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General Considerations.

Unless otherwise noted, all glassware was oven- or flame-dried, and cooled under vacuum prior to use. All non-disposable glassware and magnetic stir bars were washed with freshly prepared aqua regia prior to use to minimize the potential for trace metal contamination. Unless otherwise noted, all commercial reagents were used without further purification, with the exception of commercially available allylic halides which were purified by filtration through a short plug of basic alumina or silica (depending on base sensitivity) and distilled prior to use and thermally stable boronic acids which were recrystallized from water, toluene, ethanol or hexanes depending on solubility prior to use and stored under N_2 or argon in the freezer.

The gold catalyzed allylation reactions were run in 1 dram (15 mm x 45 mm) vials (not dried) fitted with a screw cap and stirring was carried out using an 8 mm magnetic stir bar. All reactions were carried out under air unless otherwise noted. Dichloromethane, toluene, diethyl ether, tetrahydrofuran, dimethyl formamide, and triethylamine were purified by passage through an activated alumina column under argon. Thin-layer chromatography (TLC) analysis of reaction mixtures was performed using Merck silica gel 60 F254 TLC plates, and visualized under UV or by staining with ceric ammonium molybdate or $KMnO_4$. Flash column chromatography was carried out on Merck Silica Gel 60 Å, 230 x 400 mesh. Nuclear magnetic resonance (NMR) spectra were recorded using Bruker AV-600, DRX-500, AV-500, AVB-400, AVQ-400, and AV-300 spectrometers. ^{1}H and ^{13}C chemical shifts are reported in ppm downfield of tetramethylsilane and referenced to residual solvent peak ($CHCl_3$; $\delta H = 7.26$ and $\delta C = 77.0$, CH_2Cl_2; $\delta H = 5.30$ and $\delta C = 53.5$, CH_3CN; $\delta H = 1.94$ and $\delta C = 1.3, 118.3$). Multiplicities are reported using the following abbreviations: s = singlet, d = doublet, t = triplet, q = quartet, p = pentet, m = multiplet, bs = broad singlet. Gas Chromatography was conducted on an HP 6850A Series GC System on a Chiraldex 225 β-dex column with a flame ionization detector. Ethyl benzoate was used as an internal standard. Mass spectral data were obtained from the Thermo Scientific LTQ FT Ultra mass spectrometer (ESI) or the Autospec Premier magnetic sector mass spectrometer (EI) at the Micro-Mass/Analytical Facility operated by the College of Chemistry, University of California, Berkeley. Elemental Analyses were obtained from the Microanalytical Laboratory Perkin Elmer 2400 Series II combustion analyzer operated by the College of Chemistry, University of California, Berkeley.

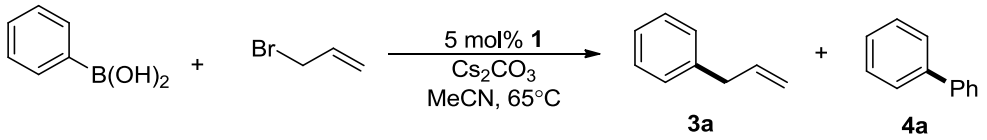
Chloro(dimethylsulfide)gold(I) was prepared from $AuCl_3$ (purchased from Strem Chemical) according to a previously reported procedure.[1] Ph_3PAuCl and tBu_3PAuCl were purchased from Strem Chemical and used without further purification.

Bis(diphenylphosphino)isopropylamine,[2] (diphenylphosphino)diisopropylamine,[3] IPrAuCl,[4] JohnphosAuCl,[5] PhO_3PAuCl,[6] $pOMePh_3PAuCl$,[7] IPrAuOH,[8] 2-phenylprop-2-en-1-ol,[9] (5,6-dihydro-2H-pyran-3-yl)methanol,[10] and (2-bromocyclohex-1-en-1-yl)methanol[11] were prepared according to previously reported literature procedures.

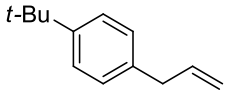
General procedure for gold catalyzed allylation with allyl bromide.

1 (5.4 mg, 0.006 mmol, carefully recrystallized and finely ground), boronic acid (0.123 mmol), and Cs_2CO_3 (120 mg, .379 mmol) were weighed into a vial equipped with a stirbar. MeCN (0.6 mL) was added followed by the allyl bromide (42 μL 0.492 mmol). The vial was equipped with a stirbar, capped tightly, and the reaction mixture was stirred vigorously for 18 hrs at 65°C in a heating block. Upon cooling, the reaction mixture was concentrated *in vacuo*, the residue was suspended in diethyl ether or dichloromethane and filtered through a pad of celite.

Effects of variation of reaction conditions



Deviation from standard conditions	GC Yield 3a	GC Yield 4a
Standard conditions	66%	9%
1:1 allyl bromide/phenylboronic acid	16%	18%
2:1 allyl bromide/ phenylboronic acid	37%	11%
10:1 allyl bromide/phenylboronic acid	71%	7%
Et_3N instead of Cs_2CO_3	3%	1%
DIPEA instead of Cs_2CO_3	12%	3%
K_2CO_3 instead of Cs_2CO_3	44%	5%
PhBPin instead of $PhB(OH)_2$	47%	10%
PhBNeop instead of $PhB(OH)_2$	62%	9%
PhSnMe3 and no base instead of PhB(OH)2	33%	12%
PhSnBu3 and no base instead of PhB(OH)2	35%	15%
Allyl iodide instead of allyl bromide	23%	6%
Allyl chloride instead of allyl bromide	5%	1%
Allyl Chloride at 80 °C	21%	5%
Allyl diethyl phosphonate instead of allyl bromide	0%	0%
Allyl mesylate instead of allyl bromide	0%	0%
Allyl acetate instead of allyl bromide	0%	0%
Room temp instead of 65°C	10%	5%
80°C instead of 65°C	63%	10%
MeOH solvent	34%	25%
$CHCl_3$ solvent	8%	5%
5:1 MeCN/MeOH	42%	21%
+ 1 equiv Bu_4N Br	10%	3%

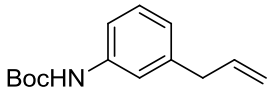


1-allyl-4-(tert-butyl)benzene, **3b**

Preperative TLC (3x elution with pentane) afforded the desired product as as colorless semisolid (15.4 mg, 72%).

^{1}H NMR (600 MHz, $CDCl_3$) δ 7.33 (d, *J* = 7.8 Hz, 2H), 7.14 (d, *J* = 7.9 Hz, 2H), 5.98 (ddt, *J* = 16.8, 9.7, 6.8 Hz, 1H), 5.13 – 5.02 (m, 2H), 3.37 (d, *J* = 6.9 Hz, 2H), 1.32 (s, 9H).

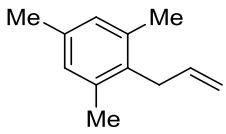
In accordance with previously reported spectra[12]



tert-butyl (3-allylphenyl)carbamate, **3c**

Column chromatography (SiO_2, eluting with 95:5 pentane/diethyl ether) afforded the desired product as a colorless film (16.4 mg, 58%).

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.25 – 7.15 (m, 3H), 6.88 (d, *J* = 7.2 Hz, 1H), 6.44 (s, 1H), 5.96 (ddt, *J* = 16.9, 10.1, 6.7 Hz, 1H), 5.17 – 4.97 (m, 2H), 3.37 (d, *J* = 6.7 Hz, 2H), 1.52 (s, 9H).
^{13}C NMR (151 MHz, $CDCl_3$) δ 152.67, 141.06, 138.38, 137.17, 128.93, 123.26, 118.61, 116.23, 115.89, 80.40, 40.18, 28.31, 28.28.
HRMS (EI) m/z: calculated for $[C_{14}H_{19}N_1O_2]^+$ 233.1416, found 233.1415.

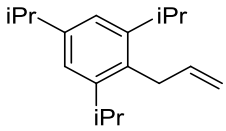


2-allyl-1,3,5-trimethylbenzene, **3d**

Column chromatography (SiO_2, eluting with pentane) afforded the desired product as a colorless oil (15.4 mg, 80%).

^{1}H NMR (600 MHz, $CDCl_3$) δ 6.86 (s, 2H), 5.89 (td, *J* = 10.5, 5.0 Hz, 1H), 4.99 (dd, *J* = 9.9, 2.4 Hz, 1H), 4.92 – 4.77 (m, 2H), 3.36 (d, *J* = 5.7 Hz, 2H), 2.27 (s, 9H).

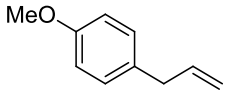
In accordance with previously reported spectra[13]



2-allyl-1,3,5-triisopropylbenzene, **3e**

Column chromatography (SiO_2, eluting with pentane) afforded the desired product as a colorless oil (10.4 mg, 35%).

^{1}H NMR (600 MHz, $CDCl_3$) δ 7.00 (s, 2H), 5.98 (ddt, *J* = 16.1, 10.5, 5.4 Hz, 1H), 5.06 – 4.95 (m, 1H), 4.89 – 4.78 (m, 1H), 3.46 (d, *J* = 5.2 Hz, 2H), 3.13 (p, *J* = 6.9 Hz, 2H), 2.88 (p, *J* = 7.0 Hz, 1H), 1.26 (d, *J* = 6.9 Hz, 6H), 1.22 (d, *J* = 6.9 Hz, 12H).
^{13}C NMR (151 MHz, $CDCl_3$) δ 147.14, 146.75, 138.06, 130.52, 121.00, 115.04, 34.28, 31.67, 29.44, 24.43, 24.23.
HRMS (EI) m/z: calculated for $[C_{18}H_{28}]^+$ 244.2191, found 244.2192.

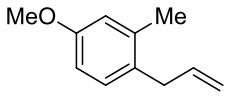


1-allyl-4-methoxybenzene, **3f**

Column chromatography (SiO_2, eluting with pentane) afforded the desired product as a colorless oil (9.3 mg, 51%).

^{1}H NMR (600 MHz, $CDCl_3$) δ 7.11 (d, *J* = 8.4 Hz, 2H), 6.84 (d, *J* = 8.5 Hz, 2H), 5.95 (ddt, *J* = 16.8, 10.1, 6.7 Hz, 1H), 5.14 – 4.96 (m, 2H), 3.79 (s, 3H), 3.33 (d, *J* = 6.6 Hz, 2H).

In accordance with previously reported spectra[14]

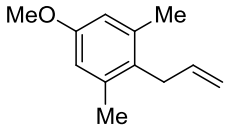


1-allyl-4-methoxy-2-methylbenzene, **3g**

Column chromatography (SiO_2, eluting with pentane) afforded the desired product as a colorless oil (14 mg, 70%).

^{1}H NMR (600 MHz, $CDCl_3$) δ 7.04 (d, *J* = 8.2 Hz, 1H), 6.72 (d, *J* = 2.6 Hz, 1H), 6.70 (d, *J* = 8.3 Hz, 1H), 5.93 (ddt, *J* = 16.6, 9.9, 6.4 Hz, 1H), 5.03 (d, *J* = 10.1 Hz, 1H), 5.01 – 4.86 (m, 1H), 3.78 (s, 3H), 3.31 (d, *J* = 6.2 Hz, 2H), 2.27 (s, 3H).

In accordance with previously reported spectra[15]

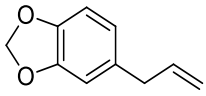


2-allyl-5-methoxy-1,3-dimethylbenzene, **3h**

Column chromatography (SiO_2, eluting with pentane) afforded the desired product as a colorless semisolid (18.2 mg, 84%).

^{1}H NMR (600 MHz, $CDCl_3$) δ 6.60 (s, 2H), 5.89 (ddt, *J* = 16.3, 10.7, 5.7 Hz, 1H), 4.98 (dd, *J* = 10.0, 2.5 Hz, 1H), 4.85 (dd, *J* = 17.1, 2.7 Hz, 1H), 3.78 (s, 3H), 3.40 – 3.27 (m, 2H), 2.28 (s, 6H).

In accordance with previously reported spectra[16]

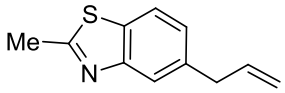


5-allylbenzo[d][1,3]dioxole, **3i**

Column chromatography (SiO_2, eluting on a gradient from pentane to 9:1 pentane/diethyl ether) afforded the desired product as a pale yellow oil (17.4 mg, 86%).

^{1}H NMR (500 MHz, $CDCl_3$) δ 6.75 (d, *J* = 7.9 Hz, 1H), 6.69 (d, *J* = 1.8 Hz, 1H), 6.64 (dd, *J* = 7.8, 1.8 Hz, 1H), 5.96-5.86 (m, 3H), 5.10 – 5.02 (m, 2H), 3.37 – 3.24 (m, 2H).

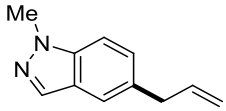
In accordance with previously reported spectra[17]



5-allyl-2-methylbenzo[d]thiazole, **3j**

Column chromatography (SiO_2, eluting with 95:5 pentane/diethyl ether) afforded the desired product as a colorless semisolid (12.2 mg, 53%).

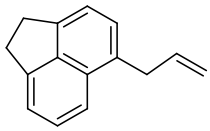
^{1}H NMR (600 MHz, $CDCl_3$) δ 7.84 (d, *J* = 8.3 Hz, 1H), 7.61 (s, 1H), 7.25 (d, *J* = 2.2 Hz, 1H), 6.11 – 5.76 (m, 1H), 5.10 (d, *J* = 5.6 Hz, 1H), 5.08 (s, 1H), 3.48 (d, *J* = 6.6 Hz, 2H), 2.80 (d, *J* = 1.9 Hz, 3H).
^{13}C NMR (151 MHz, $CDCl_3$) δ 166.40, 152.10, 137.31, 137.03, 136.07, 127.10, 122.22, 121.03, 116.32, 40.22, 20.23.
HRMS (EI) m/z: calculated for $[C_{11}H_{11}N_1S_1]^+$ 189.0612, found 189.0614.



5-allyl-1-methyl-1H-indazole, **3k**

Column chromatography (SiO_2, eluting with 9:1 pentane/diethyl ether) afforded the desired product as a pale yellow solid (10.9 mg, 52%).

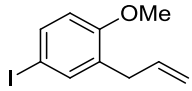
^{1}H NMR (600 MHz, $CDCl_3$) δ 7.91 (s, 1H), 7.51 (s, 1H), 7.33 (d, *J* = 8.6 Hz, 1H), 7.28 – 7.18 (m, 1H), 6.02 (ddt, *J* = 16.8, 10.1, 6.6 Hz, 1H), 5.15 – 5.00 (m, 2H), 4.06 (s, 3H), 3.50 (d, *J* = 6.7 Hz, 2H).
^{13}C NMR (151 MHz, $CDCl_3$) δ 139.08, 138.02, 132.42, 132.28, 127.91, 124.50, 120.08, 115.79, 108.94, 40.17, 35.69.
HRMS (ESI) m/z: calculated for $[C_{11}H_{12}N_2 + H]^+$ 173.1073, found 173.1073.



5-allyl-1,2-dihydroacenaphthylene, **3l**

Column chromatography (SiO_2, eluting with pentane) afforded the desired product as a pale yellow solid (11.8 mg, 50%).

^{1}H NMR (600 MHz, $CDCl_3$) δ 7.69 (d, *J* = 8.3 Hz, 1H), 7.46 (dd, *J* = 8.3, 6.9 Hz, 1H), 7.30 – 7.26 (m, 2H), 7.22 (d, *J* = 7.0 Hz, 1H), 6.09 (ddt, *J* = 16.7, 10.1, 6.4 Hz, 1H), 5.19 – 4.92 (m, 2H), 3.77 (d, *J* = 6.4 Hz, 2H), 3.46 – 3.25 (m, 5H).
^{13}C NMR (151 MHz, $CDCl_3$) δ 146.56, 144.64, 139.71, 137.48, 131.99, 130.62, 127.79, 127.70, 119.58, 119.23, 119.21, 115.85, 36.54, 30.73, 30.02.
HRMS (EI) m/z: calculated for $[C_{15}H_{14}]^+$ 194.1096, found 194.1097.

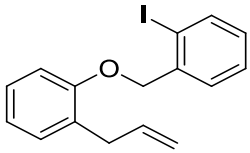


2-allyl-4-iodo-1-methoxybenzene, **3m**

Preparative TLC (SiO_2, 3x elution with pentane) afforded the desired product as a colorless solid (17.2 mg, 51%).

^{1}H NMR (500 MHz, $CDCl_3$) δ 7.47 (dd, *J* = 8.6, 2.3 Hz, 1H), 7.41 (d, *J* = 2.4 Hz, 1H), 6.61 (d, *J* = 8.6 Hz, 1H), 5.93 (ddt, *J* = 15.8, 10.5, 6.8 Hz, 1H), 5.07 (t, *J* = 1.5 Hz, 1H), 5.04 (dt, *J* = 6.0, 1.7 Hz, 1H), 3.80 (d, *J* = 1.4 Hz, 3H), 3.31 (d, *J* = 6.7 Hz, 2H).

In accordance with previously reported spectra[18]

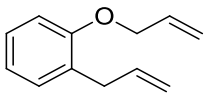


1-allyl-2-((2-iodobenzyl)oxy)benzene, **3n**

Column chromatography (SiO_2, eluting with pentane) afforded the desired product as a colorless oil (33.1 mg, 94%).

The crude reaction mixture was also analyzed by GC-MS for the presence of de-iodinated or cyclized products, with no traces found.

^{1}H NMR (600 MHz, $CDCl_3$) δ 7.88 (d, *J* = 7.8 Hz, 1H), 7.55 (d, *J* = 7.7 Hz, 1H), 7.39 (t, *J* = 7.5 Hz, 1H), 7.21 (d, *J* = 7.5 Hz, 2H), 7.04 (t, *J* = 7.6 Hz, 1H), 6.96 (t, *J* = 7.4 Hz, 1H), 6.91 (d, *J* = 8.1 Hz, 1H), 6.06 (ddt, *J* = 16.6, 9.5, 6.7 Hz, 1H), 5.15 – 5.00 (m, 4H), 3.51 (d, *J* = 6.6 Hz, 2H).
^{13}C NMR (151 MHz, $CDCl_3$) δ 156.04, 139.55, 139.26, 137.05, 130.10, 129.44, 129.09, 128.49, 128.43, 127.53, 121.22, 115.72, 111.91, 96.95, 74.04, 34.67.
HRMS (EI) m/z: calculated for $[C_{16}H_{15}O_1I_1]^+$ 350.0168, found 350.0169.



1-allyl-2-(allyloxy)benzene, **3o**

Column chromatography (SiO_2, eluting with pentane) afforded the desired product as a colorless oil (16.4 mg, 77%).

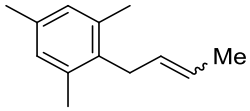
The crude reaction mixture was also analyzed by GC-MS for the presence of cyclized dihydrobenzofuran derivatives, with no traces found.

^{1}H NMR (500 MHz, $CDCl_3$) δ 7.21 – 7.14 (m, 2 H), 6.92 – 6.89 (m, 2H), 6.11-6.00 (m, 2H), 5.44 (d, *J* = 17.5 Hz, 1H), 5.26 (d, *J* = 10.5 Hz, 1H), 5.08-4.99 (m, 2H), 4.55 (d, *J* = 5 Hz, 2H), 3.39 (d, *J* = 6 Hz, 2H).

In accordance with previously reported spectra[19]

General procedure for gold catalyzed allylation with substituted allylic bromides.

1 (5.4 mg, 0.006 mmol, carefully recrystallized and finely ground), mesitylboronic acid (20.2 mg, 0.123 mmol), and Cs_2CO_3 (120 mg, .379 mmol) were weighed into a vial equipped with a stirbar. A solution of the allylic bromide (0.492 mmol) in MeCN (0.6 mL) was then added. The vial was equipped with a stirbar, capped tightly, and the reaction mixture was stirred for 18 hrs at 65°C in a heating block. Upon cooling, 100 mg of diazabicylo[2.2.2]octane (DABCO) and an additional 1 mL of MeCN was added and the mixture was stirred at room temperature for 1.5 hours. The reaction mixture was then concentrated *in vacuo*, the residue was suspended in diethyl ether and filtered through a pad of celite.



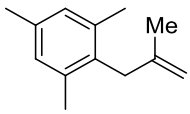
2-(but-2-en-1-yl)-1,3,5-trimethylbenzene, **5a**

Column chromatography (SiO_2, eluting with pentane) afforded the desired product as a colorless oil (17.9 mg, 82%, 2:1 *E/Z* mixture)

E isomer: ^{1}H NMR (600 MHz, $CDCl_3$) δ 6.86 (s, 2H), 5.49 (dddt, *J* = 13.5, 5.9, 4.3, 1.7 Hz, 1H), 5.40 – 5.30 (m, 1H), 3.30 (dd, *J* = 4.2, 1.8 Hz, 2H), 2.29 (s, 6H), 2.27 (s, 3H), 1.64 (dd, *J* = 6.4, 1.7 Hz, 3H).

Z isomer: ^{1}H NMR (600 MHz, $CDCl_3$) δ 6.86 (s, 2H), 5.49 (dddt, *J* = 13.5, 5.9, 4.3, 1.7 Hz, 1H), 5.27 (dtd, *J* = 10.6, 6.7, 1.9 Hz, 1H), 3.37 (d, *J* = 6.7 Hz, 2H), 2.29 (s, 3H), 2.29 (s, 6H), 1.81 – 1.76 (m, 3H).

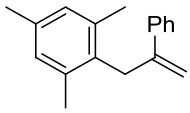
In accordance with previously reported spectra[20]



1,3,5-trimethyl-2-(2-methylallyl)benzene, **5b**

Column chromatography (SiO_2, eluting with pentane) afforded the desired product as a colorless oil (14.4 mg, 68%).

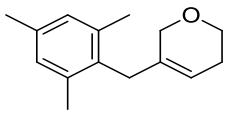
^{1}H NMR (600 MHz, $CDCl_3$) δ 6.85 (s, 2H), 4.79 – 4.61 (m, 1H), 4.24 (d, *J* = 2.4 Hz, 1H), 3.25 (s, 2H), 2.27 (s, 3H), 2.22 (s, 6H), 1.83 (s, 3H).
^{13}C NMR (151 MHz, $CDCl_3$) δ 143.31, 137.03, 135.38, 133.62, 128.73, 109.84, 37.18, 23.53, 21.01, 19.87.
HRMS (EI) m/z: calculated for $[C_{13}H_{18}]^+$ 174.1409, found 174.1409.



1,3,5-trimethyl-2-(2-phenylallyl)benzene, **5c**

Column chromatography (SiO_2, eluting with pentane) afforded the desired product as a colorless oil (16.6 mg, 57%).

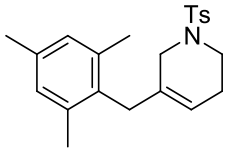
^{1}H NMR (600 MHz, $CDCl_3$) δ 7.57 (d, *J* = 7.6 Hz, 2H), 7.40 (t, *J* = 7.6 Hz, 2H), 7.33 (t, *J* = 7.4 Hz, 1H), 6.91 (s, 2H), 5.29 (s, 1H), 4.46 (d, *J* = 2.9 Hz, 1H), 3.72 (d, *J* = 3.0 Hz, 2H), 2.31 (s, 3H), 2.26 (s, 6H).
^{13}C NMR (151 MHz, $CDCl_3$) δ 145.36, 142.30, 137.20, 135.72, 133.31, 128.84, 128.47, 127.65, 125.92, 111.90, 34.54, 21.07, 19.86, 19.84.
HRMS (EI) m/z: calculated for $[C_{18}H_{20}]^+$ 236.1565, found 236.1568.



5-(2,4,6-trimethylbenzyl)-3,6-dihydro-2H-pyran, **5d**

Column chromatography (SiO_2, eluting with 9:1 pentane/diethyl ether) afforded the desired product as a colorless oil (20.2 mg, 76%).

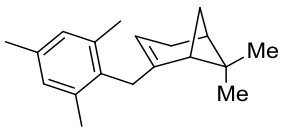
^{1}H NMR (600 MHz, $CDCl_3$) δ 6.85 (s, 2H), 5.06 (dt, *J* = 3.9, 2.0 Hz, 1H), 4.10 (q, *J* = 1.3 Hz, 2H), 3.74 (t, *J* = 5.5 Hz, 2H), 3.22 – 3.04 (m, 2H), 2.27 (s, 3H), 2.21 (s, 7H), 2.03 (dt, *J* = 4.0, 2.6 Hz, 2H).
^{13}C NMR (151 MHz, $CDCl_3$) δ 136.92, 135.42, 134.46, 131.95, 128.62, 117.62, 68.38, 64.41, 32.01, 25.07, 20.84, 19.77.
HRMS (EI) m/z: calculated for $[C_{15}H_{20}O]^+$ 216.1514, found 216.1514



1-tosyl-5-(2,4,6-trimethylbenzyl)-1,2,3,6-tetrahydropyridine, **5e**

Column chromatography (SiO_2, eluting with 9:1 pentane/diethyl ether) afforded the desired product as a colorless solid (26.4 mg, 58%).

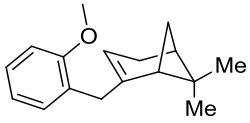
^{1}H NMR (600 MHz, $CDCl_3$) δ 7.69 (d, *J* = 8.0 Hz, 2H), 7.34 (d, *J* = 7.9 Hz, 2H), 6.83 (s, 2H), 4.91 (dt, *J* = 3.9, 2.0 Hz, 1H), 3.64 – 3.53 (m, 2H), 3.14 (s, 4H), 2.45 (s, 3H), 2.25 (s, 3H), 2.07 (dd, *J* = 5.9, 3.0 Hz, 2H).
^{13}C NMR (151 MHz, $CDCl_3$) δ 143.58, 137.01, 135.81, 133.83, 131.72, 131.69, 129.79, 128.84, 127.78, 118.51, 48.04, 42.93, 33.74, 25.03, 21.67, 20.97, 19.88..
HRMS (ESI) m/z: calculated for $[C_{22}H_{27}O_2N_1S_1 + H]^+$ 370.1835, found 370.1839.



(1R,5S)-6,6-dimethyl-2-(2,4,6-trimethylbenzyl)bicyclo[3.1.1]hept-2-ene, **5f**

Column chromatography (SiO_2, eluting with pentane) afforded the desired product as colorless film (24.5 mg, 77%).

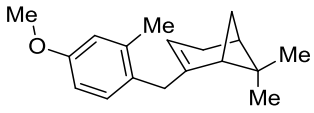
^{1}H NMR (600 MHz, $CDCl_3$) δ 6.86 (s, 2H), 4.70 – 4.49 (m, 1H), 3.28 – 3.10 (m, 2H), 2.40 (dt, *J* = 8.3, 5.5 Hz, 1H), 2.28 (s, 3H), 2.23 (s, 6H), 2.18 (dt, *J* = 17.8, 3.1 Hz, 1H), 2.11 (ddd, *J* = 14.6, 5.5, 2.8 Hz, 2H), 2.06 (td, *J* = 5.6, 1.4 Hz, 1H), 1.31 (s, 3H).
^{13}C NMR (151 MHz, $CDCl_3$) δ 145.82, 136.93, 135.17, 133.26, 128.61, 115.41, 46.89, 41.25, 38.30, 36.45, 31.86, 31.30, 26.55, 21.18, 21.03, 19.86.
HRMS (EI) m/z: calculated for $[C_{19}H_{26}]^+$ 254.2035, found 254.2035.



(1R,5S)-6,6-dimethyl-2-(2-methoxybenzyl)bicyclo[3.1.1]hept-2-ene, **5g**

Column chromatography (SiO_2, eluting with pentane) afforded the desired product as colorless film (18.1 mg, 61%).

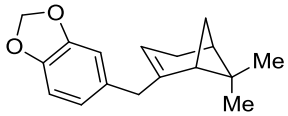
^{1}H NMR (500 MHz, $CDCl_3$) δ 7.18 (td, *J* = 7.8, 1.8 Hz, 1H), 7.10 (dd, *J* = 7.5, 1.7 Hz, 1H), 6.92 – 6.81 (m, 2H), 5.14 (dt, *J* = 3.1, 1.5 Hz, 1H), 3.80 (s, 3H), 3.29 (dddd, *J* = 17.3, 15.5, 13.6, 1.8 Hz, 2H), 2.43 – 1.94 (m, 5H), 1.22 (s, 3H), 0.76 (s, 3H).
^{13}C NMR (126 MHz, $CDCl_3$) δ 157.61, 146.83, 130.53, 128.12, 127.01, 120.18, 117.28, 110.28, 55.32, 45.83, 40.78, 37.97, 36.82, 31.80, 31.42, 26.32, 20.87.
HRMS (EI) m/z: calculated for $[C_{17}H_{22}O_1]^+$ 242.1671, found 242.1665.



(1R,5S)-6,6-dimethyl-2-(2-methyl-4-methoxybenzyl)bicyclo[3.1.1]hept-2-ene, **5h**

Column chromatography (SiO_2, eluting with pentane) afforded the desired product as colorless film (24.3 mg, 74%).

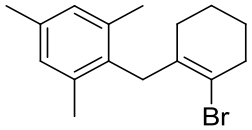
^{1}H NMR (500 MHz, $CDCl_3$) δ 7.02 (d, *J* = 8.2 Hz, 1H), 6.76 – 6.60 (m, 2H), 4.97 (dt, *J* = 3.1, 1.5 Hz, 1H), 3.81 (s, 3H), 3.21 (t, *J* = 2.1 Hz, 2H), 2.43 – 1.90 (m, 5H), 1.26 (s, 3H), 1.19 (d, *J* = 8.5 Hz, 1H), 0.81 (s, 3H).
^{13}C NMR (126 MHz, $CDCl_3$) δ 157.80, 146.91, 138.06, 130.91, 129.81, 117.01, 115.64, 110.63, 55.17, 45.88, 40.83, 40.04, 38.02, 31.72, 31.33, 26.33, 20.94, 19.70.
HRMS (EI) m/z: calculated for $[C_{18}H_{24}O_1]^+$ 256.1827, found 256.1821.



(1R,5S)-6,6-dimethyl-2-(3,4-methylenedioxybenzyl)bicyclo[3.1.1]hept-2-ene, **5i**

Column chromatography (SiO_2, eluting with pentane) afforded the desired product as colorless film (18.6 mg, 59%).

^{1}H NMR (500 MHz, $CDCl_3$) δ 6.71 (d, *J* = 7.9 Hz, 1H), 6.65 (d, *J* = 1.7 Hz, 1H), 6.60 (dd, *J* = 7.9, 1.7 Hz, 1H), 5.92 (s, 2H), 5.23 (dt, *J* = 3.0, 1.5 Hz, 1H), 3.26 – 3.08 (m, 2H), 2.36 – 2.15 (m, 4H), 2.06 (dtd, *J* = 5.9, 3.0, 1.3 Hz, 1H), 1.96 (td, *J* = 5.6, 1.5 Hz, 1H), 1.20 (s, 3H), 1.13 (d, *J* = 8.5 Hz, 1H), 0.76 (s, 3H).
^{13}C NMR (126 MHz, $CDCl_3$) δ 147.42, 147.36, 145.62, 133.41, 121.92, 117.65, 109.59, 107.86, 100.71, 45.33, 43.18, 40.66, 37.90, 31.85, 31.36, 26.23, 21.04.
HRMS (EI) m/z: calculated for $[C_{17}H_{20}O_2]^+$ 256.1463, found 256.1467.

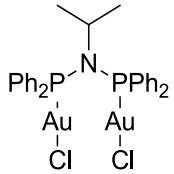


2-((2-bromocyclohex-1-en-1-yl)methyl)-1,3,5-trimethylbenzene, **5j**

Column chromatography (SiO_2, eluting with pentane) afforded the desired product as a colorless oil (21.2 mg, 59%).

^{1}H NMR (600 MHz, $CDCl_3$) δ 6.83 (s, 2H), 3.63 (s, 2H), 2.56 (tt, *J* = 4.1, 2.1 Hz, 2H), 2.26 (s, 3H), 2.25 (s, 6H), 1.74 – 1.59 (m, 4H), 1.57 – 1.44 (m, 2H).
^{13}C NMR (151 MHz, $CDCl_3$) δ 137.33, 135.57, 133.70, 132.94, 128.91, 120.02, 37.09, 36.68, 29.27, 24.99, 22.73, 20.98, 20.55.
HRMS (EI) m/z: calculated for $[C_{16}H_{21}Br]^+$ 292.0827; 294.0806, found 292.0826; 294.0804.

Preparation of gold catalysts.

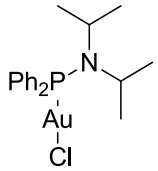


Dichloro(N-(diphenylphosphino)-N-isopropyl-1,1-diphenylphosphinamine) digold(I) (**1**)

To freshly prepared chloro(dimethylsulfide) gold(I) (310 mg, 1.45 mmol) and bis(diphenylphosphino)isopropylamine (309 mg, 0.725 mmol) under an atmosphere of N_2 was added dichloromethane (24 mL) with vigorous stirring. The reaction mixture was stirred for 20 minutes, filtered through a fine fritted funnel, and concentrated *in vacuo*. The residue was washed sequentially with pentane and ether to yield a colorless solid which was dried *in vacuo*. Recrystallization from (DCM + pentane) / Et_2O by the layering method yields colorless crystals (473 mg, 73% yield). X-ray quality crystals grown from THF / Et_2O by vapor diffusion.

^{1}H NMR (400 MHz, CD_2Cl_2) δ 7.81-7.87 (m, 8H), 7.63-7.67 (m, 4H), 7.54-7.58 (m, 8H), 3.96-4.08 (m, 1H), 1.10 (d, *J* = 5.6, 6H)
^{13}C NMR (101 MHz, CD_2Cl_2) δ 133.8-134.0 (m) 132.9, 129.9, 129.2-129.3 (m), 54.8, 24.2
^{31}P NMR (162 MHz, CD_2Cl_2) δ 75.3 (bs)
^{31}P NMR (162 MHz, CD_3CN) δ 79.2 (s)
HRMS (ESI) m/z: calculated for $[C_{27}H_{27}Au_2Cl_2NP_2 + Na]^+$ 914.0219, found 914.0224
EA: Calculated : C, 36.34; H, 3.05; N, 1.57; Found: C, 36.20; H, 3.08; N, 1.54
IR: 2957, 1572, 1432, 1113, 1099, 978, 948, 881, 850, 760, 747, 738, 713, 694, 684, 601, 544, 535, 502, 483, 472, 438

In accordance with previously reported spectra.[21]

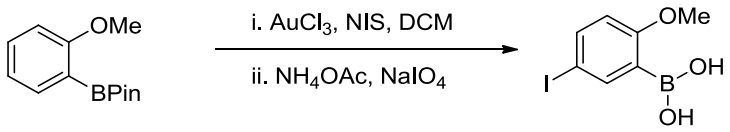


Chloro(N,N-diisopropyl-1,1-diphenylphosphinamine) gold(I) (**2**)

To chloro(dimethylsulfide) gold(I) (60 mg, 0.20 mmol) and (diphenylphosphino)diisopropylamine (60 mg, 0.21 mmol) under an atmosphere of N_2 was added dichloromethane (4.5 mL) with vigorous stirring. The reaction mixture was stirred for 20 minutes and concentrated *in vacuo*. The residue was washed sequentially with pentane, ether, and methanol to yield a colorless solid which was dried *in vacuo*. Recrystallized from DCM/Pentane by the layering method (81 mg, 80%).

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.67-7.73 (m, 4H) 7.45-7.52 (m, 6H), 3.56-3.63 (m, 2H), 1.33 (d, 12H, *J* = 6.4 Hz)
^{13}C NMR (100.6 MHz, CD_2Cl_2) δ 132.7 (d, *J* = 14.4 Hz), 132.3 (d, *J* = 69.4Hz), 131.4, 128.7 (d, *J* = 11.9 Hz), 48.0 (d, *J* = 3.0 Hz), 23.2 (d, *J* = 3.0 Hz)
^{31}P NMR (162 MHz, $CDCl_3$) δ 51.07 (s)
HRMS: (EI+) m/z: calculated for $[C_{18}H_{24}AuClNP]^+$: 517.1000, found 517.1006
EA: Calculated : C, 41.75; H, 4.67; N, 2.17; Found: C, 41.43; H, 4.35; N, 2.51
IR: 2959, 1433, 1369, 1172, 1149, 1112, 1100, 1006, 980, 749, 695, 637, 561, 543, 524, 493, 462, 455

Preparation of new arylboronic acids.

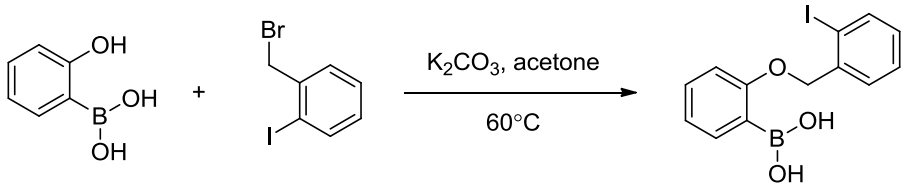


(5-iodo-2-methoxyphenyl)boronic acid, **S1**

Prepared according to a modification of a reported literature procedure:[22]

2-methoxyphenyboronic acid pinacol ester (585 mg, 2.5 mmol), $AuCl_3$ (7.6 mg, 0.025 mmol), and N-iodosuccinimide (563 mg, 2.5 mmol) were dissolved in DCE (5 mL) and the mixture was stirred overnight at room temperature. The mixture was concentrated, suspended in 2:1 Hexanes/diethyl ether, and filtered through a short SiO_2 plug. This crude material was dissolved in acetone (60 mL) and a solution of ammonium acetate (50 mL of 0.01 M aqueous solution) followed by sodium periodate (1.5 g, 7 mmol) was added. The reaction mixture was monitored by TLC for complete conversion of the boronic ester to the acid, and upon completion was quenched with 1M HCl. The aqueous layer was extracted 2x with ethyl acetate, and the combined organic layer was dried over $MgSO_4$, filtered, and concentrated. Recrystallization from ethyl acetate afforded the desired product as a pale tan solid (two crops totaling 152 mg, 20%).

^{1}H NMR (600 MHz, CD_3CN) δ 7.94 (s, 1H), 7.70 (dd, *J* = 8.9, 2.3 Hz, 2H), 6.81 (d, *J* = 8.7 Hz, 2H), 3.82 (s, 5H).
^{13}C NMR (151 MHz, CD_3CN) δ 164.81, 144.99, 141.48, 113.80, 83.71, 56.01. (Ipso C-B carbon not detected due to quadrupole broadening)
HRMS (ESI) m/z: calculated for $[C_7H_7O_3{}^{11}B_1{}^{127}I_1]^-$ 276.9538, found 276.9537

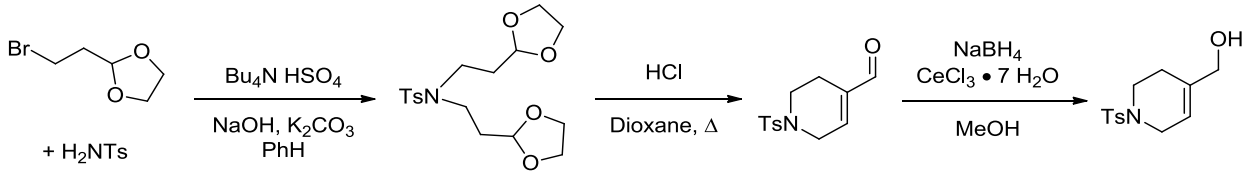


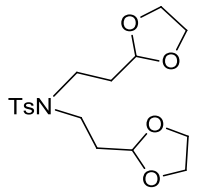
(2-((2-iodobenzyl)oxy)phenyl)boronic acid, **7**

2-hydroxyphenylboronic acid (690 mg, 5 mmol), 2-iodobenzyl bromide (1.78 g, 6 mmol), potassium carbonate (2.0 g, 15 mmol) and acetone (50 mL) were combined in a roundbottom flask equipped with a stirbar and reflux condenser. The solution was heated to reflux overnight. Upon cooling, water was added, and the mixture was extracted 3x with ethyl acetate. The combined organic layers were dried over $MgSO_4$, filtered, and concentrated. The solid was washed with hexanes, and recrystallized by slow evaporation from wet MeCN to afford the desired product as a colorless solid (two crops totaling 246 mg, 14%).

^{1}H NMR (600 MHz, CD_3CN) δ 7.95 (dd, *J* = 8.1, 1.4 Hz, 1H), 7.75 (dd, *J* = 7.2, 2.0 Hz, 1H), 7.50 (dd, *J* = 7.7, 1.8 Hz, 1H), 7.43 (tdd, *J* = 7.7, 4.4, 1.6 Hz, 2H), 7.11 (td, *J* = 7.7, 1.7 Hz, 1H), 7.02 (t, *J* = 7.9 Hz, 2H), 5.17 (s, 2H).
^{13}C NMR (151 MHz, CD_3CN) δ 163.96, 140.40, 139.44, 137.12, 133.24, 131.04, 130.60, 129.47, 121.97, 112.21, 98.64, 74.63.
HRMS (EI) m/z: calculated for $[C_{13}H_{12}B_1O_3I_1]^+$ 353.9924, found 353.9916

Preparation of N-Ts-tetrahydropyridine allylic alcohol

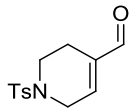




N,N-bis(2-(1,3-dioxolan-2-yl)ethyl)-4-methylbenzenesulfonamide, **S2**

Tosylamine (4.3 g, 25 mmol), 2-(bromoethyl)-1,3-dioxolane (12 mL, 100 mmol), tetrabutylammonium bisulfate (850 mg, 2.5 mmol), potassium carbonate (3.5 g, 25 mmol), and sodium hydroxide (3.5g, 88 mmol) were combined in benzene (25 mL). The mixture was stirred vigorously overnight at which time TLC showed consumption of the starting material. The mixture was diluted with ethyl acetate and washed with H_2O three times. The organic layer was dried over $MgSO_4$, filtered, and concentrated. Column chromatography (SiO_2, eluting on a gradient from 9:1 Hexanes/ethyl acetate to 1:1 hexanes/ethyl acetate) afforded the desired product as a pale yellow oil (7.1 g, 76%).

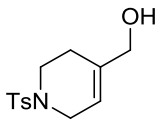
^{1}H NMR (600 MHz, $CDCl_3$) δ 7.67 (d, *J* = 8.0 Hz, 2H), 7.26 (d, *J* = 8.0 Hz, 2H), 4.83 (t, *J* = 4.6 Hz, 2H), 3.89 (d, *J* = 7.0 Hz, 4H), 3.79 (d, *J* = 3.1 Hz, 4H), 3.28 – 3.08 (m, 4H), 2.38 (s, 3H), 1.95 – 1.79 (m, 4H).
^{13}C NMR (151 MHz, $CDCl_3$) δ 143.21, 136.55, 129.70, 127.21, 102.22, 64.95, 53.55, 43.53, 32.87, 21.53.
HRMS (ESI) m/z: calculated for $[C_{17}H_{25}O_6N_1S_1 + H]^+$ 372.1475, found 372.1480.



1-tosyl-1,2,3,6-tetrahydropyridine-4-carbaldehyde, **S3**

S2 (5 g, 13.4 mmol) was dissolved in 4 mL of dioxane. 4 mL of 5 M HCl was added, and the solution was heated to reflux for 20 minutes. TLC showed consumption of product, and upon cooling the mixture was neutralized with 1M aqueous NaOH and extracted with ethyl acetate. The organic layer was washed with brine, fried over $MgSO_4$, filt. and concentrated to give a white solid (3.6 g, quantitative). Carried on without further purification.

^{1}H NMR (600 MHz, $CDCl_3$) δ 9.38 (d, *J* = 2.1 Hz, 1H), 7.67 (dd, *J* = 8.3, 2.2 Hz, 2H), 7.32 (d, *J* = 7.8 Hz, 2H), 6.84 (dd, *J* = 3.7, 2.0 Hz, 1H), 3.80 – 3.64 (m, 2H), 3.27 – 3.14 (m, 2H), 2.57 – 2.47 (m, 2H), 2.41 (d, *J* = 1.9 Hz, 3H).
^{13}C NMR (151 MHz, $CDCl_3$) δ 191.23, 147.15, 144.03, 137.83, 132.94, 129.91, 129.90, 127.79, 42.53, 42.38, 26.61, 21.62.
HRMS (ESI) m/z: calculated for $[C_{13}H_{15}O_3N_1S_1 + Na]^+$ 288.0665, found 288.0667.



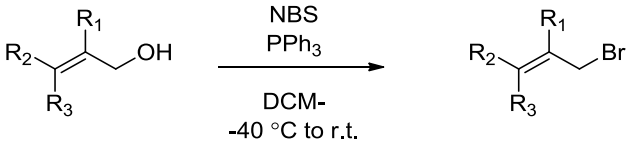
(1-tosyl-1,2,3,6-tetrahydropyridin-4-yl)methanol, **S4**

To **S3** (1.5 g, 5.6 mmol) in methanol (112 mL) was added $CeCl_3 \cdot 7\ H_2O$ (6.3 g, 17 mmol). After stirring for 10 min, $NaBH_4$ (3.2 g, 85 mmol) was added carefully in 5 portions. After stirring 1.5 hours, the reaction mixture was concentrated, and the residue was partitioned between DCM and H_2O. The layers were separated and the aqueous layer was extracted 2x with DCM. The combined organic layers were dried over $MgSO_4$, filtered, and concentrated. Column Chromatography (SiO_2, eluting with 1:1 Hexanes/Ethyl Acetate) afforded the desired product as a colorless solid (1.04 g, 70%).

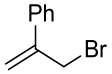
^{1}H NMR (600 MHz, $CDCl_3$) δ 7.68 (d, *J* = 8.2 Hz, 2H), 7.32 (d, *J* = 8.0 Hz, 2H), 5.74 (dt, *J* = 3.6, 2.0 Hz, 1H), 4.12 – 3.96 (m, 2H), 3.59 (d, *J* = 2.3 Hz, 2H), 3.14 (t, *J* = 5.7 Hz, 3H), 2.43 (s, 4H), 2.30 – 2.19 (m, 2H).

In accordance with previously reported spectra[23]

General procedure for the preparation of substituted allylic bromides



N-bromosuccinimide (1.1 equivalents) was dissolved in of DCM (0.15 M) under an atmosphere of N_2 and cooled to -40 ^oC in a dry ice/acetonitrile bath. Triphenyl phosphine (1.1 equivalents) was added in one portion and the mixture was stirred for 40 min at -40^oC. A solution of allylic alcohol (1 equivalent) in DCM (0.3 M) was added, and the solution was allowed to warm to room temperature overnight. The solution was poured over pentane, filtered, and concentrated *in vacuo*. The crude residue was purified by chromatography on a short plug of silica, eluting rapidly to minimize product decomposition.

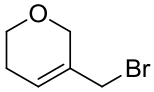


(3-bromoprop-1-en-2-yl)benzene, **S5**

3 mmol scale. Eluted with pentane to afford the desired product as a pale yellow oil (260 mg, 44%).

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.58 – 7.46 (m, 2H), 7.43 – 7.31 (m, 3H), 5.54 (dd, *J* = 27.1, 1.8 Hz, 2H), 4.40 (d, *J* = 1.8 Hz, 2H).

In accordance with previously reported spectra[24]

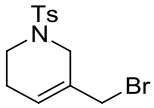


5-(bromomethyl)-3,6-dihydro-2H-pyran, **S6**

8.7 mmol scale. Eluted with pentane to afford the desired product as a pale yellow oil (954 mg, 61%).

^{1}H NMR (400 MHz, $CDCl_3$) δ 6.21 – 5.82 (m, 1H), 4.27 (d, *J* = 2.3 Hz, 2H), 3.93 (d, *J* = 1.2 Hz, 3H), 3.80 (t, *J* = 5.5 Hz, 3H), 2.22 (ddt, *J* = 5.5, 2.8, 1.4 Hz, 2H).

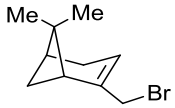
In accordance with previously reported spectra[25]



5-(bromomethyl)-1-tosyl-1,2,3,6-tetrahydropyridine, **S7**

2.62 mmol scale. Eluted with 1:1 Hexanes/Ethyl Acetate to afford the desired product as a pale yellow solid (706 mg, 82%).

^{1}H NMR (600 MHz, $CDCl_3$) δ 7.68 (d, *J* = 7.9 Hz, 2H), 7.32 (d, *J* = 8.0 Hz, 2H), 5.90 (d, *J* = 2.1 Hz, 1H), 3.89 (s, 2H), 3.69 (d, *J* = 2.3 Hz, 2H), 3.14 (t, *J* = 5.8 Hz, 2H), 2.42 (s, 3H), 2.27 – 2.11 (m, 2H).
^{13}C NMR (151 MHz, $CDCl_3$) δ 143.81, 133.37, 131.12, 129.83, 127.73, 127.72, 125.93, 45.88, 42.23, 34.60, 25.29, 21.63.
HRMS (ESI) m/z: calculated for $[C_{13}H_{16}O_2N_1S_1Br_1 + Na]^+$ 351.9977, found 351.9982.

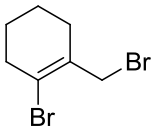


(1R,5S)-2-(bromomethyl)-6,6-dimethylbicyclo[3.1.1]hept-2-ene, **S8**

8.5 mmol scale. Eluted with pentane to afford the desired product as a colorless oil (1.14 g, 62%).

^{1}H NMR (400 MHz, $CDCl_3$) δ 5.68 (dd, *J* = 3.2, 1.7 Hz, 1H), 3.96 (dq, *J* = 2.3, 1.1 Hz, 2H), 2.45 (dt, *J* = 8.8, 5.6 Hz, 1H), 2.37 – 2.19 (m, 4H), 2.17 – 2.05 (m, 1H), 1.58 (s, 2H), 1.32 (s, 3H), 1.18 (d, *J* = 8.7 Hz, 1H), 0.83 (s, 3H).

In accordance with previously reported spectra[26]



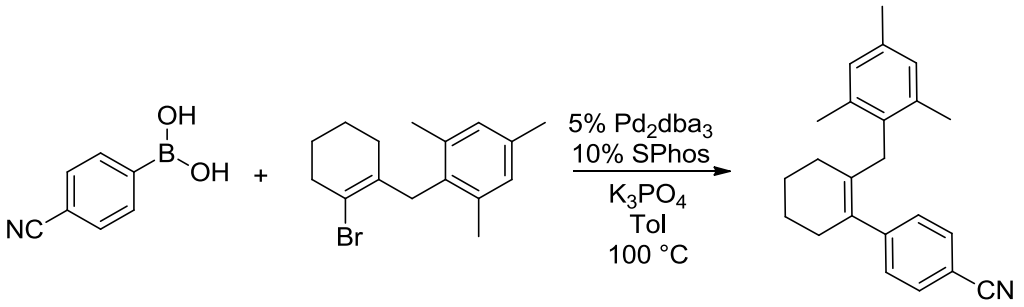
1-bromo-2-(bromomethyl)cyclohex-1-ene, **S9**

12.5 mmol scale. Eluted on a gradient from hexanes to 9:1 hexanes/diethyl ether to afford the desired product as a colorless oil (2.13 g, 67%).

^{1}H NMR (400 MHz, $CDCl_3$) δ 4.11 (s, 2H), 2.52 (s, 2H), 2.29 (s, 2H), 1.71 (s, 4H).

In accordance with previously reported spectra[27]

Palladium catalyzed elaboration of 5g and comparison experiments

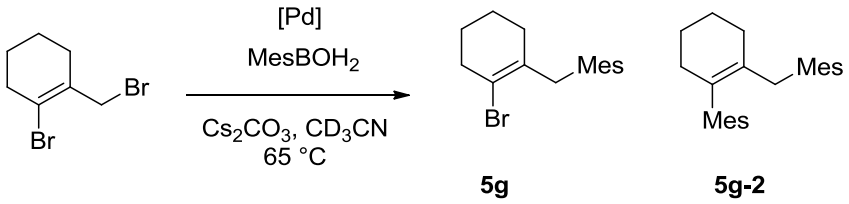


6'-(2,4,6-trimethylbenzyl)-2',3',4',5'-tetrahydro-[1,1'-biphenyl]-4-carbonitrile, **6**

Prepared by a slight modification of a previously reported procedure:[28]

Tris(dibenzylideneacetone)dipalladium(0) (2.7 mg, 0.003 mmol), Sphos (2.5 mg, 0.006 mmol), tribasic potassium phosphate (37.1 mg, 0.175 mmol), and 4-cyanophenylboronic acid (17.2 mg, 0.117 mmol) were combined in a vial equipped with a stirbar. A solution of **5g** (17.1 mg, 0.058 mmol), in 0.4 mL of dry toluene was added, and the solution was blanketed with argon and sealed tightly with a screw cap. The solution was heated to 100 ^{o}C overnight. Upon cooling, the mixture was dry loaded onto silica, and purified by column chromatography (eluting on a gradient from pentane to 10% diethyl ether in pentane) to afford the desired product as a pale yellow solid. (8.3 mg, 46% yield).

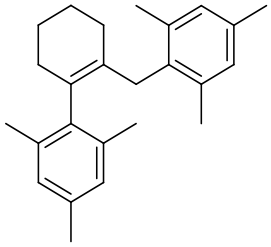
^{1}H NMR (600 MHz, $CDCl_3$) δ 7.64 (d, *J* = 8.2 Hz, 2H), 7.33 (d, *J* = 8.2 Hz, 2H), 6.76 (s, 2H), 3.28 (s, 2H), 2.25 (dt, *J* = 6.4, 3.2 Hz, 2H), 2.22 (s, 3H), 2.10 (s, 6H), 1.73 (dd, *J* = 7.6, 4.9 Hz, 2H), 1.70 – 1.64 (m, 2H), 1.58 (dd, *J* = 5.7, 2.6 Hz, 2H).
^{13}C NMR (151 MHz, $CDCl_3$) δ 149.53, 136.93, 135.34, 133.45, 132.98, 132.15, 132.14, 129.42, 128.91, 119.29, 110.04, 34.03, 32.27, 27.47, 23.20, 22.95, 20.92, 20.62.
HRMS (EI) m/z: calculated for $[C_{23}H_{25}N]^{+}$ 315.1987, found 315.1995.



Following the general procedure for substituted allylic bromides using palladium catalysts in place of **1** gave the following results (NMR yields vs. trimethoxybenzene as an internal standard):

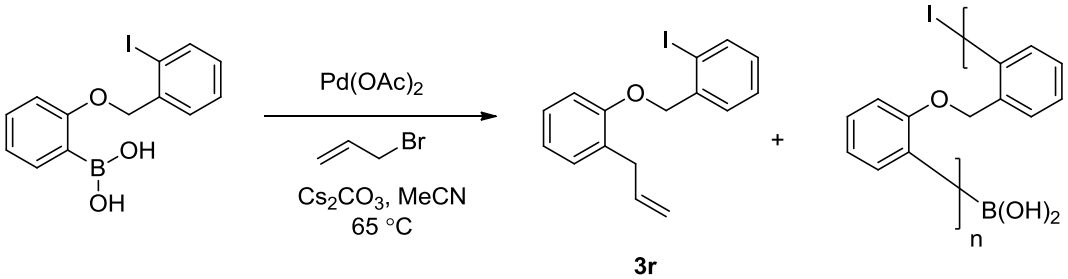
[Pd] (5 mol%)	Yield **5g**	Yield **5g-2**
$Pd(OAc)_2$	7%	1%
$Pd_2(dba)_3$	37%	5%
$Pd_2(dba)_3$ + SPhos	25%	9%
PNP • $PdCl_2$[29]	7%	1%

No **5g-2** was detected when **1** was used as a catalyst.



2',4',6'-trimethyl-6-(2,4,6-trimethylbenzyl)-2,3,4,5-tetrahydro-1,1'-biphenyl, **5g-2**

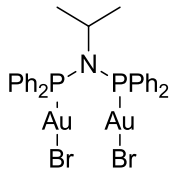
^{1}H NMR (600 MHz, $CDCl_3$) δ 6.91 (s, 2H), 6.77 (s, 2H), 3.05 (t, *J* = 2.3 Hz, 2H), 2.28 (s, 3H), 2.25 (s, 6H), 2.23 (s, 3H), 2.16 (s, 6H), 2.07 (q, *J* = 4.1 Hz, 2H), 1.71 – 1.63 (m, 2H), 1.58 (t, *J* = 2.3 Hz, 4H).
^{13}C NMR (151 MHz, $CDCl_3$) δ 139.36, 136.87, 135.46, 134.91, 134.80, 133.66, 132.17, 130.25, 128.35, 128.31, 32.72, 30.82, 27.29, 23.36, 23.07, 20.98, 20.82, 20.51, 19.17.
HRMS (EI) m/z: calculated for $[C_{25}H_{32}]^+$ 332.2504, found 332.2512



3r

Following the general procedure for allyl bromide, substituting 5 mol% of $Pd(OAc)_2$ in place of **1** gave 35% isolated yield of **3r** with substantial oligomeric material detected by crude ^{1}HNMR (not isolated). Addition of 10 mol% PPh_3 improved the yield of allylated product somewhat, yielding **3r** in 61% yield.

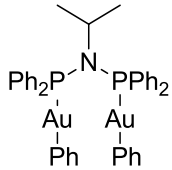
Stoichiometric Reactivity of 1 and Control Experiments



Dibromo(N-(diphenylphosphino)-N-isopropyl-1,1-diphenylphosphinamine) digold(I) (**8**)

Allyl Bromide (100 μL) was added to a solution of **1** (27.8 mg, 0.03 mmol) in MeCN (1.5 mL). The resulting mixture was stirred at 65°C overnight. The reaction mixture was concentrated and washed sequentially with pentane and ether to yield a colorless solid. Recrystallized from a saturated DCM/Pentane solution layered with diethyl ether (26 mg, 88%). X-ray quality crystals grown by slow evaporation of saturated DCM/pentane solution.

^{1}H NMR (400 MHz, CD_2Cl_2) δ 7.85 (q, *J* = 7.2 Hz, 8H), 7.66 (t, *J* = 7.4 Hz, 4H), 7.61 – 7.50 (m, 8H), 4.01 (dddd, *J* = 22.5, 16.0, 13.6, 6.9 Hz, 1H), 1.09 (d, *J* = 6.8 Hz, 6H).
^{13}C NMR (101 MHz, CD_2Cl_2) δ 133.97, 133.82, 132.91, 129.35, 129.29, 129.23, 55.01, 24.15.
^{31}P NMR (162 MHz, CD_2Cl_2) δ 77.3 (bs)
^{31}P NMR (162 MHz, CD_3CN) δ 80.3 (s)
EA: Calculated: C, 33.05; H, 2.77; N, 1.43; Found: C, 33.24; H, 3.09; N: 1.39

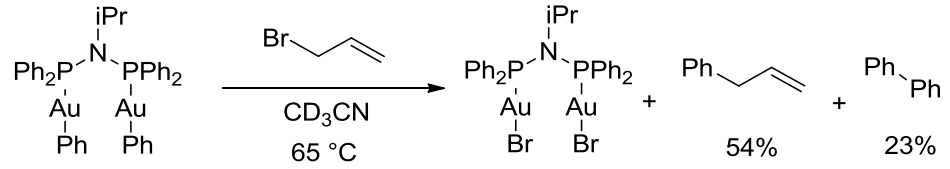


Diphenyl(N-(diphenylphosphino)-N-isopropyl-1,1-diphenylphosphinamine) digold(I) (**9**)

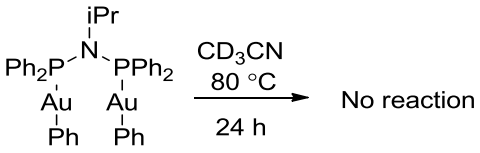
Phenylboronic acid (11 mg, 0.086 mmol), cesium carbonate (30 mg, 0.083 mmol), and **1** (22 mg, 0.024 mmol) were combined in a vial equipped with a stirbar. MeCN (0.6 mL) was added and the solution was heated to 65°C for 2 hours. The mixture was concentrated, and the residue was taken up in benzene and filtered through a celite plug. Upon concentration, the solid was washed with pentane and minimal methanol and dried *in vacuo* to give the desired product as a pale tan solid. (23.7 mg, 99%).

X-ray quality crystals were grown by vapor diffusion of hexanes into toluene.

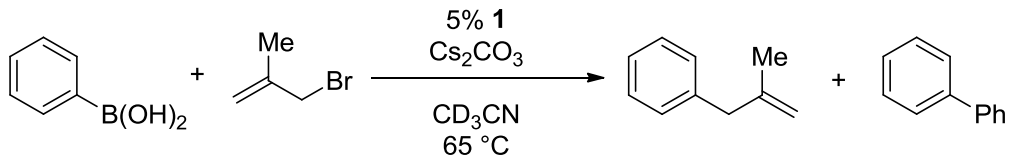
^{1}H NMR (400 MHz, CD_2Cl_2) δ 7.93-7.97 (m, 8H), 7.52-7.61 (m, 12H), 7.11 (bs, 4H), 7.02 (t, *J* = 7.6 Hz, 4H), 6.88 (t, *J* = 7.2 Hz, 2H), 3.95-4.06 (m, 1H), 1.17 (d, *J* = 6.8 Hz, 6H)
^{13}C NMR (101 MHz, CD_2Cl_2) δ 139.8, 133.8 (d, *J* = 15.6 Hz), 132.5 (d, *J* = 51 Hz) 131.7, 128.8 (d, *J* = 10.7 Hz), 127.4, 126.8 (d, *J* = 6.4 Hz), 125.0, 55.2, 24.4 [Gold aryl ipso carbon not found.]
^{31}P NMR (162 MHz, CD_2Cl_2) δ 93.3 (bs)
EA: Calculated: C, 48.01; H, 3.82; N, 1.44; Found: C, 48.36; H, 3.54; N, 1.56



To a solution of **9** (6 mg, 0.006 mmol) in CD_3CN was added allyl bromide (42 μL, 0.492 mmol) and the reaction mixture was heated to 65°C for 1.5 hours. Upon cooling, $PhCO_2Et$ (2 uL, 0.015 mmol) was added and the reaction mixture was analyzed by GC (to determine yields of allylbenzene and biphenyl) and ^{31}PNMR (showing complete consumtion of **9** and the presence of **8**).



A solution of **9** (5 mg, 0.005 mmol) in CD_3CN (0.2 mL) was heated in a vial at 80°C for 24 hrs. Upon cooling, $PhCO_2Et$ (5 uL, 0.035 mmol) was added and the reaction mixture was analyzed by GC, with no Ph-Ph detected. ^{31}PNMR indicated the persistence of **9**.

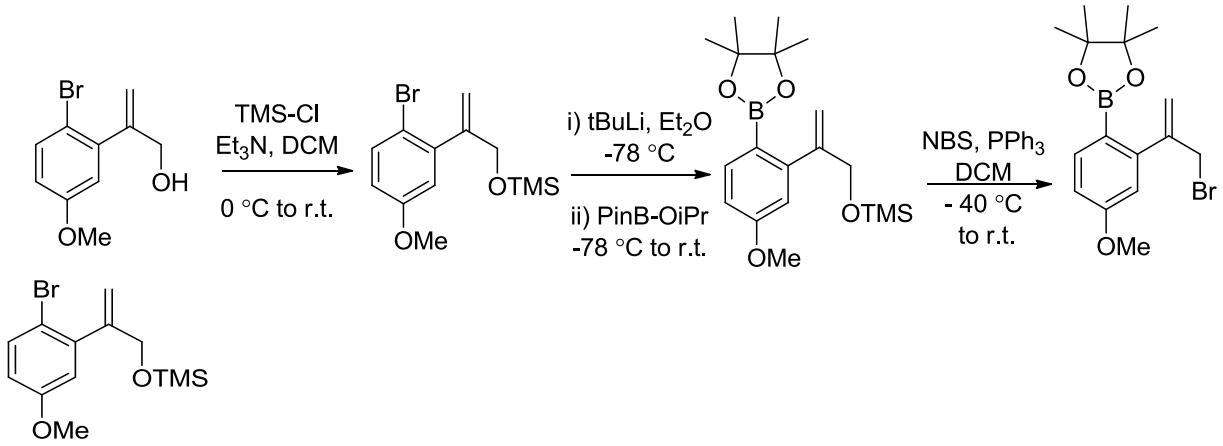


Standard Reaction Conditions	37%	23%
+ 200 mol% $Me_2C=CMe_2$	33%	21%

Following the general procedure for gold catalyzed allylation with substituted allylic bromides, substituting phenylboronic acid for mesityl boronic acid, the above results were obtained. In the latter case, 0.24 mmol (24 μL) of tetramethylethylene was added. The product ratios were determined by ^{1}HNMR vs. trimethoxybenzene as an internal standard.

\

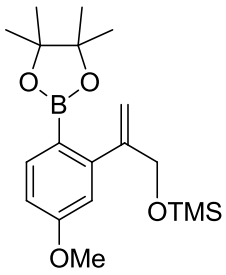
Preparation of 11



((2-(2-bromo-5-methoxyphenyl)allyl)oxy)trimethylsilane, **S10**

To a solution of 2-(2-bromo-5-methoxyphenyl)prop-2-en-1-ol[30] (681 mg, 2.8 mmol) in DCM under N_2 at 0 ^oC was added sequentially triethylamine (0.82 mL, 5.88 mmol) and chlorotrimethylsilane (0.39 mL, 3.08 mmol). The solution was stirred for 10 minutes at 0 ^oC, and then warmed to room temperature. After an additional 45 minutes, TLC showed complete consumption the starting material. The reaction mixture was concentrated directly, slurried in diethyl ether, and filtered through a fine fritted funnel. Concentration of this solution afforded the desired product as a pale yellow oil which was used without further purification. (716 mg, 81% yield)

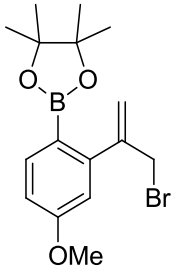
^{1}H NMR (600 MHz, $CDCl_3$) δ 7.42 (d, *J* = 8.7 Hz, 1H), 6.75 (d, *J* = 3.1 Hz, 1H), 6.71 (dd, *J* = 8.8, 3.1 Hz, 1H), 5.52 (d, *J* = 1.8 Hz, 1H), 5.09 (d, *J* = 1.7 Hz, 1H), 4.33 (t, *J* = 1.7 Hz, 2H), 3.78 (s, 3H), 0.14 (s, 9H).
^{13}C NMR (151 MHz, $CDCl_3$) δ 158.78, 148.77, 142.28, 133.33, 116.56, 114.85, 114.12, 112.88, 64.76, 55.60, -0.31.
HRMS (EI) m/z: calculated for $[C_{13}H_{19}O_2Si_1Br_1]^+$ 314.0338; 316.0317, found 314.0346; 316.0323.



((2-(5-methoxy-2-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)phenyl)allyl)oxy)trimethylsilane, **S11**

S10 (716 mg, 2.27 mmol) was dissolved in Et_2O under an atmosphere of nitrogen, and cooled to -78 ^oC. tBuLi (2.95 mL of a 1.7 M solution in pentane, 5 mmol) was added dropwise, and the solution was stirred at -78 ^oC for 1 hour. Freshly distilled 2-isopropoxy-4,4,5,5-tetramethyl-1,3,2-dioxaborolane (1.15 mL, 5.68 mmol) was added, and the solution was allowed to warm to room temperature overnight. The reaction mixture was quenched with saturated aqueous ammonium chloride, and the layers were separated. The aqueous layer was extracted with ethyl acetate, and the combined organic layers were dried over $MgSO_4$, filtered, and concentrated. Column Chromatography on silica gel (eluting on a gradient from pentane to 97:3 pentane/diethyl ether) afforded the desired product as a colorless oil. (492 mg, 55% yield).

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.72 (d, *J* = 8.3 Hz, 1H), 6.85 (dd, *J* = 8.3, 2.5 Hz, 1H), 6.79 (d, *J* = 2.5 Hz, 1H), 5.38 (d, *J* = 2.0 Hz, 1H), 5.03 (d, *J* = 1.9 Hz, 1H), 4.44 (t, *J* = 1.7 Hz, 2H), 3.85 (s, 3H), 1.34 (s, 12H), 0.19 (s, 9H).
^{13}C NMR (101 MHz, $CDCl_3$) δ 161.21, 150.64, 148.87, 137.01, 114.57, 112.18, 111.93, 83.49, 66.12, 55.21, 24.81, -0.21. [Boronic ester ipso carbon not seen due to quadrupole broadening.]
HRMS (ESI) m/z: calculated for $[C_{19}H_{31}O_4B_1Si_1 + Na]^+$ 385.1977, found 385.1981.

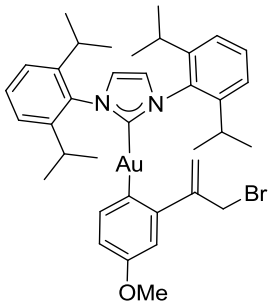


2-(2-(3-bromoprop-1-en-2-yl)-4-methoxyphenyl)-4,4,5,5-tetramethyl-1,3,2-dioxaborolane, **11**

N-bromosuccinimide (266 mg, 1.5 mmol) was dissolved in 14 mL of DCM under an atmosphere of N_2 and cooled to -40 ^{o}C in a dry ice/acetonitrile bath. Triphenylphosphine (391 mg, 1.5 mmol) was added in one portion and the mixture was stirred for 40 min at -40^{o}C. A solution of **S11** (492 mg, 1.35 mmol) in 14 mL DCM was added, and the solution was allowed to warm to room temperature overnight. The solution was poured over pentane, filtered, and concentrated *in vacuo*. The crude residue was purified by chromatography, eluting with 8:2 pentane/diethyl ether on a short plug of silica, eluting rapidly to minimize product decomposition. The desired product was isolated as a pale yellow oil which solidified upon standing. (235 mg, 67% yield).

^{1}H NMR (600 MHz, $CDCl_3$) δ 7.75 (d, *J* = 8.3 Hz, 1H), 6.85 (dd, *J* = 8.3, 2.5 Hz, 1H), 6.80 (d, *J* = 2.5 Hz, 1H), 5.48 (q, *J* = 1.1 Hz, 1H), 5.12 (d, *J* = 1.3 Hz, 1H), 4.36 (d, *J* = 1.0 Hz, 2H), 3.84 (s, 3H), 1.29 (s, 13H).
^{13}C NMR (151 MHz, $CDCl_3$) δ 161.49, 148.34, 148.23, 137.60, 118.35, 115.85, 112.42, 83.63, 55.31, 38.10, 24.90. [Ipso C-BPin not seen due to quadrupole broadening]
HRMS (EI) m/z: calculated for $[C_{16}H_{22}B_1O_3Br_1]^+$ 352.0845; 354.0825, found 352.0850; 354.0842.

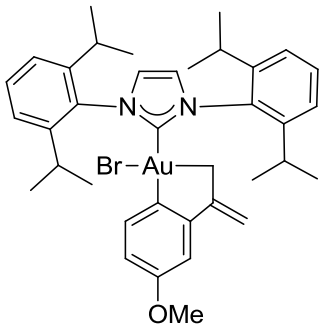
Preparation of 12-14



(1,3-bis(2,6-diisopropylphenyl)-1H-imidazol-2(3H)-ylidene)(2-(3-bromoprop-1-en-2-yl)-4-methoxyphenyl)gold(I), **12**

11 (8.7 mg, 0.024 mmol) and 1,3-bis(2,6-diisopropylphenyl)-1H-imidazol-2(3H)-ylidene gold(I) hydroxide (7.4 mg, 0.012 mmol) were dissolved in C_6D_6 (0.6 mL) and stirred at room temperature for 2 hours at which time ^{1}HNMR indicated the consumption of the gold hydroxide. The mixture was concentrated, and washed sequentially with pentane and ether to give the desired product as a colorless solid. (7.9 mg, 81%).

^{1}H NMR (600 MHz, C_6D_6) δ 7.33 (d, *J* = 8.0 Hz, 1H), 7.29 (t, *J* = 7.8 Hz, 2H), 7.13 (d, *J* = 2.7 Hz, 1H), 7.11 (d, *J* = 7.8 Hz, 4H), 6.79 (dd, *J* = 8.1, 2.7 Hz, 1H), 6.29 (s, 2H), 5.17 – 4.95 (m, 2H), 4.18 (s, 2H), 3.34 (s, 3H), 2.60 (p, *J* = 6.9 Hz, 4H), 1.43 (d, *J* = 6.9 Hz, 12H), 1.08 (d, *J* = 6.9 Hz, 12H).
^{13}C NMR (151 MHz, C_6D_6) δ 158.83, 157.94, 153.49, 150.59, 146.04, 140.93, 135.11, 130.65, 124.34, 122.47, 116.04, 114.49, 112.53, 54.56, 39.19, 29.09, 24.74, 24.01.
EA: Calculated: C, 54.75; H, 5.71; N, 3.45; Found: C, 55.12; H, 5.91; N, 3.35

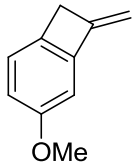


Bromo(1,3-bis(2,6-diisopropylphenyl)-1H-imidazol-2(3H)-ylidene) (1-methoxy-3-(prop-1-en-2-yl)benzene-4,3'-diyl)gold(III), **13**

12 (69 mg, 0.084 mmol) was dissolved in CD_3CN (1.5 mL) and the mixture was heated to 40 ^{o}C. Reaction progress was monitored by ^{1}HNMR for the consumption of **13**. Upon completion, the mixture was concentrated and washed with pentane and recrystallized by slow evaporation of an acetonitrile solution to yield the desired product. (80 mg, 86% yield)

X-ray quality crystals were grown by vapor diffusion of heptane into diisopropyl ether.

^{1}H NMR (600 MHz, CD_3CN) δ 7.97 (d, *J* = 8.6 Hz, 1H), 7.60 (s, 2H), 7.50 (t, *J* = 7.8 Hz, 2H), 7.35 (d, *J* = 7.8 Hz, 4H), 6.82 (d, *J* = 2.7 Hz, 1H), 6.55 (dd, *J* = 8.6, 2.8 Hz, 1H), 5.08 (d, *J* = 1.5 Hz, 1H), 4.72 (d, *J* = 1.6 Hz, 1H), 3.68 (s, 3H), 3.15 (s, 2H), 2.83 (t, *J* = 1.5 Hz, 2H), 2.70 (s, 2H), 1.37 (d, *J* = 6.5 Hz, 12H), 1.19 – 1.09 (m, 12H).
^{13}C NMR (151 MHz, CD_3CN) δ 183.86, 159.39, 156.44, 151.74, 146.69, 137.18, 135.13, 131.54, 126.65, 114.64, 106.59, 104.08, 55.53, 45.12, 29.73, 26.46. [Hindered rotation causes significant broadening of several peaks, gold aryl ipso carbon not observed.]
EA: Calculated: C, 54.75; H, 5.71; N, 3.45; Found: C, 54.90; H, 5.95; N, 3.37



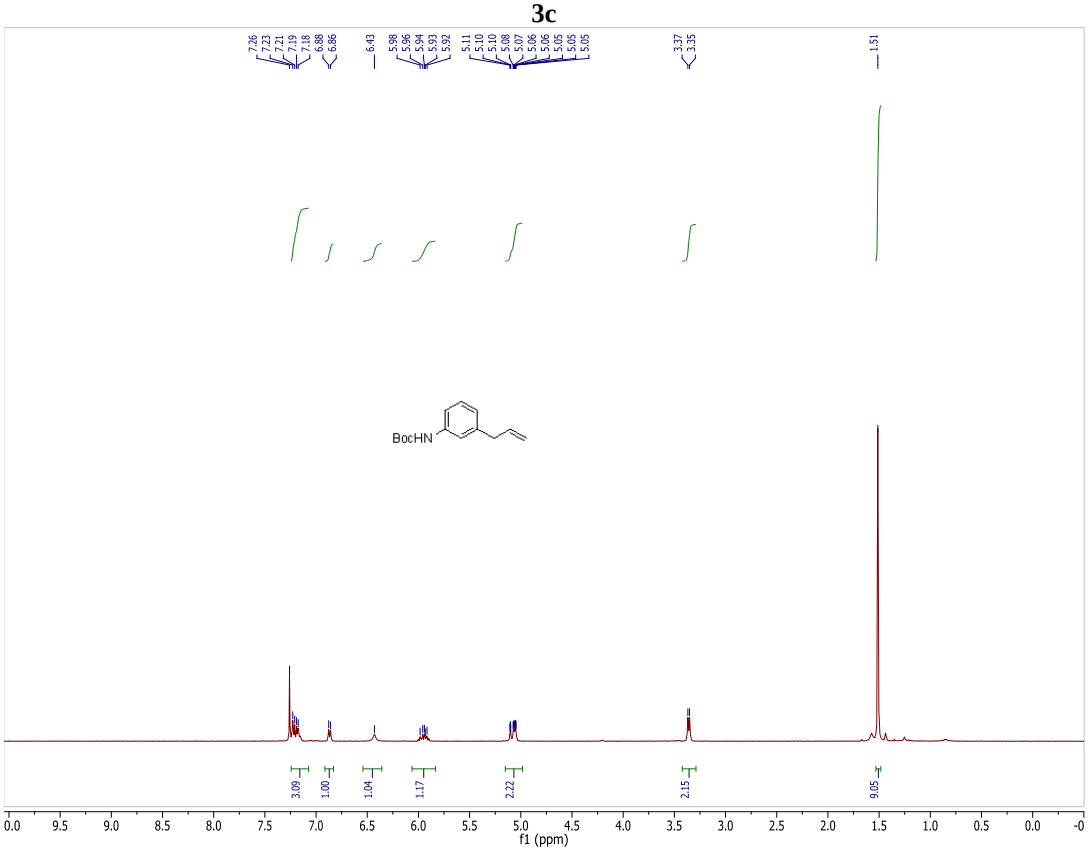
3-methoxy-8-methylenebicyclo[4.2.0]octa-1(6),2,4-triene, **14**

13 (60 mg, 0.074 mmol) was dissolved in CD_2Cl_2 (3 mL) and the mixture was added to a vial containing $AgSbF_6$ (50 mg, 0.14 mmol). A precipitate formed immediately, and the suspension was sonicated for 3 minutes before filtering through a glass fiber filter. The mixture was concentrated and the residue was purified via column chromatography on silica, eluting with 95:5 Pentane/Ethyl Acetate to afford the title compound as a colorless oil. (8 mg, 74%).

^{1}H NMR (600 MHz, $CDCl_3$) δ 7.10 (d, *J* = 8.0 Hz, 1H), 6.79 (dd, *J* = 8.0, 2.2 Hz, 1H), 6.76 (d, *J* = 2.1 Hz, 1H), 5.27 (d, *J* = 1.7 Hz, 1H), 4.92 (s, 1H), 3.79 (s, 4H), 3.54 (s, 2H).
^{13}C NMR (151 MHz, $CDCl_3$) δ 159.68, 145.69, 144.17, 137.12, 123.80, 116.29, 103.47, 102.90, 55.50, 37.69.
HRMS (EI) m/z: calculated for $[C_{10}H_{10}O_1]^+$ 146.0732, found 146.0734.

Spectra

3c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5.11
5.10
5.10
5.08
5.07
5.06
5.06
5.05
5.05
5.05
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1.00
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1.17
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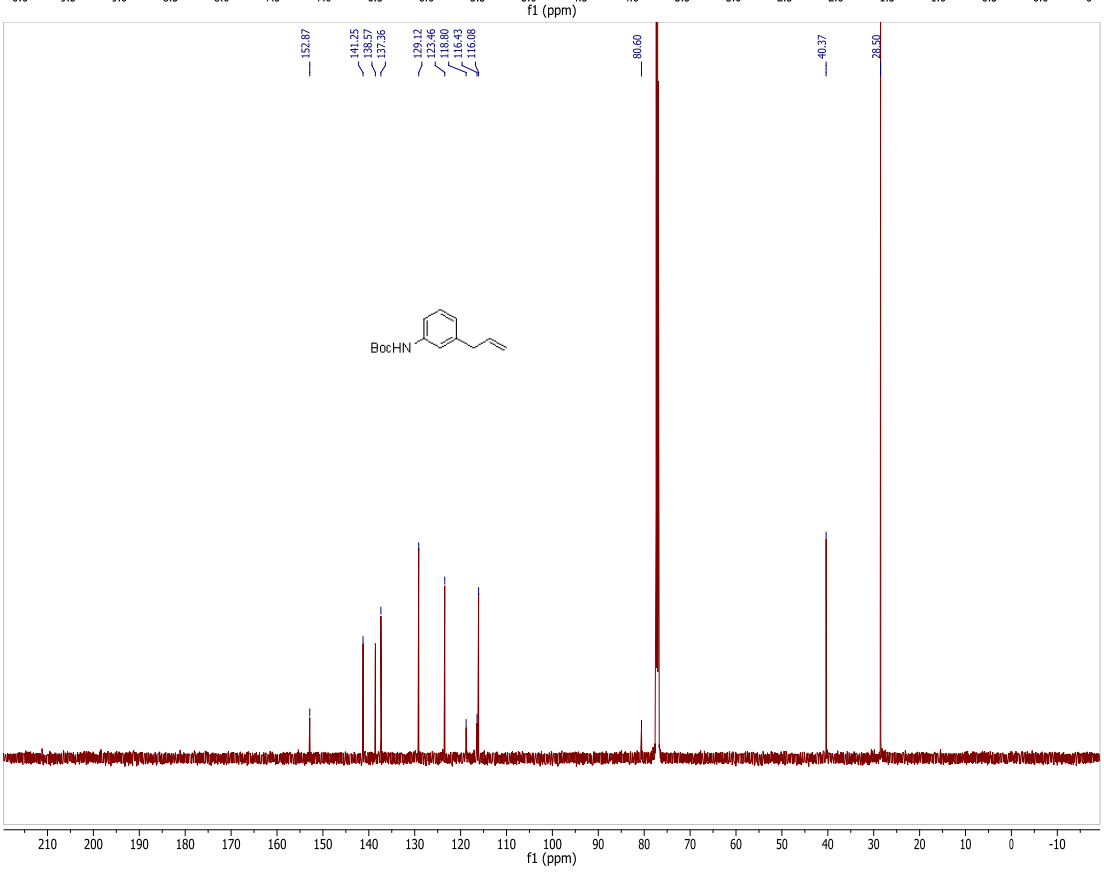
2.15
9.05
f1 (ppm)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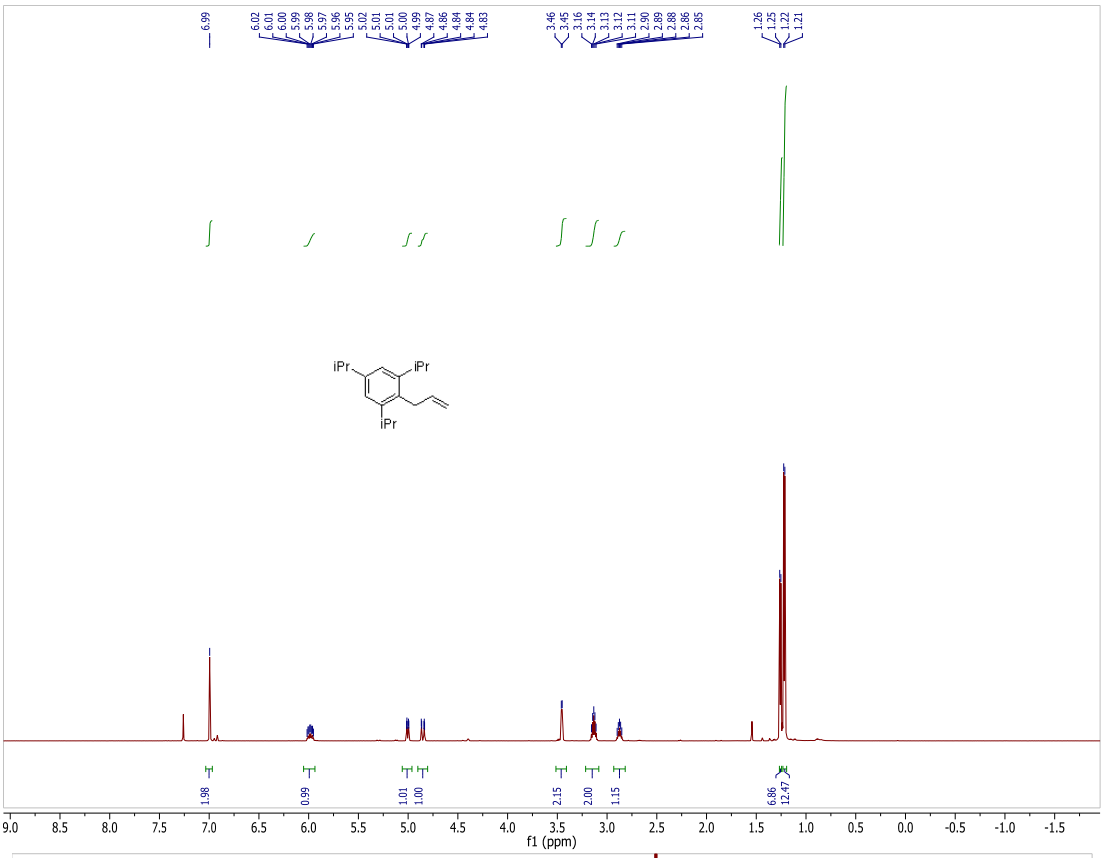
BocHN
f1 (ppm)

3e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3.11
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2.88
2.86
2.85
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1.25
1.22
1.21
iPr
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2.00
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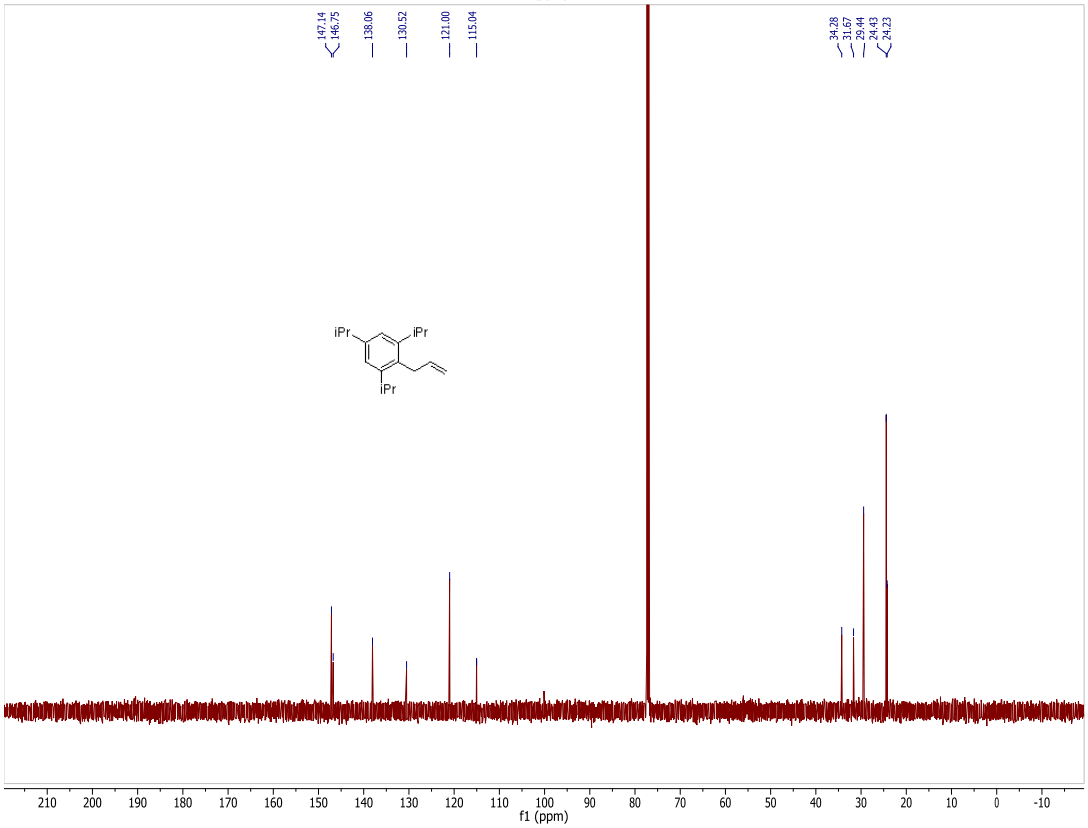
f1 (ppm)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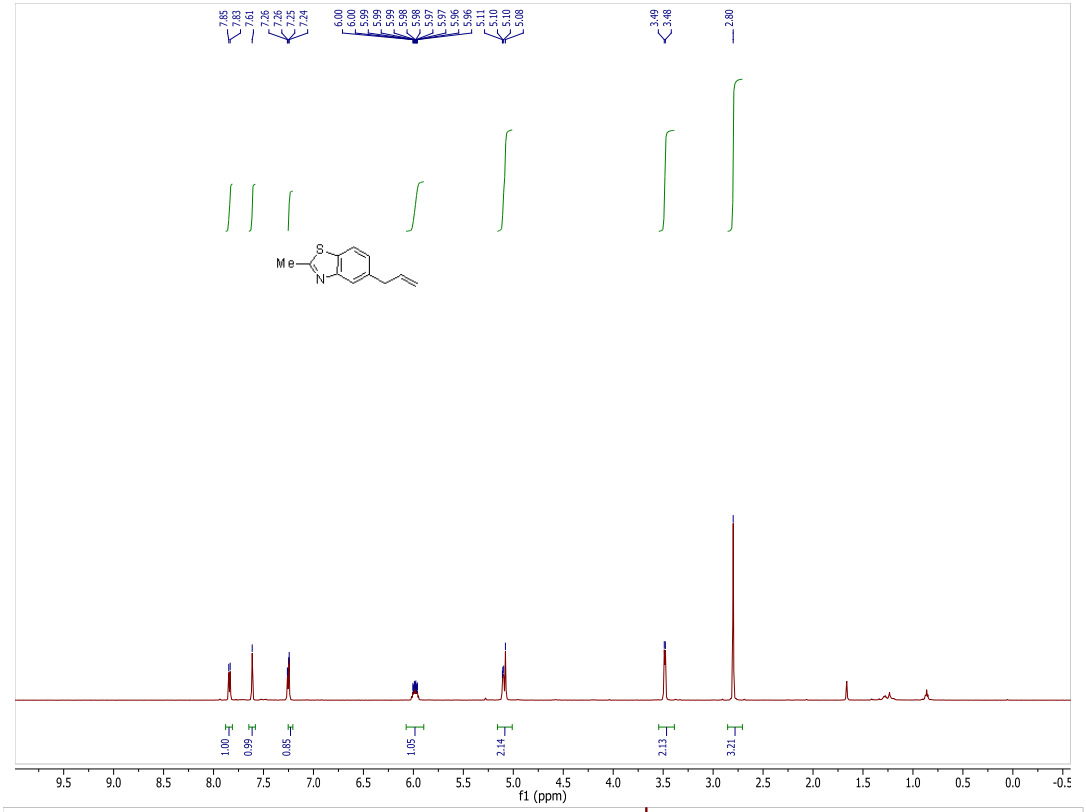
iPr
iPr
f1 (ppm)

3j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5.96
5.11
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5.10
5.08
3.49
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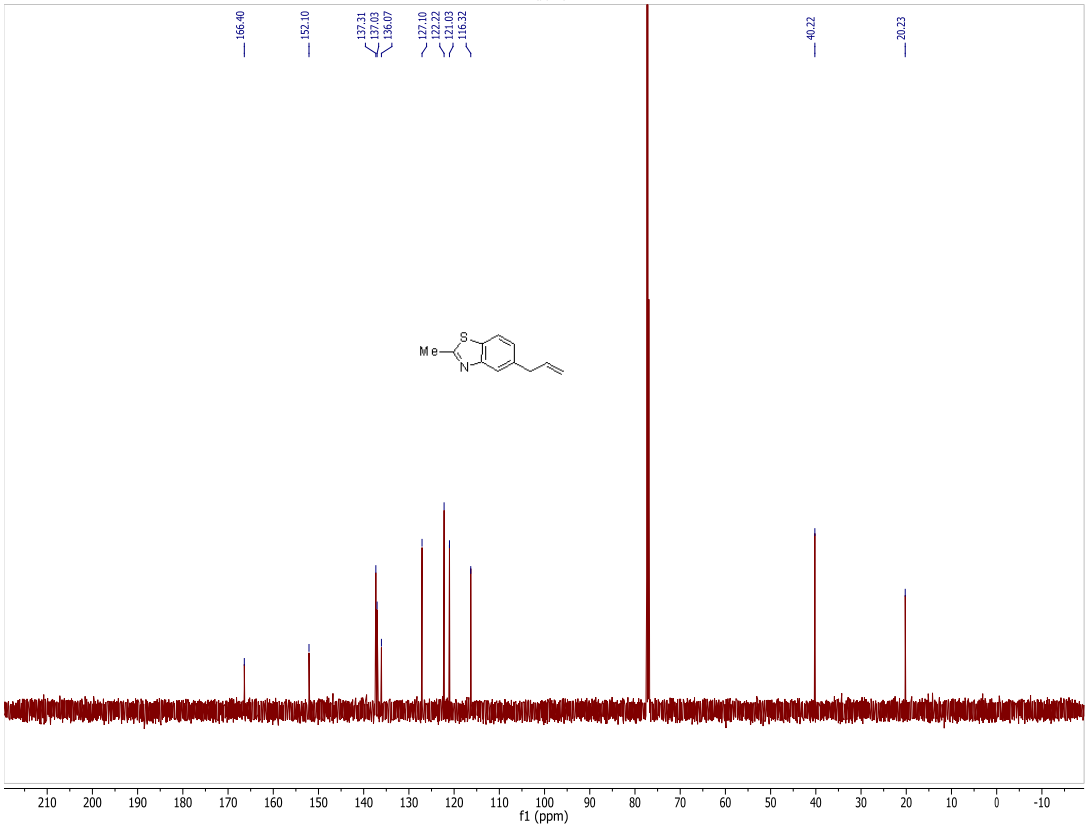
f1 (ppm)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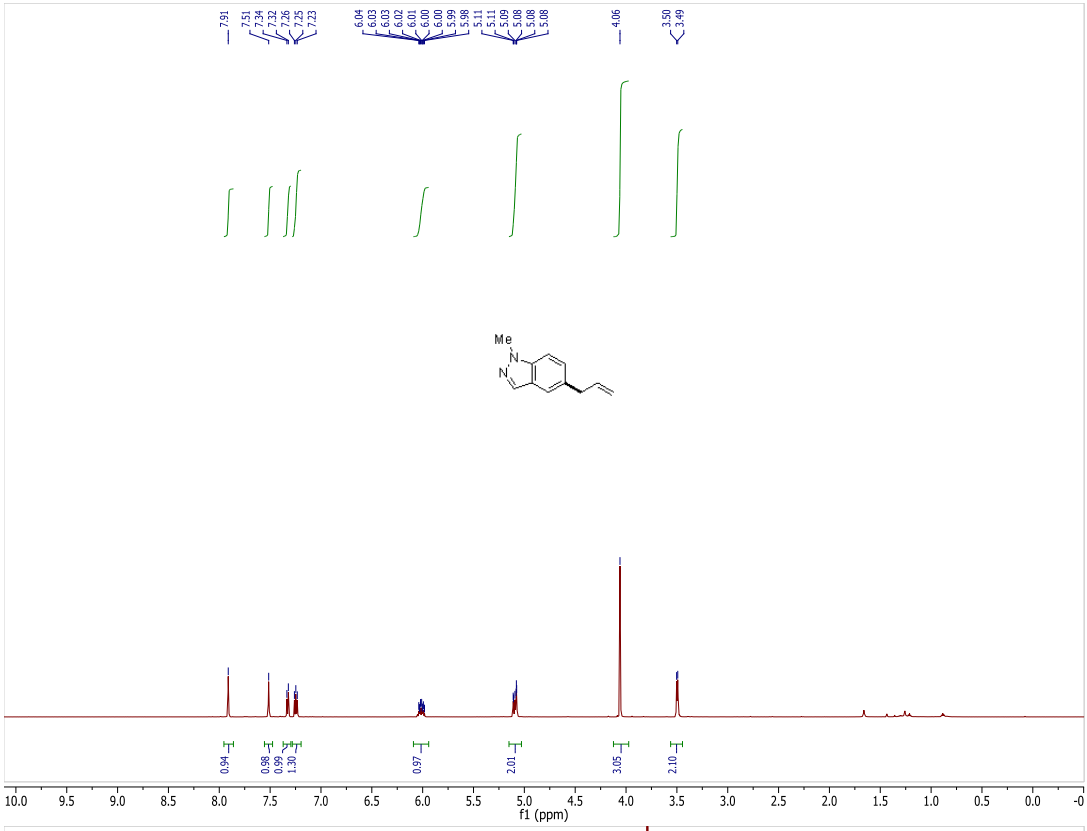
Me
S
N
f1 (ppm)

3k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5.11
5.11
5.09
5.08
5.08
5.08
4.06
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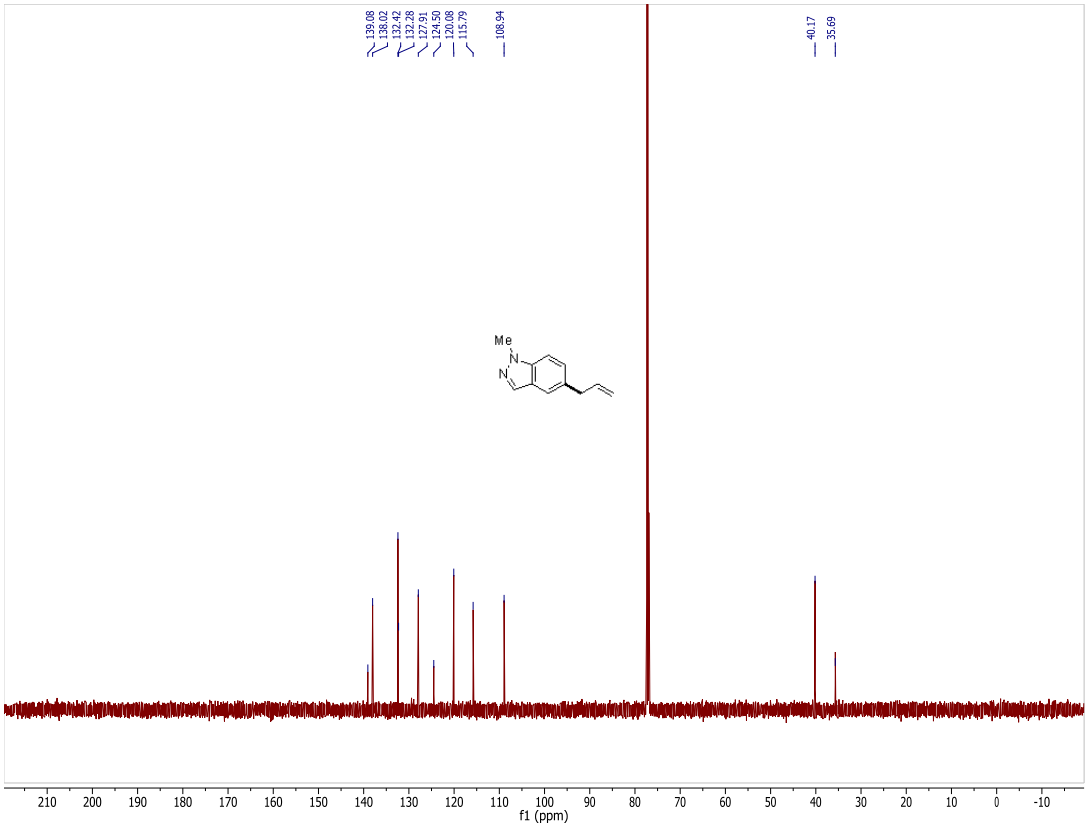
2.10
f1 (ppm)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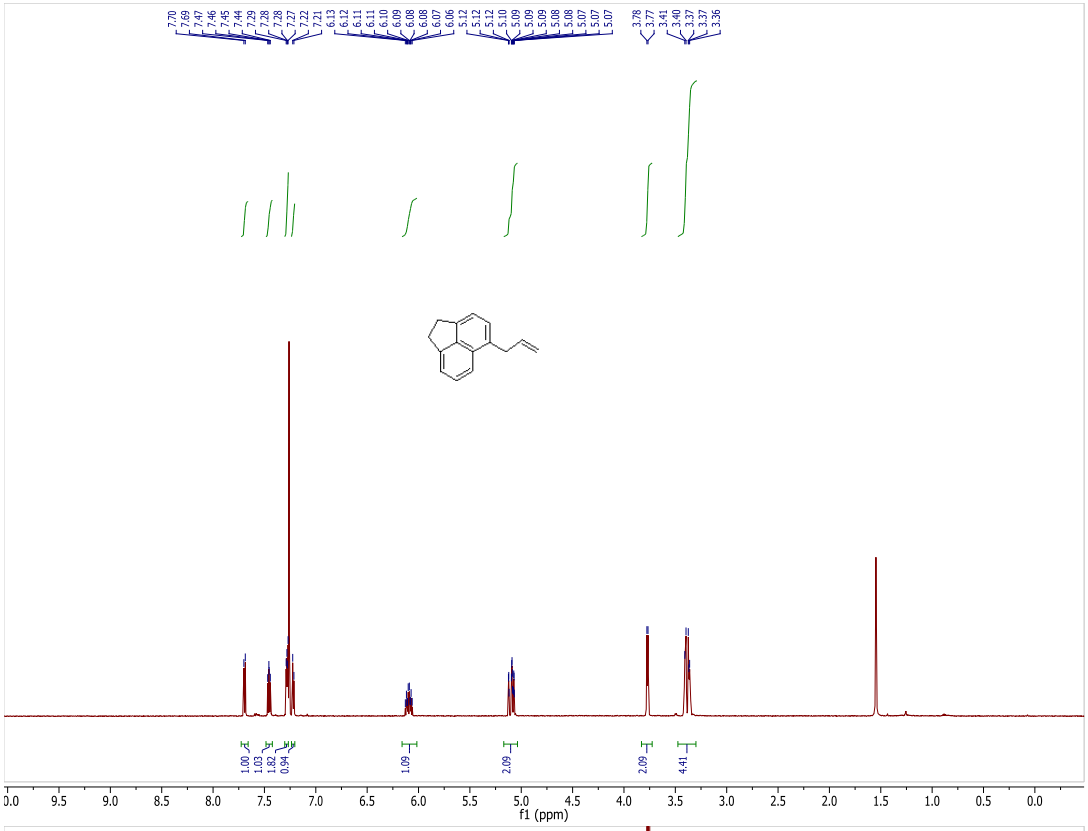
Me
f1 (ppm)

3l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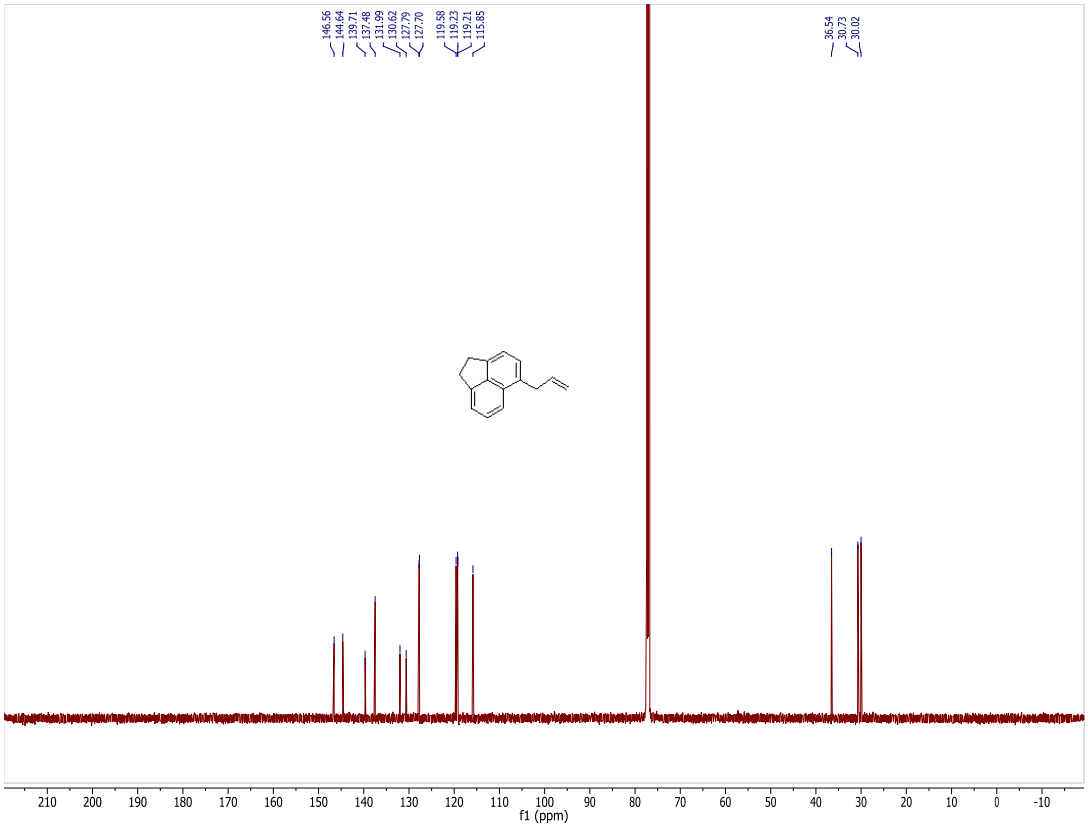
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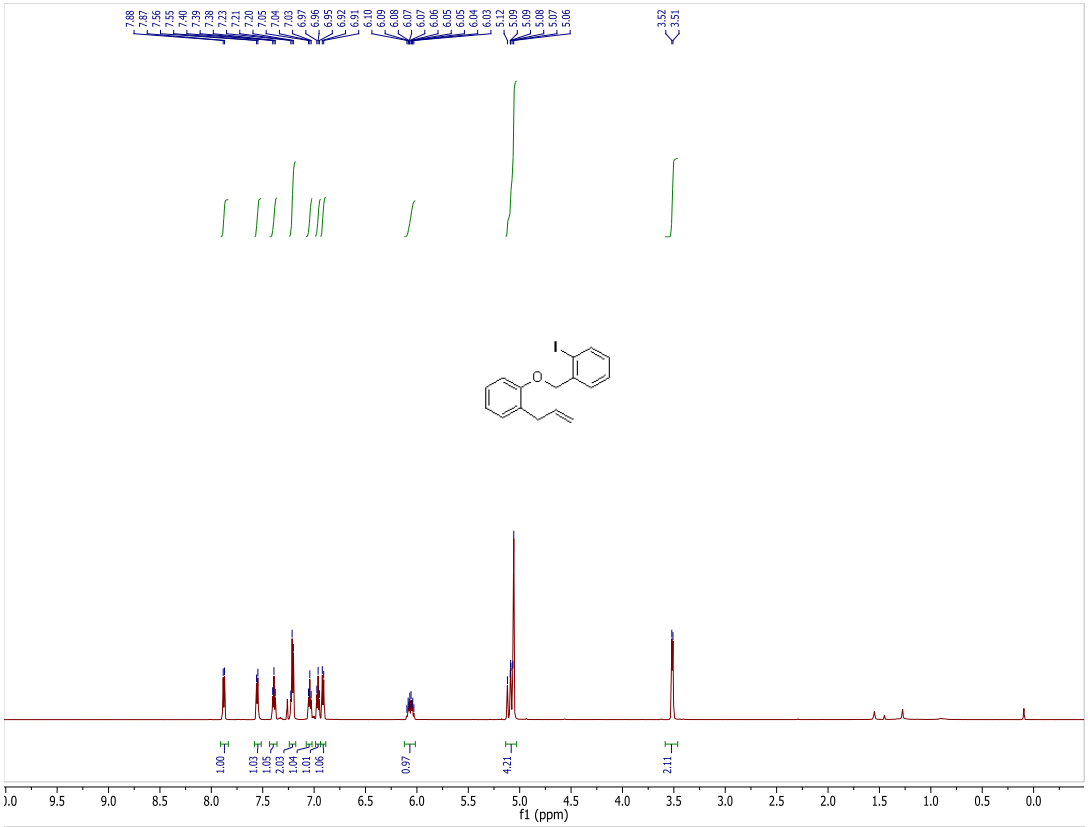
f1 (ppm)

3n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6.91
6.10
6.09
6.08
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6.07
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5.07
5.06
3.52
3.51
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1.01
1.06
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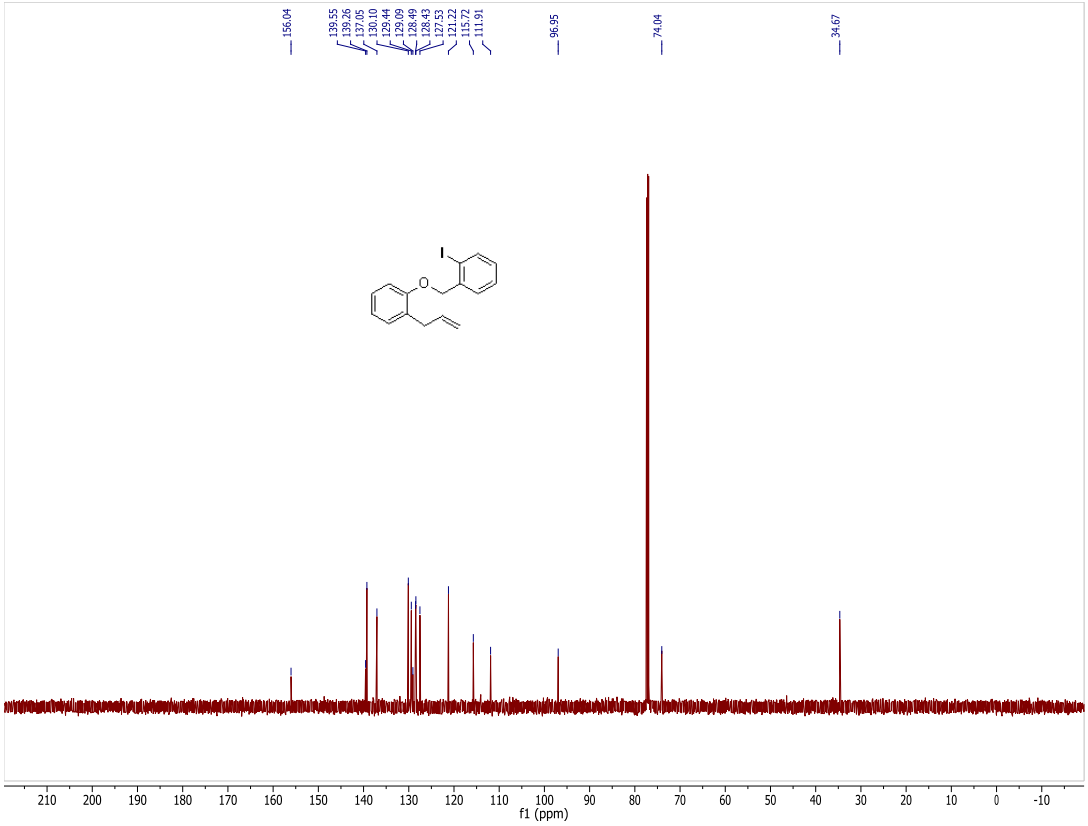
f1 (ppm)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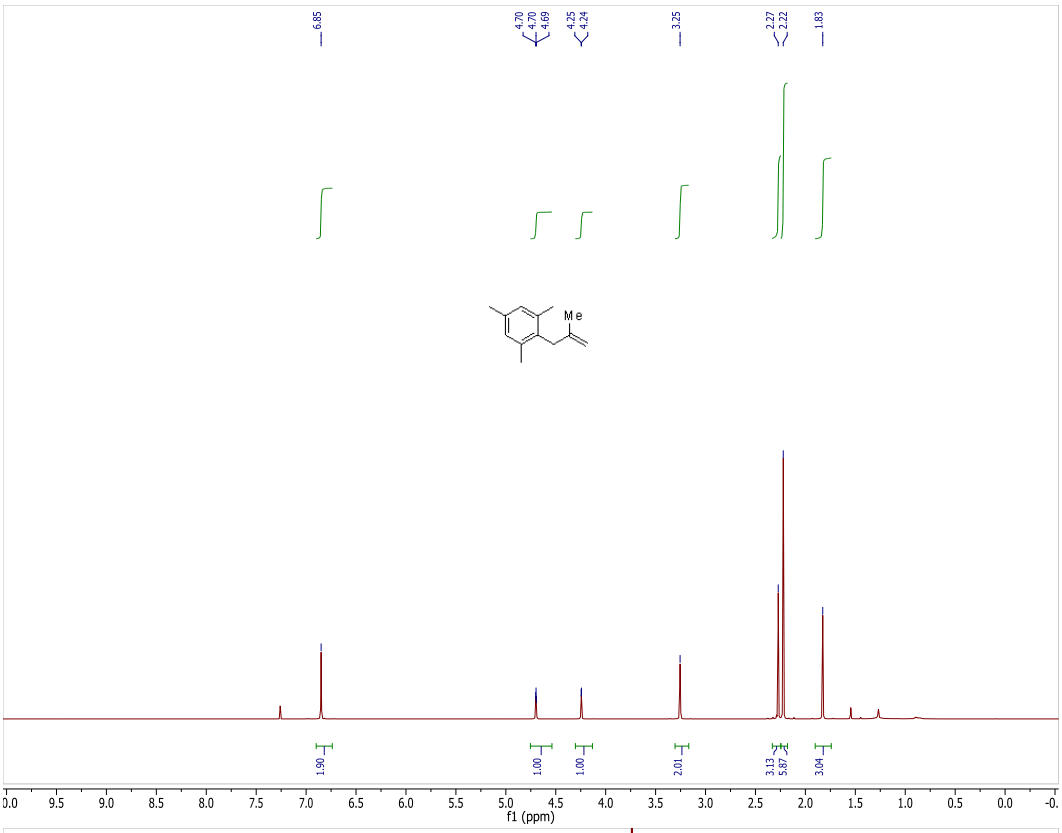
34.67
I
O
f1 (ppm)

5b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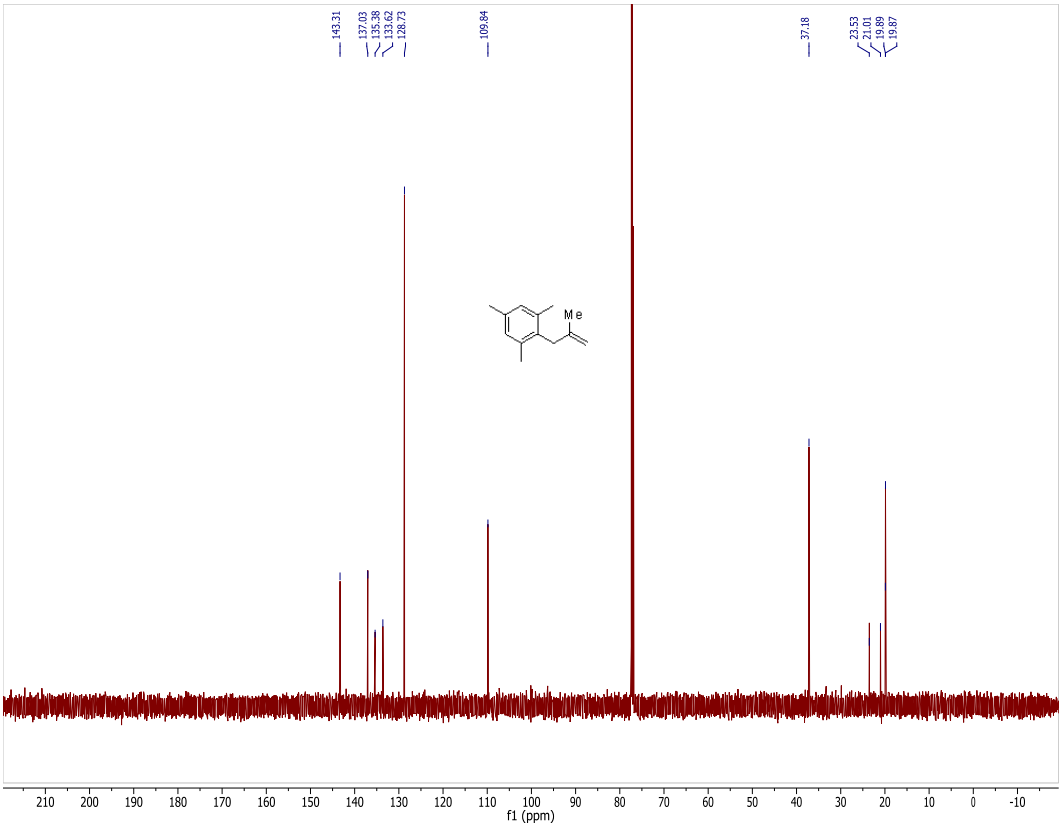
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Me
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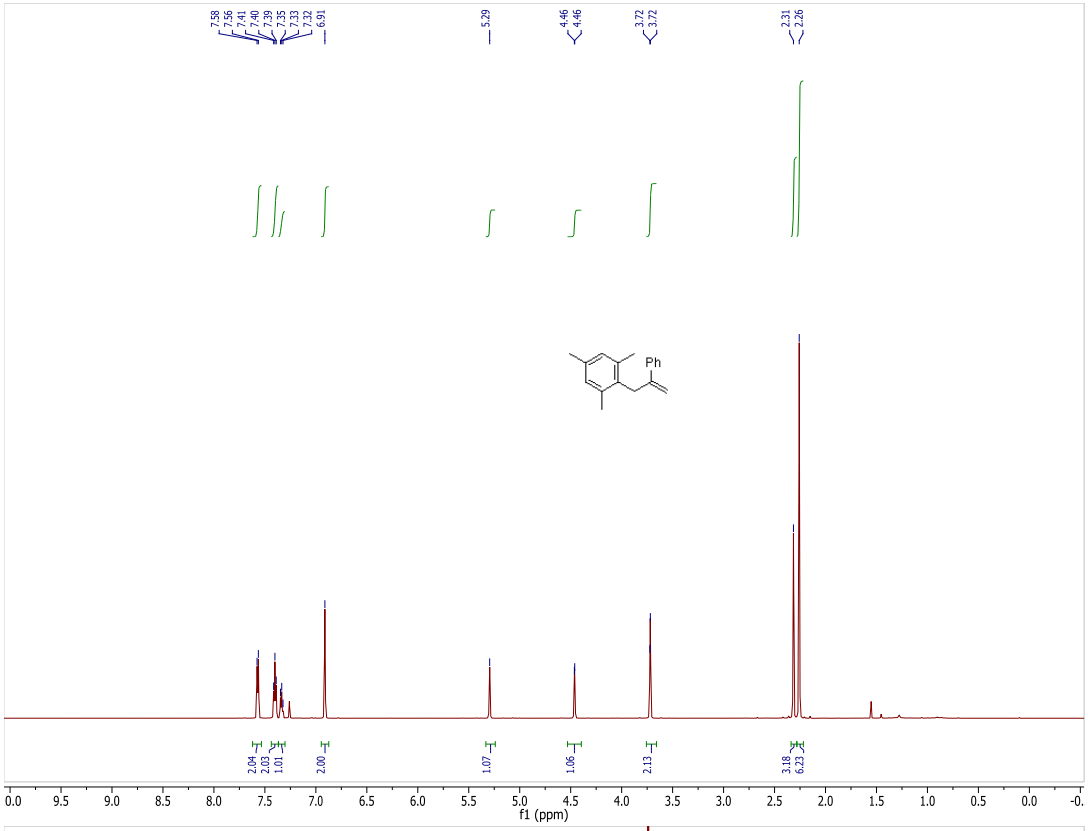
5c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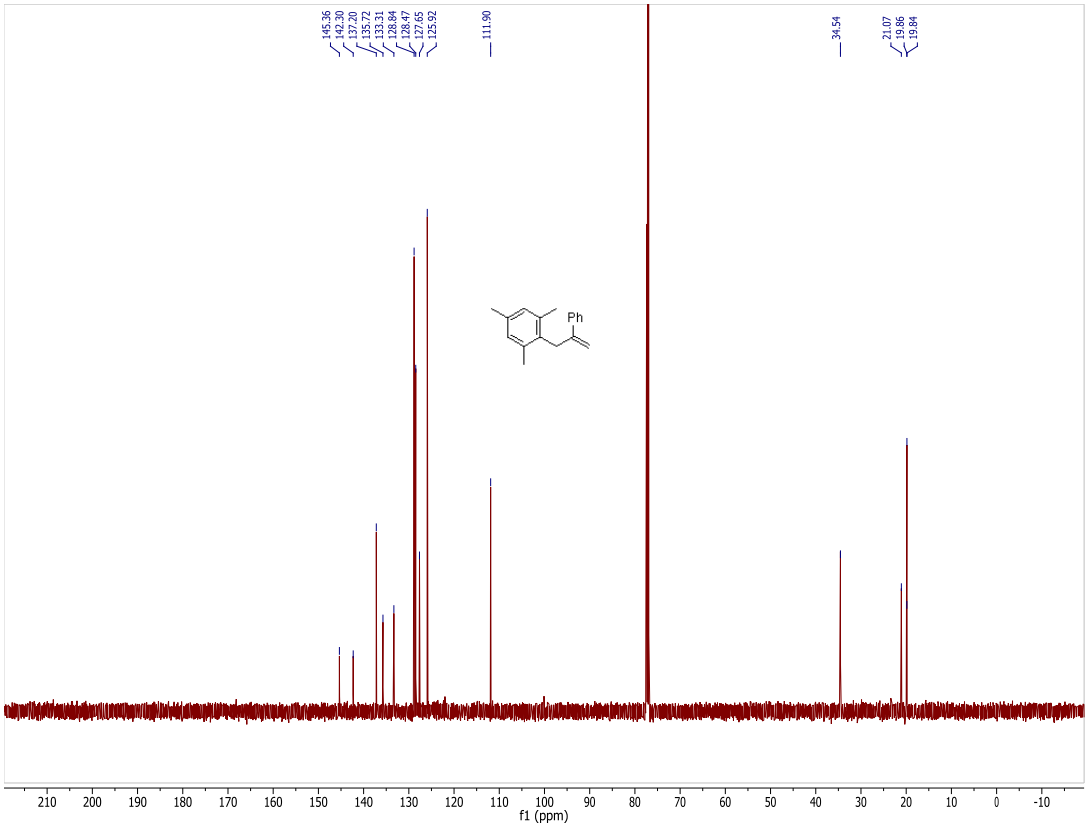
f1 (ppm)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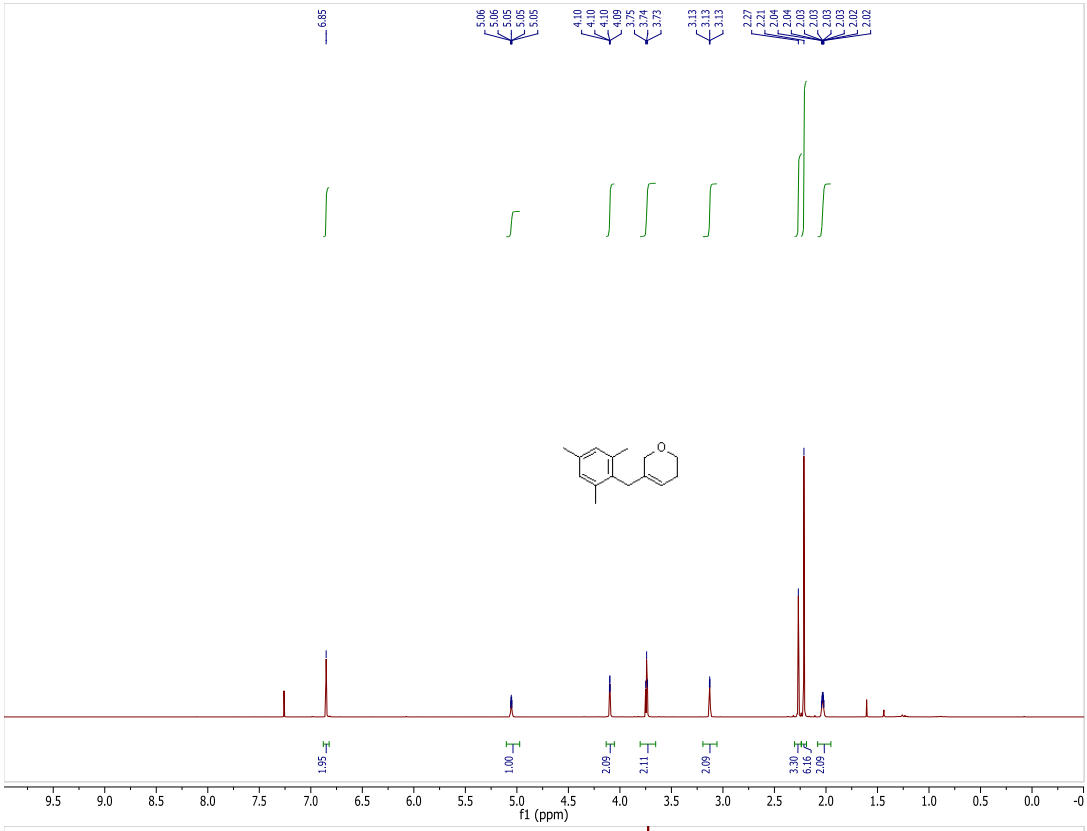
Ph
f1 (ppm)

5d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3.13
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2.02
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O
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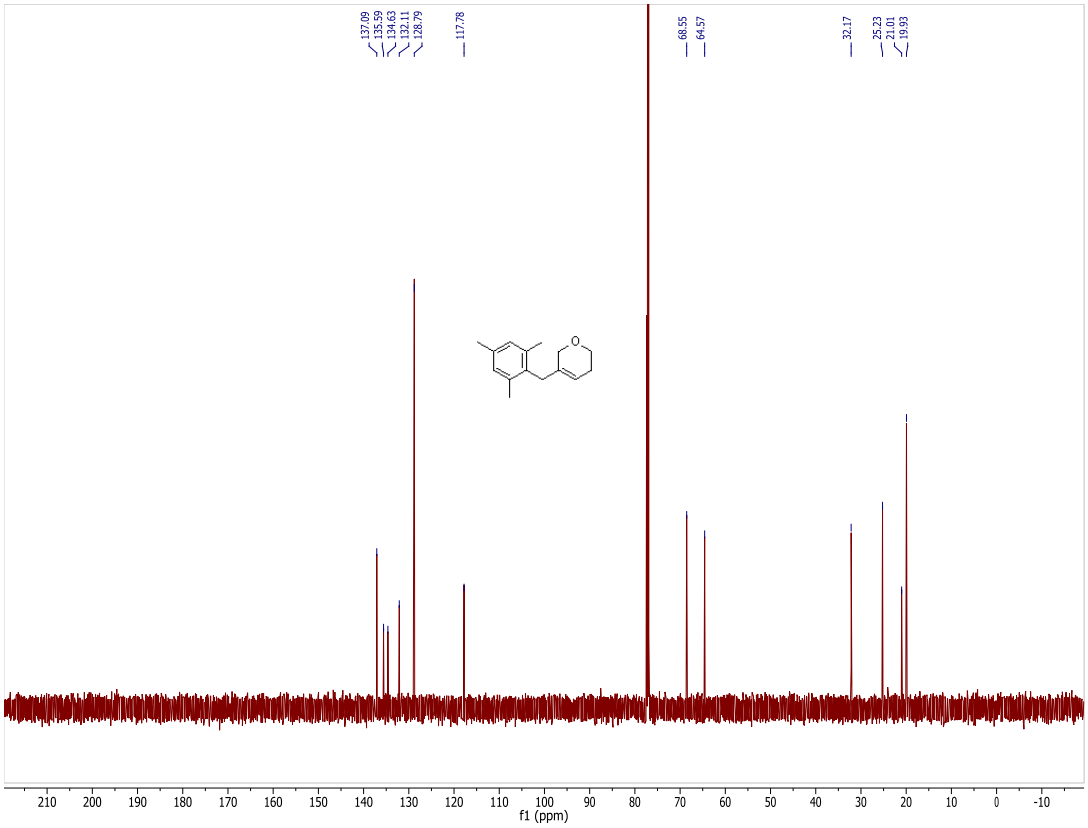
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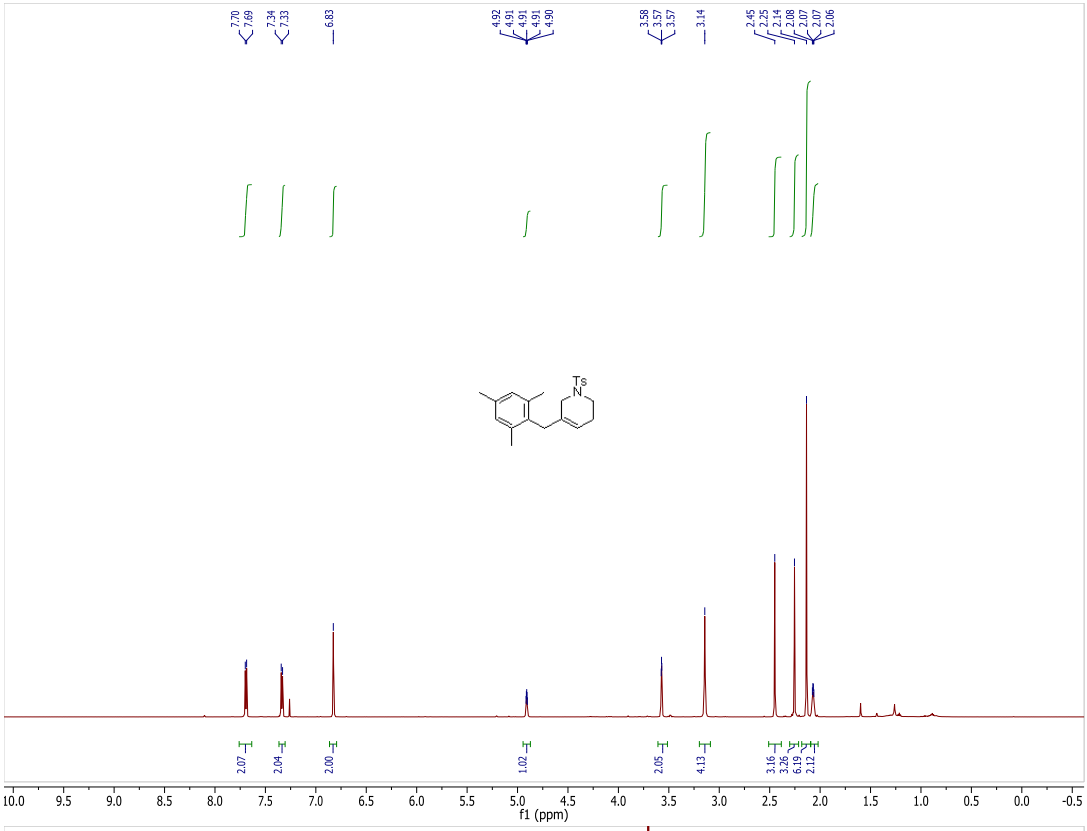
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2.07
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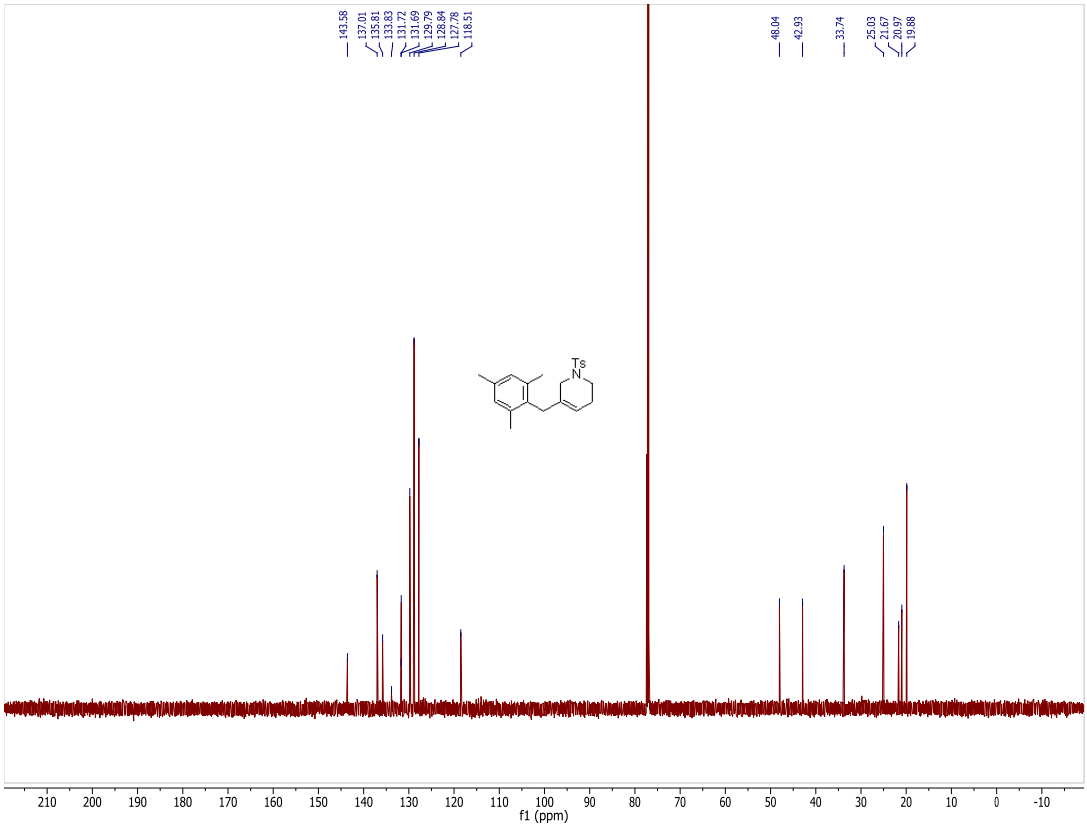
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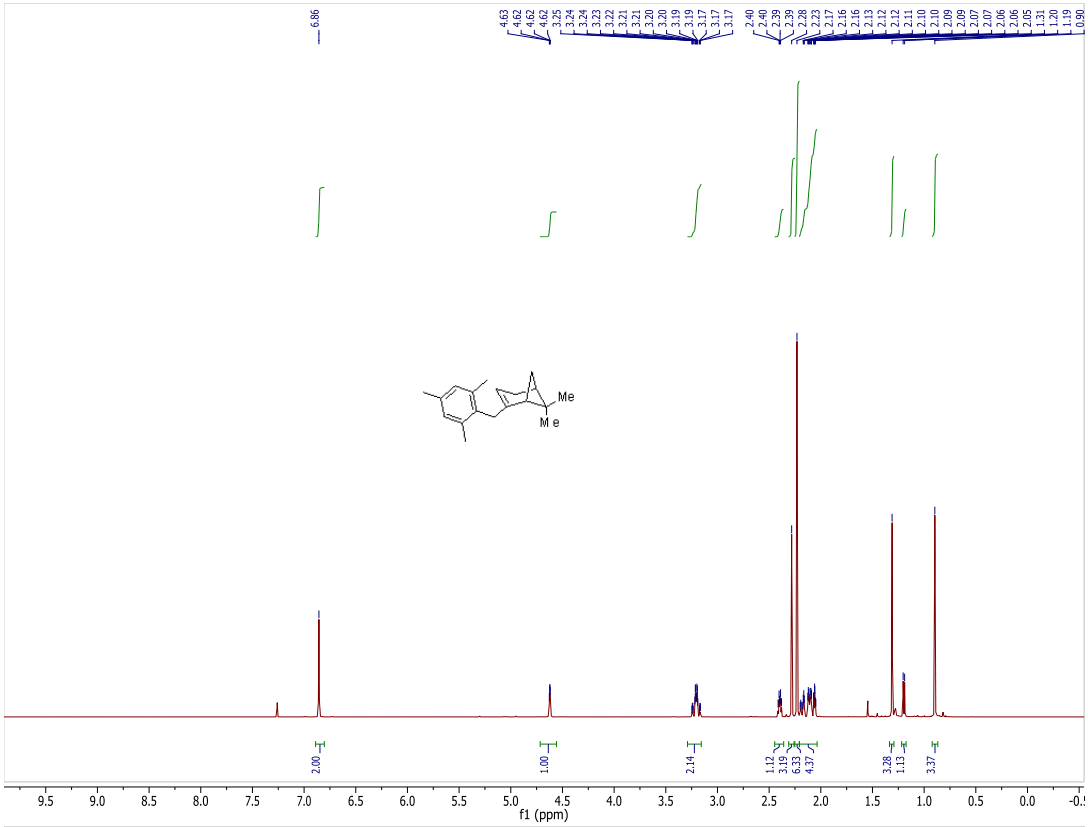
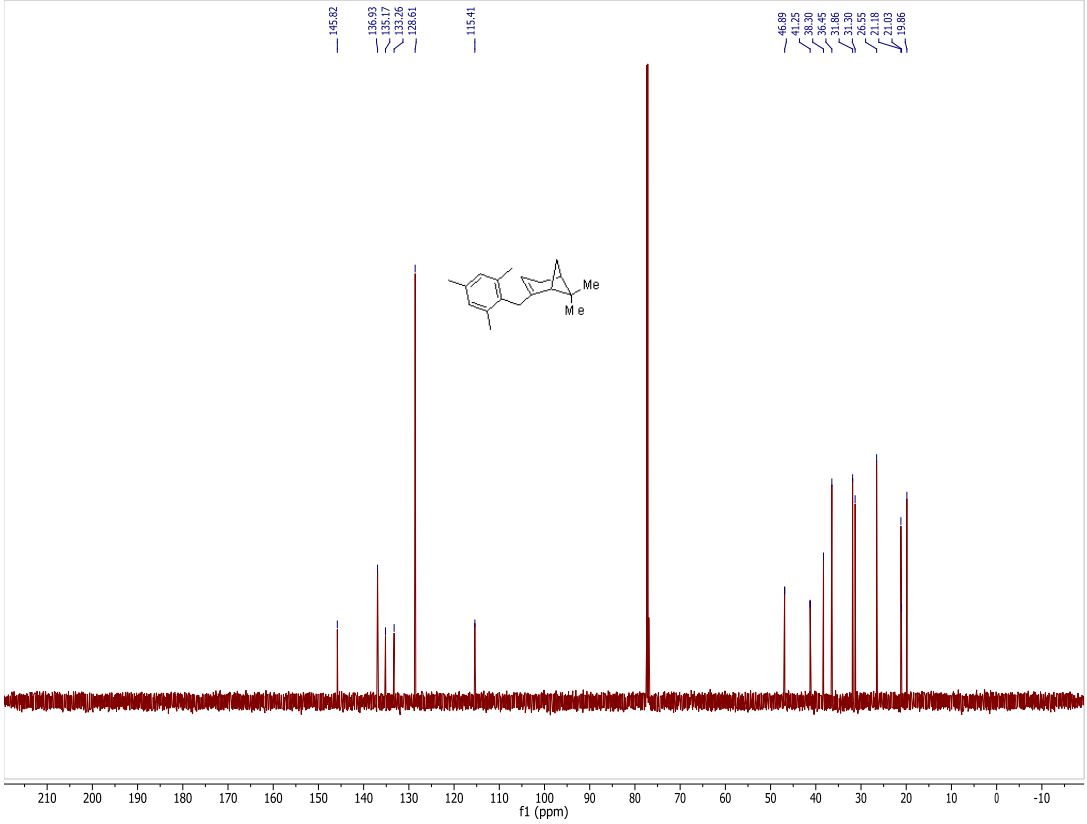
Ts
N
f1 (ppm)

5f





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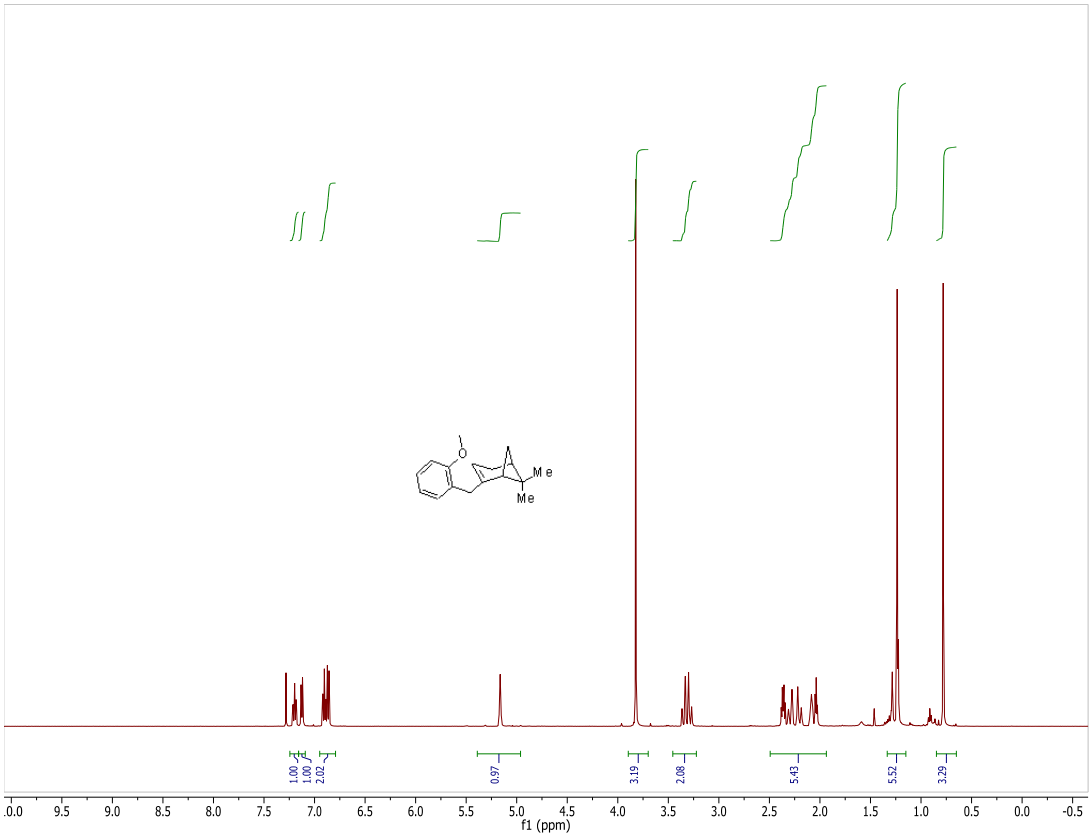
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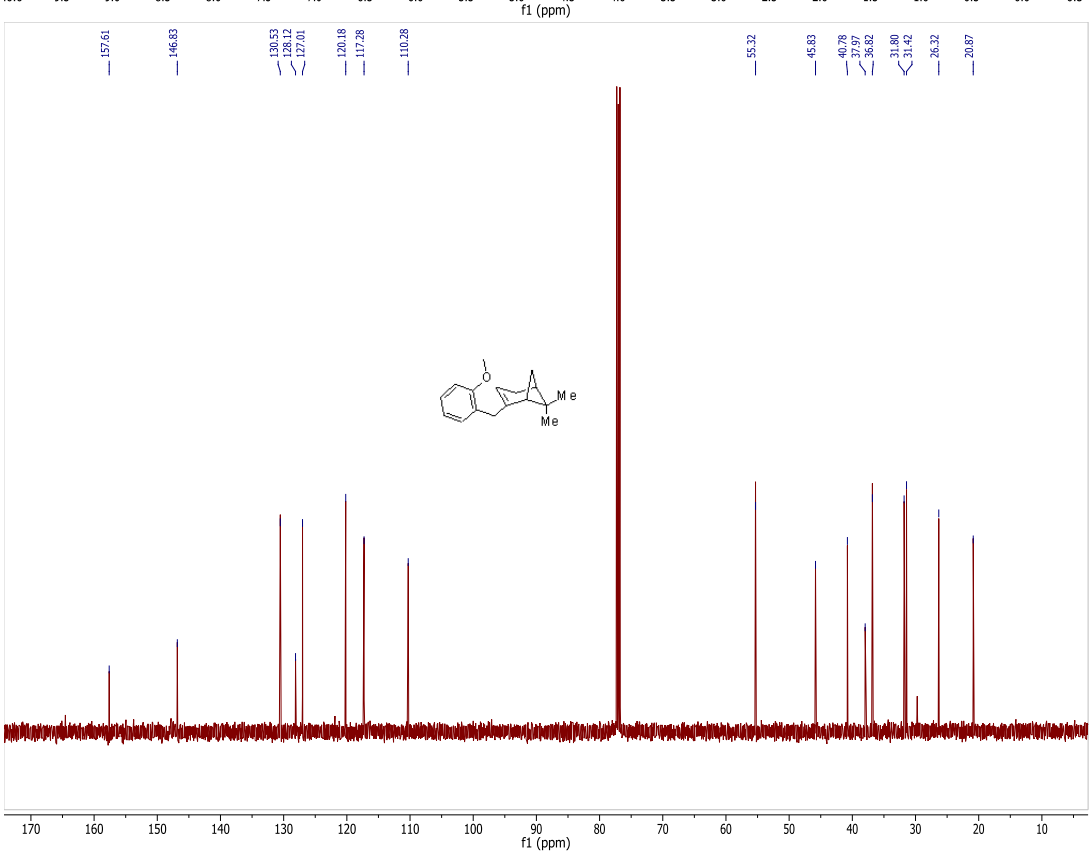
f1 (ppm)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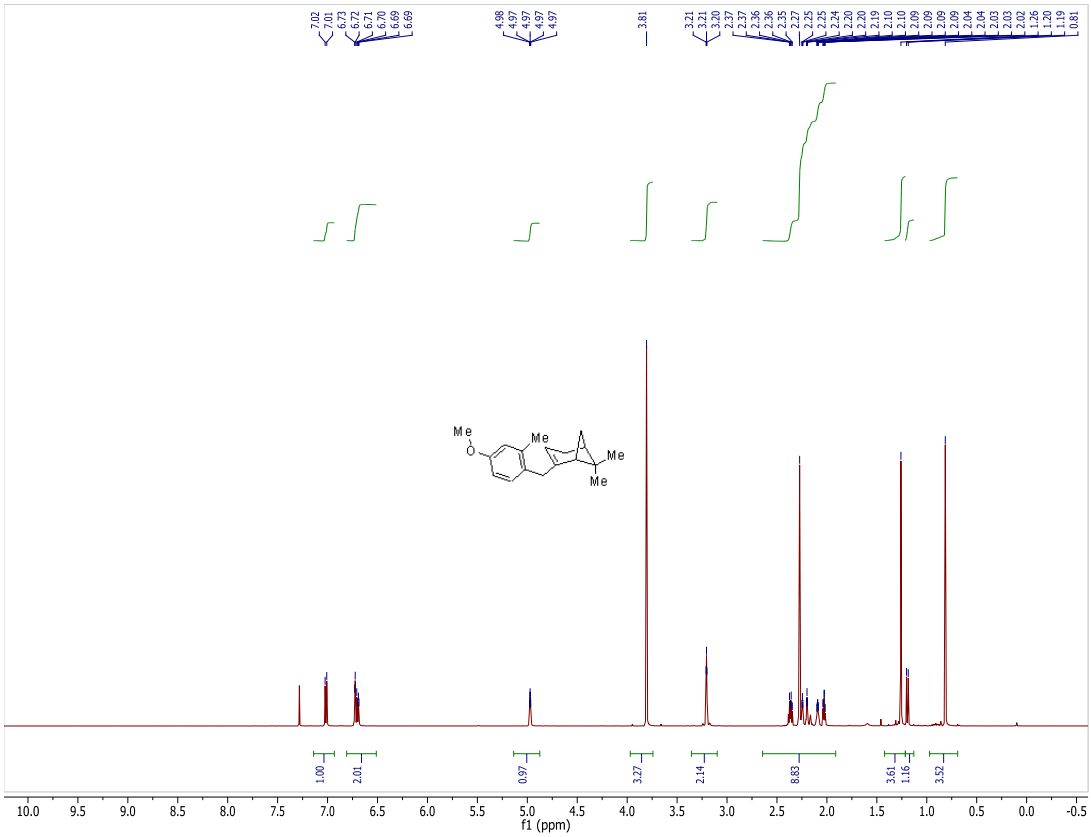
20.87
Me
Me
f1 (ppm)

5h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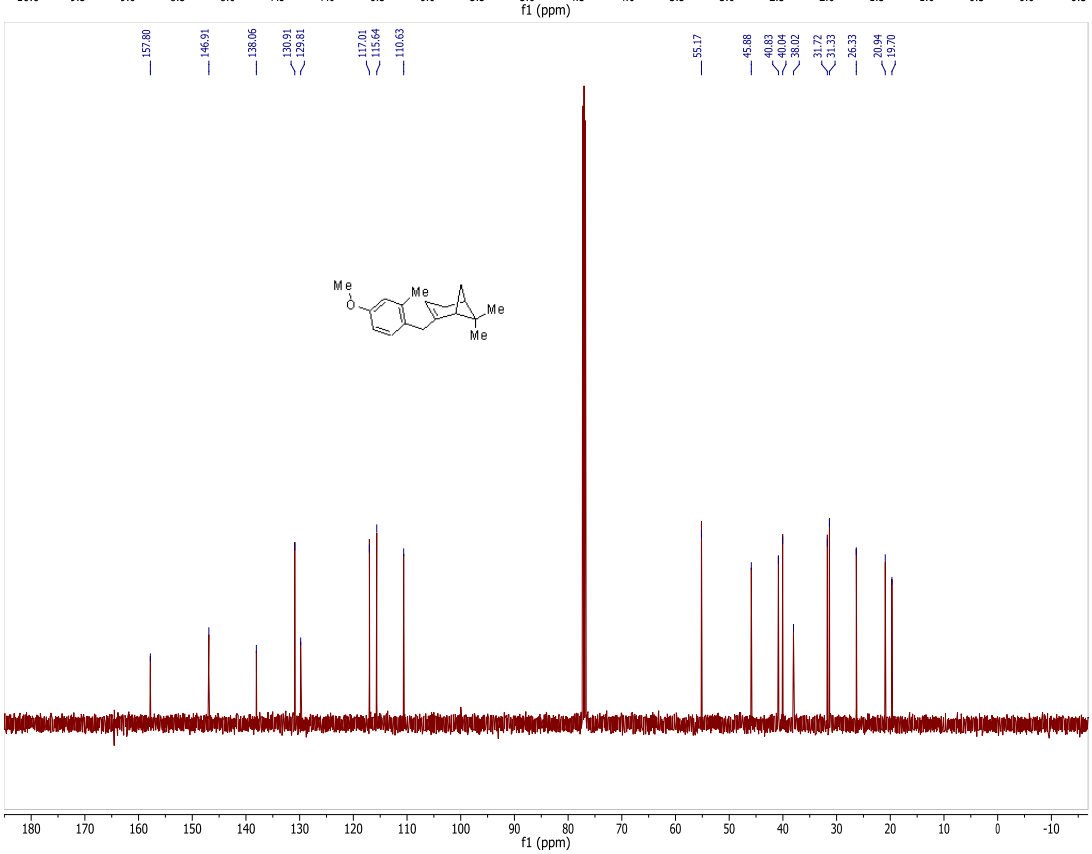
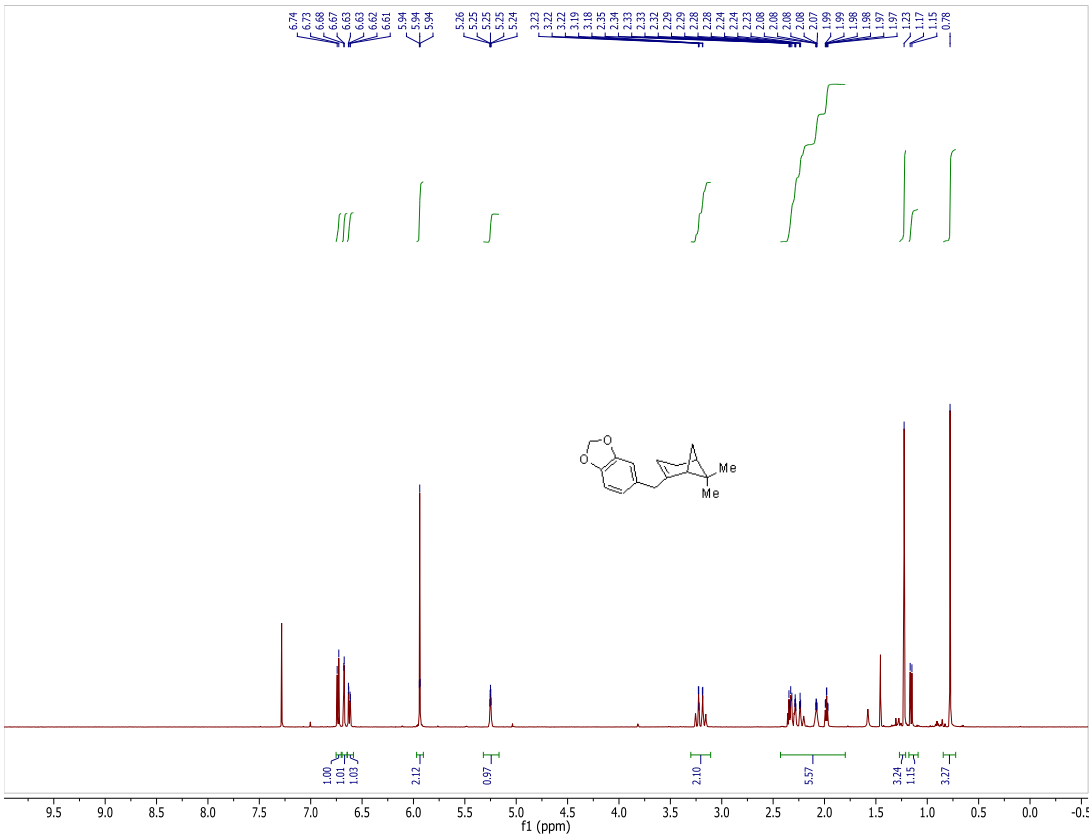
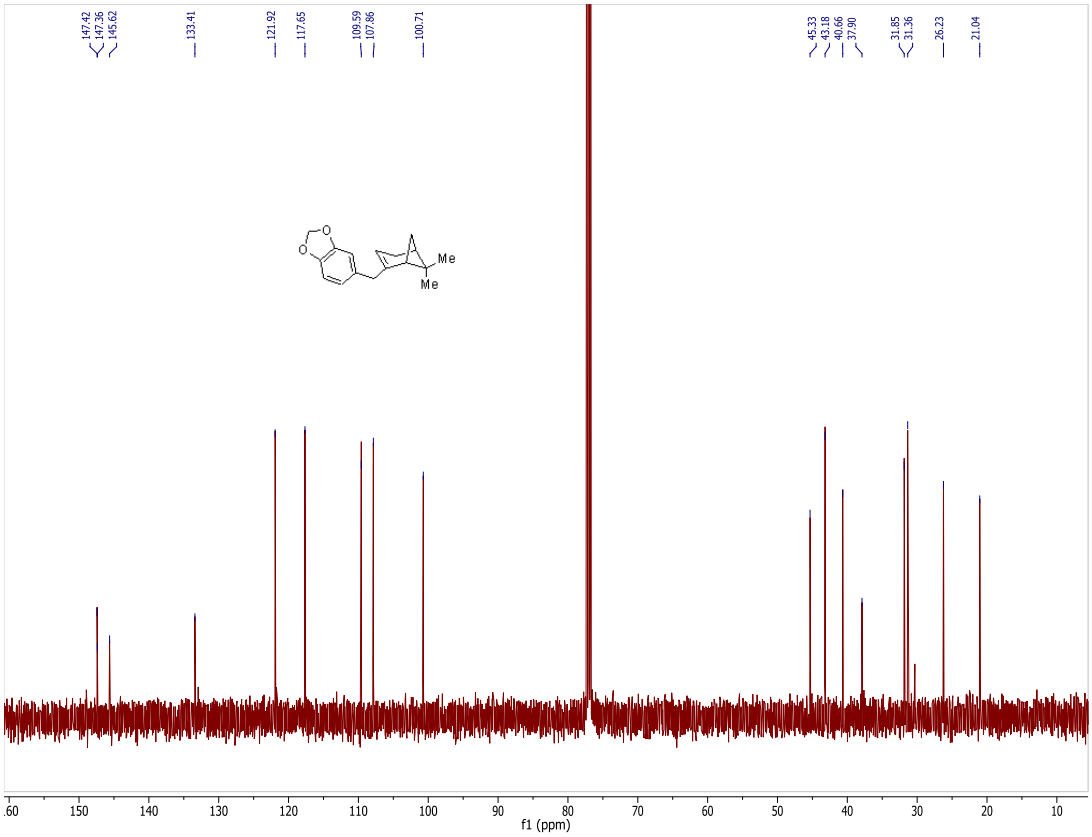
2.25
2.25
2.24
2.21
2.20
2.19
2.10
2.10
2.09
2.09
2.09
2.09
2.09
2.04
2.04
2.03
2.03
2.02
1.26
1.20
1.19
1.19
0.81
Me
O
Me
Me
Me
1.00
2.01
0.97
3.27
2.14
8.83
3.61
1.16
3.52
10.0
9.5
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
-0.5
f1 (ppm)

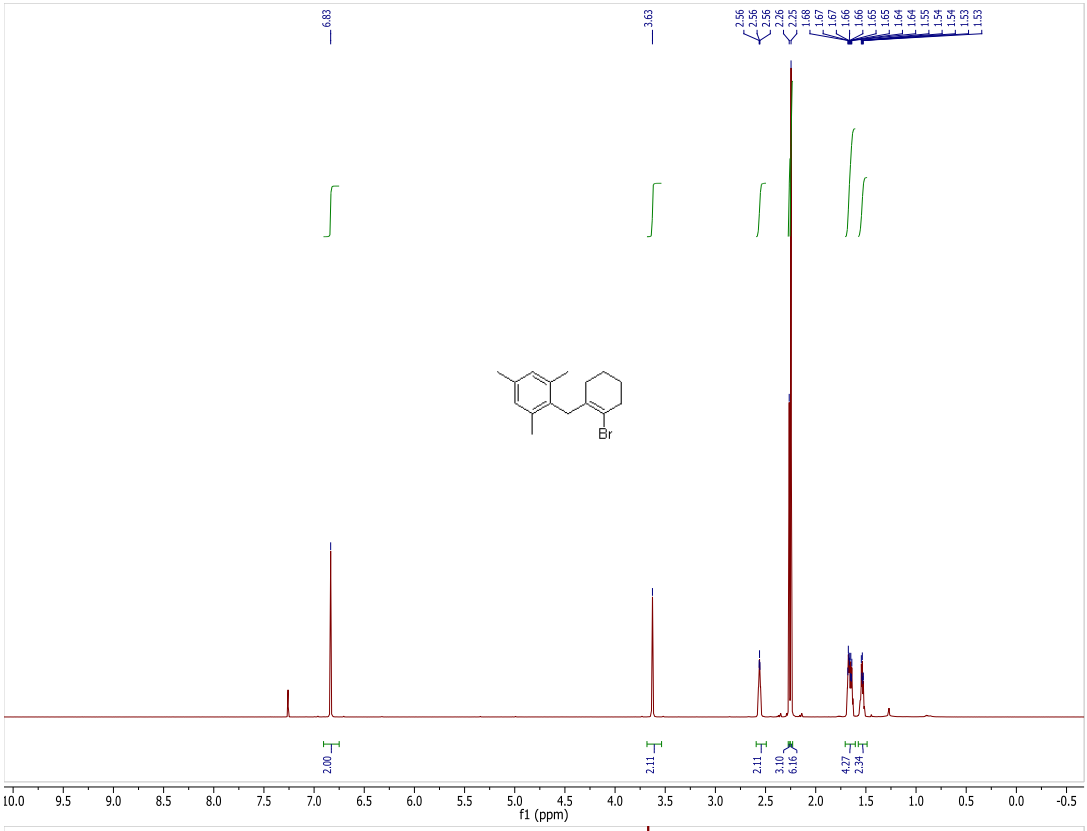

157.80
146.91
138.06
130.91
129.81
117.01
115.64
110.63
55.17
45.88
40.83
40.04
38.02
31.72
31.33
26.33
20.94
19.70
Me
O
Me
Me
Me
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
-10
f1 (ppm)

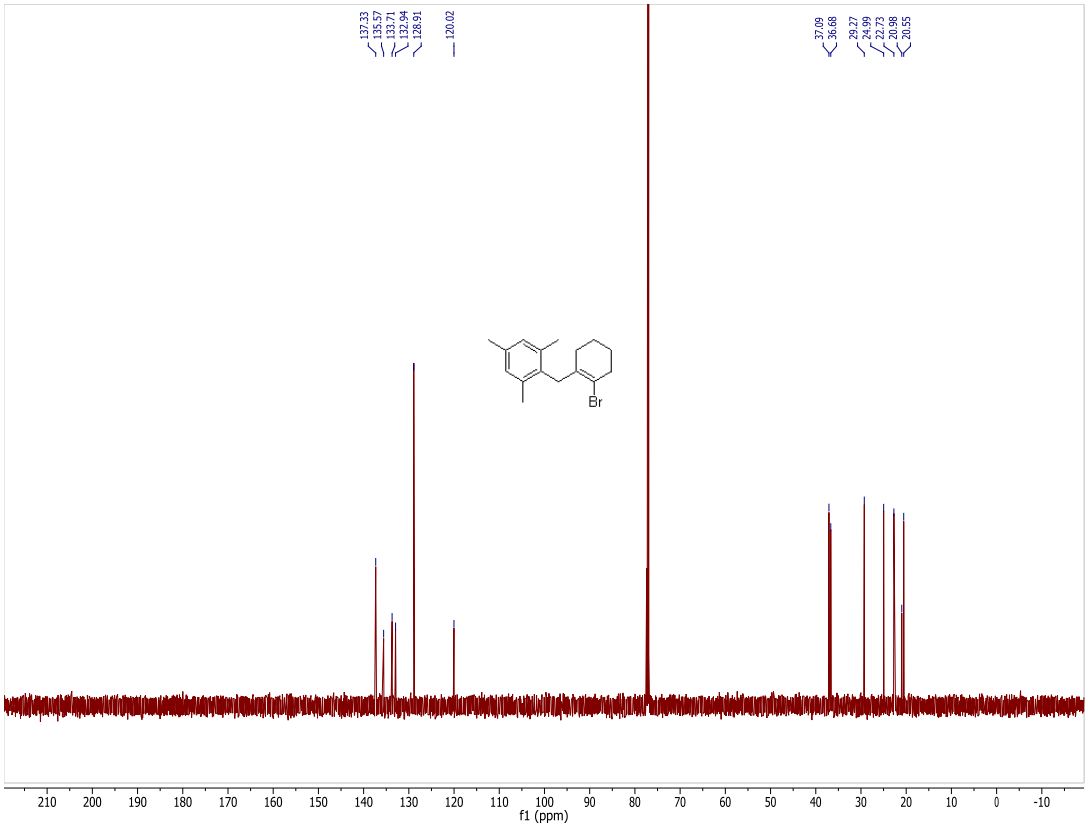
5i


6.74 6.73 6.68 6.67 6.63 6.63 6.62 6.61 5.94 5.94 5.94 5.26 5.25 5.25 5.25 5.24 3.23 3.22 3.22 3.19 3.18 2.35 2.34 2.33 2.33 2.32 2.29 2.29 2.28 2.28 2.24 2.24 2.23 2.08 2.08 2.08 2.08 2.07 1.99 1.99 1.98 1.98 1.97 1.97 1.23 1.17 1.15 0.78
Me
Me
1.00 1.01 1.03 2.12 0.97 2.10 5.57 3.24 1.15 3.27
f1 (ppm)

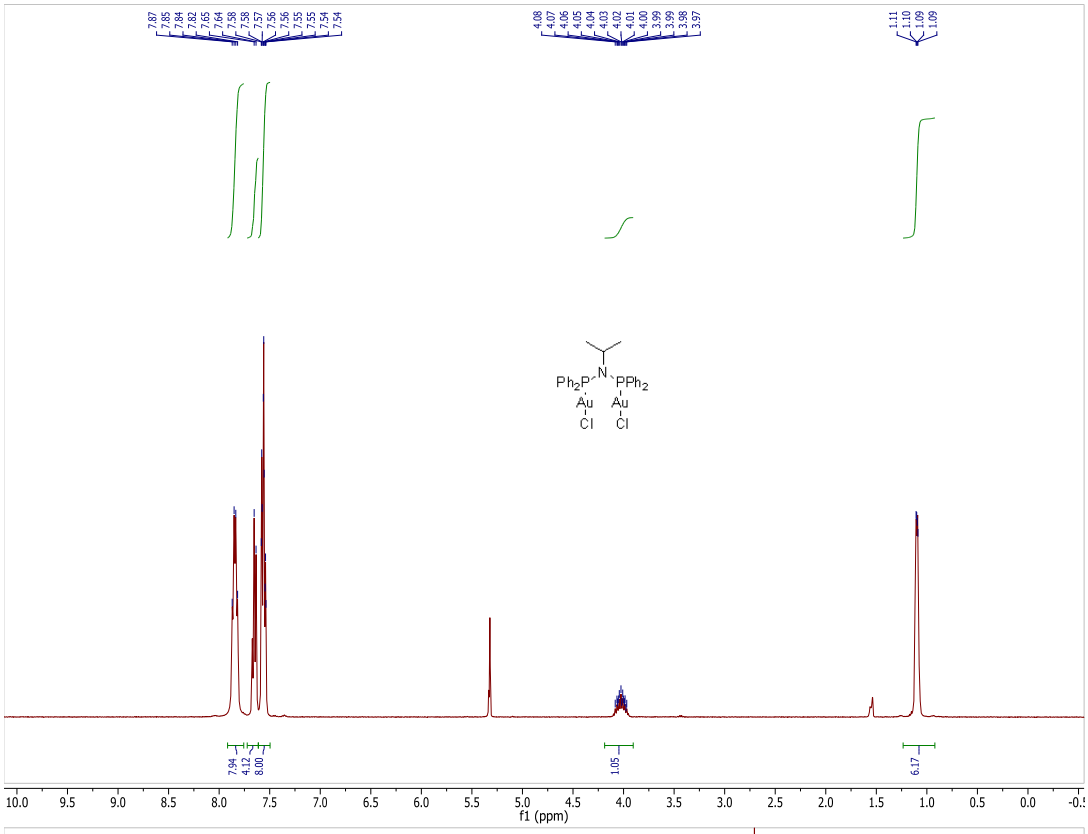

147.42 147.36 145.62 133.41 121.92 117.65 109.59 107.86 100.71 45.33 43.18 40.66 37.90 31.85 31.36 26.23 21.04
Me
Me
f1 (ppm)

5j


6.83
3.63
2.56
2.56
2.56
2.26
2.25
1.68
1.67
1.67
1.66
1.66
1.65
1.65
1.64
1.55
1.54
1.54
1.53
1.53
Br
2.00
2.11
2.11
3.10
6.16
4.27
2.34
f1 (ppm)


137.33
135.57
133.71
132.94
128.91
120.02
37.09
36.68
29.27
24.99
22.73
20.98
20.55
Br
f1 (ppm)

1


7.87
7.85
7.84
7.82
7.65
7.64
7.58
7.57
7.56
7.56
7.55
7.55
7.54
7.54
4.08
4.07
4.06
4.05
4.04
4.03
4.02
4.01
4.00
3.99
3.99
3.98
3.97
1.11
1.10
1.09
1.09
Ph2P
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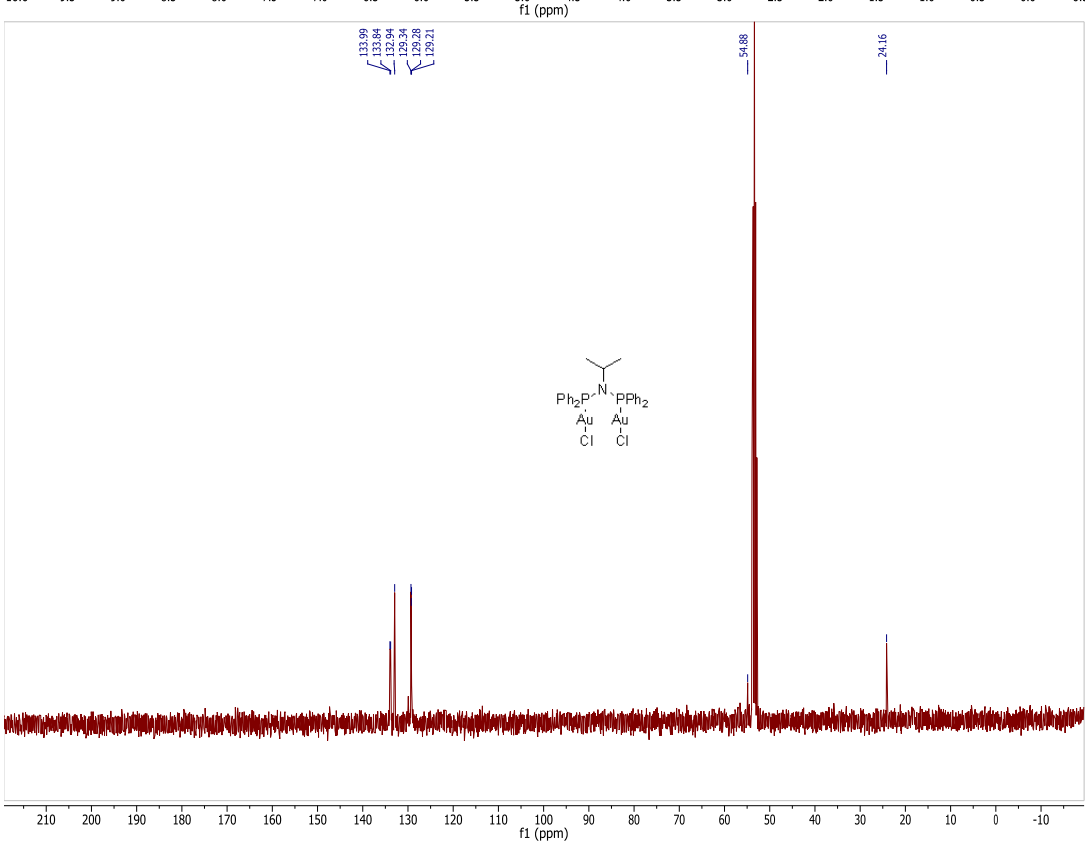
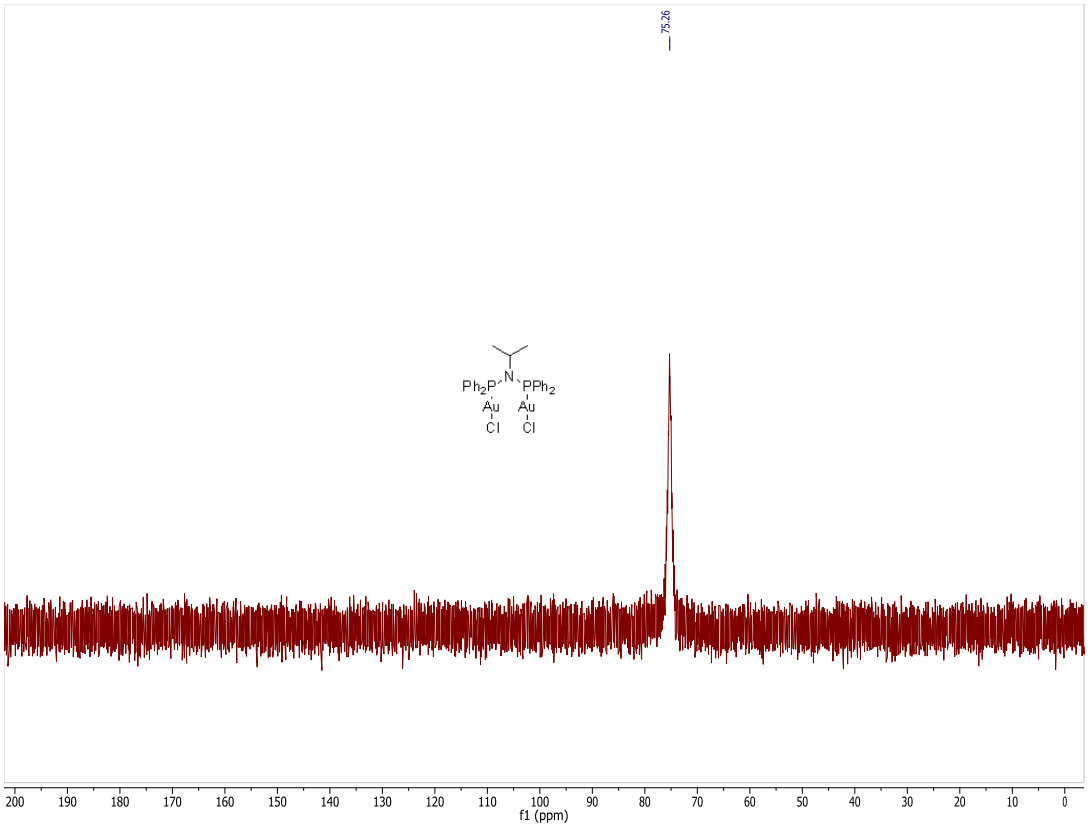
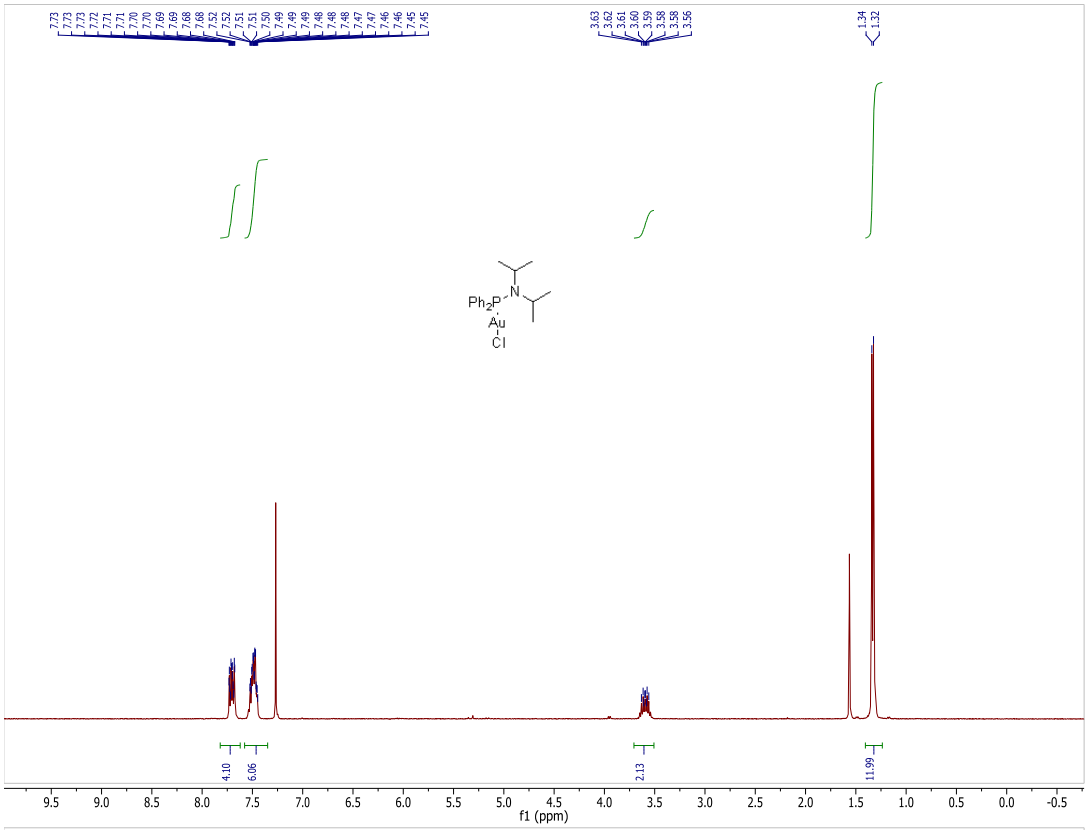
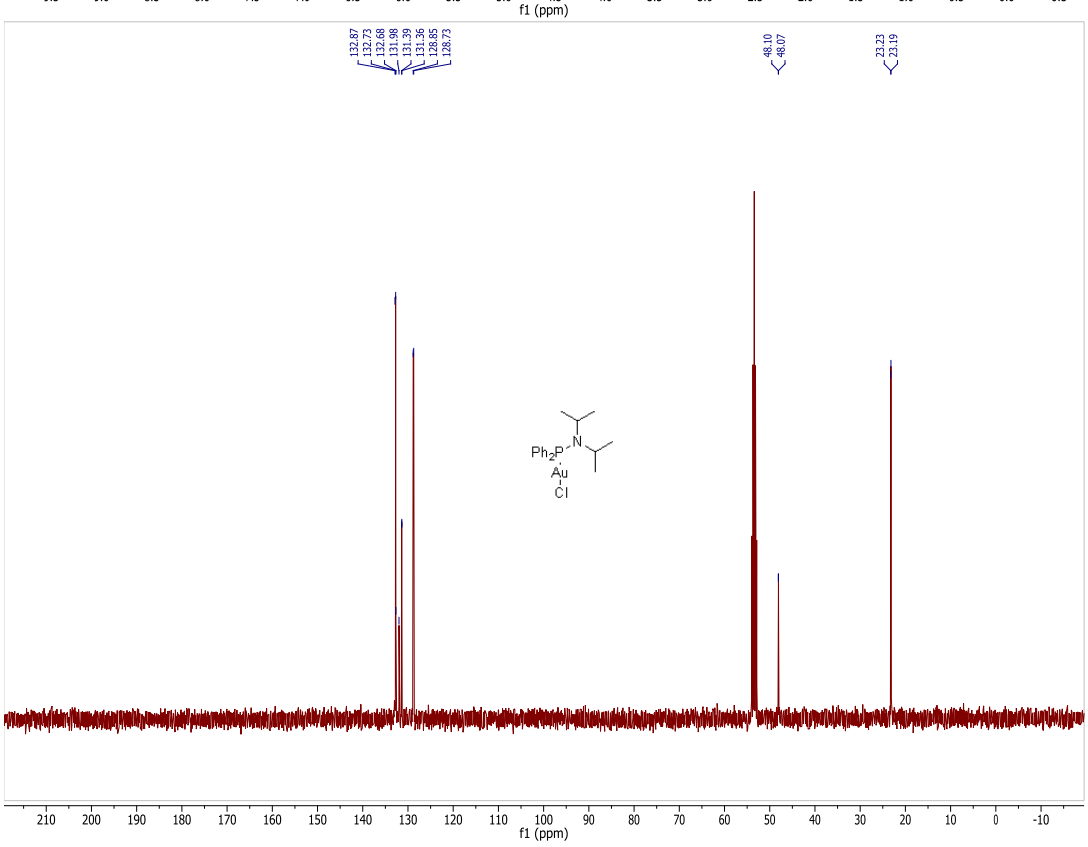
PPh2
Au
Au
Cl
Cl
7.94
4.12
8.00
1.05
6.17
f1 (ppm)

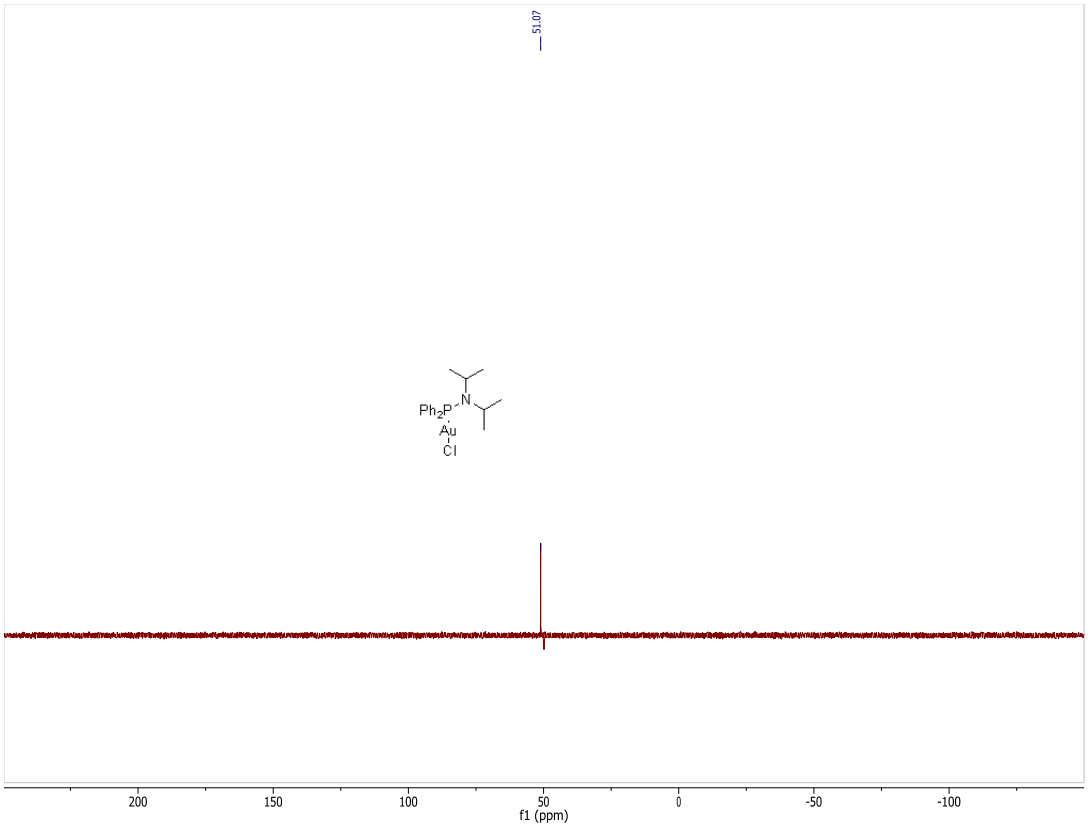

133.99
133.84
132.94
129.34
129.28
129.21
54.88
24.16
Ph2P
N
PPh2
Au
Au
Cl
Cl
f1 (ppm)


75.26
Ph2P
N
PPh2
Au
Cl
Au
Cl
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
f1 (ppm)

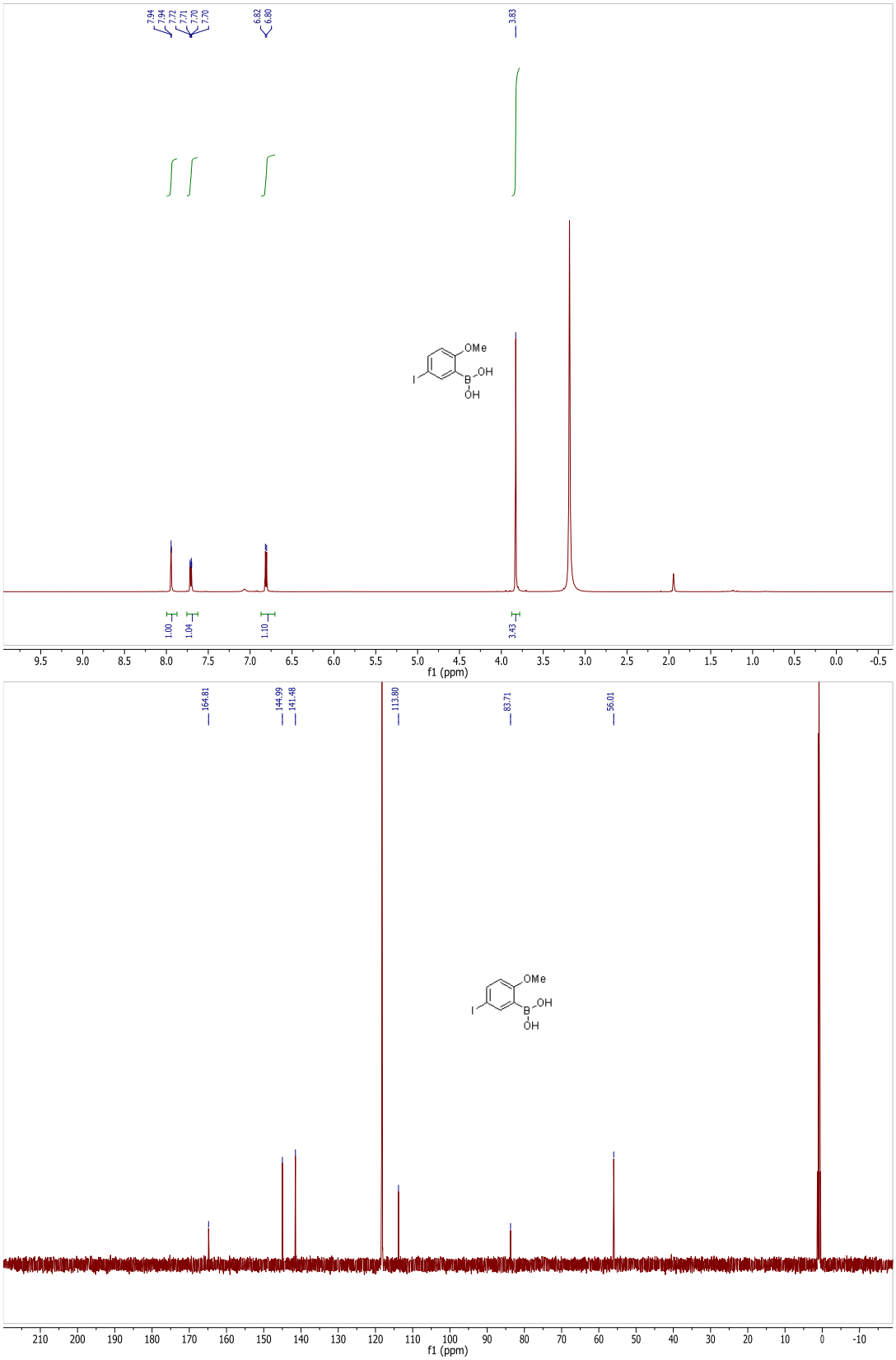
2


7.73
7.73
7.73
7.72
7.71
7.71
7.71
7.70
7.70
7.69
7.69
7.68
7.68
7.52
7.52
7.51
7.51
7.50
7.49
7.49
7.49
7.48
7.48
7.48
7.47
7.47
7.46
7.46
7.45
7.45
3.63
3.62
3.61
3.60
3.59
3.58
3.58
3.56
1.34
1.32
Ph2P
N
Au
Cl
4.10
6.06
2.13
11.99
f1 (ppm)

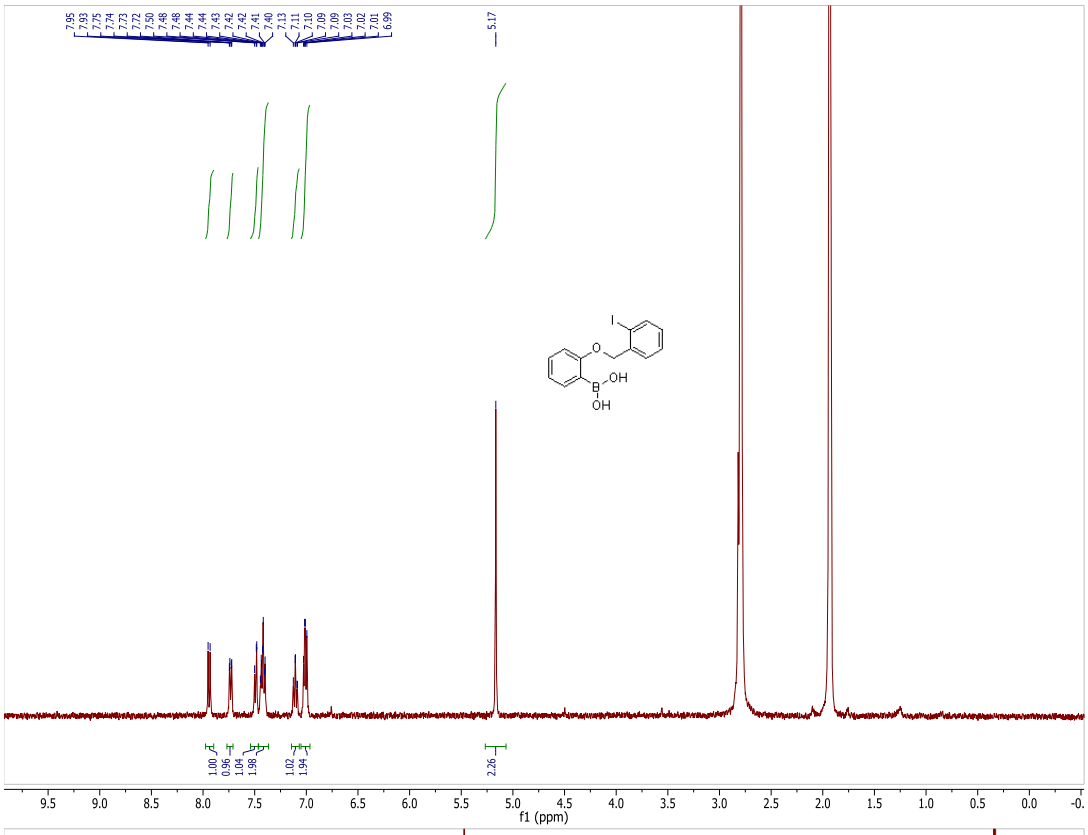

132.87
132.73
132.68
131.98
131.39
131.36
128.85
128.73
48.10
48.07
23.23
23.19
Ph2P
N
Au
Cl
f1 (ppm)

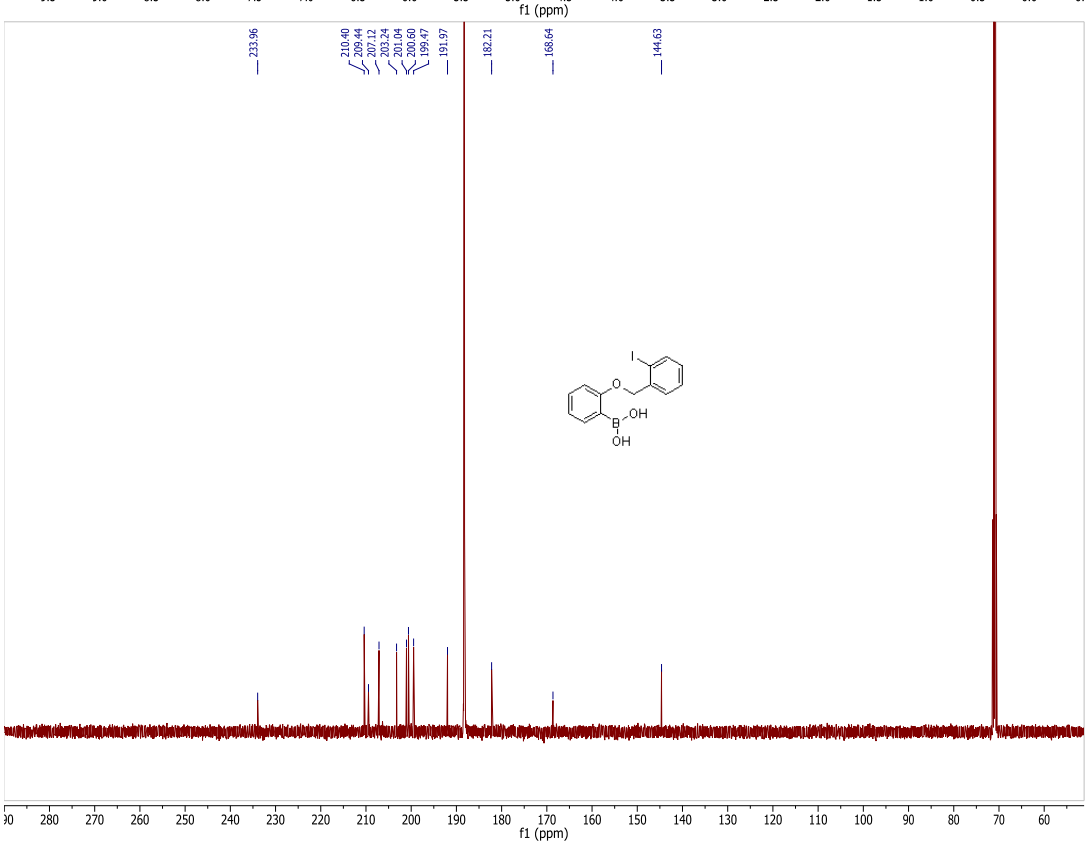

51.07
Ph2P
N
Au
Cl
200
150
100
50
0
-50
-100
f1 (ppm)

S1

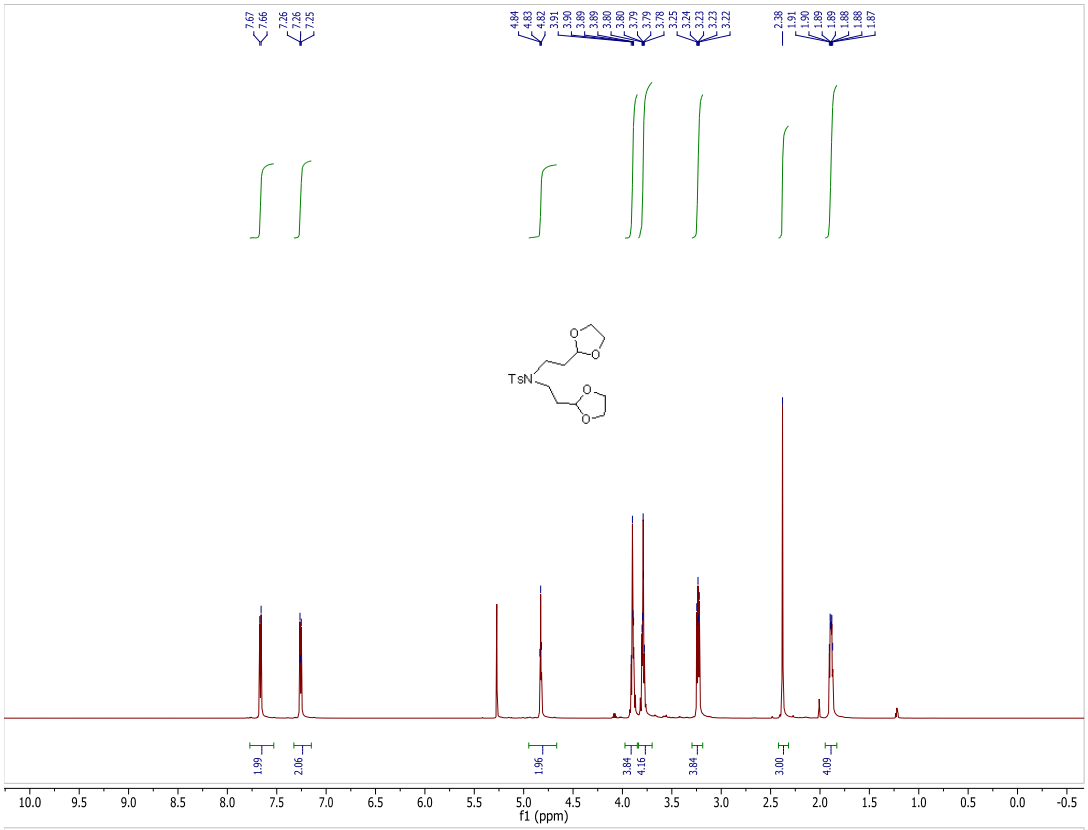

7.94
7.94
7.72
7.71
7.70
7.70
6.82
6.80
3.83
OMe
I
B
OH
OH
1.00
1.04
1.10
3.43
f1 (ppm)
164.81
144.99
141.48
113.80
83.71
56.01
OMe
I
B
OH
OH
f1 (ppm)

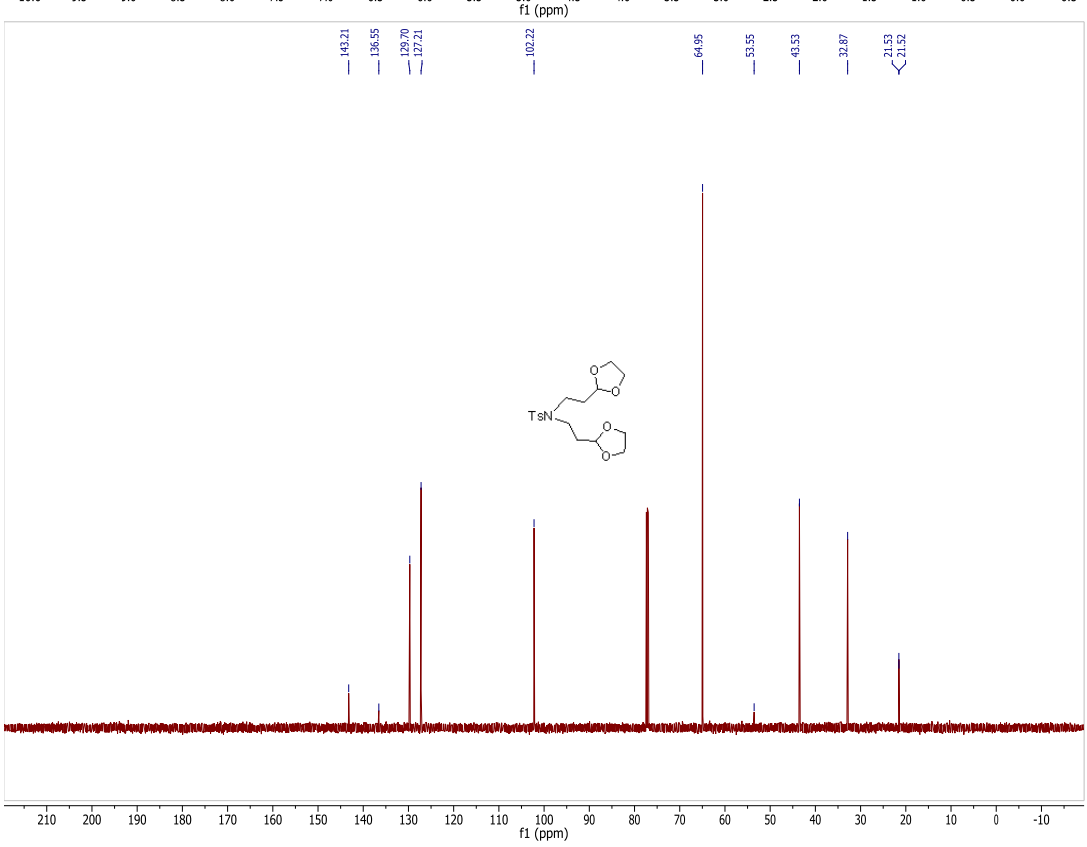
7


7.95
7.93
7.75
7.74
7.73
7.72
7.50
7.48
7.46
7.44
7.43
7.42
7.41
7.40
7.13
7.11
7.10
7.09
7.09
7.03
7.02
7.01
6.99
5.17
I
O
B
OH
OH
1.00
0.96
1.04
1.98
1.02
1.94
2.26
f1 (ppm)

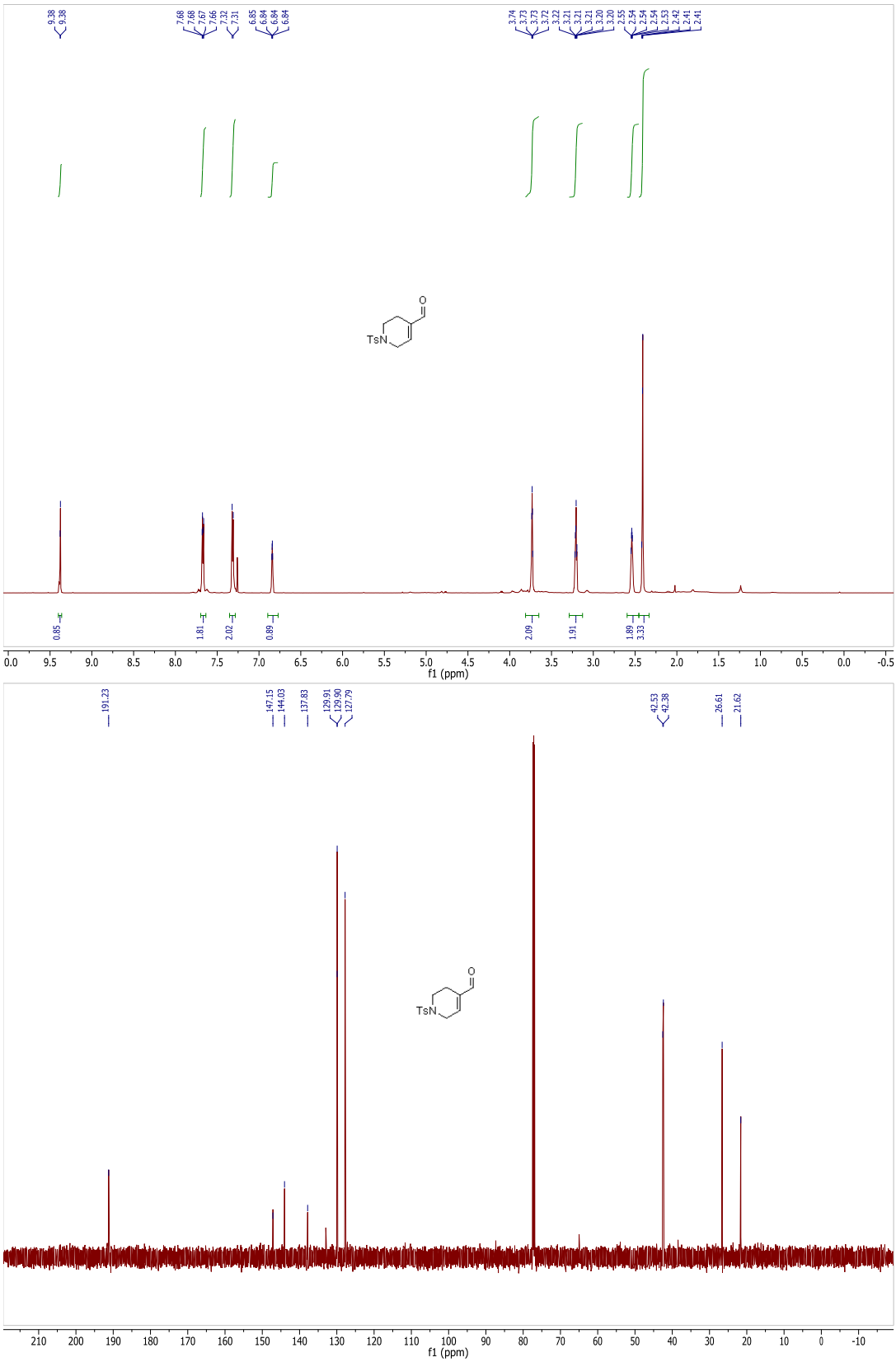

233.96
210.40
209.44
207.12
203.24
201.04
200.60
199.47
191.97
182.21
168.64
144.63
I
O
B
OH
OH
f1 (ppm)

S2

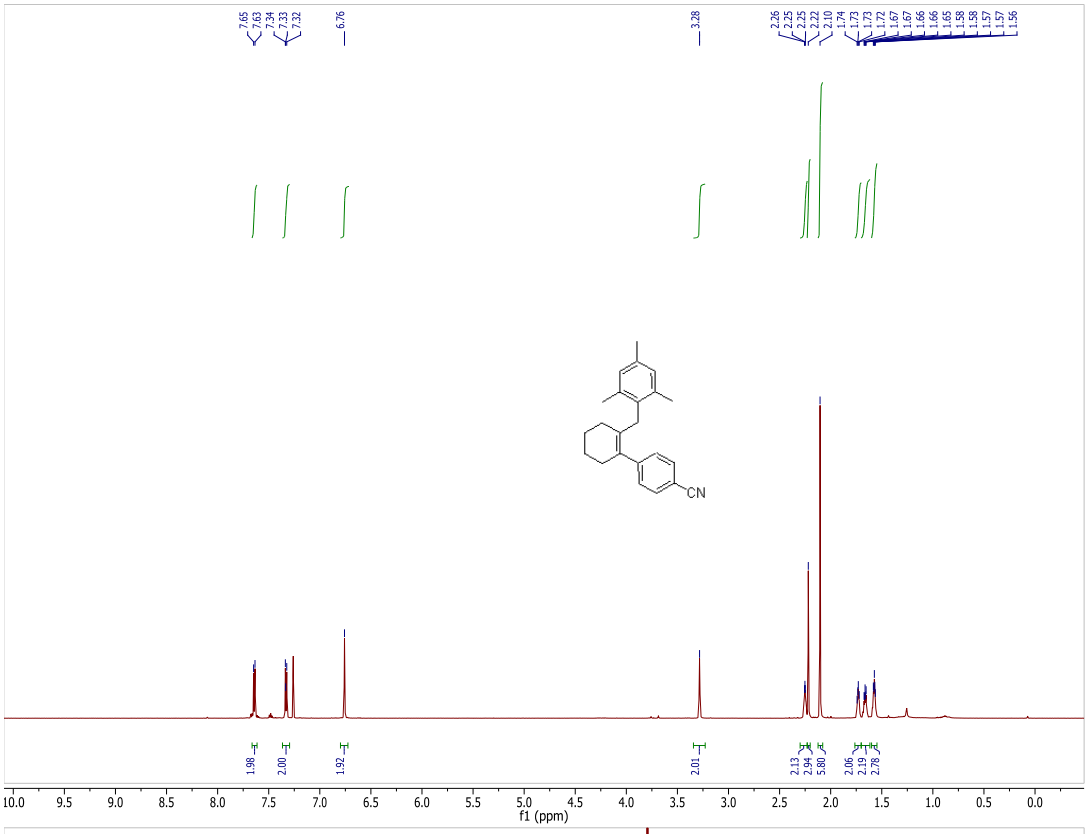

7.67
7.66
7.26
7.26
7.25
4.84
4.83
4.82
3.91
3.90
3.89
3.89
3.80
3.80
3.79
3.79
3.78
3.25
3.24
3.23
3.23
3.22
2.38
1.91
1.90
1.89
1.89
1.88
1.88
1.87
TsN
1.99
2.06
1.96
3.84
4.16
3.84
3.00
4.09
f1 (ppm)

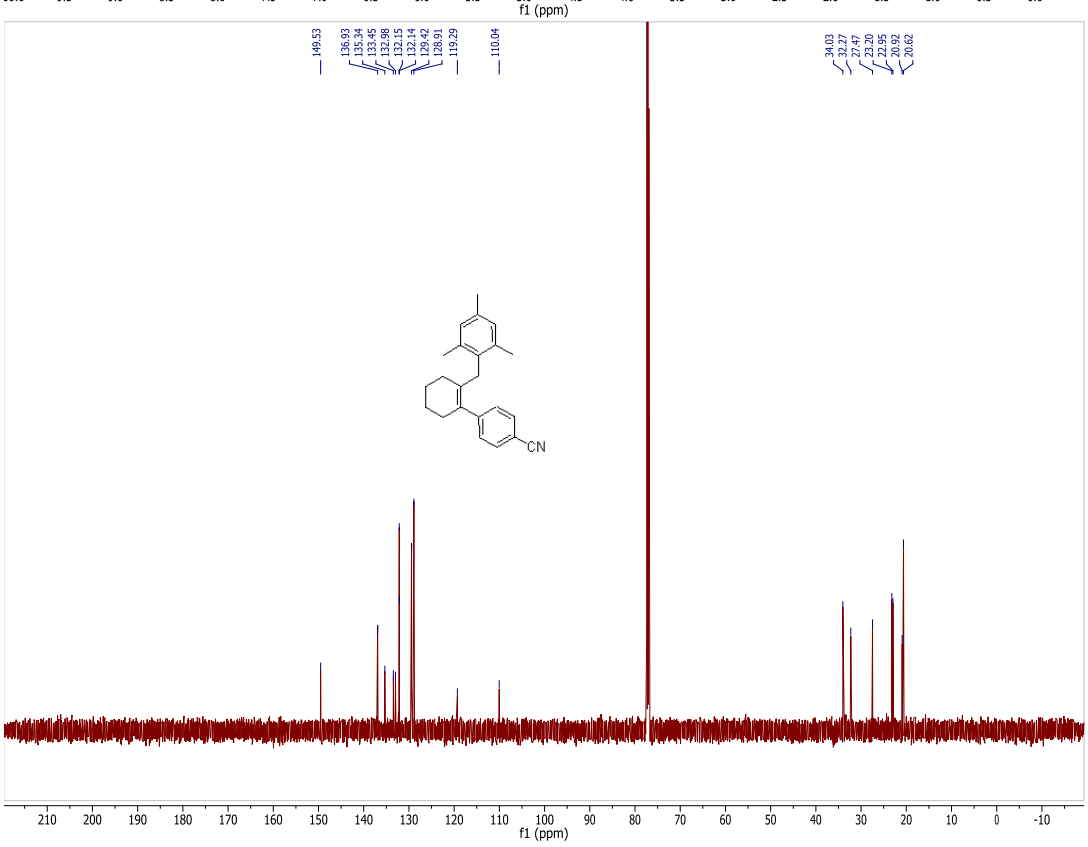

143.21
136.55
129.70
127.21
102.22
64.95
53.55
43.53
32.87
21.53
21.52
TsN
f1 (ppm)

S3

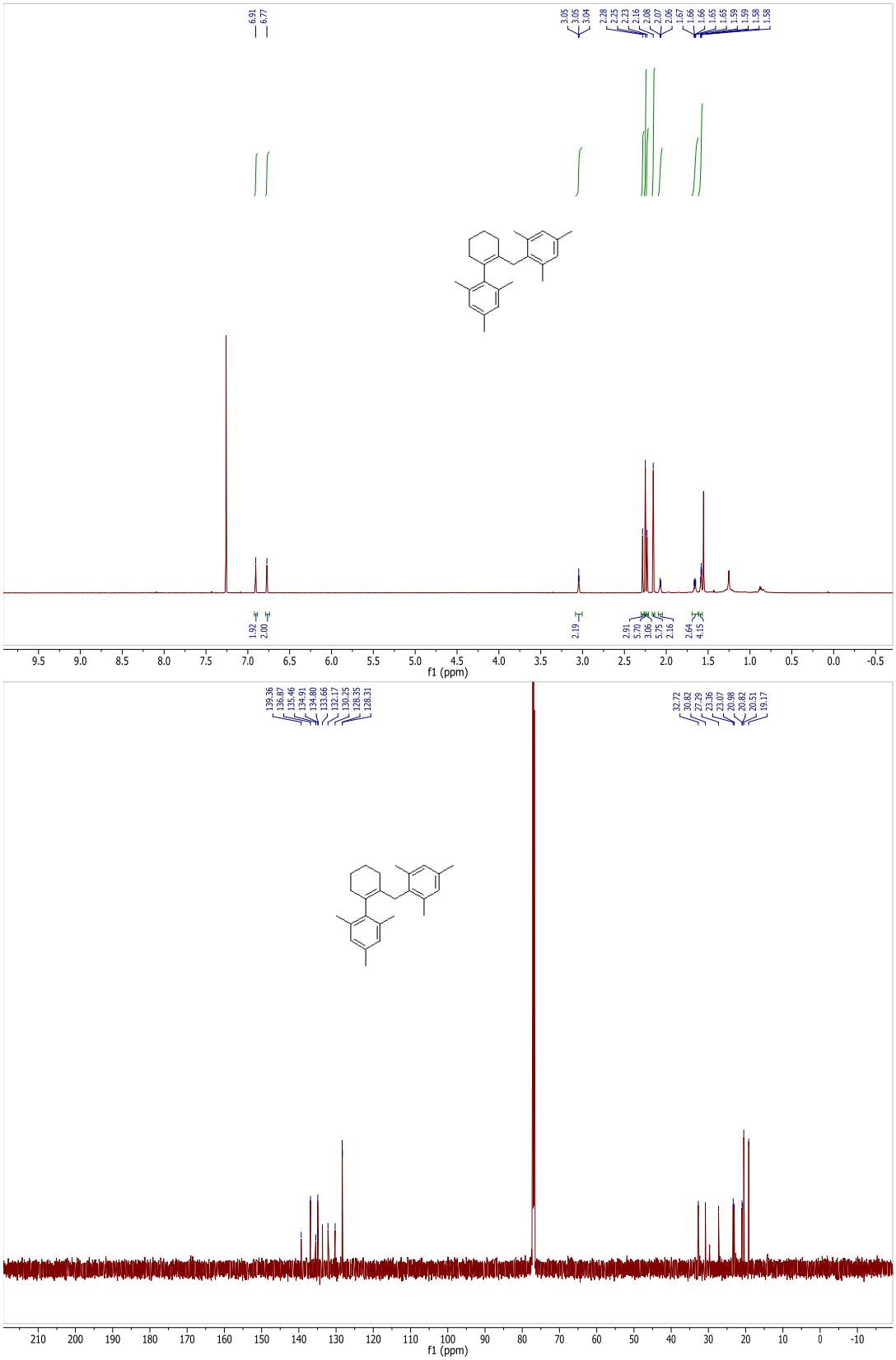

9.38
9.38
7.68
7.68
7.67
7.66
7.32
7.31
6.85
6.84
6.84
6.84
3.74
3.73
3.73
3.72
3.22
3.21
3.21
3.20
3.20
2.55
2.54
2.54
2.54
2.53
2.42
2.41
2.41
O
TsN
0.85
1.81
2.02
0.89
2.09
1.91
1.89
3.33
f1 (ppm)
191.23
147.15
144.03
137.83
129.91
129.90
127.79
42.53
42.38
26.61
21.62
O
TsN
f1 (ppm)

6

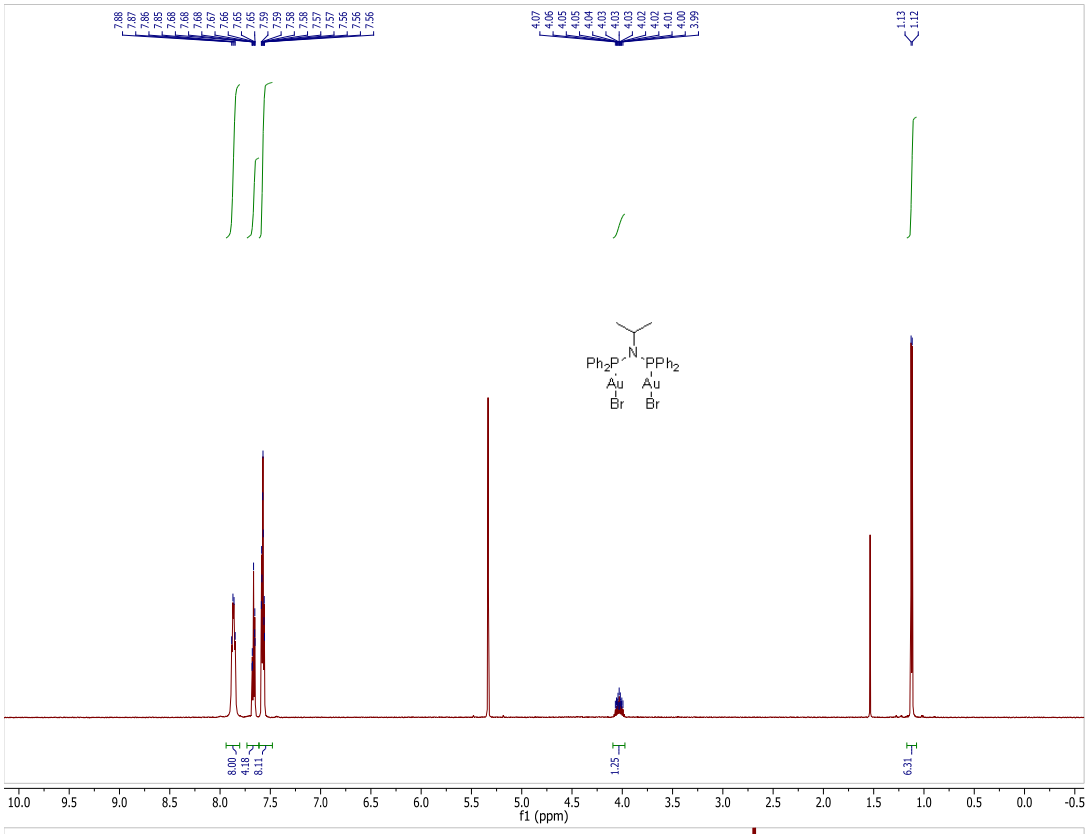

7.65
7.63
7.34
7.33
7.32
6.76
3.28
2.26
2.25
2.25
2.22
2.10
1.74
1.73
1.73
1.72
1.67
1.67
1.66
1.66
1.65
1.58
1.58
1.57
1.57
1.56
CN
1.98
2.00
1.92
2.01
2.13
2.94
5.80
2.06
2.19
2.78
f1 (ppm)

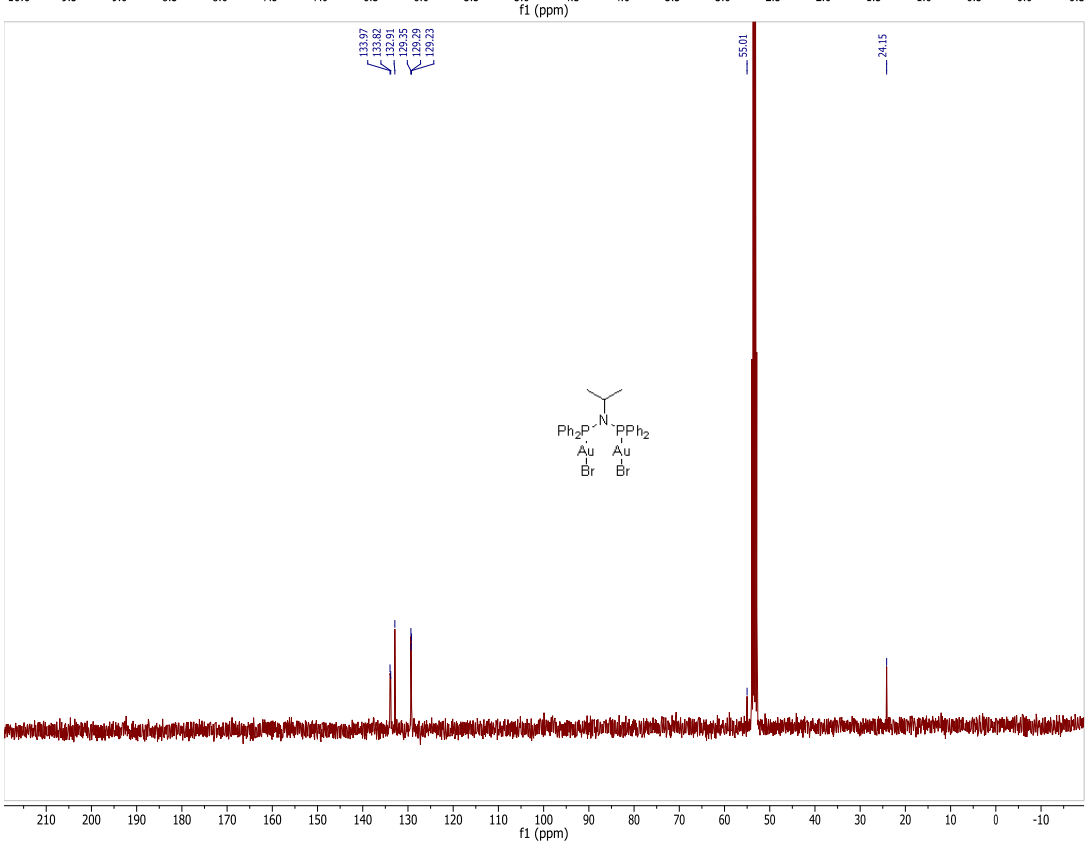

149.53
136.93
135.34
133.45
132.98
132.15
132.14
129.42
128.91
119.29
110.04
34.03
32.27
27.47
23.20
22.95
20.92
20.62
CN
f1 (ppm)

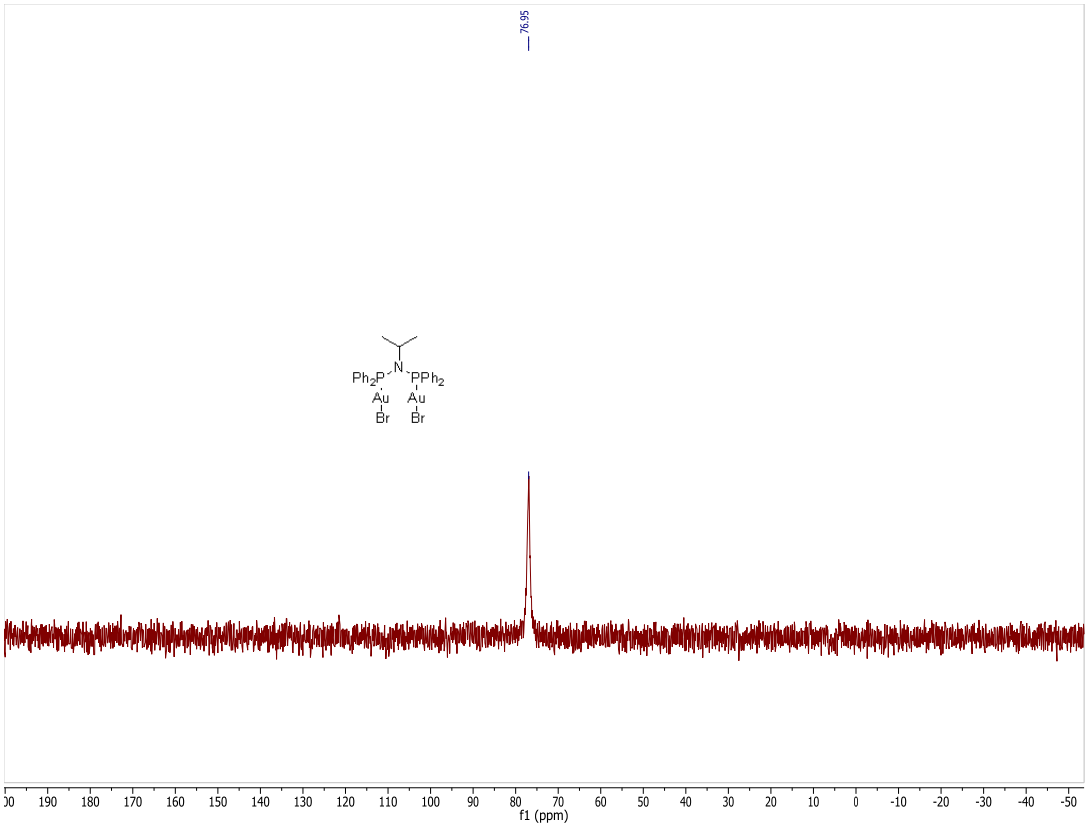
5g-2


6.91
6.77
3.05
3.05
3.04
2.28
2.25
2.23
2.16
2.08
2.07
2.06
1.67
1.66
1.66
1.65
1.59
1.59
1.58
1.58
1.92
2.00
2.19
2.91
5.70
3.06
5.75
2.16
2.64
4.15
f1 (ppm)
139.36
136.87
135.46
134.91
134.80
133.66
132.17
130.25
128.35
128.31
32.72
30.82
27.29
23.36
23.07
20.98
20.82
20.51
19.17
f1 (ppm)

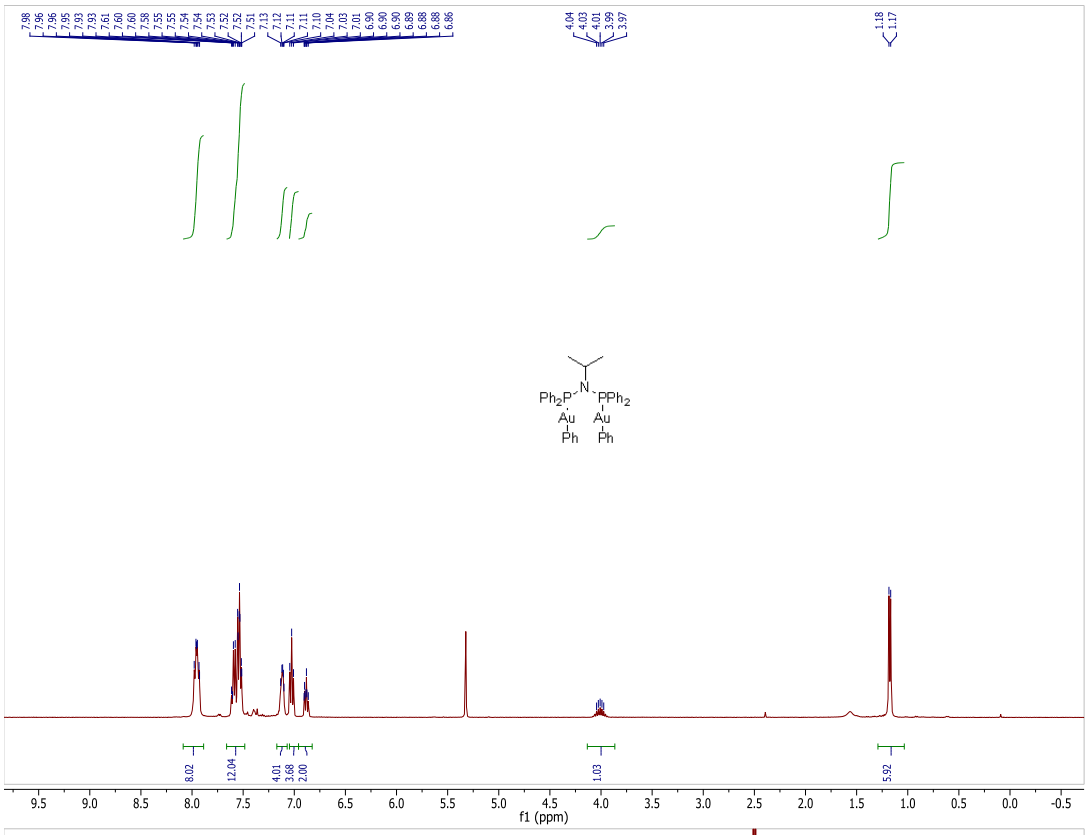
8

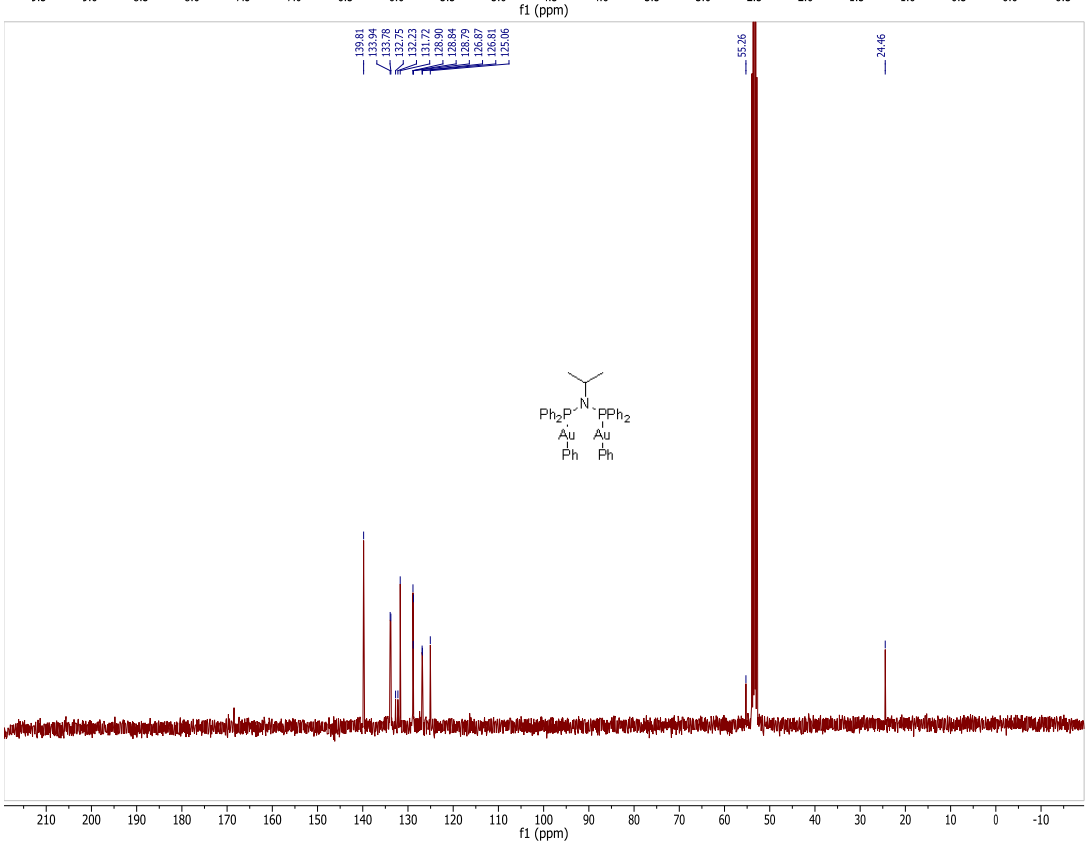

7.88
7.87
7.86
7.85
7.68
7.68
7.68
7.67
7.66
7.65
7.65
7.59
7.59
7.58
7.58
7.57
7.57
7.56
7.56
7.56
4.07
4.06
4.05
4.05
4.04
4.03
4.03
4.03
4.02
4.02
4.01
4.00
3.99
1.13
1.12
Ph2P
N
PPh2
Au
Au
Br
Br
8.00
4.18
8.11
1.25
6.31
10.0
9.5
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
-0.5
f1 (ppm)

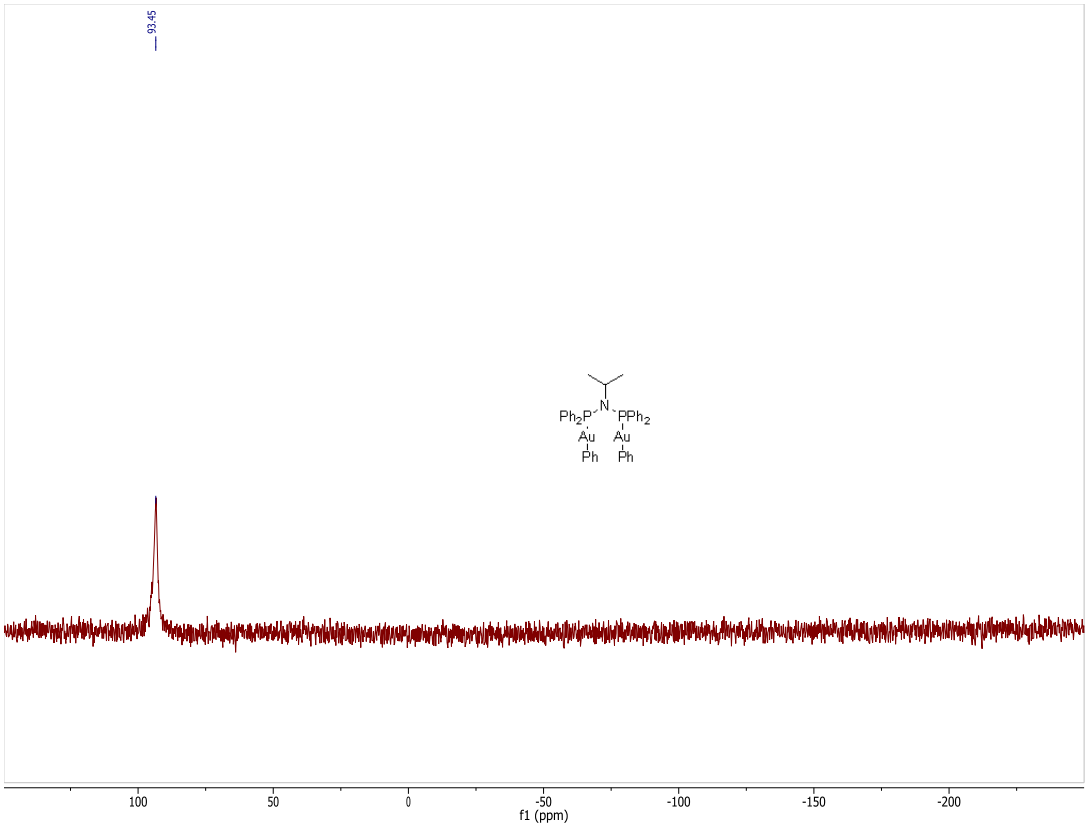

133.97
133.82
132.91
129.35
129.29
129.23
55.01
24.15
Ph2P
N
PPh2
Au
Au
Br
Br
210
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
-10
f1 (ppm)


76.95
Ph2P
N
PPh2
Au
Au
Br
Br
f1 (ppm)

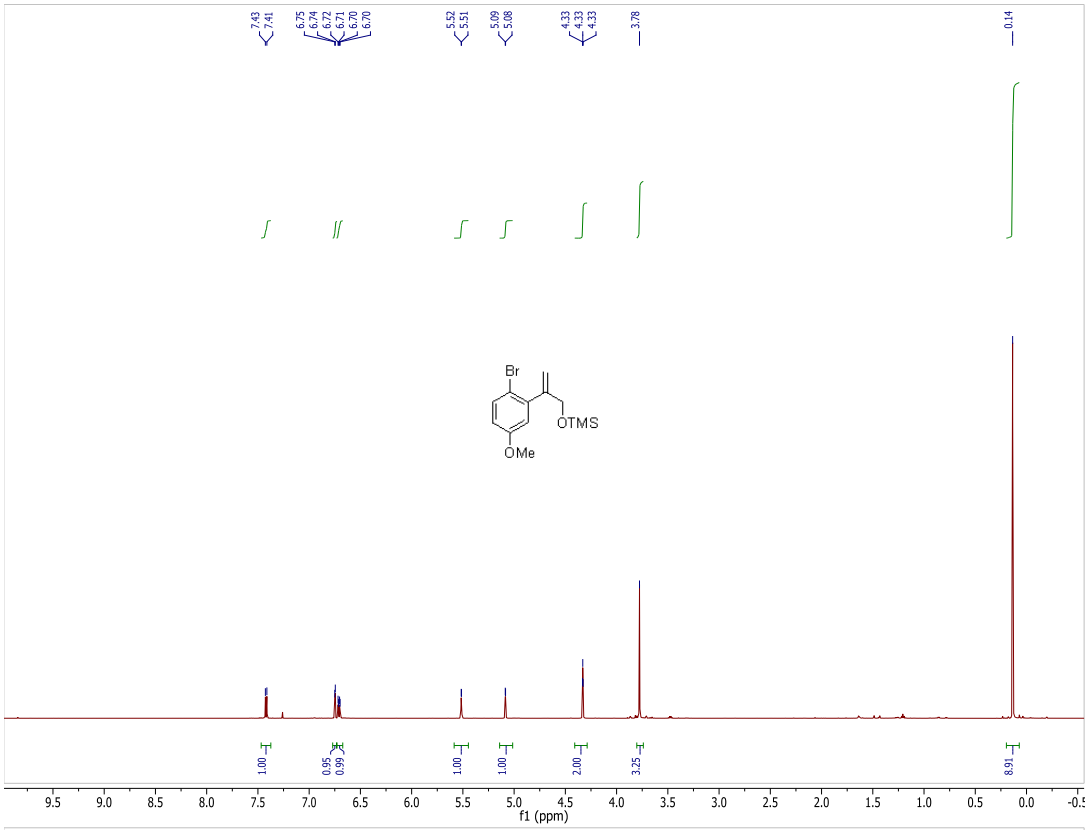
9

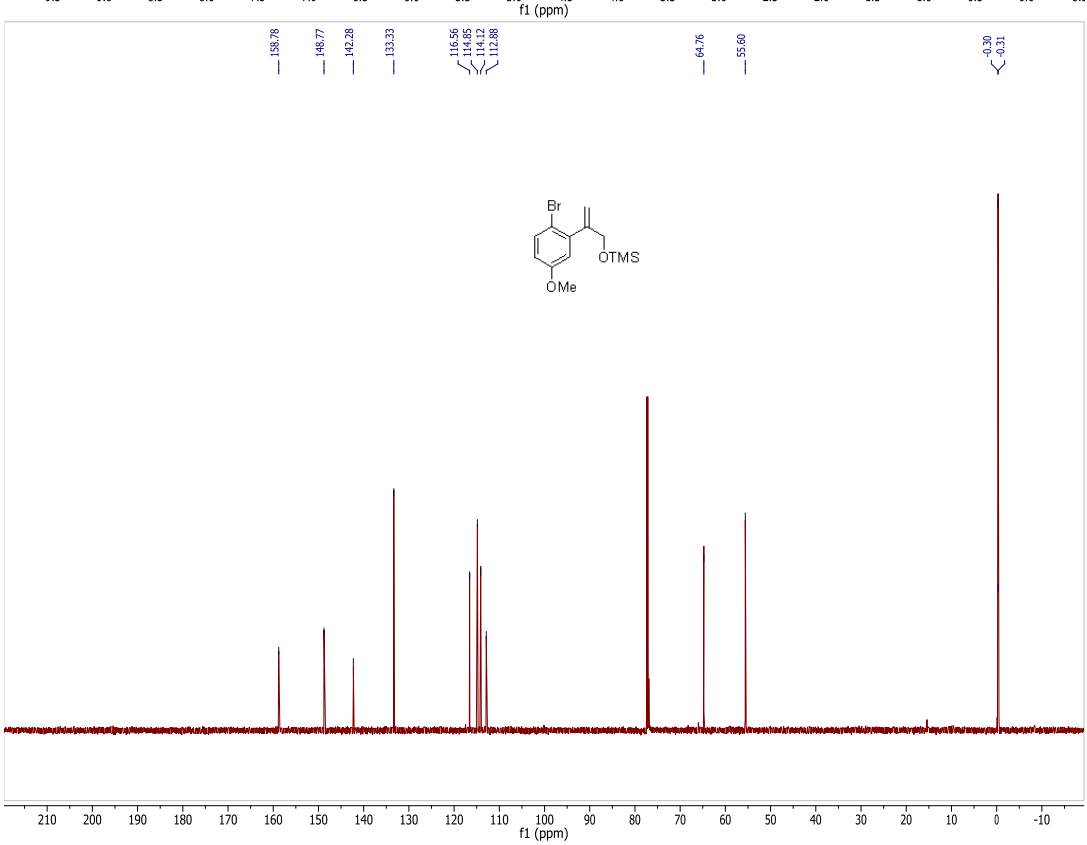

7.98 7.96 7.96 7.95 7.93 7.93 7.61 7.60 7.58 7.55 7.55 7.54 7.54 7.53 7.52 7.52 7.51 7.13 7.12 7.11 7.11 7.10 7.04 7.03 7.01 6.90 6.90 6.89 6.88 6.88 6.86
4.04 4.03 4.01 3.99 3.97
1.18 1.17
Ph2P PPh2
Au Au
Ph Ph
8.02 12.04 4.01 3.68 2.00 1.03 5.92
9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0 -0.5
f1 (ppm)

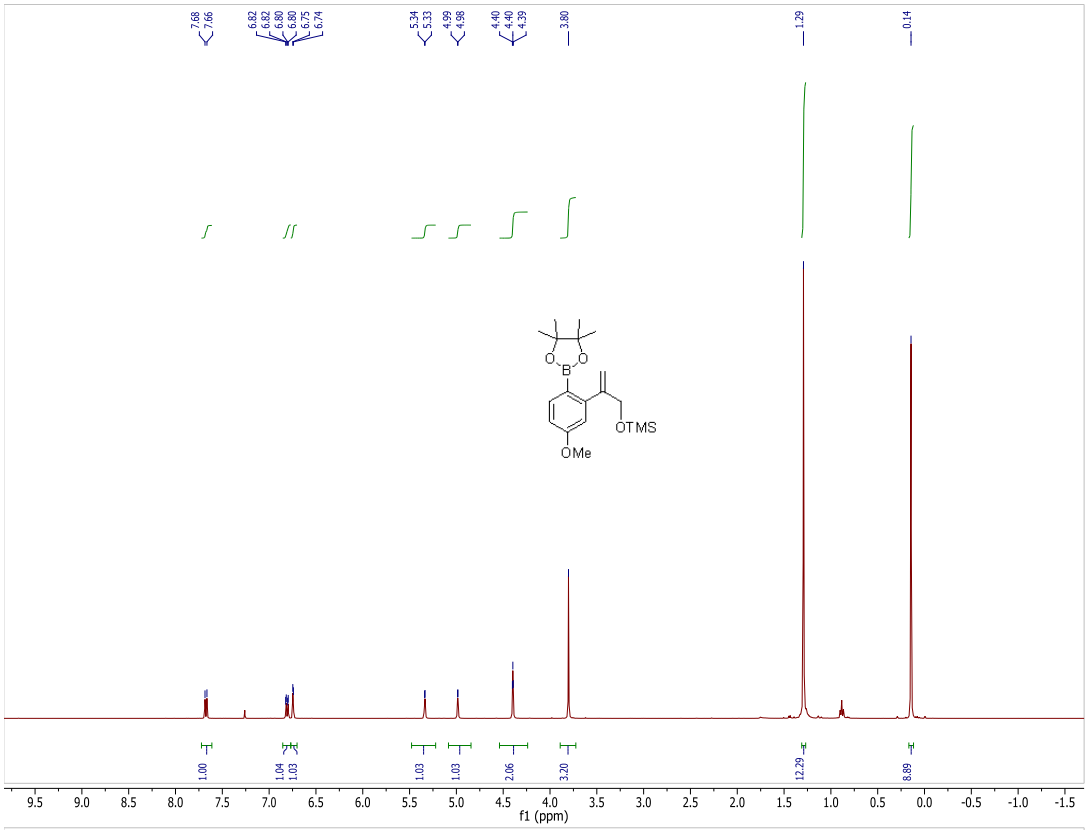

139.81 133.94 133.78 132.75 132.23 131.72 128.90 128.84 128.79 126.87 126.81 125.06
55.26
24.46
Ph2P PPh2
Au Au
Ph Ph
210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 -10
f1 (ppm)

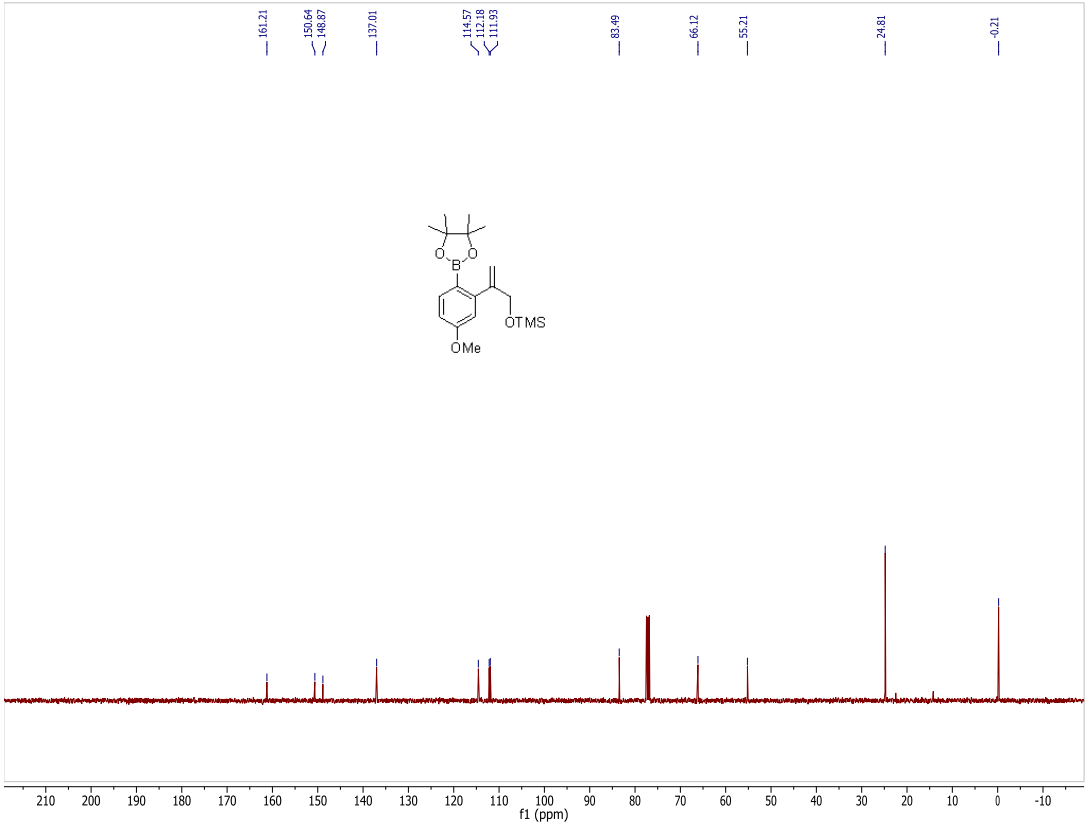

93.45
N
Ph2P
PPh2
Au
Au
Ph
Ph
100
50
0
-50
-100
-150
-200
f1 (ppm)

S10

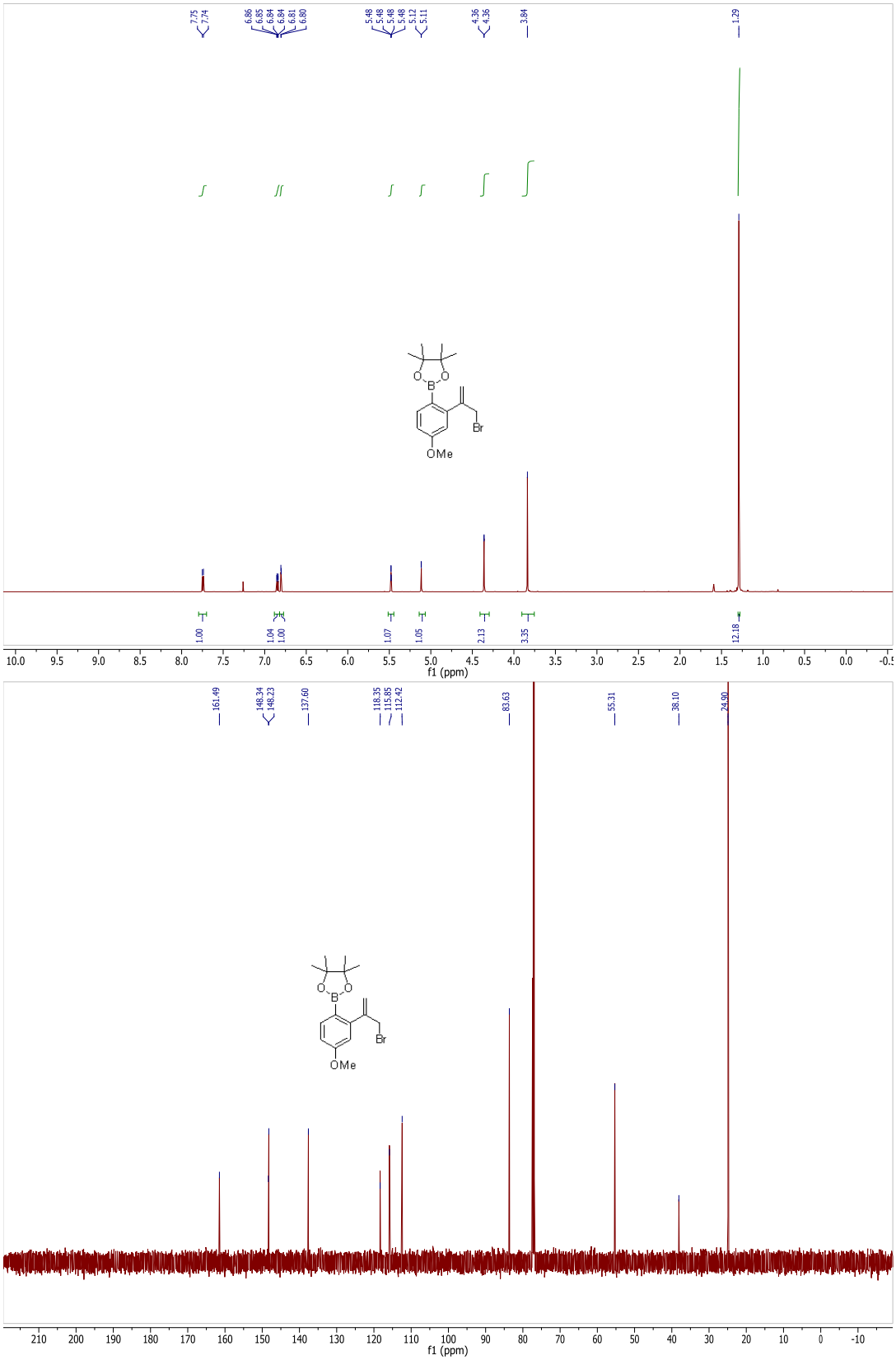

7.43
7.41
6.75
6.74
6.72
6.71
6.70
6.70
5.52
5.51
5.09
5.08
4.33
4.33
4.33
3.78
0.14
Br
OTMS
OMe
1.00
0.95
0.99
1.00
1.00
2.00
3.25
8.91
f1 (ppm)


158.78
148.77
142.28
133.33
116.56
114.85
114.12
112.88
64.76
55.60
-0.30
-0.31
Br
OTMS
OMe
f1 (ppm)

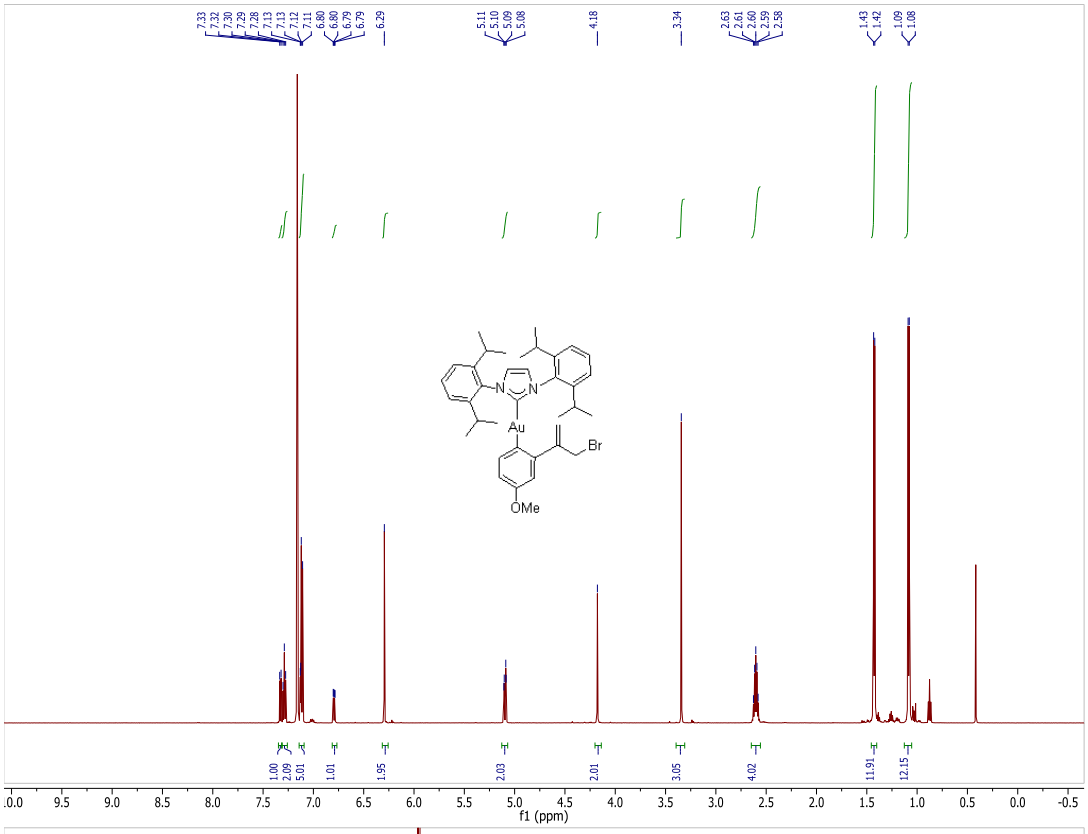

7.68
7.66
6.82
6.82
6.80
6.80
6.75
6.74
5.34
5.33
4.99
4.98
4.40
4.40
4.39
3.80
1.29
0.14
OTMS
OMe
1.00
1.04
1.03
1.03
1.03
2.06
3.20
12.29
8.89
f1 (ppm)

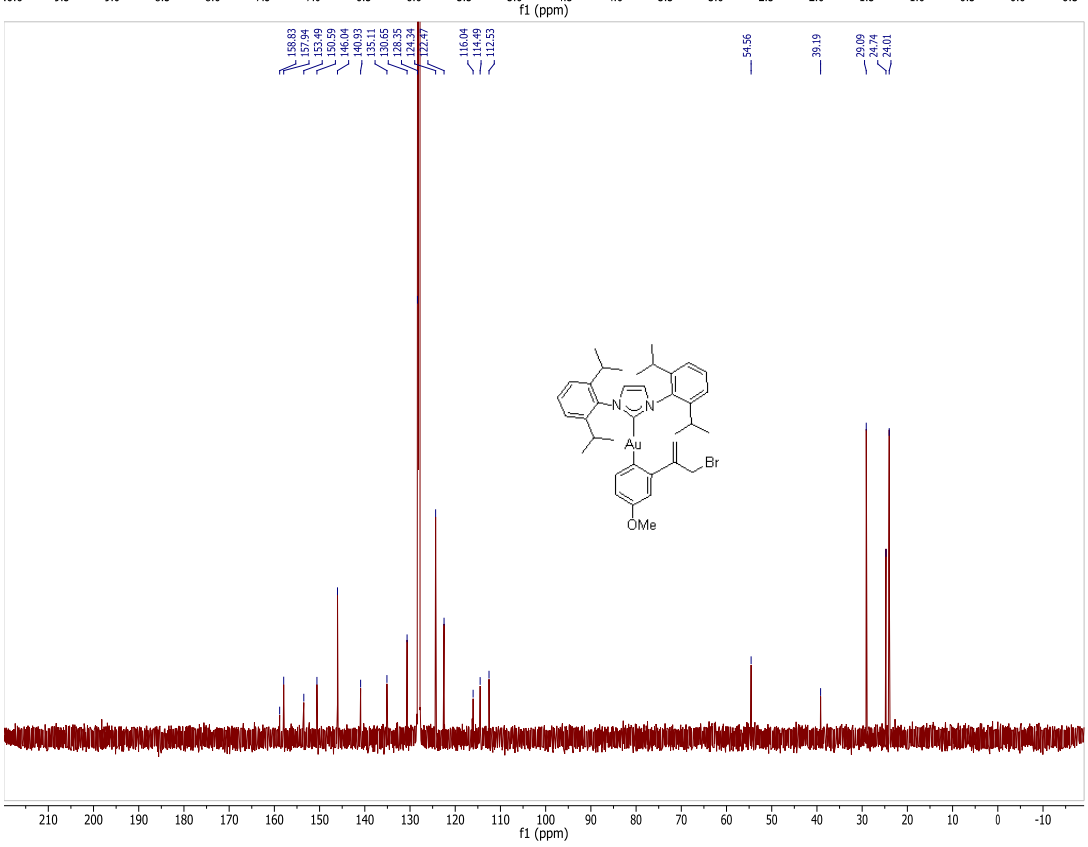

161.21
150.64
148.87
137.01
114.57
112.18
111.93
83.49
66.12
55.21
24.81
-0.21
OTMS
OMe
f1 (ppm)

11

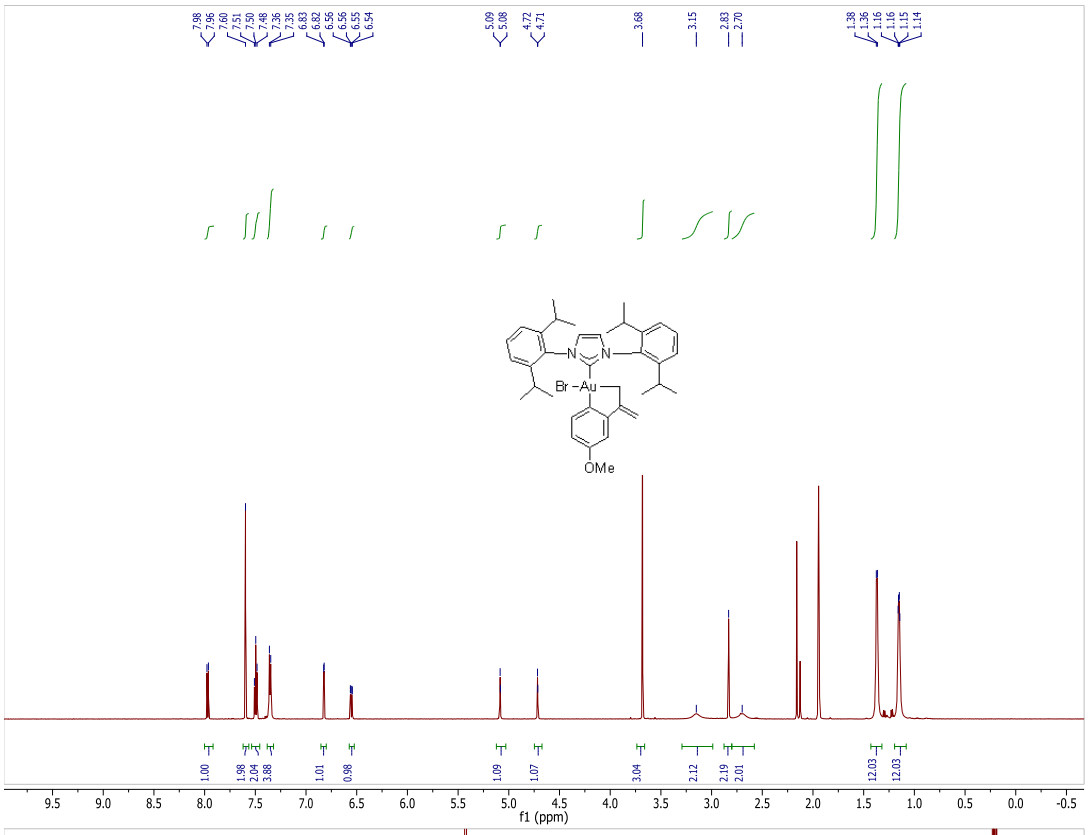

7.75
7.74
6.86
6.85
6.84
6.84
6.81
6.80
5.48
5.48
5.48
5.48
5.12
5.11
4.36
4.36
3.84
1.29
1.00
1.04
1.00
1.07
1.05
2.13
3.35
12.18
f1 (ppm)
161.49
148.34
148.23
137.60
118.35
115.85
112.42
83.63
55.31
38.10
24.90
f1 (ppm)

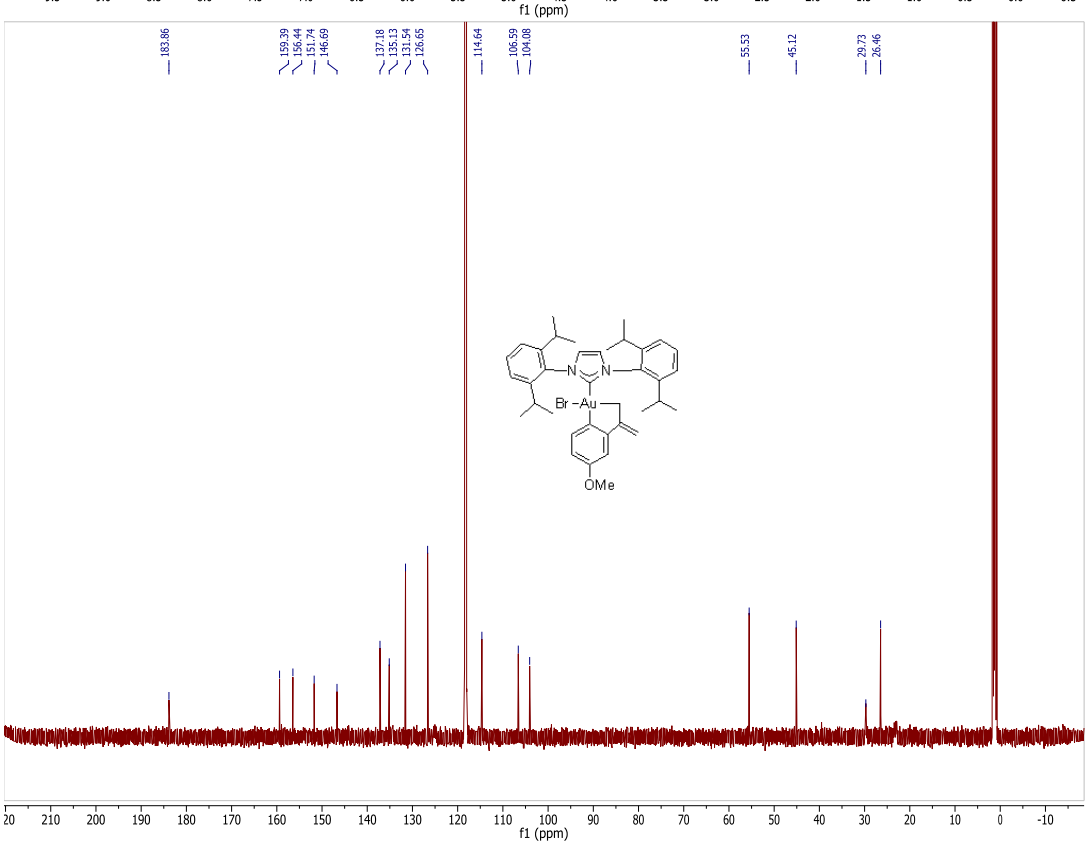
12


7.33
7.32
7.30
7.29
7.28
7.13
7.13
7.12
7.11
6.80
6.80
6.79
6.79
6.29
5.11
5.10
5.09
5.08
4.18
3.34
2.63
2.61
2.60
2.59
2.58
1.43
1.42
1.09
1.08
Au
Br
OMe
1.00
2.09
5.01
1.01
1.95
2.03
2.01
3.05
4.02
11.91
12.15
f1 (ppm)

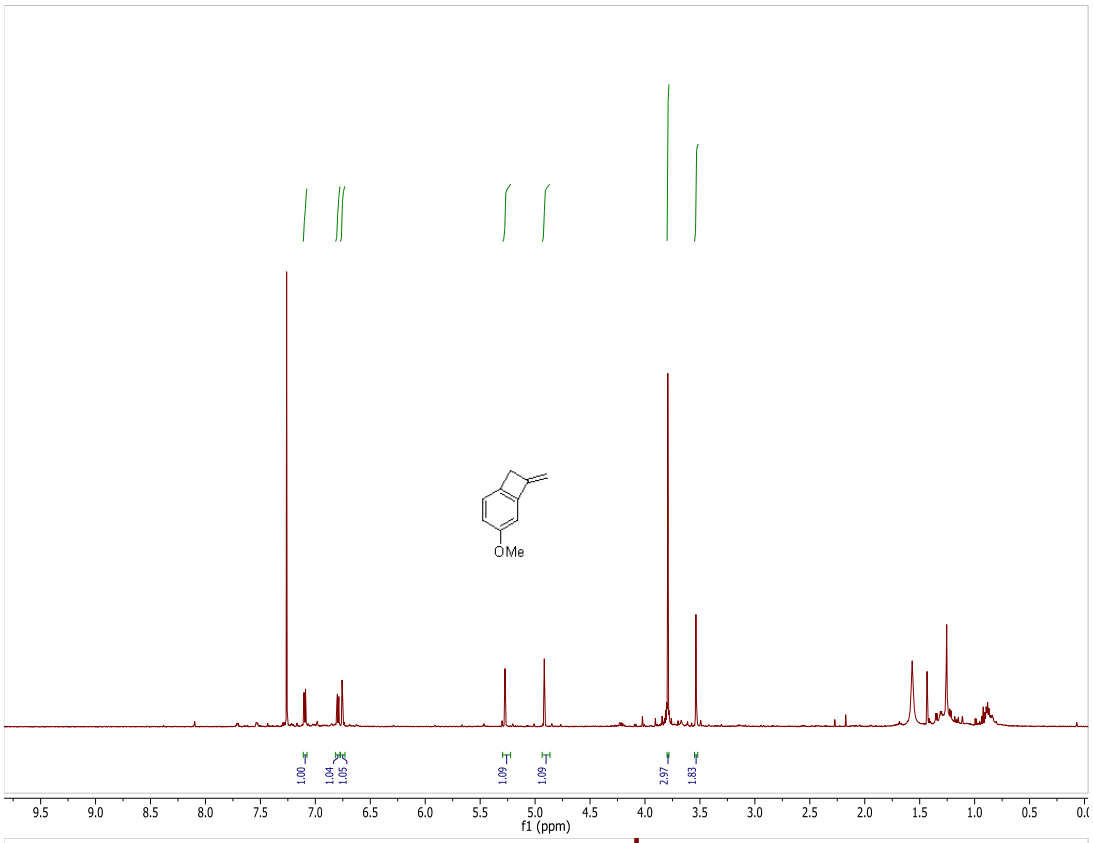

158.83
157.94
153.49
150.59
146.04
140.93
135.11
130.65
128.35
124.34
122.47
116.04
114.49
112.53
54.56
39.19
29.09
24.74
24.01
Au
Br
OMe
f1 (ppm)

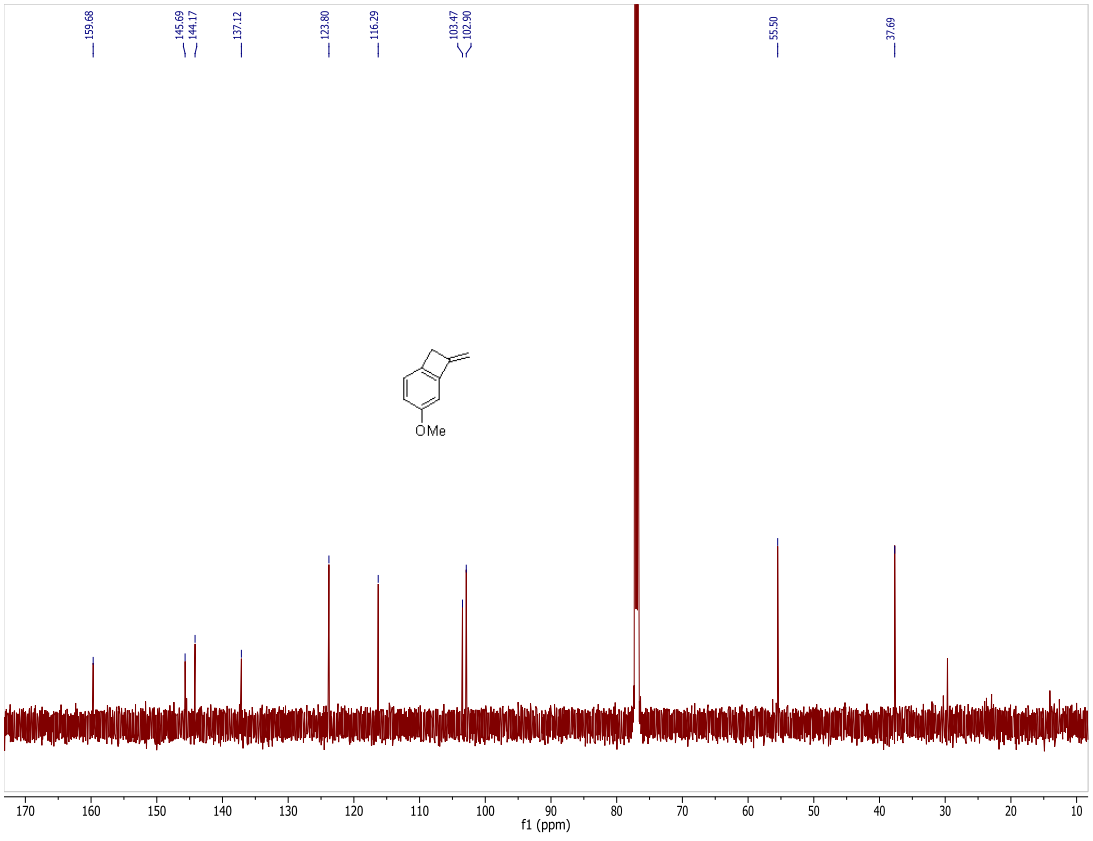
13


7.98
7.96
7.60
7.51
7.50
7.48
7.36
7.35
6.83
6.82
6.56
6.55
6.54
5.09
5.08
4.72
4.71
3.68
3.15
2.83
2.70
1.38
1.36
1.16
1.16
1.15
1.14
Br
Au
OMe
1.00
1.98
2.04
3.88
1.01
0.98
1.09
1.07
3.04
2.12
2.19
2.01
12.03
12.03
f1 (ppm)


183.86
159.39
156.44
151.74
146.69
137.18
135.13
131.54
126.65
114.64
106.59
104.08
55.53
45.12
29.73
26.46
Br
Au
OMe
f1 (ppm)

14


OMe
1.00
1.04
1.05
1.09
1.09
2.97
1.83
f1 (ppm)


159.68
145.69
144.17
137.12
123.80
116.29
103.47
102.90
55.50
37.69
OMe
f1 (ppm)

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