Electronic Supplementary Material (ESI) for Dalton Transactions.

Supporting Information

For

Hydrophenoxylation of internal alkynes catalysed by a heterobimetallic Cu-NHC/Au-NHC system

Faïma Lazreg, Stefano Guidone, Alberto Gómez-Herrera, Fady Nahra and Catherine S. J. Cazin*

Department of Inorganic and Physical Chemistry, Ghent University, Krijgslaan 281 - S3, 9000 Gent, Belgium. E-mail: Catherine.Cazin@Ugent.be

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General Information

All reactions were performed under an inert atmosphere of argon or nitrogen using standard Schlenk and glovebox techniques. Solvents were dispensed from a solvent purification system from Innovative Technology. ^{1}H, ^{13}C-{^{1}H} and ^{19}F-{^{1}H} NMR spectra were recorded on a Bruker Avance 300, Bruker Avance II 400 Ultrashield or Bruker Avance III 500 spectrometer at 298 K, unless otherwise stated. ^{1}H and ^{13}C NMR chemical shifts are reported relative to $CDCl_3$ (7.26, 77.16 ppm), CD_2Cl_2 (5.32, 54.4 ppm) and C_6D_6 (7.16, 128.06 ppm). Gas chromatography analyses were carried out using an Agilent 7890A system mounting a flame ionization detector and a (5%-Phenyl)-methylpolysiloxane column (30 m, 320 μm, film: 25 μm). Flash chromatography was conducted using 40-63 μm silica. Elemental analyses were performed by the Science Centre of the London Metropolitan University. All reagents were purchased and used as received unless otherwise noted. [Au(NTf_2)(IPr)] was synthesised according to the literature procedure.[1]

Synthesis and characterisation of complexes 1 and 2

Synthesis of [Cu(OH)(IPr)] (1)

In a glovebox, a flask was charged with [Cu(Cl)(IPr)] (2.5 g, 5 mmol, 1 equiv.), THF (50 mL) and CsOH (1.54 g, 10 mmol, 2 equiv.). The reaction mixture was stirred for 14 h. The suspension was filtered through a plug of Celite and washed with THF. The solution was concentrated (~ 4 mL) *in vacuo* and pentane (15 mL) was added. The product was collected by filtration, washed with pentane (3 x 5 mL) and dried. [Cu(OH)(IPr)] (**1**) was obtained as a colourless solid in 94% yield (2.2 g).

^{1}H NMR (400 MHz, $CDCl_3$) δ (ppm) = 7.49 (t, *J* = 7.8 Hz, 2H), 7.29 (d, *J* = 7.8 Hz, 4H), 7.13 (s, 2H), 2.64 – 2.50 (m, 4H), 1.31 (d, *J* = 6.9 Hz, 12H), 1.23 (d, *J* = 6.9 Hz, 12H). **^{1}H NMR (300 MHz, CD_2Cl_2)** δ (ppm) = 7.53 (t, *J* = 7.7 Hz, 2H), 7.34 (d, *J* = 7.7 Hz, 4H), 7.13 (s, 2H), 2.59 (sept, *J* = 6.9 Hz, 4H), 1.30 (d, *J* = 6.9 Hz, 12H), 1.22 (d, *J* = 6.9 Hz, 12H). **^{13}C NMR (126 MHz, CD_2Cl_2)** δ (ppm) = 182.1 ($C_{carbene}$), 146.3 (C_{Ar}), 135.4 (C_{Ar}), 130.77 (C_{Ar}), 124.6 (C_{Ar}), 123.6 (CH_{imid}), 29.2 ($CH(CH_3)_2$), 24.9 ($CH(CH_3)_2$), 24.1 ($CH(CH_3)_2$). **Elem. Anal. Calcd. for $C_{27}H_{37}CuN_2O$:** C, 69.12; H, 7.95; N, 5.97. **Found**: C, 68.86; H, 7.87; N, 5.85.

The data was in accordance with the literature.[2]

Synthesis of [Au(OTf)(IPr)] (2)

In a glovebox, a flask was charged with [Au(Cl)(IPr)] (500 mg, 0.805 mmol), AgOTf (419 mg, 1.74 mmol) and CH_2Cl_2 (50 mL). The reaction mixture was stirred in the absence of light for 16 h. The

suspension was filtered through a plug of celite. The solvent was removed under reduced pressure and the desired compound was obtained as a colourless solid (530 mg, 93%).

^{1}H NMR (400 MHz, $CDCl_3$) δ (ppm) = 7.55 (t, *J* = 7.8 Hz, 2H), 7.32 (d, *J* = 7.8 Hz, 4H), 7.26 (s, 2H), 2.53 – 2.43 (m, 4H), 1.33 (d, *J* = 6.9 Hz, 12H), 1.23 (d, *J* = 6.9 Hz, 12H). **^{1}H NMR (500 MHz, C_6D_6)** δ (ppm) = 7.21 – 7.18 (m, 2H), 7.01 (d, *J* = 7.8 Hz, 4H), 6.22 (s, 2H), 2.39 – 2.36 (m, 4H), 1.33 (d, *J* = 6.9 Hz, 12H), 1.01 (d, *J* = 6.8 Hz, 12H). **^{13}C NMR (101 MHz, $CDCl_3$)** δ (ppm) = 162.1 ($C_{carbene}$), 145.6 (C_{Ar}), 133.5 (C_{Ar}), 131.2 (C_{Ar}), 124.5 (C_{Ar}), 123.8 (CH_{imid}), 29.0 ($CH(CH_3)_2$), 24.3 ($CH(CH_3)_2$), 24.2 ($CH(CH_3)_2$). **^{19}F-{^{1}H} NMR (377 MHz, $CDCl_3$)** δ (ppm) = -77.12. **^{19}F-{^{1}H} NMR (282.2 MHz, CD_2Cl_2)** δ (ppm) = -78.3. **^{19}F-{^{1}H} NMR (282.2 MHz, C_6D_6)** δ (ppm) = -76.91. **Elem. Anal. Calcd. for $C_{28}H_{36}AuF_3N_2O_3S$**: C, 45.78; H, 4.94; N, 3.81. **Found:** C, 45.85; H, 4.95; N, 3.75.

The data was in accordance with the literature.[3]

Mechanistic studies

Mechanistic tests from Scheme 5

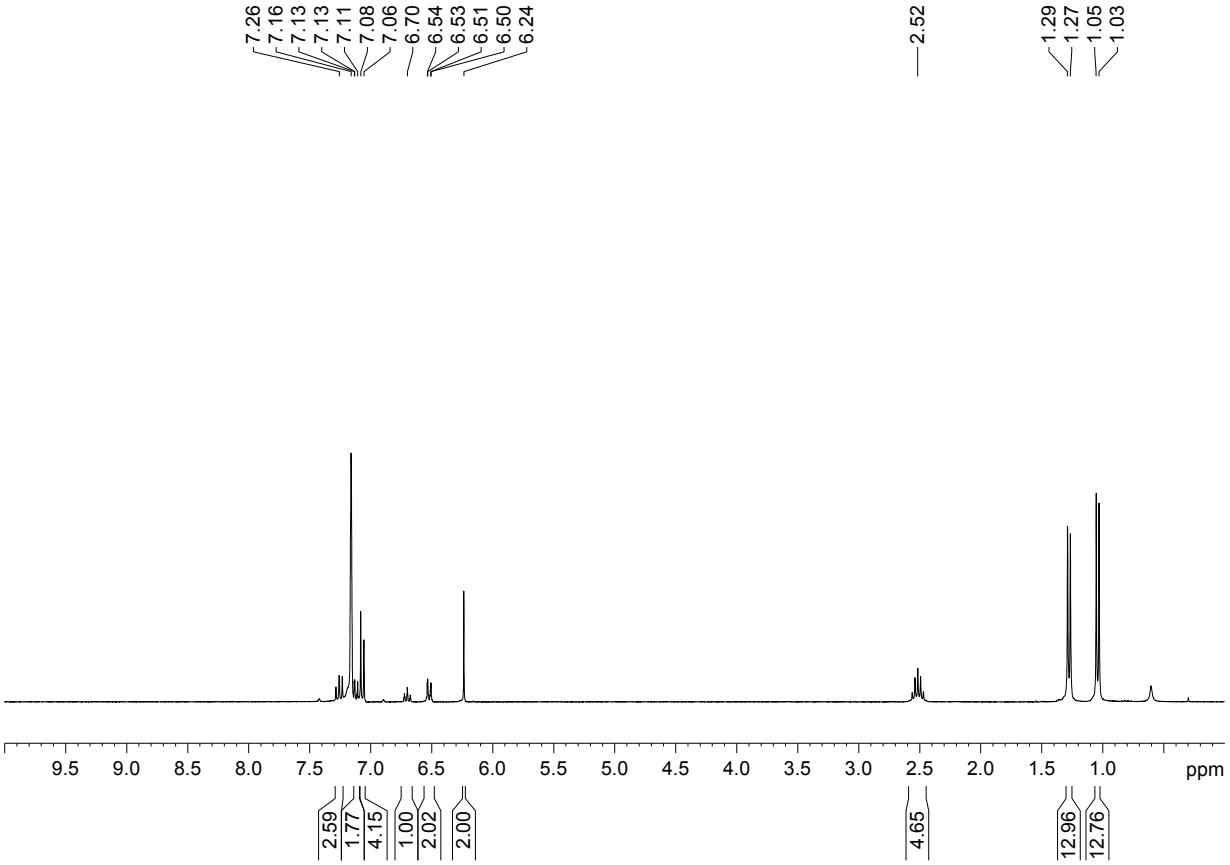
Stoichiometric reaction between [Cu(OH)(IPr)] (1) and phenol

Test 1: In a glovebox, a vial was charged with [Cu(OH)(IPr)] (1) (100 mg, 0.21 mmol, 1 equiv.) and phenol (20 mg, 0.21 mmol, 1 equiv.). Benzene-d_6 was added and the mixture was stirred at 60 °C for 16 hours. Then, a sample was taken to be analysed by ^{1}H NMR.

Test 2: In a glovebox, a vial was charged with [Cu(OH)(IPr)] (1) (100 mg, 0.21 mmol, 1 equiv.) and phenol (20 mg, 0.21 mmol, 1 equiv.). The mixture was stirred at 60 °C for 16 hours in the absence of solvent. Then, pentane was added and the product was obtained by filtration as a white solid.

The ^{1}H NMR data recorded for test 1 and 2 showed the same results.

^{1}H NMR (C_6D_6) of [Cu(OPh)(IPr)]



^{1}H NMR (300 MHz, C_6D_6) δ (ppm) = 7.26 (t, *J* = 7.8 Hz, 2H), 7.16 – 7.09 (m, 2H), 7.07 (d, *J* = 7.8 Hz, 4H), 6.71 – 6.69 (m, 1H), 6.54 – 6.50 (m, 2H), 6.24 (s, 2H), 2.52 (sept, *J* = 6.9 Hz, 4H), 1.28 (d, *J* = 6.9 Hz, 12H), 1.04 (d, *J* = 6.9 Hz, 12H). (For full characterisation see below)

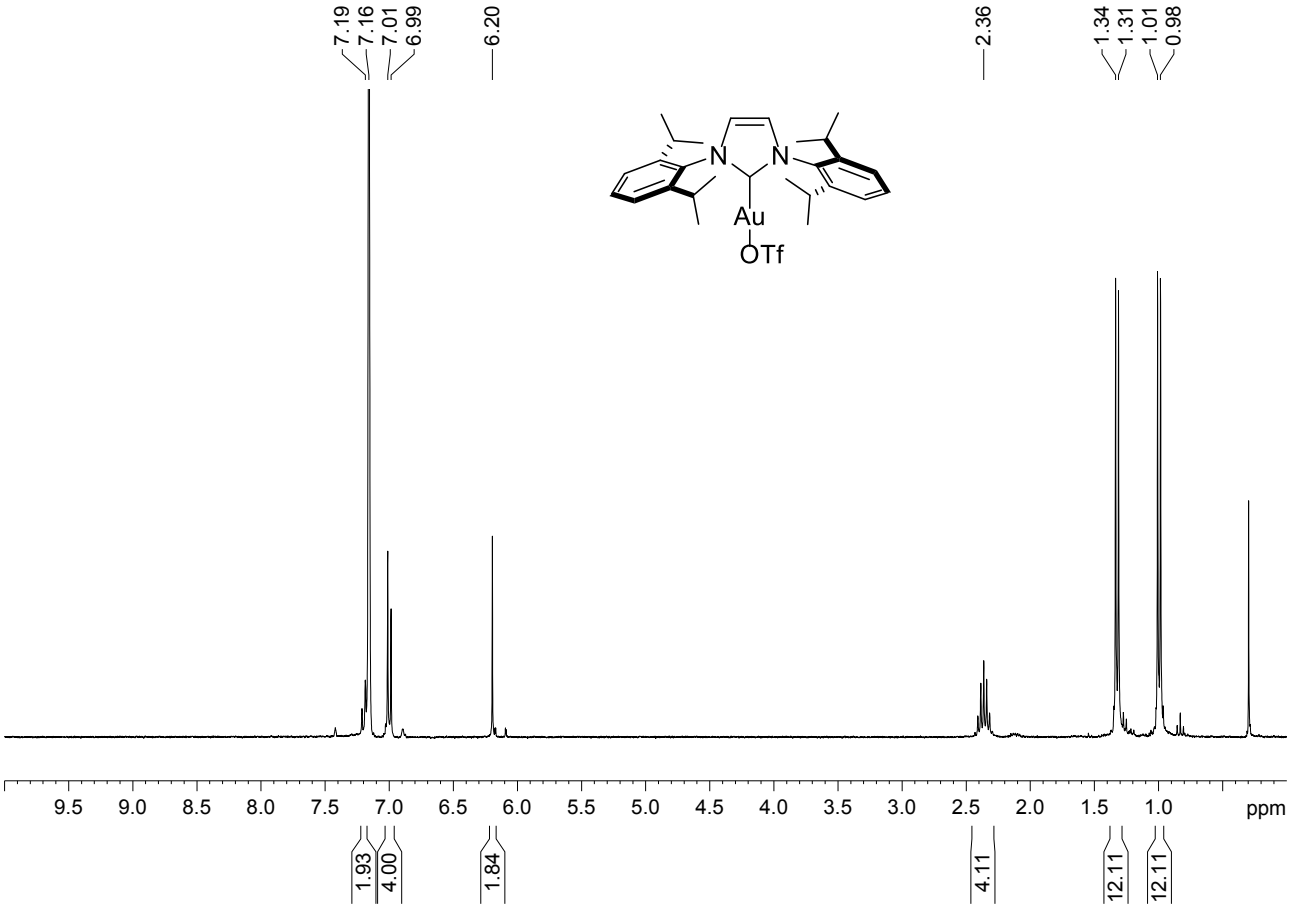
Stoichiometric reaction between [Au(OTf)(IPr)] (2) and phenol

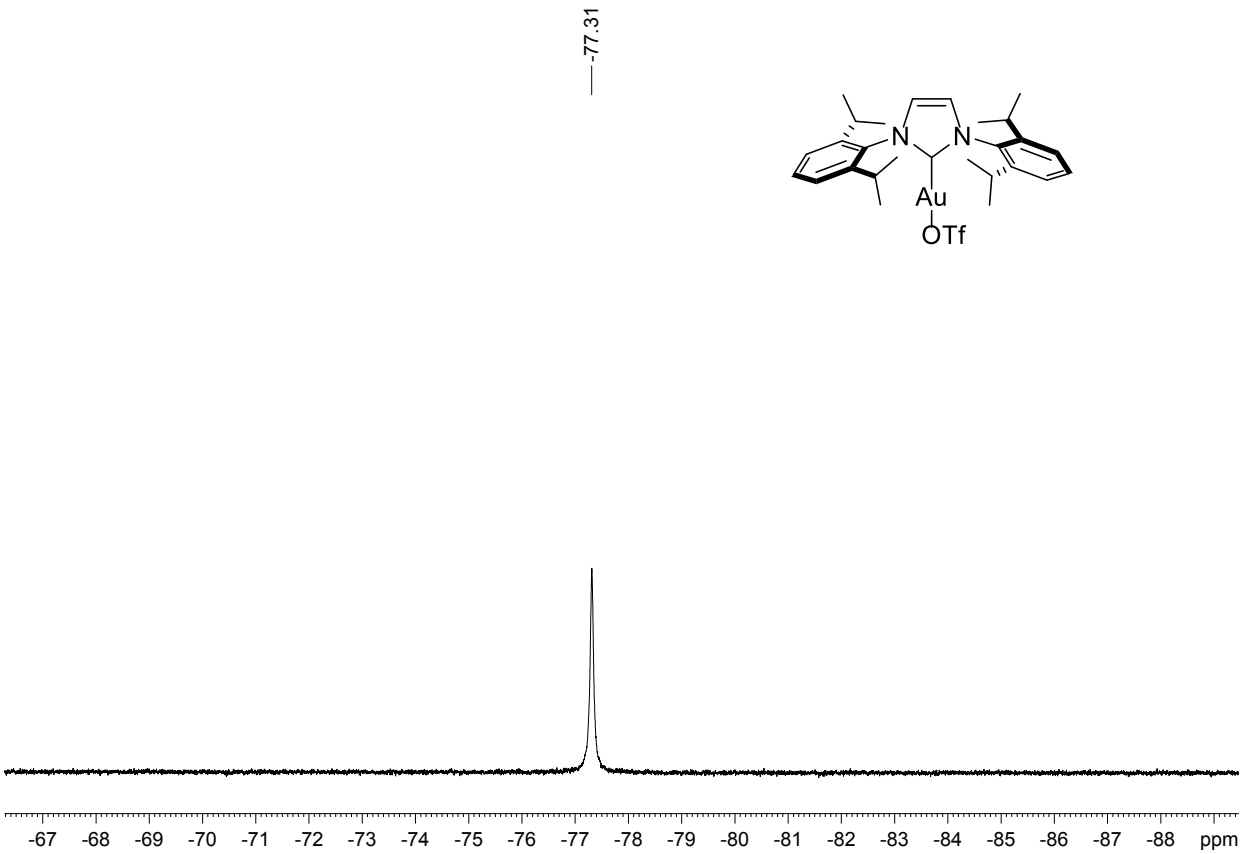
Test 1: In a glovebox, a vial was charged with [Au(OTf)(IPr)] (2) (20 mg, 0.027 mmol, 1 equiv.) and phenol (2.6 mg, 0.027 mmol, 1 equiv.). Benzene-d_6 was added and the mixture was stirred at 60 °C for 16 hours. Then, the mixture was analysed by ^{1}H NMR.

Test 2: In a glovebox, a vial was charged with [Au(OTf)(IPr)] (2) (20 mg, 0.027 mmol, 1 equiv.) and phenol (2.6 mg, 0.027 mmol, 1 equiv.). The mixture was stirred at 60 °C for 16 hours in the absence of solvent. Then, benzene-d_6 was added and the mixture was analysed by ^{1}H NMR analysis.

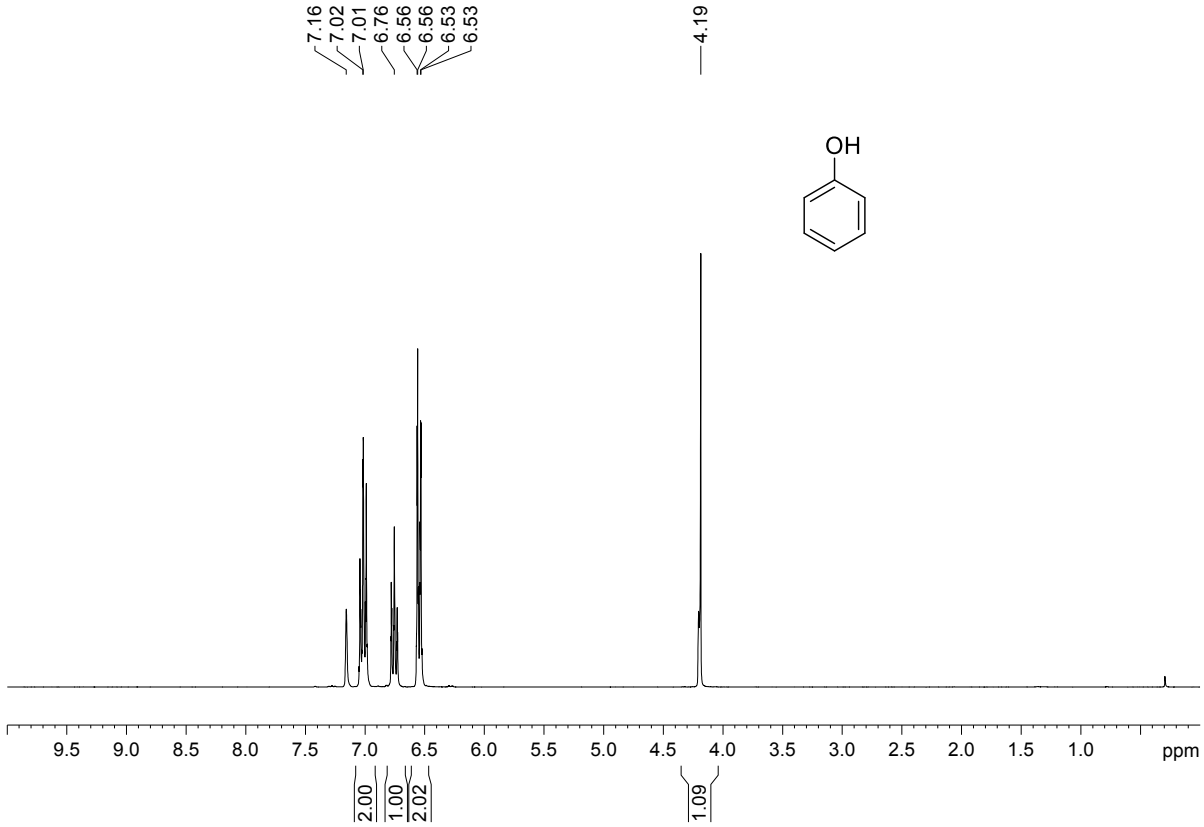
Both tests showed no reaction.

^{1}H NMR (C_6D_6) and ^{19}F-{^{1}H} NMR (C_6D_6) of [Au(OTf)(IPr)]



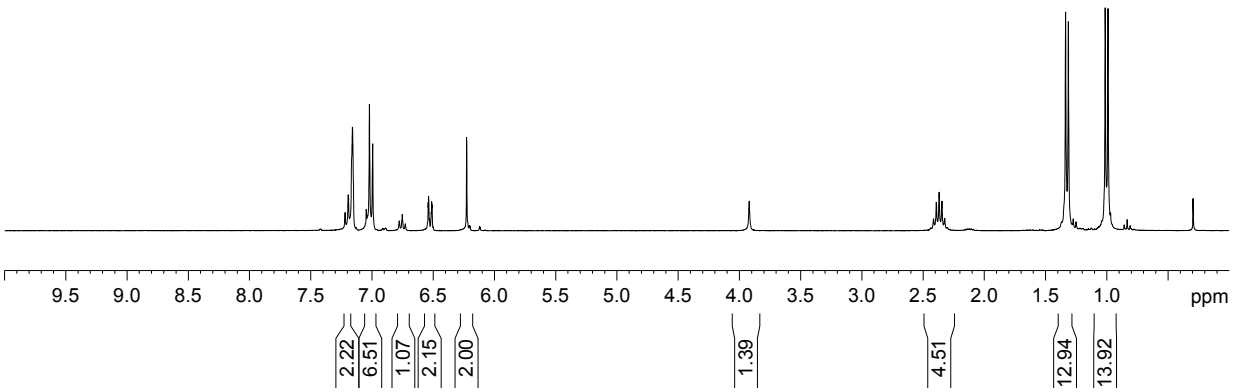


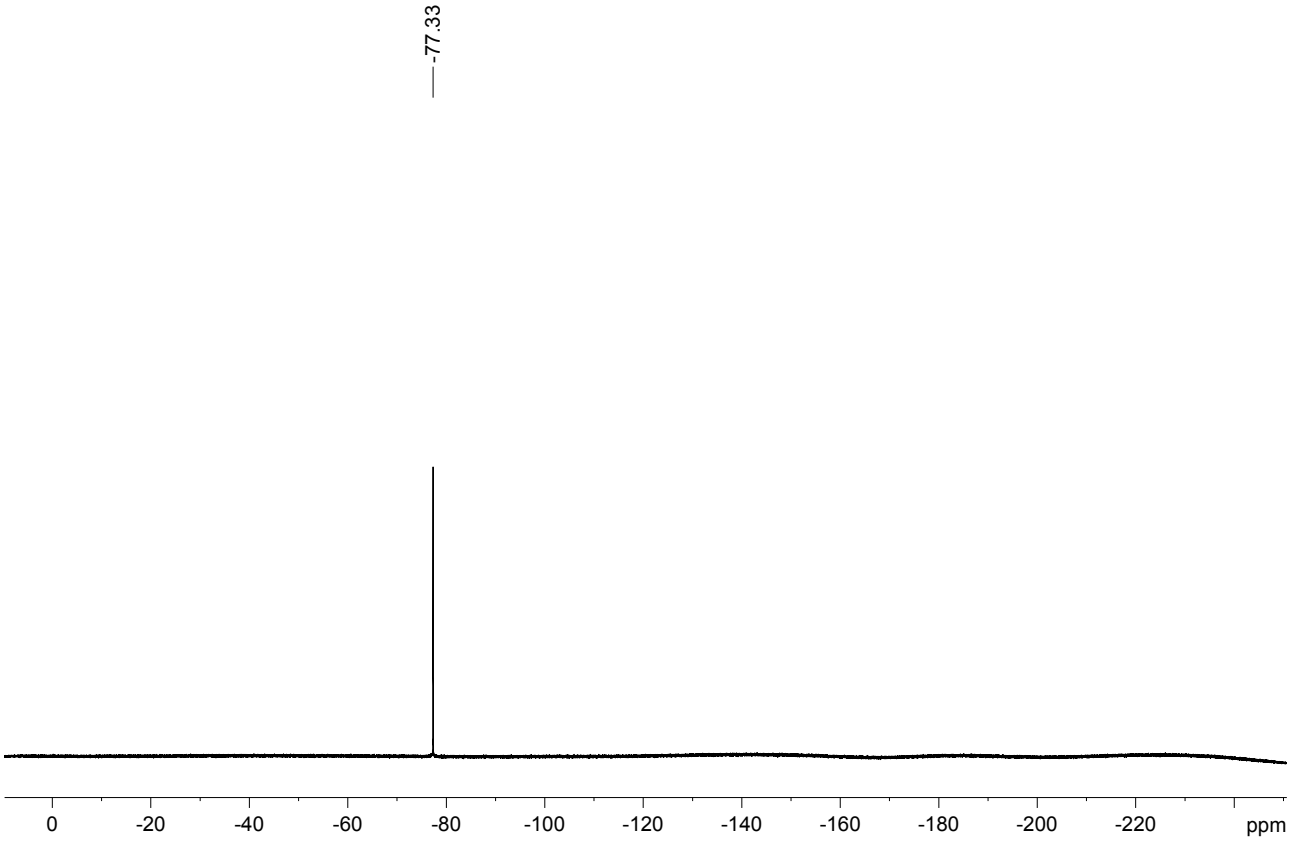
^{1}H NMR (C_6D_6) of phenol



^{1}H NMR (C_6D_6) and ^{19}F-{^{1}H} NMR (C_6D_6) of the reaction mixture

[Au(OTf)(IPr)] (2) + phenol





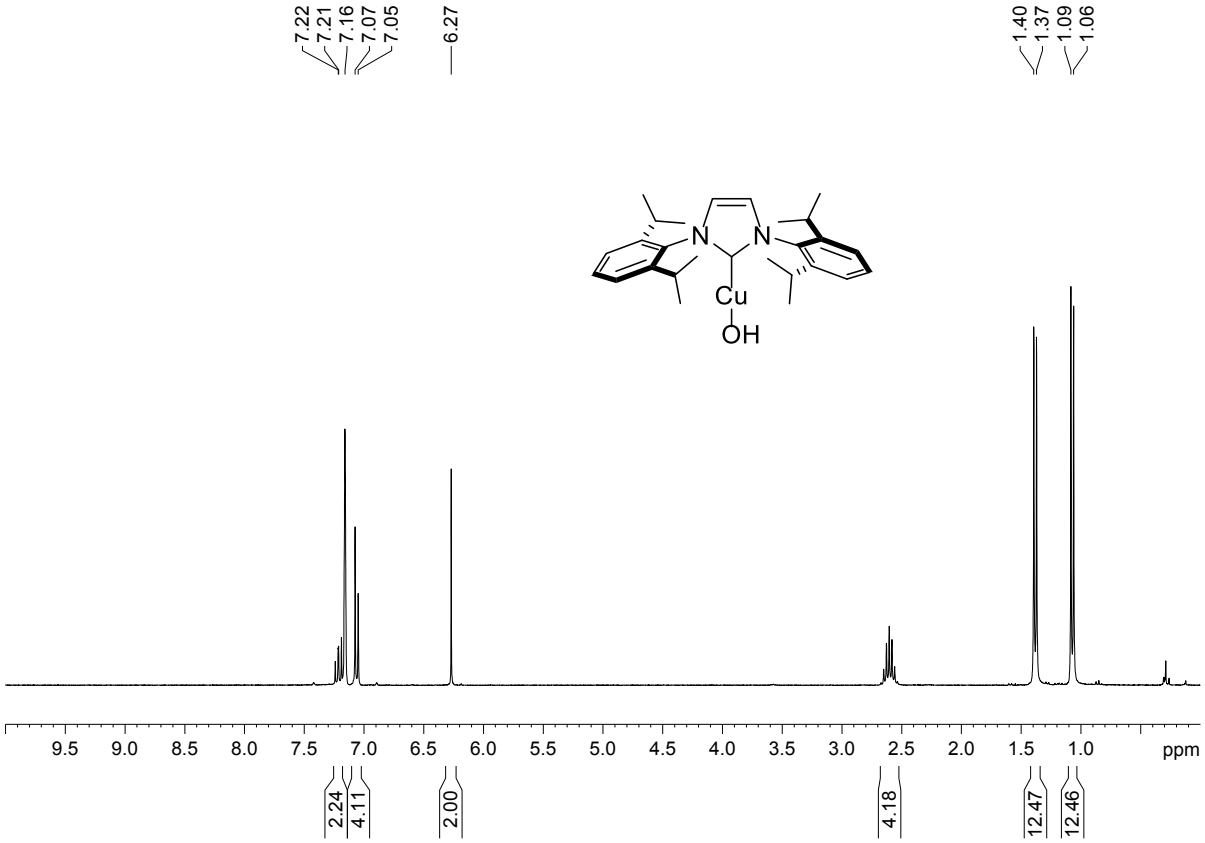
Stoichiometric reaction between [Cu(OH)(IPr)] (1) and diphenylacetylene

Test 1: In a glovebox, a vial was charged with [Cu(OH)(IPr)] (1) (20 mg, 0.043 mmol, 1 equiv.) and diphenylacetylene (7.6 mg, 0.043 mmol, 1 equiv.). Benzene-d_6 was added and the mixture was stirred at 60 °C for 16 hours. Then, the mixture was analysed by ^{1}H NMR.

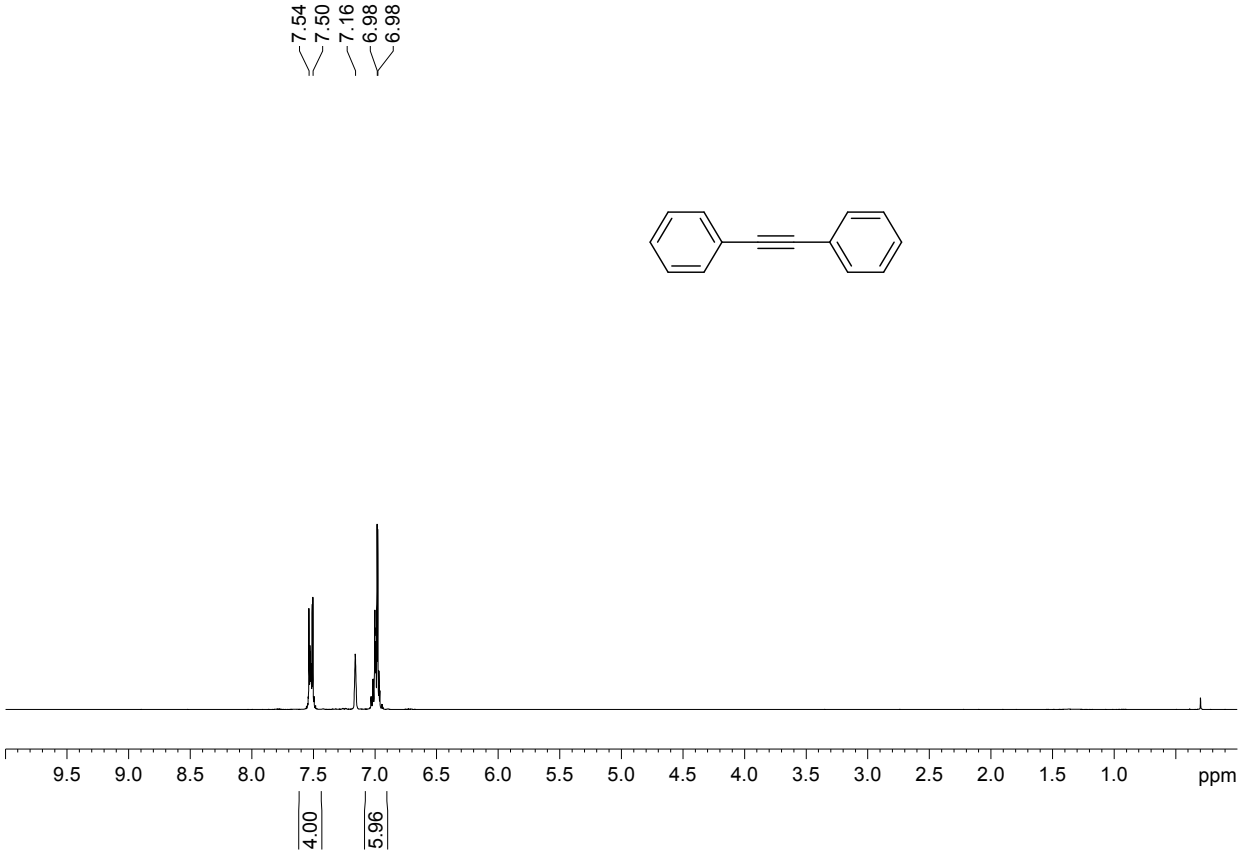
Test 2: In a glovebox, a vial was charged with [Cu(OH)(IPr)] (1) (20 mg, 0.043 mmol, 1 equiv.) and diphenylacetylene (7.6 mg, 0.043 mmol, 1 equiv.). The mixture was stirred at 60 °C for 16 hours in the absence of solvent. Then, benzene-d_6 was added and the mixture was analysed by ^{1}H NMR analysis.

Both tests showed no reaction.

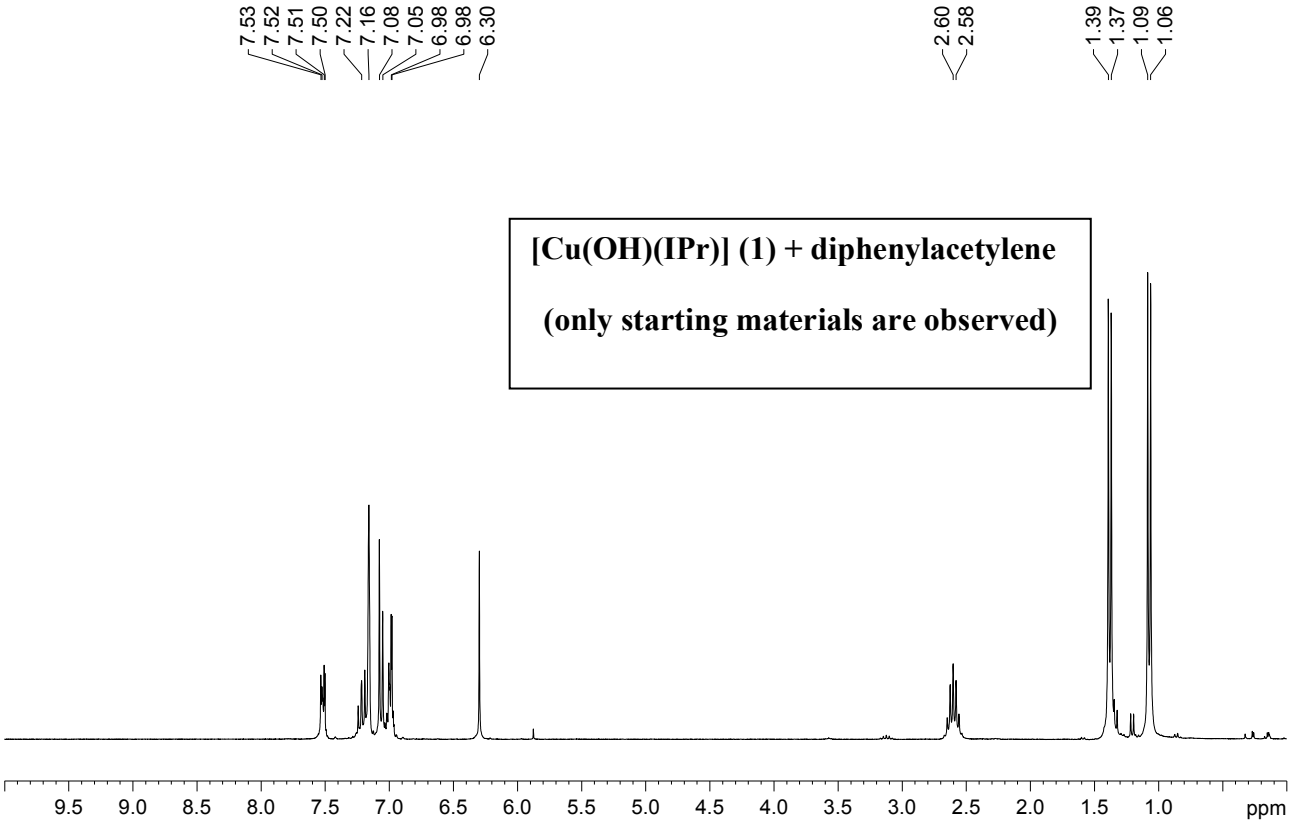
^{1}H NMR (C_6D_6) of [Cu(OH)(IPr)]



^{1}H NMR (C_6D_6) of diphenylacetylene



^{1}H NMR (C_6D_6) of reaction mixture

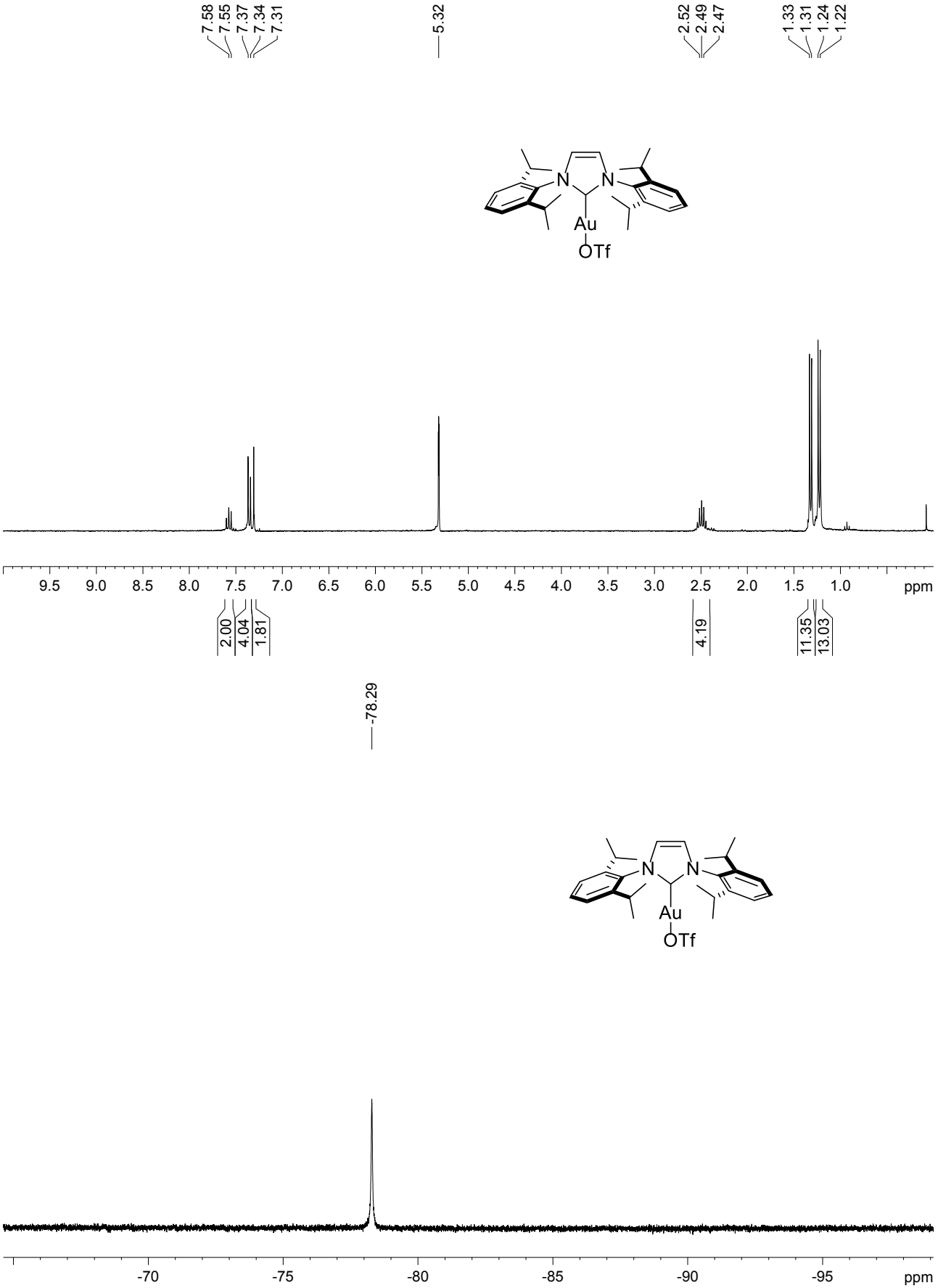


Stoichiometric reaction between [Au(OTf)(IPr)] (2) and diphenylacetylene

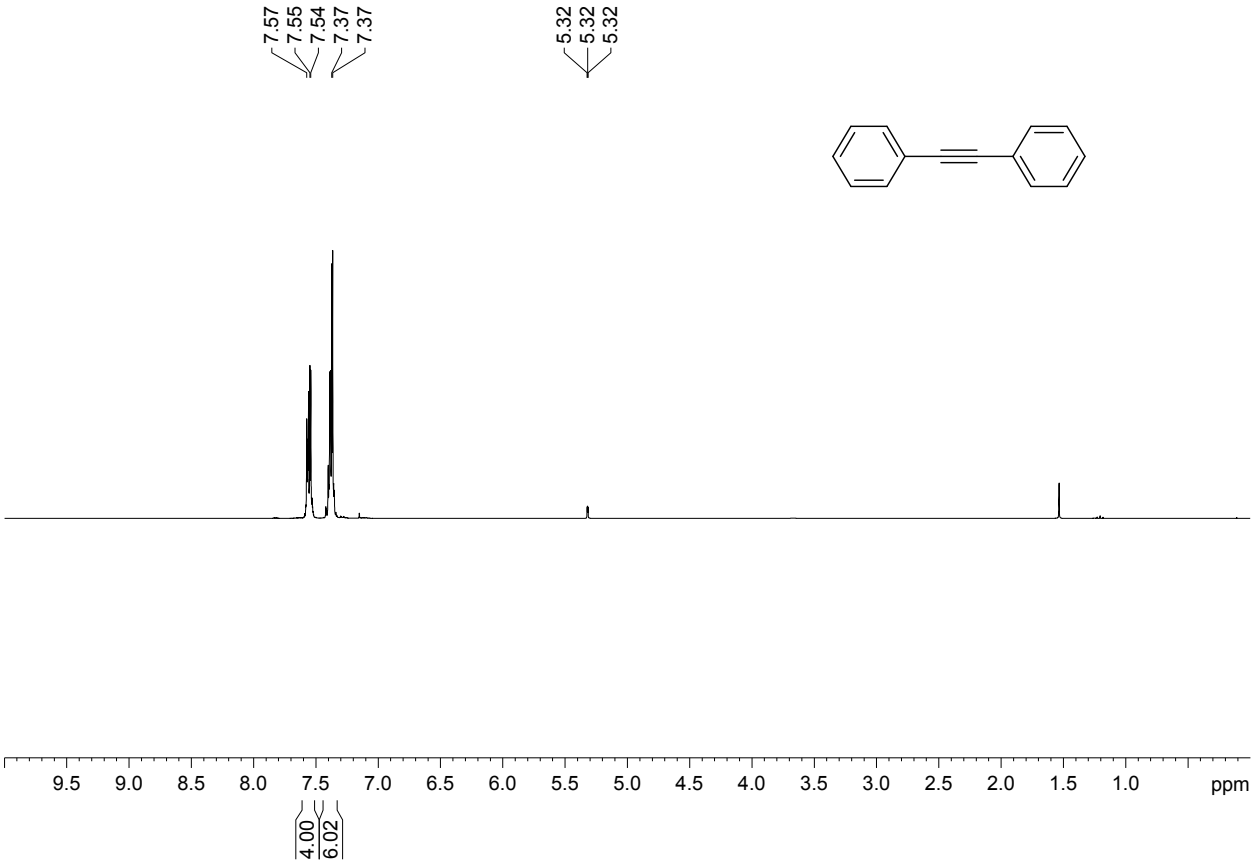
In a glovebox, a vial was charged with [Au(OTf)(IPr)] (10 mg, 0.014 mmol, 1 equiv.) and diphenylacetylene (2.4 mg, 0.014 mmol, 1 equiv.). Dichloromethane-d_2 was added and the mixture was stirred at 60 °C. The reaction was followed by ^{1}H NMR in CD_2Cl_2.

After completion (16 h), the solvent was removed under vacuo and the ^{1}H NMR was recorded in benzene-d_6.

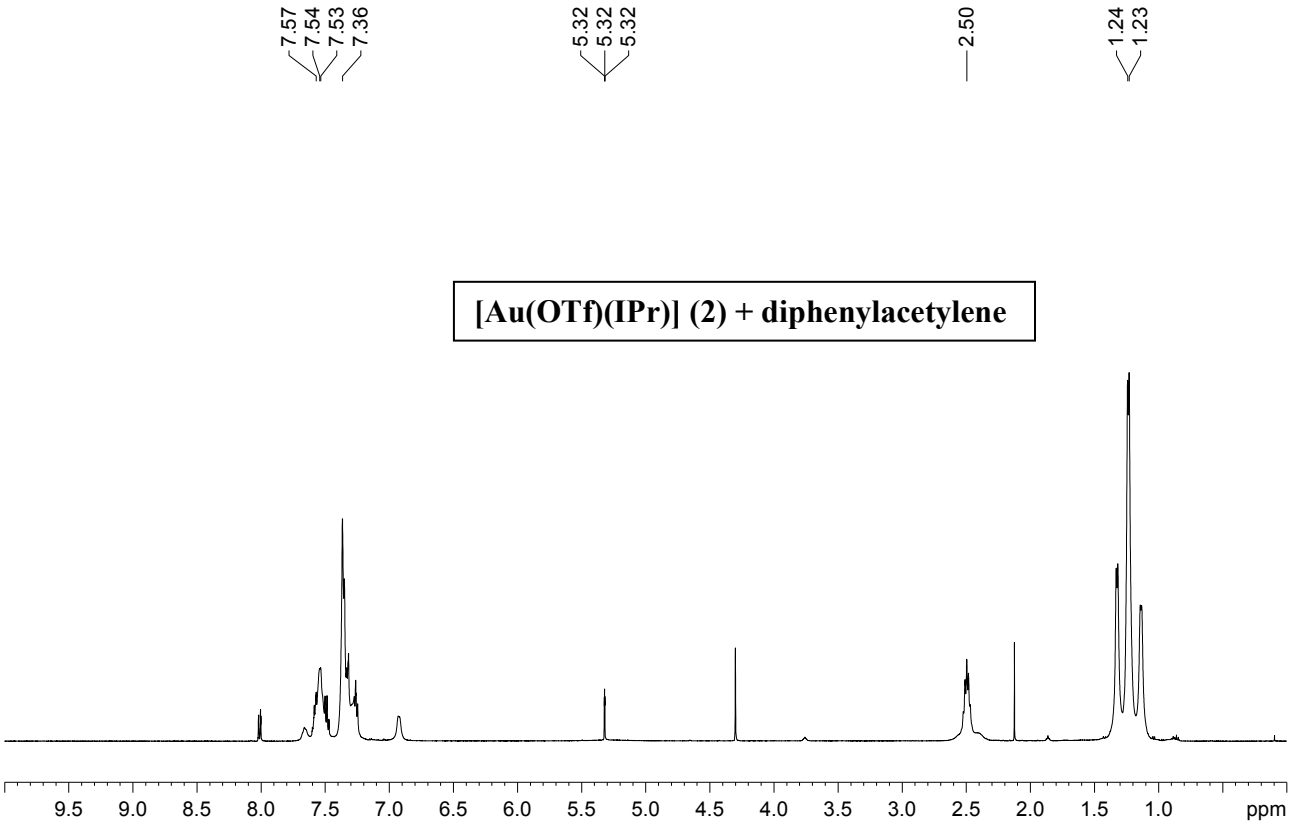
^{1}H NMR (CD_2Cl_2) and ^{19}F-{^{1}H} NMR (CD_2Cl_2) of [Au(OTf)(IPr)]

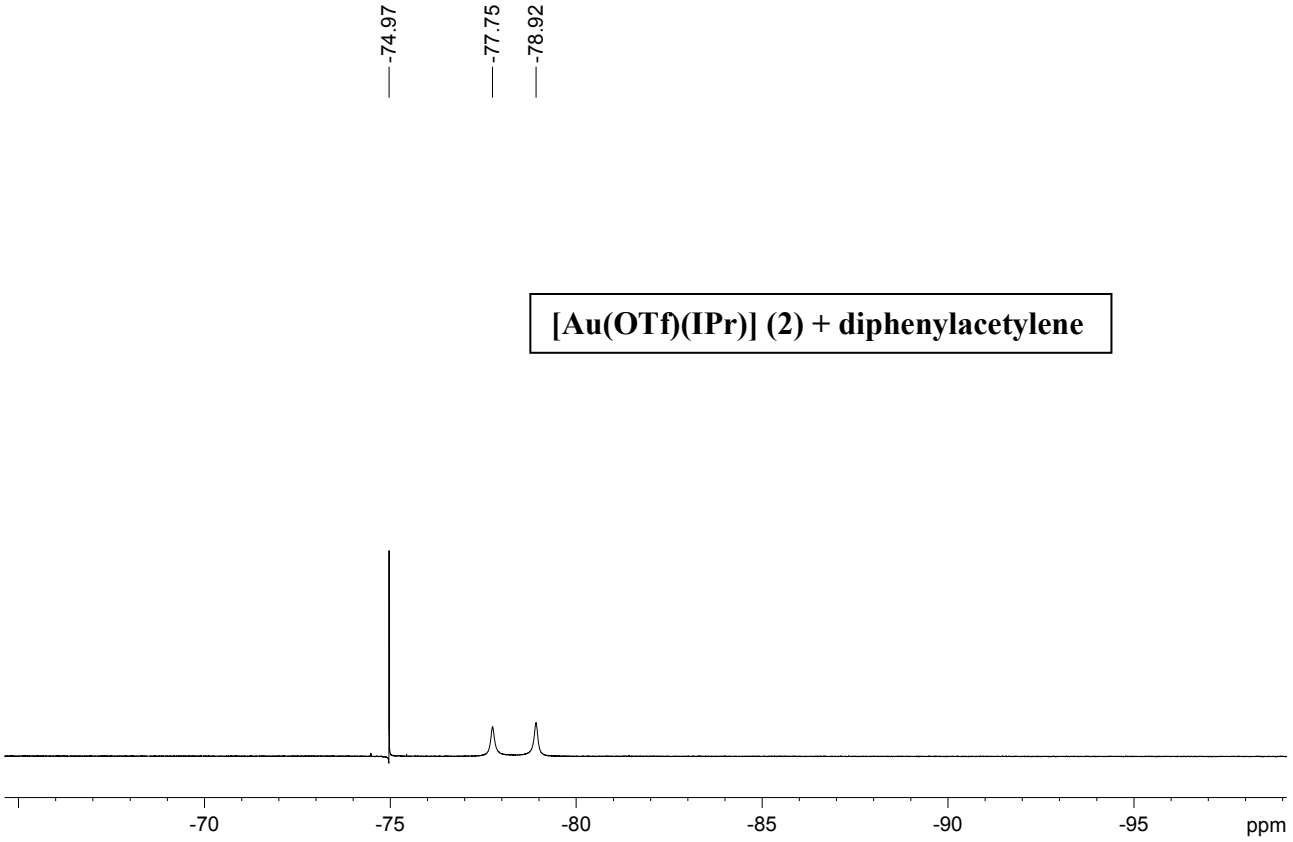


^{1}H NMR (CD_2Cl_2) of diphenylacetylene

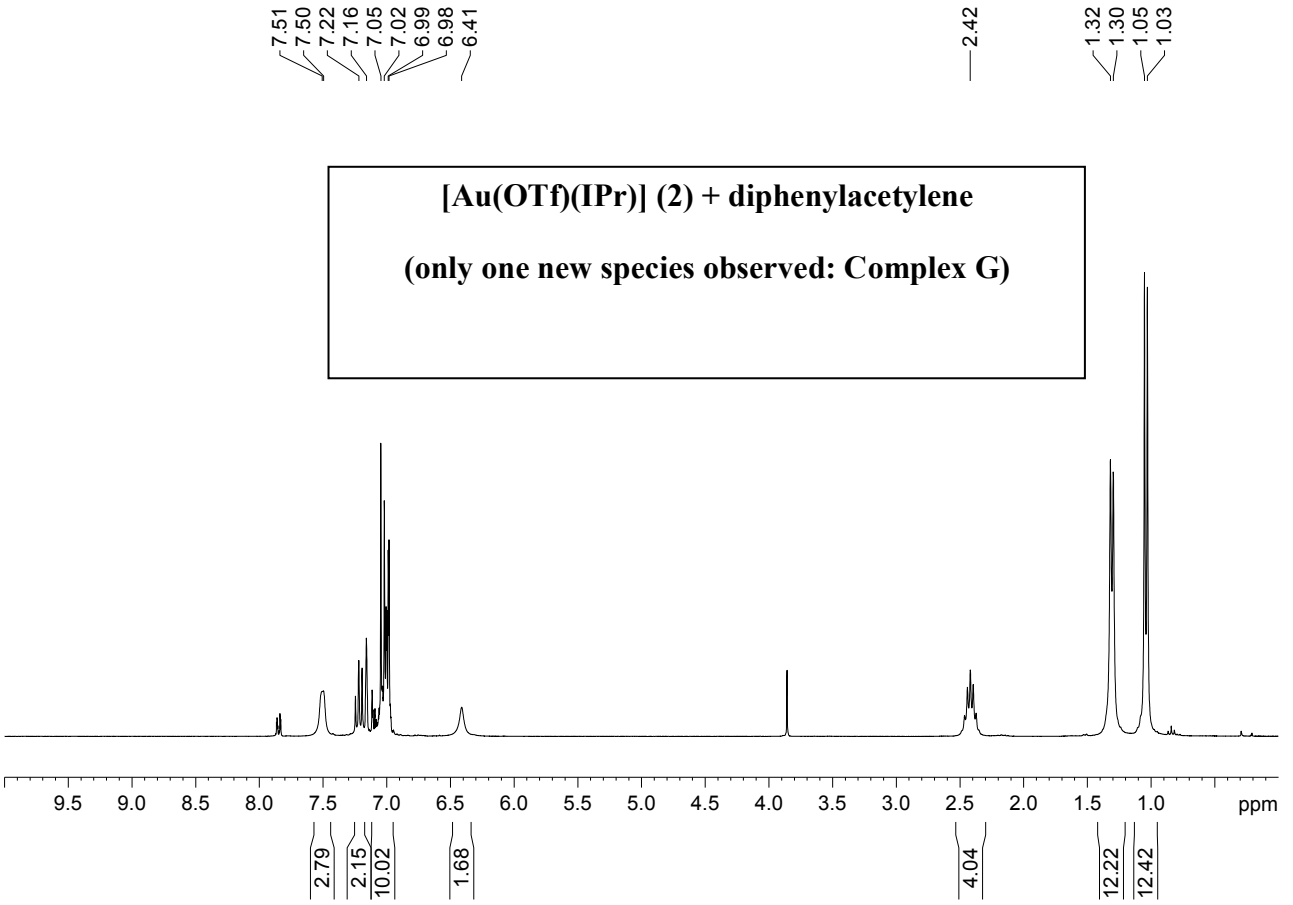


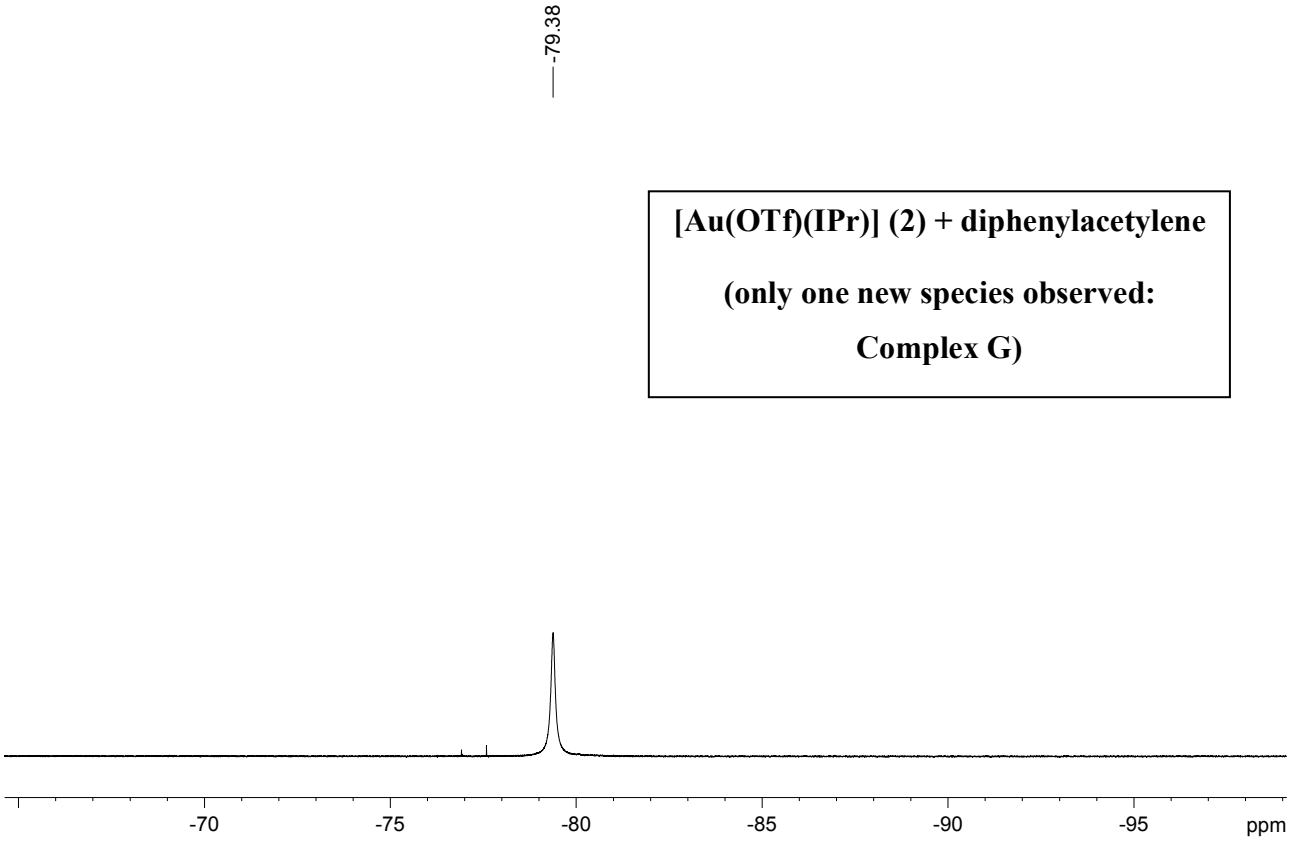
^{1}H NMR (CD_2Cl_2) and ^{19}F-{^{1}H} NMR (CD_2Cl_2) of reaction mixture after 6 hours





^{1}H NMR (C_6D_6) and ^{19}F-{^{1}H} NMR (C_6D_6) of complex G after isolation (16 h):





Mechanistic tests from Schemes 6 and 7

Synthesis of [Au(OH)(IPr)] (A)

A round-bottomed flask was charged with [Au(Cl)(IPr)] (20 g, 32.2 mmol, 1 equiv.), finely ground sodium hydroxide (9.1 g, 227.5 mmol, 7 equiv.) and THF (100 mL). *Tert*-amyl alcohol (0.9 mL, 8.1 mmol, 0.25 equiv.) was then added under stirring. After 48 hours at room temperature, the crude mixture was then filtered through celite and washed with additional THF. Water (~100 mL) was added to the solution and THF was removed under vacuum. More water was added to the white, cloudy suspension and the product was triturated. It was left to settle for 10 minutes, collected using a Büchner funnel and washed with water. It was then dried under vacuum for several days to produce a white microcrystalline solid in 99% yield (19.24 g).

^{1}H NMR (400 MHz, $CDCl_3$) δ (ppm) = 7.49 (t, *J* = 7.8 Hz, 2H), 7.28 (d, *J* = 7.8 Hz, 4H), 7.12 (s, 2H), 2.64 – 2.52 (m, 4H), 1.36 (d, *J* = 6.9 Hz, 12H), 1.21 (d, *J* = 6.9 Hz, 12H), -0.58 (s, 1H). **^{1}H NMR (500 MHz, C_6D_6)** δ (ppm) = 7.21 (t, *J* = 7.8 Hz, 2H), 7.05 (d, *J* = 7.8 Hz, 4H), 6.26 (s, 2H), 2.64 – 2.55 (m, 4H), 1.42 (d, *J* = 6.9 Hz, 12H), 1.06 (d, *J* = 6.9 Hz, 12H), -0.26 (s, 1H). **^{13}C{^{1}H}-DEPTQ NMR (125 MHz, $CDCl_3$)** δ (ppm) 171.7 ($C_{carbene}$), 145.7 (C_{Ar}), 134.4 (C_{Ar}), 130.5 (C_{Ar}), 124.1 (C_{Ar}), 122.9 (CH_{imid}), 28.8 ($CH(CH_3)_2$), 24.4 ($CH(CH_3)_2$), 24.1 ($CH(CH_3)_2$). **Anal. Calcd. for $C_{27}H_{37}AuN_2O$:** C, 53.82; H, 6.19; N, 4.65. **Found:** C, 53.80; H, 6.24; N, 4.71.

The data was in accordance with the literature.[4]

Synthesis of [Cu(OTf)(IPr)] (B)

Under argon, a vial was charged with [Cu(OH)(IPr)] (117 mg, 0.249 mmol, 1 equiv.) in toluene (2 mL), followed by TMSOTf (0.05 mL, 0.276 mmol. 1.1 equiv.). The reaction mixture was stirred for 2 h at room temperature. The solvent was removed under reduced pressure and dichloromethane was added. The solution was filtered through a plug of silica gel and washed with dichloromethane. The solvent was again removed and benzene was added. The solution was filtered through a plug of silica gel and washed with benzene. The solvent was concentrated and pentane was added. The precipitate was then triturated, filtered and washed with pentane. The desired compound was obtained as colourless solid (134.5 mg, 90%).

^{1}H NMR (400 MHz, $CDCl_3$) δ (ppm) = 7.53 (t, *J* = 7.8 Hz, 2H), 7.33 (d, *J* = 7.8 Hz, 4H), 7.20 (s, 2H), 2.51 (sept, *J* = 6.9 Hz, 4H), 1.27 (d, *J* = 6.9 Hz, 12H), 1.23 (d, *J* = 6.9 Hz, 12H). **^{13}C NMR (101 MHz, $CDCl_3$)** δ (ppm) = 178.1 ($C_{carbene}$), 145.5 (C_{Ar}), 134.0 (C_{Ar}), 131.0 (C_{Ar}), 124.5 (C_{Ar}), 123.8 (CH_{imid}), 28.9 ($CH(CH_3)_2$), 24.7 ($CH(CH_3)_2$), 24.1 ($CH(CH_3)_2$). **^{19}F-{^{1}H} NMR (377 MHz, $CDCl_3$)** δ (ppm) = -77.92. **Anal. Calcd. for $C_{28}H_{36}CuF_3N_2O_3S$:** C, 55.94; H, 6.04; N, 4.66. **Found:** C, 56.04; H, 6.18; N, 4.81.

The data was in accordance with the literature.[5]

Synthesis of [Au(OPh)(IPr)] (E)

Under argon, a vial was charged with [Au(OH)(IPr)] (100 mg, 0.166 mmol, 1 equiv.) and phenol (18 mg, 0.183 mmol. 1.1 equiv.) in toluene (2 mL). The reaction mixture was stirred overnight at room temperature. The solvent was removed under reduced pressure and diethyl ether (1 mL) was added. The precipitate was triturated in ether for 5 min, then pentane (4 mL) was added (ether/pentane = 1:4). The precipitate was collected by filtration and washed with an ether/pentane solution (1:4), followed by pure pentane. The desired compound was obtained as a colourless solid (110.5 mg, 98%).

^{1}H NMR (400 MHz, $CDCl_3$) δ (ppm) = 7.54 (t, *J* = 7.8 Hz, 2H), 7.33 (d, *J* = 7.8 Hz, 4H), 7.17 (s, 2H), 6.76 (t, *J* = 7.8 Hz, 2H), 6.35 (t, *J* = 7.2 Hz, 1H), 5.92 (d, *J* = 7.8 Hz, 2H), 2.60 (sept, *J* = 13.7, 6.8 Hz, 4H), 1.29 (d, *J* = 6.8 Hz, 12H), 1.24 (d, *J* = 6.9 Hz, 12H). **^{13}C NMR (101 MHz, $CDCl_3$)** δ (ppm) = 169.8 ($C_{carbene}$), 167.8 (C_{OPh}), 145.9 (C_{Ar}), 134.3 (C_{Ar}), 130.7 (C_{Ar}), 128.5 (C_{OPh}), 124.3 (C_{Ar}), 123.1 (CH_{imid}), 118.5 (C_{OPh}), 114.8 (C_{OPh}), 29.0 ($CH(CH_3)_2$), 24.4 ($CH(CH_3)_2$), 24.3 ($CH(CH_3)_2$). **Anal. Calcd. for $C_{33}H_{41}AuN_2O$:** C, 58.40; H, 6.09; N, 4.13. **Found:** C, 58.29; H, 6.18; N, 4.16.

The data was in accordance with the literature.[6]

Synthesis of [Cu(OPh)(IPr)] (F)

Under argon, a vial was charged with [Cu(OH)(IPr)] (78 mg, 0.166 mmol, 1 equiv.) and phenol (18 mg, 0.183 mmol. 1.1 equiv.) in toluene (2 mL). The reaction mixture was stirred overnight at room temperature. The solvent was removed under reduced pressure and diethyl ether (0.5 mL) was added. The precipitate was triturated in ether for 5 min, then pentane (4 mL) was added. The precipitate was collected by filtration and washed with an ether/pentane solution (1:7), followed by pure pentane. The desired compound was obtained as colourless solid (81.5 mg, 90%).

^{1}H NMR (400 MHz, $CDCl_3$) δ (ppm) = 7.54 (t, *J* = 7.8 Hz, 2H), 7.32 (d, *J* = 7.8 Hz, 4H), 7.21 (s, 2H), 6.85 (t, *J* = 7.8 Hz, 2H), 6.44 (t, *J* = 7.2 Hz, 1H), 6.33 (d, *J* = 7.8 Hz, 2H), 2.59 (sept, *J* = 13.7, 6.8 Hz, 4H), 1.35 (d, *J* = 6.8 Hz, 12H), 1.23 (d, *J* = 6.9 Hz, 12H). **^{13}C NMR (101 MHz, $CDCl_3$)** δ (ppm) = 181.0 ($C_{carbene}$), 167.4 (C_{OPh}), 145.9 (C_{Ar}), 134.8 (C_{Ar}), 130.6 (C_{Ar}), 128.8 (C_{OPh}), 124.4 (C_{Ar}), 123.2 (CH_{imid}), 119.0 (C_{OPh}), 114.1 (C_{OPh}), 28.9 ($CH(CH_3)_2$), 24.8 ($CH(CH_3)_2$), 24.1 ($CH(CH_3)_2$). **Anal. Calcd. for $C_{33}H_{41}CuN_2O$:** C, 72.69; H, 7.58; N, 5.14. **Found:** C, 72.54; H, 7.63; N, 5.07.

The data was in accordance with the literature.[7]

Reaction of complex 1 with complex 2: Mixture A

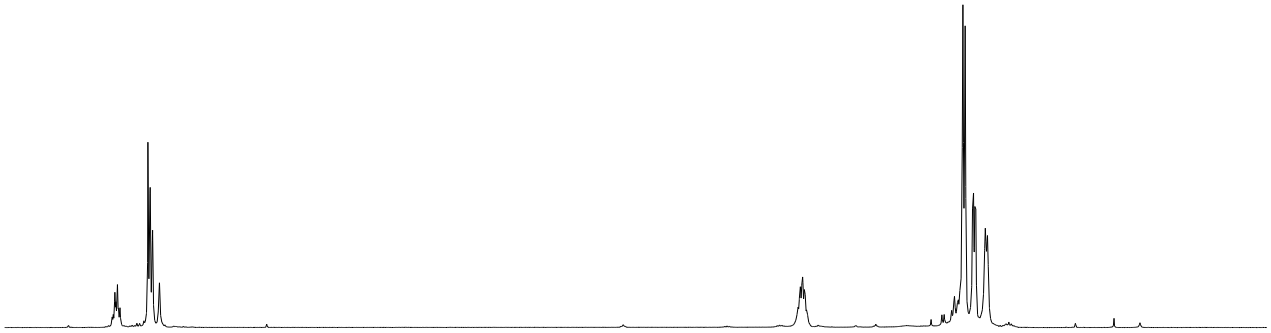
Under argon, an NMR tube was charged with [Cu(OH)(IPr)] (**1**) (5 mg, 0.011 mmol, 1 equiv.) and [Au(OTf)(IPr)] (**2**) (7.8 mg, 0.011 mmol, 1 equiv.) in 0.6 mL of $CDCl_3$. The NMR tube was heated at 45 °C for 1 h, then analysed by NMR spectroscopy. A mixture of complexes was observed: **Mixture A**.

Reaction of complex A with complex B: Mixture A

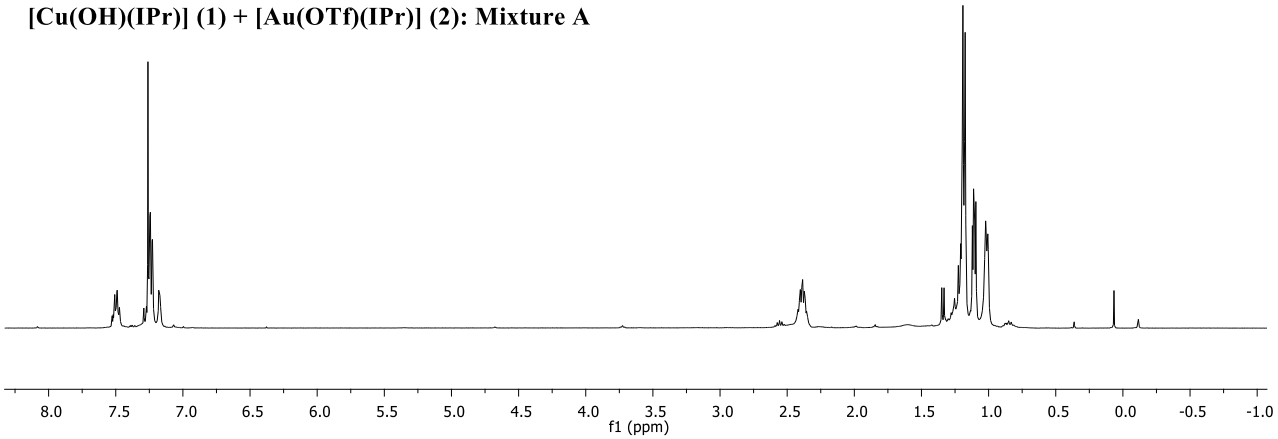
Under argon, an NMR tube was charged with [Au(OH)(IPr)] (**A**) (5 mg, 0.008 mmol, 1 equiv.) and [Cu(OTf)(IPr)] (**B**) (5 mg, 0.008 mmol, 1 equiv.) in 0.6 mL of $CDCl_3$. The NMR tube was heated at 45 °C for 1 h, then analysed by NMR spectroscopy. A mixture of complexes was observed: **Mixture A**.

^{1}H NMR ($CDCl_3$) and ^{19}F-{^{1}H} NMR ($CDCl_3$) of the reactions

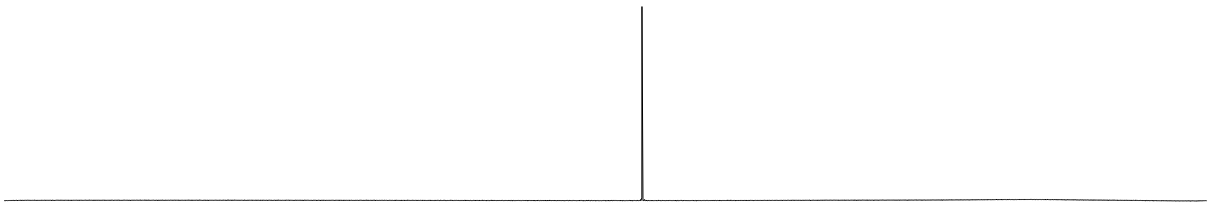
[Cu(OTf)(IPr)] (B) + [Au(OH)(IPr)] (A): Mixture A



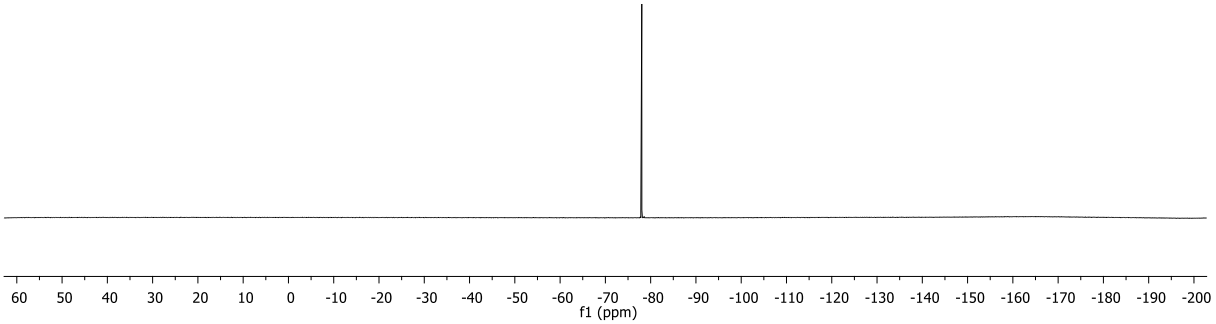
[Cu(OH)(IPr)] (1) + [Au(OTf)(IPr)] (2): Mixture A



[Cu(OTf)(IPr)] (B) + [Au(OH)(IPr)] (A): Mixture A



[Cu(OH)(IPr)] (1) + [Au(OTf)(IPr)] (2): Mixture A



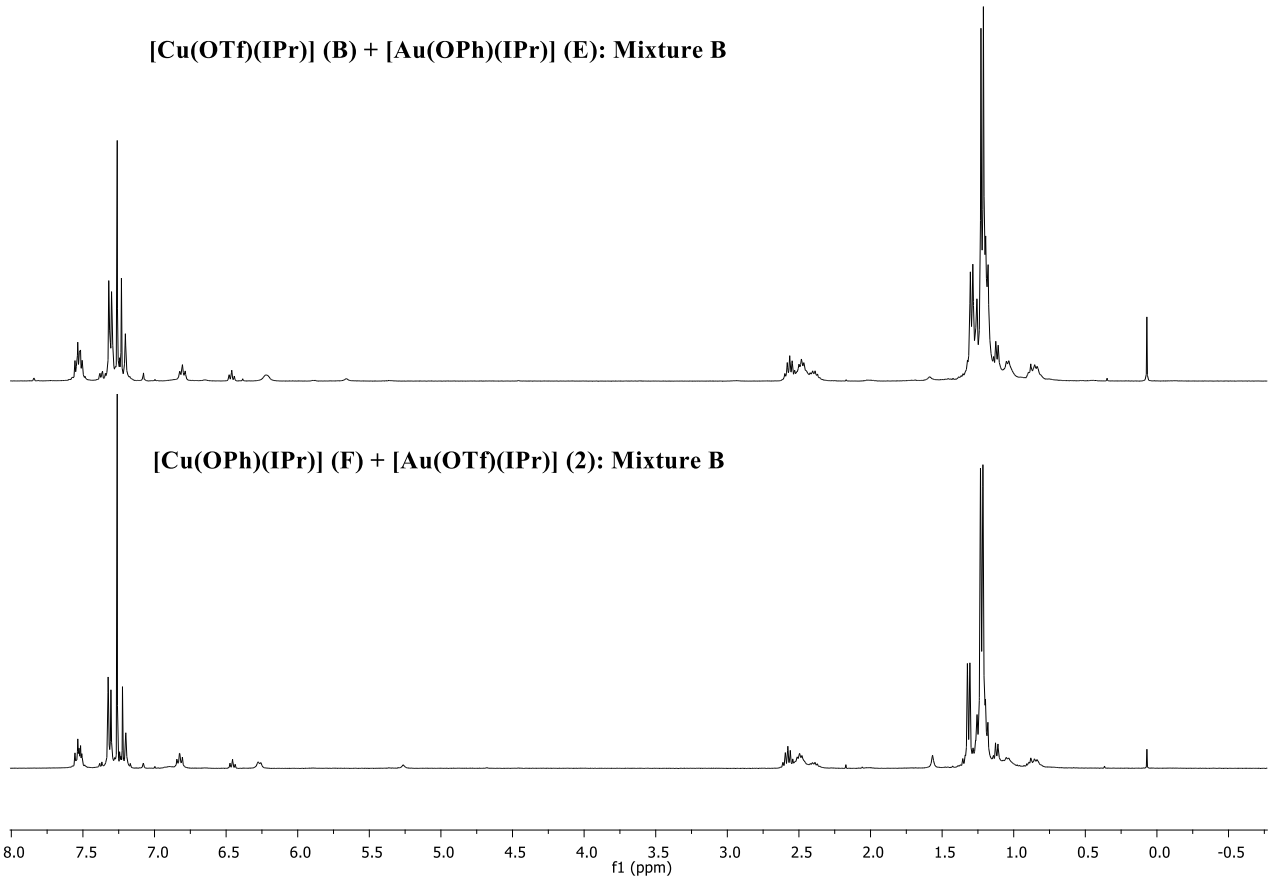
Reaction of complex F with complex 2: Mixture B

Under argon, an NMR tube was charged with [Cu(OPh)(IPr)] (**F**) (5 mg, 0.009 mmol, 1 equiv.) and [Au(OTf)(IPr)] (**2**) (6.7 mg, 0.009 mmol, 1 equiv.) in 0.6 mL of $CDCl_3$. The NMR tube was heated at 45 ^oC for 1 h, then analysed by NMR spectroscopy. A mixture of complexes was observed: **Mixture B**.

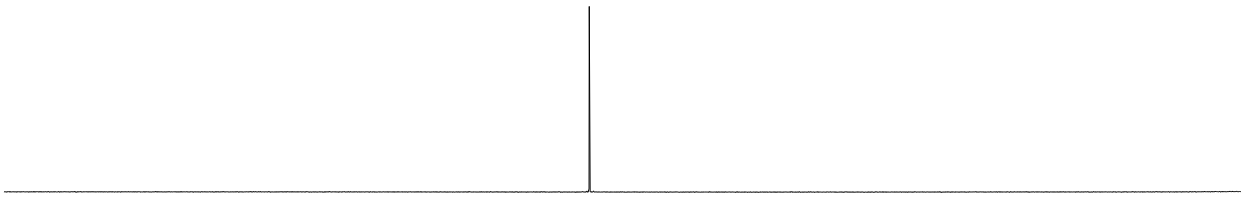
Reaction of complex E with complex B: Mixture B

Under argon, an NMR tube was charged with [Au(OPh)(IPr)] (**E**) (5.6 mg, 0.008 mmol, 1 equiv.) and [Cu(OTf)(IPr)] (**B**) (5 mg, 0.008 mmol, 1 equiv.) in 0.6 mL of $CDCl_3$. The NMR tube was heated at 45 ^oC for 1 h, then analysed by NMR spectroscopy. A mixture of complexes was observed: **Mixture B**.

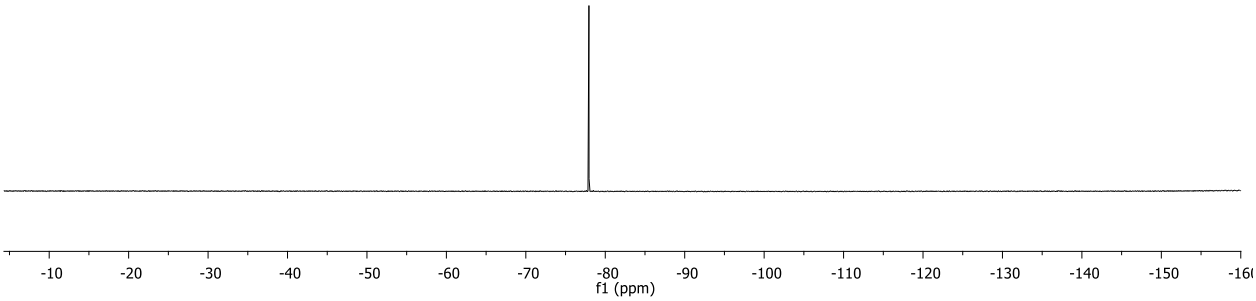
^{1}H NMR ($CDCl_3$) and ^{19}F-{^{1}H} NMR ($CDCl_3$) of the reactions



[Cu(OTf)(IPr)] (B) + [Au(OPh)(IPr)] (E): Mixture B



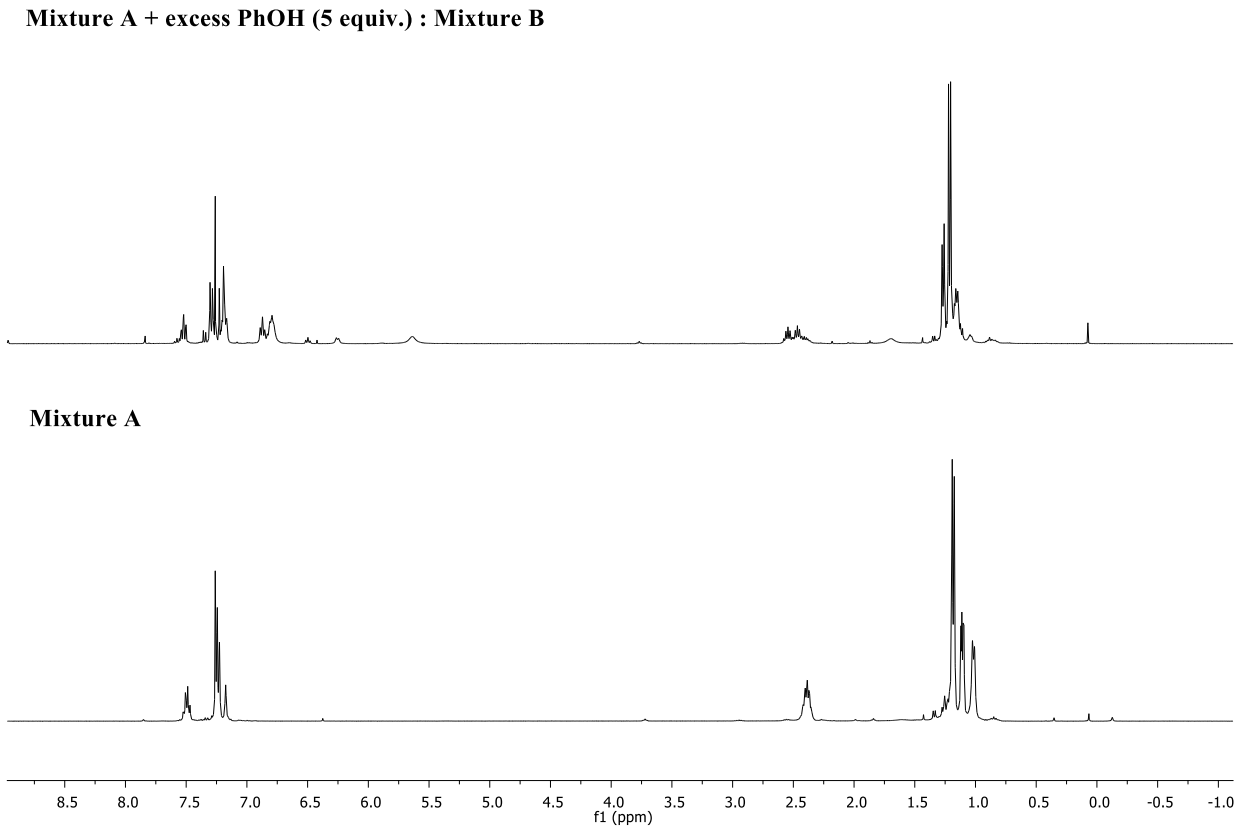
[Cu(OPh)(IPr)] (F) + [Au(OTf)(IPr)] (2): Mixture B



Reaction of Mixture A with PhOH

Under argon, an NMR tube was charged with [Au(OH)(IPr)] (**A**) (5 mg, 0.008 mmol, 1 equiv.) and [Cu(OTf)(IPr)] (**B**) (5 mg, 0.008 mmol, 1 equiv.) in 0.6 mL of $CDCl_3$. The NMR tube was heated at 45 ^{o}C for 1 h (**Mixture A**), then PhOH (5 equiv.) was added. The NMR tube was heated again at 45 ^{o}C for 1 h and then analysed by NMR spectroscopy. A mixture of complexes was observed: **Mixture B**.

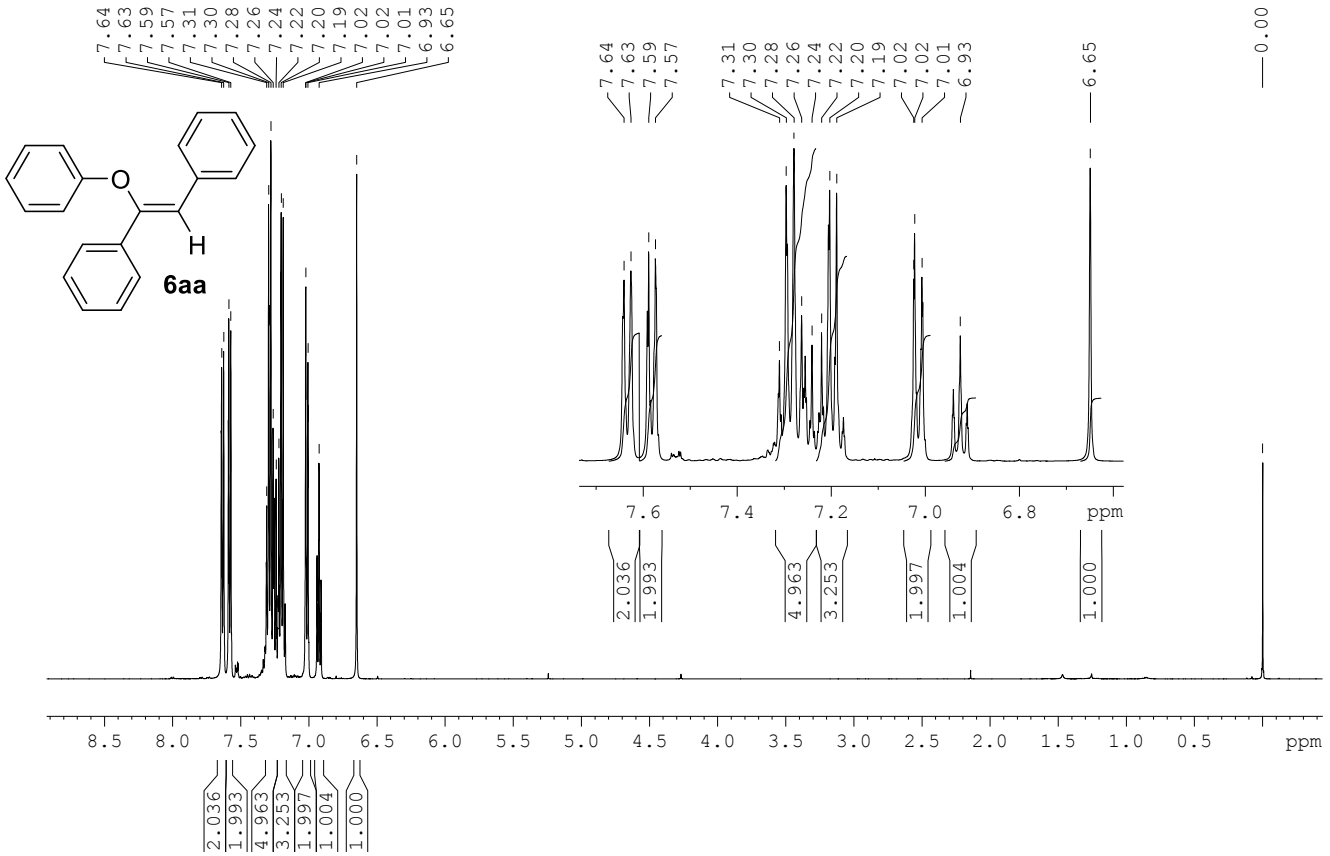
^{1}H NMR ($CDCl_3$) of the reactions



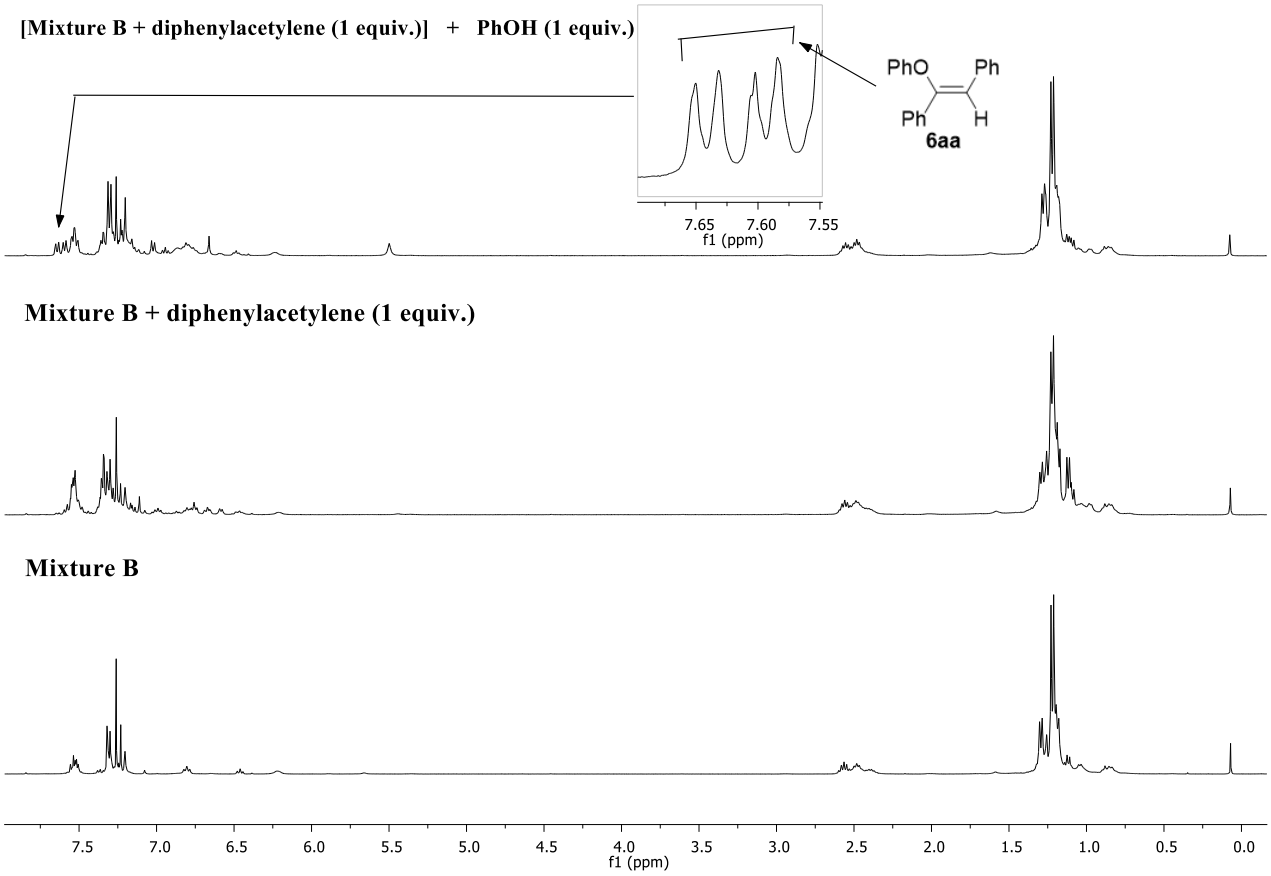
Reaction of Mixture B with diphenylacetylene and PhOH

Under argon, an NMR tube was charged with [Au(OPh)(IPr)] (**E**) (5.6 mg, 0.008 mmol, 1 equiv.) and [Cu(OTf)(IPr)] (**B**) (5 mg, 0.008 mmol, 1 equiv.) in 0.6 mL of $CDCl_3$. The NMR tube was heated at 45 ^oC for 1 h, then analysed by NMR spectroscopy. A mixture of complexes was observed: **Mixture B**. To that mixture, diphenylacetylene (1.9 mg, 0.008 mmol, 1 equiv.) was added and the NMR tube was heated at 45 ^oC for 1 h, then analysed by NMR spectroscopy (**complex reaction mixture**). Afterwards, PhOH (0.8 mg, 0.008 mmol, 1 equiv.) was added. The NMR tube was heated again at 45 ^oC for 1 h and then analysed by NMR spectroscopy. A mixture of complexes was observed: **Mixture B**.

^{1}H NMR ($CDCl_3$) of 6aa



^{1}H NMR ($CDCl_3$) of the reactions

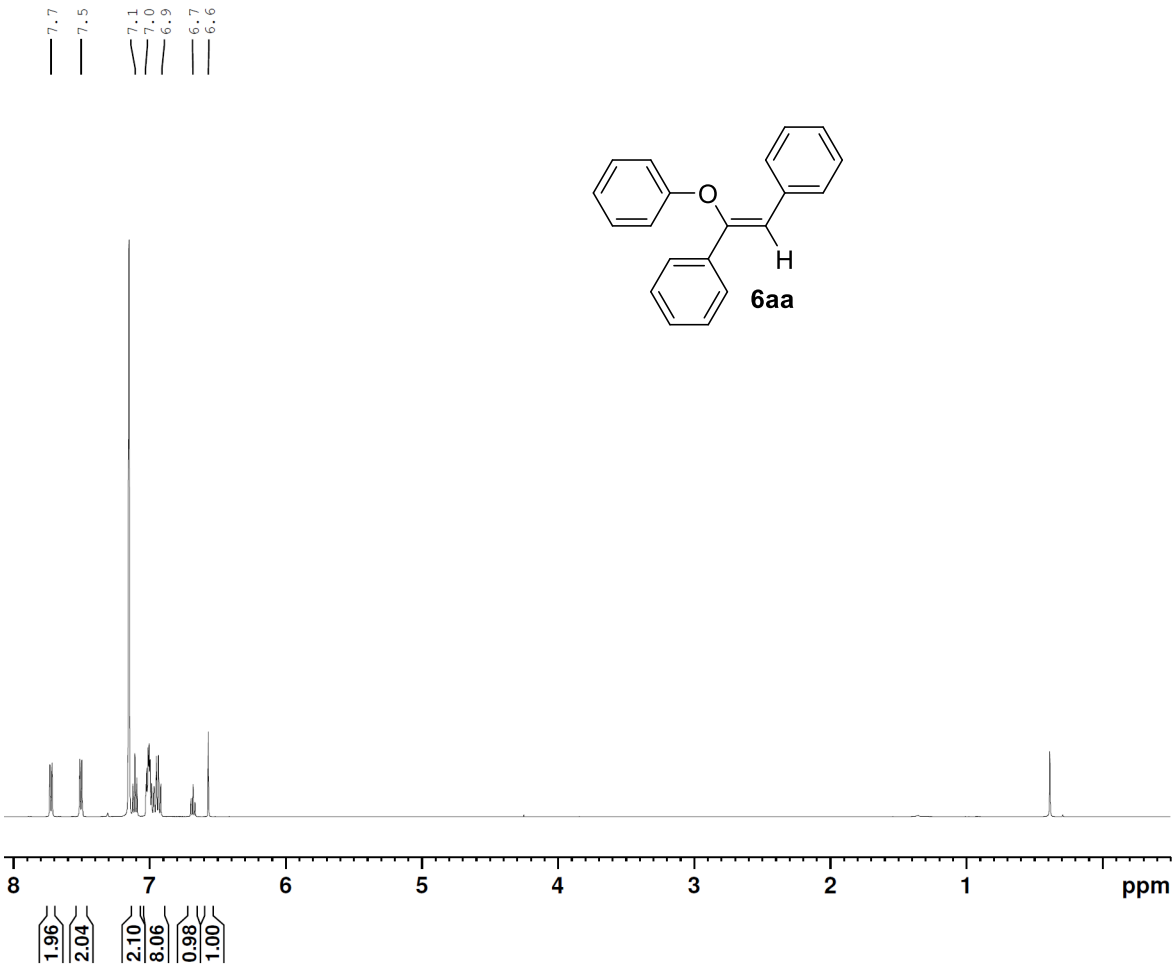


Stoichiometric reaction of complexes F and G with PhOH

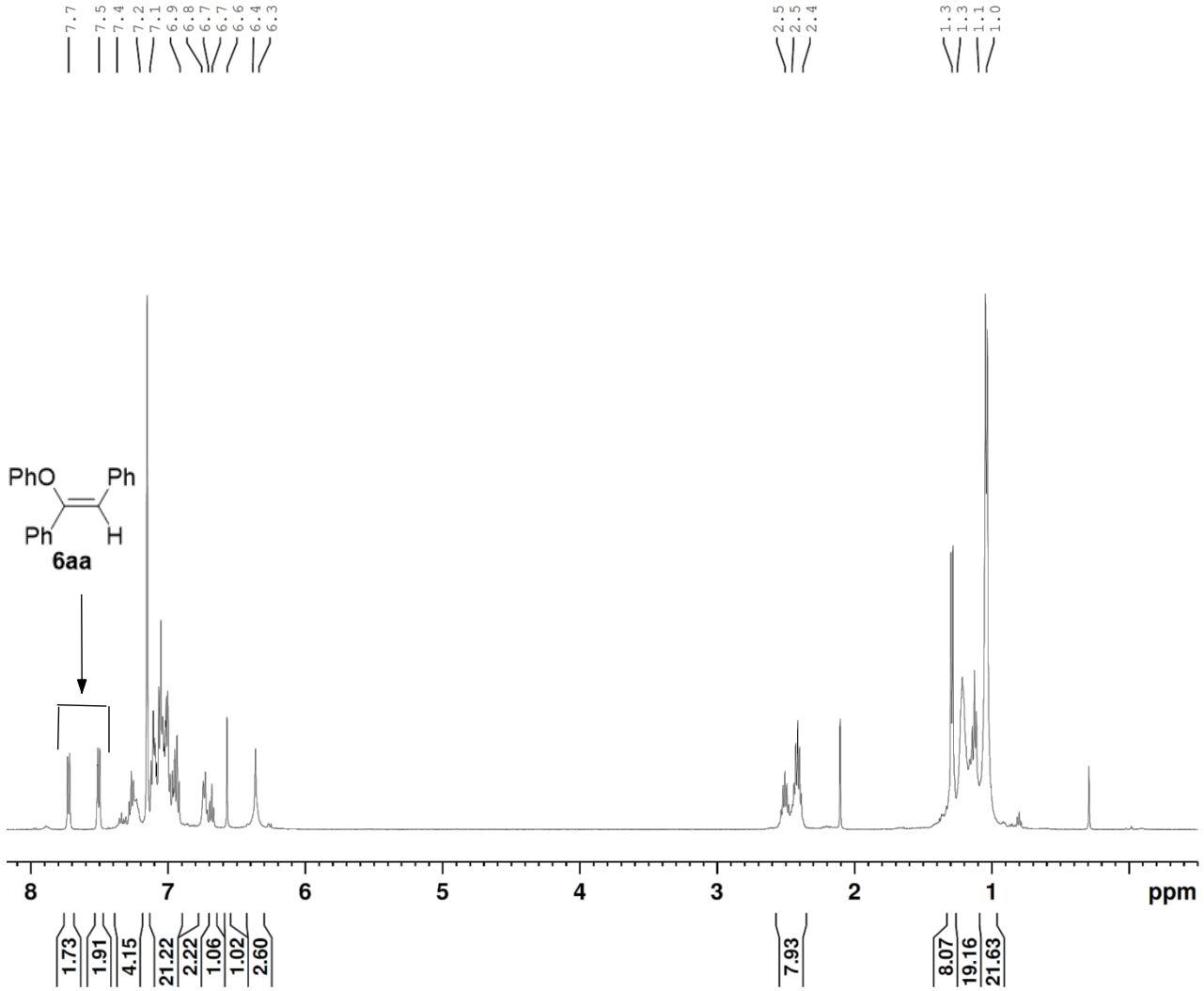
In a glovebox, a vial was charged with [Au(OTf)(IPr)] (**2**) (10 mg, 0.014 mmol, 1 equiv.) and diphenylacetylene (2.4 mg, 0.014 mmol, 1 equiv.). Dichloromethane-d_2 was added and the mixture was stirred at 60 °C. The reaction was followed by ^{1}H NMR in CD_2Cl_2. After completion (16 h), the solvent was removed under vacuo to afford complex **G**. This complex is very unstable and needs to be used directly in the next step.

To complex **G**, was added [Cu(OPh)(IPr)] (**F**) (7.6 mg, 0.014 mmol, 1 equiv.) and PhOH (1.3 mg, 0.014 mmol, 1 equiv.). The mixture was heated at 60 ^{o}C under solvent-free conditions, for 16 h. Then, benzene-d_6 was added and the mixture was analysed by NMR spectroscopy.

^{1}H NMR (C_6D_6) of 6aa



^{1}H NMR (C_6D_6) of the reaction

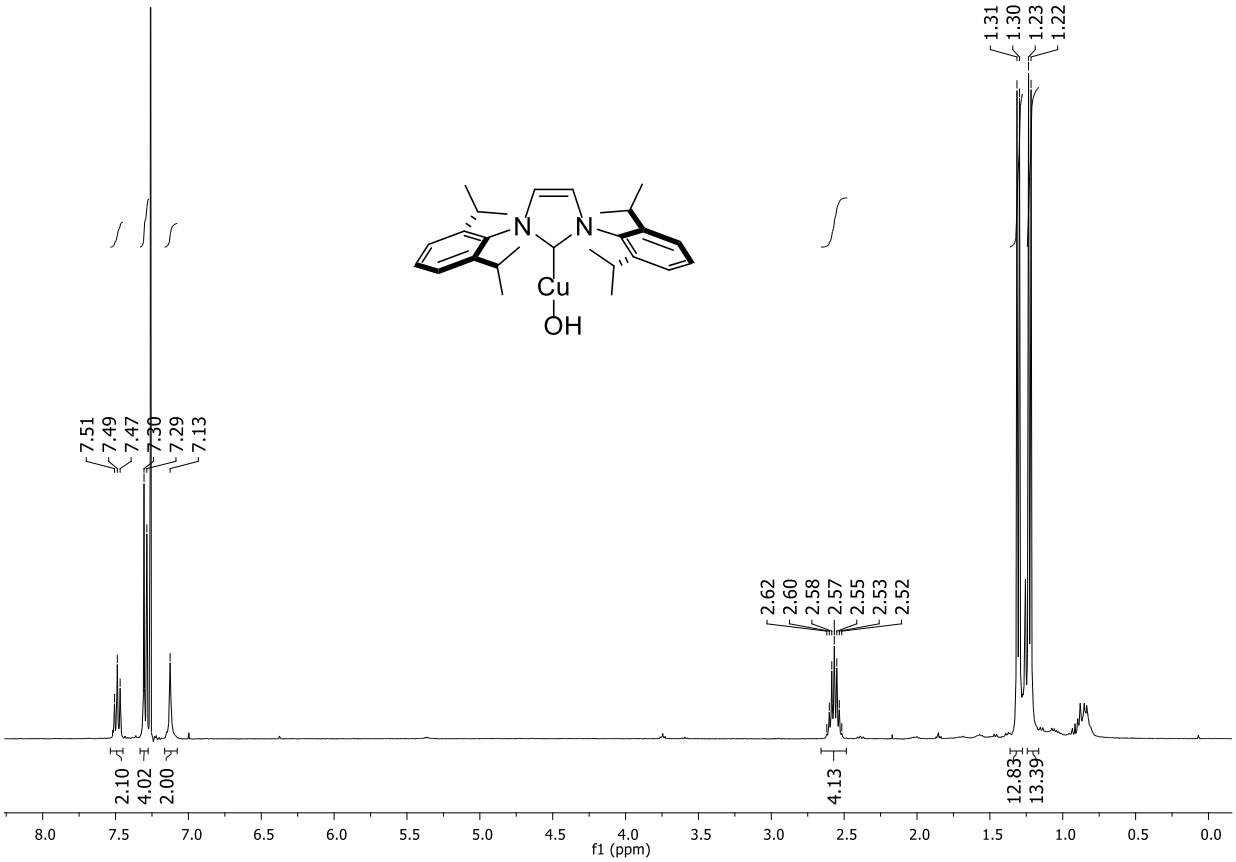


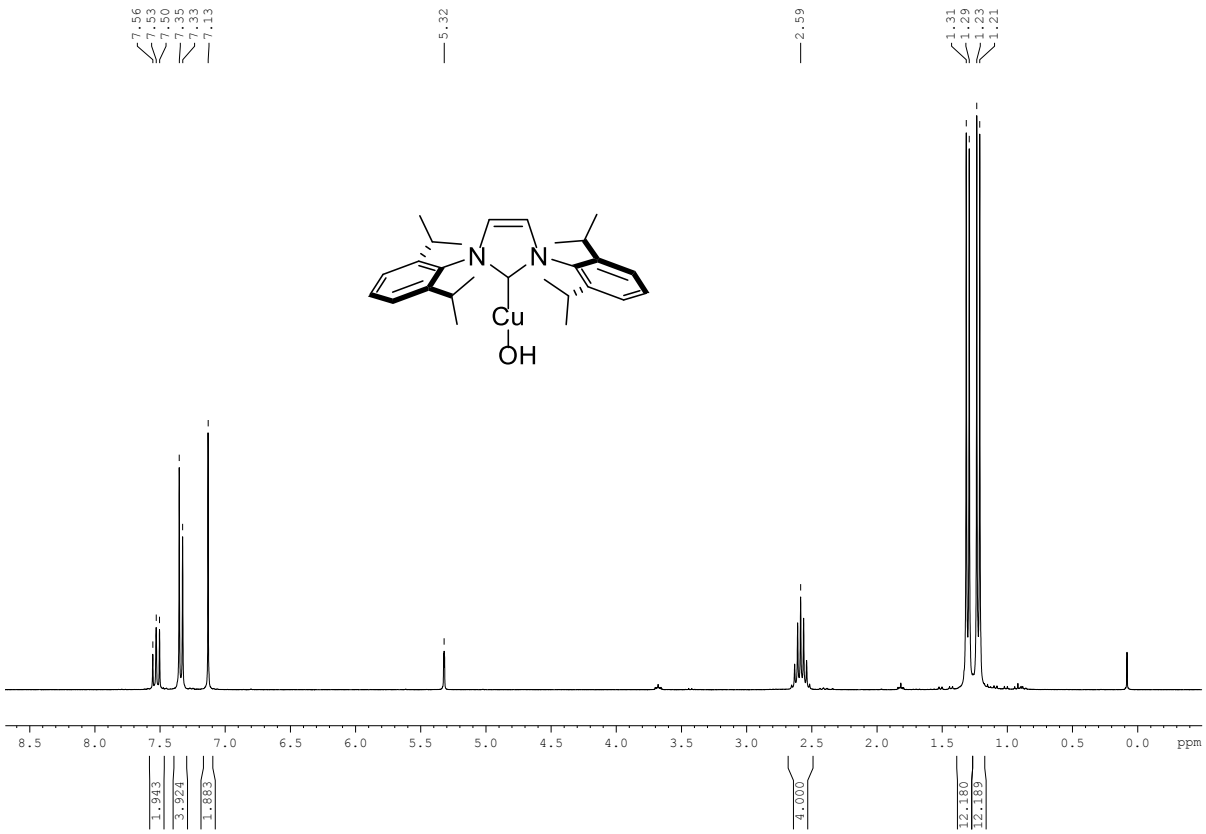
Catalytic reaction of 4a and 5a using complexes F and 2 as catalysts

In a glovebox, a vial was charged with the appropriate amounts of [Au(OTf)(IPr)] (**2**) (stock solution prepared in THF: 7.2 mg [Au] dissolved in 1 mL, 100 µL for 0.2 mol%) and [Cu(OPh)(IPr)] (**F**) (stock solution prepared in THF: 5.4 mg [Cu] dissolved in 1 mL, 100 µL for 0.2 mol%). After each addition of stock solution to the vial, THF was removed under vacuum. Alkyne **4a** (89.1 mg, 0.5 mmol, 1 equiv.) and phenol **5a** (56.5 mg, 0.6 mmol, 1.2 equiv.) were then added. The reaction mixture was removed from the glovebox and stirred at 60 ^{o}C for 16 h. The reaction residue was dissolved in dichloromethane and the conversion was determined by GC analysis. Full conversion to **6aa** was observed

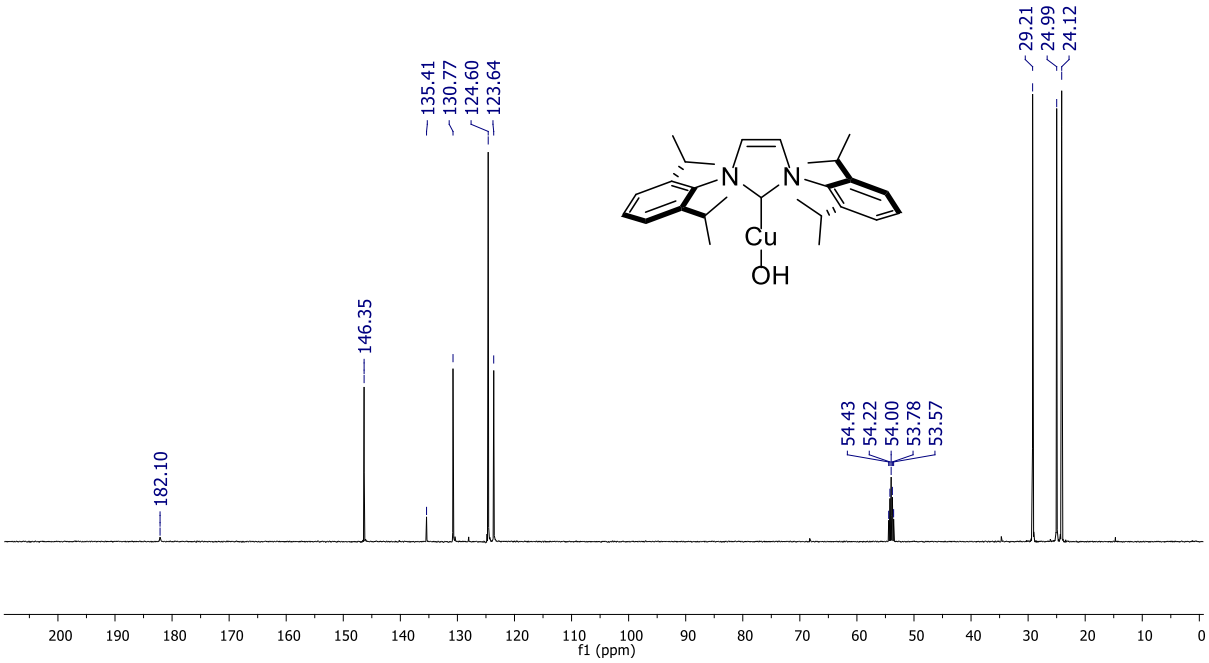
NMR Spectra of Complexes

^{1}H NMR ($CDCl_3$ and CD_2Cl_2) of [Cu(OH)(IPr)] (1)

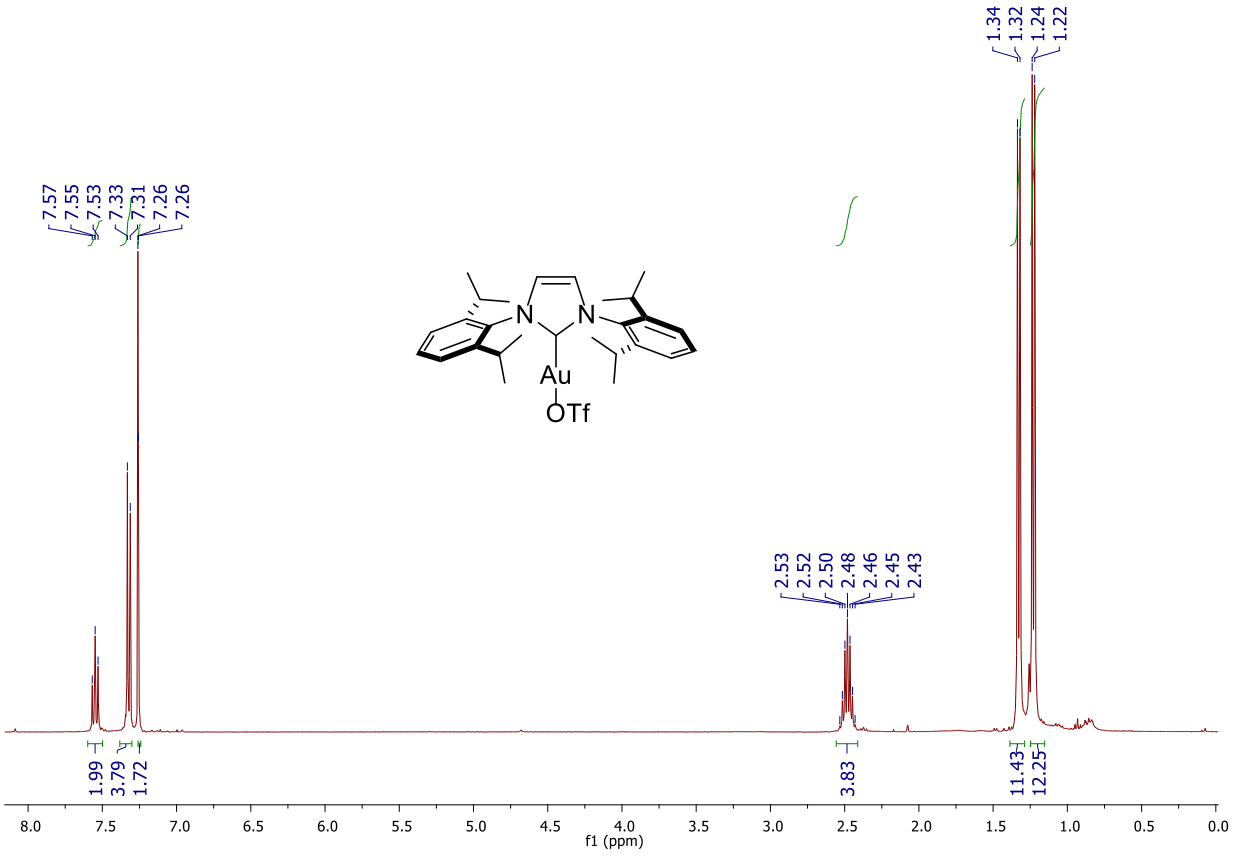


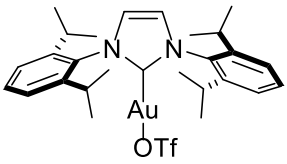


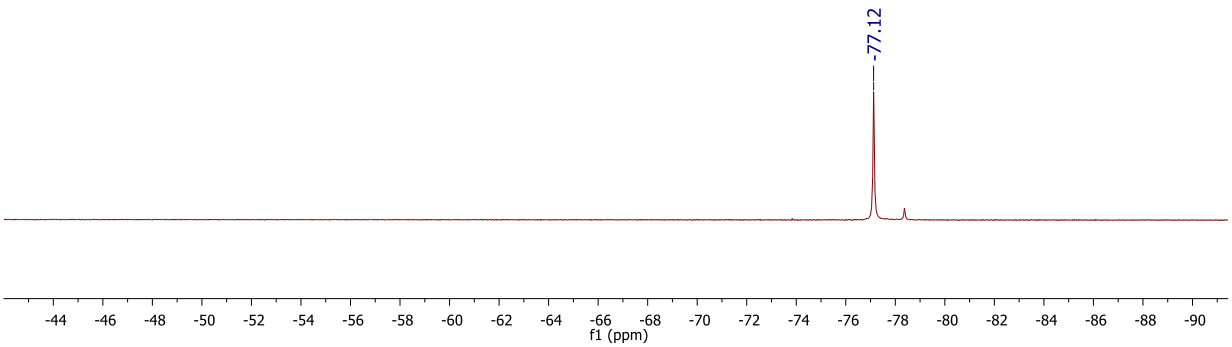
^{13}C NMR (CD_2Cl_2) of [Cu(OH)(IPr)] (1)



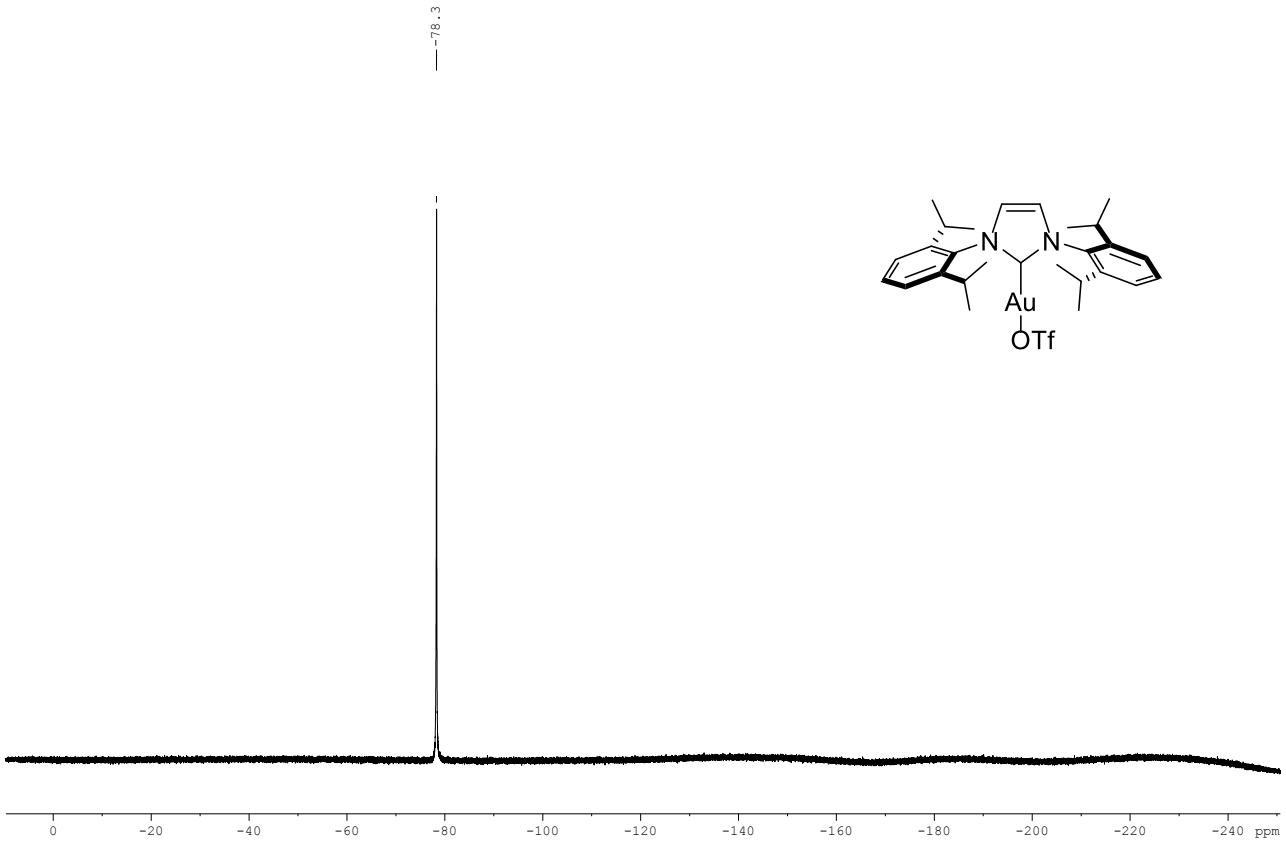
^{1}H NMR ($CDCl_3$) and ^{19}F-{^{1}H } NMR ($CDCl_3$) of [Au(OTf)(IPr)](2)



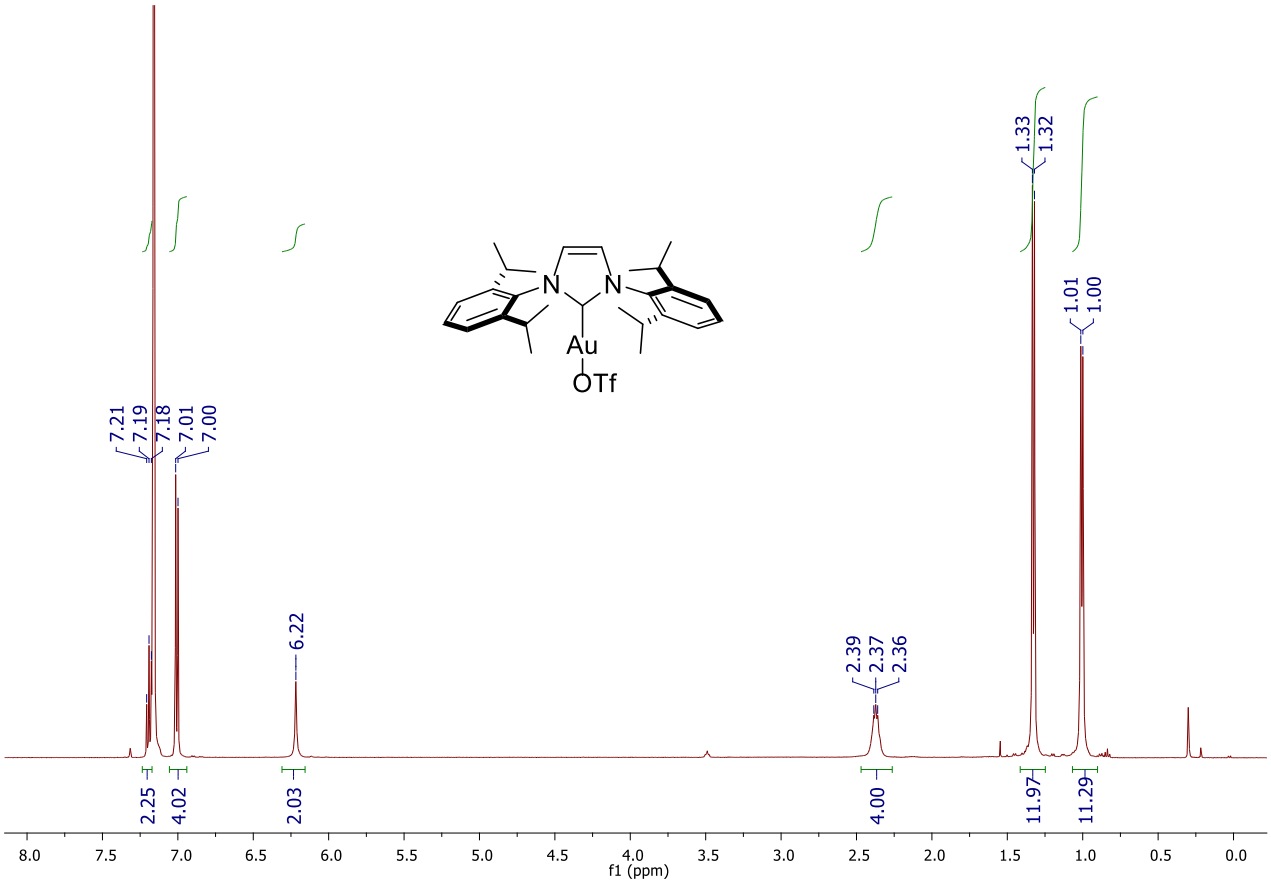


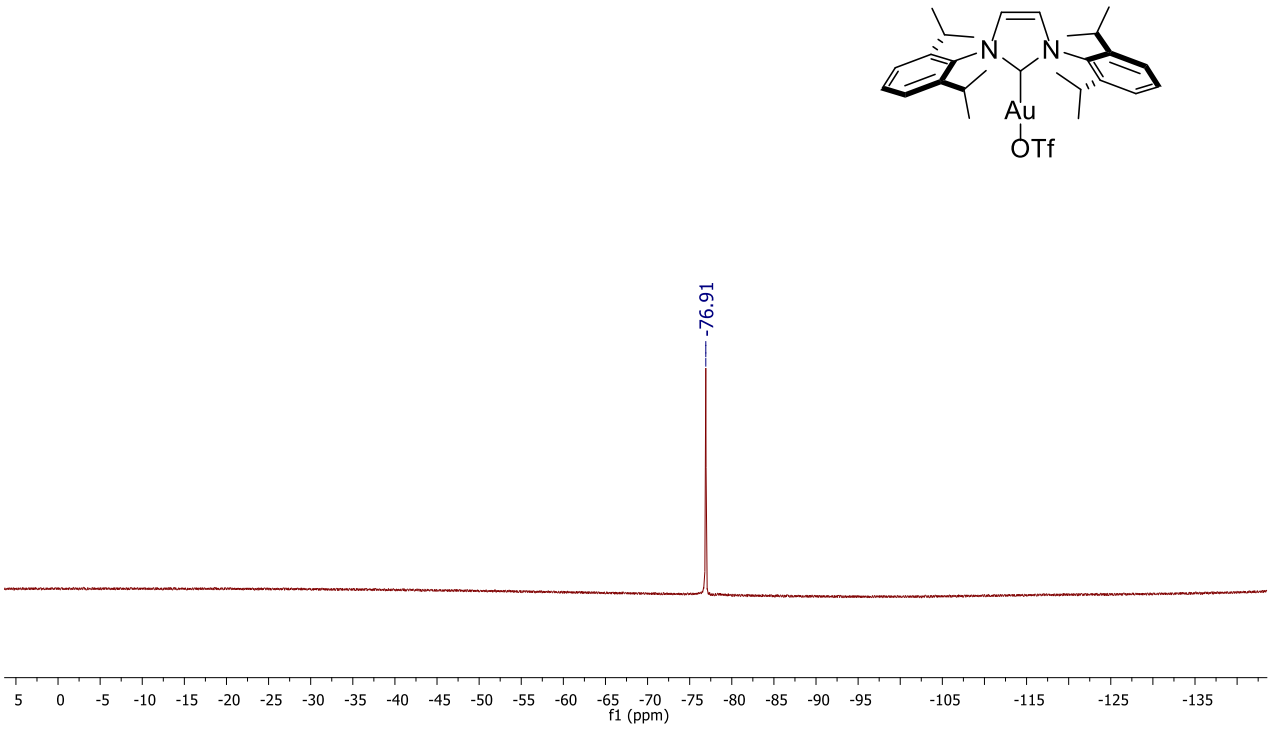


^{19}F-{^{1}H } NMR (CD_2Cl_2) of [Au(OTf)(IPr)](2)

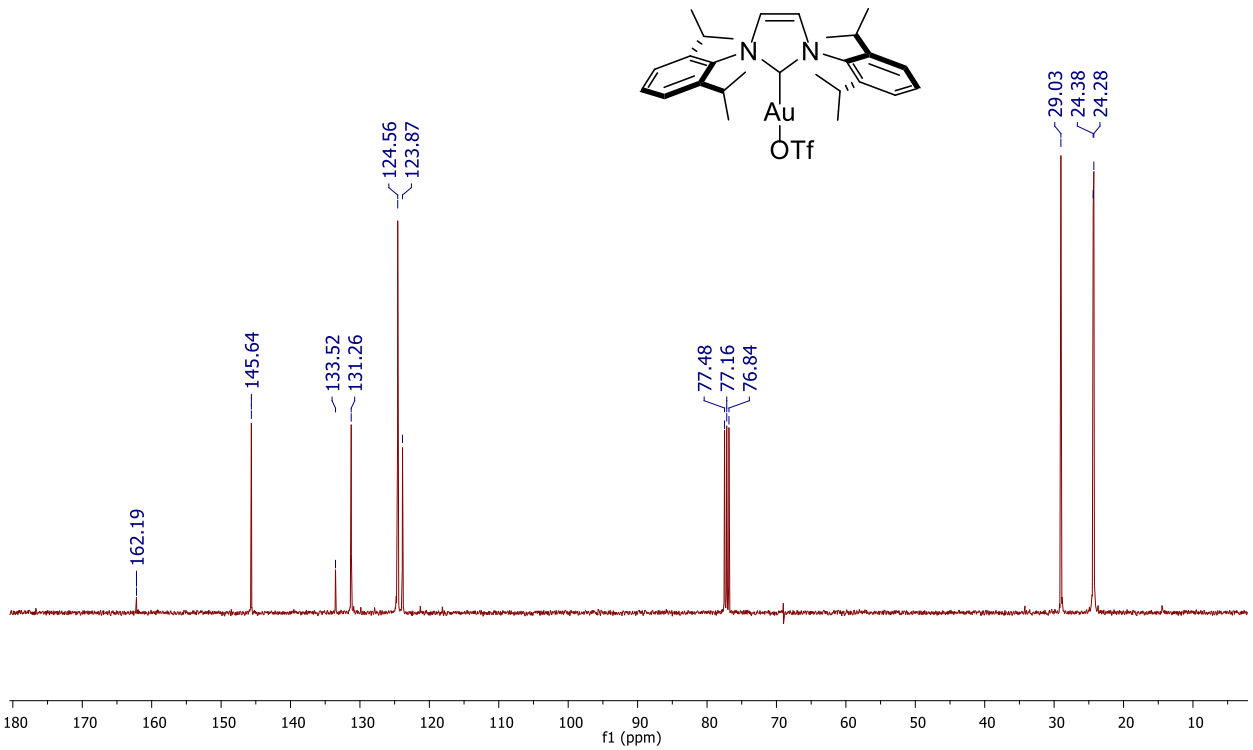


^{1}H NMR (C_6D_6) and ^{19}F-{^{1}H } NMR (C_6D_6) of [Au(OTf)(IPr)](2)

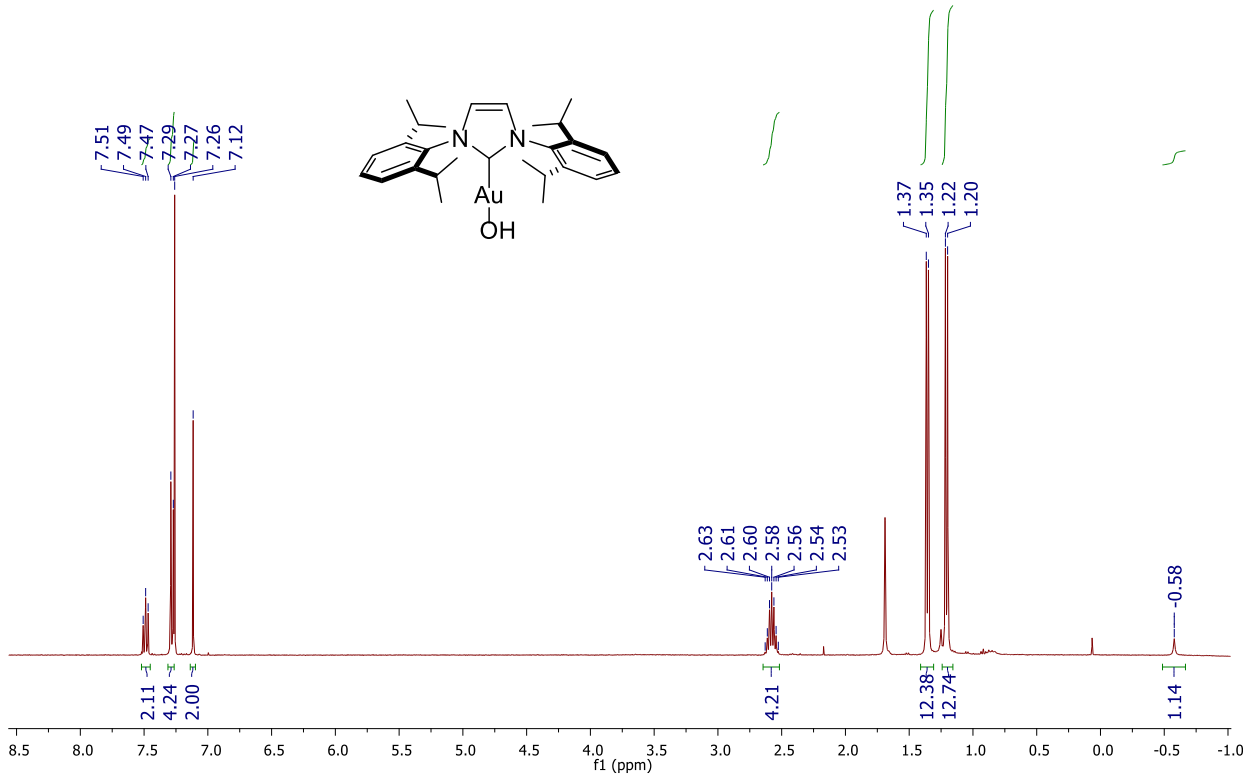




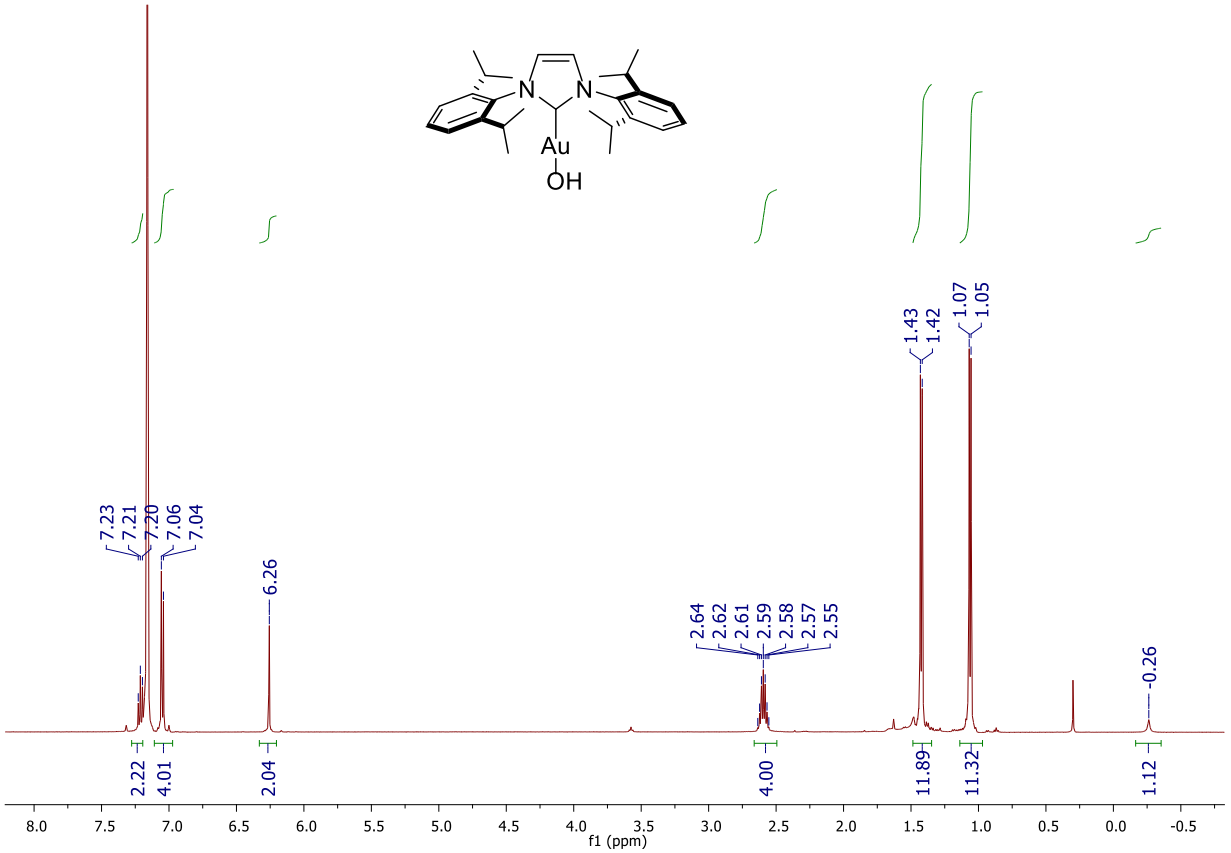
^{13}C NMR ($CDCl_3$) of [Au(OTf)(IPr)](2)



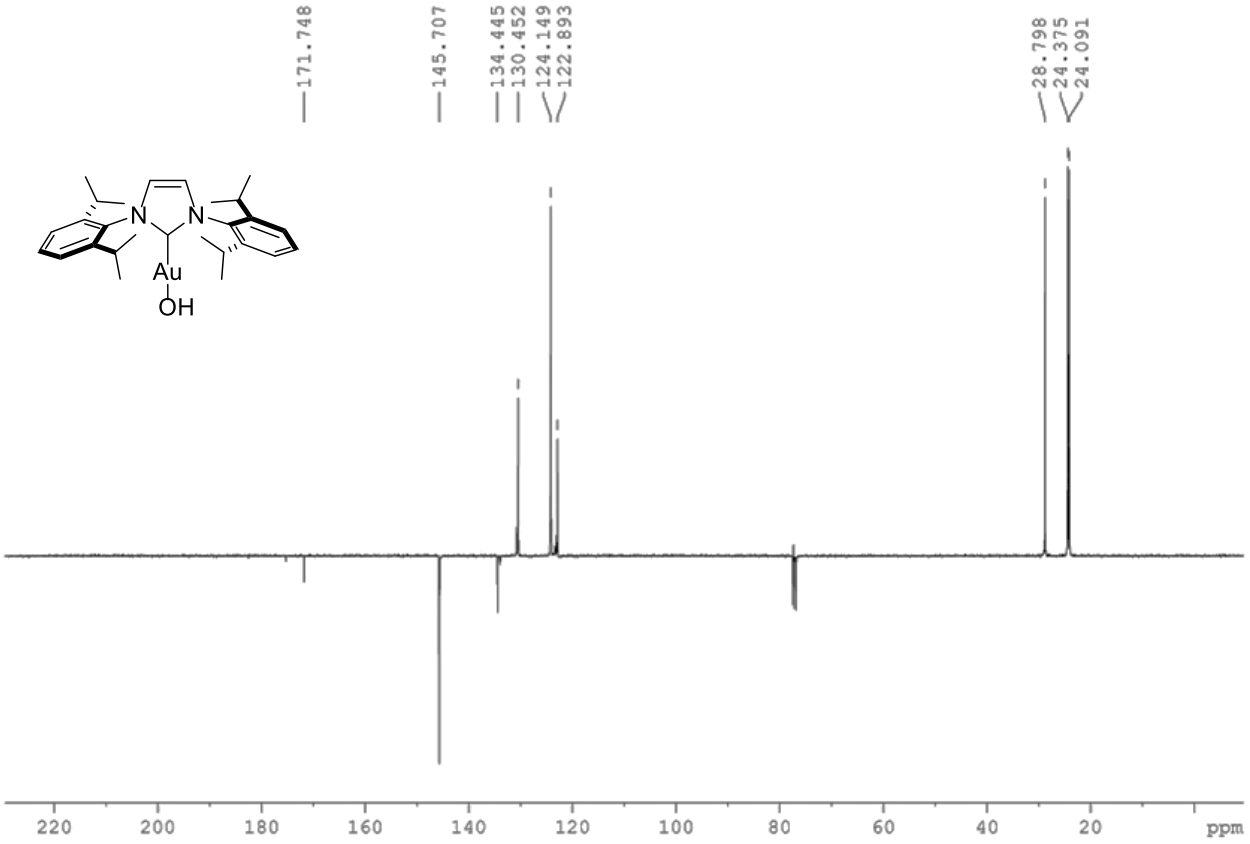
^{1}H NMR ($CDCl_3$) of [Au(OH)(IPr)] (A)



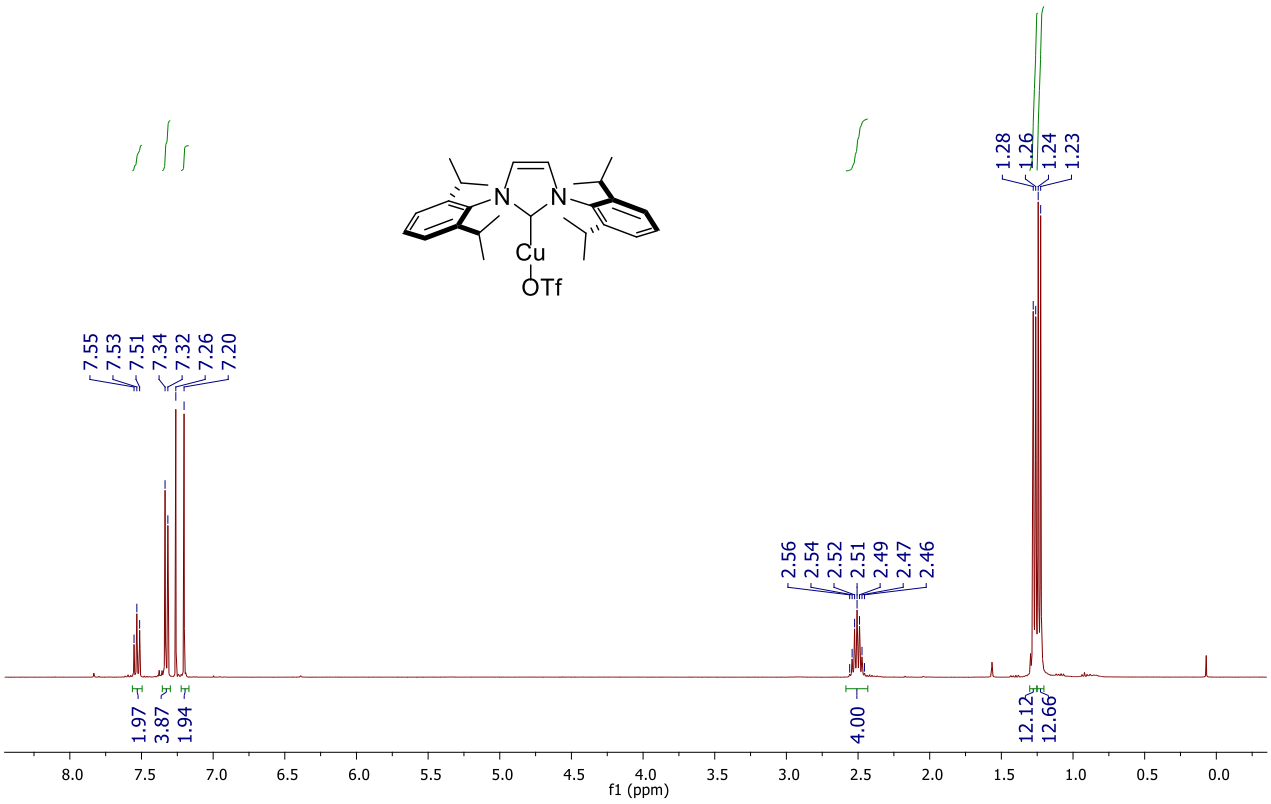
^{1}H NMR (C_6D_6) of [Au(OH)(IPr)] (A)

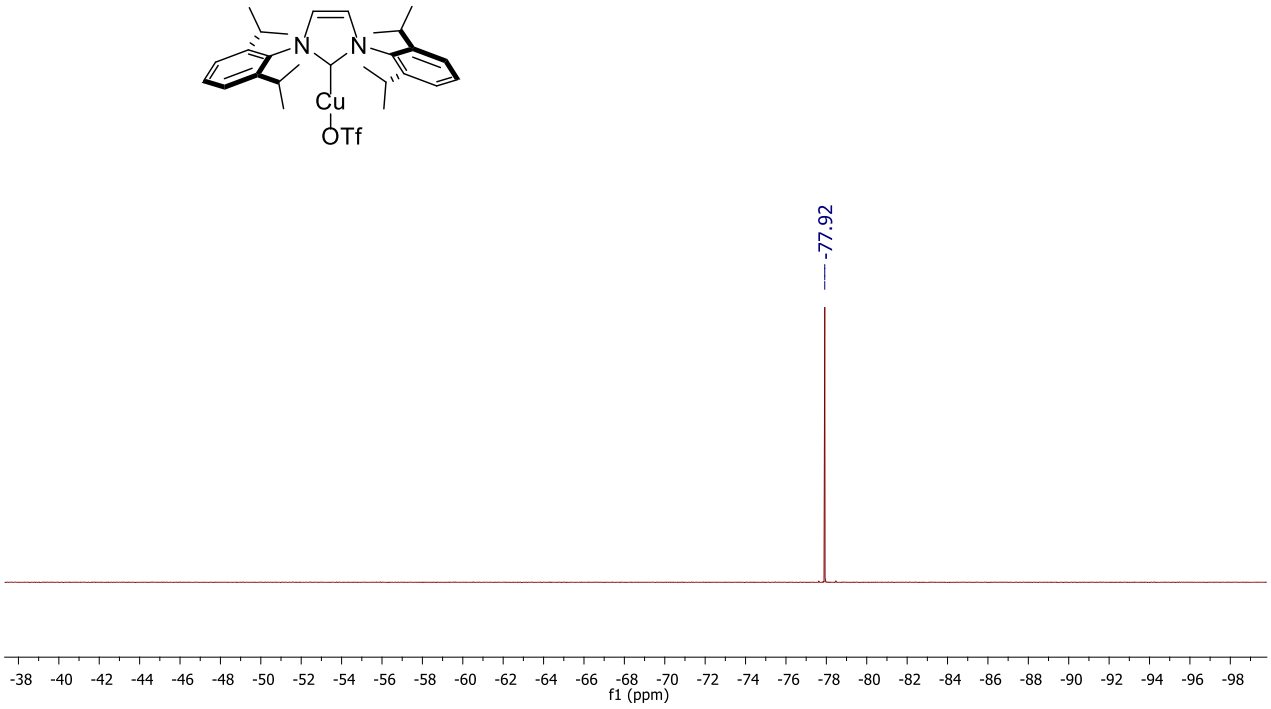


^{13}C{^{1}H}-DEPTQ NMR ($CDCl_3$) of [Au(OH)(IPr)] (A)

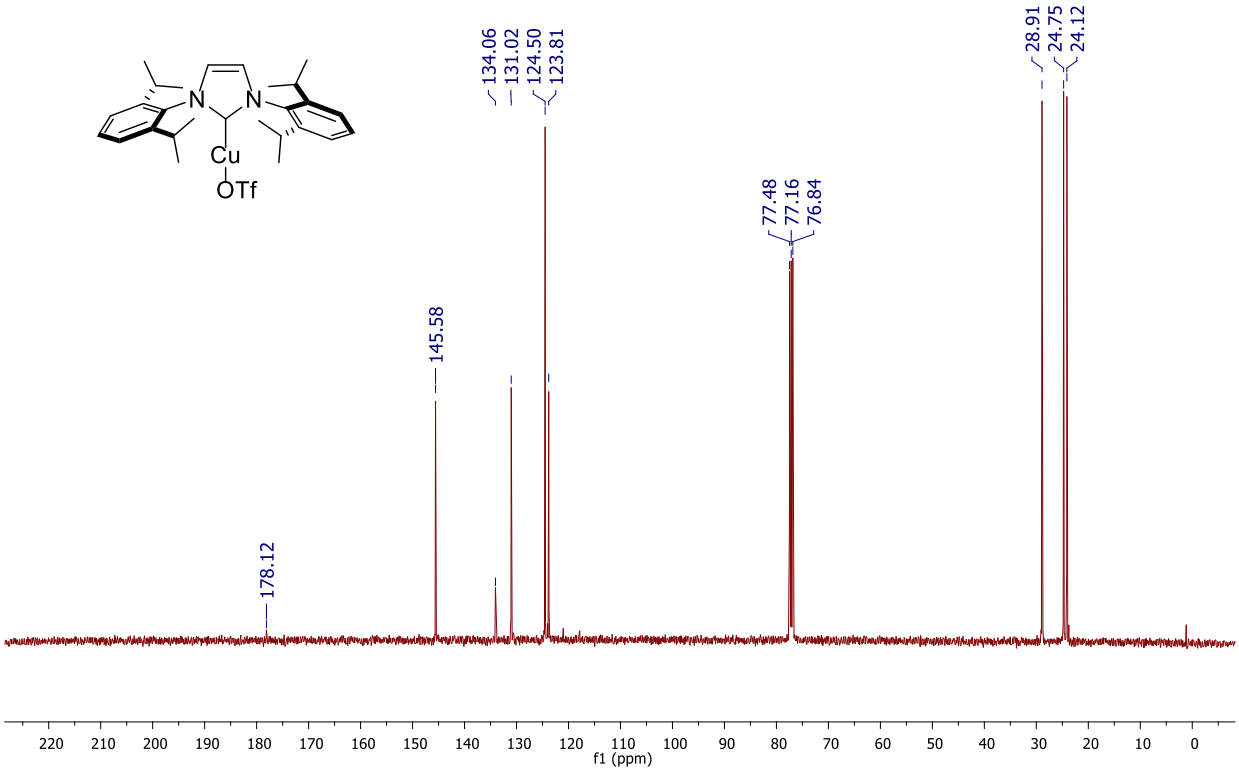


^{1}H NMR ($CDCl_3$) and ^{19}F-{^{1}H } NMR ($CDCl_3$) of [Cu(OTf)(IPr)] (B)

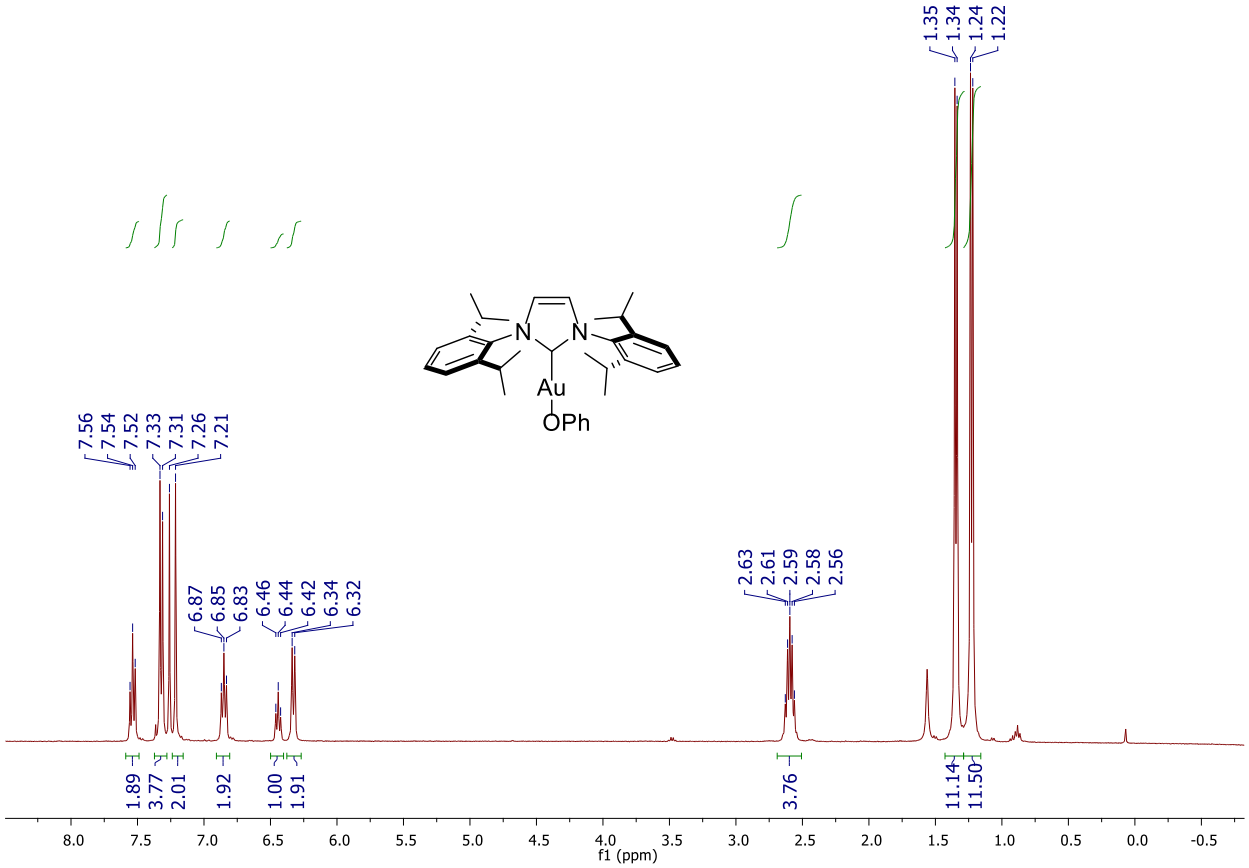




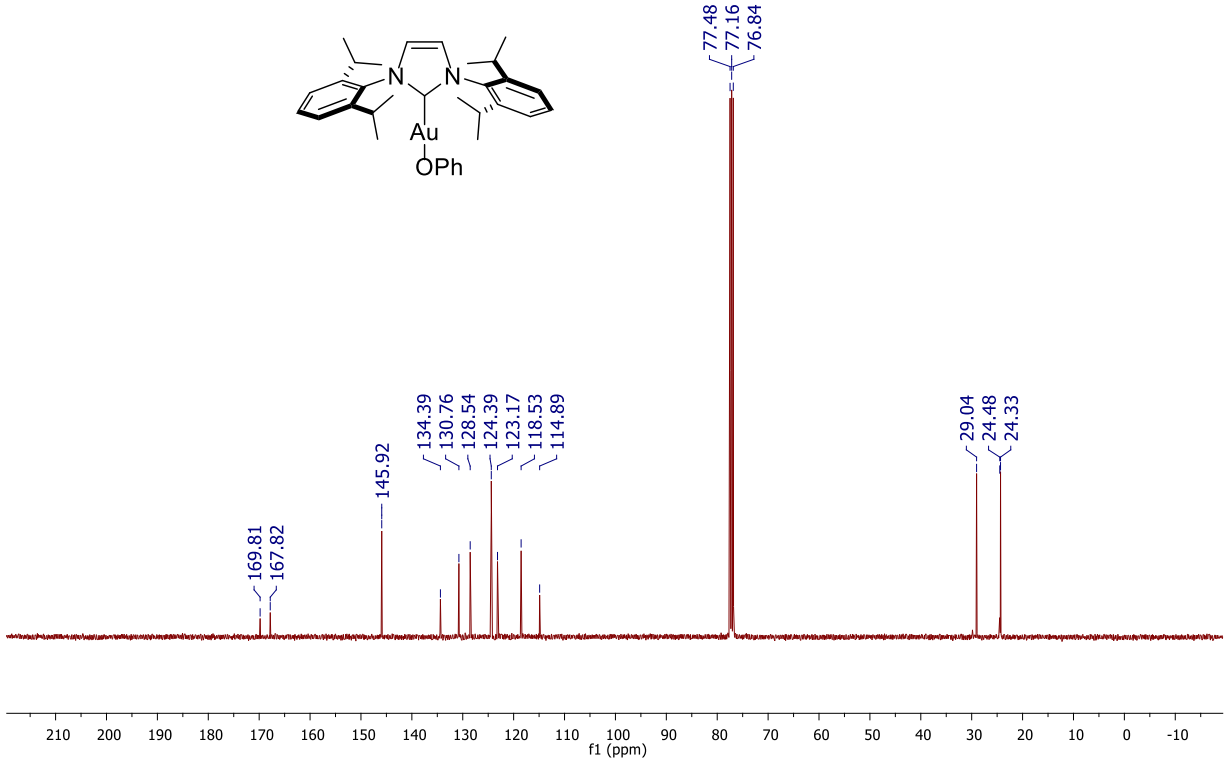
^{13}C NMR ($CDCl_3$) of [Cu(OTf)(IPr)] (B)



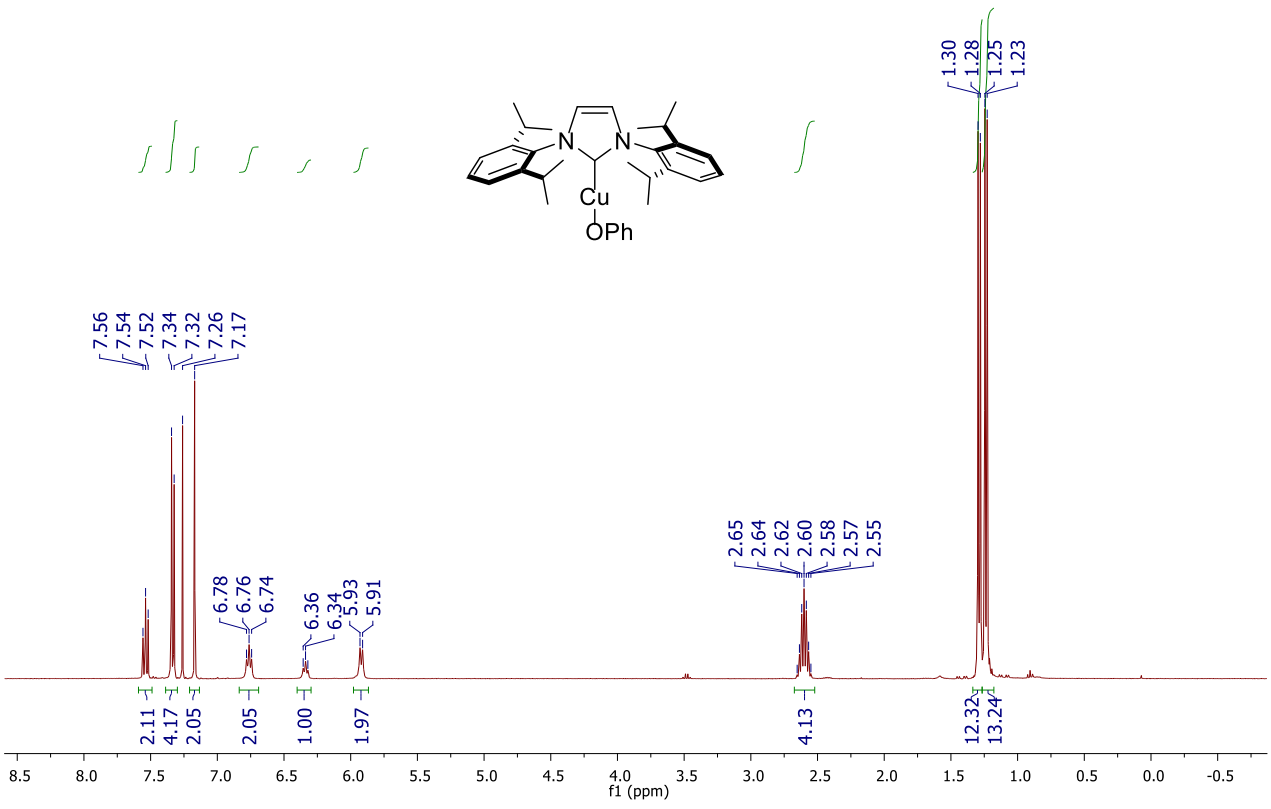
^{1}H NMR ($CDCl_3$) of [Au(OPh)(IPr)] (E)



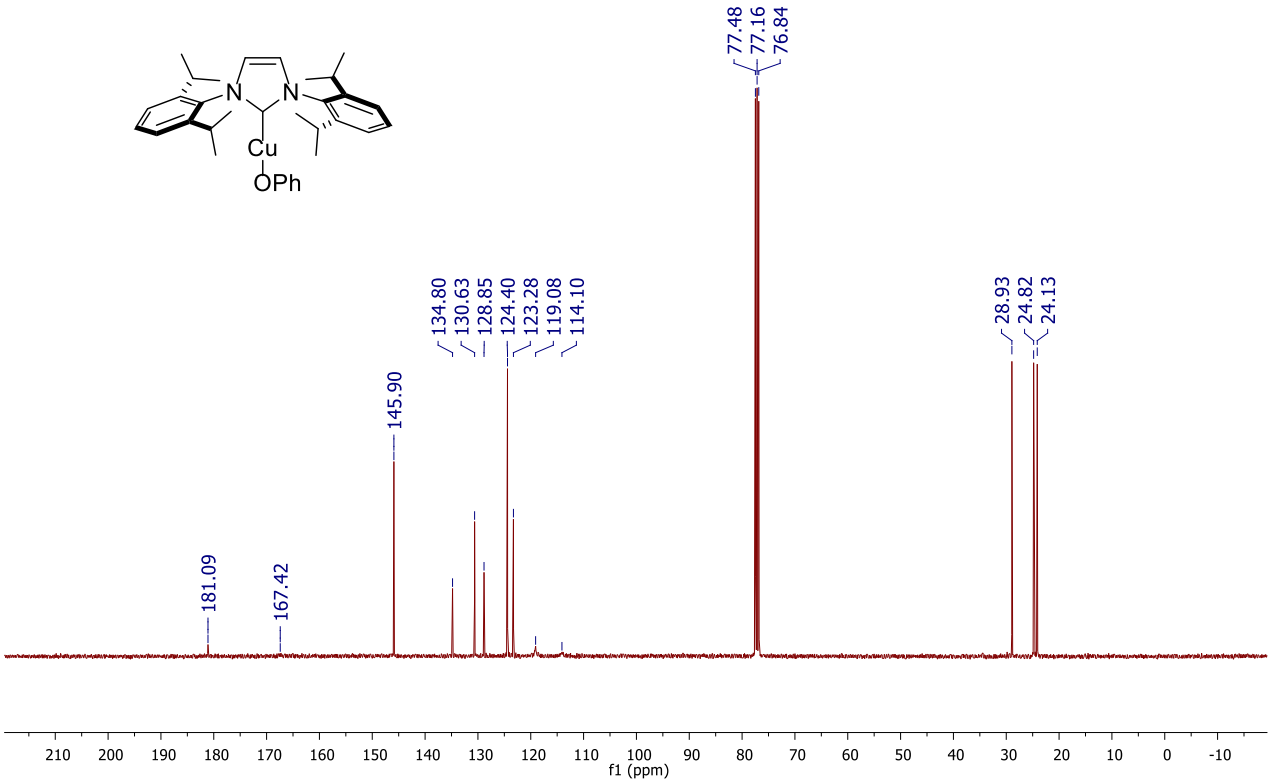
^{13}C NMR ($CDCl_3$) of [Au(OPh)(IPr)] (E)



^{1}H NMR ($CDCl_3$) of [Cu(OPh)(IPr)] (F)



^{13}C NMR ($CDCl_3$) of [Cu(OPh)(IPr)] (F)



Synthesis and characterisation of substrates 4g-j

General procedure

$[PdCl_2(PPh_3)_2]$ was synthesised according to a published procedure.[8] Internal alkynes **4g-j** were synthesised according to a general procedure given below.[9] All other substrates were purchased and used as received unless otherwise noted.

Under inert atmosphere, a Schlenk flask was charged with THF (20 mL) and triethylamine (10 mL). The aryl iodide, the alkyne, $[PdCl_2(PPh_3)_2]$ and CuI were added in this order to the flask, and the resulting mixture was stirred overnight at the corresponding temperature. Then, the mixture was cooled to room temperature and quenched by MeOH (10 mL). The solution was concentrated under reduced pressure, and diethylether (Et_2O, 100 mL) was added. After filtration, the filtrate was washed with 1N HCl(aq.) and H_2O. The organic layer was dried over $MgSO_4$, filtered and concentrated under reduced pressure to afford the crude product. The pure product was obtained by purification through silica gel column chromatography.

Substrate characterisation 4g-j

Hex-1-yn-1-ylbenzene (4g)

$[PdCl_2(PPh_3)_2]$ (25 mg, 0.035 mmol), CuI (7 mg, 0.035 mmol), iodobenzene (0.8 mL, 7.3 mmol) and 1-hexyne (0.9 mL, 8.7 mmol) were charged into a Schlenk flask. The mixture was stirred at 50 °C for 24 h. Flash chromatography (SiO_2, pentane) afforded the desired compound as an orange oil (700 mg, 61%).

^{1}H NMR (500 MHz, $CDCl_3$): δ (ppm) = 0.95 (t, *J* = 7.3 Hz, 3H, CH_3), 1.44-1.52 (m, 2H, CH_2), 1.56-1.63 (m, 2H, CH_2), 2.41 (t, *J* = 7.0 Hz, 2H, CH_2), 7.25-7.30 (m, 3H, CH_{Ar}), 7.37-7.41 (m, 2H, CH_{Ar}).

The data was in accordance with the literature.[10]

2-(hex-1-yn-1-yl)thiophene (4h)

$[PdCl_2(PPh_3)_2]$ (75 mg, 0.105 mmol), CuI (13.5 mg, 0.070 mmol), 2-iodothiophene (1.55 mL, 14.6 mmol), 1-hexyne (1.8 mL, 17.4 mmol) were charged into a Schlenk flask and stirred at 50 °C for 24 h. Flash chromatography (SiO_2, pentane) afforded the desired compound as a brown oil (1.2 g, 50%).

^{1}H NMR (500 MHz, $CDCl_3$): δ (ppm) = 0.94 (t, *J* = 7.3 Hz, 3H, CH_3), 1.43-1.51 (m, 2H, CH_2), 1.55-1.62 (m, 2H, CH_2), 2.43 (t, *J* = 7.2 Hz, 2H, CH_2), 6.93 (dd, *J* = 3.6 Hz, *J* = 5.2 Hz, 1H, CH_{thioph}), 7.11 (dd, *J* = 1.0 Hz, *J* = 3.6 Hz, 1H, CH_{thioph}), 7.16 (dd, *J* = 1.0 Hz, *J* = 5.2 Hz, 1H, CH_{thioph}).

The data was in accordance with the literature.[11]

2-(phenylethynyl)thiophene (4i)

$[PdCl_2(PPh_3)_2]$ (25 mg, 0.035 mmol), CuI (7 mg, 0.035 mmol), 2-iodothiophene (0.78 mL, 7.3 mmol), phenylacetylene (1 mL, 8.7 mmol) were charged into a Schlenk flask and stirred at 50 °C for 24 h. Flash chromatography (SiO_2, pentane) afforded the desired compound as a pale yellow solid (1.2 g, 89%).

^{1}H NMR (500 MHz, $CDCl_3$): δ (ppm) = 7.01 (m, 1H, CH_{thioph}), 7.27-7.30 (m, 2H, CH_{Ar}), 7.31-7.36 (m, 3H, CH_{Ar}), 7.50-7.54 (m, 2H, CH_{thioph}).

The data was in accordance with the literature.[12]

1-(phenylethynyl)naphthalene (4j)

$[PdCl_2(PPh_3)_2]$ (25 mg, 0.035 mmol), CuI (7 mg, 0.035 mmol), iodonaphthalene (1.1 mL, 7.3 mmol), phenylacetylene (1 mL, 8.7 mmol) were charged into a Schlenk flask and stirred at room temperature for 24 h. Flash chromatography (SiO_2, pentane) afforded the desired compound as a colourless solid (1.0 g, 60%).

^{1}H NMR (500 MHz, $CDCl_3$): δ (ppm) = 7.37-7.44 (m, 3H, CH_{Ar}), 7.47 (t, J = 7.7 Hz, 1H, CH_{Ar}), 7.54 (t, J = 7.7 Hz, 1H, CH_{Ar}), 7.60 (t, J = 7.7 Hz, 1H, CH_{Ar}), 7.64-7.68 (m, 2H, CH_{Ar}), 7.77 (d, J = 7.4 Hz, 1H, CH_{Ar}), 7.85 (d, J = 8.3 Hz, 1H, CH_{Ar}), 7.87 (d, J = 8.2 Hz, 1H, CH_{Ar}), 8.45 (d, J = 8.3 Hz, 1H, CH_{Ar}).

The data was in accordance with the literature.[13]

Catalysis

General procedure for optimisation and kinetic profiling

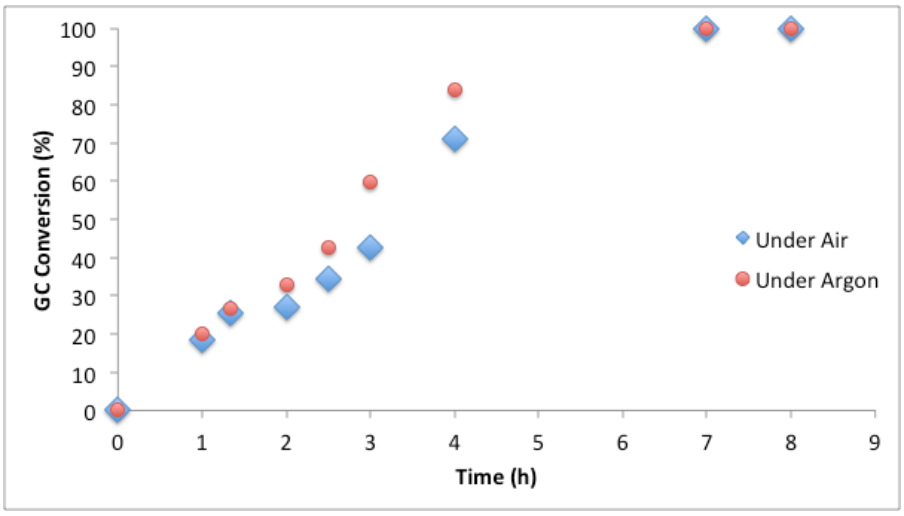
N.B.: When 0.2 and 0.1 mol% catalyst loading were used; a stock solution was prepared in THF:

- 7.2 mg [Au] dissolved in 1 mL; 100 µL for 0.2 mol% and 50 µL for 0.1 mol%.

-4.7 mg [Cu] dissolved in 1 mL, 100 µL for 0.2 mol% and 50 µL for 0.1 mol%

With solvent: In a glovebox, a vial was charged with the appropriate amount of [Au(OTf)(IPr)] (**2**) and [Cu(OH)(IPr)] (**1**) (when THF stock solutions were used, THF was removed at this point), followed by alkyne **4a** (89.1 mg, 0.5 mmol, 1 equiv.), phenol **5a** (56.5 mg, 0.6 mmol, 1.2 equiv.) and the appropriate solvent (1 mL). The reaction mixture was removed from the glovebox and stirred at 80 °C for 16 h. The solvent was then removed. The reaction residue was dissolved in dichloromethane and the conversion was determined by GC analysis.

Without solvent: In a glovebox, a vial was charged with the appropriate amount of [Au(OTf)(IPr)] (**2**) and [Cu(OH)(IPr)] (**1**) (when THF stock solutions were used, THF was removed at this point), followed by alkyne **4a** (89.1 mg, 0.5 mmol, 1 equiv.) and phenol **5a** (56.5 mg, 0.6 mmol, 1.2 equiv.). The reaction mixture was removed from the glovebox and stirred at the appropriate temperature for 16 h. The reaction residue was dissolved in dichloromethane and the conversion was determined by GC analysis. The final product **6aa** was purified by flash chromatography when indicated (Table 1, entry 14). When kinetic profiling was conducted; 0.2 mol% of [Au(OTf)(IPr)] (**2**) and 0.2 mol% of [Cu(OH)(IPr)] (**1**) were used and samples for GC analysis were taken at 60, 80, 120, 150, 180, 240, 420 and 480 minutes.



Kinetic profiling Diphenylacetylene (0.5 mmol), phenol (0.6 mmol), [Cu(OH)(IPr)]/ [Au(OTf)(IPr)] (1:1) (0.2/0.2 mol%), solvent-free, 60 °C.

General procedure for the scope

N.B.: When 0.2 and 0.4 mol% catalyst loading were used; a stock solution was prepared in THF:

- 7.2 mg [Au] dissolved in 1 mL; 100 µL for 0.2 mol% and 200 µL for 0.4 mol%.

- 4.7 mg [Cu] dissolved in 1 mL, 100 µL for 0.2 mol% and 200 µL for 0.4 mol%

In a glovebox, a vial was charged with the appropriate amount of [Au(OTf)(IPr)] (**2**) and [Cu(OH)(IPr)] (**1**) (when THF stock solutions were used, THF was removed at this point), followed by alkyne **4** (0.5 mmol, 1 equiv.) and phenol **5** (0.6 mmol, 1.2 equiv.). The reaction mixture was removed from the glovebox and stirred at 60 ^{o}C for 16 h. The reaction residue was dissolved in dichloromethane and the conversion was determined by GC analysis or ^{1}H NMR. Final products were isolated after purification *via* flash chromatography.

Characterisation of products

(*Z*)-(1-phenoxyethene-1,2-diyl)dibenzene (6aa)

The product was obtained after flash chromatography (SiO_2, pentane/Et_2O, 99:1) as a colourless solid (279 mg, 99%).

^{1}H NMR (500 MHz, $CDCl_3$, TMS): δ (ppm) = 6.65 (s, 1H, CH), 6.93 (dd, *J* = 7.3 Hz, *J* = 7.3 Hz, 1H, CH_{Ar}), 7.01 (d, *J* = 8 Hz, 2H, CH_{Ar}), 7.19-7.31 (m, 8H, CH_{Ar}), 7.58 (d, *J* = 7.3 Hz, 2H, CH_{Ar}), 7.63 (d, *J* = 7.3 Hz, 2H, CH_{Ar}).

^{13}C-{^{1}H} NMR (125.7 MHz, $CDCl_3$, TMS): δ (ppm) = 116.4 (CH), 116.9 (CH), 122.1 (CH), 126.2 (CH), 127.5 (CH), 128.5 (CH), 128.6 (CH), 128.7 (CH), 129.1 (CH), 129.8 (CH), 134.8 (C^{IV}), 136.1 (C^{IV}), 149.7 (C^{IV}), 156.4 (C^{IV}).

Data in accordance with the literature.[10]

(*Z*)-(1-(p-tolyloxy)ethene-1,2-diyl)dibenzene (6ab)

The product was obtained after flash chromatography (SiO_2, pentane/Et_2O, 9:1) as colourless solid (284 mg, 99%).

^{1}H NMR (500 MHz, $CDCl_3$, TMS): δ (ppm) = 2.22 (s, 3H, CH_3), 6.62 (s, 1H, CH), 6.90-6.92 (m, 2H, CH_{Ar}), 6.99-7.01 (m, 2H, CH_{Ar}), 7.19-7.30 (m, 6H, CH_{Ar}), 7.55-7.60 (m, 2H, CH_{Ar}), 7.62-7.66 (m, 2H, CH_{Ar}).

^{13}C-{^{1}H} NMR (126 MHz, $CDCl_3$, TMS): δ (ppm) = 20.7 (CH_3), 116.2 (CH), 116.7 (CH), 126.2 (CH), 127.4 (CH), 128.4 (CH), 128.6 (CH), 128.7 (CH), 129.0 (CH), 130.2 (CH), 131.4 (C^{IV}), 135.0 (C^{IV}), 136.2 (C^{IV}), 150.0 (C^{IV}), 154.3 (C^{IV}).

Data in accordance with the literature.[10]

(*Z*)-(1-(4-methoxyphenoxy)ethene-1,2-diyl)dibenzene (6ac)
The product was obtained after flash chromatography (SiO_2, pentane/Et_2O, 9:1) as colourless solid (288 mg, 99%).

^{1}H NMR (500 MHz, $CDCl_3$, TMS): δ (ppm) = 3.69 (s, 3H, OCH_3), 6.59 (s, 1H, CH), 6.74 (d, *J* = 7.3 Hz, 2H, CH_{Ar}), 6.94 (d, *J* = 7.3 Hz, 2H, CH_{Ar}), 7.20-7.30 (m, 6H, CH_{Ar}), 7.57 (d, *J* = 7.3 Hz, 2H, CH_{Ar}), 7.64 (d, *J* = 7.3 Hz, 2H, CH_{Ar}).

^{13}C-{^{1}H} NMR (126 MHz, $CDCl_3$, TMS): δ (ppm) = 55.7 (s, OCH_3), 114.8 (CH), 116.6 (CH), 117.2 (CH), 126.3 (CH), 127.4 (CH), 128.4 (CH), 128.6 (CH), 128.6 (CH), 129.0 (CH), 135.0 (C^{IV}), 136.2 (C^{IV}), 150.2 (C^{IV}), 150.3 (C^{IV}), 154.7 (C^{IV}).

Data in accordance with the literature.[10]

(*Z*)-2-(4-((1,2-diphenylvinyl)oxy)phenyl)-4,4,5,5-tetramethyl-1,3,2-dioxaborolane (6ad)
The product was obtained after flash chromatography (SiO_2, pentane/Et_2O, 9:1) as colourless solid (312 mg, 78%).

^{1}H NMR (300 MHz, $CDCl_3$, TMS): δ (ppm) = 1.29 (s, 12H, $C(CH_3)_2$), 6.67 (s, 1H, CH), 6.96-7.06 (m, 2H, CH_{Ar}), 7.14-7.35 (m, 6H, CH_{Ar}), 7.52-7.64 (m, 4H, CH_{Ar}), 7.65-7.74 (m, 2H, CH_{Ar}).
^{13}C-{^{1}H} NMR (75 MHz, $CDCl_3$, TMS): δ (ppm) = 25.0 ($C(CH_3)_2$), 83.7 ($C(CH_3)_2$), 115.9 (CH), 116.9 (CH), 126.1 (CH), 127.6 (C^{IV}), 128.6 (C^{IV}), 128.7 (CH), 128.7 (CH), 129.1 (CH), 134.7 (C^{IV}), 136.0 (C^{IV}), 136.8 (CH), 149.5 (C^{IV}), 159.2 (C^{IV}).

(*Z*)-(1-(4-fluorophenoxy)ethene-1,2-diyl)dibenzene (6ae)
The product was obtained after flash chromatography (SiO_2, pentane/Et_2O, 9:1) as colourless solid (278 mg, 96%).

^{1}H NMR (500 MHz, $CDCl_3$, TMS): δ (ppm) = 6.63 (s, 1H, CH), 6.84-6.98 (m, 4H, CH_{Ar}), 7.17-7.34 (m, 6H, CH_{Ar}), 7.51-7.59 (m, 2H, CH_{Ar}), 7.59-7.66 (m, 4H, CH_{Ar}).

^{19}F-{^{1}H} NMR (470 MHz, $CDCl_3$, TMS): δ (ppm) = -122.2.

^{13}C-{^{1}H} NMR (126 MHz, $CDCl_3$, TMS): δ (ppm) = 116.3 (d, J_{CF} = 23 Hz, CH), 116.9 (CH), 117.4 (d, J_{CF} = 8.1 Hz, CH), 126.2 (CH), 127.6 (CH), 128.6 (CH), 128.7 (CH), 128.7 (CH), 129.1 (CH), 134.7 (C^{IV}), 135.8 (C^{IV}), 149.9 (C^{IV}), 152.4 (C^{IV}), 158.0 (d, J_{CF} = 240 Hz, CF).

Data in accordance with the literature.[10]

(*Z*)-(1-(4-chlorophenoxy)ethene-1,2-diyl)dibenzene (6af)
The product was obtained after flash chromatography (SiO_2, pentane/Et_2O, 9:1) as colourless solid (283 mg, 92%).

^{1}H NMR (500 MHz, $CDCl_3$, TMS): δ (ppm) = 6.65 (s, 1H, CH), 6.94 (d, *J* = 7.3 Hz, 2H, CH_{Ar}), 7.15 (d, *J* = 7.3 Hz, 2H, CH_{Ar}), 7.19-7.22 (m, 1H, CH_{Ar}), 7.24-7.33 (m, 5H, CH_{Ar}), 7.55 (d, *J* = 7.3 Hz, 2H, CH_{Ar}), 7.60 (d, *J* = 7.3 Hz, 2H, CH_{Ar}).

^{13}C-{^{1}H} NMR (126 MHz, $CDCl_3$, TMS): δ (ppm) = 117.0 (CH), 117.6 (CH), 126.1 (CH), 127.1 (CH), 127.7 (CH), 128.7 (CH), 128.7 (CH), 128.8 (CH), 129.1 (CH), 129.8 (C^{IV}), 134.6 (C^{IV}), 135.6 (C^{IV}), 149.5 (C^{IV}), 155.0 (C^{IV}).

Data in accordance with the literature.[10]

(*Z*)-4-((1,2-diphenylvinyl)oxy)benzaldehyde (6ag)
The product was obtained after flash chromatography (SiO_2, pentane/Et_2O, 8:2) as colourless solid (242 mg, 81%).

^{1}H NMR (500 MHz, $CDCl_3$, TMS): δ (ppm) = 6.73 (s, 1H, CH), 7.03-7.38 (m, 8H, CH_{Ar}), 7.46-7.65 (m, 4H, CH_{Ar}), 7.66-7.83 (m, 2H, CH_{Ar}), 9.80 (s, 1H, CHO).

^{13}C-{^{1}H} NMR (126 MHz, $CDCl_3$, TMS): δ (ppm) = 116.6 (CH), 117.2 (CH), 125.8 (CH), 127.9 (CH), 128.7 (CH), 128.9 (CH), 128.9 (CH), 129.1 (CH), 131.1 (C^{IV}), 132.2 (CH), 134.1 (C^{IV}), 135.2 (C^{IV}), 148.8 (C^{IV}), 161.5 (C^{IV}), 190.7 (CO).

Data in accordance with the literature.[13]

(*Z*)-1-(4-((1,2-diphenylvinyl)oxy)phenyl)ethan-1-one (6ah)
The product was obtained after flash chromatography (SiO_2, pentane/Et_2O, 8:2) as yellow solid (291 mg, 93%).

^{1}H NMR (500 MHz, $CDCl_3$, TMS): δ (ppm) = 2.48 (s, 3H, $COCH_3$), 6.72 (s, 1H, CH), 7.03-7.09 (m, 2H, CH_{Ar}), 7.18-7.36 (m, 6H, CH_{Ar}), 7.54-7.61 (m, 4H, CH_{Ar}), 7.82-7.88 (m, 2H, CH_{Ar}).

^{13}C-{^{1}H} NMR (126 MHz, $CDCl_3$, TMS): δ (ppm) = 26.5 ($CO\mathit{C}H_3$), 116.1 (CH), 117.2 (CH), 125.9 (CH), 127.8 (CH), 128.7 (CH), 128.8 (CH), 128.9 (CH), 129.1 (CH), 130.8 (CH), 131.6 (C^{IV}), 134.3 (C^{IV}), 135.4 (C^{IV}), 149.0 (C^{IV}), 160.5 (C^{IV}), 196.8 (CO).

Data in accordance with the literature.[13]

Methyl (*Z*)-4-((1,2-diphenylvinyl)oxy)benzoate (6ai)
The product was obtained after flash chromatography (SiO_2, pentane/Et_2O, 8:2) as colourless solid (225 mg, 68%).

^{1}H NMR (500 MHz, $CDCl_3$, TMS): δ (ppm) = 3.83 (s, 3H, OCH_3), 6.72 (s, 1H, CH), 7.05 (d, *J* = 8.1 Hz, 2H, CH_{Ar}), 7.18-7.36 (m, 6H, CH_{Ar}), 7.58 (dd, *J* = 8.1 Hz, *J* = 8.1 Hz, 4H, CH_{Ar}), 7.92 (d, *J* = 8.1 Hz, 2H, CH_{Ar}).

^{13}C-{^{1}H} NMR (126 MHz, $CDCl_3$, TMS): δ (ppm) = 52.0 (s, OCH_3), 116.1 (CH), 117.1 (CH), 124.1 (C^{IV}), 125.9 (CH), 127.8 (CH), 128.7 (CH), 128.8 (CH), 128.8 (CH), 129.1 (CH), 131.9 (CH), 134.4 (C^{IV}), 135.5 (C^{IV}), 149.1 (C^{IV}), 160.3 (C^{IV}), 166.7 (CO).

Data in accordance with the literature.[13]

(*Z*)-4-((1,2-diphenylvinyl)oxy)benzonitrile (6aj)

The product was obtained after flash chromatography (SiO_2, pentane/Et_2O, 8:2) as colourless solid (193 mg, 65%).

^{1}H NMR (500 MHz, $CDCl_3$, TMS): δ (ppm) = 6.74 (s, 1H, CH), 7.03-7.10 (m, 2H, CH_{Ar}), 7.18-7.38 (m, 6H, CH_{Ar}), 7.47-7.60 (m, 6H, CH_{Ar}).

^{13}C-{^{1}H} NMR (126 MHz, $CDCl_3$, TMS): δ (ppm) = 105.7 (C^{IV}), 117.0 (CH), 117.4 (CH), 119.0 (CN), 125.8 (CH), 128.0 (CH), 128.8 (CH), 129.0 (CH), 129.0 (CH), 129.1 (CH) 134.0 (C^{IV}), 134.4 (CH), 135.0 (C^{IV}), 148.6 (C^{IV}), 159.9 (C^{IV}).

Data in accordance with the literature.[10]

(*Z*)-(1-(4-nitrophenoxy)ethene-1,2-diyl)dibenzene (6ak)

The product was obtained after flash chromatography (SiO_2, pentane:Et_2O, 9:1) as yellow oil (292 mg, 92%).

^{1}H NMR (500 MHz, $CDCl_3$, TMS): δ (ppm) = 6.77 (s, 1H, CH), 7.10 (d, J = 7.3 Hz, 2H, CH_{Ar}), 7.20-7.37 (m, 6H, CH_{Ar}), 7.56 (m, 4H, CH_{Ar}), 8.12 (d, J = 7.3 Hz, 2H, CH_{Ar}).

^{13}C-{^{1}H} NMR (126 MHz, $CDCl_3$, TMS): δ (ppm) = 116.4 (CH), 117.5 (CH), 125.7 (CH), 126.2 (CH), 128.1 (CH), 128.8 (CH), 129.0 (CH), 129.1 (CH), 129.1 (CH), 133.9 (C^{IV}), 134.9 (C^{IV}), 142.7 (C^{IV}), 148.6 (C^{IV}), 161.6 (C^{IV}).

Data in accordance with the literature.[10]

(*Z*)-(1-(m-tolyloxy)ethene-1,2-diyl)dibenzene (6al)

The product was obtained after flash chromatography (SiO_2, pentane/Et_2O, 9:1) as colourless solid (273 mg, 95%).

^{1}H NMR (500 MHz, $CDCl_3$, TMS): δ (ppm) = 2.25 (s, 3H, CH_3), 6.64 (s, 1H, CH), 6.74 (d, J = 7.5 Hz, 1H, CH_{Ar}), 6.80 (d, J = 8.1 Hz, 1H, CH_{Ar}), 6.86 (bs, 1H, CH), 7.07 (d, J = 7.8 Hz, J = 7.8 Hz, 1H, CH_{Ar}), 7.16-7.32 (m, 6H, CH_{Ar}), 7.58 (d, J = 8.1 Hz, 2H, CH_{Ar}), 7.64 (d, J = 7.8 Hz, 2H, CH_{Ar}).

^{13}C-{^{1}H} NMR (126 MHz, $CDCl_3$, TMS): δ (ppm) = 21.6 (CH_3), 113.4 (CH), 116.8 (CH), 117.1 (CH), 123.0 (CH), 126.1 (CH), 127.5 (CH), 128.4 (CH), 128.6 (CH), 128.7 (CH), 129.1 (CH), 129.4 (CH), 134.9 (C^{IV}), 136.2 (C^{IV}), 139.9 (C^{IV}), 149.8 (C^{IV}), 156.4 (C^{IV}).

Data in accordance with the literature.[13]

(*Z*)-(1-(3-fluorophenoxy)ethene-1,2-diyl)dibenzene (6am)
The product was obtained after flash chromatography (SiO_2, pentane/Et_2O, 9:1) as colourless solid (246 mg, 85%).

^{1}H NMR (500 MHz, $CDCl_3$, TMS): δ (ppm) = 6.64 (dd, *J* = 8.3 Hz, *J* = 8.3 Hz, 1H, CH_{Ar}), 6.68 (s, 1H, CH), 6.74 (dt, *J* = 10.3 Hz, *J* = 2.3 Hz, 1H, CH_{Ar}), 6.81 (dd, *J* = 8.3 Hz, *J* = 2.3 Hz, 1H, CH_{Ar}), 7.11-7.24 (m, 2H, CH_{Ar}), 7.25-7.35 (m, 5H, CH_{Ar}), 7.55-7.58 (m, 2H, CH_{Ar}), 7.59-7.63 (m, 2H, CH_{Ar}).

^{19}F-{^{1}H} NMR (470 MHz, $CDCl_3$, TMS): δ (ppm) = -111.1.

^{13}C-{^{1}H} NMR (126 MHz, $CDCl_3$, TMS): δ (ppm) = 104.2 (d, J_{CF} = 25 Hz, CH), 109.1 (d, J_{CF} = 21.5 Hz, CH), 112.1 (d, J_{CF} = 2.6 Hz, CH), 117.1 (CH), 126.0 (CH), 127.7 (C^{IV}), 128.7 (CH), 128.7 (CH), 128.8 (CH), 129.1 (CH), 130.6 (d, J_{CF} = 9.9 Hz, CH), 134.5 (C^{IV}), 135.6 (C^{IV}), 149.3 (C^{IV}), 157.7 (d, J_{CF} = 10.7 Hz, C^{IV}), 163.7 (d, J_{CF} = 246 Hz, CF).

Data in accordance with the literature.[13]

(*Z*)-(1-(3-chlorophenoxy)ethene-1,2-diyl)dibenzene (6an)
The product was obtained after flash chromatography (SiO_2, pentane/Et_2O, 99:1) as colourless solid (294 mg, 96%).

^{1}H NMR (500 MHz, $CDCl_3$, TMS): δ (ppm) = 6.67 (m, 1H, CH), 6.85-6.94 (m, 2H, CH_{Ar}), 7.01-7.05 (m, 1H, CH_{Ar}), 7.06-7.13 (m, 1H, CH_{Ar}), 7.18-7.34 (m, 6H, CH_{Ar}), 7.54-7.63 (m, 4H, CH_{Ar}).

^{13}C-{^{1}H} NMR (126 MHz, $CDCl_3$, TMS): δ (ppm) = 114.6 (CH), 116.9 (CH), 117.2 (CH), 122.5 (CH), 126.0 (CH), 127.8 (CH), 128.7 (CH), 128.7 (CH), 128.8 (CH), 129.1 (CH), 130.6 (CH), 134.5 (C^{IV}), 135.2 (C^{IV}), 135.5 (C^{IV}), 149.2 (C^{IV}), 157.2 (C^{IV}).

(*Z*)-(1-(o-tolyloxy)ethene-1,2-diyl)dibenzene (6ao)
The product was obtained after flash chromatography (SiO_2, pentane/Et_2O, 9:1) as colourless solid (231 mg, 81%).

^{1}H NMR (500 MHz, $CDCl_3$, TMS): δ (ppm) = 2.51 (s, 3H, CH_3), 6.65 (s, 1H, CH), 6.71 (d, *J* = 8.1 Hz, 1H, CH_{Ar}), 6.84 (dd, *J* = 7.3 Hz, *J* = 7.3 Hz, 1H, CH_{Ar}), 6.91 (dd, *J* = 7.7 Hz, *J* = 7.7 Hz, 1H, CH_{Ar}), 7.16-7.32 (m, 7H, CH_{Ar}), 7.53 (d, *J* = 7.7 Hz, 2H, CH_{Ar}), 7.62 (d, *J* = 7.7 Hz, 2H, CH_{Ar}).

^{13}C-{^{1}H} NMR (126 MHz, $CDCl_3$, TMS): δ (ppm) = 16.7 (CH_3), 114.4 (CH), 116.7 (CH), 121.9 (CH), 126.0 (CH), 126.7 (C^{IV}), 127.0 (CH), 127.4 (CH), 128.5 (CH), 128.6 (CH), 128.7 (C^{IV}), 128.9 (CH), 131.2 (CH), 135.0 (C^{IV}), 136.2 (C^{IV}), 150.0 (C^{IV}), 154.3 (C^{IV}).

Data in accordance with the literature.[10]

(*Z*)-2-((1,2-diphenylvinyl)oxy)-1,1'-biphenyl (6ap)

The product was obtained after flash chromatography (SiO_2, pentane/Et_2O, 9:1) as colourless solid (276 mg, 79%).

^{1}H NMR (300 MHz, $CDCl_3$, TMS): δ (ppm) = 6.60 (s, 1H, CH), 6.88-6.90 (m, 1H, CH_{Ar}), 6.97-7.01 (m, 1H, CH_{Ar}), 7.03-7.09 (m, 1H, CH_{Ar}), 7.14-7.31 (m, 6H, CH_{Ar}), 7.32-7.51 (m, 6H, CH_{Ar}), 7.60 (d, *J* = 7.3 Hz, 2H, CH_{Ar}), 7.70 (d, *J* = 7.3 Hz, 2H, CH_{Ar}).

^{13}C-{^{1}H} NMR (75 MHz, $CDCl_3$, TMS): δ (ppm) = 115.6 (CH), 116.7 (CH), 122.4 (CH), 126.1 (CH), 127.3 (CH), 127.4 (CH), 128.3 (CH), 128.5 (CH), 128.6 (CH), 128.6 (CH), 128.7 (CH), 129.0 (CH), 129.8 (CH), 131.2 (CH), 131.5 (C^{IV}), 135.0 (C^{IV}), 136.0 (C^{IV}), 138.3 (C^{IV}), 150.2 (C^{IV}), 153.1 (C^{IV}).

Data in accordance with the literature.[13]

(*Z*)-(1-(2-allylphenoxy)ethene-1,2-diyl)dibenzene (6aq)

The product was obtained after flash chromatography (SiO_2, pentane/Et_2O, 9:1) as colourless oil (234 mg, 75%).

^{1}H NMR (300 MHz, $CDCl_3$, TMS): δ (ppm) = 3.67-3.71 (m, 2H, C*H*$_2$-CHCH$_2$), 5.10-5.21 (m, 2H, CH$_2$-CHC*H*$_2$), 6.06-6.24 (m, 1H, CH$_2$-C*H*CH$_2$), 6.65 (s, 1H, CH), 6.69-6.75 (m, 1H, CH_{Ar}), 6.82-6.96 (m, 2H, CH_{Ar}), 7.11-7.32 (m, 7H, CH_{Ar}), 7.47-7.65 (m, 4H, CH_{Ar}).

^{13}C-{^{1}H} NMR (75 MHz, $CDCl_3$, TMS): δ (ppm) = 34.3 (CH$_2$-CHCH$_2$), 114.5 (CH), 116.1 (CH$_2$-CH*C*H$_2$), 116.9 (CH), 122.0 (CH), 126.0 (CH), 127.4 (CH), 127.5 (CH), 128.4 (C^{IV}), 128.5 (CH), 128.6 (CH), 128.7 (CH), 129.0 (CH), 130.6 (CH), 134.9 (C^{IV}), 136.1 (C^{IV}), 136.9 (CH$_2$-*C*HCH$_2$), 149.8 (C^{IV}), 153.8 (C^{IV}).

Data in accordance with the literature.[13]

(*Z*)-(1-(2-chlorophenoxy)ethene-1,2-diyl)dibenzene (6ar)

The product was obtained after flash chromatography (SiO_2, pentane/Et_2O, 99:1) as colourless oil (272 mg, 89%).

^{1}H NMR (300 MHz, $CDCl_3$, TMS): δ (ppm) = 6.67 (s, 1H, CH), 6.75-6.84 (m, 2H, CH_{Ar}), 6.85-6.94 (m, 1H, CH_{Ar}), 7.13-7.40 (m, 7H, CH_{Ar}), 7.53-7.60 (m, 2H, CH_{Ar}), 7.60-7.68 (m, 2H, CH_{Ar}).

^{13}C-{^{1}H} NMR (75 MHz, $CDCl_3$, TMS): δ (ppm) = 116.2 (CH), 117.1 (CH), 122.9 (CH), 123.0 (C^{IV}), 125.9 (CH), 127.7 (CH), 127.8 (CH), 128.7 (CH), 128.7 (C^{IV}), 128.8 (CH), 129.1 (CH), 130.6 (CH), 134.5 (C^{IV}), 135.4 (C^{IV}), 149.5 (C^{IV}), 151.7 (C^{IV}).

Data in accordance with the literature.[13]

(*Z*)-(1-(3,5-dimethylphenoxy)ethene-1,2-diyl)dibenzene (6as)

The product was obtained after flash chromatography (SiO_2, pentane/Et_2O, 9:1) as colourless solid (288 mg, 96%).

^{1}H NMR (300 MHz, $CDCl_3$, TMS): δ (ppm) = 2.15 (s, 6H, CH_3), 6.53 (s, 1H, CH_{Ar}), 6.60 (s, 1H, CH), 6.64 (s, 2H, CH_{Ar}) 7.10-7.30 (m, 6H, CH_{Ar}), 7.52-7.59 (m, 2H, CH_{Ar}), 7.59-7.67 (m, 2H, CH_{Ar}).

^{13}C-{^{1}H} NMR (75 MHz, $CDCl_3$, TMS): δ (ppm) = 21.4 (CH_3), 114.1 (CH), 116.7 (CH), 124.0 (CH), 126.1 (CH), 127.4 (CH), 128.4 (CH), 128.6 (CH), 129.0 (CH), 135.0 (C^{IV}), 136.3 (C^{IV}), 139.4 (C^{IV}), 139.4 (C^{IV}), 149.8 (C^{IV}), 156.4 (C^{IV}).

Data in accordance with the literature.[13]

(*Z*)-(1-(2,6-dimethylphenoxy)ethene-1,2-diyl)dibenzene (6at)

The product was obtained after flash chromatography (SiO_2, pentane/Et_2O, 9:1) as colourless solid (138 mg, 46%).

^{1}H NMR (500 MHz, $CDCl_3$, TMS): δ (ppm) = 2.30 (s, 6H, CH_3), 5.99 (s, 1H, CH), 6.78-6.83 (m, 1H, CH_{Ar}), 6.85-6.90 (m, 2H, CH_{Ar}), 7.16-7.24 (m, 4H, CH_{Ar}), 7.31-7.38 (m, 4H, CH_{Ar}), 7.76-7.82 (m, 2H, CH_{Ar})**.**

^{13}C-{^{1}H} NMR (126 MHz, $CDCl_3$, TMS): δ (ppm) = 17.4 (CH_3), 111.5 (CH), 123.7 (CH), 126.6 (C^{IV}), 127.2 (CN), 128.1 (CH), 128.4 (CH), 128.5 (CH), 129.0 (CH), 129.3 (CH), 129.4 (CH) 136.3 (C^{IV}), 136.6 (C^{IV}), 152.7 (C^{IV}), 154.6 (C^{IV}).

The data was in accordance with the literature.[13]

(*Z*)-2-((1,2-diphenylvinyl)oxy)naphthalene (6au)

The product was obtained after flash chromatography (SiO_2, pentane/Et_2O, 9:1) as colourless solid (260 mg, 81%).

^{1}H NMR (300 MHz, $CDCl_3$, TMS): δ (ppm) = 6.74 (s, 1H, CH), 7.12-7.42 (m, 10H, CH_{Ar}), 7.54-7.82 (m, 7H, CH_{Ar}).

^{13}C-{^{1}H} NMR (75 MHz, $CDCl_3$, TMS): δ (ppm) = 111.2 (CH), 117.1 (CH), 118.3 (CH), 124.3 (CH), 126.2 (CH), 126.5 (CH), 127.1 (CH), 127.6 (CH), 127.8 (CH), 128.6 (CH), 128.7 (CH), 128.8 (CH), 129.1 (CH), 129.7 (C^{IV}), 130.0 (CH), 134.5 (C^{IV}), 134.8 (C^{IV}), 136.0 (C^{IV}), 149.7 (C^{IV}), 154.3 (C^{IV}).

Data in accordance with the literature.[13]

(*Z*)-(hex-3-en-3-yloxy)benzene (6ba)

The product was obtained after flash chromatography (SiO_2, pentane/Et_2O, 99:1) as colourless oil (159 mg, 90%).

^{1}H NMR (300 MHz, $CDCl_3$, TMS): δ (ppm) = 0.94 (t, *J* = 7.5 Hz, 3H, CH_2CH_3), 1.04 (t, *J* = 7.5 Hz, 3H, CH_2CH_3), 1.95-2.08 (m, 2H, CH_2CH_3), 2.08-2.19 (m, 2H, CH_2CH_3), 5.01 (m, 1H, CH), 6.87-7.00 (m, 3H, CH_{Ar}), 7.21-7.32 (m, 2H, CH_{Ar}).

^{13}C-{^{1}H} NMR (75 MHz, $CDCl_3$, TMS): δ (ppm) = 11.7 (CH_2CH_3), 14.2 (CH_2CH_3), 18.7 (CH_2CH_3), 25.5 (CH_2CH_3), 116.0 (CH), 116.8 (CH), 121.4 (CH), 129.6 (CH), 151.8 (C^{IV}), 157.0 (C^{IV}).

Data in accordance with the literature.[10]

(*Z*)-(pent-2-en-2-yloxy)benzene (6ca) and (*Z*)-(pent-2-en-3-yloxy)benzene (6'ca) (6ca/6'ca = 60/40)

The product was obtained after flash chromatography (SiO_2, pentane/Et_2O, 99:1) as colourless oil (112 mg, 69%).

^{1}H NMR (400 MHz, $CDCl_3$, TMS): δ (ppm) = 0.85 (t, *J* = 7.5 Hz, 3H, CH_2CH_3), 0.95 (t, *J* = 7.5 Hz, 3H, CH_2CH_3'), 1.46 (dt, *J* = 6.8 Hz, *J* = 1.4 Hz, 3H, $CHCH_3$'), 1.68-1.62 (m, 3H, $CHCH_3$), 1.89-2.00 (m, 2H, CH_2CH_3), 2.01-2.09 (m, 2H, CH_2CH_3'), 4.87-4.93 (m, 1H, CH), 4.95-5.03 (m, 1H, CH'), 6.79-6.91 (m, 6H, CH_{Ar} and CH_{Ar}'), 7.14-7.22 (m, 4H, CH_{Ar} and CH_{Ar}').

^{13}C-{^{1}H} NMR (101 MHz, $CDCl_3$, TMS): δ (ppm) = 10.7 (CH_3'), 11.6 (CH_3'), 14.2 (CH_3), 18.5 (CH_3), 18.8 (CH_2), 25.7 (CH_2'), 109.2 (CH'), 115.9 (CH), 116.1 (CH), 118.5 (CH'), 121.4 (CH'), 121.6 (CH), 129.6 (CH'), 129.6 (CH), 146.5 (C^{IV}), 153.0 (C^{IV}'), 156.7 (C^{IV}), 156.8 (C^{IV}').

(*Z*)-(hex-2-en-2-yloxy)benzene (6da) and (*Z*)-(hex-2-en-3-yloxy)benzene (6'da) (6da/6'da = 65/35)

The product was obtained after flash chromatography (SiO_2, pentane/Et_2O, 99:1) as colourless oil (133 mg, 76%).

^{1}H NMR (400 MHz, $CDCl_3$, TMS): δ (ppm) = 0.76-0.85 (m, 6H, $CH_2CH_2CH_3$ and $CH_2CH_2CH_3$'), 1.22-1.33 (m, 2H, $CH_2CH_2CH_3$), 1.34-1.43 (m, 2H, $CH_2CH_2CH_3$'), 1.45-1.49 (m, ^{3}H, $CHCH_3$'), 1.70-1.74 (m, 3H, $CHCH_3$), 1.87-1.96 (m, 2H, $CH_2CH_2CH_3$), 1.97-2.04 (m, 2H, $CH_2CH_2CH_3$'), 4.89-4.95 (m, 1H, CH), 4.96-5.03 (m, 1H, CH'), 6.81-6.92 (m, 6H, CH_{Ar} and CH_{Ar}'), 7.15-7.22 (m, 4H, CH_{Ar} and CH_{Ar}').

^{13}C-{^{1}H} NMR (101 MHz, $CDCl_3$, TMS): δ (ppm) = 10.7 (CH_3'), 13.8 (CH_3'), 14.0 (CH_3), 18.5 (CH_3), 20.2 (CH_2'), 22.8 (CH_2), 27.4 (CH_2), 34.6 (CH_2'), 110.4(CH'), 115.9(CH), 116.2(CH),

116.7(CH'), 121.4(CH), 121.6 (CH'), 129.6 (CH), 147.0 (C^{IV}), 151.4 ($C^{IV'}$), 156.6 (C^{IV}), 156.8 ($C^{IV'}$).

(*Z*)-(1-phenoxyprop-1-en-1-yl)benzene (6ea) and (*Z*)-(2-phenoxyprop-1-en-1-yl)benzene (6'ea) (6ea/6'ea = 42/58)

The product was obtained after flash chromatography (SiO_2, pentane/Et_2O, 99:1) as colourless oil (167 mg, 80%).

^{1}H NMR (500 MHz, $CDCl_3$, TMS): δ (ppm) = 1.70-1.77 (m, 3H, CH_3), 1.91-1.97 (m, 3H, CH_3'), 5.82-5.88 (m, 1H, CH'), 5.88-5.96 (m, 1H, CH), 6.85-7.33 (m, 16H, CH_{Ar} and CH'_{Ar}), 7.42-7.49 (m, 2H, CH_{Ar}), 7.49-7.56 (m, 2H, CH'_{Ar}).

^{13}C-{^{1}H} NMR (126 MHz, $CDCl_3$, TMS): δ (ppm) = 11.6 (CH_3), 19.7 (CH_3'), 112.6 (CH), 115.0 (CH'), 115.4 (CH), 117.7 (CH'), 121.5 (CH), 122.8 (CH'), 125.2 (CH'), 126.6 (CH), 127.9 (CH), 128.2 (CH'), 128.4 (CH'), 128.5 (CH), 129.7 (CH), 129.7 (CH'), 135.3 (C^{IV}'), 135.6 (C^{IV}), 149.3 (C^{IV}'), 149.7 (C^{IV}), 155.4 (C^{IV}'), 157.4 (C^{IV}).

Data in accordance with the literature.[13]

(*Z*)-(1-phenoxybut-1-en-1-yl)benzene (6fa) and (*Z*)-(2-phenoxybut-1-en-1-yl)benzene (6'fa) (6fa/6'fa = 55/45)

The product was obtained after flash chromatography (SiO_2, pentane/Et_2O, 99:1) as colourless oil (202 mg, 90%).

^{1}H NMR (300 MHz, $CDCl_3$, TMS): δ (ppm) = 0.96-1.07 (m, 3H, CH_3), 1.07-1.17 (m, 3H, CH_3'), 2.12-2.36 (m, 4H, CH_2 and CH_2'), 5.76-5.89 (m, 1H, CH), 5.89-5.97 (m, 1H, CH'), 6.83-7.35 (m, 16H, CH_{Ar} and CH'_{Ar}), 7.40-7.58 (m, 4H, CH_{Ar} and CH'_{Ar}).

^{13}C-{^{1}H} NMR (75 MHz, $CDCl_3$, TMS): δ (ppm) = 12.0 (CH_3'), 14.0 (CH_3), 19.5 (CH_3), 26.4 (CH_3'), 114.1 (CH'), 115.5 (CH), 117.3 (CH'), 119.9 (CH), 121.4 (CH), 122.5 (CH'), 125.4 (CH), 126.7 (CH'), 127.9 (CH'), 128.4 (CH), 128.5 (CH'), 128.5 (CH), 129.6 (CH), 129.7 (CH'), 135.3 (C^{IV}'), 135.6 (C^{IV}), 148.4 (C^{IV}'), 154.4 (C^{IV}), 155.6 (C^{IV}'), 157.7 (C^{IV}).

Data in accordance with the literature.[13]

(*Z*)-(1-phenoxyhex-1-en-1-yl)benzene (6ga) and (*Z*)-(2-phenoxyhex-1-en-1-yl)benzene (6'ga) (6ga/6'ga = 68/32)

The product was obtained after flash chromatography (SiO_2, pentane/Et_2O, 99:1) as colourless oil (195 mg, 77%).

^{1}H NMR (300 MHz, $CDCl_3$, TMS): δ (ppm) = 0.83-0.91 (m, 6H, CH_3 and CH_3'), 1.28-1.56 (m, 8H, CH_2 and CH_2'), 2.20 (dt, *J* = 7.4 Hz, *J* = 7.4 Hz, 2H, CHC*H*$_2$), 2.27 (t, *J* = 7.4 Hz, 2H,

CHCH_2'), 5.86 (t, J = 7.4 Hz, 1H, CH), 5.92 (s, 1H, CH'), 6.88-7.31 (m, 16H, CH_{Ar} and CH'_{Ar}), 7.45-7.50 (m, 2H, CH_{Ar}), 7.50-7.54 (m, 2H, CH_{Ar}').

^{13}C-{^{1}H} NMR (75 MHz, $CDCl_3$, TMS): δ (ppm) = 14.0 (CH_3'), 14.1 (CH_3), 22.2 (CH_2'), 22.6 (CH_2), 25.7 (CH_2), 29.4 (CH_2'), 31.6 (CH_2), 32.9 (CH_2'), 115.1 (CH'), 115.6 (CH), 117.3 (CH'), 118.5 (CH), 121.4 (CH), 122.4 (CH'), 125.3 (CH), 126.7 (CH'), 127.9 (CH'), 128.4 (CH), 128.5 (CH'), 128.5 (CH), 129.6 (CH), 129.7 (CH'), 135.3 (C^{IV}'), 135.6 (C^{IV}), 148.8 (C^{IV}), 153.0 (C^{IV}'), 155.6 (C^{IV}'), 157.6 (C^{IV}).

Data in accordance with the literature.[10]

(*Z*)-2-(1-phenoxyhex-1-en-1-yl)thiophene (6ha)

The product was obtained after flash chromatography (SiO_2, pentane/Et_2O, 99:1) as pale yellow oil (83 mg, 32%).

^{1}H NMR (400 MHz, $CDCl_3$, TMS): δ (ppm) = 0.83-0.90 (m, 3H, CH_3), 1.26-1.44 (m, 4H, CH_2), 2.10-2.20 (m, 2H, CHCH_2), 5.72-5.79 (m, 1H, CH), 6.84-6.90 (m, 1H, CH_{Ar}), 6.91-7.03 (m, 4H, CH_{Ar}) 7.08-7.13 (m, 1H, CH_{Ar}), 7.21-7.28 (m, 2H, CH_{Ar}).

^{13}C-{^{1}H} NMR (101 MHz, $CDCl_3$, TMS): δ (ppm) = 14.0 (CH_3), 22.5 (CH_2), 25.6 (CH_2), 31.4 (CH_2), 115.4 (CH), 118.0 (CH), 121.7 (CH), 124.2 (CH), 124.5 (CH), 127.5 (CH), 129.6 (CH), 139.9 (C^{IV}), 144.3 (C^{IV}), 157.5 (C^{IV}).

(*Z*)-2-(2-phenoxyhex-1-en-1-yl)thiophene (6'ha)

The product was obtained after flash chromatography (SiO_2, pentane/Et_2O, 99:1) as dark orange oil (99 mg, 38%).

^{1}H NMR (400 MHz, $CDCl_3$, TMS): δ (ppm) = 0.84-0.92 (m, 3H, CH_3), 1.27-1.40 (m, 2H, CH_2), 1.45-1.56 (m, 2H, CH_2), 2.23-2.31 (m, 2H, CHCH_2), 6.27 (s, 1H, CH), 6.89-7.13 (m, 6H, CH_{Ar}), 7.26-7.34 (m, 2H, CH_{Ar}).

^{13}C-{^{1}H} NMR (101 MHz, $CDCl_3$, TMS): δ (ppm) = 13.9 (CH_3), 22.1 (CH_2), 29.2 (CH_2), 31.8 (CH_2), 109.7 (CH), 117.2 (CH), 122.6 (CH), 125.1 (CH), 125.6 (CH), 126.1 (CH), 129.6 (CH), 137.7 (C^{IV}), 151.2 (C^{IV}), 155.0 (C^{IV}).

(*Z*)-2-(1-phenoxy-2-phenylvinyl)thiophene (6ia) and (Z)-2-(2-phenoxy-2-phenylvinyl)thiophene (6'ia) (6ia/6'ia = 19/81)

The product was obtained after flash chromatography (SiO_2, pentane/Et_2O, 99:1) as pale yellow solid (180 mg, 65%).

^{1}H NMR (500 MHz, $CDCl_3$, TMS): δ (ppm) = 6.63 (s, 1H, CH), 6.89-7.11 (m, 10H, CH' and CH_{Ar} and CH'_{Ar}), 7.14-7.33 (m, 14H, CH_{Ar} and CH'_{Ar}), 7.52-7.57 (m, 2H, CH_{Ar}'), 7.57-7.60 (m, 2H, CH_{Ar}).

^{13}C-{^{1}H} NMR (126 MHz, $CDCl_3$, TMS): δ (ppm) = 111.2 (CH'), 116.0 (CH), 116.1 (CH), 116.2 (CH'), 122.3 (CH'), 122.4 (CH), 125.6 (CH), 125.7 (CH), 125.7 (CH'), 126.6 (CH'), 126.9 (CH'), 127.6 (CH), 127.8 (CH), 127.8 (CH'), 128.4 (CH'), 128.7 (CH), 128.8 (CH'), 129.0 (CH), 129.7 (CH'), 129.8 (CH), 134.4 (C^{IV}), 134.9 (C^{IV}'), 137.6 (C^{IV}'), 140.2 (C^{IV}), 144.8 (C^{IV}), 147.5 (C^{IV}'), 156.0 (C^{IV}'), 156.4 (C^{IV}).

(*Z*)-1-(1-phenoxy-2-phenylvinyl)naphthalene (6ja) and (Z)-1-(2-phenoxy-2-phenylvinyl) naphthalene (6'ja) (6ja/6'ja = 50/50)

The product was obtained after flash chromatography (SiO_2, pentane/Et_2O, 99:1) as colourless oil (200 mg, 62%).

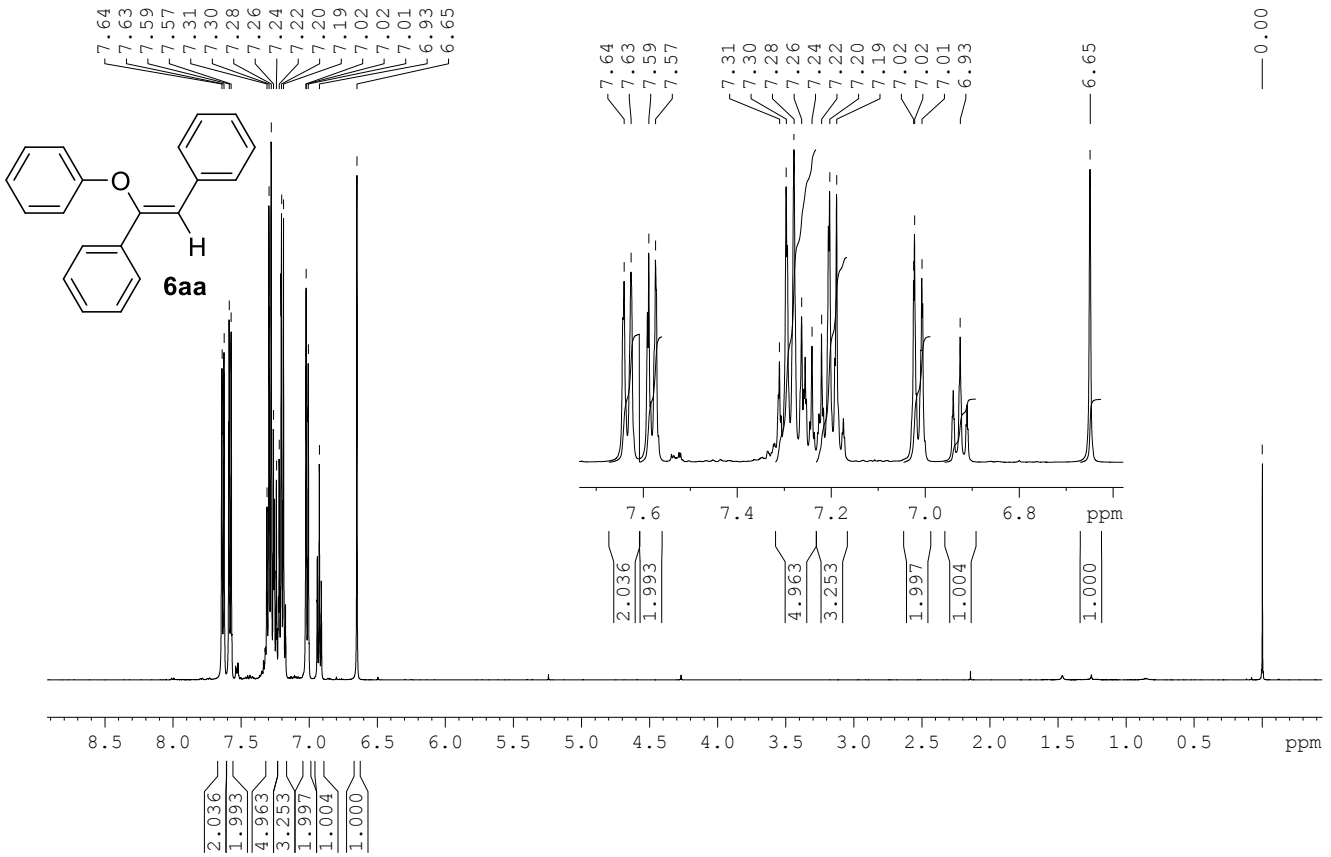
^{1}H NMR (500 MHz, $CDCl_3$, TMS): δ (ppm) = 6.35 (s, 1H, CH), 6.76-6.85 (m, 2H, CH_{Ar} and CH_{Ar}), 6.93-6.98 (m, 2H, CH_{Ar}), 6.99-7.06 (m, 4H, CH and CH_{Ar}), 7.08-7.13 (m, 2H, CH_{Ar}), 7.18-7.34 (m, 9H, CH_{Ar} and CH_{Ar}), 7.37-7.51 (m, 4H, CH_{Ar} and CH_{Ar}), 7.60-7.74 (m, 8H, CH_{Ar} and CH_{Ar}), 7.76 (d, *J* = 7.9 Hz, 1H, CH_{Ar}), 7.87 (d, *J* = 7.2 Hz, 1H, CH_{Ar}), 8.14 (d, *J* = 8.4 Hz, 1H, CH'_{Ar}), 8.56 (d, *J* = 8.5 Hz, 1H, CH_{Ar}).

^{13}C-{^{1}H} NMR (126 MHz, $CDCl_3$, TMS): δ (ppm) = 113.3 (CH), 116.5 (CH), 117.7 (CH), 119.9 (CH), 121.9 (CH), 122.5 (CH), 124.1 (CH), 125.1 (CH), 125.7 (CH), 125.7 (CH), 125.8 (CH), 126.0 (CH), 126.1 (CH), 126.3 (CH), 126.6 (CH), 126.7 (CH), 127.4 (CH), 127.9 (CH), 128.1 (CH), 128.5 (CH), 128.7 (CH), 128.8 (CH), 128.9 (CH), 129.3 (CH), 129.4 (CH), 129.6 (CH), 131.0 (C^{IV}), 131.3 (C^{IV}), 131.9 (C^{IV}), 133.7 (C^{IV}), 133.8 (C^{IV}), 134.2 (C^{IV}), 135.3 (C^{IV}), 136.2 (C^{IV}), 150.4 (C^{IV}), 150.9 (C^{IV}), 155.9 (C^{IV}), 157.1 (C^{IV}).

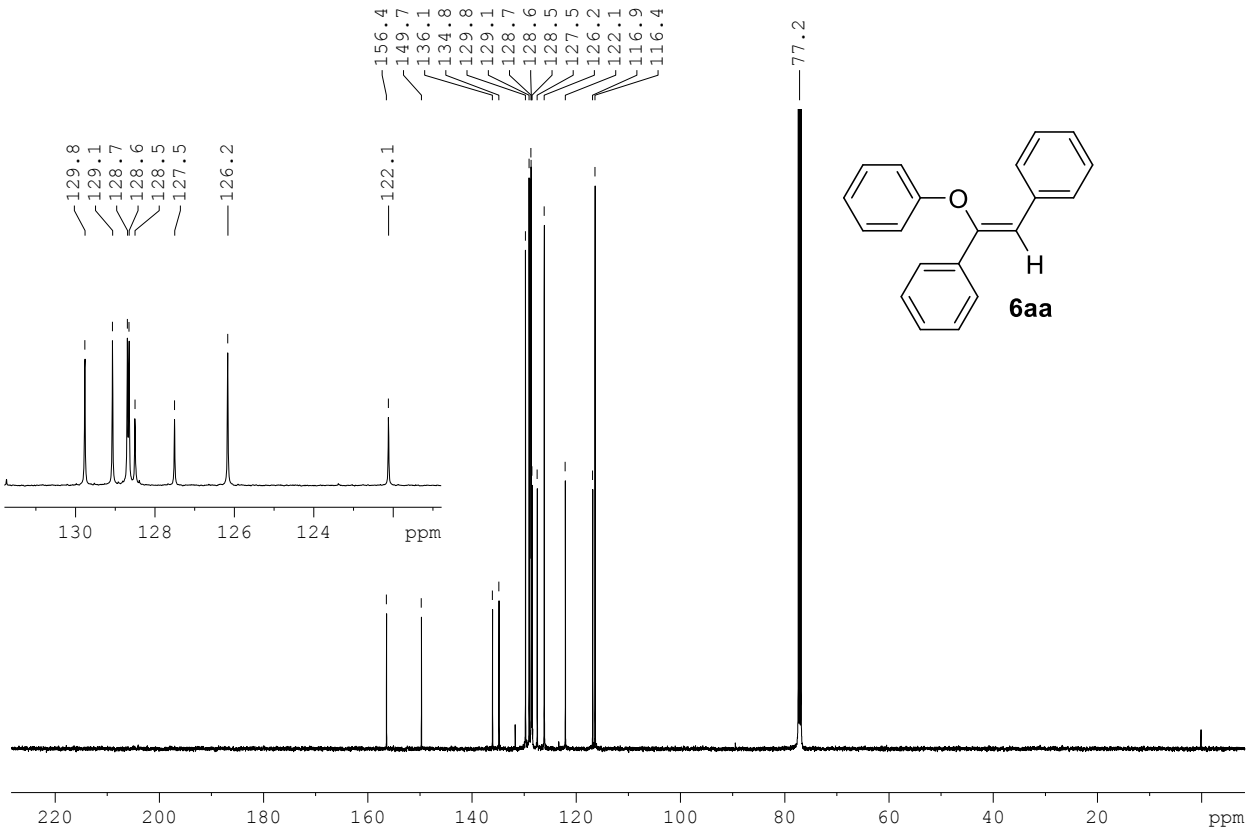
Data in accordance with the literature.[13]

NMR Spectra of Products

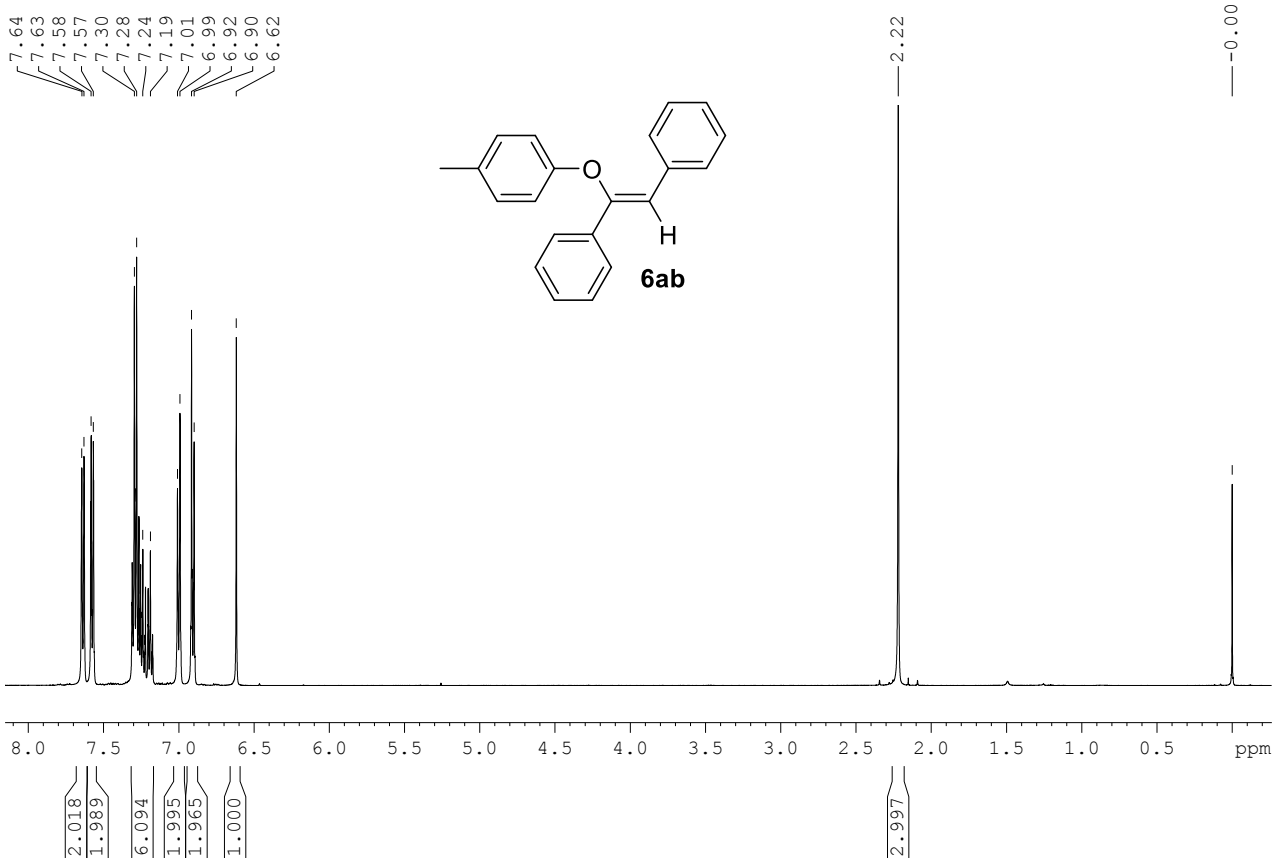
^{1}H NMR ($CDCl_3$) of 6aa



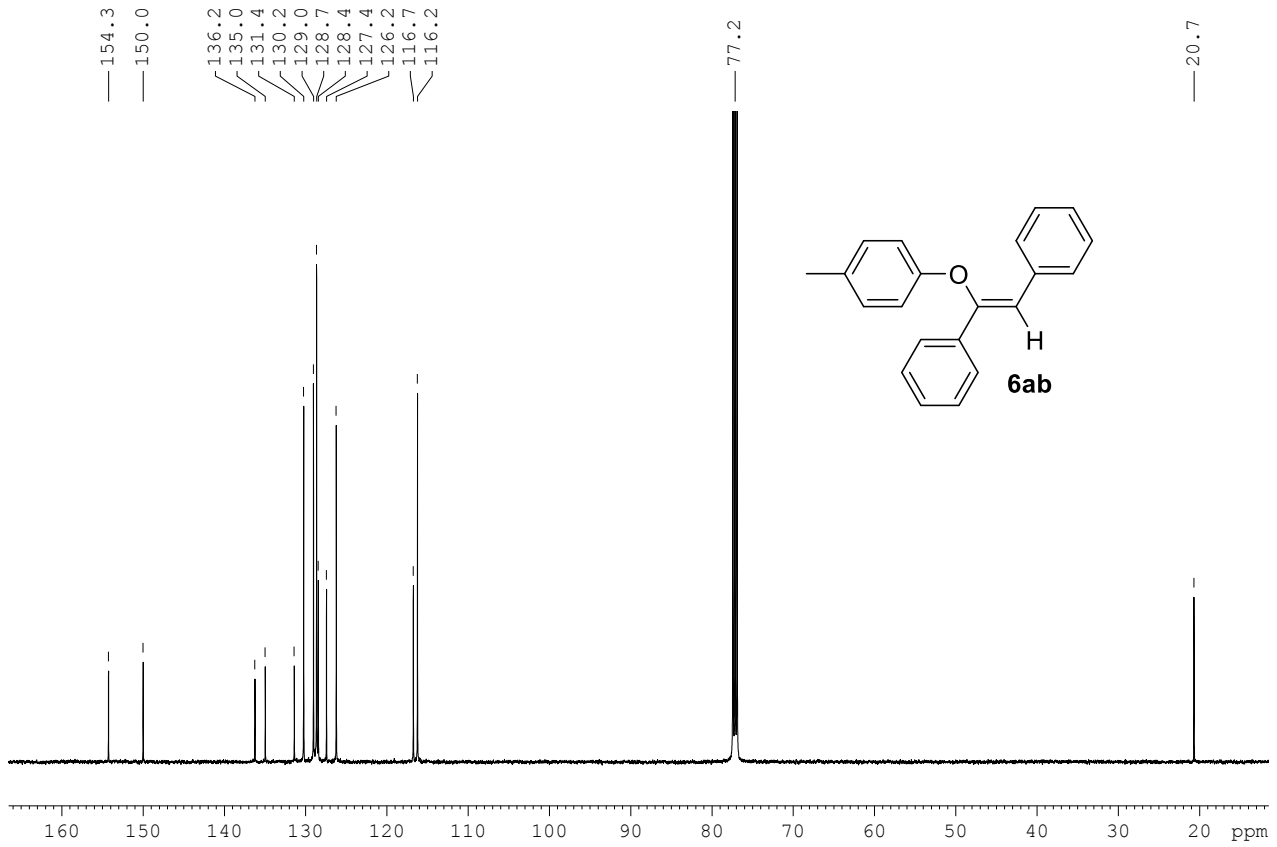
^{13}C-{^{1}H} NMR ($CDCl_3$) of 6aa



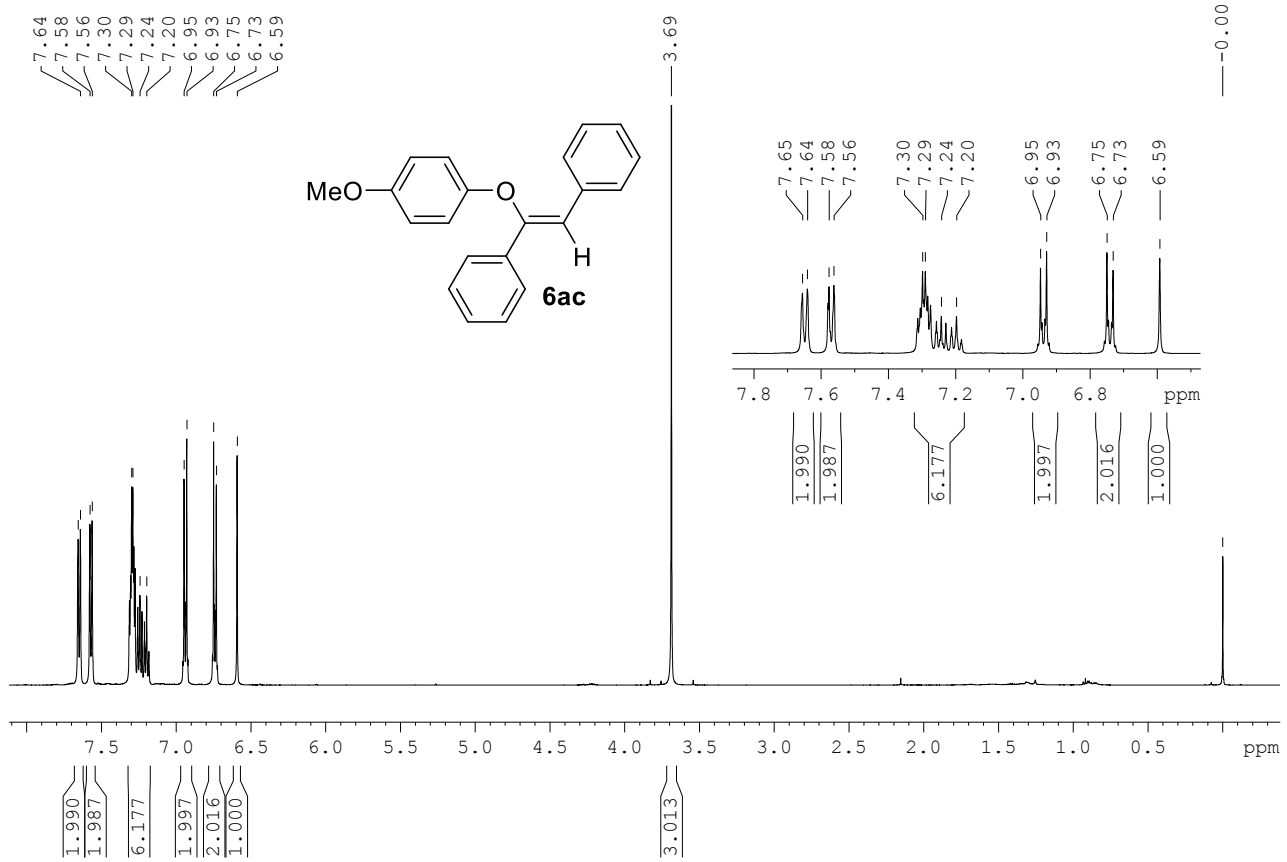
^{1}H NMR ($CDCl_3$) of 6ab



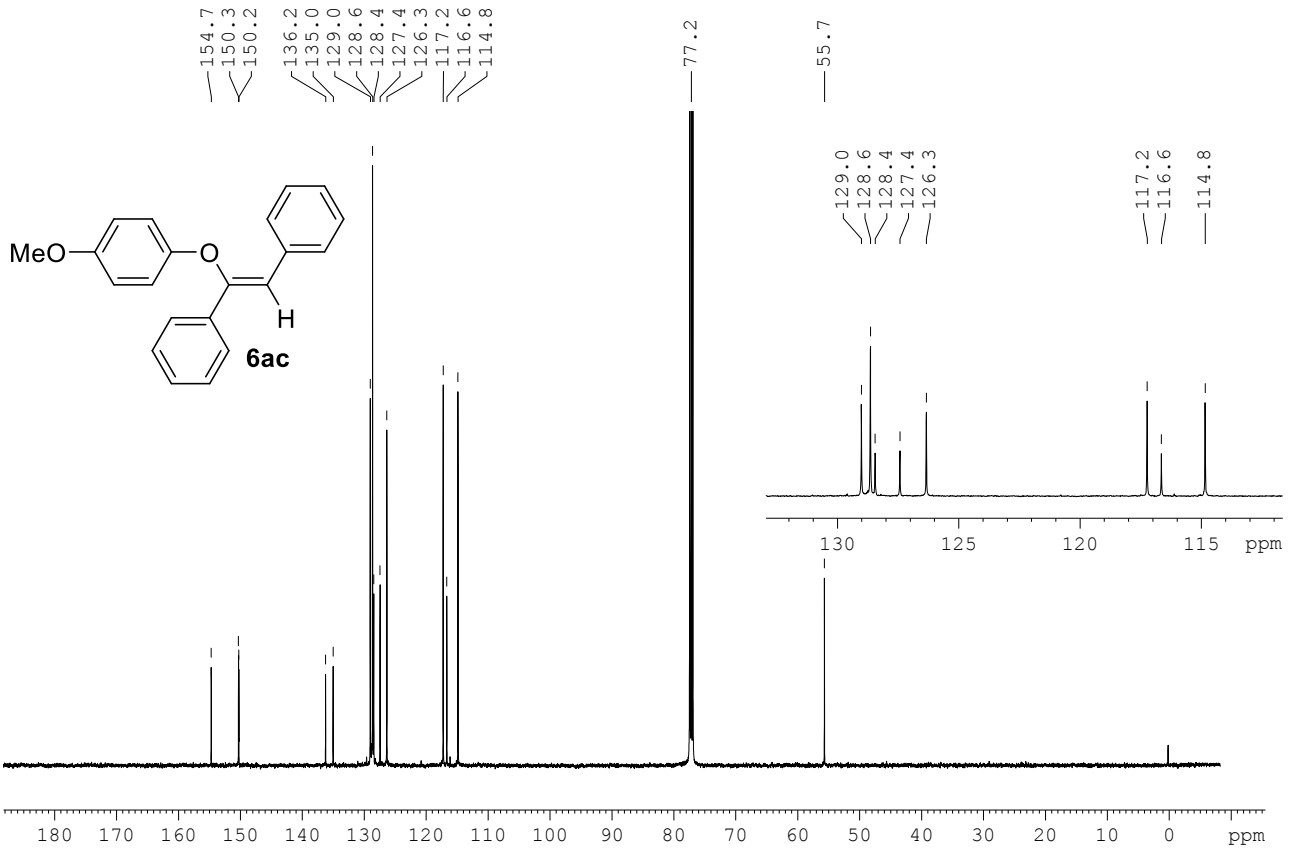
^{13}C-{^{1}H} NMR ($CDCl_3$) of 6ab



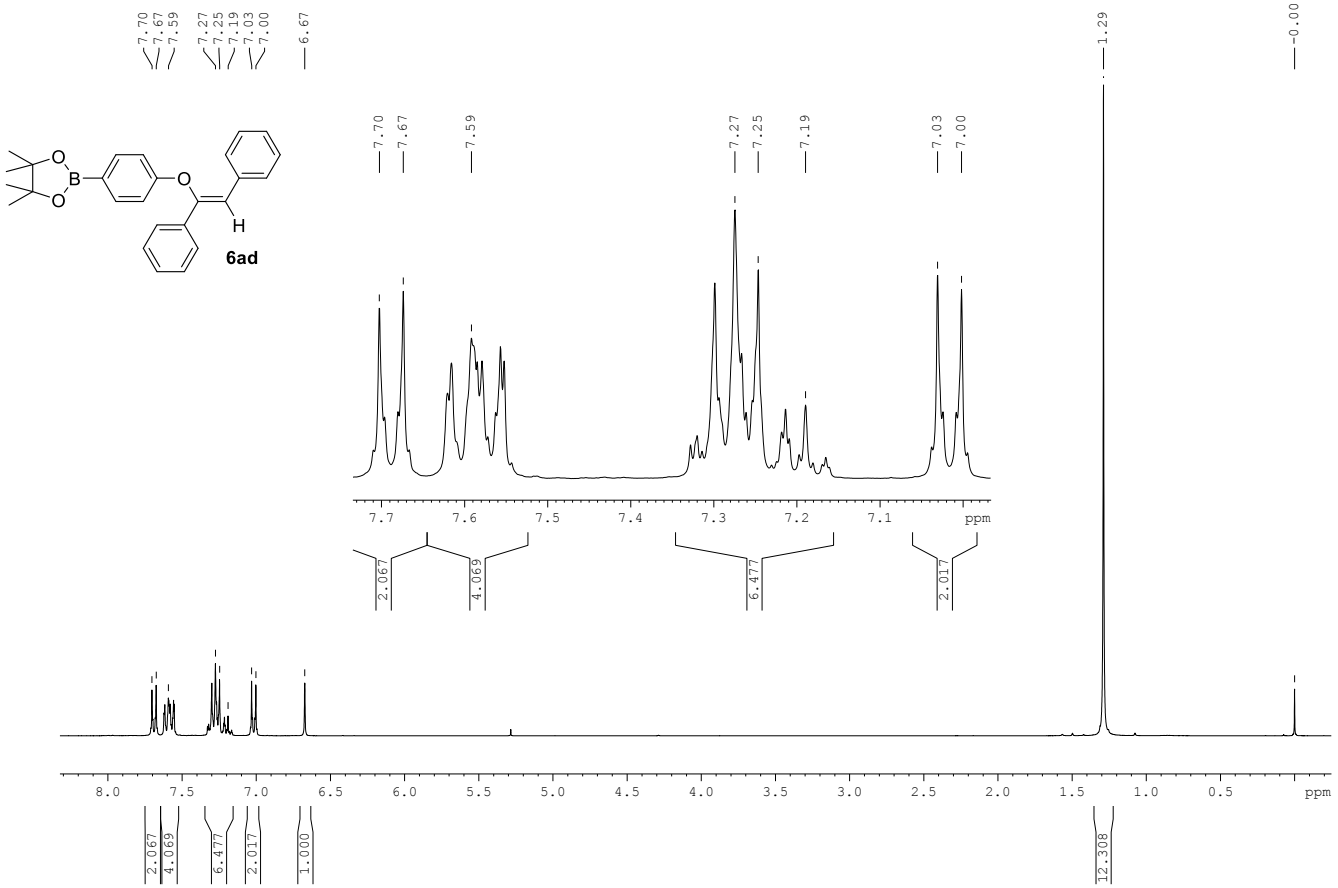
^{1}H NMR ($CDCl_3$) of 6ac



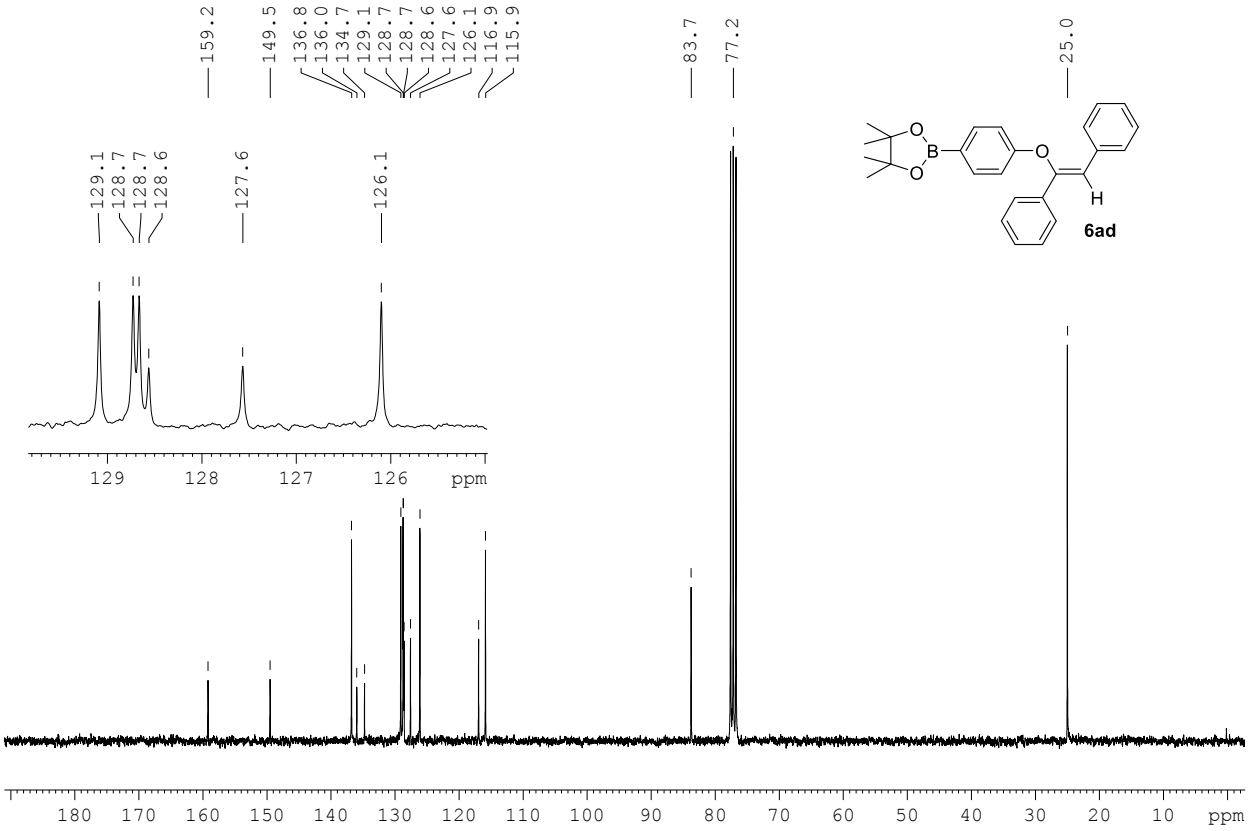
^{13}C-{^{1}H} NMR ($CDCl_3$) of 6ac



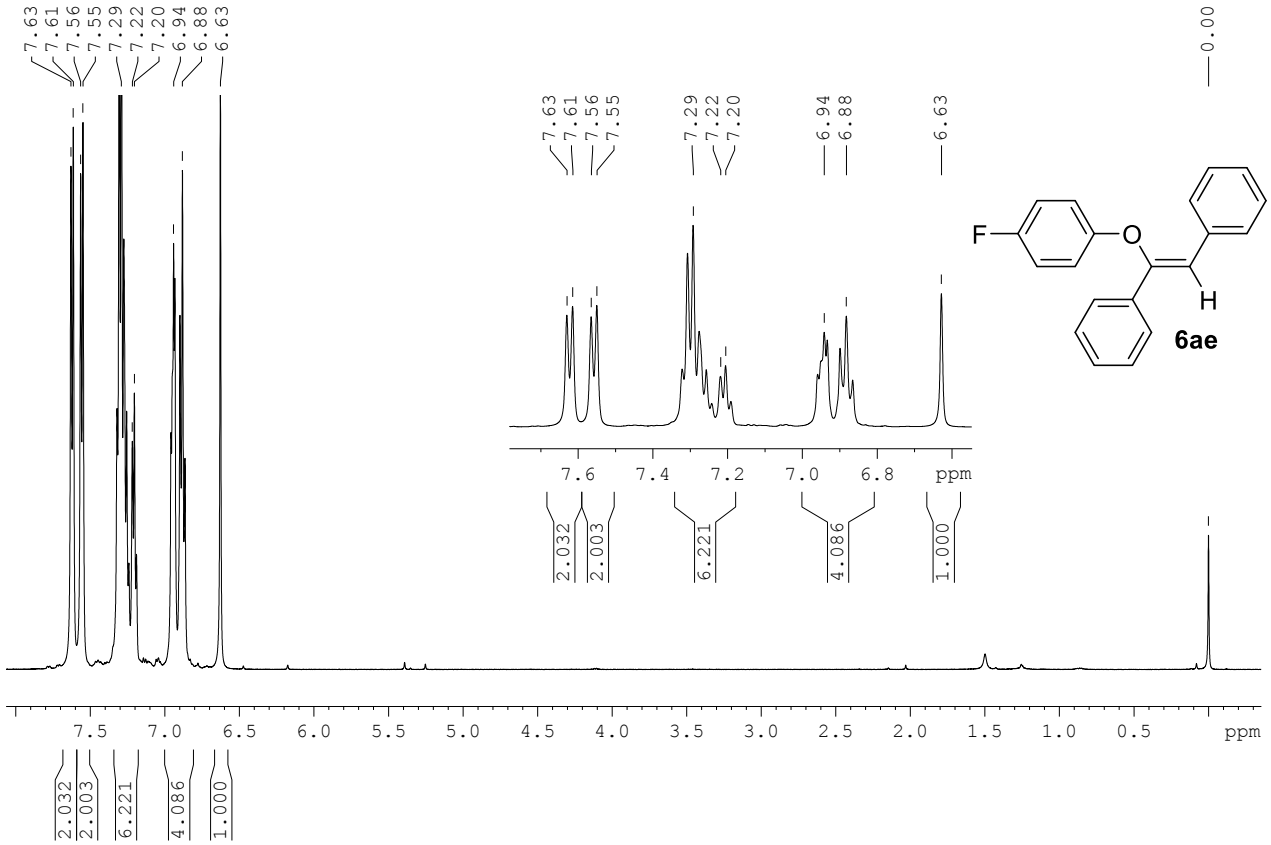
^{1}H NMR ($CDCl_3$) of 6ad



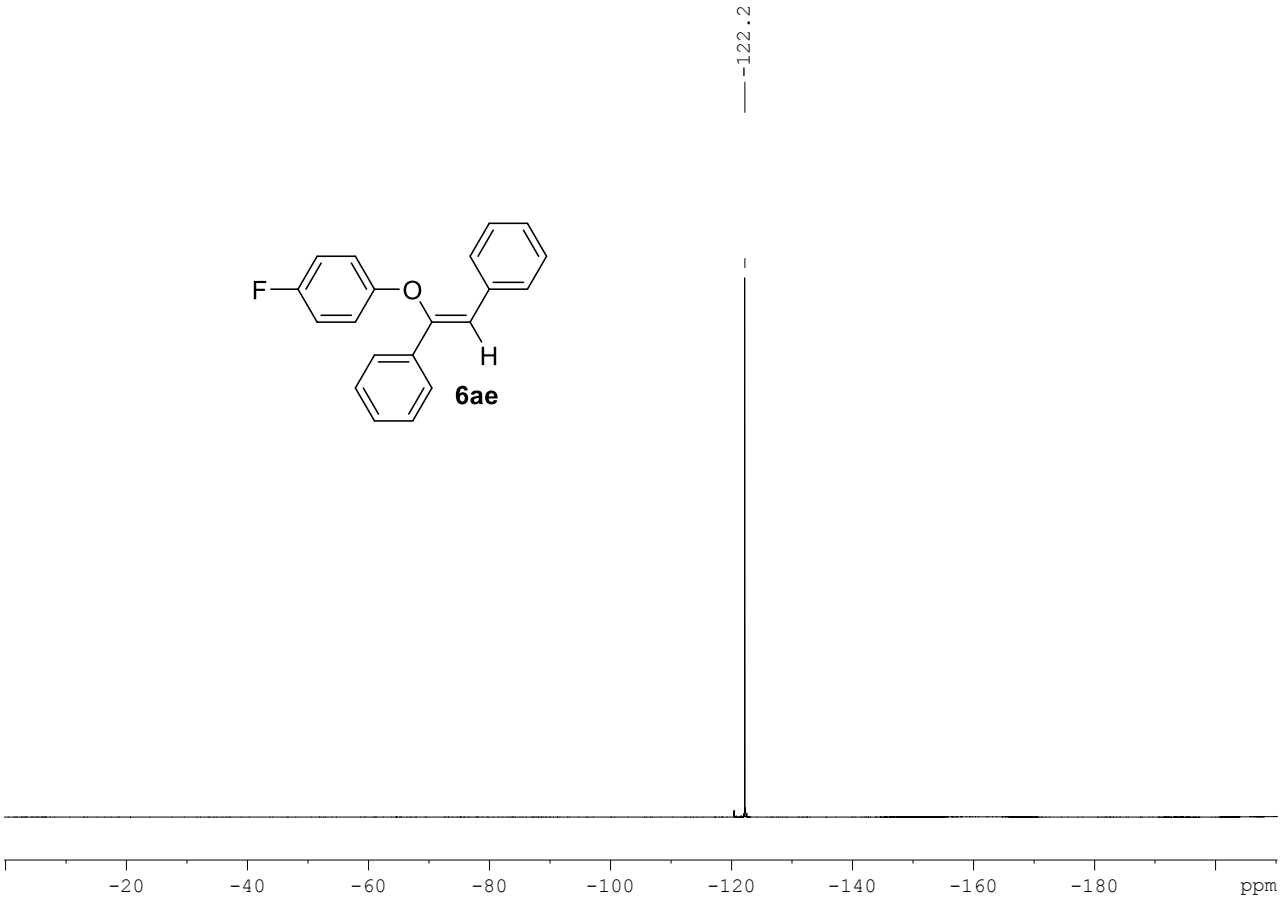
^{13}C-{^{1}H} NMR ($CDCl_3$) of 6ad



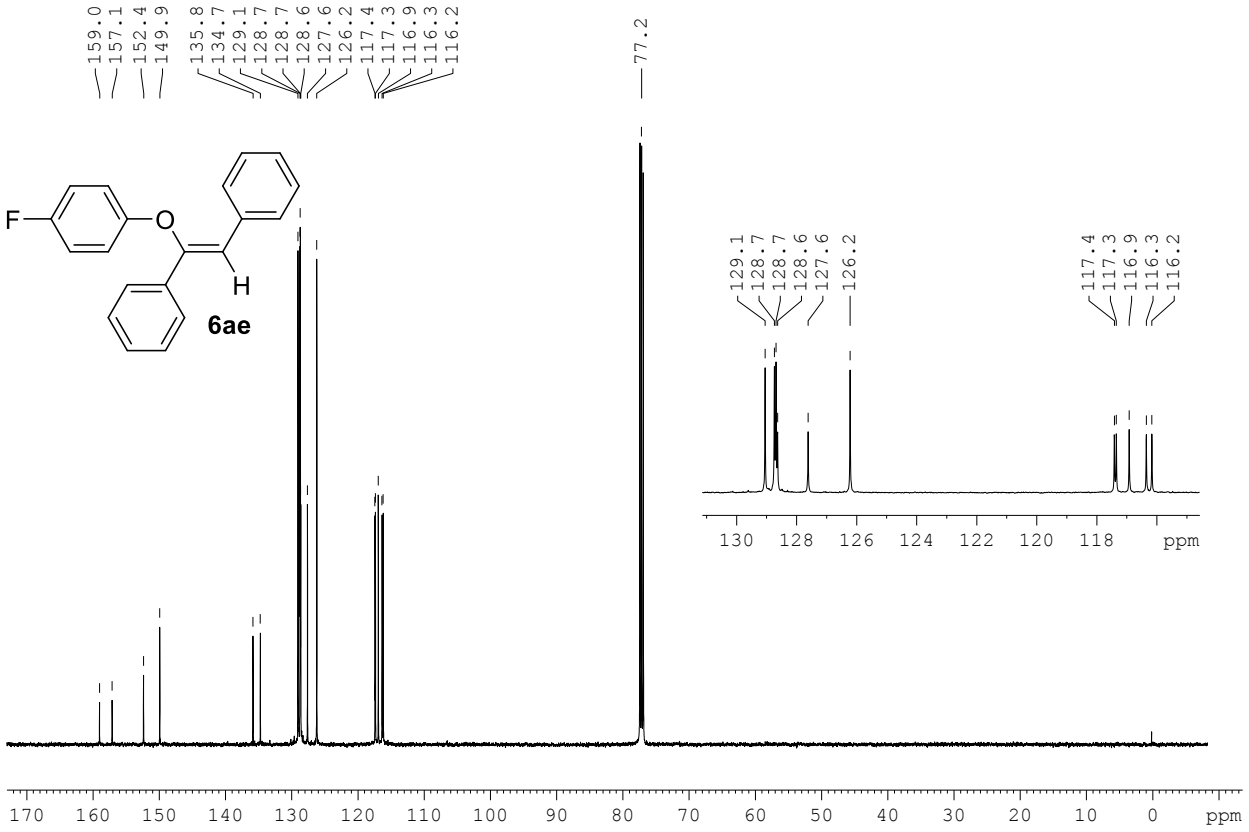
^{1}H NMR ($CDCl_3$) of 6ae



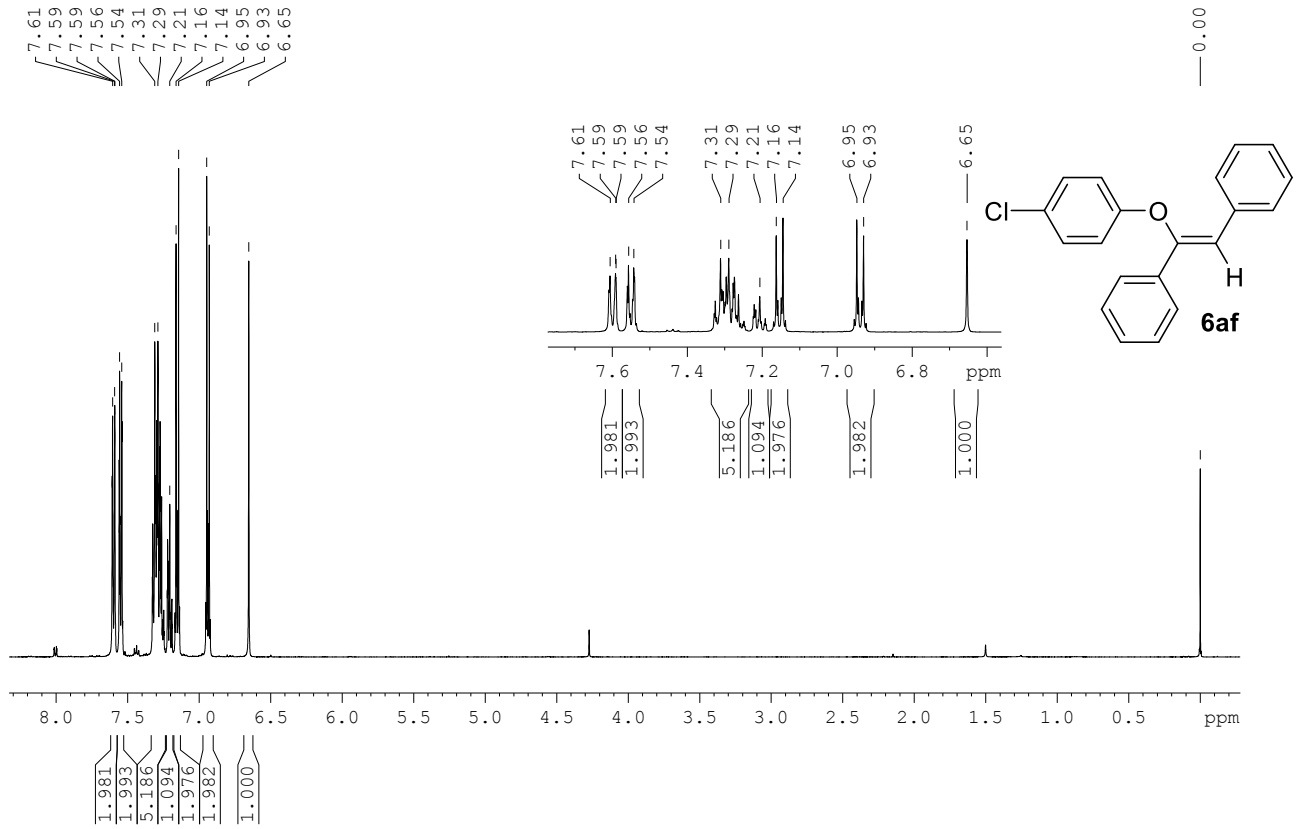
^{19}F-{^{1}H} NMR ($CDCl_3$) of 6ae



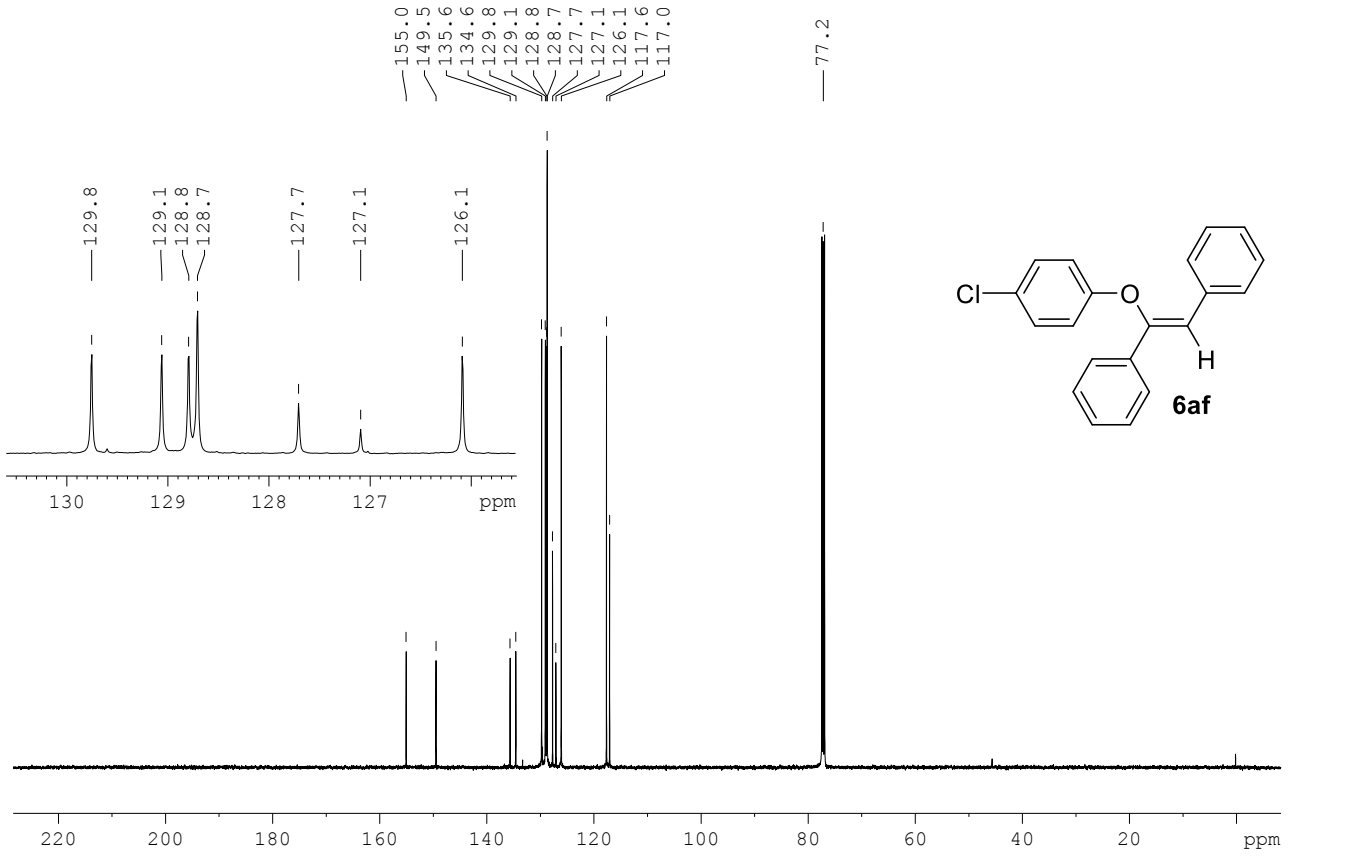
^{13}C-{^{1}H} NMR ($CDCl_3$) of 6ae



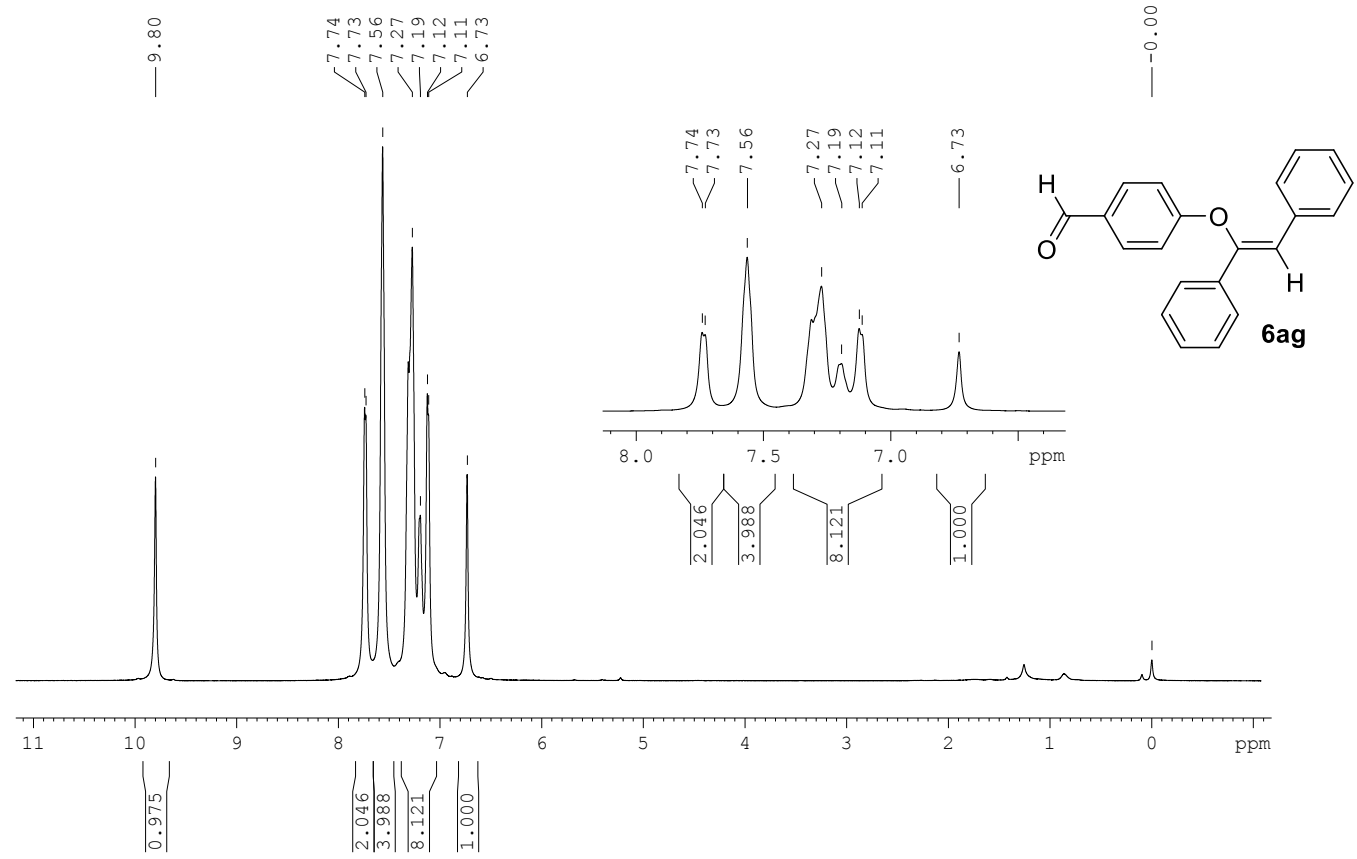
^{1}H NMR ($CDCl_3$) of 6af



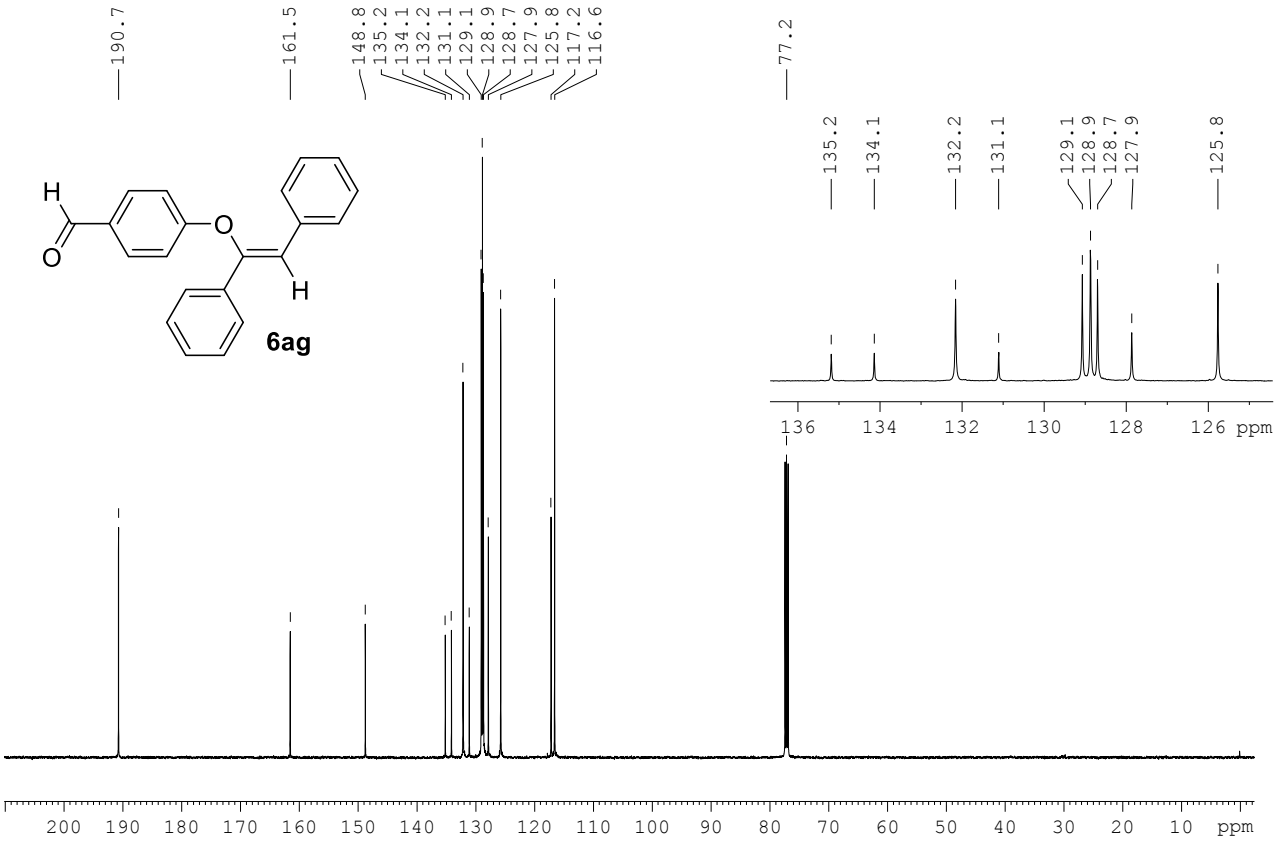
^{13}C-{^{1}H} NMR ($CDCl_3$) of 6af



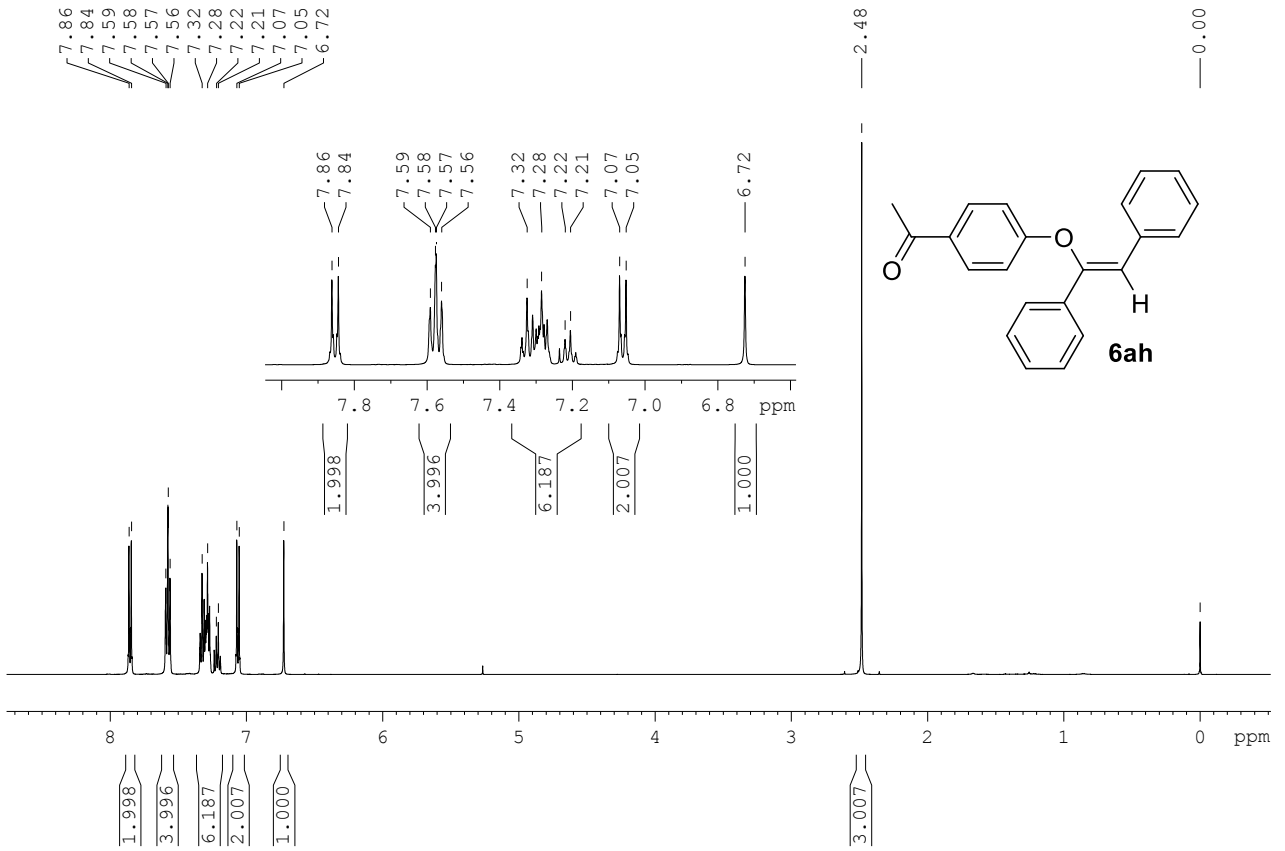
^{1}H NMR ($CDCl_3$) of 6ag



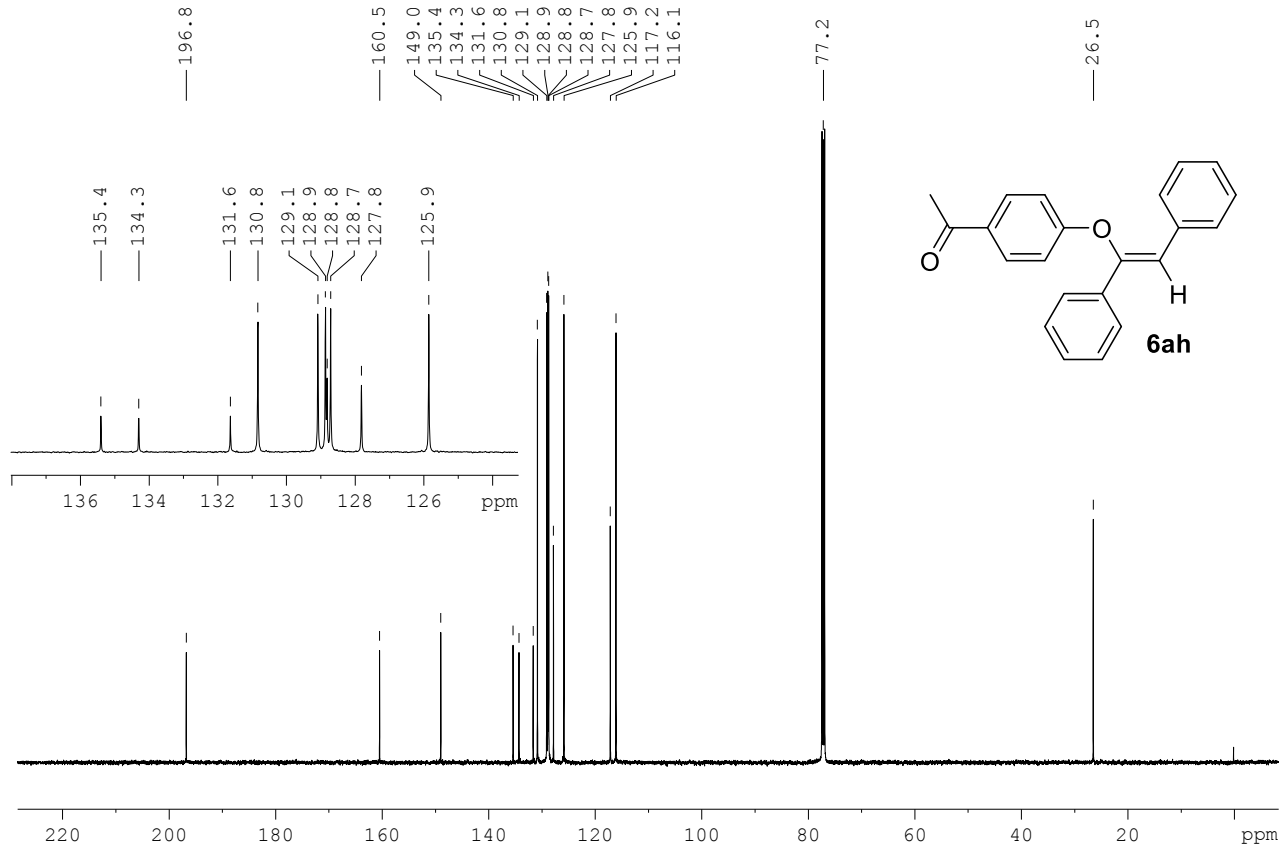
^{13}C-{^{1}H} NMR ($CDCl_3$) of 6ag



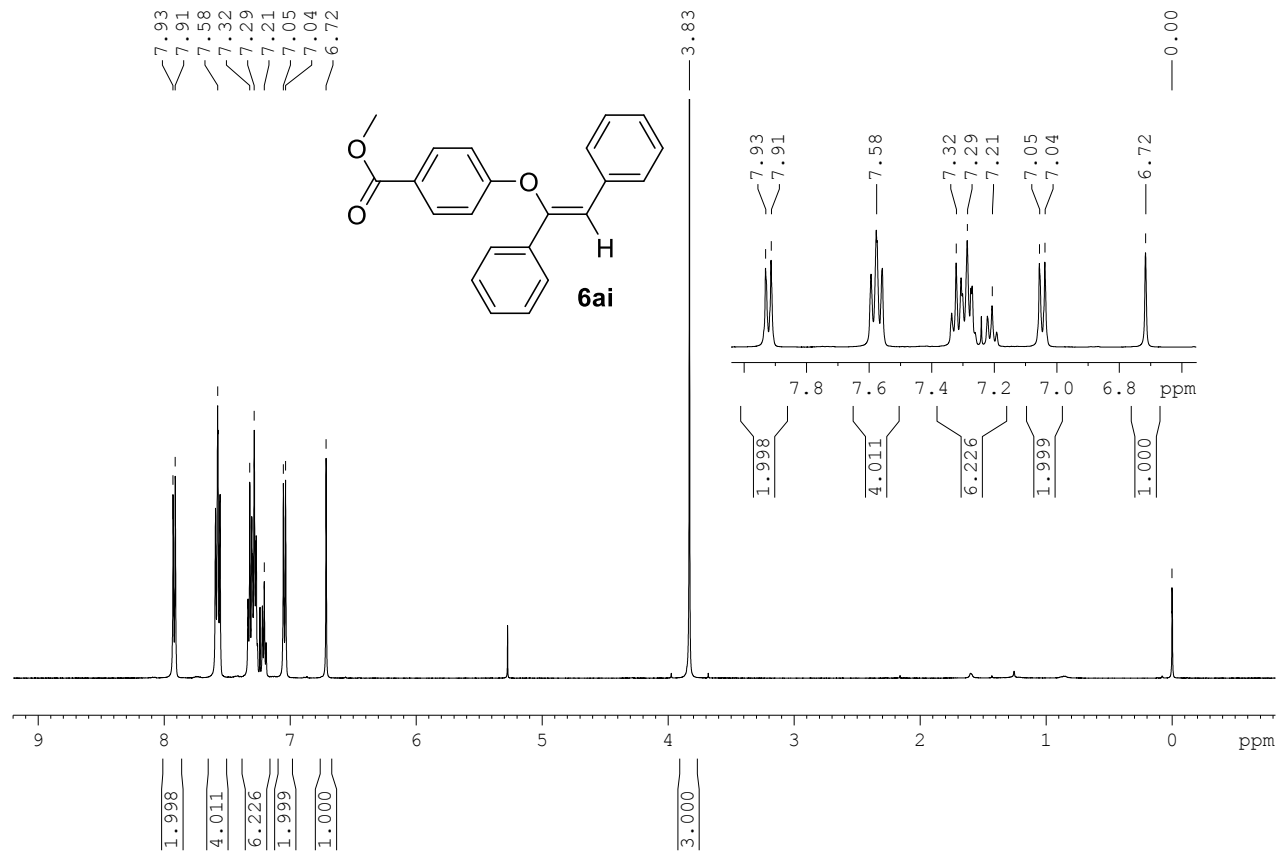
^{1}H NMR ($CDCl_3$) of 6ah



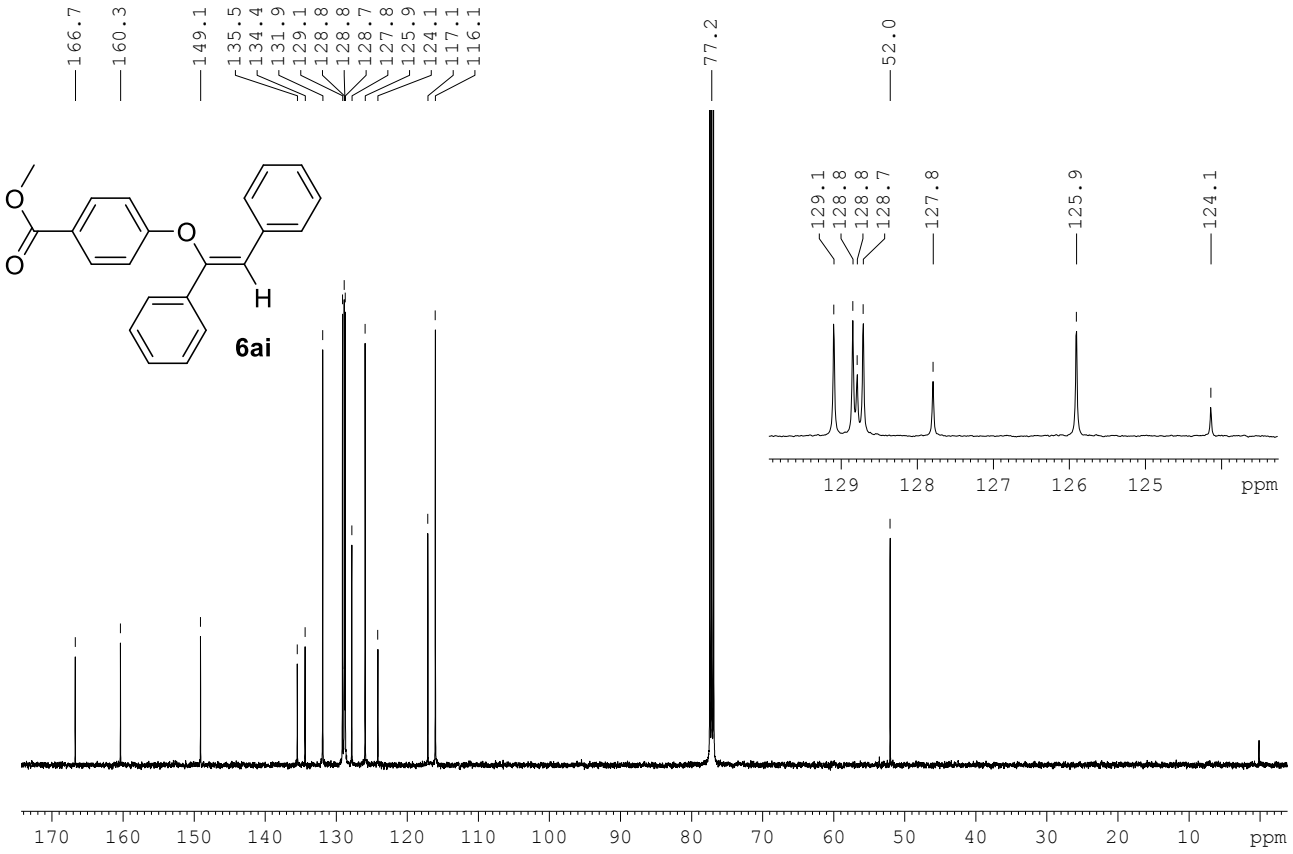
^{13}C-{^{1}H} NMR ($CDCl_3$) of 6ah



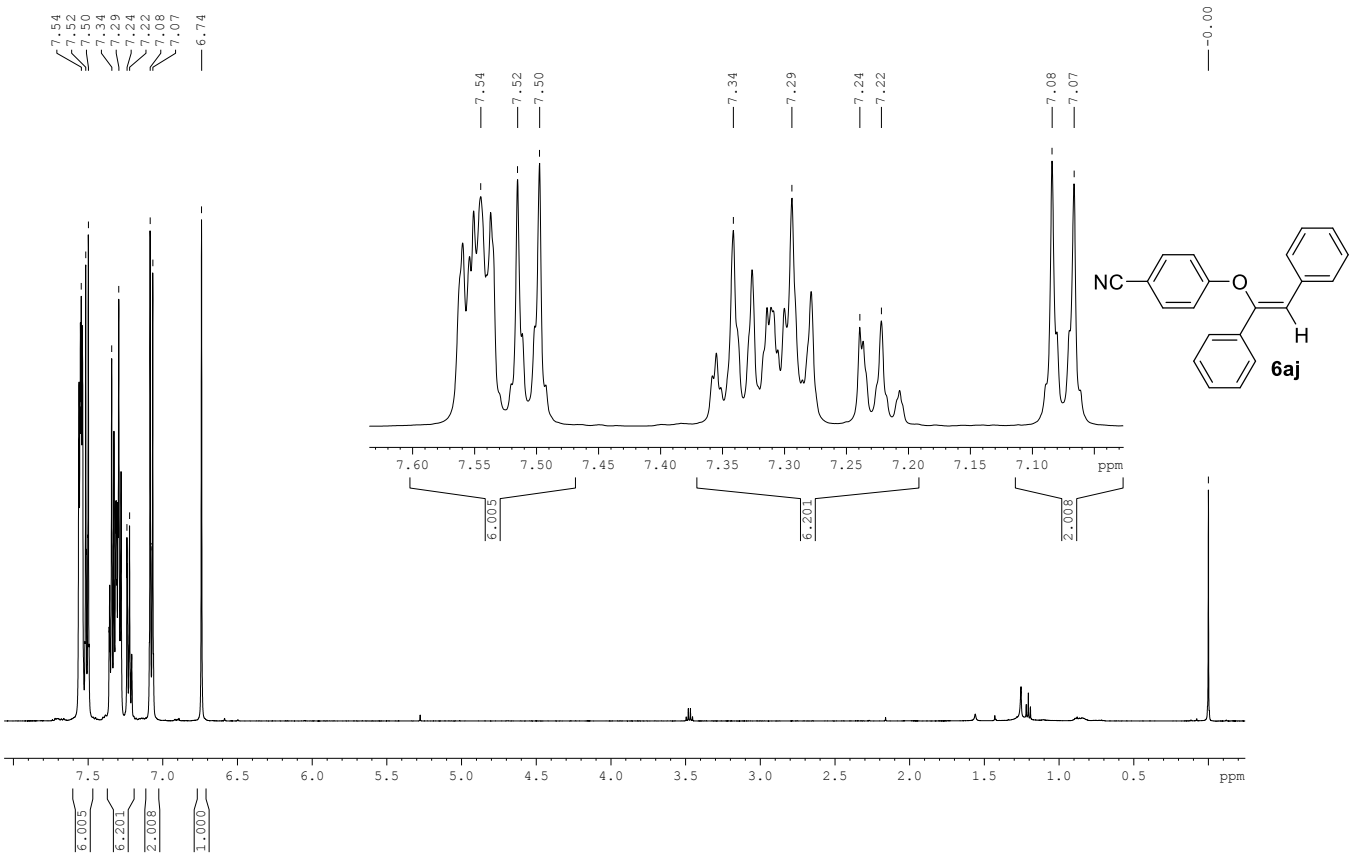
^{1}H NMR ($CDCl_3$) of 6ai



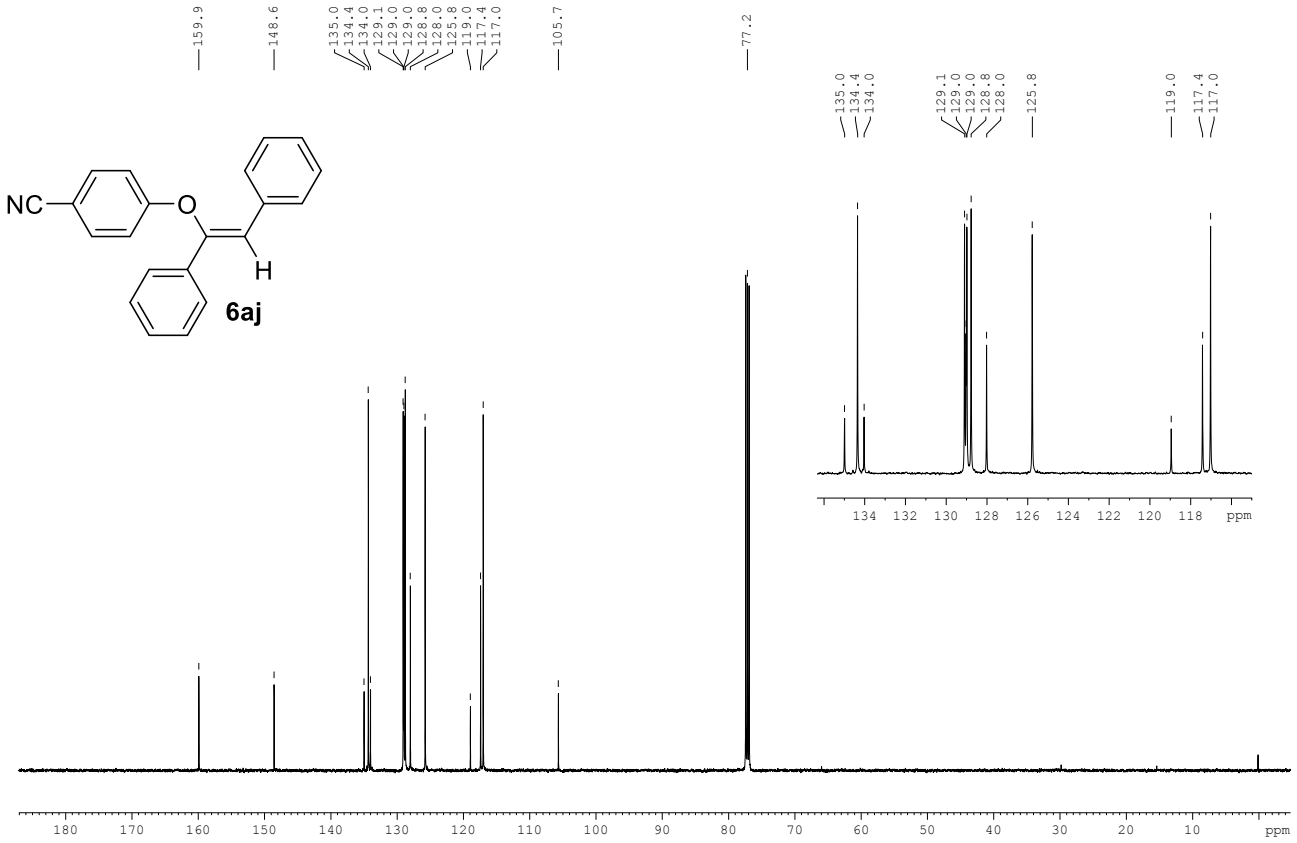
^{13}C-{^{1}H} NMR ($CDCl_3$) of 6ai



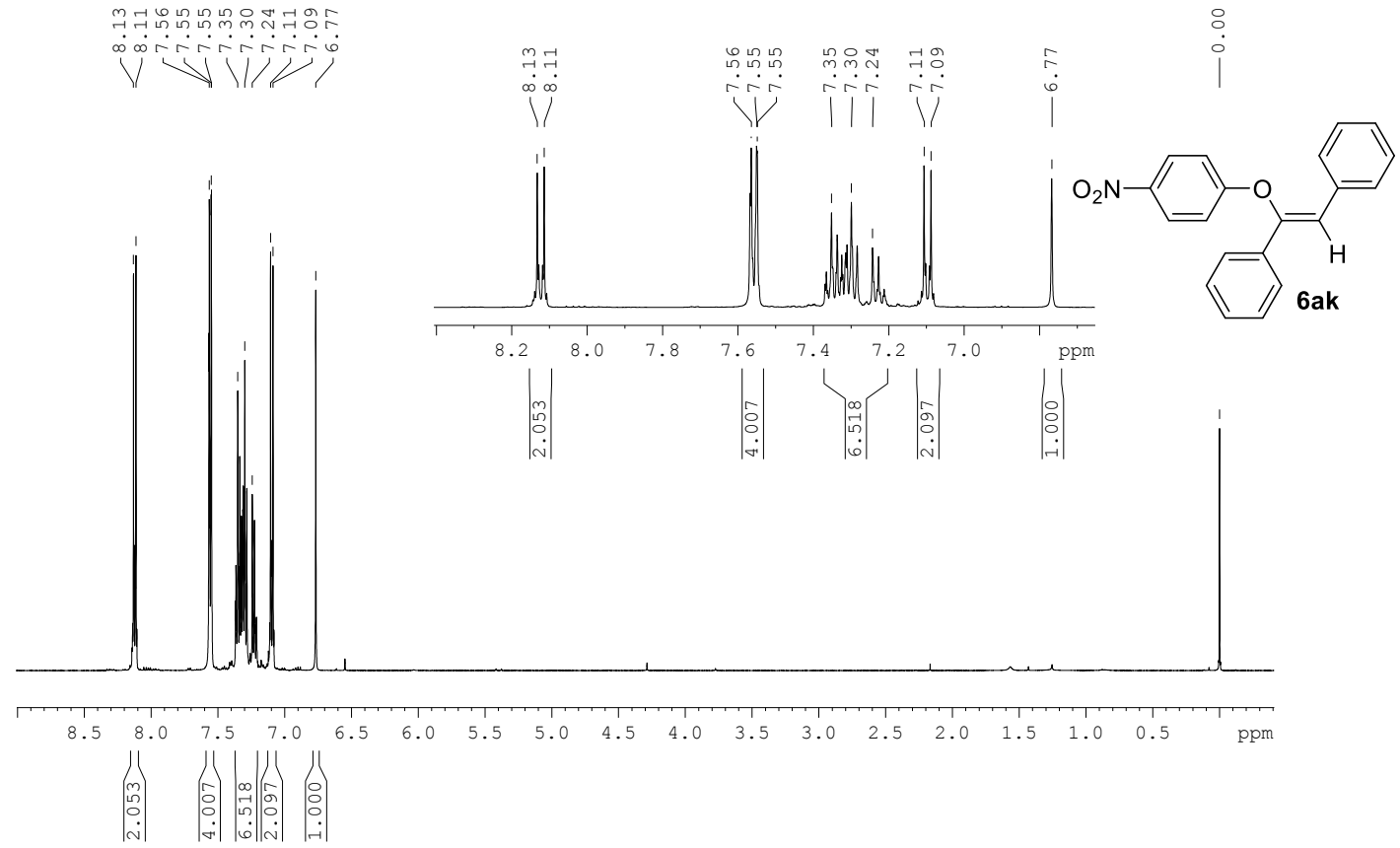
^{1}H NMR ($CDCl_3$) of 6aj



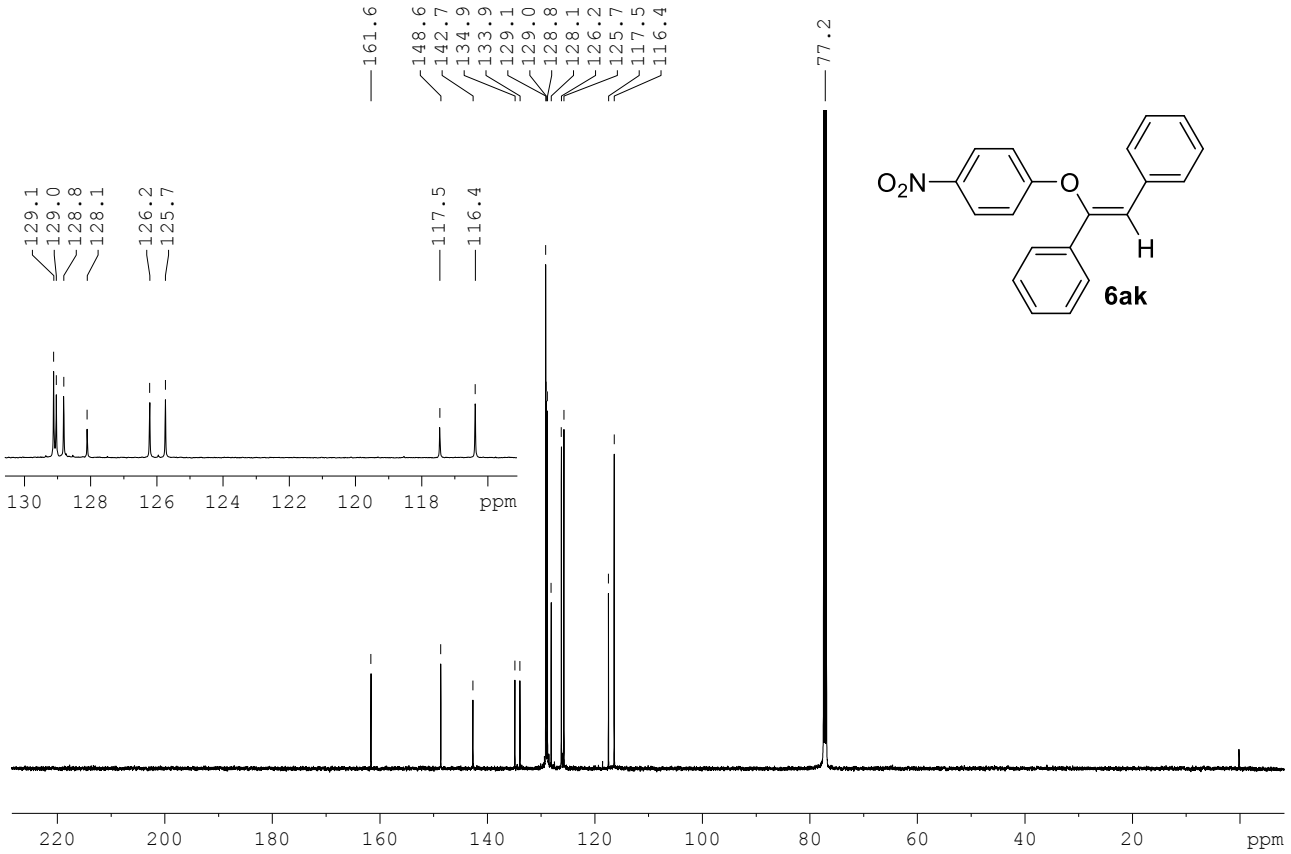
^{13}C-{^{1}H} NMR ($CDCl_3$) of 6aj



^{1}H NMR ($CDCl_3$) of 6ak

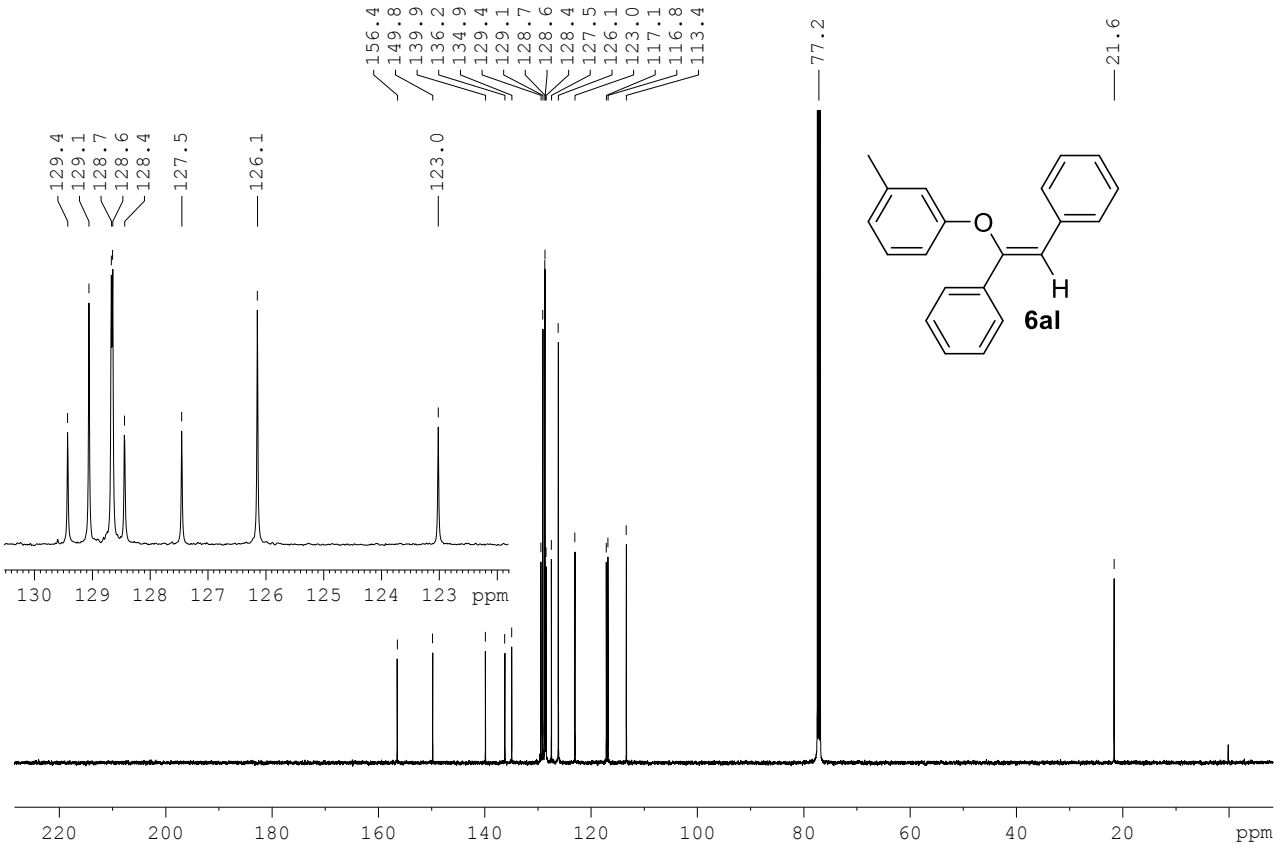


^{13}C-{^{1}H} NMR ($CDCl_3$) of 6ak

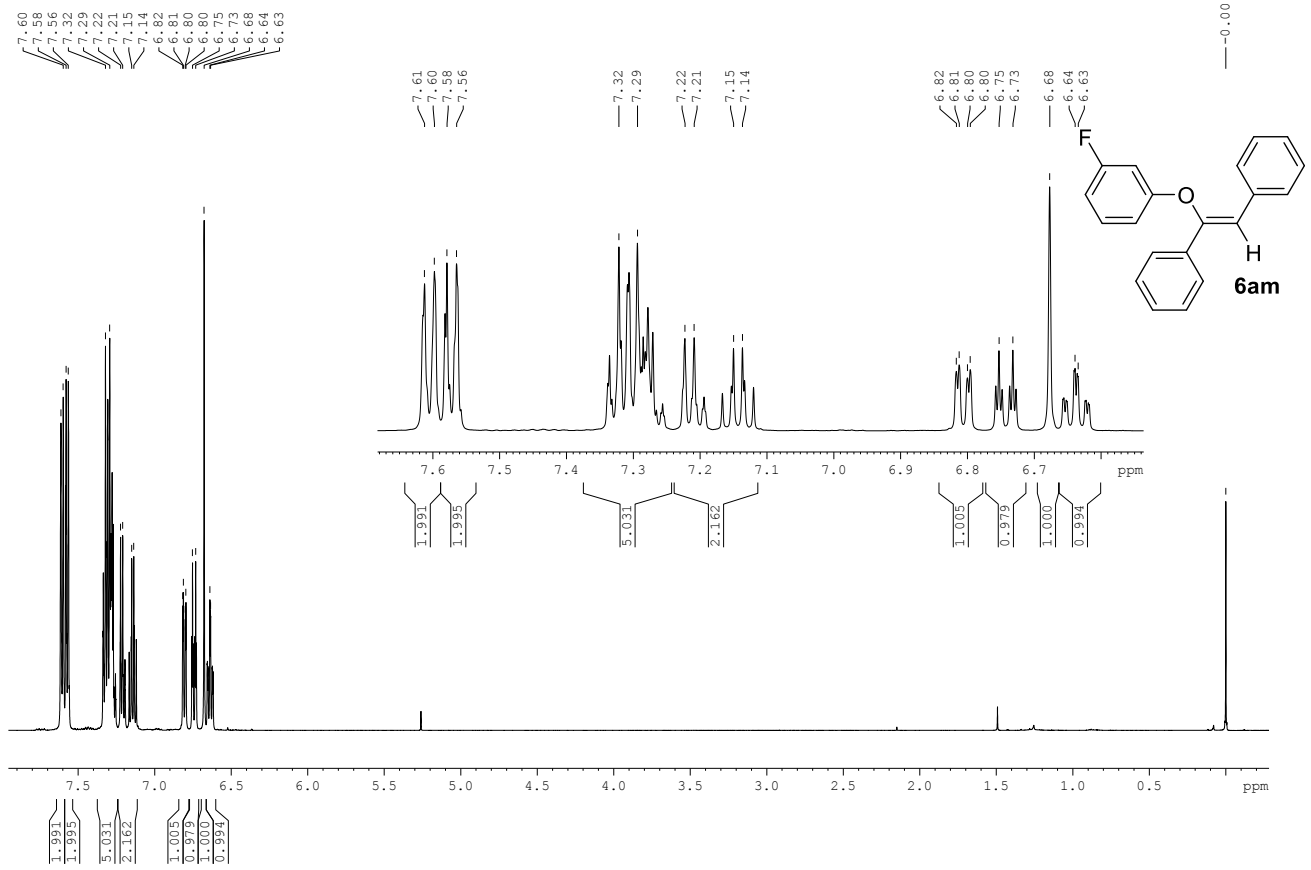


^{1}H NMR ($CDCl_3$) of 6al

^{13}C-{^{1}H} NMR ($CDCl_3$) of 6al

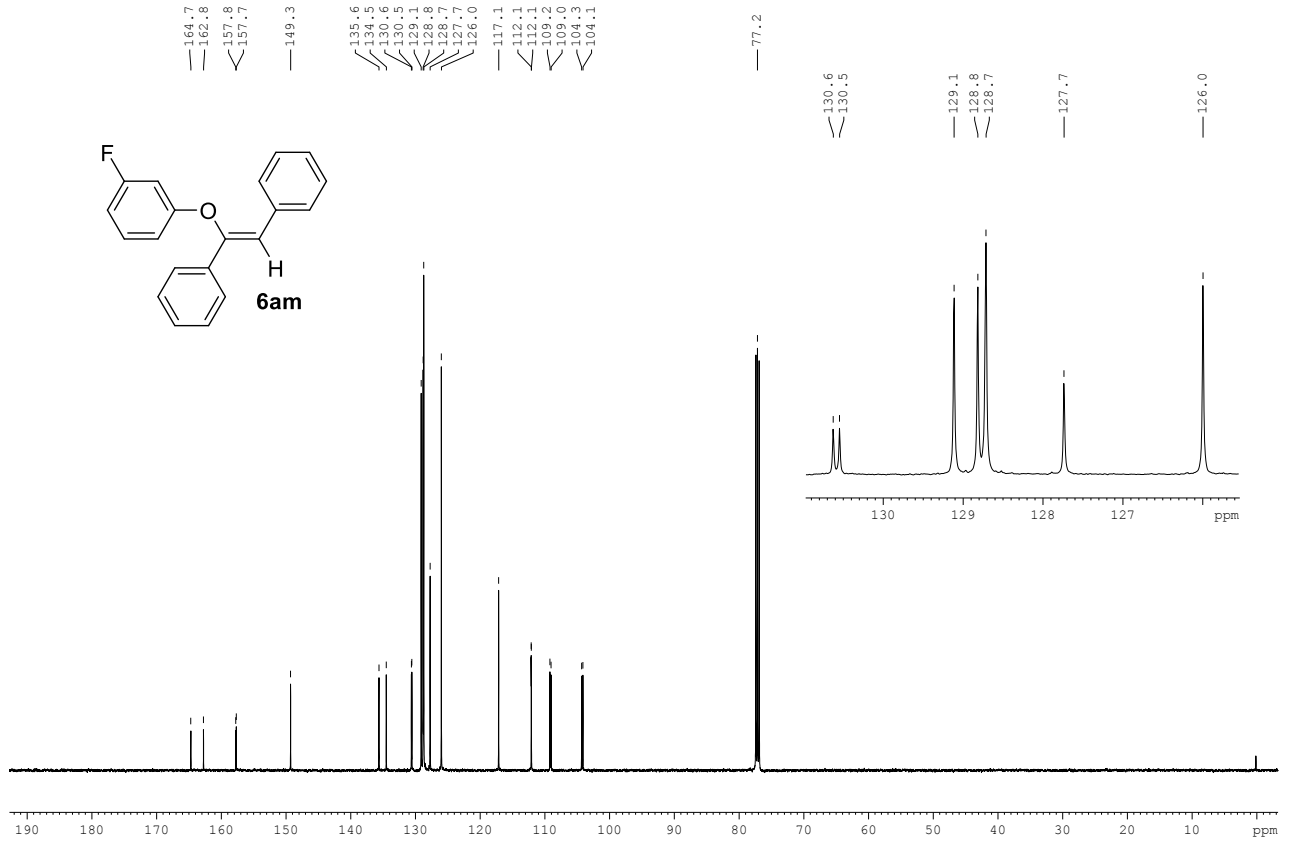


^{1}H NMR ($CDCl_3$) of 6am

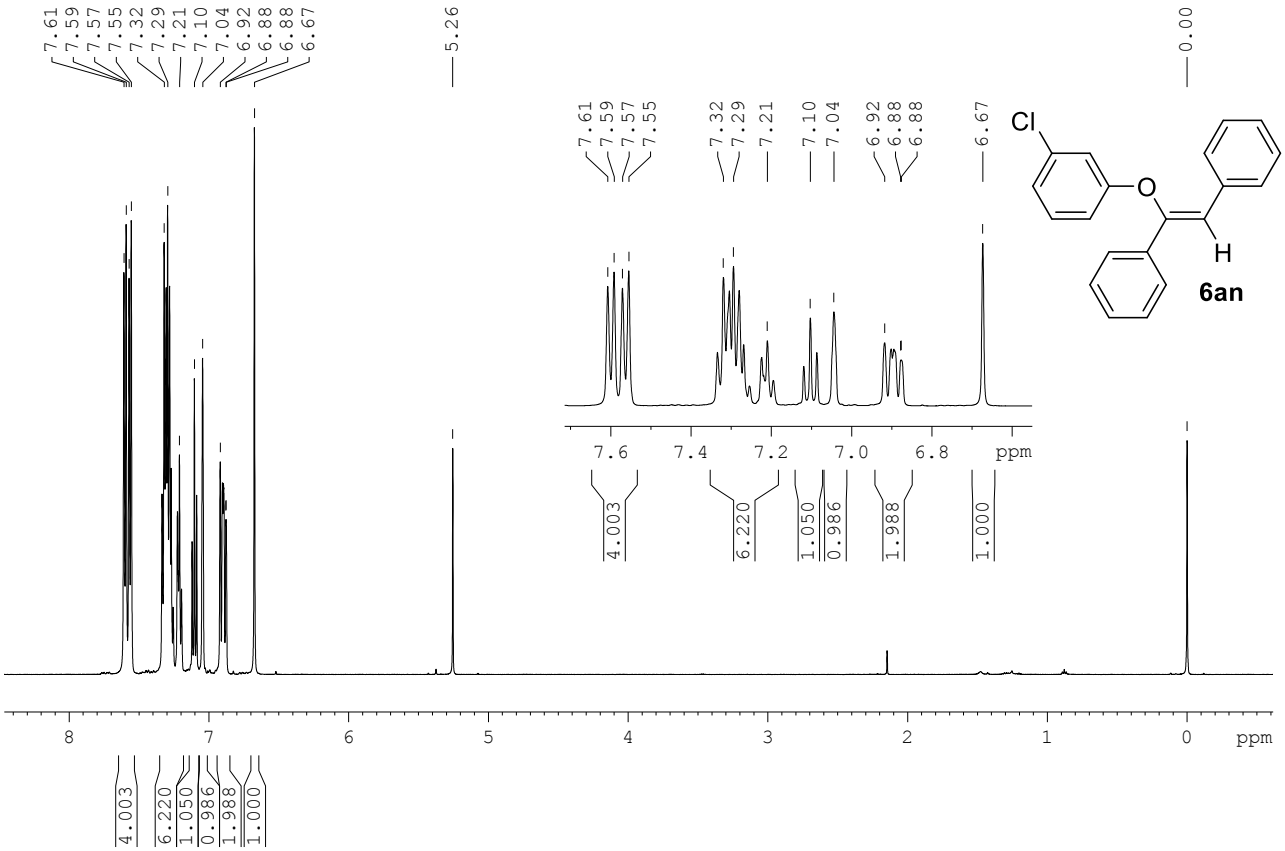


^{19}F-{^{1}H} NMR ($CDCl_3$) of 6am

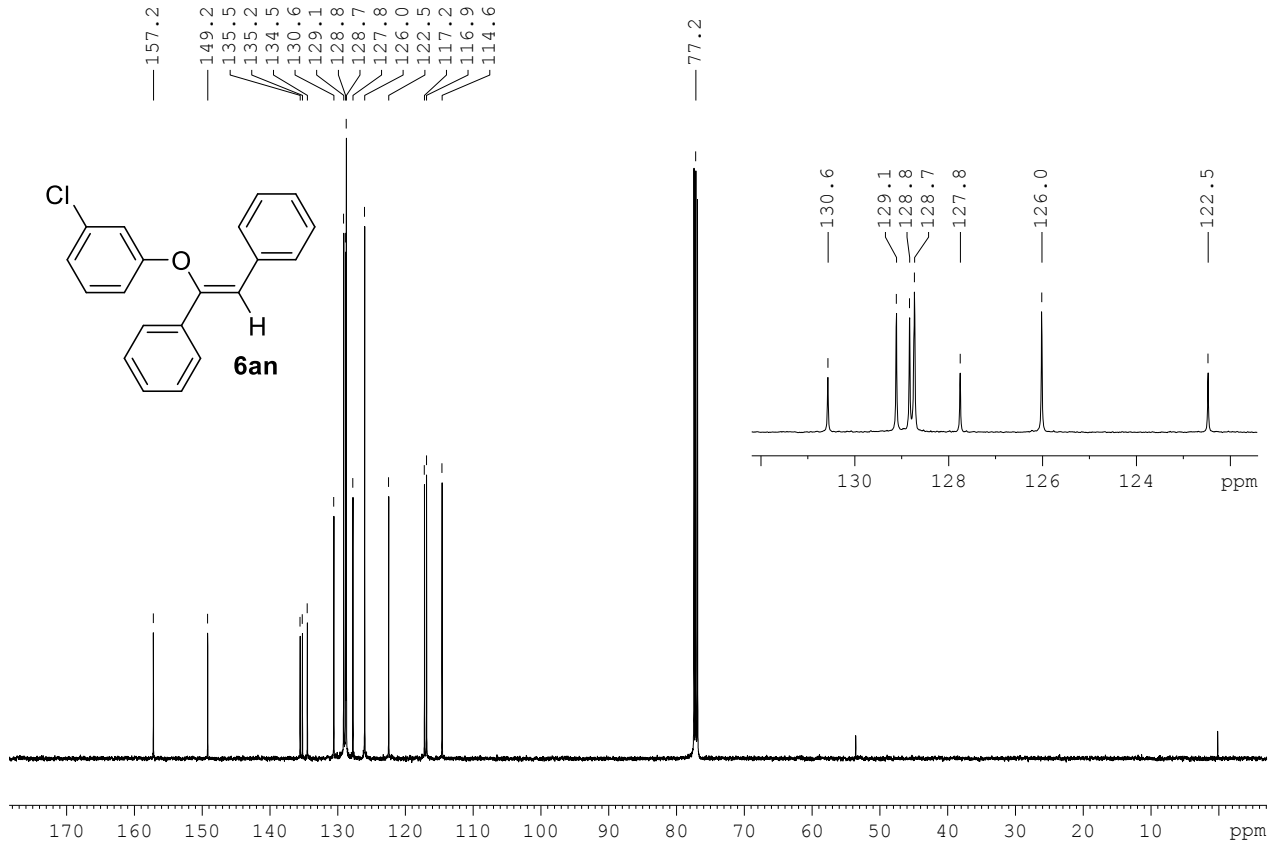
^{13}C-{^{1}H} NMR ($CDCl_3$) of 6am



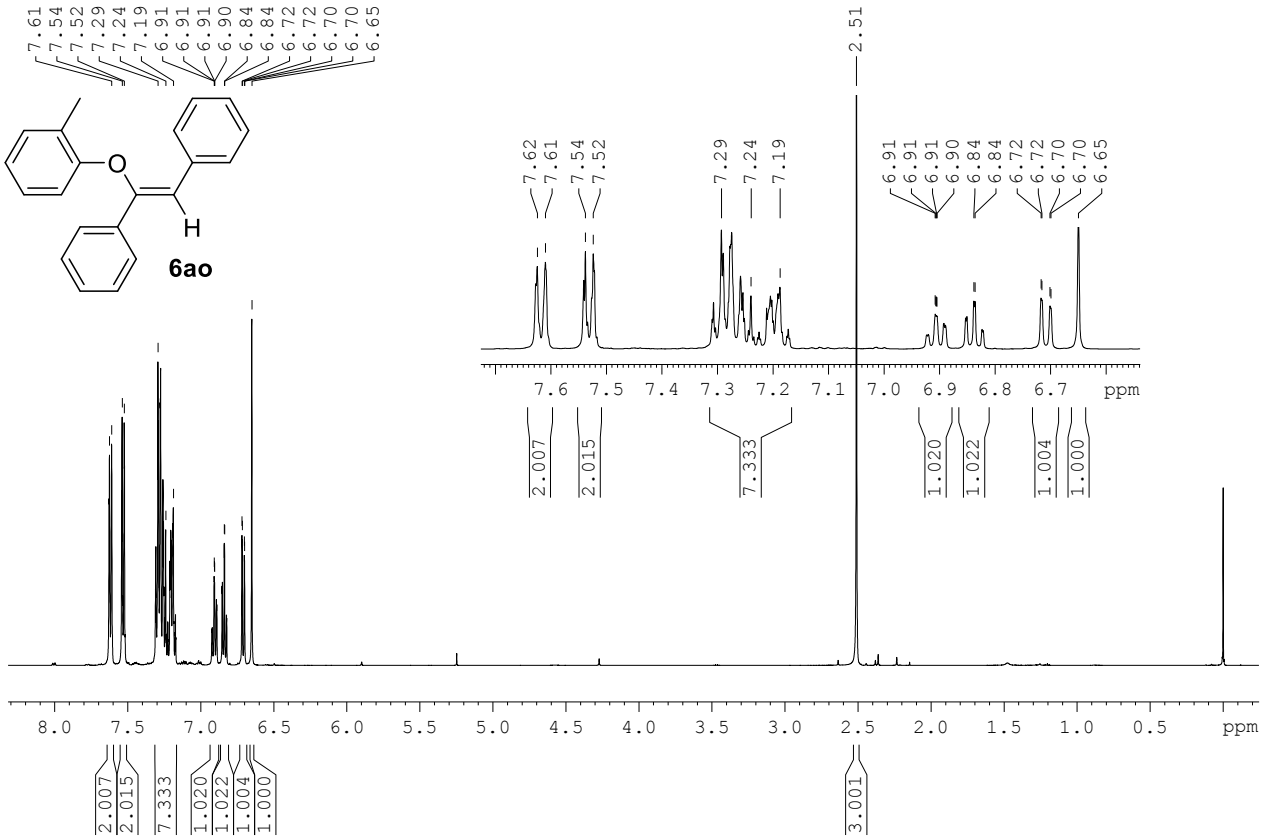
^{1}H NMR ($CDCl_3$) of 6an



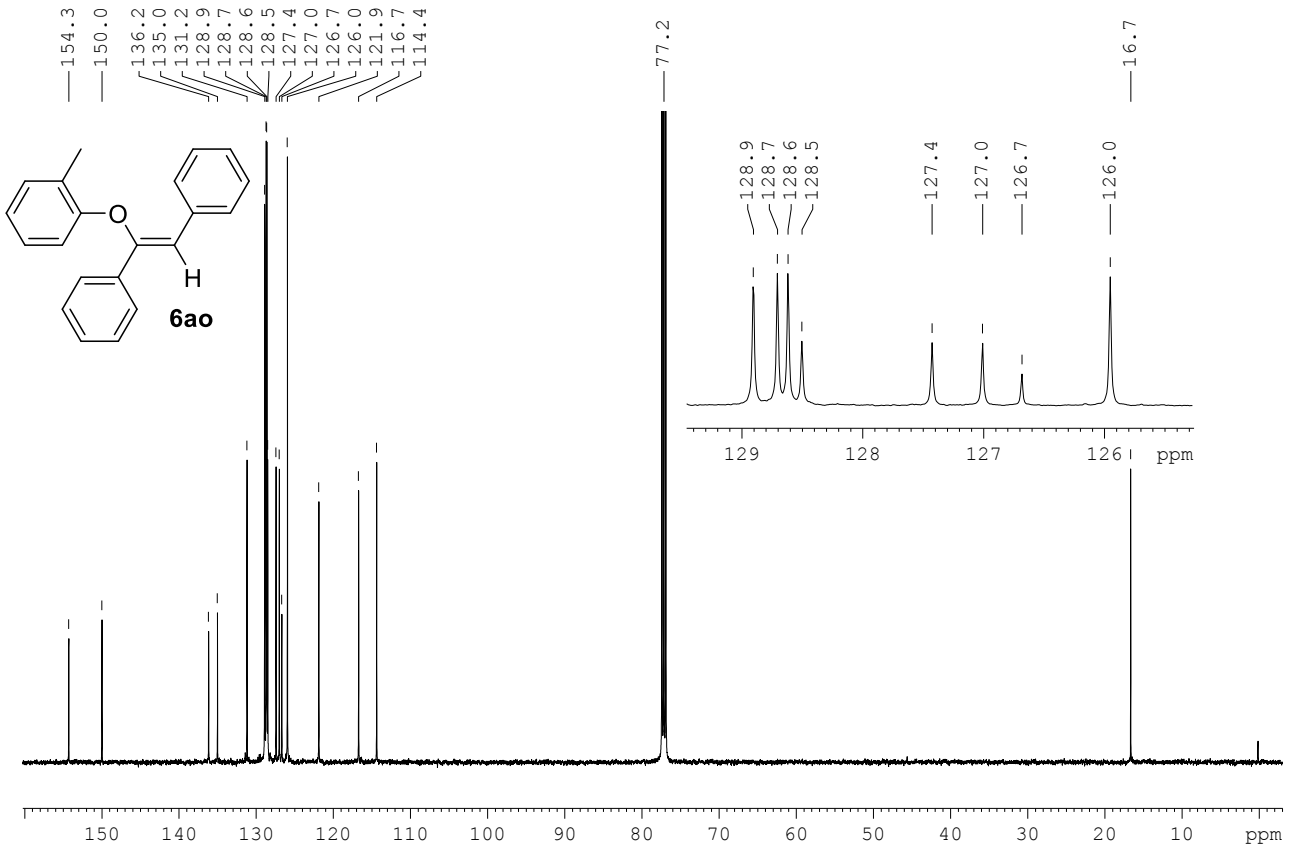
^{13}C-{^{1}H} NMR ($CDCl_3$) of 6an



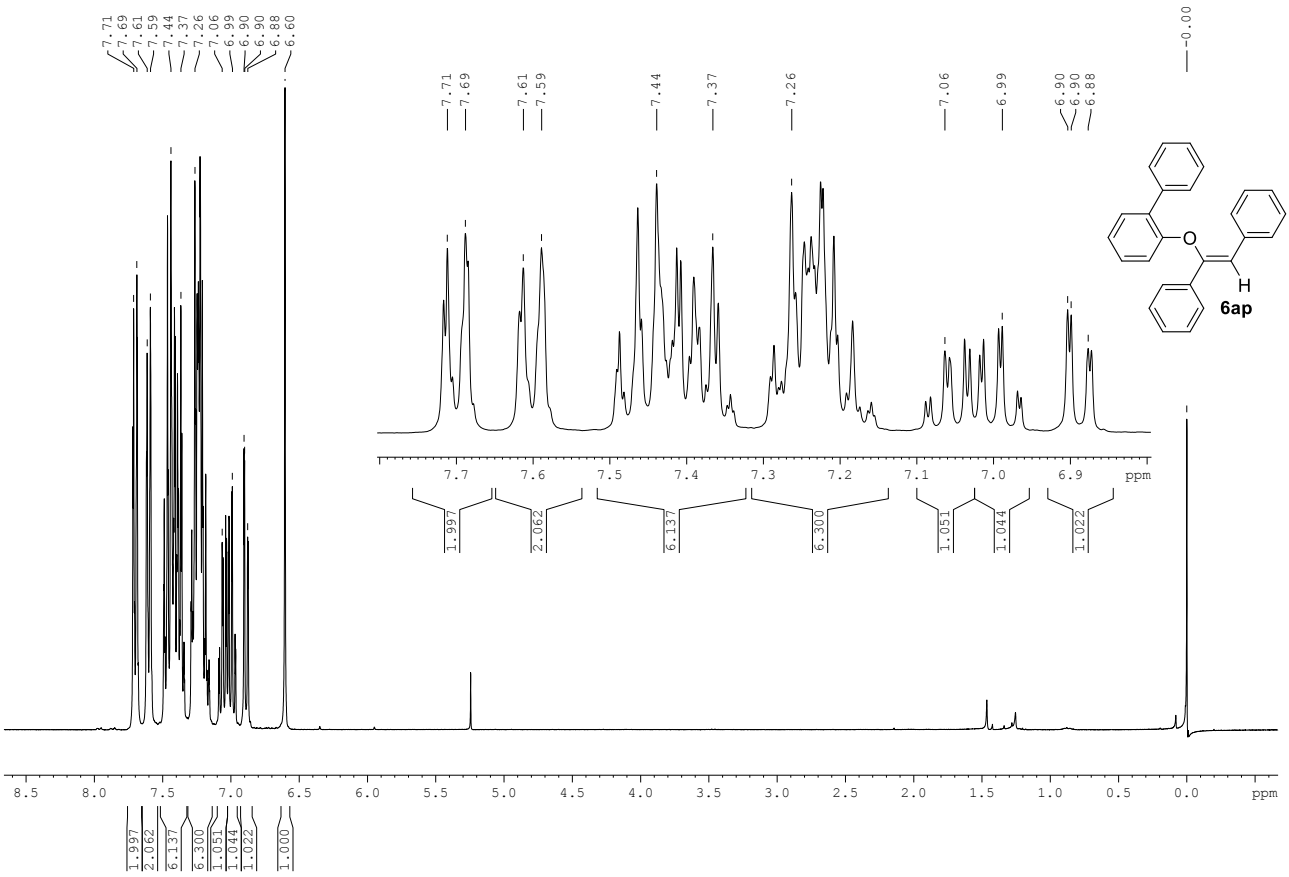
^{1}H NMR ($CDCl_3$) of 6ao



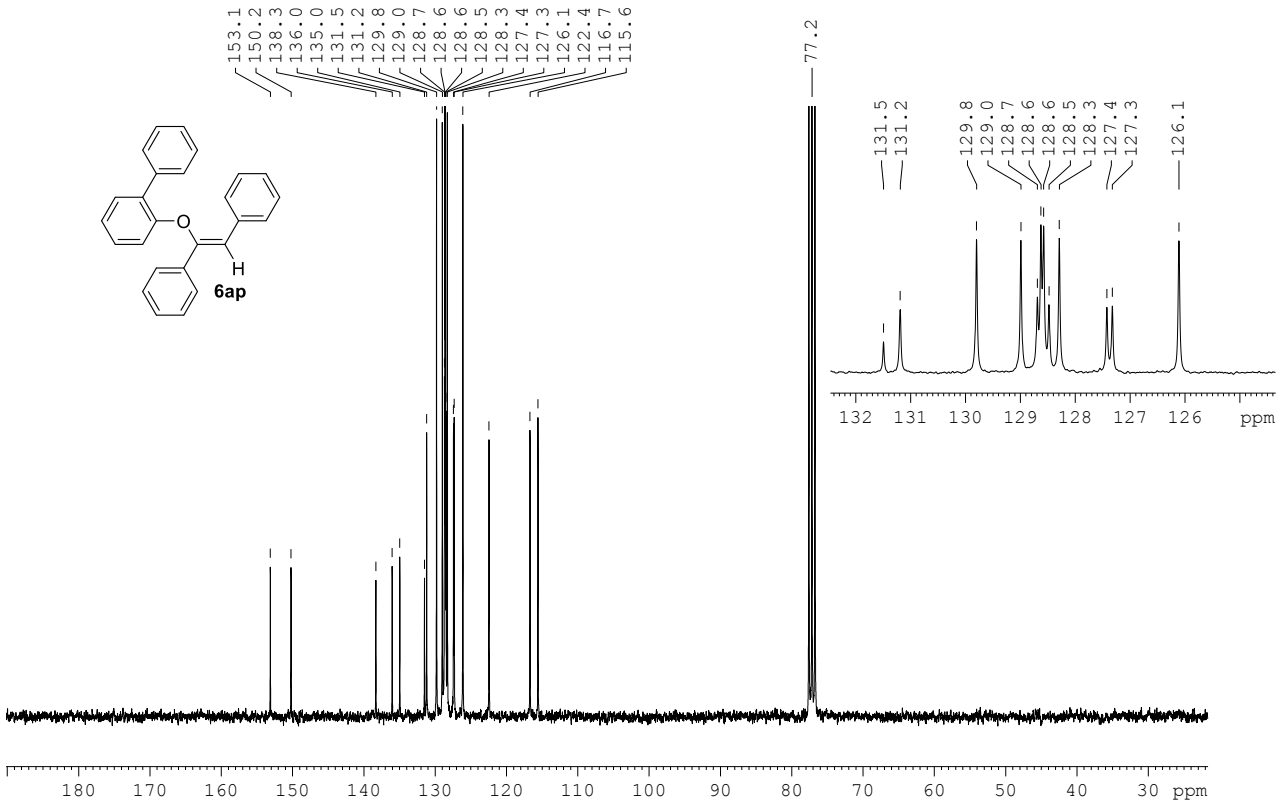
^{13}C-{^{1}H} NMR ($CDCl_3$) of 6ao



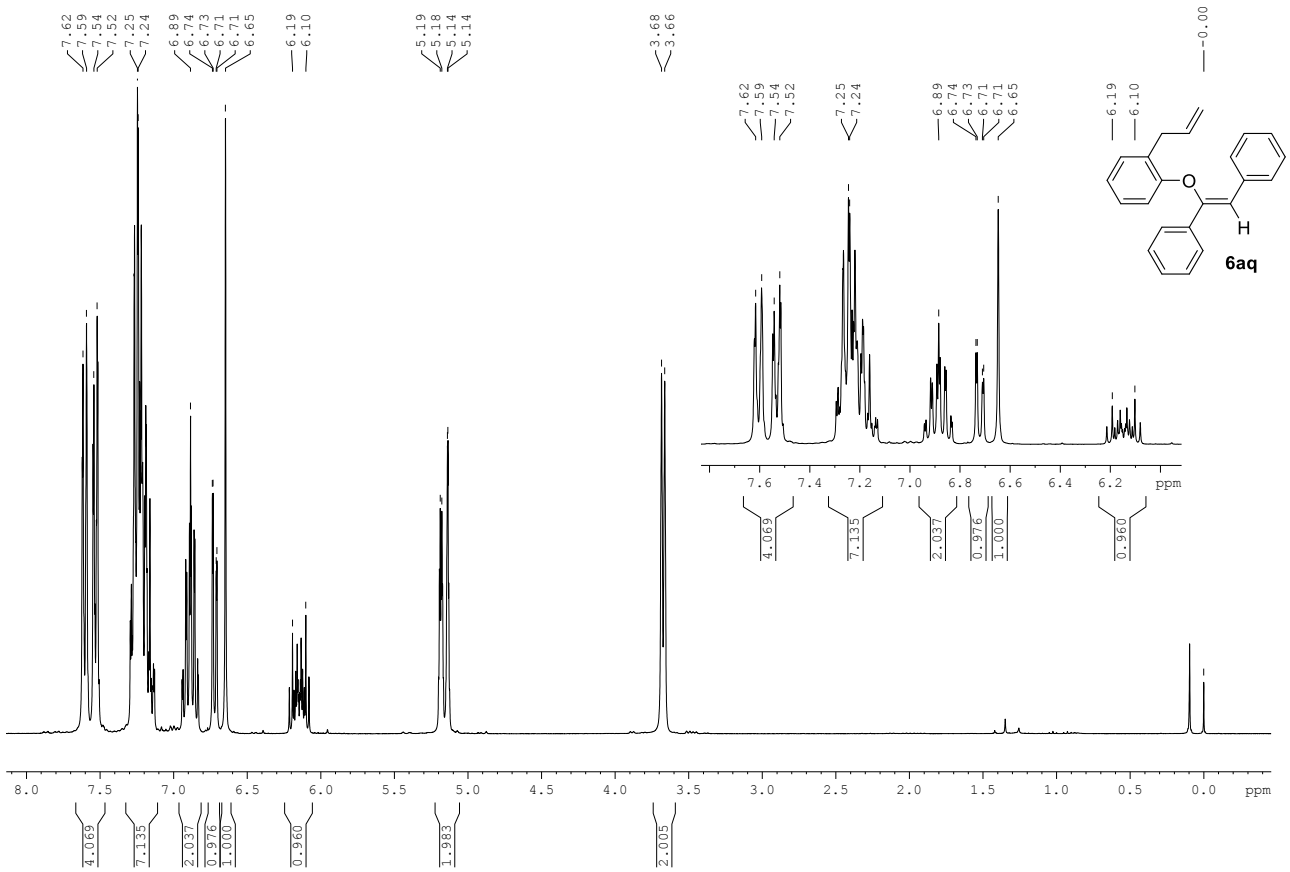
^{1}H NMR ($CDCl_3$) of 6ap



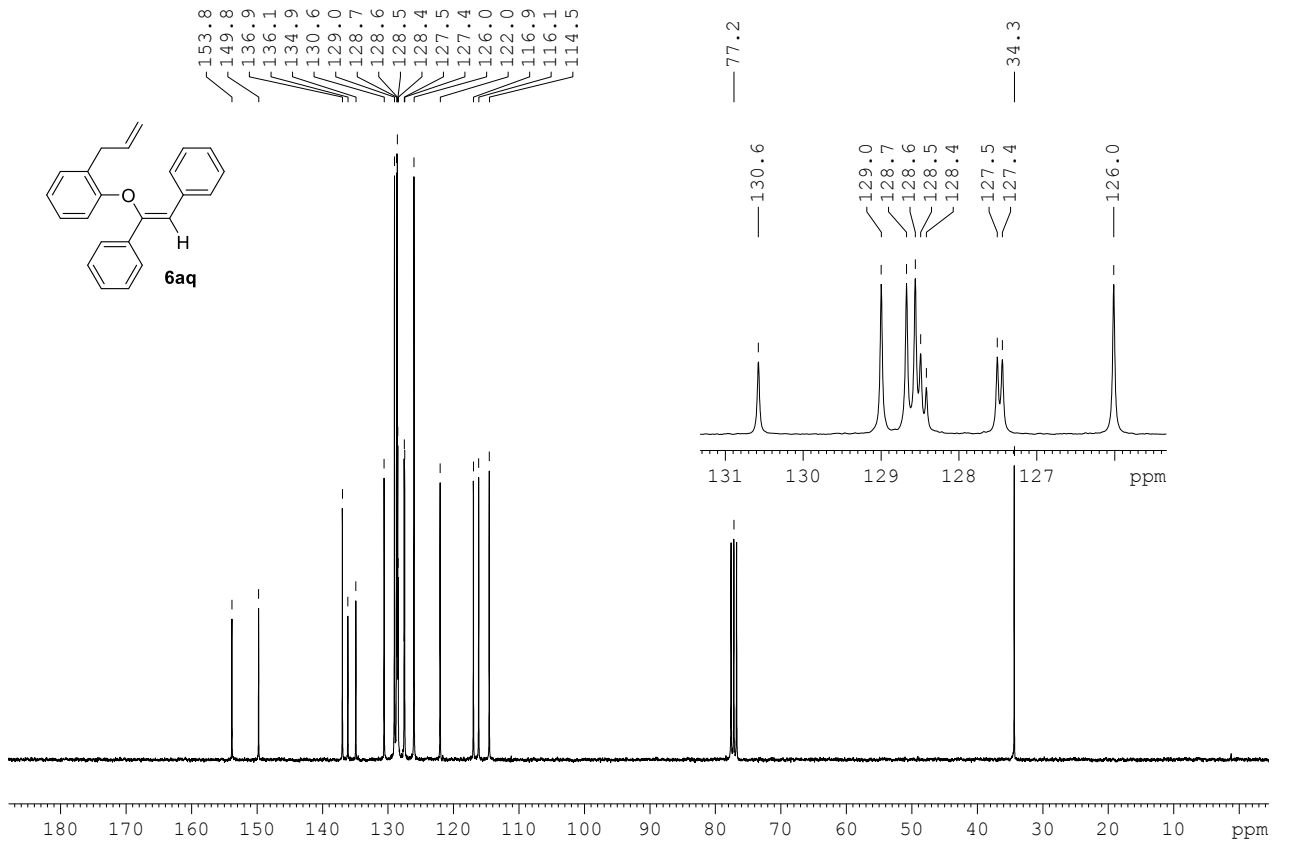
^{13}C-{^{1}H} NMR ($CDCl_3$) of 6ap



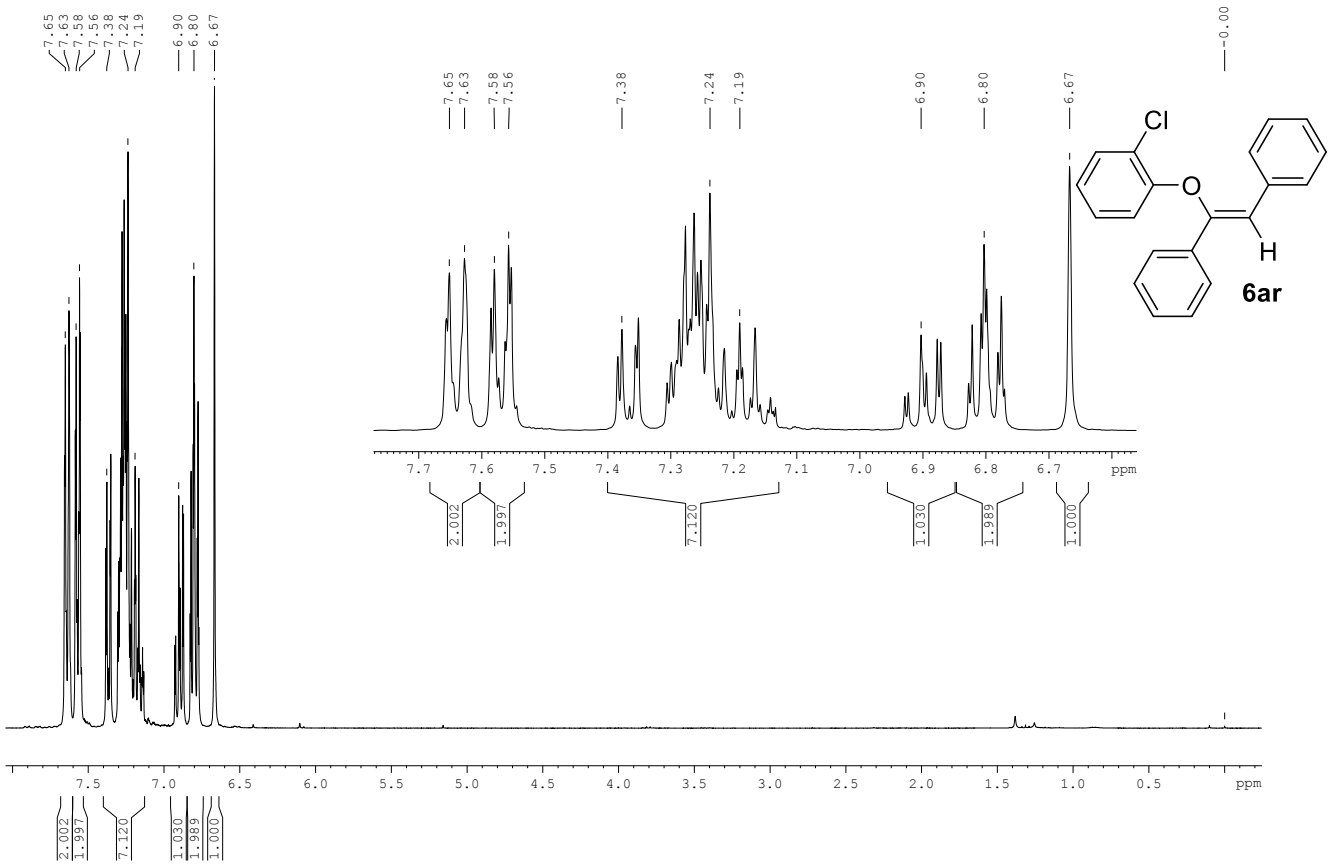
^{1}H NMR ($CDCl_3$) of 6aq



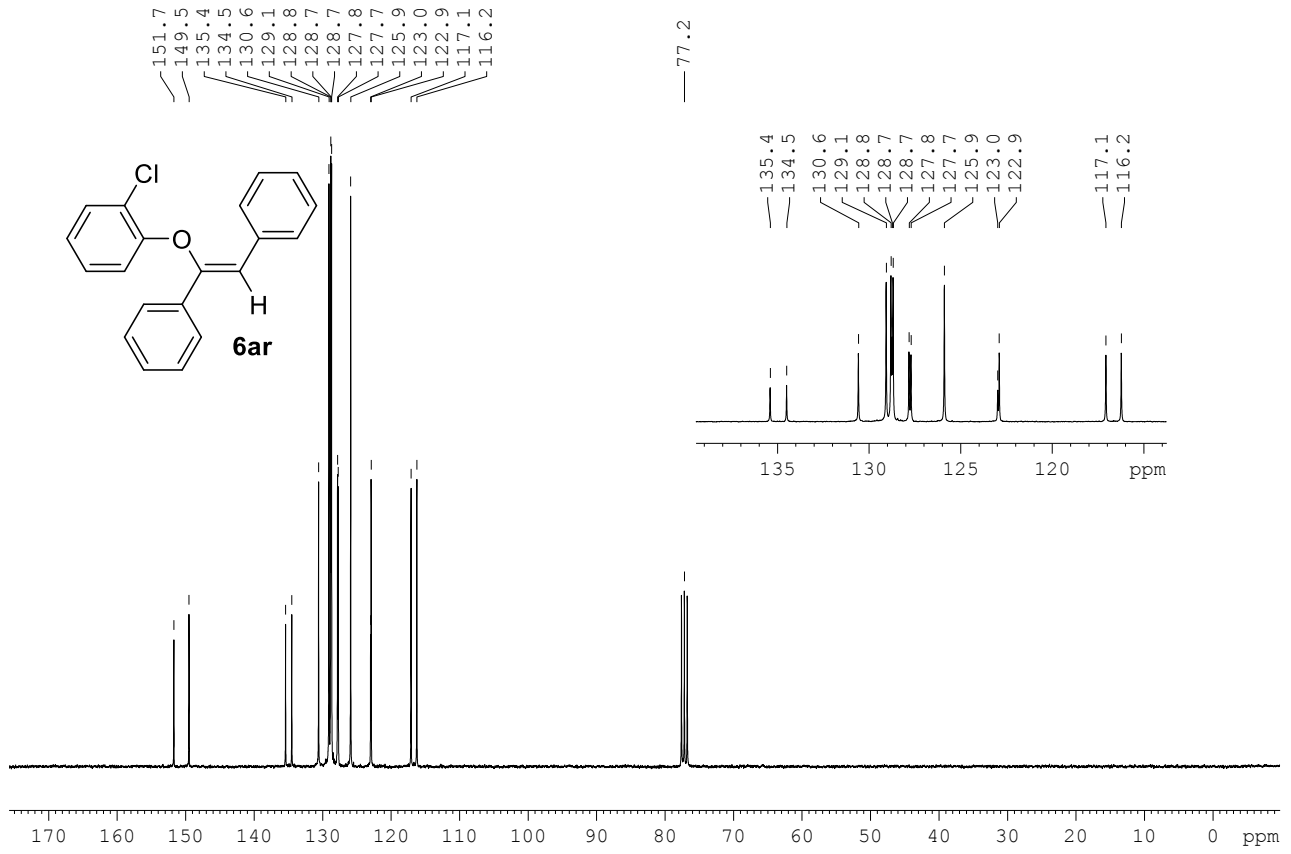
^{13}C-{^{1}H} NMR ($CDCl_3$) of 6aq



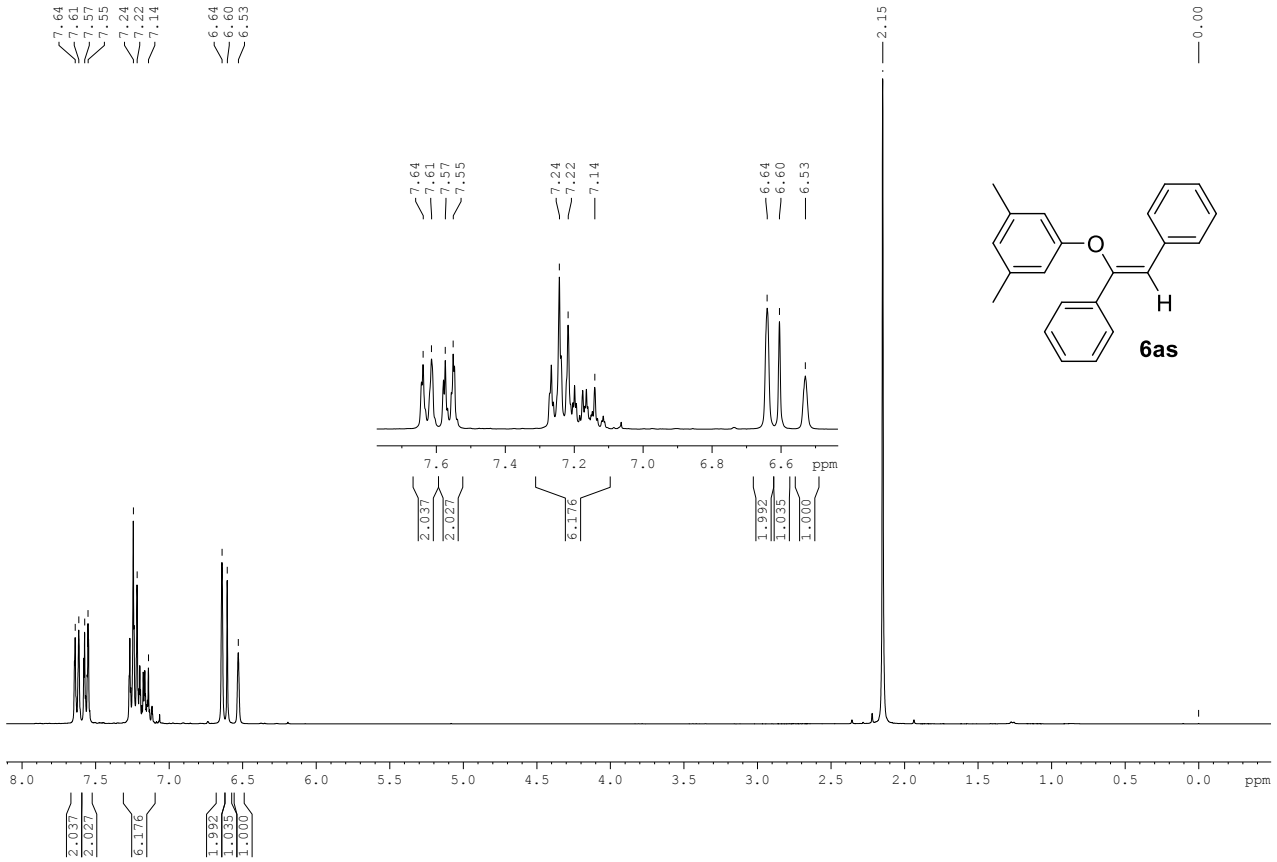
^{1}H NMR ($CDCl_3$) of 6ar



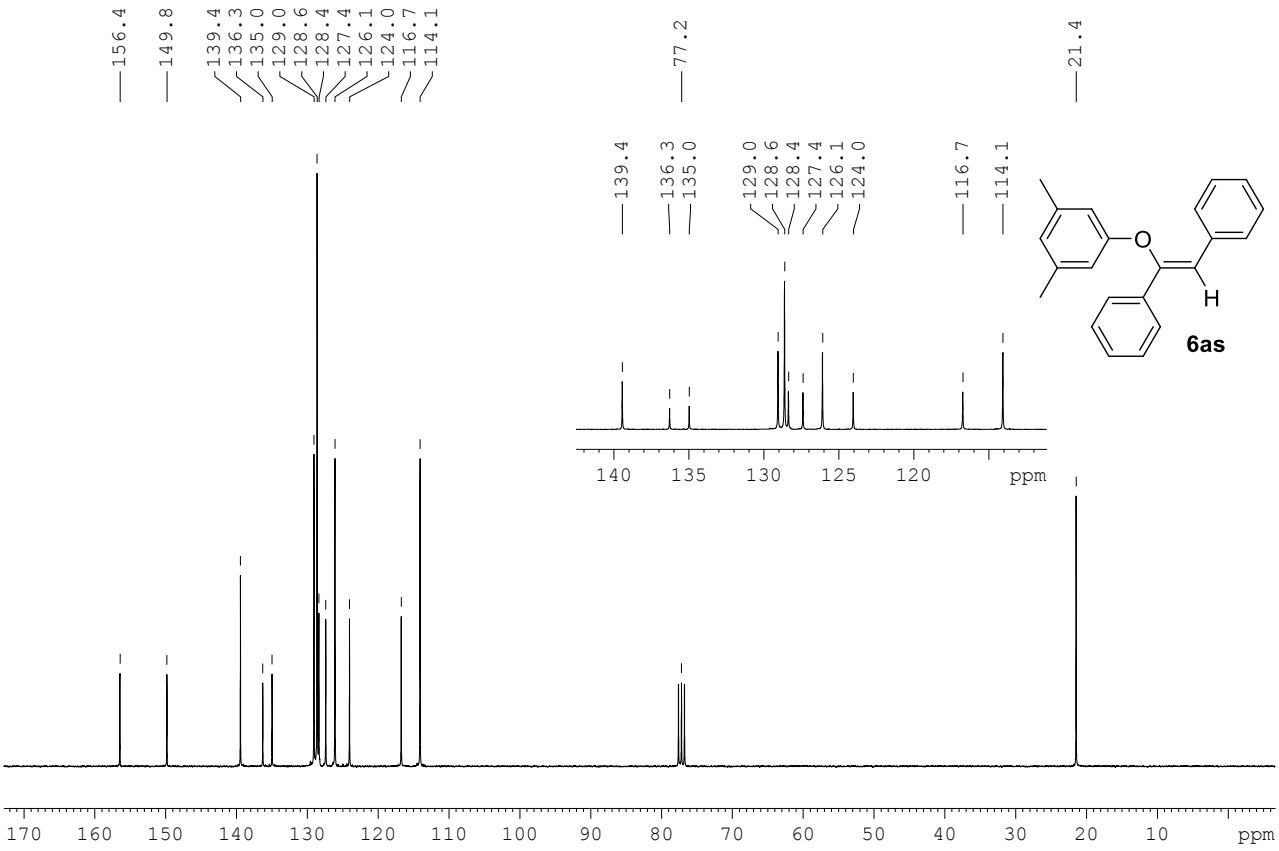
^{13}C-{^{1}H} NMR ($CDCl_3$) of 6ar



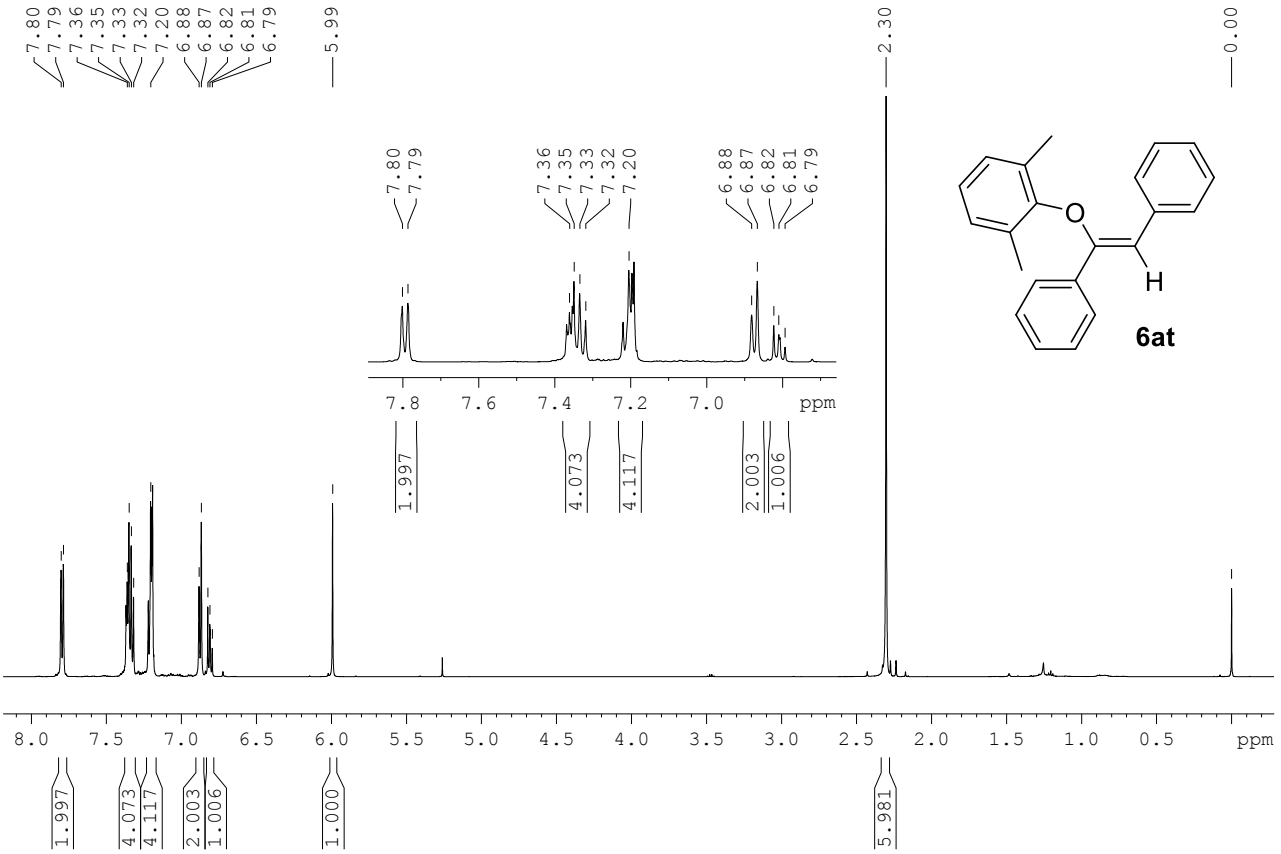
^{1}H NMR ($CDCl_3$) of 6as



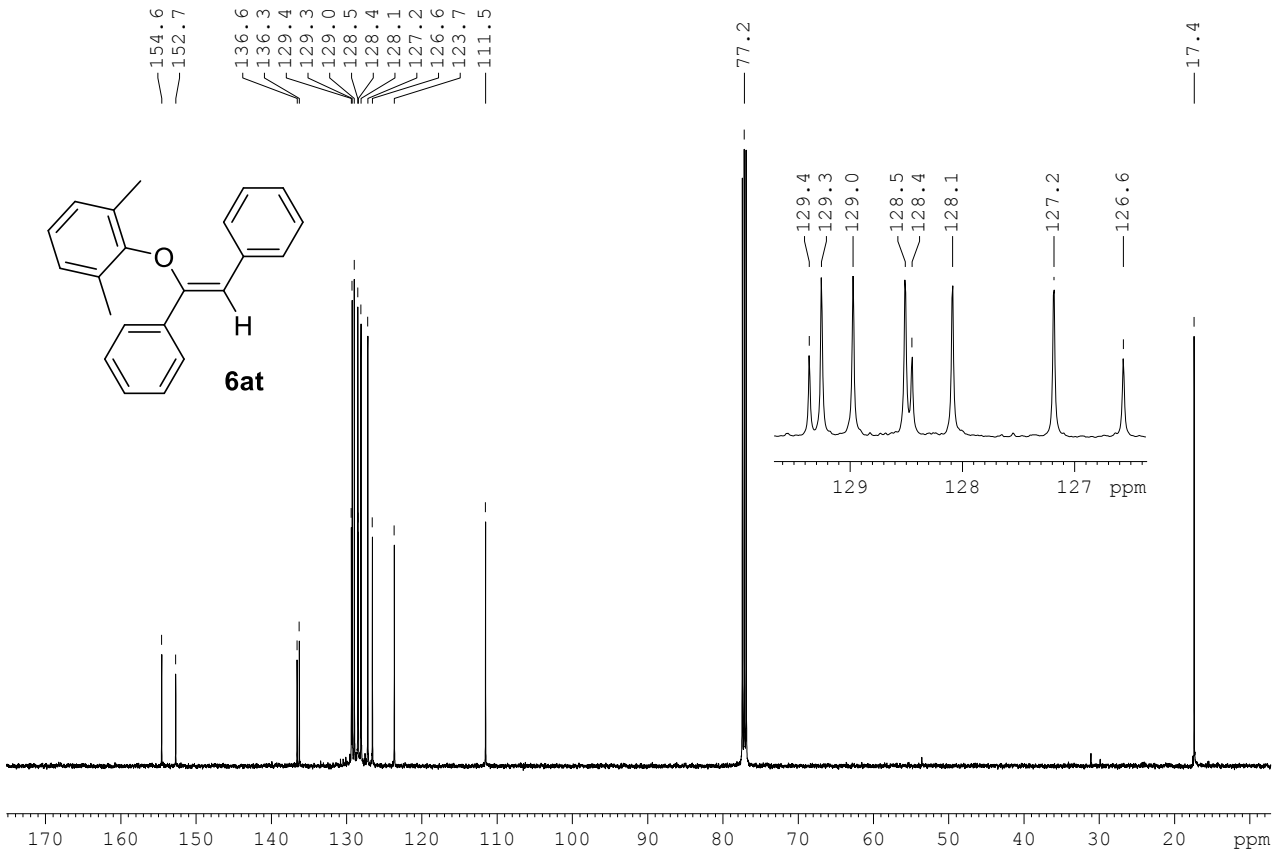
^{13}C-{^{1}H} NMR ($CDCl_3$) of 6as



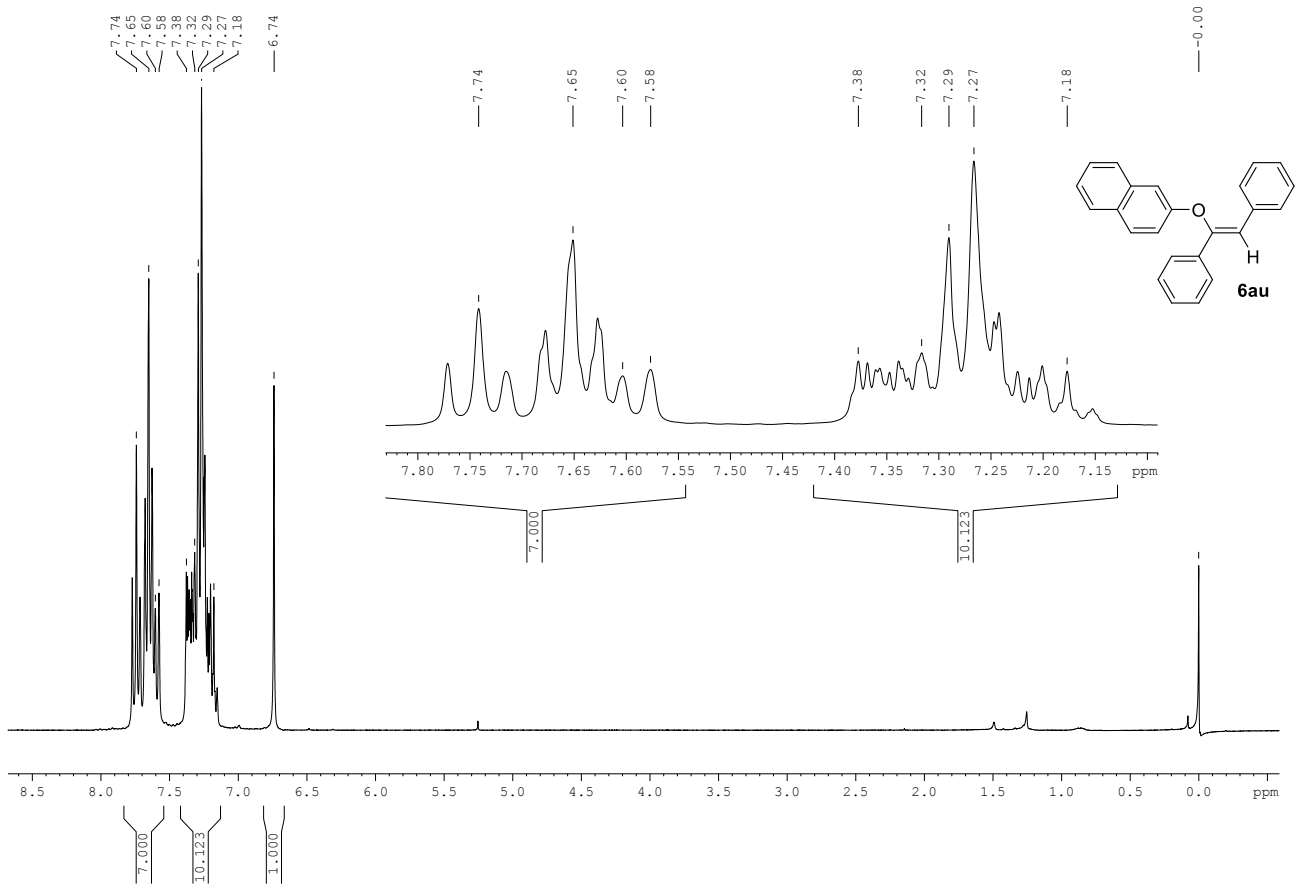
^{1}H NMR ($CDCl_3$) of 6at



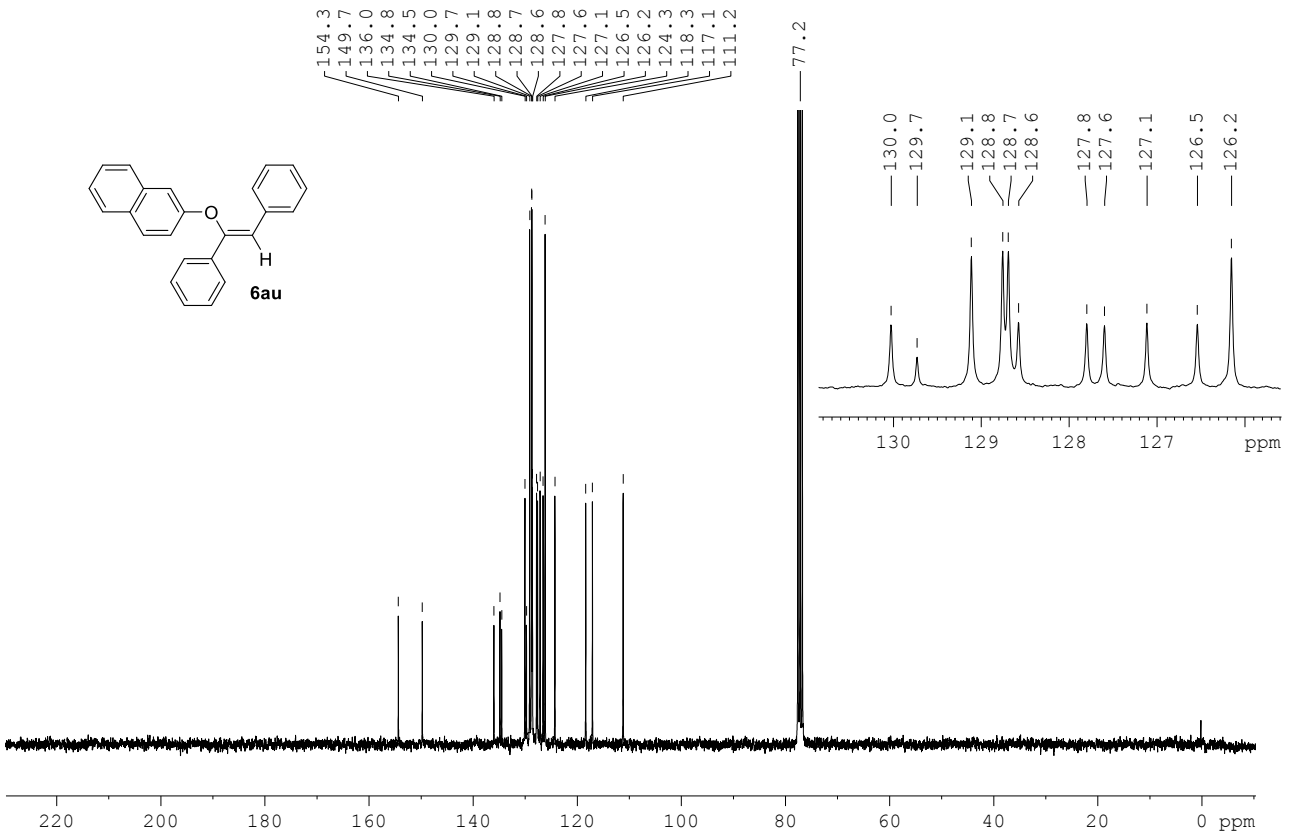
^{13}C-{^{1}H} NMR ($CDCl_3$) of 6at



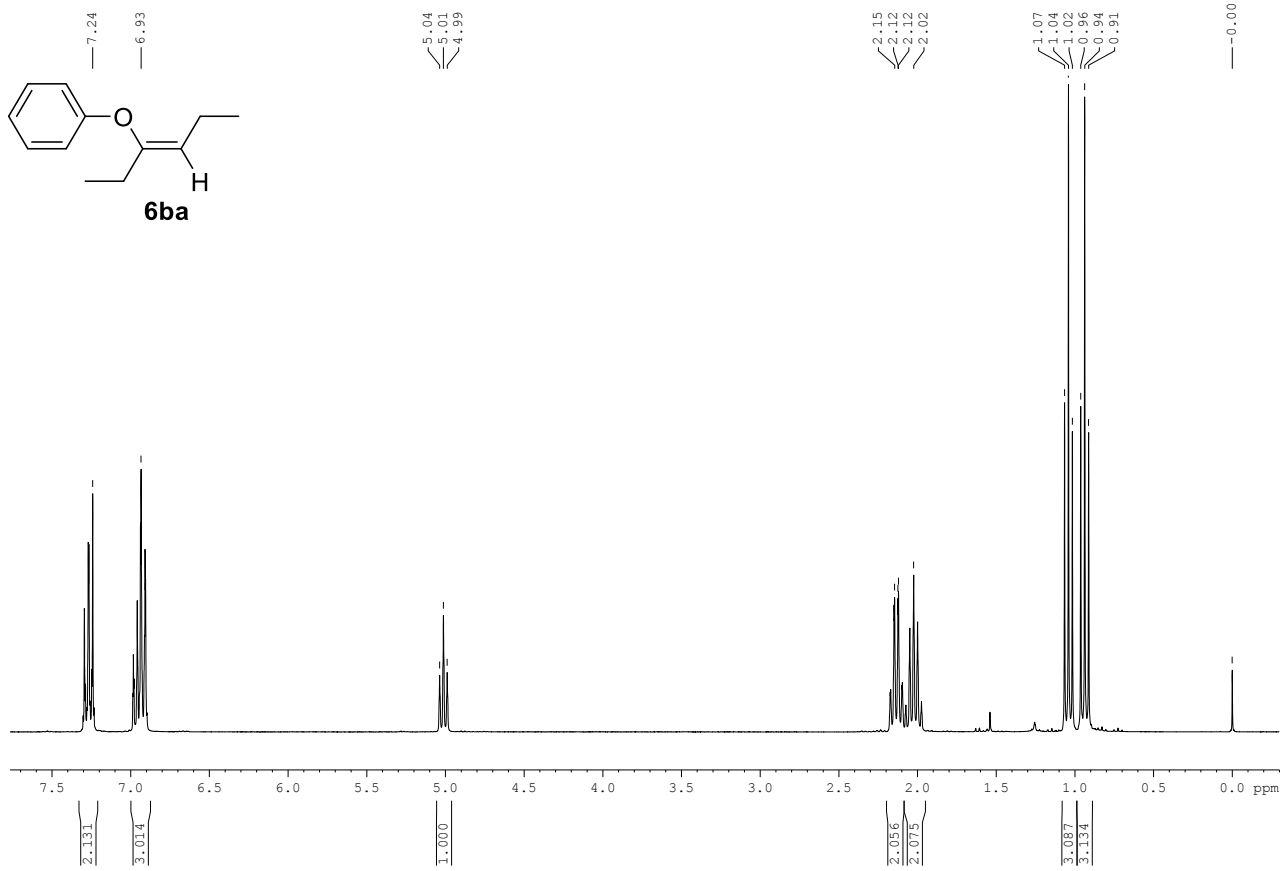
^{1}H NMR ($CDCl_3$) of 6au



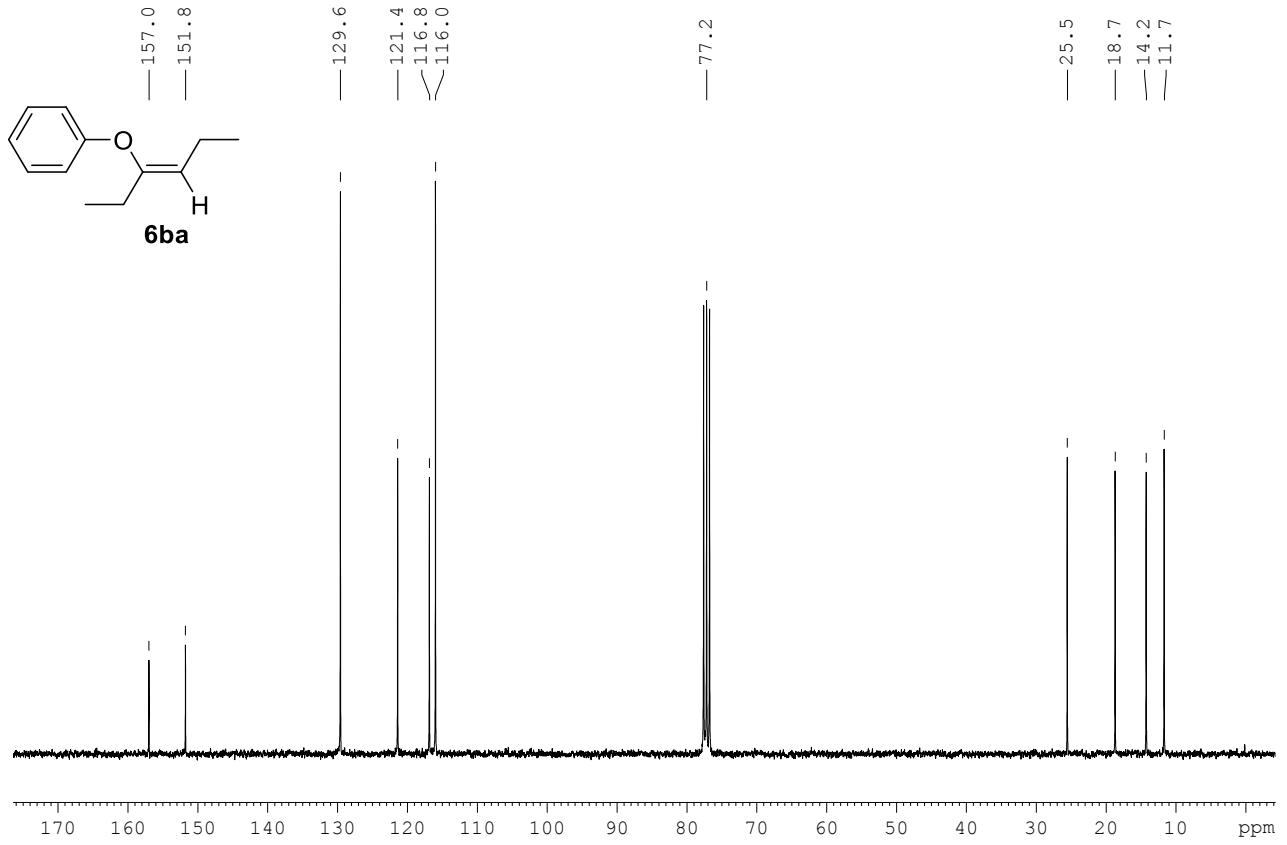
^{13}C-{^{1}H} NMR ($CDCl_3$) of 6au



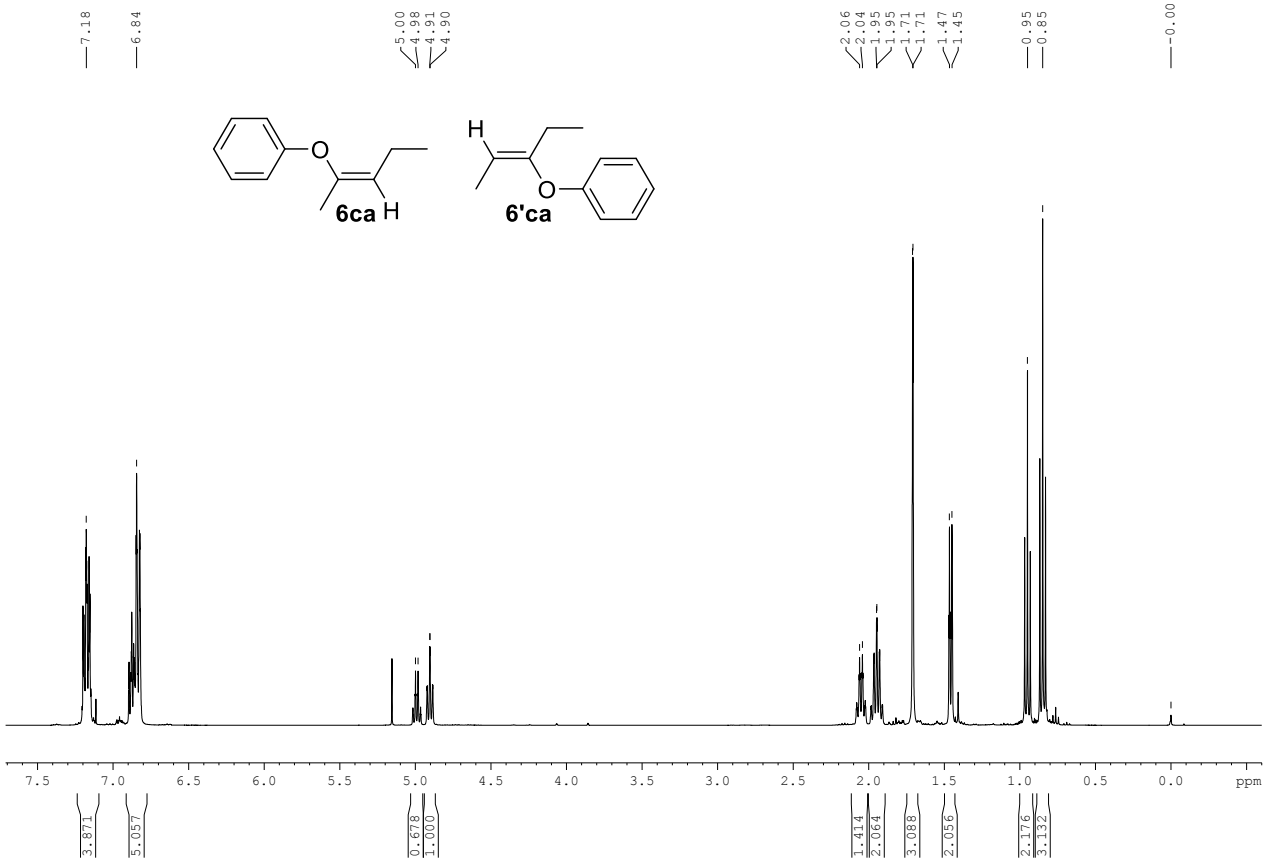
^{1}H NMR ($CDCl_3$) of 6ba



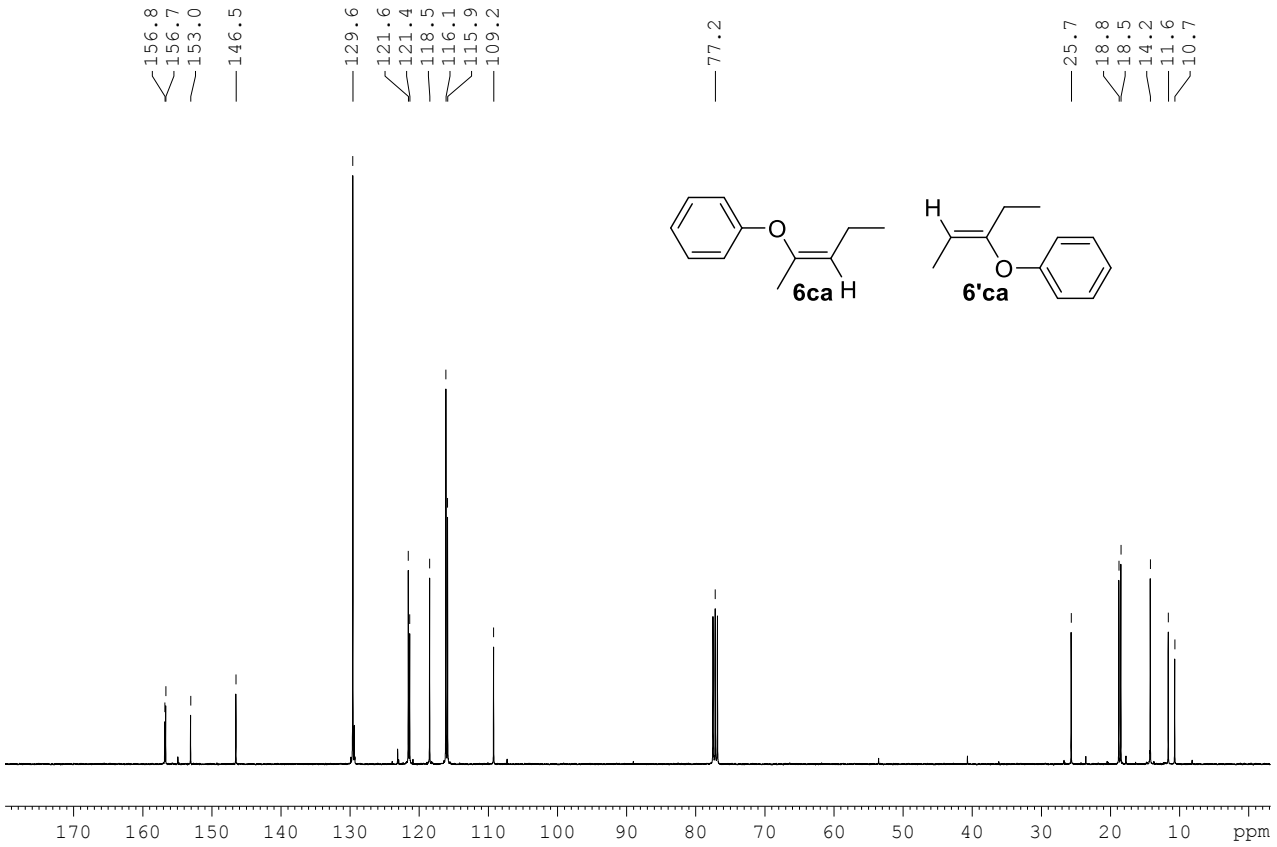
^{13}C-{^{1}H} NMR ($CDCl_3$) of 6ba



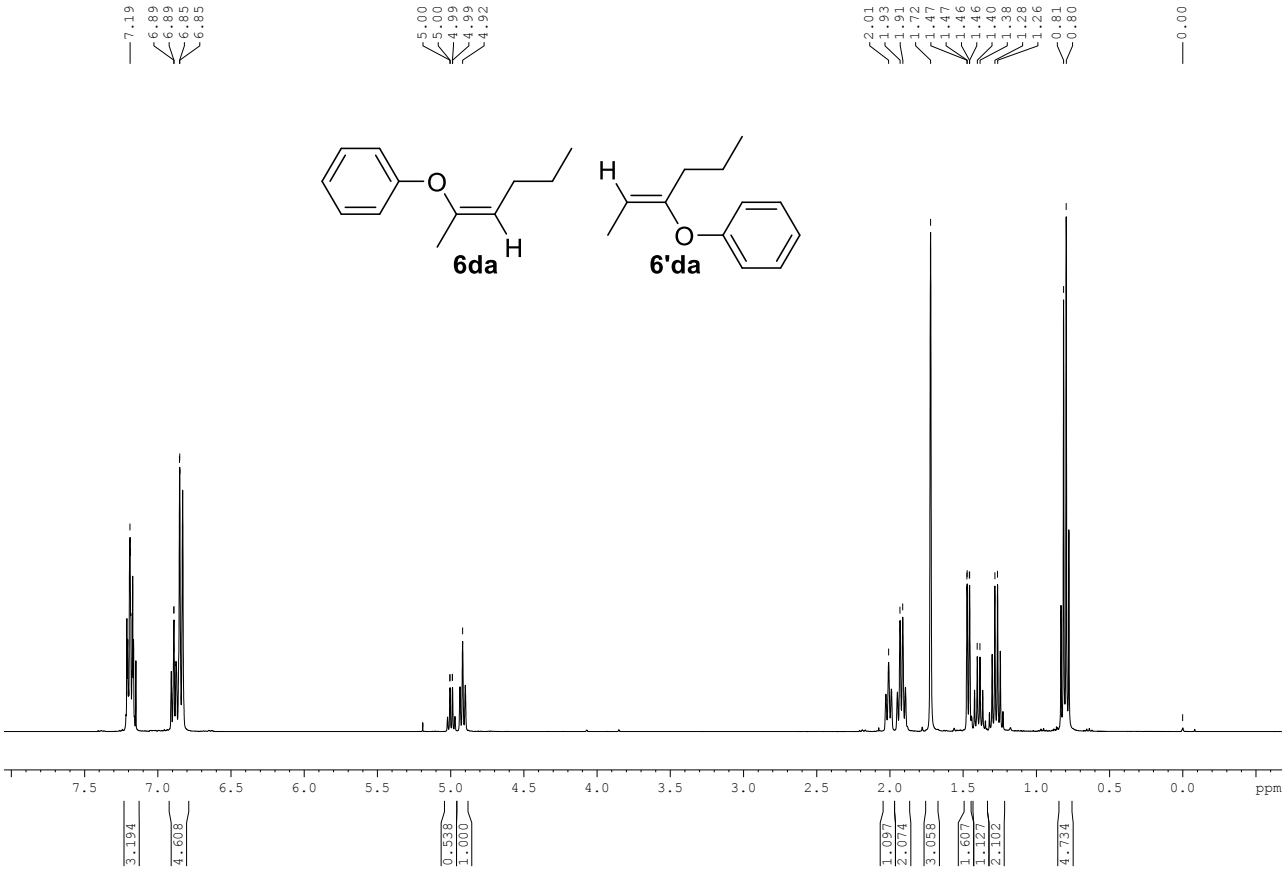
^{1}H NMR ($CDCl_3$) of 6ca/6'ca (6ca/6'ca = 60/40)



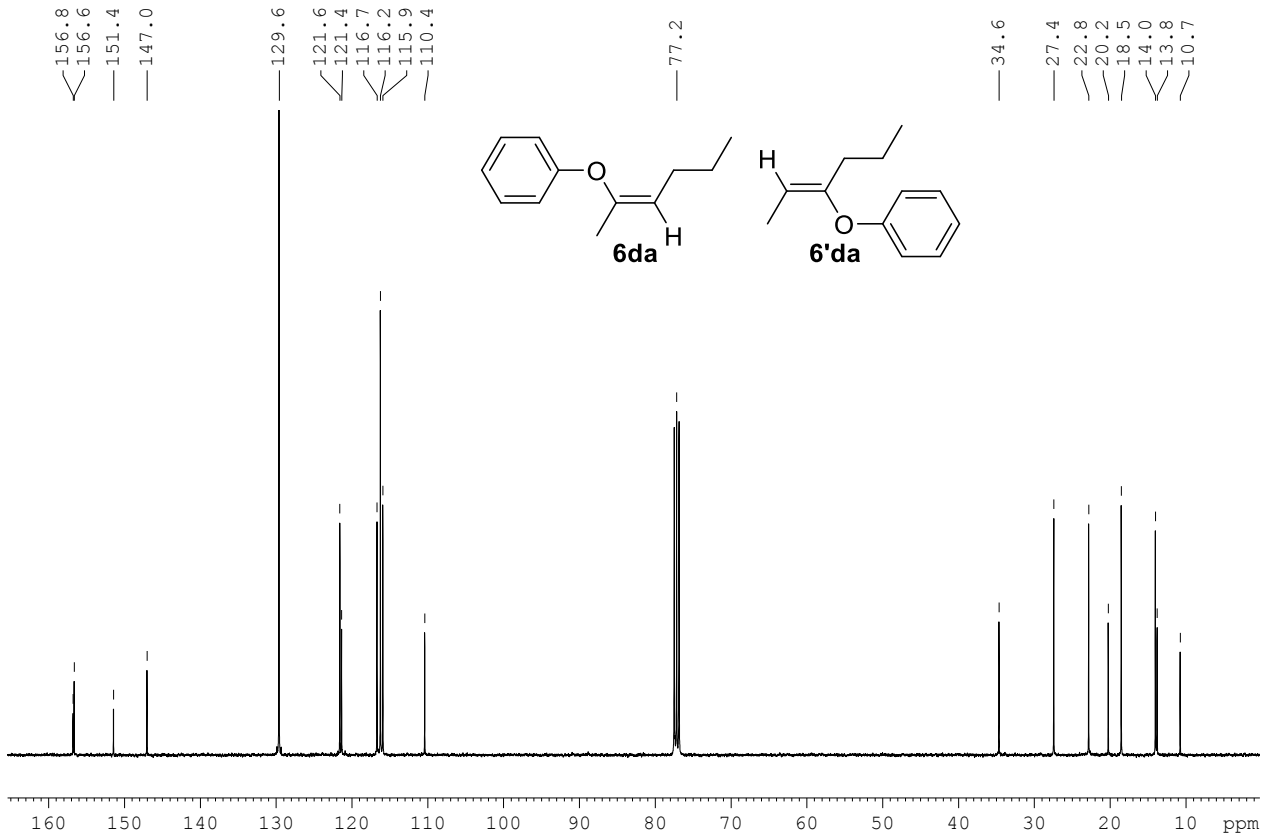
^{13}C-{^{1}H} NMR ($CDCl_3$) of 6ca/6'ca (6ca/6'ca = 60/40)



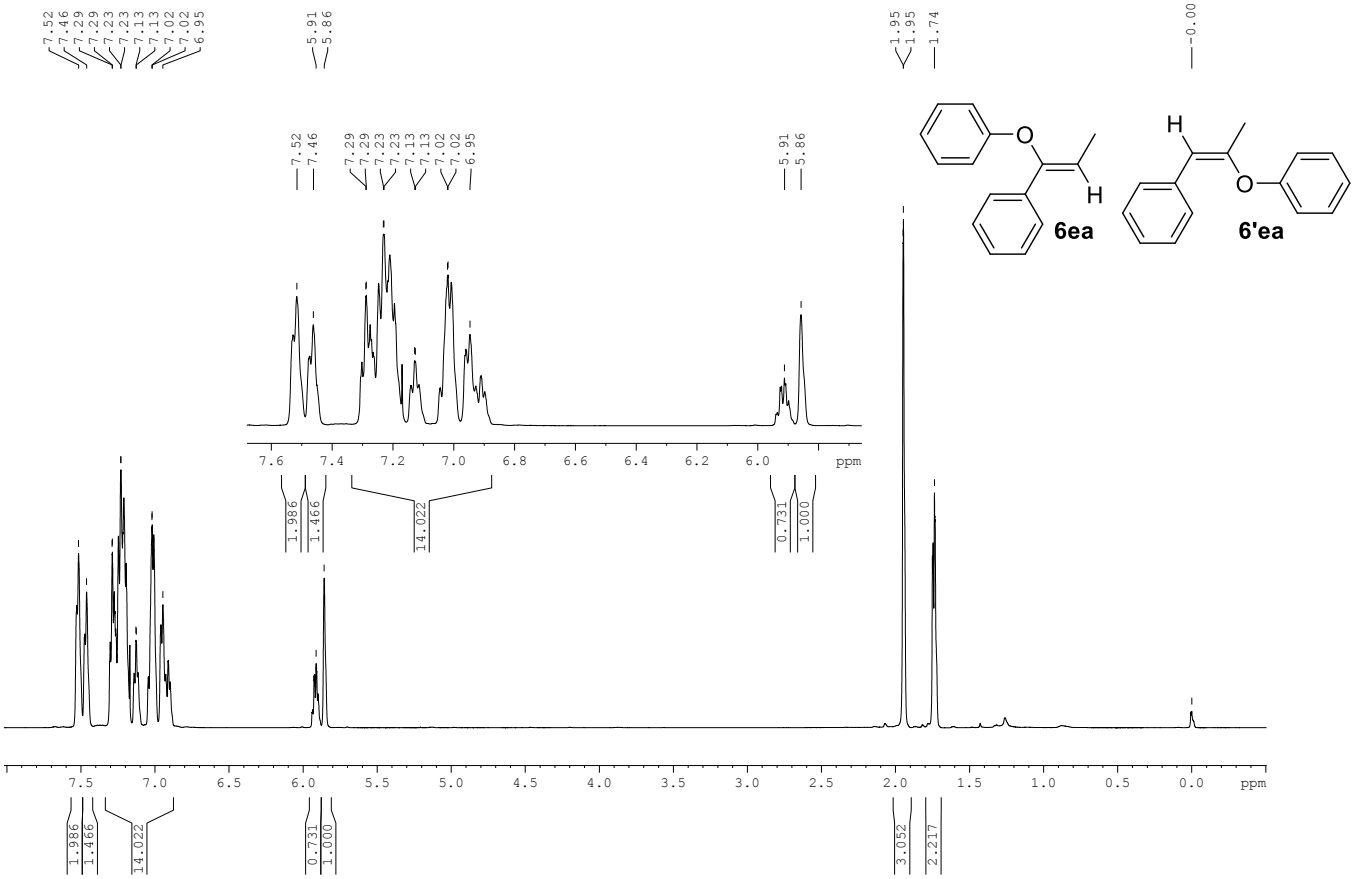
^{1}H NMR ($CDCl_3$) of 6da/6'da (6da/6'da = 65/35)



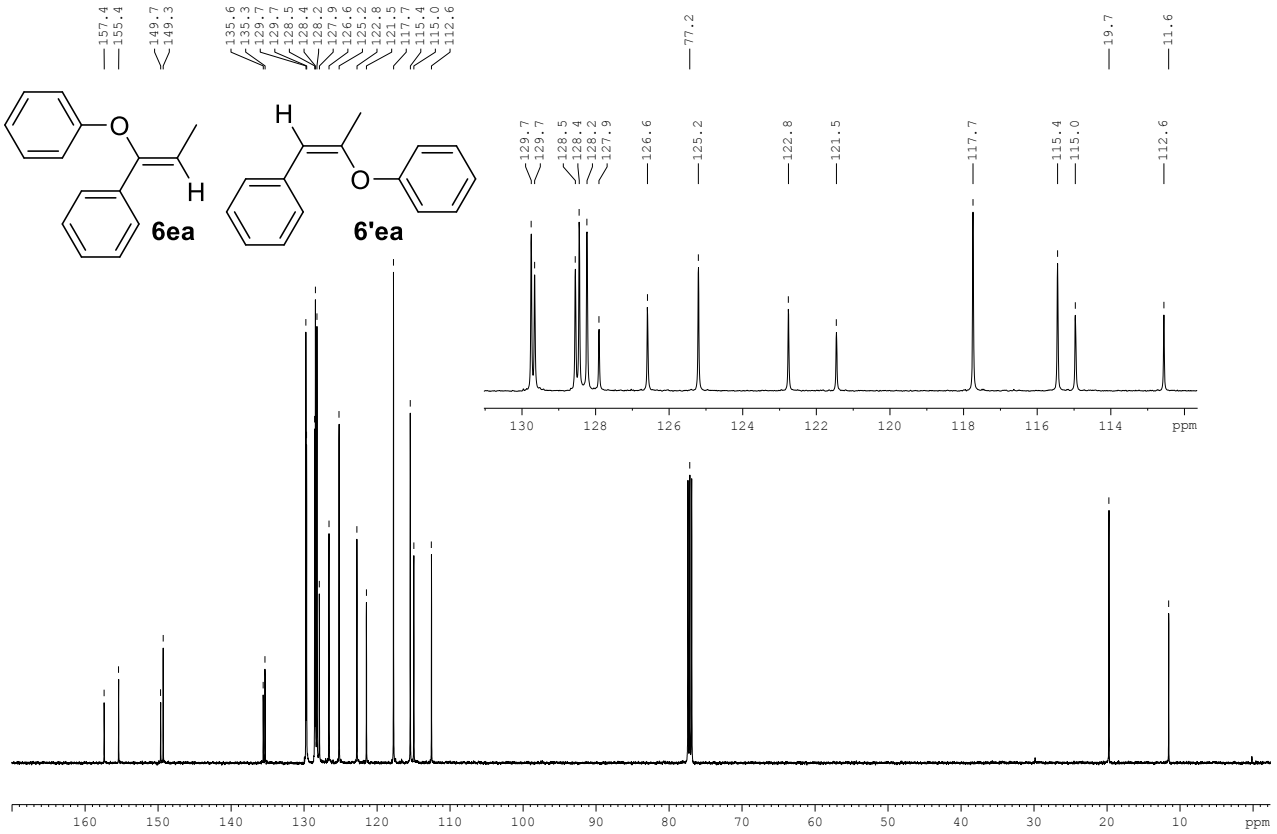
^{13}C-{^{1}H} NMR ($CDCl_3$) of 6da/6'da (6da/6'da = 65/35)



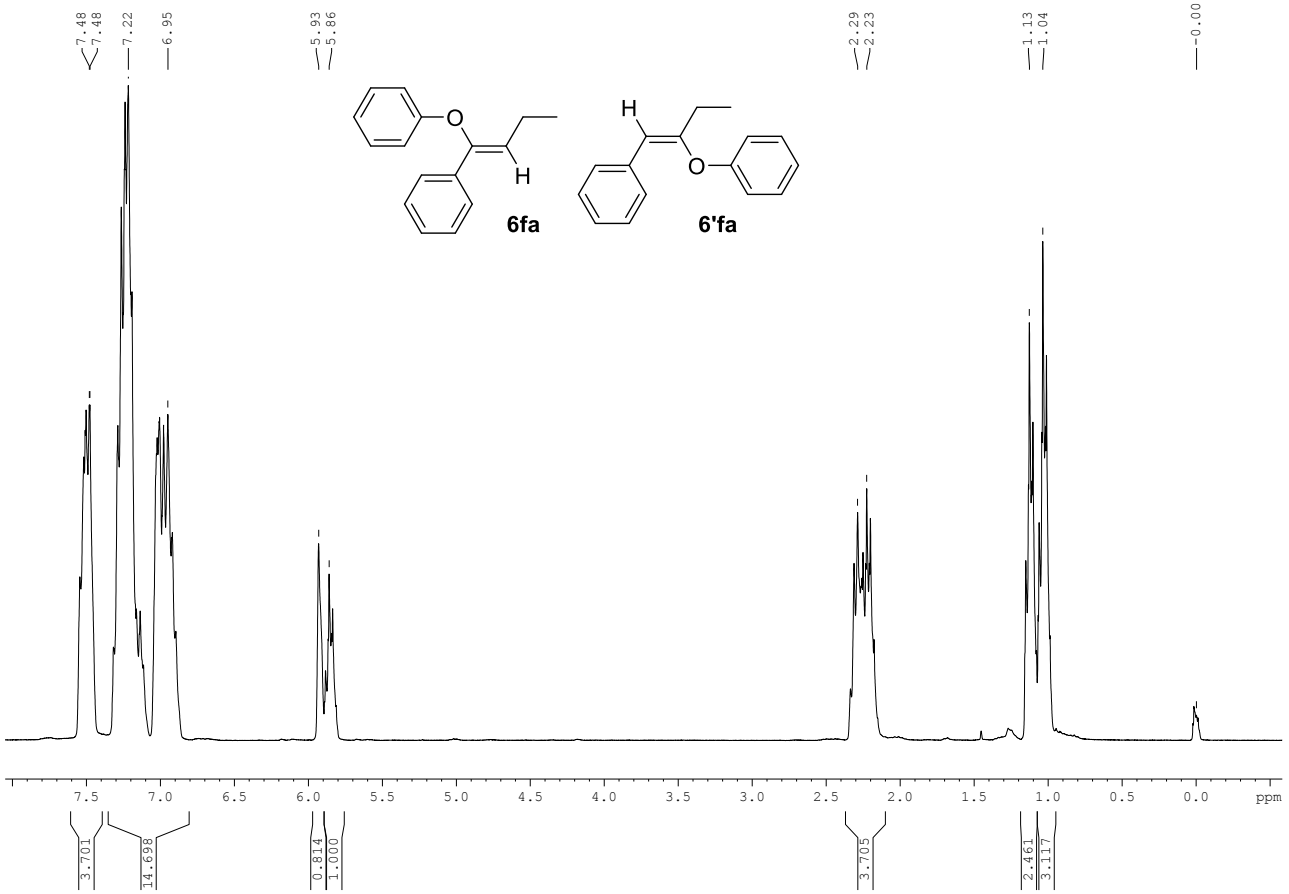
^{1}H NMR ($CDCl_3$) of 6ea/6'ea (6ea/6'ea = 42/58)



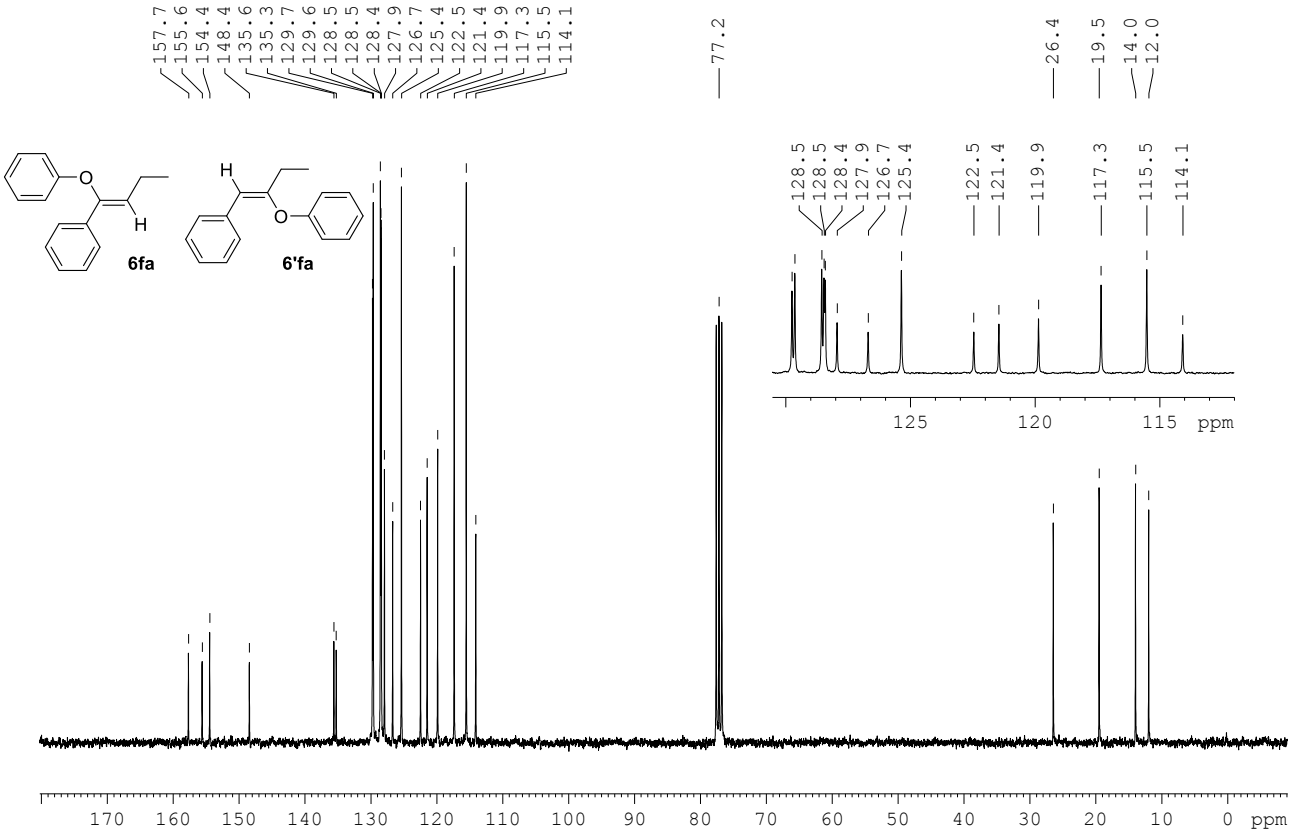
^{13}C-{^{1}H} NMR ($CDCl_3$) of 6ea/6'ea (6ea/6'ea = 42/58)



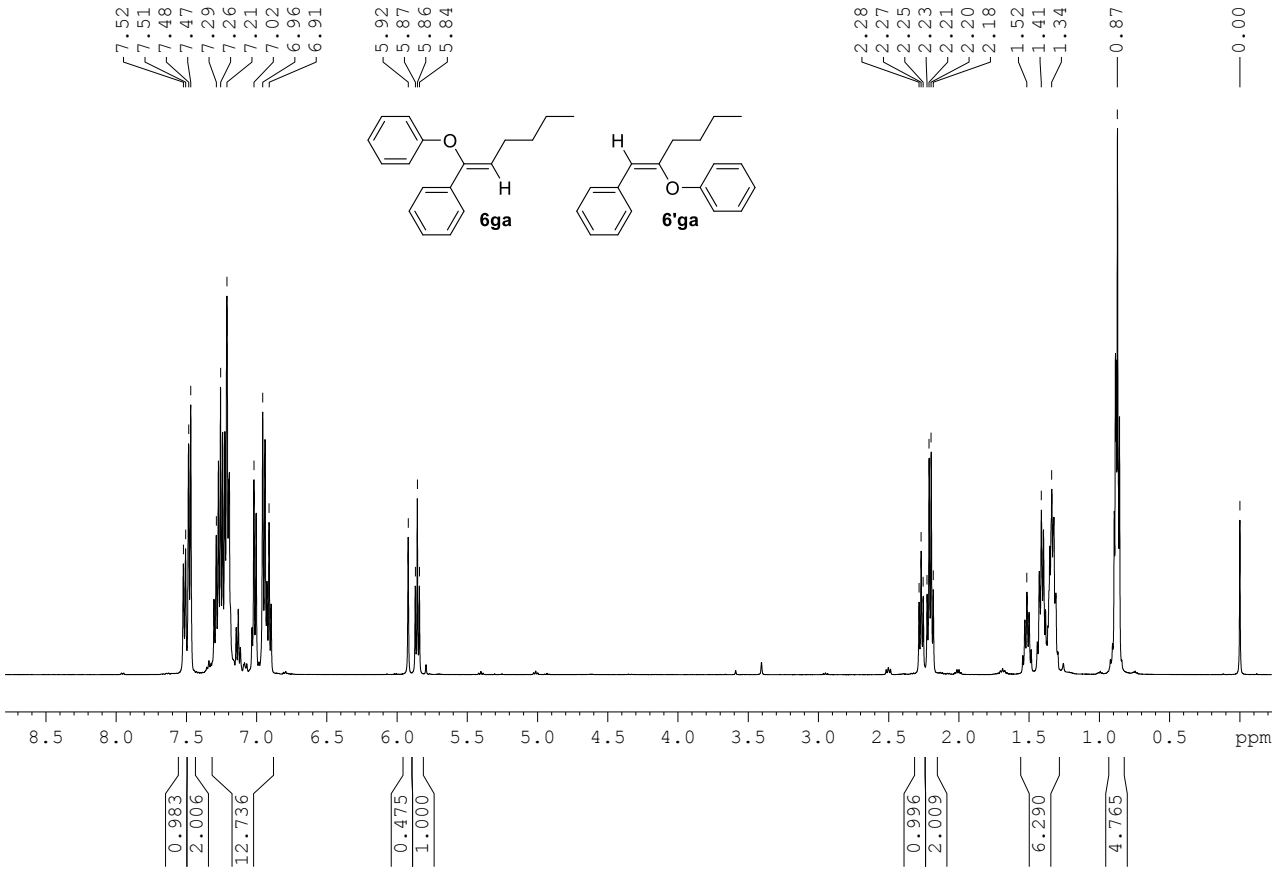
^{1}H NMR ($CDCl_3$) of 6fa/6'fa (6fa/6'fa = 55/45)



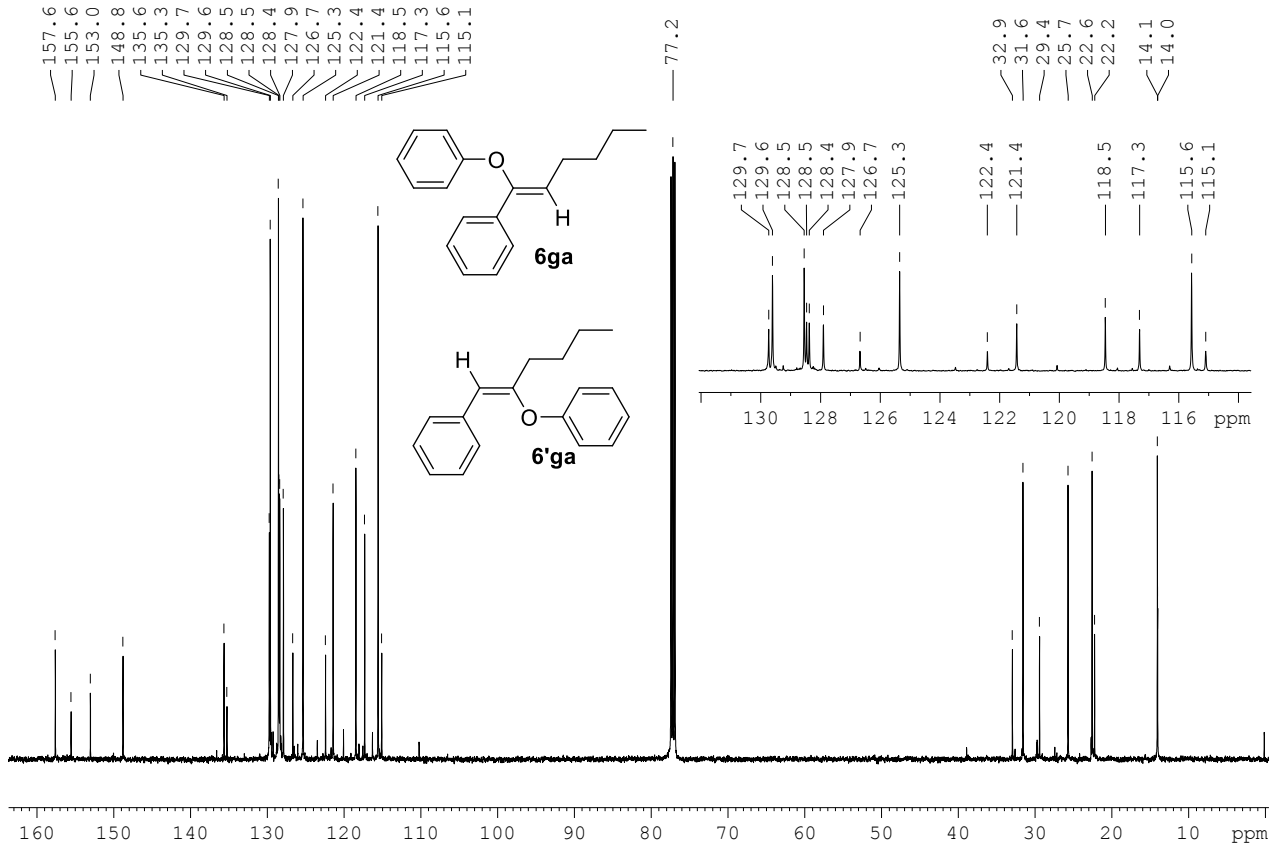
^{13}C-{^{1}H} NMR ($CDCl_3$) of 6fa/6'fa (6fa/6'fa = 55/45)



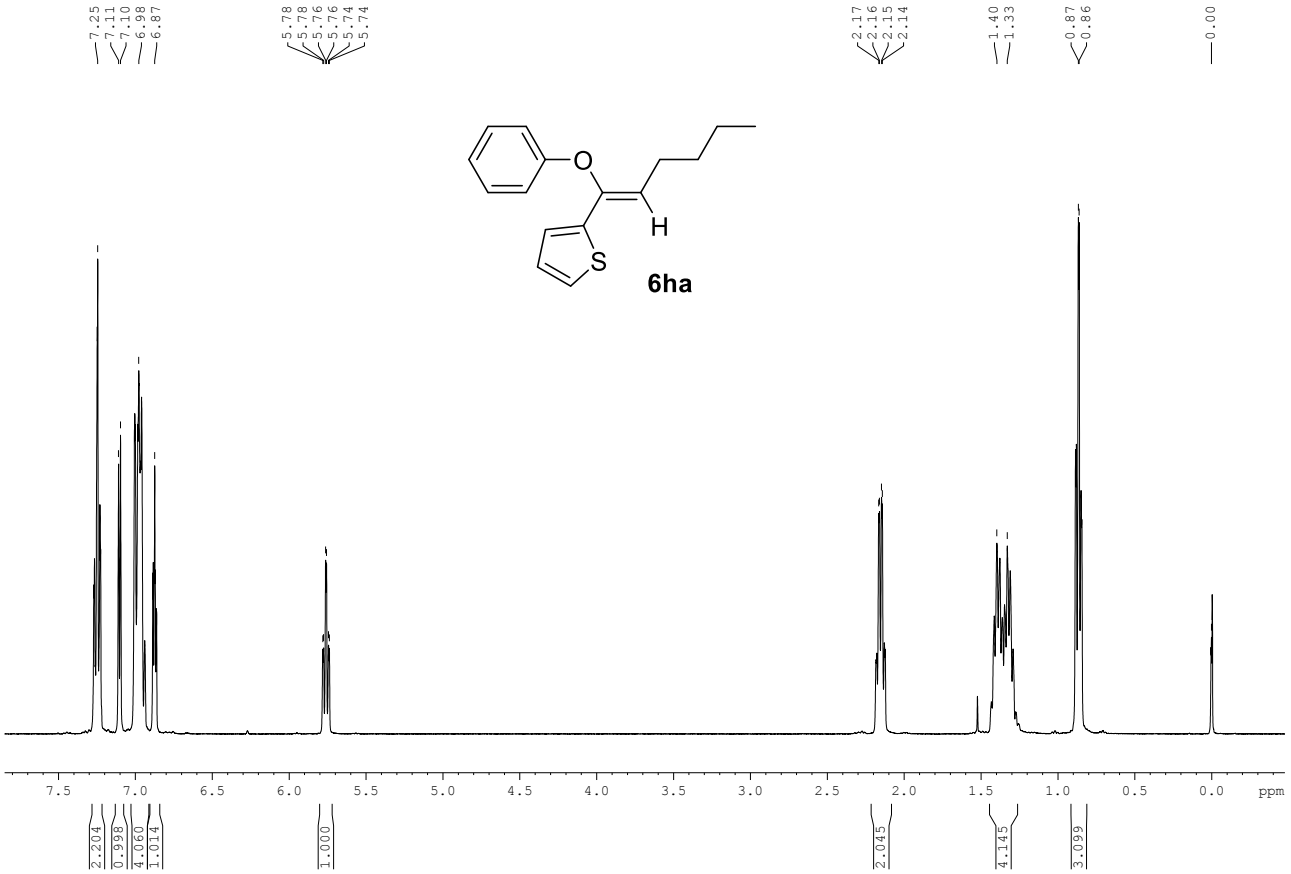
^{1}H NMR ($CDCl_3$) of 6ga/6'ga (6ga/6'ga = 68/32)



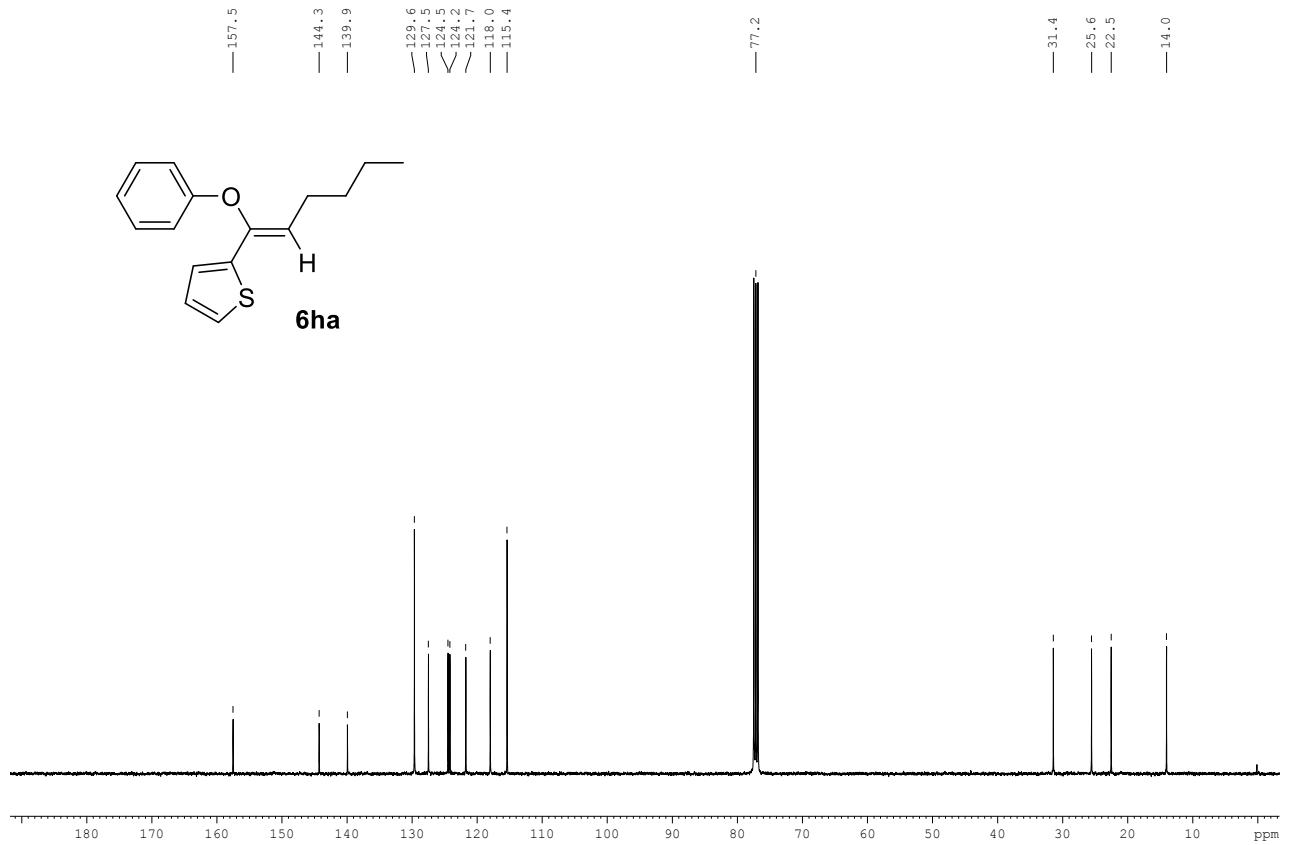
^{13}C-{^{1}H} NMR ($CDCl_3$) of 6ga/6'ga (6ga/6'ga = 68/32)



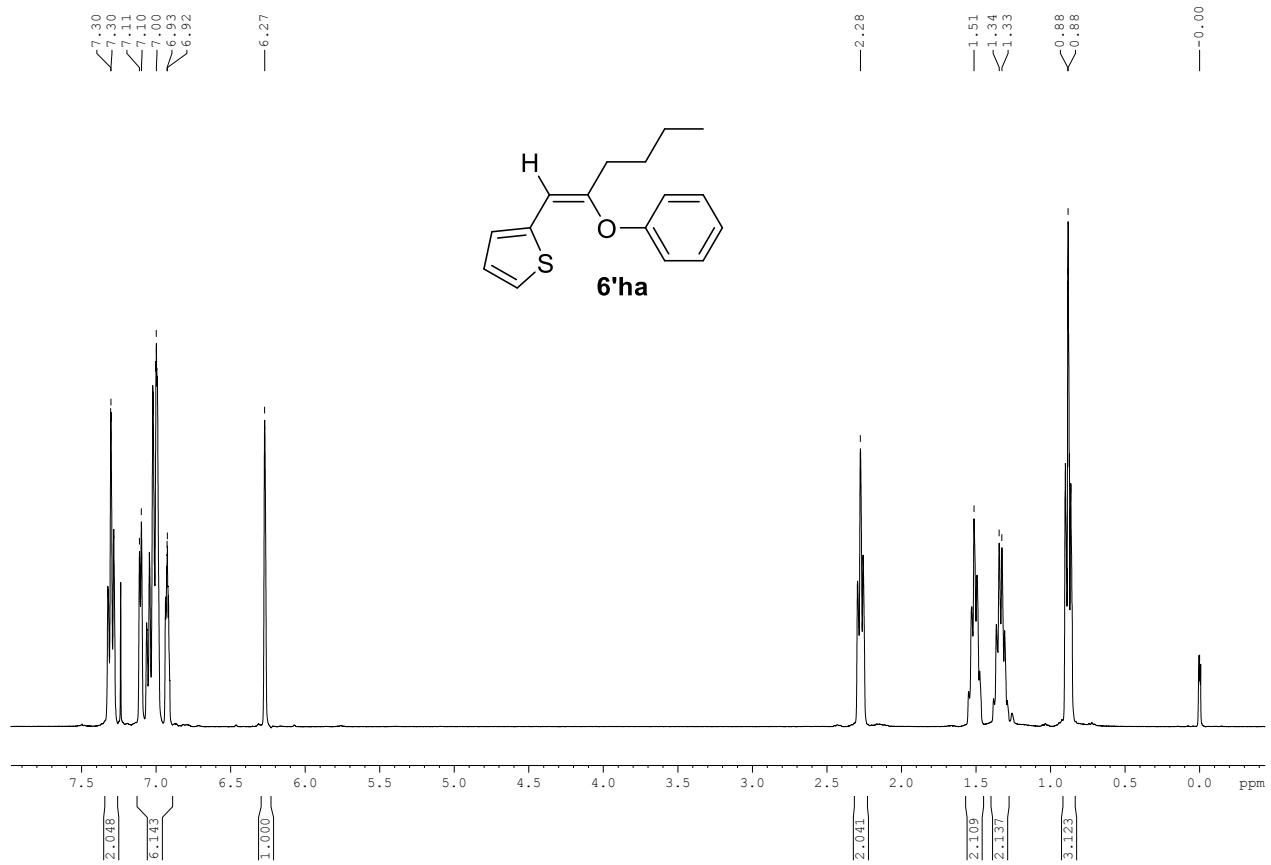
^{1}H NMR ($CDCl_3$) of 6ha



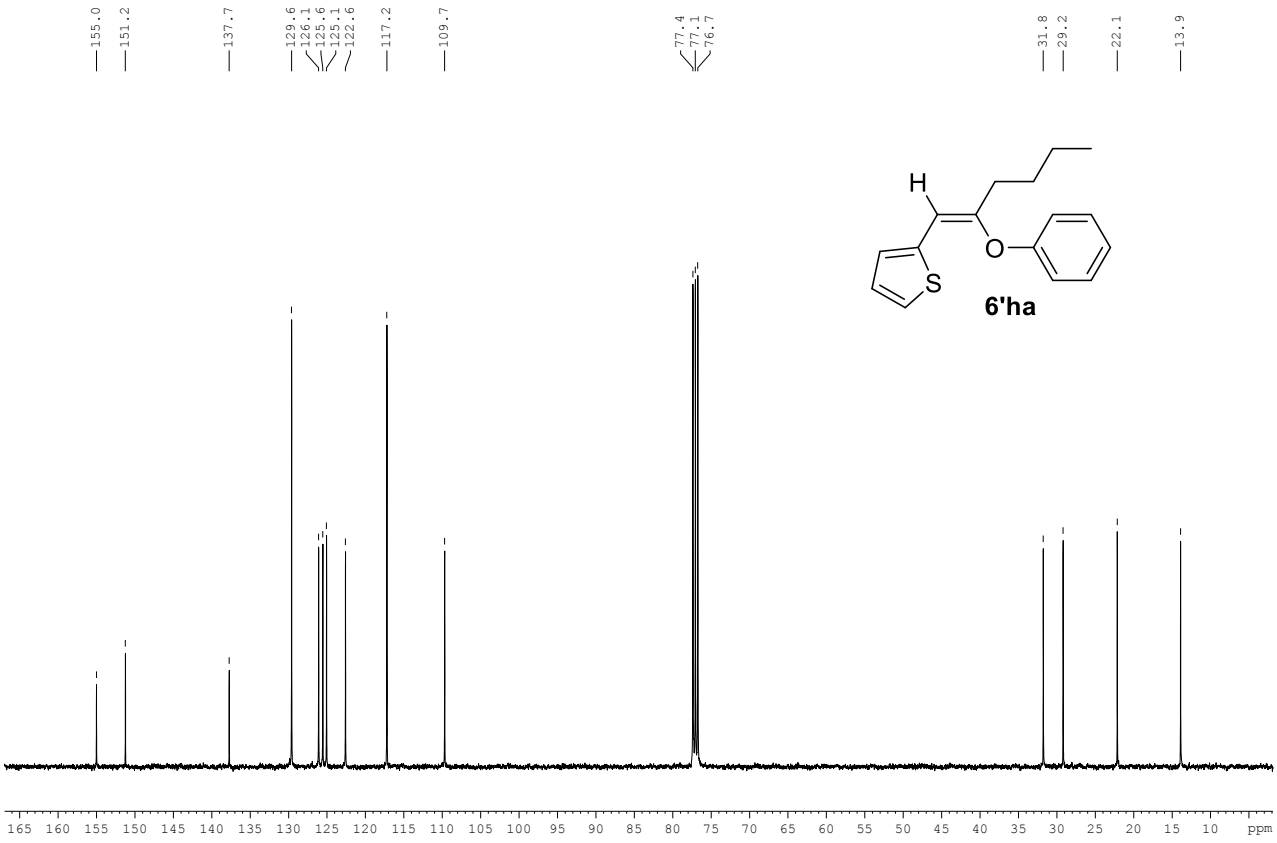
^{13}C-{^{1}H} NMR ($CDCl_3$) of 6ha



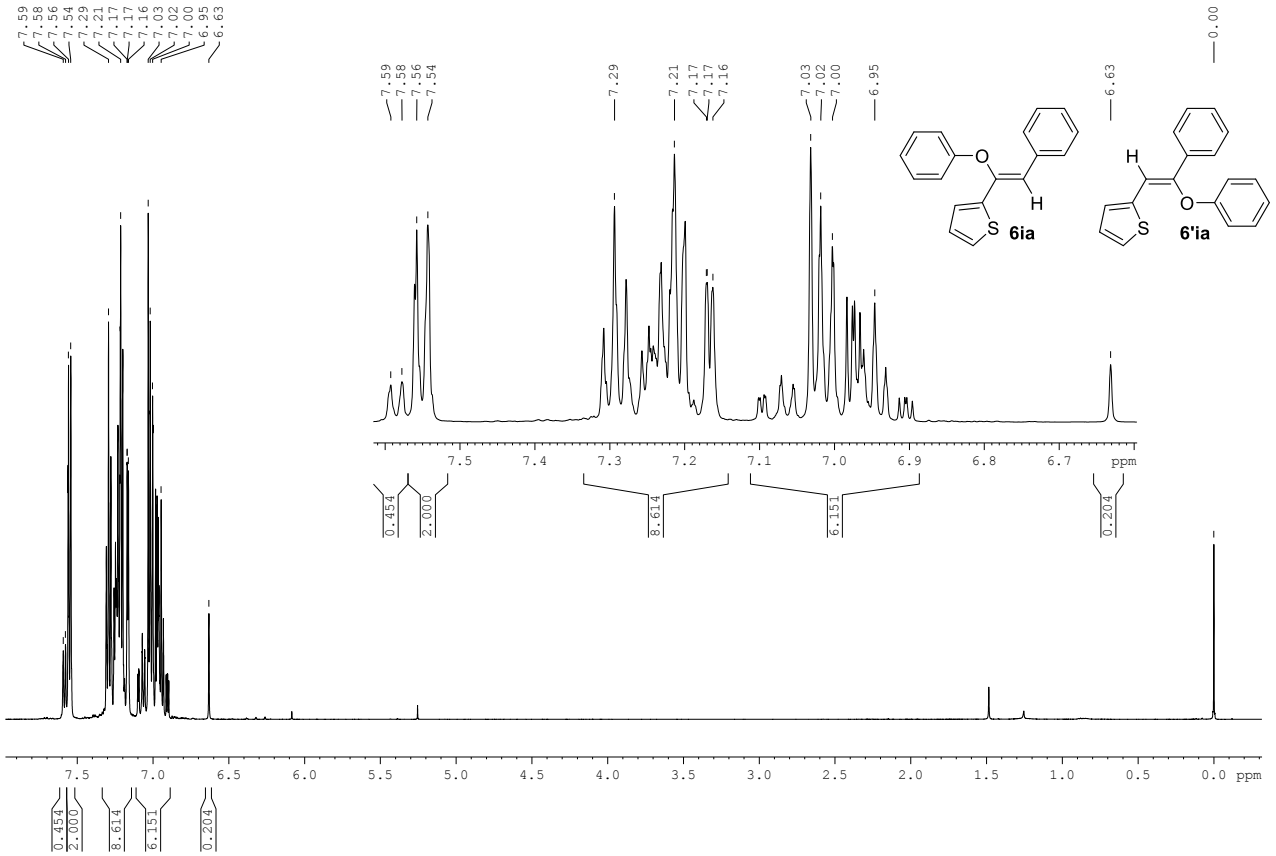
^{1}H NMR ($CDCl_3$) of 6'ha



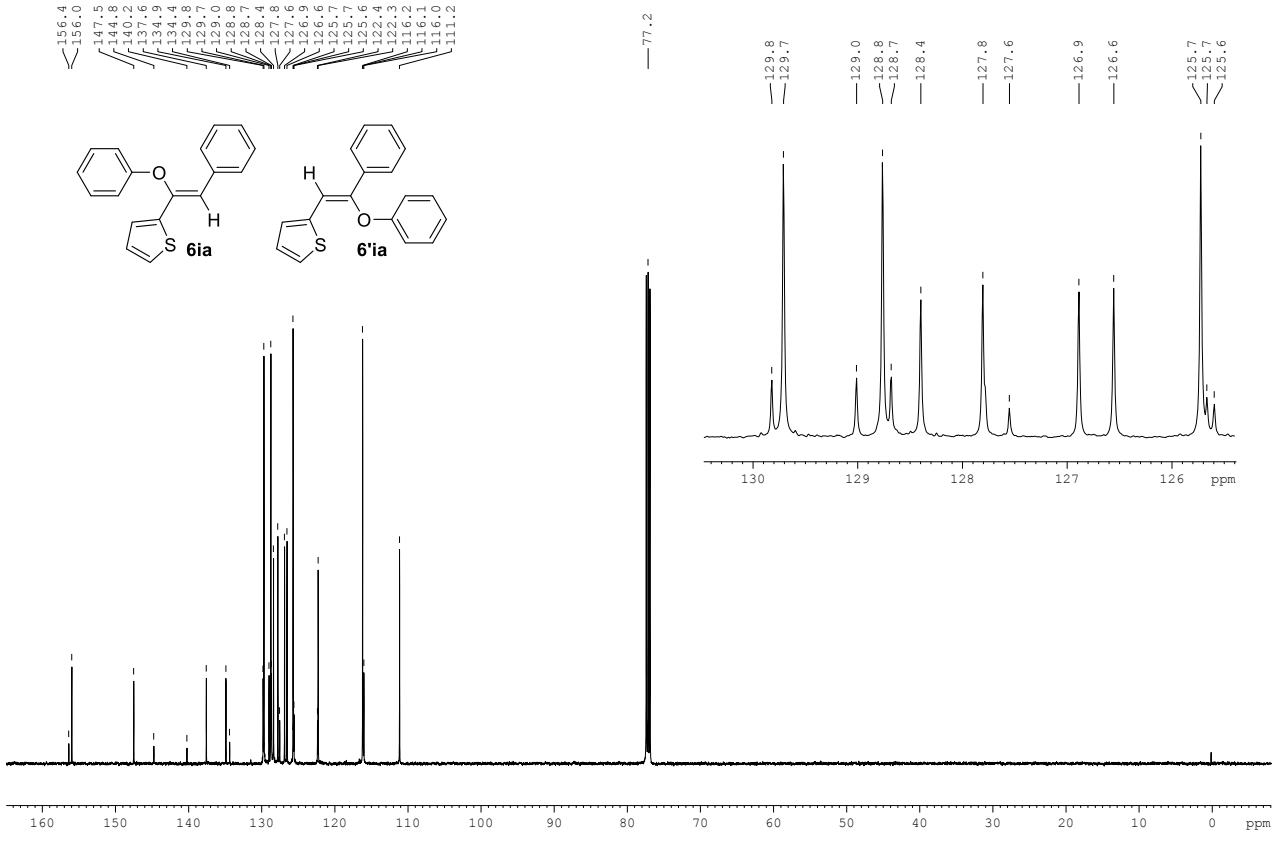
^{13}C-{^{1}H} NMR ($CDCl_3$) of 6'ha



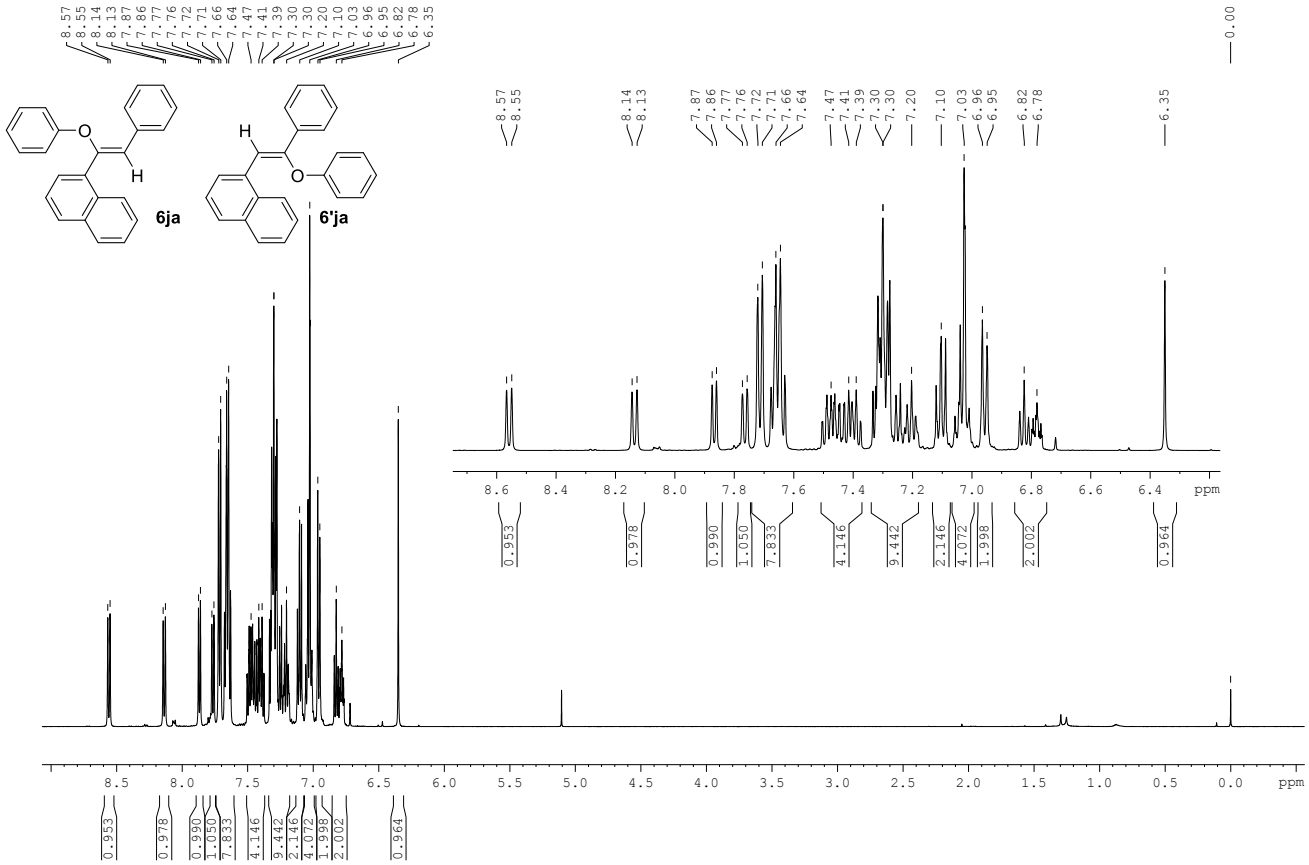
^{1}H NMR ($CDCl_3$) of 6ia/6'ia (6ia/6'ia = 19/81)



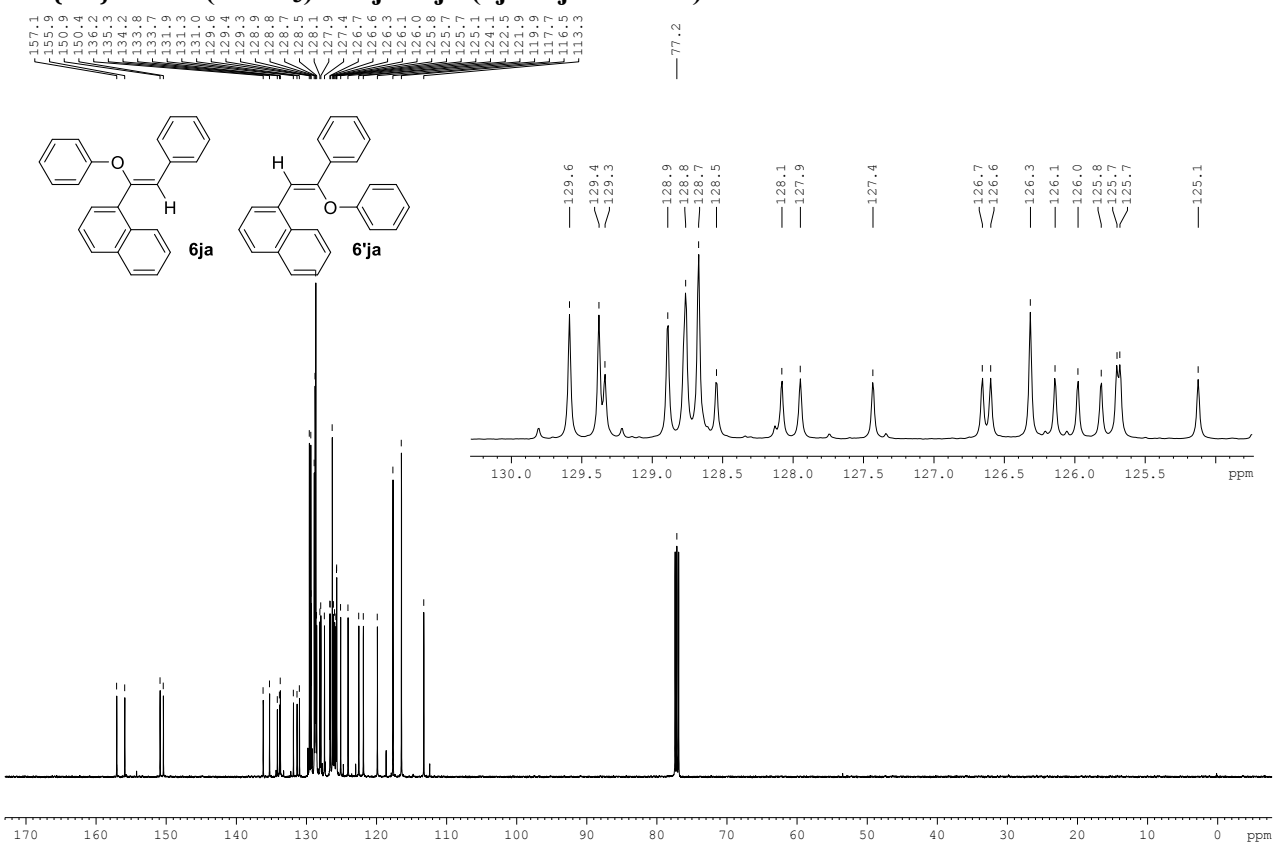
^{13}C-{^{1}H} NMR ($CDCl_3$) of 6ia/6'ia (6ia/6'ia = 19/81)



^{1}H NMR ($CDCl_3$) of 6ja/6'ja (6ja/6'ja = 50/50)



^{13}C-{^{1}H} NMR ($CDCl_3$) of 6ja/6'ja (6ja/6'ja = 50/50)



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