



Nickel-Mediated Oxidative Fluorination for PET with Aqueous [(¹⁸F)] Fluoride

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Supporting Information

Nickel-Mediated Oxidative Fluorination for PET with Aqueous [^{18}F]Fluoride

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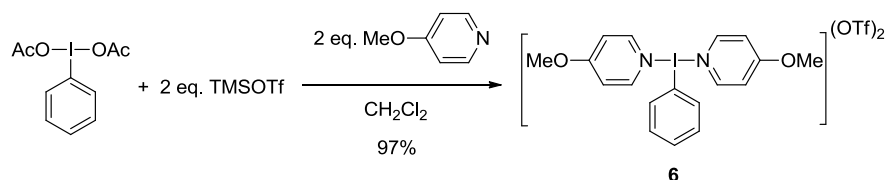
Materials and Methods

All air- and moisture-insensitive reactions were carried out under an ambient atmosphere, magnetically stirred, and monitored by thin layer chromatography (TLC) using EMD TLC plates pre-coated with 250 μm thickness silica gel 60 F254 plates and visualized by fluorescence quenching under UV light. Flash chromatography was performed on Dynamic Adsorbents Silica Gel 40–63 μm particle size using a forced flow of eluent at 0.3–0.5 bar pressure.¹ All air- and moisture-sensitive manipulations were performed using oven-dried glassware, including standard Schlenk and glovebox techniques under an atmosphere of nitrogen. Methylene chloride, diethyl ether, toluene, and pentane were purged with nitrogen, dried by passage through activated alumina, and stored over 3Å molecular sieves.² Benzene, benzene- d_6 , dioxane and THF were distilled from deep purple sodium benzophenone ketyl. Methylene chloride- d_2 was dried over CaH_2 and vacuum-distilled. Acetonitrile and acetonitrile- d_3 were dried over P_2O_5 and vacuum-distilled. Pyridine and tetramethylethylenediamine (TMEDA) were dried over CaH_2 and distilled. DMSO was distilled from sodium triphenylmethanide and stored over 3Å sieves.³ Acetone was distilled over B_2O_3 . MeOH was degassed at $-30\text{ }^\circ\text{C}$ under dynamic vacuum (10^{-4} Torr) for one hour and stored over 3Å sieves. Anhydrous DMF and dioxane bottles equipped with a SureSeal™ were purchased from Sigma Aldrich®. 18-Crown-6 was sublimed. KF was ground finely and dried at $200\text{ }^\circ\text{C}$ under dynamic vacuum (10^{-4} Torr) before use. $\text{Ni}(\text{COD})_2$ and all other chemicals were used as received. All deuterated solvents were purchased from Cambridge Isotope Laboratories. $\text{Ni}(\text{COD})_2$ and 18-crown-6 were purchased from Strem Chemicals. (Diacetoxyiodo)benzene, potassium fluoride, 4-methoxypyridine, pyrrolidine, *p*-toluenesulfonic acid, *p*-methoxybenzenesulfonamide, and F-TEDA- BF_4 (Selectfluor®) were purchased from Sigma-Aldrich®. TMSOTf and trifluoroacetic acid were purchased from Oakwood Products. NMR spectra were recorded on either a Varian Unity/Inova 600 spectrometer operating at 600 MHz for ^1H acquisitions, a Varian Unity/Inova 500 spectrometer operating at 500 MHz and 125 MHz for ^1H and ^{13}C acquisitions, respectively, a Varian Mercury 400 spectrometer operating at 375 MHz and 101 MHz for ^{19}F and ^{13}C acquisitions, respectively, or a Varian Mercury 300 spectrometer operating at 100 MHz for ^{11}B acquisitions. Chemical shifts were referenced to the residual proton solvent peaks (^1H : CDCl_3 , δ 7.26; C_6D_6 , δ 7.16; CD_2Cl_2 , δ 5.32; D_2O , δ 4.79; $(\text{CD}_3)_2\text{SO}$, δ 2.50; CD_3CN , δ 1.94), solvent ^{13}C signals (CDCl_3 , δ 77.16; C_6D_6 , δ 128.06; CD_2Cl_2 , δ 53.84; CD_3CN , δ 1.32, $(\text{CD}_3)_2\text{SO}$, δ 39.52),⁴ dissolved or external neat PhF (^{19}F , δ -113.15 relative to CFCl_3) or dissolved 3-nitrofluorobenzene (-112.0 ppm). Signals are listed in ppm, and multiplicity identified as s = singlet, br = broad, d = doublet, t = triplet, q = quartet, quin = quintet, sep = septet, m = multiplet; coupling constants in Hz; integration. Concentration under reduced pressure was performed by rotary evaporation at $25\text{--}30\text{ }^\circ\text{C}$ at appropriate pressure. Purified compounds were further dried under high vacuum ($0.01\text{--}0.05$ Torr). Yields refer to purified and spectroscopically pure compounds.

Experimental Data

Synthesis of hypervalent iodine oxidant (6) and (2-(2-pyridinyl)phenyl-2-nitrobenzenesulfonamide)silver(I) complex (8)

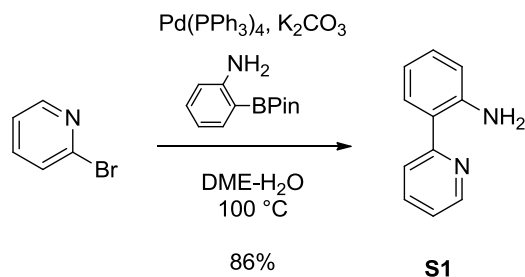
1,1'-(phenyl- λ^3 -iodanediyl)bis(4-methoxypyridinium) bis(trifluoromethanesulfonate) (6)⁵



All manipulations were carried out in a dry box under a N₂ atmosphere. To (diacetoxyiodo)benzene (3.00 g, 9.31 mmol, 1.00 equiv) dissolved in CH₂Cl₂ (100 mL) in a round-bottom flask was added TMSOTf (4.14 g, 18.6 mmol, 2.00 equiv) drop-wise over 1 minute at 23 °C. 4-Methoxypyridine (2.03 g, 18.6 mmol, 2.00 equiv) in CH₂Cl₂ (15 mL) was added to the solution drop-wise over 5 minutes. The reaction mixture was then concentrated in vacuo until a white solid was observed. To the reaction mixture was added 100 mL of Et₂O to precipitate a white solid while stirring vigorously, and the resulting solid was collected on a frit. The solid was washed with Et₂O (3 × 10 mL) and subsequently dried under vacuum to afford 6.52 g of the title compound as a colorless solid (97%).

NMR Spectroscopy: ¹H NMR (500 MHz, CD₃CN, 23 °C, δ): 8.77 (d, J = 7.5 Hz, 4H), 8.60 (d, J = 8.5 Hz, 2H), 7.79 (t, J = 7.5 Hz, 1H), 7.64 (t, J = 8.5 Hz, 2H), 7.19 (d, J = 7.5 Hz, 4H), 3.99 (s, 3H). ¹³C NMR (125 MHz, CD₃CN, 23 °C, δ): 172.1, 149.9, 136.1, 135.7, 134.2, 125.7, 121.9 (q, J = 319 Hz, triflate), 115.3, 58.5. ¹⁹F NMR (375 MHz, CD₃CN, 23 °C, δ): -77.5. Anal: calcd for C₂₀H₁₉F₆IN₂O₈S₂: C, 33.34; H, 2.66; N, 3.89; found: C, 33.05; H, 2.59; N, 3.73.

2-(2-Pyridinyl)aniline (S1)

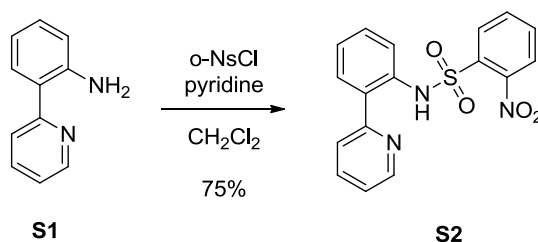


Under air, to 2-bromopyridine (4.54 g, 28.7 mmol, 1.00 equiv) in DME-H₂O (1:1, 100 mL) at 23 °C was added K₂CO₃ (5.96 g, 43.1 mmol, 1.50 equiv), 2-aminophenylboronic acid pinacol ester (6.30 g, 28.7 mmol, 1.00 equiv), and tetrakis(triphenylphosphine)palladium (1.66 g, 1.44 mmol,

5.00 mol%). The reaction mixture was stirred at 100 °C for 3.0 h. After cooling to 23 °C, the phases were separated and the aqueous phase was extracted with EtOAc (3 × 50 mL). The combined organic phases were washed with brine (100 mL) and dried (Na₂SO₄). The filtrate was concentrated in vacuo and the residue was purified by chromatography on silica gel eluting with hexanes/EtOAc 4:1 (v/v) to afford 4.20 g of the title compound as a red-brown oil (86%).

R_f = 0.38 (hexanes/EtOAc 3:1 (v/v)). NMR Spectroscopy: ¹H NMR (500 MHz, CDCl₃, 23 °C, δ): 8.61–8.60 (m, 1H), 7.78–7.75 (m, 1H), 7.65 (d, *J* = 7.9 Hz, 1H), 7.51 (dd, *J* = 7.6 Hz, 1.4 Hz, 1H), 7.19–7.16 (m, 2H), 6.80–6.76 (m, 2H), 5.72 (br s, 2H). ¹³C NMR (125 MHz, CDCl₃, 23 °C, δ): 159.5, 147.9, 146.6, 136.9, 129.9, 129.4, 122.2, 122.2, 121.0, 117.6, 117.2. These spectroscopic data correspond to previously reported data.⁶

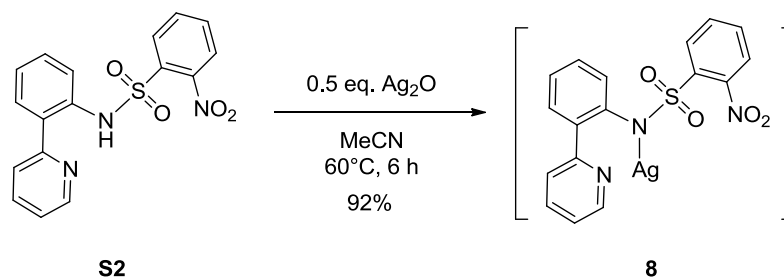
2-(2-Pyridinyl)-2-nitrobenzenesulfonamide (S2)



To 2-(2-pyridinyl)aniline (**S1**) (851 mg, 5.00 mmol, 1.00 equiv) in CH₂Cl₂ (10 mL) at 0 °C was added pyridine (1.60 mL, 20.0 mmol, 4.00 equiv) and 2-nitrobenzenesulfonyl chloride (2.20 g, 10.0 mmol, 2.00 equiv). The reaction mixture was warmed to 23 °C and stirred for 2.0 hr before the addition of water (10 mL). The phases were separated and the aqueous layer was extracted with CH₂Cl₂ (3 × 8 mL). The combined organic phases were washed with brine (30 mL) and dried (Na₂SO₄). The filtrate was concentrated in vacuo and the residue was purified by chromatography on silica gel eluting with hexanes/EtOAc 3:7 (v/v) to afford 1.33 g of the title compound as a pale-yellow solid (75%).

R_f = 0.12 (hexanes/EtOAc 7:3 (v/v)). Melting Point: 91–94 °C. NMR Spectroscopy: ¹H NMR (500 MHz, CDCl₃, 23 °C, δ): 8.73 (d, *J* = 5.0 Hz, 1H), 7.94 (dd, *J* = 7.5 Hz, 2.0 Hz, 1H), 7.82 (dd, *J* = 8.0 Hz, 1.0 Hz, 1H), 7.74 (ddd, *J* = 7.5 Hz, 7.5 Hz, 2.0 Hz, 1H), 7.63–7.52 (m, 5H), 7.38 (ddd, *J* = 7.5 Hz, 7.5 Hz, 1.5 Hz, 1H), 7.27–7.24 (m, 1H), 7.18 (ddd, *J* = 7.5 Hz, 7.5 Hz, 1.0 Hz, 1H). ¹³C NMR (125 MHz, CDCl₃, 23 °C, δ): 156.9, 156.2, 148.0, 137.9, 136.4, 133.6, 132.2, 131.0, 130.0, 129.0, 127.1, 125.0, 124.7, 122.4, 121.9, 121.9, 110.9. Mass Spectrometry: HRMS-FIA (m/z): Calcd for [C₁₇H₁₃N₃O₄S + H], 356.06995. Found, 356.07008. These spectroscopic data correspond to previously reported data.⁷

Synthesis of (2-(2-Pyridinyl)phenyl-2-nitrobenzenesulfonamide)silver(I) (**8**)

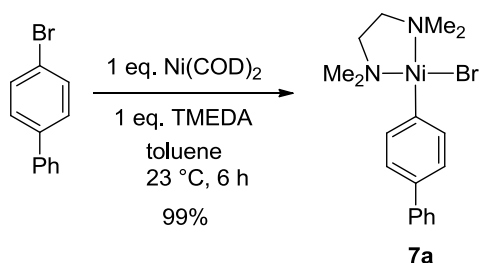


To silver(I) oxide (4.99 g, 21.5 mmol, 0.500 equiv) in CH₃CN (200 mL) at 23 °C was added 2-(2-pyridinyl)phenyl-2-nitrobenzenesulfonamide (**S2**) (15.3 g, 43.1 mmol, 1.00 equiv). After stirring for 12 h at 65 °C, the resulting light gray solid was collected on a frit and dried in vacuo to afford 18.3 g of the title compound as a light gray solid (92%).

Anal: calcd for C₁₇H₁₂AgN₃O₄S: C, 44.17; H, 2.62; N, 9.09; found: C, 44.06; H, 2.66; N, 9.00. ¹H and ¹³C NMR spectra were not obtained due to low solubility.

Synthesis of aryl and alkenyl nickel complexes (**1a–1l**)

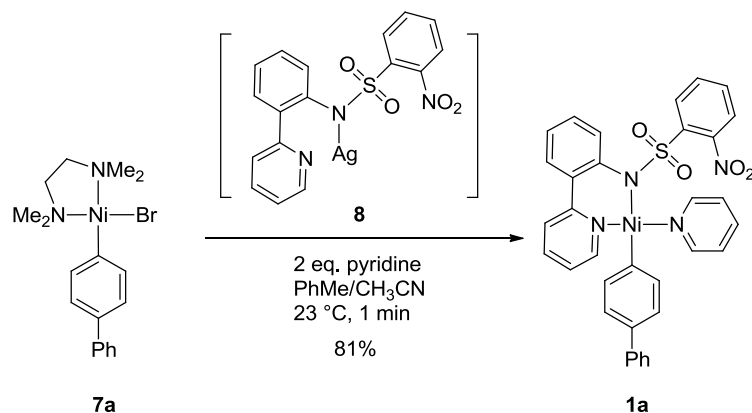
Synthesis of nickel aryl bromide complex **7a**⁸



To a solution of TMEDA (83.0 mg, 0.107 mL, 0.717 mmol, 1.00 equiv) and 4-bromobiphenyl (167 mg, 0.717 mmol, 1.00 equiv) in toluene (4 mL) was added Ni(COD)₂ (200 mg, 0.717 mmol, 1.00 equiv), and the mixture was stirred at room temperature for 2 h. Pentane (16 mL) was added to the mixture and the resulting solid was collected on a frit. The solid was washed with pentane (3 × 5 mL) and dried in vacuo to afford 288 mg of the title compound as an orange solid (99%).

NMR Spectroscopy: ¹H NMR (500 MHz, CD₂Cl₂, δ): 7.59 (d, *J* = 8.0 Hz, 2H), 7.52 (d, *J* = 7.5 Hz, 1H), 7.38–7.35 (m, 2H), 7.24–7.21 (m, 1H), 7.10 (d, *J* = 7.7 Hz, 2H), 2.56–2.26 (br, 16H). ¹³C NMR (125 MHz, CD₂Cl₂, δ): 142.2, 137.9, 134.6, 128.9, 126.9, 126.5, 123.5, 61.5 (br), 57.4 (br), 59.5 (br), 48.4 (br). Broadness of TMEDA signals in ¹H and ¹³C NMR spectra was previously reported for a similar nickel complex.^{8a} Anal: calcd for C₁₈H₂₅BrN₂Ni: C, 52.99; H, 6.18; N, 6.87; found: C, 52.69; H, 6.16; N, 6.84.

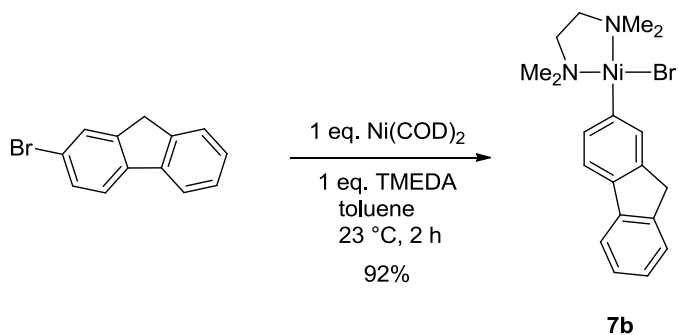
Synthesis of nickel aryl complex 1a



To (2-(2-pyridinyl)phenyl-2-nitrobenzenesulfonamide)silver(I) (**8**) (0.227 g, 0.490 mmol, 1.00 equiv) and nickel aryl bromide complex **7a** (0.200 g, 0.490 mmol, 1.00 equiv) in a 20 mL vial was added a toluene solution (4 mL) that contained pyridine (78.0 mg, 79.0 μL , 0.980 mmol, 2.00 equiv) at 23 $^\circ\text{C}$, followed by addition of acetonitrile (1 mL). After stirring for 1 min at 23, the solution was filtered through a glass frit, and the filtered cake was extracted further with dichloromethane (3×5 mL). The combined filtrate was concentrated in vacuo and the resulting residue was dissolved in dichloromethane (8 mL), the solution was filtered through a pad of Celite, and the filtrate was concentrated in vacuo. The resulting residue was recrystallized by dissolving the solid in CH_2Cl_2 (3 mL) and layering with pentane (17 mL). After one hour, the solid was collected by filtration to afford 0.256 g of the title compound as a yellow solid (81%).

NMR Spectroscopy: ^1H NMR (500 MHz, CDCl_3 , δ): 9.17 (d, $J = 5.4$ Hz, 2H), 8.25 (d, $J = 5.4$ Hz, 1H), 7.57–7.47 (m, 6H), 7.43–7.36 (m, 3H), 7.32–7.28 (m, 3H), 7.21–6.97 (m, 10H), 6.61–6.59 (m, 1H). ^{13}C NMR (125 MHz, CDCl_3 , δ): 156.0, 154.9, 152.7, 151.4, 147.0, 141.6, 141.2, 137.2, 136.7, 136.5, 135.8, 135.6, 135.5, 131.6, 130.4, 130.2, 129.9, 128.7, 128.6, 128.3, 126.6, 126.4, 124.4, 124.3, 124.2, 122.8, 122.6, 121.8. Anal: calcd for $\text{C}_{34}\text{H}_{26}\text{N}_4\text{NiO}_4\text{S}$: C, 63.28; H, 4.06; N, 8.68; found: C, 63.02; H, 4.31; N, 8.48.

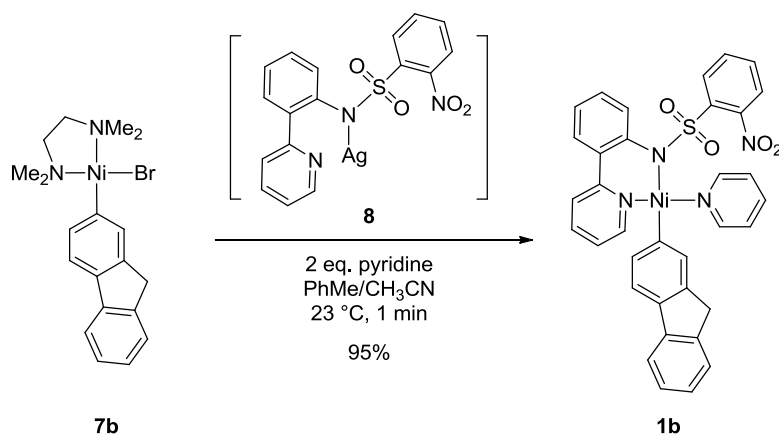
Synthesis of nickel aryl bromide complex 7b



To a solution of TMEDA (104 mg, 0.133 mL, 0.896 mmol, 1.00 equiv) and 2-bromofluorene (220 mg, 0.896 mmol, 1.00 equiv) in toluene (4 mL) was added $\text{Ni}(\text{COD})_2$ (250 mg, 0.896 mmol, 1.00 equiv), and the mixture was stirred at room temperature for 2 h. Pentane (16 mL) was added to the mixtures and the resulting solid was collected on a frit. The solid was washed with pentane (3×5 mL) and dried in vacuo to afford 348 mg of the title compound as a pink solid (92%).

^1H NMR (500 MHz, CD_2Cl_2 , δ): 7.73 (s, 1H), 7.62 (d, $J = 6.4$ Hz, 1H), 7.53 (d, $J = 6.4$ Hz, 1H), 7.45 (d, $J = 6.4$ Hz, 1H), 7.31–7.26 (m, 2H), 7.18–7.15 (m, 1H), 3.78 (br s, 2H), 2.55–2.23 (br, 16H). ^{13}C NMR (125 MHz, CD_2Cl_2 , δ): 143.1, 142.4, 140.3, 136.3, 135.0, 134.0, 126.6, 125.6, 125.1, 118.9, 116.1, 61.4 (br), 57.3 (br), 49.4 (br), 48.3 (br), 36.5. Anal: calcd for $\text{C}_{19}\text{H}_{25}\text{BrN}_2\text{Ni}$: C, 54.33; H, 6.00; N, 6.67; found: C, 53.98; H, 5.85; N, 6.56.

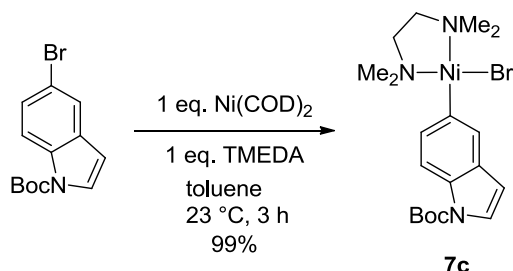
Synthesis of nickel aryl complex 1b



To (2-(2-pyridinyl)phenyl-2-nitrobenzenesulfonamide)silver(I) (**8**) (110 mg, 0.238 mmol, 1.00 equiv) and nickel aryl bromide complex **7b** (100 mg, 0.238 mmol, 1.00 equiv) in a 20 mL vial was added a toluene solution (4 mL) that contained pyridine (37.7 mg, 38.4 μL , 0.476 mmol, 2.00 equiv) at 23 °C, followed by addition of acetonitrile (0.5 mL). After stirring for 1 min at 23, the solution was filtered through a glass frit, and the filtered cake was extracted further with dichloromethane (3×3 mL). The combined filtrate was concentrated in vacuo, and the resulting residue was purified by chromatography on silica gel eluting with hexanes/EtOAc 1:2 (v/v) and further recrystallized by dissolving the solid in CH_2Cl_2 (2 mL) and layering with pentane (20 mL) to afford 0.148 g of the title compound as a yellow solid (95%).

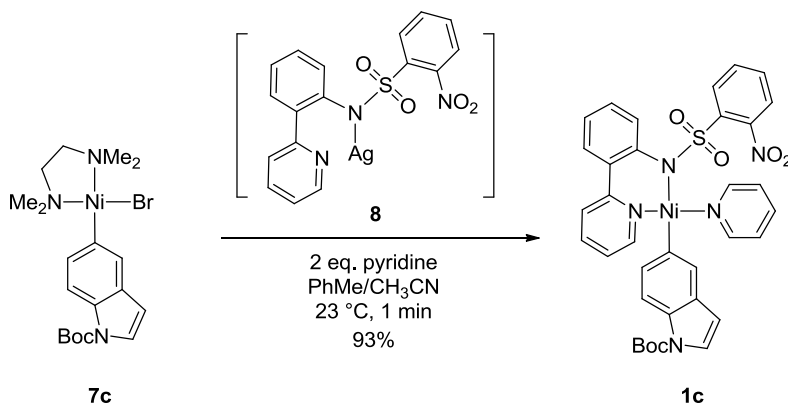
$R_f = 0.53$ (hexanes/EtOAc 1:2 (v/v)). NMR Spectroscopy: ^1H NMR (500 MHz, CDCl_3 , 23 °C, δ): 9.18 (d, $J = 5.3$ Hz, 2H), 8.24 (d, $J = 6.4$ Hz, 1H), 7.65 (s, 1H), 7.58–7.46 (m, 6H), 7.40–7.37 (m, 2H), 7.29–7.21 (m, 3H), 7.16–7.07 (m, 6H), 7.02–6.97 (m, 2H), 6.57–6.54 (m, $J = 6.3$, 1H), 3.72–3.58 (m, 2H). ^{13}C NMR (125 MHz, CDCl_3 , 23 °C, δ): 156.0, 155.2, 152.6, 151.4, 147.0, 142.6, 142.2, 141.3, 141.0, 137.1, 137.1, 136.7, 136.6, 135.6, 133.0, 131.8, 131.6, 130.4, 130.2, 129.9, 128.7, 128.3, 126.5, 125.6, 124.9, 124.4, 124.1, 122.8, 122.7, 121.7, 118.9, 117.1, 36.4. Anal: calcd for $\text{C}_{35}\text{H}_{26}\text{N}_4\text{NiO}_4\text{S} \cdot (\text{CH}_2\text{Cl}_2)_{0.1}$: C, 63.31; H, 3.97; N, 8.41; found: C, 63.04; H, 4.18; N,

8.36.

Synthesis of nickel aryl bromide complex 7c

To a solution of TMEDA (122 mg, 0.157 mL, 1.05 mmol, 1.00 equiv) and *tert*-butyl 5-bromindole-1-carboxylate (311 mg, 1.05 mmol, 1.00 equiv) in toluene (5 mL) was added Ni(COD)₂ (293 mg, 1.05 mmol, 1.00 equiv), and the mixture was stirred at room temperature for 3 h. Pentane (16 mL) was added to the mixtures and the resulting solid was collected on a frit. The solid was washed with pentane (3 × 5 mL) and dried in vacuo to afford 491 mg of the title compound as a peach solid (99%).

¹H NMR (600 MHz, CD₂Cl₂, δ): 7.64 (d, *J* = 7.4 Hz, 1H), 7.55 (s, 1H), 7.48 (d, *J* = 8.6 Hz, 1H), 7.36 (d, *J* = 3.3 Hz, 1H), 6.38 (d, *J* = 3.6 Hz, 1H), 2.56–2.21 (br, 16H). ¹³C NMR (125 MHz, CD₂Cl₂, δ): 150.3, 132.9, 129.3, 129.0, 128.5, 124.2, 111.8, 106.4, 83.1, 61.4 (br), 57.3 (br), 49.3 (br), 48.4 (br), 28.0. Anal: calcd for C₁₉H₃₀BrN₃NiO₂: C, 48.44; H, 6.42; N, 8.92; found: C, 48.14; H, 6.22; N, 8.84.

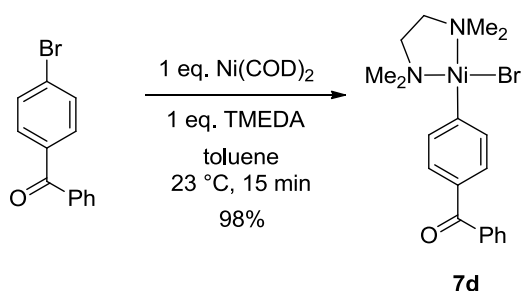
Synthesis of nickel aryl complex 1c

To (2-(2-pyridinyl)phenyl-2-nitrobenzenesulfonamide)silver(I) (**8**) (98.0 mg, 0.212 mmol, 1.00 equiv) and nickel aryl bromide complex **7c** (100 mg, 0.212 mmol, 1.00 equiv) in a 20 mL vial was added a toluene solution (3 mL) that contained pyridine (33.6 mg, 34.2 μL, 0.425 mmol, 2.00 equiv) at 23 °C, followed by addition of acetonitrile (0.5 mL). After stirring for 1 min at 23, the solution was filtered through a glass frit, and the filtered cake was extracted further with

dichloromethane (3 × 3 mL). The combined filtrate was concentrated in vacuo and the resulting residue was purified by chromatography on silica gel eluting with hexanes/EtOAc 1:2 (v/v) and further recrystallized by dissolving the solid in CH₂Cl₂ (2 mL) and layering with pentane (20 mL) to afford 140 mg of the title compound as a yellow solid (93%).

R_f = 0.53 (hexanes/EtOAc 1:2 (v/v)). NMR Spectroscopy: ¹H NMR (500 MHz, CDCl₃, 23 °C, δ): 9.10 (d, J = 4.3 Hz, 2H), 8.16 (d, J = 5.3 Hz, 1H), 7.59–7.39 (m, 6H), 7.33–7.29 (m, 2H), 7.21–7.18 (m, 2H), 7.09–7.00 (m, 5H), 6.93–6.91 (m, 2H), 6.48–6.47 (m, 1H), 6.23 (d, J = 4.3, 1H), 1.50 (s, 9H). ¹³C NMR (125 MHz, CDCl₃, 23 °C, δ): 156.0, 152.7, 151.5, 150.1, 147.0, 146.8, 141.3, 137.0, 136.6, 136.6, 135.7, 131.6, 130.7, 130.4, 130.1, 129.9, 129.3, 128.8, 128.3, 126.7, 124.4, 124.3, 124.1, 122.8, 122.6, 121.7, 112.6, 83.1, 28.0. Anal: calcd for C₃₅H₃₁N₅NiO₆S (CH₂Cl₂)_{0.1}: C, 58.81; H, 4.39; N, 9.77; found: C, 58.49; H, 4.39; N, 9.81. X-ray quality crystals were obtained from 2 mL CH₂Cl₂ solution that contained 10.0 mg of the title compound slowly layered with 8.0 mL pentane at 23 °C. For crystallography data, see X-ray section.

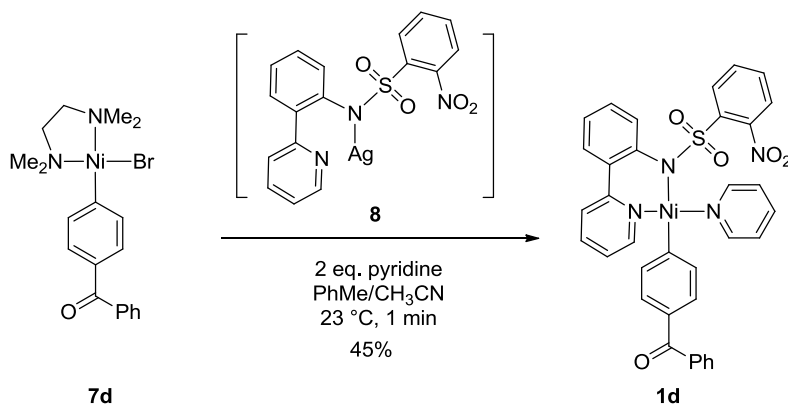
Synthesis of nickel aryl bromide complex 7d



To a solution of TMEDA (83.0 mg, 0.107 mL, 0.717 mmol, 1.00 equiv) and 4-bromobenzophenone (187 mg, 0.717 mmol, 1.00 equiv) in toluene (4 mL) was added Ni(COD)₂ (200 mg, 0.717 mmol, 1.00 equiv), and the mixture was stirred at room temperature for 15 min. Pentane (16 mL) was added to the mixtures and the resulting solid was collected on a frit. The solid was washed with pentane (3 × 5 mL) and dried in vacuo to afford 305 mg of the title compound as an orange solid (98%).

¹H NMR (600 MHz, CD₂Cl₂, δ): 7.77 (d, J = 7.5 Hz, 2H), 7.70 (d, J = 6.4 Hz, 2H), 7.56–7.52 (m, 1H), 7.46–7.43 (m, 2H), 7.24 (d, J = 7.5 Hz, 2H), 2.56–2.22 (br, 16H). ¹³C NMR (125 MHz, CD₂Cl₂, δ): 197.3, 162.4, 139.2, 137.4, 131.7, 129.9, 128.3, 125.6, 111.0, 61.5 (br), 57.4 (br), 49.7 (br), 48.4 (br), 36.5. Anal: calcd for C₁₉H₂₅BrN₂NiO (PhMe)_{0.1}: C, 53.15; H, 5.84; N, 6.29; found: C, 53.41; H, 5.84; N, 6.18.

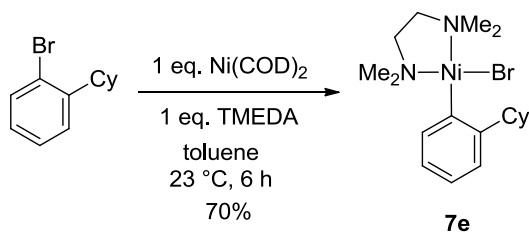
Synthesis of nickel aryl complex **1d**



To (2-(2-pyridinyl)phenyl-2-nitrobenzenesulfonamide)silver(I) (**8**) (212 mg, 0.459 mmol, 1.00 equiv) and nickel aryl bromide complex **7d** (200 mg, 0.459 mmol, 1.00 equiv) in a 20 mL vial was added a toluene solution (4 mL) that contained pyridine (78.0 mg, 79.0 μL , 0.980 mmol, 2.00 equiv) at 23 $^\circ\text{C}$, followed by addition of acetonitrile (1.0 mL). After stirring for 1 min at 23, the solution was filtered through a glass frit, and the filtered cake was extracted further with dichloromethane (3×5 mL). The combined filtrate was concentrated in vacuo and the resulting residue was purified by chromatography on silica gel eluting with hexanes/EtOAc 1:2 (v/v) and further recrystallized by dissolving the solid in CH_2Cl_2 (2 mL) and layering with pentane (20 mL) to afford 138 mg of the title compound as a yellow solid (45%).

$R_f = 0.41$ (hexanes/EtOAc 1:2 (v/v)). NMR Spectroscopy: ^1H NMR (500 MHz, CD_2Cl_2 , 23 $^\circ\text{C}$, δ): 9.13 (d, $J = 5.3$ Hz, 2H), 8.17 (d, $J = 5.3$ Hz, 1H), 7.69 (d, $J = 7.6$ Hz, 2H), 7.66–7.56 (m, 5H), 7.52–7.49 (m, 1H), 7.41–7.35 (m, 5H), 7.26–7.23 (m, 2H), 7.19–7.16 (m, 4H), 7.08 (d, $J = 8.3$ Hz, 1H), 7.02 (br s, 2H), 6.67–6.64 (m, 1H). ^{13}C NMR (125 MHz, CD_2Cl_2 , 23 $^\circ\text{C}$, δ): 197.1, 169.1, 156.2, 152.5, 151.5, 147.3, 141.2, 138.8, 138.0, 137.4, 136.6, 136.0, 135.6, 132.8, 131.9, 131.8, 130.9, 130.8, 130.3, 130.0, 128.8, 128.7, 128.3, 126.9, 124.8, 124.6, 123.4, 123.0, 122.4. Anal: calcd for $\text{C}_{35}\text{H}_{26}\text{N}_4\text{NiO}_5\text{S}$ (CH_2Cl_2) $_{0.15}$: C, 61.53; H, 3.86; N, 8.17; found: C, 61.19; H, 4.20; N, 8.58.

Synthesis of nickel aryl bromide complex **7e**

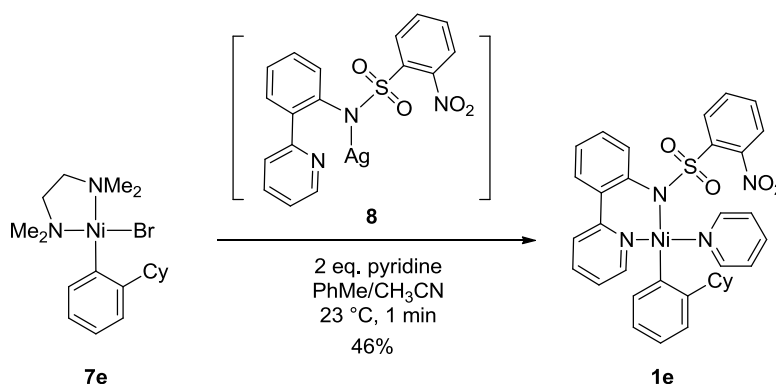


To a solution of TMEDA (83.0 mg, 0.107 mL, 0.717 mmol, 1.00 equiv) and 1-bromo-2-cyclohexylbenzene (171 mg, 0.717 mmol, 1.00 equiv) in toluene (4 mL) was added Ni(COD)_2

(200 mg, 0.717 mmol, 1.00 equiv), and the mixture was stirred at room temperature for 6 h. Pentane (16 mL) was added to the mixtures and the resulting solid was collected on a frit. The solid was washed with pentane (3×5 mL) and dried in vacuo to afford 208 mg of the title compound as a pink solid (70%).

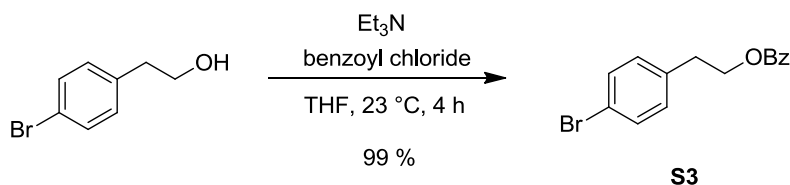
^1H NMR (600 MHz, CD_2Cl_2 , δ): 7.37 (d, $J = 7.5$ Hz, 2H), 6.68–6.62 (m, 3H), 5.55–5.45 (m, 1H), 2.75–2.23 (br, 16H), 2.05–1.73 (m, 8H), 2.05–1.73 (m, 8H), 1.48–1.41 (m, 1H), 1.15 (br s, 1H). ^{13}C NMR (125 MHz, CD_2Cl_2 , δ): 153.3, 143.2, 136.8, 123.1, 123.0, 122.3, 61.4 (br), 57.2 (br), 50.8 (br), 49.9, 48.9 (br), 48.2 (br), 47.5 (br), 35.8 (br), 34.3 (br), 28.4 (br), 27.2. Anal: calcd for $\text{C}_{18}\text{H}_{31}\text{BrN}_2\text{Ni}$: C, 52.21; H, 7.55; N, 6.77; found: C, 51.87; H, 7.43; N, 6.73.

Synthesis of nickel aryl complex **1e**



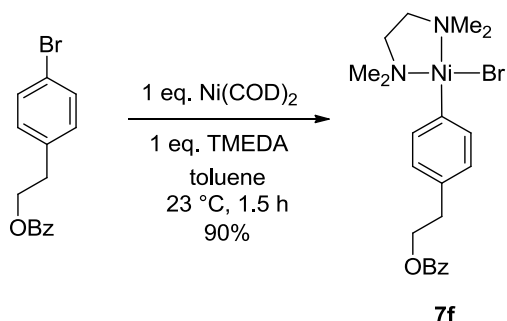
To (2-(2-pyridinyl)phenyl-2-nitrobenzenesulfonamide)silver(I) (**8**) (223 mg, 0.483 mmol, 1.00 equiv) and nickel aryl bromide complex **7e** (200 mg, 0.483 mmol, 1.00 equiv) in a 20 mL vial was added a toluene solution (4 mL) that contained pyridine (76.0 mg, 78.0 μL , 0.966 mmol, 2.00 equiv) at 23 °C, followed by addition of acetonitrile (1.0 mL). After stirring for 1 min at 23, the solution was filtered through a glass frit, and the filtered cake was extracted further with dichloromethane (3×5 mL). The combined filtrate was concentrated in vacuo and the resulting residue was purified by chromatography on silica gel eluting with hexanes/EtOAc 1:2 (v/v) and further recrystallized by dissolving the solid in CH_2Cl_2 (2 mL) and layering with pentane (20 mL) to afford 146 mg of the title compound as a yellow solid (46%).

$R_f = 0.66$ (hexanes/EtOAc 1:2 (v/v)). NMR Spectroscopy: ^1H NMR (500 MHz, CDCl_3 , 23 °C, δ): 9.09 (d, $J = 5.3$ Hz, 2H), 8.33 (d, $J = 5.3$ Hz, 1H), 8.18 (d, $J = 7.5$ Hz, 1H), 7.62–7.46 (m, 4H), 7.40–7.37 (m, 1H), 7.29–7.26 (m, 1H), 7.15–7.09 (m, 5H), 7.00–6.93 (m, 3H), 6.73–6.70 (m, 1H), 6.59–6.56 (m, 1H), 6.49 (d, $J = 7.4$, 1H), 4.86–4.82 (m, 1H), 1.73–1.01 (m, 10H). ^{13}C NMR (125, CDCl_3 , 23 °C, δ): 156.2, 156.1, 153.1, 151.8, 151.2, 147.0, 141.2, 137.0, 136.6, 135.4, 134.2, 131.8, 130.3, 130.1, 129.8, 128.9, 128.6, 125.1, 124.1, 124.0, 123.0, 122.7, 122.5, 121.7, 49.0, 35.5, 34.5, 27.4, 26.9, 26.4. Anal: calcd for $\text{C}_{34}\text{H}_{32}\text{N}_4\text{NiO}_4\text{S}$ (CH_2Cl_2)_{0.1}: C, 62.07; H, 4.92; N, 8.49; found: C, 61.91; H, 4.92; N, 8.69.

4-bromophenethyl benzoate (S3)

To a mixture of 2-(4-bromophenyl)ethanol (1.00 g, 4.97 mmol, 1.00 equiv) and Et₃N (0.763 mL, 0.554 g, 5.47 mmol, 1.10 equiv) in a round-bottom flask in THF (20 mL) was added benzoyl chloride (0.589 mL, 0.713 g, 5.07 mmol, 1.02 equiv). The reaction mixture was stirring for 4 h at 23 °C and concentrated in vacuo. The residue was purified by chromatography on silica gel eluting with hexanes/EtOAc 1:1 (v/v) to afford 1.50 g of the title compound as a colorless solid (99%).

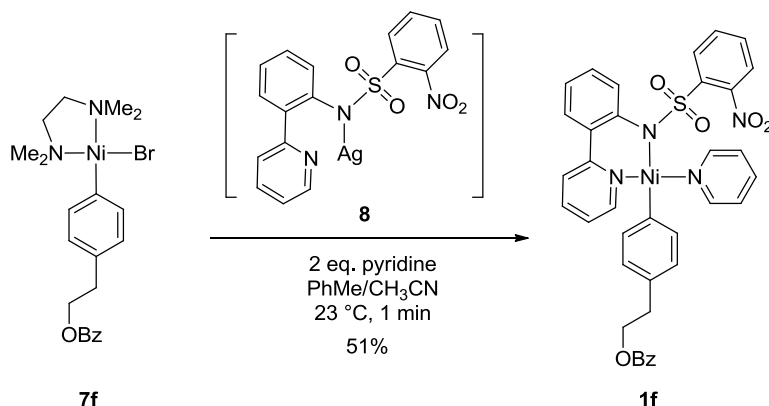
R_f = 0.70 (hexanes/EtOAc 1:1 (v/v)). NMR Spectroscopy: ¹H NMR (500 MHz, CDCl₃, 23 °C, δ): 8.00 (d, *J* = 7.2 Hz, 1H), 7.58–7.54 (m, 1H), 7.45–7.42 (m, 4H), 7.16 (d, *J* = 8.4 Hz, 2H), 4.51 (t, *J* = 6.4 Hz, 2H), 3.04 (t, *J* = 6.4 Hz, 2H). ¹³C NMR (125 MHz, CDCl₃, 23 °C, δ): 166.6, 137.1, 133.1, 131.8, 130.8, 130.3, 129.7, 128.5, 120.6, 65.2, 34.8. HRMS-FIA (*m/z*): calcd for C₁₅H₁₃BrO₂ [M + Na]⁺, 326.9991; found, 327.0007.

Synthesis of nickel aryl bromide complex 7f

To a solution of TMEDA (83 mg, 0.107 mL, 0.717 mmol, 1.00 equiv) and 4-bromophenethyl benzoate (219 mg, 0.717 mmol, 1.00 equiv) in toluene (4 mL) was added Ni(COD)₂ (200 mg, 0.717 mmol, 1.00 equiv), and the mixture was stirred at room temperature for 1.5 h. Pentane (16 mL) was added to the mixtures and the resulting solid was collected on a frit. The solid was washed with pentane (3 × 5 mL) and dried in vacuo to afford 208 mg of the title compound as an orange-pink solid (90%).

¹H NMR (600 MHz, CD₂Cl₂, δ): 7.98 (d, *J* = 6.9 Hz, 2H), 7.57–7.55 (m, 1H), 7.45–7.42 (m, 4H), 6.77 (d, *J* = 5.5 Hz, 2H), 4.41 (t, *J* = 6.2 Hz, 2H), 2.90 (t, *J* = 6.2 Hz, 2H), 2.53–2.15 (br, 16H).. ¹³C NMR (125 MHz, CD₂Cl₂, δ): 166.4, 142.4, 137.3, 132.9, 130.8, 130.8, 129.6, 128.5, 125.7, 66.4, 61.1 (br), 57.2 (br), 49.3 (br), 49.2 (br), 34.5. Anal: calcd for C₂₁H₂₉BrN₂NiO₂: C, 52.54; H, 6.09; N, 5.84; found: C, 52.81; H, 5.95; N, 5.53.

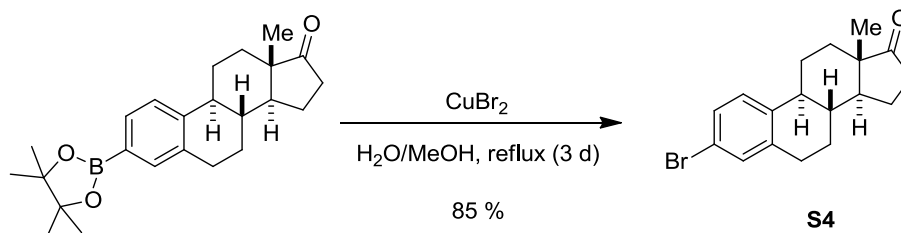
Synthesis of nickel aryl complex **1f**



To (2-(2-pyridinyl)phenyl-2-nitrobenzenesulfonamide)silver(I) (**8**) (193 mg, 0.417 mmol, 1.00 equiv) and nickel aryl bromide complex **7f** (200 mg, 0.417 mmol, 1.00 equiv) in a 20 mL vial was added a toluene solution (4 mL) that contained pyridine (65.9 mg, 67.1 μL , 0.833 mmol, 2.00 equiv) at 23 $^\circ\text{C}$, followed by addition of acetonitrile (1.0 mL). After stirring for 1 min at 23, the solution was filtered through a glass frit, and the filtered cake was extracted further with dichloromethane (3×5 mL). The combined filtrate was concentrated in vacuo and the resulting residue was purified by chromatography on silica gel eluting with hexanes/EtOAc 1:2 (v/v) to afford 152 mg of the title compound as a yellow solid (51%).

$R_f = 0.52$ (hexanes/EtOAc 1:2 (v/v)). NMR Spectroscopy: ^1H NMR (400 MHz, CDCl_3 , 23 $^\circ\text{C}$, δ): 9.13 (d, $J = 5.6$ Hz, 2H), 8.17 (d, $J = 5.2$ Hz, 1H), 7.94 (d, $J = 8.0$ Hz, 2H), 7.55–7.45 (m, 5H), 7.41–7.28 (m, 6H), 7.17–7.07 (m, 5H), 7.01–6.97 (m, 2H), 6.68 (d, $J = 7.6$, 2H), 6.57–6.54 (m, 1H), 4.32 (t, $J = 7.2$ Hz, 2H), 2.81 (t, $J = 7.2$ Hz, 2H). ^{13}C NMR (125 MHz CDCl_3 , 23 $^\circ\text{C}$, δ): 166.7, 156.0, 152.6, 152.3, 151.5, 147.1, 141.3, 137.1, 136.7, 136.6, 136.3, 135.6, 135.5, 132.9, 131.8, 131.6, 130.6, 130.4, 130.1, 129.8, 129.6, 128.8, 128.5, 128.4, 128.3, 127.2, 126.7, 124.3, 124.1, 122.8, 122.6, 121.7, 66.1, 34.6. Anal: calcd for $\text{C}_{37}\text{H}_{30}\text{N}_4\text{NiO}_6\text{S}$: C, 61.94; H, 4.21; N, 7.81; found: C, 61.58; H, 4.16; N, 7.47.

Synthesis of 3-deoxy-3-bromoestrone (**S4**)

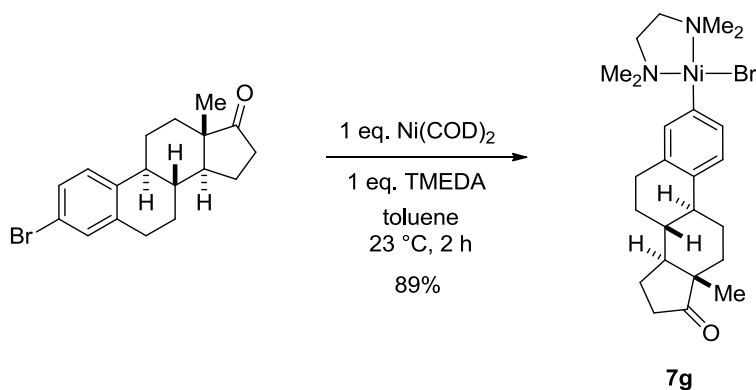


To 3-pinacolatoboroestra-1,3,5-(10)-triene-17-one (3.50 g, 9.20 mmol, 1.00 equiv)⁹ in a round-bottom flask in MeOH (70 mL) was added copper(II) bromide (11.0 g, 49.2 mmol, 5.00 equiv) in H_2O (70 mL) in one portion. The reaction mixture was stirred at reflux for 3 d. The reaction

mixture was cooled to 23 °C and subsequently poured into H₂O (200 mL). The colorless precipitate was collected on a frit, followed by washing with water (3 × 30 mL). CH₂Cl₂ (100 mL) was added to the solid and the solution was filtered through a pad of Celite. The filtrate was concentrated, triturated with Et₂O (3 × 5 mL) and dried to afford 2.60 g of the title compound as a colorless solid (85% yield).

NMR Spectroscopy: ¹H NMR (500 MHz, CDCl₃, 23 °C, δ): 7.28 (d, *J* = 8.6 Hz, 1H), 7.26 (s, 1H), 7.17 (d, *J* = 8.6 Hz, 1H), 2.92–2.90 (m, 2H), 2.56–2.50 (m, 2H), 2.28–2.23 (m, 1H), 2.21–1.98 (m, 4H), 1.69–1.41 (m, 6H), 0.93 (s, 3 H). ¹³C NMR (125 MHz, CDCl₃, 23 °C, δ): 220.7, 139.0, 138.9, 131.8, 128.8, 127.3, 119.7, 50.5, 48.0, 44.2, 38.0, 35.9, 31.6, 29.3, 26.4, 25.8, 21.7, 13.9. HRMS-FIA (*m/z*): calcd for C₁₈H₂₁BrO [M + Na]⁺, 333.0849; found, 333.0861.

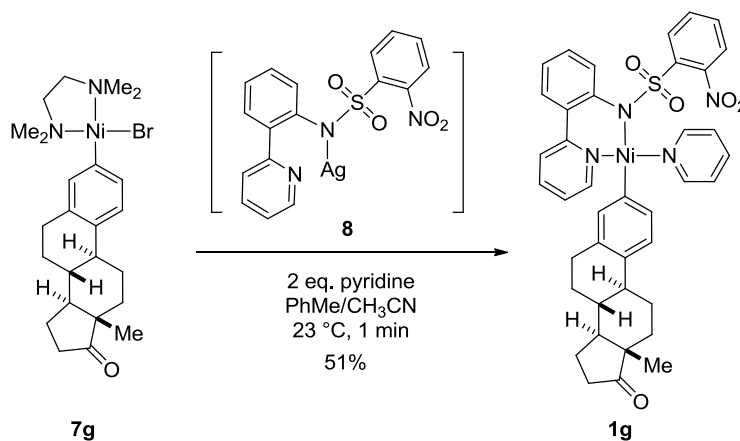
Synthesis of nickel aryl bromide complex 7g



To a solution of TMEDA (83.0 mg, 0.134 mL, 0.896 mmol, 1.00 equiv) and 3-deoxy-3-bromoestrone (299 mg, 0.896 mmol, 1.00 equiv) in toluene (5 mL) was added (Ni(COD)₂ (200 mg, 0.896 mmol, 1.00 equiv), and the mixture was stirred at room temperature for 2 h. Pentane (16 mL) was added to the mixtures and the resulting solid was collected on a frit. The solid was washed with pentane (3 × 5 mL) and dried in vacuo to afford 406 mg of the title compound as a peach solid (89%).

NMR Spectroscopy: ¹H NMR (600 MHz, CD₂Cl₂, δ): 7.21 (d, *J* = 8.2 Hz, 1H), 7.16 (s, 1H), 6.73 (d, *J* = 6.9 Hz, 1H), 2.83 (br s, 2H), 2.52–2.23 (br, 18H), 2.10–1.85 (m, 6H), 1.59–1.29 (4H), 0.87 (m, 3H). ¹³C NMR (125 MHz, CD₂Cl₂, δ): 220.9, 137.8, 135.0, 133.1, 133.1, 121.9, 110.9, 61.4 (br), 57.3 (br), 50.9, 49.4 (br), 48.3, 44.3, 38.8 (br), 36.1, 32.1, 29.7, 27.2, 26.1, 21.8, 14.0. Anal: calcd for C₂₄H₃₇BrN₂NiO: C, 56.73; H, 7.34; N, 5.51; found: C, 52.92; H, 6.91; N, 5.50. Numerous attempts (recrystallization using different solvents) were made to obtain satisfactory elemental analysis data but none of them was successful. However, this material was of sufficient quality to allow preparation of analytically pure **1g** (see below). HRMS-FIA (*m/z*): calcd for C₂₄H₃₇N₂NiO [M – Br]⁺, 427.2259; found, 427.2263.

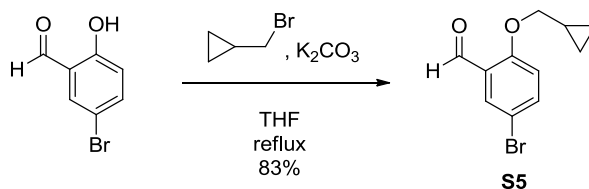
Synthesis of nickel aryl complex **1g**



To (2-(2-pyridinyl)phenyl-2-nitrobenzenesulfonamide)silver(I) (**8**) (193 mg, 0.417 mmol, 1.00 equiv) and nickel aryl bromide complex **7g** (200 mg, 0.417 mmol, 1.00 equiv) in a 20 mL vial was added a toluene solution (4 mL) that contained pyridine (65.9 mg, 67.1 μ L, 0.833 mmol, 2.00 equiv) at 23 °C, followed by addition of acetonitrile (1.0 mL). After stirring for 1 min at 23, the solution was filtered through a glass frit, and the filtered cake was extracted further with dichloromethane (3×5 mL). The combined filtrate was concentrated in vacuo and the resulting residue was purified by chromatography on silica gel eluting with hexanes/EtOAc 1:2 (v/v) and further recrystallized by dissolving the solid in CH_2Cl_2 (2 mL) and layering with pentane (20 mL) to afford 152 mg of the title compound as a yellow solid (51%).

$R_f = 0.35$ (hexanes/EtOAc 1:2 (v/v)). NMR Spectroscopy: ^1H NMR (500 MHz, CDCl_3 , 23 °C, δ): 9.14 (d, $J = 4.9$ Hz, 2H), 8.28–8.26 (m, 1H), 7.54–7.45 (m, 4H), 7.36–7.28 (m, 2H), 7.16–6.97 (m, 9H), 6.66–6.62 (m, 2H), 2.77–2.60 (m, 2H), 2.47–2.41 (m, 2H), 2.21–1.85 (m, 6H), 1.55–1.27 (4H), 0.82 (m, 3H). ^{13}C NMR (125 MHz CDCl_3 , 23 °C, δ): 221.3, 156.0, 152.7, 152.7, 151.5, 150.7, 150.6, 147.0, 141.3, 137.0, 136.6, 135.9, 135.8, 135.7, 133.9, 133.8, 133.7, 133.1, 132.9, 131.6, 131.3, 130.5, 130.4, 130.1, 129.7, 128.8, 128.4, 128.3, 124.4, 124.2, 124.1, 122.8, 122.7, 122.7, 122.6, 121.7, 50.7, 48.2, 44.2, 44.2, 38.4, 38.3, 36.0, 31.8, 29.5, 29.5, 26.9, 25.6, 25.6, 21.7, 14.0. Anal: calcd for $\text{C}_{40}\text{H}_{38}\text{N}_4\text{NiO}_5\text{S}$ (CH_2Cl_2) $_{0.1}$: C, 63.88; H, 5.11; N, 7.43; found: C, 63.62; H, 5.26; N, 7.06.

5-Bromo-2-(cyclopropylmethoxy)benzaldehyde (**S5**)⁹

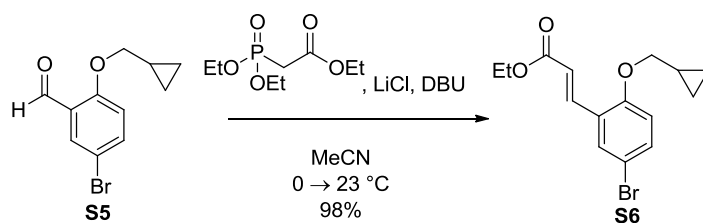


To 5-bromo-2-hydroxybenzaldehyde (1.00 g, 4.97 mmol, 1.00 equiv) and K_2CO_3 (3.44 g, 24.9

mmol, 5.00 equiv) in THF (10 mL) in an oven-dried round-bottom flask fitted with a reflux condenser under a N₂ atmosphere at 23 °C was added (bromomethyl)cyclopropane (1.01 g, 0.724 mL, 7.46 mmol, 1.50 equiv). The reaction mixture was warmed in an oil heating bath at a temperature of 70 °C and heated at reflux with vigorous stirring for 40 hours. The reaction mixture was cooled to 23 °C and poured into H₂O (30 mL) in a separatory funnel. CHCl₃ (30 mL) was added, the funnel was shaken and the organic phase collected. The aqueous phase was then extracted with CHCl₃ (2 × 30 mL). The combined organic phases were washed with brine (30 mL), dried with Na₂SO₄, and concentrated in vacuo. The residue was purified by chromatography on silica gel, eluting with 2–7% EtOAc in hexanes (v/v) to afford 1.05 g of the title compound as a colorless solid (83% yield).

R_f = 0.30 (hexanes/EtOAc 19:1 (v/v)). NMR Spectroscopy: ¹H NMR (600 MHz, CDCl₃, 23 °C, δ): 10.45 (s, 1H), 7.91 (d, *J* = 2.5 Hz, 1H), 7.58 (dd, *J* = 8.9, 2.6 Hz, 1H), 6.84 (d, *J* = 8.9 Hz, 1H), 3.91 (d, *J* = 7.2 Hz, 2H), 1.32–1.26 (m, 1H), 0.71–0.63 (m, 2H), 0.41–0.34 (m, 2H). ¹³C NMR (125 MHz, CDCl₃, 23 °C, δ): 188.7, 160.5, 138.3, 130.9, 126.5, 115.0, 113.5, 73.9, 10.1, 3.4. HRMS-FIA (*m/z*): calcd for C₁₁H₁₁BrNaO₂ [M + Na]⁺, 276.9840; found, 276.9820.

(E)-ethyl 3-(5-bromo-2-(cyclopropylmethoxy)phenyl)acrylate (S6)

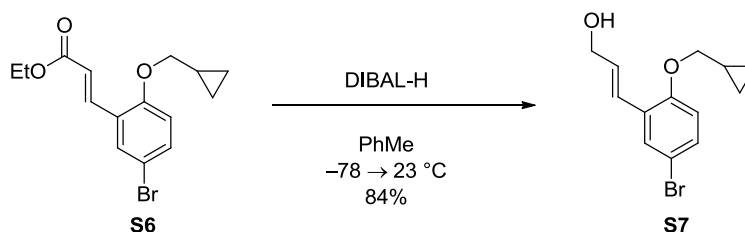


To 5-bromo-2-(cyclopropylmethoxy)benzaldehyde (S5) (3.10 g, 12.2 mmol, 1.00 equiv) and LiCl (0.541 g, 12.8 mmol, 1.05 equiv) in MeCN (45 mL) in a round-bottom flask under a N₂ atmosphere at 0 °C was added triethyl phosphonoacetate (3.00 g, 2.68 mL, 13.4 mmol, 1.10 equiv) and 1,8-diazabicycloundec-7-ene (DBU) (2.04 g, 2.02 mL, 13.4 mmol, 1.10 equiv). Upon the addition of DBU, the reaction mixture turned yellow. The reaction mixture was warmed to 23 °C and stirred for 15 hours. The reaction mixture was poured into H₂O (75 mL) in a separatory funnel. CHCl₃ (75 mL) was added and the funnel was shaken and the organic phase collected. The aqueous phase was extracted from with CHCl₃ (2 × 50 mL). All organic phases were combined and washed with brine (50 mL), dried with Na₂SO₄, and concentrated in vacuo. The residue was purified by chromatography on silica gel, eluting with 5–10% EtOAc in hexanes (v/v) to afford 3.89 g of the title compound as a colorless solid (98% yield).

R_f = 0.25 (hexanes/EtOAc 19:1 (v/v)). NMR Spectroscopy: ¹H NMR (500 MHz, CDCl₃, 23 °C, δ): 7.93 (d, *J* = 16.1 Hz, 1H), 7.60 (d, *J* = 2.4 Hz, 1H), 7.37 (dd, *J* = 8.8, 2.5 Hz, 1H), 6.74 (d, 8.8 Hz, 1H), 6.53 (d, *J* = 16.1 Hz, 1H), 4.26 (q, *J* = 6.8 Hz, 2H), 3.84 (d, *J* = 6.8 Hz, 2H), 1.34–1.25 (m, 4H), 0.70–0.61 (m, 2H), 0.40–0.31 (m, 2H). ¹³C NMR (125 MHz, CDCl₃, 23 °C, δ): 167.3, 156.9, 138.7, 133.7, 131.3, 125.9, 120.0, 114.4, 113.0, 73.9, 60.6, 14.4, 10.2, 3.4. HRMS-FIA

(*m/z*): calcd for $C_{15}H_{18}BrO_3 [M + H]^+$, 325.0439; found, 325.0428.

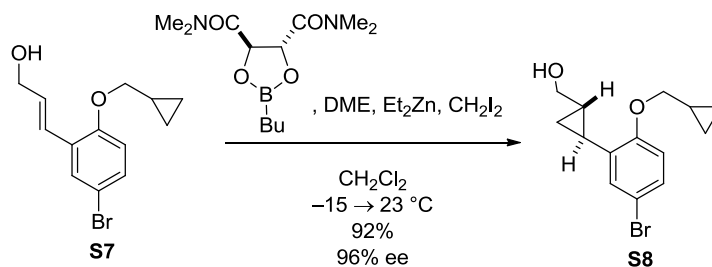
(*E*)-3-(5-bromo-2-(cyclopropylmethoxy)phenyl)prop-2-en-1-ol (S7)



To (*E*)-ethyl 3-(5-bromo-2-(cyclopropylmethoxy)phenyl)acrylate (**S6**) (3.78 g, 11.6 mmol, 1.00 equiv) in PhMe (30 mL) in a flame-dried round-bottom flask under a N_2 atmosphere at $-78\text{ }^\circ\text{C}$ was added a 1.0 M solution of diisobutylaluminum hydride (DIBAL-H) in PhMe (26 mL, 26 mmol, 2.2 equiv) in 6 portions dropwise every 10 minutes for 1 hour. The reaction was warmed to $0\text{ }^\circ\text{C}$ over 2 hours and then warmed to $23\text{ }^\circ\text{C}$ and stirred at this temperature for 1 hour. The reaction mixture was poured onto a concentrated aqueous Rochelle's salt (potassium sodium tartrate) solution (400 mL). EtOAc (400 mL) was added and the mixture was stirred for 3 hour until two liquid phases separated cleanly. The phases were partitioned and the aqueous phase was extracted from with EtOAc (300 mL). The organic phases were combined and washed with brine (200 mL), dried with Na_2SO_4 , and concentrated in vacuo. The residue was purified by chromatography on silica gel, eluting with a gradient of 10–25% EtOAc in hexanes (v/v) to afford 2.77 g of the title compound as a colorless solid (84% yield).

$R_f = 0.15$ (hexanes/EtOAc 6:1 (v/v)). NMR Spectroscopy: 1H NMR (500 MHz, $CDCl_3$, $23\text{ }^\circ\text{C}$, δ): 7.53 (d, $J = 2.4$ Hz, 1H), 7.26 (dd, $J = 8.8, 2.4$ Hz, 1H), 6.88 (d, $J = 16.1$ Hz, 1H), 6.69 (d, $J = 8.8$ Hz, 1H), 6.39 (dt, $J = 16.1, 5.9$ Hz, 1H), 4.33 (br dd, $J = 4.6, 4.6$ Hz, 2H), 3.79 (d, $J = 6.8$ Hz, 2H), 1.71 (br t, $J = 5.1$ Hz, 1H), 1.31–1.23 (m, 1H), 0.68–0.58 (m, 2H), 0.38–0.30 (m, 2H). ^{13}C NMR (125 MHz, $CDCl_3$, $23\text{ }^\circ\text{C}$, δ): 155.4, 131.2, 130.5, 129.7, 128.2, 125.0, 114.2, 113.2, 73.7, 64.1, 10.3, 3.4. HRMS-FIA (*m/z*): calcd for $C_{13}H_{15}BrNaO_2 [M + Na]^+$, 305.0153; found, 305.0123.

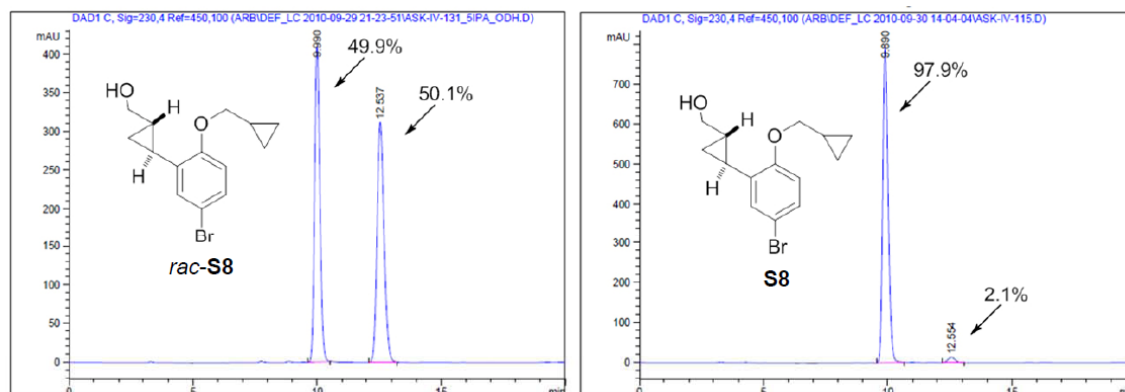
((1*S*,2*S*)-2-(5-bromo-2-(cyclopropylmethoxy)phenyl)cyclopropyl)methanol (S8)



Following a published procedure for asymmetric allylic cyclopropanation:¹⁰ To dimethoxyethane (DME) (1.39 g, 1.60 mL, 15.4 mmol, 1.90 equiv) in CH_2Cl_2 (50 mL) in a flame-dried round-

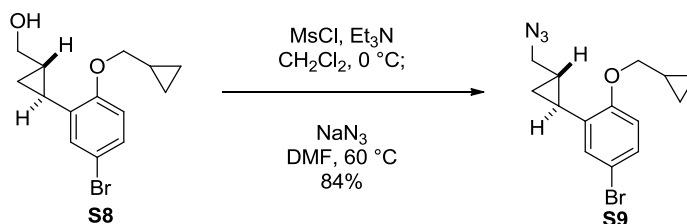
bottom flask under a N₂ atmosphere cooled in an ethyleneglycol/CO₂ bath at –15 °C was added diethylzinc (2.01 g, 1.67 mL, 16.3 mmol, 2.00 equiv), while maintaining the bath temperature between –15 and –10 °C. CH₂I₂ (8.70 g, 2.62 mL, 32.5 mmol, 4.00 equiv) was added dropwise over 20 minutes at –15 °C. The reaction mixture was stirred at –15 °C for 10 minutes. A solution of (4*R*,5*R*)-2-butyl-*N,N,N',N'*-tetramethyl-1,3,2-dioxaborolane-4,5-dicarboxamide (2.63 g, 2.46 mL, 9.75 mmol, 1.20 equiv) in CH₂Cl₂ (10 mL) from a separate flame-dried round-bottom flask under a N₂ atmosphere was added over 5 minutes via syringe. A solution of (*E*)-3-(5-bromo-2-(cyclopropylmethoxy)phenyl)prop-2-en-1-ol (**S7**) (2.30 g, 8.12 mmol, 1.00 equiv) in CH₂Cl₂ (10 mL) from a separate flame-dried round-bottom flask under a N₂ atmosphere was added over 5 minutes via syringe. The reaction mixture was allowed to warm to 23 °C and stirred for 20 hours. Saturated aqueous NH₄Cl solution (10 mL) and 1M HCl (50 mL) were added to the reaction mixture. The reaction mixture was transferred to a separatory funnel. Diethyl ether (200 mL) was added and the separatory funnel was shaken and the organic phase was separated. The aqueous phase was extracted from with diethyl ether (200 mL) and then again with diethyl ether (100 mL). The combined organic phases were transferred to an Erlenmeyer flask. 2 M NaOH solution (60 mL) and 30% H₂O₂ solution (15 mL) were added. The reaction mixture was stirred vigorously for 5 minutes. The reaction mixture was transferred into a separatory funnel and partitioned. The organic phase was washed with 1.0 M aqueous HCl (75 mL), saturated aqueous Na₂CO₃ solution (75 mL), saturated aqueous NaHCO₃ solution (75 mL) and brine (75 mL). The organic phase was dried with MgSO₄, and concentrated in vacuo. The residue was purified by chromatography on silica gel, eluting with a gradient of 10–30% EtOAc in hexanes (v/v) to afford 2.21 g of the title compound as a colorless oil (92% yield and 96% *ee* as determined on a Chiracel ODH column with 5% isopropanol/hexanes eluent (see Figure S4). Racemic **S8** was synthesized using the above procedures omitting the addition of (4*R*,5*R*)-2-butyl-*N,N,N',N'*-tetramethyl-1,3,2-dioxaborolane-4,5-dicarboxamide. Absolute stereochemistry was assigned by analogy.¹⁰

R_f = 0.20 (hexanes/EtOAc 6:1 (v/v)). NMR Spectroscopy: ¹H NMR (500 MHz, CDCl₃, 23 °C, δ): 7.24 (dd, *J* = 8.8, 2.4 Hz, 1H), 7.09 (d, *J* = 2.4 Hz, 1H), 6.65 (d, *J* = 8.8 Hz, 1H), 3.95 (ddd, *J* = 10.7, 8.8, 4.9 Hz, 1H), 3.82 (d, *J* = 7.3 Hz, 2H), 3.19 (ddd, *J* = 10.7, 10.7, 2.0, 1H), 2.40 (dd, *J* = 8.5, 2.0 Hz, 1H), 1.86 (ddd, *J* = 8.5, 5.0, 5.0 Hz, 1H), 1.34–1.27 (m, 1H), 1.20–1.15 (m, 1H), 1.14–1.09 (m, 1H), 0.86 (ddd, *J* = 9.0, 5.0, 5.0 Hz, 1H), 0.71–0.65 (m, 2H), 0.40–0.34 (m, 2H). ¹³C NMR (125 MHz, CDCl₃, 23 °C, δ): 157.2, 132.4, 130.2, 129.9, 112.8, 112.6, 73.6, 67.3, 24.5, 17.2, 10.2, 9.9, 3.7, 3.2. HRMS-FIA (*m/z*): calcd for C₁₄H₁₇BrNaO₂ [M + Na]⁺, 319.0310; found, 319.0327.

Figure S1: Enantiodiscriminating HPLC trace of S8

HPLC method: Chiralcel ODH column with 5% isopropanol/hexanes eluent for racemic **S8** and enantioenriched **S8**. Percent of total integration listed for each peak.

2-((1S,2S)-2-(azidomethyl)cyclopropyl)-4-bromo-1-(cyclopropylmethoxy)benzene (**S9**)

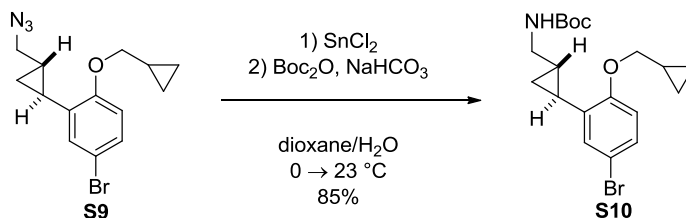


To ((1S,2S)-2-(5-bromo-2-(cyclopropylmethoxy)phenyl)cyclopropyl)methanol (**S8**) (2.15 g, 7.23 mmol, 1.00 equiv) in CH_2Cl_2 (30 mL) in an oven-dried round-bottom flask under a N_2 atmosphere at 0 °C was added Et_3N (2.20 g, 3.03 mL, 21.7 mmol, 3.00 equiv) and MsCl (1.66 g, 1.13 mL, 14.5 mmol, 2.00 equiv). The reaction mixture was stirred at 0 °C for 2 hours. The reaction mixture turned yellow and a precipitate formed. The reaction mixture was poured into a separatory funnel with saturated NH_4Cl solution (40 mL). The funnel was shaken and the organic phase collected. The aqueous phase was extracted from with diethyl ether (3×75 mL). The organic phases were combined and washed with saturated NaHCO_3 (100 mL) and brine (100 mL), dried with MgSO_4 , and concentrated in vacuo. The residue was dissolved in DMF (30 mL) and NaN_3 (1.88 g, 28.9 mmol, 4.00 equiv) was added. The reaction mixture was heated at 60 °C for 1 hour. The reaction mixture was cooled and poured into 60 mL of water. The reaction mixture was extracted from with diethyl ether (3×75 mL). The combined organic phases were washed with brine (100 mL), dried with MgSO_4 , and concentrated in vacuo. The residue was purified by chromatography on silica gel, eluting with a gradient of 5–10% EtOAc in hexanes (v/v) to afford 1.95 g of the title compound as a colorless oil (84% yield).

R_f = 0.60 (hexanes/EtOAc 19:1 (v/v)). NMR Spectroscopy: ^1H NMR (500 MHz, CDCl_3 , 23 °C, δ): 7.21 (dd, J = 8.7, 2.3 Hz, 1H), 6.96 (d, J = 2.3 Hz, 1H), 6.66 (d, J = 8.7 Hz, 1H), 3.84–3.78 (m,

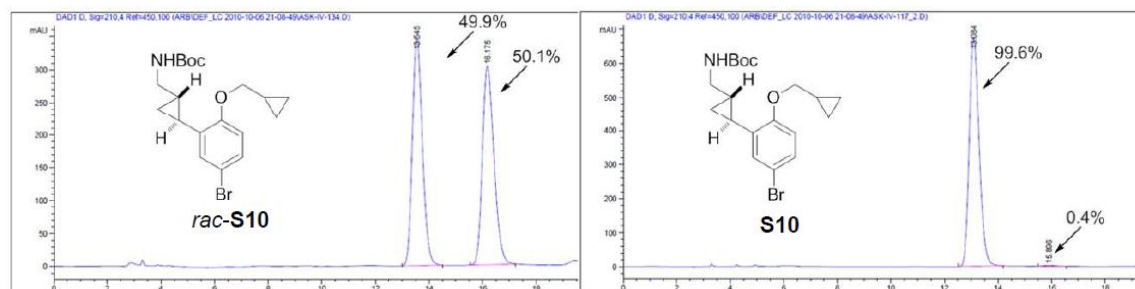
2H), 3.40 (dd, $J = 12.8, 6.4$, 1H), 3.24 (dd, $J = 12.8, 7.1$ Hz, 1H), 2.11 (ddd, $J = 8.7, 5.0, 5.0$ Hz, 1H), 1.38–1.32 (m, 1H), 1.31–1.25 (m, 1H), 1.08–1.04 (m, 1H), 0.98–0.94 (m, 1H), 0.68–0.58 (m, 2H), 0.40–0.31 (m, 2H). ^{13}C NMR (125 MHz, CDCl_3 , 23 °C, δ): 156.9, 132.8, 129.5, 128.8, 113.4, 112.9, 73.3, 55.3, 20.8, 16.2, 12.8, 10.4, 3.3, 3.2. HRMS-FIA (m/z): calcd for $\text{C}_{14}\text{H}_{16}\text{BrN}_3\text{NaO}$ [$\text{M} + \text{Na}$] $^+$, 344.0374; found, 344.0363.

***t*-Butyl (((1*S*,2*S*)-2-(5-bromo-2-(cyclopropylmethoxy)phenyl)cyclopropyl)methyl) carbamate (S10)⁹**



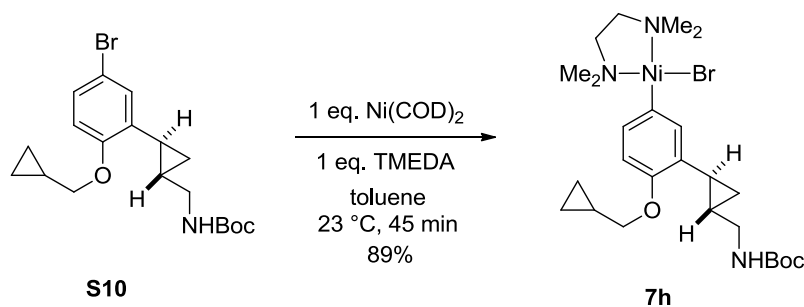
To 2-((1*S*,2*S*)-2-(azidomethyl)cyclopropyl)-4-bromo-1-(cyclopropylmethoxy)benzene (**S9**) (1.90 g, 5.90 mmol, 1.00 equiv) in a round-bottom flask open to air in a 2:1 solution of dioxane: H_2O (45 mL) cooled to 0 °C was added tin(II) chloride (5.59 g, 29.5 mmol, 5.00 equiv). The reaction mixture was allowed to warm to 23 °C and stirred for 15 hours. Saturated aqueous NaHCO_3 solution (50 mL) was carefully added. The addition was accompanied by foaming. H_2O (15 mL) was added followed by Boc_2O (3.86 g, 4.11 mL, 17.7 mmol, 3.00 equiv). The reaction mixture was stirred for 3 hours and then transferred to a separatory funnel. The reaction mixture was extracted from with EtOAc (3×75 mL). The combined organic phases were washed with brine (75 mL), dried with Na_2SO_4 , and concentrated in vacuo. The residue was purified by chromatography on silica gel, eluting with a gradient of 5–20% EtOAc in hexanes (v/v) to afford 1.96 g of the title compound as a colorless solid (85% yield). The enantioenriched product could be recrystallized by suspending the solid in hexanes (10 mL), heating the suspension to reflux to dissolve the solid, cooling the solution, and collecting the solid by filtration, affording the title compound in >99% *ee* as determined on a Chiracel ODH column with 5% isopropanol/hexanes eluent (see Figure S5).

$R_f = 0.25$ (hexanes/EtOAc 19:1 (v/v)). NMR Spectroscopy: ^1H NMR (500 MHz, CDCl_3 , 23 °C, δ): 7.23 (dd, $J = 8.3, 2.4$ Hz, 1H), 7.06 (br d, $J = 2.0$ Hz, 1H), 6.66 (d, $J = 8.8$ Hz, 1H), 5.27 (br, 1H), 3.97 (dd, $J = 9.5, 7.1$ Hz, 1H), 3.72–3.66 (m, 2H), 2.66 (br dd, $J = 10.0, 10.0$, 1H), 1.83 (ddd, $J = 6.6, 6.6, 4.9$ Hz, 1H), 1.43 (br, 10H), 1.06–0.99 (br m, 2H), 0.83–0.80 (br m, 1H), 0.67 (br m, 2H), 0.38 (br m, 2H). ^{13}C NMR (125 MHz, CDCl_3 , 23 °C, δ): 157.2, 155.9, 132.6, 130.3, 129.7, 112.8, 112.7, 79.1, 73.5, 45.7, 28.6, 21.1, 17.4, 10.6, 10.3, 3.5. HRMS-FIA (m/z): calcd for $\text{C}_{19}\text{H}_{26}\text{BrNNaO}_3$ [$\text{M} + \text{Na}$] $^+$, 418.0988; found, 418.0994.

Figure S2. Enantiodiscriminating HPLC trace of S10

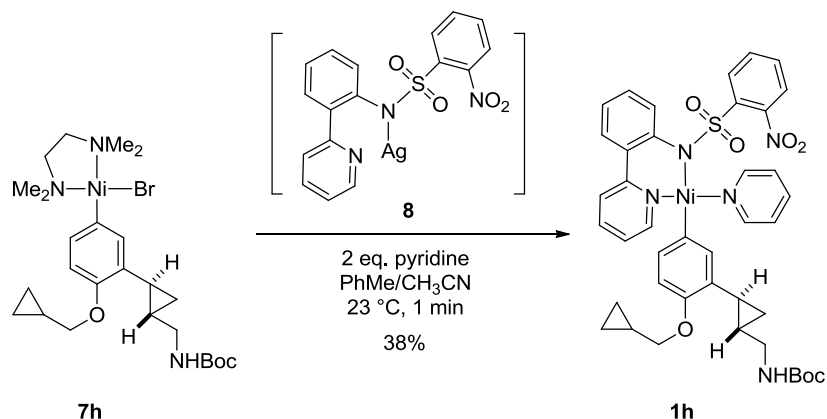
HPLC method: Chiralcel ODH column with 5% isopropanol/hexanes eluent for racemic **S10** and enantioenriched **S10**. Percent of total integration listed for each peak.

Synthesis of nickel aryl bromide complex **7h**



To a solution of TMEDA (41.6 mg, 53.7 μ L, 0.358 mmol, 1.00 equiv) and *t*-butyl (((1*S*,2*S*)-2-(5-bromo-2-(cyclopropylmethoxy)phenyl)cyclopropyl)methyl) carbamate (**S10**) (0.142 g, 0.358 mmol, 1.00 equiv) in toluene (3 mL) was added $\text{Ni}(\text{COD})_2$ (0.100 g, 0.358 mmol, 1.00 equiv), and the mixture was stirred at room temperature for 45 min. Pentane (16 mL) was added to the mixtures and the resulting solid was collected on a frit. The solid was washed with pentane (3×5 mL) and dried in vacuo to afford 0.183 g of the title compound as a peach solid (89%).

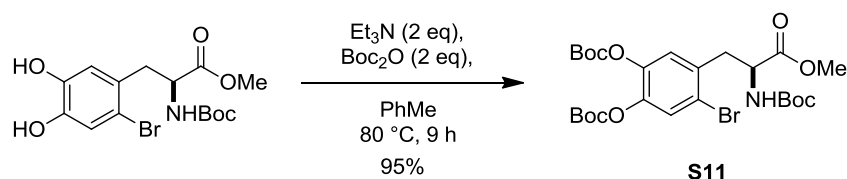
Reliable ^1H NMR and ^{13}C NMR data could not be obtained due to the instability of **7h** in most organic solvents. However, some representative peaks were observed in CD_2Cl_2 . NMR Spectroscopy: ^1H NMR (500 MHz, CD_2Cl_2 , 23 $^\circ\text{C}$, δ): 7.15 (d, $J = 7.8$ Hz, 1H), 7.02 (s, 1H), 6.47 (d, $J = 7.8$ Hz, 1H), 5.43 (br, 1H), 3.86 (br s, 1H), 3.62 (br s, 1H), 2.52–2.19 (br, 18H), 1.41 (s, 9H), 0.61 (br m, 2H), 0.33 (br s, 2H). ^{13}C NMR (125 MHz, CD_2Cl_2 , 23 $^\circ\text{C}$, δ): 156.5, 155.4, 135.5, 135.2, 127.9, 110.2, 79.1, 74.0, 61.9 (br), 58.0 (br), 50.1 (br), 49.0 (br), 46.8, 29.1, 21.7 (br), 18.3 (br), 11.3, 11.1, 4.0, 3.8. Anal: calcd for $\text{C}_{25}\text{H}_{42}\text{BrN}_3\text{NiO}_3$: C, 52.57; H, 7.41; N, 7.36; found: C, 50.08; H, 7.03; N, 7.10. Numerous attempts (recrystallization using different solvents) were made to obtain satisfactory elemental analysis data but none of them was successful. However, this material is of sufficient purity for use in the preparation of analytically pure **1h** in the next step. HRMS-FIA (m/z): calcd for $\text{C}_{25}\text{H}_{42}\text{N}_3\text{NiO}_3$ [$\text{M} - \text{Br}$] $^+$, 490.2574; found, 490.2590.

Synthesis of nickel aryl complex **1h**

To (2-(2-pyridinyl)phenyl-2-nitrobenzenesulfonamide)silver(I) (**8**) (0.113 g, 0.245 mmol, 1.00 equiv) and nickel aryl bromide complex **7h** (0.140 g, 0.245 mmol, 1.00 equiv) in a 20 mL vial was added a toluene solution (3 mL) that contained pyridine (38.8 mg, 39.5 μ L, 0.490 mmol, 2.00 equiv) at 23 °C, followed by addition of acetonitrile (0.5 mL). After stirring for 1 min at 23, the solution was filtered through a glass frit, and the filtered cake was extracted further with dichloromethane (3 $\times$ 5 mL). The combined filtrate was concentrated in vacuo and the resulting residue was purified by chromatography on silica gel eluting with hexanes/EtOAc 1:2 (v/v) and further recrystallized by dissolving the solid in CH₂Cl₂ (2 mL) and layering with pentane (20 mL) to afford 75.0 mg of the title compound as a yellow solid (38%).

R_f = 0.47 (hexanes/EtOAc 1:2 (v/v)). NMR Spectroscopy: ¹H NMR (500 MHz, CD₂Cl₂, 23 °C, δ): 9.09 (d, J = 3.4 Hz, 2H), 8.15 (dd, J = 8.9, 6.0 Hz, 1H), 7.61–7.63 (m, 3H), 7.39–7.32 (m, 3H), 7.21–7.18 (m, 3H), 7.15–7.13 (m, 3H), 7.04–6.99 (m, 2H), 6.85 (s, 1H), 6.63–6.60 (m, 1H), 6.36–6.31 (m, 1H), 5.29 (br, 1H), 3.75 (br s, 1H), 3.56–3.48 (m, 1H), 2.57–2.52 (br m, 1H), 2.58–2.50 (br m, 2H), 1.62 (br s, 1H), 1.42–1.29 (m, 10H), 0.67–0.62 (br m, 2H), 0.57–0.54 (m, 2H) 0.26–0.24 (m, 2H). ¹³C NMR (125 MHz, CD₂Cl₂, 23 °C, δ): 155.4, 152.7, 151.7, 141.5, 137.7, 137.1, 136.7, 136.1, 133.2, 131.6, 130.7, 130.7, 130.0, 128.8, 128.7, 124.6, 124.3, 123.2, 123.1, 122.9, 122.1, 73.1, 38.4, 28.5, 21.2, 10.7, 3.4. Note: A conformational isomer was observed in the ¹H NMR spectrum. Reliable ¹³C NMR data were not obtained due to the decomposition of **1h** in the solvent over time. Anal: calcd for C₄₁H₄₃N₅NiO₇S: C, 60.90; H, 5.36; N, 8.66; found: C, 60.21; H, 5.57; N, 8.66. HRMS-FIA (m/z): calcd for C₃₆H₃₉N₄NiO₇S [M – pyridine + H]⁺, 729.1887; found, 729.1843.

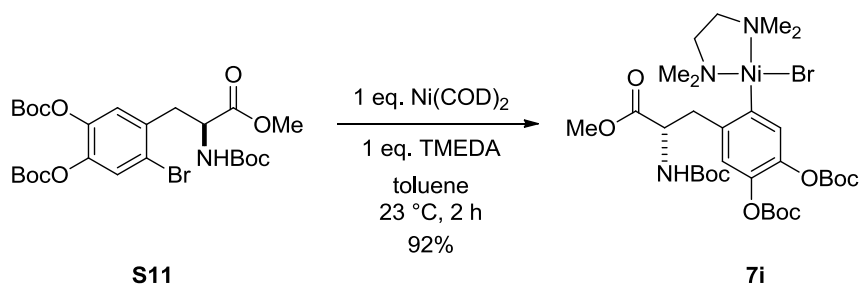
***N*-(*tert*-butoxycarbonyl)-3,4-di(*tert*-butoxycarbonyloxy)-6-bromo-*L*-phenylalaninemethyl ester (**S11**)**



(*S*)-*N*-(*tert*-butoxycarbonyl)-2-bromo-4,5-dihydroxyphenylalanine methyl ester was prepared by a published method.¹¹ To the mixture of (*S*)-*N*-(*tert*-butoxycarbonyl)-2-bromo-4,5-dihydroxyphenylalanine methyl ester (8.00 g, 20.5 mmol, 1.00 equiv) and Et₃N (5.72 ml, 4.15 g, 164 mmol, 2.00 equiv) in a round-bottom flask in PhMe (100 ml) was added Boc₂O (3.86 g, 4.11 mL, 17.7 mmol, 3.00 equiv) in one portion. The reaction mixture was stirring under nitrogen atmosphere at 80 °C for 9 h. The reaction mixture was cooled to 23 °C and was concentrated in vacuo. The residue was purified by chromatography on silica gel, eluting with a gradient of 30% EtOAc in hexanes (v/v) to afford 11.5 g of the title compound as a light yellow solid (95% yield).

R_f = 0.53 (hexanes/EtOAc 2:1 (v/v)). NMR Spectroscopy: ¹H NMR (500 MHz, CDCl₃, 23 °C, δ): 7.46 (s, 1H), 7.11 (s, 1H), 5.10 (d, J = 8.4 Hz, 1H), 4.61–4.57 (m, 1H), 3.68 (s, 3H), 3.25–3.20 (m, 1H), 3.11–3.06 (m, 1H), 1.51 (s, 18H), 1.37 (s, 9 H). ¹³C NMR (125 MHz, CDCl₃, 23 °C, δ): 172.2, 155.0, 150.3, 141.8, 141.7, 134.6, 127.2, 125.3, 120.8, 84.3, 84.1, 80.1, 53.3, 52.5, 38.2, 28.3, 27.6, 27.5. HRMS-FIA (m/z): calcd for C₂₅H₃₆BrNO₁₀ [M + Na]⁺, 612.1415; found, 612.1413.

Synthesis of nickel aryl bromide complex **7i**

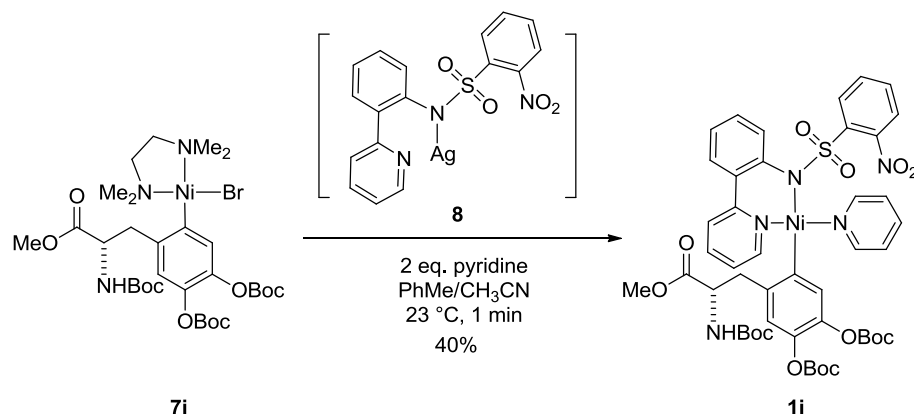


To a solution of TMEDA (125 mg, 0.161 mL, 1.08mmol, 1.00 equiv) and *N*-(*tert*-butoxycarbonyl)-3,4-di(*tert*-butoxycarbonyloxy)-6-bromo-*L*-phenylalaninemethyl ester (**S11**) (635 mg, 1.08mmol, 1.00 equiv) in toluene (8 mL) was added Ni(COD)₂ (300 mg, 1.08mmol, 1.00 equiv), and the mixture was stirred at room temperature for 2 h. The solution was concentrated in vacuo and pentane (16 mL) was added to the mixtures and the resulting solid was collected on a frit. The solid was washed with pentane (3 × 5 mL) and dried in vacuo to afford 735 mg of the title compound as a red solid (92%).

NMR Spectroscopy: ¹H NMR (500 MHz, CD₃CN 23 °C, δ): 7.39 (s, 1H), 6.73 (s, 1H), 5.50 (br s,

1H), 4.51 (br s, 1H), 3.84 (s, 3H), 3.80–3.70 (m, 1H), 2.63–2.22 (br, 18H), 1.54 (s, 9H), 1.50 (s, 9H), 1.35 (s, 9H). ¹³C NMR (125 MHz, CD₃CN 23 °C, δ): 174.2, 156.1, 151.8, 151.6, 144.5, 140.5, 139.1, 137.5, 129.7, 118.4, 83.4, 79.1, 61.3 (br), 57.3 (br), 56.5 (br), 52.3, 50.0 (br), 48.7 (br), 48.0 (br), 47.1 (br), 40.1, 29.2, 28.1, 27.5, 27.4. Note: Conformational isomers were observed in the ¹H NMR spectrum. Anal: calcd for C₃₁H₅₂BrN₃NiO₁₀ (PhMe)_{0.2}: C, 49.65; H, 6.89; N, 5.36; found: C, 49.29; H, 6.65; N, 4.74.

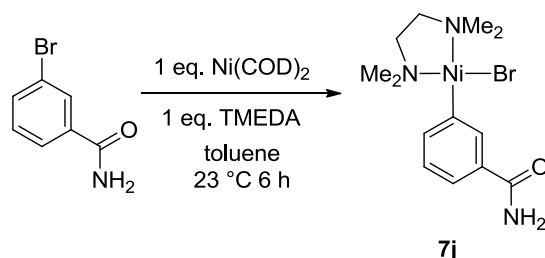
Synthesis of nickel aryl complex **1i**



To (2-(2-pyridinyl)phenyl-2-nitrobenzenesulfonamide)silver(I) (**7**) (302 mg, 0.650 mmol, 1.00 equiv) and nickel aryl bromide complex **7i** (500 mg, 0.650 mmol, 1.00 equiv) in a round-bottom flask was added a toluene solution (8 mL) that contained pyridine (103 mg, 105 μ L, 1.31 mmol, 2.00 equiv) at 23 °C, followed by addition of acetonitrile (2.0 mL). After stirring for 1 min at 23, the solution was filtered through a glass frit, and the filtered cake was extracted further with dichloromethane (3 $\times$ 5 mL). The combined filtrate was concentrated in vacuo and the resulting residue was purified by chromatography on silica gel eluting with hexanes/EtOAc 1:3 (v/v) (0.5% Et₃N) to afford 260 mg of the title compound as a yellow solid (40%).

R_f = 0.40 (hexanes/EtOAc 1:2 (v/v)). NMR Spectroscopy: ¹H NMR (500 MHz, CD₂Cl₂, 23 °C, δ): 9.04 (d, *J* = 4.9 Hz, 2H), 8.32 (d, *J* = 5.4 Hz, 0.4H), 8.26 (d, *J* = 5.4 Hz, 0.6H), 8.05 (s, 1H), 7.66–7.32 (m, 7H), 7.27–7.15 (m, 5H), 7.08–7.01 (m, 4H), 6.73–6.63 (m, 1H), 6.40 (s, 0.6H), 6.32 (s, 0.4H), 4.35–4.22 (m, 1H), 4.07–3.93 (m, 1H), 3.88–3.80 (m, 2H), 3.54–3.41 (m, 3H), 1.59 (s, 5H), 1.58 (s, 5H), 1.44 (s, 9H), 1.31 (s, 8H). ¹³C NMR (125 MHz CD₂Cl₂, 23 °C, δ): 173.2, 156.2, 155.3, 154.5, 151.8, 151.5, 151.4, 147.2, 140.8, 140.7, 139.7, 139.5, 139.3, 138.3, 138.0, 137.6, 137.5, 136.6, 136.3, 135.8, 132.0, 130.9, 130.8, 130.2, 129.1, 129.1, 128.6, 127.9, 127.8, 124.8, 124.7, 124.6, 123.6, 123.0, 122.7, 122.5, 119.4, 119.2, 83.5, 83.4, 79.8, 54.6, 52.3, 40.8, 28.4, 28.1, 27.9, 27.7. Note: Conformational isomers were observed in the ¹H NMR spectrum, which is possibly due to slow rotation about bonds as seen for similar complexes.¹² Anal: calcd for C₄₇H₅₃N₅NiO₁₄S: C, 56.30; H, 5.33; N, 6.98; found: C, 55.98; H, 5.18; N, 6.90. HRMS-FIA (m/z): calcd for C₄₂H₄₉N₄NiO₁₄S [M – pyridine + H]⁺, 923.2314; found, 923.2276.

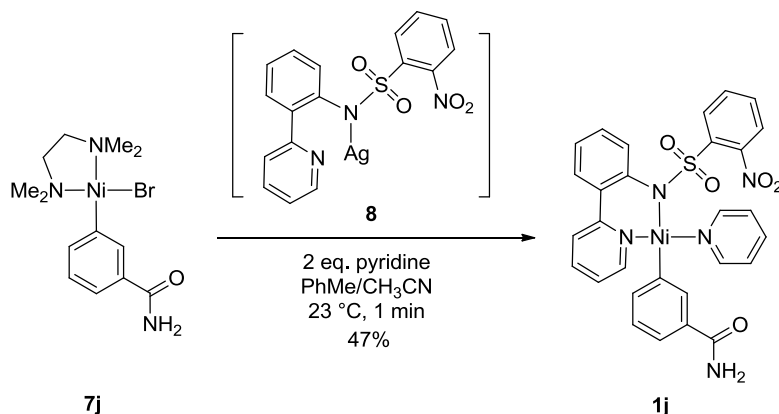
Synthesis of nickel aryl bromide complex **7j**



To a solution of TMEDA (83.0 mg, 0.107 mL, 0.717 mmol, 1.00 equiv) and 3-bromobenzamide (143 mg, 0.717 mmol, 1.00 equiv) in toluene (4 mL) was added $\text{Ni}(\text{COD})_2$ (200 mg, 0.717 mmol, 1.00 equiv), and the mixture was stirred at room temperature for 6 h. Pentane (16 mL) was added to the mixtures and the resulting solid was collected on a frit. The solid was washed with pentane (3×5 mL) and dried in vacuo to afford 225 mg of the title compound as a pink solid (84%).

^1H NMR (600 MHz, CD_2Cl_2 , δ): 7.97 (s, 1H), 7.71 (d, $J = 7.5$ Hz, 1H), 7.07 (d, $J = 7.5$ Hz, 1H), 6.90–6.88 (m, 1H), 6.10 (br s, 1H), 5.32 (br s, 1H), 2.56–2.20 (br, 16H). ^{13}C NMR spectra were not obtained due to low solubility. Anal: calcd for $\text{C}_{13}\text{H}_{22}\text{BrN}_3\text{NiO}$: C, 41.64; H, 5.91; N, 11.21; found: C, 41.36; H, 5.78; N, 10.95.

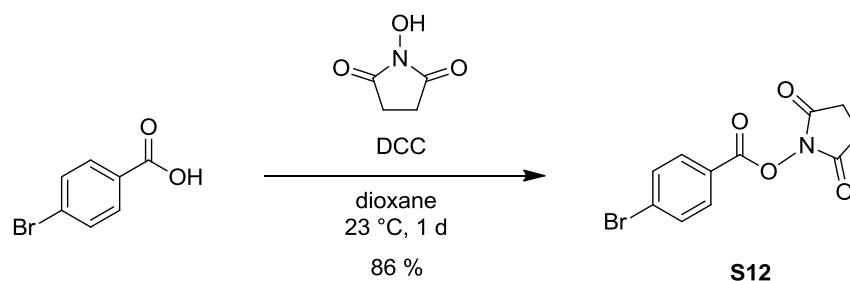
Synthesis of nickel aryl complex **1j**



To (2-(2-pyridinyl)phenyl-2-nitrobenzenesulfonamide)silver(I) (**8**) (247 mg, 0.533 mmol, 1.00 equiv) and nickel aryl bromide complex **7j** (200 mg, 0.533 mmol, 1.00 equiv) in a 20 mL vial was added a toluene solution (4 mL) that contained pyridine (84.0 mg, 86.0 μL , 1.07 mmol, 2.00 equiv) at 23 °C, followed by addition of acetonitrile (1.0 mL). After stirring for 1 min at 23, the solution was filtered through a glass frit, and the filtered cake was extracted further with dichloromethane (3×5 mL). The combined filtrate was concentrated in vacuo and the resulting residue was purified by chromatography on silica gel eluting with EtOAc and further recrystallized by dissolving the solid in CH_2Cl_2 (2 mL) and layering with pentane (20 mL) to afford 154 mg of the title compound as a yellow solid (47%).

R_f = 0.26 (EtOAc). NMR Spectroscopy: ^1H NMR (500 MHz, CD_2Cl_2 , 23 °C, δ): 9.13 (d, J = 4.9 Hz, 2H), 8.15 (d, J = 5.4 Hz, 1H), 7.86 (s, 1H), 7.78 (d, J = 7.2 Hz, 1H), 7.63–7.56 (m, 3H), 7.42–7.32 (m, 3H), 7.23–7.17 (m, 4H), 7.08–7.02 (m, 4H), 6.87–6.84 (m, 1H), 6.64–6.61 (m, 1H), 5.94 (br s, 1H), 5.32 (br s, 1H). ^{13}C NMR (125 MHz CD_2Cl_2 , 23 °C, δ): 157.1, 156.2, 152.5, 151.5, 147.3, 141.3, 139.5, 137.9, 137.3, 136.7, 136.0, 134.1, 131.7, 130.9, 130.8, 130.2, 128.8, 128.7, 126.0, 124.8, 124.5, 123.4, 123.0, 122.3. Anal: calcd for $\text{C}_{29}\text{H}_{23}\text{N}_5\text{NiO}_5\text{S}$ (CH_2Cl_2) $_{0.25}$: C, 55.46; H, 3.74; N, 11.05; found: C, 55.22; H, 3.82; N, 11.28.

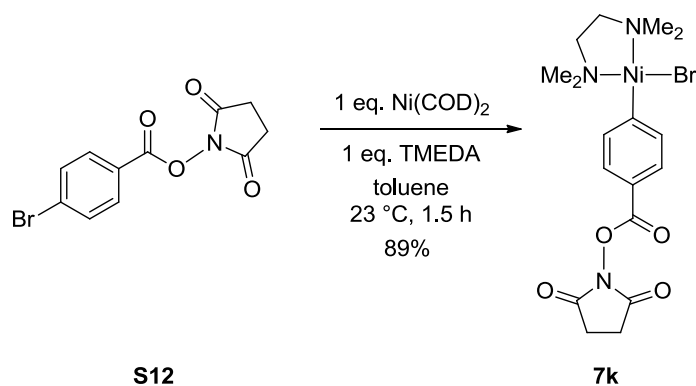
4-bromobenzoic acid succinimidyl ester (S12)



To 4-bromobenzoic acid (5.00 g, 24.9 mmol, 1.00 equiv) and *N*-hydroxysuccinimide (3.66 g, 31.8 mmol, 1.28 equiv) in a round-bottom flask in dioxane (120 mL) was added an dioxane solution (30 mL) that contained 1,3-dicyclohexylcarbodiimide (DCC) (6.77 g, 32.8 mmol, 1.32 equiv) dropwise over 5 min at 23 °C. The reaction mixture was stirring at 23 °C for 24 h. The reaction mixture was concentrated in vacuo and the crude product was obtained by recrystallization in a cold acetone. The crude product was further purified by chromatography on silica gel eluting with hexanes/EtOAc 2:1 (v/v) to afford 6.34 g of the title compound as a colorless solid (86%).

R_f = 0.25 (hexanes/EtOAc 2:1 (v/v)). NMR Spectroscopy: ^1H NMR (500 MHz, CDCl_3 , 23 °C, δ): 7.99 (d, J = 8.7 Hz, 2H), 7.67 (d, J = 8.7 Hz, 1H), 2.90 (s, 4H). ^{13}C NMR (125 MHz, CDCl_3 , 23 °C, δ): 169.2, 161.5, 132.5, 132.1, 130.6, 124.2, 25.8. These spectroscopic data correspond to the reported data.¹³

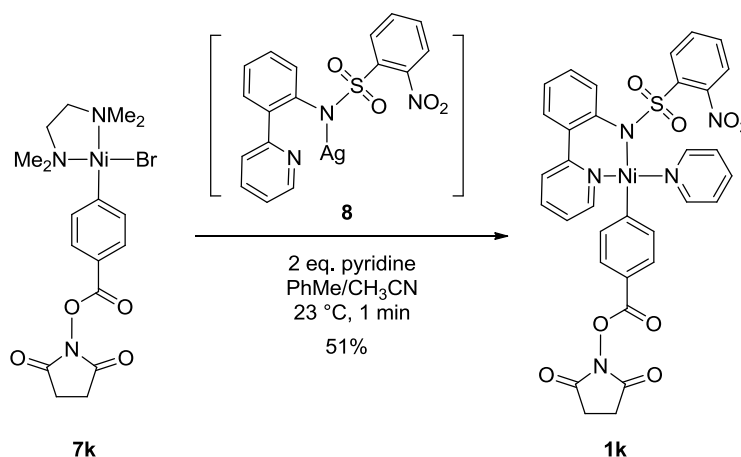
Synthesis of nickel aryl bromide complex 7k



To a solution of TMEDA (83.0 mg, 0.107 mL, 0.717 mmol, 1.00 equiv) and 4-bromobenzoic acid succinimidyl ester (**S12**) (214 mg, 0.717 mmol, 1.00 equiv) in toluene (4 mL) was added Ni(COD)_2 (200 mg, 0.717 mmol, 1.00 equiv), and the mixture was stirred at room temperature for 1.5 h. Pentane (16 mL) was added to the mixtures and the resulting solid was collected on a frit. The solid was washed with pentane (3×5 mL) and dried in vacuo to afford 300 mg of the title compound as an orange solid (89%).

^1H NMR (500 MHz, CD_2Cl_2 , δ): 7.86 (d, $J = 8.2$ Hz, 2H), 7.49 (d, $J = 6.9$ Hz, 2H), 2.83 (br s, 4H), 2.57–2.22 (br, 16H). ^{13}C NMR (125 MHz, CD_2Cl_2 , δ): 170.1, 163.6, 138.2, 124.9, 118.6, 111.1, 61.5 (br), 57.5 (br), 49.7 (br), 48.4 (br), 26.1. Anal: calcd for $\text{C}_{17}\text{H}_{24}\text{BrN}_3\text{NiO}_4$: C, 43.17; H, 5.11; N, 8.88; found: C, 43.65; H, 4.54; N, 7.48.

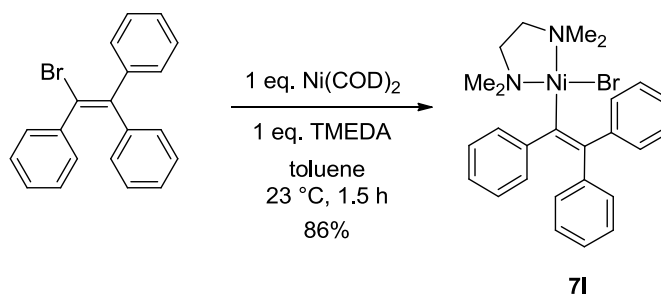
Synthesis of nickel aryl complex **1k**



To (2-(2-pyridinyl)phenyl-2-nitrobenzenesulfonamide)silver(I) (**8**) (195 mg, 0.423 mmol, 1.00 equiv) and nickel aryl bromide complex **7k** (200 mg, 0.423 mmol, 1.00 equiv) in a 20 mL vial was added a toluene solution (4 mL) that contained pyridine (66.9 mg, 68.1 μL , 0.833 mmol, 2.00 equiv) at 23°C , followed by addition of acetonitrile (1.0 mL). After stirring for 1 min at 23°C , the solution was filtered through a glass frit, and the filtered cake was extracted further with dichloromethane (3×5 mL). The combined filtrate was concentrated in vacuo and the resulting residue was purified by chromatography on silica gel eluting with hexanes/EtOAc 1:2 (v/v) to afford 152 mg of the title compound as a yellow solid (51%).

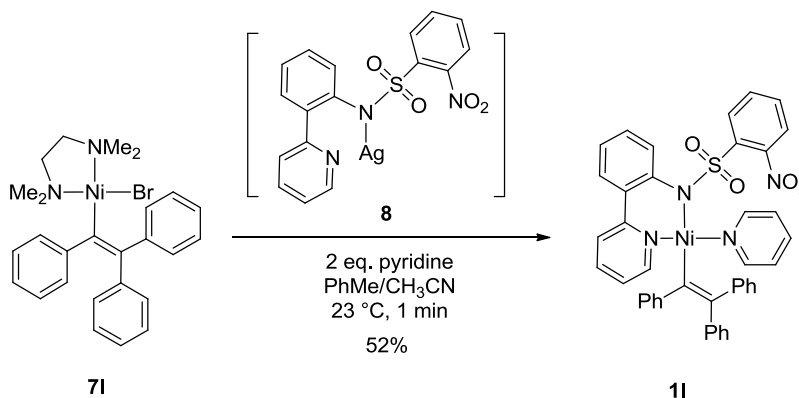
$R_f = 0.47$ (hexanes/EtOAc 1:6 (v/v)). NMR Spectroscopy: ^1H NMR (500 MHz, CDCl_3 , 23°C , δ): 9.10 (d, $J = 5.2$ Hz, 2H), 8.05 (d, $J = 5.6$ Hz, 1H), 7.7 (d, $J = 7.9$ Hz, 2H), 7.58–7.54 (m, 3H), 7.47–7.32 (m, 5H), 7.19–7.11 (m, 4H), 7.05–6.97 (m, 3H), 6.63–6.61 (m, 1H), 2.81 (s, 4H). ^{13}C NMR (125 MHz CDCl_3 , 23°C , δ): 174.2, 169.7, 162.9, 155.9, 152.3, 151.2, 147.0, 140.9, 137.6, 137.1, 136.4, 136.0, 135.4, 131.8, 130.5, 130.4, 130.1, 128.6, 128.4, 126.4, 124.6, 124.4, 122.9, 122.8, 122.0, 119.5, 25.7. Anal: calcd for $\text{C}_{33}\text{H}_{25}\text{N}_5\text{NiO}_8\text{S}$: C, 55.80; H, 3.55; N, 9.86; found: C, 55.53; H, 3.50; N, 9.61.

Synthesis of nickel alkenyl bromide complex **7I**



To a solution of TMEDA (83.0 mg, 0.107 mL, 0.717 mmol, 1.00 equiv) and bromotriphenylethylene (240 mg, 0.717 mmol, 1.00 equiv) in toluene (4 mL) was added Ni(COD)_2 (200 mg, 0.717 mmol, 1.00 equiv), and the mixture was stirred at room temperature for 40 min. Pentane (16 mL) was added to the mixtures and the resulting solid was collected on a frit. The solid was washed with pentane (3 $\times$ 5 mL) and dried in vacuo to afford 305 mg of the title compound as a pink solid (86%). ^1H NMR (500 MHz, C_6D_6 , δ): 9.41 (d, J = 7.2 Hz, 2H), 8.20 (d, J = 7.2 Hz, 2H), 7.51–7.48 (m, 2H), 7.32–7.29 (m, 1H), 7.01–6.98 (m, 2H), 6.91–6.88 (m, 1H), 1.89 (br, 16H). ^{13}C NMR (125 MHz, C_6D_6 , δ): 148.3, 147.7, 145.2, 144.2, 143.5, 132.2, 131.2, 131.0, 126.1, 125.5, 124.6, 50.0 (br), 48.2 (br). Attempts (recrystallization using different solvents) were made to obtain satisfactory elemental analysis data but none of them was successful. However, this material is of sufficient purity for use in the preparation of analytically pure **1I** in the next step. HRMS-FIA (m/z): calcd for $\text{C}_{26}\text{H}_{31}\text{N}_2\text{Ni} [\text{M} - \text{Br}]^+$, 429.1841; found, 429.1845.

Synthesis of nickel alkenyl complex **1I**



To (2-(2-pyridinyl)phenyl-2-nitrobenzenesulfonamide)silver(I) (**8**) (93.0 mg, 0.417 mmol, 1.00 equiv) and nickel alkenyl bromide complex **7I** (0.100 mg, 0.417 mmol, 1.00 equiv) in a 20 mL vial was added a toluene solution (3 mL) that contained pyridine (32.0 mg, 32.5 μL , 0.833 mmol, 2.00 equiv) at 23 °C, followed by addition of acetonitrile (0.5 mL). After stirring for 1 min at 23, the solution was filtered through a glass frit, and the filtered cake was extracted further with

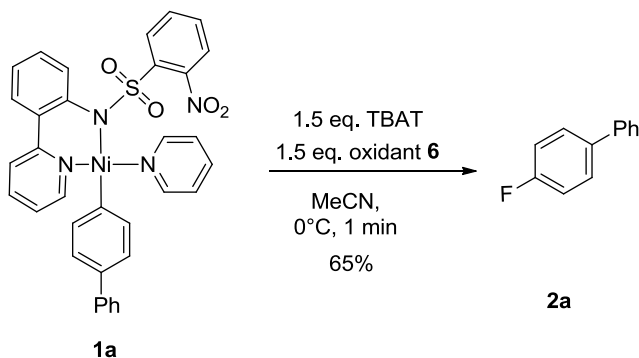
dichloromethane (3×5 mL). The combined filtrate was concentrated in vacuo and the resulting residue was purified by chromatography on silica gel eluting with hexanes/EtOAc 1:2 (v/v) and further recrystallized by dissolving the solid in CH_2Cl_2 (2 mL) and layering with pentane (20 mL) to afford 78.0 mg of the title compound as a yellow solid (52%).

$R_f = 0.66$ (hexanes/EtOAc 1:2 (v/v)). NMR Spectroscopy: ^1H NMR (500 MHz, CDCl_3 , 23 °C, δ): 9.85 (d, $J = 7.5$ Hz, 1H), 8.77–8.60 (m, 3H), 7.80 (d, $J = 7.3$ Hz, 1H), 7.74–7.70 (m, 1H), 7.49–7.30 (m, 6H), 7.24–6.82 (m, 15H), 6.69–6.59 (m, 4H), 6.40 (d, $J = 7.1$ Hz, 1H). ^{13}C NMR (125 MHz, CDCl_3 , 23 °C, δ): 160.7, 156.7, 156.5, 154.6, 152.3, 152.0, 151.9, 151.6, 148.0, 147.9, 147.3, 146.9, 145.2, 143.7, 143.2, 142.4, 141.8, 141.0, 137.4, 136.8, 136.5, 136.2, 135.9, 135.8, 135.2, 131.4, 131.1, 131.0, 130.7, 130.6, 130.3, 130.1, 130.0, 130.0, 129.9, 129.5, 129.4, 129.1, 128.9, 128.7, 128.2, 127.6, 127.5, 127.4, 127.2, 127.0, 127.0, 127.0, 126.5, 125.8, 125.3, 125.0, 124.6, 123.5, 123.4, 123.2, 123.0, 122.8, 122.6, 122.4, 122.0, 121.6. There are more ^{13}C peaks than could be expected, possibly due to slow rotation about bonds as seen for similar complexes.⁹ Anal: calcd for $\text{C}_{42}\text{H}_{32}\text{N}_4\text{NiO}_4\text{S}(\text{CH}_2\text{Cl}_2)_{0.15}$: C, 66.59; H, 4.28; N, 7.37; found: C, 66.71; H, 4.24; N, 7.51. HRMS-FIA (m/z): calcd for $\text{C}_{37}\text{H}_{27}\text{N}_3\text{NaNiO}_4\text{S}[\text{M} - \text{pyridine} + \text{H}]^+$, 668.1149; found, 668.1150.

Fluorination of nickel aryl complexes and preparation of authentic 2

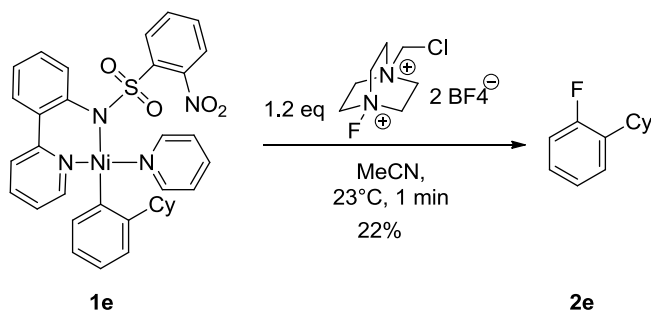
Most of the aryl fluorides were either purchased from a commercial source or synthesized by previous methods. **2b** and **2j** were purchased from Matrix Scientific and Aldrich, respectively. **2c**,¹⁴ **2d**,¹⁵ **2g**,⁹ **2h**,⁹ **2i**,¹⁵ and **2k**¹⁶ were synthesized based on reported procedures. **2e**, **2f**, and **2l** were synthesized by electrophilic fluorination of **1e**, **1f**, and **1l** with Selectfluor®.

4-Fluorobiphenyl (**2a**)



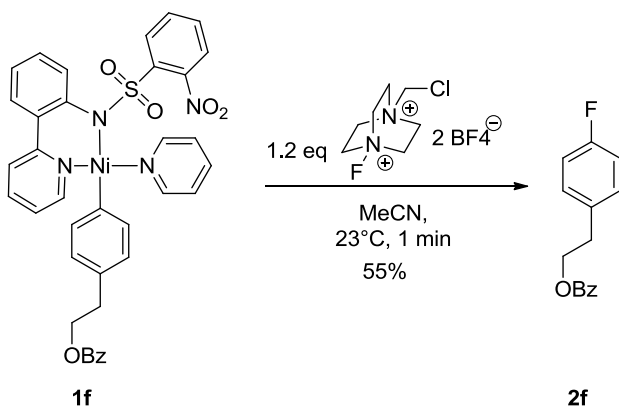
In a glove box under a N₂ atmosphere, nickel aryl complex **1a** (40 mg, 0.062 mmol, 1.0 equiv), tetrabutylammonium difluorotriphenylsilicate (TBAT) (50 mg, 0.093 mmol, 1.5 equiv), and oxidant **6** (69 mg, 0.093 mmol, 1.5 equiv) were placed in a 20 mL vial. The vial was taken out of the glove box, and immersed in an ice bath at 0 °C for 5 minutes. To the reaction mixture was added quickly pre-cooled acetonitrile (4 mL) at 0 °C in one portion and the solution was stirred for 1 min at 0 °C. After warming to 23 °C, the solution was concentrated in vacuo and the residue was purified by chromatography on silica gel eluting with hexane/EtOAc 99:1 (v/v) to afford 6.9 mg of the title compound as a white solid (65% yield).

R_f = 0.60 (hexanes/EtOAc 19:1 (v/v)). ¹H-NMR (500 MHz, CDCl₃, 23 °C, δ): δ 7.56–7.54 (m, 4H), 7.45–7.42 (m, 2H), 7.36–7.33 (m, 1H), 7.15–7.11 (m, 2H). ¹³C-NMR (125 MHz, CDCl₃, 23 °C, δ): 162.7 (d, *J* = 244 Hz), 140.5, 137.6, 129.0, 128.9 (d, *J* = 8.5 Hz), 127.5, 127.3, 115.8 (d, *J* = 21 Hz); ¹⁹F-NMR (375 MHz, CDCl₃, 23 °C): δ –116.2. These spectroscopic data correspond to previously reported data.¹²

1-Cyclohexyl-2-fluorobenzene (2e)

Nickel aryl complex **1e** (50 mg, 0.077 mmol, 1.0 equiv) and 1-chloromethyl-4-fluoro-1,4-diazoniabicyclo[2.2.2]octane bis(tetrafluoroborate) (Selectfluor®) (33 mg, 0.092 mmol, 1.5 equiv) were placed in a 20 mL vial. To the reaction mixture was added acetonitrile (4 mL) at 23 °C in one portion and the solution was stirred for 1min at 23 °C. The solution was concentrated in vacuo and the residue is purified by chromatography on silica gel eluting with pentane to afford 8.1 mg of the title compound and cyclohexylbenzene as a 1:2 mixture (a colorless oil, 22% yield based on 1-cyclohexyl-2-fluorobenzene). Due to the difficulty of purification of the title compound and its volatility,¹⁷ the above mixture was used without further purification for identifying [¹⁸F]**2e** by HPLC analysis.

R_f = 0.67 (pentane). NMR Spectroscopy: Selected ¹H NMR (400 MHz, CDCl₃, 23 °C, δ): 7.07–7.03 (m, 1H), 2.94–2.89 (m, 1H). ¹⁹F NMR (375 MHz, CD₃CN, 23 °C, δ): –120.0. These spectroscopic data correspond to previously reported data.¹⁷

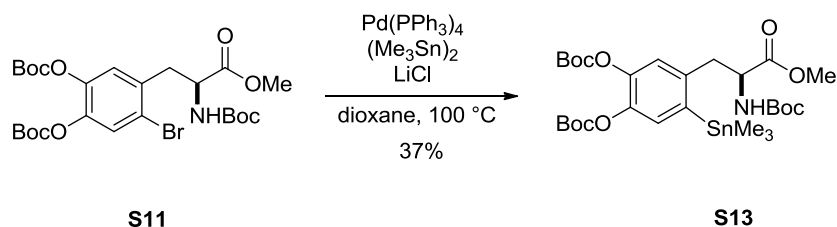
2-(4-Fluorophenyl)ethyl benzoate (2f)

Nickel aryl complex **1f** (30 mg, 0.042 mmol, 1.0 equiv) and Selectfluor® (18 mg, 0.050 mmol, 1.2 equiv) were placed in a 20 mL vial. To the reaction mixture was added quickly acetonitrile (3 mL) at 23 °C in one portion and the solution was stirred for 1min at 23 °C. The solution was subsequently concentrated in vacuo and the residue is purified by chromatography on silica gel eluting with hexane/EtOAc 4:1 (v/v) to afford 5.6 mg of the title compound as a colorless solid

(55% yield).

R_f = 0.47 (hexanes/EtOAc 4:1 (v/v)). NMR Spectroscopy: ^1H NMR (500 MHz, CDCl_3 , 23 °C, δ): 7.00 (d, J = 7.5 Hz, 2H), 7.57–7.54 (m, 1H), 7.45–7.42 (m, 2H), 7.26–7.23 (m, 2H), 7.02–6.99 (m, 2H), 5.51 (t, J = 6.5 Hz, 2H), 3.06 (t, J = 6.5 Hz, 2H). ^{13}C NMR (125 MHz, CDCl_3 , 23 °C, δ): 166.6, 161.9 (d, J = 243 Hz), 133.7 (d, J = 2.9 Hz), 133.1 (s), 130.5 (s), 130.4 (d, J = 27 Hz), 129.7, 128.5, 115.5 (d, J = 22 Hz), 65.5, 34.6. ^{19}F NMR (375 MHz, CDCl_3 , 23 °C, δ): –116.8. HRMS-FIA (m/z): calcd for $\text{C}_{15}\text{H}_{13}\text{FO}_2$ [$\text{M} + \text{H}$] $^+$, 245.0972; found, 245.0982.

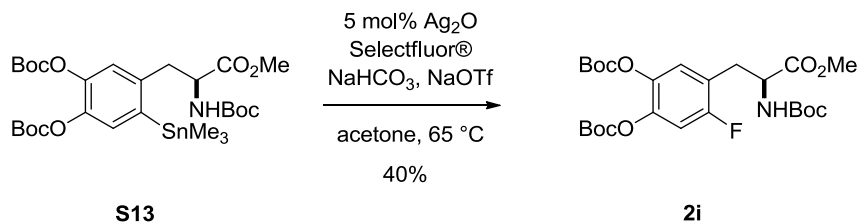
***N*-(*tert*-butoxycarbonyl)-3,4-di(*tert*-butoxycarbonyloxy)-6-trimethylstannyl-L-phenylalaninemethyl ester (S13)**



To *N*-(*tert*-butoxycarbonyl)-3,4-di(*tert*-butoxycarbonyloxy)-6-bromo-L-phenylalaninemethyl ester (**S11**) (1.00 g, 1.69 mmol, 1.00 equiv) in dioxane (20 mL) at 23 °C was added lithium chloride (0.359 g, 8.47 mmol, 5.0 equiv), tetrakis(triphenylphosphine)palladium (0.391 g, 0.339 mmol, 20.0 mol%) and bis(trimethyltin) (1.11 g, 3.39 mmol, 2.00 equiv). After stirring for 5 hr at 100 °C, the reaction mixture was cooled to 23 °C and concentrated in vacuo. The residue was purified by chromatography on silica gel, eluting with hexanes/EtOAc 5:1 (v/v), to afford 420 mg of the title compound as a colorless oil (37% yield).

R_f = 0.55 (hexane/EtOAc 3:1 (v/v)). NMR Spectroscopy: ^1H NMR (500 MHz, CDCl_3 , 23 °C, δ): 7.26 (br s, 1H), 7.08 (br s, 1H), 4.89 (d, J = 7.6 Hz, 1H), 4.53–4.48 (m, 1H), 3.70 (s, 3H), 3.10–3.00 (m, 2H), 1.54 (s, 9H), 1.53 (s, 9H), 1.39 (s, 9H), 0.35 (s, 9H). ^{13}C NMR (125 MHz, CDCl_3 , 23 °C, δ): 172.7, 155.2, 150.9, 150.8, 142.7, 141.7, 141.5, 141.0, 130.4, 123.4, 110.8, 83.8, 80.2, 54.5, 52.5, 40.4, 28.3, 27.7, 27.7, –7.7. HRMS-FIA (m/z): calcd for $\text{C}_{28}\text{H}_{45}\text{NO}_{10}\text{Sn}$ [$\text{M} + \text{H}$] $^+$, 676.2144; found, 676.2171.

***N*-Boc-O-Boc-6-fluoro-DOPA methyl ester (2i)**

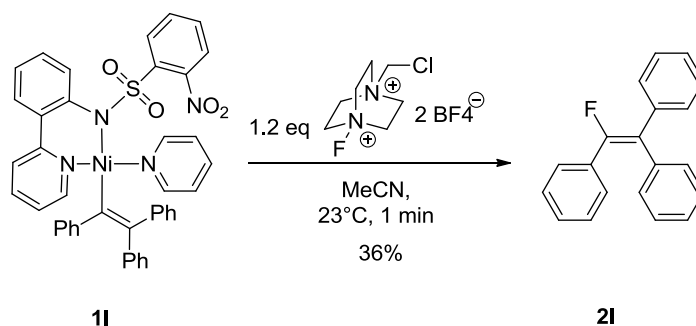


To *N*-Boc-O-Boc-6-trimethylstannyl-DOPA methyl ester (**S13**) (142 mg, 0.211 mmol, 1.00 equiv)

in acetone (4 mL) at 23 °C was added silver oxide (2.45 mg, 0.0106 mmol, 5.0 mol%), sodium bicarbonate (35.5 mg, 0.422 mmol, 2.0 equiv), sodium trifluoromethanesulfonate (36.3 mg, 0.211 mmol, 1.0 equiv) and Selectfluor® (112 mg, 0.317 mmol, 1.50 equiv). The reaction mixture was stirred for 5 hr at 65 °C in a sealed vial. After cooling to 23 °C, the reaction mixture was filtered through a pad of celite, eluting with CH₂Cl₂ and the filtrate was concentrated in vacuo. The residue was purified by chromatography on silica gel, eluting with hexane/EtOAc 4:1 (v/v), to afford 45.0 mg of the title compound as a colorless solid (40% yield).

R_f = 0.37 (hexane/EtOAc 3:1 (v/v)). NMR Spectroscopy: ¹H NMR (500 MHz, CDCl₃, 23 °C, δ): 7.05 (d, J = 6.9 Hz, 1H), 7.02 (d, J = 9.6 Hz, 1H), 5.07 (d, J = 7.7 Hz, 1H), 4.57–4.53 (m, 1H), 3.71 (s, 3H), 3.18–3.04 (m, 2H), 1.54 (s, 9H), 1.53 (s, 9H), 1.41 (s, 9H). ¹³C NMR (125 MHz, CDCl₃, 23 °C, δ): 172.0, 158.2 (d, J = 246 Hz), 155.1, 150.8, 150.4, 142.1 (d, J = 12 Hz), 138.6, 125.4 (d, J = 5.6 Hz), 121.5 (d, J = 18 Hz), 110.8 (d, J = 28 Hz), 84.4, 84.1, 80.2, 53.5, 52.6, 31.7, 28.4, 27.7, 27.7. ¹⁹F NMR (375 MHz, CDCl₃, 23 °C, δ): –117.6. Mass HRMS-FIA (m/z): calcd for C₂₅H₃₆FNO₁₀ [M + Na]⁺, 552.2215; found, 552.2214.

1-Fluoro-1,2,2-triphenylethylene (2I)



Nickel aryl complex **1I** (30 mg, 0.040 mmol, 1.0 equiv) and Selectfluor® (17 mg, 0.048 mmol, 1.2 equiv) were placed in a 20 mL vial. To the reaction mixture was added quickly acetonitrile (3 mL) at 23 °C in one portion and the solution was stirred for 1min at 23 °C. The solution was subsequently concentrated in vacuo and the residue is purified by chromatography on silica gel eluting with Et₂O/CH₂Cl₂ 2:1 (v/v) to afford 4.0 mg of the title compound as a colorless solid (36% yield).

R_f = 0.88 (Et₂O/CH₂Cl₂ 2:1 (v/v)). NMR Spectroscopy: ¹H NMR (500 MHz, CDCl₃, 23 °C, δ): 7.39–6.95 (m, 15H). ¹³C NMR (125 MHz, CDCl₃, 23 °C, δ): 130.8 (d, J = 2.8 Hz), 130.1 (d, J = 3.4 Hz), 130.8 (d, J = 2.8 Hz), 129.2 (d, J = 4.6 Hz), 128.7, 128.3, 128.2, 128.1, 128.1, 128.0, 127.7, 127.6, 127.5, 127.1. ¹⁹F NMR (375 MHz, CDCl₃, 23 °C, δ): –101.2. These spectroscopic data correspond to previously reported data.¹⁸

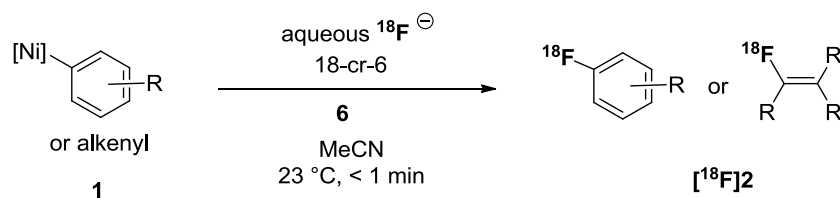
Radiochemistry

General methods

No-carrier-added [^{18}F]fluoride was produced from water 97% enriched in ^{18}O (ISOFLEX, USA) by the nuclear reaction $^{18}\text{O}(\text{p},\text{n})^{18}\text{F}$ using a Siemens Eclipse HP cyclotron and a silver-bodied target at Massachusetts General Hospital Athinoula A. Martinos Center for Biomedical Imaging. The produced [^{18}F]fluoride in water was transferred from the cyclotron target by helium push. An Agilent Eclipse XDB-C18, 5 μm , 4.6 x 150 mm HPLC column was used for analysis. Analytical HPLC used the following mobile phases: 0.1% $\text{CF}_3\text{CO}_2\text{H}$ in water (A) 0.1% $\text{CF}_3\text{CO}_2\text{H}$ in acetonitrile (B). Program: 5% (B) and 95% (A) for 10 minutes. In the HPLC analysis of the ^{18}F -labeled compounds, isotopically unmodified (^{19}F -containing) substances were used as references for identification. Radioactivity was measured in a Capintec, Inc. CRC-25PET ion chamber.

Solvents and reagents for radiochemical experiments: Acetonitrile was distilled over P_2O_5 . Water was obtained from a Millipore Milli-Q Integral Water Purification System. 18-crown-6 was sublimed.

Radiosynthesis of ^{18}F -labeled Molecules



A portion of aqueous [^{18}F]fluoride solution (20–50 μL , 2–5 mCi) obtained from a cyclotron was added to an acetonitrile solution (2.0–5.0 mL) of 20 mg of 18-cr-6. The resulting solution (200–500 μL) was added quickly to a septum-capped vial containing 1.0 mg nickel complex **1** and 1.0 equiv of **6** (relative to **1**). The solution immediately became pink, red, or yellow, depending on the nickel complex used, and then became colorless 5 to 10 seconds later. A capillary tube was used to spot part of the solution on a silica gel TLC plate. The TLC plate was developed in an appropriate organic solvent mixture. The TLC plate was scanned with a Bioscan AR-2000 Radio TLC Imaging Scanner.

Calculation of equivalents of [^{18}F]fluoride relative to nickel complex¹⁹

Method to calculate the number of [^{18}F]fluoride atoms that exhibit radioactivity of 1.0 Ci:

$$N (\text{atoms}) \times \lambda (\text{s}^{-1}) = 1.0 \text{ Ci} = 3.7 \times 10^{10} (\text{Bq})$$

$$N = 3.7 \times 10^{10} / \lambda \quad (\lambda \text{ is the decay constant in } (\text{s}^{-1}): \lambda ([^{18}\text{F}]\text{fluoride}) \text{ is } 1.5 \times 10^{-4} \text{ s}^{-1})$$

Typical radioactivity for a reaction: 0.5 mCi

$$N ([^{18}\text{F}]\text{fluoride}) \times \lambda (\text{s}^{-1}) = 0.5 \text{ mCi} = 1.9 \times 10^7 (\text{Bq})$$

$$N = 1.9 \times 10^7 \text{ (Bq)} / \lambda = 1.9 \times 10^7 / 1.5 \times 10^{-4} = 1.3 \times 10^{11}$$

$$\text{Mole of } [^{18}\text{F}]\text{fluoride: } 1.3 \times 10^{11} / 6.02 \times 10^{23} = 0.21 \text{ pmol}$$

Reaction conditions: For the aqueous solutions of [^{18}F]fluoride (2–5 μl , 100–500 μCi ; 500 μCi in 5 μl water corresponds to a concentration of 42 nM in [^{18}F]).

Measurement of Radiochemical Yield

Radiochemical yield was determined by multiplying the percentage of radioactivity in the solution and the relative peak integrations of a radio TLC scan. After spotting the solution on a silica gel TLC plate, the TLC plate was eluted with an appropriate solvent mixture, and then the TLC plate was scanned with a Bioscan AR-2000 Radio TLC Imaging Scanner. The Radiochemical TLC (RTLC) yield was calculated by dividing the area of the product peak by the total area of all peaks, and multiplying by 100% to convert to percentage units.

The remaining reaction solution was transferred to another vial. The radioactivity of the solution was measured in an ion chamber and the amount of radioactivity left on the walls of the initial vial was also measured in this way, and the % of ^{18}F in solution was determined by dividing the radioactivity of the solution by the sum of the radioactivity of the solution and the empty vial, and multiplying by 100% to convert to percentage units. The radiochemical yield (RCY) was determined by multiplying the RTLC yield by the fraction of radioactivity in solution (typically 0.75–0.85).

Table S1. Radiochemical Yield Data

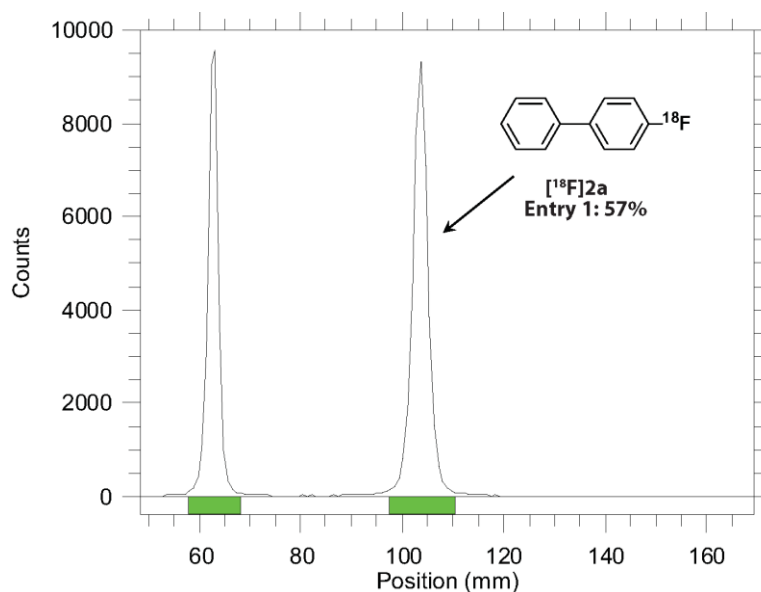
Entry	Molecule	RTLC yield (%)	^{18}F in solution (%)	RCY (%)	Average RCY (%)
1	$[^{18}\text{F}]\mathbf{2a}$	57	83	47	42
2		68	80	54	
3		49	82	40	
4		48	82	39	
5		49	81	40	
6		38	82	31	
7	$[^{18}\text{F}]\mathbf{2b}$	69	83	58	51
8		61	83	51	
9		52	77	40	
10		47	83	39	
11		73	82	60	
12		69	80	55	
13	$[^{18}\text{F}]\mathbf{2c}$	54	81	44	53
14		72	84	61	
15		72	84	60	
16		64	84	54	
17		57	78	45	
18		69	80	56	

19	$[^{18}\text{F}]\mathbf{2d}$	28	78	22	17
20		18	80	14	
21		19	79	15	
22		19	79	15	
23		24	79	19	
24		21	76	16	
25	$[^{18}\text{F}]\mathbf{2e}$	40	80	32	21
26		24	82	20	
27		21	82	17	
28		25	78	19	
29		26	73	19	
30		26	73	19	
31	$[^{18}\text{F}]\mathbf{2f}$	57	83	47	54
32		57	84	48	
33		54	82	44	
34		72	86	62	
35		78	84	66	
36		75	75	56	
37	$[^{18}\text{F}]\mathbf{2g}$	70	89	62	58
38		66	88	58	
39		76	87	66	
40		66	84	55	
41		61	79	48	
42		72	81	58	
43	$[^{18}\text{F}]\mathbf{2h}$	60	83	50	43
44		66	84	55	
45		52	81	42	
46		44	73	32	
47		42	80	34	
48		56	80	45	
49		24	70	17	
50		22	65	14	

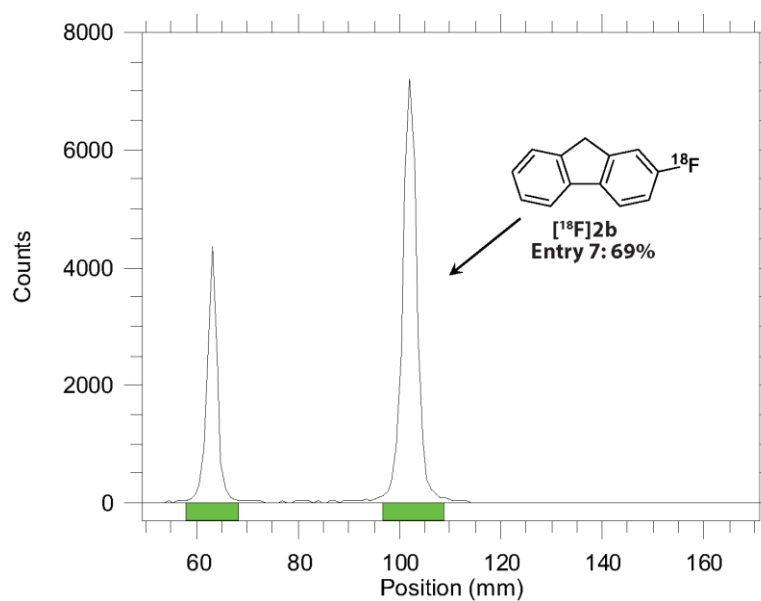
51	$[^{18}\text{F}]\mathbf{2i}$	41	68	28	15
52		14	76	11	
53		17	59	10	
54		13	64	8	
55	$[^{18}\text{F}]\mathbf{2j}$	45	84	38	38
56		53	83	44	
57		51	78	40	
58		51	79	40	
59		33	77	25	
60		49	79	39	
61	$[^{18}\text{F}]\mathbf{2k}$	27	74	20	21
62		30	75	23	
63		34	76	26	
64		32	77	25	
65		21	79	17	
66		20	75	15	
67	$[^{18}\text{F}]\mathbf{2l}$	11	86	9	13
68		14	82	11	
69		15	84	13	
70		14	81	11	
71		20	82	16	
72		17	86	15	

Example Radio TLC Scans:

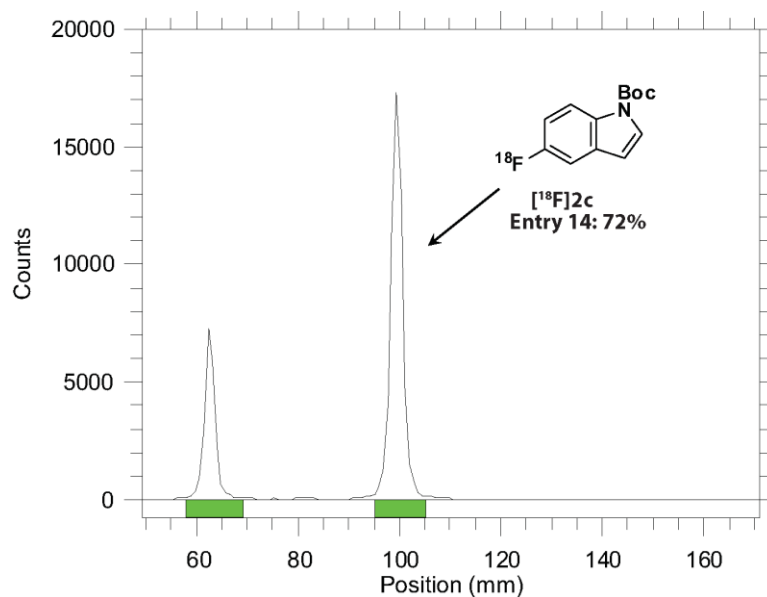
(Note: the baseline of the TLC plate where the reaction mixture was spotted corresponds to about 60mm on the horizontal axis of the following radio TLC scans).

Figure S3. Example Radio TLC Scan of [^{18}F]2a

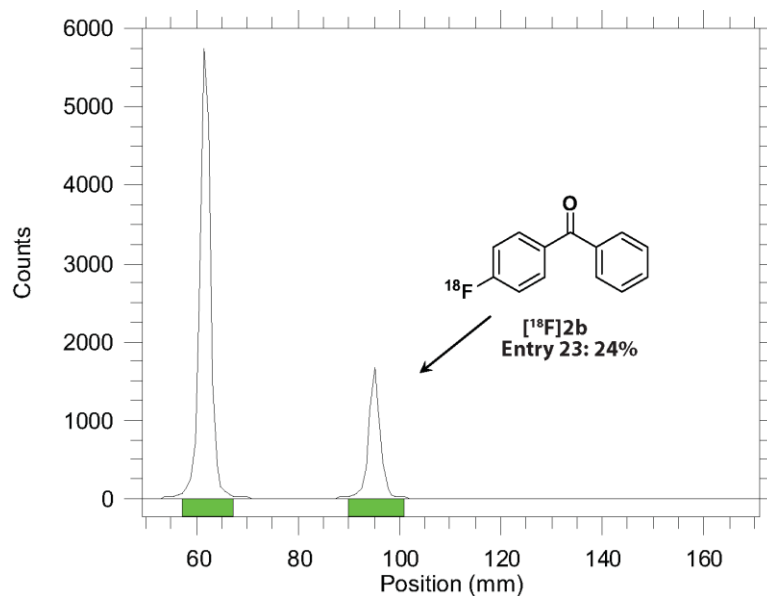
Entry 1 of Table S1. Percent of total integration listed for [^{18}F]2a

Figure S4. Example Radio TLC Scan of [^{18}F]2b

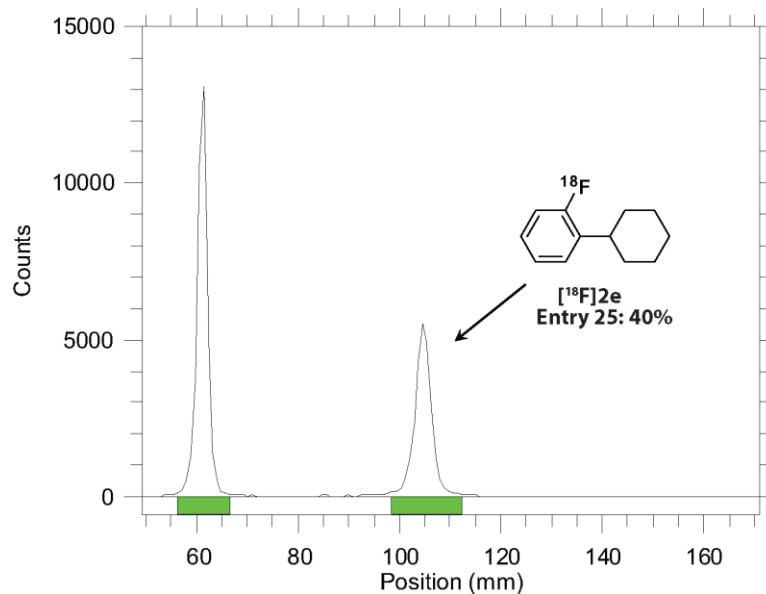
Entry 7 of Table S1. Percent of total integration listed for [^{18}F]2b

Figure S5. Example Radio TLC Scan of [^{18}F]2c

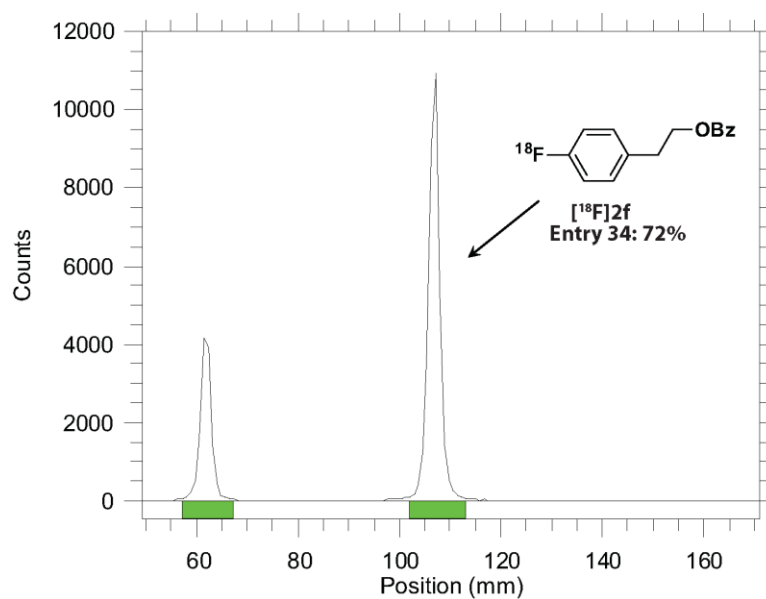
Entry 14 of Table S1. Percent of total integration listed for [^{18}F]2c

Figure S6. Example Radio TLC Scan of [^{18}F]2d

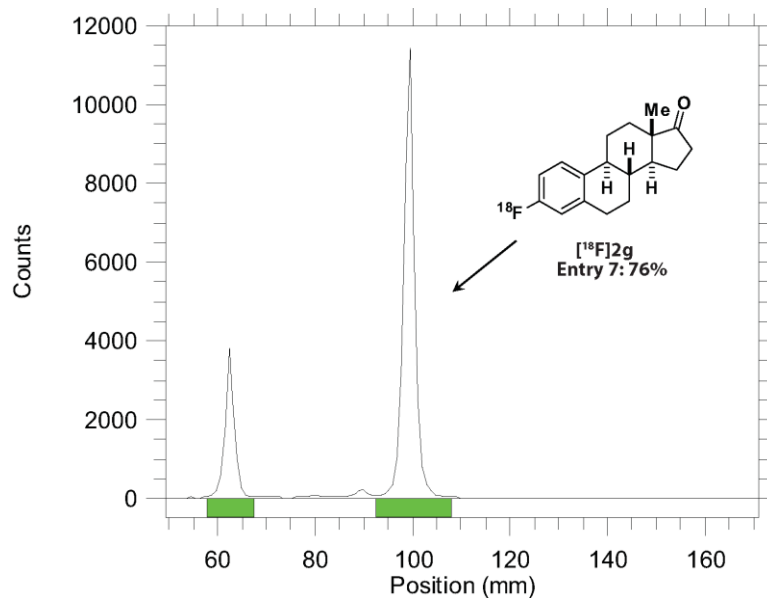
Entry 23 of Table S1. Percent of total integration listed for [^{18}F]2d

Figure S7. Example Radio TLC Scan of [^{18}F]2e

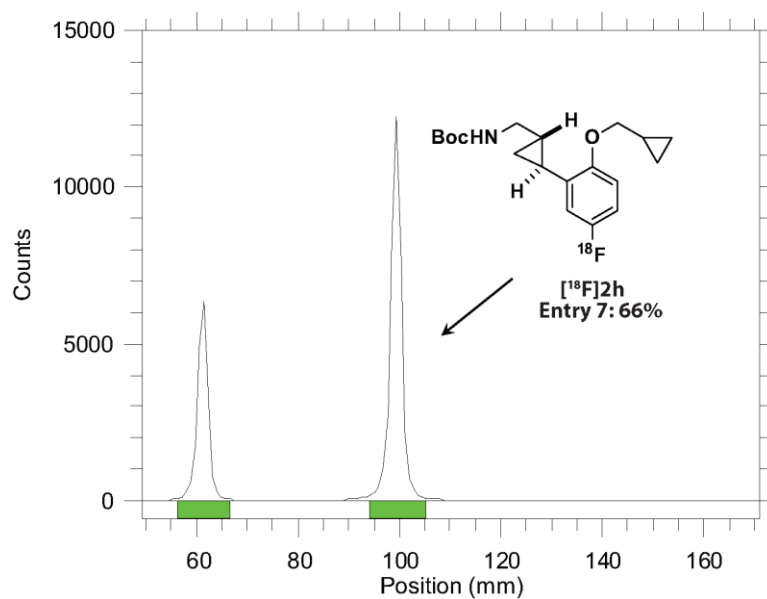
Entry 25 of Table S1. Percent of total integration listed for [^{18}F]2e

Figure S8. Example Radio TLC Scan of [^{18}F]2f

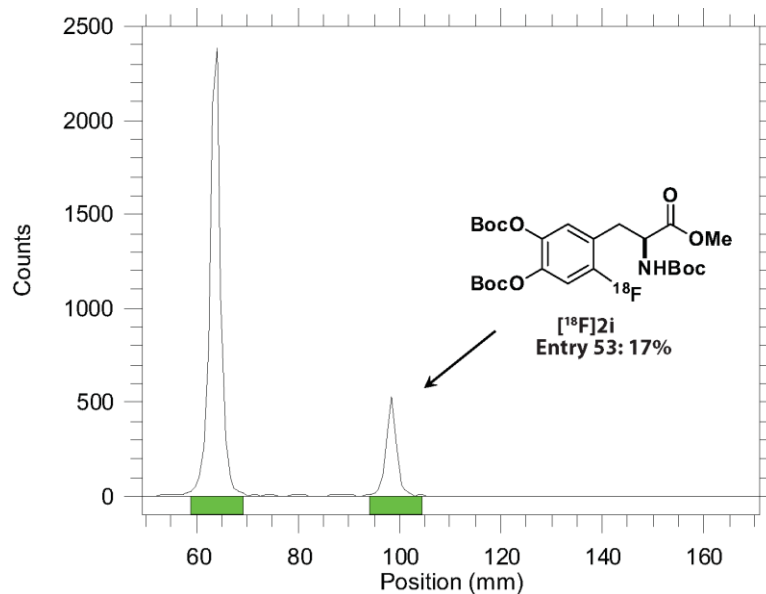
Entry 34 of Table S1. Percent of total integration listed for [^{18}F]2f

Figure S9. Example Radio TLC Scan of [^{18}F]2g

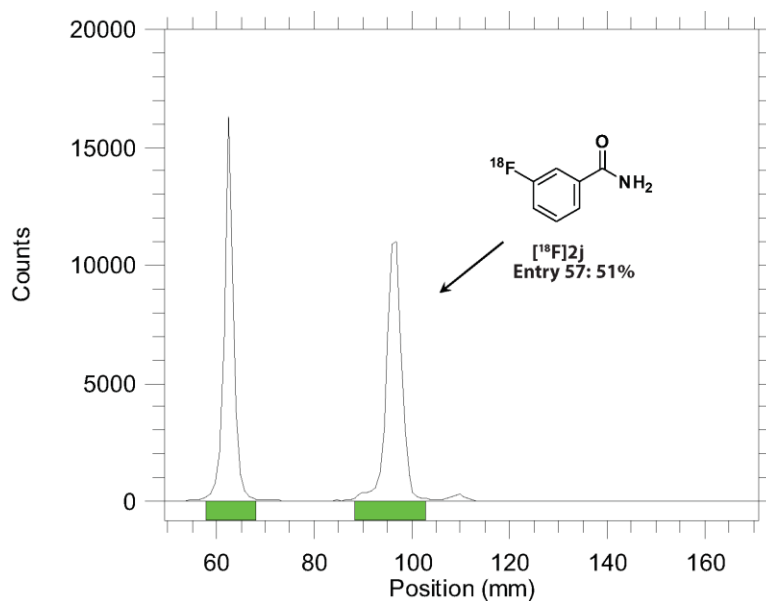
Entry 39 of Table S1. Percent of total integration listed for [^{18}F]2g

Figure S10. Example Radio TLC Scan of [^{18}F]2h

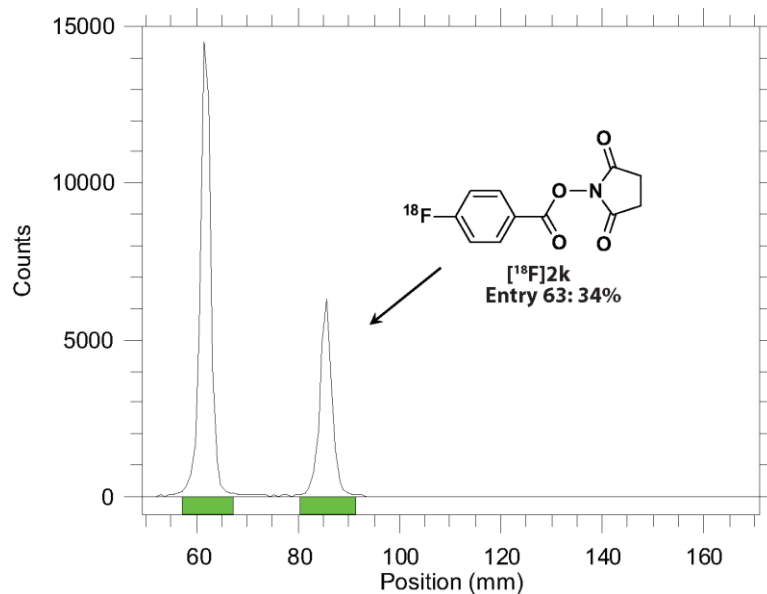
Entry 44 of Table S1. Percent of total integration listed for [^{18}F]2h

Figure S11. Example Radio TLC Scan of [^{18}F]2i

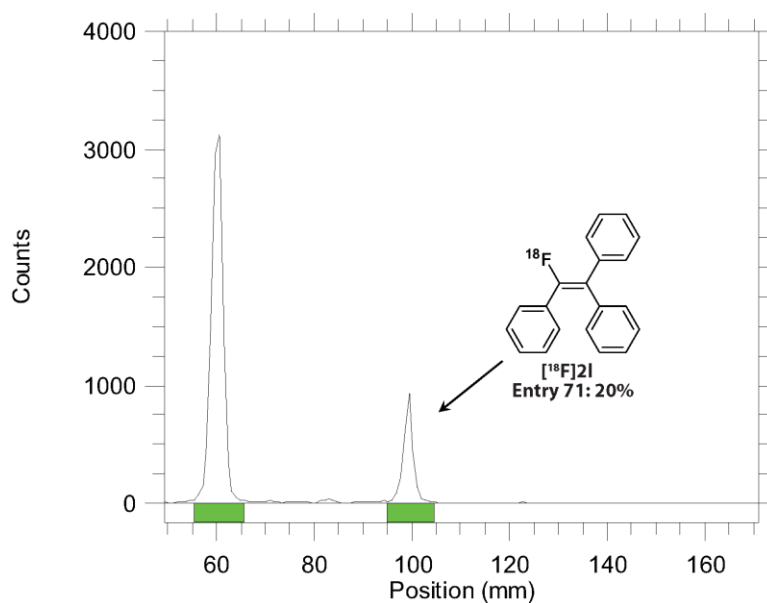
Entry 53 of Table S1. Percent of total integration listed for [^{18}F]2i

Figure S12. Example Radio TLC Scan of [^{18}F]2j

Entry 57 of Table S1. Percent of total integration listed for [^{18}F]2j

Figure S13. Example Radio TLC Scan of [^{18}F]2k

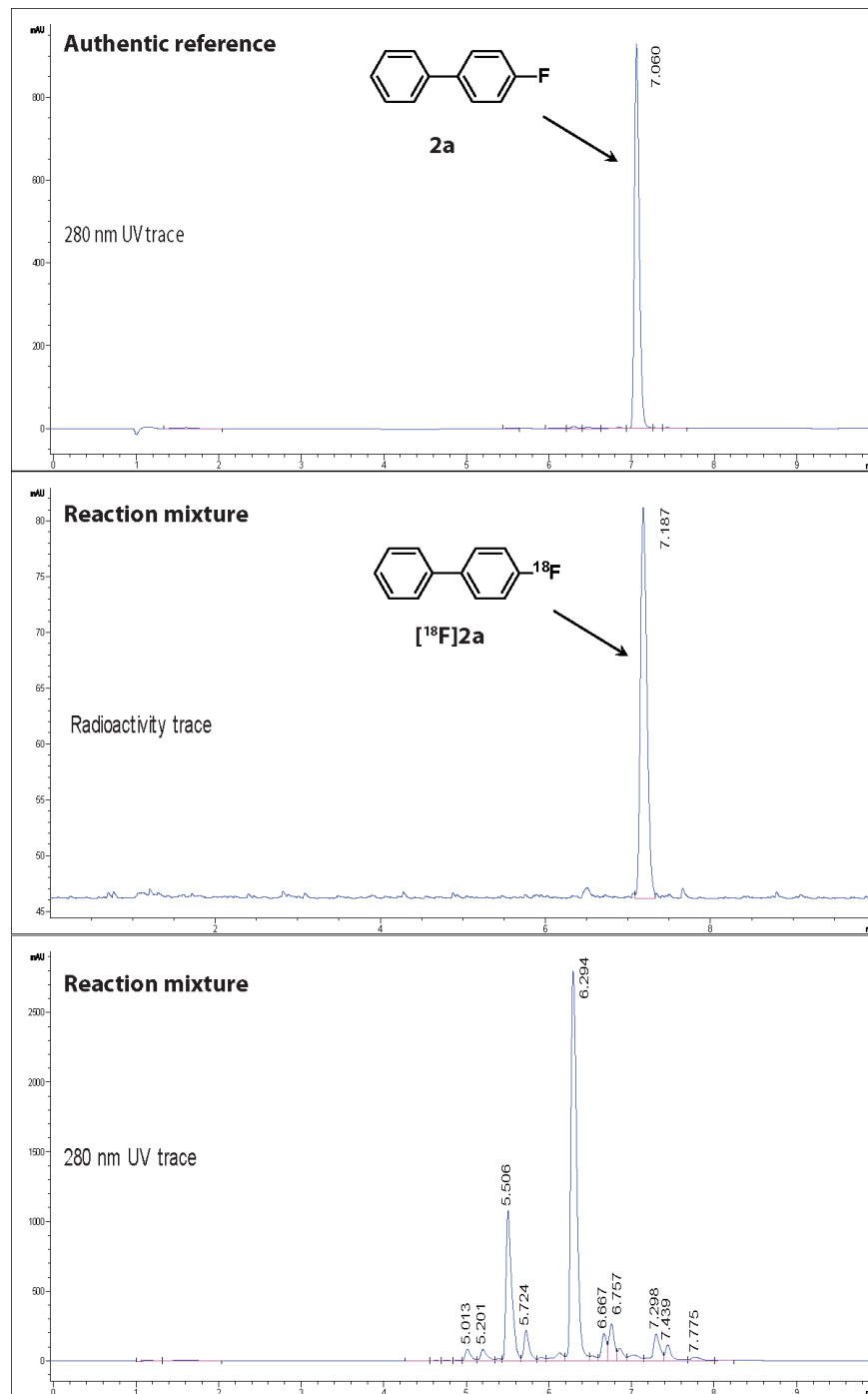
Entry 63 of Table S1. Percent of total integration listed for [^{18}F]2k

Figure S14. Example Radio TLC Scan of [^{18}F]2l

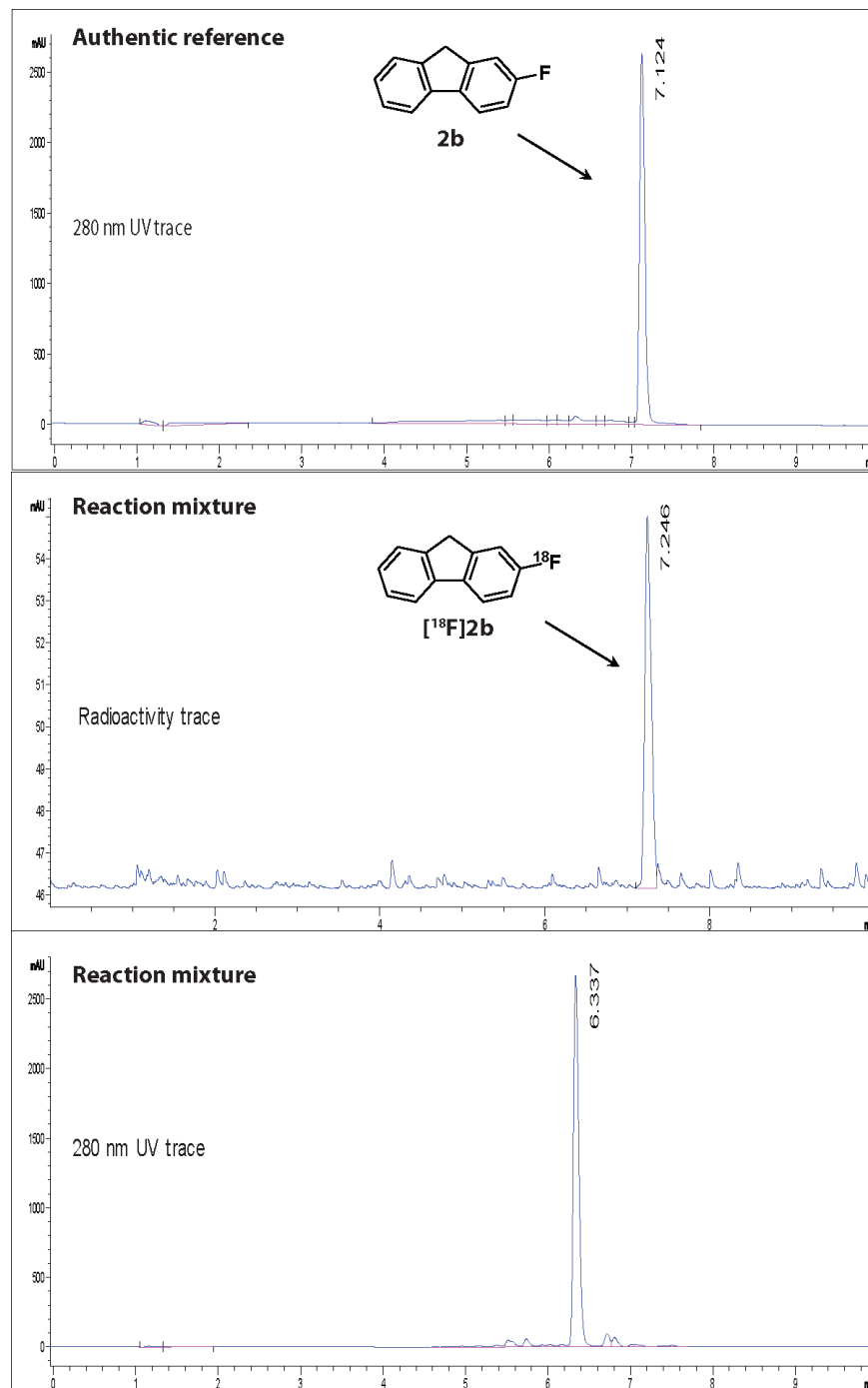
Entry 71 of Table S1. Percent of total integration listed for [^{18}F]2l

Characterization of ^{18}F -labeled Molecules

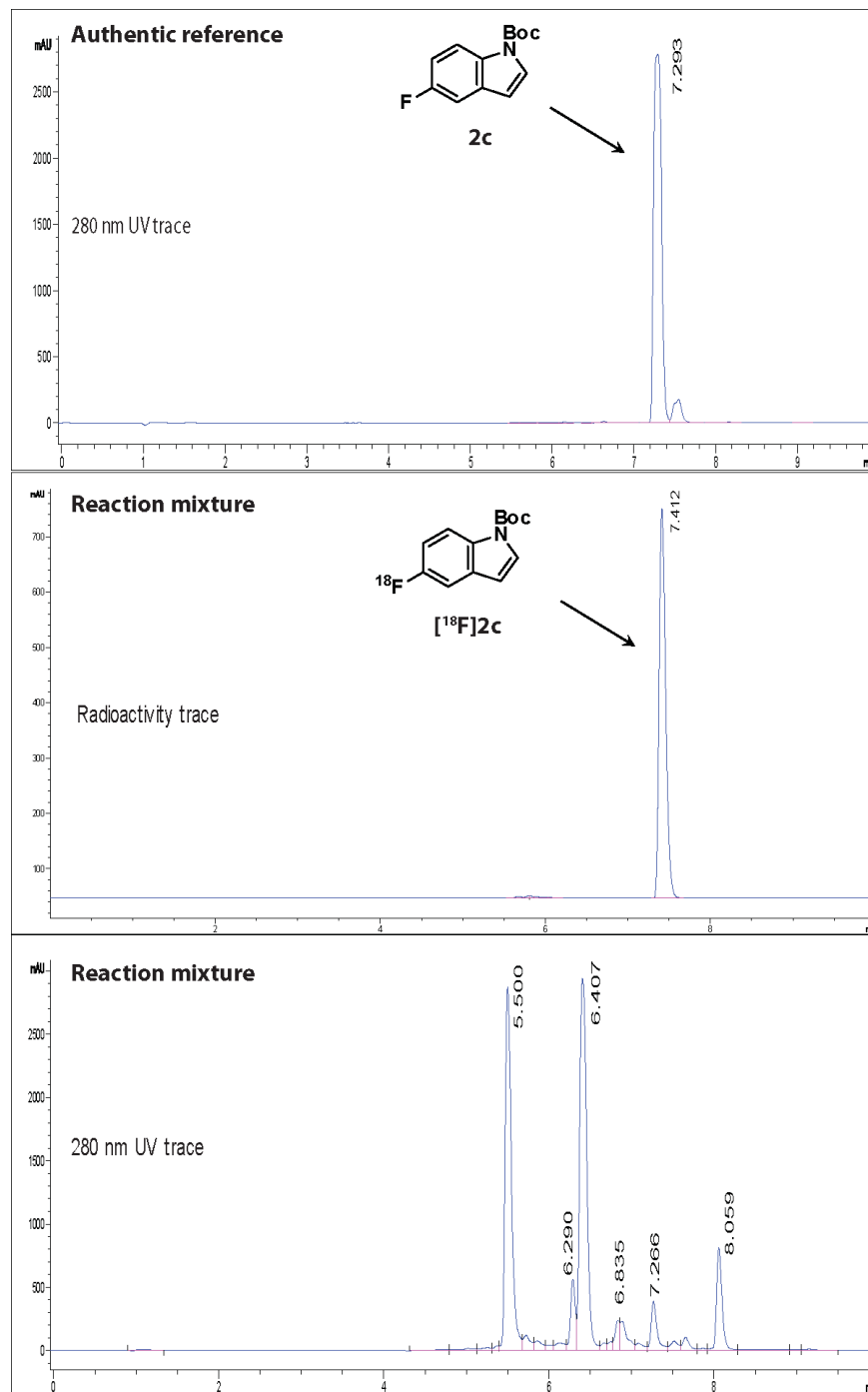
All ^{18}F -labeled molecules were characterized by comparing the HPLC trace (measured by radioactivity) of the crude reaction mixture to the HPLC trace (measured by UV) of the corresponding authentic ^{19}F -containing reference sample. An Agilent Eclipse XDB-C18, 5 μm , 4.6 x 150 mm HPLC column was used for analytical HPLC analysis. Analytical HPLC used the following mobile phases: 0.1% $\text{CF}_3\text{CO}_2\text{H}$ in water (A) 0.1% $\text{CF}_3\text{CO}_2\text{H}$ in acetonitrile (B). Program: 95% (A) and 5% (B) for 10 minutes. Note: radioactivity chromatographs have been offset (-0.125 min) to account for the delay volume (time) between the UV diode array detector and the radioactivity detector.

Figure S15. Characterization of [^{18}F]2a

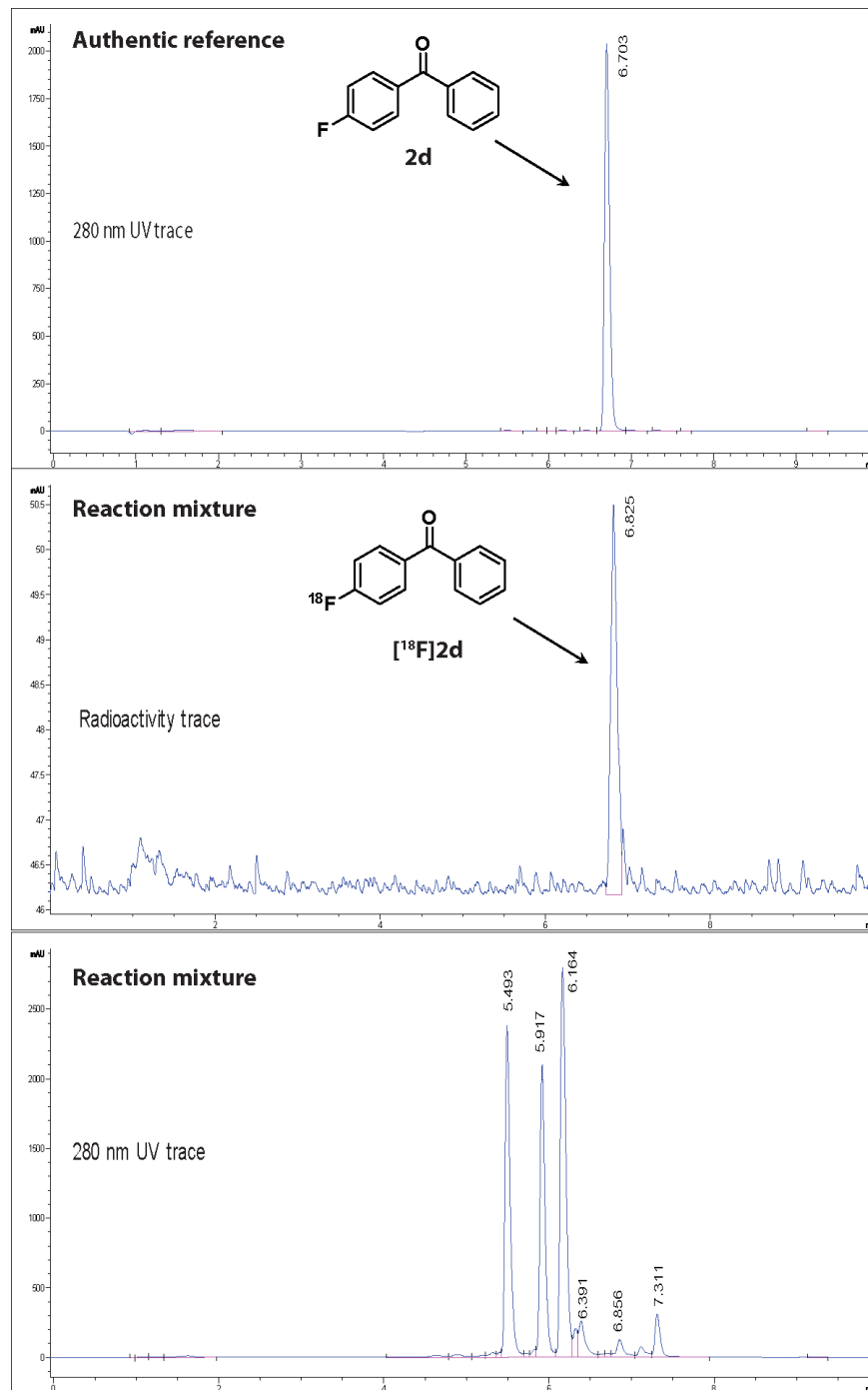
280 nm UV trace (top) of authentic sample (**2a**), radioactivity trace of the reaction mixture (middle) containing [^{18}F]2a, and 280 nm UV trace (bottom) of the reaction mixture. Note: radioactivity chromatographs have been offset (-0.125 min) to account for the delay volume (time) between the diode array detector and the radioactivity detector.

Figure S16. Characterization of [^{18}F]2b

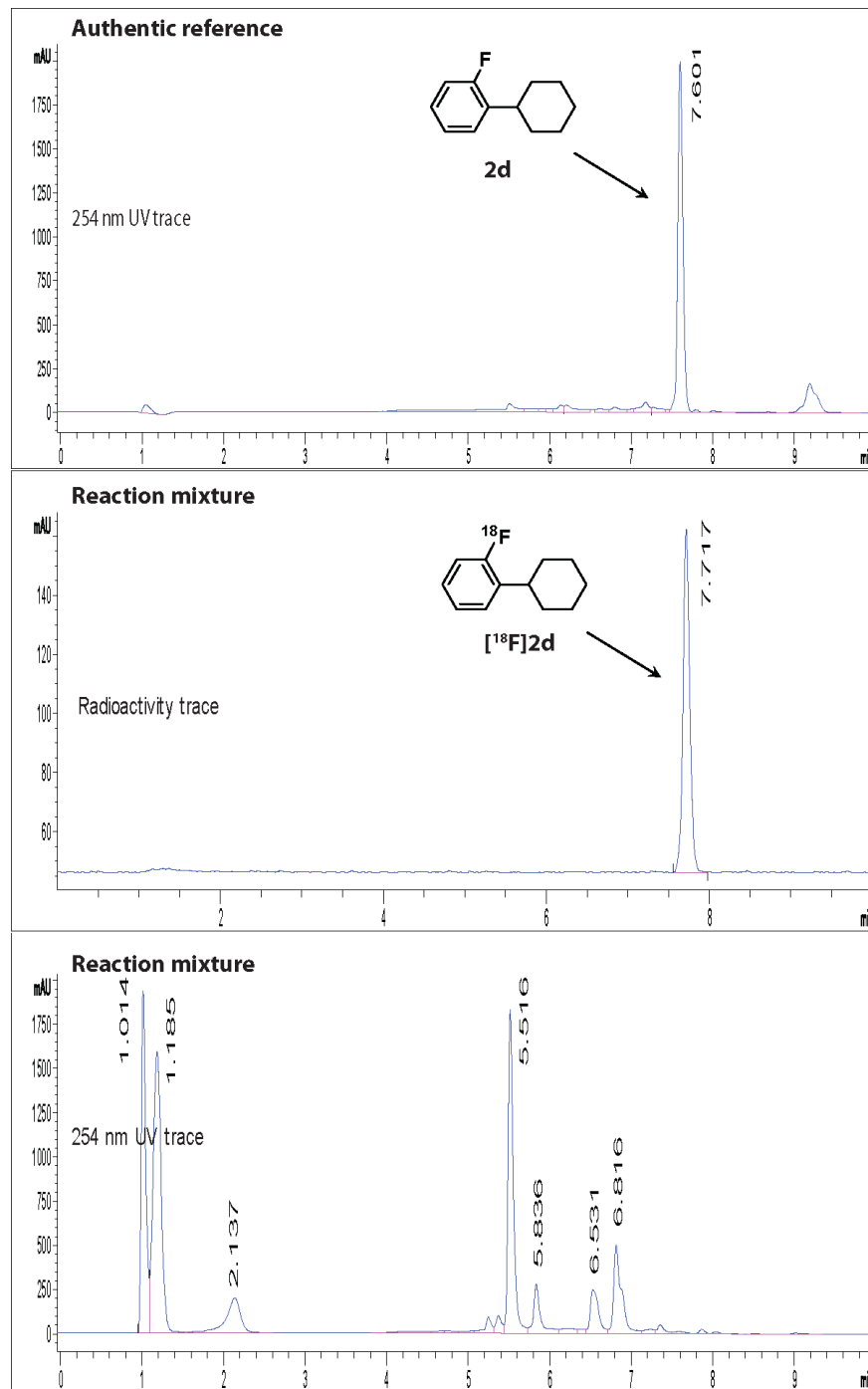
280 nm UV trace (top) of authentic sample (**2b**), radioactivity trace of the reaction mixture (middle) containing [^{18}F]2b, and 280 nm UV trace (bottom) of the reaction mixture. Note: radioactivity chromatographs have been offset (-0.125 min) to account for the delay volume (time) between the diode array detector and the radioactivity detector.

Figure S17. Characterization of [^{18}F]2c

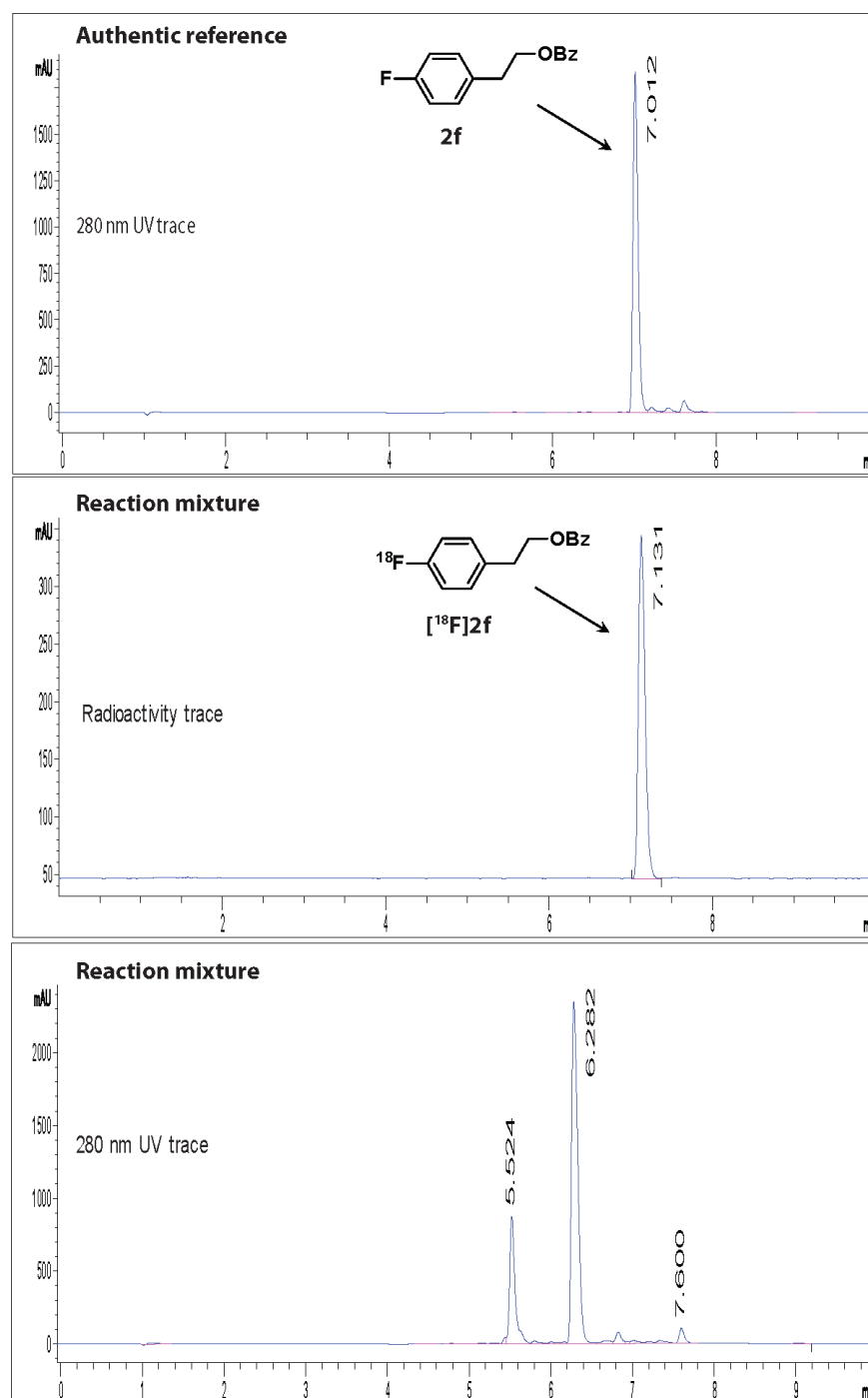
280 nm UV trace (top) of authentic sample (**2c**), radioactivity trace of the reaction mixture (middle) containing [^{18}F]2c, and 280 nm UV trace (bottom) of the reaction mixture. Note: radioactivity chromatographs have been offset (-0.125 min) to account for the delay volume (time) between the diode array detector and the radioactivity detector.

Figure S18. Characterization of [^{18}F]2d

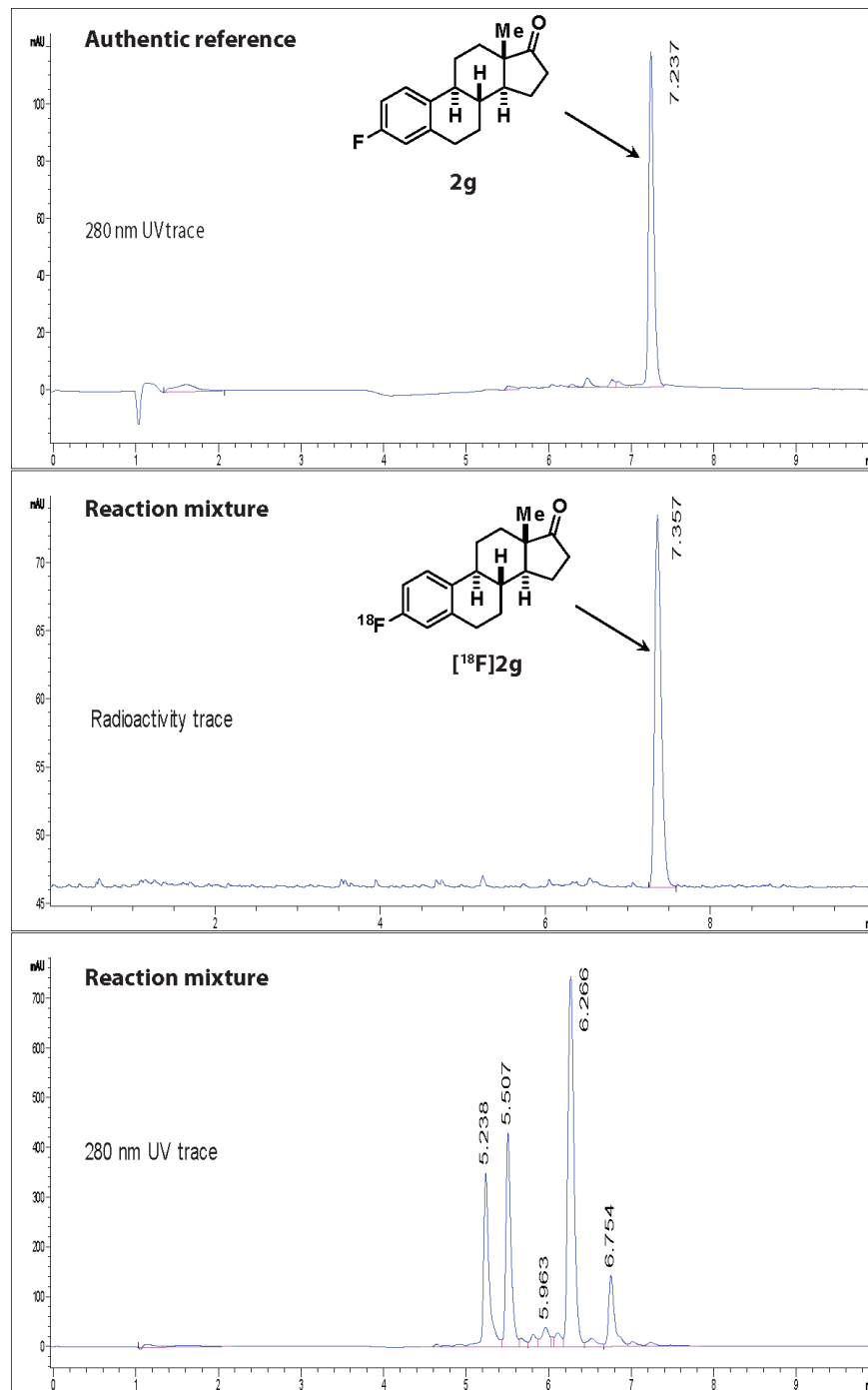
280 nm UV trace (top) of authentic sample (**2d**), radioactivity trace of the reaction mixture (middle) containing [^{18}F]**2d**, and 280 nm UV trace (bottom) of the reaction mixture. Note: radioactivity chromatographs have been offset (-0.125 min) to account for the delay volume (time) between the diode array detector and the radioactivity detector.

Figure S19. Characterization of [^{18}F]2e

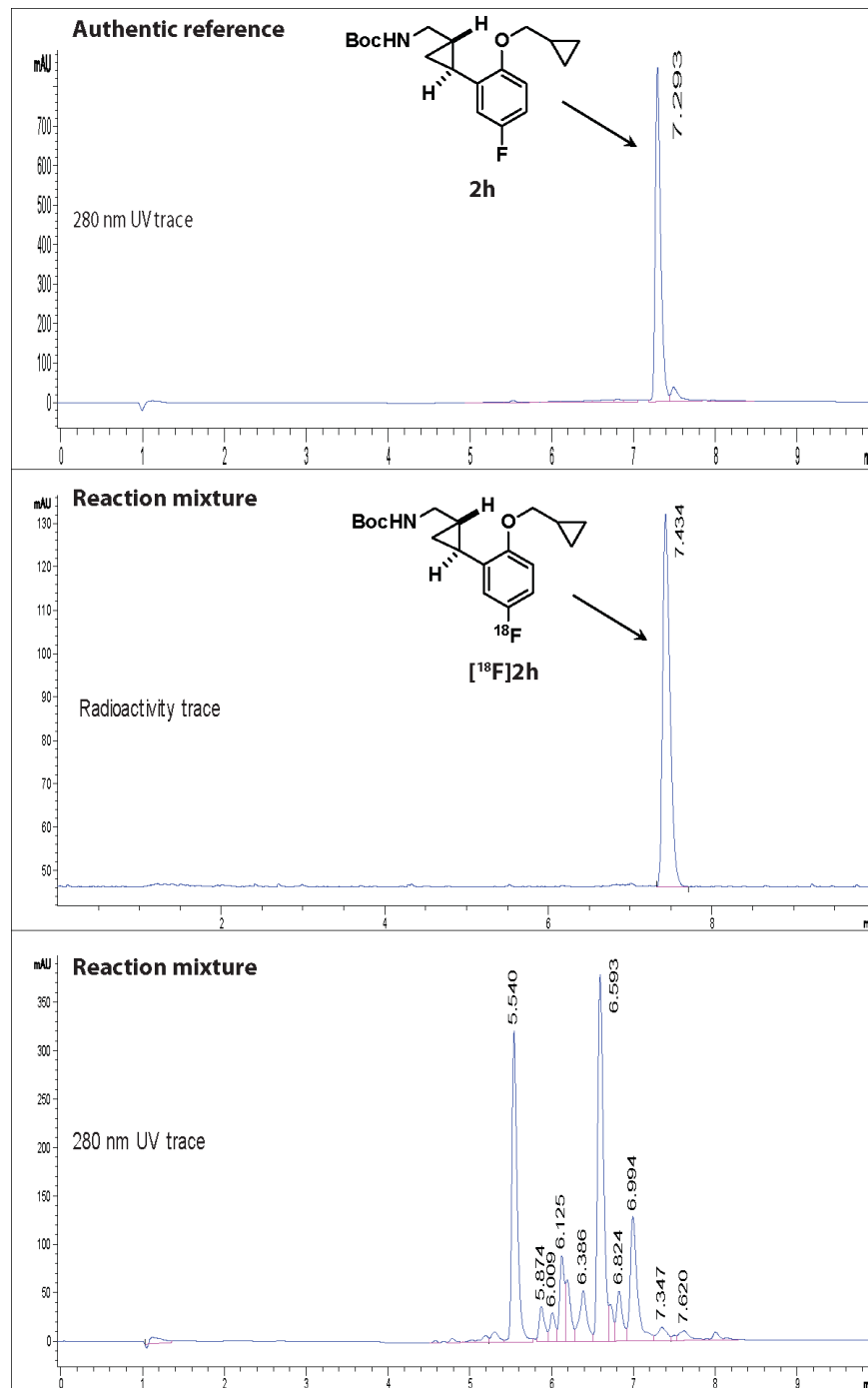
254 nm UV trace (top) of authentic sample (2e and cyclohexylbenzene as a 1:2 mixture), radioactivity trace of the reaction mixture (middle) containing [^{18}F]2e, and 254 nm UV trace (bottom) of the reaction mixture. Note: radioactivity chromatographs have been offset (-0.125 min) to account for the delay volume (time) between the diode array detector and the radioactivity detector.

Figure S20. Characterization of [^{18}F]2f

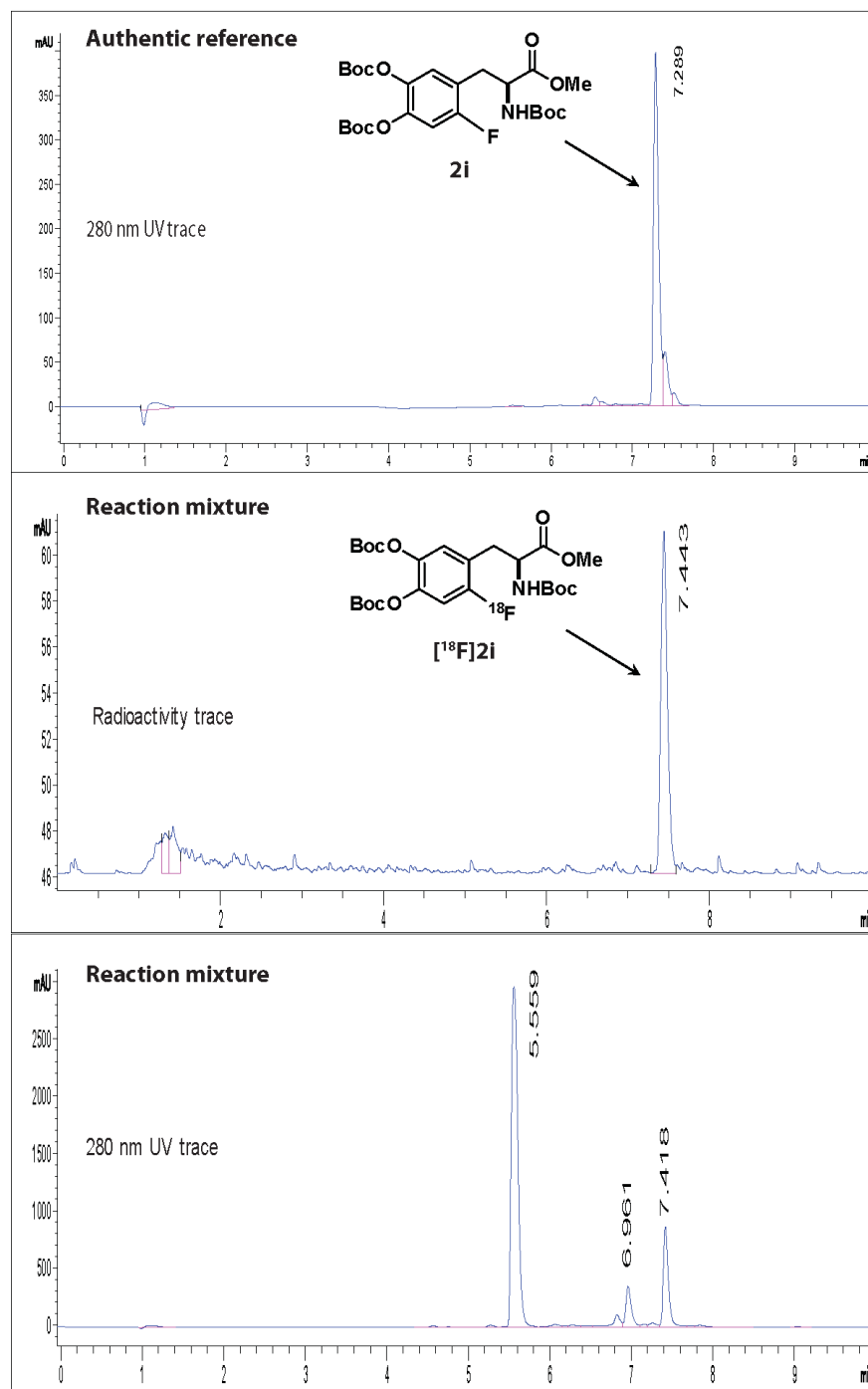
280 nm UV trace (top) of authentic sample (**2f**), radioactivity trace of the reaction mixture (middle) containing [^{18}F]2f, and 280 nm UV trace (bottom) of the reaction mixture. Note: radioactivity chromatographs have been offset (-0.125 min) to account for the delay volume (time) between the diode array detector and the radioactivity detector.

Figure S21. Characterization of [^{18}F]2g

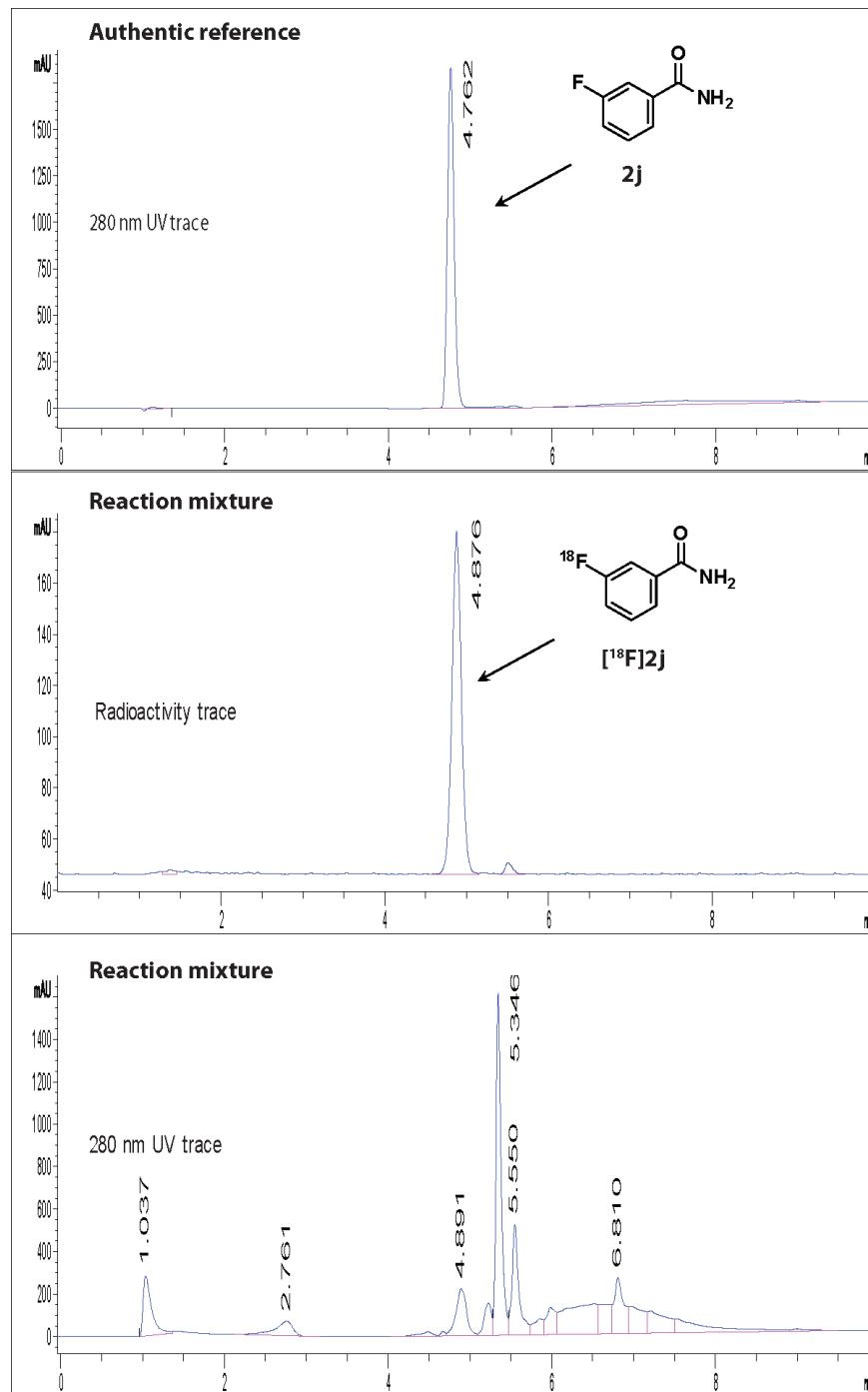
280 nm UV trace (top) of authentic sample (**2g**), radioactivity trace of the reaction mixture (middle) containing [^{18}F]**2g**, and 280 nm UV trace (bottom) of the reaction mixture. Note: radioactivity chromatographs have been offset (-0.125 min) to account for the delay volume (time) between the diode array detector and the radioactivity detector.

Figure S22. Characterization of [^{18}F]2h

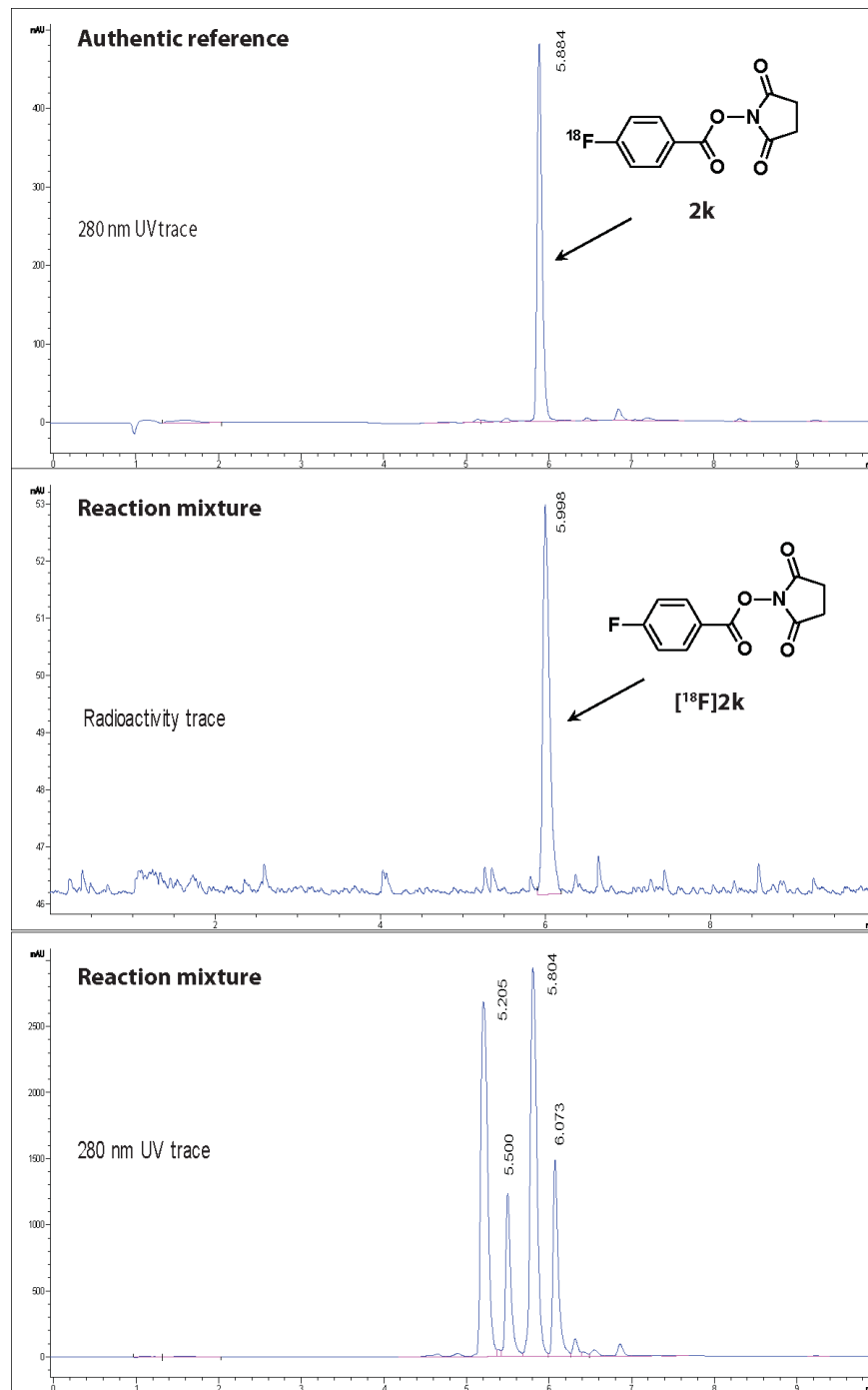
280 nm UV trace (top) of authentic sample (**2h**), radioactivity trace of the reaction mixture (middle) containing [^{18}F]2h, and 280 nm UV trace (bottom) of the reaction mixture. Note: radioactivity chromatographs been been offset (-0.125 min) to account for the delay volume (time) between the diode array detector and the radioactivity detector.

Figure S23. Characterization of [^{18}F]2i

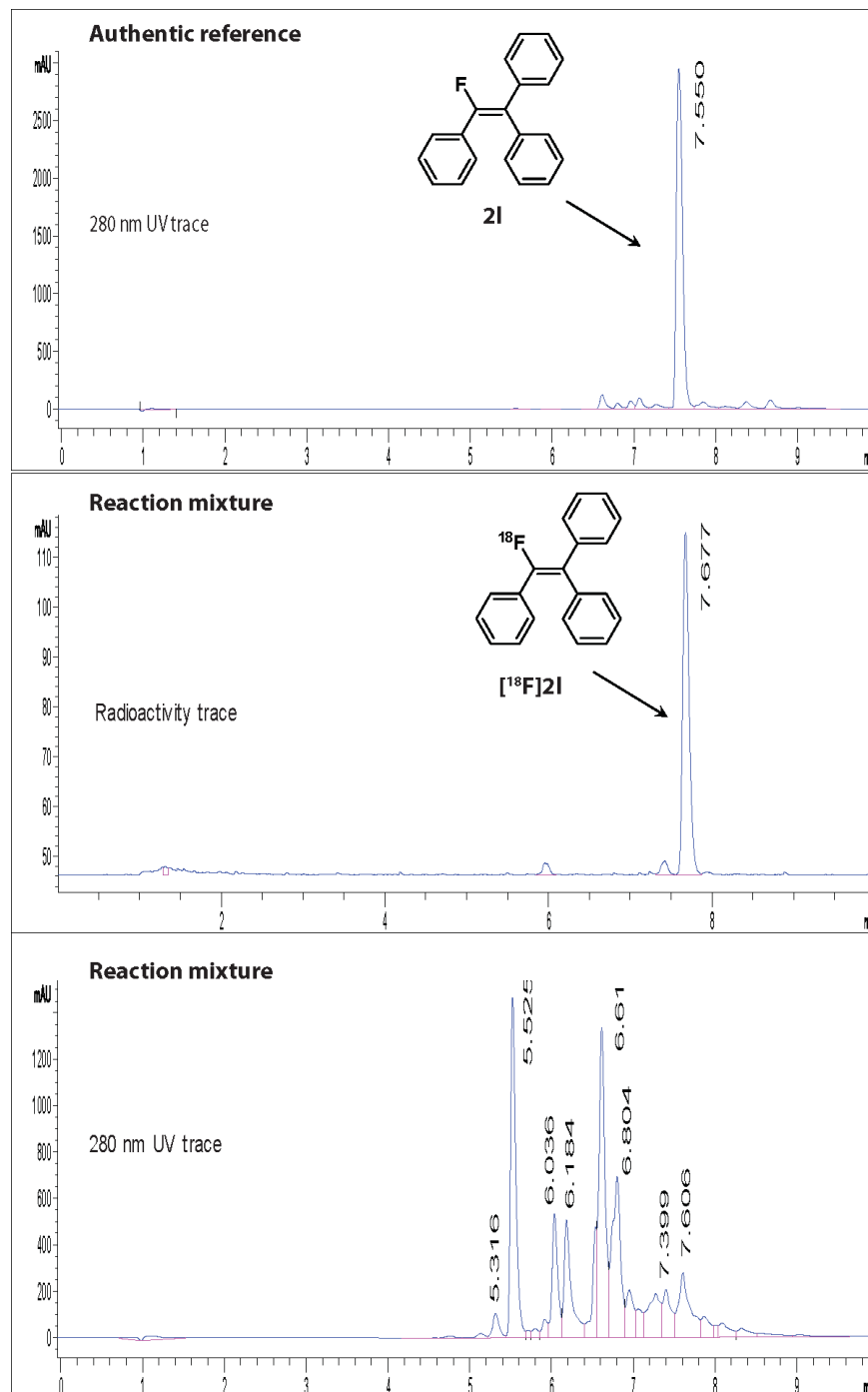
280 nm UV trace (top) of authentic sample (**2i**), radioactivity trace of the reaction mixture (middle) containing [^{18}F]2i, and 280 nm UV trace (bottom) of the reaction mixture. Note: radioactivity chromatographs have been offset (-0.125 min) to account for the delay volume (time) between the diode array detector and the radioactivity detector.

Figure S24. Characterization of [^{18}F]2j

280 nm UV trace (top) of authentic sample (**2j**), radioactivity trace of the reaction mixture (middle) containing [^{18}F]2j, and 280 nm UV trace (bottom) of the reaction mixture. Note: radioactivity chromatographs have been offset (-0.125 min) to account for the delay volume (time) between the diode array detector and the radioactivity detector.

Figure S25. Characterization of [^{18}F]2k

280 nm UV trace (top) of authentic sample (**2k**), radioactivity trace of the reaction mixture (middle) containing [^{18}F]2k, and 280 nm UV trace (bottom) of the reaction mixture. Note: radioactivity chromatographs have been offset (-0.125 min) to account for the delay volume (time) between the diode array detector and the radioactivity detector.

Figure S26. Characterization of [^{18}F]2I

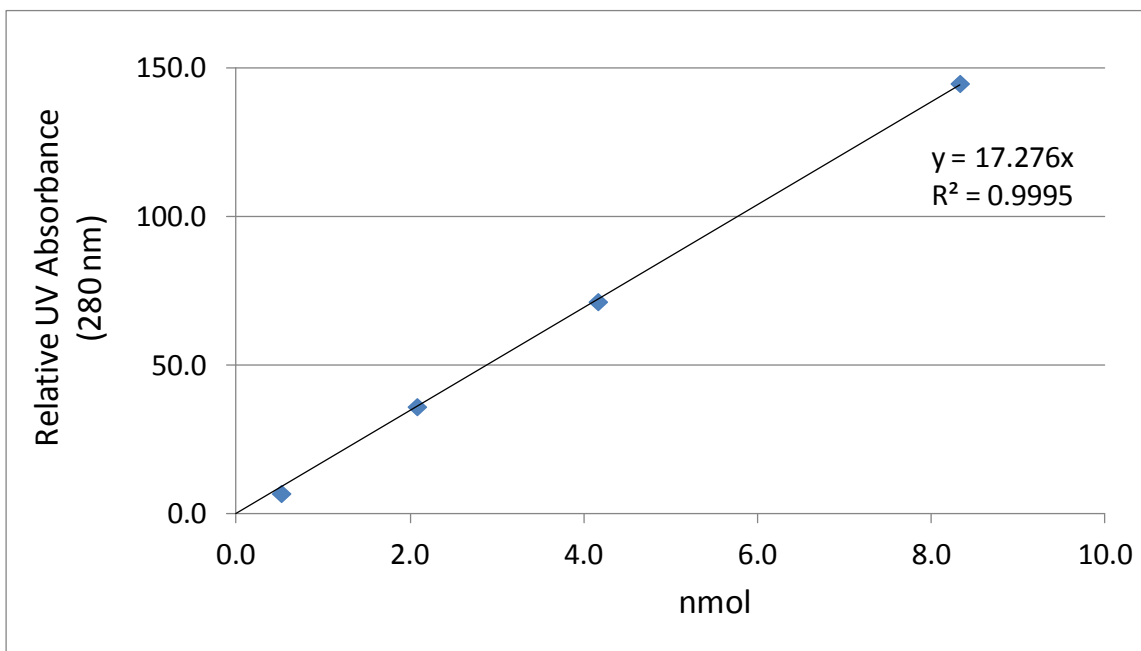
280 nm UV trace (top) of authentic sample (**2I**), radioactivity trace of the reaction mixture (middle) containing [^{18}F]**2I**, and 280 nm UV trace (bottom) of the reaction mixture. Note: radioactivity chromatographs have been offset (–0.125 min) to account for the delay volume (time) between the diode array detector and the radioactivity detector.

Determination of specific activity of [^{18}F]2g

Specific activity of [^{18}F]2g was determined by measuring the UV absorbance of a known amount of radioactivity and comparing to a standard curve of UV absorbance vs amount of unlabeled 2g. For 595 μCi of [^{18}F]2g a UV absorbance of 9.7 was measured corresponding to 0.56 nmol for a specific activity of 1.1 Ci/ μmol (41 GBq/ μmol) at time of injection (TOI). The standard curve was generated by integration of the UV absorbance signal (at 280 nm) of 4 different known amounts of 2g (see Tables S1 and Figures S11).

Table S2. Data for standard curve of UV absorbance vs amount of 2g

nmol 2g	UV Absorbance
0.5	6.6
2.1	35.9
4.2	71.2
8.3	144.6

Figure S27. Standard curve of UV absorbance vs amount of 2g

X-ray Crystallographic Analysis

Experimental (nickel aryl complex 1c) (CCDC 896034)

A crystal mounted on a diffractometer was collected data at 100 K. The intensities of the reflections were collected by means of a Bruker APEX II CCD diffractometer ($\text{Mo}_{\text{K}\alpha}$ radiation, $\lambda=0.71073$ Å), and equipped with an Oxford Cryosystems nitrogen flow apparatus. The collection method involved 0.5° scans in ω at 28° in 2θ . Data integration down to 0.82 Å resolution was carried out using SAINT V7.46 A (Bruker diffractometer, 2009) with reflection spot size optimization. Absorption corrections were made with the program SADABS (Bruker diffractometer, 2009). The structure was solved by the direct methods procedure and refined by least-squares methods against F^2 using SHELXS-97 and SHELXL-97 (Sheldrick, 2008) with OLEX 2 interface (Dolomanov, et al., 2009). Non-hydrogen atoms were refined anisotropically, and hydrogen atoms were allowed to ride on the respective atoms. Crystal data as well as details of data collection and refinement are summarized in Table 2, geometric parameters are shown in Table 3 and hydrogen-bond parameters are listed in Table 4. The Ortep plots produced with SHELXL-97 program, and the other drawings were produced with Accelrys DS Visualizer 2.0 (Accelrys, 2007).

Figure S28. The structure of 1c. The atoms are depicted with 50% probability ellipsoids.

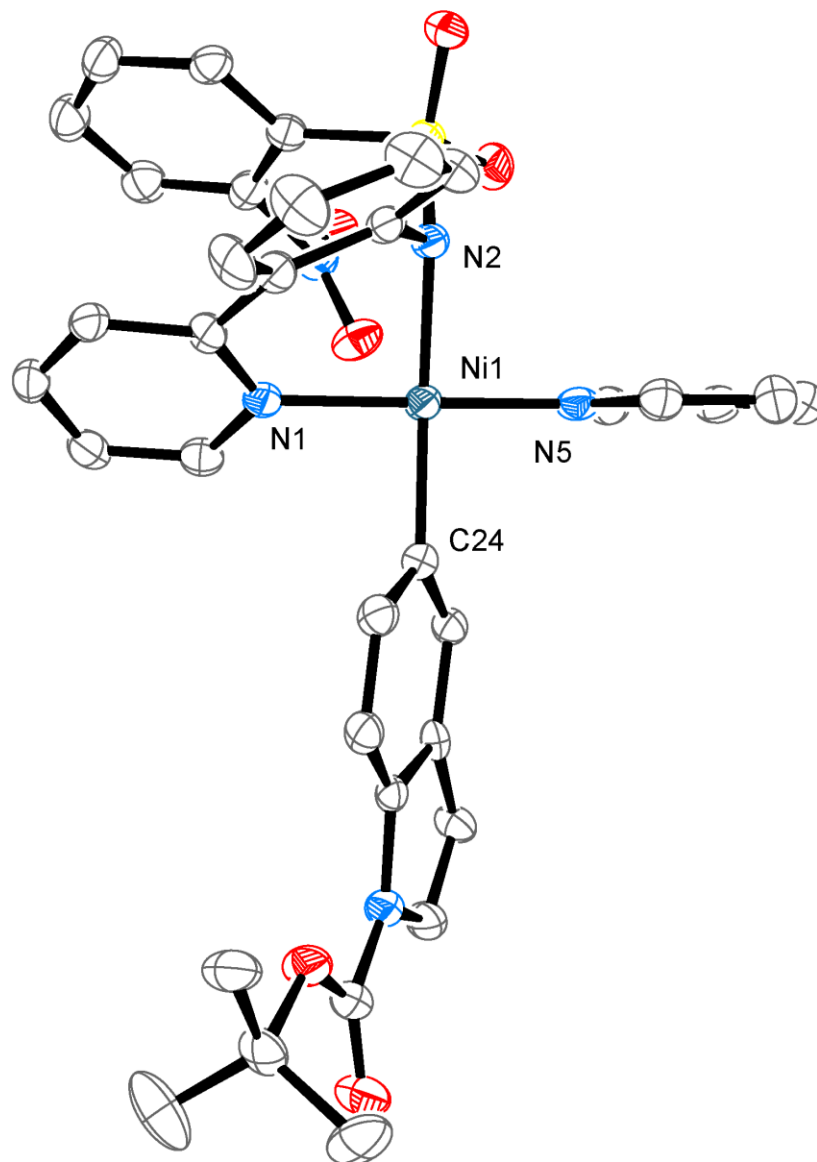


Table S3. Experimental details

	1c
Crystal data	
Chemical formula	C ₇₅ H ₇₄ N ₁₀ Ni ₂ O ₁₂ S ₂

M_r	1488.98
Crystal system, space group	Monoclinic, $P2_1/c$
Temperature (K)	100
a, b, c (Å)	14.5704 (11), 15.7185 (12), 30.632 (2)
β (°)	96.597 (1)
V (Å ³)	6969.0 (9)
Z	4
Radiation type	Mo $K\alpha$
μ (mm ⁻¹)	0.67
Crystal size (mm)	0.32 × 0.26 × 0.24
Data collection	
Diffractometer	Bruker D8 goniometer with CCD area detector diffractometer
Absorption correction	Multi-scan <i>SADABS</i>
$T_{\min}, T_{\max}$	0.814, 0.856
No. of measured, independent and observed [$I > 2\sigma(I)$] reflections	77361, 13259, 8722
R_{int}	0.107
$(\sin \theta/\lambda)_{\text{max}}$ (Å ⁻¹)	0.611
Refinement	
$R[F^2 > 2\sigma(F^2)], wR(F^2), S$	0.061, 0.163, 1.01
No. of reflections	13259
No. of parameters	936
No. of restraints	62
H-atom treatment	H-atom parameters constrained
$\Delta\rho_{\text{max}}, \Delta\rho_{\text{min}}$ (e Å ⁻³)	1.06, -0.73

Computer programs: *APEX2* v2009.3.0 (Bruker-AXS, 2009), *SAINT* 7.46A (Bruker-AXS, 2009), *SHELXS97* (Sheldrick, 2008), *SHELXL97* (Sheldrick, 2008), Bruker *SHELXTL* (Sheldrick, 2008).

Table S4. Selected geometric parameters (Å, °)

C1P—C2P	1.360 (12)	C92—C93	1.381 (8)
C1P—H1PA	0.9800	C92—H92	0.9500
C1P—H1PB	0.9800	C93—C94	1.375 (8)
C1P—H1PC	0.9800	C93—H93	0.9500
C2P—C3P	1.343 (11)	C94—C95	1.387 (7)
C2P—H2PA	0.9900	C94—H94	0.9500
C2P—H2PB	0.9900	C95—N10	1.345 (6)
C3P—C4P	1.237 (11)	C95—H95	0.9500
C3P—H3PA	0.9900	N6—Ni2	1.911 (4)
C3P—H3PB	0.9900	N7—S2	1.578 (3)
C4P—C5P	1.309 (12)	N7—Ni2	1.963 (3)
C4P—H4PA	0.9900	N8—O9	1.220 (5)
C4P—H4PB	0.9900	N8—O10	1.230 (5)
C5P—H5PA	0.9800	N10—Ni2	1.889 (4)
C5P—H5PB	0.9800	O7—S2	1.442 (3)
C5P—H5PC	0.9800	O8—S2	1.443 (3)
C1S—C2S	1.323 (12)	C1—N1	1.357 (5)
C1S—H1SA	0.9800	C1—C2	1.374 (6)
C1S—H1SB	0.9800	C1—H1	0.9500
C1S—H1SC	0.9800	C2—C3	1.381 (6)
C2S—C3S	1.252 (11)	C2—H2	0.9500
C2S—H2SA	0.9900	C3—C4	1.377 (6)
C2S—H2SB	0.9900	C3—H3	0.9500
C3S—C4S	1.319 (12)	C4—C5	1.393 (6)
C3S—H3SA	0.9900	C4—H4	0.9500
C3S—H3SB	0.9900	C5—N1	1.351 (5)
C4S—C5S	1.345 (12)	C5—C6	1.482 (6)
C4S—H4SA	0.9900	C6—C7	1.391 (6)

C4S—H4SB	0.9900	C6—C11	1.418 (6)
C5S—H5SA	0.9800	C7—C8	1.381 (7)
C5S—H5SB	0.9800	C7—H7	0.9500
C5S—H5SC	0.9800	C8—C9	1.392 (7)
C51—N6	1.351 (6)	C8—H8	0.9500
C51—C52	1.375 (7)	C9—C10	1.383 (6)
C51—H51	0.9500	C9—H9	0.9500
C52—C53	1.378 (7)	C10—C11	1.387 (6)
C52—H52	0.9500	C10—H10	0.9500
C53—C54	1.376 (7)	C11—N2	1.434 (5)
C53—H53	0.9500	C12—C13	1.390 (6)
C54—C55	1.394 (6)	C12—C17	1.396 (6)
C54—H54	0.9500	C12—S1	1.793 (4)
C55—N6	1.352 (6)	C13—C14	1.383 (6)
C55—C56	1.475 (6)	C13—H13	0.9500
C56—C57	1.391 (6)	C14—C15	1.378 (7)
C56—C61	1.416 (6)	C14—H14	0.9500
C57—C58	1.382 (7)	C15—C16	1.386 (7)
C57—H57	0.9500	C15—H15	0.9500
C58—C59	1.386 (7)	C16—C17	1.390 (6)
C58—H58	0.9500	C16—H16	0.9500
C59—C60	1.382 (6)	C17—N3	1.470 (5)
C59—H59	0.9500	C21—C22	1.390 (6)
C60—C61	1.382 (6)	C21—C26	1.408 (6)
C60—H60	0.9500	C21—N4	1.415 (5)
C61—N7	1.437 (5)	C22—C23	1.380 (6)
C62—C67	1.389 (6)	C22—H22	0.9500
C62—C63	1.393 (6)	C23—C24	1.402 (6)
C62—S2	1.790 (4)	C23—H23	0.9500

C63—C64	1.379 (6)	C24—C25	1.390 (6)
C63—H63	0.9500	C24—Ni1	1.894 (4)
C64—C65	1.386 (6)	C25—C26	1.403 (6)
C64—H64	0.9500	C25—H25	0.9500
C65—C66	1.385 (6)	C26—C27	1.450 (6)
C65—H65	0.9500	C27—C28	1.348 (6)
C66—C67	1.377 (6)	C27—H27	0.9500
C66—H66	0.9500	C28—N4	1.399 (5)
C67—N8	1.486 (5)	C28—H28	0.9500
C71—C72	1.393 (6)	C29—O6	1.202 (5)
C71—C76	1.405 (6)	C29—O5	1.332 (5)
C71—N9	1.419 (5)	C29—N4	1.394 (6)
C72—C73	1.389 (6)	C30—C33	1.487 (7)
C72—H72	0.9500	C30—O5	1.493 (5)
C73—C74	1.413 (6)	C30—C32	1.499 (7)
C73—H73	0.9500	C30—C31	1.504 (7)
C74—C75	1.391 (6)	C31—H31A	0.9800
C74—Ni2	1.901 (4)	C31—H31B	0.9800
C75—C76	1.402 (6)	C31—H31C	0.9800
C75—H75	0.9500	C32—H32A	0.9800
C76—C77	1.454 (6)	C32—H32B	0.9800
C77—C78	1.343 (6)	C32—H32C	0.9800
C77—H77	0.9500	C33—H33A	0.9800
C78—N9	1.401 (5)	C33—H33B	0.9800
C78—H78	0.9500	C33—H33C	0.9800
C79—O12	1.205 (5)	C41—N5	1.351 (5)
C79—O11	1.329 (5)	C41—C42	1.387 (6)
C79—N9	1.392 (5)	C41—H41	0.9500
C80—O11	1.490 (5)	C42—C43	1.379 (7)

C80—C82	1.513 (7)	C42—H42	0.9500
C80—C83	1.525 (7)	C43—C44	1.377 (7)
C80—C81	1.535 (7)	C43—H43	0.9500
C81—H81A	0.9800	C44—C45	1.384 (6)
C81—H81B	0.9800	C44—H44	0.9500
C81—H81C	0.9800	C45—N5	1.341 (6)
C82—H82A	0.9800	C45—H45	0.9500
C82—H82B	0.9800	N1—Ni1	1.921 (3)
C82—H82C	0.9800	N2—S1	1.577 (3)
C83—H83A	0.9800	N2—Ni1	1.962 (3)
C83—H83B	0.9800	N3—O3	1.225 (5)
C83—H83C	0.9800	N3—O4	1.235 (5)
C91—N10	1.356 (6)	N5—Ni1	1.886 (4)
C91—C92	1.383 (7)	O1—S1	1.441 (3)
C91—H91	0.9500	O2—S1	1.439 (3)
C2P—C1P—H1PA	109.5	C61—N7—Ni2	108.6 (3)
C2P—C1P—H1PB	109.5	S2—N7—Ni2	129.2 (2)
H1PA—C1P—H1PB	109.5	O9—N8—O10	124.1 (4)
C2P—C1P—H1PC	109.5	O9—N8—C67	119.4 (4)
H1PA—C1P—H1PC	109.5	O10—N8—C67	116.5 (4)
H1PB—C1P—H1PC	109.5	C79—N9—C78	122.0 (4)
C3P—C2P—C1P	147.5 (14)	C79—N9—C71	130.1 (4)
C3P—C2P—H2PA	99.9	C78—N9—C71	107.9 (3)
C1P—C2P—H2PA	99.9	C95—N10—C91	118.5 (4)
C3P—C2P—H2PB	99.9	C95—N10—Ni2	120.1 (3)
C1P—C2P—H2PB	99.9	C91—N10—Ni2	121.1 (3)
H2PA—C2P—H2PB	104.2	C79—O11—C80	121.0 (3)
C4P—C3P—C2P	133.8 (14)	O7—S2—O8	117.58 (19)

C4P—C3P—H3PA	103.8	O7—S2—N7	108.85 (18)
C2P—C3P—H3PA	103.8	O8—S2—N7	112.83 (19)
C4P—C3P—H3PB	103.8	O7—S2—C62	107.04 (19)
C2P—C3P—H3PB	103.8	O8—S2—C62	104.47 (19)
H3PA—C3P—H3PB	105.4	N7—S2—C62	105.08 (19)
C3P—C4P—C5P	163.9 (16)	N10—Ni2—C74	91.06 (17)
C3P—C4P—H4PA	95.0	N10—Ni2—N6	175.21 (16)
C5P—C4P—H4PA	95.0	C74—Ni2—N6	91.06 (17)
C3P—C4P—H4PB	95.0	N10—Ni2—N7	89.44 (15)
C5P—C4P—H4PB	95.0	C74—Ni2—N7	167.58 (17)
H4PA—C4P—H4PB	103.2	N6—Ni2—N7	89.41 (14)
C4P—C5P—H5PA	109.5	N1—C1—C2	122.8 (4)
C4P—C5P—H5PB	109.5	N1—C1—H1	118.6
H5PA—C5P—H5PB	109.5	C2—C1—H1	118.6
C4P—C5P—H5PC	109.5	C1—C2—C3	118.6 (4)
H5PA—C5P—H5PC	109.5	C1—C2—H2	120.7
H5PB—C5P—H5PC	109.5	C3—C2—H2	120.7
C3S—C2S—C1S	168.7 (17)	C4—C3—C2	119.2 (4)
C3S—C2S—H2SA	93.5	C4—C3—H3	120.4
C1S—C2S—H2SA	93.5	C2—C3—H3	120.4
C3S—C2S—H2SB	93.5	C3—C4—C5	120.1 (4)
C1S—C2S—H2SB	93.5	C3—C4—H4	120.0
H2SA—C2S—H2SB	103.1	C5—C4—H4	120.0
C2S—C3S—C4S	133.9 (14)	N1—C5—C4	120.6 (4)
C2S—C3S—H3SA	103.7	N1—C5—C6	118.6 (4)
C4S—C3S—H3SA	103.7	C4—C5—C6	120.8 (4)
C2S—C3S—H3SB	103.7	C7—C6—C11	119.2 (4)
C4S—C3S—H3SB	103.7	C7—C6—C5	120.2 (4)
H3SA—C3S—H3SB	105.4	C11—C6—C5	120.6 (4)

C3S—C4S—C5S	141.1 (15)	C8—C7—C6	121.2 (4)
C3S—C4S—H4SA	101.7	C8—C7—H7	119.4
C5S—C4S—H4SA	101.7	C6—C7—H7	119.4
C3S—C4S—H4SB	101.7	C7—C8—C9	119.2 (4)
C5S—C4S—H4SB	101.7	C7—C8—H8	120.4
H4SA—C4S—H4SB	104.7	C9—C8—H8	120.4
N6—C51—C52	123.4 (5)	C10—C9—C8	120.6 (5)
N6—C51—H51	118.3	C10—C9—H9	119.7
C52—C51—H51	118.3	C8—C9—H9	119.7
C51—C52—C53	118.7 (5)	C9—C10—C11	120.7 (4)
C51—C52—H52	120.7	C9—C10—H10	119.6
C53—C52—H52	120.7	C11—C10—H10	119.6
C54—C53—C52	118.9 (5)	C10—C11—C6	119.0 (4)
C54—C53—H53	120.5	C10—C11—N2	120.7 (4)
C52—C53—H53	120.5	C6—C11—N2	120.0 (4)
C53—C54—C55	120.0 (5)	C13—C12—C17	117.4 (4)
C53—C54—H54	120.0	C13—C12—S1	117.8 (3)
C55—C54—H54	120.0	C17—C12—S1	124.8 (3)
N6—C55—C54	121.2 (4)	C14—C13—C12	120.3 (4)
N6—C55—C56	118.3 (4)	C14—C13—H13	119.9
C54—C55—C56	120.5 (4)	C12—C13—H13	119.9
C57—C56—C61	118.3 (4)	C15—C14—C13	121.6 (4)
C57—C56—C55	119.9 (4)	C15—C14—H14	119.2
C61—C56—C55	121.7 (4)	C13—C14—H14	119.2
C58—C57—C56	121.0 (4)	C14—C15—C16	119.5 (4)
C58—C57—H57	119.5	C14—C15—H15	120.2
C56—C57—H57	119.5	C16—C15—H15	120.2
C57—C58—C59	120.2 (5)	C15—C16—C17	118.5 (4)
C57—C58—H58	119.9	C15—C16—H16	120.7

C59—C58—H58	119.9	C17—C16—H16	120.7
C60—C59—C58	119.7 (5)	C16—C17—C12	122.7 (4)
C60—C59—H59	120.1	C16—C17—N3	114.4 (4)
C58—C59—H59	120.1	C12—C17—N3	122.9 (4)
C59—C60—C61	120.7 (4)	C22—C21—C26	120.9 (4)
C59—C60—H60	119.6	C22—C21—N4	132.2 (4)
C61—C60—H60	119.6	C26—C21—N4	106.9 (4)
C60—C61—C56	120.0 (4)	C23—C22—C21	117.6 (4)
C60—C61—N7	121.4 (4)	C23—C22—H22	121.2
C56—C61—N7	118.5 (4)	C21—C22—H22	121.2
C67—C62—C63	116.8 (4)	C22—C23—C24	123.3 (4)
C67—C62—S2	126.1 (3)	C22—C23—H23	118.3
C63—C62—S2	117.1 (3)	C24—C23—H23	118.3
C64—C63—C62	121.4 (4)	C25—C24—C23	118.4 (4)
C64—C63—H63	119.3	C25—C24—Ni1	125.7 (3)
C62—C63—H63	119.3	C23—C24—Ni1	115.8 (3)
C63—C64—C65	120.1 (4)	C24—C25—C26	119.8 (4)
C63—C64—H64	120.0	C24—C25—H25	120.1
C65—C64—H64	120.0	C26—C25—H25	120.1
C66—C65—C64	119.9 (4)	C25—C26—C21	119.9 (4)
C66—C65—H65	120.0	C25—C26—C27	132.8 (4)
C64—C65—H65	120.0	C21—C26—C27	107.3 (4)
C67—C66—C65	118.7 (4)	C28—C27—C26	107.7 (4)
C67—C66—H66	120.6	C28—C27—H27	126.2
C65—C66—H66	120.6	C26—C27—H27	126.2
C66—C67—C62	123.0 (4)	C27—C28—N4	109.9 (4)
C66—C67—N8	115.2 (4)	C27—C28—H28	125.0
C62—C67—N8	121.8 (4)	N4—C28—H28	125.0
C72—C71—C76	121.0 (4)	O6—C29—O5	127.8 (4)

C72—C71—N9	131.6 (4)	O6—C29—N4	122.4 (4)
C76—C71—N9	107.3 (3)	O5—C29—N4	109.8 (4)
C73—C72—C71	117.2 (4)	C33—C30—O5	109.0 (4)
C73—C72—H72	121.4	C33—C30—C32	112.2 (5)
C71—C72—H72	121.4	O5—C30—C32	101.1 (4)
C72—C73—C74	123.5 (4)	C33—C30—C31	110.8 (5)
C72—C73—H73	118.3	O5—C30—C31	109.6 (4)
C74—C73—H73	118.3	C32—C30—C31	113.6 (4)
C75—C74—C73	117.8 (4)	C30—C31—H31A	109.5
C75—C74—Ni2	126.3 (3)	C30—C31—H31B	109.5
C73—C74—Ni2	115.9 (3)	H31A—C31—H31B	109.5
C74—C75—C76	120.1 (4)	C30—C31—H31C	109.5
C74—C75—H75	119.9	H31A—C31—H31C	109.5
C76—C75—H75	119.9	H31B—C31—H31C	109.5
C75—C76—C71	120.2 (4)	C30—C32—H32A	109.5
C75—C76—C77	133.0 (4)	C30—C32—H32B	109.5
C71—C76—C77	106.8 (4)	H32A—C32—H32B	109.5
C78—C77—C76	108.2 (4)	C30—C32—H32C	109.5
C78—C77—H77	125.9	H32A—C32—H32C	109.5
C76—C77—H77	125.9	H32B—C32—H32C	109.5
C77—C78—N9	109.9 (4)	C30—C33—H33A	109.5
C77—C78—H78	125.1	C30—C33—H33B	109.5
N9—C78—H78	125.1	H33A—C33—H33B	109.5
O12—C79—O11	127.8 (4)	C30—C33—H33C	109.5
O12—C79—N9	122.5 (4)	H33A—C33—H33C	109.5
O11—C79—N9	109.7 (4)	H33B—C33—H33C	109.5
O11—C80—C82	108.8 (4)	N5—C41—C42	122.4 (4)
O11—C80—C83	110.5 (4)	N5—C41—H41	118.8
C82—C80—C83	112.9 (4)	C42—C41—H41	118.8

O11—C80—C81	101.3 (3)	C43—C42—C41	119.3 (5)
C82—C80—C81	110.7 (4)	C43—C42—H42	120.4
C83—C80—C81	112.0 (4)	C41—C42—H42	120.4
C80—C81—H81A	109.5	C44—C43—C42	118.5 (5)
C80—C81—H81B	109.5	C44—C43—H43	120.7
H81A—C81—H81B	109.5	C42—C43—H43	120.7
C80—C81—H81C	109.5	C43—C44—C45	119.3 (5)
H81A—C81—H81C	109.5	C43—C44—H44	120.3
H81B—C81—H81C	109.5	C45—C44—H44	120.3
C80—C82—H82A	109.5	N5—C45—C44	122.8 (5)
C80—C82—H82B	109.5	N5—C45—H45	118.6
H82A—C82—H82B	109.5	C44—C45—H45	118.6
C80—C82—H82C	109.5	C5—N1—C1	118.7 (4)
H82A—C82—H82C	109.5	C5—N1—Ni1	122.5 (3)
H82B—C82—H82C	109.5	C1—N1—Ni1	118.6 (3)
C80—C83—H83A	109.5	C11—N2—S1	118.5 (3)
C80—C83—H83B	109.5	C11—N2—Ni1	107.8 (3)
H83A—C83—H83B	109.5	S1—N2—Ni1	128.6 (2)
C80—C83—H83C	109.5	O3—N3—O4	124.1 (4)
H83A—C83—H83C	109.5	O3—N3—C17	118.9 (4)
H83B—C83—H83C	109.5	O4—N3—C17	116.9 (4)
N10—C91—C92	121.9 (5)	C29—N4—C28	122.0 (4)
N10—C91—H91	119.1	C29—N4—C21	129.6 (4)
C92—C91—H91	119.1	C28—N4—C21	108.2 (3)
C93—C92—C91	119.5 (5)	C45—N5—C41	117.5 (4)
C93—C92—H92	120.3	C45—N5—Ni1	122.4 (3)
C91—C92—H92	120.3	C41—N5—Ni1	120.1 (3)
C94—C93—C92	118.6 (5)	C29—O5—C30	121.4 (4)
C94—C93—H93	120.7	O2—S1—O1	117.78 (19)

C92—C93—H93	120.7	O2—S1—N2	112.58 (19)
C93—C94—C95	120.0 (5)	O1—S1—N2	108.63 (18)
C93—C94—H94	120.0	O2—S1—C12	104.50 (19)
C95—C94—H94	120.0	O1—S1—C12	106.71 (19)
N10—C95—C94	121.6 (5)	N2—S1—C12	105.72 (19)
N10—C95—H95	119.2	N5—Ni1—C24	90.46 (17)
C94—C95—H95	119.2	N5—Ni1—N1	174.11 (16)
C51—N6—C55	117.7 (4)	C24—Ni1—N1	90.12 (16)
C51—N6—Ni2	119.5 (3)	N5—Ni1—N2	91.33 (15)
C55—N6—Ni2	122.4 (3)	C24—Ni1—N2	165.86 (17)
C61—N7—S2	117.7 (3)	N1—Ni1—N2	89.53 (14)
C1P—C2P—C3P—C4P	17 (3)	C61—N7—Ni2—N6	62.1 (3)
C2P—C3P—C4P—C5P	19 (6)	S2—N7—Ni2—N6	-93.0 (3)
C1S—C2S—C3S—C4S	-25 (8)	N1—C1—C2—C3	-0.5 (7)
C2S—C3S—C4S—C5S	21 (3)	C1—C2—C3—C4	-1.2 (7)
N6—C51—C52—C53	-1.1 (7)	C2—C3—C4—C5	1.1 (7)
C51—C52—C53—C54	-1.1 (7)	C3—C4—C5—N1	0.5 (6)
C52—C53—C54—C55	1.3 (7)	C3—C4—C5—C6	-177.5 (4)
C53—C54—C55—N6	0.6 (7)	N1—C5—C6—C7	-139.7 (4)
C53—C54—C55—C56	-178.8 (4)	C4—C5—C6—C7	38.4 (6)
N6—C55—C56—C57	-142.2 (4)	N1—C5—C6—C11	38.9 (6)
C54—C55—C56—C57	37.3 (6)	C4—C5—C6—C11	-143.0 (4)
N6—C55—C56—C61	39.5 (6)	C11—C6—C7—C8	-0.7 (7)
C54—C55—C56—C61	-141.0 (4)	C5—C6—C7—C8	177.9 (5)
C61—C56—C57—C58	-1.3 (7)	C6—C7—C8—C9	-1.1 (8)
C55—C56—C57—C58	-179.7 (4)	C7—C8—C9—C10	1.6 (8)
C56—C57—C58—C59	-0.6 (8)	C8—C9—C10—C11	-0.4 (8)
C57—C58—C59—C60	1.8 (8)	C9—C10—C11—C6	-1.4 (7)

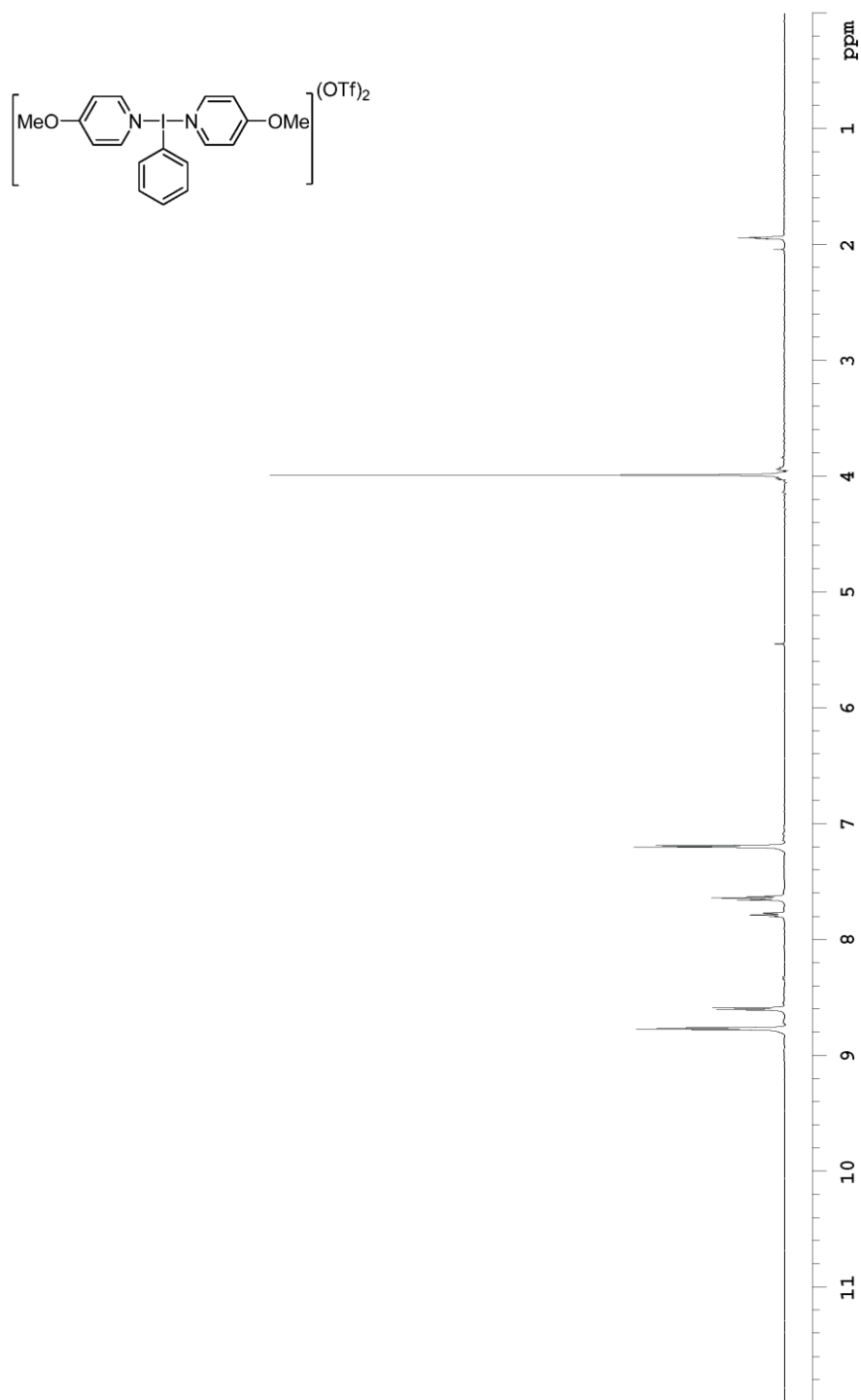
C58—C59—C60—C61	-1.1 (7)	C9—C10—C11—N2	-175.8 (4)
C59—C60—C61—C56	-0.9 (7)	C7—C6—C11—C10	2.0 (6)
C59—C60—C61—N7	-176.7 (4)	C5—C6—C11—C10	-176.6 (4)
C57—C56—C61—C60	2.1 (6)	C7—C6—C11—N2	176.4 (4)
C55—C56—C61—C60	-179.6 (4)	C5—C6—C11—N2	-2.2 (6)
C57—C56—C61—N7	178.0 (4)	C17—C12—C13—C14	0.9 (6)
C55—C56—C61—N7	-3.7 (6)	S1—C12—C13—C14	-178.4 (3)
C67—C62—C63—C64	0.0 (6)	C12—C13—C14—C15	-1.8 (7)
S2—C62—C63—C64	-177.7 (3)	C13—C14—C15—C16	0.4 (7)
C62—C63—C64—C65	0.6 (7)	C14—C15—C16—C17	1.7 (7)
C63—C64—C65—C66	-1.6 (7)	C15—C16—C17—C12	-2.6 (7)
C64—C65—C66—C67	1.9 (7)	C15—C16—C17—N3	179.6 (4)
C65—C66—C67—C62	-1.3 (7)	C13—C12—C17—C16	1.3 (6)
C65—C66—C67—N8	-179.2 (4)	S1—C12—C17—C16	-179.4 (4)
C63—C62—C67—C66	0.3 (6)	C13—C12—C17—N3	178.9 (4)
S2—C62—C67—C66	177.8 (3)	S1—C12—C17—N3	-1.9 (6)
C63—C62—C67—N8	178.1 (4)	C26—C21—C22—C23	2.5 (6)
S2—C62—C67—N8	-4.4 (6)	N4—C21—C22—C23	-177.8 (4)
C76—C71—C72—C73	3.8 (6)	C21—C22—C23—C24	-1.2 (7)
N9—C71—C72—C73	-179.7 (4)	C22—C23—C24—C25	-1.1 (7)
C71—C72—C73—C74	-1.5 (7)	C22—C23—C24—Ni1	176.3 (3)
C72—C73—C74—C75	-1.8 (7)	C23—C24—C25—C26	2.1 (6)
C72—C73—C74—Ni2	178.0 (4)	Ni1—C24—C25—C26	-175.1 (3)
C73—C74—C75—C76	2.7 (6)	C24—C25—C26—C21	-0.8 (6)
Ni2—C74—C75—C76	-177.0 (3)	C24—C25—C26—C27	178.9 (4)
C74—C75—C76—C71	-0.4 (6)	C22—C21—C26—C25	-1.6 (6)
C74—C75—C76—C77	-178.2 (4)	N4—C21—C26—C25	178.6 (4)
C72—C71—C76—C75	-3.0 (6)	C22—C21—C26—C27	178.7 (4)
N9—C71—C76—C75	179.8 (4)	N4—C21—C26—C27	-1.1 (4)

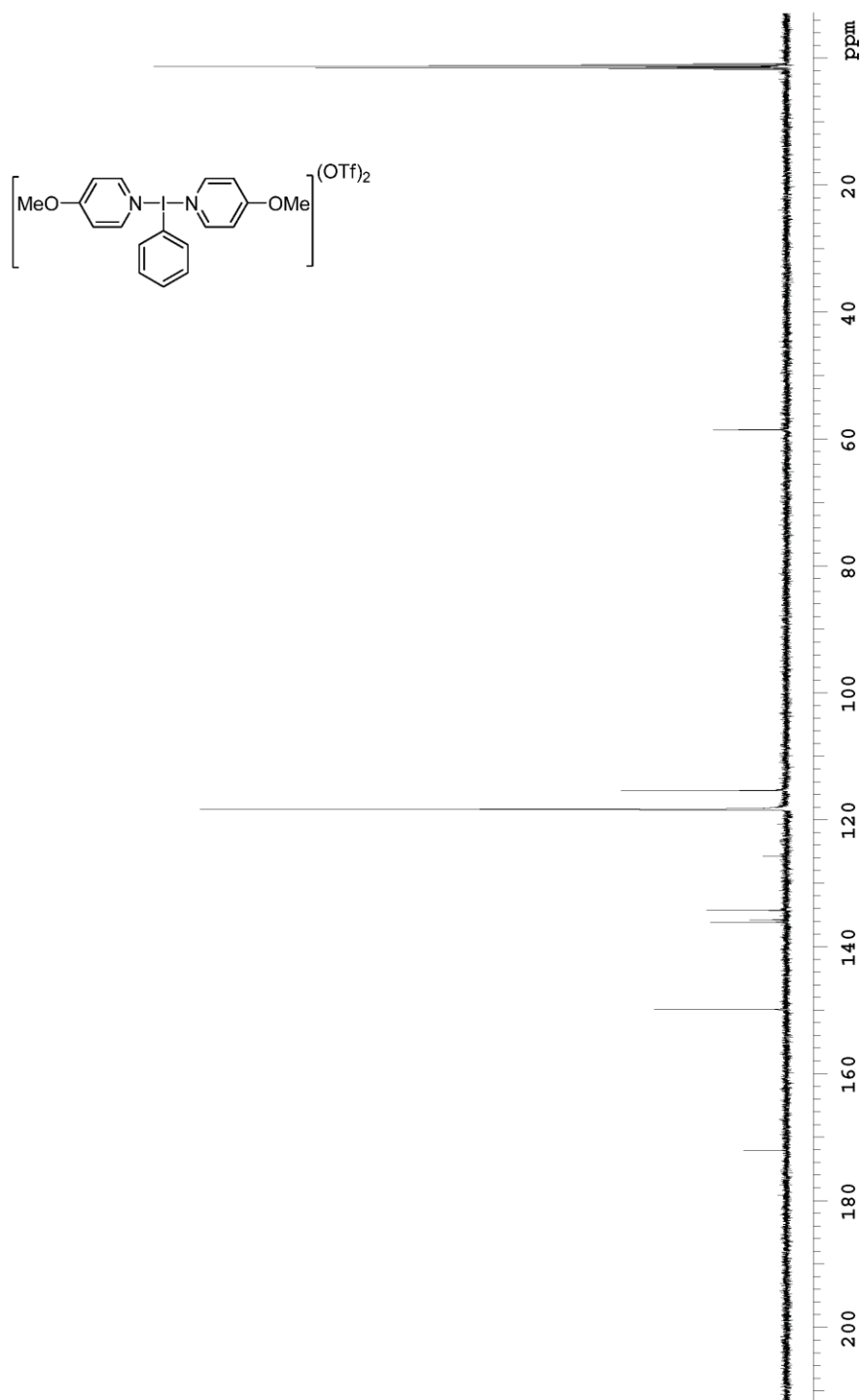
C72—C71—C76—C77	175.3 (4)	C25—C26—C27—C28	-179.6 (4)
N9—C71—C76—C77	-2.0 (4)	C21—C26—C27—C28	0.1 (5)
C75—C76—C77—C78	179.4 (4)	C26—C27—C28—N4	1.0 (5)
C71—C76—C77—C78	1.5 (5)	N5—C41—C42—C43	0.9 (7)
C76—C77—C78—N9	-0.4 (5)	C41—C42—C43—C44	-1.7 (7)
N10—C91—C92—C93	0.8 (7)	C42—C43—C44—C45	1.2 (7)
C91—C92—C93—C94	1.2 (8)	C43—C44—C45—N5	0.3 (7)
C92—C93—C94—C95	-1.8 (7)	C4—C5—N1—C1	-2.1 (6)
C93—C94—C95—N10	0.5 (7)	C6—C5—N1—C1	175.9 (4)
C52—C51—N6—C55	2.9 (7)	C4—C5—N1—Ni1	171.7 (3)
C52—C51—N6—Ni2	-170.8 (4)	C6—C5—N1—Ni1	-10.2 (5)
C54—C55—N6—C51	-2.7 (6)	C2—C1—N1—C5	2.1 (6)
C56—C55—N6—C51	176.8 (4)	C2—C1—N1—Ni1	-171.9 (3)
C54—C55—N6—Ni2	170.9 (3)	C10—C11—N2—S1	-81.1 (5)
C56—C55—N6—Ni2	-9.7 (5)	C6—C11—N2—S1	104.6 (4)
C60—C61—N7—S2	-77.2 (5)	C10—C11—N2—Ni1	121.9 (4)
C56—C61—N7—S2	106.9 (4)	C6—C11—N2—Ni1	-52.4 (4)
C60—C61—N7—Ni2	124.4 (4)	C16—C17—N3—O3	-118.6 (5)
C56—C61—N7—Ni2	-51.4 (4)	C12—C17—N3—O3	63.7 (6)
C66—C67—N8—O9	-115.6 (5)	C16—C17—N3—O4	58.5 (5)
C62—C67—N8—O9	66.5 (6)	C12—C17—N3—O4	-119.2 (5)
C66—C67—N8—O10	62.4 (5)	O6—C29—N4—C28	3.3 (7)
C62—C67—N8—O10	-115.6 (5)	O5—C29—N4—C28	-177.0 (4)
O12—C79—N9—C78	0.5 (6)	O6—C29—N4—C21	-170.6 (4)
O11—C79—N9—C78	-179.8 (4)	O5—C29—N4—C21	9.2 (6)
O12—C79—N9—C71	-176.3 (4)	C27—C28—N4—C29	-176.7 (4)
O11—C79—N9—C71	3.4 (6)	C27—C28—N4—C21	-1.7 (5)
C77—C78—N9—C79	-178.3 (4)	C22—C21—N4—C29	-3.5 (8)
C77—C78—N9—C71	-0.9 (5)	C26—C21—N4—C29	176.2 (4)

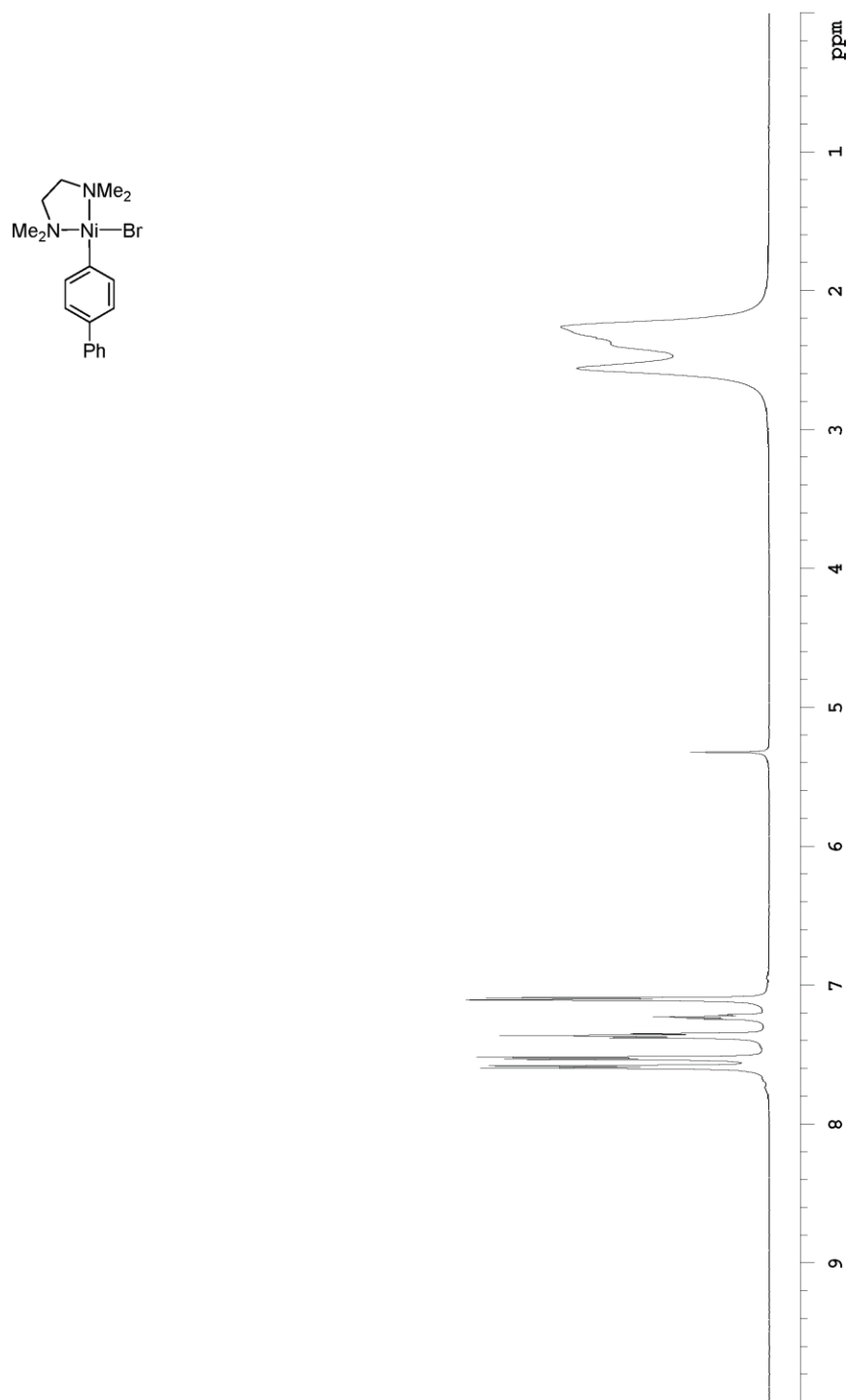
C72—C71—N9—C79	2.0 (7)	C22—C21—N4—C28	-178.0 (4)
C76—C71—N9—C79	178.9 (4)	C26—C21—N4—C28	1.7 (5)
C72—C71—N9—C78	-175.1 (4)	C44—C45—N5—C41	-1.1 (6)
C76—C71—N9—C78	1.8 (4)	C44—C45—N5—Ni1	-179.3 (3)
C94—C95—N10—C91	1.5 (6)	C42—C41—N5—C45	0.5 (6)
C94—C95—N10—Ni2	174.4 (3)	C42—C41—N5—Ni1	178.7 (3)
C92—C91—N10—C95	-2.2 (7)	O6—C29—O5—C30	0.7 (7)
C92—C91—N10—Ni2	-175.0 (4)	N4—C29—O5—C30	-179.0 (4)
O12—C79—O11—C80	8.2 (7)	C33—C30—O5—C29	-67.3 (6)
N9—C79—O11—C80	-171.5 (3)	C32—C30—O5—C29	174.3 (4)
C82—C80—O11—C79	56.7 (5)	C31—C30—O5—C29	54.2 (6)
C83—C80—O11—C79	-67.8 (5)	C11—N2—S1—O2	35.0 (4)
C81—C80—O11—C79	173.4 (4)	Ni1—N2—S1—O2	-173.4 (2)
C61—N7—S2—O7	171.8 (3)	C11—N2—S1—O1	167.3 (3)
Ni2—N7—S2—O7	-35.0 (3)	Ni1—N2—S1—O1	-41.1 (3)
C61—N7—S2—O8	39.4 (4)	C11—N2—S1—C12	-78.5 (3)
Ni2—N7—S2—O8	-167.4 (2)	Ni1—N2—S1—C12	73.1 (3)
C61—N7—S2—C62	-73.8 (3)	C13—C12—S1—O2	-28.6 (4)
Ni2—N7—S2—C62	79.4 (3)	C17—C12—S1—O2	152.2 (4)
C67—C62—S2—O7	25.5 (4)	C13—C12—S1—O1	-154.0 (3)
C63—C62—S2—O7	-157.0 (3)	C17—C12—S1—O1	26.7 (4)
C67—C62—S2—O8	150.9 (4)	C13—C12—S1—N2	90.4 (4)
C63—C62—S2—O8	-31.6 (4)	C17—C12—S1—N2	-88.8 (4)
C67—C62—S2—N7	-90.2 (4)	C45—N5—Ni1—C24	-92.6 (4)
C63—C62—S2—N7	87.3 (4)	C41—N5—Ni1—C24	89.2 (3)
C95—N10—Ni2—C74	91.6 (3)	C45—N5—Ni1—N2	73.4 (3)
C91—N10—Ni2—C74	-95.7 (4)	C41—N5—Ni1—N2	-104.8 (3)
C95—N10—Ni2—N7	-100.8 (3)	C25—C24—Ni1—N5	-58.4 (4)
C91—N10—Ni2—N7	71.9 (3)	C23—C24—Ni1—N5	124.4 (3)

C75—C74—Ni2—N10	-51.7 (4)	C25—C24—Ni1—N1	115.7 (4)
C73—C74—Ni2—N10	128.6 (4)	C23—C24—Ni1—N1	-61.5 (3)
C75—C74—Ni2—N6	124.0 (4)	C25—C24—Ni1—N2	-155.7 (5)
C73—C74—Ni2—N6	-55.7 (4)	C23—C24—Ni1—N2	27.0 (9)
C75—C74—Ni2—N7	-143.9 (6)	C5—N1—Ni1—C24	132.1 (3)
C73—C74—Ni2—N7	36.3 (10)	C1—N1—Ni1—C24	-54.0 (3)
C51—N6—Ni2—C74	-53.0 (3)	C5—N1—Ni1—N2	-33.7 (3)
C55—N6—Ni2—C74	133.6 (4)	C1—N1—Ni1—N2	140.1 (3)
C51—N6—Ni2—N7	139.4 (3)	C11—N2—Ni1—N5	-124.1 (3)
C55—N6—Ni2—N7	-34.0 (3)	S1—N2—Ni1—N5	82.0 (3)
C61—N7—Ni2—N10	-122.6 (3)	C11—N2—Ni1—C24	-26.9 (8)
S2—N7—Ni2—N10	82.4 (3)	S1—N2—Ni1—C24	179.2 (6)
C61—N7—Ni2—C74	-30.2 (9)	C11—N2—Ni1—N1	61.7 (3)
S2—N7—Ni2—C74	174.8 (6)	S1—N2—Ni1—N1	-92.2 (3)

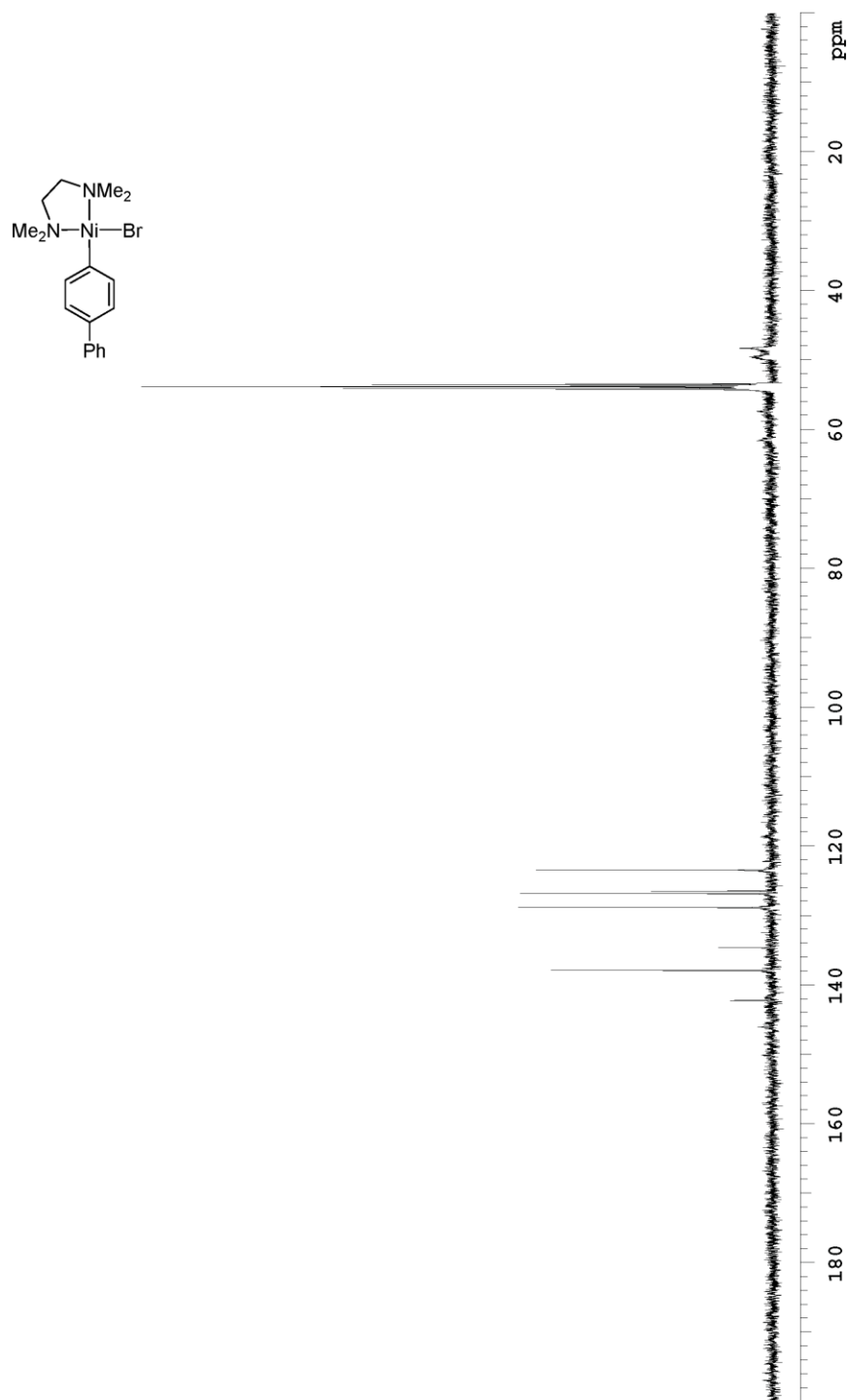
Spectroscopic Data

¹H NMR (CD₃CN, 23 °C) of **6**

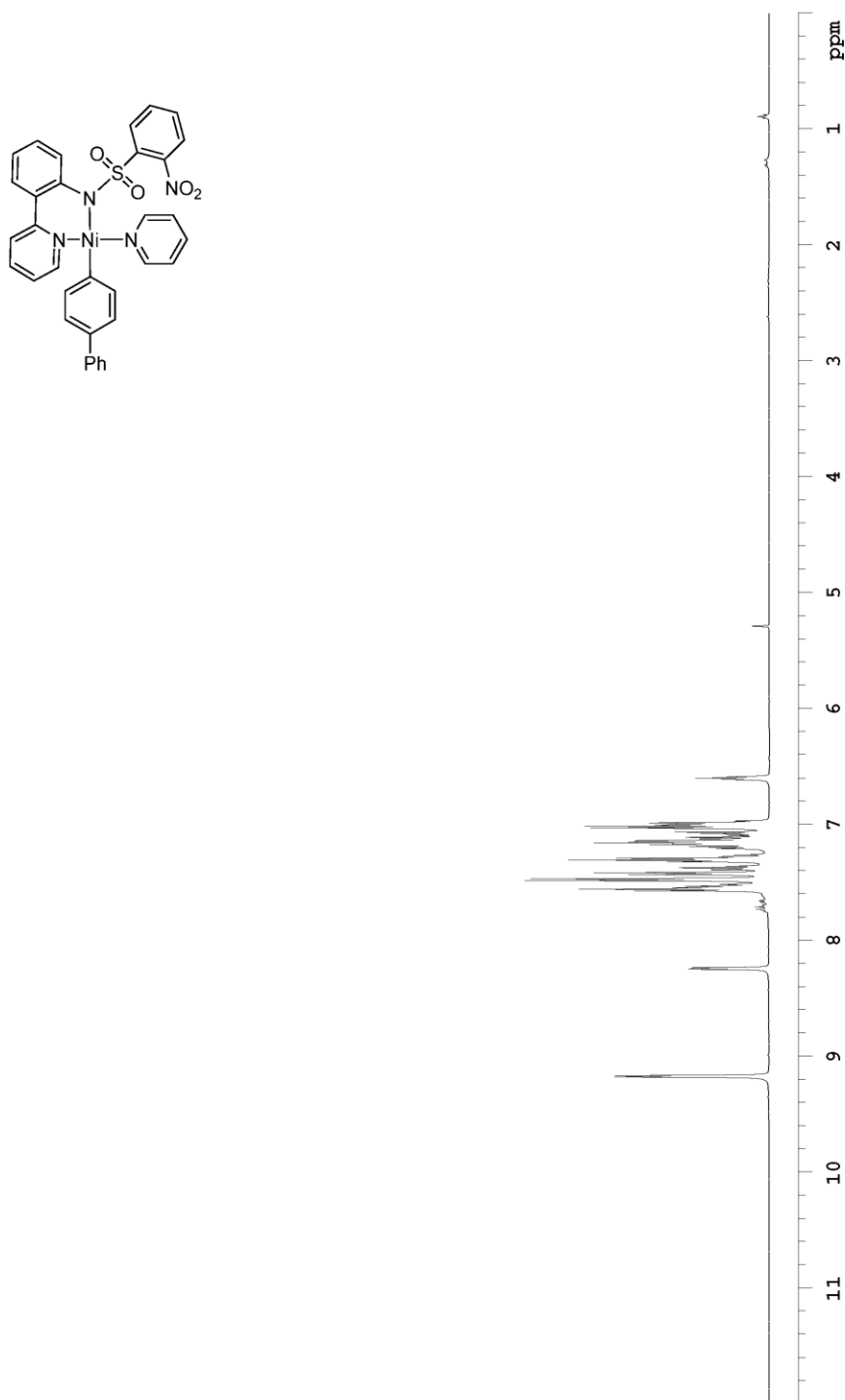
 ^{13}C NMR (CD_3CN , $23\text{ }^\circ\text{C}$) of **6**

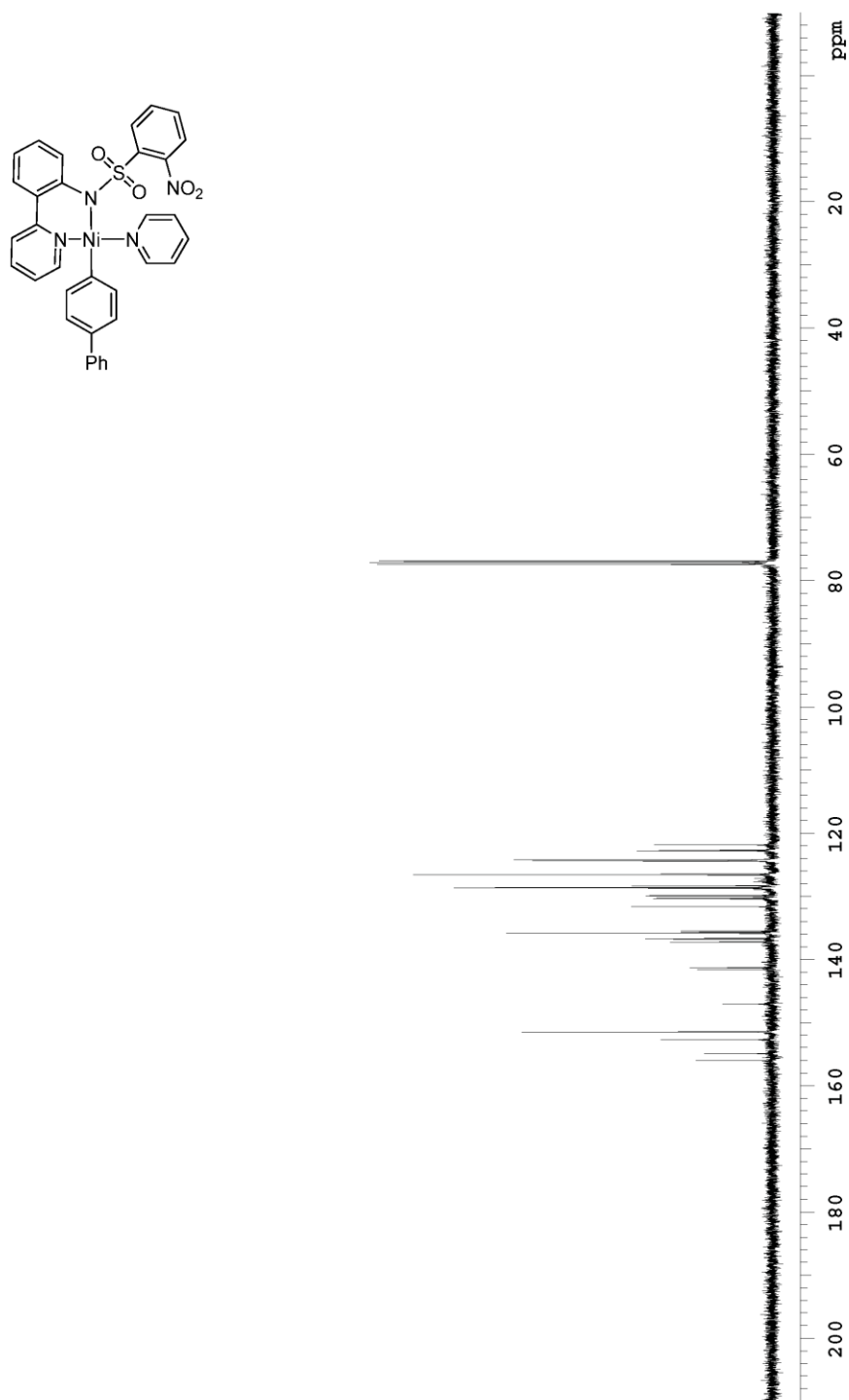


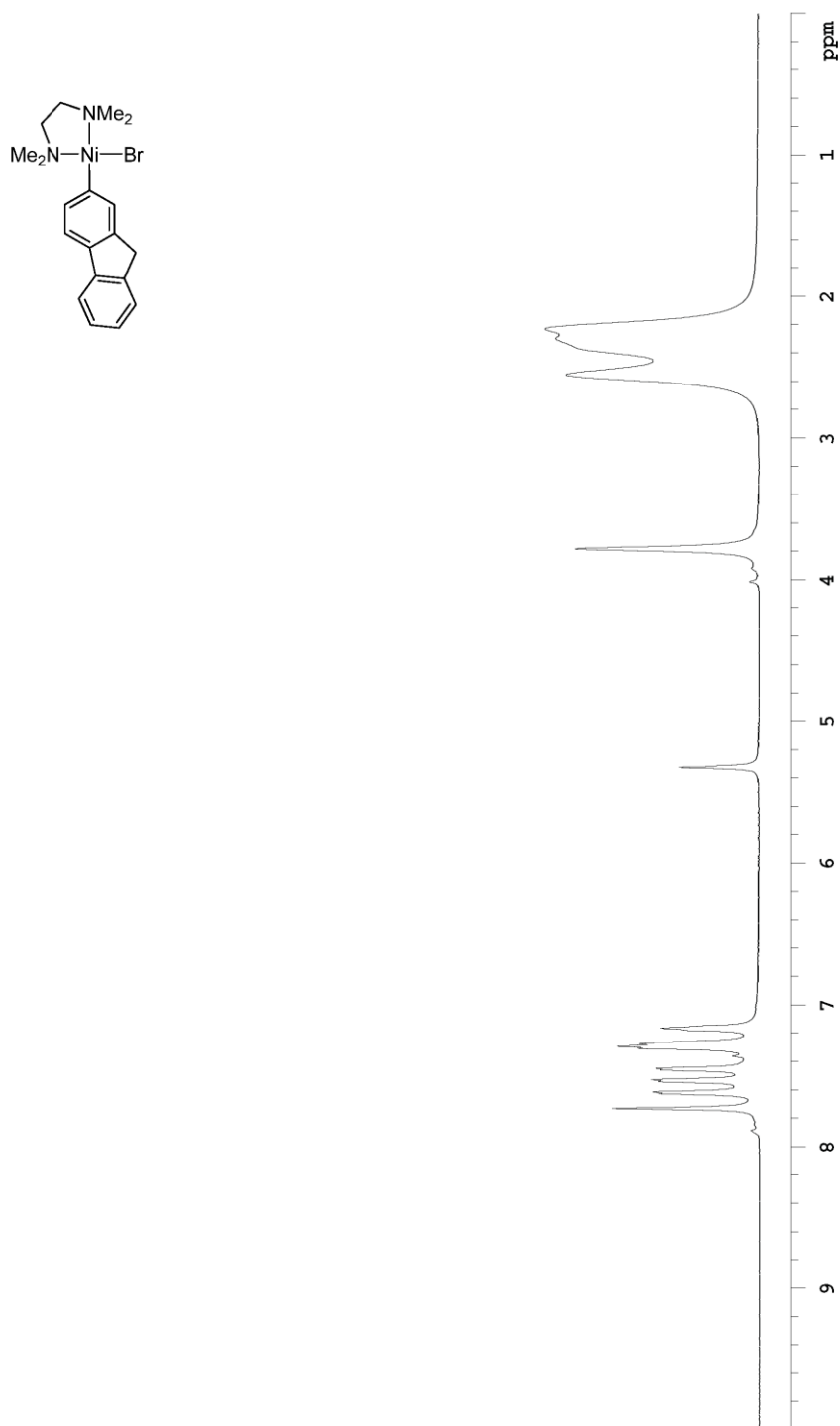
^1H NMR (CD₂Cl₂, 23 °C) of **7a**

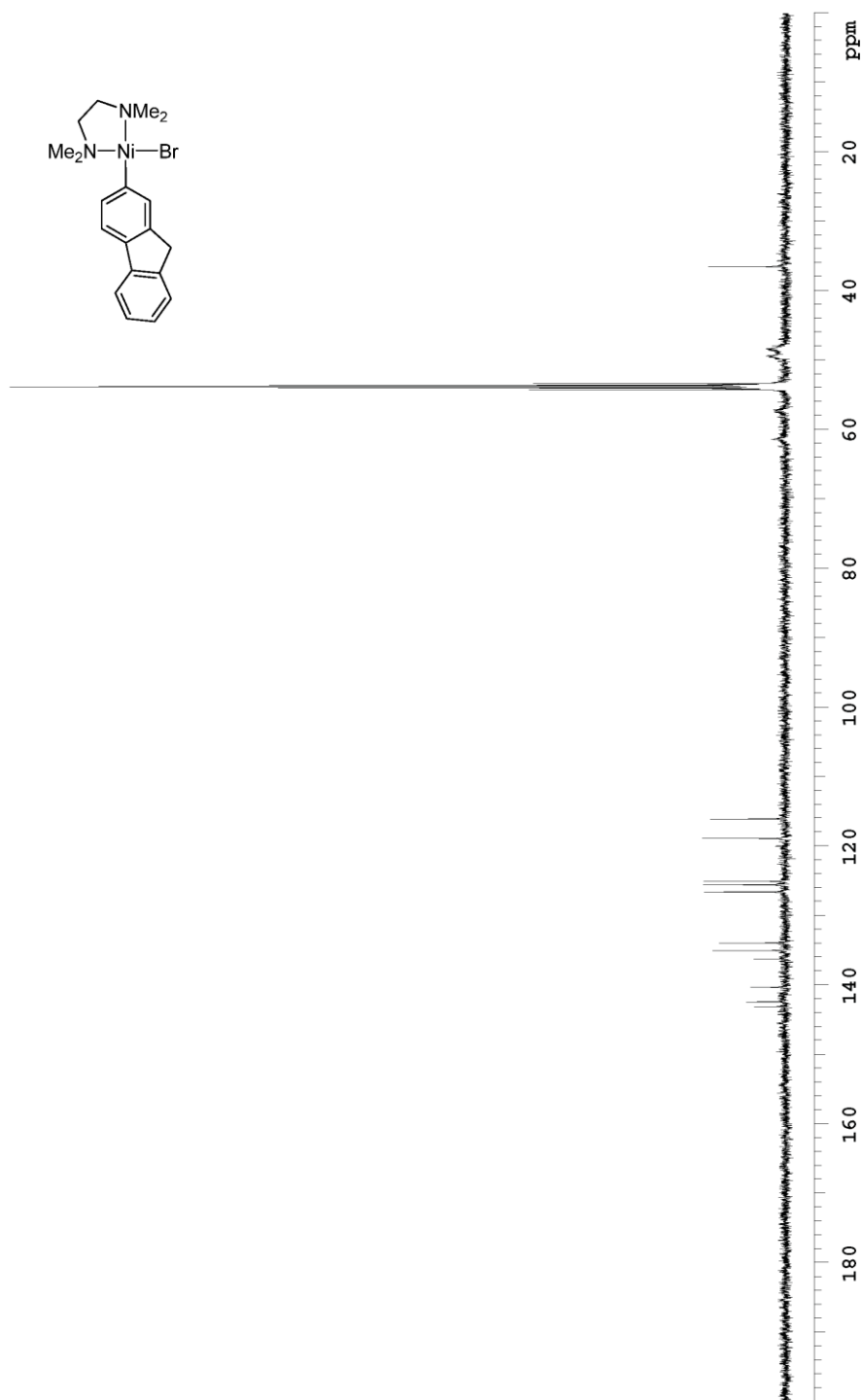


^{13}C NMR (CD₂Cl₂, 23 °C) of **7a**

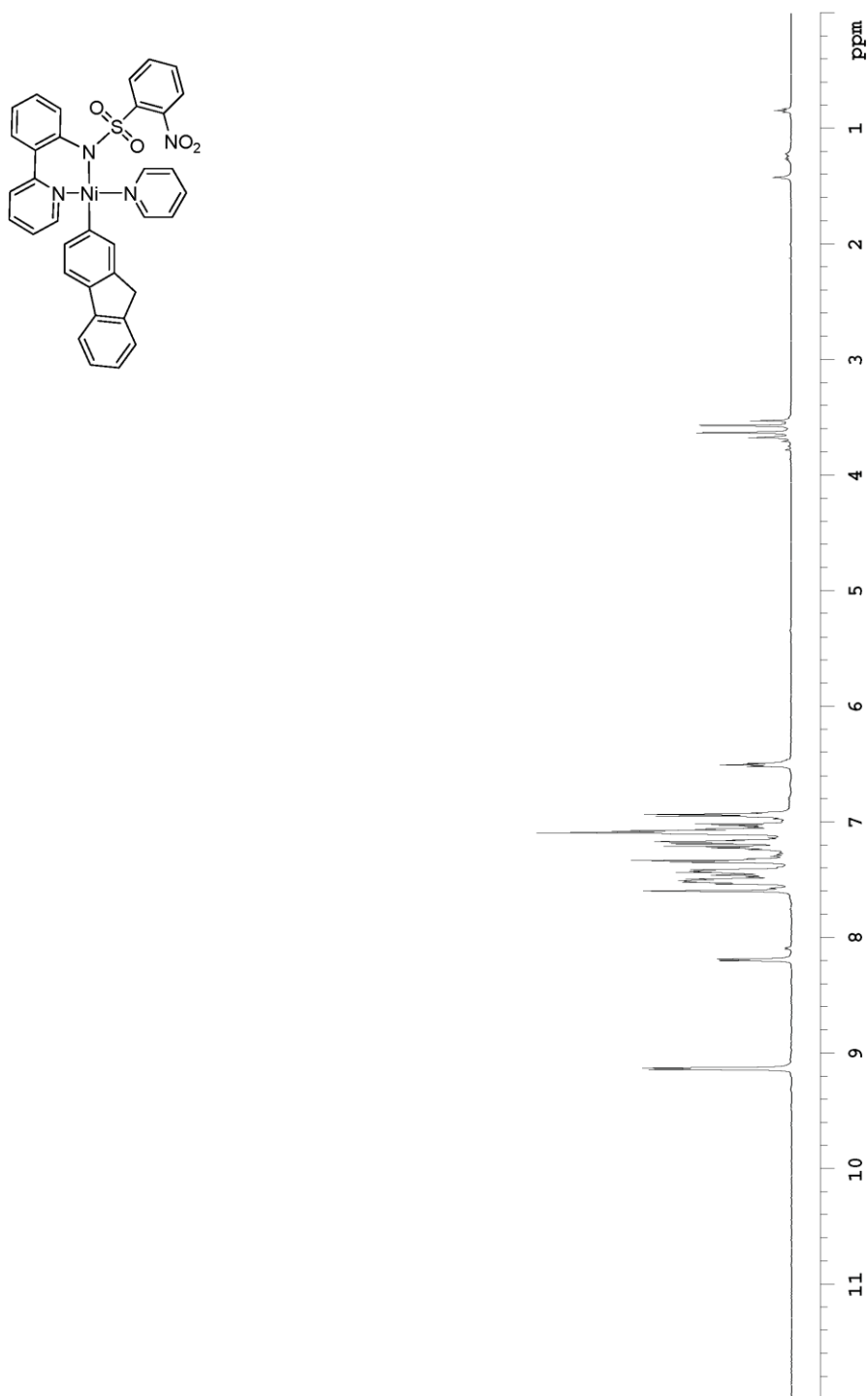
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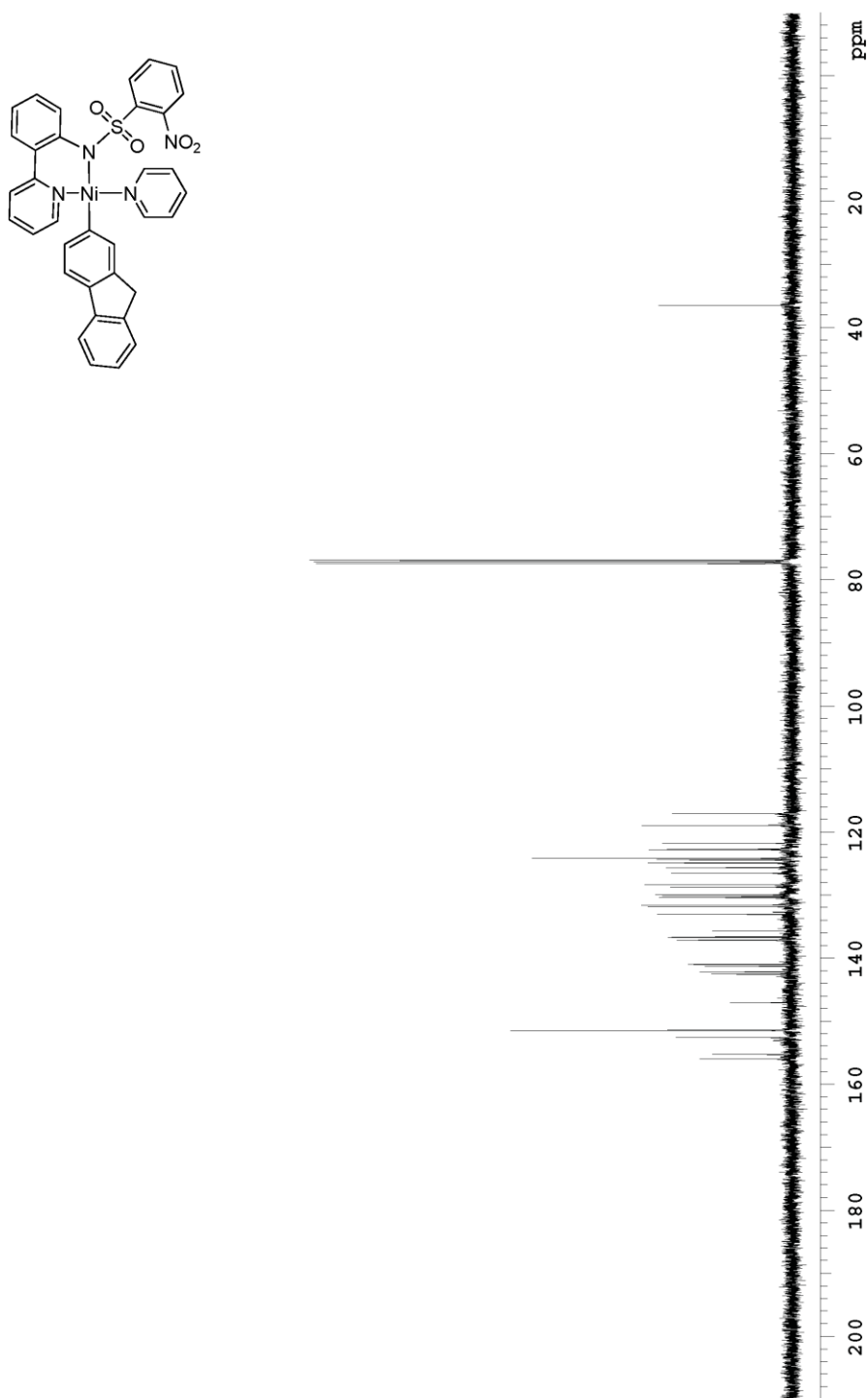
 ^1H NMR (CDCl₃, 23 °C) of **1a**

 ^1H NMR (CD₂Cl₂, 23 °C) of **7b**

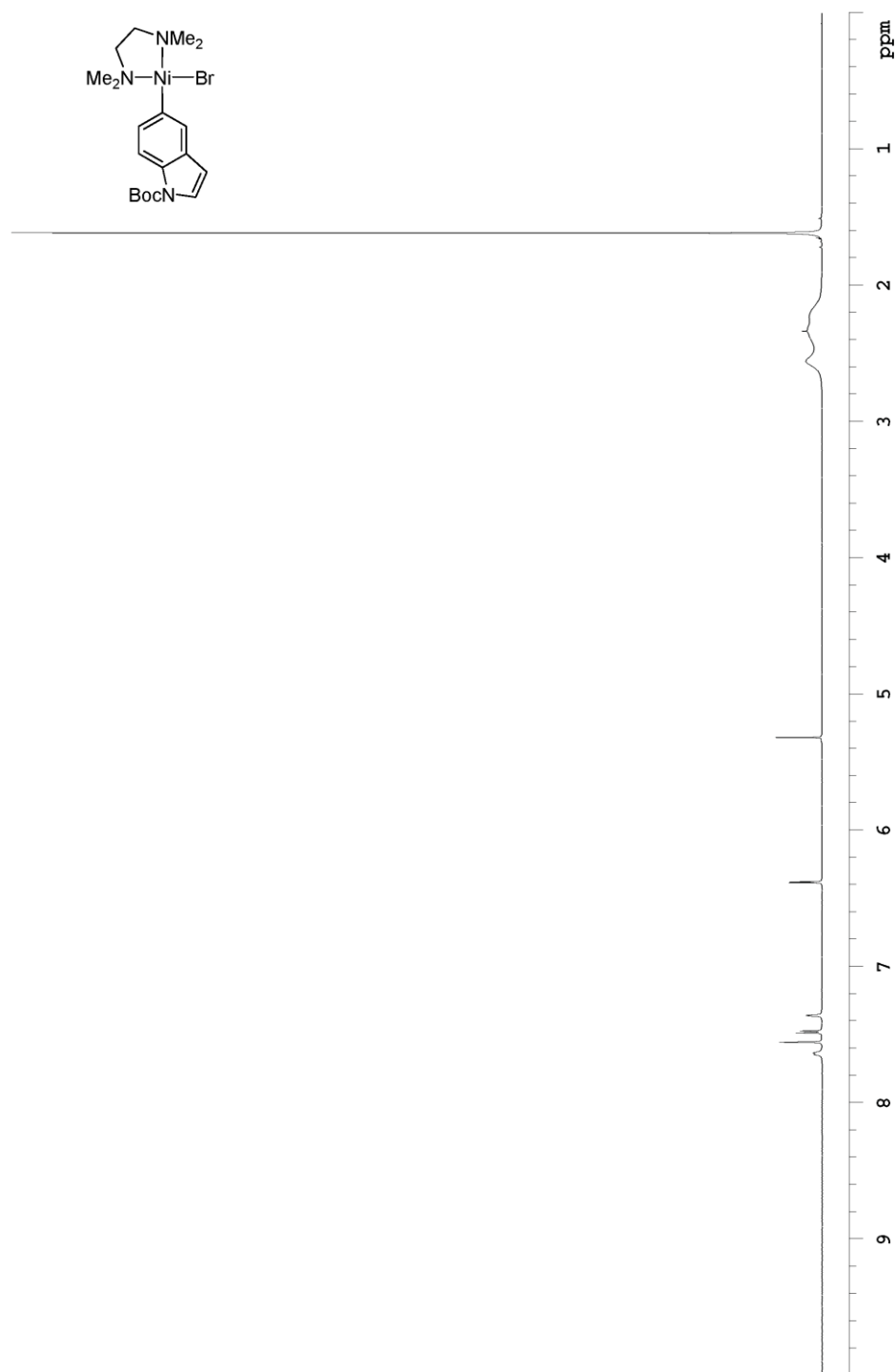


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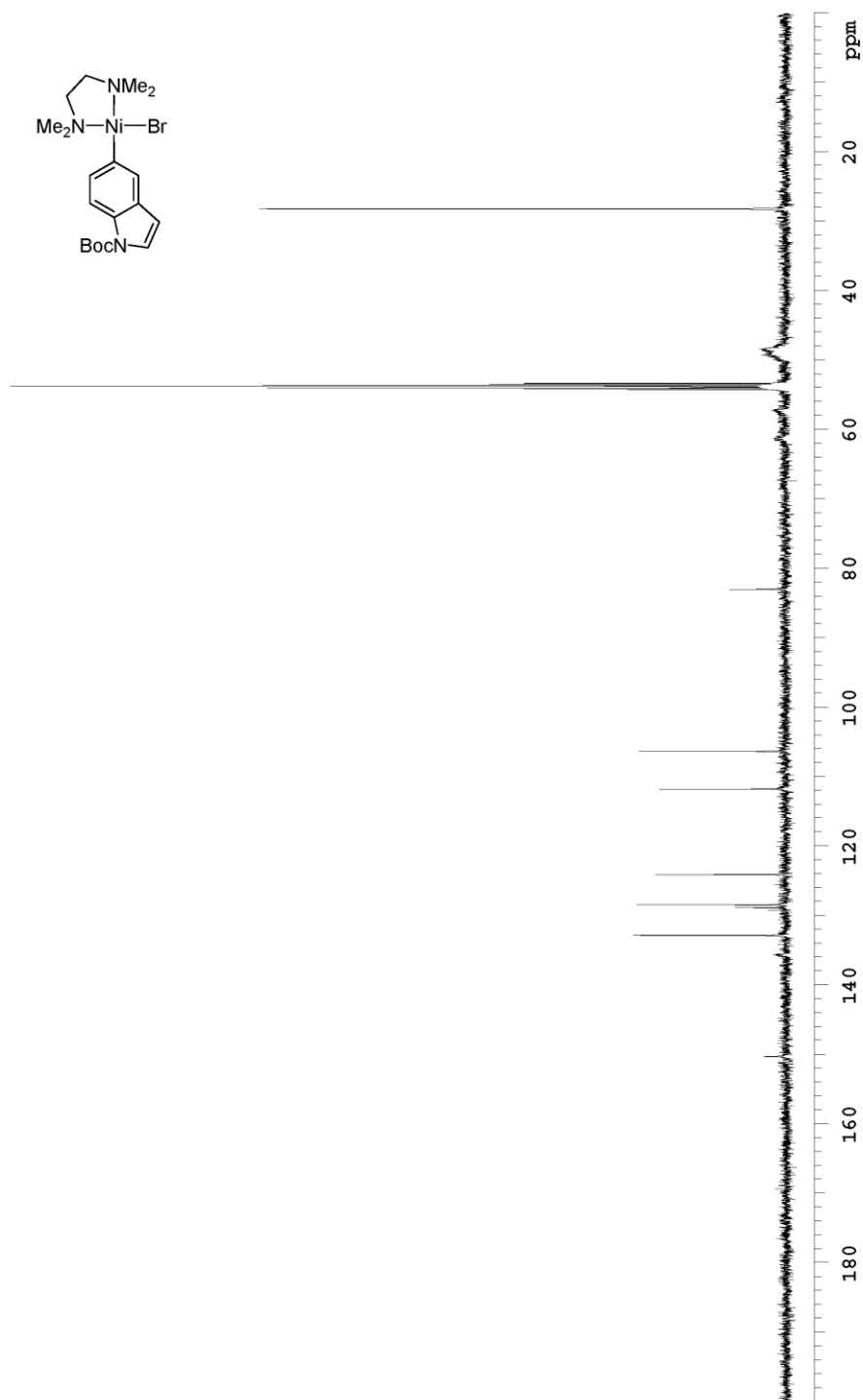
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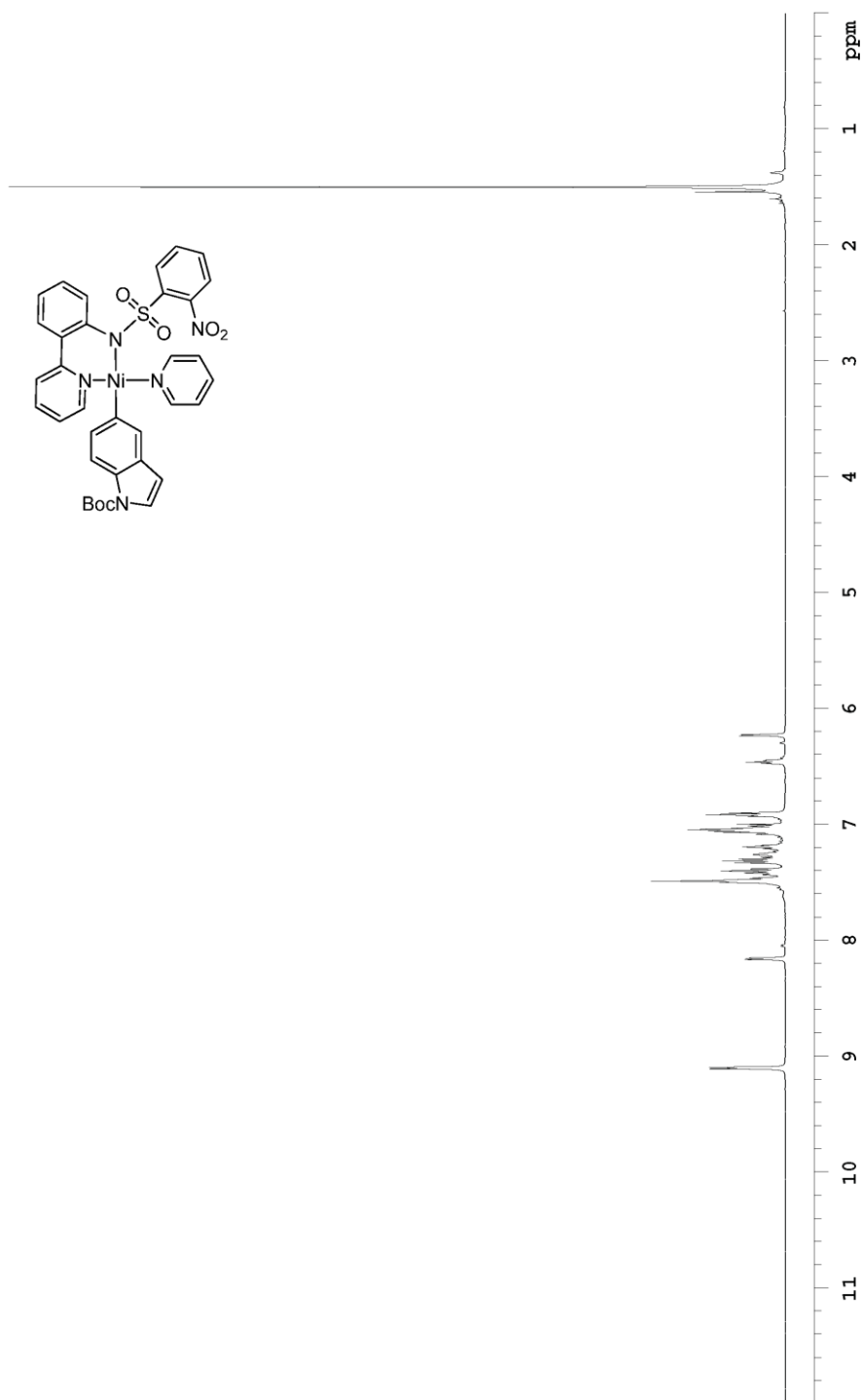
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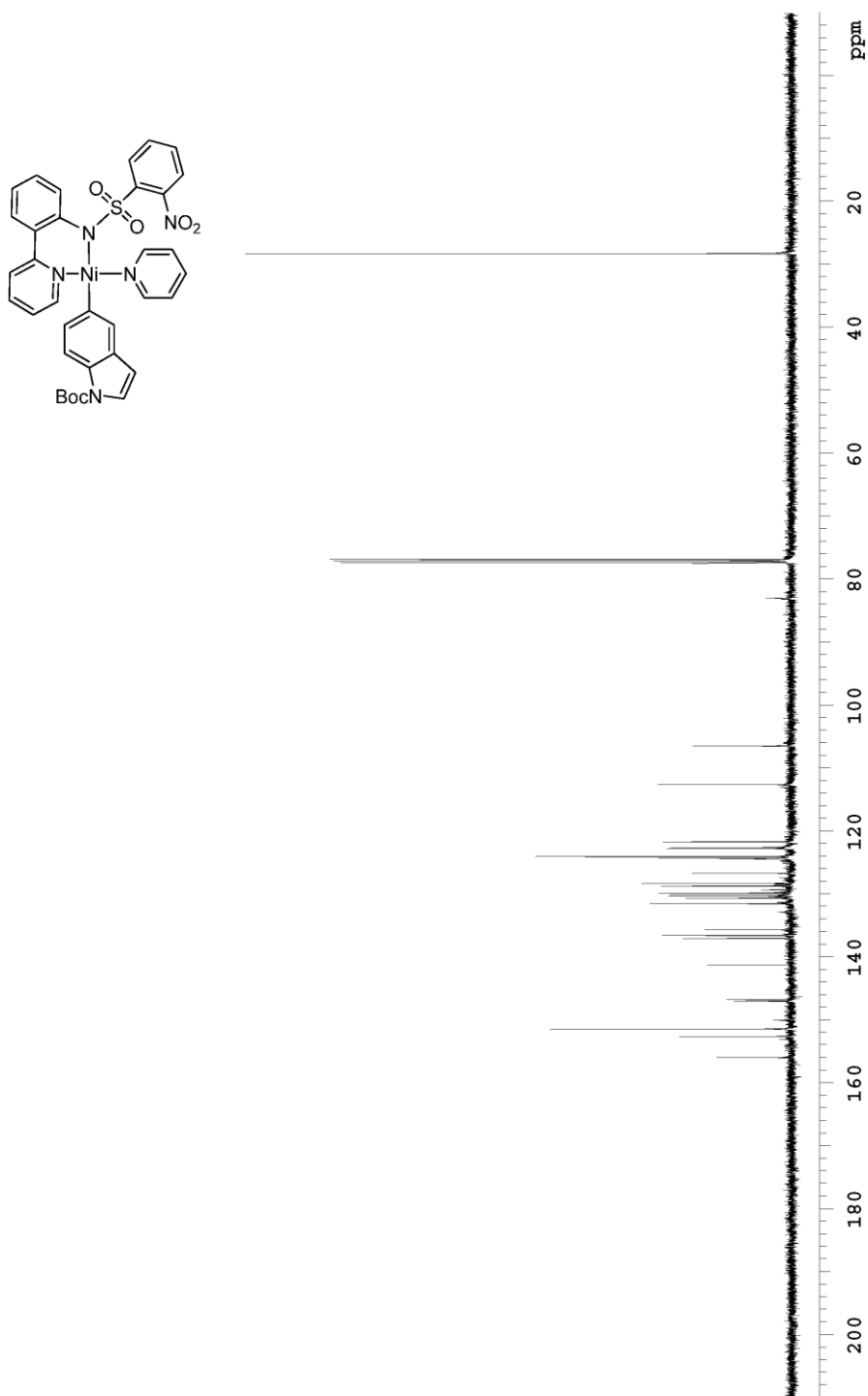
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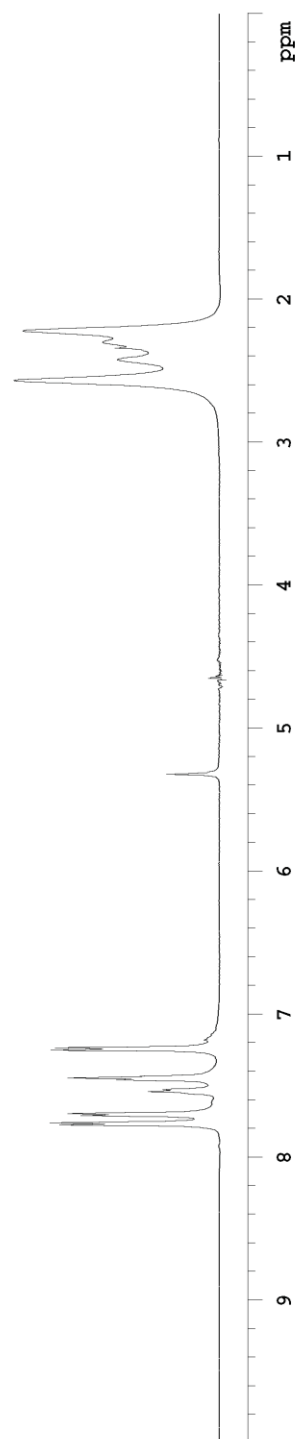
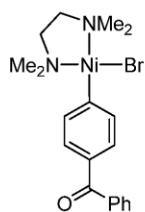


^{13}C NMR (CD₂Cl₂, 23 °C) of 7c

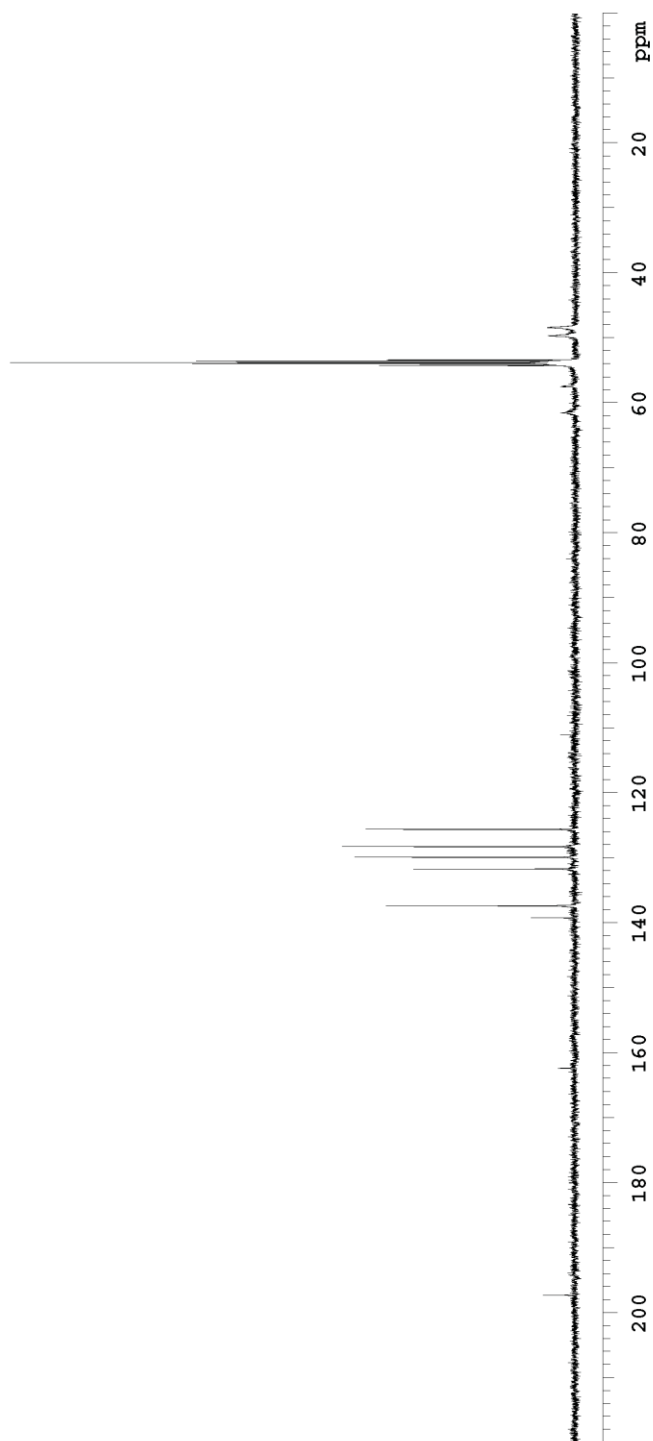
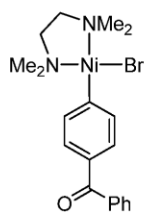


^1H NMR (CDCl_3 , 23 °C) of **1c**

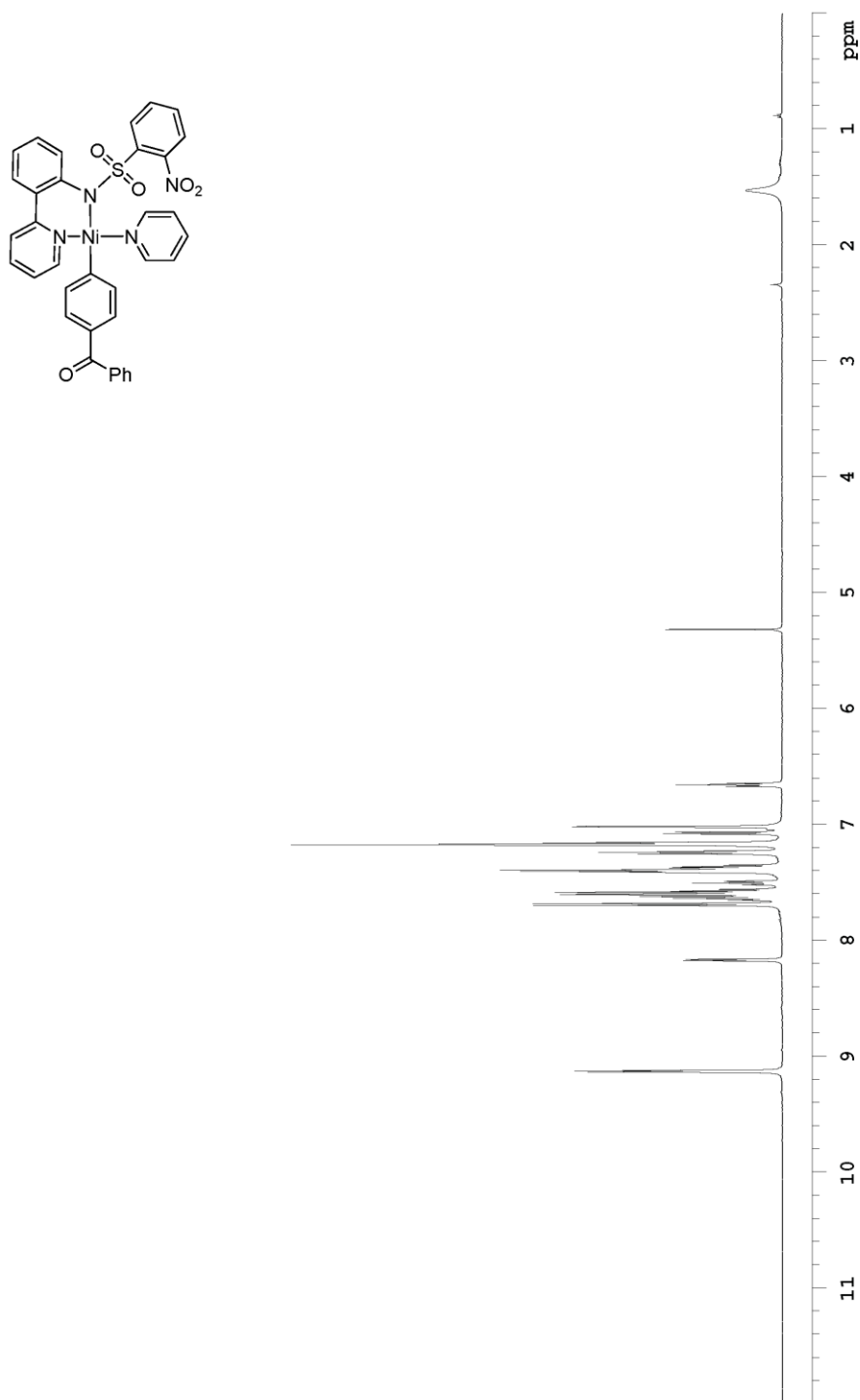
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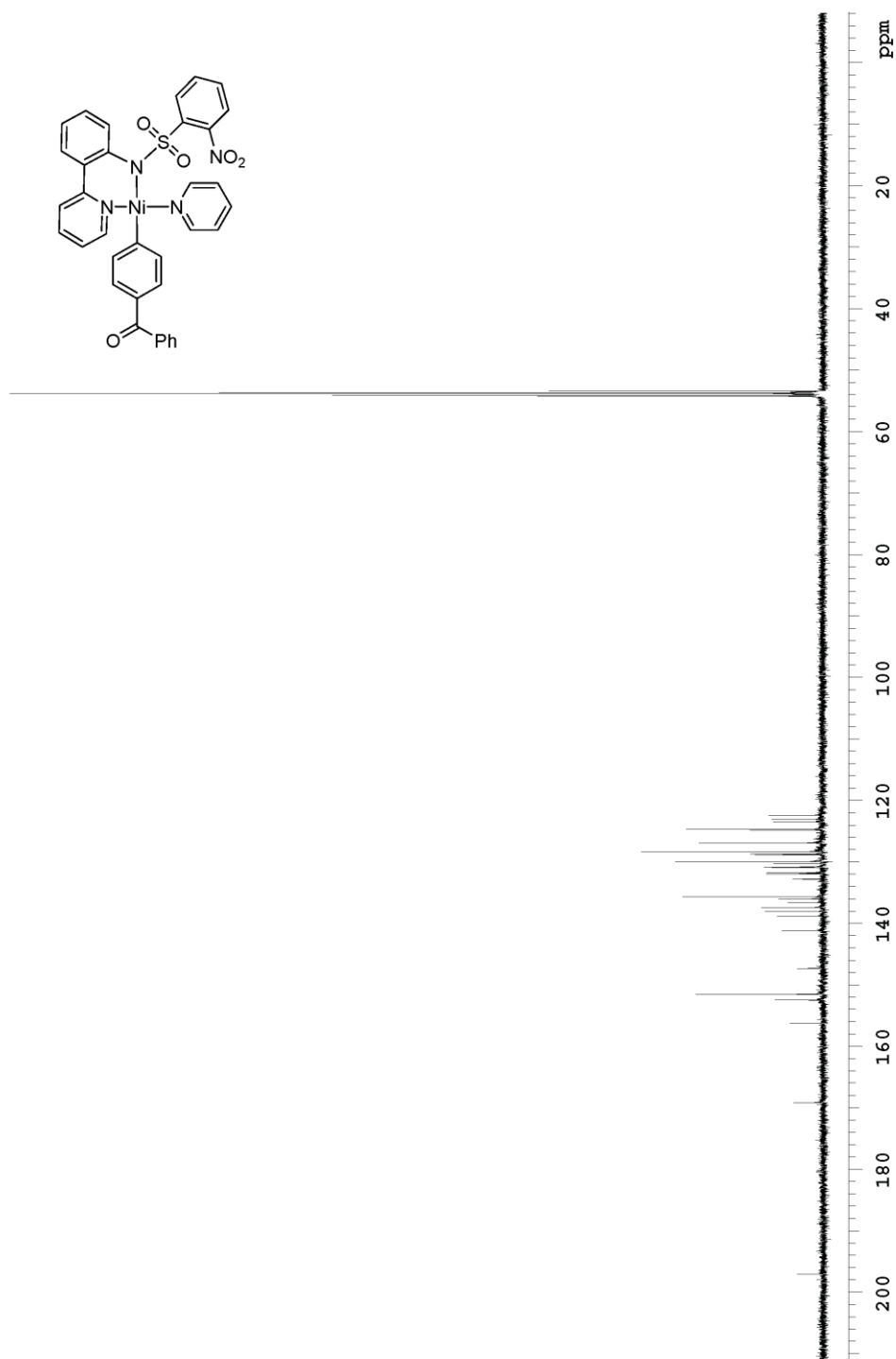
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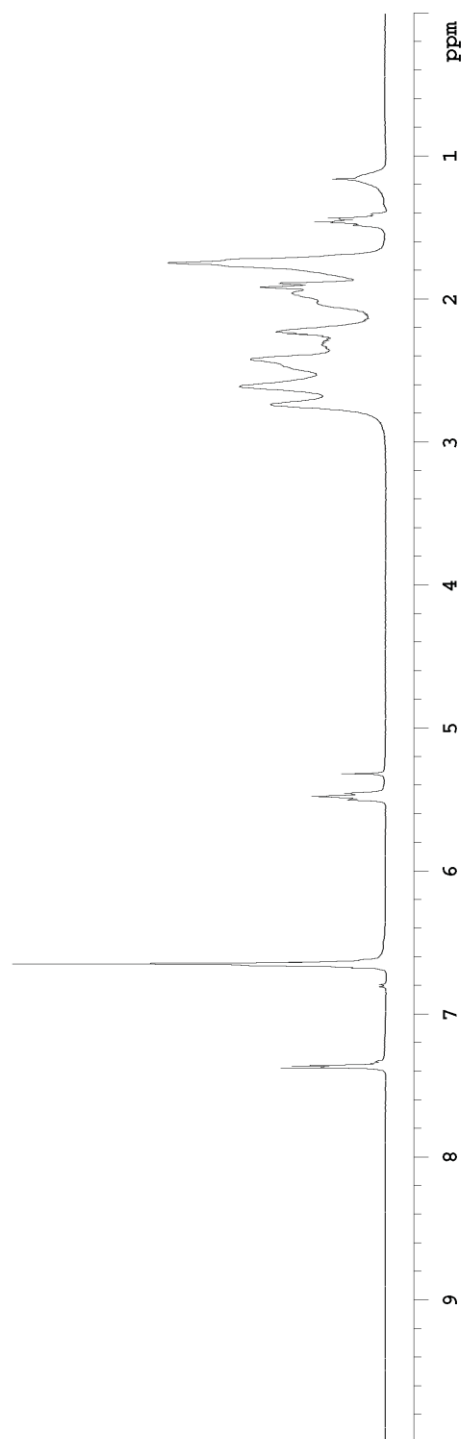
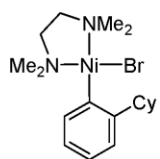


^{13}C NMR (CD_2Cl_2 , 23 °C) of **7d**

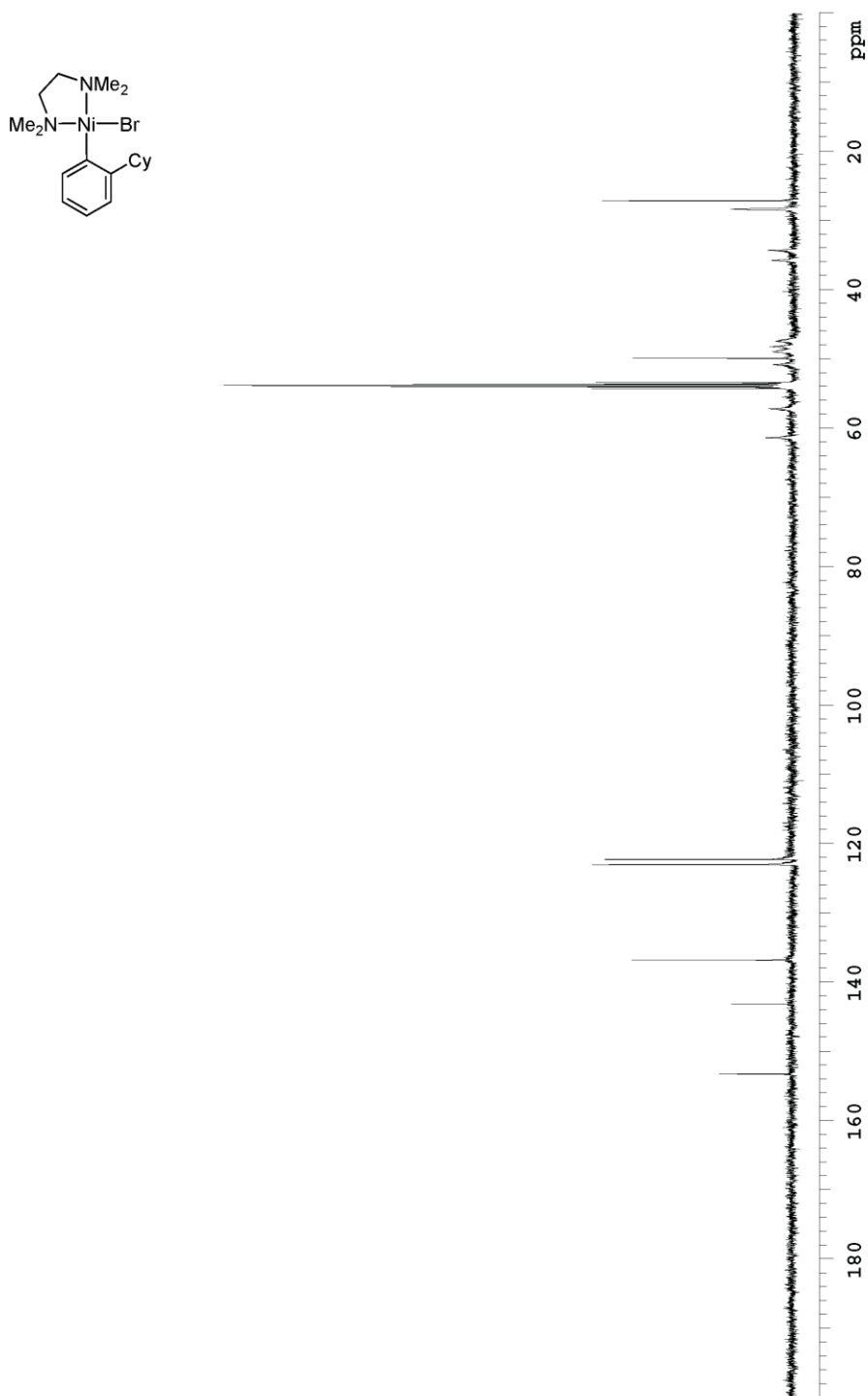


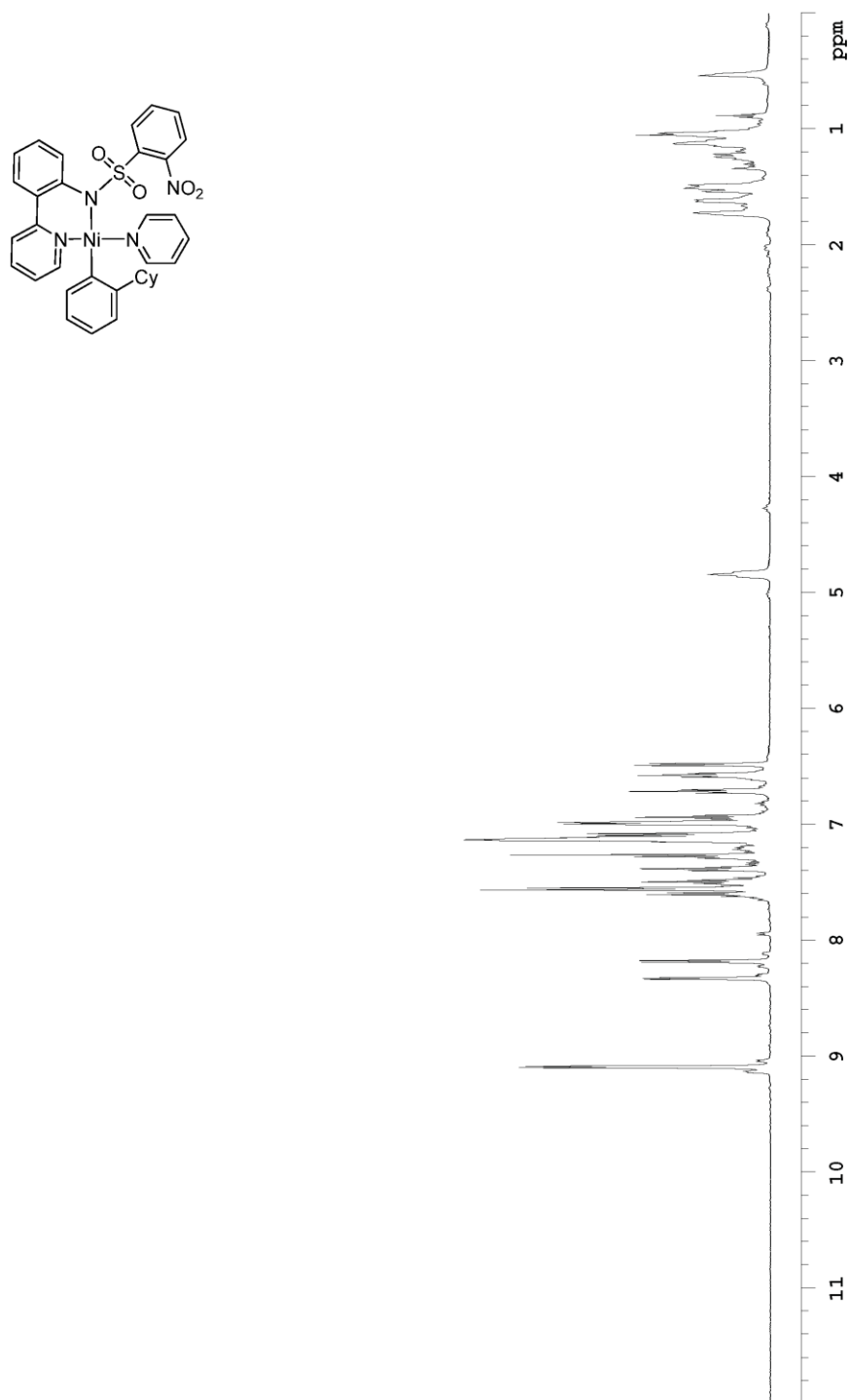
¹H NMR (CDCl₃, 23 °C) of **1d**

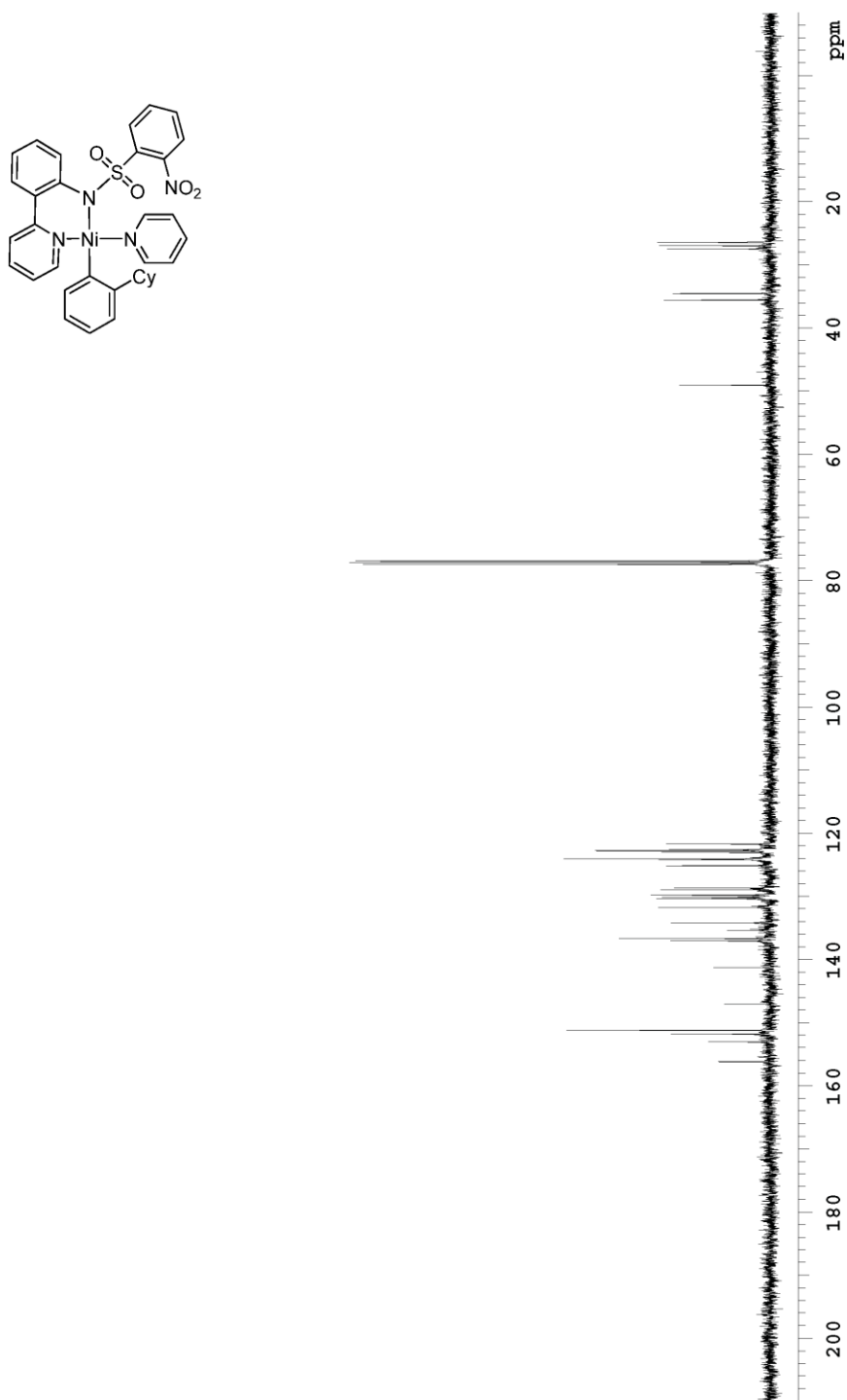
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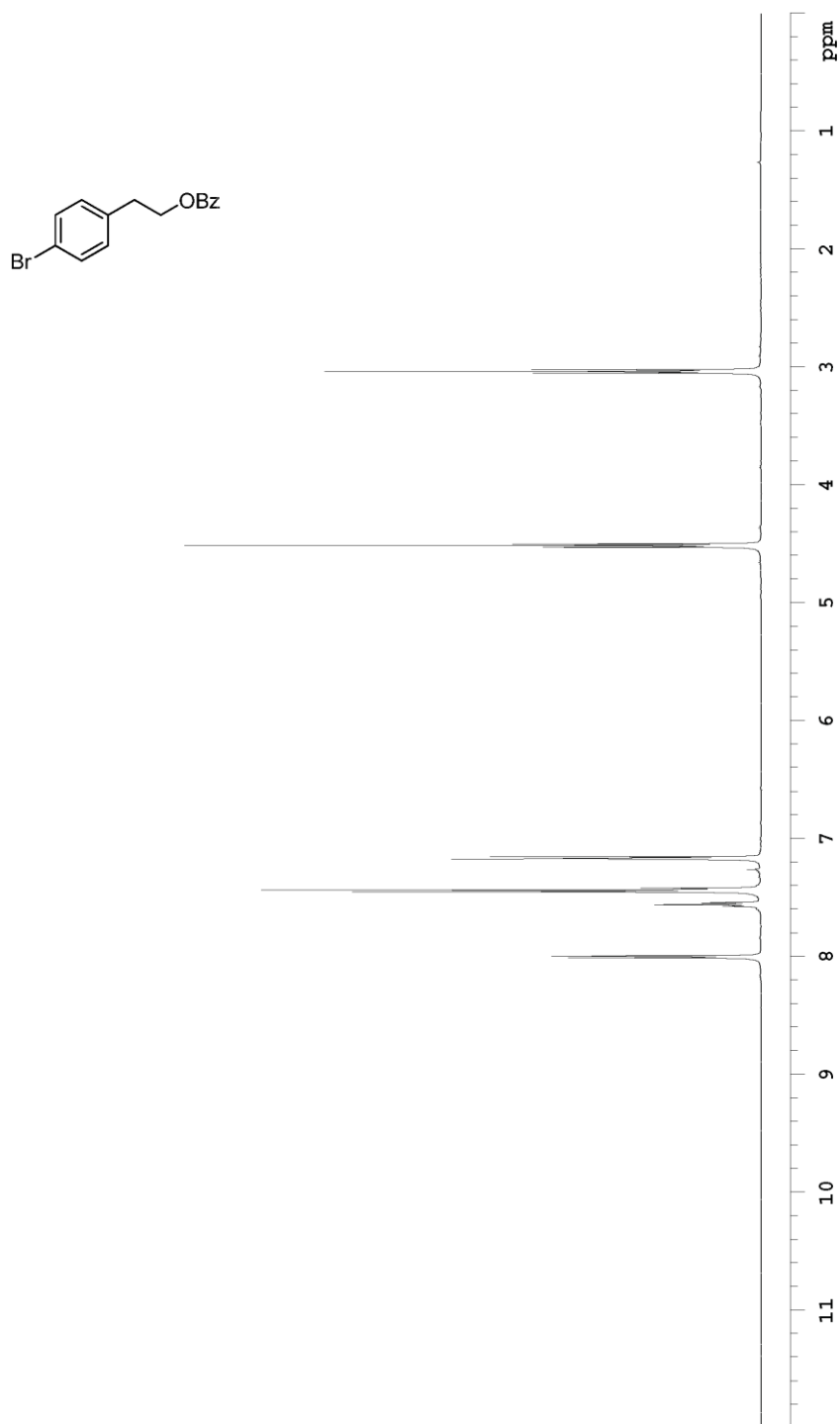
^1H NMR (CD_2Cl_2 , 23 °C) of **7e**

 ^{13}C NMR (CD_2Cl_2 , 23 °C) of **7e**

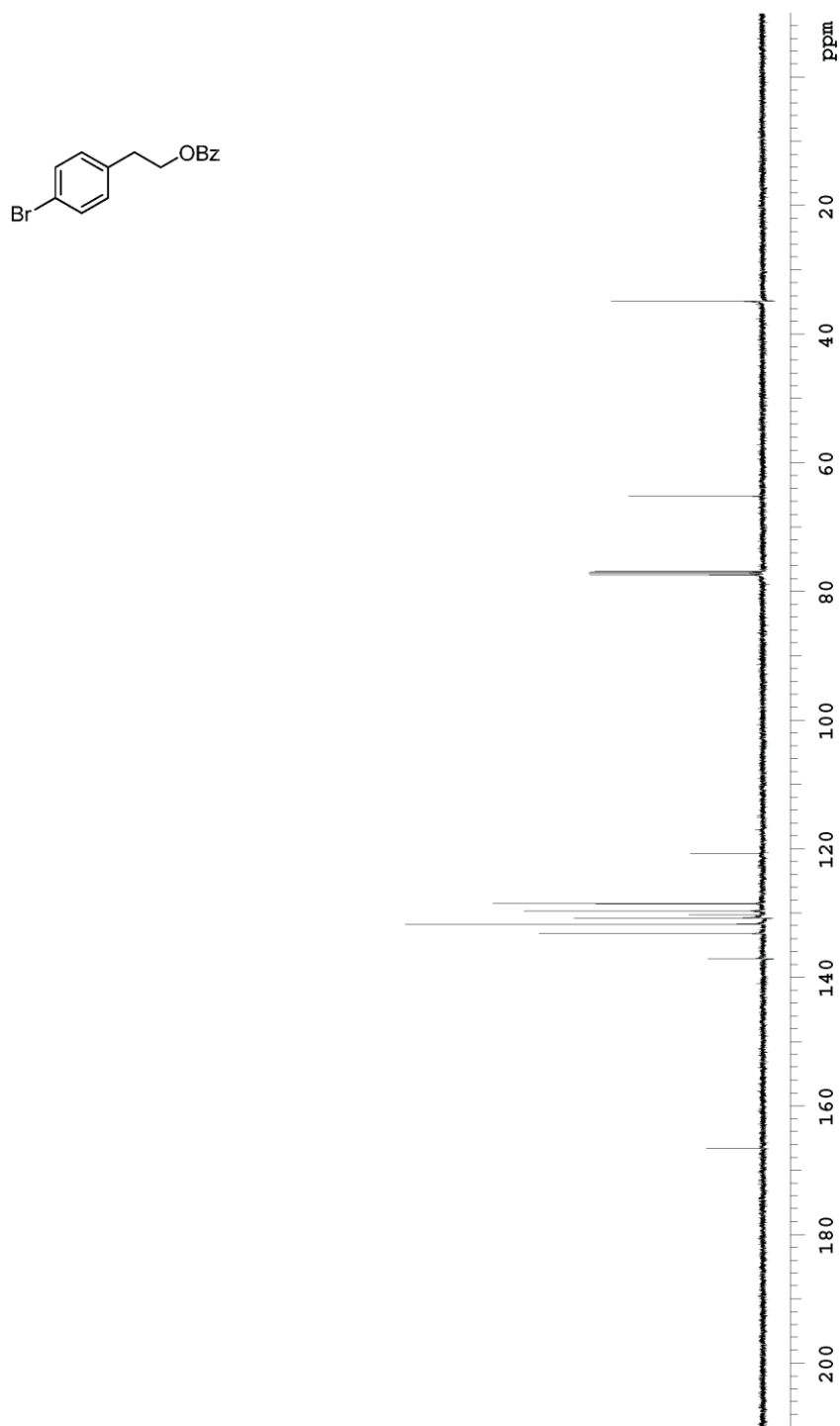
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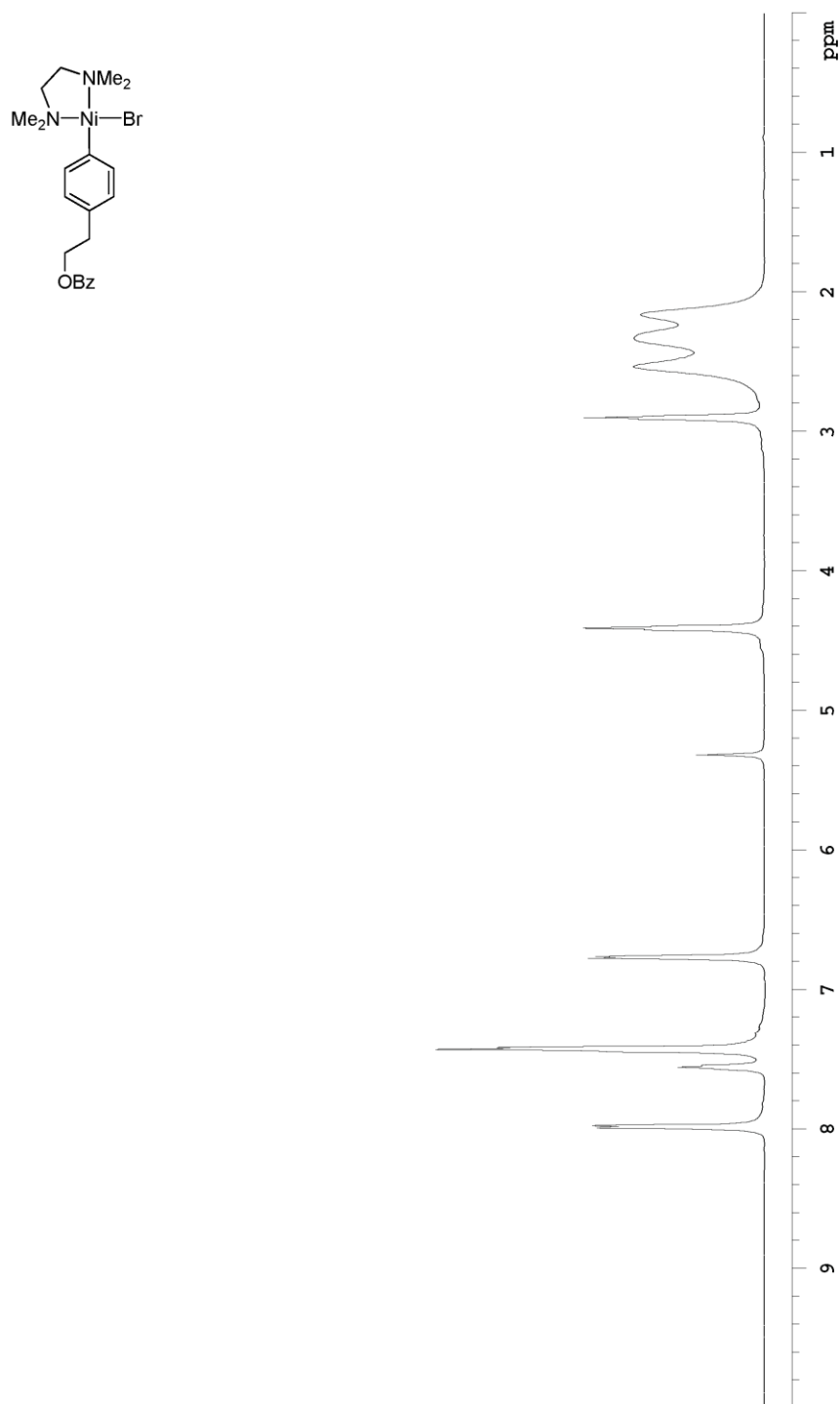


¹³C NMR (CDCl₃, 23 °C) of **1e**

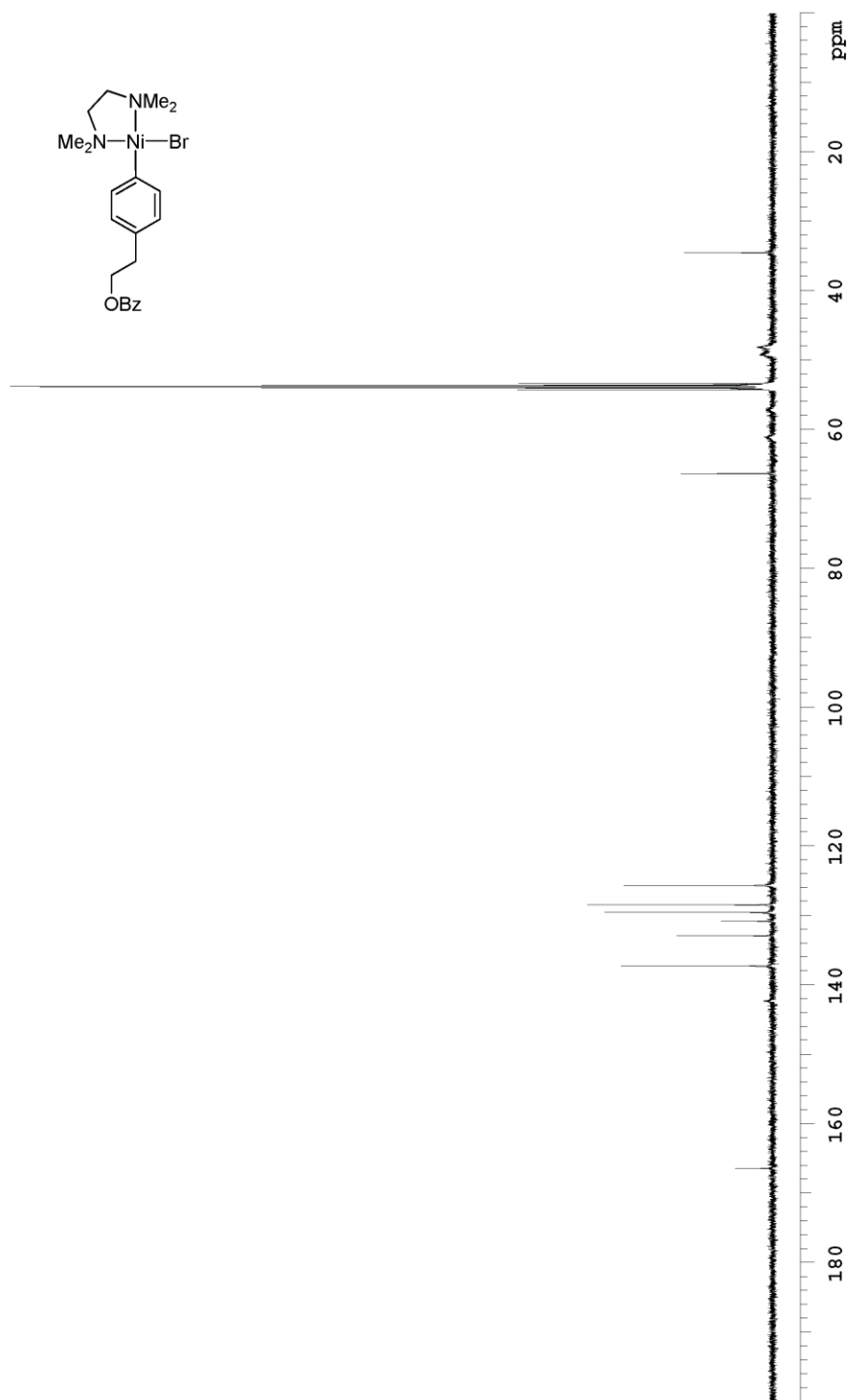


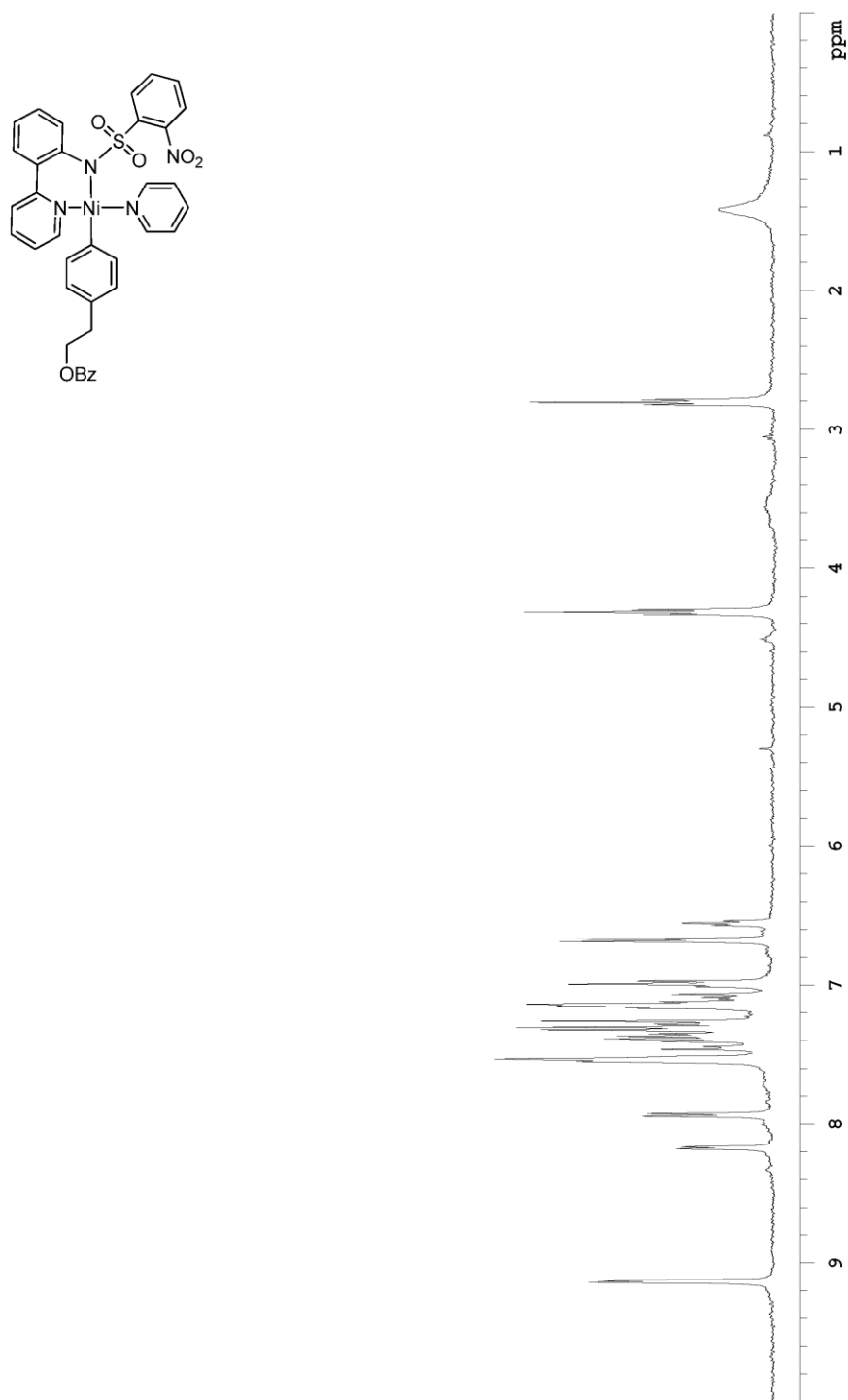
^1H NMR (CDCl₃, 23 °C) of S3

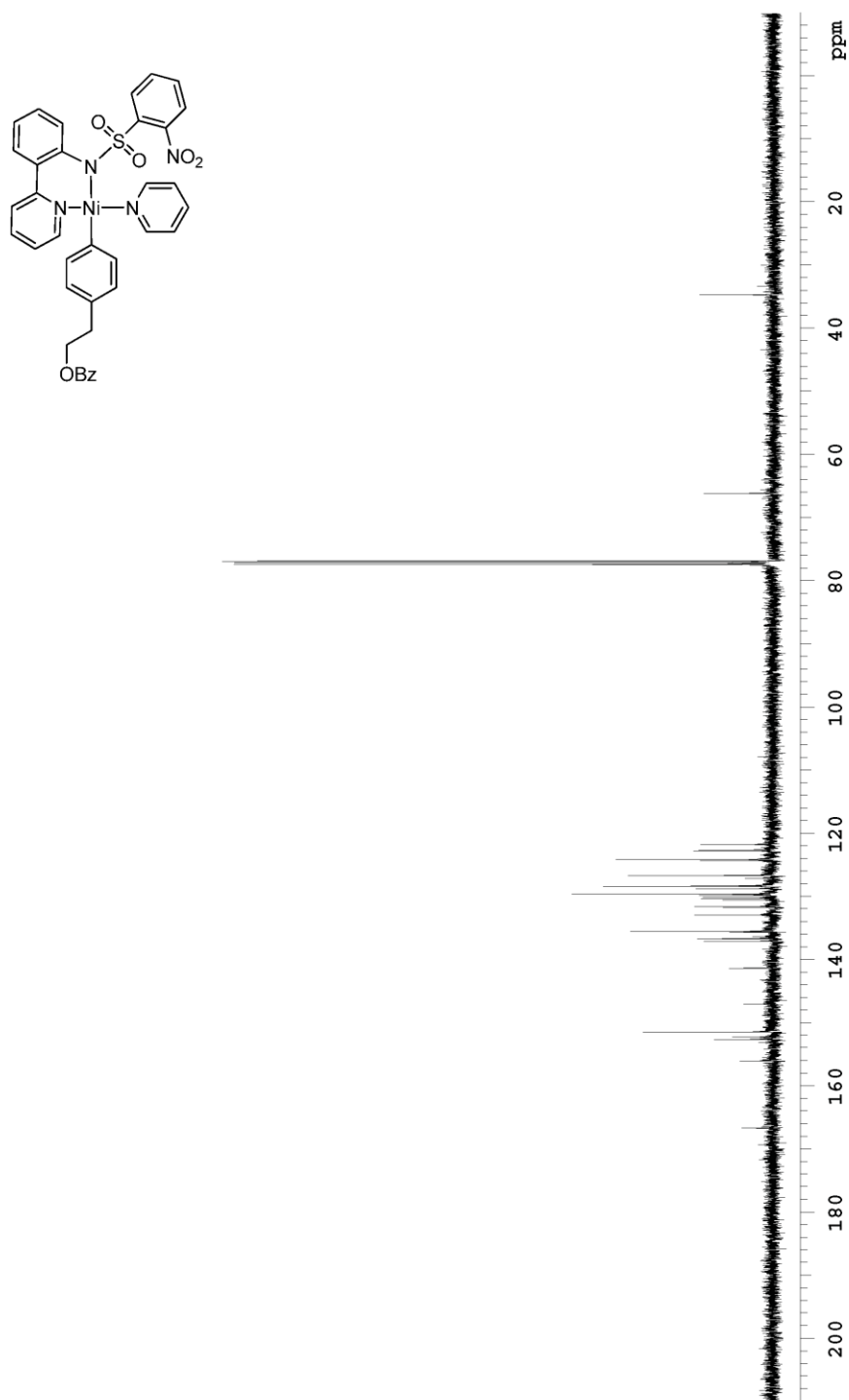
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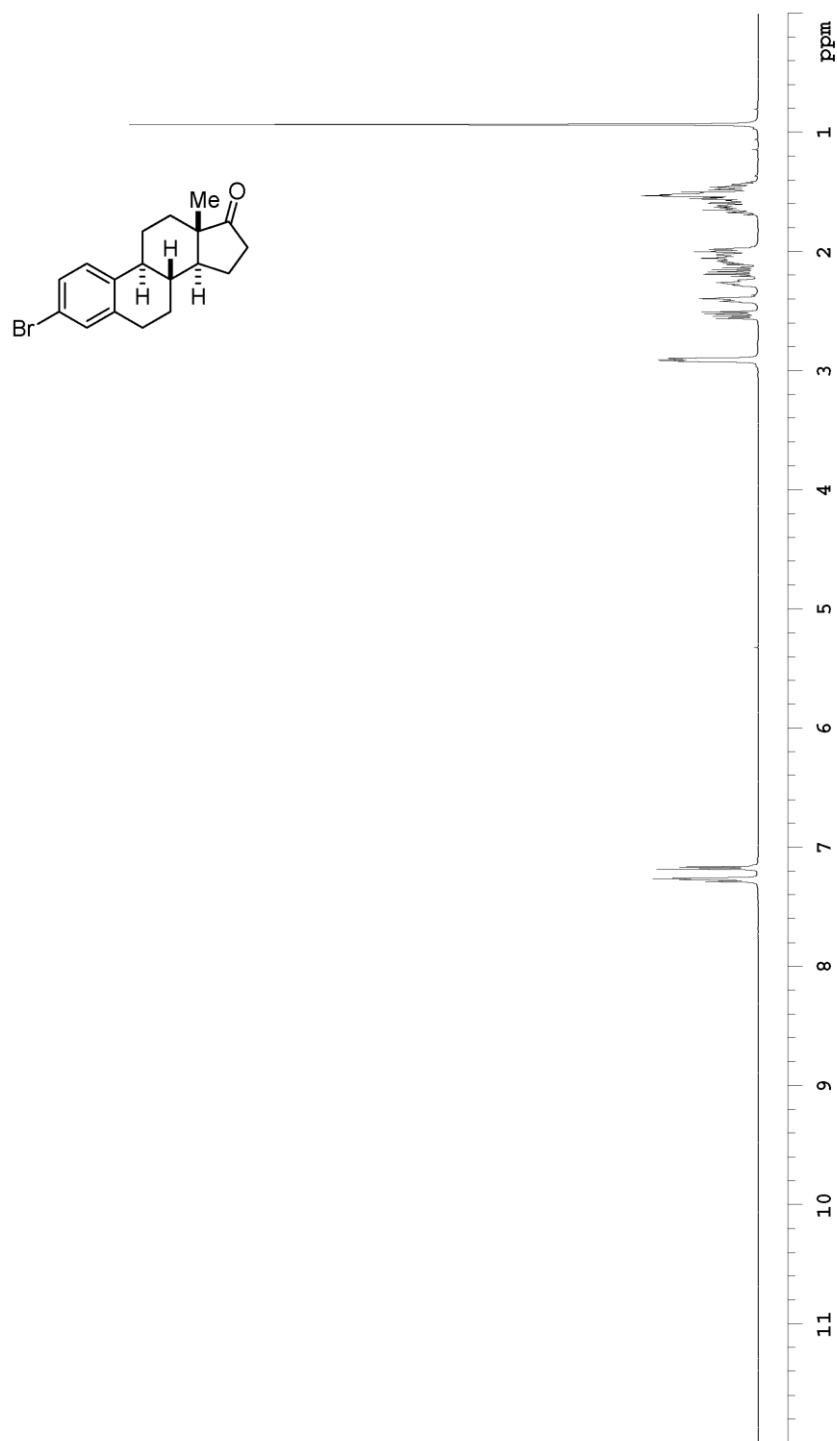


¹H NMR (CD₂Cl₂, 23 °C) of **7f**

 ^{13}C NMR (CD_2Cl_2 , 23 °C) of **7f**

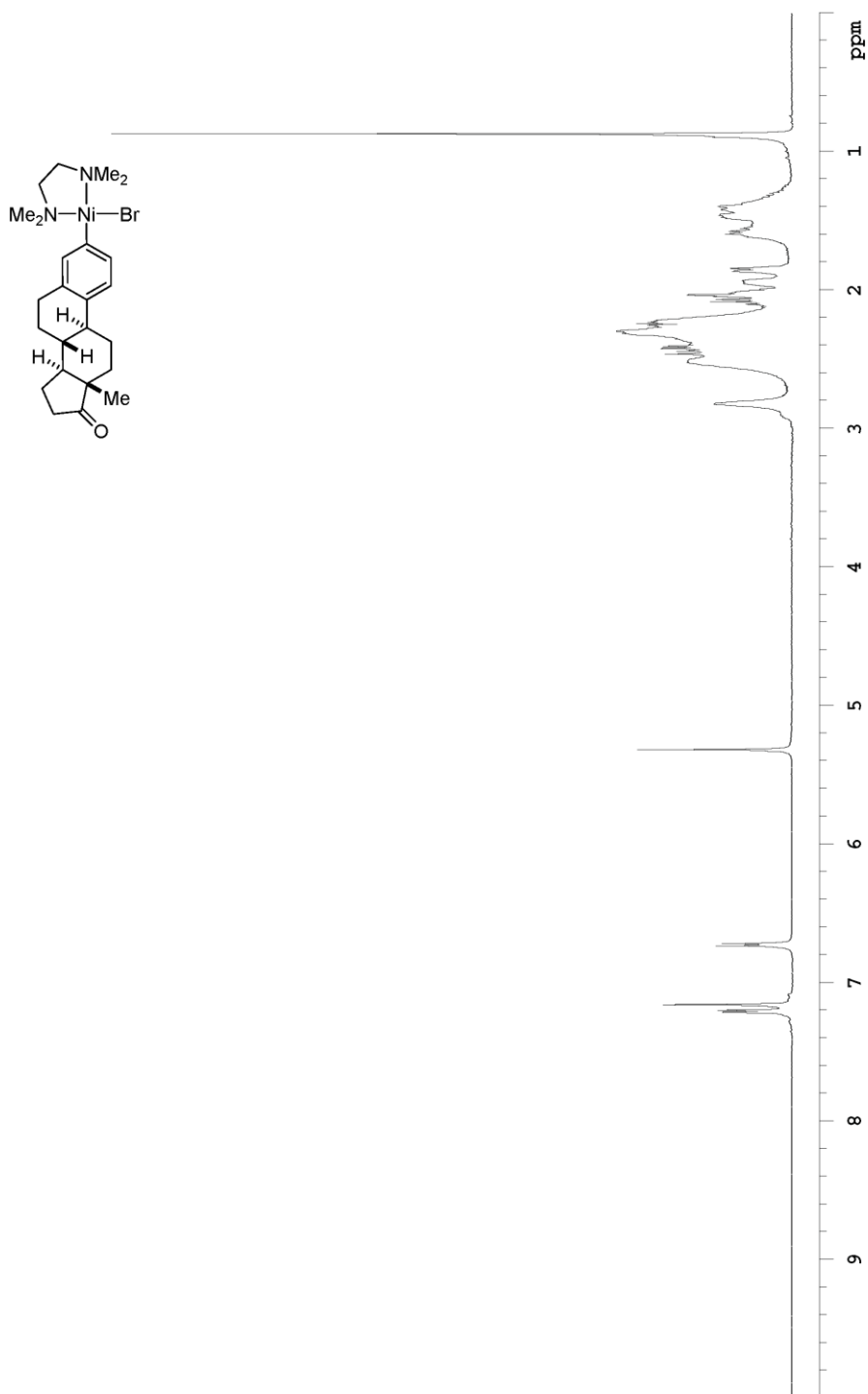
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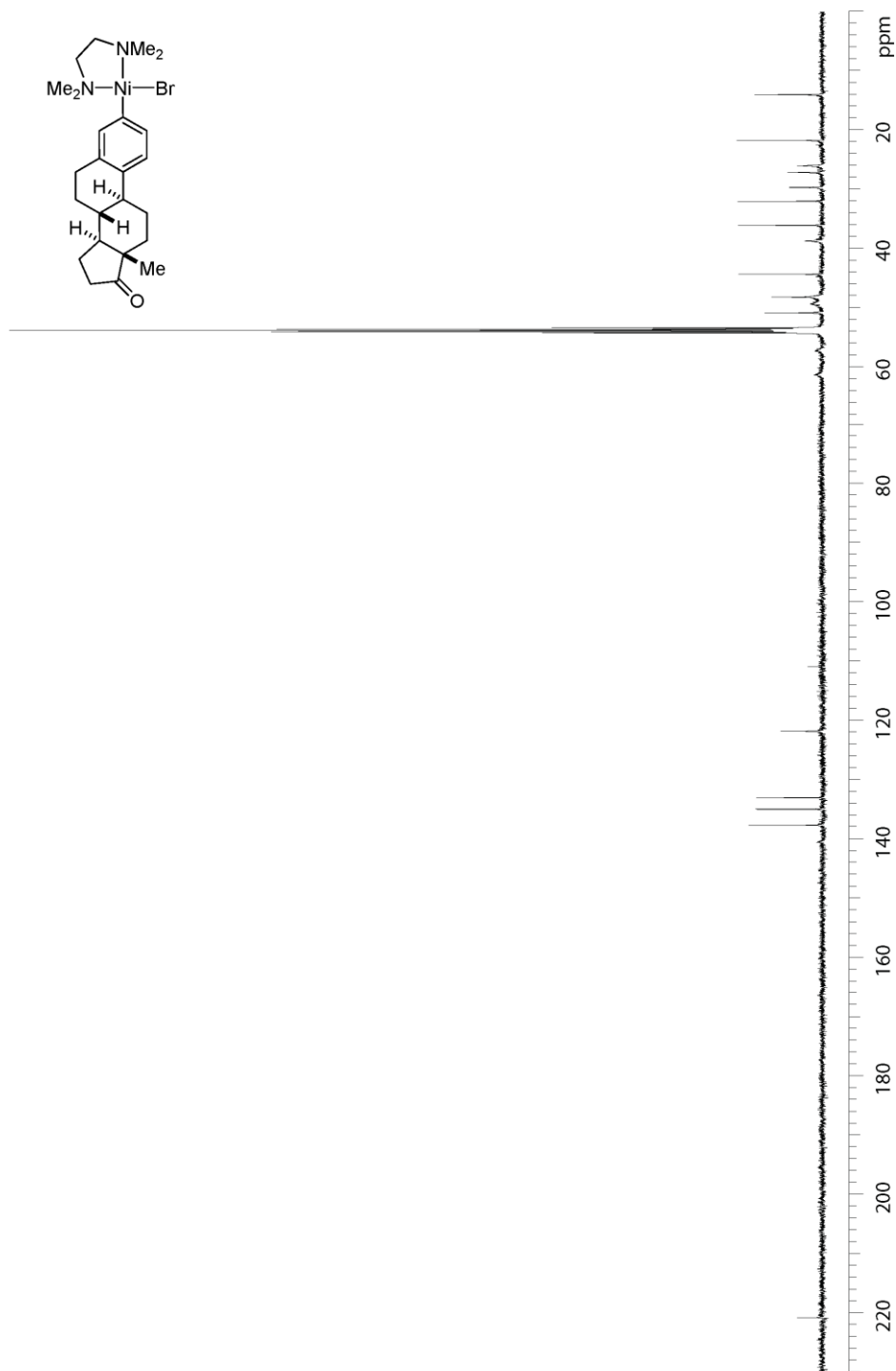
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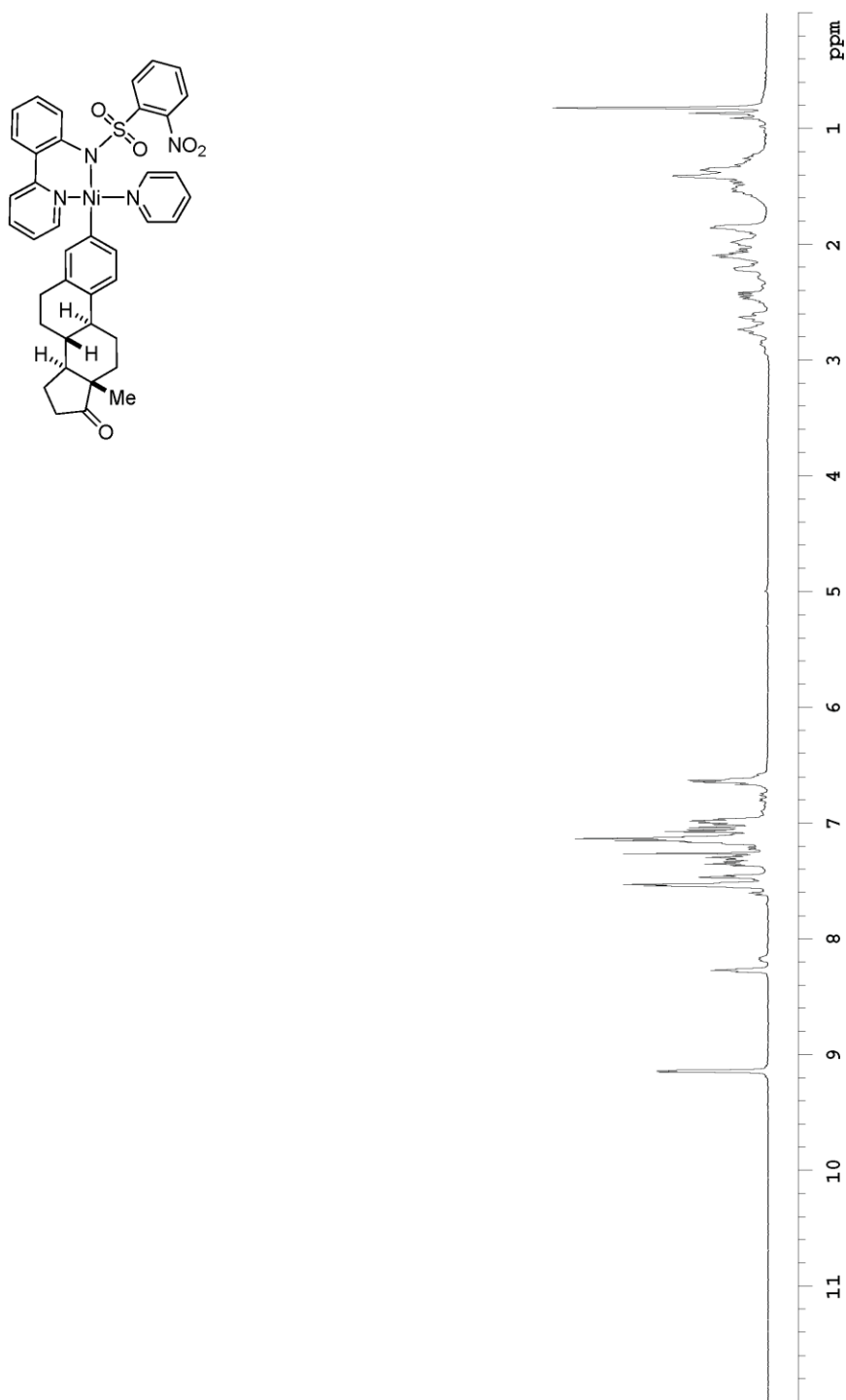


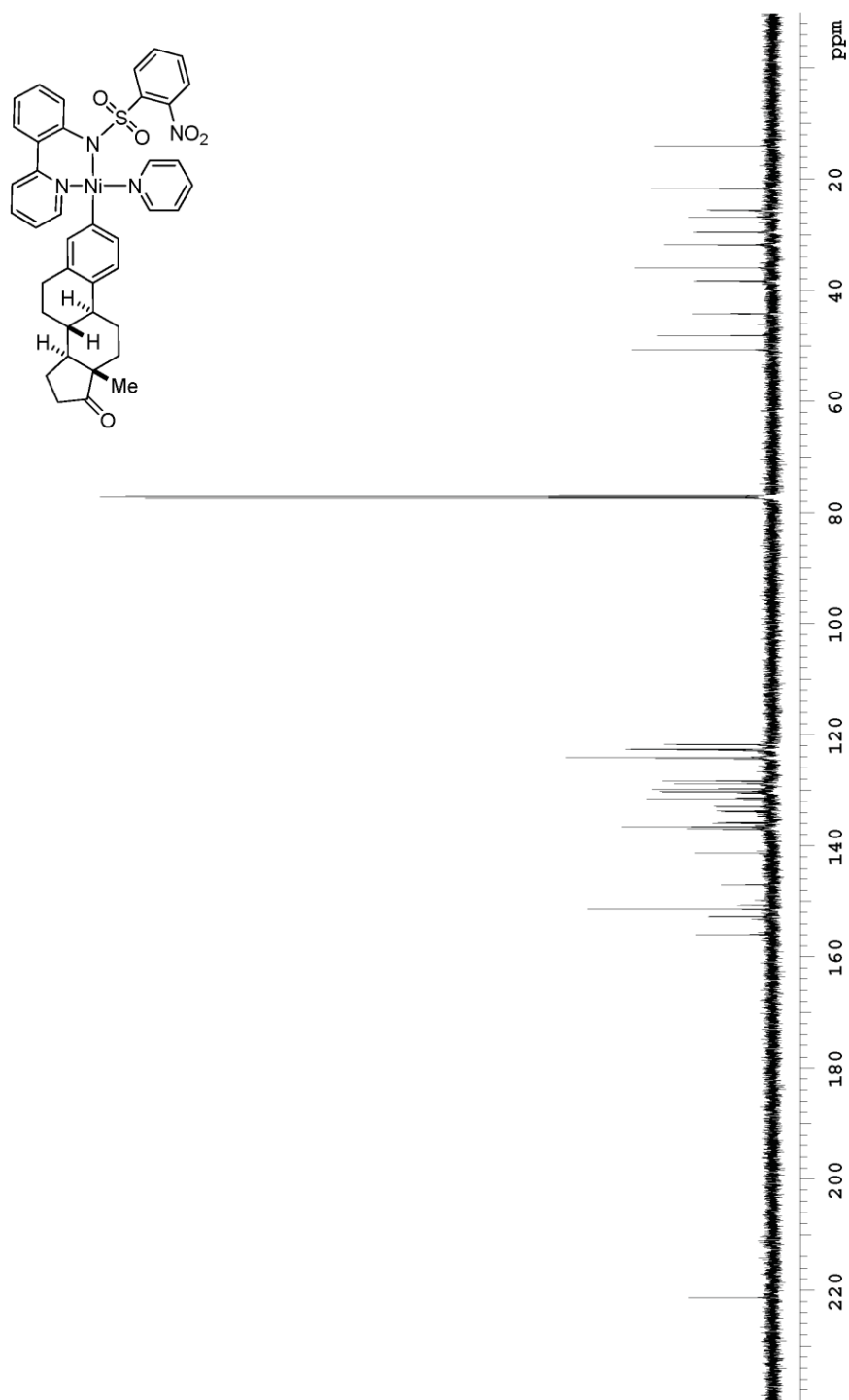
^1H NMR (CDCl₃, 23 °C) of S4

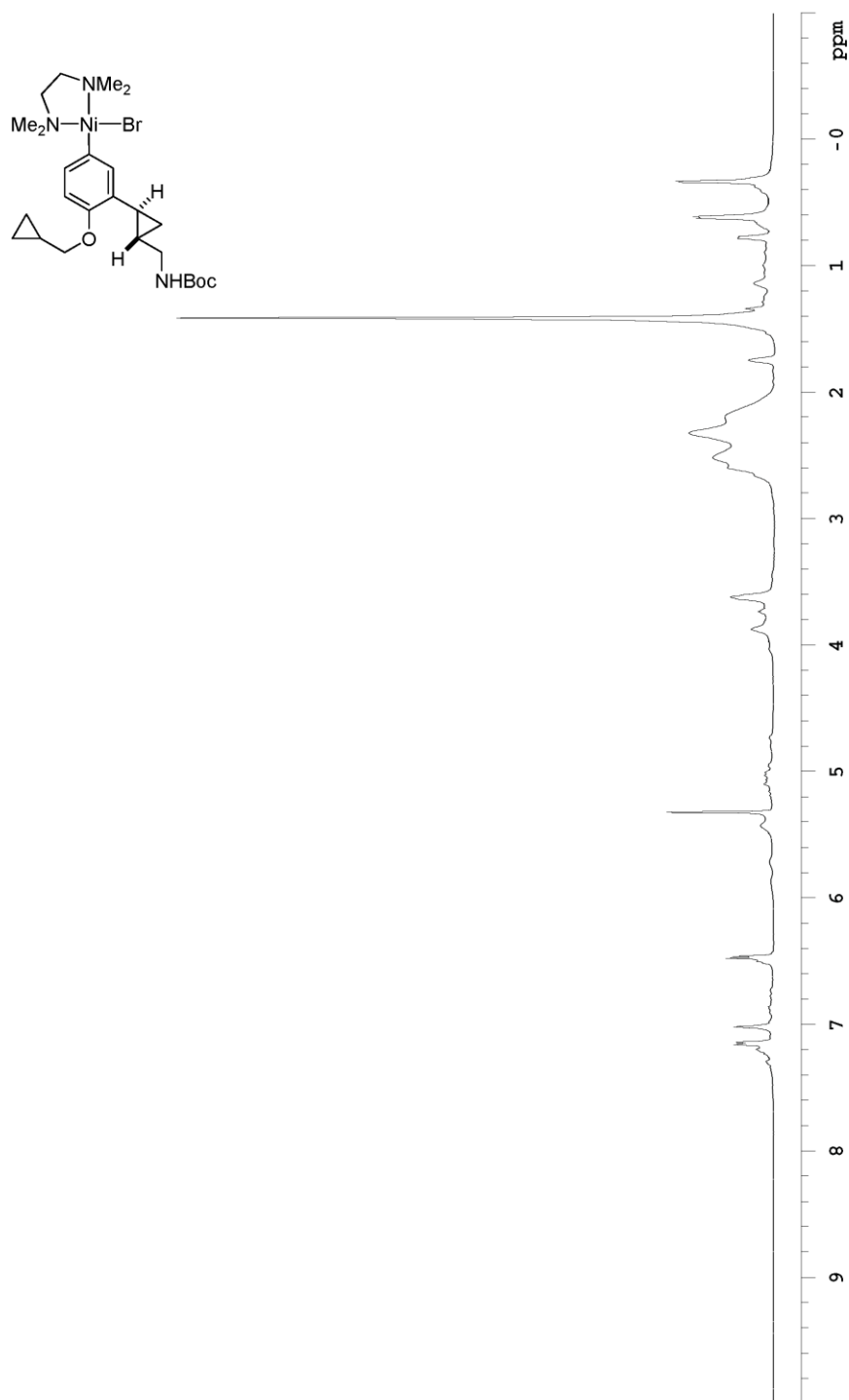


 ^1H NMR (CD $_2$ Cl $_2$, 23 °C) of **7g**

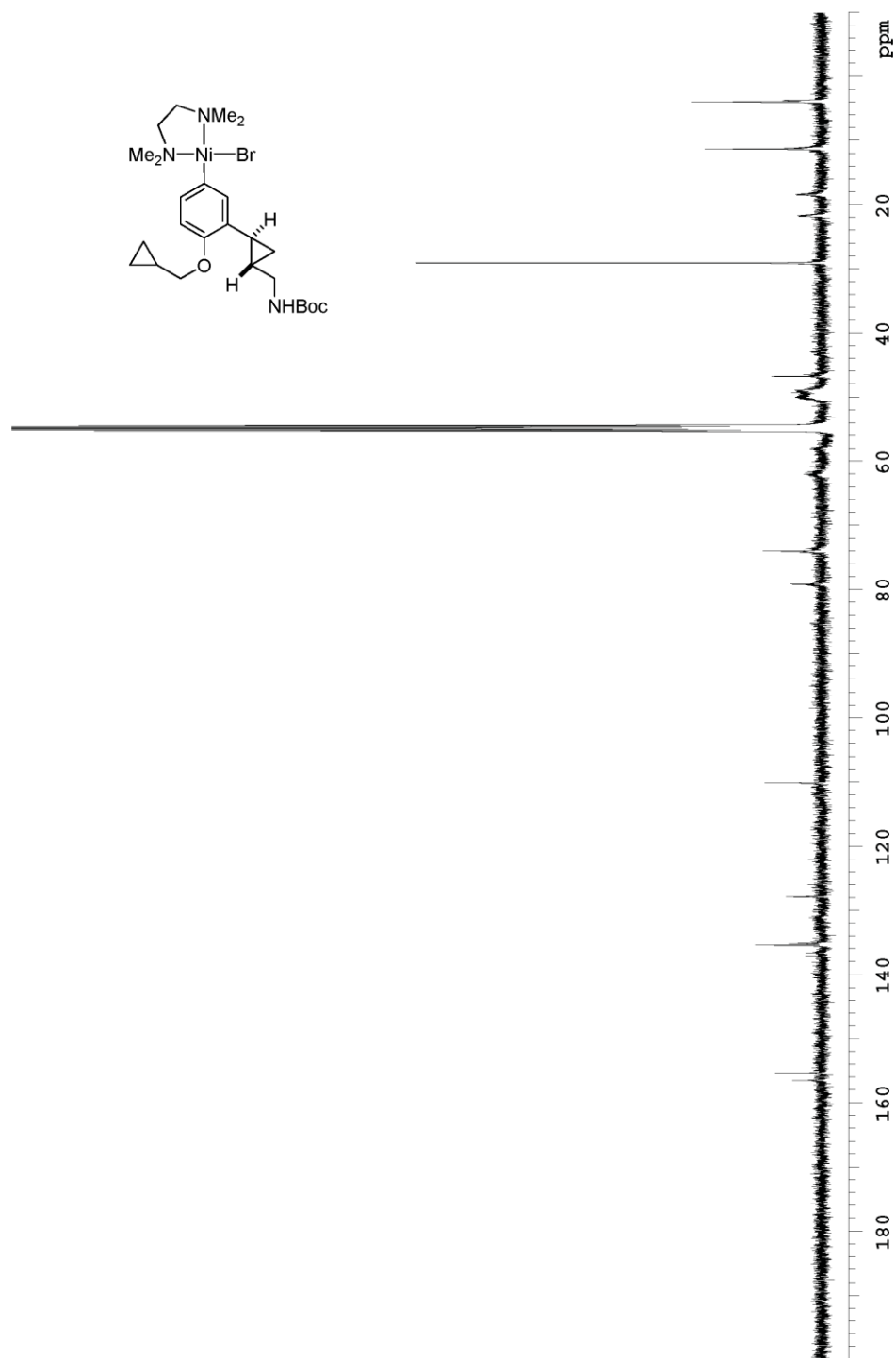
 ^{13}C NMR (CD₂Cl₂, 23 °C) of **7g**

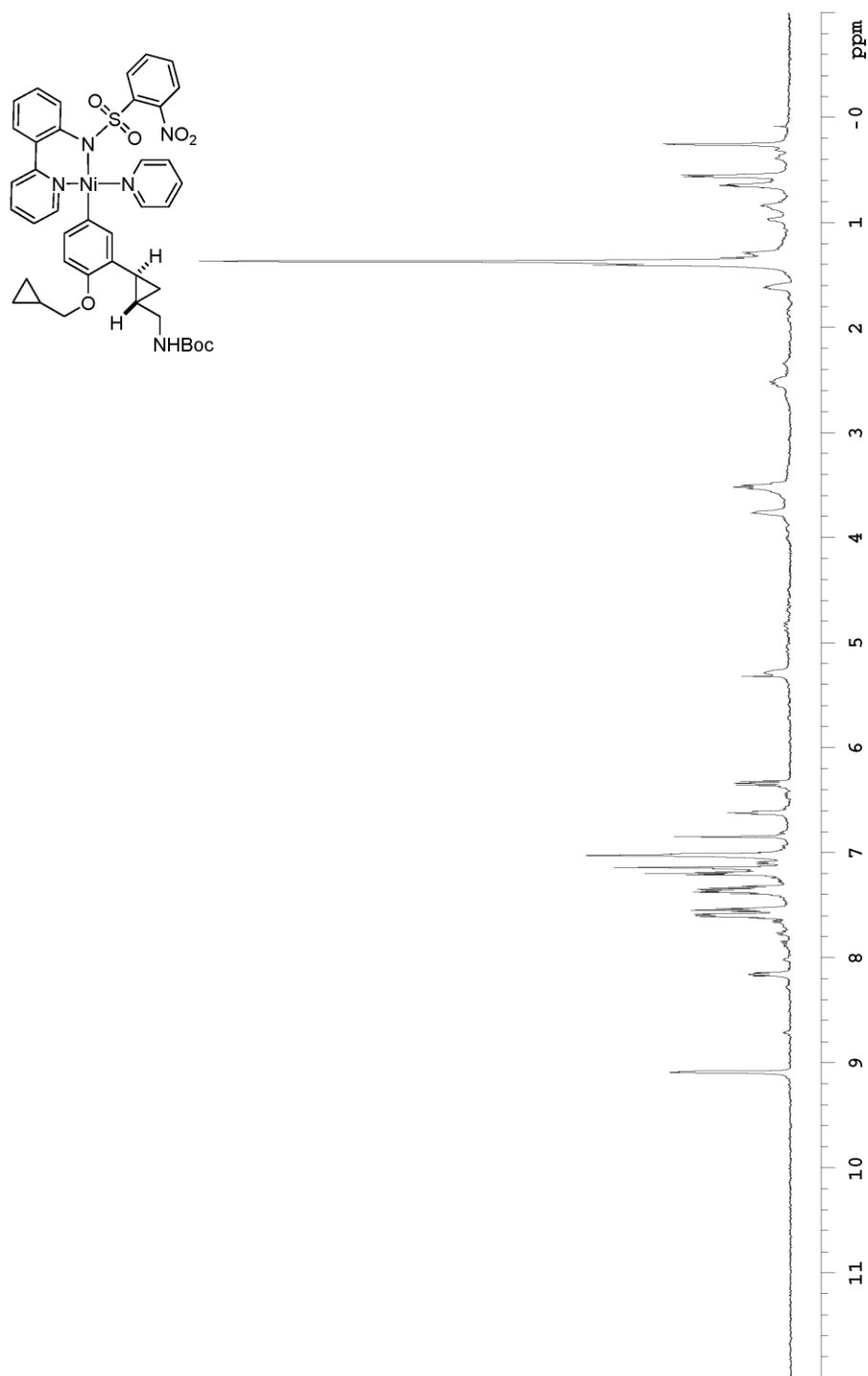
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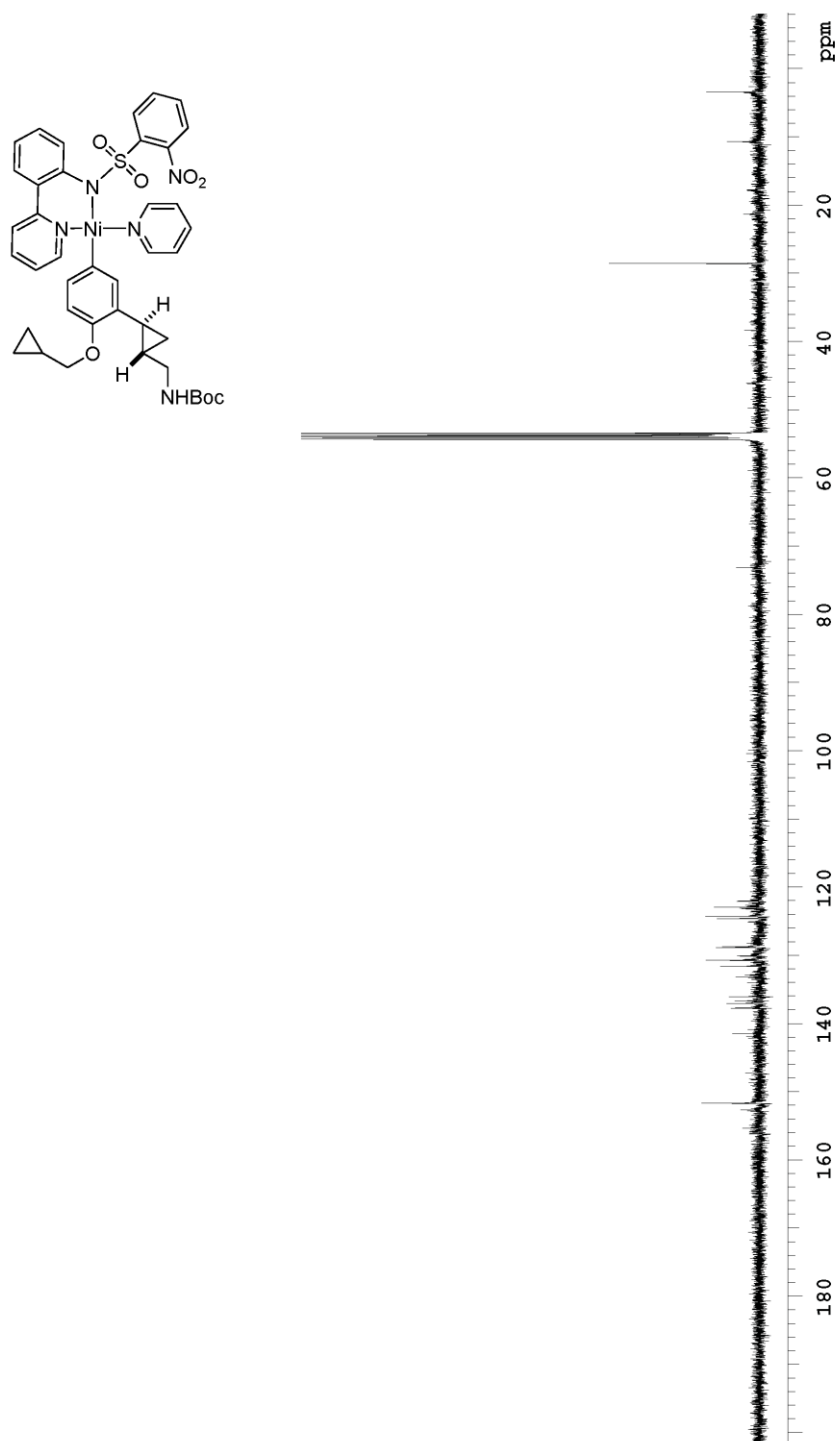
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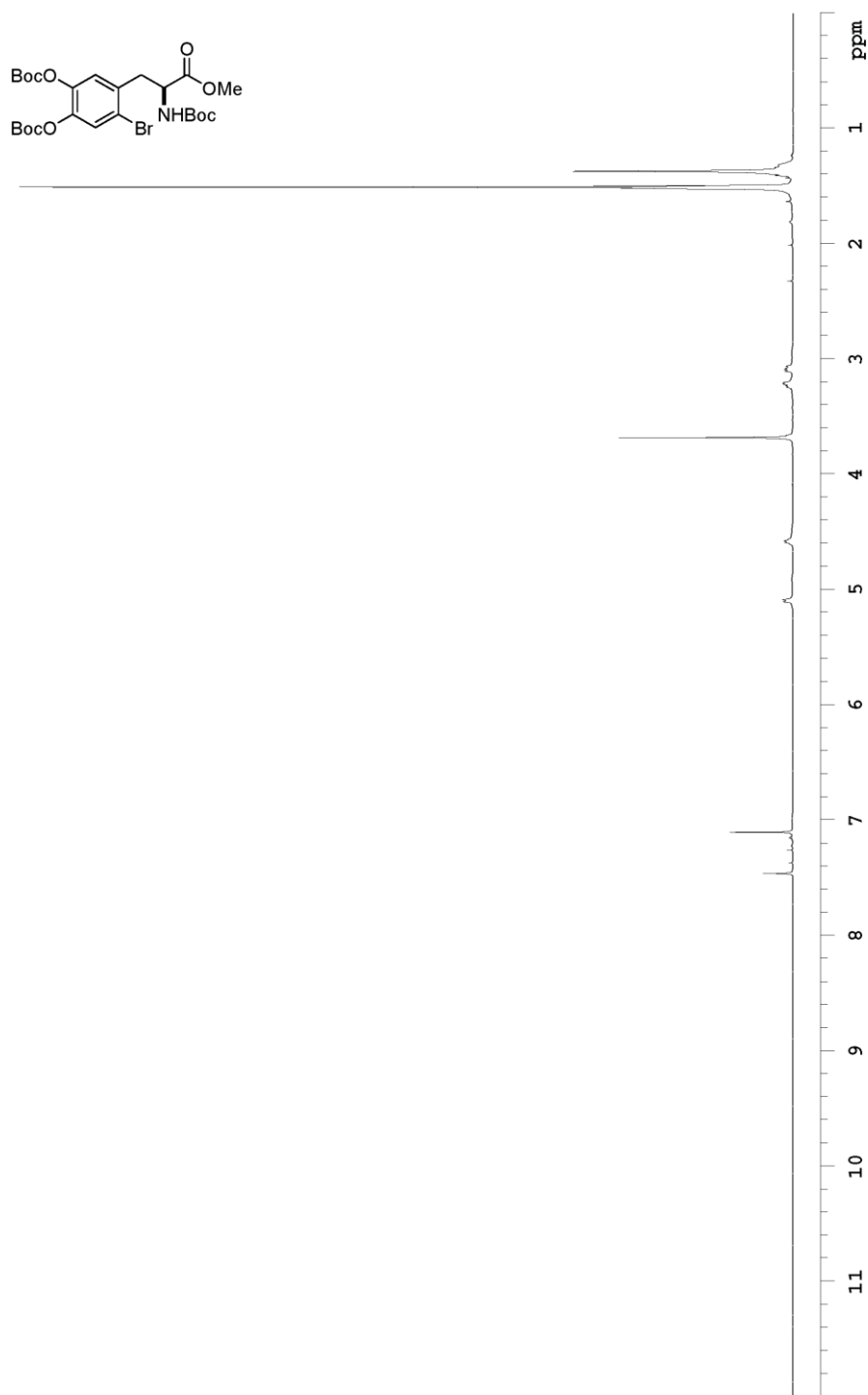


^1H NMR (CD₂Cl₂, 23 °C) of **7h**

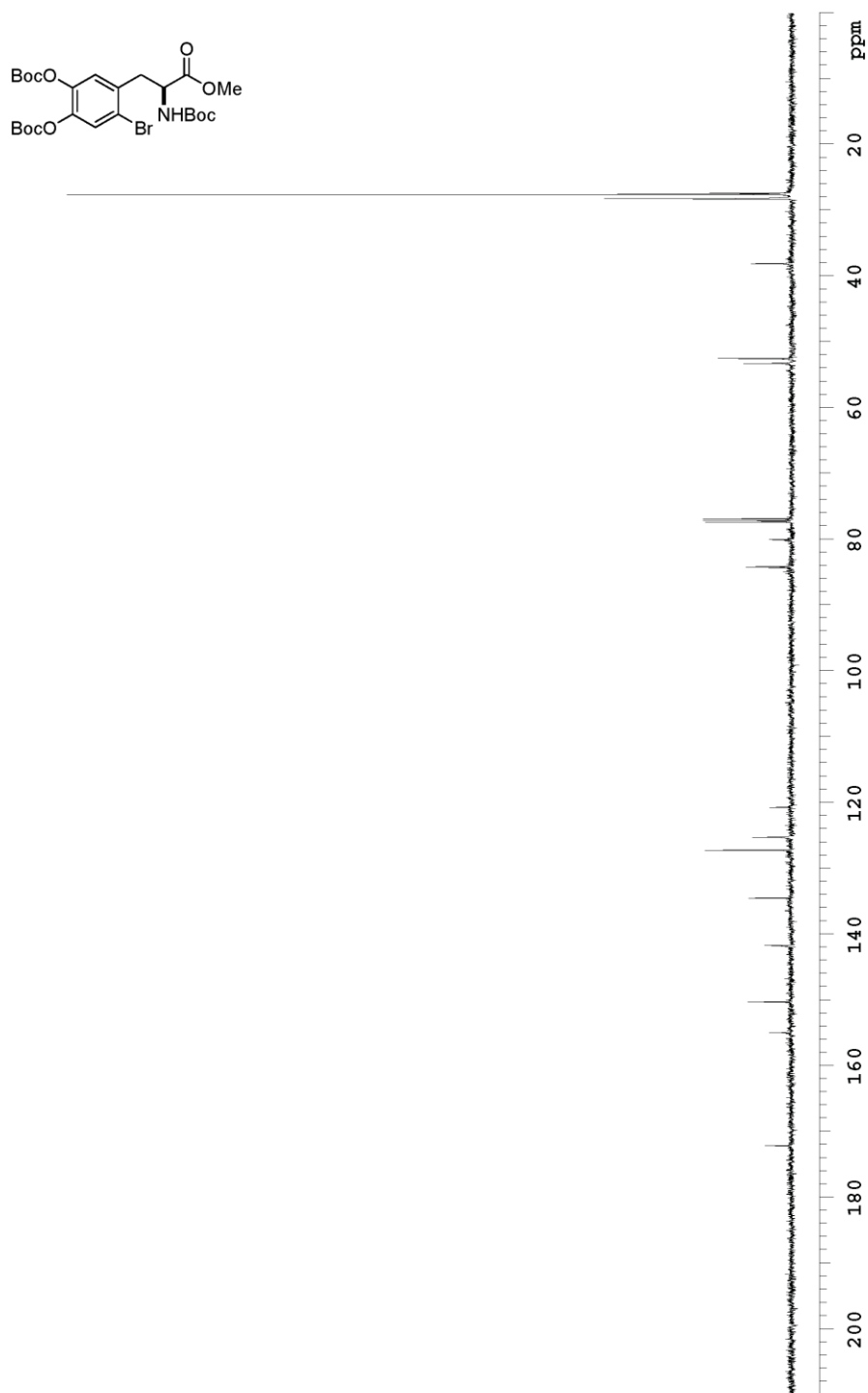
 ^{13}C NMR (CD_2Cl_2 , 23 °C) of **7h**

 ^1H NMR (CD_2Cl_2 , 23 °C) of **1h**

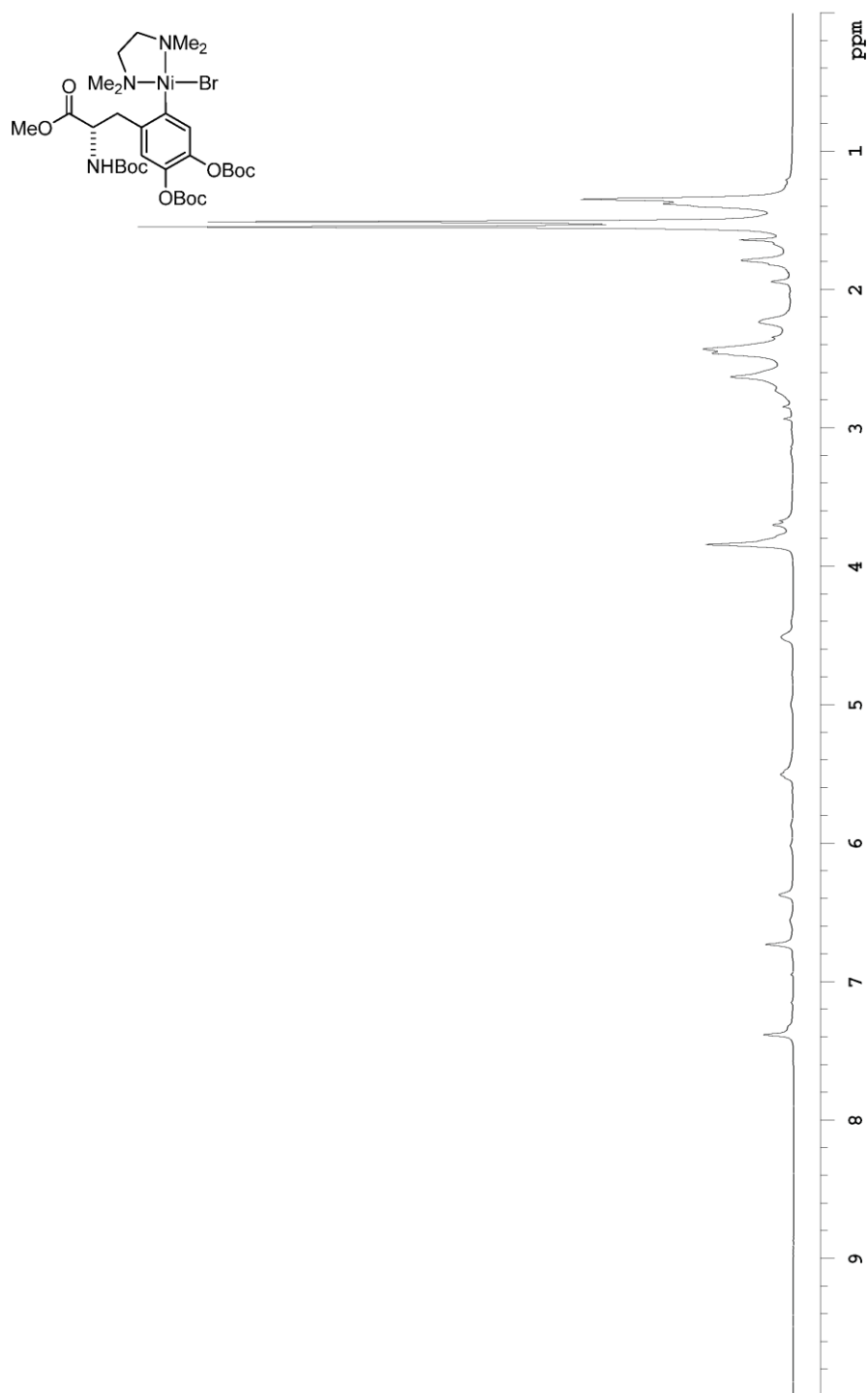
 ^{13}C NMR (CD_2Cl_2 , 23 °C) of **1h**



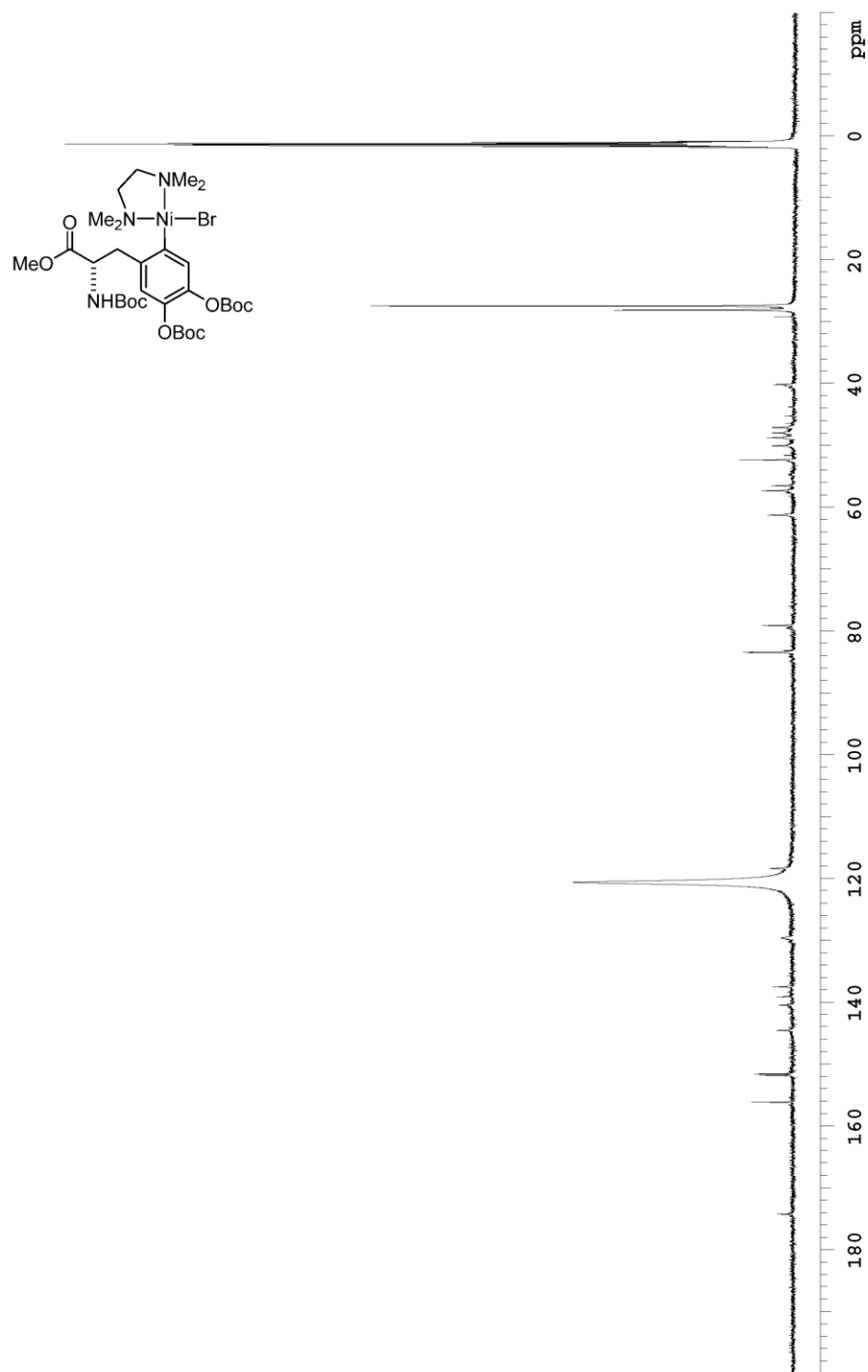
¹H NMR (CDCl₃, 23 °C) of S11

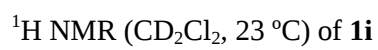


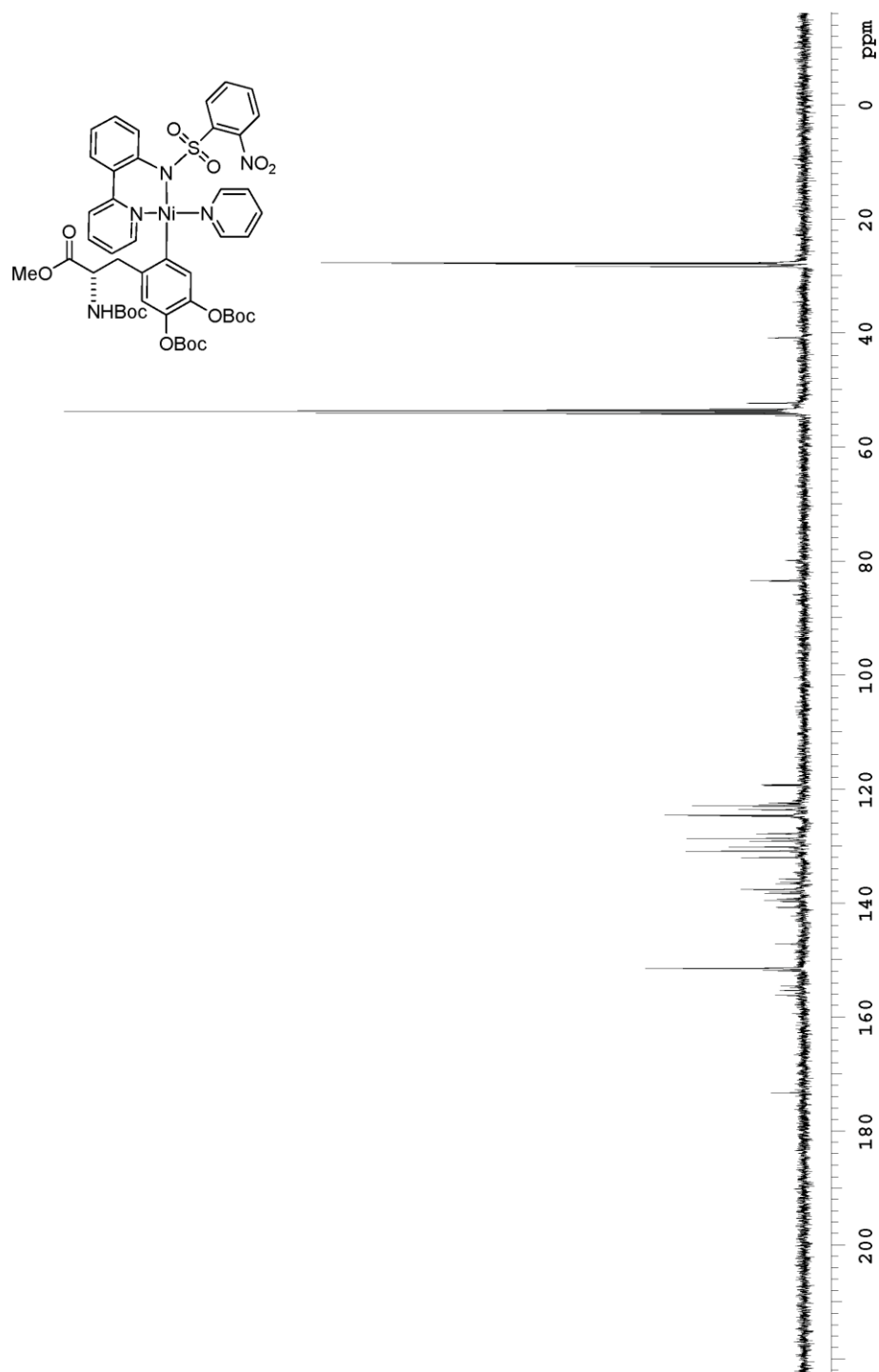
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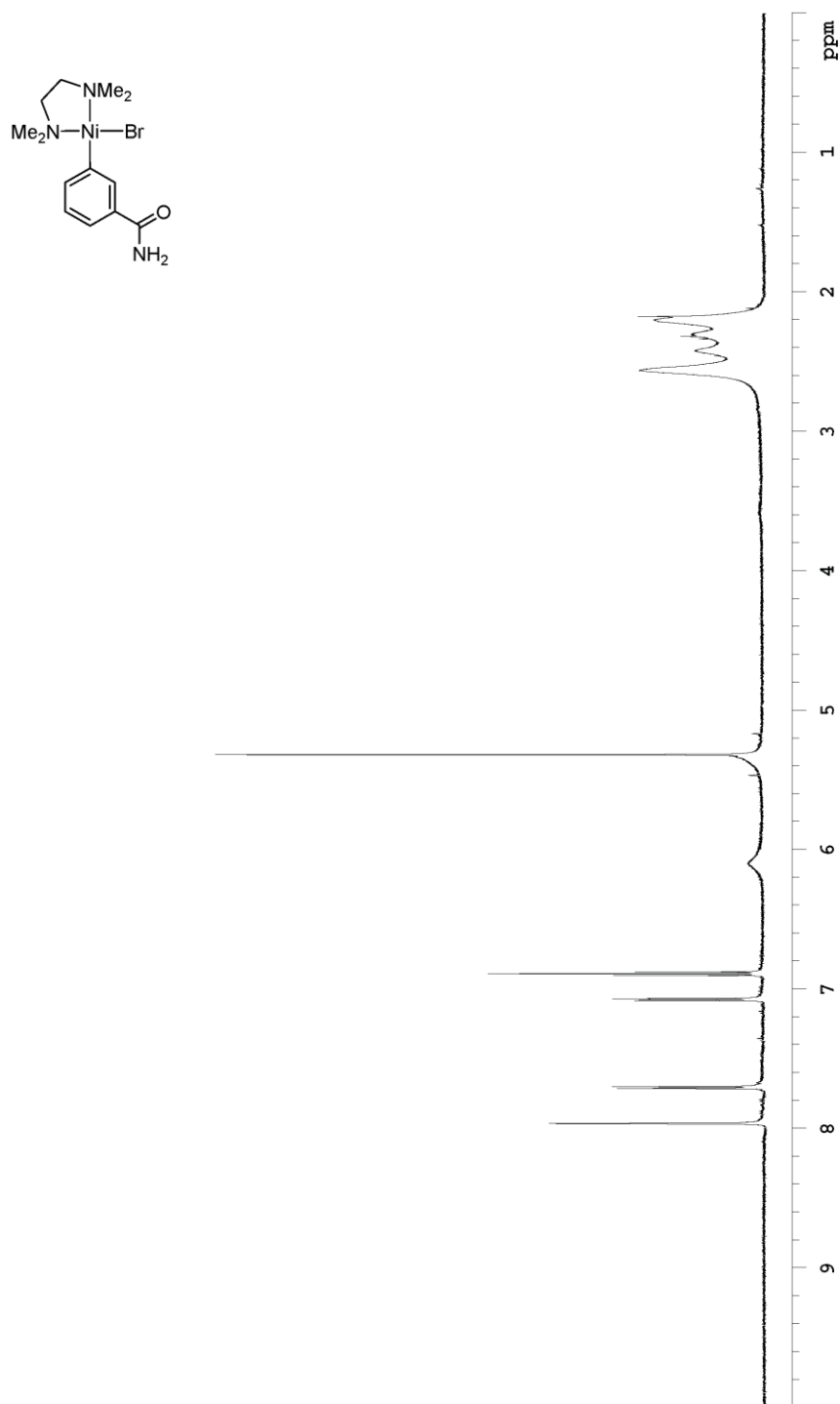


¹H NMR (CD₃CN, 23 °C) of **7i**

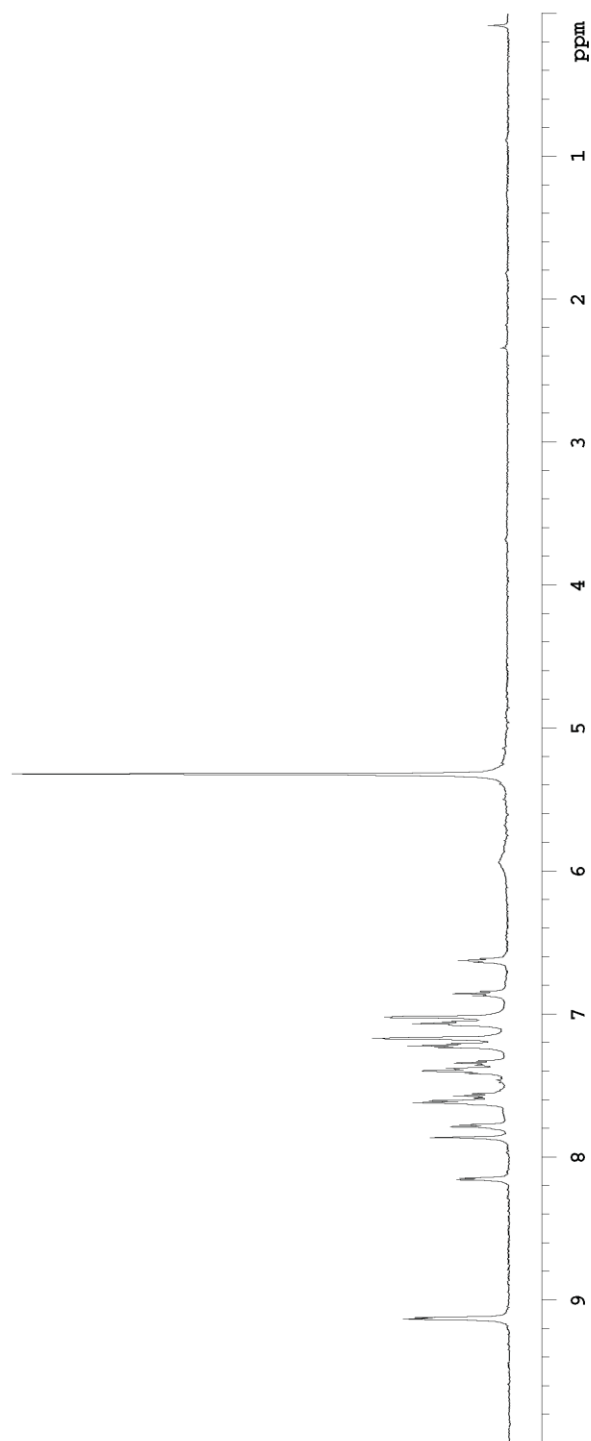
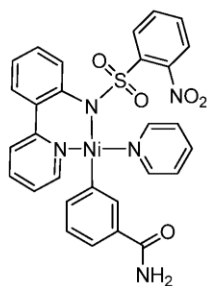
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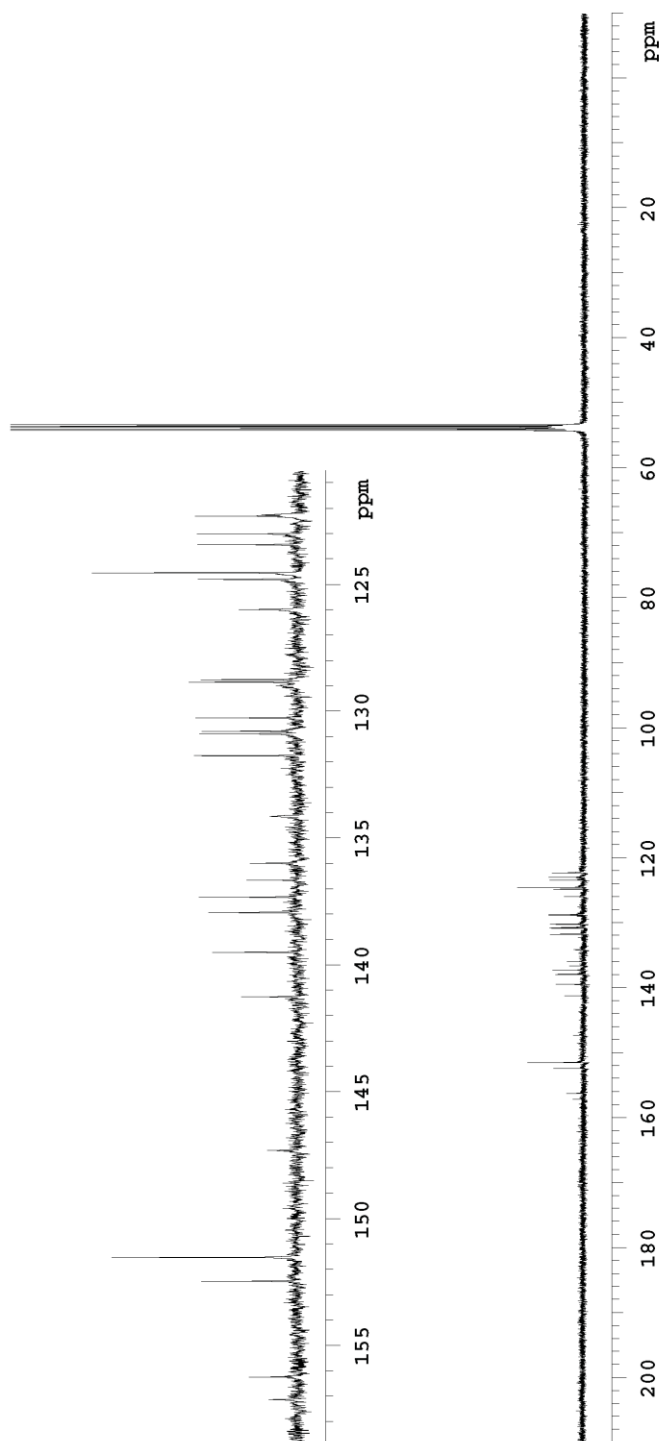
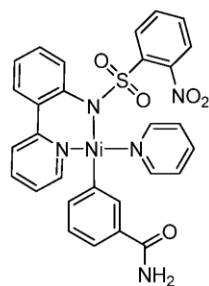
 ^{13}C NMR (CD_2Cl_2 , 23 °C) of **1i**



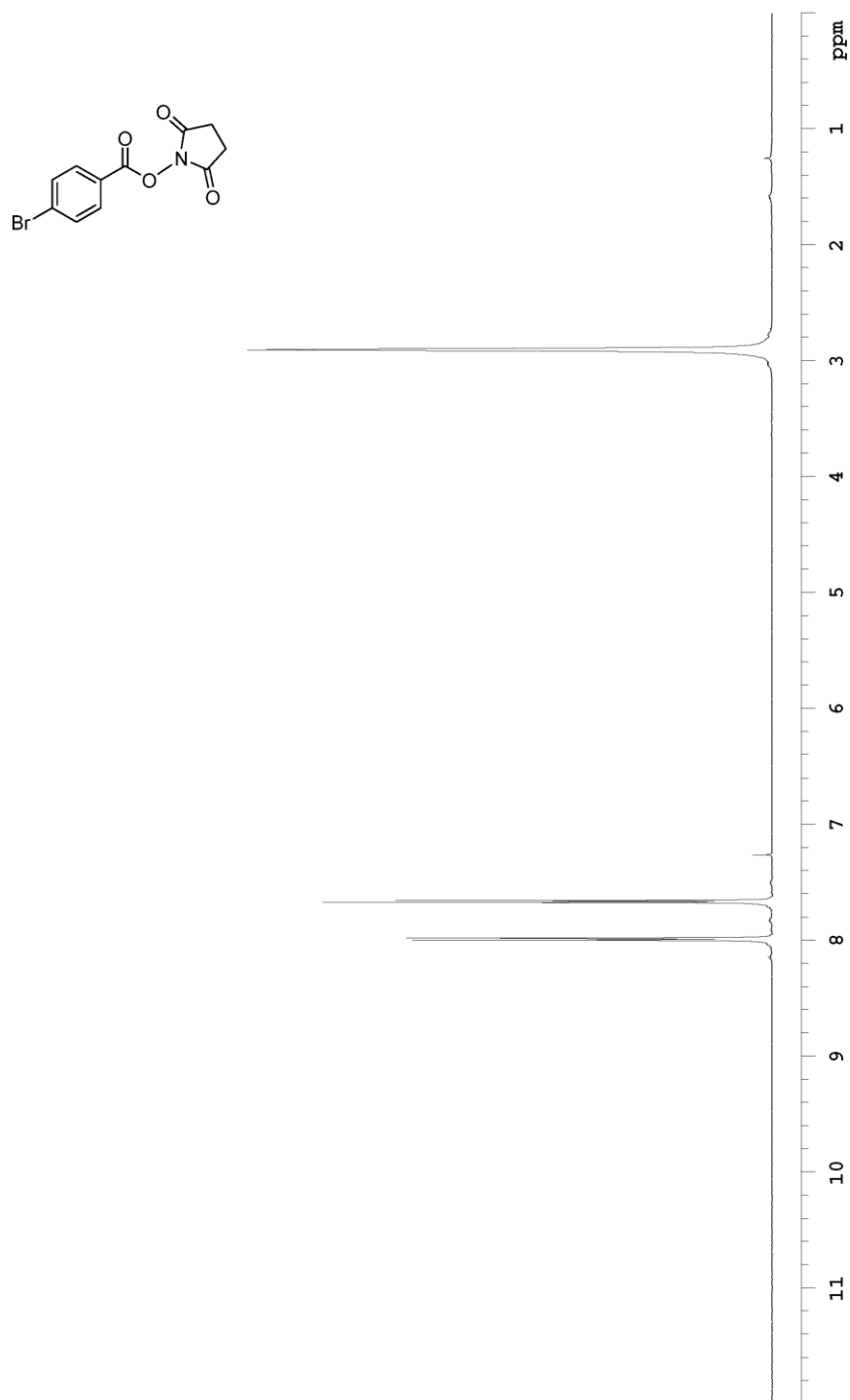
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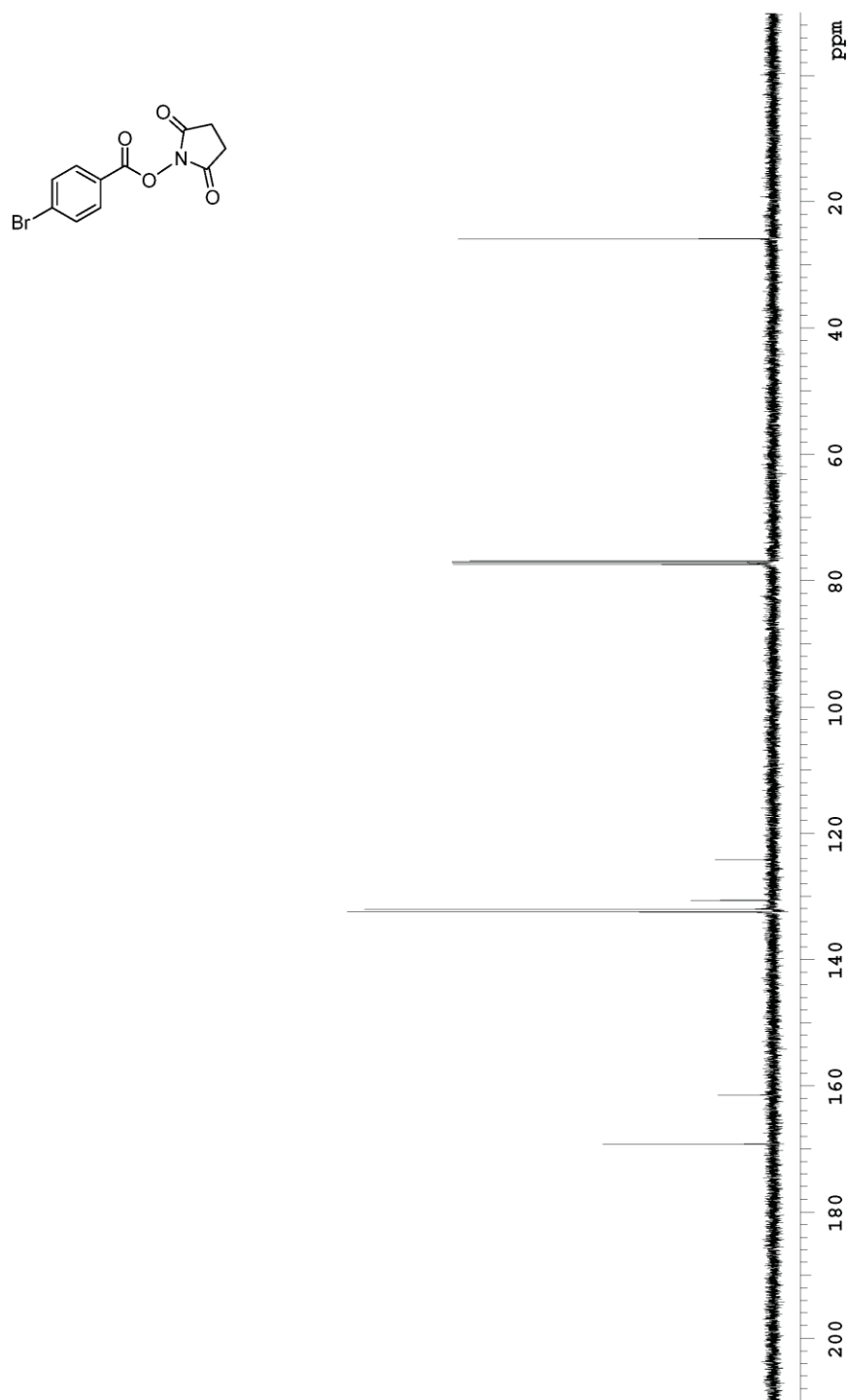


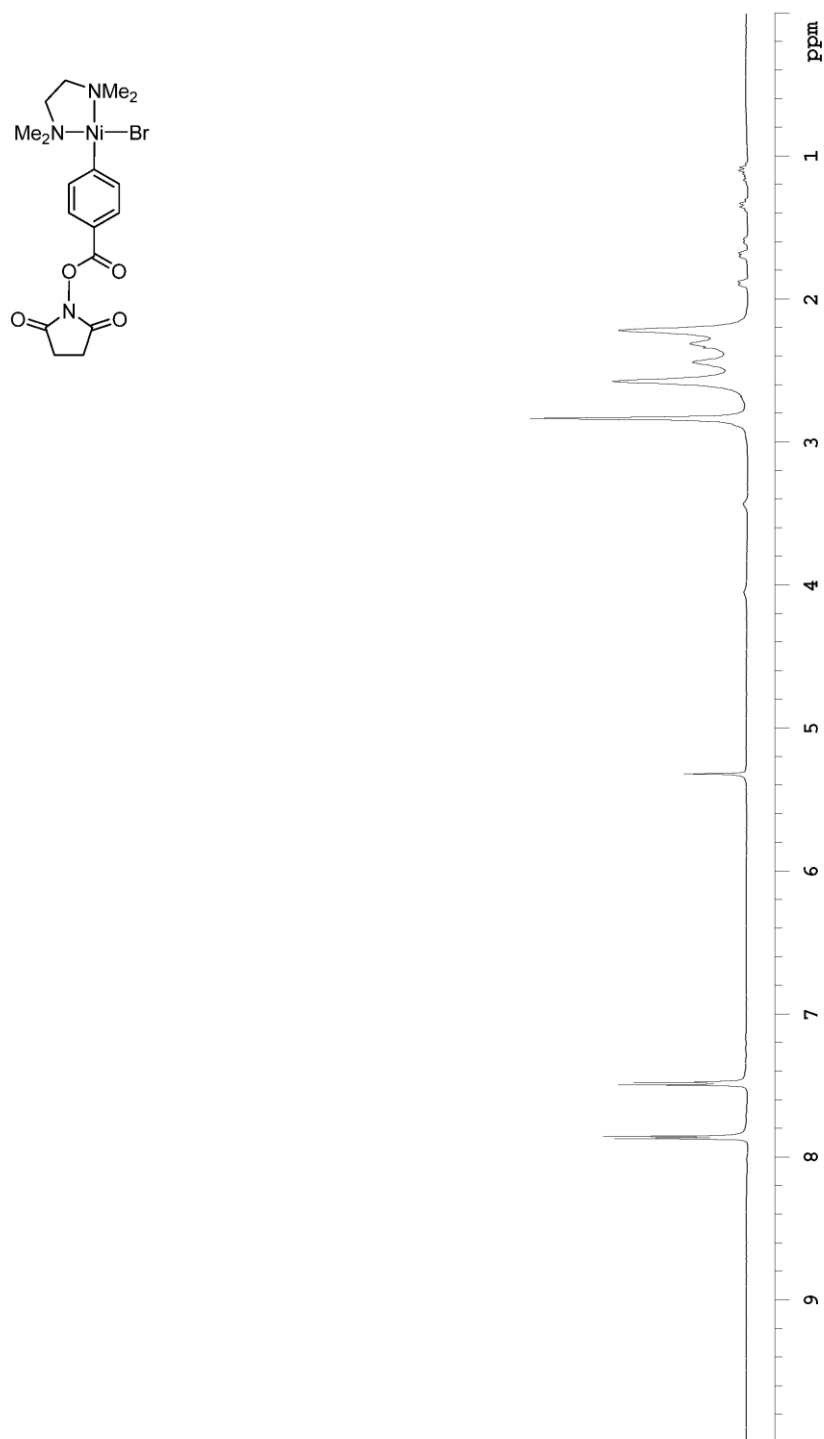
^1H NMR (CD_2Cl_2 , 23 °C) of **1j**

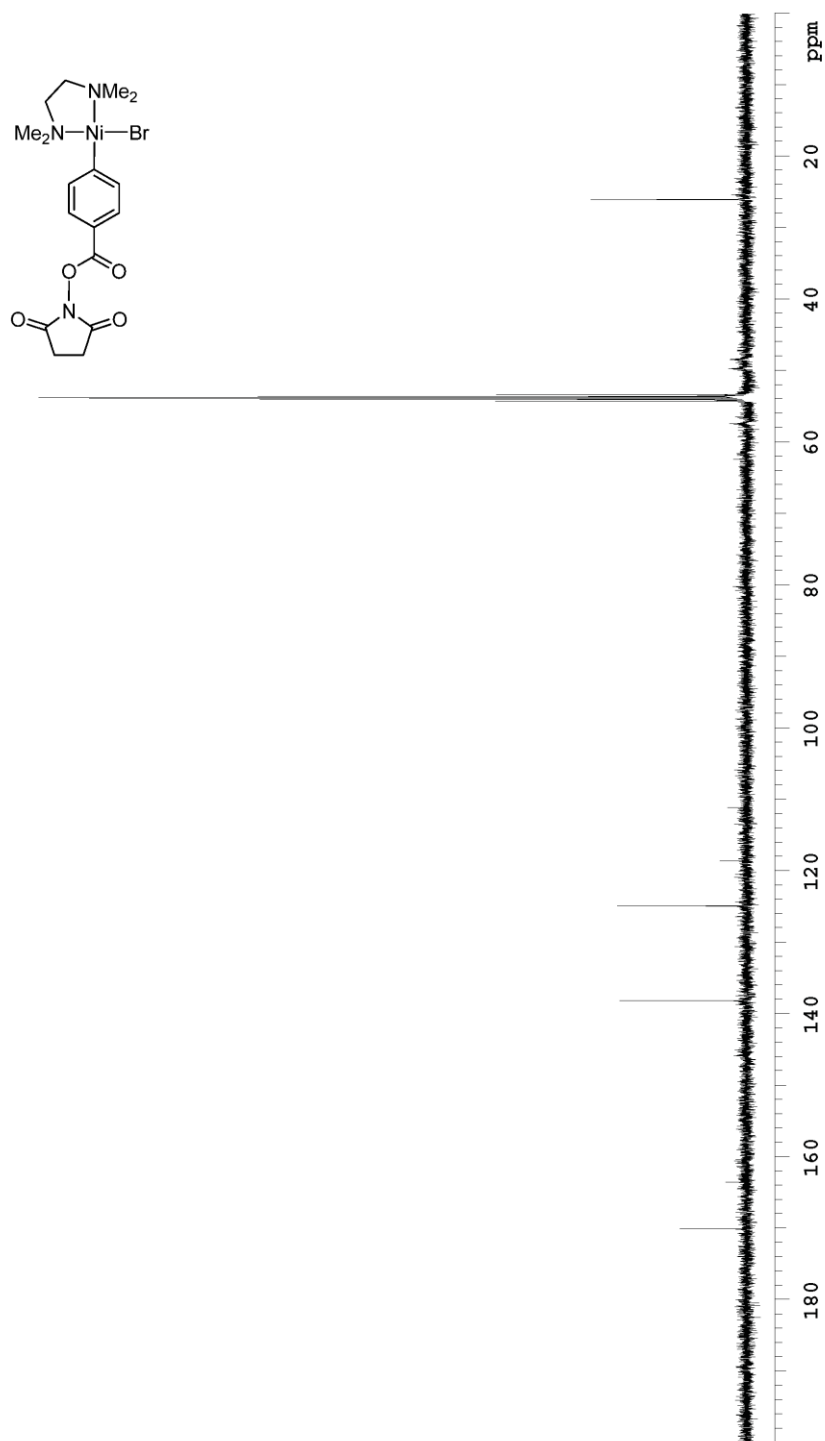


^{13}C NMR (CD_2Cl_2 , 23 °C) of **1j**

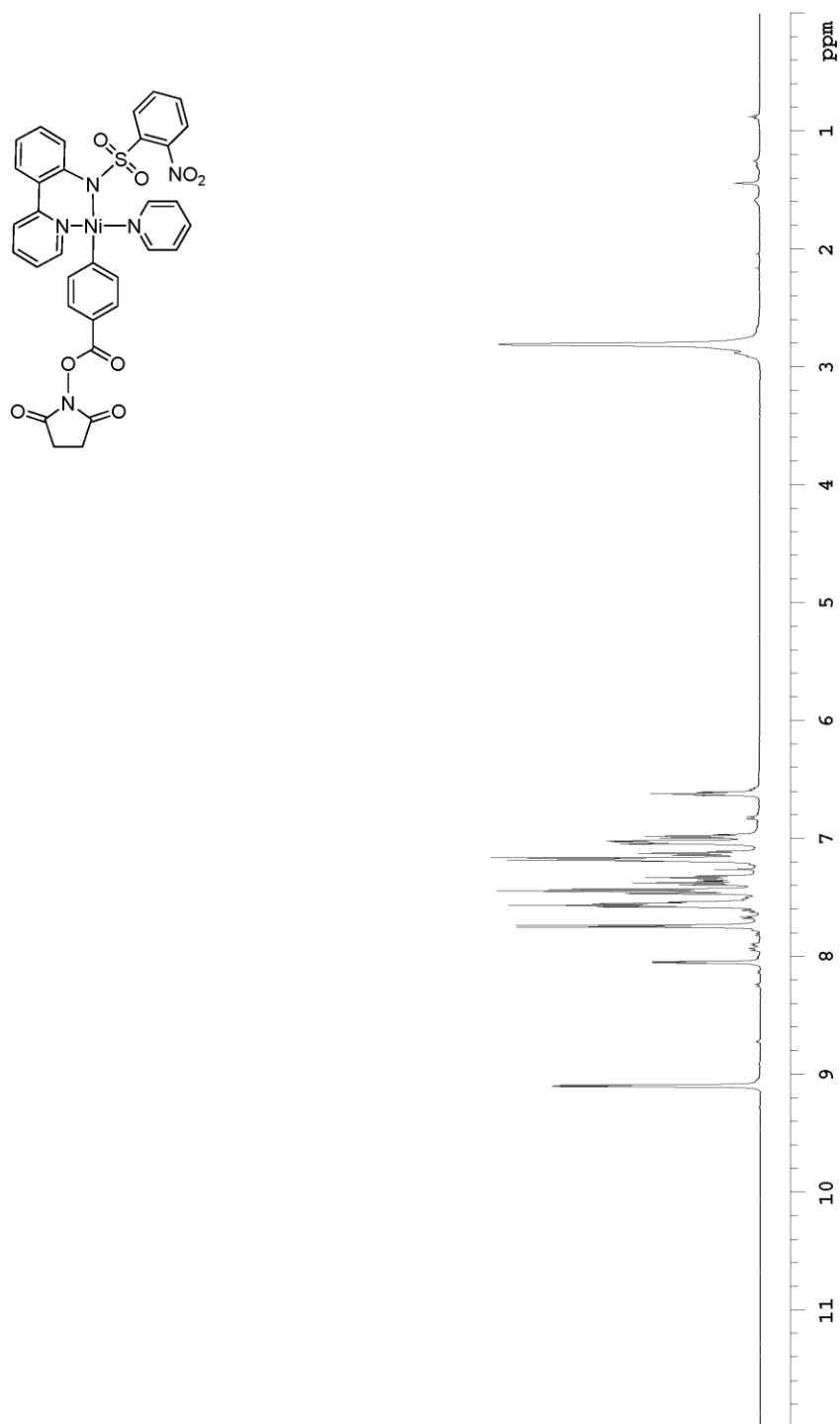
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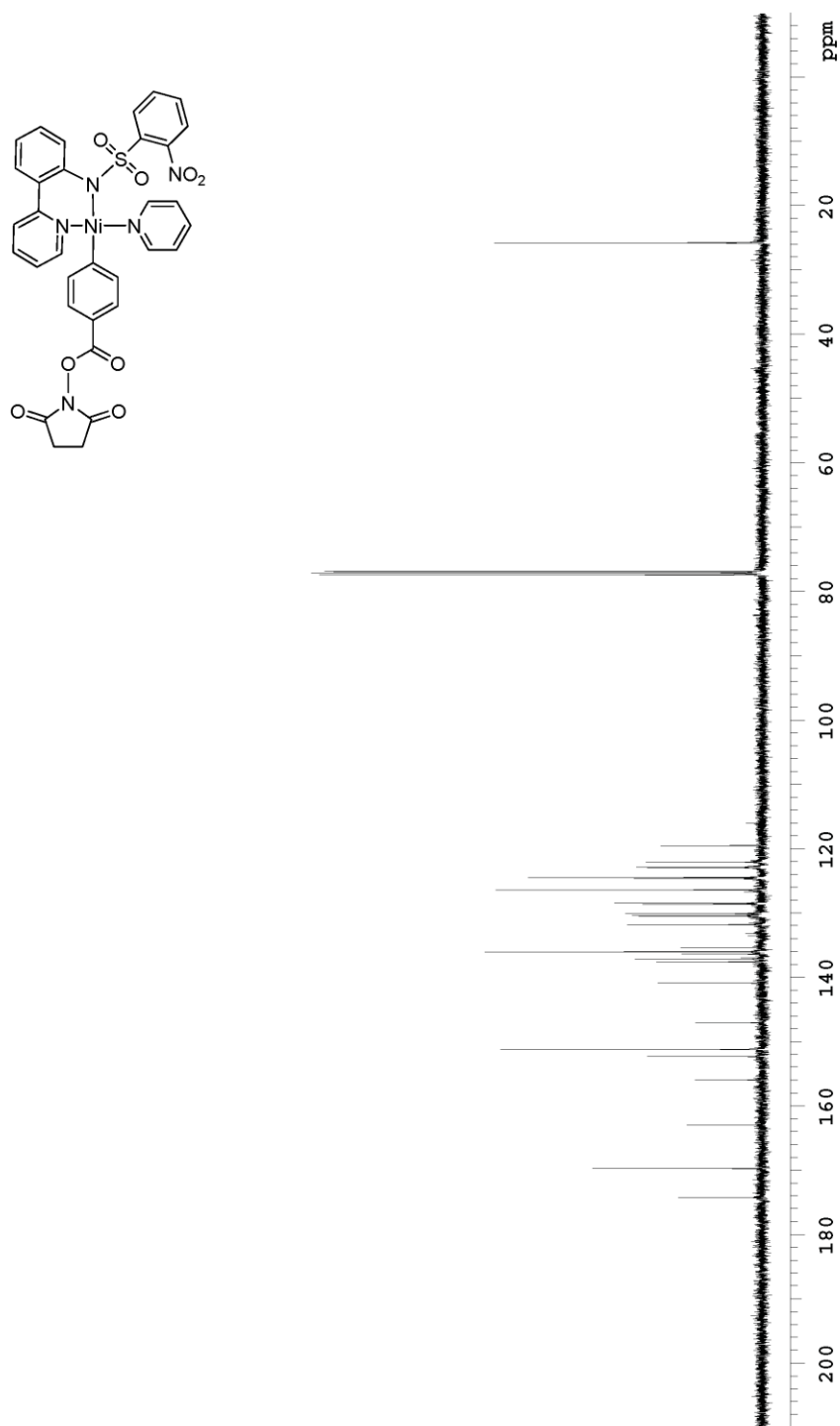
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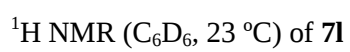
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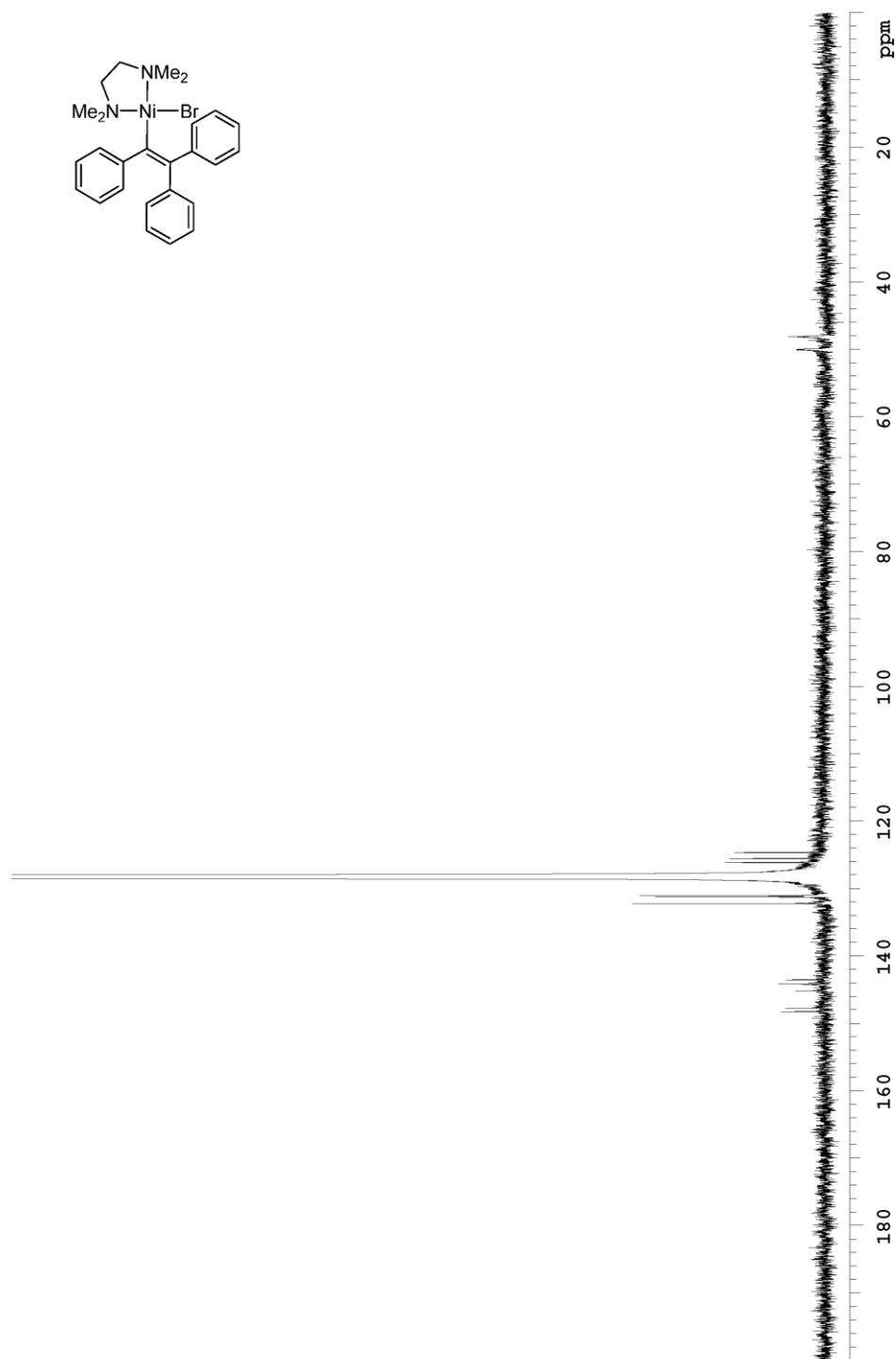


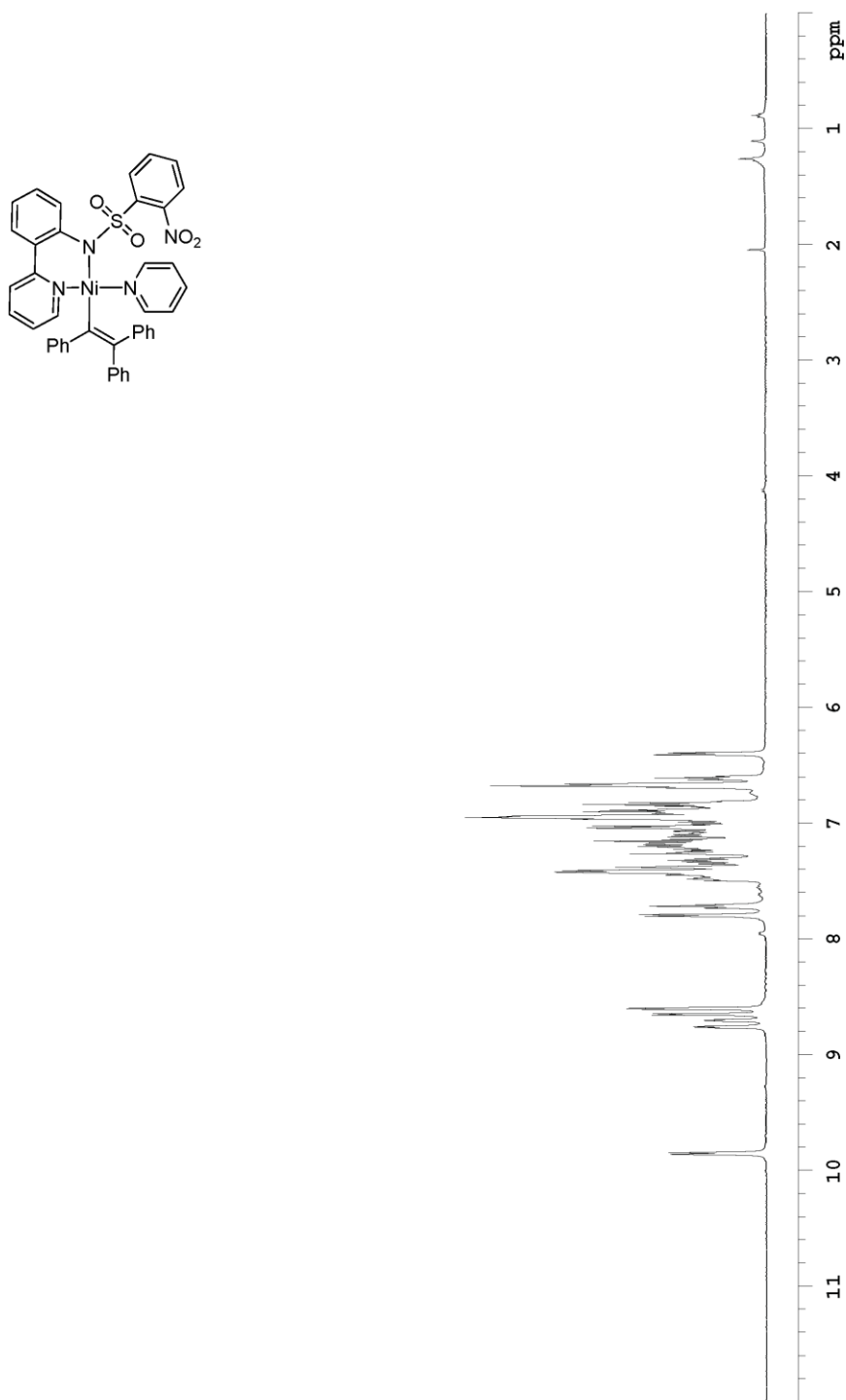
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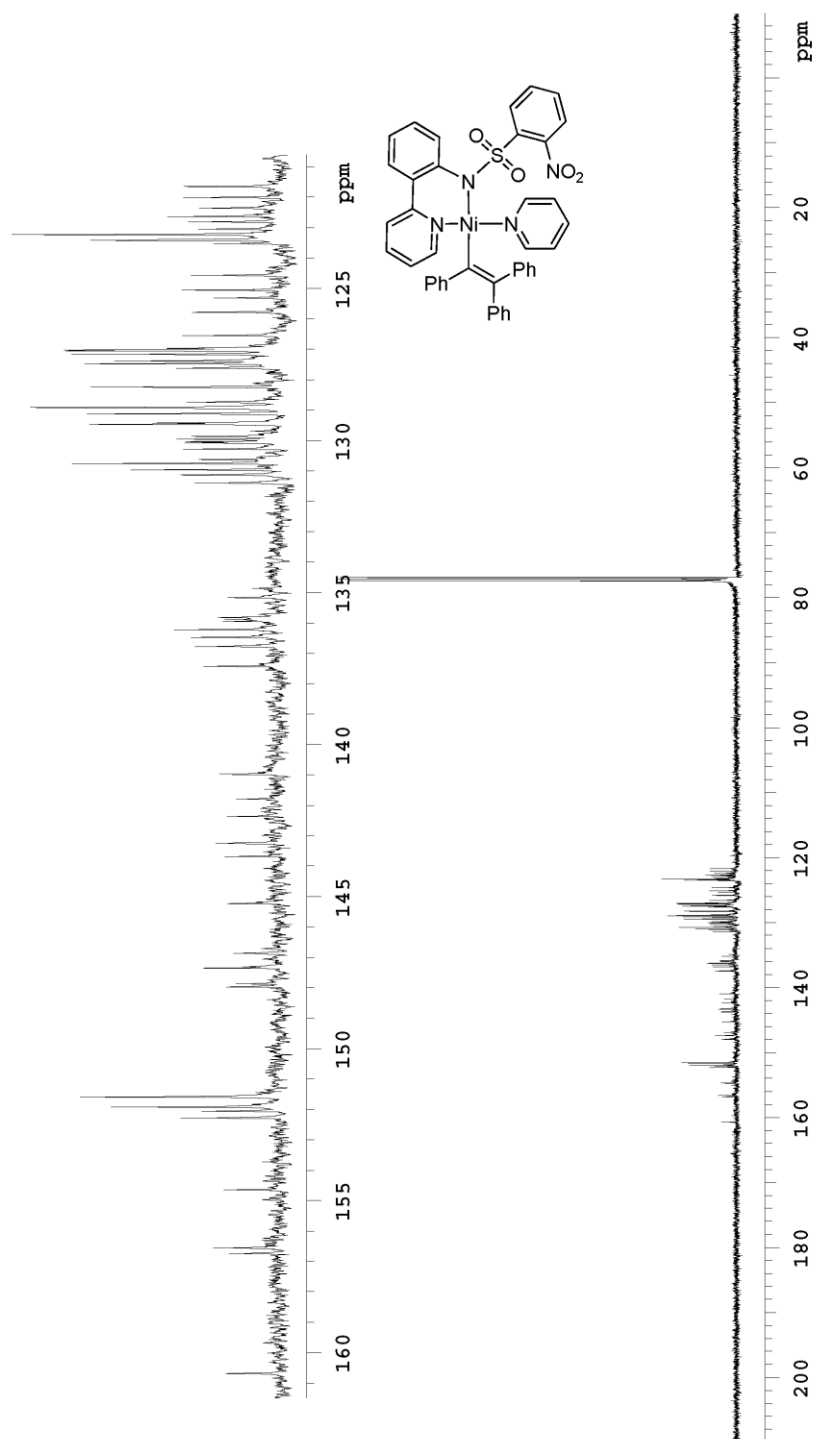
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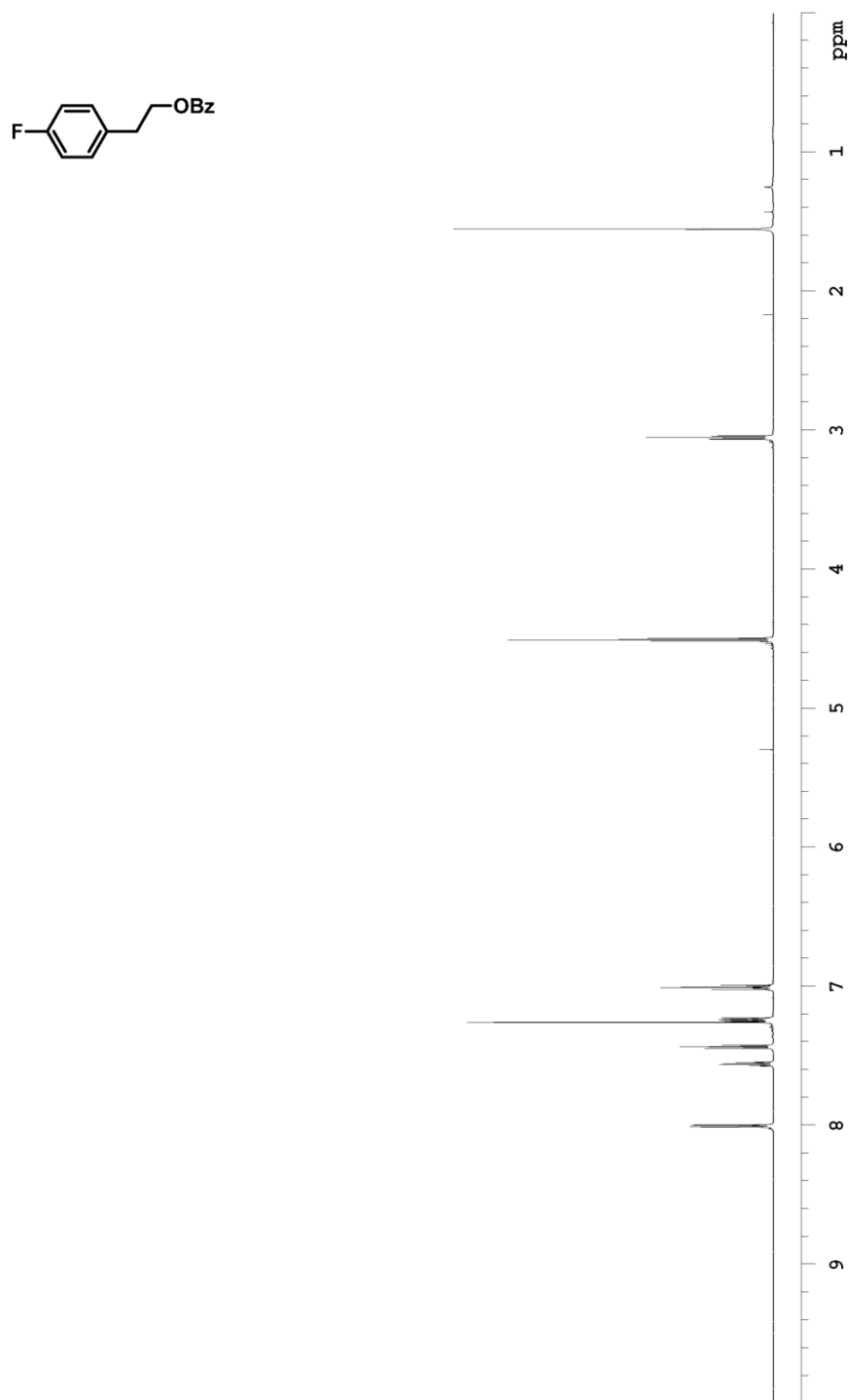
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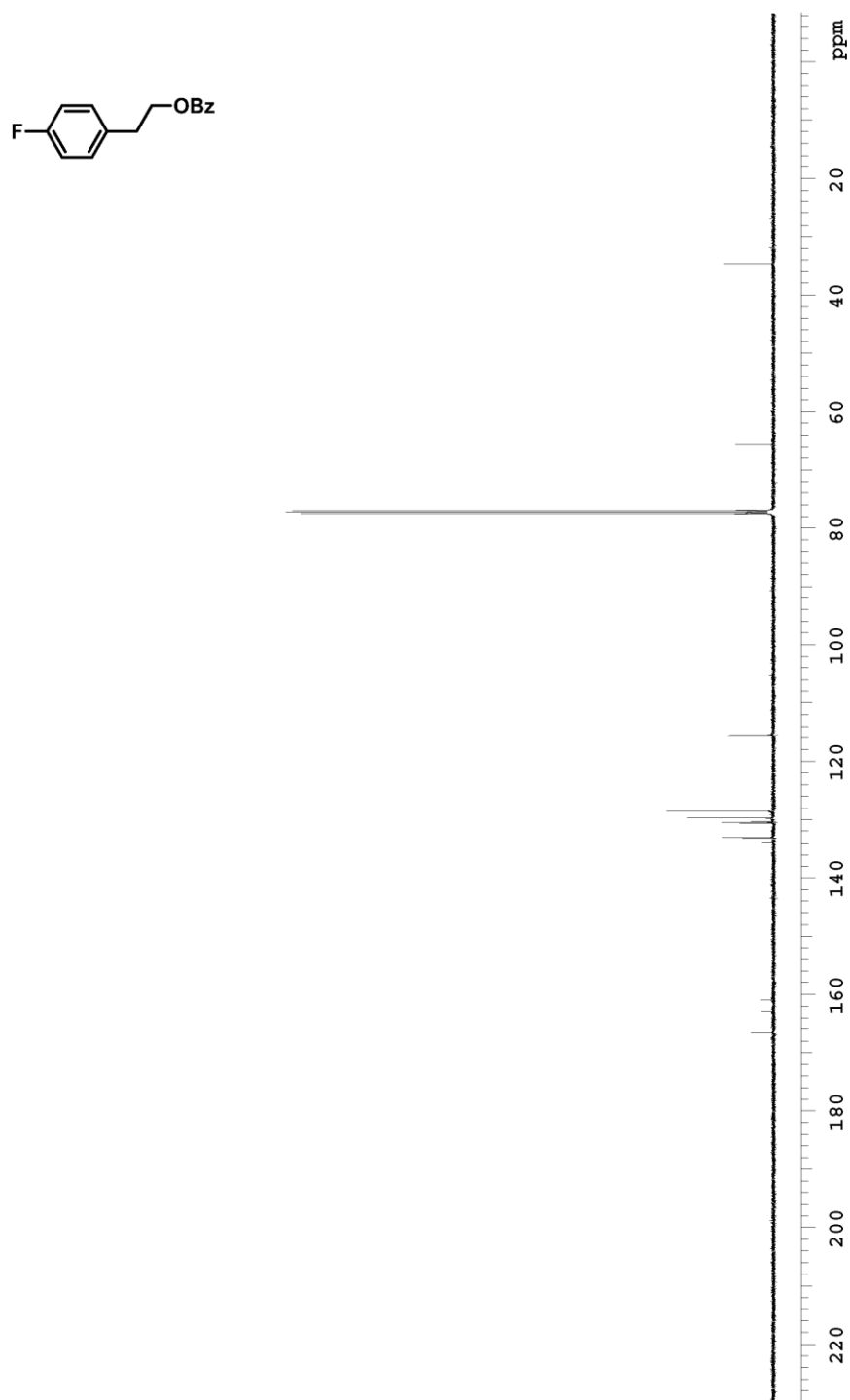


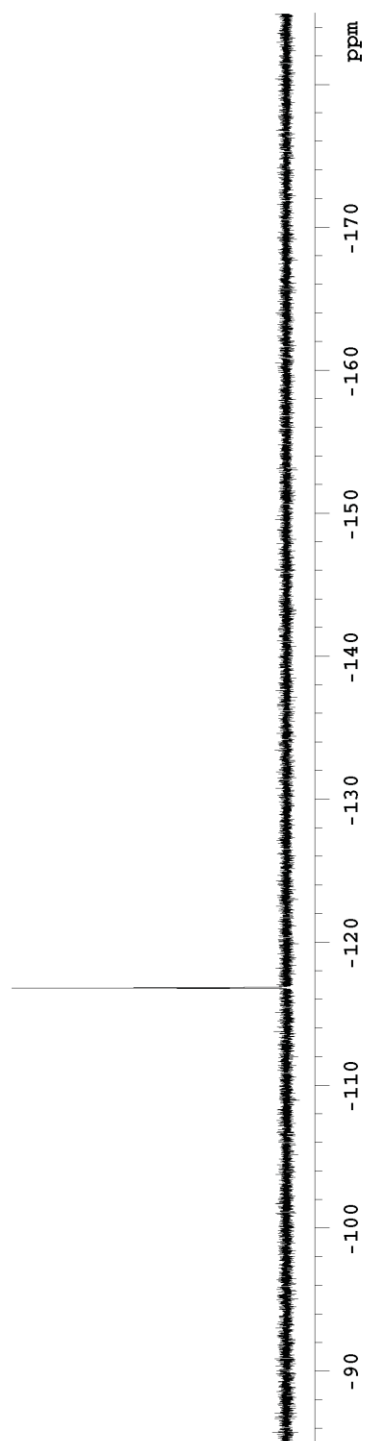
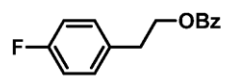
 ^{13}C NMR (C_6D_6 , 23 °C) of **7I**

 ^1H NMR (CDCl_3 , 23°C) of **11**

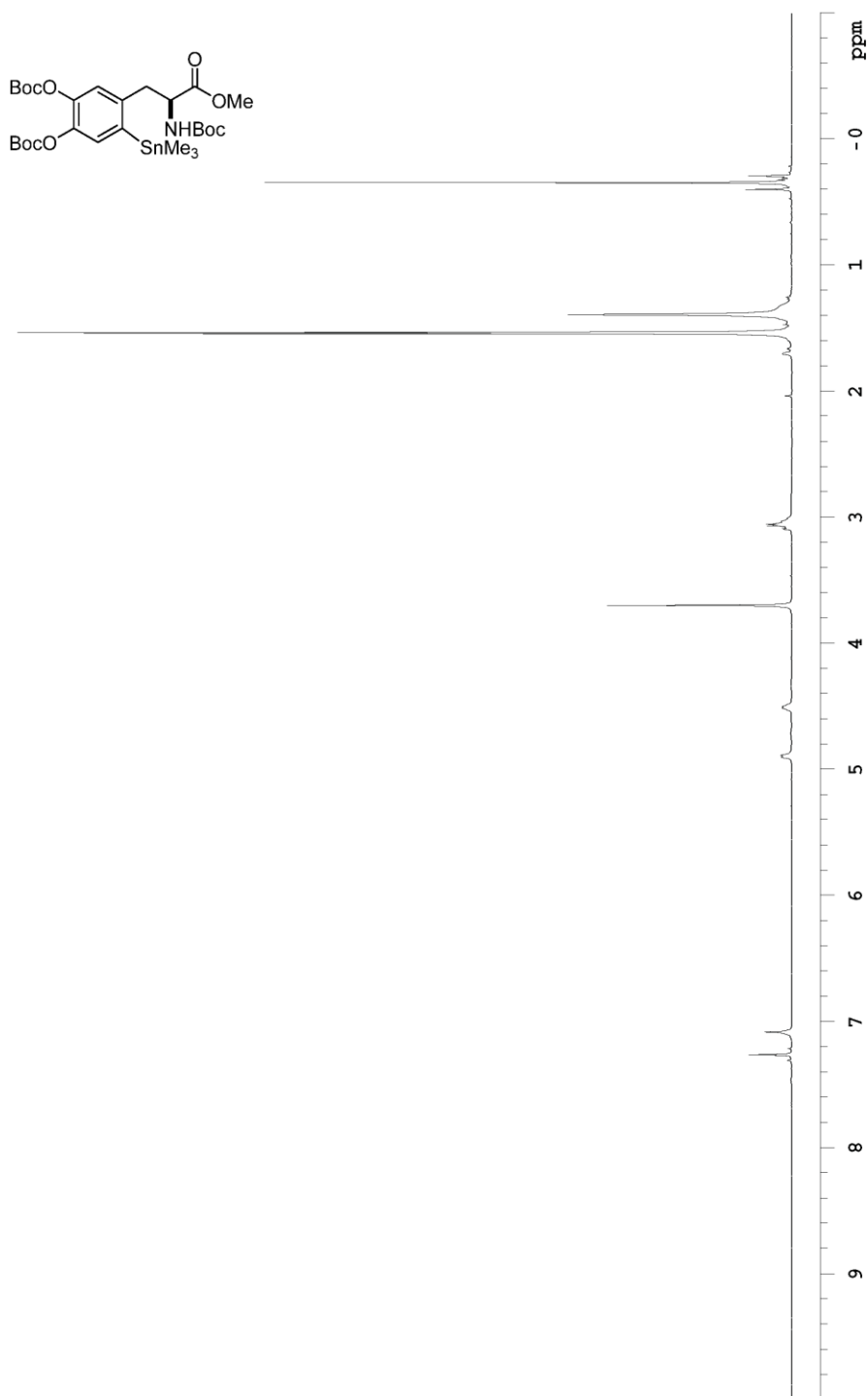
 ^{13}C NMR (CDCl_3 , 23 °C) of **11**

 ^1H NMR (CDCl_3 , 23 °C) of **2f**

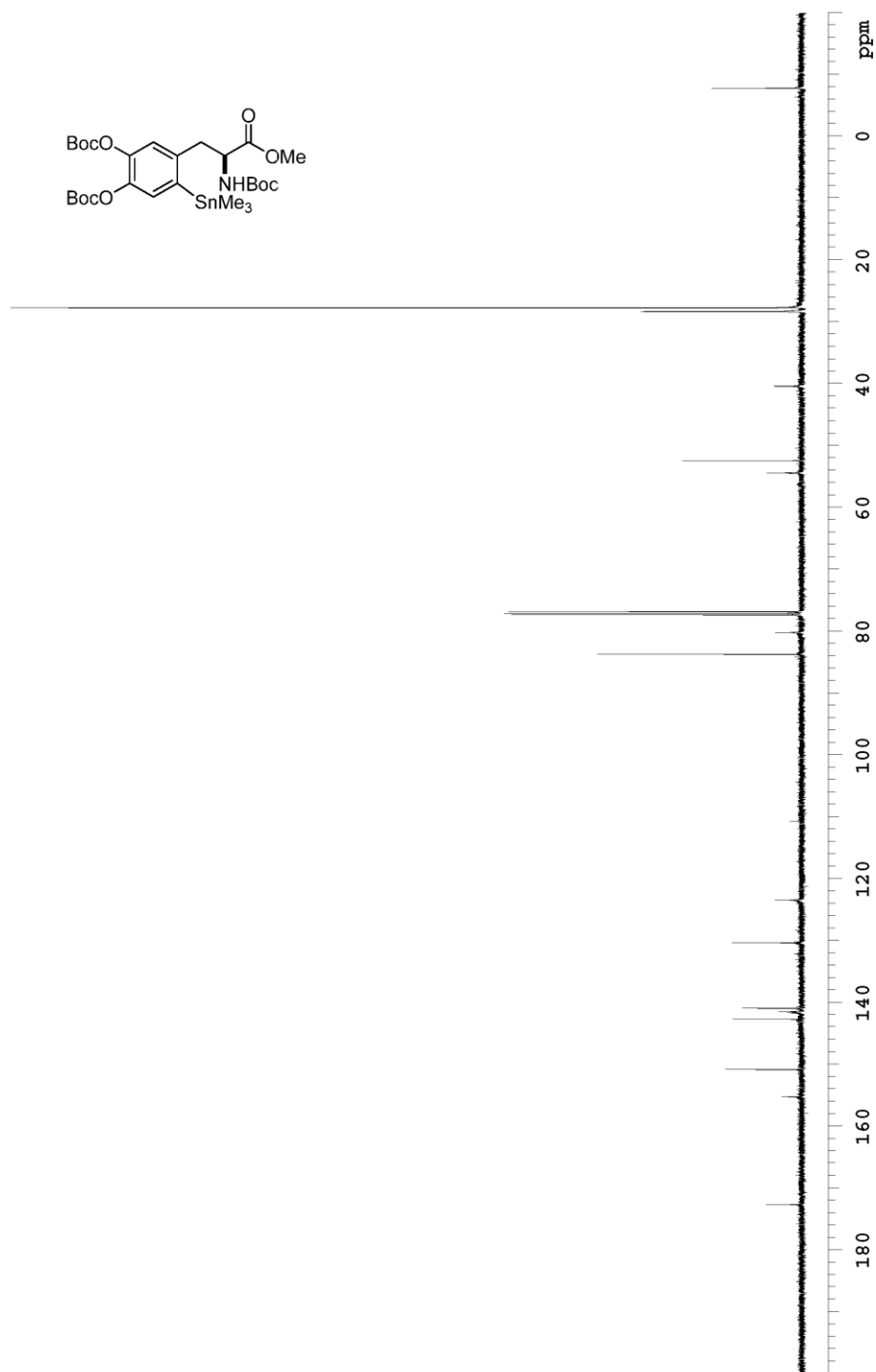
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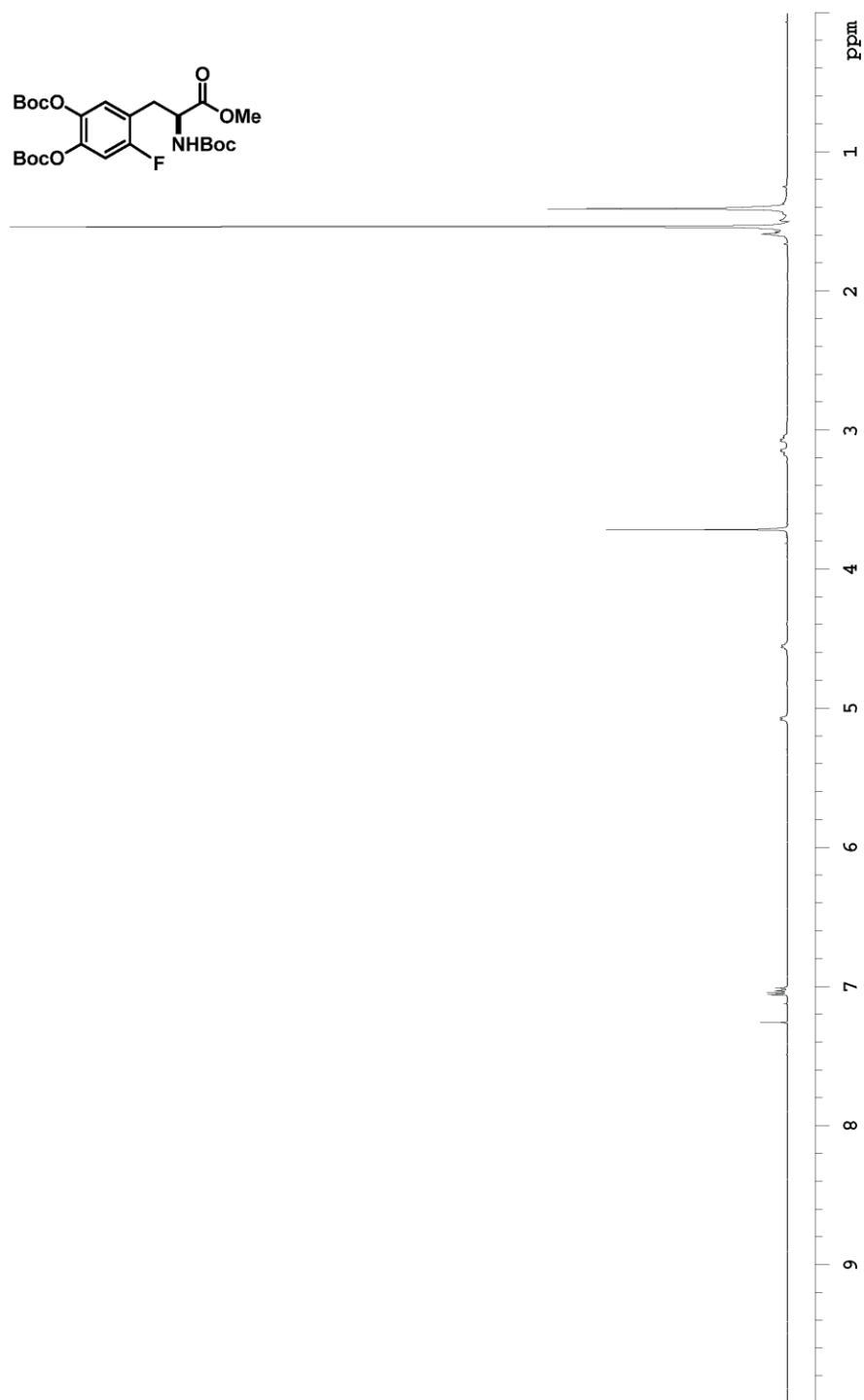


^{19}F NMR (CDCl_3 , 23 °C) of **2f**

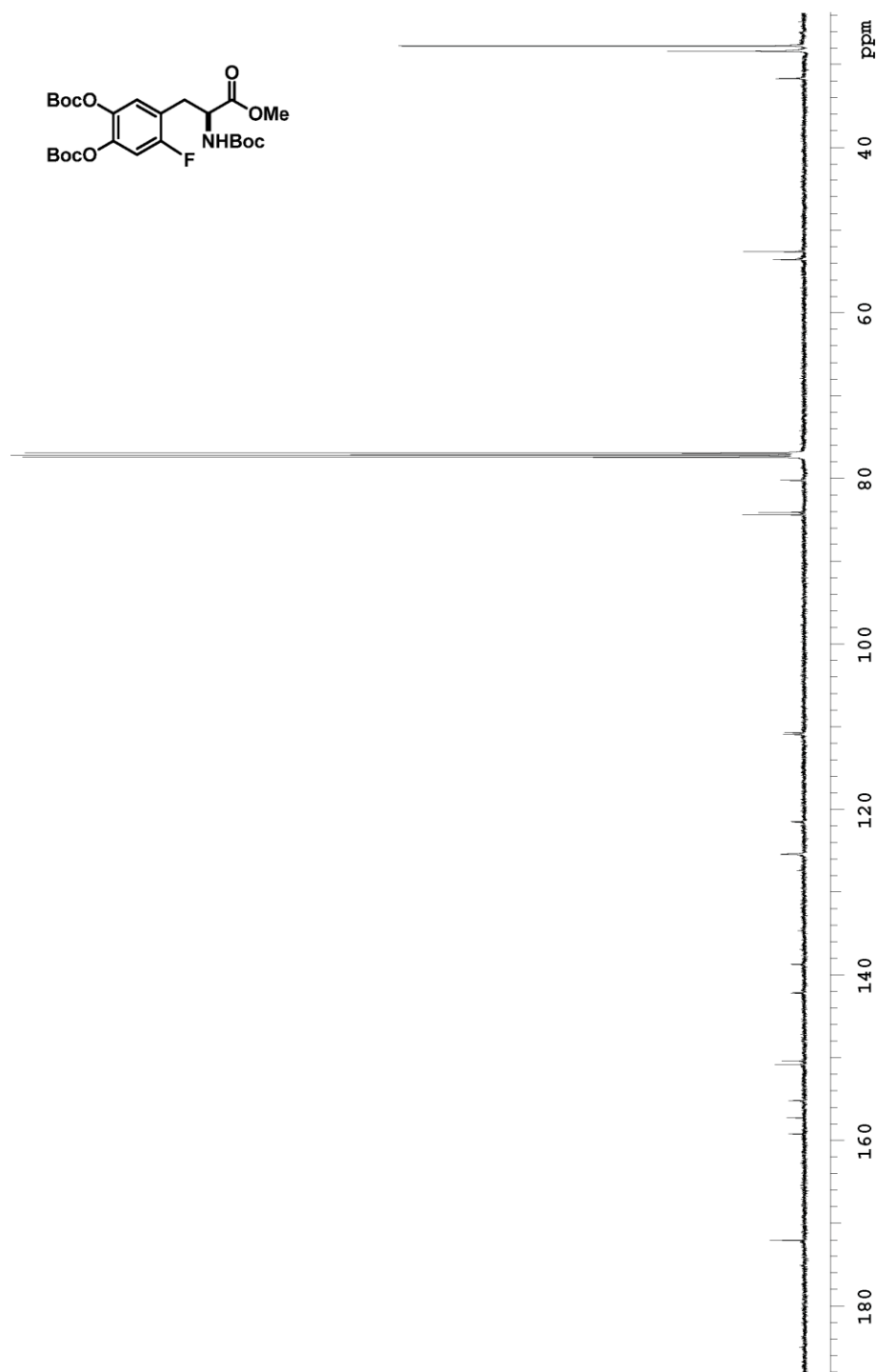


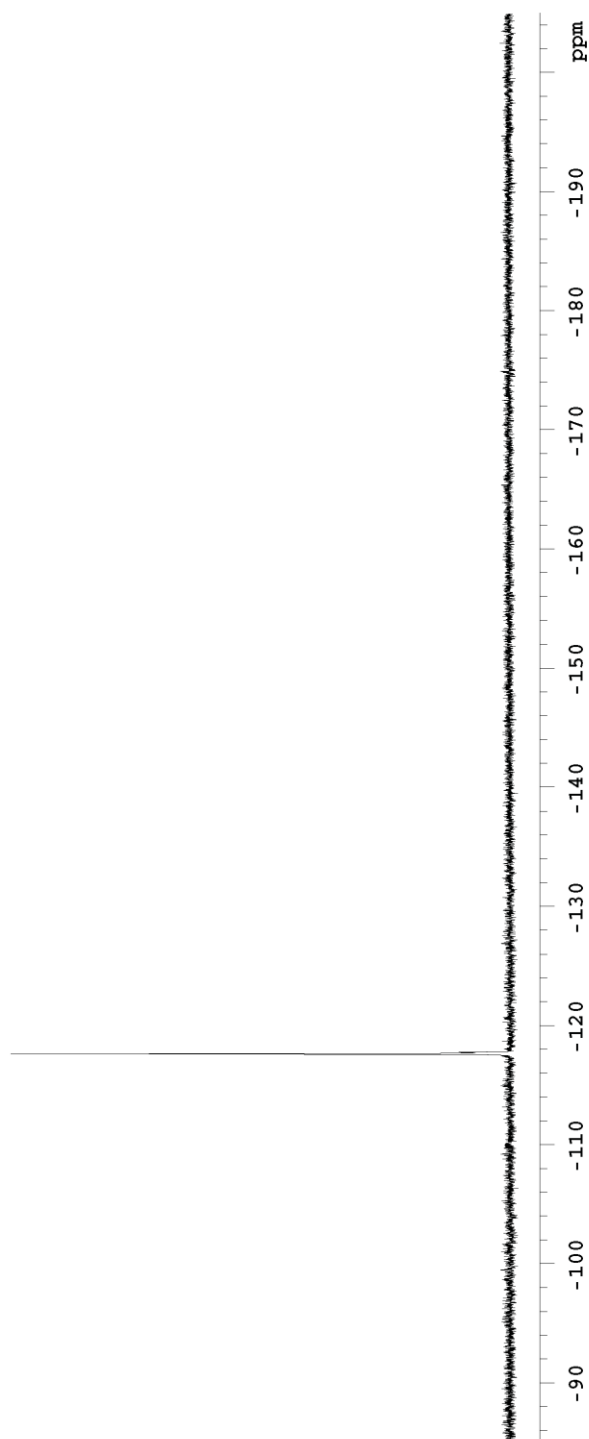
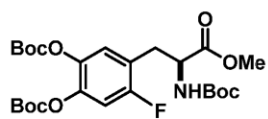
¹H NMR (CDCl₃, 23 °C) of S13

 ^{13}C NMR (CDCl₃, 23 °C) of **S13**

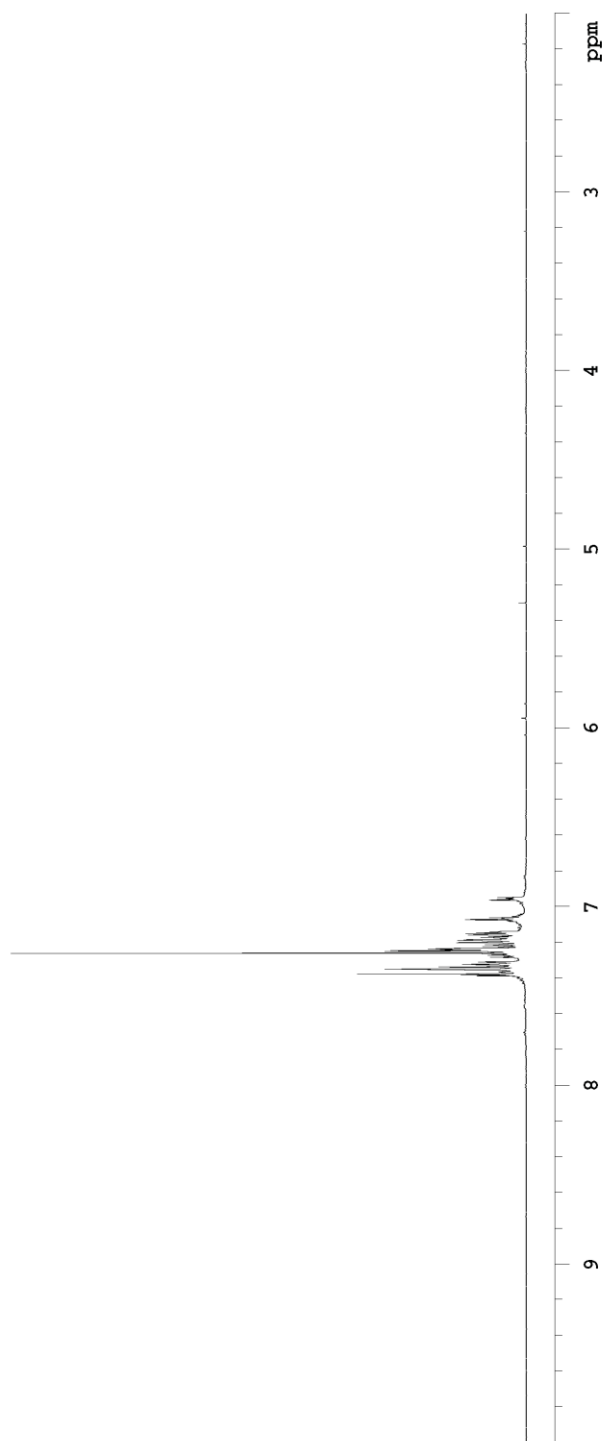
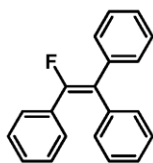


¹H NMR (CDCl₃, 23 °C) of **2i**

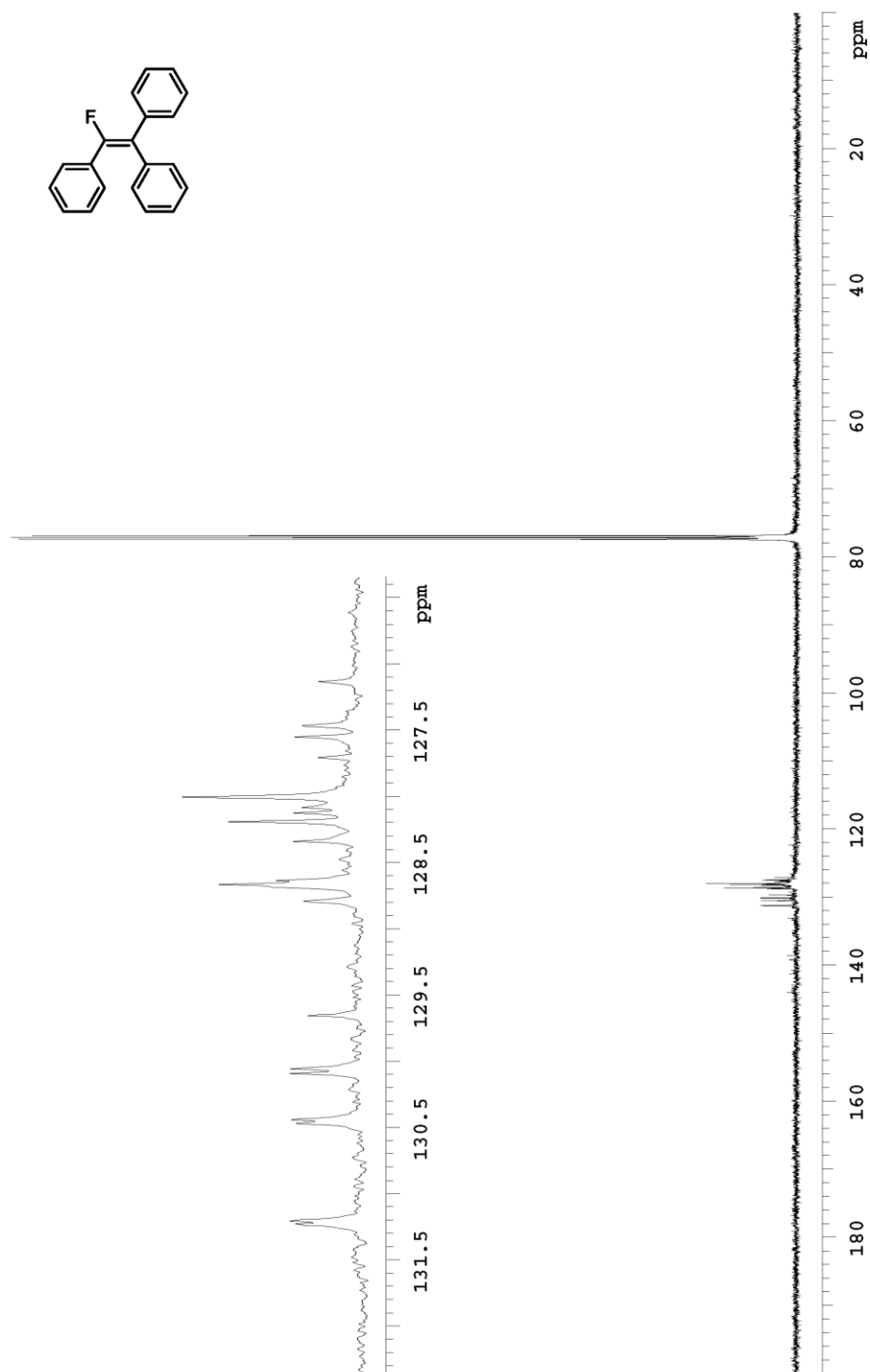
 ^{13}C NMR (CDCl₃, 23 °C) of **2i**

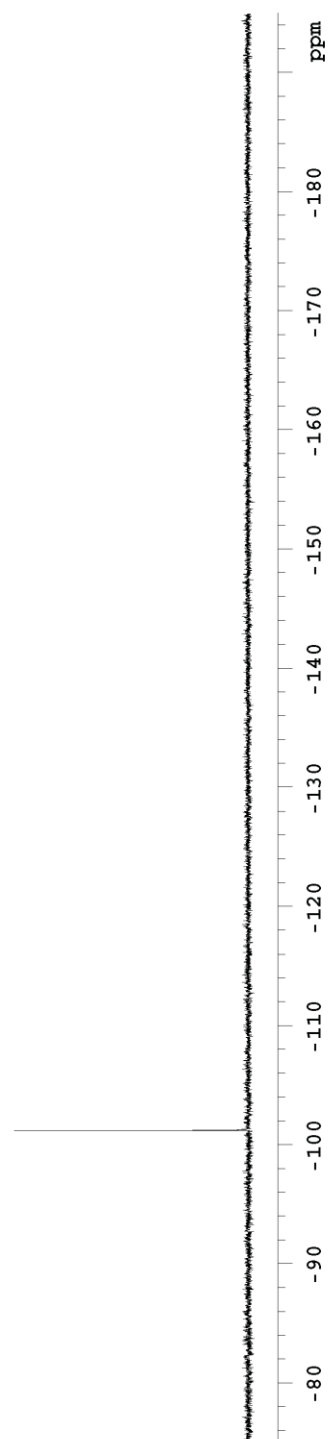
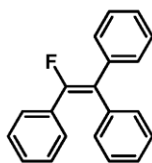


¹⁹F NMR (CDCl₃, 23 °C) of **2f**



¹H NMR (CDCl₃, 23 °C) of **21**

 ^{13}C NMR (CDCl_3 , 23 °C) of **21**

 ^{19}F NMR (CDCl_3 , 23 °C) of **21**

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