# Influence of Carbene and Phosphine Ligands on the Catalytic Activity of Gold Complexes in the Hydroamination and Hydrohydrazination of Alkynes

Sima Yazdani,[†,‡] Glen P. Junor,[†] Jesse L. Peltier,[†] Milan Gembicky,[†] Rodolphe Jazzar,[*,†] Douglas B. Grotjahn,[*,‡] Guy Bertrand[*,†]

[†] UCSD-CNRS Joint Research Laboratory (UMI 3555), Department of Chemistry and Biochemistry, University of California, San Diego, La Jolla, California 92093-0358, United States

[‡] Department of Chemistry and Biochemistry, San Diego State University, 5500 Campanile Drive, San Diego, California 92182-1030, United States

**Corresponding Author E-mail Addresses:**

gbertrand@ucsd.edu
dbgrotjahn@sdsu.edu
rjazzar@ucsd.edu

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# I. General Considerations

All the catalytic experiments were performed in air using commercial grade solvents and reagents unless otherwise noted. All the kinetic experiments were performed three times to verify the reproducibility of the results. All other manipulations were performed using standard glovebox and Schlenk techniques. Glassware was dried in an oven overnight at 150 °C or flame-dried, and solvent were dried and degassed before use. Benzene, diethyl ether, and n-pentane and were freshly distilled over Na metal. Hexanes, dichloromethane, and chloroform were freshly distilled over $CaH_2$.

**NMR**: Deuterium-labeled solvents were purchased from Cambridge Isotope Laboratories. NMR: Multinuclear NMR data were recorded on a Varian INOVA 500 MHz, a Bruker Avance 300 MHz at UCSD or a Bruker 400 MHz and Bruker 600 MHz at SDSU. Chemical shifts (δ) are reported in parts per million (ppm) and are referenced to residual solvent signals ($^1H$, $^{13}C$). Coupling constants J are given in hertz (Hz). NMR multiplicities are abbreviated as follows: s = singlet, d = doublet, t = triplet, q = quartet, sext = sextet, sept = septet, m = multiplet, br = broad. All spectra were recorded at 298 K unless otherwise noted.

**X-Ray Crystallography**: Single-crystal X-ray structure determinations were carried out at low temperature on a Bruker P4, Platform, or Kappa diffractometer equipped with a Mo (λ = 0.710 73 Å) or Cu (λ = 1.541 78 Å) radiation source and a Bruker APEX detector. Crystals were selected under oil, mounted on nylon loops, then immediately placed in a cold stream of nitrogen. All structures were solved by direct methods with SIR 2004 or SHELXS and refined by full-matrix least-squares procedures utilizing SHELXL within the Olex 2 small-molecule solution,[1] refinement, and analysis software package.

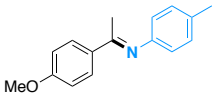
# II. Experimental methods

## II.1. Hydroamination scope – (*cf.* Scheme 3)

### A. General procedure

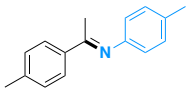
In air, a scintillation vial (3 mL) was charged with ($^{IPr}$BiCAAC)AuCl (2.5 mol%, 0.029 mmol), KBAr$^{F}$ (2.5 mol%, 0.029 mmol), $C_6H_6$ (1 mL) and the alkyne (1.163 mmol, 1.0 eq.). After stirring for two minutes, the amine (1.163 mmol, 1.0 eq.) was added as a solution in $C_6H_6$ (0.5 mL). The mixture was then set stirring according to reaction time and temperature listed in scheme 3. The products were purified by column chromatography using Florisil eluting with a gradient mixture of DCM/hexane. To confirm the reproducibility of results some reactions were repeated up to 4 times.

**1a**



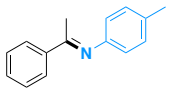

Compound **1a** was isolated in 95% yield (0.264 g) and agrees with a previous literature report.[2] $^{1}$H NMR (300 MHz, $CDCl_3$) δ 7.95 (d, *J* = 9.0 Hz, 2H), 7.18 – 7.13 (m, 2H), 6.96 (d, *J* = 8.9 Hz, 2H), 6.71 (d, *J* = 8.2 Hz, 2H), 3.87 (s, 3H), 2.36 (s, 3H), 2.21 (s, 3H). $^{13}$C{$^{1}$H} (126 MHz, $CDCl_3$) δ 164.7, 161.4, 149.2, 132.4, 132.3, 129.5, 128.8, 119.65, 113.6, 55.4, 20.97, 17.2.

**1b**



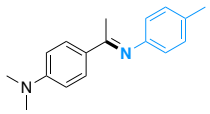

Compound **1b** was isolated in 90% yield (0.234 g) and agrees with a previous literature report.[2] $^{1}$H NMR (300 MHz, $CDCl_3$) δ 8.11 (d, *J* = 8.2 Hz, 2H), 7.48 (d, *J* = 7.7 Hz, 2H), 7.39 (d, *J* = 7.7 Hz, 2H), 6.94 (d, *J* = 8.2 Hz, 2H), 2.65 (s, 3H), 2.59 (s, 3H), 2.46 (s, 3H). $^{13}$C{$^{1}$H} NMR (75 MHz, $CDCl_3$) δ 165.4, 149.3, 140.7, 137.1, 132.6, 129.6, 129.1, 119.6, 21.5, 21.0, 17.4.

**1c**



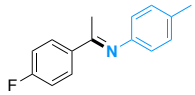

Compound **1c** was isolated in 95% yield (0.231 g) and agrees with a previous literature report.[2] $^{1}$H NMR (300 MHz, $CDCl_3$) δ 8.00 – 7.95 (m, 2H), 7.47 – 7.43 (m, 3H), 7.16 (d, *J* = 8.0 Hz, 2H), 6.71 (d, *J* = 8.2 Hz, 2H), 2.36 (s, 3H), 2.24 (s, 3H). $^{13}$C{$^{1}$H} NMR (126 MHz, $CDCl_3$) δ 165.7, 149.1, 139.8, 132.7, 130.5, 129.6, 128.5, 127.3, 119.5, 21.0, 17.5.

**1d**



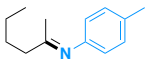

Compound **1d** was isolated in 97% yield (0.284 g) and agrees with a previous literature report.[3] $^{1}$H NMR (300 MHz, $CDCl_3$) δ 7.89 (d, *J* = 9.0 Hz, 2H), 7.13 (d, *J* = 7.9 Hz, 2H), 6.71 (dd, *J* = 8.7, 7.4 Hz, 4H), 3.03 (s, 6H), 2.34 (s, 3H), 2.18 (s, 3H). $^{13}$C{$^{1}$H}NMR (126 MHz, $CDCl_3$) δ 164.7, 152.0, 149.8, 132.1, 129.5, 128.6, 127.5, 120.0, 111.4, 40.4, 21.0, 17.0.

**1e**



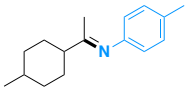

Compound **1e** was isolated in 90% yield (0.238 g) and agrees with a previous literature report.[4] $^{1}$H NMR (300 MHz, $C_6D_6$) δ 7.88 (dd, *J* = 9.0, 5.5 Hz, 2H), 7.13 (d, *J* = 7.9 Hz, 2H), 6.94 – 6.87 (m, 2H), 6.81 (d, *J* = 8.2 Hz, 2H), 2.27 (s, 3H), 1.88 (s, 3H). $^{13}$C{$^{1}$H} NMR (126 MHz, $C_6D_6$) δ 165.6, 163.6, 163.1, 149.8, 136.1 (d, *J* = 3.1 Hz), 132.6, 129.9, 129.7 (dd, *J* = 8.3, 2.1 Hz), 119.8, 115.5 – 115.1 (m), 20.9, 16.6 (d, *J* = 2.6 Hz). $^{19}$F NMR (282 MHz, $C_6$D6) δ -111.54

**1f**



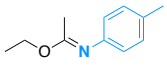

Compound **1f** was isolated in 92% yield (0.202 g) and agrees with a previous literature report.[5] $^{1}$H NMR (300 MHz, $C_6D_6$) 7.01 (d, *J* = 8.0 Hz, 2H), 6.70 (d, *J* = 8.2 Hz, 2H), 2.16 (s, 3H), 2.25 – 2.11 (m, 3H), 1.71 – 1.54 (m, 2H), 1.48 (s, 3H), 1.41 – 1.27 (m, 3H), 0.91 (t, *J* = 7.3 Hz, 3H). $^{13}$C{$^{1}$H} NMR (126 MHz, $C_6D_6$) δ 170.2, 150.3, 131.95, 129.8, 119.8, 41.3, 28.5, 22.8, 20.9, 19.2, 14.3.

**1g**



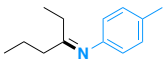
Compound **1g** was isolated in 93% yield (0.248 g) and agrees with a previous literature report.[3] $^1$H NMR (300 MHz, $C_6D_6$) δ 7.01 (d, *J* = 8.1 Hz, 2H), 6.68 (d, *J* = 8.2 Hz, 2H), 2.16 (s, 3H), 1.88 (dd, *J* = 11.2, 2.9 Hz, 2H), 1.79 – 1.56 (m, 4H), 1.51 (s, 3H), 1.27 – 1.07 (m, 5H). $^{13}$C{$^1$H} NMR (126 MHz, $C_6D_6$) δ 173.8, 150.4, 131.8, 129.8, 119.6, 49.2, 30.6, 26.6, 26.6, 20.9, 17.8.

**1h**



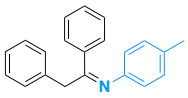
Compound **1h** was isolated in 97% yield (0.200 g). $^1$H NMR (300 MHz, $CDCl_3$) δ 7.10 (d, *J* = 7.9 Hz, 2H), 6.68 (d, *J* = 8.2 Hz, 2H), 4.24 (q, *J* = 7.1 Hz, 2H), 2.33 (s, 3H), 1.84 (s, 3H), 1.36 (t, *J* = 7.1 Hz, 3H). $^{13}$C{$^1$H} NMR (75 MHz, $CDCl_3$) δ 160.9, 146.3, 131.6, 129.1, 120.6, 61.0, 20.4, 15.8, 13.9.

**1i**



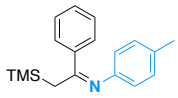
Compound **1i** was isolated in 50% yield (0.110 g) as a mixture of cis/trans isomers. $^1$H NMR (300 MHz, $C_6D_6$) δ 6.99 (dd, *J* = 8.2, 2.0 Hz, 4H), 6.69 (dd, *J* = 8.2, 2.0 Hz, 4H), 2.20 (q, *J* = 7.4 Hz, 3H), 2.15 (d, *J* = 3.3 Hz, 6H), 2.03 – 1.87 (m, 4H), 1.84 – 1.65 (m, 2H), 1.23 (t, *J* = 7.3 Hz, 6H), 0.96 (t, *J* = 7.3 Hz, 3H), 0.75 (t, *J* = 7.7 Hz, 3H), 0.61 (t, *J* = 7.3 Hz, 3H). $^{13}$C{$^1$H} $^{13}$C NMR (126 MHz, $C_6D_6$) δ 174.3 (d, *J* = 41.5 Hz), 150.1 (d, *J* = 3.7 Hz), 131.7 (d, *J* = 2.5 Hz), 129.8 (d, *J* = 4.3 Hz), 119.6 (d, *J* = 5.4 Hz), 39.9, 35.2, 31.5, 26.5, 20.9, 20.7, 19.6, 14.2, 14.2, 11.8, 10.6.

**1j**



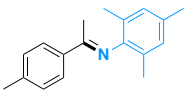
Compound **1j** was isolated in 76% yield (0.252 g) and agrees with a previous literature report.[6] $^1$H NMR (300 MHz, $C_6D_6$) δ 8.11 – 8.04 (m, 2H), 7.56 – 7.48 (m, 2H), 7.08 (dd, *J* = 4.8, 2.1 Hz, 4H), 6.94 (d, *J* = 8.2 Hz, 1H), 6.85 (d, *J* = 8.2 Hz, 1H), 3.92 (s, 2H), 2.10 (s, 3H). $^{13}$C{$^1$H} NMR (126 MHz, $C_6D_6$) δ 165.5, 149.4, 138.75, 138.0, 132.8, 131.95, 130.5, 129.9, 128.9, 128.6, 128.5, 126.45, 119.4, 36.0, 20.9.

**1k**



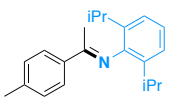

Compound **1k** (58% NMR yield) : $^1$H NMR (300 MHz, $CDCl_3$) δ 8.03 – 7.91 (m, 2H), 7.46 (td, *J* = 5.6, 5.1, 2.7 Hz, 3H), 7.30 (dd, *J* = 5.1, 2.0 Hz, 2H), 7.17 (d, *J* = 8.0 Hz, 2H), 6.72 (d, *J* = 8.2 Hz, 2H), 2.36 (s, 2H), 2.25 (s, 3H), 0.27 (s, 9H). $^{13}$C{$^1$H} (126 MHz, $CDCl_3$) δ 165.6, 149.2, 139.8, 132.1, 130.5, 129.6, 128.5 (t, *J* = 18.7 Hz), 127.3, 119.5, 105.2, 94.2, 19.2 (d, *J* = 446.9 Hz), 0.1.

**1l**



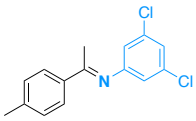
Compound **1l** was isolated in 95% yield (0.278 g) and agrees with a previous literature report.[7] $^1$H NMR (300 MHz, $C_6D_6$) δ 7.99 (d, *J* = 8.2 Hz, 2H), 7.05 (d, *J* = 8.0 Hz, 2H), 6.88 (s, 2H), 2.24 (s, 3H), 2.12 (s, 3H), 2.03 (s, 6H), 1.78 (s, 3H). $^{13}$C{$^1$H} (126 MHz, $C_6D_6$) δ 164.4, 147.6, 140.5, 137.0, 131.7, 129.2, 129.0, 127.6, 125.65, 21.3, 20.95, 18.2, 16.9.

**1m**



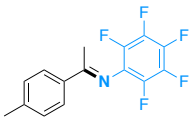

Compound **1m** was isolated in 99% yield (0.338 g). $^1$H NMR (500 MHz, $C_6D_6$) δ 7.96 (d, *J* = 7.9 Hz, 2H), 7.20 – 7.07 (m, 3H), 7.03 (d, *J* = 7.9 Hz, 2H), 2.87 (p, *J* = 6.8 Hz, 2H), 2.10 (s, 3H), 1.83 (s, 3H), 1.13 (dd, *J* = 22.2, 7.1 Hz, 12H). $^{13}$C NMR (126 MHz, $C_6D_6$) δ 164.3, 147.6, 140.7, 136.8, 136.3, 129.4, 127.6, 123.8, 123.4, 28.8, 23.5, 23.0, 21.3, 17.7.

**1n**



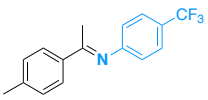

Compound **1n** was isolated in 94% yield (0.304 g). $^1$H NMR (300 MHz, $C_6D_6$) δ 7.80 (d, *J* = 8.3 Hz, 2H), 7.00 (d, *J* = 8.0 Hz, 2H), 6.94 (t, *J* = 1.9 Hz, 1H), 6.52 (d, *J* = 1.9 Hz, 1H), 2.10 (s, 3H), 1.60 (s, 3H). $^{13}$C{$^1$H} NMR (126 MHz, $C_6D_6$) δ 166.0, 154.5, 141.4, 136.3, 135.5, 129.3, 127.8, 123.1, 118.4, 21.4, 16.9.

**1o**



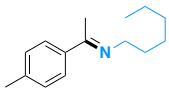
Compound **1o** was isolated in 96% yield (0.334 g). $^{1}$H NMR (500 MHz, $C_6D_6$) δ 7.82 (d, *J* = 8.3 Hz, 2H), 6.95 (d, *J* = 8.0 Hz, 2H), 2.07 (s, 3H), 1.71 (s, 3H). $^{13}$C{$^{1}$H} (126 MHz, $C_6D_6$) δ 172.7 (d, *J* = 1.3 Hz), 142.3, 139.6– 138.8(m), 138.5– 137.9(m), 137.6–136.9 (m), 136.6–136.0(m), 135.5, 129.3, 21.3, 18.3. $^{19}$F NMR (282 MHz, $C_6D_6$) δ -153.7, -164.7.

**1p**



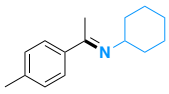
Compound **1p** was isolated in 42% yield (0.135 g) and agrees with previous literature report.[4] $^{1}$H NMR (500 MHz, $C_6D_6$) δ 7.88 (d, *J* = 7.9 Hz, 2H), 7.36 (d, *J* = 8.1 Hz, 2H), 7.03 (d, *J* = 7.9 Hz, 2H), 6.54 (d, *J* = 8.1 Hz, 1H), 2.12 (s, 3H), 1.72 (s, 3H). $^{13}$C{$^{1}$H} NMR (126 MHz, $C_6D_6$) δ 165.2, 155.7, 141.3, 136.5, 129.3, 127.8, 126.5 (d, *J* = 3.8 Hz), 119.8, 21.3, 16.9. $^{19}$F NMR (282 MHz, $C_6D_6$) δ -62.09.

**1q**



Compound **1q** was isolated under anhydrous conditions as a mixture of cis/trans isomers in 87% yield (0.220 g). 1H NMR (500 MHz, $C_6D_6$) 1H NMR (300 MHz, $C_6D_6$) δ 7.92 (d, J = 8.2 Hz, 2H), 7.75 (d, J = 8.2 Hz, 2H), 7.04 (d, J = 8.0 Hz, 2H), 6.87 (d, J = 8.0 Hz, 2H), 3.37 (t, J = 6.9 Hz, 2H), 2.12 (s, 3H), 2.11 (s, 3H), 1.99 (s, 3H), 1.83 (s, 3H), 1.59 – 1.42 (m, 4H), 1.40 – 1.28 (m, 8H), 1.15 – 1.08 (m, 2H), 0.95 – 0.83 (m, 6H), 0.77 – 0.50 (m, 3H). $^{13}$C{$^{1}$H} NMR (126 MHz, C6D6) δ 163.1, 139.3 – 138.2 (m), 132.4, 129.3 (d, J = 6.0 Hz), 129.0, 127.1, 84.1, 77.3, 52.3, 32.0 (d, J = 70.6 Hz), 27.9, 22.2 (d, J = 249.9 Hz), 15.3 – 11.8 (m).

**1r**

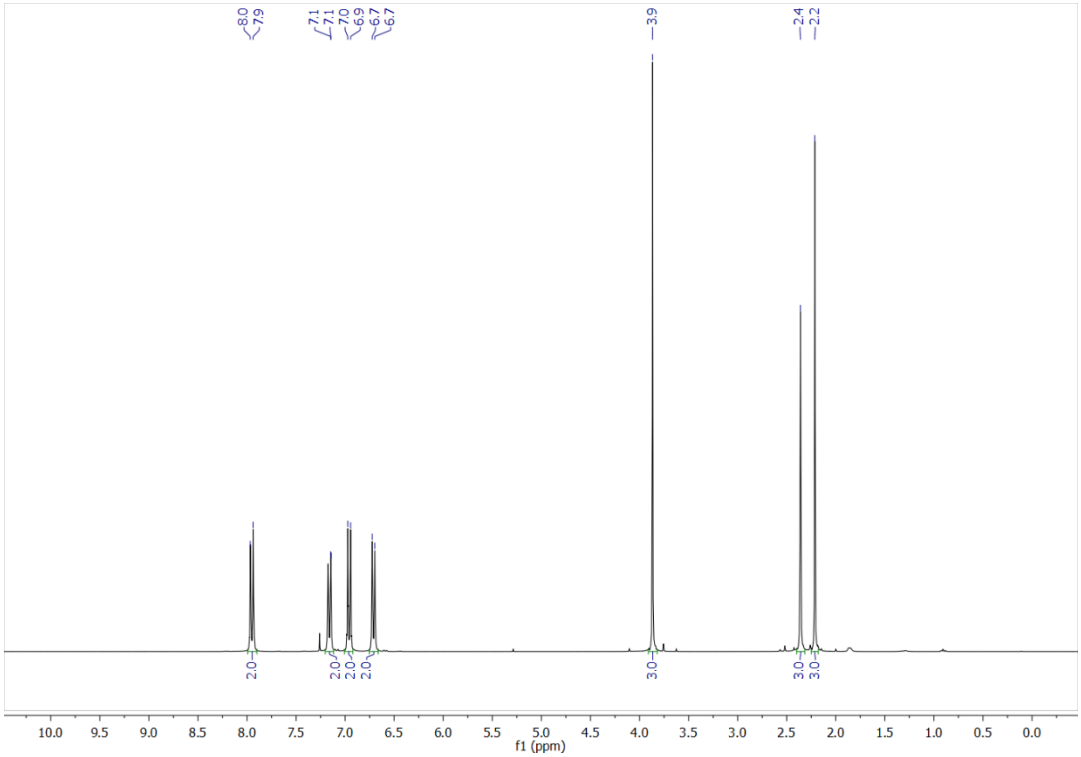


Compound **1r** was isolated in 67% yield (0.168 g). $^{1}$H NMR (300 MHz, $CDCl_3$) δ 7.66 (d, *J* = 8.2 Hz, 2H), 7.16 (d, *J* = 8.0 Hz, 2H), 3.47 (tt, *J* = 10.2, 4.1 Hz, 1H), 2.36 (s, 3H), 2.23 (s, 3H), 1.93 – 1.10 (m, 10H). $^{13}$C NMR (126 MHz, $CDCl_3$) δ 162.4, 139.3, 139.7, 128.9, 126.7, 59.9, 33.7, 25.9, 25.1, 21.4, 15.3.

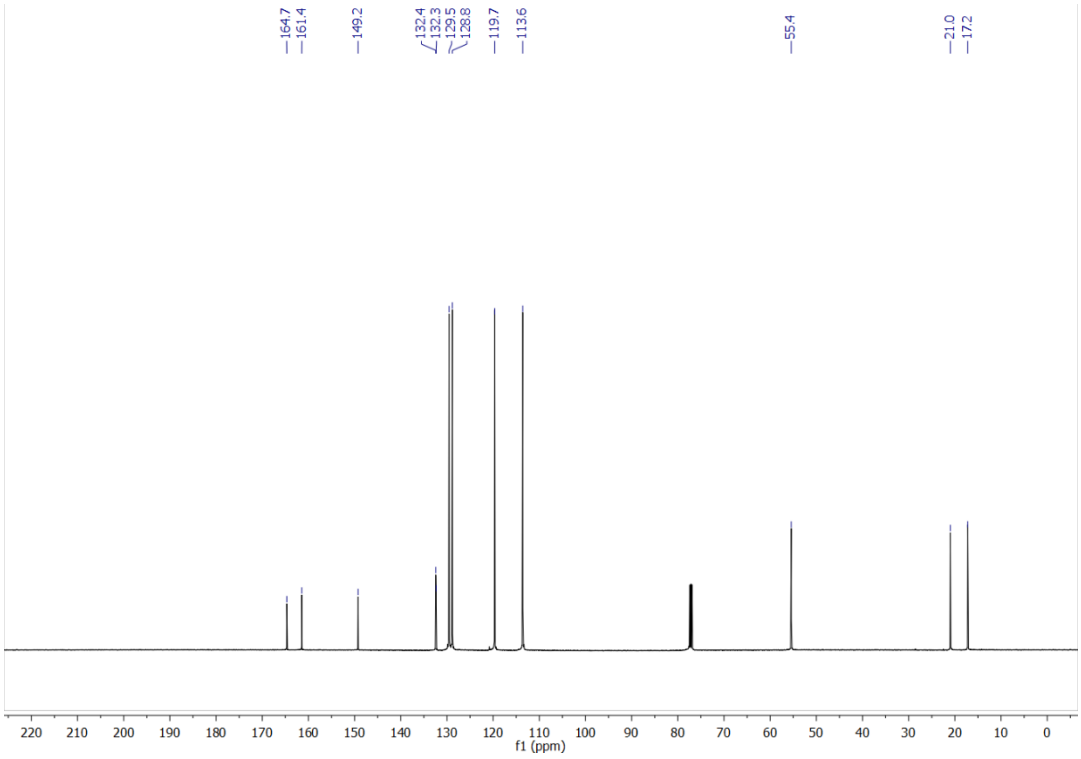
## B. NMR spectra

**Compound 1a.**

$^{1}$H spectrum

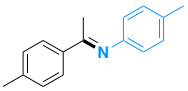



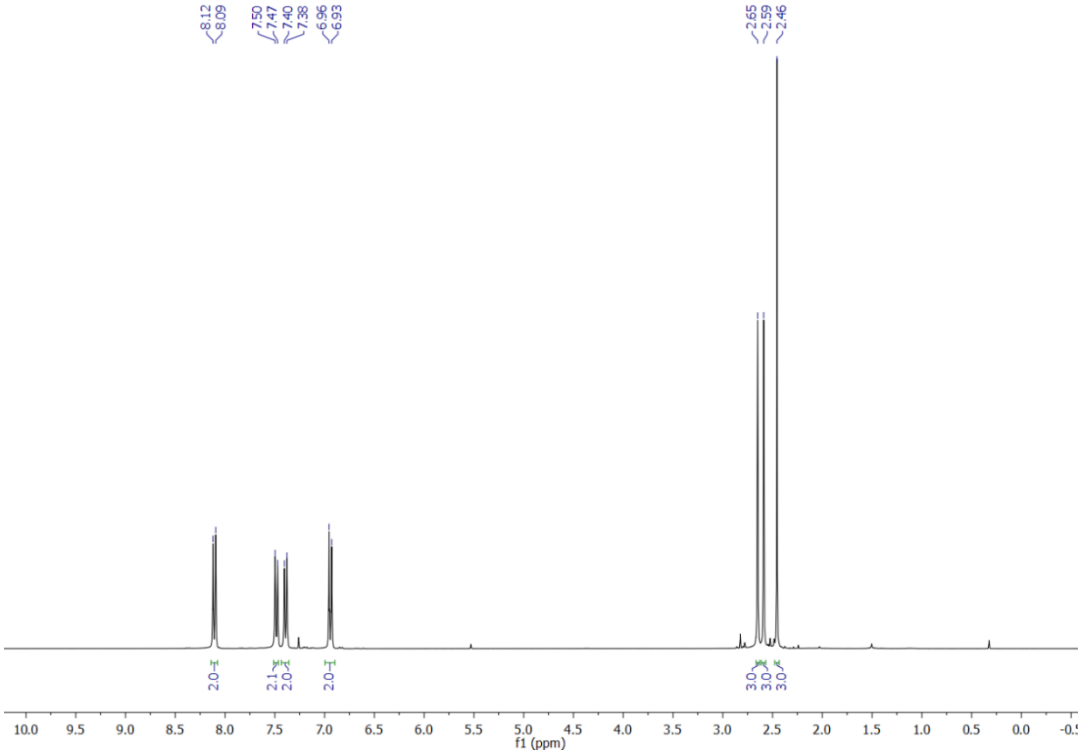

$^{13}$C{$^{1}$H} spectrum



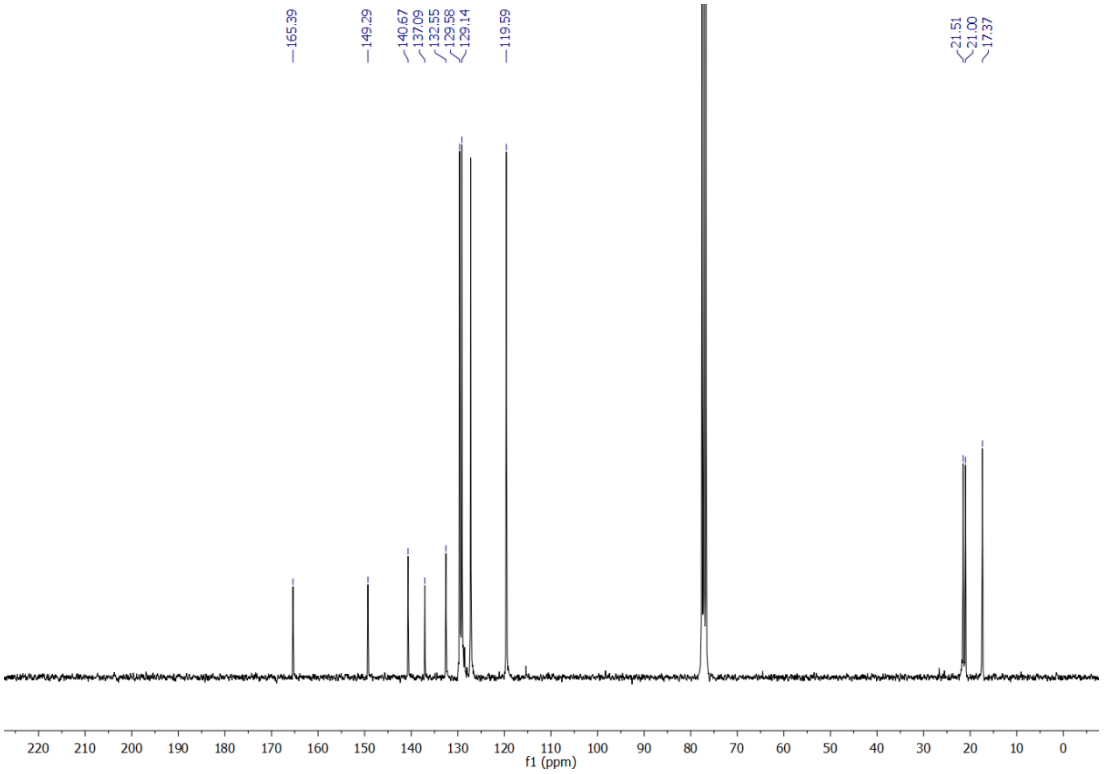
**Compound 1b.**

$^{1}$H spectrum



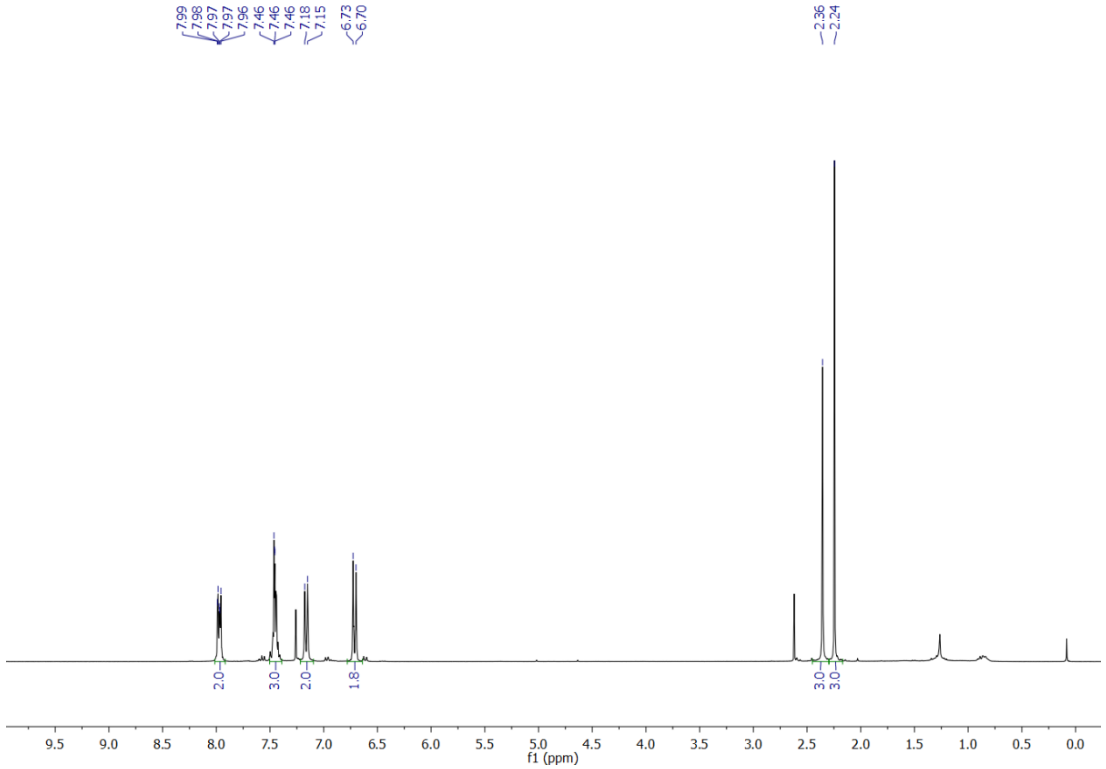



$^{13}$C{$^{1}$H} spectrum

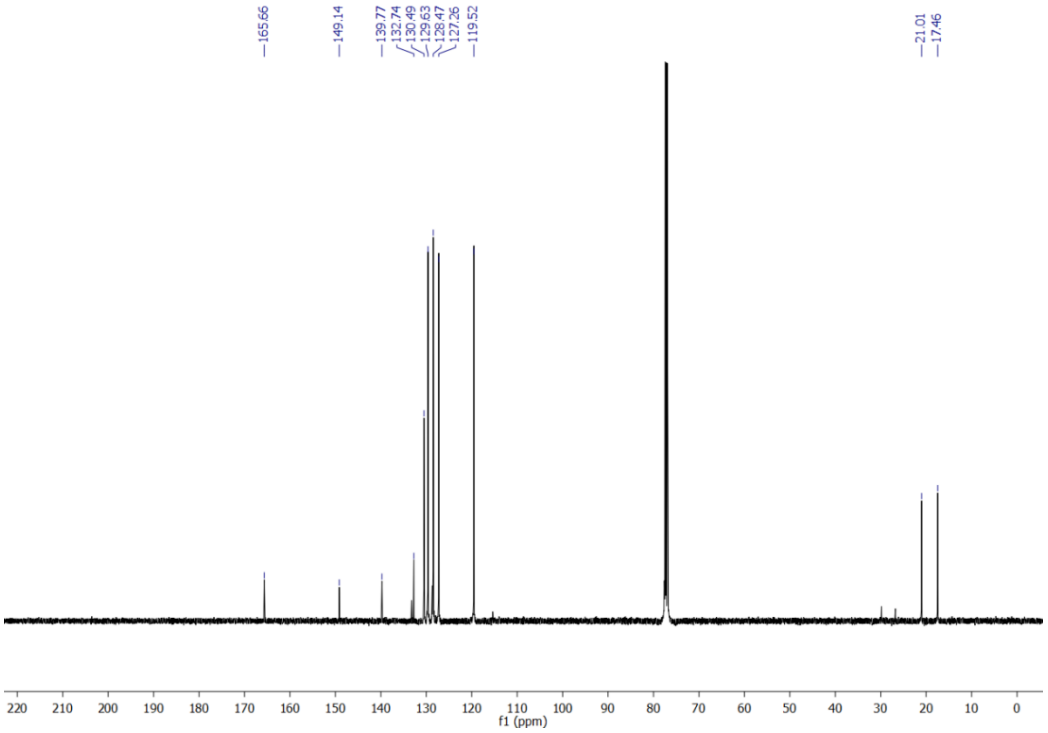


**Compound 1c.**

$^{1}$H spectrum

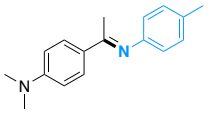


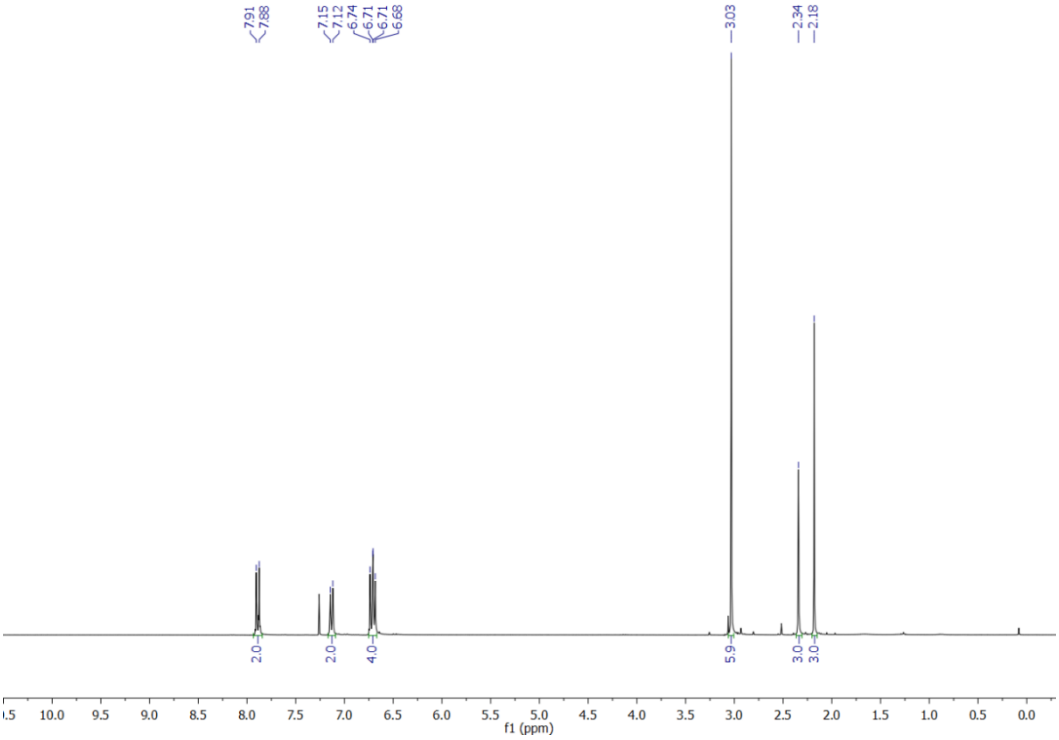

$^{13}$C{$^{1}$H} spectrum



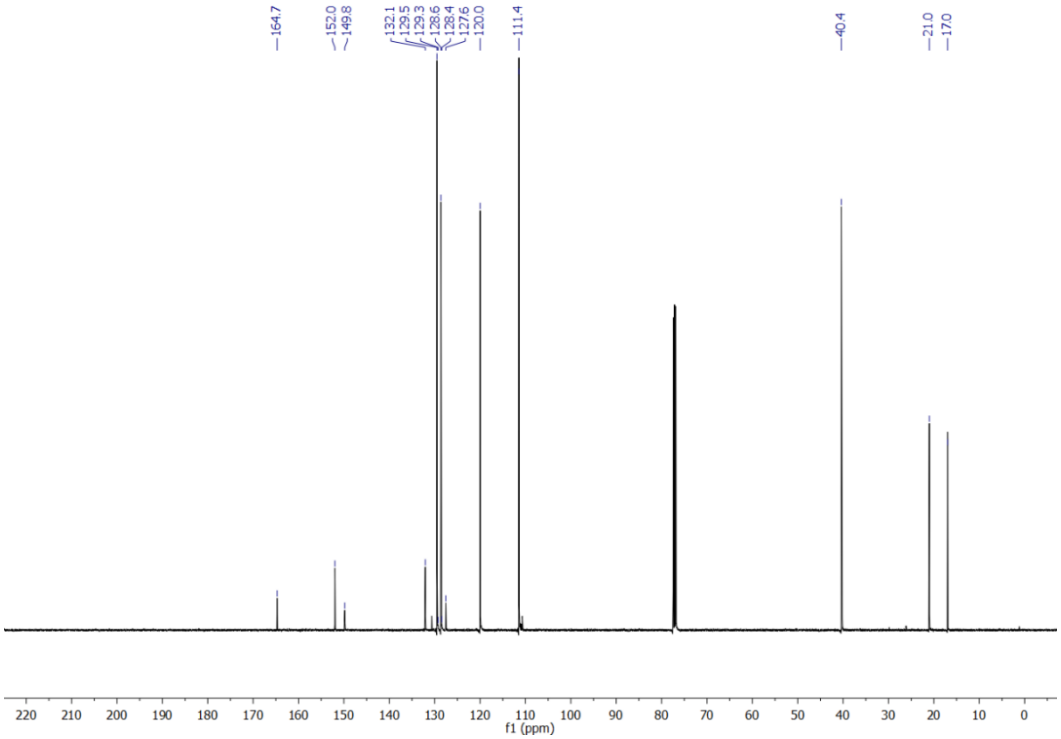
**Compound 1d.**

$^{1}$H spectrum



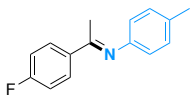


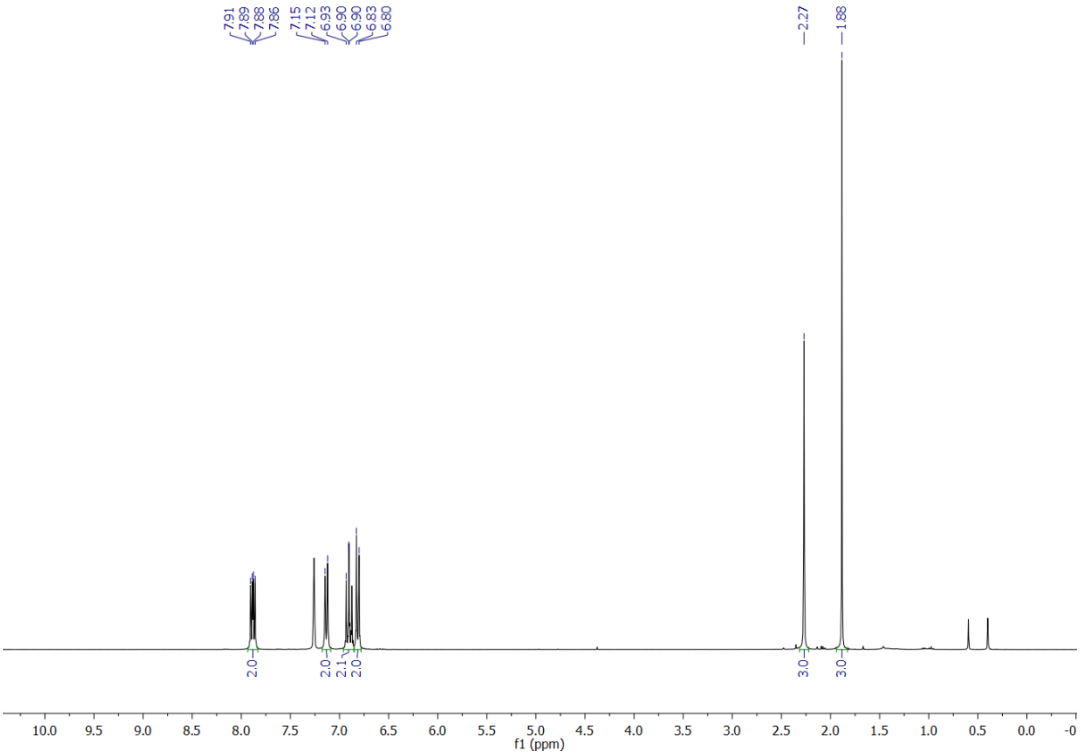

$^{13}$C{$^{1}$H} spectrum



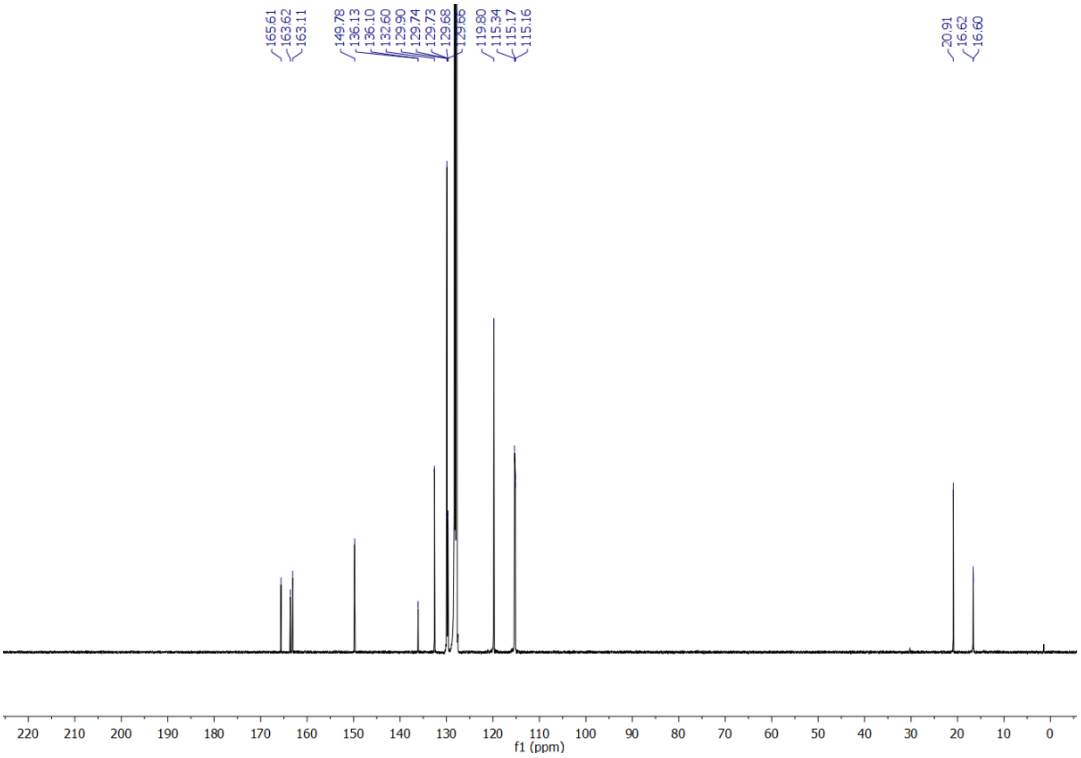
**Compound 1e.**

$^{1}$H spectrum



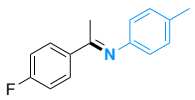



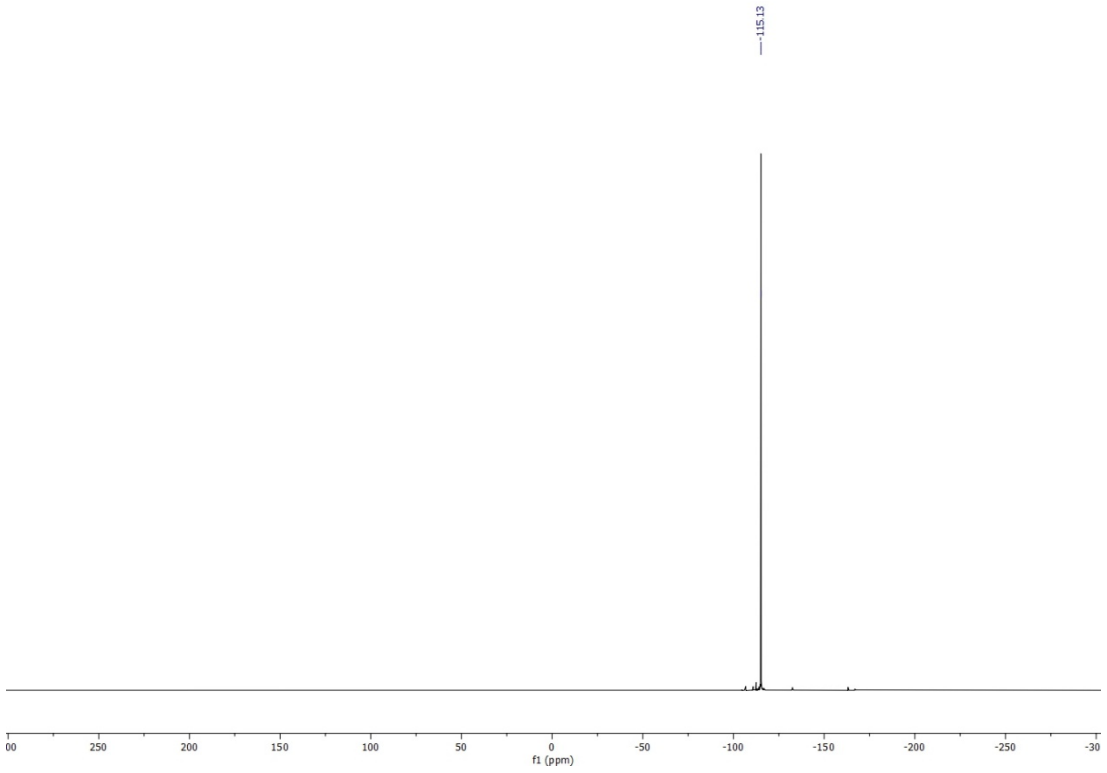

$^{13}$C{$^{1}$H} spectrum



**Compound 1e.**

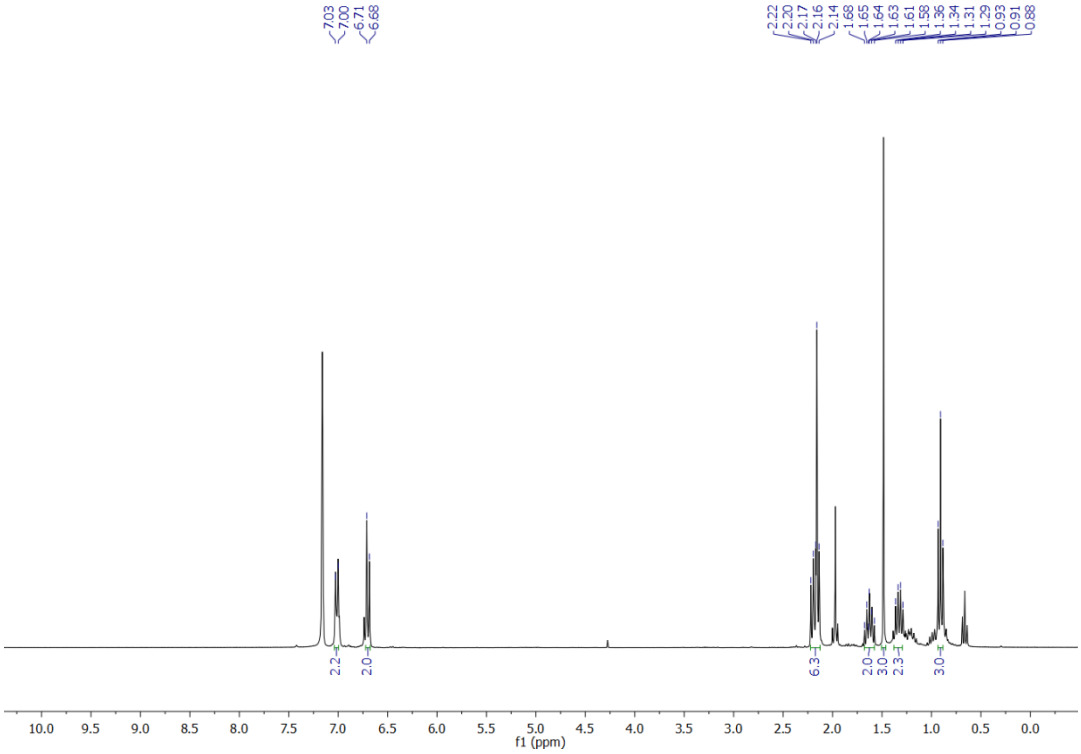
$^{19}F$ spectrum



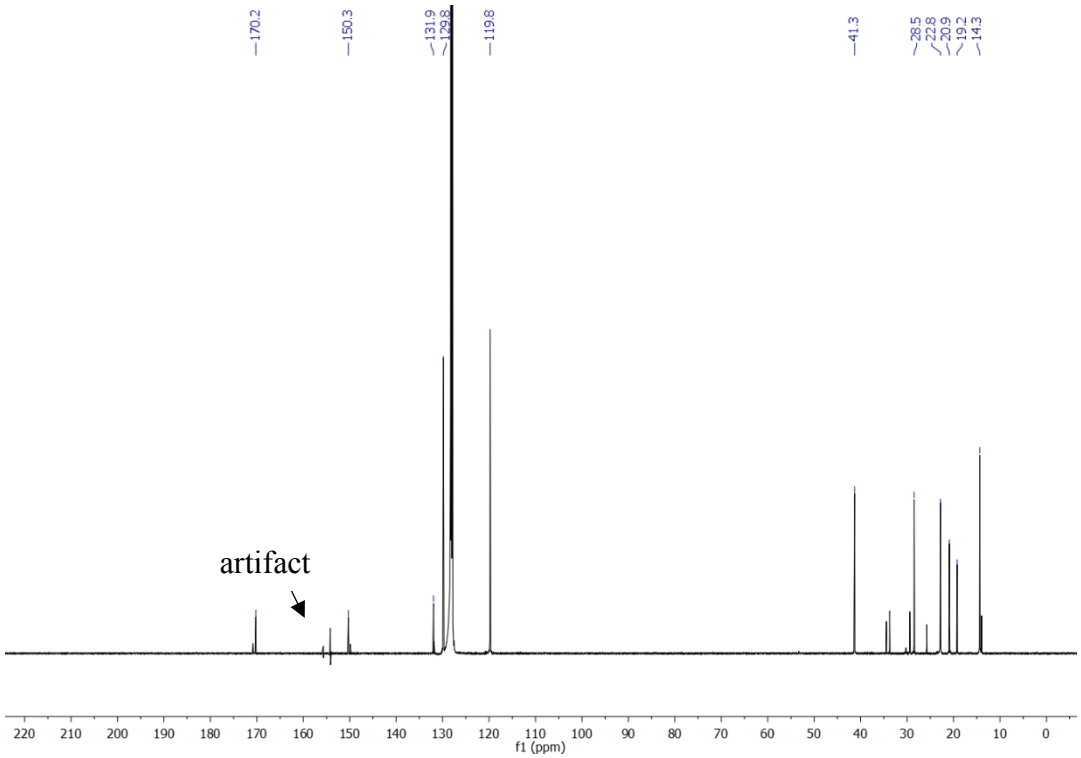



**Compound 1f.**

$^{1}$H spectrum

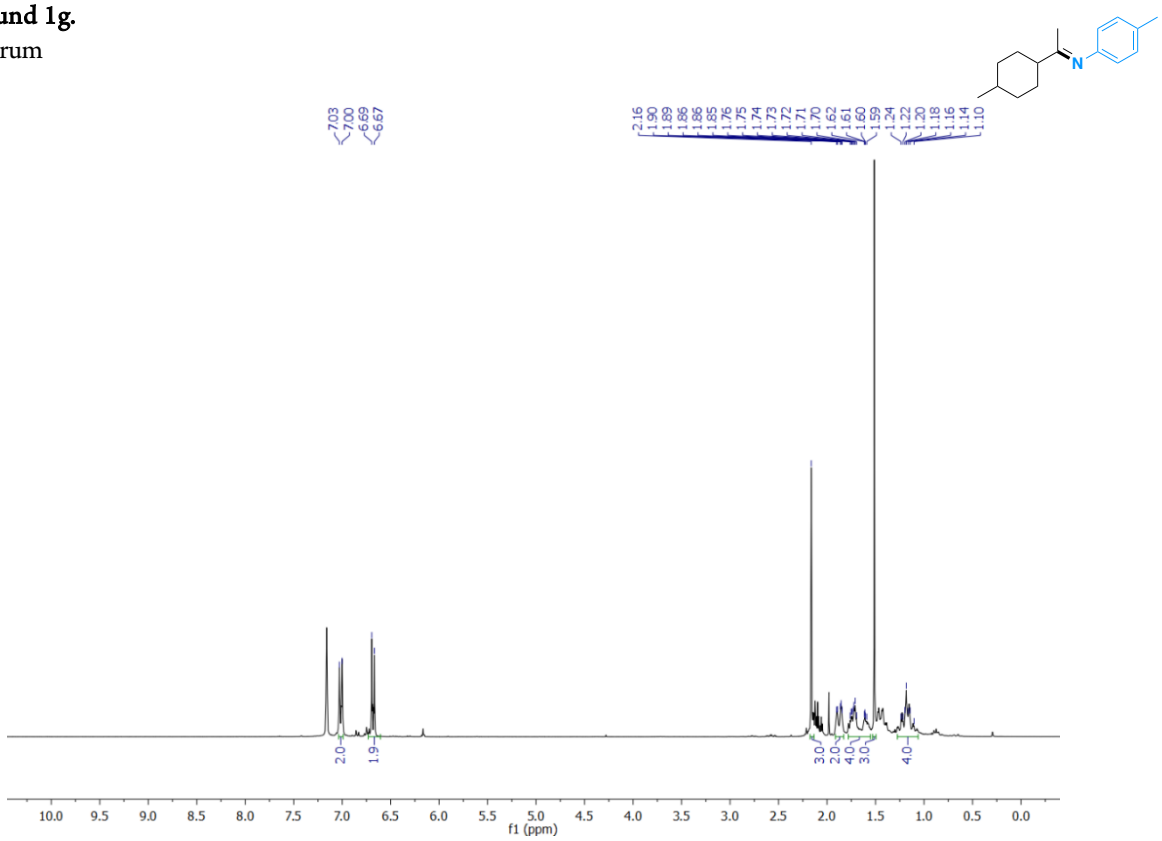



$^{13}$C{$^{1}$H} spectrum

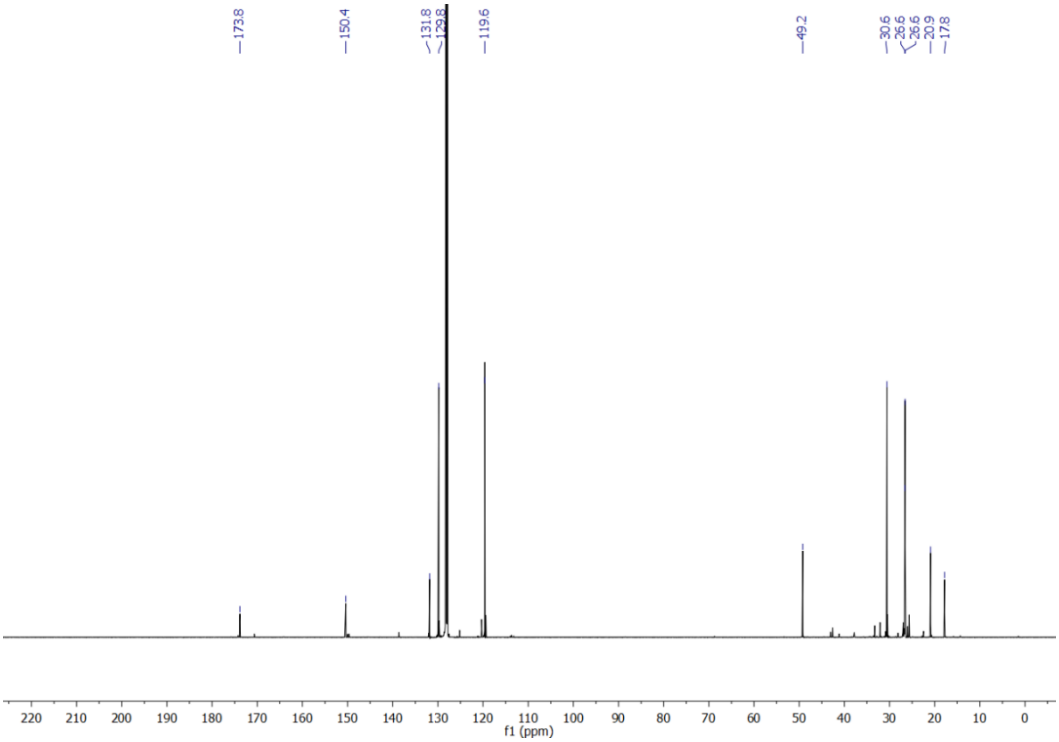


**Compound 1g.**

$^{1}H$ spectrum

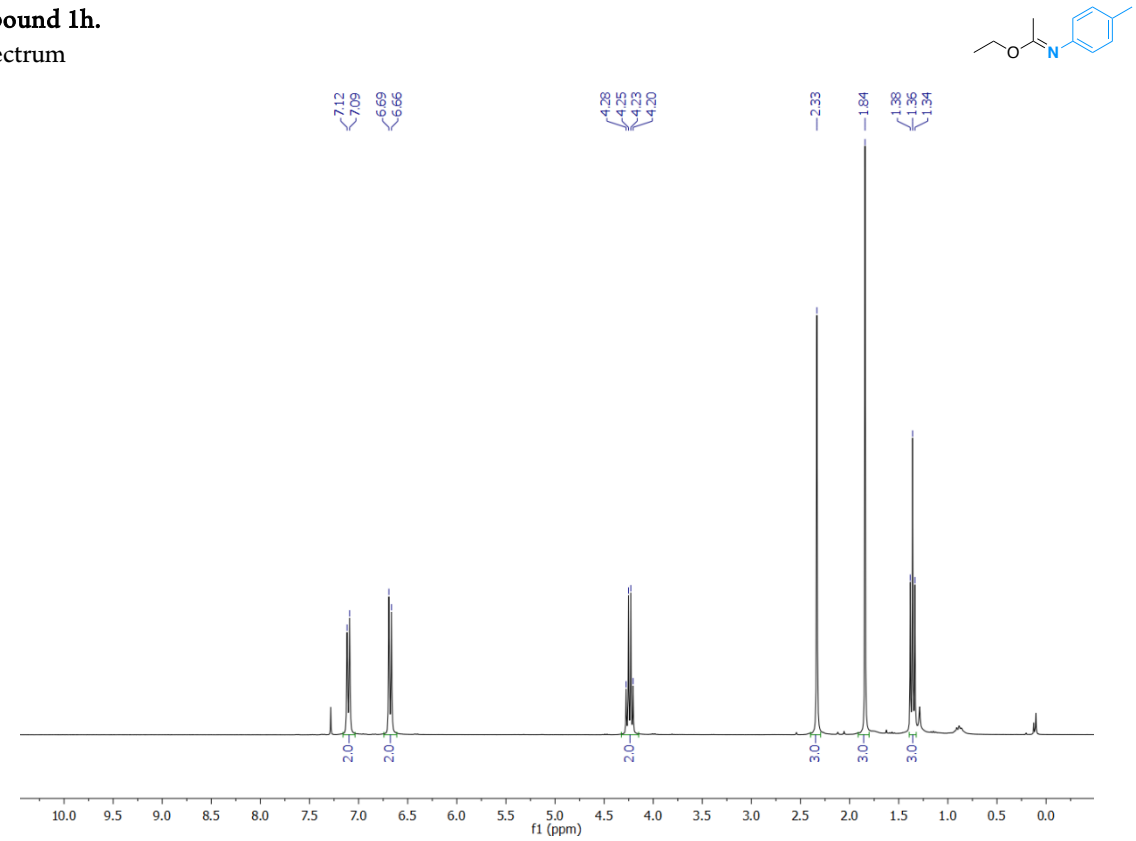



$^{13}C\{^{1}H\}$ spectrum

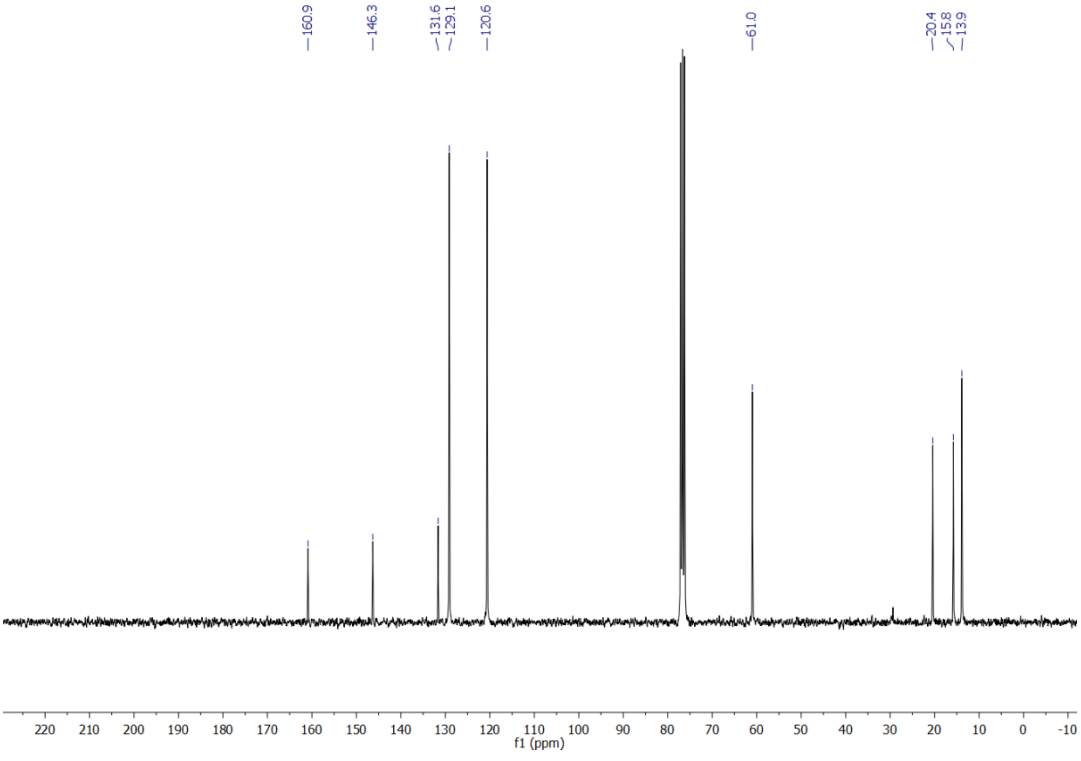


**Compound 1h.**

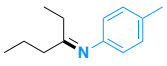
$^{1}H$ spectrum



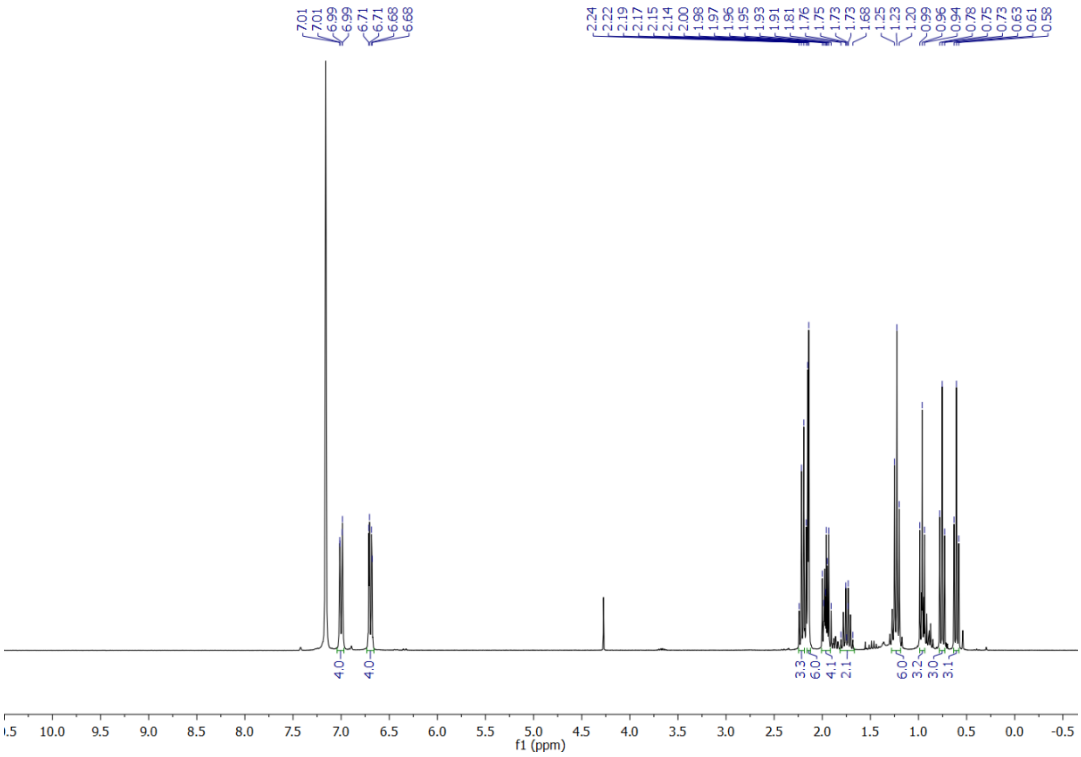

$^{13}C\{^{1}H\}$ spectrum



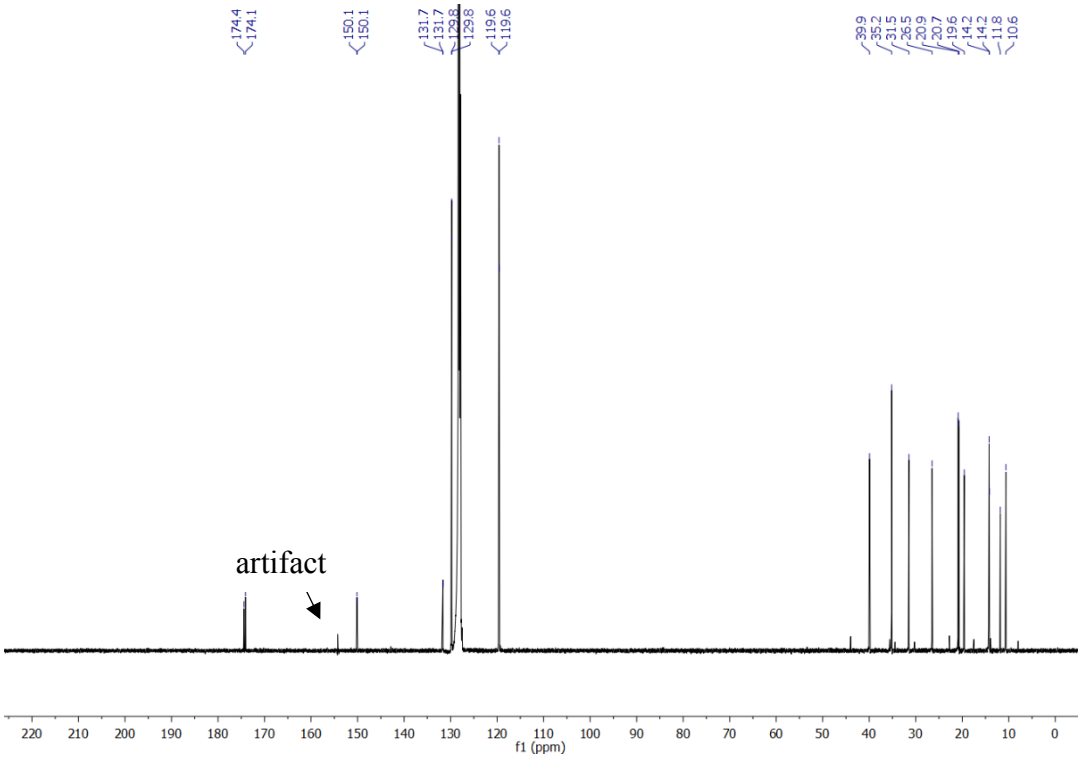
**Compound 1i**



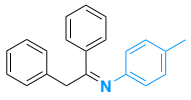
$^{1}H$ spectrum



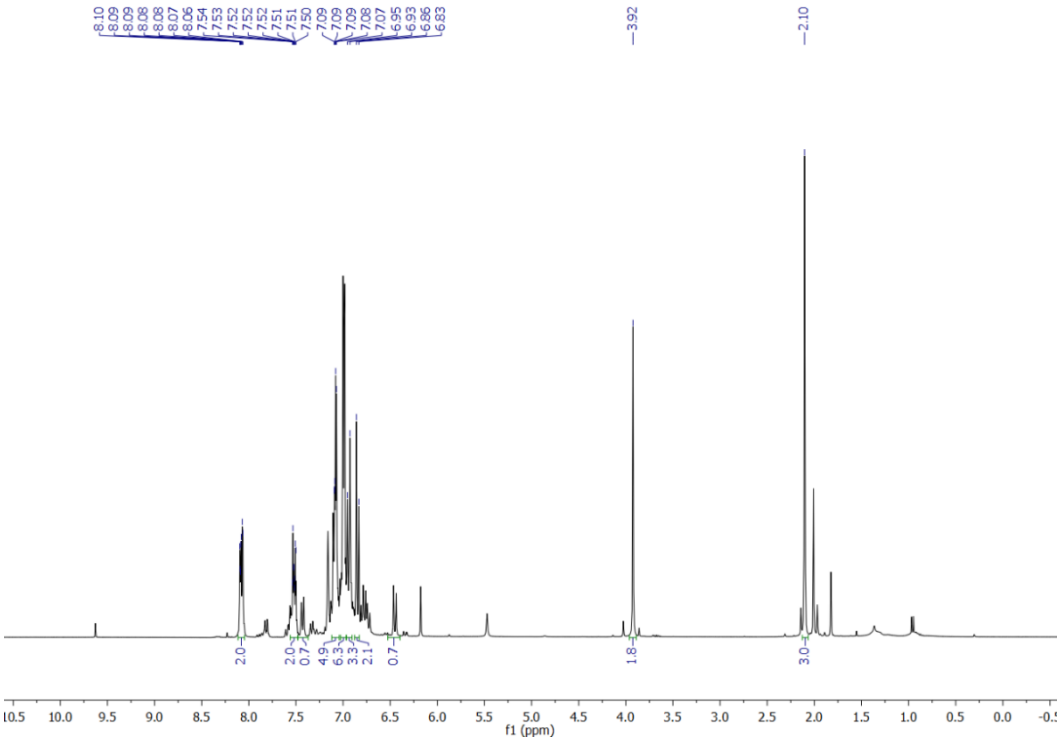

$^{13}C\{^{1}H\}$ spectrum



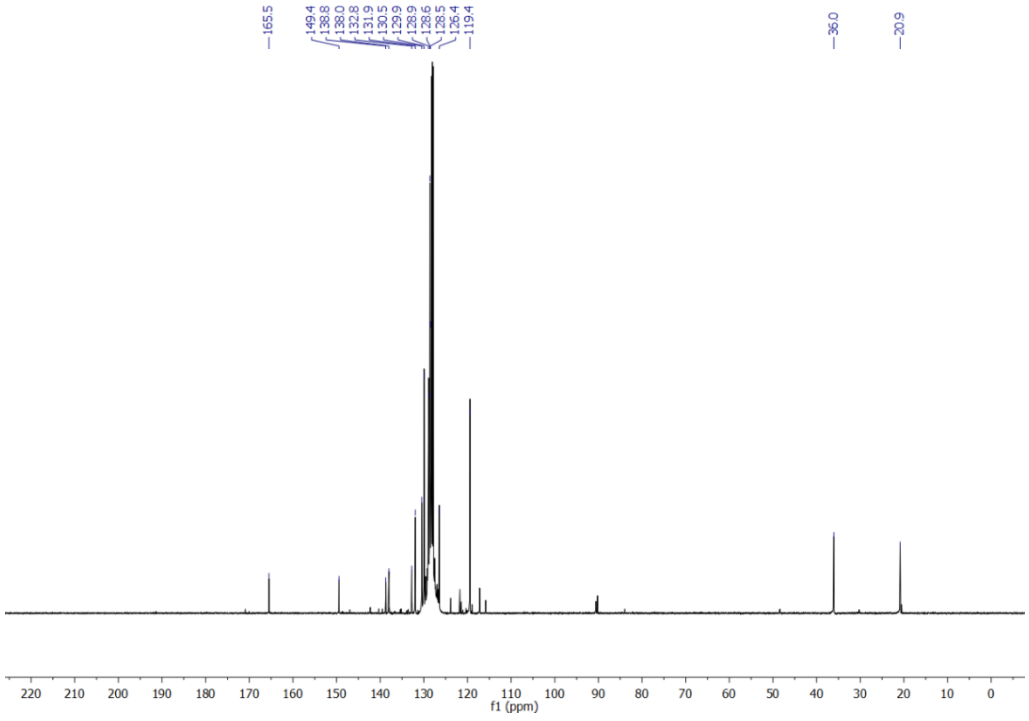
**Compound 1j**



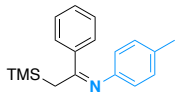
$^{1}H$ spectrum



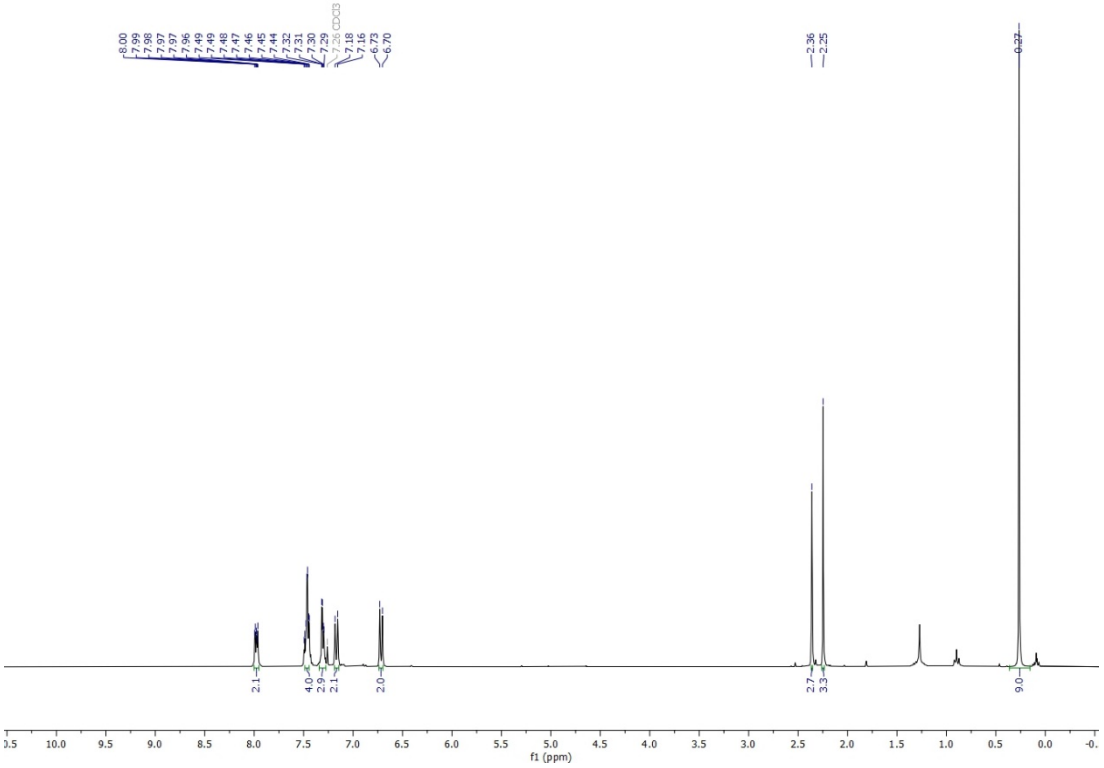

$^{13}C\{^{1}H\}$ spectrum



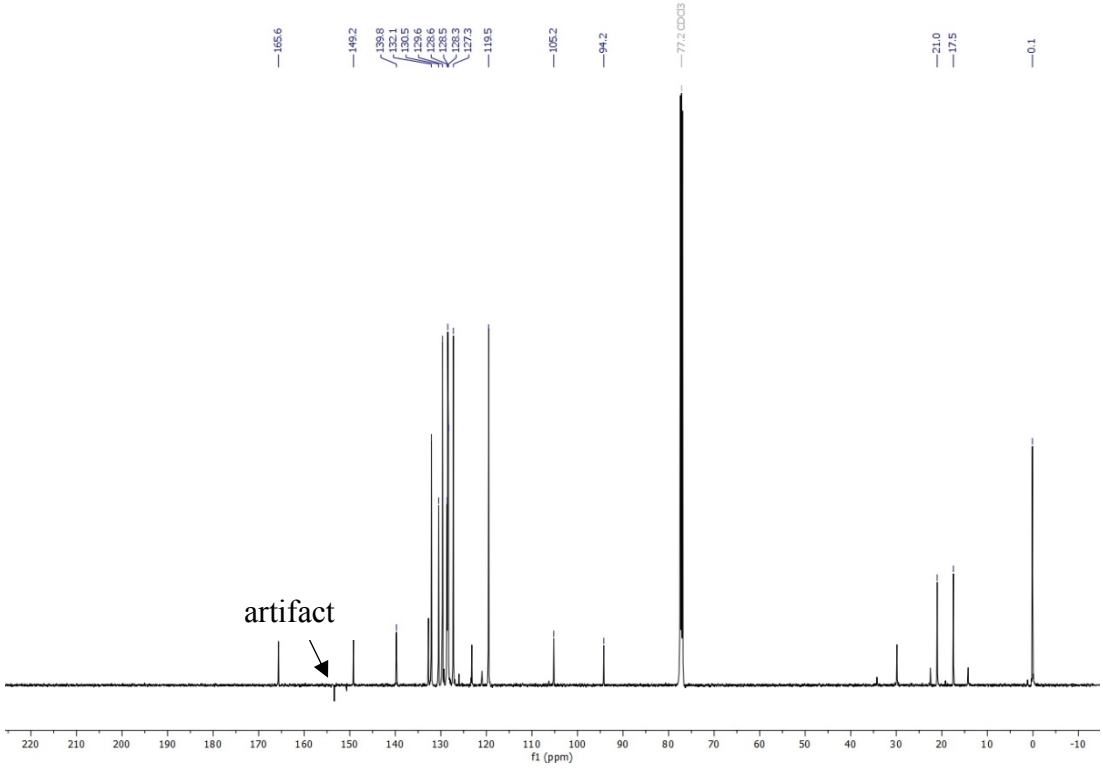
**Compound 1k**



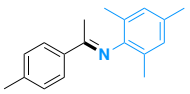

$^{1}H$ spectrum



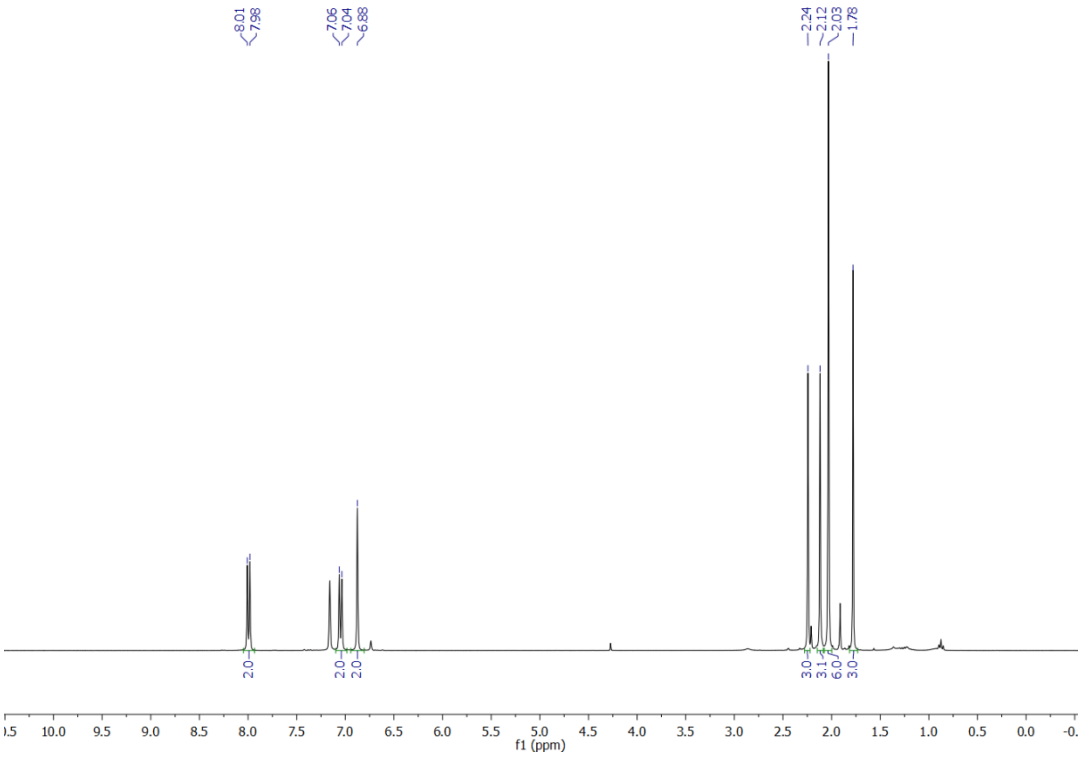

$^{13}C\{^{1}H\}$ spectrum



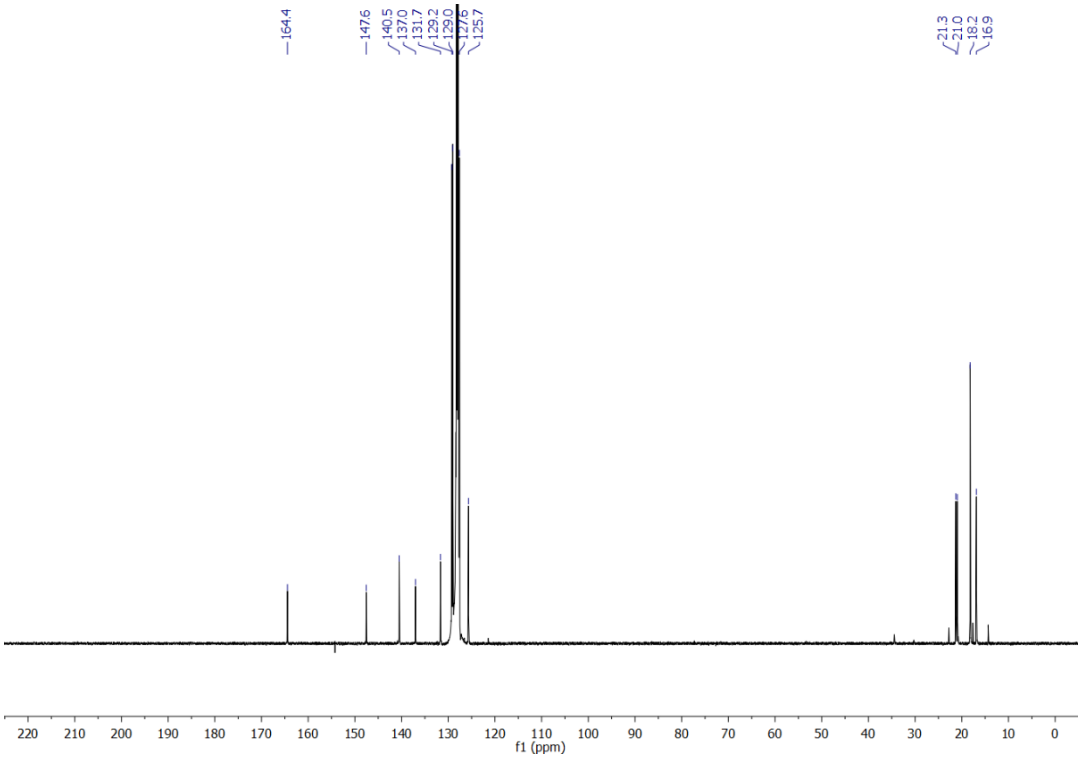
**Compound 1l**



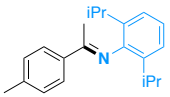
$^{1}H$ spectrum



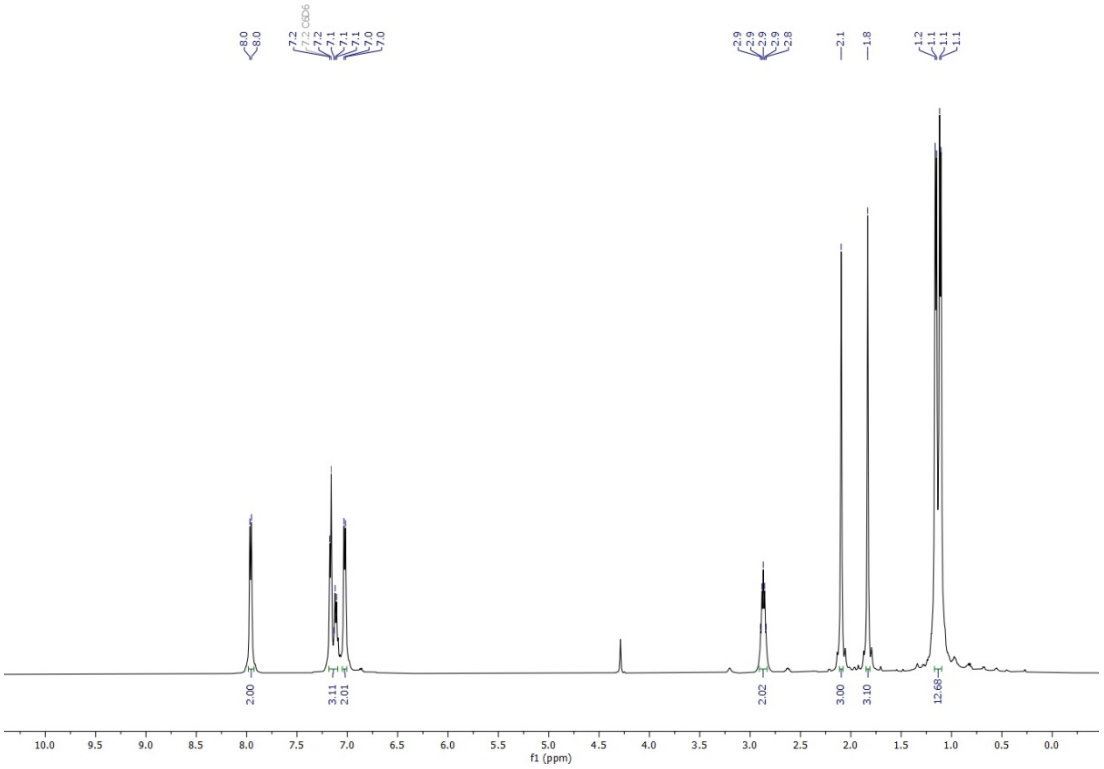

$^{13}C\{^{1}H\}$ spectrum



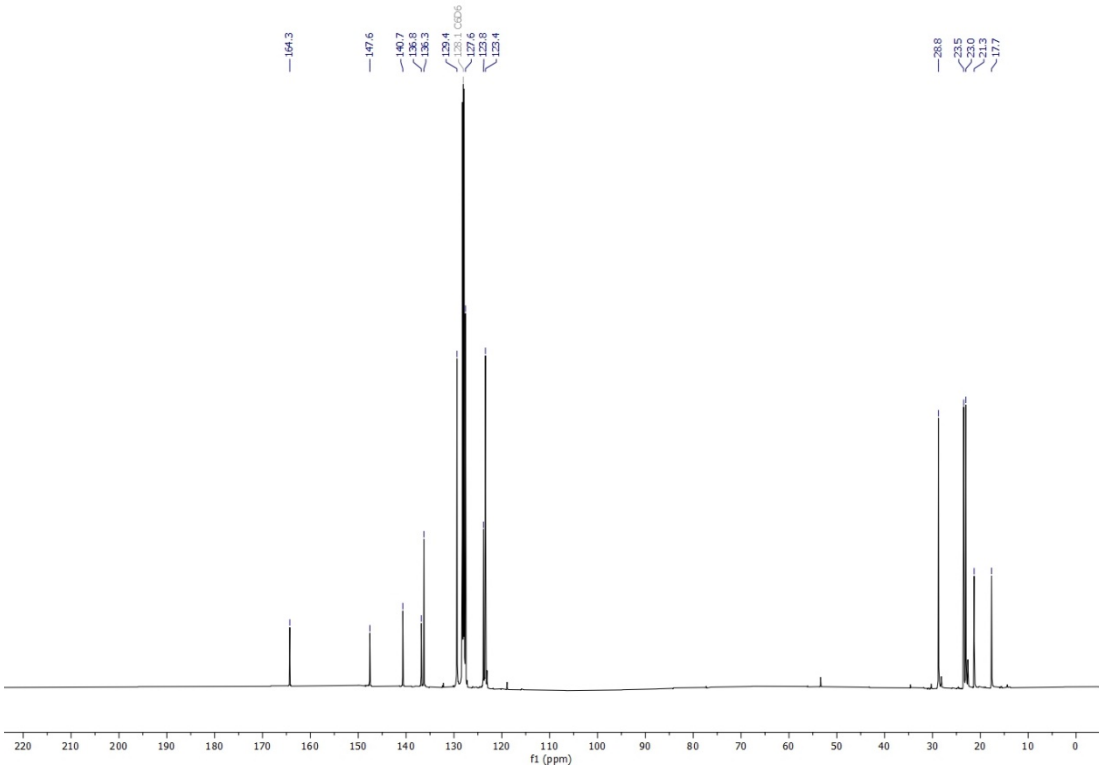
**Compound 1m**



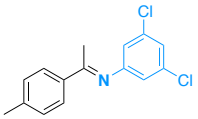

$^{1}$H spectrum



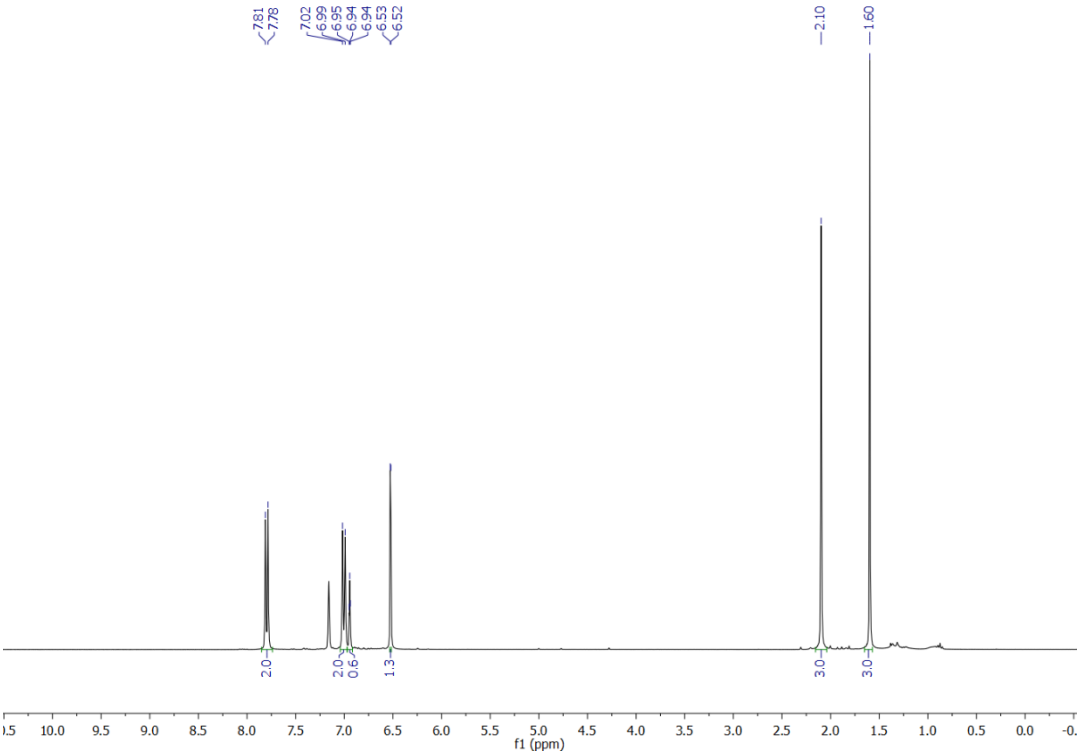

$^{13}$C{$^{1}$H} spectrum



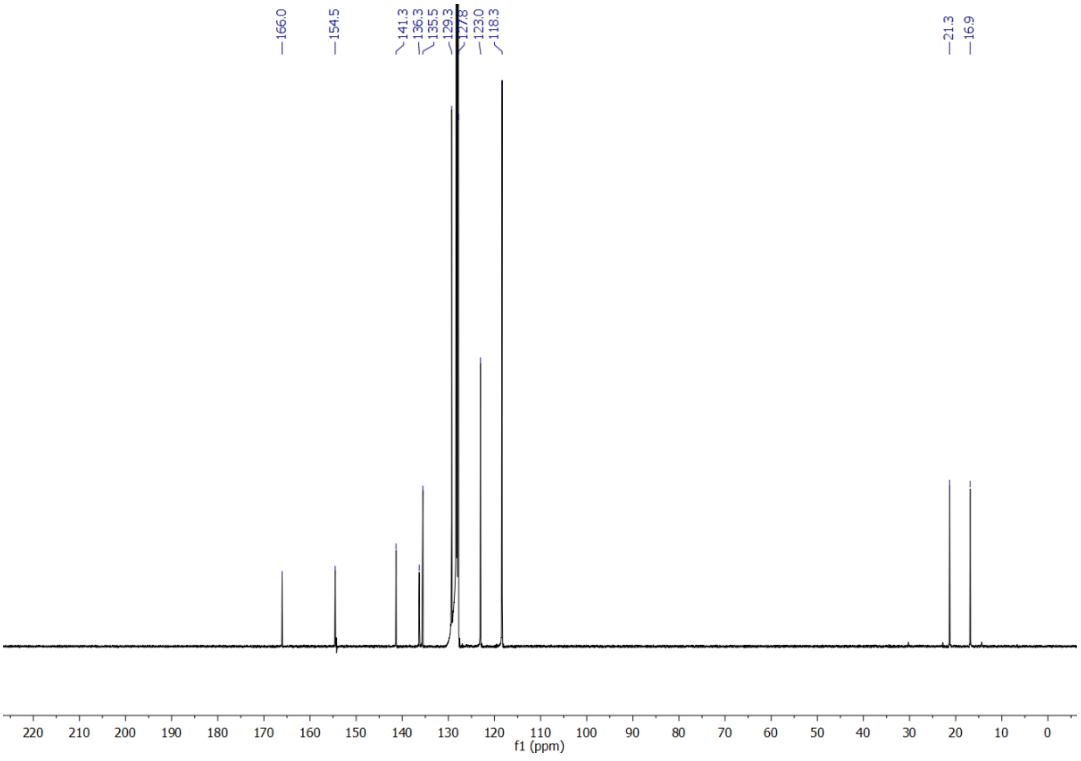
**Compound 1n**



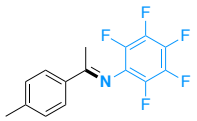

$^{1}H$ spectrum



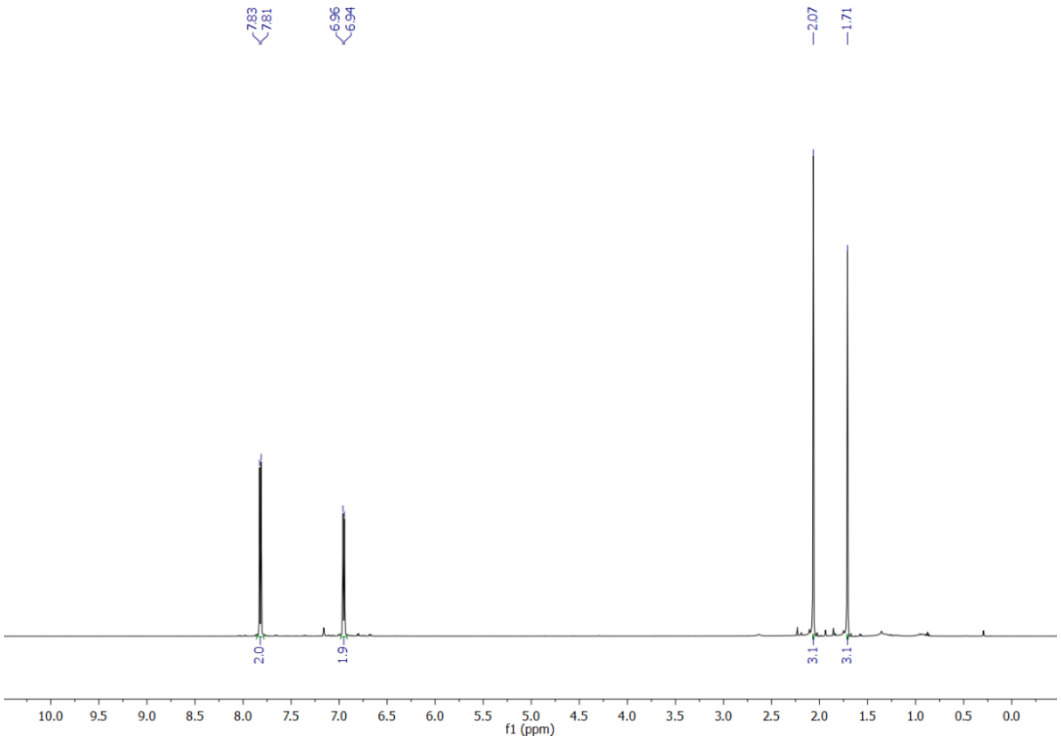

$^{13}C\{^{1}H\}$ spectrum



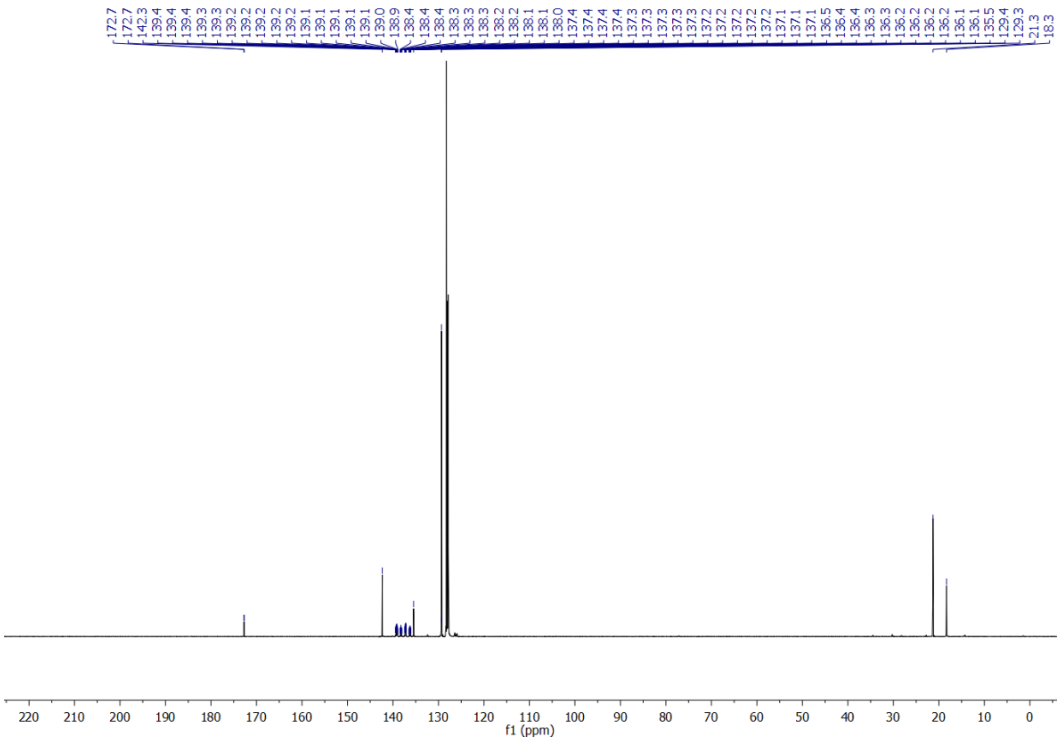
**Compound 1o**



$^{1}$H spectrum

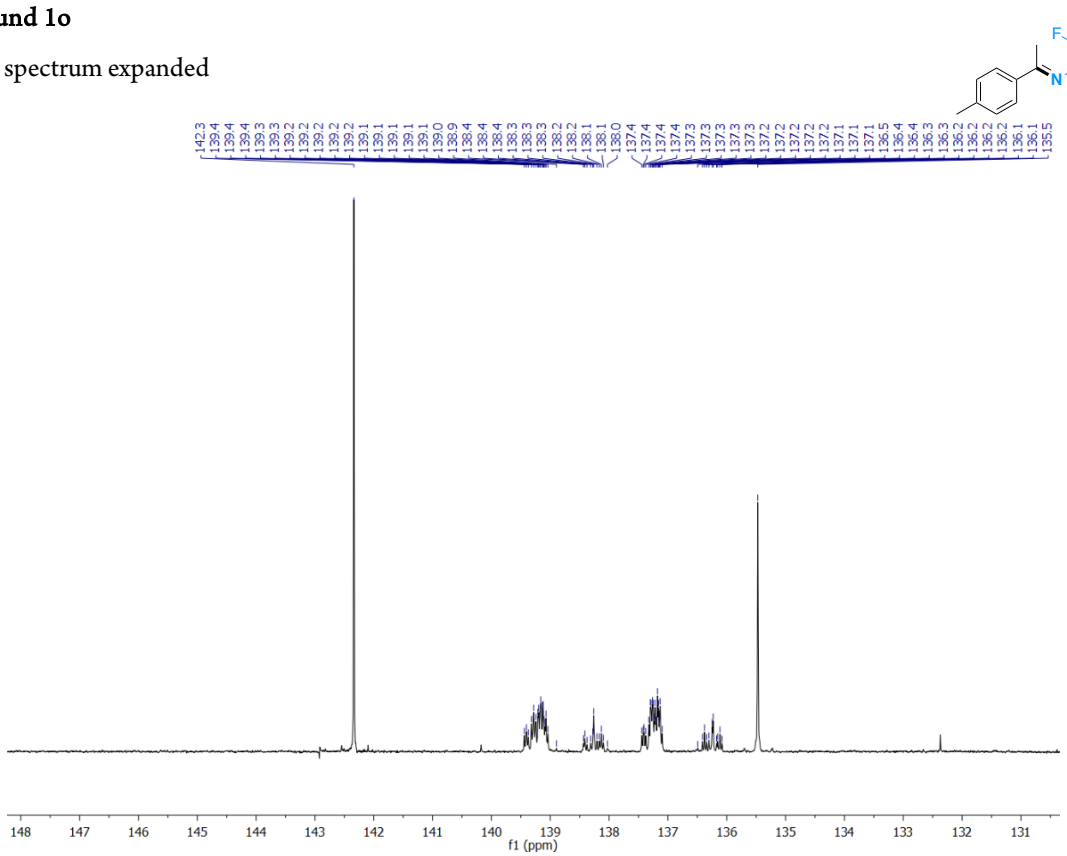



$^{13}$C{$^{1}$H} spectrum

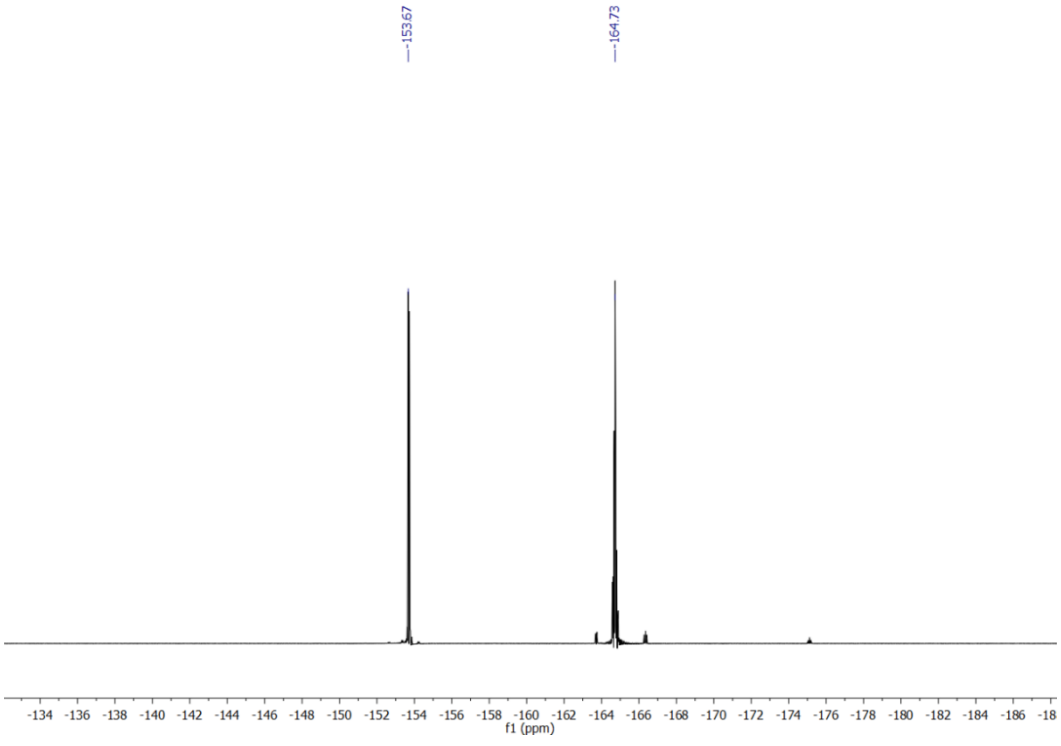


**Compound 1o**

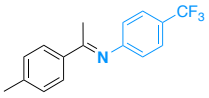
$^{13}C\{^{1}H\}$ spectrum expanded



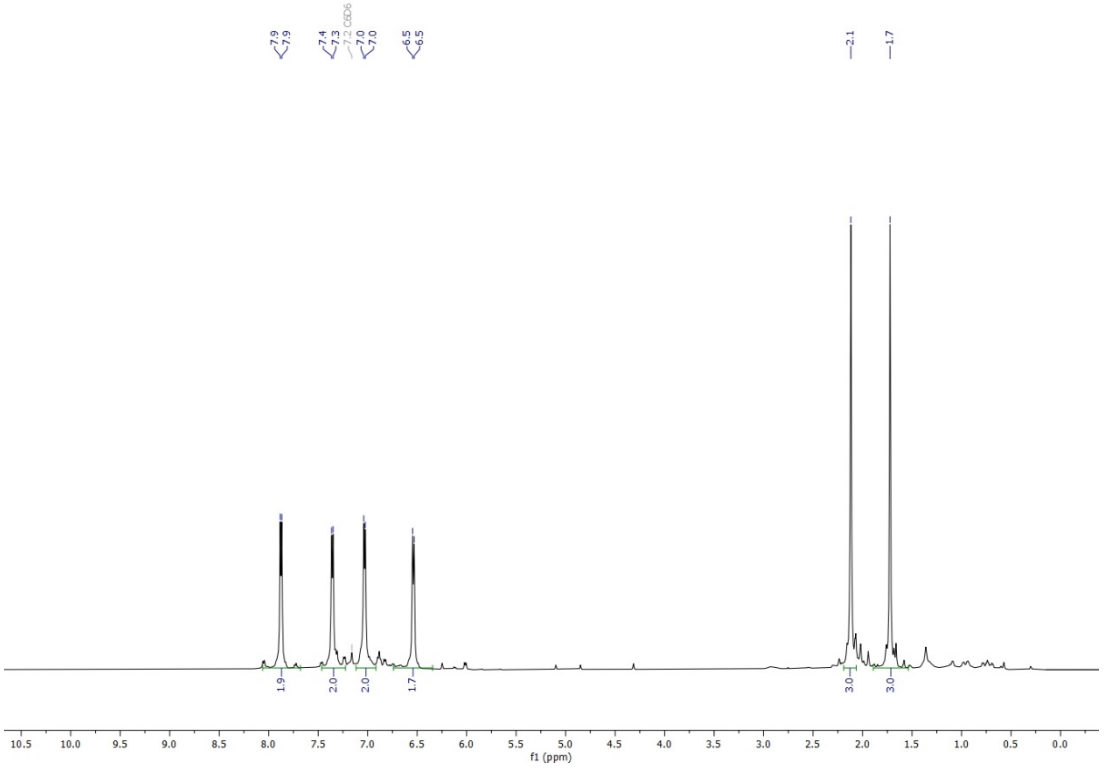

$^{19}F$ spectrum expanded



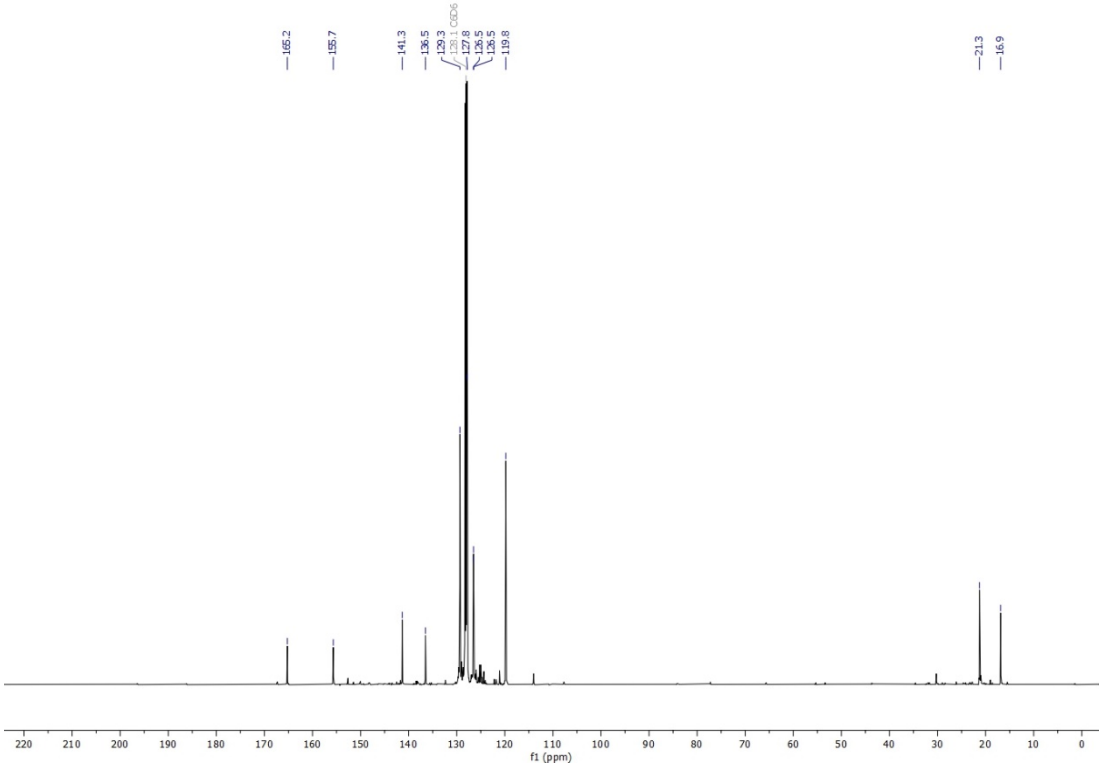
**Compound 1p**



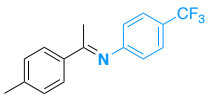

$^{1}$H spectrum



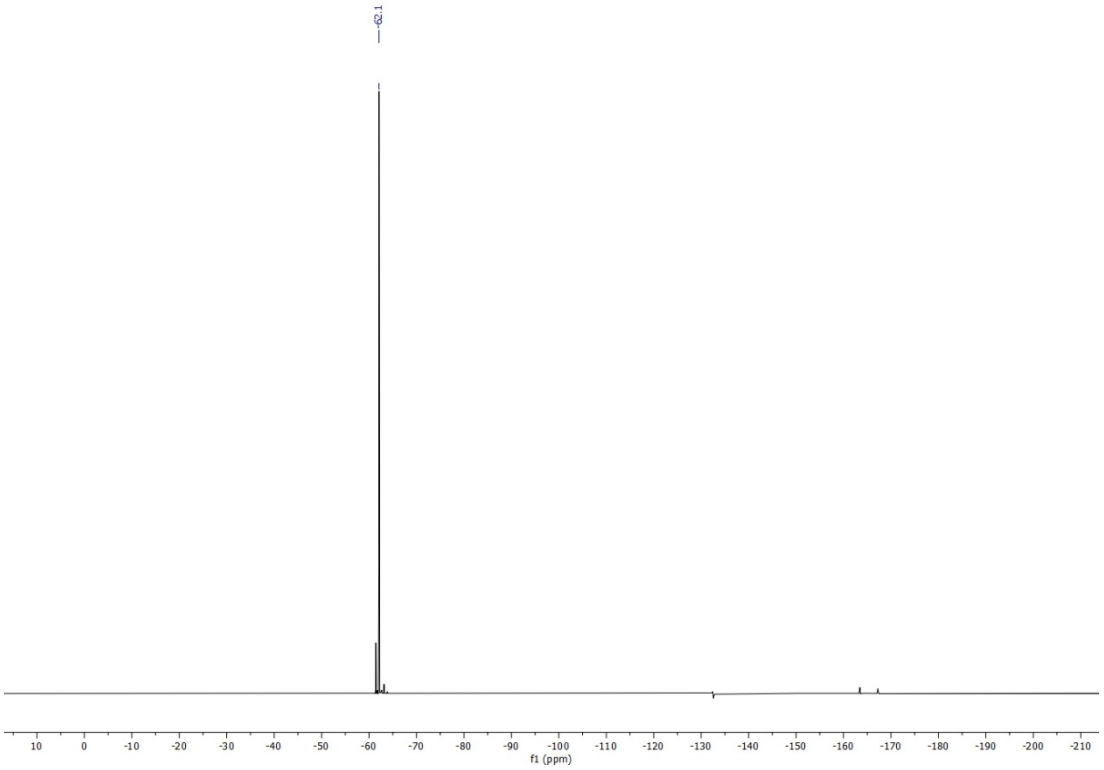

$^{13}$C{$^{1}$H} spectrum



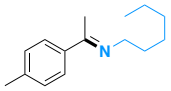
**Compound 1p**



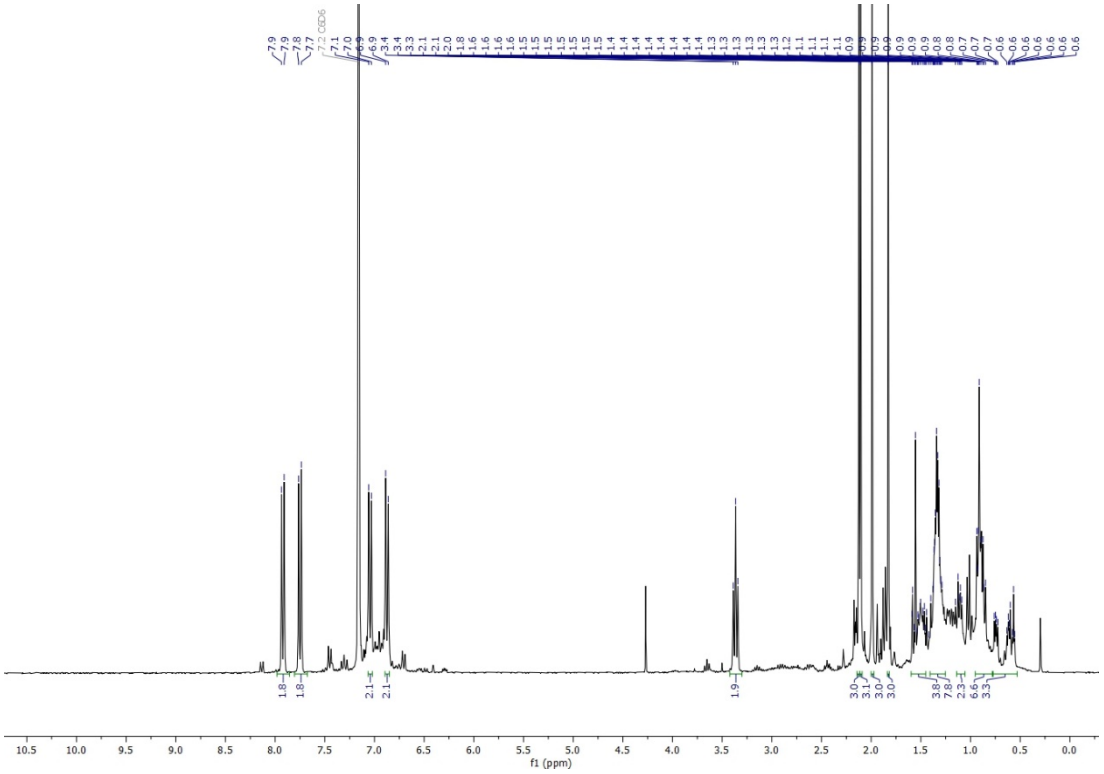

$^{19}F$ spectrum



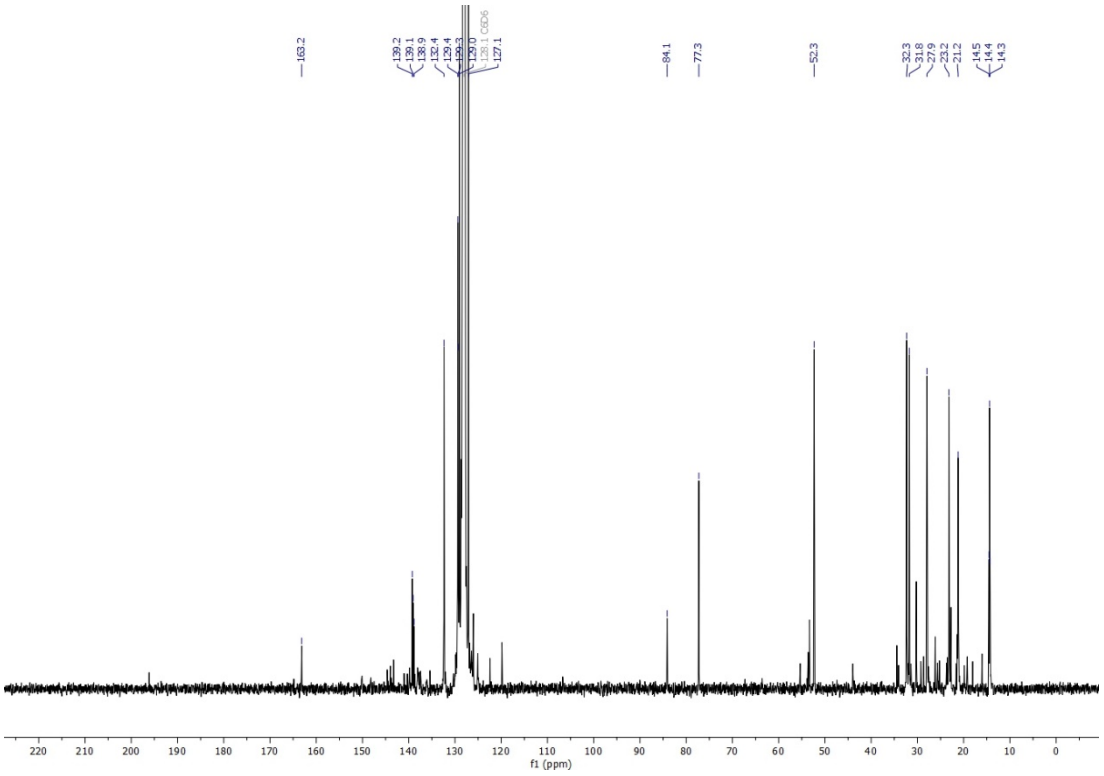
**Compound 1q**




$^{1}H$ spectrum

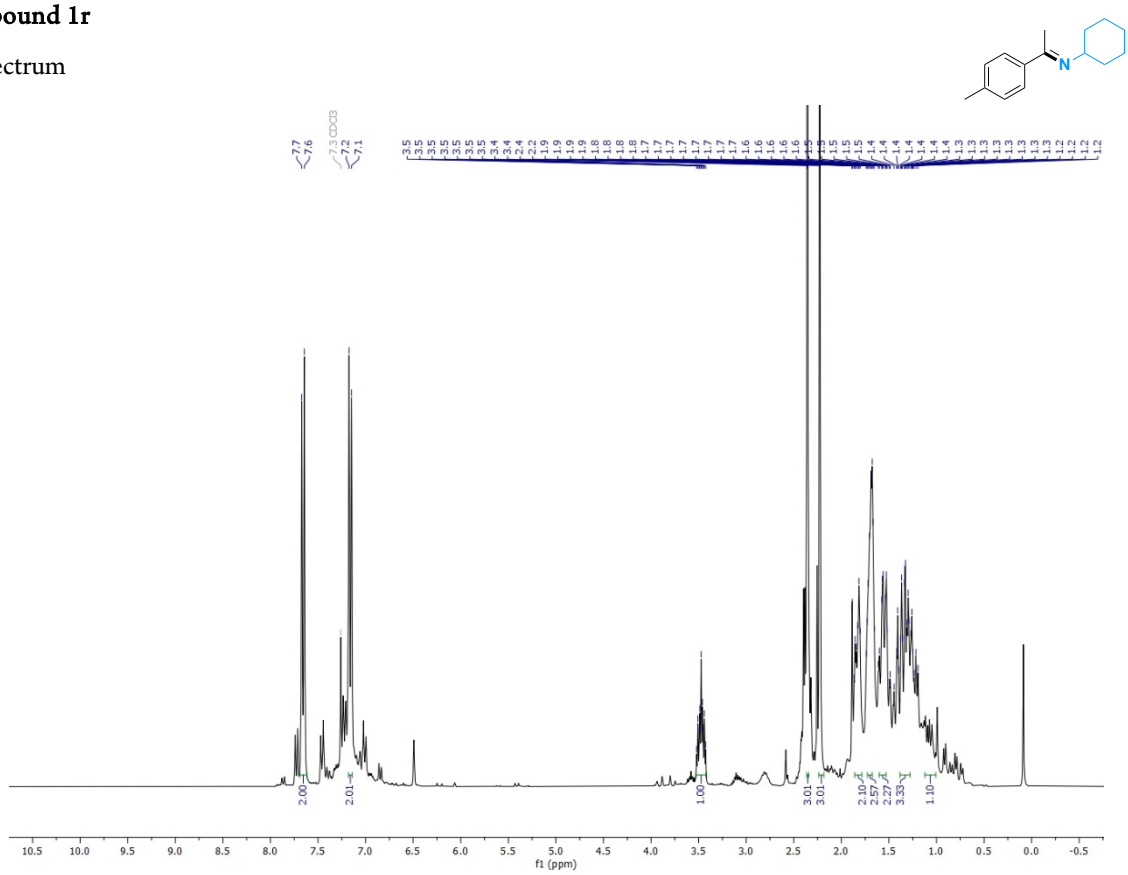



$^{13}C\{^{1}H\}$ spectrum

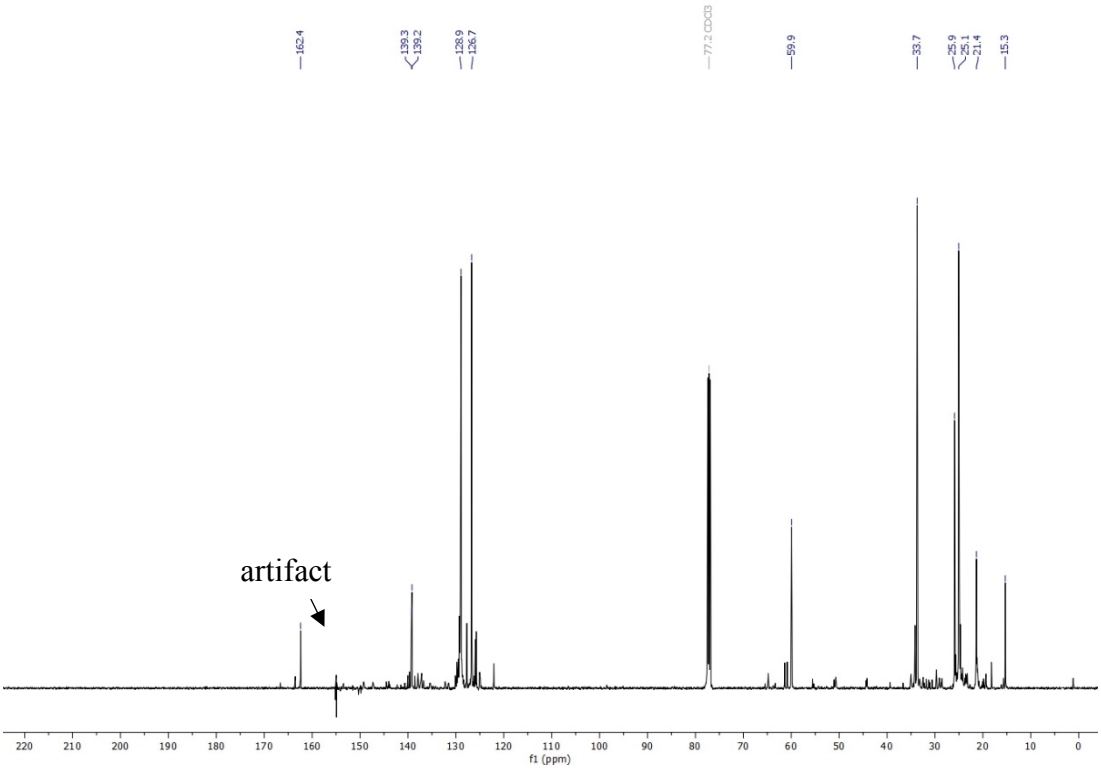


**Compound 1r**

$^{1}$H spectrum



$^{13}$C{$^{1}$H} spectrum

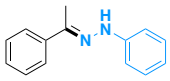


## II.2. Hydrohydrazination scope (*cf.* Scheme 4)

### A. General procedure

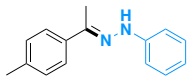
In air, a scintillation vial (3 mL) was charged with ($^{IPr}$BiCAAC)AuCl (**2a**-**2e** : 0.5 mol%, 0.001784 mmol; **2f**-**2p** : 2.5 mol%, 0.00892 mmol ), KBAr$^F$ (**2a**-**2e** : 0.5 mol%, 0.001784 mmol; **2f**-**2p** : 2.5 mol%, 0.00892 mmol), $C_6H_6$ (200 µL) and the alkyne (0.357 mmol, 1.0 eq.). After stirring for two minutes, the amine (0.357 mmol, 1.0 eq.) was added as a solution in $C_6H_6$ (200 µL). The mixture was then set stirred according to the reaction time and temperature listed in scheme 4. The products were purified by column chromatography using Florisil eluting with a gradient mixture of $CH_2Cl_2$/hexane. NB: Air sensitive products were purified under argon using dried Florisil. To confirm the reproducibility of results some reactions were repeated up to 4 times.

**2a**



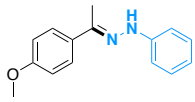
For this reaction, 1.1 equivalent of hydrazine was added (0.043 g, 0.393 mmol). Compound **2a** was isolated in 100% yield (0.075 g) and agrees with previous literature report.[8] $^1$H NMR (500 MHz, $C_6D_6$) δ 7.76 (d, *J* = 7.4 Hz, 2H), 7.28 – 7.13 (m, 8H), 6.88 (tt, *J* = 6.9, 1.4 Hz, 1H), 6.81 (s, 1H), 1.42 (s, 3H). $^{13}$C{$^1$H} NMR (126 MHz, $C_6D_6$) δ 145.8, 140.8, 139.7, 129.6, 128.6, 125.9, 120.5, 113.7, 11.0.

**2b**



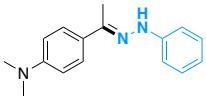
Compound **2b** was isolated in 95% yield (0.076 g) and agrees with previous literature report.[8] $^1$H NMR (500 MHz, $C_6D_6$) δ 7.76 (d, *J* = 8.3 Hz, 2H), 7.29 – 7.24 (m, 2H), 7.24 – 7.19 (m, 2H), 7.09 (d, *J* = 7.9 Hz, 2H), 6.89 (tt, *J* = 7.2, 1.3 Hz, 2H), 6.81 (s, 1H), 2.15 (s, 3H), 1.45 (s, 3H). $^{13}$C{$^1$H} NMR (126 MHz, $C_6D_6$) δ 146.0, 141.1, 137.7, 137.1, 129.6, 129.3, 125.9, 120.4, 113.7, 21.2, 11.1.

**2c**



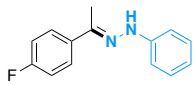
Compound **2c** was isolated in 99% yield (0.085 g). $^1$H NMR (500 MHz, $C_6D_6$) δ 7.75 (d, *J* = 8.9 Hz, 2H), 7.29 (ddd, *J* = 8.8, 6.9, 1.7 Hz, 2H), 7.24 – 7.22 (m, 2H), 6.90 (td, *J* = 7.1, 1.3 Hz, 1H), 6.86 (d, *J* = 9.1 Hz, 2H), 6.80 (s, 1H), 3.33 (s, 3H), 1.47 (s, 3H). $^{13}$C{$^1$H} NMR (126 MHz, $C_6D_6$) δ 160.1, 146.2, 141.2, 132.3, 129.6, 127.2, 120.2, 114.0, 113.6, 54.9, 11.2.

**2d**



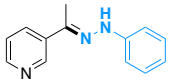
Compound **2d** was isolated in 95% yield (0.086 g). $^1$H NMR (300 MHz, $C_6D_6$) δ 7.75 (d, *J* = 8.4 Hz, 2H), 7.04 (d, *J* = 7.1 Hz, 2H), 6.82 – 6.62 (m, 2H), 6.53 (d, *J* = 8.5 Hz, 2H), 6.43 (s, 1H), 2.42 (s, 6H), 1.49 (s, 3H). $^{13}$C{$^1$H} NMR (126 MHz, $C_6D_6$) δ 150.7, 146.6, 142.4, 129.6, 129.3, 127.1, 120.0, 119.1, 113.7, 112.4, 112.4, 40.0, 11.2.

**2e**



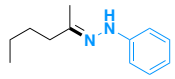
Compound **2e** was isolated in 95% yield (0.077 g). $^1$H NMR (300 MHz, $C_6D_6$) δ 7.55 – 7.45 (m, 2H), 7.25 (dd, *J* = 8.6, 7.2 Hz, 2H), 7.17 – 7.07 (m, 2H), 6.93 – 6.79 (m, 3H), 6.78 (s, 1H), 1.35 (s, 3H). $^{13}$C{$^1$H} NMR (126 MHz, $C_6D_6$) δ 164.0, 162.1, 145.7, 139.9, 139.9, 135.8, 135.7, 129.6, 127.5, 127.5, 120.6, 115.4, 115.2, 113.6, 10.9. $^{19}$F NMR (282 MHz, $C_6D_6$) δ -115.13.

**2f**



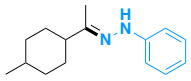
Compound **2f** was isolated in 93% yield (0.070 g). $^1$H NMR (300 MHz, $C_6D_6$) δ 9.09 (br, 1H), 8.52 (s, 1H), 7.83 (d, *J* = 8.1 Hz, 1H), 7.25 (dd, *J* = 8.6, 7.2 Hz, 2H), 7.14 – 7.10 (m, 2H), 6.93 – 6.86 (m, 2H), 6.82 – 6.76 (m, 1H), 1.29 (s, 3H). $^{13}$C{$^1$H} NMR (126 MHz, $C_6D_6$) δ 148.8, 147.2, 145.1, 137.7, 131.8, 129.2, 127.3, 122.8, 120.5, 113.3, 10.2.

**2g**



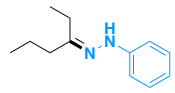
For these substrates, 1.1 equivalent of hydrazine was used (0.393 mmol). Compound **2g** was isolated in 91% yield (0.062 g) and agrees with previous literature report.[8] $^{1}$H NMR (300 MHz, $C_6D_6$) δ 7.27 – 7.20 (m, 2H), 7.17 (d, *J* = 7.6 Hz, 2H), 6.84 (tt, *J* = 7.1, 1.4 Hz, 1H), 6.51 (br, 1H), 2.18 – 2.10 (m, 2H), 1.51 – 1.39 (m, 2H), 1.35 – 1.19 (m, 2H), 1.15 (s, 3H)0.88 (t, *J* = 7.3 Hz, 3H). $^{13}$C{$^{1}$H} NMR (126 MHz, $C_6D_6$) δ 146.7, 145.5, 129.5, 119.8, 113.4, 38.8, 29.1, 22.7, 14.2, 13.6.

**2h**



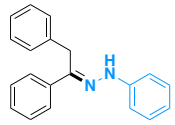
Compound **2h** was isolated in 99% yield (0.081 g). $^{1}$H NMR (300 MHz, $C_6D_6$) δ 7.24 (dd, *J* = 8.6, 7.1 Hz, 2H), 7.17 – 7.13 (m, 2H), 6.87 – 6.80 (m, 1H), 6.52 (s, 1H), 2.04 (ddt, *J* = 11.2, 6.8, 3.3 Hz, 1H), 1.84 – 1.67 (m, 4H), 1.60 (ddt, *J* = 8.1, 3.6, 1.5 Hz, 1H), 1.40 – 1.22 (m, 4H), 1.17 (s, 3H). $^{13}$C{$^{1}$H} NMR (126 MHz, $C_6D_6$) δ 148.95, 146.8, 129.5, 119.7, 113.4, 47.1, 30.8, 26.65, 26.6, 12.3.

**2i**



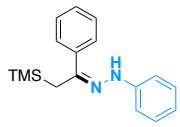
Compound **2i** was isolated in 99% yield (0.069 g) as a mixture of cis/trans isomers. $^{1}$H NMR (300 MHz, $C_6D_6$) δ 7.32 – 7.19 (m, 7H), 7.19 – 7.13 (m, 5H), 7.13 – 7.04 (m, 1H), 6.89 – 6.77 (m, 1H), 2.66 (q, *J* = 7.5 Hz, 2H), 2.38 – 2.25 (m, 2H), 2.17 (s, 2H), 2.14 – 2.05 (m, 3H), 1.71 – 1.49 (m, 5), 1.41 – 1.27 (m, 2H), 1.26 – 1.16 (m, 3H), 1.13 (t, *J* = 7.4 Hz, 34H), 0.93 (td, *J* = 7.4, 2.2 Hz, 4H), 0.78 (t, *J* = 7.3 Hz, 2H), 0.69 (q, *J* = 7.5 Hz, 5H). $^{13}$C{$^{1}$H}NMR (126 MHz, $C_6D_6$) δ 149.7, 149.6, 146.8, 146.8, 129.5, 119.7, 113.4, 38.6, 38.6, 30.2, 30.21, 21.3, 20.2, 18.6, 14.4, 14.4, 14.2, 14.9, 11.2, 11.2, 9.4.

**2j**



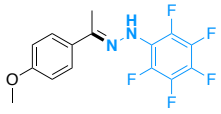
Compound **2j** was isolated in 86% yield (0.087 g). $^{1}$H NMR (300 MHz, $C_6D_6$) δ 7.90 – 7.81 (m, 2H), 7.33 (br, 1H), 7.23 – 7.16 (m, 4H), 7.14 – 7.10 (m, 2H), 7.07 – 7.01 (m, 4H), 6.81 (ddt, *J* = 7.2, 5.5, 1.3 Hz, 1H), 3.60 (s, 3H). $^{13}$C{$^{1}$H} NMR (126 MHz, $C_6D_6$) δ 145.5, 142.3, 139.5, 135.7, 129.5, 129.4, 128.8, 126.0, 120.7, 113.7, 32.2.

**2k**



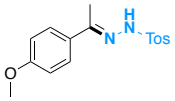

Compound **2k** was isolated in 76% yield (0.077 g). $^{1}$H NMR (300 MHz, $C_6D_6$) δ 7.76 – 7.72 (m, 2H), 7.28 – 7.18 (m, 4H), 7.17 (t, *J* = 1.1 Hz, 1H), 7.15 – 7.13 (m, 1H), 6.91 – 6.82 (m, 2H), 1.46 (s, 2H), 0.13 (s, 9H). $^{13}$C{$^{1}$H} (126 MHz, $C_6D_6$) δ 145.9, 141.0, 139.7, 129.6, 128.6, 128.5, 125.88, 120.5, 113.7, 11.1, 2.1.

**2l**



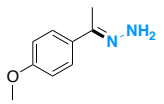
Compound **2l** was isolated in 99% yield (0.117 g). $^{1}$H NMR (300 MHz, $C_6D_6$) δ 7.65 (d, *J* = 8.9 Hz, 2H), 6.76 (d, *J* = 9.0 Hz, 2H), 6.37 (t, *J* = 3.4 Hz, 1H), 3.32 (s, 3H), 1.50 (s, 3H). $^{13}$C{$^{1}$H} NMR (126 MHz, $C_6D_6$) δ 160.9, 147.9, 139.5 (ddd, *J* = 28.7, 12.3, 7.7 Hz), 137.9– 137.19 (m), 130.9, 127.5, 114.1, 54.8, 10.9. $^{19}$F NMR (282 MHz, $C_6D_6$) δ -157.70 (dd, *J* = 22.9, 5.0 Hz), -164.88 – -165.31 (m), -168.85 – -169.31 (m). Crystals suitable for X-ray diffraction study were obtained from vapor diffusion from DCM solution with pentane.

**2m**



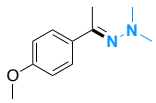

This reaction Compound **2m** was isolated in 56% yield (0.064 g) and agrees with previous literature report.[9] $^{1}$H NMR (300 MHz, $CDCl_3$) δ 7.92 (d, *J* = 8.3 Hz, 2H), 7.60 (d, *J* = 8.9 Hz, 2H), 7.34 – 7.29 (m, 2H), 6.85 (d, *J* = 8.9 Hz, 2H), 3.81 (s, 3H), 2.41 (s, 3H), 2.12 (s, 3H). $^{13}$C{$^{1}$H} NMR (126 MHz, $CDCl_3$) δ 160.9, 152.7, 144.2, 135.4, 129.9, 129.7, 128.25, 127.9, 113.7, 55.45, 21.78, 13.4.

**2n**



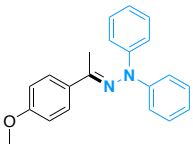
Hydrous hydrazine ($nH_2O.NH_2$-$NH_2$, 50-60%) was used for this reaction. Compound **2n** was isolated in 73% yield (0.043 g) and agrees with previous literature report.[10]. $^{1}$H NMR (300 MHz, $C_6D_6$) δ 7.70 (d, *J* = 8.9 Hz, 2H), 6.80 (d, *J* = 8.9 Hz, 2H), 4.76 (br, 2H), 3.32 (s, 3H), 1.65 (s, 3H). $^{13}$C{$^{1}$H} NMR (126 MHz, $C_6D_6$) δ 160.0, 145.4, 132.9, 127.1, 113.9, 54.8, 10.9.

**2o**



Compound **2o** was isolated in 81% yield (0.056 g) and agrees with previous literature report.[11] $^{1}$H NMR (300 MHz, $C_6D_6$) δ 7.84 (d, $J$ = 8.9 Hz, 2H), 6.78 (d, $J$ = 8.9 Hz, 2H), 3.28 (s, 3H), 2.52 (s, 6H), 2.16 (s, 3H). $^{13}$C{$^{1}$H} NMR (126 MHz, $C_6D_6$) δ 161.1, 160.9, 131.9, 128.2, 113.7, 54.8, 47.5, 14.6.

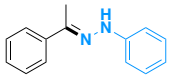
**2p**



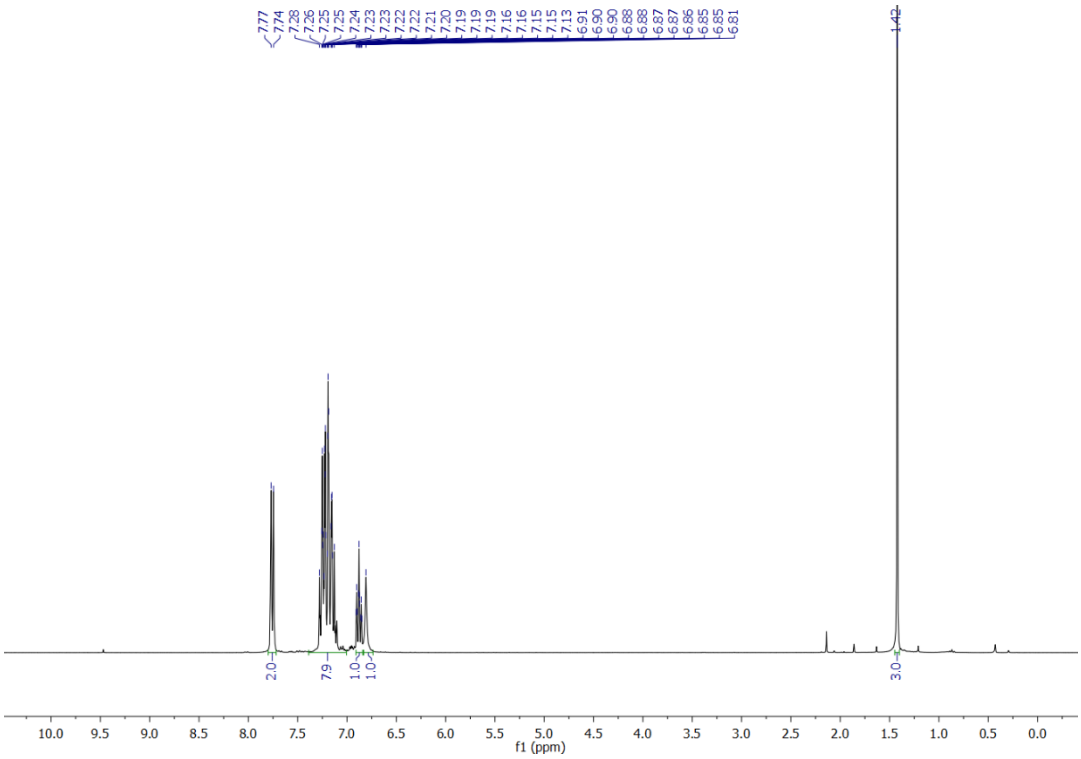
Despite several attempts **1k** was found to be too sensitive to purify by standard chromatographic methods even under anhydrous conditions. Consequently, the yield was determined by NMR (19%) as presented in the NMR spectrum of the crude reaction mixture.

## B. NMR spectra

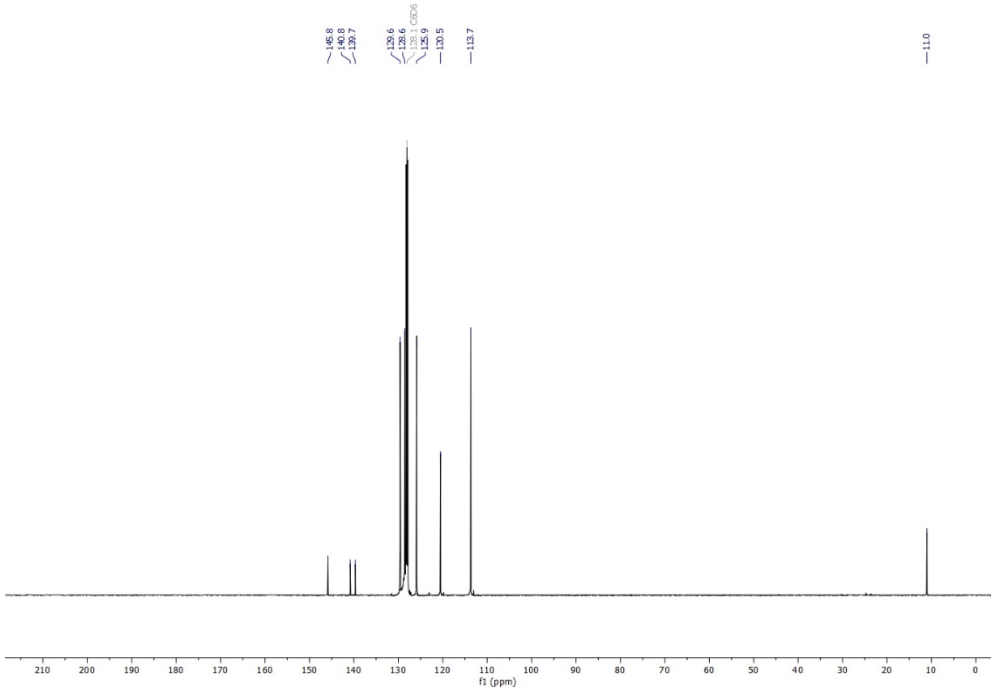
**Compound 2a**



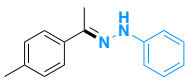
$^{1}H$ spectrum



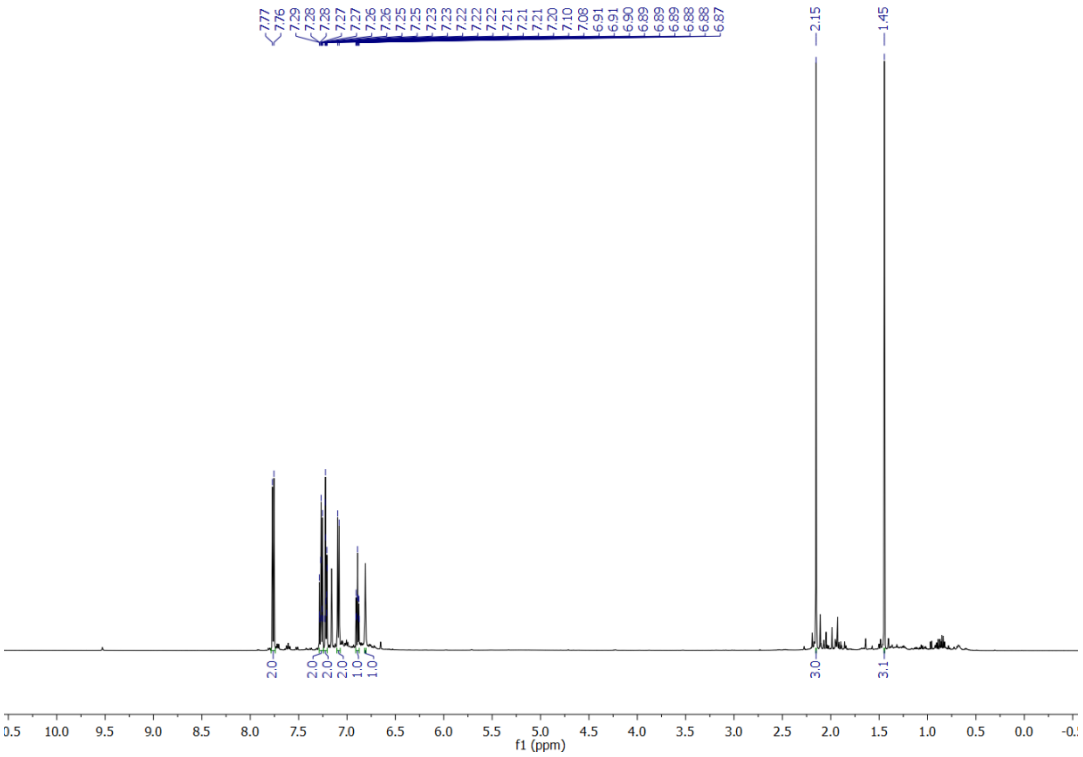

$^{13}C\{^{1}H\}$ spectrum



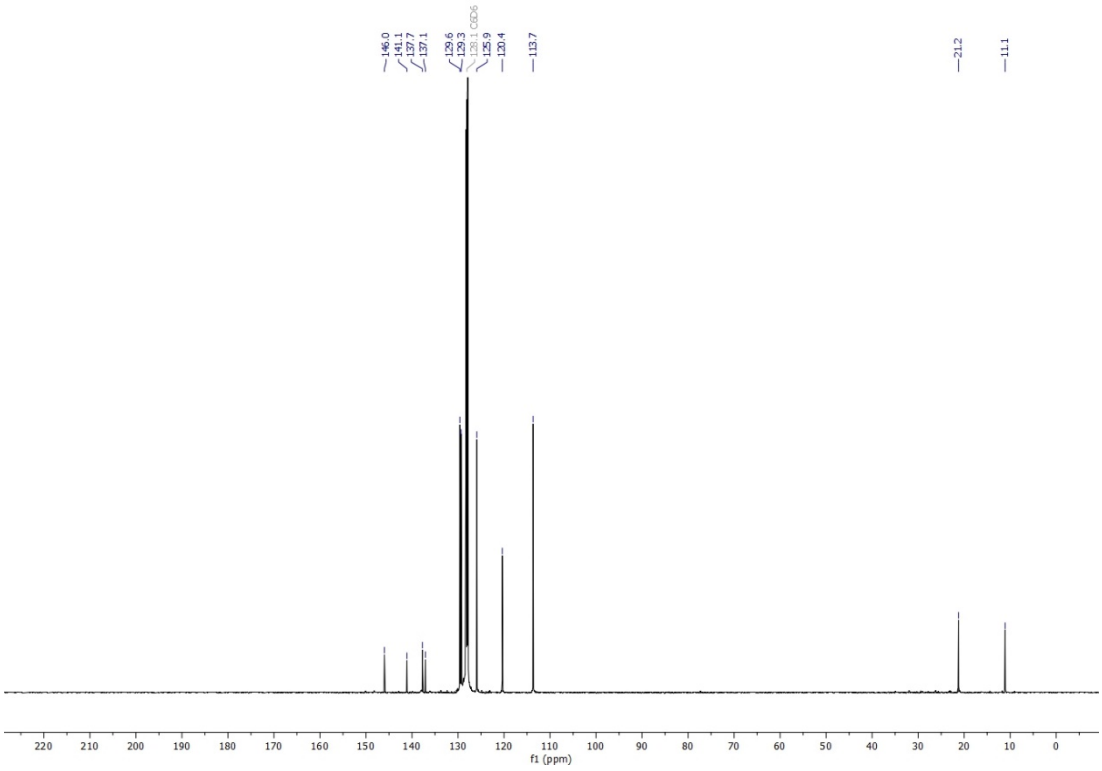
**Compound 2b**



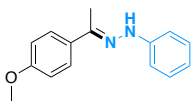
$^{1}H$ spectrum



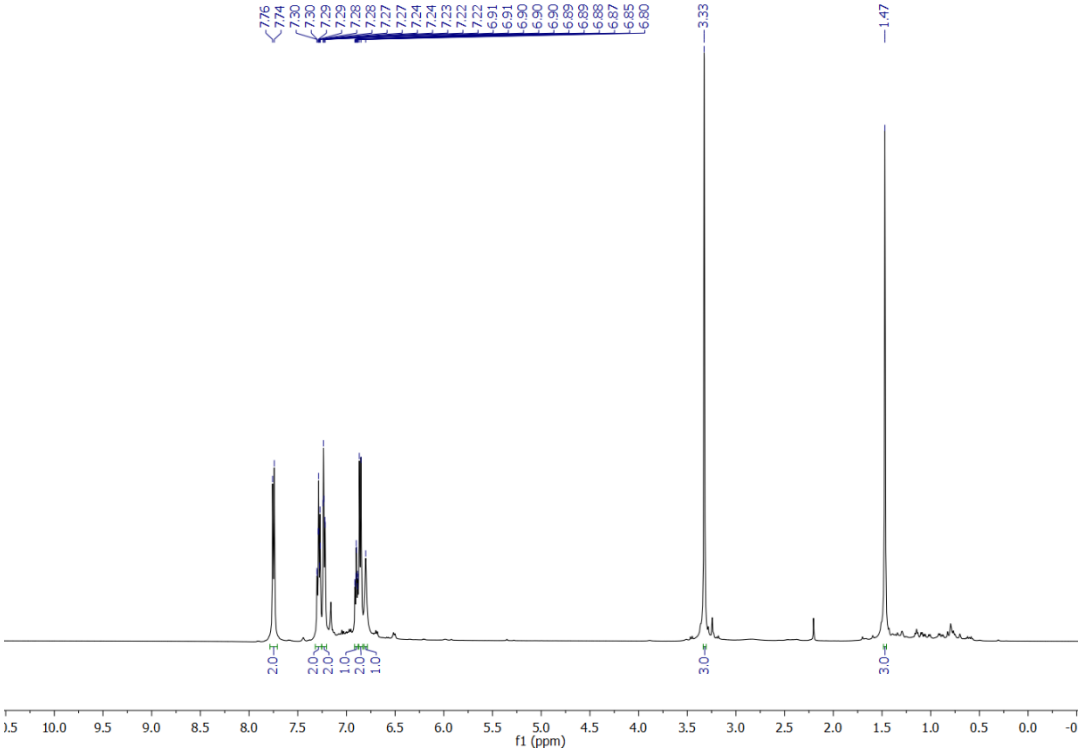

$^{13}C\{^{1}H\}$ spectrum



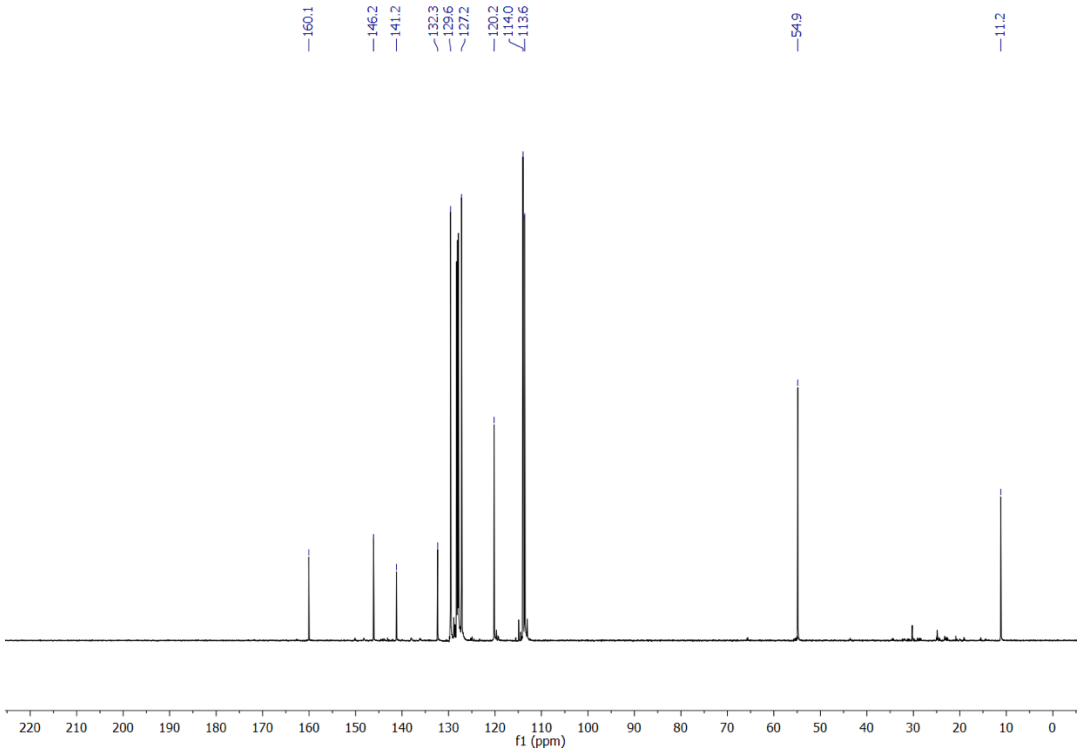
**Compound 2c**



$^{1}$H spectrum

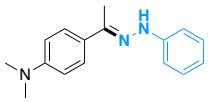


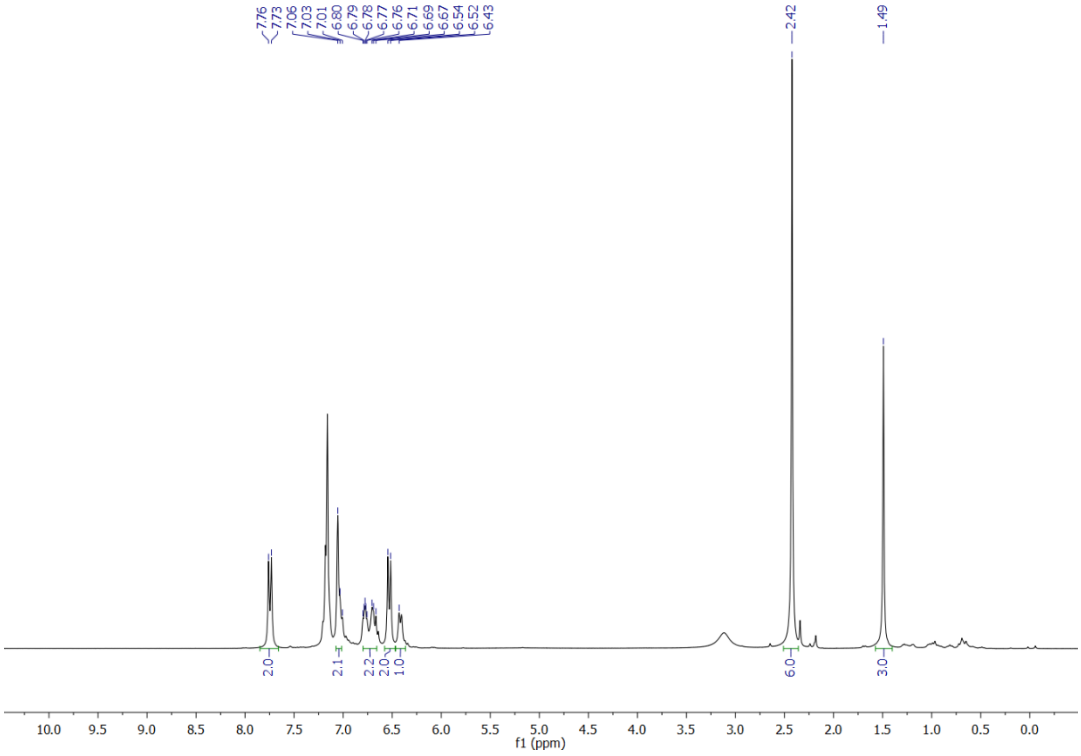

$^{13}$C{$^{1}$H} spectrum



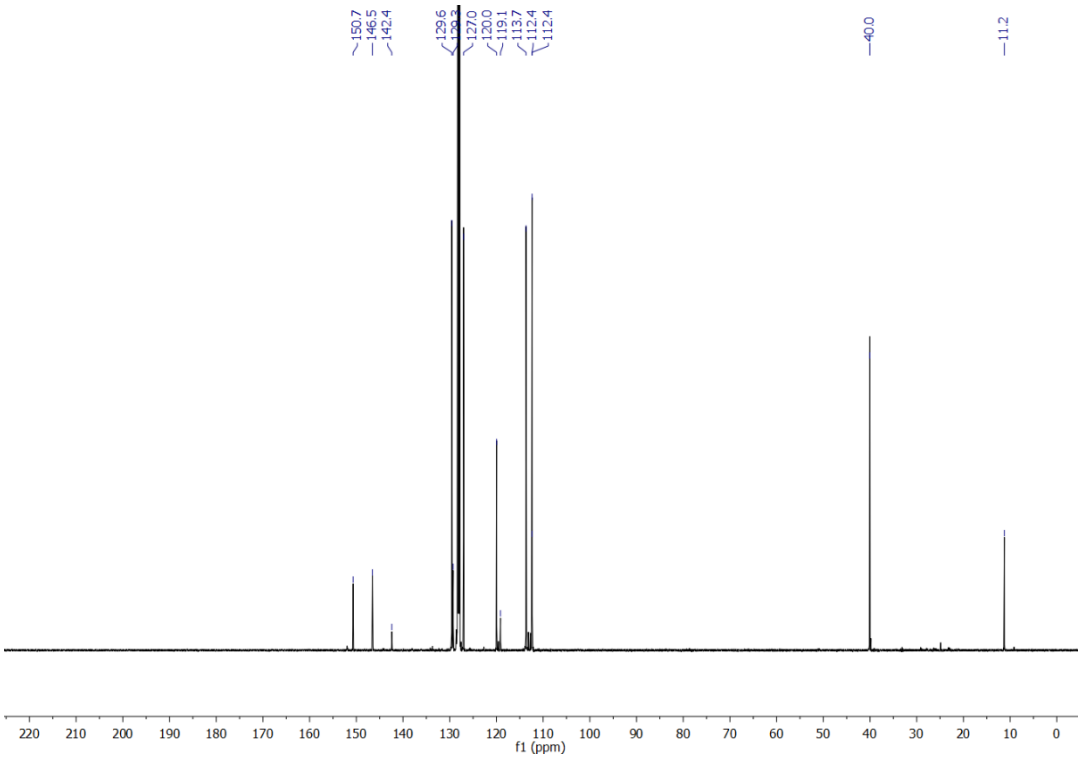
**Compound 2d**

$^{1}$H spectrum



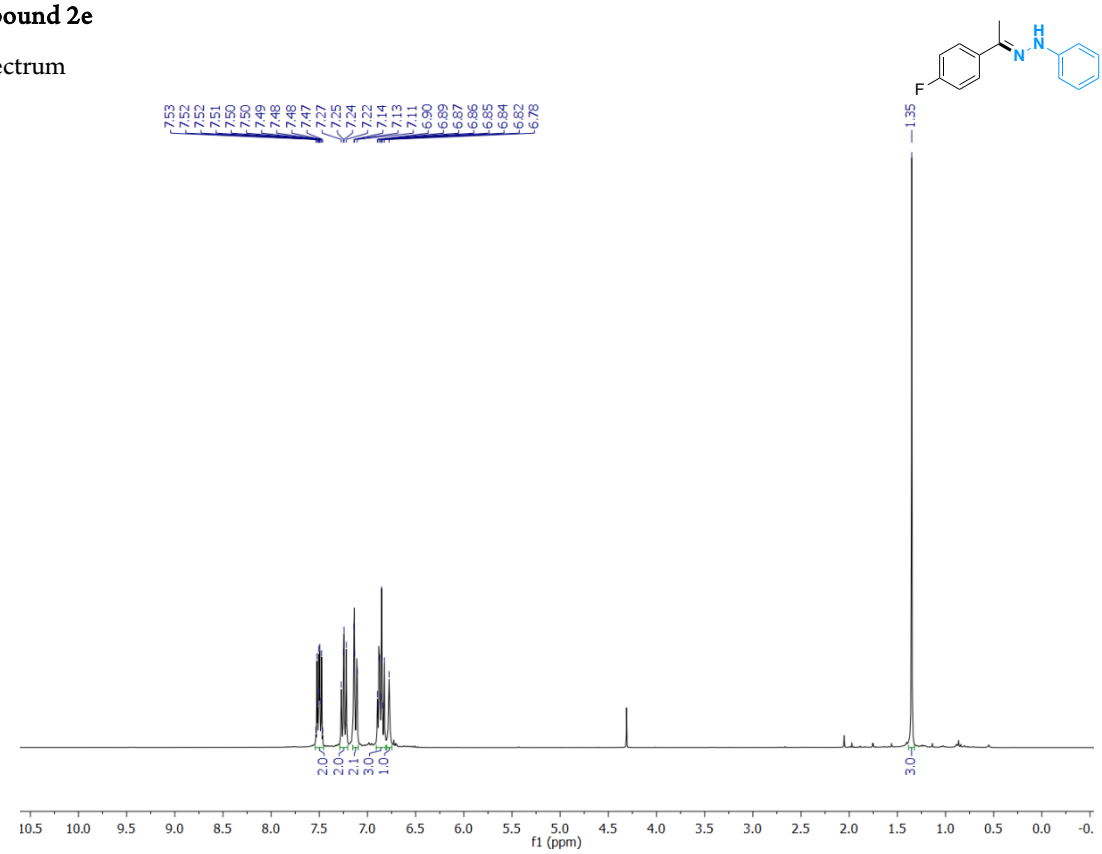



$^{13}$C{$^{1}$H} spectrum

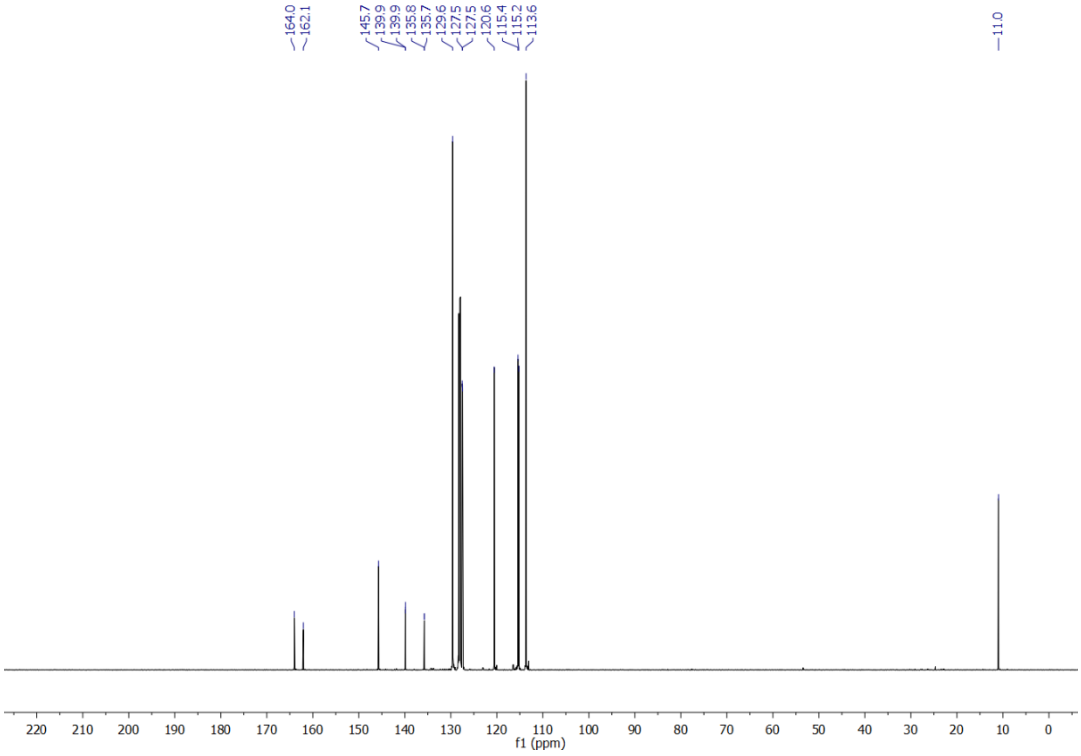


**Compound 2e**

$^{1}$H spectrum

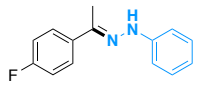


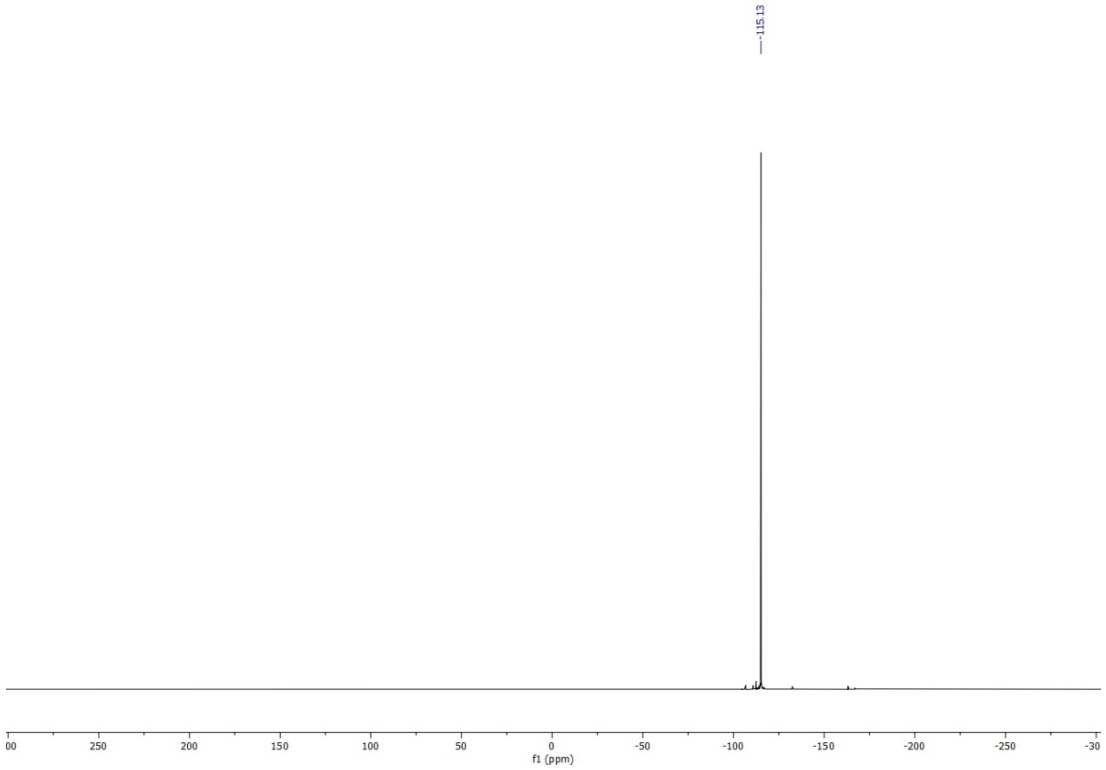

$^{13}$C{$^{1}$H} spectrum



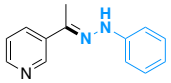
**Compound 2e**

$^{19}F$ spectrum

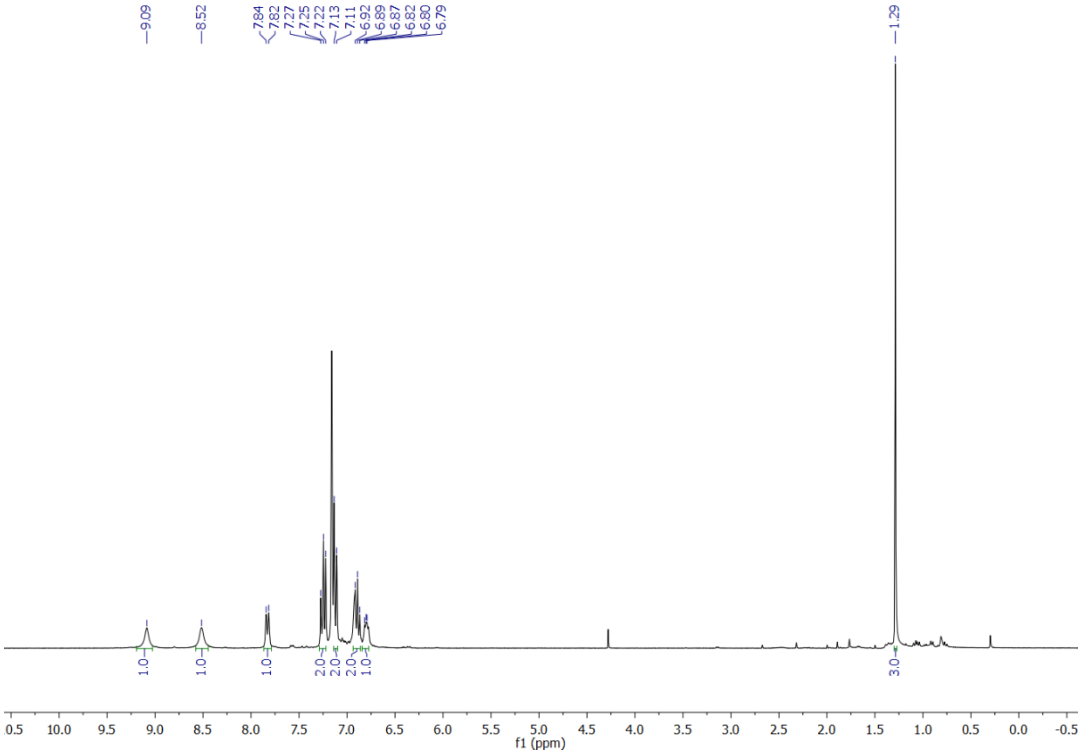


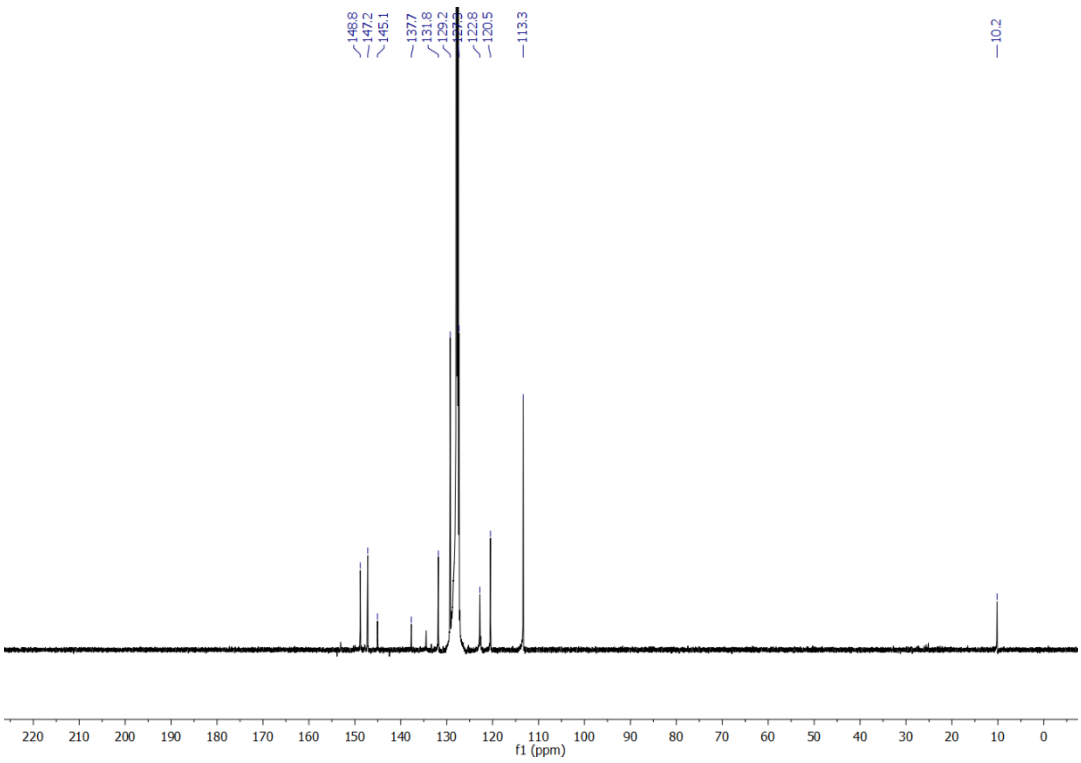
**Compound 2f**



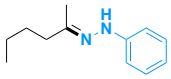
$^{1}$H spectrum



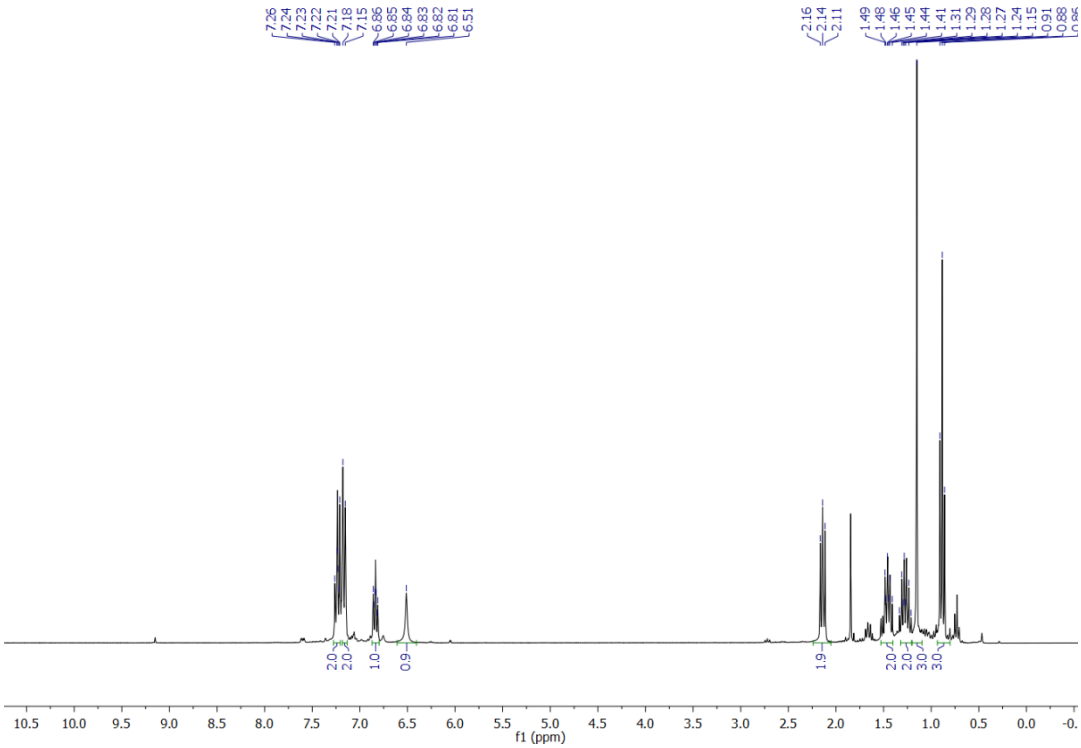

$^{13}$C{$^{1}$H} spectrum



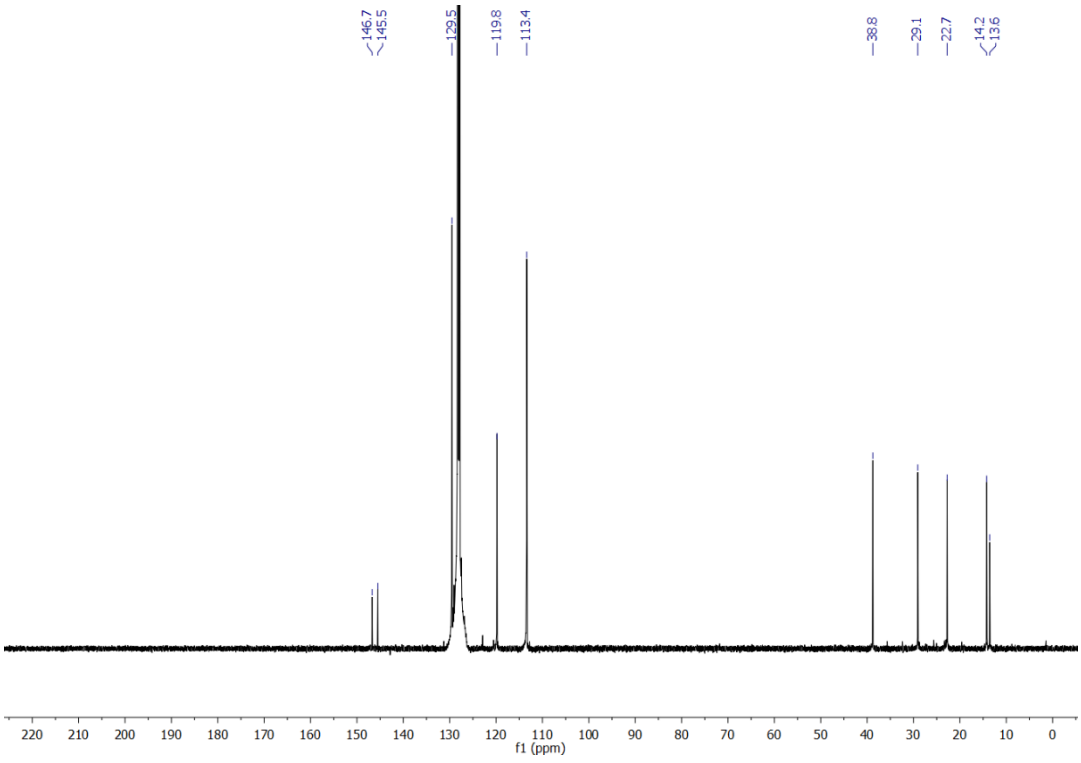
**Compound 2g**



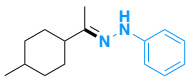
$^{1}H$ spectrum



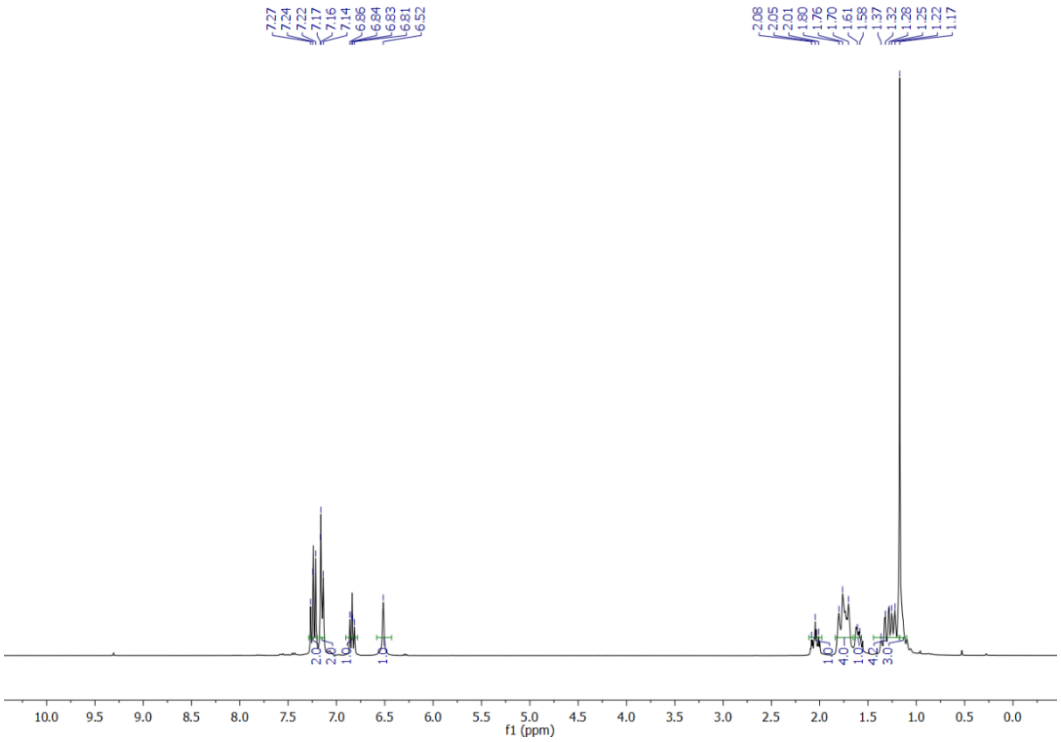

$^{13}C\{^{1}H\}$ spectrum



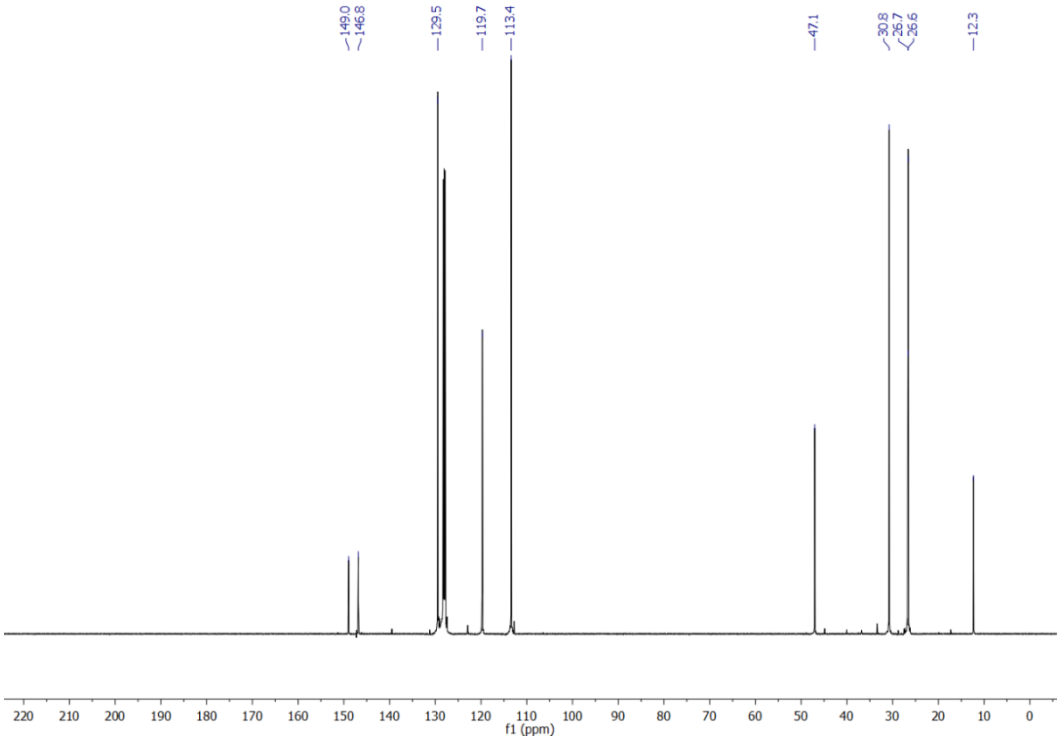
**Compound 2h**



$^{1}H$ spectrum

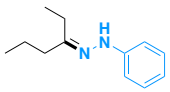


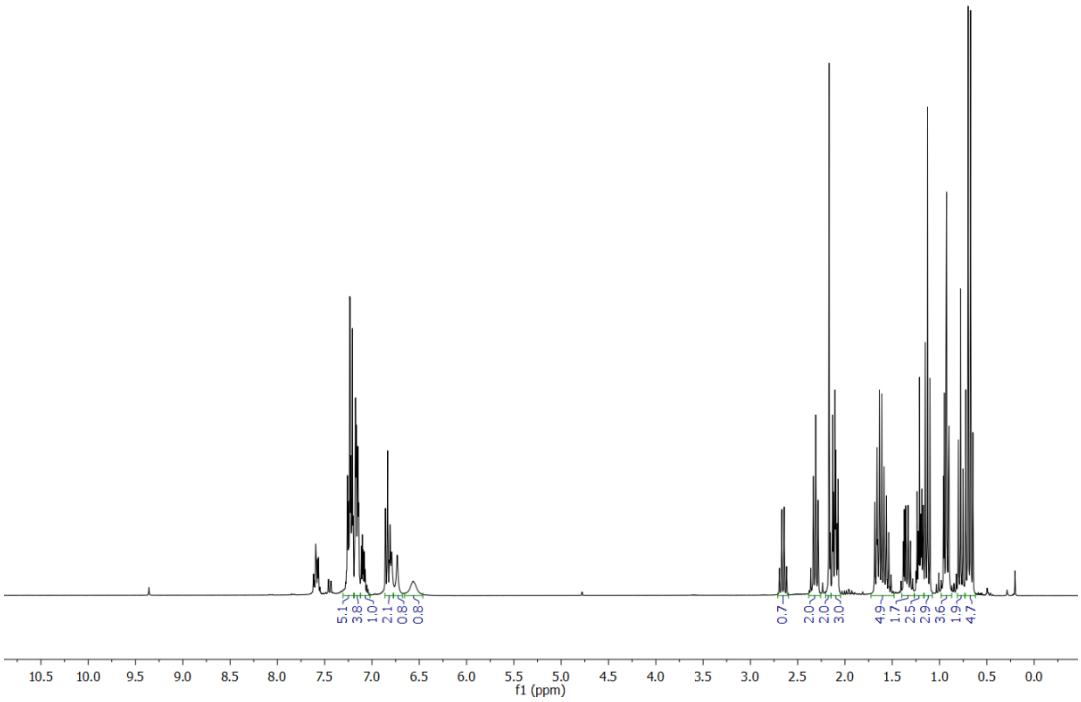

$^{13}C\{^{1}H\}$ spectrum



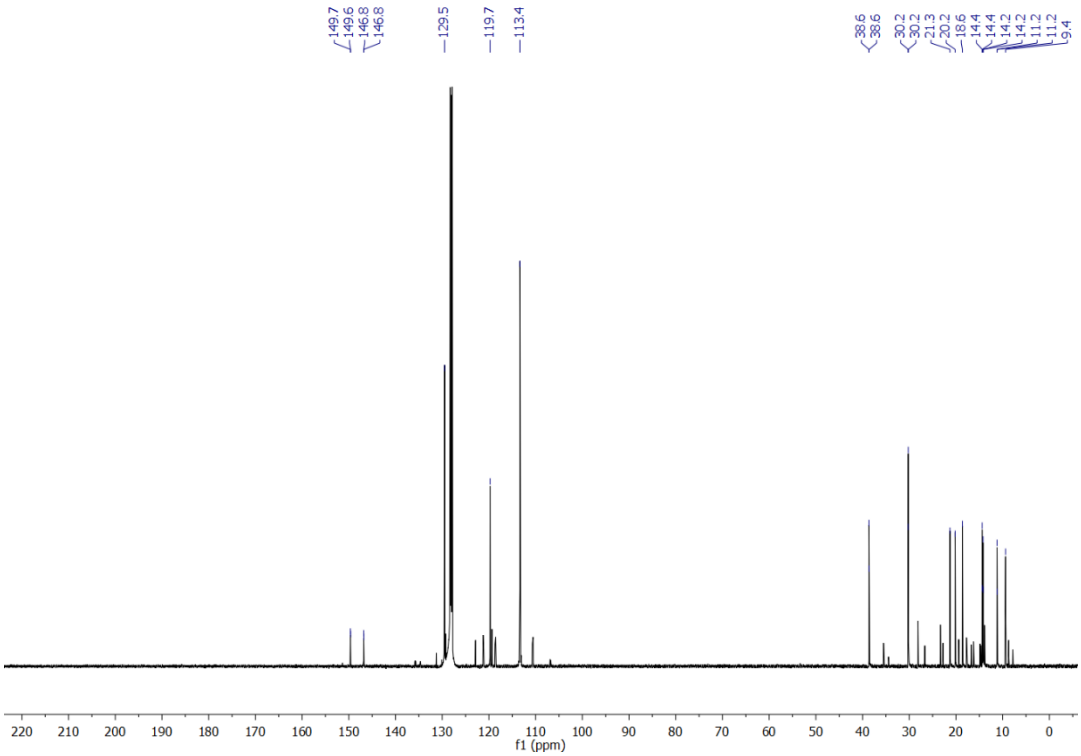
**Compound 2i**

$^{1}H$ spectrum



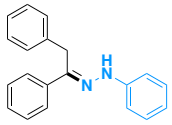


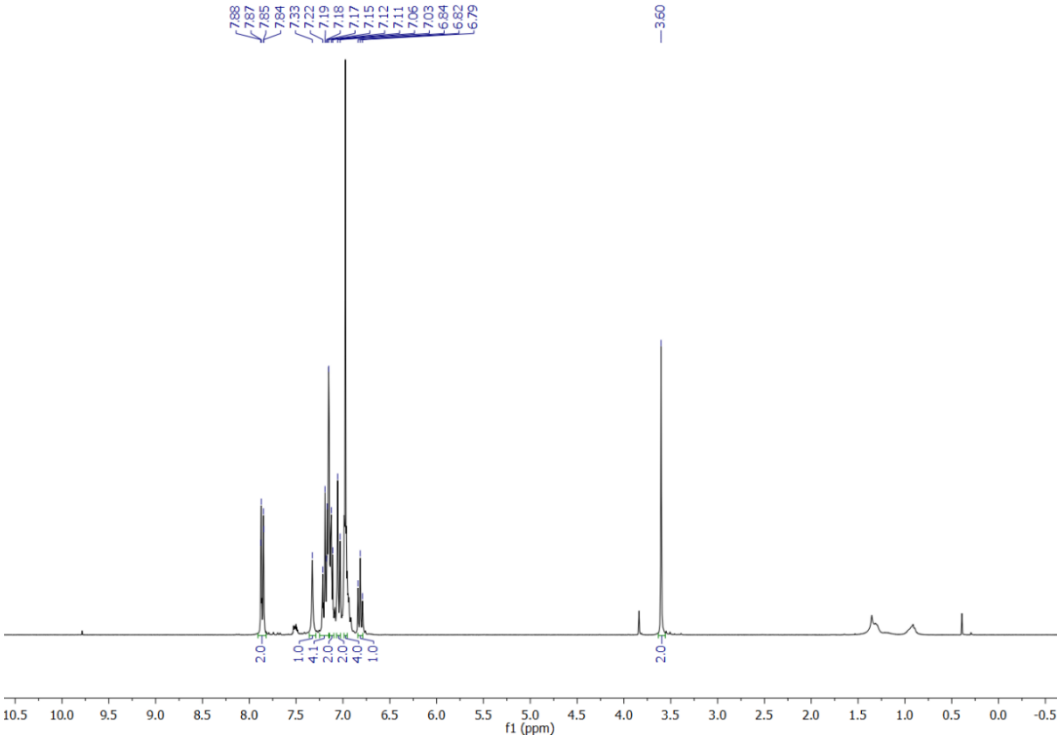

$^{13}C\{^{1}H\}$ spectrum



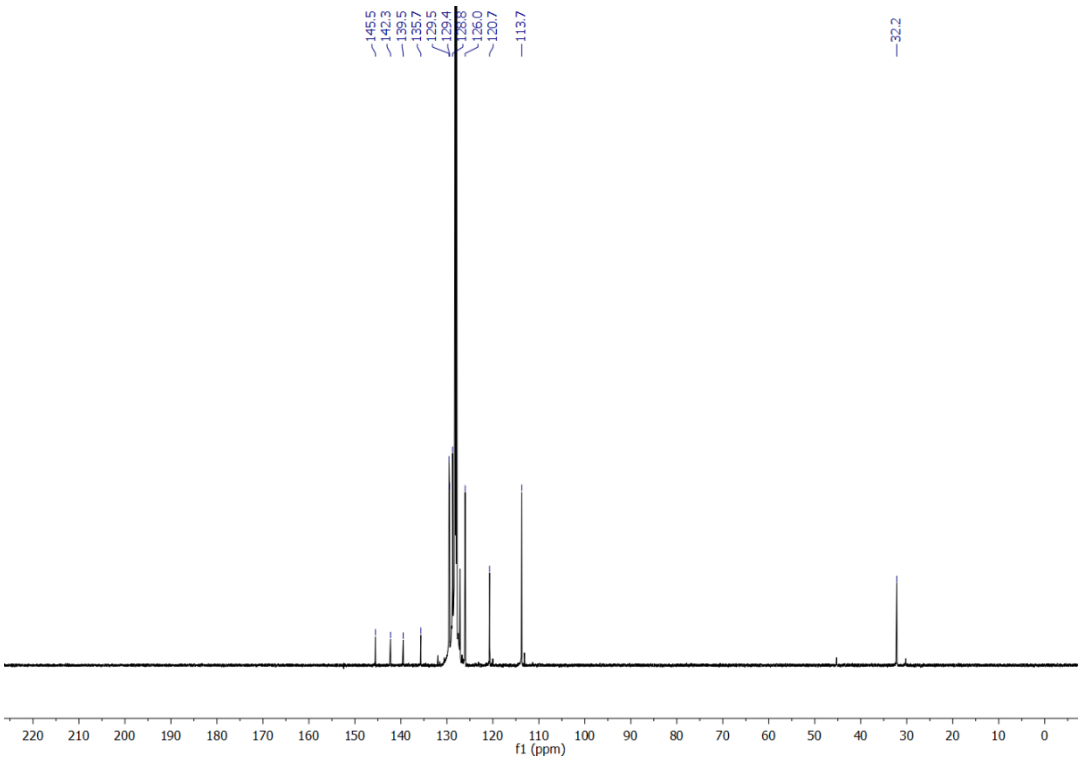
**Compound 2j**

$^{1}$H spectrum

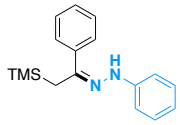




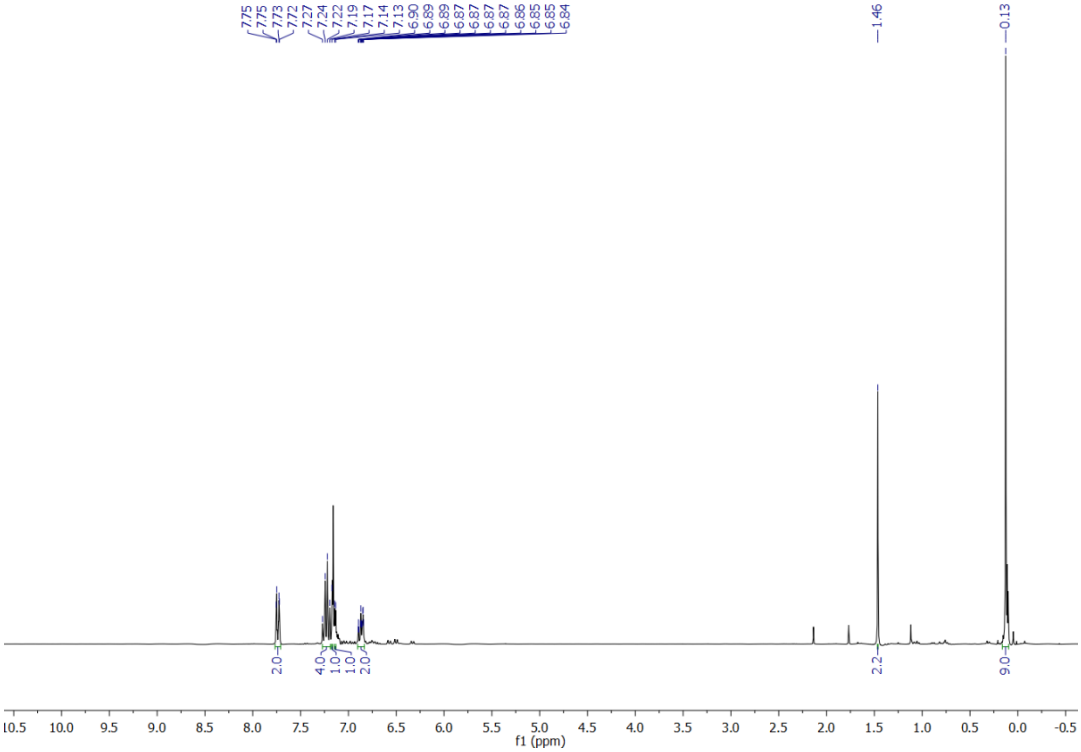

$^{13}$C{$^{1}$H} spectrum



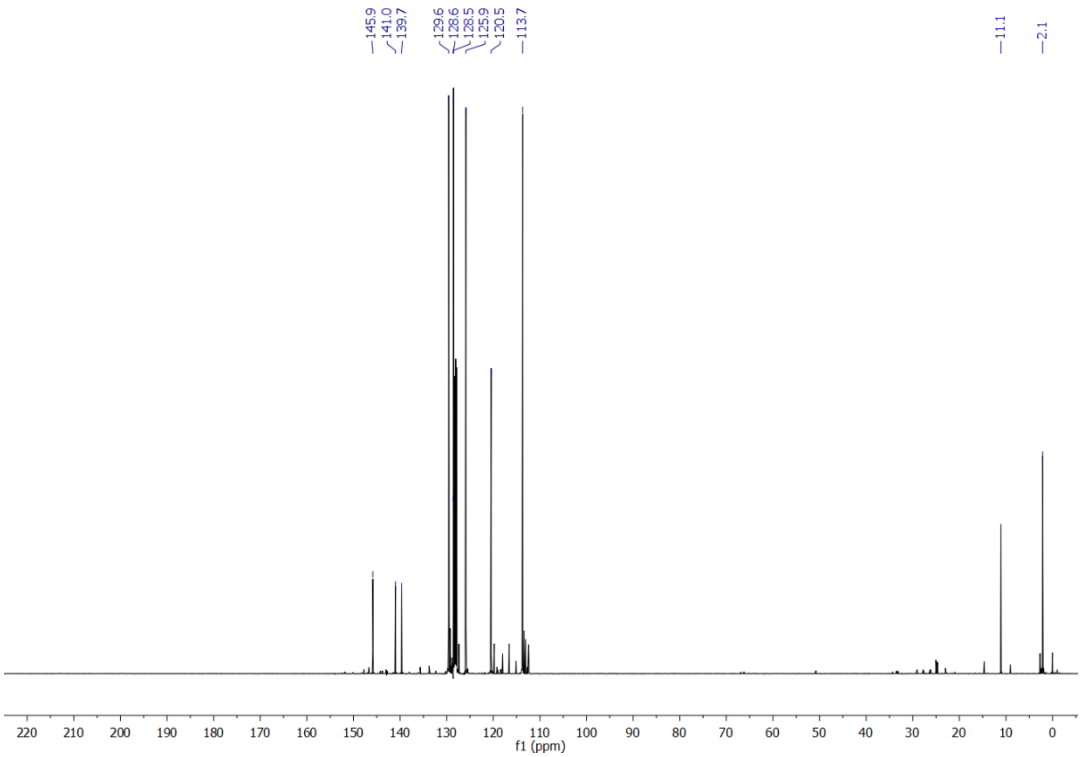
**Compound 2k**



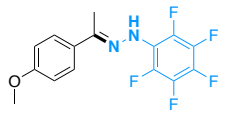

$^{1}$H spectrum



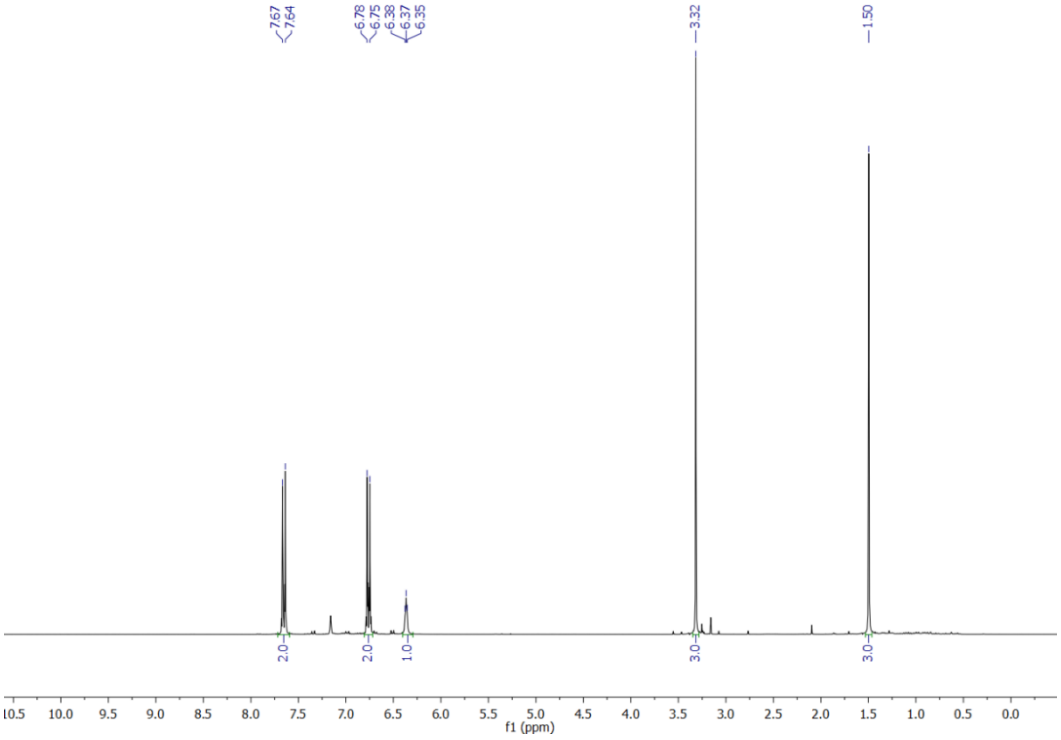

$^{13}$C{$^{1}$H} spectrum



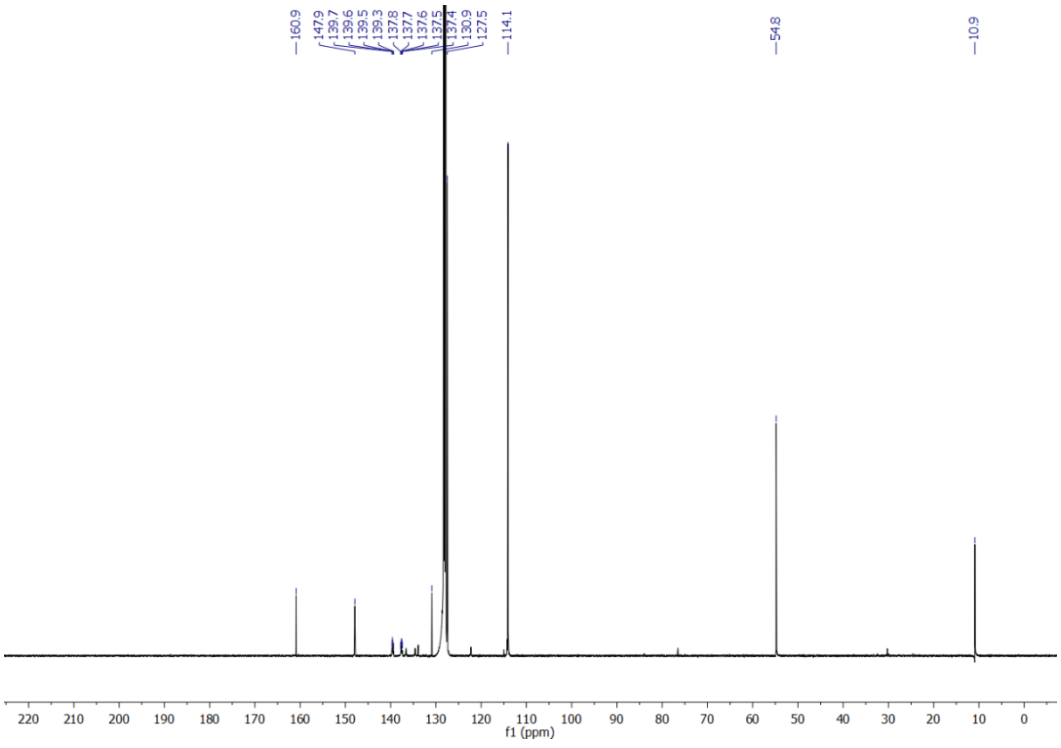
**Compound 2l**



$^{1}$H spectrum

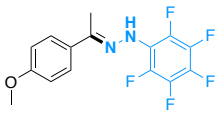


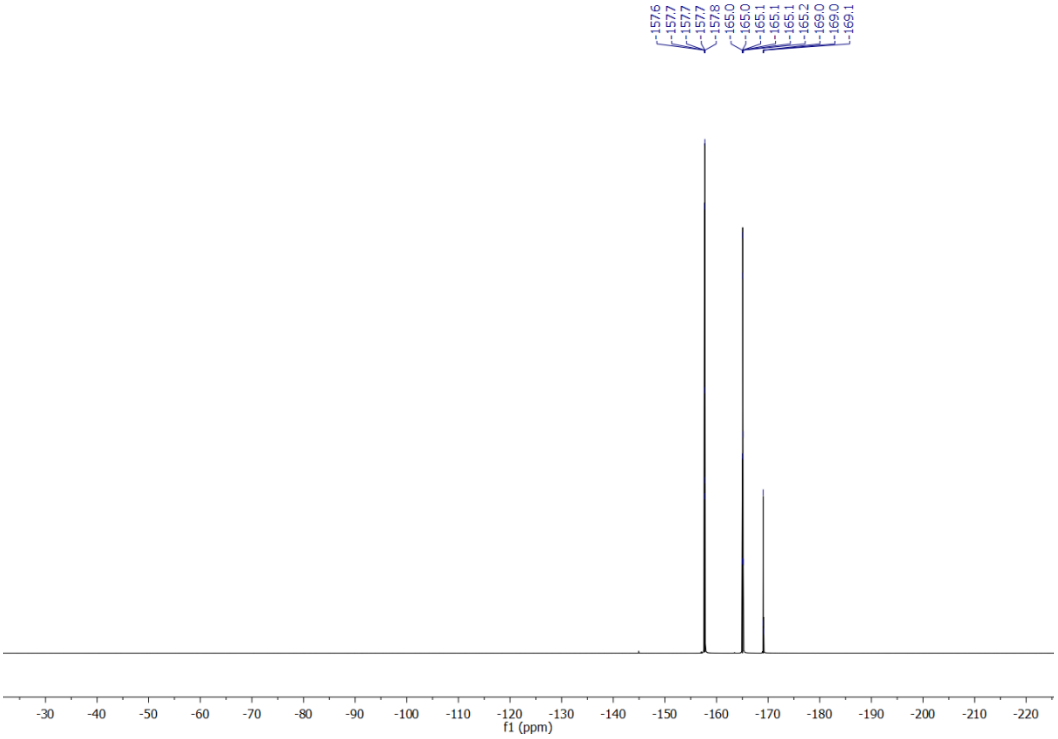

$^{13}$C{$^{1}$H} spectrum



**Compound 2l**

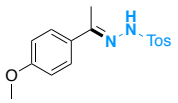
$^{19}F$ spectrum

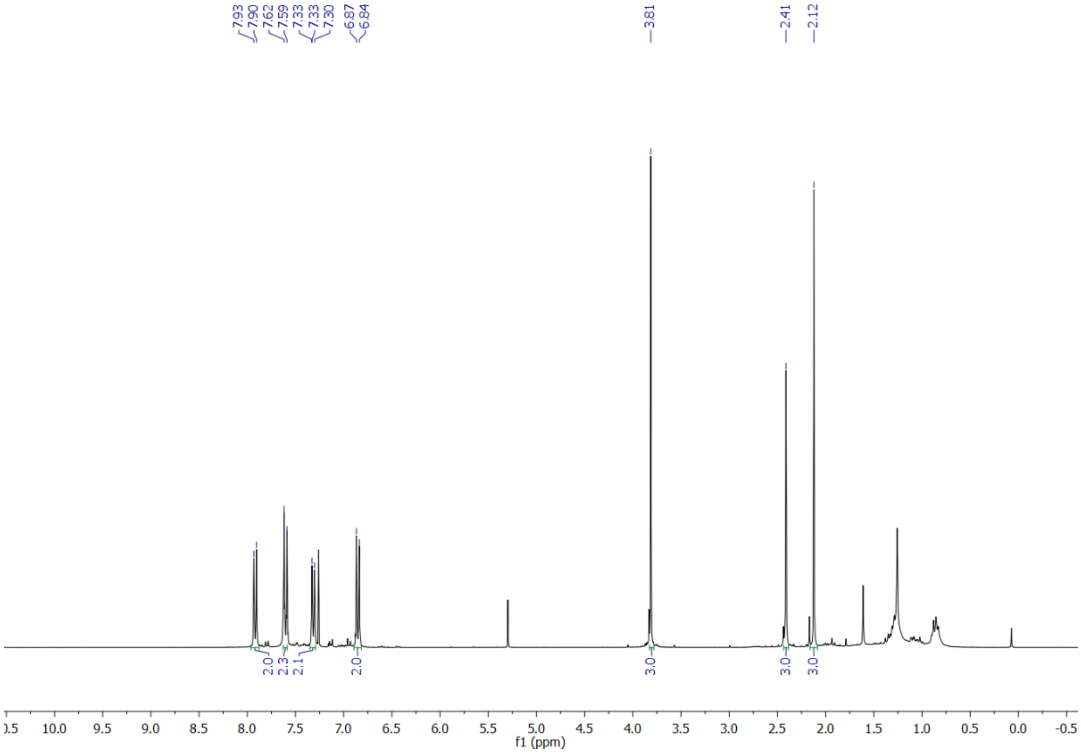


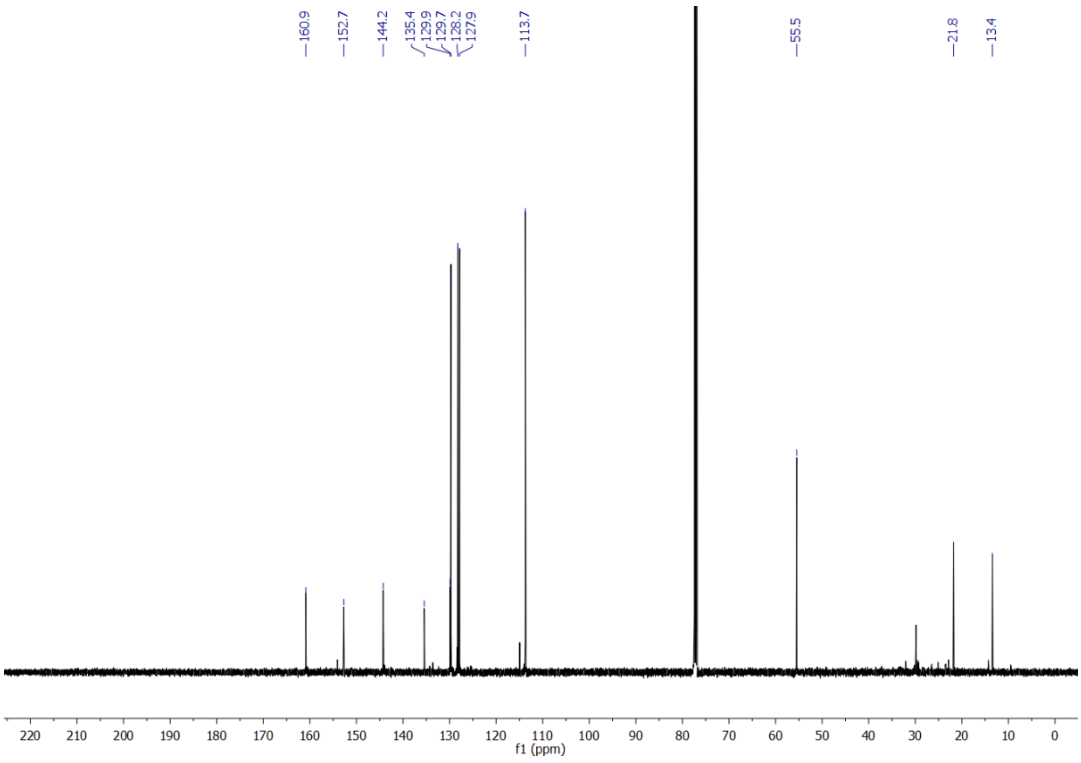
**Compound 2f**

$^{1}$H spectrum



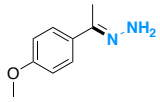



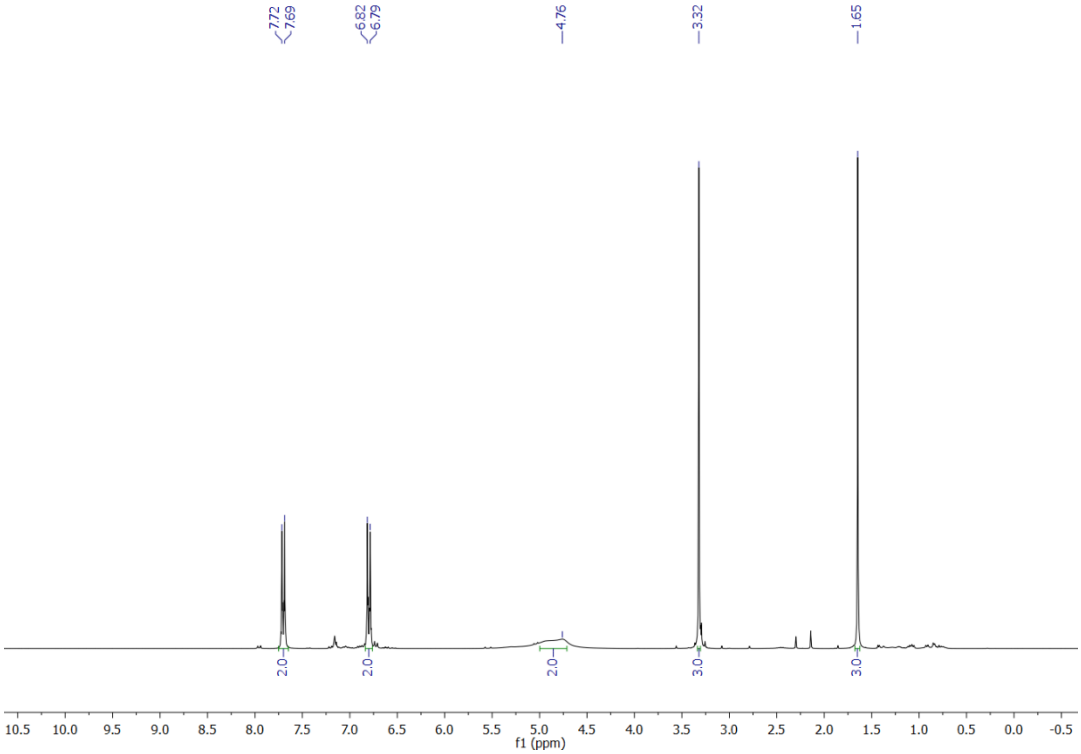

$^{13}$C{$^{1}$H} spectrum



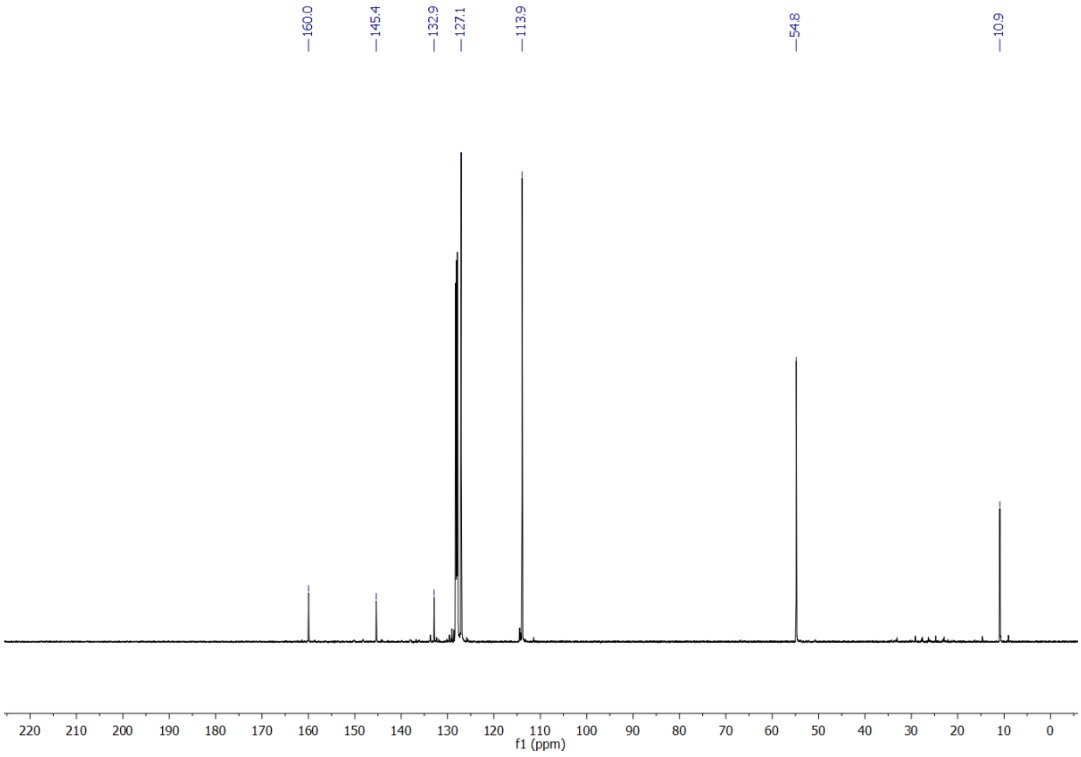
**Compound 2n**

$^{1}$H spectrum



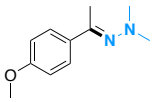



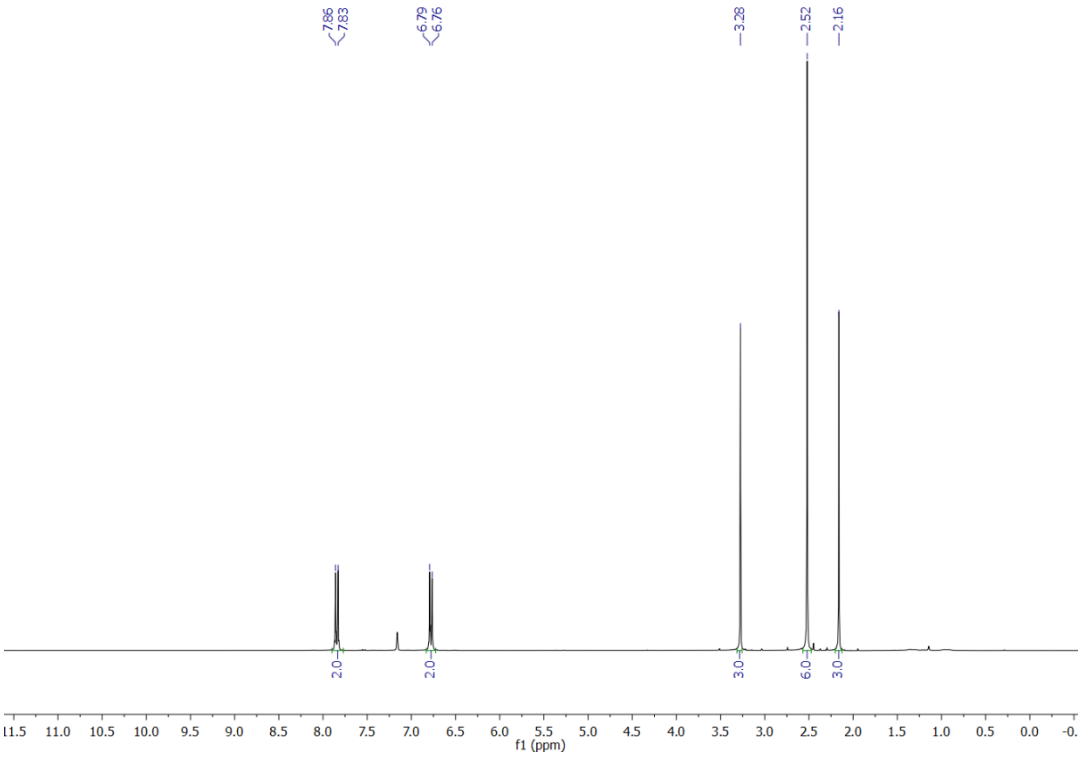

$^{13}$C{$^{1}$H} spectrum



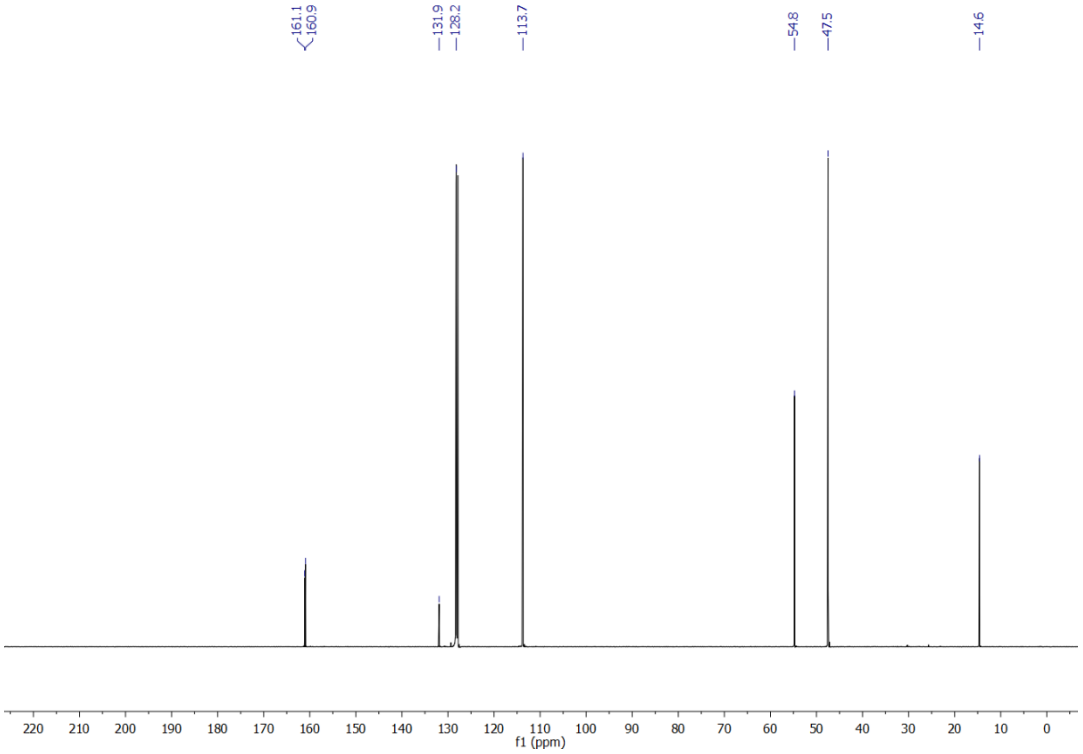
**Compound 2o**

$^{1}H$ spectrum

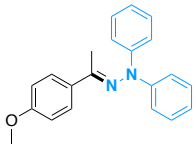




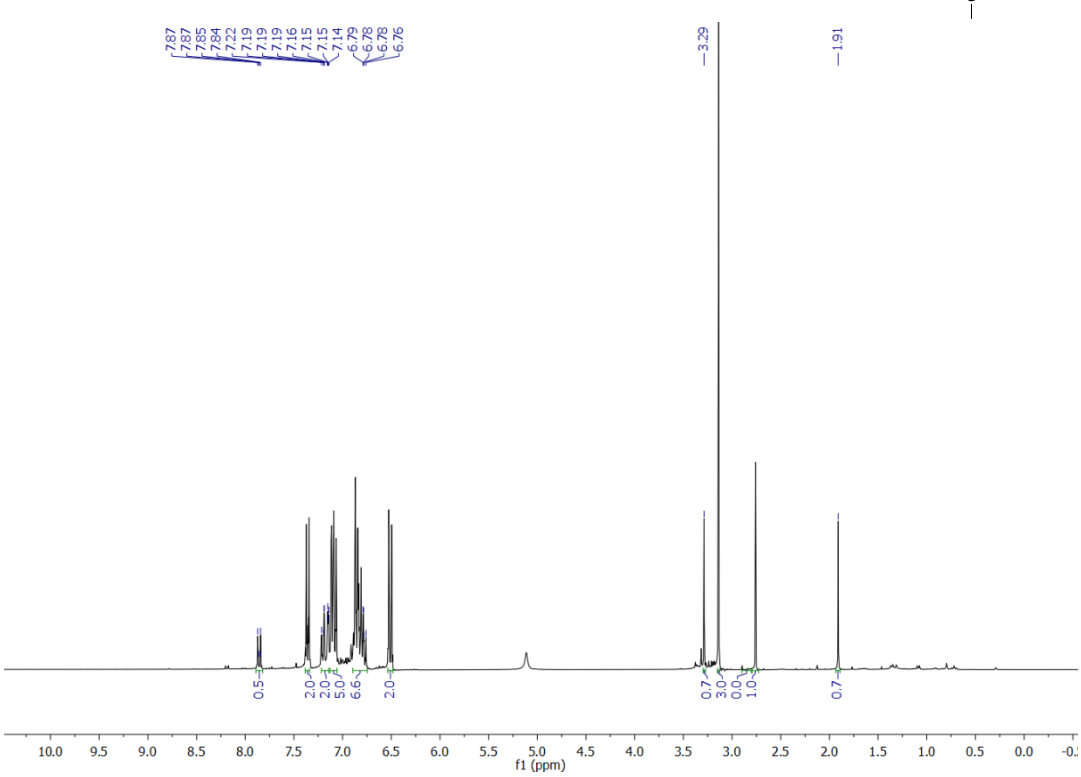

$^{13}C\{^{1}H\}$ spectrum



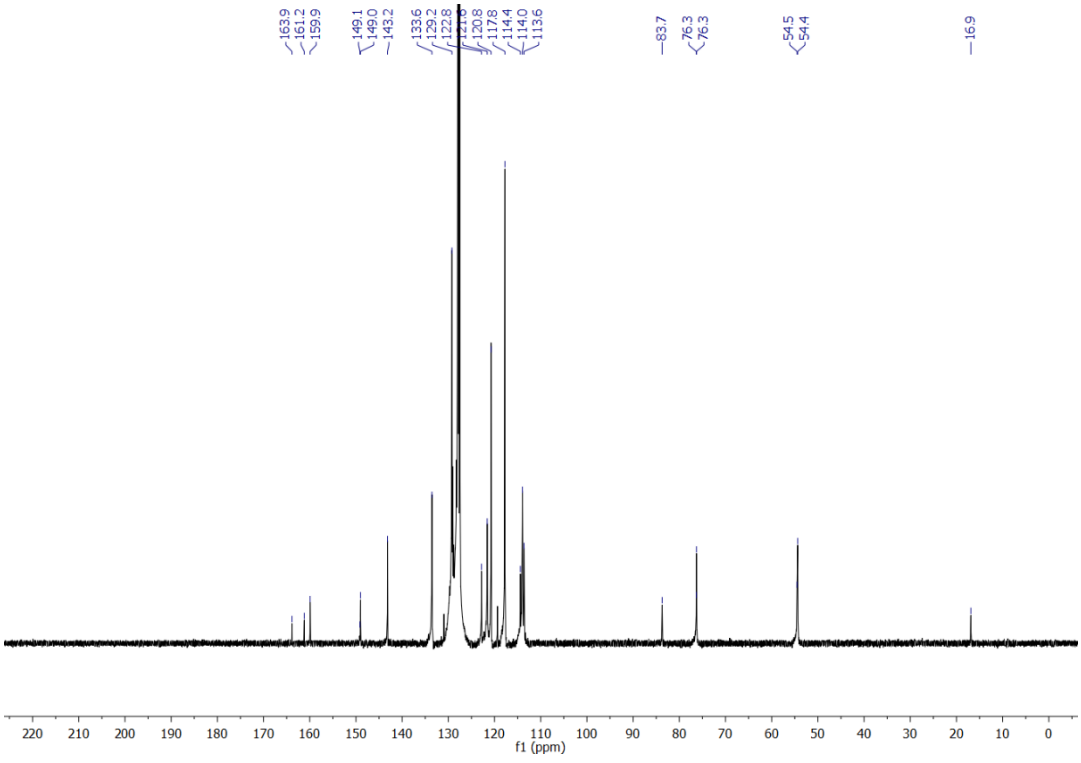
**Compound 2p**



$^{1}H$ spectrum




$^{13}C\{^{1}H\}$ spectrum

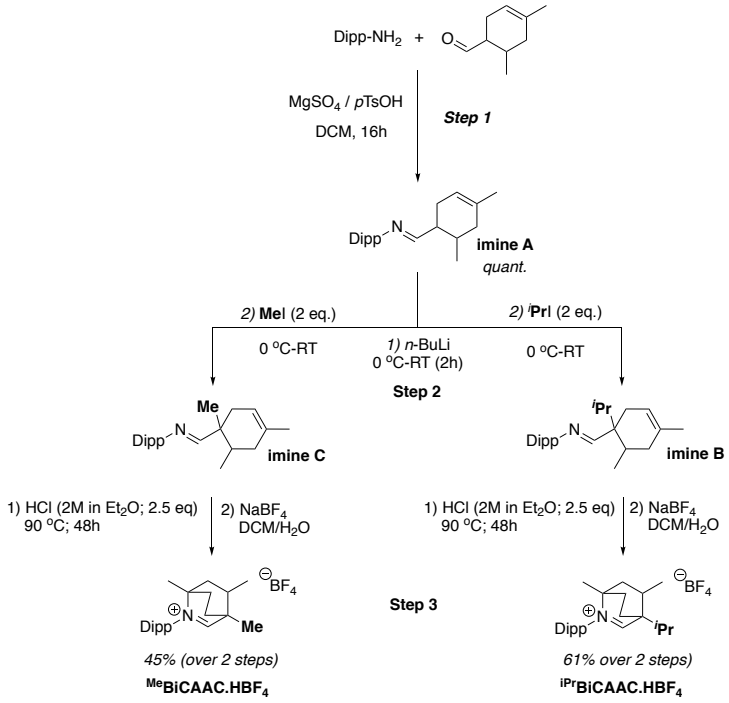


## II.3. Gold complexes and catalysts

### A. Literature procedures

$^{Et}$CAAC-5,[12] $^{Et}$CAAC-6,[13] $^{Ad}$CAAC-5,[14] and IMes[15] ligands, as well as [(THT)Au(Cl)][16] (THT = tetrahydrothiophene), [($PPh_3$)Au(Cl)],[17] [(IMes)AuCl],[18] [($^{Et}$CAAC-5)Au(Cl)],[19] [($^{Ad}$CAAC-5)Au(Cl)],[14] [($PPh_3$)Au(Ph)] gold precursors were prepared according to known literature procedures.

### B. Preparation of BICAAC ligands



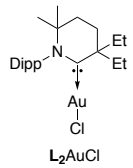

$^{IPr}$BICAAC and $^{Me}$BICAAC were prepared according to a modified literature procedure.[20]

**Step 1**: Commercially available 2,4-dimethyl-3-cyclohexene carboxaldehyde (50 mL; 0.339 mol) was dissolved in 300 mL of dichloromethane followed by the addition of 2,6-diisopropylaniline ($DippNH_2$; 54 mL; 0.282 mol), anhydrous $MgSO_4$ (large excess) and *p*-toluene-sulfonic acid (catalytic - 0.1 g). The mixture was stirred at room temperature for 16h. After confirming full consumption of the aniline, the mixture was filtered and the volatiles were removed under vacuum. Evaporation of the volatiles afforded an oily residue, which was further distillated at 100 °C under high vacuum to remove the residual excess aldehyde, thus affording an off-yellow oil. (Note that the purity of **imine A** is largely affected by the purity of the 2,6-diisopropylaniline. In such case, the imine can be further purified through distillation or purified over silica gel). The purity of **imine A** was confirmed by NMR[20,21] and it was used in the next step without further purification. **Step 2**: **imine A** (30g; 0.100 mol) was dissolved in dry diethyl ether (180 mL) under argon atmosphere and the solution was cooled down to 0 °C. n-Butyl lithium (45 mL; 2.5 M in hexanes, 1.1 eqv.) was carefully added over 10 minutes (**! Exert caution** when working in large scale as the reaction is exothermic) and the mixture was allowed to warm up to room temperature. After 2 h the mixture was cooled down to 0 °C and the corresponding alkyl halide (2 eqv.) was added dropwise over 30 minutes (**! Exert caution** when working in large scale as the reaction is exothermic). The reaction mixture was brought back to room temperature and stirred overnight. Following aqueous workup $H_2O$ (3 x 50 mL), and washing with $NaHSO_3$ (*saturated aqueous, sat.*; 2 x 50 mL), the organic phase was dried over $MgSO_4$ to afford a crude oily residue. The latter was further dried under high vacuum with the help of the heat gun to eliminate residual water (Note: Any traces of water at this stage will significantly impact the yield of the next step). The purity of **imine B** and **C** were confirmed by NMR,[20] and these imines were used in the next step without further purification. **Step 3**: **imine B** (or **C**) obtained in the previous step was transferred via cannula to a heavy wall pressure schlenk of 250 mL with help of 2x 50 mL of dry toluene under argon atmosphere. The toluene was then removed under high vacuum, before adding 2.5 equivalents (with respect to imine **A**) of hydrogen chloride (126 mL; 2M in $Et_2O$) at 0 °C (**Note**: precipitation should be observed immediately). The mixture was sealed and stirred under argon atmosphere at 90 °C for 48h. After this time the pressure schlenk was brought back to room temperature and left stirring for 2h to enforce precipitation of the product before being carefully opened to argon line. Removal of the supernatant via canula, and further washing with dry $Et_2O$ (3x 50 mL) afforded an off-white powder. The latter was dissolved in DCM (100 mL), to which was added an aqueous solution of sodium tetrafluoroborate (22g in 100mL; 2 eqv./**imine A**). After stirring the biphasic mixture for 1h at room temperature, the organic phase was washed with water (3x 50 mL) and

dried over $MgSO_4$. Following evaporation of the DCM under vacuum the iminium was obtained as a white crystalline powder, which was further triturated in pentane/$Et_2O$ (1:1; 100ml) thus affording after filtration and evaporation **$^{iPr}$BiCAAC.HBF$_4$** in 61% (26.25 g) yield as confirmed by NMR.[20] Similarly, **$^{Me}$BiCAAC.HBF$_4$** was obtained in 45% (18.1 g) yield as confirmed by NMR.[20]

## C. Preparation of gold catalysts

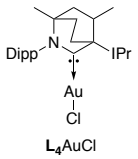
**Synthesis of [($^{Et}$CAAC-6)Au(Cl)] / ($L_2$)AuCl:**



**$L_2$AuCl**

Under an argon atmosphere, a 50 mL schlenk flask was charged with [($L_2$)AuPh][13] (1.000 g, 1.702 mmol, 1.0 eq.)and 15 mL of anhydrous THF. The solution was then cooled to -78 °C and stirred for 15 min, before adding a 2M HCl solution in $Et_2O$ (1.28 mL, 1.5 eq.) dropwise. Warming up to room temperature slowly over the course of 5h, and evaporation of the volatiles in vacuo afforded **($L_2$)AuCl** as a white powder (0.919 g, 99% yield). $^1$H NMR (300 MHz, $CDCl_3$) δ 7.58 – 7.49 (m, 1H), 7.38 (dd, *J* = 8.3, 7.1 Hz, 1H), 7.22 (d, *J* = 7.7 Hz, 1H), 2.72 (p, *J* = 6.7 Hz, 2H), 2.08 – 1.99 (m, 4H), 1.96 – 1.88 (m, 2H), 1.47 (d, *J* = 6.7 Hz, 6H), 1.33 (d, 6H), 1.30 (d, 6H), 1.30 (s, 3H), 1.10 (d, *J* = 6.2 Hz, 2H), 1.01 (t, *J* = 7.4 Hz, 6H).$^{13}$C{$^1$H} NMR (126 MHz, $CDCl_3$) δ 240.9, 143.8, 141.7, 141.7, 134.3, 132.1, 129.6, 125.4, 64.9, 51.0, 35.2, 33.5, 29.3, 28.7, 26.6, 23.8, 21.5, 9.5.

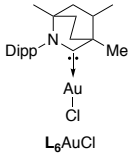
**Synthesis of [($^{iPr}$BICAAC)Au(Cl)] / ($L_4$)AuCl:**



**$L_4$AuCl**

**($L_4$)AuCl** was prepared in a two-step procedure from the free carbene.[8] **Step 1** - **($L_4$)AuPh**: Under an argon atmosphere, a 50 mL schlenk flask was charged with 20 mL of THF, the free carbene **$L_4$** (1.000 g, 2.945 mmol, 1.01 eq.) and [($PPh_3$)AuPh] (1.563 g, 2.916 mmol, 1.0 eq.). After stirring the solution at room temperature for 2 hours, the volatiles were removed in vacuo and the oily crude residue was triturated with pentane to enforce precipitation of the titled compound. After filtration and further drying under vacuum **($L_4$)AuPh** was obtained as a white solid (1.396 g, 80% yield). $^1$H NMR (300 MHz, $CDCl_3$) δ 7.38 (t, *J* = 7.7 Hz, 1H), 7.27 – 7.16 (m, 2H), 7.11 – 7.00 (m, 4H), 6.90 – 6.81 (m, 1H), 3.29 (p, *J* = 6.8 Hz, 1H), 3.05 (p, *J* = 6.8 Hz, 1H), 2.63 (p, *J* = 6.8 Hz, 1H), 2.26 – 2.13 (m, 1H), 1.75 – 1.85 (m, 1H), 2.11 – 2.00 (m, 1H), 1.70 (d, *J* = 1.4 Hz, 2H), 1.56 (d, *J* = 6.8 Hz, 4H), 1.51 (d, *J* = 6.7 Hz, 4H), 1.38 (d, *J* = 6.8 Hz, 3H), 1.33 (d, *J* = 6.9 Hz, 3H), 1.25 (d, *J* = 6.9 Hz, 3H), 1.09 – 0.98 (m, 9H). $^{13}$C{$^1$H} NMR (126 MHz, $CDCl_3$) δ 269.0, 169.5, 144.8, 144.1, 141.1, 141.0, 129.1, 126.6, 124.7, 124.6, 124.4, 62.9, 55.1, 44.5, 34.0, 32.8, 31.1, 29.3, 28.6, 25.5, 25.1, 24.1, 23.9, 23.5, 21.4, 19.8, 19.7, 16.2. **Step 2 - ($L_4$)AuCl:** Under an argon atmosphere, a 50 mL schlenk flask was charged with **($L_4$)AuPh** complex (1.000 g, 1.671 mmol, 1.0 eq.) and 15 mL of anhydrous THF. The solution was then cooled to -78 °C and stirred for 15 min, before adding a 2M HCl solution in $Et_2O$ (1.52 mL, 1.5 eq.) dropwise. Upon warming up to room temperature slowly over the course of 5h, and evaporating the volatiles in vacuo afforded **($L_4$)AuCl** as a white powder (0.921 g, 99% yield). $^1$H NMR (300 MHz, $CDCl_3$) δ 7.40 (t, *J* = 7.7 Hz, 1H), 7.25 – 7.14 (m, 2H), 3.10 (p, *J* = 6.8 Hz, 1H), 2.94 (p, *J* = 6.8 Hz, 1H), 2.53 (p, *J* = 6.8 Hz, 1H), 2.26 (ddd, *J* = 10.5, 7.4, 5.0 Hz, 1H), 2.09 (dd, *J* = 13.5, 10.4 Hz, 1H), 1.77 – 1.69 (m, 2H), 1.65 – 1.49 (m, 3H), 1.43 (t, *J* = 6.6 Hz, 6H), 1.34 (dd, *J* = 14.2, 6.8 Hz, 6H), 1.25 (d, *J* = 6.9 Hz, 3H), 1.08 – 0.94 (m, 9H). $^{13}$C{$^1$H} NMR (126 MHz, $CDCl_3$) δ 243.2, 144.3, 143.8, 141.2, 129.8, 125.1, 124.9, 64.3, 55.1, 44.2, 34.4, 32.5, 31.9, 29.2, 28.6, 25.5, 25.2, 24.2, 23.8, 23.4, 21.2, 20.3, 19.4, 16.3.

**[(*Me*BICAAC)Au(Cl)] / (L$_6$)AuCl**:

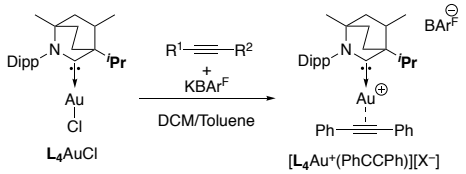


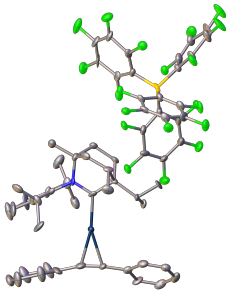
**L$_6$AuCl**

Following the same general procedure described for **(L$_4$)AuCl**, **(L$_6$)AuCl** was prepared in a two-step procedure from the free carbene (0.840 g, 95% yield,).[8] $^1$H NMR (500 MHz, $CDCl_3$) δ 7.39 (td, *J* = 7.7, 3.1 Hz, 1H), 7.26 (d, *J* = 3.2 Hz, 1H), 7.22 (dt, *J* = 7.5, 3.3 Hz, 2H), 2.90 (dd, *J* = 8.5, 5.3 Hz, 1H), 2.56 (dd, *J* = 8.5, 5.3 Hz, 1H), 2.14 – 2.04 (m, 2H), 1.79 (dd, *J* = 10.4, 3.7 Hz, 3H), 1.71 (s, 3H), 1.61 – 1.56 (m, 2H), 1.39 – 1.33 (m, 6H), 1.30 (d, *J* = 7.2 Hz, 3H), 1.25 (d, *J* = 7.1 Hz, 3H), 1.03 (s, 6H). $^{13}$C{$^1$H} NMR (126 MHz, $CDCl_3$) δ 241.6, 144.3, 143.9, 140.6, 129.9, 125.2, 124.9, 64.7, 50.5, 44.1, 37.1, 33.0, 31.0, 29.2, 28.5, 26.4, 25.5, 25.5, 24.1, 24.0, 23.3, 20.3.

## D. Catalyst Behavior Studies

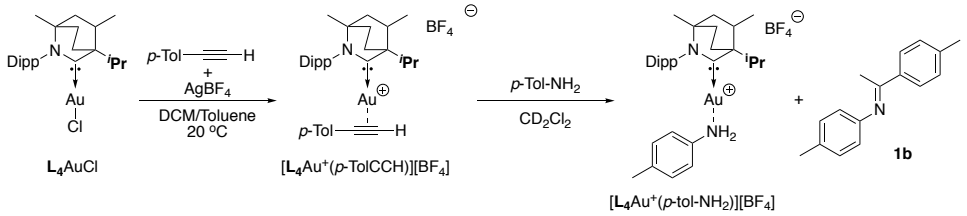
**Complex [(*iPr*BICAAC)Au$^+$(1,2-diphenylethyne)(X)$^-$] / [(L$_4$)Au$^+$(PhCCPh)(X)$^-$]**



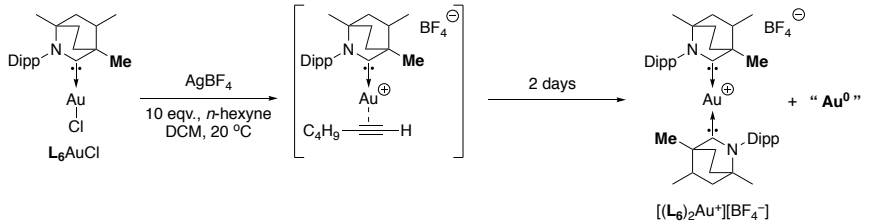
**[(*iPr*BICAAC)Au$^+$(PhCCPh)(BAr$^F$)$^-$]**. Under an argon atmosphere, a 25 mL schlenk flask was charged with 2 mL of Toluene/DCM mixture (50:50), KBAr$^F$ (0.250 g, 0.349 mmol, 1.0 eq.) and [(*iPr*BICAAC)Au(Cl)] (0.200 g, 0.349 mmol, 1.0 eq.). The reaction was stirred for 1h at room temperature and then filtered through celite into a separate reaction flask to remove KCl. The volatiles were removed under vacuum to afford an off-white residue. Following the addition of 2 mL of $CH_2Cl_2$ and diphenylacetylene (0.0622 g, 0.349 mmol, 1.0 eq.), the reaction mixture was stirred overnight at 50 °C. Removal of the volatiles under vacuum, trituration in pentane, filtration, and drying of precipitate afforded the titled compound as a greenish solid. X-ray quality crystals were obtained from a $CH_2Cl_2$/Pentane mixture. **[(*iPr*BICAAC)Au$^+$(PhCCPh)(BF$_4$)$^-$].** Under an argon atmosphere, a 25 mL schlenk flask was charged with 2 mL of Toluene, $AgBF_4$ (0.068 g, 0.349 mmol, 1.0 eq.) and [(*iPr*BICAAC)Au(Cl)] (0.200 g, 0.349 mmol, 1.0 eq.). The reaction was stirred for 1h at room temperature and then filtered into a separate reaction flask to remove AgCl. The volatiles were removed under vacuum to afford a brown residue. Following the addition of 2 mL of $CH_2Cl_2$ and diphenylacetylene (0.0622 g, 0.349 mmol, 1.0 eq.), the reaction mixture was stirred overnight at 50 °C. Removal of volatiles under vacuum, trituration in pentane, filtration, and drying of precipitate afforded the titled compound as a greenish solid (0.288 g, 95% yield). $^1$H NMR (500 MHz, $CD_2Cl_2$) δ 7.61 – 7.58 (m, 2H), 7.58 – 7.54 (m, 1H), 7.49 – 7.42 (m, 2H), 7.42 – 7.39 (m, 4H), 7.29 (dd, *J* = 7.9, 6.8 Hz, 1H), 7.27 – 7.22 (m, 1H), 7.17 (dd, *J* = 7.8, 1.6 Hz, 2H), 2.88 (p, *J* = 6.8 Hz, 1H), 2.52 (dp, *J* = 23.1, 6.8 Hz, 1H), 2.48 (dp, *J* = 23.1, 6.8 Hz, 1H), 2.24 (dd, *J* = 13.8, 10.4 Hz, 1H), 1.90 – 1.81 (m, 2H), 1.80 – 1.58 (m, 2H), 1.29 (d, *J* = 6.9 Hz, 3H), 1.25 (dd, *J* = 6.9, 3.4 Hz, 9H), 1.11 (d, *J* = 6.8 Hz, 3H), 1.02 (s, 3H), 0.99 (d, *J* = 7.2 Hz, 3H), 0.94 (dd, *J* = 9.9, 6.7 Hz, 6H). $^{13}$C{$^1$H} NMR (126 MHz, $CD_2Cl_2$) δ 244.2, 144.6, 143.6, 141.2, 140.8, 132.4, 132.3, 132.0, 131.0, 131.0, 129.4, 128.9, 128.3, 128.1, 127.2, 127.0, 126.8, 125.8, 122.3, 122.1, 117.7, 88.8, 67.3, 56.1, 43.5, 35.2, 32.2, 32.1, 29.2, 28.6, 25.1, 23.6, 23.3, 22.8, 21.3, 20.8, 20.4, 19.2, 15.7. $^{19}$F{$^1$H} NMR (282 MHz, $CDCl_3$) δ -153.68. $^{11}$B{$^1$H} NMR (96 MHz, $CDCl_3$) δ -1.01. NB : Reagents and solvents were stored over molecular sieves before use.

**Reactivity of transient [(L$_4$)Au$^+$(TolCCH)(BF$_4$)$^-$] with Tol-NH$_2$:**



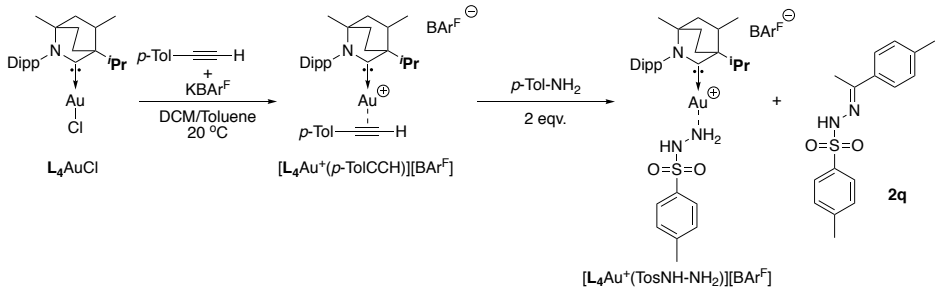

Under an argon atmosphere, a 5 mL schlenk flask was charged with 1 mL of Toluene/DCM mixture (50:50), $AgBF_4$ (0.017 g, 0.087 mmol, 1.0 eq.) and [($^{iPr}$BICAAC)Au(Cl)] (0.050 g, 0.087 mmol, 1.0 eq.). The reaction was stirred for 1h at room temperature and then filtered through celite into a separate reaction flask to remove AgCl. The volatiles were removed under vacuum to afford an off-white residue. The residue was transferred to a J-Young NMR tube using 0.5 mL of $CD_2Cl_2$, followed by the addition of *p*-tolyl-acetylene (0.011 g, 0.087 mmol, 1.0 eq.). After confirming the formation of **[(L$_4$)Au$^+$(TolCCH)(BF$_4$)$^-$]** by NMR (δ 237.4 ppm characteristic signal by $^{13}C\{^1H\}$ NMR), tolyl-amine was added to the NMR tube (0.093 g, 0.087 mmol, 1.0 eq.). The reaction mixture was monitored after 1h at room temperature showing the formation of **1b** and **[(L$_4$)Au$^+$(*p*-tol-NH$_2$)(BF$_4$)$^-$]**. Removal of volatiles under vacuum, trituration in pentane, filtration, and drying of precipitate afforded the latter as a white solid. This compound was successfully recrystallized by layering a DCM solution with pentane. $^1H$ NMR (300 MHz, $CD_2Cl_2$) δ 7.48 – 7.14 (m, 1H), 7.26 – 7.14 (d, 1H), 6.97 (d, *J* = 7.9 Hz, 1H), 6.55 (d, *J* = 7.8 Hz, 1H), 5.45 (s, 1H), 2.90 (dp, *J* = 20.5, 6.8 Hz, 2H), 2.43 (p, *J* = 6.8 Hz, 1H), 2.31 (s, 5H), 2.16 (dd, *J* = 13.7, 10.4 Hz, 1H), 1.78 (d, *J* = 5.1 Hz, 3H), 1.68 – 1.47 (m, 2H), 1.43 (d, *J* = 6.7 Hz, 3H), 1.32 (d, *J* = 6.8 Hz, 3H), 1.25 (d, *J* = 6.9 Hz, 3H), 1.18 (d, *J* = 6.7 Hz, 6H), 1.09 (t, *J* = 3.5 Hz, 6H), 1.04 (d, *J* = 7.1 Hz, 3H). $^{13}C\{^1H\}$ NMR (126 MHz, $CD_2Cl_2$) δ 240.5, 144.8, 143.9, 142.1, 136.9, 135.7, 130.3, 130.1, 128.7, 125.6, 121.5, 65.8, 55.7, 44.3, 35.1, 32.8, 32.1, 29.4, 28.8, 25.1, 24.8, 24.0 (d, *J* = 3.0 Hz), 23.3, 21.2, 20.5, 19.6, 16.2. $^{19}F\{^1H\}$ NMR (282 MHz, $CD_2Cl_2$) δ -153.7. $^{11}B\{^1H\}$ NMR (96 MHz, $CD_2Cl_2$) δ 0.82. NB : Reagents and solvents were stored over molecular sieves before use.

**Synthesis of complex [($^{Me}$BICAAC)$_2$Au$^+$(BF$_4$)$^-$] / [(L$_6$)$_2$Au$^+$(BF$_4$)]:**




Following the same general procedure described for **[(L$_4$)Au$^+$(PhCCPh)(BF$_4$)$^-$]**, but instead using **[($^{iPr}$BICAAC)Au(Cl)]** (0.150 g, 0.261 mmol, 1.0 eq.) and *n*-hexyne (0.214 g, 2.610 mmol, 10.0 eq.), we monitored the reaction by NMR. The slow formation of **[($^{Me}$BICAAC)$_2$Au$^+$(BF$_4$)$^-$]** was observed upon stirring the reaction mixture at room temperature over 2 days. The title compound was isolated as a white powder by evaporation of the volatiles in vacuo, and trituration with pentane. This compound was successfully recrystallized by layering a DCM solution with pentane. $^1H$ NMR (300 MHz, $C_6D_6$) δ 7.33 (td, *J* = 7.8, 4.9 Hz, 2H), 7.20-7.16 (m, 2H), 7.15-7.12 (m, 2H), 2.75 (p, *J* = 6.9 Hz, 2H), 2.36 (dp, *J* = 15.0, 6.9 Hz, 2H), 2.23 – 1.99 (m, 4H), 1.95 – 1.67 (m, 4H), 1.61 – 1.40 (m, 9H), 1.18 (dt, *J* = 10.4, 5.2 Hz, 24H), 0.98 (s, 6H), 0.93 (d, *J* = 6.7 Hz, 6H). $^{13}C\{^1H\}$ NMR (126 MHz, $C_6D_6$) δ 235.7, 144.8, 144.0, 141.1, 130.2, 125.3, 124.9, 67.3, 53.4, 51.4, 50.9, 43.7, 36.9, 36.8, 32.7, 31.0, 30.6, 29.0, 28.5, 26.5, 25.6, 25.4, 23.8, 23.6, 23.0, 20.5. $^{19}F\{^1H\}$ NMR (282 MHz, $CD_2Cl_2$) δ -151.0. $^{11}B\{^1H\}$ NMR (96 MHz, $CD_2Cl_2$) δ 0.25. NB : Reagents and solvents were stored over molecular sieves before use.

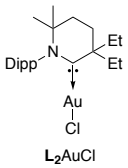
**Reactivity of transient [(L$_4$)Au$^+$(TolCCH)(BAr$^F$)$^-$] with Tol-NHNH$_2$:**




Under an argon atmosphere, a 5 mL schlenk flask was charged with 1 mL of Toluene/DCM mixture (50:50), $KBAr^F$ (0.062 g, 0.087 mmol, 1.0 eq.) and [(*iPr*BICAAC)Au(Cl)] (0.050 g, 0.087 mmol, 1.0 eq.). The reaction was stirred for 1h at room temperature and then filtered through celite into a separate reaction flask to remove KCl. The volatiles were removed under vacuum to afford an off-white residue. The residue was transferred to a J-Young NMR tube using 0.5 mL of $CD_2Cl_2$, followed by the addition of *p*-tolyl-acetylene (0.010 g, 0.087 mmol, 1.0 eq.). After confirming the formation of **[(L$_4$)Au$^+$(TolCCH)(BAr$^F$)$^-$]** by NMR (δ 237.4 ppm characteristic signal by $^{13}C\{^1H\}$ NMR), Tosyl-hydrazine was added to the NMR tube (0.016 g, 0.087 mmol, 1.0 eq.). The reaction mixture was monitored after 1h at room temperature showing the formation of **2q** and **[(L$_4$)Au$^+$(TosNH-NH$_2$)(BAr$^F$)$^-$]**. Evaporation of the volatiles and addition of $C_6H_6$ (0.5 mL), resulted in the slow crystallization of **2q** overnight in the NMR tube which was confirmed by X-ray crystallography. Subsequent transfer of the mother liquor to a 5 mL schlenk flask, removal of volatiles under vacuum, trituration in pentane and filtration, afforded **[(L$_4$)Au$^+$(TosNH-NH$_2$)(BAr$^F$)$^-$]** as a white solid. **[(L$_4$)Au$^+$(TolCCH)(BAr$^F$)$^-$]:** $^1H$ NMR (300 MHz, $CD_2Cl_2$) δ 7.48 – 7.34 (m, 1H), 7.27 (q, *J* = 7.9 Hz, 1H), 7.21 – 7.10 (m, 1H), 6.90 (d, *J* = 7.3 Hz, 2H), 6.39 (q, *J* = 6.2, 4.8 Hz, 2H), 4.29 (s, 1H), 3.00 – 2.87 (m, 2H), 2.60 – 2.44 (m, 2H), 2.35 (s, 3H), 2.25 – 2.04 (m, 3H), 1.80 (d, *J* = 10.0 Hz, 6H), 1.64 – 1.46 (m, 3H), 1.45 – 1.21 (m, 6H), 1.13 (p, *J* = 5.5 Hz, 6H), 1.09 (m, 6H). $^{13}C\{^1H\}$ NMR (126 MHz, $CD_2Cl_2$) δ 237.4, 149.4, 147.5, 144.8, 143.8, 141.6, 139.6, 137.6, 135.7, 130.5, 130.4, 129.3, 125.5, 124.7, 76.7, 66.4, 55.7, 44.2, 35.2, 34.5, 32.6, 29.5, 28.9, 25.5, 25.2, 23.8, 23.1, 22.7, 21.1, 20.7, 19.4, 16.3, 14.2. $^{19}F\{^1H\}$ NMR (282 MHz, $CD_2Cl_2$) δ -133.85 (d, *J* = 14.2 Hz), -164.44 (t, *J* = 20.3 Hz), -168.28 (t, *J* = 19.9 Hz). $^{11}B\{^1H\}$ NMR (96 MHz, $CD_2Cl_2$) δ -16.62. **[(L$_4$)Au$^+$(TosNH-NH$_2$)(BAr$^F$)$^-$]:** $^1H$ NMR (300 MHz, $CD_2Cl_2$) δ 7.69 (d, *J* = 7.9 Hz, 2H), 7.43 (t, *J* = 7.8 Hz, 1H), 7.33 (d, *J* = 8.0 Hz, 2H), 7.25 (t, *J* = 6.4 Hz, 2H), 5.92 (s, 1H), 3.83 (s, 2H), 2.84 (dp, *J* = 19.6, 6.8 Hz, 2H), 2.42 (s, 3H), 2.31 (m, 1H), 2.17 (dd, *J* = 13.7, 10.3 Hz, 1H), 1.80 (s, 3H), 1.55 (ddt, *J* = 22.9, 10.8, 5.8 Hz, 3H), 1.38 – 1.33 (m, 4H), 1.30 (m, 3H), 1.29 – 1.22 (m, 8H), 1.05 (m, 6H), 1.00 (m, 3H). $^{13}C\{^1H\}$ NMR (126 MHz, $CD_2Cl_2$) δ δ 149.4 (broad), 147.5, 144.8, 143.9, 141.7, 139.55, 137.6, 135.7, 130.5, 130.4, 128.4, 125.5, 66.3, 55.7, 44.2, 35.1, 32.6, 32.5, 29.5, 28.9, 25.5, 25.2, 24.0, 23.7, 23.1, 21.7, 21.1, 20.7, 19.4, 16.2. $^{19}F\{^1H\}$ NMR (282 MHz, $CD_2Cl_2$) δ -133.14 – -135.72 (m), -164.37 (t, *J* = 20.3 Hz), -168.23 (t, *J* = 19.4 Hz). $^{11}B\{^1H\}$ NMR (96 MHz, $CD_2Cl_2$) δ -16.62. NB : Reagents and solvents were stored over molecular sieves before use.

## E. NMR Spectra

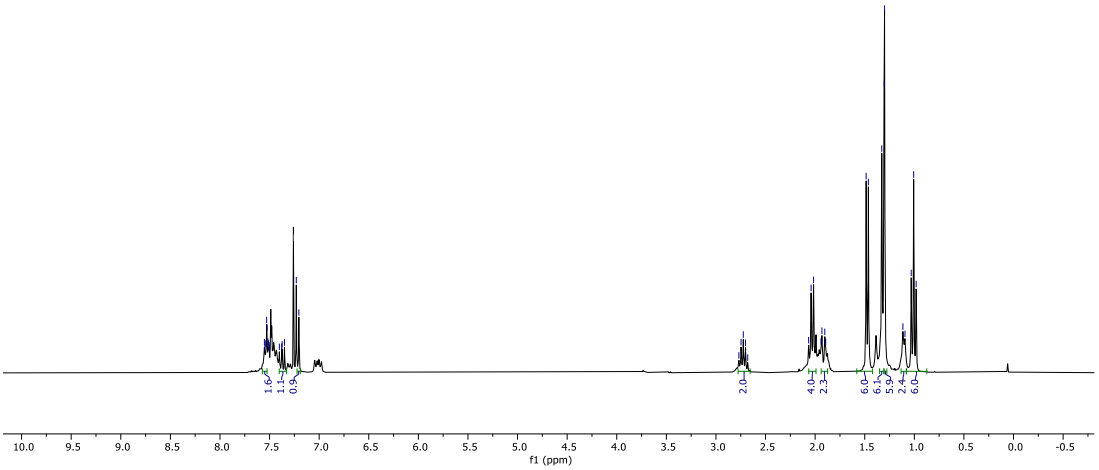
**Complex [(*Et*CAAC-6)Au(Cl)]**



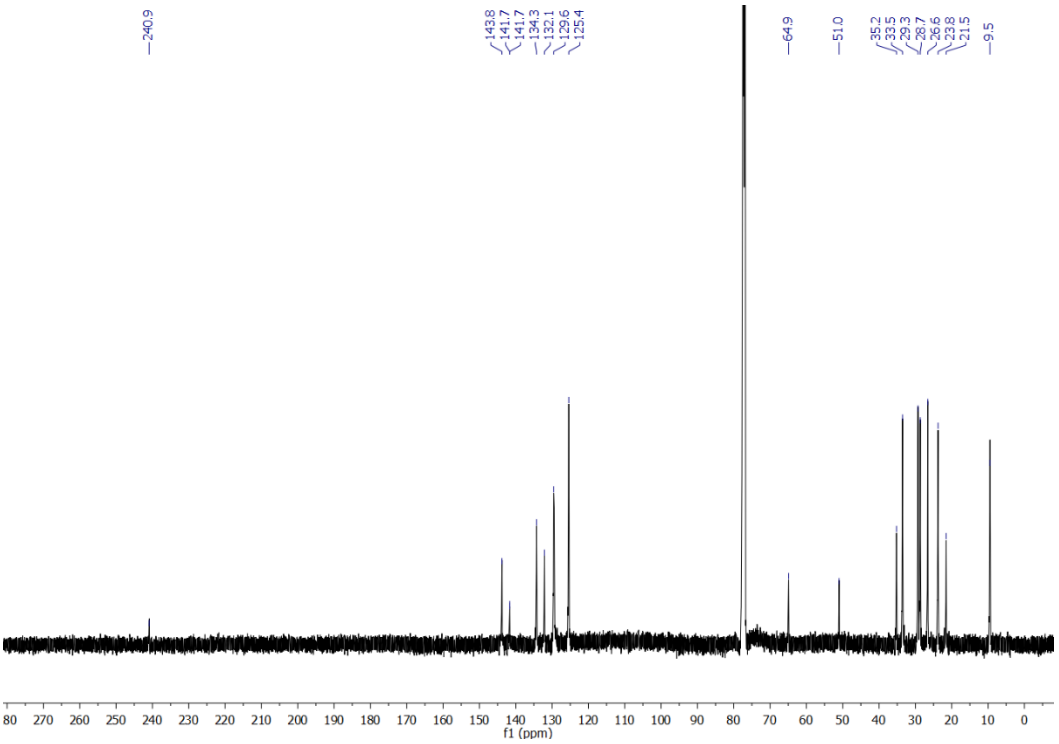

$L_2AuCl$

$^1H$ spectrum

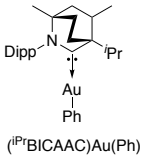





$^{13}C\{^1H\}$ spectrum

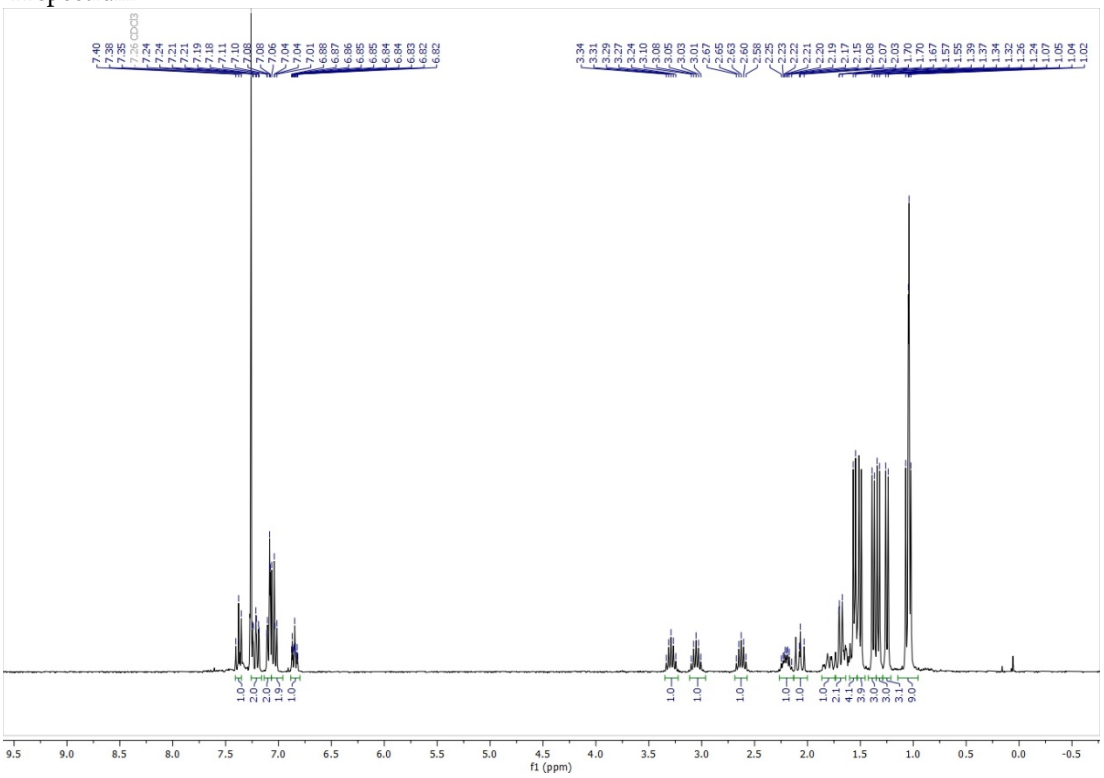


**Complex [(*iPr*BICAAC)Au(Ph)]**

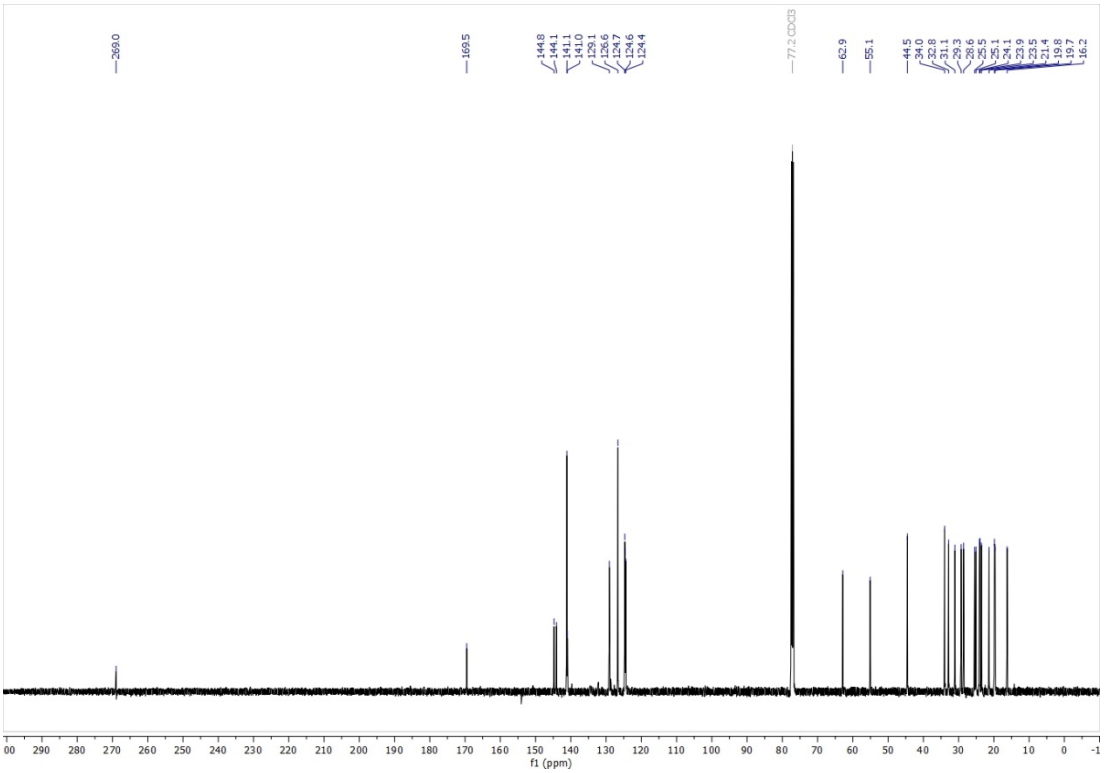


(*iPr*BICAAC)Au(Ph)

$^{1}H$ spectrum

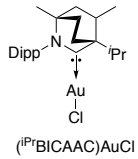



$^{13}C\{^{1}H\}$ spectrum

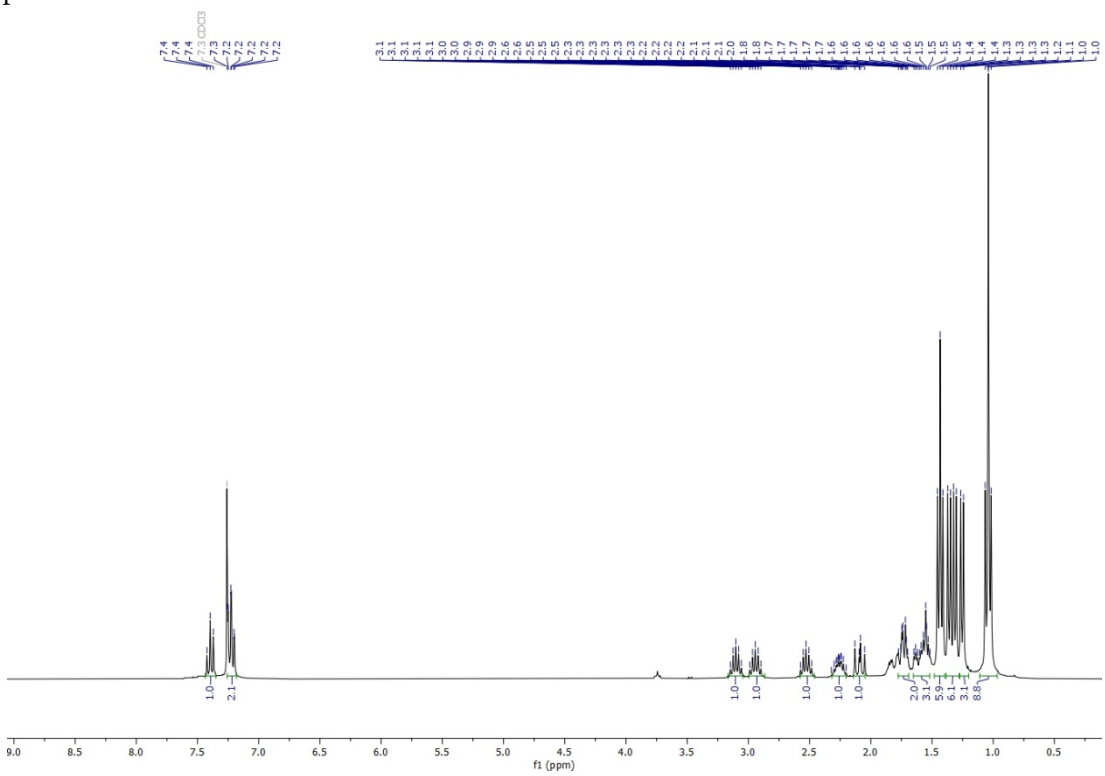


**Complex [(*iPr*BICAAC)Au(Cl)]**

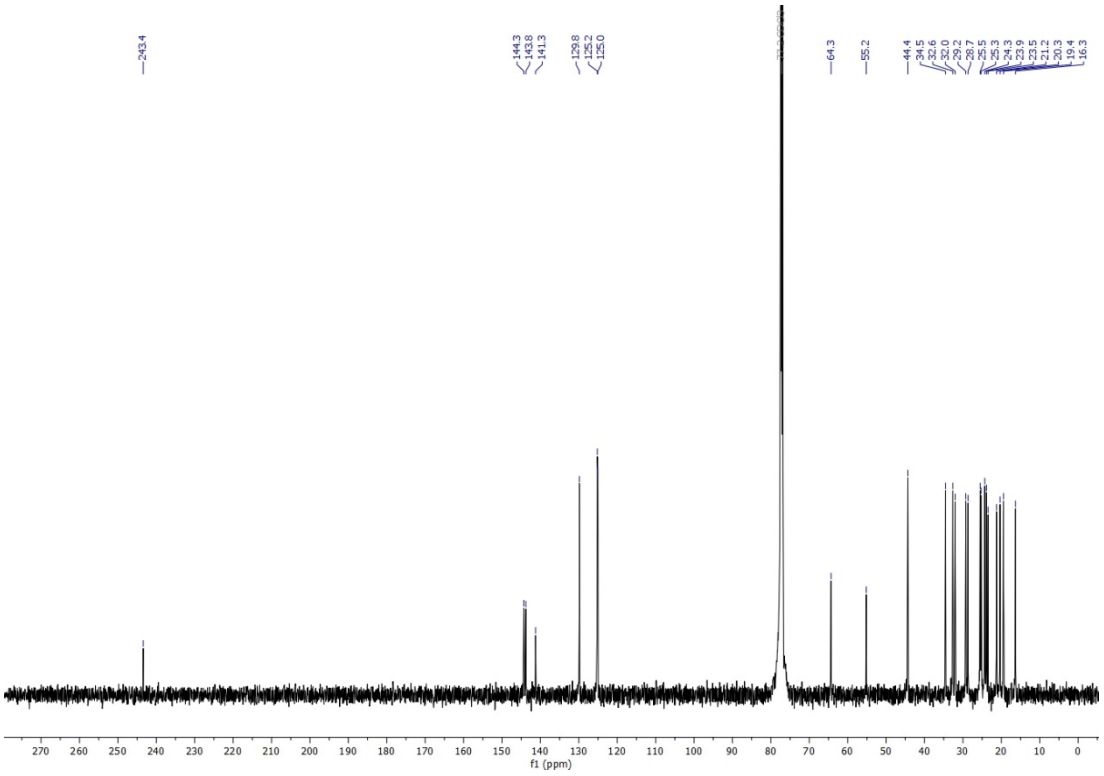
$^{1}$H spectrum



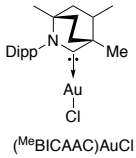
($^{iPr}$BICAAC)AuCl




$^{13}$C{$^{1}$H} spectrum



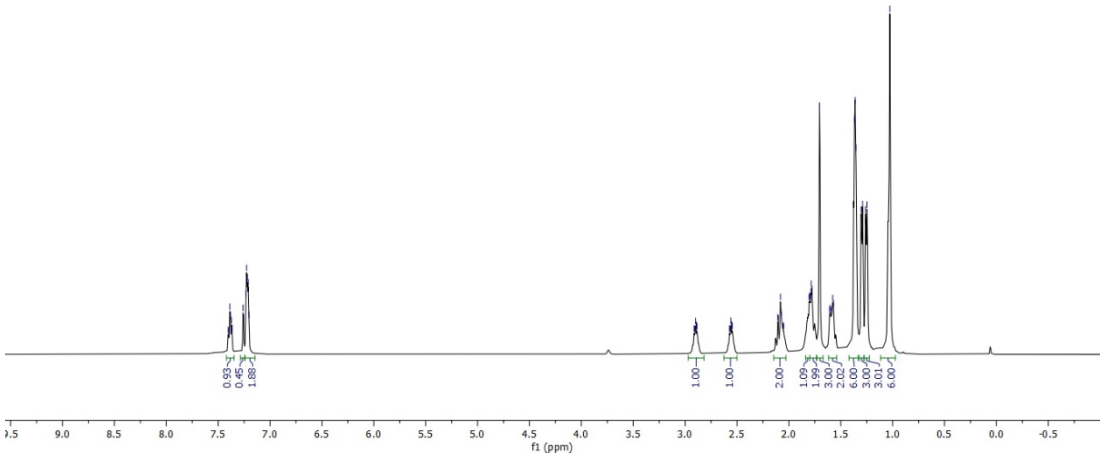
**Complex [(*Me*BICAAC)Au(Cl)]**



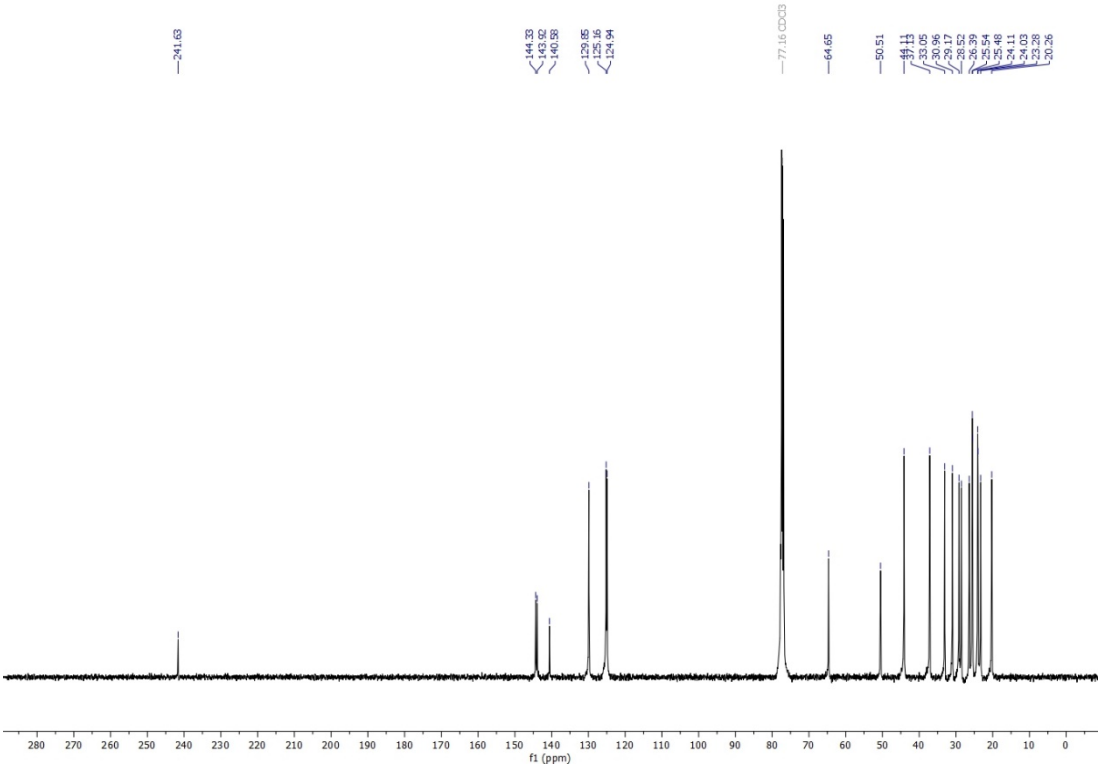
($^{Me}$BICAAC)AuCl

$^{1}$H spectrum

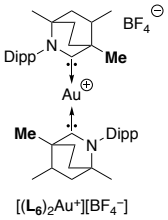




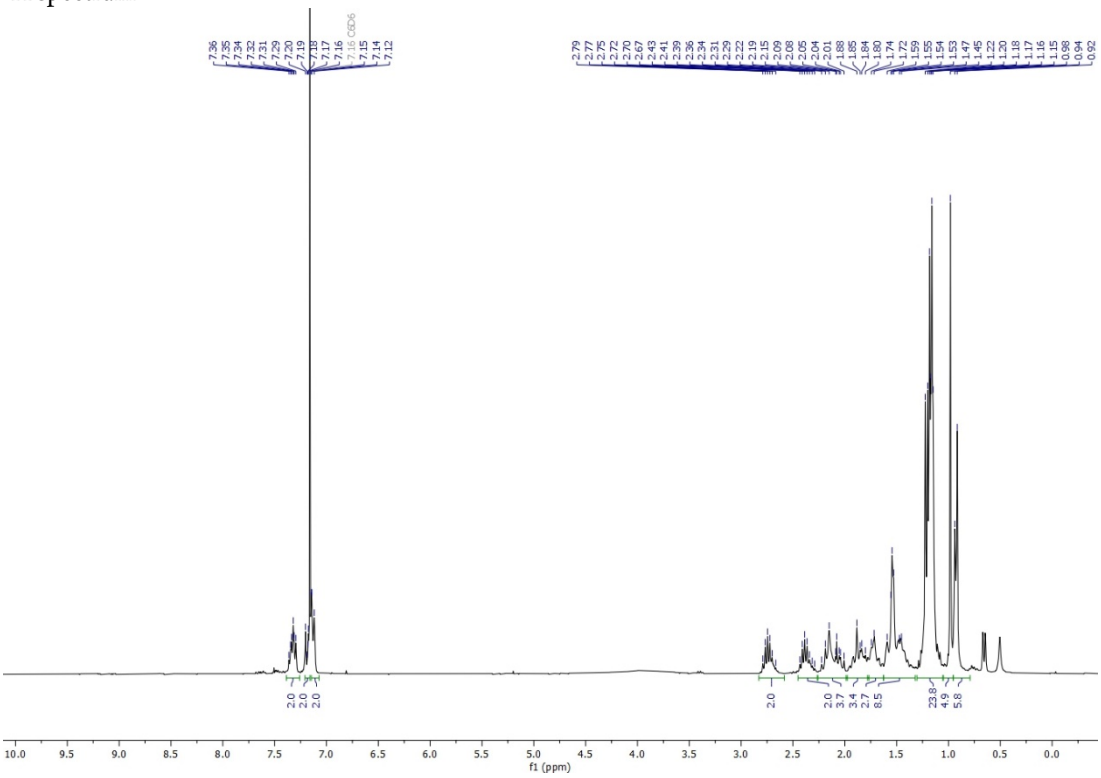

$^{13}$C{$^{1}$H} spectrum



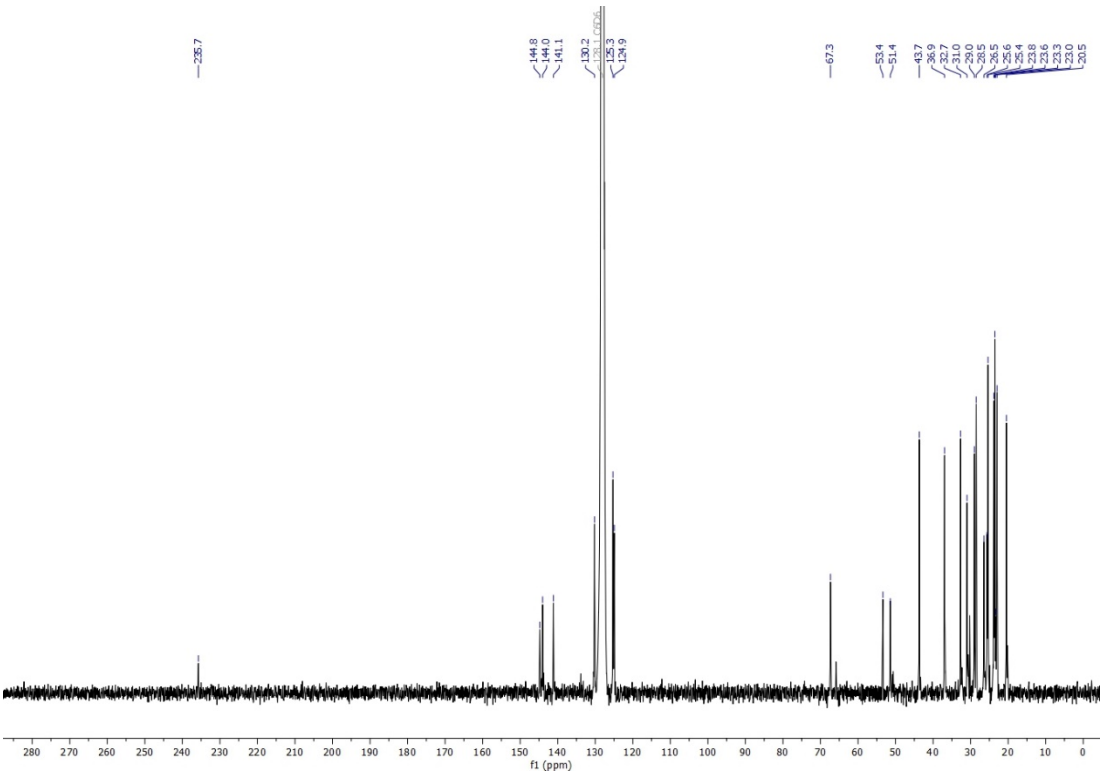
**Complex [($^{Me}$BICAAC)$_2$Au$^+$(BF$_4$)$^-$]**



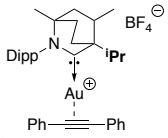

$^1$H spectrum



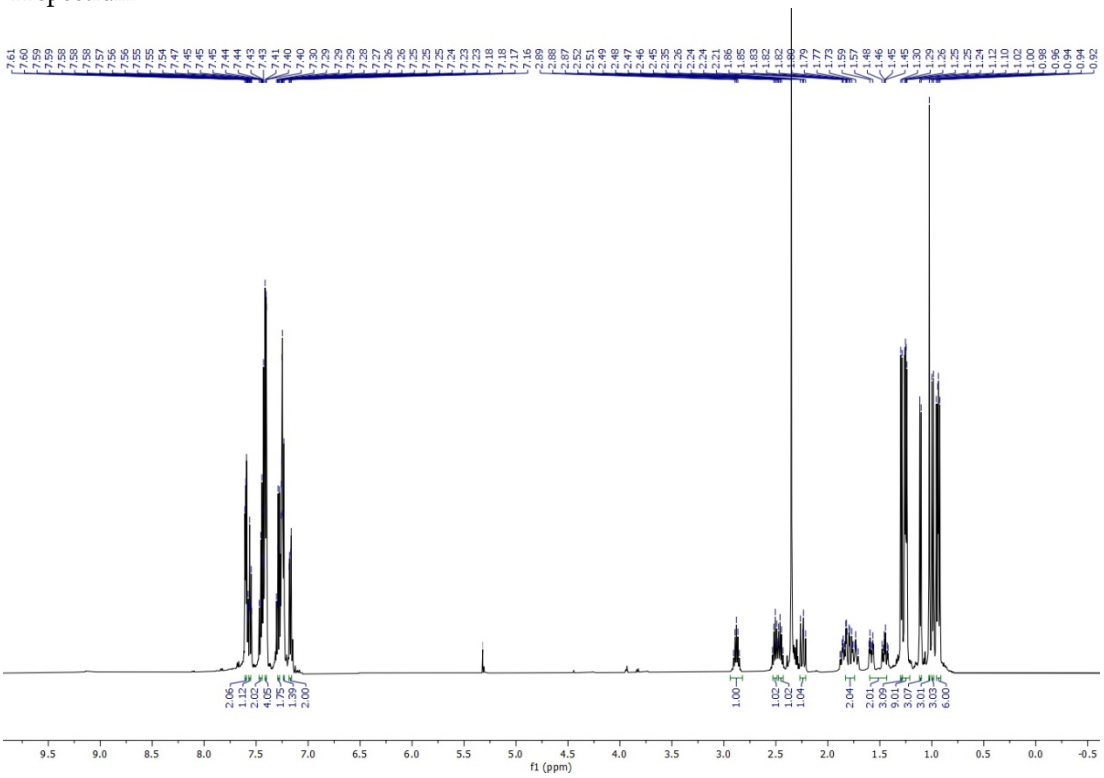

$^{13}$C{$^1$H} spectrum



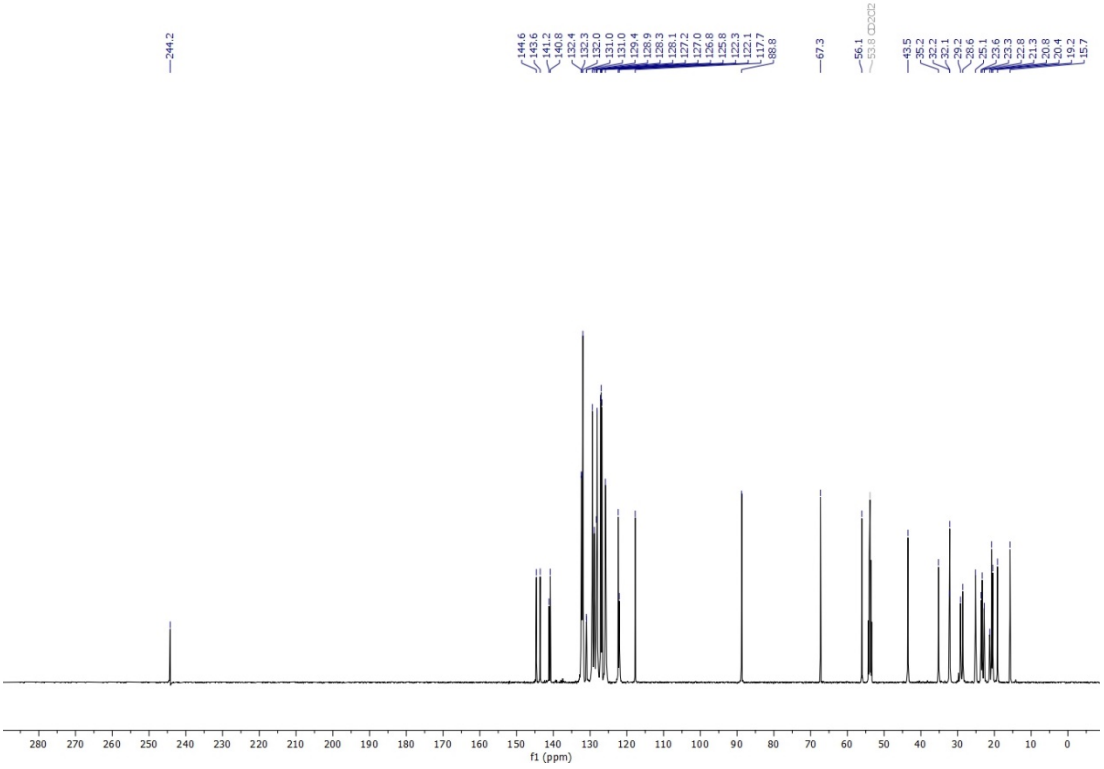
**Complex [(*iPr*BICAAC)Au$^{+}$(1,2-diphenylethyne)($BF_4$)$^{-}$]**



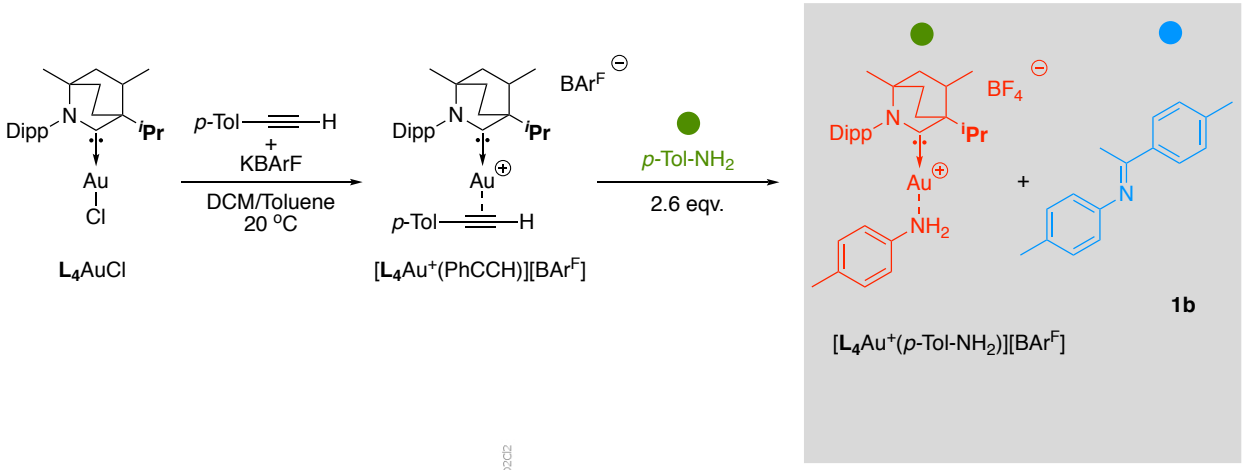

$^{1}$H spectrum

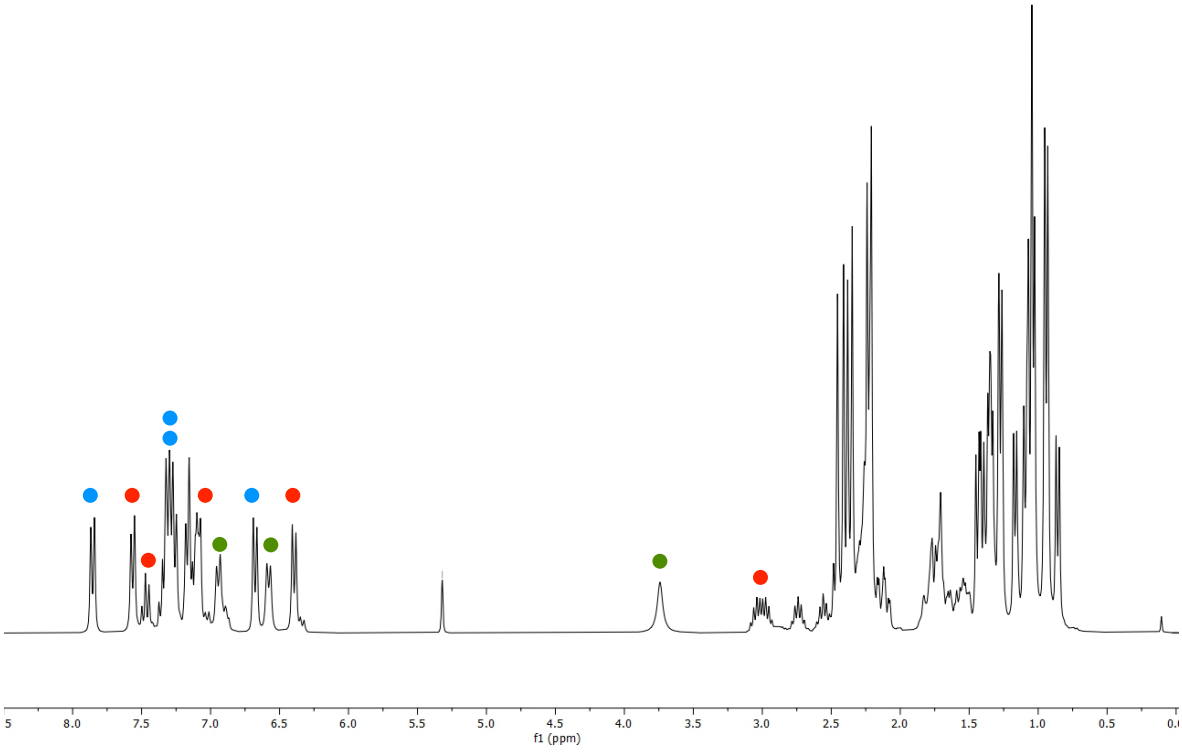



$^{13}$C{$^{1}$H} spectrum

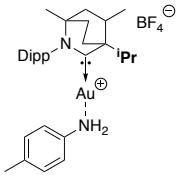


**Evidence for the formation of $[(L_4)Au^+(p\text{-}TolNH_2)(BF_4)^-]$ and 1b.**

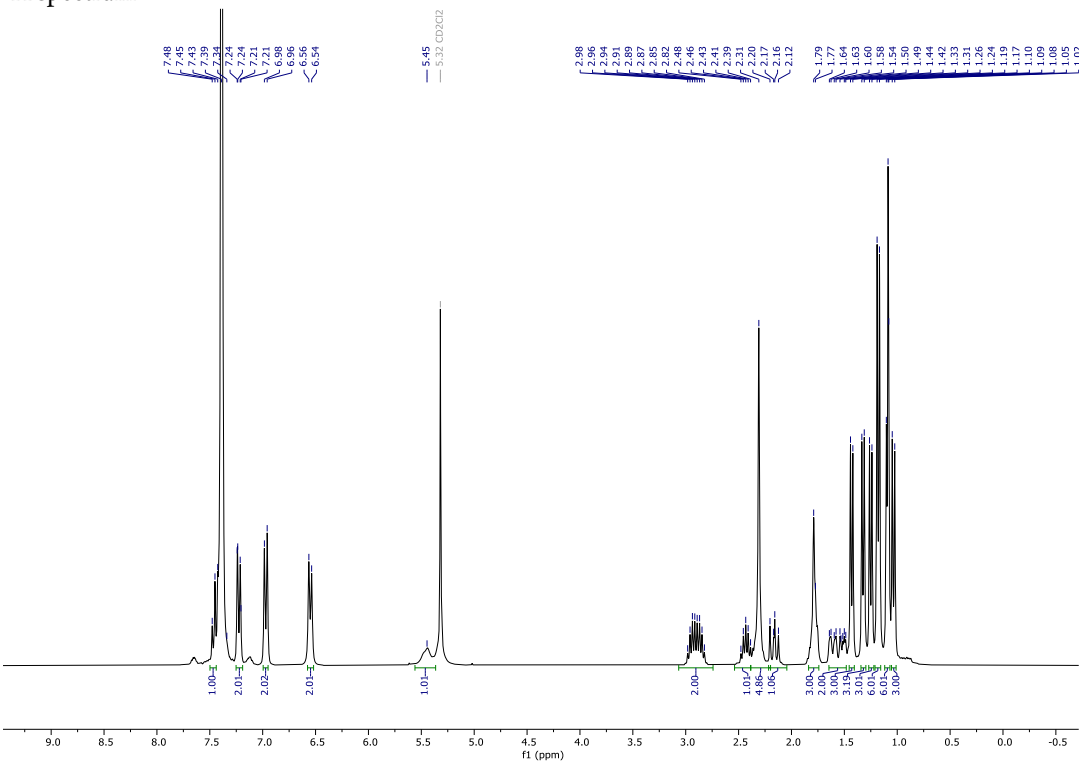


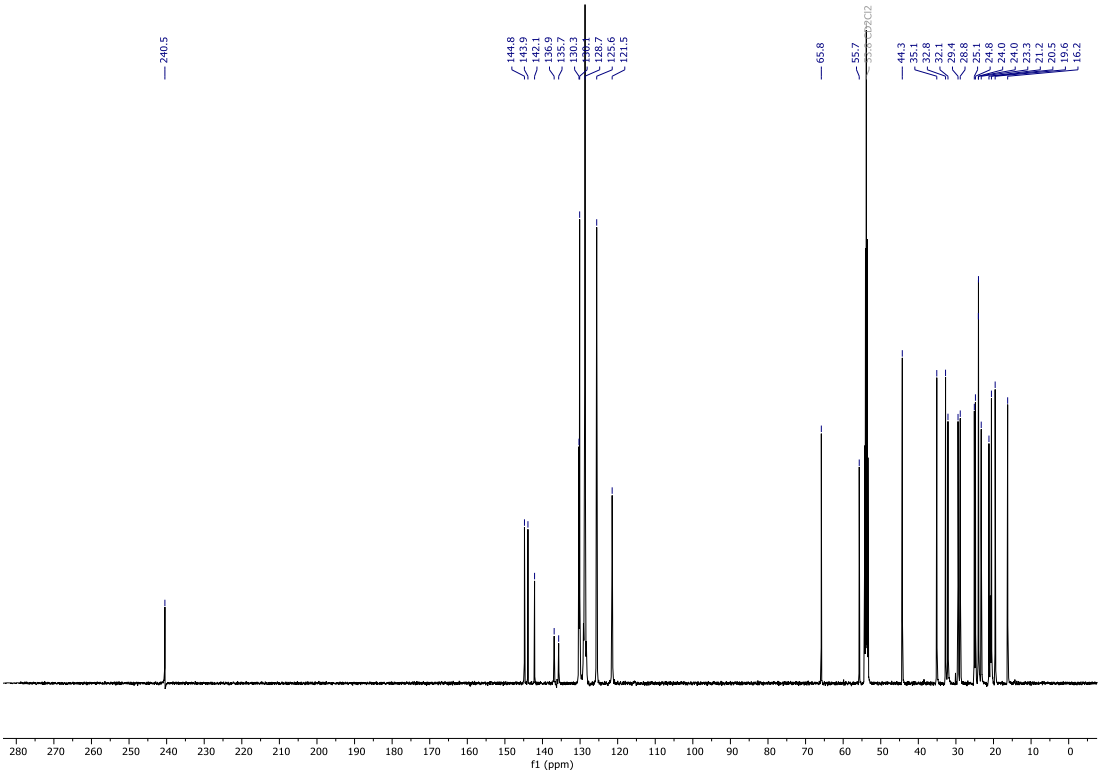
**Complex [(*iPr*BICAAC)Au$^+$(*p*-TolNH$_2$)(BF$_4$)$^-$]**



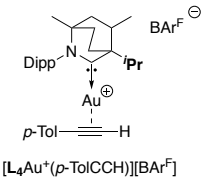

$^1$H spectrum




$^{13}$C{$^1$H} spectrum

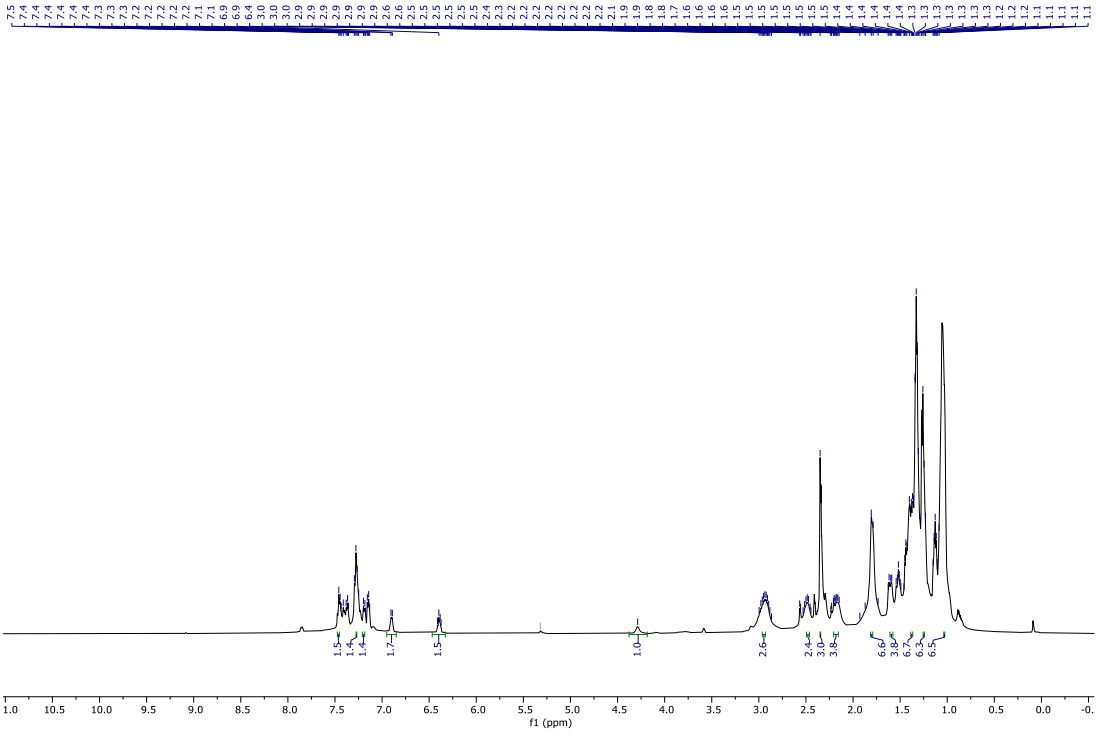


**Complex [(*iPr*BICAAC)Au⁺(TolCCH)(BAr$^F$)⁻]**

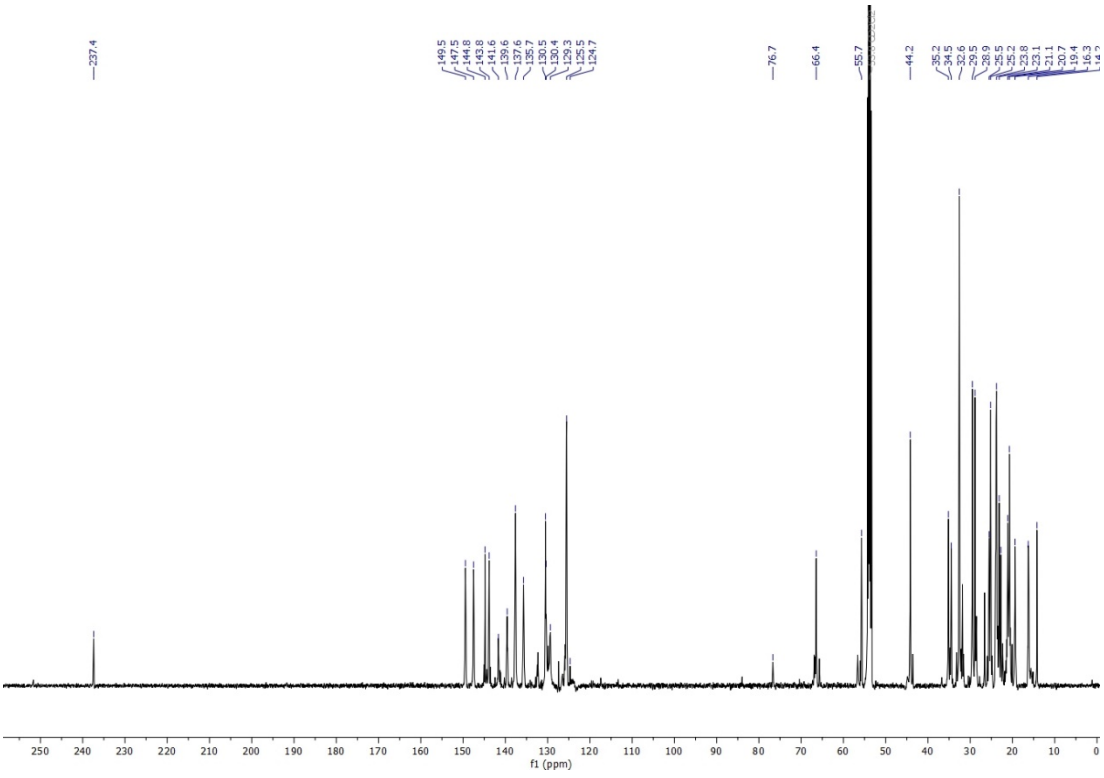



[$L_4$Au⁺(*p*-TolCCH)][BAr$^F$]

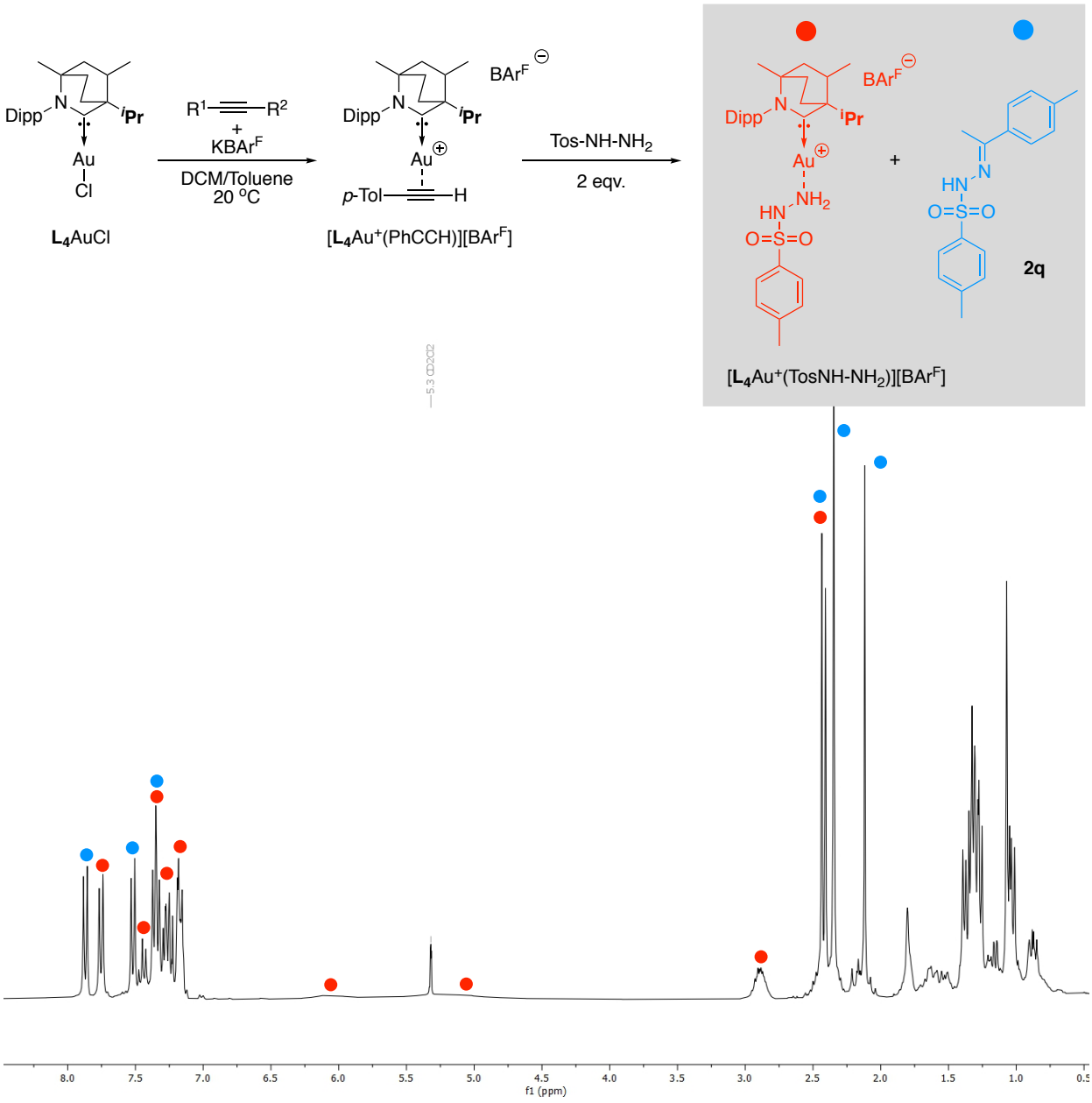
$^1$H spectrum



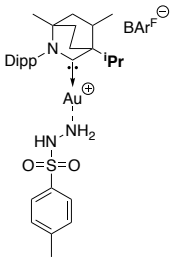

$^{13}$C{$^1$H} spectrum



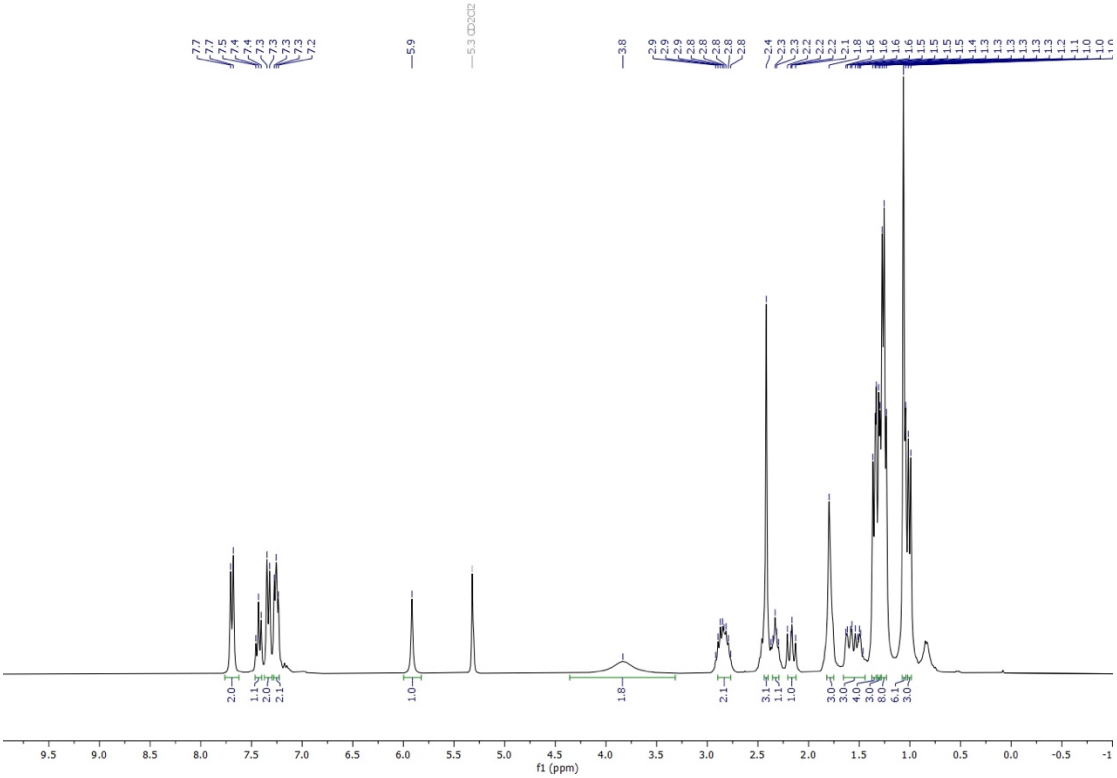
**Evidence for the formation of [(L$_4$)Au$^+$(*p*-TosNH-NH$_2$)(BAr$^F$)$^-$] and 2q.**



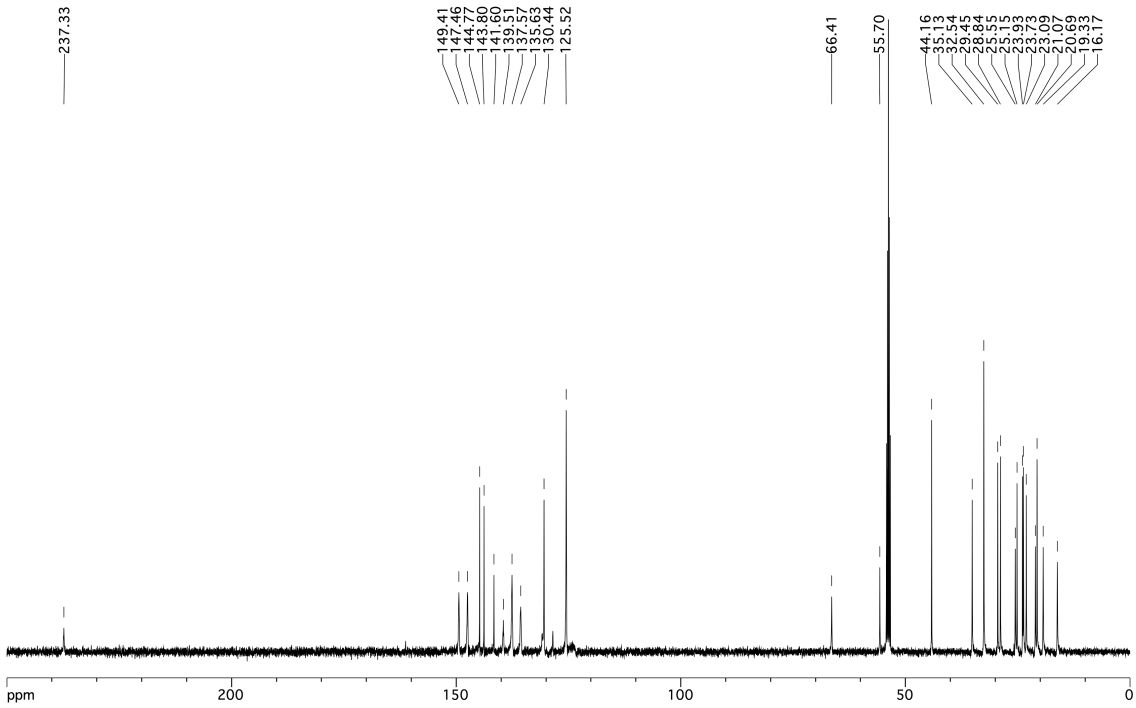
**Complex [($^{iPr}$BICAAC)Au$^{+}$(*p*-TosNH-NH$_2$)(BAr$^{F}$)$^{-}$]**




$^{1}$H spectrum

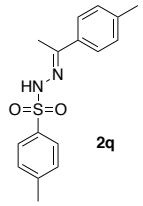


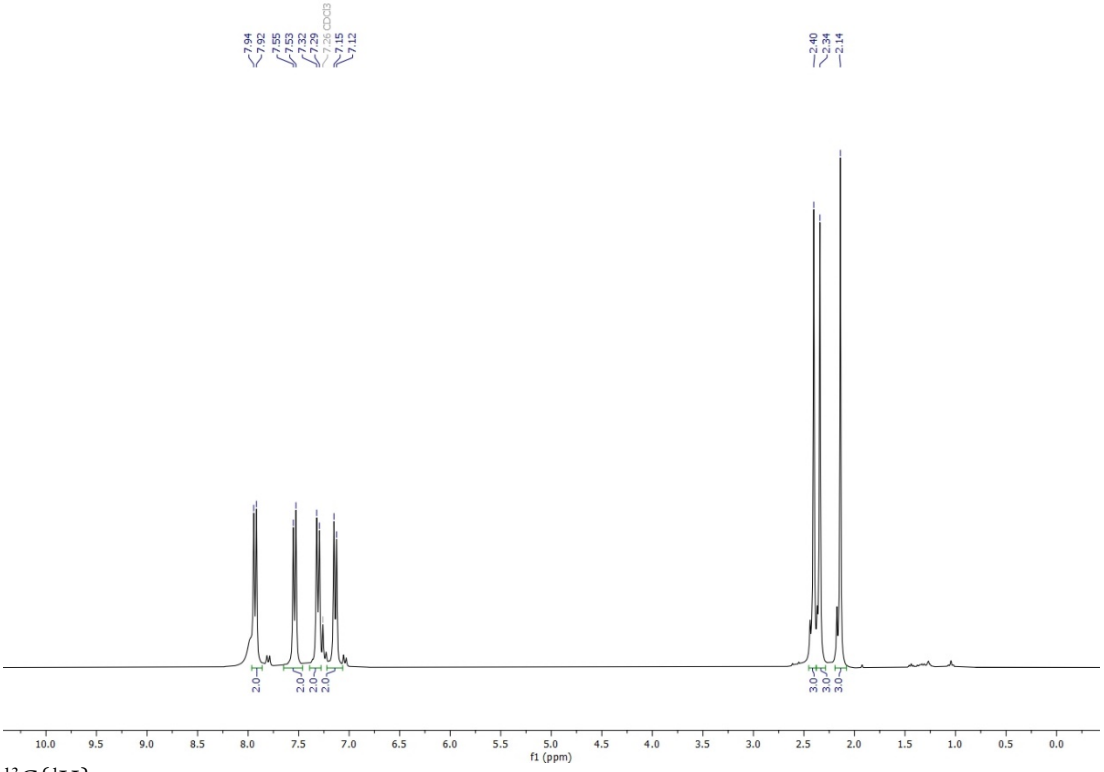

$^{13}$C{$^{1}$H} spectrum



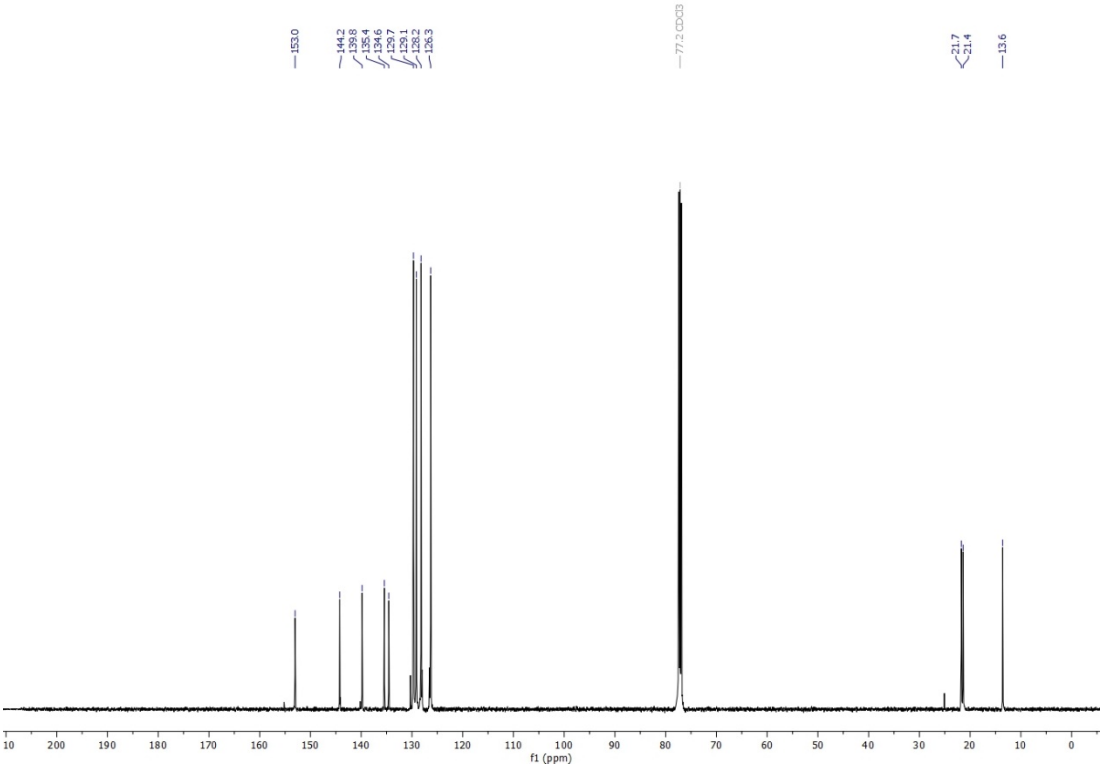
**Compound 2q**

$^{1}H$ spectrum




$^{13}C\{^{1}H\}$ spectrum



## II.4. Reaction optimization using Kinetic studies (*cf.* Figure 2 and 6).

All the kinetic measurements were performed in an NMR tube at room temperature on a Bruker 300MHz NMR machine using the multi_zgvd command. In a typical experiment, the NMR tube was charged with the Au catalyst and $KB(C_6F_5)_4$ (1:1 ratio), 4-ethynylanisole (0.047 g, 0.356 mmol, 1.0 eq.) and the corresponding amount of deuterated solvent. The tube was locked and shimmed (T0) before starting the kinetic measurement. Following the addition of toluidine (0.356 mmol, 1.0 eq. - Figure 2) or phenylhydrazine (0.356 mmol, 1.0 eq. - Figure 6) the reaction was monitored as a function of the time at a constant temperature of 20 °C. Conversions were quantified by tracking the change in characteristic signals for the starting material and the product (imine). In all cases, and as highlighted bellow the kinetic measurements were repeated 3-4 times to confirm the reproducibility of our results.

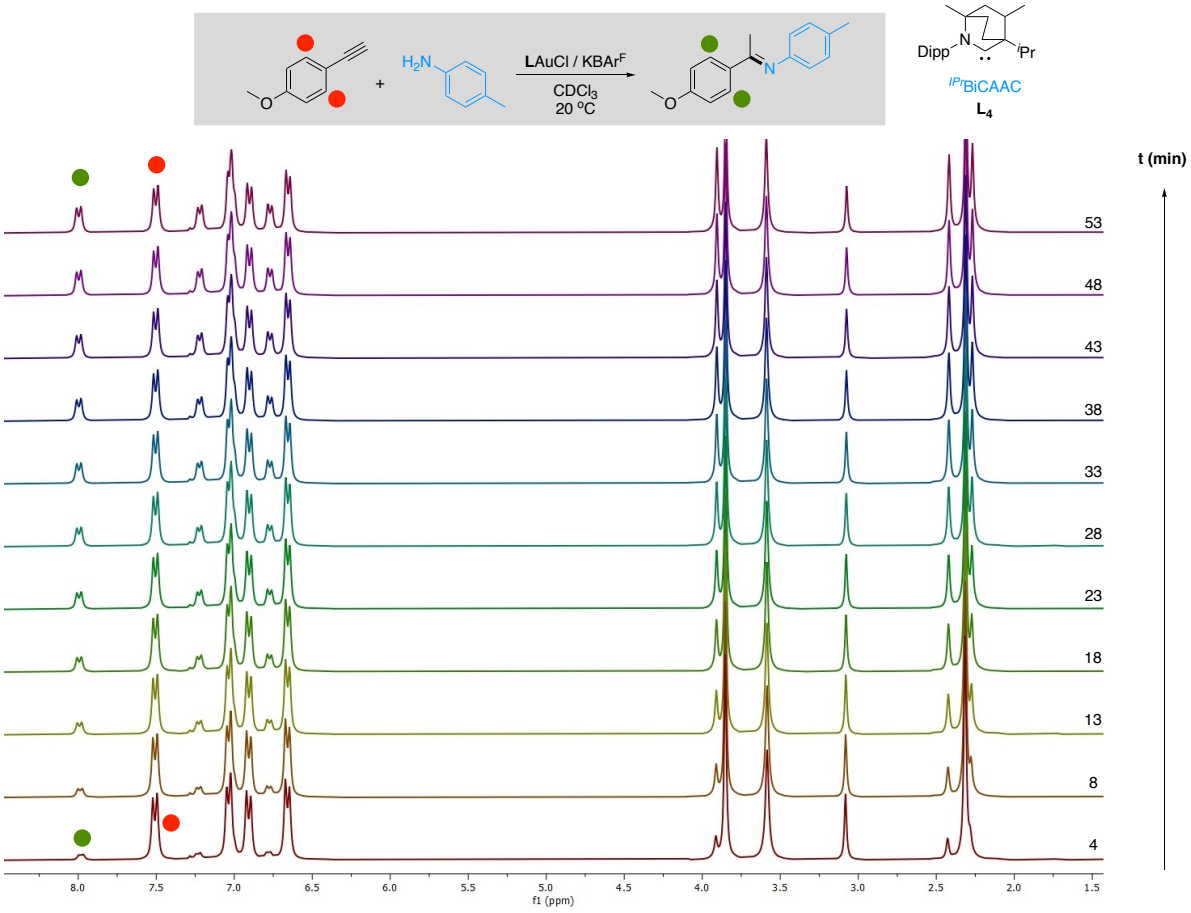



*Figure illustrating the kinetics of the hydroamination reaction by $^1H$ NMR ($CDCl_3$)*

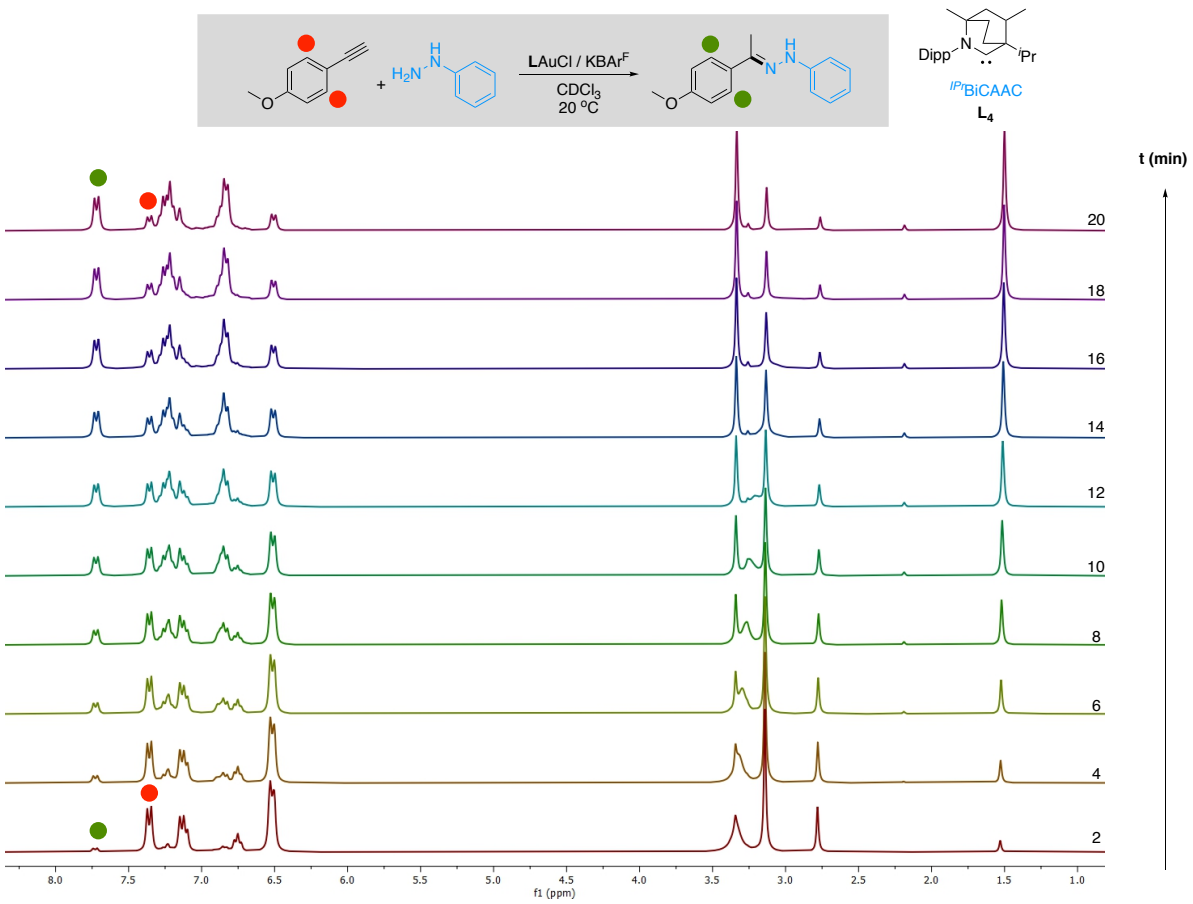



*Figure illustrating the kinetics of the hydrazination reaction by $^1H$ NMR ($CDCl_3$)*

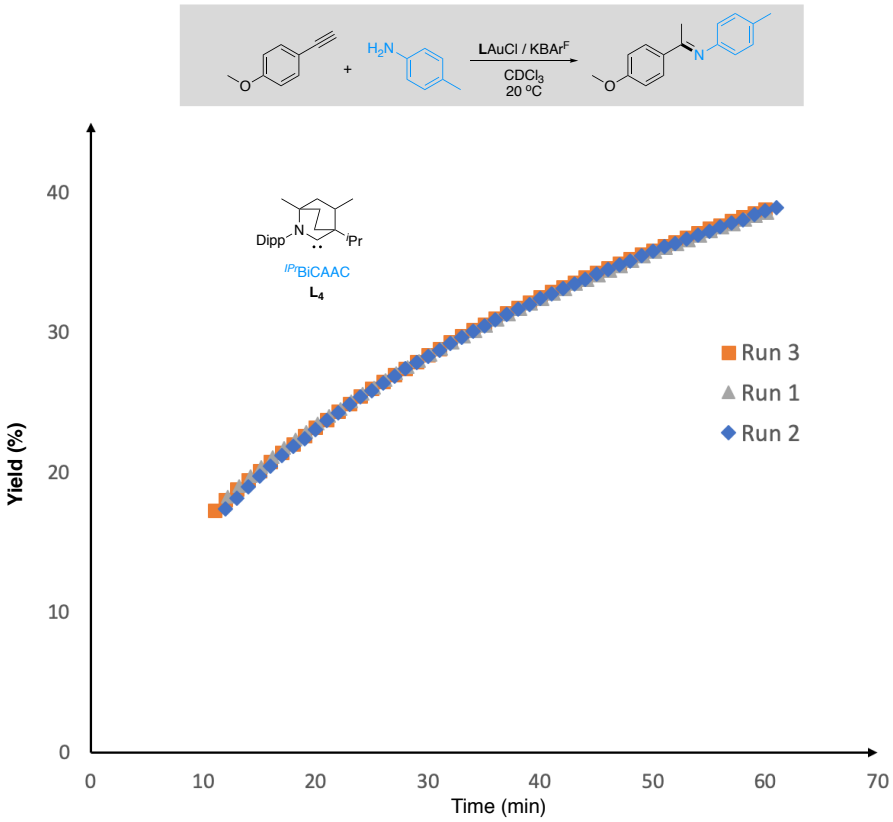



*Figure illustrating the reproducibility of the kinetic measurements by $^1H$ NMR ($CDCl_3$)*

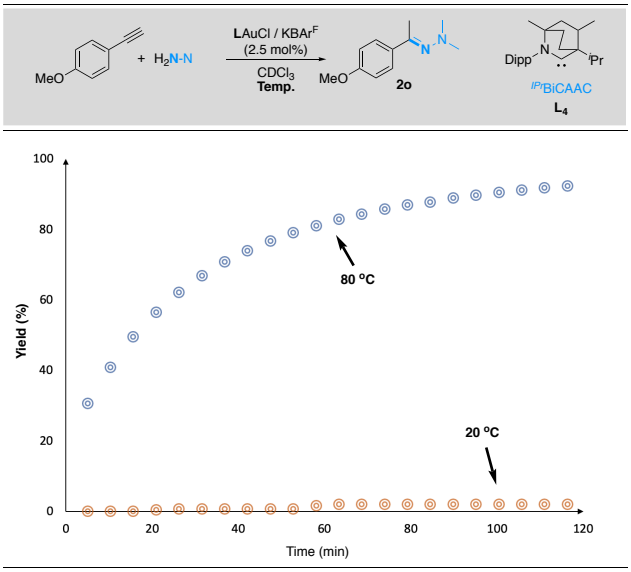
### II.5. Hammett correlations of rates and substituents (*cf.* Figure 4 and 7).

All the kinetic measurements were performed in an NMR tube at room temperature on a Bruker 300MHz NMR machine using the multi_zgvd command. In a typical experiment, the NMR tube was charged with the Au catalyst and $KB(C_6F_5)_4$ [2.5 mol% (Fig. 4); 0.5 mol% (Fig. 7); 1:1 ratio)], the alkyne (0.356 mmol, 1.0 eq.) and the corresponding amount of deuterated solvent [$C_6D_6$ (1.5 M) – Fig. 4; $CDCl_3$ (1.8 M) Fig. 7]. The tube was locked and shimmed (T0) before starting the kinetic measurement. Following the addition of amine (0.356 mmol, 1.0 eq. - Figure 2) or phenylhydrazine (0.356 mmol, 1.0 eq. - Figure 6) the reaction was monitored as a function of the time at constant temperature (20 °C). Conversions were quantified by tracking the change in characteristic signals for the starting material and the product (imine). In all cases, the kinetic measurements were repeated up to 2-3 times to confirm the reproducibility of our results.

### II.6. Rate dependence of concentration of alkyne and hydrazine (*cf.* Figure 5 and 8).

All the kinetic measurements were performed in an NMR tube at room temperature on a Bruker 300MHz NMR machine using the multi_zgvd command. In a typical experiment, the NMR tube was charged with the Au catalyst and $KB(C_6F_5)_4$ [2.5 mol% (Fig. 5); 0.5 mol% (Fig. 8); 1:1 ratio)], the alkyne (0.178 - 1.068 mmol, from 0.5 to 3 eq.) and the corresponding amount of deuterated solvent ($C_6D_6$ – Fig. 4; $CDCl_3$ Fig. 7). The tube was locked and shimmed (T0) before starting the kinetic measurement. Following the addition of amine (Figure 2) or phenylhydrazine (Figure 6) (0.178 - 1.068 mmol, from 0.5 to 3 eq.) the reaction was monitored as a function of the time at constant temperature (20 °C). Conversions were quantified by tracking the change in characteristic signals for the starting material and the product (imine). In all cases, the kinetic measurements were repeated up to 2-3 times to confirm the reproducibility of our results.

## II.7. Comparing the reactivity of 1,1-disubstituted hydrazines at RT and at 80 °C (*cf.* Ref. 27)




Temperature dependence study for **2o**.

## II.8. Procedure for investigating ligand effects on cationic gold degradation (*cf.* Figure 9)

All NMR measurements were performed in an NMR tube at room temperature on a Bruker 300MHz NMR machine. In a typical experiment, the NMR tube was charged with the specified Au catalyst (0.0367 mmole, 1.0 eq.), $KB(C_6F_5)_4$ (0.0264 g, .0367 mmole, 1.0 eq.), 1-Hexyne (0.030 g, 3.668 mmol, 10.0 eq.) and 0.5 mL of $CDCl_3$. Complex degradation was quantified by tracking the change of the characteristic signals for the $[(L)Au^+(\pi\text{-alkyne})][BAr^{F-}]$ using TMSCl as an internal standard.

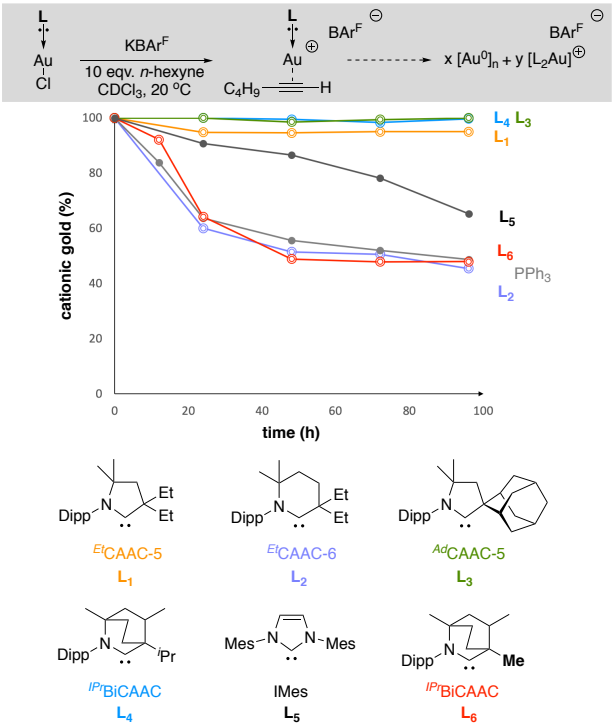



*Figure illustrating the Ligand effects on the decay of $[LAu(alkyne)^+][BAr^{F-}]$.*

### II.9. TON- hydroamination and Hydrazination of phenylacetylene with aniline/ and phenylhydrazine

All reaction performed in 25 mL pressure tube and in the presence of 0.01-0.0025 mol% of ($^{iPr}$BICAAC)Au(Cl) ($5.10^{-4}$-$1.25.10^{-4}$ mmol). The corresponding amount of catalyst loading was achieved by preparing a stock solution of ($^{iPr}$BICAAC)Au(Cl) in $CH_2Cl_2$ ($2.796.10^{-3}$ mol.L$^{-1}$ obtained by dissolving $5.592.10^{-3}$ mmol in 2 mL).

**In a typical experimental protocol**: a 25 mL pressure tube was loaded with 179 µL of catalyst stock solution (0.0025 mol%). The pressure tube was evaporated to remove the $CH_2Cl_2$ which left 0.0005 mmol of solid ($^{iPr}$BICAAC)Au(Cl) catalyst precursor. KBAr$^F$ (0.0057 mg, 0.008 mmol, 0.04%), immediately followed by aniline (2.0488, 22 mmol) or phenylhydrazine (2.379, 22 mmol) was added. Finally, phenylacetylene (2.0427 g, 20 mmol) was added to this mixture and the pressure tube was sealed with a Teflon-screw cap and placed in a pre-heated oil bath (80 °C). After 19h, the reaction mixture was cooled and the TON was quantified by $^1$H spectroscopy in $CDCl_3$, by direct integration of the characteristic aromatic peaks of the starting material and the product. **NB**: For consistency with previous reports,[22] the reactions were performed under argon using commercial reagents pre-dried over molecular sieves (4 Å).

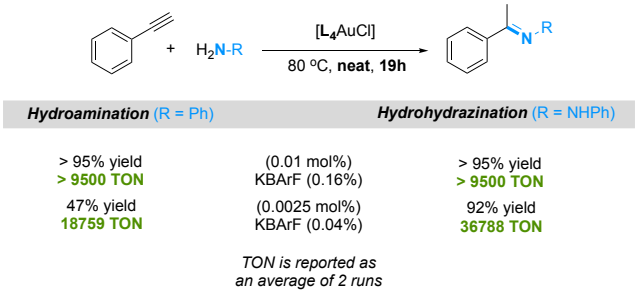


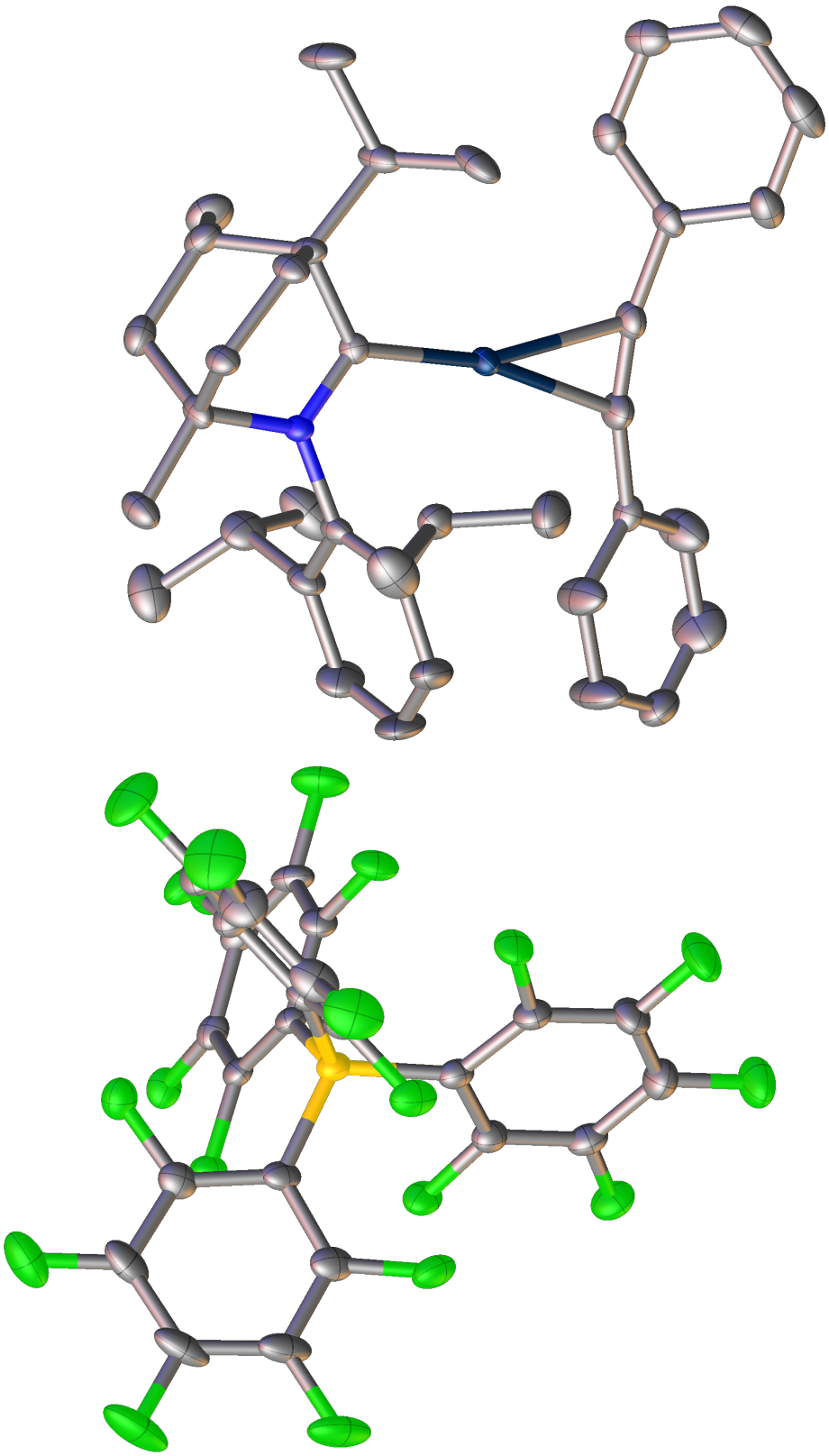

*Figure illustrating the benchmarking the catalytic activity of $^{IPr}$BiCAAC gold chloride ($L_4AuCl$) against state-of-the-art ligands.*

# III. Crystallographic data

**Crystal data and structure refinement for [(L$_4$)AuPhCCPh][BArF] (CCDC # 1983926)**

| | |
|---|---|
| Identification code | L4AuPhCCPhBArF |
| Empirical formula | $C_{62}H_{47}AuBF_{20}N$ |
| Formula weight | 1393.78 |
| Temperature/K | 100.15 |
| Crystal system | triclinic |
| Space group | P-1 |
| a/Å | 15.2805(9) |
| b/Å | 18.4692(12) |
| c/Å | 20.3195(13) |
| α/° | 78.4450(10) |
| β/° | 80.9370(10) |
| γ/° | 82.2190(10) |
| Volume/Å$^3$ | 5516.1(6) |
| Z | 4 |
| $\rho_{calc}$g/cm$^3$ | 1.678 |
| μ/mm$^{-1}$ | 2.777 |
| F(000) | 2760.0 |
| Crystal size/mm$^3$ | 0.15 × 0.11 × 0.05 |
| Radiation | MoKα (λ = 0.71073) |
| 2Θ range for data collection/° | 2.77 to 52.744 |
| Index ranges | -19 ≤ h ≤ 19, -23 ≤ k ≤ 23, -25 ≤ l ≤ 25 |
| Reflections collected | 116457 |
| Independent reflections | 22551 [$R_{int}$ = 0.0320, $R_{sigma}$ = 0.0229] |
| Data/restraints/parameters | 22551/91/1633 |
| Goodness-of-fit on F$^2$ | 1.043 |
| Final R indexes [I>=2σ (I)] | $R_1$ = 0.0263, $wR_2$ = 0.0555 |
| Final R indexes [all data] | $R_1$ = 0.0412, $wR_2$ = 0.0615 |
| Largest diff. peak/hole / e Å$^{-3}$ | 1.37/-0.44 |

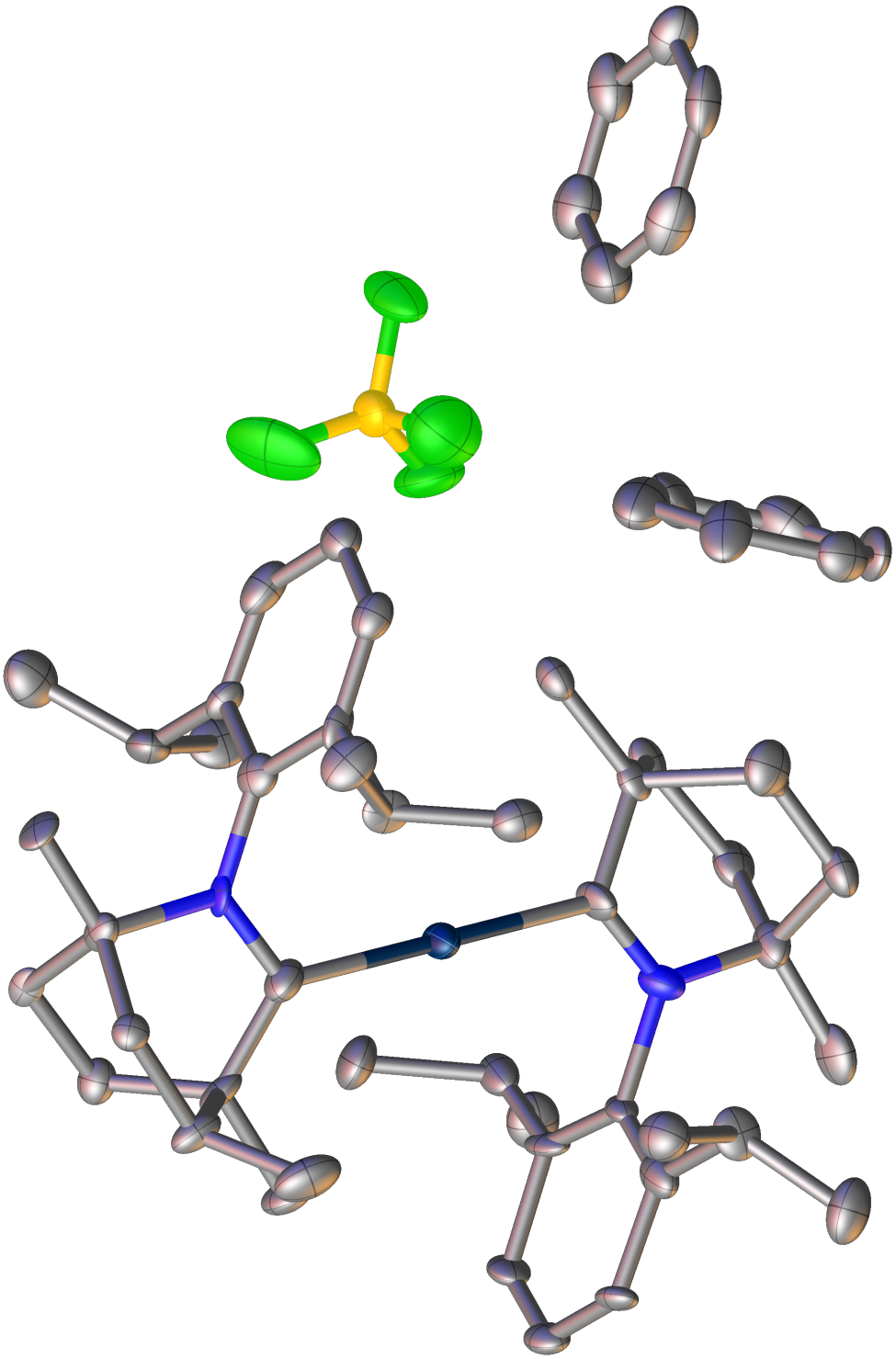
Note: Additional weak reflections support unit cell with larger volume.



**X-ray structure of [(L4)AuPhCCPh][BArF] with ellipsoids shown at 50% probability. Hydrogen atoms are omitted for clarity.**

**Crystal data and structure refinement for $[(L_6)_2Au][BF_4]$ (CCDC # 1983924)**

| | |
|---|---|
| Identification code | [(L6)2Au][BF4] |
| Empirical formula | $C_{56}H_{78}AuBF_4N_2$ |
| Formula weight | 1062.98 |
| Temperature/K | 100.0 |
| Crystal system | monoclinic |
| Space group | Cc |
| a/Å | 17.9392(11) |
| b/Å | 18.2892(10) |
| c/Å | 17.3878(10) |
| α/° | 90 |
| β/° | 118.402(2) |
| γ/° | 90 |
| Volume/Å$^3$ | 5018.1(5) |
| Z | 4 |
| $\rho_{calc}$g/cm$^3$ | 1.407 |
| μ/mm$^{-1}$ | 2.985 |
| F(000) | 2192.0 |
| Crystal size/mm$^3$ | 0.12 × 0.06 × 0.05 |
| Radiation | MoKα (λ = 0.71073) |
| 2Θ range for data collection/° | 3.408 to 52.794 |
| Index ranges | -22 ≤ h ≤ 22, -22 ≤ k ≤ 22, -21 ≤ l ≤ 21 |
| Reflections collected | 44280 |
| Independent reflections | 10265 [$R_{int}$ = 0.0340, $R_{sigma}$ = 0.0272] |
| Data/restraints/parameters | 10265/278/686 |
| Goodness-of-fit on F$^2$ | 1.040 |
| Final R indexes [I>=2σ (I)] | $R_1$ = 0.0188, $wR_2$ = 0.0427 |
| Final R indexes [all data] | $R_1$ = 0.0310, $wR_2$ = 0.0476 |
| Largest diff. peak/hole / e Å$^{-3}$ | 0.53/-0.24 |
| Flack parameter | 0.52(2) |

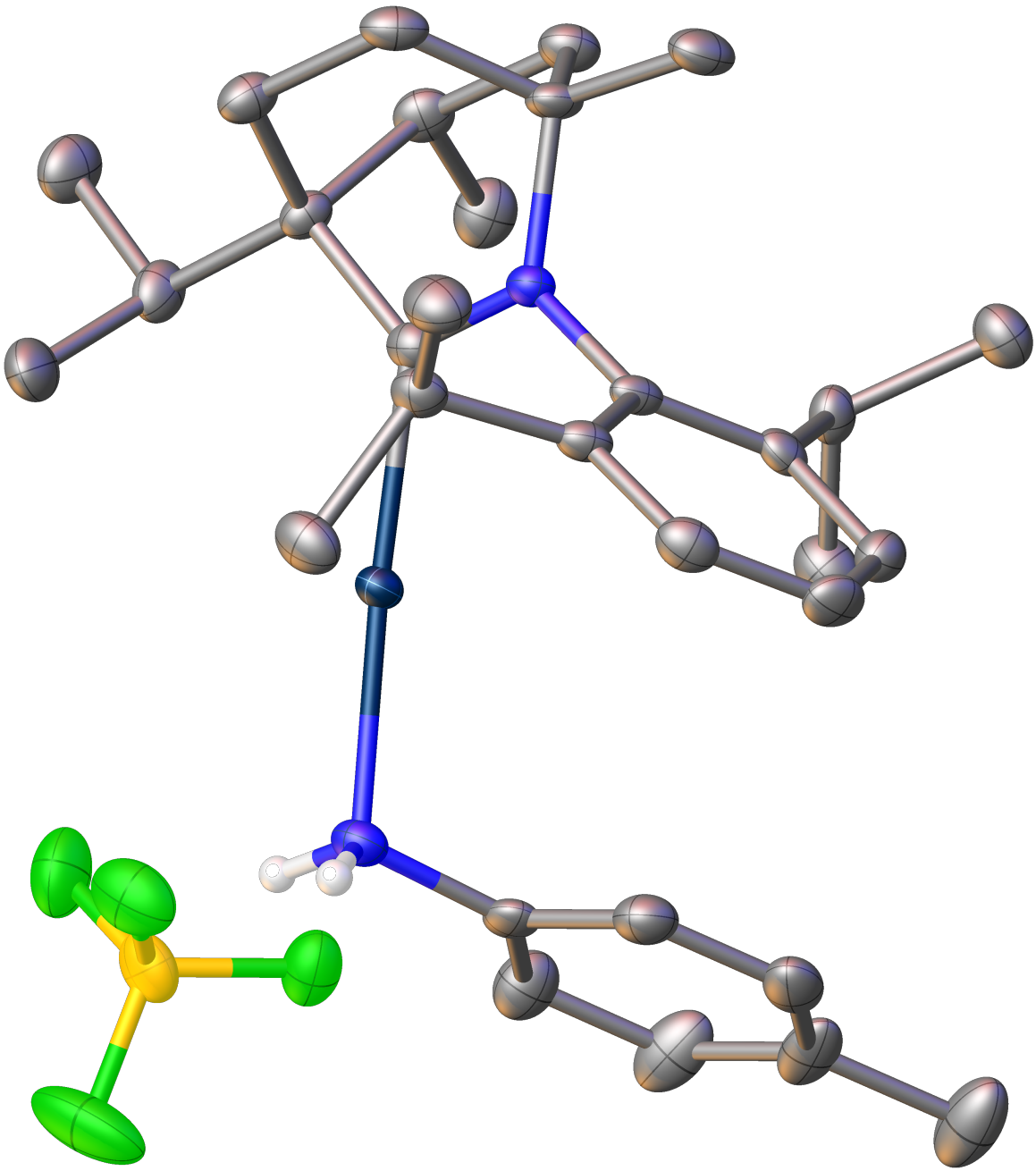


**X-ray structure of $[(L_6)_2Au][BF_4]$ with ellipsoids shown at 50% probability. Hydrogen atoms are omitted for clarity.**

**Crystal data and structure refinement for $(L_4)Au(TolNH_2)$_sq.**

| | |
|---|---|
| Identification code | $(L_4)Au(TolNH_2)$_sq |
| Empirical formula | $C_{31}H_{46}AuBF_4N_2$ |
| Formula weight | 730.47 |
| Temperature/K | 100.0 |
| Crystal system | monoclinic |
| Space group | $P2_1/c$ |
| a/Å | 11.0290(5) |
| b/Å | 13.8947(7) |
| c/Å | 23.6350(9) |
| α/° | 90 |
| β/° | 102.050(2) |
| γ/° | 90 |
| Volume/Å$^3$ | 3542.1(3) |
| Z | 4 |
| $\rho_{calc}$g/cm$^3$ | 1.370 |
| μ/mm$^{-1}$ | 4.194 |
| F(000) | 1464.0 |
| Crystal size/mm$^3$ | 0.35 × 0.33 × 0.22 |
| Radiation | MoKα (λ = 0.71073) |
| 2Θ range for data collection/° | 6.392 to 51.34 |
| Index ranges | -13 ≤ h ≤ 13, -16 ≤ k ≤ 16, -28 ≤ l ≤ 28 |
| Reflections collected | 41355 |
| Independent reflections | 6714 [$R_{int}$ = 0.0441, $R_{sigma}$ = 0.0321] |
| Data/restraints/parameters | 6714/0/361 |
| Goodness-of-fit on F$^2$ | 1.048 |
| Final R indexes [I>=2σ (I)] | $R_1$ = 0.0222, $wR_2$ = 0.0468 |
| Final R indexes [all data] | $R_1$ = 0.0310, $wR_2$ = 0.0492 |
| Largest diff. peak/hole / e Å$^{-3}$ | 1.08/-0.56 |

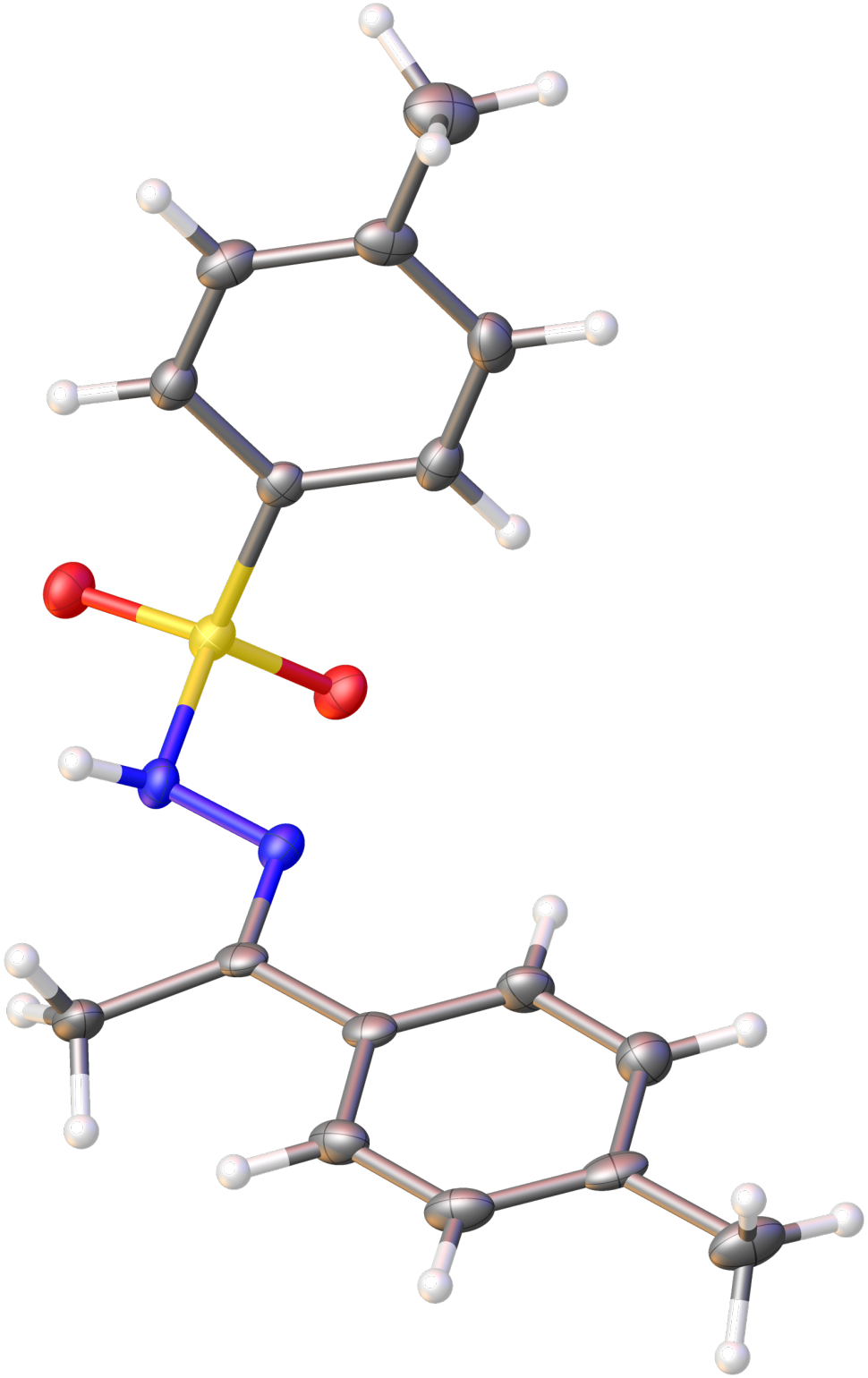
Note: A disordered benzene molecule was squeezed from the final solution.



**X-ray structure of $[(L_4)Au(TolNH_2)][BF_4]$ with ellipsoids shown at 50% probability. Hydrogen atoms are omitted for clarity.**

**Crystal data and structure refinement for 2q** **(CCDC # 1983923)**

| | |
|---|---|
| Identification code | GB_RJ_SY_20191021_0m_a |
| Empirical formula | $C_{16}H_{18}N_2O_2S$ |
| Formula weight | 302.38 |
| Temperature/K | 100.0 |
| Crystal system | monoclinic |
| Space group | $P2_1/n$ |
| a/Å | 5.2585(18) |
| b/Å | 15.779(3) |
| c/Å | 18.526(4) |
| α/° | 90 |
| β/° | 95.843(14) |
| γ/° | 90 |
| Volume/Å$^3$ | 1529.1(7) |
| Z | 4 |
| $\rho_{calc}$g/cm$^3$ | 1.313 |
| μ/mm$^{-1}$ | 0.217 |
| F(000) | 640.0 |
| Crystal size/mm$^3$ | 0.05 × 0.05 × 0.01 |
| Radiation | MoKα (λ = 0.71073) |
| 2Θ range for data collection/° | 3.398 to 50.888 |
| Index ranges | -6 ≤ h ≤ 6, -19 ≤ k ≤ 19, -19 ≤ l ≤ 22 |
| Reflections collected | 15315 |
| Independent reflections | 2819 [$R_{int}$ = 0.0539, $R_{sigma}$ = 0.0469] |
| Data/restraints/parameters | 2819/0/197 |
| Goodness-of-fit on $F^2$ | 1.019 |
| Final R indexes [I>=2σ (I)] | $R_1$ = 0.0415, $wR_2$ = 0.0837 |
| Final R indexes [all data] | $R_1$ = 0.0680, $wR_2$ = 0.0925 |
| Largest diff. peak/hole / e Å$^{-3}$ | 0.25/-0.38 |



**X-ray structure of 2q with ellipsoids shown at 50% probability.**

## IV. Computational Methods

Different computational methods were used based on the Gaussian09 program suite,[23] all used ultrafine[24] (99,590) integration grids. First, the electronic structure of carbene cores to obtain HOMO, LUMO, and Singlet-Triplet gap values were performed at the B3LYP[25]/def2-TZVPP[26] level of theory to maintain homogeneity with other studies.[13,20,27] Second, the energy of isopropyl rotation on $^{iPr}$BiCAAC-AuCl used the ωB97X-D[28] functional with cc-pVDZ-pp basis set and pseudopotential for the Au atom,[29] and 6-31g**[30] basis set for all other atoms. Third, the ligand exchange structures were optimized with the ωB97X-D functional and 6-31g** basis set for all atoms except Au, which was treated with the SDD[31] basis set and ECP. Solvent was treated as a polarizable continuum of benzene.[32] Structures were found to be minima by checking there were no imaginary frequencies at the same level of theory. All results (.chk, .fchk, and .log files) are made available for download from UCSD Library Digital Collections.[33]

## V. References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