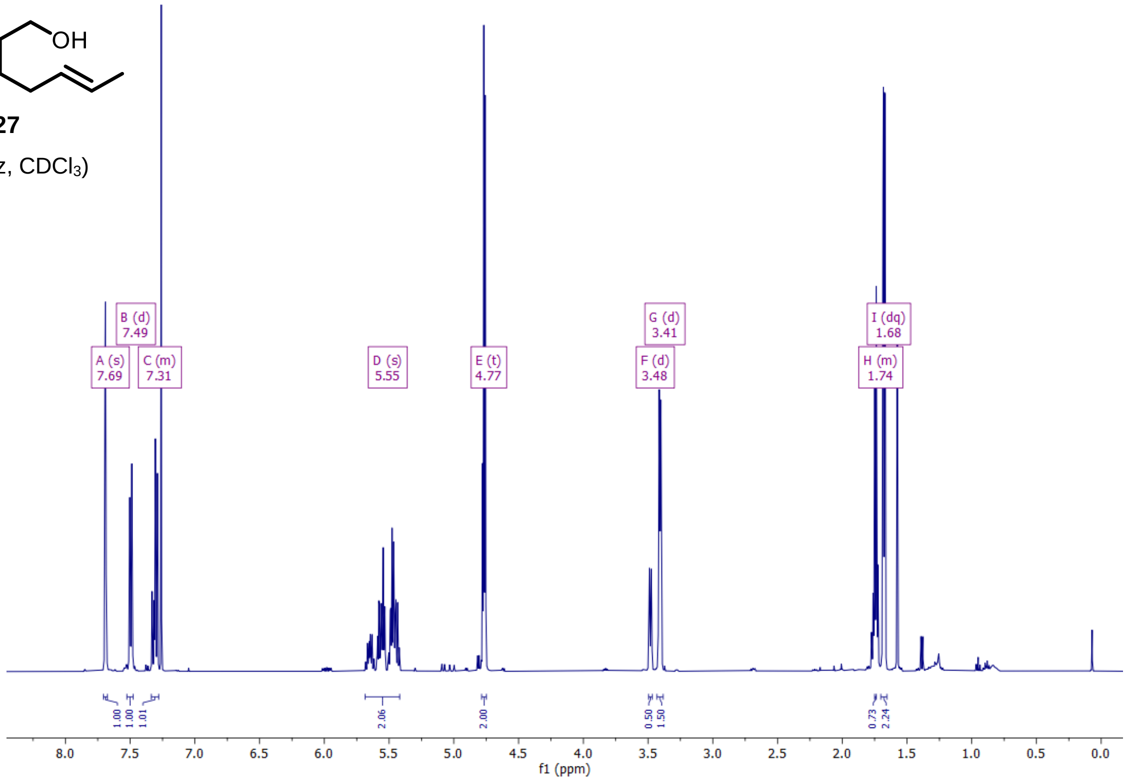
(282 MHz, $CDCl_3$)

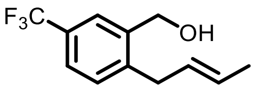




S27

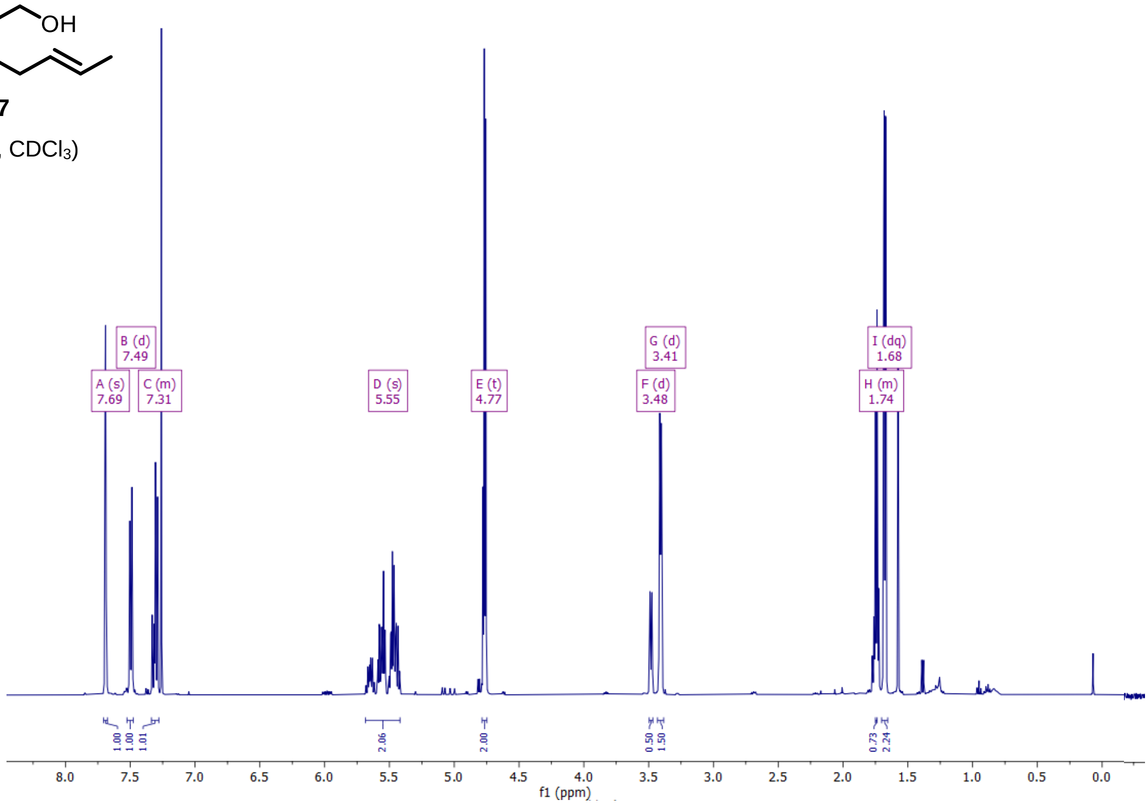
(500 MHz, $CDCl_3$)

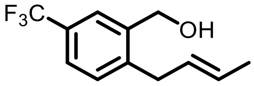




S27

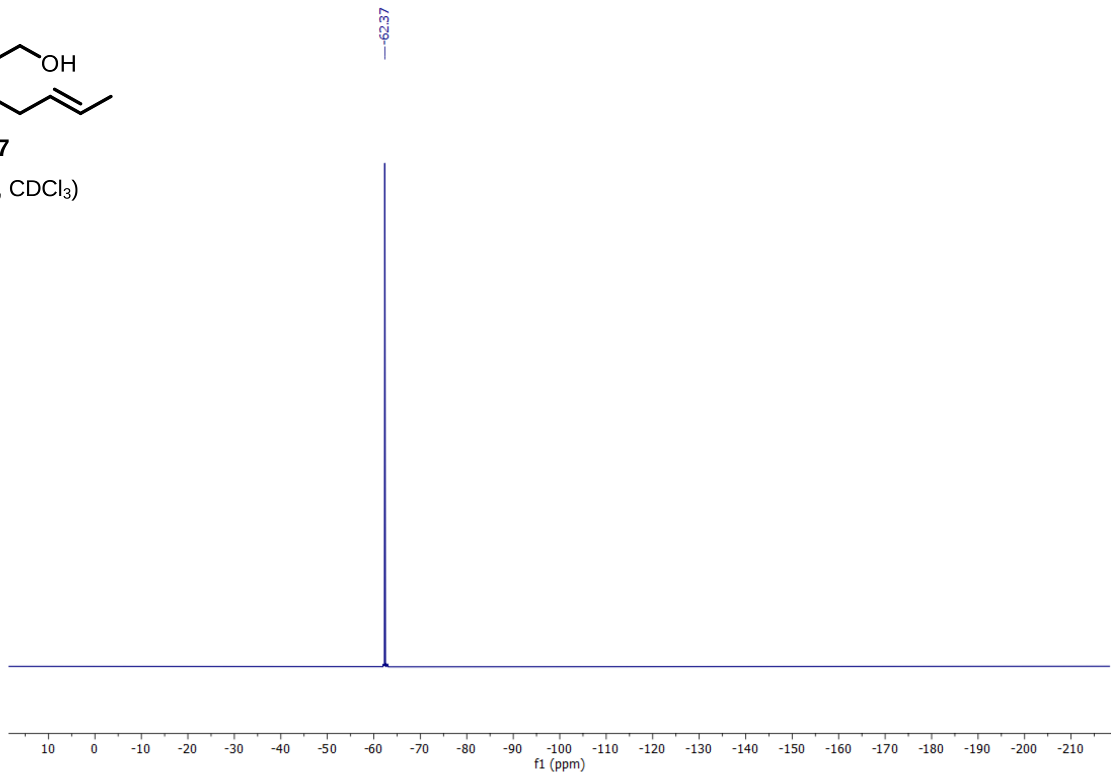
(126 MHz, $CDCl_3$)

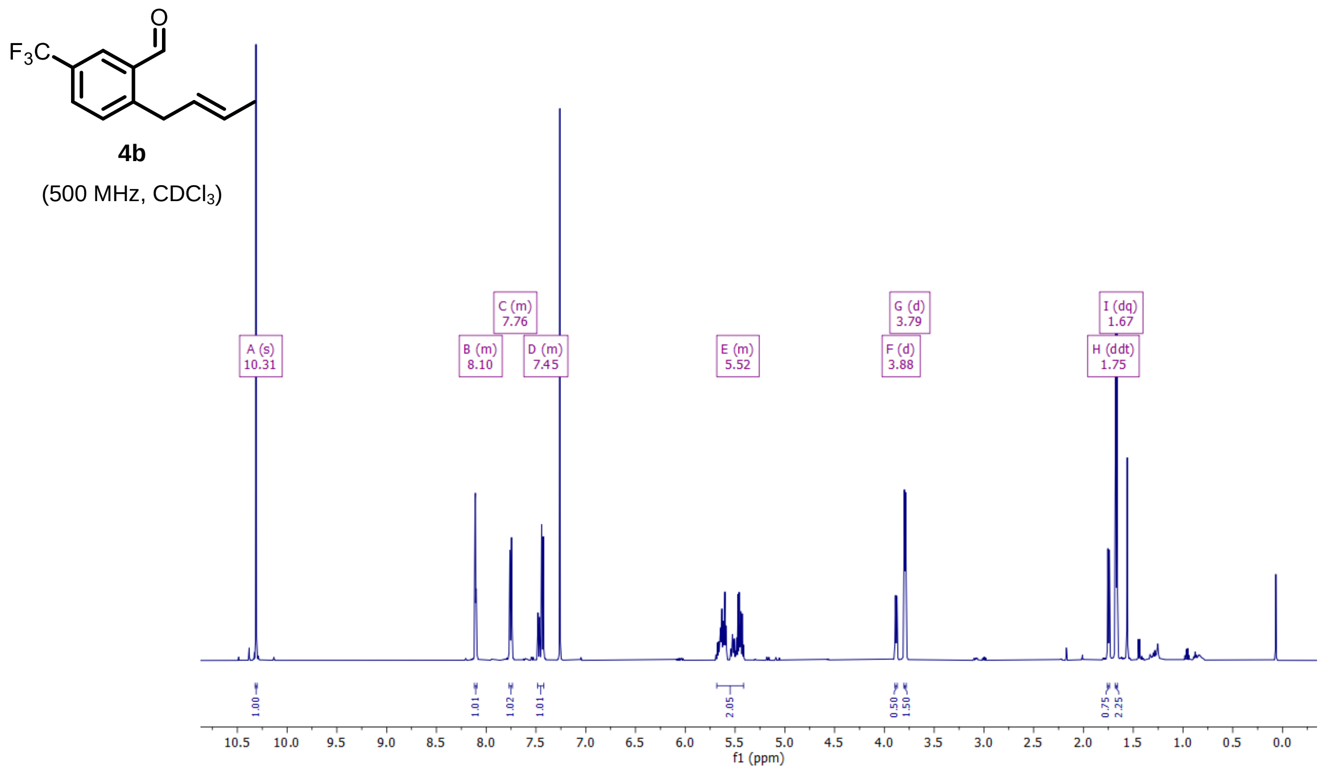




S27

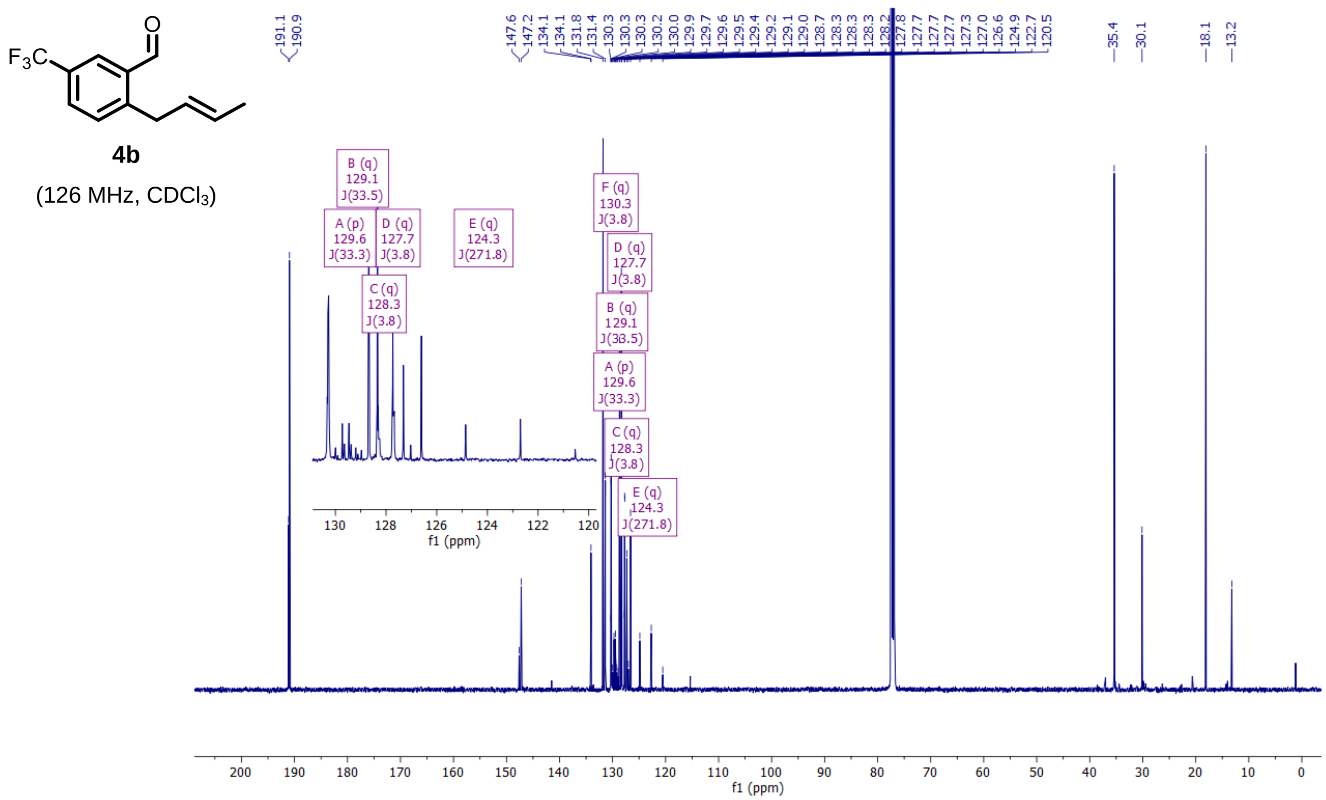
(282 MHz, $CDCl_3$)





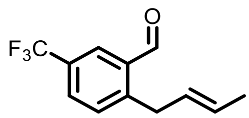
4b

(500 MHz, $CDCl_3$)



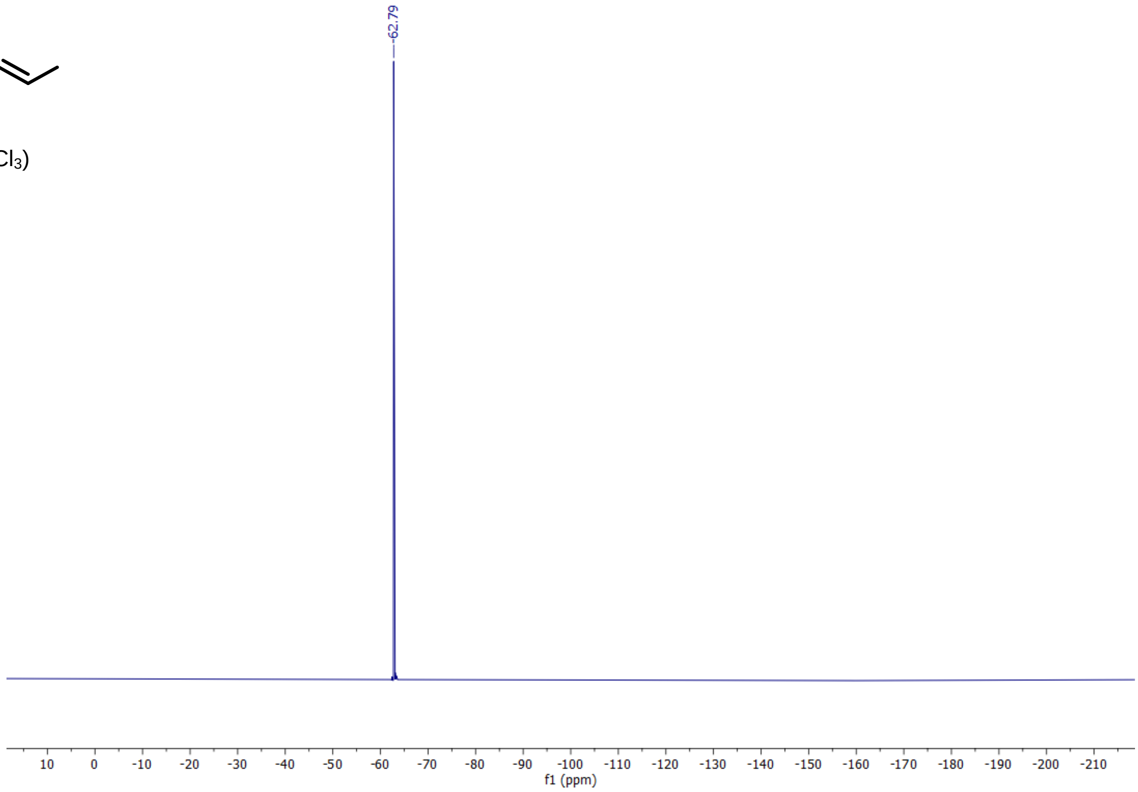
4b

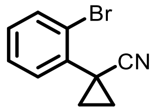
(126 MHz, $CDCl_3$)



4b

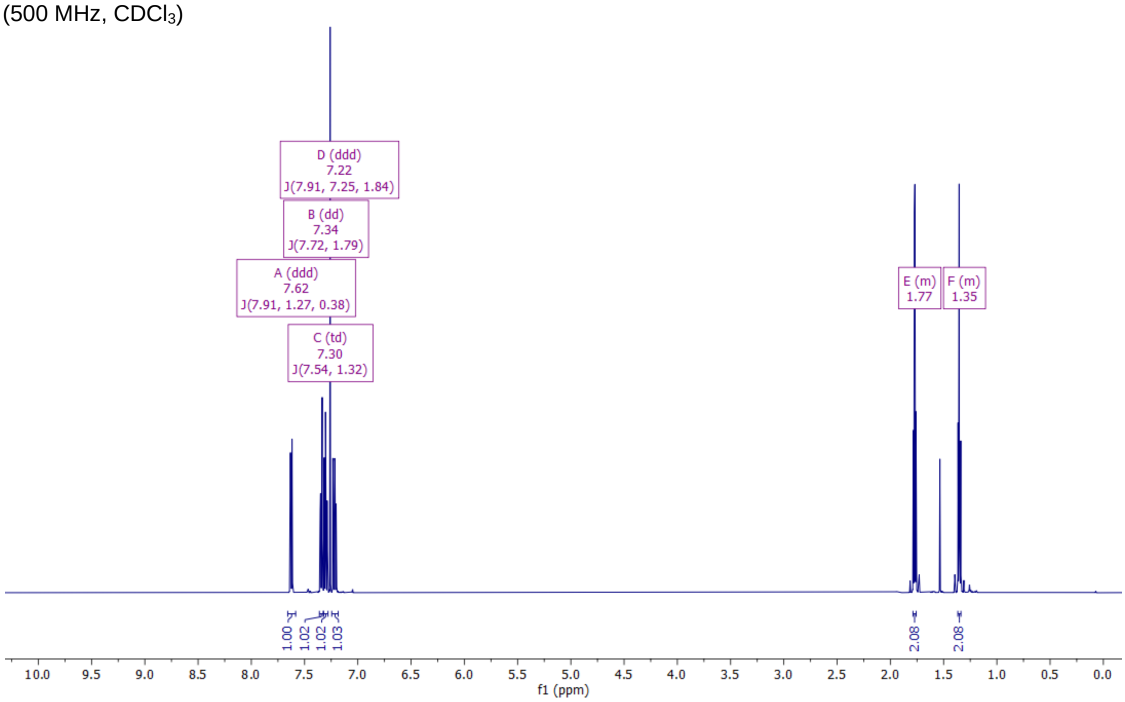
(282 MHz, $CDCl_3$)

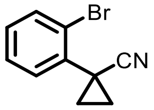




1S3

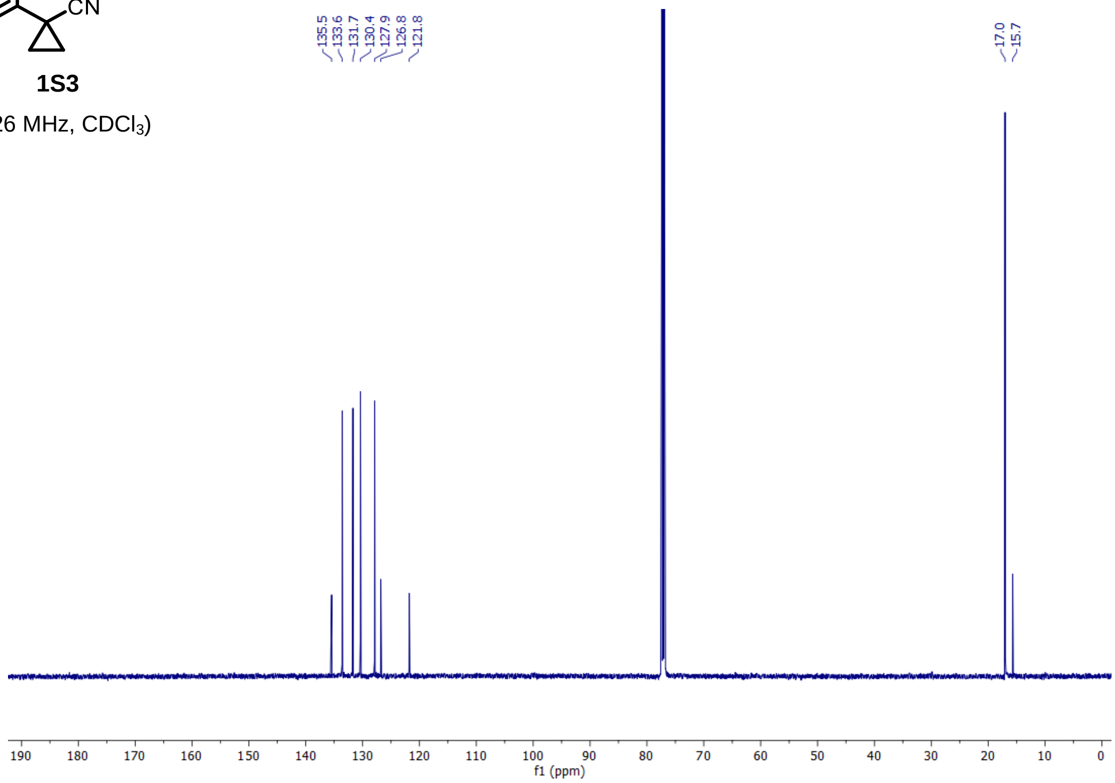
(500 MHz, $CDCl_3$)

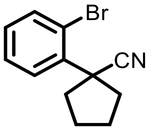




1S3

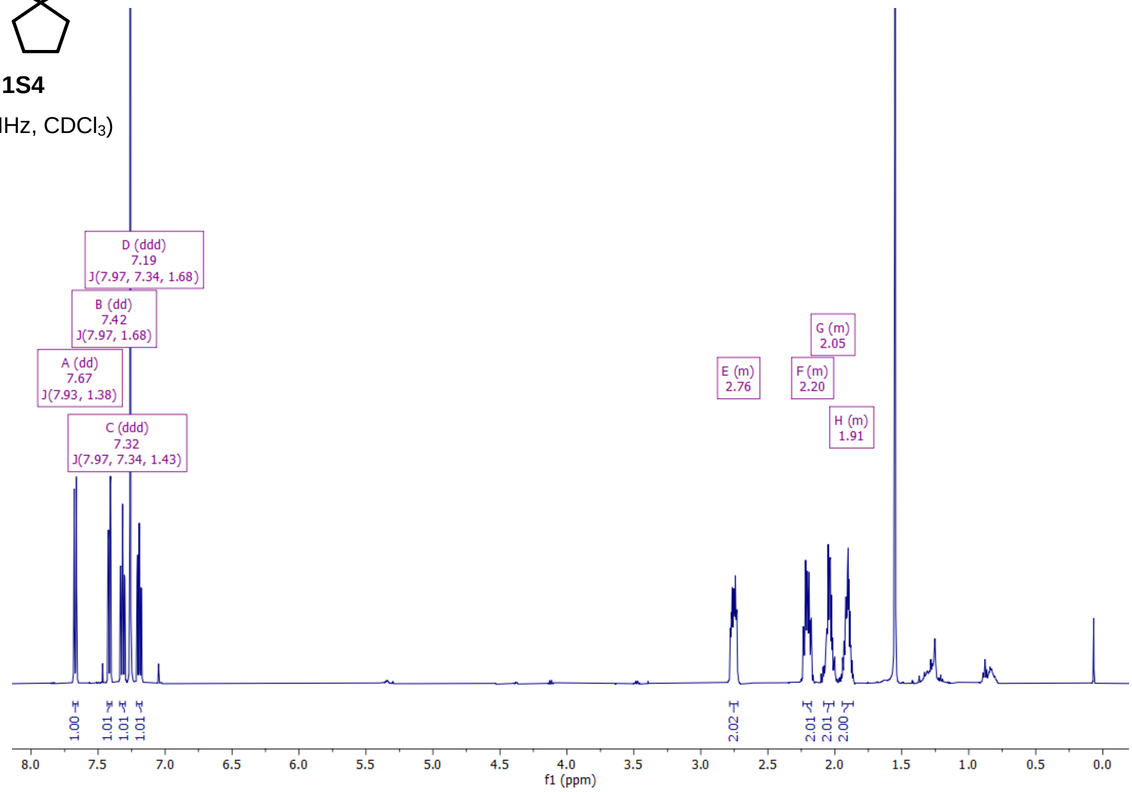
(126 MHz, $CDCl_3$)

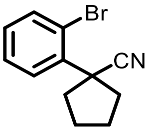




1S4

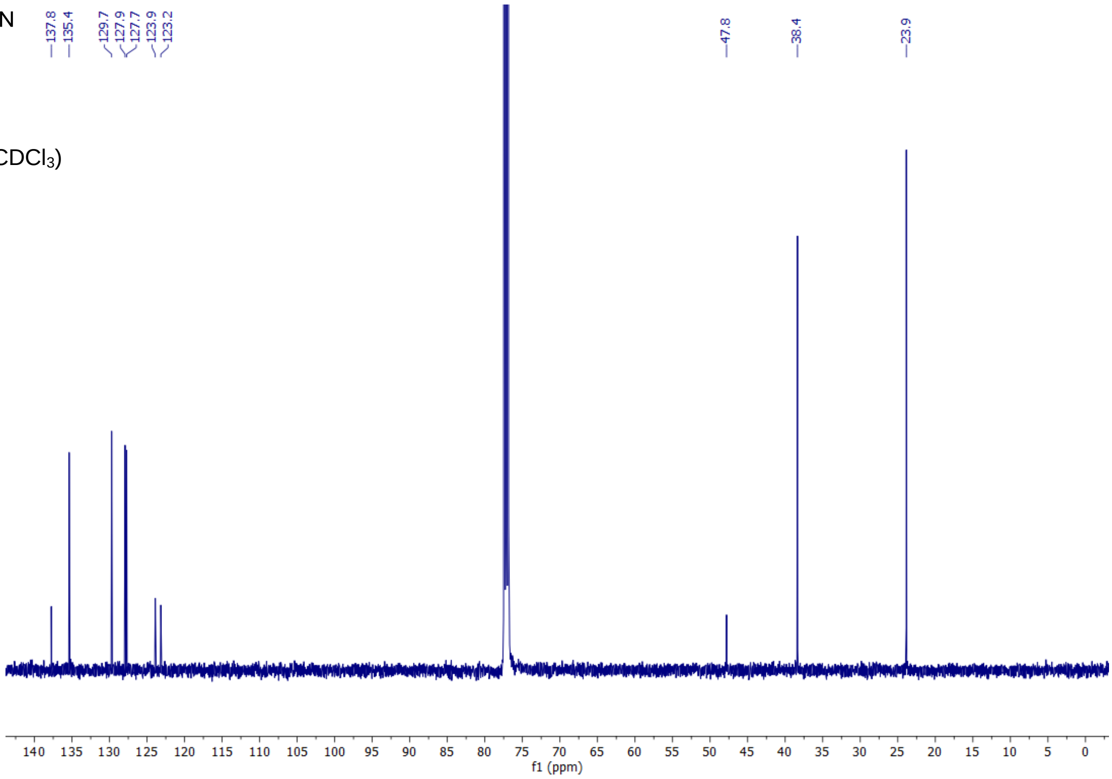
(500 MHz, $CDCl_3$)

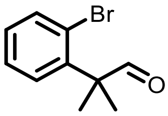




1S4

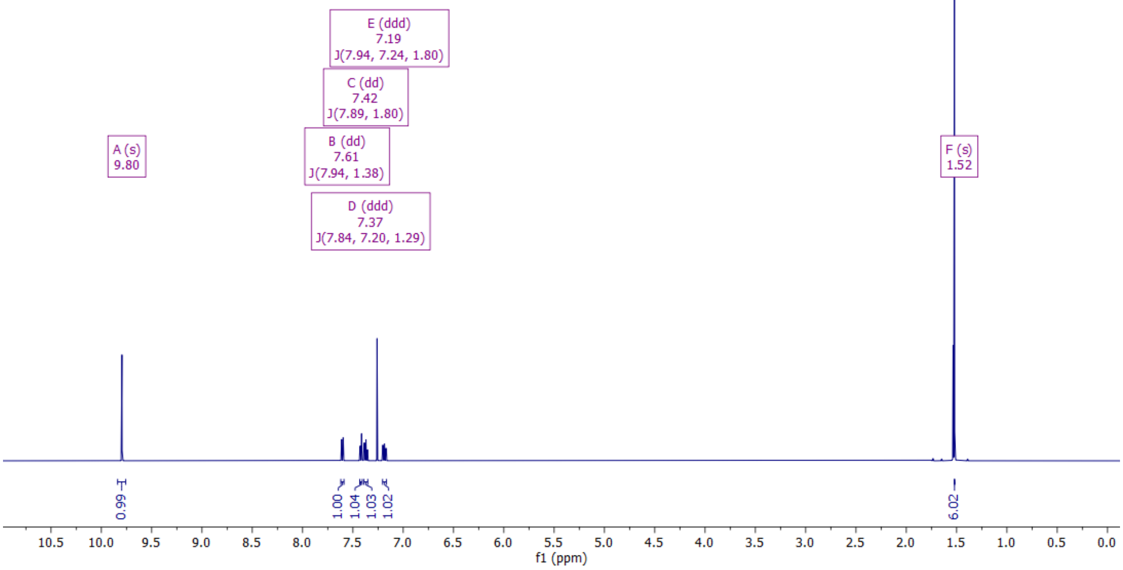
(126 MHz, $CDCl_3$)

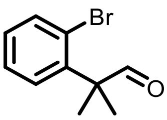




2S1

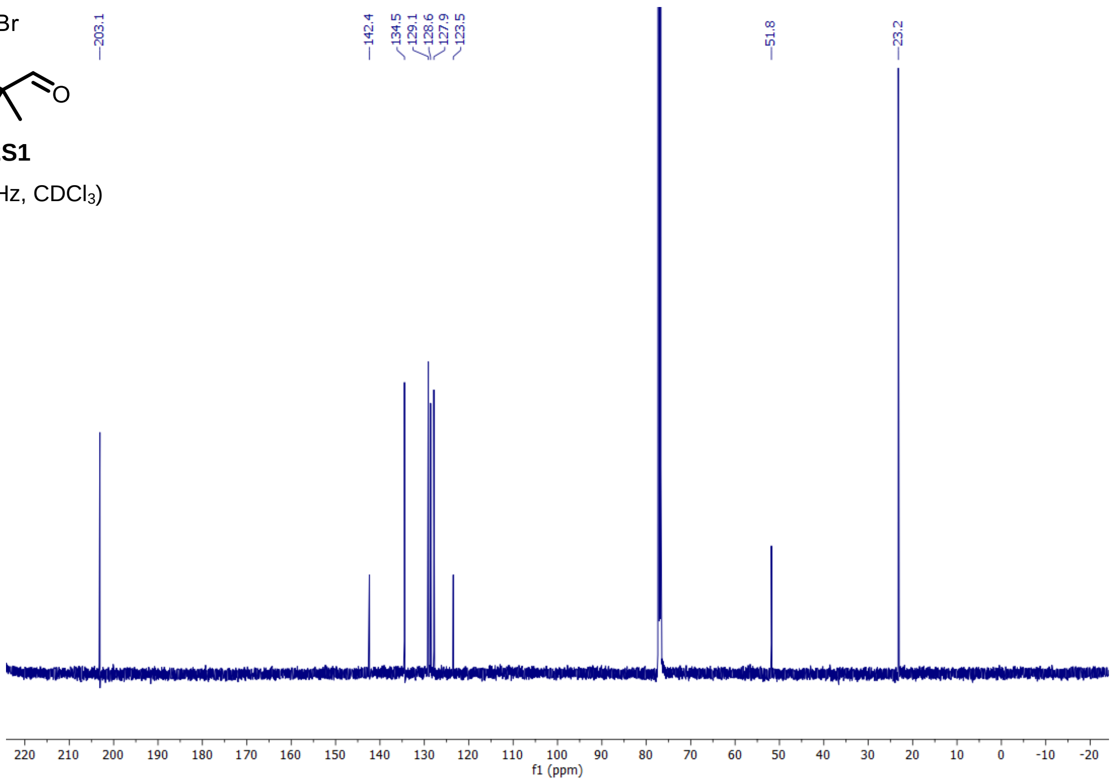
(500 MHz, $CDCl_3$)

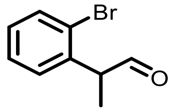




2S1

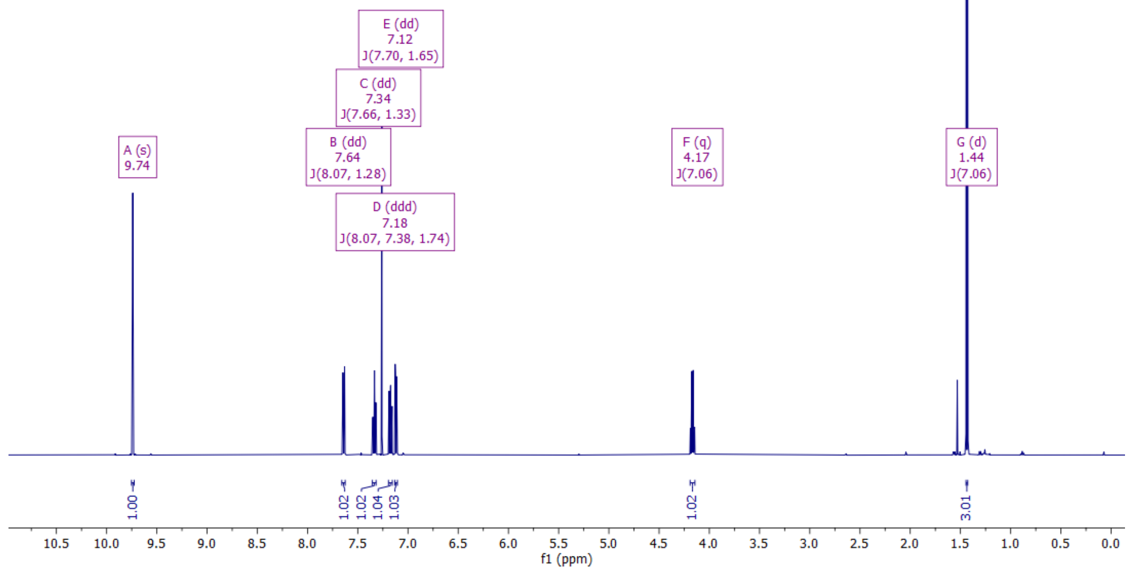
(126 MHz, $CDCl_3$)

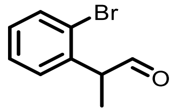




2S2

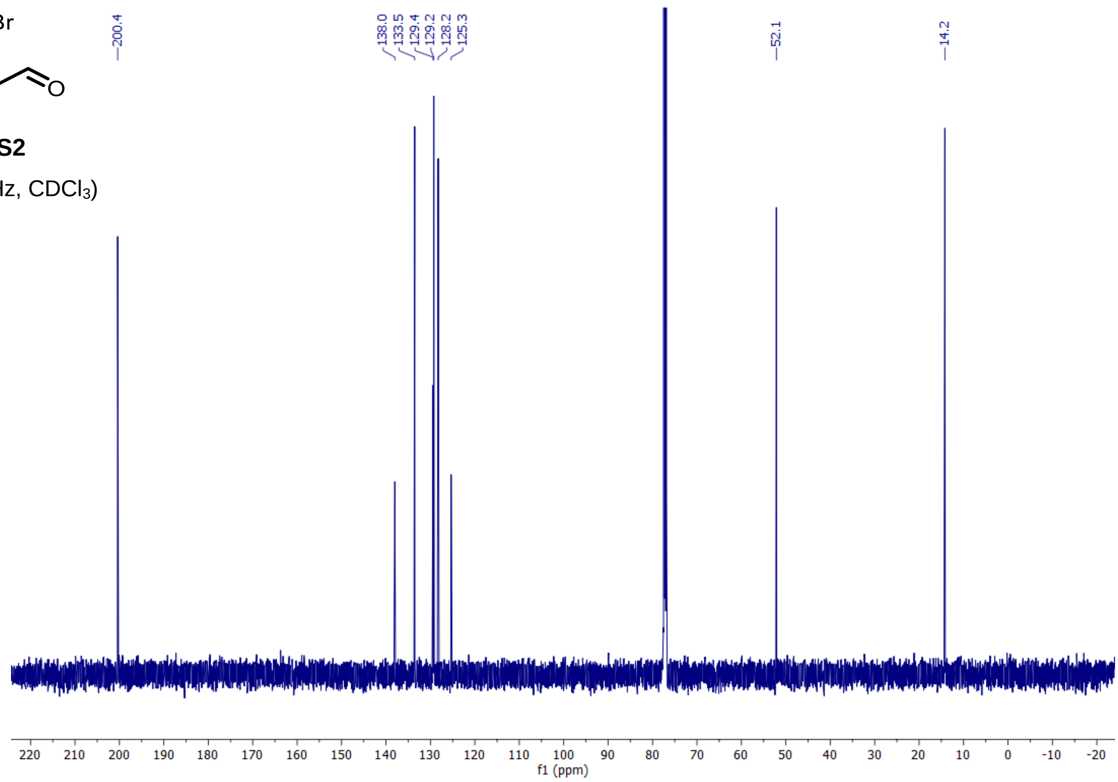
(500 MHz, $CDCl_3$)

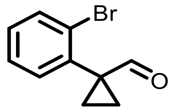




2S2

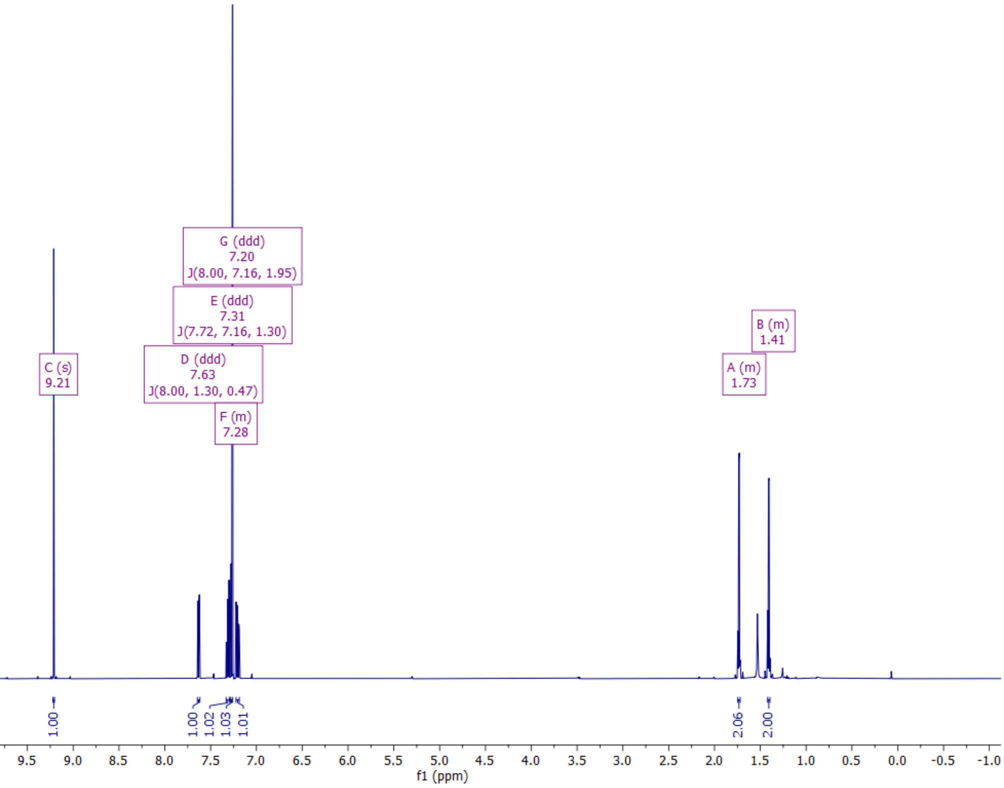
(126 MHz, $CDCl_3$)

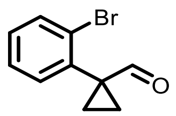




2S3

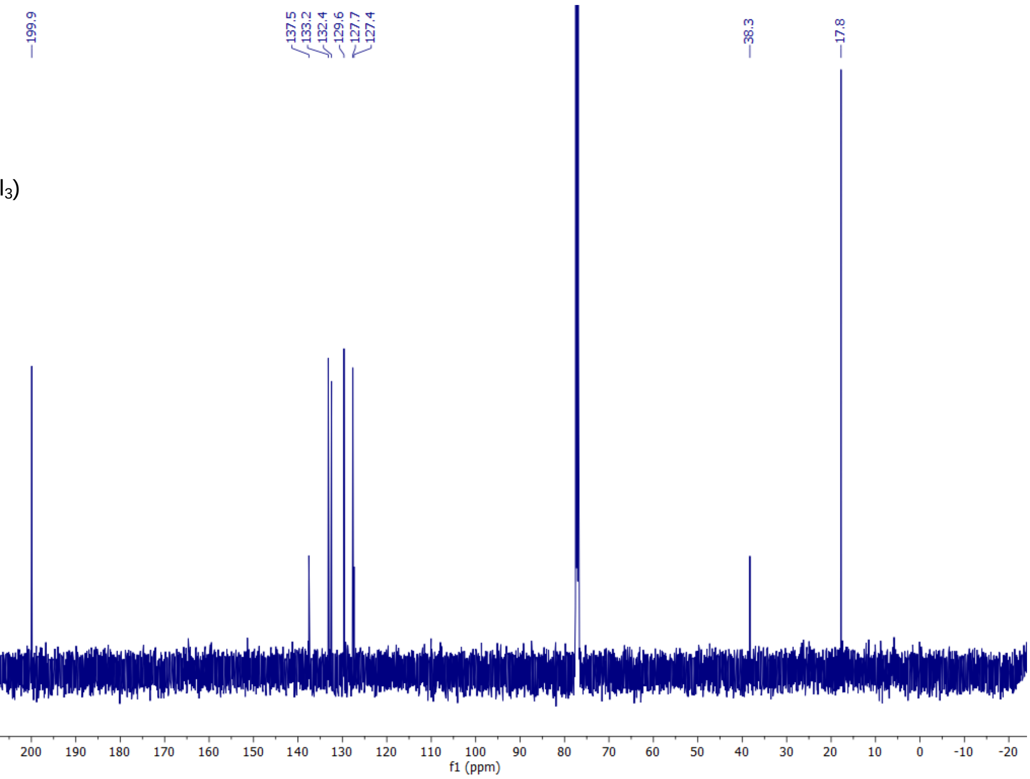
(500 MHz, $CDCl_3$)

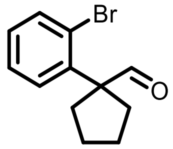




2S3

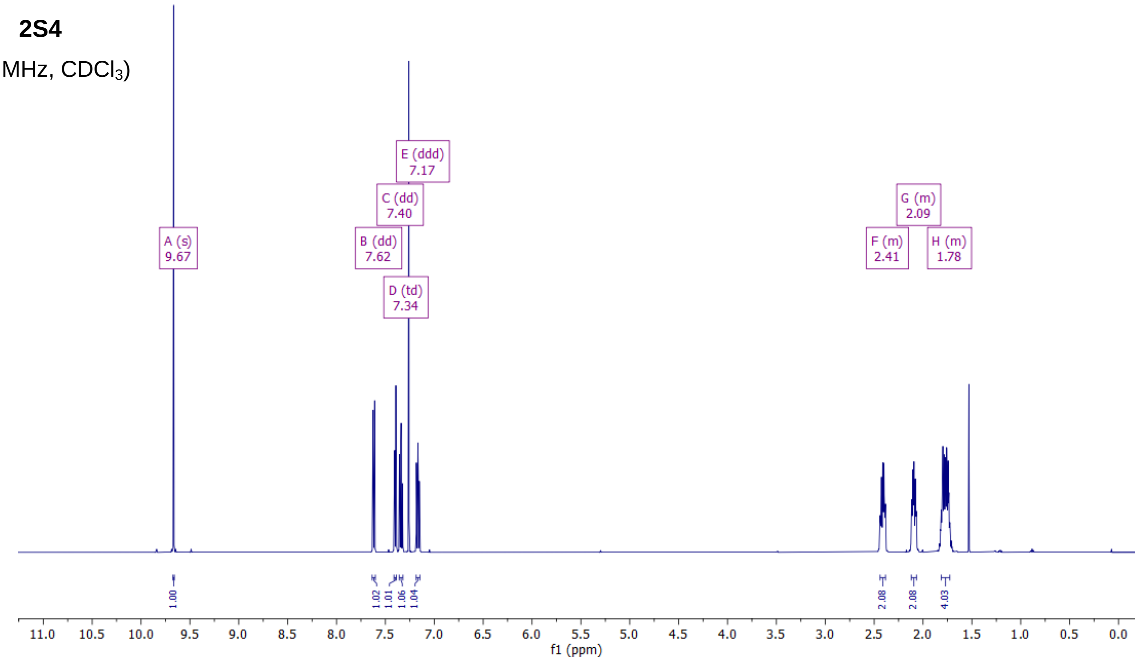
(126 MHz, $CDCl_3$)

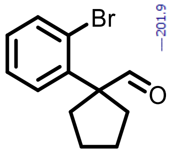




2S4

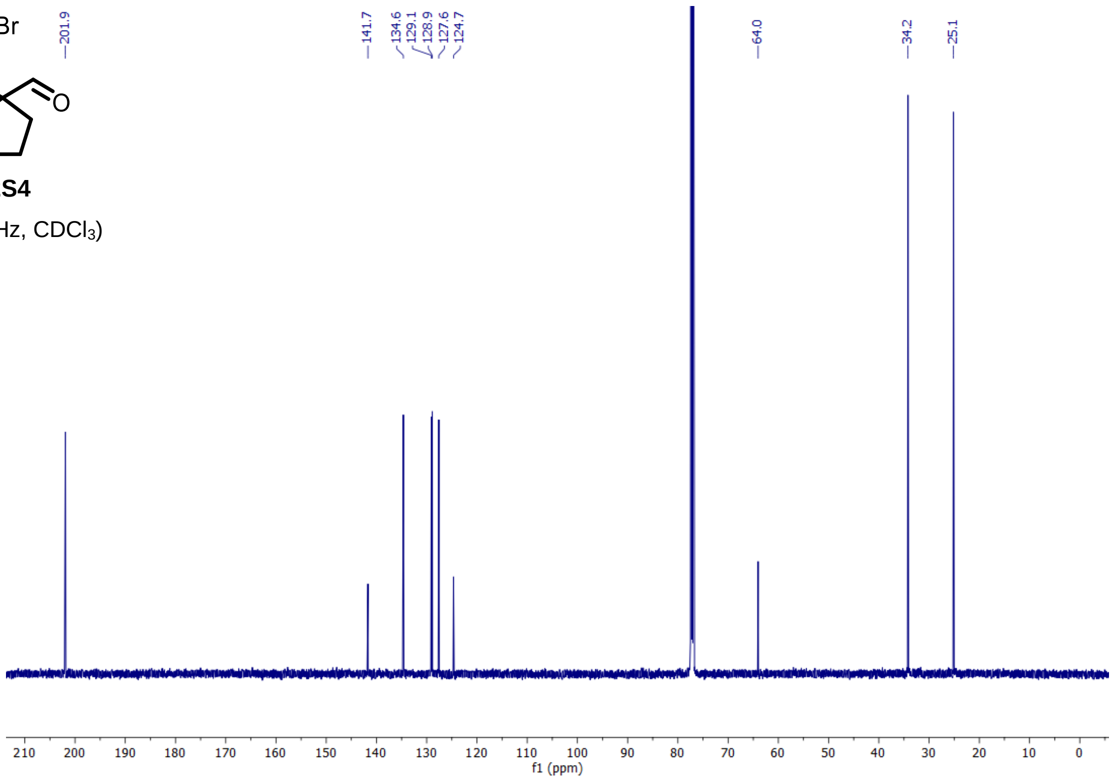
(500 MHz, $CDCl_3$)

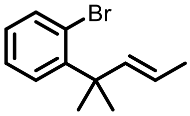




2S4

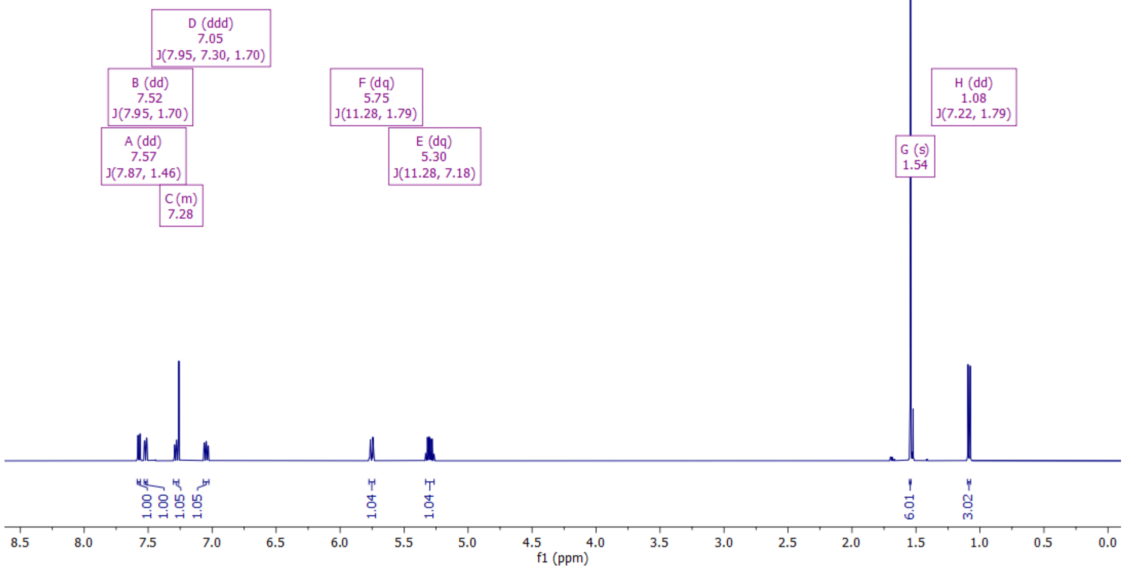
(126 MHz, $CDCl_3$)

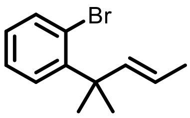




5S1

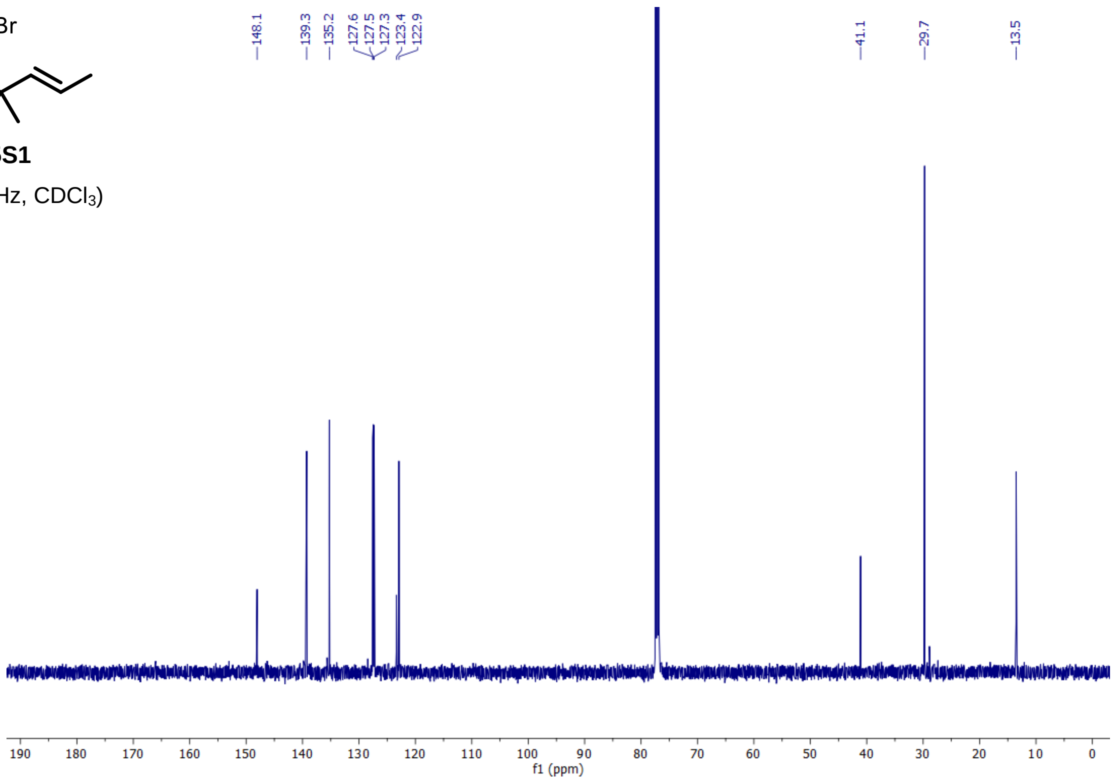
(500 MHz, $CDCl_3$)

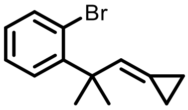




5S1

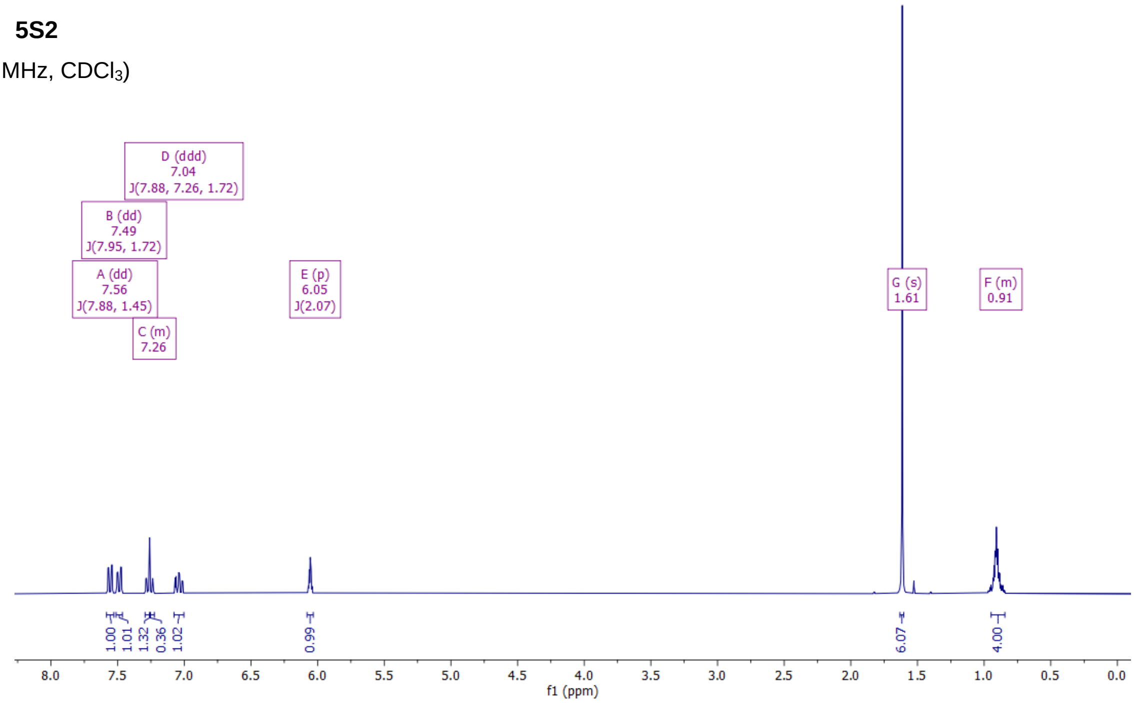
(126 MHz, $CDCl_3$)

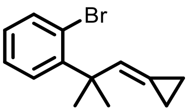




5S2

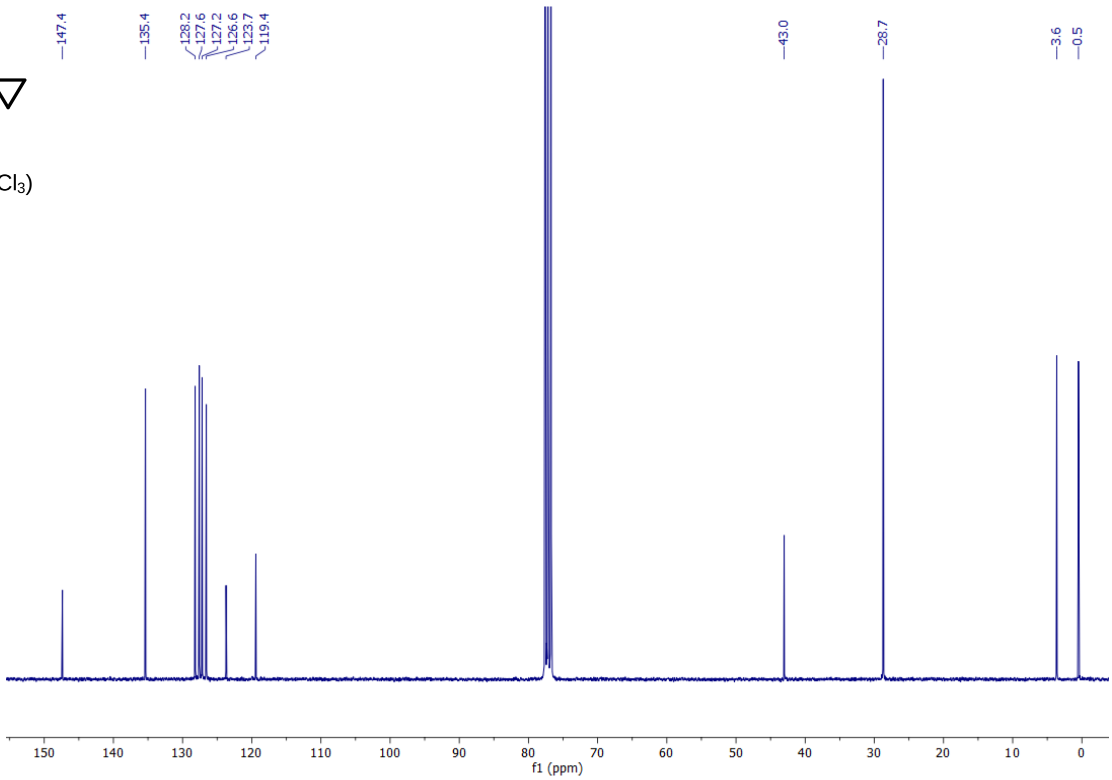
(300 MHz, $CDCl_3$)

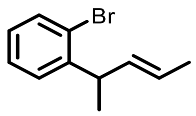




5S2

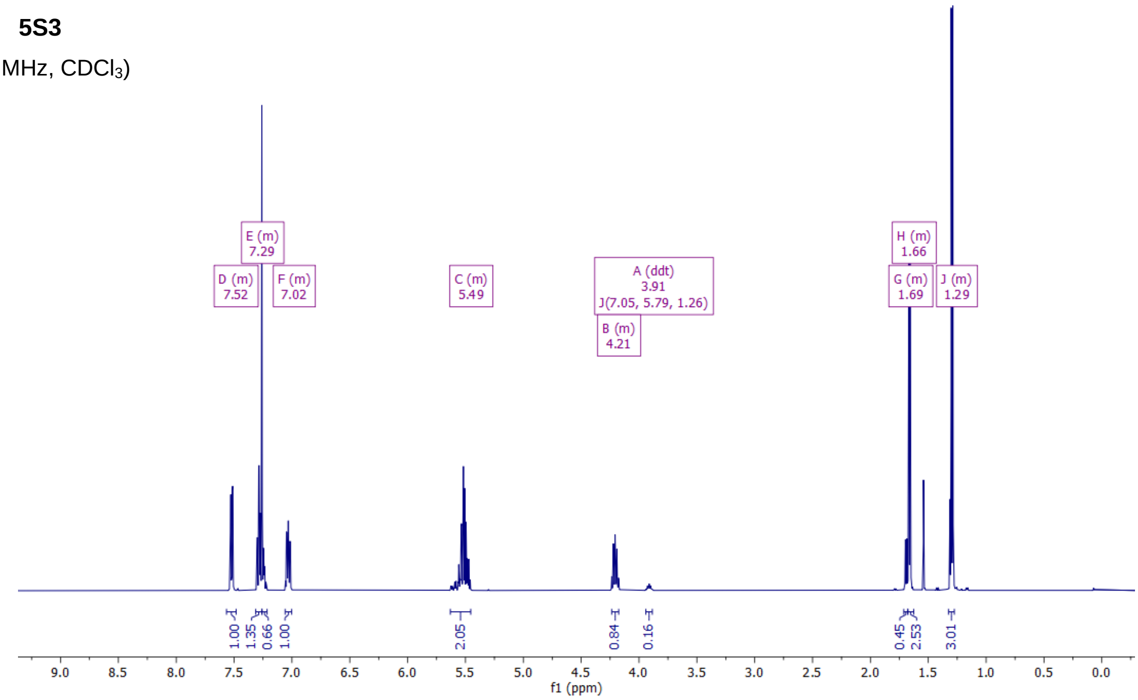
(76 MHz, $CDCl_3$)

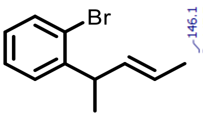




5S3

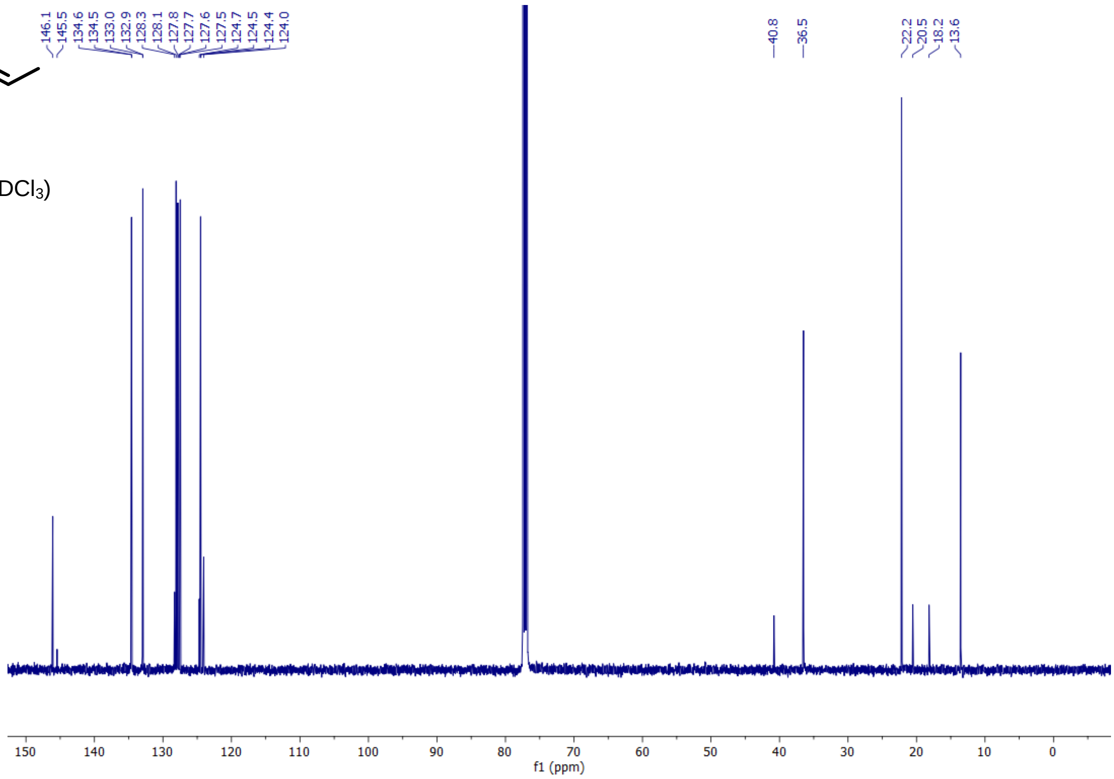
(500 MHz, $CDCl_3$)

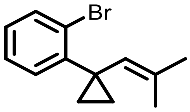




5S3

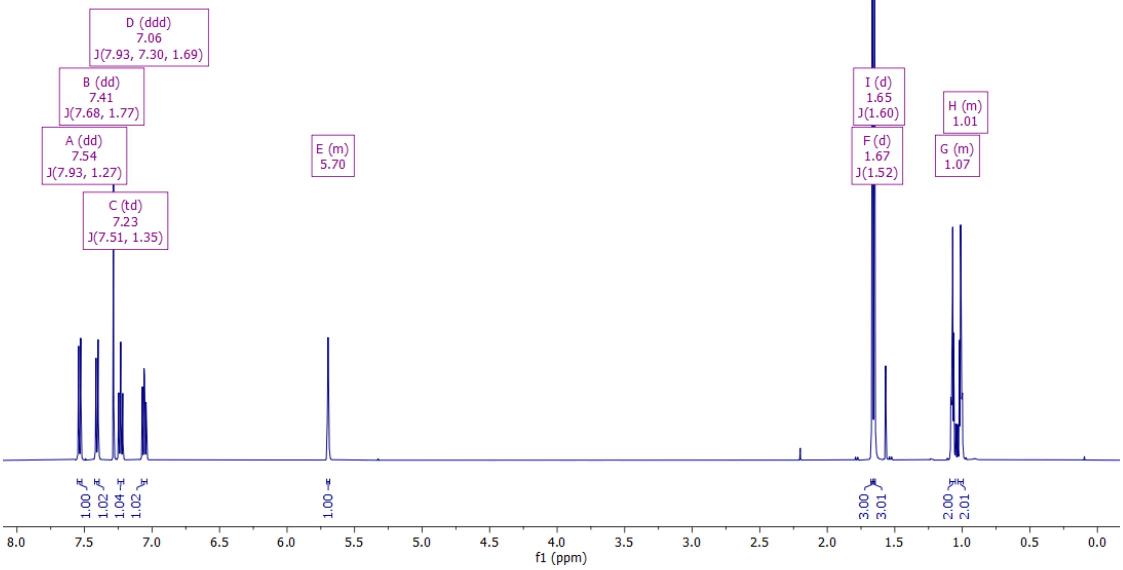
(126 MHz, $CDCl_3$)

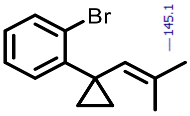




5S4

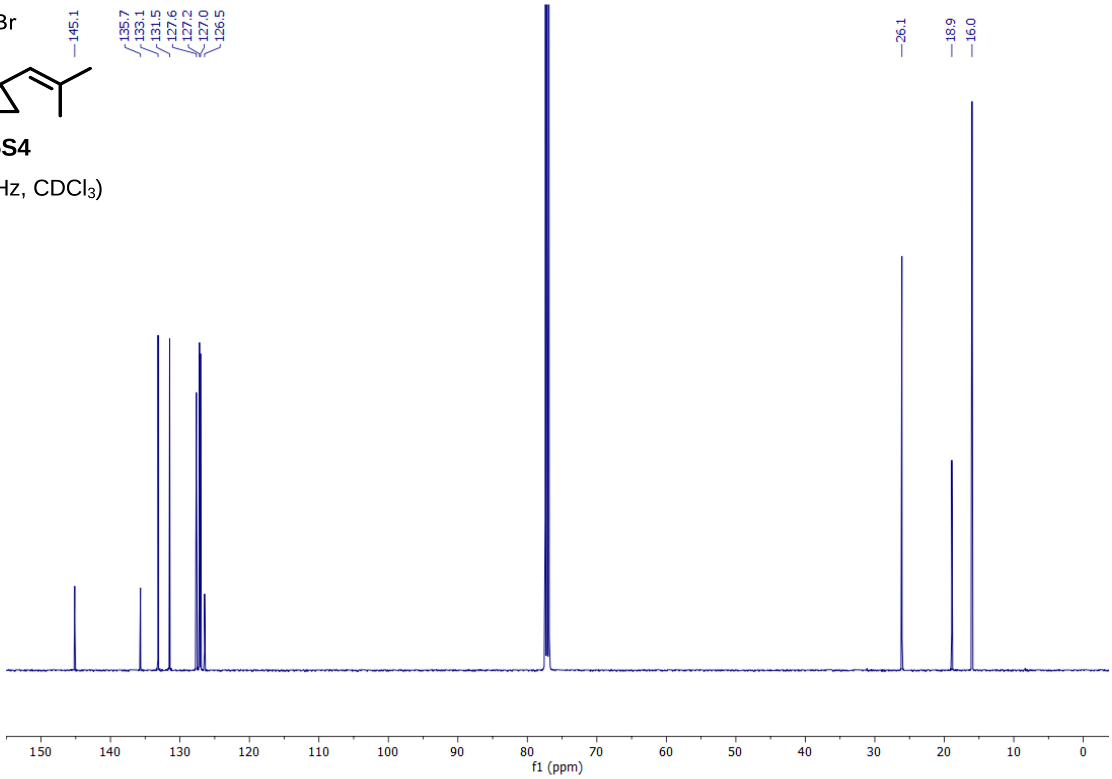
(500 MHz, $CDCl_3$)

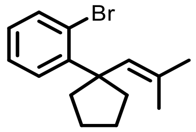




5S4

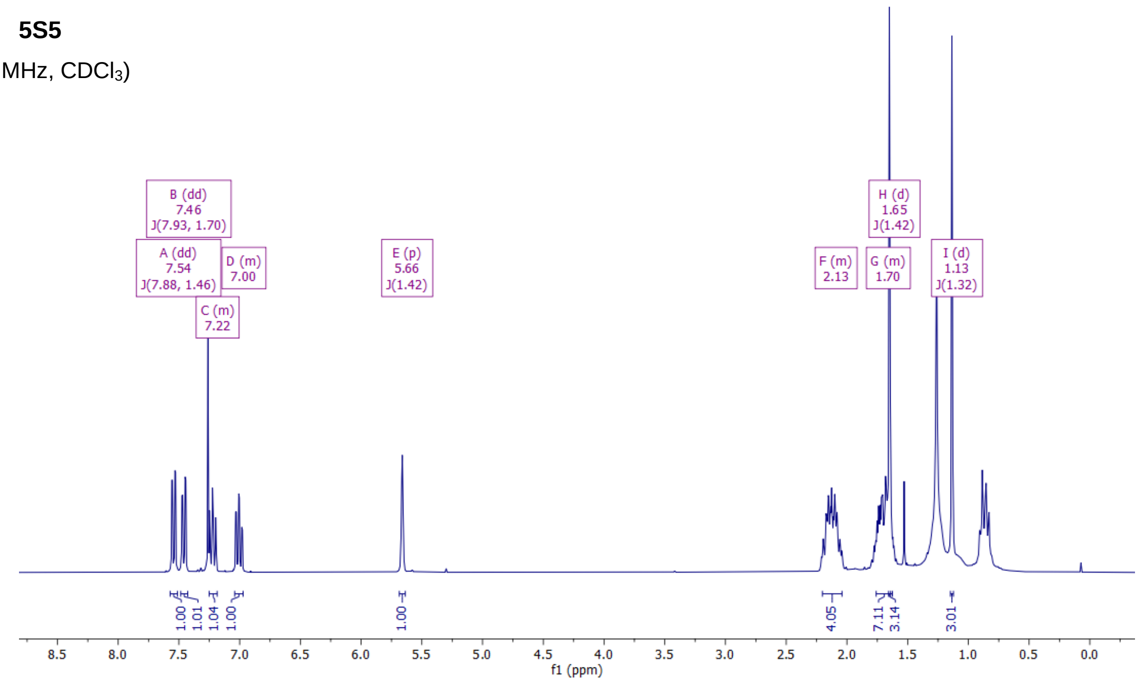
(126 MHz, $CDCl_3$)

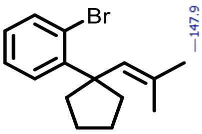




5S5

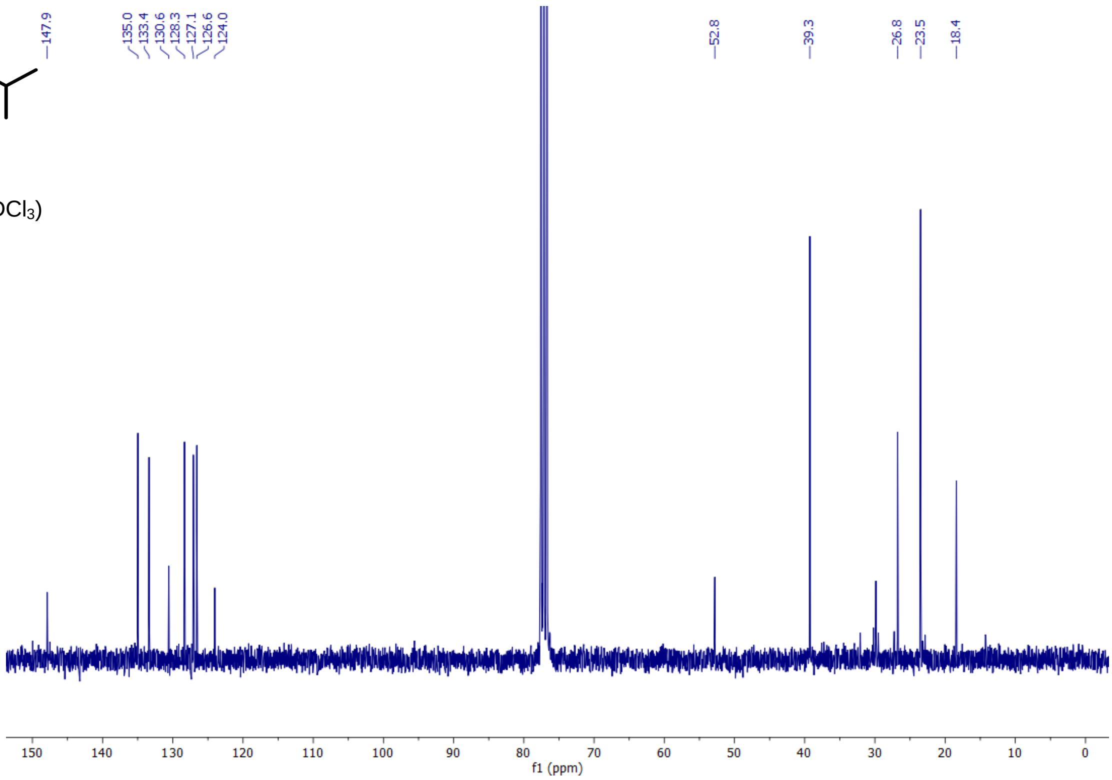
(300 MHz, $CDCl_3$)

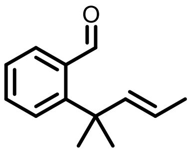




5S5

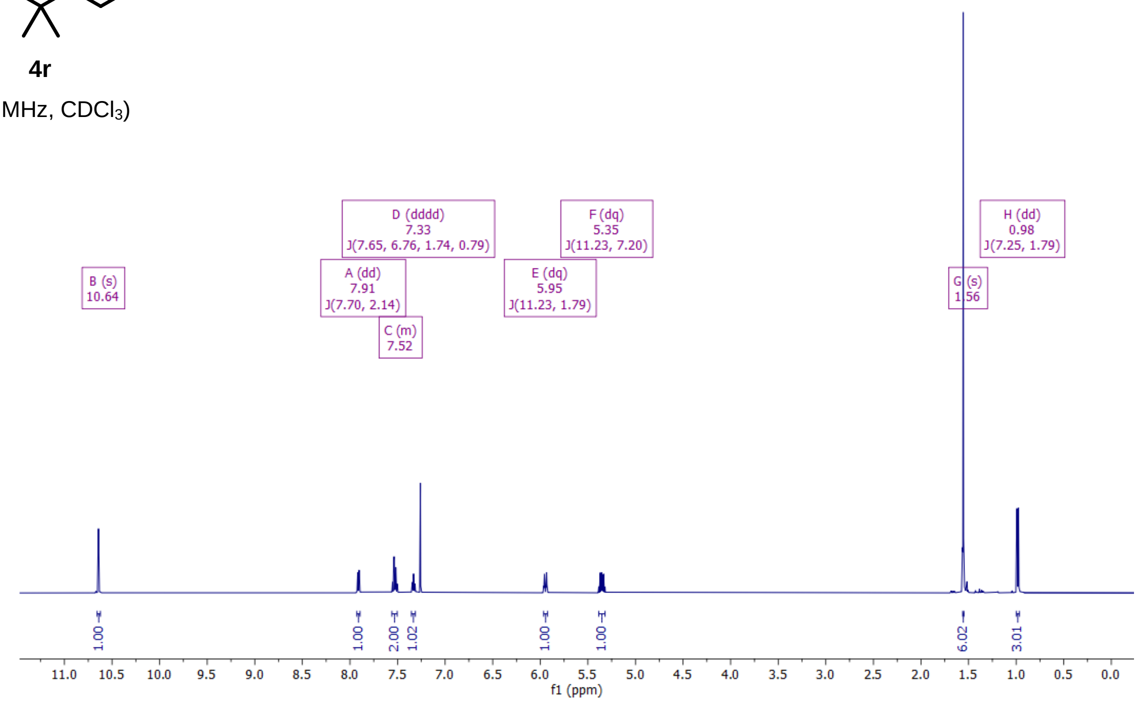
(75 MHz, $CDCl_3$)

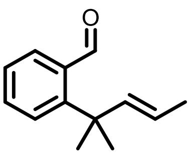




4r

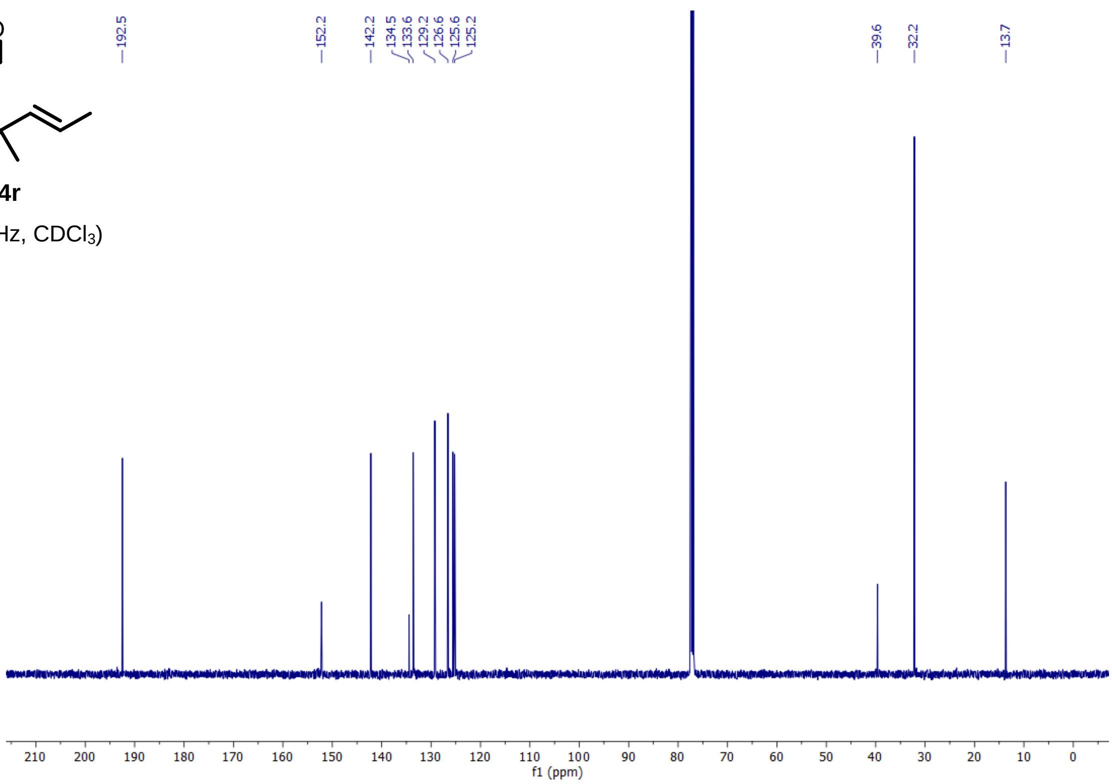
(500 MHz, $CDCl_3$)

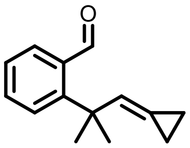




4r

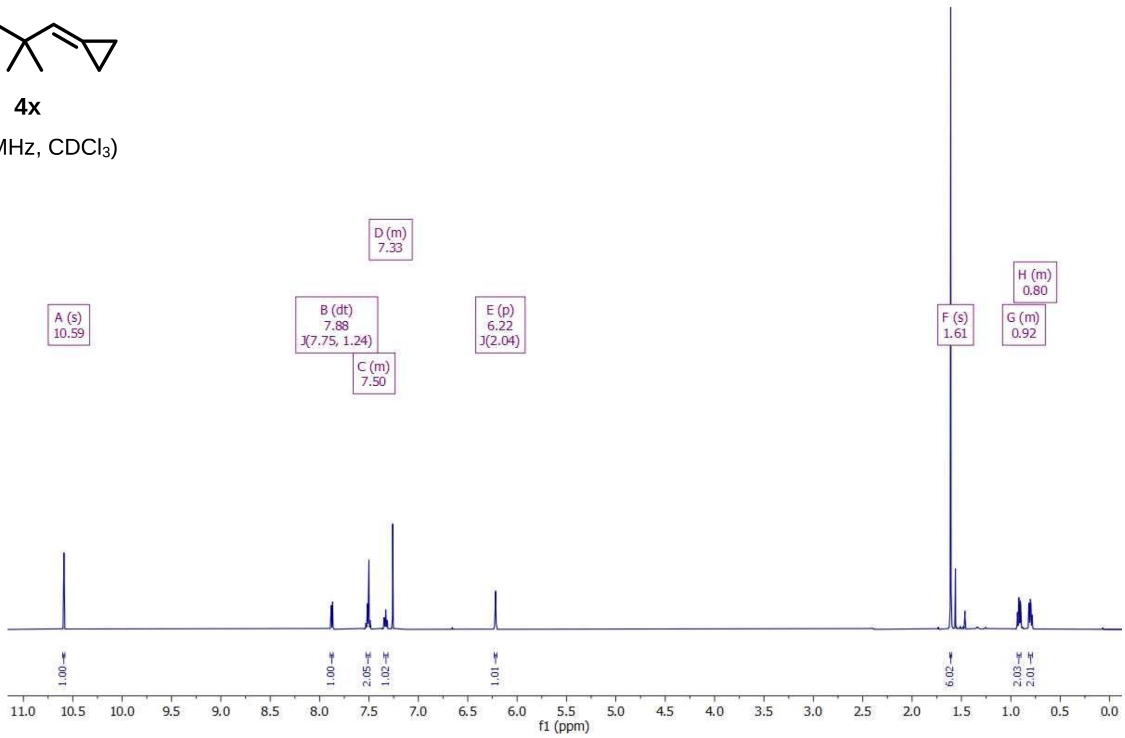
(126 MHz, $CDCl_3$)

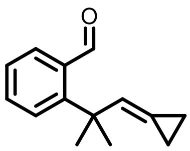




4x

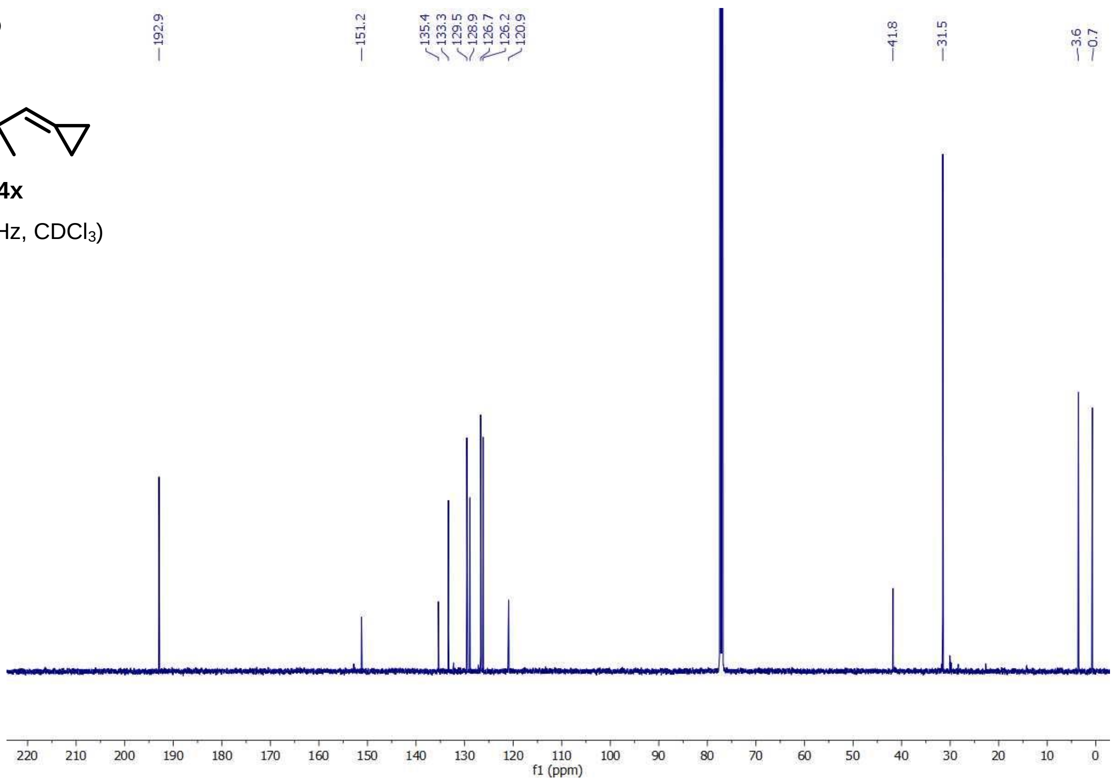
(500 MHz, $CDCl_3$)

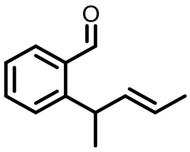




4x

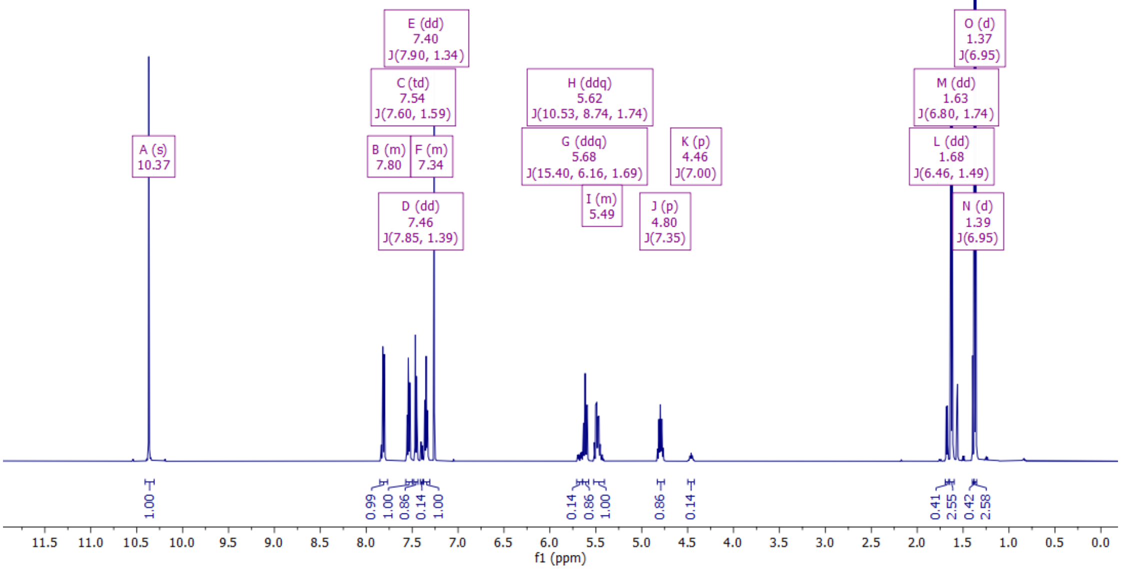
(126 MHz, $CDCl_3$)

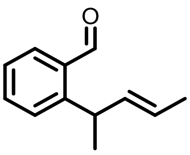




4n

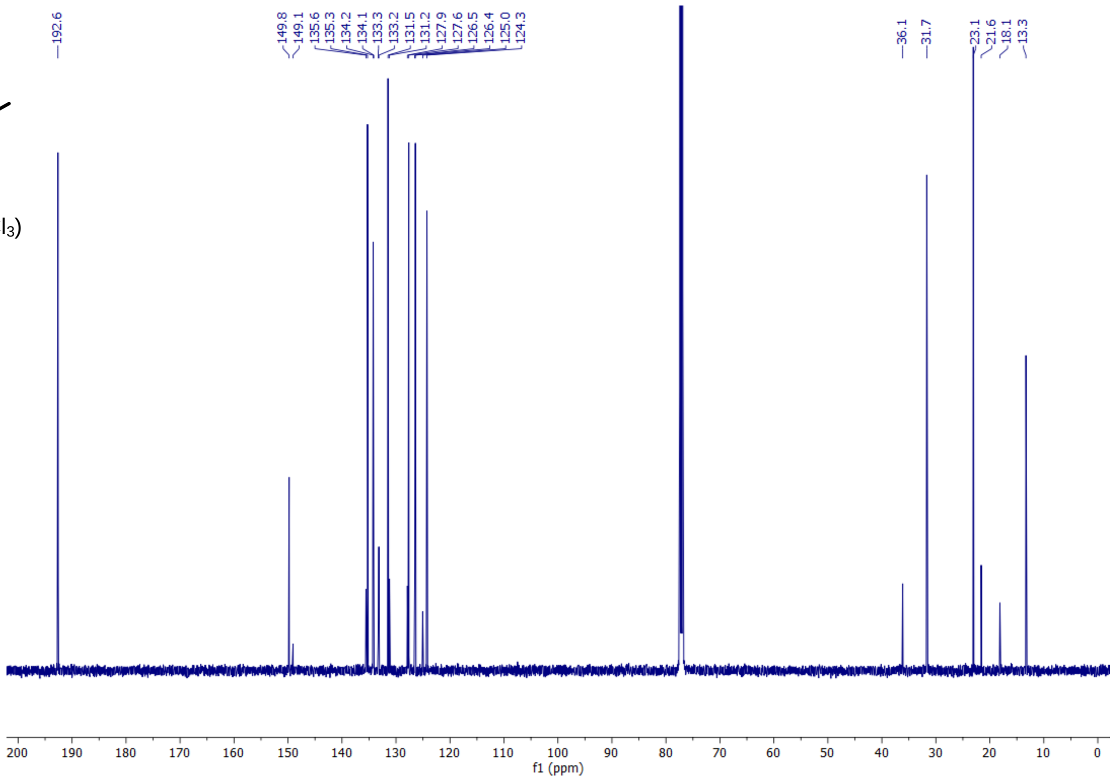
(500 MHz, $CDCl_3$)

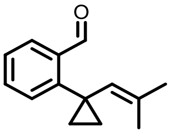




4n

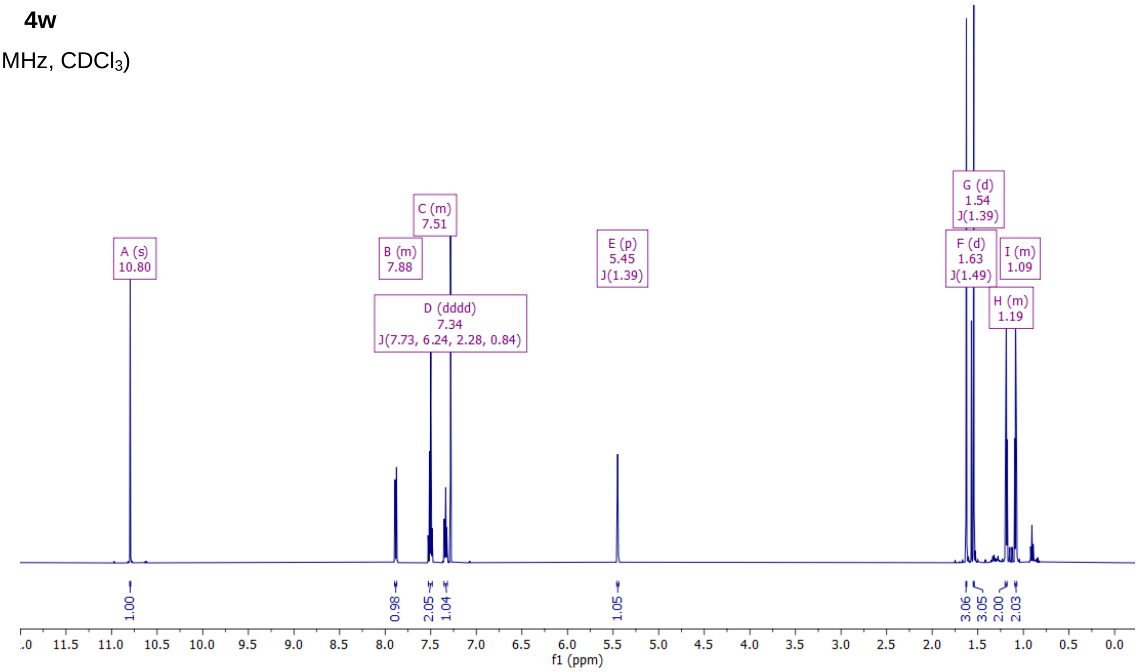
(126 MHz, $CDCl_3$)

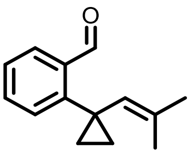




4w

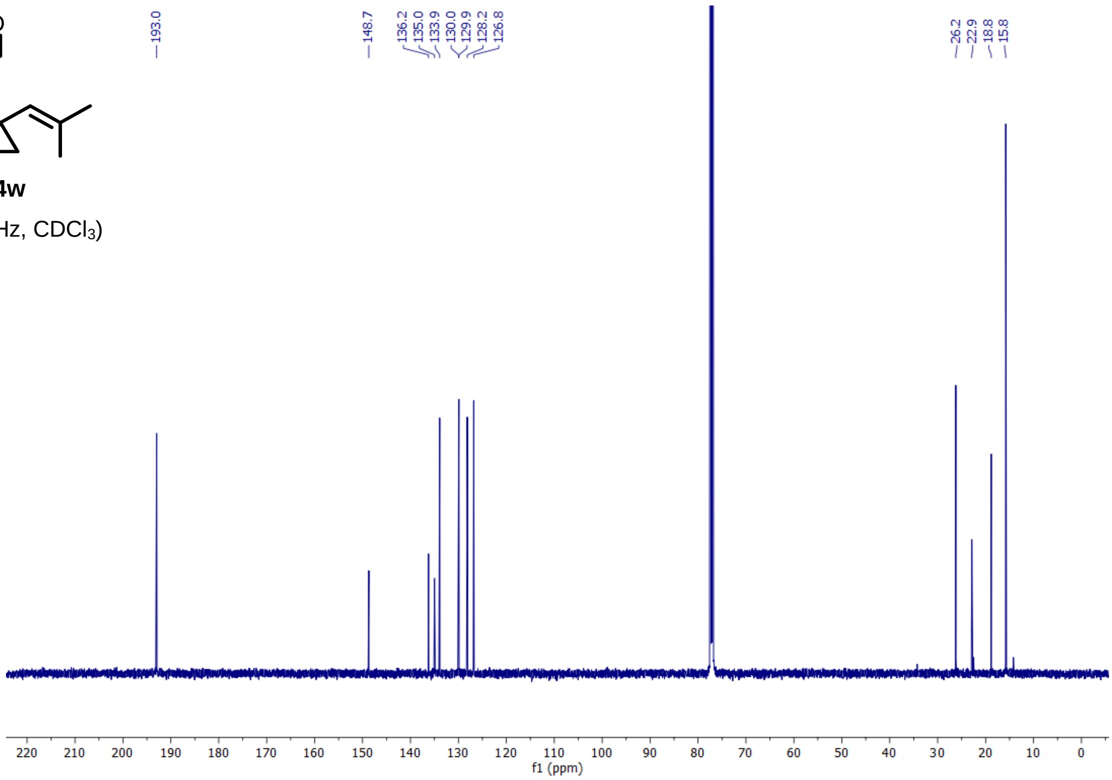
(500 MHz, $CDCl_3$)

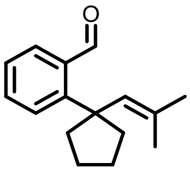




4w

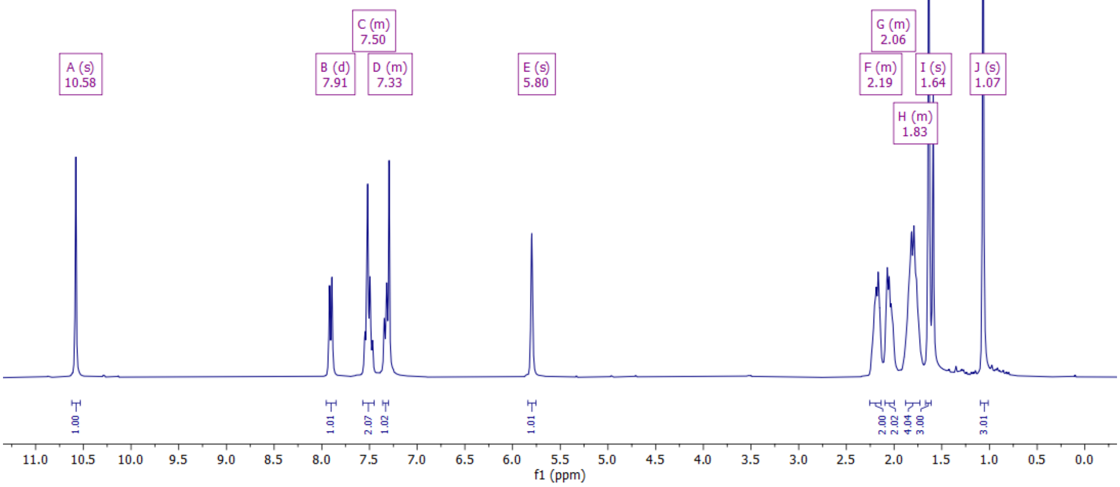
(126 MHz, $CDCl_3$)

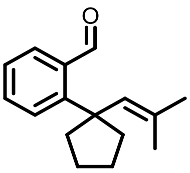




4s

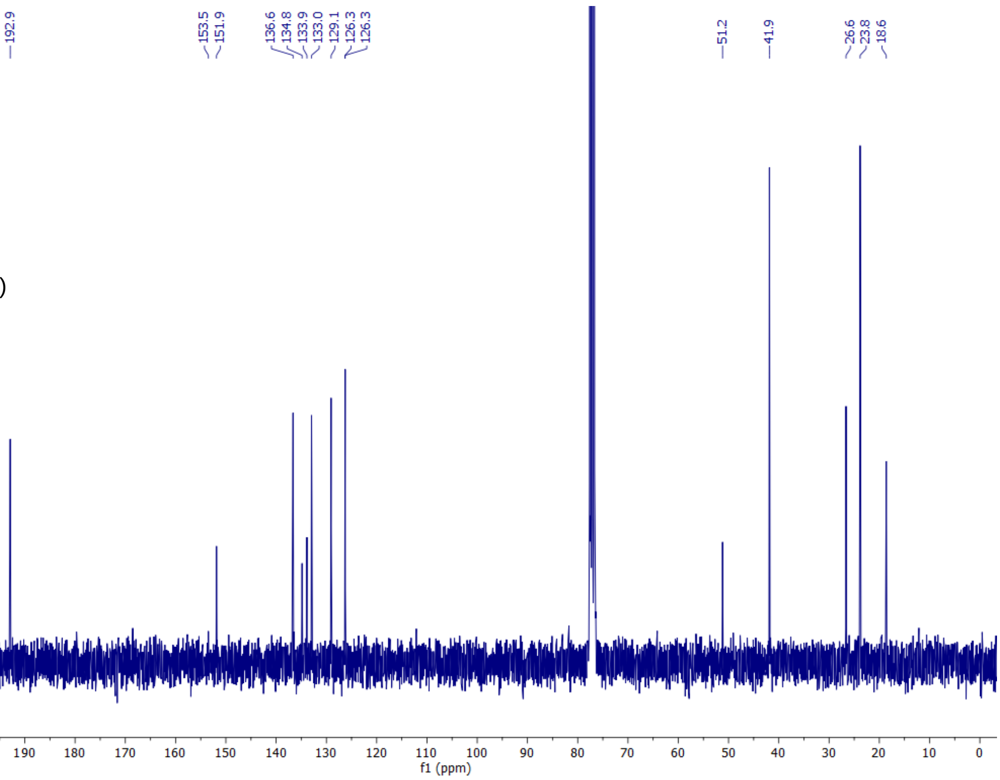
(300 MHz, $CDCl_3$)

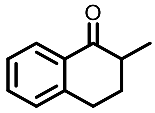




4s

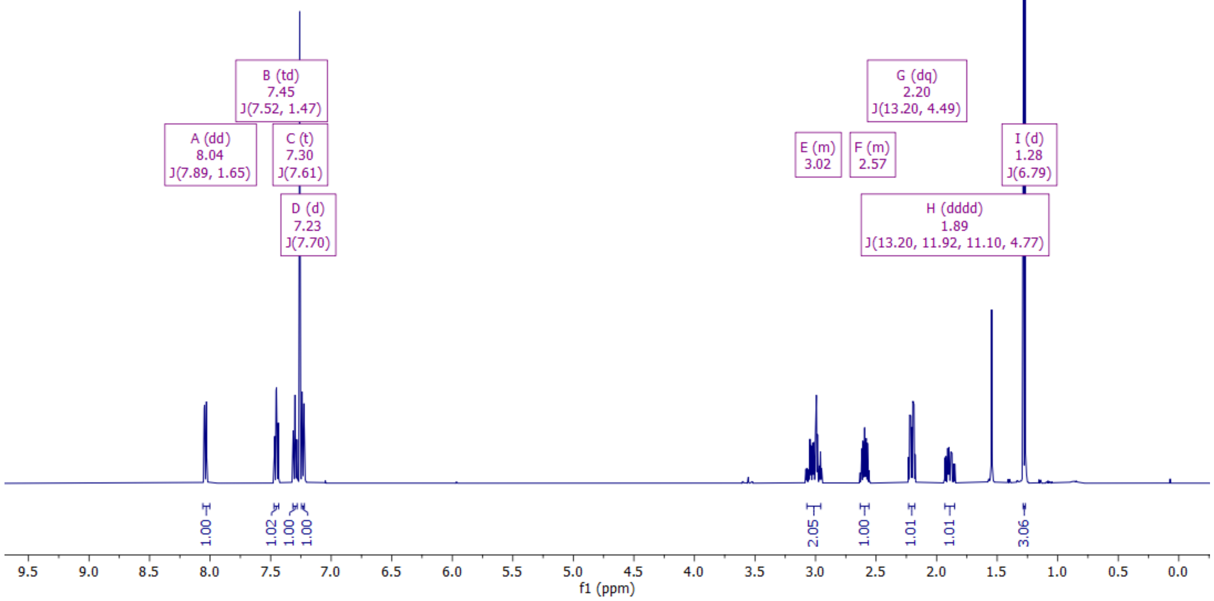
(126 MHz, $CDCl_3$)

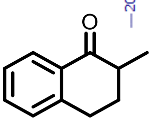




6k

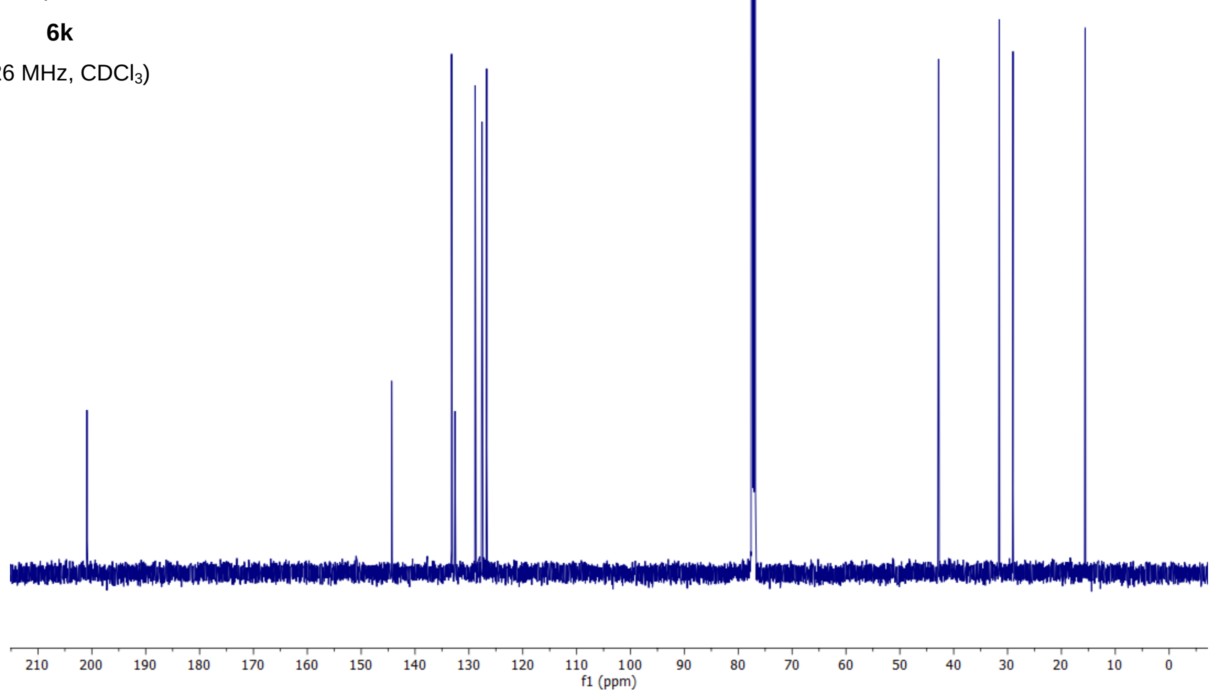
(500 MHz, $CDCl_3$)

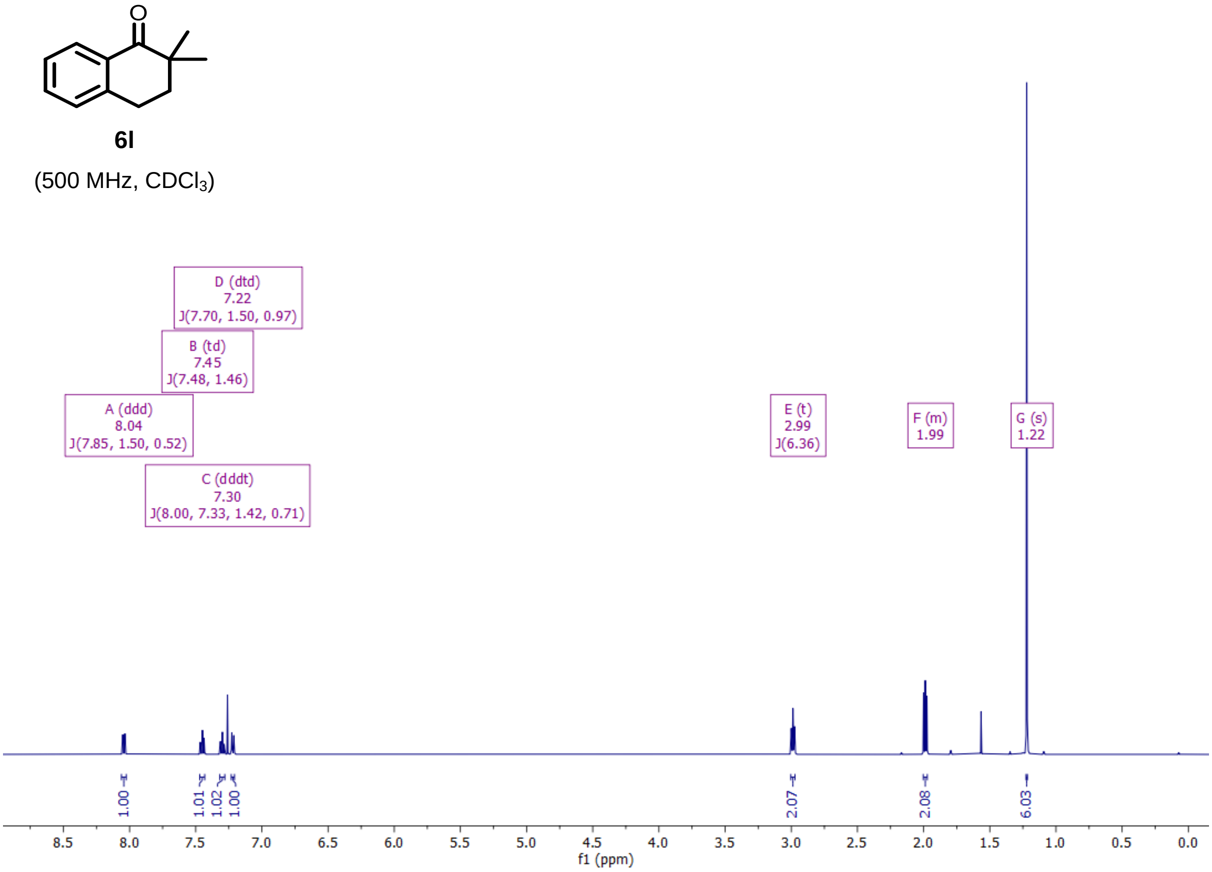




6k

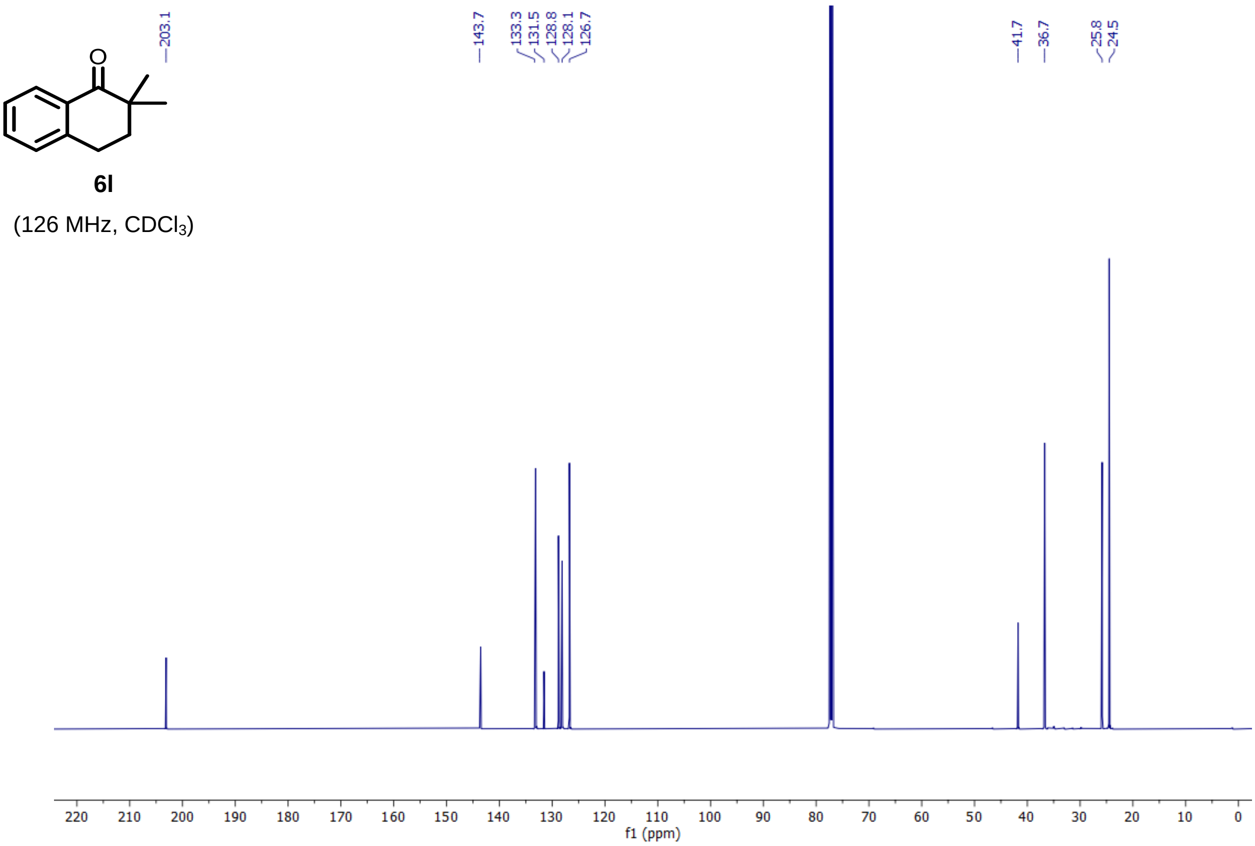
(126 MHz, $CDCl_3$)





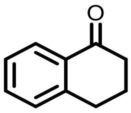
6l

(500 MHz, $CDCl_3$)



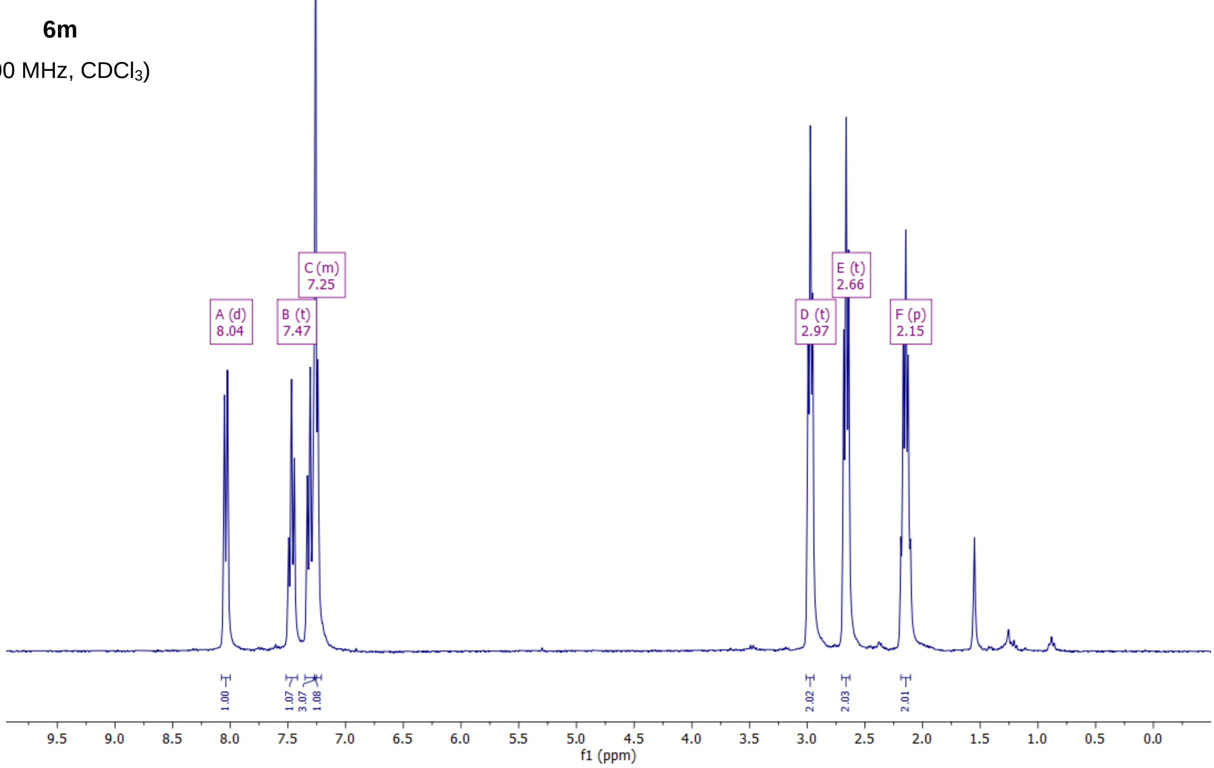
6l

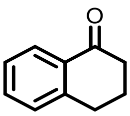
(126 MHz, $CDCl_3$)



6m

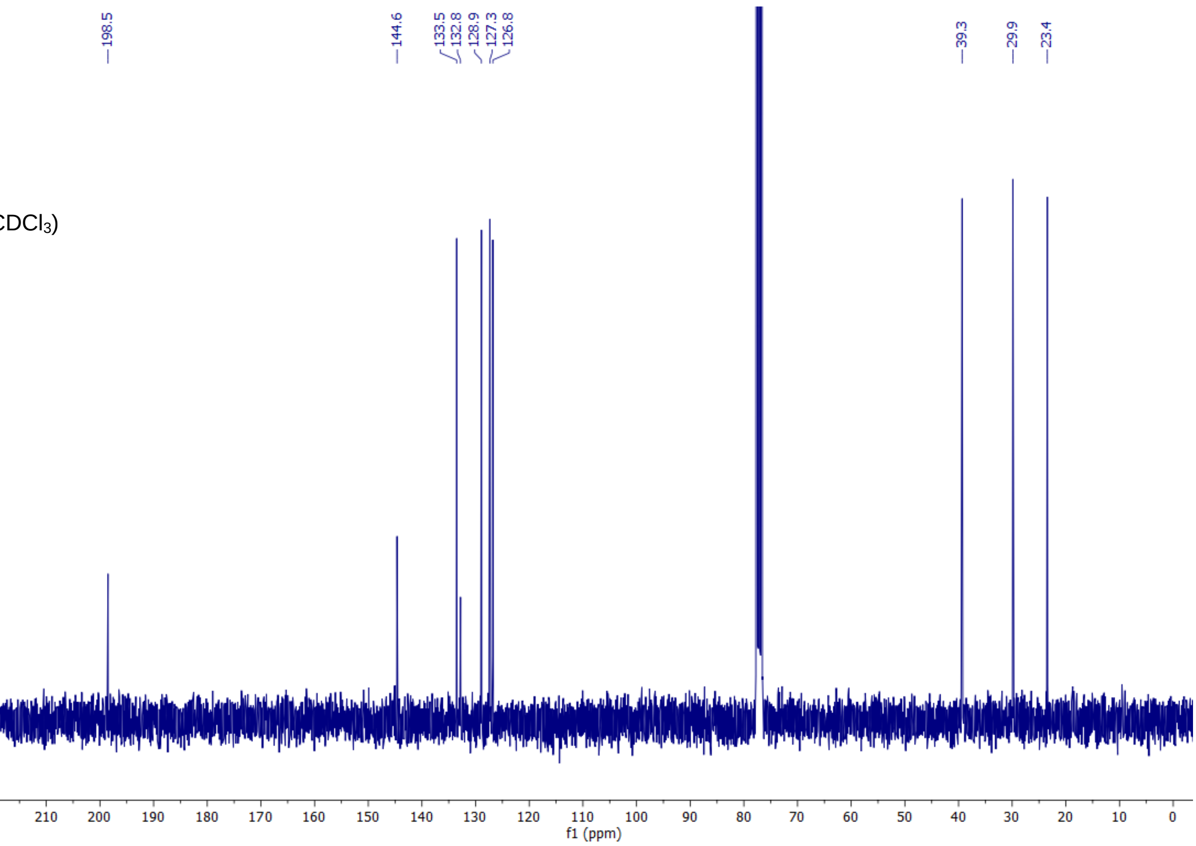
(300 MHz, $CDCl_3$)

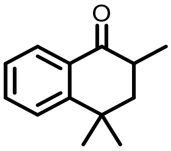




6m

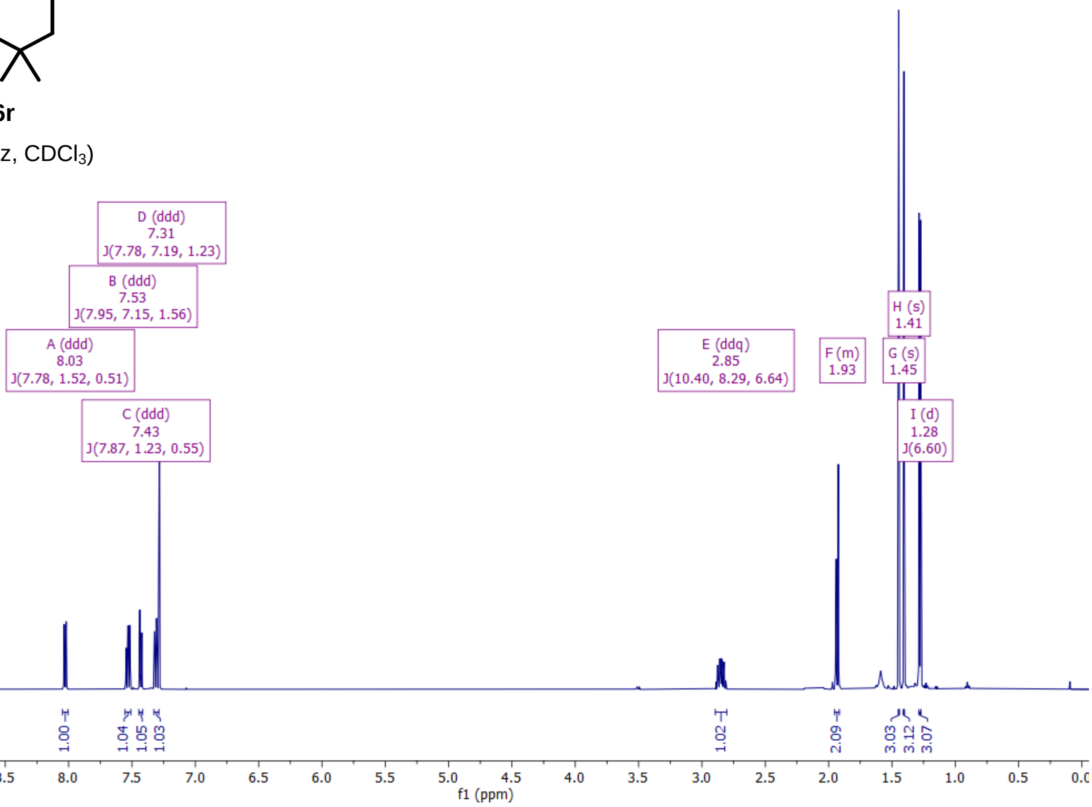
(75 MHz, $CDCl_3$)

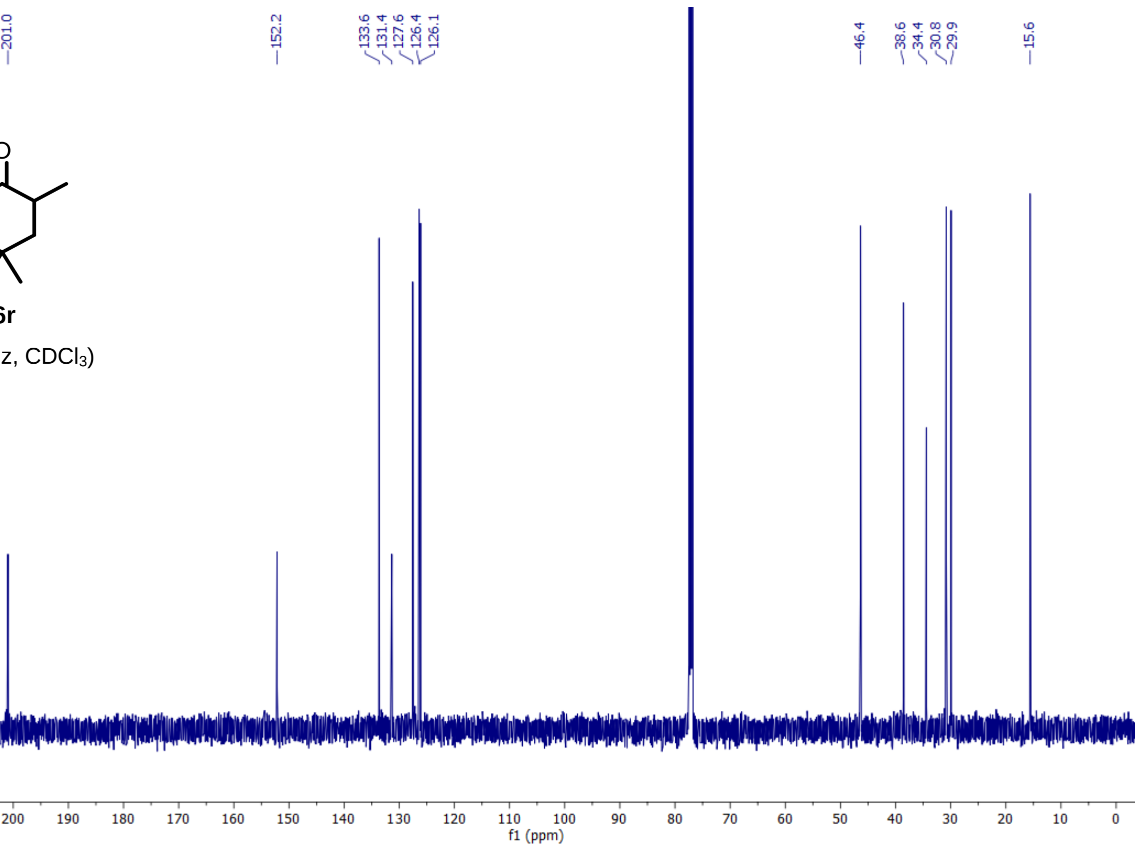


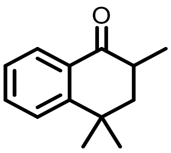


6r

(500 MHz, $CDCl_3$)

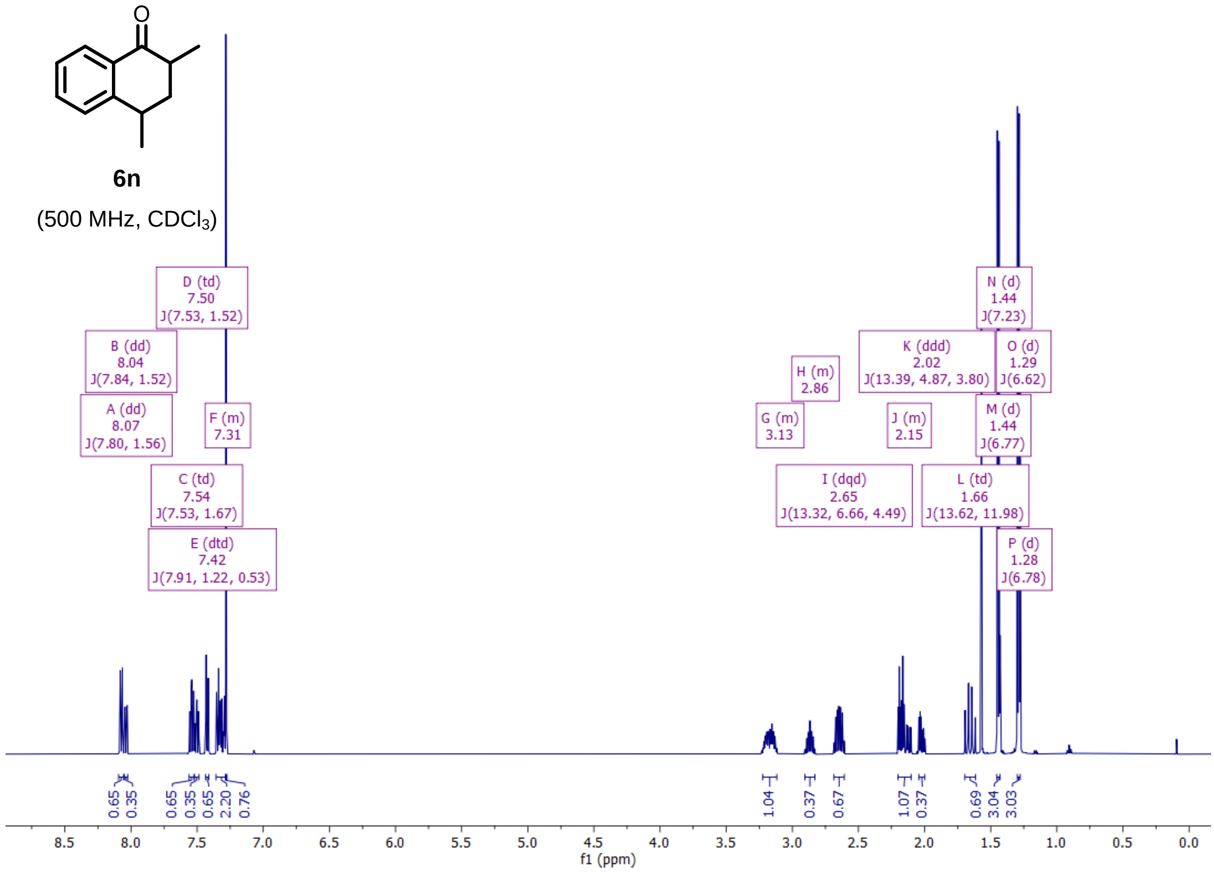






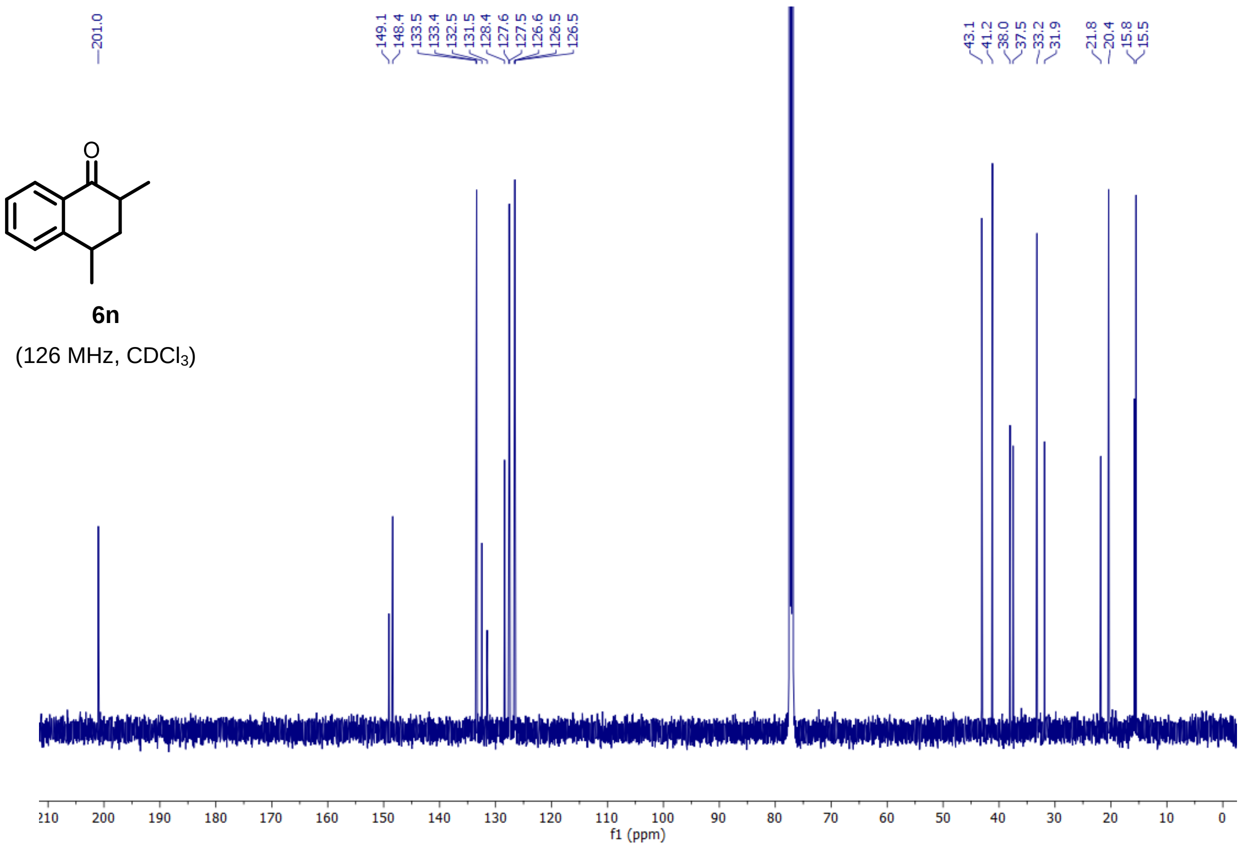
6r

(126 MHz, $CDCl_3$)



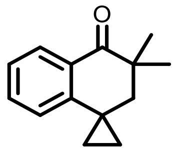
6n

(500 MHz, $CDCl_3$)



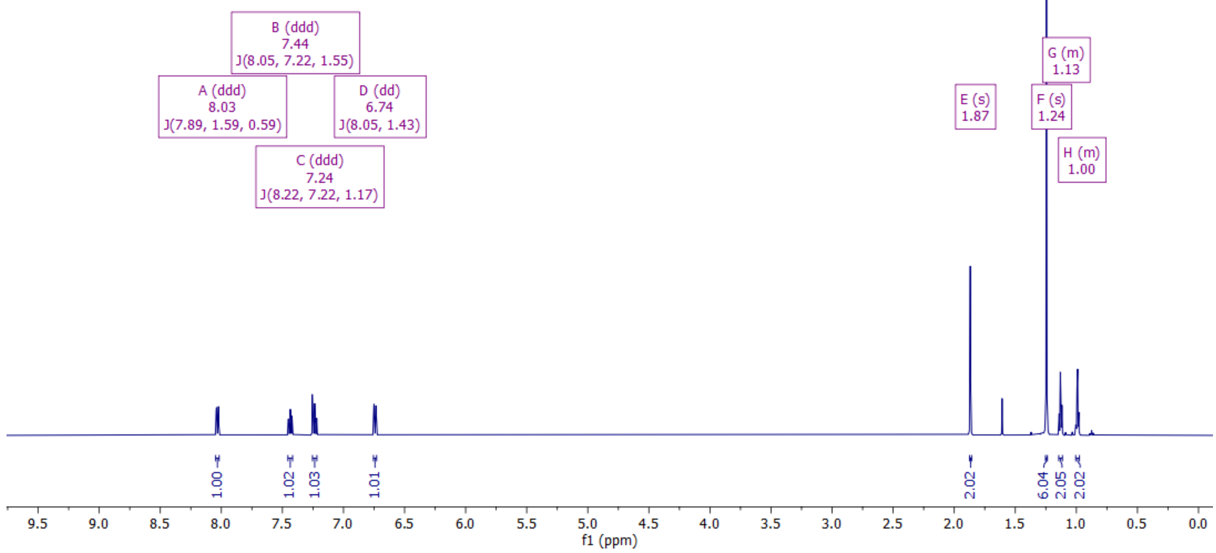
6n

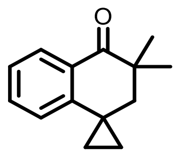
(126 MHz, $CDCl_3$)



6w

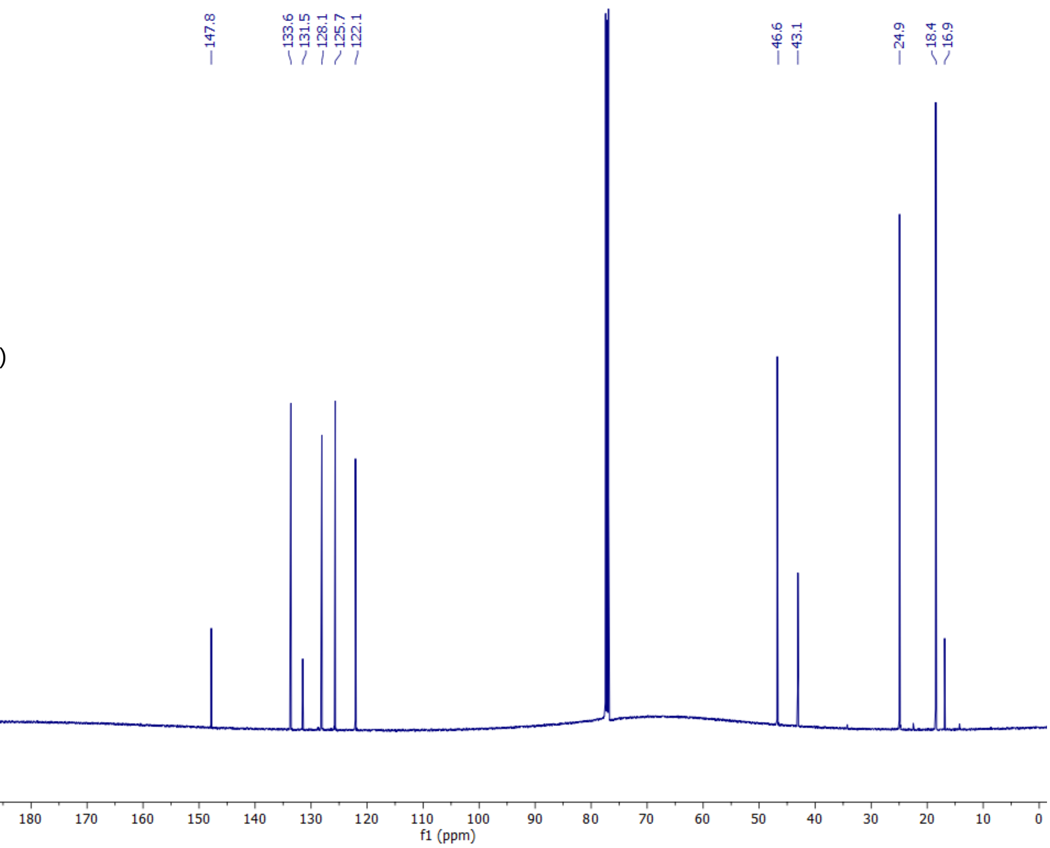
(500 MHz, $CDCl_3$)

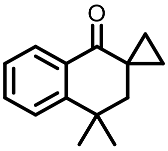




6w

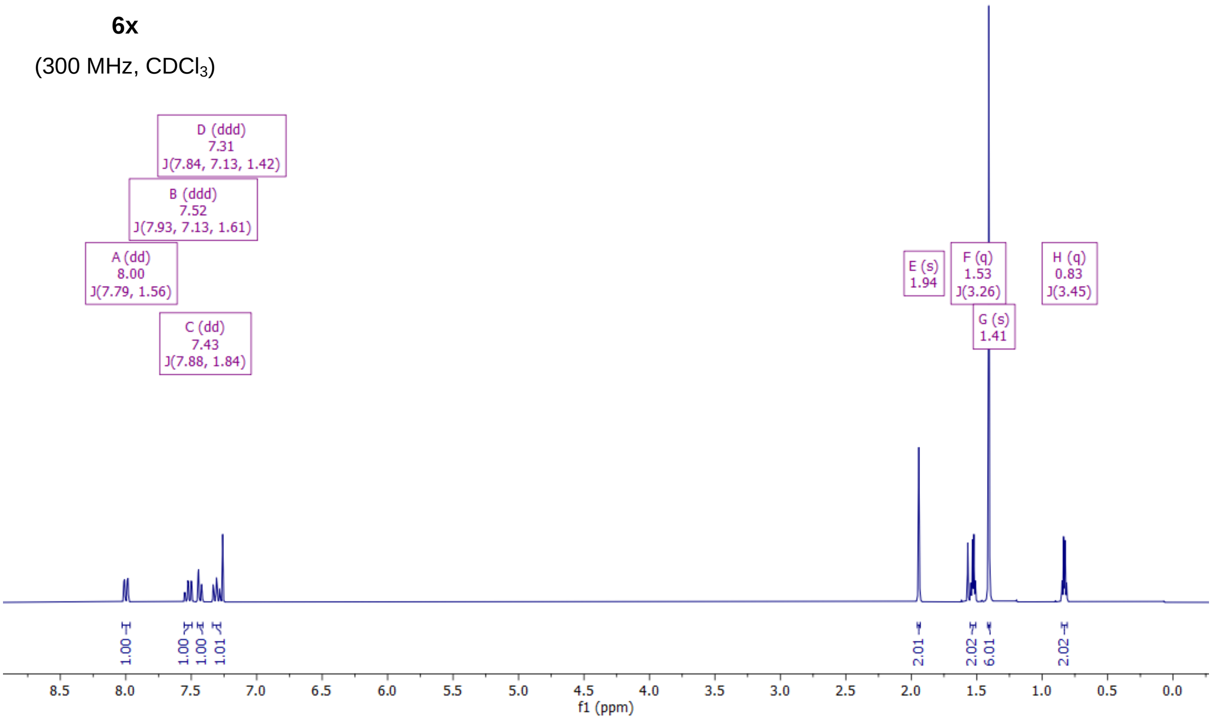
(126 MHz, $CDCl_3$)

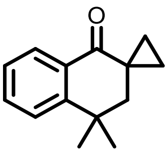




6x

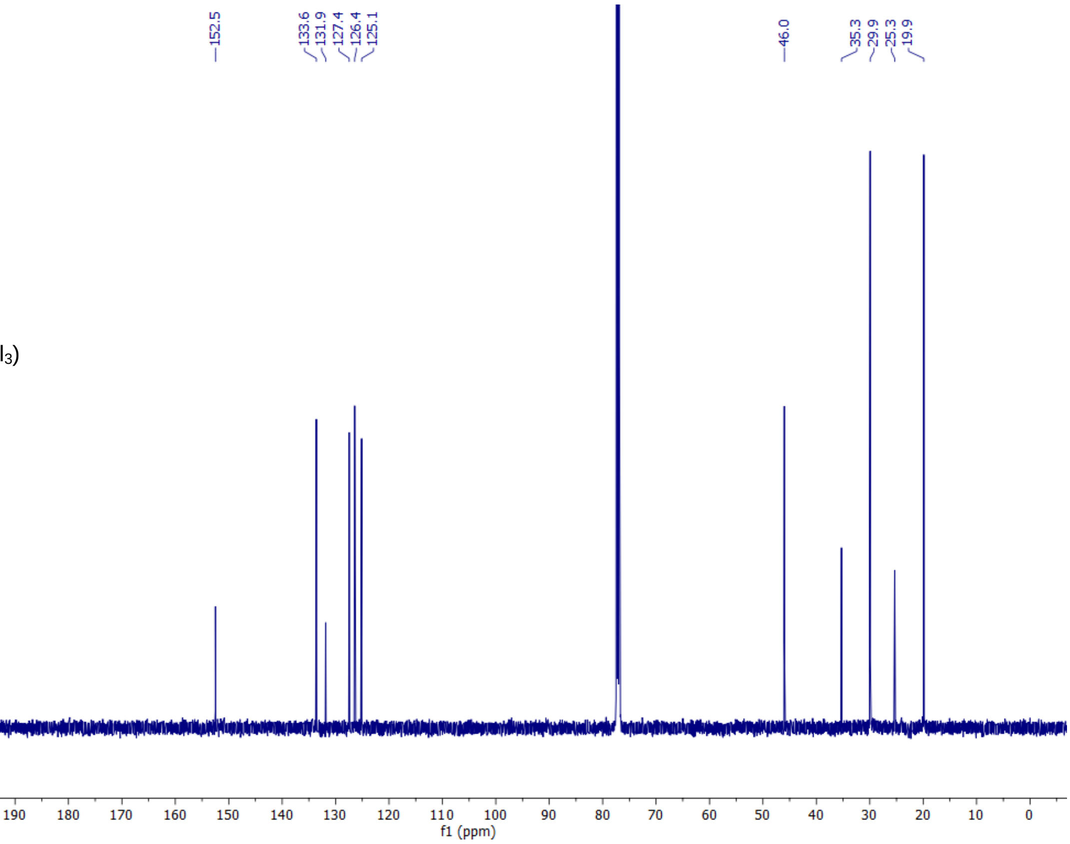
(300 MHz, $CDCl_3$)

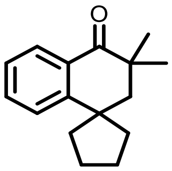




6x

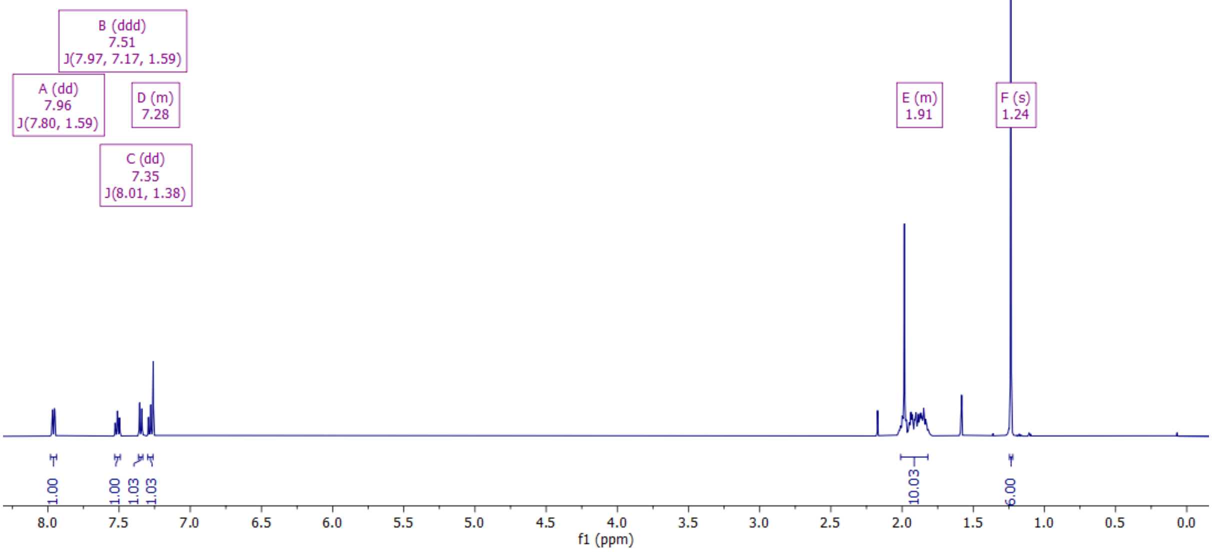
(75 MHz, $CDCl_3$)

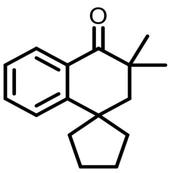




6s

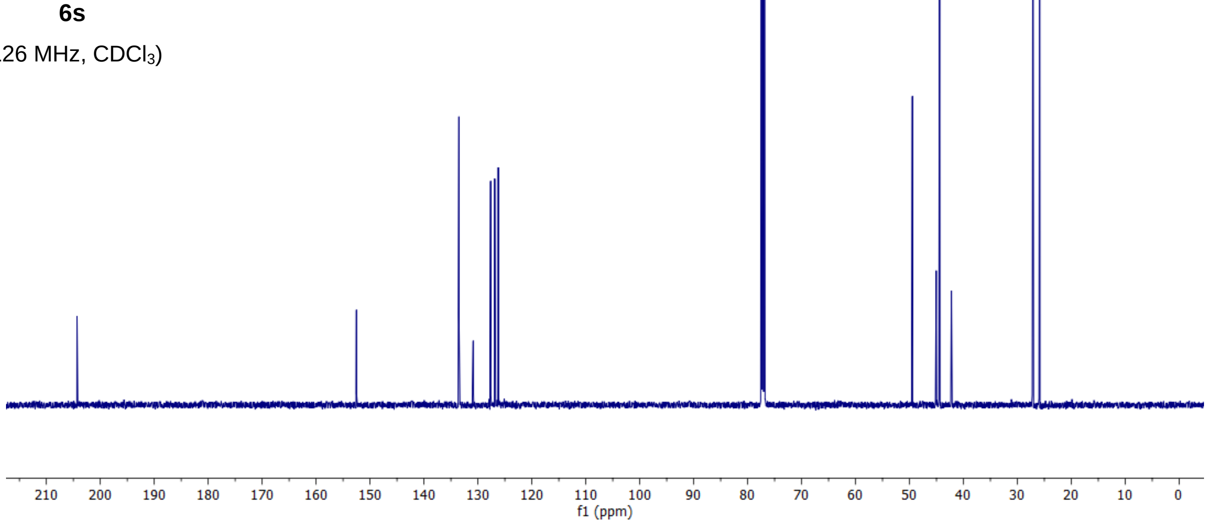
(500 MHz, $CDCl_3$)

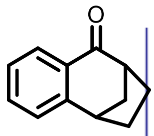




6s

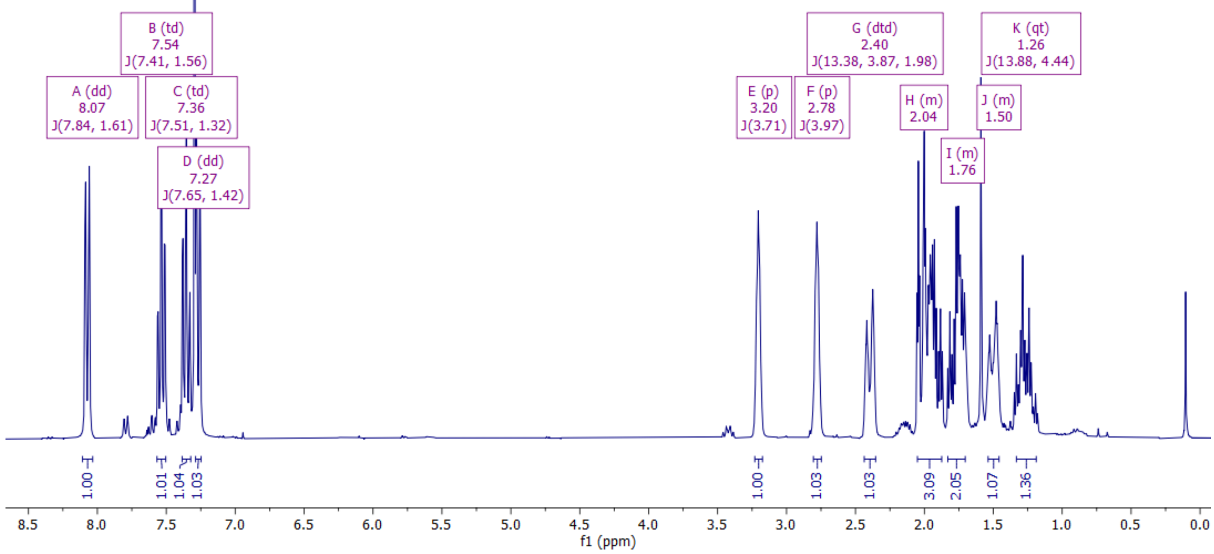
(126 MHz, $CDCl_3$)

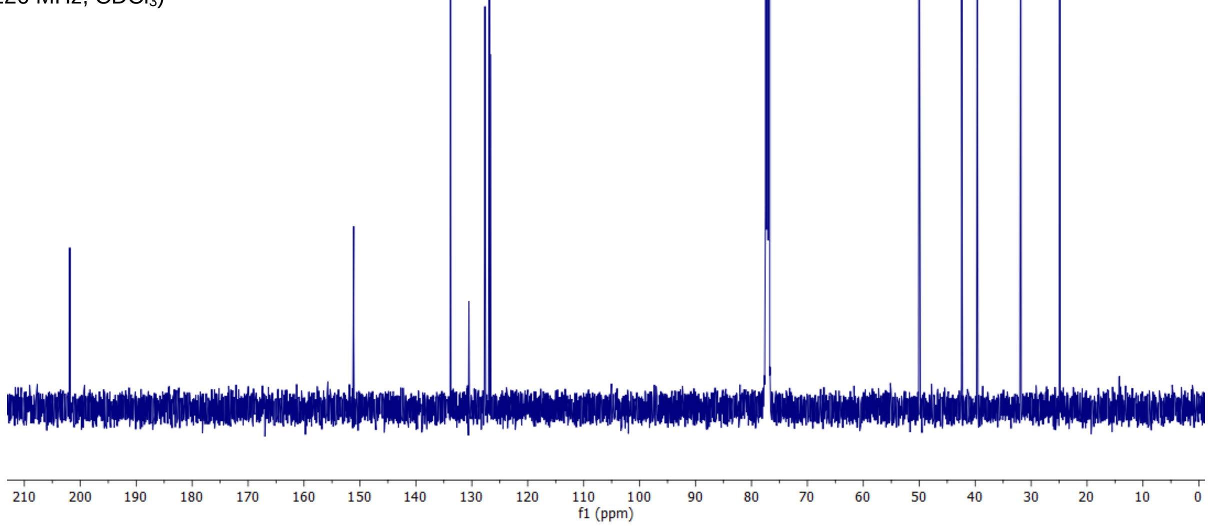


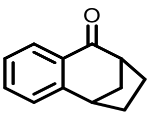


6o

(500 MHz, $CDCl_3$)

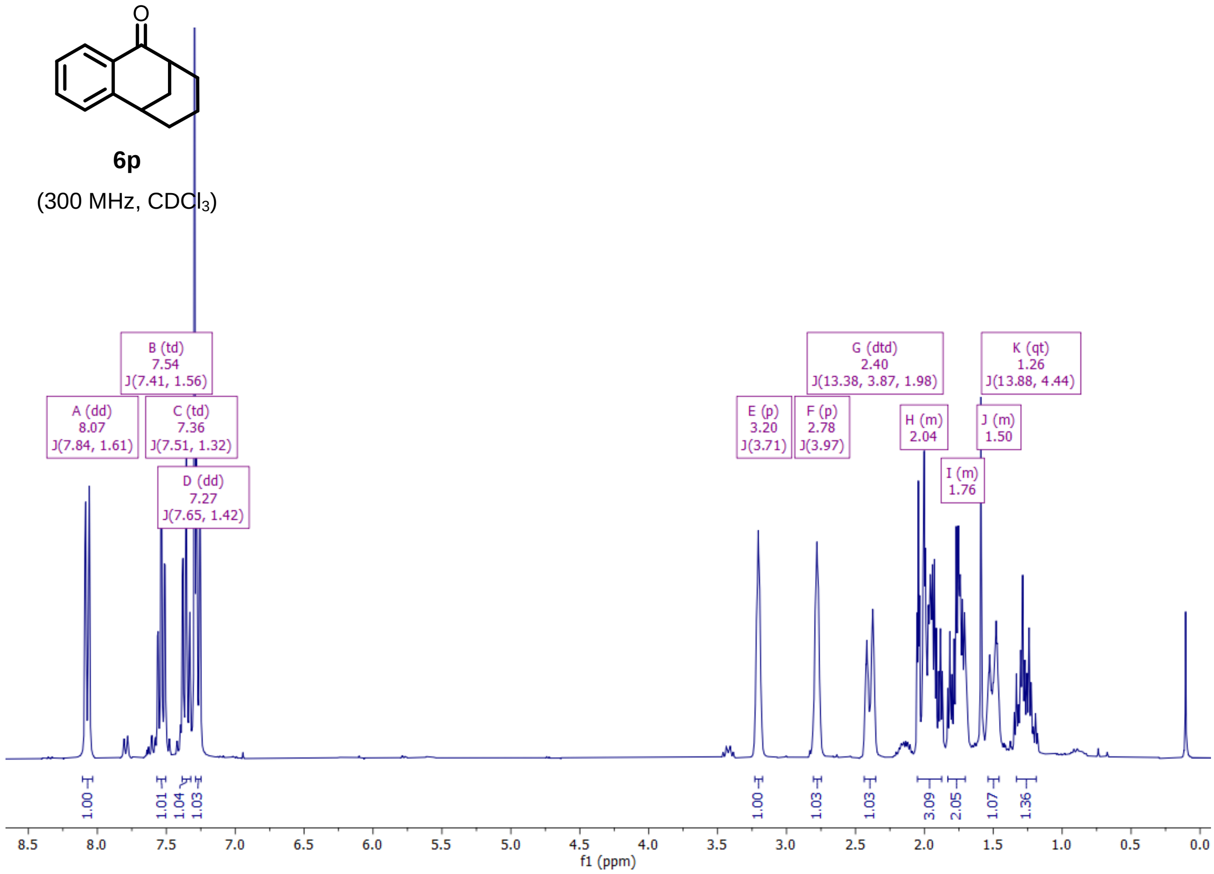






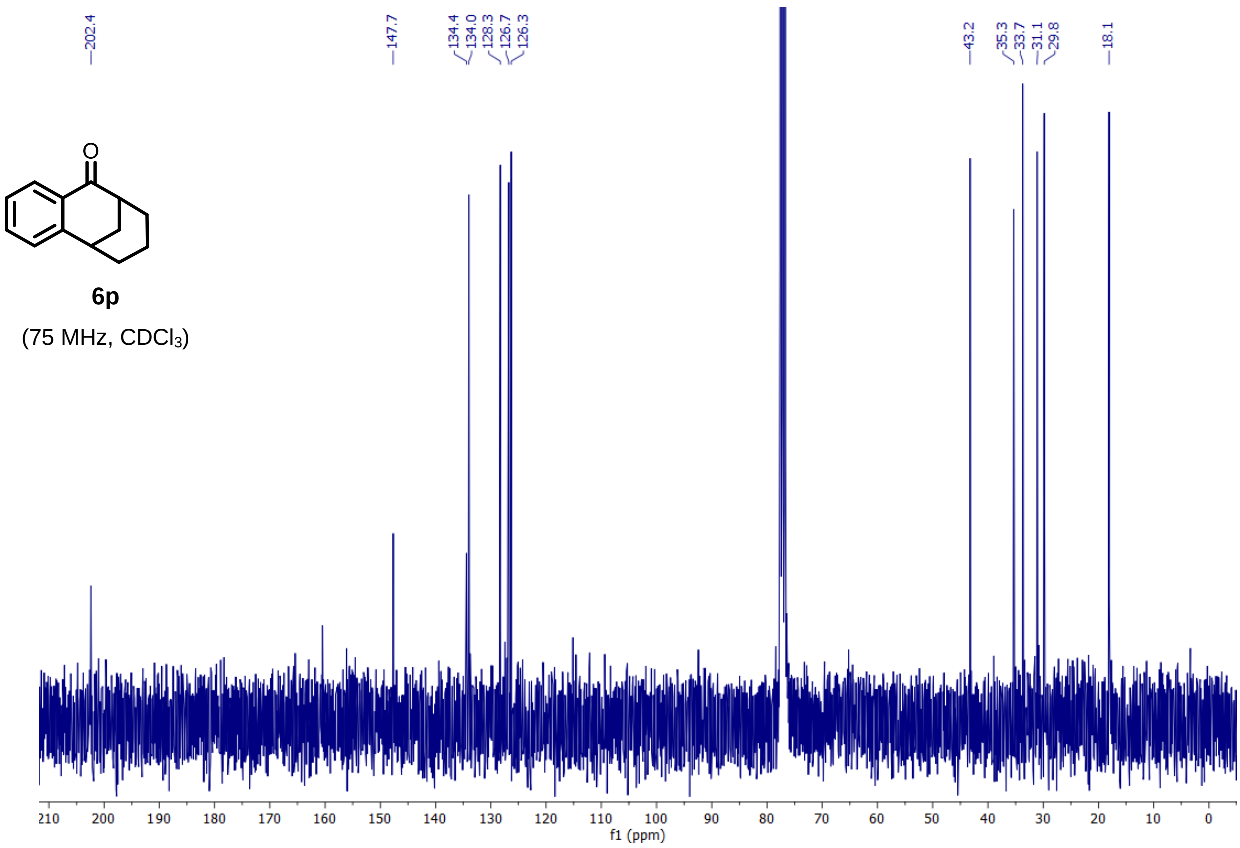
6o

(126 MHz, $CDCl_3$)



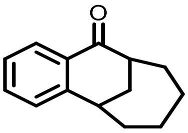
6p

(300 MHz, $CDCl_3$)



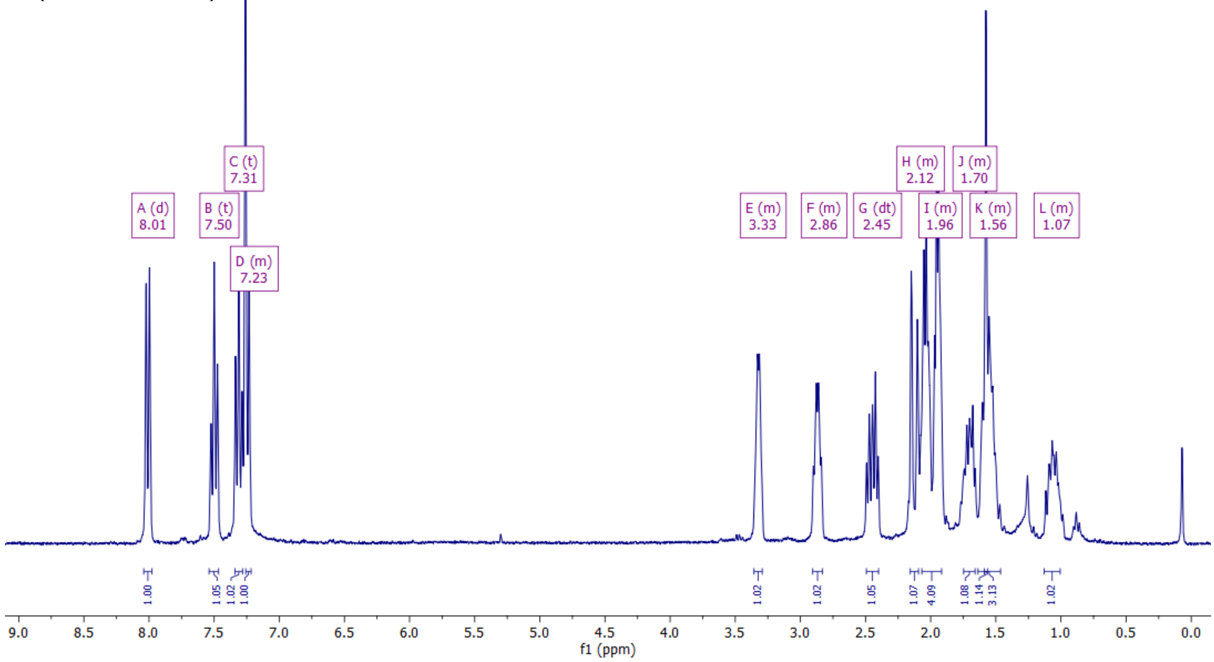
6p

(75 MHz, $CDCl_3$)



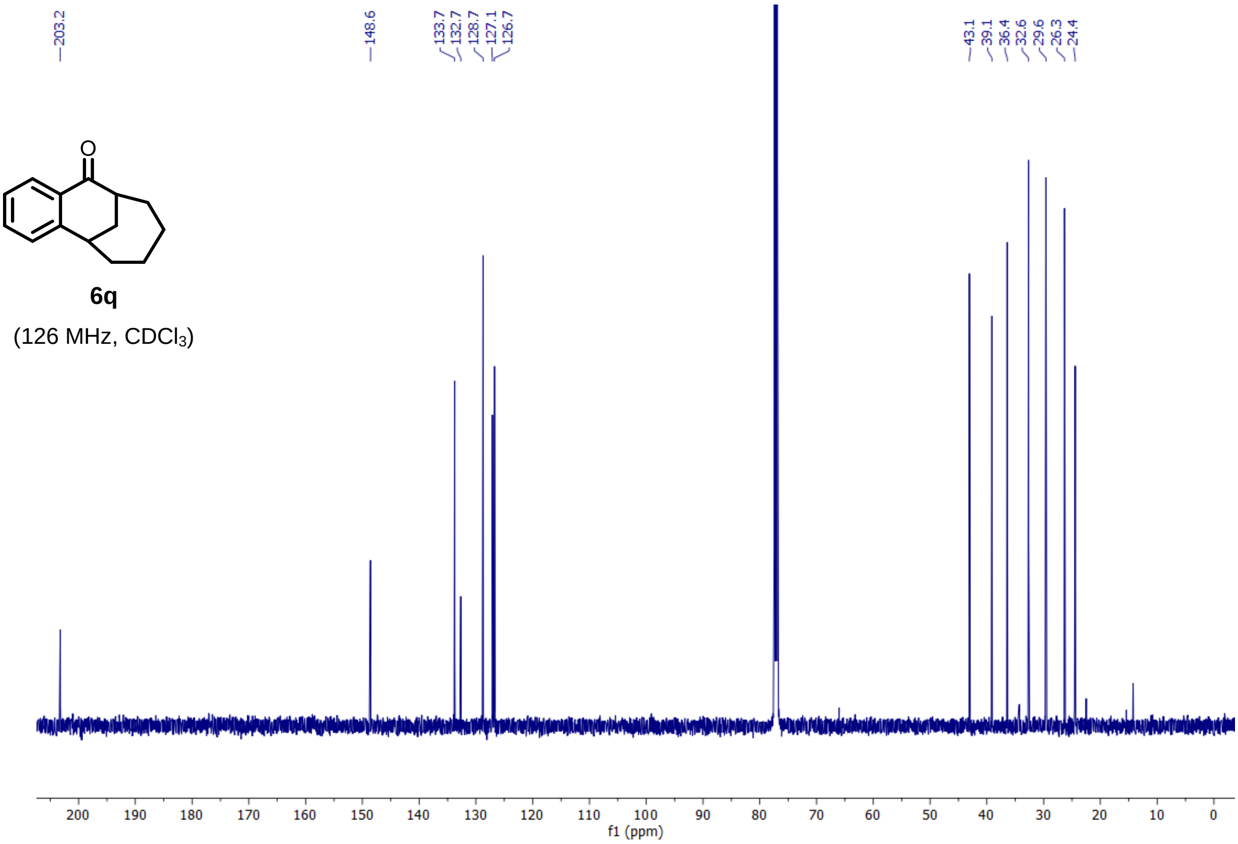
6q

(300 MHz, $CDCl_3$)

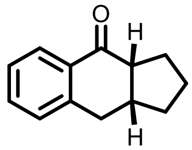


6q

(126 MHz, $CDCl_3$)

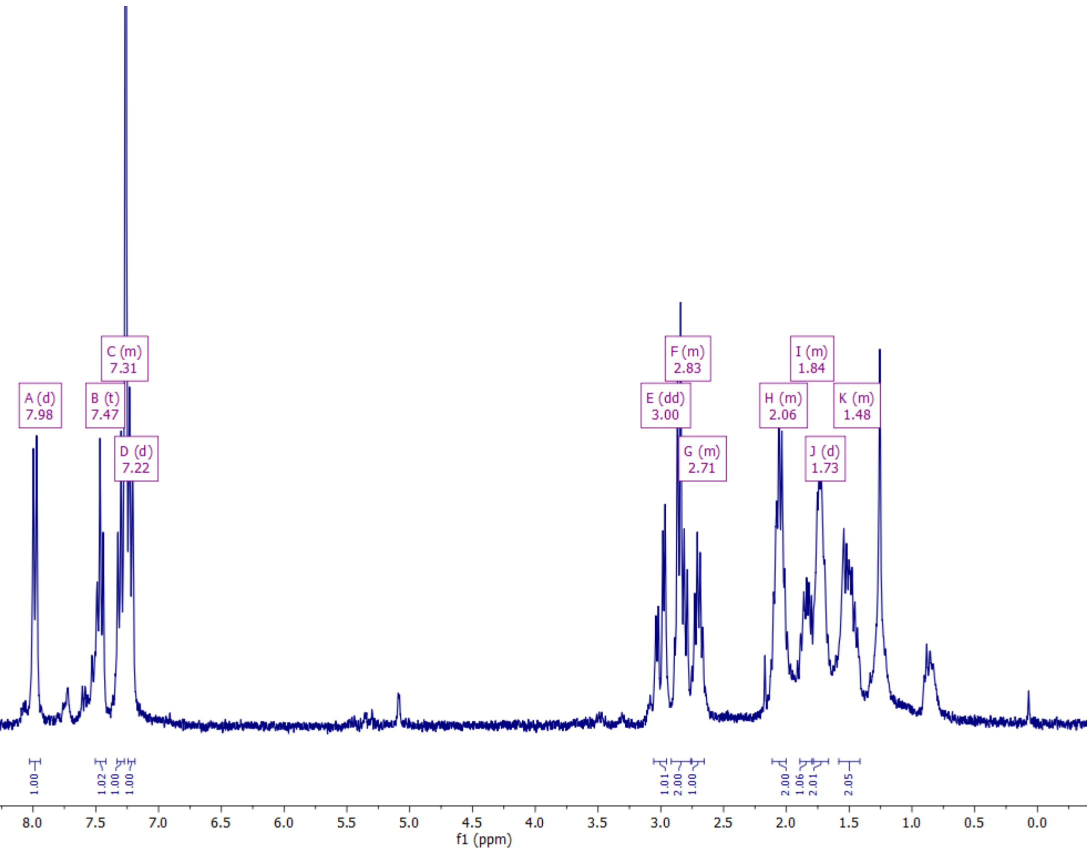


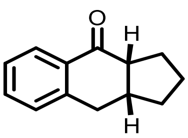
I



6t (cis)

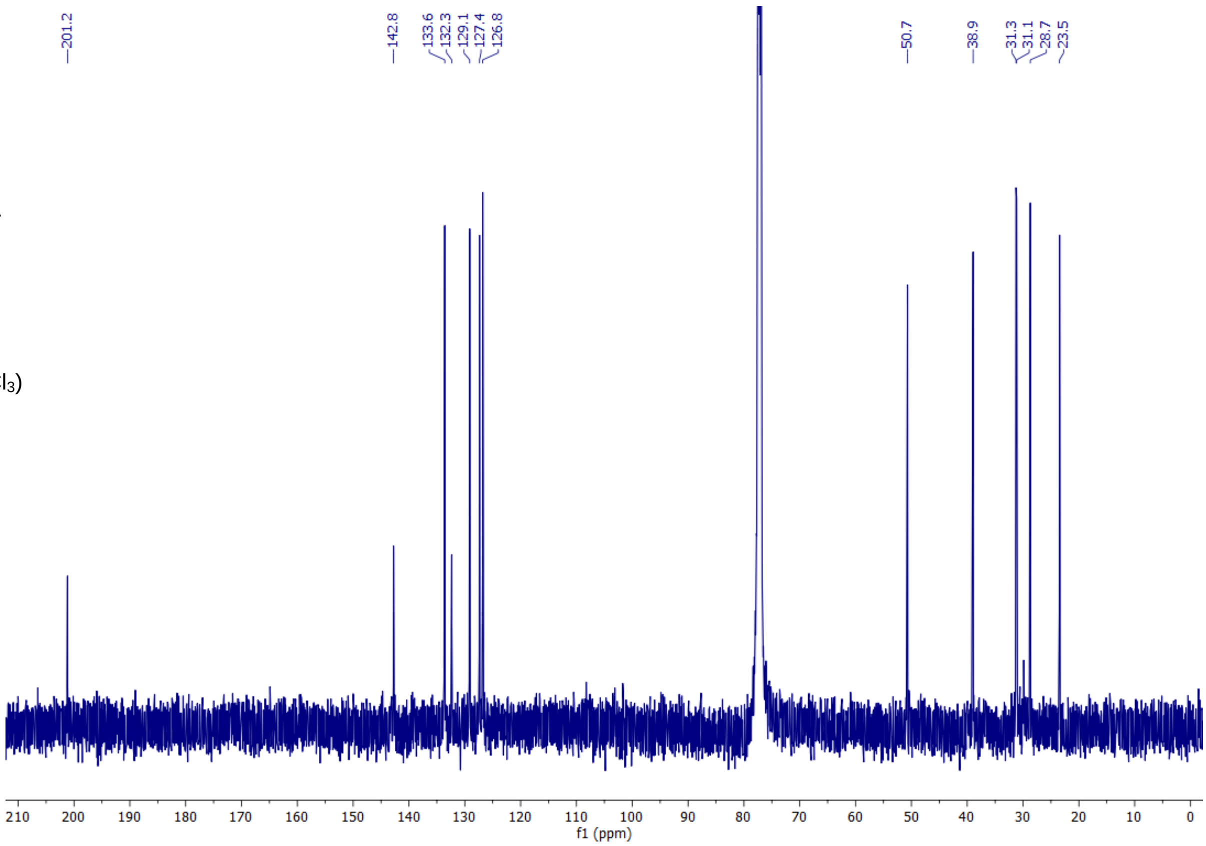
(300 MHz, $CDCl_3$)

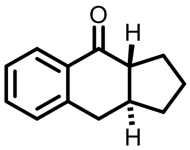




6t (cis)

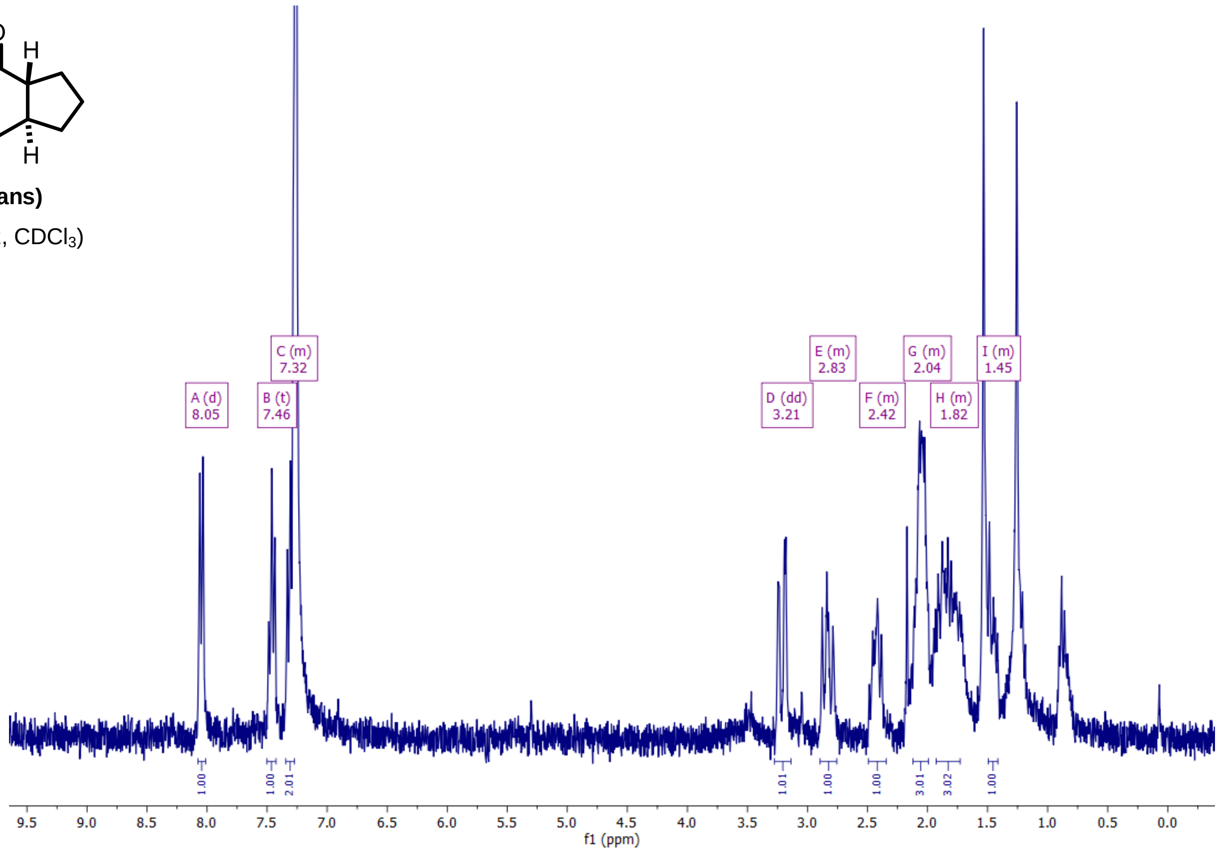
(126 MHz, $CDCl_3$)

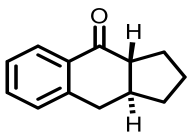




6t (trans)

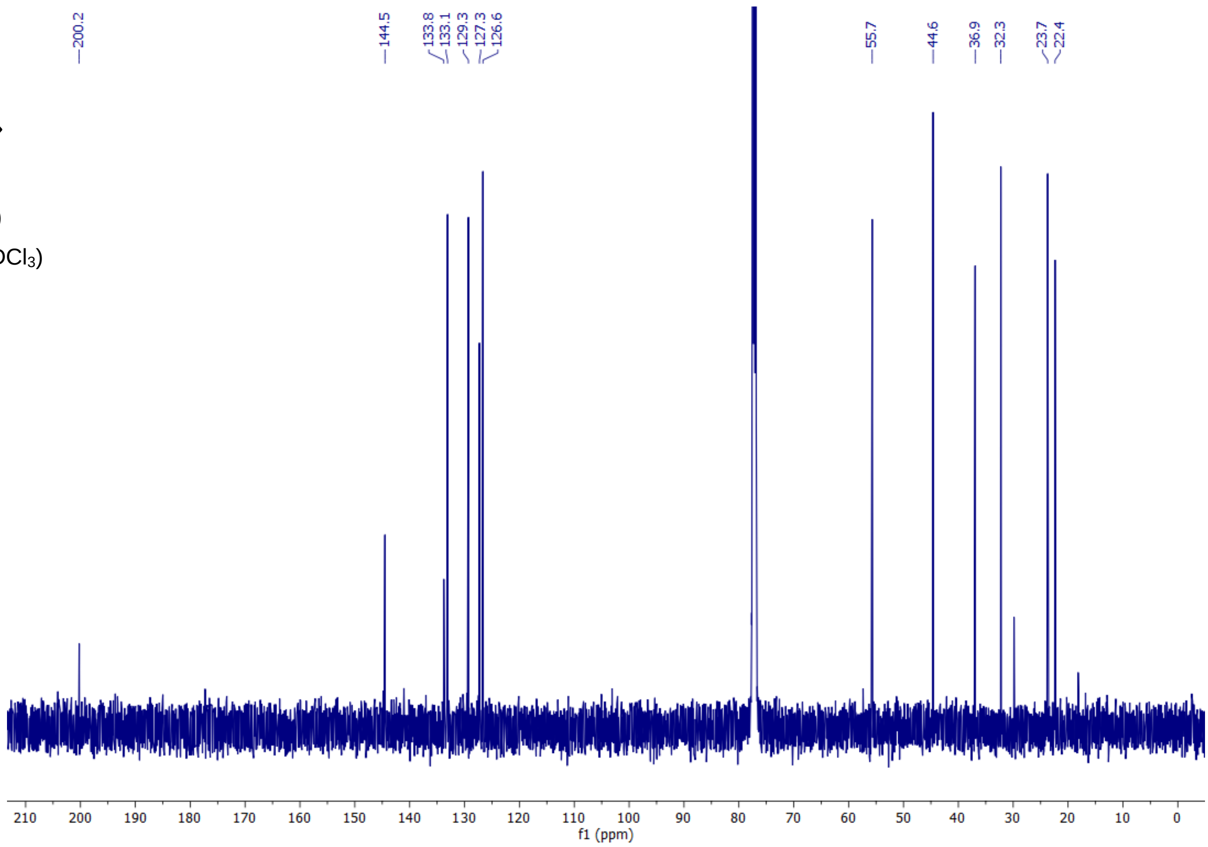
(300 MHz, $CDCl_3$)

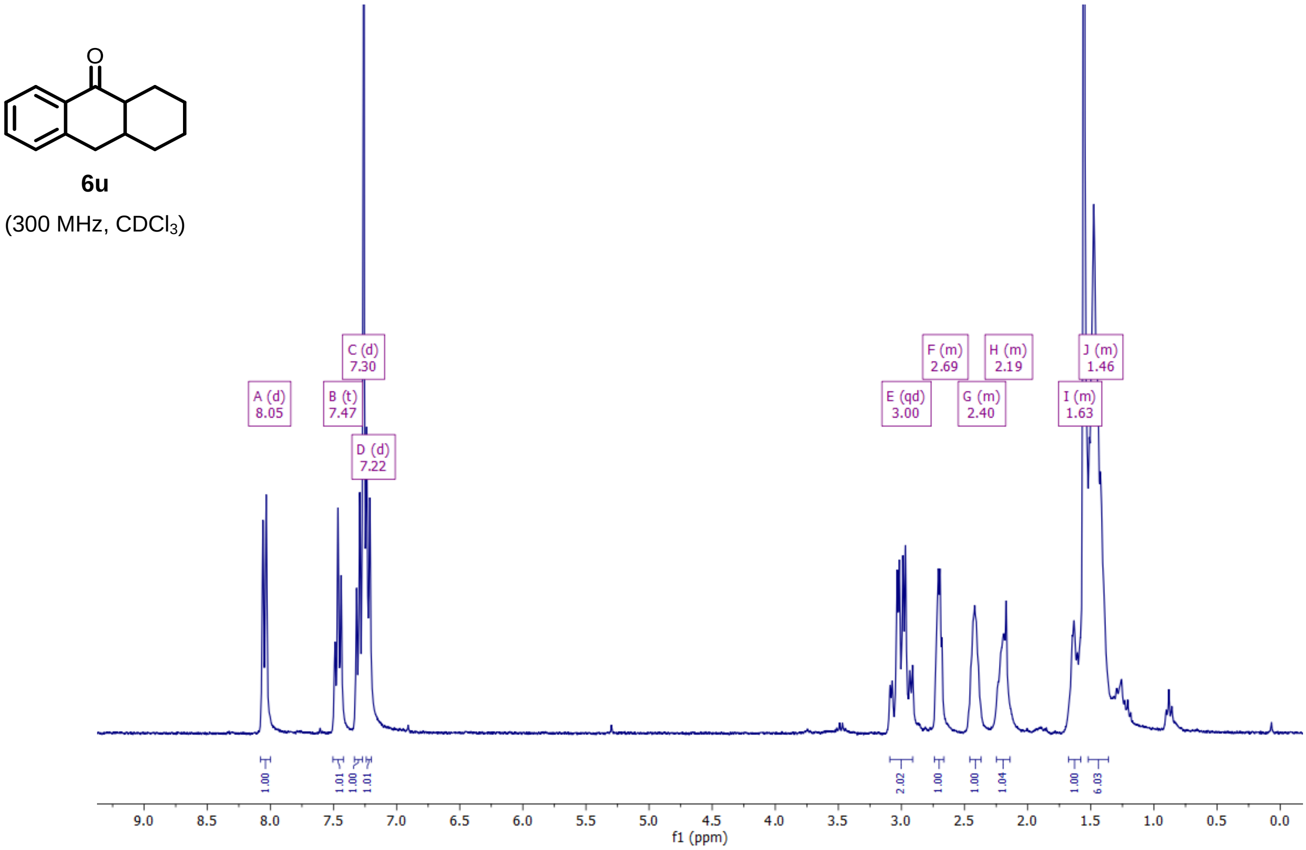




6t (trans)

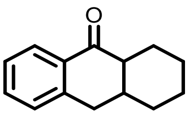
(126 MHz, $CDCl_3$)





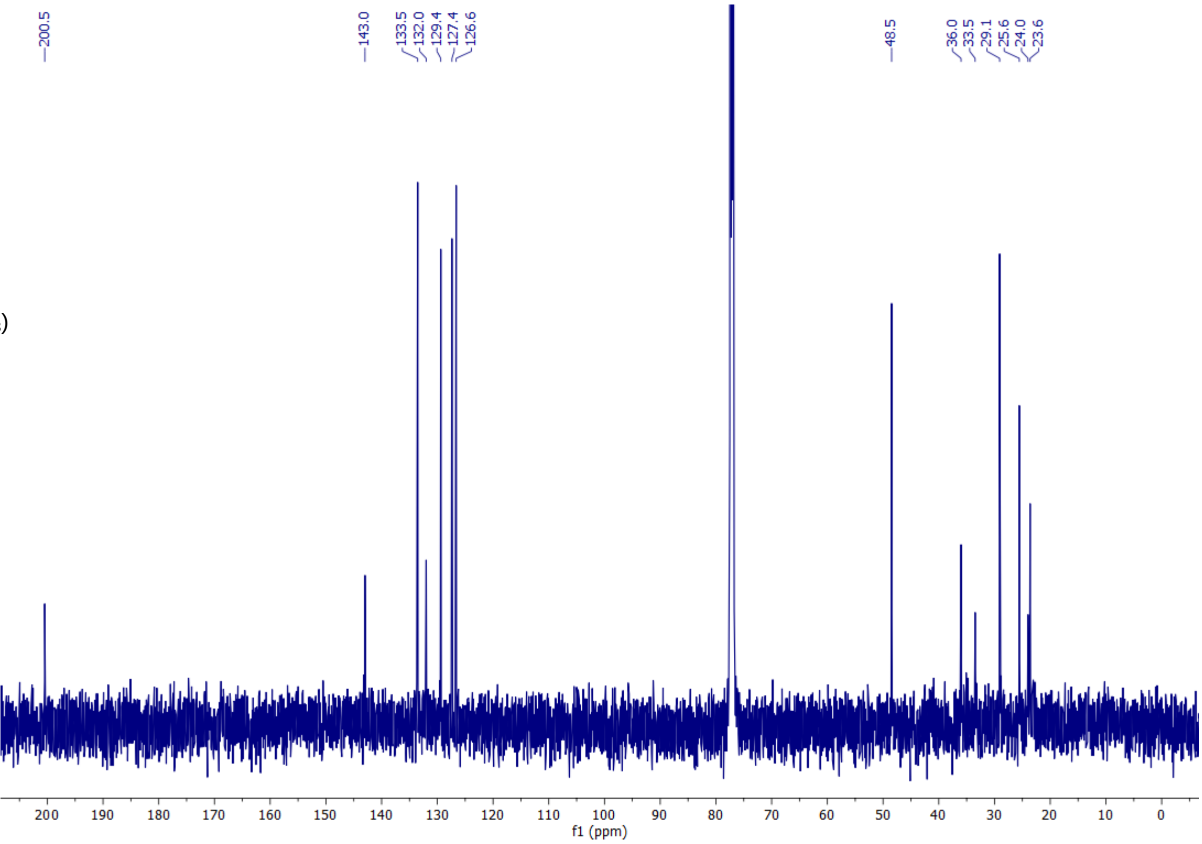
6u

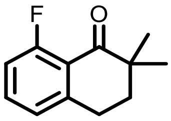
(300 MHz, $CDCl_3$)



6u

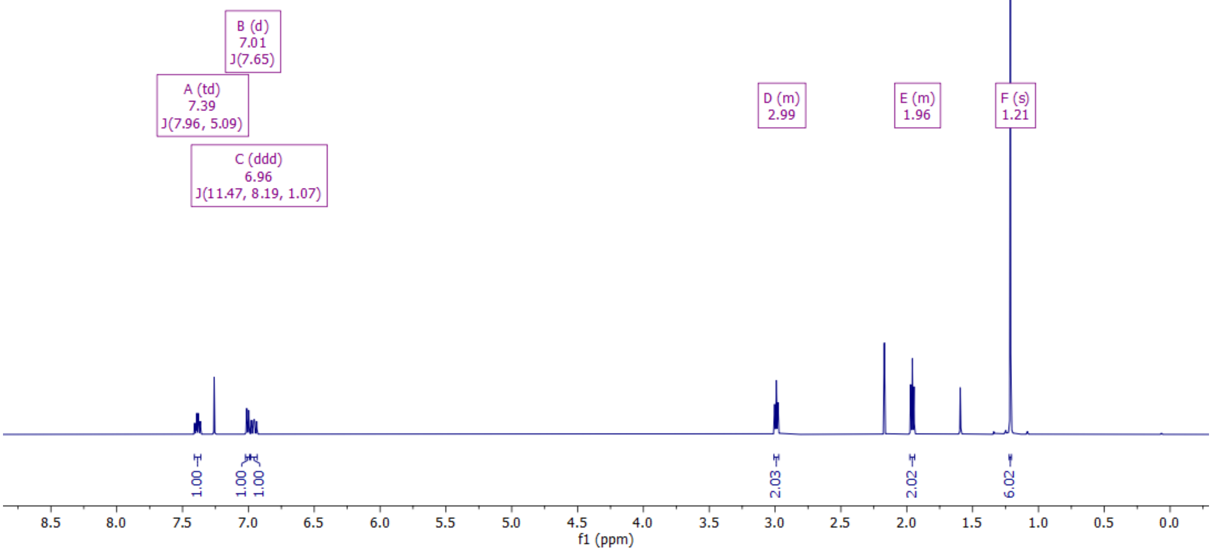
(126 MHz, $CDCl_3$)

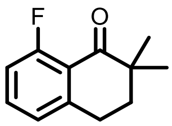




6d

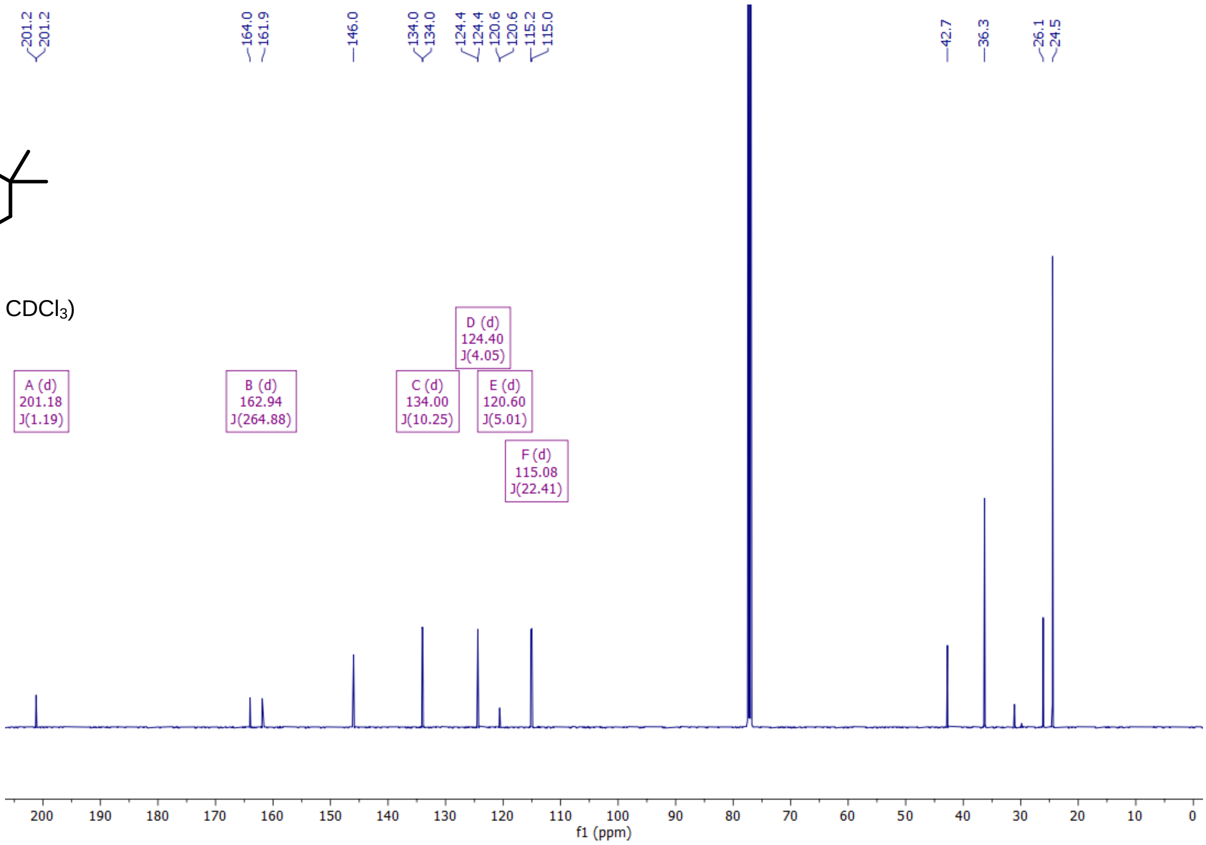
(500 MHz, $CDCl_3$)

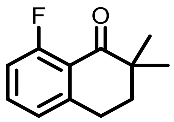




6d

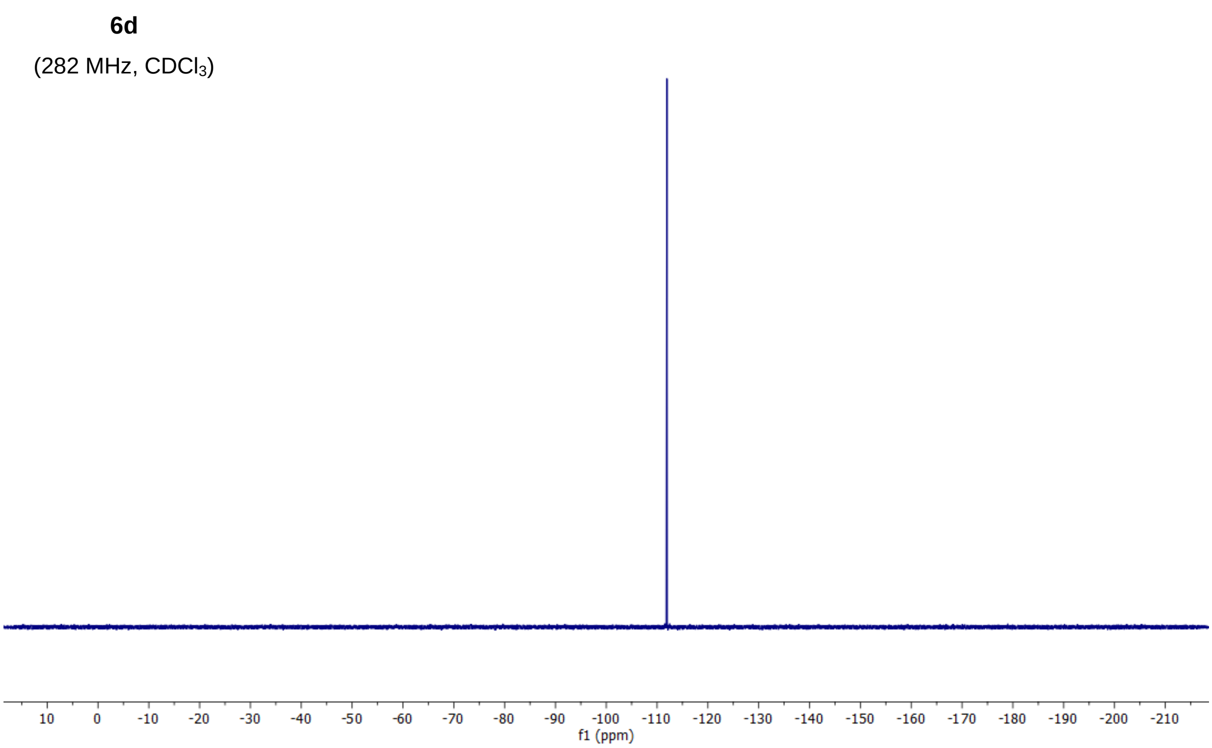
(126 MHz, $CDCl_3$)

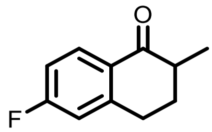




6d

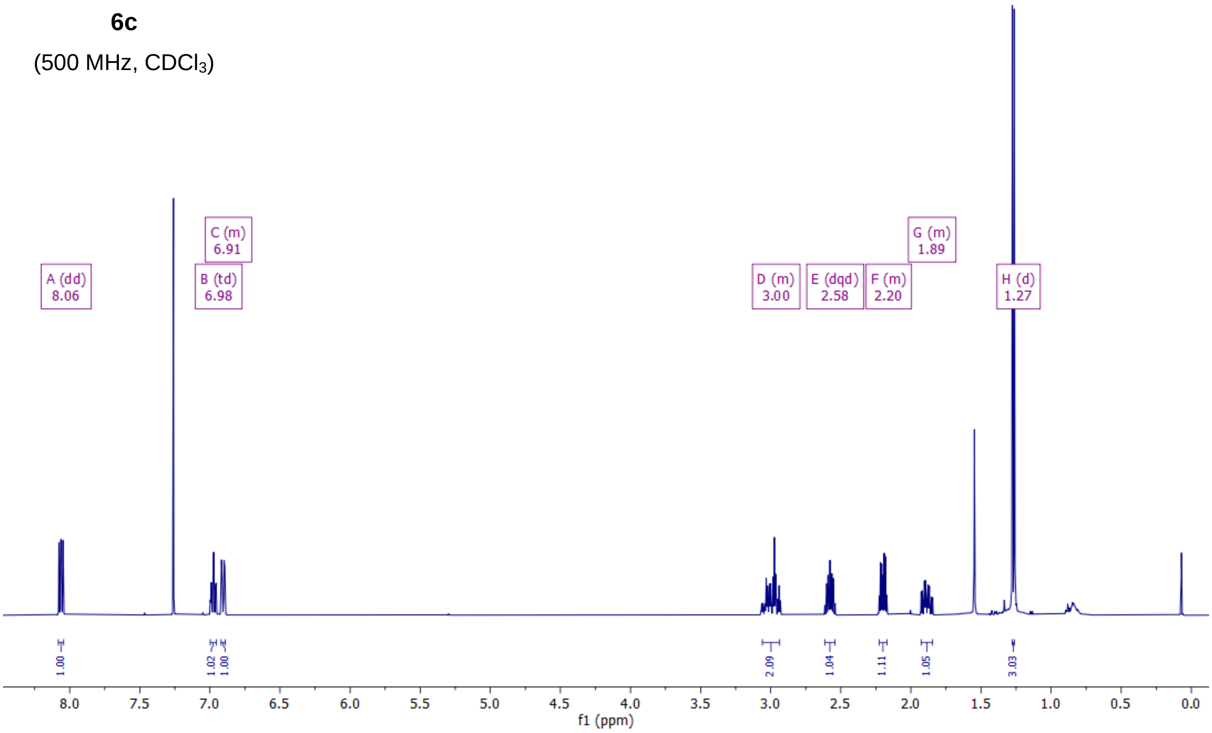
(282 MHz, $CDCl_3$)

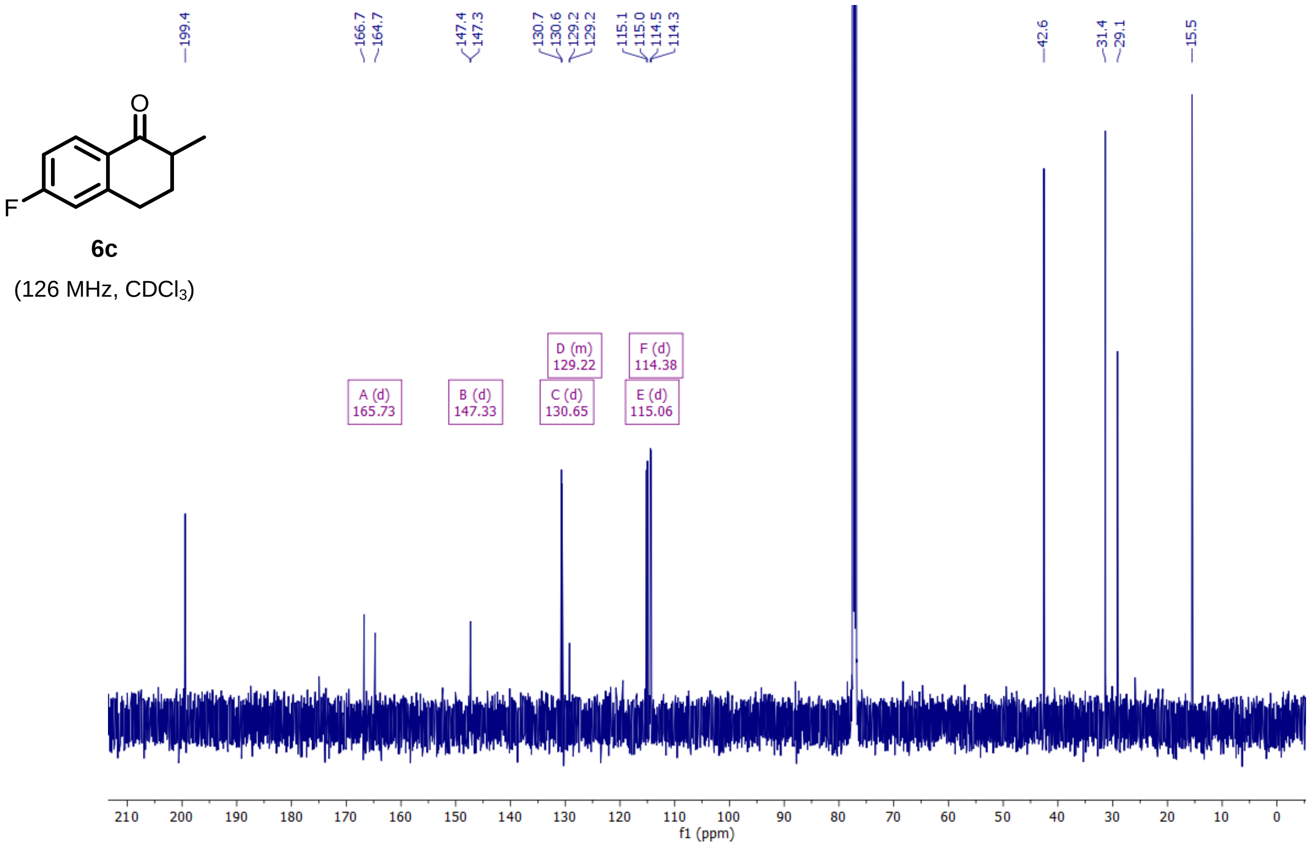




6c

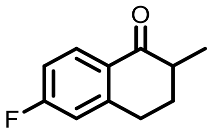
(500 MHz, $CDCl_3$)





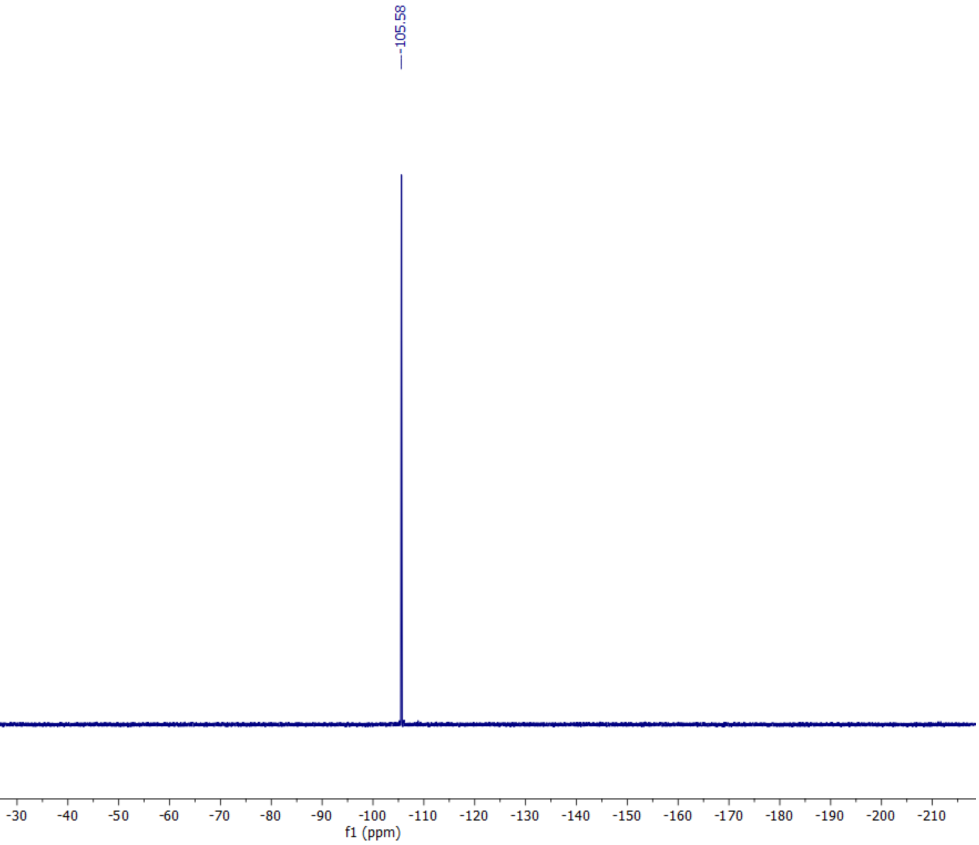
6c

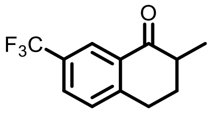
(126 MHz, $CDCl_3$)



6c

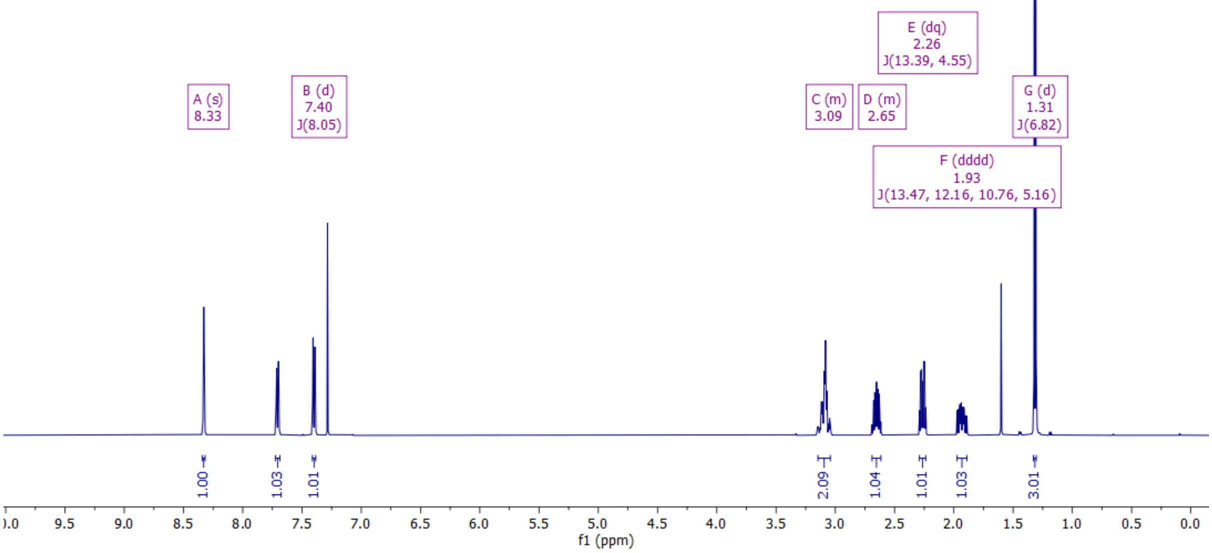
(282 MHz, $CDCl_3$)

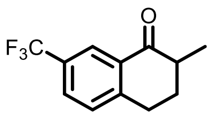




6b

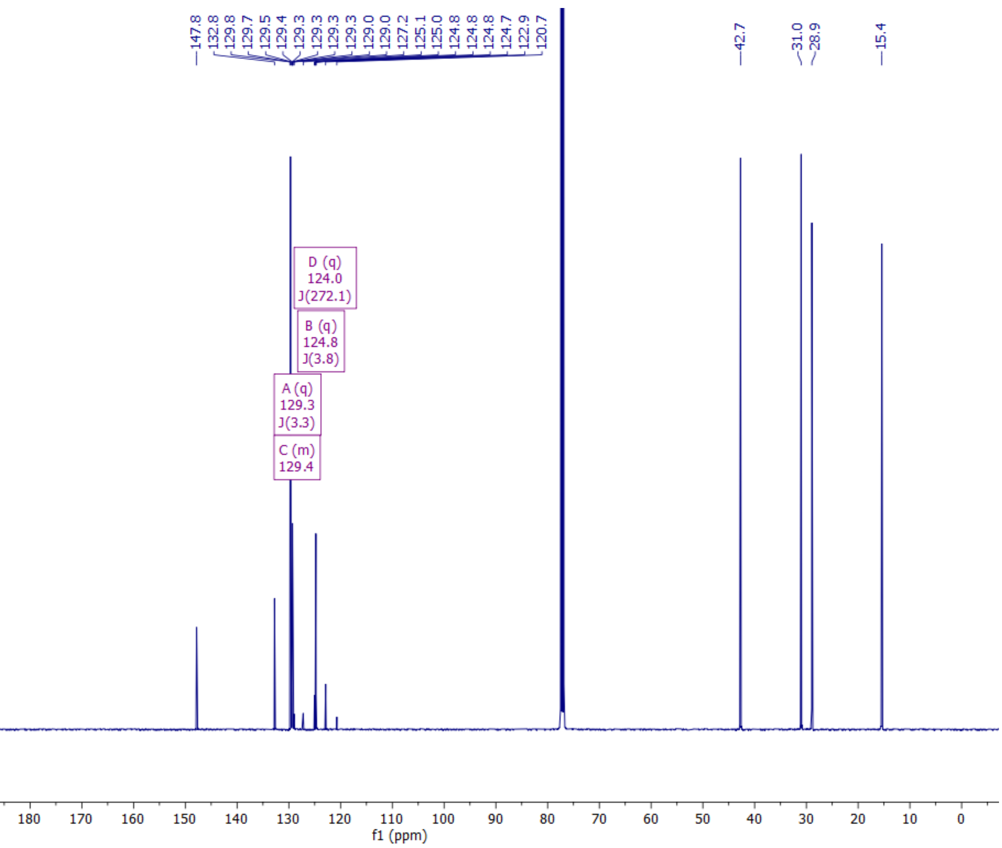
(500 MHz, $CDCl_3$)

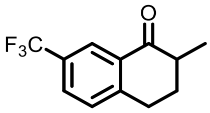




6b

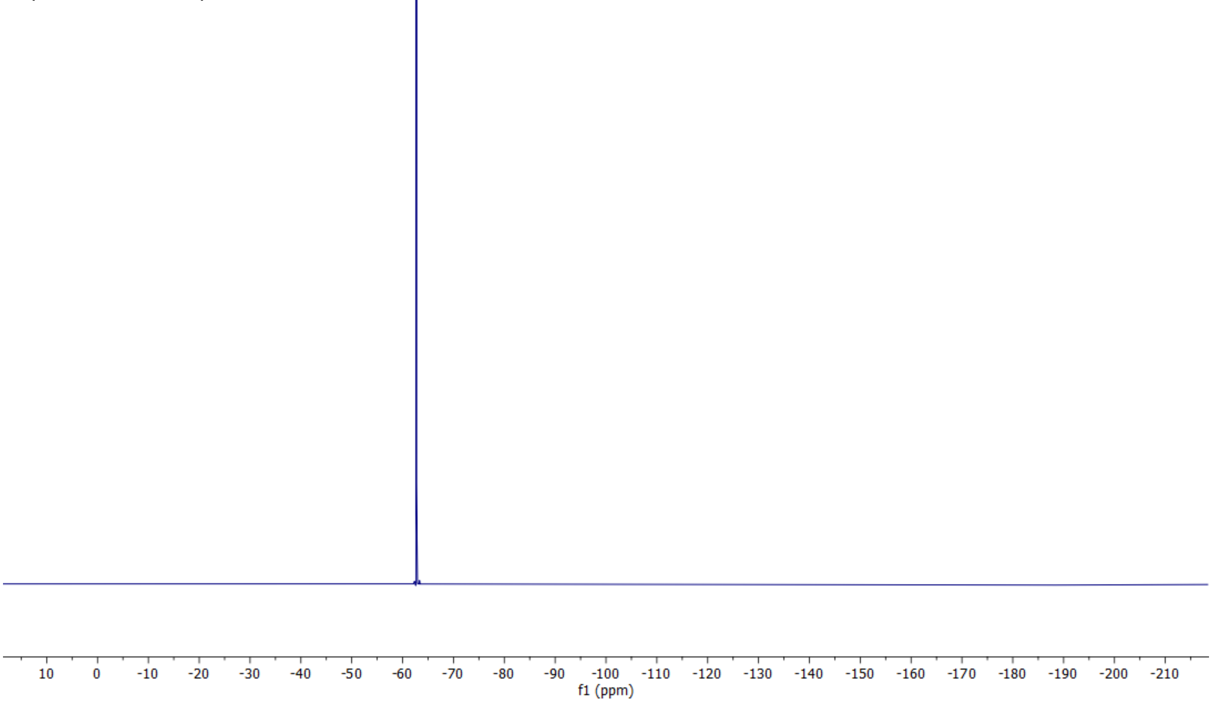
(126 MHz, $CDCl_3$)

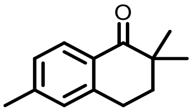




6b

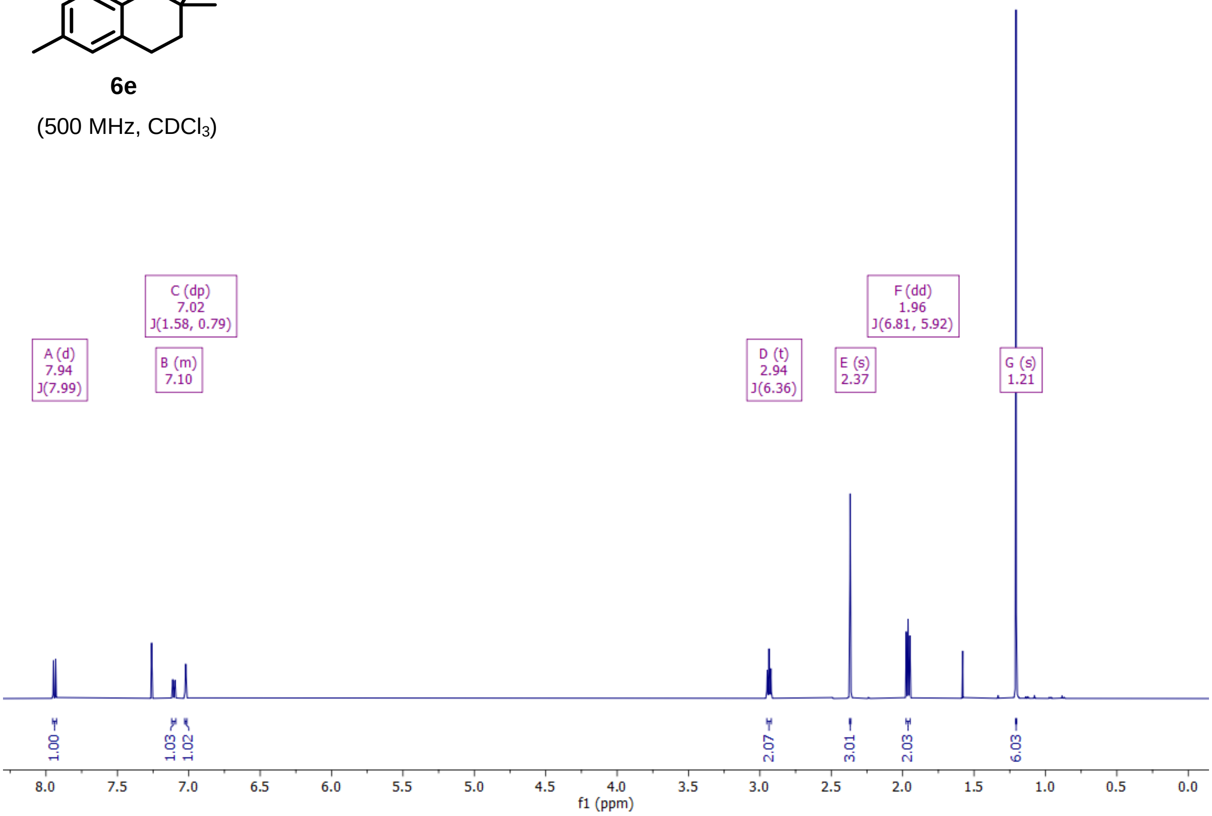
(282 MHz, $CDCl_3$)





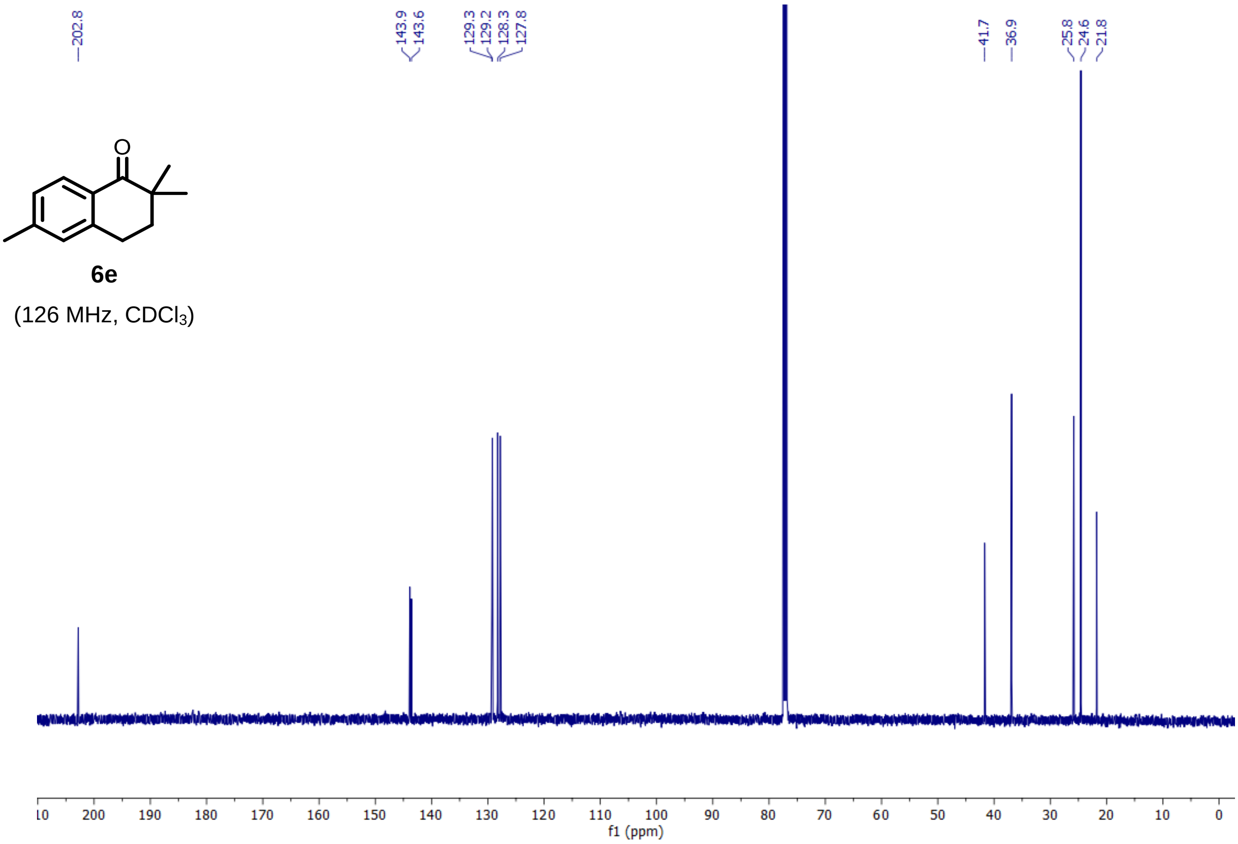
6e

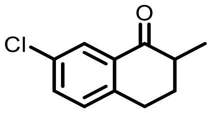
(500 MHz, $CDCl_3$)



6e

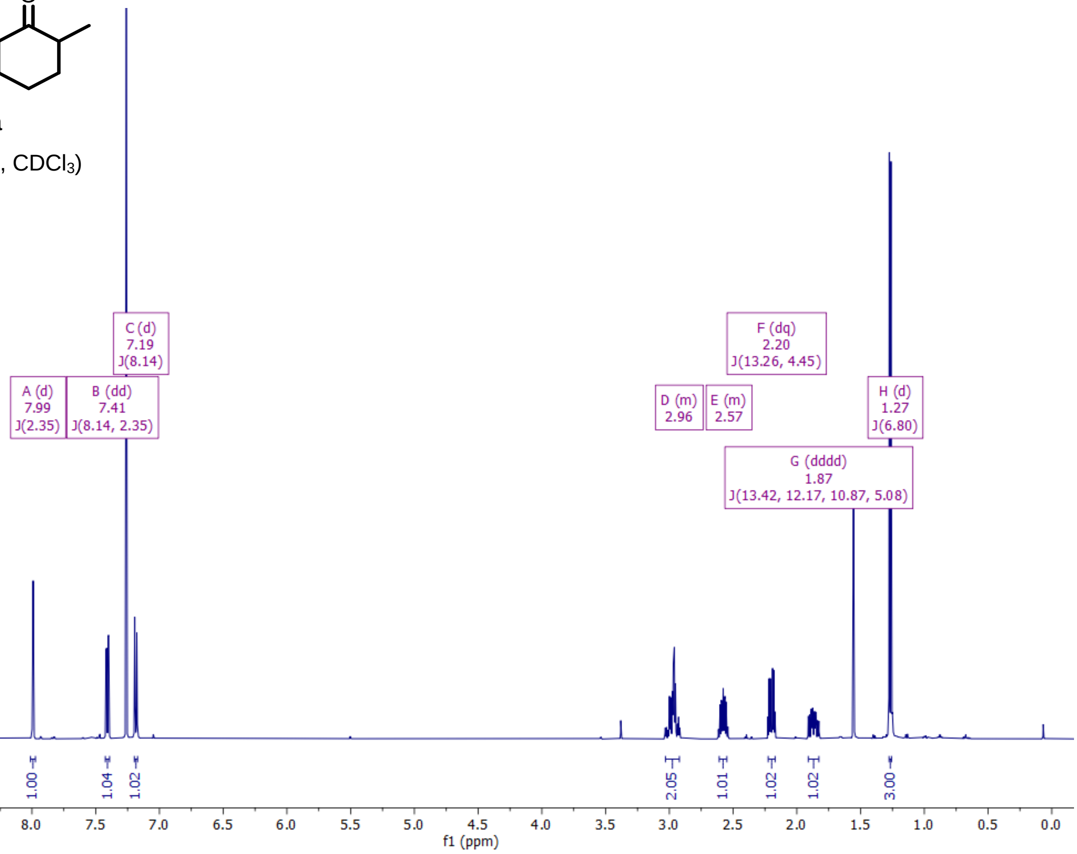
(126 MHz, $CDCl_3$)

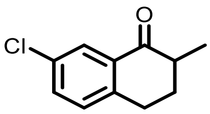




6a

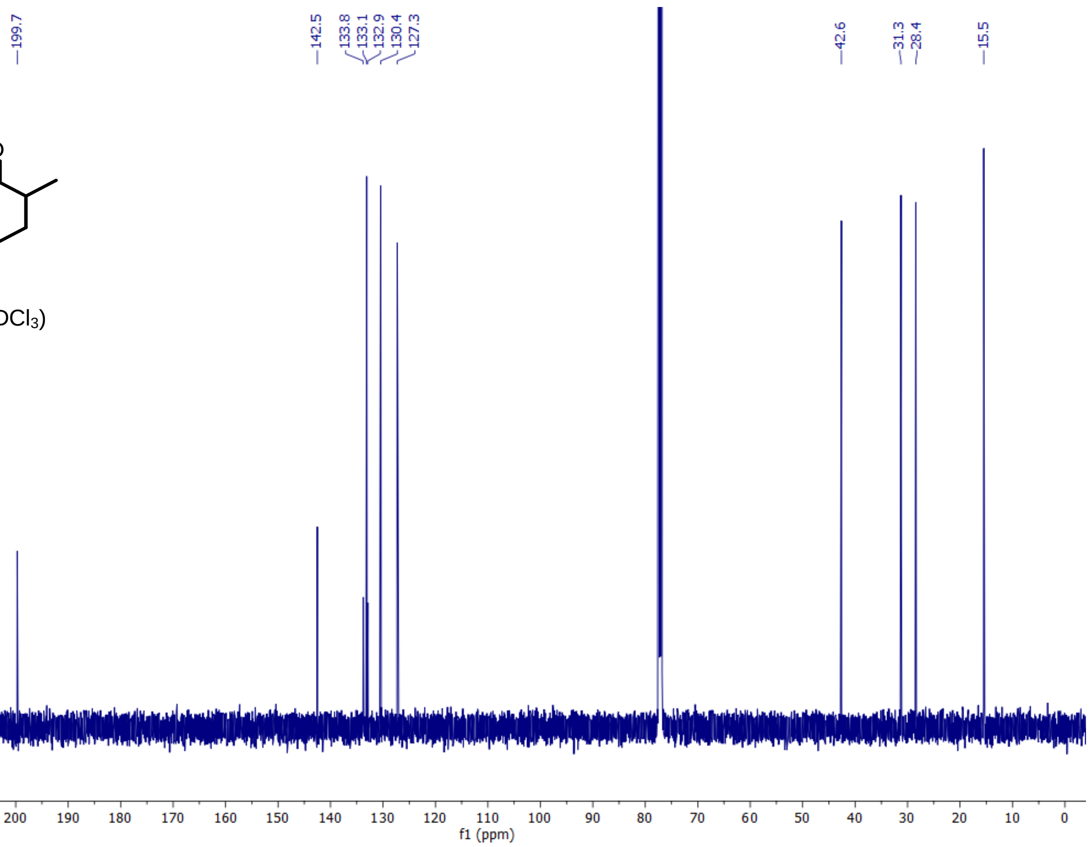
(500 MHz, $CDCl_3$)

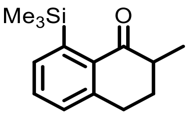




6a

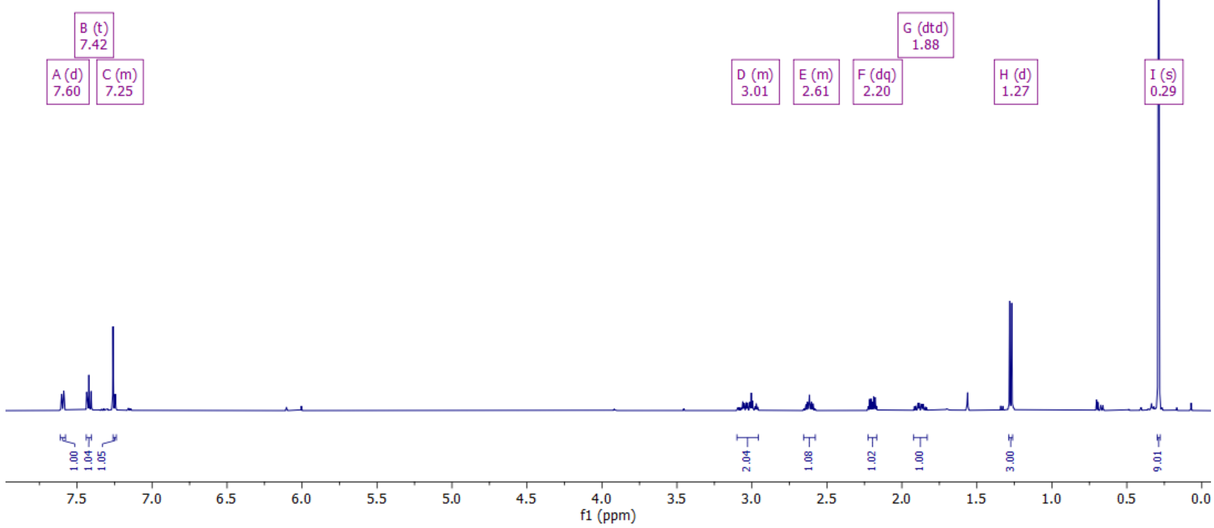
(126 MHz, $CDCl_3$)

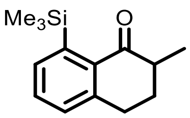




6f

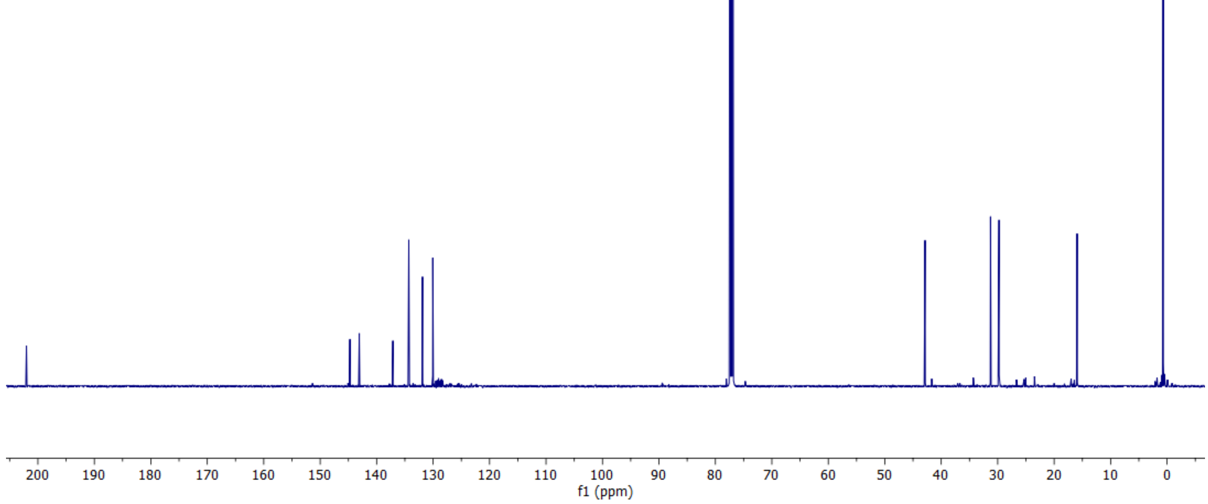
(500 MHz, $CDCl_3$)

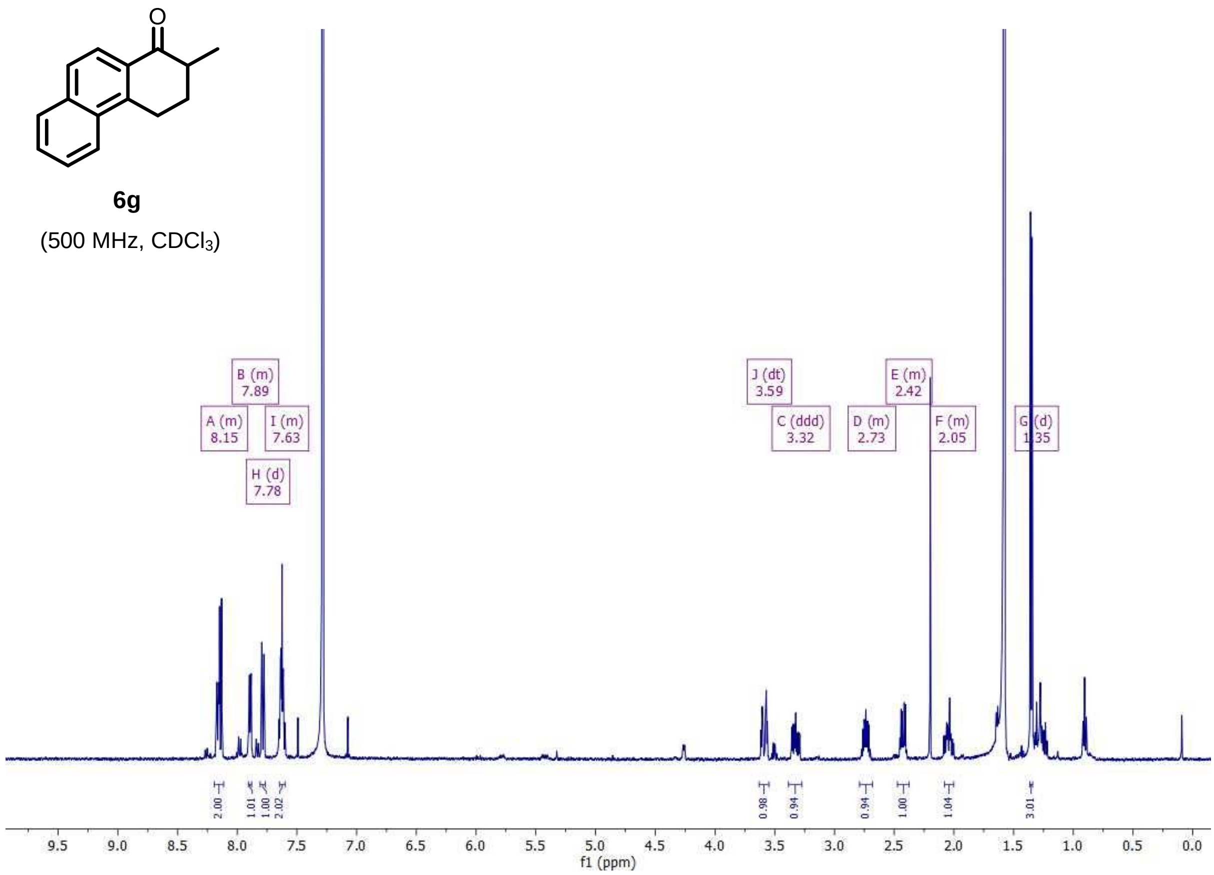




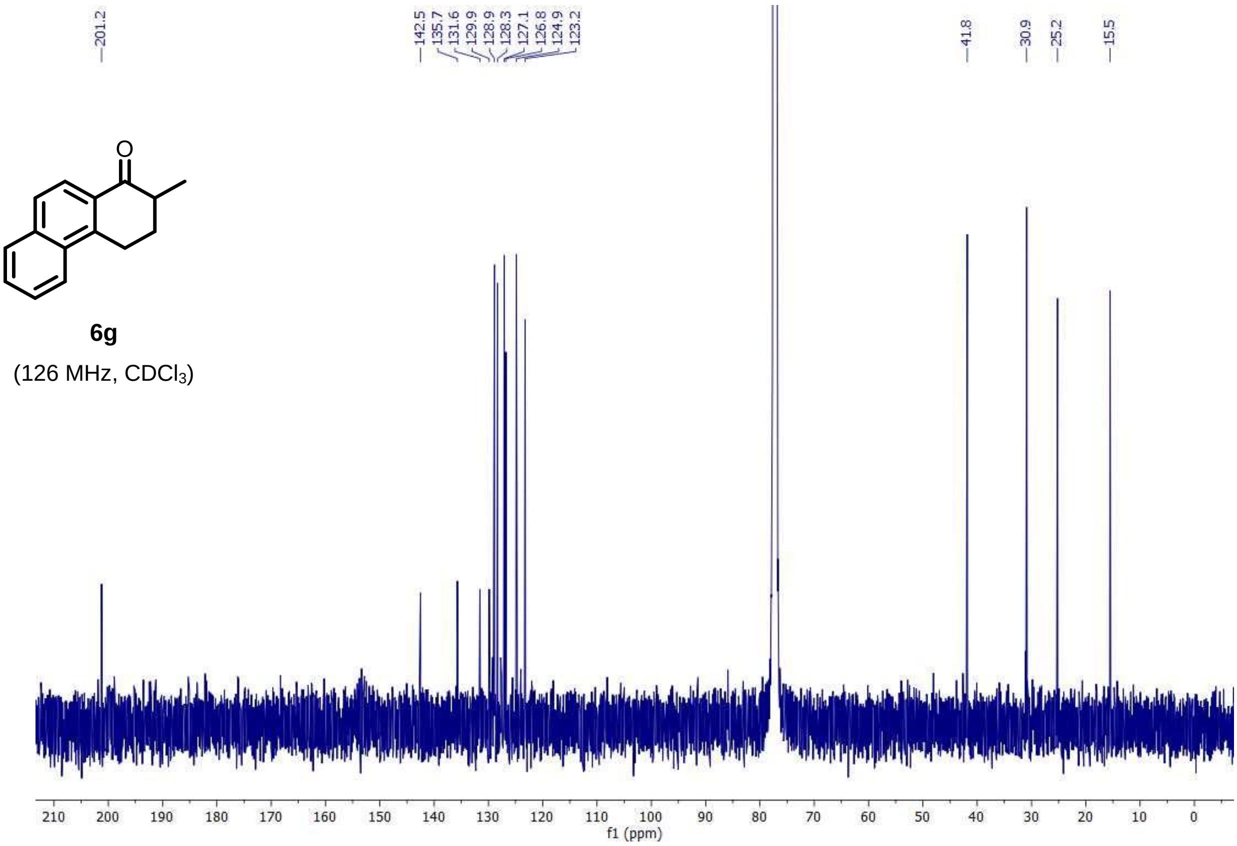
6f

(126 MHz, $CDCl_3$)

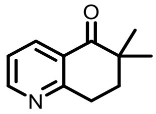




6g
(500 MHz, $CDCl_3$)

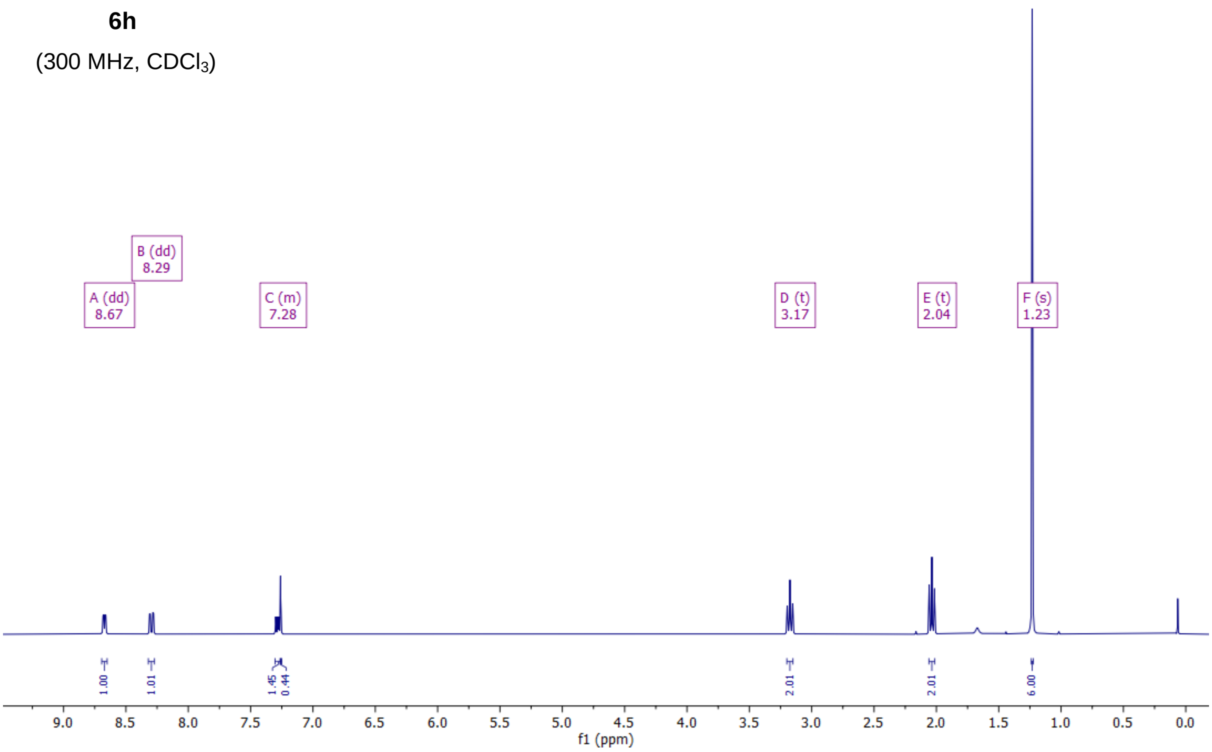


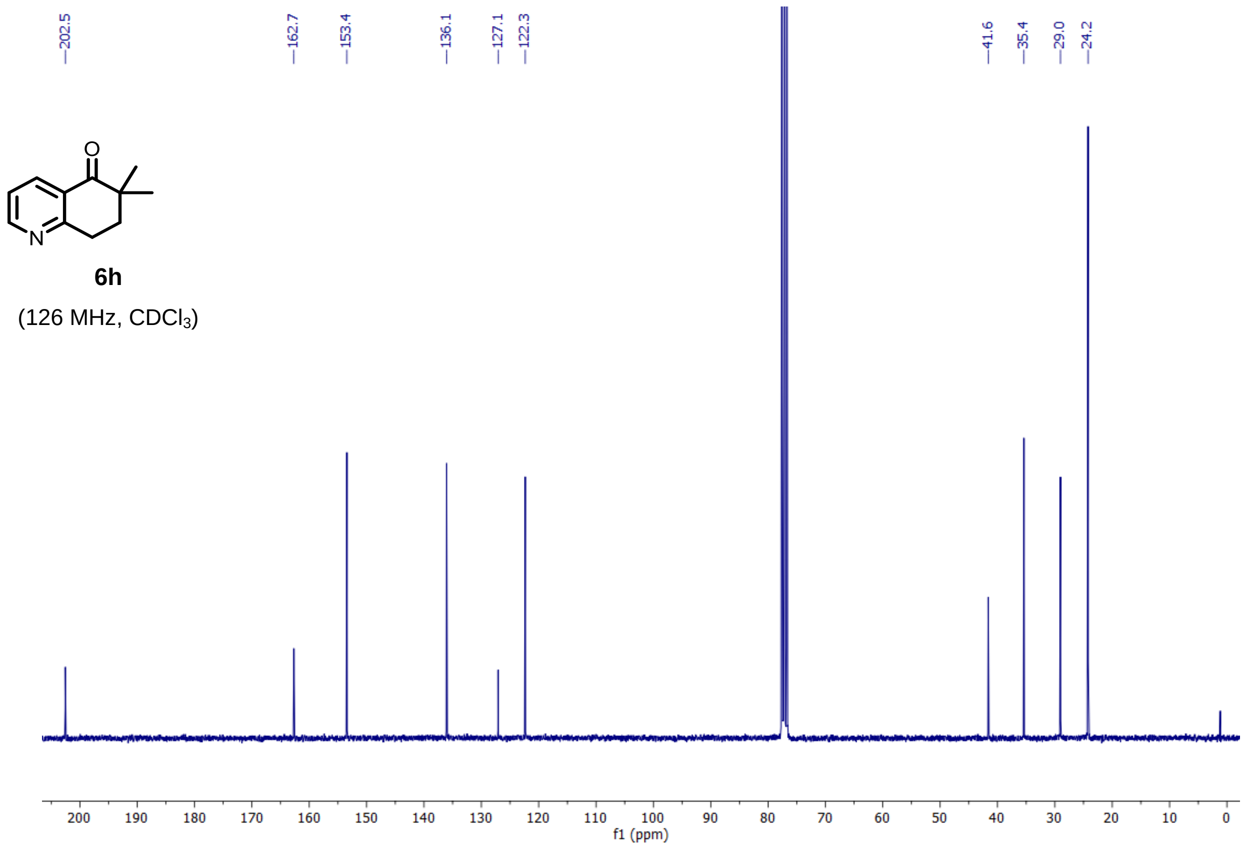
6g
(126 MHz, $CDCl_3$)



6h

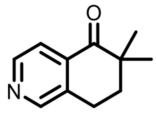
(300 MHz, $CDCl_3$)





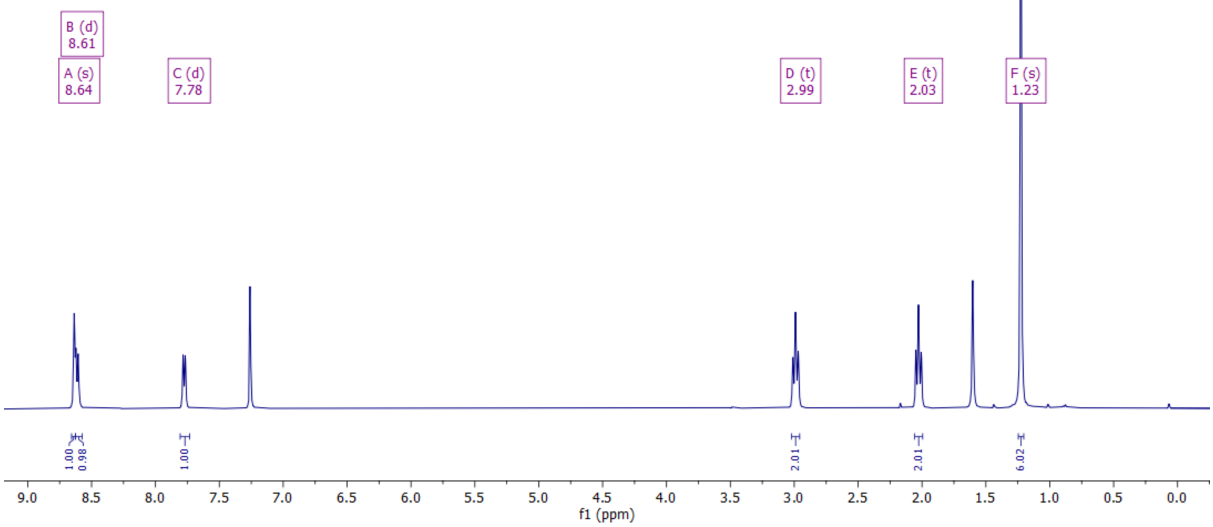
6h

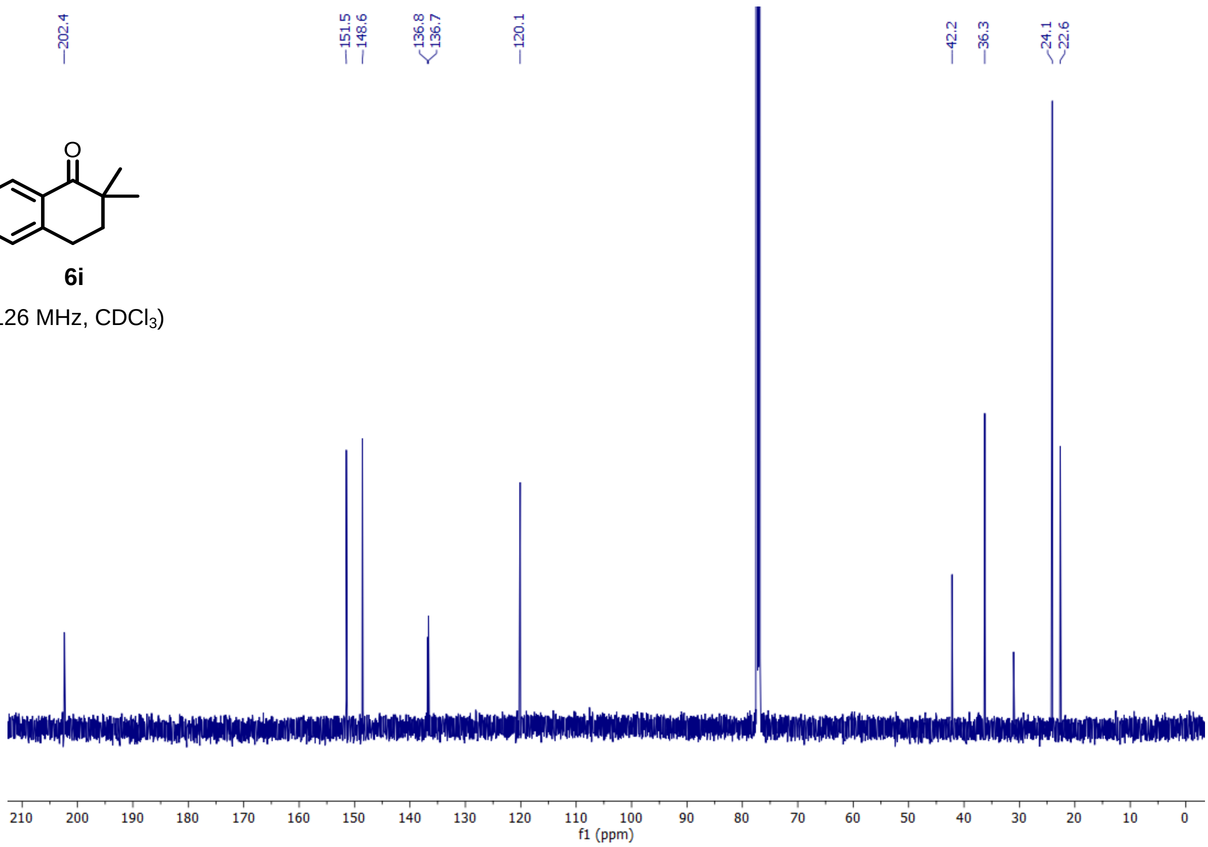
(126 MHz, $CDCl_3$)



6i

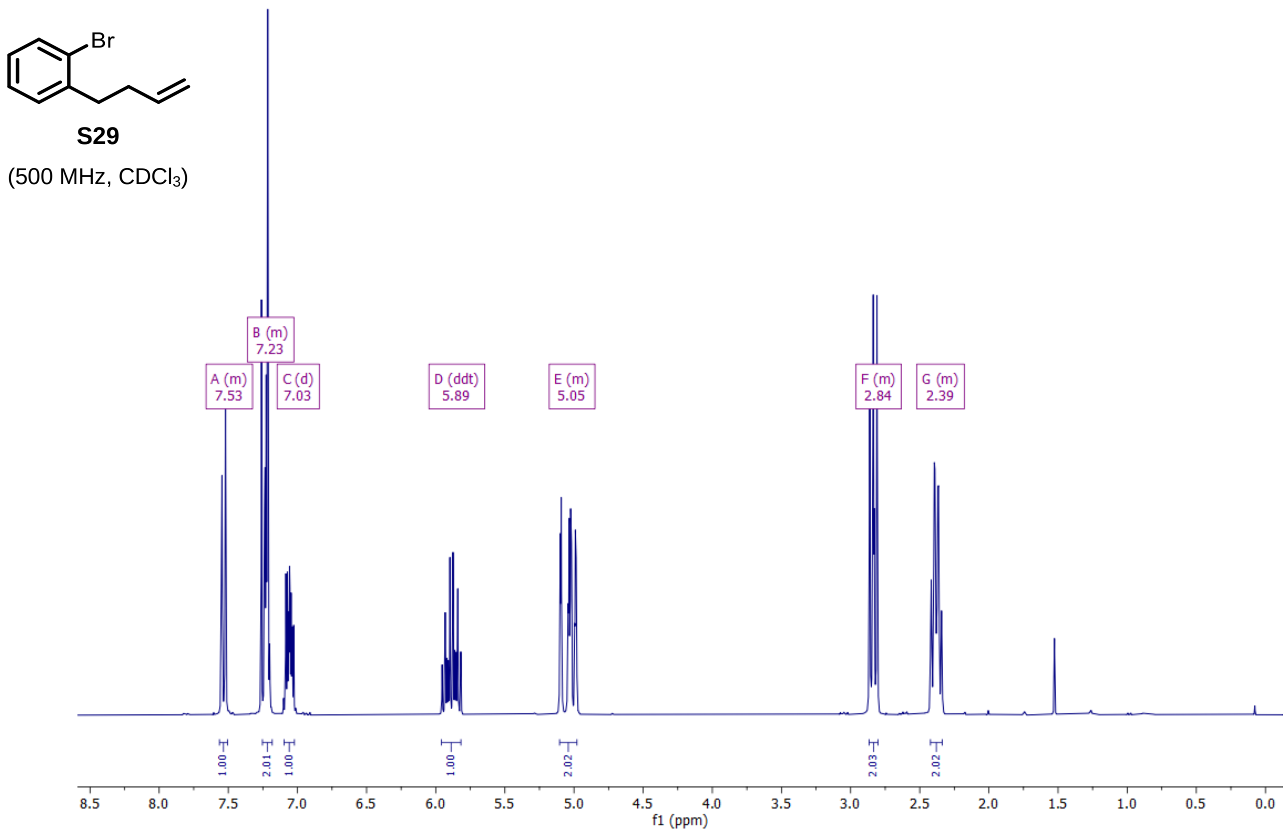
(300 MHz, $CDCl_3$)

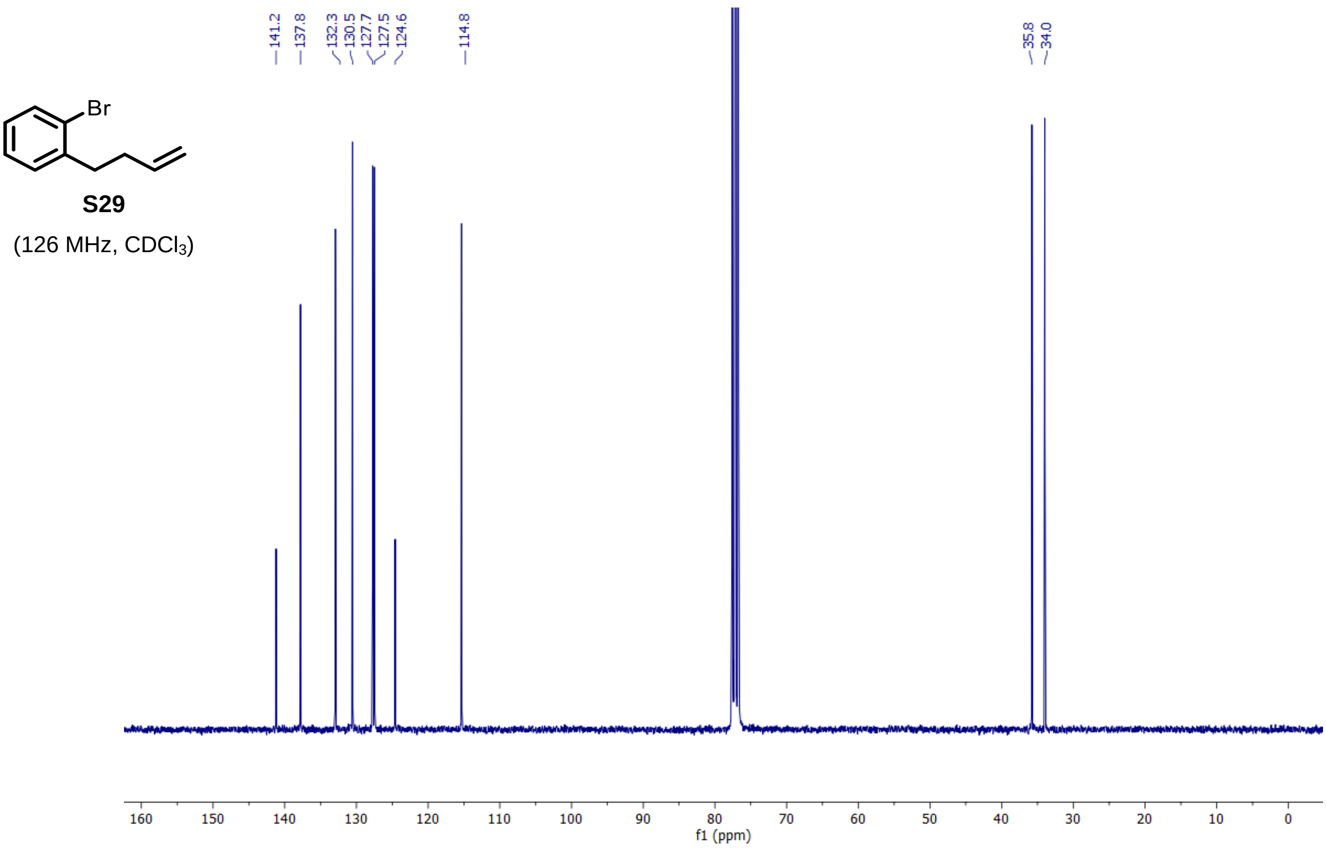


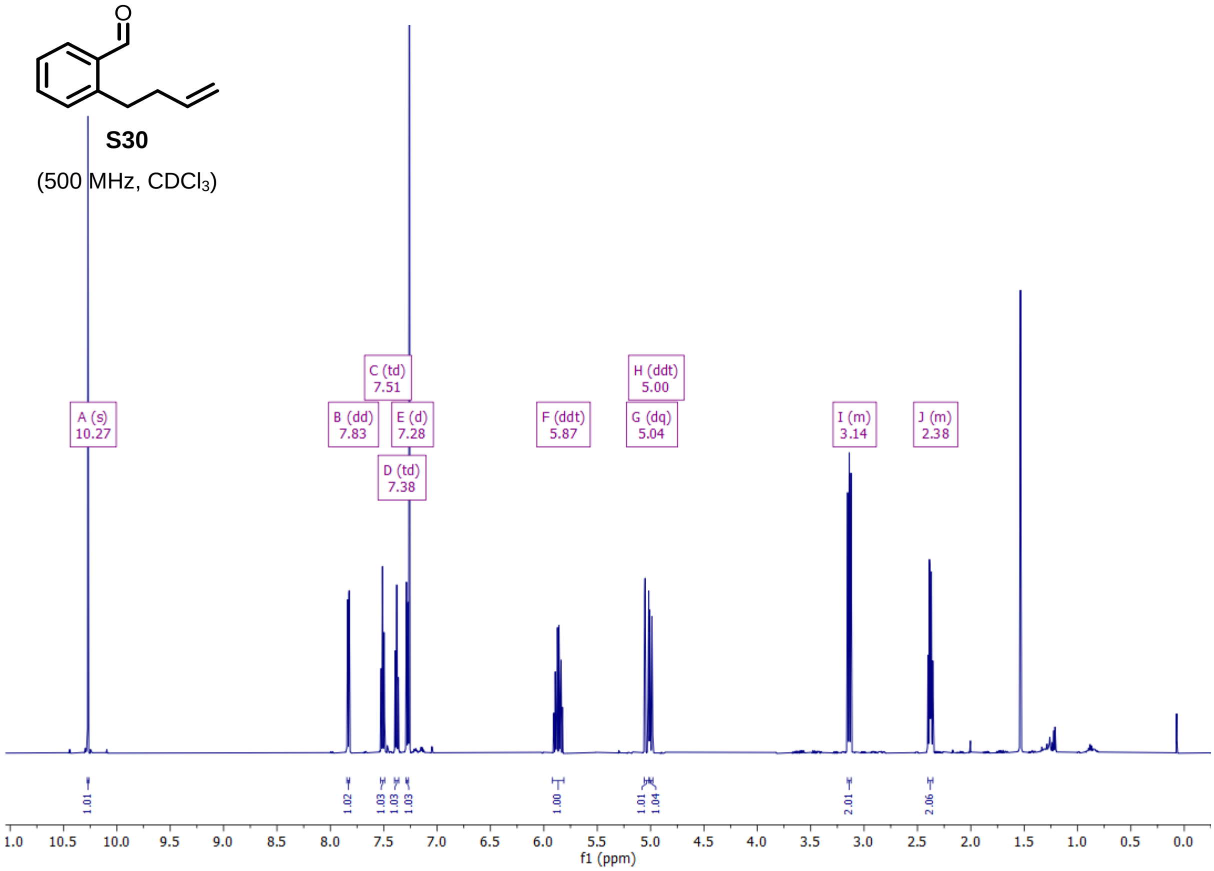


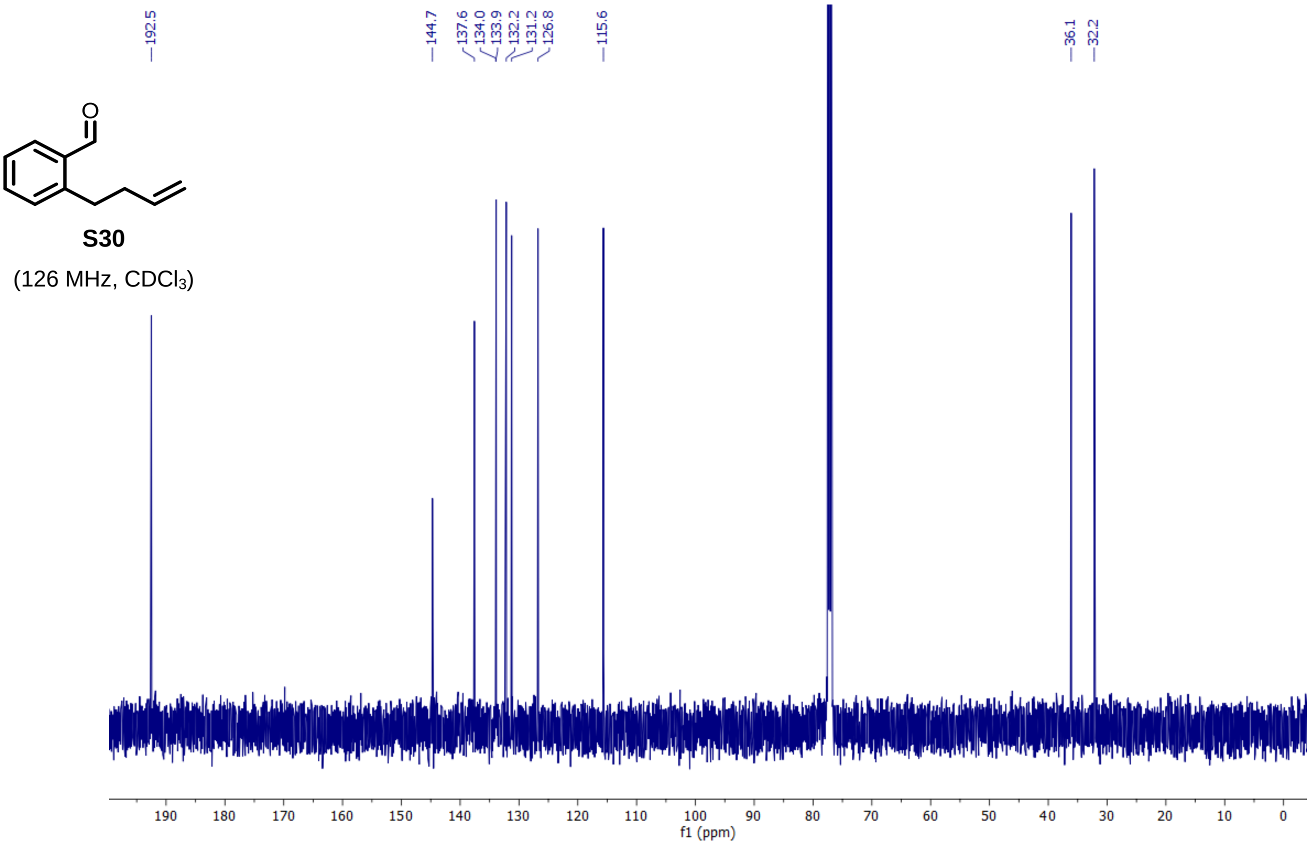
6i

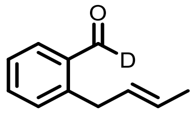
(126 MHz, $CDCl_3$)


Br
S29
(500 MHz, CDCl3)
A (m) 7.53
B (m) 7.23
C (d) 7.03
D (ddt) 5.89
E (m) 5.05
F (m) 2.84
G (m) 2.39
1.00
2.01
1.00
1.00
2.02
2.03
2.02
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
f1 (ppm)


141.2
137.8
132.3
130.5
127.7
127.5
124.6
114.8
35.8
34.0
Br
S29
(126 MHz, CDCl3)
160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0
f1 (ppm)

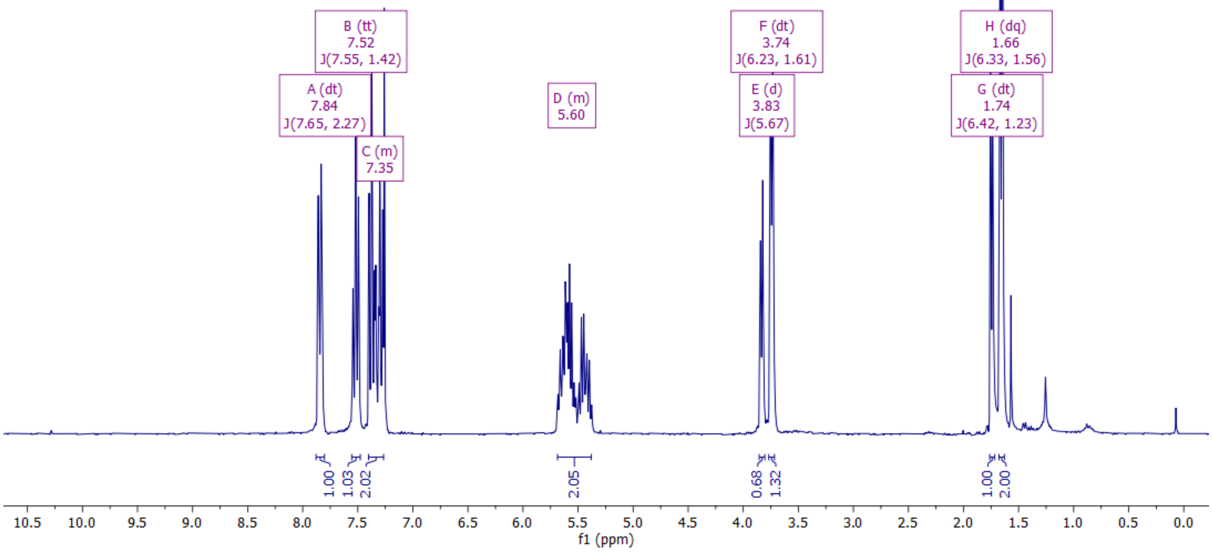

S30
(500 MHz, $CDCl_3$)
A (s) 10.27
B (dd) 7.83
C (td) 7.51
D (td) 7.38
E (d) 7.28
F (ddt) 5.87
G (dq) 5.04
H (ddt) 5.00
I (m) 3.14
J (m) 2.38
1.01
1.02
1.03
1.03
1.03
1.00
1.01
1.04
2.01
2.06
f1 (ppm)


192.5
144.7
137.6
134.0
133.9
132.2
131.2
126.8
115.6
36.1
32.2
S30
(126 MHz, $CDCl_3$)
f1 (ppm)



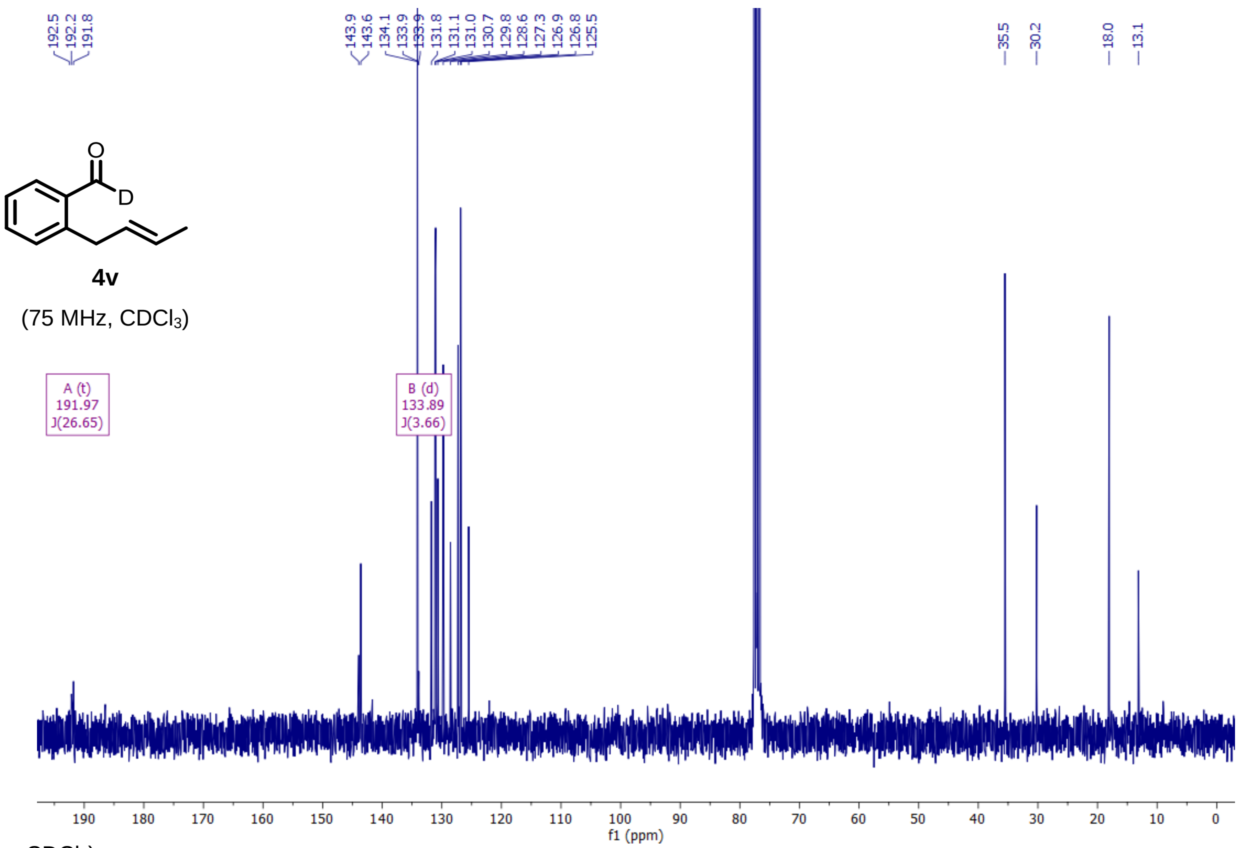
4v

(300 MHz, $CDCl_3$)

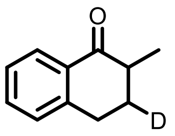


4v

(75 MHz, $CDCl_3$)

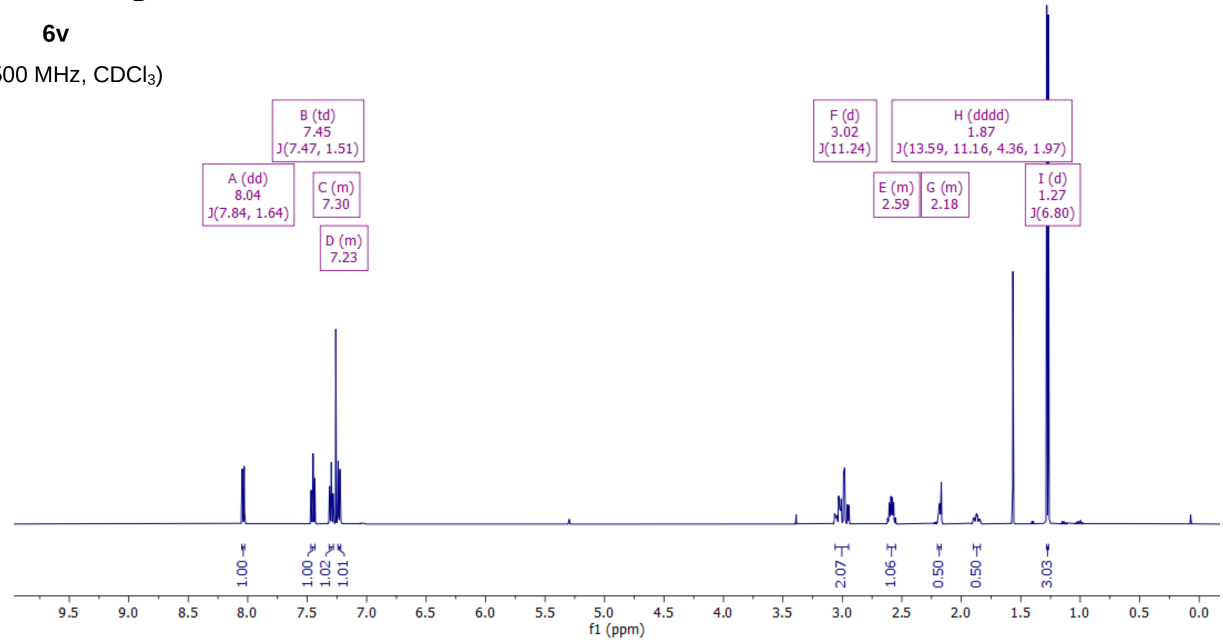


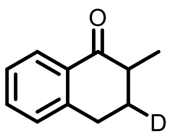
Hz, $CDCl_3$)



6v

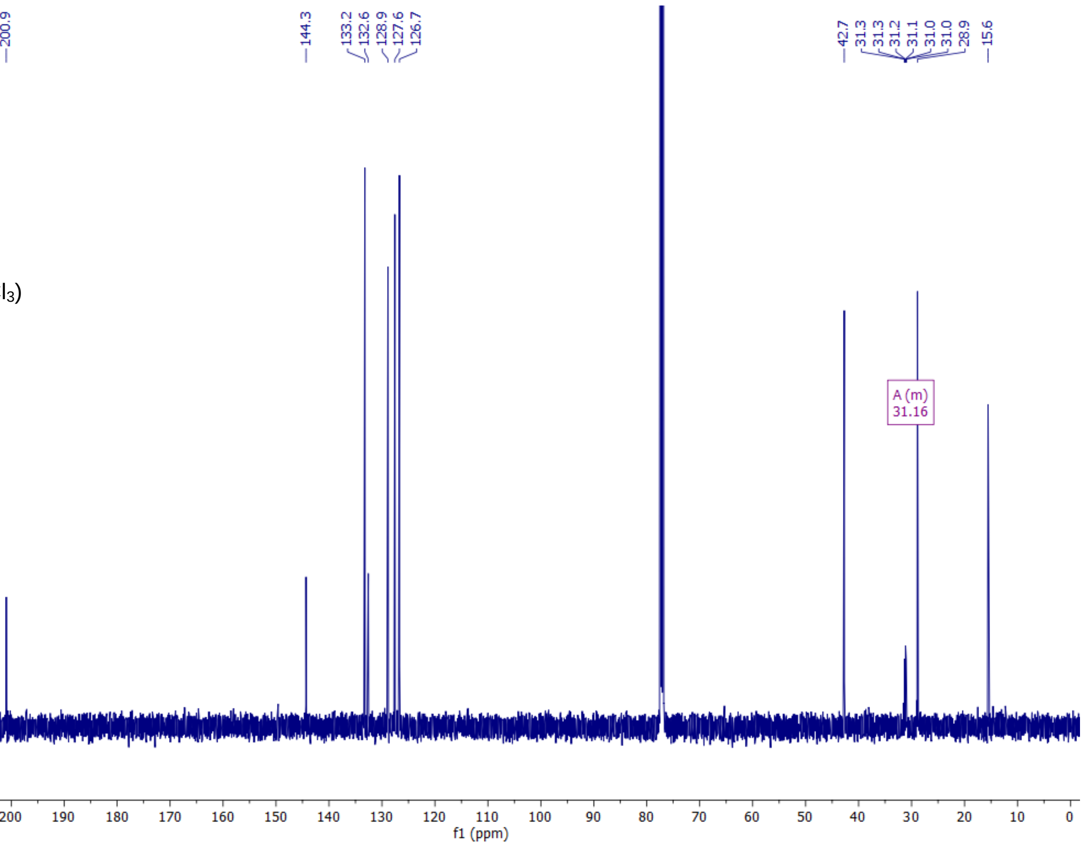
(500 MHz, $CDCl_3$)

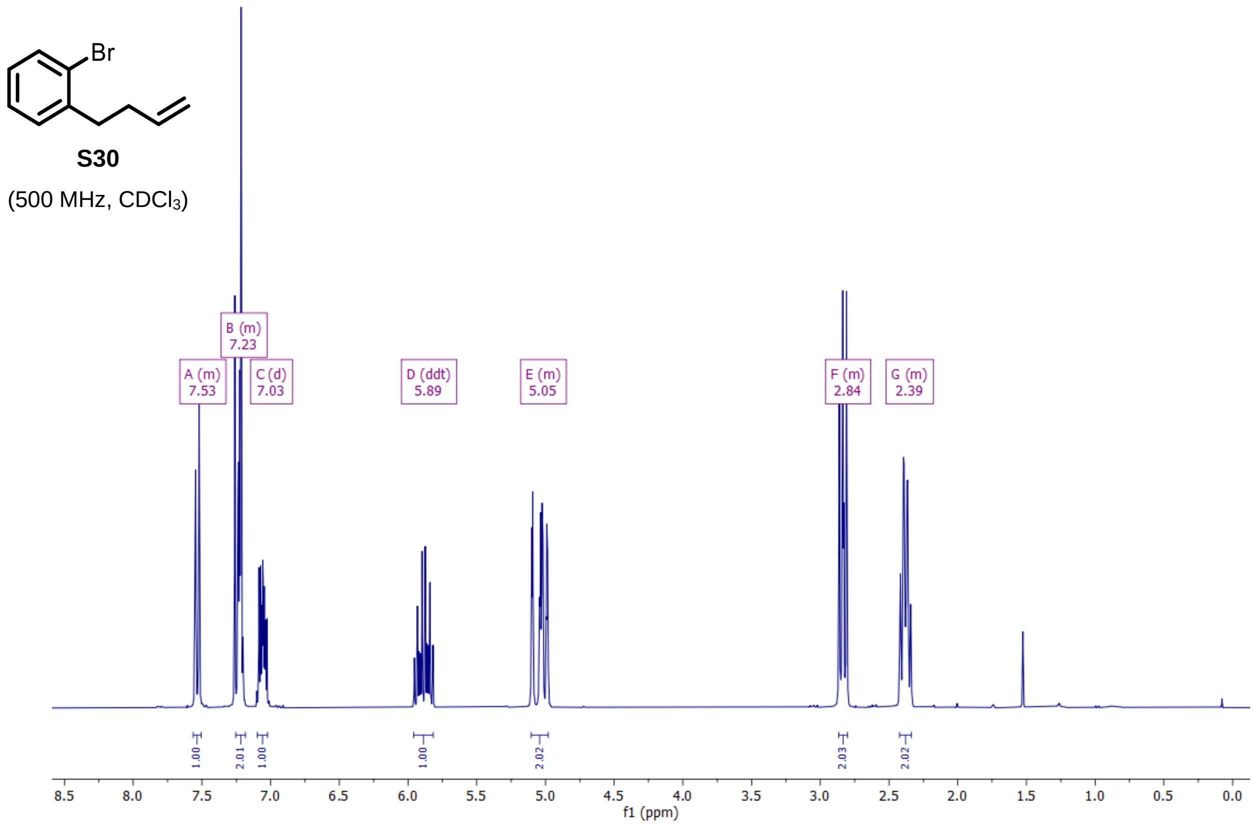


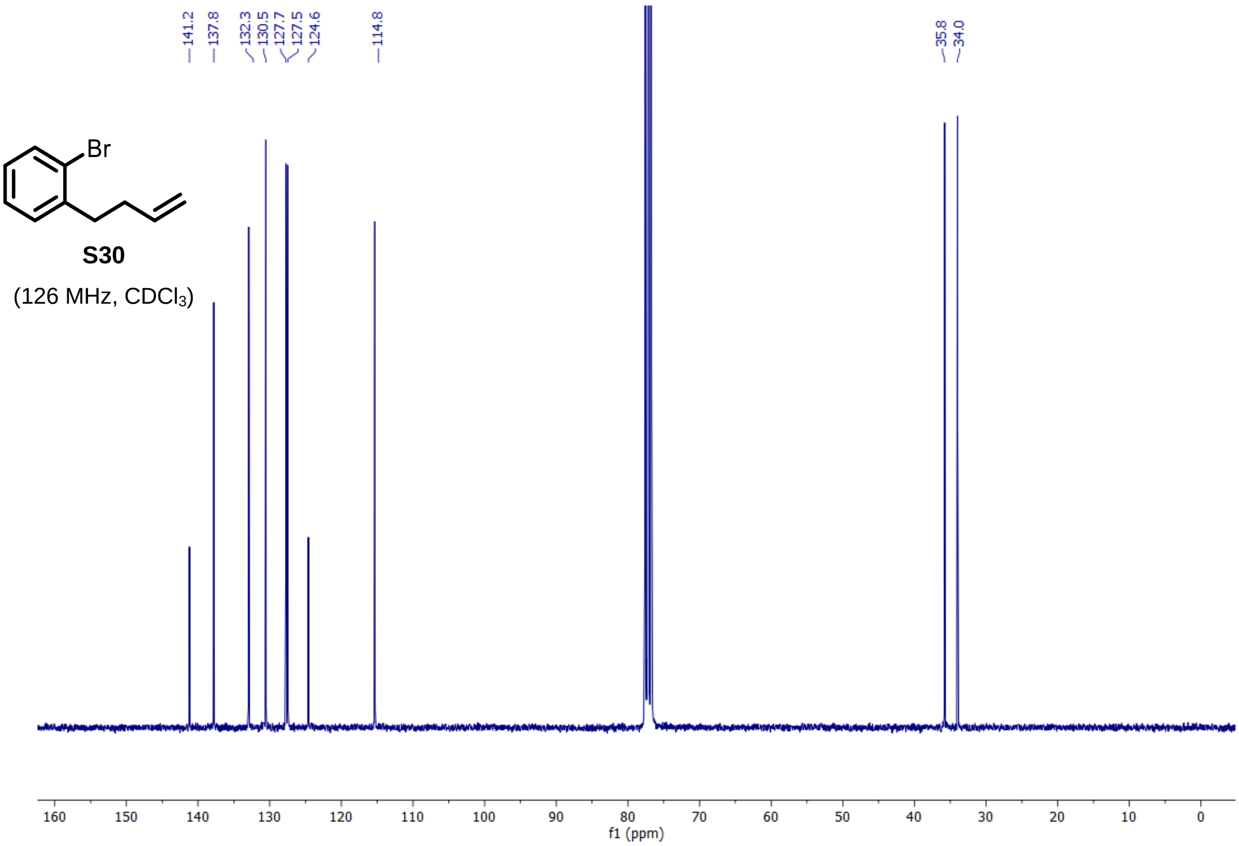


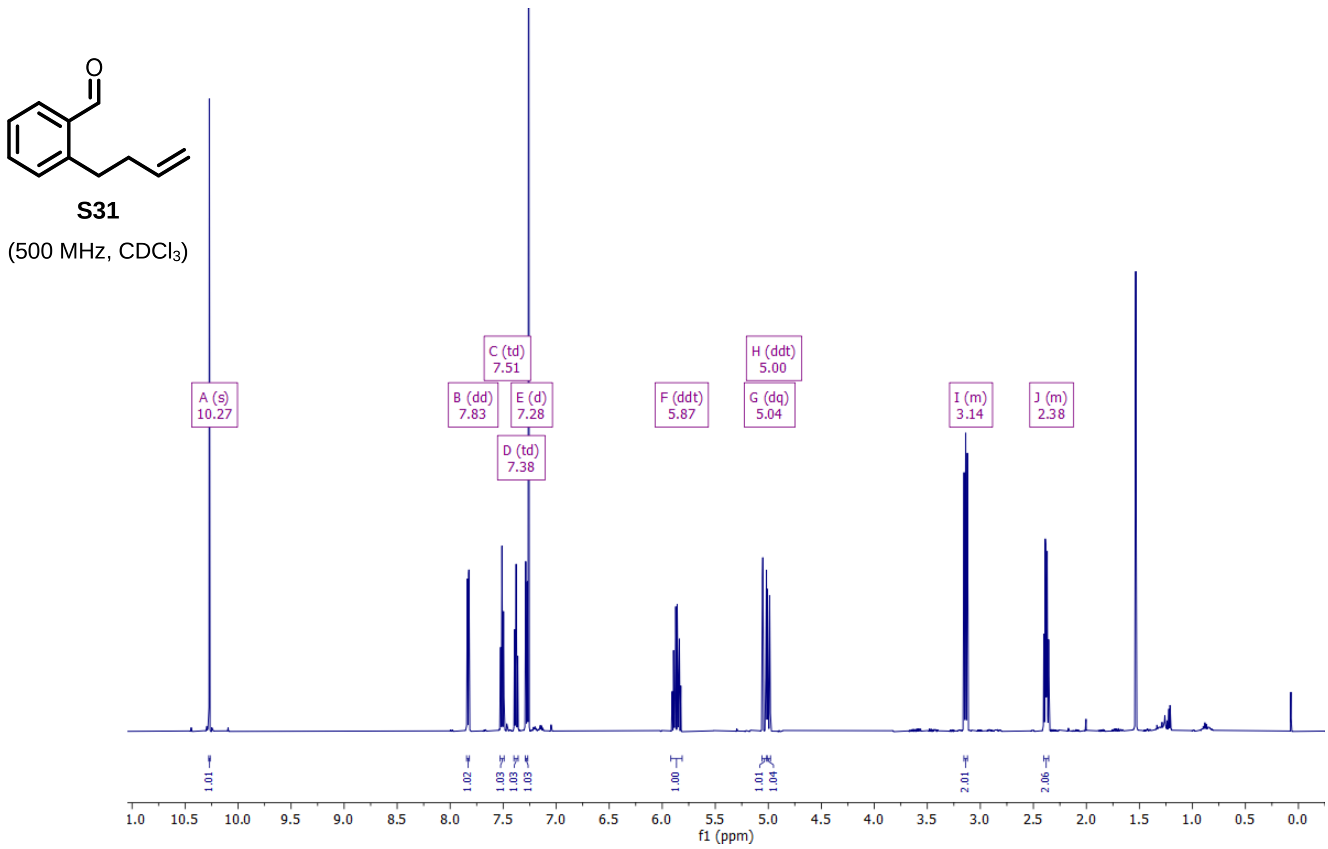
6v

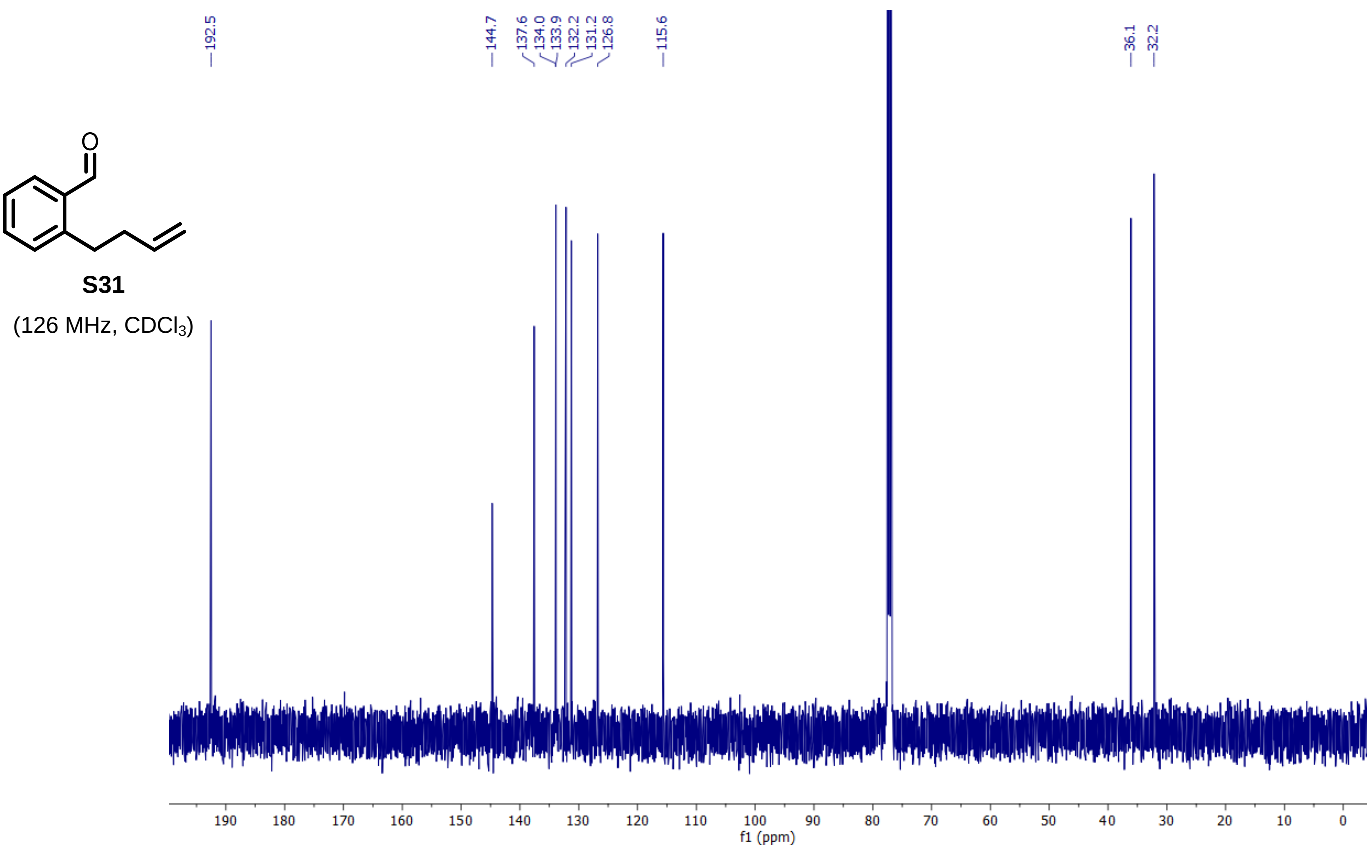
(126 MHz, $CDCl_3$)




Br
S30
(500 MHz, CDCl3)
A (m) 7.53
B (m) 7.23
C (d) 7.03
D (ddt) 5.89
E (m) 5.05
F (m) 2.84
G (m) 2.39
1.00
2.01
1.00
1.00
2.02
2.03
2.02
f1 (ppm)


141.2
137.8
132.3
130.5
127.7
127.5
124.6
114.8
35.8
34.0
Br
S30
(126 MHz, CDCl3)
f1 (ppm)


O
S31
(500 MHz, CDCl3)
A (s)
10.27
B (dd)
7.83
C (td)
7.51
D (td)
7.38
E (d)
7.28
F (ddt)
5.87
G (dq)
5.04
H (ddt)
5.00
I (m)
3.14
J (m)
2.38
1.01
1.02
1.03
1.03
1.03
1.00
1.01
1.04
2.01
2.06
f1 (ppm)


192.5
144.7
137.6
134.0
133.9
132.2
131.2
126.8
115.6
36.1
32.2
O
S31
(126 MHz, CDCl3)
f1 (ppm)

References

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13 Author Contributions

U. Koert administered the project. U. Koert & V. Schmalz conceived and planned the project. V. Schmalz conducted the experimental work.t