Electronic Supplementary Material (ESI) for ChemComm.

Isolation and Structural Characterization of a Titanacyclopropane as Key Intermediate in the Double Aryl Grignard Addition to 2-(Arylethynyl)pyridine Derivatives

Francesco Foschi,[a] Torsten Roth,[a] Markus Enders,[a] Hubert Wadepohl,[a] Eric Clot[b] and Lutz H. Gade[a,*]

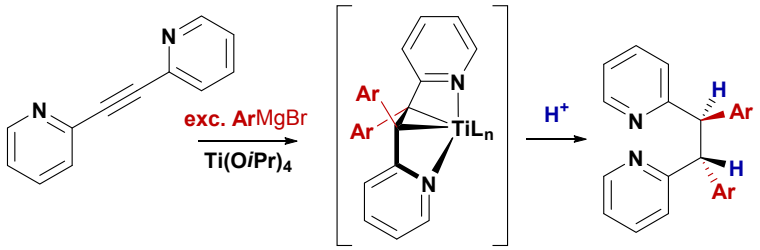


Table of contents

[a] Anorganisch-Chemisches Institut, Universität Heidelberg, Im Neuenheimer Feld 270, 69120 Heidelberg, Germany.
[b] ICGM - Equipe CTMM c.c. 1501 Place E. Bataillon 34095 Montpellier cedex 5.
*E-mail: lutz.gade@uni-heidelberg.

Experimental Section

Unless otherwise stated, all reactions were carried out in oven-dried flasks (150 °C) under dry inert gas atmosphere, according to Schlenk standard techniques. As inert gas Argon 5.0 purchased from Messer Group GmbH was used after drying over Granusic© phosphorus pentoxide granulate. If not indicated otherwise all reagents were obtained from commercial sources (Sigma Aldrich®, ACROS ORGANICS, abcr GmbH).

Solvents: THF, diethyl ether, dichloromethane, toluene and hexane were dried over activated alumina columns using a M. Braun SPS 800 solvent purification system, and stored under argon atmosphere in glass ampules. Column chromatography solvents (petrolether, ethyl acetate, triethylamine) were used without any preliminar treatment.

General remarks

All novel compounds were characterized by multinuclear magnetic resonance spectroscopy (NMR), high resolution mass spectroscopy (HRMS), and in selected cases single-crystal X-ray diffraction.

^{1}H NMR spectroscopy: NMR spectra were recorded in deuterated chloroform-d_1, benzene-d_6 or toluene-d_8 at room temperature on a Bruker Avance II (400MHz) or a Bruker Avance III (600MHz) spectrometer. Chemical shifts are reported in parts per million (ppm) and referenced internally to the chloroform, benzene or toluene residual proton signals (δ = 7,26, 7.16 or 2.08 ppm, respectively). NMR resonances are reported as chemical shift, multiplicity, coupling constant *J* and integration. The multiplicity is reported by the labels s (singlet), d (doublet), t (triplet), q (quartet), quin (quintet). Furthermore the abbreviations m (multiplet) and br (broad signal) are used.

^{13}C NMR spectroscopy: NMR spectra were recorded and described as indicated for ^{1}H-NMR spectra. Chemical shifts are reported in parts per million (ppm) and referenced internally to choloroform-d_1, benzene-d_6 or toluene-d_8 carbon atoms (δ = 77,16, 128.06 or 20.43 ppm, respectively).

^{19}F NMR spectroscopy: NMR spectra were recorded in toluene-d_8 at room temperature on a Bruker Avance II (400MHz). Chemical shifts are reported in parts per million (ppm) and referenced to an external standard ($CFCl_3$).

Identification of diastereoisomers and determination of diastereoisomeric ratios by use of a chiral shift reagent (Eu(ufc)$_3$)

Products **1a-e** were obtained as a mixture of *anti* diastereoisomer (racemate) and *meso* diastereoisomer. The identification of the *anti* and *meso* diastereoisomers and the determination of their relative amount (dr) were performed by use of a chiral lanthanide shift reagent (Eu(hfc)$_3$), hence inducing splitting of selected signals in the ^{1}H and ^{13}C NMR spectra of the *anti* diastereoisomer (racemate resolution). The assigned NMR shifts are marked in the following way:

Anti diastereoisomer: red, underscore.

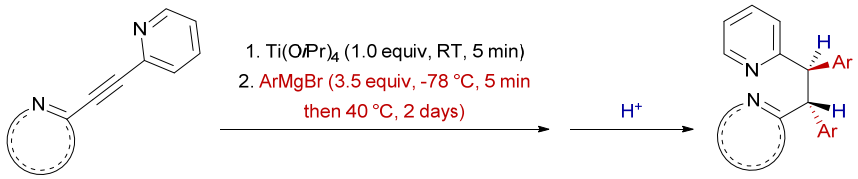
Meso diastereoisomer: blue.

Splitting of signals induced by Eu(hfc)$_3$: xxx turns into the couple of signals ***xxx*/*xxx*** or into the broad signal indication ***xxx (br)*** (bold, italic). Layout for exemplary description of ^{1}H NMR split signals: ***5.62*/*5.60* (s/s, 2 H)**. Layout for exemplary description of ^{13}C NMR split and broad signals: ***130.90*/*130.89* (d/d, *J*= 7.7 Hz)**, ***58.13*/*58.12***, ***162.3* (br)**.

Mass Spectrometry: mass spectra and high-resolution mass spectra were measured by the University of Heidelberg Mass Spectrometry Facility. High resolution mass spectra were acquired on Brucker ApexQe Hybrid 9.4 T FT-ICR and JEOL JMS-700 magnetic sector (EI, LIFDI) spectrometers.

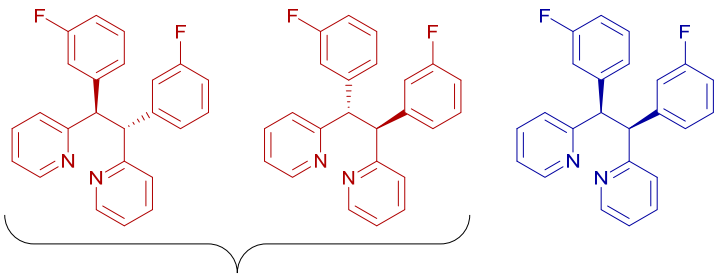
Synthetic Procedures

General Procedure 1 (GP-1, 1,2-diaryl-1,2-di(pyridin-2-yl)ethanes)



To a solution of 1,2-di(pyridin-2-yl)ethyne (0.10 g, 0.55 mmol) in dry THF (2.0 mL), [Ti(O*i*Pr)$_4$] (0.16 g, 0.16 mL, 1.0 equiv) was added and the mixture was stirred for 5 min at room temperature. After cooling to –78 °C, a solution of a Grignard reagent (1.0 M in THF, 1.9 mL, 3.5 equiv) was added dropwise, then the cooling bath was removed and the mixture was stirred at 40 °C for two days, thus turning black. The reaction vessel was then

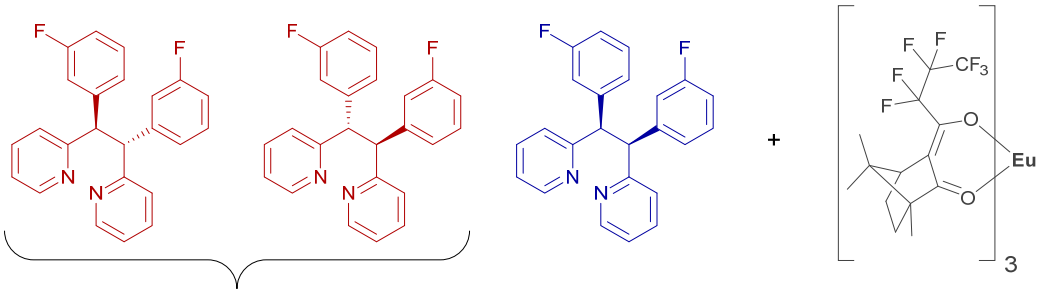
cooled to 0 °C in an ice bath and trifluoroacetic acid (0.28 g, 0.19 mL, 4.5 equiv) was added dropwise and the mixture was stirred for 15 min under argon atmosphere. The ice bath was replaced by a water bath and the mixture was stirred for 30 min at room temperature, hence fine white precipitate was observed. A potassium carbonate aqueous solution (10 g, 25% w/w) was poured in small portions and the mixture was stirred for 30 minutes, then 50 mL of dichloromethane were added and the mixture was stirred vigorously for 2 hours, turning from black to pale orange with white slurry. Filtration through a celite pad (75 mL) gave a clear orange solution, which was dried over magnesium sulfate. The crude product was adsorbed over celite and purified by column chromatography (SiO_2, eluent gradient: petroleum ether:ethylacetate = 15:1 to 2:1, 0.5 vol% NEt_3). Evaporation of the volatiles gave the products as racemate of the *anti* diastereoisomers (**1b**–**e**) as white to pale yellow solid. The co-eluted *meso* diastereoisomer was spectroscopically characterized as a minor by-product. Further purification by column chromatography could not significatively increase the *anti*/*meso* diastereoisomeric ratio. Identification of the main product as a racemate of the *anti* diastereoisomers and evaluation of the diastereoisomeric ratio with respect to the *meso* by-product were performed spectroscopically (^{1}H NMR, ^{13}C{^{1}H} NMR) by addition of a chiral shift reagent to NMR probes of **1b**–**e** (saturated Eu(hfc)$_3$ solution in C_6D_6, 0.013 mL of saturated solution *per* μmol of tetraarylalkane, ~0.05–0.1 equivalents of lanthanide shift reagent).



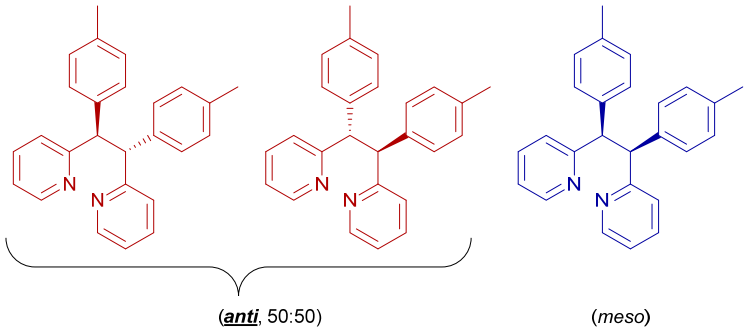
(***anti***, 50:50) (*meso*)

1b (*anti* and *meso*) (white solid, 0.15 g, 0.40 mmol, 73%, dr (*anti*:*meso*) = 15:1). ArMgBr: 3-fluorophenylmagnesium bromide. ^{1}H NMR (600.13 MHz; C_6D_6; 295.0 K): δ [ppm] = 8.39 – 8.36 (m, 2 H), 8.36 – 8.23 (m, 2 H), 7.68 – 7.61 (m, 2 H), 7.54 – 7.40 (m, 2 H), 7.38 – 7.35 (m, 2 H), 7.11 – 7.05 (m, 2 H), 7.05 – 7.01 (m, 2 H), 7.00 – 6.94 (m, 2 H), 6.85 – 6.79 (m, 2 H), 6.77 – 6.74 (m, 2 H), 6.72 – 6.68 (m, 2 H), 6.67 – 6.65 (m, 2 H), 6.56 – 6.44 (m, 2 H + 2 H), 6.39 – 6.30 (m, 2 H + 2 H), 5.42 (s, 2 H), 5.34 (s, 2 H). ^{13}C{^{1}H} NMR (150.90

MHz; C_6D_6; 295.0 K): δ [ppm] = 163.2 (d, *J*= 245.1 Hz), 163.1 (d, *J*= 244.4 Hz), 162.2, 161.5, 149.6, 149.2, 145.6 (d, *J*= 7.3 Hz), 143.3 (d, *J*= 7.2 Hz), 136.0, 135.8, 129.8 (d, *J*= 8.2 Hz), 129.6 (d, *J*= 8.2 Hz), 125.14 (d, *J*= 2.7 Hz), 125.08 (d, *J*= 2.7 Hz), 124.7, 124.2, 121.3, 121.1, 116.05 (d, *J*= 21.6 Hz), 116.01 (d, *J*= 21.2 Hz), 113.5 (d, *J*= 21.1 Hz), 113.4 (d, *J*= 21.0 Hz), 58.3 (d, *J*= 1.5 Hz), 57.9 (d, *J*= 1.5 Hz). MS (HR-DART(+)): calcd 373.1516 ($C_{24}H_{19}F_2N_2$, $[M+H]^+$), found 373.1509.

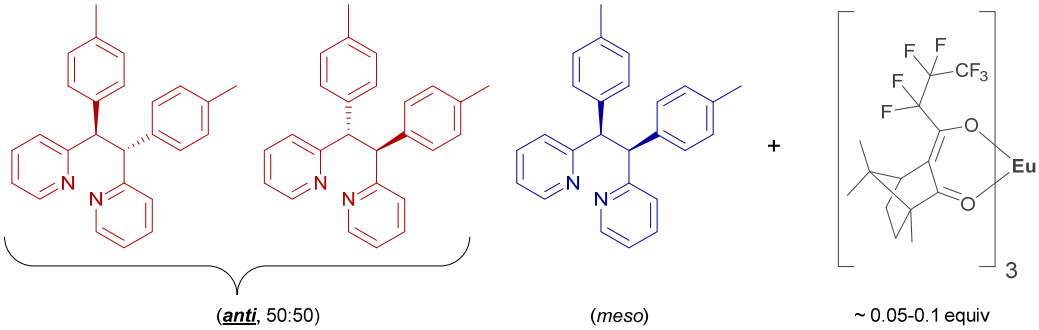


1b (*anti* and *meso* + $Eu(hfc)_3$) (**1b**: 20 mg, 0.054 mmol, $Eu(hfc)_3$: 0.70 mL (saturated C_6D_6 solution)). ^{1}H NMR (600.13 MHz; C_6D_6; 295.0 K): δ [ppm] = 8.45 – 8.33 (m, 2 H + 2 H), 7.71 – 7.67 (m, 2 H), 7.57 – 7.49 (m, 2 H), 7.45 – 7.41 (m, 2 H), 7.22 – 7.17 (m, 2 H + 2 H), 7.05 – 7.00 (m, 2 H), 6.88 – 6.81 (m, 2 H), 6.78 – 6.75 (m, 2 H), 6.74 – 6.70 (m, 2 H), 6.70 – 6.67 (m, 2 H), 6.57 – 6.48 (m, 2 H + 2 H), 6.41 – 6.33 (m, 2 H + 2 H), ***5.62/5.60 (s/s, 2 H)***, 5.43 (s, 2 H). $^{13}C\{^1H\}$ NMR (150.90 MHz; C_6D_6; 295.0 K): δ [ppm] = 163.3 (d, *J*= 245.0 Hz), 163.1 (d, *J*= 244.2 Hz), ***162.3 (br)***, 161.6, 149.6, 149.4, 145.7 (d, *J*= 7.1 Hz), 145.3 (d, *J*= 7.1 Hz), 136.1, 135.9, 129.8 (d, *J*= 8.2 Hz), 129.6 (d, *J*= 8.5 Hz), 125.2 (d, *J*= 2.5 Hz), 125.1 (d, *J*= 2.8 Hz), 124.7, 124.2, 121.3, 121.2, 116.09 (d, *J*= 21.8 Hz), 116.07 (d, *J*= 21.6 Hz), 113.6 (d, *J*= 21.2 Hz), 113.4 (d, *J*= 21.3 Hz), 58.4 (br), ***58.1 (br)***.



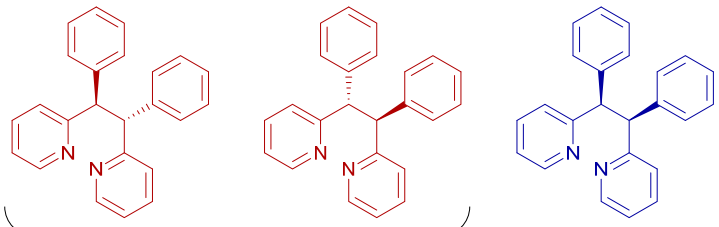
1c (*anti* and *meso*) (white solid, 92 mg, 0.26 mmol, 46%, dr (*anti*:*meso*) = 11:1). ArMgBr: *p*-tolylmagnesium bromide. ^{1}H NMR (600.13 MHz; C_6D_6; 295.0 K): δ [ppm] = 8.47 – 8.44

(m, 2 H), 8.44 – 8.35 (m, 2 H), 7.75 – 7.70 (m, 4 H), 7.60 – 7.49 (m, 4 H), 7.15 – 7.13 (m, 1 H + 1 H), 7.05 – 6.76 (m, 7 H + 7 H), 6.40 – 6.31 (m, 2 H + 2 H), 5.65 (s, 2 H), 5.58 (s, 2 H), 1.92 (s, 6 H), 1.90 (s, 6 H). $^{13}C\{^{1}H\}$ NMR (150.90 MHz; C_6D_6; 295.0 K): δ [ppm] = 163.9, 163.2, 149.4, 149.1, 140.4, 140.2, 135.8, 135.7, 135.53, 135.48, 129.4, 129.3, 129.2, 129.1, 124.7, 124.1, 120.9, 120.7, 58.3, 58.0, 20.92, 20.90. MS (HR-DART(+)): calcd 365.2018 ($C_{26}H_{25}N_2$, $[M+H]^+$), found 365.2010.



(***anti***, 50:50) (*meso*) ~ 0.05-0.1 equiv

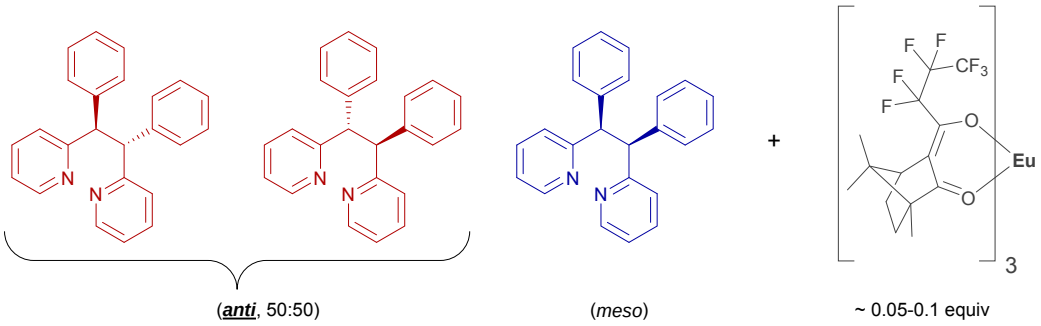
1c (*anti* and *meso* + $Eu(hfc)_3$) (**1c**: 20 mg, 0.055 mmol, $Eu(hfc)_3$: 0.72 mL (saturated C_6D_6 solution)). ^{1}H NMR (600.13 MHz; C_6D_6; 295.0 K): δ [ppm] = 8.53 – 8.43 (m, 2 H + 2 H), 7.81 – 7.79 (m, 4 H), 7.67 – 7.58 (m, 4 H), 7.25 – 7.18 (m, 2 H), 7.05 – 7.02 (m, 2 H), 6.93 – 6.84 (m, 6 H + 6 H), 6.40 – 6.35 (m, 2 H + 2 H), ***5.86/5.85 (s/s, 2 H)***, 5.72 (s, 2 H), 1.924 (s, 6 H), 1.916 (s, 6 H). $^{13}C\{^{1}H\}$ NMR (150.90 MHz; C_6D_6; 295.0 K): δ [ppm] = 164.0, 163.3, 149.5, 149.2, 140.5, ***140.271/140.266***, 135.9, 135.8, 135.6, 135.5, 129.5, 129.3, 129.2, 129.1, 124.6, 124.2, 120.9, 120.8, 58.5, ***58.13/58.12***, 20.93, 20.91.



(***anti***, 50:50) (*meso*)

1d (*anti* and *meso*) (white solid, 75 mg, 0.22 mmol, 41%, dr (*anti*:*meso*) = 7:1). ArMgBr: phenylmagnesium bromide. ^{1}H NMR (600.13 MHz; C_6D_6; 295.0 K): δ [ppm] = 8.47 – 8.42 (m, 2 H), 8.42 – 8.30 (m, 2 H), 7.84 – 7.75 (m, 4 H), 7.63 – 7.49 (m, 4 H), 7.14 – 7.07 (m, 2 H + 2 H), 7.06 – 6.97 (m, 4 H + 4 H), 6.86 – 6.73 (m, 4 H + 4 H), 6.43 – 6.28 (m, 2 H + 2 H) 5.61 (s, 2 H), 5.54 (s, 2 H). $^{13}C\{^{1}H\}$ NMR (150.90 MHz; C_6D_6; 295.0 K): δ [ppm] = 163.4, 162.7, 149.5, 149.1, 143.3, 143.1, 135.8, 135.7, 129.5, 129.4, 128.3 (br), 128.3 (br),

126.40, 126.39, 124.8, 124.2, 120.9, 120.8, 58.8, 58.4. MS (HR-DART(+)): calcd 337.1705 ($C_{24}H_{21}N$, $[M+H]^+$), found 337.1700.



1d (*anti* and *meso* + $Eu(hfc)_3$) (**1d**: 20 mg, 0.059 mmol, $Eu(hfc)_3$: 0.77 mL (saturated C_6D_6 solution)). ^{1}H NMR (600.13 MHz; C_6D_6; 295.0 K): δ [ppm] = 8.59 – 8.44 (m, 2 H + 2 H), 7.95 – 7.86 (m, 4 H), 7.79 – 7.58 (m, 4 H), 7.22 – 7.18 (m, 2 H + 2 H), 7.08 – 7.01 (m, 4 H + 4 H), 6.91 – 6.76 (m, 4 H + 4 H), 6.46 – 6.27 (m, 2 H + 2 H), ***5.94*/*5.91* (*s*/*s*, *2 H*)**, 5.75 (s, 2 H). ^{13}C{^{1}H} NMR (150.90 MHz; C_6D_6; 295.0 K): δ [ppm] = ***163.60*/*163.59***, 162.8, 149.6, ***149.31*/*149.30***, 143.37, ***143.14*/*143.13***, 135.9, 135.8, ***129.56*/*129.55***, 129.47, ***128.424*/*128.421***, 128.3, 126.48, 126.45, 124.8, 124.3, 121.0, 120.9, 58.9, ***58.65*/*58.63***.

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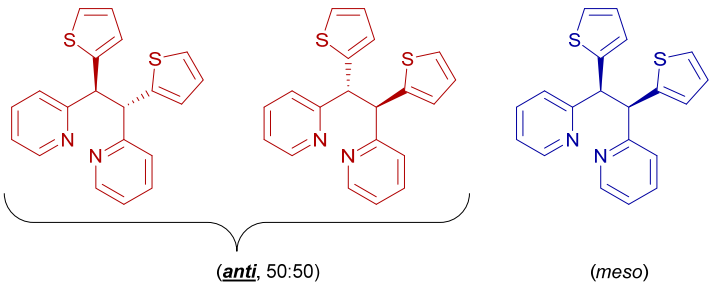
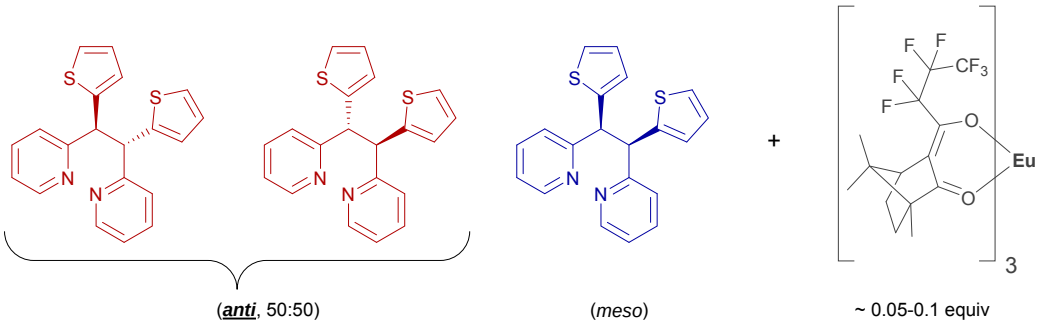


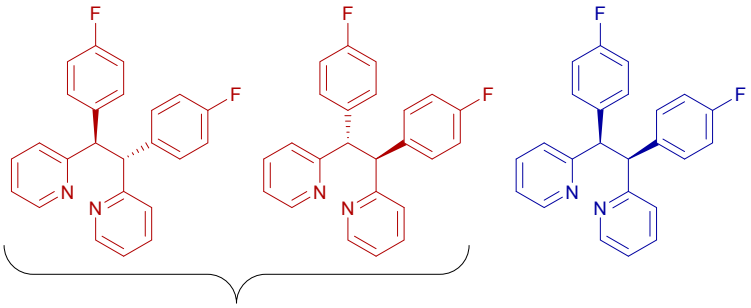
1e (*anti* and *meso*) (pale yellow solid, 0.10 g, 0.29 mmol, 52%, dr (*anti*:*meso*) = 5:1). ArMgBr: 2-thienylmagnesium bromide. ^{1}H NMR (600.13 MHz; C_6D_6; 295.0 K): δ [ppm] = 8.60 – 8.52 (m, 2 H), 8.47 – 8.29 (m, 2 H), 7.00 – 6.92 (m, 2 H + 2 H), 6.92 – 6.85 (m, 2 H), 6.83 – 6.71 (m, 4 H + 4 H), 6.71 – 6.68 (m, 2 H), 6.64 – 6.57 (m, 2 H), 6.52 – 6.48 (m, 2 H), 6.46 – 6.41 (m, 2 H), 6.37 – 6.29 (m, 2 H), 5.76 (s, 2 H), 5.68 (s, 2 H). ^{13}C{^{1}H} NMR (150.90 MHz; C_6D_6; 295.0 K): δ [ppm] = 162.2, 161.8, 149.6, 149.2, 145.8, 145.5, 136.0, 135.8, 126.3, 126.2, 126.1, 126.0, 125.0, 124.8, 124.3, 124.2, 121.5, 121.2, 56.3, 55.9. MS (HR-DART(+)): calcd 349.0833 ($C_{20}H_{17}N_2S_2$, $[M+H]^+$), found 349.0827.



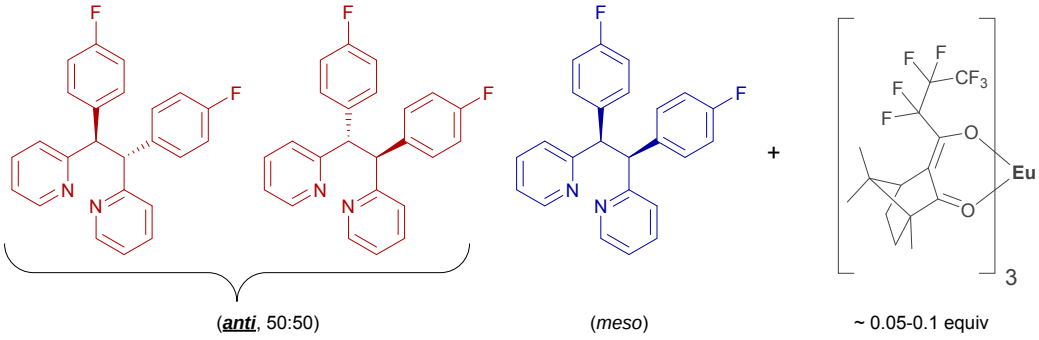
1e (*anti* and *meso* + $Eu(hfc)_3$) (**1e**: 15 mg, 0.043 mmol. $Eu(hfc)_3$: 0.56 mL (saturated C_6D_6 solution)). ^{1}H NMR (600.13 MHz; C_6D_6; 295.0 K): δ [ppm] = 8.65 – 8.57 (m, 2 H), 8.57 – 8.38 (m, 2 H), 7.06 – 7.02 (m, 2 H + 2 H), 7.00 – 6.94 (m, 2 H), 6.89 – 6.74 (m, 4 H + 4 H), 6.73 – 6.69 (m, 2 H), 6.65 – 6.60 (m, 2 H), 6.54 – 6.49 (m, 2 H), 6.48 – 6.42 (m, 2 H), 6.40 – 6.31 (m, 2 H), ***6.00*/*5.97* (*s*/*s*, *2 H*)**, 5.84 (s, 2 H). ^{13}C{^{1}H} NMR (150.90 MHz; C_6D_6; 295.0 K): δ [ppm] = ***162.4*/*162.3***, 161.9, 149.6, ***149.41*/*149.40***, ***145.83*/*145.82***, 145.5, 136.1, ***135.92*/*135.91***, 126.4, ***126.30*/*126.29***, 126.2, 126.1, 125.1, 124.9, 124.4, 124.2, 121.5, 121.2, 56.4, ***56.04*/*56.02***.

Procedure 1-II (P-1-II, 1,2-diaryl-1,2-di(pyridin-2-yl)ethanes)

The reaction was carried out according to **GP-1**, with exception that quenching was performed adding water (1.0 mL) instead of trifluoroacetic acid, while keeping the reaction vessel in a water cooling bath at room temperature. The mixture was stirred for two hours, the white solid precipitate was removed by filtration and the crude product was purified as described for **GP-1**, hence giving **1a** as a white solid (0.15 g, 0.40 mmol, 73%, dr (*anti*:*meso*) = 14:1). The co-eluted *meso* diastereoisomer was spectroscopically characterized as a minor by-product. Identification of the main product as a racemate of the *anti* diastereoisomers and evaluation of the diastereoisomeric ratio with respect to the *meso* by-product were performed spectroscopically (^{1}H NMR, ^{13}C{^{1}H) NMR) as described in **GP-1**. Recrystallization in benzene/pentane gave single crystals of **1a** suitable for X-ray diffraction analysis.



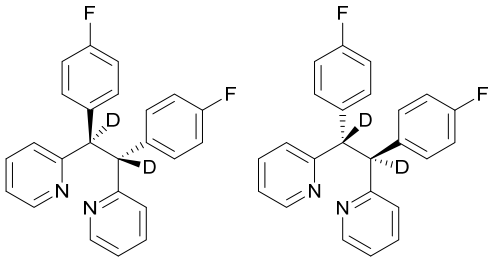
1a (*anti* and *meso*) ArMgBr: 4-fluorophenylmagnesium bromide. ^{1}H NMR (600.13 MHz; C_6D_6; 295.0 K): δ [ppm] = 8.43 – 8.40 (m, 2 H), 8.40 – 8.31 (m, 2 H), 7.62 – 7.52 (m, 4 H), 7.34 – 7.23 (m, 4 H), 7.15 – 7.12 (m, 2 H), 7.02 – 6.97 (m, 2 H), 6.88 – 6.82 (m, 2 H), 6.78 – 6.75 (m, 2 H), 6.71 – 6.68 (m, 4 H), 6.68 – 6.62 (m, 4 H), 6.43 – 6.33 (m, 2 H + 2 H), 5.37 (s, 2 H), 5.29 (s, 2 H). ^{13}C{^{1}H} NMR (150.90 MHz; C_6D_6; 295.0 K): δ [ppm] = 162.8, 162.2, 161.89 (d, *J*= 244.4 Hz), 161.85 (d, *J*= 244.2 Hz), 149.5, 149.1, 138.7 (d, *J*= 3.3 Hz), 138.6 (d, *J*= 3.2 Hz), 136.0, 135.8, 130.80 (d, *J*= 7.8 Hz), 130.77 (d, *J*= 7.6 Hz), 124.6, 124.2, 121.2, 121.0, 115.1 (d, *J*= 21.1 Hz), 115.0 (d, *J*= 21.0 Hz), 58.2, 57.7. MS (HR-DART(+)): calcd 373.1516 ($C_{24}H_{19}F_2N_2$, $[M+H]^+$), found 373.1509.



1a (*anti* and *meso* + Eu(hfc)$_3$) (**1a**: 20 mg, 0.054 mmol. Eu(hfc)$_3$: 0.70 mL (saturated C_6D_6 solution)). ^{1}H NMR (600.13 MHz; C_6D_6; 295.0 K): δ [ppm] = 8.63 – 8.33 (m, 2 H + 2 H), 7.71 – 7.63 (m, 4 H), 7.50 – 7.29 (m, 4 H), 7.12 – 7.01 (m, 2 H + 2 H), 6.93 – 6.87 (m, 2 H), 6.81 – 6.77 (m, 2 H), 6.76 – 6.71 (m, 4 H), 6.71 – 6.66 (m, 4 H), 6.46 – 6.34 (m, 2 H + 2 H), ***5.67*/*5.65* (*s*/*s*, *2 H*)**, 5.46 (s, 2 H). ^{13}C{^{1}H} NMR (150.90 MHz; C_6D_6; 295.0 K): δ [ppm] = ***163.03*/*163.02***, 162.3, 161.94 (d, *J*= 244.5 Hz), 149.6, ***149.36*/*149.35***, ***138.64*/*138.63* (*d*/*d*, *J*= 3.2 Hz)**, 136.0, 135.9, ***130.90*/*130.89* (*d*/*d*, *J*= 7.7 Hz)**, 124.7, 124.2, 121.2, 121.1, 115.2 (d, *J*= 21.0 Hz), 115.0 (d, *J*= 20.9 Hz), 58.3, ***57.92*/*57.91***. Three signals pertaining to the *meso* by-product were not detectable.

Procedure 1-III (P-1-III, 1,2-diaryl-1,2-di(pyridin-2-yl)ethanes)

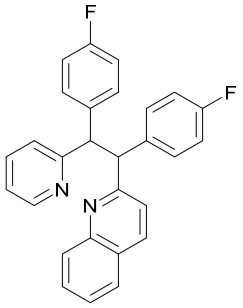
The reaction was carried out according to **P-1-II**, with exception that quenching was performed adding deuterium oxide (2.0 mL) under argon atmosphere, hence giving **1a-d$_2$** as a white solid (0.15 g, 0.40 mmol, 73%, dr (*anti*:*meso*) = 14:1). Further purification by column chromatography (SiO_2, eluent gradient: petroleum ether:ethylacetate = 20:1, 0.25 vol% NEt_3) lead to the increase of the *anti*/*meso* diastereoisomeric ratio (>20:1) although with severe drop of the overall isolated yield (72 mg, 0.19 mmol, 35%).



^{1}H NMR (399.89 MHz; $CDCl_3$; 294.6 K): δ [ppm] = 8.51 – 8.36 (m, 2 H), 7.56 – 7.28 (m, 8 H), 7.04 – 6.96 (m, 2 H), 6.85 – 6.77 (m, 4 H). ^{13}C{^{1}H} NMR (100.55 MHz; $CDCl_3$; 295.3 K): δ [ppm] = 161.6 (d, *J*= 245.0 Hz), 161.4 (br), 147.9 (br), 137.6 (br), 136.9 (br), 130.3 (d, *J*= 8.0 Hz), 124.9, 121.7, 115.3 (d, *J*= 21.2 Hz), 55.8 (t, *J*= 19.8 Hz). MS (HR-DART(+)): calcd 375.1642 ($C_{24}H_{17}D_2F_2N_2$, $[M+H]^+$), found 375.1631.

Procedure 1-IV (P-1-IV, 2-(1,2-bis(4-fluorophenyl)-2-(pyridin-2-yl)ethyl)quinoline)

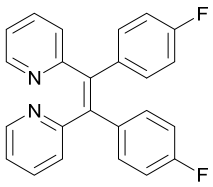
To a solution of 2-(pyridin-2-ylethynyl)quinoline (0.10 g, 0.43 mmol) in dry THF (3.0 mL), Ti(O*i*Pr)$_4$ (0.12 g, 0.13 mL, 1.0 equiv) was added and the mixture was stirred for 5 min at room temperature. After cooling to –78 °C, a solution of 4-fluorophenylmagnesium bromide (1.0 M in THF, 1.5 mL, 3.5 equiv) was added dropwise, then the cooling bath was removed and the mixture was stirred at 40 °C for two days, thus turning black. The heated bath was replaced with a water bath at room temperature, and water (1.0 mL) was added dropwise. The mixture was stirred for two hours, the white solid was removed by filtration and the crude product was purified as described for **GP-1**, hence giving **1f** as a white solid (0.15 g, 0.36 mmol, 83%). The configuration of **1f** was not established.



^{1}H NMR (399.89 MHz; C_6D_6; 295.1 K): δ [ppm] = 8.36 – 8.25 (m, 1 H), 8.25 – 8.17 (m, 1 H), 7.41 – 7.19 (m, 7 H), 7.16 – 7.02 (m, 3 H), 6.86 – 6.79 (m, 1 H), 6.72 – 6.59 (m, 4 H), 6.33 – 6.24 (m, 1 H), 5.67 – 5.50 (m, 2 H). ^{13}C{^{1}H} NMR (100.55 MHz; C_6D_6; 296.0 K): δ [ppm] = 163.07, 163.05, 161.95 (d, *J*= 244.7 Hz), 161.92 (d, *J*= 244.4 Hz), 148.9, 148.2, 138.7 (d, *J*= 3.3 Hz), 138.2 (d, *J*= 3.2 Hz), 135.9, 135.7, 131.0 (d, *J*= 7.8 Hz), 130.9 (d, *J*= 7.7 Hz), 129.4, 129.3, 127.0, 125.9, 124.8, 123.4, 121.0, 115.22 (d, *J*= 21.1 Hz), 115.15 (d, *J*= 21.1 Hz), 58.2, 57.5. MS (HR-DART(+)): calcd 423.1673 ($C_{28}H_{21}F_2N_2$, $[M+H]^+$), found 423.1667. One signal expected for a ^{13}C nucleus, possibly eclipsed by the solvent signal, was not detectable.

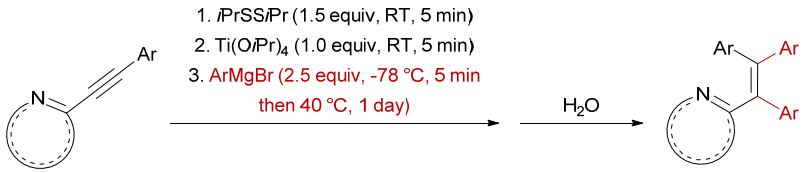
Procedure 2 (P-2, (Z)-1,2-bis(4-fluorophenyl)-1,2-di(pyridin-2-yl)ethene)

To a solution of 1,2-di(pyridin-2-yl)ethyne (0.20 g, 1.1 mmol) in dry THF (4.0 mL), Ti(O*i*Pr)$_4$ (0.31 g, 0.33 mL, 1.0 equiv) was added and the mixture was stirred for 5 min at room temperature. After cooling to –78 °C, a solution of 4-fluorophenylmagnesium bromide (1.0 M in THF, 3.9 mL, 3.5 equiv) was added dropwise, then the cooling bath was removed and the mixture was stirred at 40 °C for two days, thus turning black. The mixture was then cooled again to –78 °C and a iodine solution (0.84 g, 3.0 equiv in 10 mL (THF)) was added dropwise. After 30 minutes the cooling bath was replaced by an ice bath, which in turn was replaced after 30 min by a water bath at room temperature. Water (3.0 mL) was added dropwise and the mixture was stirred for 1 h, then THF (5.0 mL) and dichloromethane (40mL) were subsequently added. After stirring vigorously for 1 h the white precipitate was removed by filtration and the crude product was adsorbed over celite and purified by column chromatography (SiO_2, eluent gradient: petroleum ether:ethylacetate = 5:1 to 1:1.5, 0.5 vol% NEt_3). Evaporation of the volatiles gave **2** as pale yellow solid (0.24 g, 0.66 mmol, 60%). Recrystallization in ethyl acetate/pentane gave single crystals of **2** suitable for X-ray diffraction analysis.

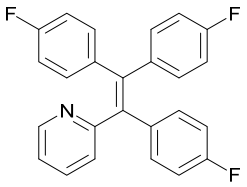


^{1}H NMR (399.89 MHz; C_6D_6; 295.2 K): δ [ppm] = 8.36 – 8.26 (m, 2 H), 7.00 – 6.84 (m, 8 H), 6.63 – 6.57 (m, 4 H), 6.50 – 6.44 (m, 2 H). ^{13}C{^{1}H} NMR (100.55 MHz; C_6D_6; 296.0 K): δ [ppm] = 162.2 (d, *J*= 247.1 Hz), 162.0, 149.4, 142.3, 138.2 (d, *J*= 3.5 Hz), 135.3, 133.2 (d, *J*= 8.0 Hz), 126.2, 121.5, 115.2 (d, *J*= 21.4 Hz). MS (HR-DART(+)): calcd 371.1360 ($C_{24}H_{17}F_2N_2$, $[M+H]^+$), found 371.1353.

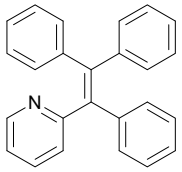
General Procedure 3 (GP-3, 2-(1,2,2-triarylvinyl)pyridines, 2-(1,2,2-triarylvinyl)quinolines)



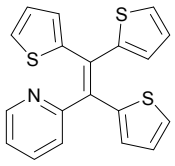
To a solution of 2-(arylethynyl)pyridine or 2-(arylethynyl)quinoline in dry THF (2.0 mL), isopropyl disulfide (1.5 equiv, diethyl and di-t-butyl disulfide could also be used but gave rise to lower yields in the preparation of the target compounds) and Ti(O*i*Pr)$_4$ (1.0 equiv) were added consecutively while stirring the solution at room temperature. After cooling the mixture to –78 °C, a THF solution of arylmagnesium bromide (2.5 equiv) was added dropwise, the cooling bath was then removed and the mixture was stirred at 40 °C for 24 h, hence turning black. The reaction vessel was cooled to rt in a water bath, distilled water (1.0 mL) was added dropwise and the mixture was stirred for 1 h. After addition of THF (3.0 mL) and dichloromethane (20 mL) the mixture was stirred vigorously for 2 h. The white precipitate was removed by filtration, the crude product was adsorbed over celite and purified by column chromatography (SiO_2, eluent gradient: petroleum ether:ethylacetate = 25:1 to 4:1, 0.5 vol% NEt_3). After evaporation of the volatiles, products **3a**–**e** were obtained as white to pale yellow solid. Recrystallization in ethyl acetate/pentane gave single crystals of **3b** suitable for X-ray diffraction analysis.



3a (white solid, 0.12 g, 0.31 mmol, 61%). Alkyne: 2-((4-fluorophenyl)ethynyl)pyridine (0.10 g, 0.51 mmol); *i*PrSS*i*Pr (0.11 g, 0.12 mL, 1.5 equiv); Ti(O*i*Pr)$_4$ (0.14 g, 0.15 mL, 1.0 equiv); ArMgBr: 4-fluorophenylmagnesium bromide (1.0 M THF solution, 1.3 mL, 2.5 equiv). ^{1}H NMR (399.89 MHz; C_6D_6; 294.8 K): δ [ppm] = 8.39 – 8.26 (m, 1 H), 6.89 – 6.73 (m, 8 H), 6.65 – 6.56 (m, 6 H), 6.50 – 6.45 (m, 1 H). ^{13}C{^{1}H} NMR (100.55 MHz; C_6D_6; 295.7 K): δ [ppm] = 162.21 (d, *J*= 247.5 Hz), 162.19 (d, *J*= 247.1 Hz), 162.1, 162.0 (d, *J*= 246.7 Hz), 149.8, 141.1, 140.8, 139.5 (d, *J*= 3.4 Hz), 139.0 (d, *J*= 3.4 Hz), 138.6 (d, *J*= 3.5 Hz), 135.4, 133.4 – 133.0 (m), 126.3, 121.4, 115.4 – 114.9 (m). MS (HR-DART(+)): calcd 388.1313 ($C_{25}H_{17}F_3N$, $[M+H]^+$), found 388.1315.

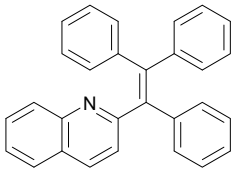


3b (pale yellow solid, 0.11 g, 0.33 mmol, 59%). Alkyne: 2-(phenylethynyl)pyridine (0.10 g, 0.56 mmol); *i*PrSS*i*Pr (0.13 g, 0.13 mL, 1.5 equiv); Ti(O*i*Pr)$_4$ (0.16 g, 0.17 mL, 1.0 equiv); ArMgBr: phenylmagnesium bromide (1.0 M THF solution, 1.4 mL, 2.5 equiv). **3b** is known compound. ^{1}H NMR (600.13 MHz; C_6D_6; 295.0 K): δ [ppm] = 8.42 – 8.33 (m, 1 H), 7.21 – 7.17 (m, 6 H), 6.97 – 6.88 (m, 10 H), 6.85 – 6.81 (m, 1 H), 6.46 – 6.42 (m, 1 H). ^{13}C{^{1}H} NMR (150.90 MHz; C_6D_6; 295.0 K): δ [ppm] = 162.9, 149.7, 144.2, 143.6, 143.23, 143.15, 141.8, 135.1, 131.8, 131.63, 131.60, 128.4, 128.15, 128.12, 127.1, 127.0, 126.8, 126.5, 121.1. MS (HR-DART(+)): calcd 334.1596 ($C_{25}H_{20}N$, $[M+H]^+$), found 334.1590.

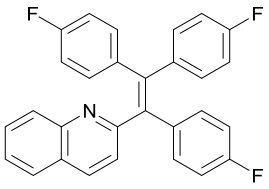


3c (pale yellow solid, 92 mg, 0.26 mmol, 48%). Alkyne: 2-(thiophen-2-ylethynyl)pyridine (0.10 g, 0.54 mmol); *i*PrSS*i*Pr (0.12 g, 0.13 mL, 1.5 equiv); Ti(O*i*Pr)$_4$ (0.15 g, 0.16 mL, 1.0 equiv); ArMgBr: 2-thienylmagnesium bromide (1.0 M THF solution, 1.4 mL, 2.5 equiv). ^{1}H

NMR (600.13 MHz; C_6D_6; 295.0 K): δ [ppm] = 8.60 – 8.44 (m, 1 H), 7.09 – 6.90 (m, 4 H), 6.81 – 6.75 (m, 1 H), 6.75 – 6.64 (m, 4 H), 6.63 – 6.58 (m, 1 H), 6.57 – 6.52 (m, 1 H), 6.48 – 6.41 (m, 1 H). $^{13}C\{^1H\}$ NMR (150.90 MHz; C_6D_6; 294.9 K): δ [ppm] = 161.1, 150.2, 145.8, 144.6, 143.8, 136.2, 136.0, 130.3, 130.2, 130.0, 127.9, 127.7, 127.6, 127.4, 127.1, 126.5, 126.4, 125.9, 122.4. MS (HR-DART(+)): calcd 352.0288 ($C_{19}H_{14}NS_3$, $[M+H]^+$), found 352.0286.



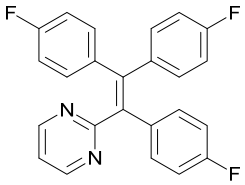
3d (pale yellow solid, 87 mg, 0.23 mmol, 40%). Alkyne: 2-(phenylethynyl)quinoline (0.13 g, 0.57 mmol); *i*PrSS*i*Pr (0.13 g, 0.14 mL, 1.5 equiv); Ti(O*i*Pr)$_4$ (0.16 g, 0.17 mL, 1.0 equiv); ArMgBr: phenylmagnesium bromide (1.0 M THF solution, 1.4 mL, 2.5 equiv). ^1H NMR (600.13 MHz; C_6D_6; 295.0 K): δ [ppm] = 8.15 – 7.92 (m, 1 H), 7.38 – 7.17 (m, 9 H), 7.10 – 6.79 (m, 11 H). $^{13}C\{^1H\}$ NMR (150.90 MHz; C_6D_6; 294.9 K): δ [ppm] = 163.1, 148.9, 144.1, 143.9, 143.6, 143.3, 142.0, 135.0, 131.84, 131.78, 131.70, 130.2, 129.3, 128.20, 128.18, 128.10, 127.5, 127.24, 127.22, 126.9, 126.8, 126.4, 125.0. MS (HR-DART(+)): calcd 384.1752 ($C_{29}H_{22}N$, $[M+H]^+$), found 384.1748.



3e (pale yellow solid, 0.11 g, 0.25 mmol, 63%). Alkyne: 2-((4-fluorophenyl)ethynyl)quinoline (0.10 g, 0.40 mmol); *i*PrSS*i*Pr (90 mg, 0.10 mL, 1.5 equiv); Ti(O*i*Pr)$_4$ (0.11 g, 0.12 mL, 1.0 equiv); ArMgBr: 4-fluorophenylmagnesium bromide (1.0 M THF solution, 1.0 mL, 2.5 equiv). ^1H NMR (399.89 MHz; C_6D_6; 295.4 K): δ [ppm] = 8.12 – 7.97 (m, 1 H), 7.42 – 7.32 (m, 2 H), 7.25 – 7.20 (m, 1 H), 7.12 – 7.07 (m, 1 H), 6.98 – 6.78 (m, 7 H), 6.70 – 6.55 (m, 4 H), 6.52 – 6.40 (m, 2 H). $^{13}C\{^1H\}$ NMR (100.55 MHz; C_6D_6; 296.0 K): δ [ppm] = 162.30 (d, *J*= 247.5 Hz), 162.28, 162.1 (d, *J*= 247.0 Hz), 148.8, 141.9, 141.1, 139.3 (d, *J*= 3.3 Hz), 139.0 (d, *J*= 3.5 Hz), 138.8 (d, *J*= 3.5 Hz), 135.2, 133.4 – 133.1 (m), 130.1, 129.7, 128.4, 127.5, 126.8, 124.5, 115.4 – 115.0 (m). MS (HR-DART(+)): calcd 438.1470 ($C_{29}H_{19}F_3N$, $[M+H]^+$), found 438.1465.

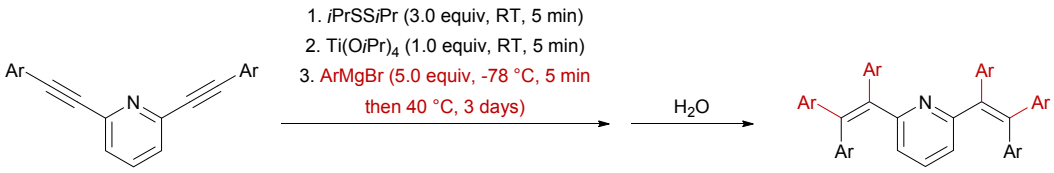
General Procedure 3-II (GP-3-II, 2-(1,2,2-triarylvinyl)pyridines, 2-(1,2,2-triarylvinyl)quinolines, 2-(1,2,2-triarylvinyl)pyrimidines).

Products **3a-f** were yielded by use of General Procedure 3-II (**GP-3-II**), analogous to **GP-3** with the exception that a catalytic amount of Ti(O*i*Pr)$_4$ (10 mol% for **3a**–**d**, 20 mol% for **3e,f**) was used and the mixture was stirred for 7 days (at rt for **3e**, 40°C for **3a**–**d**, 50°C for **3f**). Products **3a**, **3b**, **3c**, **3d**, **3e** and **3f** were obtained with isolated yields of 52%, 45%, 35%, 35%, 60% and 60%, respectively. Recrystallization in ethyl acetate/pentane gave single crystals of **3f** suitable for X-ray diffraction analysis.



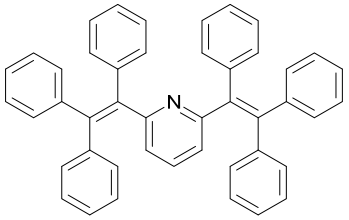
3f (pale yellow solid, 0.11 g, 0.28 mmol, 60%). Alkyne: 2-((4-fluorophenyl)ethynyl)pyrimidine (0.094 g, 0.47 mmol); *i*PrSS*i*Pr (0.11 g, 0.11 mL, 1.5 equiv); Ti(O*i*Pr)$_4$ (0.13 g, 0.14 mL, 1.0 equiv); ArMgBr: 4-fluorophenylmagnesium bromide (1.0 M THF solution, 1.2 mL, 1.2 mmol). ^{1}H NMR (399.89 MHz; C_6D_6; 295.2 K): δ [ppm] = 8.05 (d, *J*= 4.7 Hz, 2 H), 7.03 – 6.85 (m, 6 H), 6.68 – 6.53 (m, 6 H), 6.05 (t, *J*= 4.8 Hz, 1 H). ^{13}C{^{1}H} NMR (100.55 MHz; C_6D_6; 295.2 K): δ [ppm] = 170.5, 162.4 (d, *J*= 247.8 Hz), 162.3 (d, *J*= 246.7 Hz), 162.1 (d, *J*= 247.0 Hz), 156.7, 142.7, 139.7, 139.6 (d, *J*= 3.4 Hz), 138.3 (d, *J*= 3.4 Hz), 137.7 (d, *J*= 3.5 Hz), 133.3 (d, *J*= 8.0 Hz), 132.8 (d, *J*= 8.0 Hz), 132.6 (d, *J*= 8.0 Hz), 118.3, 115.5 – 114.9 (m). MS (HR-DART(+)): calcd 389.1266 ($C_{24}H_{16}F_3N_2$, $[M+H]^+$), found 389.1259.

General Procedure 3-III (GP-3-III, 2,6-bis(1,2,2-triarylvinyl)pyridines)

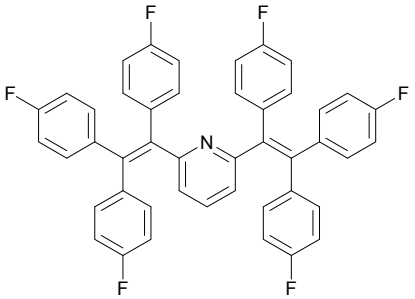


To a solution of a 2,6-bis(arylethynyl)pyridine in dry THF (3.0 mL), isopropyl disulfide (3.0 equiv) and Ti(O*i*Pr)$_4$ (1.0 equiv) were added consecutively while stirring the solution at room temperature. After cooling the mixture to –78 °C, a THF solution of arylmagnesium bromide (5.0 equiv) was added dropwise, the cooling bath was then removed and the

mixture was stirred at 40 °C for 3 days, hence turning black. The reaction vessel was cooled to rt in a water bath, distilled water (1.0 mL) was added dropwise and the mixture was stirred for 1 h. After addition of THF (3.0 mL) and dichloromethane (20 mL) the mixture was stirred vigorously for 2 h. The white precipitate was removed by filtration, the crude product was adsorbed over celite and purified by column chromatography (SiO_2, eluent gradient: petroleum ether:ethylacetate = 100:1 to 25:1, 0.25 vol% NEt_3). After evaporation of the volatiles, products **4g,h** were obtained as white solid. Recrystallization in benzene/pentane gave single crystals of **4g,h** suitable for X-ray diffraction analysis.



3g (white solid, 0.038 g, 0.065 mmol, 50%). Alkyne: 2,6-bis(phenylethynyl)pyridine (35 mg, 0.13 mmol); *i*PrSS*i*Pr (0.059 g, 0.062 mL, 3.0 equiv); Ti(O*i*Pr)$_4$ (0.037 g, 0.038 mL, 1.0 equiv); ArMgBr: phenylmagnesium bromide (1.0 M THF solution, 0.65 mL, 5.0 equiv). ^{1}H NMR (600.13 MHz; C_6D_6; 295.0 K): δ [ppm] = 7.14 – 6.86 (m, 30 H), 6.73 – 6.65 (m, 3 H) . ^{13}C{^{1}H} NMR (150.90 MHz; C_6D_6; 295.0 K): δ [ppm] = 162.4, 144.1, 143.3, 142.5, 142.4, 141.4, 135.3, 131.74, 131.67, 131.4, 128.4, 128.1, 127.1, 126.8, 126.7, 123.9. One signal expected for a ^{13}C nucleus, possibly eclipsed by the solvent signal, was not detectable. MS (HR-DART(+)): calcd 588.2691 ($C_{45}H_{34}N$, $[M+H]^+$), found 588.2683.



3h (white solid, 0.045 g, 0.064 mmol, 46%). Alkyne: 2,6-bis((4-fluorophenyl)ethynyl)pyridine (0.045 g, 0.14 mmol); *i*PrSS*i*Pr (63 mg, 0.067 mL, 3.0 equiv); Ti(O*i*Pr)$_4$ (40 mg, 0.041 mL, 1.0 equiv); ArMgBr: 4-fluorophenylmagnesium bromide (1.0 M THF solution, 0.70 mL, 5.0 equiv). ^{1}H NMR (399.89 MHz; C_6D_6; 295.0 K): δ [ppm] = 6.86 – 6.62 (m, 21 H), 6.61 – 6.51 (m, 6 H). ^{13}C{^{1}H} NMR (100.55 MHz; C_6D_6; 295.7 K): δ [ppm] =

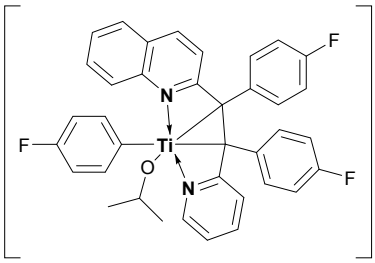
162.2 (d, *J*= 247.7 Hz), 162.13 (d, *J*= 247.2 Hz), 162.05 (d, *J*= 247.2 Hz), 161.9, 140.6, 140.3, 139.4 (d, *J*= 3.4 Hz), 138.4 (d, *J*= 3.4 Hz), 138.0 (d, *J*= 3.5 Hz), 135.7, 133.11 (d, *J*= 7.9 Hz), 133.07 (d, *J*= 7.8 Hz), 132.7 (d, *J*= 7.9 Hz), 123.8, 115.4 – 114.8 (m). MS (HR-DART(+)): calcd 696.2126 ($C_{45}H_{28}F_6N$, $[M+H]^+$), found 696.2116.

Procedure 4 (P-4, titanacyclopropane Ti-*if*, crystallization)

To a solution of 2-(pyridin-2-ylethynyl)quinoline (0.20 g, 0.87 mmol) in dry THF (4.0 mL), Ti(O*i*Pr)$_4$ (0.25 g, 0.26 mL, 1.0 equiv) was added and the mixture was stirred for 5 min at room temperature. After cooling to –78 °C, a solution of 4-fluorophenylmagnesium bromide (1.0 M in THF, 2.6 mL, 3.0 equiv) was added dropwise, then the cooling bath was removed and the mixture was stirred at 40 °C for two days, thus turning black. The volatiles were removed under vacuum and the black solid residue was extracted with a mixture of dry toluene:pentane = 15:1 (15 mL). The solid residue was separated by filtration through a dry celite pad, hence single crystals suitable for X-ray diffraction analysis were obtained upon storing the black filtrate for 2 weeks at –40 °C. All operations were carried out under argon atmosphere.

Procedure 4-II (P-4-II, titanacyclopropane Ti-*if*, NMR characterization)

The titanacyclopropane synthesis was performed according to the previously described **P-4**, except for extracting the solid residue with a mixture of toluene (12 mL) and 1,4-dioxane (0.34 g, 0.33 mL, 4.5 equiv) for 18 h. The solid residue was removed by filtration through a dry celite pad, thus obtaining a black solution. The volatiles were evaporated and the black solid residue was extracted in tol-d_8 for full NMR characterization (^{1}H, ^{13}C{^{1}H}, ^{19}F{^{1}H}). All operations were performed under argon atmosphere.

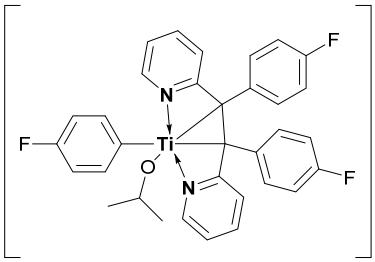


Ti-*if* (black solid, 0.35 g, 0.056 mmol, 65%). ^{1}H NMR (399.89 MHz; Tol-d_8; 295.2 K): δ [ppm] = 7.67 – 7.61 (m, 1 H), 7.55 – 7.51 (m, 1 H), 7.51 – 7.43 (m, 2 H), 7.32 – 7.27 (m, 2 H), 7.26 – 7.20 (m, 2 H), 7.08 – 7.05 (m, 1 H), 6.85 – 6.63 (m, 11 H), 6.52 – 6.48 (m, 1 H),

6.17 – 6.08 (m, 1 H), 4.62 – 4.55 (m, 1 H), 1.13 (d, *J*= 6.1 Hz, 3 H), 1.11 (d, *J*= 6.1 Hz, 3 H). $^{13}C\{^1H\}$ NMR (100.55 MHz; Tol-d_8; 295.9 K): δ [ppm] = 181.9 (d, *J*= 3.8 Hz), 163.0 (d, *J*= 245.3 Hz), 161.9 (d, *J*= 245.6 Hz), 160.8 (d, *J*= 242.9 Hz), 158.6, 149.3, 148.6, 146.4, 140.2, 139.4 (d, *J*= 2.9 Hz), 135.6 (d, *J*= 3.0 Hz), 135.2, 134.7 (d, *J*= 5.7 Hz), 130.7 – 130.3 (m), 126.5 (d, *J*= 7.4 Hz), 122.7, 121.0, 120.2, 118.9, 117.5, 115.6 (d, *J*= 21.3 Hz), 115.1 (d, *J*= 21.3 Hz), 113.1 (d, *J*= 17.8 Hz), 110.3, 89.1, 78.8, 26.7, 26.6. $^{19}F\{^1H\}$ NMR (376.27 MHz; Tol-d_8; 295.3 K): –112.0 (s, 1 F), –115.5 (s, 1 F), –117.9 (s, 1 F). MS (LIFDI(+)): calcd 622.1712 ($C_{37}H_{29}F_3N_2OTi$, $[M]^+$), found 622.1715. Despite numerous attempts a correct elemental analysis could not be obtained which we attribute to the formation of Ti-carbide in the combustion process.

Procedure 4-II' (P-4-II', titanacyclopropane Ti-*i*a, NMR characterization)

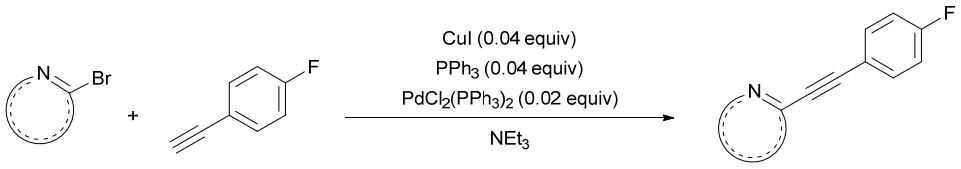
The titanacyclopropane synthesis was performed according to the previously described **P-4**, except for starting from a solution of 1,2-di(pyridin-2-yl)ethyne (0.40 g, 2.2 mmol) in dry THF (8.0 mL). [Ti(O*i*Pr)$_4$] (0.63 g, 0.65 mL, 1.0 equiv); ArMgBr: 4-fluorophenylmagnesium bromide (1.0 M in THF, 6.6 mL, 3.0 equiv).



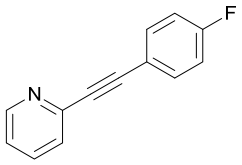
Ti-*i*a (black solid, 0.57 g, 1.0 mmol, 45%). ^1H NMR (399.89 MHz; Tol-d_8; 294.9 K): δ [ppm] = 7.55 – 7.44 (m, 4 H), 7.24 – 7.19 (m, 2 H), 7.07 – 7.05 (m, 2 H), 6.92 – 6.80 (m, 4 H), 6.75 – 6.71 (m, 4 H), 6.64 – 6.61 (m, 1 H), 6.36 – 6.29 (m, 1 H), 6.08 – 6.02 (m, 1 H), 5.51 – 5.36 (m, 1 H), 4.57 – 4.47 (m, 1 H), 1.13 (d, *J*= 6.0 Hz, 3 H), 1.11 (d, *J*= 6.0 Hz, 3 H). $^{13}C\{^1H\}$ NMR (100.55 MHz; Tol-d_8; 295.6 K): δ [ppm] = 184.0 (d, *J*= 3.8 Hz), 163.0 (d, *J*= 245.2 Hz), 161.4 (d, *J*= 243.6 Hz), 161.0 (d, *J*= 242.8 Hz), 158.1, 153.6, 148.3, 144.0, 140.1, 137.8 (br), 137.2, 136.6 (d, *J*= 3.1 Hz), 135.5 (d, *J*= 5.0 Hz), 129.3 (br), 128.5, 127.0 (d, *J*= 7.4 Hz), 118.4, 118.2, 117.3, 115.4 (d, *J*= 21.2 Hz), 114.9 (d, *J*= 21.2 Hz), 113.1 (d, *J*= 17.7 Hz), 108.4, 91.6, 78.0, 26.9 (br). $^{19}F\{^1H\}$ NMR (376.27 MHz; Tol-d_8; 295.1 K): –112.2 (s, 1 F), –117.1 (s, 1 F), –118.0 (s, 1 F). MS (LIFDI(+)): calcd 632.2130 ($C_{36}H_{35}F_3N_2O_2Ti$**, Ti-*i*a** + isopropanol (1 equiv), $[M]^+$), found 632.2134. Despite numerous

attempts a correct elemental analysis could not be obtained which we attribute to the formation of Ti-carbide in the combustion process.

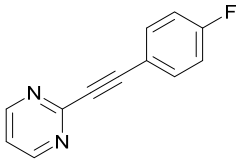
General Procedure 5 (GP-5, 2-((4-fluorophenyl)ethynyl)pyridine and 2-((4-fluorophenyl)ethynyl)pyrimidine)



To a stirring mixture of 2-bromopyridine or 2-bromopyrimidine (2.0 g, 13 mmol), CuI (0.10 g, 0.040 equiv), triphenylphosphine (0.14 g, 0.040 equiv) and $PdCl_2(PPh_3)_2$ (0.18 g, 0.020 equiv) in degassed triethylamine (20 mL), 1-ethynyl-4-fluorobenzene (1.6 g, 1.5 mL, 1.0 equiv) was added dropwise. The mixture was stirred at 70 °C for 2 days, then cooled to RT and filtered. The filtrate was adsorbed over celite and purified by column chromatography (SiO_2, eluent gradient: petroleum ether:ethylacetate = 25:1 to 2:1, 0.5 vol% NEt_3), thus yielding 2-((4-fluorophenyl)ethynyl)pyridine and 2-((4-fluorophenyl)ethynyl)pyrimidine as pale yellow solid with isolated yields of 70% and 82%, respectively.



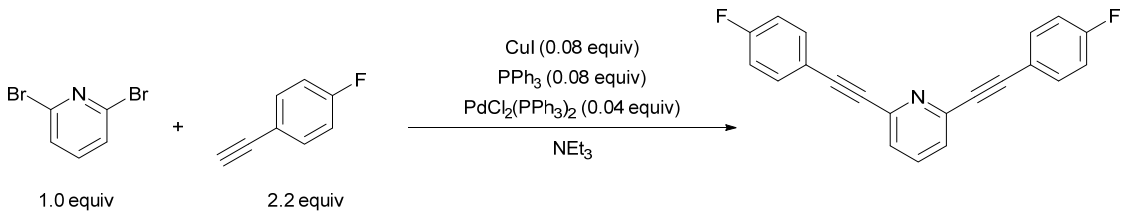
2-((4-fluorophenyl)ethynyl)pyridine (pale yellow solid, 1.8 g, 9.1 mmol, 70%).^{1}H NMR (399.89 MHz; C_6D_6; 297.2 K): δ [ppm] = 8.71 – 8.58 (m, 1 H), 7.74 – 7.68 (m, 1 H), 7.62 – 7.56 (m, 2 H), 7.55 – 7.50 (m, 1 H), 7.30 – 7.23 (m, 1 H), 7.09 – 7.03 (m, 2 H). ^{13}C{^{1}H} NMR (100.55 MHz; C_6D_6; 298.0K): δ [ppm] = 163.2 (d, *J*= 251.0 Hz), 149.2, 142.6, 137.4, 134.4 (d, *J*= 8.6 Hz), 127.5, 123.2, 118.2 (d, *J*= 3.4 Hz), 116.0 (d, *J*= 22.3 Hz), 90.1 (br), 87.5 (br). MS (HR-EI(+)): calcd 197.0641 ($C_{13}H_8FN$, $[M]^+$), found 197.0621.



2-((4-fluorophenyl)ethynyl)pyrimidine (pale yellow solid, 2.1 g, 11 mmol, 82%). ^{1}H NMR (399.89 MHz; C_6D_6; 295.2 K): δ [ppm] = 8.10 (d, *J*= 4.9 Hz, 2 H), 7.16 – 7.11 (m, 2 H), 6.59

– 6.34 (m, 2 H), 6.08 (t, *J*= 4.9 Hz, 1 H). $^{13}C\{^1H\}$ NMR (100.55 MHz; C_6D_6; 296.0 K): δ [ppm] = 163.4 (d, *J*= 250.7 Hz), 157.1, 154.2, 134.9 (d, *J*= 8.6 Hz), 128.4, 119.4, 118.1 (d, *J*= 3.5 Hz), 115.9 (d, *J*= 22.2 Hz), 89.5, 86.5. MS (EI(+)): calcd 198.0593 ($C_{12}H_7FN_2$, $[M]^+$), found 198.0587.

Procedure 5 (GP-5, 2,6-bis((4-fluorophenyl)ethynyl)pyridine)

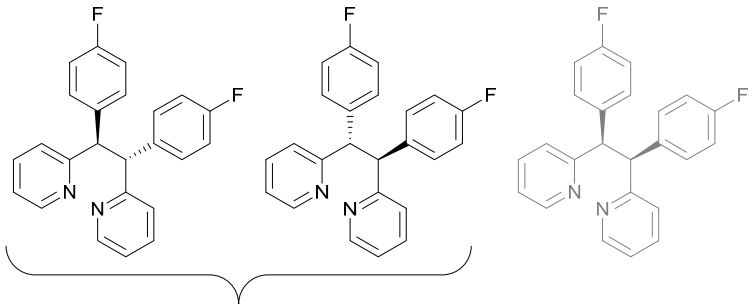


To a stirring mixture of 2,6-dibromopyridine (2.0 g, 8.4 mmol), CuI (0.13 g, 0.080 equiv), triphenylphosphine (0.18 g, 0.080 equiv) and $PdCl_2(PPh_3)_2$ (0.24 g, 0.040 equiv) in degassed triethylamine (20 mL), 1-ethynyl-4-fluorobenzene (2.2 g, 2.1 mL, 2.2 equiv) was added dropwise. The mixture was stirred at 70 °C for 7 days, then cooled to RT and filtered. The filtrate was adsorbed over celite and purified by column chromatography (SiO_2, eluent gradient: petroleum ether:ethylacetate = 50:1 to 4:1, 0.5 vol% NEt_3), thus yielding 2,6-bis((4-fluorophenyl)ethynyl)pyridine as pale yellow solid (2.1 g, 6.7 mmol, 79%). ^1H NMR (600.13 MHz; C_6D_6; 295.0 K): δ [ppm] = 7.29 – 7.20 (m, 4 H), 7.04 (d, *J*= 7.8 Hz, 2 H), 6.80 (t, *J*= 7.8 Hz, 1 H), 6.60 – 6.52 (m, 4 H). $^{13}C\{^1H\}$ NMR (150.90 MHz; C_6D_6; 295.0 K): δ [ppm] = 163.3 (d, *J*= 250.6 Hz), 144.4, 136.2, 134.3 (d, *J*= 8.5 Hz), 126.0, 118.7 (d, *J*= 3.5 Hz), 116.0 (d, *J*= 22.1 Hz), 89.2 (d, *J*= 1.4 Hz), 88.6. MS (HR-EI(+)): calcd 316.0938 ($C_{21}H_{12}F_2N$, $[M+H]^+$), found 316.0931.

Synthesis of 2-(arylethynyl)pyridines

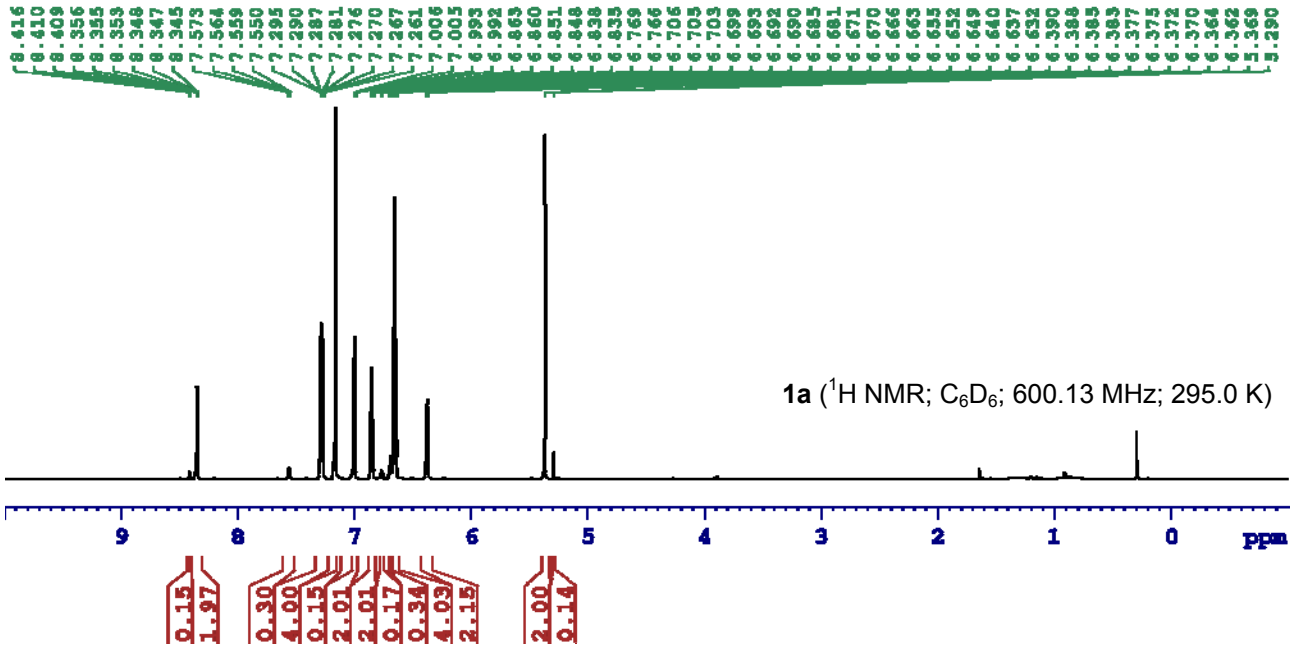
1,2-di(pyridin-2-yl)ethyne,[1] 2-(pyridin-2-ylethynyl)quinoline,[2] 2-(phenylethynyl)pyridine,[3] 2-(thiophen-2-ylethynyl)pyridine,[4] 2-((4-fluorophenyl)ethynyl)quinoline,[5] 2-(phenylethynyl)quinoline[6] and 2,6-bis(phenylethynyl)pyridine[3] are known compound, which were synthesized by Sonogashira coupling according to previously reported procedures.

^{1}H NMR - ^{13}C{^{1}H} - ^{19}F{^{1}H} NMR Spectra

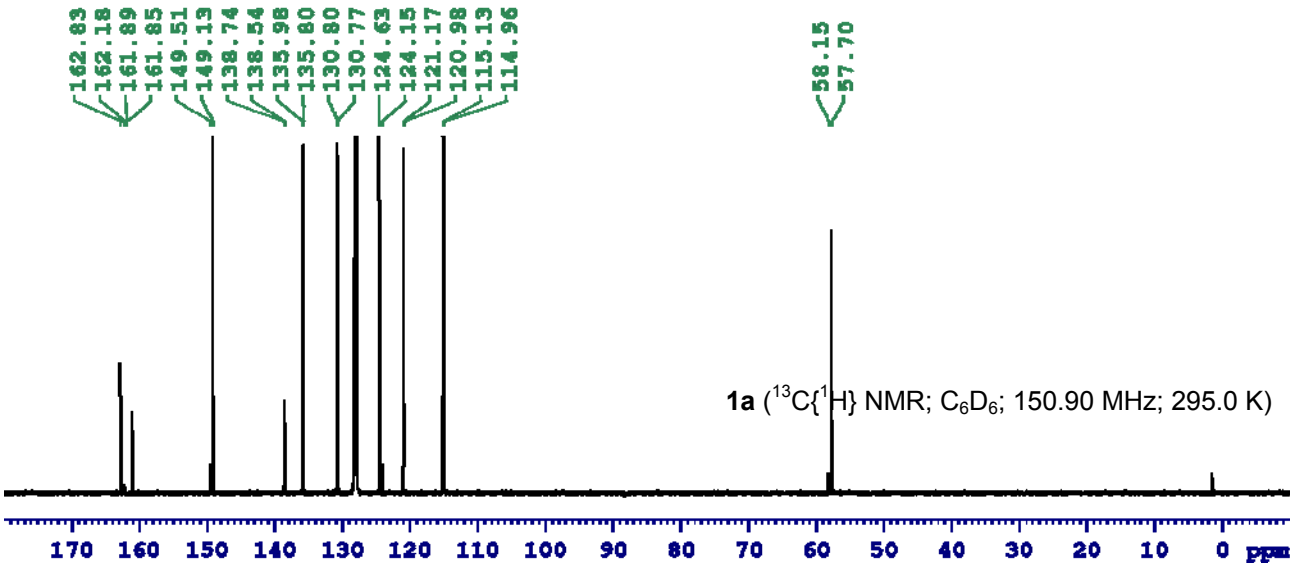


(***anti***, 50:50) (*meso*)

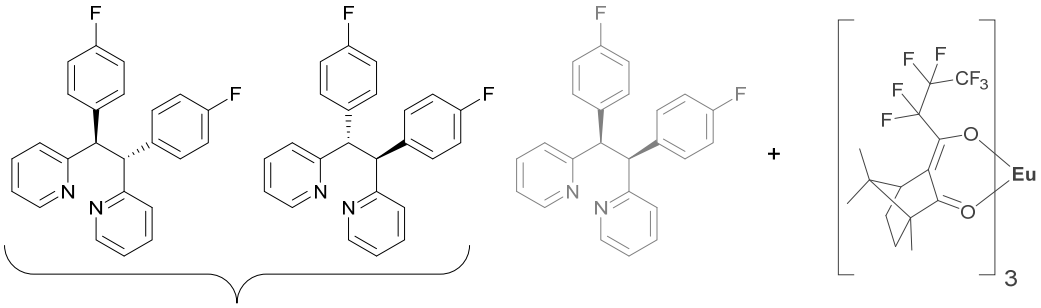
dr (***anti***:*meso*) = 14:1



1a (^{1}H NMR; C_6D_6; 600.13 MHz; 295.0 K)

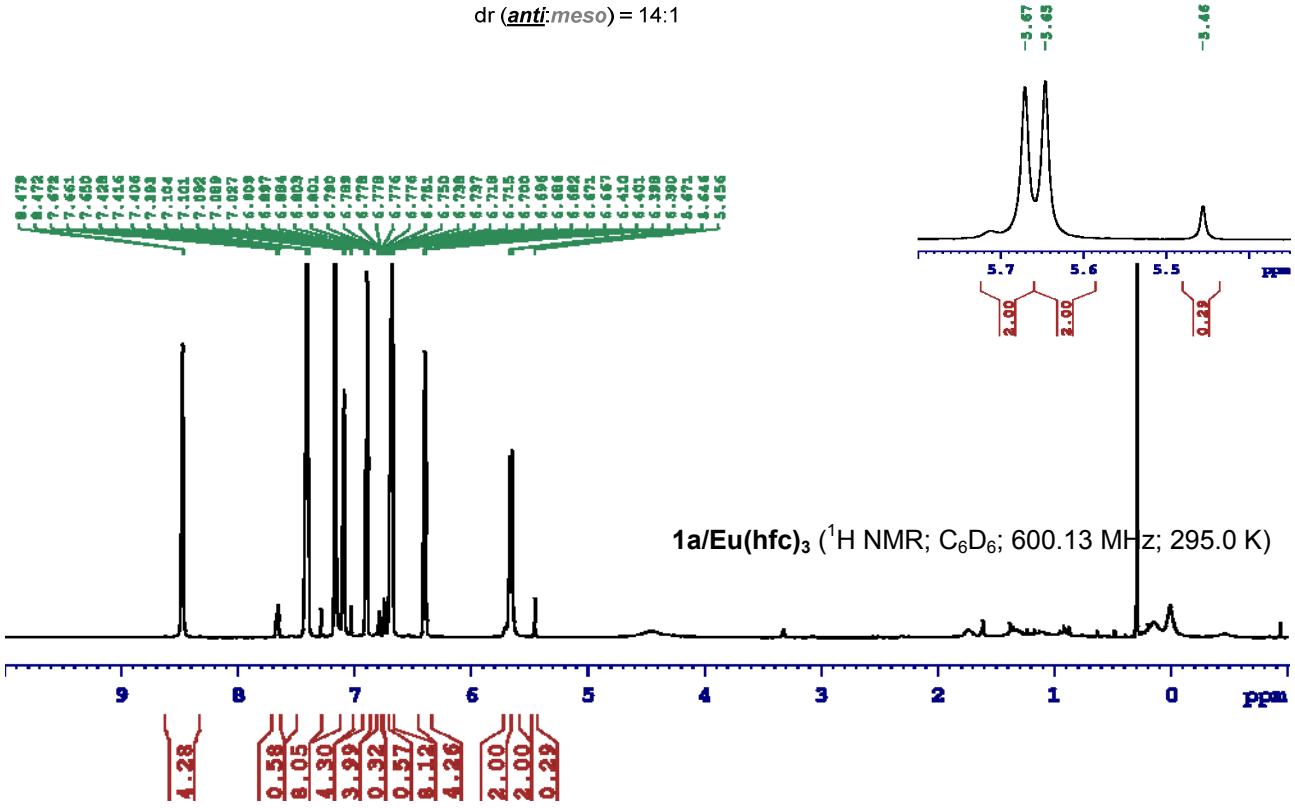


1a (^{13}C{^{1}H} NMR; C_6D_6; 150.90 MHz; 295.0 K)

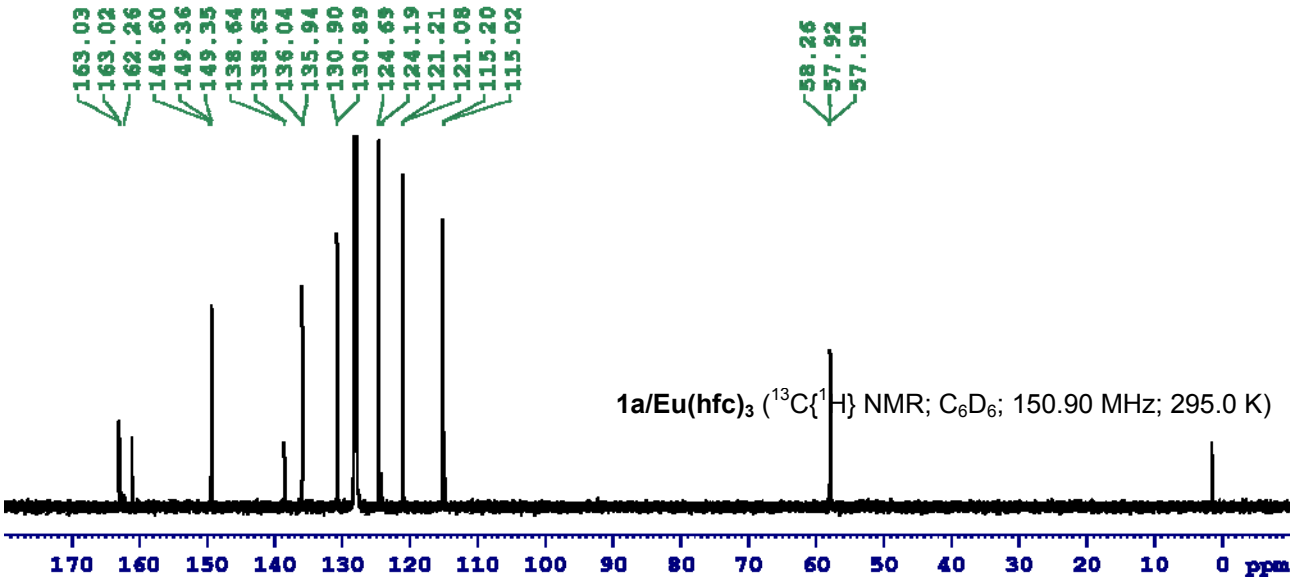


(***anti***, 50:50) (*meso*) ~ 0.05-0.1 equiv

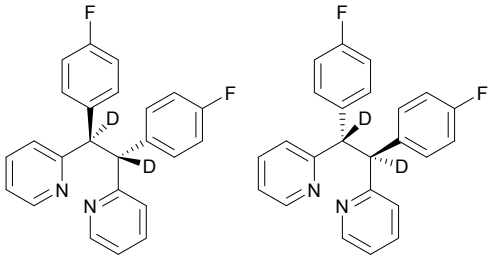
dr (***anti***:*meso*) = 14:1

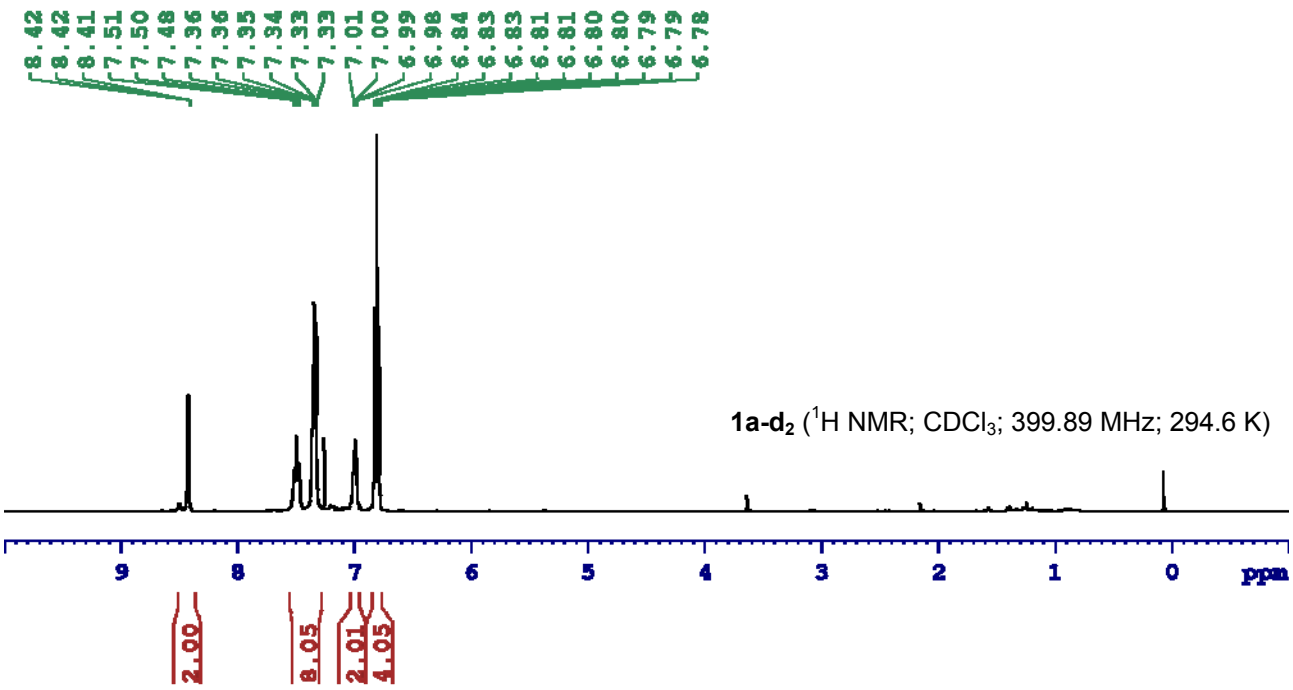


1a/Eu(hfc)$_3$ (^{1}H NMR; C_6D_6; 600.13 MHz; 295.0 K)

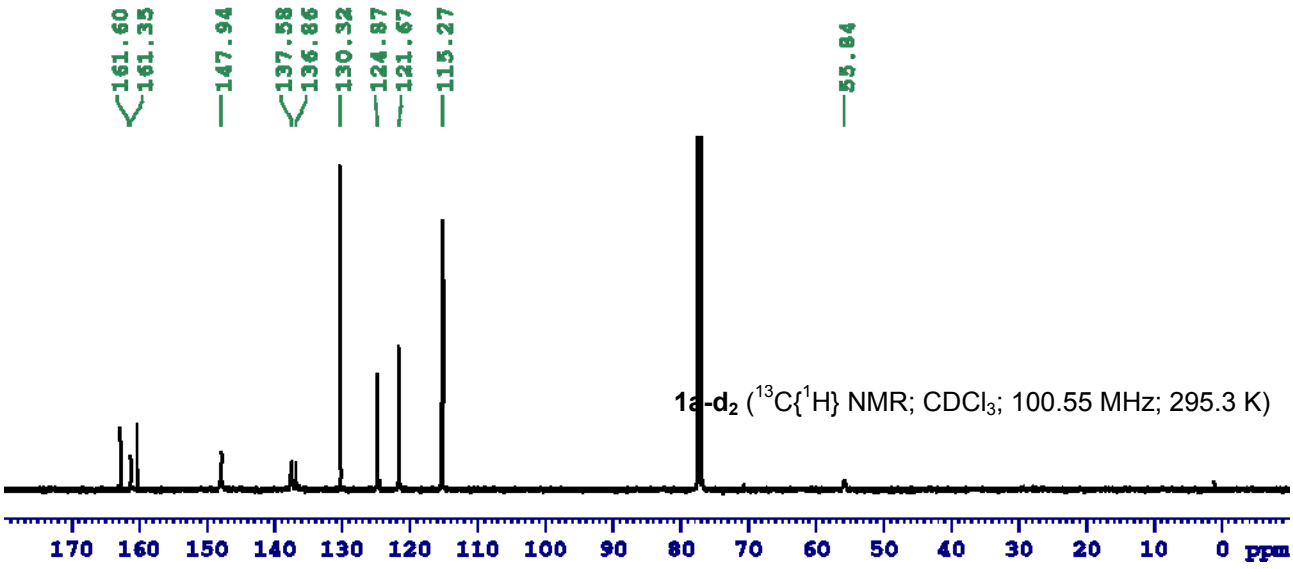


1a/Eu(hfc)$_3$ (^{13}C{^{1}H} NMR; C_6D_6; 150.90 MHz; 295.0 K)

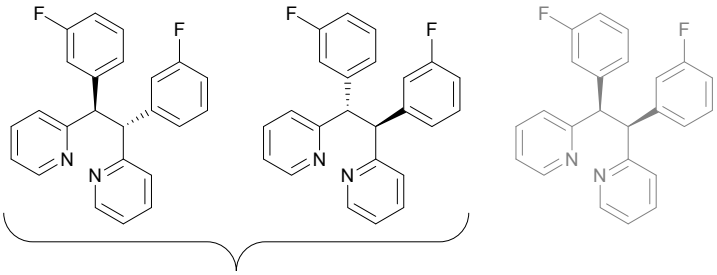




1a-d$_2$ (^{1}H NMR; $CDCl_3$; 399.89 MHz; 294.6 K)

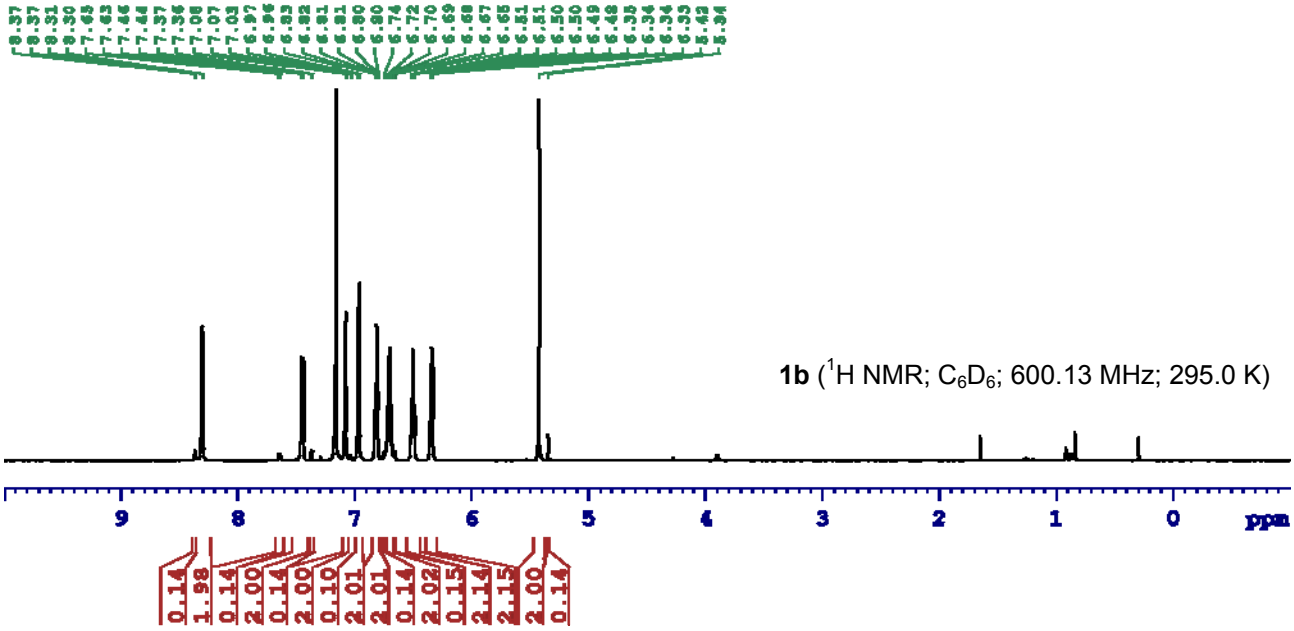


1a-d$_2$ ($^{13}C\{^1H\}$ NMR; $CDCl_3$; 100.55 MHz; 295.3 K)

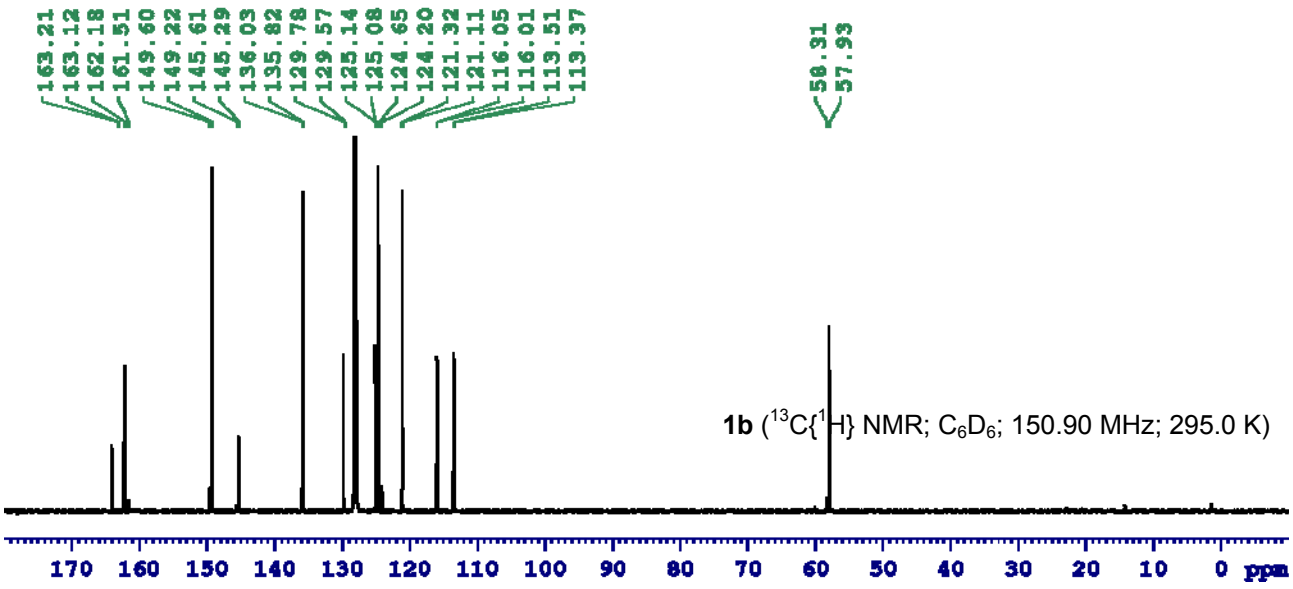


(***anti***, 50:50) (*meso*)

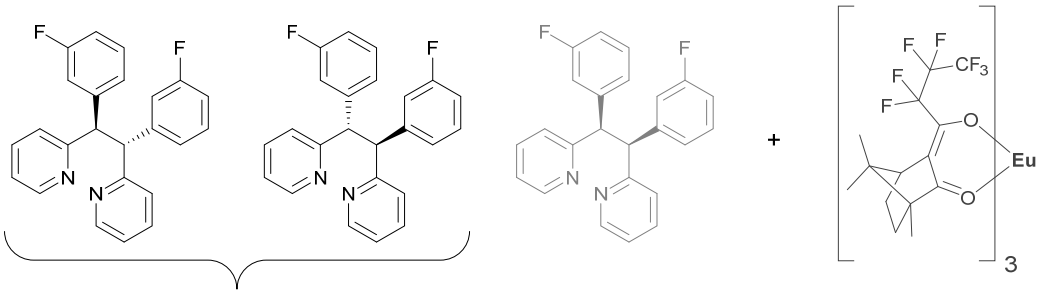
dr (***anti***:***meso***) = 15:1



1b (^{1}H NMR; C_6D_6; 600.13 MHz; 295.0 K)

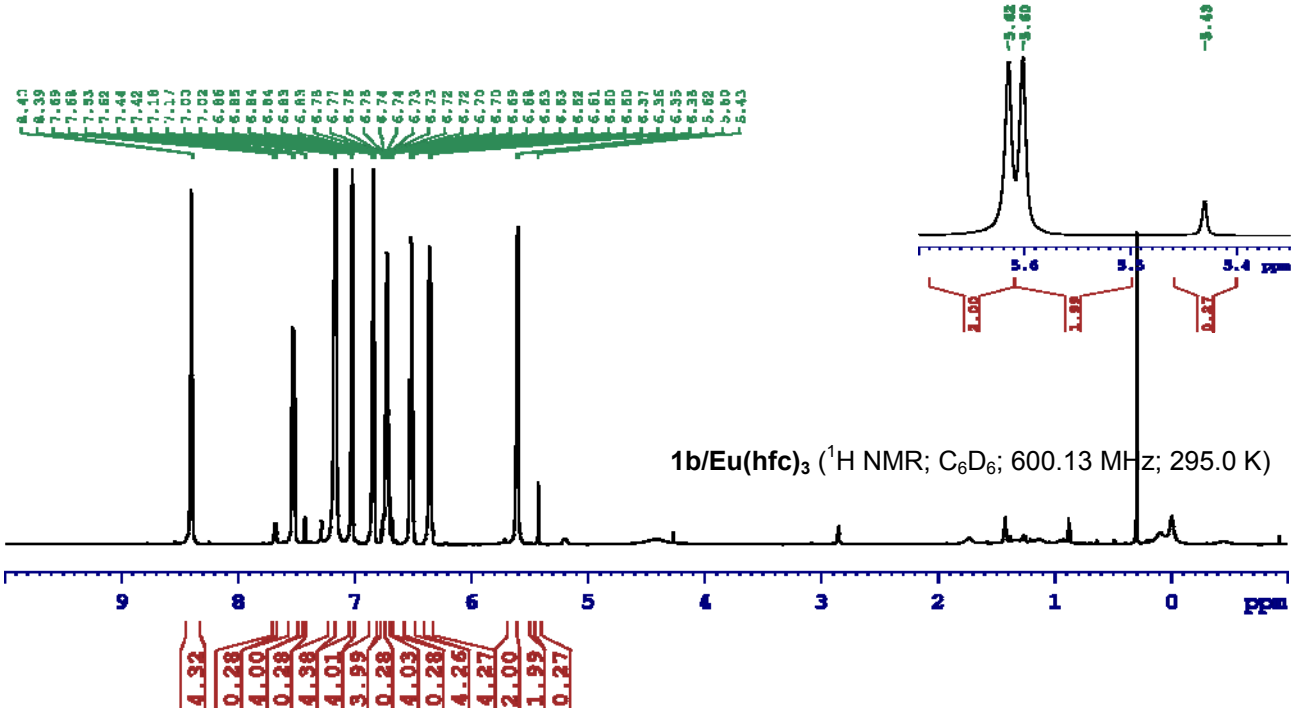


1b (^{13}C{^{1}H} NMR; C_6D_6; 150.90 MHz; 295.0 K)

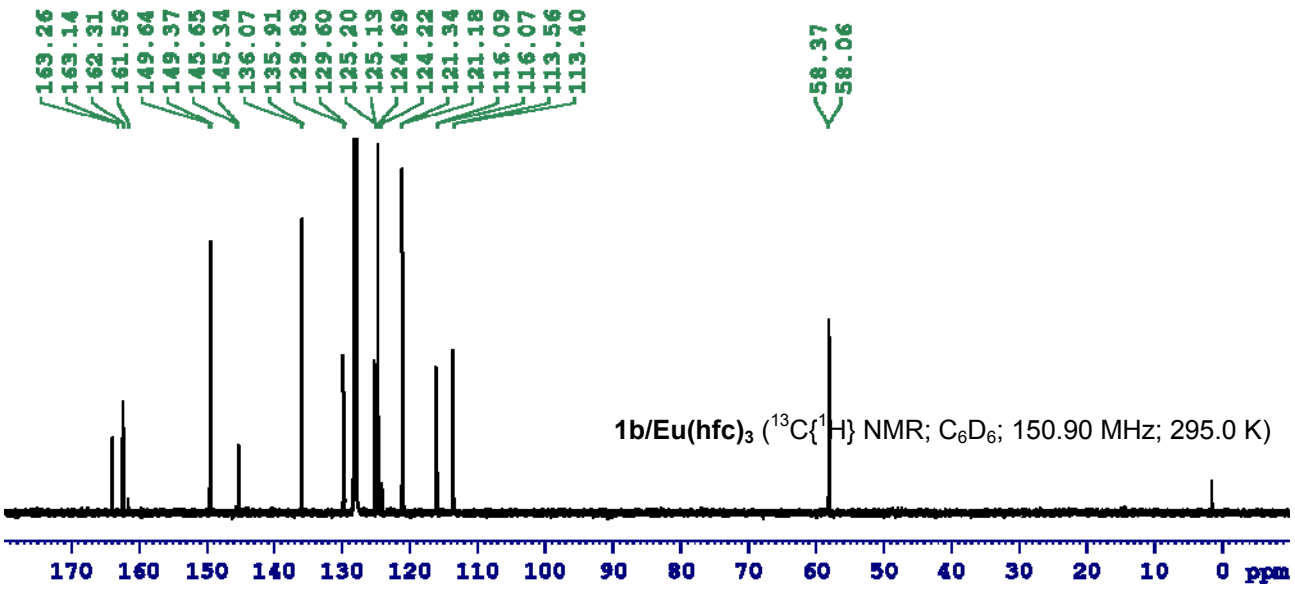


(***anti***, 50:50) (*meso*) ~ 0.05-0.1 equiv

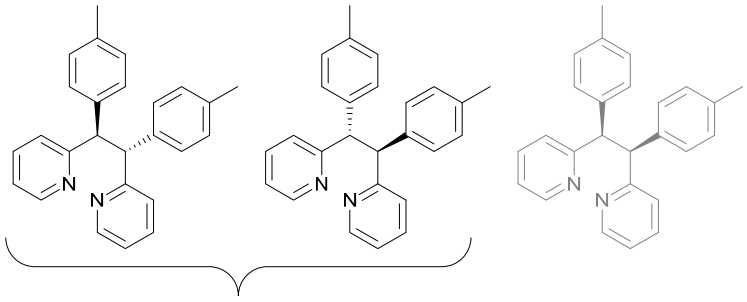
dr (***anti***:*meso*) = 15:1



1b/Eu(hfc)$_3$ (^{1}H NMR; C_6D_6; 600.13 MHz; 295.0 K)

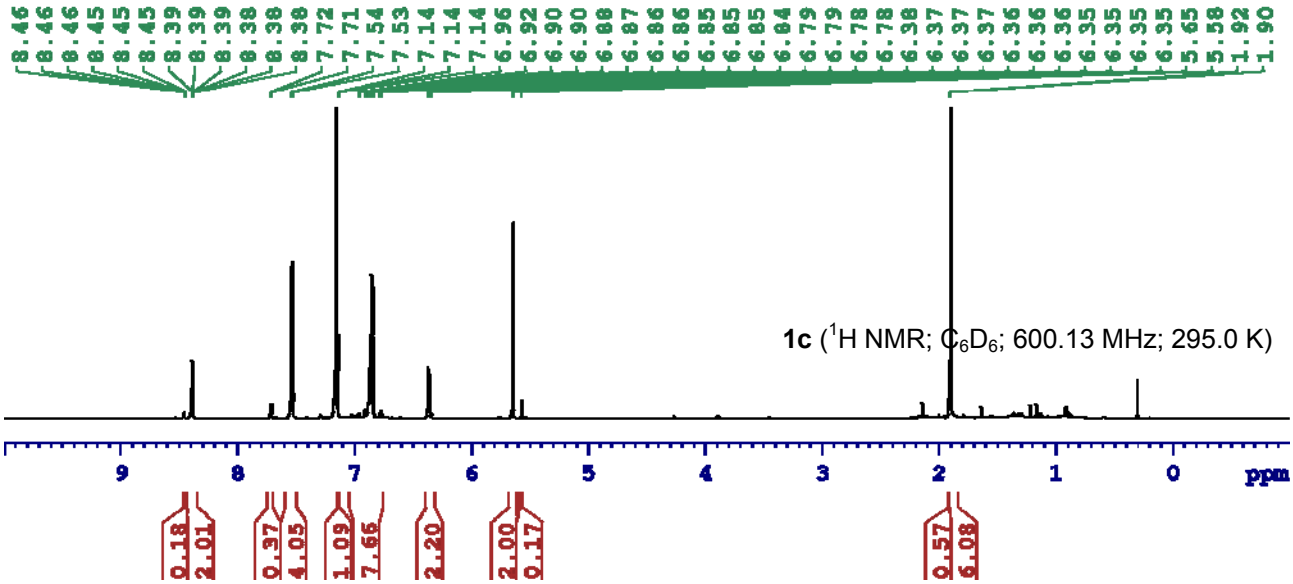


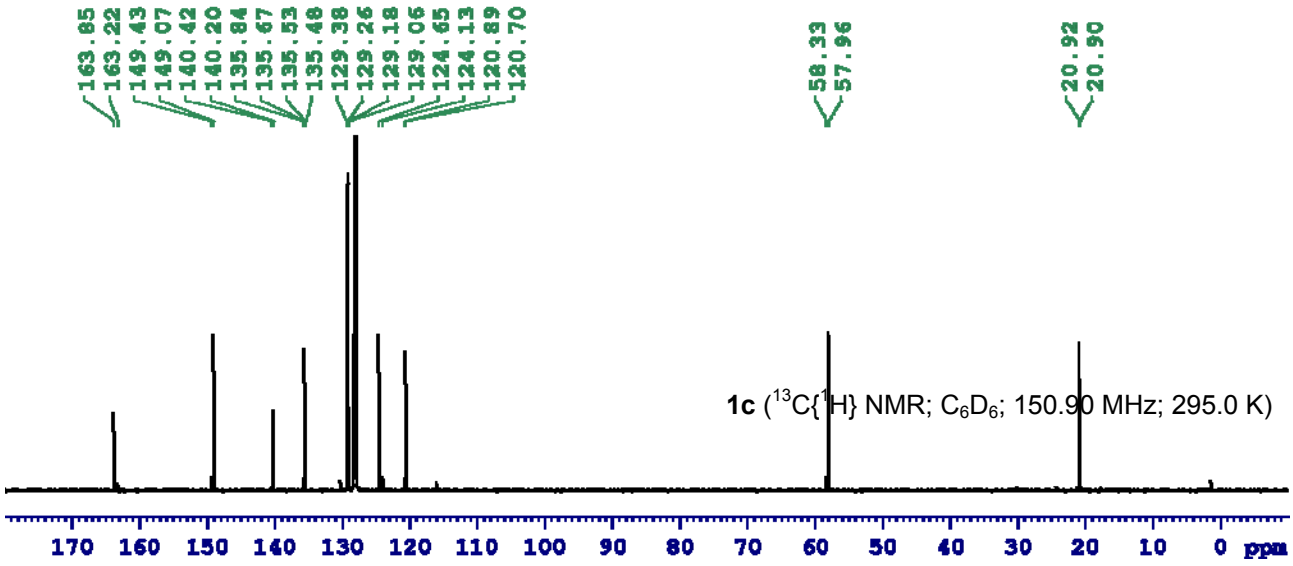
1b/Eu(hfc)$_3$ ($^{13}C\{^1H\}$ NMR; C_6D_6; 150.90 MHz; 295.0 K)

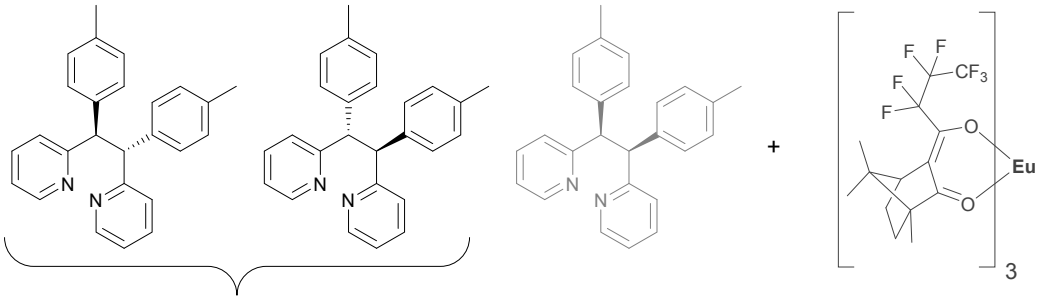


(***anti***, 50:50) (*meso*)

dr (***anti***:*meso*) = 11:1

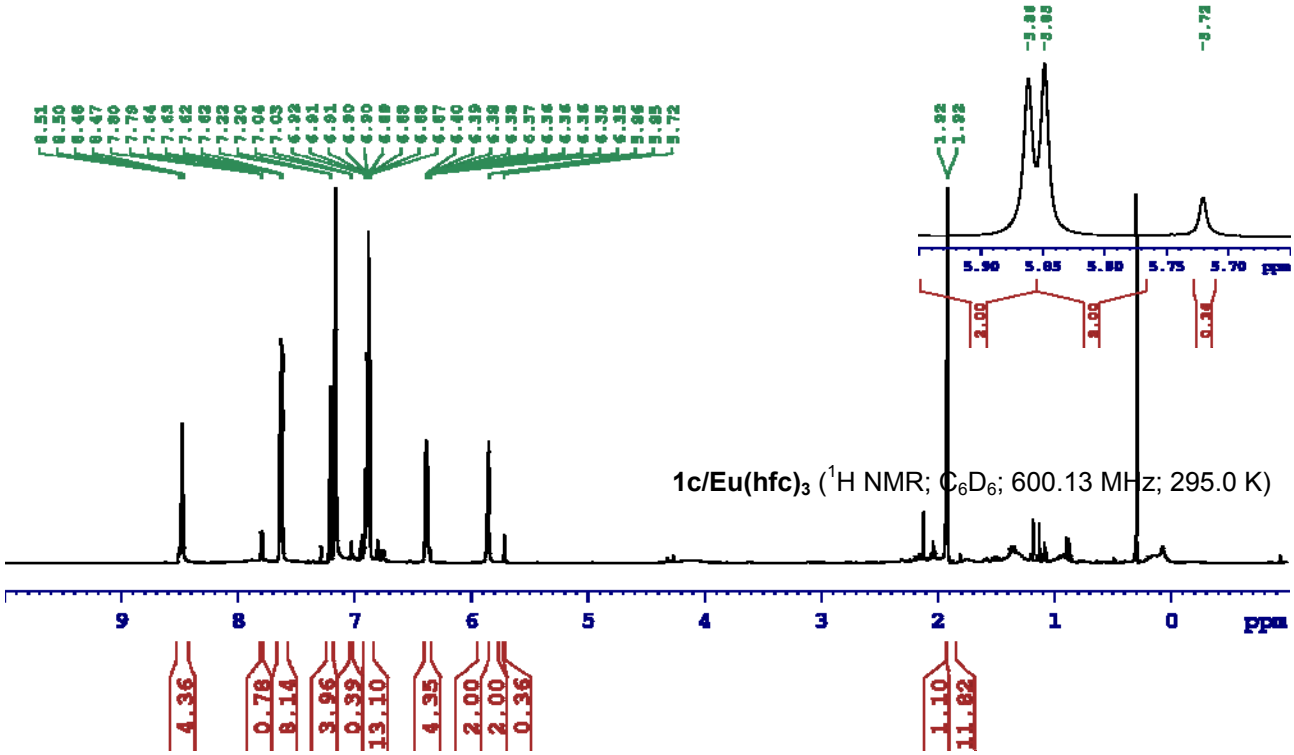




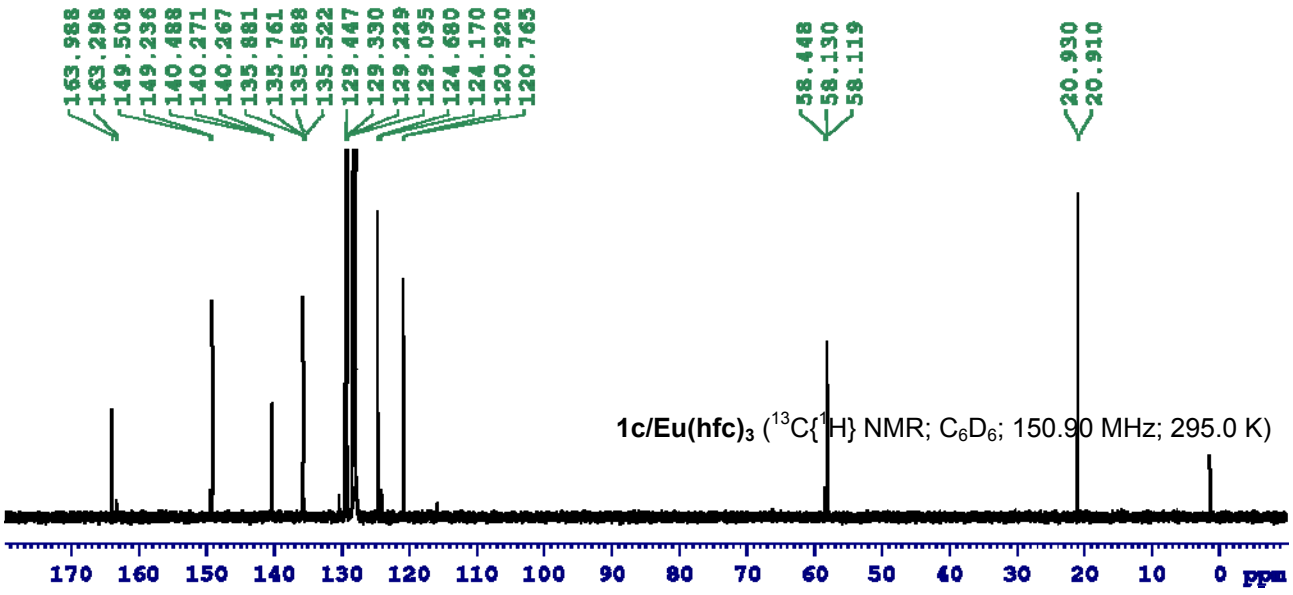


(***anti***, 50:50) (*meso*) ~ 0.05-0.1 equiv

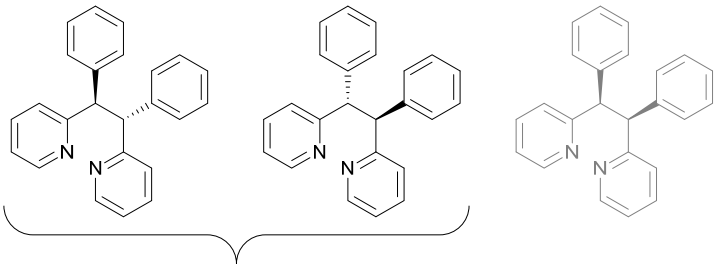
dr (***anti***:*meso*) = 11:1



1c/Eu(hfc)$_3$ (^{1}H NMR; C_6D_6; 600.13 MHz; 295.0 K)

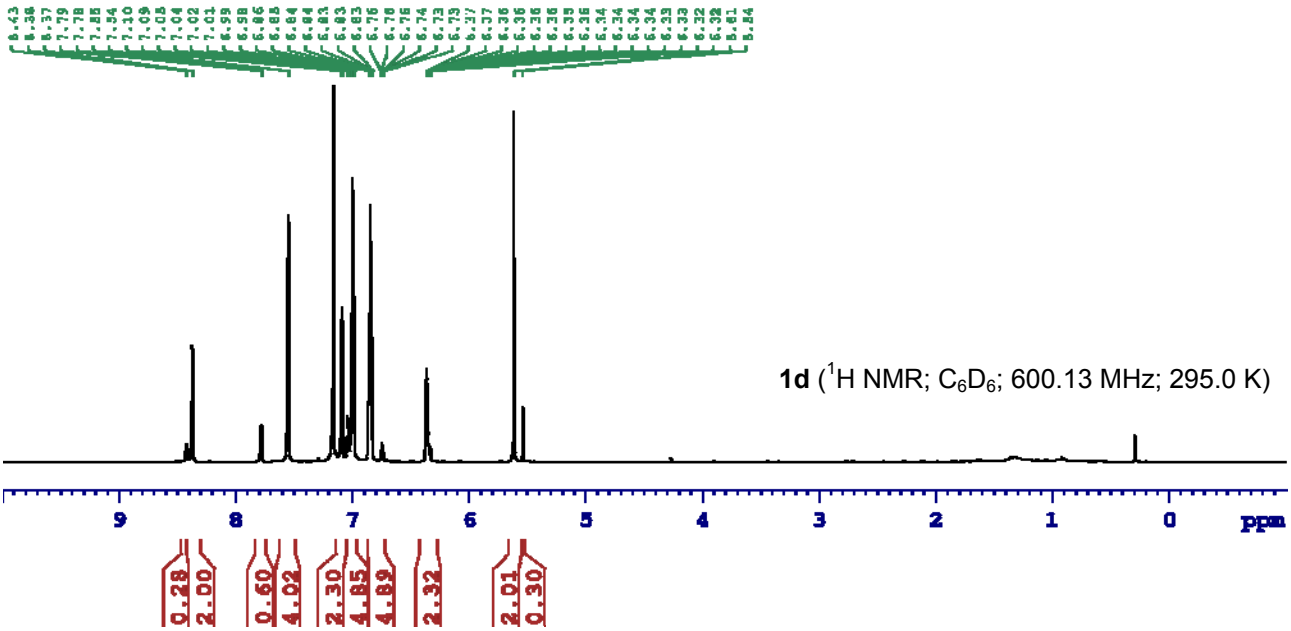


1c/Eu(hfc)$_3$ (^{13}C{^{1}H} NMR; C_6D_6; 150.90 MHz; 295.0 K)

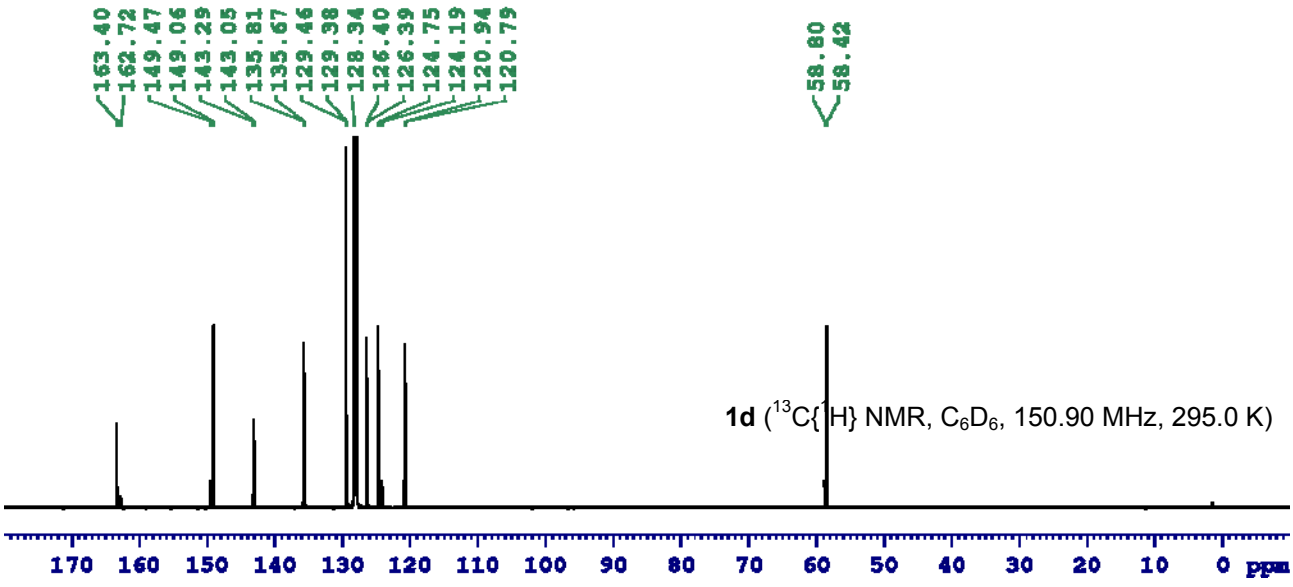


(***anti***, 50:50) (*meso*)

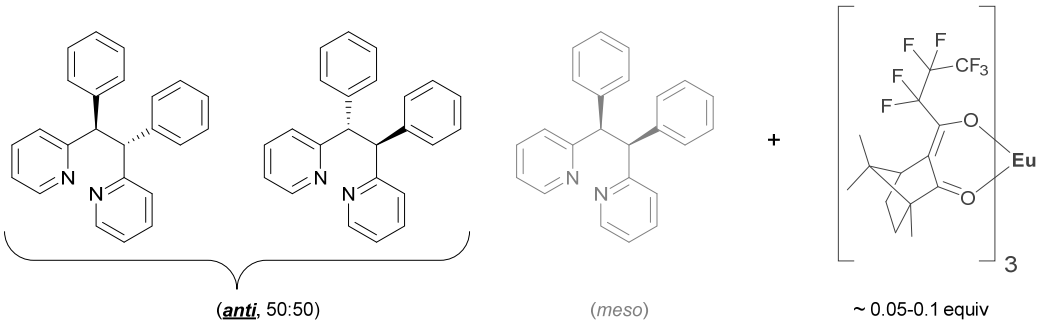
dr (***anti***:*meso*) = 7:1



1d (^{1}H NMR; C_6D_6; 600.13 MHz; 295.0 K)

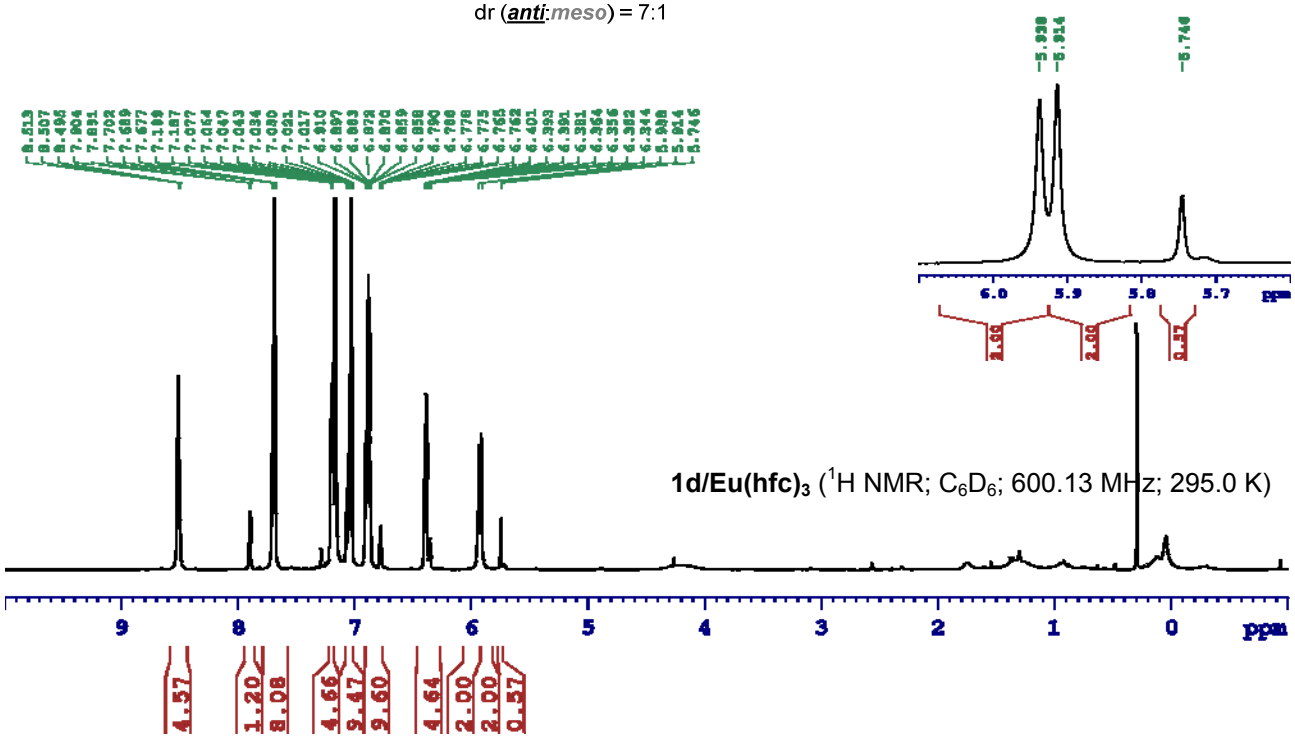


1d (^{13}C{^{1}H} NMR, C_6D_6, 150.90 MHz, 295.0 K)

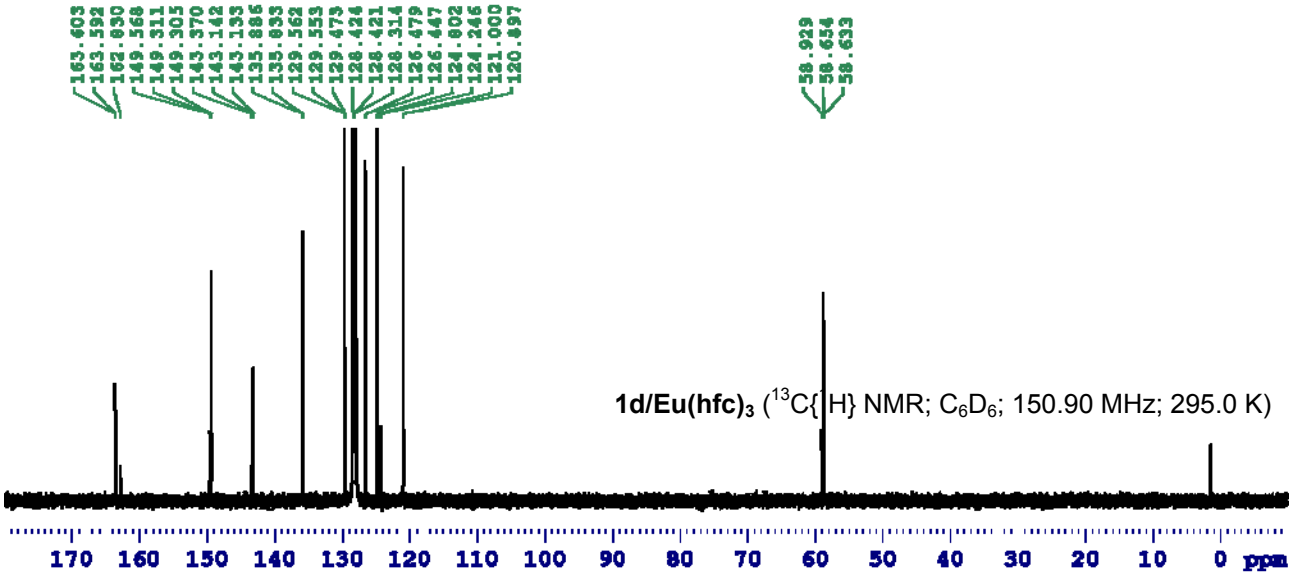


(***anti***, 50:50) (*meso*) ~ 0.05-0.1 equiv

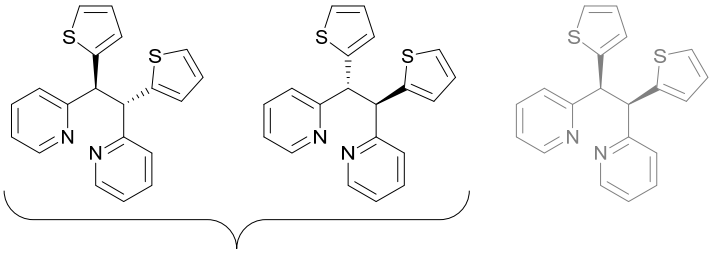
dr (***anti***:*meso*) = 7:1



1d/Eu(hfc)$_3$ (^{1}H NMR; C_6D_6; 600.13 MHz; 295.0 K)

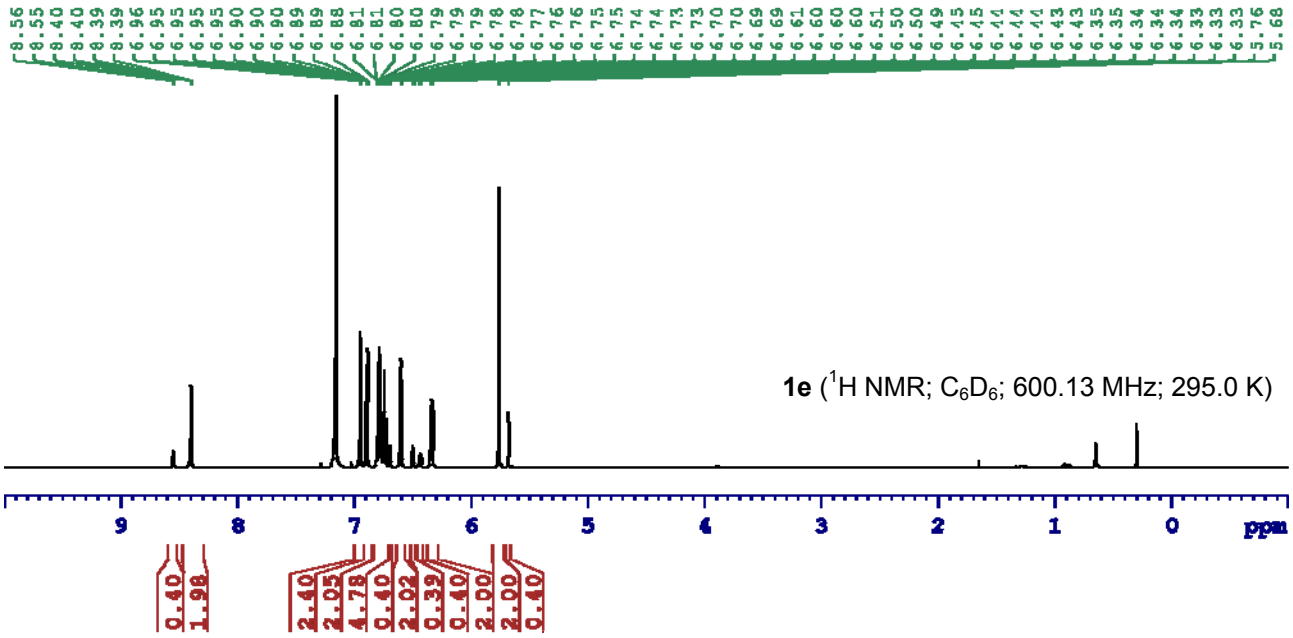


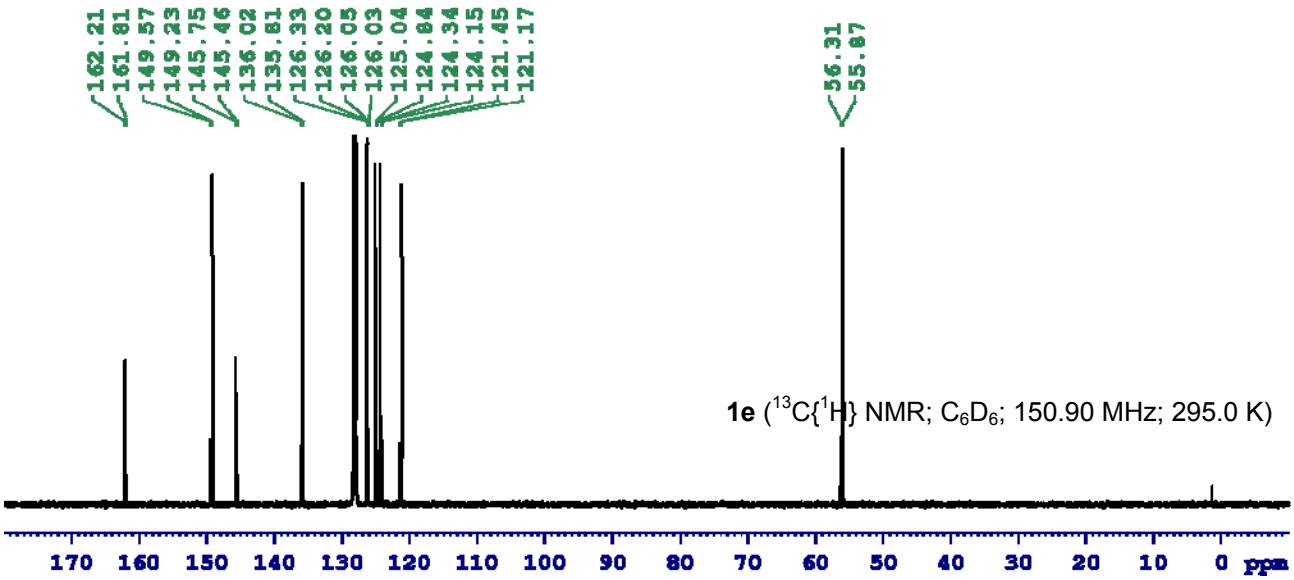
1d/Eu(hfc)$_3$ (^{13}C{^{1}H} NMR; C_6D_6; 150.90 MHz; 295.0 K)

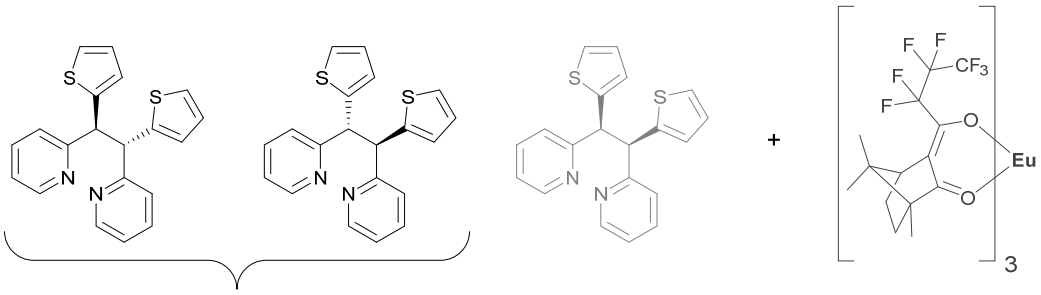


(***anti***, 50:50) (*meso*)

dr (***anti***:*meso*) = 5:1

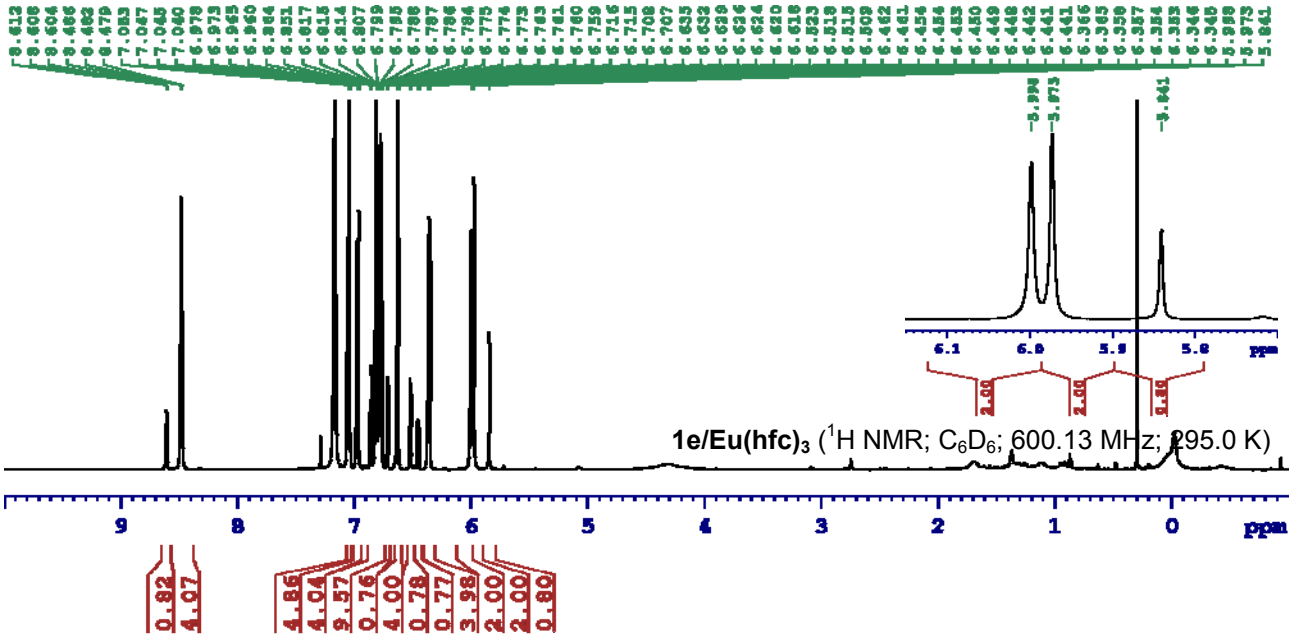


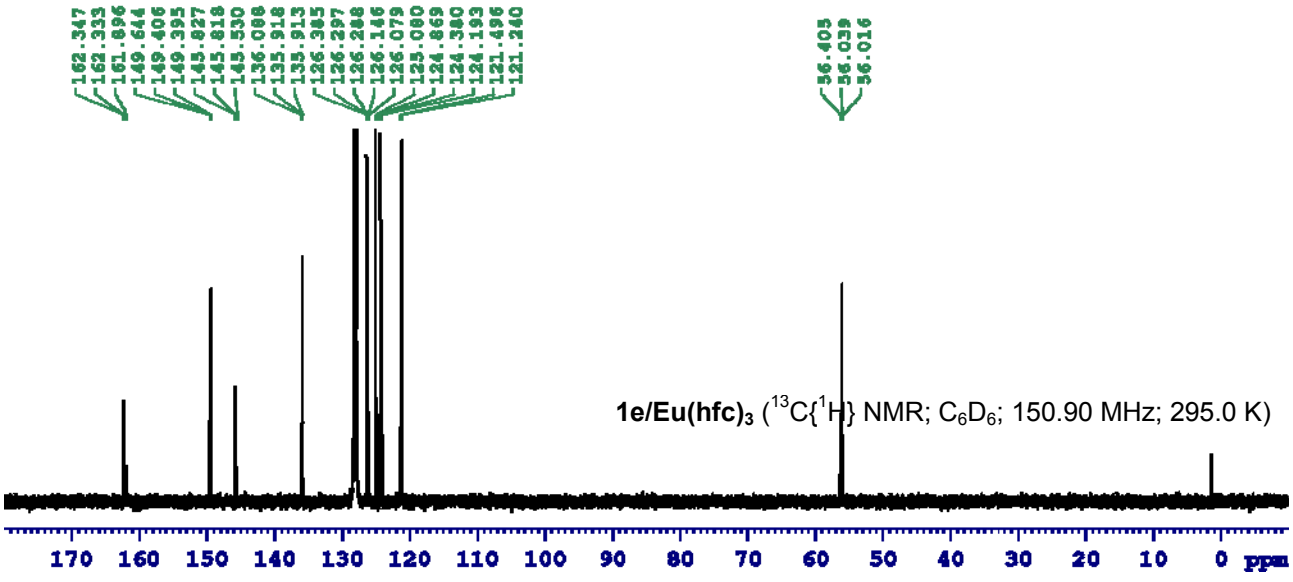


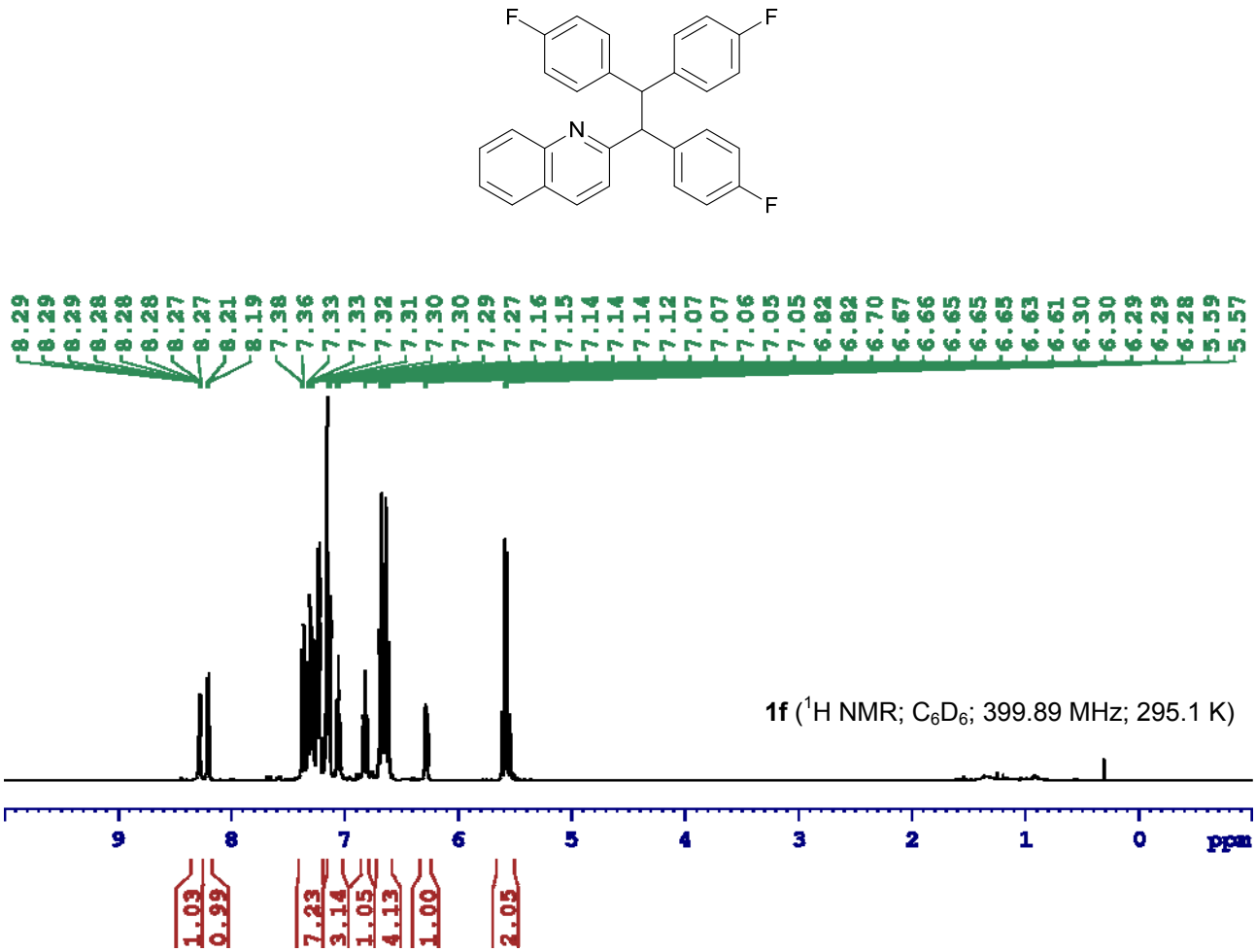


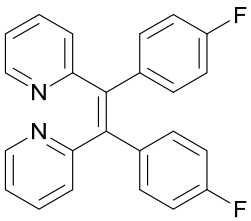
(***anti***, 50:50) (*meso*) + ~ 0.05-0.1 equiv

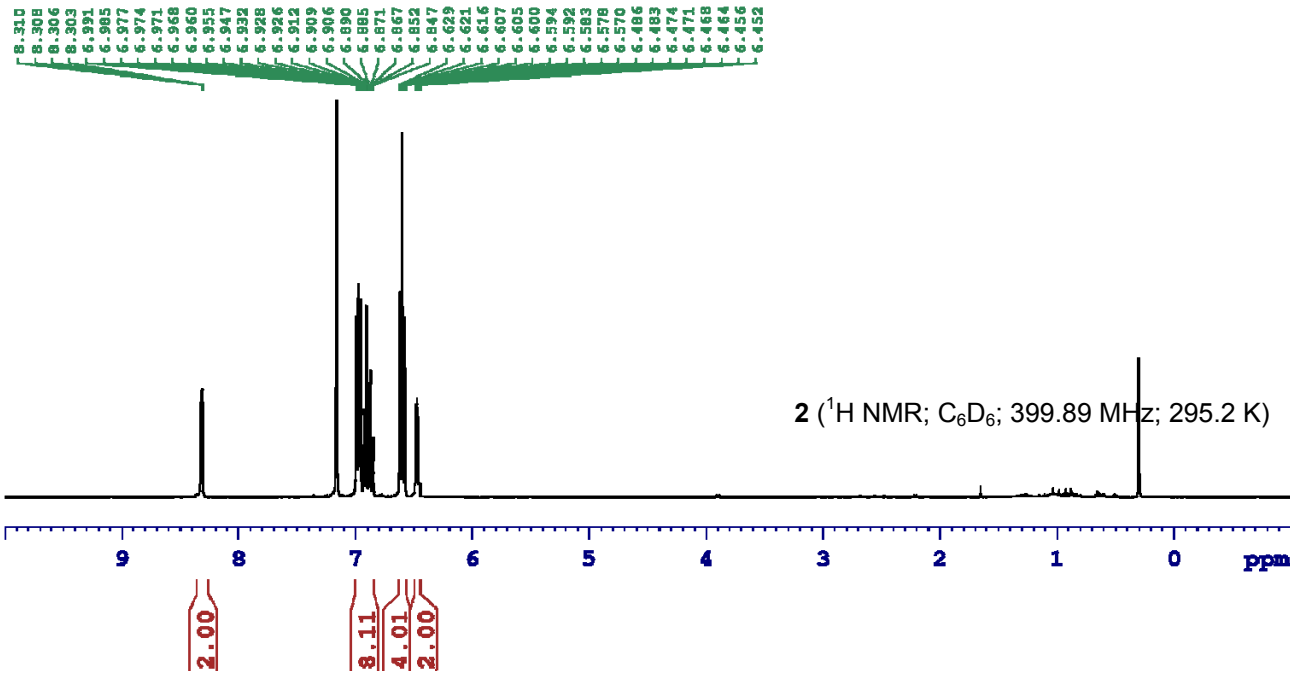
dr (***anti***:*meso*) = 5:1



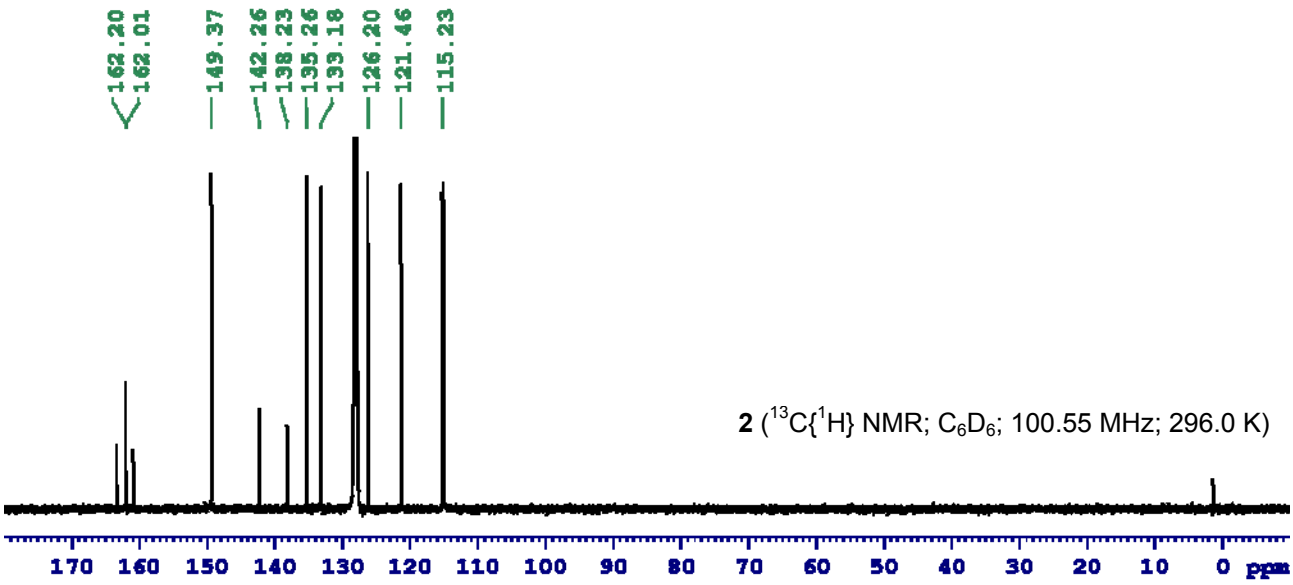



F
F
N
F
8.29 8.29 8.29 8.28 8.28 8.28 8.27 8.27 8.21 8.19 7.38 7.36 7.33 7.33 7.32 7.31 7.30 7.30 7.29 7.27 7.16 7.15 7.14 7.14 7.14 7.12 7.07 7.07 7.06 7.05 7.05 6.82 6.82 6.70 6.67 6.66 6.65 6.65 6.63 6.61 6.30 6.30 6.29 6.29 6.28 5.59 5.57
1f (1H NMR; C6D6; 399.89 MHz; 295.1 K)
9 8 7 6 5 4 3 2 1 0 ppm
1.03 0.99 7.23 3.14 1.05 4.13 1.00 2.05
163.07 163.05 161.95 161.92 148.94 148.22 138.67 138.18 135.88 135.74 131.03 130.87 129.43 129.26 127.02 125.92 124.79 123.40 120.95 115.22 115.15
58.16 57.49
1f (13C{1H} NMR; C6D6; 100.55 MHz; 296.0 K)
170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 ppm

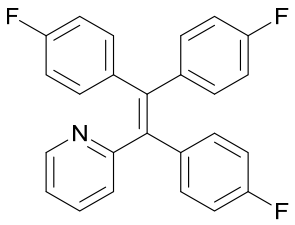


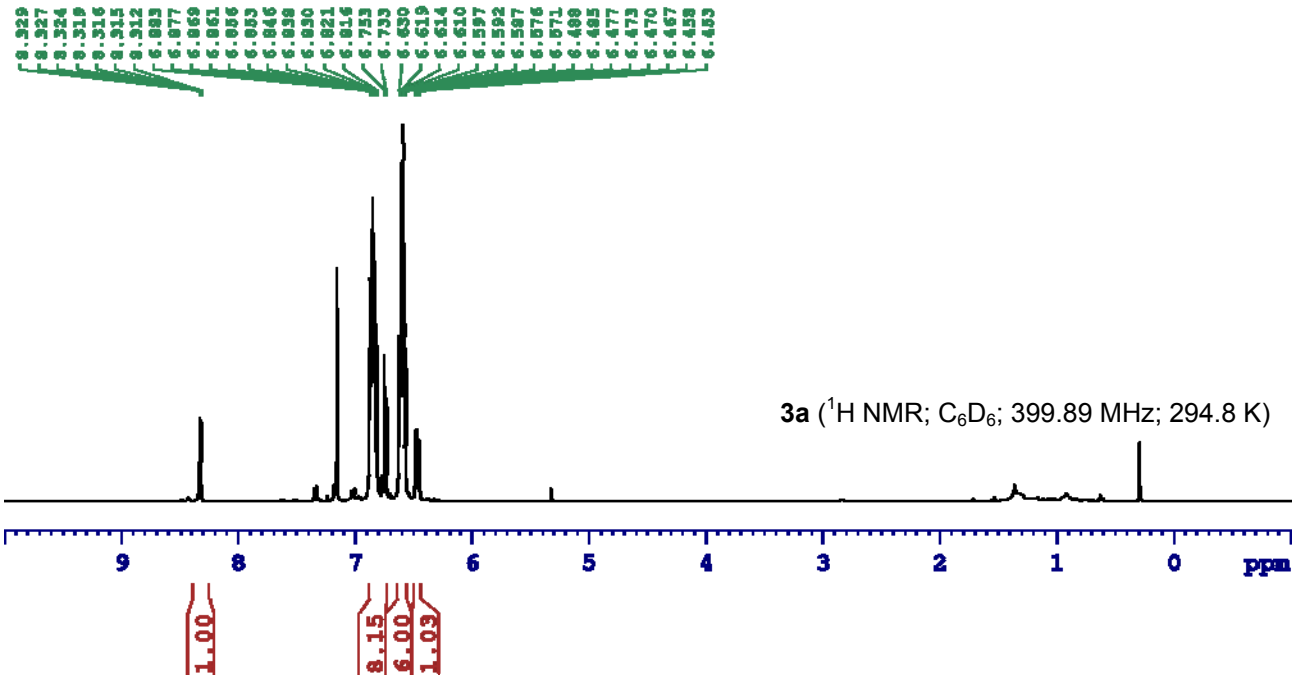


2 (^{1}H NMR; C_6D_6; 399.89 MHz; 295.2 K)

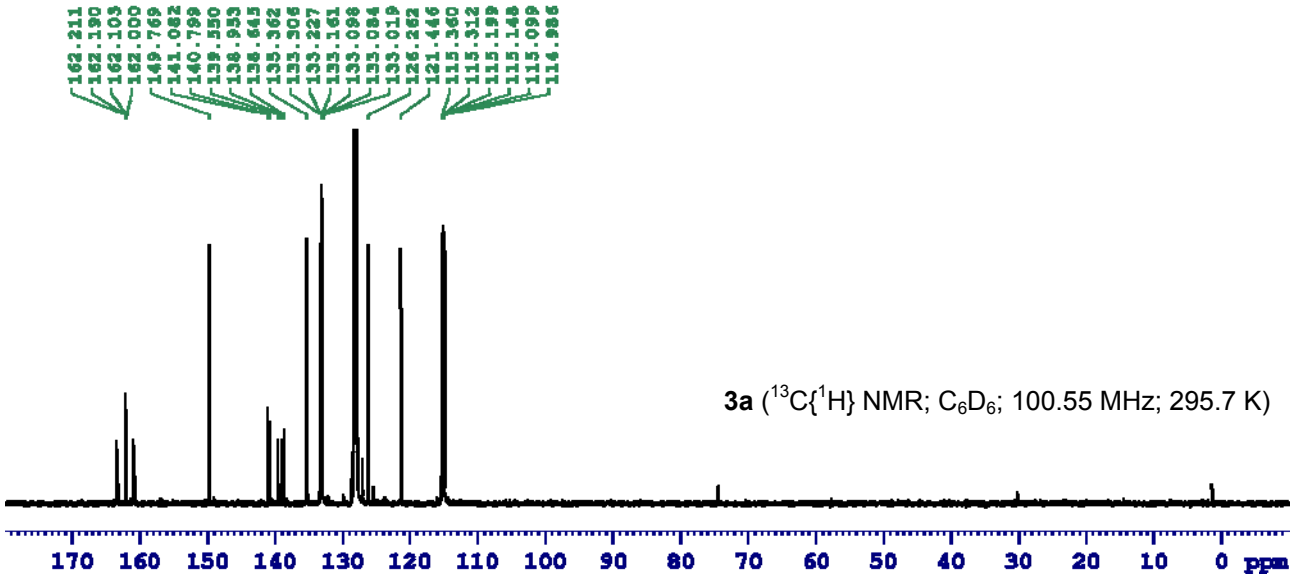


2 (^{13}C{^{1}H} NMR; C_6D_6; 100.55 MHz; 296.0 K)

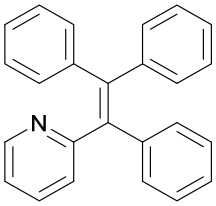


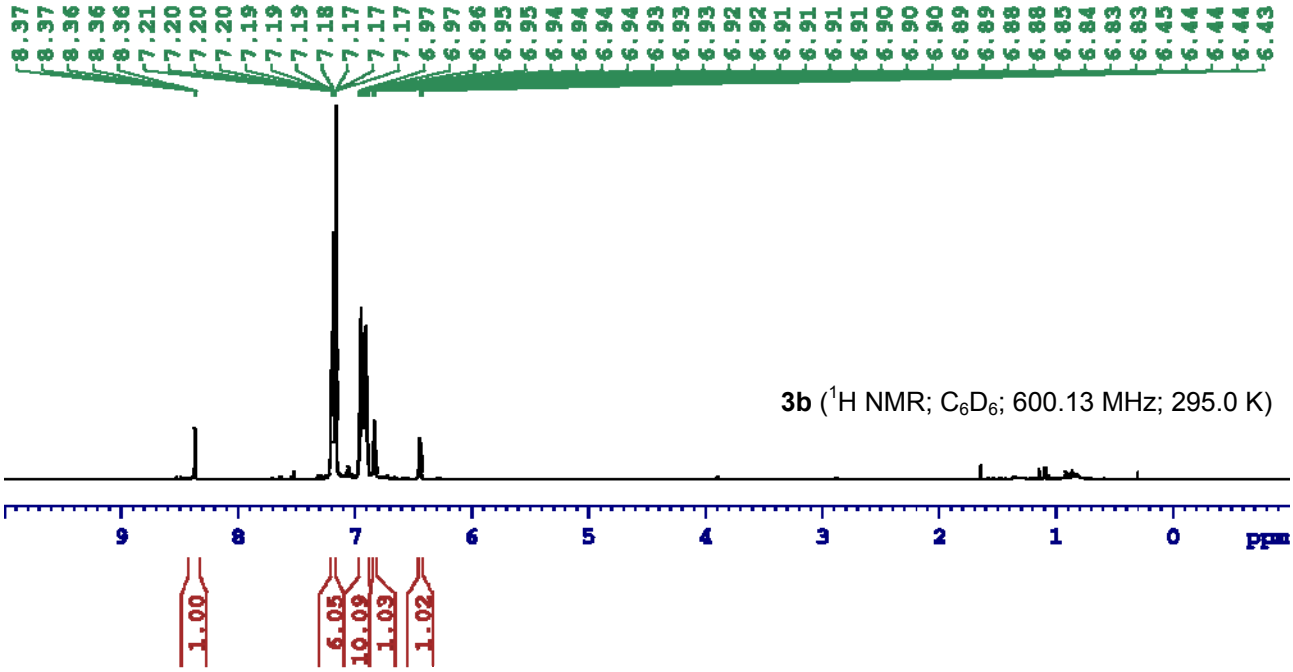


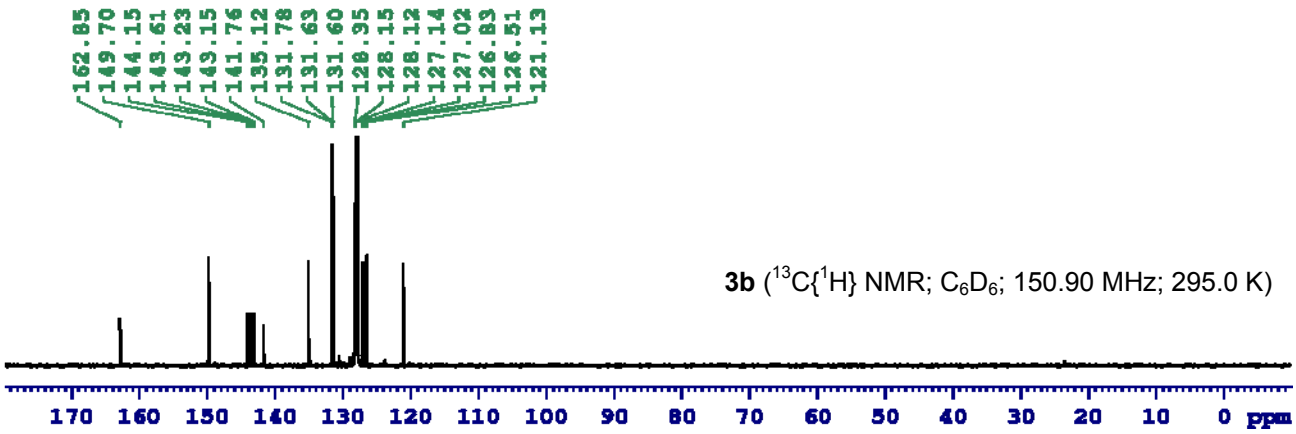
3a (^{1}H NMR; C_6D_6; 399.89 MHz; 294.8 K)

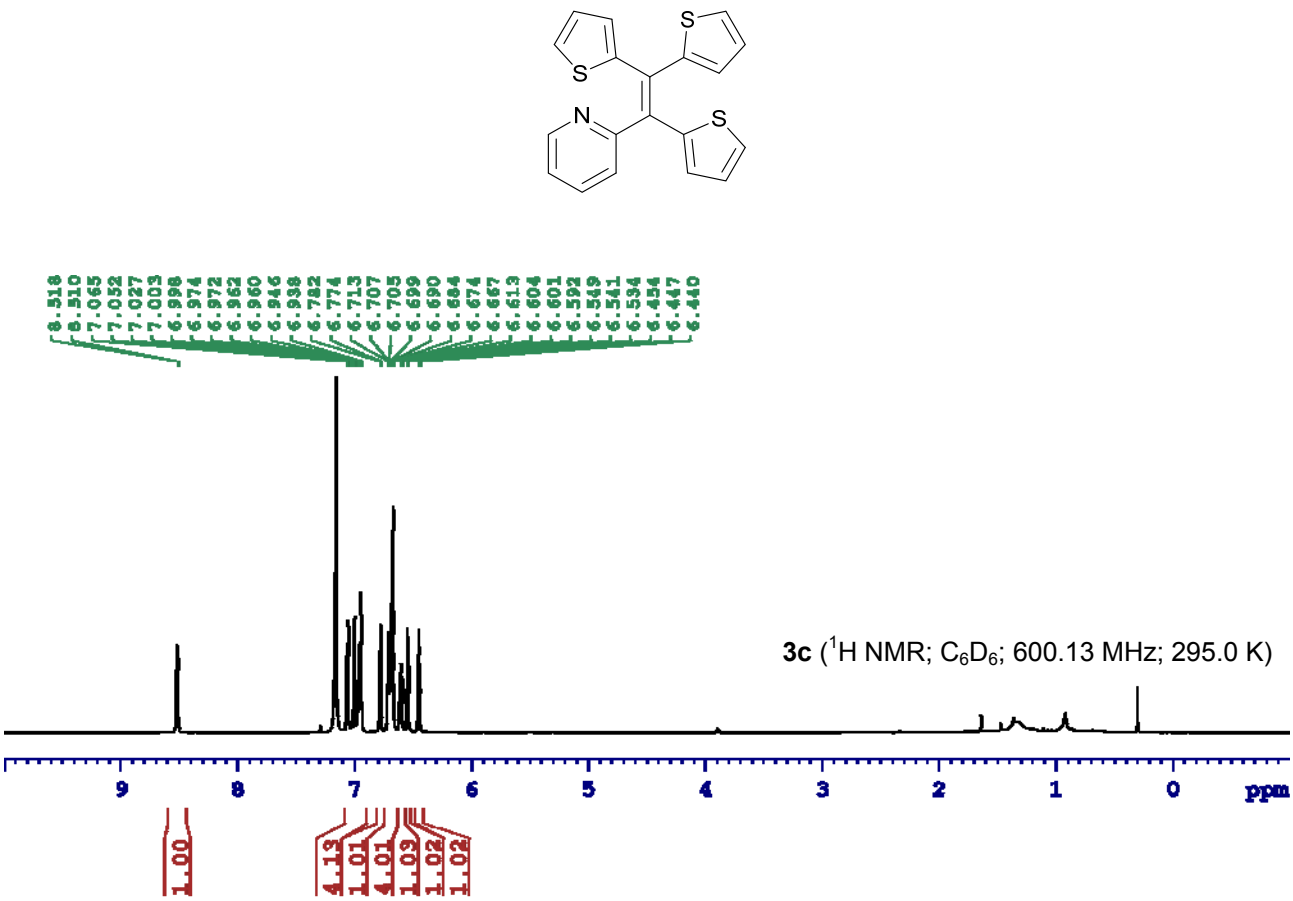


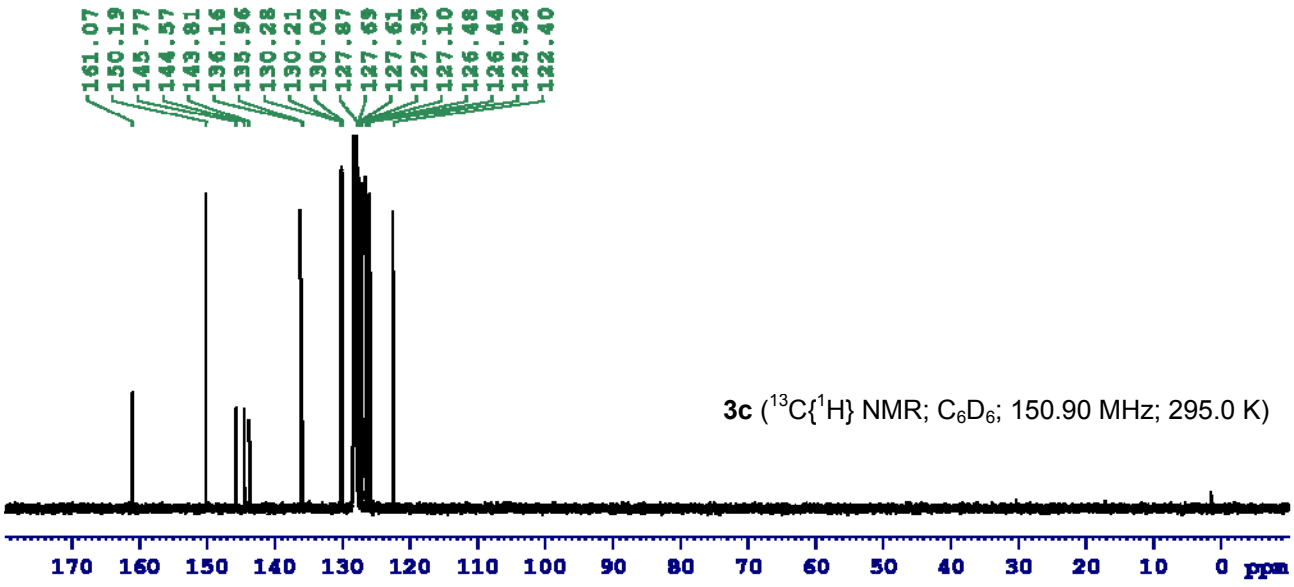
3a (^{13}C{^{1}H} NMR; C_6D_6; 100.55 MHz; 295.7 K)

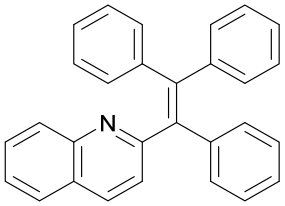

N

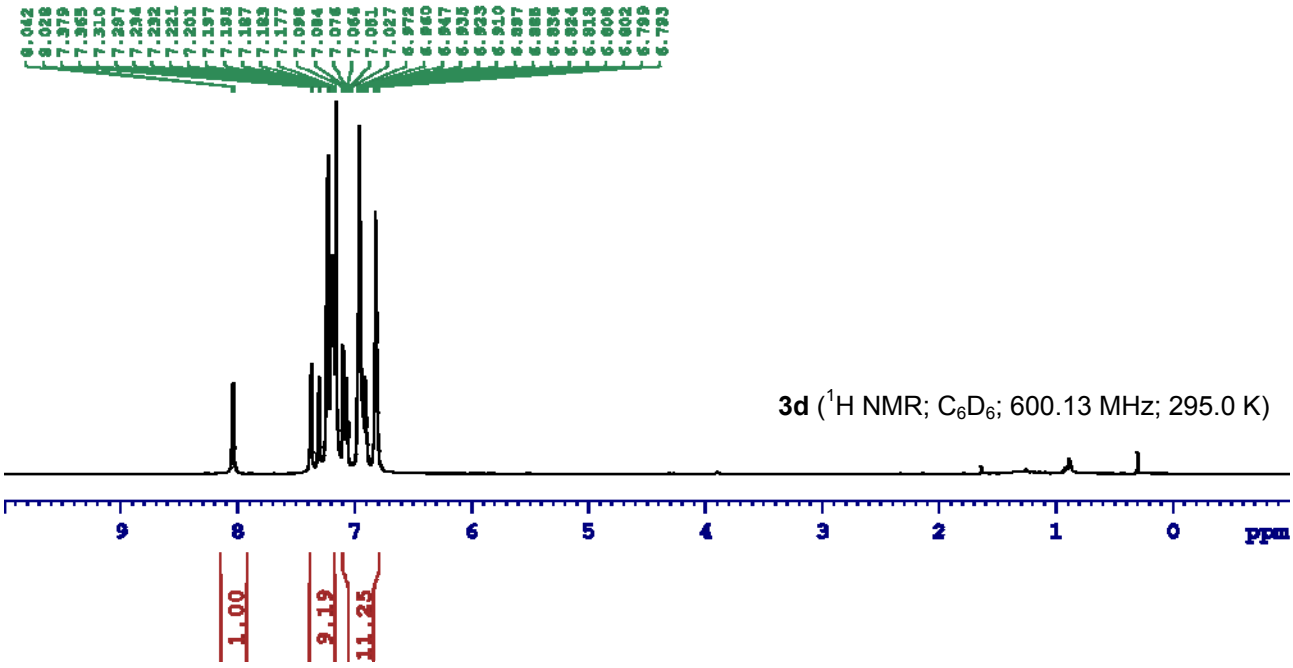

8.37
8.37
8.36
8.36
8.36
7.21
7.20
7.20
7.19
7.19
7.19
7.18
7.17
7.17
7.17
6.97
6.97
6.96
6.95
6.95
6.94
6.94
6.94
6.94
6.93
6.93
6.93
6.92
6.92
6.91
6.91
6.91
6.91
6.90
6.90
6.90
6.89
6.89
6.88
6.88
6.85
6.84
6.83
6.83
6.45
6.44
6.44
6.44
6.43
3b (1H NMR; C6D6; 600.13 MHz; 295.0 K)
9
8
7
6
5
4
3
2
1
0
ppm
1.00
6.05
10.09
1.03
1.02


162.85
149.70
144.15
143.61
143.23
143.15
141.76
135.12
131.78
131.63
131.60
128.95
128.15
128.12
127.14
127.02
126.83
126.51
121.13
3b (13C{1H} NMR; C6D6; 150.90 MHz; 295.0 K)
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
ppm

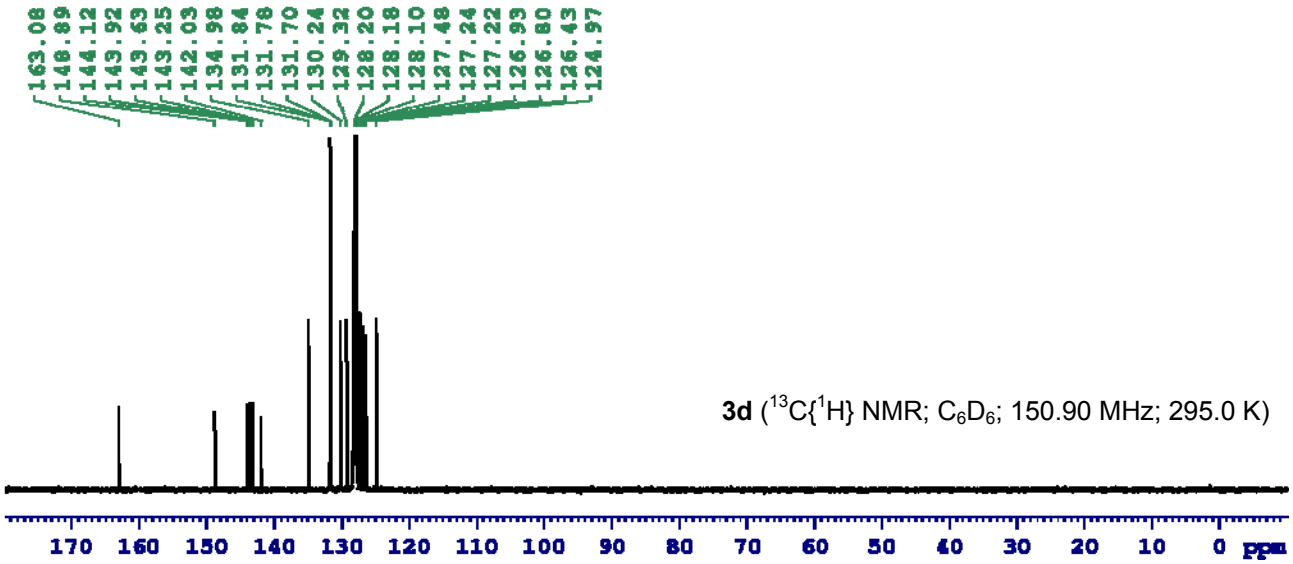

8.318
8.310
7.065
7.052
7.027
7.003
6.898
6.874
6.872
6.862
6.860
6.846
6.838
6.782
6.774
6.713
6.707
6.705
6.699
6.690
6.684
6.674
6.667
6.613
6.604
6.601
6.592
6.549
6.541
6.534
6.454
6.447
6.440
3c (1H NMR; C6D6; 600.13 MHz; 295.0 K)
9
8
7
6
5
4
3
2
1
0
ppm
1.00
4.13
1.01
4.01
1.03
1.02
1.02


161.07
150.19
145.77
144.57
143.81
136.16
135.96
130.28
130.21
130.02
127.87
127.69
127.61
127.35
127.10
126.48
126.44
125.92
122.40
3c (13C{1H} NMR; C6D6; 150.90 MHz; 295.0 K)
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
ppm

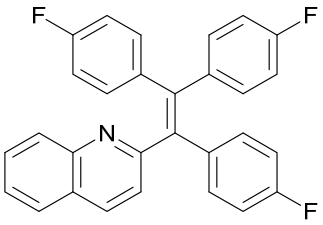


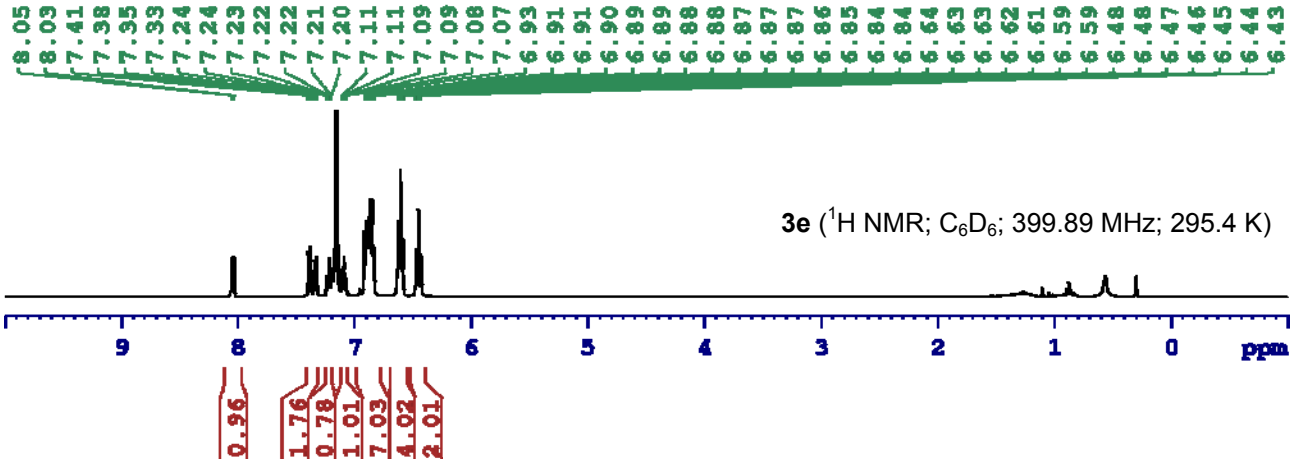


3d (^{1}H NMR; C_6D_6; 600.13 MHz; 295.0 K)

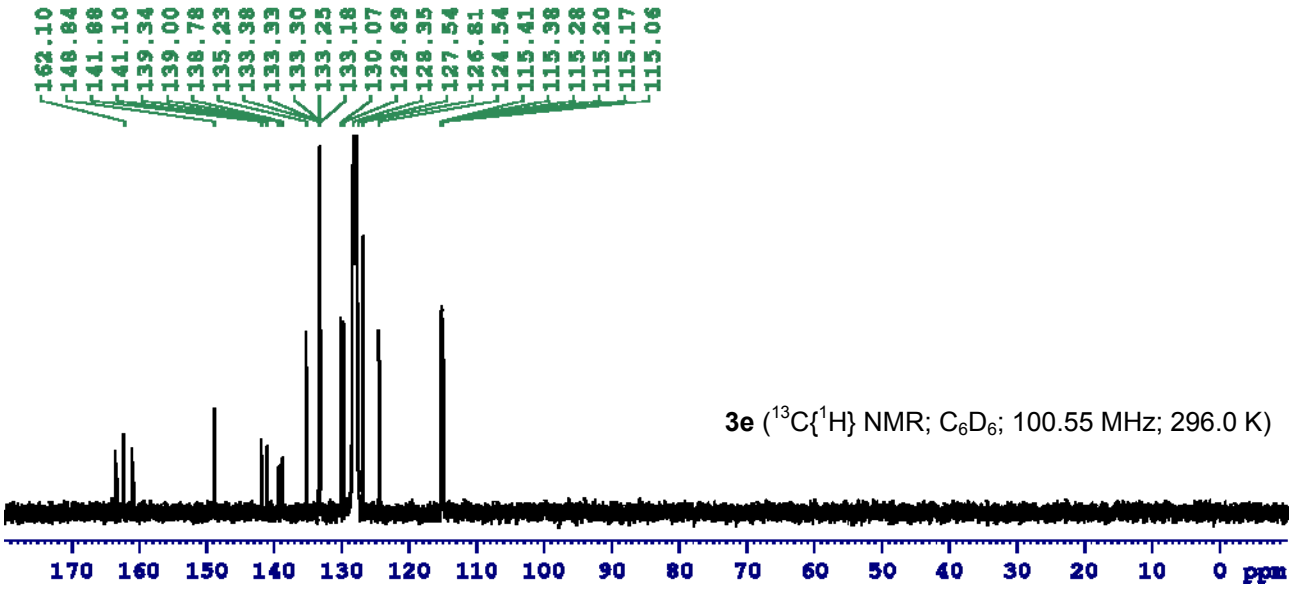


3d (^{13}C{^{1}H} NMR; C_6D_6; 150.90 MHz; 295.0 K)

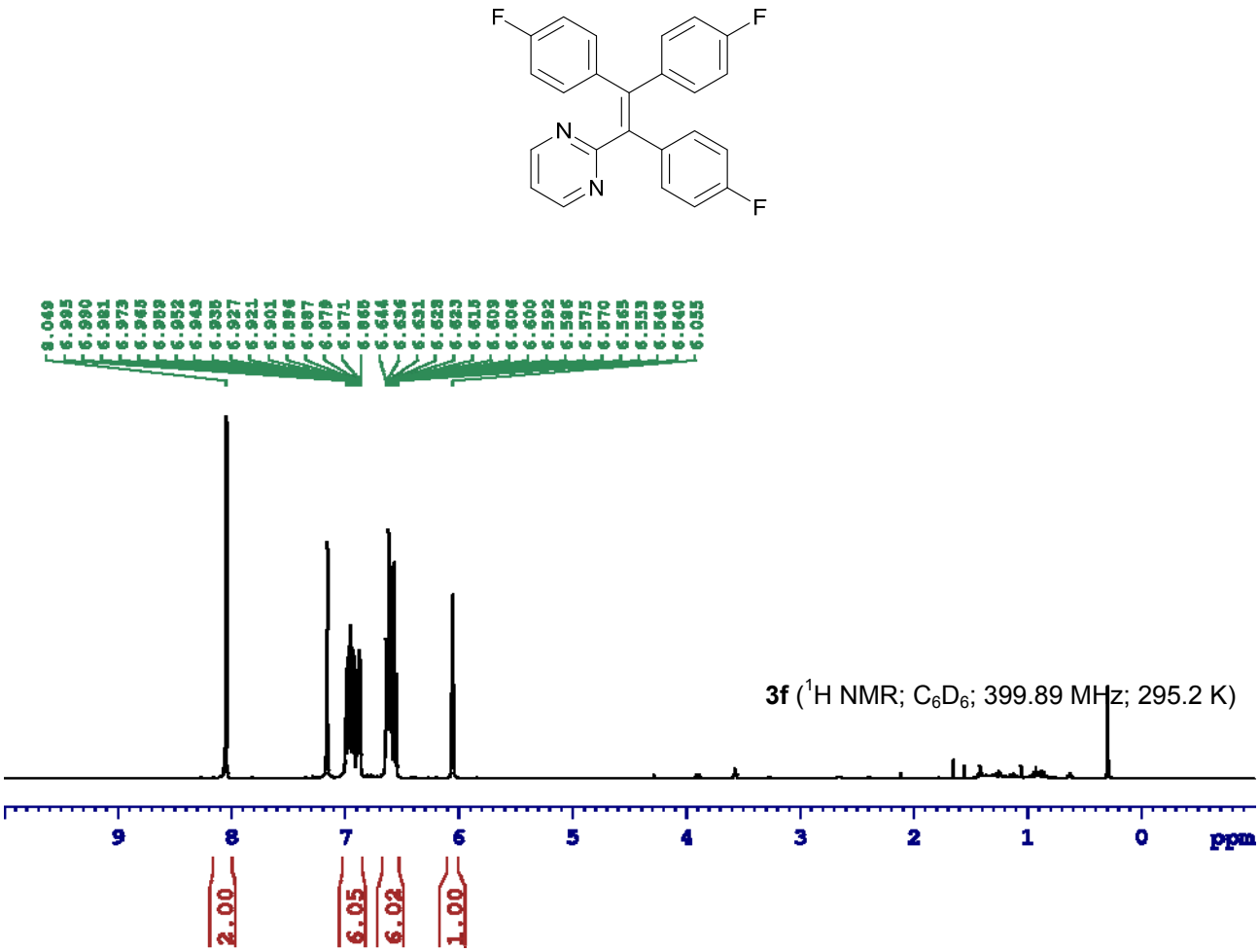




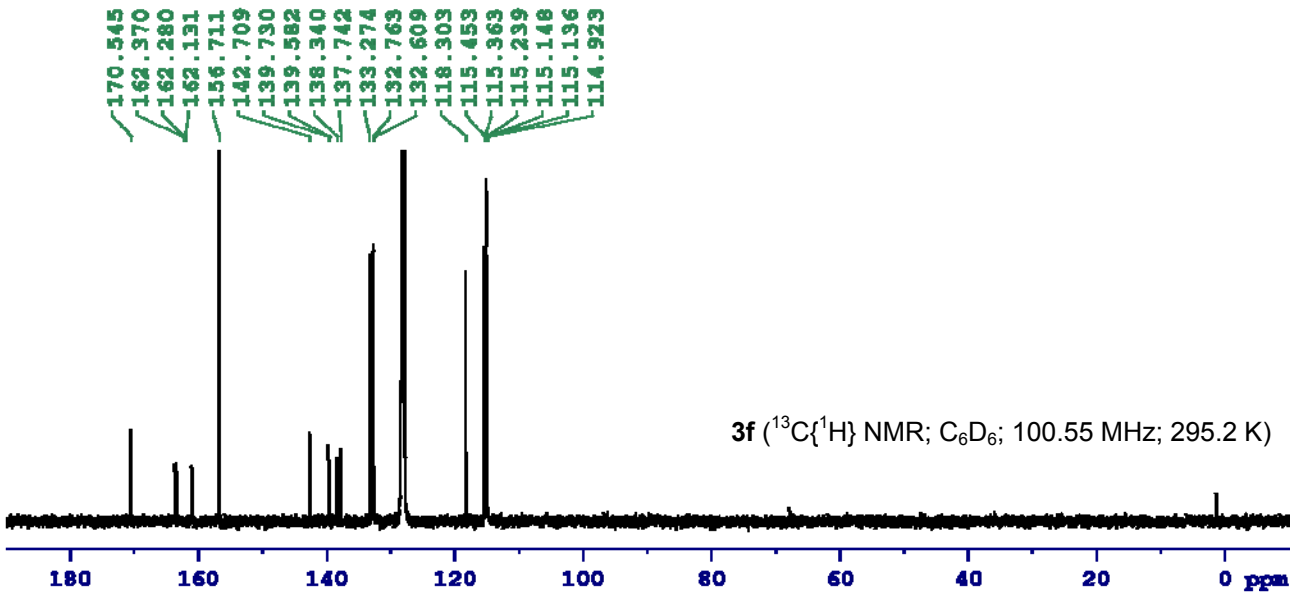
3e (^{1}H NMR; C_6D_6; 399.89 MHz; 295.4 K)



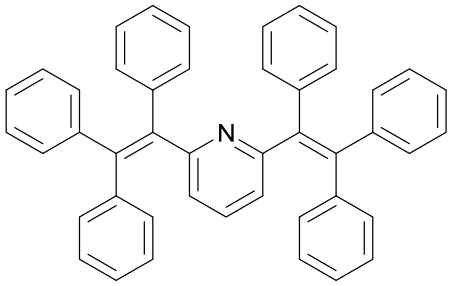
3e (^{13}C{^{1}H} NMR; C_6D_6; 100.55 MHz; 296.0 K)

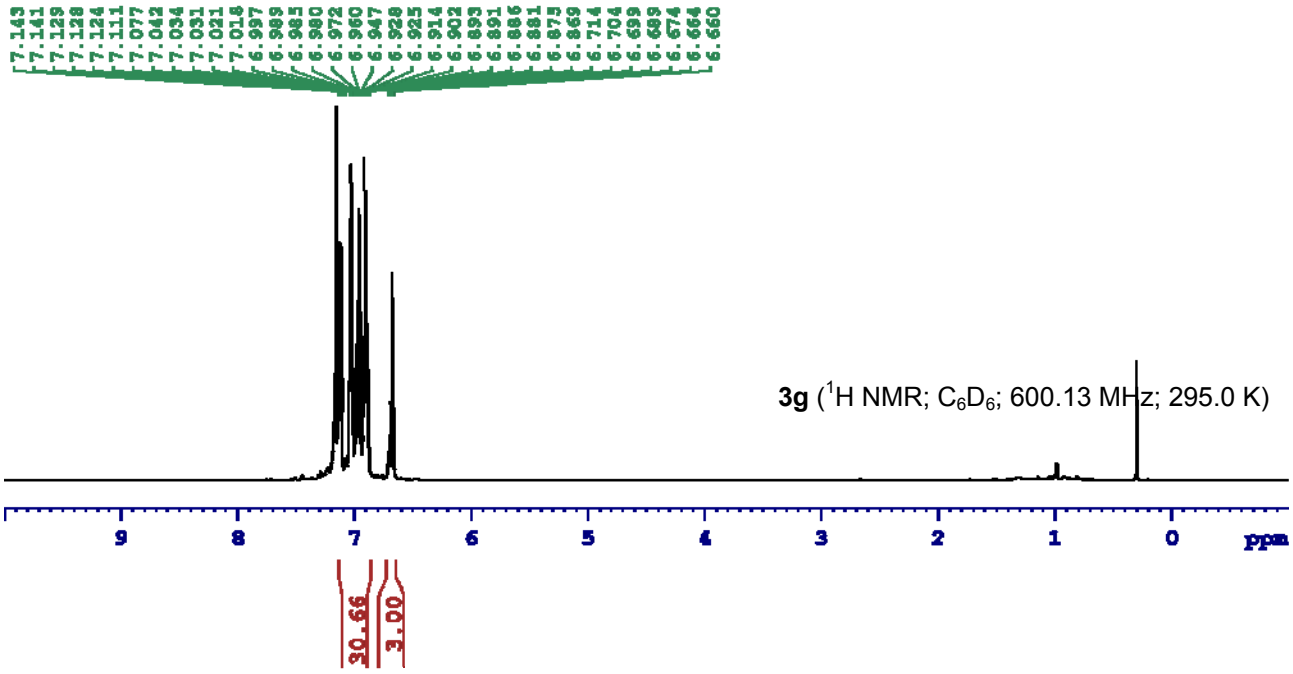


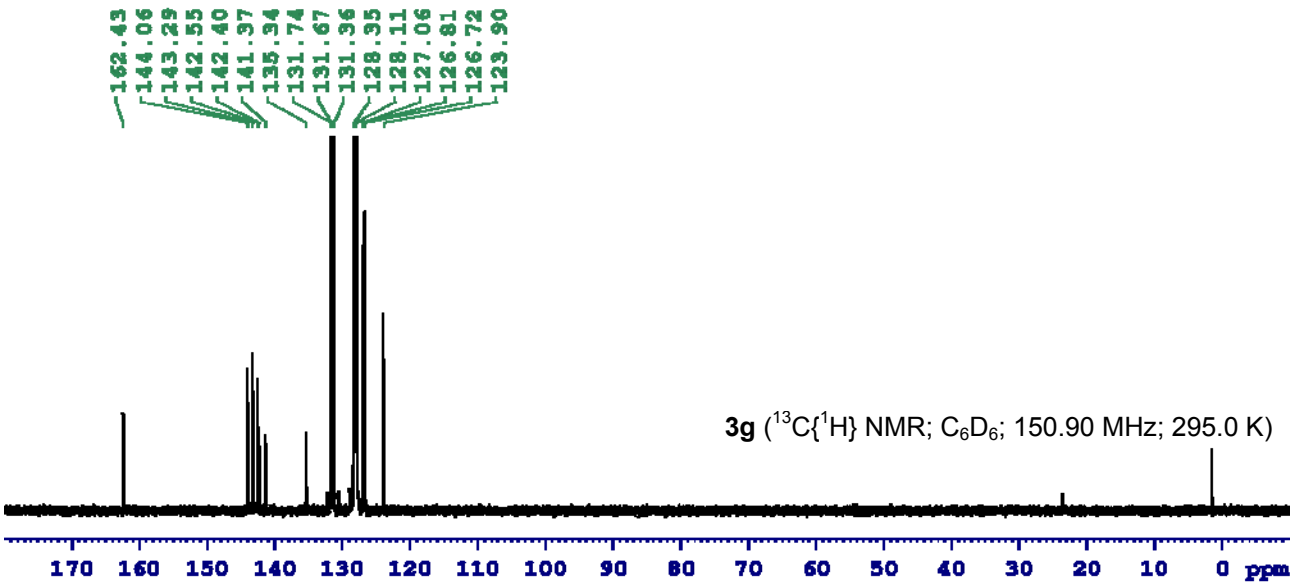
3f (^{1}H NMR; C_6D_6; 399.89 MHz; 295.2 K)

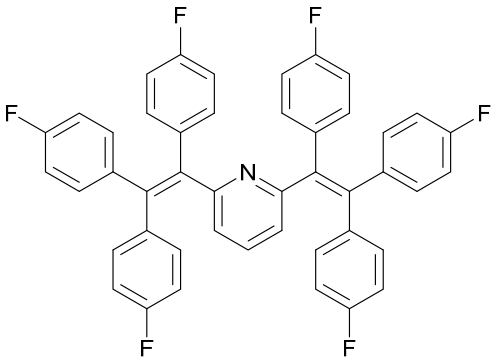


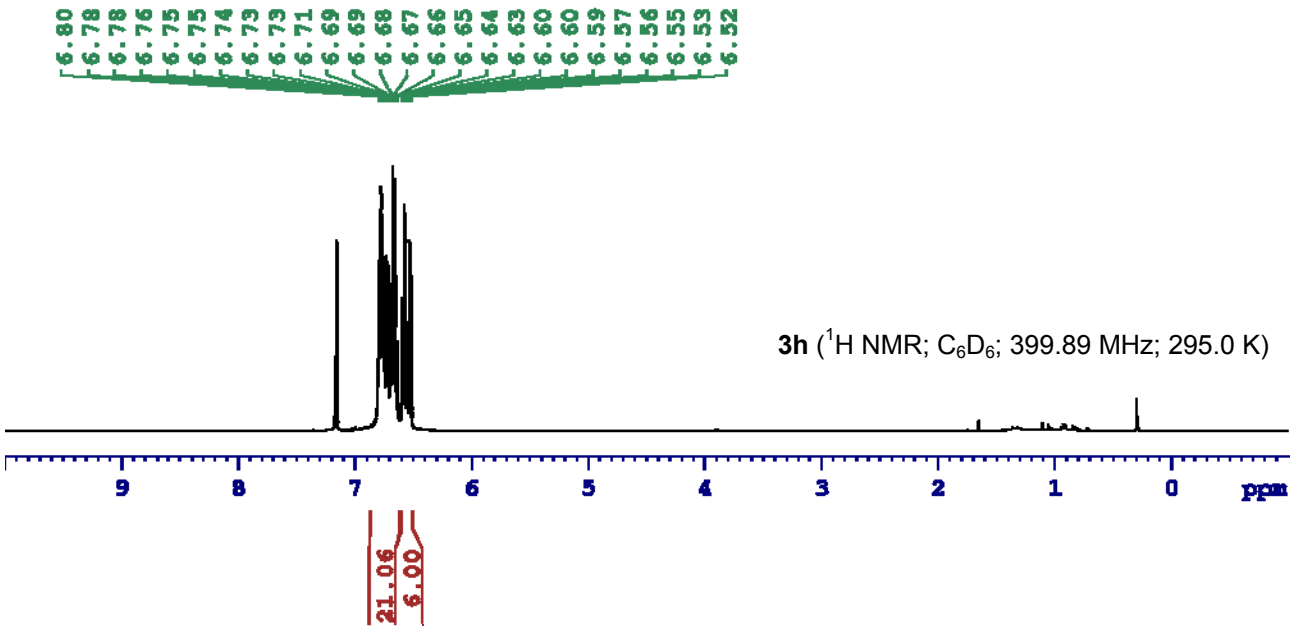
3f (^{13}C{^{1}H} NMR; C_6D_6; 100.55 MHz; 295.2 K)


N

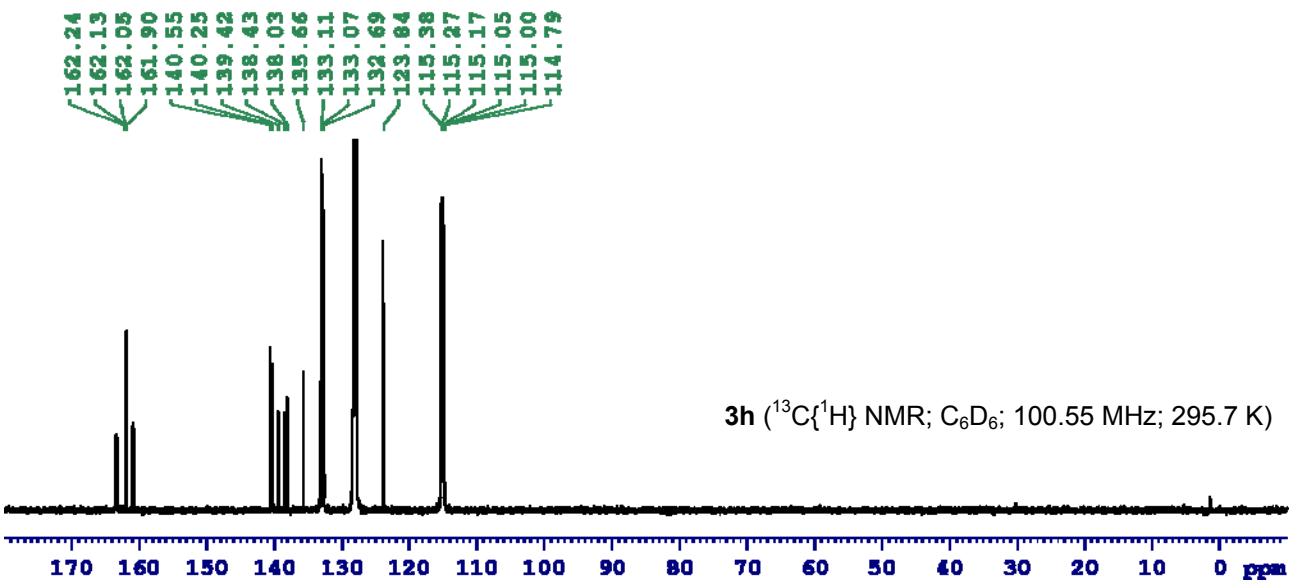

7.143
7.141
7.129
7.128
7.124
7.111
7.077
7.042
7.034
7.031
7.021
7.018
6.997
6.989
6.983
6.980
6.972
6.960
6.947
6.928
6.925
6.914
6.902
6.893
6.891
6.886
6.881
6.873
6.869
6.714
6.704
6.699
6.689
6.674
6.664
6.660
3g (1H NMR; C6D6; 600.13 MHz; 295.0 K)
9
8
7
6
5
4
3
2
1
0
ppm
30.66
3.00


162.43
144.06
143.29
142.55
142.40
141.37
135.34
131.74
131.67
131.36
128.35
128.11
127.06
126.81
126.72
123.90
3g (13C{1H} NMR; C6D6; 150.90 MHz; 295.0 K)
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
ppm

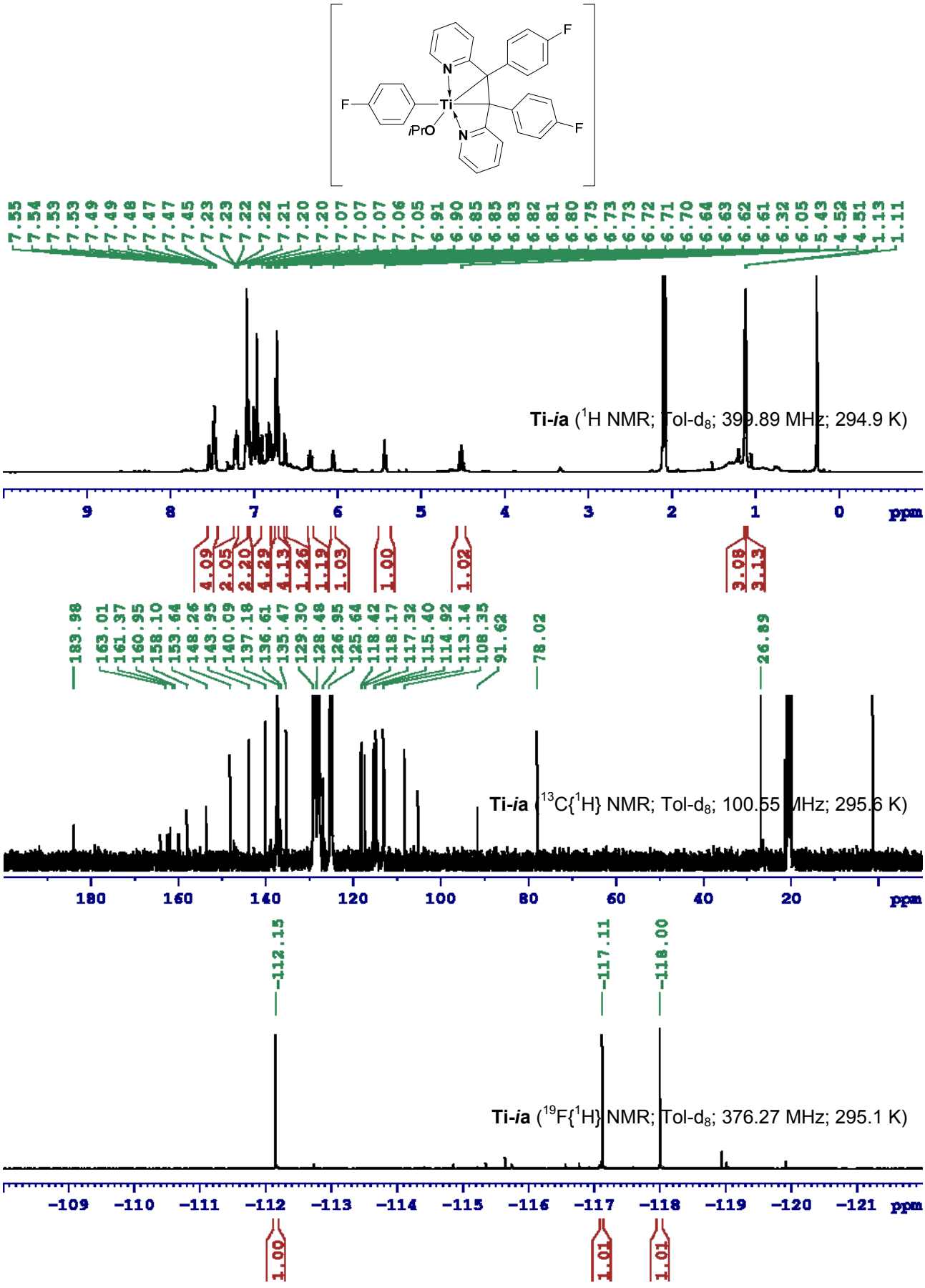


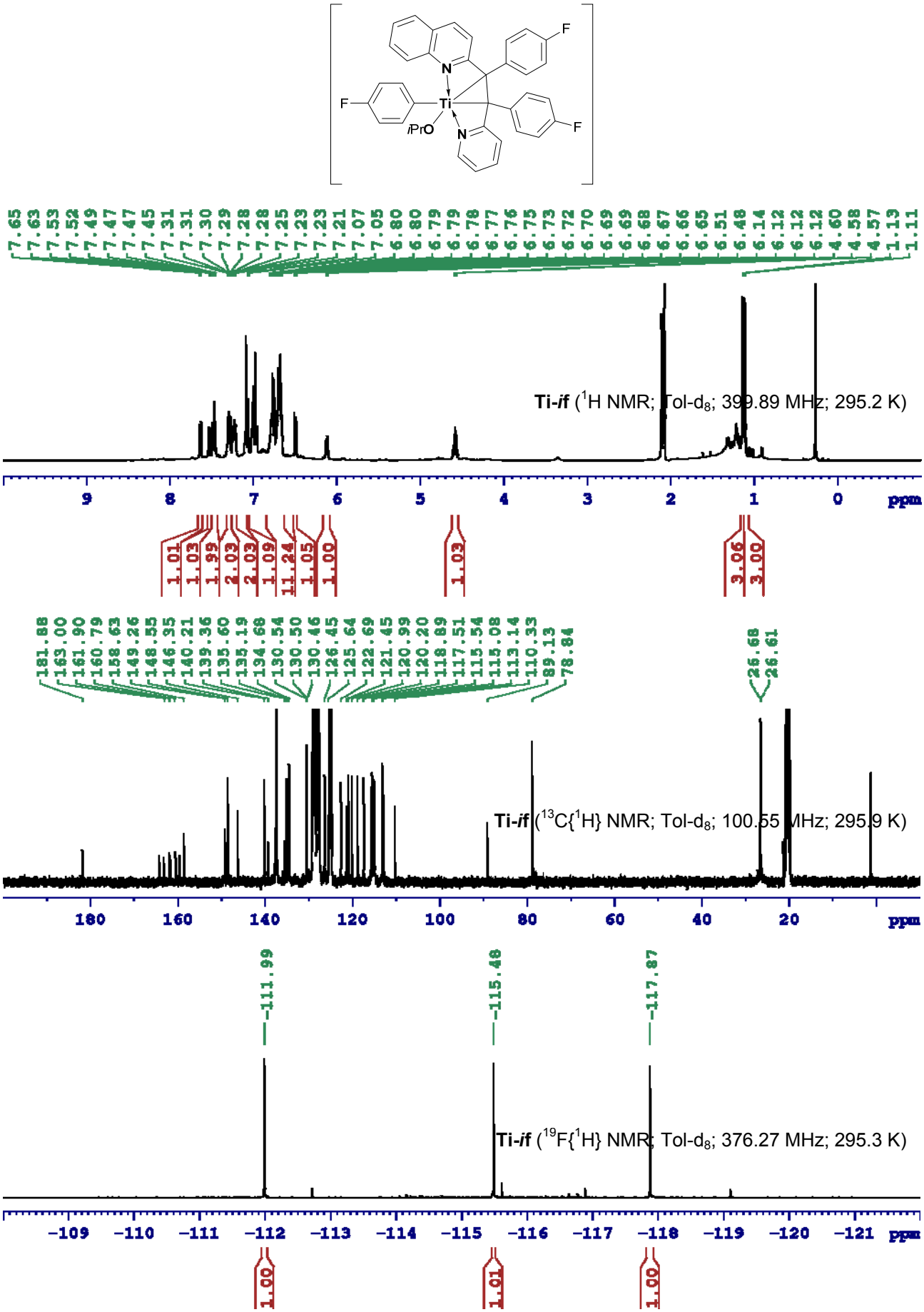


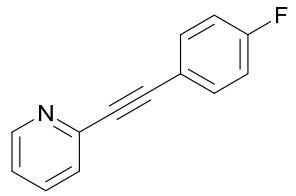
3h (^{1}H NMR; C_6D_6; 399.89 MHz; 295.0 K)

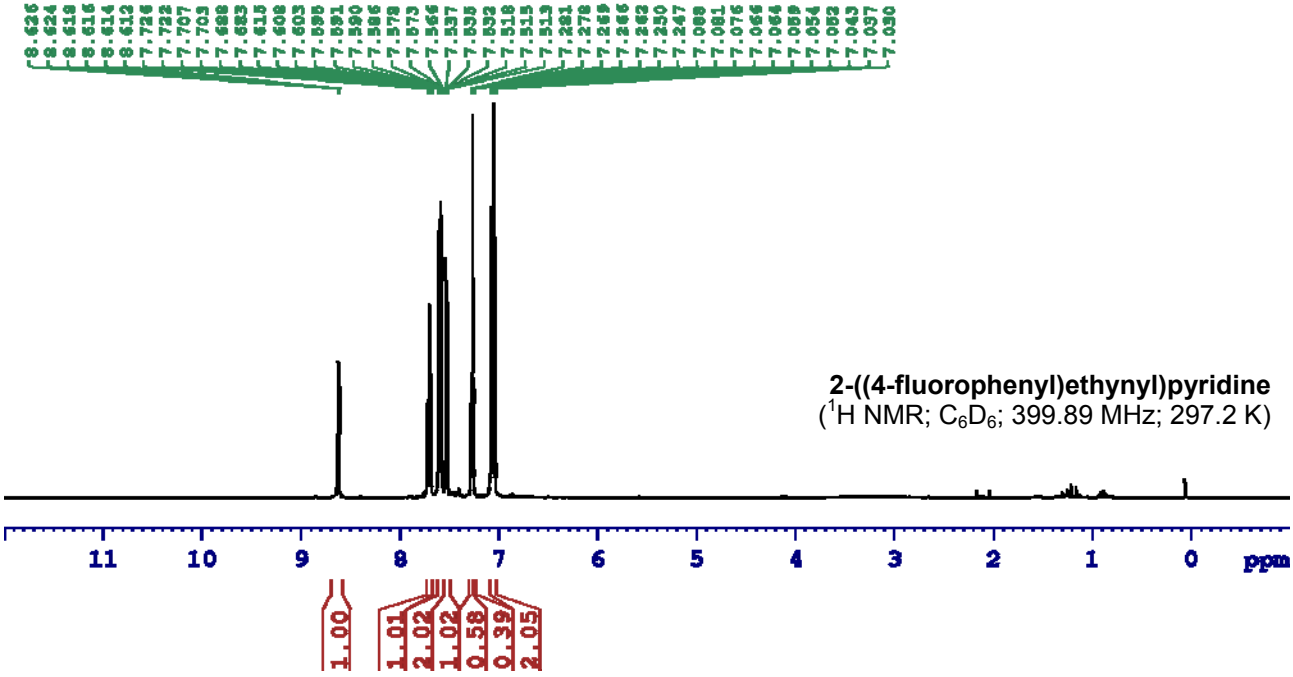


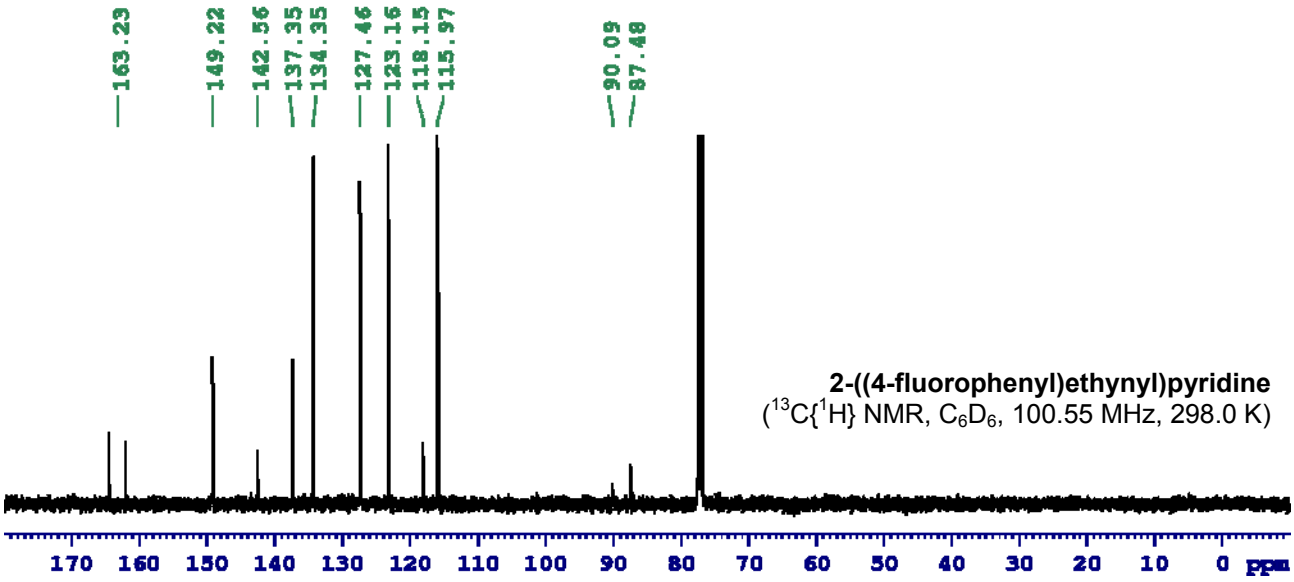
3h (^{13}C{^{1}H} NMR; C_6D_6; 100.55 MHz; 295.7 K)

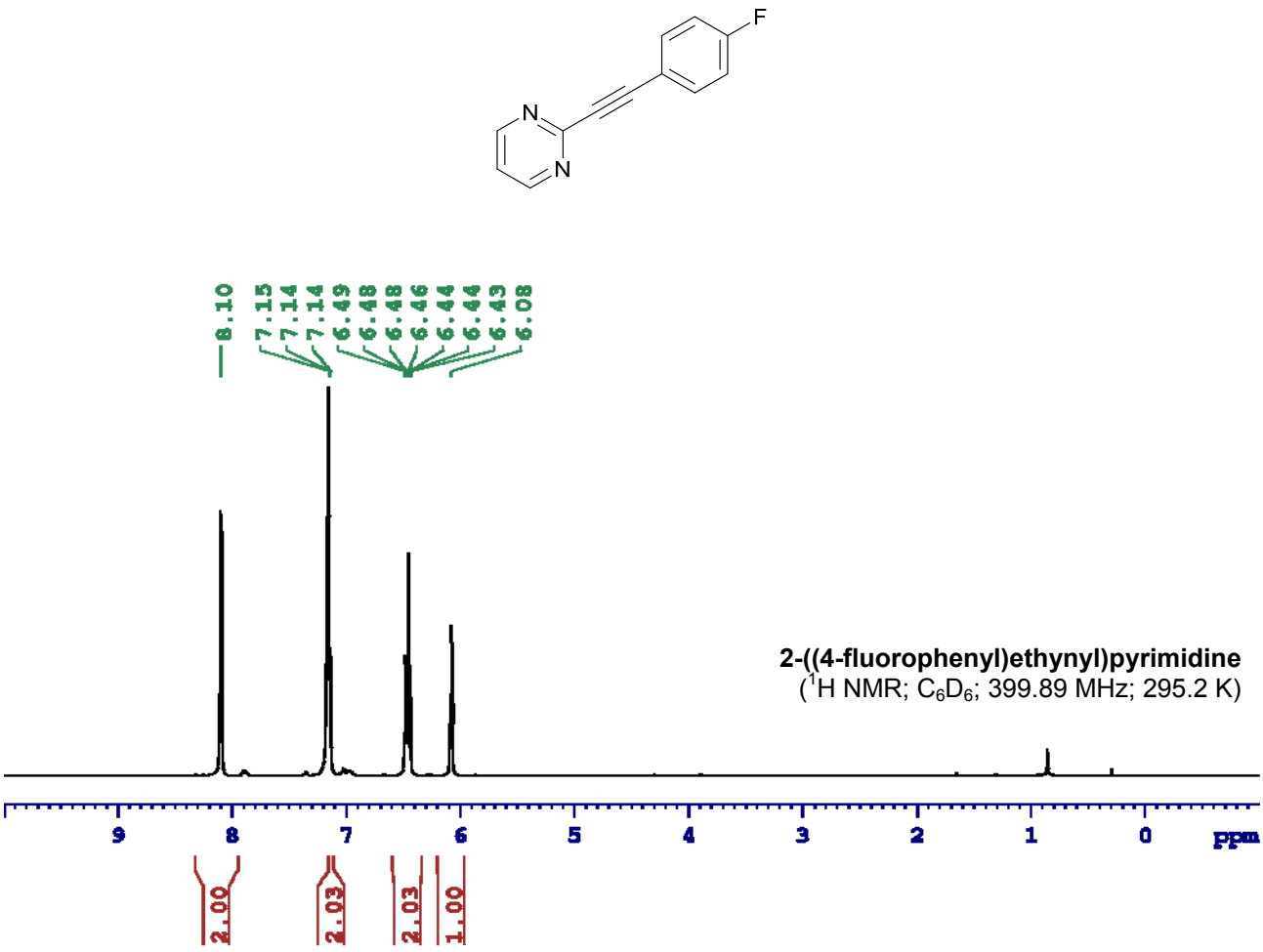

Ti-*ia* (^{1}H NMR; Tol-d$_8$; 399.89 MHz; 294.9 K)
Ti-*ia* (^{13}C{^{1}H} NMR; Tol-d$_8$; 100.55 MHz; 295.6 K)
Ti-*ia* (^{19}F{^{1}H} NMR; Tol-d$_8$; 376.27 MHz; 295.1 K)
ppm

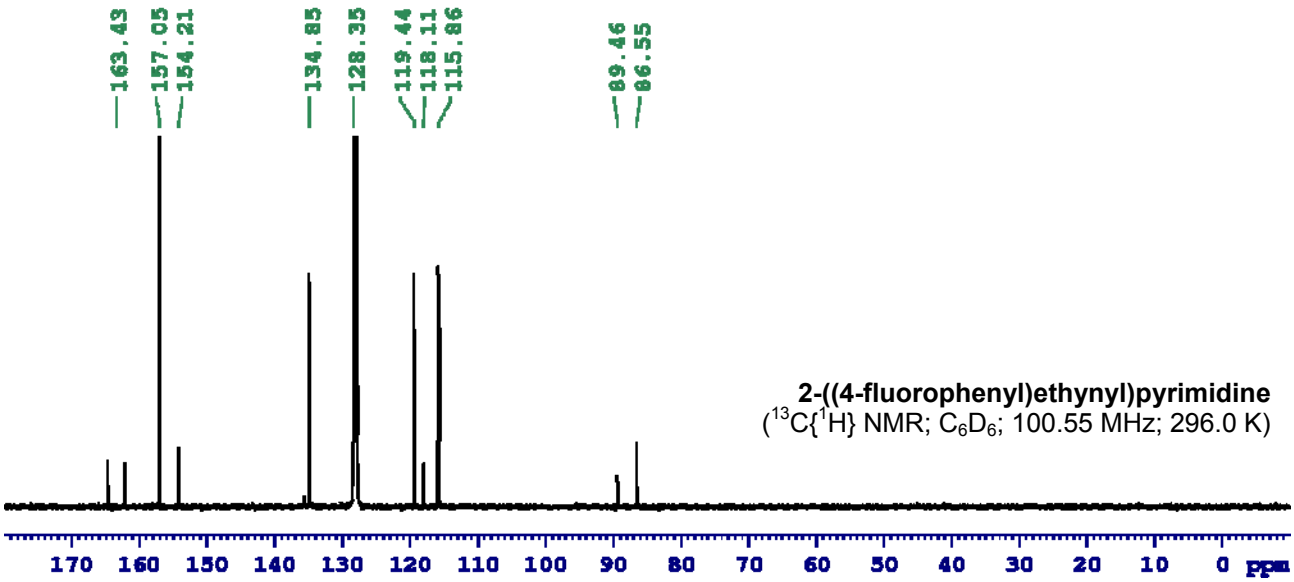

F
N
Ti
F
iPrO
N
F
7.65 7.63 7.53 7.52 7.49 7.47 7.47 7.45 7.31 7.31 7.30 7.29 7.28 7.28 7.25 7.23 7.23 7.21 7.07 7.05 6.80 6.80 6.79 6.79 6.78 6.77 6.76 6.75 6.73 6.72 6.70 6.69 6.69 6.68 6.67 6.66 6.65 6.51 6.48 6.14 6.12 6.12 6.12 4.60 4.58 4.57 1.19 1.11
Ti-if (1H NMR; Tol-d8; 399.89 MHz; 295.2 K)
9 8 7 6 5 4 3 2 1 0 ppm
1.01 1.03 1.99 2.03 2.03 1.09 11.24 1.05 1.00 1.03 3.06 3.00
181.88 163.00 161.90 160.79 158.63 149.26 148.55 146.35 140.21 139.36 135.60 135.19 134.68 130.54 130.50 130.46 126.45 125.64 122.69 121.45 120.99 120.20 118.89 117.51 115.54 115.08 113.14 110.33 89.13 78.84 26.68 26.61
Ti-if (13C{1H} NMR; Tol-d8; 100.55 MHz; 295.9 K)
180 160 140 120 100 80 60 40 20 ppm
-111.99 -115.48 -117.87
Ti-if (19F{1H} NMR; Tol-d8; 376.27 MHz; 295.3 K)
-109 -110 -111 -112 -113 -114 -115 -116 -117 -118 -119 -120 -121 ppm
1.00 1.01 1.00

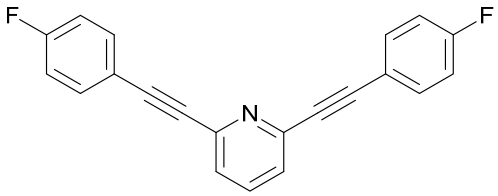

F
N

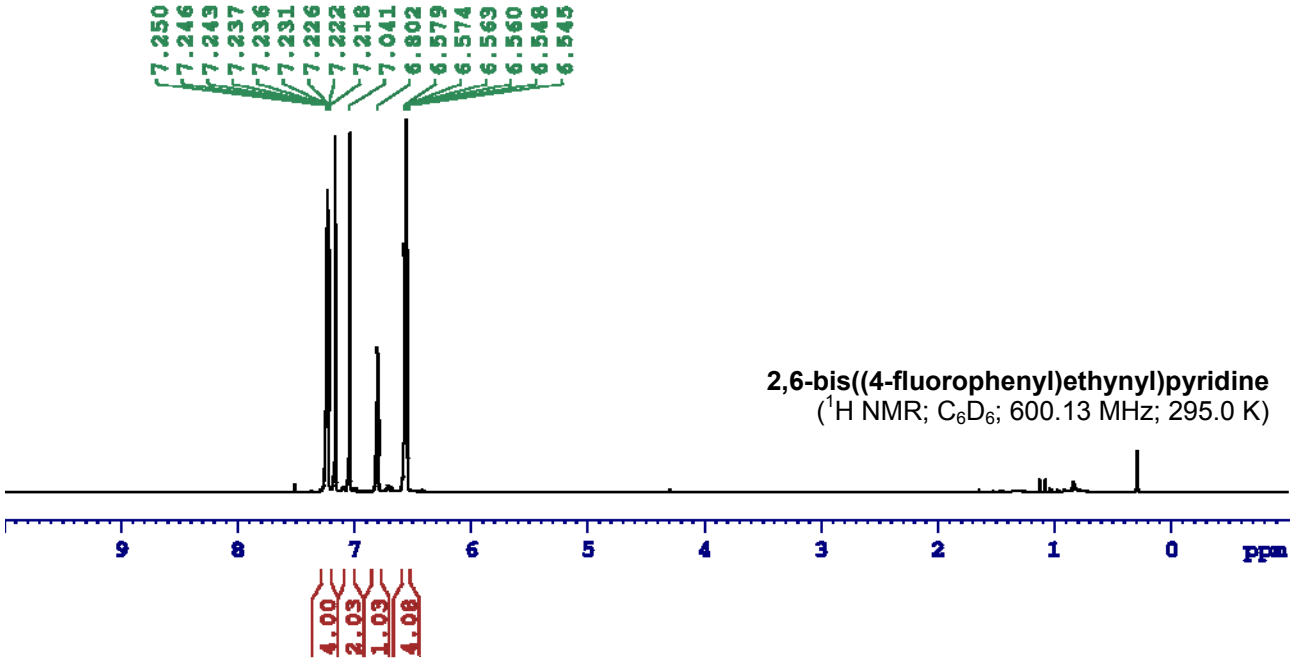

8.626
8.624
8.618
8.616
8.614
8.613
7.726
7.722
7.707
7.703
7.688
7.683
7.615
7.608
7.603
7.590
7.581
7.580
7.578
7.573
7.566
7.537
7.535
7.532
7.518
7.515
7.513
7.281
7.278
7.269
7.266
7.262
7.250
7.247
7.008
7.001
7.076
7.066
7.064
7.059
7.054
7.052
7.043
7.037
7.030
2-((4-fluorophenyl)ethynyl)pyridine
(1H NMR; C6D6; 399.89 MHz; 297.2 K)
11
10
9
8
7
6
5
4
3
2
1
0
ppm
1.00
1.01
2.02
1.02
0.58
0.39
2.05


163.23
149.22
142.56
137.35
134.35
127.46
123.16
118.15
115.97
90.09
87.48
2-((4-fluorophenyl)ethynyl)pyridine
(13C{1H} NMR, C6D6, 100.55 MHz, 298.0 K)
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
ppm

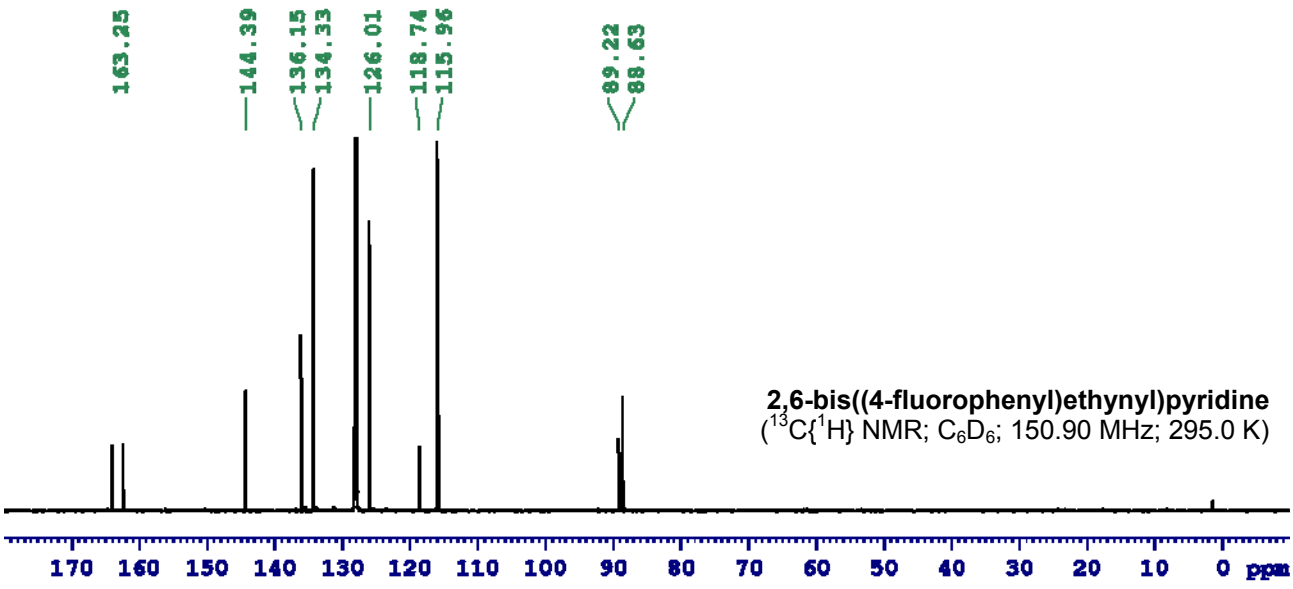

F
N
N
8.10
7.15
7.14
7.14
6.49
6.48
6.48
6.46
6.44
6.44
6.43
6.08
2-((4-fluorophenyl)ethynyl)pyrimidine
(1H NMR; C6D6; 399.89 MHz; 295.2 K)
9
8
7
6
5
4
3
2
1
0
ppm
2.00
2.03
2.03
1.00


163.43
157.05
154.21
134.85
128.35
119.44
118.11
115.86
89.46
86.55
2-((4-fluorophenyl)ethynyl)pyrimidine
(13C{1H} NMR; C6D6; 100.55 MHz; 296.0 K)
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
ppm





2,6-bis((4-fluorophenyl)ethynyl)pyridine
(^{1}H NMR; C_6D_6; 600.13 MHz; 295.0 K)



2,6-bis((4-fluorophenyl)ethynyl)pyridine
(^{13}C{^{1}H} NMR; C_6D_6; 150.90 MHz; 295.0 K)

Computational Details

Geometry optimization of **Ti-*if*** has been performed with the Gaussian 09 package[7] at the B3LYP level of hybrid density functional theory.[8] The geometry, as Cartesian coordinates, of the optimized structure is given below. The atoms were represented by a 6-311G basis set.[9] The Natural Bonding Orbital (NBO) analysis was performed with NBO6[10] on the B3LYP/6-311G density. The Atoms in Molecules (AIM)[11] analysis of the B3LYP/6-311G density was carried out with the AIMAll program[12].

Geometry Ti-*if*:

Ti	-0.307082	-0.615379	0.763950
F	-1.223740	6.356415	-2.094337
F	6.626642	-0.708951	-0.498464
F	-6.562649	-0.984494	0.369100
O	0.141285	-1.790209	2.028445
N	0.175360	-1.252388	-1.079361
N	-0.381633	1.269830	1.907362
C	0.037295	-0.003357	-1.659558
C	-0.405466	0.066464	-3.032394
H	-0.555341	1.037101	-3.485756
C	-0.539142	-1.069330	-3.758771
H	-0.820426	-1.013567	-4.806648
C	-0.282110	-2.363919	-3.185846
C	-0.379228	-3.560356	-3.916120
H	-0.656998	-3.513412	-4.965306
C	-0.129685	-4.782120	-3.314233
H	-0.207038	-5.699996	-3.886785
C	0.223517	-4.825885	-1.957772
H	0.421696	-5.781681	-1.483119
C	0.329657	-3.661839	-1.214962
H	0.611455	-3.689602	-0.168674
C	0.081577	-2.415522	-1.815436
C	0.352561	1.097535	-0.834735
C	-0.084063	2.471531	-1.171016
C	0.802168	3.552006	-1.009036
H	1.807533	3.363336	-0.649742
C	0.429137	4.855616	-1.318608
H	1.117547	5.685004	-1.201135
C	-0.851986	5.090021	-1.793766
C	-1.764821	4.059494	-1.959018
H	-2.765027	4.280672	-2.314596
C	-1.378532	2.761463	-1.640275
H	-2.101693	1.959827	-1.736715
C	1.267985	0.861247	0.330648
C	2.681854	0.458021	0.105425
C	3.461693	-0.068841	1.153038
H	3.021439	-0.189390	2.137363
C	4.784018	-0.452595	0.961585
H	5.379278	-0.857163	1.772718
C	5.341216	-0.329273	-0.302792
C	4.609347	0.168463	-1.367953
H	5.072477	0.250205	-2.344985
C	3.290122	0.560112	-1.156956
H	2.719296	0.953928	-1.989992

C	0.899329	1.562169	1.565167
C	1.675219	2.381758	2.403150
H	2.709508	2.585947	2.155768
C	1.078534	2.940711	3.523959
H	1.651935	3.604337	4.163959
C	-0.260282	2.667814	3.825146
H	-0.746436	3.102869	4.689640
C	-0.952663	1.800973	2.990200
H	-1.976276	1.499821	3.188075
C	-2.433424	-0.584986	0.706146
C	-3.054512	-1.848167	0.673381
H	-2.454133	-2.753148	0.737381
C	-4.437016	-1.997826	0.557096
H	-4.909475	-2.974043	0.528573
C	-5.218414	-0.855820	0.479405
C	-4.664617	0.415159	0.515579
H	-5.313368	1.282821	0.453711
C	-3.279183	0.535078	0.631186
H	-2.854875	1.534268	0.657617
C	0.543358	-2.439198	3.224608
H	1.116769	-1.709900	3.813347
C	-0.691034	-2.854644	4.021003
H	-1.324270	-1.990039	4.229625
H	-0.403327	-3.309404	4.973461
H	-1.284641	-3.580595	3.458992
C	1.452532	-3.618064	2.885239
H	0.901567	-4.379856	2.326237
H	1.842266	-4.081535	3.796062
H	2.298059	-3.288976	2.277477

X-ray Crystal Structure Determinations

Crystal data and details of the structure determinations are compiled in Tables S1 and S2. Full shells of intensity data were collected at low temperature with a Bruker AXS Smart 1000 CCD diffractometer (Mo-K_α radiation, sealed X-ray tube, graphite monochromator, compound **3b** or an Agilent Technologies Supernova-E CCD diffractometer (Mo-K_α radiation, microfocus X-ray tube, multilayer mirror optics). Detector frames (typically ω-, occasionally φ-scans, scan width 0.4...1°) were integrated by profile fitting.[13,14,15] Data were corrected for air and detector absorption, Lorentz and polarization effects[14,15] and scaled essentially by application of appropriate spherical harmonic functions.[14,16,17,18] Absorption by the crystal was treated numerically (Gaussian grid)[16,19] or with a semiempirical multiscan method (as part of the scaling process), and augmented by a spherical correction.[16,17,18] The structures were solved by dual space methods (compound **2**: SHELXD,[20,21] compound **3g**: VLD procedure,[22] all other compunds: charge flip procedure[23]) and refined by full-matrix least squares methods based on F^2 against all unique reflections.[21,24] All non-hydrogen atoms were given anisotropic displacement

parameters. Hydrogen atoms were generally input at calculated positions and refined with a riding model.[25] When justified by the quality of the data the positions of some or all hydrogen atoms were taken from difference Fourier syntheses and refined. When found necessary, disordered groups and/or solvent molecules were subjected to suitable geometry and adp restraints or constraints.

CCDC 1815806 and 1817687-1817692 contain the supplementary crystallographic data for this paper. These data can be obtained free of charge from The Cambridge Crystallographic Data Centre via https://www.ccdc.cam.ac.uk/data_request/cif.

Table S1. Details of the crystal structure determination of **Ti-*if*** ·1.5 toluene, **1a**, **2** and **3b**.

	Ti-*if* · 1.5 toluene	**1a**	**2**	**3b**
formula	$C_{47.50}H_{41}F_3N_2OTi$	$C_{24}H_{18}F_2N_2$	$C_{24}H_{16}F_2N_2$	$C_{25}H_{19}N$
crystal system	triclinic	orthorhombic	trigonal	monoclinic
space group	*P* -1	*P n a* 2_1	*P* 3_2	*P* 2_1
a /Å	9.83402(10)	14.1238(3)	28.9605(16)	9.652(5)
b /Å	10.87734(15)	8.54517(18)		9.262(4)
c /Å	19.1786(3)	15.8226(3)	5.6946(3)	10.579(5)
α /°	104.5042(12)			
β /°	103.2734(10)			107.030(14)
γ /°	91.6813(10)			
V /Å^3	1924.82(4)	1909.64(7)	4136.3(5)	904.2(7)
Z	2	4	9	2
M_r	760.72	372.40	370.39	333.41
F_{000}	794	776	1728	352
d_c /Mg·m^{-3}	1.313	1.295	1.338	1.225
μ /mm^{-1}	0.276	0.736	0.093	0.071
max., min. transmission factors	0.9546, 0.9322 [a]	1.000, 0.646 [b]	0.987, 0.956 [a]	0.8623, 0.8055 [a]
X-radiation, λ /Å	Mo-*K*α, 0.71073	Cu-*K*α, 1.54184	Mo-*K*α, 0.71073	Mo-*K*α, 0.71073
data collect. temperat. /K	120(1)	110(1)	110(1)	100(1)
θ range /°	2.5 to 32.4	5.6 to 67.4	3.2 to 25.2	2.0 to 30.5
index ranges *h*,*k*,*l*	-14 ... 14, -16 ... 16, -28 ... 28	-16 ... 16, -10 ... 10, -18 ... 18	-34 ... 34, -34 ... 34, -6 ... 6	-13 ... 13, -13 ... 13, -15 ... 14
reflections measured	98052	56245	76183	21932
unique [R_{int}]	13318 [0.0541]	3420 [0.1686]	9873 [0.1830]	5499 [0.0434]
observed [$I \geq 2\sigma(I)$]	10506	2778	7376	4474
data / restraints /parameters	13318 / 141 / 556	3420 / 1 / 253	9873 / 1 / 758	5499 / 86 / 320
GooF on F^2	1.015	1.226	1.054	1.048
R indices [$F>4\sigma(F)$] $R(F)$, $wR(F^2)$	0.0482, 0.1186	0.0928, 0.2666	0.0742, 0.1207	0.0449, 0.0937
R indices (all data) $R(F)$, $wR(F^2)$	0.0687, 0.1257	0.1151, 0.3170	0.1034, 0.1330	0.0608, 0.1009
absolute structure parameter		-0.3(4)	0.3(7)	0.0(10)
largest residual peaks /e·Å^{-3}	0.645, -0.487	0.359, -0.390	0.353, -0.213	0.253, -0.211
CCDC	1815806	1817688	1817689	1817690

[a] semi-emirical absorption correction. [b] numerical absorption correction.

Table S2. Details of the crystal structure determination of **3f**, **3g**·*n*-pentane and **3h**.

	3f	**3g** · *n*-pentane	**3h**
formula	$C_{24}H_{15}F_3N_2$	$C_{47.50}H_{39}N$	$C_{45}H_{27}F_6N$
crystal system	monoclinic	monoclinic	monoclinic
space group	*P* $2_1/n$	*P* $2_1/n$	*P* $2_1/n$
a /Å	9.06788(17)	17.51974(11)	16.1155(4)
b /Å	5.50360(16)	9.24966(5)	10.2929(3)
c /Å	37.4304(11)	22.74222(19)	20.6155(5)
α /°			
β /°	96.012(2)	107.3819(8)	90.803(2)
γ /°			
V /Å^3	1857.73(8)	3517.12(4)	3419.27(14)
Z	4	4	4
M_r	388.38	623.79	695.67
F_{000}	800	1324	1432
d_c /Mg·m^{-3}	1.389	1.178	1.351
μ /mm^{-1}	0.863	0.508	0.101
max., min. transmission factors	0.964, 0.833 [a]	1.000, 0.924 [b]	1.000, 0.804 [a]
X-radiation, λ /Å	Cu-*K*α, 1.54184	Cu-*K*α, 1.54184	Mo-*K*α, 0.71073
data collect. temperat. /K	110(1)	120(1)	120(1)
θ range /°	4.8 to 70.9	3.8 to 70.9	2.2 to 30.5
index ranges *h*,*k*,*l*	-11 ... 11, -6 ... 6, -45 ... 42	-21 ... 21, -11 ... 11, -27 ... 27	-23 ... 23, -14 ... 14, -29 ... 29
reflections measured	53581	175052	73029
unique [R_{int}]	3543 [0.1176]	6766 [0.0472]	10459 [0.0795]
observed [$I \geq 2\sigma(I)$]	3027	6216	6833
data / restraints /parameters	3543 / 0 / 307	6766 / 22 / 460	10459 / 0 / 550
GooF on F^2	1.064	1.042	1.026
R indices [$F>4\sigma(F)$] $R(F)$, $wR(F^2)$	0.0398, 0.1029	0.0497, 0.1152	0.0574, 0.1125
R indices (all data) $R(F)$, $wR(F^2)$	0.0472, 0.1090	0.0545, 0.1185	0.0967, 0.1288
largest residual peaks /e·Å^{-3}	0.228, -0.275	0.698, -0.668	0.342, -0.245
CCDC	1817687	1817692	1817691

[a] numerical absorption correction. [b] semi-emirical absorption correction.

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