SUPPORTING INFORMATION

Arynes in green solvent: employing *o*-silylaryl triflates with propylene carbonate

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Table of contents

1. General information

General: All chemicals were used directly as obtained from commercial sources without prior purification. Dry tetrahydrofuran (THF) and dichloromethane (DCM) were obtained from the MB SPS-80 solvent purification machine. Acetonitrile (MeCN) and propylene carbonate (PC) were purchased from commercial sources and stored over molecular sieves before use. Reactions requiring anhydrous conditions were carried out in oven-dried apparatus under nitrogen. 2-(Trimethylsilyl)phenyl trifluoromethanesulfonate **1** was purchased from commercial suppliers and used without additional purification.

Chromatography: Flash column chromatography was carried out using 40-63 µm silica gel or Biotage Isolera One flash purification system using KP-Sil or KP-NH (amine modified) Snap cartridges. Thin-layer chromatography (TLC) was performed on aluminium backed plates pre-coated with Silica Gel 60 F_{254} and visualized using a UV lamp (254 nm) or Dragendorff reagent stain.

Nuclear Magnetic Resonance Spectroscopy: ^{1}H, ^{13}C and ^{19}F NMR spectra were recorded on a Bruker Avance UltraShield AV400 or AV(III)400 (400 MHz, 376 MHz and 101 MHz). ^{1}H and ^{13}C NMR spectra were recorded in $CDCl_3$ and referenced to the residual solvent peak at 7.26 ppm and solvent peak at 77.2 ppm. ^{19}F NMR spectra were recorded in C_6F_6 referenced to the solvent peak at –164.9 ppm. Chemical shifts are quoted in parts per million (ppm) to 2 dp for ^{1}H NMR spectra and 1 dp for the ^{13}C and ^{19}F NMR spectra. Coupling constants (J) were measured in Hertz (Hz) to 1 dp. Spectral data are reported as follows: chemical shift, integration, multiplicity (s = singlet, d = doublet, t = triplet, q = quartet, quint = quintet, sep = septet, dd = doublet of doublets, ddd = doublet of doublets of doublets, m = multiplet, br = broad) and coupling constant (J).

Infrared (IR) spectroscopy: IR spectra were recorded as solids or neat liquids on the PerkinElmer Spectrum 65 FT-IR spectrometer fitted with a Universal ATR sampling accessory and are reported in wavenumbers (cm^{-1}) to the nearest integer.

Mass Spectrometry: Low resolution mass spectra were recorded on the Agilent 1100 series LC-MS (comprising a 6310 ion trap) under electrospray ionization (ESI) or on the Agilent GC-MS (comprising a 6890 GC and 5973 MSD) under electron ionization (EI).

Determination of ^{1}H NMR Yields: Folowing work-up of the reactions dibromomethane (1 equiv.) as an internal standard was added to the evaporated residues using a microliter syringe. The yields were calculated by ^{1}H NMR measurements of the reaction mixtures with dibromomethane (2H, 4.93 ppm) as an internal standard. The yields were corrected according to this value.

2. Experimental Data

2.1. Synthesis of starting materials

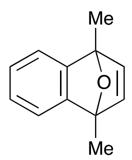
Aryne precursors **4a-h** were prepared according to literature procedures and data obtained were consistent with those reported.[1-3]

2.2. Synthesis and characterization of Diels-Alder adducts

General procedure for the synthesis of Diels-Alder adducts:

According to a modified literature procedure,[4] *ortho*-silylaryl triflate precursor (1.0 eq.), cesium fluoride (5.0 eq.) and furan **7a-d** (3.0 eq.) were added to a microwave vial, sealed and purged with nitrogen. The mixture was dissolved in either (a) acetonitrile or (b) propylene carbonate [0.1 M] and heated to 50 °C under N_2. The reaction was monitored by TLC and once all of the aryne precursor was consumed, the reaction was quenched with cold $NaHCO_3$ (sat. aq., 15 mL) and extracted three times with either (a) diethyl ether or (b) *n*-hexane, respectively. The combined organic layers were washed with brine (15 mL) and dried over magnesium sulfate, filtered and concentrated *in vacuo*. The resulting residue was then submitted for ^{1}H NMR spectroscopic analysis with dibromomethane as the internal standard. The crude material acquired from the reaction in PC was then purified by silica gel flash chromatography.

1,4-Dimethyl-1,4-dihydro-1,4-epoxynaphthalene, 8a



2-(Trimethylsilyl)phenyl trifluoromethanesulfonate **1** (30 µL, 0.124 mmol) and 2,5-dimethyl furan **7a** (40.1 µL, 0.371 mmol) were subjected to the general procedure for the synthesis of Diels-Alder adducts. Following ^{1}H NMR spectroscopic analyses of the crude mixtures, the reaction conducted in PC solvent was purified by silica gel flash chromatography (1:5 ethyl acetate:*n*-hexane) to afford 1,4-dimethyl-1,4-dihydro-1,4-epoxynaphthalene, **8a** (18.5 mg, 0.108 mmol, 87%) as a colourless oil; R_f 0.25 (1:5 ethyl acetate:*n*-hexane).

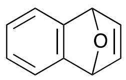
a) **In MeCN:** NMR yield = 91%
b) **In PC:** NMR yield = 90% (isolated yield 87%)

^{1}H NMR (400 MHz, $CDCl_3$): δ 7.13 (dd, J = 5.1, 3.0 Hz, 2H), 6.98 (dd, J = 5.1, 3.0 Hz, 2H), 6.78 (s, 2H), 1.90 (s, 6H).

^{13}C NMR (101 MHz, $CDCl_3$): δ 152.9, 146.9, 124.8, 118.5, 88.7, 15.4.

Data is consistent with previously reported literature values.[4]

1,4-Dihydro-1,4-epoxynaphthalene, 8b



2-(Trimethylsilyl)phenyl trifluoromethanesulfonate **1** (30 µL, 0.124 mmol) and furan **7b** (26.9 µL, 0.371 mmol) were subjected to the general procedure for the synthesis of Diels-Alder adducts. Following ^{1}H NMR spectroscopic analyses of the crude mixtures, the reaction conducted in PC solvent was purified by silica gel flash chromatography (1:5 ethyl acetate:*n*-hexane) yielded 1,4-dihydro-1,4-epoxynaphthalene, **8b** (16.0 mg, 0.111 mmol, 90%) as a colourless oil; R_f 0.30 (1:5 ethyl acetate:*n*-hexane).

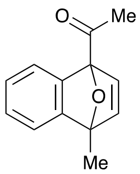
a) **In MeCN:** NMR yield = 94%
b) **In PC:** NMR yield = 95% (isolated yield 90%)

^{1}H NMR (400 MHz, $CDCl_3$): δ 7.17 (dd, *J* = 5.1, 3.0 Hz, 2H), 6.95 (t, *J* = 1.0 Hz, 2H), 6.89 (dd, *J* = 5.1, 3.0 Hz, 2H), 5.63 (s, 2H).

^{13}C NMR (101 MHz, $CDCl_3$): δ 149.1, 143.2, 125.1, 120.4, 82.4.

Data is consistent with previously reported literature values.[4]

1-(4-Methyl-1,4-epoxynaphthalen-1(4H)-yl)ethan-1-one, 8c



2-(Trimethylsilyl)phenyl trifluoromethanesulfonate **1** (30 µL, 0.124 mmol) and 2-acetyl-5-methylfuran **7c** (43.0 µL, 0.371 mmol) were subjected to the general procedure for the synthesis of Diels-Alder adducts. Following ^{1}H NMR spectroscopic analyses of the crude mixtures, the reaction conducted in PC solvent was purified by silica gel flash chromatography (1:5 ethyl acetate:*n*-hexane) yielded 1-(4-methyl-1,4-epoxynaphthalen-1(4H)-yl)ethan-1-one, **8c** (21.3 mg, 0.106 mmol, 86%) as a colourless oil; R_f 0.28 (1:5 ethyl acetate:*n*-hexane).

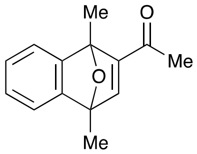
a) **In MeCN:** NMR yield = 88%
b) **In PC:** NMR yield = 89% (isolated yield 86%)

^{1}H NMR (400 MHz, $CDCl_3$): δ_H 7.22 – 7.17 (m, 2H), 7.06 (d, *J* = 5.3 Hz, 1H), 7.04 – 6.95 (m, 2H), 6.78 (d, *J* = 5.2 Hz, 1H), 2.40 (s, 3H), 1.97 (s, 3H).

^{13}C NMR (101 MHz, $CDCl_3$): δ_C 205.6, 150.6, 149.2, 146.1, 143.6, 125.7, 125.1, 119.3, 119.2, 95.3, 89.9, 27.0, 15.3.

Data is consistent with previously reported literature values.[5]

1-(1,4-Dimethyl-1,4-dihydro-1,4-epoxynaphthalen-2-yl)ethan-1-one, 8d



2-(Trimethylsilyl)phenyl trifluoromethanesulfonate **1** (30 µL, 0.124 mmol) and 3-acetyl-2,5-dimethylfuran **7d** (49.3 µL, 0.371 mmol) were subjected to the general procedure for the synthesis of Diels-Alder adducts. Following ^{1}H NMR spectroscopic analyses of the crude mixtures, the reaction conducted in PC solvent was purified by silica gel flash chromatography (1:5 ethyl acetate:*n*-hexane) yielded 1-(1,4-dimethyl-1,4-dihydro-1,4-epoxynaphthalen-2-yl)ethan-1-one, **8d** (15.9 mg, 0.074 mmol, 60%) as a colourless oil; R_f 0.22 (1:5 ethyl acetate:*n*-hexane).

a) **In MeCN:** NMR yield = 97%
b) **In PC:** NMR yield = 62% (isolated yield 60%)

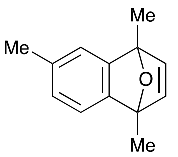
^{1}H NMR (400 MHz, CDCl$_3$): δ_H 7.43 (s, 1H), 7.30 – 7.27 (m, 1H), 7.18 – 7.14 (m, 1H), 7.04 – 7.00 (m, 2H), 2.23 (s, 3H), 2.02 (s, 3H), 1.95 (s, 3H).

^{13}C NMR (101 MHz, CDCl$_3$): δ_C 194.5, 157.9, 156.9, 151.8, 150.3, 125.8, 125.3, 119.6, 119.2, 89.6, 87.6, 27.5, 15.1, 14.8.

IR (neat): ν_{max}/cm^{-1} 2978, 2934, 1703, 1667, 1381, 1354, 1132, 1034, 858, 753, 673, 654.

LCMS (ESI) [M+H]+ calcd. for $C_{14}H_{15}O_2$ 215.11, found 215.10.

1,4,6-Trimethyl-1,4-dihydro-1,4-epoxynaphthalene, 9a



4-Methyl-2-(trimethylsilyl)phenyl trifluoromethanesulfonate **4a** (30 µL, 0.117 mmol) and 2,5-dimethyl furan **7a** (38.0 µL, 0.352 mmol) were subjected to the general procedure for the synthesis of Diels-Alder adducts. Following ^{1}H NMR spectroscopic analyses of the crude mixtures, the reaction conducted in PC solvent was purified by silica gel flash chromatography (1:5 ethyl acetate:*n*-hexane) to afford 1,4,6-trimethyl-1,4-dihydro-1,4-epoxynaphthalene, **9a** (19.6 mg, 0.105 mmol, 90%) as a colourless oil; R_f 0.30 (1:5 ethyl acetate:*n*-hexane).

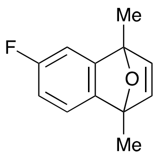
a) **In MeCN:** NMR yield = 85%
b) **In PC:** NMR yield = 94% (isolated yield 90%)

^{1}H NMR (400 MHz, CDCl$_3$): δ 7.01 (d, J = 7.2 Hz, 1H), 6.96 (s, 1H), 6.76 (m, 3H), 2.30 (s, 3H), 1.88 (s, 6H).

^{13}C NMR (101 MHz, CDCl$_3$): δ 153.2, 147.2, 146.7, 134.6, 124.8, 119.9, 118.2, 88.6, 21.4, 15.4 (2 x C).

Data is consistent with previously reported literature values.[6]

6-Fluoro-1,4-dimethyl-1,4-dihydro-1,4-epoxynaphthalene, 9b



4-Fluoro-2-(trimethylsilyl)phenyl trifluoromethanesulfonate **4b** (30 µL, 0.126 mmol) and 2,5-dimethyl furan **7a** (40.9 µL, 0.379 mmol) were subjected to the general procedure for the synthesis of Diels-Alder adducts. Following ^{1}H NMR spectroscopic analyses of the crude mixtures, the reaction conducted in PC solvent was purified by silica gel flash chromatography (1:5 ethyl acetate:*n*-hexane) to afford 6-fluoro-1,4-dimethyl-1,4-dihydro-1,4-epoxynaphthalene, **9b** (15.4 mg, 0.081 mmol, 64%) as a colourless oil; R_f 0.20 (1:5 ethyl acetate:*n*-hexane).

a) **In MeCN:** NMR yield = 73%
b) **In PC:** NMR yield = 70% (isolated yield 64%)

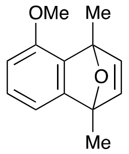
^{1}H NMR (400 MHz, CDCl$_3$): δ 7.01 (dd, J = 7.7, 4.5 Hz, 1H), 6.86 (dd, J = 7.7, 2.2 Hz, 1H), 6.81 – 6.74 (m, 2H), 6.62 (ddd, J = 9.9, 7.8, 2.2 Hz, 1H), 1.88 (s, 3H), 1.87 (s, 3H).

^{13}C NMR (101 MHz, CDCl$_3$): δ 160.8 (d, $^{1}J_{C-F}$ = 244.0 Hz), 155.9 (d, $^{3}J_{C-F}$ = 7.0 Hz), 148.2, 147.4, 146.5, 119.0 (d, $^{3}J_{C-F}$ = 9.0 Hz), 110.0 (d, $^{2}J_{C-F}$ = 23.0 Hz), 108.0 (d, $^{2}J_{C-F}$ = 25.0 Hz), 88.7, 88.6, 15.4, 15.3.

^{19}F NMR (377 MHz, CDCl$_3$): δ –77.2 (s).

Data is consistent with previously reported literature values.[7]

5-Methoxy-1,4-dimethyl-1,4-dihydro-1,4-epoxynaphthalene, 9c



5-Methoxy-1,4-dimethyl-1,4-dihydro-1,4-epoxynaphthalene **4c** (30 µL, 0.118 mmol) and 2,5-dimethyl furan **7a** (38.2 µL, 0.354 mmol) were subjected to the general procedure for the synthesis of Diels-Alder adducts. Following ^{1}H NMR spectroscopic analyses of the crude mixtures, the reaction conducted in PC solvent was purified by silica gel flash chromatography (1:5 ethyl acetate:*n*-hexane) to afford 5-methoxy-1,4-dimethyl-1,4-dihydro-1,4-epoxynaphthalene, **9c** (21.5 mg, 0.0106 mmol, 90%) as a colourless oil; R_f 0.25 (1:5 ethyl acetate:*n*-hexane).

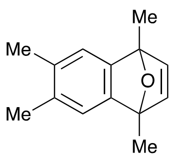
a) **In MeCN:** NMR yield = 98%
b) **In PC:** NMR yield = 97% (isolated yield 90%)

^{1}H NMR (400 MHz, CDCl$_3$): δ 6.97 (dd, *J* = 8.3, 7.1 Hz, 1H), 6.87 (d, *J* = 5.3 Hz, 1H), 6.79 (d, *J* = 7.0 Hz, 1H), 6.76 (d, *J* = 5.3 Hz, 1H), 6.60 (d, *J* = 8.4 Hz, 1H), 3.80 (s, 3H), 2.02 (s, 3H), 1.88 (s, 3H).

^{13}C NMR (101 MHz, CDCl$_3$): δ 156.0, 153.5, 147.5, 146.8, 138.0, 127.0, 112.0, 110.3, 89.5, 88.7, 55.7, 17.3, 15.5.

Data is consistent with previously reported literature values.[8]

1,4,6,7-Tetramethyl-1,4-dihydro-1,4-epoxynaphthalene, 9d



4,5-Dimethyl-2-(trimethylsilyl)phenyl trifluoromethanesulfonate **4d** (30 µL, 0.113 mmol) and 2,5-dimethyl furan **7a** (36.6 µL, 0.339 mmol) were subjected to the general procedure for the synthesis of Diels-Alder adducts. Following ^{1}H NMR spectroscopic analyses of the crude mixtures, the reaction conducted in PC solvent was purified by silica gel flash chromatography (1:5 ethyl acetate:*n*-hexane) to afford 1,4,6,7-tetramethyl-1,4-dihydro-1,4-epoxynaphthalene, **9d** (18.6 mg, 0.0927 mmol, 82%) as a colourless oil; R_f 0.30 (1:5 ethyl acetate:*n*-hexane).

a) **In MeCN:** NMR yield = 79%
b) **In PC:** NMR yield = 88% (isolated yield 82%)

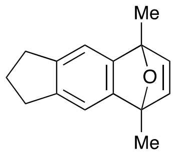
^{1}H NMR (400 MHz, CDCl$_3$): δ_H 6.94 (s, 2H), 6.76 (s, 2H), 2.21 (s, 6H), 1.87 (s, 6H).

^{13}C NMR (101 MHz, CDCl$_3$): δ_C 150.6, 147.0, 132.3, 120.5, 88.6, 19.9, 15.5.

IR (neat): ν_{max}/cm^{-1} 3059, 2953, 1645, 1577, 1462, 1451, 1383, 1236, 1128, 1033, 868, 743, 683, 644.

LCMS (ESI) [M+H]+ calcd. for $C_{14}H_{17}O$ 211.13, found 211.20.

5,8-Dimethyl-2,3,5,8-tetrahydro-1H-5,8-epoxycyclopenta[b]naphthalene, 9e



6-(Trimethylsilyl)-2,3-dihydro-1H-inden-5-yl trifluoromethanesulfonate **4e** (30 µL, 0.114 mmol) and 2,5-dimethyl furan **7a** (37.1 µL, 0.343 mmol) were subjected to the general procedure for the synthesis of Diels-Alder adducts. Following ^{1}H NMR spectroscopic analyses of the crude mixtures, the reaction conducted in PC solvent was purified by silica gel flash chromatography (1:5 ethyl acetate:*n*-hexane) yielded 5,8-dimethyl-2,3,5,8-tetrahydro-1H-5,8-epoxycyclopenta[b]naphthalene, **9e** (21.8 mg, 0.103 mmol, 90%) as a colourless oil; R_f 0.30 (1:5 ethyl acetate:*n*-hexane).

a) **In MeCN:** NMR yield = 88%
b) **In PC:** NMR yield = 94% (isolated yield 90%)

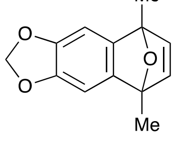
^{1}H NMR (400 MHz, CDCl$_3$): δ_H 7.01 (s, 2H), 6.78 (s, 2H), 2.82 (t, J = 7.4 Hz, 4H), 2.13 – 2.05 (m, 2H), 1.88 (s, 6H).

^{13}C NMR (101 MHz, CDCl$_3$): δ_C 151.6, 147.1, 140.4, 115.3, 88.6, 32.7, 25.7, 15.5.

IR (neat): ν_{max}/cm^{-1} 2930, 2843, 1614, 1439, 1381, 1304, 1209, 1142, 880, 858, 692,646.

LCMS (ESI) [M+H]+ calcd. for $C_{15}H_{17}O$ 213.13, found 213.10.

5,8-Dimethyl-5,8-dihydro-5,8-epoxynaphtho[2,3-d][1,3]dioxole, 9f



6-(Trimethylsilyl)benzo[d][1,3]dioxol-5-yl trifluoromethanesulfonate **4f** (30 µL, 0.124 mmol) and 2,5-dimethyl furan **7a** (40.3 µL, 0.373 mmol) were subjected to the general procedure for the synthesis of Diels-Alder adducts. Following ^{1}H NMR spectroscopic analyses of the crude mixtures, the reaction conducted in PC solvent was purified by silica gel flash chromatography (1:5 ethyl acetate:*n*-hexane) yielded 5,8-dimethyl-5,8-dihydro-5,8-epoxynaphtho[2,3-d][1,3]dioxole, **9f** (23.7 mg, 0.1095 mmol, 88%) as a colourless oil; R_f 0.20 (1:5 ethyl acetate:*n*-hexane).

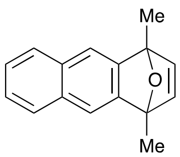
a) **In MeCN:** NMR yield = 92%
b) **In PC:** NMR yield = 89% (isolated yield 88%)

^{1}H NMR (400 MHz, CDCl$_3$): δ_H 6.80 (s, 2H), 6.71 (s, 2H), 5.91 (dd, J = 12.6, 1.4 Hz, 2H), 1.85 (s, 6H).

^{13}C NMR (101 MHz, CDCl$_3$): δ_C 147.4, 147.3 144.3, 102.5, 101.3, 88.9, 15.5.

Data is consistent with previously reported literature values.[9]

1,4-Dimethyl-1,4-dihydro-1,4-epoxyanthracene, 9g



3-(Trimethylsilyl)naphthalen-2-yl trifluoromethanesulfonate **4g** (30 µL, 0.112 mmol) and 2,5-dimethyl furan **7a** (36.6 µL, 0.338 mmol) were subjected to the general procedure for the synthesis of Diels-Alder adducts. Following ^{1}H NMR spectroscopic analyses of the crude mixtures, the reaction conducted in PC solvent was purified by silica gel flash chromatography (1:5 ethyl acetate:*n*-hexane) yielded 1,4-dimethyl-1,4-dihydro-1,4-epoxyanthracene, **9g** (4.26 mg, 0.0192 mmol, 17%) as a colourless oil; R_f 0.20 (1:5 ethyl acetate:*n*-hexane).

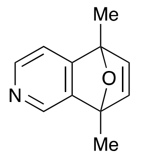
a) **In MeCN:** NMR yield = 19%
b) **In PC:** NMR yield = 18% (isolated yield 17%)

^{1}H NMR (400 MHz, CDCl$_3$): δ_H 7.72 (dt, J = 6.5, 3.3 Hz, 2H), 7.46 – 7.40 (m, 4H), 6.72 (s, 2H), 1.98 (s, 6H).

^{13}C NMR (101 MHz, CDCl$_3$): δ_C 148.7, 145.6, 131.9, 128.2, 126.2, 116.9, 88.2, 15.5.

Data is consistent with previously reported literature values.[10]

5,8-Dimethyl-5,8-dihydro-5,8-epoxyisoquinoline, 9h



4-(Trimethylsilyl)pyridin-3-yl trifluoromethanesulfonate **4h** (30 µL, 0.133 mmol) and 2,5-dimethyl furan **7a** (43.2 µL, 0.400 mmol) were subjected to the general procedure for the synthesis of Diels-Alder adducts. Following ^{1}H NMR spectroscopic analyses of the crude mixtures, the reaction conducted in PC solvent was purified by silica gel flash chromatography (1:5 ethyl acetate:*n*-hexane) yielded 5,8-dimethyl-5,8-dihydro-5,8-epoxyisoquinoline **9h** (5.06 mg, 0.0293 mmol, 22%) as a colourless oil; R_f 0.20 (1:5 ethyl acetate:*n*-hexane).

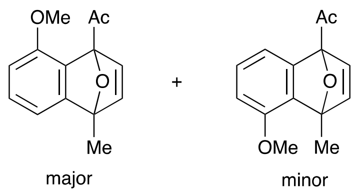
a) **In MeCN:** NMR yield = 21%
b) **In PC:** NMR yield = 23% (isolated yield 22%)

^{1}H NMR (400 MHz, CDCl$_3$): δ_H 8.36 – 8.29 (m, 2H), 7.11 (dd, *J* = 4.5, 0.9 Hz, 1H), 6.81 (d, *J* = 5.3 Hz, 1H), 6.74 (d, *J* = 5.3 Hz, 1H), 1.95 (s, 3H), 1.88 (s, 3H).

^{13}C NMR (101 MHz, CDCl$_3$): δ_C 162.7, 147.8, 147.6 147.3, 146.0, 138.3, 114.3, 88.6, 88.2 15.3, 15.0.

Data is consistent with previously reported literature values.[11]

1-(8-Methoxy-4-methyl-1,4-epoxynaphthalen-1(*4H*)-yl)ethan-1-one and 1-(5-methoxy-4-methyl-1,4-epoxynaphthalen-1(*4H*)-yl)ethan-1-one, 9i & 9i'



5-Methoxy-1,4-dimethyl-1,4-dihydro-1,4-epoxynaphthalene **4c** (50 µL, 0.196 mmol) and 2-acetyl-5-methylfuran **7c** (68.6 µL, 0.589 mmol) were subjected to the general procedure for the synthesis of Diels-Alder adducts. Following ^{1}H NMR spectroscopic analyses of the crude mixtures, the reaction conducted in PC solvent was purified by silica gel flash chromatography (1:5 ethyl acetate:*n*-hexane) to afford an inseparable mixture of 1-(8-methoxy-4-methyl-1,4-epoxynaphthalen-1(*4H*)-yl)ethan-1-one **(9i)** and 1-(5-methoxy-4-methyl-1,4-epoxynaphthalen-1(*4H*)-yl)ethan-1-one **(9i')** (20.3 mg, 0.088 mmol, 45%) as a colourless oil; R_f 0.20 (1:5 ethyl acetate:*n*-hexane).

a) **In MeCN:** NMR yield = 43%
b) **In PC:** NMR yield = 47% (isolated yield 45%)

1-(8-Methoxy-4-methyl-1,4-epoxynaphthalen-1(*4H*)-yl)ethan-1-one, 9i, major

^{1}H NMR (400 MHz, CDCl$_3$): δ_H 6.95 (d, J = 5.0 Hz, 1H), 6.86 (d, J = 8.0 Hz, 1H), 6.80 – 6.76 (m, 2H), 6.54 (d, J = 8.3 Hz, 1H), 3.71 (s, 3H), 2.30 (s, 3H), 2.00 (s, 3H).

^{13}C NMR (101 MHz, CDCl$_3$): δ_C 205.6, 153.9, 152.1, 146.6, 143.2, 135.7, 127.2, 112.5, 110.9, 95.4, 90.6, 55.6, 26.9, 17.1.

1-(5-methoxy-4-methyl-1,4-epoxynaphthalen-1(*4H*)-yl)ethan-1-one, 9i', minor

^{1}H NMR (400 MHz, CDCl$_3$): δ_H 7.20 (d, J = 5.3 Hz, 1H), 6.90 (d, J = 16.9 Hz, 1H), 6.75 (s, 1H), 6.68 (d, J = 5.3 Hz, 1H), 6.51 (d, J = 8.4 Hz, 1H), 3.66 (s, 3H), 2.31 (s, 3H), 1.85 (s, 3H).

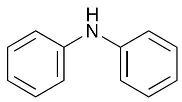
^{13}C NMR (101 MHz, CDCl$_3$): δ_C 203.6, 154.4, 152.6, 145.9, 142.1, 136.2, 128.0, 112.6, 110.2, 94.6, 90.7, 55.8, 26.6, 15.4.

IR (neat): ν_{max}/cm^{-1} 2924, 2688, 1723, 1680, 1381, 1354, 1132, 1034, 990, 858, 730, 673, 654.

LCMS (ESI) [M+H]+ calcd. for $C_{14}H_{15}O_3$ 231.27, found 231.25

2.3. Synthesis and characterisation of nucleophilic addition

Diphenylamine, 10



According to a modified literature procedure,[11] 2-(trimethylsilyl)phenyl trifluoromethanesulfonate **1** (50 µL, 0.206 mmol), cesium fluoride (62.6 mg, 0.412 mmol) and aniline (18.8 µL, 0.206 mmol) were added to a microwave vial, sealed and purged with nitrogen. The mixture was dissolved in either (a) acetonitrile or (b) propylene carbonate [0.1 M] and stirred at room temperature for 24 hours. The reaction was quenched with cold brine (sat. aq., 15 mL) and the mixture extracted with diethyl ether (3 x 10 mL). The combined organic layers were dried over $MgSO_4$ and concentrated *in vacuo*. The resulting residue was then submitted for ^{1}H NMR spectroscopic analysis with dibromomethane as the internal standard. The crude material acquired from the reaction in PC was then purified by silica gel flash chromatography (1:9 ethyl acetate:*n*-hexane) to afford diphenylamine **10** (12.2 mg, 0.072 mmol, 35%) as an amorphous white solid; R_f 0.12 (1:9 ethyl acetate:*n*-hexane).

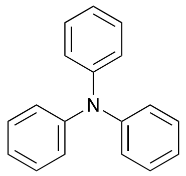
a) **In MeCN:** NMR yield = 92%
b) **In PC:** NMR yield = 37% (isolated yield = 35%)

^{1}H NMR (400 MHz, CDCl$_3$): δ_H 7.21 – 7.15 (m, 4H), 6.99 (dd, *J* = 8.6, 1.0 Hz, 4H), 6.88 – 6.82 (m, 2H), 5.60 (s, 1H).

^{13}C NMR (101 MHz, CDCl$_3$): δ_C 143.3, 129.5, 121.1, 117.9.

Data is consistent with previously reported literature values.[12]

Triphenylamine, 11



According to a modified literature procedure,[11] 2-(trimethylsilyl)phenyl trifluoromethanesulfonate **1** (70 µL, 0.289 mmol), cesium fluoride (87.6 mg, 0.577 mmol) and aniline (11.0 µL, 0.121 mmol) were added to a microwave vial, sealed and purged with nitrogen. The mixture was dissolved in either (a) acetonitrile or (b) propylene carbonate [0.1 M] and stirred at room temperature for 72 hours. The reaction was quenched with cold brine (sat. aq., 15 mL) and the mixture extracted with diethyl ether (3 x 10 mL). The combined organic layers were dried over $MgSO_4$ and concentrated *in vacuo*. The resulting residue was then submitted for ^{1}H NMR spectroscopic analysis with dibromomethane as the internal standard. The crude material acquired from the reaction in PC was then purified by silica gel flash chromatography (1:9 ethyl acetate:*n*-hexane) to afford triphenylamine **11** (14.2 mg, 0.058 mmol, 48%) as an amorphous white solid; R_f 0.12 (1:9 ethyl acetate:*n*-hexane).

a) **In MeCN:** NMR yield = 57%
b) **In PC:** NMR yield = 53% (isolated yield = 48%)

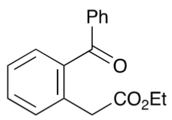
^{1}H NMR (400 MHz, CDCl$_3$): δ_H 7.34 – 7.27 (m, 6H), 7.14 – 7.08 (m, 6H), 7.01 – 6.93 (m, 3H).

^{13}C NMR (101 MHz, CDCl$_3$): δ_C 143.3, 129.5, 121.1, 118.0.

Data is consistent with previously reported literature values.[12]

2.4. Synthesis and characterisation of sigma-bond insertion

Ethyl 2-(2-benzoylphenyl)acetate, 12



According to a modified literature procedure,[12] 2-(trimethylsilyl)phenyl trifluoromethanesulfonate **1** (50 µL, 0.206 mmol), cesium fluoride (78.3 mg, 0.515 mmol) and ethyl 3-oxo-3-phenylpropanoate (35.7 µL, 0.206 mmol) were added to a microwave vial, sealed and purged with nitrogen. The mixture was dissolved in either (a) acetonitrile or (b) propylene carbonate [0.1 M] and heated to 80 °C for 1 hour. The reaction was quenched with cold brine (sat. aq., 15 mL) and the mixture extracted with diethyl ether (3 x 10 mL). The combined organic layers were dried over $MgSO_4$ and concentrated *in vacuo*. The resulting residue was then submitted for ^{1}H NMR spectroscopic analysis with dibromomethane as the internal standard. The crude material acquired from the reaction in PC was then purified by silica gel flash chromatography (1:9 ethyl acetate:*n*-hexane) to afford ethyl 2-(2-benzoylphenyl)acetate **12** (19.3 mg, 0.0721 mmol, 35%) as an amorphous white solid; R_f 0.23 (1:9 ethyl acetate:*n*-hexane).

a) **In MeCN:** NMR yield = 51%
b) **In PC:** NMR yield = 39% (isolated yield = 35%)

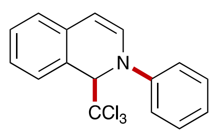
^{1}H NMR (400 MHz, $CDCl_3$): δ_H 7.84 – 7.79 (m, 2H), 7.58 (t, *J* = 7.4 Hz, 1H), 7.47 (d, *J* = 7.9 Hz, 2H), 7.36 (m, 4H), 4.02 (q, *J* = 7.1 Hz, 2H), 3.88 (s, 2H), 1.11 (t, *J* = 7.1 Hz, 3H).

^{13}C NMR (101 MHz, $CDCl_3$): δ_C 198.2, 171.4, 138.5, 138.0, 134.2, 133.1, 131.9, 131.0, 130.5, 130.1, 128.4, 126.6, 61.0, 39.0, 14.2.

Data is consistent with previously reported literature values.[13]

2.5. Synthesis and characterisation of multi-component reaction

2-Phenyl-1-(trichloromethyl)-1,2-dihydroisoquinoline, 13



According to a modified literature procedure,[14] 2-(trimethylsilyl)phenyl trifluoromethanesulfonate **1** (43.7 µL, 0.180 mmol), cesium fluoride (76.0 mg, 0.500 mmol), isoquinoline (17.6 µL, 0.150 mmol) and chloroform (0.40 mL) were added to a microwave vial, sealed and purged with nitrogen. The mixture was dissolved in either (a) acetonitrile or

(b) propylene carbonate (0.40 mL) and heated to 70 °C for 12 hours. The reaction was quenched with water (20 mL) and the mixture extracted with ethyl acetate (2 x 20 mL). The combined organic layers were dried over $MgSO_4$ and concentrated *in vacuo*. The resulting residue was then submitted for ^{1}H NMR spectroscopic analysis with dibromomethane as the internal standard. The crude material acquired from the reaction in PC was then purified by silica gel flash chromatography (1:200 ethyl acetate:*n*-hexane) to afford 2-phenyl-1-(trichloromethyl)-1,2-dihydroisoquinoline **13** (41.4 mg, 0.128 mmol, 85%) as a white solid; R_f 0.20 (1:200 ethyl acetate:*n*-hexane).

a) **In MeCN:** NMR yield = 80%
b) **In PC:** NMR yield = 90% (isolated yield = 85%)

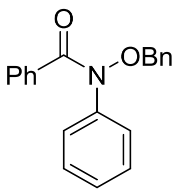
^{1}H NMR (400 MHz, CDCl$_3$): δ_H 7.48 (dd, *J* = 7.6, 0.6 Hz, 1H), 7.41 – 7.33 (m, 3H), 7.30 – 7.26 (m, 3H), 7.25 – 7.21 (m, 1H), 7.06 (tt, *J* = 7.5, 1.1 Hz, 1H), 6.79 (dd, *J* = 7.3, 1.5 Hz, 1H), 6.13 (d, *J* = 7.3 Hz, 1H), 5.82 (d, *J* = 1.3 Hz, 1H).

^{13}C NMR (101 MHz, CDCl$_3$): δ_C 147.0, 133.4, 130.2, 129.5, 129.4, 129.3 126.0, 124.4, 123.7, 122.8, 118.8, 109.0, 105.0, 74.8.

Data is consistent with previously reported literature values.[14]

2.6. Synthesis and characterisation of *N*-arylation of *O*-benzyl hydroxamate

***N*-(Benzyloxy)-*N*-phenylbenzamide, 14**



According to a modified literature procedure,[15] 2-(trimethylsilyl)phenyl trifluoromethanesulfonate **1** (29.1 µL, 0.120 mmol), cesium fluoride (76.0 mg, 0.500 mmol) and *N*-(benzyloxy)benzamide (22.7 mg, 0.100 mmol) were added to a microwave vial, sealed and purged with nitrogen. The mixture was dissolved in either (a) acetonitrile or (b) propylene carbonate [0.1 M] and stirred at room temperature for 12 hours. Afterwards, the solvent was removed *in vacuo* and the resulting residue was then submitted for ^{1}H NMR spectroscopic analysis with dibromomethane as the internal standard. The crude material acquired from the reaction in PC was then purified by silica gel flash chromatography (1:9 ethyl acetate:*n*-hexane) to afford *N*-(benzyloxy)-*N*-phenylbenzamide **14** (19.7 mg, 0.0650 mmol, 65%) as a pale yellow oil; R_f 0.20 (1:9 ethyl acetate:*n*-hexane).

a) **In MeCN:** NMR yield = 66%
b) **In PC:** NMR yield = 69% (isolated yield = 65%)

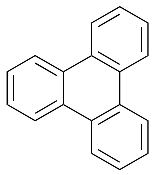
^{1}H NMR (400 MHz, CDCl$_3$): δ_H 7.52 (dd, *J* = 8.3, 1.3 Hz, 2H), 7.43 (d, *J* = 7.8 Hz, 2H), 7.37 – 7.13 (m, 9H), 7.07 – 6.99 (m, 2H), 4.74 (s, 2H).

^{13}C NMR (101 MHz, CDCl$_3$): δ_C 168.6, 139.8, 134.9, 134.2, 130.7, 129.7, 129.1, 129.0, 128.7, 128.6, 128.0, 127.0, 124.2, 76.5.

Data is consistent with previously reported literature values.[15]

2.7. Synthesis and characterisation of metal-catalysed cyclotrimerization

Triphenylene, 15



According to a modified literature procedure,[16] 2-(trimethylsilyl)phenyl trifluoromethanesulfonate **1** (50 µL, 0.206 mmol), cesium fluoride (62.6 mg, 0.412 mmol) and Pd(PPh$_3$)$_4$ (238 mg, 0.206 mmol) were added to a microwave vial, sealed and purged with nitrogen. The mixture was dissolved in either (a) acetonitrile or (b) propylene carbonate [0.1 M] and stirred at 50 °C for 12 hours. The reaction was quenched with cold NaHCO$_3$ (sat. aq., 15 mL) and the mixture extracted with petroleum ether (3 x 10 mL). The combined organic layers were dried over MgSO$_4$ and concentrated *in vacuo*. The resulting residue was then submitted for ^{1}H NMR spectroscopic analysis with dibromomethane as the internal standard. The crude material acquired from the reaction in PC was then purified by silica gel flash chromatography (100 % *n*-hexane) to afford triphenylene **15** (22.1 mg, 0.097 mmol, 47%) as an amorphous white solid; R_f 0.12 (100% *n*-hexane).

a) **In MeCN:** NMR yield = 77%
b) **In PC:** NMR yield = 55% (isolated yield = 47%)

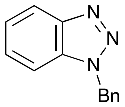
^{1}H NMR (400 MHz, CDCl$_3$): δ_H 8.71 – 8.63 (m, 6H), 7.71 – 7.63 (m, 6H).

^{13}C NMR (101 MHz, CDCl$_3$): δ_C 129.9, 127.4, 123.4.

Data is consistent with previously reported literature values.[16]

2.8. Synthesis and characterisation of 1,3-dipolar cycloaddition

1-Benzyl-1H-benzo[d][1,2,3]triazole, 16



According to a modified literature procedure,[17] 2-(trimethylsilyl)phenyl trifluoromethanesulfonate **1** (70 µL, 0.289 mmol), cesium fluoride (87.7 mg, 0.577 mmol) and benzyl azide (30.9 µL, 0.248 mmol) were added to a microwave vial, sealed and purged with nitrogen. The mixture was dissolved in either (a) acetonitrile or (b) propylene carbonate [0.1 M] and stirred at 50 ˚C for 24 hours. The reaction was quenched with cold $NaHCO_3$ (sat. aq., 15 mL) and the mixture extracted with petroleum ether (3 x 10 mL). The combined organic layers were dried over $MgSO_4$ and concentrated *in vacuo*. The resulting residue was submitted for ^1H NMR spectroscopic analysis with dibromomethane as the internal standard. The crude material acquired from the reaction in PC was then purified by silica gel flash chromatography (1:1 ethyl acetate:n-hexane) to afford 1-benzyl-1H-benzo[d][1,2,3]triazole **16** (27.0 mg, 0.129 mmol, 52%) as a dark orange amorphous solid; R_f 0.21 (1:1 ethyl acetate:*n*-hexane).

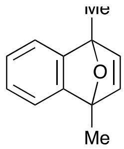
a) **In MeCN:** NMR yield = 90%
b) **In PC:** NMR yield = 62% (isolated yield = 52%)

^{1}H NMR (400 MHz, CDCl$_3$): δ_H 7.98 (d, J = 8.2 Hz, 1H), 7.34 – 7.16 (m, 8H), 5.76 (s, 2H).

^{13}C NMR (101 MHz, CDCl$_3$): δ_C 146.4, 134.9, 132.9, 129.1, 128.6, 127.7, 127.5, 124.0, 120.2, 109.8, 52.4.

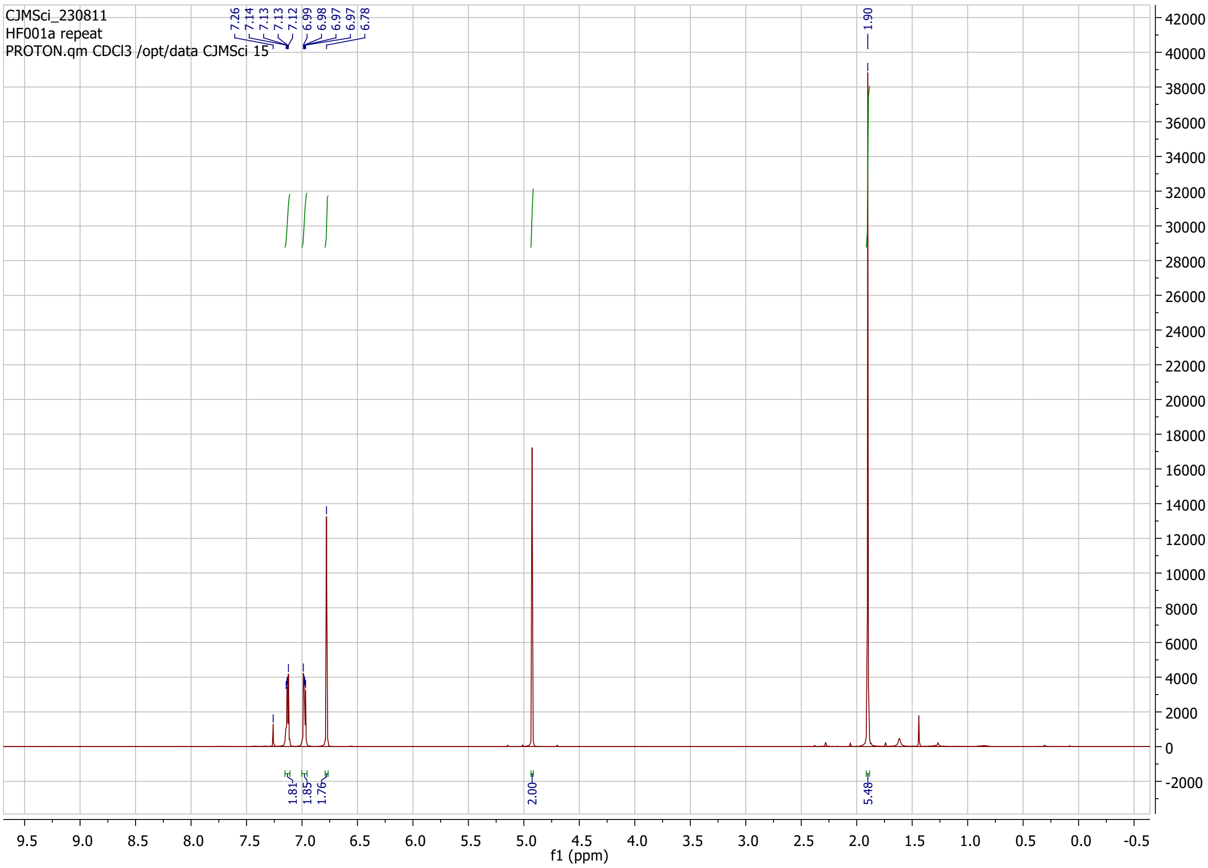
Data is consistent with previously reported literature values.[17]

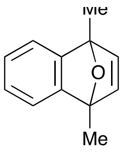
3. ^{1}H NMR Spectra of reaction mixtures for quantitative analyses



8a

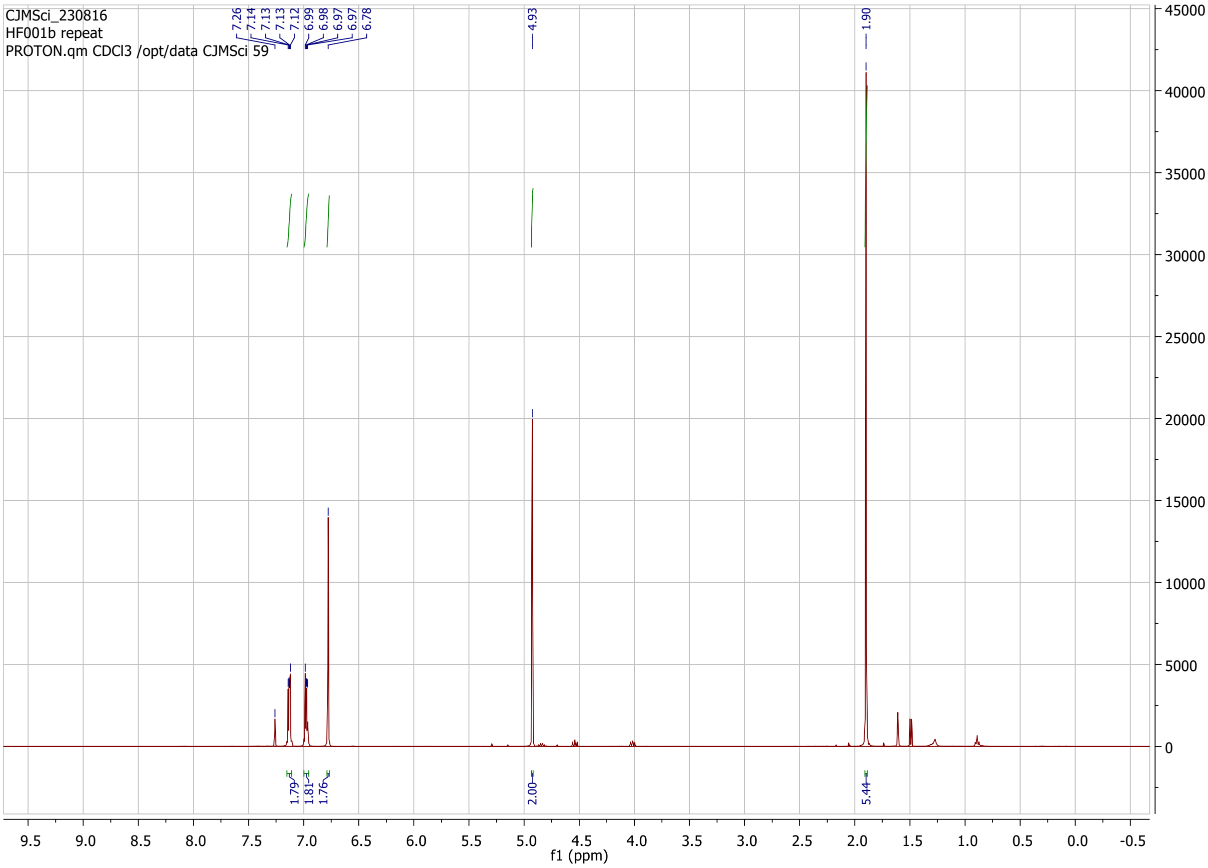
^{1}H NMR (400 MHz, $CDCl_3$) in MeCN

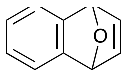




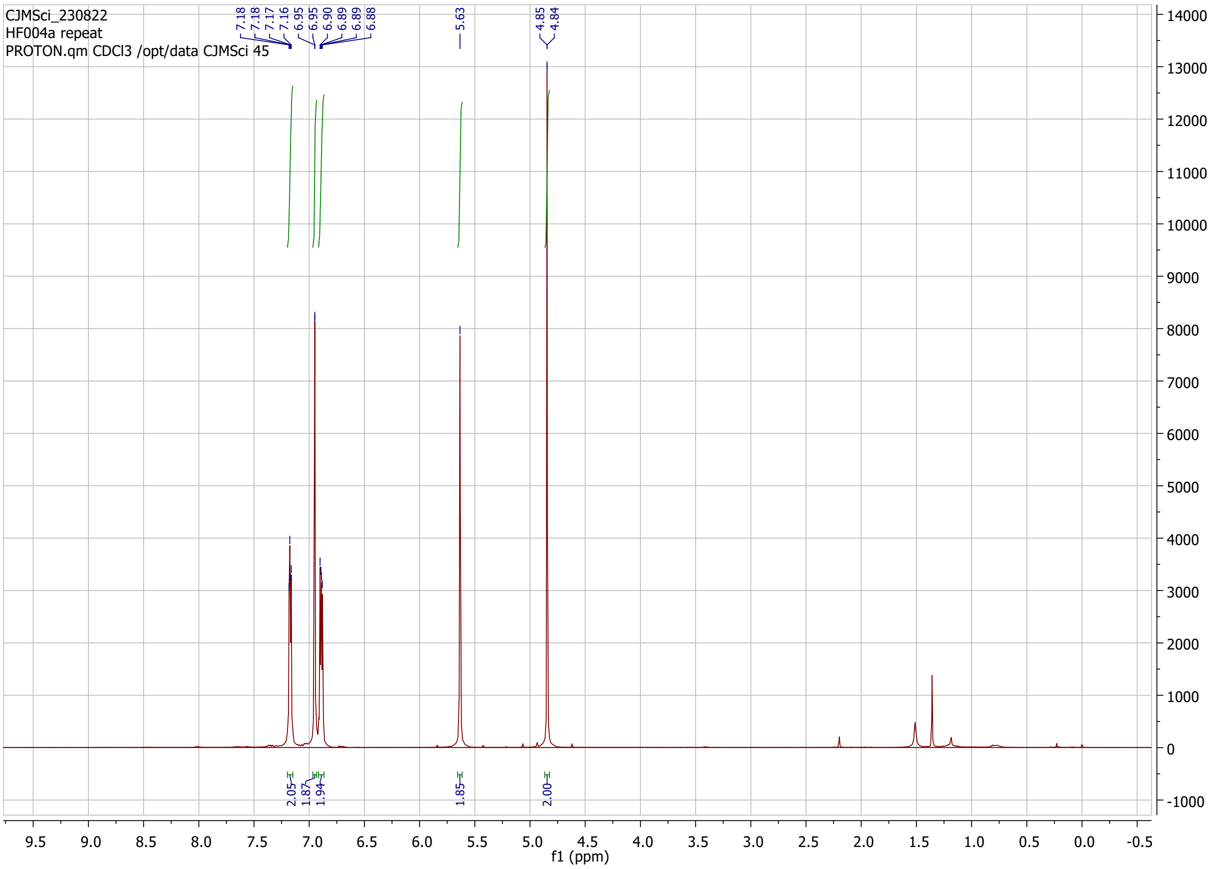
8a

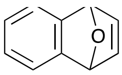
^{1}H NMR (400 MHz, $CDCl_3$) in PC



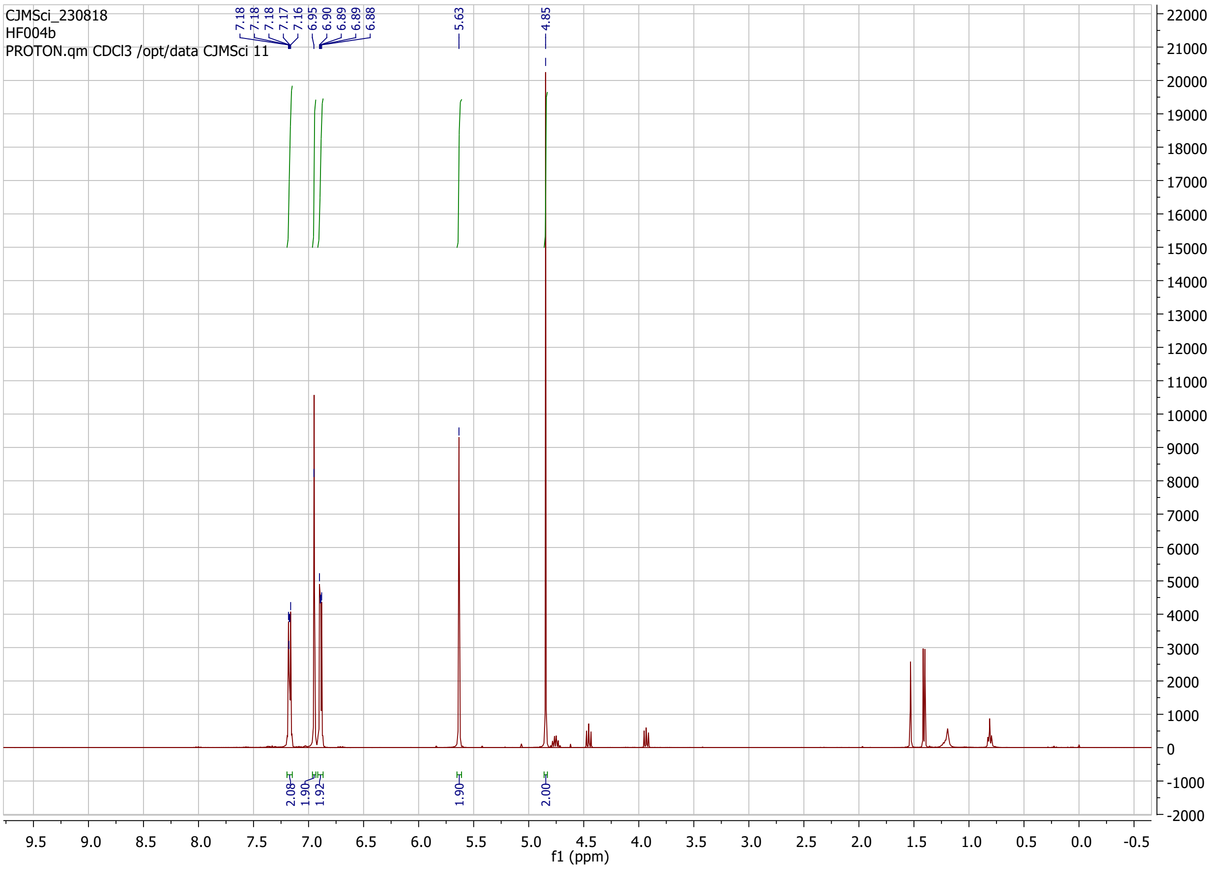


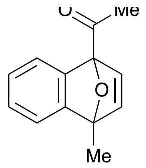
8b ^{1}H NMR (400 MHz, $CDCl_3$) in MeCN





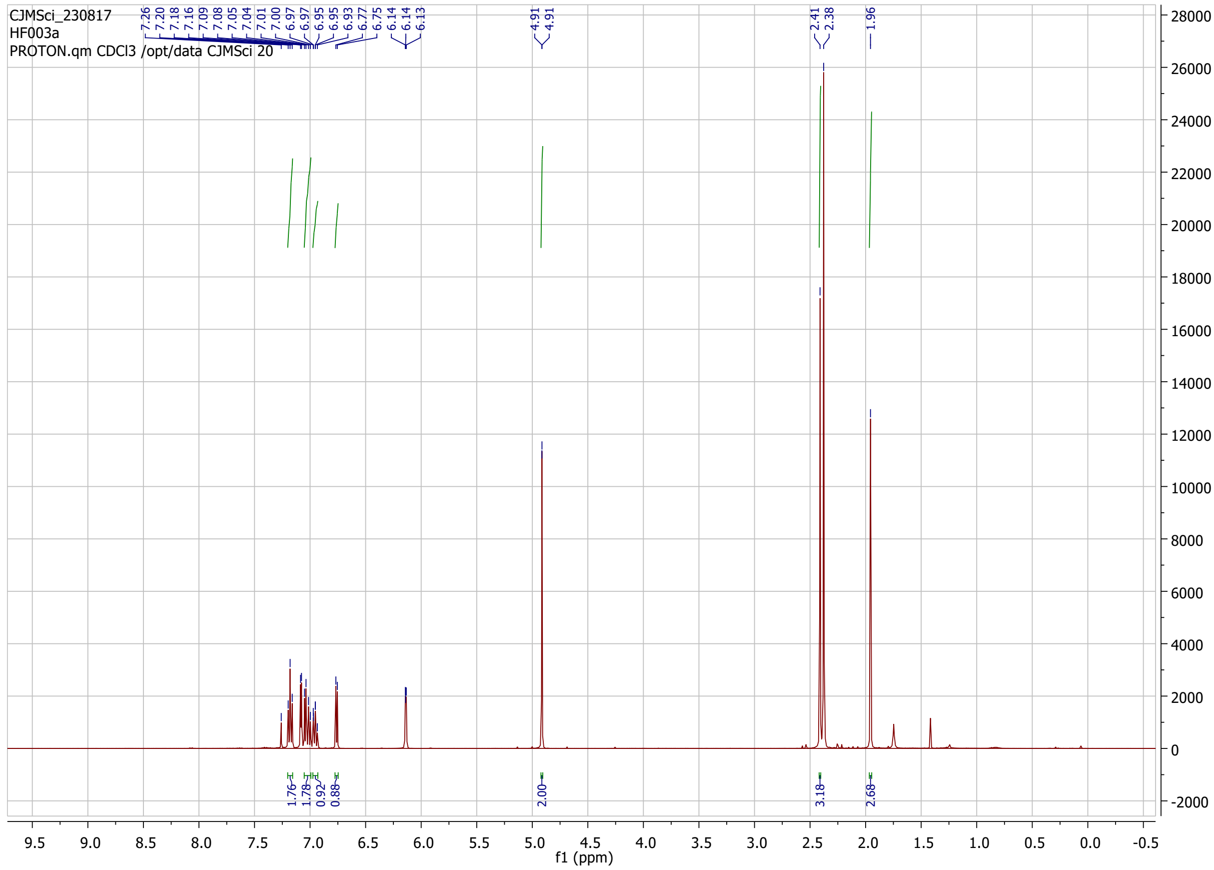
8b ^{1}H NMR (400 MHz, $CDCl_3$) in PC

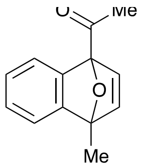




8c

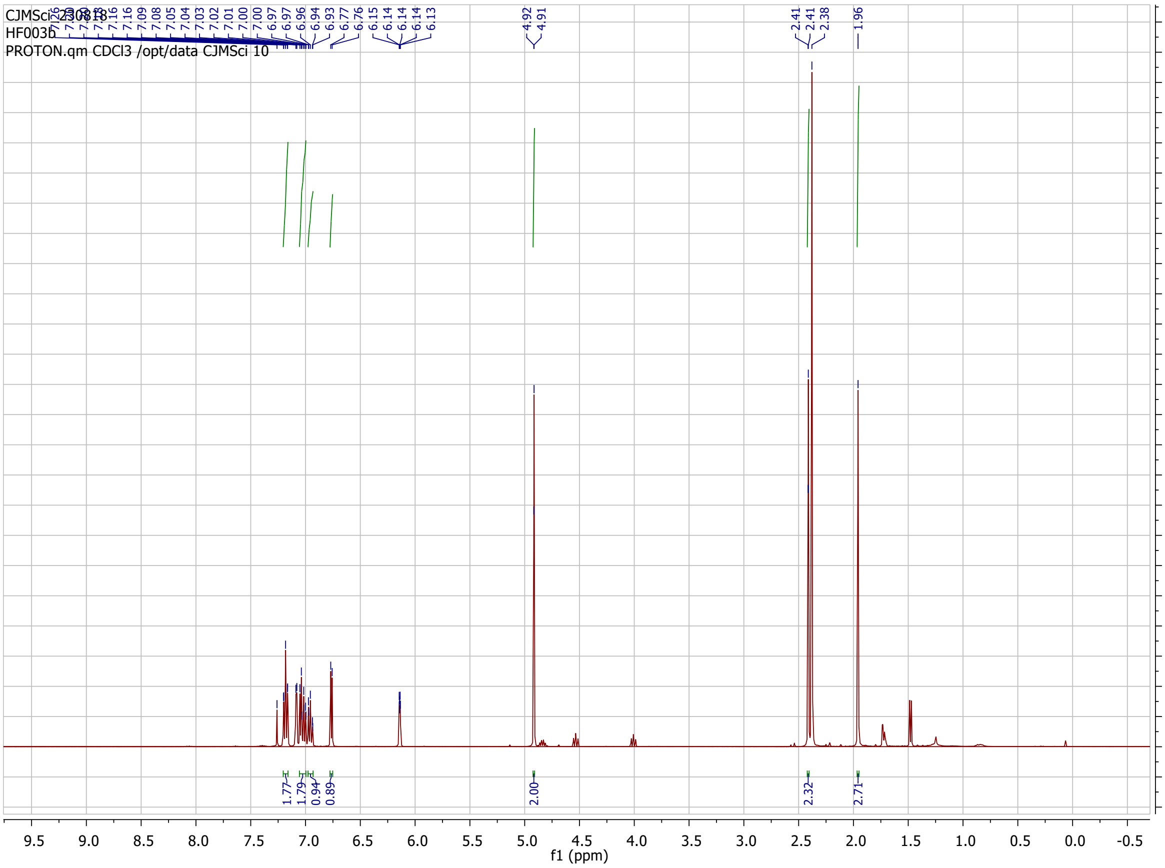
^{1}H NMR (400 MHz, $CDCl_3$) in MeCN

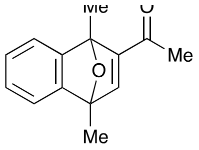




8c

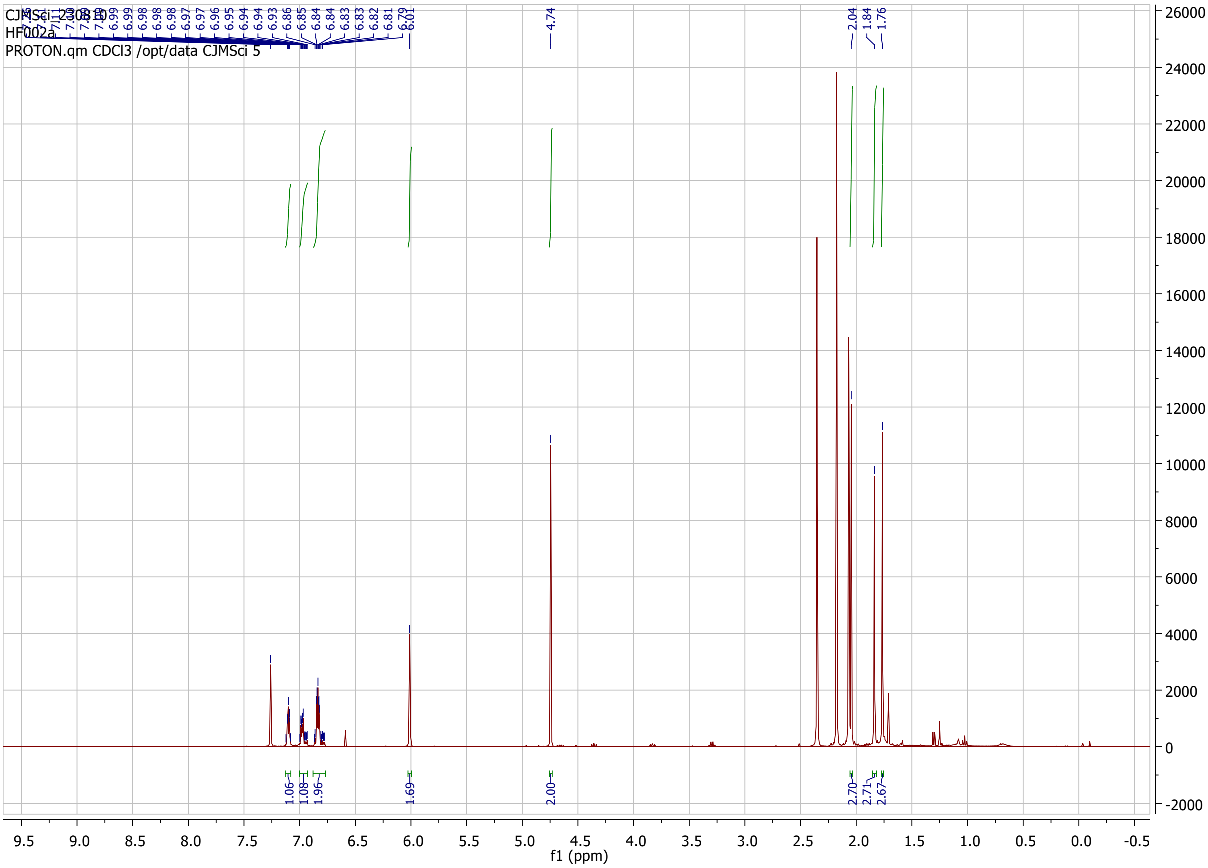
^{1}H NMR (400 MHz, $CDCl_3$) in PC

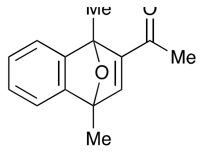




8d

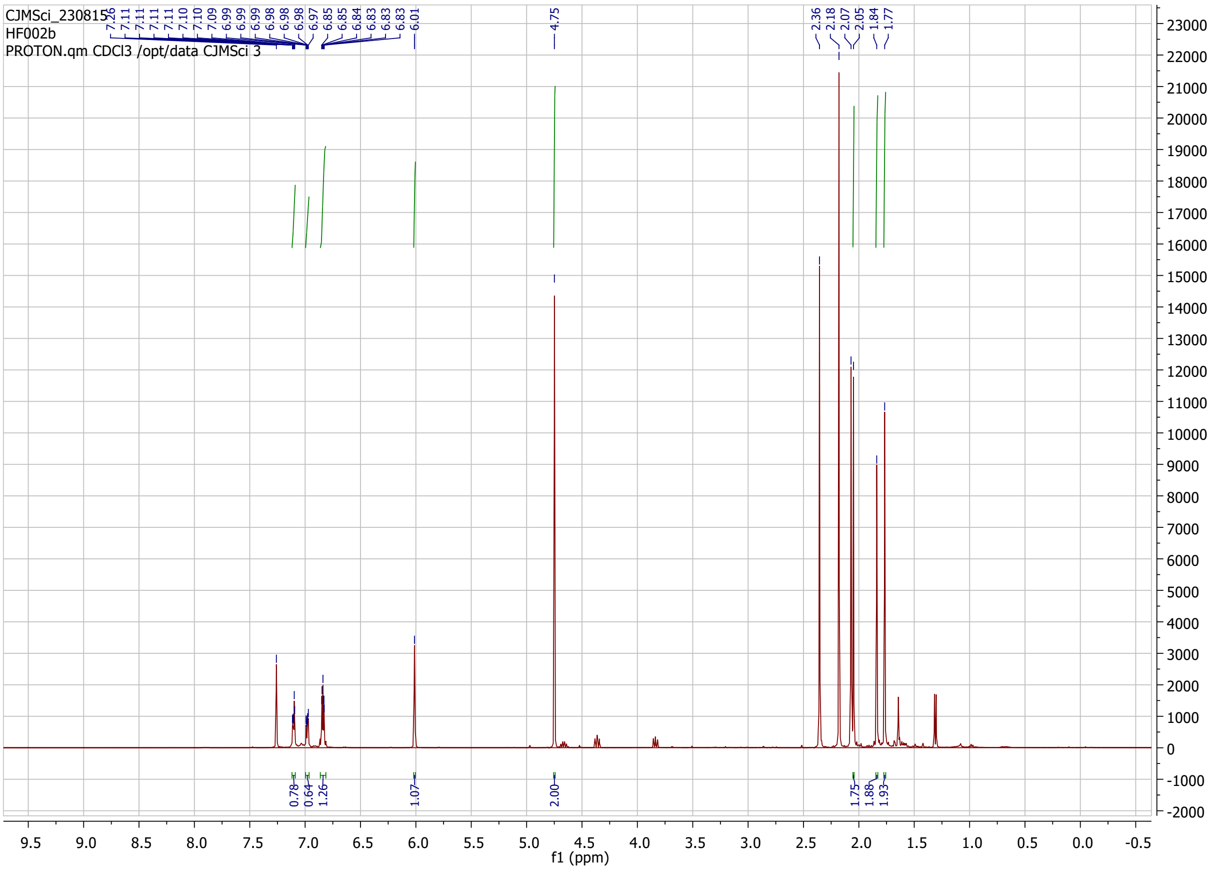
^{1}H NMR (400 MHz, $CDCl_3$) in MeCN

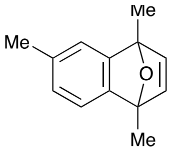




8d

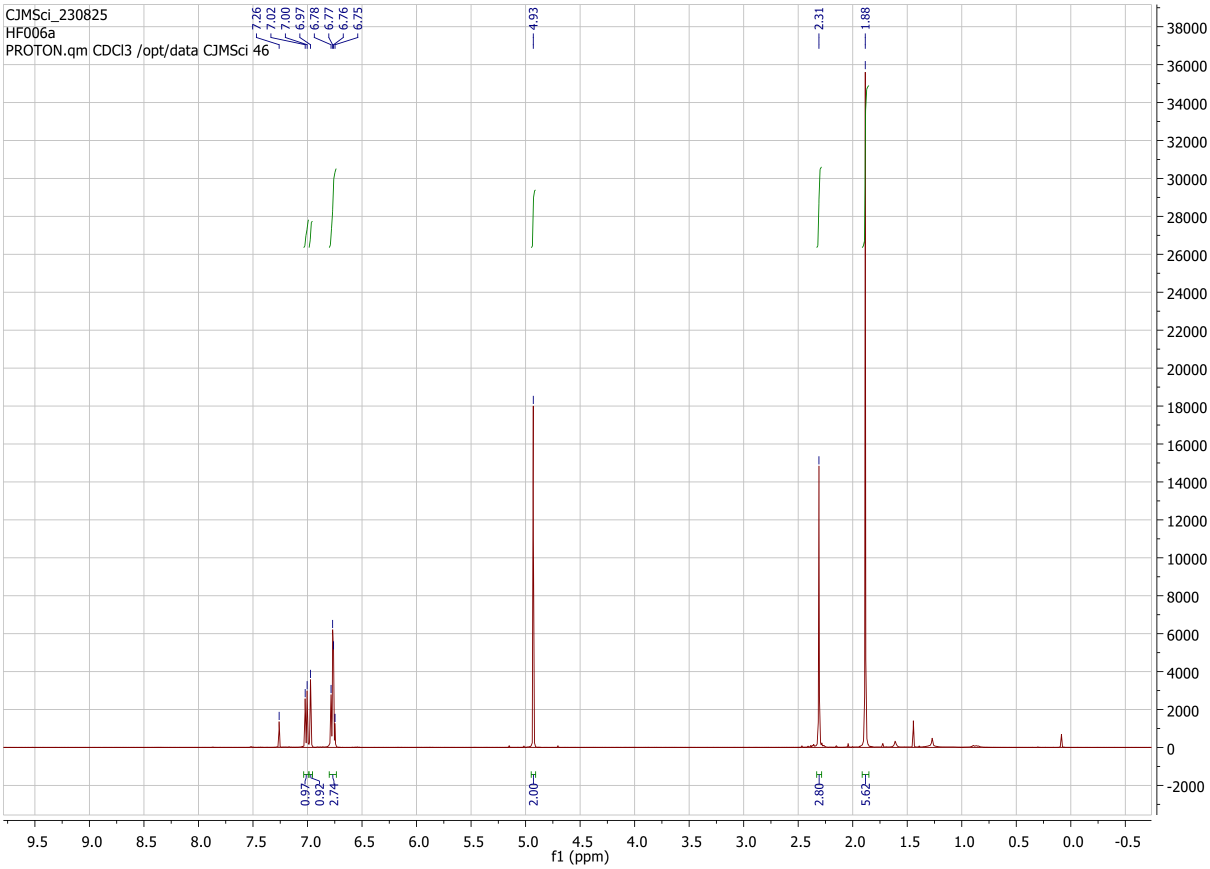
^{1}H NMR (400 MHz, $CDCl_3$) in PC

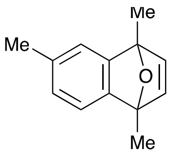




9a

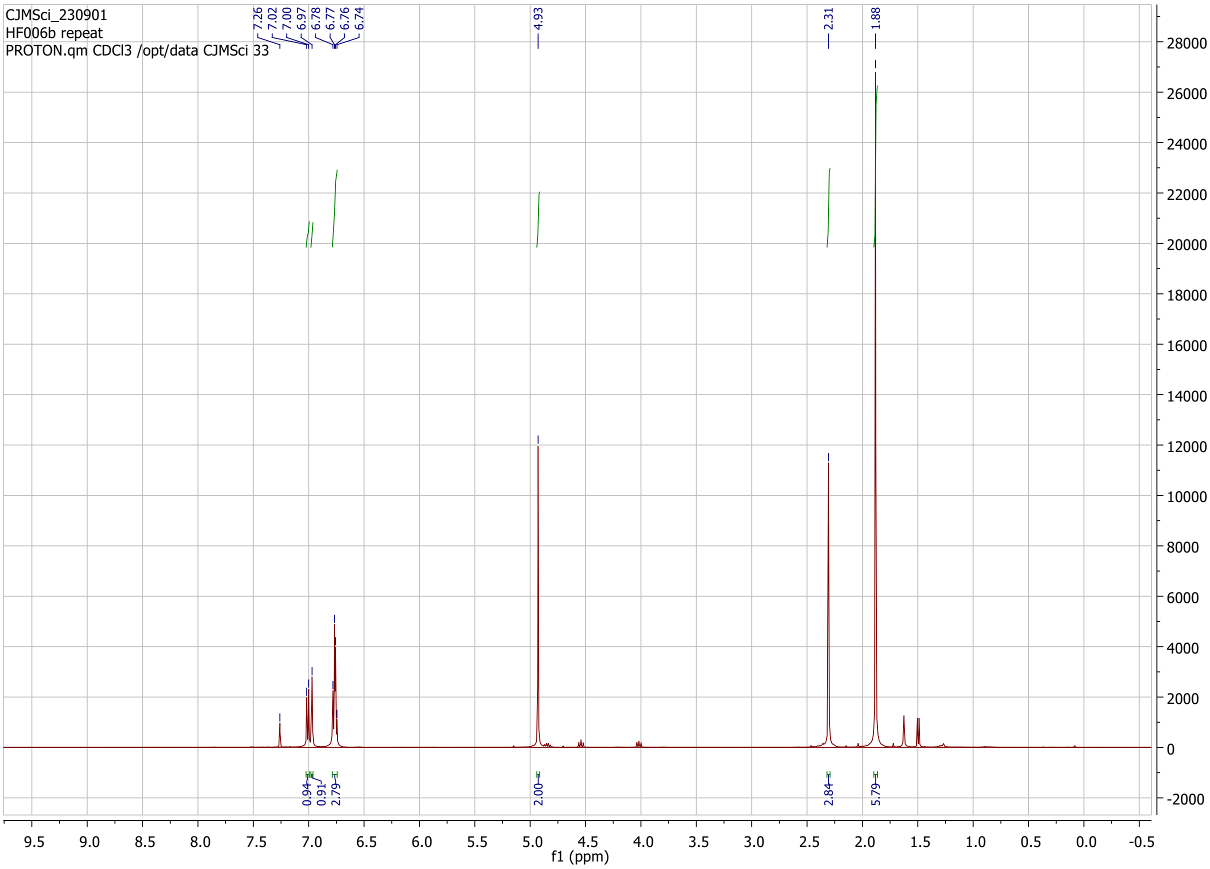
^{1}H NMR (400 MHz, $CDCl_3$) in MeCN

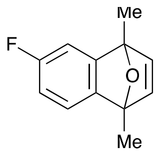




9a

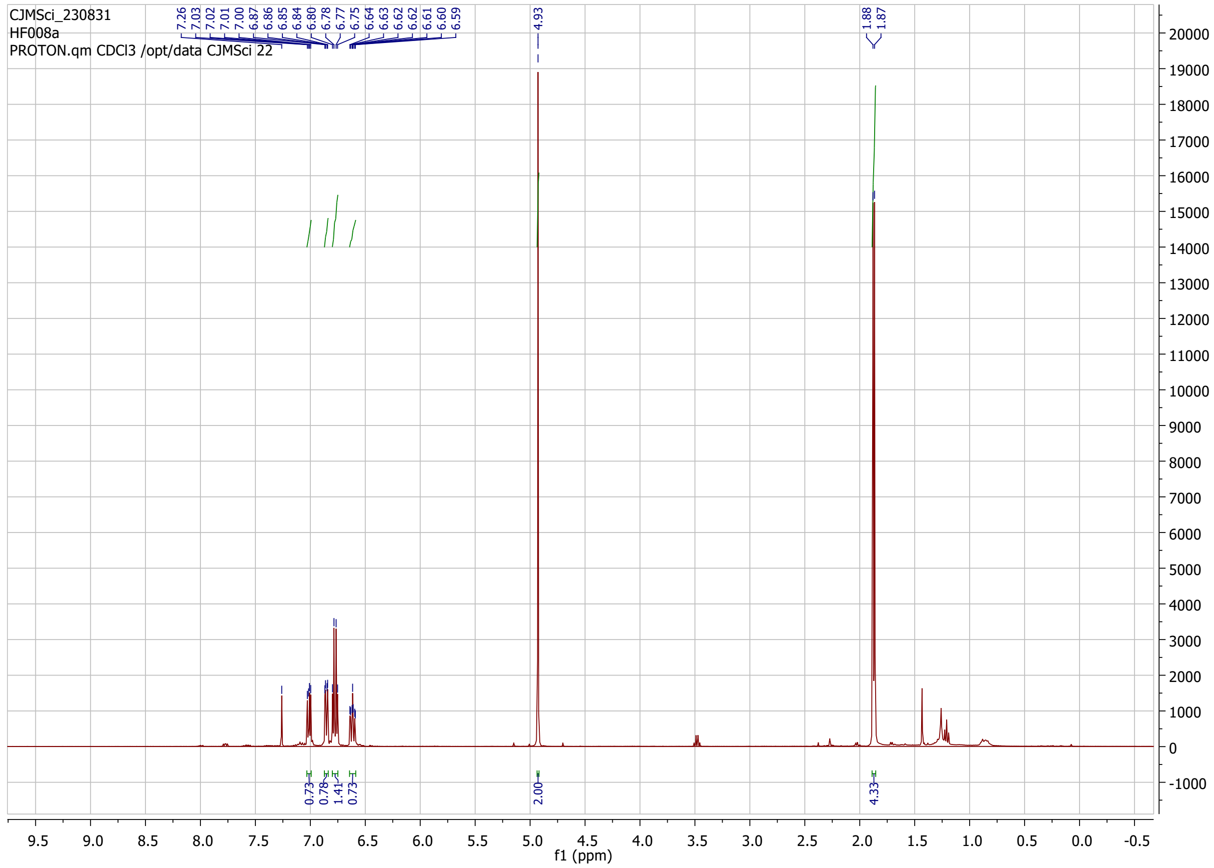
^{1}H NMR (400 MHz, $CDCl_3$) in PC

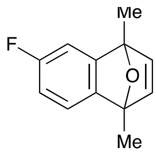




9b

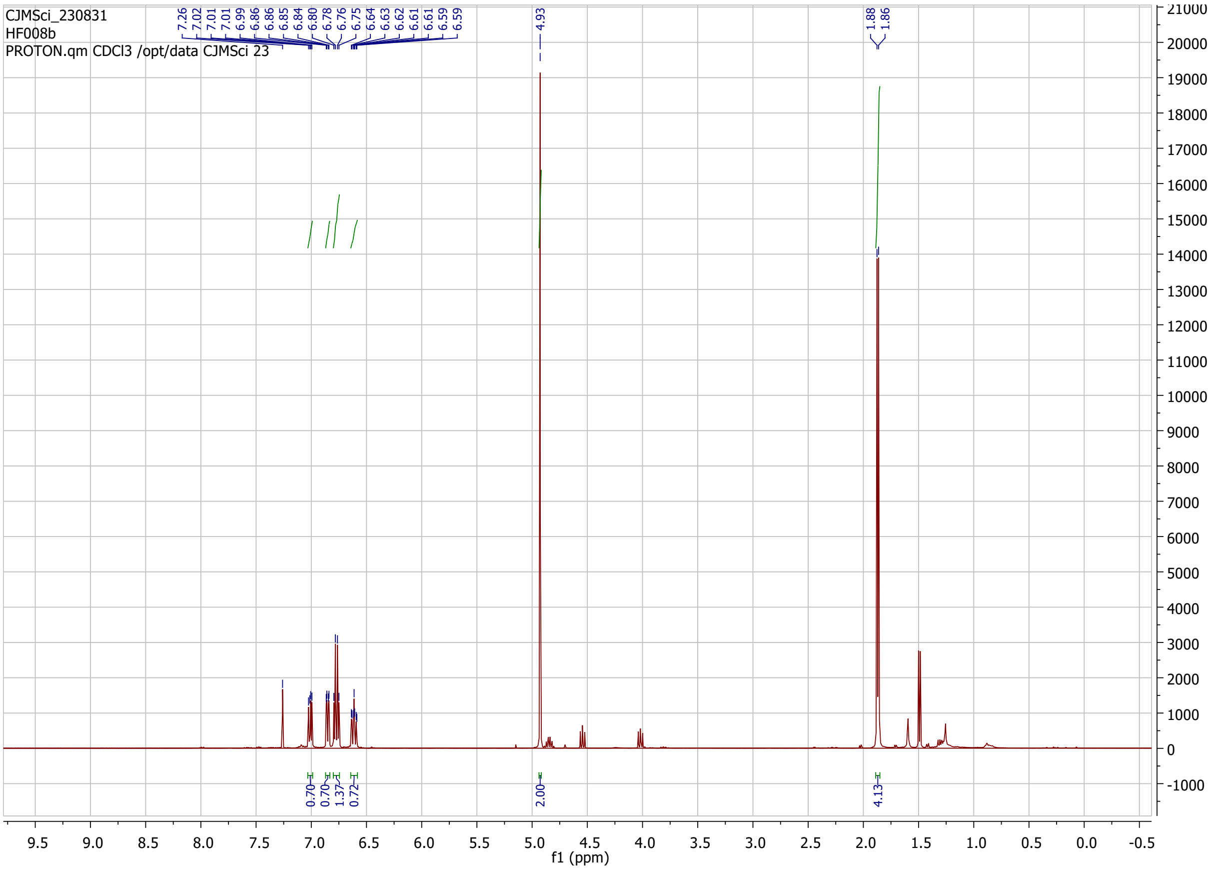
^{1}H NMR (400 MHz, $CDCl_3$) in MeCN

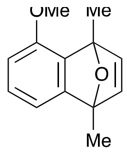




9b

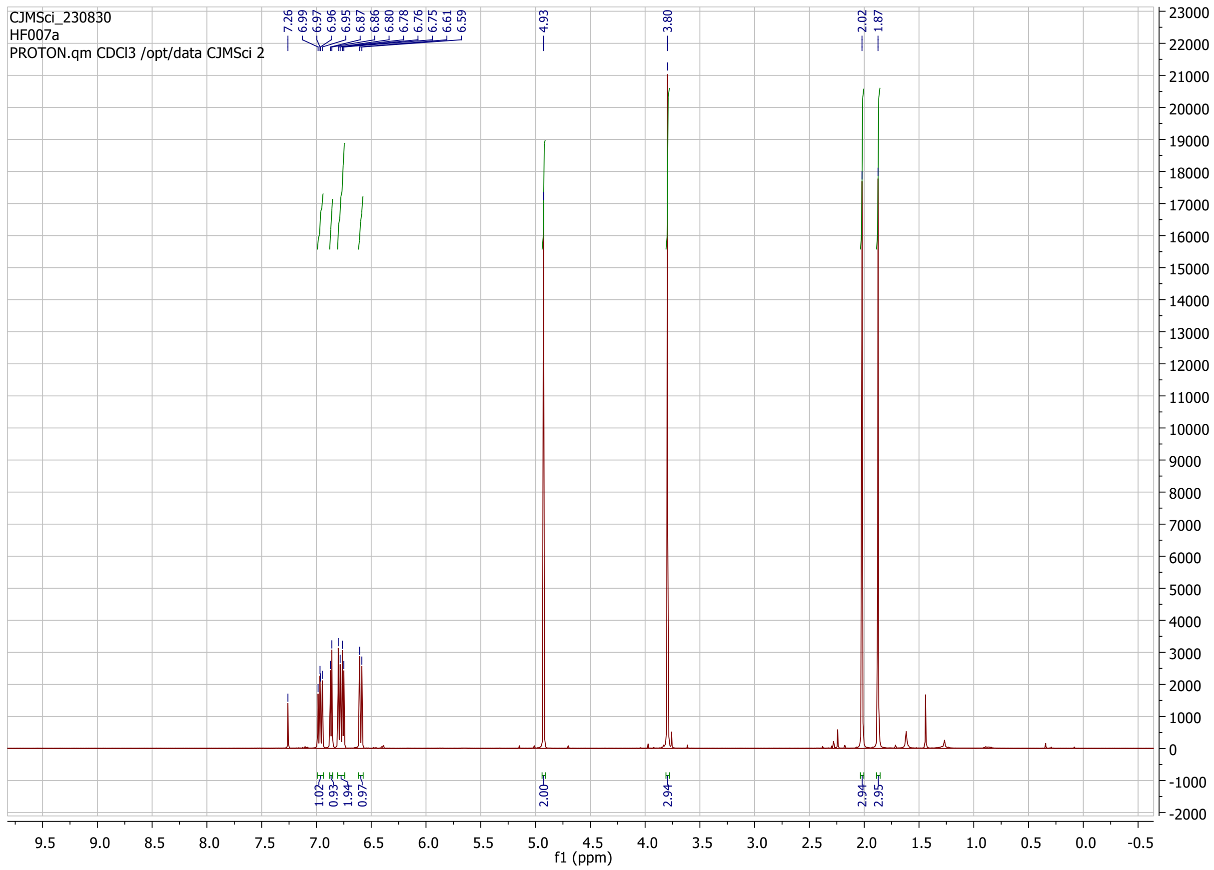
^{1}H NMR (400 MHz, $CDCl_3$) in PC

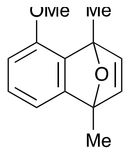




9c

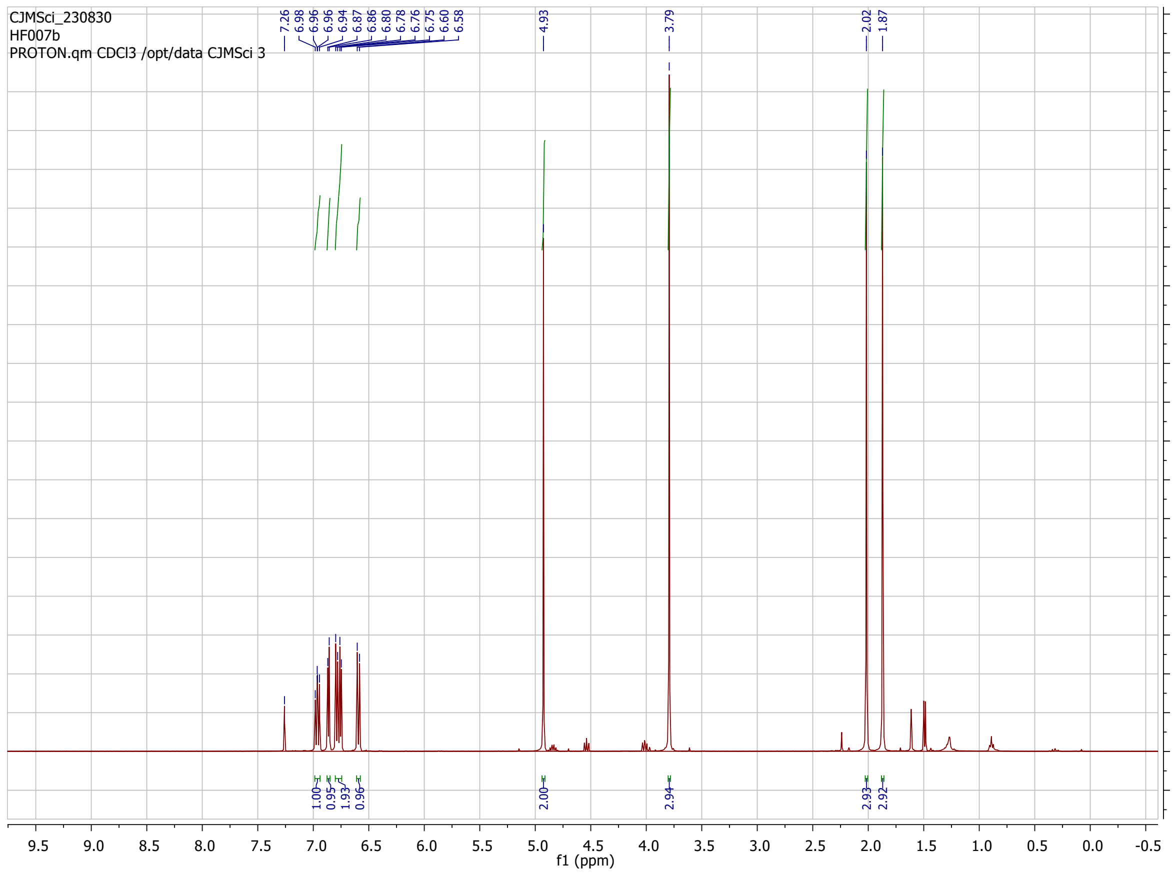
^{1}H NMR (400 MHz, $CDCl_3$) in MeCN

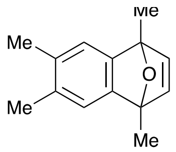




9c

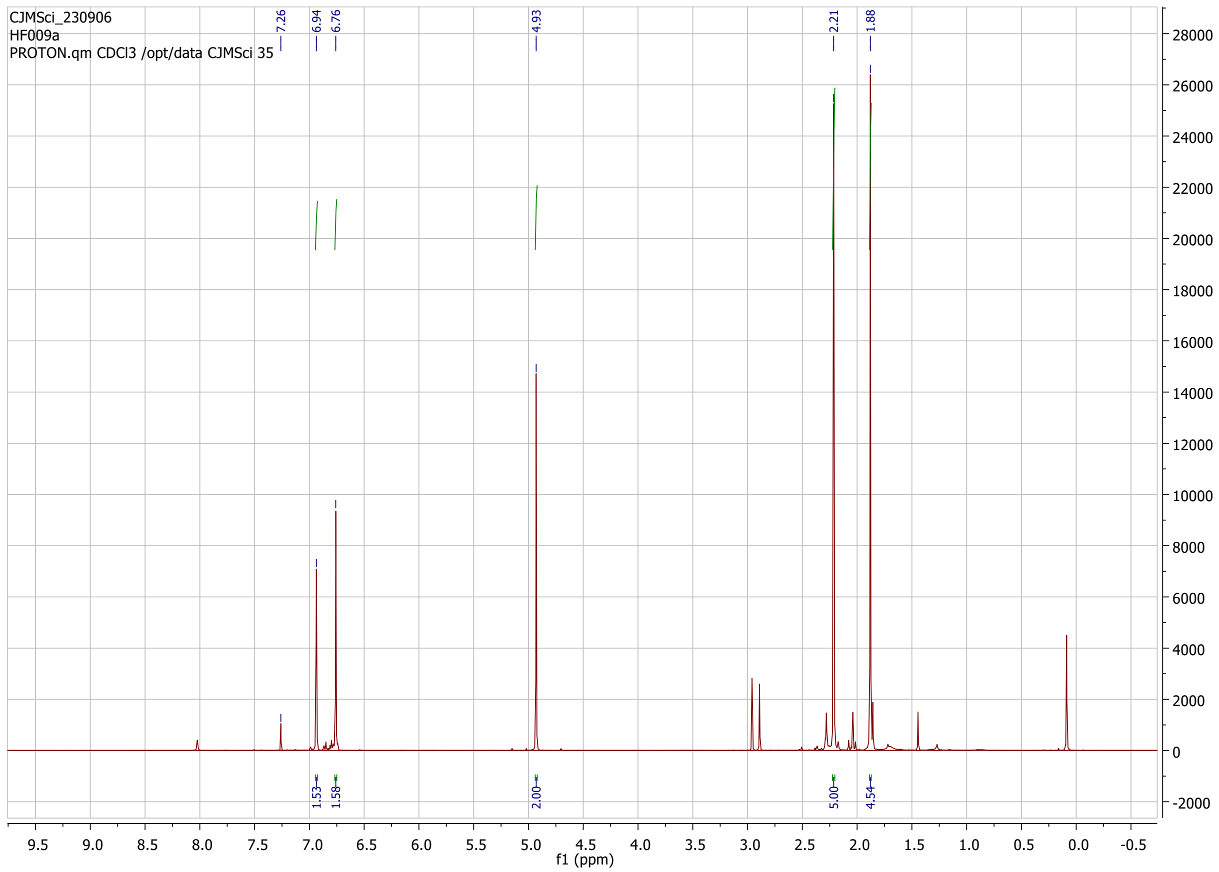
^{1}H NMR (400 MHz, $CDCl_3$) in PC

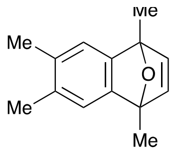




9d

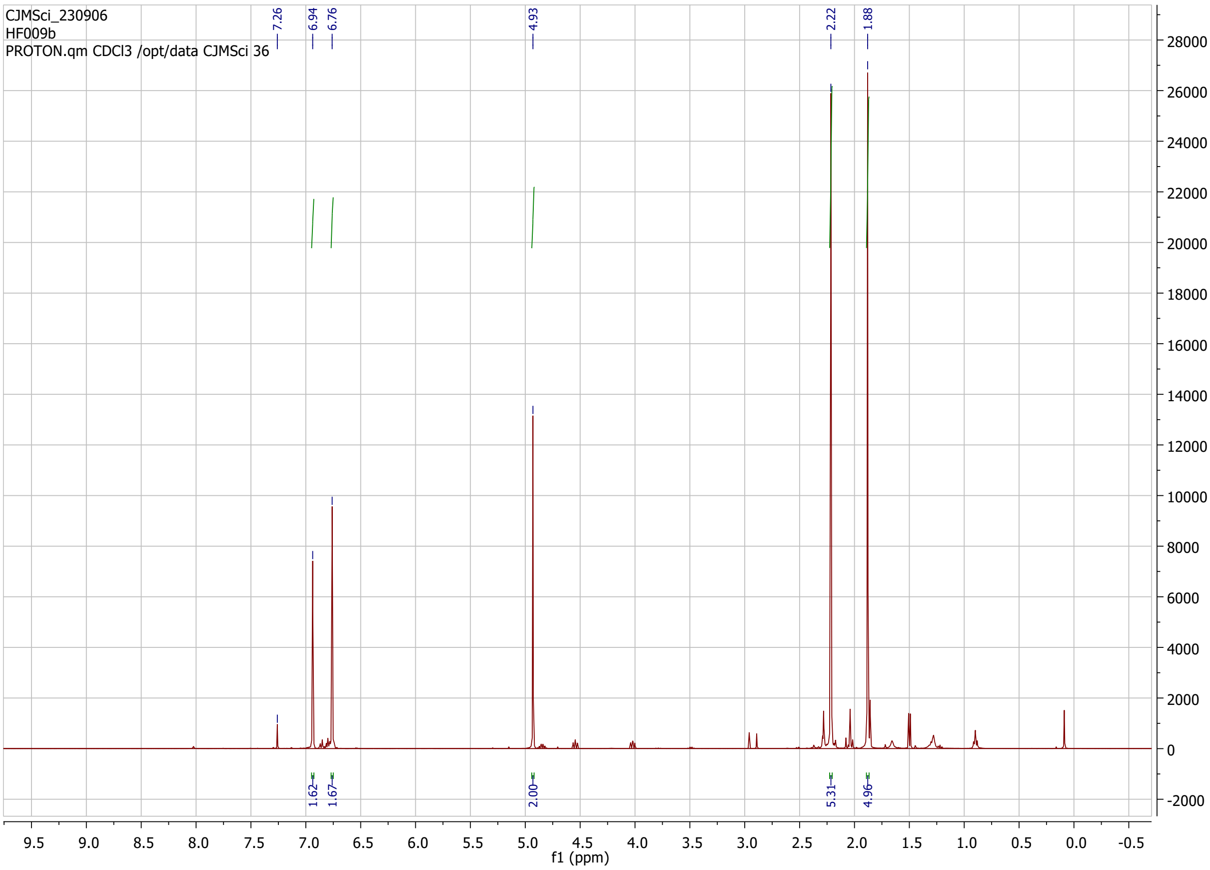
^{1}H NMR (400 MHz, $CDCl_3$) in MeCN

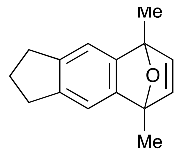




9d

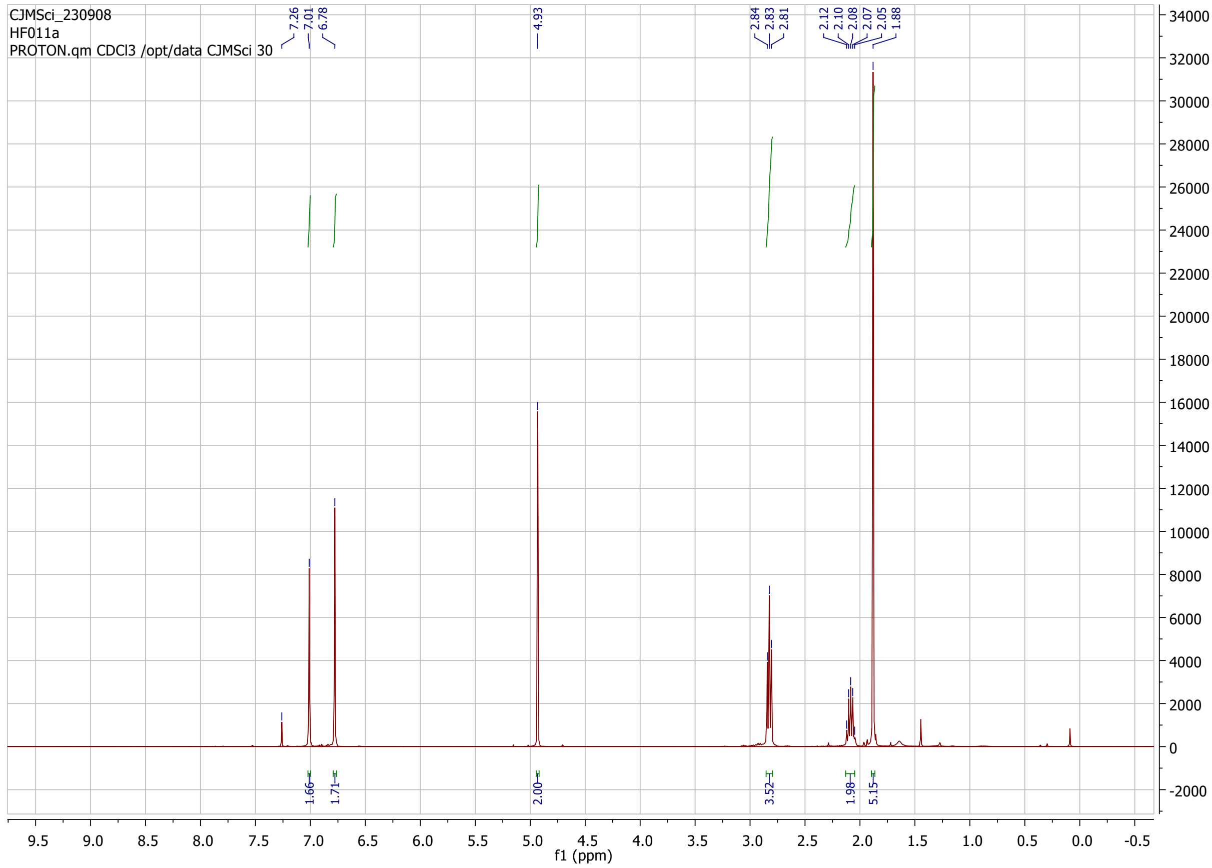
^{1}H NMR (400 MHz, $CDCl_3$) in PC

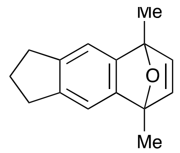




9e

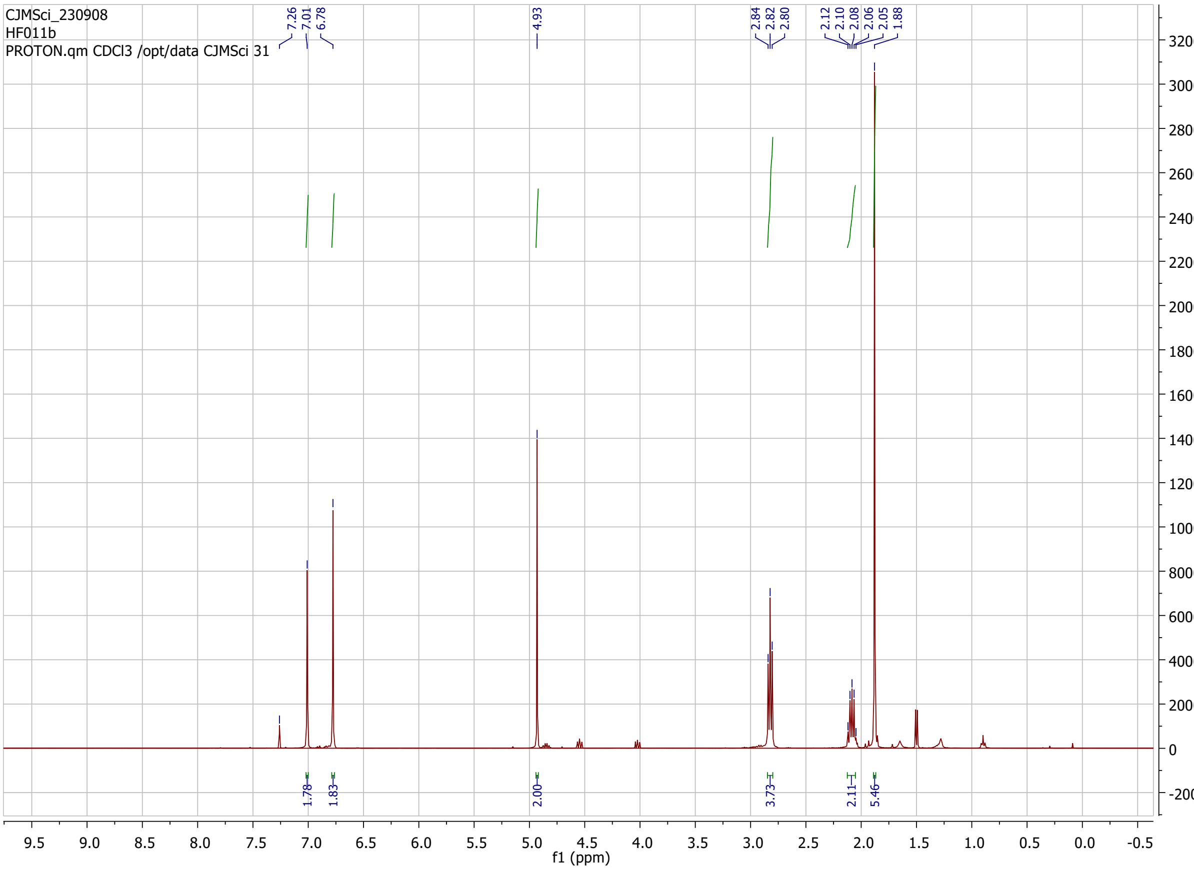
^{1}H NMR (400 MHz, $CDCl_3$) in MeCN

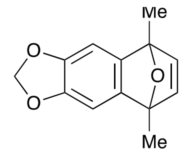




9e

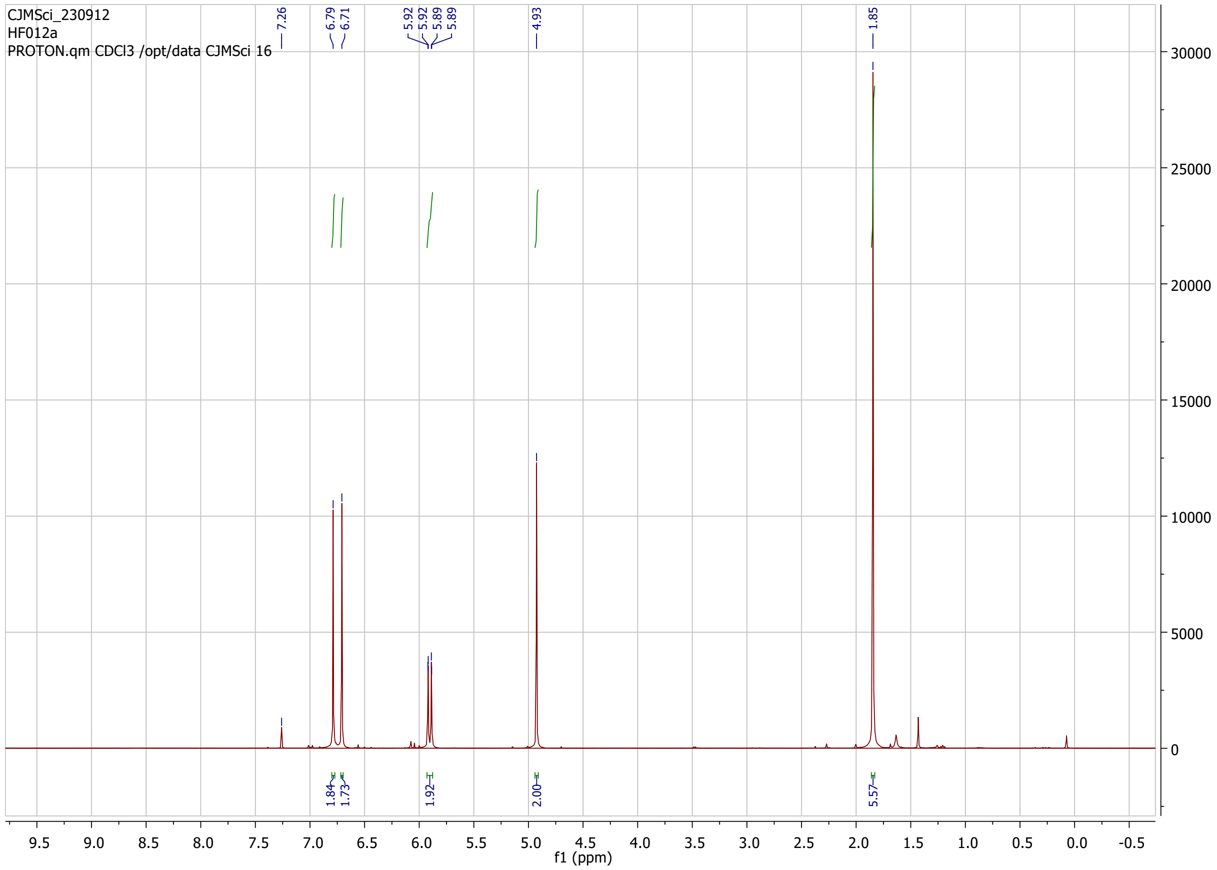
^{1}H NMR (400 MHz, $CDCl_3$) in PC

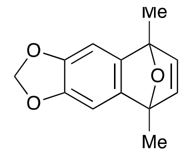




9f

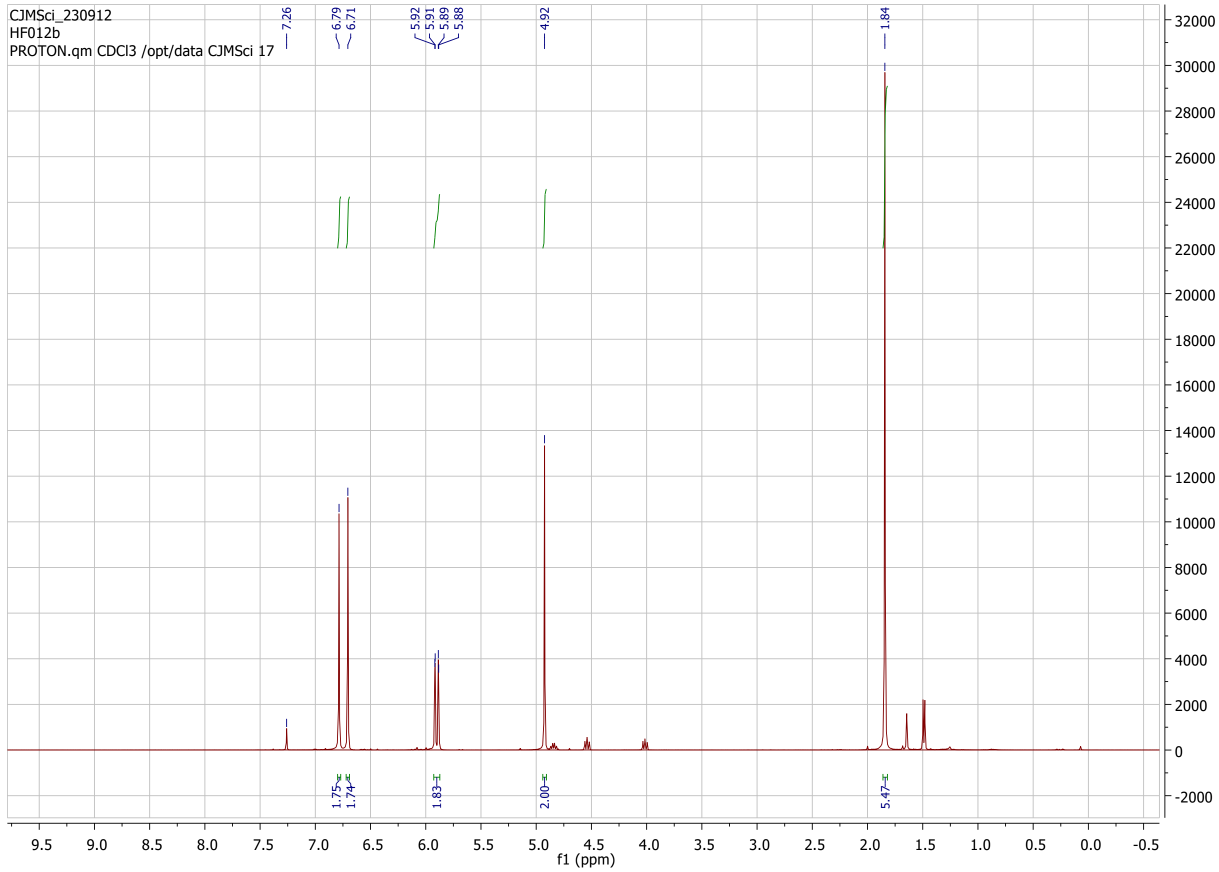
^{1}H NMR (400 MHz, $CDCl_3$) in MeCN

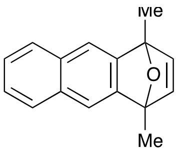




9f

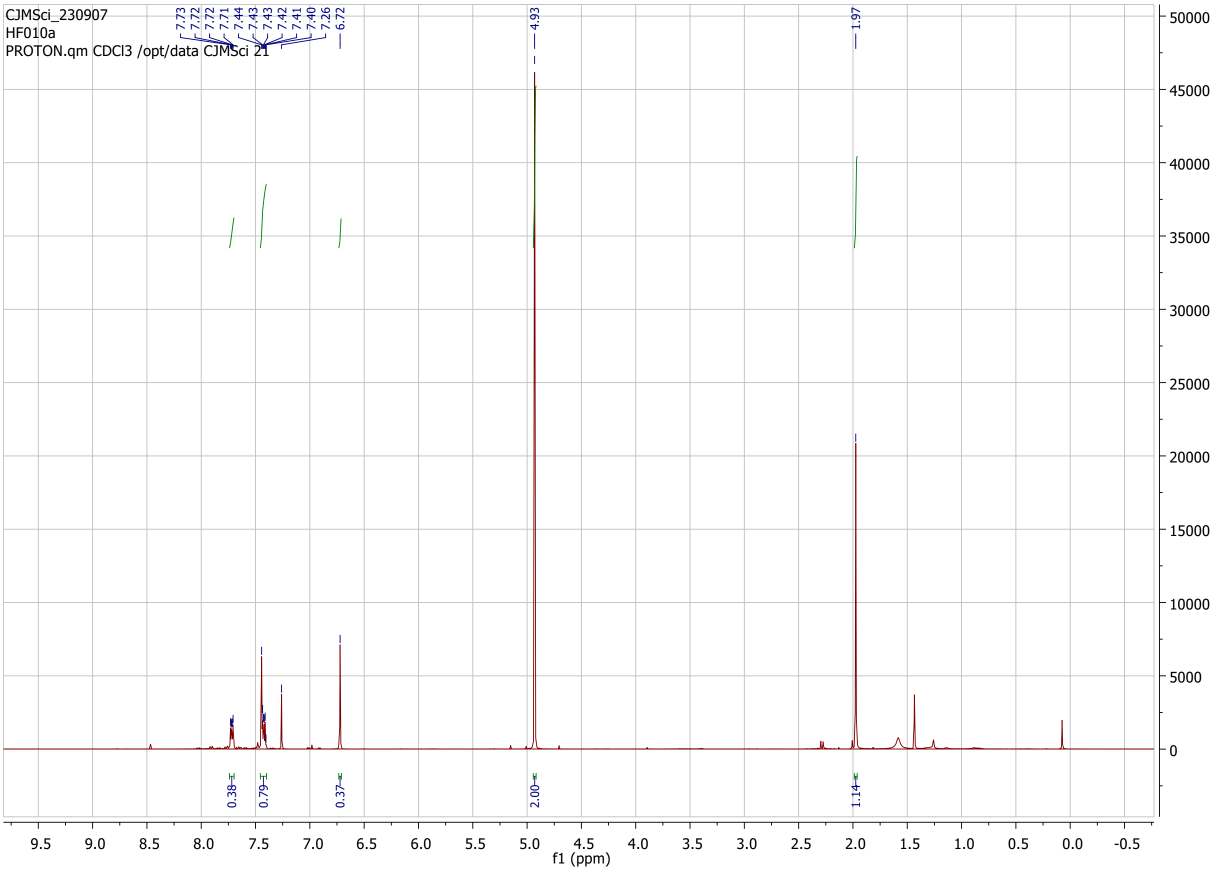
^{1}H NMR (400 MHz, $CDCl_3$) in PC

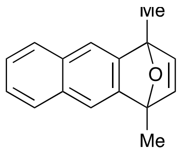




9g

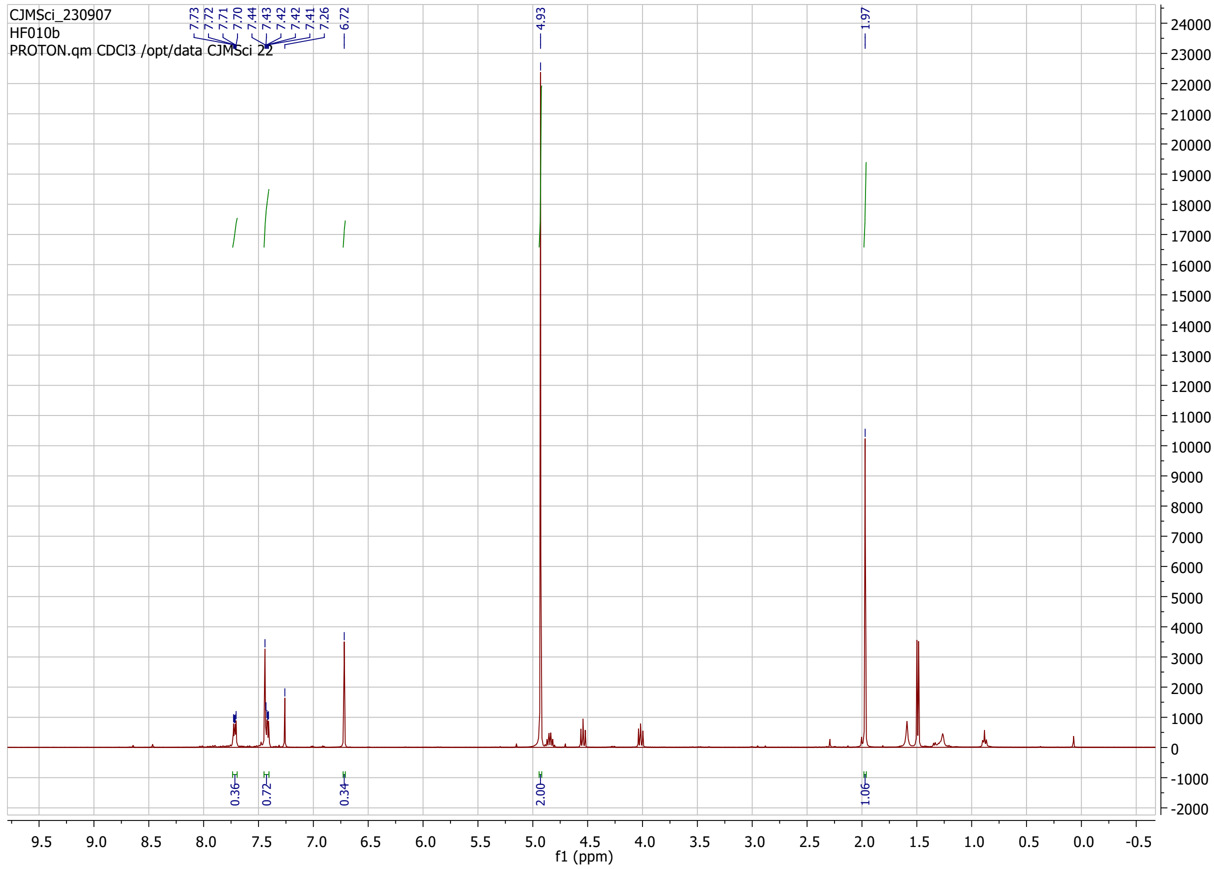
^{1}H NMR (400 MHz, $CDCl_3$) in MeCN

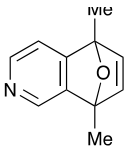




9g

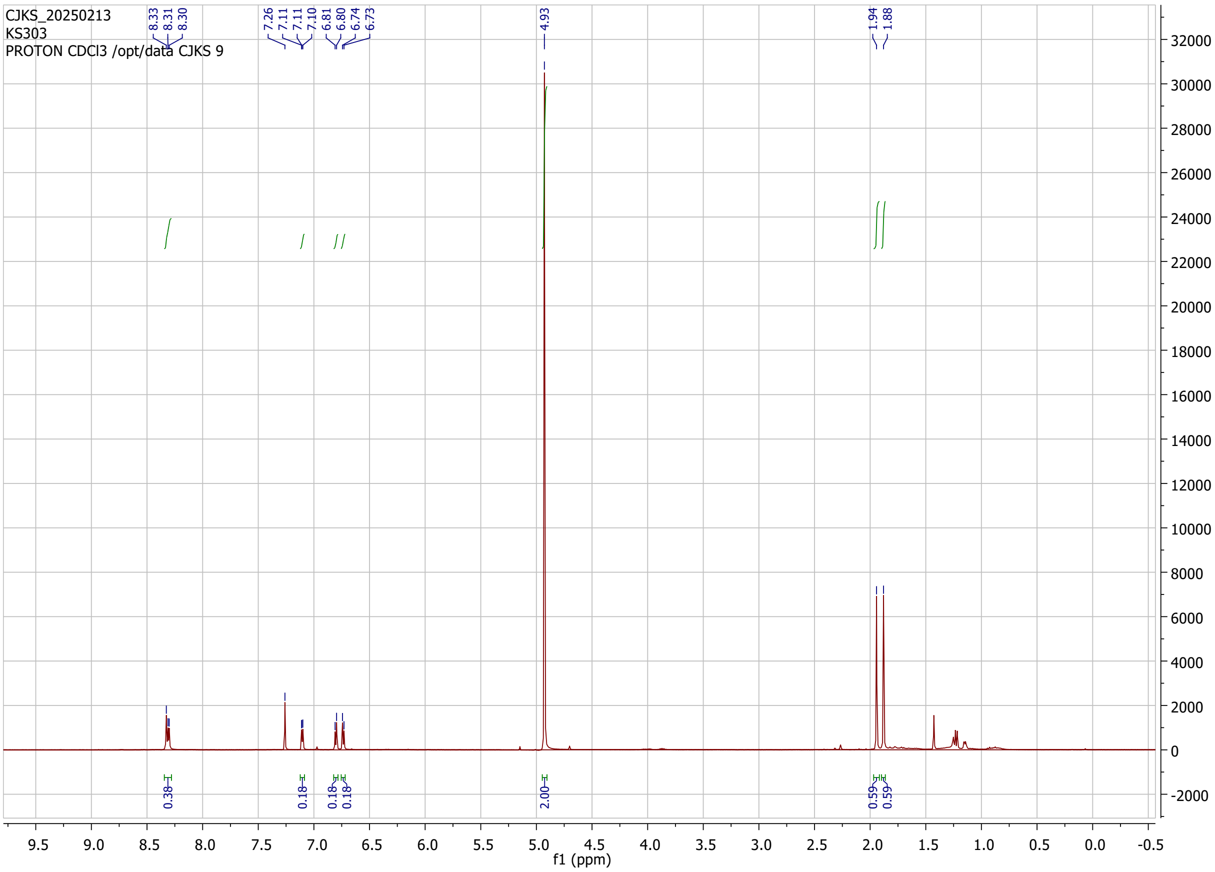
^{1}H NMR (400 MHz, $CDCl_3$) in PC

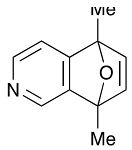




9h

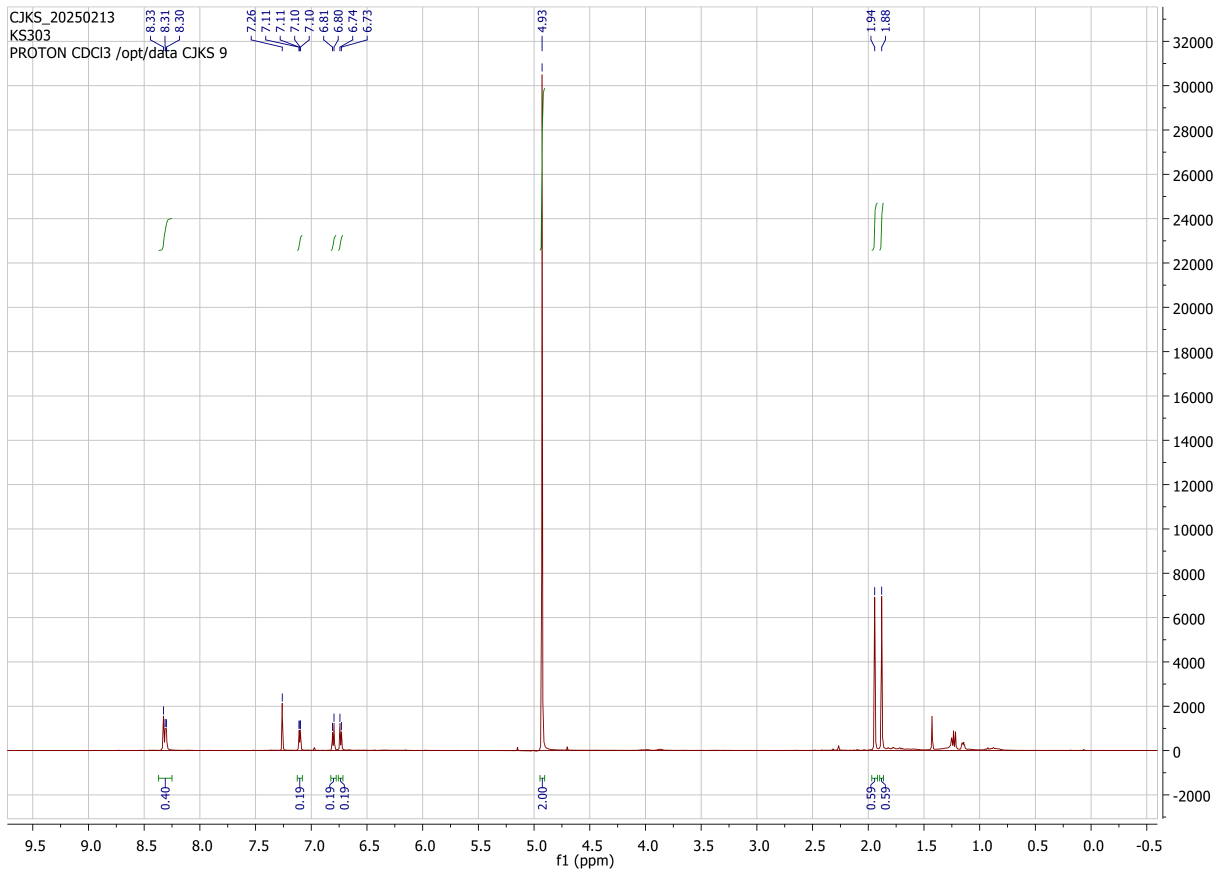
^{1}H NMR (400 MHz, $CDCl_3$) in MeCN

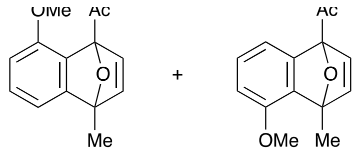




9h

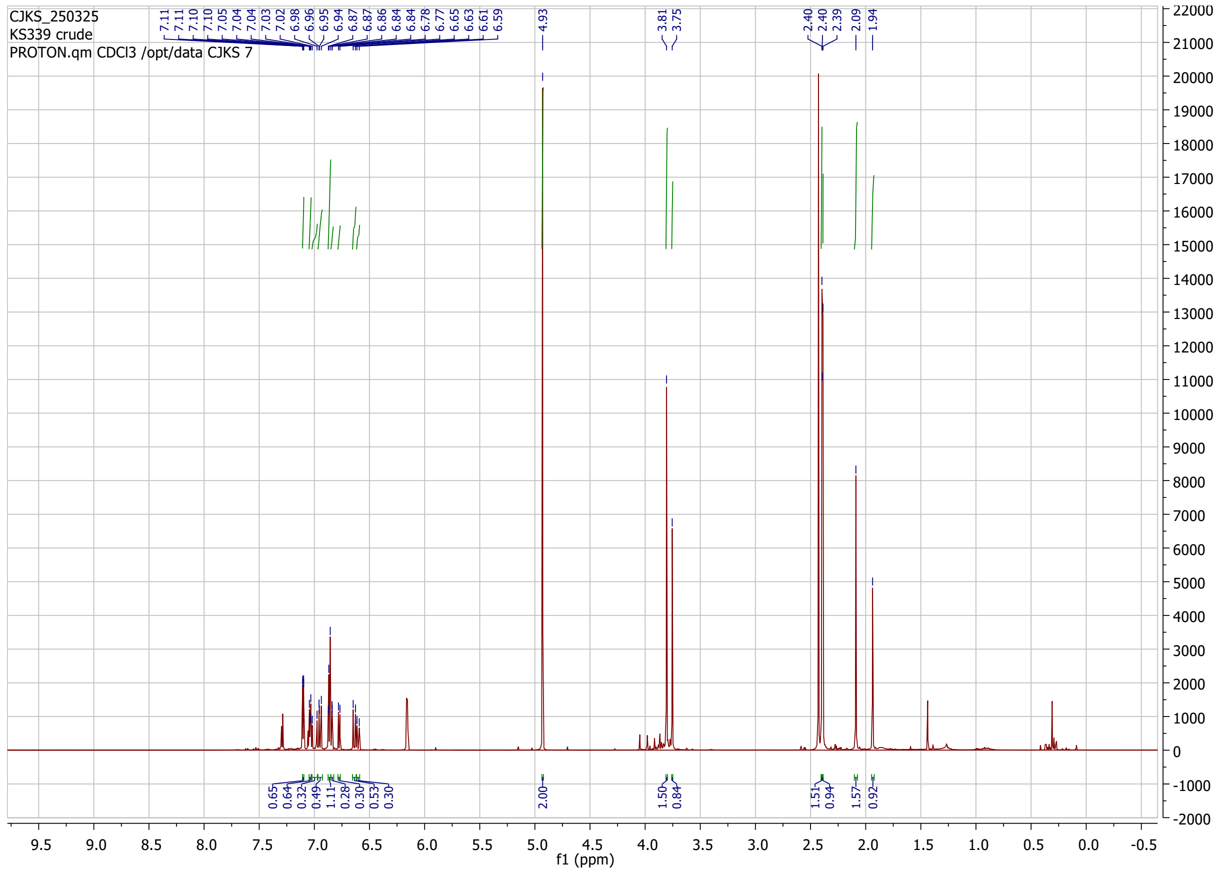
^{1}H NMR (400 MHz, $CDCl_3$) in PC

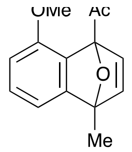




9i + **9i'**

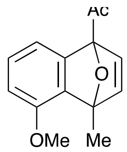
^{1}H NMR (400 MHz, $CDCl_3$) in MeCN





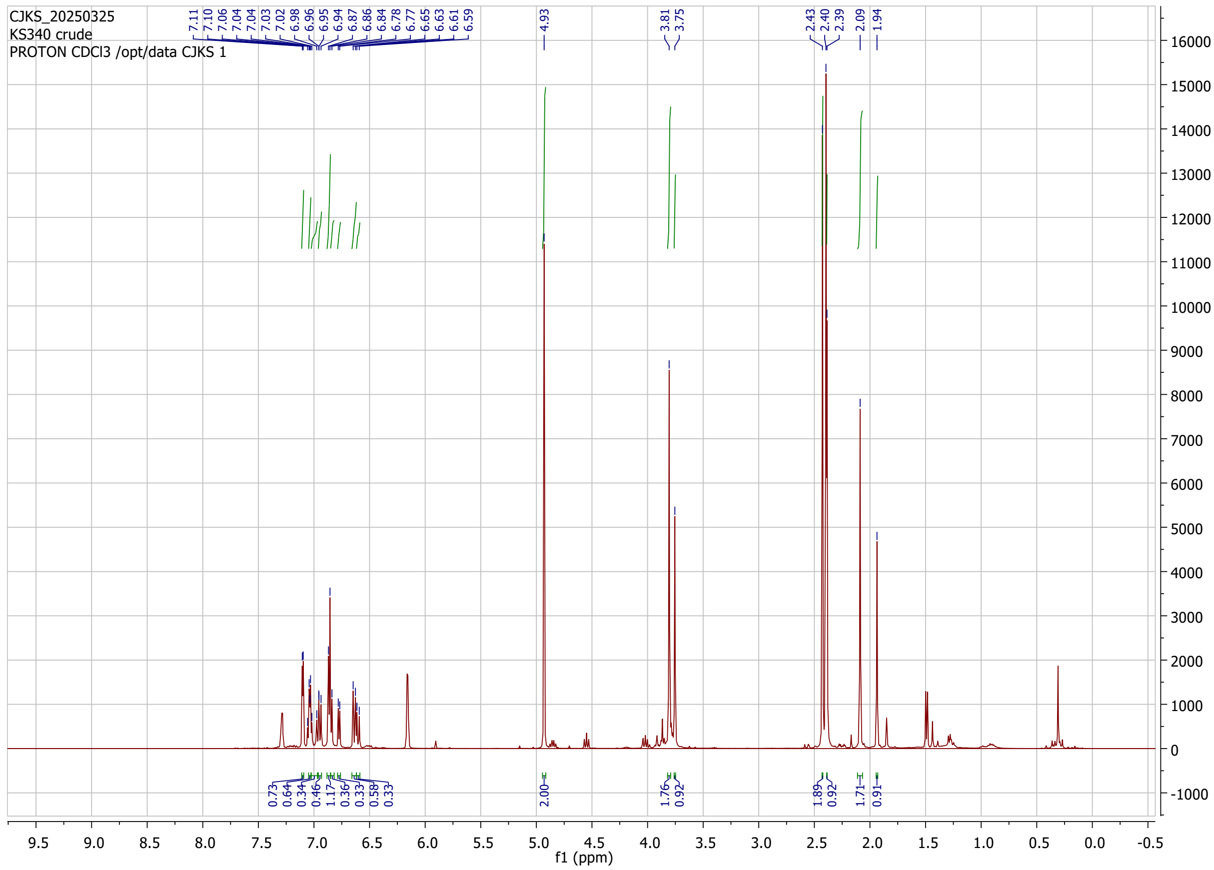
9i

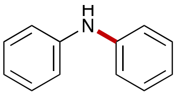
+



9i'

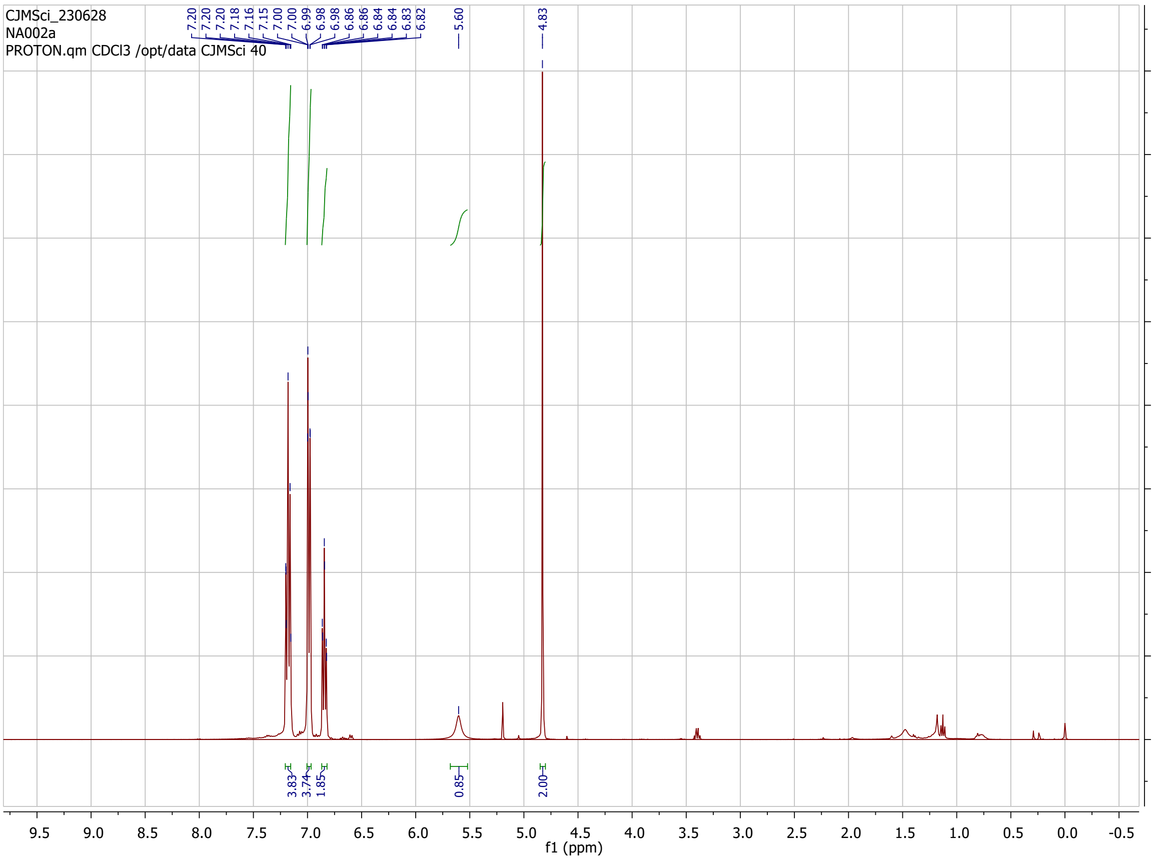
^{1}H NMR (400 MHz, $CDCl_3$) in PC

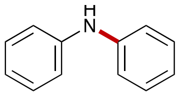




10

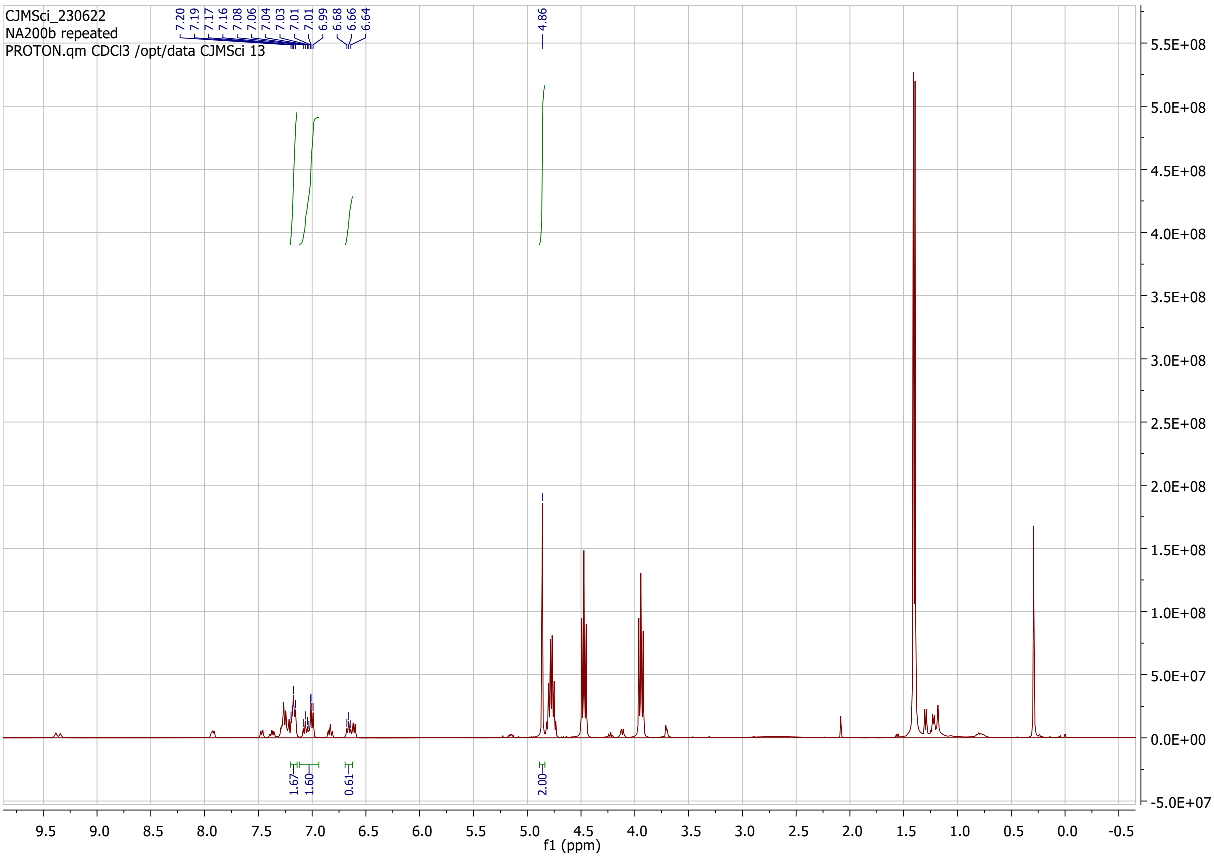
^{1}H NMR (400 MHz, $CDCl_3$) in MeCN

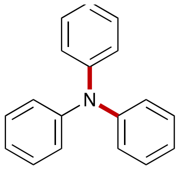




10

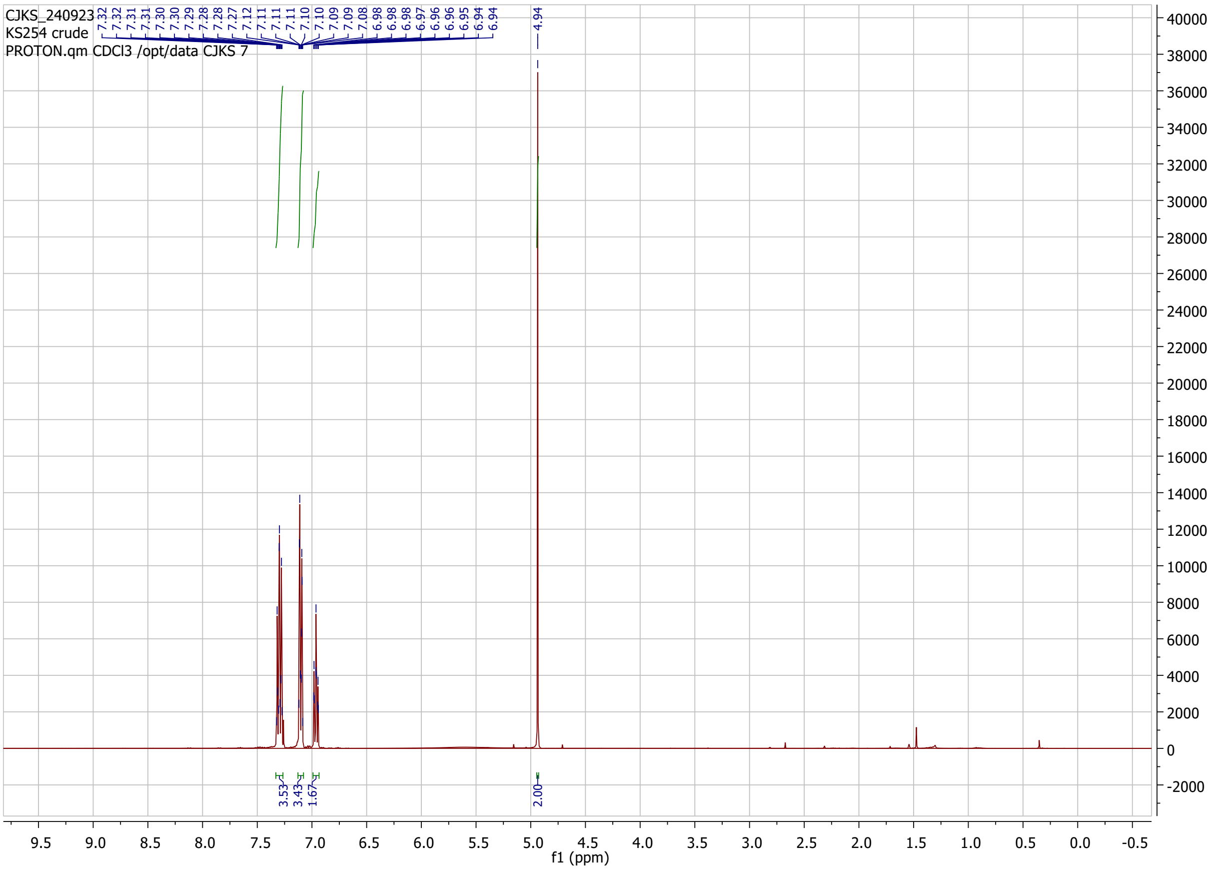
^{1}H NMR (400 MHz, $CDCl_3$) in PC

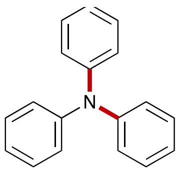




11

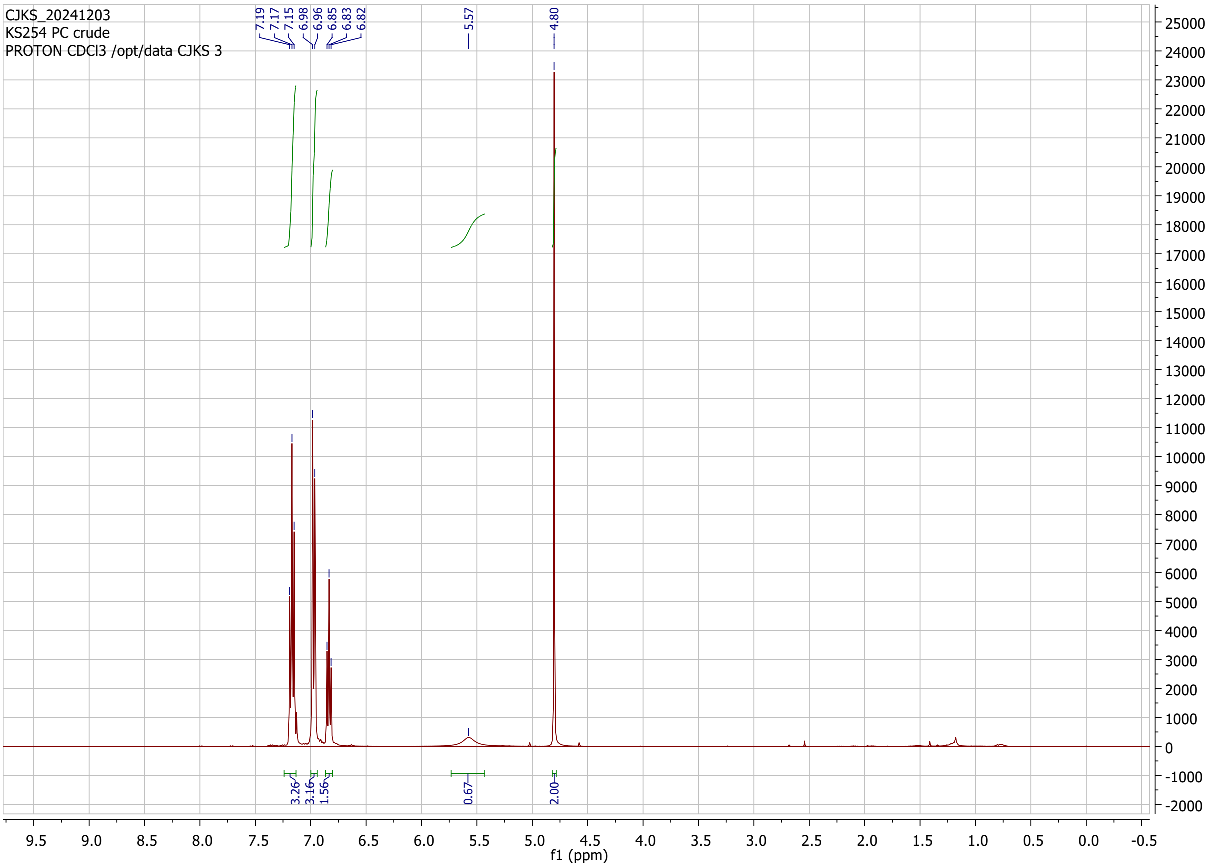
^{1}H NMR (400 MHz, $CDCl_3$) in MeCN

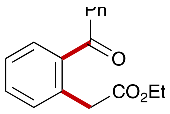




11

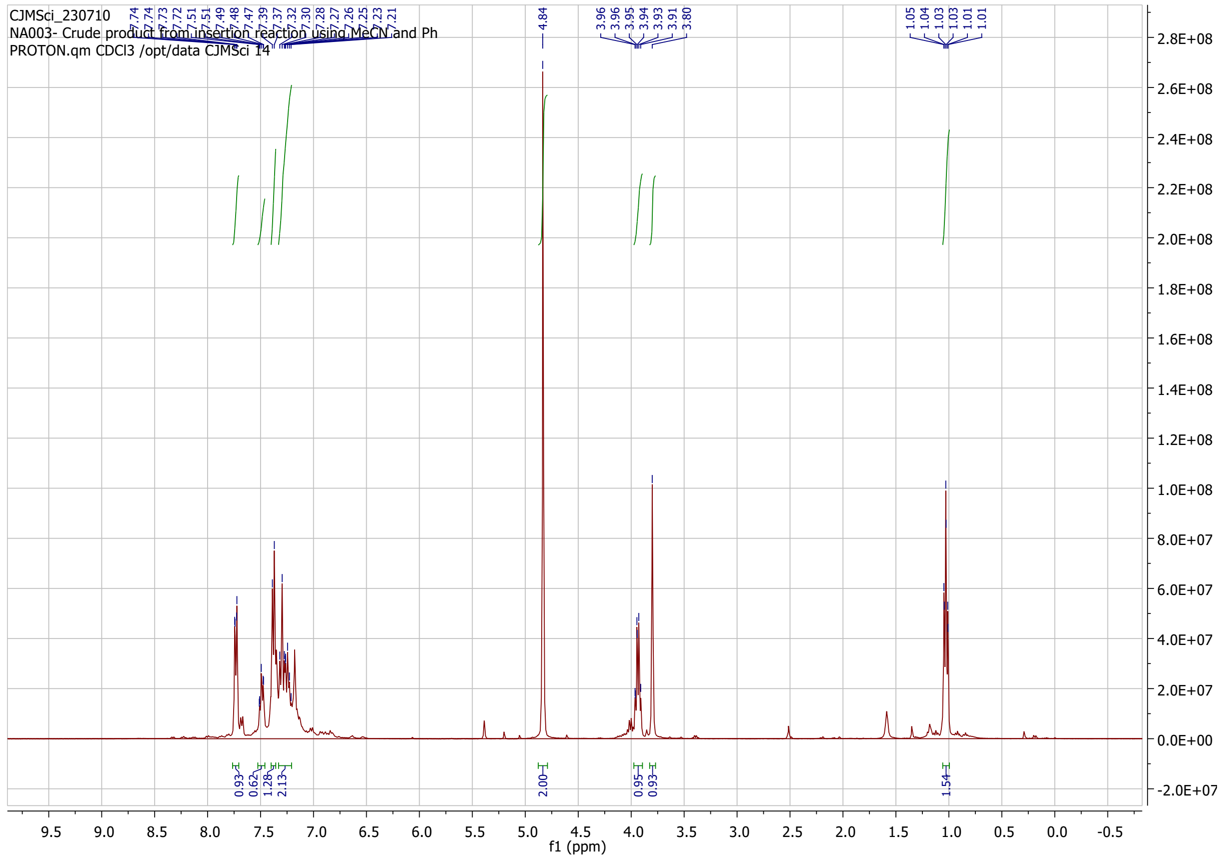
^{1}H NMR (400 MHz, $CDCl_3$) in PC

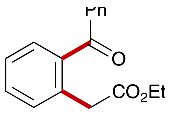




12

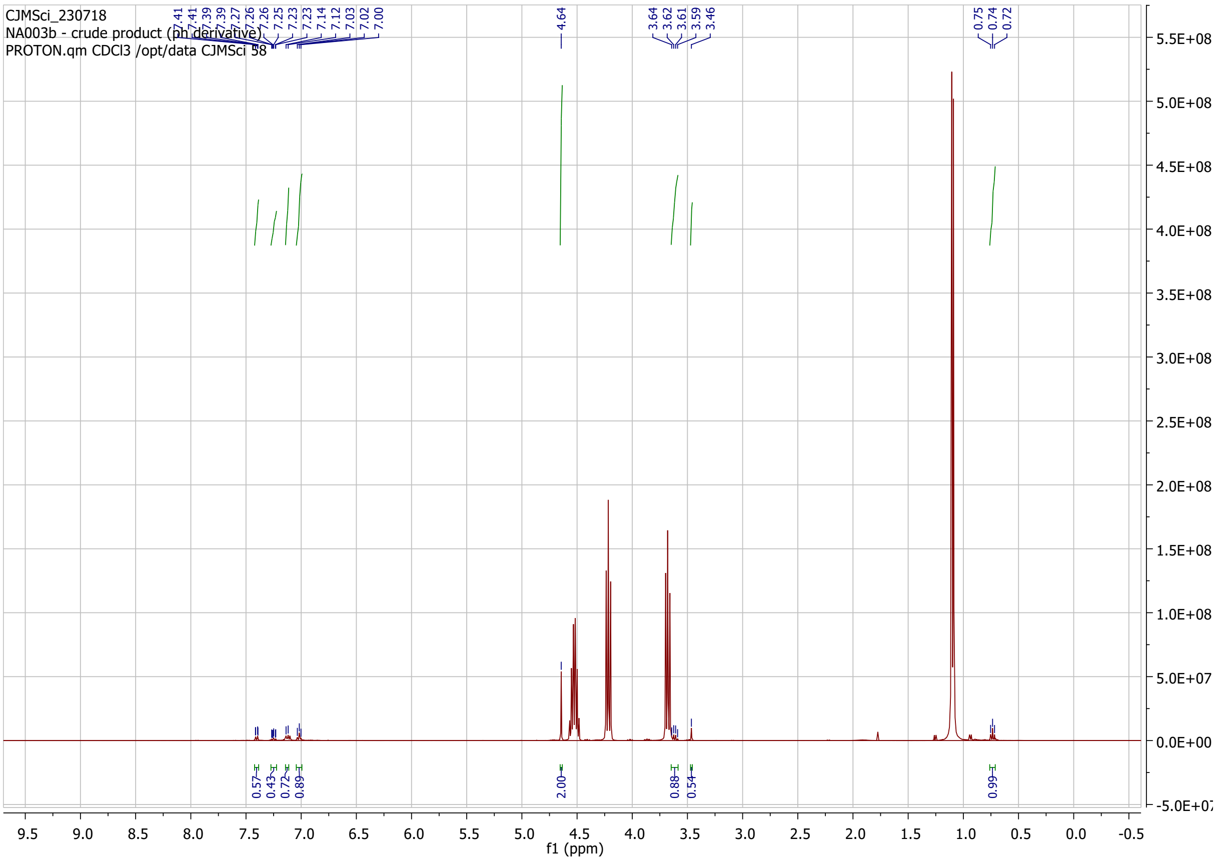
^{1}H NMR (400 MHz, $CDCl_3$) in MeCN

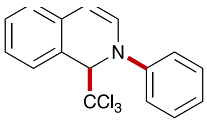




12

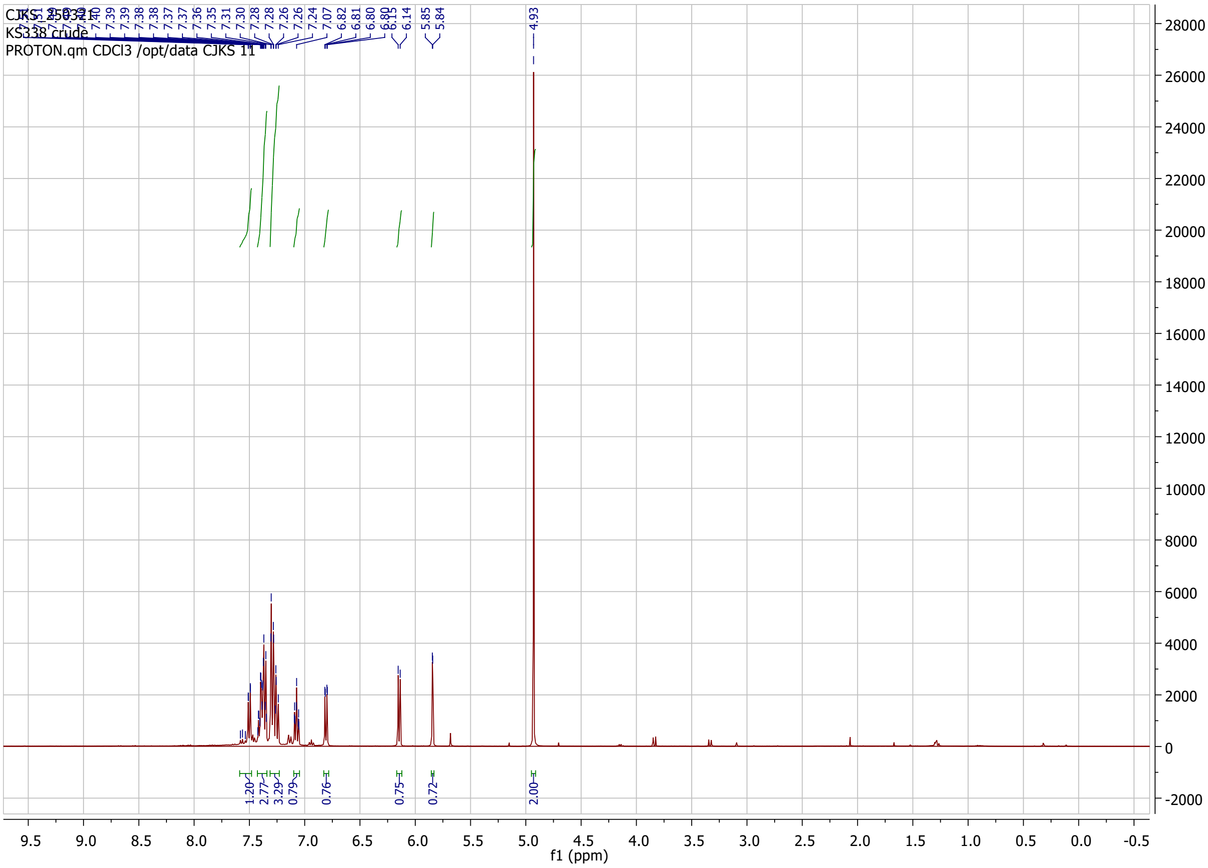
^{1}H NMR (400 MHz, $CDCl_3$) in PC

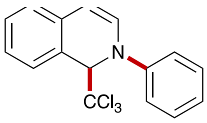




13

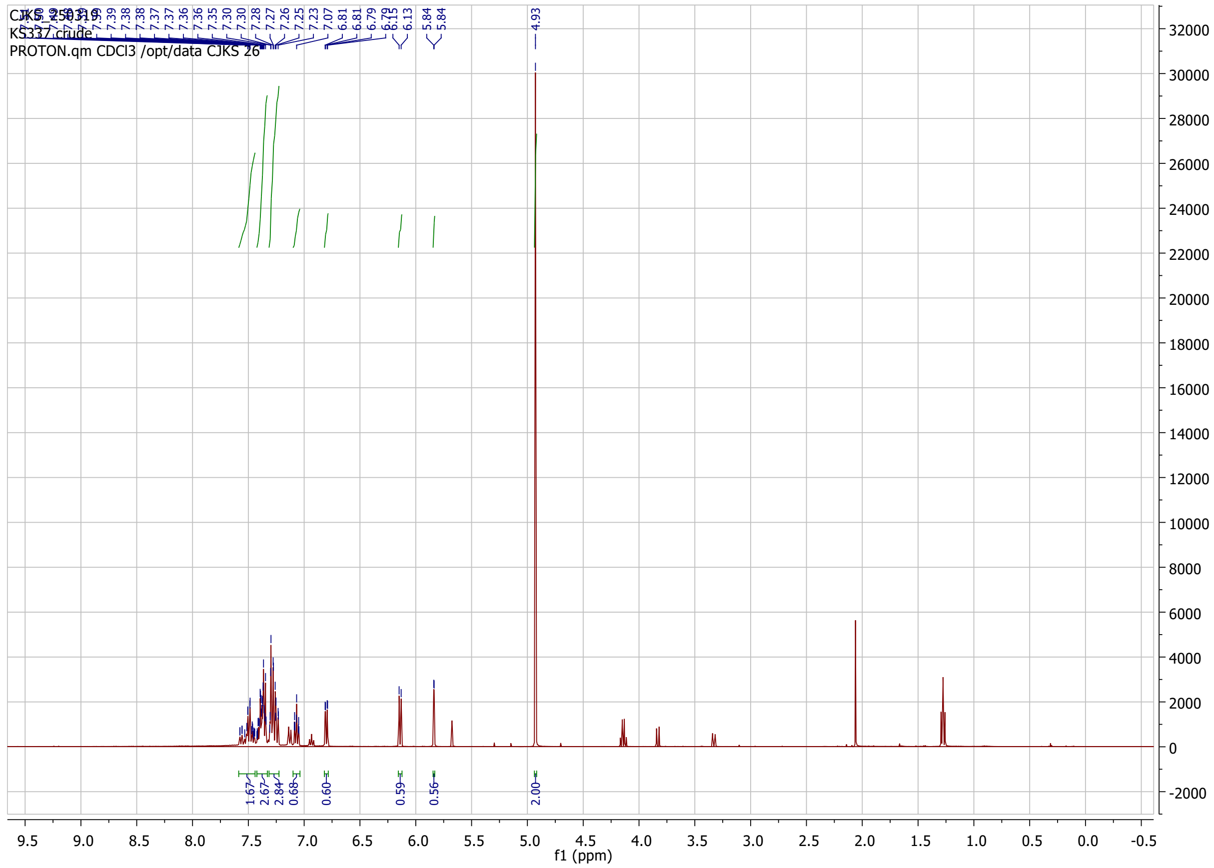
^{1}H NMR (400 MHz, $CDCl_3$) in MeCN

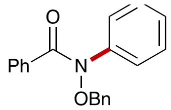




13

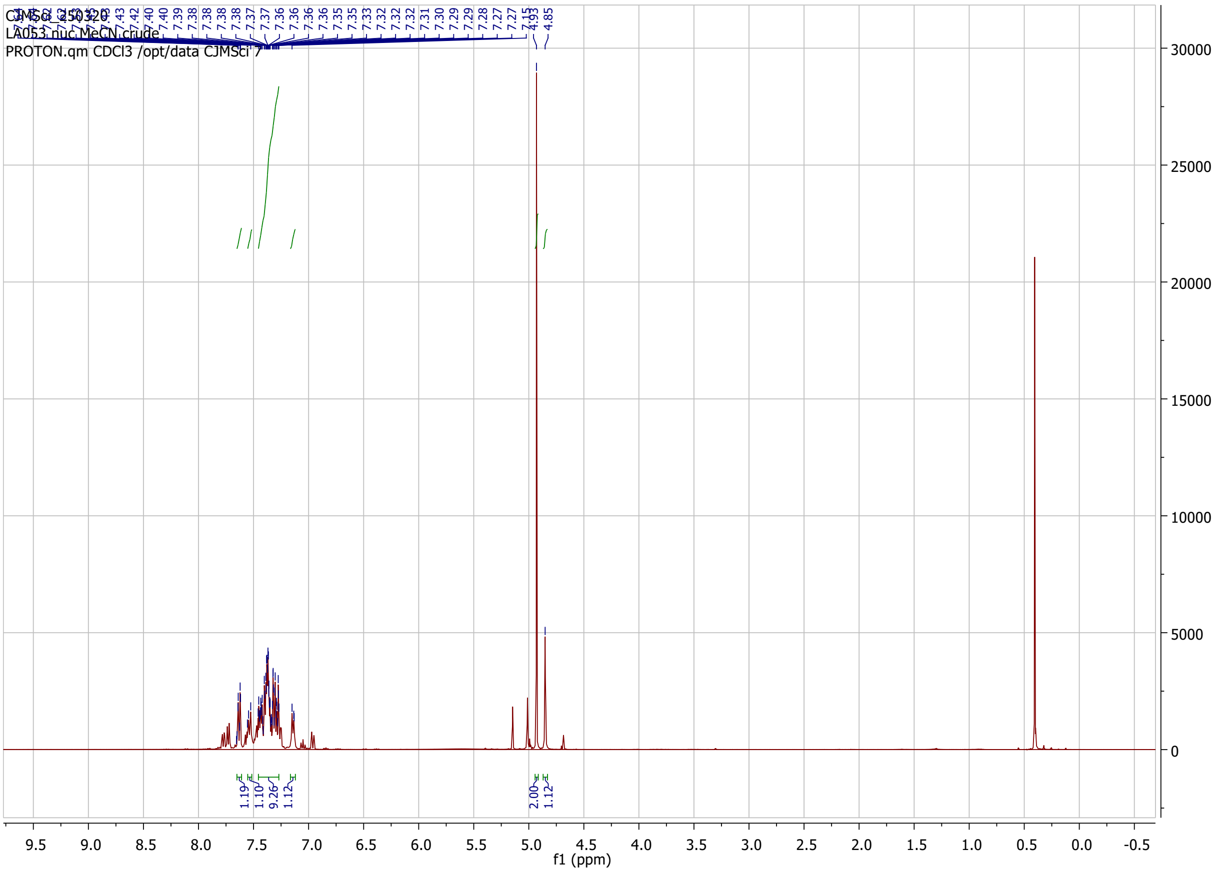
^{1}H NMR (400 MHz, $CDCl_3$) in PC

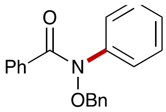




14

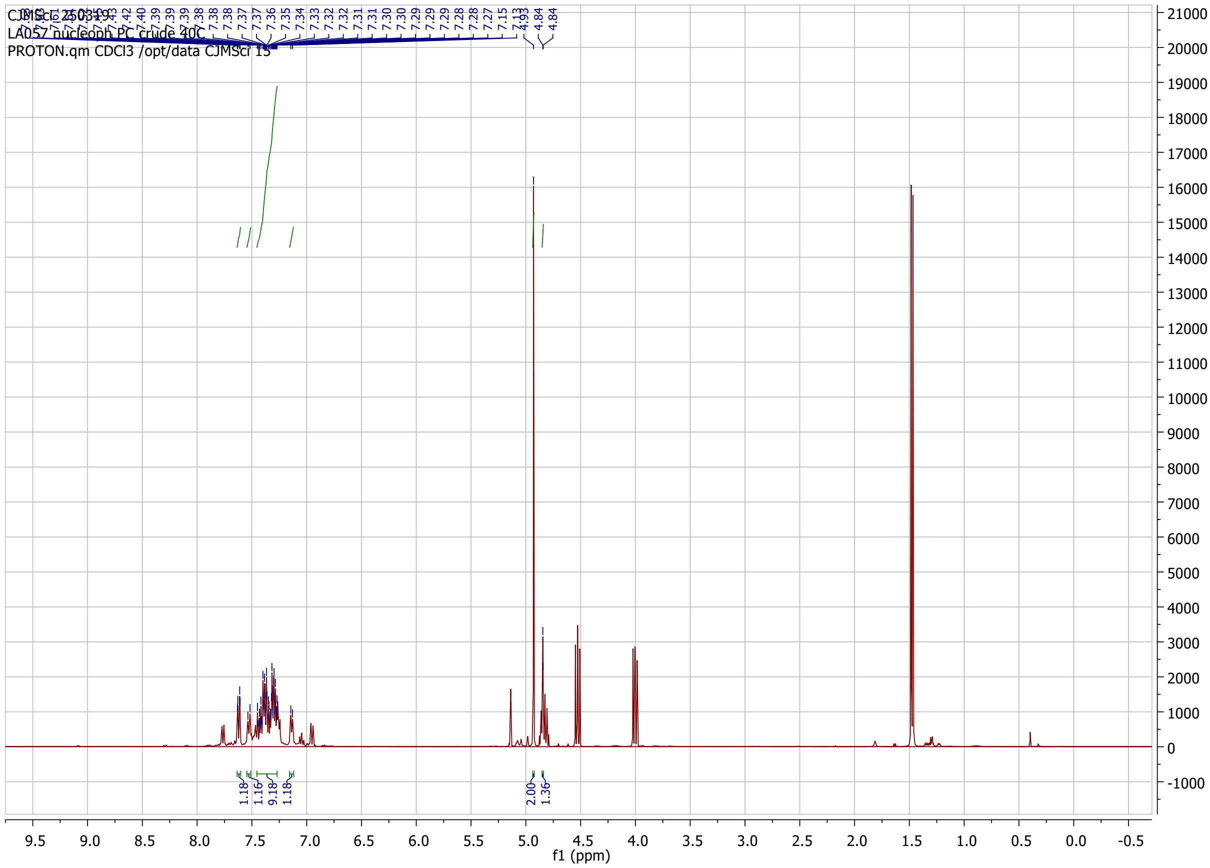
^{1}H NMR (400 MHz, $CDCl_3$) in MeCN

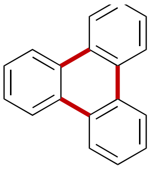




14

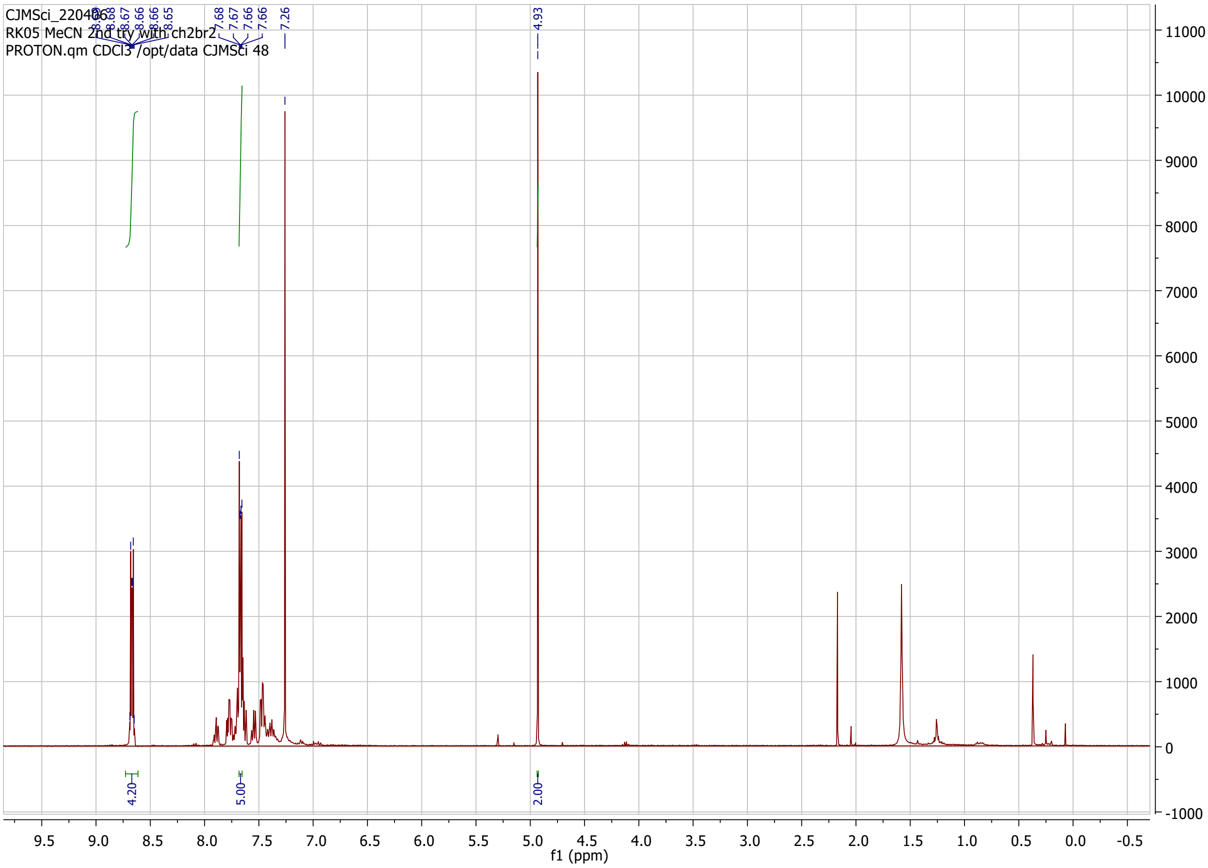
^{1}H NMR (400 MHz, $CDCl_3$) in PC

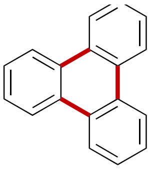




15

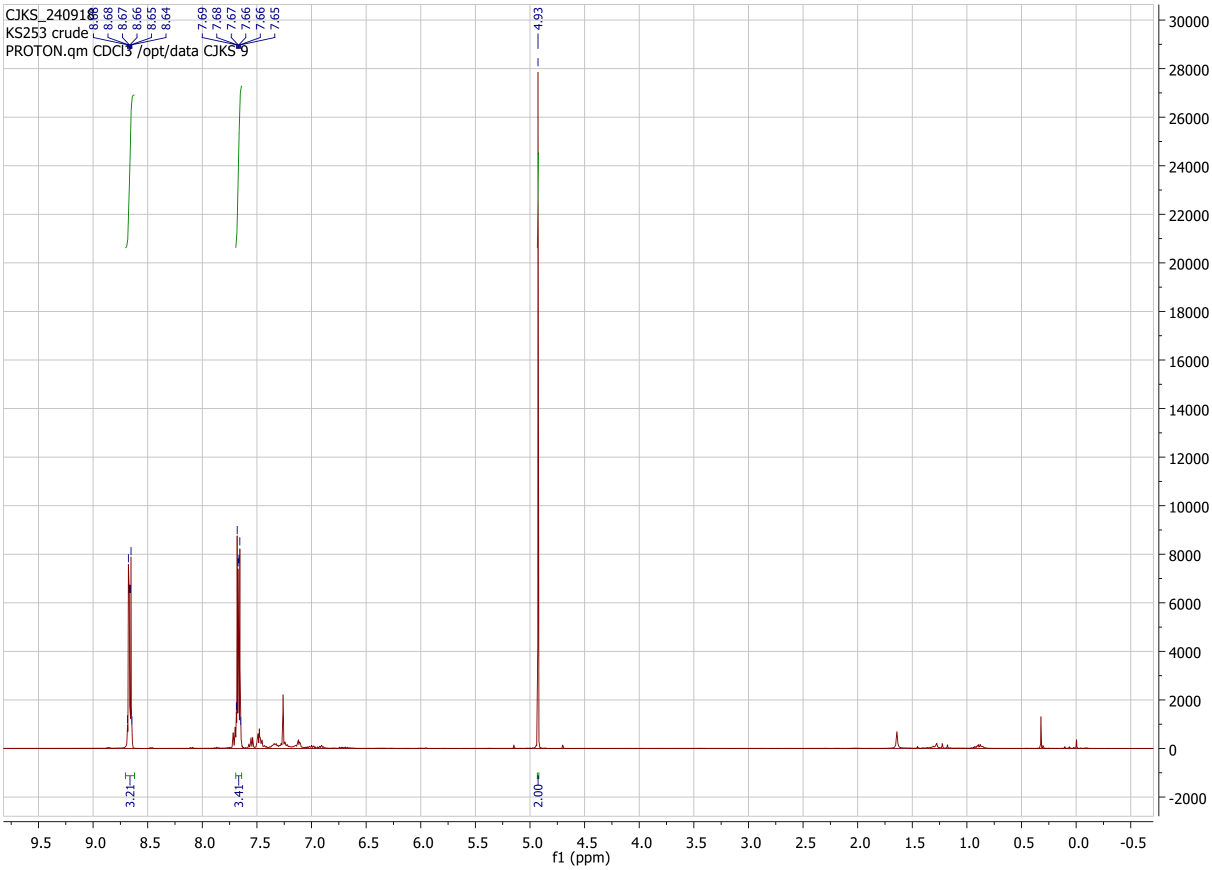
[1]H NMR (400 MHz, $CDCl_3$) in MeCN

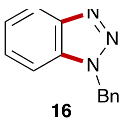




15

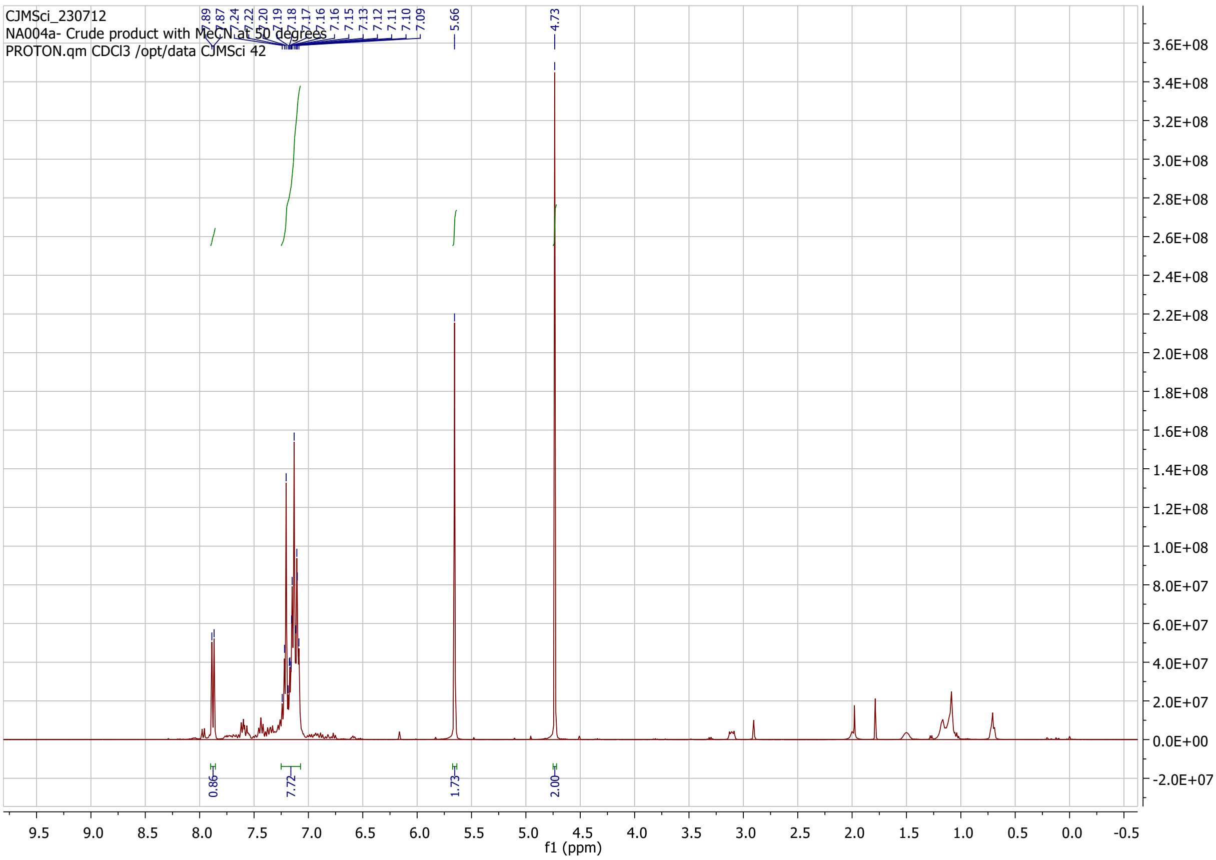
[1]H NMR (400 MHz, $CDCl_3$) in PC

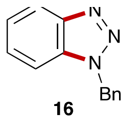




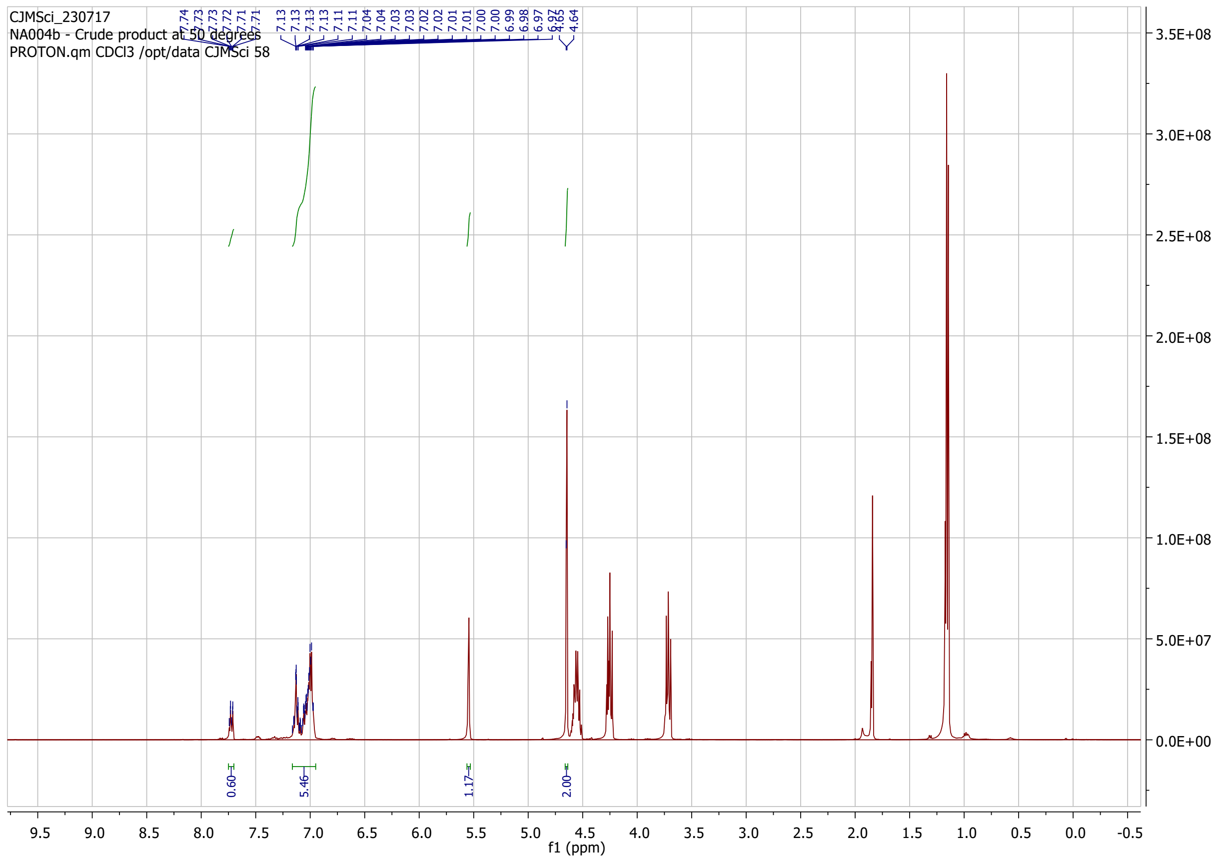
16

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

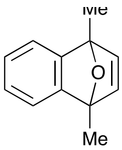




16 ^{1}H NMR (400 MHz, $CDCl_3$) in PC

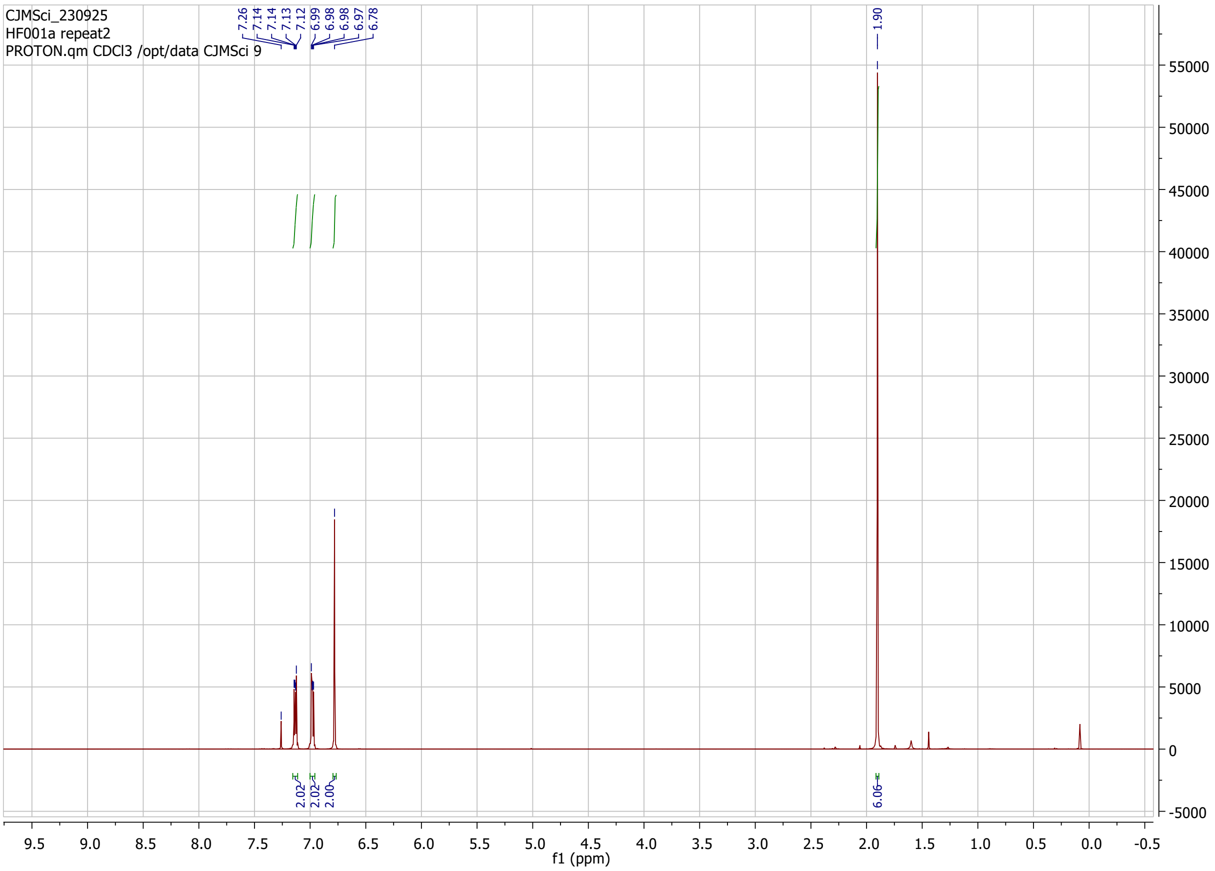


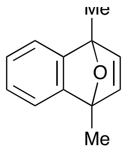
4. NMR spectra of isolated compounds



8a

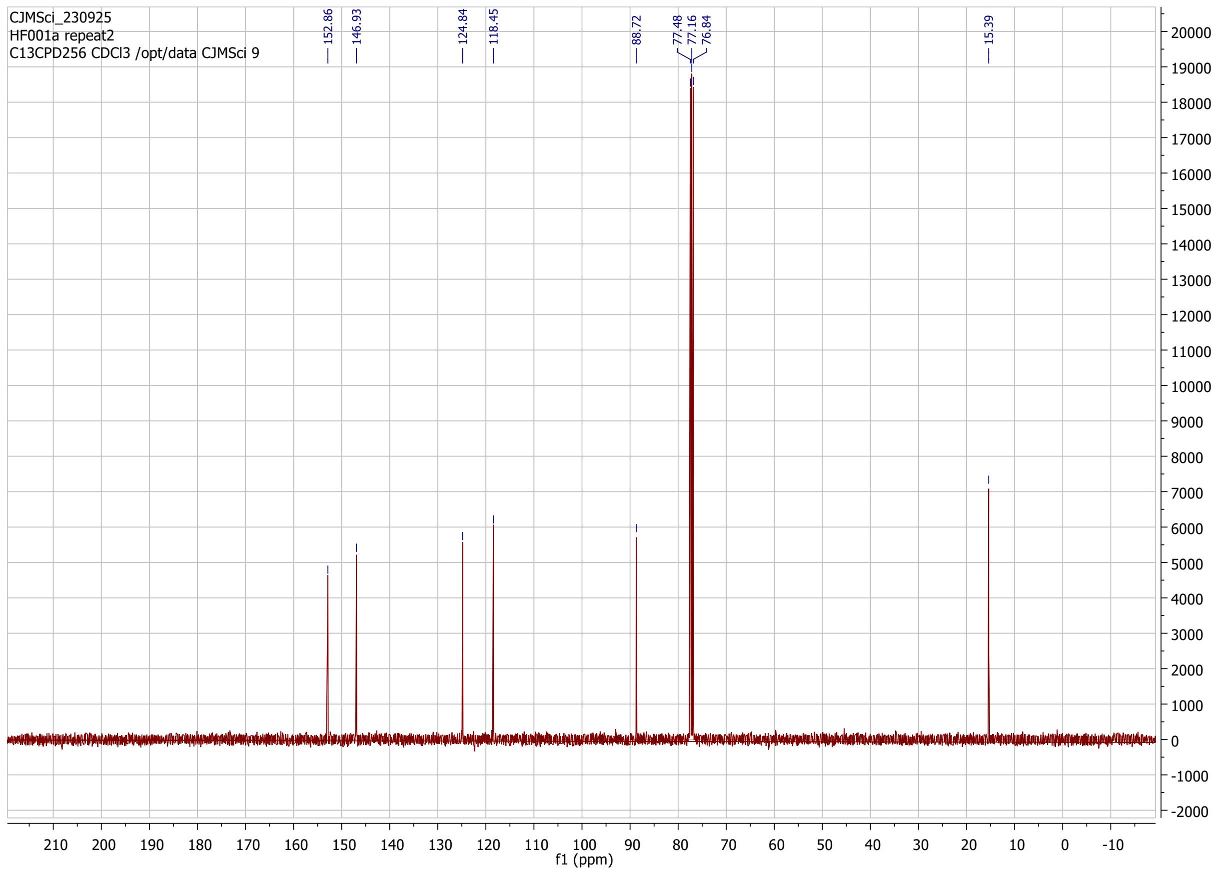
^{1}H NMR (400 MHz, $CDCl_3$)

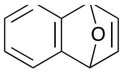




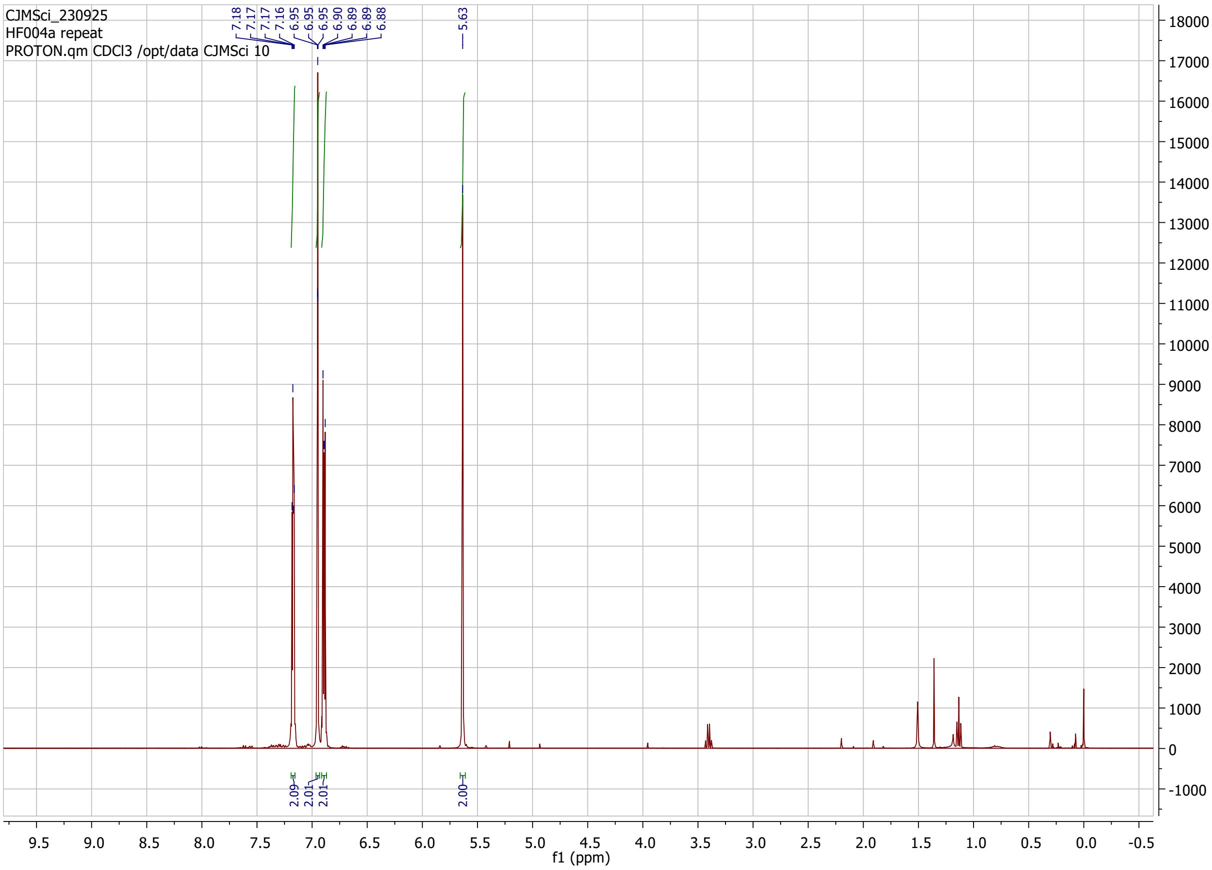
8a

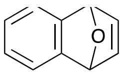
^{13}C NMR (101 MHz, $CDCl_3$)



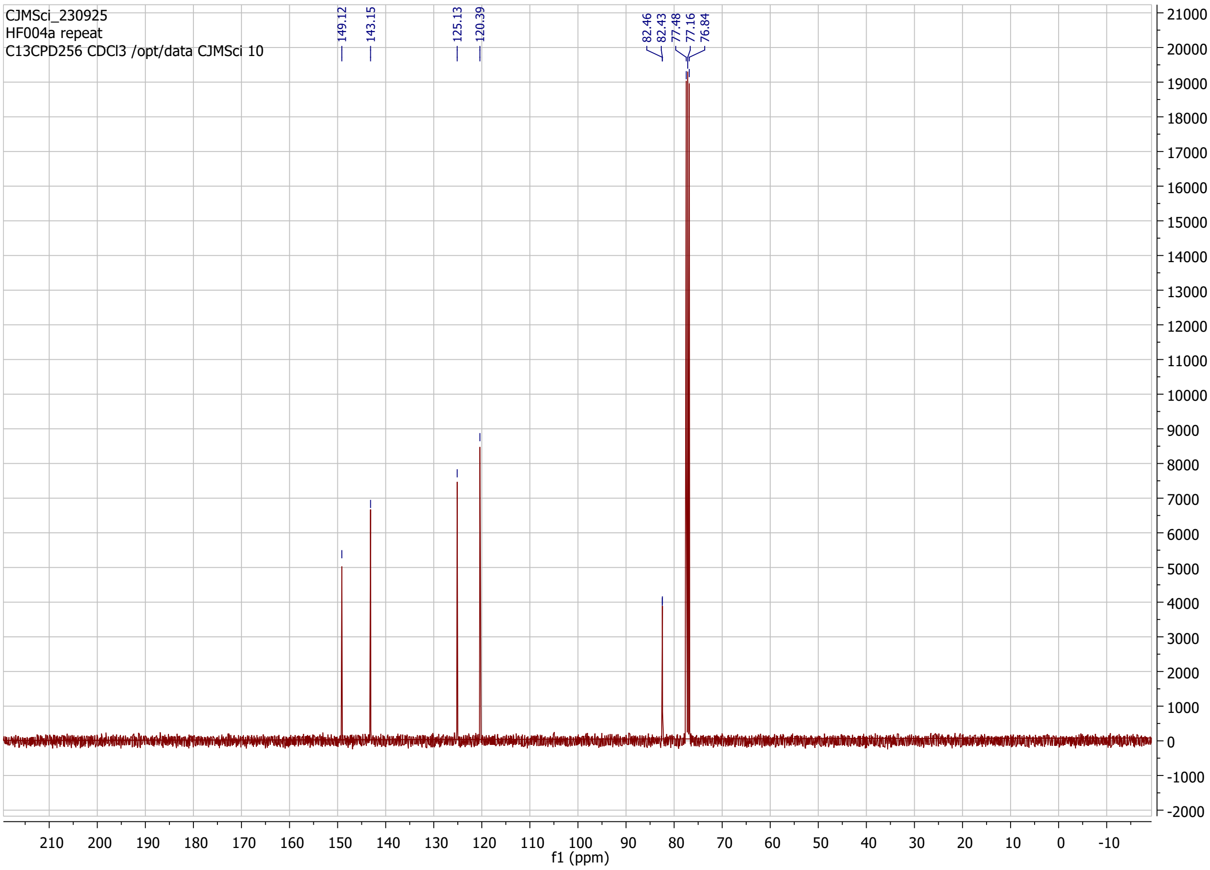


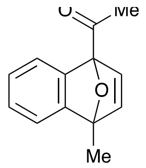
8b ^{1}H NMR (400 MHz, $CDCl_3$)





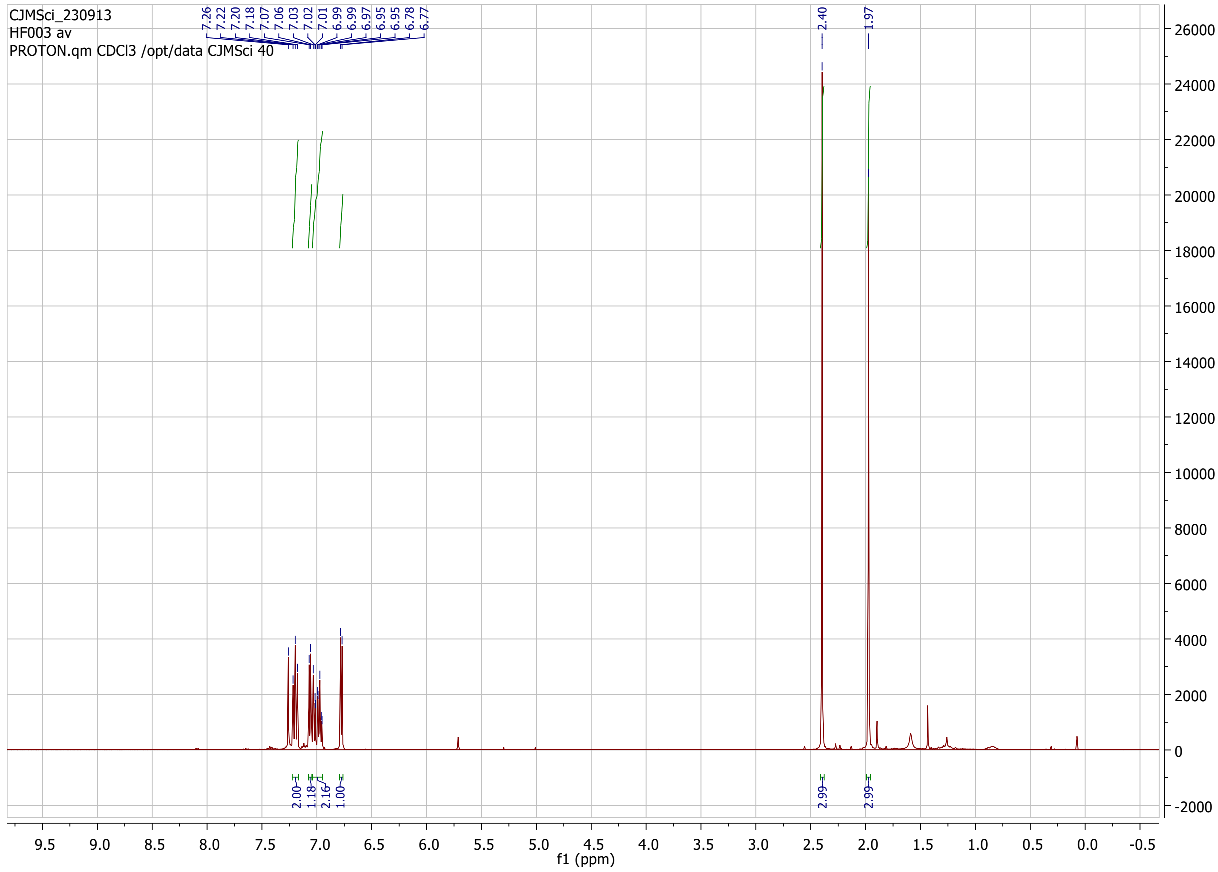
8b ^{13}C NMR (101 MHz, $CDCl_3$)

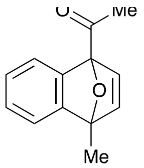




8c

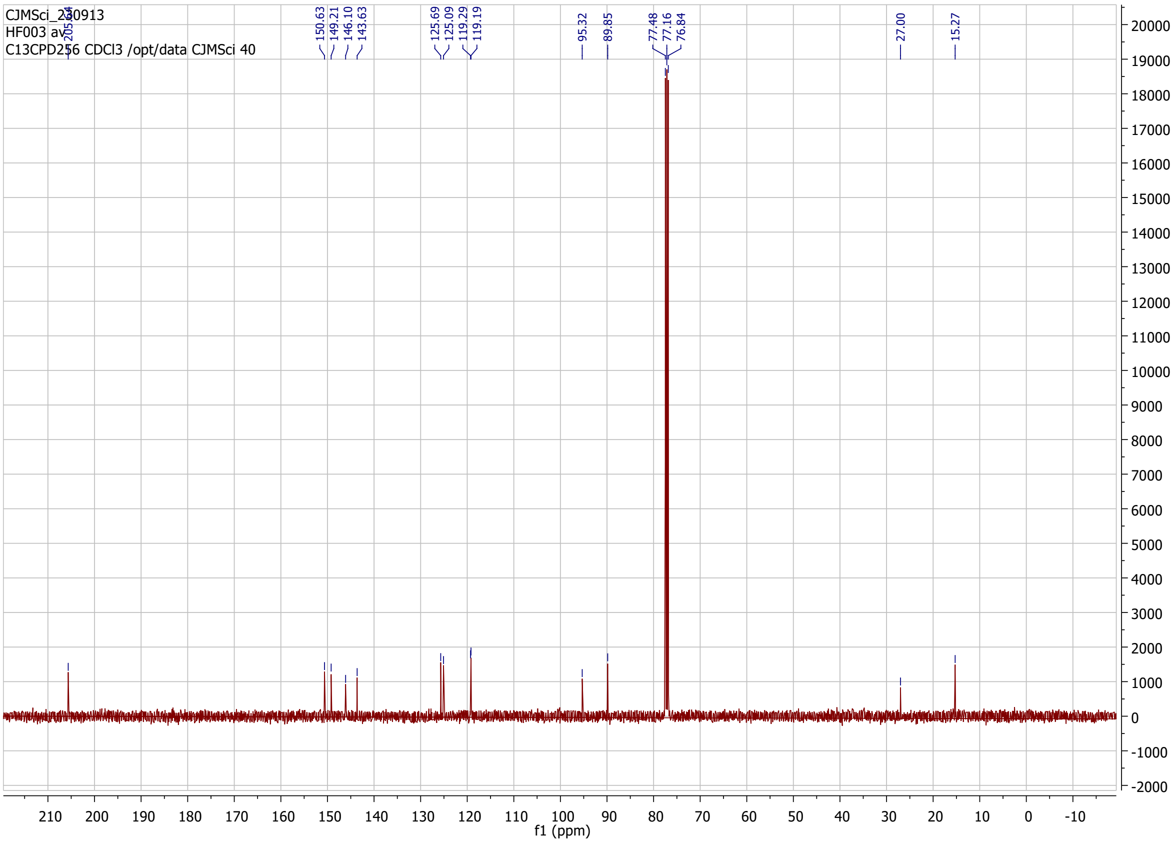
^{1}H NMR (400 MHz, $CDCl_3$)

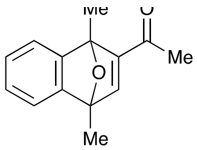




8c

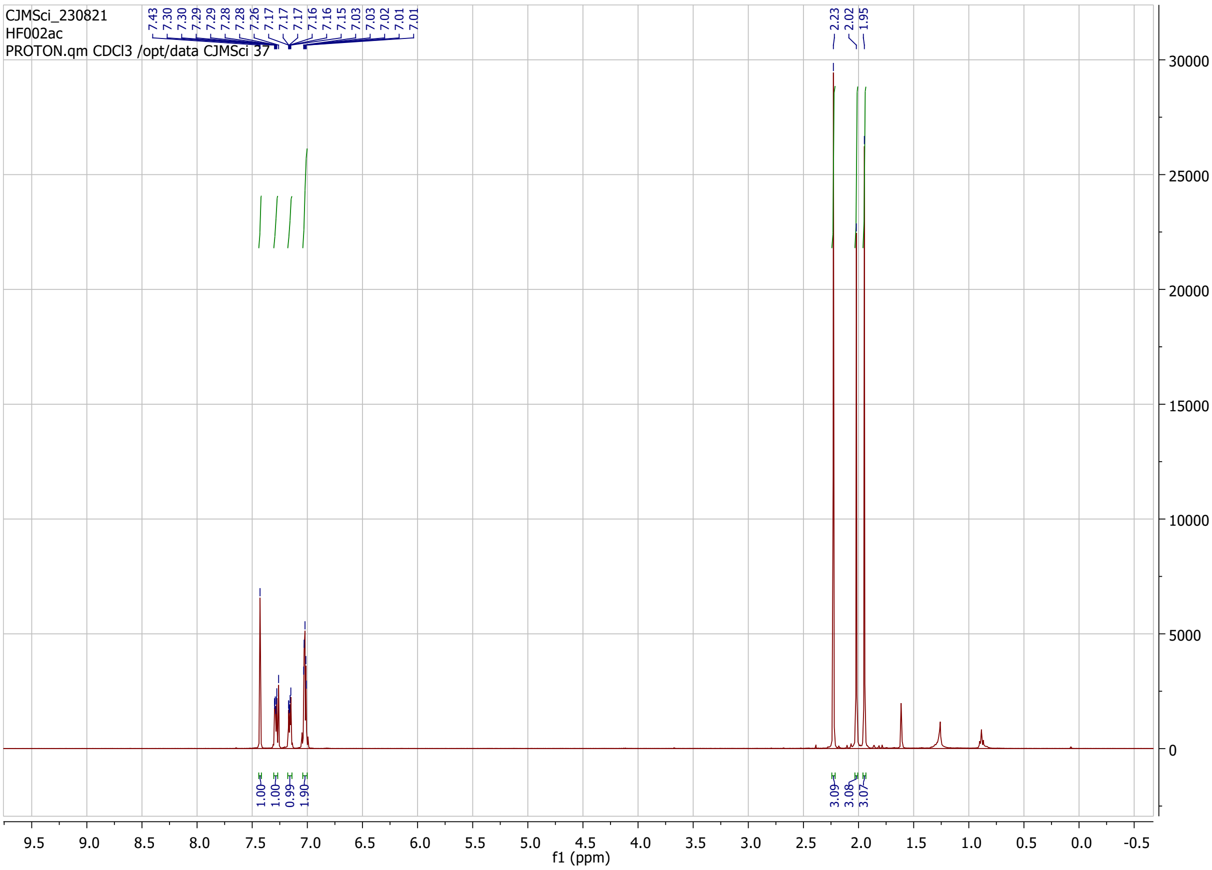
^{13}C NMR (101 MHz, $CDCl_3$)

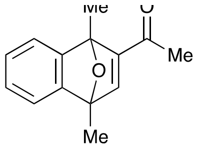




8d

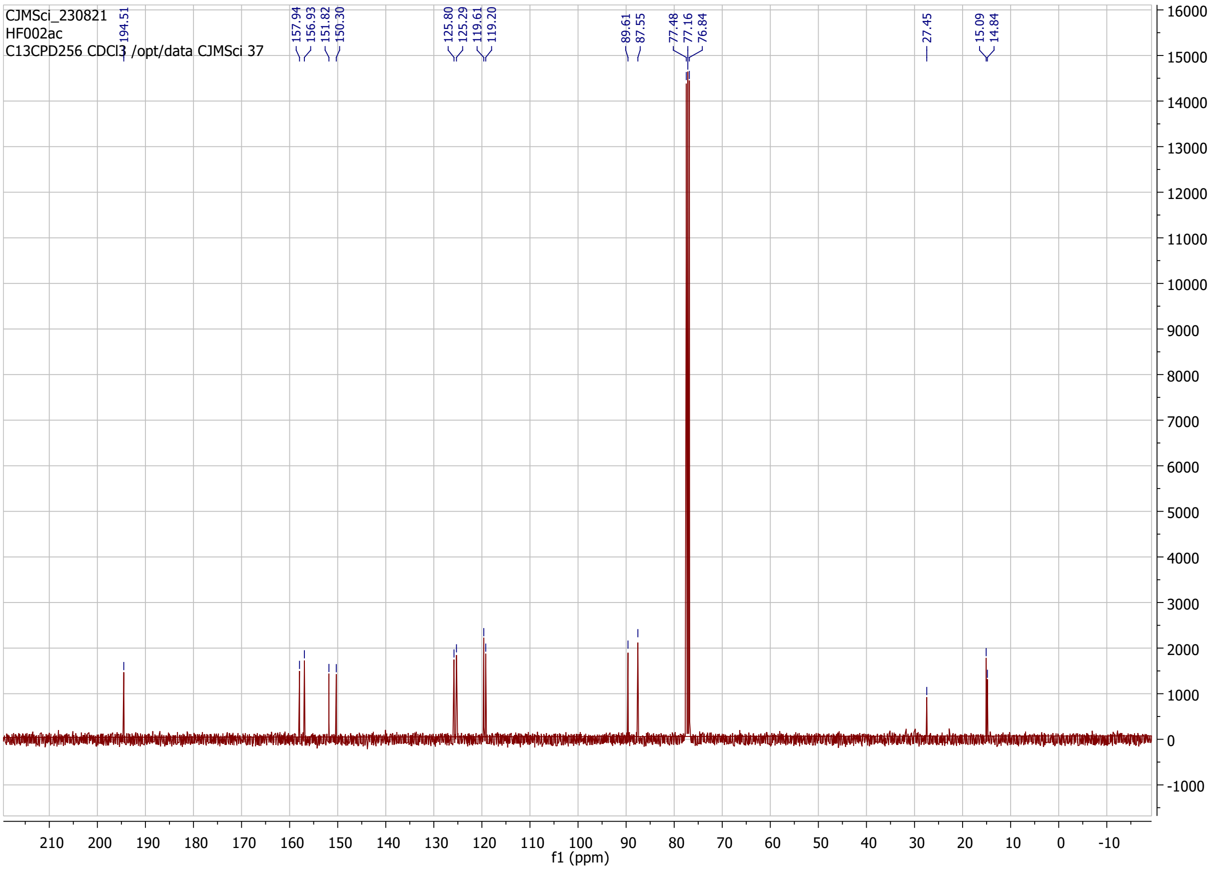
^{1}H NMR (400 MHz, $CDCl_3$)

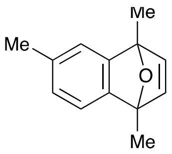




8d

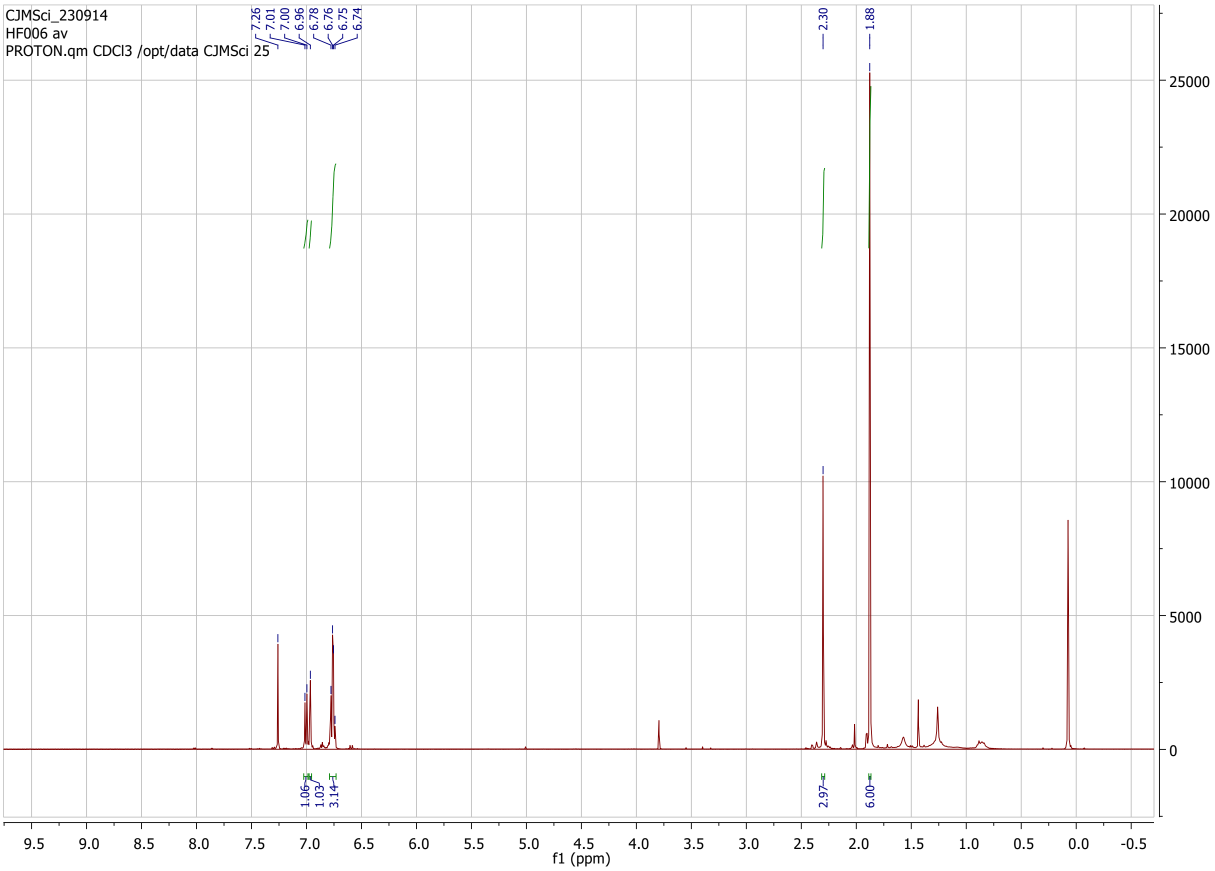
^{13}C NMR (101 MHz, $CDCl_3$)

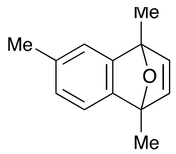




9a

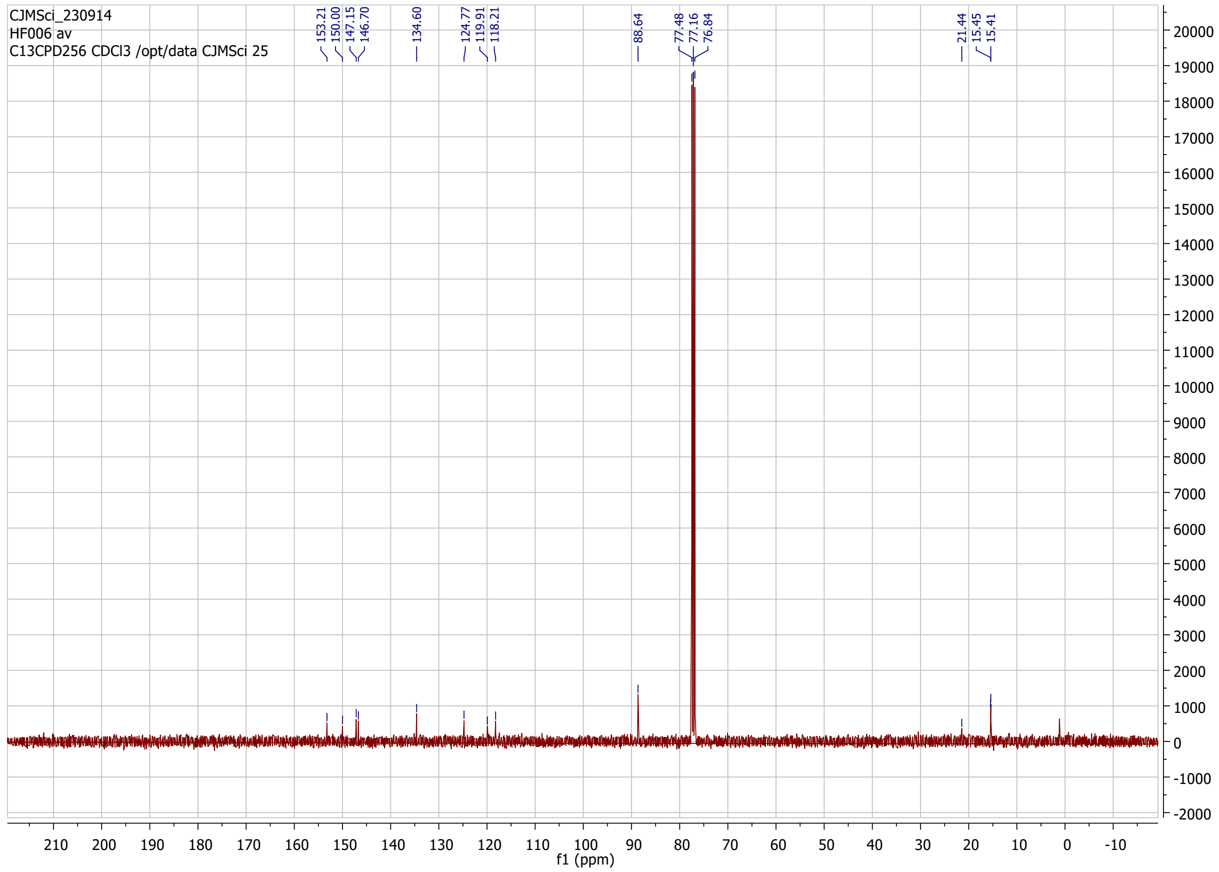
^{1}H NMR (400 MHz, $CDCl_3$)

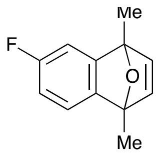




9a

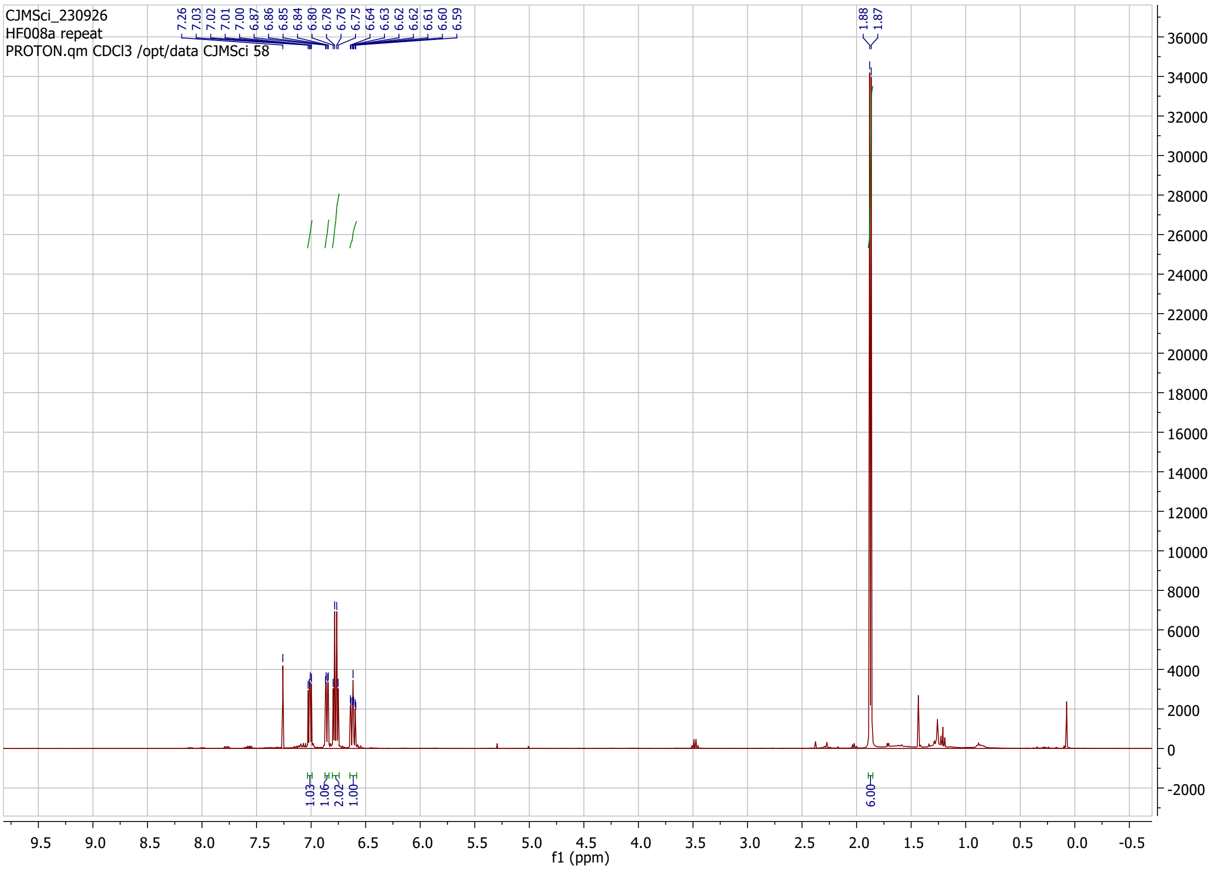
^{13}C NMR (101 MHz, $CDCl_3$)

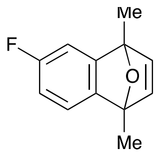




9b

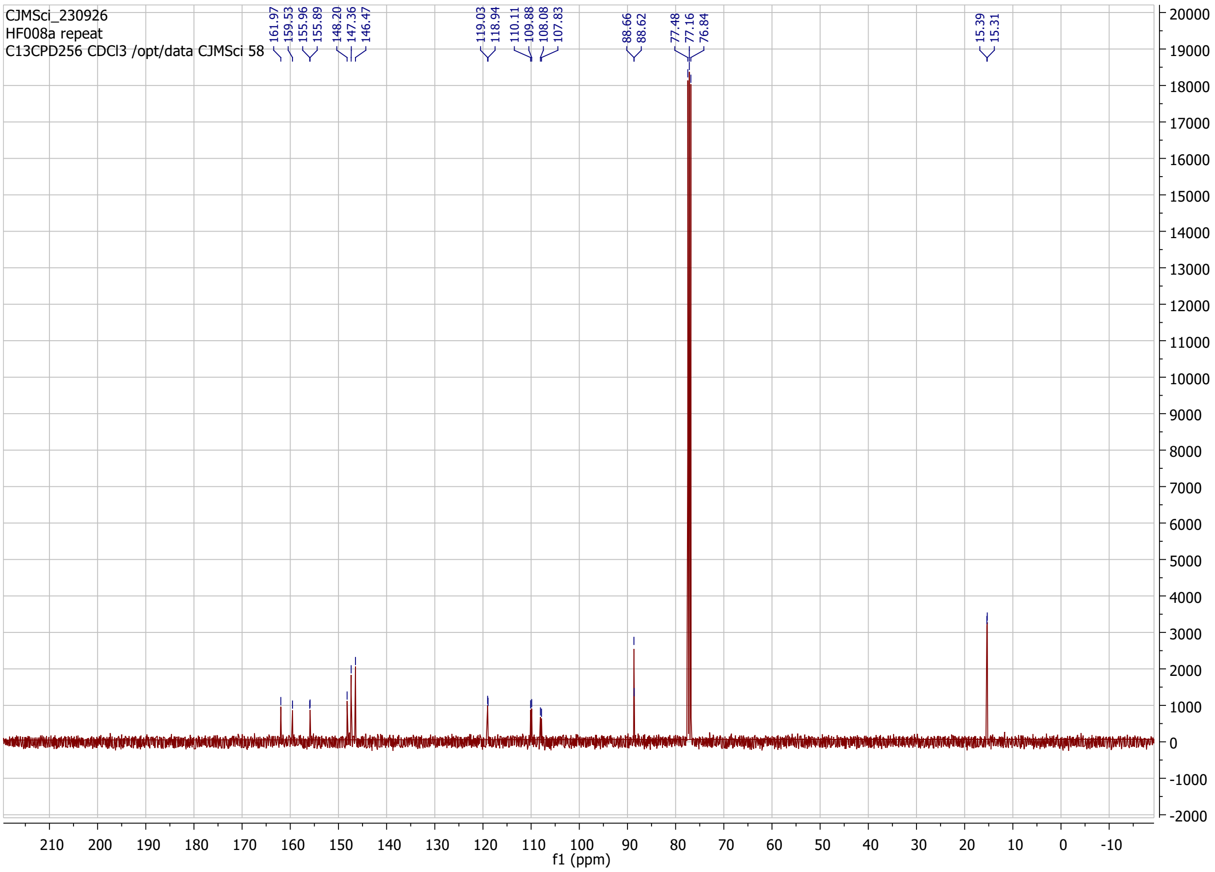
^{1}H NMR (400 MHz, $CDCl_3$)

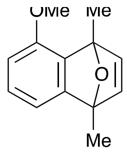




9b

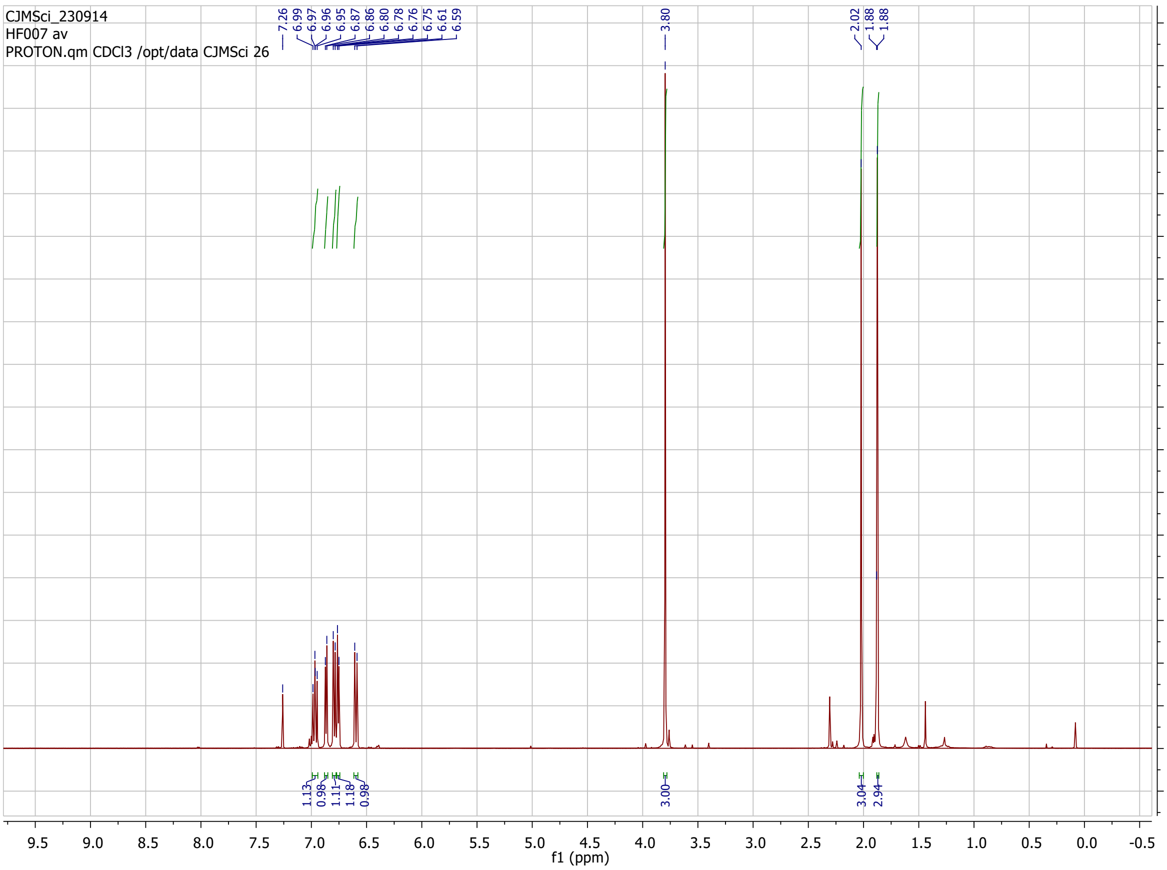
^{13}C NMR (101 MHz, $CDCl_3$)

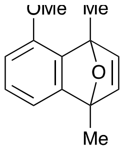




9c

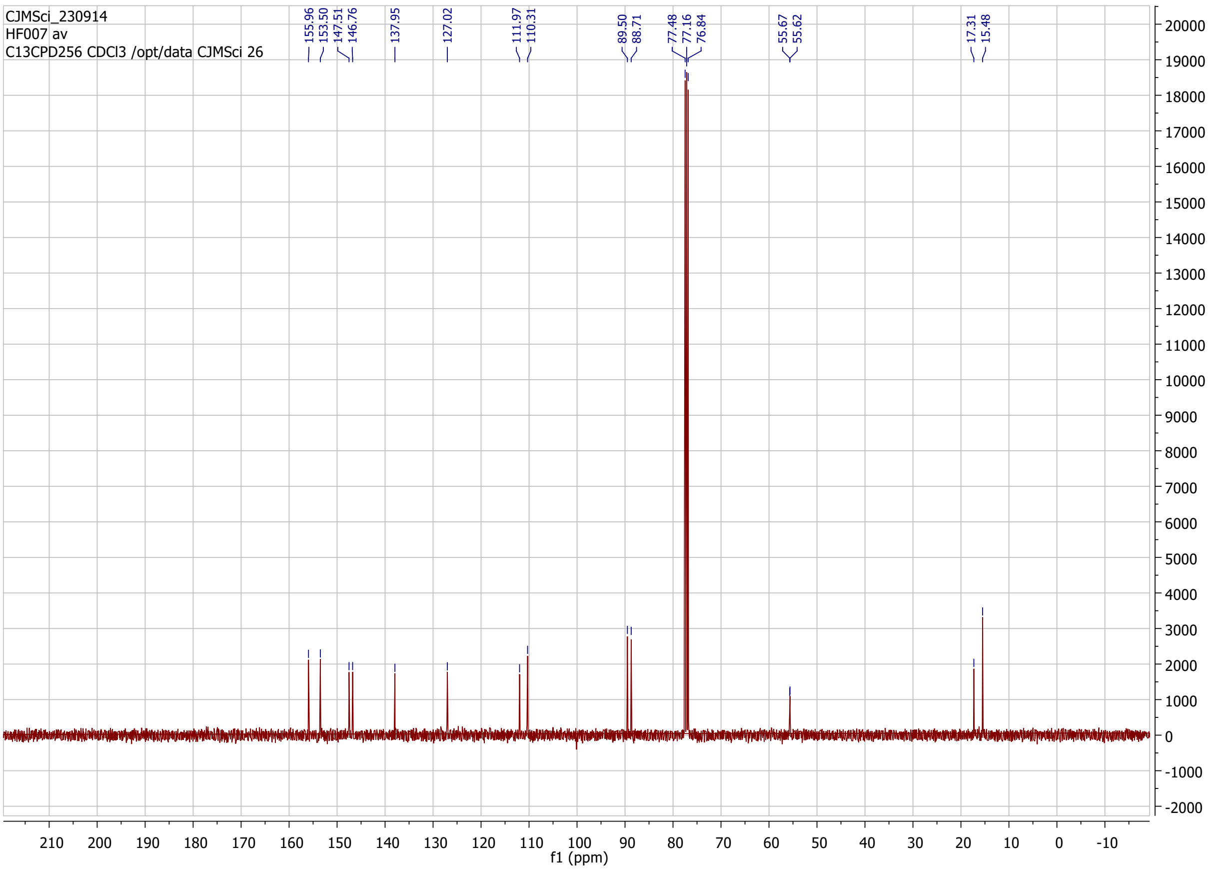
^{1}H NMR (400 MHz, $CDCl_3$)

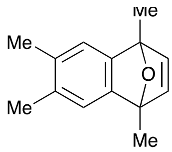




9c

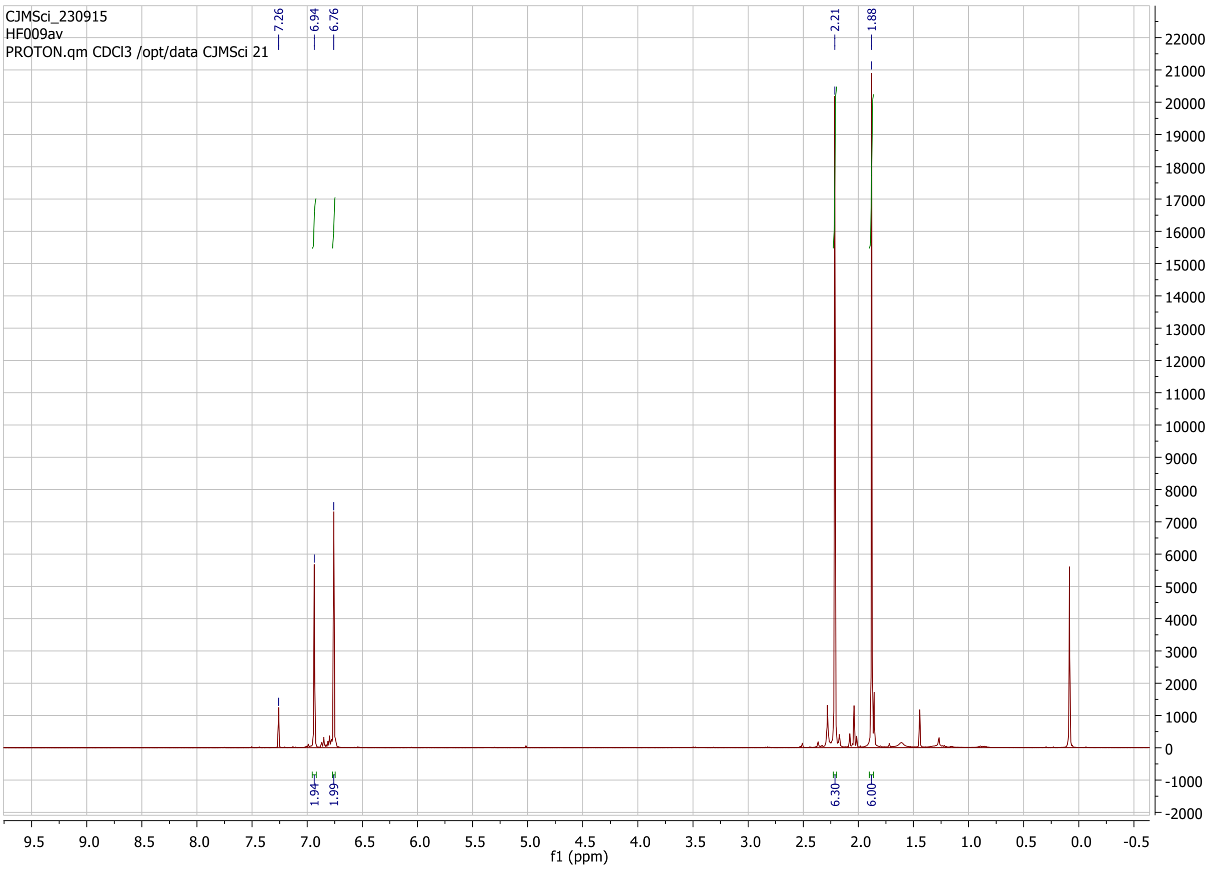
^{13}C NMR (101 MHz, $CDCl_3$)

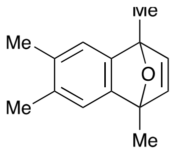




9d

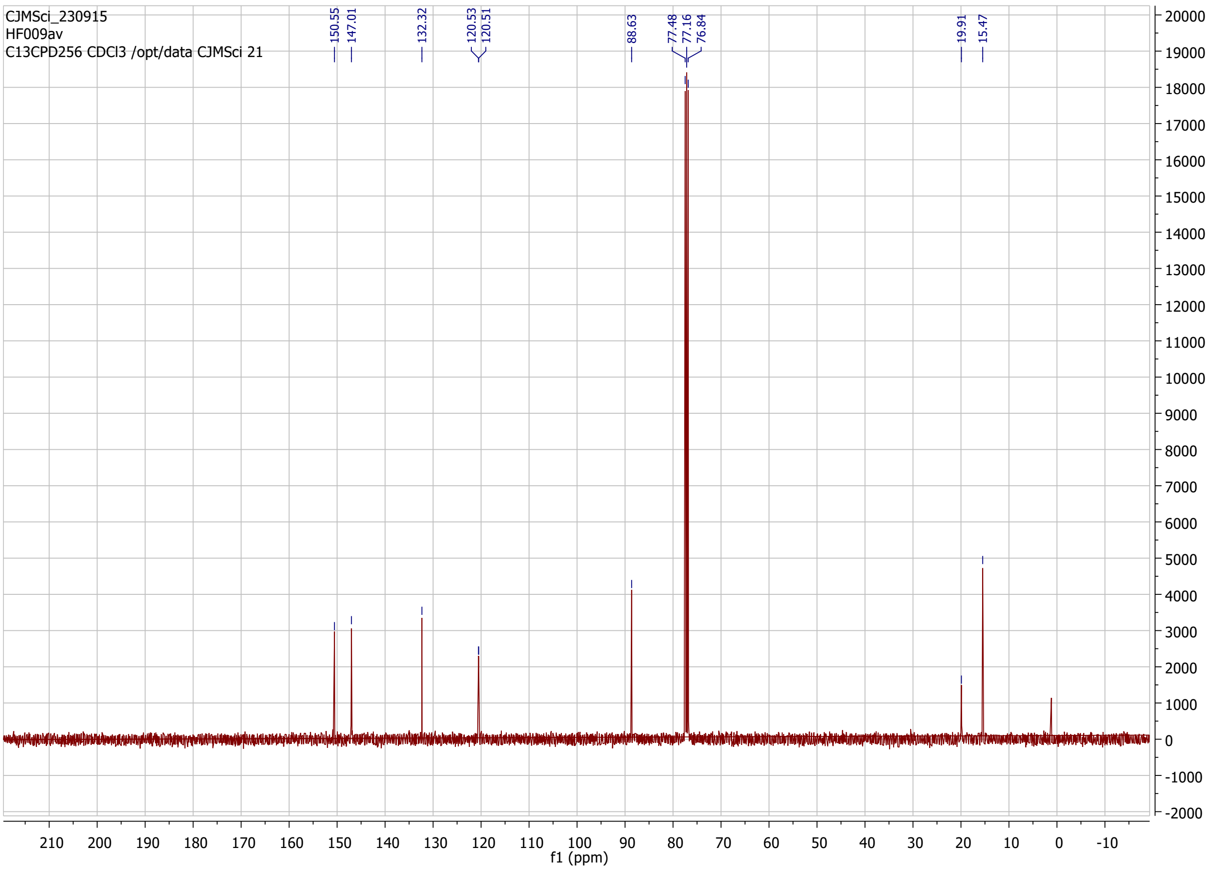
^{1}H NMR (400 MHz, $CDCl_3$)

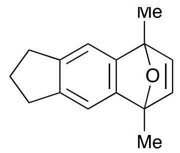




9d

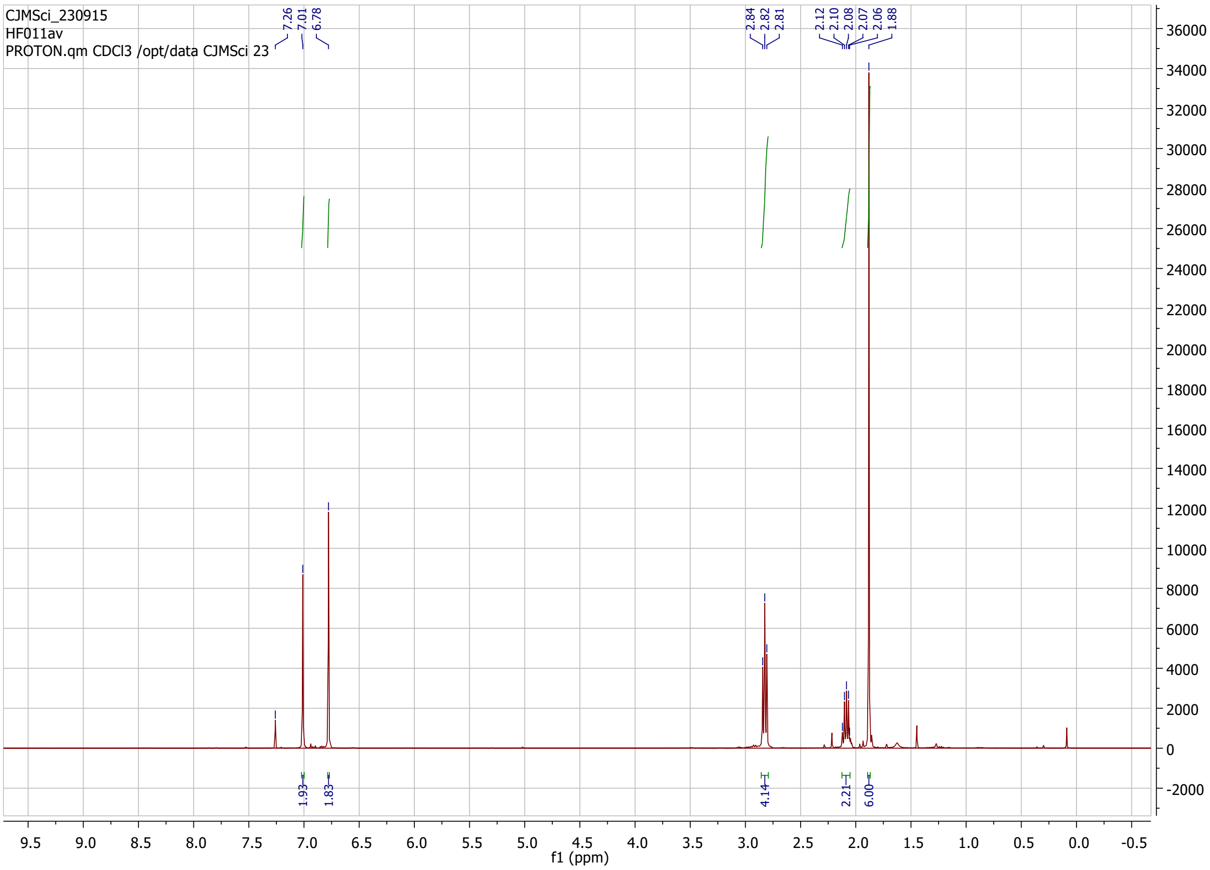
^{13}C NMR (101 MHz, $CDCl_3$)

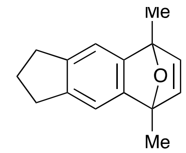




9e

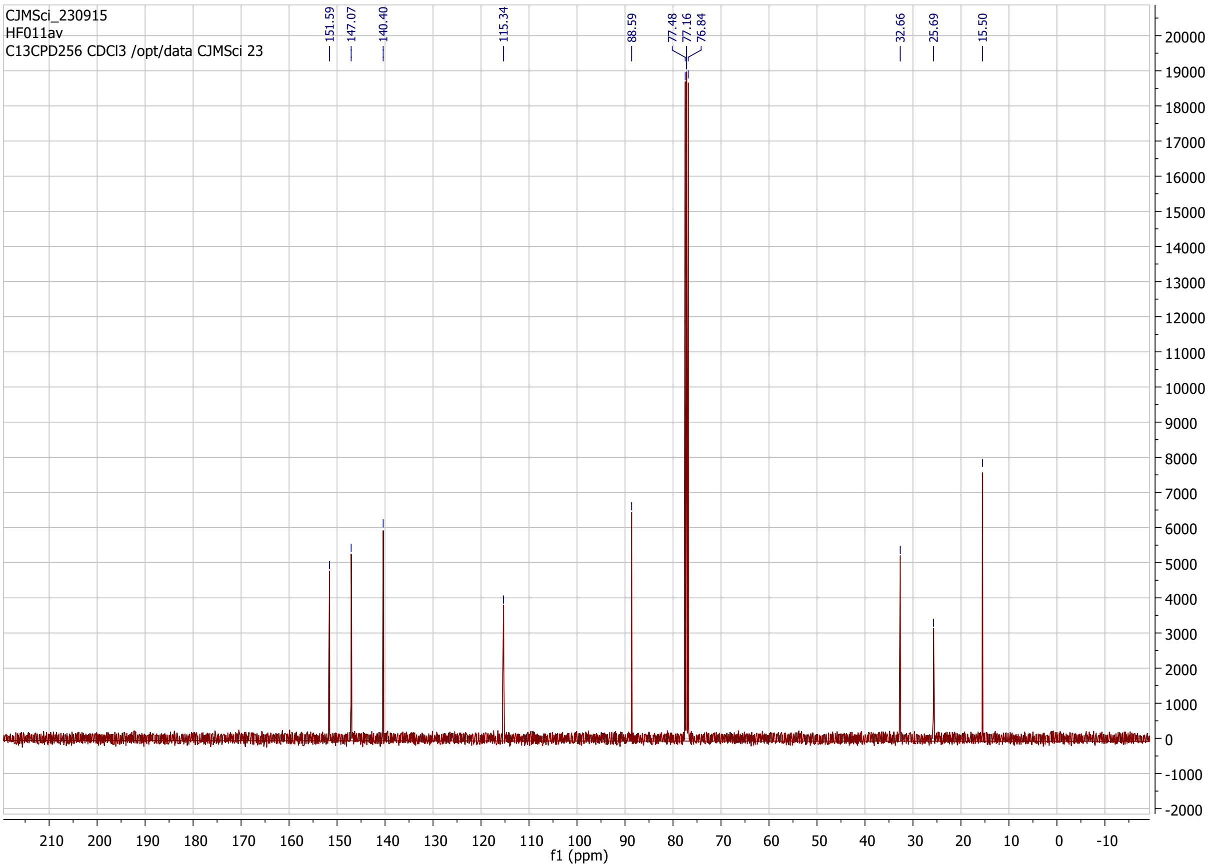
^1H NMR (400 MHz, $CDCl_3$)

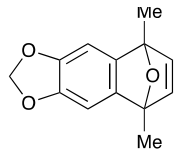




9e

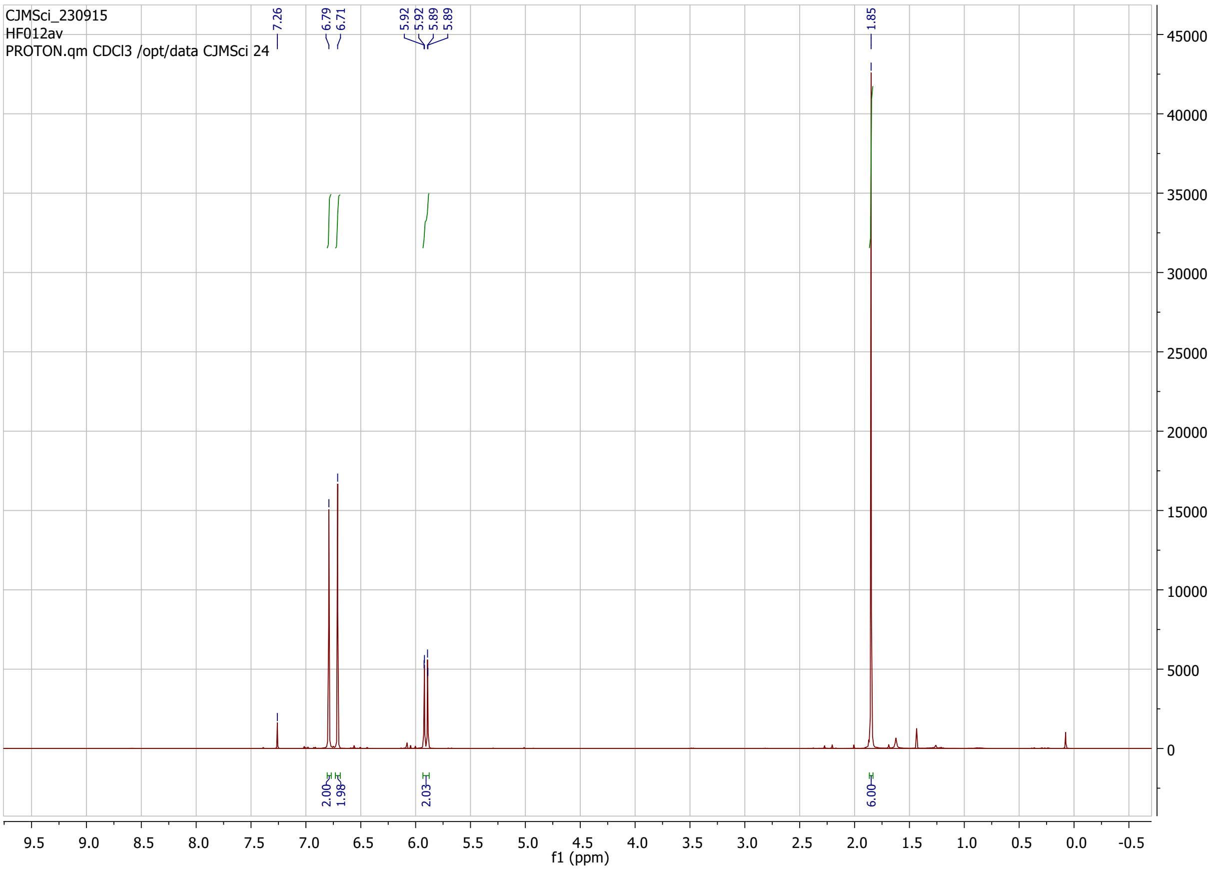
^{13}C NMR (101 MHz, $CDCl_3$)

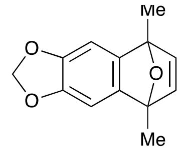




9f

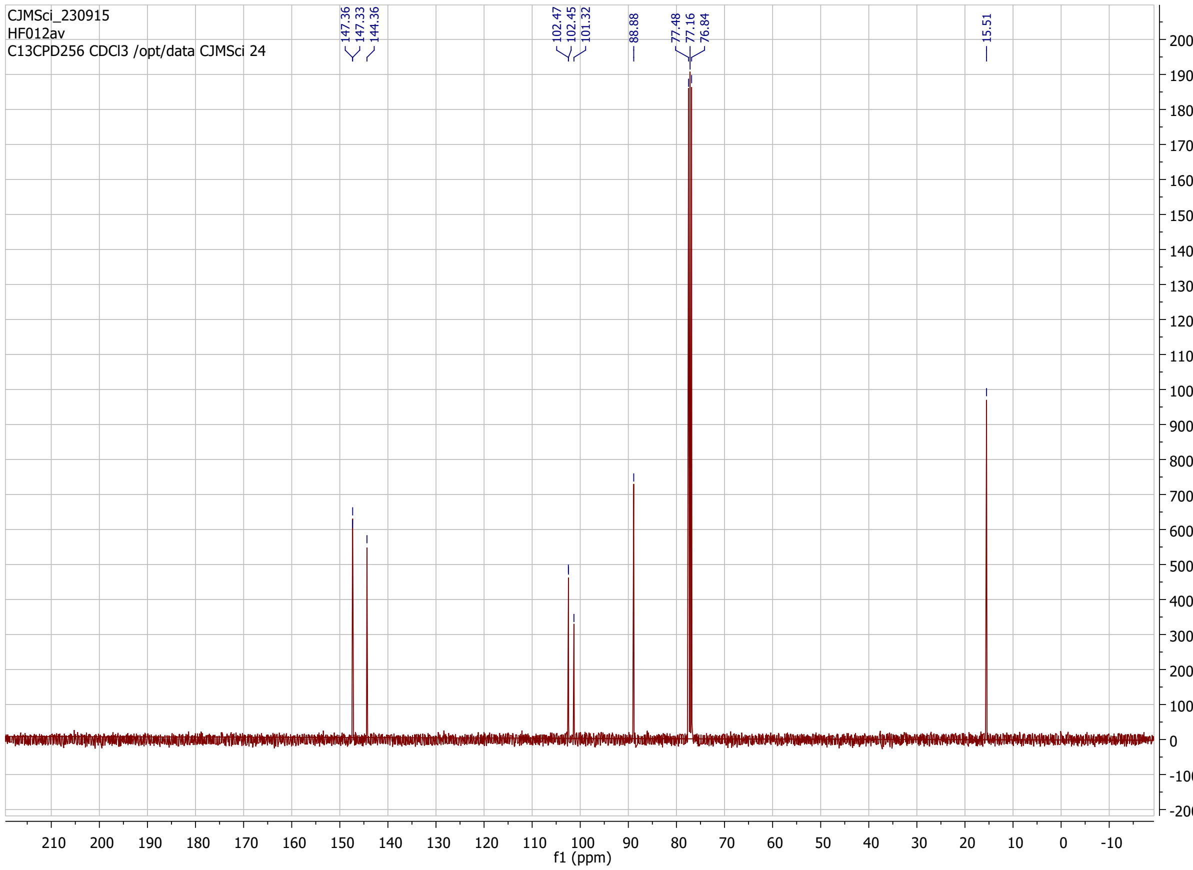
^{1}H NMR (400 MHz, $CDCl_3$)

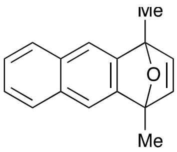




9f

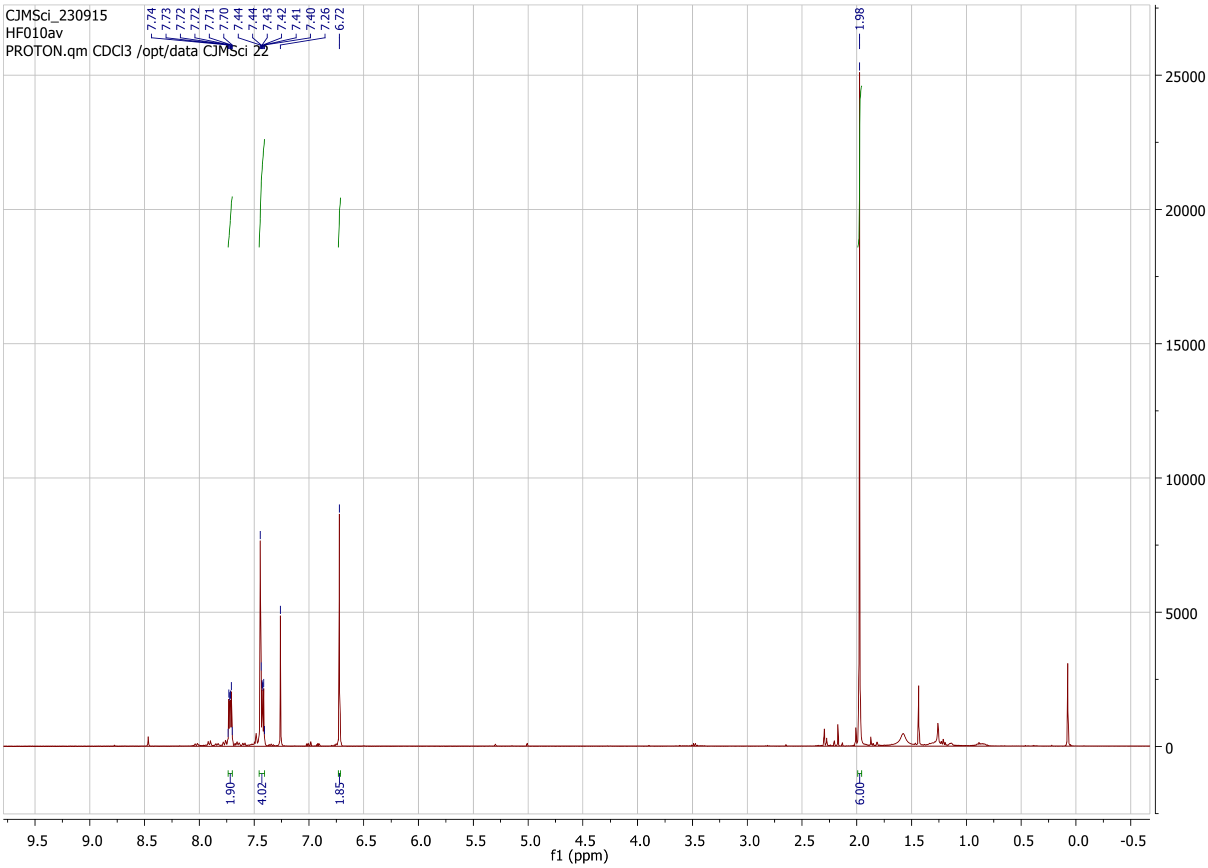
^{13}C NMR (101 MHz, $CDCl_3$)

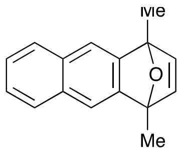




9g

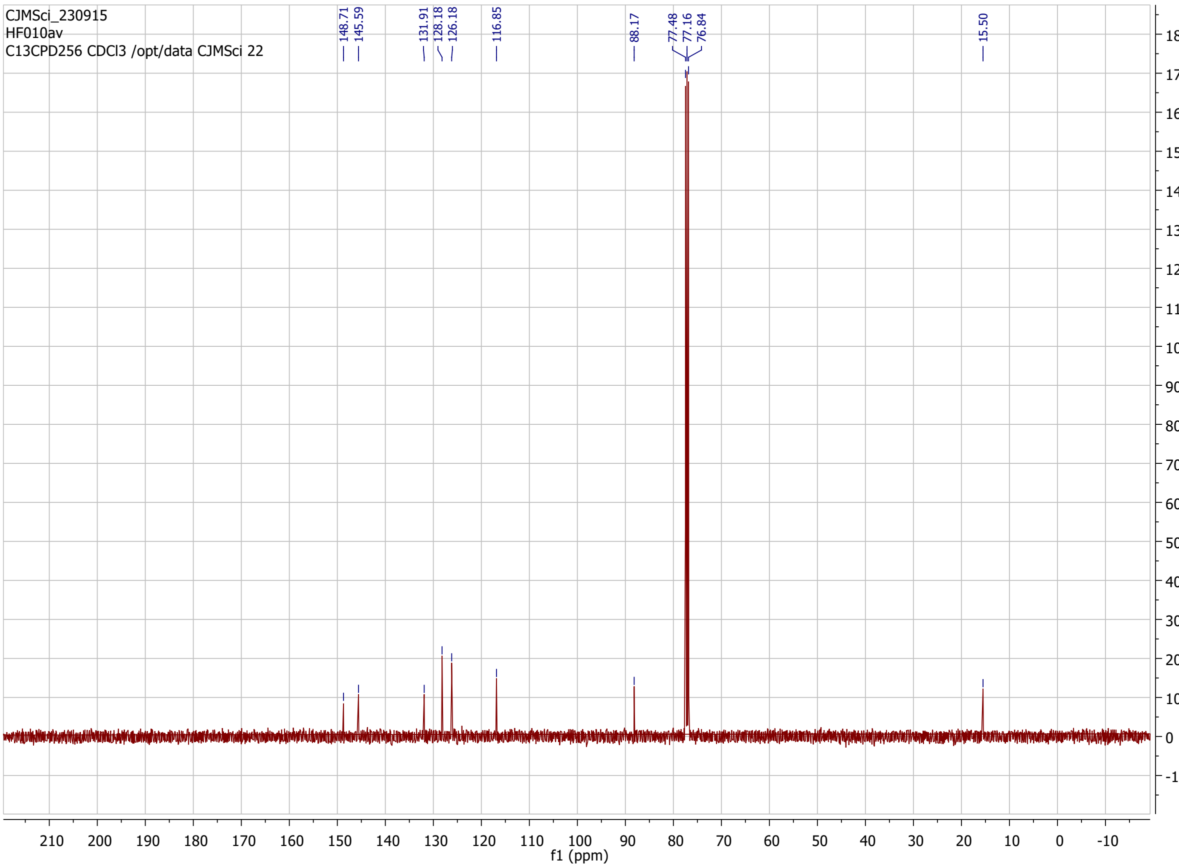
^{1}H NMR (400 MHz, $CDCl_3$)

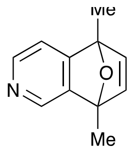




9g

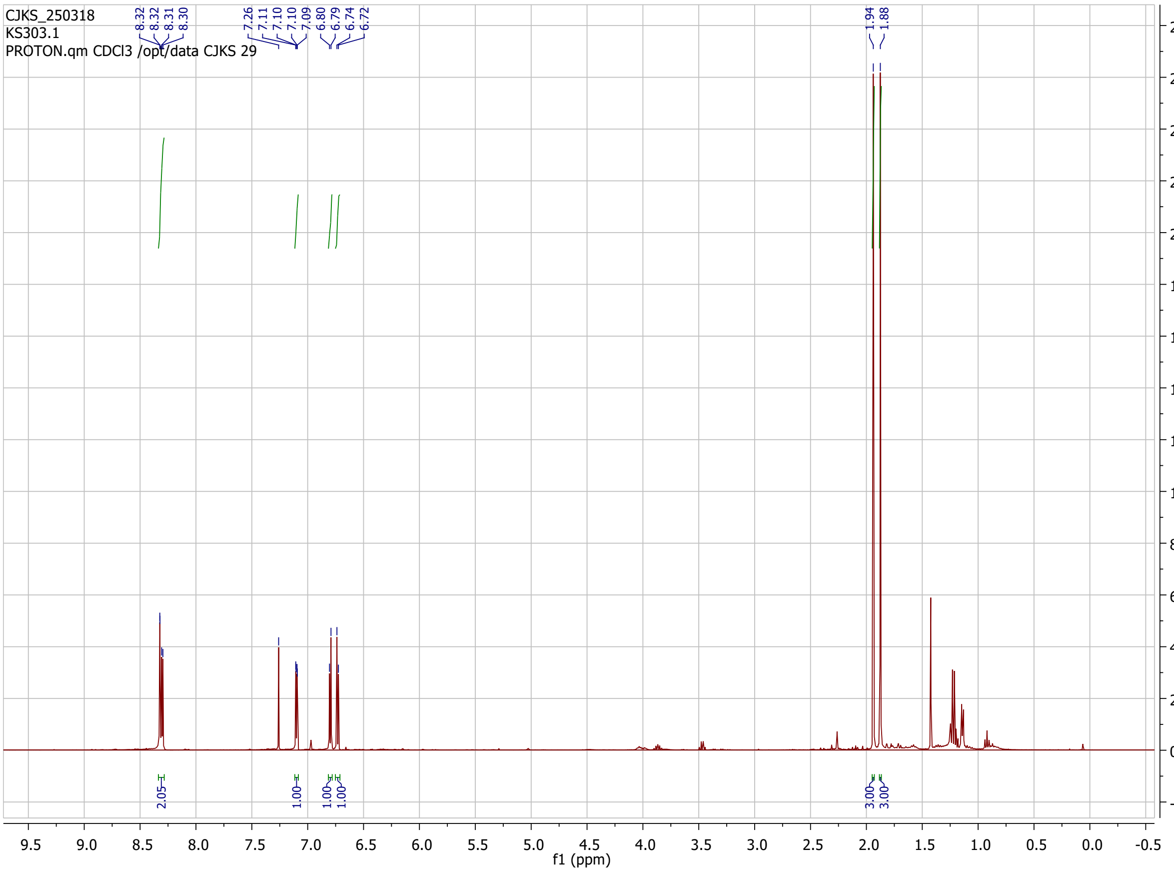
^{13}C NMR (101 MHz, $CDCl_3$)

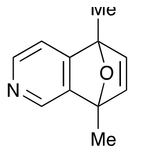




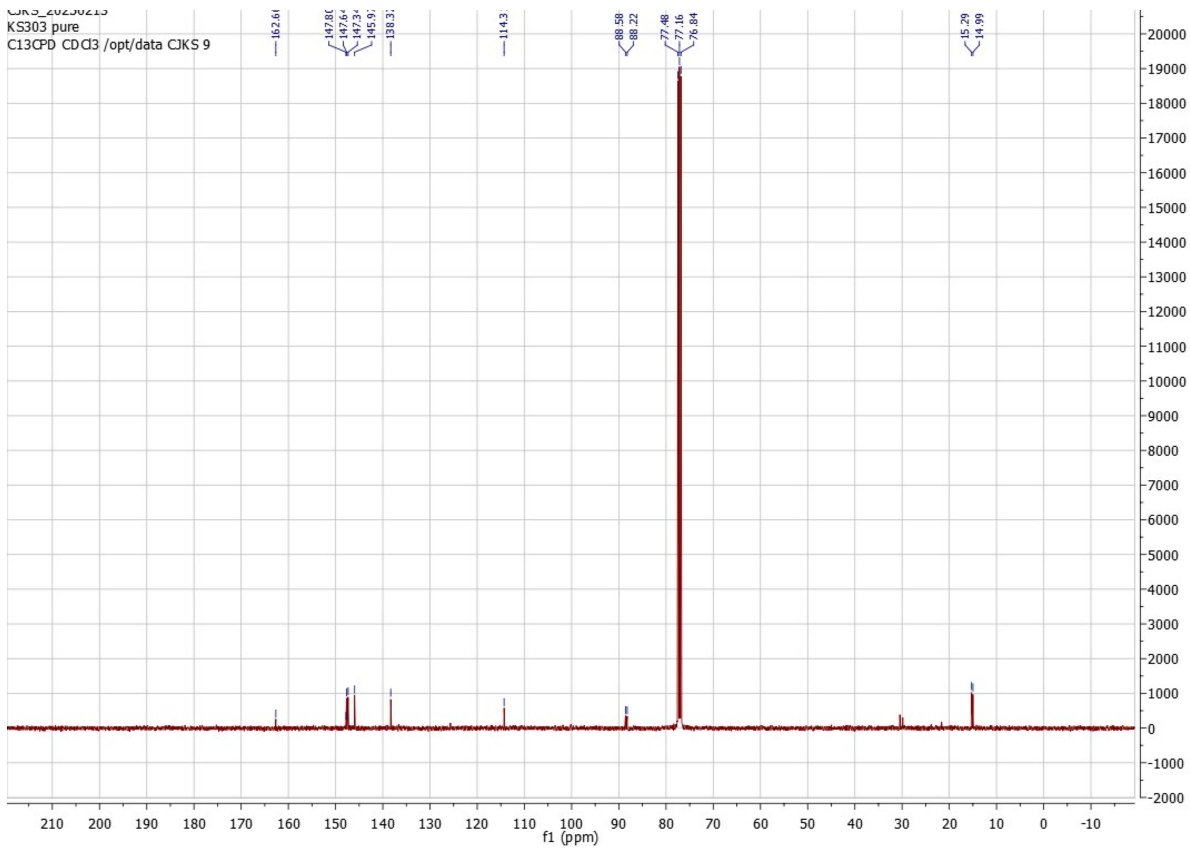
9h

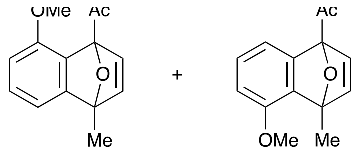
^{1}H NMR (400 MHz, $CDCl_3$)





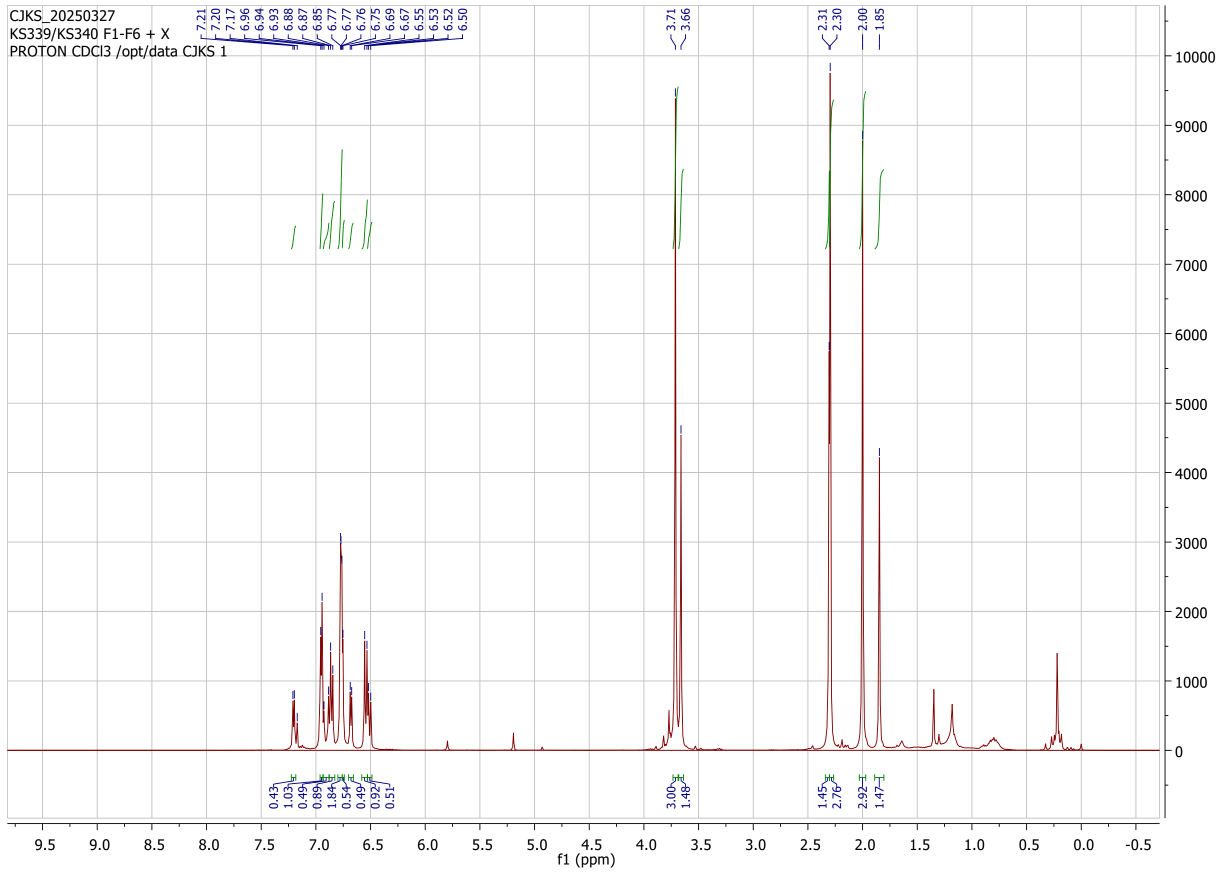
9h ^{13}C NMR (101 MHz, $CDCl_3$)

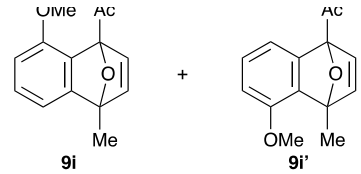




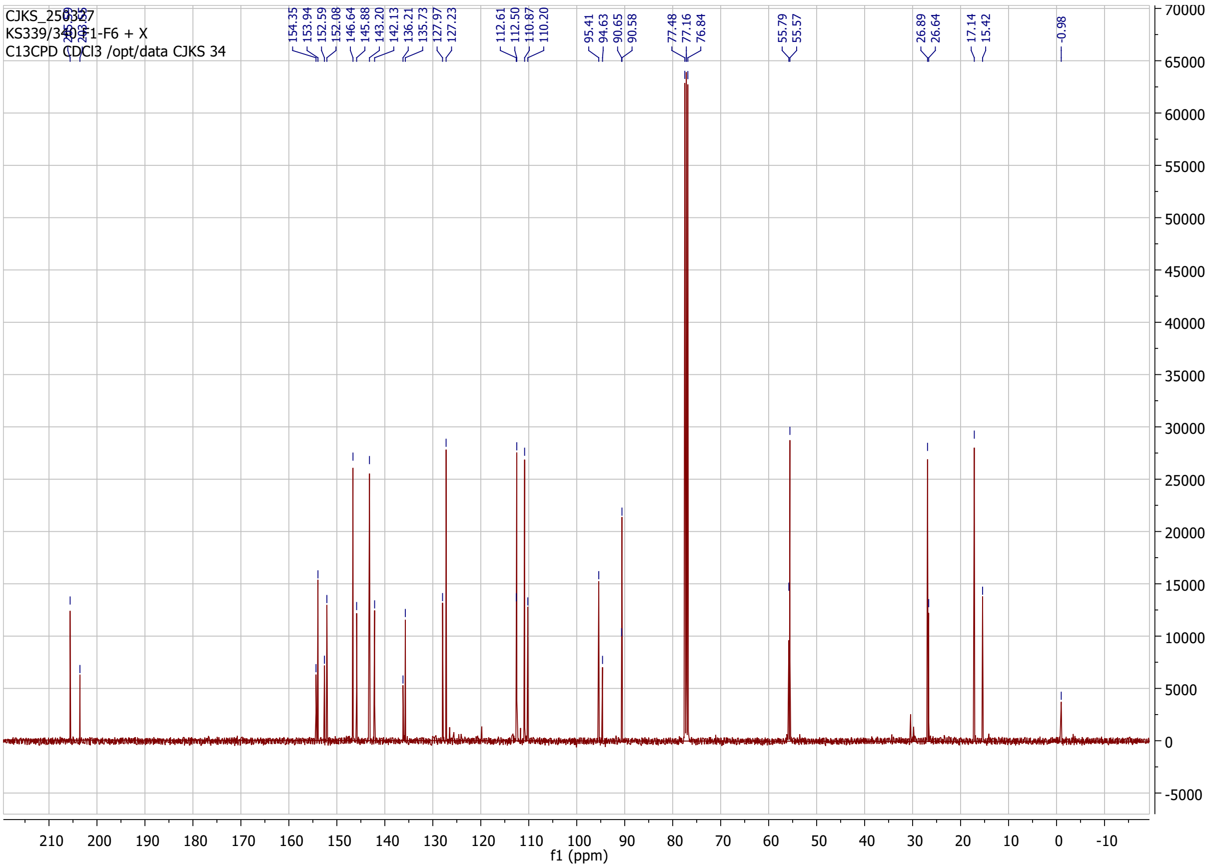
9i **9i'**

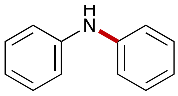
^{1}H NMR (400 MHz, $CDCl_3$)





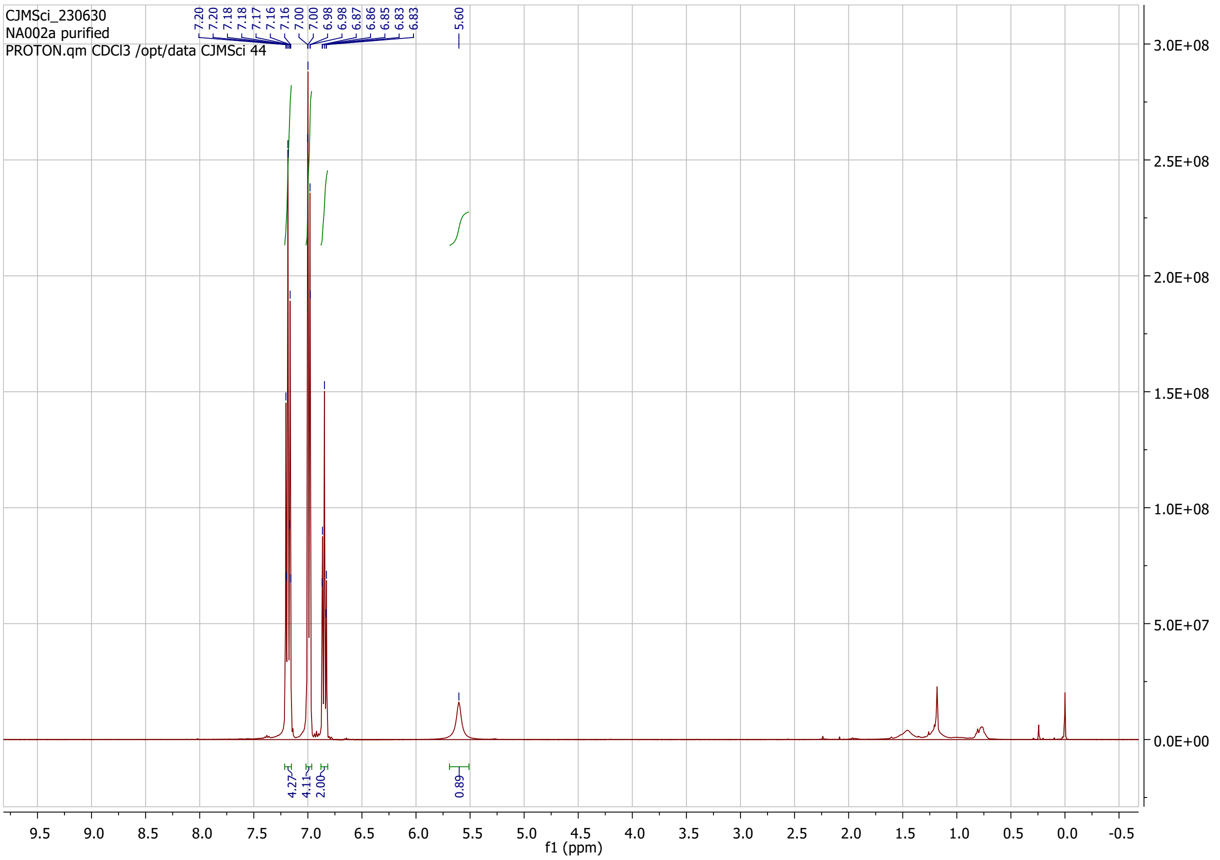
^{13}C NMR (101 MHz, $CDCl_3$)

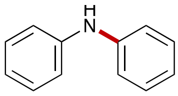




10

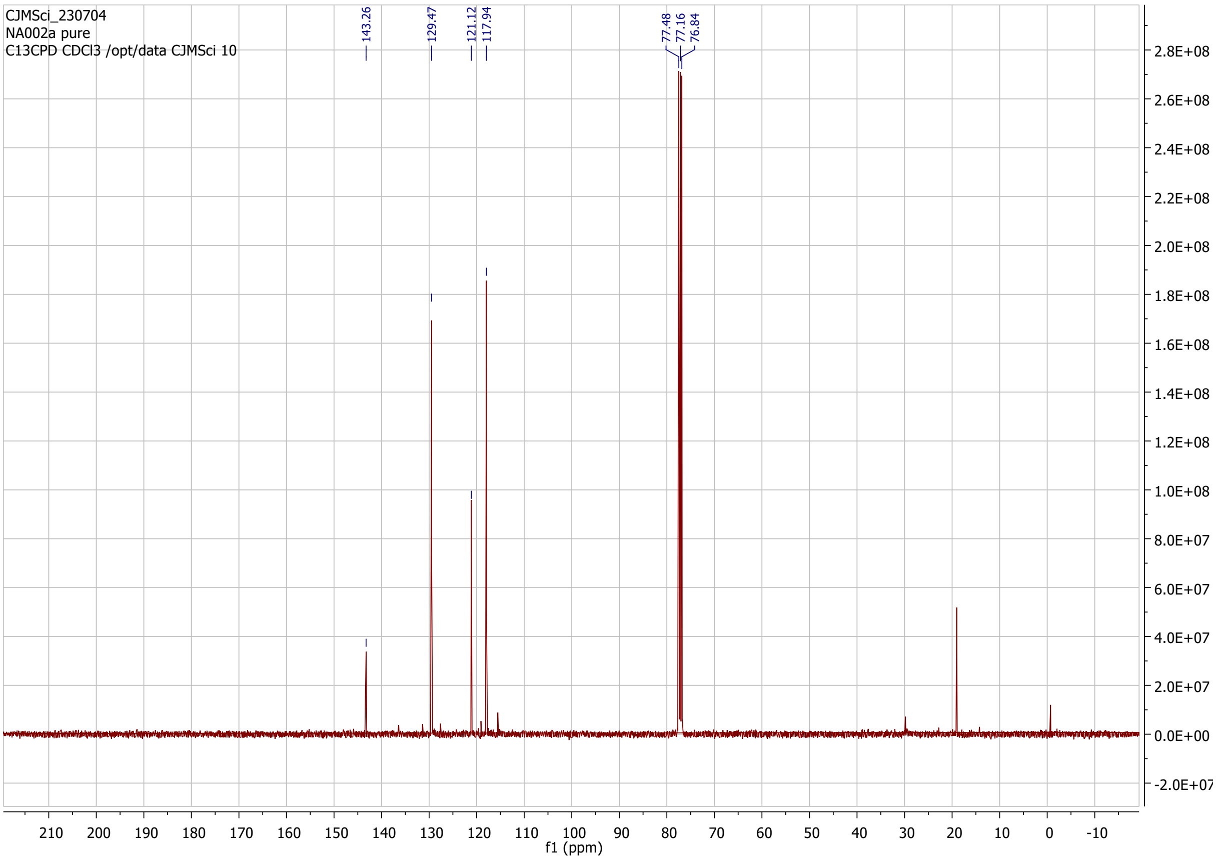
^1H NMR (400 MHz, $CDCl_3$)

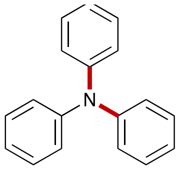




10

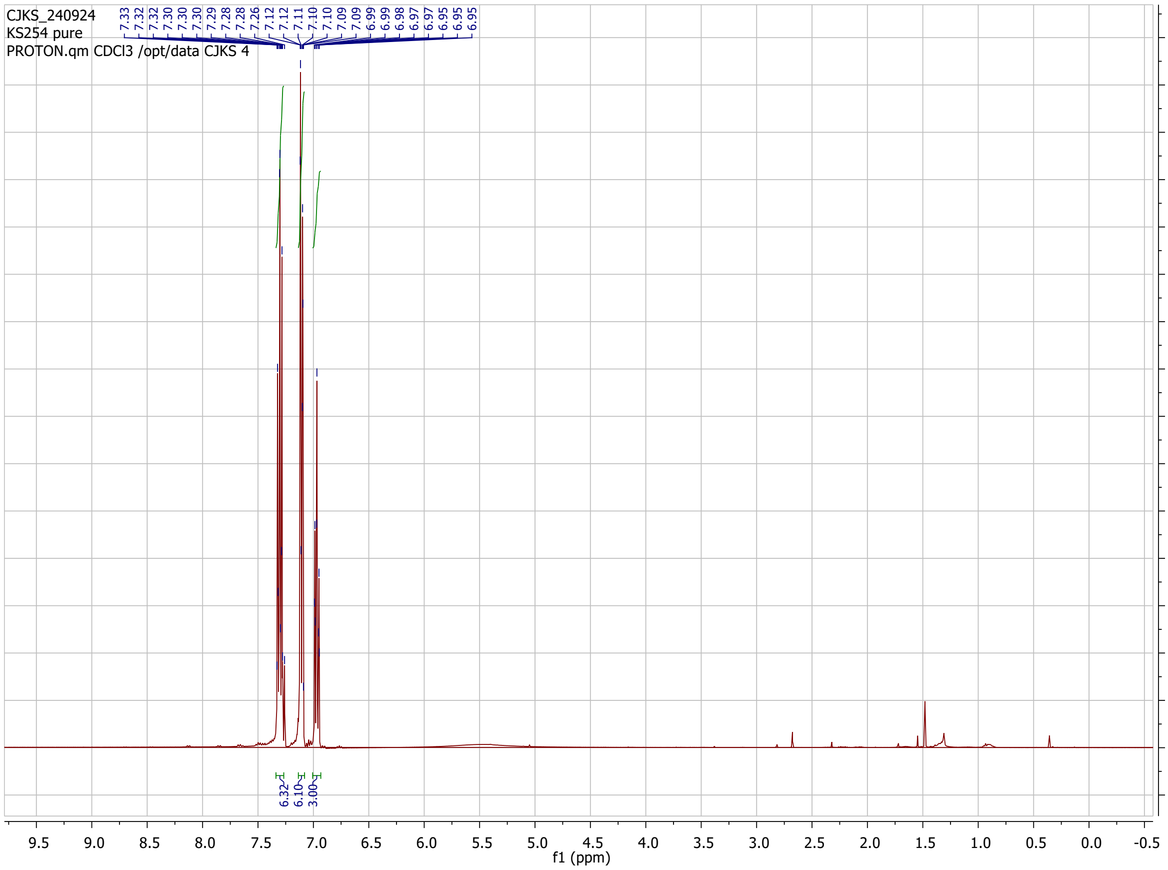
^{13}C NMR (101 MHz, $CDCl_3$)

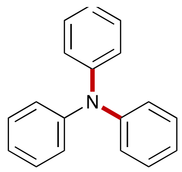




11

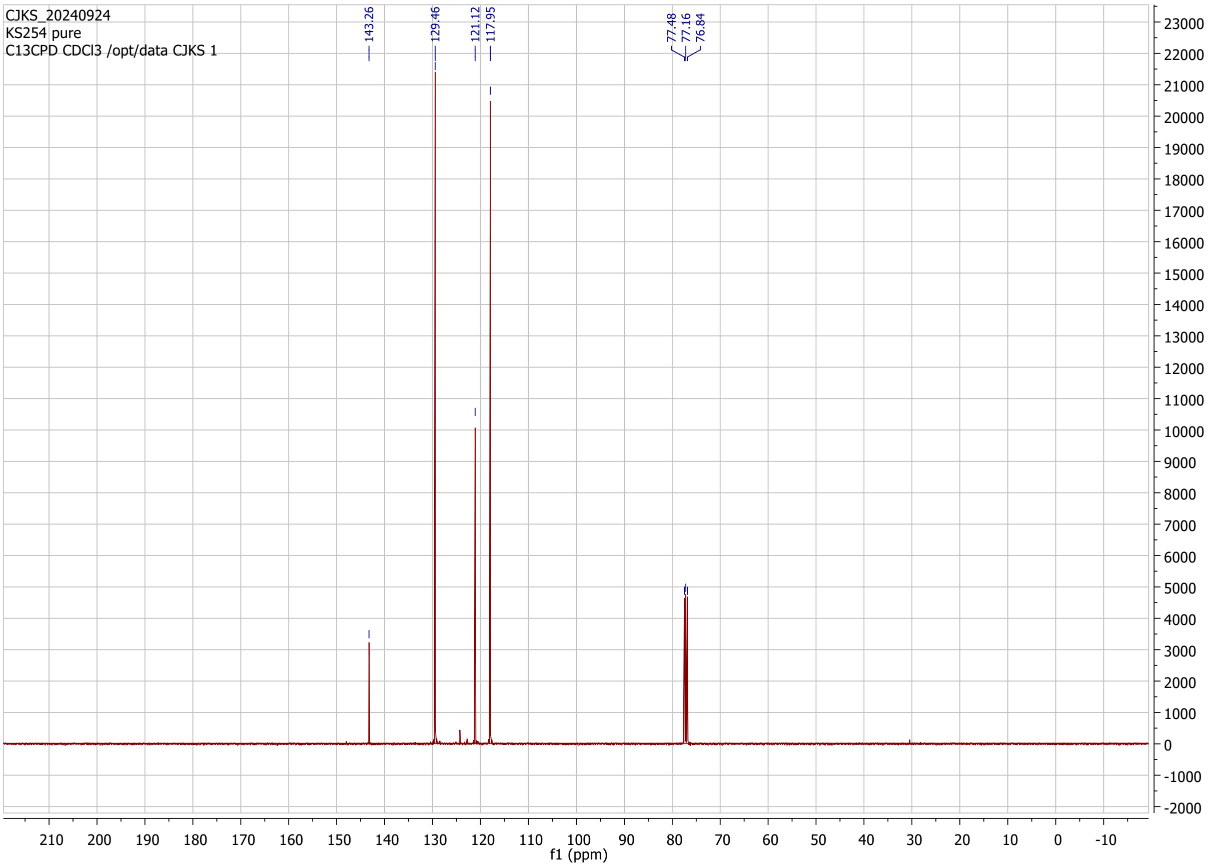
^{1}H NMR (400 MHz, $CDCl_3$)

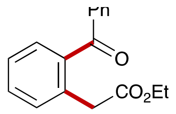




11

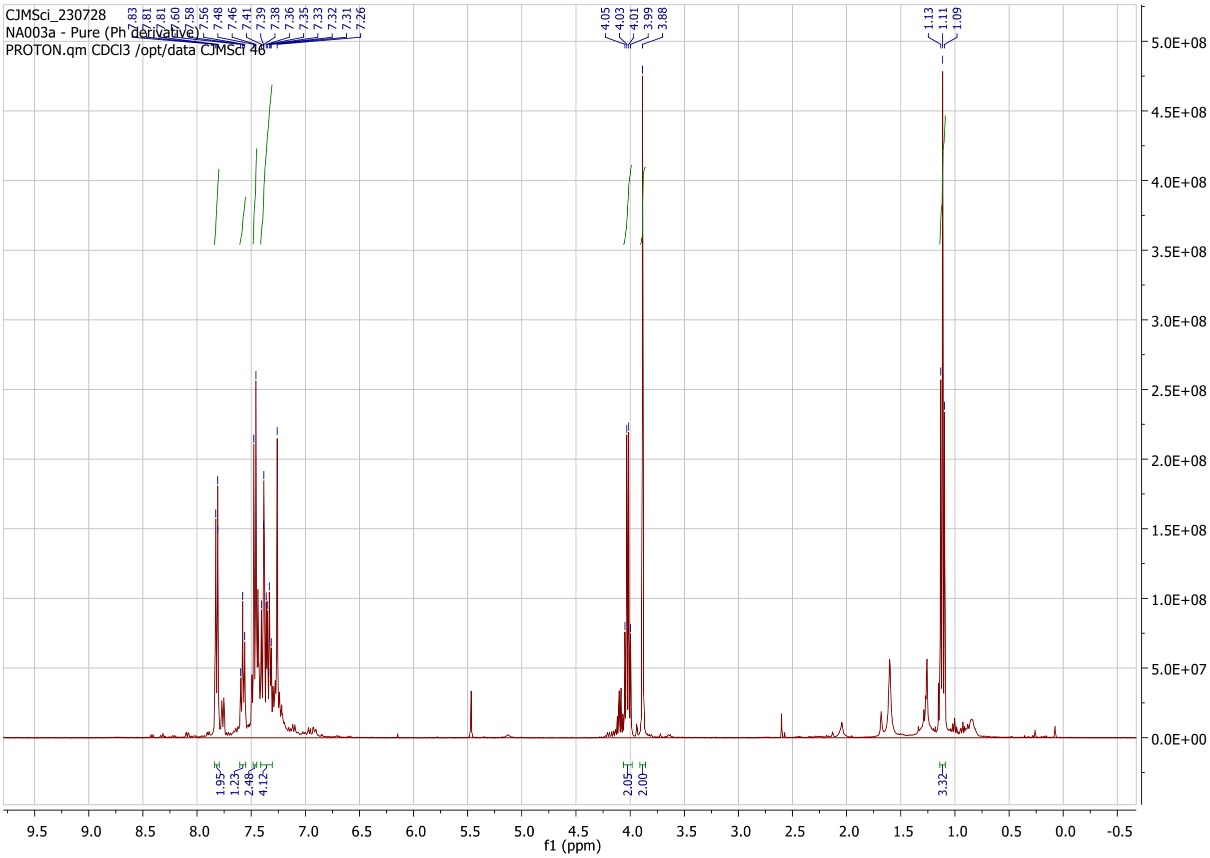
^{13}C NMR (101 MHz, $CDCl_3$)

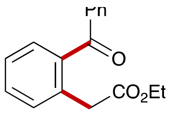




12

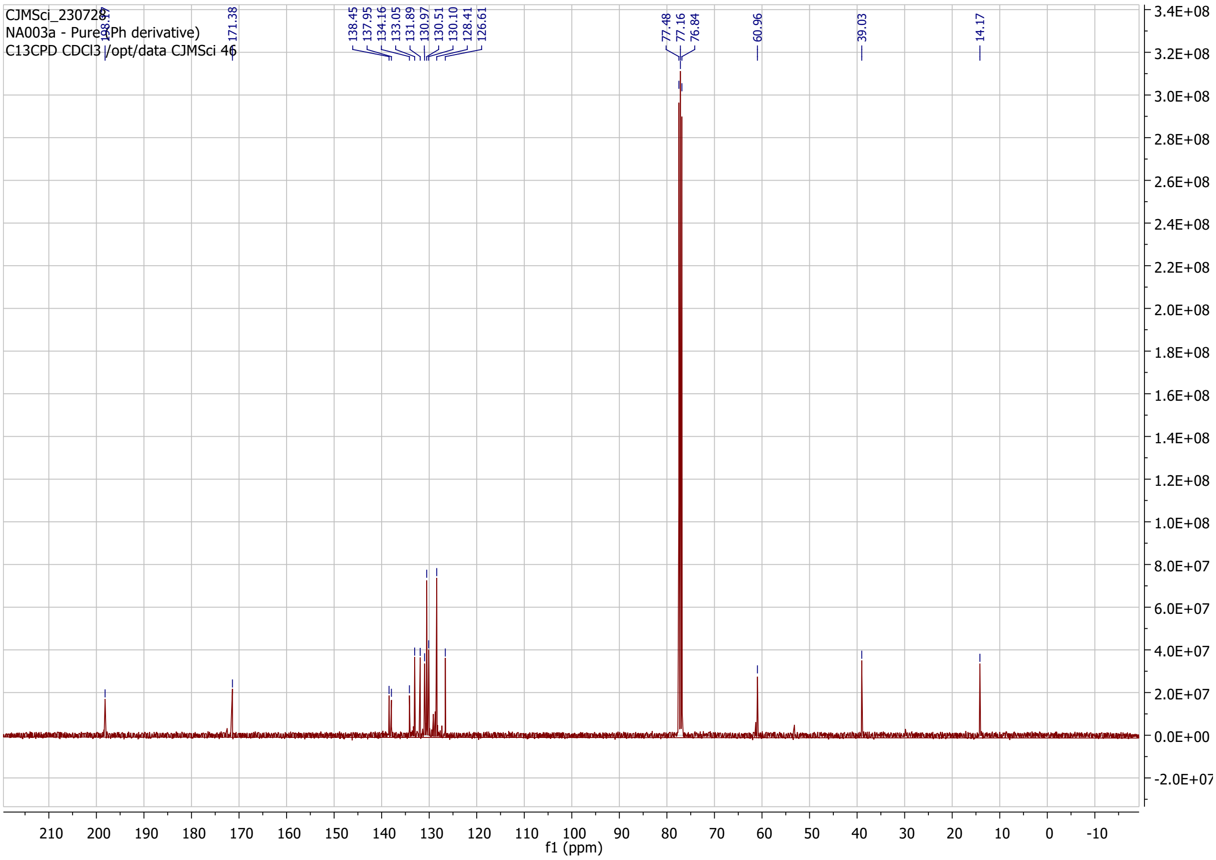
^{1}H NMR (400 MHz, $CDCl_3$)

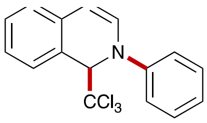




12

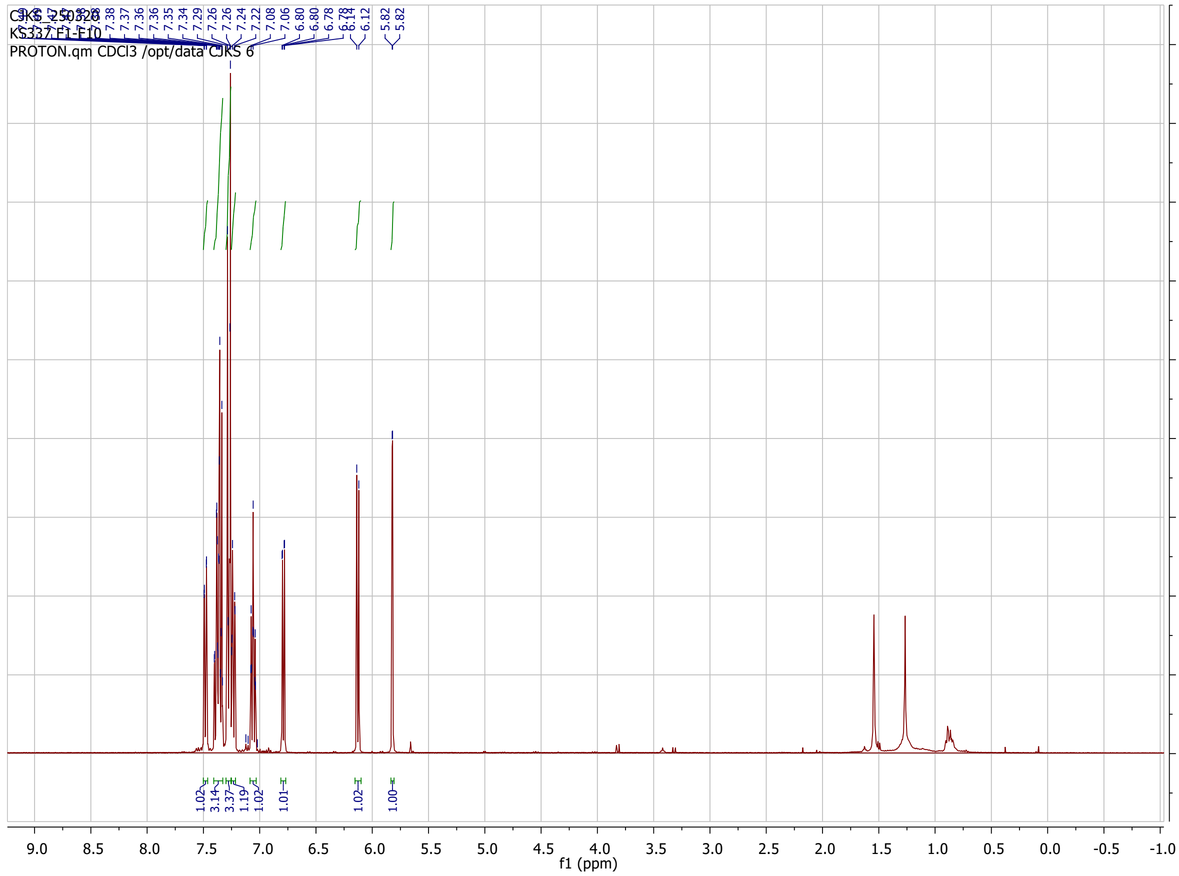
^{13}C NMR (101 MHz, $CDCl_3$)

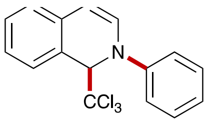




13

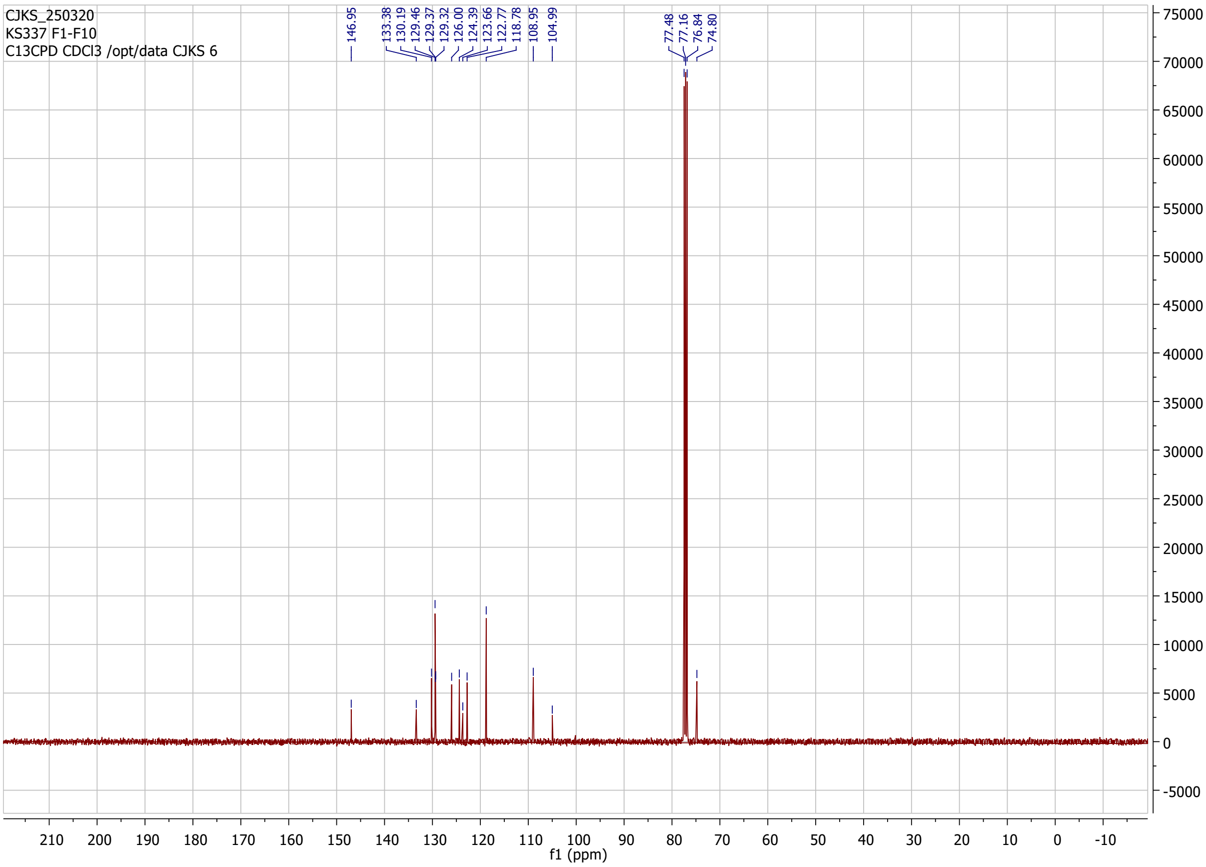
^{1}H NMR (400 MHz, $CDCl_3$)

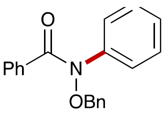




13

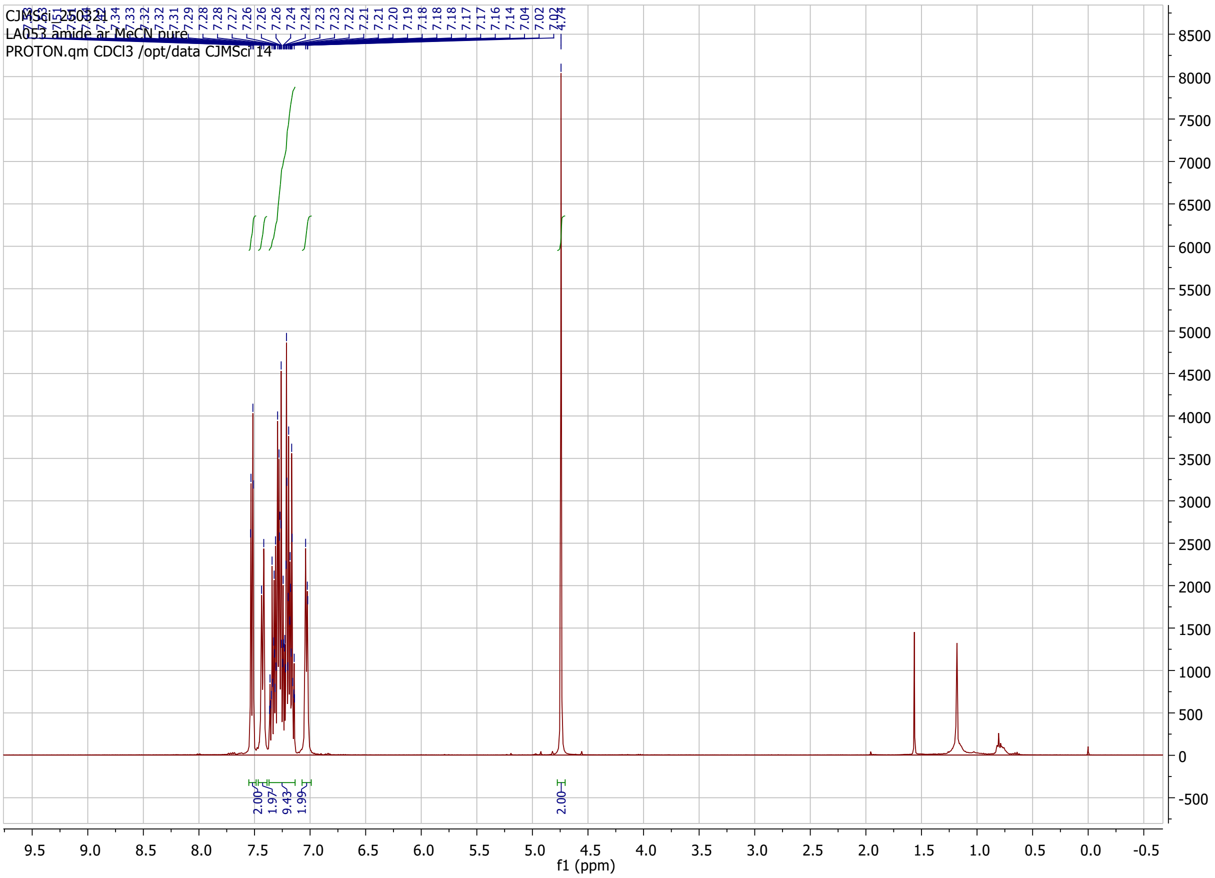
^{13}C NMR (101 MHz, $CDCl_3$)

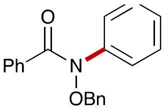




14

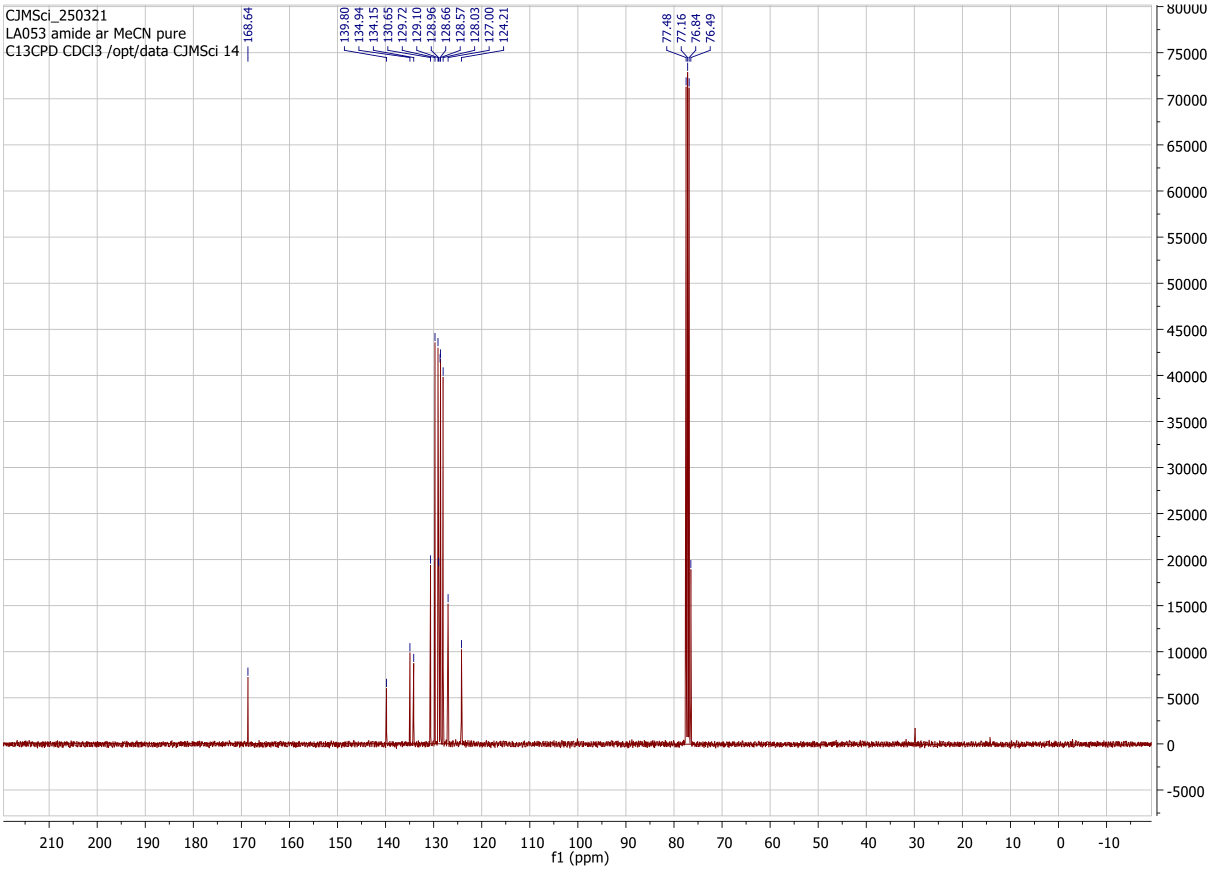
^{1}H NMR (400 MHz, $CDCl_3$)

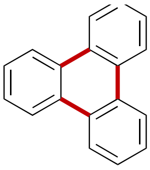




14

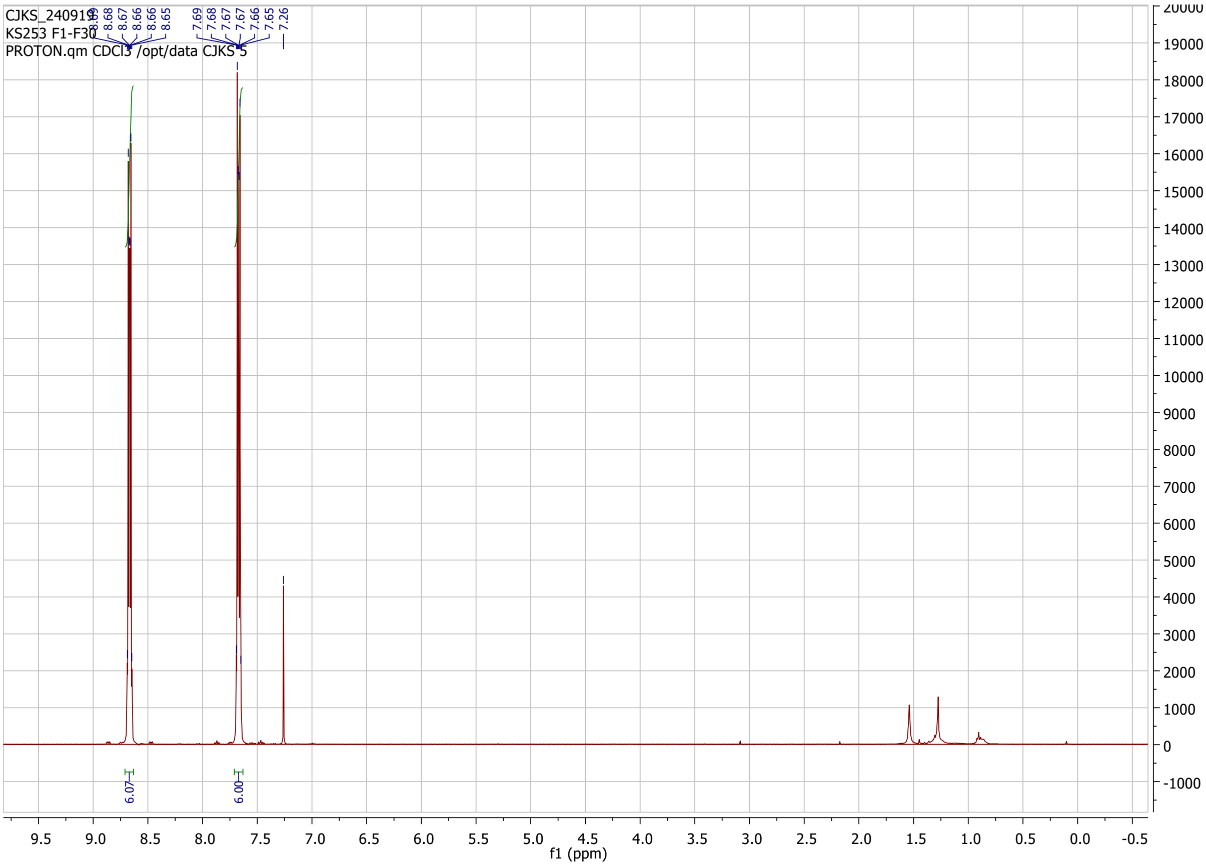
^{13}C NMR (101 MHz, $CDCl_3$)

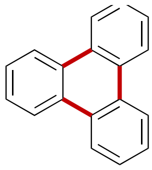




15

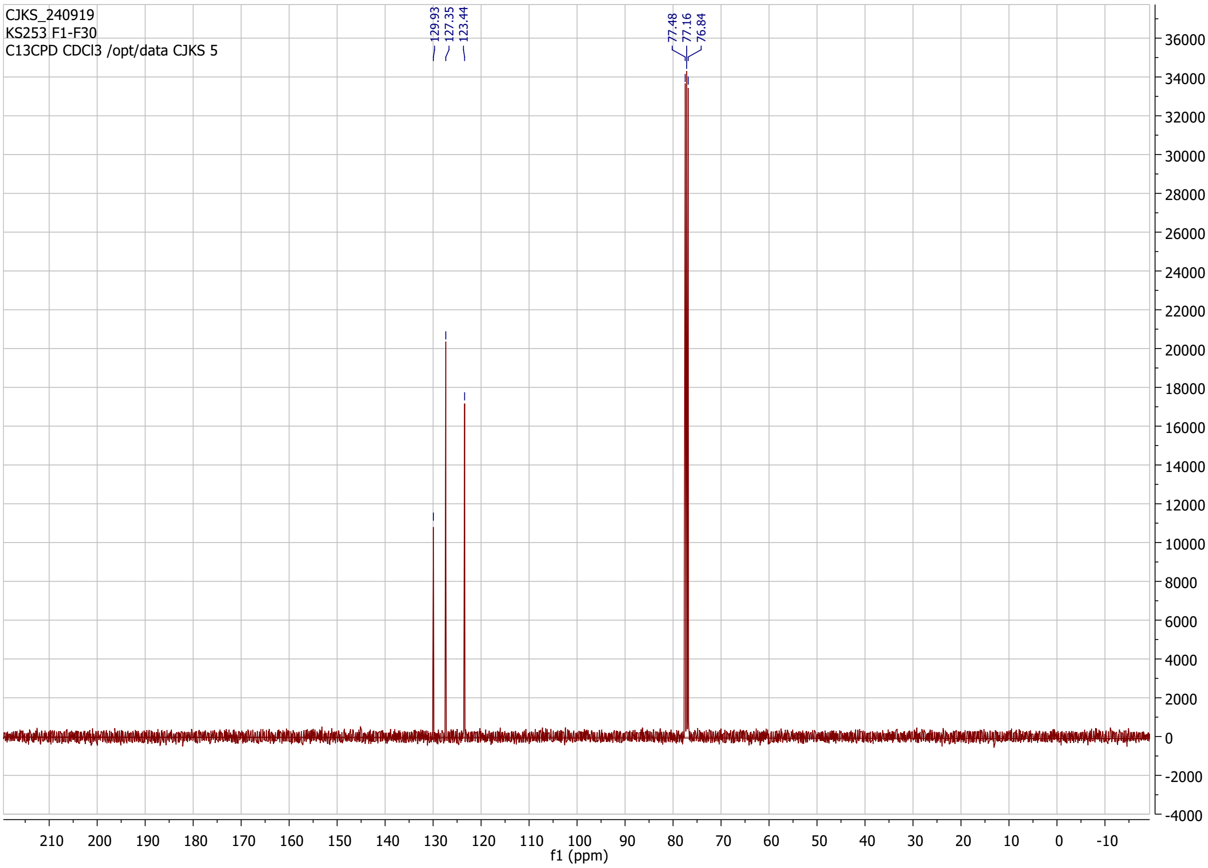
^{1}H NMR (400 MHz, $CDCl_3$)

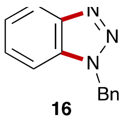




15

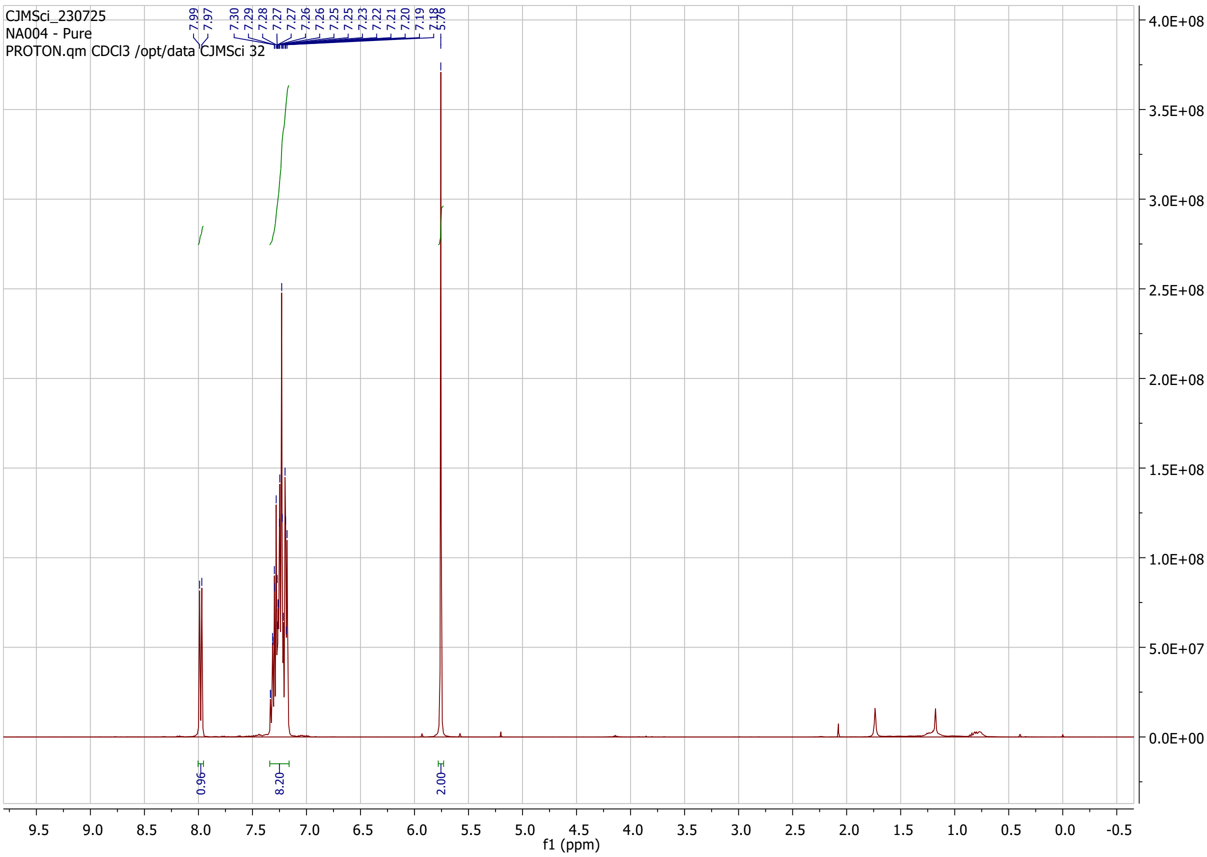
^{13}C NMR (101 MHz, $CDCl_3$)

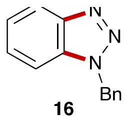




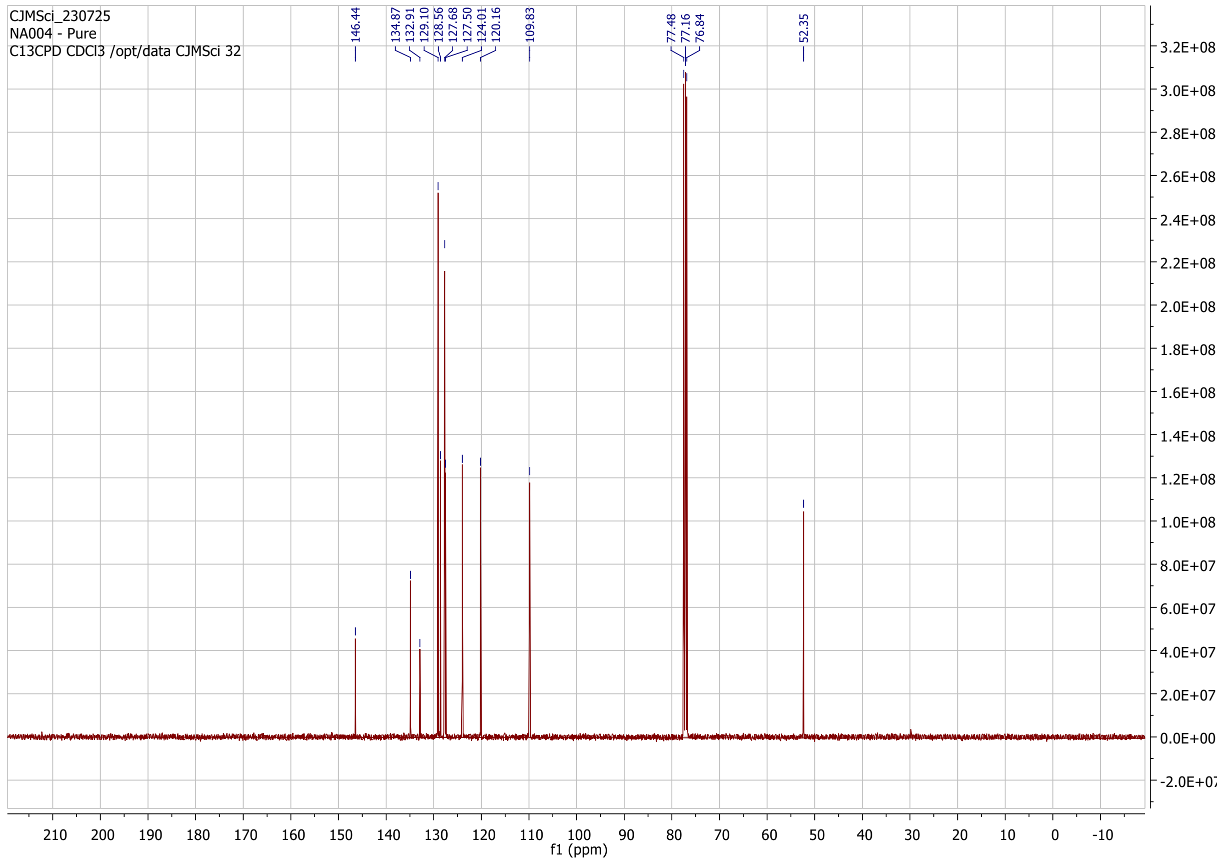
16

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

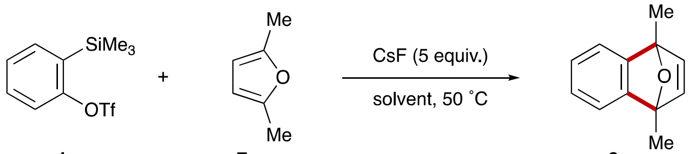




16 ^{13}C NMR (101 MHz, $CDCl_3$)

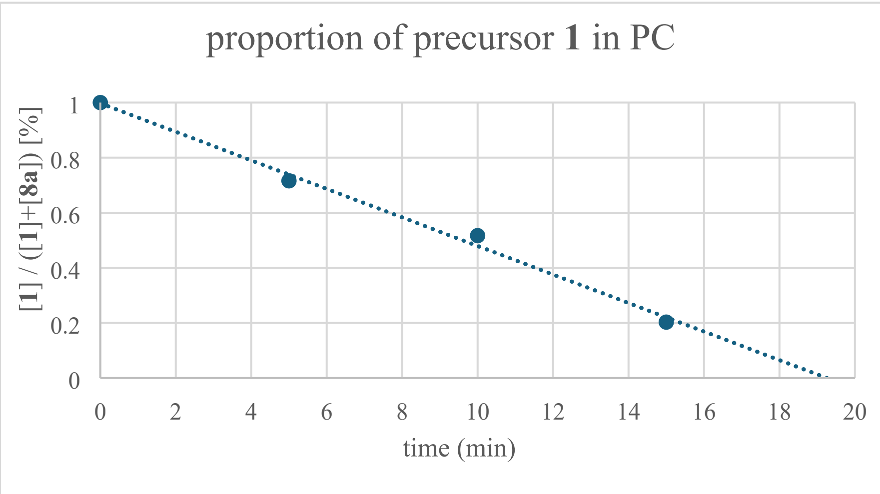


5. Rate of aryne formation in PC and acetonitrile



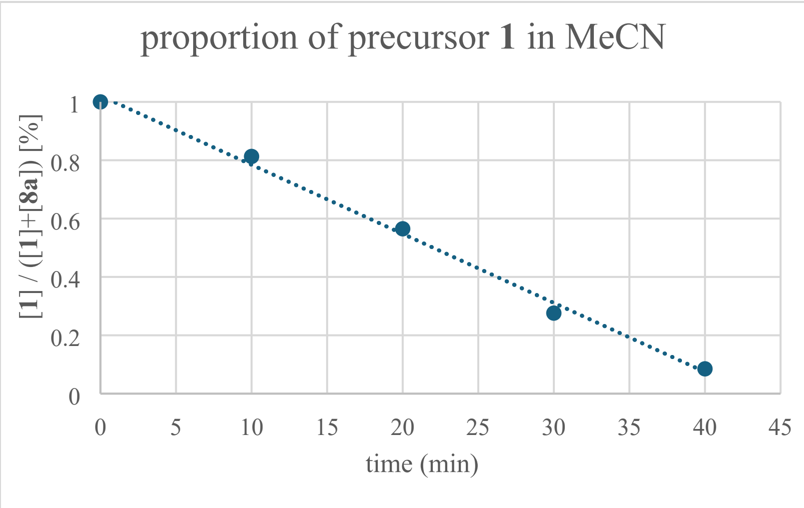
Aliquots taken from an aryne Diels-Alder reaction in PC and proportion of precursor **1** vs Diels-Alder adduct **8a** calculated from [1]H NMR spectra:

time (min)	[**1**] / ([**1**]+[**8a**])
0	1
5	0.716
10	0.517
15	0.203



Aliquots taken from an aryne Diels-Alder reaction in acetonitrile and proportion of precursor **1** vs Diels-Alder adduct **8a** calculated from [1]H NMR spectra:

time (min)	[**1**] / ([**1**]+[**8a**])
0	1
10	0.813
20	0.565
30	0.276
40	0.085



6. References

1. X. Li, Y. Sun, X. Huang, L. Zhang, L. Kong and B. Peng, *Org. Lett.*, 2017, **19**, 838.
2. B. Michel and M. F. Greaney, *Org. Lett.*, 2014, **16**, 2684.
3. B. S. Shaibu, R. K. Kawade and R.-S. Liu, *Org. Biomol. Chem*, 2012, **10**, 6834.
4. K. J. Hoon, 2017.
5. C. Bracken, A. S. Batsanov and M. Baumann, *SynOpen*, 2021, **5**, 29.
6. M. Ito, H. Yamazaki, A. Ito, R. Oda, M. Komiya, K. Higuchi and S. Sugiyama, *Eur. J. Org. Chem.*, 2023, **26**, e202300458.
7. R. A. Enríquez-Figueroa, A. Pineda-Contreras, O. F. Vázquez-Vuelvas, J. S. González-González and S. Fomine, *Macromol. Chem. Phys.*, 2023, **224**, 2300138.
8. Y. Sumida, T. Kato and T. Hosoya, *Org. Lett.*, 2013, **15**, 2806.
9. M. Lei, H. Miao, X. Wang, W. Zhang, C. Zhu, X. Lu, J. Shen, Y. Qin, H. Zhang and S. Sha, *Tetrahedron Lett.*, 2019, **60**, 1389.
10. T. Kitamura, N. Fukatsu and Y. Fujiwara, *J. Org. Chem.*, 1998, **63**, 8579.
11. M. Ito, Y. Yamabayashi, M. Oikawa, E. Kano, K. Higuchi and S. Sugiyama, *Org. Chem. Front.*, 2021, **8**, 2963-2969.
12. Z. Liu and R. C. Larock, *J. Org. Chem.,* 2006, **71**, 3198.
13. K. Okuma, Y. Tanabe, N. Nagahora and K. Shioji, *Bull. Chem. Soc. Jpn.*, 2015, **88**, 1064.
14. J. Tan, B. Liu and S. Su, *Org. Chem. Front*., 2018, **5**, 3093.
15. L. Zhang, Y. Geng and Z. Jin, *J. Org. Chem. Soc*., 2016, **81**, 3542.
16. D. Peña, S. Escudero, D. Pérez, E. Guitián and L. Castedo, *Angew. Chem. Int. Ed*., 1998, **37**, 2659.
17. F. Shi, J. P. Waldo, Y. Chen and R. C. Larock, *Org. Lett*., 2008, **10**, 2409.