Origins of Enantioselectivity in Allylic Substitution Reactions Catalyzed by Metallacyclic Iridium Complexes

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Supporting information

General Procedures. All reactions were conducted in flame or oven-dried round-bottomed flasks fitted with rubber septa under a positive pressure of argon or nitrogen, or in 1-dram vials sealed with a screw cap fitted with PTFE silicon septum under an atmosphere of Argon, unless otherwise stated. Air and moisture-sensitive reagents were transferred via syringe, or were handled in an argon-filled or nitrogen-filled drybox (Innovative Technologies, Newburyport, Massachusetts) equipped with an oxygen sensor (working oxygen level <5 ppm) and low-temperature refrigeration unit (–35 °C). Organic solutions were concentrated by rotary evaporation at 23–35 °C. Flash-column chromatography was performed as described by Still et. al.[1] employing silica gel (40–63 μm particle size) purchased from Silicycle. Analytical thin-layer chromatography (TLC) was performed using glass plates pre-coated with silica gel (0.25 mm). TLC plates were visualized by exposure to ultraviolet light (UV) or submersion in aqueous potassium permanganate solution (KMnO4), followed by brief heating by a heat gun (175 °C, 3–5 s).

Instrumentation. Proton nuclear magnetic resonance spectra (^{1}H NMR) were recorded at 500 MHz at 22 °C unless otherwise stated. Chemical shifts are expressed in parts per million (ppm, δ scale) downfield from tetramethylsilane and are referenced to residual protium in the NMR solvent (CHCl3, δ 7.26; THF, δ 1.73, 3.58; CH_2Cl_2, δ 5.32). Data are represented as follows: chemical shift, multiplicity (s = singlet, d = doublet, t = triplet, q = quartet, m = multiplet and/or multiple resonances, br = broad, app = apparent), integration, coupling constant in Hertz. Proton-decoupled carbon nuclear magnetic resonance spectra (^{13}C NMR) were recorded at 125 MHz at 22 °C. Chemical shifts are expressed in parts per million (ppm, δ scale) downfield from tetramethylsilane and are referenced to the carbon resonances of the solvent (CDCl3, δ 77.0; THF, δ 25.5, 67.7; CH_2Cl_2, δ 53.5) or to an external standard ($CFCl_3$ = 0 for ^{19}F and 85% H_3PO_4 = 0 for 31P). Two-dimensional COSY (Correlation Spectroscopy) and Heteronuclear Multiple Quantum Coherence (HMQC) were recorded at 500 MHz at 22 °C. Gas chromatography was performed using an HP 6890 series gas chromatograph equipped with an HP-5 column (25 m, 0.2 mm I.D., 0.33 μm film). GC/MS analyses were performed on an Agilent 6890N GC equipped with a 5973 MS and an HP-5ms column (30 m x 0.25 mm ID x 0.25 μm film). HPLC analyses were carried out on a Waters chromatography system (1525 binary pump, 717+autosampler, 2487 dual wavelength detector). Elemental analyses were obtained at the University of Illinois Microanalysis Laboratory.

Materials. Commercial solvents and reagents were used as received with the following exceptions. Tetrahydrofuran, dichloromethane and benzene were deoxygenated and dried by sparging with argon and passing through columns of activated alumina and supported copper according to the method of Pangborn et al.[2] Aniline, *N*-methylaniline and octylamine were all dried over KOH, distilled under reduced pressure and freeze pump thawed before transferring into the drybox. Sodium dimethylmalonate was prepared by the reaction of 1 equiv. of the corresponding malonate with 1 equiv NaH in THF or THF-*d*8 directly before use. Lithium phenolate was prepared by reaction of 1 equiv. phenol with 1 equiv. of a 2.5 molar solution of n-butyllithium in hexane at 0℃. Triethylamine was dried over $CaSO_4$ and distilled before use. All allylic carbonates (**4b, 4b-D-(*R*)** and **6**) were synthesized by the reaction of the corresponding allylic alcohols with alkyl chloroformate in the presence of pyridine. Monodeuterated enantioenriched alcohols (±)-(*E*)-1-[$^2H_1$]-3-Phenylprop-2-en-1-ol (corresponding to **4b-D-(*R*)**) and (*S*)-5-phenylpent-1-en-3-ol (corresponding to **5b-(*S*)**) were prepared according to the method described previously.[3-4] Ethylene complex **1a** was prepared according to an earlier report by our group.[5] Cinnamyliridium complex **3e** containing the ligand **1b** was prepared according to the procedure reported previously by Helmchen and coworkers.[6]

Synthesis of allylic trifluoroacetates: Triethylamine (1.2 euiv.) was added to the solution of allylic alcohol (1 equiv) in THF (0.5 M). The resulting solution was cooled to 0℃, and acetic acid anhydride (1 equiv.) was added. The reaction mixture was allowed to stir for 4 hours while allowing the system to reach room temperature. The solvents were removed under reduced pressure, and the crude product was purified by column chromatography over silica gel with 8:2 hexane:EtOAc as the eluent.

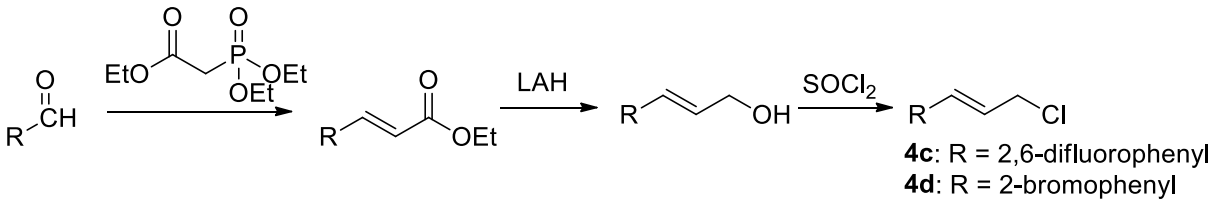
Cinnamyl trifluoromethylacetate, 4a: Colorless oil, 97% isolated yield. ^{1}H NMR (499 MHz, Benzene) δ 7.07 – 6.97 (m, 5H), 6.21 (d, J = 15.9 Hz, 1H), 5.74 (dt, J = 15.9, 6.8 Hz, 1H), 4.29 (d, J = 6.8 Hz, 1H). ^{13}C NMR (126 MHz, Benzene) δ 157.2 (q, J_F = 42.0 Hz), 136.8, 135.6, 128.7, 128.6, 127.0, 120.1, 115.1 (q, J_F = 285.8 Hz), 68.4.

5-phenylpent-1-en-3-yl 2,2,2-trifluoroacetate, 5b: Colorless oil, 80% isolated yield**.** ^{1}H NMR (499 MHz, $CDCl_3$) δ 7.36 – 7.29 (m, 2H), 7.29 – 7.22 (m, 1H), 7.19 (dd, J = 7.8, 0.9 Hz, 2H), 5.91 – 5.81 (m, 1H), 5.45 – 5.32 (m, 3H), 2.81 – 2.61 (m, 2H), 2.22 – 2.11 (m, 1H), 2.10 – 2.00 (m, 1H). ^{13}C NMR (126 MHz, $CDCl_3$) δ 156.9 (q, J_F = 41.6 Hz), 140.4, 134.0, 128.7, 128.4, 126.5, 119.7, 114.7 (q, J_F = 287.0 Hz), 79.1, 35.5, 31.2.

5-phenylpent-2-en-1-yl 2,2,2-trifluoroacetate, 5l: Colorless oil, 88% yield. ^{1}H NMR (499 MHz, $CDCl_3$) δ 7.40 – 7.12 (m, 5H), 6.01 – 5.92 (m, 1H), 5.71 – 5.59 (m, 1H), 4.79 (d, J = 6.7 Hz, 2H), 2.80 – 2.71 (m, 2H), 2.51 – 2.37 (m, 2H). ^{13}C NMR (126 MHz, $CDCl_3$) ^{13}C NMR (126 MHz, $CDCl_3$) δ 157.6 (q, J_F = 42.2 Hz), 141.4, 138.8, 128.6, 126.3, 122.3, 122.4, 114.8 (q, J_F = 285.8 Hz), 68.8, 35.3, 34.2.

Synthesis of allylic chlorides:
Allylic chlorides **4c** and **4d** were prepared starting from corresponding aldehydes by a Horner-Wadsworth-Emmons reaction, followed by reduction with lithium aluminum hydride to form the allylic alcohol. The allylic alcohol was subsequently converted to the allylic chloride with $SOCl_2$ to give **4c** or **4d** (Scheme S1).

Scheme S1



(2,6-difluoro)cinnamylchloride, 4c: ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.22 – 7.12 (m, 1H), 6.94 – 6.82 (m, 2H), 6.76 – 6.61 (m, 2H), 4.25 (d, J = 6.3 Hz, 2H). ^{13}C NMR (126 MHz, $CDCl_3$) δ 161.1 (dd, J_F = 252.2, 7.5 Hz), 131.8 (t, J_F = 8.2 Hz), 129.0 (t, J_F = 10.9 Hz), 120.5, 113.4, 111.7 (dd, J_F = 20.8, 5.4 Hz), 46.0.

(2-bromo)cinnamylchloride, 4d: ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.62 – 7.47 (m, 2H), 7.32 – 7.23 (m, 1H), 7.17 – 7.08 (m, 1H), 7.01 (d, J = 15.6 Hz, 1H), 6.27 (dt, J = 15.5, 7.1 Hz, 1H), 4.27 (d, J = 7.1 Hz, 2H). ^{13}C NMR (126 MHz, $CDCl_3$) δ 135.8, 133.1, 132.7, 129.6, 127.9, 127.7, 127.3, 123.9, 45.1.

Synthesis of allyliridium complexes

Cinnamyliridium complex 2c: 100 mg of Ir(I) ethylene complex **1a-(*R,R,R*)** (0.115 mmol) was dissolved in 5 ml THF, and 53.0 mg of cinnamyl trfiluoroacetate **4a** (0.230 mmol, method A) or 44.0 mg of methylcinnamyl carbonate **4b** (0.230 mmol, method B) was added to the solution. The solution was allowed to stir for 5 min, after which time 22.4 mg $AgBF_4$ (0.115 mmol) was added. Large amounts of dark precipitate formed quickly upon addition of the $AgBF_4$. The precipitate was removed by syringe filtration through a 25 mm diameter and 0.2 μm pore size filter, and the filtrate was added dropwise to 10 ml of pentane while stirring vigorously. The precipitated product was collected by filtration and died under vacuum to give 90 mg (75%, Method A) or 96 mg (80%, Method B) of allyliridium complex **2c** after drying. Crystals suitable for single-crystal structural analysis were obtained by dissolving **2c** in a small amount THF and layering with benzene. Anal. Calc'd for $C_{59}H_{56}BF_4IrNO_2P$: C, 63.21; H, 5.03; N, 1.25. Found: C, 63.45; H, 5.21; N, 1.45. ^{1}H NMR (500 MHz, CD_2Cl_2) δ 8.32 (d, *J* = 8.9 Hz, 1H), 8.25 (d, *J* = 8.8 Hz, 1H), 8.14 – 8.07 (m, 2H), 7.84 (d, *J* = 8.8 Hz, 1H), 7.71 (d, *J* = 8.8 Hz, 1H), 7.67 – 7.56 (m, 4H), 7.56 – 7.34 (m, 15H), 7.22 – 7.15 (m, 2H), 5.63 (t, *J* = 12.1 Hz, 1H), 5.26 – 5.14 (m, 1H), 4.93 – 4.78 (m, 1H), 4.24 – 4.14 (m, 1H), 4.02 – 3.88 (m, 2H), 3.56 – 3.47 (m, 1H), 3.02 – 2.89 (m, 2H), 2.89 – 2.71 (m, 2H), 2.55 – 2.38 (m, 2H), 2.27 – 2.16 (m, 1H), 2.15 – 2.04 (m, 2H), 1.93 – 1.79 (m, 1H), 1.69 – 1.54 (m, 2H), 1.24 (t, *J* = 12.3 Hz, 1H), 0.61 (d, *J* = 7.4 Hz, 3H). ^{13}C NMR (126 MHz, CD_2Cl_2) δ 148.83, 148.70, 147.50, 147.43, 142.42, 142.32, 140.22, 133.96, 133.91, 133.17, 132.92, 132.24, 132.19, 132.10, 131.95, 129.92, 129.68, 128.97, 128.87, 128.78, 128.67, 128.56, 128.54, 128.49, 128.40, 128.36, 127.61, 127.57, 127.38, 127.17, 126.67, 126.54, 126.24, 124.49, 122.80, 121.93, 121.19, 121.16, 120.97, 101.48, 97.22, 92.84, 91.02, 86.55, 84.15, 66.12, 65.87, 60.62, 39.95, 35.08, 33.32, 28.13, 26.85, 18.66, 17.47. ^{31}P NMR (202 MHz, THF) δ 118.5.

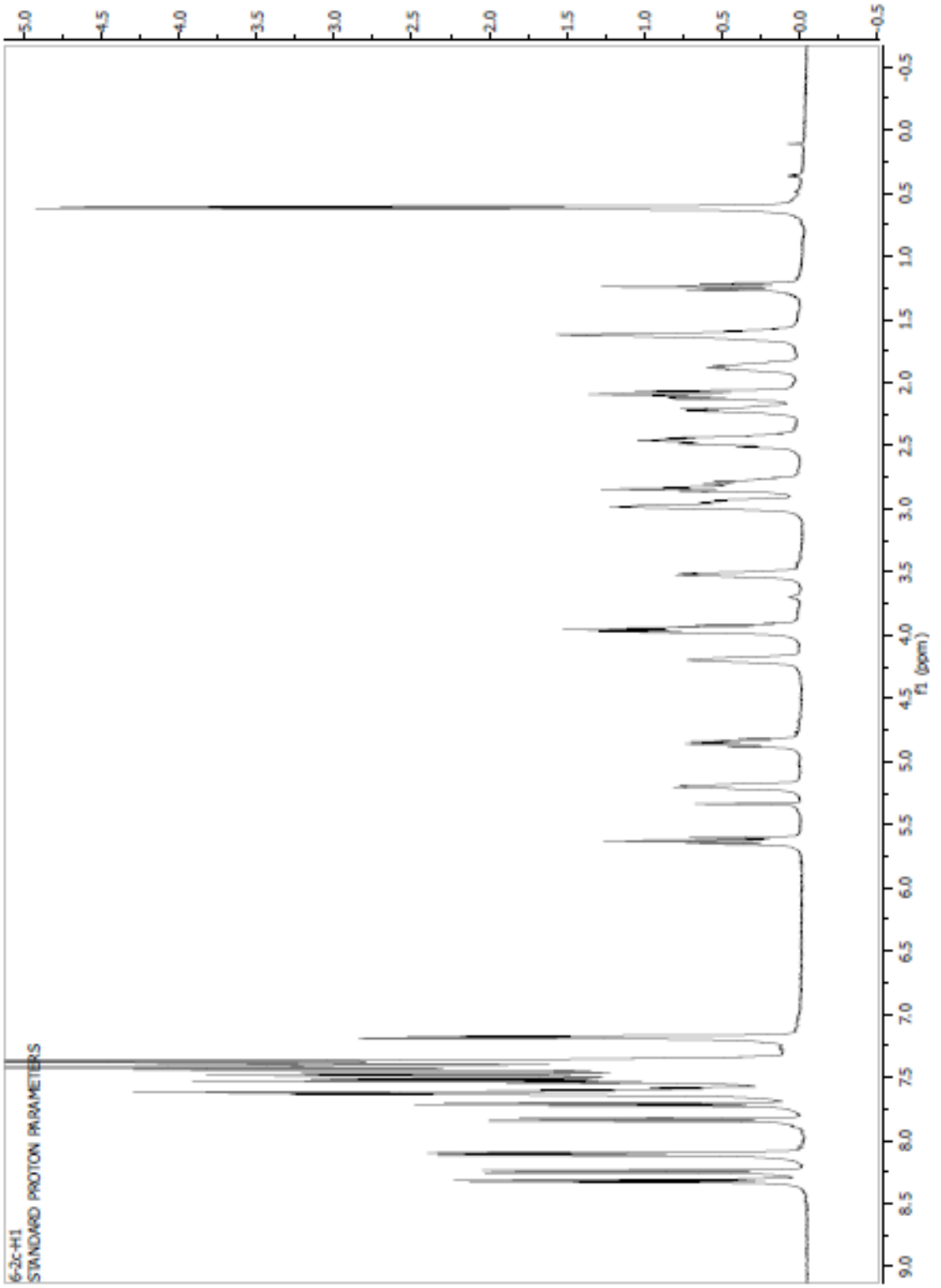
(2,6-difluoro)cinnamyliridium complex 2d: 100.0 mg of Ir(I) ethylene complex **1a-(*R,R,R*)** (0.115 mmol) was dissolved in 5 ml benzene, and 23.9 mg (2,6-difluoro)cinnamylchloride **4c** (0.127 mmol) was added. The resulting solution was added to a solution for 22.4 mg $AgBF_4$ (0.115 mmol) in 2 ml THF, and the resulting mixture was allowed to stir vigorously for 15 min. The precipitate was removed by syringe filtration through a 25 mm diameter and 0.2 μm pore size filter, and the filtrate was left in an argon-filled dry-box with the cap slightly unscrewed for 48 h. Complex **4c** (86 mg, 65% yield) crystallized and was collected after drying under vacuum. Anal. Calc. for $C_{59}H_{54}BF_6IrNO_2P$: 61.24; H, 4.70; N, 1.21. Found: C, 61.32; H, 4.81; N, 1.33. ^{1}H NMR (500 MHz, THF) δ 8.30 (d, *J* = 8.9 Hz, 1H), 8.22 (d, *J* = 8.8 Hz, 1H), 8.08 (dd, *J* = 8.2, 2.8 Hz, 2H), 7.81 (d, *J* = 8.8 Hz, 1H), 7.68 (d, *J* = 8.8 Hz, 1H), 7.64 – 7.54 (m, 2H), 7.51 – 7.44 (m, 3H), 7.42 – 7.30 (m, 10H), 7.17 – 7.11 (m, 2H), 7.06 (dd, *J* = 10.4, 8.6 Hz, 2H), 5.58 (t, *J* = 12.3 Hz, 1H), 5.48 – 5.37 (m, 1H), 5.25 (dd, *J* = 14.6, 6.4 Hz, 1H), 4.44 – 4.25 (m, 1H), 4.01 – 3.81 (m, 2H), 3.49 (dd, *J* = 20.9, 14.2 Hz, 2H), 3.20 – 3.07 (m, 1H), 2.80 (t, *J* = 7.1 Hz, 1H), 2.65 – 2.48 (m, 2H), 2.47 – 2.33 (m, 2H), 2.24 (dd, *J* = 14.6, 7.6 Hz, 1H), 1.99 (d, *J* = 11.0 Hz, 1H), 1.95 – 1.85 (m, 1H), 1.61 (dddd, *J* = 18.5, 14.4, 12.0, 6.8 Hz, 2H), 1.17 (t, *J* = 12.1 Hz, 1H), 0.58 (d, *J* = 7.4 Hz, 3H). ^{13}C NMR (126 MHz, CD_2Cl_2) δ 147.38, 141.96, 141.85, 140.02, 133.14, 132.90, 132.28, 132.20, 132.14, 132.02, 130.91, 129.63, 128.96, 128.89, 128.77, 128.75, 128.49, 128.35, 128.33, 127.69, 127.65, 127.39, 127.16, 126.76, 126.62, 126.17, 124.60, 120.97, 120.95, 120.89, 120.88, 113.66, 113.47, 110.00, 102.39, 93.98, 93.22, 85.34, 74.30, 74.06, 66.42, 66.18, 60.59, 60.55, 54.09, 53.87, 53.65, 53.44, 53.22, 40.48, 35.21, 35.11, 27.88, 27.64, 18.45. ^{31}P NMR (202 MHz, THF) δ 115.6.

(2-bromo)cinnamyliridium complex 2e: Ir(I) ethylene complex **1a-(*R,R,R*)** (50.0 mg, 0.058 mmol) was dissolved in 3 ml of either benzene, THF or CH_2Cl_2. (2-bromo)cinnamylchloride (26.8 mg, 0.115 mmol) (**4d**) was added to the solution. The resulting solution was added to 11.3 mg of $AgBF_4$ (0.058 mmol) dissolved in 1 ml of THF and allowed to stir vigorously for 15 min. The resulting precipitate was removed by filtration through a 25 mm diameter, 0.2 μm pore size filter, and the filtrate was added dropwise to 10 ml of pentane while stirring vigorously. The precipitated product was collected on a glass frit and dried under vacuum. Yield: 40 mg (60%) from the reaction in benzene, 31 mg (50%) from the reaction in THF, and 36 mg (55%) from the reaction in CH_2Cl_2. Crystals suitable for solid-state structural analysis were obtained by dissolving the complex in a small amount of THF and layering the resulting solution with benzene. Anal. Calc. for $C_{59}H_{55}BBrF_4IrNO_2P$: 59.05; H, 4.62; N, 1.17. Found: C, 59.17; H, 4.76; N, 1.39. ^{1}H NMR (500 MHz, CD_2Cl_2) δ 8.33 (d, *J* = 8.9 Hz, 1H), 8.25 (d, *J* = 8.8 Hz, 1H), 8.11 (dd, *J* = 8.2, 2.6 Hz, 2H), 7.85 (d, *J* = 8.8 Hz, 1H), 7.76 (dd, *J* = 7.8, 1.3 Hz, 1H), 7.71 (d, *J* = 8.8 Hz, 1H), 7.66 – 7.57 (m, 3H), 7.55 (t, *J* = 7.6 Hz, 2H), 7.50 – 7.31 (m, 12H), 7.24 – 7.13 (m, 2H), 5.90 (t, *J* = 12.0 Hz, 1H), 5.40 – 5.27 (m, 1H), 5.02 – 4.87 (m, 1H), 4.35 (d, *J* = 5.3 Hz, 1H), 4.07 – 3.86 (m, 2H), 3.64 – 3.56 (m, 1H), 3.23 (b, *J* = 9.3 Hz, 2H), 2.75 (t, *J* = 6.8 Hz, 1H), 2.56 – 2.39 (m, 3H), 2.35 (dd, *J* = 12.0, 4.5 Hz, 1H), 2.24 (dd, *J* = 14.5, 7.8 Hz, 1H), 2.02 (d, *J* = 10.6 Hz, 1H), 1.95 (b, *J* = 19.2 Hz, 1H), 1.74

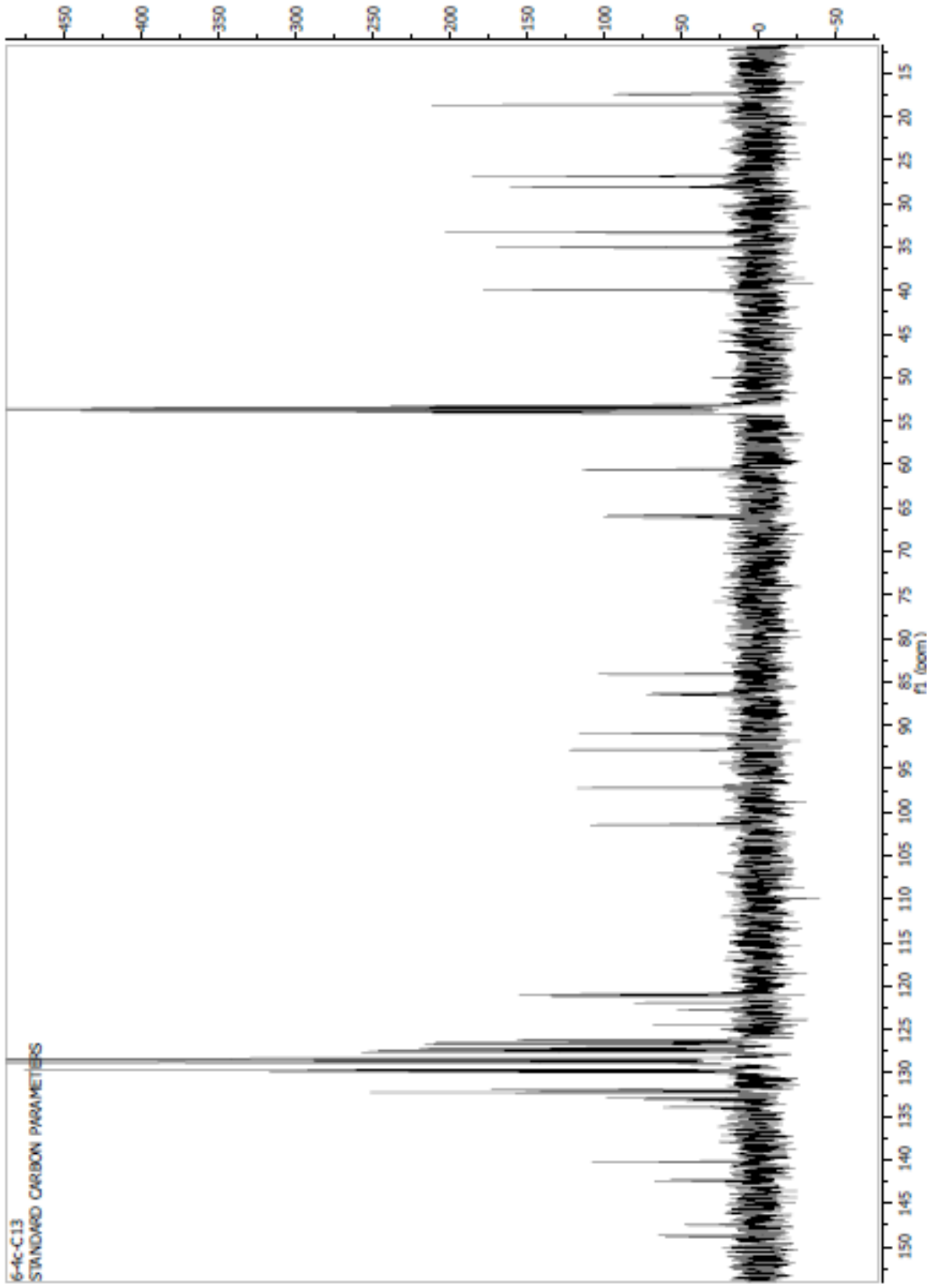
– 1.53 (m, 2H), 1.39 (t, *J* = 12.4 Hz, 1H), 0.61 (d, *J* = 7.4 Hz, 3H). ^{13}C NMR (126 MHz, CD_2Cl_2) δ 148.74, 148.62, 147.47, 147.40, 142.12, 142.02, 139.99, 135.21, 134.09, 134.03, 133.17, 132.93, 132.28, 132.20, 132.15, 132.06, 130.48, 129.75, 129.12, 128.96, 128.89, 128.79, 128.70, 128.52, 128.42, 127.67, 127.63, 127.42, 127.16, 126.75, 126.61, 126.35, 122.76, 121.86, 121.08, 120.94, 103.13, 99.14, 94.38, 93.15, 86.13, 85.92, 85.66, 65.88, 65.63, 60.66, 38.22, 37.17, 35.07, 28.82, 27.80, 18.58, 16.19. ^{31}P NMR (202 MHz, THF) δ 118.5. ^{31}P NMR (202 MHz, THF) δ 115.4.

Phenethylallyliridium complex 2f-BF_4: 100.0 mg of $[Ir(COD)Cl]_2$ (0.149 mmol) and 160.7 mg phosphoramidite ligand **L1a-(*R,R,R*)** (0.298 mmol) were dissolved in 4 ml THF and 58.0 mg $AgBF_4$ (0.298 mmol) dissolved in 1 ml THF was added to the resulting solution followed by 132.0 mg of methyl (5-phenylpent-2-en-1-yl) carbonate. The reaction mixture was allowed to stir for 12 h. The large amount of white precipitate that forms over the course of the reaction was filtered out by syringe filtration through a 25 mm diameter, 0.2 μm pore size filter. The filtrate was added dropwise to 15 ml pentane while stirring vigorously. The precipitated product was collected over a glass frit and dried under vacuum. Yield: 271 mg (85%). ^{1}H NMR (500 MHz, CD_2Cl_2) δ 8.32 (d, *J* = 8.9 Hz, 1H), 8.23 (d, *J* = 8.8 Hz, 1H), 8.11 (dd, *J* = 7.6, 6.4 Hz, 2H), 7.84 (d, *J* = 8.8 Hz, 1H), 7.67 (d, *J* = 8.8 Hz, 1H), 7.64 – 7.59 (m, 2H), 7.49 (t, *J* = 7.5 Hz, 2H), 7.46 – 7.27 (m, 15H), 7.08-7.18 (m, 2H), 5.08 (dd, *J* = 13.9, 7.8 Hz, 1H), 4.45 (dd, *J* = 19.2, 10.9 Hz, 1H), 4.19 (dd, *J* = 8.3, 4.0 Hz, 1H), 3.99-3.79 (m, 2H), 3.66 (dd, *J* = 11.8, 5.6 Hz, 1H), 3.38 – 3.20 (m, 2H), 3.12 (dtd, *J* = 21.0, 13.9, 7.4 Hz, 2H), 3.00 (dd, *J* = 14.6, 8.2 Hz, 1H), 2.79 (t, *J* = 7.7 Hz, 1H), 2.76 – 2.66 (m, 1H), 2.55 – 2.40 (m, 2H), 2.39 – 2.26 (m, 1H), 2.20-2.07 (m, 2H), 1.92 (d, *J* = 11.3 Hz, 1H), 1.89 – 1.80 (m, 1H), 1.71 – 1.50 (m, 3H), 1.10 (t, *J* = 11.8 Hz, 1H), 0.58 (d, *J* = 7.4 Hz, 3H). ^{31}P NMR (202 MHz, $CDCl_3$) δ 120.57. ^{13}C NMR (126 MHz, CD_2Cl_2) δ 146.81, 145.44, 140.35, 140.26, 138.67, 138.29, 131.21, 130.94, 130.15, 129.89, 127.51, 127.06, 126.91, 126.70, 126.52, 126.28, 125.55, 125.39, 125.15, 124.75, 124.65, 124.50, 124.31, 120.81, 119.94, 119.13, 119.02, 103.71, 100.51, 90.51, 86.70, 80.47, 76.19, 75.94, 64.03, 63.76, 58.47, 42.09, 34.81, 34.62, 32.98, 30.55, 26.09, 23.92, 16.62, 12.47.

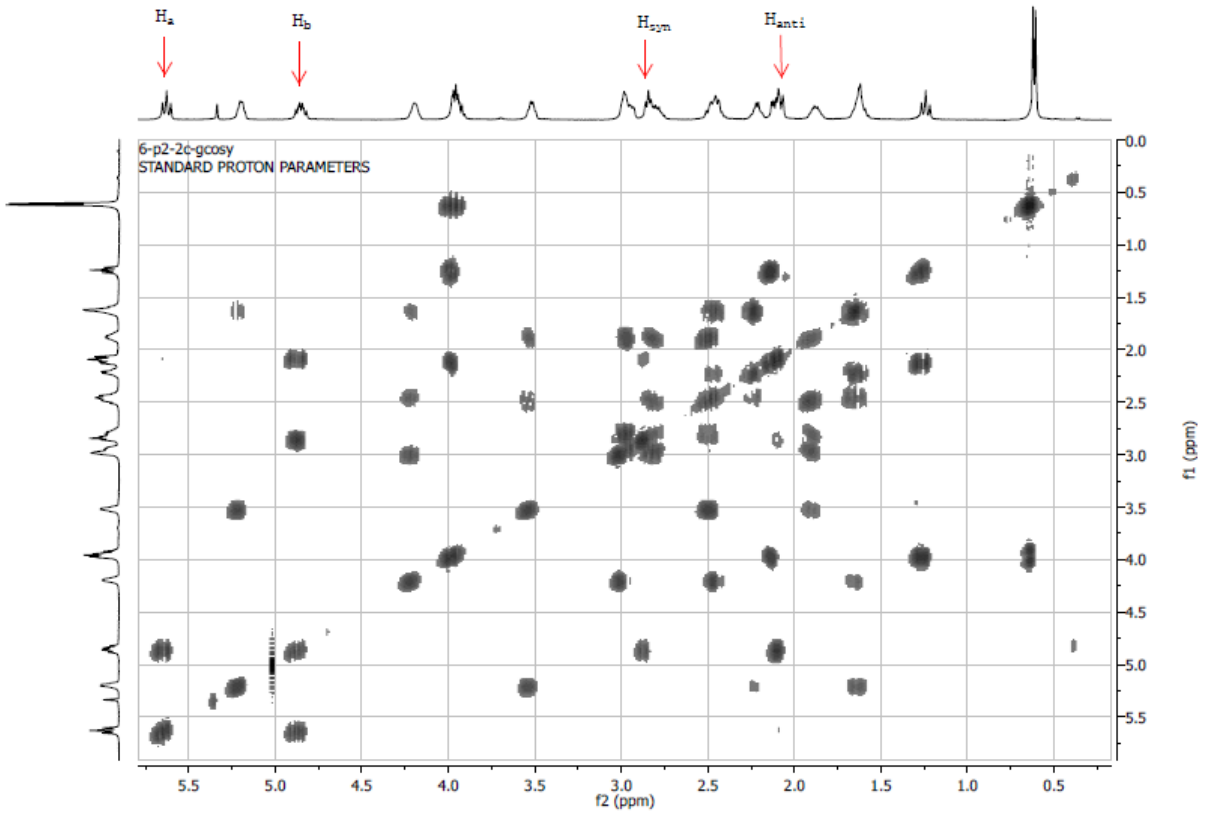
NMR spectra of allyliridium compexes.
Cinnamyliridium complex 2c:
^{1}H-NMR spectrum:



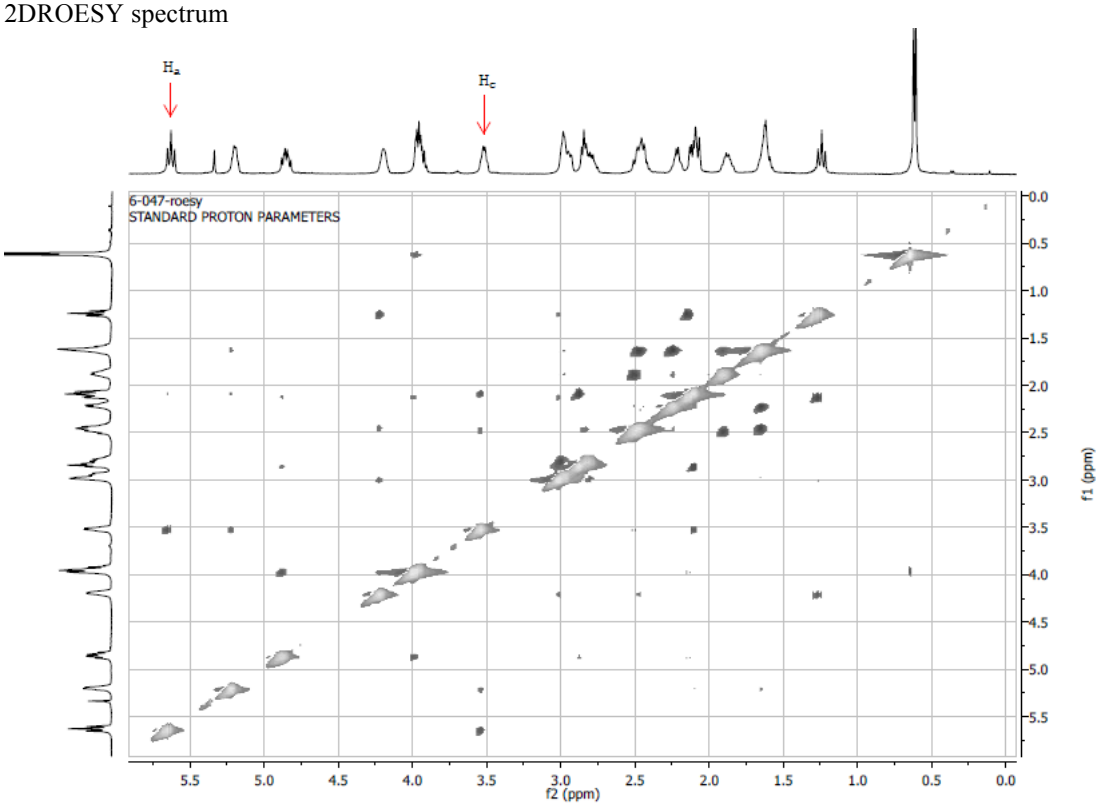
^{13}C-NMR spectrum:



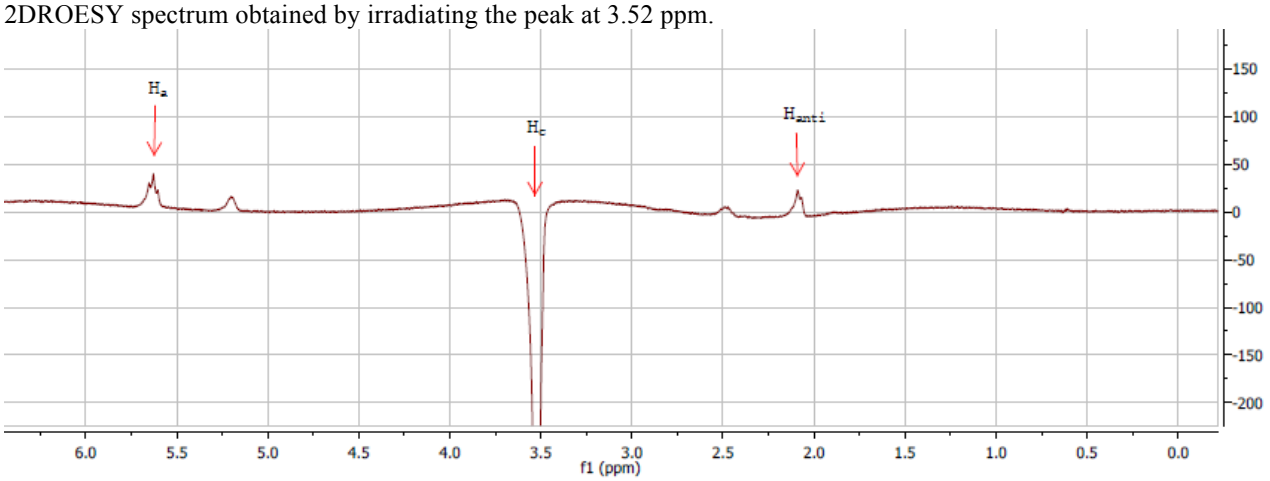
gCOSY spectrum:

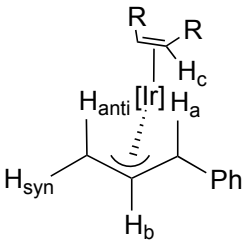


2DROESY spectrum



2DROESY spectrum obtained by irradiating the peak at 3.52 ppm.

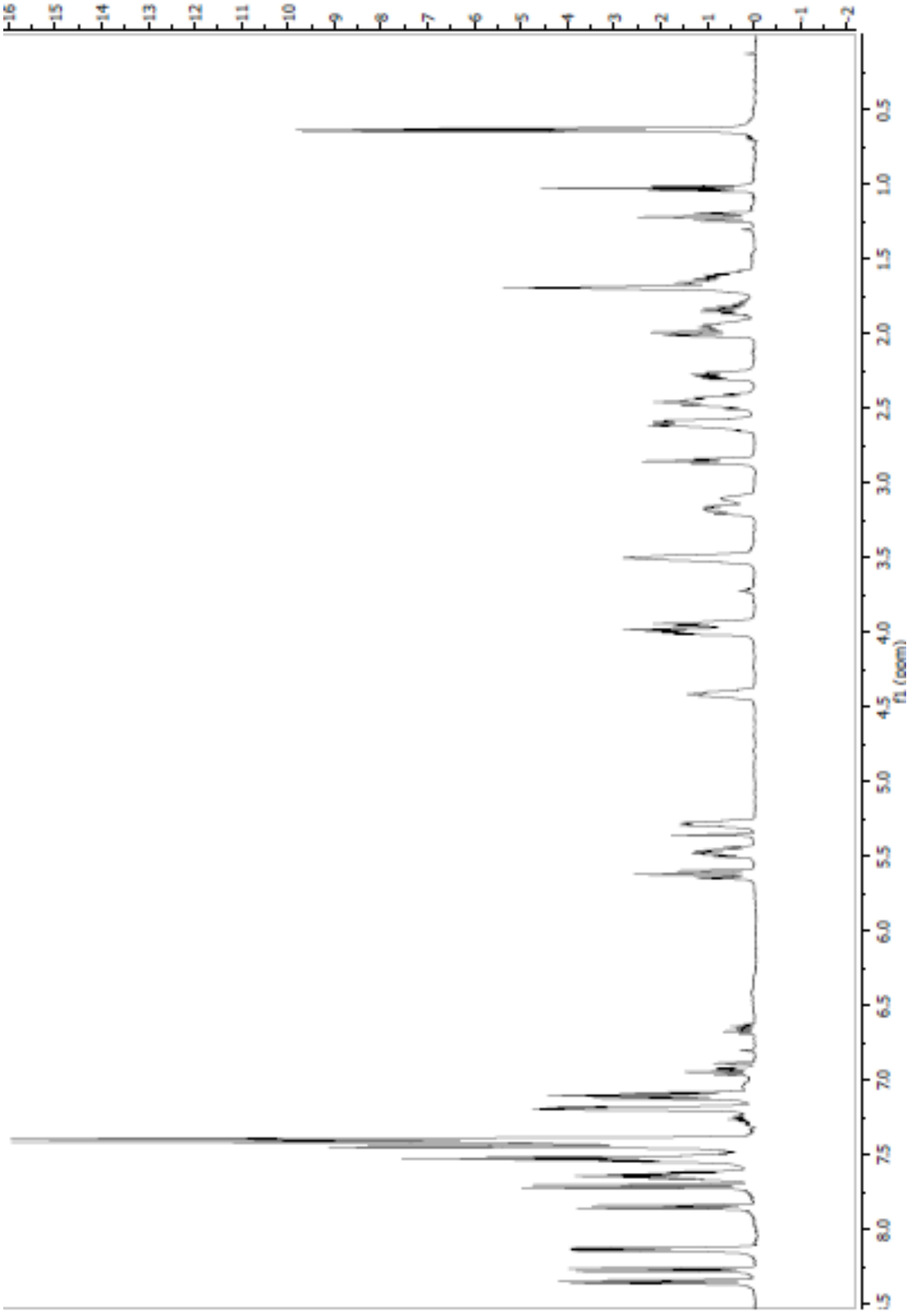




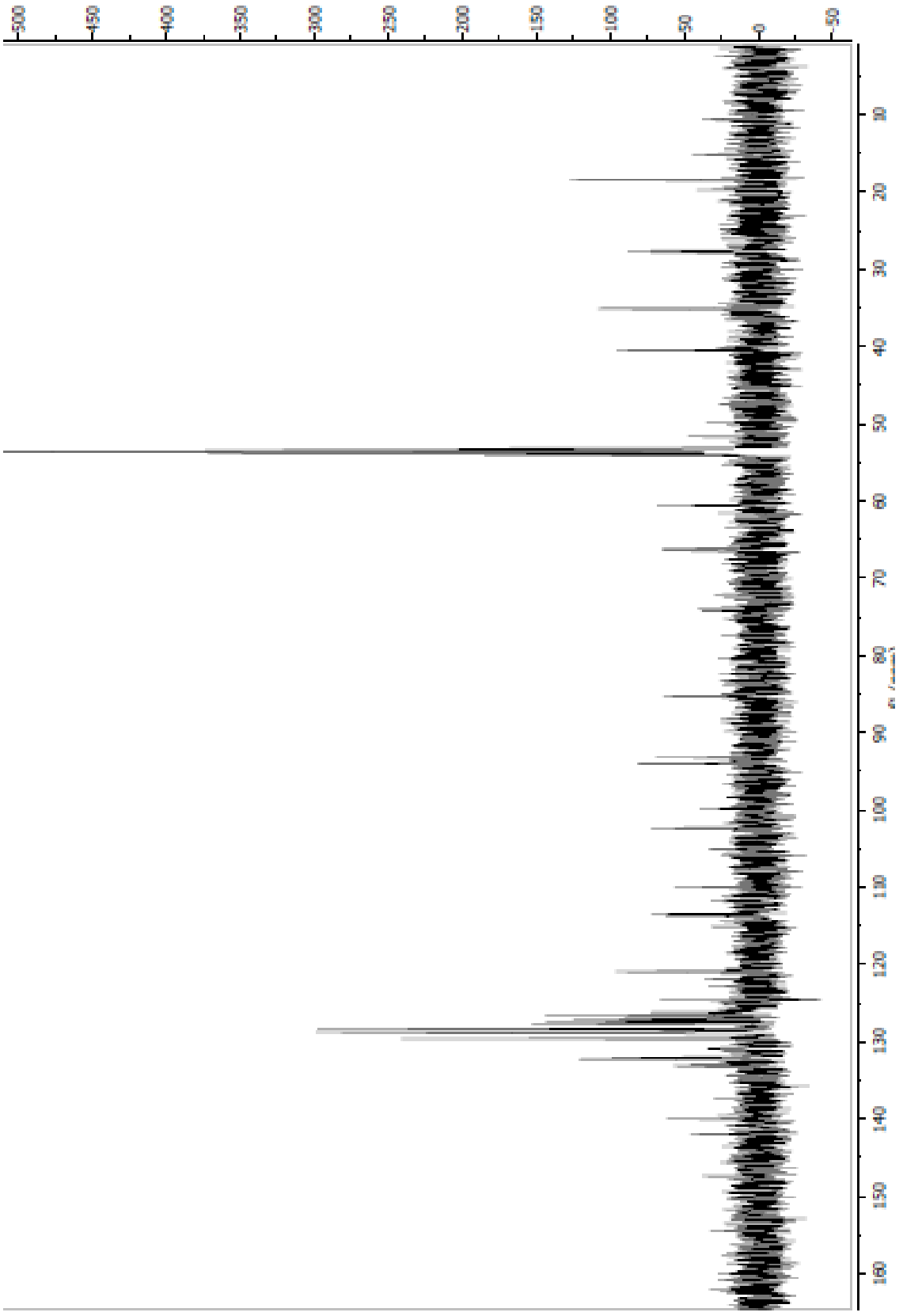
Assignment of the *anti* and *syn* allylic hydrogens:

The benzylic proton of the allyl (H_a as depicted in the figure above) should have the most downfield chemical shift among the allylic hydrogens and couple to only one other proton (H_b) in the gCOSY spectrum. Only the signal at 5.61 ppm meets these criteria; this peak was assigned to H_a. The proton coupled to H_a should be H_b and the signal at 4.85 ppm was assigned to H_b. H_b is coupled to two other protons which should be H_{anti} and H_{syn}. The signals at 2.83 and 2.05 are the remaining signals coupled to that of H_b. H_{anti} is located closer to the metal than H_{syn} (2.23 Å vs. 2.77 Å). Because of this structural feature H_{anti} will experience a stronger shielding from the metal than H_{syn}.[7-8] The peak at 2.05 ppm was, therefore, assigned to H_{anti} and the peak at 2.83 ppm was assigned to H_{syn}. This assignment of allylic protons was confirmed by 1D and 2D-ROESY NMR spectroscopy. The solid-state structure of the allyliridium complex shows that both H_a and H_{anti} should be close enough to the olefin proton (labeled as H_c) to observe an NOE (The H_a-H_c distance is 2.011 Å, and the H_{anti}-H_c distance is 2.383 Å), whereas H_{syn} is located too far (The H_{syn}-H_c distance is 4.001 Å) from H_c to observe an NOE. The 2D-ROESY NMR spectrum of the cinnamyliridium complex shows a strong NOE between H_a 5.61 ppm and the multiplet at 3.52 ppm. Thus, the multiplet at 3.52 ppm was assigned to H_c. The 2D-ROESY spectrum also shows that the peak at 3.52 ppm is close in space to the proton with a chemical shift close to 2.05 ppm. Because there are two protons at this chemical shift in ^{1}H-NMR spectrum, one corresponding to the allylic proton and the other to a proton from cyclooctadiene, we could not immediately assign the chemical shift at 2.05 ppm to H_{syn}. A 1D-ROESY spectrum was obtained with irradiation at the chemical shift of 3.52 ppm (H_c) to observe the peak shape of the coupled proton at 2.05 ppm. The peak shape of the coupled proton at 2.05 ppm is an apparent doublet, which is the peak shape observed in the ^{1}H-NMR spectrum for the allylic proton. No coupling was observed between H_c and protons with a chemical shift of 2.83. Thus the chemical shift at 2.05 ppm was assigned to H_{anti}, and the chemical shift at 2.83 ppm was assigned to H_{syn}. The outcome of the ROESY-NMR was in good agreement with our assignment of syn and anti allylic protons based on the ^{1}H NMR chemical shifts.

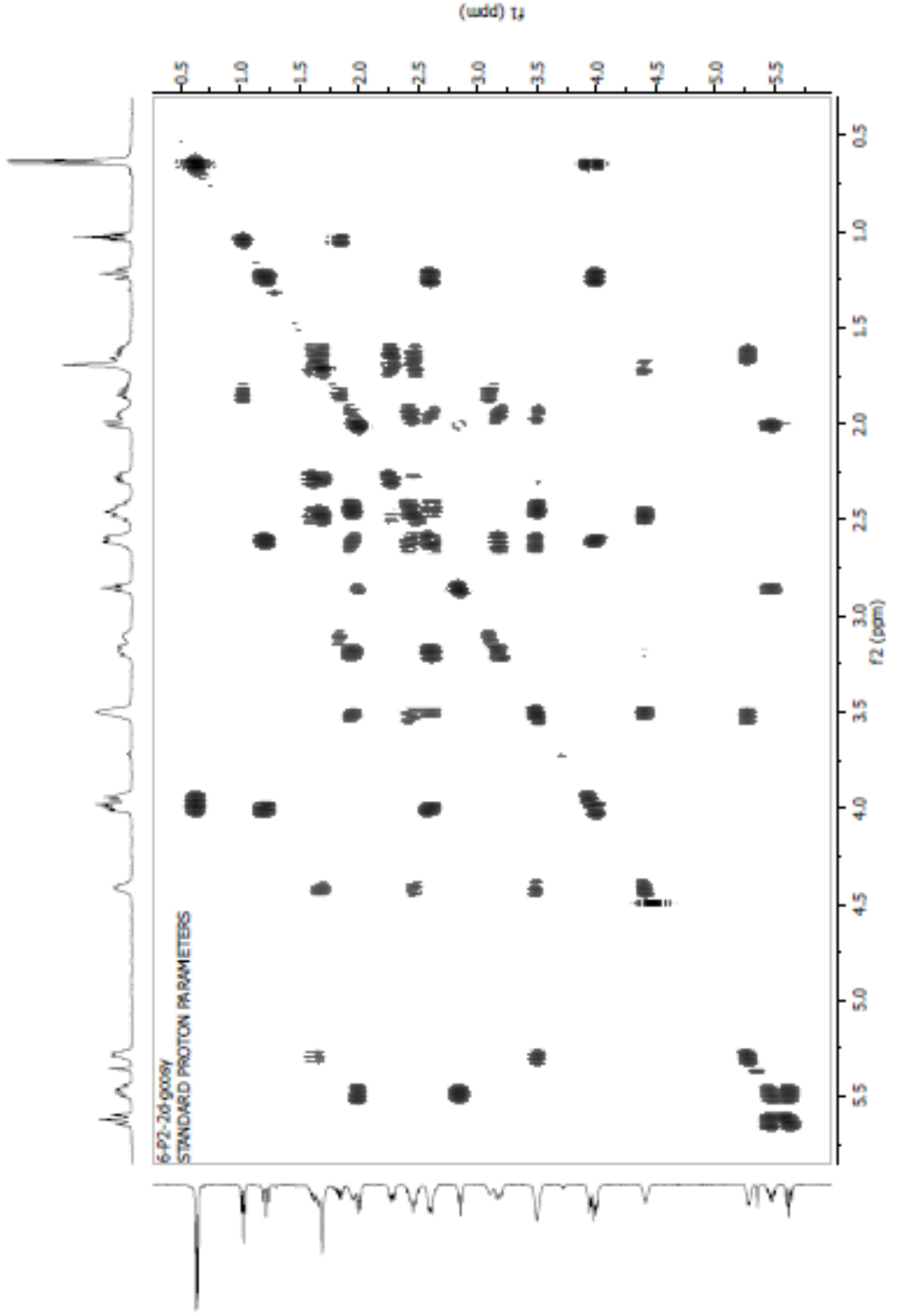
(2,6-difluoro)cinnamyliridium complex 2d:
^{1}H-NMR spectrum:



^{13}C-NMR spectrum:

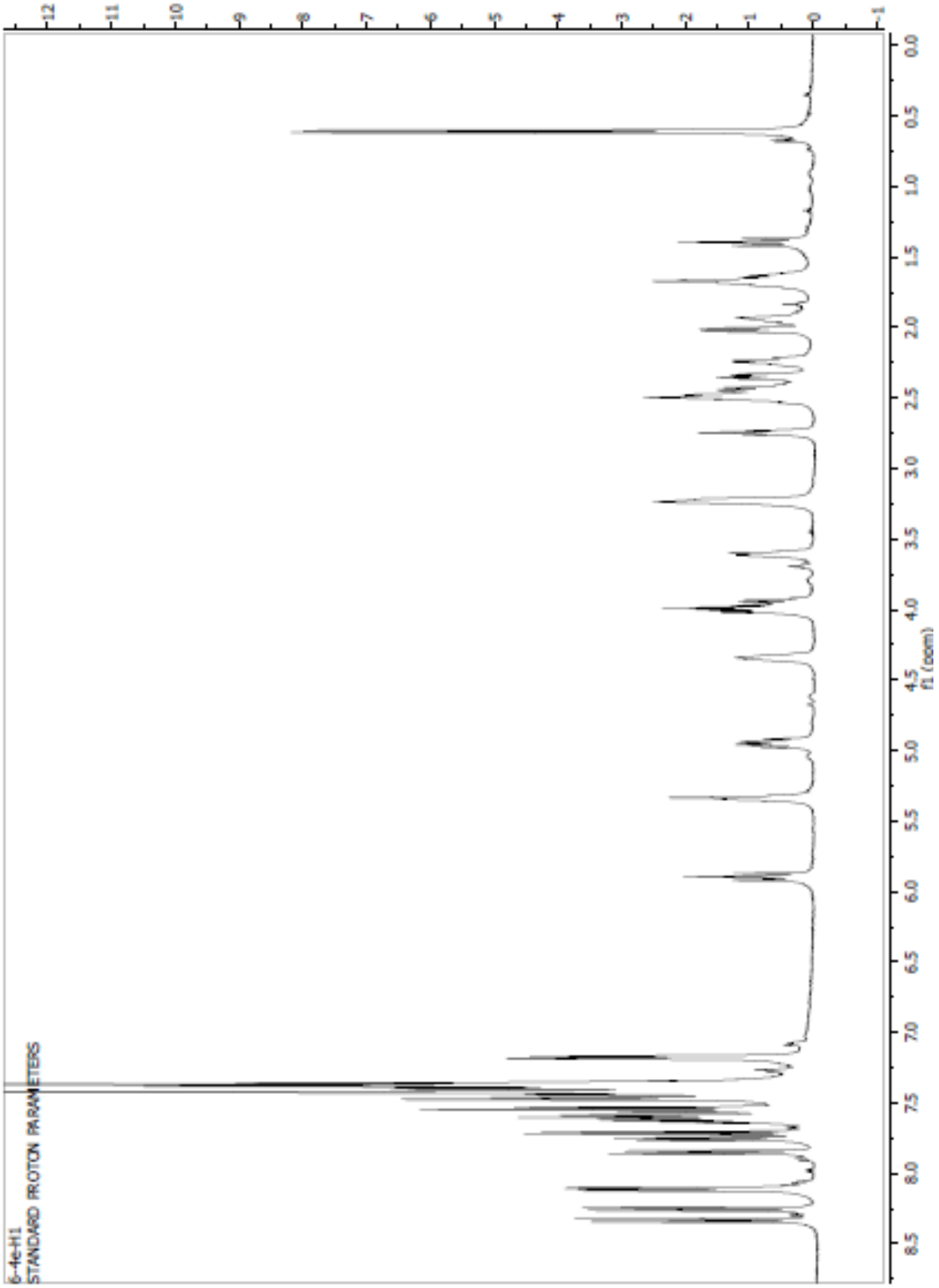


gCOSY spectrum:

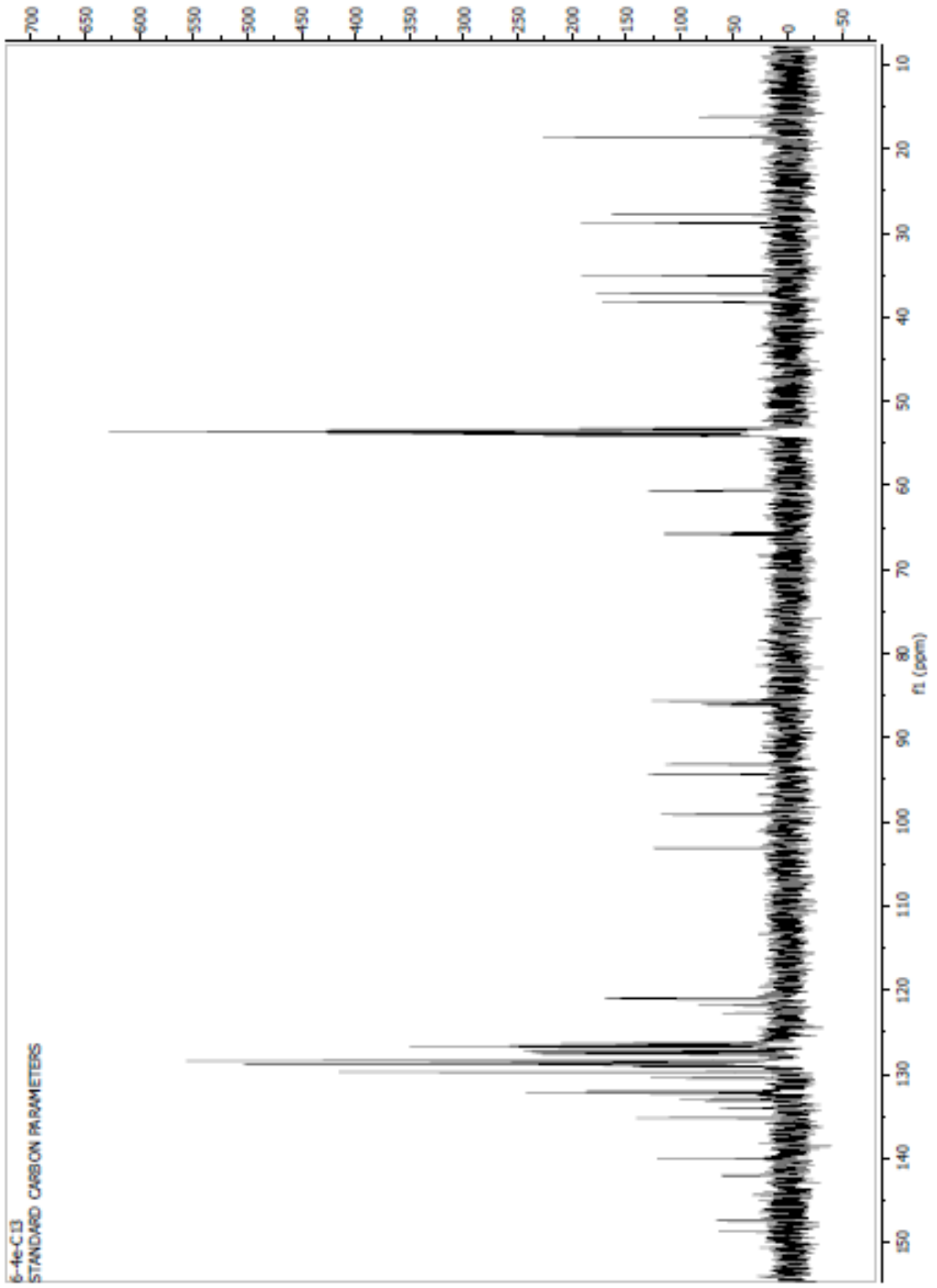


(2-bromo)cinnamyliridium complex 2e:

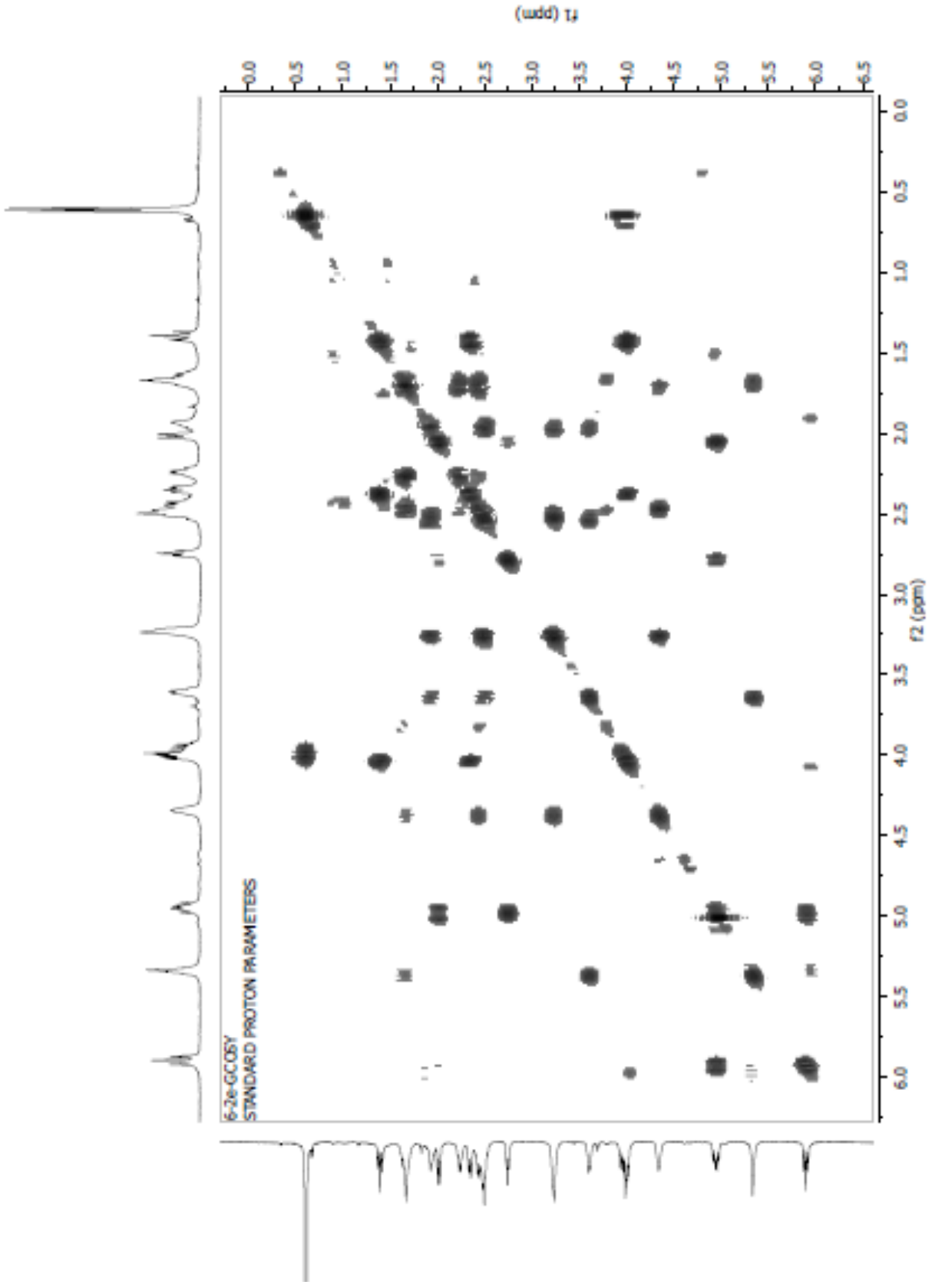
^{1}H-NMR spectrum:



^{13}C-NMR spectrum:

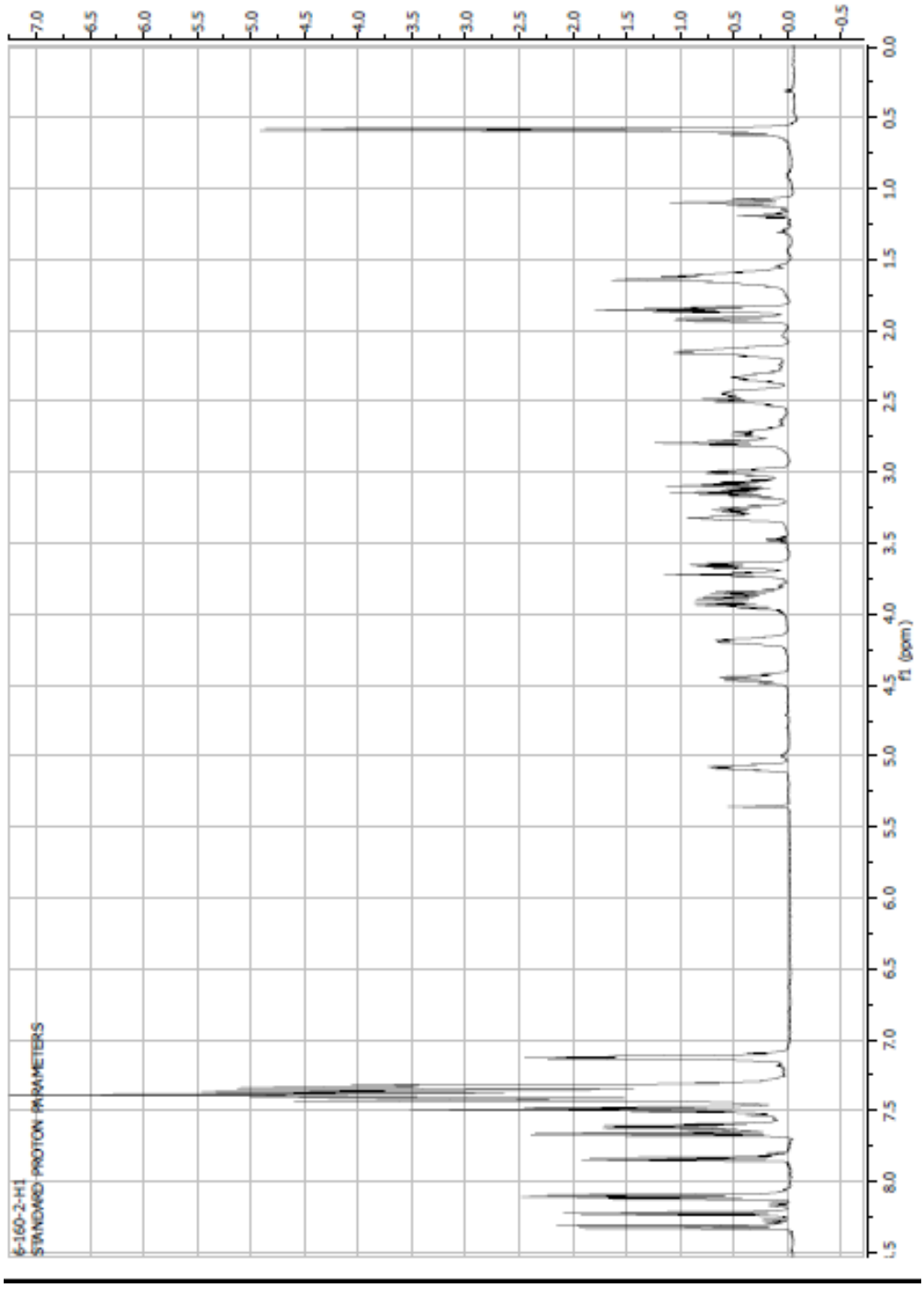


gCOSY spectrum:

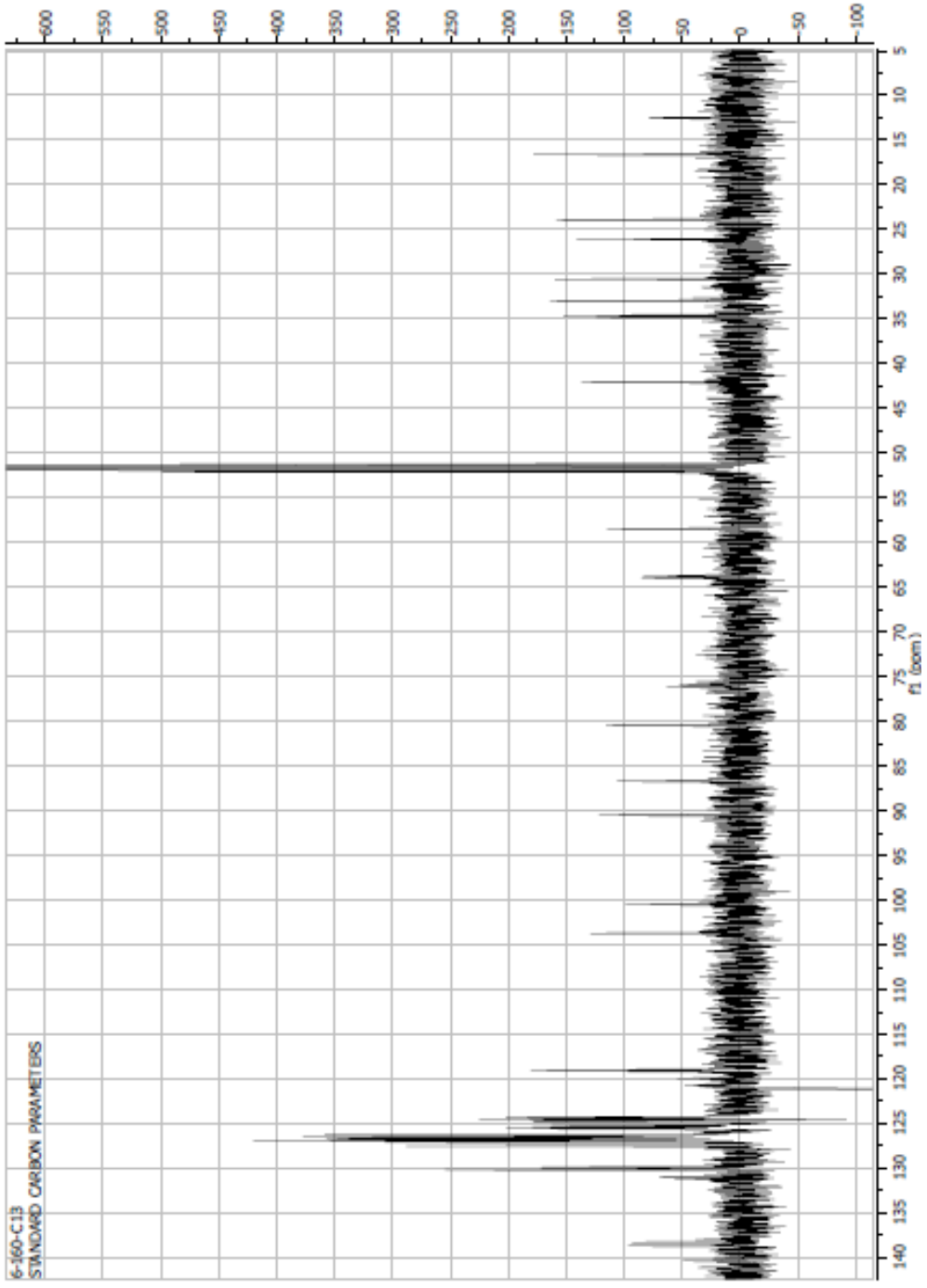


Phenethylallyliridium complex 2f-BF4

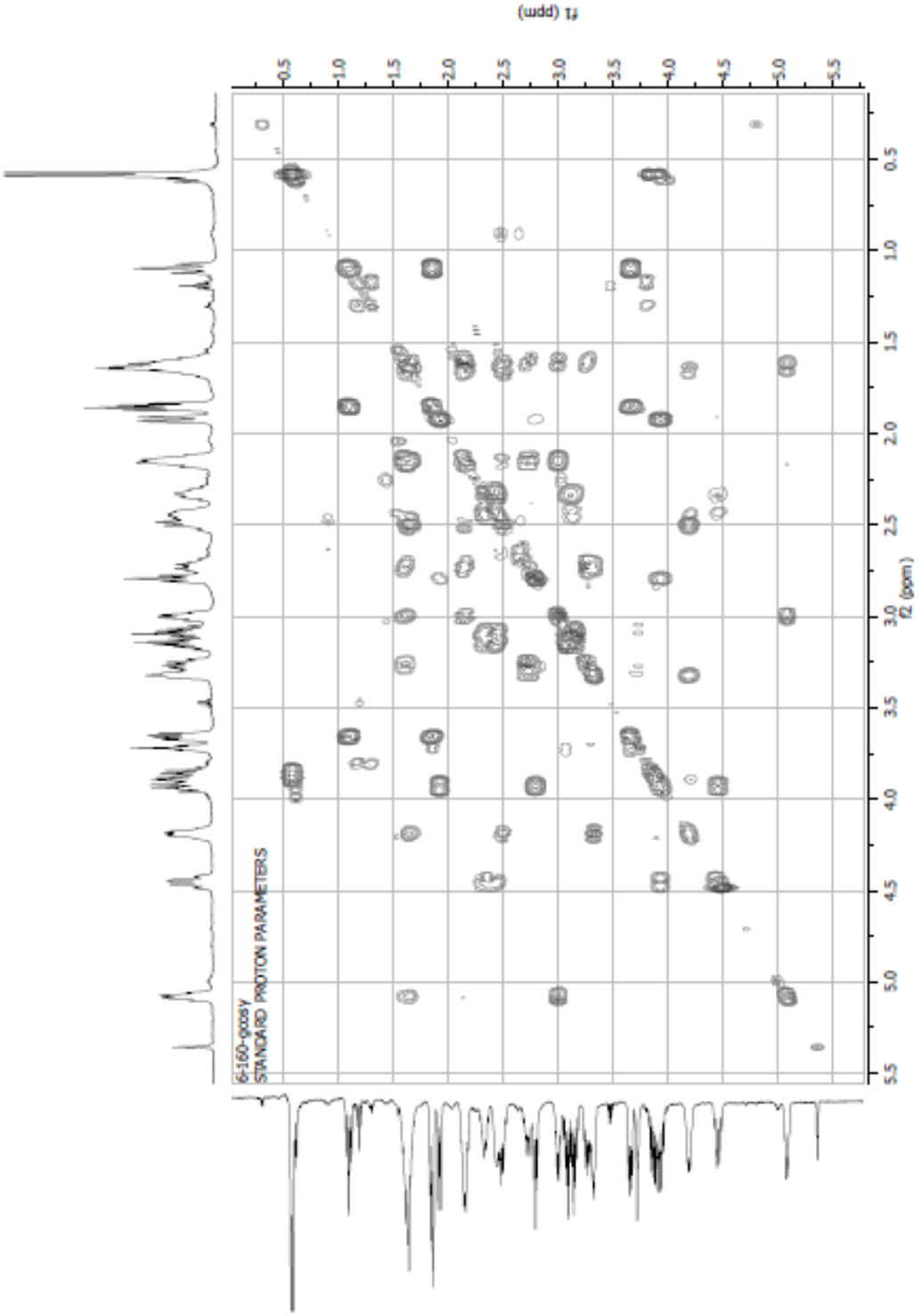
^{1}H-NMR spectrum:



^{13}C-NMR spectrum:



gCOSY spectrum:



Kinetic studies:

Rate of interconversion of allyliridium diastereomers:
General procedure for the measurement of the rate of interconversion:
1a-(*S,S,S*) (40 mg, 0.046 mmol) was dissolved in THF (1 ml for the reaction at -40℃ and 0.7 ml for the reaction at -30℃) and transferred into a screw capped NMR tube with a sealed capillary tube containing ^{31}P internal standard. The tube was placed in a dry-ice acetone bath and **5b-(*S*)** was added by syringe (62 µl, 0.28 mmol). The tube was transferred to NMR-probe cooled to -30 or -40℃ and decay of **1a-(*S,S,S*)** as well as formation and decay of **2f-TFA-(*S,S,S,R*)** was monitored.

Reaction at -40℃.

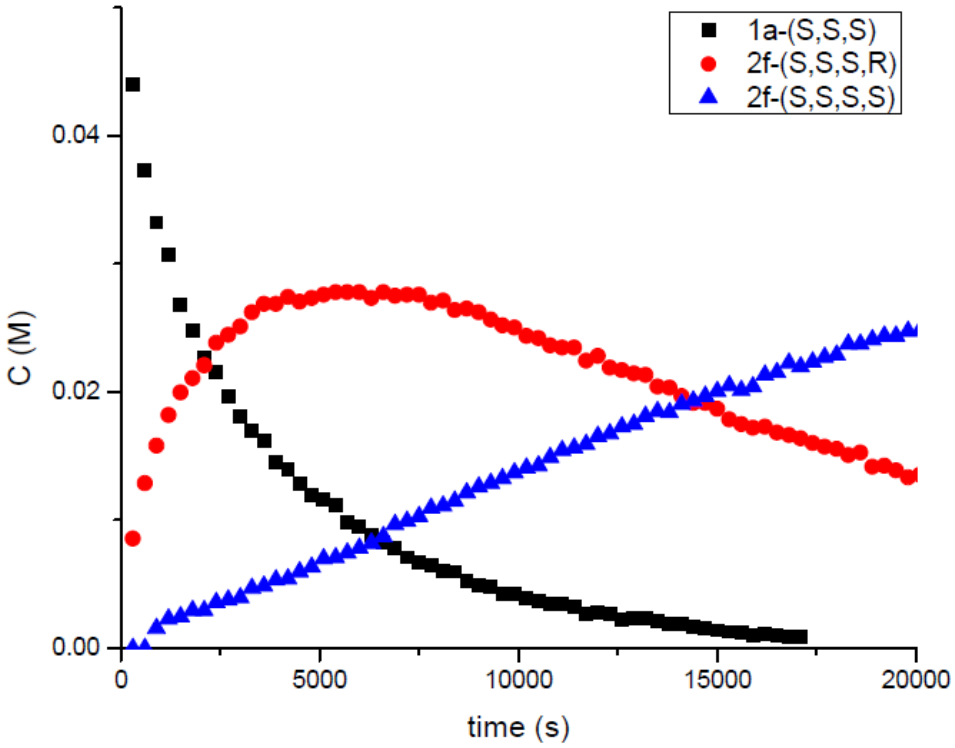


Figure S1. Plots of the change of concentration over time for **1a-(*S,S,S*), 2f-TFA-(*S,S,S,R*)** and **2f-TFA-(*S,S,S,S*)** at -40℃

The 1st order decay of **1a-(*S,S,S*)** corresponds to oxidative addition of **5b-(*S*)** to **1a-(*S,S,S*).** The rate constant for oxidative addition can be determined by plotting ln**[1a-(*S,S,S*)]** versus time.

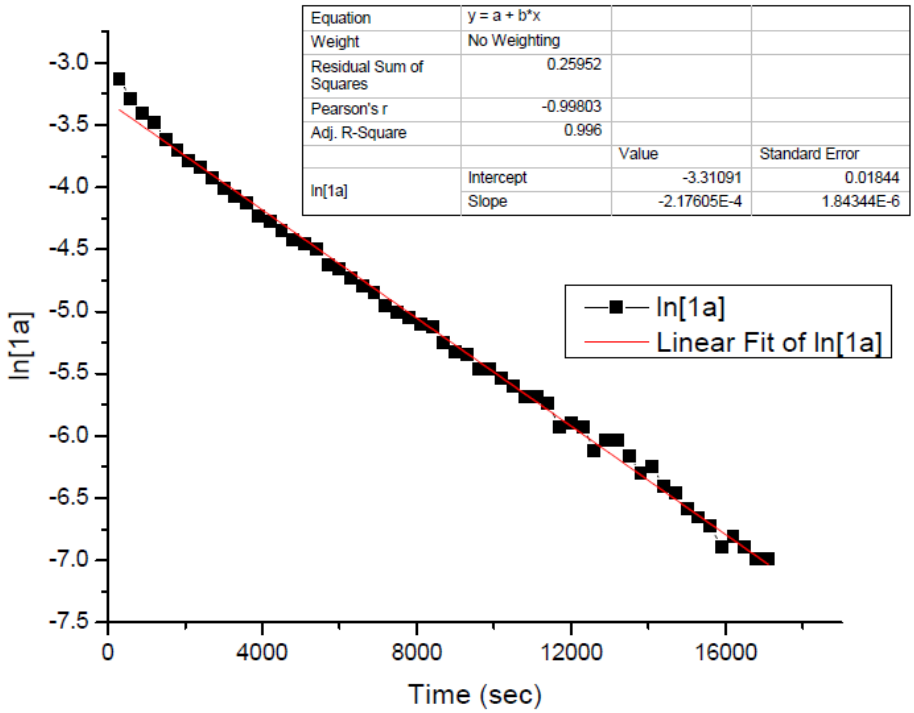


Figure S2. Plot ln**[1a-(*S,S,S*)]** versus time for the reaction of **1a-(*S,S,S*)** with **5b-(*S*)** at -40℃.

Isomerization at -30℃.

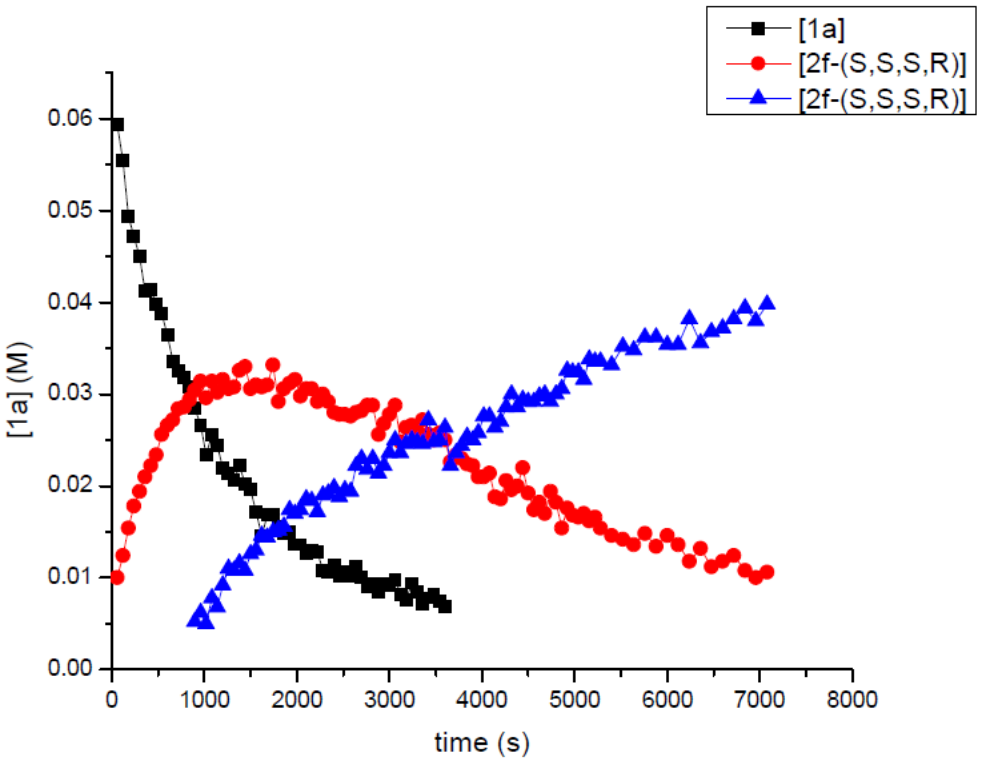


Figure S3. Plots of the change of concentration over time for **1a-(*S,S,S*)**, **2f-TFA-(*S,S,S,R*)** and **2f-TFA-(*S,S,S,S*)** at -30℃.

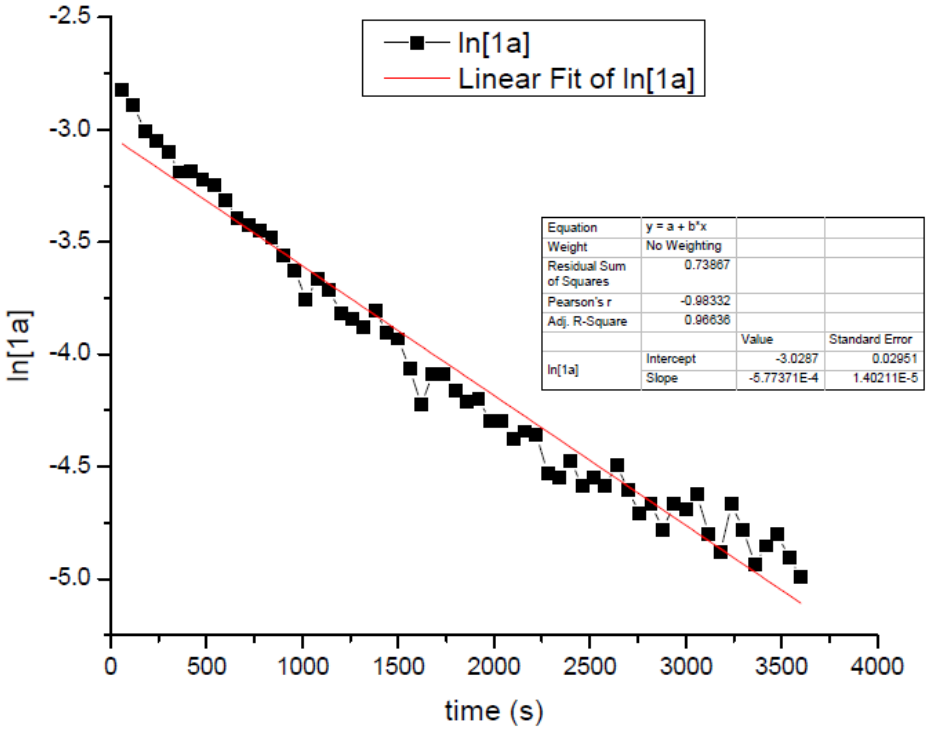


Figure S4. Plot ln[**1a-(*S,S,S*)**] versus time for the reaction of **1a-(*S,S,S*)** with **5b-(*S*)** at -30℃.

Calculation of the rate of isomerization of 2f-TFA-(*S,S,S,R*).[9-10]

2f-TFA-minor is produced by **1a-(*S,S,S*)** and depleted by production of **2f-TFA-major**. The change in concentration of **2f-TFA-minor** is governed by the relationship:

$$d[\mathbf{2f-minor}]/dt = k_1[\mathbf{1a-(S,S,S)}] - k_2[\mathbf{2f-minor}] \quad (1)$$

Integrating gives the single transcendental equation:

$$[\mathbf{2f-minor}] = \{([\mathbf{1a-(S,S,S)}]_0 k_1)/(k_2 - k_1)\}(e^{-k_1 t} - e^{-k_2 t}) \quad (2)$$

Equation 2 cannot be solved exactly but can be accurately approximated via the mathematical treatment of Emanuel.[11] Equation 2 can be simplified to

$$\beta_{max} = \kappa[\kappa/(1-\kappa)] \quad (3)$$ (this equation corresponds to the equation 2 in the paper)

where $\beta_{max} = ([\mathbf{2f-minor}]_{max}/[\mathbf{1a-(S,S,S)}]_0)$ and $\kappa = k_2/k_1$

The value of βmax was obtained directly from Figure 5 (for -40℃) or Figure S3 (for -30℃), and κ can be calculated iteratively so that equation 3 is satisfied. The value of k_2 is calculated from the product of κ and k_1.

Measurements of the rates of nucleophilic attack

The rate of nucleophlic attack on allyliridium complexes was measured by ^{31}P NMR spectroscopy on an Unity Inova 400 MHz instrument at -30, -40 or -60℃. The rate constants for nucleophilic attack on allyliridium complexes **2c**, **2d, 2f(*S,S,S,S*)** and **3c** were determined by conducting reactions of the complexes with 10 equiv of tetrabutyl ammonium acetate or a combination of 25 equiv of primary or a secondary amine nucleophile and 25 equiv of triethylamine as proton acceptor. The rate constants were determined by measuring the decay of the ^{31}P-NMR signal of the starting iridium complex. The rate constants for nucleophilic attack were determined by plotting the natural logarithms of concentration vs. time.

Reaction of 2c with aniline at -30℃ in CH_2Cl_2 (table 2, entry 1)

Complex 2c (20.0 mg, 0.0178 mmol) was dissolved in 0.6 ml CH_2Cl_2 and transferred into a screw capped NMR tube and cooled in a dry-ice acetone bath. 41 µl of aniline (0.45 mmol) and 62 µl of triethylamine (0.45 mmol) were added to the NMR tube by syringes. The NMR tube was placed into a probe cooled to -30℃ and ^{31}P-NMR spectra were recorded every 3 min.

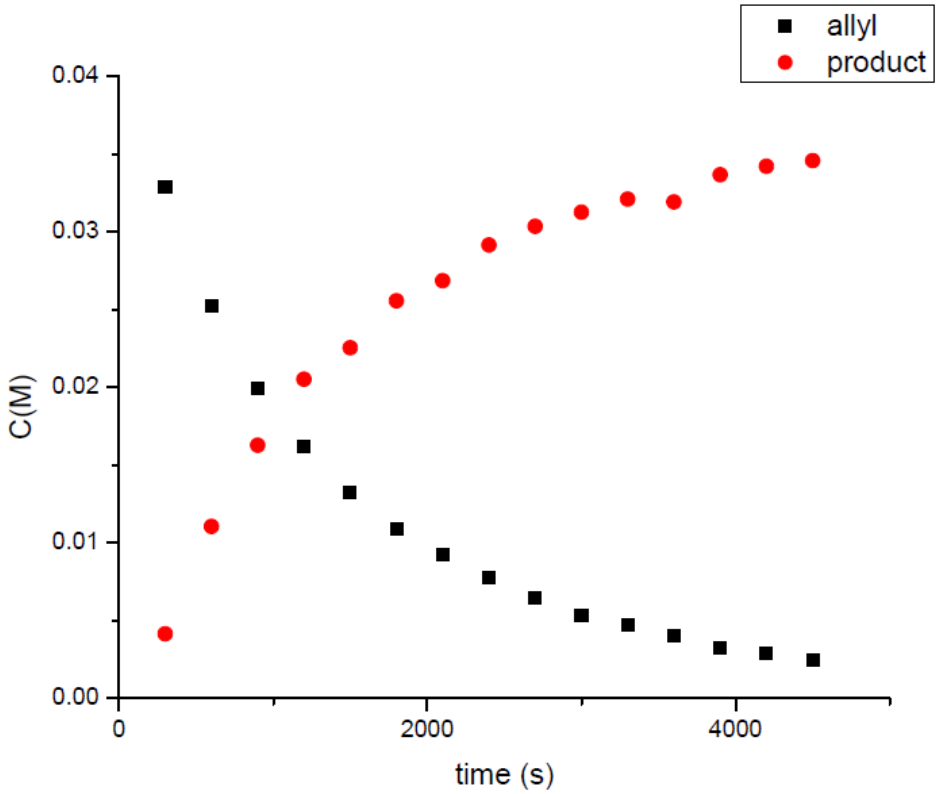


Figure S5. Plot of the change of concentration over time for the reaction of **2c** with aniline in CH_2Cl_2 at -30℃.

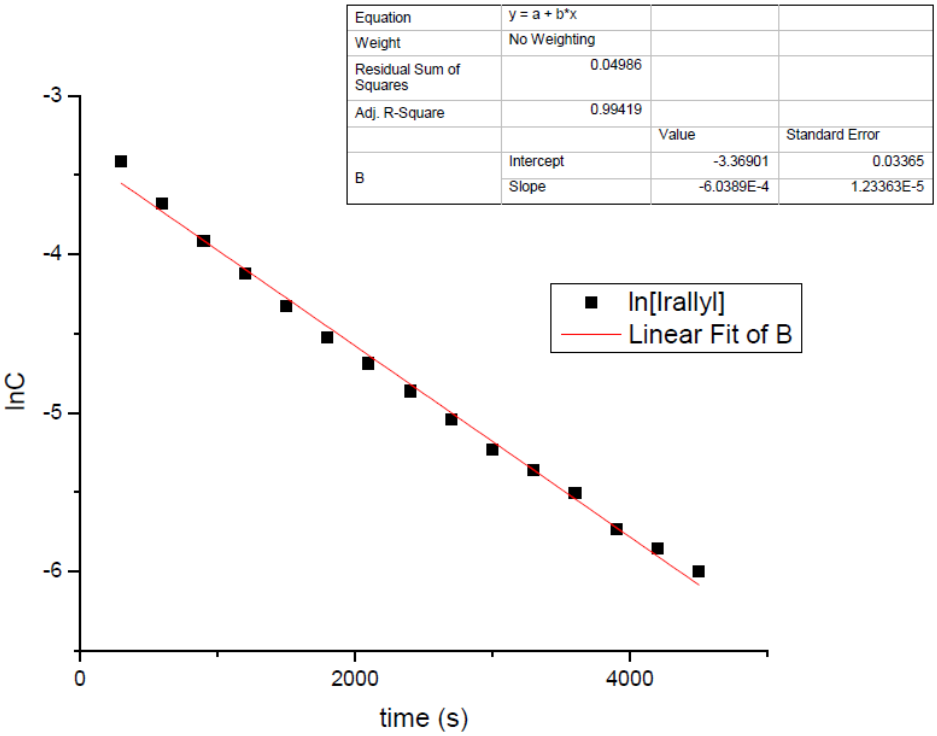


Figure S6. Graph of ln[**2c**] vs. time for the reaction of **2c** with aniline in CH_2Cl_2 at -30 ℃.

Reaction of 2c with aniline at -40 ℃ in THF (table 2, entry 2)
2c (30 mg, 0.026 mmol) was dissolved in 0.6 ml THF and transferred into a screw capped NMR tube and cooled in a dry-ice acetone bath. 61 µl aniline (0.65 mmol) and 84 µl triethylamine (0.445 mmol) were injected into the NMR tube. The NMR tube was placed into a probe cooled to -40 ℃ and ^{31}P-NMR spectra were recorded every min.

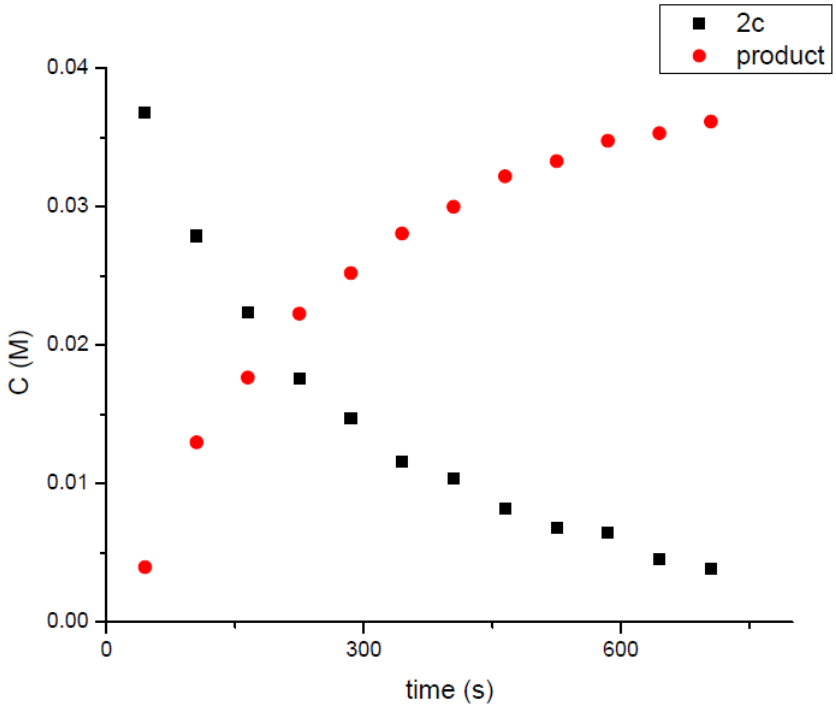


Figure S7. Plot of the change of concentration over time for the reaction of **2c** with aniline in THF at -40 ℃.

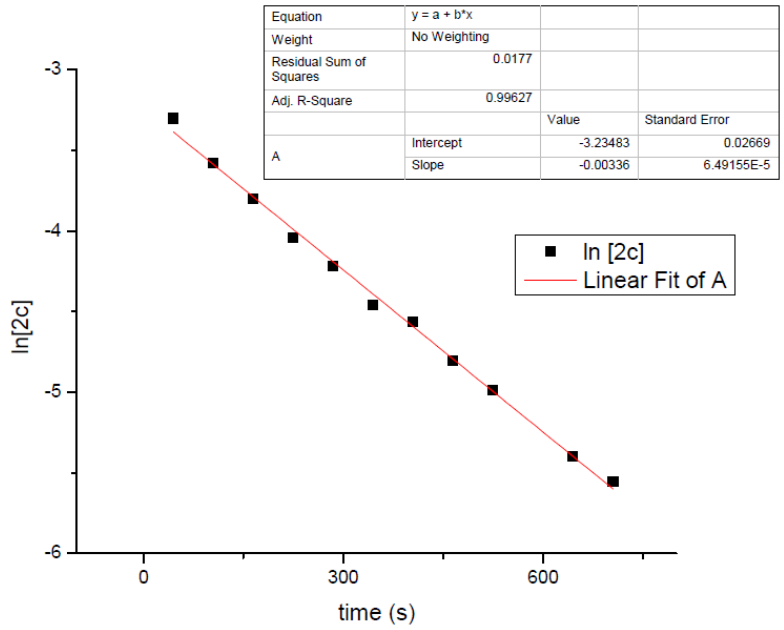


Figure S8. Graph of ln[**2c**] vs. time for the reaction of **2c** with aniline in THF at -40℃.

Reaction of 2d with aniline at -30℃ in CH_2Cl_2 (table 2, entry 4)
2d (30 mg, 0.026 mmol) was dissolved in 0.6 ml CH_2Cl_2 and transferred into a screw capped NMR tube and cooled in a dry-ice acetone bath. 61 µl aniline (0.445 mmol) and 84 µl triethylamine (0.445 mmol) were injected into the NMR tube. The NMR tube was placed into a probe cooled to -30℃ and ^{31}P-NMR spectra were recorded every 4 min.

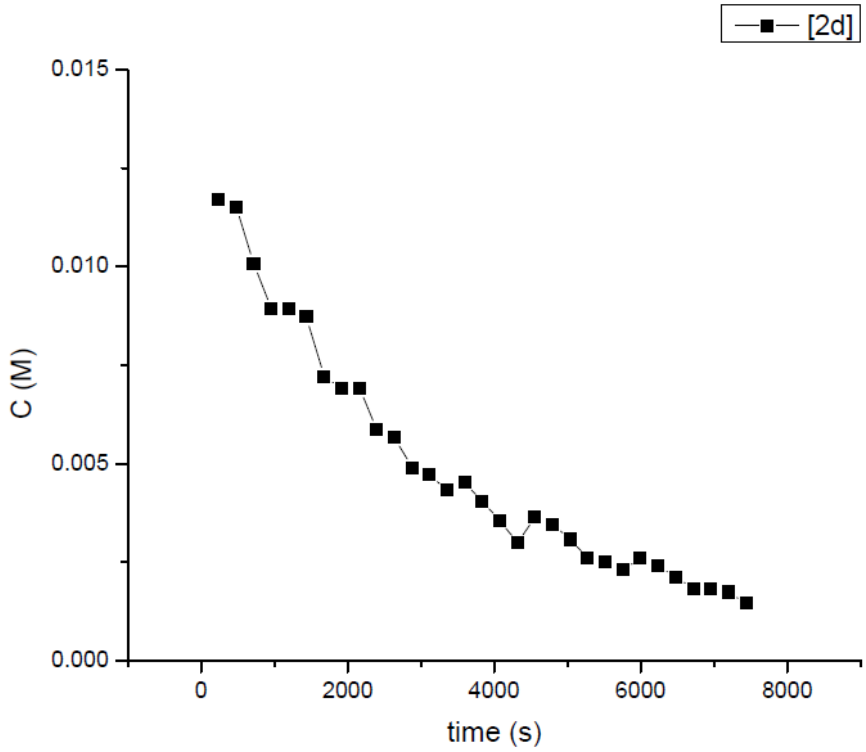


Figure S9. Plot of the change of concentration over time for the reaction of **2d** with aniline in CH_2Cl_2 at -30℃.

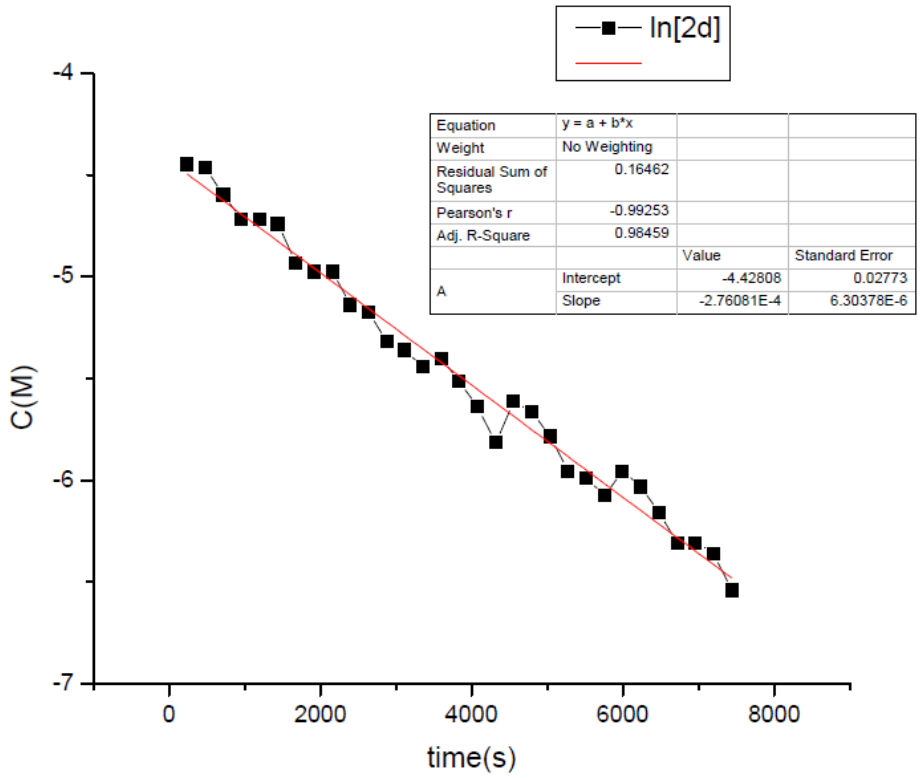


Figure S10. Graph of ln[**2d**] vs. time for the reaction of **2d** with aniline in CH_2Cl_2 at -30℃.

Reaction of 2d with N-methyl aniline at -30℃ in CH_2Cl_2 (table 2, entry 5)
2d (40 mg, 0.037 mmol) was dissolved in 0.6 ml CH_2Cl_2 and transferred into a screw-capped NMR tube and cooled in a dry-ice acetone bath. 113 µl of *N*-methyl aniline (1.05 mmol) and 56 µl of triethylamine (1.05 mmol) were injected into the NMR tube. The NMR tube was placed into a probe cooled to -30℃, and ^{31}P-NMR spectra were recorded every 4 min.

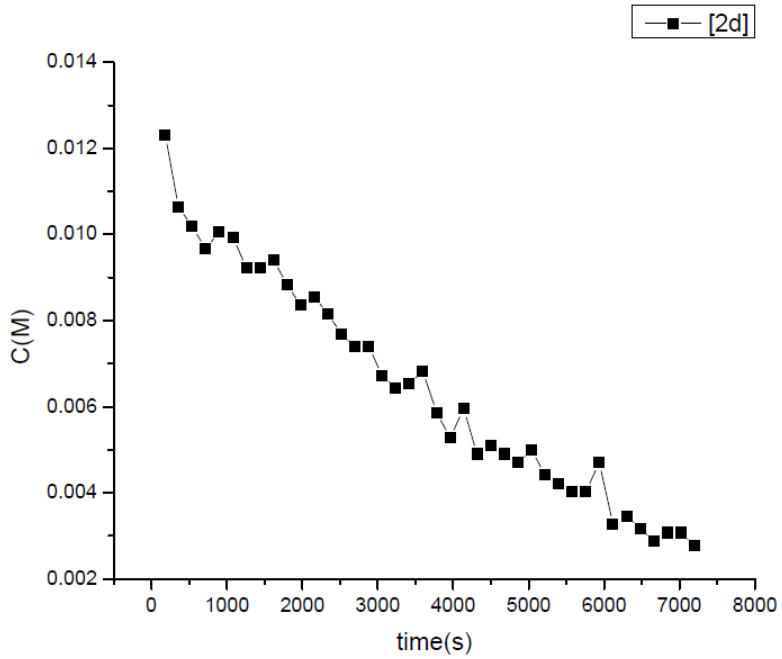


Figure S11. Plot of the change of concentration over time for the reaction of **2d** with N-methyl aniline in CH_2Cl_2 at -30℃.

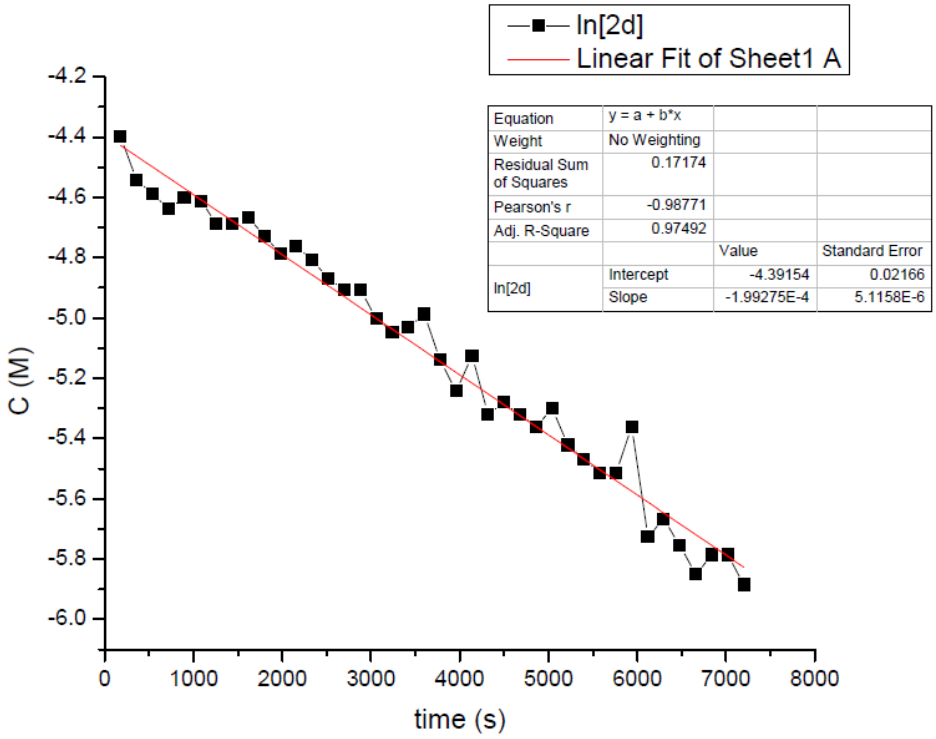


Figure S12. Graph of ln[**2d**] vs. time for the reaction of **2d** with *N*-methyl aniline in CH_2Cl_2 at -30℃.

Reaction of 3c with aniline at -40℃ in THF (table 2, entry 6)
3c (20 mg, 0.018 mmol) was dissolved in 0.6 ml THF and transferred into a screw capped NMR tube and cooled in a dry-ice acetone bath. 41 µl aniline (0.45 mmol) and 62 µl triethylamine (0.45 mmol) were injected into the NMR tube. The NMR tube was placed into a probe cooled to -40℃ and ^{31}P-NMR spectra were recorded every 4 min.

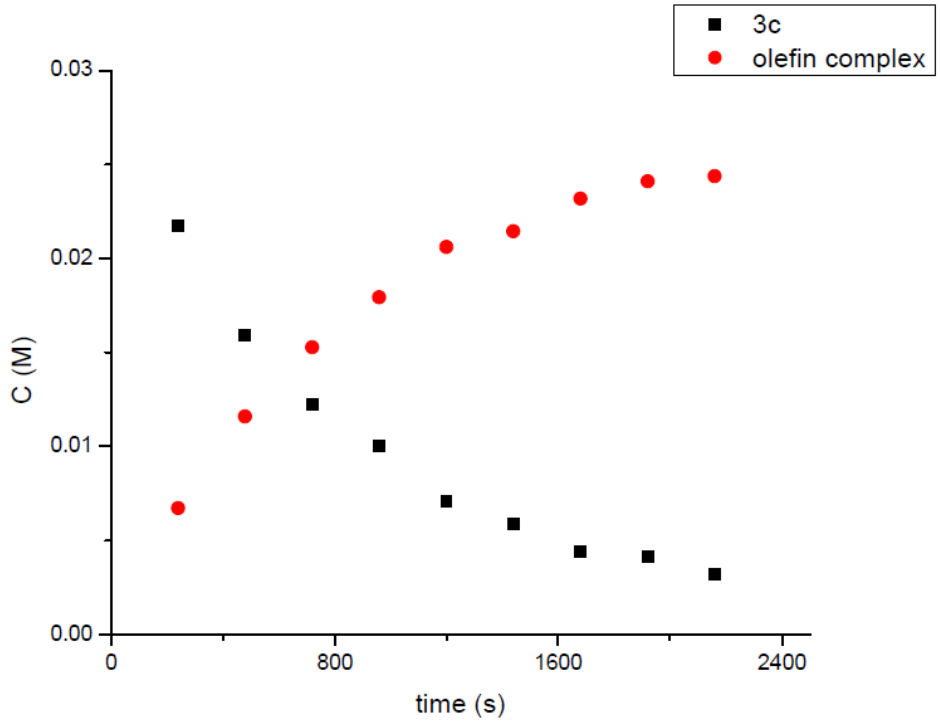


Figure S13. Plot of the change of concentration over time for the reaction of **3c** with aniline in THF at -40℃.

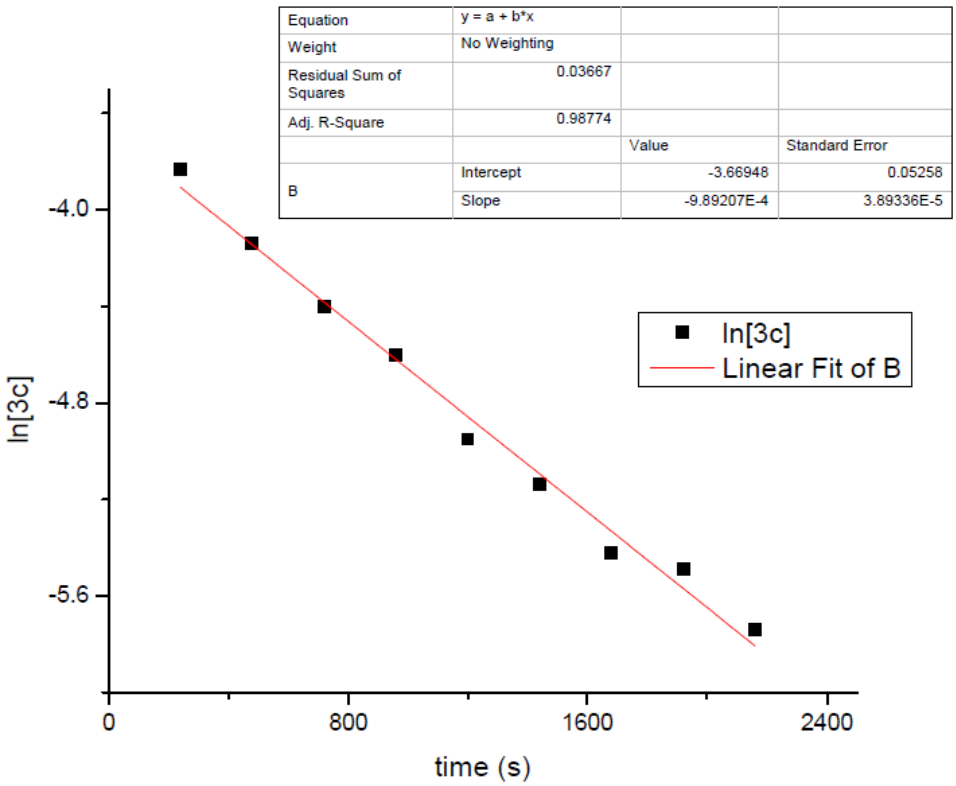


Figure S14. Graph of ln[**3c**] vs. time for the reaction of **3c** with aniline in THF at -40℃.

Reaction of 2f(*S,S,S,S*) with aniline at -40℃ in THF (table 2, entry 8)
1a(*R,R,R*) (40 mg, 0.046 mmol) was dissolved in 1 ml THF and 5-phenylpent-2-en-1-yl 2,2,2-trifluoroacetate, **5l** (12 µl, 51 mmol) was added to the solution and allowed to stir for 15 min. The reaction mixture was transferred into a screw capped NMR tube and cooled in a dry-ice acetone bath. 93 µl aniline (1 mmol) and 139 µl triethylamine (1 mmol) were injected into the NMR tube. The NMR tube was placed into a probe cooled to -40℃ and ^{31}P-NMR spectra were recorded every min.

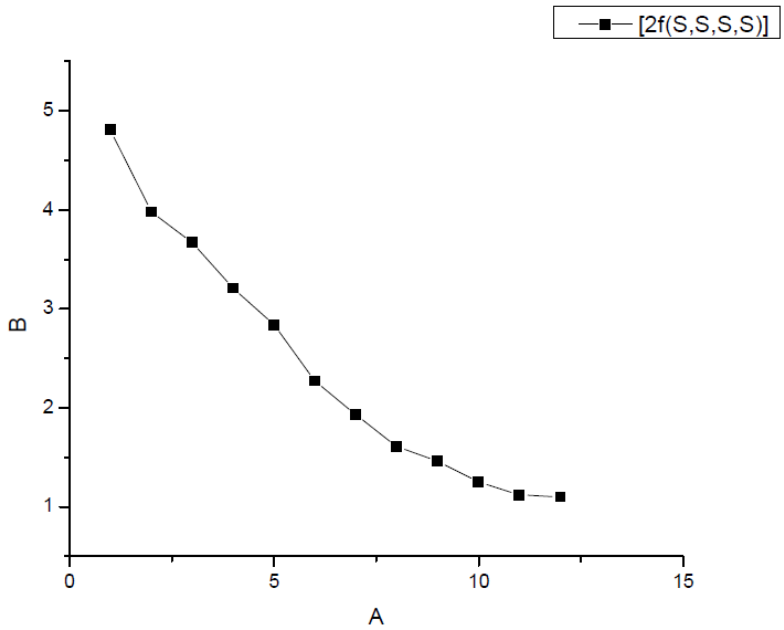


Figure S15. Plot of the change of concentration over time for the reaction of **2f(*S,S,S,S*)** with aniline in THF at -40℃.

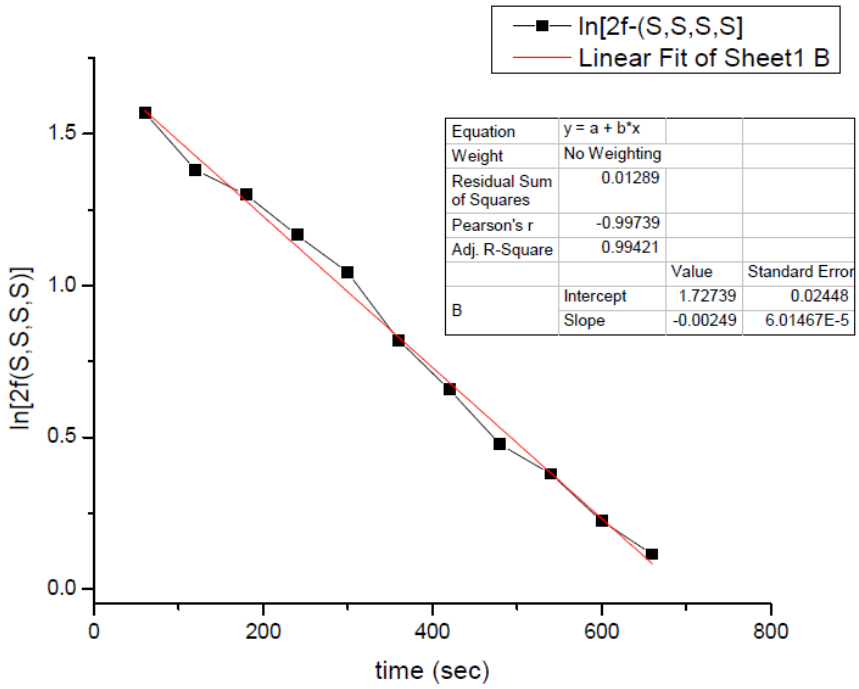


Figure S16. Graph of ln[**2f(*S,S,S,S*)**] vs. time for the reaction of **2f(*S,S,S,S*)** with aniline in THF at -40℃.

Measurement of activation parameters of nucleophilic attack

Reaction of 2f(*R,R,R,R*)-BF_4 with aniline at -40,-30,-20 and -10℃ in THF:

2f(*R,R,R,R*)-BF_4 (40 mg, 0.037 mmol) was dissolved in 0.5 ml THF and transferred into a screw capped NMR tube and cooled in a dry-ice acetone bath. 86 µl aniline (0.94 mmol) and 130 µl triethylamine (0.94 mmol) dissolved in 0.3 ml THF were injected into the NMR tube, making the overall volume of the solution 1 ml. The NMR tube was placed into a probe cooled to -40, -30, -20 or -10℃ and ^{31}P-NMR spectra were recorded every 3 min.

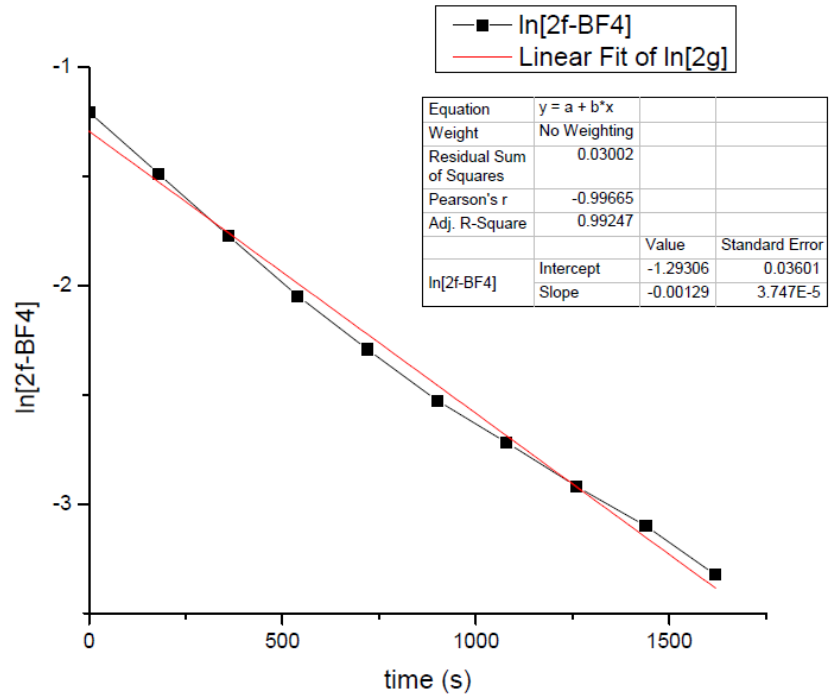


Figure S17. Graph of ln[**2f(*S,S,S,S*)-BF_4**] vs. time for the reaction of **2f(*S,S,S,S*)-BF_4** with aniline in THF at -10℃.

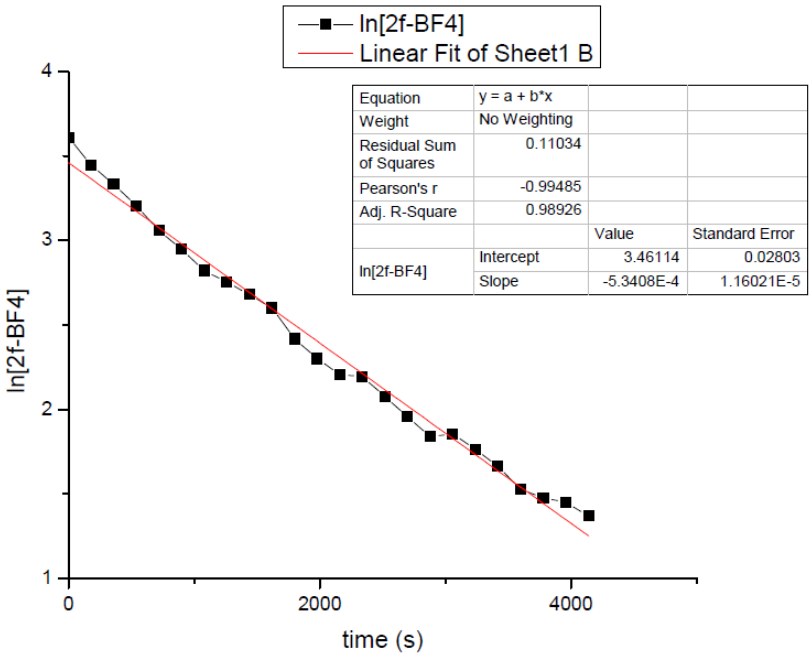


Figure S18. Graph of ln[**2f(*S*,*S*,*S*,*S*)-BF$_4$**] vs. time for the reaction of **2f(*S*,*S*,*S*,*S*)-BF$_4$** with aniline in THF at -20℃.

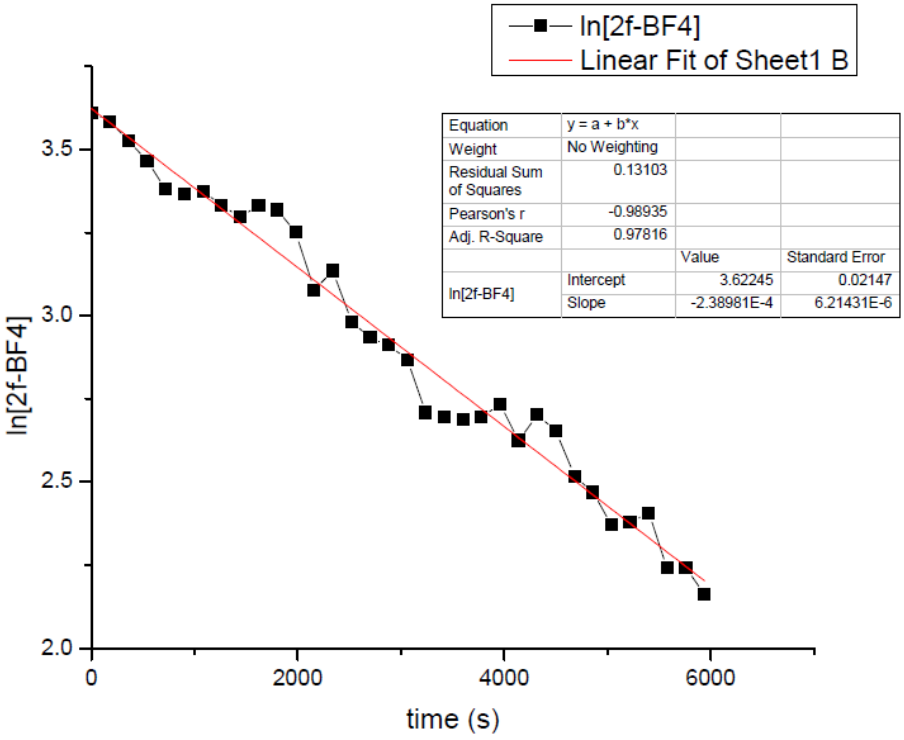


Figure S19. Graph of ln[**2f(*S*,*S*,*S*,*S*)-BF$_4$**] vs. time for the reaction of **2f(*S*,*S*,*S*,*S*)-BF$_4$** with aniline in THF at -30℃.

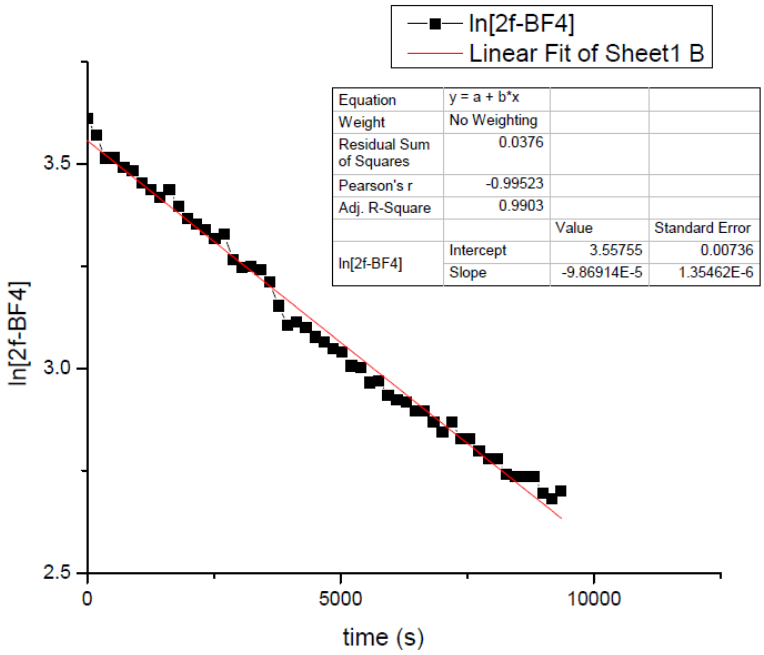


Figure S20. Graph of ln[**2f(*S,S,S,S*)-BF$_4$**] vs. time for the reaction of **2f(*S,S,S,S*)-BF$_4$** with aniline in THF at -40℃.

Eyring plot for the reaction of 2f-BF$_4$ with aniline:

The natural logarithms of the rate constants divided by temperature (ln(k/T)) for the reaction of **2f-BF$_4$** with aniline measured at -10, -20, -30 and -40℃ were plotted against the reciprocal of the temperature (1/T) to determine the activation parameters for the nucleophilic attack.

	T (℃)	k_{Nu}	T (K)	1/T	ln(k/T)
1	-40	9.9 x 10^{-5}	233	0.004292	-14.671
2	-30	2.4 x 10^{-4}	243	0.004115	-13.827
3	-20	5.3 x 10^{-4}	253	0.003953	-13.076
4	-10	1.3 x 10^{-3}	263	0.03802	-12.225

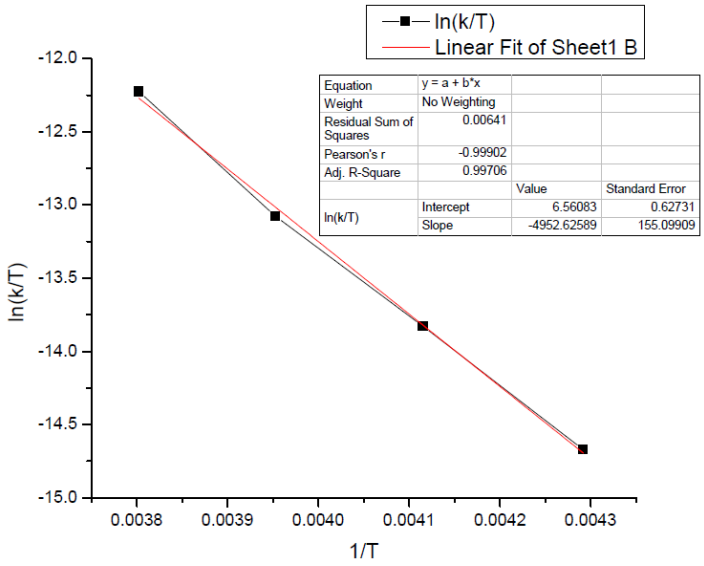


Figure S21. Eyring plot for the reaction of 2f-BF_4 with aniline.

From Figure S21:

Slope = -4952 = -ΔH/R;
$\Delta H^{\ddagger}_{nuc}$ = 4952 x 8.314 = 41.2 kJ/mol = 9.8 kcal/mol

Intercept = 6.6 = ln(k_B/h) + ΔS/R ;
$\Delta S^{\ddagger}_{nuc}$ = [6.6 - ln(1.38x10^{-23}/6.27x10^{-34})] x 8.314 = (6.6-23.8) x 8.314 = -143 J/mol•K = -34.2 eu

Thus, the nucleophilic attack on a representative allyliridium complex has a typical entropy of activation for a bimolecular reaction.

For the reaction of aniline with **2f-TFA**

At -40 °C $\Delta G^{\ddagger}_{nuc}$ = 75.7 kJ/mol

Estimation of the value of $\Delta\Delta H^{\ddagger}$ for nucleophilic attack versus isomerization at -40 ℃ from $\Delta\Delta G^{\ddagger}$ and $\Delta\Delta S^{\ddagger}$.

$\Delta\Delta G^{\ddagger} = \Delta\Delta H^{\ddagger} - T\bullet\Delta\Delta S^{\ddagger}$;

Assuming that $\Delta S^{\ddagger}_{nuc}$ for **2f-TFA** is similar to that for **2f-BF_4** and that $\Delta S^{\ddagger}_{epi}$ is close to zero because it is unimolecular reaction,

$\Delta\Delta S^{\ddagger}$ = -143 J/mol•K

At T = 233 K ;

$\Delta\Delta H^{\ddagger} = \Delta\Delta G^{\ddagger} + T\bullet\Delta\Delta S^{\ddagger}$

$\Delta\Delta G^{\ddagger}$ = -7.6 kJ/mol from the ratio of rate constants for nucleophilic attack and epimerization of **2f-TFA**.

$T\bullet\Delta\Delta S^{\ddagger}$ = 143 x 233 = -33.3 kJ/mol

And $\Delta\Delta H^{\ddagger}$ = -40.9 kJ/mol;

The temperature dependence of the ratio of rate constants of nucleophilic attack and epimerization can be derived as follows:

$$k_{Nu} = \frac{k_B T}{h} e^{\Delta H^{\ddagger}/RT + \Delta S^{\ddagger}/R} \quad (3)$$

$$k_{epi} = \frac{k_B T}{h} e^{\Delta H^{\ddagger}/RT + \Delta S^{\ddagger}/R} \quad (4)$$

$$\frac{k_{Nu}}{k_{epi}} = e^{\Delta\Delta H^{\ddagger}/RT} \times e^{\Delta\Delta S^{\ddagger}/R} \quad (5)$$

$$\frac{\left(\frac{k_{Nu}}{k_{epi}}\right)_{T_1}}{\left(\frac{k_{Nu}}{k_{epi}}\right)_{T_2}} = \frac{e^{\Delta\Delta H^{\ddagger}/RT_1 \; x \; e^{\Delta\Delta S^{\ddagger}/R}}}{e^{\Delta\Delta H^{\ddagger}/RT_2 \; x \; e^{\Delta\Delta S^{\ddagger}/R}}} \quad (6)$$

$$\frac{\left(\frac{k_{Nu}}{k_{epi}}\right)_{T_1}}{\left(\frac{k_{Nu}}{k_{epi}}\right)_{T_2}} = e^{(\Delta\Delta H^{\ddagger}/RT_1) - (\Delta\Delta H^{\ddagger}/RT_2)} \quad (7)$$

To determine the change in relative rate constants with temperature, the two temperatures and the value of $\Delta\Delta H^{\ddagger}$ are used:

For the two temperatures T_1 = -40 ℃; T_2 = 25 ℃

$(k_{Nu}/k_{epi})_{T2}/(k_{Nu}/k_{epi})_{T1}$ = e^[(-40900/(8.314 x 298)) – (-40900/(8.314 x 233))] = 100.

For the two temperatures T_1 = -40 ℃; T_2 = 50 ℃

$(k_{Nu}/k_{epi})_{T2}/(k_{Nu}/k_{epi})_{T1}$ = e^[(-40900/(8.314 x 323)) – (-40900/(8.314 x 233))] = 360.

Thus, a temperature increase from -40 ℃ to 25 ℃ and to 50 ℃ will result in 100 and 360 times increase respectively in the ratio of rate constants for epimerization versus nucleophilic attack.

Catalytic reactions of 2-bromocinnamyl carbonate 5: Ethyl 3-(2-bromophenyl)-2-propen-1-yl carbonate **5** (0.50 mmol, 143 mg) was added to the solution of **1a** (0.02 mmol 17.4 mg) in 1 ml THF followed by nucleophile (0.3 mmol). The solution was allowed to stir for the indicated time at indicated temperature. After removing the solvent yields were determined by ^{1}H-NMR with mesitylene as internal standart. The products were purified by flash column chromatography through silica using with Hex:EtOAc eluent.

N-(1-(2-bromophenyl)allyl)aniline, 7a: ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.58 (dd, *J* = 8.0, 1.1 Hz, 1H), 7.44 (dd, *J* = 7.8, 1.7 Hz, 1H), 7.30 – 7.24 (m, 1H), 7.16 – 7.09 (m, 3H), 6.74 – 6.63 (m, 1H), 6.53 (dd, *J* = 8.6, 0.9 Hz, 2H), 6.04 (ddd, *J* = 17.1, 10.3, 5.6 Hz, 1H), 5.36 (t, *J* = 5.4 Hz, 1H), 5.26 (dt, *J* = 10.3, 1.2 Hz, 1H), 5.24 – 5.19 (m, 1H), 4.13 (b, 1H). ^{13}C NMR (126 MHz, $CDCl_3$) δ 146.89, 140.57, 137.53, 133.33, 129.39, 129.10, 128.58, 128.11, 124.02, 118.04, 117.22, 113.61, 59.48. HRMS-ESI (m/z): $[MH]^+$ calcd. for $C_{15}H_{15}BrN$, 289.1903; found, 289.1901. HPLC conditions: Daicel CHIRALCEL OJ-H (0.46 cm x 25 cm); hexane/2-propanol =99.5/0.5; flow rate = 1 mL/min; detection wave length = 254 nm; TR = 12.1 (*R*), 14.3 (*S*) min.

dimethyl 2-(1-(2-bromophenyl)allyl)malonate, 7b: ^{1}H NMR (499 MHz, $CDCl_3$) δ 7.58 (dd, *J* = 8.0, 1.2 Hz, 1H), 7.30 – 7.25 (m, 1H), 7.23 (dd, *J* = 7.8, 1.7 Hz, 1H), 7.12 – 7.06 (m, 1H), 5.97 (ddd, *J* = 17.1, 10.2, 8.0 Hz, 1H), 5.15 (dd, *J* = 15.0, 14.0 Hz, 2H), 4.70 (dd, *J* = 10.6, 8.1 Hz, 1H), 4.02 (d, *J* = 10.6 Hz, 1H), 3.75 (s, 3H), 3.56 (s, 3H). ^{13}C NMR (126 MHz, $CDCl_3$) δ 168.20, 167.81, 139.38, 136.43, 133.68, 128.77, 128.66, 127.86, 124.99, 117.92, 56.43, 52.85, 52.77, 48.14. HRMS-ESI (m/z): $[MH]^+$ calcd. for $C_{15}H_{15}BrN$, 328.1784; found, 328.1781. HPLC conditions: Daicel

CHIRALCEL OJ-H (0.46 cm x 25 cm); hexane/2-propanol =95/5; flow rate = 1 mL/min; detection wave length = 254 nm; t_R = 32.1 (*S*), 35.3 (*R*) min.

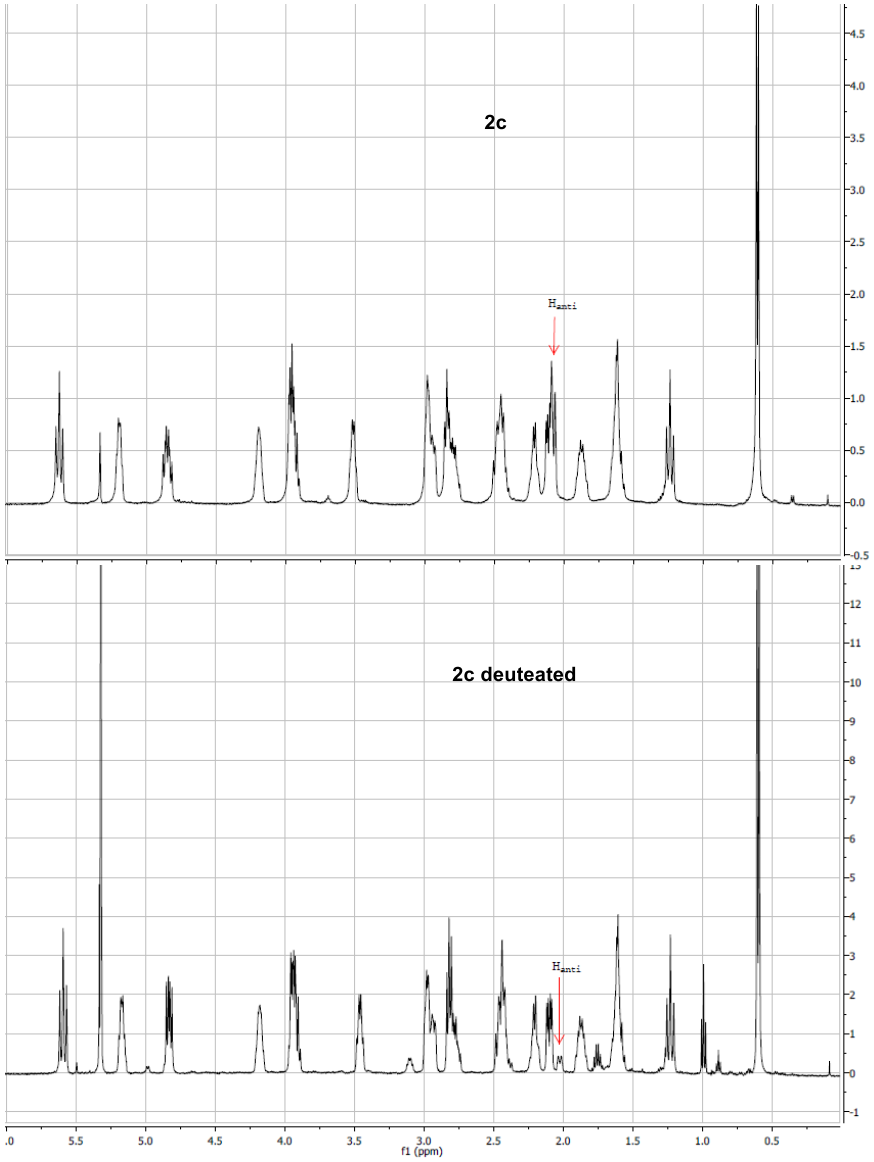
1-bromo-2-(1-phenoxyallyl)benzene, 7c: ^{1}H NMR (499 MHz, $CDCl_3$) δ 7.60 (dd, *J* = 19.8, 7.9 Hz, 2H), 7.40 – 7.23 (m, 3H), 7.23 – 7.09 (m, 1H), 7.01 – 6.82 (m, 3H), 6.25 – 6.03 (m, 2H), 5.48 (d, *J* = 16.5 Hz, 1H), 5.34 (d, *J* = 9.9 Hz, 1H). ^{13}C NMR (126 MHz, $CDCl_3$) δ 157.51, 139.27, 136.06, 132.87, 129.54, 129.38, 128.36, 128.17, 122.63, 121.17, 117.07, 115.85, 78.67. HRMS-ESI (m/z): $[MH]^+$ calcd. for $C_{15}H_{15}BrN$, 290.1751; found, 290.1750. HPLC conditions: Daicel CHIRALCEL OJ-H (0.46 cm x 25 cm); hexane/2-propanol =99.5/0.5; flow rate = 1 mL/min; detection wave length = 254 nm; t_R = 29.3 (*S*), 31.5 (*R*) min.

Stereochemical route of the reaction:

Oxidative addition:

Reaction between 1a and monodeuterated cinnamyl trifluoroacetate, 4a-D: 1a-(*R,R,R*) (30 mg, 0.035 mmol) was dissolved in 1 ml C_6H_6, and **4a-D** (10.2 mg, 0.042 mmol) was added to it. $AgBF_4$ (6.8 mg, 0.035 mmol) was dissolved in 0.5 ml THF and added to the first solution. The mixture was allowed to stir for 5 min. Precipitated AgCl was removed by filtration, and the solution was left in the drybox overnight with the cap slightly unscrewed. Crystals formed overnight and were washed with C_6H_6 and dried under vacuum. The obtained crystals were dissolved in CD_2Cl_2, and the ratio between the *syn* and *anti* deuterated complexes was determined by ^{1}H-NMR spectroscopy.

NMR spectra of fully protiated **2c** and **2c** obtained after reaction with **4a-D.**



Stereochemistry of nucleophilic attack.

Cinnamyliridium complex **2c** monodeutrated at anti allylic hydrogen (40 mg 0.038 mmol) was dissolved in 0.5 ml CH_2Cl_2. Aniline (7 µl, 0.076 mmol) and triethylamine (11 µl 0.076 mmol) was added to the solution. The reaction mixture was allowed to stir for 15 min. Triphenylphosphine (20 mg, 0.076 mmol) was added to the solution to free the olefin. The product was purified by preparatory TLC plate chromatography over silicagel with 9:1 Hexane : Ethylacetate eluent. The ratio between the cis and trans deuterated product was determined through ^{1}H-NMR of the $CDCl_3$ solution of the product. Ee was determined by chiral HLPC. HPLC conditions: Daicel CHIRALCEL OJ-H (0.46 cm x 25 cm); hexane/2-propanol =99/1; flow rate= 1 mL/min; detection wave length = 254 nm; TR = 29 (R), 31 (S) min.

Catalytic reactions to determine the stereochemical route.

Reactions of 4b-D-(*R*) with aniline catalyzed by 1a-(*R*,*R*,*R*), 1a-(*S*,*S*,*S*) or **1b-(*S*,*S*,*S*)**:

In a small, vial linear allylic carbonate **4b-D-(*R*)** (39 mg, 0.2 mmol) was combined with the catalyst (either one of **1a-(*R*,*R*,*R*)** 7 mg, 0.08 mmol; **1a-(*S*,*S*,*S*)** 7mg, 0.08 mmol or **1b-(*S*,*S*,*S*)** 7.5 mg, 0.08 mmol) in 1ml THF. Aniline (22 µl, 0.24 mmol) was added to each of the vials. The reaction mixture was allowed to stir for 1h. Solvents were removed under reduced pressure. Yields and branched to linear ratios were determined by ^{1}H-NMR with mesitylene standard. The crude reaction product was purified by flash column chromatography with 9:1 hexane:ethylacetate eluent phase. Ees were determined by chiral HLPC. HPLC conditions: Daicel CHIRALCEL OJ-H (0.46 cm x 25 cm); hexane/2-propanol =99/1; flow rate= 1 mL/min; detection wave length = 254 nm; TR = 29 (R), 31 (S) min.

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