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Bis-phosphine allene ligands: coordination chemistry and preliminary applications in catalysis

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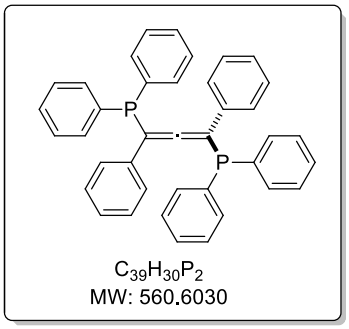
1. General information

All reactions were performed in oven-dried glassware under argon atmosphere. All solvents were freshly distilled prior to use: Et_2O and THF over sodium and benzophenone; CH_2Cl_2 over CaH_2. DMF was dried and degassed before using. Technical grade solvents for extraction and chromatography were used without distillation. *n*-Butyllithium was purchased as 2.5 M solutions in hexanes and titrated before using. NaH was purchased as a 60% suspension in mineral oil and washed with pentane under argon atmosphere before using. Column chromatography was performed on Merck Geduran SI 60 A silica gel (35-70 mm). Analytical Thin-layer chromatography (TLC) was performed on Merck 60 F_{254} silica gel and visualized either with a UV lamp (254 nm), or using solutions of *p*-anisaldehyde-sulfuric acid-acetic acid in EtOH or $KMnO_4$-K_2CO_3 in water followed by heating. ^1H NMR spectra were recorded at 400 MHz, 300 MHz or 600 MHz and data are reported as follows: chemical shift in ppm with the solvent as an internal indicator ($CDCl_3$ δ 7.26, CD_2Cl_2 δ 5.32, C_6D_6 δ 7.16), multiplicity (s = singlet, d = doublet, t = triplet, q = quartet or m = multiple and b = broad) and integration. ^{13}C NMR spectra were recorded at 100 MHz, 75 MHz or 151 MHz and data are reported as follows: chemical shift in ppm with the solvent as an internal indicator ($CDCl_3$ δ 77.16, CD_2Cl_2 δ 54.00, C_6D_6 δ 128.06). ^{31}P NMR spectra were recorded at 122 MHz or 162 MHz and data are reported as follows: chemical shift in ppm with an internal probe of H_3PO_4 (85% in H_2O, δ 0.0). Coupling constants (*J*) are given in Hertz (Hz). High-resolution mass spectra (HRMS) were obtained using a mass spectrometer MicroTOF from Bruker with an electron spray ion source (ESI) and a TOF detector at Institut Parisien de Chimie Moléculaire. Melting points (m.p.) were recorded with a SMP3 Stuart Scientific melting point apparatus. Infrared (IR) spectra were measured using Tensor 27 (ATR Diamond) Bruker spectrometer. IR data are reported as characteristic band (cm^{-1}) in their maximal intensity. Optical rotations were determined using a JASCO P2000. Chiral HPLC analyses were achieved on an Agilent 1260 infinity unit with pump, autosampler, oven, DAD and Jasco CD-2095 circular dichroism detector, controlled by a SRA Instrument software (Marcy l'Etoile, France) at Institut des Sciences Moléculaires de Marseille.

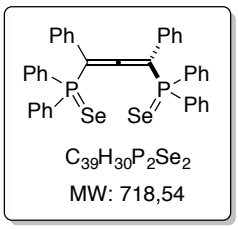
2. Experimental details and analytical data

1,3-Bis(diphenylphosphino)-1,3-diphenylpropa-1,2-diene (1)



To a solution of 1,3-diphenyl-1-propyne [1] (1.50 g, 7.80 mmol, 1 equiv) in THF (80 mL) was added *n*-BuLi (6.24 mL of 2.5 M in hexane, 15.60 mmol, 2 equiv) at –78 °C. The solution of chlorodiphenylphosphine (2.9 mL, 15.60 mmol, 2 equiv) in THF (10 mL) was slowly added into the mixture at the same temperature. The mixture was slowly warmed to room temperature for 15 h and concentrated under reduce pressure. The residue was precipitated in the mixture of ethanol and water (1:1) to obtain **1** (2.12 g, 48% yield) as a white solid. (*Note*: The product was stable in the solid under argon atmosphere and slowly oxidized in small amount of oxygen).
The characterization data were identical to those previously reported.[2]
m.p. = 160–163 °C.
IR (neat): ῡ (cm^{-1}) = 3057, 2226, 1902, 1595, 1492, 1437, 1187, 1120, 910, 729, 694.
^{1}H NMR (400 MHz, $CDCl_3$) δ 7.47 (d, *J* = 8.4 Hz, 5H), 7.35-7.12 (m, 22H), 7.01 (t, *J* = 7.7 Hz, 3H).
^{13}C NMR (100 MHz, $CDCl_3$) δ 209.9 (d, $^{2}J_{CP}$ = 3.5 Hz, C), 136.0, 135.9, 135.8, 135.6, 135.2, 135.0, 134.9, 134.8, 133.8 (2CH), 133.6, 132.0, 131.7, 131.6, 129.6, 129.2 (2CH), 128.8, 128.7, 128.6, 128.5, 128.4, 128.3 (2CH), 128.2 (2CH), 128.1 (2CH), 128.0, 127.7, 127.4, 127.2 , 127.1, 127.0 (CH), 105.0 (d, $^{1}J_{CP}$ = 3.6 Hz, C), 104.8 (d, $^{1}J_{CP}$ = 3.0 Hz, C)
^{31}P NMR (162 MHz, $CDCl_3$) δ – 8.8.
HRMS (ESI) calcd. for $C_{39}H_{30}P_2H$ ($[M + H]^+$) 561.18955 found 561.18941.

1,3-Bis(diphenylphosphoroselenoyl)-1,3-diphenylpropa-1,2-diene (2)

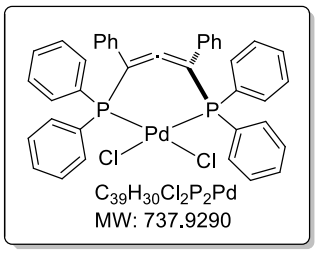


The solution of **1** (0.10 g, 0.18 mmol, 1 equiv) and small pieces of selenium (0.08 g, 1.03 mmol, 7.2 equiv) in $CDCl_3$ (17 mL) was stirred at reflux overnight (24 h). After monitoring the reaction by ^{31}P NMR, the mixture was filtered to remove selenium and concentrated to afford **2** (0.17 g, quant) as a yellow solid.
The characterization data were identical to those previously reported.[2]

m.p. = 207–208 °C.
IR (neat): ῡ (cm^{-1}) = 3079, 2221, 1899, 1594, 1492, 1435, 1335, 1184, 1095, 1029, 999, 908, 715.
^{1}H NMR (300 MHz, $CDCl_3$) δ 7.63-7.46 (m, 10H), 7.41-7.19 (m, 20H).
^{13}C NMR (100 MHz, $CDCl_3$) δ 211.8 (t, $^{2}J_{CP}$ = 5.0 Hz), 133.2, 133.1, 132.7, 132.6, 132.0, 131.4, 130.8, 130.7, 129.7, 128.8, 128.7, 128.6, 128.5, 105.4 (d, $^{1}J_{CP}$ = 8.1 Hz), 105.0 (d, $^{1}J_{CP}$ = 8.3 Hz).

^{31}P NMR (162 MHz, $CDCl_3$) δ 35.5 (d, $^4J_{PP}$ = 15.7 Hz), 33.2 (P=Se, $^1J_{PSe}$ = 751 Hz), 30.86 (d, $^4J_{PP}$ = 16.0 Hz).
(Se = ^{77}Se isotope)

Dichloropalladium(II)-(1,3-Diphenylpropa-1,2-diene-1,3-diyl)-bis(diphenylphosphine) (3)



A solution of **1** (0.07 g, 0.12 mmol, 1 equiv) and *cis*-bis(acetonitrile)dichloropalladium(II) (32 mg, 0.12 mmol, 1 equiv) in toluene (1.4 mL) was stirred at 80 °C for 4 h. The mixture was concentrated under reduced pressure. The orange solid was washed with Et_2O and dried under vacuum to give **3** (74 mg, 84% yield) as a yellow solid. The latter was dissolved in dichloromethane (1 mL) and cyclohexane was added slowly in order to obtain a biphasic solution. Overnight crystallization occurred to give crystals of expected complex.

m.p.= 236-237 °C

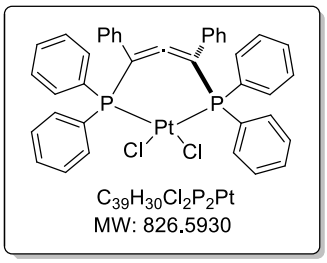
IR (neat): ῡ (cm^{-1}) = 3055, 1734, 1597, 1493, 1481, 1310, 1098, 729, 690.

^{1}H NMR (400 MHz, CD_2Cl_2) δ 8.62 (bdd, *J* = 12.0, 7.2 Hz, 4H), 7.80-7.72 (m, 6H), 7.35-7.33 (m, 2H), 7.24-7.19 (m, 8H), 7.05 (t, *J* = 7.6 Hz, 2H), 6.86 (t, *J* = 7.6 Hz, 4H,), 6.10 (d, *J* = 7.6 Hz, 4H).

^{13}C NMR (100 MHz, CD_2Cl_2) δ 193.3 (t, $^2J_{CP}$ = 3.8 Hz), 136.9, 136.8, 136.7, 134.0, 133.9, 133.5, 133.3, 133.3, 133.1, 131.9 (2CH), 130.1 (2CH), 130.0, 129.9, 129.8, 129.5, 129.1, 129.0, 128.8, 128.7, 128.5, 128.4, 128.4, 128.3, 105.6 (t, $^1J_{CP}$ = 21.7 Hz).

^{31}P NMR (162 MHz, CD_2Cl_2) δ 128.3.

Dichloroplatinum(II)-(1,3-Diphenylpropa-1,2-diene-1,3-diyl)-bis(diphenylphosphine) (4)



A solution of **1** (0.15 g, 0.27 mmol, 1 equiv) and *cis*-bis(benzonitrile)dichloroplatinum(II) (0.12 g, 0.27 mmol, 1 equiv) in toluene (6 mL) was stirred at 80 °C for 20 h. The mixture was filtered over a short pad of Celite® and concentrated under reduced pressure. The product was recrystallized by diffusion of toluene into the solution of the crude product in $CHCl_3$ to give **4** (0.24 g, quant) as a brown solid. (*Note*: the product is not air stable).

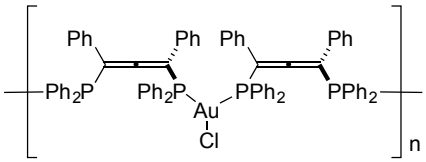
IR (neat): ῡ (cm^{-1}) = 3080, 3058, 2228, 1903, 1714, 1593, 1482, 1436, 1215, 1099, 758, 716.

^{1}H NMR (300 MHz, $CDCl_3$) δ 10.54-10.47 (m, 3H), 9.73-9.66 (m, 6H), 9.28-9.13 (m, 11H), 8.98 (t, *J* = 7.5 Hz, 3H), 8.79 (t, *J* = 7.7 Hz, 4H), 8.07 (d, *J* = 7.6 Hz, 3H).

^{13}C NMR (100 MHz, CD_2Cl_2) δ 198.9 (t, $^2J_{CP}$ = 5.1 Hz, C), 136.6 (2CH), 136.5, 134.2 (2CH), 134.1, 133.2 (2CH), 131.8 (2CH), 131.7, 131.1, 130.0 (2CH), 129.9 (2CH), 129.8 (4CH), 129.7, 129.2, 128.9 (4CH), 128.7 (6CH), 128.5, 128.4, 128.3, 128.2, 128.0, 104.5 (dd, $^1J_{CP}$ = 32.8, 21.5 Hz, 2C).

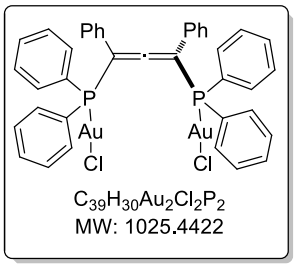
^{31}P NMR (162 MHz, CDCl3) δ 98.7 (P-Pt, $^1J_{P\text{-}Pt}$ = 4371 Hz).

Synthesis of polymer 6



To a solution of **1** (0.1 g, 0.18 mmol, 1 equiv) in CH_2Cl_2 (4 mL) at –20 °C was added AuCl(Me_2S) (0.051 g, 0.18 mmol, 1 equiv) in solution in CH_2Cl_2 (1 mL). The temperature was slowly warmed to room temperature and the mixture was stirred for 4h. The mixture was concentrated under reduced pressure. The residue was dissolved in CH_2Cl_2 and precipitated with pentane to obtain **6** as a white solid. The latter was recrystallized by diffusion of pentane into the solution of crude product in CH_2Cl_2 to give **6** as a colorless crystals (0.1 g, quant).
^{1}H NMR (400 MHz, CD_2Cl_2) δ 7.50-7.38 (m, n10H, H_{ar}), 7.32-7.11 (m, n 20H, H_{ar}).
^{31}P NMR (162 MHz, CD_2Cl_2) δ 12.3 (bs), 27.9 (s).

Dichlorogold(I)-(1,3-Diphenylpropa-1,2-diene-1,3-diyl)-bis(diphenylphosphine) (*rac-7*)



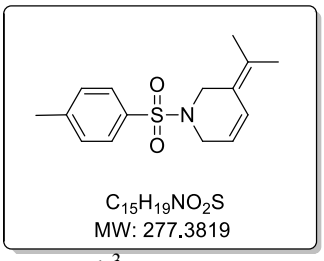
A solution of AuCl(Me_2S) (0.106 g, 0.36 mmol, 2 equiv) and **1** (0.1 g, 0.18 mmol, 1 equiv) in CH_2Cl_2 (5 mL) was stirred at room temperature for 3 h. The mixture was concentrated under reduced pressure. The residue was dissolved in CH_2Cl_2 and precipitated with pentane to obtain ***rac*-7** (0.184 g, quant) as a white solid. The latter was recrystallized by diffusion of cyclohexane into the solution of crude product in CH_2Cl_2 to give colorless crystals quantitatively.

m.p. = 259–261 °C
IR (neat): ϋ (cm^{-1}) = 3055, 2924, 2237, 1908, 1490, 1436, 1101, 911, 730, 689.
^{1}H NMR (400 MHz, $CDCl_3$) δ 7.60-7.31 (m, 30H, H_{ar}).
^{13}C NMR (100 MHz, $CDCl_3$) δ 213.1 (t, $^2J_{CP}$ = 3.5 Hz), 135.2, 135.1, 135.0, 134.1, 134.0, 133.5, 132.9, 132.7, 132.4, 131.8, 131.5, 130.3, 130.2, 130.1, 129.8, 129.7, 129.6, 129.5, 129.4, 129.3, 129.2, 129.1 (CH), 129.0, 128.9, 127.8, 127.7, 127.5, 127.2, 126.8, 126.6, 104.4 (d, $^1J_{CP}$ = 8.1 Hz), 103.9 (d, $^1J_{CP}$ = 8.1 Hz).
^{31}P NMR (162 MHz, $CDCl_3$) δ 30.2.
HRMS (ESI) calcd for $C_{39}H_{30}Au_2Cl_2P_2$ ($[M + Na]^+$) 1047.04230, found 1047.04241

GP: Gold(I)-catalyzed cycloisomerization of enynes

To a solution of ***rac*-7** (0.03 equiv) in dry and degassed solvent was added AgX (X= SbF_6, OTf, BF_4 or OTs) (0.06 equiv). After 10 min stirring at room temperature, the precipitation of AgCl occurred (white solid). Then, a solution of 1,6-enyne (1 equiv) in dry and degassed solvent was added (final concentration 0.05 M). The mixture was stirred and monitored by TLC. When the reaction was complete, the mixture was filtered over a short pad of Celite® and washed with CH_2Cl_2. The solution was concentrated under reduced pressure. Subsequent purification by flash-chromatography on silica gel afforded the desired products.

3-(Propan-2-ylidene)-1-tosyl-1,2,3,6-tetrahydropyridine (9a)



According to the general procedure **GP**: using ***rac*-7** (11 mg, 0.0108 mmol), $AgSbF_6$ (7.4 mg, 0.022 mmol) and **8a** (100 mg, 0.36 mmol) .The reaction mixture in CH_2Cl_2 (7 mL) was stirred at room temperature for 2h. Silica gel chromatography (Rf = 0.11, cyclohexane/AcOEt, 10/1) gave **9a** as a white solid (77 mg, 77%) The characterization data were identical to those previously reported.[3]

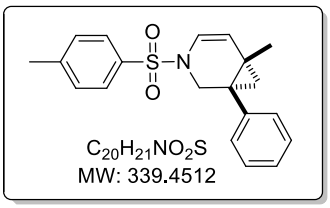
R_f = 0.11 (EtOAc/Cyclohexane: 1/10).

IR (neat): ῡ (cm^{-1}) = 2956, 2854, 1597, 1494, 1381, 1346, 1164, 1091, 1035, 955, 910, 816, 734, 664.

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.64 (d, *J* = 8.2, 2H), 7.26 (d, *J* = 7.9 Hz, 2H), 6.32 (dt, *J* = 10.4, 2.1 Hz, 1H), 5.51 (dt, *J* = 10.4, 3.6 Hz, 1H), 3.89 (s, 2H), 3.75 (bs, 2H), 2.39 (s, 3H, H_1), 1.75 (s, 3H), 1.66 (s, 3H).

^{13}C NMR (100 MHz, $CDCl_3$) δ 143.4, 134.3, 129.9, 129.4, 127.7, 124.6, 122.4, 121.0, 45.1, 21.6, 20.4, 19.7.

6-Methyl-1-phenyl-3-tosyl-3-azabicyclo[4.1.0]hept-4-ene (8b)



According to the general procedure **GP**: using ***rac*-7** (11 mg, 0.0108 mmol), $AgSbF_6$ (7.4 mg, 0.022 mmol) and **8b** (122 mg, 0.36 mmol).The reaction mixture in CH_2Cl_2 (7 mL) was stirred at room temperature for 2h. Silica gel chromatography (Rf = 0.3, pentane/AcOEt, 10/1) gave **9b** as a white solid (103.7 mg, 85%) The characterization data were identical to those previously reported.[3]

IR (neat): ῡ (cm^{-1}) = 3059, 3027, 2973, 2926, 2869, 2255, 1642, 1597, 1494, 1445, 1349, 1306, 1237, 1125, 1026, 981, 907, 814.

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.66 (d, *J* = 8.3 Hz, 2H), 7.34-7.22 (m, 7H), 6.40 (dd, *J* = 8.0, 1.0 Hz, 1H), 5.38 (d, *J* = 8.0 Hz, 1H), 3.97 (d, *J* = 11.5 Hz, 1H), 3.02 (d, *J* = 11.5, 1H), 2.45 (s, 3H), 1.22 (d, *J* = 4.6 Hz, 1H), 0.99 (dd, *J* = 4.6, 1.3 Hz, 1H), 0.87 (s, 3H).

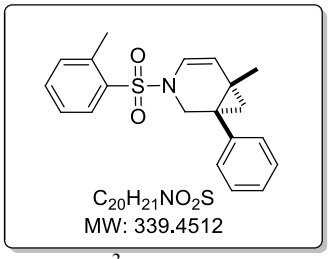
^{13}C NMR (100 MHz, $CDCl_3$) δ 143.8, 139.1, 135.1, 129.9 (4CH), 128.6 (2CH), 127.3, 127.2 (2CH), 121.0, 118.1, 48.2, 39.8, 24.3, 21.7, 20.9, 18.9.

Chiral HPLC analysis: Prepared **9b** by using **8b** (1 equiv), (*aR*)-(+)-**7** (3 mol%) and $AgSbF_6$ (6 mol%) in CH_2Cl_2 at –20°C for15 h.

Chiralpak AS-H, 95/5 *n*-heptane/*i*-PrOH, 1 mL/min. Retention time for minor enantiomer = 9.91 min; for major enantiomer = 11.45 min (*ee* = 29%); $[\alpha_D]$ = 28.9 (*c* 0.1, $CHCl_3$).

{$[\alpha_D]$ (*ent*-**9b**) = – 72 (*c* 0.85, $CHCl_3$, *ee* = 52%)}[4]

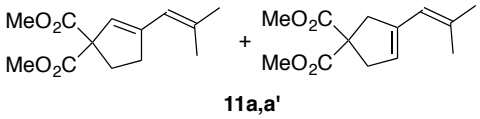
6-Methyl-1-phenyl-3-(o-tolylsulfonyl)-3-azabicyclo[4.1.0]hept-4-ene (21)



According to the general procedure **GP**: using ***rac*-7** (11 mg, 0.0108 mmol), $AgSbF_6$ (7.4 mg, 0.022 mmol) and **20** (122.2 mg, 0.36 mmol). The reaction mixture in CH_2Cl_2 (7 mL) was stirred at room temperature for 1h. Silica gel chromatography (Rf = 0.4, pentane/AcOEt, 10/1) gave **21** as a white solid (122.2 mg, quant) The characterization data were identical to those previously reported.[3]

IR (neat): ϋ (cm^{-1}) = 3061, 2927, 2871, 2851, 2361, 2257, 1643, 1600, 1496, 1446, 1348, 1329, 1281, 1242, 1177, 1161, 1092, 1069, 979, 906.
^{1}H NMR (300 MHz, $CDCl_3$) δ 7.89 (d, *J* = 7.7 Hz, 1H), 7.44 (d, *J* = 7.1 Hz, 1H), 7.33-7.21 (m, 7H), 6.47 (d, *J* = 7.9 Hz, 1H), 5.39 (d, *J* = 8.0 Hz, 1H), 3.81 (d, *J* = 12.0 Hz, 1H), 3.19 (d, *J* = 11.9 Hz, 1H), 2.61 (s, 3H), 1.19 (d, *J* = 4.4 Hz, 1H), 1.02 (d, *J* = 4.1 Hz, 1H), 0.88 (s, 3H).
^{13}C NMR (100 MHz, $CDCl_3$) δ 139.0, 137.7, 136.9, 133.1, 132.9, 130.1, 129.9, 128.6, 127.3, 126.4, 120.9, 117.6, 48.0, 40.1, 24.6, 21.0, 20.9, 19.1.
Chiral HPLC analysis: Prepared **21** by using **20** (1 equiv), (*aR*)-(+)-**7** (3 mol%) and $AgSbF_6$ (6 mol%) in CH_2Cl_2 at –20°C for15 h.
Chiralpak AS-H, 95/5 *n*-heptane/*i*-PrOH, 1 mL/min. Retention time for minor enantiomer = 6.46 min; for major enantiomer =7.89 min (*ee* =32%); $[\alpha_D]$ = 68.9 (*c* 0.1, $CHCl_3$).
{$[\alpha_D]$ (*ent*-**21**) = – 206 (*c* 1.42, $CHCl_3$, *ee* = 75%)}.[4]

Inseparable mixture of dimethyl-5-(propan-2-ylidene)cyclopent-2-ene-1,1-dicarboxylate (a) and dimethyl 5-(propan-2-ylidene)cyclopent-3-ene-1,1-dicarboxylate (a') with a ratio (2:1) (11a,a')



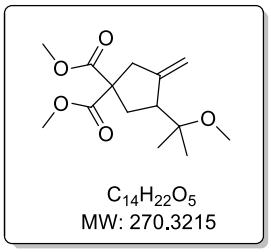
11a,a'
$C_{13}H_{18}O_4$
MW: 238.2796

According to the general procedure **GP**: using ***rac*-7** (11 mg, 0.0108 mmol), $AgSbF_6$ (7.4 mg, 0.022 mmol) and **10a** (85.8 mg, 0.36 mmol) .The reaction mixture in CH_2Cl_2 (7 mL) was stirred at room temperature for 1h. Silica gel chromatography (Rf = 0.4, pentane/AcOEt, 10/1) gave **11a** and **11a'** as an inseparable mixture (2:1) of colorless oil. The characterization data were identical to those previously reported.

IR (neat): ϋ (cm^{-1}) = 2954, 2911, 1731, 1453, 1379, 1248, 1155, 1060, 865.
^{1}H NMR (300 MHz, $CDCl_3$) δ 5.79 (s, 1H, a), 5.72 (s, 1H, b), 5.58 (s, 1H, a), 5.37 (s, 1H, b), 3.73 (s, 6H, b), 3.71 (s, 6H, a), 3.18 (bs, 2H, b), 3.01 (bs, 2H, a), 2.64 (t, *J* = 6.6 Hz, 2H, b), 2.48-2.45 (m, 2H, a), 1.83 (s, 3H, a), 1.81 (s, 3H, b), 1.79 (s, 3H, a), 1.77 (s, 3H, b).

^{13}C NMR (75 MHz, $CDCl_3$) δ 172.7 (b), 172.1 (a), 146.2 (a), 138.9 (b), 138.1 (a), 135.8 (b), 125.0 (a), 124.5 (b), 120.8 (2CH, a, b) , 66.1 (a), 59.5 (b), 52.9 (b), 52.7 (a), 43.4 (b), 40.4 (b), 34.9 (a), 32.2 (a), 27.5 (a), 27.4 (b), 20.0 (CH_3, a), 19.9 (CH_3, b).

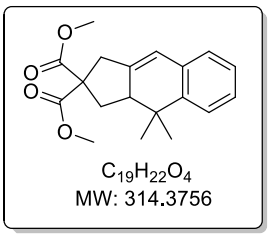
3-(2-Methoxypropan-2-yl)-4-methylene-1-tosylpyrrolidine (12)



To a solution of ***rac*-7** (13.0 mg, 0.01 mmol, 0.03 equiv) in dry and degassed MeOH (4 mL) was added $AgSbF_6$ (2.52 mL of 0.01 M in MeOH, 0.02 mmol, 0.06 equiv). After 5 min stirring at room temperature, a solution of **10a** (100 mg, 0.42 mmol, 1 equiv) in methanol (1.9 mL) (final concentration 0.05 M) was added. The mixture was stirred at room temperature. After 24 h, the mixture was filtered over a short pad of silica and washed with Et_2O. The solution was concentrated under reduced pressure. Purification by flash chromatography on silica gel (Rf = 0.38, EtOAc/pentane, 1/10) afforded **12** (80mg, 70% yield) as colorless oil.
The characterization data were identical to those previously reported.[5]

IR (neat): ῡ (cm^{-1}) = 2953, 1733, 1434, 1364, 1272, 1230, 1202, 1077.
^{1}H NMR (300 MHz, $CDCl_3$) δ, 5.03(bs, 1H), 5.00 (bs, 1H), 3.72 (s, 3H), 3.71 (s, 3H), 3.18 (s, 3H), 2.96-2.84 (m, 3H), 2.57 (dd, *J* = 15.0, 9.0 Hz, 1H), 2.00 (dd, *J* = 12.0, 9.0 Hz, 1H), 1.17 (s, 3H), 1.11 (s, 3H).
^{13}C NMR (75 MHz, $CDCl_3$) δ 172.2, 172.1, 148.3, 110.7, 76.9, 58.7, 52.8, 52.8, 49.3, 49.2, 43.5, 36.1, 22.8, 22.3.

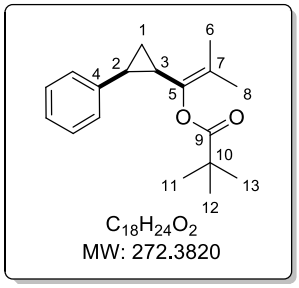
Dimethyl 4,4-dimethyl-3a,4-dihydro-1H-cyclopenta[b]naphthalene-2,2(*3H*)-dicarboxylate (14)



According to the general procedure **GP**: using ***rac*-7** (11 mg, 0.0108 mmol), $AgSbF_6$ (7.4 mg, 0.022 mmol) and **13** (113.2 mg, 0.36 mmol). The reaction mixture in CH_2Cl_2 (7 mL) was stirred at room temperature for 1h. Silica gel chromatography (Rf = 0.14, pentane/AcOEt, 10/1) gave **14** as a white solid (113.2 mg, quant). The characterization data were identical to those previously reported.[6]

IR (neat): ῡ (cm^{-1}) = 2954, 2868, 2843, 1731, 1433, 1200, 1129, 1113, 1066, 989, 888, 752.
^{1}H NMR (400 MHz, $CDCl_3$) δ 7.31-7.29 (m, 1H), 7.16-7.13 (m, 2H), 7.03-7.01 (m, 1H), 6.37 (d, *J* = 2.2 Hz, 1H), 3.78 (s, 3H), 3.73 (s, 3H), 3.32 (dd, *J* = 18.0, 1.5 Hz, 1H), 3.01 (dt, *J* = 18.0 Hz, 3 Hz, 1H), 2.75-2.70 (m, 1H), 2.62 (ddd, *J* = 12.3, 7.5, 1.4 Hz, 1H), 2.17 (t, *J* = 12.4 Hz, 1H), 1.44 (s, 3H), 0.94 (s, 3H).
^{13}C NMR (100 MHz, $CDCl_3$) δ 172.2, 172.0, 144.1, 143.0, 134.0, 127.0, 126.4, 126.3, 123.5, 119.5, 59.0, 52.9, 52.9, 48.5, 39.3, 36.7, 34.9, 25.7, 22.1.

2-Methyl-1-(2-phenylcyclopropyl)prop-1-en-1-yl pivalate (16)



To a solution of ***rac*-7** (15 mg, 14.75 mmol, 0.025 equiv) in $MeNO_2$ (3 mL) was added a solution of $AgSbF_6$ (2.52 mL of 0.01 M in $MeNO_2$, 0.02 mmol, 0.05 equiv) at room temperature. The mixture was stirred for 5 min. Styrene (0.27 mL, 2.38 mmol, 4 equiv) and the solution of 2-methylbut-3-yne pivalate **15** (99.1 mg, 0.59 mmol, 1 equiv) in $MeNO_2$ (final concentration = 0.05 M) was added into the mixture at room temperature. After stirring for 15 h, the mixture was filtered over a short pad of silica and washed with Et_2O, and then concentrated under reduced pressure. Purification by column chromatography on silica gel (Rf = 0.45, EtOAc/pentane, 1/20) afforded **16** as a colorless oil in a 20:1 ratio of inseparable mixture of diastereomers (97 mg, 60%).

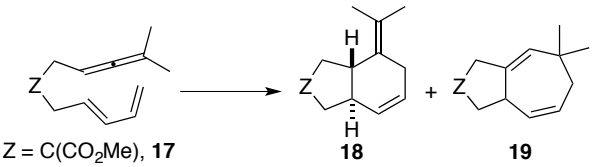
The characterization data were identical to those previously reported.[5]

IR (neat): $\tilde{\upsilon}$ (cm^{-1}) = 2979, 2933, 2872, 1738, 1604, 1395, 1363, 1257, 1157, 767, 697.

^{1}H NMR (300 MHz, $CDCl_3$) δ 7.30-7.18 (m, 3H), 7.05-7.02 (m, 2H), 2.32 (bt, *J* = 7.1 Hz, 2H), 1.53 (s, 3H), 1.46 (s, 3H), 1.29-1.28 (m, 1H), 1.27 (s, 9H), 1.05 (dd, *J* = 11.8 Hz, 6.3 Hz, 1H).

^{13}C NMR (75 MHz, $CDCl_3$) δ 176.8, 139.6, 138.2, 127.6, 127.4, 125.6, 123.2, 39.0, 27.4, 24.1, 21.9, 18.7, 17.4, 11.9.

Inseparable mixture of dimethyl 7-(propan-2-ylidene)-3,3a,7,7a-tetrahydro-1*H*-indene-2,2(6*H*)-dicarboxylate (18) and dimethyl 3,3a,6,7-tetrahydroazulene-2,2(1*H*)-dicarboxylate (19)



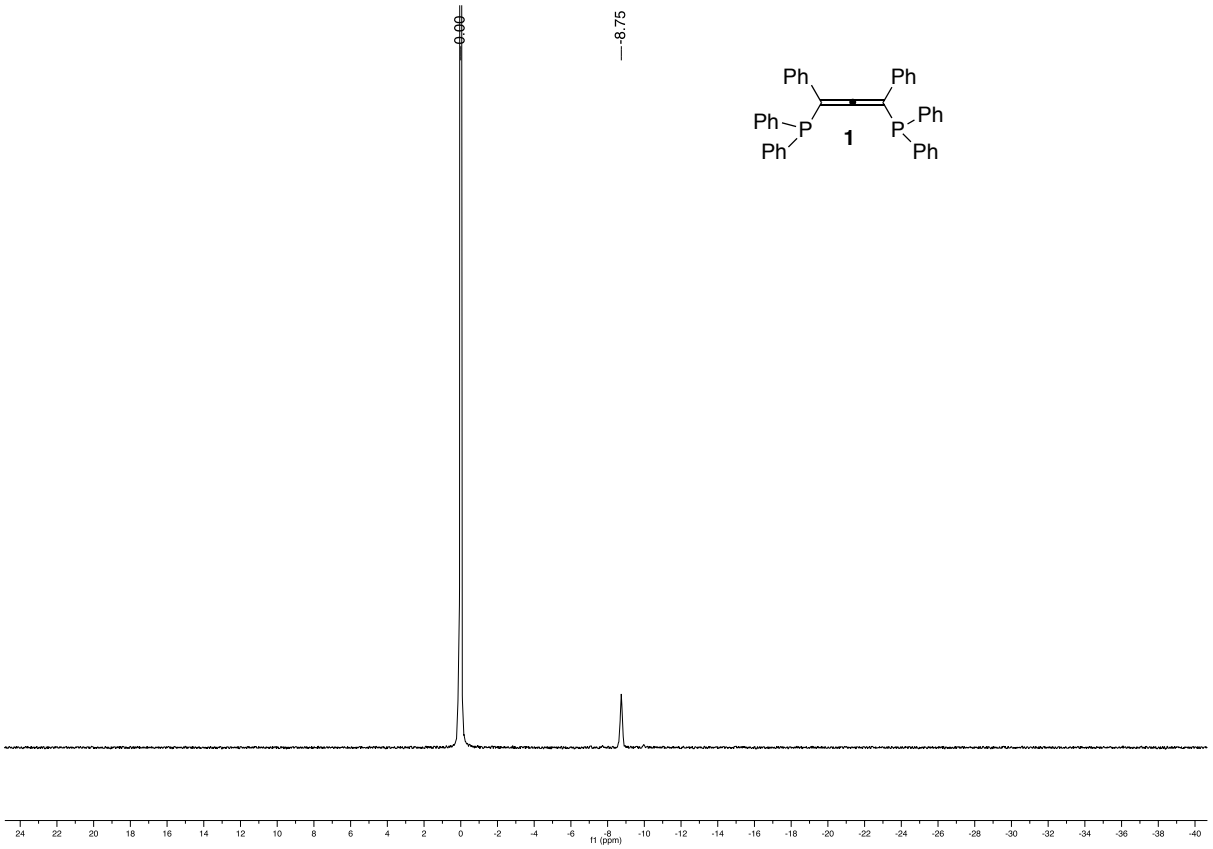
According to the general procedure **GP**: using ***rac*-7** (11 mg, 0.0108 mmol), $AgSbF_6$ (7.4 mg, 0.022 mmol) and **17** (100.2 mg, 0.36 mmol). The reaction mixture in CH_2Cl_2 (7 mL) was stirred at room temperature for 1h. Silica gel chromatography (Rf = 0.24, pentane/AcOEt, 10/1) gave an inseparable mixture of **18** and **19** (4:1, 67.1 mg, 67%) in favor of **18** as a colorless oil.

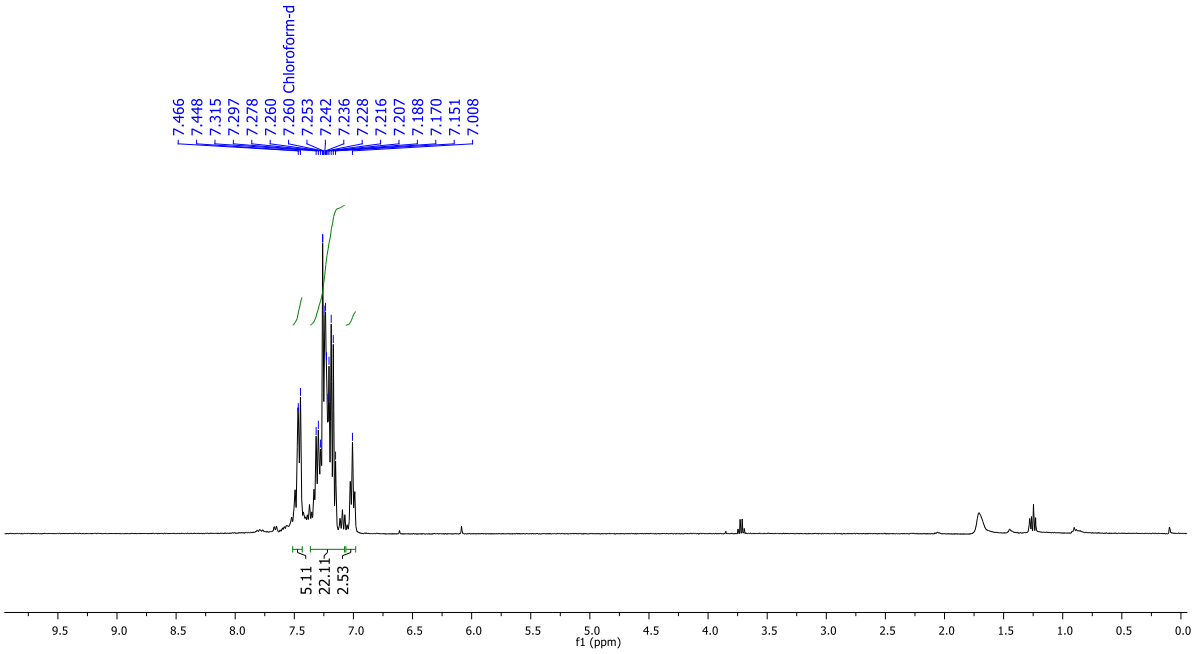
The characterization data were identical to those previously reported.[7]

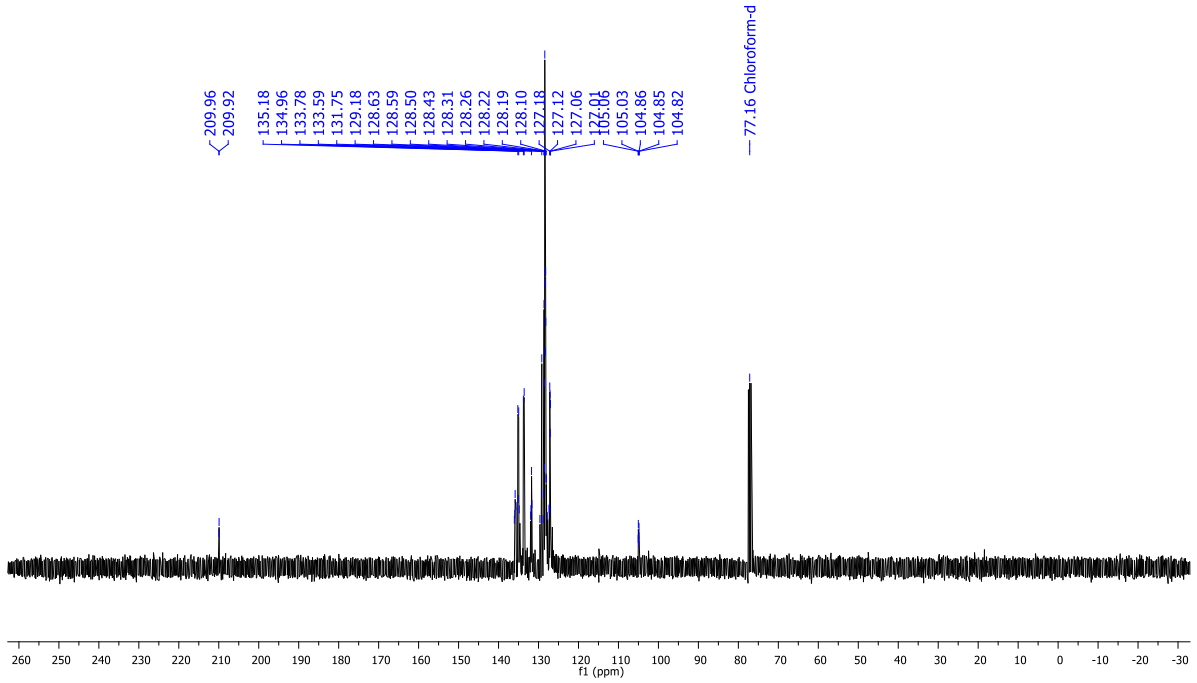
^{1}H NMR (300 MHz, $CDCl_3$) δ 5.85-5.82(m, 1H), 5.70-5.69 (m, 1H), 5.16 (bs, 0.5H), 3.71 (m, 10H), 2.99-2.60 (m, 6H, 2.20-2.14 (bm, 3H), 1.77 (s, 3H), 1.71-1.67 (m, 1H), 1.63 (s, 3H), 0.99 (s, 1H), 0.94 (s, 1H).

^{13}C NMR (75 MHz, $CDCl_3$) δ 173.3, 172.3, 136.7, 135.1, 132.6, 129.2, 129.1, 128.1, 124.0, 58.5, 52.8, 48.3, 44.5, 42.1, 41.1, 39.9, 39.2, 39.1, 37.6, 34.4, 31.6, 28.7, 22.1, 21.9.

3. Spectral data



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209.92
135.18
134.96
133.78
133.59
131.75
129.18
128.63
128.59
128.50
128.43
128.31
128.26
128.22
128.19
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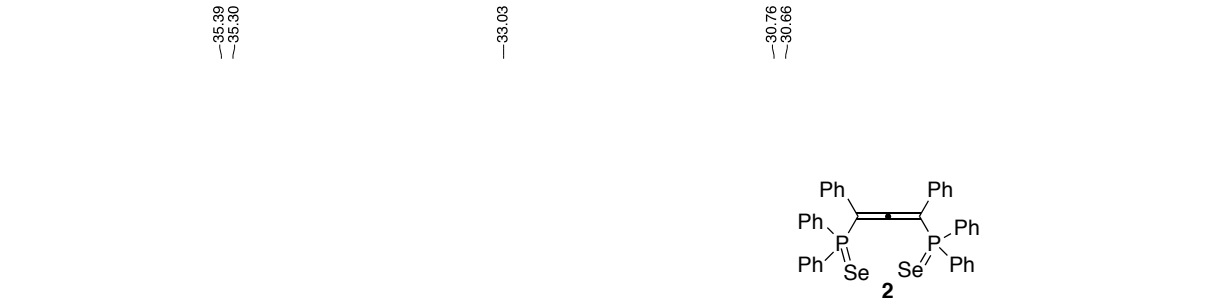
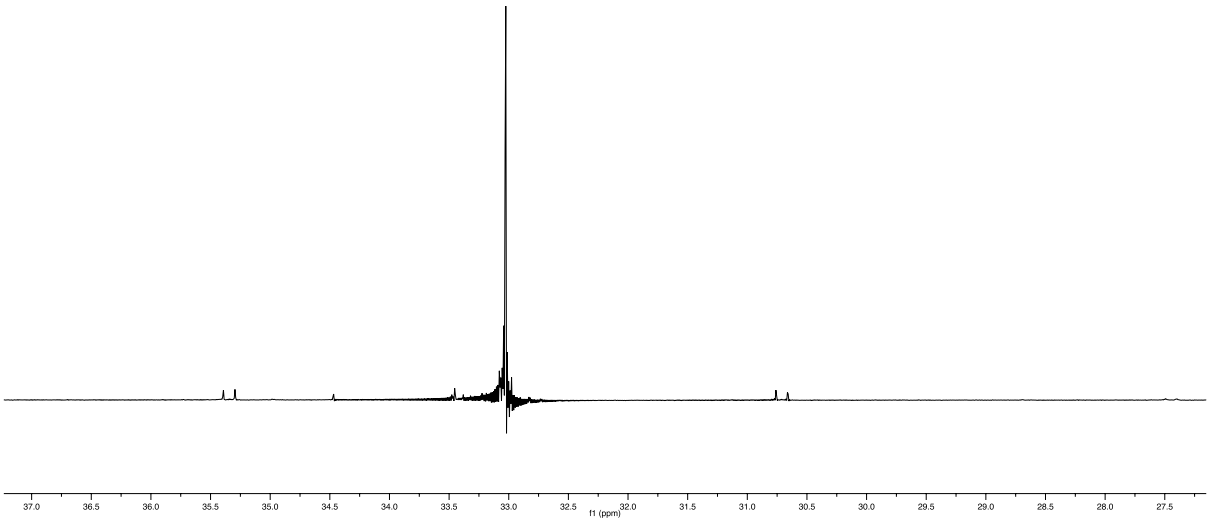
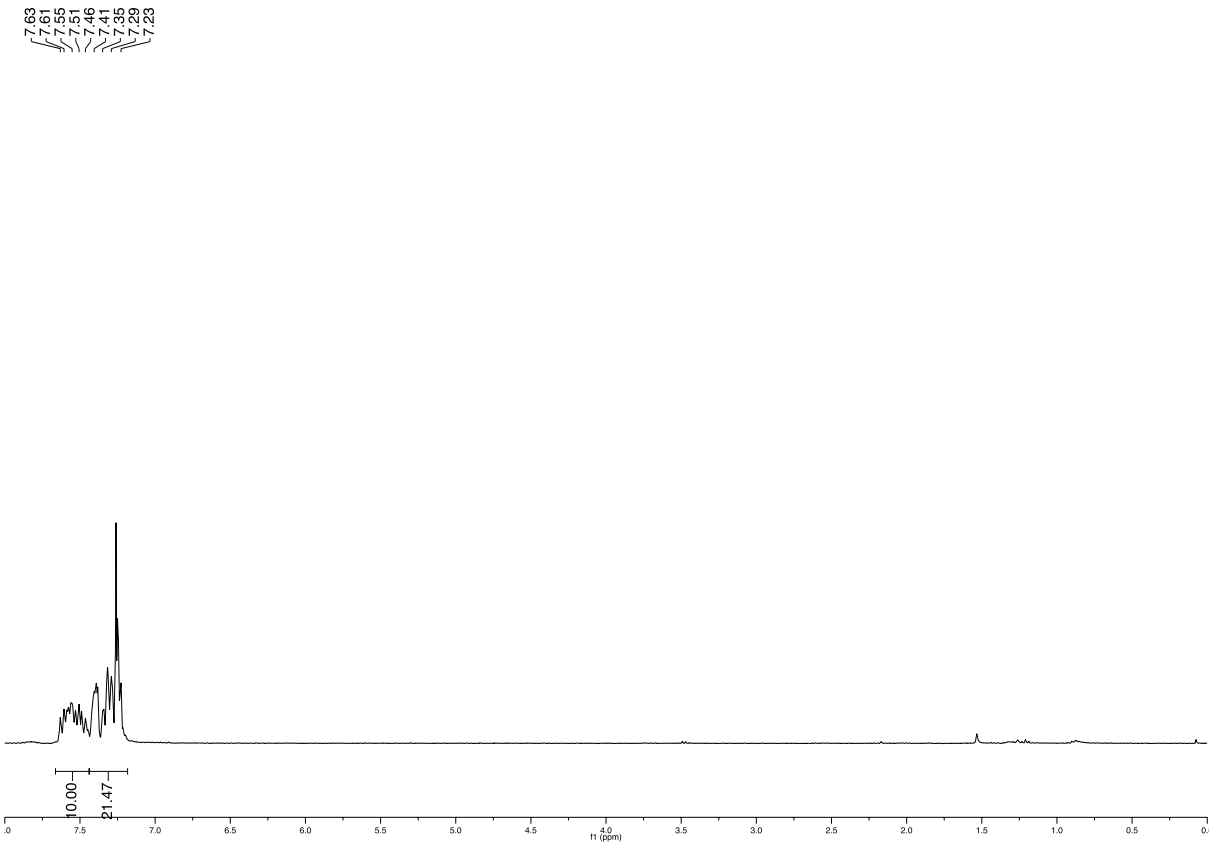
104.85
104.82
77.16 Chloroform-d
f1 (ppm)


35.39
35.30
33.03
30.76
30.66

Ph
Ph
Ph
P
Se
Ph
Ph
Ph
P
Se
Ph

2


f1 (ppm)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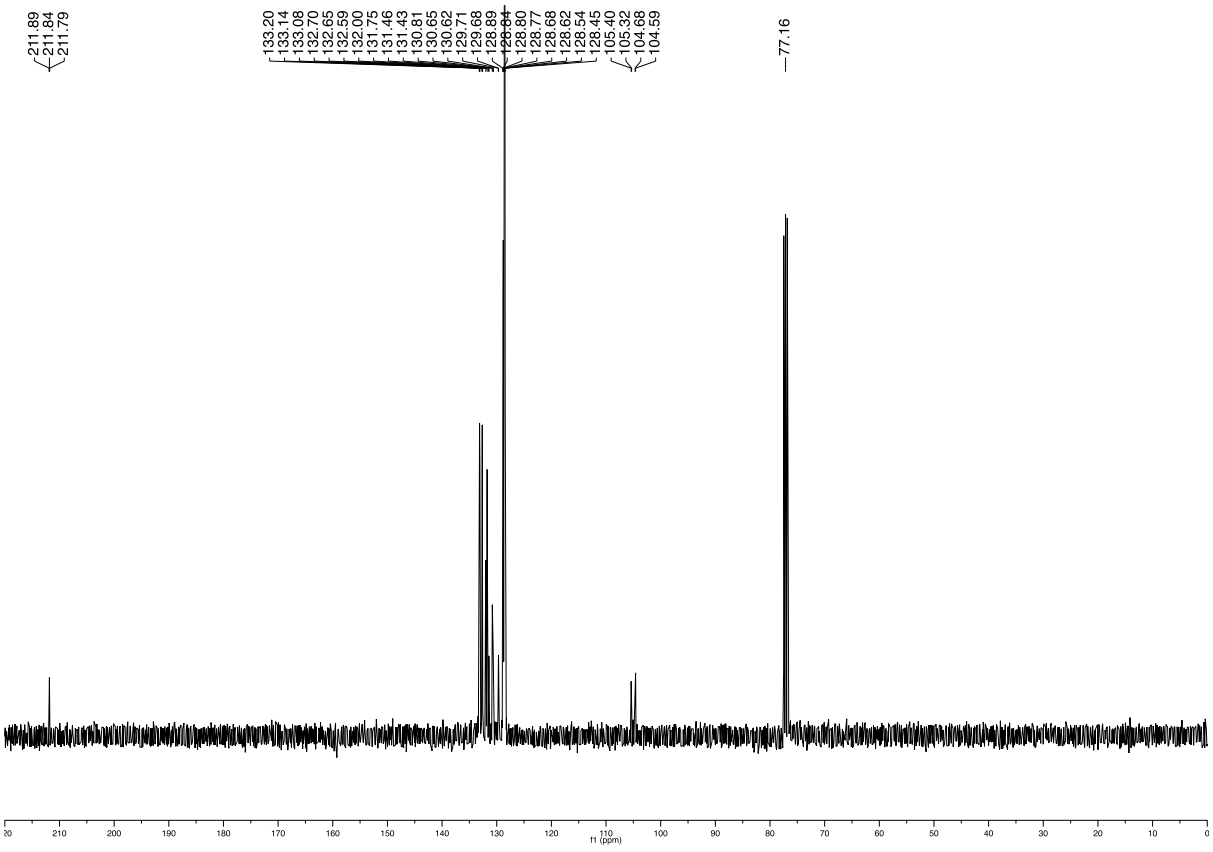
7.41
7.35
7.29
7.23
10.00
21.47
f1 (ppm)


211.89
211.84
211.79
133.20
133.14
133.08
132.70
132.65
132.59
132.00
131.75
131.46
131.43
130.81
130.65
130.62
129.71
129.68
128.89
128.84
128.80
128.77
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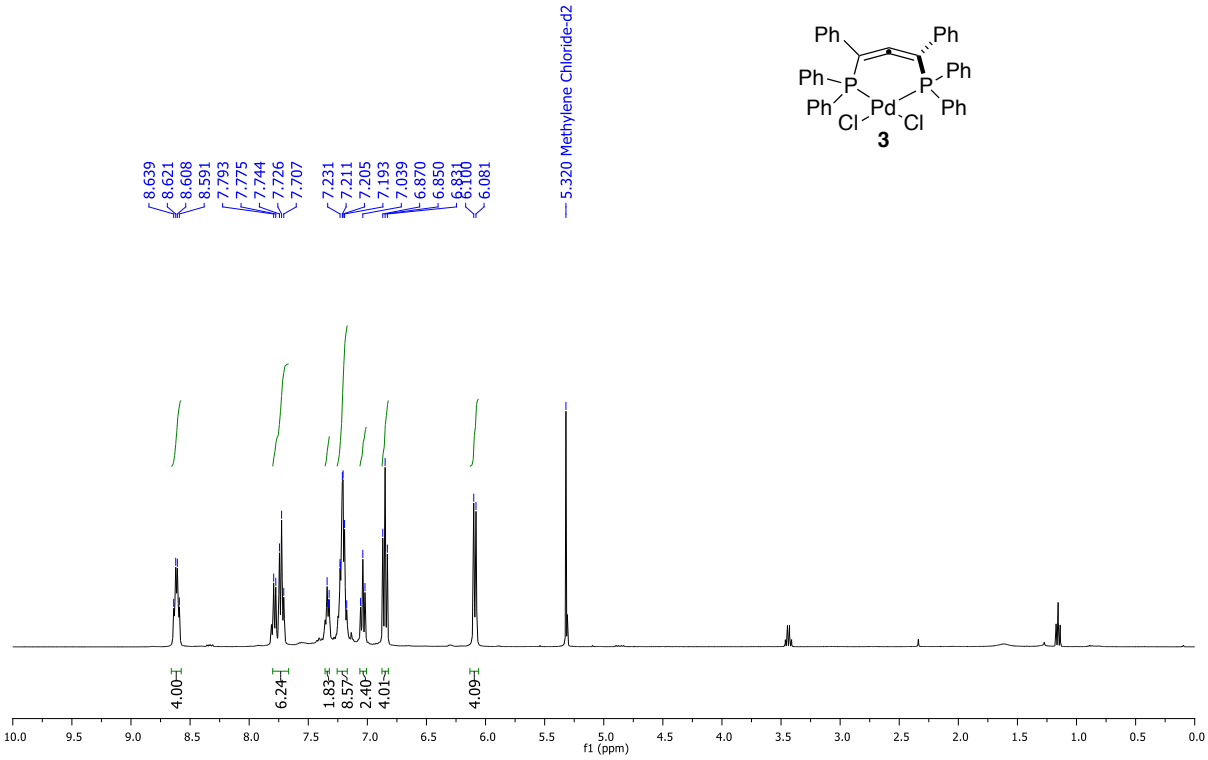
128.62
128.54
128.45
105.40
105.32
104.68
104.59
77.16
f1 (ppm)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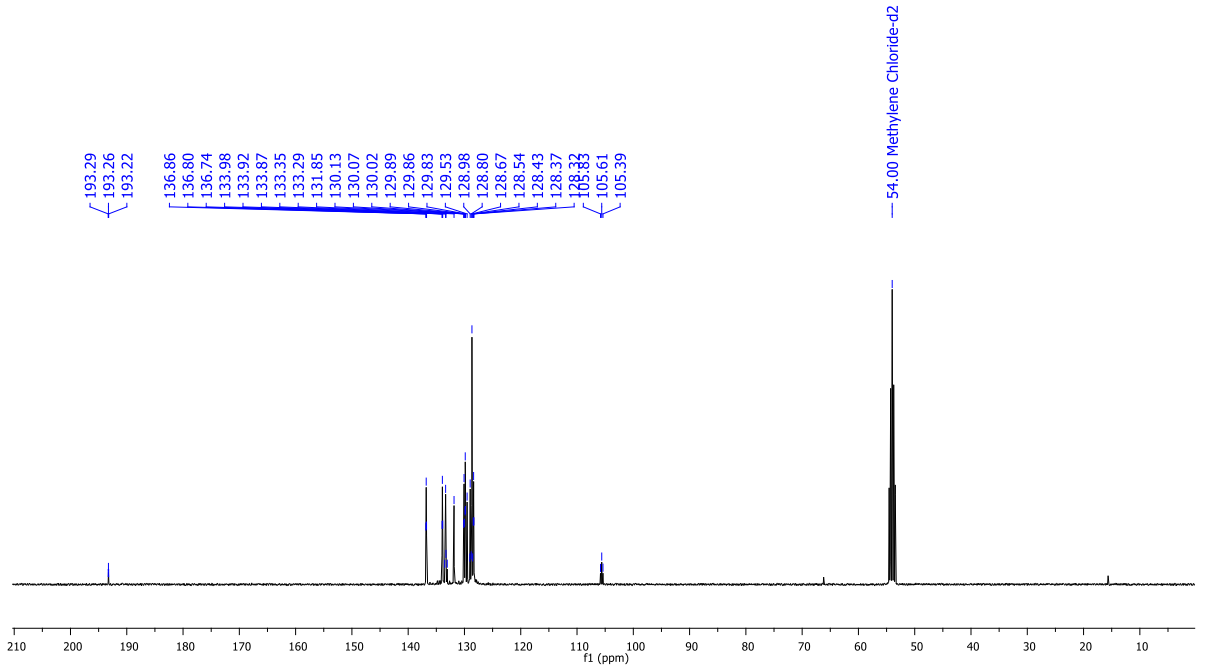
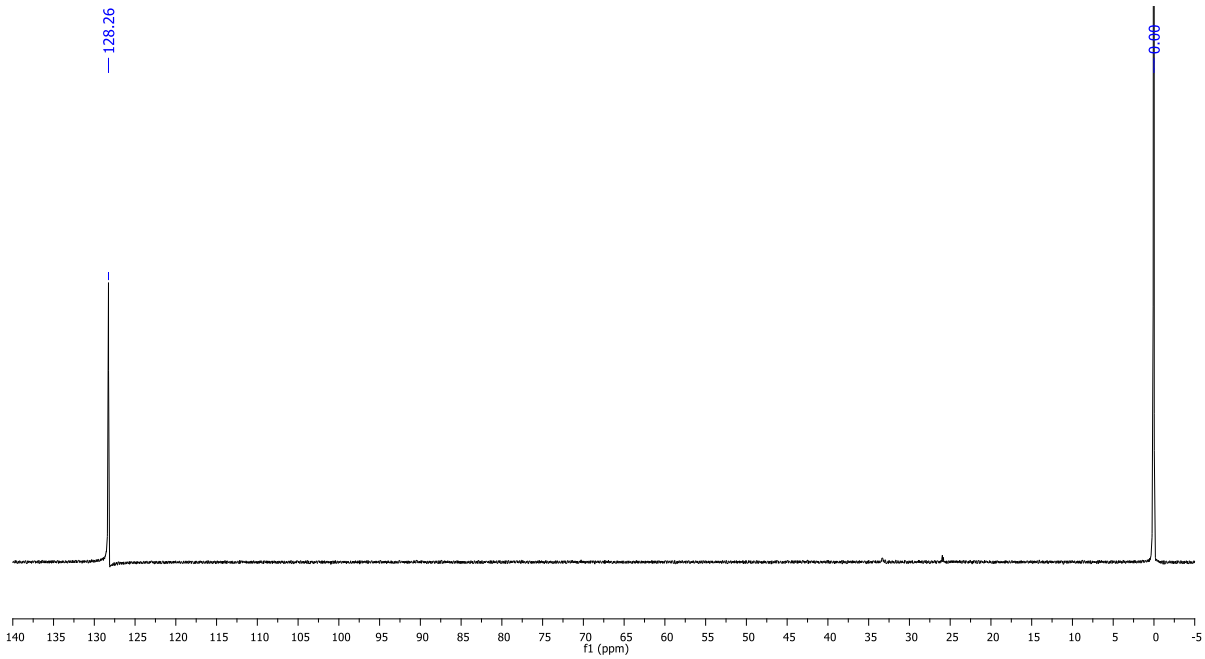
8.621
8.608
8.591
7.793
7.775
7.744
7.726
7.707
7.231
7.211
7.205
7.193
7.039
6.870
6.850
6.831
6.100
6.081
5.320 Methylene Chloride-d2
4.00
6.24
1.83
8.57
2.40
4.01
4.09
f1 (ppm)

Ph
Ph
Ph
P
P
Ph
Ph
Pd
Ph
Cl
Cl

3


193.29
193.26
193.22
136.86
136.80
136.74
133.98
133.92
133.87
133.35
133.29
131.85
130.13
130.07
130.02
129.89
129.86
129.83
129.53
128.98
128.80
128.67
128.54
128.43
128.37
128.32
105.83
105.61
105.39
54.00 Methylene Chloride-d2
f1 (ppm)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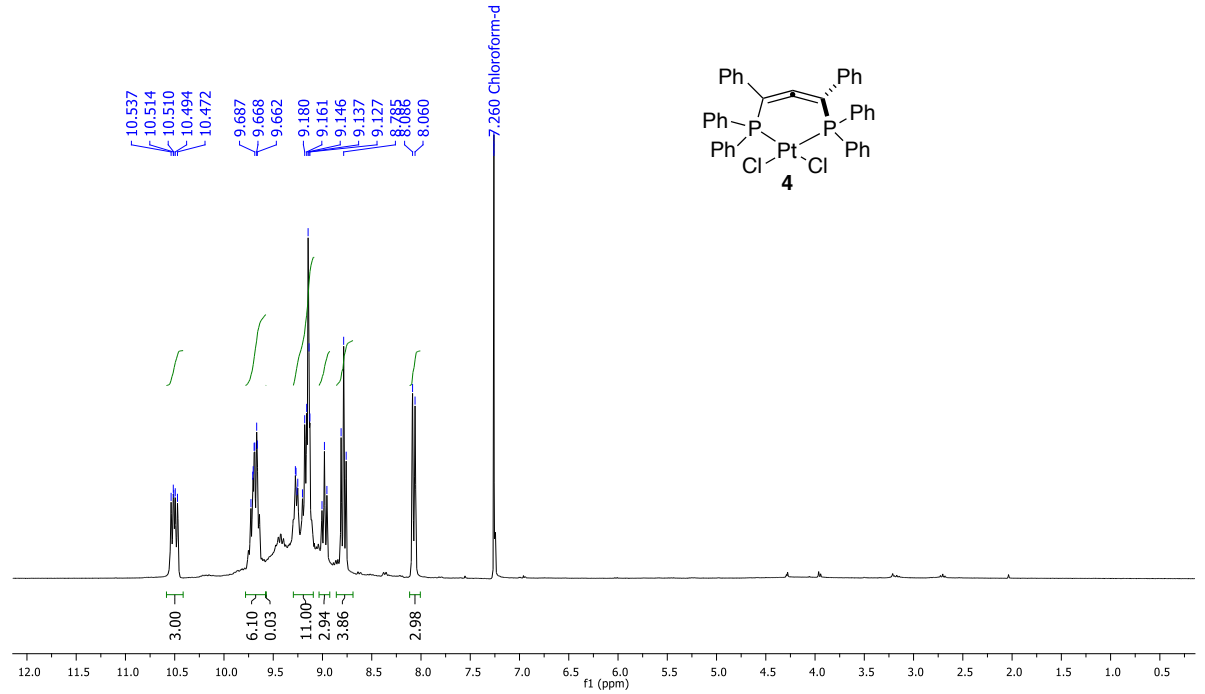
0.00
f1 (ppm)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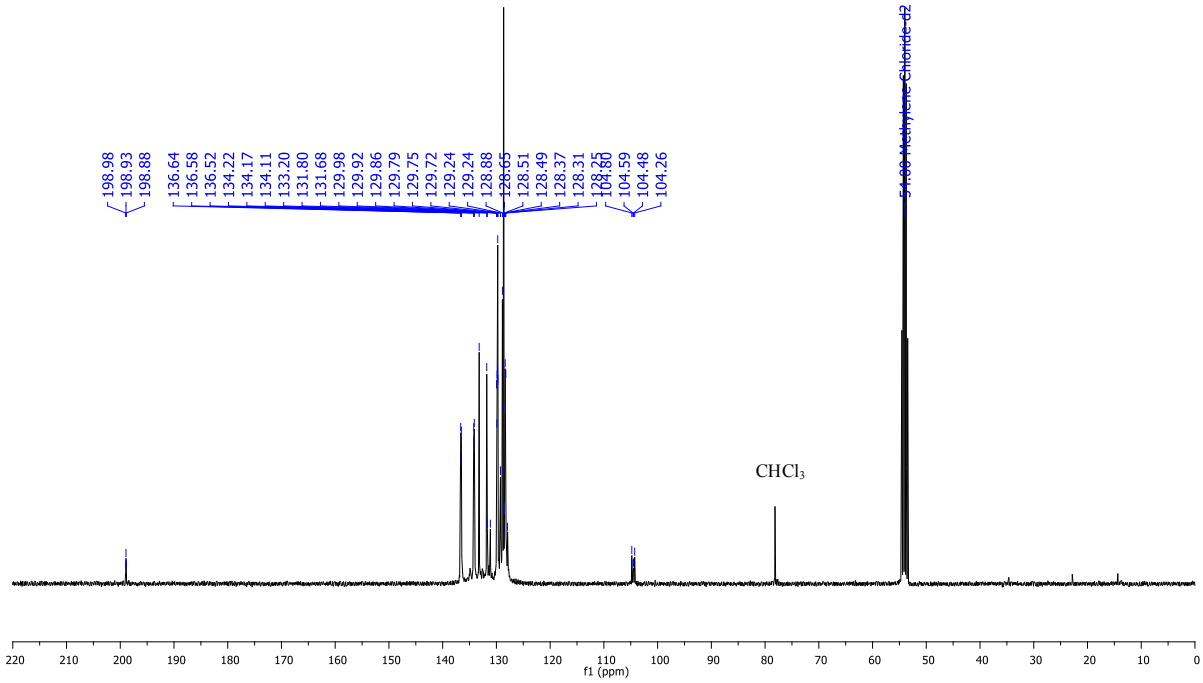
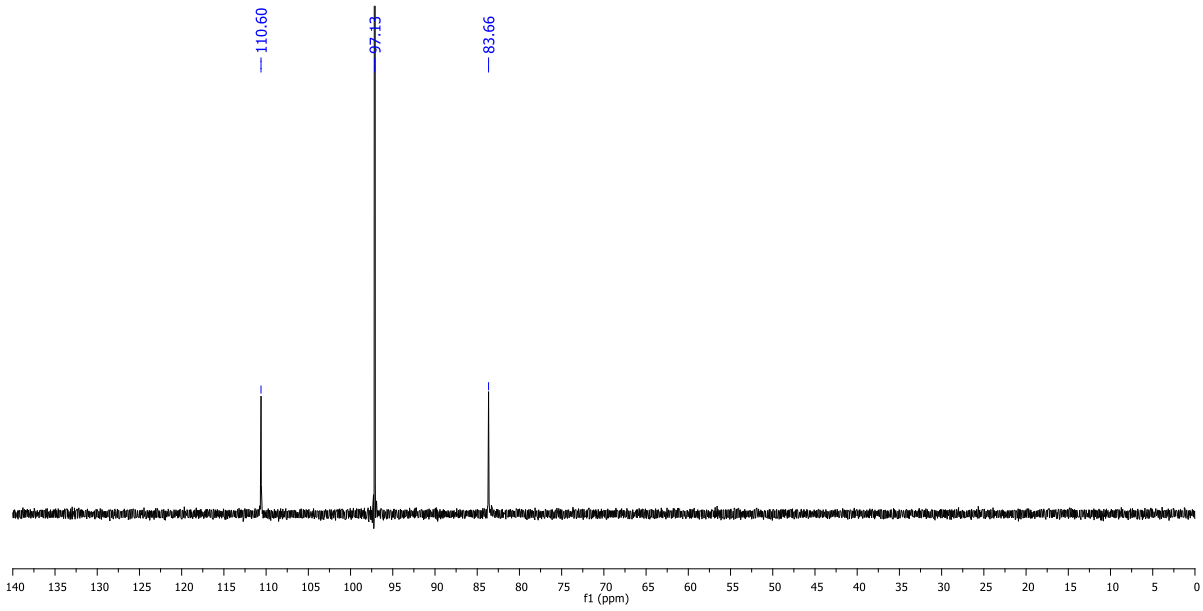
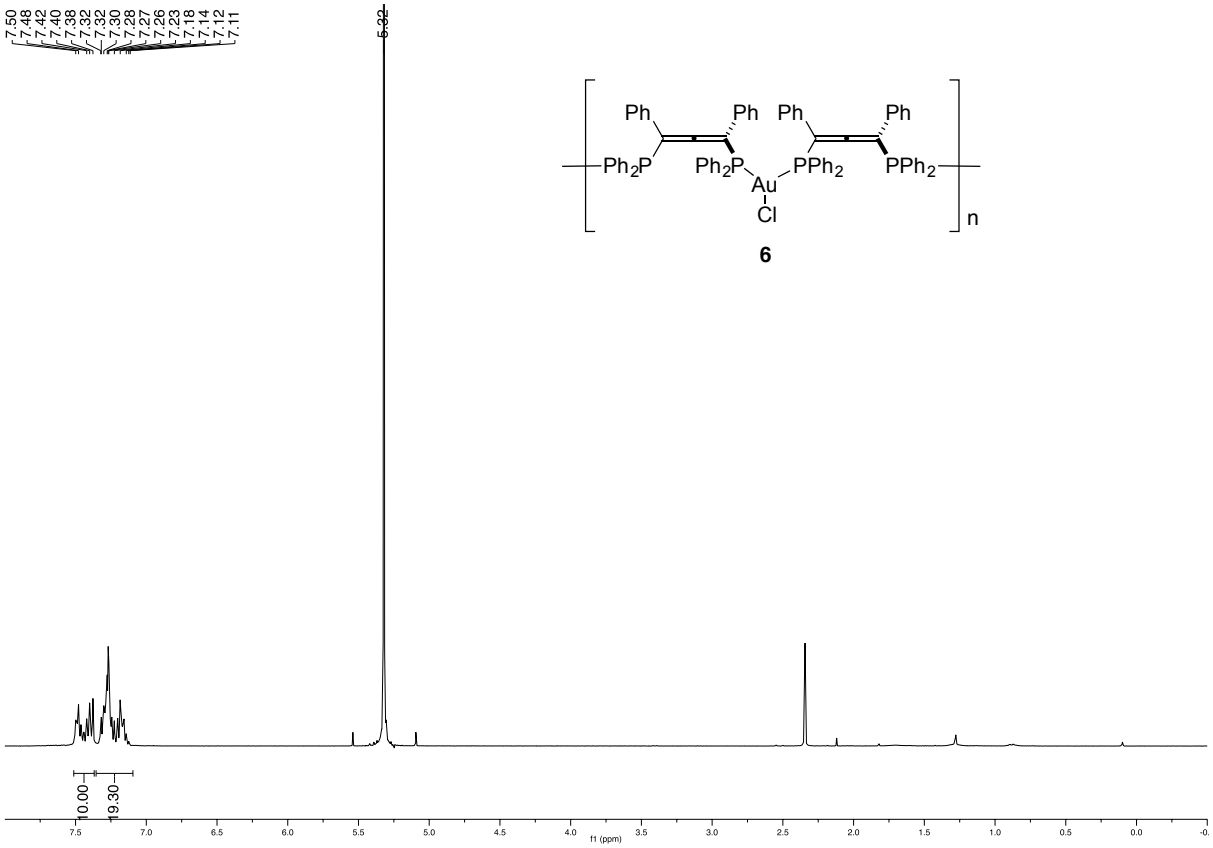
10.510
10.494
10.472
9.687
9.668
9.662
9.180
9.161
9.146
9.137
9.127
8.785
8.060
7.260 Chloroform-d
3.00
6.10
0.03
11.00
2.94
3.86
2.98
f1 (ppm)

Ph
Ph
Ph
P
P
Ph
Ph
Pt
Ph
Cl
Cl

4

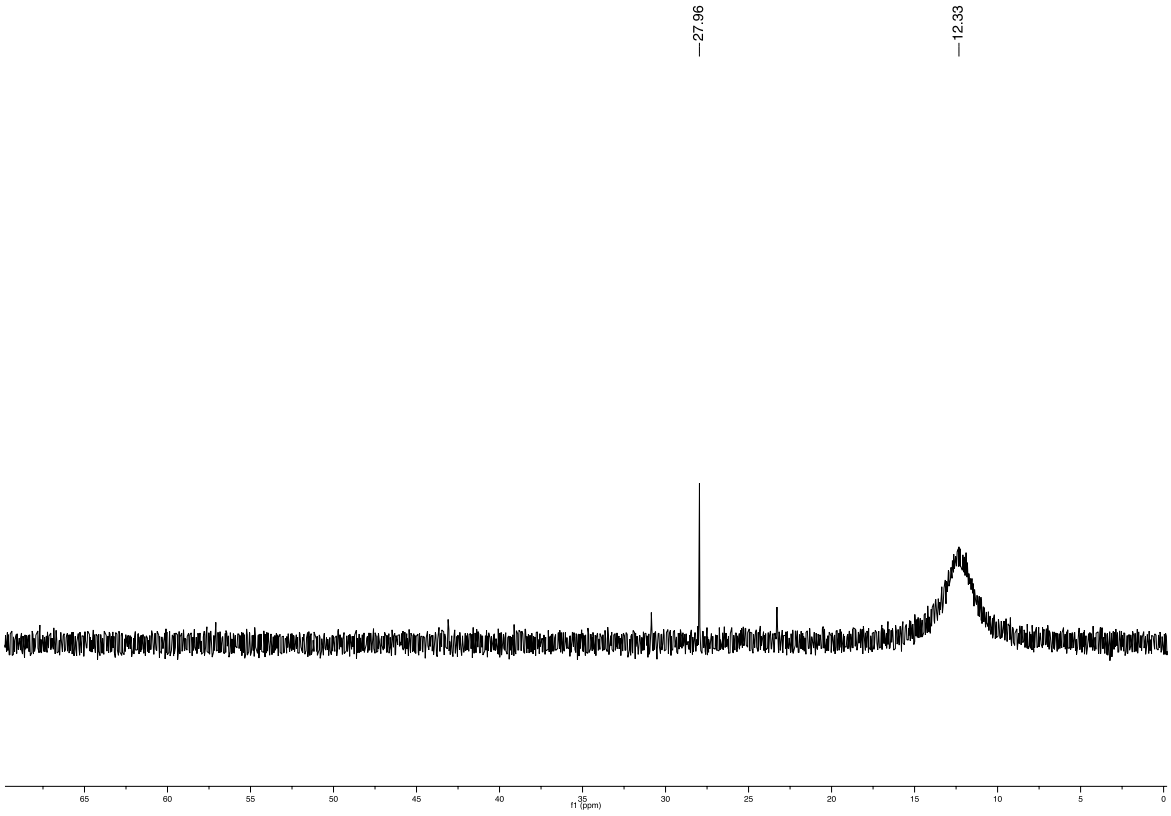

198.98
198.93
198.88
136.64
136.58
136.52
134.22
134.17
134.11
133.20
131.80
131.68
129.98
129.92
129.86
129.79
129.75
129.72
129.24
129.24
128.88
128.65
128.51
128.49
128.37
128.31
104.80
104.59
104.48
104.26
54.00 Methylene Chloride-d2
CHCl3
220 210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0
f1 (ppm)

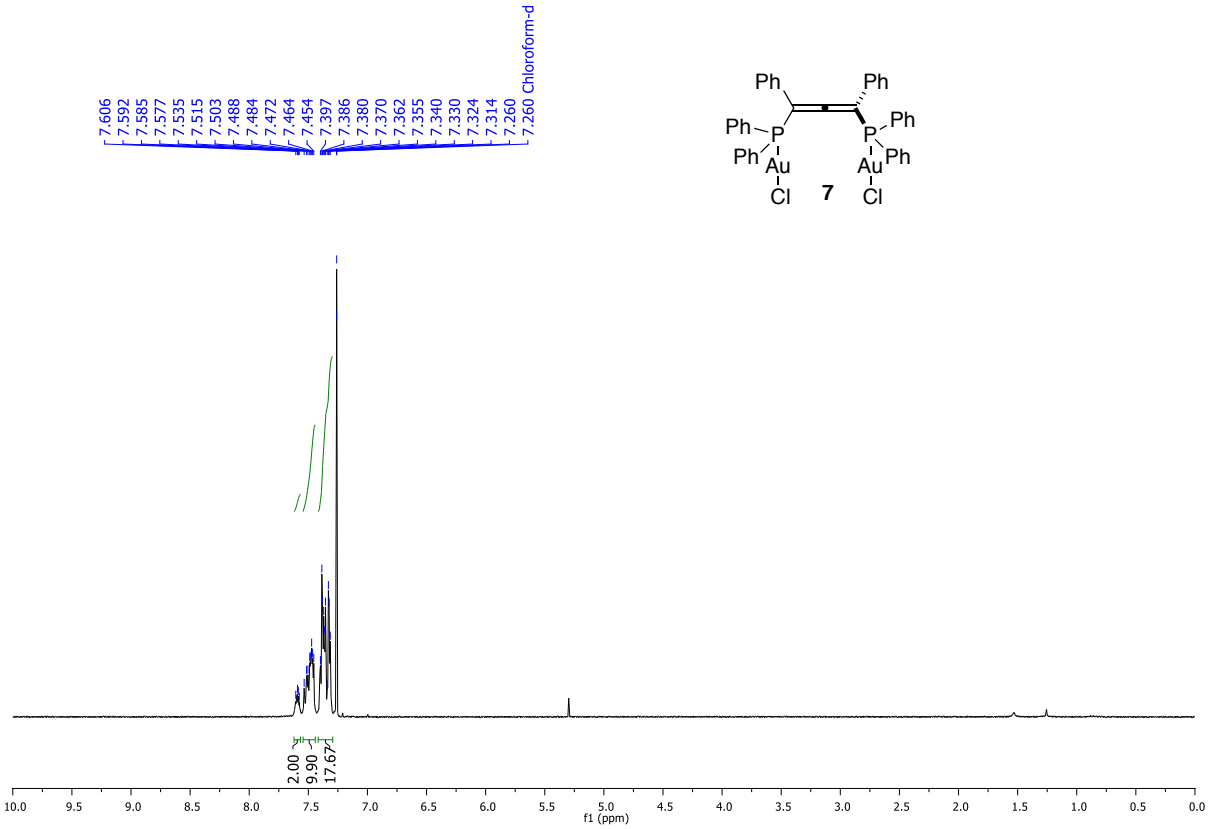

110.60
97.13
83.66
140 135 130 125 120 115 110 105 100 95 90 85 80 75 70 65 60 55 50 45 40 35 30 25 20 15 10 5 0
f1 (ppm)


7.50
7.48
7.42
7.40
7.38
7.32
7.32
7.30
7.28
7.27
7.26
7.23
7.18
7.14
7.12
7.11
5.32
10.00
19.30
f1 (ppm)

Ph
Ph
Ph
Ph
Ph2P
Ph2P
Au
Cl
PPh2
PPh2
n

6


27.96
12.33
f1 (ppm)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7.515
7.503
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7.472
7.464
7.454
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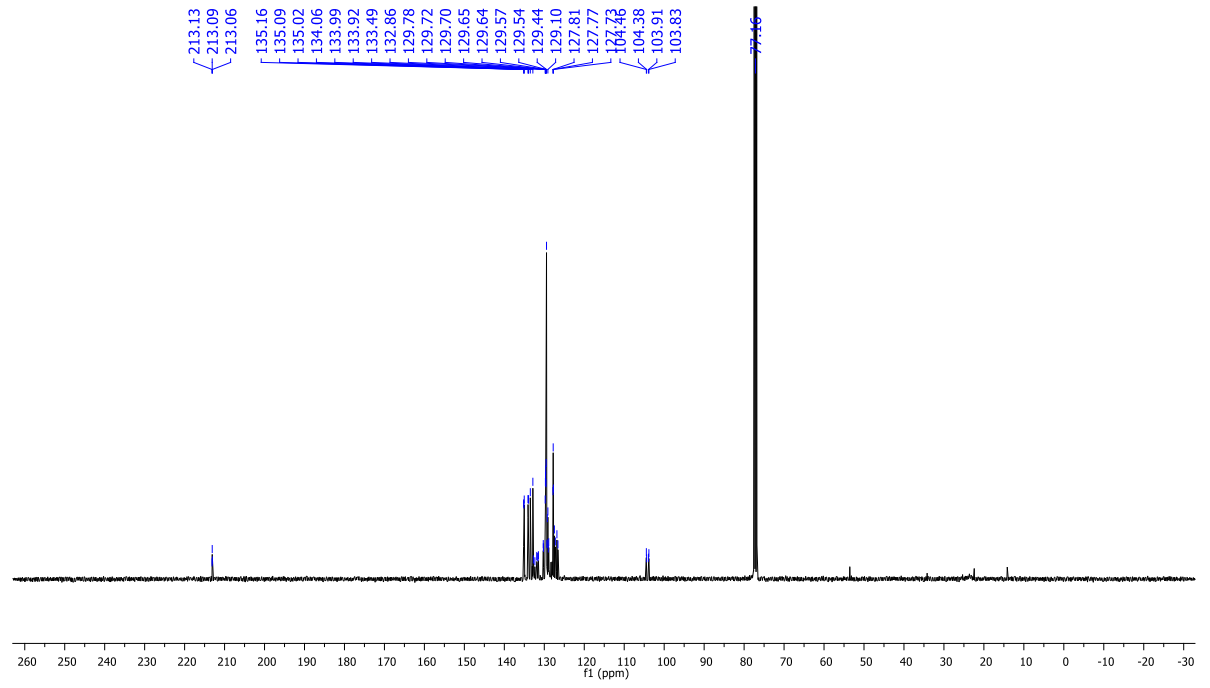
7.386
7.380
7.370
7.362
7.355
7.340
7.330
7.324
7.314
7.260
7.260 Chloroform-d
Ph
Ph
Ph
P
Ph
Au
Cl
Ph
P
Ph
Au
Cl
7
2.00
9.90
17.67
10.0
9.5
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
f1 (ppm)


213.13
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213.06
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135.09
135.02
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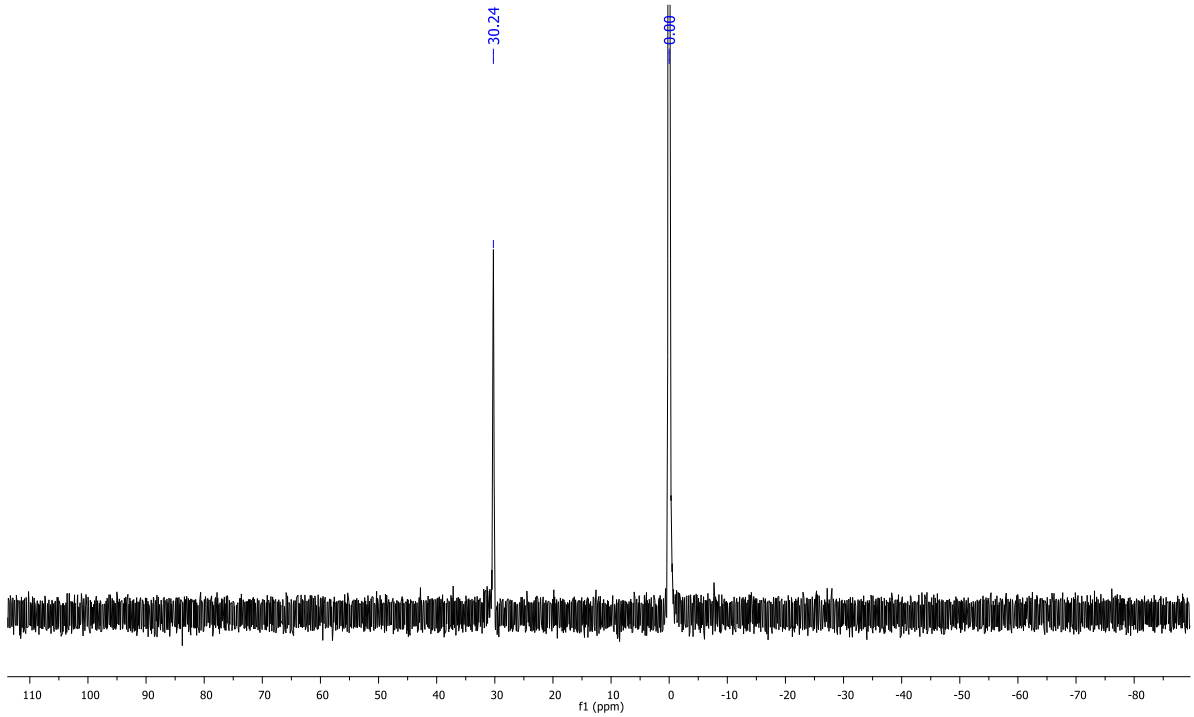
133.49
132.86
129.78
129.72
129.70
129.65
129.64
129.57
129.54
129.44
129.10
127.81
127.77
104.43
104.38
103.91
103.83
77.16
260
250
240
230
220
210
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
-10
-20
-30
f1 (ppm)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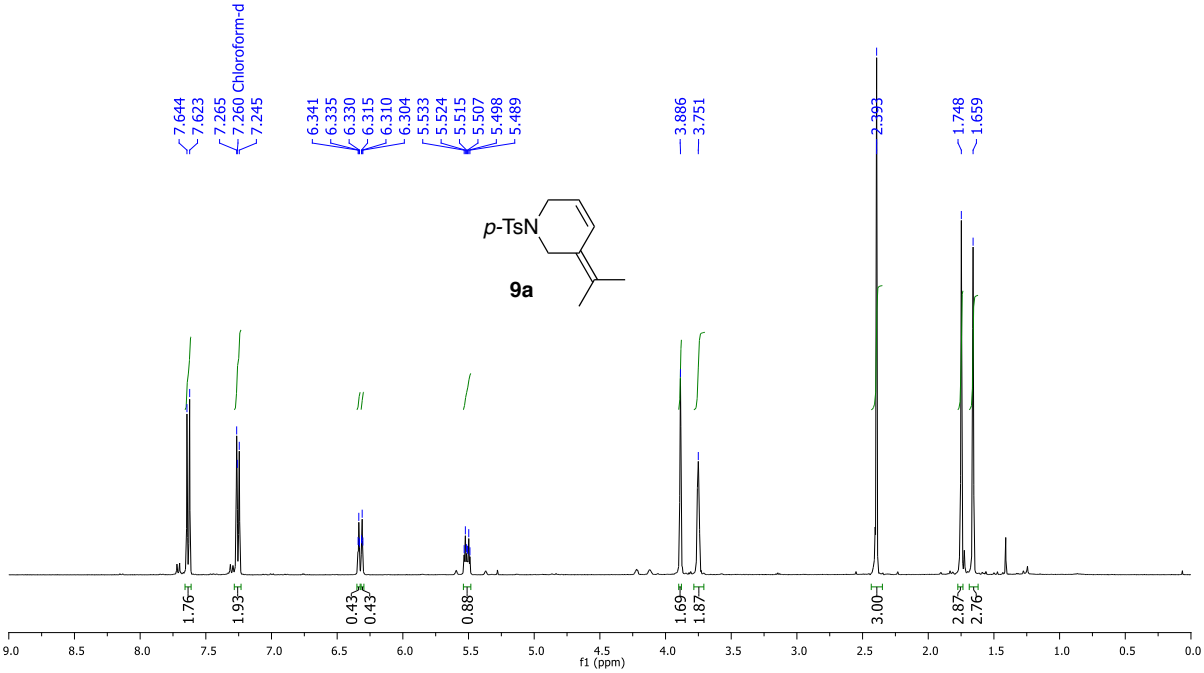
0.00
110 100 90 80 70 60 50 40 30 20 10 0 -10 -20 -30 -40 -50 -60 -70 -80
f1 (ppm)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7.623
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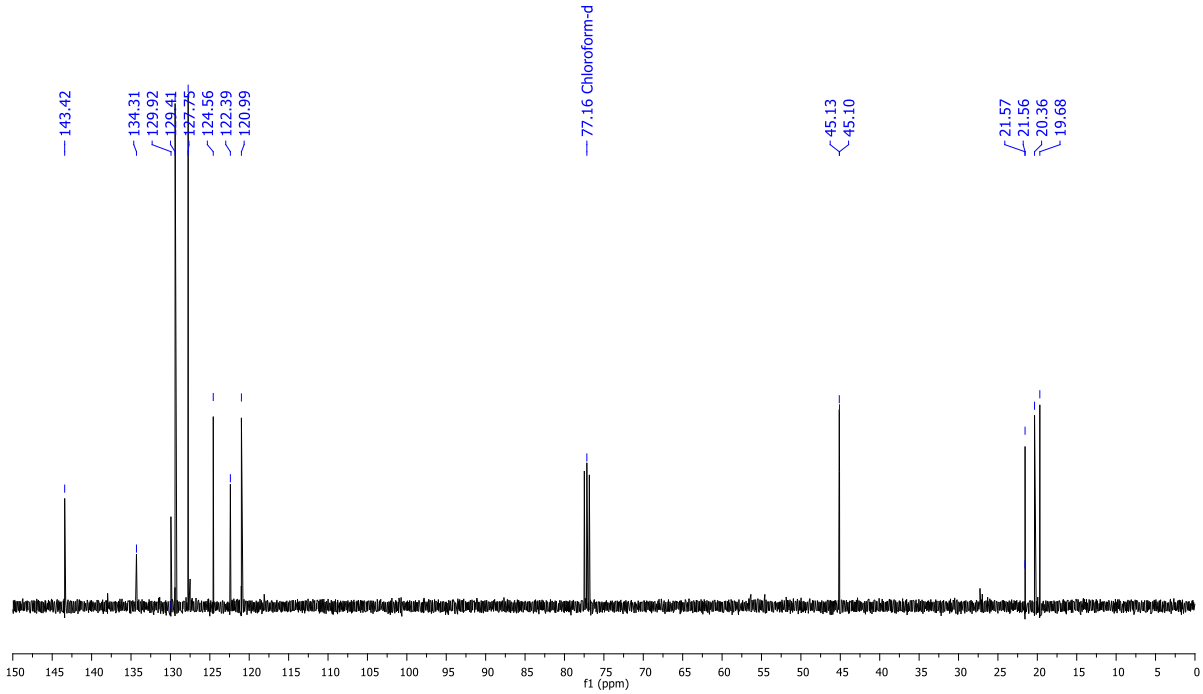
7.260 Chloroform-d
7.245
6.341
6.335
6.330
6.315
6.310
6.304
5.533
5.524
5.515
5.507
5.498
5.489
3.886
3.751
2.393
1.748
1.659
p-TsN
9a
1.76
1.93
0.43
0.43
0.88
1.69
1.87
3.00
2.87
2.76
9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0
f1 (ppm)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129.41
127.75
124.56
122.39
120.99
77.16 Chloroform-d
45.13
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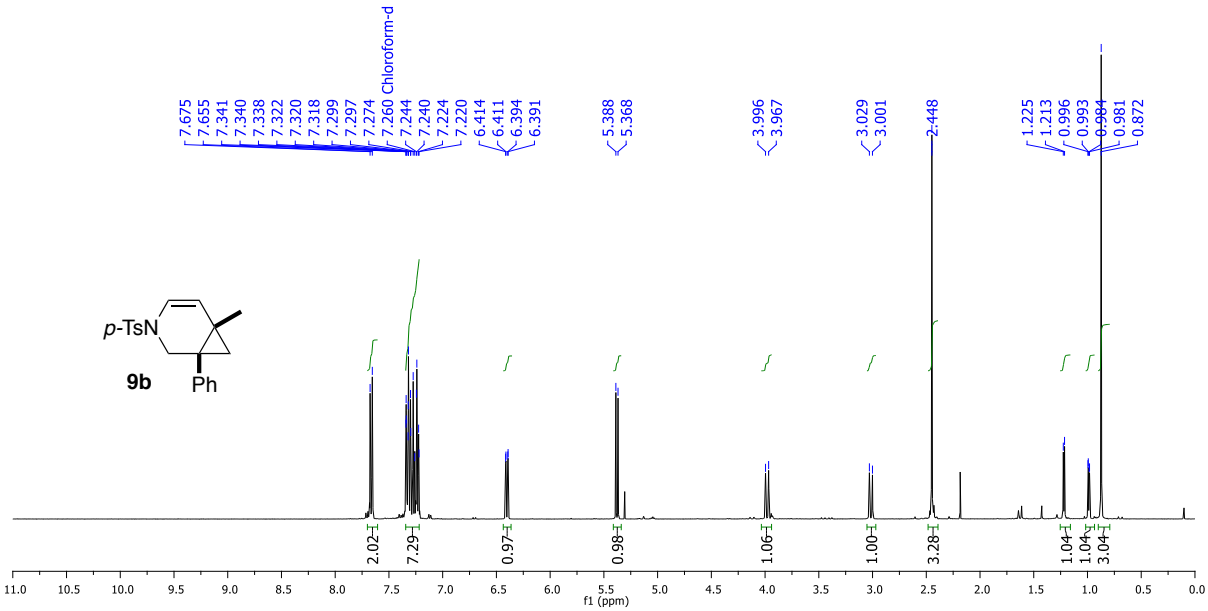
21.56
20.36
19.68
f1 (ppm)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7.340
7.338
7.322
7.320
7.318
7.299
7.297
7.274
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7.244
7.240
7.224
7.220
6.414
6.411
6.394
6.391
5.388
5.368
3.996
3.967
3.029
3.001
2.448
1.225
1.213
0.996
0.993
0.984
0.981
0.872
p-TsN
9b
Ph
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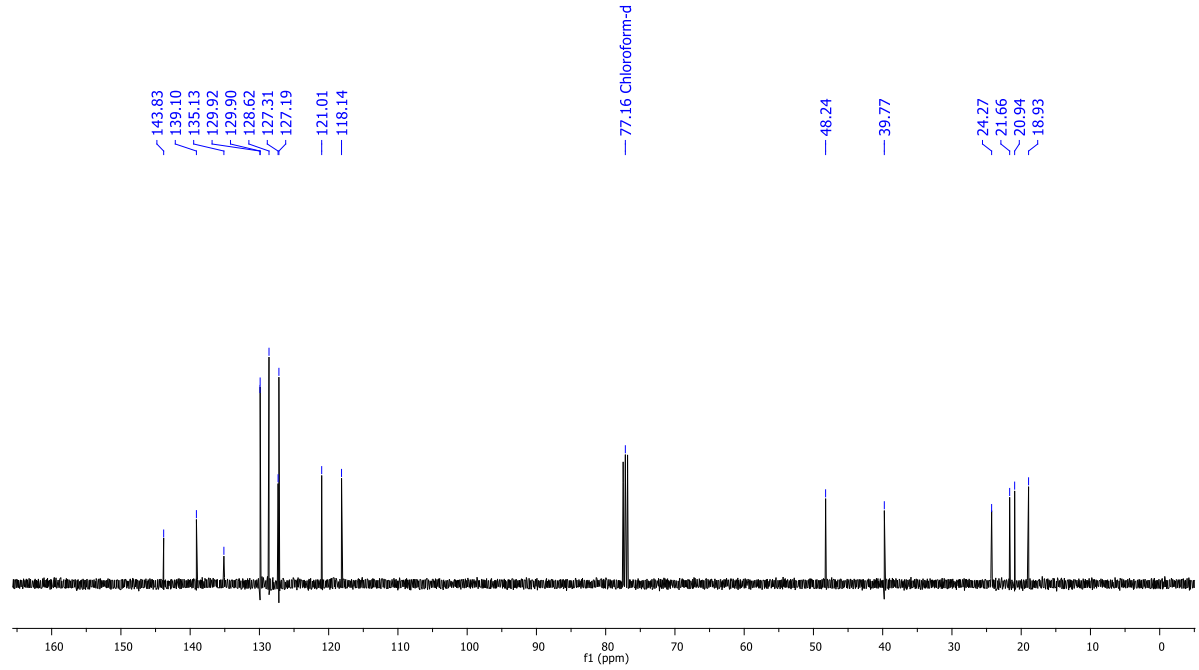
0.97
0.98
1.06
1.00
3.28
1.04
1.04
3.04
f1 (ppm)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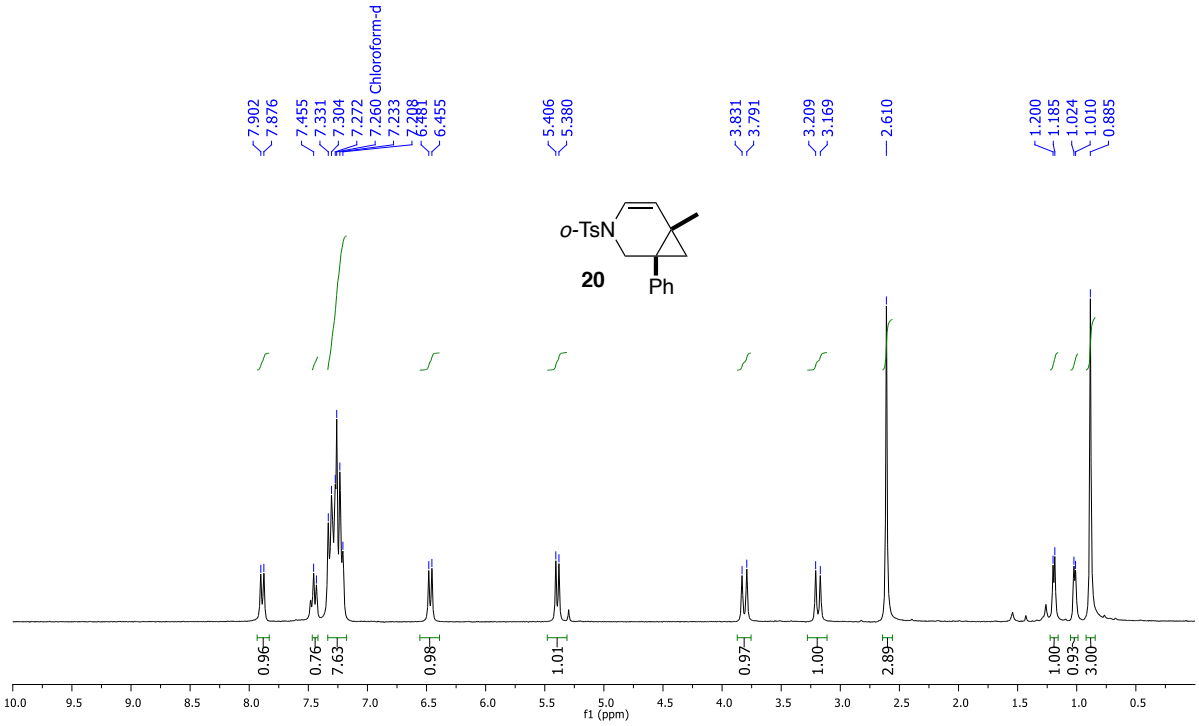
129.92
129.90
128.62
127.31
127.19
121.01
118.14
77.16 Chloroform-d
48.24
39.77
24.27
21.66
20.94
18.93
f1 (ppm)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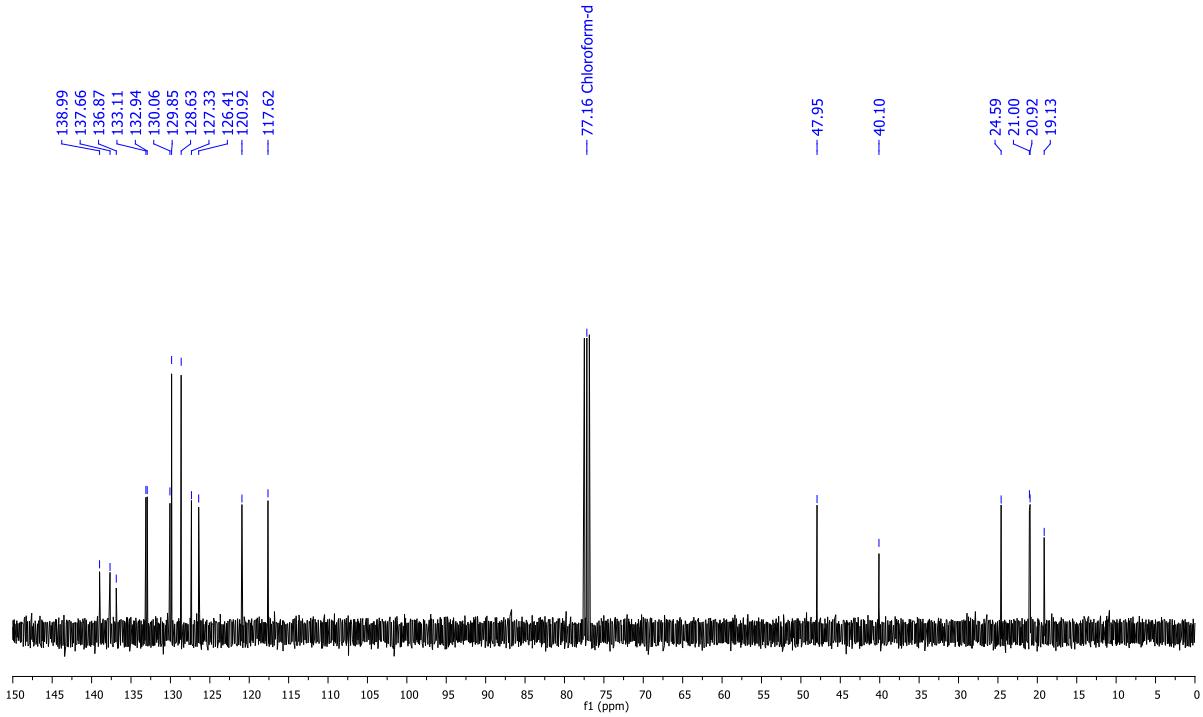
7.876
7.455
7.331
7.304
7.272
7.260 Chloroform-d
7.233
7.208
6.488
6.455
5.406
5.380
3.831
3.791
3.209
3.169
2.610
1.200
1.185
1.024
1.010
0.885
o-TsN
20
Ph
0.96
0.76
7.63
0.98
1.01
0.97
1.00
2.89
1.00
0.93
3.00
f1 (ppm)


138.99
137.66
136.87
133.11
132.94
130.06
129.85
128.63
127.33
126.41
120.92
117.62
77.16 Chloroform-d
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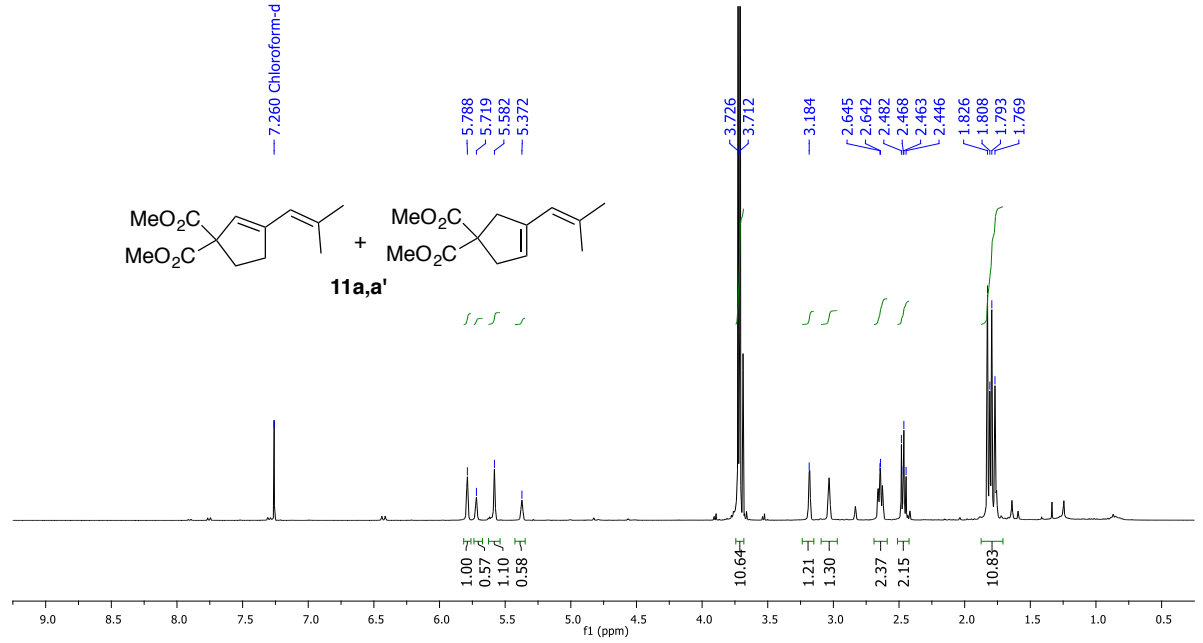
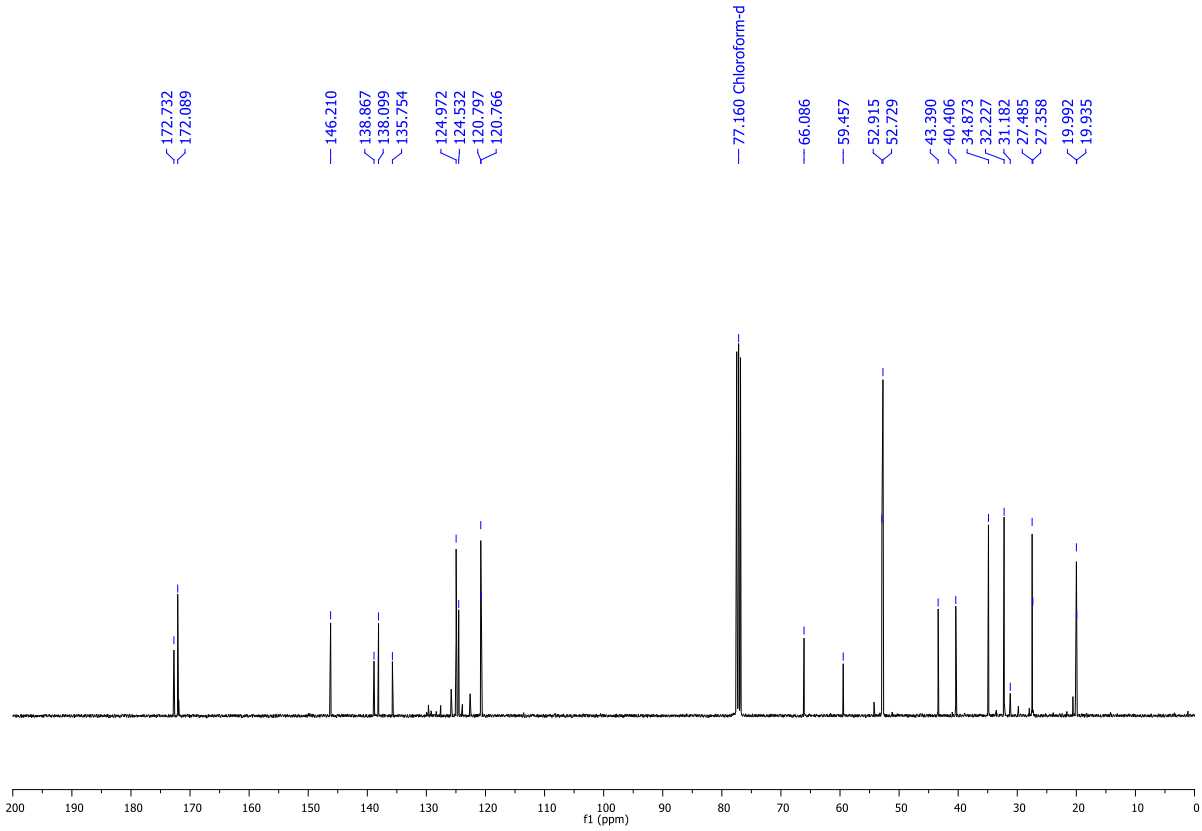
40.10
24.59
21.00
20.92
19.13
f1 (ppm)


7.260 Chloroform-d
5.788
5.719
5.582
5.372
3.726
3.712
3.184
2.645
2.642
2.482
2.468
2.463
2.446
1.826
1.808
1.793
1.769
MeO2C
MeO2C
+
MeO2C
MeO2C
11a,a'
1.00
0.57
1.10
0.58
10.64
1.21
1.30
2.37
2.15
10.83
f1 (ppm)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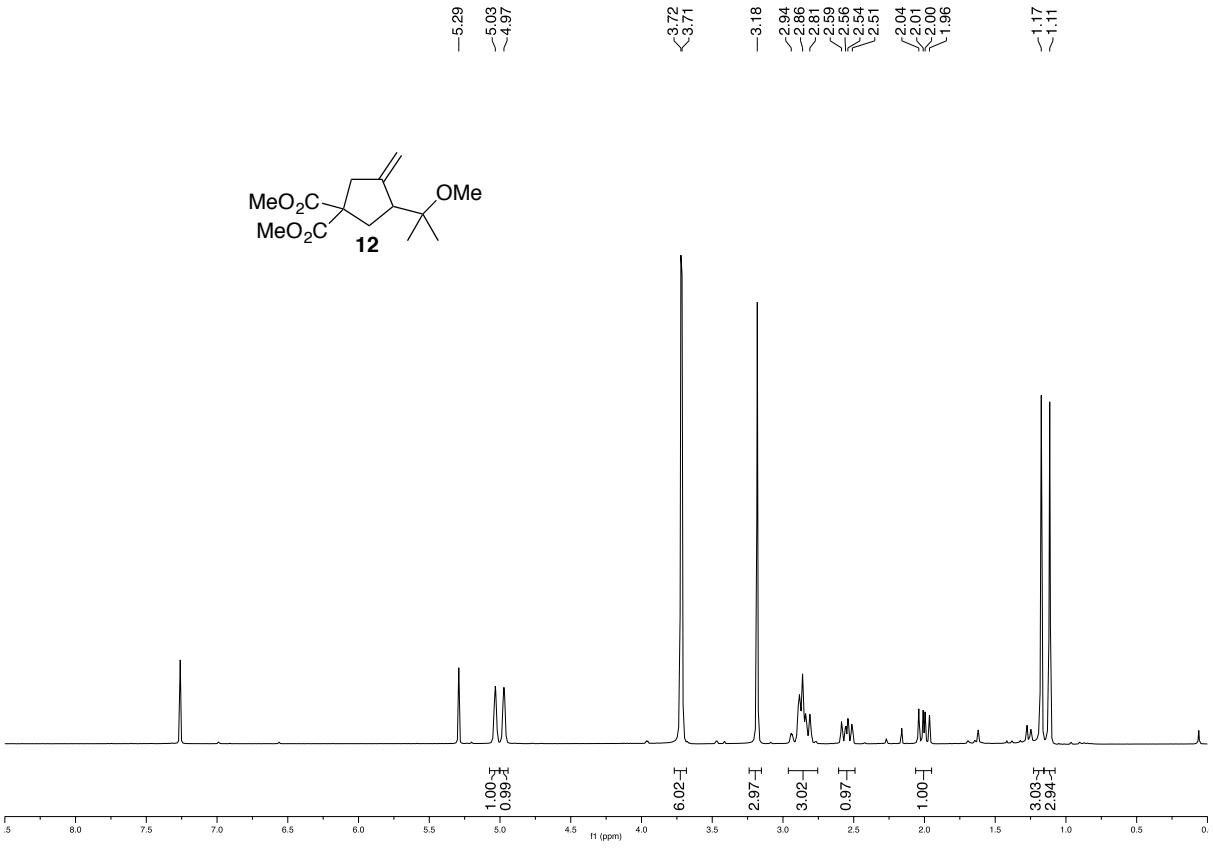
172.089
146.210
138.867
138.099
135.754
124.972
124.532
120.797
120.766
77.160 Chloroform-d
66.086
59.457
52.915
52.729
43.390
40.406
34.873
32.227
31.182
27.485
27.358
19.992
19.935
f1 (ppm)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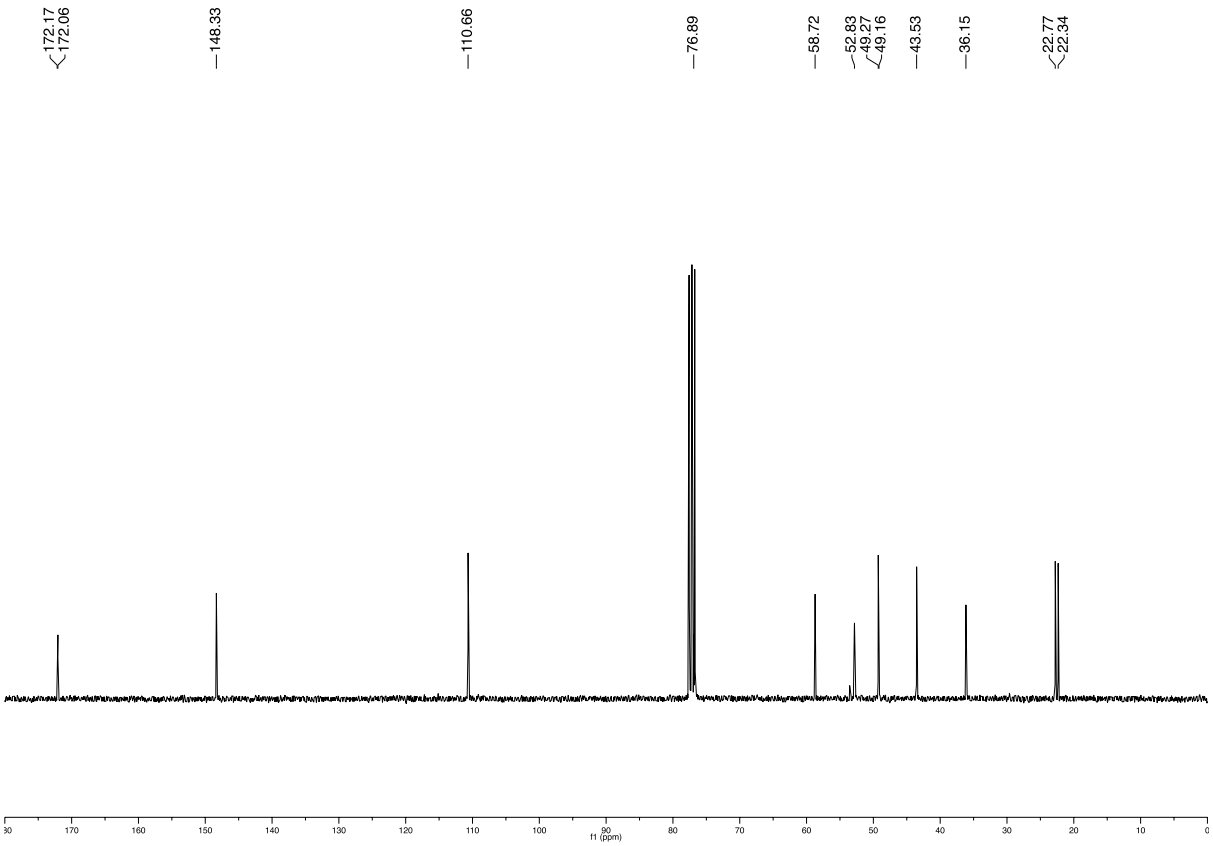
5.03
4.97
3.72
3.71
3.18
2.94
2.86
2.81
2.59
2.56
2.54
2.51
2.04
2.01
2.00
1.96
1.17
1.11
MeO2C
MeO2C
OMe
12
1.00
0.99
6.02
2.97
3.02
0.97
1.00
3.03
2.94
f1 (ppm)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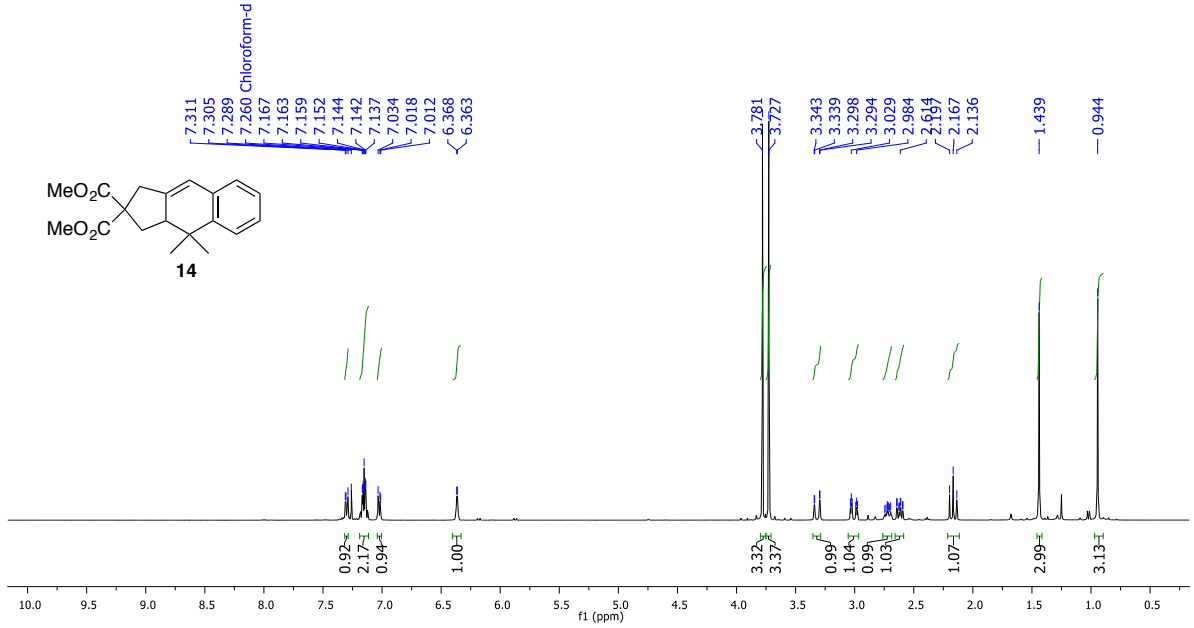
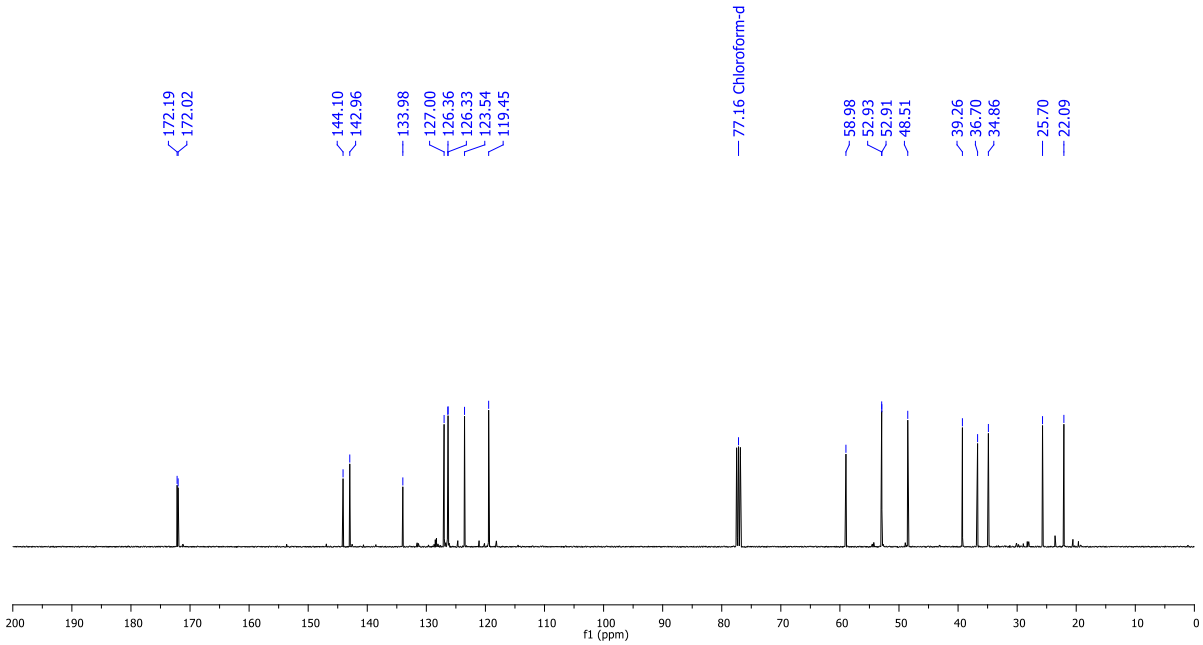
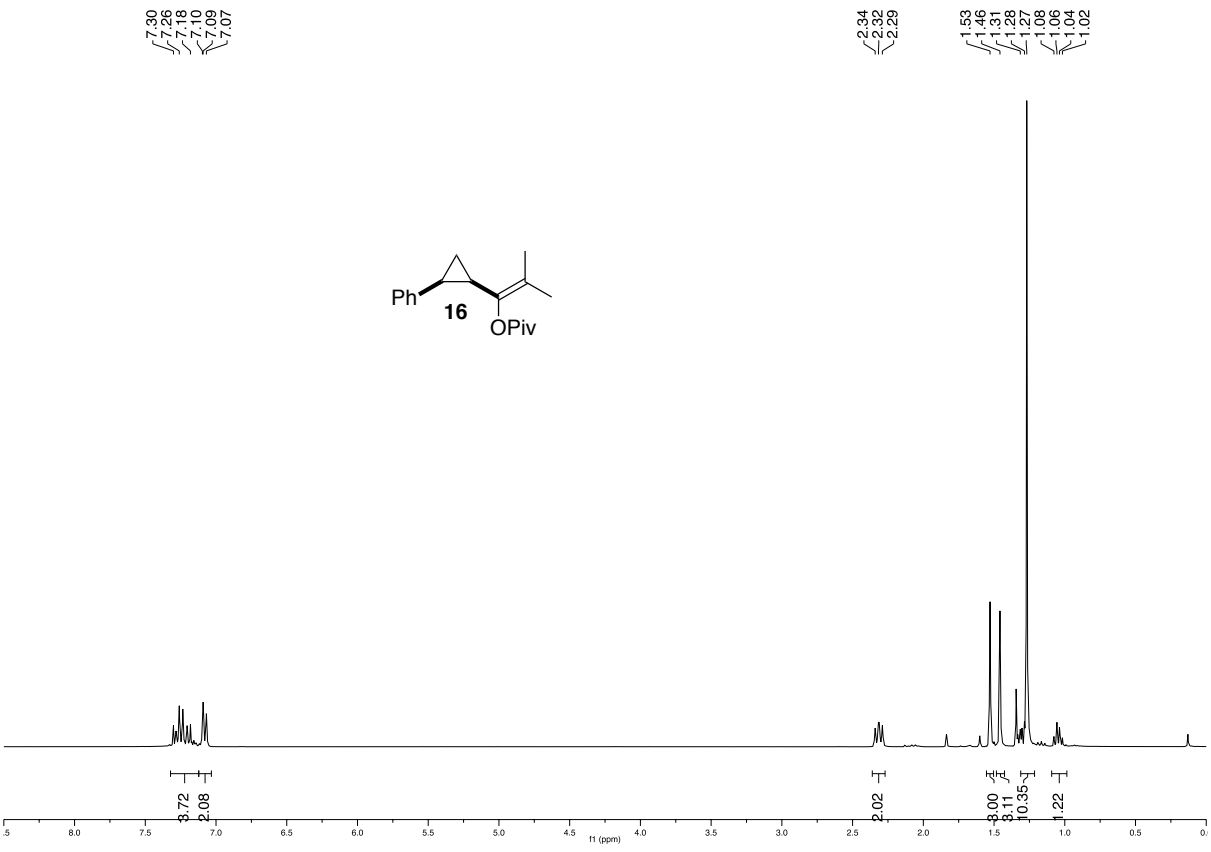
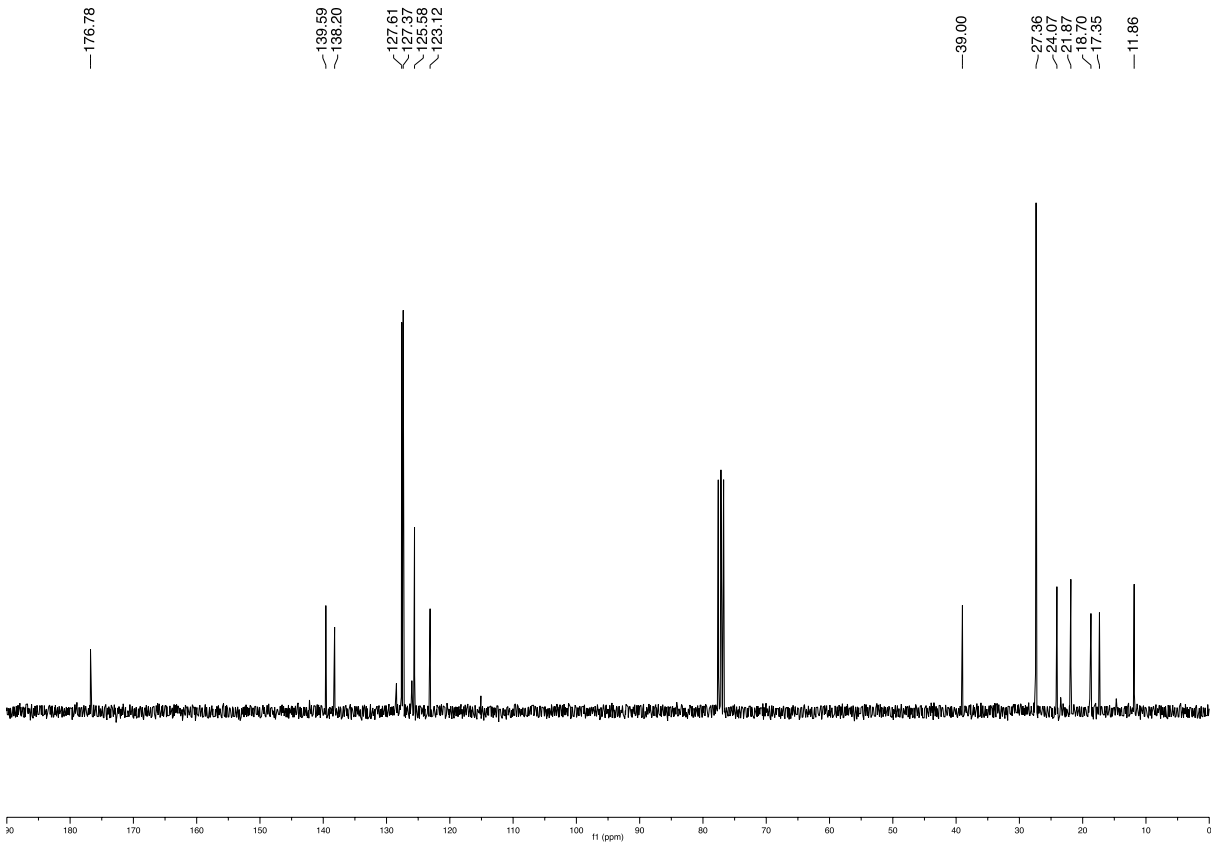
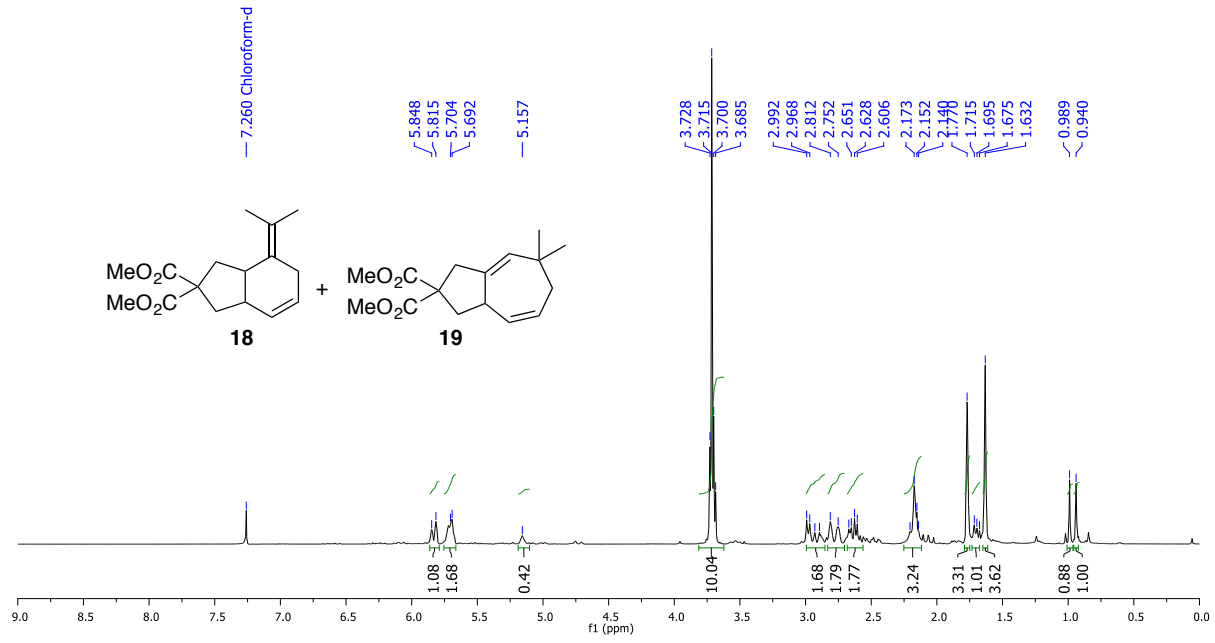
172.06
148.33
110.66
76.89
58.72
52.83
49.27
49.16
43.53
36.15
22.77
22.34
f1 (ppm)

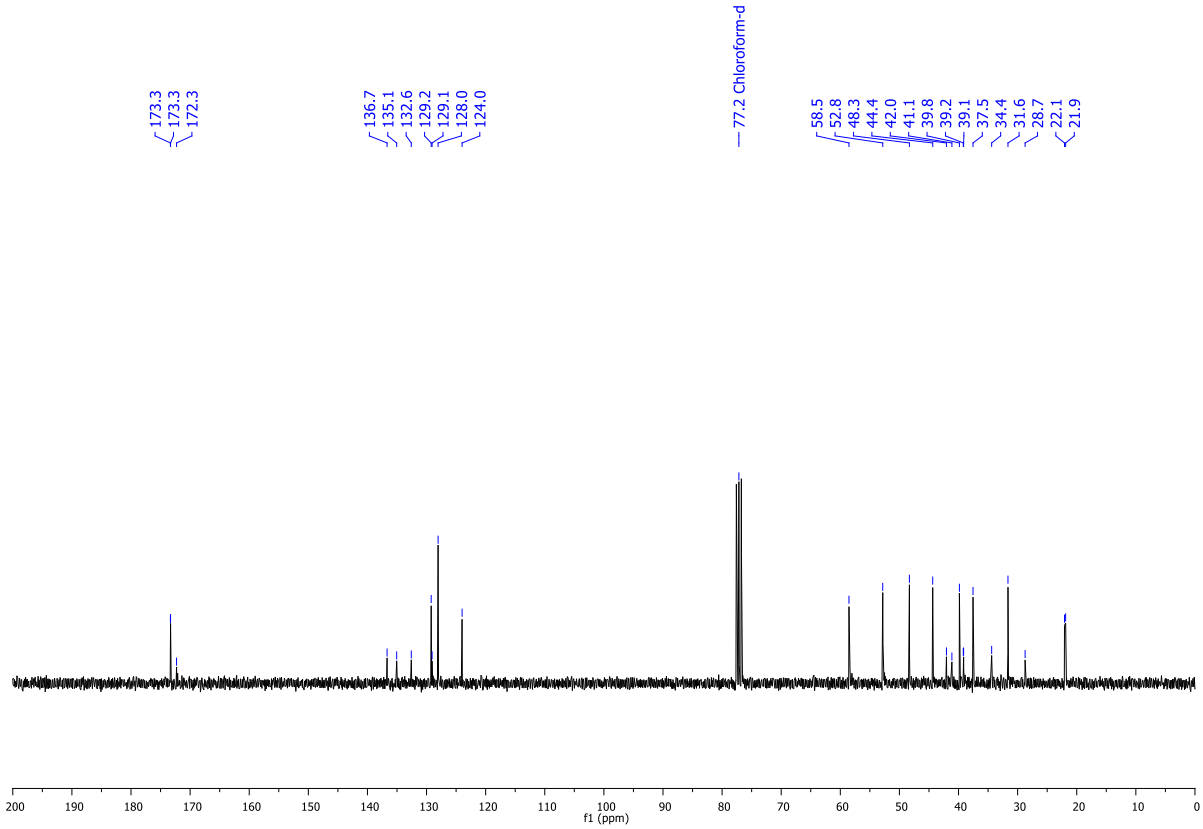

7.311
7.305
7.289
7.260 Chloroform-d
7.167
7.163
7.159
7.152
7.144
7.142
7.137
7.034
7.018
7.012
6.368
6.363
3.781
3.727
3.343
3.339
3.298
3.294
3.029
2.984
2.614
2.597
2.167
2.136
1.439
0.944
MeO2C
MeO2C
14
0.92
2.17
0.94
1.00
3.32
3.37
0.99
1.04
0.99
1.03
1.07
2.99
3.13
f1 (ppm)


172.19
172.02
144.10
142.96
133.98
127.00
126.36
126.33
123.54
119.45
77.16 Chloroform-d
58.98
52.93
52.91
48.51
39.26
36.70
34.86
25.70
22.09
f1 (ppm)


7.30
7.26
7.18
7.10
7.09
7.07
2.34
2.32
2.29
1.53
1.46
1.31
1.28
1.27
1.08
1.06
1.04
1.02
Ph
16
OPiv
3.72
2.08
2.02
3.00
8.11
10.35
1.22
f1 (ppm)

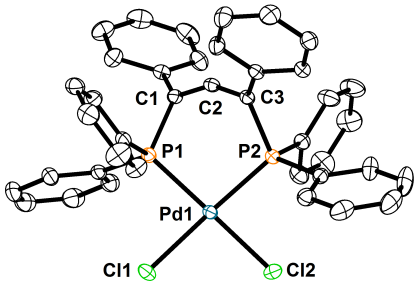

176.78
139.59
138.20
127.61
127.37
125.58
123.12
39.00
27.36
24.07
21.87
18.70
17.35
11.86
f1 (ppm)


7.260 Chloroform-d
5.848
5.815
5.704
5.692
5.157
3.728
3.715
3.700
3.685
2.992
2.968
2.812
2.752
2.651
2.628
2.606
2.173
2.152
2.140
1.770
1.715
1.695
1.675
1.632
0.989
0.940
MeO2C
MeO2C
18
+
MeO2C
MeO2C
19
1.08
1.68
0.42
10.04
1.68
1.79
1.77
3.24
3.31
1.01
3.62
0.88
1.00
f1 (ppm)



4. X-Ray crystal structure determination

Compound 3

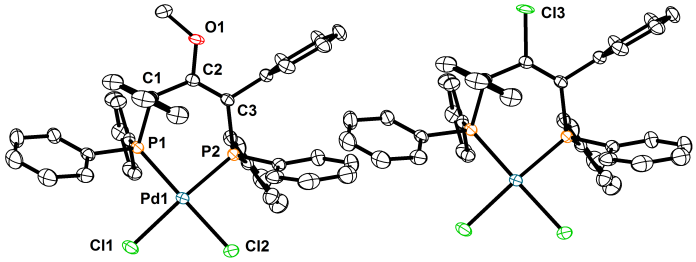


A single crystal was selected, mounted and transferred into a cold nitrogen gas stream. Intensity data was collected with a Bruker Kappa-APEX2 system using micro-source Cu-Kα radiation. Unit-cell parameters determination, data collection strategy and integration were carried out with the Bruker APEX2 suite of programs. Multi-scan absorption correction was applied.[8] The structure was solved with SHELXT-2014[9] and refined anisotropically by full-matrix least-squares methods with SHELXL-2014[9] using the WinGX suite.[10] The structure was deposited at the Cambridge Crystallographic Data Centre with number CCDC 1448365 and can be obtained free of charge via www.ccdc.cam.ac.uk.

Empirical formula	C40 H32 Cl4 P2 Pd
Formula weight	822.79

Temperature	200(1) K	
Wavelength	1.54178 Å	
Crystal system	Monoclinic	
Space group	P 21/c	
Unit cell dimensions	a = 9.8924(2) Å	α= 90°
	b = 19.0871(5) Å	β= 100.6180(10)°
	c = 19.8273(4) Å	γ = 90°
Volume	3679.63(14) $Å^3$	
Z	4	
Density (calculated)	1.485 $g.cm^{-3}$	
Absorption coefficient	7.777 mm^{-1}	
F(000)	1664	
Crystal size	0.4 x 0.3 x 0.1 mm^3	
θ range for data collection	3.241° to 66.657°	
Index ranges	-11<=h<=11, -22<=k<=14, -23<=l<=23	
Reflections collected	38783	
Independent reflections	6496 [R(int) = 0.0256]	
Completeness to θ = 66.500°	99.8 %	
Absorption correction	Semi-empirical from equivalents	
Max. and min. transmission	0.519 and 0.152	
Refinement method	Full-matrix least-squares on F^2	
Data / restraints / parameters	6496 / 0 / 424	
Goodness-of-fit on F^2	1.032	
Final R indices [I > 2σ(I)]	R1 = 0.0263, wR2 = 0.0682	
R indices (all data)	R1 = 0.0271, wR2 = 0.0688	
Largest difference peak and hole	0.928 and -0.671 $e.Å^{-3}$	

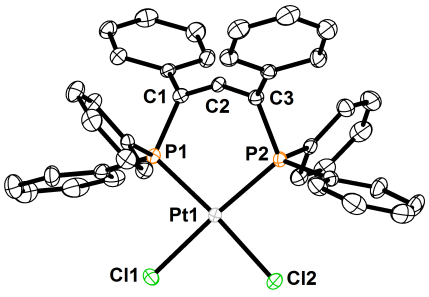
MeOH and HCl adducts on 3



A single crystal was selected, mounted and transferred into a cold nitrogen gas stream. Intensity data was collected with a Bruker Kappa-APEX2 system using micro-source Cu-Kα radiation. Unit-cell parameters determination, data collection strategy and integration were carried out with the Bruker APEX2 suite of programs. Multi-scan absorption correction was applied.[8] The structure was solved with SHELXT-2014[9] and refined anisotropically by full-matrix least-squares methods with SHELXL-2014[9] using the WinGX suite.[10] Crystal absolute structure was determined by anomalous scattering effects analysis.[11] The structure was deposited at the Cambridge Crystallographic Data Centre with number CCDC 1448366 and can be obtained free of charge via www.ccdc.cam.ac.uk.

Empirical formula	C40.80 H35.40 Cl4.20 O0.80 P2 Pd	
Formula weight	855.72	
Temperature	200(1) K	
Wavelength	1.54178 Å	
Crystal system	Monoclinic	
Space group	C c	
Unit cell dimensions	a = 20.1238(7) Å	α= 90°
	b = 12.6403(4) Å	β= 119.991(2)°
	c = 17.4640(6) Å	γ = 90°
Volume	3847.5(2) $Å^3$	
Z	4	
Density (calculated)	1.477 $g.cm^{-3}$	
Absorption coefficient	7.600 mm^{-1}	
F(000)	1736	
Crystal size	0.2 x 0.2 x 0.1 mm^3	
θ range for data collection	4.321° to 66.778°	
Index ranges	-23<=h<=23, -14<=k<=15, -20<=l<=20	
Reflections collected	30800	
Independent reflections	6637 [R(int) = 0.0223]	
Completeness to θ = 66.500°	100.0 %	
Absorption correction	Semi-empirical from equivalents	
Max. and min. transmission	0.678 and 0.399	
Refinement method	Full-matrix least-squares on F^2	
Data / restraints / parameters	6637 / 2 / 460	
Goodness-of-fit on F^2	1.062	
Final R indices [I > 2σ(I)]	R1 = 0.0232, wR2 = 0.0603	
R indices (all data)	R1 = 0.0233, wR2 = 0.0605	
Absolute structure parameter	-0.024(3)	
Largest difference peak and hole	0.667 and -0.527 $e.Å^{-3}$	

Compound 4

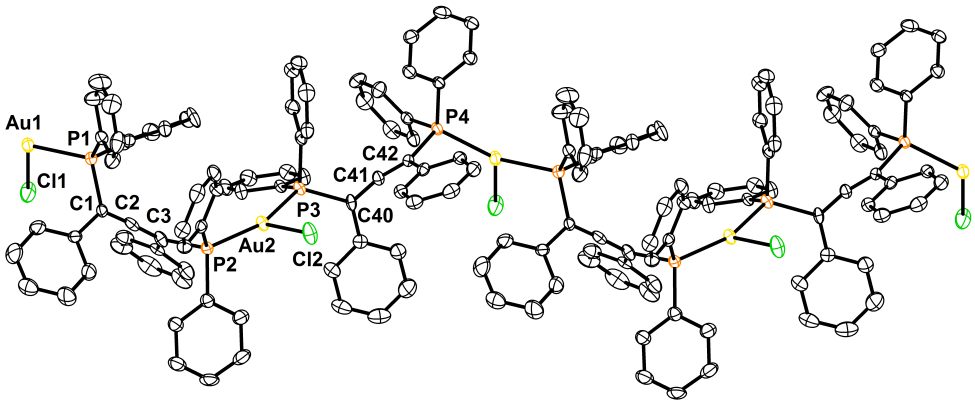


A single crystal was selected, mounted and transferred into a cold nitrogen gas stream. Intensity data was collected with a Bruker Kappa-APEX2 system using micro-source Cu-Kα radiation. Unit-cell parameters determination, data collection strategy and integration were carried out with the Bruker APEX2 suite of programs. Multi-scan absorption correction was applied.[8] The structure was solved with SIR-92[12] and refined anisotropically by full-matrix least-squares methods with SHELXL-2014[9] using the WinGX suite.[10] Crystal absolute structure was determined by anomalous scattering effects analysis. Chemical absolute configuration was then deduced.[11] The structure was deposited at the Cambridge

Crystallographic Data Centre with number CCDC 1448367 and can be obtained free of charge via www.ccdc.cam.ac.uk.

Empirical formula	C41 H32 Cl8 P2 Pt	
Formula weight	1065.29	
Temperature	200(1) K	
Wavelength	1.54178 Å	
Crystal system	Monoclinic	
Space group	P 21	
Unit cell dimensions	a = 9.9582(3) Å	α= 90°
	b = 21.3845(7) Å	β= 103.135(2)°
	c = 10.1108(3) Å	γ = 90°
Volume	2096.77(11) $Å^3$	
Z	2	
Density (calculated)	1.687 $g.cm^{-3}$	
Absorption coefficient	11.903 mm^{-1}	
F(000)	1044	
Crystal size	0.3 x 0.15 x 0.05 mm^3	
θ range for data collection	4.134° to 66.651°	
Index ranges	-11<=h<=9, -25<=k<=25, -9<=l<=12	
Reflections collected	14108	
Independent reflections	6633 [R(int) = 0.0143]	
Completeness to θ = 66.500°	99.0 %	
Absorption correction	Semi-empirical from equivalents	
Max. and min. transmission	0.715 and 0.242	
Refinement method	Full-matrix least-squares on F^2	
Data / restraints / parameters	6633 / 1 / 469	
Goodness-of-fit on F^2	1.032	
Final R indices [I > 2σ(I)]	R1 = 0.0183, wR2 = 0.0464	
R indices (all data)	R1 = 0.0184, wR2 = 0.0466	
Absolute structure parameter	-0.027(5)	
Largest difference peak and hole	0.730 and -0.377 $e.Å^{-3}$	

Compound 6



A single crystal was selected, mounted and transferred into a cold nitrogen gas stream. Intensity data was collected with a Bruker Kappa-APEX2 system using micro-source Cu-Kα radiation. Unit-cell parameters determination, data collection strategy and integration were carried out with the Bruker APEX2 suite of programs. Multi-scan absorption correction was applied.[8] The structure was solved with SHELXT-2014[9] and refined anisotropically by full-matrix least-squares methods with SHELXL-2014[9] using the WinGX suite.[10] The structure was deposited at the Cambridge Crystallographic Data Centre with number CCDC 1448368 and can be obtained free of charge via www.ccdc.cam.ac.uk.

Empirical formula	C82 H68 Au2 Cl4 O P4	
Formula weight	1728.97	
Temperature	200(1) K	
Wavelength	1.54178 Å	
Crystal system	Triclinic	
Space group	P -1	
Unit cell dimensions	a = 12.7889(5) Å	α= 93.515(3)°
	b = 16.3920(6) Å	β= 96.512(3)°
	c = 19.0982(7) Å	γ = 112.335(3)°
Volume	3655.6(2) $Å^3$	
Z	2	
Density (calculated)	1.571 $g.cm^{-3}$	
Absorption coefficient	9.957 mm^{-1}	
F(000)	1708	
Crystal size	0.25 x 0.2 x 0.1 mm^3	
θ range for data collection	3.773° to 66.902°	
Index ranges	-15<=h<=15, -19<=k<=19, -18<=l<=22	
Reflections collected	71019	
Independent reflections	12773 [R(int) = 0.0573]	
Completeness to θ = 66.500°	98.9 %	
Absorption correction	Semi-empirical from equivalents	
Max. and min. transmission	0.659 and 0.270	
Refinement method	Full-matrix least-squares on F^2	
Data / restraints / parameters	12773 / 96 / 874	
Goodness-of-fit on F^2	1.132	
Final R indices [I > 2σ(I)]	R1 = 0.0603, wR2 = 0.1429	
R indices (all data)	R1 = 0.0818, wR2 = 0.1610	
Largest difference peak and hole	2.920 and -1.575 $e.Å^{-3}$	

Compound *rac*-7

A single crystal was selected, mounted and transferred into a cold nitrogen gas stream. Intensity data was collected with a Bruker Kappa-APEX2 system using fine-focus sealed tube Mo-Kα radiation. Unit-cell parameters determination, data collection strategy and integration were carried out with the Bruker APEX2 suite of programs. Multi-scan absorption correction was applied.[8] The structure was solved with SIR-92[12] and refined anisotropically by full-matrix least-squares methods with SHELXL-2014[9] using the WinGX suite.[10] The structure was deposited at the Cambridge Crystallographic Data Centre with number CCDC 1448369 and can be obtained free of charge via www.ccdc.cam.ac.uk.

Empirical formula	C40 H32 Au2 Cl4 P2	
Formula weight	1110.33	
Temperature	200(1) K	
Wavelength	0.71073 Å	
Crystal system	Monoclinic	
Space group	P 21/n	
Unit cell dimensions	a = 12.6409(3) Å	α= 90°
	b = 16.9730(4) Å	β= 104.6610(10)°
	c = 18.0808(5) Å	γ = 90°
Volume	3753.00(16) $Å^3$	
Z	4	
Density (calculated)	1.965 $g.cm^{-3}$	
Absorption coefficient	8.208 mm^{-1}	
F(000)	2112	
Crystal size	0.5 x 0.2 x 0.15 mm^3	
θ range for data collection	2.053° to 30.533°	
Index ranges	-18<=h<=18, -24<=k<=24, -25<=l<=25	
Reflections collected	55873	
Independent reflections	11469 [R(int) = 0.0200]	
Completeness to θ = 25.242°	100.0 %	
Absorption correction	Semi-empirical from equivalents	
Max. and min. transmission	0.419 and 0.165	
Refinement method	Full-matrix least-squares on F^2	
Data / restraints / parameters	11469 / 0 / 433	
Goodness-of-fit on F^2	1.083	
Final R indices [I > 2σ(I)]	R1 = 0.0191, wR2 = 0.0439	
R indices (all data)	R1 = 0.0248, wR2 = 0.0462	
Largest difference peak and hole	0.791 and -0.979 $e.Å^{-3}$	

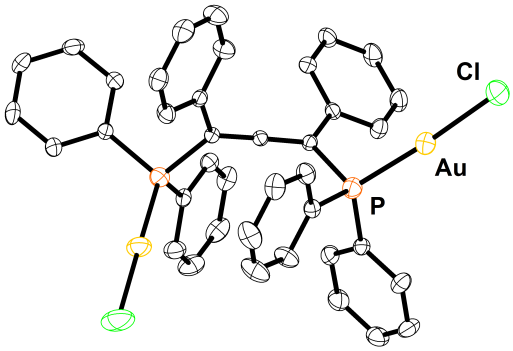
Compound a*R*-(+)-7

A single crystal was selected, mounted and transferred into a cold nitrogen gas stream. Intensity data was collected with a Bruker Kappa-APEX2 system using micro-source Cu-Kα radiation. Unit-cell parameters determination, data collection strategy and integration were carried out with the Bruker APEX2 suite of programs. Multi-scan absorption correction was applied.[8] The structure was solved with SIR-92[12] and refined anisotropically by full-matrix least-squares methods with SHELXL-2014[9] using the WinGX suite.[10] Crystal absolute structure was determined by anomalous scattering effects analysis. Chemical absolute configuration was then deduced.[11] The structure was deposited at the Cambridge Crystallographic Data Centre with number CCDC 1448370 and can be obtained free of charge via www.ccdc.cam.ac.uk.

Empirical formula	C39.50 H31 Au2 Cl3 P2	
Formula weight	1067.86	
Temperature	200(1) K	
Wavelength	1.54178 Å	
Crystal system	Monoclinic	
Space group	C 2	
Unit cell dimensions	a = 34.7999(22)Å	α= 90°

	b = 9.8414(6) Å	β= 96.507(3)°
	c = 10.8355(7) Å	γ = 90°
Volume	3687.0(4) Å^3	
Z	4	
Density (calculated)	1.924 g.cm^{-3}	
Absorption coefficient	17.776 mm^{-1}	
F(000)	2028	
Crystal size	0.10 x 0.07 x 0.03 mm^3	
θ range for data collection	2.556° to 66.578°	
Index ranges	-41<=h<=41, -11<=k<=11, -12<=l<=12	
Reflections collected	22843	
Independent reflections	6498 [R(int) = 0.0226]	
Completeness to θ = 66.500°	100.0 %	
Absorption correction	Semi-empirical from equivalents	
Max. and min. transmission	0.686 and 0.299	
Refinement method	Full-matrix least-squares on F^2	
Data / restraints / parameters	6498 / 1 / 425	
Goodness-of-fit on F^2	1.032	
Final R indices [I > 2σ(I)]	R1 = 0.0179, wR2 = 0.0445	
R indices (all data)	R1 = 0.0184, wR2 = 0.0447	
Absolute structure parameter	-0.040(7)	
Largest difference peak and hole	0.322 and -0.370 e.Å^{-3}	

Compound a*S*-(−)-7



A single crystal was selected, mounted and transferred into a cold nitrogen gas stream. Intensity data was collected with a Bruker Kappa-APEX2 system using micro-source Cu-Kα radiation. Unit-cell parameters determination, data collection strategy and integration were carried out with the Bruker APEX2 suite of programs. Multi-scan absorption correction was applied.[8] The structure was solved with SIR-92[12] and refined anisotropically by full-matrix least-squares methods with SHELXL-2014[9] using the WinGX suite.[10] Crystal absolute structure was determined by anomalous scattering effects analysis. Chemical absolute configuration was then deduced.[11] The structure was deposited at the Cambridge Crystallographic Data Centre with number CCDC 1448371 and can be obtained free of charge via www.ccdc.cam.ac.uk.

Empirical formula	C39.50 H31 Au2 Cl3 P2

Formula weight	1067.86	
Temperature	200(1) K	
Wavelength	1.54178 Å	
Crystal system	Monoclinic	
Space group	C 2	
Unit cell dimensions	a = 34.8079(11) Å	α= 90°
	b = 9.8397(3) Å	β= 96.441(2)°
	c = 10.8227(4) Å	γ = 90°
Volume	3683.4(2) $Å^3$	
Z	4	
Density (calculated)	1.926 $g.cm^{-3}$	
Absorption coefficient	17.794 mm^{-1}	
F(000)	2028	
Crystal size	0.2 x 0.1 x 0.03 mm^3	
θ range for data collection	2.555° to 66.682°	
Index ranges	-41<=h<=41, -10<=k<=11, -12<=l<=12	
Reflections collected	35967	
Independent reflections	6278 [R(int) = 0.0248]	
Completeness to θ = 66.500°	100.0 %	
Absorption correction	Semi-empirical from equivalents	
Max. and min. transmission	0.654 and 0.174	
Refinement method	Full-matrix least-squares on F^2	
Data / restraints / parameters	6278 / 1 / 425	
Goodness-of-fit on F^2	1.069	
Final R indices [I > 2σ(I)]	R1 = 0.0141, wR2 = 0.0359	
R indices (all data)	R1 = 0.0142, wR2 = 0.0359	
Absolute structure parameter	-0.034(3)	
Largest difference peak and hole	0.598 and -0.287 $e.Å^{-3}$	

5. Chiral HPLC analyses

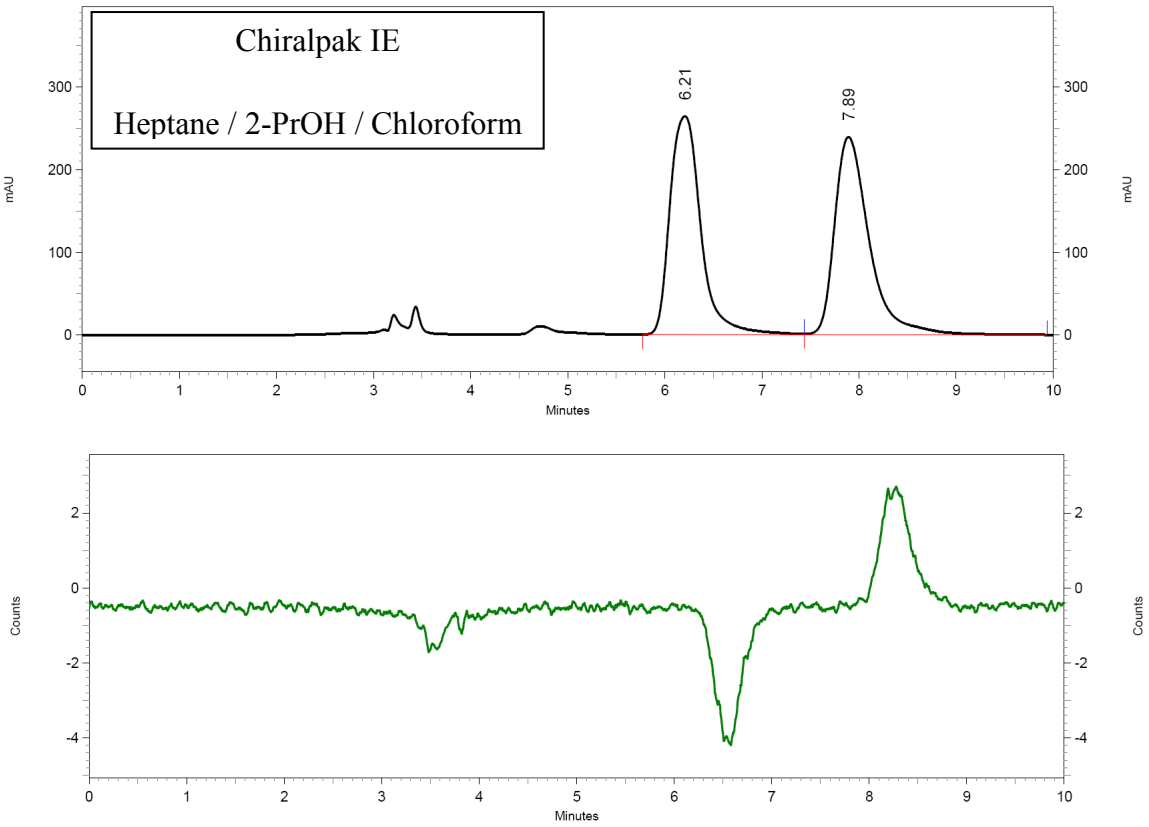
The enantiomers of complex (**7**) are separated by analytical chiral chromatography, on Chiralpak IE column with an enantioselectivity of 1.52 and a resolution of 2.94. The first eluted enantiomer has a negative CD sign at 254 nm in the ternary mixture heptane / 2-PrOH / chloroform (5/2/3) used as mobile phase. A preparative separation on 1 cm diameter column allowed the collection of 200 mg of each enantiomer with ees higher than 98%, after 150 successive injections. Retention times Rt in minutes, retention factors $k_i = (Rt_i-Rt_0)/Rt_0$, enantioselectivity factor $\alpha = k_2/k_1$ and resolution $Rs = 2 (Rt_2 - Rt_1) / (w_1 + w_2)$ are given. Rt_0 was determined by injection of tri-tertio-butyl benzene and w_i was the width of the peak.

Analytical chiral HPLC separation for compound ***rac*-7**

• The sample is dissolved in chloroform, injected on the chiral columns, and detected with an UV detector at 254 nm and circular dichroism detector at 254 nm. The flow-rate is 1 mL/min.

Column	Mobile Phase	t1	k1	t2	k2	α	Rs

Chiralpak IE	Heptane / 2-PrOH / Chloroform (5/2/3)	6.21 (-)	1.07	7.89 (+)	1.63	1.52	2.94



1: 254 nm, 4 nm

Results

Retention Time	Area	Area %	Capacity factor	Relative RT	Resolution (USP)
6.21	23419527	49.75	1.07	0.00	0.00
7.89	23657344	50.25	1.63	0.00	2.94
Totals	47076871	100.00			

Semi-preparative separation for compound ***rac*-7** :

• Sample preparation: about 577 mg of compound ***rac*-7** are dissolved in 33 mL of chloroform.

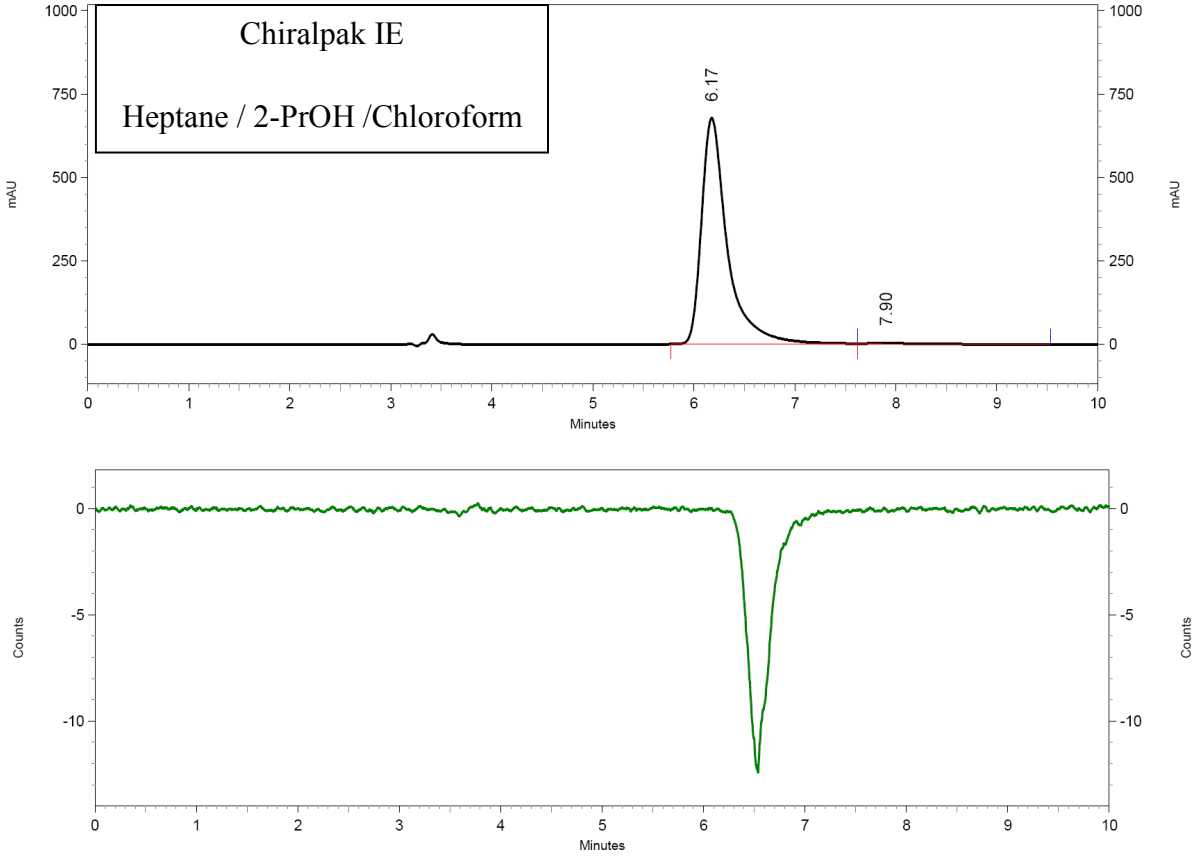
• Chromatographic conditions: Chiralpak IE (250 x 10 mm), hexane / 2-PrOH / Chloroform (5/2/3) as mobile phase, flow-rate = 5 mL/min, UV detection at 254 nm.

• Injections: 150 times 220 µL, every 4.5 minutes.

• First fraction: 257 mg of the first eluted ((-, CD 254nm)-enantiomer) with ee > 98.5%

• Second fraction: 207 mg of the second eluted ((+, CD 254nm)-enantiomer) with ee > 99.5%

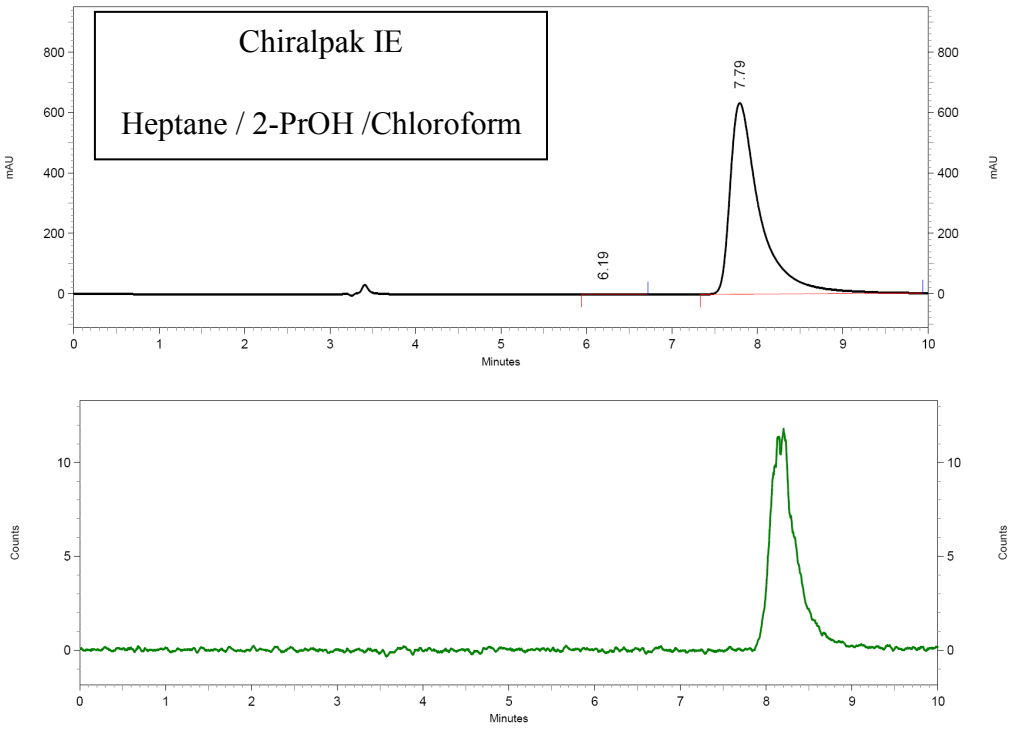
• Chromatograms of the collected fractions:



1: 254 nm, 4 nm

Results

Retention Time	Area	Area %	Capacity factor	Relative RT	Resolution (USP)
6.17	48323179	99.18	1.06	0.00	0.00
7.90	399201	0.82	1.63	0.00	3.02
Totals	48722380	100.00			



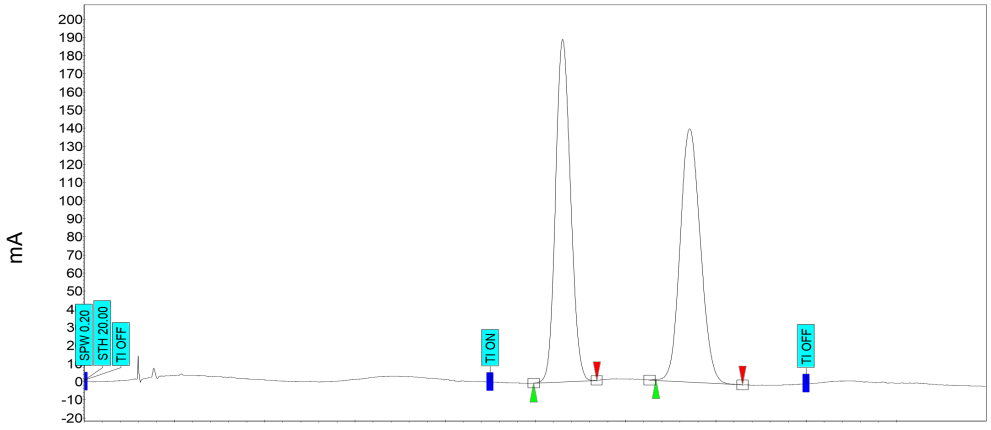
1: 254 nm, 4 nm

Results

Retention Time	Area	Area %	Capacity factor	Relative RT	Resolution (USP)
6.19	14384	0.02	1.06	0.00	0.00
7.79	61412146	99.98	1.60	0.00	3.00
Totals	61426530	100.00			

Chromatograms for **9b**

Chromatogram recorded on a CO_2 supercritical HPLC using AD-H column, with a debit of 5 mL/min and 8 % MeOH as eluant at λ = 220 nm. (±)-6-methyl-1-phenyl-3-(*p*-tolylsulfonyl)-3-azabicyclo[4.1.0]hept-4-ene was obtained.

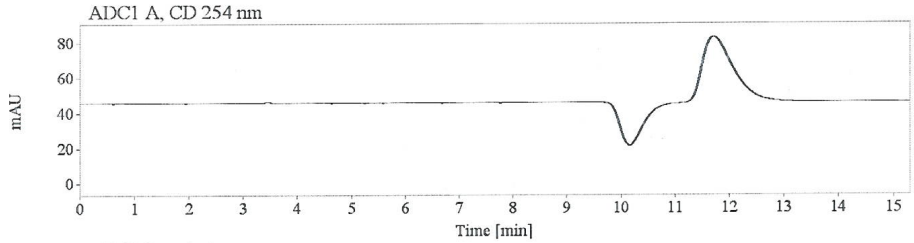


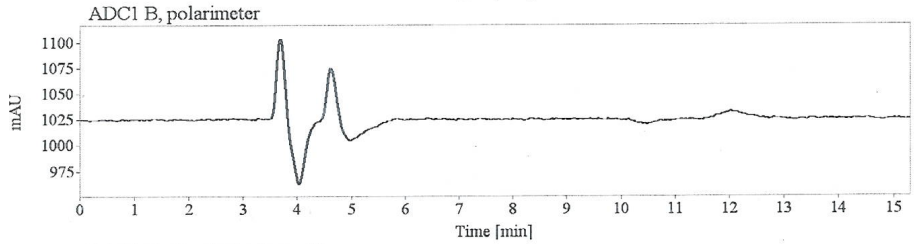
Index	Time [Min]	Area [%]
1	5.30	50.060
2	6.71	49.940
Total		100.000

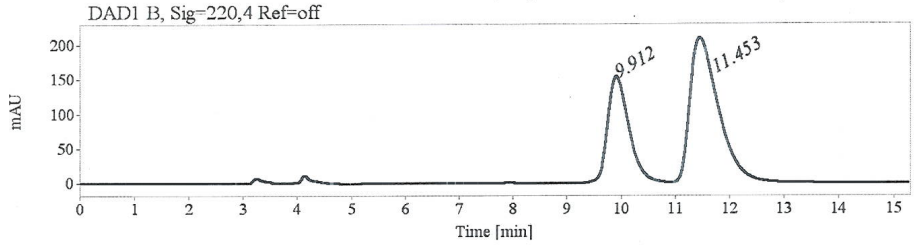
Chiral HPLC report

Sample name: Vmav473
Column: Chiralpak AS-H

Temperature: 25 degres
Mobile phase: Heptane/isopropanol (95/5), 1 mL/min







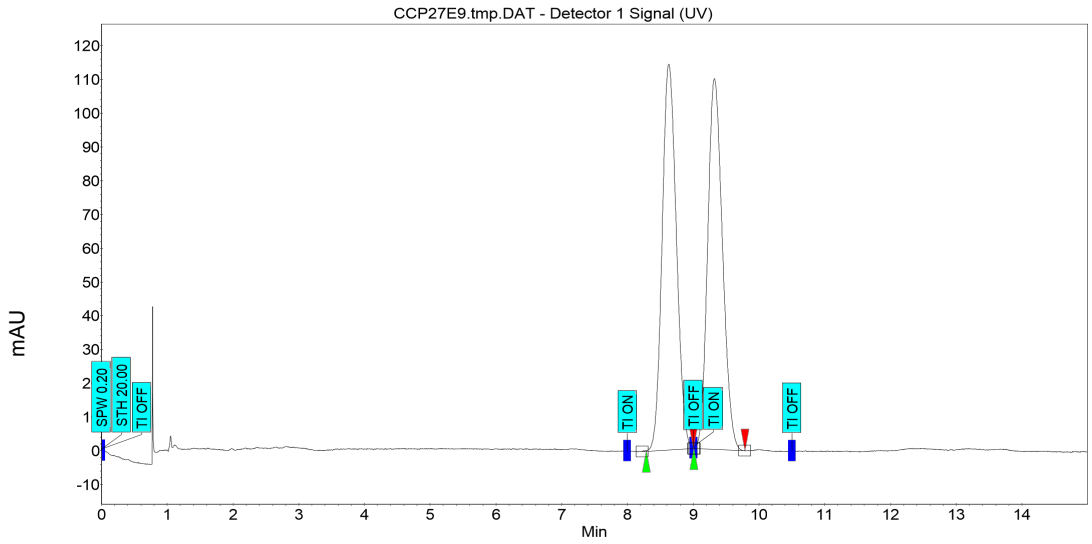
Signal: DAD1 B, Sig=220,4 Ref=off

RT [min]	Area	Area%	Capacity Factor	Enantioselectivity	Resolution (USP)
9.91	4208	35.66	2.36		
11.45	7592	64.34	2.88	1.22	1.87
Sum	11800	100.00			

Data file: C:\CHEM32\1\DATA\FENSTERBANK\MESURES-NOV-2014\VMAV473_ASH_1.D
Injection date: 11/8/2014 12:28:43 AM
Injection volume: 10.000
Acq. method: I-5-CD254NM-20MIN.M
Analysis method: I-5-CD254NM-RAPVMAV441-AS-H.M
Last changed: 11/10/2014 2:16:06 PM
Location: Vial 20
Column void time (min) 2.950

Chromatograms for **21**

Chromatogram recorded on a CO_2 supercritical HPLC using OD-H column, with a debit of 5 mL/min and 8 % MeOH as eluant at λ = 220 nm. (±)-6-methyl-1-phenyl-3-(*o*-tolylsulfonyl)-3-azabicyclo[4.1.0]hept-4-ene was obtained.



Index	Time [Min]	Area [%]
1	8.63	50.001
2	9.32	49.999
Total		100.000

Chiral HPLC report

Signal: DAD1 A, Sig=205,4 Ref=off

RT [min]	Area	Area%	Capacity Factor	Enantioselectivity	Resolution (USP)
5.92	4766	39.71	1.01		
6.84	320	2.67	1.32	1.31	0.65
12.52	6917	57.63	3.24	2.46	3.35
Sum	12003	100.00			

Signal: DAD1 B, Sig=220,4 Ref=off

RT [min]	Area	Area%	Capacity Factor	Enantioselectivity	Resolution (USP)
5.92	788	56.56	1.01		
12.52	605	43.44	3.24	3.22	16.85
Sum	1393	100.00			

Data file: C:\CHEM32\1\DATA\FENSTERBANK\MESURES-NOV-2014 \VMAV520_LC2_1.D

Injection date: 11/8/2014 2:43:29 PM **Injection volume:** 10.000

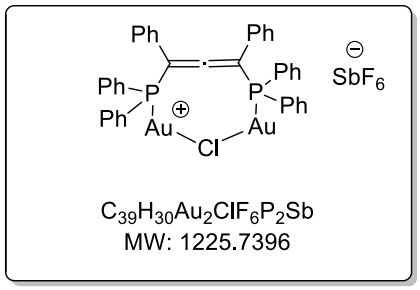
Acq. method: I-5-CD254NM-20MIN.M **Analysis method:** I-5-CD254NM-RAPCT600-LUXC2.M

Last changed: 11/10/2014 6:16:28 PM **Location:** Vial 14

Column void time (min) 2.950

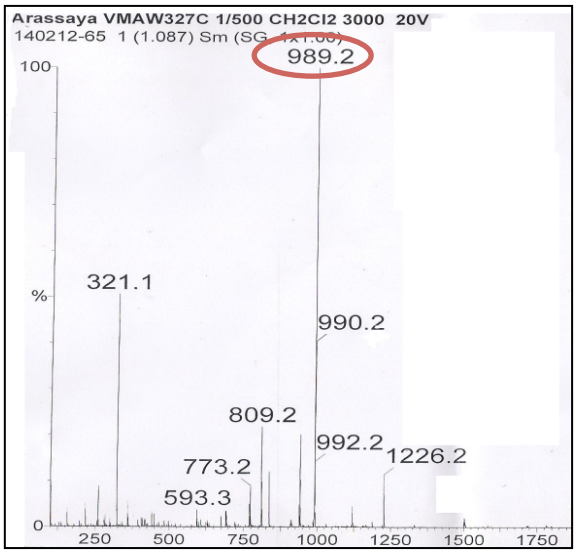
6. MS of bridged gold complex

Chloride bridged-(1,3-diphenylpropa-1,2-diene-1,3-diyl)-bis(gold(I) diphenylphosphine)



$C_{39}H_{30}Au_2ClF_6P_2Sb$
MW: 1225.7396

A solution of **1** (20 mg, 0.02 mmol, 1 equiv) and $AgSbF_6$ (6.8 mg, 0.02 mmol, 1 equiv) in CD_2Cl_2 (0.4 mL) was stirred for 3 h. The mixture was concentrated under reduced pressure to obtain the bridge gold complex (20 mg, quant).as a brown solid. (*Note*: This product cannot characterized by NMR analysis)
MS (ESI) calcd for $C_{39}H_{30}Au_2ClP_2$ 989.1, found 989.2



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