Palladium Catalyzed Alkene Carboalkoxylation Reactions of Phenols and Alcohols for the Synthesis of Carbocycles

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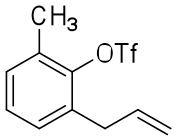
Supporting Information

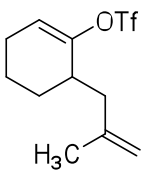
General Considerations: All reactions were carried out under a nitrogen atmosphere using oven or flame-dried glassware. All palladium sources and reagents were obtained from commercial sources and used without further purification unless otherwise noted, and all liquid alcohols were distilled over CaH_2 prior to use. Aryl or alkenyl triflate starting materials were synthesized according to published procedures: 2-allylphenyl trifluoromethanesulfonate,[1,3] 2-allylnaphthalen-1-yl trifluoromethanesulfonate,[2,3] 2-allyl-4-methoxyphenyl trifluoromethanesulfonate,[3] 2-allyl-4-fluorophenyl trifluoromethanesulfonate,[3] 2-(but-3-en-2-yl)phenyl trifluoromethanesulfonate,[5] 2-allylcyclohexan-1-one,[4] 3,3-diallylhexa-1,5-dien-2-yl trifluoromethanesulfonate,[5] ethyl 1-allyl-2-{[(trifluoromethyl)sulfonyl]oxy}cyclopent-2-ene-1-carboxylate,[5] 6-(but-3-en-1-yl)-6-methylcyclohex-1-en-1-yl trifluoromethanesulfonate,[5] *tert*-butyl 3-allyl-4-

{[(trifluoromethyl)sulfonyl]oxy}-3,6-dihydropyridine-1(2*H*)-carboxylate,[5] 3-allyl-3,6-dihydro-2*H*-pyran-4-yl trifluoromethanesulfonate,[5] 2-allyl-3,4-dihydronaphthalen-1-yl trifluoromethanesulfonate,[5] methyl 1-allylcyclopentane-1-carboxylate,[6] 3-methylhexa-1,5-dien-2-yl trifluoromethanesulfonate,[5] and 3-(benzyloxy)hex-5-en-2-one.[7] Alkenyl triflates were stored in a freezer due to observed instability/decomposition of 5-(2-methylallyl)cyclopent-1-en-1-yl trifluoromethanesulfonate at ambient temperature on the bench. Toluene, tetrahydrofuran, diethyl ether, diisopropylamine and dichloromethane were purified using a GlassContour solvent system. All yields refer to isolated compounds that are estimated to be ≥95% pure as judged by ^{1}H NMR analysis, unless noted otherwise.

Preparation and Characterization of Substrates

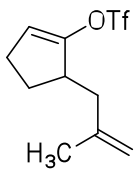


2-Allyl-6-methylphenyl trifluoromethanesulfonate (4d). A flame-dried round bottom flask charged with 2-allyl-6-methylphenol (0.93 g, 6.3 mmol) and dichloromethane (13 mL). The mixture was cooled to 0 °C and triflic anhydride (1.27 mL, 7.5 mmol) was added dropwise. The reaction mixture was allowed to warm to rt with stirring overnight. The crude mixture was filtered through a cotton plug, concentrated *in vacuo*, and purified by flash chromatography on silica gel using 5% ethyl acetate/hexanes as the eluant to afford 1.46 g (83%) of the title product as a clear liquid. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.24 – 7.18 (m, 1H), 7.15 (d, *J* = 7.4 Hz, 2H), 5.91 (ddt, *J* = 16.8, 10.2, 6.6 Hz, 1H), 5.19 – 5.04 (m, 2H), 3.51 (d, *J* = 6.6 Hz, 2H), 2.40 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 146.18, 135.20, 133.73, 131.88, 130.56, 129.17, 128.32, 118.75 (q, J_{C-F} = 318.4 Hz), 117.36, 34.55, 17.38; IR (film) 1404, 1441 cm^{-1}; MS (EI) 280.0373 (280.0381 calcd for $C_{11}H_{11}F_3O_3S$, M^+).



(±)-6-(2-Methylallyl)cyclohex-1-en-1-yl trifluoromethanesulfonate (6c). Using the procedure by Gridnev and Zhang[4], a mixture of DPPF (333 mg, 6 mol %) and $[Pd(\eta^3\text{-}C_3H_5)Cl]_2$ (92 mg, 2.5 mol %) in dry MeOH (40 mL) was stirred at rt under N_2 (g) for 1 h. 2-methyl-2-propen-1-ol (926 µL, 11 mmol) was added and the mixture was stirred for another 10 min, followed by addition of pyrrolidine (167 µL, 2 mmol) and cyclohexanone (1.04 mL, 10 mmol). The mixture was stirred at rt overnight and was then quenched with ice-cooled satd. NH_4Cl (aq). The mixture was extracted with ether (20 mL x 3) and the combined organic phase was washed with water, brine, and dried over Na_2SO_4. The solvent was evaporated and the residue was purified by flash chromatography on silica gel using 10% ethyl acetate/hexanes as the eluant to give 2-(2-methylallyl)cyclohexan-1-one[4] (702 mg, 46%) as a clear oil.

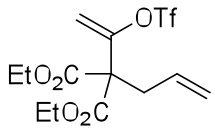
The title compound was prepared following the procedure described below for the synthesis of 5-(2-methylallyl)cyclopent-1-en-1-yl trifluoromethanesulfonate, except using 2-(2-methylallyl)cyclohexan-1-one (702 mg, 4.6 mmol) as the substrate. The product was purified via flash chromatography on silica gel using hexanes as the eluant. This procedure afforded the volatile enol triflate title compound (988 mg, 75%) as a clear liquid. ^{1}H NMR (500 MHz, $CDCl_3$) δ 5.78 (t, J = 3.7 Hz, 1H), 4.82 (s, 1H), 4.73 (s, 1H), 2.62 – 2.52 (m, 1H), 2.45 (dd, J = 13.8, 3.5 Hz, 1H), 2.20 – 2.15 (m, 2H), 2.01 (dd, J = 13.7, 10.9 Hz, 1H), 1.81 – 1.69 (m, 4H), 1.65 – 1.55 (m, 3H); ^{13}C NMR (125 MHz, $CDCl_3$) δ 152.36, 142.53, 119.19, 118.67 (q, $J_{C\text{-}F}$ = 318.1 Hz), 113.37, 40.09, 35.29, 27.20, 24.51, 21.85, 18.43; IR (film) 1413, 1200 cm^{-1}; MS (EI) 284.0690 (284.0694 calcd for $C_{11}H_{15}F_3O_3S$, M^+).



(±)-5-(2-Methylallyl)cyclopent-1-en-1-yl trifluoromethanesulfonate (6g). The allylation of cyclopentanone was accomplished using the procedure for the synthesis of 2-(2-methylallyl)cyclohexan-1-one[4] except with cyclopentanone (1.33 mL, 15 mmol) as

the substrate. The product was purified via flash chromatography on silica gel using 5% ethyl acetate/hexanes as the eluant. This procedure afforded 2-(2-methylallyl)cyclopentan-1-one (1.35 g, 65%) as a clear oil.

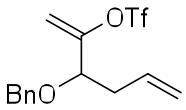
A flame-dried 250 mL round-bottom flask equipped with a stir bar was cooled under a stream of N_2 and charged with diisopropylamine (880 µL, 6.3 mmol) and THF (16 mL). The solution was cooled to 0 ºC and *n*-BuLi (2.5 M in hexanes, 2.34 mL, 5.9 mmol) was added dropwise and stirred for an additional 15 min at 0 ºC before cooling to -78 ºC in a dry ice/acetone bath. A solution of 2-(2-methylallyl)cyclopentan-1-one (735 mg, 5.3 mmol) in THF (11 mL) was added dropwise and stirred for an additional 1.5 h at -78 ºC. Then, a solution of *N*-(2-pyridyl)bis(trifluoromethanesulfonimide) (2.49 g, 6.9 mmol) in THF (13 mL) was added dropwise and the resulting solution was warmed to 0 ºC and stirred for an additional 1.5 h when the solution became an orange, cloudy suspension. The mixture was then cooled to 0 ºC, the reaction was quenched with satd. NH_4Cl (aq.) and the aqueous layer was extracted with Et_2O (3 x 25 mL). The combined organic layers were dried over anhydrous $MgSO_4$, filtered through a cotton plug, concentrated *in vacuo*, and purified by flash chromatography on silica gel using hexanes as the eluant to afford 971 mg (68%) of the title product as a clear liquid. Note: The enol triflate product decomposes upon standing even at 2-8 ºC, as such the compound was stored under N_2 in a freezer. ^{1}H NMR (500 MHz, $CDCl_3$) δ 5.64 (d, *J* = 2.3 Hz, 1H), 4.80 (s, 1H), 4.72 (s, 1H), 3.05 - 2.96 (m, 1H), 2.45 – 2.34 (m, 3H), 2.15 (dtd, *J* = 14.0, 8.7, 5.5 Hz, 1H), 1.95 (dd, *J* = 14.2, 10.6 Hz, 1H), 1.73 (s, 3H), 1.71 – 1.64 (m, 1H); ^{13}C NMR (175 MHz, $CDCl_3$) δ 152.05, 142.85, 118.72 (q, $J_{C\text{-}F}$ = 318.7 Hz), 116.97, 112.44, 41.33, 40.95, 27.20, 26.52, 22.33; IR (film) 1421, 1202 cm^{-1}; MS (EI) 270.0533 (270.0537 calcd for $C_{10}H_{13}F_3O_3S$, M^+).



Diethyl 2-allyl-2-(1-{[(trifluoromethyl)sulfonyl]oxy}vinyl)malonate (8a). To a cooled solution of diethyl 2-acetylmalonate (1.8 mL, 9.9 mmol) in THF (33 mL) at 0 ºC was added sodium hydride (60% dispersion in mineral oil, 436 mg, 18.2 mmol) portionwise,

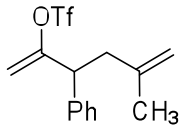
and the resulting mixture was stirred for 30 min at 0 ºC. Allyl bromide (943 µL, 10.9 mmol) was then added dropwise and the resulting mixture was heated to reflux overnight. The mixture was then cooled to rt, quenched with H_2O (25 mL), and the aqueous layer was extracted using Et_2O (3 x 20 mL). The combined organic layers were dried over anhydrous $MgSO_4$, concentrated *in vacuo*, and the crude mixture was purified via flash chromatography on silica gel using 10% ether/pentane as the eluant to afford 1.02 g (42%) of diethyl 2-acetyl-2-allylmalonate (**8a'**) as a clear oil. ^{1}H NMR (400 MHz, $CDCl_3$) δ 5.87 (ddt, *J* = 17.2, 10.1, 7.2 Hz, 1H), 5.18 – 4.99 (m, 2H), 4.25 (q, *J* = 7.1 Hz, 4H), 2.83 (d, *J* = 7.2 Hz, 2H), 2.33 (s, 3H), 1.32 – 1.24 (m, 6H).

The enol triflate was prepared according to the procedure used for the synthesis of 1-(1-allylcyclopentyl)vinyl trifluoromethanesulfonate except with diethyl 2-acetyl-2-allylmalonate (518 mg, 2.14 mmol) in place of 1-(1-allylcyclopentyl)ethan-1-one. The product was purified via flash chromatography on silica gel using 10% ethyl acetate/hexanes as the eluant. This procedure afforded 703 mg (88%) of the title compound as a clear oil. ^{1}H NMR (400 MHz, $CDCl_3$) δ 5.80 (ddt, *J* = 17.3, 10.2, 7.2 Hz, 1H), 5.59 (d, *J* = 4.8 Hz, 1H), 5.46 (d, *J* = 4.8 Hz, 1H), 5.21 – 5.11 (m, 2H), 4.25 (qq, *J* = 7.2, 3.7 Hz, 4H), 2.86 (d, *J* = 7.2 Hz, 2H), 1.28 (t, *J* = 7.1 Hz, 6H); ^{13}C NMR (125 MHz, $CDCl_3$) δ 166.78, 150.37, 131.57, 120.06, 118.35 (q, $J_{C\text{-}F}$ = 317.5 Hz), 107.44, 62.67, 62.59, 37.99, 13.97; IR (film) 1739, 1204 cm^{-1}; MS (ESI) 375.0720 (375.072 calcd for $C_{13}H_{17}F_3O_7S$, M + H^+).



(±)-3-(Benzyloxy)hexa-1,5-dien-2-yl trifluoromethanesulfonate (8d). The title compound was prepared using the procedure employed for the synthesis of 5-methyl-3-phenylhexa-1,5-dien-2-yl trifluoromethanesulfonate except with 3-(benzyloxy)hex-5-en-2-one[7] (990 mg, 4.85 mmol) in place of 5-methyl-3-phenylhex-5-en-2-one. The product was purified via flash chromatography on silica gel using 5% ethyl acetate/hexanes as the eluant. This procedure afforded the title compound (1.26 g, 77%) as a clear oil. ^{1}H

NMR (500 MHz, $CDCl_3$) δ 7.38 - 7.28 (m, 5H), 5.75 (ddt, *J* = 17.2, 10.2, 7.0 Hz, 1H), 5.35 (d, *J* = 3.6 Hz, 1H), 5.25 (d, *J* = 3.7 Hz, 1H), 5.16 – 5.05 (m, 2H), 4.71 (d, *J* = 11.8 Hz, 1H), 4.42 (d, *J* = 11.8 Hz, 1H), 3.92 (t, *J* = 6.5 Hz, 1H), 2.46 (t, *J* = 6.6 Hz, 2H); ^{13}C NMR (125 MHz, $CDCl_3$) δ 153.84, 137.39, 132.76, 128.62, 128.05, 118.57 (q, J_{C-F} = 317.8 Hz), 118.51, 106.31, 77.88, 71.37, 37.44; IR (film) 1416, 1207 cm^{-1}; MS (EI) 336.0638 (336.0643 calcd for $C_{14}H_{15}F_2O_4S$, M^+).



(±)-5-Methyl-3-phenylhexa-1,5-dien-2-yl trifluoromethanesulfonate (8e). Following a slightly modified procedure by Aïssa and Yip[8], diisopropylamine (3.5 mL, 25 mmol) was dissolved in THF (31 mL) and cooled to 0 ºC. *n*-BuLi (9.2 mL, 23 mmol, 2.5M in hexanes) was added slowly and stirred for 15 min at 0 ºC before cooling to -78 ºC. Methyl phenylacetate (2.82 mL, 20 mmol) in THF (67 mL) was added dropwise and stirred for an additional 40 min at -78 ºC. Then, 3-bromo-2-methylpropene (2.2 mL, 22 mmol) was added dropwise at -78 ºC and the resulting mixture was warmed to rt with stirring for 16 h. The reaction mixture was cooled to 0 ºC, quenched with saturated aq. NH_4Cl, and the aqueous layer was extracted with Et_2O (3 x 20 mL). The organic layer was dried with anhydrous $MgSO_4$, filtered through a cotton plug, and concentrated *in vacuo*. The crude mixture was purified by flash chromatography on silica gel using 5% ethyl acetate/hexanes as the eluant to afford 2.84 g (69%) of methyl 4-methyl-2-phenylpent-4-enoate as a clear oil. Characterization data matched those previously reported in the literature.[8]

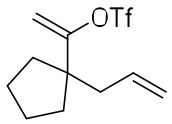
In a flame-dried round bottom flask was added methyl 4-methyl-2-phenylpent-4-enoate (839 mg, 4.1 mmol) and THF (21 mL). *N,O*-dimethylhydroxylamine hydrochloride (816 mg, 8.6 mmol) was added and the reaction mixture was cooled to 0 ºC. *i*-PrMgCl (8.2 mL, 16.4 mmol, 2M in THF) was added dropwise and the resulting mixture was stirred at 0 °C for 1 h. The reaction was quenched with saturated aq. NH_4Cl

(15 mL) and the aqueous layer was extracted using EtOAc (3 x 15 mL). The organic fractions were combined and washed with brine, dried over anhydrous Na_2SO_4, filtered through a cotton plug, and concreted *in vacuo*. The crude *N*-methoxy-*N*,4-dimethyl-2-phenylpent-4-enamide product was used without further purification.

A flame-dried round bottom flask was charged with *N*-methoxy-*N*,4-dimethyl-2-phenylpent-4-enamide (934 mg, 4 mmol) and THF (8 mL) and cooled to 0 ºC. Methyl magnesium bromide (1.6 mL, 4.8 mmol, 3M in THF) was added dropwise and the resulting mixture was stirred at 0 ºC for 1 h. The reaction mixture was quenched with saturated aq. NH_4Cl (10 mL) and the aqueous layer was extracted with EtOAc (3 x 10 mL). The combined organic layers were dried over anhydrous Na_2SO_4, filtered through a cotton plug, and concentrated *in vacuo*. The crude mixture was purified by flash chromatography on silica gel using 5% ethyl acetate/hexanes as the eluant to afford 610 mg (81%) of 5-methyl-3-phenylhex-5-en-2-one as a clear oil. ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.32 (t, *J* = 7.4 Hz, 2H), 7.28 – 7.17 (m, 3H), 4.70 (s, 1H), 4.59 (s, 1H), 3.87 (t, *J* = 7.5 Hz, 1H), 2.82 (dd, *J* = 14.9, 7.6 Hz, 1H), 2.38 (dd, *J* = 14.9, 7.3 Hz, 1H), 2.08 (s, 3H), 1.67 (s, 3H).

A flame-dried round bottom flask was charged wtih diisopropylamine (0.63 mL, 4.5 mmol) and THF (14 mL) and cooled to 0 ºC. *n*-BuLi (1.7 mL, 4.2 mmol, 2.5M in hexanes) was added slowly and the resulting mixture was stirred at 0 ºC for 15 min before cooling to -78 ºC. A solution of 5-methyl-3-phenylhex-5-en-2-one (610 mg, 3.2 mmol) in THF (6.5 mL) was added dropwise and the resulting mixture was stirred for 2 h at -78 ºC. A solution of *N*-(2-pyridyl)bis(trifluoromethanesulfonimide) (1.5 g, 4.2 mmol) in THF (8 mL) was added dropwise at -78 ºC followed by warming to 0 ºC with stirring for an additional 3 hours. The reaction mixture was quenched at 0 ºC using saturated aq. NH_4Cl (15 mL) and the aqueous phase was extracted using Et_2O (3 x 15 mL). The combined organic fractions were dried over anhydrous $MgSO_4$, filtered through a cotton plug, and concentrated *in vacuo*. The crude mixture was purified by flash chromatography on silica gel using 5% ethyl acetate/hexanes as the eluant to afford 621 mg (60%) of the title product as a clear oil. ^{1}H NMR (700 MHz, $CDCl_3$) δ 7.34 (t, *J* = 7.7 Hz, 2H), 7.28 (t, *J* = 7.4 Hz, 1H), 7.22 (d, *J* = 8.0 Hz, 2H), 5.22 (d, *J* = 3.9 Hz, 1H),

5.06 (d, J = 3.9 Hz, 1H), 4.76 (s, 1H), 4.66 (s, 1H), 3.76 (t, J = 7.7 Hz, 1H), 2.67 (dd, J = 14.5, 7.0 Hz, 1H), 2.51 (dd, J = 14.5, 8.5 Hz, 1H), 1.69 (d, J = 1.4 Hz, 3H); ^{13}C NMR (175 MHz, $CDCl_3$) δ 158.39, 141.49, 138.64, 128.84, 128.17, 127.73, 118.5 (q, $J_{C\text{-}F}$ = 319 Hz), 113.74, 104.51, 48.30, 41.38, 22.23; IR (film) 1416, 1205 cm^{-1}; MS (EI) 320.0692 (320.0694 calcd for $C_{14}H_{15}F_3O_3S$, M^+).

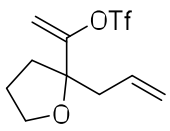


1-(1-Allylcyclopentyl)vinyl trifluoromethanesulfonate (8f). A round bottom flask with a stir bar was charged with methyl 1-allylcyclopentane-1-carboxylate[6] (2.5 g, 15 mmol), methanol (60 mL), and de-ionized water (30 mL). Then, solid KOH (5 g, 88 mmol) was added and the mixture was heated to reflux overnight. The mixture was cooled to rt and concentrated *in vacuo*. The resulting mixture of water and product was washed with dichloromethane (30 mL), then the aqueous layer was acidified to pH = 1 using aq. HCl (6 M), and then was extracted with dichloromethane (3 x 20 mL). The combined organic layers were dried using anhydrous $MgSO_4$ and concentrated *in vacuo*. The 1-allylcyclopentane-1-carboxylic acid was used without further purification. ^{1}H NMR (500 MHz, $CDCl_3$) δ 5.77 (ddt, J = 17.3, 10.2, 7.2 Hz, 1H), 5.12 – 5.01 (m, 2H), 2.38 (d, J = 7.2 Hz, 2H), 2.10 (dt, J = 10.3, 4.6 Hz, 2H), 1.74 – 1.51 (m, 6H).

A flame-dried round bottom flask with a stir bar was charged with 1-allylcyclopentane-1-carboxylic acid (1 g, 6.5 mmol) and Et_2O (29 mL). The mixture was cooled to -78 ^{o}C in an acetone/dry ice bath. MeLi (10.1 mL, 1.6 M in Et_2O) was added slowly and the resulting mixture was stirred for 1 h at -78 ^{o}C. Then, the mixture was placed in an oil bath and refluxed for 4 h. The crude mixture was cooled to 0 ^{o}C in an ice bath and slowly quenched with de-ionized water (15 mL). The aqueous layer was extracted with Et_2O (3 x 15 mL) and the combined organic layers were dried over anhydrous $MgSO_4$, filtered through a cotton plug, concentrated *in vacuo*, and isolated via flash chromatography on silica gel using 10% ethyl acetate/hexanes as the eluant.

This procedure afforded 525 mg (53%) of 1-(1-allylcyclopentyl)ethan-1-one as a clear oil. ^{1}H NMR (700 MHz, $CDCl_3$) δ 5.64 (ddt, *J* = 17.2, 10.2, 7.1 Hz, 1H), 5.11 – 4.96 (m, 2H), 2.37 (d, *J* = 7.1 Hz, 2H), 2.14 (s, 3H), 2.02 (dt, *J* = 12.5, 6.2 Hz, 2H), 1.70 – 1.54 (m, 4H), 1.49 (dt, *J* = 12.3, 6.3 Hz, 2H); ^{13}C NMR (175 MHz, $CDCl_3$) δ 212.14, 134.72, 117.59, 60.02, 42.78, 34.29, 25.94, 25.28.

A flame-dried round bottom flask with a stir bar was charged with KHMDS (826 mg, 4.14 mmol) and THF (28 mL). After cooling to -78 ºC in an acetone/dry ice bath, a solution of 1-(1-allylcyclopentyl)ethan-1-one (525 mg, 3.45 mmol) in THF (7 mL) was added dropwise and the mixture was stirred for 30 min at -78 ºC. A solution of phenyl triflimide (1.36 g, 3.8 mmol) in THF (8 mL) was added dropwise and stirred for an additional 20 min at -78 ºC. The mixture was then warmed to RT and stirred for 2 h. The reaction was quenched with saturated aq. NH_4Cl (20 mL), the aqueous layer was extracted with Et_2O (3 x 20 mL), the combined organic layers were dried over anhydrous $MgSO_4$, filtered through a cotton plug, concentrated *in vacuo*, and isolated via flash chromatography on silica gel using pentane as the eluant. Note: The enol triflate product decomposes slowly on silica gel, thus high flow rate was necessary in order to avoid substantial product loss. This procedure afforded 463 mg (47%) of the title product as a clear, volatile liquid. ^{1}H NMR (700 MHz, $CDCl_3$) δ 5.70 (ddt, *J* = 17.4, 10.2, 7.3 Hz, 1H), 5.15 (d, *J* = 4.3 Hz, 1H), 5.10 – 5.03 (m, 2H), 4.91 (d, *J* = 4.4 Hz, 1H), 2.24 (dd, *J* = 7.3, 1.2 Hz, 2H), 1.81 – 1.75 (m, 2H), 1.75 – 1.68 (m, 4H), 1.63 – 1.58 (m, 2H); ^{13}C NMR (175 MHz, $CDCl_3$) δ 161.26, 133.93, 118.51 (q, $J_{C\text{-}F}$ = 317.7 Hz), 118.13, 101.62, 51.70, 40.83, 35.44, 23.48; IR (film) 1405, 1204 cm^{-1}; MS (EI) 134.1099 (134.1090 calcd for $C_{10}H_{14}^+$, $M^+ - HOSO_2CF_3$).



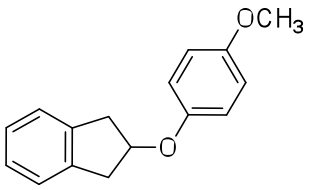
1-(2-allyltetrahydrofuran-2-yl)vinyl trifluoromethanesulfonate (8g). The title compound was prepared using the procedure employed for the synthesis of 1-(1-

allylcyclopentyl)vinyl trifluoromethanesulfonate except methyl 2-allyltetrahydrofuran-2-carboxylate[6] (851 mg, 5 mmol) was used in place of methyl 1-allylcyclopentane-1-carboxylate.[6] The product was purified via flash chromatography on silica gel using 5% ether/pentane to 10% ether/pentane as the eluant. This 3-step procedure afforded 584 mg (41% overall yield) of the title compound as a clear liquid. ^{1}H NMR (500 MHz, $CDCl_3$) δ 5.77 (dddd, J = 16.6, 10.8, 7.6, 6.7 Hz, 1H), 5.24 (d, J = 3.8 Hz, 1H), 5.21 (d, J = 3.8 Hz, 1H), 5.17 – 5.08 (m, 2H), 3.98 – 3.87 (m, 2H), 2.51 (ddt, J = 14.3, 6.7, 1.3 Hz, 1H), 2.41 (ddt, J = 14.3, 7.6, 1.2 Hz, 1H), 2.10 (ddd, J = 12.3, 7.0, 5.2 Hz, 1H), 2.01 – 1.90 (m, 2H), 1.90 – 1.81 (m, 1H); ^{13}C NMR (125 MHz, $CDCl_3$) δ 157.29, 132.60, 118.96, 118.51 (q, J_{CF} = 317 Hz), 102.53, 84.41, 69.09, 42.06, 34.16, 25.52; IR (film) 1417, 1207 cm^{-1}; MS (ESI) 245.0098 (245.0090 calcd for $C_7H_8F_3O_4S^+$, M^+ – allyl).

Preparation and Characterization of Products

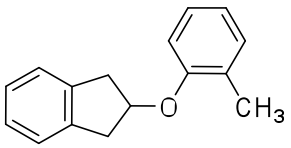
General Procedure for Pd-Catalyzed Alkene Carboalkoxylation Reactions

A flame-dried Schlenk tube, test tube, or vial equipped with a stir bar was cooled under a stream of N_2 and charged with $Pd(OAc)_2$ (4 mol %), RuPhos (10 mol %), the phenol or alcohol nucleophile (0.12 mmol, 1.2 equiv), and LiO^tBu (0.14 mmol, 1.4 equiv). A solution of the aryl or alkenyl triflate (0.1 mmol, 1.0 equiv) in toluene (0.5 mL) was added via syringe, followed by toluene (0.5 mL) to wash the inside of the tube so all reagents were in solution. The reaction mixture was heated to 95 ^{o}C (unless otherwise noted) until the starting material was completely consumed as judged by ^{1}H NMR analysis of an aliquot removed from the reaction mixture. The mixture was cooled to rt, quenched with saturated aqueous NH_4Cl (2 mL), and the aqueous layer was extracted with ethyl acetate (3 x 5 mL). The combined organic layers were dried over anhydrous Na_2SO_4, filtered through a cotton plug, and concentrated *in vacuo*. The crude mixtures were purified by flash chromatography on silica gel unless otherwise noted.

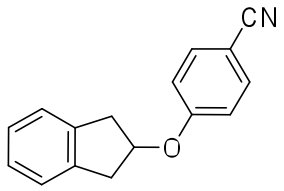


(±)-2-(4-Methoxypheoxy)-2,3-dihydro-1*H*-indene (5a). The general procedure was used for the coupling of 4-methoxyphenol (14.9 mg, 0.12 mmol) and 2-allylphenyl trifluoromethanesulfonate (26.6 mg, 0.1 mmol) except the reaction was conducted in xylenes solvent (1 mL) at 130 ºC for 1 h. The product was purified by flash chromatography on silica gel using 5% ethyl acetate/hexanes as the eluant. This procedure afforded 22.7 mg (94%) of the title compound as a solid (m.p. = 89-92 ºC). ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.29 – 7.15 (m, 4H), 6.86 (app. s, 4H), 5.10 (tt, *J* = 6.4, 3.3 Hz, 1H), 3.79 (s, 3H), 3.34 (dd, *J* = 16.6, 6.3 Hz, 2H), 3.18 (dd, *J* = 16.6, 3.3 Hz, 2H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 153.98, 151.83, 140.92, 126.79, 124.89, 116.78, 114.81, 78.40, 55.85, 39.85; IR (film) 1240, 1491 cm^{-1}; MS (ESI) 258.1492 (258.1489 calcd for $C_{16}H_{16}O_2$, M + NH_4^+).

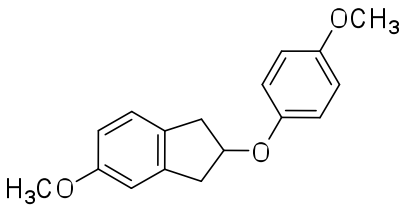
(±)-2-(4-Methoxypheoxy)-2,3-dihydro-1*H*-indene (5a). The general procedure was used for the coupling of 4-methoxyphenol (149 mg, 1.2 mmol) and 2-allylphenyl trifluoromethanesulfonate (266 mg, 1 mmol) except the reaction was conducted in xylenes solvent (10 mL) at 130 ºC for 1 h. The product was purified by flash chromatography on silica gel using 100% hexanes to 5% ethyl acetate/hexanes as the eluant. This procedure afforded 233 mg (97%) of the title compound as a solid (m.p. = 89-92 ºC). Characterization data were identical to those reported above.



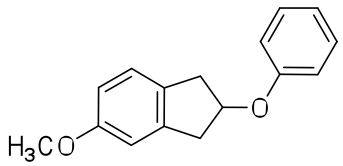
(±)-2-(*o*-Tolyloxy)-2,3-dihydro-1*H*-indene (5b). The general procedure was used for the coupling of *o*-cresol (12.4 μL, 0.12 mmol) and 2-allylphenyl trifluoromethanesulfonate (26.6 mg, 0.1 mmol) except the reaction was conducted in xylenes solvent (1 mL) at 130 °C for 4 h. The product was purified by flash chromatography on silica gel using hexanes as the eluant. The procedure afforded 20.2 mg (90%) of the title compound as a clear oil. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.26 – 7.10 (m, 6H), 6.93 – 6.82 (m, 2H), 5.18 (tt, *J* = 6.6, 3.5 Hz, 1 H), 3.39 (dd, *J* = 16.6, 6.5 Hz, 2H), 3.19 (dd, *J* = 16.6, 3.5 Hz, 2H), 2.13 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 156.04, 141.02, 131.00, 127.88, 126.75, 126.74, 124.83, 120.51, 112.53, 77.91, 40.10, 16.48; IR (film) 1491, 1241 cm^{-1}; MS (EI) 224.1202 (224.1201 calcd for $C_{16}H_{16}O$, M^+).



(±)-4-[(2,3-Dihydro-1*H*-inden-2-yl)oxy]benzonitrile (5c). The general procedure was used for the coupling of 4-cyanophenol (14.3 mg, 0.12 mmol) and 2-allylphenyl trifluoromethanesulfonate (26.6 mg, 0.1 mmol) except the reaction was conducted in mesitylene solvent at 160 °C for 16 h. The product was purified by flash chromatography on silica gel using 10% ether/hexanes as the eluant. This procedure afforded 9.8 mg (42%) of the title compound as a white solid (m.p. = 136-138 °C). ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.63 – 7.55 (m, 2H), 7.30 – 7.17 (m, 4H), 6.99 – 6.91 (m, 2H), 5.21 (tt, *J* = 6.1, 2.8 Hz, 1H), 3.42 (dd, *J* = 16.8, 6.2 Hz, 2H), 3.18 (dd, *J* = 16.8, 2.8 Hz, 2H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 161.23, 140.27, 134.16, 127.11, 124.90, 119.37, 116.17, 104.00, 78.31, 39.77; IR (film) 1506, 1254 cm^{-1}; MS (EI) 235.0998 (235.0997 calcd for $C_{16}H_{13}NO$, M^+).

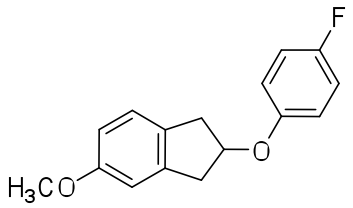


(±)-5-Methoxy-2-(4-methoxyphenoxy)-2,3-dihydro-1*H*-indene (5d). The general procedure was used for the coupling of 4-methoxyphenol (14.9 mg, 0.12 mmol) and 2-allyl-4-methoxyphenyl trifluoromethanesulfonate (29.6 mg, 0.1 mmol) except the reaction was conducted in xylenes solvent at 130 ºC for 16 h. The product was purified by flash chromatography on silica gel using 10% ethyl acetate/hexanes as the eluant. The procedure afforded 23.9 mg (88%) of the title compound as a solid (m.p. = 80-83 ºC). ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.13 (d, *J* = 8.2 Hz, 1H), 6.90 – 6.67 (m, 6H), 5.09 (tt, *J* = 6.4, 3.3 Hz, 1H), 3.79 (s, 3H), 3.78 (s, 3H), 3.29 (td, *J* = 16.1, 6.3 Hz, 2H), 3.11 (ddd, *J* = 19.4, 16.5, 3.3 Hz, 2H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 159.09, 153.97, 151.85, 142.36, 132.85, 125.40, 116.77, 114.81, 112.80, 110.32, 78.87, 55.86, 55.56, 40.11, 39.00; IR (film) 1504, 1228 cm $^{-1}$; MS (ESI) 271.1333 (271.1329 calcd for $C_{17}H_{18}O_3$, M + H^+).

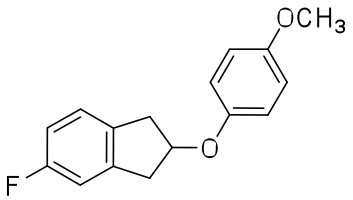


(±)-5-Methoxy-2-phenoxy-2,3-dihydro-1*H*-indene (5e). The general procedure was used for the coupling of phenol (11.3 mg, 0.12 mmol) and 2-allyl-4-methoxyphenyl trifluoromethanesulfonate (29.6 mg, 0.1 mmol) except the reaction was conducted in xylenes solvent at 130 ºC for 16 h. The product was purified by flash chromatography on silica gel using 10% ethyl acetate/hexanes as the eluant. The procedure afforded 22.7 mg (94 %) of the title compound as a white solid (m.p. = 77-79 ºC). ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.30 (t, *J* = 7.7 Hz, 2H), 7.15 (d, *J* = 8.2 Hz, 1H), 7.00 – 6.89 (m, 3H), 6.85 – 6.80 (m, 1H), 6.76 (dd, *J* = 8.2, 2.5 Hz, 1H), 5.18 (tt, *J* = 6.4, 3.2 Hz, 1H), 3.80 (s, 3H), 3.34 (td, *J* = 15.9, 6.3 Hz, 2H), 3.14 (ddd, *J* = 19.3, 16.5, 3.2 Hz, 2H); ^{13}C NMR

(100 MHz, $CDCl_3$) δ 159.12, 157.81, 142.32, 132.80, 129.62, 125.39, 120.76, 115.61, 112.86, 110.29, 78.06, 55.56, 40.15, 39.05; IR (film) 1240, 1491 cm^{-1}; MS (ESI) 241.1225 (241.1223 calcd for $C_{16}H_{16}O_2$, M + H^+).

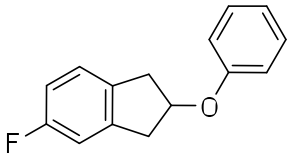


(±)-2-(4-Fluorophenoxy)-5-methoxy-2,3-dihydro-1*H*-indene (5f). The general procedure was used for the coupling of 4-fluorophenol (13.5 mg, 0.12 mmol) and 2-allyl-4-methoxyphenyl trifluoromethanesulfonate (29.6 mg, 0.1 mmol) except the reaction was conducted in xylenes solvent at 130 ºC for 16 h. The product was purified by flash chromatography on silica gel using 5% ethyl acetate/hexanes as the eluant. The procedure afforded 22.8 mg (88%) of the title compound as clear oil. ^1H NMR (400 MHz, $CDCl_3$) δ 7.14 (d, *J* = 8.2 Hz, 1H), 7.03 – 6.93 (m, 2H), 6.90 – 6.70 (m, 4H), 5.10 (dtt, *J* = 6.3, 3.2, 1.9 Hz, 1H), 3.79 (s, 3H), 3.31 (td, *J* = 16.1, 6.3 Hz, 2H), 3.11 (ddd, *J* = 19.5, 16.5, 3.1 Hz, 2H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 159.19, 158.56, 155.05 (d, $J_{C1\text{-}F}$ = 228 Hz), 142.19, 132.66, 125.41,116.70 (d, $J_{C3\text{-}F}$ = 7 Hz), 115.99 (d, $J_{C2\text{-}F}$ = 23 Hz), 112.92, 110.34, 78.89, 55.58, 40.08, 38.98; IR (film) 1502, 1198 cm^{-1}; MS (EI) 258.1060 (258.1056 calcd for $C_{16}H_{15}FO_2$, M^+).

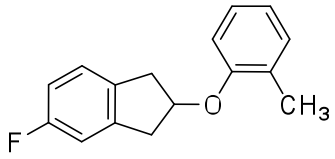


(±)-5-Fluoro-2-(4-methoxyphenoxy)-2,3-dihydro-1*H*-indene (5g). The general procedure was used for the coupling of 4-methoxyphenol (14.9 mg, 0.12 mmol) and 2-allyl-4-fluorophenyl trifluoromethanesulfonate (29.2 mg, 0.1 mmol) with a reaction time

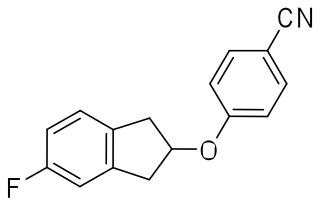
of 1 h. The product was purified by flash chromatography on silica gel using 5% ethyl acetate/hexanes as the eluant. This procedure afforded 22.5 mg (87%) of the title compound as a white solid (m.p. = 71-74 ºC). ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.16 (dd, *J* = 8.1, 5.2 Hz, 1H), 6.95 – 6.80 (m, 6H), 5.10 (tt, *J* = 6.2, 3.1 Hz, 1H), 3.78 (s, 3H), 3.29 (td, *J* = 15.4, 14.3, 6.2 Hz, 2H), 3.13 (td, *J* = 15.9, 15.3, 2.5 Hz, 2H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 162.38 (d, $J_{C1\text{-}F}$ = 242 Hz), 154.12, 151.67, 143.03 (d, $J_{C3\text{-}F}$ = 8 Hz), 136.30 (d, $J_{C4\text{-}F}$ = 3 Hz), 125.75 (d, $J_{C3\text{-}F}$ = 9 Hz), 116.83, 114.87, 113.70 (d, $J_{C2\text{-}F}$ = 22 Hz), 111.94 (d, $J_{C2\text{-}F}$ = 22 Hz), 78.81, 55.86, 40.01 (d, $J_{C4\text{-}F}$ = 2 Hz), 39.09; IR (film) 1505, 1227 cm^{-1}; MS (EI) 258.1066 (258.1056 calcd for $C_{16}H_{15}FO_2$, M^+).



(±)-5-Fluoro-2-phenoxy-2,3-dihydro-1*H*-indene (5h). The general procedure was used for the coupling of phenol (11.3 mg, 0.12 mmol) and 2-allyl-4-fluorophenyl trifluoromethanesulfonate (29.2 mg, 0.1 mmol) with a reaction time of 2 h. The product was purified by flash chromatography on silica gel using 2% ethyl acetate/hexanes as the eluant. This procedure afforded 19.5 mg (85 %) of the title compound as an oil. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.30 (t, *J* = 7.7 Hz, 2H), 7.17 (dd, *J* = 8.2, 5.3 Hz, 1H), 7.01 – 6.82 (m, 5H), 5.19 (tt, *J* = 6.2, 3.0 Hz, 1H), 3.34 (td, *J* = 15.4, 14.3, 6.3 Hz, 2H), 3.24 – 3.07 (m, 2H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 162.41 (d, $J_{C1\text{-}F}$ = 242 Hz), 157.65, 143.00 (d, $J_{C3\text{-}F}$ = 8 Hz), 136.26 (d, $J_{C4\text{-}F}$ = 3 Hz), 129.68, 125.75 (d, $J_{C3\text{-}F}$ = 8 Hz), 120.96, 115.63, 113.65 (d, $J_{C2\text{-}F}$ = 22 Hz), 111.94 (d, $J_{C2\text{-}F}$ = 23 Hz), 77.97, 40.07 (d, $J_{C4\text{-}F}$ = 3 Hz), 39.14; IR (film) 1484, 1239 cm^{-1}; MS (EI) 228.0950 (229.0950 calcd for $C_{15}H_{13}FO$, M^+).

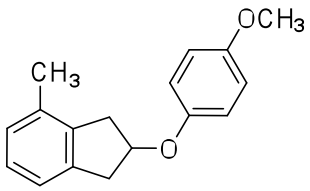


(±)-5-Fluoro-2-(*o*-tolyloxy)-2,3-dihydro-1*H*-indene (5i). The general procedure was used for the coupling of *o*-cresol (12.4 μL, 0.12 mmol) and 2-allyl-4-fluorophenyl trifluoromethanesulfonate (28.4 mg, 0.1 mmol) except the reaction was conducted in xylenes (1 mL) at 130 °C for 4 h. The product was purified by flash chromatography on silica gel using 2% ethyl acetate/hexanes as the eluant. This procedure afforded 20.7 mg (85%) of the title compound as an oil. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.20 – 7.12 (m, 3H), 7.01 – 6.81 (m, 4H), 5.19 (tt, *J* = 6.4, 3.3 Hz, 1H), 3.35 (td, *J* = 15.5, 14.5, 6.4 Hz, 2H), 3.15 (td, *J* = 16.2, 3.2 Hz, 2H), 2.12 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 162.36 (d, $J_{C1\text{-}F}$ = 242 Hz), 155.84, 143.12 (d, $J_{C3\text{-}F}$ = 9 Hz), 136.39 (d, $J_{C4\text{-}F}$ = 3 Hz), 131.07, 127.90, 126.76, 125.69 (d, $J_{C3\text{-}F}$ = 9 Hz), 120.66, 113.67 (d, $J_{C2\text{-}F}$ = 22 Hz), 112.51, 111.87 (d, $J_{C2\text{-}F}$ = 22 Hz), 78.24, 40.23 (d, $J_{C4\text{-}F}$ = 2 Hz), 39.30, 16.45; IR (film) 1488, 1238 cm^{-1}; MS (EI) 242.1097 (242.1107 calcd for $C_{16}H_{16}FO$, M^+).

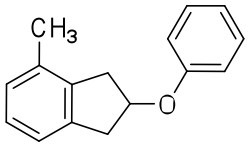


(±)-4-[(5-Fluoro-2,3-dihydro-1*H*-inden-2-yl)oxy]benzonitrile (5j). The general procedure was used for the coupling of 4-cyanophenol (14.3 mg, 0.12 mmol) and 2-allyl-4-fluorophenyl trifluoromethanesulfonate (29.2 mg, 0.1 mmol) except the reaction was conducted in mesitylene solvent at 160 °C for 16 h. The product was purified by flash chromatography on silica gel using 10% ethyl acetate/hexanes as the eluant. This procedure afforded 20.4 mg (80%) of the title compound as an opaque solid (m.p. = 108-111 °C). ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.59 (d, *J* = 8.8 Hz, 2H), 7.18 (dd, *J* = 8.2, 5.2 Hz, 1H), 7.03 – 6.80 (m, 4H), 5.22 (tt, *J* = 5.9, 2.7 Hz, 1H), 3.38 (td, *J* = 15.6, 14.7, 6.2 Hz, 2H), 3.14 (td, *J* = 16.1, 15.7, 2.6 Hz, 2H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 162.50 (d,

$J_{C1\text{-}F}$ = 242 Hz), 161.03, 142.38 (d, $J_{C3\text{-}F}$ = 9 Hz), 135.65 (d, $J_{C4\text{-}F}$ = 2 Hz), 134.19, 125.81 (d, $J_{C3\text{-}F}$ = 8 Hz), 119.30, 116.13, 114.08 (d, $J_{C2\text{-}F}$ = 22 Hz), 111.97 (d, $J_{C2\text{-}F}$ = 22 Hz), 104.16, 78.60, 39.90 (d, $J_{C4\text{-}F}$ = 2 Hz), 39.00; IR (film) 1255, 2222 cm^{-1}; MS (ESI) 276.0799 (276.0795 calcd for $C_{16}H_{12}FNO$, M + Na^+).

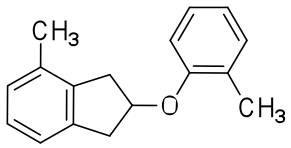


(±)-2-(4-Methoxyphenoxy)-4-methyl-2,3-dihydro-1*H*-indene (5k). The general procedure was used for the coupling of 4-methoxyphenol (14.9 mg, 0.12 mmol) and 2-allyl-6-methylphenyl trifluoromethanesulfonate (28.0 mg, 0.1 mmol) except the reaction was conducted in xylenes solvent at 130 ºC for 16 h. The product was purified by flash chromatography on silica gel using 5% ethyl acetate/hexanes as the eluant. This procedure afforded 19.6 mg (72%) of the title compound as a white solid (m.p. = 80-82 ºC). ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.16 – 7.05 (m, 2H), 7.01 (d, *J* = 7.1 Hz, 1H), 6.90 – 6.82 (m, 4H), 5.11 (tt, *J* = 6.4, 3.2 Hz, 1H), 3.78 (s, 3H), 3.40 – 3.01 (m, 4H), 2.26 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 153.98, 151.90, 140.65, 139.82, 134.28, 127.63, 127.03, 122.14, 116.76, 114.85, 78.00, 55.88, 40.14, 38.64, 19.29; IR (film) 1228, 1505 cm^{-1}; MS (ESI) 272.1649 (272.1645 calcd for $C_{17}H_{18}O_2$, M + NH_4^+).

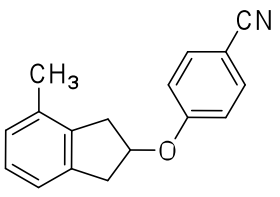


(±)-4-Methyl-2-phenoxy-2,3-dihydro-1*H*-indene (5l). The general procedure was used for the coupling of phenol (11.3 mg, 0.12 mmol) and 2-allyl-6-methylphenyl trifluoromethanesulfonate (28.0 mg, 0.1 mmol) except the reaction was conducted in xylenes solvent at 130 ºC for 1 h. The product was purified by flash chromatography on

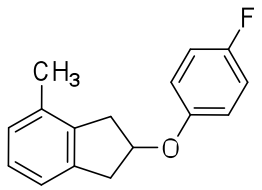
silica gel using 10% ethyl acetate/hexanes as the eluant. This procedure afforded 17.5 mg (78%) of the title compound as a yellow solid (m.p. = 94-96 °C). ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.35 – 7.27 (m, 2H), 7.16 – 7.05 (m, 2H), 7.02 (d, *J* = 7.1 Hz, 1H), 7.00 – 6.89 (m, 3H), 5.20 (tt, *J* = 6.4, 3.1 Hz, 1H), 3.36 (ddd, *J* = 35.6, 16.8, 6.5 Hz, 2H), 3.17 (ddd, *J* = 39.4, 16.8, 3.1 Hz, 2H), 2.28 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 157.86, 140.61, 139.78, 134.29, 129.64, 127.66, 127.06, 122.13, 120.76, 115.63, 77.20, 40.20, 38.71, 19.30; IR (film) 1238, 1494 cm^{-1}; MS (EI) 224.1207 (224.1201 calcd for $C_{16}H_{16}O$, M^+).



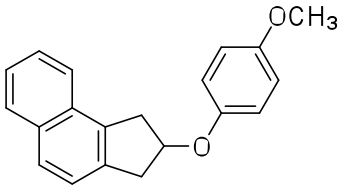
(±)-4-Methyl-2-(*o*-tolyloxy)-2,3-dihydro-1*H*-indene (5m). The general procedure was used for the coupling of *o*-cresol (12.4 μL, 0.12 mmol) and 2-allyl-6-methylphenyl trifluoromethanesulfonate (28.0 mg, 0.1 mmol) except the reaction was conducted in xylenes solvent at 130 °C for 1 h. The product was purified by flash chromatography on silica gel using hexanes as the eluant. This procedure afforded 18.1 mg (75%) of the title compound as a clear oil. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.22 – 7.07 (m, 4H), 7.03 (d, *J* = 7.1 Hz, 1H), 6.96 – 6.83 (m, 2H), 5.20 (tt, *J* = 6.9, 3.5 Hz, 1H), 3.39 (ddd, *J* = 35.5, 16.7, 6.8 Hz, 2H), 3.17 (ddd, *J* = 43.5, 16.8, 3.5 Hz, 2H), 2.28 (s, 3H), 2.16 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 156.10, 140.74, 139.88, 134.23, 131.00, 127.83, 127.57, 126.99, 126.74, 122.08, 120.47, 112.46, 77.48, 40.41, 38.90, 19.30, 16.51; IR (film) 1491, 1236 cm^{-1}; MS (EI) 238.1350 (238.1358 calcd for $C_{17}H_{18}O$, M^+).



(±)-4-[(4-Methyl-2,3-dihydro-1*H*-inden-2-yl)oxy]benzonitrile (5n). The general procedure was used for the coupling of 4-cyanophenol (14.3 mg, 0.12 mmol) and 2-allyl-6-methylphenyl trifluoromethanesulfonate (28.0 mg, 0.1 mmol) except the reaction was conducted in mesitylene solvent (1 mL) at 160 °C for 13.5 h. The product was purified by flash chromatography on silica gel using 5% ethyl acetate/hexanes as the eluant. This procedure afforded 10.5 mg (42%) of the title compound as a solid (m.p. = 112-114 °C). ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.60 (dd, *J* = 9.7, 2.9 Hz, 2H), 7.21 – 6.85 (m, 5H), 5.22 (tt, *J* = 6.2, 2.8 Hz, 1H), 3.38 (ddd, *J* = 37.9, 16.9, 6.4 Hz, 2H), 3.15 (ddd, *J* = 38.3, 17.0, 2.7 Hz, 2H), 2.27 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 161.07, 139.84, 139.01, 134.17, 133.99, 127.74, 127.16, 121.96, 119.22, 115.99, 103.79, 77.74, 39.87, 38.40, 19.10; IR (film) 2224, 1604 cm^{-1}; MS (EI) 249.1147 (249.1154 calcd for $C_{17}H_{15}NO$, M^+).

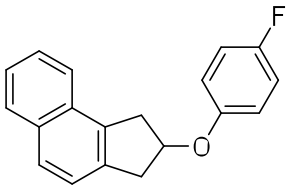


(±)-2-(4-Fluorophenoxy)-4-methyl-2,3-dihydro-1H-indene (5o). The general procedure was used for the coupling of 4-fluorophenol (13.5 mg, 0.12 mmol) and 2-allyl-6-methylphenyl trifluoromethanesulfonate (28.0 mg, 0.1 mmol) except the reaction was conducted in xylenes solvent (1 mL) at 130 °C for 1 h. The product was purified by flash chromatography on silica gel using 5% ethyl acetate/hexanes as the eluant. This procedure afforded 21.2 mg (87%) of the title compound as a yellow solid (m.p. = 63-65 °C). ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.16 – 7.07 (m, 2H), 7.05 – 6.95 (m, 3H), 6.90 – 6.83 (m, 2H), 5.16 – 5.09 (m, 1H), 3.33 (ddd, *J* = 35.8, 16.8, 6.5 Hz, 2H), 3.14 (ddt, *J* = 38.6, 16.9, 2.5 Hz, 2H), 2.28 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 157.36 (d, $J_{C1\text{-}F}$ = 237 Hz), 153.92 (d, $J_{C4\text{-}F}$ = 2.2 Hz) 140.46, 139.64, 134.29, 127.71, 127.12, 122.14, 116.65 (d, $J_{C3\text{-}F}$ = 7.9 Hz), 115.99 (d, $J_{C2\text{-}F}$ = 22.9 Hz) 77.98, 40.09, 38.60, 19.28; IR (film) 1501, 1202 cm^{-1}; MS (EI) 242.1110 (242.1107 calcd for $C_{16}H_{15}FO$, M^+).

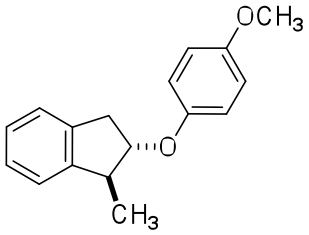


(±)-2-(4-Methoxyphenoxy)-2,3-dihydro-1H-cyclopenta[a]naphthalene (5p). The general procedure was used for the coupling of 4-methoxyphenol (14.9 mg, 0.12 mmol) and 2-allylnaphthalen-1-yl trifluoromethanesulfonate (31.6 mg, 0.1 mmol) with a reaction time of 16 h. The product was purified by flash chromatography on silica gel using 5% ethyl acetate/hexanes as the eluant. This procedure afforded 28.7 mg (98%) of the title compound as a yellow solid (m.p. = 124-128 ºC). ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.86 (d, *J* = 8.0 Hz, 1H), 7.75 (dd, *J* = 16.7, 8.2 Hz, 2H), 7.54 – 7.36 (m, 3H), 6.94 – 6.83 (m, 4H), 5.29 (dt, *J* = 6.6, 3.3 Hz, 1H), 3.79 (s, 3H), 3.66 (dd, *J* = 16.9, 6.5 Hz, 1H), 3.60 – 3.46 (m, 2H), 3.34 (dd, *J* = 16.8, 2.9 Hz, 1H); ^{13}C NMR (125 MHz, $CDCl_3$) δ 154.04, 151.87, 137.89, 136.44, 132.88, 130.53, 128.65, 127.52, 126.27, 125.15, 124.27, 123.35, 116.74, 114.90, 78.09, 55.89, 41.00, 38.48; IR (film) 1504.8 cm^{-1}, 1226.5 cm^{-1}; MS (EI) 290.1302 (290.1307 calcd for $C_{20}H_{18}O_2$, M^+).

2-(4-Methoxyphenoxy)-2,3-dihydro-1H-cyclopenta[a]naphthalene (5p). The general procedure was used for the asymmetric coupling of 4-methoxyphenol (14.9 mg, 0.12 mmol) and 2-allylnaphthalen-1-yl trifluoromethanesulfonate (31.6 mg, 0.1 mmol) except using (*R*)-SDP (3.5 mg, 6 mol %) as ligand in place of RuPhos with a reaction time of 16 h. The product was purified by flash chromatography on silica gel using 5% ethyl acetate/hexanes as the eluant. This procedure afforded 8 mg (27%) of the title compound as a yellow solid. The material was judged to have 96:4 e.r by chiral HPLC analysis (Chiralpak ADH, 25 cm x 4.6 mm, 1% IPA/Hexanes (+0.1% diethylamine), 1.5 mL/min, λ 285 nm, R_T = 8.441 min and 10.970 min. A melting point and optical rotation was not obtained due to the small amount of material isolated.

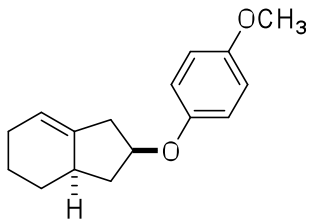


(±)-2-(4-Fluorophenoxy)-2,3-dihydro-1*H*-cyclopenta[*a*]naphthalene (5q). The general procedure was used for the coupling of 4-fluorophenol (13.5 mg, 0.12 mmol) and 2-allylnaphthalen-1-yl trifluoromethanesulfonate (31.6 mg, 0.1 mmol) with a reaction time of 16 h. The product was purified by flash chromatography on silica gel using 5% ethyl acetate/hexanes as the eluant. This procedure afforded 24.6 mg (88%) of the title compound as a yellow solid (m.p. = 134-137 ºC). ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.87 (d, *J* = 8.1 Hz, 1H), 7.75 (dd, *J* = 13.3, 8.2 Hz, 2H), 7.55 – 7.37 (m, 3H), 7.00 (t, *J* = 8.6 Hz, 2H), 6.89 (dd, *J* = 9.1, 4.3 Hz, 2H), 5.30 (m, 1H), 3.68 (dd, *J* = 16.9, 6.5 Hz, 1H), 3.62 – 3.46 (m, 2H), 3.34 (dd, *J* = 16.9, 2.8 Hz, 1H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 157.38 (d, $J_{C1\text{-}F}$ = 237.2 Hz), 153.85, 137.72, 136.27, 132.87, 130.46, 128.67, 127.61, 126.33, 125.22, 124.22, 123.28, 116.61 (d, $J_{C3\text{-}F}$ = 7.8 Hz), 116.05 (d, $J_{C2\text{-}F}$ = 22.9 Hz), 78.04, 40.94, 38.43.; IR (film) 1500, 1198 cm^{-1}; MS (EI) 278.1105 (278.1107 calcd for $C_{19}H_{15}FO$, M^+).

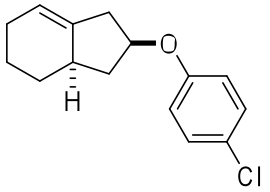


(±)-(1*S,2*S**)-2-(4-Methoxyphenoxy)-1-methyl-2,3-dihydro-1*H*-indene (5r).** The general procedure was used for the coupling of 4-methoxyphenol (14.9 mg, 0.12 mmol) and 2-(but-3-en-2-yl)phenyl trifluoromethanesulfonate[5] (27.8 mg, 0.1 mmol) except the reaction was conducted using RuPhos as ligand (6 mol %) and NaO^{t}Bu as base (13.5 mg, 0.14 mmol) and a reaction time of 4.5 h. The product was purified by flash chromatography on silica gel using 2% ethyl acetate/hexanes to 5% ethyl acetate/hexanes as the eluant. This procedure afforded 24.9 mg (98%) of the product

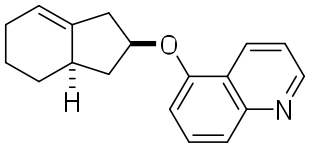
as a clear oil. This material was obtained as a >20:1 mixture of diastereomers as judged by ^{1}H NMR analysis. Data are for the major isomer. ^{1}H NMR (700 MHz, $CDCl_3$) δ 7.25 – 7.19 (m, 4H), 6.91 – 6.84 (m, 4H), 4.63 – 4.56 (m, 1H), 3.79 (s, 3H), 3.46 – 3.35 (m, 2H), 3.02 (dd, *J* = 16.2, 4.9 Hz, 1H), 1.38 (d, *J* = 7.2 Hz, 3H); ^{13}C NMR (175 MHz, $CDCl_3$) δ 154.08, 152.35, 145.70, 139.79, 127.00, 126.99, 124.86, 123.79, 116.95, 114.84, 86.09, 55.86, 45.78, 37.98, 18.17; IR (film) 1504, 1227 cm^{-1}; MS (EI) 254.1311 (254.1307 calcd for $C_{17}H_{18}O_2$, M^+).



(±)-(2*S,3a*R**)-2-(4-Methoxyphenoxy)-2,3,3a,4,5,6-hexahydro-1*H*-indene (7a).** The general procedure was used for the coupling of 4-methoxyphenol (14.9 mg, 0.12 mmol) and 6-allylcyclohex-1-en-1-yl trifluoromethanesulfonate (27.0 mg, 0.1 mmol) except BrettPhos (10 mol %) was used as ligand and the reaction was conducted for 15 h. The product was purified by flash chromatography on silica gel using 5% ethyl acetate/hexanes as the eluant. The reaction afforded 21.1 mg (86%) of the title compound as a yellow solid (m.p. = 44-46 °C). This material was obtained as a >20:1 mixture of diastereomers as judged by ^{1}H NMR analysis. Data are for the major isomer. ^{1}H NMR (500 MHz, $CDCl_3$) δ 6.82 (d, *J* = 1.1 Hz, 4H), 5.44 (s, 1H), 4.67 (dtd, *J* = 8.1, 6.8, 4.6 Hz, 1H), 3.76 (s, 3H), 2.84 – 2.67 (m, 1H), 2.48 – 2.19 (m, 3H), 2.10 – 1.93 (m, 3H), 1.86 – 1.74 (m, 1H), 1.51 – 1.35 (m, 2H), 1.19 – 1.08 (m, 1H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 153.83, 152.41, 141.35, 118.70, 116.80, 114.72, 77.48, 55.86, 40.19, 38.57, 38.24, 29.27, 25.23, 22.52; IR (film) 1506, 1229 cm^{-1}; MS (EI) 244.1470 (244.1463 calcd for $C_{16}H_{20}O_2$, M^+).

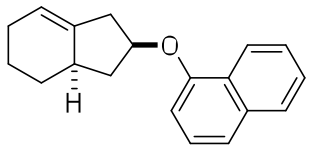


(±)-(2*S,3a*R**)-2-(4-Chlorophenoxy)-2,3,3a,4,5,6-hexahydro-1*H*-indene (7b).** The general procedure was used for the coupling of 4-chlorophenol (15.4 mg, 0.12 mmol) and 6-allylcyclohex-1-en-1-yl trifluoromethanesulfonate (27.0 mg, 0.1 mmol) except BrettPhos as ligand (10 mol %), NaO^{t}Bu as base (13.5 mg, 0.14 mmol), and a reaction time of 16 h. The product was purified by flash chromatography on silica gel using 100% hexanes to 2% ethyl acetate/hexanes as the eluant. This procedure afforded 19.2 mg (78%) of the title compound as a white solid (m.p. = 38-40 ^{o}C). This material was obtained as a >20:1 mixture of diastereomers as judged by ^{1}H NMR analysis. Data are for the major isomer. ^{1}H NMR (700 MHz, $CDCl_3$) δ 7.21 (d, *J* = 8.9 Hz, 2H), 6.79 (d, *J* = 8.9 Hz, 2H), 5.45 (s, 1H), 4.72 – 4.68 (m, 1H), 2.82 – 2.74 (m, 1H), 2.45 (dt, *J* = 13.3, 7.1 Hz, 1H), 2.34 (d, *J* = 16.6 Hz, 1H), 2.27 (app. br s, 1H), 2.07 – 1.96 (m, 3H), 1.81 (dt, *J* = 14.0, 4.2 Hz, 1H), 1.50 – 1.36 (m, 2H), 1.13 (tdd, *J* = 13.4, 10.9, 2.8 Hz, 1H); ^{13}C NMR (175 MHz, $CDCl_3$) δ 156.93, 140.99, 129.38, 125.39, 118.93, 116.94, 77.19, 40.05, 38.51, 38.18, 29.27, 25.20, 22.47; IR (film) 1489, 1238 cm $^{-1}$; MS (EI) 248.0971 (248.0968 calcd for $C_{15}H_{17}ClO$, M^+).



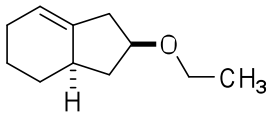
(±)-(2*S,3a*R**)-5-[(2,3,3a,4,5,6-Hexahydro-1*H*-inden-2-yl)oxy]quinoline (7c).** The general procedure was used for the coupling of 5-hydroxyquinoline (17.4 mg, 0.12 mmol) and 6-allylcyclohex-1-en-1-yl trifluoromethanesulfonate (27.0 mg, 0.1 mmol) except using BrettPhos as ligand (10 mol %), NaO^{t}Bu as base (13.5 mg, 0.14 mmol), and a reaction time of 16 h. After the reaction had proceeded to completion, H_2O (5 mL) was added and the aqueous layer was extracted with EtOAc (5 mL x 3). The combined

organic layers were dried over anhydrous Na_2SO_4, filtered, and concentrated *in vacuo*. The crude product was purified by flash chromatography on silica gel using 40% ethyl acetate/hexanes as the eluant to afford 20.2 mg (77%) of the title compound as a yellow solid (m.p. = 66-67 ºC). This material was obtained as a >20:1 mixture of diastereomers as judged by ^{1}H NMR analysis. Data are for the major isomer. ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.88 (dd, *J* = 4.2, 1.8 Hz, 1H), 8.55 (ddd, *J* = 8.4, 1.8, 0.8 Hz, 1H), 7.67 (d, *J* = 8.5 Hz, 1H), 7.59 (dd, *J* = 7.7, 7.7 Hz, 1H), 7.35 (dd, *J* = 8.4, 4.2 Hz, 1H), 6.85 (d, *J* = 0.9 Hz, 1H), 5.48 (s, 1H), 5.00 – 4.90 (m, 1H), 2.95 – 2.84 (m, 1H), 2.58 (ddd, *J* = 12.7, 7.9, 6.4 Hz, 1H), 2.48 (ddt, *J* = 16.6, 4.1, 1.9 Hz, 1H), 2.35 (app. br s, 1H), 2.10 - 2.00 (m, 3H), 1.83 (dp, *J* = 13.9, 3.8 Hz, 1H), 1.63 – 1.40 (m, 2H), 1.16 (dddd, *J* = 13.5, 12.2, 10.7, 2.8 Hz, 1H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 153.76, 150.66, 141.13, 131.36, 129.55, 121.26, 120.18, 119.00, 106.52, 77.52, 40.01, 38.42, 38.38, 29.42, 25.23, 22.49; IR (film) 1588, 1267 cm^{-1}; MS (ESI) 266.1546 (266.1539 calcd for $C_{18}H_{19}NO$, M + H^+).

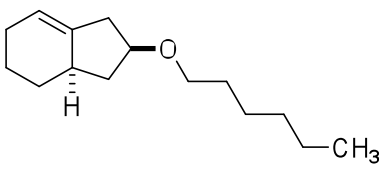


(±)-(2*S,3a*R**)-1-[(2,3,3a,4,5,6-Hexahydro-1*H*-inden-2-yl)oxy]naphthalene (7d).** The general procedure was used for the coupling of 1-naphthol (17.3 mg, 0.12 mmol) and 6-allylcyclohex-1-en-1-yl trifluoromethanesulfonate (27.0 mg, 0.1 mmol) except using BrettPhos as ligand (10 mol %), NaO^{t}Bu as base (13.5 mg, 0.14 mmol), and a reaction time of 14.5 h. The product was purified by flash chromatography on silica gel using 100% hexanes to 5% ethyl acetate/hexanes as the eluant. This procedure afforded 24.7 mg (93%) of the title compound as a white solid (m.p. = 78-80 ºC). This material was obtained as a >20:1 mixture of diastereomers as judged by ^{1}H NMR analysis. Data are for the major isomer. ^{1}H NMR (500 MHz, $CDCl_3$) δ 8.26 (d, *J* = 7.6 Hz, 1H), 7.79 (d, *J* = 7.7 Hz, 1H), 7.52 – 7.33 (m, 4H), 6.81 (d, *J* = 7.4 Hz, 1H), 5.49 (s, 1H), 4.95 – 4.93 (m, 1H), 2.98 – 2.84 (m, 1H), 2.64 – 2.47 (m, 2H), 2.43 – 2.29 (m, 1H), 2.12 – 2.02 (m, 3H), 1.89 – 1.81 (m, 1H), 1.62 (ddd, *J* = 12.6, 10.9, 6.7 Hz, 1H), 1.51 (dddd, *J* = 21.2, 13.2,

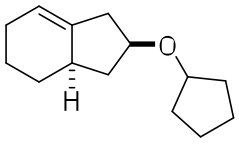
9.6, 2.9 Hz, 1H), 1.20 (tdd, *J* = 13.4, 10.9, 2.8 Hz, 1H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 154.01, 141.41, 134.71, 127.51, 126.41, 126.25, 125.96, 125.11, 122.46, 120.01, 118.81, 106.16, 77.11, 40.12, 38.49, 38.44, 29.41, 25.27, 22.55; IR (film) 1579, 1269 cm^{-1}; MS (EI) 264.1513 (264.1514 calcd for $C_{19}H_{20}O$, M^+).



(±)-(2*S,3a*R**)-2-Ethoxy-2,3,3a,4,5,6-hexahydro-1*H*-indene (7e).** The general procedure was used for the coupling of ethanol (1 mL) and 6-allylcyclohex-1-en-1-yl trifluoromethanesulfonate (27.0 mg, 0.1 mmol) except ethanol was used as solvent, BrettPhos as ligand (10 mol %), NaO^{t}Bu as base (13.5 mg, 0.14 mmol), and a reaction time of 15 h at 70 °C. The product was purified by flash chromatography on silica gel using 2% ethyl acetate/hexanes to 5% ethyl acetate/hexanes as the eluant. Despite a 62% crude yield by ^{1}H NMR integration against phenanthrene as a standard, the procedure afforded 4.7 mg (28%) of the compound as a clear oil due to volatility of the product. This material was obtained as a >20:1 mixture of diastereomers as judged by ^{1}H NMR analysis. Data are for the major isomer. ^{1}H NMR (400 MHz, $CDCl_3$) δ 5.40 (s, 1H), 3.94 (tt, *J* = 8.4, 6.0 Hz, 1H), 3.46 (q, *J* = 7.1 Hz, 2H), 2.73 – 2.56 (m, 1H), 2.34 – 2.07 (m, 3H), 2.07 – 1.87 (m, 3H), 1.78 (dt, *J* = 13.4, 3.8 Hz, 1H), 1.50 – 1.35 (m, 1H), 1.22 – 1.03 (m, 5H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 141.60, 118.32, 78.58, 64.58, 40.19, 38.79, 37.51, 29.10, 25.30, 22.55, 15.69; IR (film) 1098, 2927 cm^{-1}; MS (EI) 166.1350 (166.1358 calcd for $C_{11}H_{18}O$, M^+).

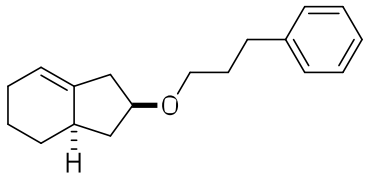


(±)-(2*S,3a*R**)-2-(Hexyloxy)-2,3,3a,4,5,6-hexahydro-1*H*-indene (7f).** The general procedure was used for the coupling of hexyl alcohol (15.1 μL, 0.12 mmol) and 6-allylcyclohex-1-en-1-yl trifluoromethanesulfonate (26.8 mg, 0.1 mmol) except using BrettPhos as ligand (10 mol %), NaO^{t}Bu as base (13.5 mg, 0.14 mmol), and a reaction time of 15.5 h. The product was purified by flash chromatography on silica gel using 5% ether/pentane as the eluant. Despite a 67% crude yield by ^{1}H NMR integration against phenanthrene as a standard, the procedure afforded 11.9 mg (54%) of the title compound as a clear oil due to volatility of the product. This material was obtained as a >20:1 mixture of diastereomers as judged by ^{1}H NMR analysis. Data are for the major isomer. ^{1}H NMR (500 MHz, $CDCl_3$) δ 5.39 (s, 1H), 3.92 (tt, *J* = 8.4, 6.0 Hz, 1H), 3.38 (td, *J* = 6.8, 2.3 Hz, 2H), 2.69 – 2.57 (m, 1H), 2.25 (dt, *J* = 12.4, 6.5 Hz, 1H), 2.21 – 2.09 (m, 2H), 2.05 – 1.90 (m, 3H), 1.78 (dt, *J* = 13.3, 3.7 Hz, 1H), 1.60 – 1.49 (m, 2H), 1.49 – 1.36 (m, 1H), 1.36 – 1.22 (m, 6H), 1.19 – 1.03 (m, 2H), 0.88 (t, *J* = 6.7 Hz, 3H); ^{13}C NMR (125 MHz, $CDCl_3$) δ 141.71, 118.27, 78.70, 69.53, 40.16, 38.79, 37.51, 31.87, 30.16, 29.12, 26.09, 25.31, 22.79, 22.57, 14.21; IR (film) 1457, 1117 cm^{-1}; MS (EI) 222.1992 (222.1984 calcd for $C_{15}H_{26}O$, M^+).

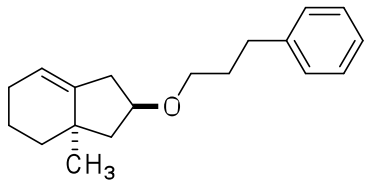


(±)-(2*S,3a*R**)-2-(Cyclopentyloxy)-2,3,3a,4,5,6-hexahydro-1*H*-indene (7g).** The general procedure was used for the coupling of cyclopentanol (10.9 μL, 0.12 mmol) and 6-allylcyclohex-1-en-1-yl trifluoromethanesulfonate (26.8 mg, 0.1 mmol) except using BrettPhos as ligand (10 mol %), NaO^{t}Bu as base (13.5 mg, 0.14 mmol), and a reaction time of 15.5 h. The product was purified by flash chromatography on silica gel using 5% ether/pentane as the eluant. Despite a 70% crude yield by ^{1}H NMR integration against phenanthrene as a standard, the procedure afforded 10.2 mg (50%) of the title compound as a clear oil due to volatility of the product. This material was obtained as a >20:1 mixture of diastereomers as judged by ^{1}H NMR analysis. Data are for the major isomer. ^{1}H NMR (500 MHz, $CDCl_3$) δ 5.38 (s, 1H), 4.04 – 3.88 (m, 2H), 2.73 – 2.58 (m,

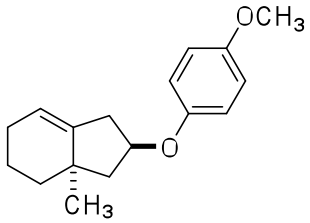
1H), 2.29 – 2.07 (m, 3H), 1.97 (ddq, *J* = 35.5, 12.1, 3.8 Hz, 3H), 1.85 – 1.36 (m, 10H), 1.19 – 1.02 (m, 2H); ^{13}C NMR (125 MHz, $CDCl_3$) δ 141.70, 118.21, 79.97, 76.88, 40.71, 38.89, 37.77, 32.88, 32.80, 29.02, 25.34, 23.57, 22.56; IR (film) 1344, 1098 cm^{-1}; MS (EI) 206.1675 (206.1671 calcd for $C_{14}H_{22}O$, M^+).



(±)-(2*S,3a*R**)-2-(3-Phenylpropoxy)-2,3,3a,4,5,6-hexahydro-1*H*-indene (7h).** The general procedure was used for the coupling of 3-phenyl-1-propanol (16.2 μL, 0.12 mmol) and 6-allylcyclohex-1-en-1-yl trifluoromethanesulfonate (27.4 mg, 0.1 mmol) except using BrettPhos as ligand (10 mol %), NaO*t*Bu as base (13.5 mg, 0.14 mmol), and a reaction time of 15.5 h. The product was purified by flash chromatography on silica gel using 2% ethyl acetate/hexanes to 5% ethyl acetate/hexanes as the eluant. The procedure afforded 19.1 mg (74%) of the product as a clear oil. This material was obtained as a >20:1 mixture of diastereomers as judged by ^{1}H NMR analysis. Data are for the major isomer. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.31 – 7.23 (m, 2H), 7.19 (d, *J* = 7.6 Hz, 3H), 5.40 (s, 1H), 3.92 (tt, *J* = 8.4, 5.9 Hz, 1H), 3.47 – 3.33 (m, 2H), 2.74 – 2.55 (m, 3H), 2.32 – 2.07 (m, 3H), 2.07 – 1.83 (m, 5H), 1.79 (dt, *J* = 13.6, 3.7 Hz, 1H), 1.43 (dddd, *J* = 21.4, 13.2, 8.2, 2.9 Hz, 1H), 1.22 – 1.03 (m, 2H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 142.23, 141.68, 128.62, 128.41, 125.84, 118.31, 78.83, 68.46, 40.15, 38.77, 37.52, 32.57, 31.66, 29.13, 25.31, 22.56; IR (film) 1110, 1452 cm^{-1}; MS (EI) 256.1837 (256.1827 calcd for $C_{18}H_{24}O$, M^+).

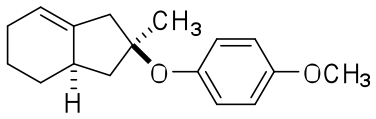


(±)-(2*S,3a*R**)-3a-Methyl-2-(3-phenylpropoxy)-2,3,3a,4,5,6-hexahydro-1*H*-indene (7i).** The general procedure was used for the coupling of 3-phenyl-1-propanol (16.2 μL, 0.12 mmol) and 6-(but-3-en-1-yl)-6-methylcyclohex-1-en-1-yl trifluoromethanesulfonate (28.4 mg, 0.1 mmol) except using BrettPhos as ligand (6 mol %), NaO^{t}Bu as base (13.5 mg, 0.14 mmol), and a reaction time of 14 h. The product was purified by flash chromatography on silica gel using 2% ethyl acetate/hexanes as the eluant. The procedure afforded 18.1 mg (67%) of the product as a clear oil. This material was obtained as a >20:1 mixture of diastereomers as judged by ^{1}H NMR analysis. Data are for the major isomer. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.31 – 7.23 (m, 2H), 7.18 (d, *J* = 7.4 Hz, 3H), 5.33 (s, 1H), 4.09 (dtd, *J* = 8.5, 7.0, 4.0 Hz, 1H), 3.37 (t, *J* = 6.5 Hz, 2H), 2.77 (ddq, *J* = 18.5, 9.1, 3.3 Hz, 1H), 2.67 (dd, *J* = 8.6, 6.8 Hz, 2H), 2.19 (ddd, *J* = 16.7, 4.0, 2.0 Hz, 1H), 2.08 (dd, *J* = 12.3, 6.8 Hz, 1H), 2.04 – 1.97 (m, 2H), 1.93 – 1.83 (m, 2H), 1.72 (dt, *J* = 12.3, 3.4 Hz, 1H), 1.67 – 1.60 (m, 2H), 1.36 – 1.28 (m, 2H), 0.96 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 144.84, 142.24, 128.62, 128.41, 125.84, 118.06, 77.97, 68.41, 49.17, 40.30, 37.04, 36.37, 32.59, 31.65, 25.44, 25.31, 18.79; IR (film) 1102, 1454 cm^{-1}; MS (EI) 270.1984 (270.1984 calcd for $C_{19}H_{26}O$, M^+).

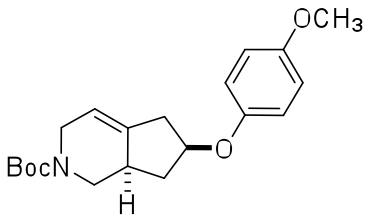


(±)-(2*S,3a*R**)-2-(4-Methoxyphenoxy)-3a-methyl-2,3,3a,4,5,6-hexahydro-1*H*-indene (7j).** The general procedure was used for the coupling of 4-methoxyphenol (14.9 mg, 0.12 mmol) and 6-(but-3-en-1-yl)-6-methylcyclohex-1-en-1-yl trifluoromethanesulfonate (28.5 mg, 0.1 mmol) except using BrettPhos (6 mol %) as ligand and a reaction time of 14 h. The product was purified by flash chromatography on silica gel using 2% ethyl acetate/hexanes as the eluant. The procedure afforded 12.8 mg (50 %) of the product as a viscous clear oil. This material was obtained as an 8:1 mixture of diastereomers as

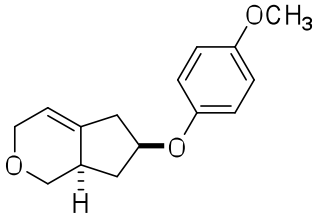
judged by ^{1}H NMR analysis. Data are for the major isomer. ^{1}H NMR (400 MHz, $CDCl_3$) δ 6.81 (s, 4H), 5.37 (d, *J* = 3.2 Hz, 1H), 4.86 - 4.78 (m, 1H), 3.77 (s, 3H), 3.01 – 2.86 (m, 1H), 2.37 – 2.21 (m, 2H), 2.07 - 1.98 (m, 2H), 1.76 (dt, *J* = 12.4, 3.4 Hz, 1H), 1.70 – 1.62 (m, 2H), 1.57 (dd, *J* = 12.8, 6.8 Hz, 1H), 1.35 (td, *J* = 12.2, 3.5 Hz, 1H), 1.04 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 118.49, 116.65, 114.74, 76.73, 55.87, 49.25, 40.29, 37.67, 36.34, 25.67, 25.25, 18.84; IR (film) 1505, 1227 cm^{-1}; MS (ESI) 259.1691 (259.1693 calcd for $C_{17}H_{22}O_2$, M + H^+).



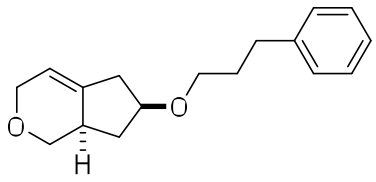
(±)-(2*S,3a*R**)-2-(4-Methoxyphenoxy)-2-methyl-2,3,3a,4,5,6-hexahydro-1*H*-indene (7k).** The general procedure was used for the coupling of 4-methoxyphenol (14.9 mg, 0.12 mmol) and 6-allylcyclohex-1-en-1-yl trifluoromethanesulfonate (31.0 mg, 0.1 mmol) except using BrettPhos as ligand (10 mol %), NaO^{t}Bu as base (13.5 mg, 0.14 mmol), and a reaction time of 14 h. The product was purified by flash chromatography on silica gel using 2% ethyl acetate/hexanes to 5% ethyl acetate/hexanes as the eluant. The reaction afforded 18.9 mg (67%) of the title compound as a clear oil. This material was obtained as an 8:1 mixture of diastereomers as judged by ^{1}H NMR analysis. Data are for the major isomer. ^{1}H NMR (500 MHz, C_6D_6) δ 6.93 (d, *J* = 9.0 Hz, 2H), 6.72 (d, *J* = 9.0 Hz, 2H), 5.38 (s, 1H), 3.32 (s, 3H), 2.88 (d, *J* = 16.4 Hz, 1H), 2.36 (d, *J* = 16.4 Hz, 1H), 2.18 – 2.09 (m, 1H), 2.01 – 1.94 (m, 2H), 1.91 – 1.85 (m, 2H), 1.81 (ddt, *J* = 12.0, 4.9, 3.4 Hz, 1H), 1.72 – 1.64 (m, 1H), 1.44 – 1.33 (m, 1H), 1.31 (s, 3H), 1.10 (dddd, *J* = 13.6, 12.2, 10.8, 2.8 Hz, 1H); ^{13}C NMR (125 MHz, C_6D_6) δ 156.16, 150.74, 142.74, 123.73, 119.19, 115.12, 86.05, 55.67, 47.74, 45.68, 39.86, 29.95, 27.13, 26.07, 23.47; IR (film) 1505, 1210 cm^{-1}; MS (EI) 258.1628 (258.1620 calcd for $C_{17}H_{22}O_2$, M^+).



(±)-(2*S,3a*R**)-*tert*-Butyl 6-(4-methoxyphenoxy)-1,3,5,6,7,7a-hexahydro-2*H*-cyclopenta[*c*]pyridine-2-carboxylate (7l).** The general procedure was used for the coupling of 4-methoxyphenol (14.9 mg, 0.12 mmol) and *tert*-butyl 3-allyl-4-{[(trifluoromethyl)sulfonyl]oxy}-3,6-dihydropyridine-1(2*H*)-carboxylate (37.1 mg, 0.1 mmol) except using BrettPhos as ligand (6 mol %) and a reaction time of 14 h. The product was purified by flash chromatography on silica gel using 20% ethyl acetate/hexanes as the eluant. This procedure afforded 28.2 mg (82%) of the product as a yellow oil. Note: The peaks in the NMR spectra were broadened and complex due to the presence of rotamers. ^{1}H NMR (500 MHz, $CDCl_3$) δ 6.86 – 6.74 (m, 4H), 5.46 (d, *J* = 18.7 Hz, 1H), 4.80 – 4.67 (m, 1H), 4.51 – 4.05 (m, 2H), 3.76 (s, 3H), 3.65 – 3.43 (m, 1H), 2.82 – 2.68 (m, 1H), 2.56 – 2.28 (m, 4H), 1.53 - 1.44 (m, 10H); ^{13}C NMR (175 MHz, $CDCl_3$) δ ^{13}C NMR (100 MHz, $CDCl_3$) δ 154.04, 151.97, 116.92, 114.78, 79.69, 77.66, 55.84, 38.16, 37.65, 36.33, 28.64; IR (film) 1682, 1504, 1225 cm^{-1}; MS (ESI) 368.1839 (368.1832 calcd for $C_{20}H_{27}NO_4$, M + Na^+). The diastereomeric ratio for the title product was determined by ^{1}H NMR analysis after cleavage of the boc group using TFA/CH_2Cl_2 and was found to be >20:1 dr. Proton NMR and MS data are provided for the deprotected product **7l-H**: ^{1}H NMR (500 MHz, $CDCl_3$) δ 6.81 (s, 4H), 5.47 (s, 1H), 4.72 (ddt, *J* = 9.8, 7.3, 4.9 Hz, 1H), 3.76 (s, 3H), 3.43 – 3.31 (m, 3H), 2.95 (s, 1H), 2.76 (ddd, *J* = 13.9, 6.9, 3.0 Hz, 1H), 2.48 – 2.34 (m, 4H), 1.41 (ddd, *J* = 11.1, 9.1, 5.8 Hz, 1H); MS (ESI) 246.1491 (246.1489 calcd for $C_{15}H_{19}NO_2$, M + H^+).

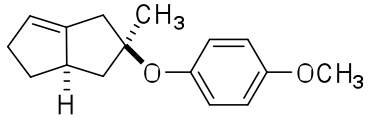


(±)-(2*S,3a*R**)-6-(4-Methoxyphenoxy)-1,3,5,6,7,7a-hexahydrocyclopenta[*c*]pyran (7m).** The general procedure was used for the coupling of 4-methoxyphenol (14.9 mg, 0.12 mmol) and 3-allyl-3,6-dihydro-2*H*-pyran-4-yl trifluoromethanesulfonate (22.8 mg, 0.08 mmol) except using BrettPhos as ligand (6 mol %) and a reaction time of 14 h. The product was purified by flash chromatography on silica gel using 20% ethyl acetate/hexanes as the eluant. This procedure afforded 19.2 mg (93%) of the product as a pale solid (m.p. = 56-58 ºC). This material was obtained as a >20:1 mixture of diastereomers as judged by ^{1}H NMR analysis. Data are for the major isomer. ^{1}H NMR (400 MHz, $CDCl_3$) δ 6.81 (s, 4H), 5.48 (s, 1H), 4.75 (dtd, *J* = 7.7, 6.2, 3.9 Hz, 1H), 4.26 – 4.04 (m, 3H), 3.76 (s, 3H), 3.15 (t, *J* = 10.2 Hz, 1H), 2.84 – 2.68 (m, 1H), 2.60 (app. br s, 1H), 2.46 (ddt, *J* = 16.4, 3.9, 1.9 Hz, 1H), 2.39 – 2.27 (m, 1H), 1.40 (ddd, *J* = 13.1, 10.2, 6.0 Hz, 1H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 154.03, 139.64, 117.22, 116.86, 114.79, 77.48 (incidental overlap with $CDCl_3$), 69.45, 65.22, 55.84, 38.12, 37.30, 35.33; IR (film) 1505, 1226 cm^{-1}; MS (ESI) 269.1154 (269.1148 calcd for $C_{15}H_{18}O_3$, M + Na^+).

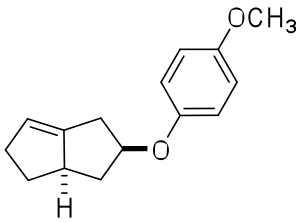


(±)-(2*S,3a*R**)-6-(3-Phenylpropoxy)-1,3,5,6,7,7a-hexahydrocyclopenta[*c*]pyran (7n).** The general procedure was used for the coupling of 3-phenyl-1-propanol (16.3 µL, 0.12 mmol) and 3-allyl-3,6-dihydro-2*H*-pyran-4-yl trifluoromethanesulfonate (27.3 mg, 0.1 mmol) except using BrettPhos as ligand (6 mol %) and a reaction time of 14 h. The product was purified by flash chromatography on silica gel using 20% ethyl acetate/hexanes as the eluant. This procedure afforded 19.9 mg (77%) of the product as a clear yellow oil. This material was obtained as a >20:1 mixture of diastereomers as judged by ^{1}H NMR analysis. Data are for the major isomer. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.31 – 7.24 (m, 2H), 7.21 – 7.16 (m, 3H), 5.44 (d, *J* = 2.3 Hz, 1H), 4.22 – 4.05 (m, 3H), 4.05 – 3.93 (m, 1H), 3.40 (t, *J* = 6.4 Hz, 2H), 3.12 (t, *J* = 10.1 Hz, 1H), 2.74 – 2.58 (m, 3H), 2.49 (app. br s, 1H), 2.29 (ddt, *J* = 16.6, 4.7, 2.2 Hz, 1H), 2.17 (ddd, *J* = 12.4, 7.6,

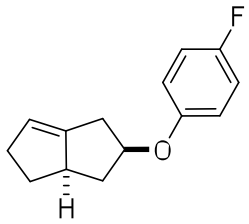
6.2 Hz, 1H), 1.94 – 1.82 (m, 2H), 1.15 (ddd, *J* = 12.3, 11.1, 7.5 Hz, 1H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 142.09, 139.93, 128.59, 128.43, 125.90, 116.84, 78.82, 69.45, 68.54, 65.29, 37.55, 37.33, 35.41, 32.52, 31.59; IR (film) 1723, 749 cm^{-1}; MS (ESI) 276.1955 (276.1958 calcd for $C_{17}H_{22}O_2$, M + H$^+$).



(±)-(2*S,3a*R**)-2-(4-Methoxyphenoxy)-2-methyl-1,2,3,3a,4,5-hexahydropentalene (7o).** The general procedure was used for the coupling of 4-methoxyphenol (14.9 mg, 0.12 mmol) and 5-(2-methylallyl)cyclopent-1-en-1-yl trifluoromethanesulfonate (27 mg, 0.1 mmol) except using BrettPhos as ligand (10 mol %), NaO*t*Bu as base (13.5 mg, 0.14 mmol), and a reaction time of 15 h. The product was purified by flash chromatography on silica gel using 2% ethyl acetate/hexanes to 5% ethyl acetate/hexanes as the eluant. The reaction afforded 17.1 mg (70%) of the title product as a clear oil. Note: The product decomposes upon standing in ambient conditions on the benchtop. This material was obtained as a >20:1 mixture of diastereomers as judged by ^{1}H NMR analysis. Data are for the major isomer. ^{1}H NMR (500 MHz, $CDCl_3$) δ 6.89 (d, *J* = 9.0 Hz, 2H), 6.79 (d, *J* = 9.0 Hz, 2H), 5.36 (s, 1H), 3.77 (s, 3H), 3.00 – 2.82 (m, 1H), 2.74 (d, *J* = 16.9 Hz, 1H), 2.62 – 2.39 (m, 2H), 2.35 – 2.23 (m, 1H), 2.15 (dt, *J* = 12.8, 6.8 Hz, 1H), 2.02 (dd, *J* = 12.1, 7.6 Hz, 1H), 1.71 (t, *J* = 11.3 Hz, 1H), 1.56 – 1.37 (m, 4H); ^{13}C NMR (125 MHz, $CDCl_3$) δ 155.17, 150.41, 149.37, 123.16, 119.82, 114.21, 91.29, 55.69, 49.61, 46.12, 39.07, 36.75, 32.97, 27.36; IR (film) 1505, 1215 cm^{-1}; MS (EI) 244.1472 (244.1463 calcd for $C_{16}H_{20}O_2$, M$^+$).

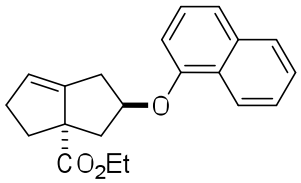


(±)-(2*S,3a*R**)-2-(4-Methoxyphenoxy)-1,2,3,3a,4,5-hexahydropentalene (7p).** The general procedure was used for the coupling of 4-methoxyphenol (14.9 mg, 0.12 mmol) and 5-allylcyclopent-1-en-1-yl trifluoromethanesulfonate (28.5 mg, 0.1 mmol) except using BrettPhos as ligand (10 mol %), NaO^{t}Bu as base (13.5 mg, 0.14 mmol), and a reaction time of 15 h. The product was purified by flash chromatography on silica gel using 2% ethyl acetate/hexanes to 5% ethyl acetate/hexanes as the eluant. This procedure afforded 21.8 mg (95%) of the title product as a pale solid (m.p. = 54-56 °C). This material was obtained as a >20:1 mixture of diastereomers as judged by ^{1}H NMR analysis. Data are for the major isomer. ^{1}H NMR (500 MHz, $CDCl_3$) δ 6.82 (s, 4H), 5.36 (s, 1H), 4.91 (qd, *J* = 7.3, 4.9 Hz, 1H), 3.77 (s, 3H), 2.88 (app. br s, 1H), 2.68 (ddt, *J* = 12.5, 6.0, 2.1 Hz, 1H), 2.63 – 2.40 (m, 3H), 2.37 – 2.28 (m, 1H), 2.15 (dt, *J* = 12.7, 7.0 Hz, 1H), 1.50 (dq, *J* = 11.7, 9.4 Hz, 1H), 1.35 (ddd, *J* = 12.2, 10.8, 7.3 Hz, 1H); ^{13}C NMR (175 MHz, $CDCl_3$) δ 153.88, 152.33, 149.75, 119.67, 116.74, 114.75, 82.28, 55.85, 49.34, 39.61, 37.09, 32.59, 32.42; IR (film) 1506, 1227 cm^{-1}; MS (EI) 230.1311 (230.1307 calcd for $C_{15}H_{18}O_2$, M^+).



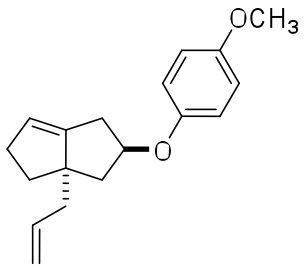
(±)-(2*S,3a*R**)-2-(4-Fluorophenoxy)-1,2,3,3a,4,5-hexahydropentalene (7q).** The general procedure was used for the coupling of 4-fluorophenol (13.5 mg, 0.12 mmol) and 5-allylcyclopent-1-en-1-yl trifluoromethanesulfonate (28.3 mg, 0.1 mmol) except using BrettPhos as ligand (10 mol %), NaO^{t}Bu as base (13.5 mg, 0.14 mmol), and a reaction time of 16 h. The product was purified by flash chromatography on silica gel using 2% ethyl acetate/hexanes as the eluant. This procedure afforded 19.8 mg (91%) of the title product as a clear oil. Note: The product co-eluted with 4% of the alkene regioisomer, data are for the major regioisomer. This material was obtained as a >20:1 mixture of diastereomers as judged by ^{1}H NMR analysis. Data are for the major

diastereomer. ^{1}H NMR (500 MHz, $CDCl_3$) δ 6.95 (t, *J* = 8.7 Hz, 2H), 6.80 (dd, *J* = 9.1, 4.3 Hz, 2H), 5.37 (s, 1H), 4.95 – 4.85 (m, 1H), 2.95 – 2.82 (m, 1H), 2.69 (dddd, *J* = 16.8, 8.4, 4.4, 2.2 Hz, 1H), 2.64 – 2.42 (m, 3H), 2.33 (app. br d, *J* = 18.5 Hz, 1H), 2.16 (dtd, *J* = 12.1, 7.0, 1.1 Hz, 1H), 1.50 (dq, *J* = 12.1, 9.4 Hz, 1H), 1.36 (ddd, *J* = 12.5, 10.7, 7.2 Hz, 1H); ^{13}C NMR (125 MHz, $CDCl_3$) δ 157.28 (d, $J_{C1\text{-}F}$ = 236.3 Hz), 154.32, 149.49, 119.86, 116.66 (d, $J_{C3\text{-}F}$ = 7.7 Hz), 115.89 (d, $J_{C2\text{-}F}$ = 22.5 Hz), 82.25, 49.33, 39.52, 37.12, 32.61, 32.38; IR (film) 1502, 1206 cm^{-1}; MS (EI) 218.1105 (218.1107 calcd for $C_{14}H_{15}FO$, M^+).

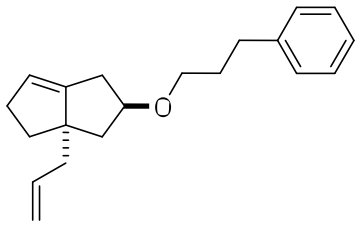


(±)-(2*R,3a*S**)-Ethyl 2-(naphthalen-1-yloxy)-2,3,4,5-tetrahydropentalene-3a(1*H*)-carboxylate (7r).** The general procedure was used for the coupling of 1-naphthol (17.3 mg, 0.12 mmol) and ethyl 1-allyl-2-{[(trifluoromethyl)sulfonyl]oxy}cyclopent-2-ene-1-carboxylate (32.6 mg, 0.1 mmol) except using RuPhos as ligand (6 mol %), NaO^{t}Bu as base (13.5 mg, 0.14 mmol), and a reaction time of 15 h. No aqueous work-up was performed. Instead, the reaction mixture was concentrated *in vacuo* and the crude product was purified via silica gel chromatography. The product was purified by flash chromatography on silica gel using 2% ethyl acetate/hexanes to 10% ethyl acetate/hexanes as the eluant. This procedure afforded 28.8 mg (90%) of the product as a clear oil. This material was obtained as a >20:1 mixture of diastereomers as judged by ^{1}H NMR analysis. Data are for the major isomer. ^{1}H NMR (500 MHz, $CDCl_3$) δ 8.23 (dd, *J* = 7.9, 1.6 Hz, 1H), 7.79 (dd, *J* = 7.6, 1.6 Hz, 1H), 7.53 – 7.32 (m, 4H), 6.78 (d, *J* = 7.5 Hz, 1H), 5.59 (s, 1H), 5.42 – 5.34 (m, 1H), 4.18 (p, *J* = 7.0 Hz, 2H), 3.01 (dd, *J* = 13.5, 6.9 Hz, 1H), 2.96 – 2.81 (m, 2H), 2.65 – 2.50 (m, 3H), 1.91 (dt, *J* = 12.6, 9.2 Hz, 1H), 1.82 (dd, *J* = 13.5, 5.6 Hz, 1H), 1.30 (t, *J* = 7.1 Hz, 3H); ^{13}C NMR (125 MHz, $CDCl_3$) δ 175.91, 153.66, 148.36, 134.75, 127.57, 126.47, 126.14, 125.98, 125.19,

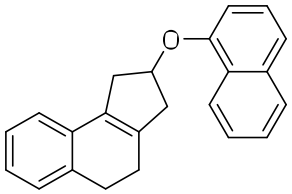
124.20, 122.34, 120.23, 106.17, 81.38, 65.01, 60.91, 43.55, 37.84, 37.12, 32.60, 14.39; IR (film) 1716, 1153 cm^{-1}; MS (ESI) 323.1639 (323.1642 calcd for $C_{21}H_{22}O_3$, M + H^+).



(±)-(2*S,3a*S**)-3a-Allyl-2-(4-methoxyphenoxy)-1,2,3,3a,4,5-hexahydropentalene (7s).** The general procedure was used for the coupling of 4-methoxyphenol (14.9 mg, 0.12 mmol) and 5,5-diallylcyclopent-1-en-1-yl trifluoromethanesulfonate (29.6 mg, 0.1 mmol) except using BrettPhos as ligand (10 mol %), NaO^{t}Bu as base (13.5 mg, 0.14 mmol), and a reaction time of 24 h. The product was purified by flash chromatography on silica gel using 2% ethyl acetate/hexanes to 5% ethyl acetate/hexanes as the eluant. This procedure afforded 26.1 mg (97%) of the product as a clear oil. This material was obtained as a >20:1 mixture of diastereomers as judged by ^{1}H NMR analysis. Data are for the major isomer. ^{1}H NMR (500 MHz, $CDCl_3$) δ 6.87 – 6.73 (m, 4H), 5.83 (ddt, *J* = 17.2, 10.0, 7.3 Hz, 1H), 5.36 (s, 1H), 5.13 – 5.01 (m, 2H), 5.01 – 4.91 (m, 1H), 3.77 (s, 3H), 2.76 – 2.55 (m, 2H), 2.51 – 2.40 (m, 1H), 2.36 (dd, *J* = 13.5, 6.5 Hz, 2H), 2.16 – 1.93 (m, 3H), 1.74 (dt, *J* = 12.3, 9.4 Hz, 1H), 1.54 (dd, *J* = 13.2, 6.2 Hz, 1H); ^{13}C NMR (175 MHz, $CDCl_3$) δ 153.80, 152.19, 152.12, 136.06, 120.15, 117.07, 116.60, 114.73, 81.46, 58.52, 55.84, 44.39, 41.45, 37.69, 35.69, 31.93; IR (film) 1506, 1227 cm^{-1}; MS (ESI) 271.1692 (271.1693 calcd for $C_{18}H_{22}O_2$, M+H^+).

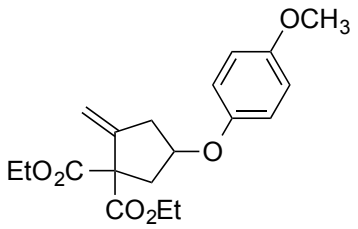


(±)-(2*S,3a*S**)-3a-Allyl-2-(3-phenylpropoxy)-1,2,3,3a,4,5-hexahydropentalene (7t).** The general procedure was used for the coupling of 3-phenyl-1-propanol (16.3 µL, 0.12 mmol) and 5,5-diallylcyclopent-1-en-1-yl trifluoromethanesulfonate (29.8 mg, 0.1 mmol) except using BrettPhos as ligand (6 mol %) and a reaction time of 16 h. The product was purified by flash chromatography on silica gel using 5% ethyl acetate/hexanes as the eluant. This procedure afforded 26.4 mg (94%) of the product as a clear oil. This material was obtained as a >20:1 mixture of diastereomers as judged by ^{1}H NMR analysis. Data are for the major isomer. ^{1}H NMR (700 MHz, $CDCl_3$) δ 7.28 (t, *J* = 7.6 Hz, 2H), 7.19 (d, *J* = 7.4 Hz, 3H), 5.80 (ddt, *J* = 17.1, 9.8, 7.3 Hz, 1H), 5.31 (s, 1H), 5.06 – 5.01 (m, 2H), 4.25 (qd, *J* = 7.2, 3.7 Hz, 1H), 3.38 (dt, *J* = 6.5, 3.3 Hz, 2H), 2.68 (t, *J* = 7.7 Hz, 2H), 2.62 – 2.51 (m, 2H), 2.44 – 2.38 (m, 1H), 2.25 – 2.17 (m, 2H), 2.06 (dd, *J* = 13.8, 6.7 Hz, 1H), 2.01 – 1.94 (m, 2H), 1.88 (p, *J* = 7.0 Hz, 2H), 1.71 – 1.65 (m, 1H), 1.30 (dd, *J* = 12.6, 7.1 Hz, 1H); ^{13}C NMR (175 MHz, $CDCl_3$) δ 152.65, 142.18, 136.25, 128.61, 128.42, 125.86, 119.51, 116.79, 83.08, 68.47, 58.44, 44.40, 41.14, 37.44, 35.62, 32.56, 31.59, 31.24; IR (film) 1098, 698 cm^{-1}; MS (ESI) 283.2051 (283.2056 calcd for $C_{20}H_{26}O$, M + H$^+$).

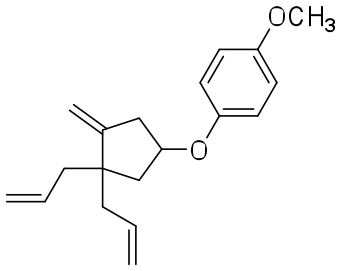


(±)-2-(Naphthalen-1-yloxy)-2,3,4,5-tetrahydro-1*H*-cyclopenta[*a*]naphthalene (7u). The general procedure was used for the coupling of 1-naphthol (17.3 mg, 0.12 mmol) and 2-allyl-3,4-dihydronaphthalen-1-yl trifluoromethanesulfonate[5] (31.6 mg, 0.1 mmol) except using BrettPhos (6 mol %) as ligand and a reaction time of 15.5 h. The product was purified by flash chromatography on silica gel using 2% ethyl acetate/hexanes to 5% ethyl acetate/hexanes as the eluant. This procedure afforded 22.7 mg (73%) of the title product as a clear oil. ^{1}H NMR (500 MHz, $CDCl_3$) δ 8.28 (d, *J* = 8.2 Hz, 1H), 7.81 (d, *J* = 8.1 Hz, 1H), 7.53 – 7.37 (m, 4H), 7.22 – 7.09 (m, 3H), 7.05 (d, *J* = 7.4 Hz, 1H), 6.88 (d, *J* = 7.3 Hz, 1H), 5.40 – 5.32 (m, 1H), 3.26 (dd, *J* = 16.3, 6.2 Hz, 1H), 3.13 (dd, *J* =

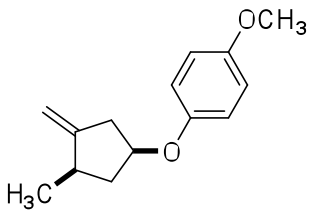
18.0, 6.9 Hz, 1H), 3.05 (d, *J* = 16.5 Hz, 1H), 2.95 (sextet, *J* = 7.6 Hz, 2H), 2.88 (d, *J* = 18.6 Hz, 1H), 2.39 (septet, *J* = 8.5 Hz, 2H); ^{13}C NMR (125 MHz, $CDCl_3$) δ 153.95, 137.50, 135.45, 135.06, 133.68, 132.24, 127.79, 126.80, 126.77, 126.76, 126.53, 126.18, 125.46, 122.82, 122.74, 120.43, 106.12, 76.89, 44.07, 39.16, 28.86, 24.48; IR (film) 1577, 1266 cm^{-1}; MS (EI) 312.1506 (312.1514 calcd for $C_{23}H_{20}O$, M^+).



(±)-Diethyl 4-(4-methoxyphenoxy)-2-methylenecyclopentane-1,1-dicarboxylate (9a). The general procedure was used for the coupling of 4-methoxylphenol (14.9 mg, 0.12 mmol) and diethyl 2-allyl-2-(1-{[(trifluoromethyl)sulfonyl]oxy}vinyl)malonate (37.8 mg, 0.1 mmol) except using RuPhos as ligand (6 mol %), NaO^{t}Bu as base (13.5 mg, 0.14 mmol), and a reaction time of 1 h. The product was purified by flash chromatography on silica gel using 5% ethyl acetate/hexanes to 10% ethyl acetate/hexanes as the eluant. This procedure afforded 16.3 mg (46%) of the title compound as clear oil. ^{1}H NMR (500 MHz, $CDCl_3$) δ 6.83 – 6.74 (m, 4H), 5.41 (s, 1H), 5.33 (s, 1H), 4.76 (p, *J* = 4.5 Hz, 1H), 4.20 (dq, *J* = 15.1, 7.2 Hz, 4H), 3.76 (s, 3H), 2.81 (dd, *J* = 14.1, 4.6 Hz, 2H), 2.76 – 2.64 (m, 2H), 1.27 (t, *J* = 7.1 Hz, 3H), 1.20 (t, *J* = 7.1 Hz, 3H); ^{13}C NMR (126 MHz, $CDCl_3$) δ 170.35, 169.88, 154.20, 151.40, 144.96, 117.03, 114.76, 114.00, 76.42, 62.59, 62.05, 61.77, 55.84, 41.09, 39.89, 14.14, 14.10; IR (film) 1729, 1506 cm^{-1}; MS (ESI) 349.1646 (349.1646 calcd for $C_{19}H_{24}O_6$, M + H^+).

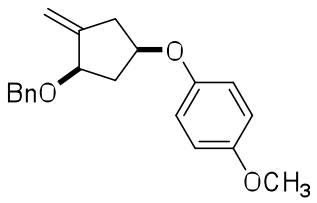


(±)-1-[(3,3-Diallyl-4-methylenecyclopentyl)oxy]-4-methoxybenzene (9b). The general procedure was used for the coupling of 4-methoxyphenol (14.9 mg, 0.12 mmol) and 3,3-diallylhexa-1,5-dien-2-yl trifluoromethanesulfonate (32.0 mg, 0.1 mmol) except using RuPhos as ligand (6 mol %), NaO^{t}Bu as base (13.5 mg, 0.14 mmol), and a reaction time of 15.5 h. No aqueous work-up was performed. Instead, the reaction mixture was concentrated *in vacuo* and the crude product was purified via flash chromatograpy on silica gel using 2% ethyl acetate/hexanes to 5% ethyl acetate/hexanes as the eluant. This procedure afforded 20.8 mg (73%) of the product as a clear oil. ^{1}H NMR (500 MHz, $CDCl_3$) δ 6.91 – 6.70 (m, 4H), 5.79 (dtt, *J* = 17.9, 10.7, 7.3 Hz, 2H), 5.11 – 4.92 (m, 5H), 4.83 (s, 1H), 4.65 (p, *J* = 5.7 Hz, 1H), 3.77 (s, 3H), 2.79 (dd, *J* = 16.8, 6.4 Hz, 1H), 2.68 – 2.51 (m, 1H), 2.30 (d, *J* = 7.3 Hz, 2H), 2.17 (d, *J* = 7.3 Hz, 2H), 2.05 – 1.86 (m, 2H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 154.95, 153.85, 152.09, 135.42, 135.32, 117.77, 117.68, 116.68, 114.76, 106.90, 76.61, 55.86, 47.60, 44.79, 44.41, 41.54, 41.25; IR (film) 1505, 1228 cm^{-1}; MS (ESI) 285.1853 (285.1849 calcd for $C_{19}H_{24}O_2$, M + H$^+$).



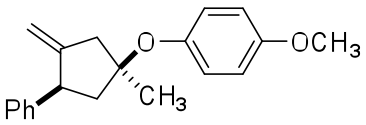
(±)-(1*S,3*R**)-1-Methoxy-4-[(3-methyl-4-methylenecyclopentyl)oxy]benzene (9c).** The general procedure was used for the coupling of 4-methoxyphenol (14.9 mg, 0.12 mmol) and 3-methylhexa-1,5-dien-2-yl trifluoromethanesulfonate[5] (24.4 mg, 0.1 mmol) except using CPhos as ligand (6 mol %), NaO^{t}Bu as base (13.5 mg, 0.14 mmol), and a

reaction time of 4.5 h. No aqueous work-up was performed. Instead, the reaction mixture was concentrated *in vacuo* and the crude product was purified via flash chromatograpy on silica gel using 5% ether/pentane as the eluant. This procedure afforded 19.1 mg (88%) of the product as a clear oil. This material was obtained as a >20:1 mixture of diastereomers as judged by ^{1}H NMR analysis. Data are for the major isomer. ^{1}H NMR (500 MHz, $CDCl_3$) δ 6.82 (s, 4H), 4.91 (q, *J* = 2.4 Hz, 1H), 4.86 (q, *J* = 2.7 Hz, 1H), 4.65 (p, *J* = 6.1 Hz, 1H), 3.77 (s, 3H), 2.82 (dd, *J* = 17.0, 7.1 Hz, 1H), 2.59 – 2.46 (m, 2H), 2.34 (ddd, *J* = 13.4, 7.8, 5.9 Hz, 1H), 1.56 (ddd, *J* = 13.0, 9.0, 6.3 Hz, 1H), 1.18 (d, *J* = 6.8 Hz, 3H); ^{13}C NMR (175 MHz, $CDCl_3$) δ 154.43, 153.92, 152.24, 116.88, 114.75, 105.80, 77.42, 55.85, 41.00, 40.03, 36.65, 19.61; IR (film) 1504, 1225 cm^{-1}; MS (EI) 218.1308 (218.1307 calcd for $C_{14}H_{18}O_2$, M^+).

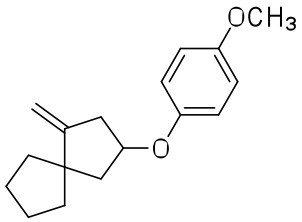


(±)-(1*R,3*R**)-1-{[3-(Benzyloxy)-4-methylenecyclopentyl]oxy}-4-methoxybenzene (9d).** The general procedure was used for the coupling of 4-methoxyphenol (14.9 mg, 0.12 mmol) and 3-(benzyloxy)hexa-1,5-dien-2-yl trifluoromethanesulfonate (33.6 mg, 0.1 mmol), except using CPhos as ligand (6 mol %), NaO^{t}Bu as base (13.5 mg, 0.14 mmol), and a reaction time of 15 min. No aqueous work-up was performed. Instead, the reaction mixture was concentrated *in vacuo* and the crude product was directly purified via flash chromatograpy on silica gel using 10% ethyl acetate/hexanes as the eluant. This procedure afforded 25.6 mg (88%) of the product as a clear oil. This material was obtained as a 4:1 mixture of diastereomers as judged by ^{1}H NMR analysis. Data are for the major isomer. ^{1}H NMR (700 MHz, $CDCl_3$) δ 7.39 – 7.32 (m, 4H), 7.28 (t, *J* = 7.3 Hz, 1H), 6.86 – 6.78 (m, 4H), 5.21 (s, 1H), 5.14 (s, 1H), 4.65 (ddd, *J* = 12.2, 6.8, 5.4 Hz, 1H), 4.61 – 4.53 (m, 2H), 4.23 (ddd, *J* = 6.7, 5.0, 1.6 Hz, 1H), 3.77 (s, 3H), 2.77 (dd, J = 14.4, 6.4 Hz, 1H), 2.69 (ddd, *J* = 16.3, 5.3, 2.2 Hz, 1H), 2.43 (dt, *J* = 13.8, 6.8 Hz, 1H), 2.06 (dt, *J* = 13.9, 5.1 Hz, 1H); ^{13}C NMR (175 MHz, $CDCl_3$) δ 153.98, 152.05, 148.40,

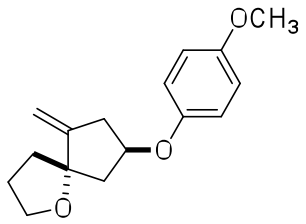
138.71, 128.46, 127.80, 127.58, 117.01, 114.71, 110.88, 79.13, 76.09, 70.31, 55.83, 38.80, 38.29; IR (film) 1504, 1226, 731 cm^{-1}; MS (ESI) 311.1641 (311.1642 calcd for $C_{20}H_{22}O_3$, M + H^+).



(±)-(1*S,4*R**)-1-Methoxy-4-[(-1-methyl-3-methylene-4-phenylcyclopentyl)oxy]benzene (9e).** The general procedure was used for the coupling of 4-methoxyphenol (14.9 mg, 0.12 mmol) and 5-methyl-3-phenylhexa-1,5-dien-2-yl trifluoromethanesulfonate (32 mg, 0.1 mmol) except using CPhos as ligand (6 mol %), NaO*t*Bu as base (13.5 mg, 0.14 mmol), and a reaction time of 1 h. No aqueous work-up was performed. Instead, the reaction mixture was concentrated *in vacuo* and the crude product was purified via flash chromatograpy on silica gel using 5% ethyl acetate/hexanes as the eluant. This procedure afforded 16.5 mg (56%) of the title product as a clear oil. This material was obtained as a >20:1 mixture of diastereomers as judged by ^{1}H NMR analysis. ^{1}H NMR (700 MHz, $CDCl_3$) δ 7.34 – 7.27 (m, 4H), 7.24 – 7.19 (m, 1H), 6.94 (d, *J* = 9.0 Hz, 2H), 6.80 (d, *J* = 9.0 Hz, 2H), 5.03 (q, *J* = 2.3 Hz, 1H), 4.60 (q, *J* = 2.2 Hz, 1H), 3.78 (s, 3H), 3.71 (tt, *J* = 8.7, 2.6 Hz, 1H), 3.00 (dd, *J* = 16.0, 2.8 Hz, 1H), 2.59 (dd, *J* = 16.0, 2.0 Hz, 1H), 2.37 (dd, *J* = 12.8, 10.2 Hz, 1H), 2.32 (ddd, *J* = 12.8, 8.7, 1.6 Hz, 1H), 1.43 (s, 3H); ^{13}C NMR (175 MHz, $CDCl_3$) δ 155.60, 153.33, 149.12, 144.55, 128.53, 128.51, 126.38, 123.86, 114.20, 109.69, 85.24, 55.68, 48.85, 48.82, 47.00, 24.64; IR (film) 1504, 1214 cm^{-1}; MS (EI) 294.1610 (294.1620 calcd for $C_{20}H_{22}O_2$, M^+).



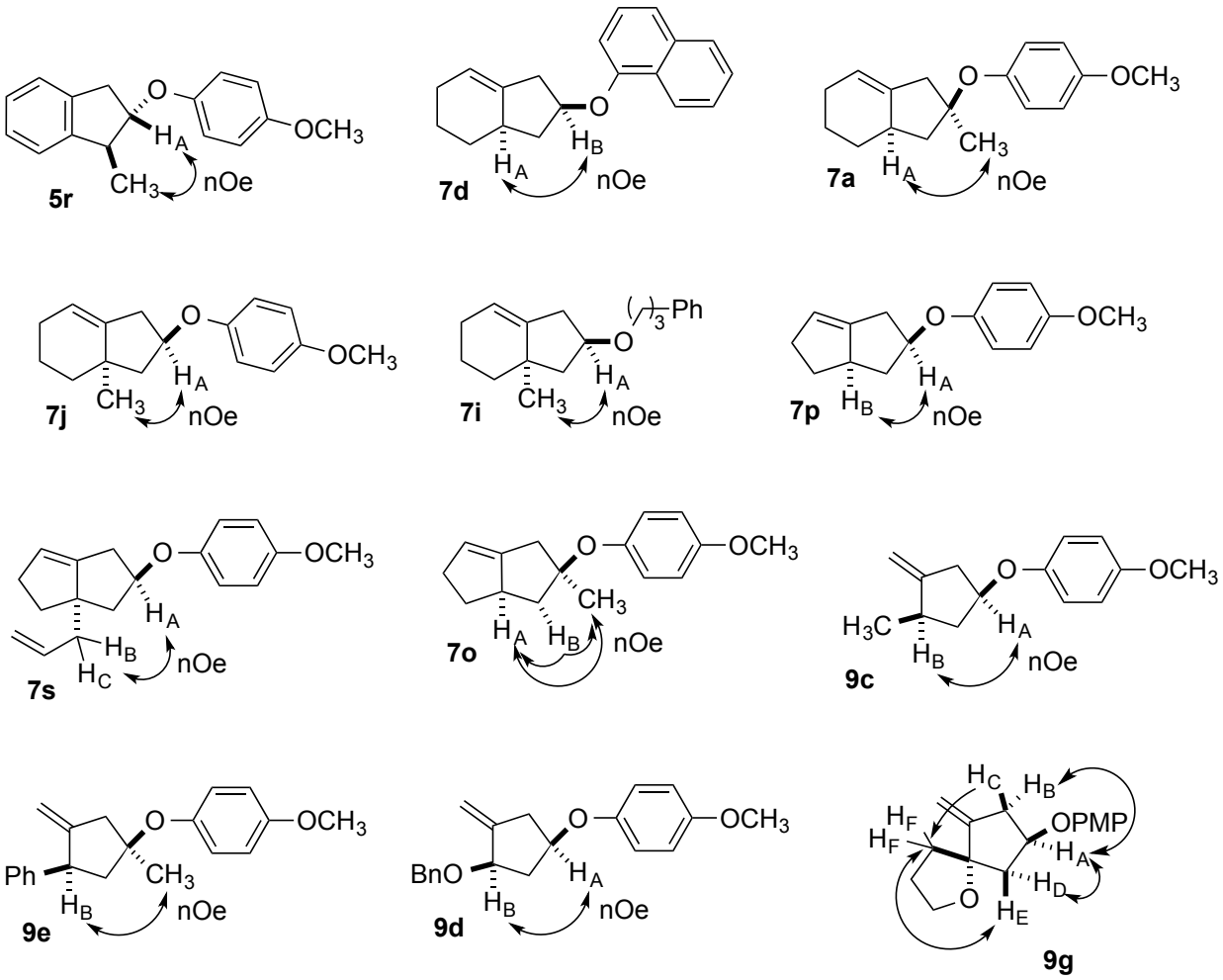
(±)-3-(4-Methoxyphenoxy)-1-methylenespiro[4.4]nonane (9f). The general procedure was used for the coupling of 4-methoxyphenol (14.9 mg, 0.12 mmol) and 1-(1-allylcyclopentyl)vinyl trifluoromethanesulfonate (28.4 mg, 0.1 mmol) except using RuPhos as ligand (6 mol %), NaO^{t}Bu as base (13.5 mg, 0.14 mmol), and a reaction time of 1 h. The product was purified by flash chromatography on silica gel using 35% hexanes in dichloromethane as the eluant. This procedure afforded 18.6 mg (71%) of the title product as a clear oil. ^{1}H NMR (700 MHz, $CDCl_3$) δ 6.82 (s, 4H), 4.86 (d, *J* = 7.9 Hz, 2H), 4.68 (ddd, *J* = 10.7, 6.1, 4.6 Hz, 1H), 3.77 (s, 3H), 2.87 (dd, *J* = 16.8, 6.5 Hz, 1H), 2.70 – 2.59 (m, 1H), 1.98 (dd, *J* = 13.2, 5.8 Hz, 1H), 1.93 (dd, *J* = 13.2, 4.6 Hz, 1H), 1.79 – 1.70 (m, 4H), 1.70 – 1.59 (m, 3H), 1.59 – 1.54 (m, 1H); ^{13}C NMR (175 MHz, $CDCl_3$) δ 158.10, 153.86, 152.16, 116.87, 114.76, 104.41, 76.94, 55.86, 52.58, 46.30, 41.16, 40.87, 40.62, 24.89, 24.85; IR (film) 1504, 1225 cm^{-1}; MS (ESI) 258.1686 (259.1963 calcd for $C_{17}H_{22}O_2$, M + H$^+$).



(5*S,8*R**)-8-(4-Methoxyphenoxy)-6-methylene-1-oxaspiro[4.4]nonane (9g).** The general procedure was used for the coupling of 1-(2-allyltetrahydrofuran-2-yl)vinyl trifluoromethanesulfonate (28.2 mg, 0.1 mmol) and 4-methoxyphenol (14.9 mg, 0.12 mmol) except using RuPhos as ligand (6 mol %), NaO^{t}Bu as base (13.5 mg, 0.14 mmol), and a reaction time of 1 h. The product was purified by flash chromatography on silica gel using 5% ethyl acetate/hexanes to 10% ethyl acetate/hexanes to 15% ethyl acetate/hexanes as the eluant. This procedure afforded 21.4 mg (83%) of the product as a clear liquid. This material was obtained as a 5:1 mixture of diastereomers as judged by ^{1}H NMR analysis. Data are for the mixture. ^{1}H NMR (500 MHz, $CDCl_3$) δ 6.87 – 6.73 (m, 4H), 5.09 (s, 1H), 5.01 – 4.95 (m, 1H), 4.82 – 4.71 (m, 0.83H), 4.59 (p, 6.4 Hz, 0.18H), 4.01 – 3.81 (m, 2H), 3.76 (s, 3H), 2.96 (dd, *J* = 17.3, 6.6 Hz, 0.83H), 2.85

(dd, J = 17.0, 7.2 Hz, 0.18H), 2.66 (ddt, J = 17, 5.2, 2.8 Hz, 0.18H), 2.59 (dd, J = 17.3, 2 Hz, 0.84H) 1H), 2.28 – 2.11 (m, 1.18H), 2.10 – 1.79 (m, 5H); ^{1}H NMR (500 MHz, C_6D_6) δ 6.82 – 6.69 (m, 4H), 5.16 – 5.12 (m, 1H), 4.91 (s, 0.83H), 4.87 (s, 0.19H), 4.56 (tt, *J* = 6.6, 3.7 Hz, 1H), 4.36 (p, J = 6.4 Hz, 0.18H), 3.75 (q, *J* = 7.4 Hz, 1H), 3.68 (q, *J* = 7.2 Hz, 1H), 3.34 (s, 3H), 2.76 (dd, *J* = 17.2, 6.7 Hz, 1H), 2.56 (d, *J* = 17.1 Hz, 1H), 2.31 (dd, J = 13.1, 6.6 Hz, 0.17H), 2.21 (dd, *J* = 13.6, 6.2 Hz, 0.83H), 2.02 (dd, *J* = 13.5, 3.4 Hz, 1H), 1.94 – 1.83 (m, 1.65H), 1.70 – 1.52 (m, 2.2H); ^{13}C NMR (125 MHz, $CDCl_3$) δ 153.91, 153.47, 151.76, 117.19, 116.67, 114.79, 114.69, 107.42, 107.18, 88.38, 75.29, 75.20, 68.19, 67.84, 55.84, 55.82, 45.42, 45.17, 38.58, 38.48, 38.06, 37.50, 29.85, 26.13, 25.90, 19.16, 1.17; IR (film) 1504, 1225 cm^{-1}; MS (ESI) 261.1488 (261.1485 calcd for $C_{16}H_{20}O_3$, M + H^+).

Relative Stereochemical Assignments – Significant nOe Correlations



References

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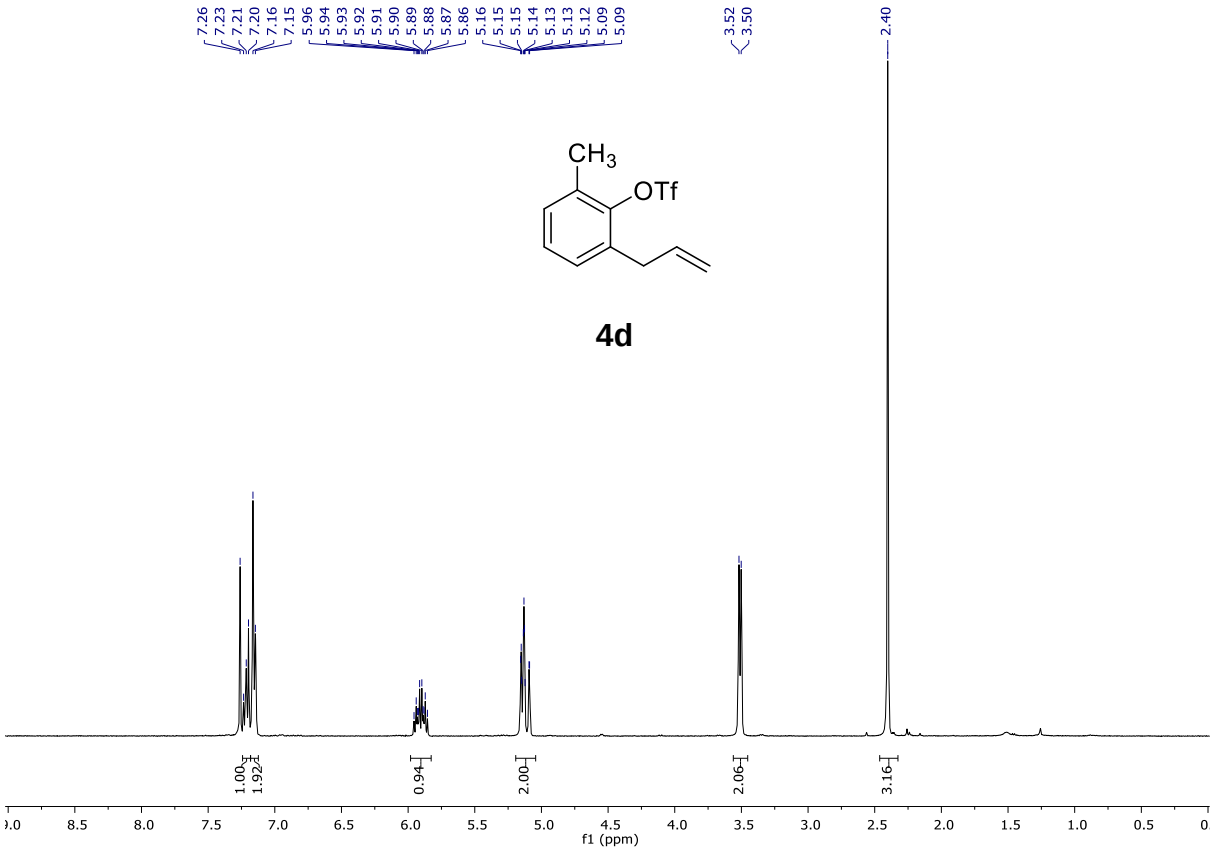
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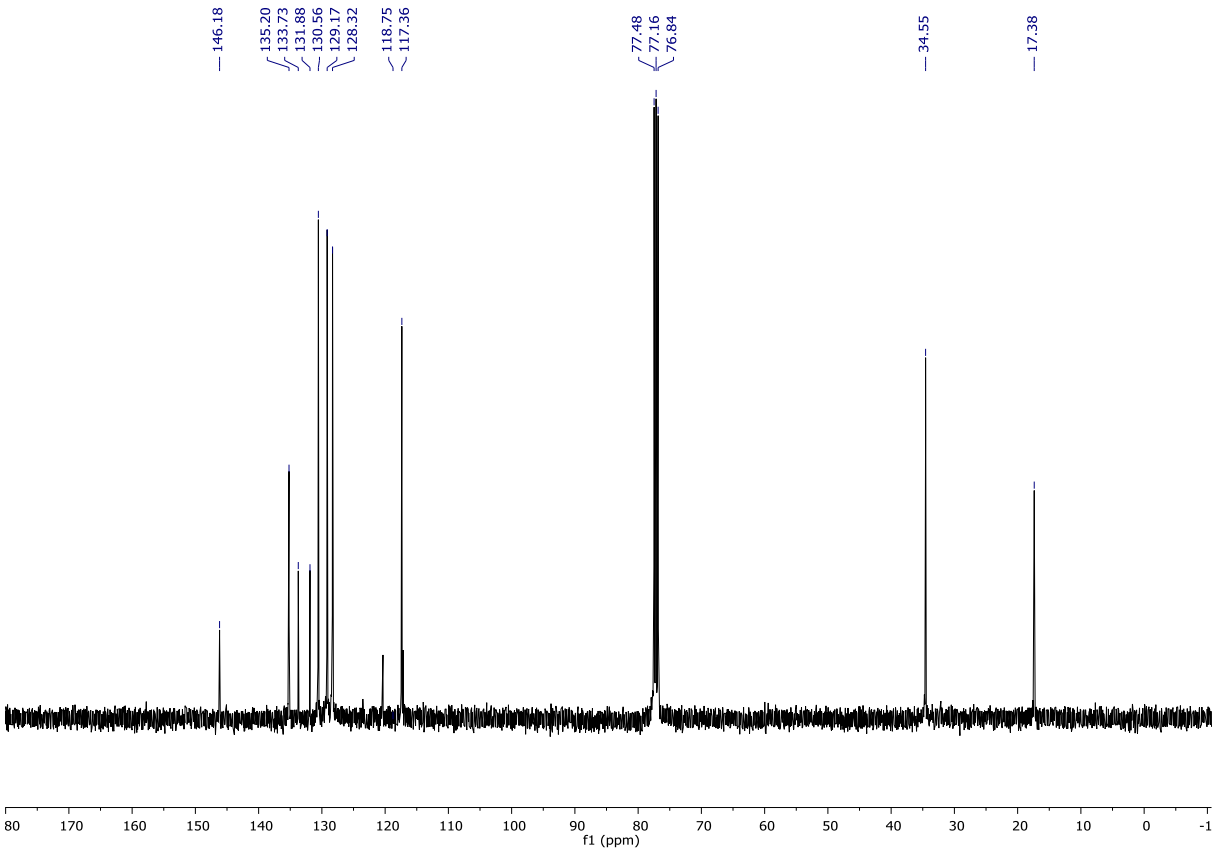
7.23
7.21
7.20
7.16
7.15
5.96
5.94
5.93
5.92
5.91
5.90
5.89
5.88
5.87
5.86
5.16
5.15
5.15
5.14
5.13
5.13
5.12
5.09
5.09
3.52
3.50
2.40
CH3
OTf
1.00
1.92
0.94
2.00
2.06
3.16
f1 (ppm)

4d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135.20
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131.88
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129.17
128.32
118.75
117.36
77.48
77.16
76.84
34.55
17.38
f1 (ppm)


7.26
5.79
5.78
5.77
4.82
4.73
2.59
2.58
2.58
2.57
2.56
2.56
2.55
2.47
2.46
2.44
2.44
2.20
2.19
2.19
2.18
2.18
2.18
2.17
2.17
2.16
2.16
2.04
2.01
2.01
1.99
1.80
1.79
1.78
1.77
1.77
1.76
1.76
1.75
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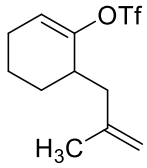
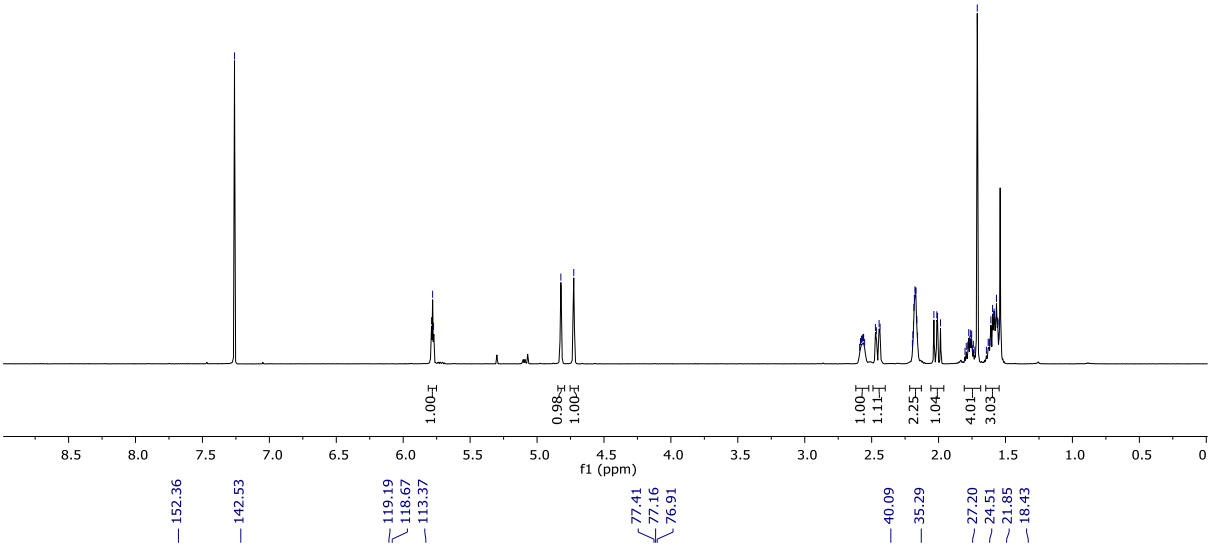
1.55


OTf
H3C

6c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1.11
2.25
1.04
4.01
3.03
8.5
8.0
7.5
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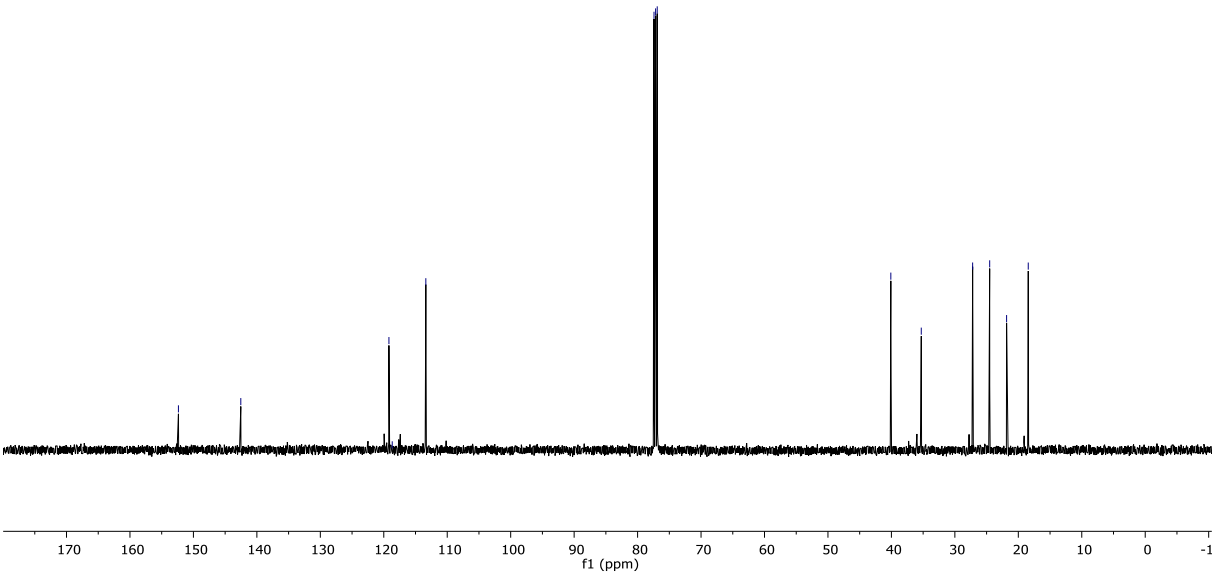
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0
f1 (ppm)

152.36
142.53
119.19
118.67
113.37
77.41
77.16
76.91
40.09
35.29
27.20
24.51
21.85
18.43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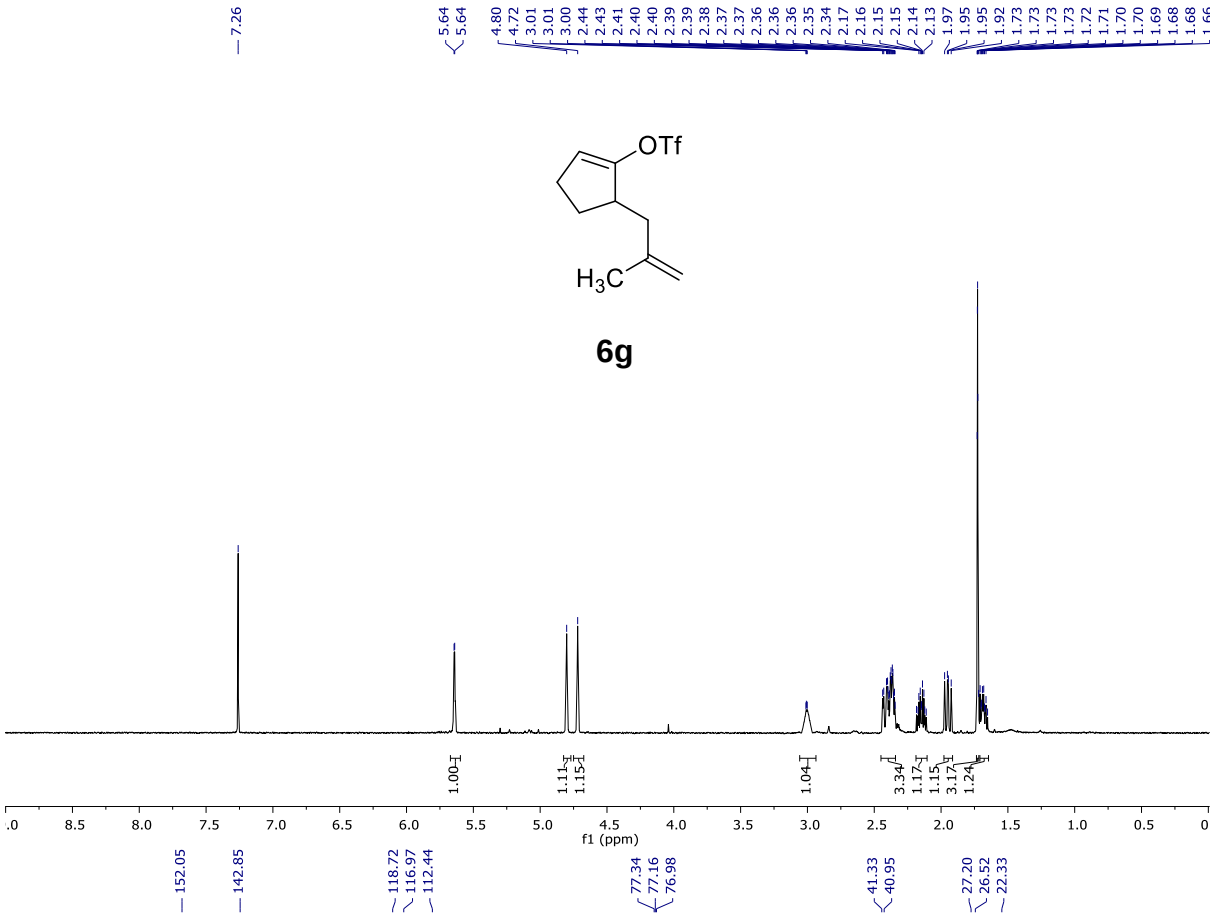
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
-1
f1 (ppm)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2.43
2.41
2.40
2.40
2.39
2.39
2.38
2.37
2.36
2.36
2.36
2.35
2.34
2.17
2.16
2.15
2.15
2.14
2.13
1.97
1.95
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1.92
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1.73
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1.72
1.71
1.70
1.70
1.69
1.68
1.68
OTf
H3C
1.00
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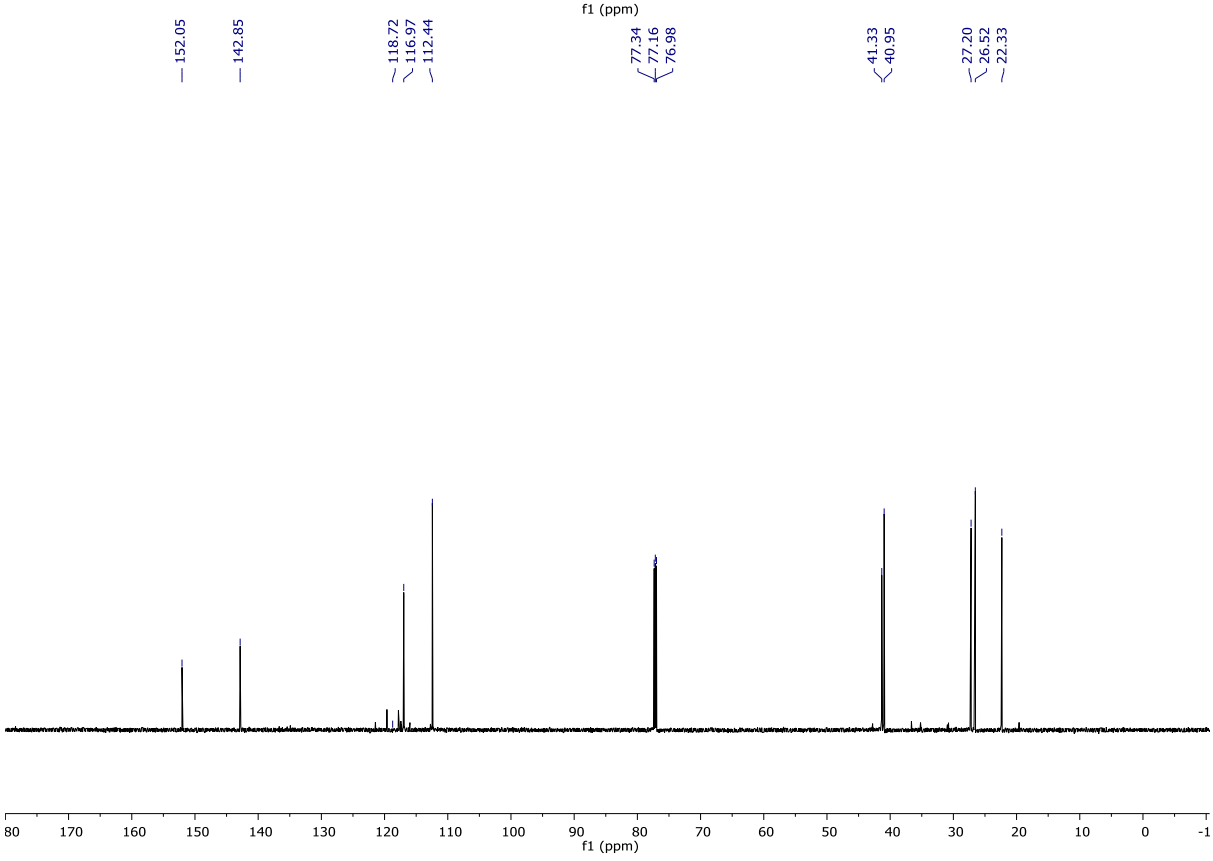
1.15
1.04
3.34
1.17
1.15
3.17
1.24
f1 (ppm)

6g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76.98
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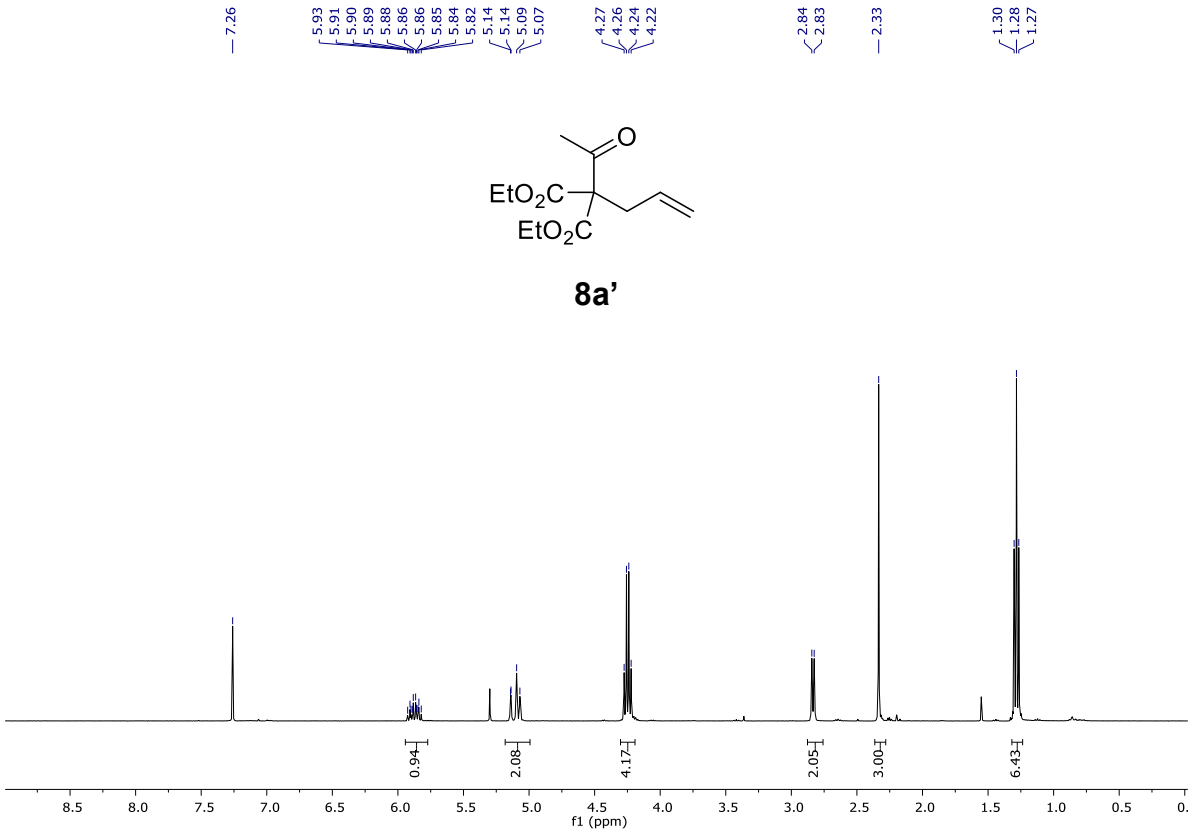
22.33
f1 (ppm)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5.09
5.07
4.27
4.26
4.24
4.22
2.84
2.83
2.33
1.30
1.28
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O
EtO2C
EtO2C
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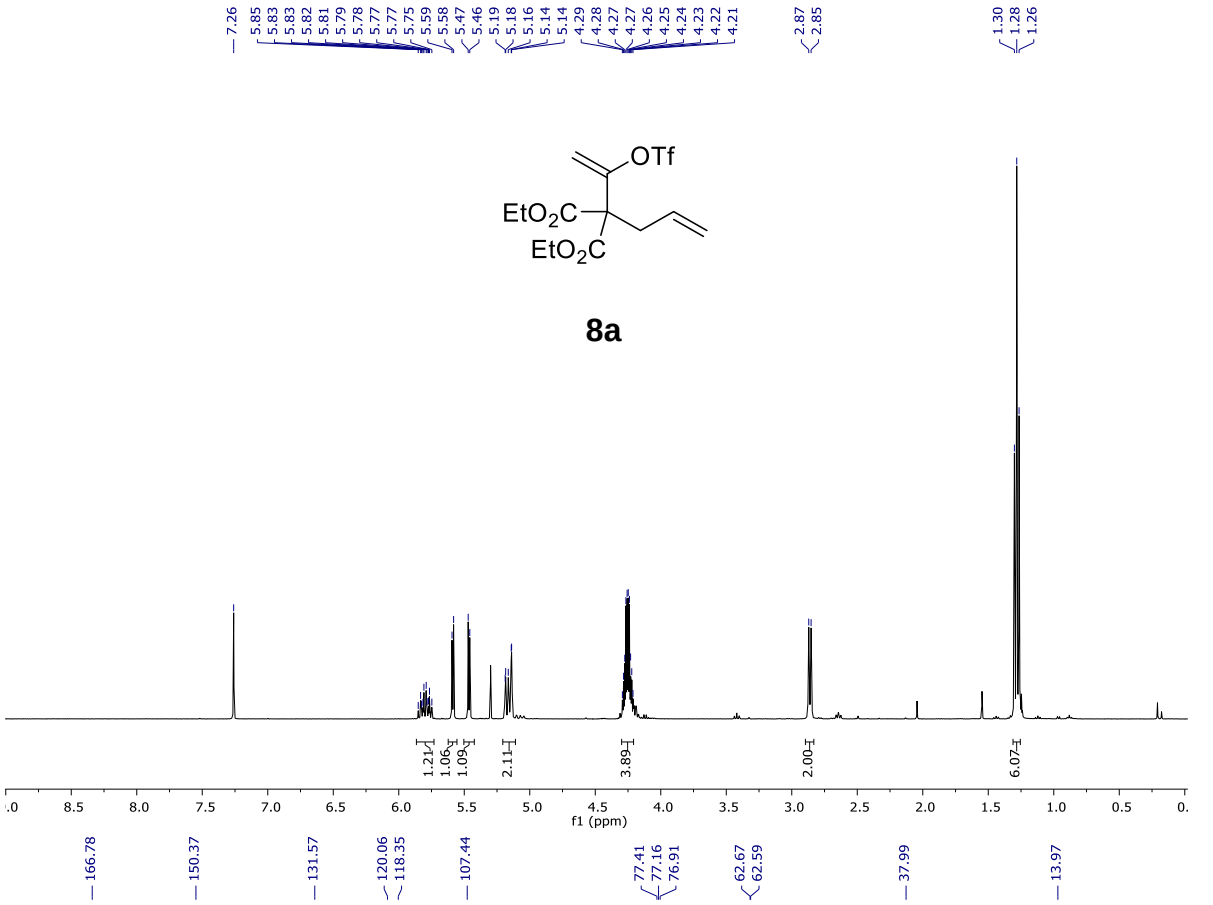
3.00
6.43
f1 (ppm)

8a'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5.77
5.77
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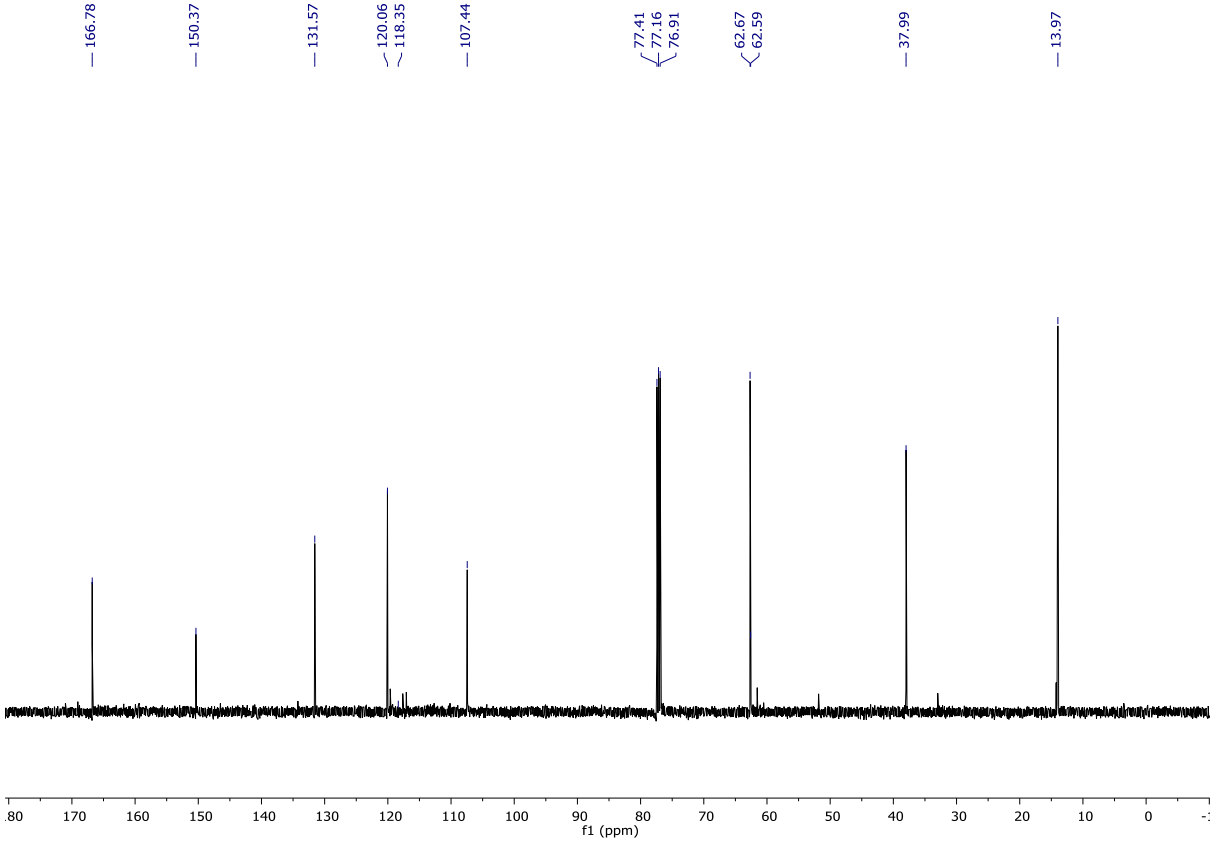
5.58
5.47
5.46
5.19
5.18
5.16
5.14
5.14
4.29
4.28
4.27
4.27
4.26
4.25
4.24
4.23
4.22
4.21
2.87
2.85
1.30
1.28
1.26
OTf
EtO2C
EtO2C
1.21
1.06
1.09
2.11
3.89
2.00
6.07
f1 (ppm)

8a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62.67
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13.97
f1 (ppm)


7.38
7.38
7.37
7.36
7.36
7.36
7.35
7.34
7.34
7.33
7.32
7.32
7.31
7.31
7.30
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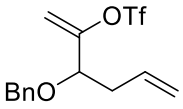
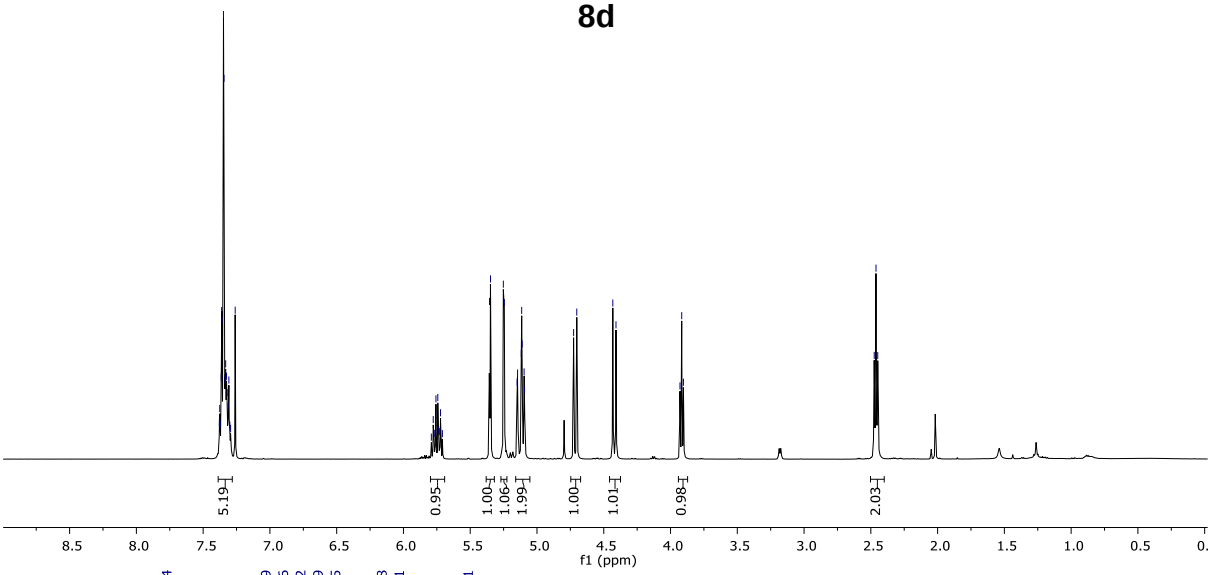

OTf
BnO

8d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6.0
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2.5
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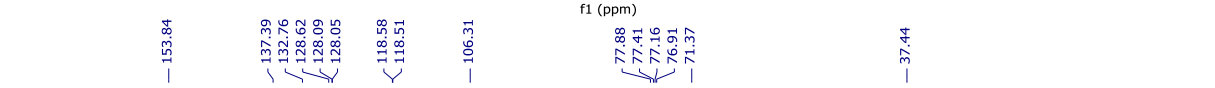
0.
f1 (ppm)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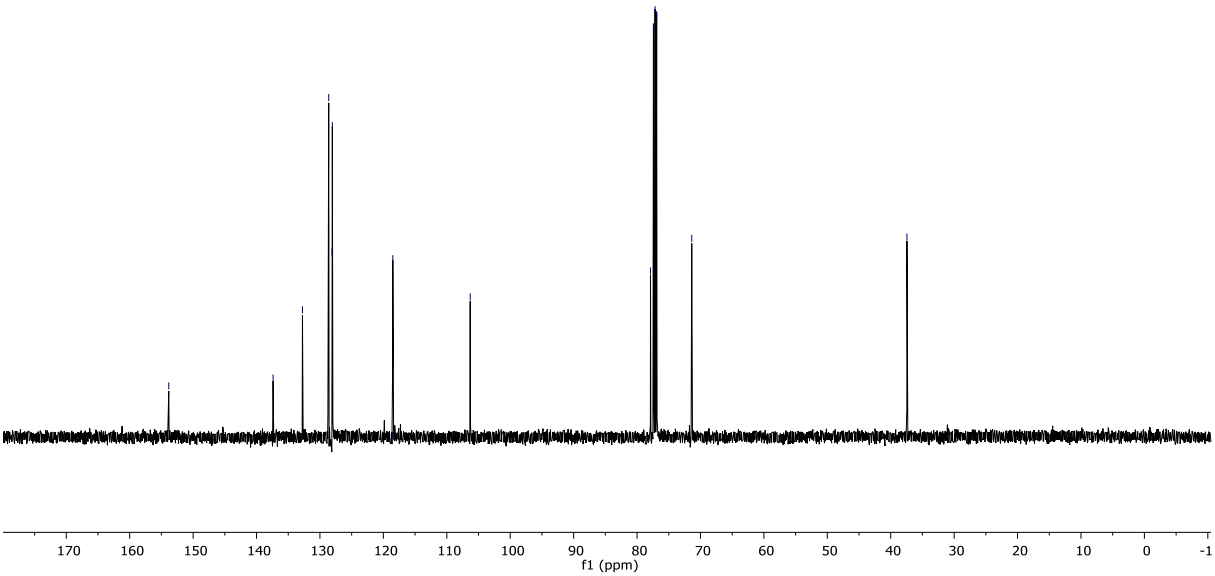
37.44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0
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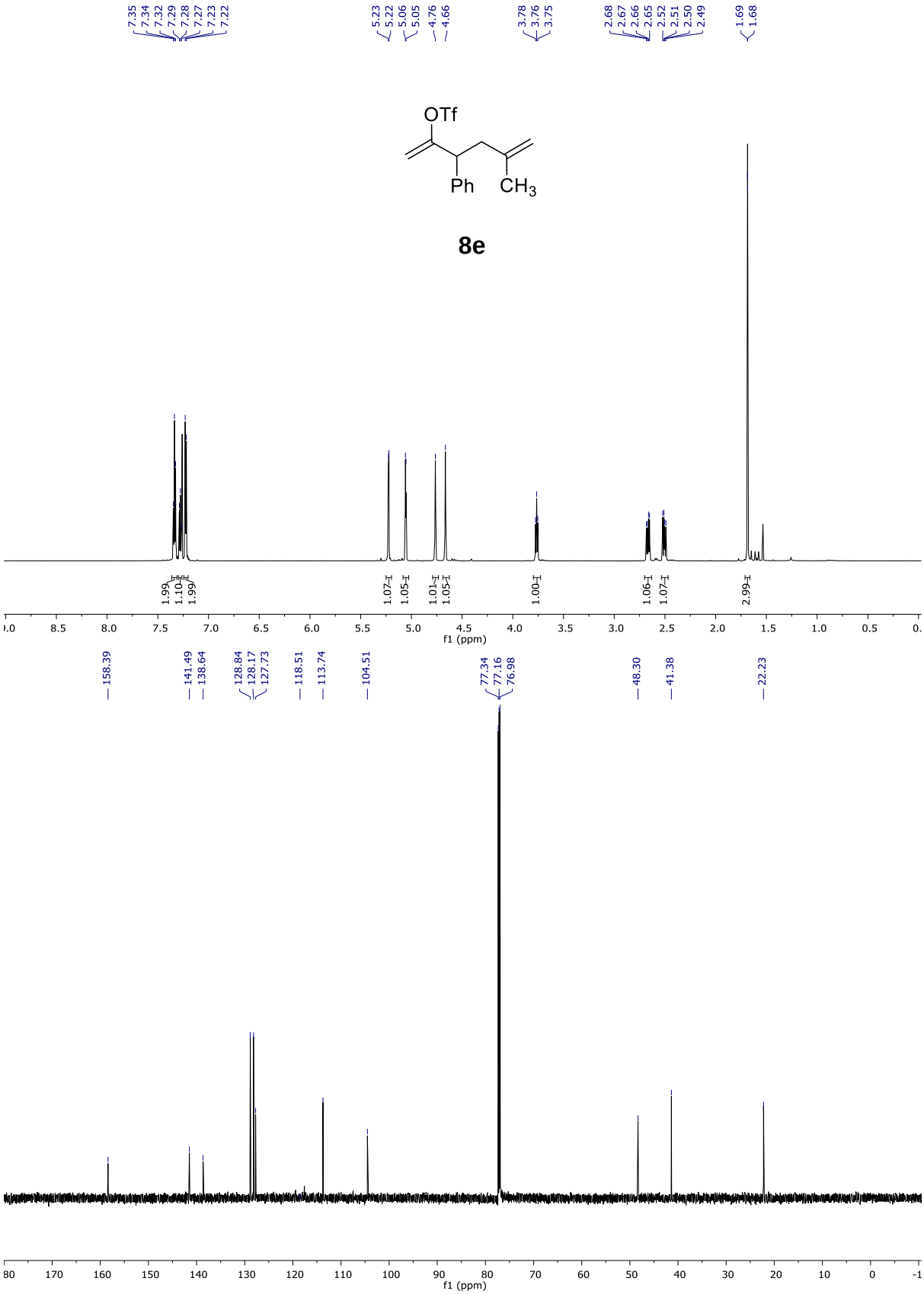
f1 (ppm)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3.78
3.76
3.75
2.68
2.67
2.66
2.65
2.52
2.51
2.50
2.49
1.69
1.68
OTf
Ph
CH3
1.99
1.10
1.99
1.07
1.05
1.01
1.05
1.00
1.06
1.07
2.99
f1 (ppm)
158.39
141.49
138.64
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128.17
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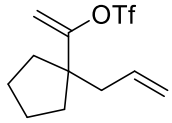
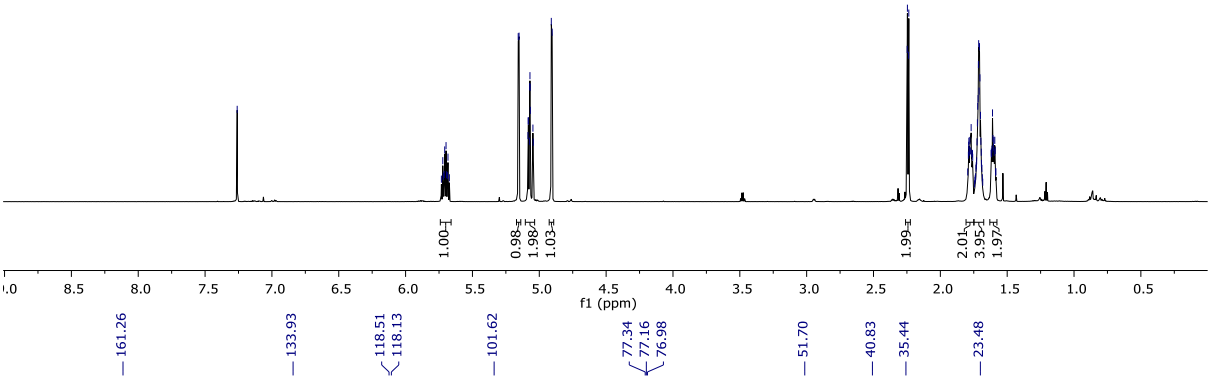
22.23
f1 (ppm)

8e


OTf

8f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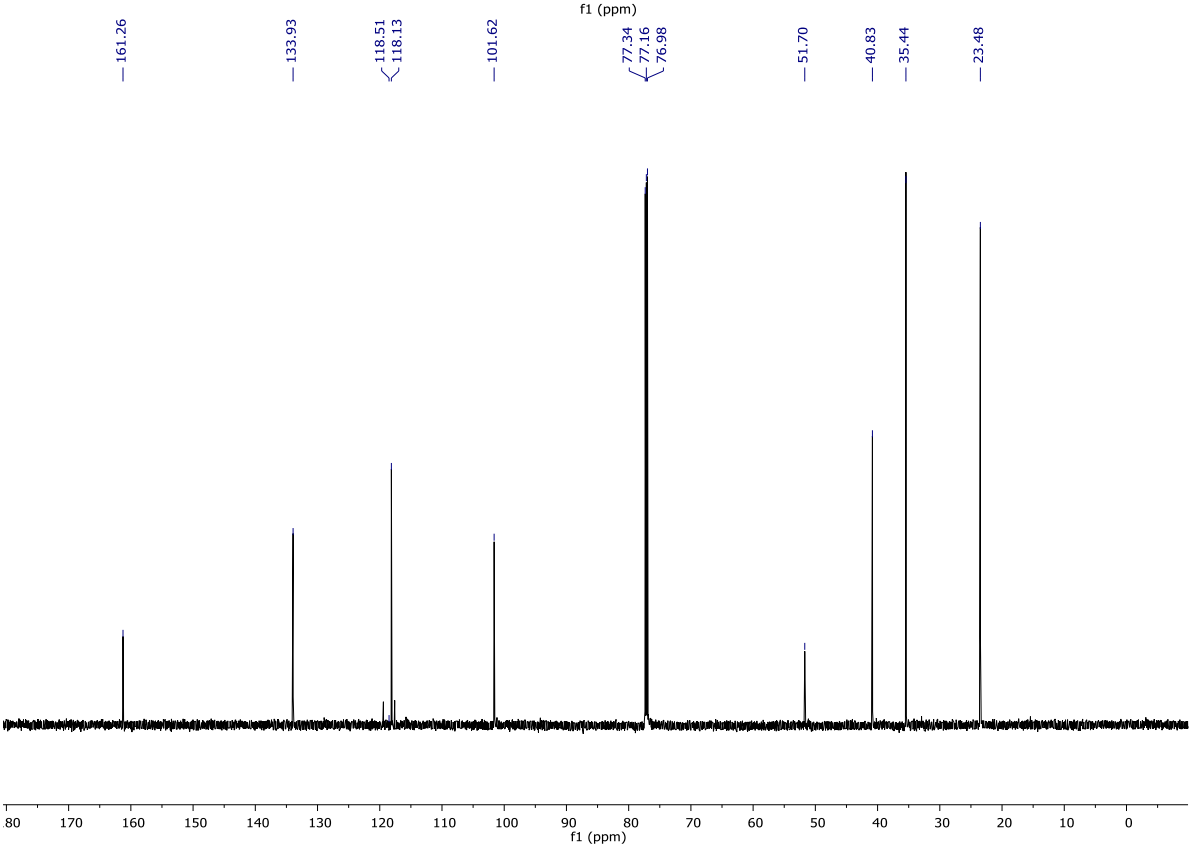
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40.83
35.44
23.48
f1 (ppm)


7.26
5.78
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5.78
5.77
5.76
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5.74
5.24
5.24
5.21
5.21
5.14
5.14
5.13
5.13
5.12
5.11
5.11
5.11
5.10
3.95
3.95
3.94
3.94
3.93
3.92
3.92
2.53
2.52
2.51
2.50
2.50
2.49
2.49
2.49
2.43
2.43
2.43
2.42
2.42
2.41
2.40
2.39
2.13
2.12
2.11
2.10
2.09
2.09
2.08
1.98
1.97
1.96
1.96
1.95
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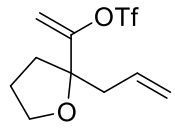
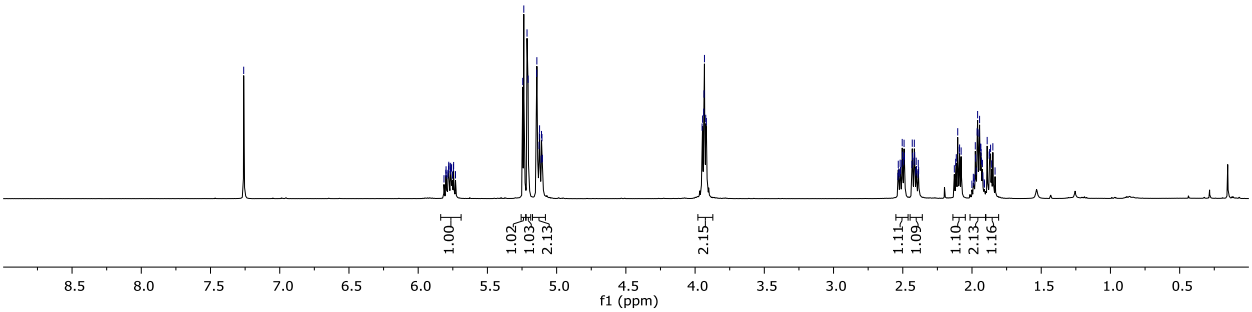
1.86
1.85


OTf
O

8g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1.10
2.13
1.16
8.5
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7.5
7.0
6.5
6.0
5.5
5.0
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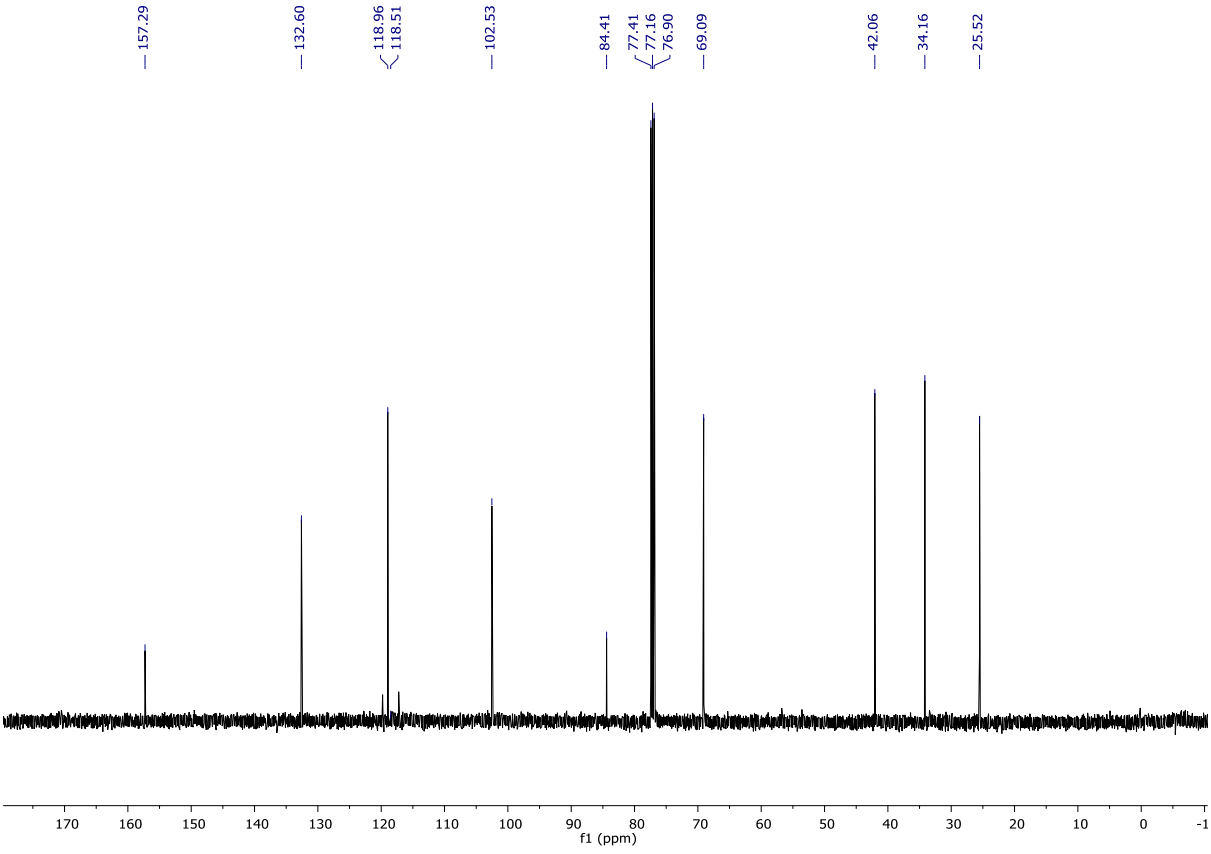
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
f1 (ppm)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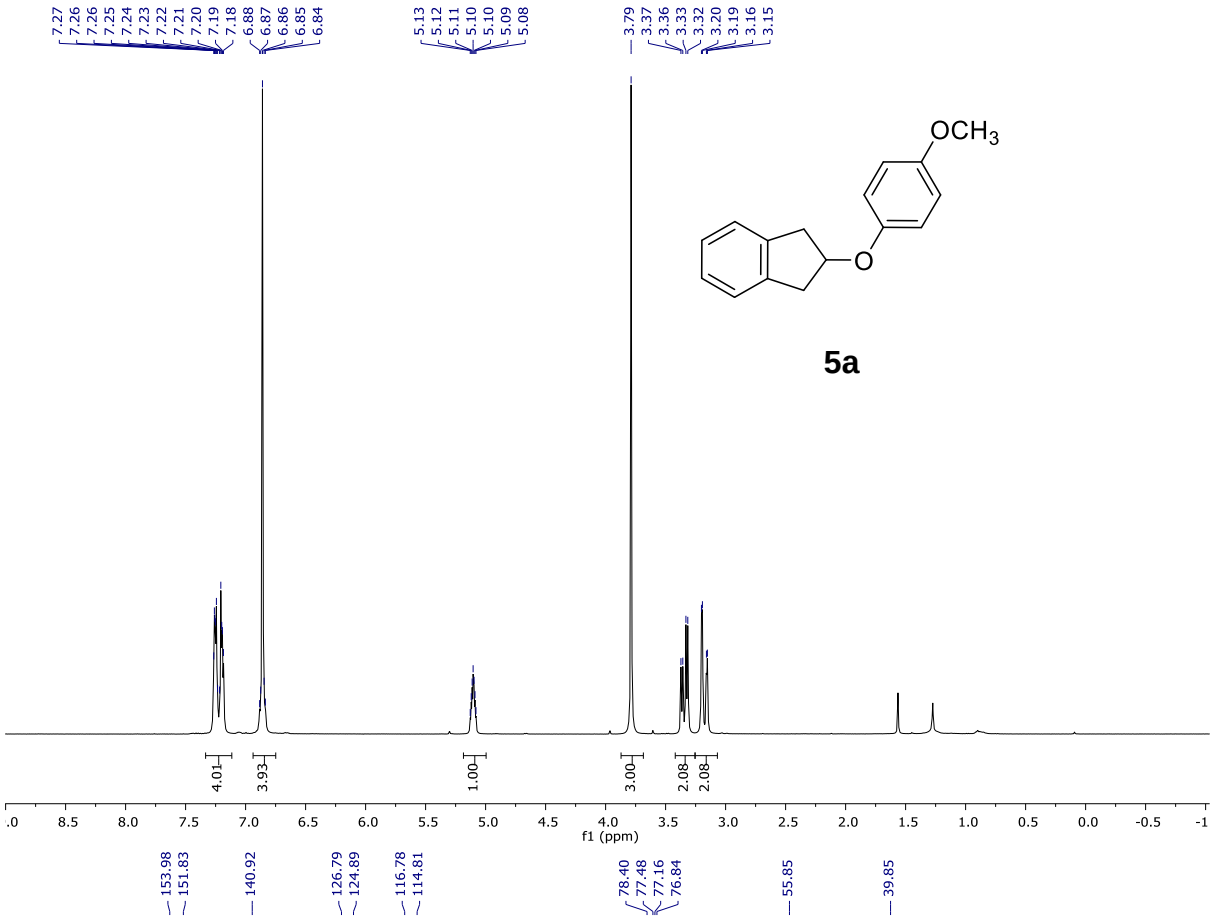
84.41
77.41
77.16
76.90
69.09
42.06
34.16
25.52
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
-1
f1 (ppm)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7.19
7.18
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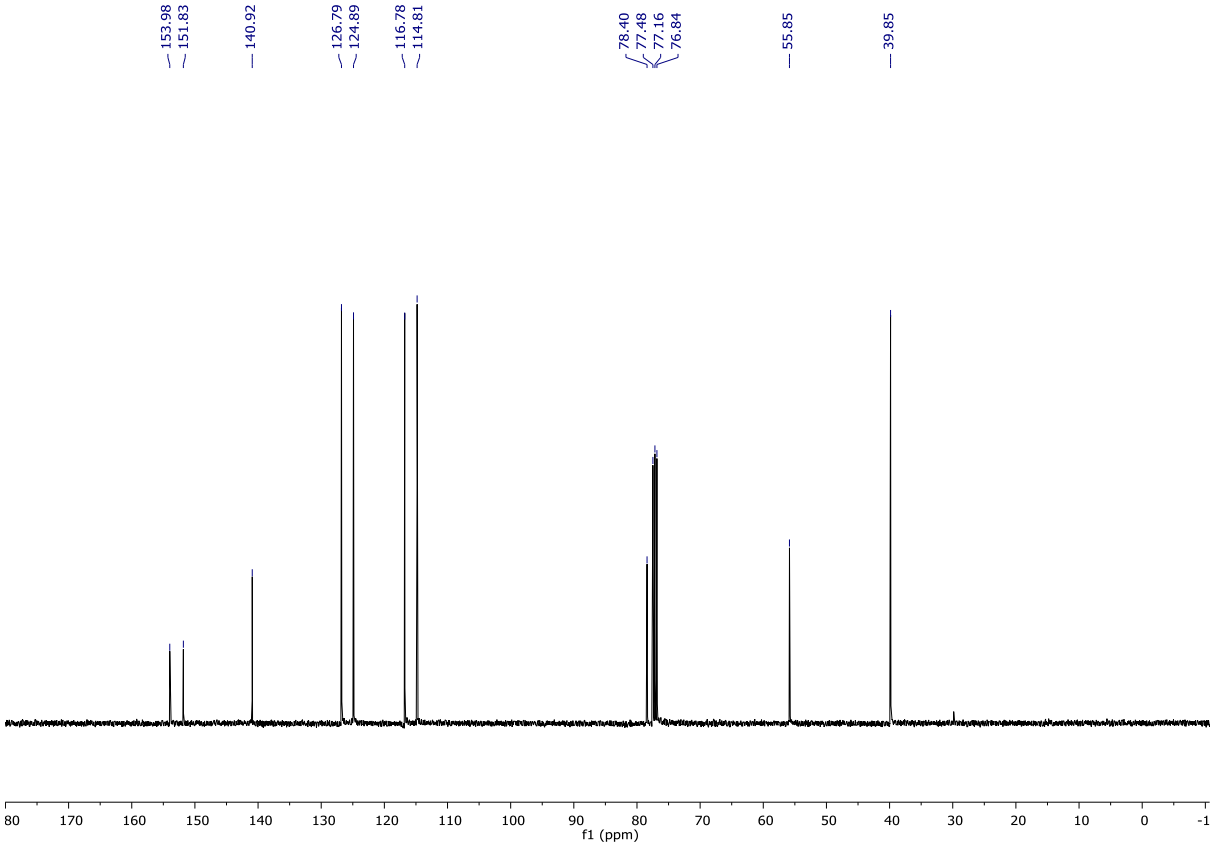
6.87
6.86
6.85
6.84
5.13
5.12
5.11
5.10
5.10
5.09
5.08
3.79
3.37
3.36
3.33
3.32
3.20
3.19
3.16
3.15
OCH3
O
4.01
3.93
1.00
3.00
2.08
2.08
f1 (ppm)

5a


153.98
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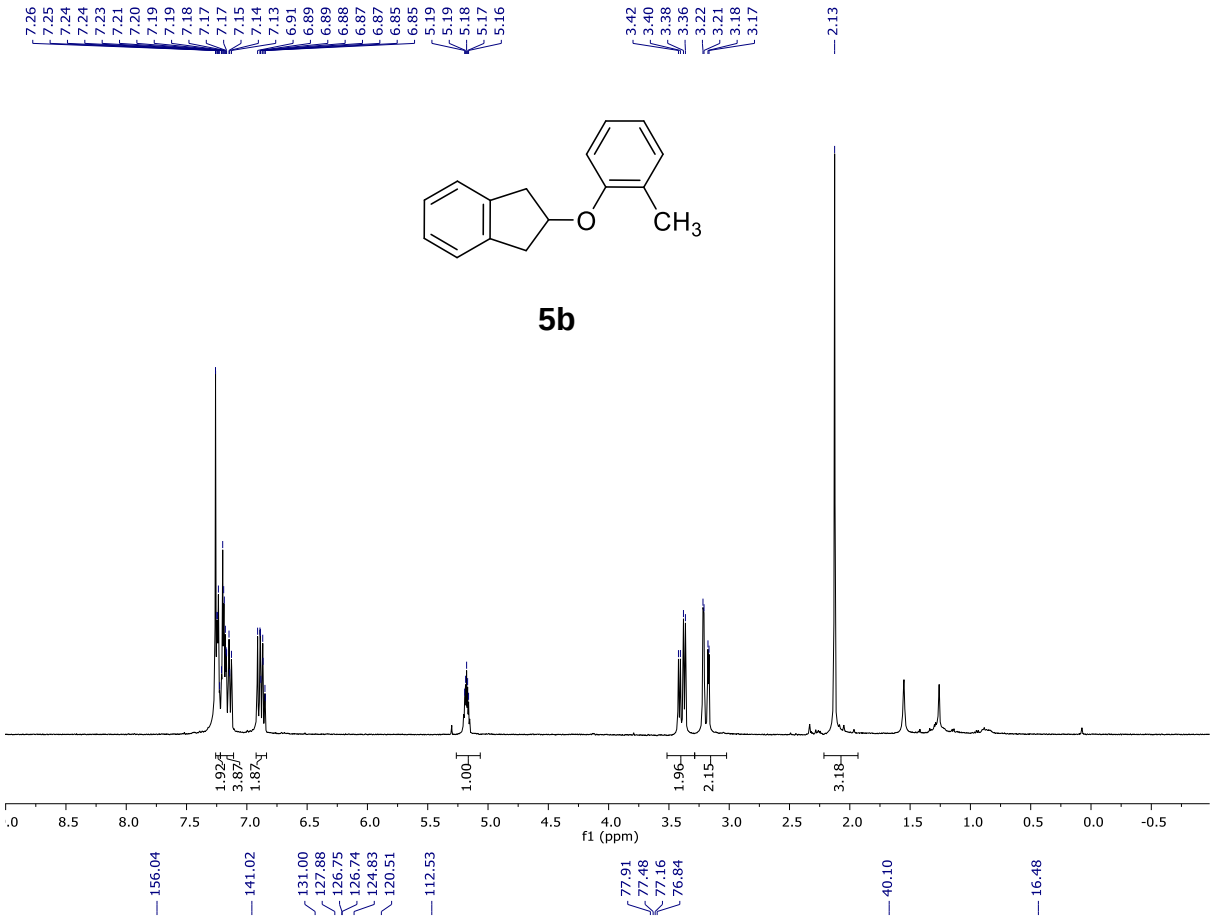
126.79
124.89
116.78
114.81
78.40
77.48
77.16
76.84
55.85
39.85
f1 (ppm)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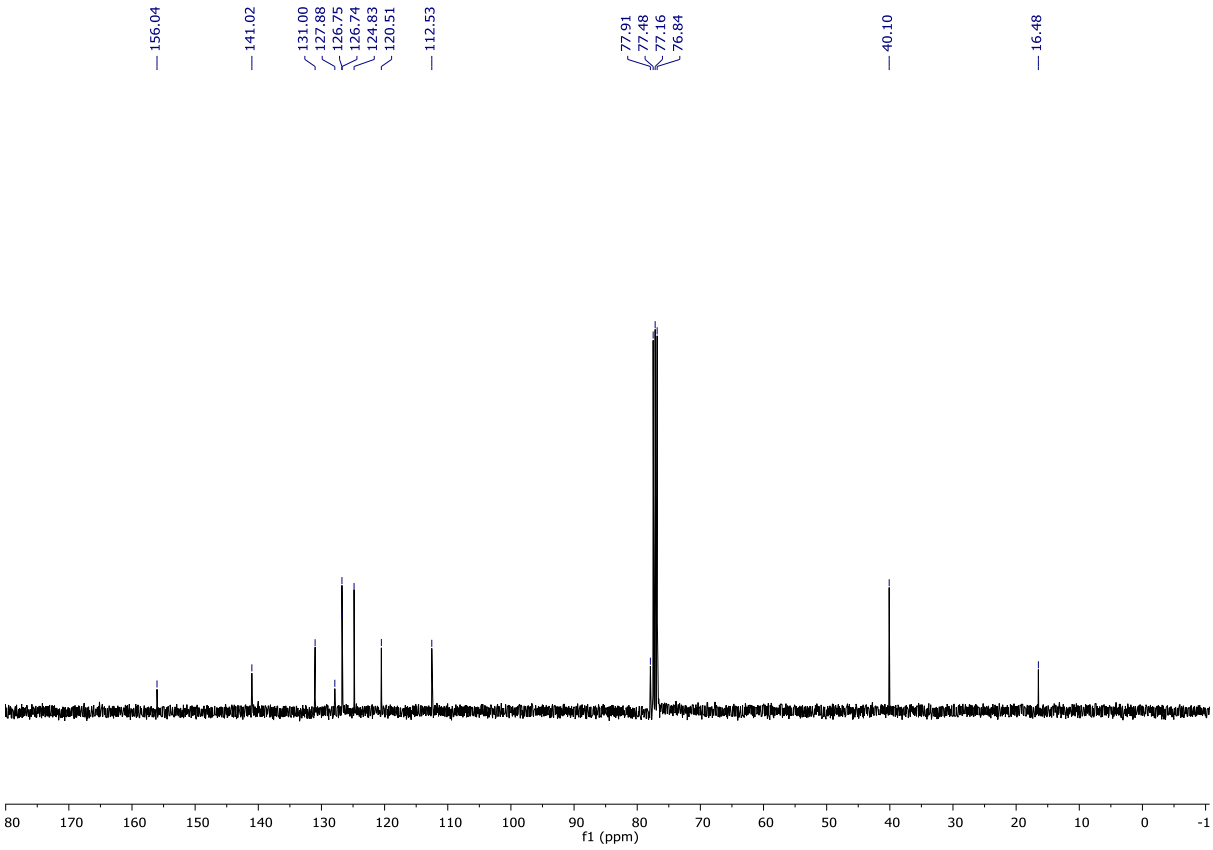
7.19
7.18
7.17
7.17
7.15
7.14
7.13
6.91
6.89
6.89
6.88
6.87
6.87
6.85
6.85
5.19
5.19
5.18
5.17
5.16
3.42
3.40
3.38
3.36
3.22
3.21
3.18
3.17
2.13
O
CH3
1.92
3.87
1.87
1.00
1.96
2.15
3.18
f1 (ppm)

5b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141.02
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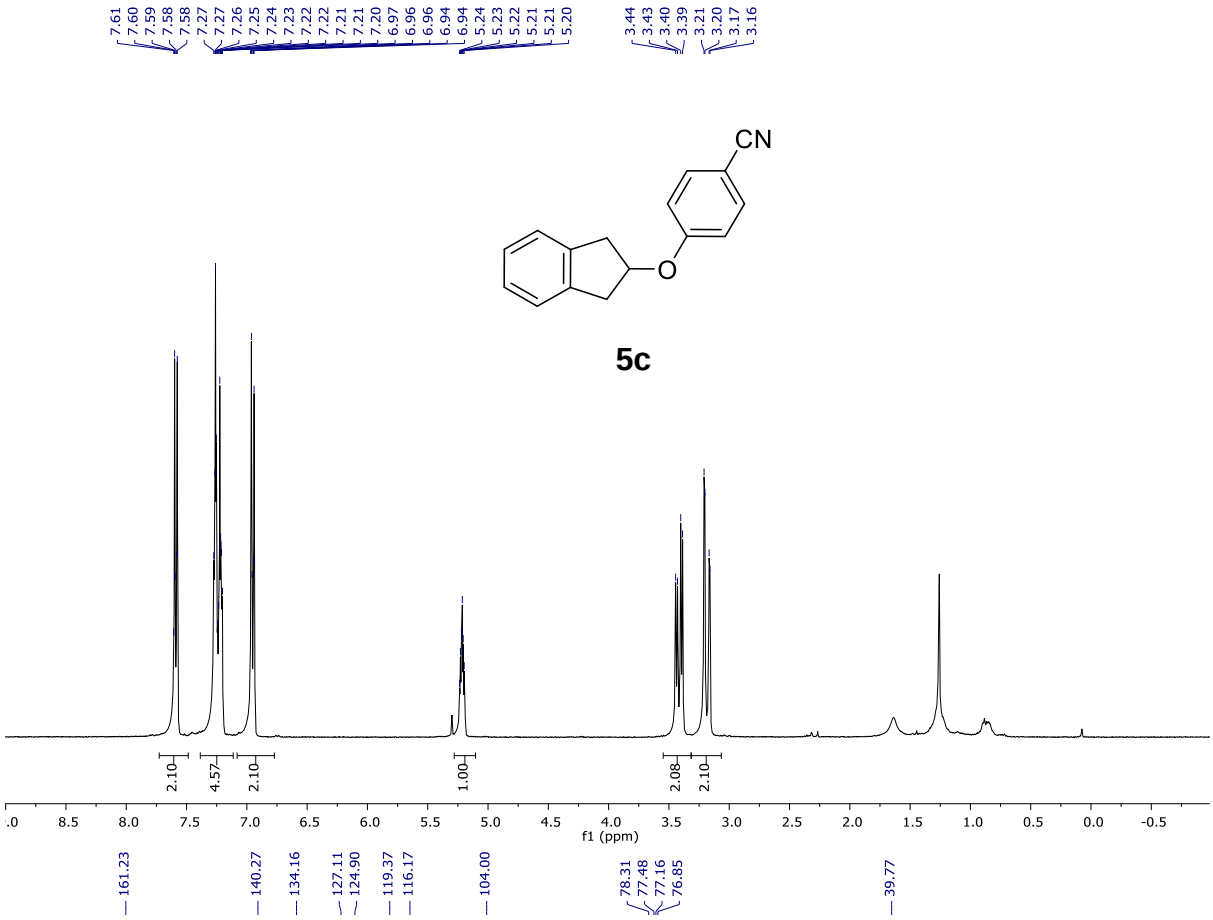
127.88
126.75
126.74
124.83
120.51
112.53
77.91
77.48
77.16
76.84
40.10
16.48
f1 (ppm)


7.61
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7.58
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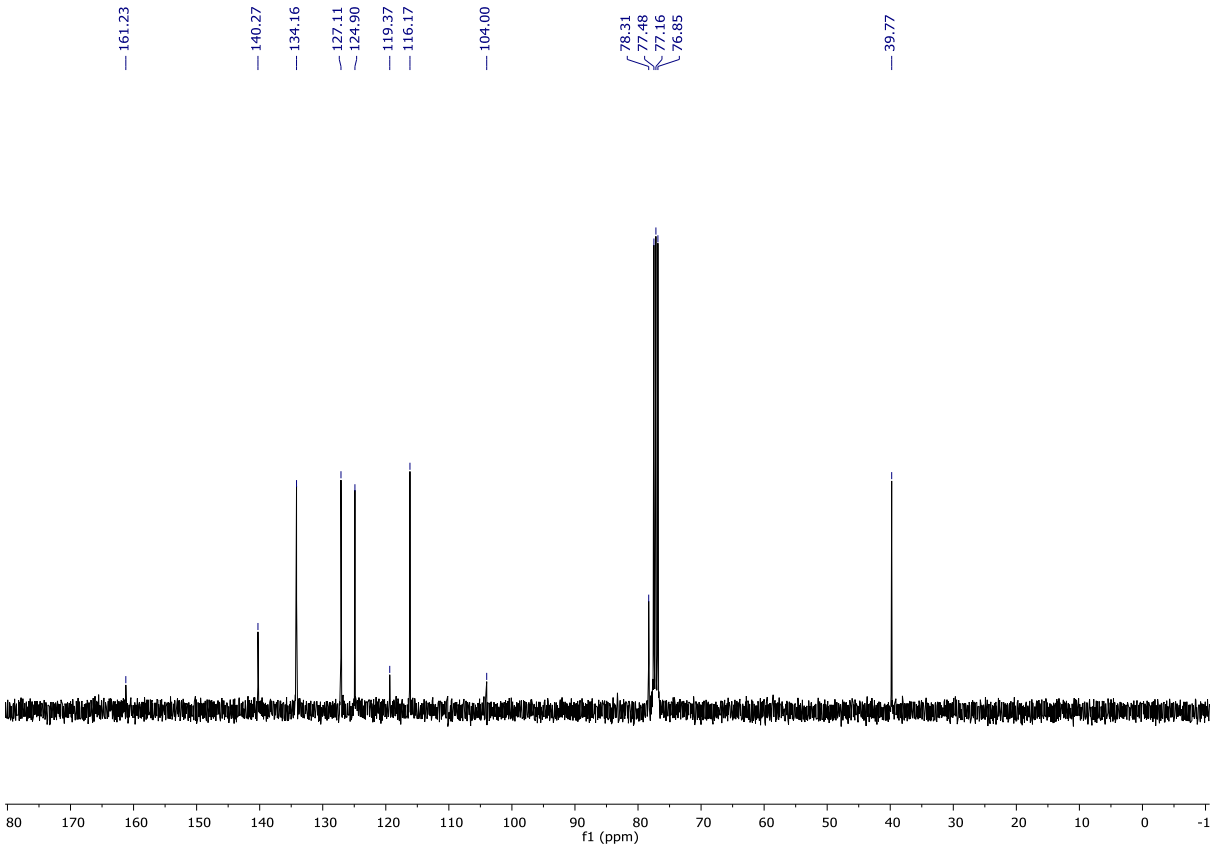
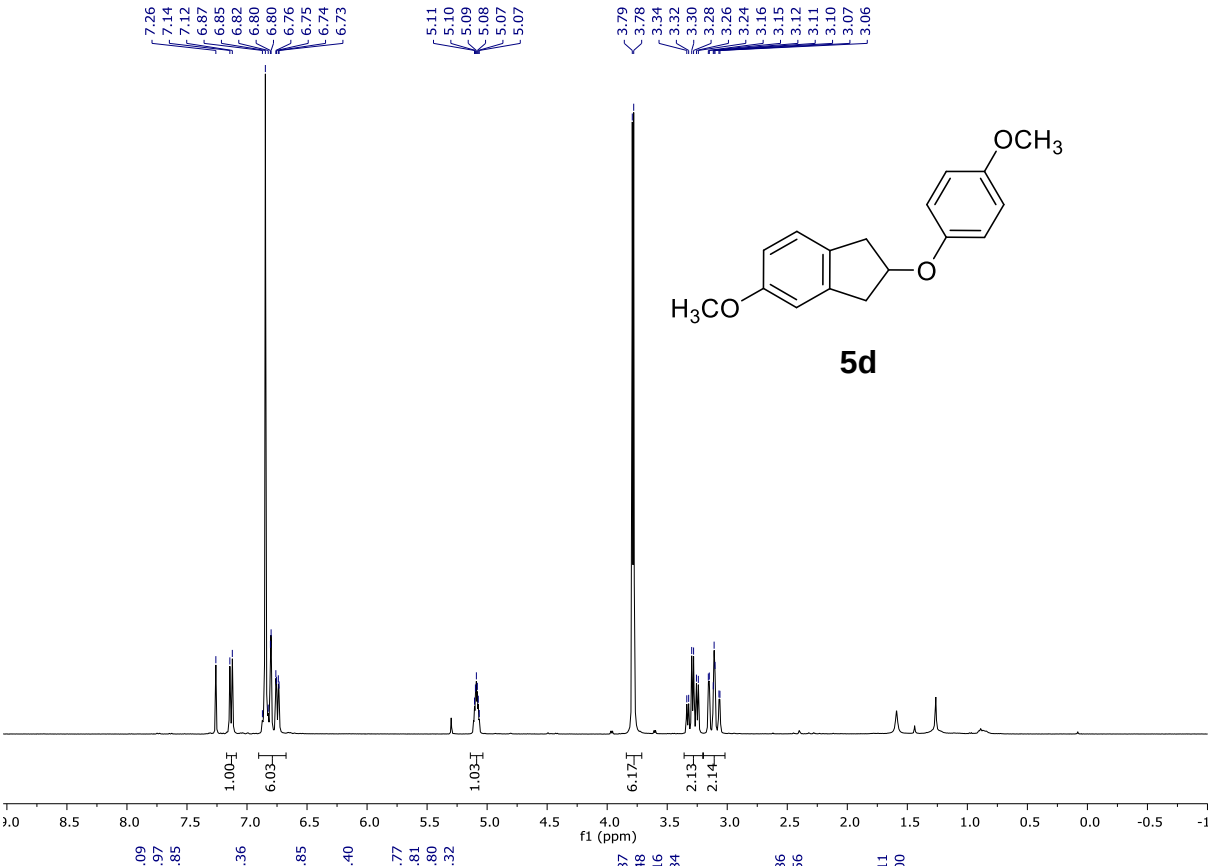
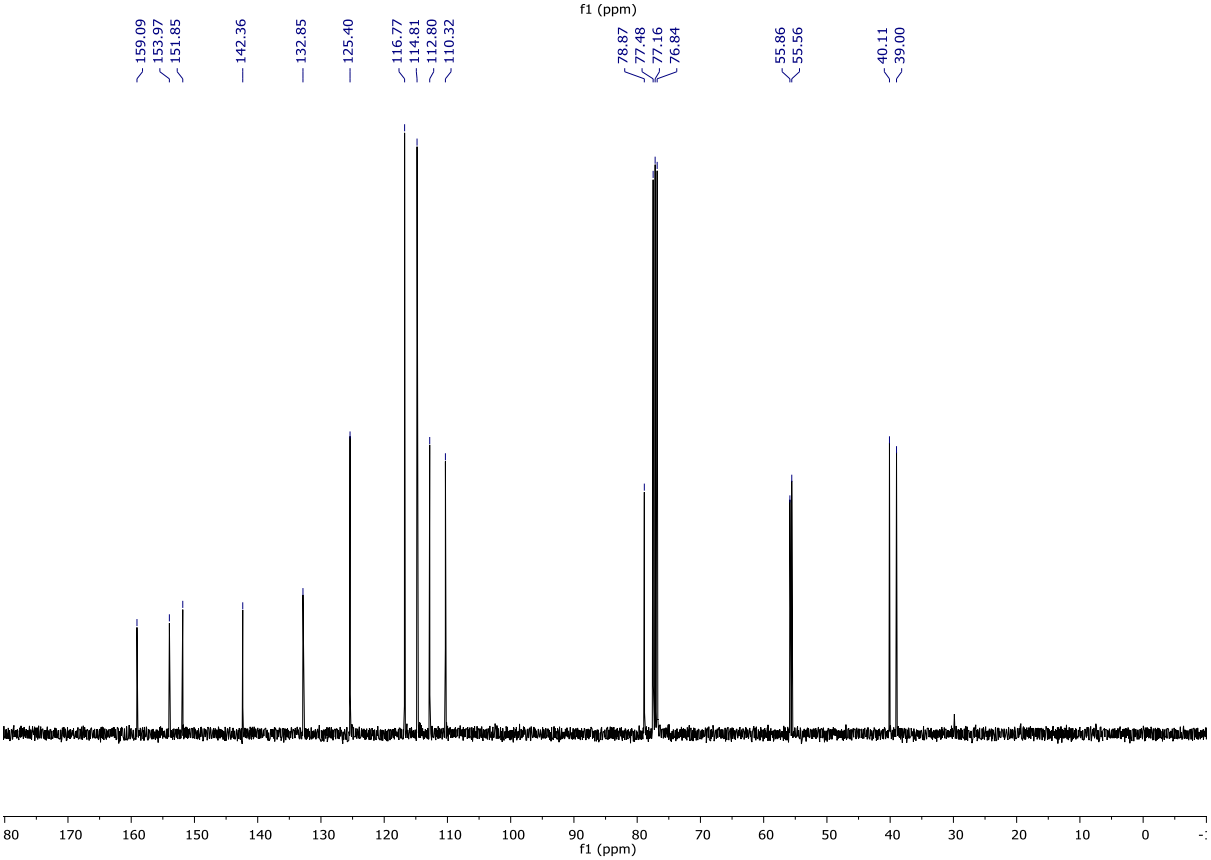
7.26
7.25
7.24
7.23
7.22
7.22
7.21
7.21
7.20
6.97
6.96
6.96
6.94
6.94
5.24
5.23
5.22
5.21
5.21
5.20
3.44
3.43
3.40
3.39
3.21
3.20
3.17
3.16
CN
O
5c
2.10
4.57
2.10
1.00
2.08
2.10
f1 (ppm)


161.23
140.27
134.16
127.11
124.90
119.37
116.17
104.00
78.31
77.48
77.16
76.85
39.77
f1 (ppm)


7.26
7.14
7.12
6.87
6.85
6.82
6.80
6.80
6.76
6.75
6.74
6.73
5.11
5.10
5.09
5.08
5.07
5.07
3.79
3.78
3.34
3.32
3.30
3.28
3.26
3.24
3.16
3.15
3.12
3.11
3.10
3.07
3.06
1.00
6.03
1.03
6.17
2.13
2.14
f1 (ppm)

OCH3
O
H3CO

5d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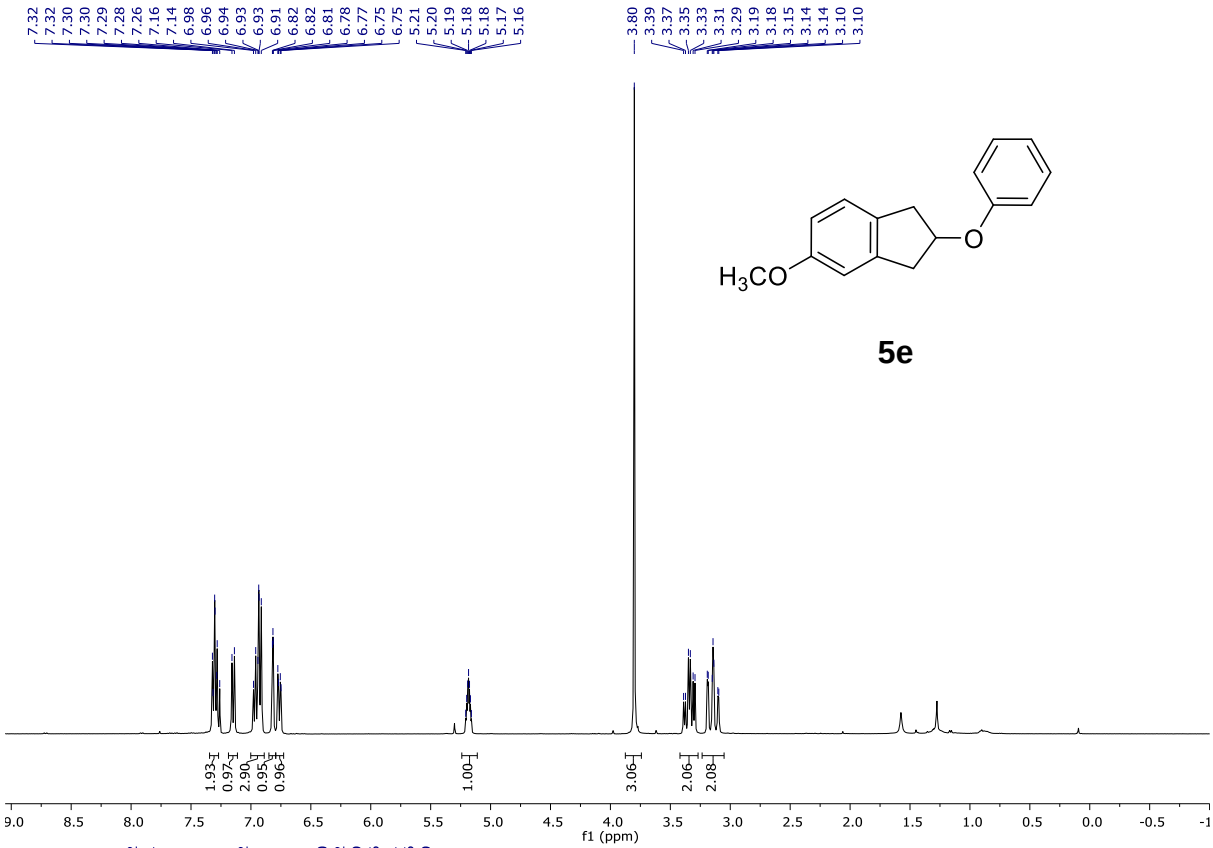
153.97
151.85
142.36
132.85
125.40
116.77
114.81
112.80
110.32
78.87
77.48
77.16
76.84
55.86
55.56
40.11
39.00
f1 (ppm)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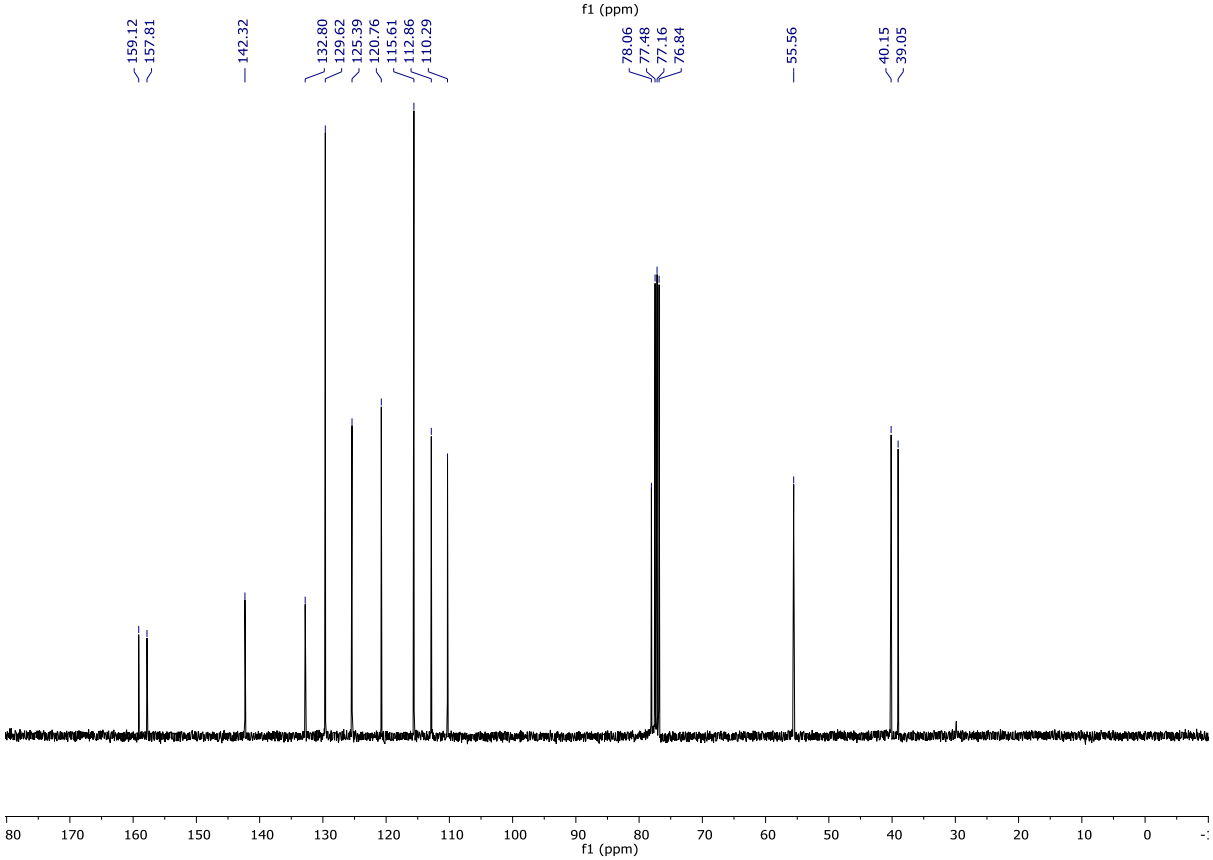
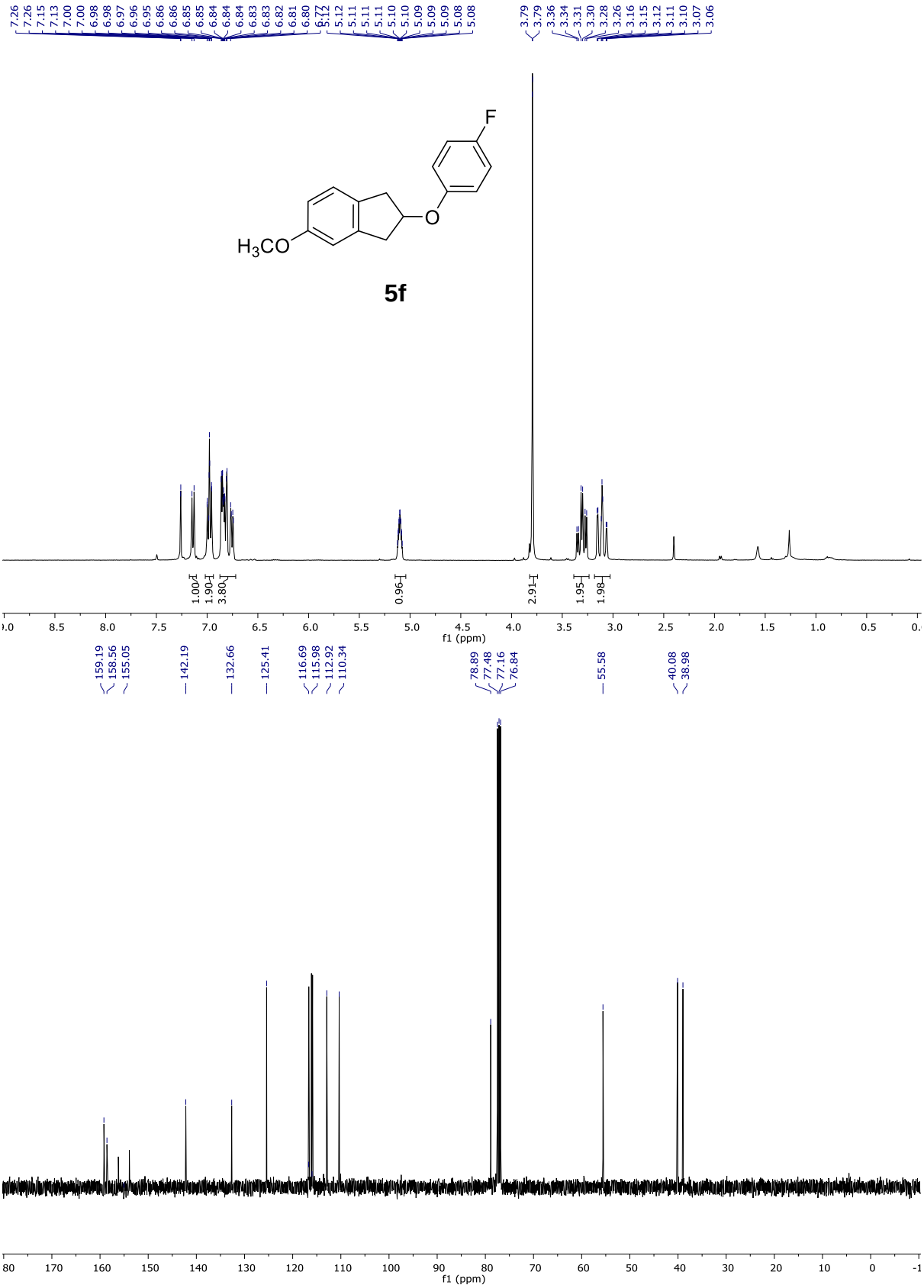
7.32
7.30
7.30
7.29
7.28
7.26
7.16
7.14
6.98
6.96
6.94
6.93
6.93
6.91
6.82
6.82
6.81
6.78
6.77
6.75
6.75
5.21
5.20
5.19
5.18
5.18
5.17
5.16
3.80
3.39
3.37
3.35
3.33
3.31
3.29
3.19
3.18
3.15
3.14
3.14
3.10
3.10
H3CO
O
1.93
0.97
2.90
0.95
0.96
1.00
3.06
2.06
2.08
f1 (ppm)

5e


159.12
157.81
142.32
132.80
129.62
125.39
120.76
115.61
112.86
110.29
78.06
77.48
77.16
76.84
55.56
40.15
39.05
f1 (ppm)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7.26
7.15
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7.00
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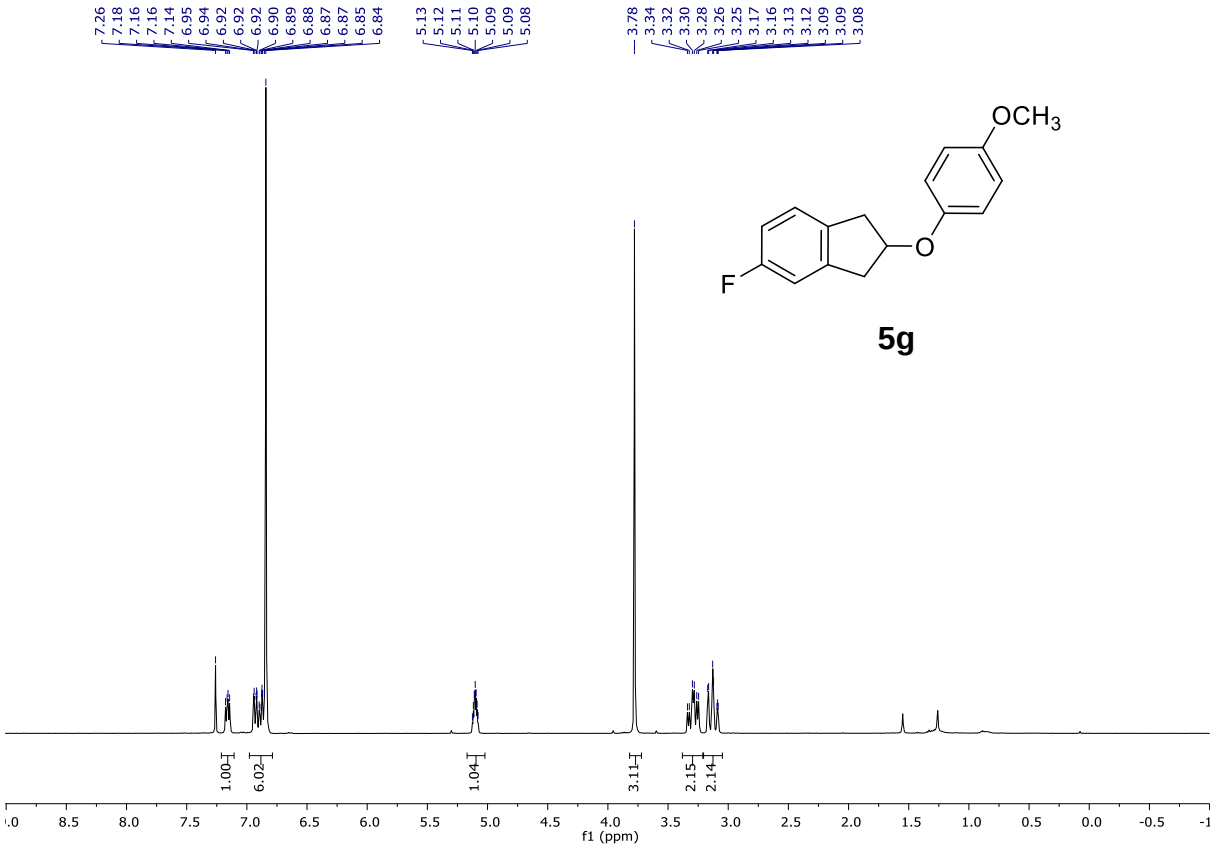
6.98
6.97
6.96
6.95
6.86
6.86
6.85
6.84
6.84
6.84
6.83
6.83
6.82
6.81
6.80
5.12
5.12
5.11
5.11
5.11
5.10
5.10
5.09
5.09
5.09
5.08
5.08
3.79
3.79
3.36
3.34
3.31
3.30
3.28
3.26
3.16
3.15
3.12
3.11
3.10
3.07
3.06
F
O
H3CO
5f
1.00
1.90
3.80
0.96
2.91
1.95
1.98
f1 (ppm)
159.19
158.56
155.05
142.19
132.66
125.41
116.69
115.98
112.92
110.34
78.89
77.48
77.16
76.84
55.58
40.08
38.98
f1 (ppm)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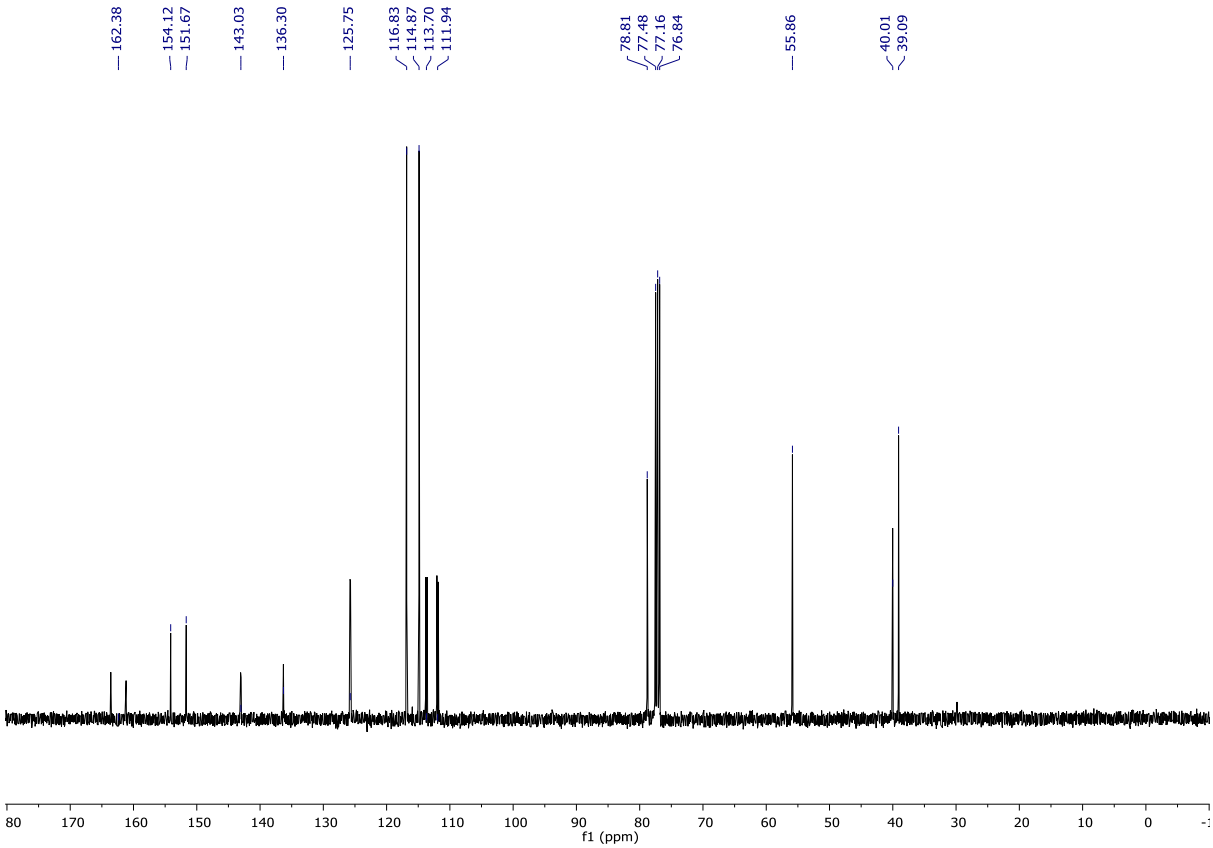
7.18
7.16
7.16
7.14
6.95
6.94
6.92
6.92
6.92
6.90
6.89
6.88
6.87
6.87
6.85
6.84
5.13
5.12
5.11
5.10
5.09
5.09
5.08
3.78
3.34
3.32
3.30
3.28
3.26
3.25
3.17
3.16
3.13
3.12
3.09
3.09
3.08
OCH3
O
F
1.00
6.02
1.04
3.11
2.15
2.14
f1 (ppm)

5g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125.75
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114.87
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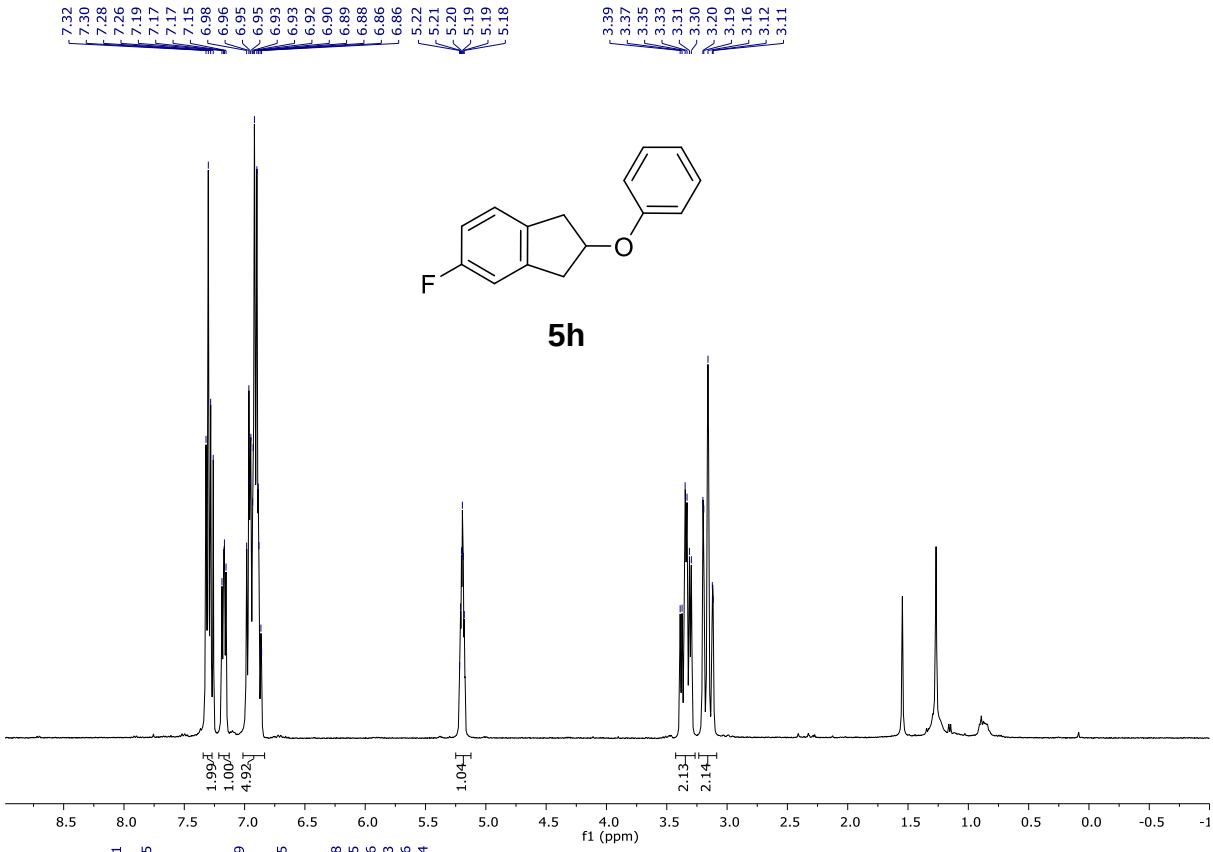
111.94
78.81
77.48
77.16
76.84
55.86
40.01
39.09
f1 (ppm)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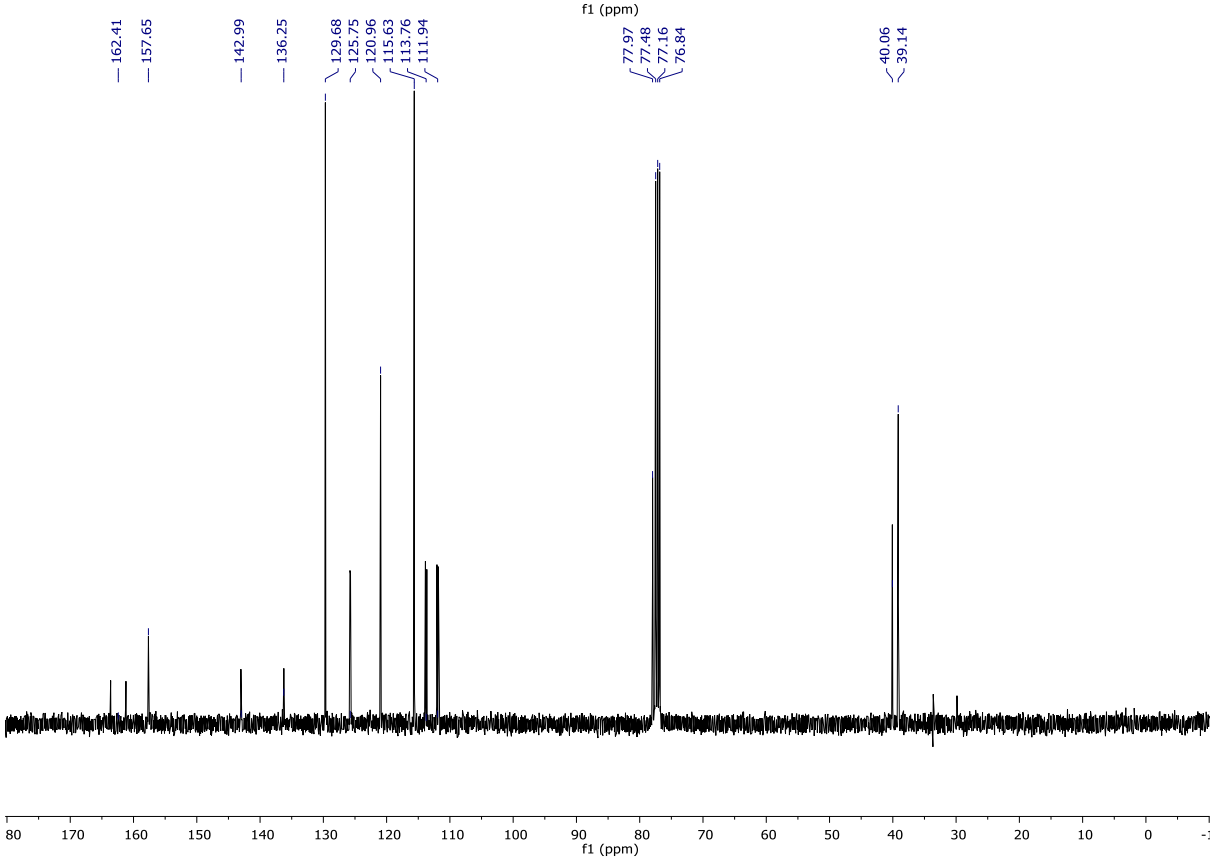
7.17
7.17
7.15
6.98
6.96
6.95
6.95
6.93
6.93
6.92
6.90
6.89
6.88
6.86
6.86
5.22
5.21
5.20
5.19
5.19
5.18
3.39
3.37
3.35
3.33
3.31
3.30
3.20
3.19
3.16
3.12
3.11
F
O
1.99
1.00
4.92
1.04
2.13
2.14
f1 (ppm)

5h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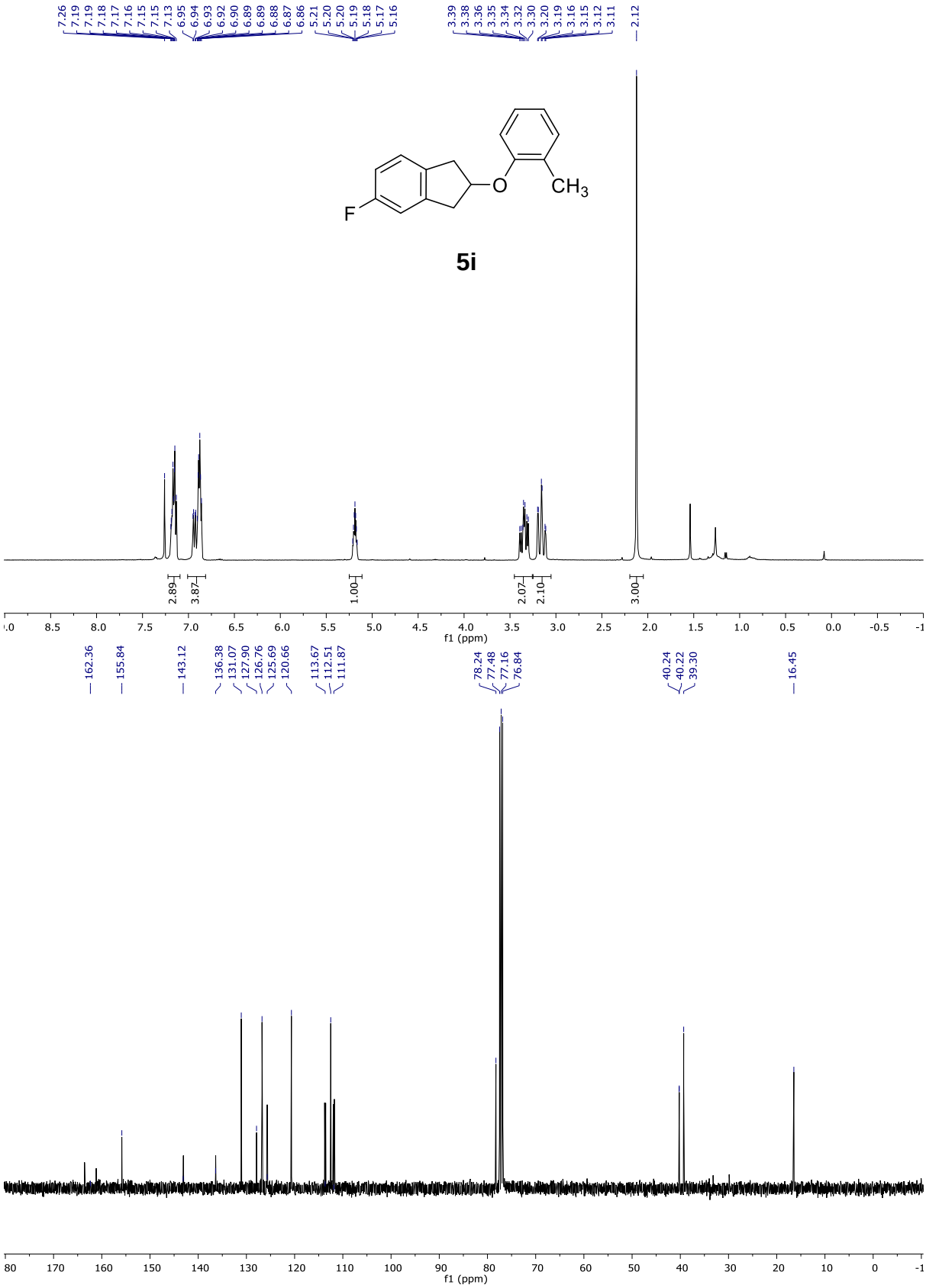
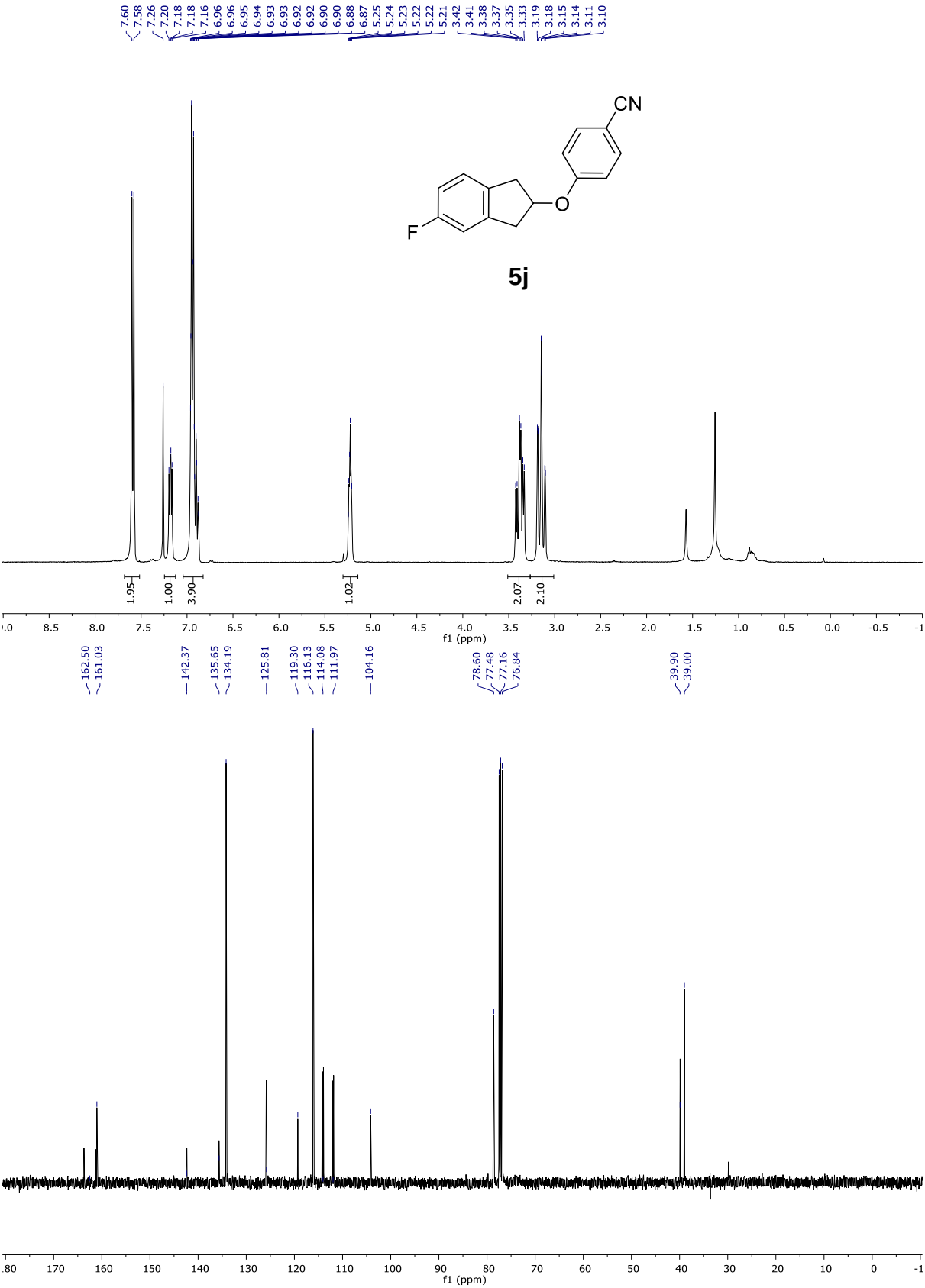
120.96
115.63
113.76
111.94
77.97
77.48
77.16
76.84
40.06
39.14
f1 (ppm)


7.26
7.19
7.19
7.18
7.17
7.16
7.15
7.15
7.13
6.95
6.94
6.93
6.92
6.90
6.89
6.89
6.88
6.87
6.86
5.21
5.20
5.20
5.19
5.18
5.17
5.16
3.39
3.38
3.36
3.35
3.34
3.32
3.30
3.20
3.19
3.16
3.15
3.12
3.11
2.12
F
O
CH3
2.89
3.87
1.00
2.07
2.10
3.00
f1 (ppm)
162.36
155.84
143.12
136.38
131.07
127.90
126.76
125.69
120.66
113.67
112.51
111.87
78.24
77.48
77.16
76.84
40.24
40.22
39.30
16.45
f1 (ppm)

5i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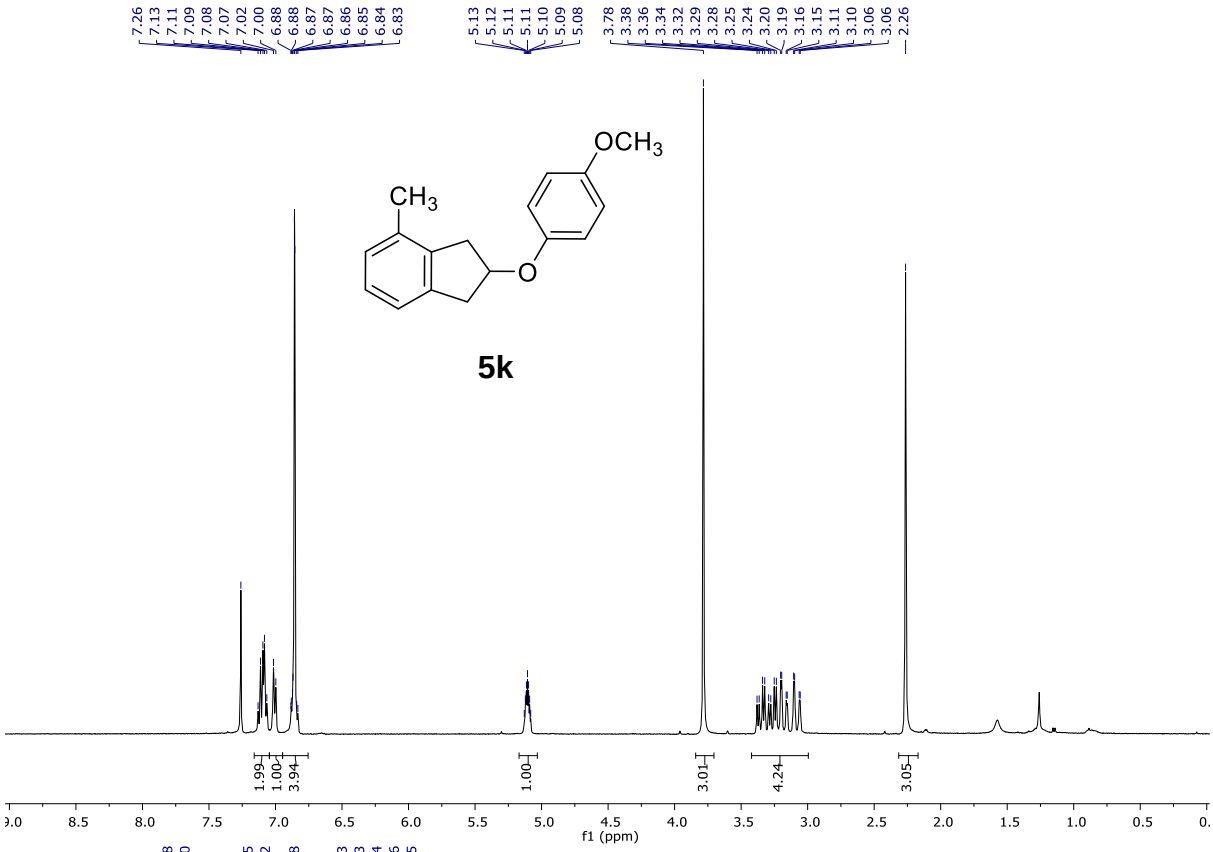
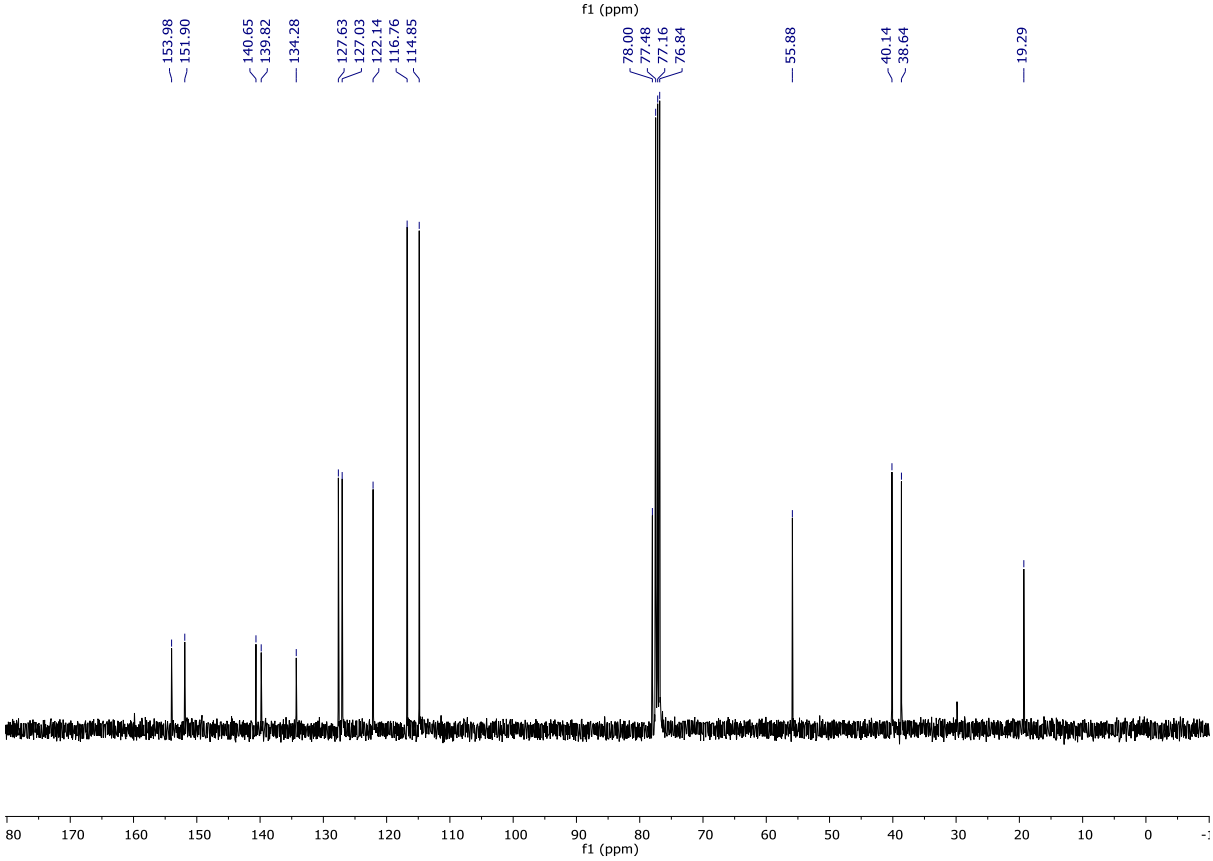
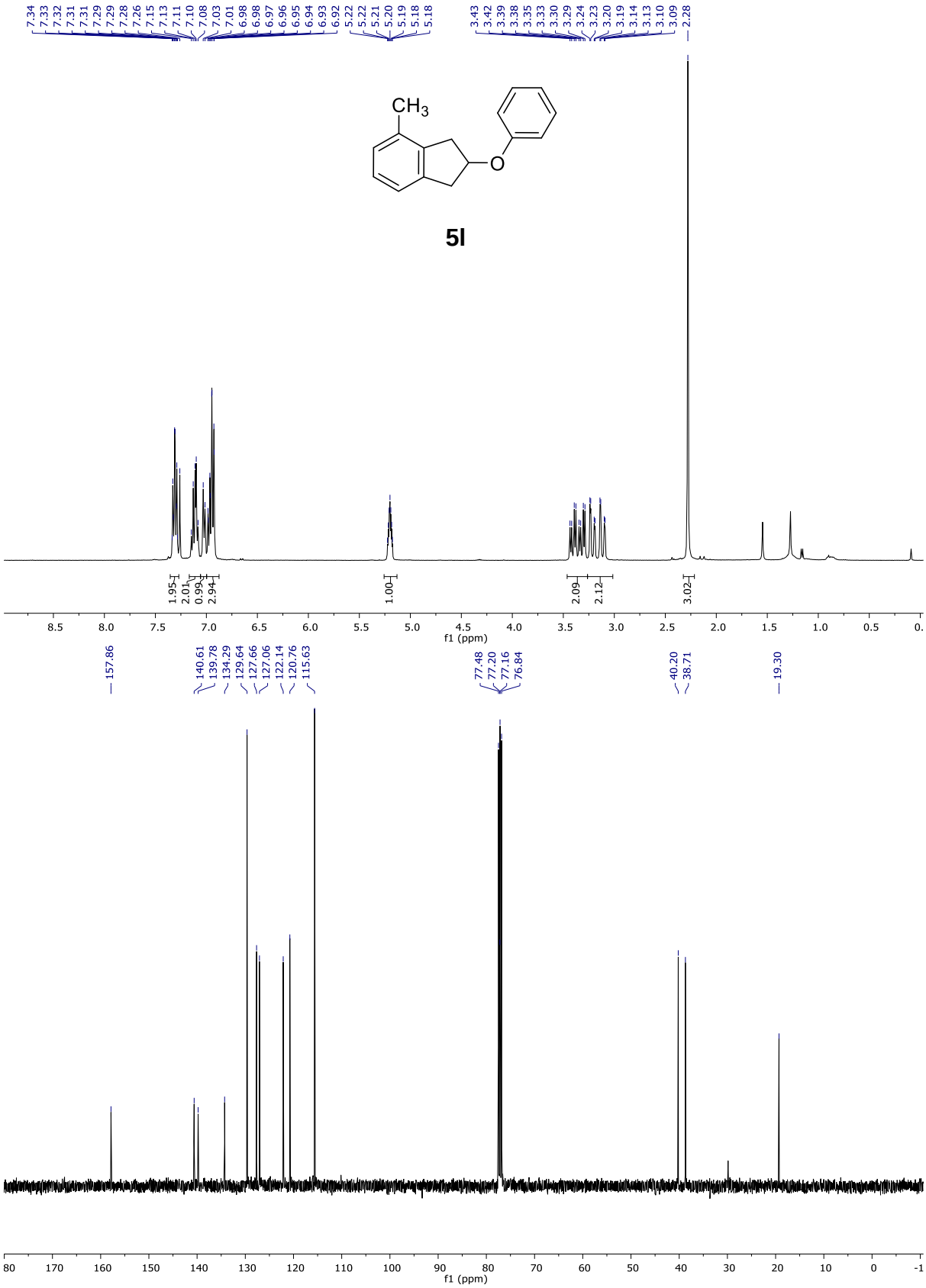
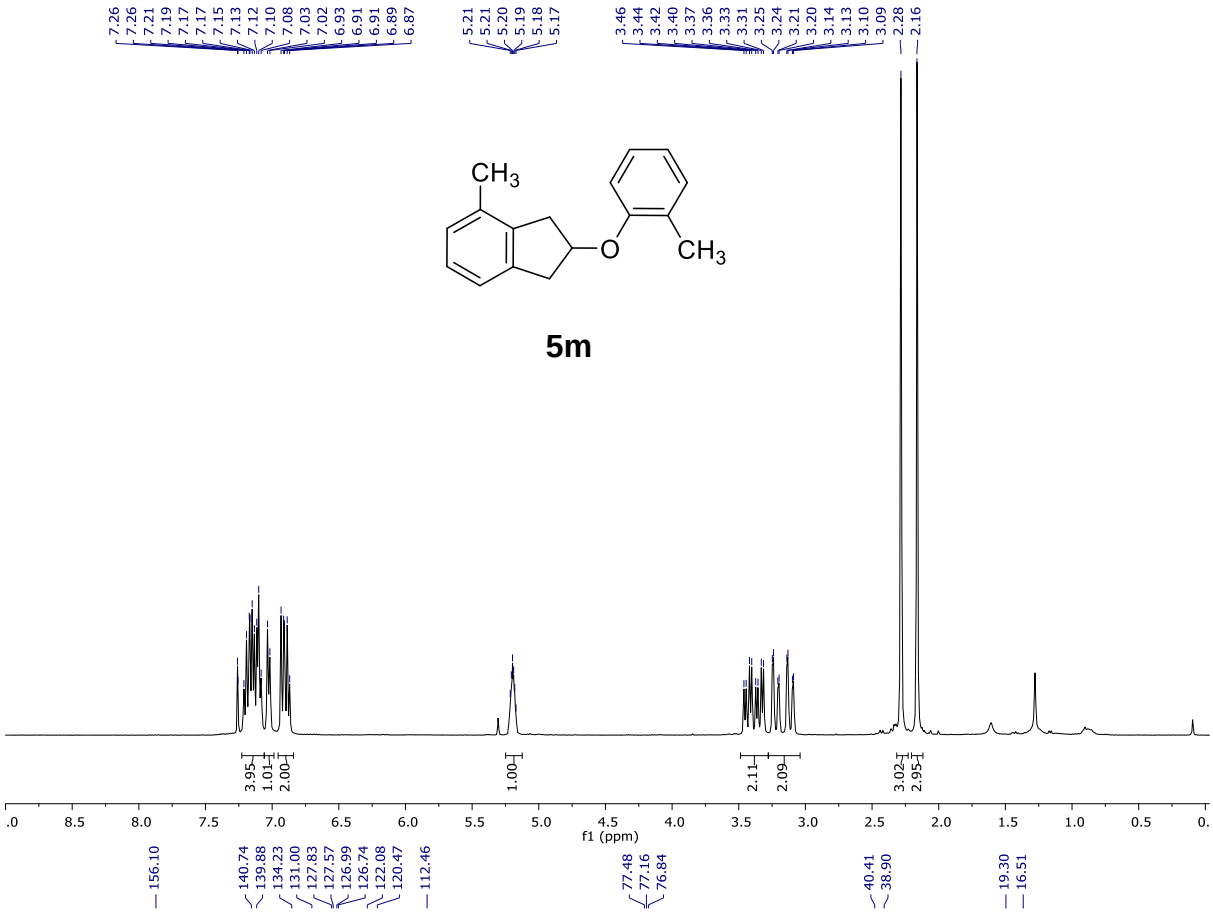
7.16
6.96
6.96
6.95
6.94
6.93
6.93
6.92
6.92
6.90
6.90
6.88
6.87
5.25
5.24
5.23
5.22
5.22
5.21
3.42
3.41
3.38
3.37
3.35
3.33
3.19
3.18
3.15
3.14
3.11
3.10
CN
O
F
5j
1.95
1.00
3.90
1.02
2.07
2.10
f1 (ppm)
162.50
161.03
142.37
135.65
134.19
125.81
119.30
116.13
114.08
111.97
104.16
78.60
77.48
77.16
76.84
39.90
39.00
f1 (ppm)

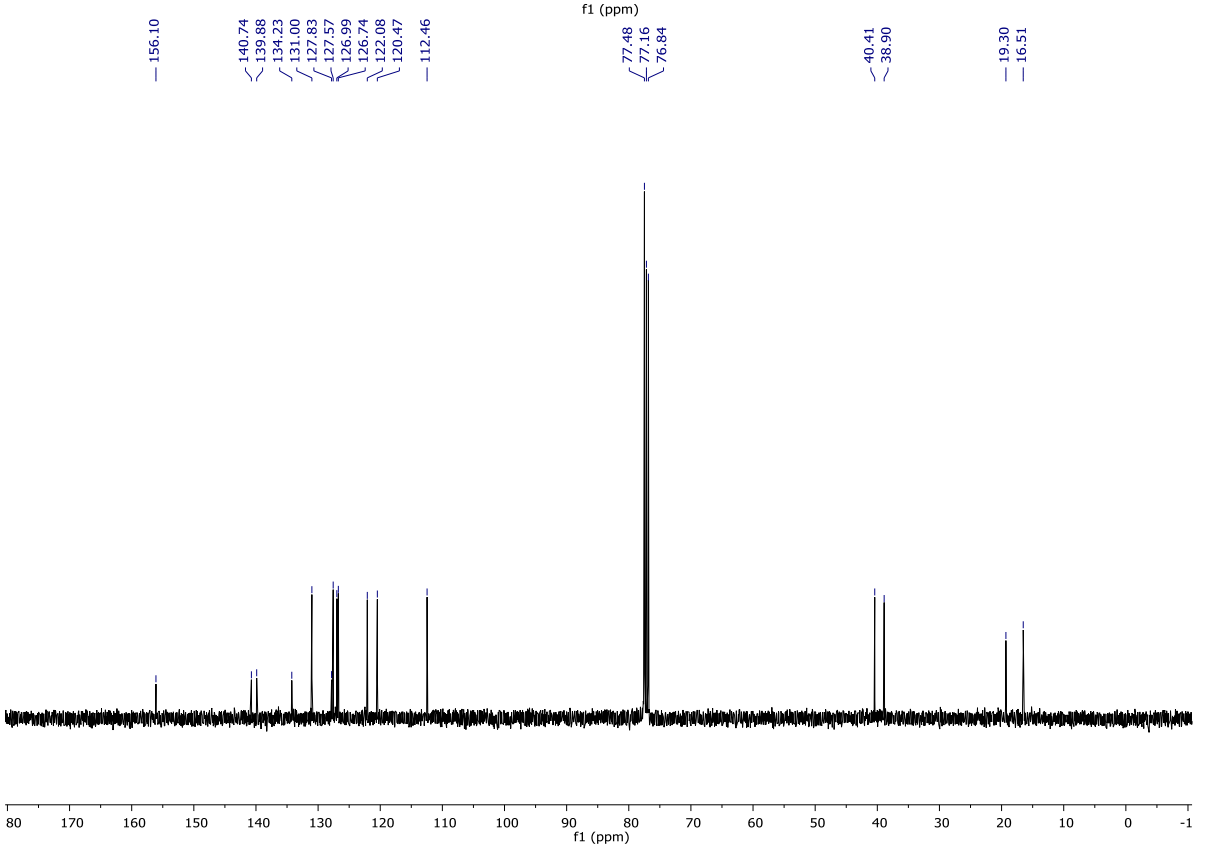

7.26
7.13
7.11
7.09
7.08
7.07
7.02
7.00
6.88
6.87
6.87
6.86
6.85
6.84
6.83
5.13
5.12
5.11
5.11
5.10
5.09
5.08
3.78
3.38
3.36
3.34
3.32
3.29
3.28
3.25
3.24
3.20
3.19
3.16
3.15
3.11
3.10
3.06
3.06
2.26
OCH3
CH3
O
1.99
1.00
3.94
1.00
3.01
4.24
3.05
f1 (ppm)

5k


153.98
151.90
140.65
139.82
134.28
127.63
127.03
122.14
116.76
114.85
78.00
77.48
77.16
76.84
55.88
40.14
38.64
19.29
f1 (ppm)


7.34 7.33 7.32 7.31 7.31 7.29 7.29 7.28 7.26 7.15 7.13 7.11 7.10 7.08 7.03 7.01 6.98 6.98 6.97 6.96 6.95 6.94 6.93 6.92 5.22 5.22 5.21 5.20 5.19 5.18 5.18 3.43 3.42 3.39 3.38 3.35 3.33 3.30 3.29 3.24 3.23 3.20 3.19 3.14 3.13 3.10 3.09 2.28
CH3
O
5l
1.95 2.01 0.99 2.94 1.00 2.09 2.12 3.02
f1 (ppm)
157.86 140.61 139.78 134.29 129.64 127.66 127.06 122.14 120.76 115.63 77.48 77.20 77.16 76.84 40.20 38.71 19.30
f1 (ppm)


7.26
7.26
7.21
7.19
7.17
7.17
7.15
7.13
7.12
7.10
7.08
7.03
7.02
6.93
6.91
6.89
6.87
5.21
5.21
5.20
5.19
5.18
5.17
3.46
3.44
3.42
3.40
3.37
3.36
3.33
3.31
3.25
3.24
3.21
3.20
3.14
3.13
3.10
3.09
2.28
2.16
CH3
O
CH3
5m
3.95
1.01
2.00
1.00
2.11
2.09
3.02
2.95
f1 (ppm)


156.10
140.74
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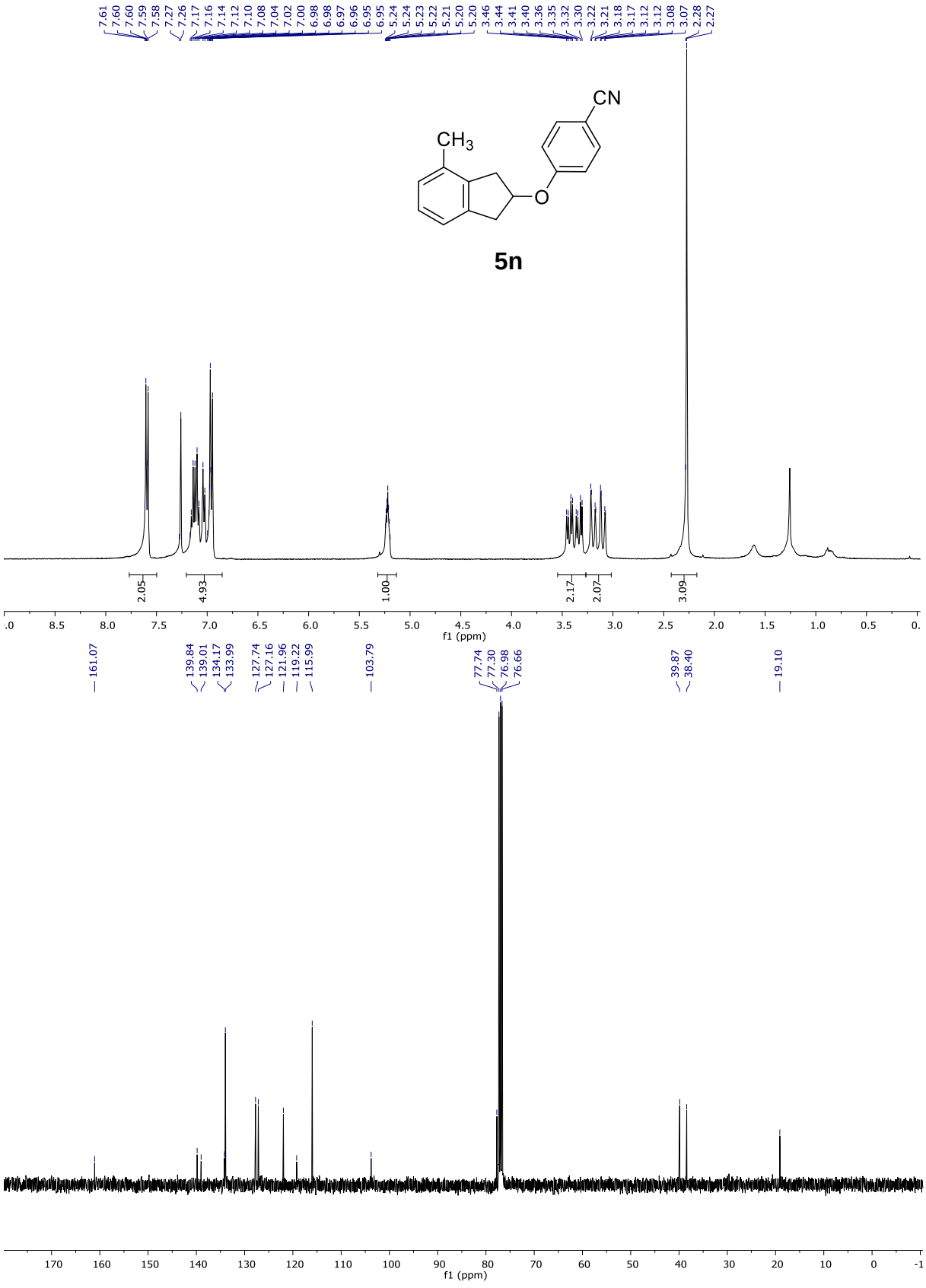
134.23
131.00
127.83
127.57
126.99
126.74
122.08
120.47
112.46
77.48
77.16
76.84
40.41
38.90
19.30
16.51
f1 (ppm)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7.14
7.12
7.10
7.08
7.04
7.02
7.00
6.98
6.97
6.96
6.95
6.95
5.24
5.24
5.23
5.22
5.21
5.20
5.20
3.46
3.44
3.41
3.40
3.36
3.35
3.32
3.30
3.22
3.21
3.18
3.17
3.12
3.12
3.08
3.07
2.28
2.27
CN
CH3
O
5n
2.05
4.93
1.00
2.17
2.07
3.09
f1 (ppm)
161.07
139.84
139.01
134.17
133.99
127.74
127.16
121.96
119.22
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103.79
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77.30
76.98
76.66
39.87
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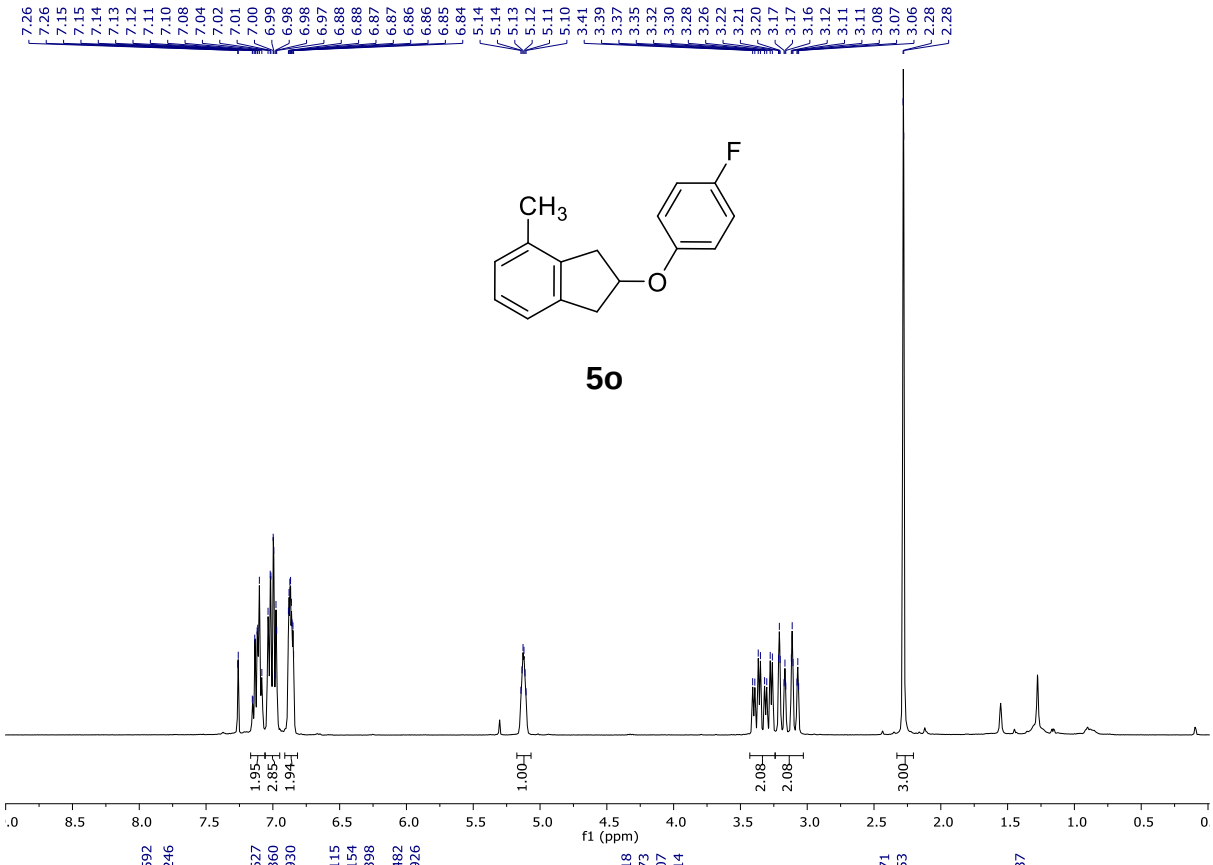
19.10
f1 (ppm)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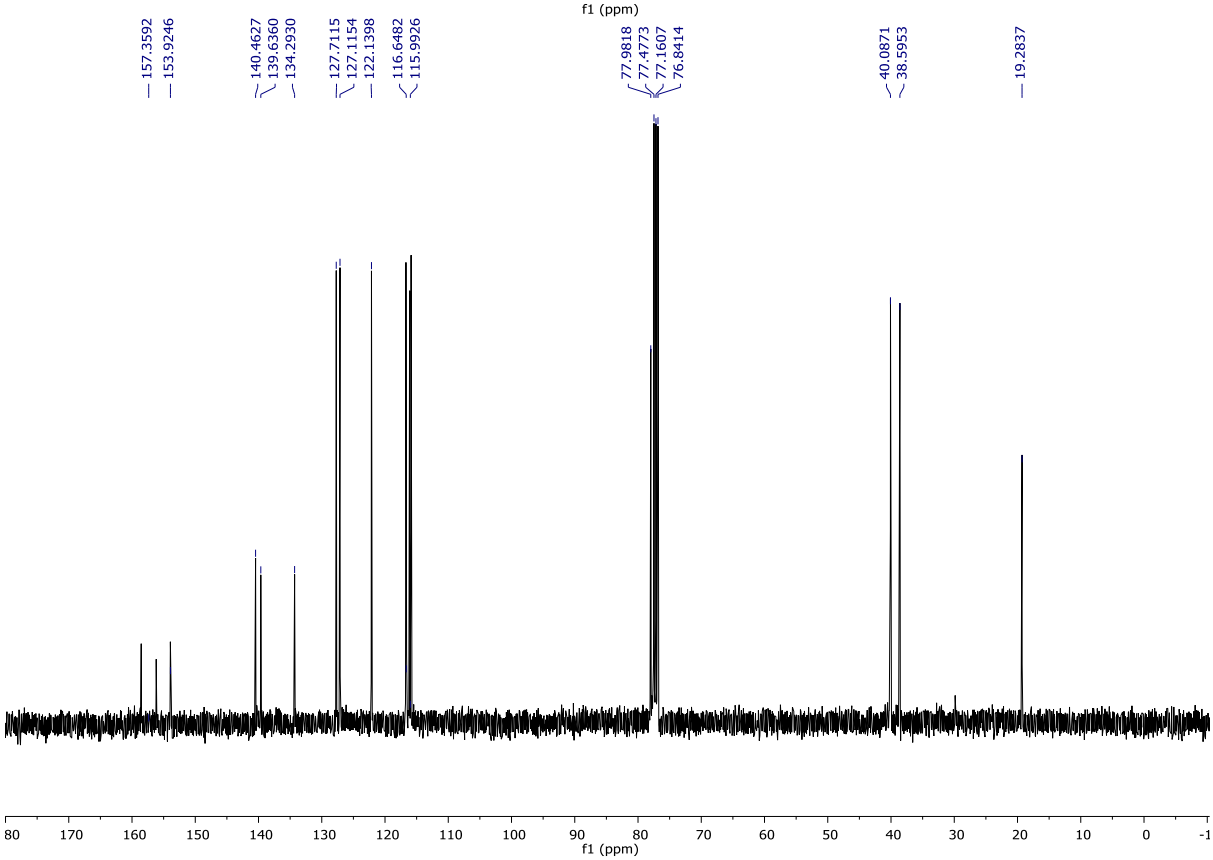
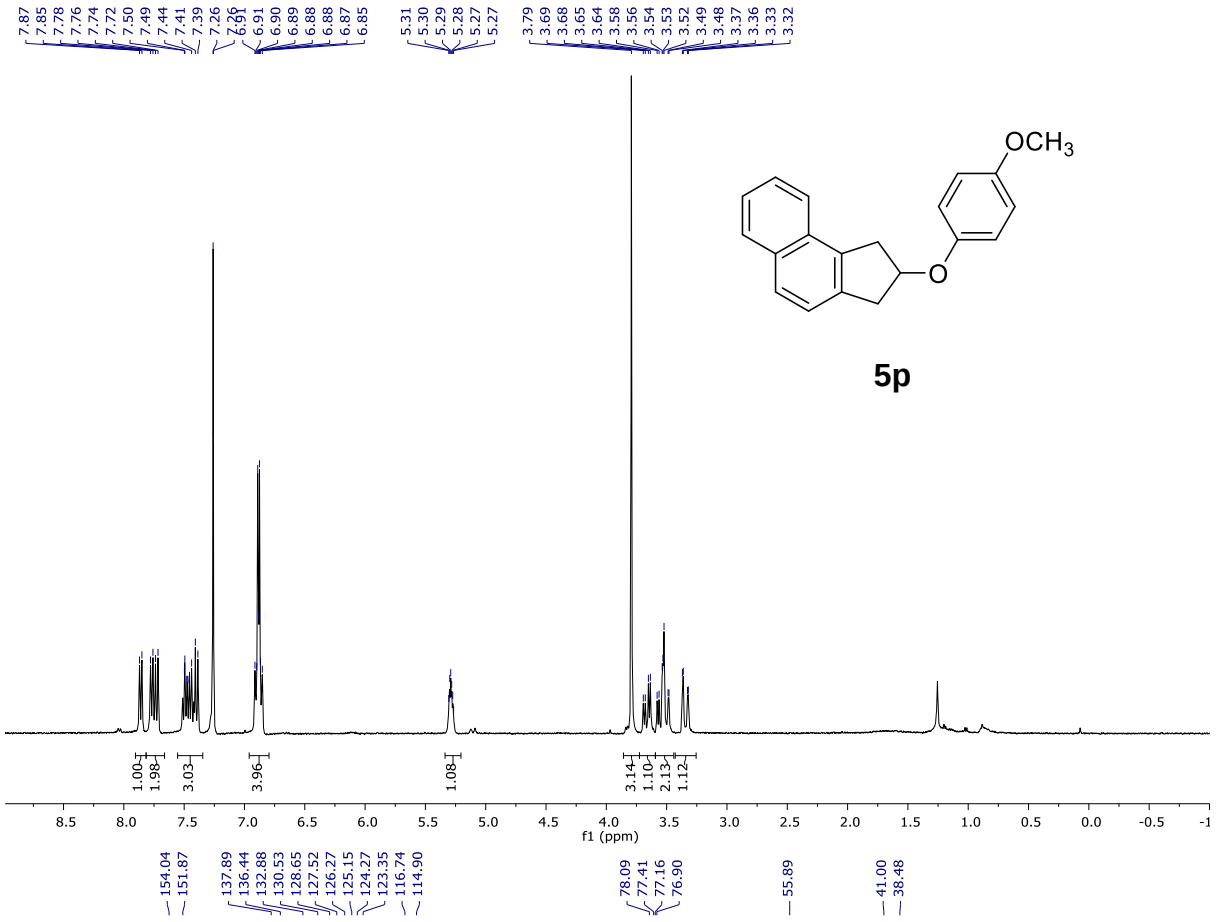
F
CH3
O
1.95 2.85 1.94 1.00 2.08 2.08 3.00
f1 (ppm)

5o


157.3592 153.9246 140.4627 139.6360 134.2930 127.7115 127.1154 122.1398 116.6482 115.9926 77.9818 77.4773 77.1607 76.8414 40.0871 38.5953 19.2837
f1 (ppm)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7.49
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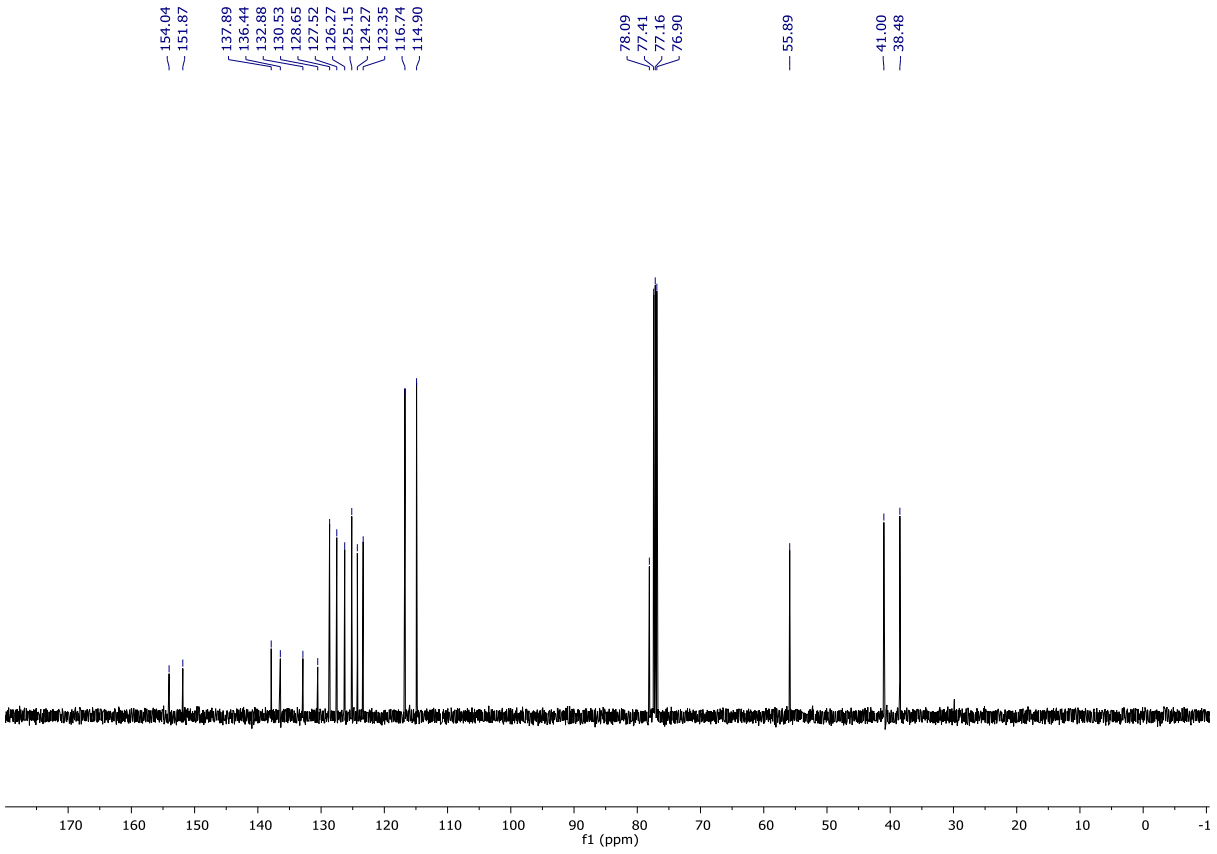
7.41
7.39
7.26
6.91
6.90
6.89
6.88
6.88
6.87
6.85
5.31
5.30
5.29
5.28
5.27
5.27
3.79
3.69
3.68
3.65
3.64
3.58
3.56
3.54
3.53
3.52
3.49
3.48
3.37
3.36
3.33
3.32
OCH3
O
1.00
1.98
3.03
3.96
1.08
3.14
1.10
2.13
1.12
f1 (ppm)

5p


154.04
151.87
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136.44
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127.52
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55.89
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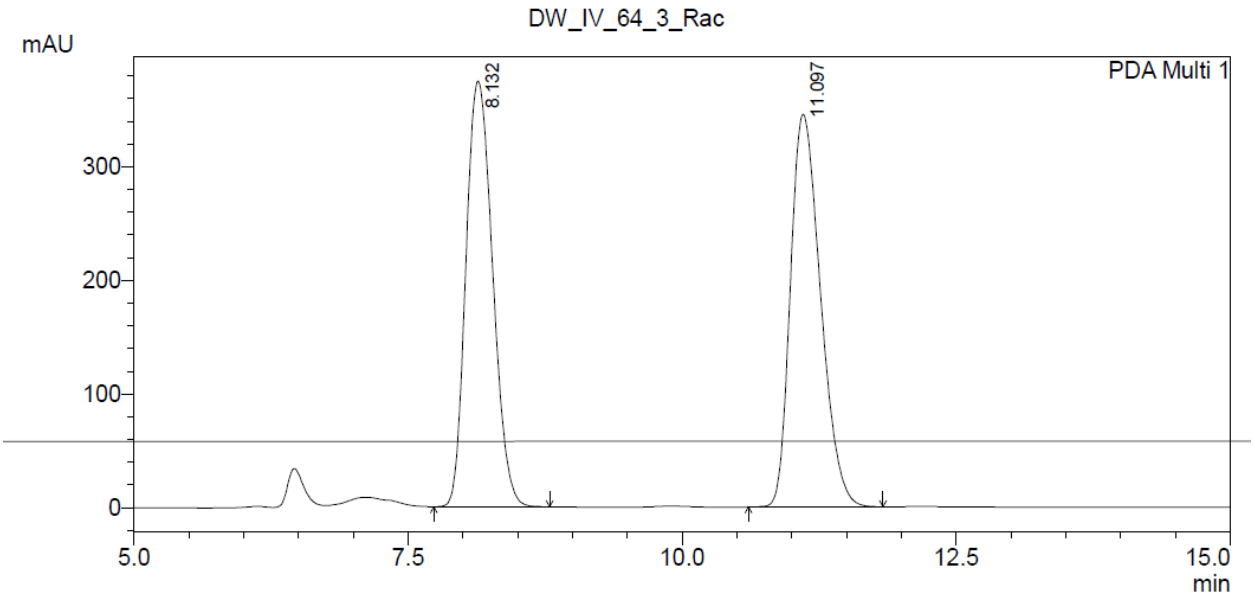
38.48
f1 (ppm)

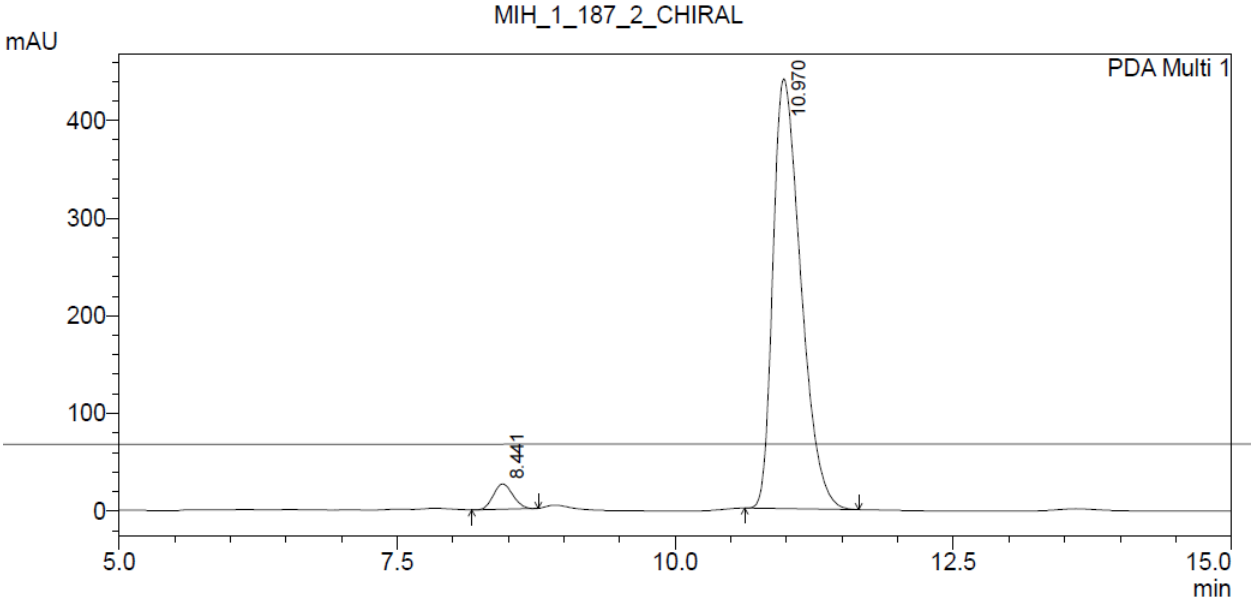


1 PDA Multi 1/285nm 4nm

PeakTable

PDA Ch1 285nm 4nm

Peak#	Ret. Time	Area	Height	Area %	Height %
1	8.132	6341010	374538	49.038	52.017
2	11.097	6589739	345496	50.962	47.983
Total		12930749	720034	100.000	100.000



1 PDA Multi 1/285nm 4nm

PeakTable

PDA Ch1 285nm 4nm

Peak#	Ret. Time	Area	Height	Area %	Height %
1	8.441	316553	25953	3.961	5.566
2	10.970	7675190	440299	96.039	94.434
Total		7991743	466252	100.000	100.000


7.88
7.86
7.78
7.76
7.75
7.73
7.52
7.52
7.51
7.50
7.49
7.48
7.47
7.46
7.45
7.43
7.41
7.39
7.26
7.03
7.02
7.00
6.99
6.98
6.92
6.91
6.89
6.89
6.88
6.88
6.87
5.32
5.31
5.31
5.30
5.29
5.28
5.28
3.71
3.69
3.67
3.65
3.60
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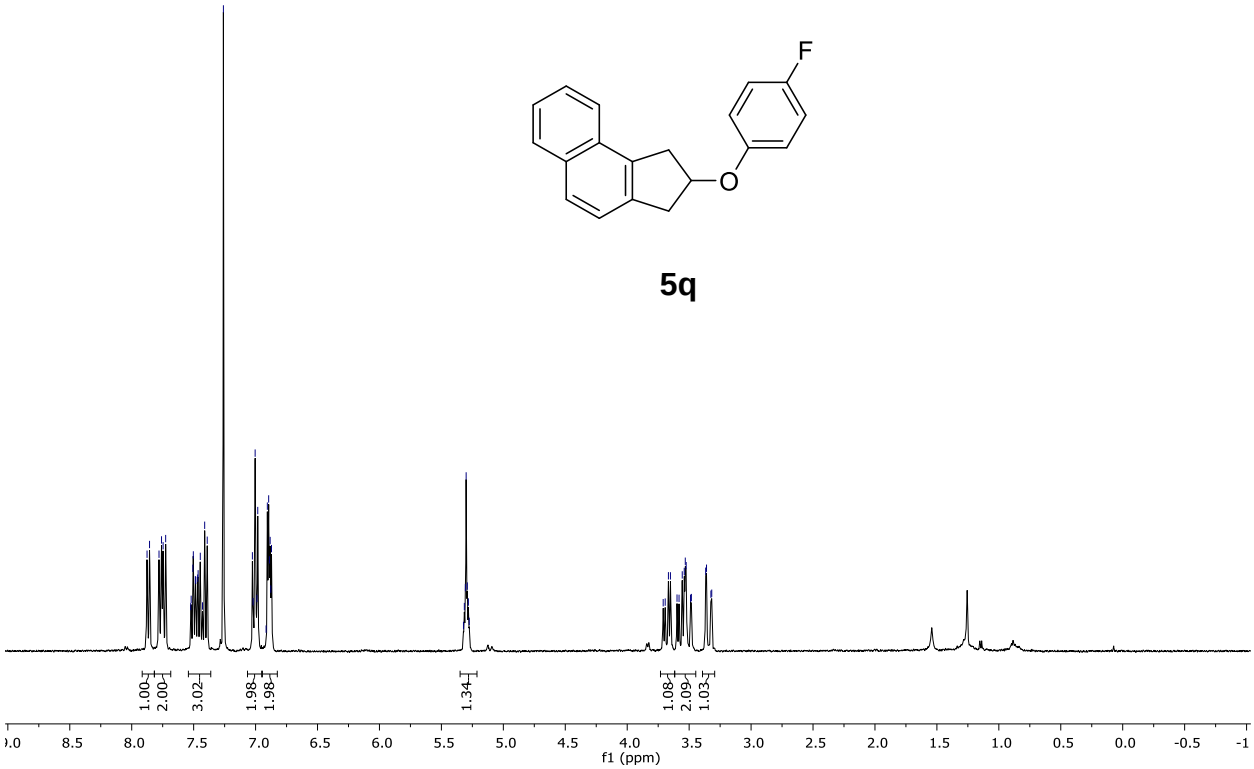
3.52
3.49
3.48
3.37
3.36
3.32
3.32


F
O
1.00
2.00
3.02
1.98
1.98
1.34
1.08
2.09
1.03
f1 (ppm)

5q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156.1979
153.8513
137.7163
136.2688
132.8745
130.4636
128.6708
127.6142
126.3335
125.2223
124.2172
123.2779
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116.1595
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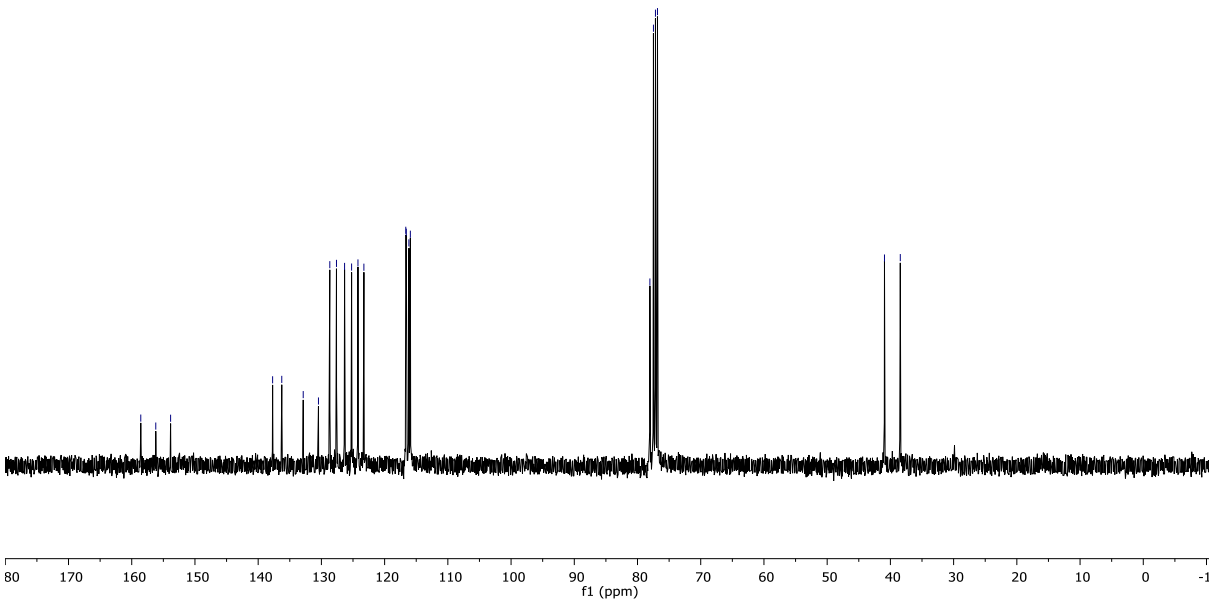
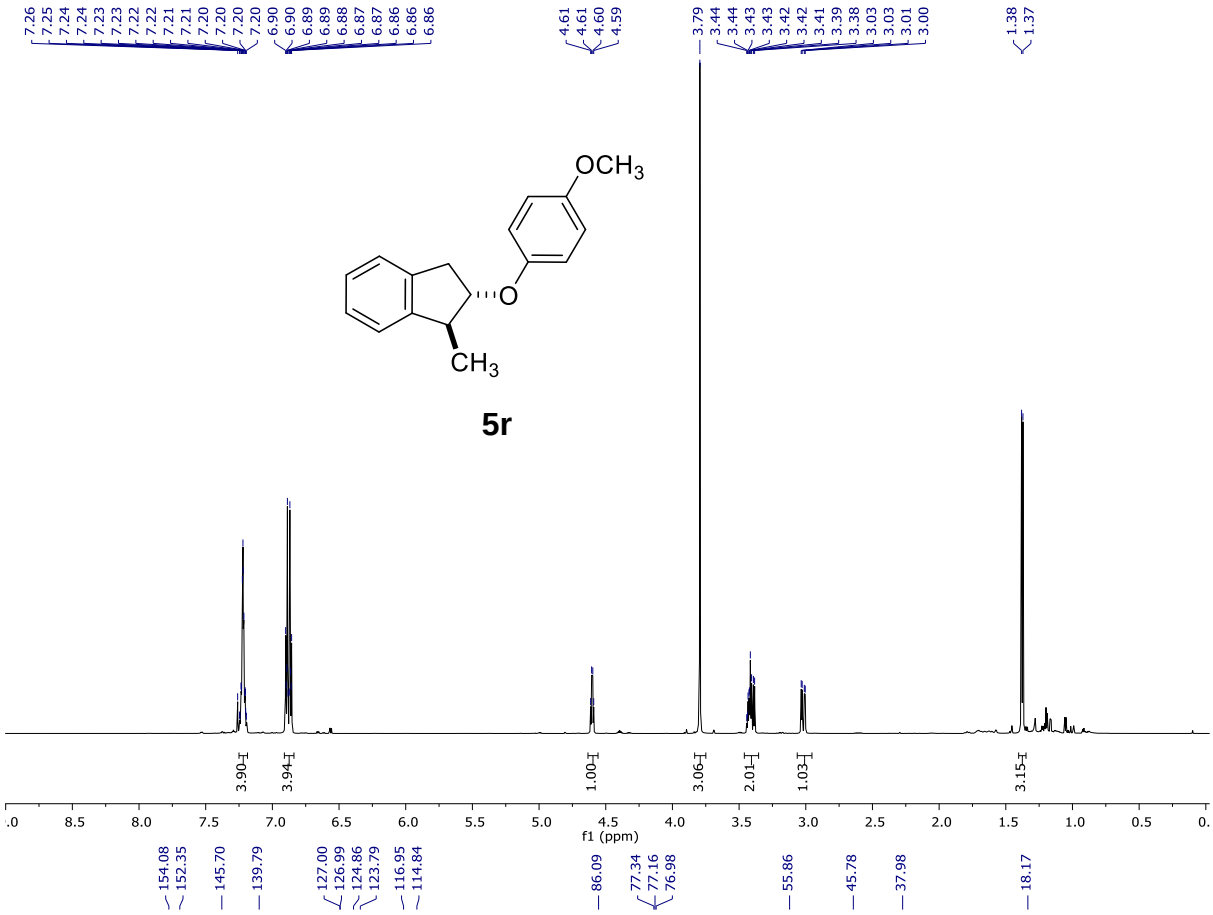
77.1598
76.8420
40.9364
38.4345


f1 (ppm)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7.20
7.20
7.20
7.20
6.90
6.90
6.89
6.89
6.88
6.87
6.87
6.86
6.86
6.86
6.86
4.61
4.61
4.60
4.59
3.79
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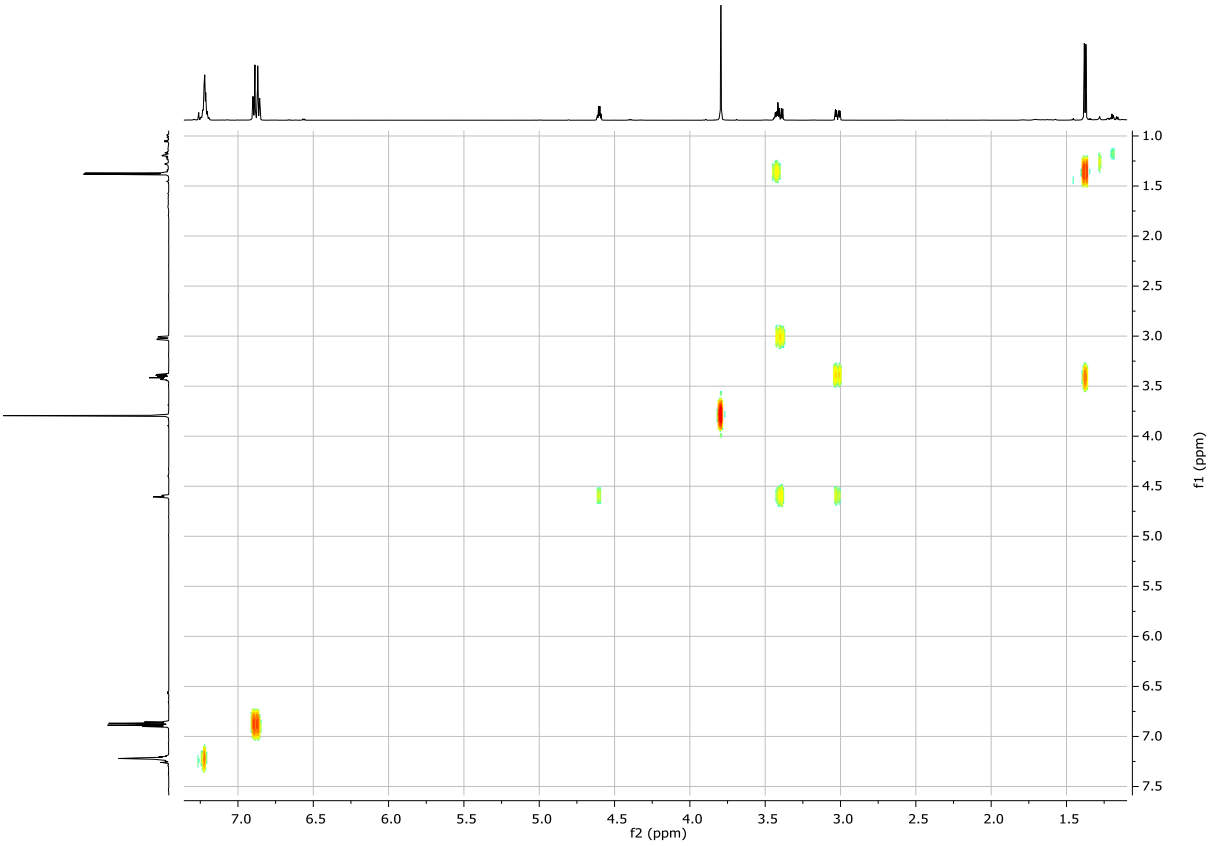
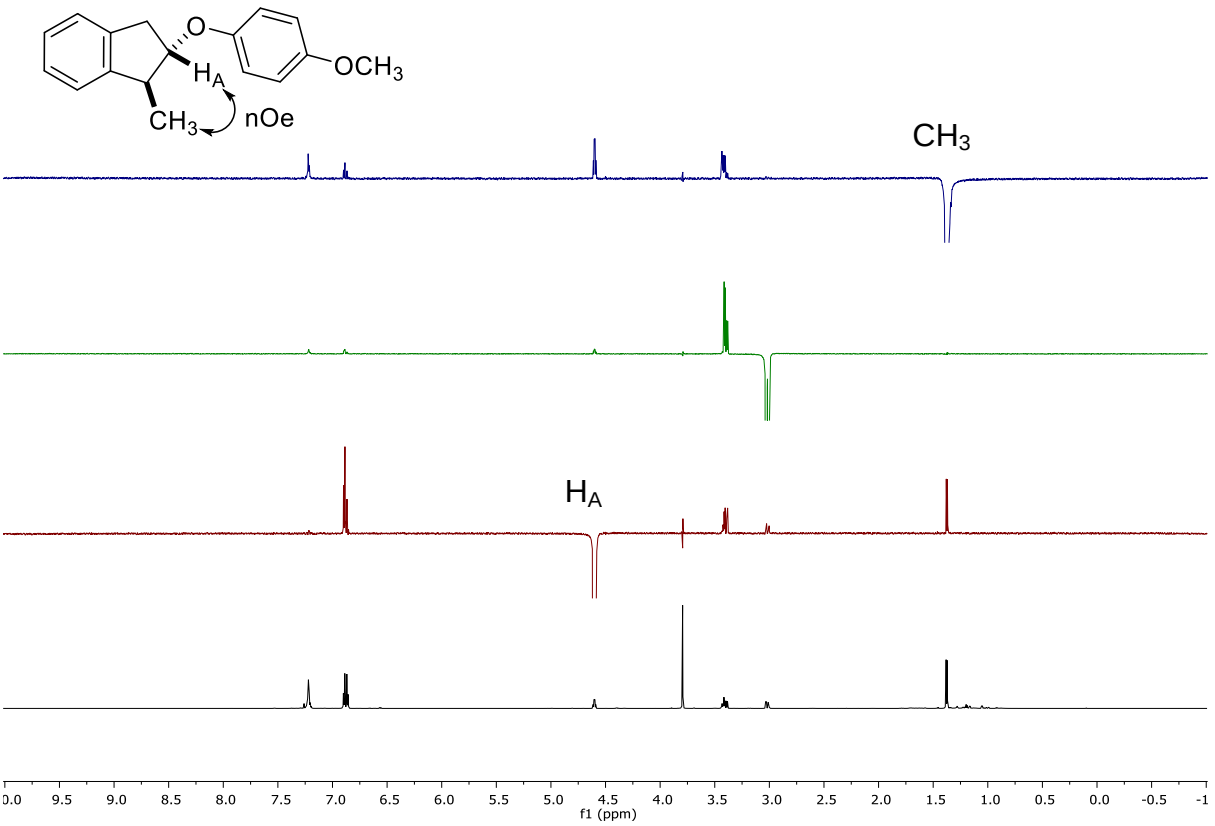
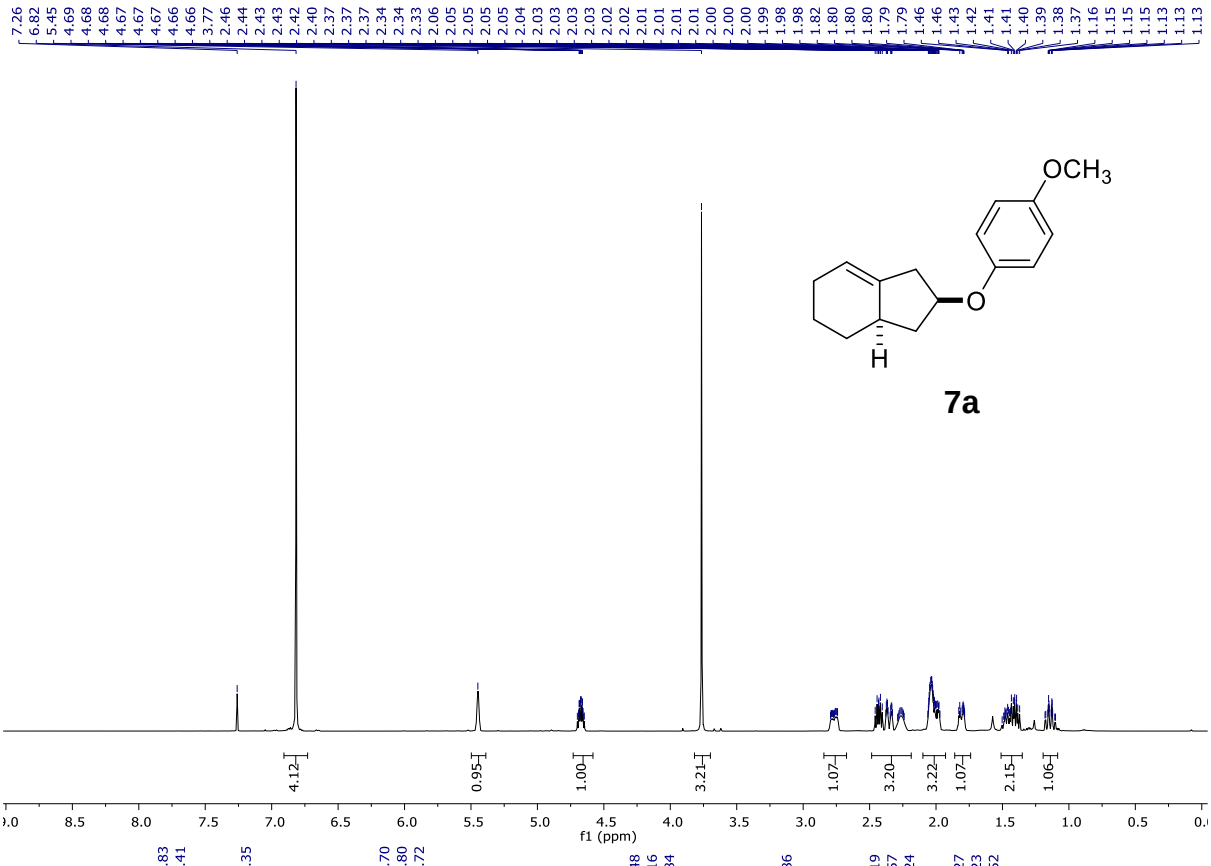
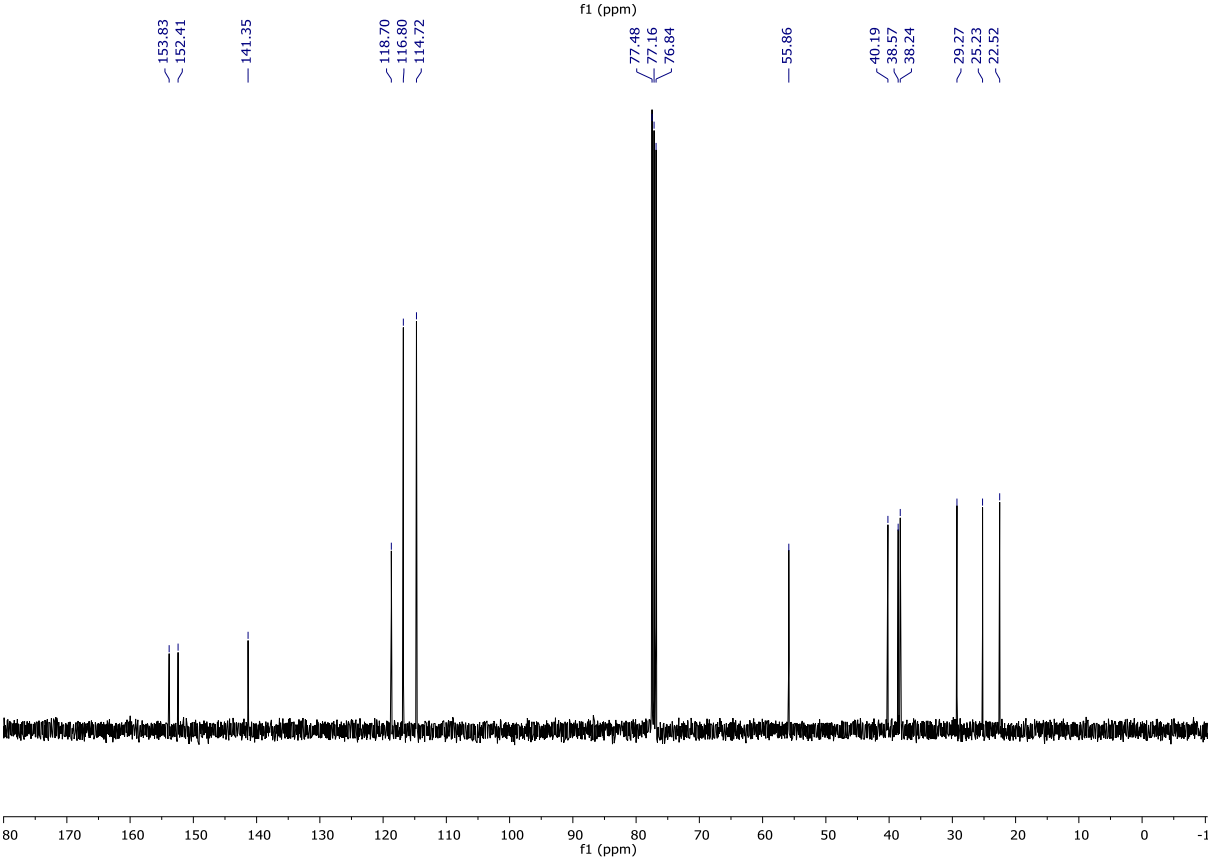
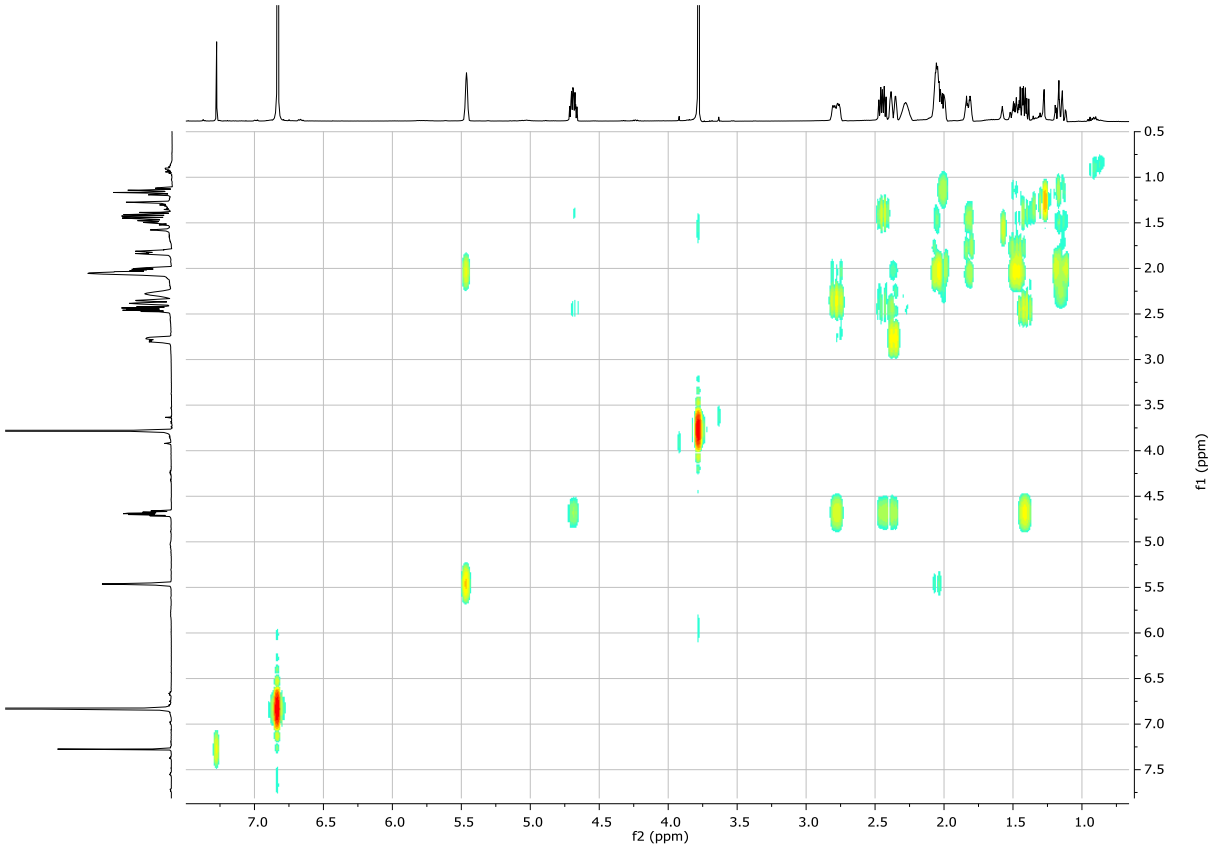
3.44
3.43
3.43
3.42
3.42
3.41
3.39
3.38
3.03
3.03
3.01
3.00
1.38
1.37
OCH3
O
CH3
5r
3.90
3.94
1.00
3.06
2.01
1.03
3.15
f1 (ppm)
154.08
152.35
145.70
139.79
127.00
126.99
124.86
123.79
116.95
114.84
86.09
77.34
77.16
76.98
55.86
45.78
37.98
18.17
f1 (ppm)

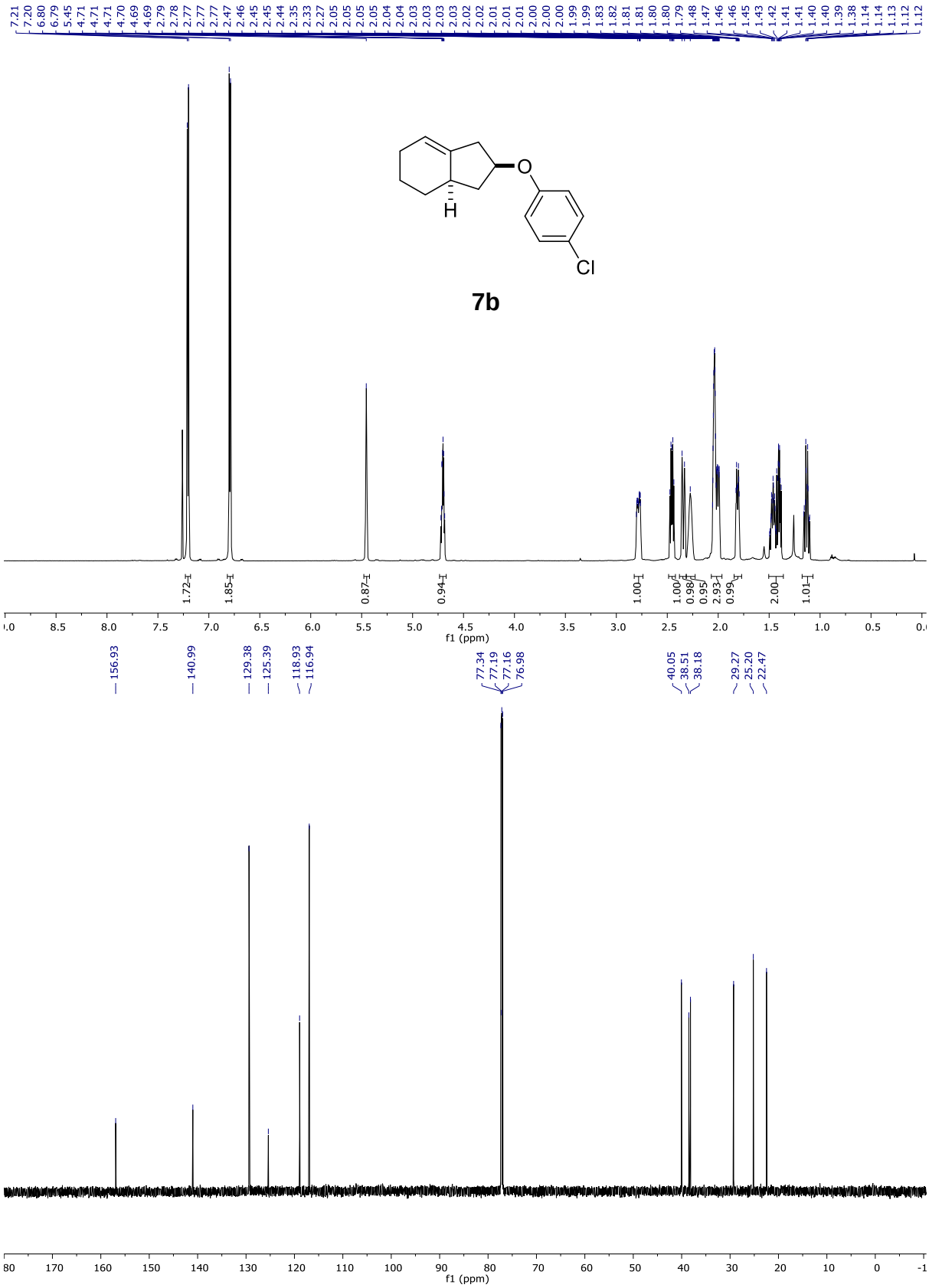

f2 (ppm)
f1 (ppm)


O
H_A
OCH_3
CH_3
nOe
CH_3
H_A
f1 (ppm)


7.26 6.82 5.45 4.69 4.68 4.68 4.67 4.67 4.67 4.67 4.66 4.66 3.77 2.46 2.44 2.43 2.43 2.42 2.40 2.37 2.37 2.37 2.34 2.34 2.33 2.06 2.05 2.05 2.05 2.05 2.04 2.03 2.03 2.03 2.03 2.02 2.02 2.01 2.01 2.01 2.01 2.00 2.00 2.00 2.00 1.99 1.98 1.98 1.82 1.80 1.80 1.80 1.79 1.79 1.46 1.46 1.43 1.42 1.41 1.41 1.40 1.39 1.38 1.37 1.16 1.15 1.15 1.15 1.13 1.13 1.13
OCH3
O
H
7a
4.12 0.95 1.00 3.21 1.07 3.20 3.22 1.07 2.15 1.06
f1 (ppm)


153.83 152.41 141.35 118.70 116.80 114.72 77.48 77.16 76.84 55.86 40.19 38.57 38.24 29.27 25.23 22.52
f1 (ppm)


f2 (ppm)
f1 (ppm)


7.21 7.20 6.80 6.79 5.45 4.71 4.71 4.71 4.70 4.69 4.69 2.79 2.78 2.77 2.77 2.77 2.47 2.46 2.45 2.45 2.44 2.35 2.33 2.27 2.05 2.05 2.05 2.04 2.04 2.03 2.03 2.03 2.03 2.02 2.02 2.01 2.01 2.01 2.00 2.00 2.00 1.99 1.99 1.83 1.82 1.81 1.81 1.80 1.80 1.79 1.48 1.47 1.46 1.46 1.45 1.43 1.42 1.41 1.41 1.40 1.40 1.39 1.38 1.14 1.14 1.13 1.12 1.12
O
H
Cl
7b
1.72 1.85 0.87 0.94 1.00 1.00 0.98 0.95 2.93 0.99 2.00 1.01
f1 (ppm)
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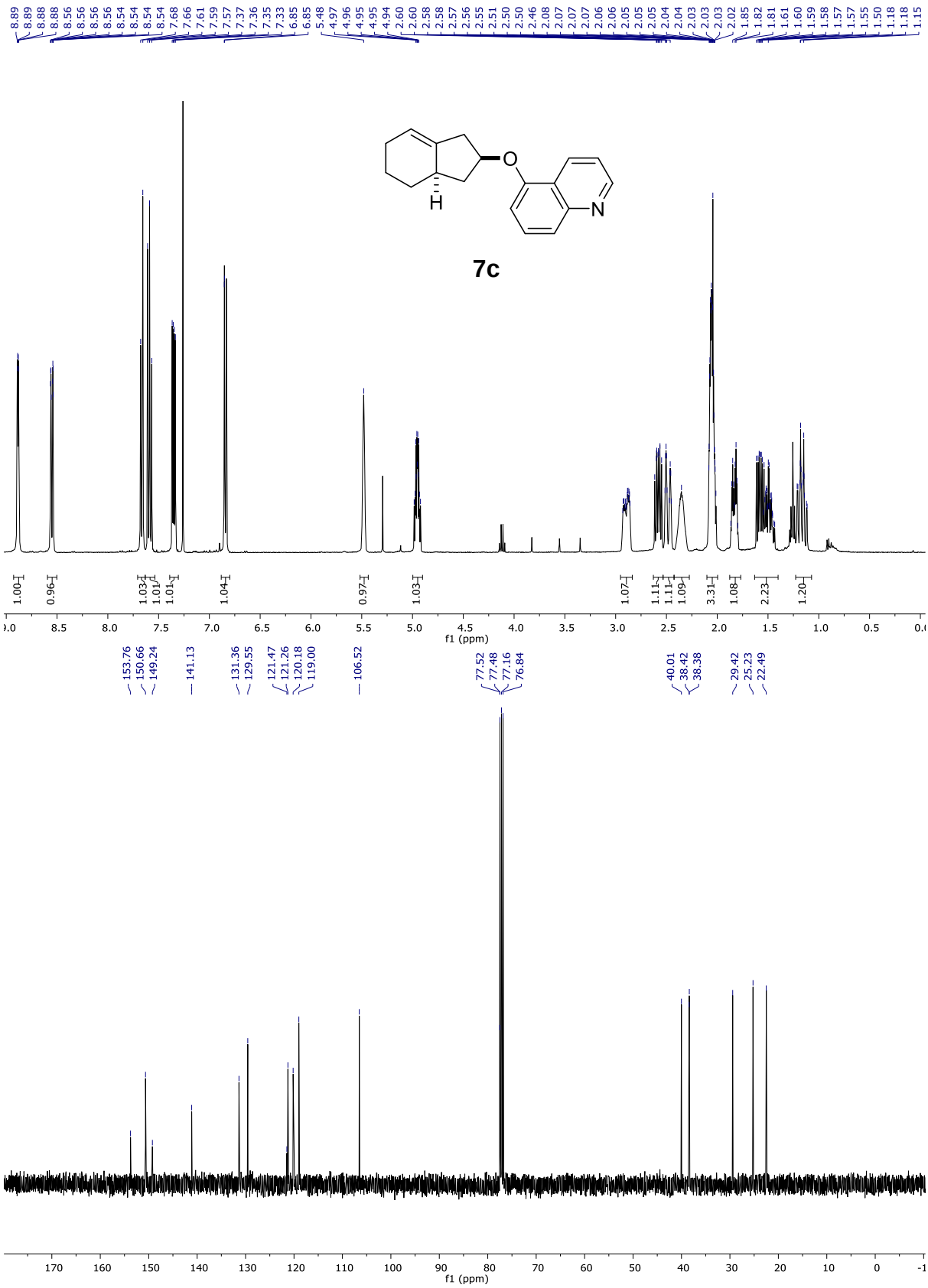
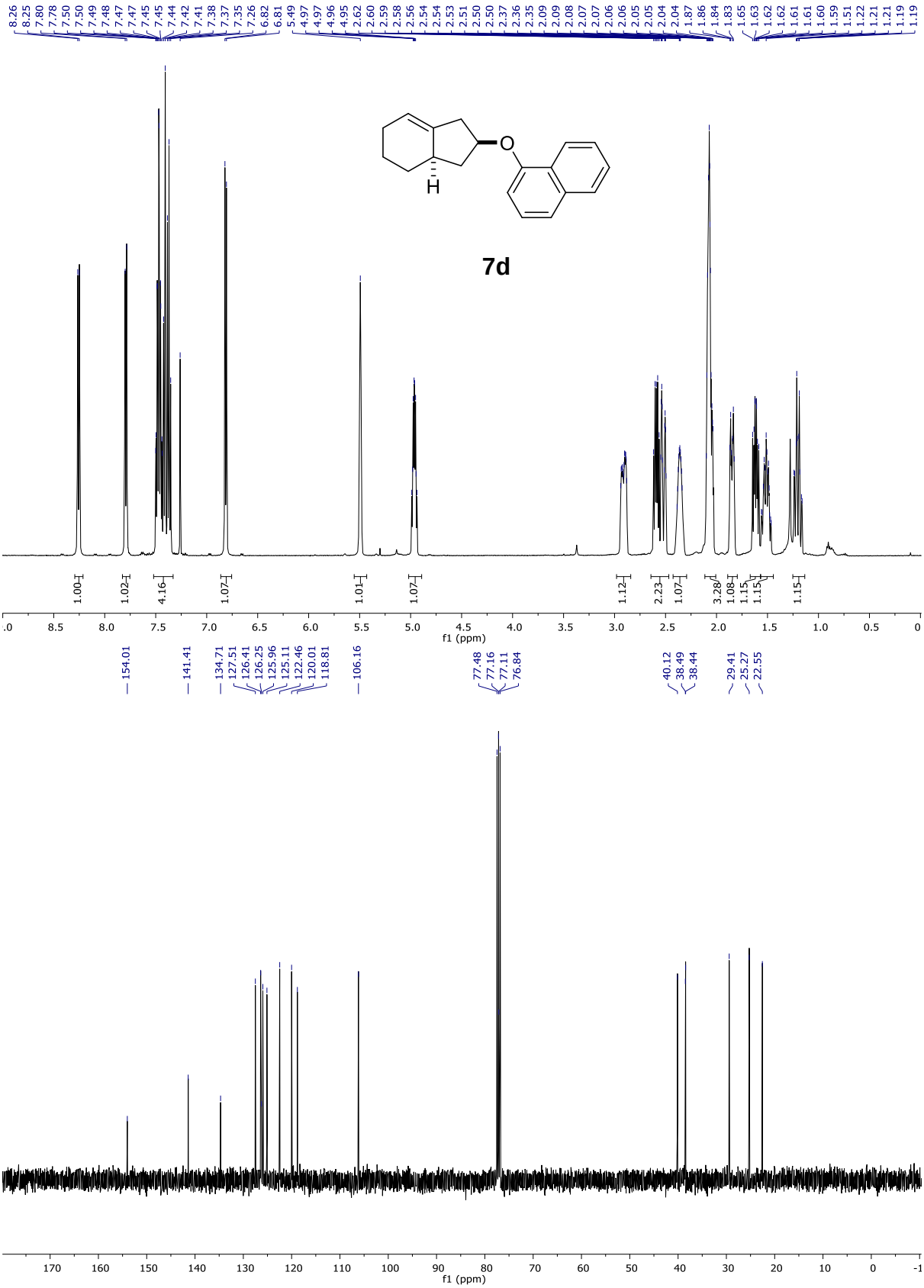
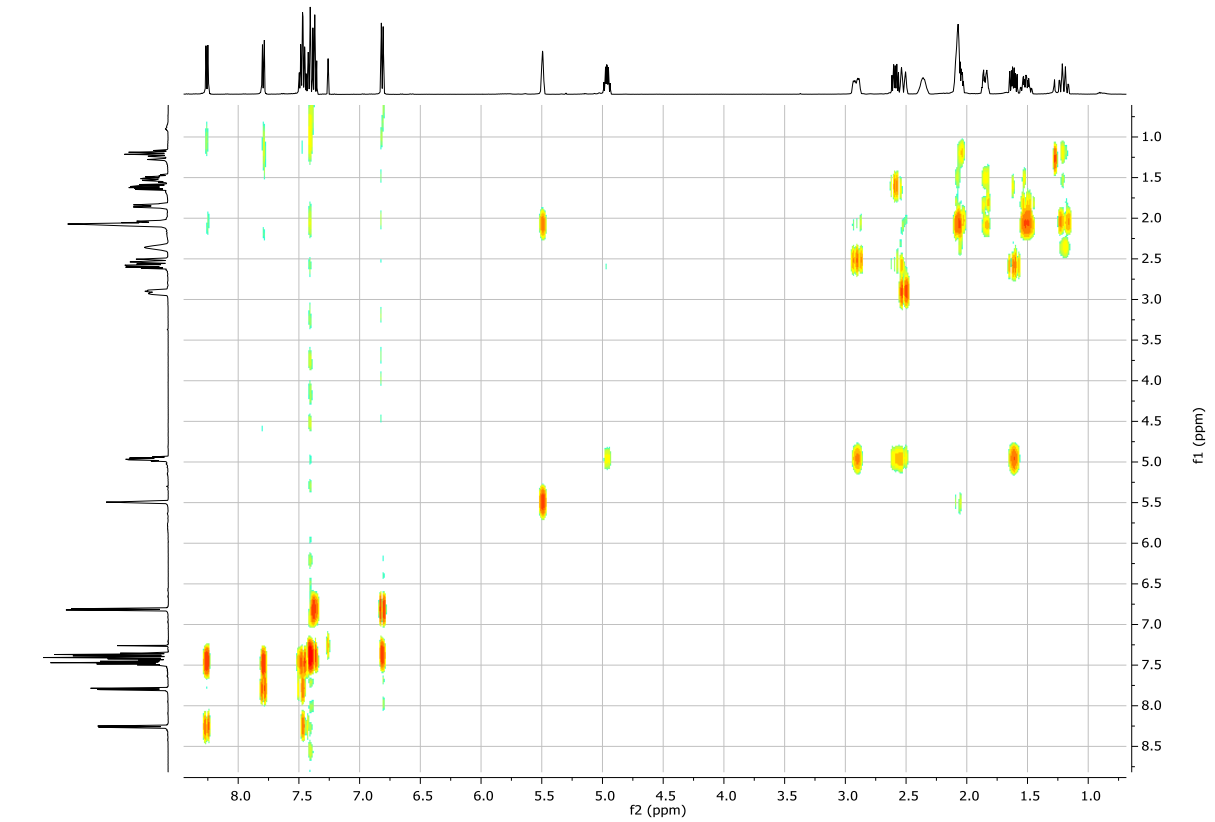
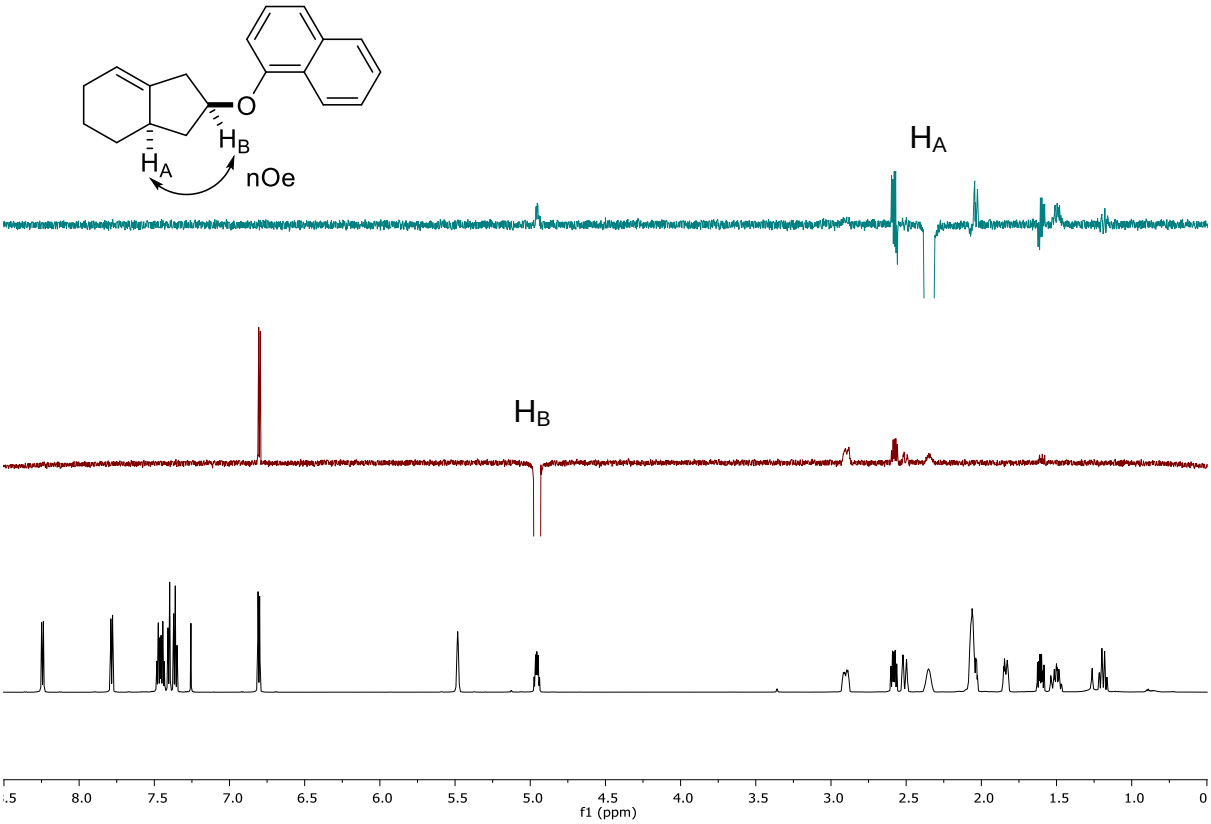
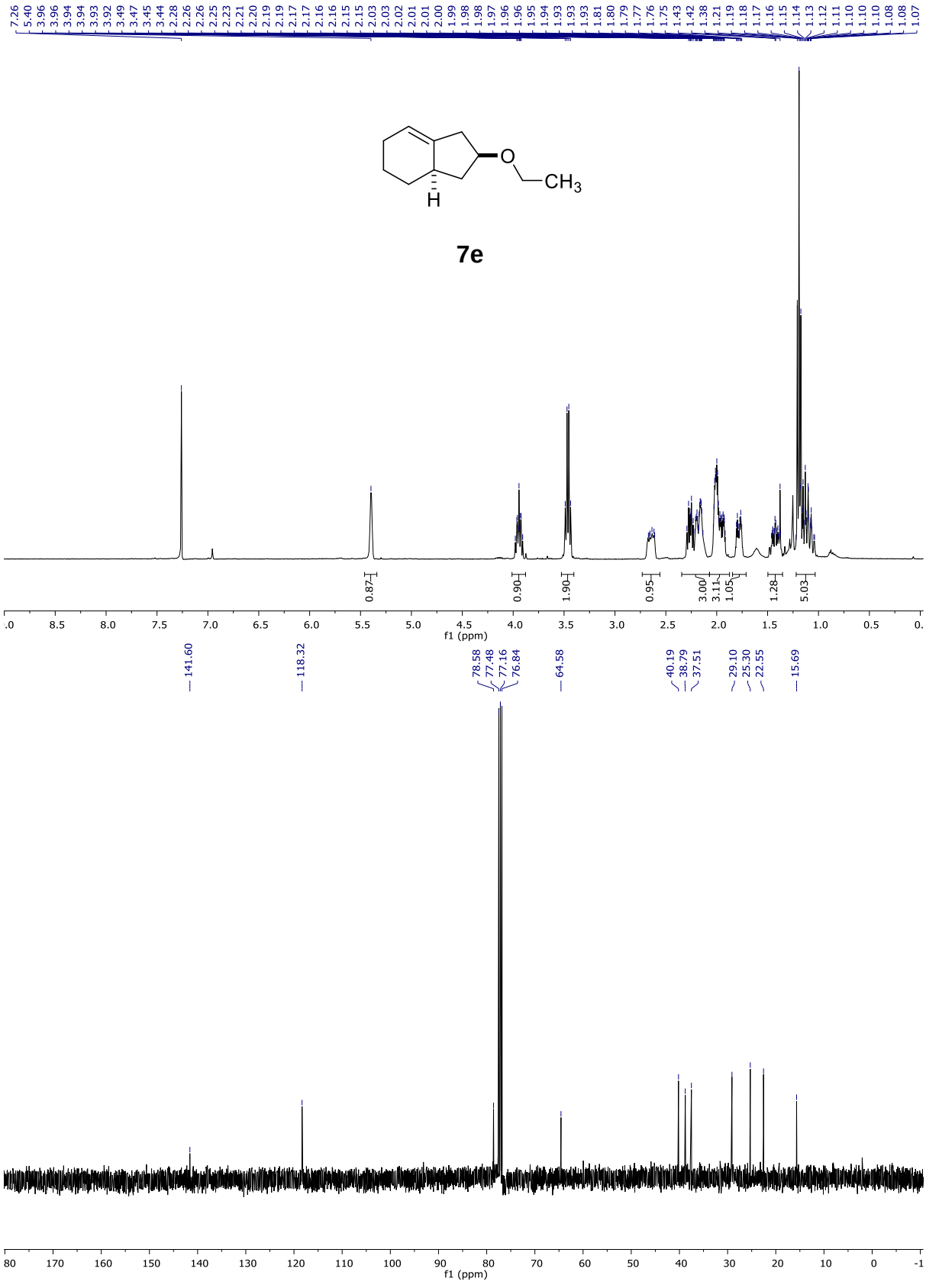
f1 (ppm)


O
H
N
7c
f1 (ppm)


8.26 8.25 7.80 7.78 7.50 7.50 7.49 7.48 7.47 7.47 7.45 7.45 7.44 7.42 7.41 7.38 7.37 7.35 7.26 6.82 6.81 5.49 4.97 4.97 4.96 4.95 2.62 2.60 2.59 2.58 2.56 2.54 2.54 2.53 2.51 2.50 2.50 2.37 2.36 2.35 2.09 2.09 2.08 2.07 2.07 2.06 2.06 2.05 2.05 2.04 2.04 1.87 1.86 1.84 1.83 1.65 1.63 1.62 1.62 1.61 1.61 1.60 1.59 1.51 1.22 1.21 1.21 1.19 1.19
O
H
7d
1.00 1.02 4.16 1.07 1.01 1.07 1.12 2.23 1.07 3.28 1.08 1.15 1.15 1.15
f1 (ppm)
154.01 141.41 134.71 127.51 126.41 126.25 125.96 125.11 122.46 120.01 118.81 106.16 77.48 77.16 77.11 76.84 40.12 38.49 38.44 29.41 25.27 22.55
f1 (ppm)


f2 (ppm)
f1 (ppm)


O
H_B
H_A
nOe
H_A
H_B
f1 (ppm)


7.26 5.40 3.96 3.96 3.94 3.94 3.93 3.92 3.49 3.47 3.45 3.44 2.28 2.26 2.26 2.25 2.23 2.21 2.20 2.19 2.19 2.17 2.17 2.16 2.16 2.15 2.15 2.03 2.03 2.02 2.01 2.01 2.00 1.99 1.98 1.98 1.97 1.96 1.96 1.95 1.94 1.93 1.93 1.93 1.81 1.80 1.79 1.77 1.76 1.75 1.43 1.42 1.38 1.21 1.19 1.18 1.17 1.16 1.15 1.14 1.13 1.12 1.11 1.10 1.10 1.10 1.08 1.08 1.07
O
CH3
H
0.87 0.90 1.90 0.95 3.00 3.11 1.05 1.28 5.03
f1 (ppm)
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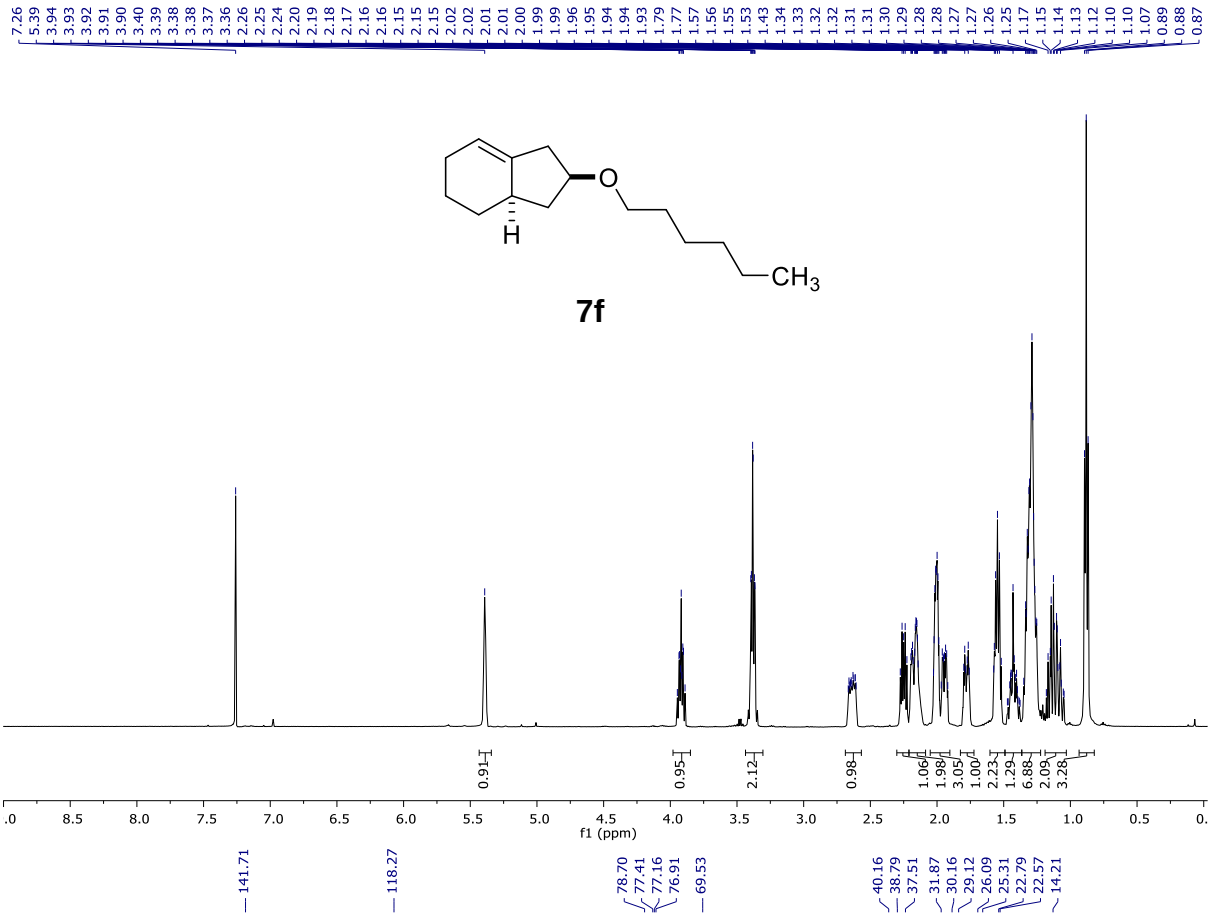
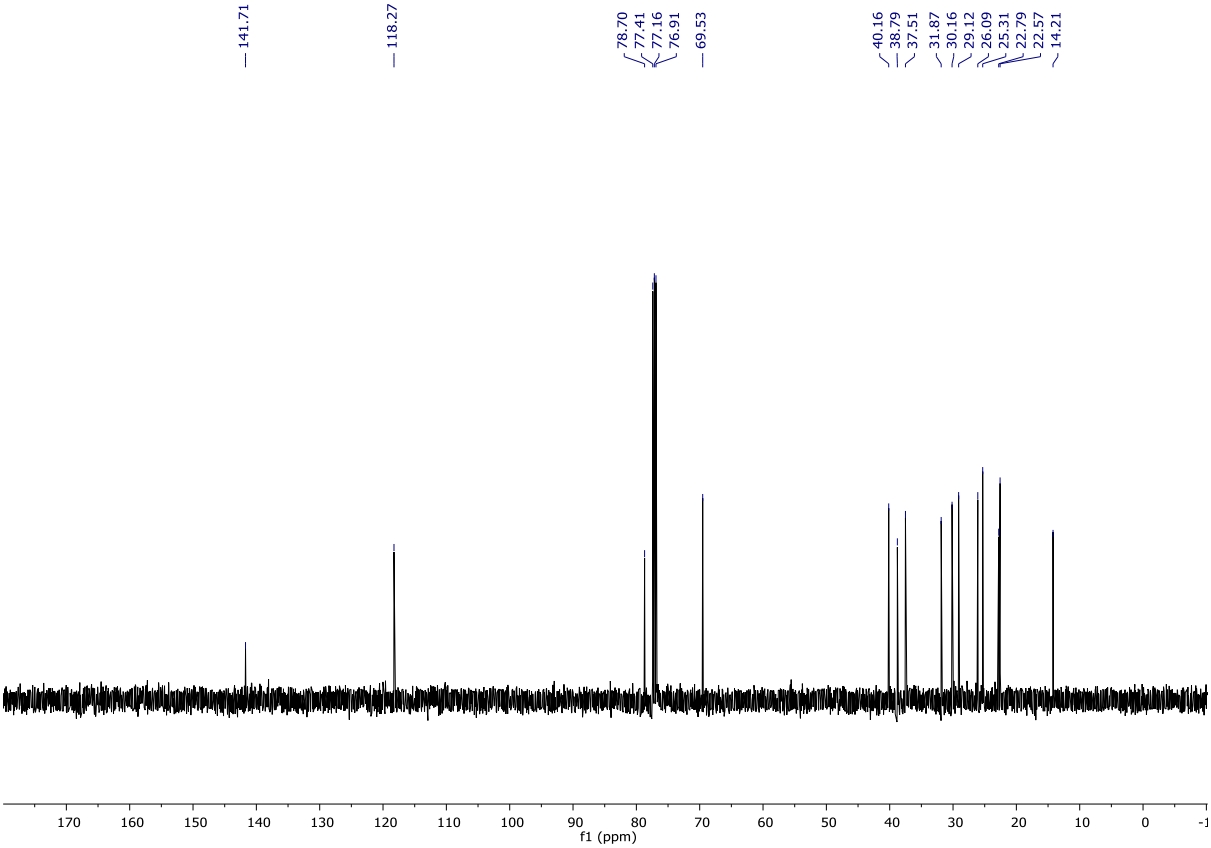
f1 (ppm)

7e


7.26 5.39 3.94 3.93 3.92 3.91 3.90 3.40 3.39 3.38 3.38 3.37 3.36 2.26 2.25 2.24 2.20 2.19 2.18 2.17 2.16 2.16 2.15 2.15 2.15 2.02 2.02 2.01 2.01 2.00 1.99 1.99 1.96 1.95 1.94 1.94 1.93 1.79 1.77 1.57 1.56 1.55 1.53 1.43 1.34 1.33 1.32 1.32 1.31 1.31 1.30 1.29 1.28 1.28 1.27 1.27 1.26 1.25 1.17 1.15 1.14 1.13 1.12 1.10 1.10 1.07 0.89 0.88 0.87
O
H
CH3
7f
0.91 0.95 2.12 0.98 1.06 1.98 3.05 1.00 2.23 1.29 6.88 2.09 3.28
f1 (ppm)


141.71 118.27 78.70 77.41 77.16 76.91 69.53 40.16 38.79 37.51 31.87 30.16 29.12 26.09 25.31 22.79 22.57 14.21
f1 (ppm)


5.38
3.99
3.99
3.97
3.96
3.96
3.95
3.94
3.94
3.93
3.92
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2.22
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2.13
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2.01
2.01
2.00
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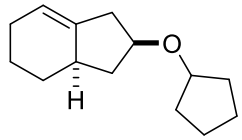
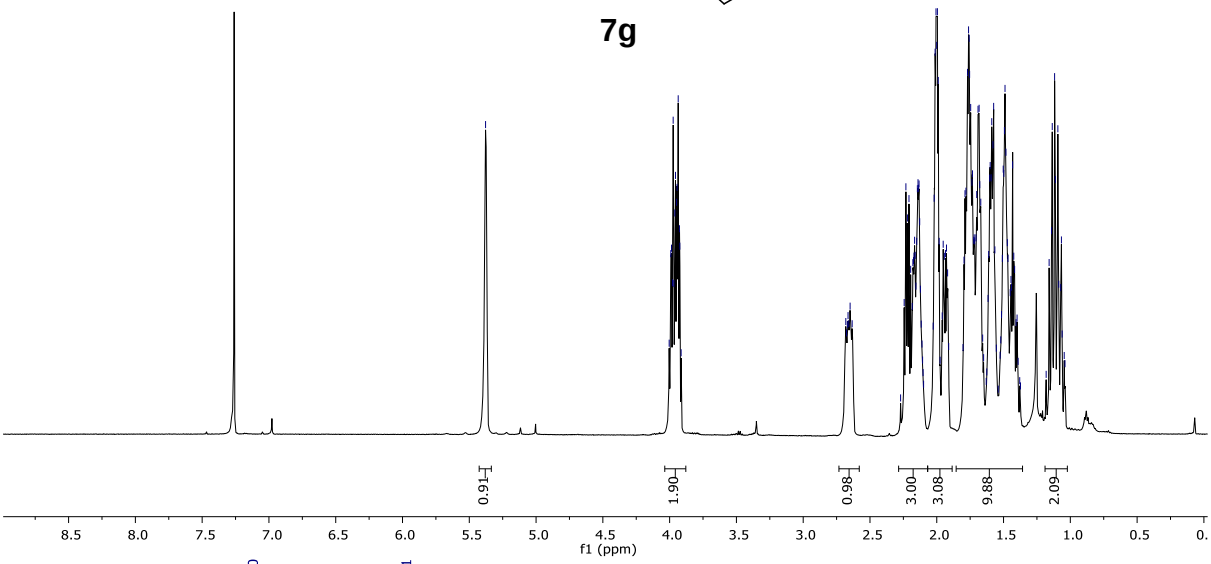
1.09
1.07


O
H

7g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2.09
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7.5
7.0
6.5
6.0
5.5
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4.5
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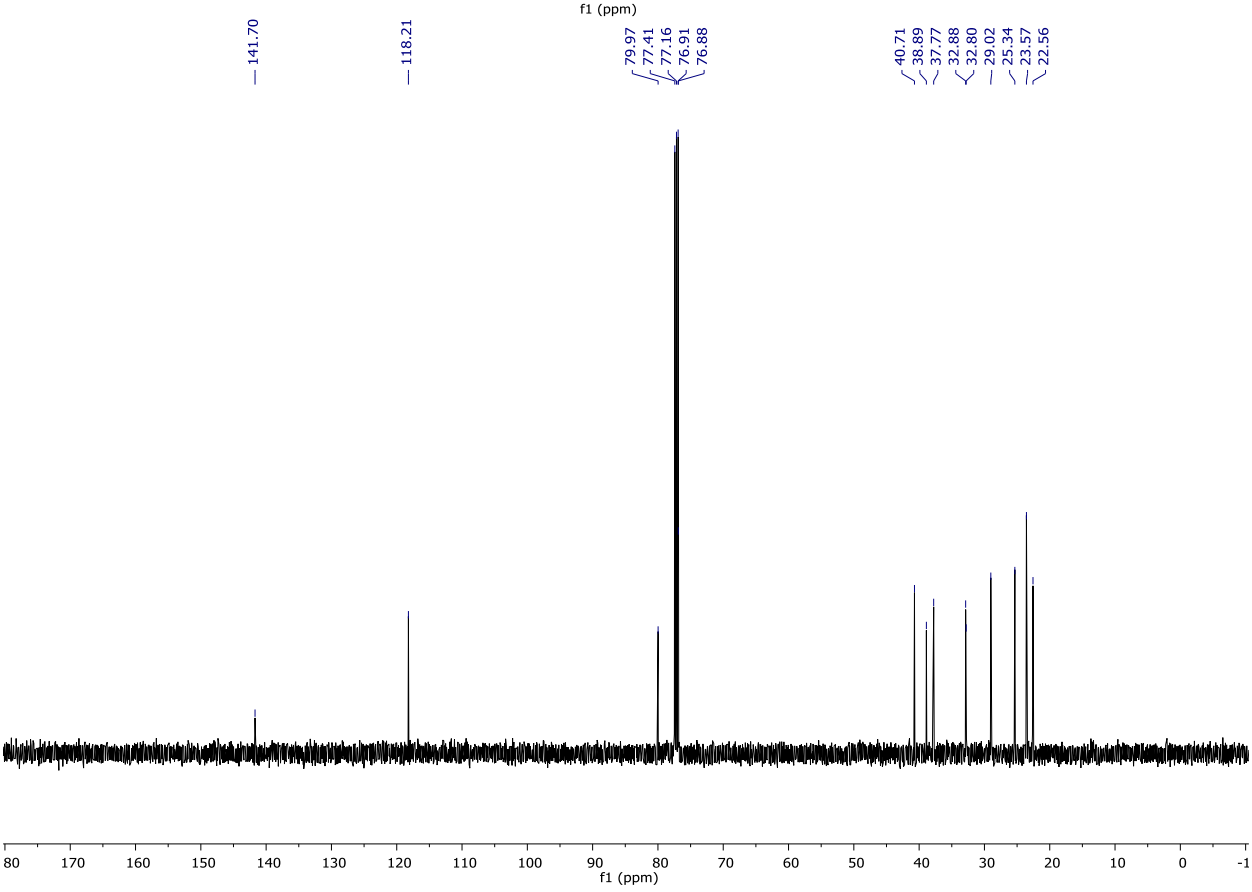
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.
f1 (ppm)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38.89
37.77
32.88
32.80
29.02
25.34
23.57
22.56
80
170
160
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140
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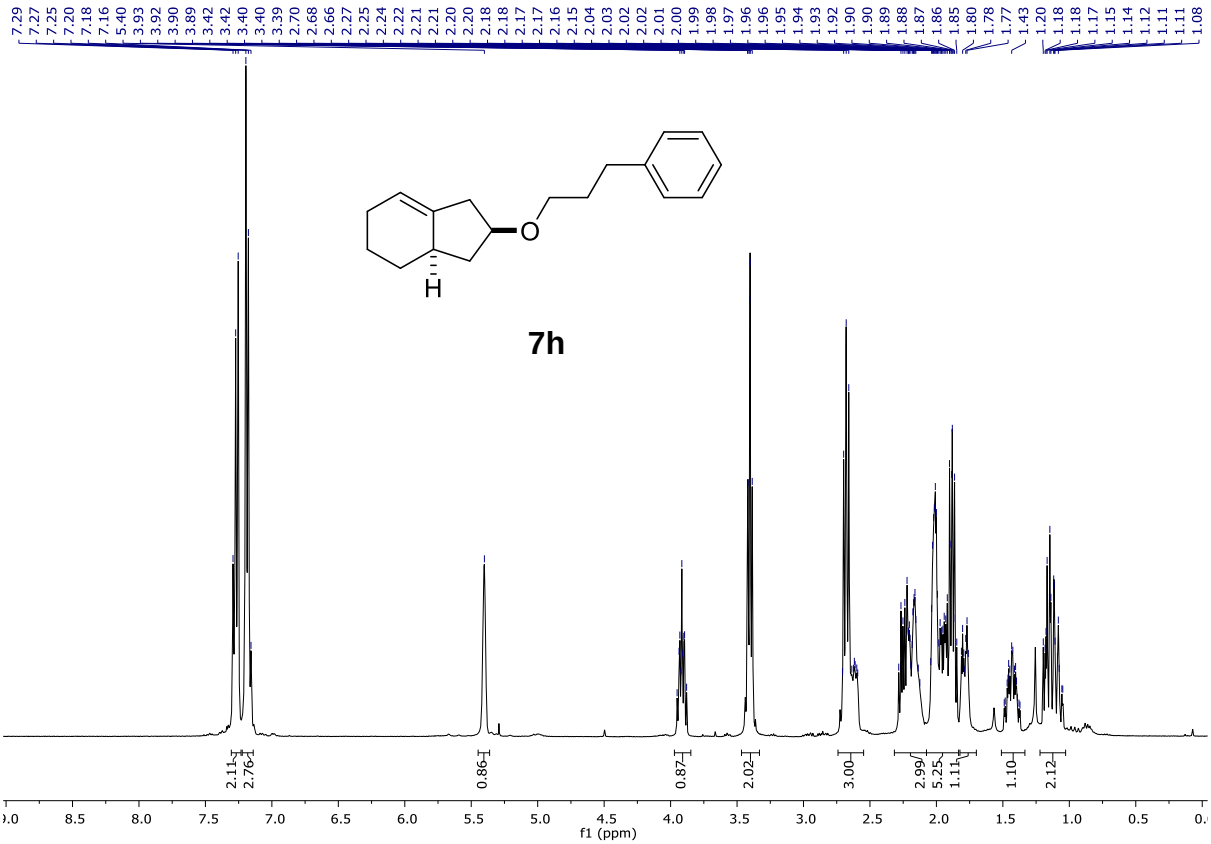
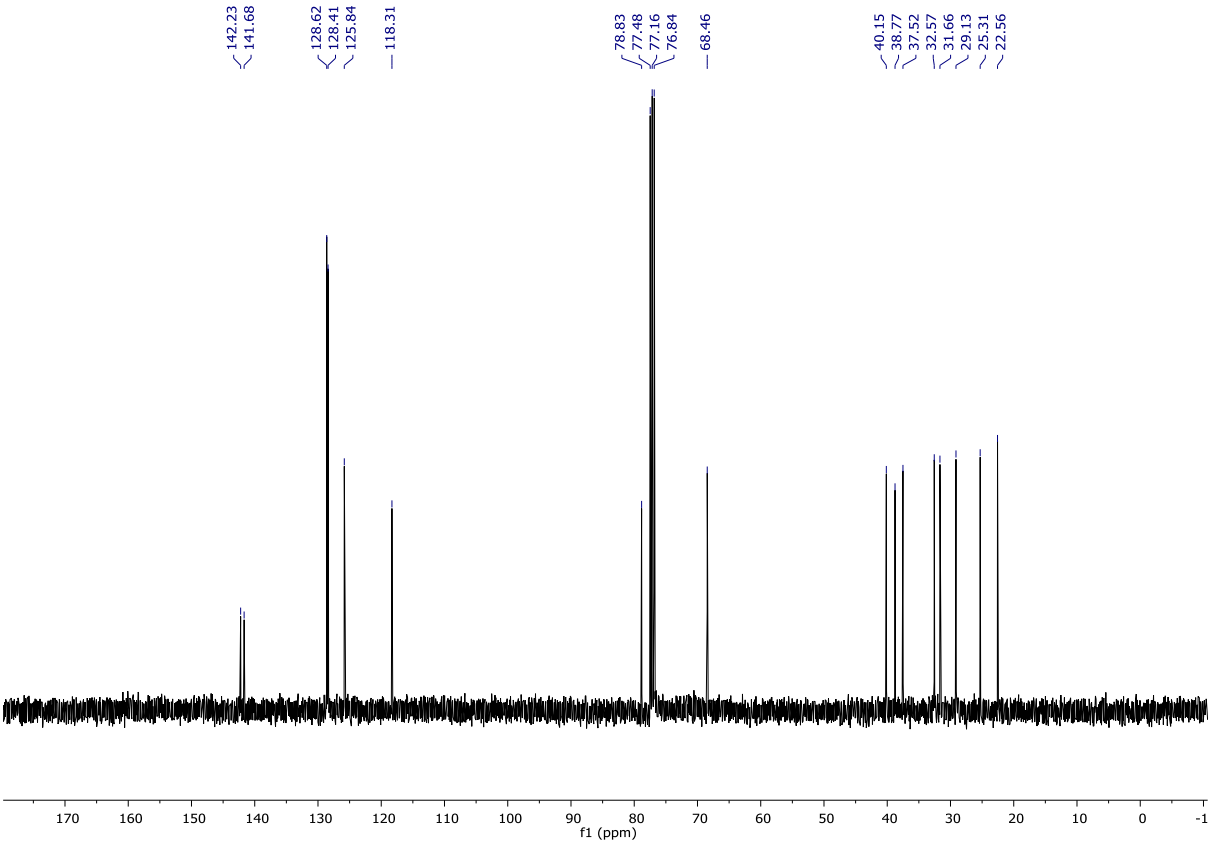
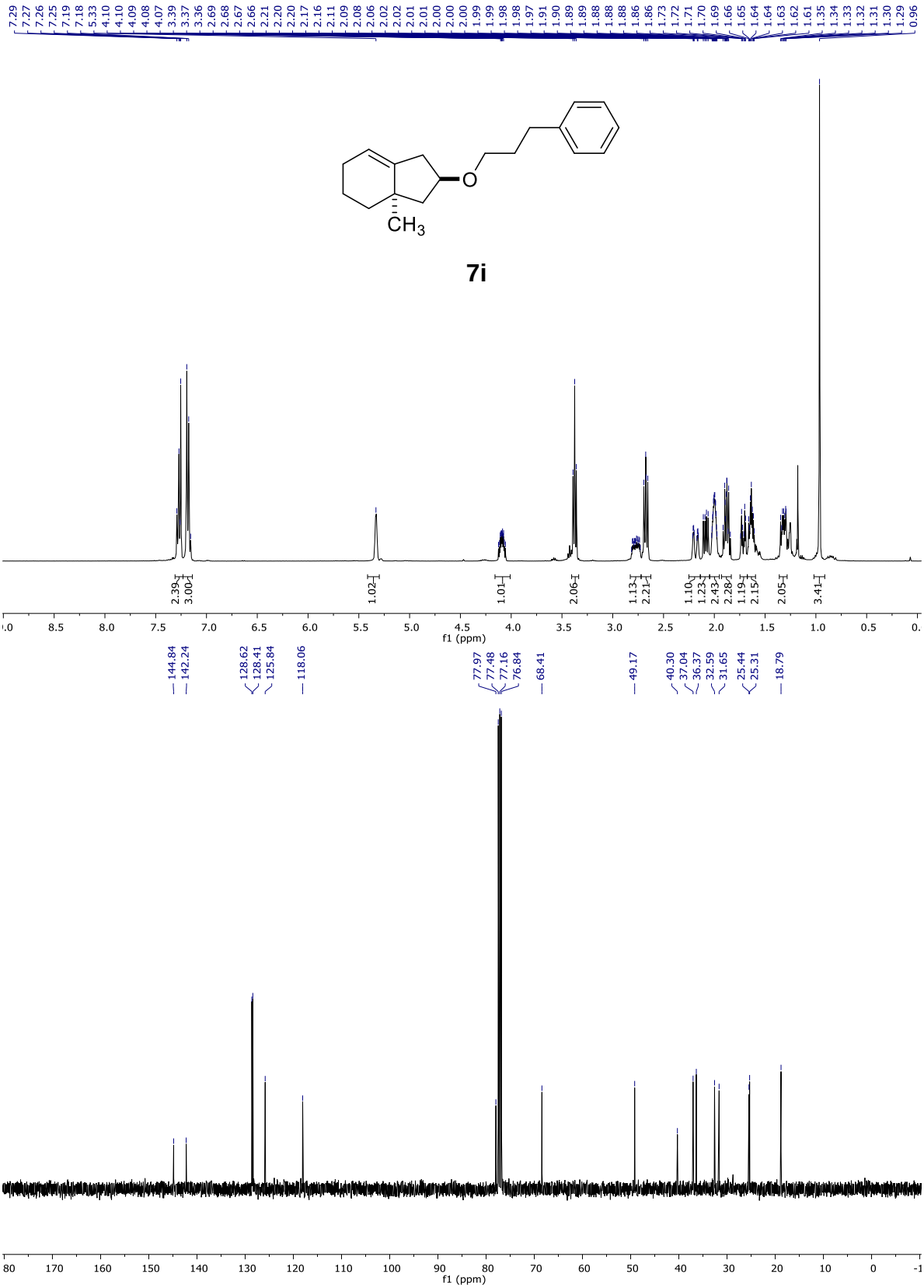
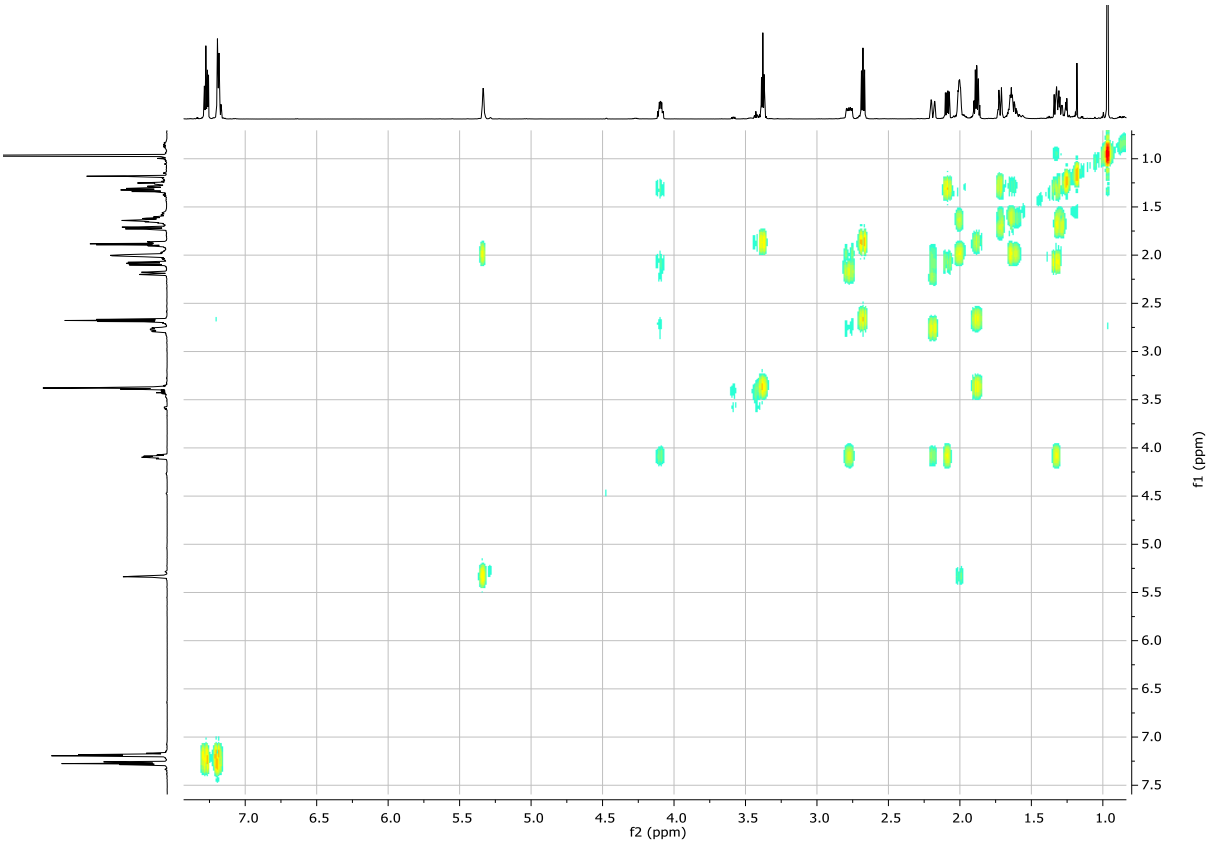
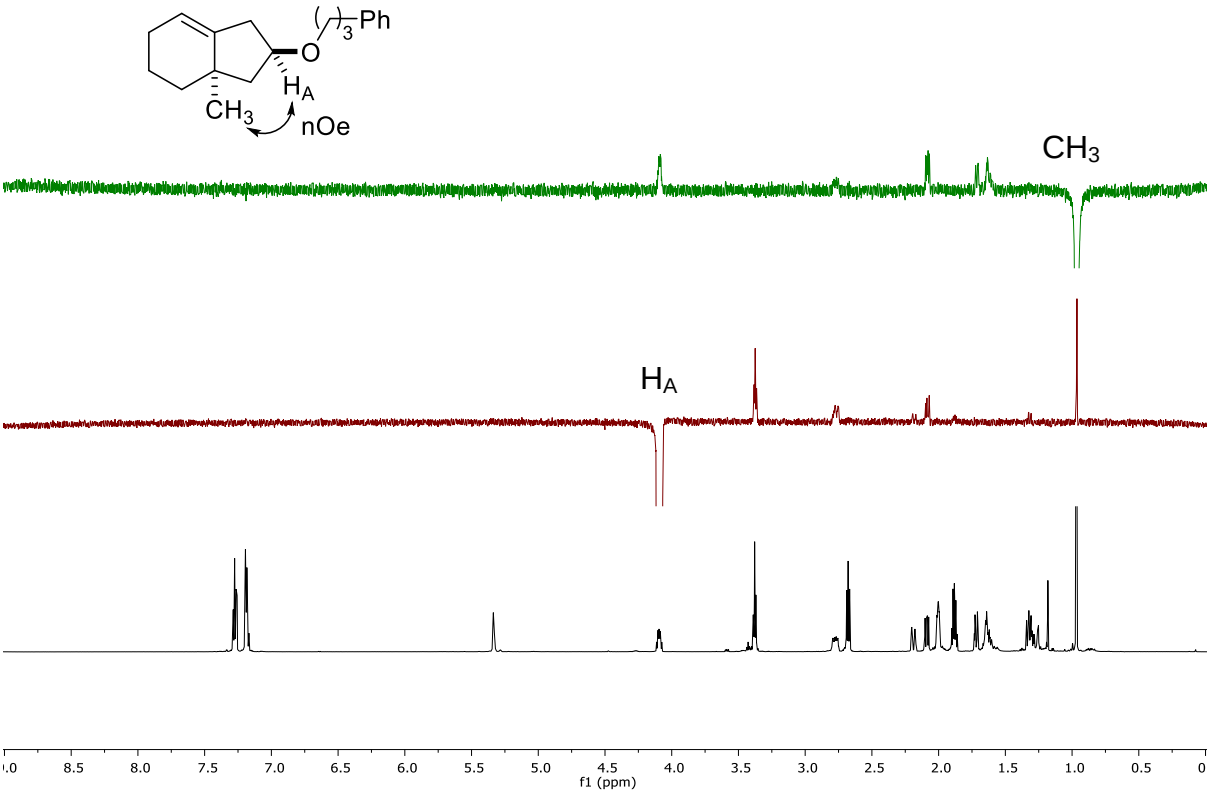
120
110
100
90
80
70
60
50
40
30
20
10
0
-1
f1 (ppm)

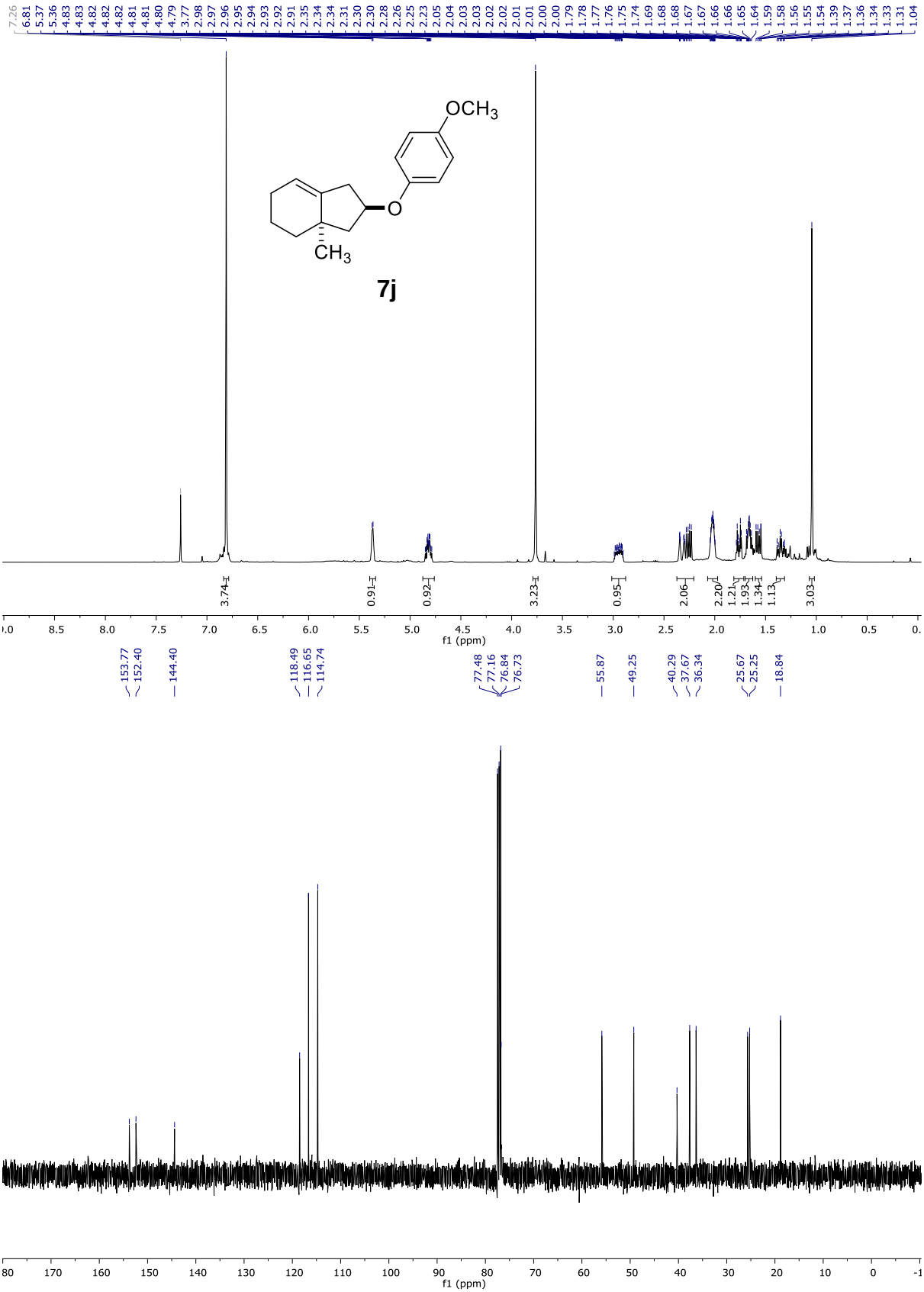

7.29 7.27 7.25 7.20 7.18 7.16 5.40 3.93 3.92 3.90 3.89 3.42 3.42 3.40 3.40 3.39 2.70 2.68 2.66 2.27 2.25 2.24 2.22 2.21 2.21 2.20 2.20 2.18 2.18 2.17 2.17 2.16 2.15 2.04 2.03 2.02 2.02 2.01 2.00 1.99 1.98 1.97 1.96 1.96 1.95 1.94 1.93 1.92 1.90 1.90 1.89 1.88 1.87 1.86 1.85 1.80 1.78 1.77 1.43 1.20 1.18 1.18 1.17 1.15 1.14 1.12 1.11 1.11 1.08
O
H
7h
2.11
2.76
0.86
0.87
2.02
3.00
2.99
5.25
1.11
1.10
2.12
f1 (ppm)

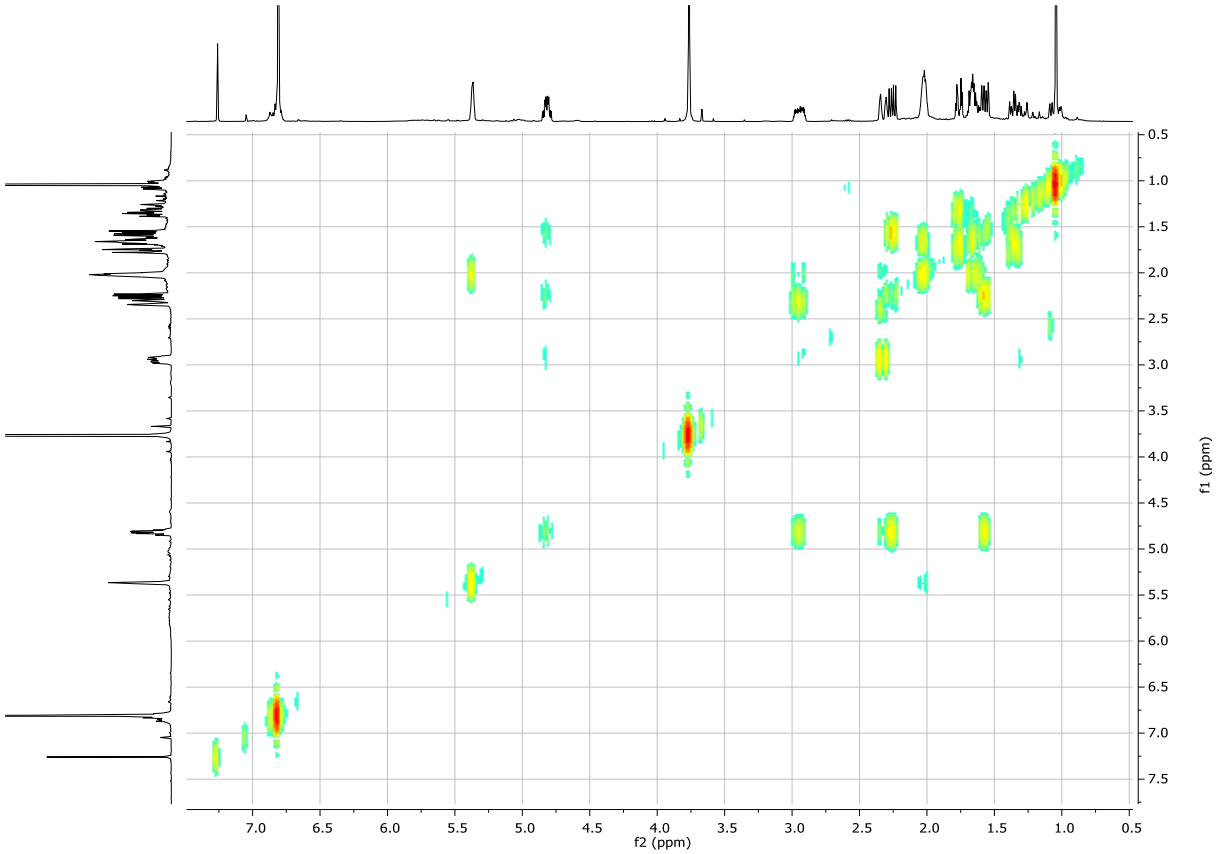

142.23
141.68
128.62
128.41
125.84
118.31
78.83
77.48
77.16
76.84
68.46
40.15
38.77
37.52
32.57
31.66
29.13
25.31
22.56
f1 (ppm)

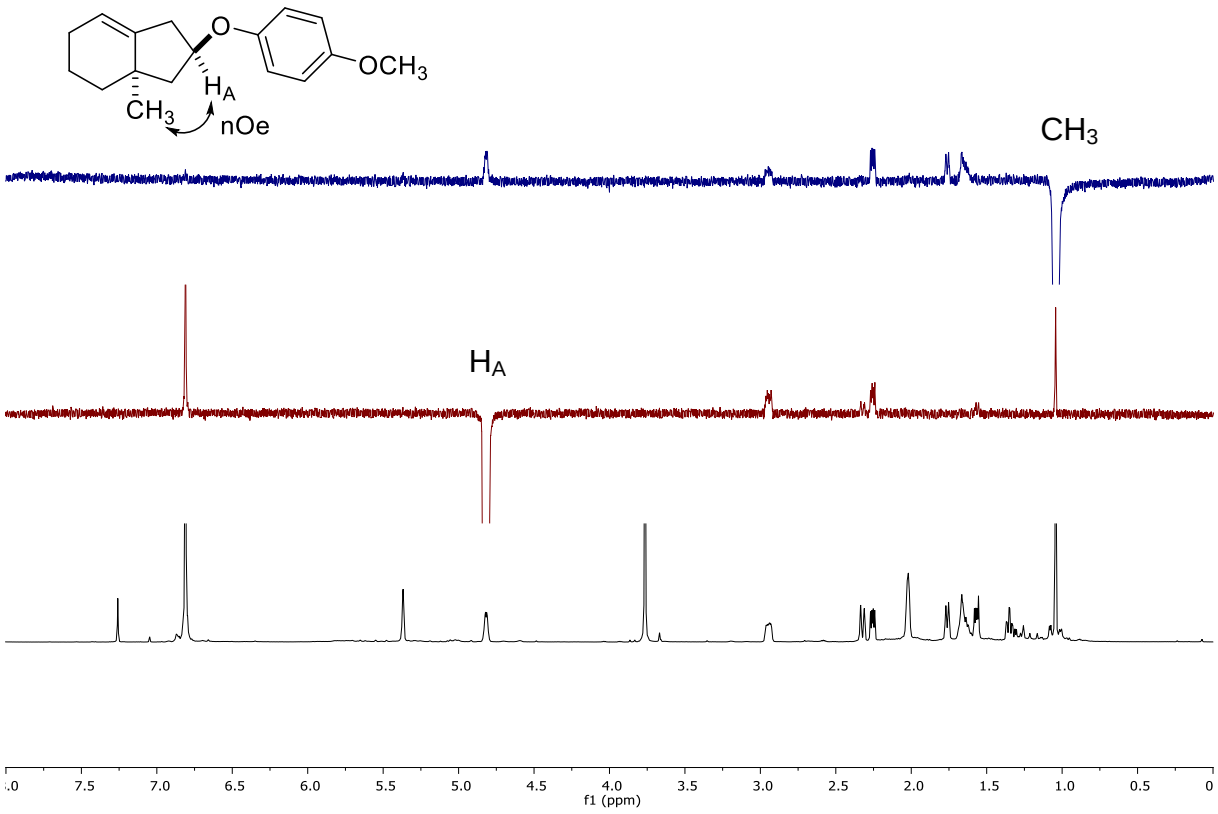

7.29 7.27 7.26 7.25 7.19 7.18 5.33 4.10 4.09 4.08 4.07 3.39 3.37 3.36 2.69 2.68 2.67 2.66 2.21 2.20 2.20 2.17 2.16 2.11 2.09 2.08 2.06 2.02 2.02 2.01 2.01 2.00 2.00 2.00 1.99 1.99 1.98 1.98 1.97 1.91 1.90 1.89 1.89 1.88 1.88 1.88 1.86 1.86 1.73 1.72 1.71 1.70 1.69 1.66 1.65 1.64 1.64 1.63 1.62 1.61 1.35 1.34 1.33 1.32 1.31 1.30 1.29 0.96
O
CH3
7i
2.39 3.00 1.02 1.01 2.06 1.13 2.21 1.10 1.23 2.43 2.28 1.19 2.15 2.05 3.41
f1 (ppm)
144.84 142.24 128.62 128.41 125.84 118.06 77.97 77.48 77.16 76.84 68.41 49.17 40.30 37.04 36.37 32.59 31.65 25.44 25.31 18.79
f1 (ppm)

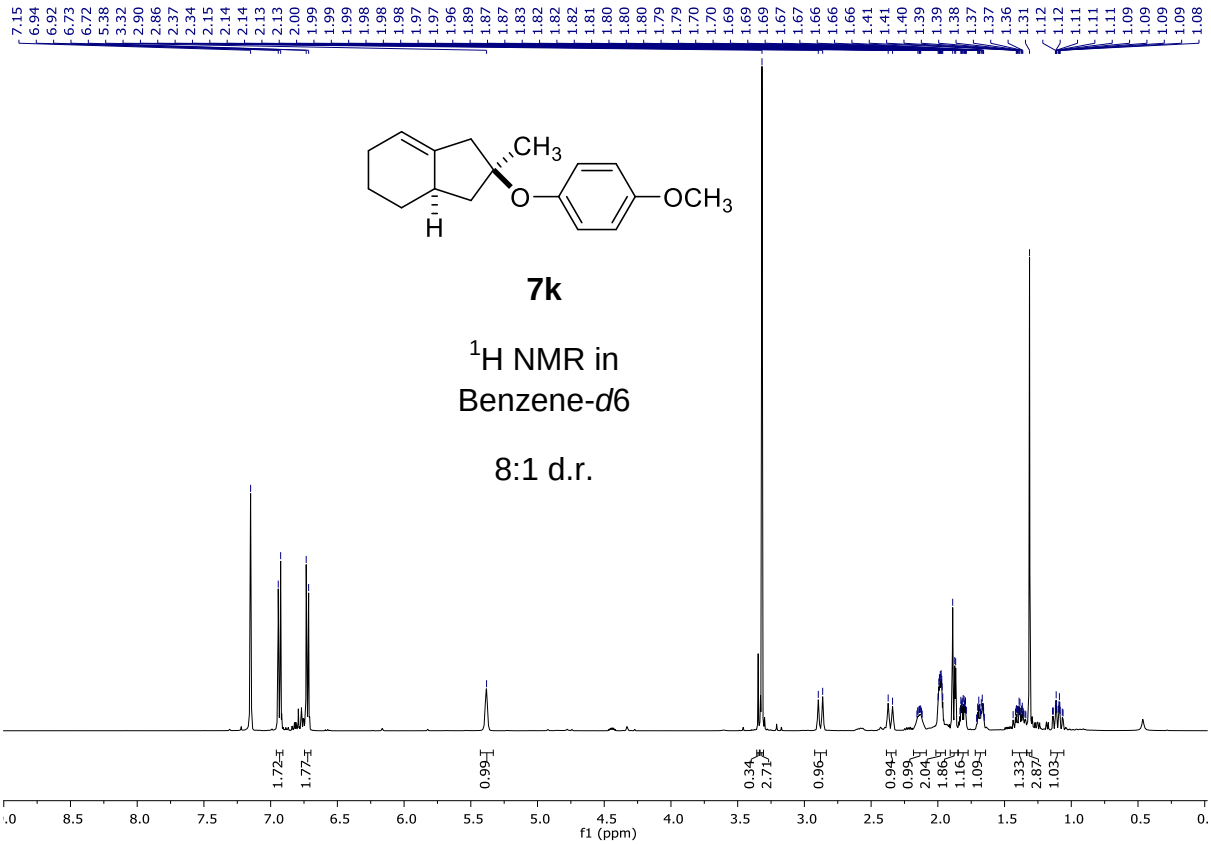

f2 (ppm)
f1 (ppm)


Ph
O
H_A
CH_3
nOe
CH_3
H_A
f1 (ppm)


OCH3
O
CH3
7j
f1 (ppm)
f1 (ppm)


f2 (ppm)
f1 (ppm)

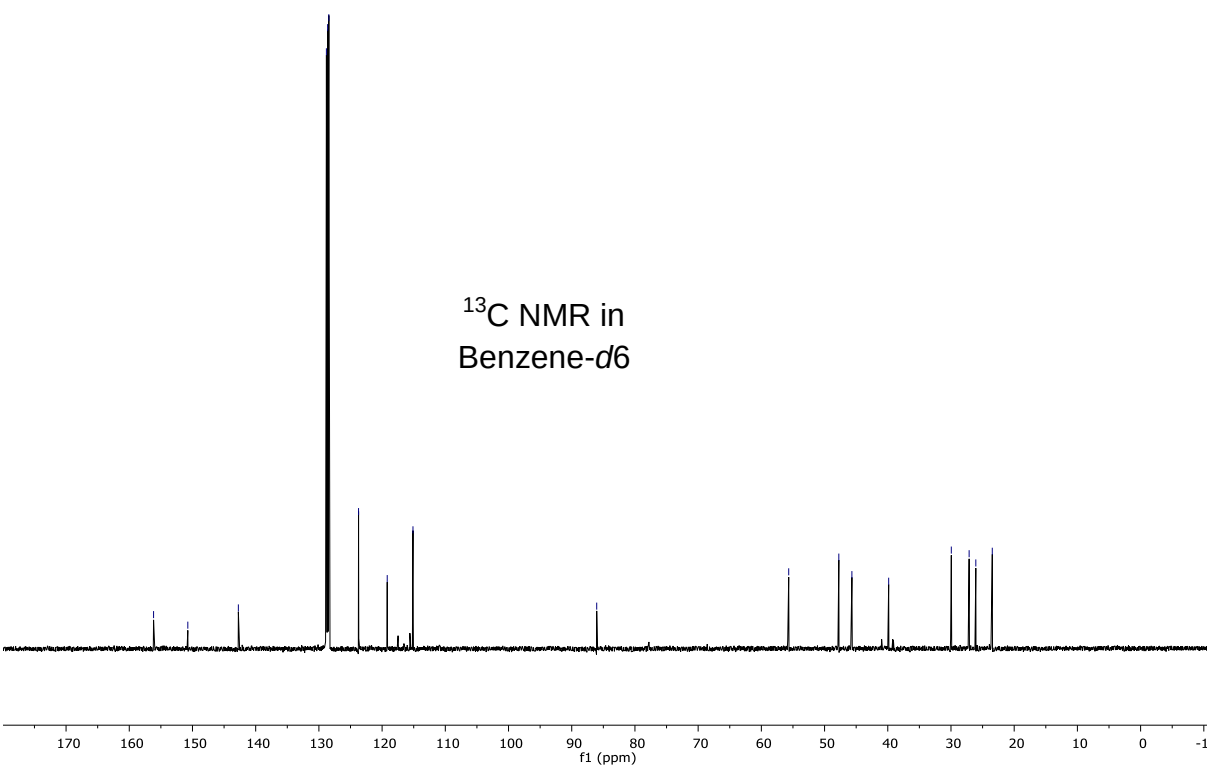

O
OCH3
HA
CH3
nOe
CH3
HA
f1 (ppm)



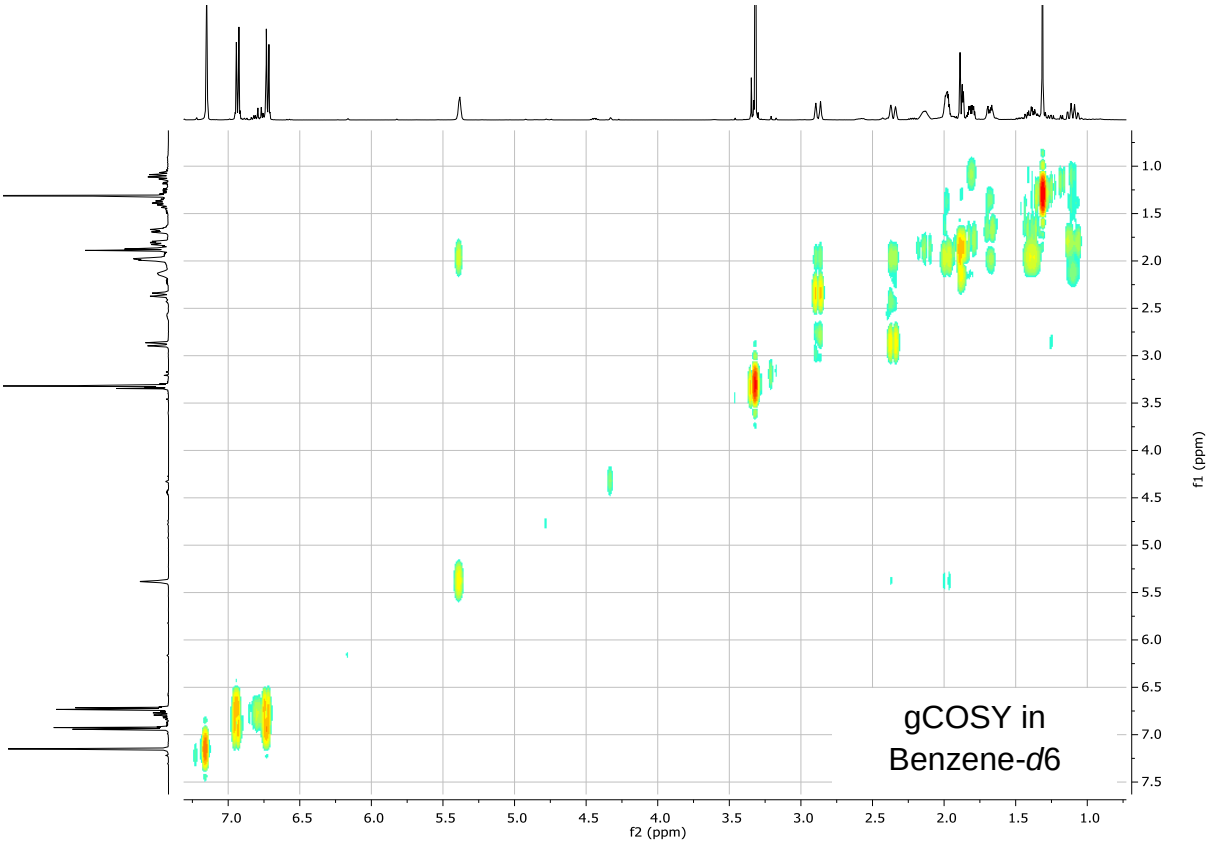
7k

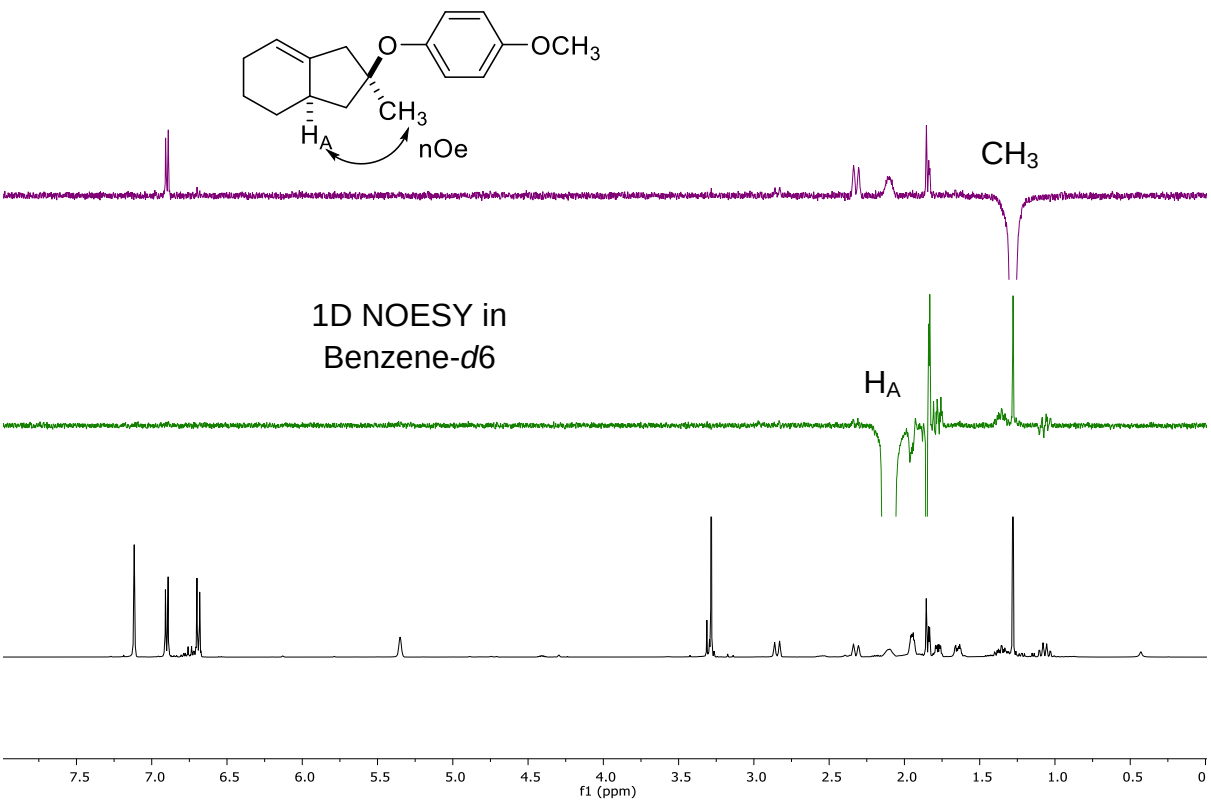
^{1}H NMR in Benzene-*d*6

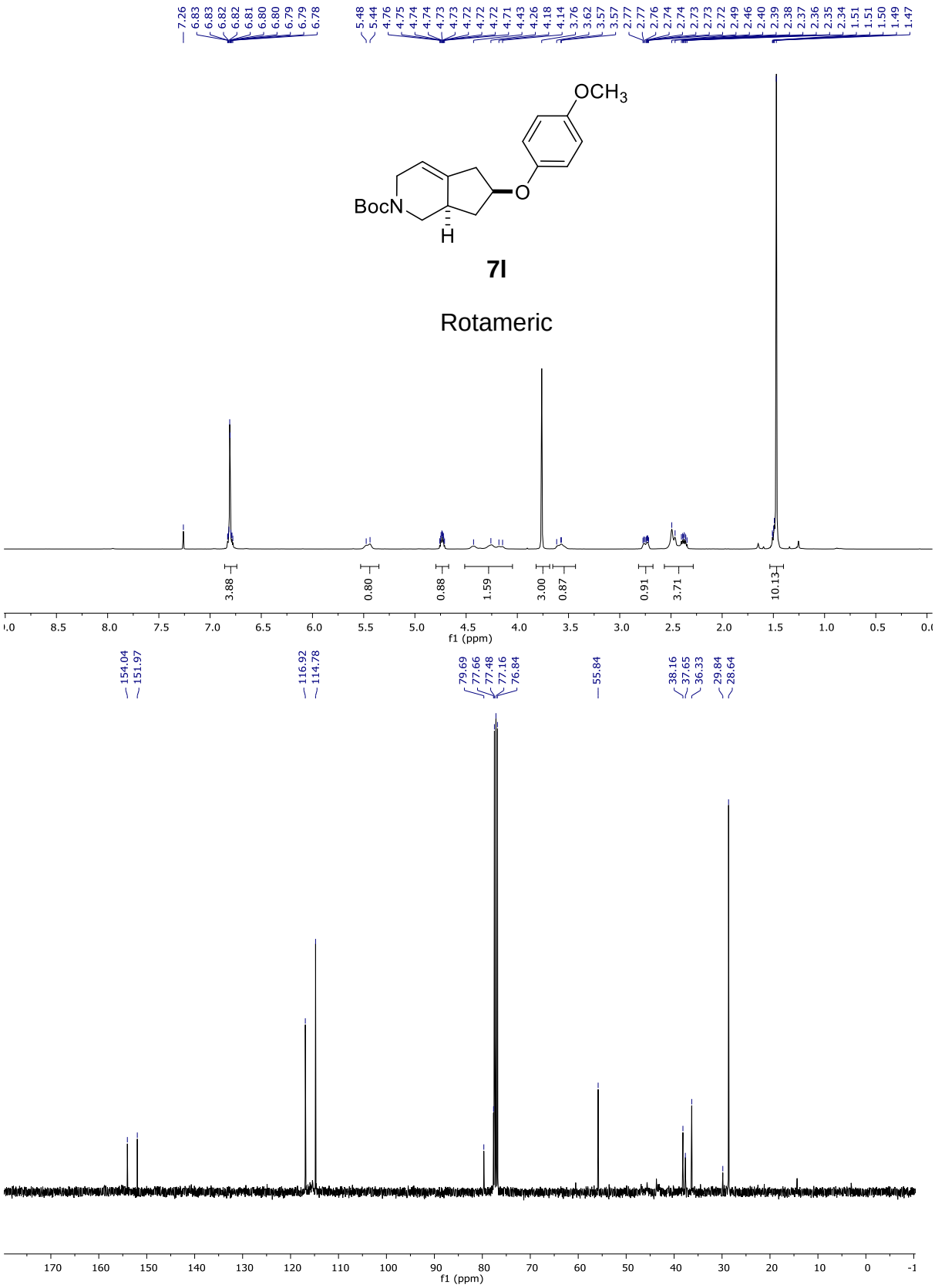
8:1 d.r.

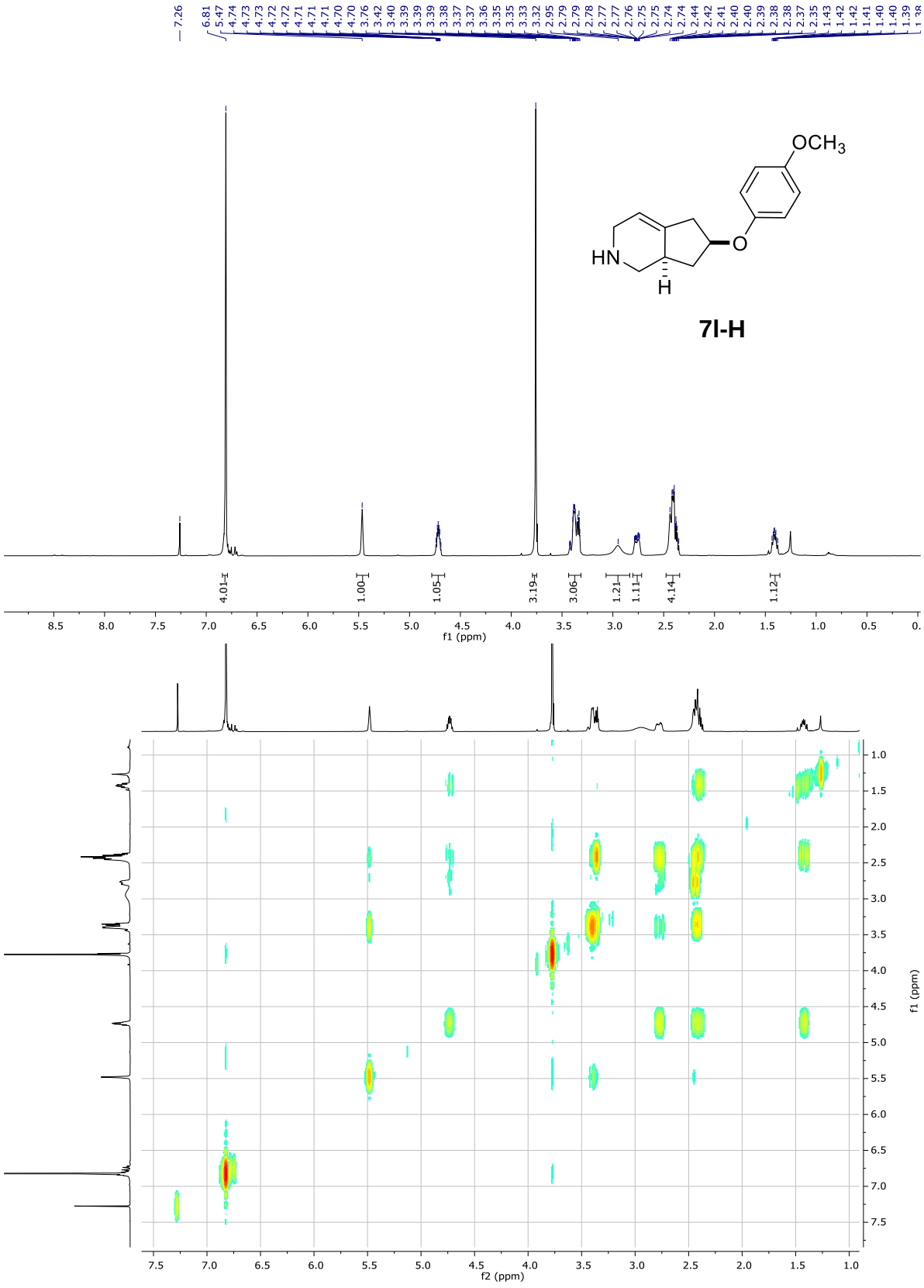


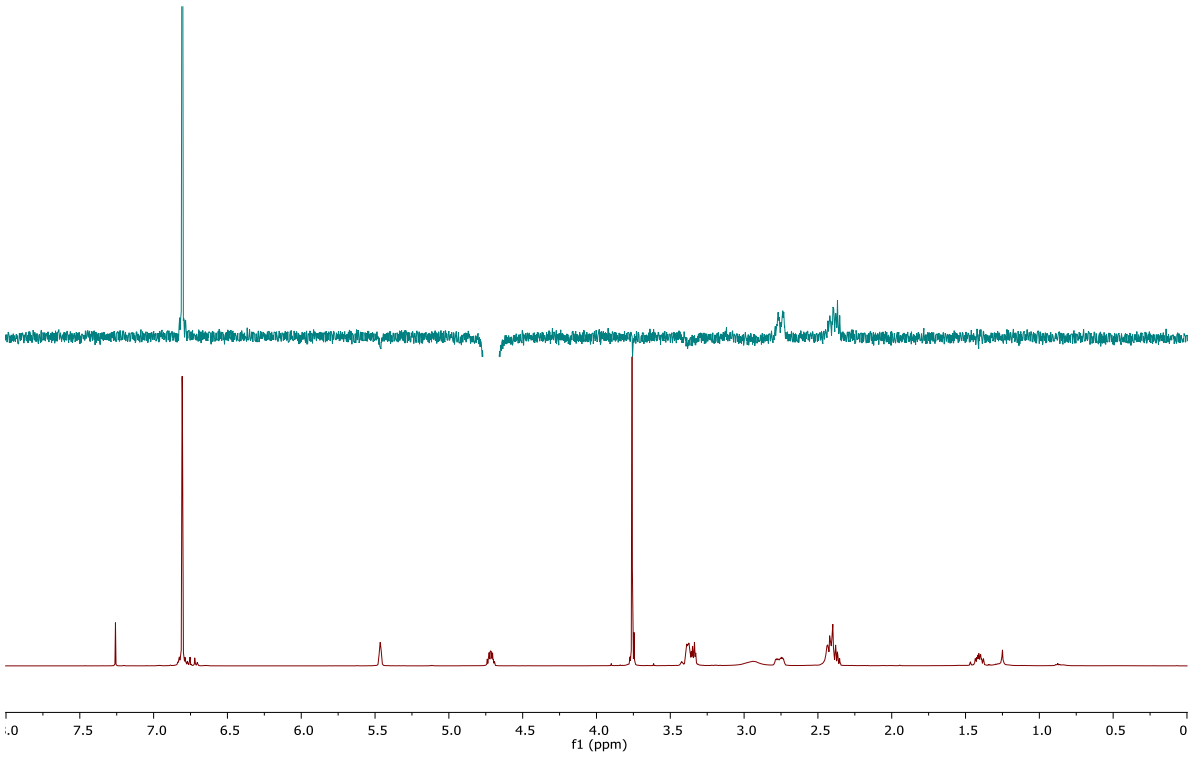
^{13}C NMR in Benzene-*d*6

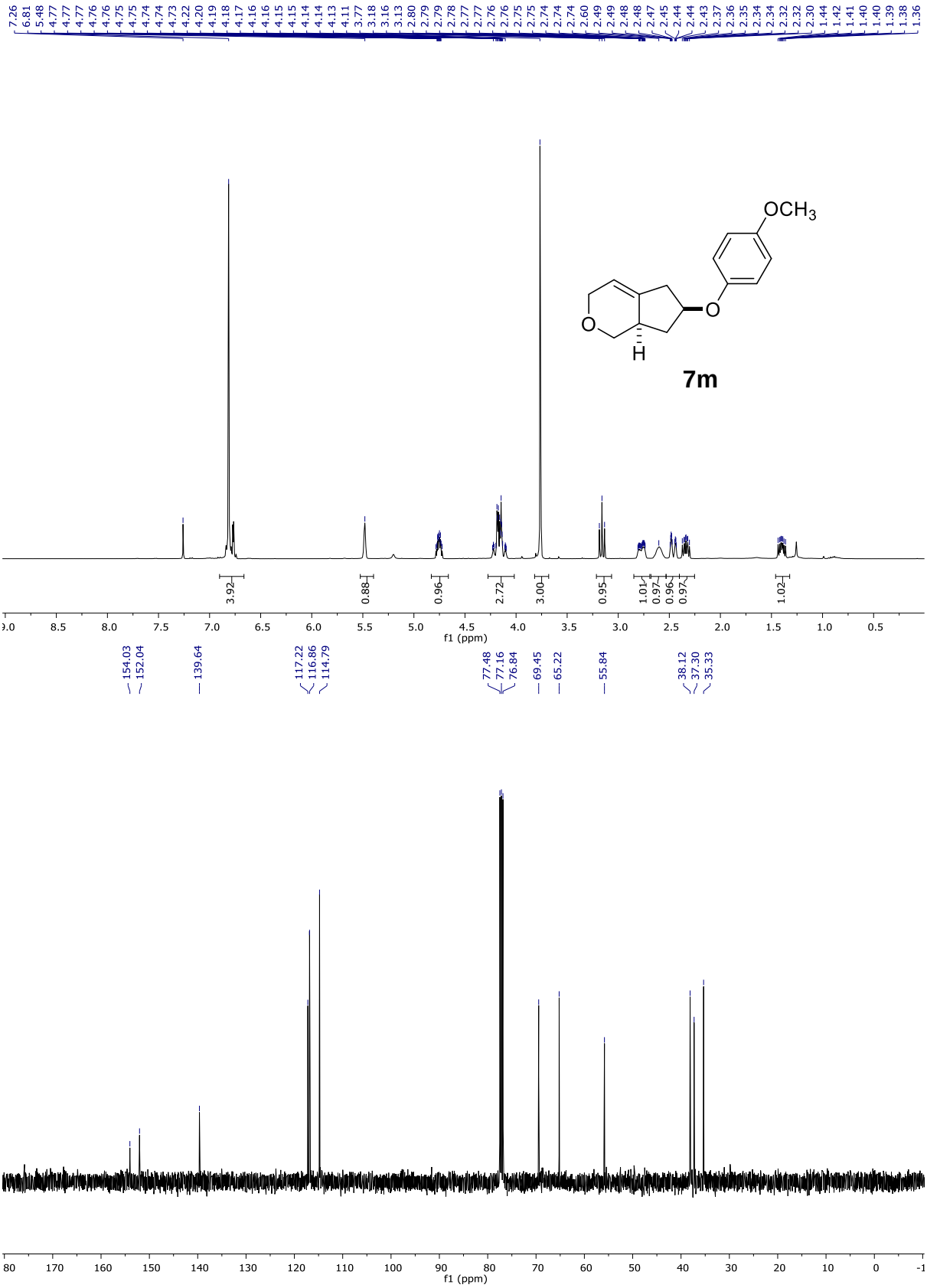

gCOSY in
Benzene-d6
f2 (ppm)
f1 (ppm)

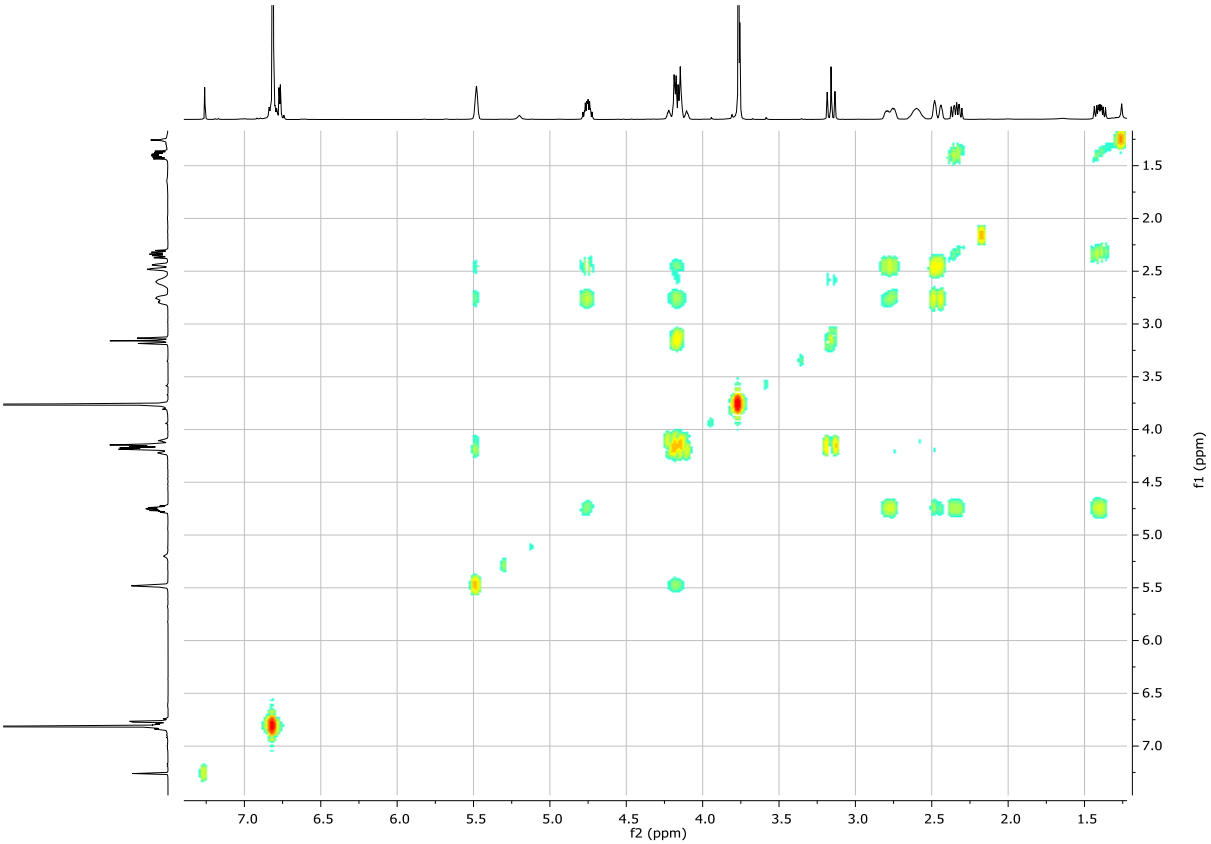

O
OCH3
CH3
HA
nOe
CH3
1D NOESY in
Benzene-d6
HA
f1 (ppm)

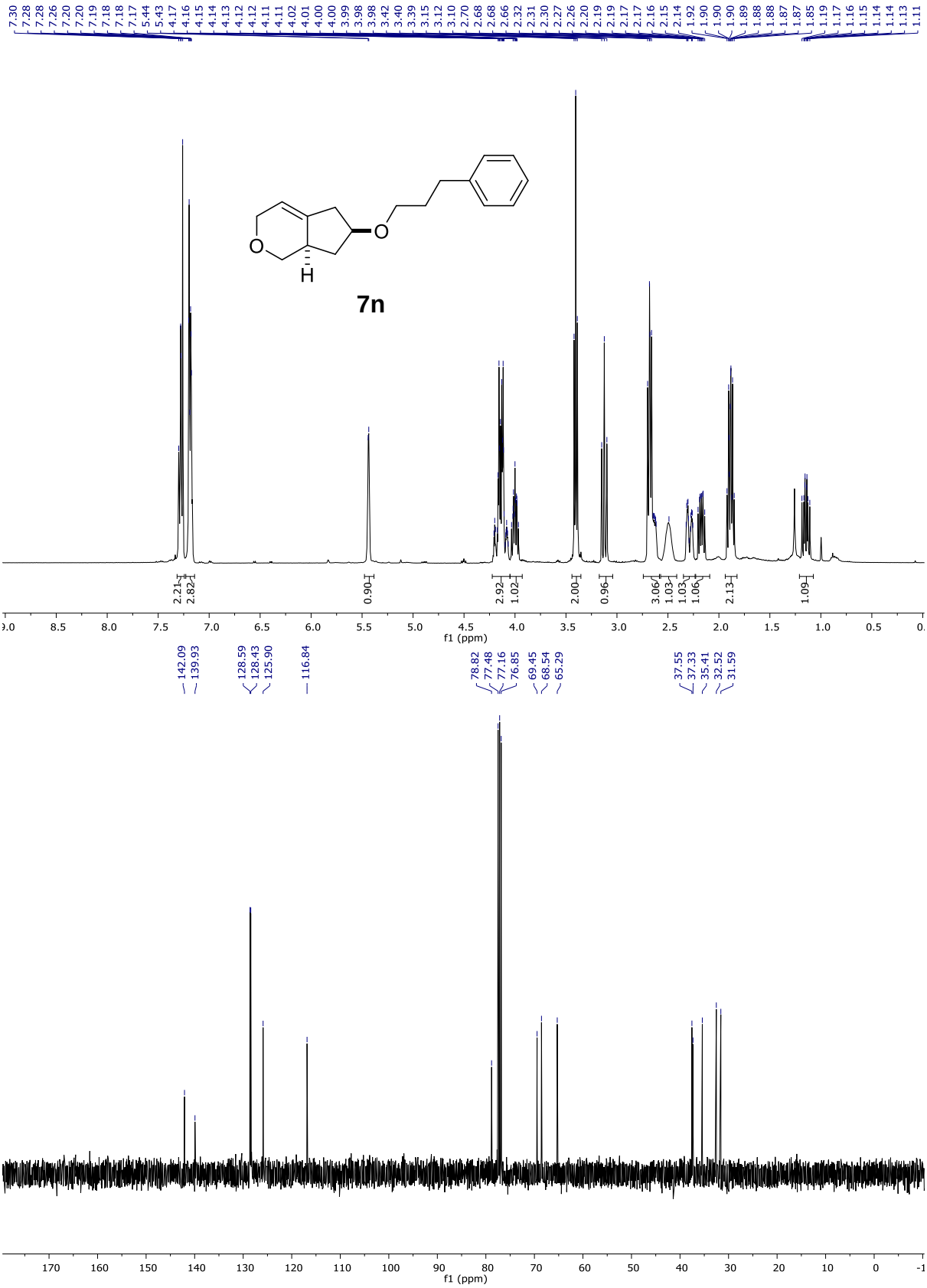

7.26
6.83
6.83
6.82
6.82
6.81
6.80
6.80
6.79
6.79
6.78
5.48
5.44
4.76
4.75
4.74
4.74
4.74
4.73
4.73
4.72
4.72
4.72
4.71
4.43
4.26
4.18
4.14
3.76
3.62
3.57
3.57
2.77
2.77
2.76
2.74
2.74
2.73
2.73
2.72
2.49
2.46
2.40
2.39
2.38
2.37
2.36
2.35
2.34
1.51
1.51
1.50
1.49
1.47
OCH3
BocN
O
H
7l
Rotameric
3.88
0.80
0.88
1.59
3.00
0.87
0.91
3.71
10.13
f1 (ppm)
154.04
151.97
116.92
114.78
79.69
77.66
77.48
77.16
76.84
55.84
38.16
37.65
36.33
29.84
28.64
f1 (ppm)

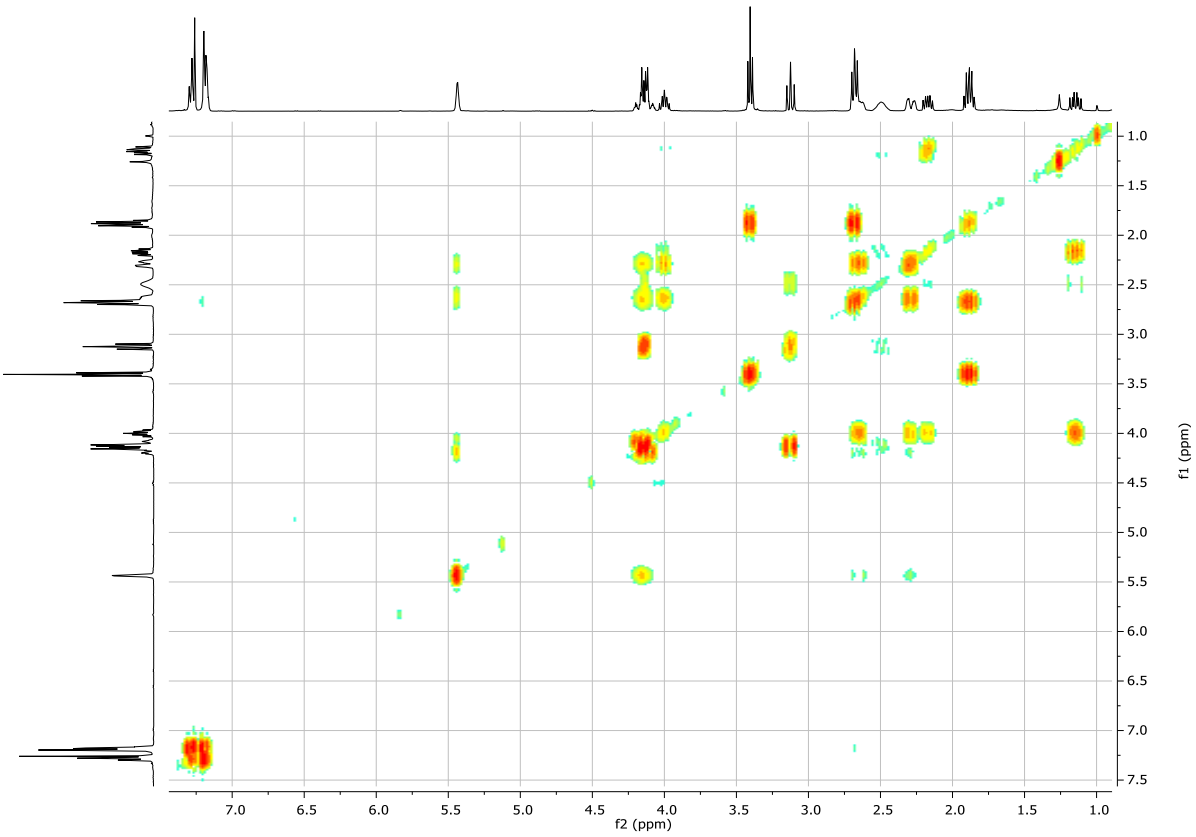

7.26
6.81
5.47
4.74
4.73
4.73
4.72
4.72
4.72
4.71
4.71
4.71
4.70
4.70
3.76
3.42
3.40
3.39
3.39
3.39
3.38
3.37
3.37
3.36
3.35
3.35
3.33
3.32
2.95
2.79
2.79
2.78
2.77
2.77
2.76
2.75
2.75
2.74
2.74
2.44
2.42
2.41
2.40
2.40
2.39
2.38
2.38
2.37
2.35
1.43
1.42
1.42
1.41
1.40
1.40
1.39
OCH3
HN
O
H
7l-H
4.01
1.00
1.05
3.19
3.06
1.21
1.11
4.14
1.12
f1 (ppm)
f2 (ppm)
f1 (ppm)

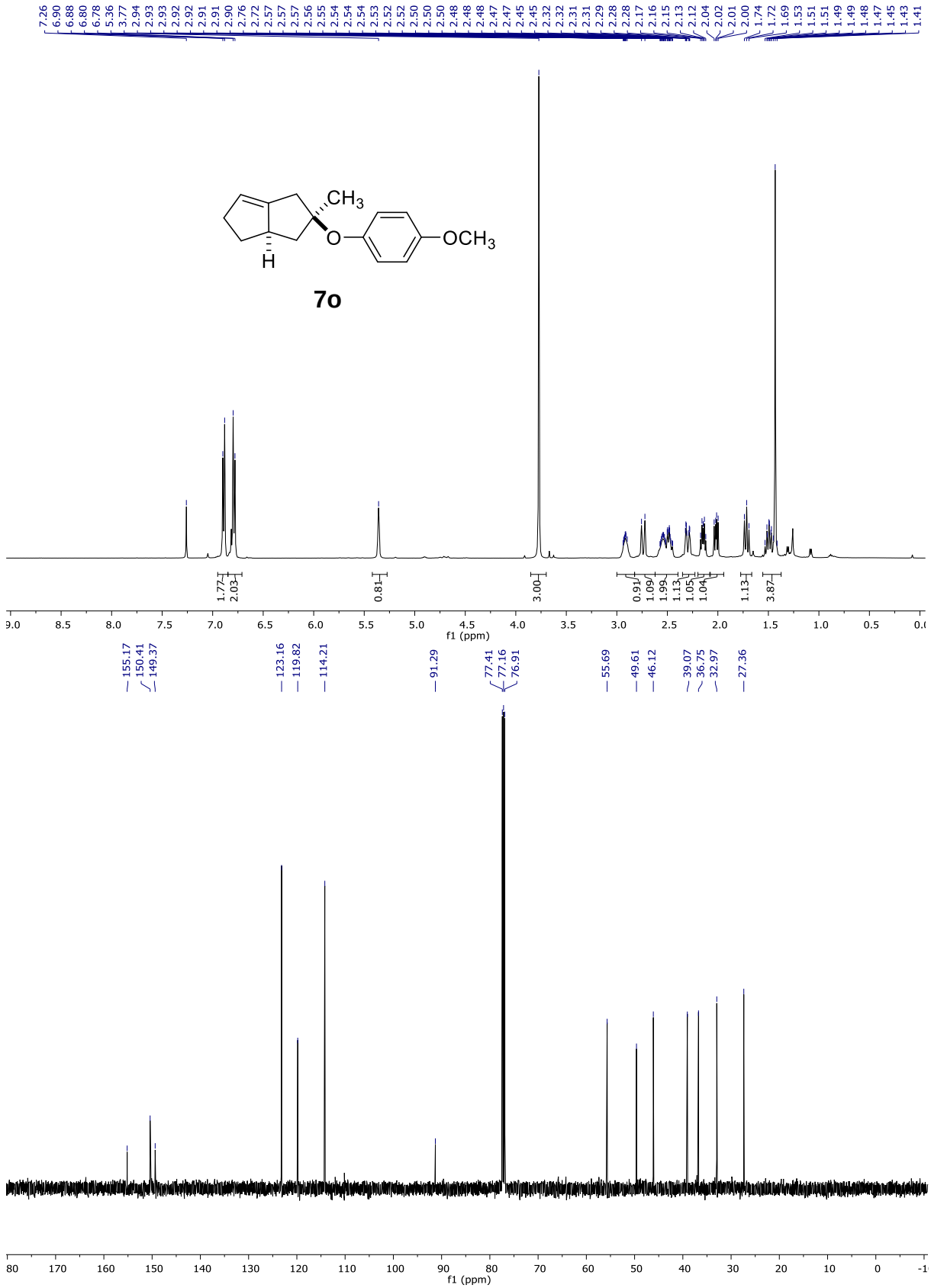

7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0
f1 (ppm)

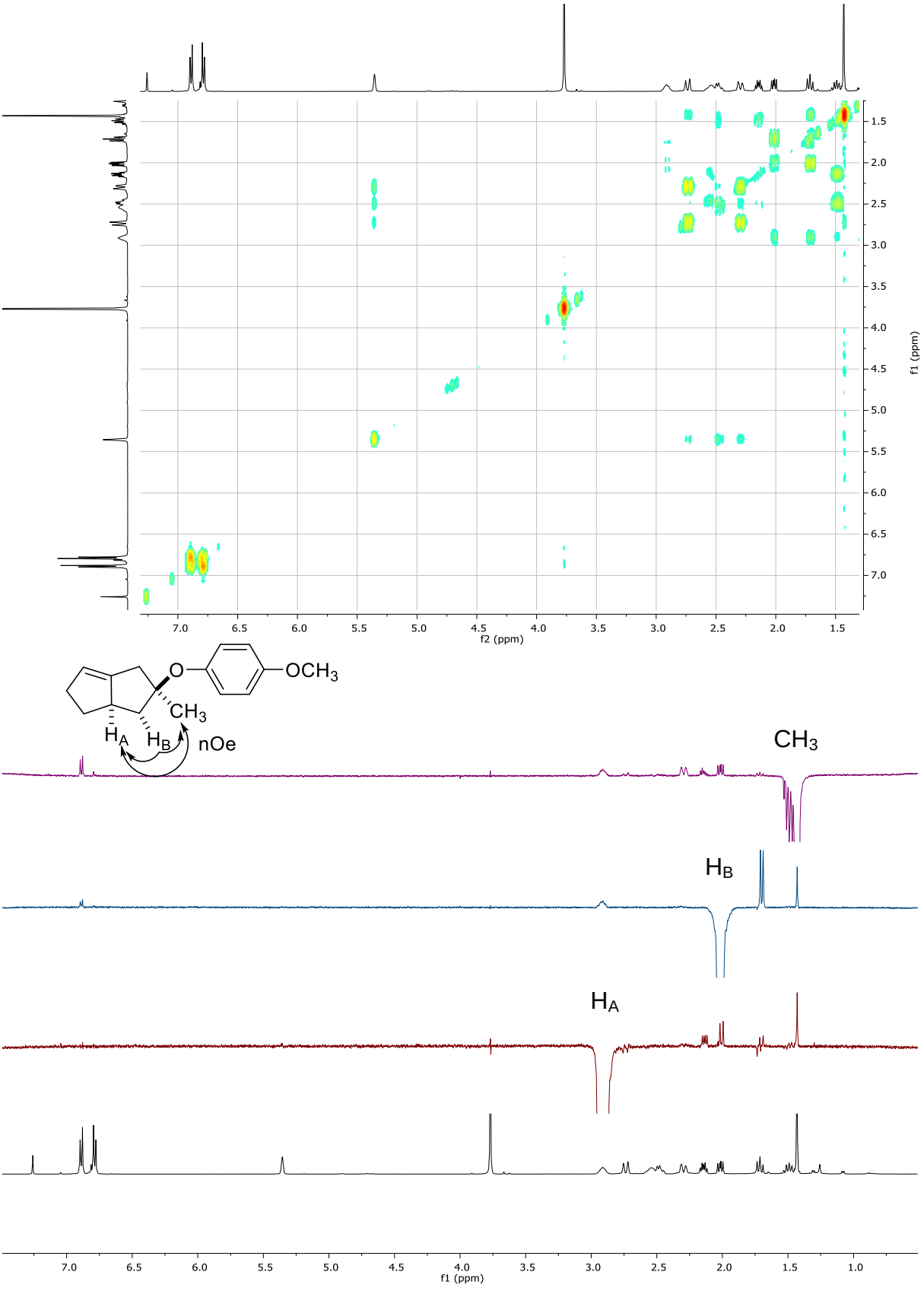

7.26 6.81 5.48 4.77 4.77 4.77 4.77 4.76 4.76 4.76 4.75 4.75 4.74 4.74 4.73 4.22 4.20 4.19 4.18 4.17 4.16 4.16 4.15 4.15 4.15 4.14 4.14 4.13 4.11 3.77 3.18 3.16 3.13 2.80 2.79 2.79 2.78 2.77 2.77 2.76 2.76 2.75 2.75 2.74 2.74 2.74 2.60 2.49 2.49 2.48 2.48 2.47 2.45 2.44 2.44 2.43 2.37 2.36 2.35 2.34 2.34 2.32 2.32 2.30 1.44 1.42 1.41 1.40 1.40 1.39 1.38 1.36
OCH3
O
O
H
7m
3.92 0.88 0.96 2.72 3.00 0.95 1.01 0.97 0.96 0.97 1.02
f1 (ppm)
154.03 152.04 139.64 117.22 116.86 114.79 77.48 77.16 76.84 69.45 65.22 55.84 38.12 37.30 35.33
f1 (ppm)


7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
f2 (ppm)
1.5
2.0
2.5
3.0
3.5
4.0
4.5
5.0
5.5
6.0
6.5
7.0
f1 (ppm)


7.30 7.28 7.28 7.26 7.20 7.20 7.19 7.18 7.18 7.17 5.44 5.43 4.17 4.16 4.15 4.14 4.13 4.12 4.12 4.11 4.11 4.02 4.01 4.00 4.00 3.99 3.98 3.98 3.42 3.40 3.39 3.15 3.12 3.10 2.70 2.68 2.68 2.66 2.32 2.31 2.30 2.27 2.26 2.20 2.19 2.19 2.17 2.17 2.16 2.15 2.14 1.92 1.90 1.90 1.90 1.89 1.88 1.88 1.87 1.87 1.85 1.19 1.17 1.16 1.15 1.14 1.14 1.13 1.11
O
O
H
7n
2.21 2.82 0.90 2.92 1.02 2.00 0.96 3.06 1.03 1.03 1.06 2.13 1.09
f1 (ppm)
142.09 139.93 128.59 128.43 125.90 116.84 78.82 77.48 77.16 76.85 69.45 68.54 65.29 37.55 37.33 35.41 32.52 31.59
f1 (ppm)


f2 (ppm)
f1 (ppm)


7.26 6.90 6.88 6.80 6.78 5.36 3.77 2.94 2.93 2.93 2.92 2.92 2.91 2.91 2.90 2.76 2.72 2.57 2.57 2.57 2.56 2.55 2.54 2.54 2.54 2.53 2.52 2.52 2.50 2.50 2.50 2.48 2.48 2.48 2.47 2.47 2.45 2.45 2.32 2.32 2.31 2.31 2.29 2.28 2.28 2.17 2.16 2.15 2.13 2.12 2.04 2.02 2.01 2.00 1.74 1.72 1.69 1.53 1.51 1.51 1.49 1.49 1.48 1.47 1.45 1.43 1.41
CH3
O
OCH3
H
7o
1.77
2.03
0.81
3.00
0.91
1.09
1.99
1.13
1.05
1.04
1.13
3.87
f1 (ppm)
155.17
150.41
149.37
123.16
119.82
114.21
91.29
77.41
77.16
76.91
55.69
49.61
46.12
39.07
36.75
32.97
27.36
f1 (ppm)


f2 (ppm)
f1 (ppm)
OCH3
CH3
HA
HB
nOe
CH3
HB
HA
f1 (ppm)


7.26
6.82
5.36
4.93
4.92
4.92
4.91
4.90
4.90
4.89
4.89
4.88
3.77
2.88
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2.13
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1.52
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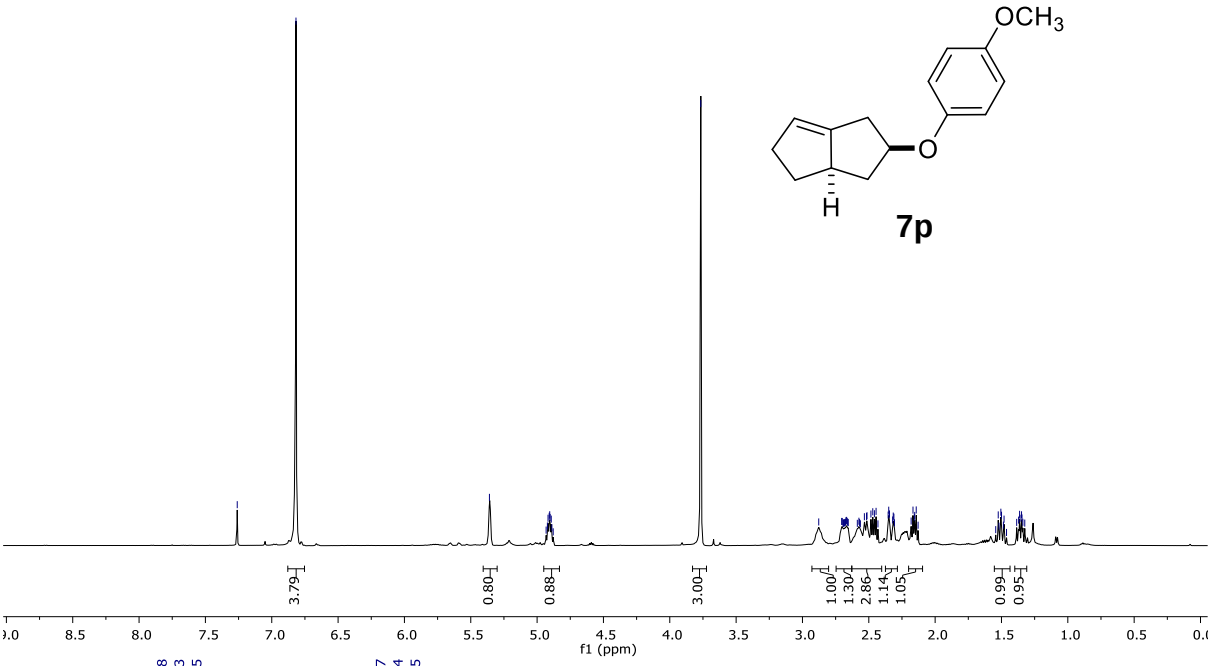
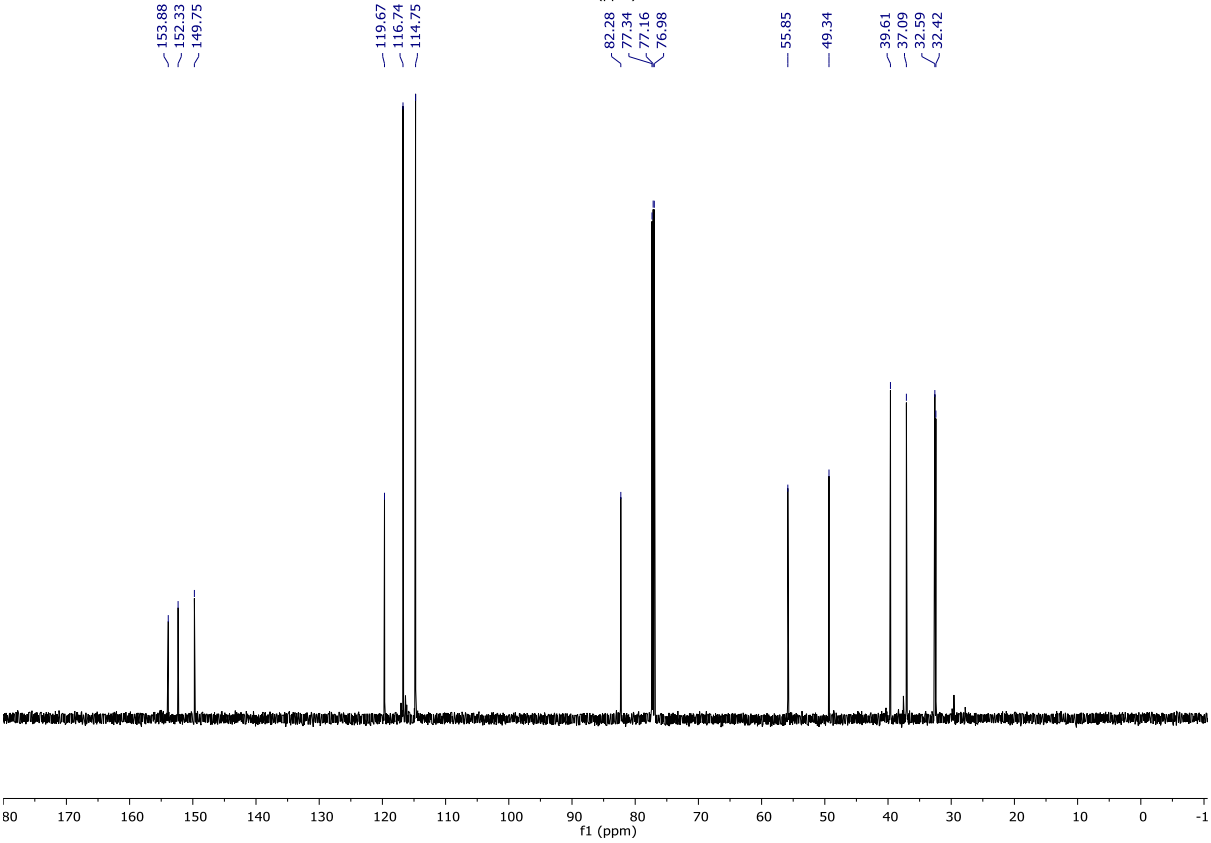
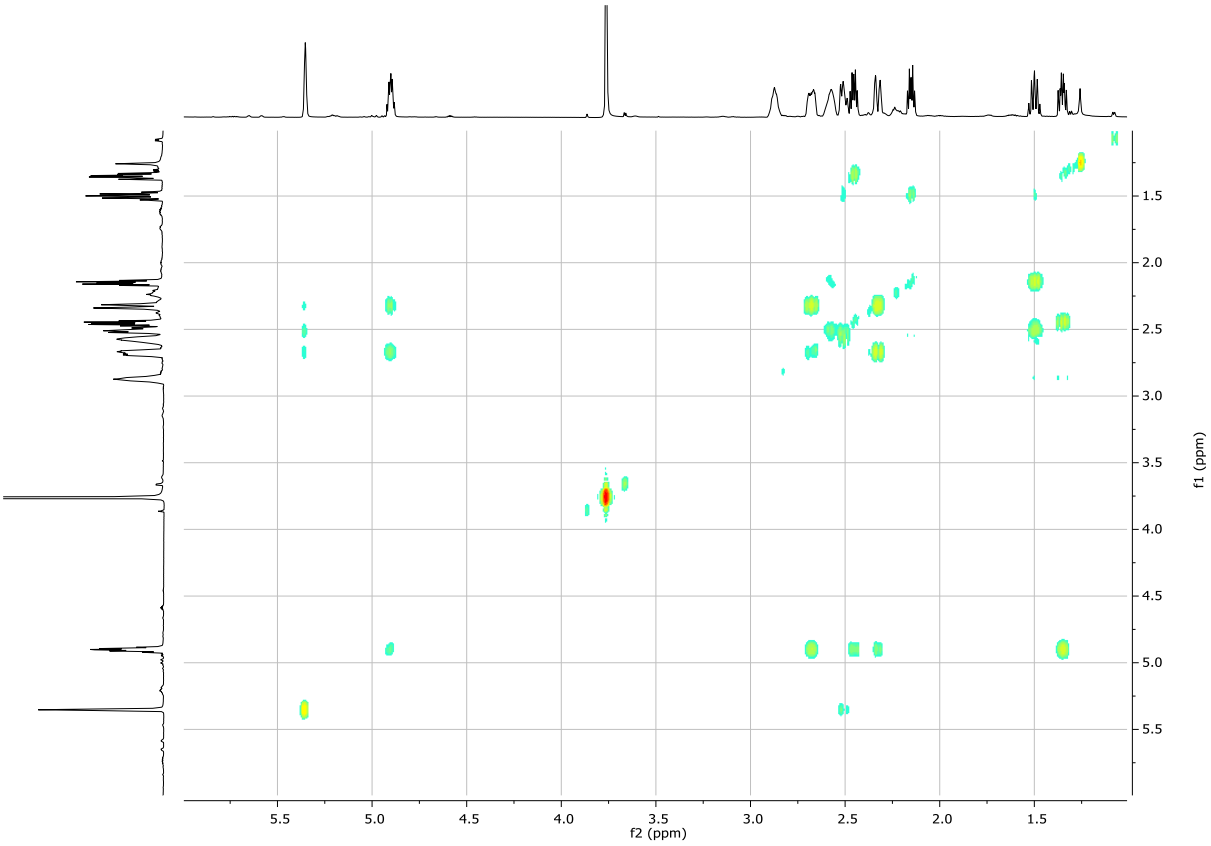
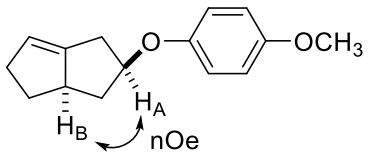
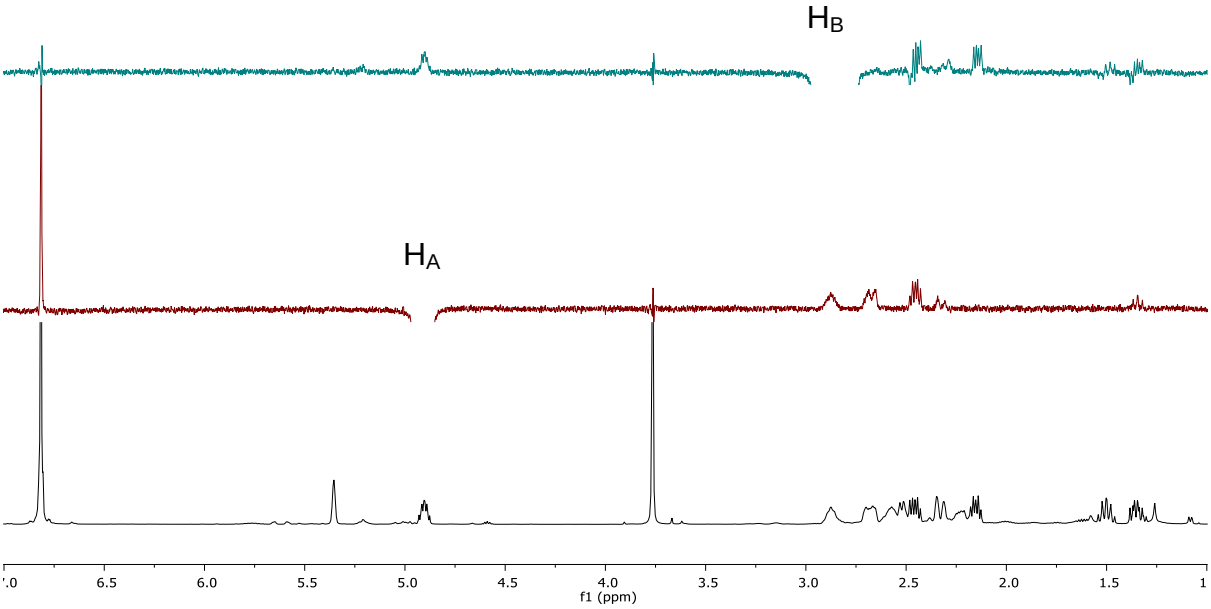
1.34
1.32

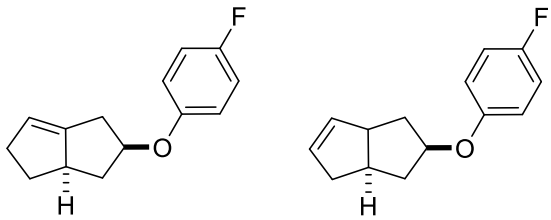

OCH3
O
H
7p
3.79
0.80
0.88
3.00
1.00
1.30
2.86
1.14
1.05
0.99
0.95
f1 (ppm)


153.88
152.33
149.75
119.67
116.74
114.75
82.28
77.34
77.16
76.98
55.85
49.34
39.61
37.09
32.59
32.42
f1 (ppm)

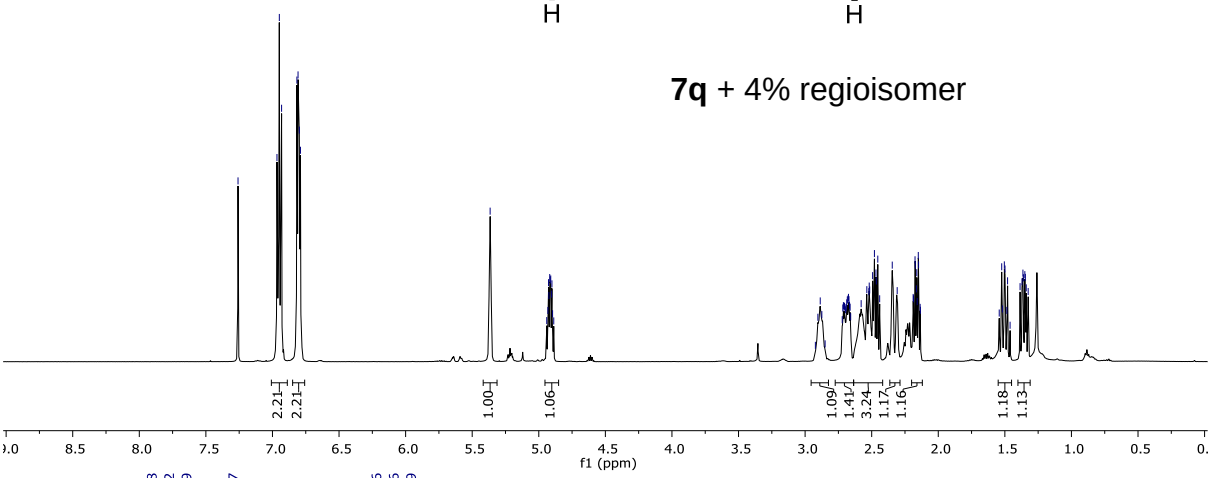

5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
f2 (ppm)
f1 (ppm)

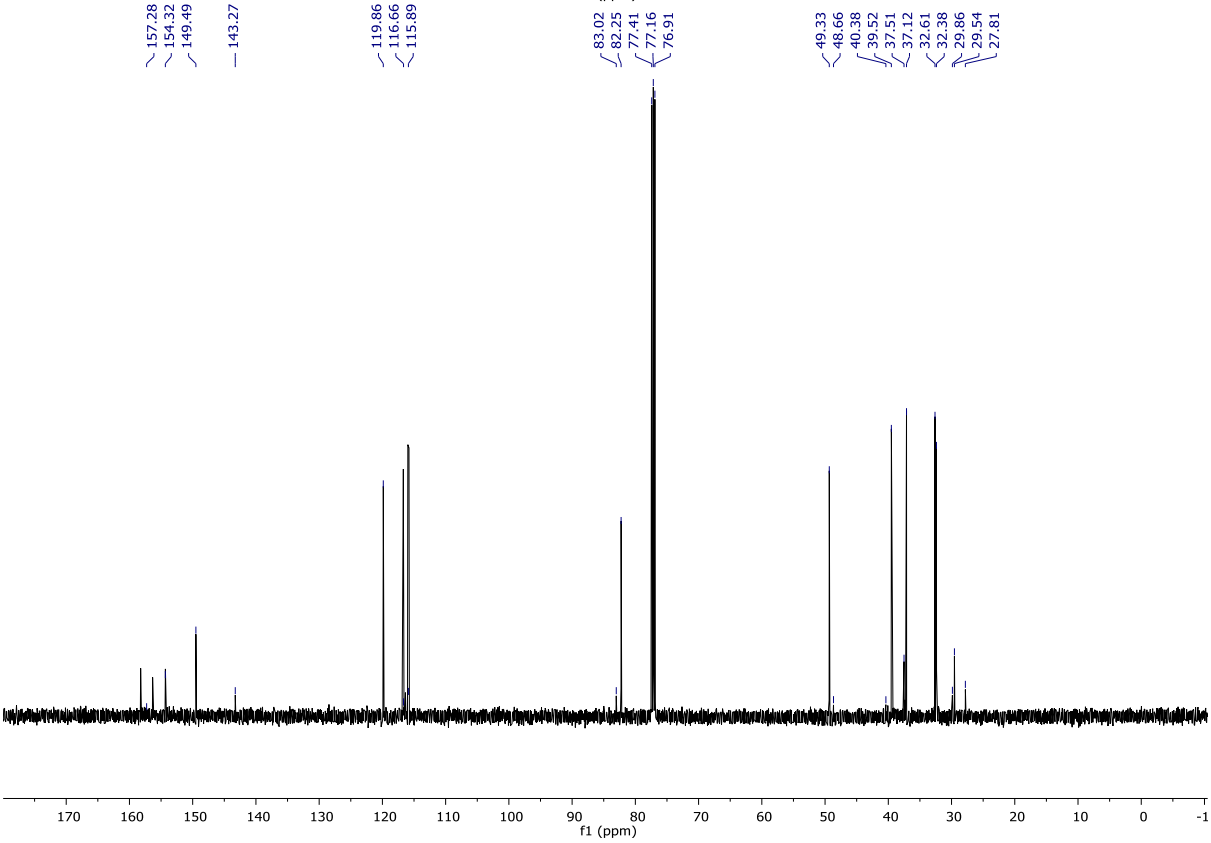

O
OCH3
HA
HB
nOe

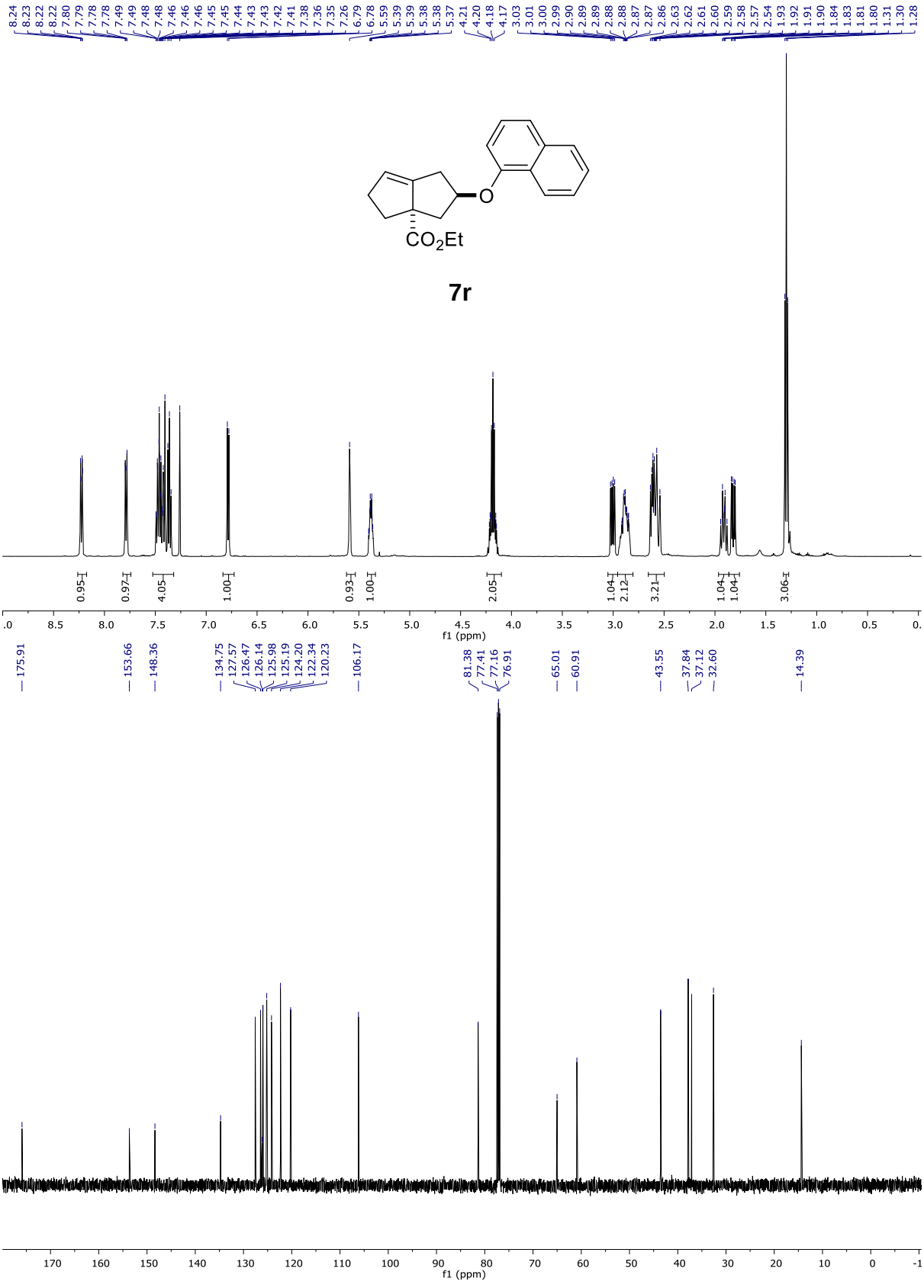

HB
HA
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
f1 (ppm)



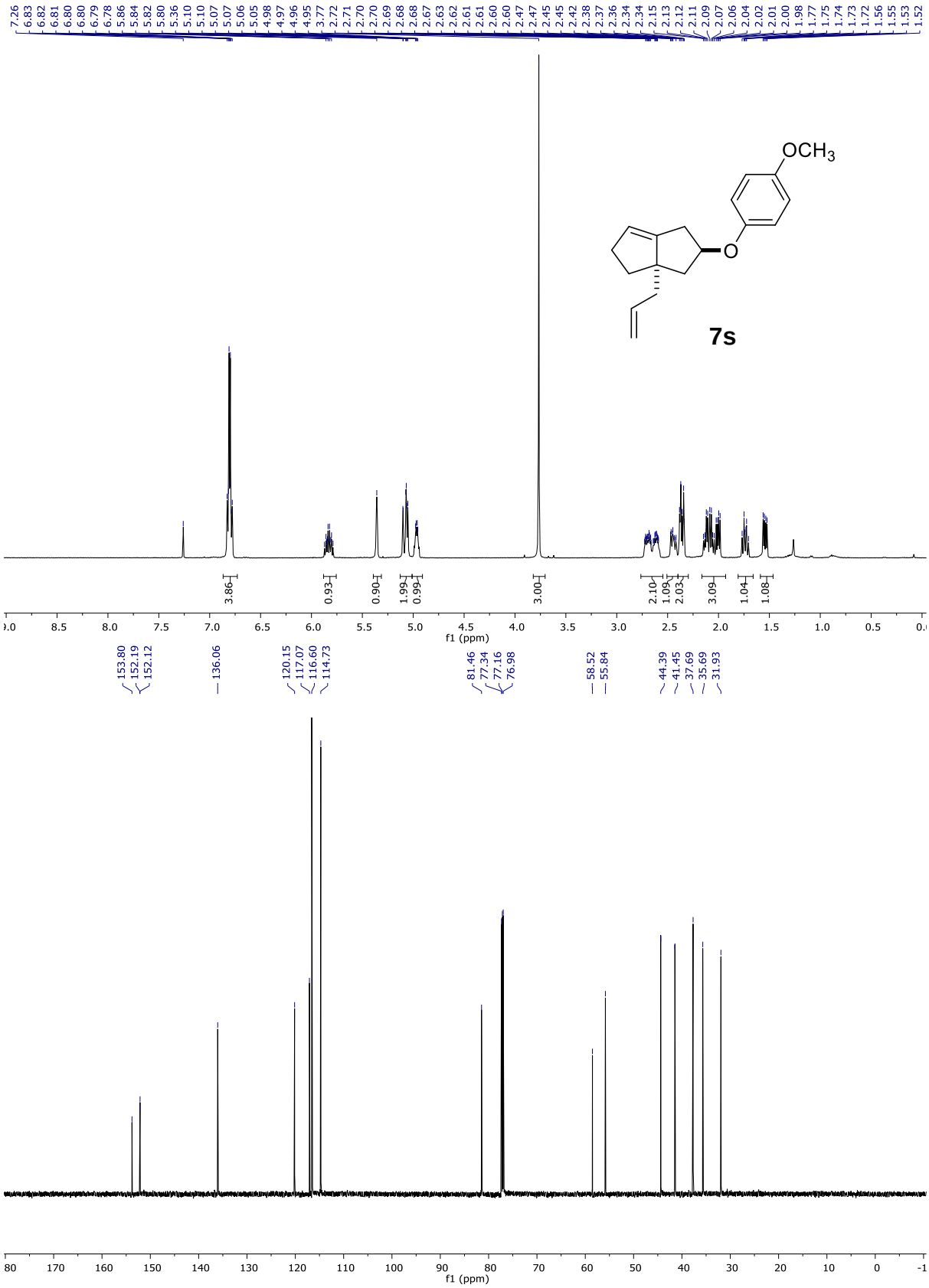
7q + 4% regioisomer

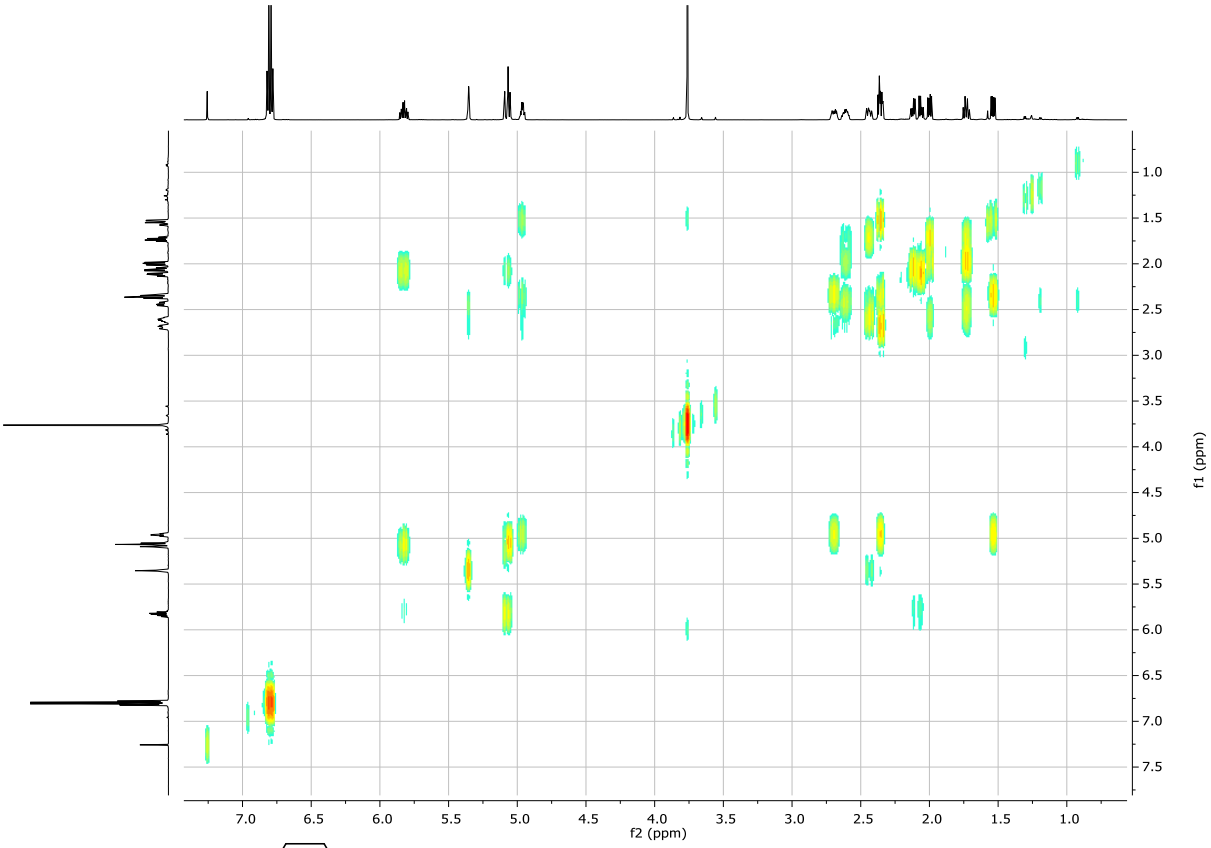


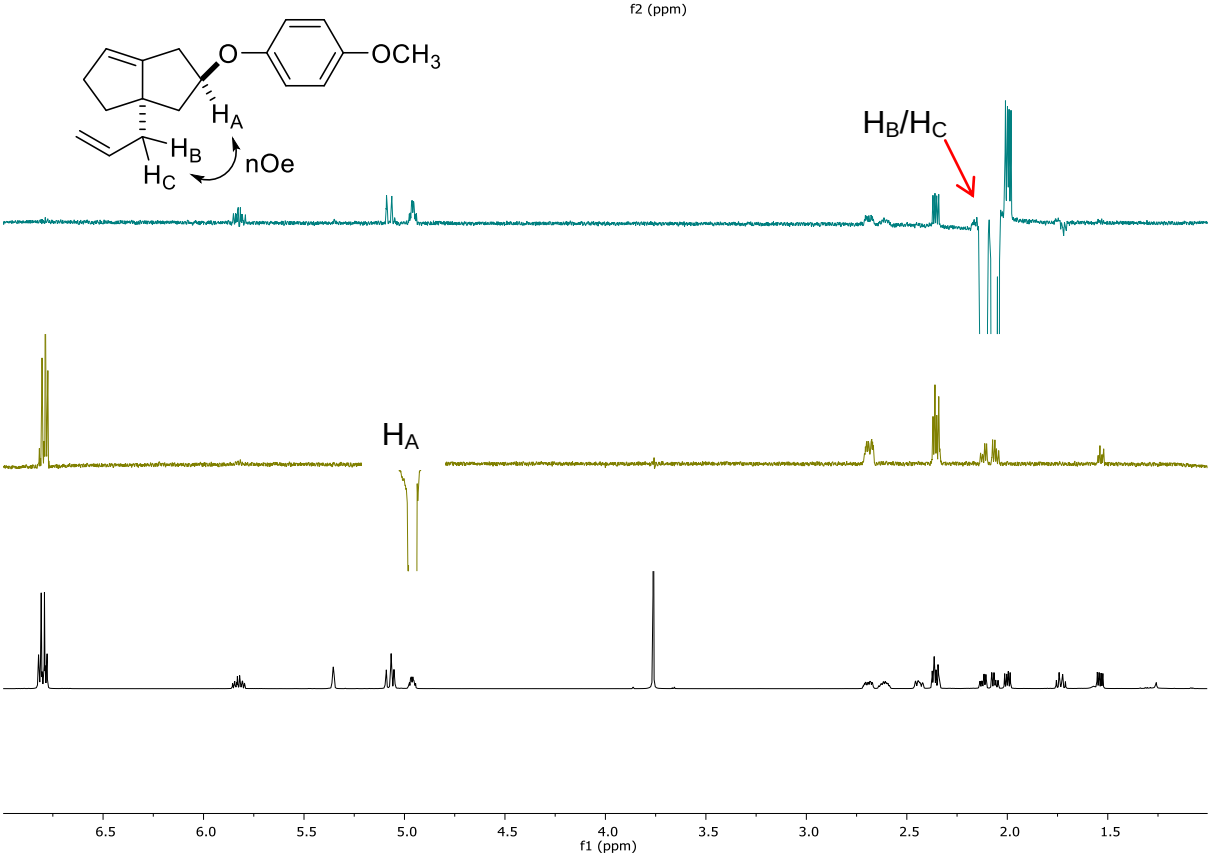


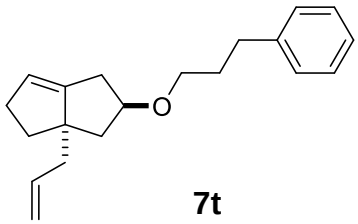

8.24 8.23 8.22 8.22 7.80 7.79 7.78 7.78 7.49 7.49 7.48 7.48 7.46 7.46 7.46 7.45 7.45 7.44 7.43 7.43 7.42 7.41 7.38 7.36 7.35 7.26 6.79 6.78 5.59 5.39 5.39 5.38 5.38 5.37 4.21 4.20 4.18 4.17 3.03 3.01 3.00 2.99 2.90 2.89 2.89 2.88 2.88 2.87 2.87 2.86 2.63 2.62 2.61 2.60 2.59 2.58 2.57 2.54 1.93 1.92 1.91 1.90 1.84 1.83 1.81 1.80 1.31 1.30 1.28
O
CO2Et
7r
0.95 0.97 4.05 1.00 0.93 1.00 2.05 1.04 2.12 3.21 1.04 1.04 3.06
f1 (ppm)
175.91 153.66 148.36 134.75 127.57 126.47 126.14 125.98 125.19 124.20 122.34 120.23 106.17 81.38 77.41 77.16 76.91 65.01 60.91 43.55 37.84 37.12 32.60 14.39
f1 (ppm)


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
f2 (ppm)
1.0
1.5
2.0
2.5
3.0
3.5
4.0
4.5
5.0
5.5
6.0
6.5
7.0
7.5
8.0
8.5
f1 (ppm)

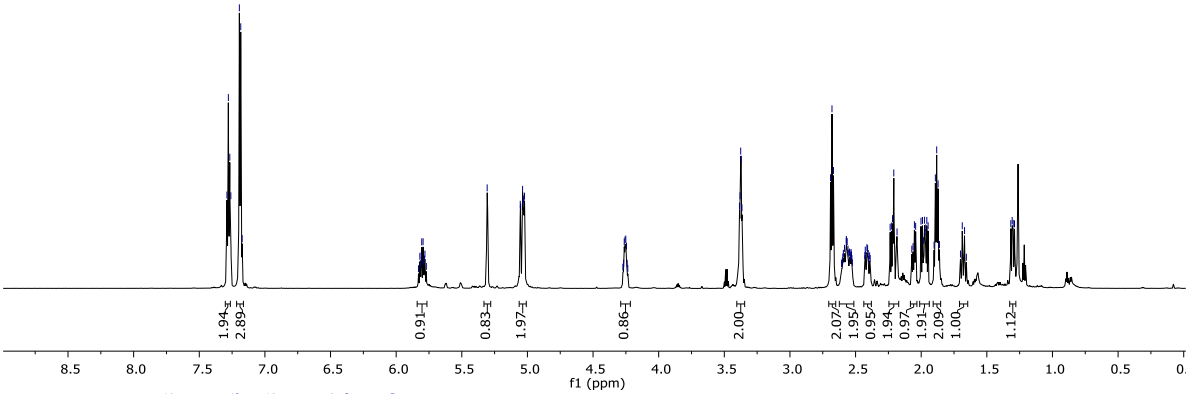

7.26 6.83 6.82 6.81 6.80 6.80 6.80 6.79 6.78 6.86 5.84 5.82 5.80 5.36 5.10 5.10 5.07 5.07 5.06 5.05 4.98 4.97 4.96 4.95 3.77 2.72 2.71 2.70 2.70 2.69 2.68 2.68 2.67 2.63 2.62 2.61 2.61 2.60 2.60 2.47 2.47 2.45 2.45 2.42 2.38 2.37 2.36 2.34 2.34 2.15 2.13 2.12 2.11 2.09 2.07 2.06 2.04 2.02 2.01 2.00 1.98 1.77 1.75 1.74 1.73 1.72 1.56 1.55 1.53 1.52
OCH3
O
7s
3.86 0.93 0.90 1.99 0.99 3.00 2.10 1.09 2.03 3.09 1.04 1.08
f1 (ppm)
153.80 152.19 152.12 136.06 120.15 117.07 116.60 114.73 81.46 77.34 77.16 76.98 58.52 55.84 44.39 41.45 37.69 35.69 31.93
f1 (ppm)

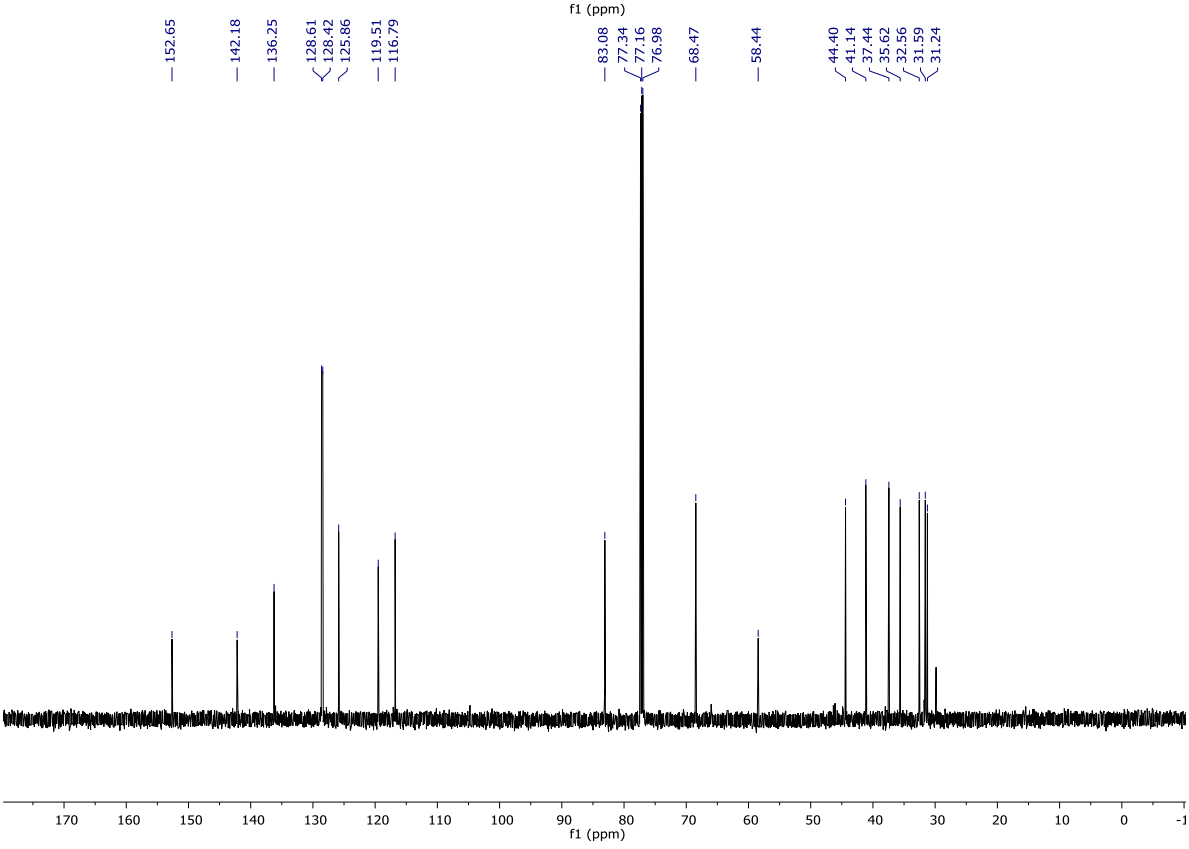

f2 (ppm)
f1 (ppm)


O
OCH3
HA
HB
HC
nOe
HB/HC
HA
f1 (ppm)

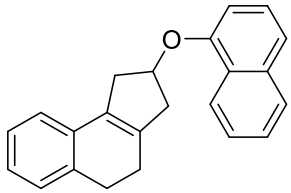


7t

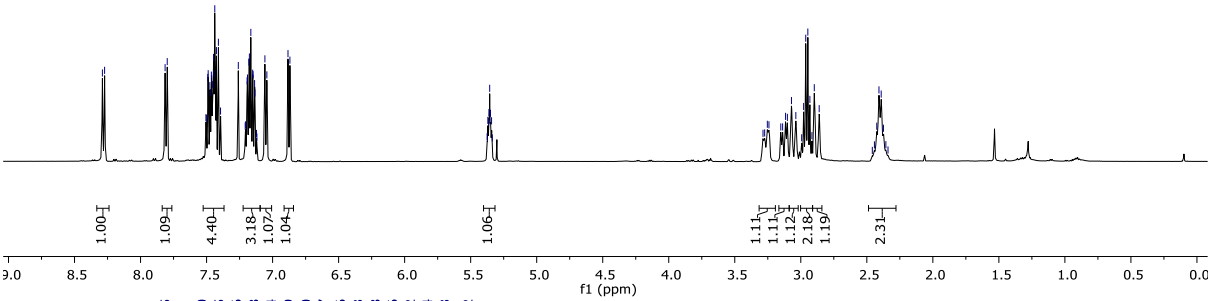


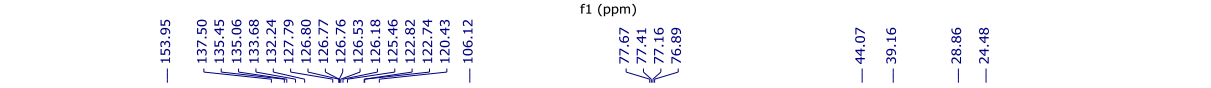


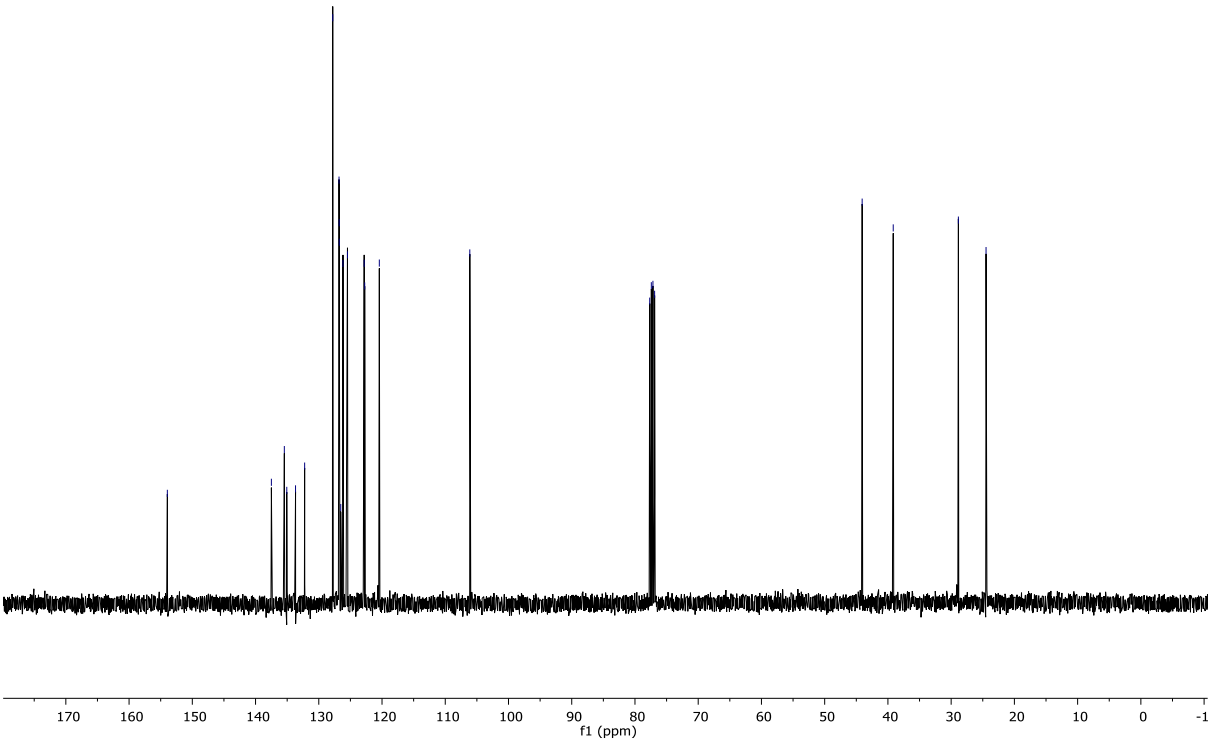

8.29 8.27 7.81 7.80 7.50 7.50 7.49 7.49 7.47 7.47 7.46 7.46 7.45 7.45 7.44 7.44 7.43 7.41 7.39 7.26 7.21 7.20 7.19 7.19 7.18 7.18 7.16 7.15 7.15 7.14 7.13 7.12 7.12 7.06 7.04 6.88 6.87 5.38 5.37 5.36 5.36 5.36 5.35 5.34 5.34 3.29 3.27 3.25 3.24 3.15 3.14 3.12 3.10 3.07 3.04 2.99 2.98 2.96 2.95 2.93 2.92 2.90 2.86 2.44 2.42 2.41 2.39 2.37 2.36

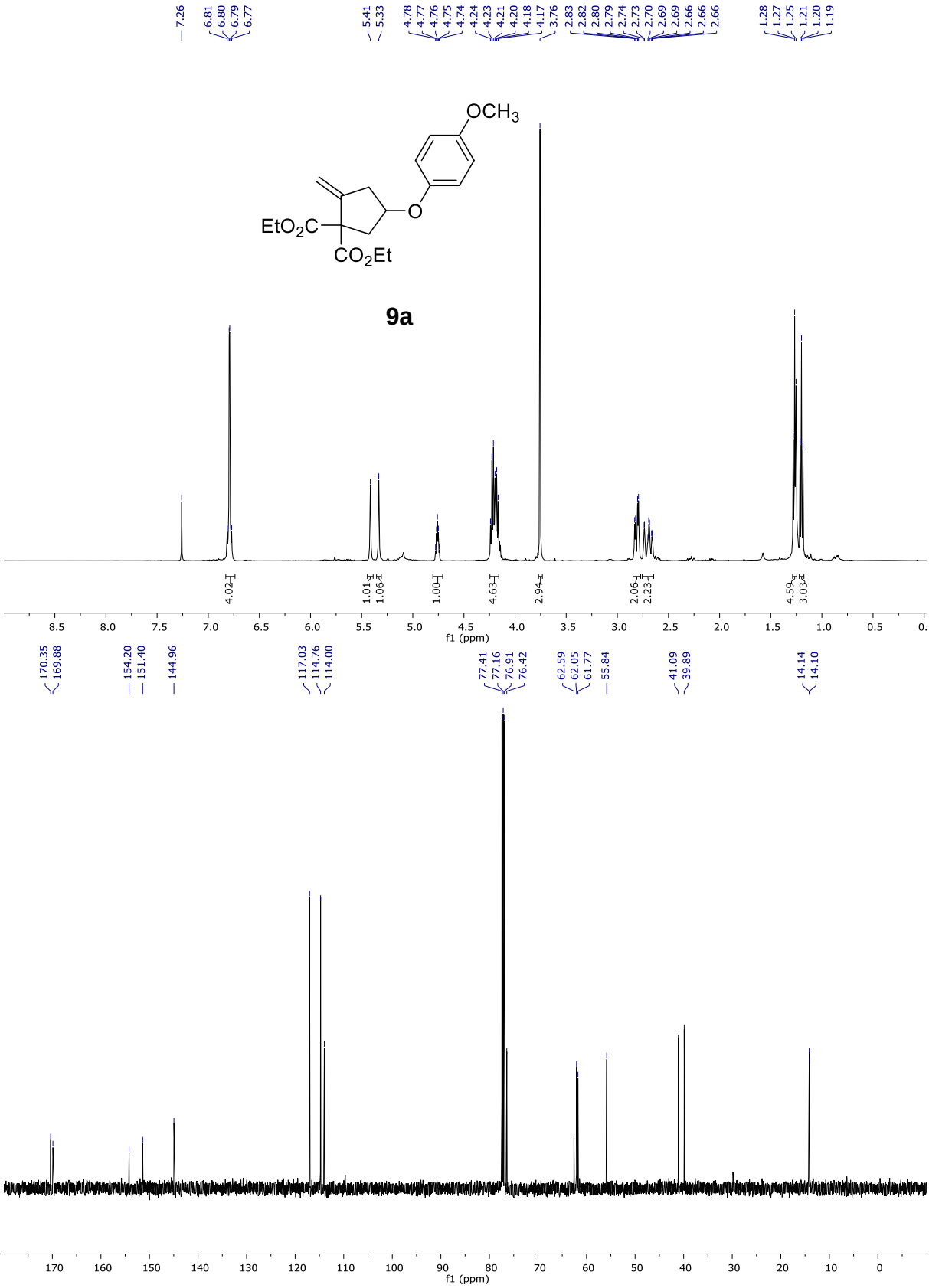

O

7u

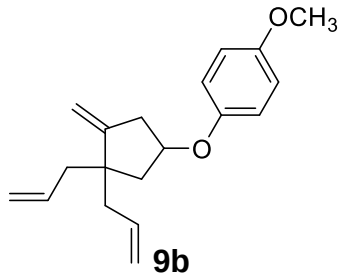

1.00 1.09 4.40 3.18 1.07 1.04 1.06 1.11 1.11 1.12 2.18 1.19 2.31
9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0
f1 (ppm)


153.95 137.50 135.45 135.06 133.68 132.24 127.79 126.80 126.77 126.76 126.53 126.18 125.46 122.82 122.74 120.43 106.12 77.67 77.41 77.16 76.89 44.07 39.16 28.86 24.48

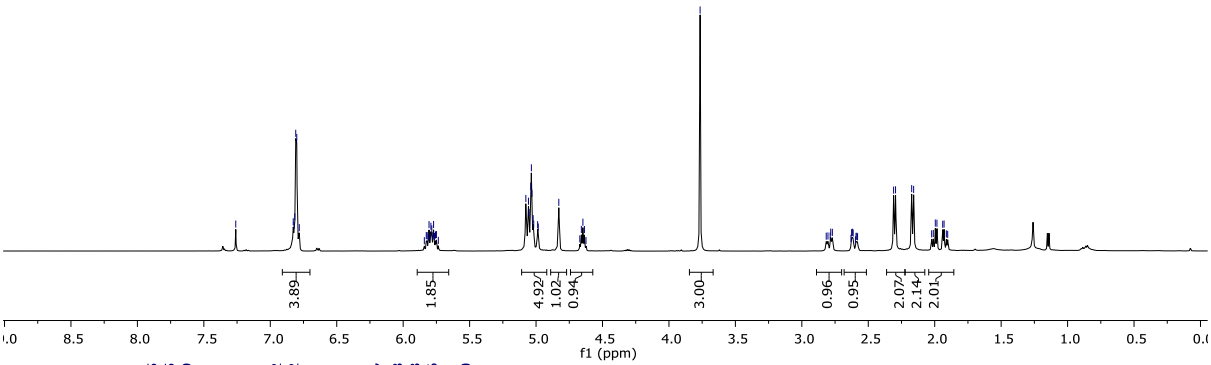

170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 -1
f1 (ppm)

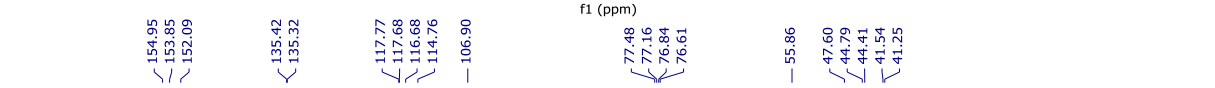

7.26
6.81
6.80
6.79
6.77
5.41
5.33
4.78
4.77
4.76
4.75
4.74
4.24
4.23
4.21
4.20
4.18
4.17
3.76
2.83
2.82
2.80
2.79
2.74
2.73
2.70
2.69
2.66
2.66
2.66
1.28
1.27
1.25
1.21
1.20
1.19
OCH3
O
EtO2C
CO2Et
9a
4.02
1.01
1.06
1.00
4.63
2.94
2.06
2.23
4.59
3.03
f1 (ppm)
170.35
169.88
154.20
151.40
144.96
117.03
114.76
114.00
77.41
77.16
76.91
76.42
62.59
62.05
61.77
55.84
41.09
39.89
14.14
14.10
f1 (ppm)

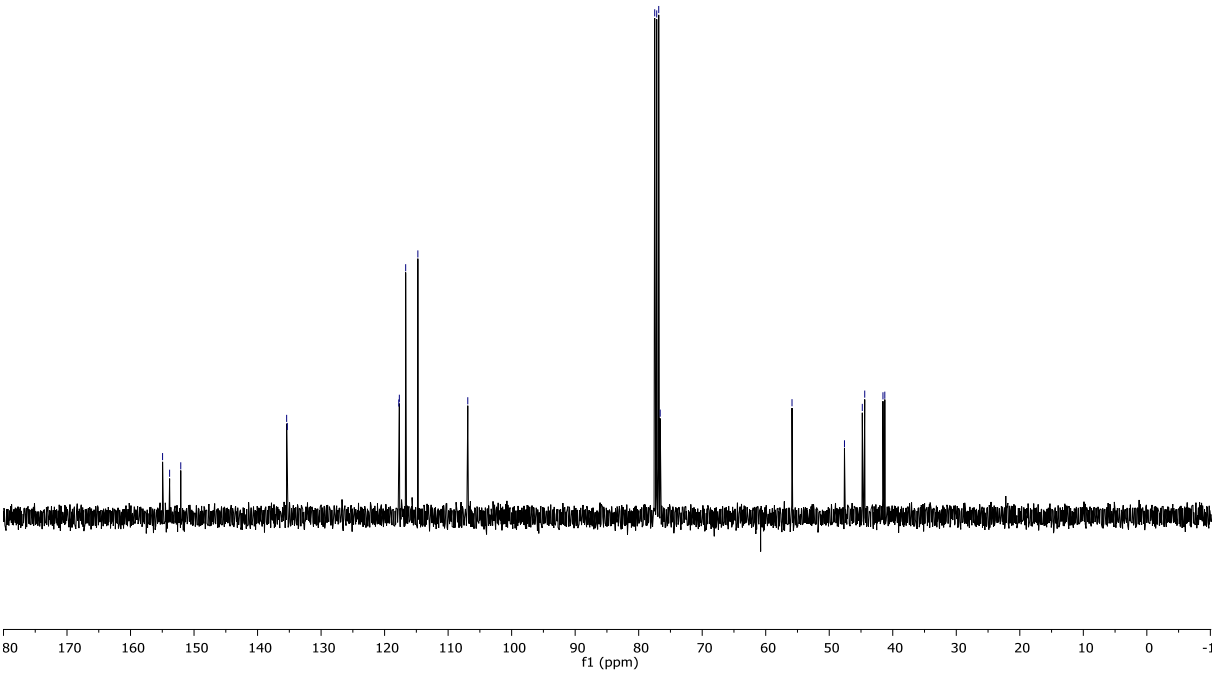

7.26
6.83
6.82
6.82
6.81
6.80
6.78
5.83
5.82
5.81
5.80
5.79
5.78
5.78
5.77
5.76
5.76
5.75
5.08
5.06
5.05
5.04
5.04
5.03
5.02
5.02
4.99
4.98
4.83
4.66
4.65
4.64
3.77
2.82
2.80
2.79
2.78
2.77
2.63
2.62
2.61
2.59
2.59
2.58
2.31
2.29
2.17
2.16
2.02
2.01
2.00
1.98
1.94
1.93
1.91

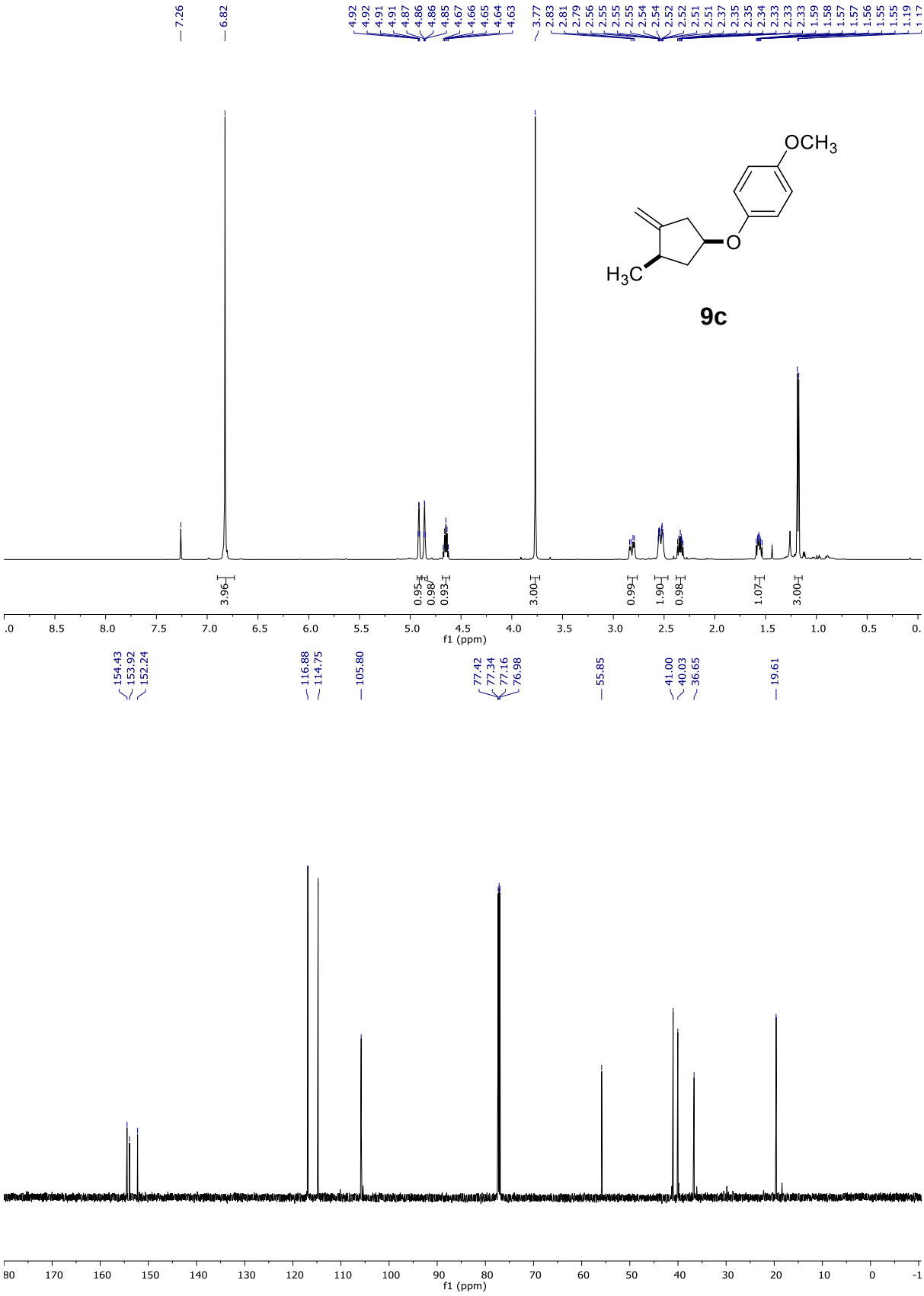

OCH3
O

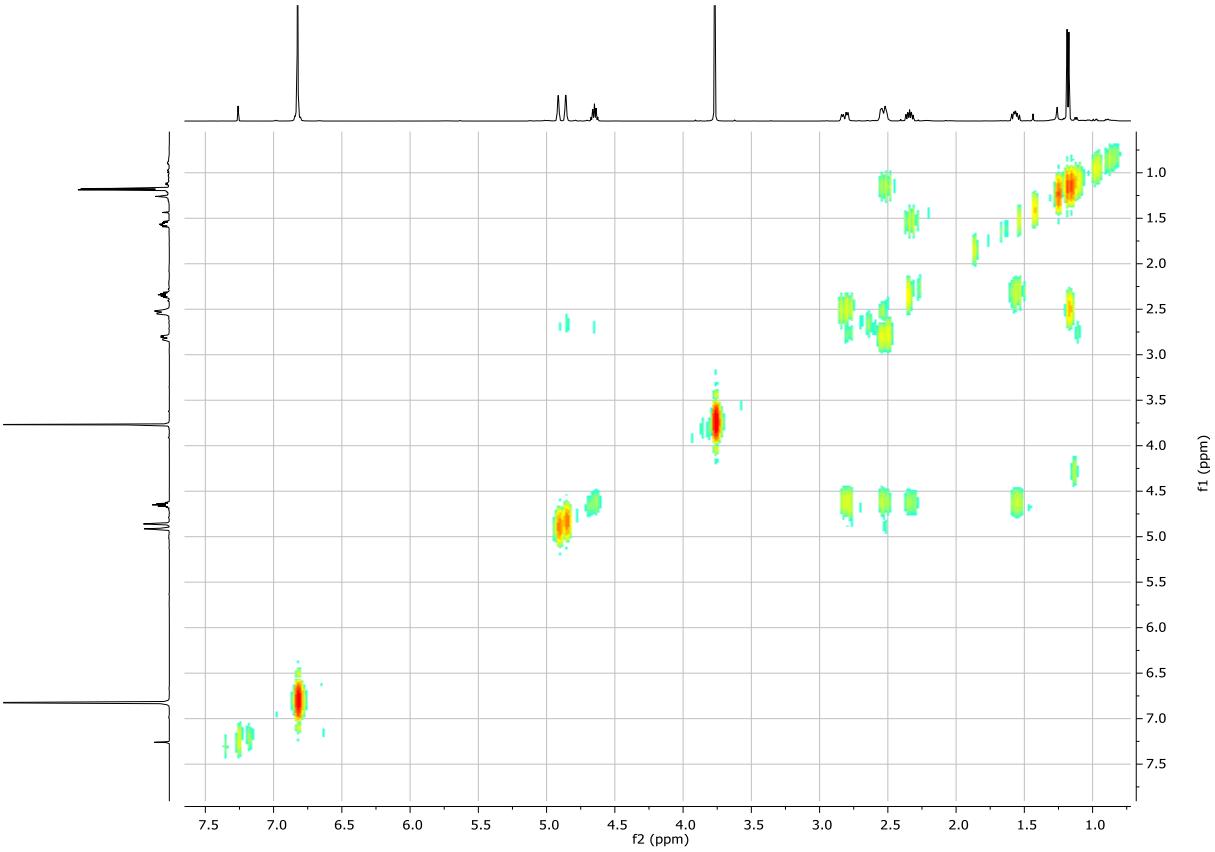
9b

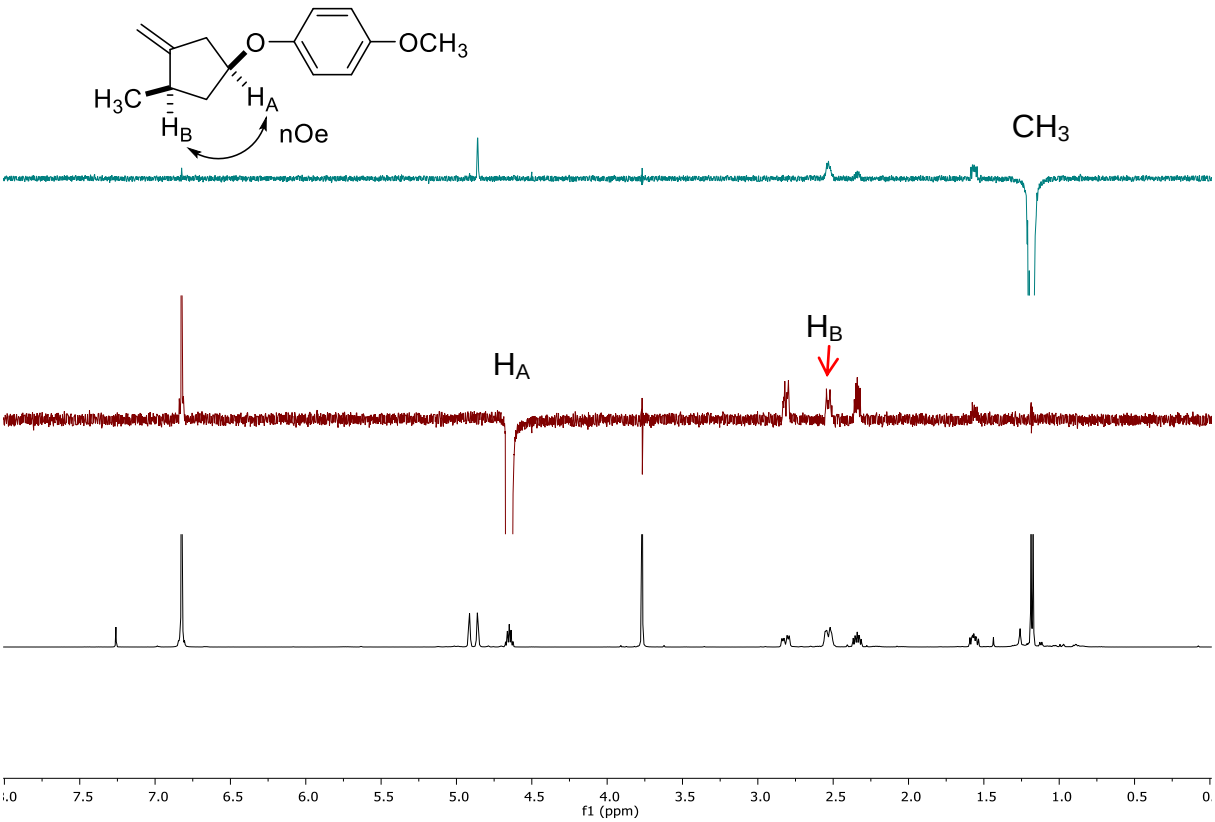

3.89
1.85
4.92
1.02
0.94
3.00
0.96
0.95
2.07
2.14
2.01
f1 (ppm)

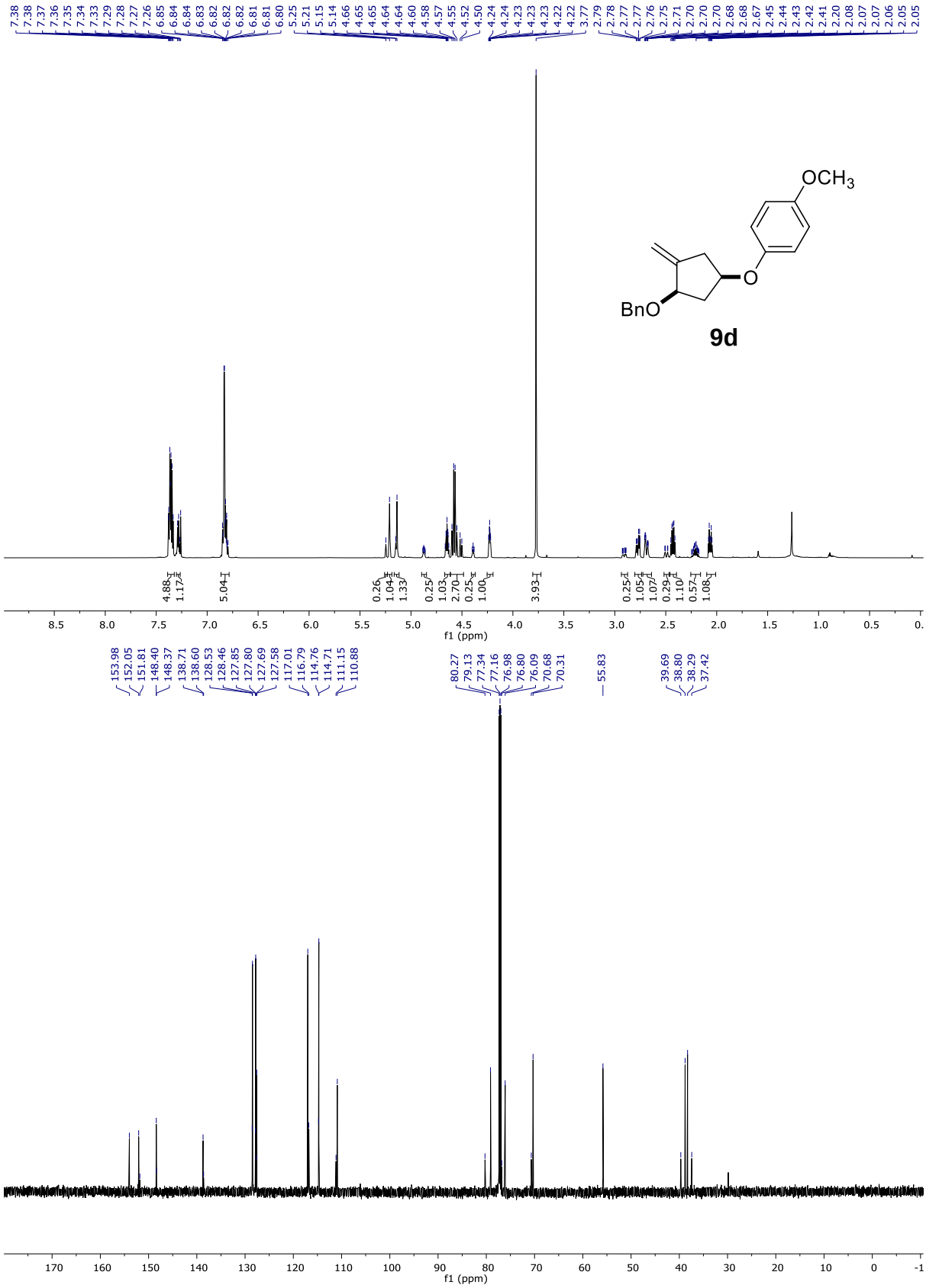

154.95
153.85
152.09
135.42
135.32
117.77
117.68
116.68
114.76
106.90
77.48
77.16
76.84
76.61
55.86
47.60
44.79
44.41
41.54
41.25

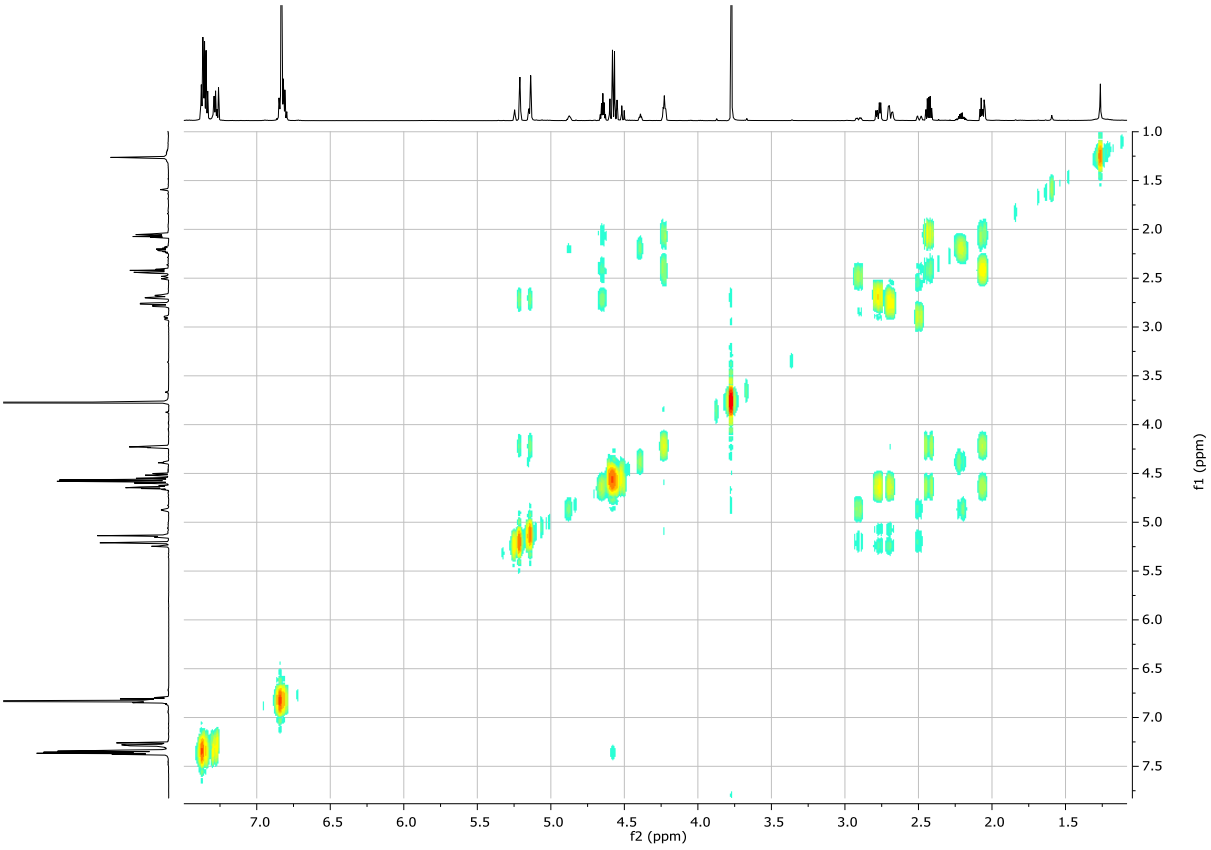

f1 (ppm)

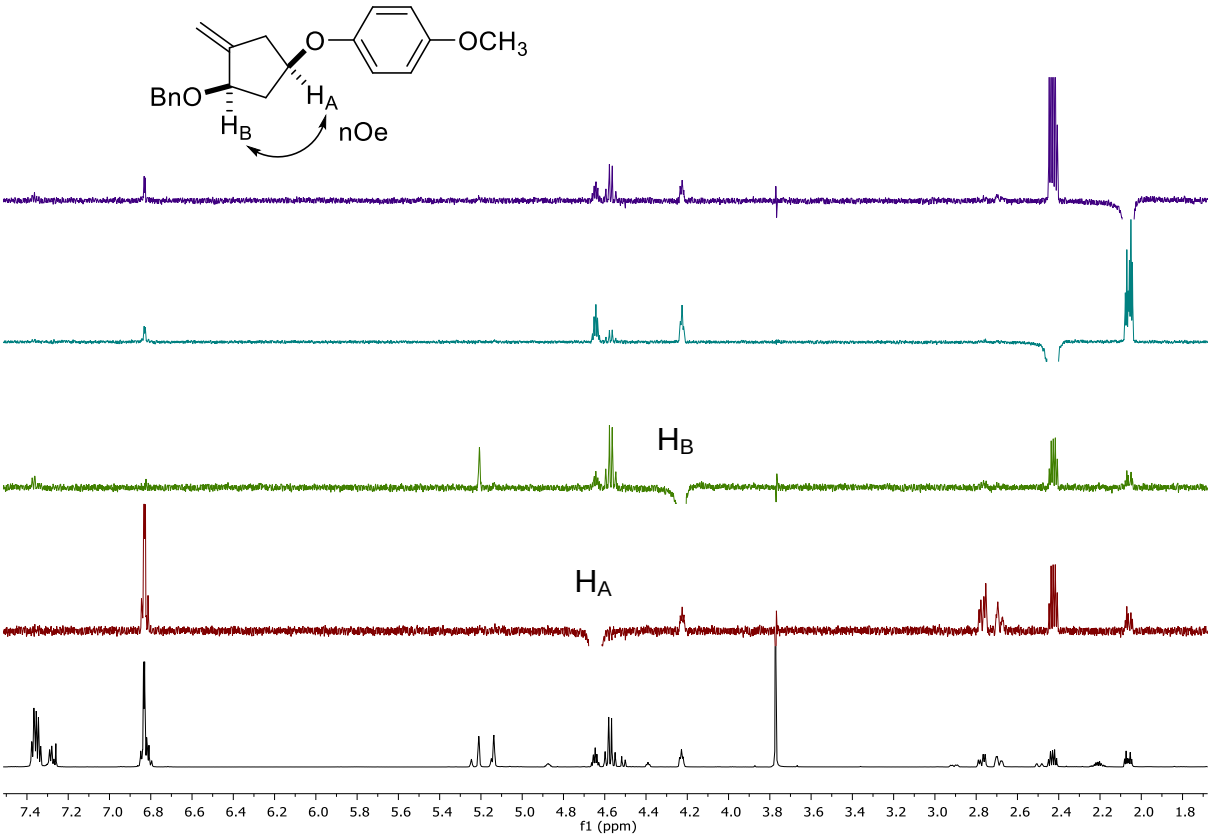

7.26
6.82
4.92
4.92
4.91
4.91
4.87
4.86
4.86
4.85
4.67
4.66
4.65
4.64
4.63
3.77
2.83
2.81
2.79
2.56
2.55
2.55
2.55
2.54
2.54
2.52
2.52
2.51
2.51
2.37
2.35
2.35
2.34
2.33
2.33
2.33
1.59
1.58
1.57
1.57
1.56
1.55
1.55
1.19
OCH3
O
H3C
9c
3.96
0.95
0.98
0.93
3.00
0.99
1.90
0.98
1.07
3.00
f1 (ppm)
154.43
153.92
152.24
116.88
114.75
105.80
77.42
77.34
77.16
76.98
55.85
41.00
40.03
36.65
19.61
f1 (ppm)

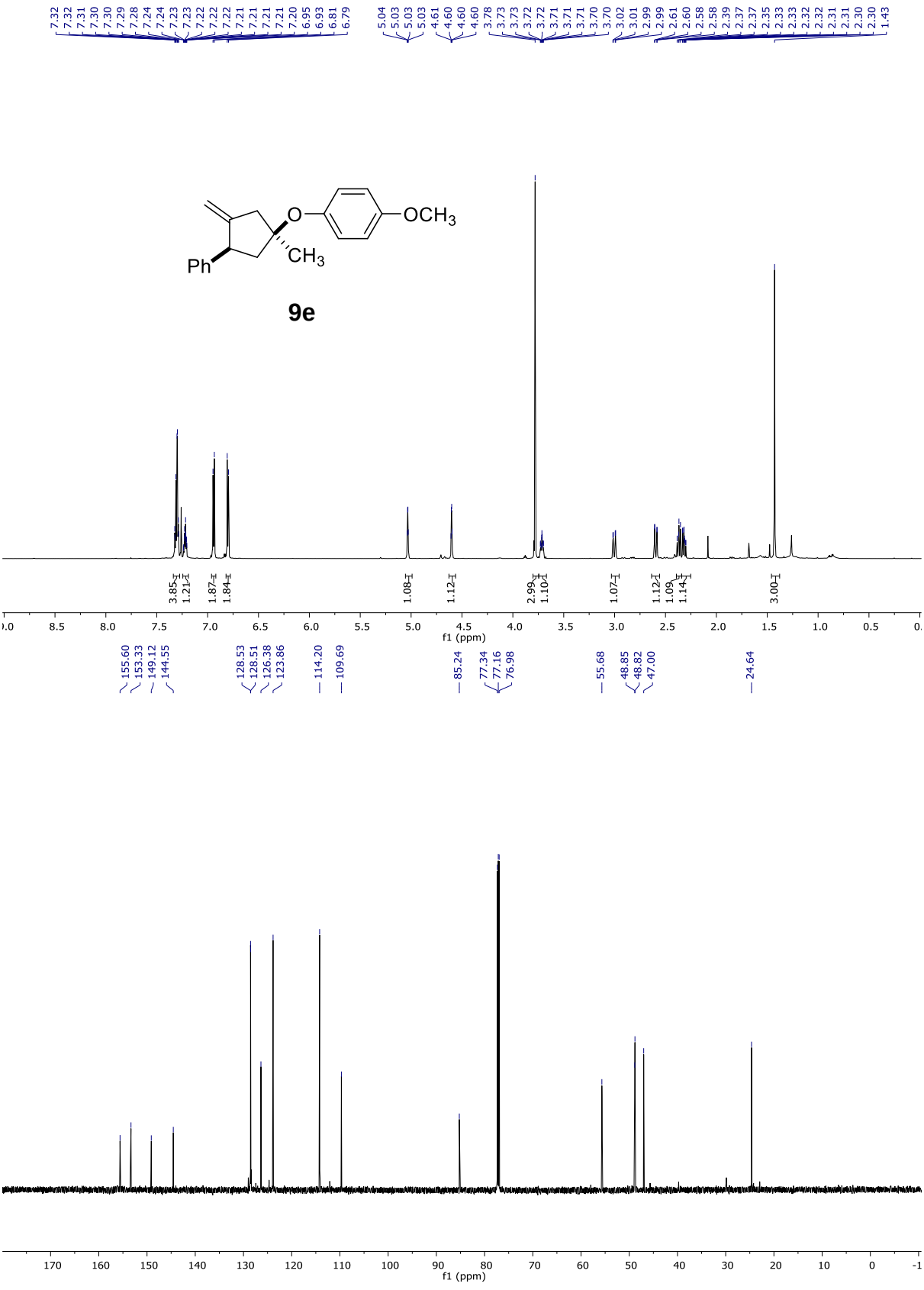

f2 (ppm)
f1 (ppm)

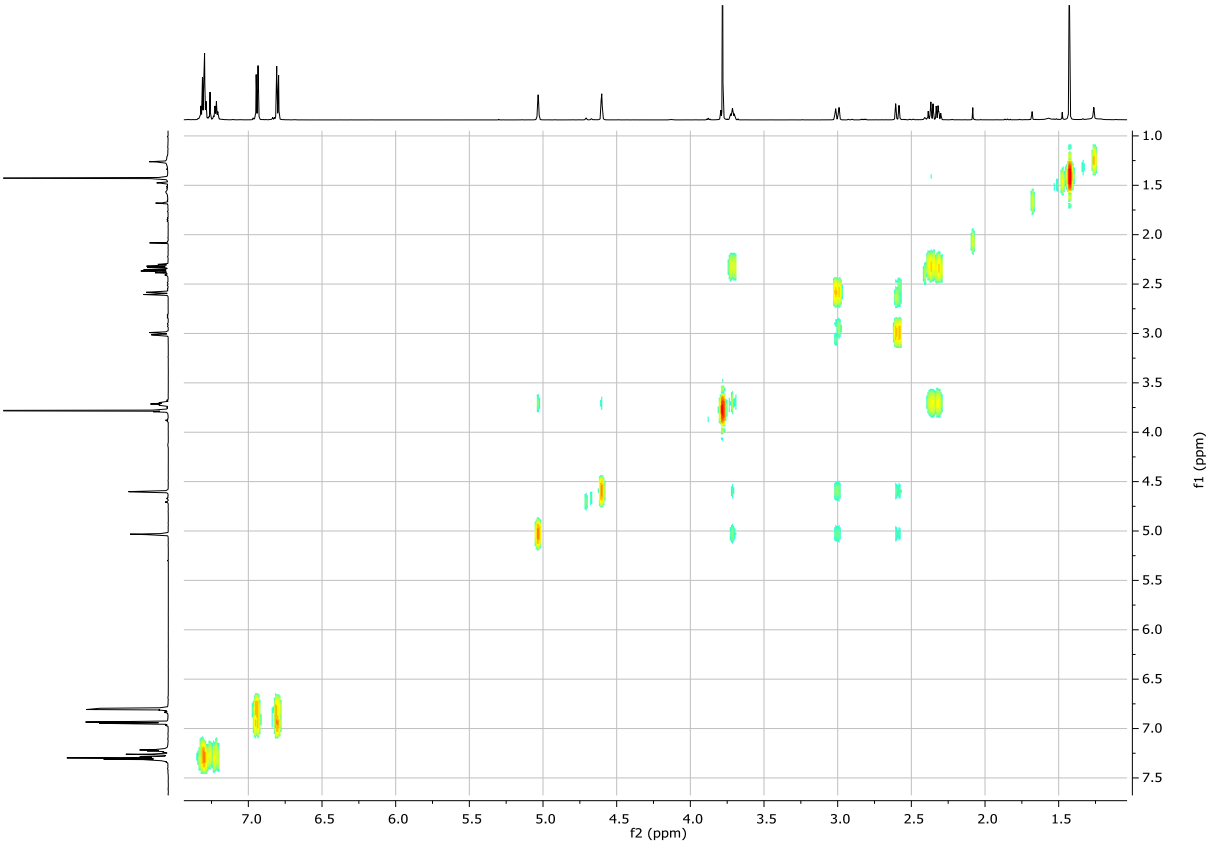

O
OCH3
H3C
HA
HB
nOe
CH3
HA
HB
f1 (ppm)

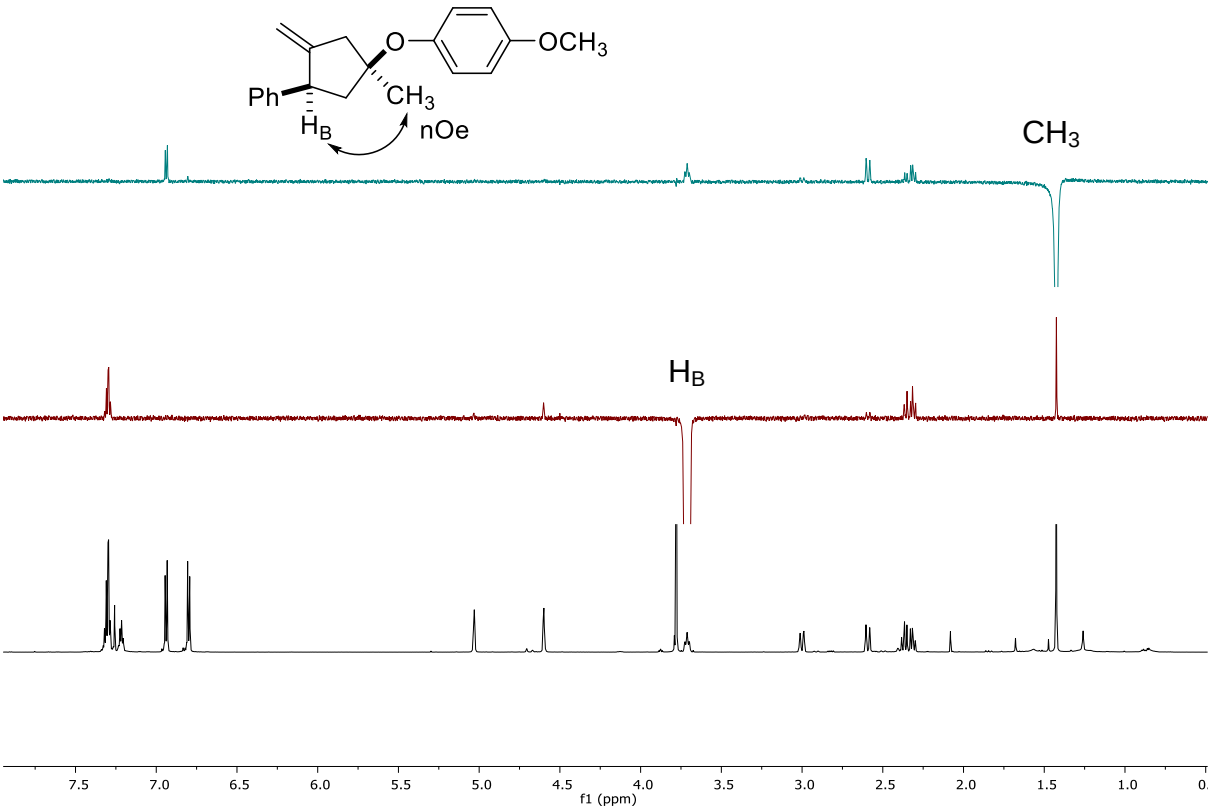

OCH3
O
BnO
9d
f1 (ppm)
f1 (ppm)

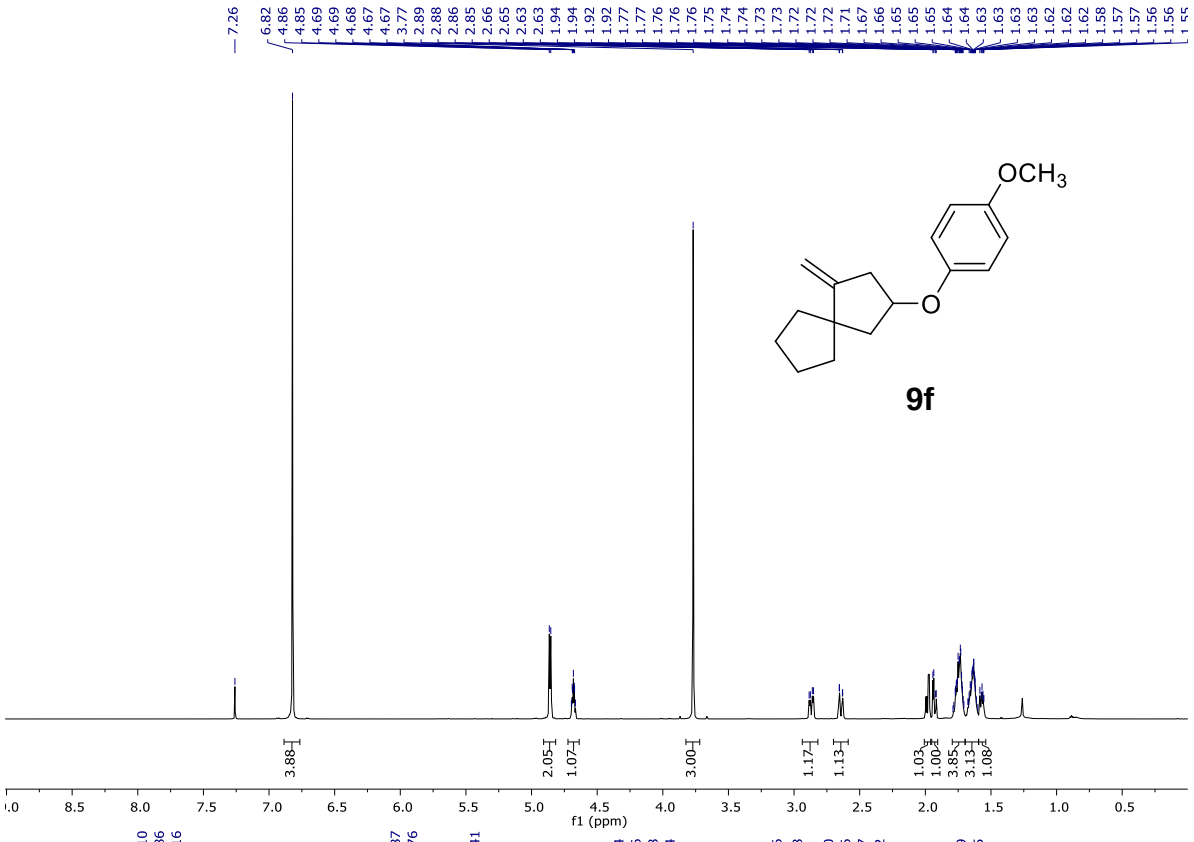

f2 (ppm)
f1 (ppm)

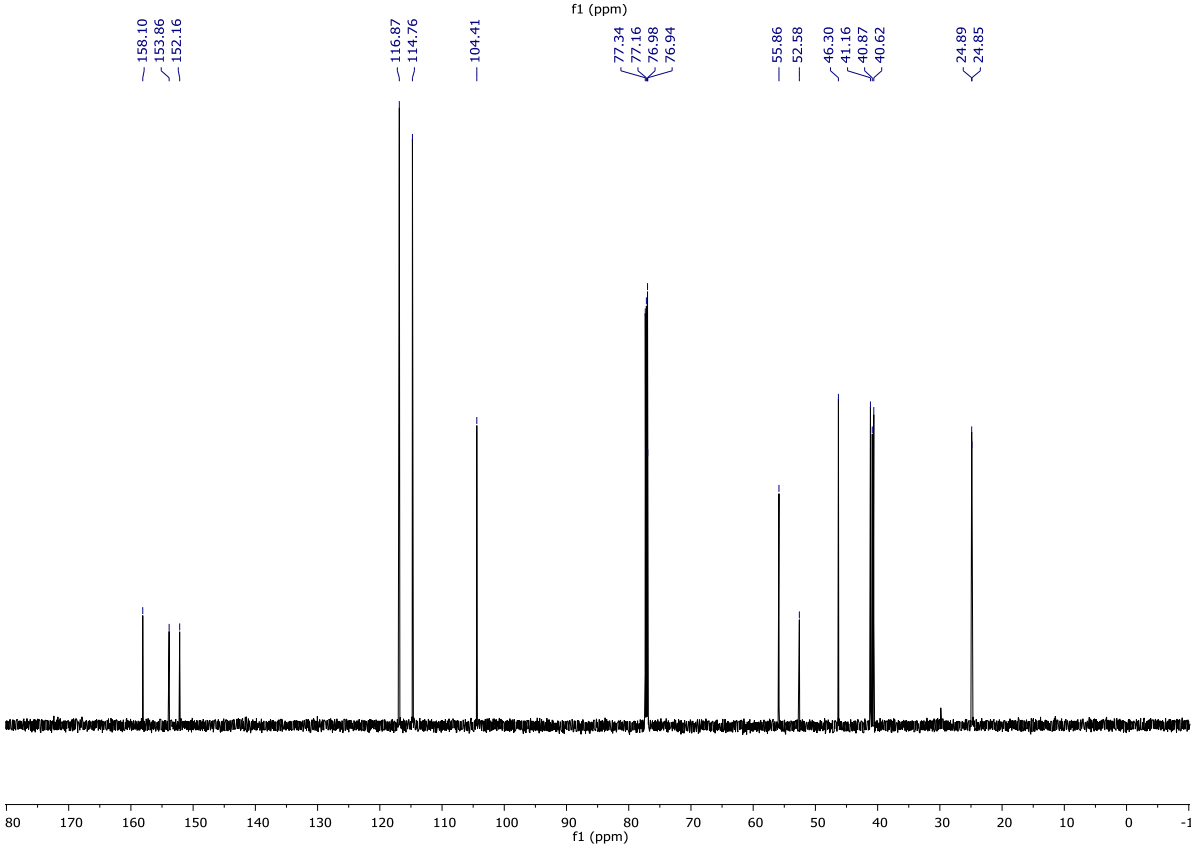

O
OCH3
BnO
HA
HB
nOe
HB
HA
f1 (ppm)

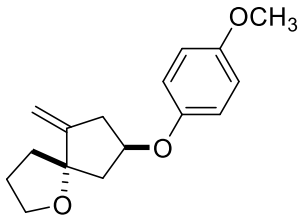

7.32 7.32 7.31 7.30 7.30 7.29 7.28 7.24 7.24 7.23 7.23 7.22 7.22 7.22 7.21 7.21 7.21 7.21 7.20 6.95 6.93 6.81 6.79
5.04 5.03 5.03 5.03 4.61 4.60 4.60 4.60 3.78 3.73 3.73 3.72 3.72 3.71 3.71 3.71 3.70 3.70 3.02 3.01 2.99 2.99 2.61 2.60 2.58 2.58 2.39 2.37 2.37 2.35 2.33 2.33 2.32 2.31 2.31 2.30 2.30 1.43
O
OCH3
CH3
Ph
9e
3.85 1.21 1.87 1.84 1.08 1.12 2.99 1.10 1.07 1.12 1.09 1.14 3.00
f1 (ppm)
155.60 153.33 149.12 144.55 128.53 128.51 126.38 123.86 114.20 109.69 85.24 77.34 77.16 76.98 55.68 48.85 48.82 47.00 24.64
f1 (ppm)


f2 (ppm)
f1 (ppm)


O
OCH3
Ph
CH3
HB
nOe
CH3
HB
f1 (ppm)


7.26
6.82
4.86
4.85
4.69
4.69
4.68
4.68
4.67
4.67
3.77
2.89
2.88
2.86
2.85
2.66
2.65
2.63
2.63
1.94
1.94
1.92
1.92
1.77
1.77
1.76
1.76
1.76
1.75
1.74
1.74
1.73
1.73
1.72
1.72
1.72
1.71
1.67
1.66
1.65
1.65
1.65
1.64
1.64
1.63
1.63
1.63
1.63
1.62
1.62
1.62
1.58
1.57
1.57
1.56
1.56
OCH3
O
9f
3.88
2.05
1.07
3.00
1.17
1.13
1.03
1.00
3.85
3.13
1.08
f1 (ppm)

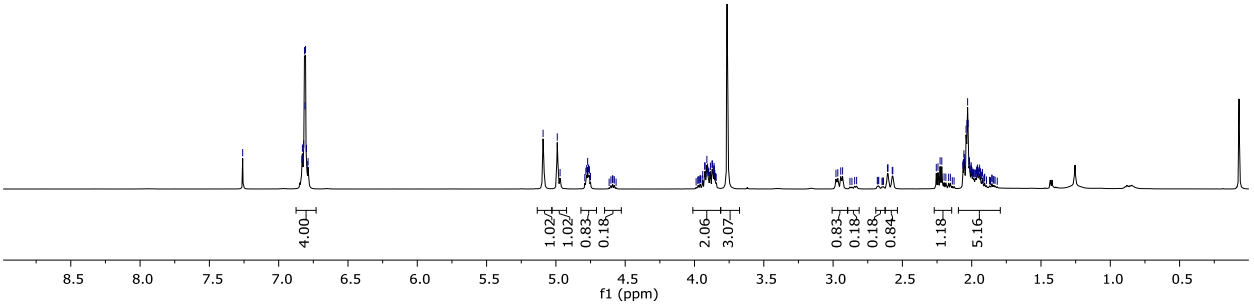

158.10
153.86
152.16
116.87
114.76
104.41
77.34
77.16
76.98
76.94
55.86
52.58
46.30
41.16
40.87
40.62
24.89
24.85
f1 (ppm)

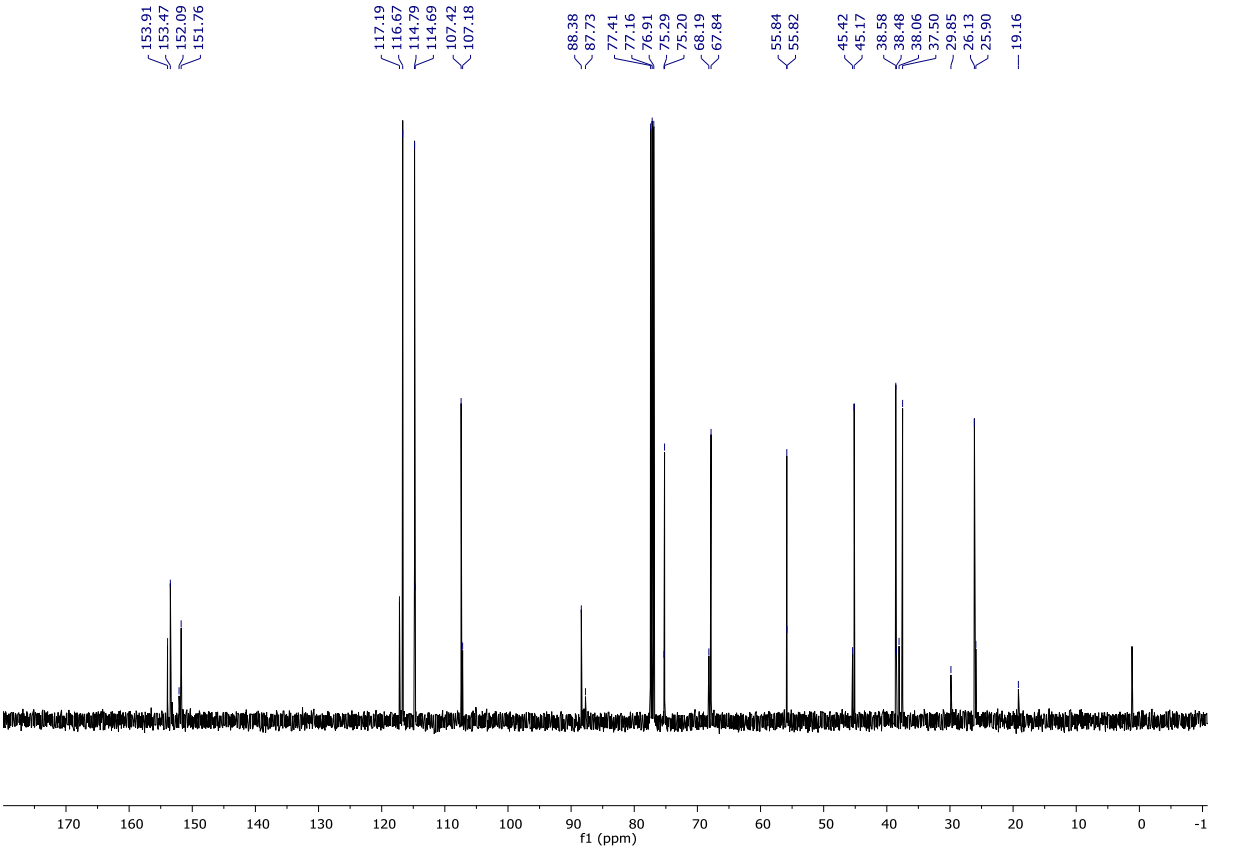


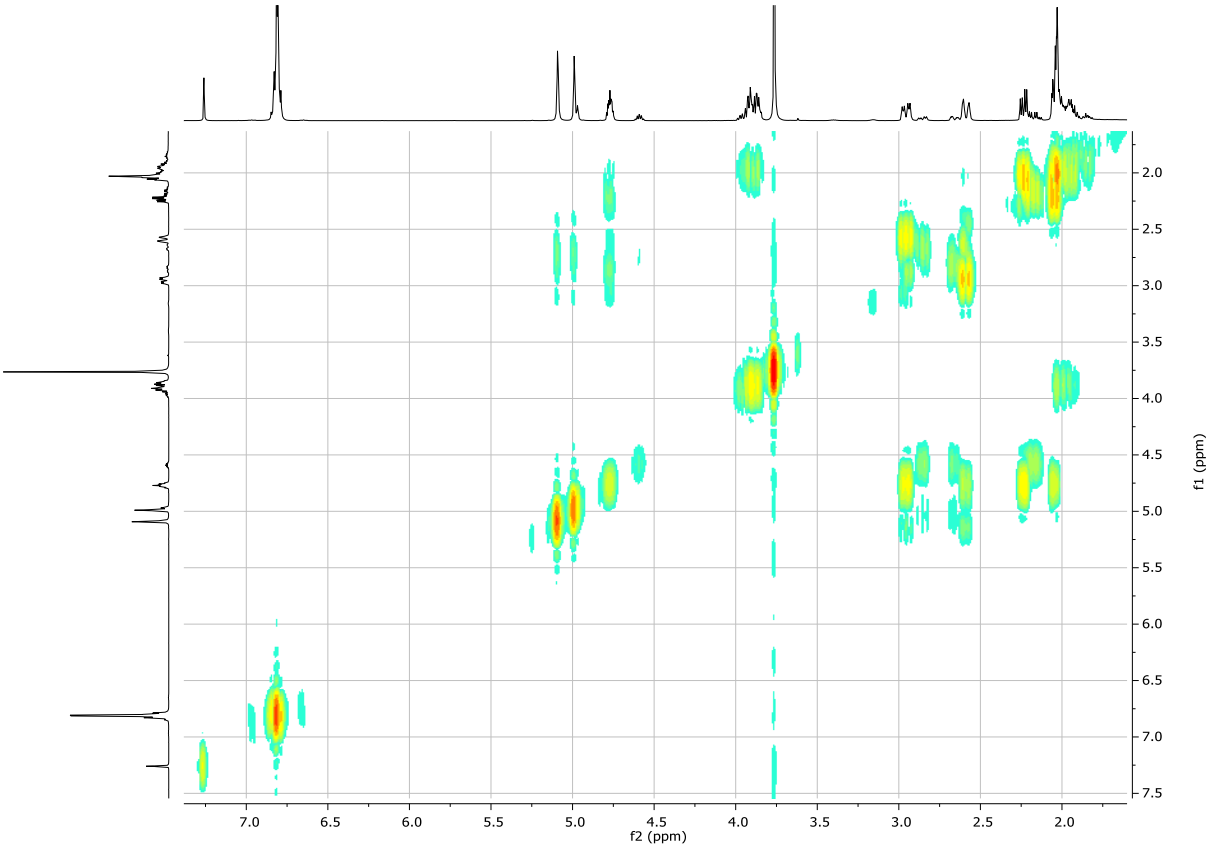
9g

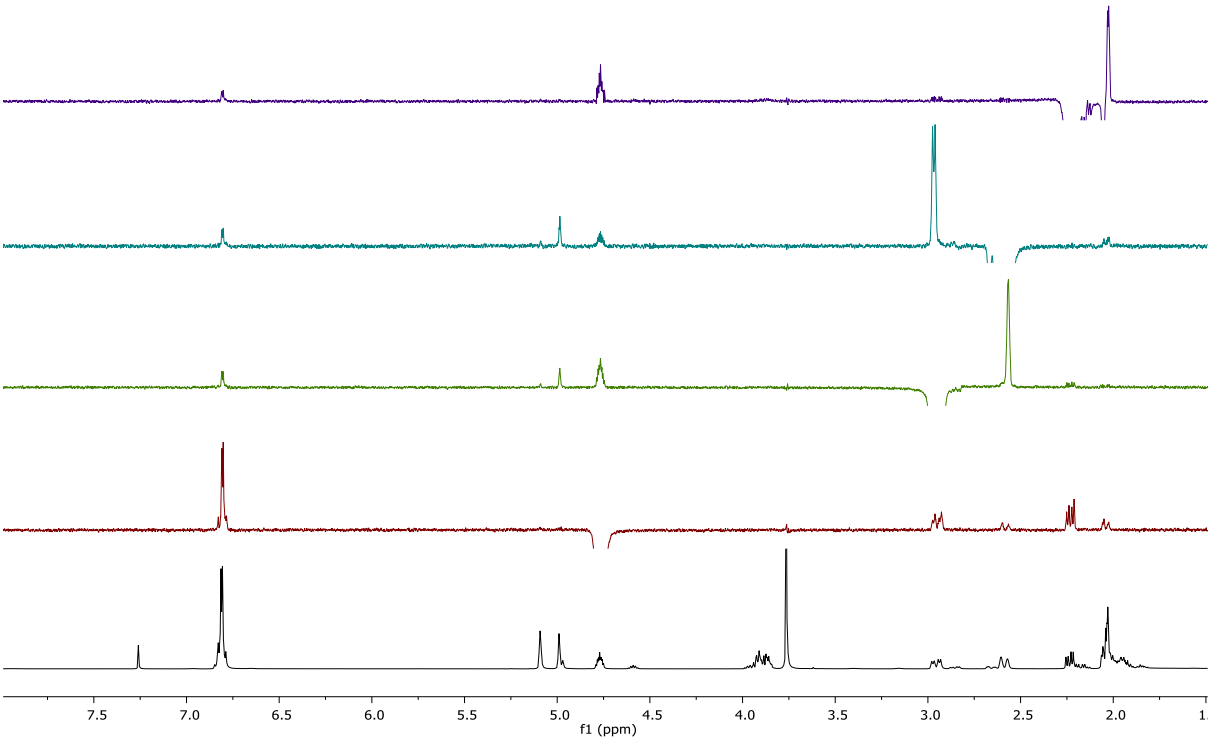
5:1 dr

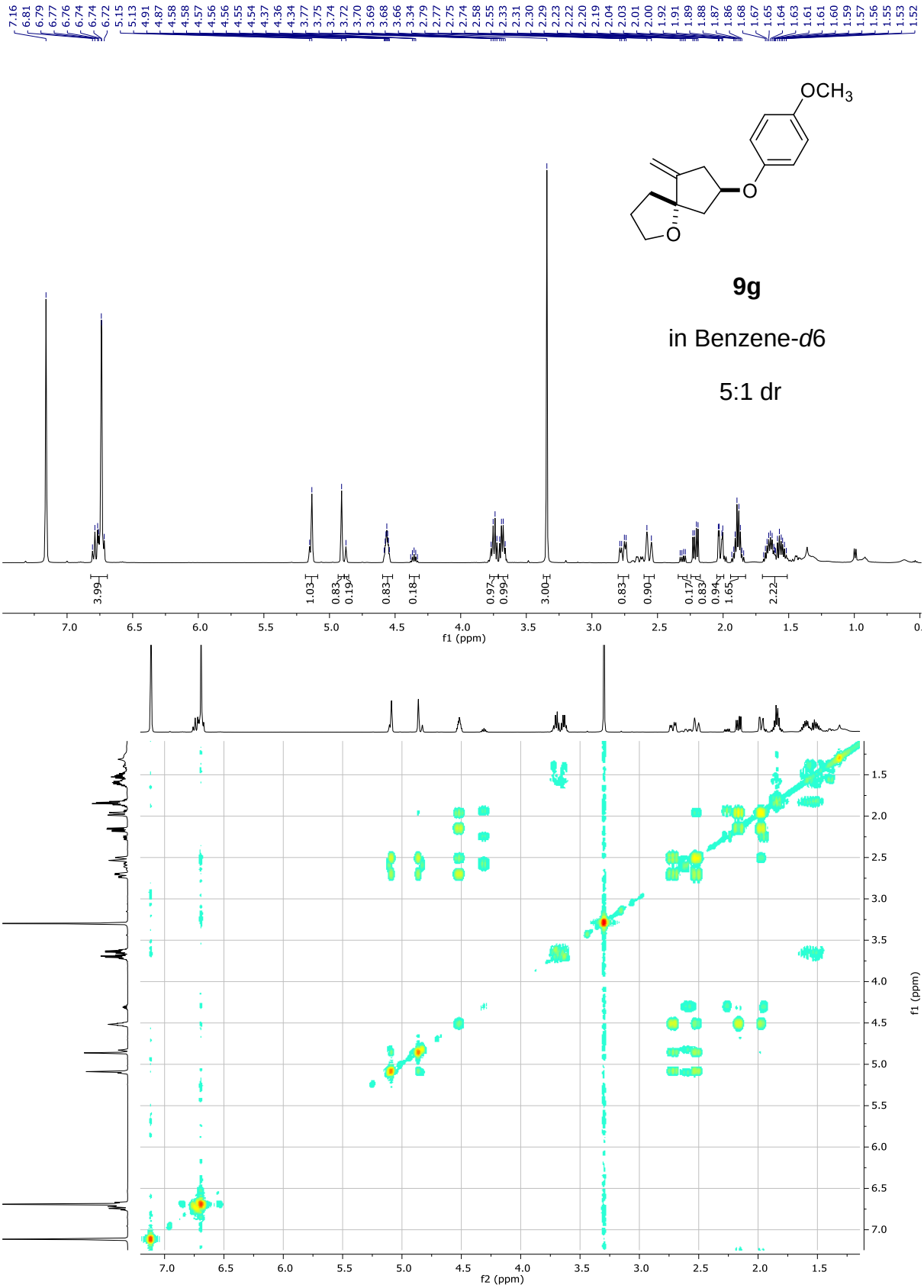
(Contains silicone grease impurity)

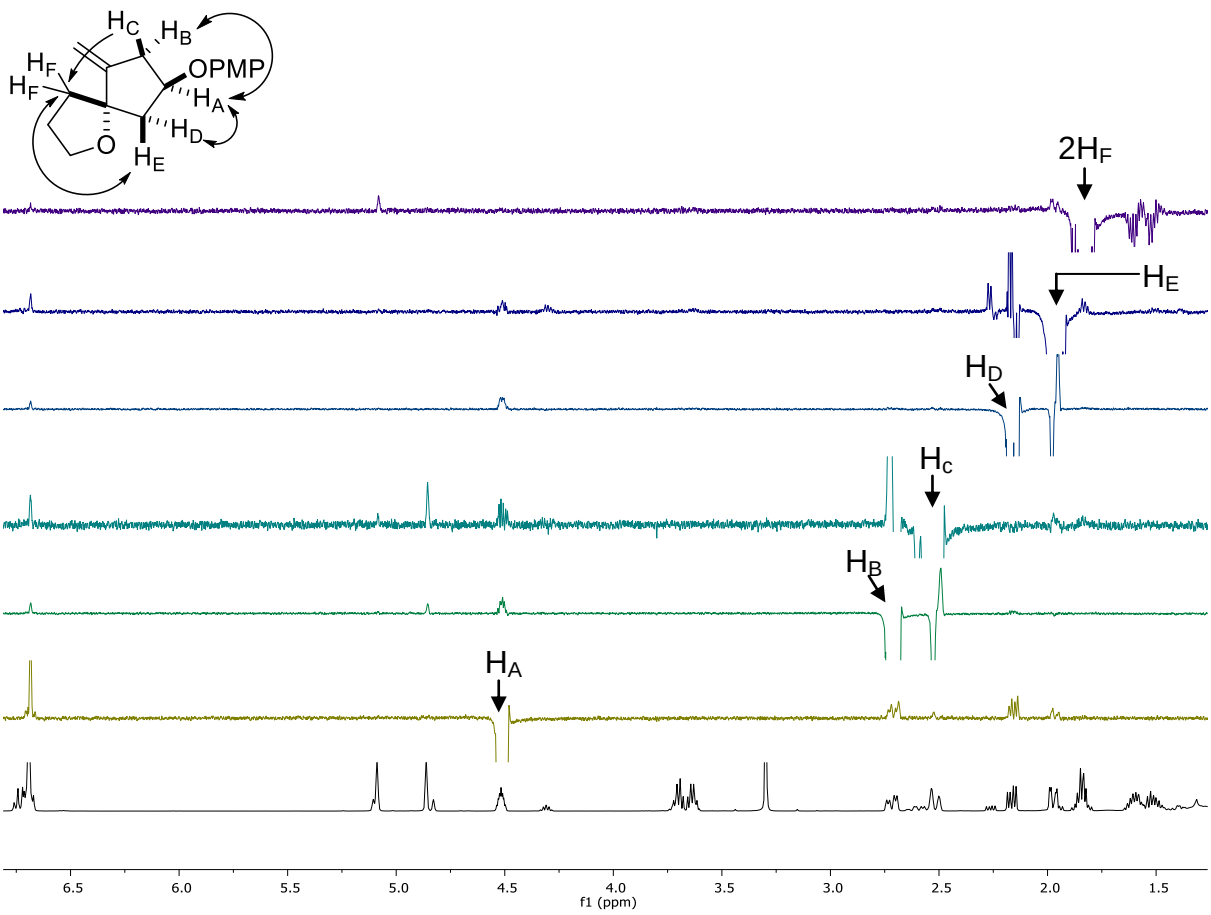





f2 (ppm)
f1 (ppm)


f1 (ppm)


OCH3
O
O
9g
in Benzene-d6
5:1 dr
f1 (ppm)
f2 (ppm)


H_C
H_B
H_F
H_F
OPMP
H_A
H_D
O
H_E
2H_F
H_E
H_D
H_c
H_B
H_A
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
f1 (ppm)