Supporting Information

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

Eunsung Lee,[†] Jacob M. Hooker,[‡,§] and Tobias Ritter*[,†,§]

† Department of Chemistry and Chemical Biology, Harvard University, 12 Oxford Street,
Cambridge, Massachusetts 02138, United States

‡ Athinoula A.Martinos Center for Biomedical Imaging, Massachusetts General Hospital and
Harvard Medical School, Charlestown,MA 02129, United States

§ Division of Nuclear Medicine and Molecular Imaging, Department of Radiology,
Massachusetts General Hospital, Boston, MA 02114, United States

E-mail: ritter@chemistry.harvard.edu

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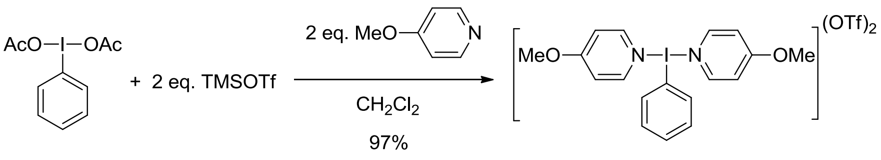
## Materials and Methods

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 ºC 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 ºC under dynamic vacuum ($10^{-4}$ Torr) before use. $Ni(COD)_2$ and all other chemicals were used as received. All deutrated solvents were purchased from Cambridge Isotope Laboratories. $Ni(COD)_2$ 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 $^1$H acquisitions, a Varian Unity/Inova 500 spectrometer operating at 500 MHz and 125 MHz for $^1$H 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 ($^1$H: $CDCl_3$, δ 7.26; $C_6D_6$, δ 7.16; $CD_2Cl_2$, δ 5.32; $D_2O$, δ 4.79; $(CD_3)_2SO$, 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, $(CD_3)_2SO$, 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 25–30 ºC at appropriate pressure. Purified compounds were further dried under high vacuum (0.01–0.05 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-$\lambda^3$-iodanediyl)bis(4-methoxypyridinium) bis(trifluoromethanesulfonate) (6)[5]

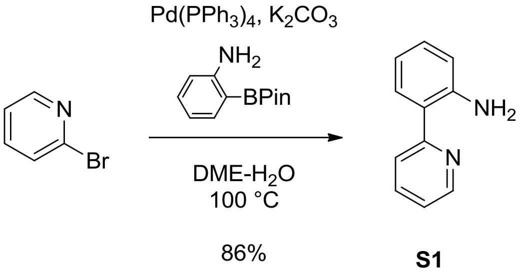


**6**

All manipulations were carried out in a dry box under a $N_2$ atmosphere. To (diacetoxyiodo)benzene (3.00 g, 9.31 mmol, 1.00 equiv) dissolved in $CH_2Cl_2$ (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 $CH_2Cl_2$ (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 $Et_2O$ to precipitate a white solid while stirring vigorously, and the resulting solid was collected on a frit. The solid was washed with $Et_2O$ (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, $CD_3CN$, 23 ºC, 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). $^{13}C$ NMR (125 MHz, $CD_3CN$, 23 ºC, δ): 172.1, 149.9, 136.1, 135.7, 134.2, 125.7, 121.9 (q, *J* = 319 Hz, triflate), 115.3, 58.5. $^{19}F$ NMR (375 MHz, $CD_3CN$, 23 ºC, δ): –77.5. Anal: calcd for $C_{20}H_{19}F_6IN_2O_8S_2$: C, 33.34; H, 2.66; N, 3.89; found: C, 33.05; H, 2.59; N, 3.73.

### 2-(2-Pyridinyl)aniline (S1)

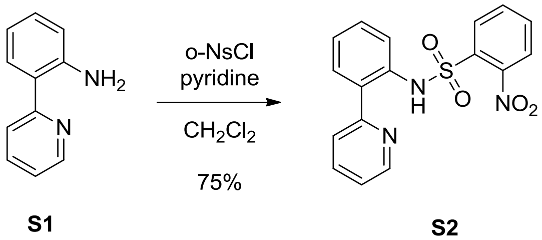


**S1**

Under air, to 2-bromopyridine (4.54 g, 28.7 mmol, 1.00 equiv) in DME–$H_2O$ (1:1, 100 mL) at 23 ºC was added $K_2CO_3$ (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 ºC, 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 ($Na_2SO_4$). 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: $^1$H NMR (500 MHz, $CDCl_3$, 23 ºC, 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). $^{13}$C NMR (125 MHz, $CDCl_3$, 23 ºC, 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]

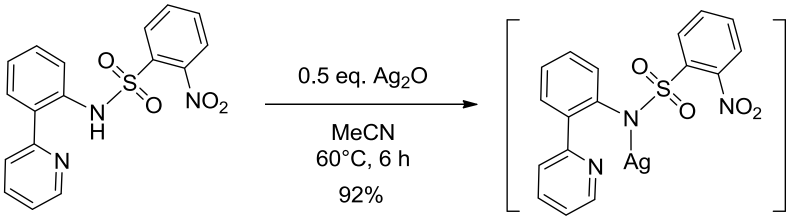
### 2-(2-Pyridinyl)-2-nitrobenzenesulfonanilide (S2)



To 2-(2-pyridinyl)aniline (**S1**) (851 mg, 5.00 mmol, 1.00 equiv) in $CH_2Cl_2$ (10 mL) at 0 ºC 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 ºC and stirred for 2.0 hr before the addition of water (10 mL). The phases were separated and the aqueous layer was extracted with $CH_2Cl_2$ (3 × 8 mL). The combined organic phases were washed with brine (30 mL) and dried ($Na_2SO_4$). 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 ºC. NMR Spectroscopy: $^1$H NMR (500 MHz, $CDCl_3$, 23 ºC, 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). $^{13}$C NMR (125 MHz, $CDCl_3$, 23 ºC, 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 [$C_{17}H_{13}N_3O_4S$ + 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)



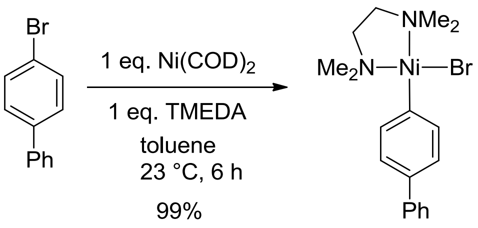
**S2** **8**

To silver(I) oxide (4.99 g, 21.5 mmol, 0.500 equiv) in $CH_3CN$ (200 mL) at 23 ºC was added 2-(2-pyridinyl)phenyl-2-nitrobenzenesulfonanilide (**S2**) (15.3 g, 43.1 mmol, 1.00 equiv). After stirring for 12 h at 65 ºC, 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 $C_{17}H_{12}AgN_3O_4S$: C, 44.17; H, 2.62; N, 9.09; found: C, 44.06; H, 2.66; N, 9.00. $^1H$ and $^{13}C$ 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]

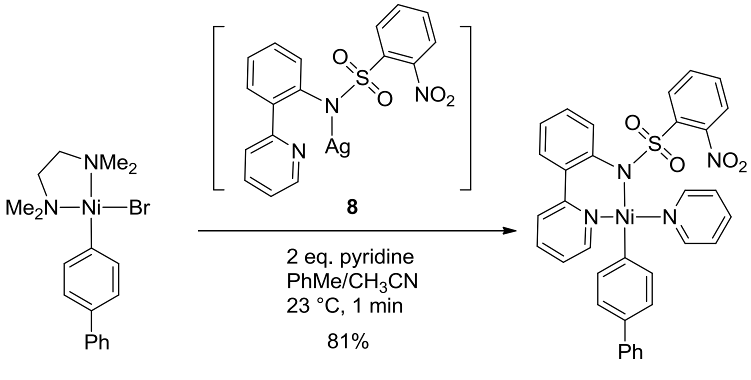


**7a**

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, $CD_2Cl_2$, 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). $^{13}C$ NMR (125 MHz, $CD_2Cl_2$, 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 $^{13}C$ NMR spectra was previously reported for a similar nickel complex.[8a] Anal: calcd for $C_{18}H_{25}BrN_2Ni$: 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

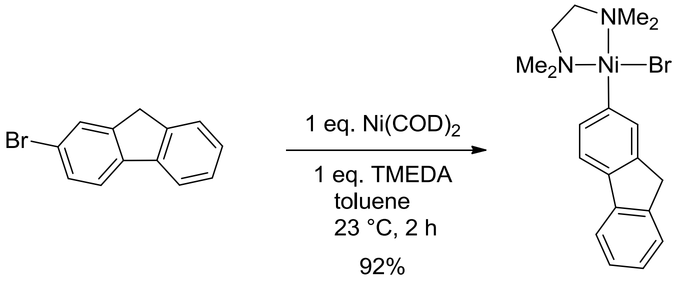


**7a** **1a**

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 ºC, 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: $^1$H 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 $C_{34}H_{26}N_4NiO_4S$: 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

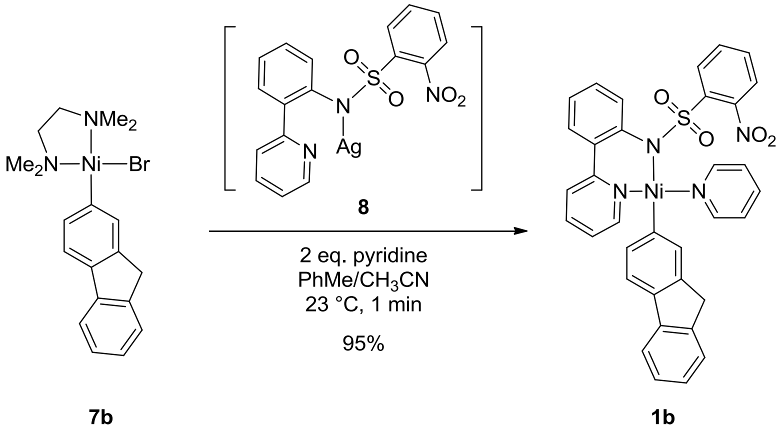


**7b**

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 Ni(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%).

$^1$H NMR (500 MHz, CD$_2$Cl$_2$, 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$_2$Cl$_2$, 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 $C_{19}H_{25}BrN_2Ni$: C, 54.33; H, 6.00; N, 6.67; found: C, 53.98; H, 5.85; N, 6.56.

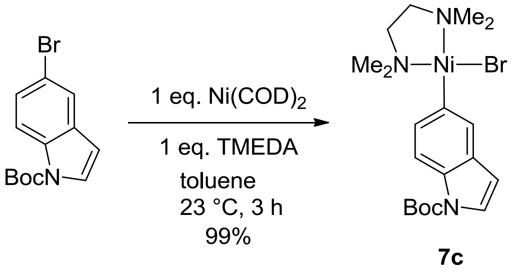
**Synthesis of nickel aryl complex 1b**



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 ºC, 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$_2$Cl$_2$ (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: $^1$H NMR (500 MHz, CDCl$_3$, 23 ºC, 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 ºC, 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 $C_{35}H_{26}N_4NiO_4S\cdot(CH_2Cl_2)_{0.1}$: C, 63.31; H, 3.97; N, 8.41; found: C, 63.04; H, 4.18; N, 8.36.

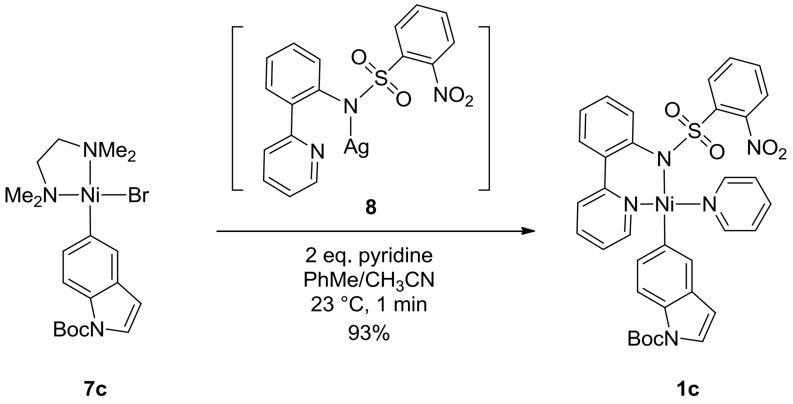
**Synthesis of nickel aryl bromide complex 7c**



To a solution of TMEDA (122 mg, 0.157 mL, 1.05 mmol, 1.00 equiv) and *tert*-butyl 5-bromoindole-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%).

$^1$H NMR (600 MHz, $CD_2Cl_2$, 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). $^{13}$C NMR (125 MHz, $CD_2Cl_2$, 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 $C_{19}H_{30}BrN_3NiO_2$: C, 48.44; H, 6.42; N, 8.92; found: C, 48.14; H, 6.22; N, 8.84.

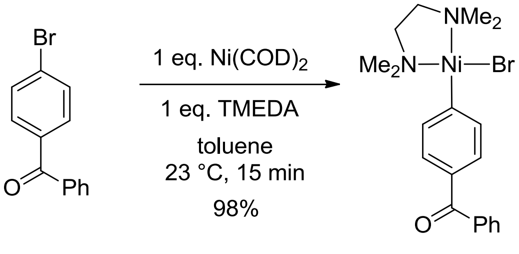
**Synthesis of nickel aryl complex 1c**



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 ºC, 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 140 mg of the title compound as a yellow solid (93%).

$R_f$ = 0.53 (hexanes/EtOAc 1:2 (v/v)). NMR Spectroscopy: $^1$H NMR (500 MHz, $CDCl_3$, 23 ºC, 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). $^{13}$C NMR (125 MHz, $CDCl_3$, 23 ºC, 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 $C_{35}H_{31}N_5NiO_6S$ $(CH_2Cl_2)_{0.1}$: 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 $CH_2Cl_2$ solution that contained 10.0 mg of the title compound slowly layered with 8.0 mL pentane at 23 ºC. For crystallography data, see X-ray section.

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

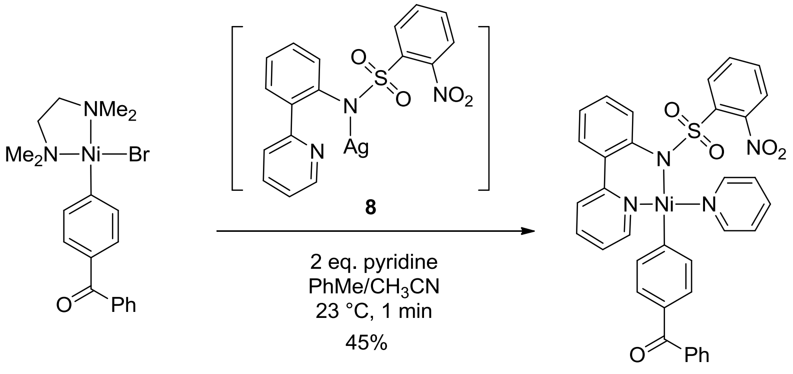


**7d**

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%).

$^1$H NMR (600 MHz, $CD_2Cl_2$, 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). $^{13}$C NMR (125 MHz, $CD_2Cl_2$, 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 $C_{19}H_{25}BrN_2NiO$ $(PhMe)_{0.1}$: 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

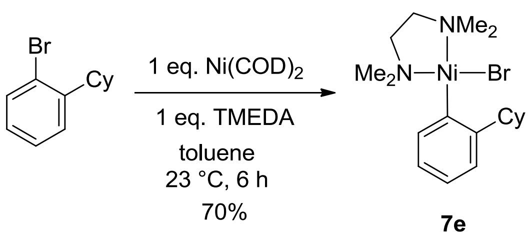


**7d** **1d**

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 ºC, 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: $^1$H NMR (500 MHz, $CD_2Cl_2$, 23 ºC, 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 ºC, 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 $C_{35}H_{26}N_4NiO_5S\ (CH_2Cl_2)_{0.15}$: 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



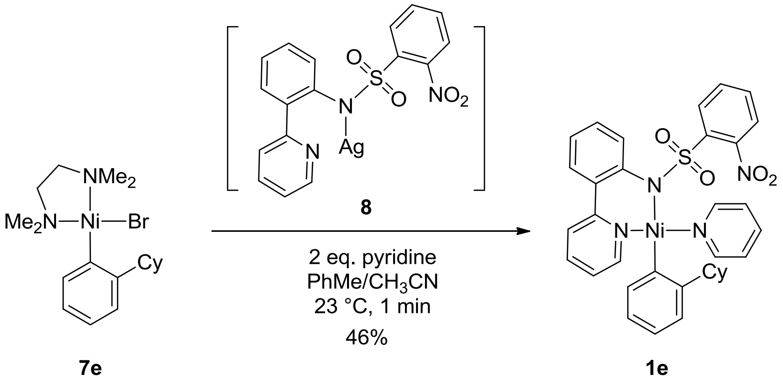
**7e**

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%).

$^{1}$H 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 $C_{18}H_{31}BrN_2Ni$: C, 52.21; H, 7.55; N, 6.77; found: C, 51.87; H, 7.43; N, 6.73.

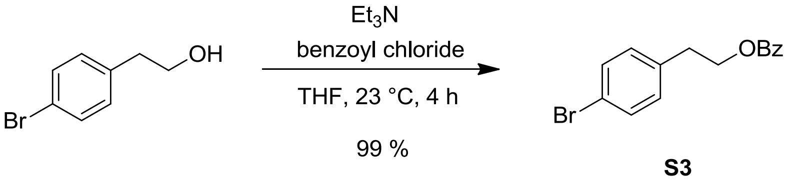
**Synthesis of nickel aryl complex 1e**



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 ºC, 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: $^{1}$H NMR (500 MHz, $CDCl_3$, 23 ºC, 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 ºC, 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 $C_{34}H_{32}N_4NiO_4S\ (CH_2Cl_2)_{0.1}$: C, 62.07; H, 4.92; N, 8.49; found: C, 61.91; H, 4.92; N, 8.69.

### 4-bromophenethyl benzoate (S3)

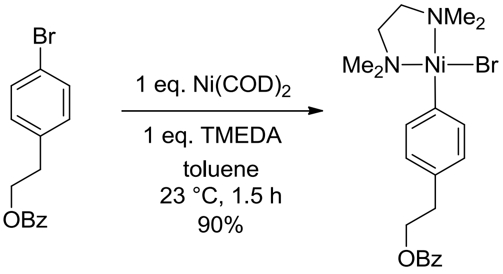


**S3**

To a mixture of 2-(4-bromophenyl)ethanol (1.00 g, 4.97 mmol, 1.00 equiv) and $Et_3N$ (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 ºC 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: $^1$H NMR (500 MHz, $CDCl_3$, 23 ºC, 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). $^{13}$C NMR (125 MHz, $CDCl_3$, 23 ºC, 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 $C_{15}H_{13}BrO_2$ $[M + Na]^+$, 326.9991; found, 327.0007.

### Synthesis of nickel aryl bromide complex 7f

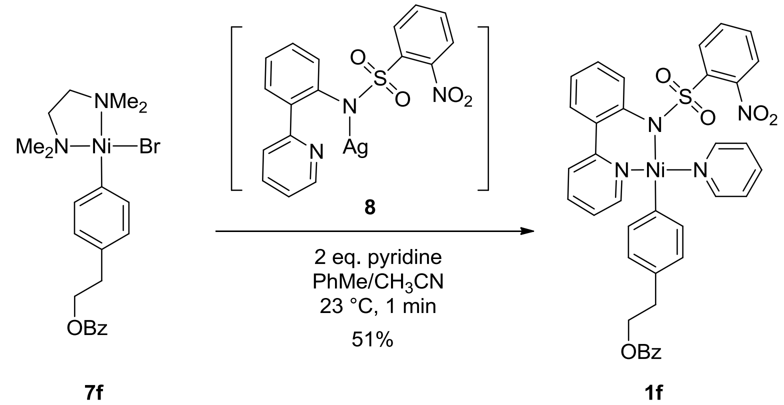


**7f**

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%).

$^1$H NMR (600 MHz, $CD_2Cl_2$, 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).. $^{13}$C NMR (125 MHz, $CD_2Cl_2$, 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 $C_{21}H_{29}BrN_2NiO_2$: C, 52.54; H, 6.09; N, 5.84; found: C, 52.81; H, 5.95; N, 5.53.

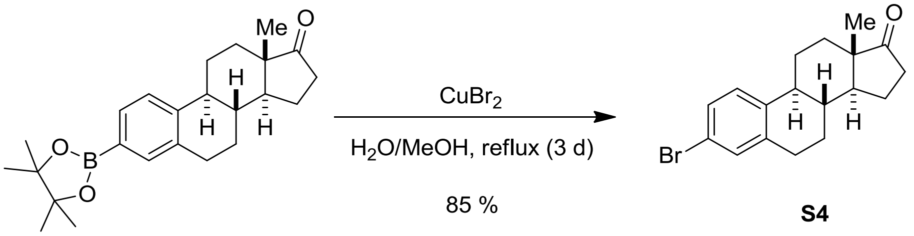
**Synthesis of nickel aryl complex 1f**



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 ºC, 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: $^1$H NMR (400 MHz, $CDCl_3$, 23 ºC, 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 ºC, 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 $C_{37}H_{30}N_4NiO_6S$: C, 61.94; H, 4.21; N, 7.81; found: C, 61.58; H, 4.16; N, 7.47.

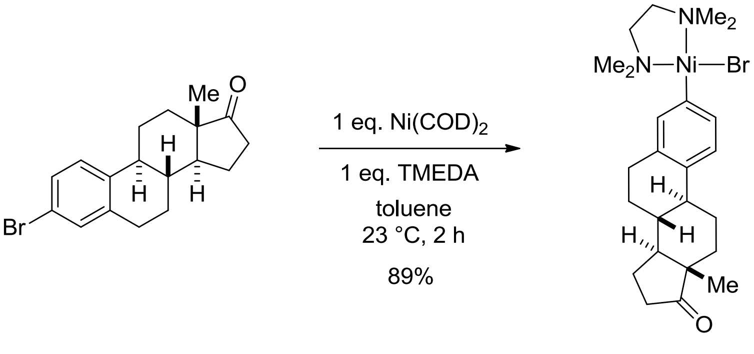
**Synthesis of 3-deoxy-3-bromoestrone (S4)**



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 ºC and subsequently poured into $H_2O$ (200 mL). The colorless precipitate was collected on a frit, followed by washing with water (3 × 30 mL). $CH_2Cl_2$ (100 mL) was added to the solid and the solution was filtered though a pad of Celite. The filtrate was concentrated, triturated with $Et_2O$ (3 × 5 mL) and dried to afford 2.60 g of the title compound as a colorless solid (85% yield).

NMR Spectroscopy: $^1$H NMR (500 MHz, $CDCl_3$, 23 ºC, 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). $^{13}$C NMR (125 MHz, $CDCl_3$, 23 ºC, 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 $C_{18}H_{21}BrO$ $[M + Na]^+$, 333.0849; found, 333.0861.

### Synthesis of nickel aryl bromide complex 7g

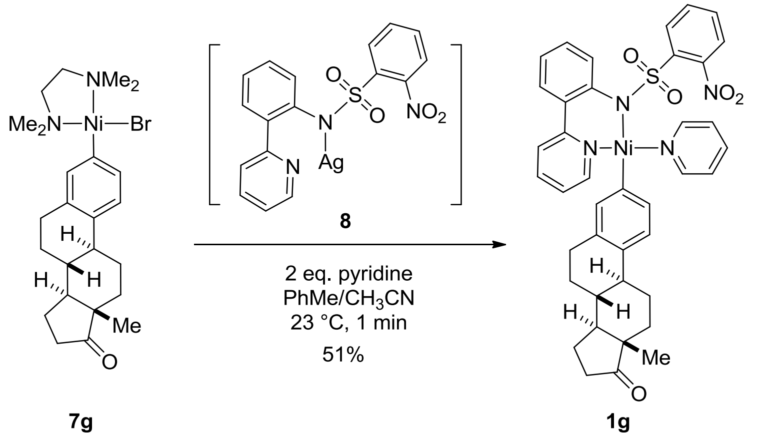


**7g**

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: $^1$H NMR (600 MHz, $CD_2Cl_2$, 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). $^{13}$C NMR (125 MHz, $CD_2Cl_2$, 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 $C_{24}H_{37}BrN_2NiO$: 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 $C_{24}H_{37}N_2NiO$ $[M – Br]^+$, 427.2259; found, 427.2263.

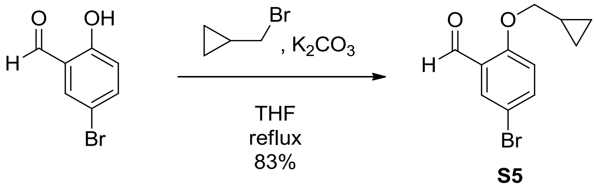
### Synthesis of nickel aryl complex 1g



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 µL, 0.833 mmol, 2.00 equiv) at 23 ºC, 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: $^1$H NMR (500 MHz, $CDCl_3$, 23 ºC, 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 ºC, 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 $C_{40}H_{38}N_4NiO_5S$ $(CH_2Cl_2)_{0.1}$: 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]

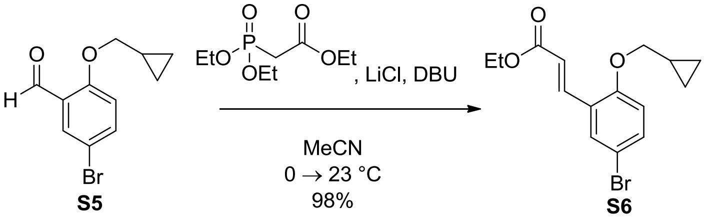


To 5-bromo-2-hydroxybenzaldehyde (1.00 g, 4.97 mmol, 1.00 equiv) and $K_2CO_3$ (3.44 g, 24.9

mmol, 5.00 equiv) in THF (10 mL) in an oven-dried round-bottom flask fitted with a reflux condenser under a $N_2$ atmosphere at 23 ºC 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 ºC and heated at reflux with vigorous stirring for 40 hours. The reaction mixture was cooled to 23 ºC and poured into $H_2O$ (30 mL) in a separatory funnel. $CHCl_3$ (30 mL) was added, the funnel was shaken and the organic phase collected. The aqueous phase was then extracted with $CHCl_3$ (2 × 30 mL). The combined organic phases were washed with brine (30 mL), dried with $Na_2SO_4$, 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: $^1$H NMR (600 MHz, $CDCl_3$, 23 ºC, 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). $^{13}$C NMR (125 MHz, $CDCl_3$, 23 ºC, 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 $C_{11}H_{11}BrNaO_2$ [M + Na]$^+$, 276.9840; found, 276.9820.

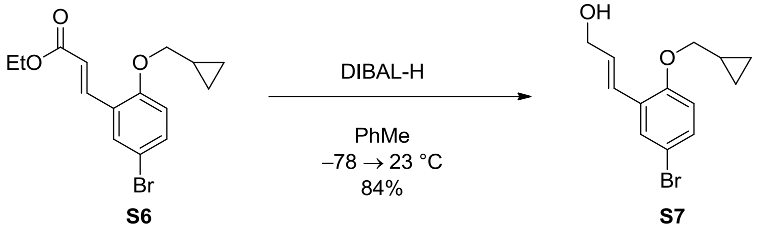
**(*E*)-ethyl 3-(5-bromo-2-(cyclopropylmethoxy)phenyl)acrylate (S6)**



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 $N_2$ atmosphere at 0 ºC 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 ºC and stirred for 15 hours. The reaction mixture was poured into $H_2O$ (75 mL) in a separatory funnel. $CHCl_3$ (75 mL) was added and the funnel was shaken and the organic phase collected. The aqueous phase was extracted from with $CHCl_3$ (2 × 50 mL). All organic phases were combined and washed with brine (50 mL), dried with $Na_2SO_4$, 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: $^1$H NMR (500 MHz, $CDCl_3$, 23 ºC, 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). $^{13}$C NMR (125 MHz, $CDCl_3$, 23 ºC, 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.

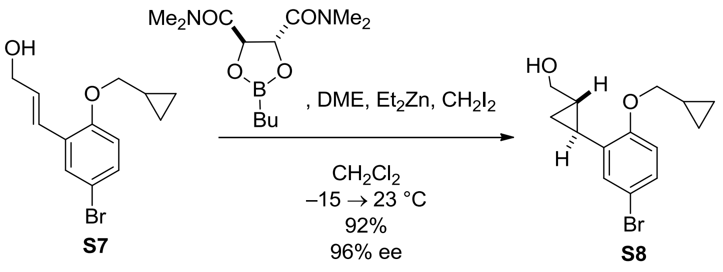
### (*E*)-3-(5-bromo-2-(cyclopropylmethoxy)phenyl)prop-2-en-1-ol (S7)



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 ºC 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 ºC over 2 hours and then warmed to 23 ºC 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: $^1$H NMR (500 MHz, $CDCl_3$, 23 ºC, 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 ºC, 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.

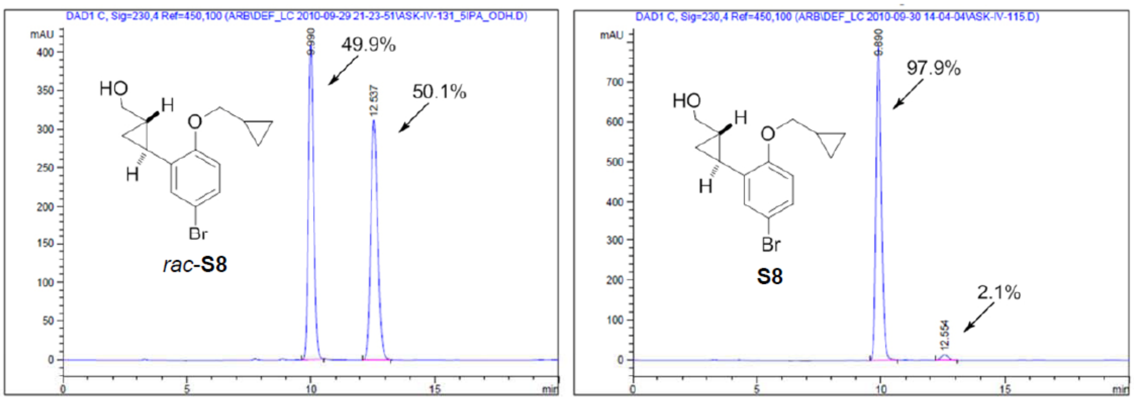
### ((1*S*,2*S*)-2-(5-bromo-2-(cyclopropylmethoxy)phenyl)cyclopropyl)methanol (S8)



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 $N_2$ atmosphere cooled in an ethyleneglycol/$CO_2$ bath at –15 ºC was added diethylzinc (2.01 g, 1.67 mL, 16.3 mmol, 2.00 equiv), while maintaining the bath temperature between –15 and –10 ºC. $CH_2I_2$ (8.70 g, 2.62 mL, 32.5 mmol, 4.00 equiv) was added dropwise over 20 minutes at –15 ºC. The reaction mixture was stirred at –15 ºC 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 $CH_2Cl_2$ (10 mL) from a separate flame-dried round-bottom flask under a $N_2$ 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 $CH_2Cl_2$ (10 mL) from a separate flame-dried round-bottom flask under a $N_2$ atmosphere was added over 5 minutes via syringe. The reaction mixture was allowed to warm to 23 ºC and stirred for 20 hours. Saturated aqueous $NH_4Cl$ 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% $H_2O_2$ 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 $Na_2CO_3$ solution (75 mL), saturated aqueous $NaHCO_3$ solution (75 mL) and brine (75 mL). The organic phase was dried with $MgSO_4$, 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]

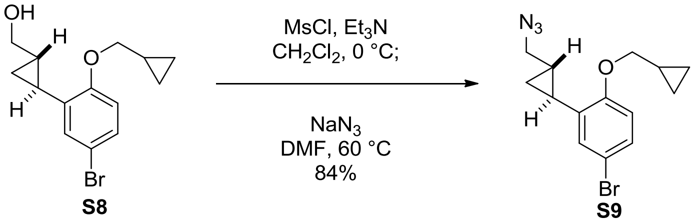
$R_f$ = 0.20 (hexanes/EtOAc 6:1 (v/v)). NMR Spectroscopy: $^1H$ NMR (500 MHz, $CDCl_3$, 23 ºC, δ): 7.24 (dd, *J* = 8.8, 2.4 Hz, 1H), 7.09 (d, *J* = 2.4 Hz, 1H), 6.65 (d, *J* = 8.8 Hz, 1H), 3.95 (ddd, *J* = 10.7, 8.8, 4.9 Hz, 1H), 3.82 (d, *J* = 7.3 Hz, 2H), 3.19 (ddd, *J* = 10.7, 10.7, 2.0, 1H), 2.40 (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). $^{13}C$ NMR (125 MHz, $CDCl_3$, 23 ºC, 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 $C_{14}H_{17}BrNaO_2$ $[M + Na]^+$, 319.0310; found, 319.0327.

**Figure S1: Enantiodiscriminating HPLC trace of S8**



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

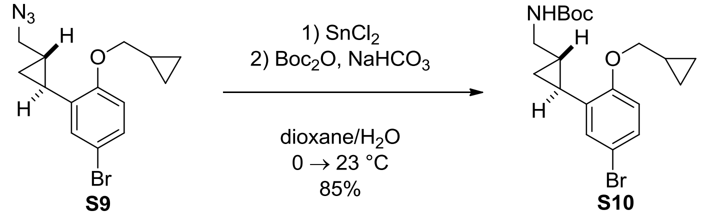
**2-((1*S*,2*S*)-2-(azidomethyl)cyclopropyl)-4-bromo-1-(cyclopropylmethoxy)benzene (S9)**



To ((1*S*,2*S*)-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 ºC 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 ºC 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 ºC 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: $^1$H NMR (500 MHz, $CDCl_3$, 23 ºC, 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 ºC, 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 $C_{14}H_{16}BrN_3NaO$ [M + Na]$^+$, 344.0374; found, 344.0363.

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

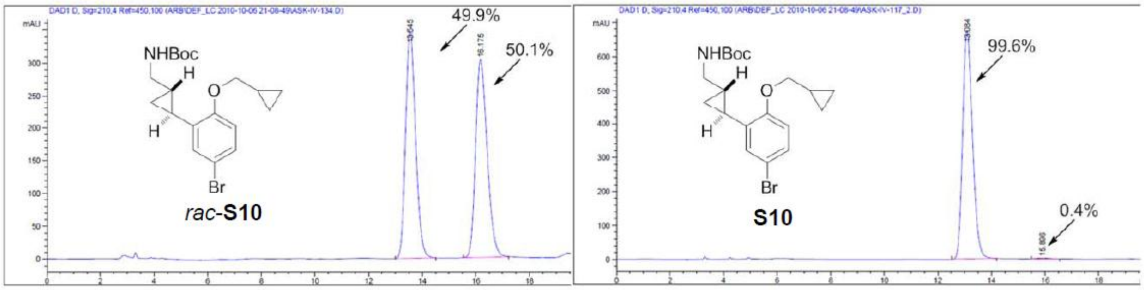


**S9** **S10**

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 ºC was added tin(II) chloride (5.59 g, 29.5 mmol, 5.00 equiv). The reaction mixture was allowed to warm to 23 ºC 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).

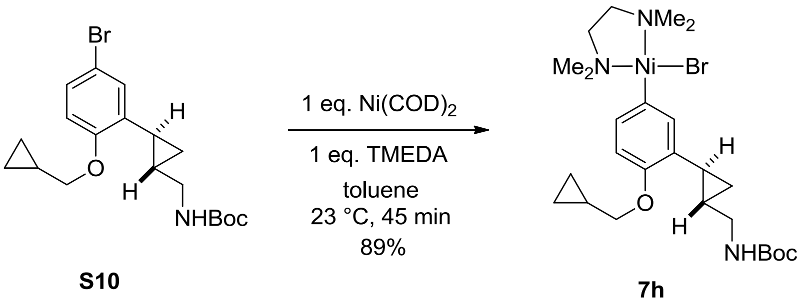
$R_f$ = 0.25 (hexanes/EtOAc 19:1 (v/v)). NMR Spectroscopy: $^1$H NMR (500 MHz, $CDCl_3$, 23 ºC, δ): 7.23 (dd, *J* = 8.3, 2.4 Hz, 1H), 7.06 (br d, *J* = 2.0 Hz, 1H), 6.66 (d, *J* = 8.8 Hz, 1H), 5.27 (br, 1H), 3.97 (dd, *J* = 9.5, 7.1 Hz, 1H), 3.72–3.66 (m, 2H), 2.66 (br dd, *J* = 10.0, 10.0, 1H), 1.83 (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 ºC, 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 $C_{19}H_{26}BrNNaO_3$ [M + Na]$^+$, 418.0988; found, 418.0994.

**Figure S2. Enantiodiscriminating HPLC trace of S10**



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

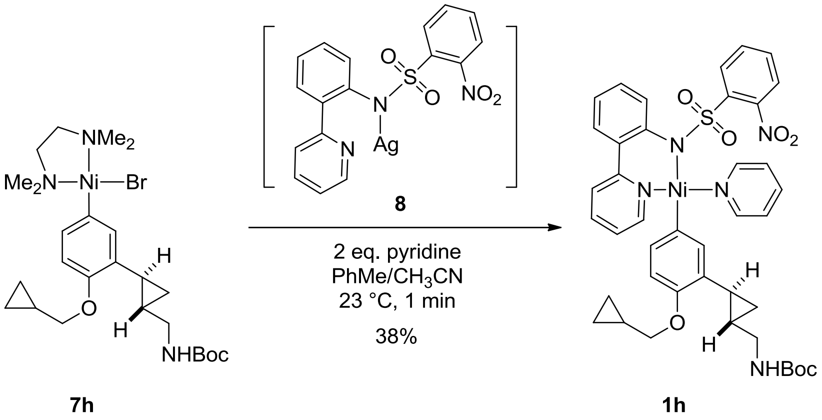
**Synthesis of nickel aryl bromide complex 7h**



To a solution of TMEDA (41.6 mg, 53.7 µL, 0.358 mmol, 1.00 equiv) and *t*-butyl (((1S,2S)-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 Ni(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 $^{1}$H 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$_2$Cl$_2$. NMR Spectroscopy: $^{1}$H NMR (500 MHz, CD$_2$Cl$_2$, 23 ºC, 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$_2$Cl$_2$, 23 ºC, 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 $C_{25}H_{42}BrN_3NiO_3$: 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 $C_{25}H_{42}N_3NiO_3$ $[M - Br]^+$, 490.2574; found, 490.2590.

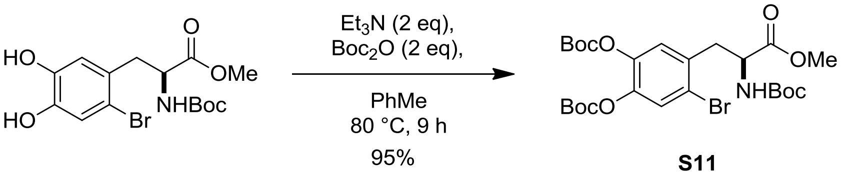
## Synthesis of nickel aryl complex 1h



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 μL, 0.490 mmol, 2.00 equiv) at 23 ºC, 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 75.0 mg of the title compound as a yellow solid (38%).

$R_f$ = 0.47 (hexanes/EtOAc 1:2 (v/v)). NMR Spectroscopy: $^1$H NMR (500 MHz, $CD_2Cl_2$, 23 ºC, 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). $^{13}$C NMR (125 MHz, $CD_2Cl_2$, 23 ºC, 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 $^1$H NMR spectrum. Reliable $^{13}$C NMR data were not obtained due to the decomposition of **1h** in the solvent over time. Anal: calcd for $C_{41}H_{43}N_5NiO_7S$: 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 $C_{36}H_{39}N_4NiO_7S$ $[M – pyridine + H]^+$, 729.1887; found, 729.1843.

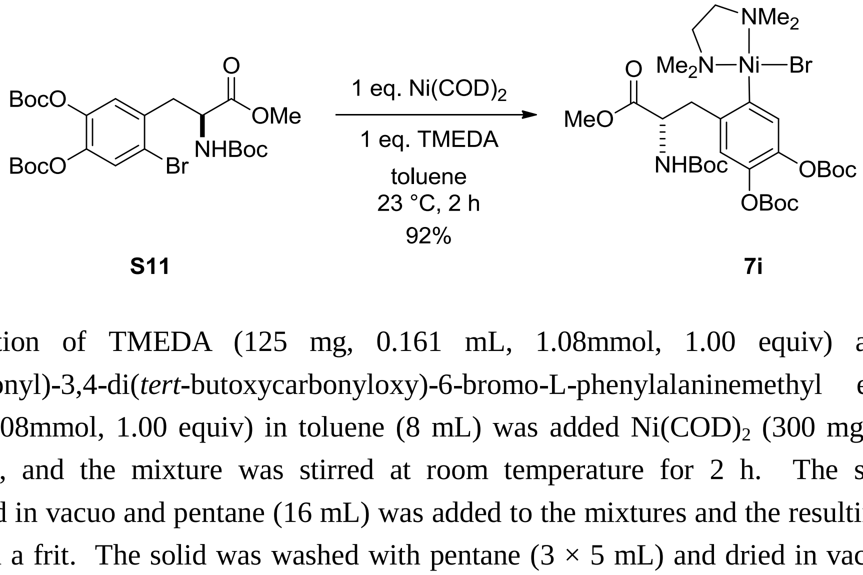
### *N*-(*tert*-butoxycarbonyl)-3,4-di(*tert*-butoxycarbonyloxy)-6-bromo-*L*-phenylalaninemethyl ester (S11)



(S)-*N*-(*tert*-butyloxycarbonyl)-2-bromo-4,5-dihydroxyphenylalanine methyl ester was prepared by a published method.[11] To the mixture of (S)-*N*-(*tert*-butyloxycarbonyl)-2-bromo-4,5-dihydroxyphenylalanine methyl ester (8.00 g, 20.5 mmol, 1.00 equiv) and $Et_3N$ (5.72 ml, 4.15 g, 164 mmol, 2.00 equiv) in a round-bottom flask in PhMe (100 ml) was added $Boc_2O$ (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 ºC 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: $^1$H NMR (500 MHz, $CDCl_3$, 23 ºC, 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). $^{13}$C NMR (125 MHz, $CDCl_3$, 23 ºC, 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 $C_{25}H_{36}BrNO_{10}$ $[M + Na]^+$, 612.1415; found, 612.1413.

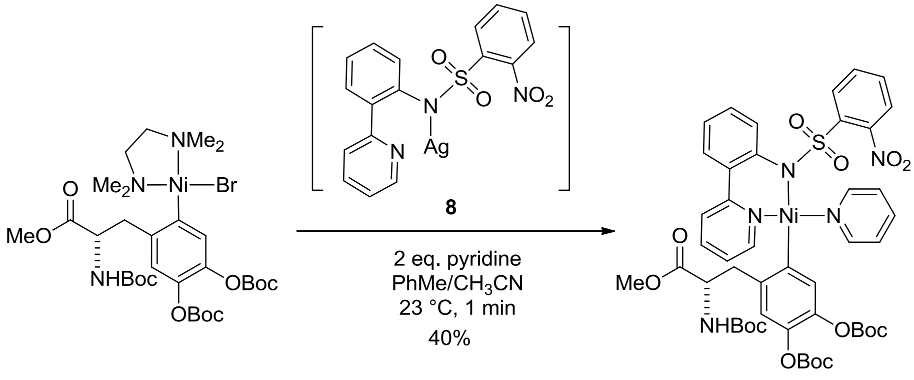
### Synthesis of nickel aryl bromide complex 7i



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: $^1$H NMR (500 MHz, $CD_3CN$ 23 ºC, 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). $^{13}$C NMR (125 MHz, $CD_3CN$ 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 $^1$H NMR spectrum. Anal: calcd for $C_{31}H_{52}BrN_3NiO_{10}$ $(PhMe)_{0.2}$: 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**

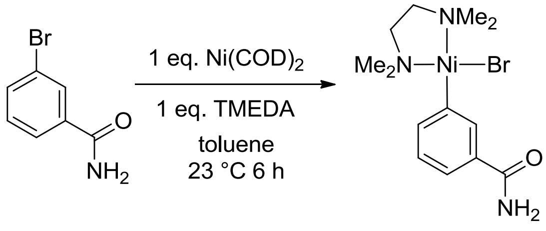


**7i** **1i**

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 μL, 1.31 mmol, 2.00 equiv) at 23 ºC, 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 × 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% $Et_3N$) 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: $^1$H NMR (500 MHz, $CD_2Cl_2$, 23 ºC, 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). $^{13}$C NMR (125 MHz $CD_2Cl_2$, 23 ºC, 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 $^1$H NMR spectrum, which is possibly due to slow rotation about bonds as seen for similar complexes.[12] Anal: calcd for $C_{47}H_{53}N_5NiO_{14}S$: 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 $C_{42}H_{49}N_4NiO_{14}S$ $[M – pyridine + H]^+$, 923.2314; found, 923.2276.

### Synthesis of nickel aryl bromide complex 7j

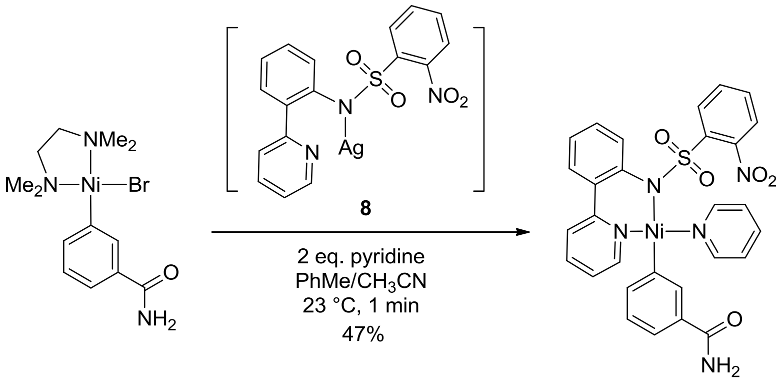


**7j**

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 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 225 mg of the title compound as a pink solid (84%).

$^1$H NMR (600 MHz, CD$_2$Cl$_2$, 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 $C_{13}H_{22}BrN_3NiO$: 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

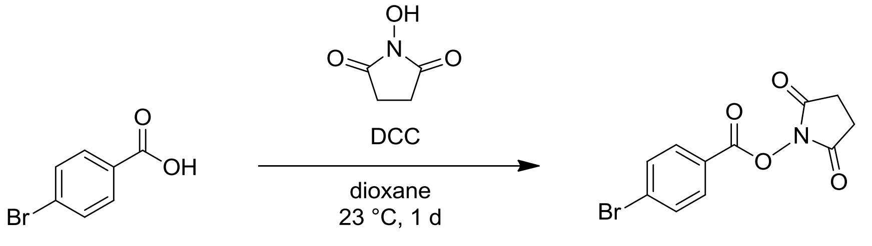


**7j** **1j**

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 ºC, 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$_2$Cl$_2$ (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: $^1$H NMR (500 MHz, $CD_2Cl_2$, 23 ºC, 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 ºC, 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 $C_{29}H_{23}N_5NiO_5S\ (CH_2Cl_2)_{0.25}$: 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)**

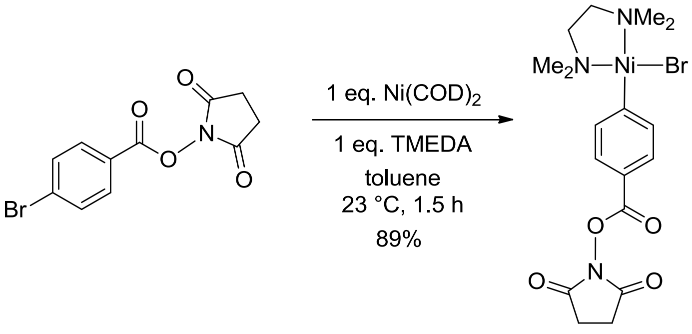


**S12**

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 ºC. 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: $^1$H NMR (500 MHz, $CDCl_3$, 23 ºC, 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 ºC, 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**

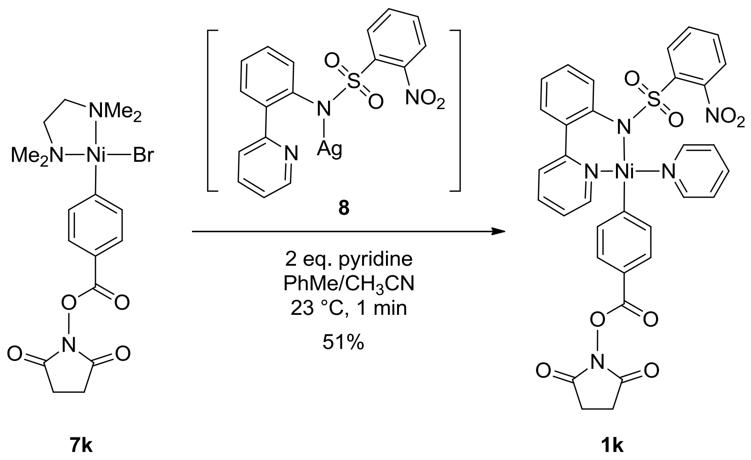


**S12** **7k**

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%).

$^1$H NMR (500 MHz, CD$_2$Cl$_2$, 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$_2$Cl$_2$, 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 $C_{17}H_{24}BrN_3NiO_4$: C, 43.17; H, 5.11; N, 8.88; found: C, 43.65; H, 4.54; N, 7.48.

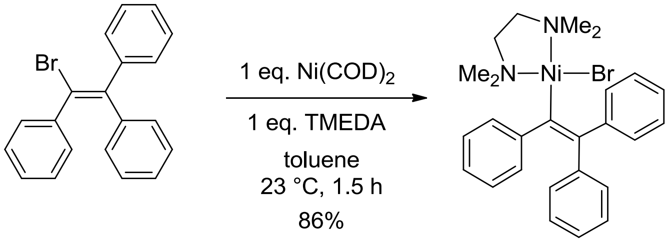
**Synthesis of nickel aryl complex 1k**



To (2-(2-pyridinyl)phenyl-2-nitrobenzenesulfonamide)silver(I) (**8**) (195 mg, 0.423mmol, 1.00 equiv) and nickel aryl bromide complex **7k** (200 mg, 0.423mmol, 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 ºC, 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$_f$ = 0.47 (hexanes/EtOAc 1:6 (v/v)). NMR Spectroscopy: $^1$H NMR (500 MHz, CDCl$_3$, 23 ºC, 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 ºC, 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 $C_{33}H_{25}N_5NiO_8S$: C, 55.80; H, 3.55; N, 9.86; found: C, 55.53; H, 3.50; N, 9.61.

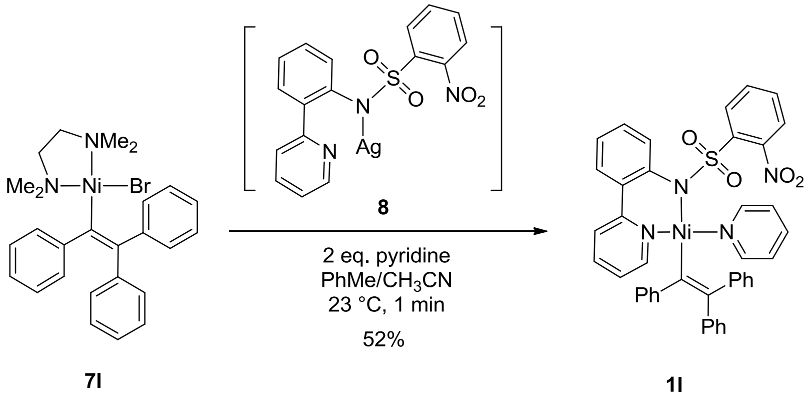
### Synthesis of nickel alkenyl bromide complex 7l



**7l**

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 × 5 mL) and dried in vacuo to afford 305 mg of the title compound as a pink solid (86%). $^{1}$H 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 **1l** in the next step. HRMS-FIA (m/z): calcd for $C_{26}H_{31}N_2Ni$ [M – Br]$^+$, 429.1841; found, 429.1845.

### Synthesis of nickel alkenyl complex 1l



**7l** **1l**

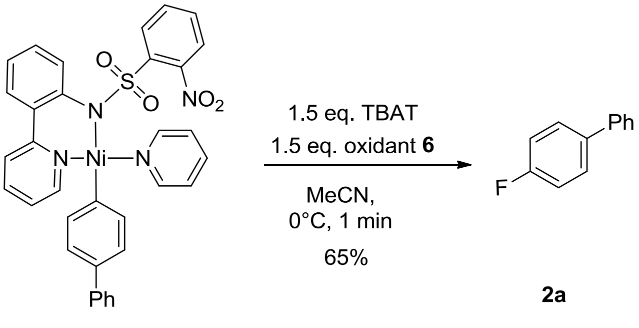
To (2-(2-pyridinyl)phenyl-2-nitrobenzenesulfonamide)silver(I) (**8**) (93.0 mg, 0.417 mmol, 1.00 equiv) and nickel alkenyl bromide complex **7l** (0.100 mg, 0.417 mmol, 1.00 equiv) in a 20 mL vial was added a toluene solution (3 mL) that contained pyridine (32.0 mg, 32.5 µL, 0.833 mmol, 2.00 equiv) at 23 ºC, 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: $^1$H NMR (500 MHz, $CDCl_3$, 23 ºC, 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 ºC, 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 $C_{42}H_{32}N_4NiO_4S$ $(CH_2Cl_2)_{0.15}$: 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 $C_{37}H_{27}N_3NaNiO_4S$ $[M - \text{pyridine} + H]^+$, 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-Flurobiphenyl (2a)

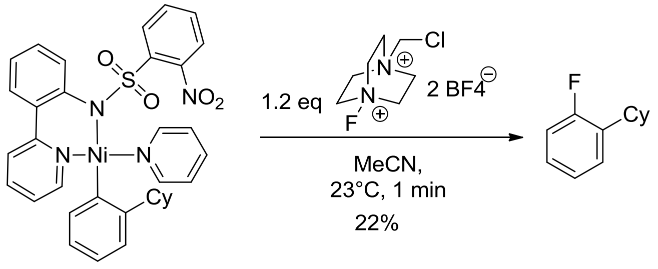


**1a**

In a glove box under a $N_2$ 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 ºC for 5 minutes. To the reaction mixture was added quickly pre-cooled acetonitrile (4 mL) at 0 ºC in one portion and the solution was stirred for 1min at 0 ºC. After warming to 23 ºC, 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)). $^1$H-NMR (500 MHz, $CDCl_3$, 23 ºC, δ): $\delta$ 7.56–7.54 (m, 4H), 7.45–7.42 (m, 2H), 7.36–7.33 (m, 1H), 7.15–7.11 (m, 2H). $^{13}$C-NMR (125 MHz, $CDCl_3$, 23 ºC, 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); $^{19}$F-NMR (375 MHz, $CDCl_3$, 23 ºC): $\delta$ –116.2. These spectroscopic data correspond to previously reported data.[12]

### 1-Cyclohexyl-2-fluorobenzene (2e)

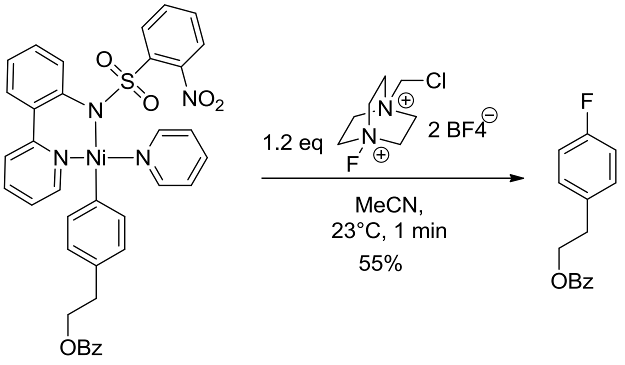


**1e** **2e**

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 ºC in one portion and the solution was stirred for 1min at 23 ºC. 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 **$[^{18}F]$2e** by HPLC analysis.

$R_f$ = 0.67 (pentane). NMR Spectroscopy: Selected $^1H$ NMR (400 MHz, $CDCl_3$, 23 ºC, δ): 7.07–7.03 (m, 1H), 2.94–2.89 (m, 1H). $^{19}F$ NMR (375 MHz, $CD_3CN$, 23 ºC, δ): –120.0. These spectroscopic data correspond to previously reported data.[17]

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



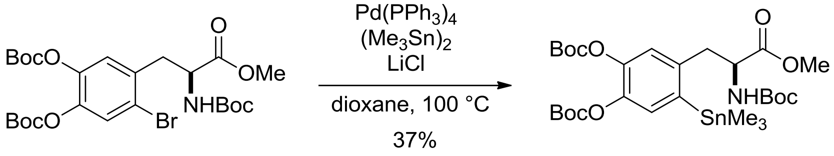
**1f** **2f**

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 ºC in one portion and the solution was stirred for 1min at 23 ºC. 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: $^1$H NMR (500 MHz, CDCl$_3$, 23 ºC, 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 ºC, 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 ºC, δ): –116.8. HRMS-FIA (m/z): calcd for $C_{15}H_{13}FO_2$ [M + H]$^+$, 245.0972; found, 245.0982.

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

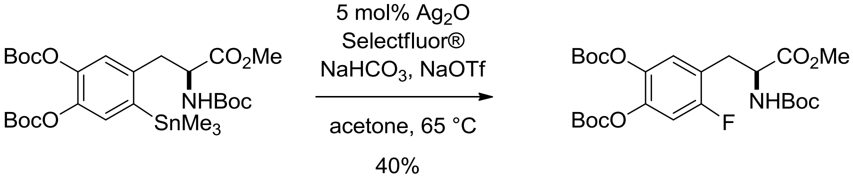


**S11** **S13**

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 ºC 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 ºC, the reaction mixture was cooled to 23 ºC 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: $^1$H NMR (500 MHz, CDCl$_3$, 23 ºC, 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 ºC, 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 $C_{28}H_{45}NO_{10}Sn$ [M + H]$^+$, 676.2144; found, 676.2171.

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

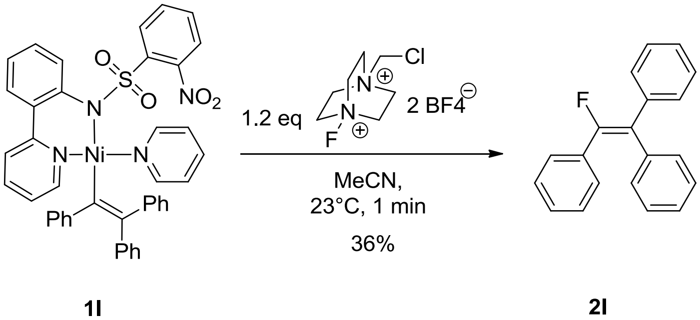


**S13** **2i**

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 ºC 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 ºC in a sealed vial. After cooling to 23 ºC, the reaction mixture was filtered through a pad of celite, eluting with $CH_2Cl_2$ 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: $^1$H NMR (500 MHz, $CDCl_3$, 23 ºC, 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). $^{13}$C NMR (125 MHz, $CDCl_3$, 23 ºC, 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. $^{19}$F NMR (375 MHz, $CDCl_3$, 23 ºC, δ): –117.6. Mass HRMS-FIA (m/z): calcd for $C_{25}H_{36}FNO_{10}$ $[M + Na]^+$, 552.2215; found, 552.2214.

**l-Fluoro-1,2,2-triphenylethylene (2l)**



Nickel aryl complex **1l** (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 ºC in one portion and the solution was stirred for 1min at 23 ºC. The solution was subsequently concentrated in vacuo and the residue is purified by chromatography on silica gel eluting with $Et_2O/CH_2Cl_2$ 2:1 (v/v) to afford 4.0 mg of the title compound as a colorless solid (36% yield).

$R_f$ = 0.88 ($Et_2O/CH_2Cl_2$ 2:1 (v/v)). NMR Spectroscopy: $^1$H NMR (500 MHz, $CDCl_3$, 23 ºC, δ): 7.39–6.95 (m, 15H). $^{13}$C NMR (125 MHz, $CDCl_3$, 23 ºC, 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. $^{19}$F NMR (375 MHz, $CDCl_3$, 23 ºC, 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 $^{18}$O(p,n)$^{18}$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% $CF_3CO_2H$ in water (A) 0.1% $CF_3CO_2H$ 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 complex[19]

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

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

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

Typical radioactivity for a reaction: 0.5 mCi

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

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

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

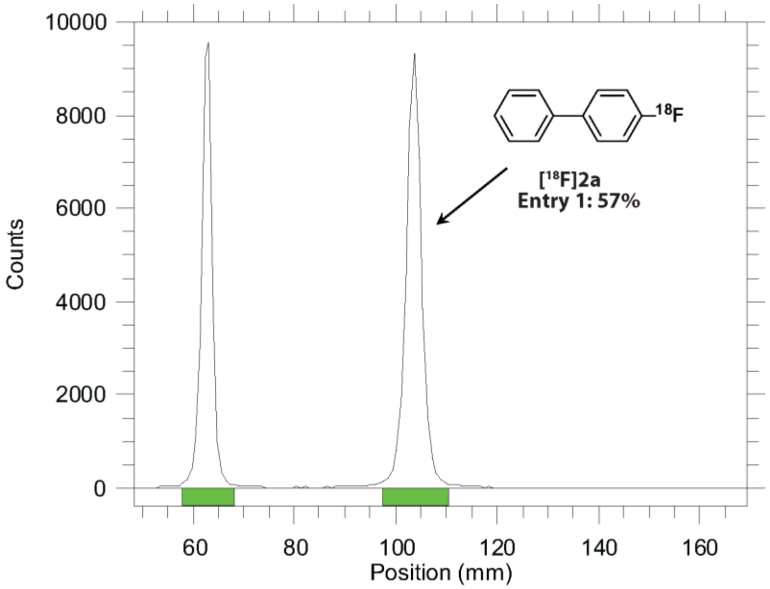
| | | | | | |
|---|---|---|---|---|---|
| 19 | **[$^{18}$F]2d** | 28 | 78 | 22 | 17 |
| 20 | | 18 | 80 | 14 | |
| 21 | | 19 | 79 | 15 | |
| 22 | | 19 | 79 | 15 | |
| 23 | | 24 | 79 | 19 | |
| 24 | | 21 | 76 | 16 | |
| 25 | **[$^{18}$F]2e** | 40 | 80 | 32 | 21 |
| 26 | | 24 | 82 | 20 | |
| 27 | | 21 | 82 | 17 | |
| 28 | | 25 | 78 | 19 | |
| 29 | | 26 | 73 | 19 | |
| 30 | | 26 | 73 | 19 | |
| 31 | **[$^{18}$F]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 | **[$^{18}$F]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 | **[$^{18}$F]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 | **[$^{18}$F]2i** | 41 | 68 | 28 | 15 |
| 52 | | 14 | 76 | 11 | |
| 53 | | 17 | 59 | 10 | |
| 54 | | 13 | 64 | 8 | |
| 55 | **[$^{18}$F]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 | **[$^{18}$F]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 | **[$^{18}$F]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:**

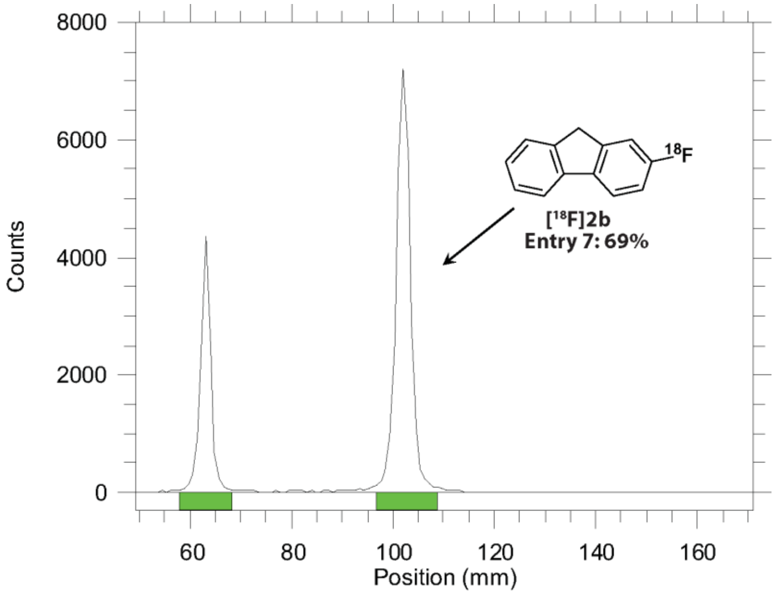
(Note: the baseline of the TLC plate where the reaction mixture was spotted corresponds to about 60mm on the horizontal axis of the following radio TLC scans).

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



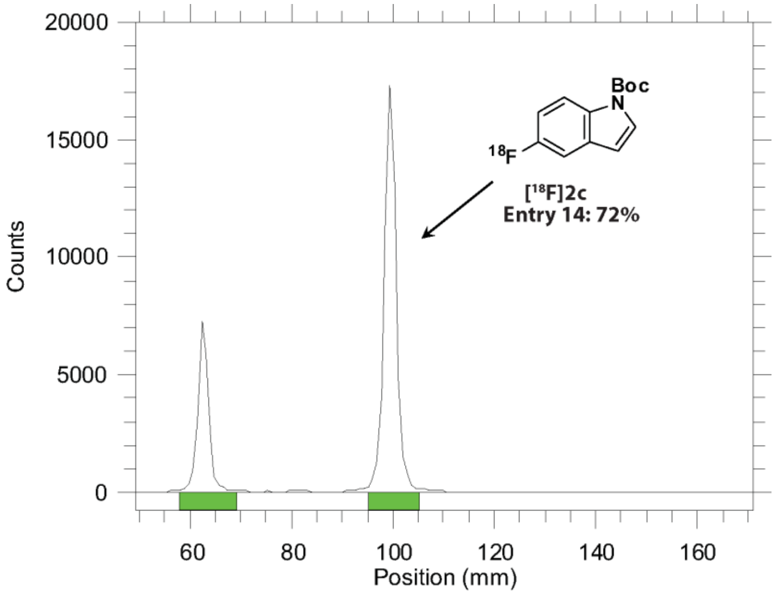
Entry 1 of Table S1. Percent of total integration listed for **[$^{18}$F]2a**

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



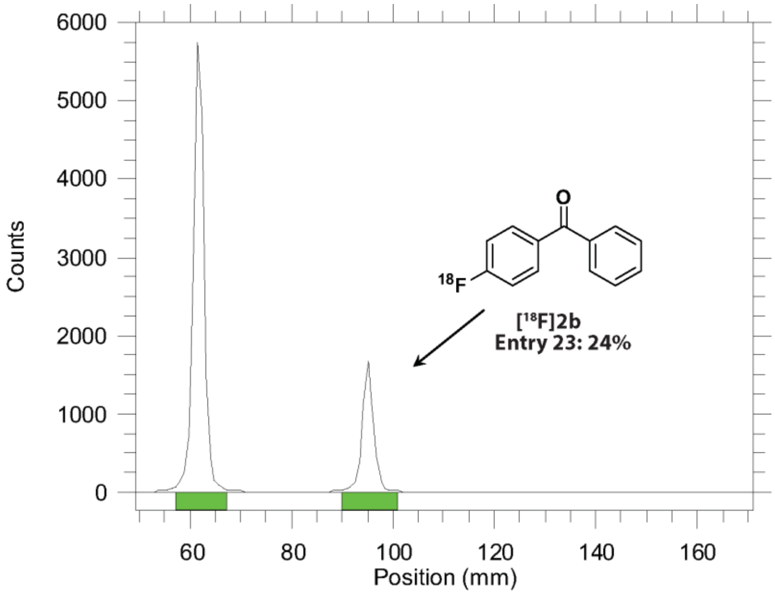
Entry 7 of Table S1. Percent of total integration listed for **[$^{18}$F]2b**

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



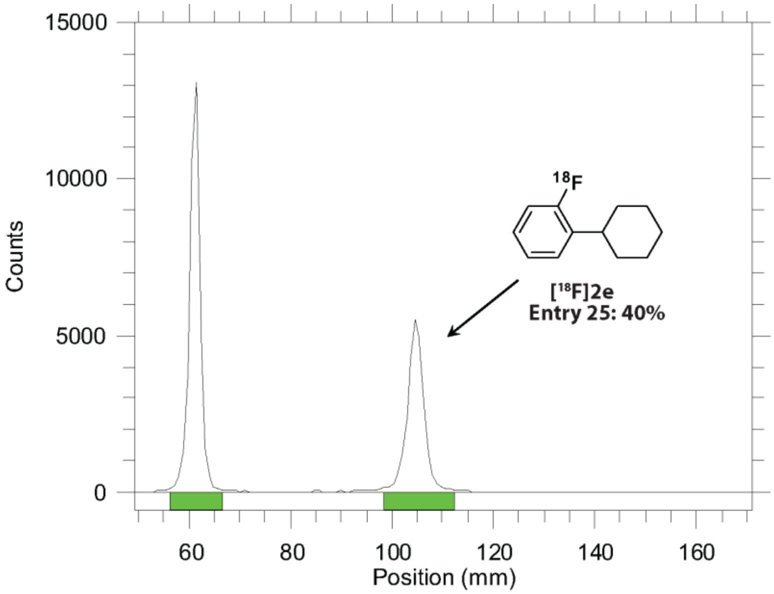
Entry 14 of Table S1. Percent of total integration listed for **[$^{18}$F]2c**

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



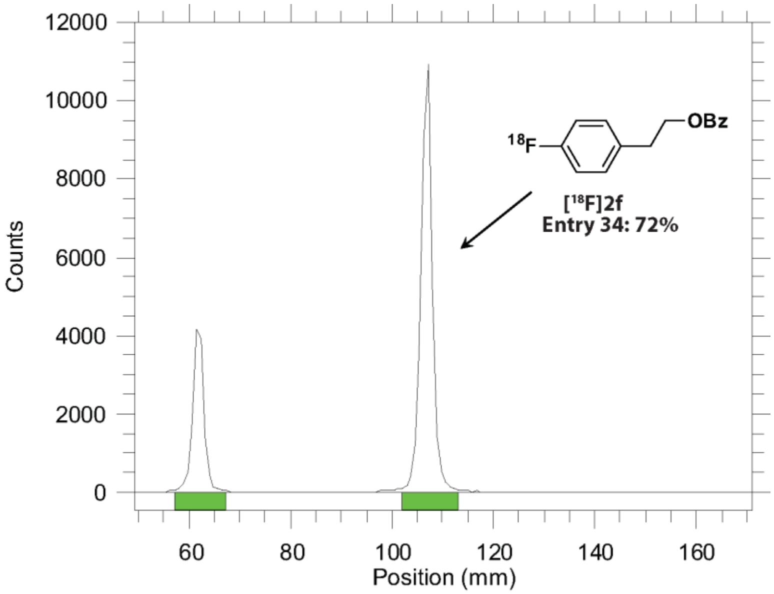
Entry 23 of Table S1. Percent of total integration listed for **[$^{18}$F]2d**

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



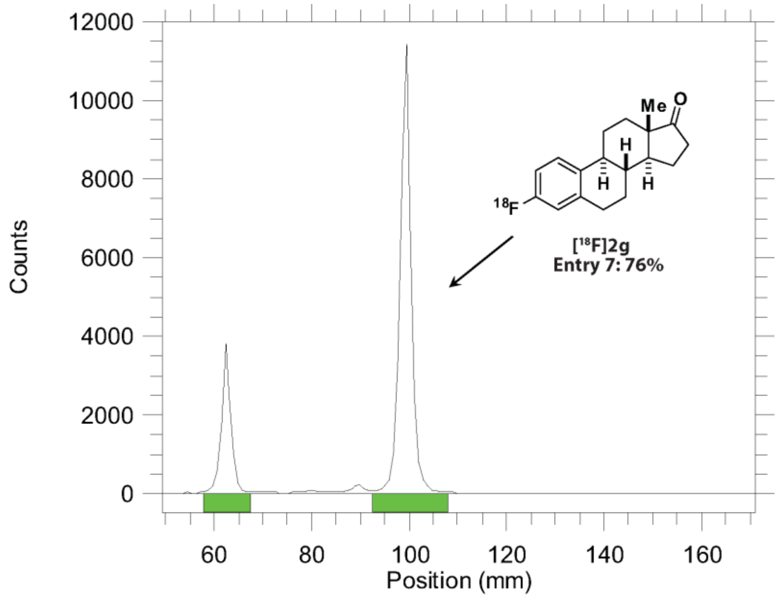
Entry 25 of Table S1. Percent of total integration listed for **[$^{18}$F]2e**

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



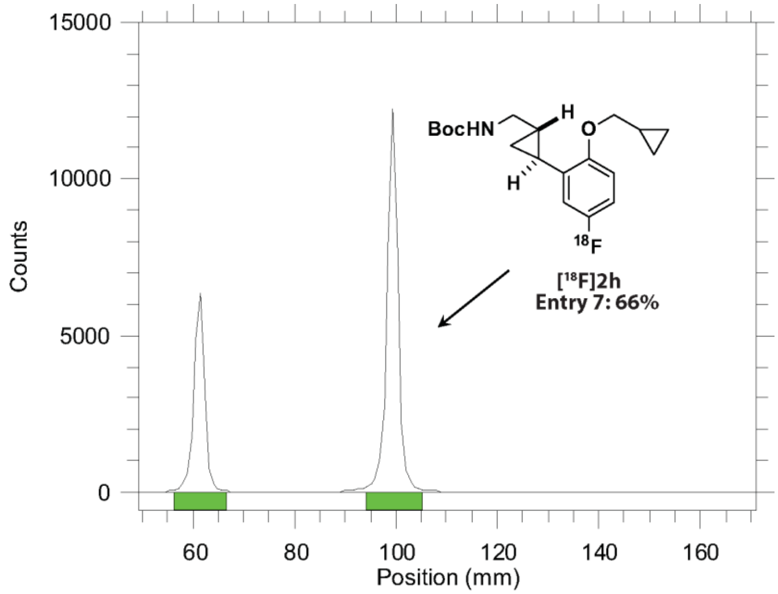
Entry 34 of Table S1. Percent of total integration listed for **[$^{18}$F]2f**

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



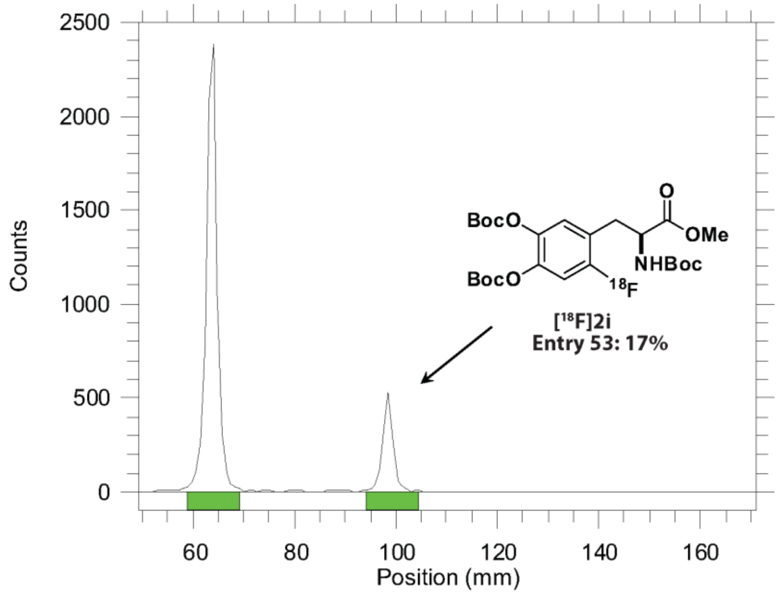
Entry 39 of Table S1. Percent of total integration listed for **[$^{18}$F]2g**

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



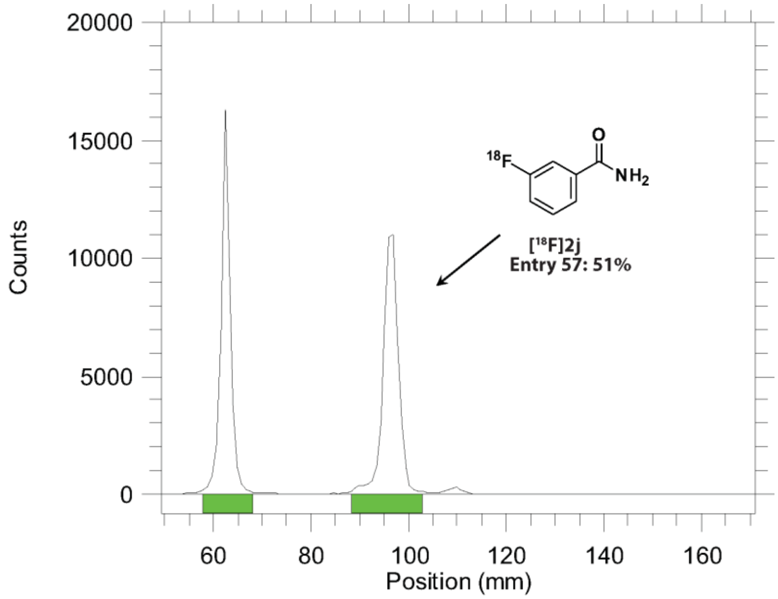
Entry 44 of Table S1. Percent of total integration listed for **[$^{18}$F]2h**

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



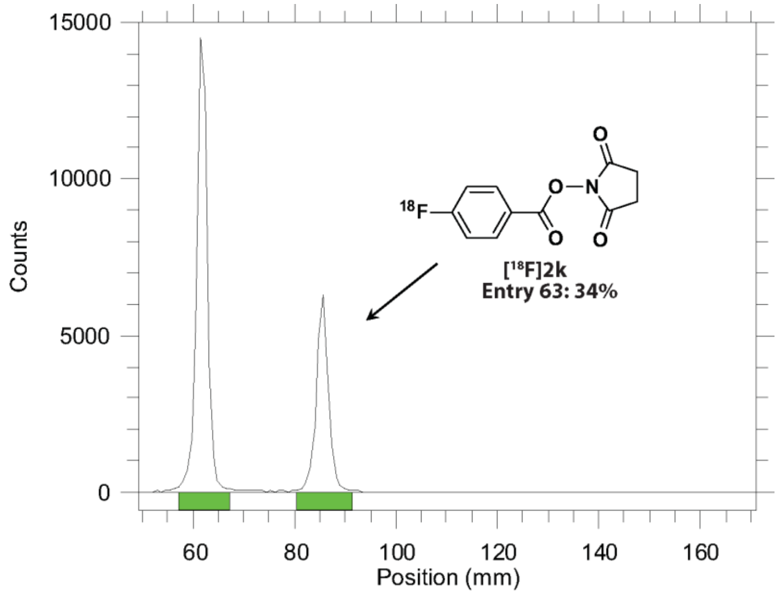
Entry 53 of Table S1. Percent of total integration listed for **[$^{18}$F]2i**

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



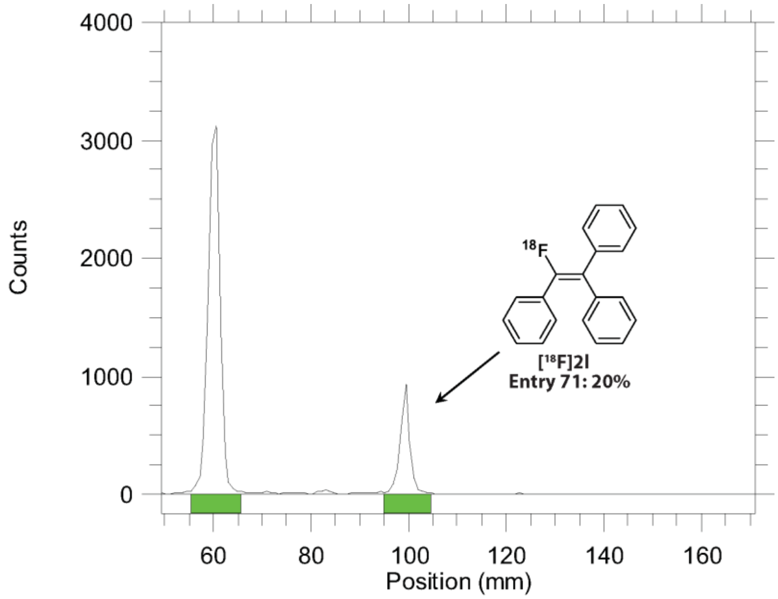
Entry 57 of Table S1. Percent of total integration listed for **[$^{18}$F]2j**

**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**

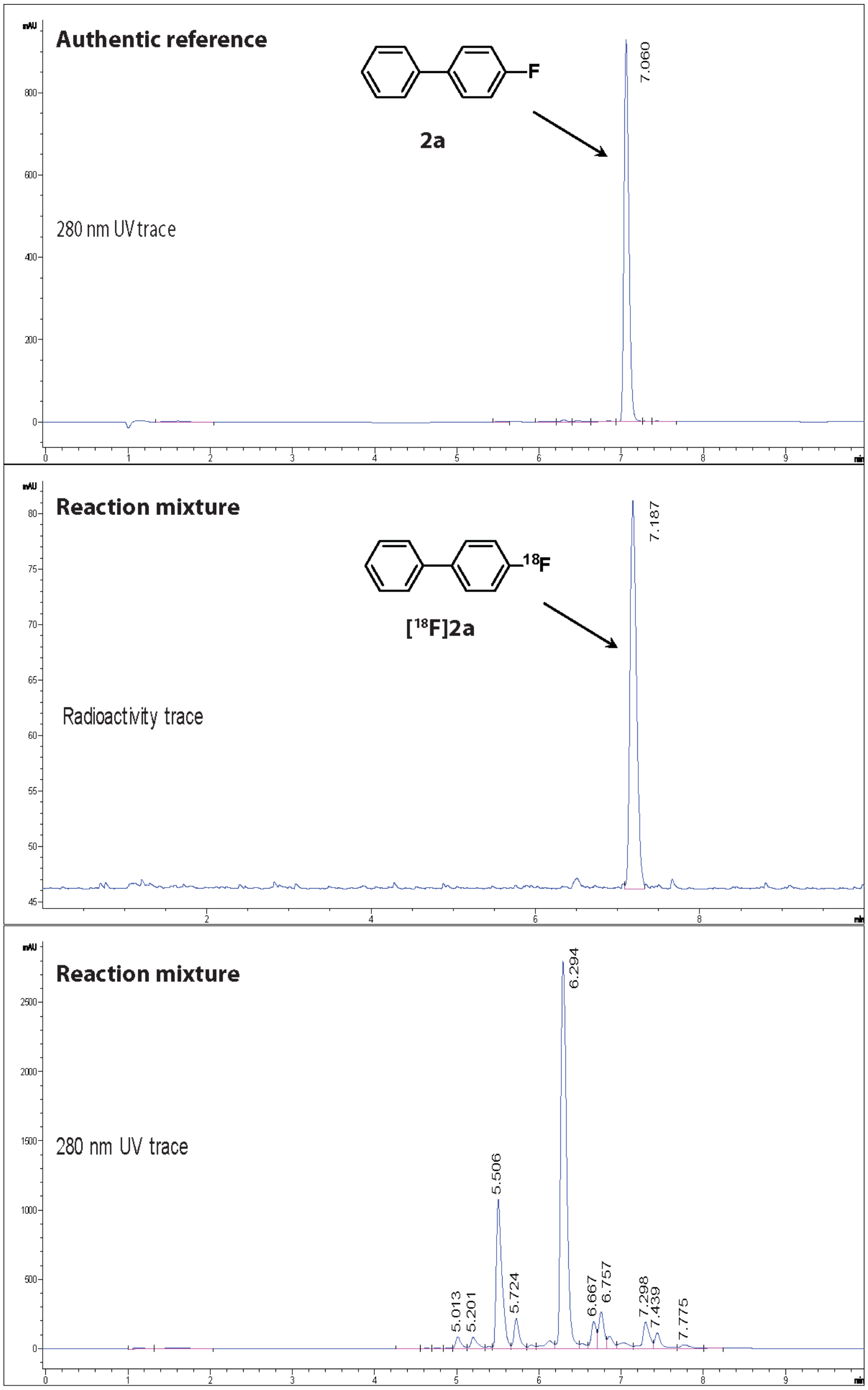


Entry 71 of Table S1. Percent of total integration listed for **[$^{18}$F]2l**

## Characterization of $^{18}$F-labeled Molecules

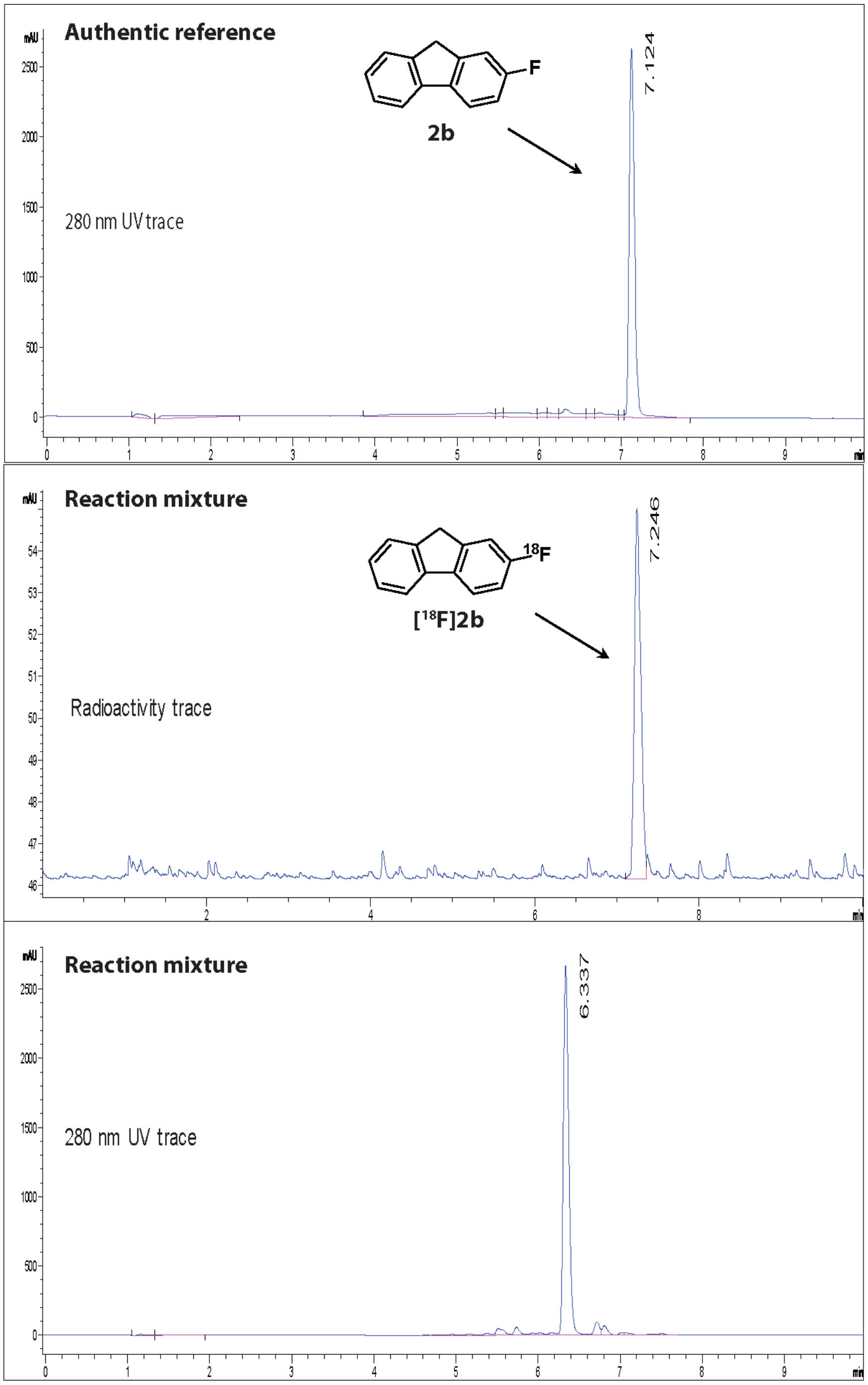
All $^{18}$F-labeled molecules were characterized by comparing the HPLC trace (measured by radioactivity) of the crude reaction mixture to the HPLC trace (measured by UV) of the corresponding authentic $^{19}$F-containing reference sample. An Agilent Eclipse XDB-C18, 5 µm, 4.6 x 150 mm HPLC column was used for analytical HPLC analysis. Analytical HPLC used the following mobile phases: 0.1% $CF_3CO_2H$ in water (A) 0.1% $CF_3CO_2H$ 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**



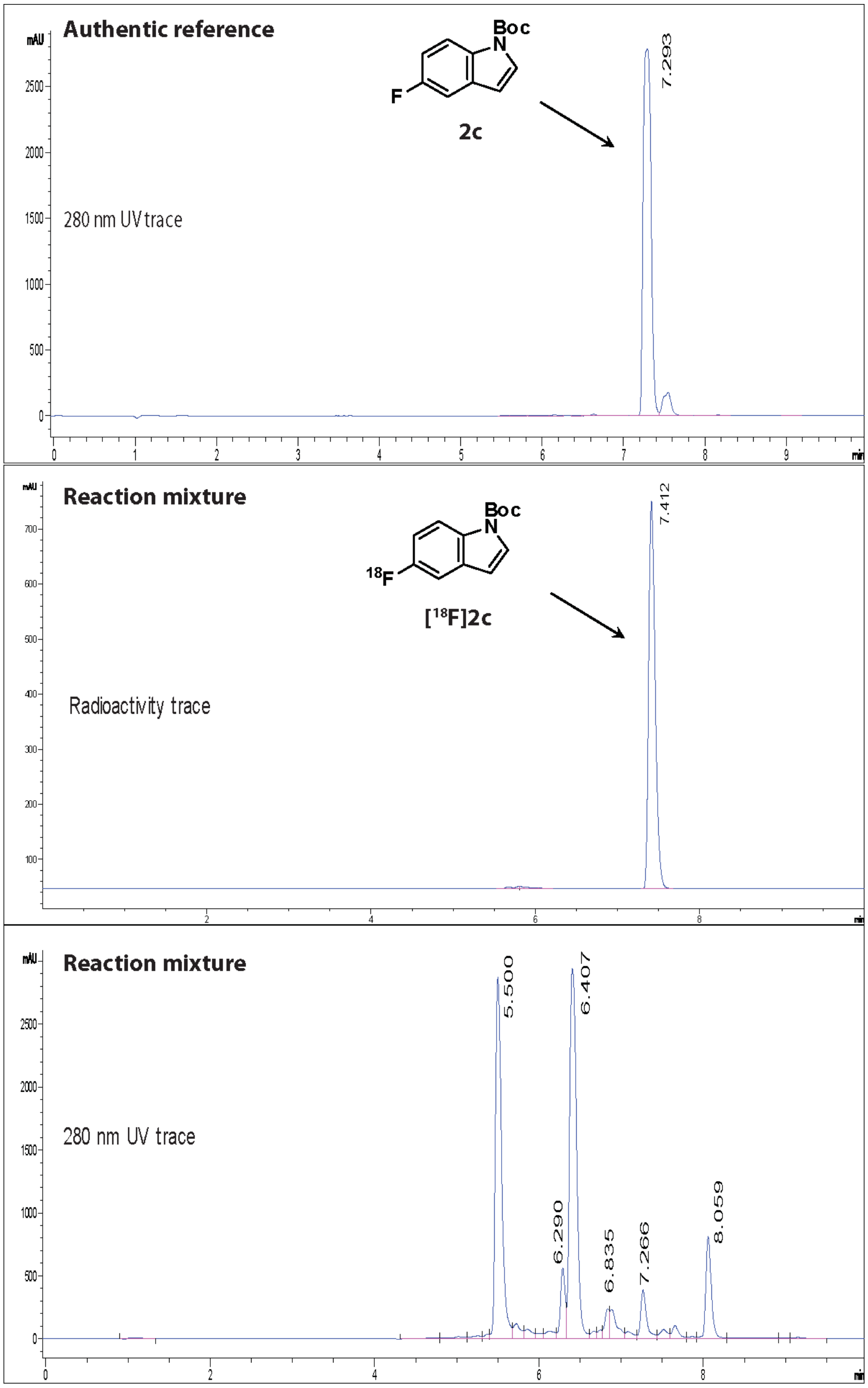
280 nm UV trace (top) of authentic sample (**2a**), radioactivity trace of the reaction mixture (middle) containing **[$^{18}$F]2a**, and 280 nm UV trace (bottom) of the reaction mixture. Note: radioactivity chromatographs have been offset (–0.125 min) to account for the delay volume (time) between the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

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



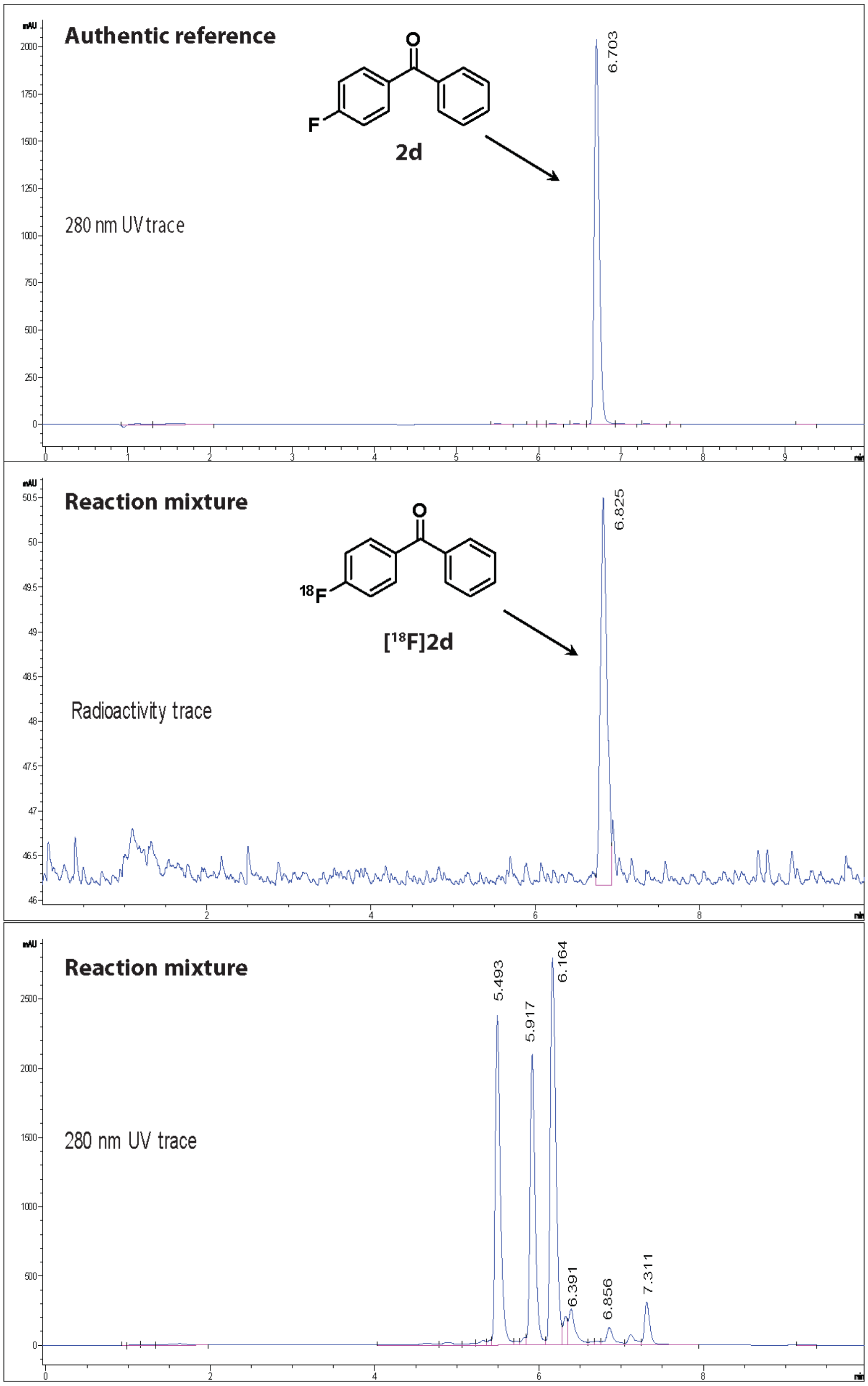
280 nm UV trace (top) of authentic sample (**2b**), radioactivity trace of the reaction mixture (middle) containing **[$^{18}$F]2b**, and 280 nm UV trace (bottom) of the reaction mixture. Note: radioactivity chromatographs have been offset (–0.125 min) to account for the delay volume (time) between the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

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



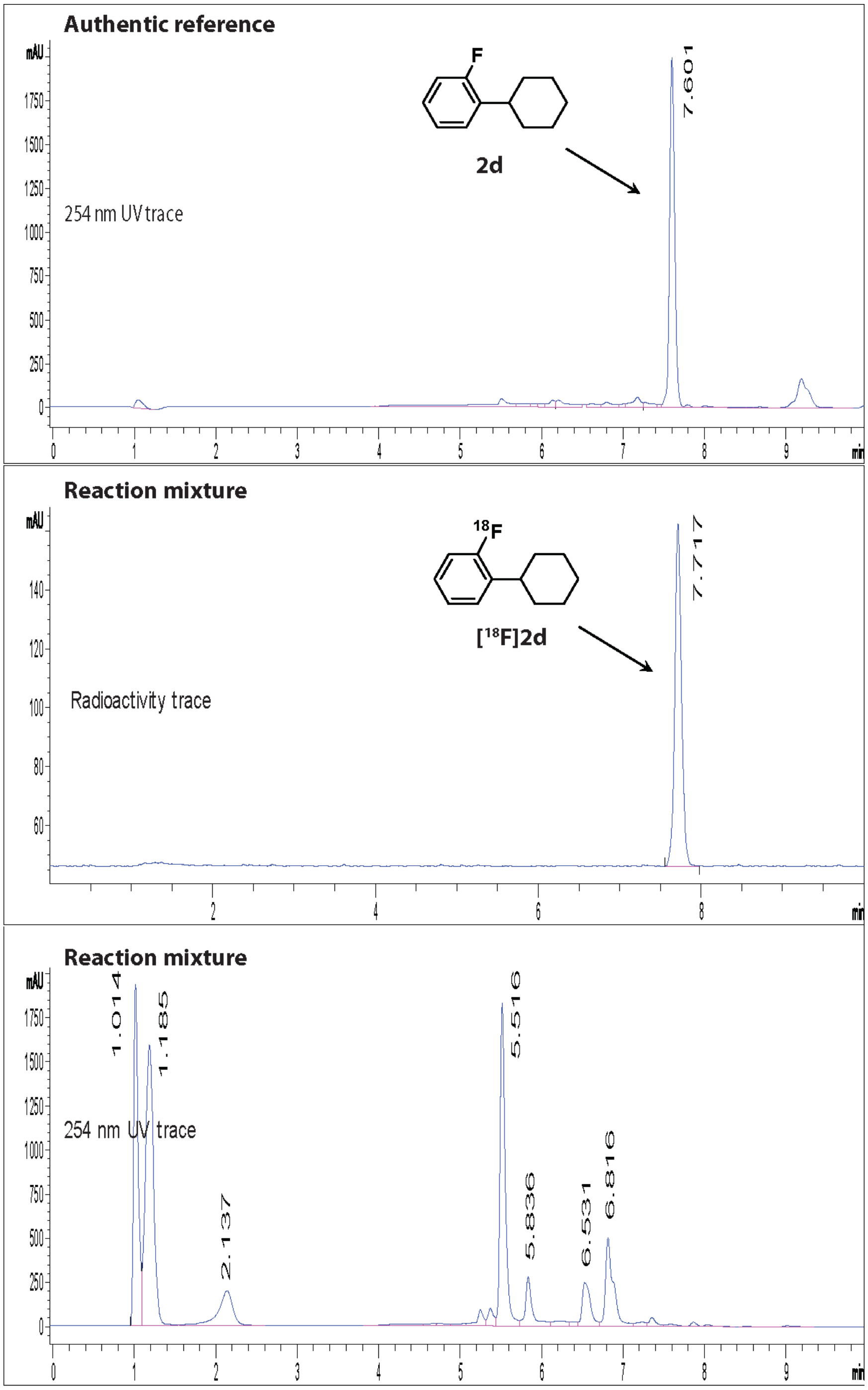
280 nm UV trace (top) of authentic sample (**2c**), radioactivity trace of the reaction mixture (middle) containing **[$^{18}$F]2c**, and 280 nm UV trace (bottom) of the reaction mixture. Note: radioactivity chromatographs have been offset (–0.125 min) to account for the delay volume (time) between the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

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



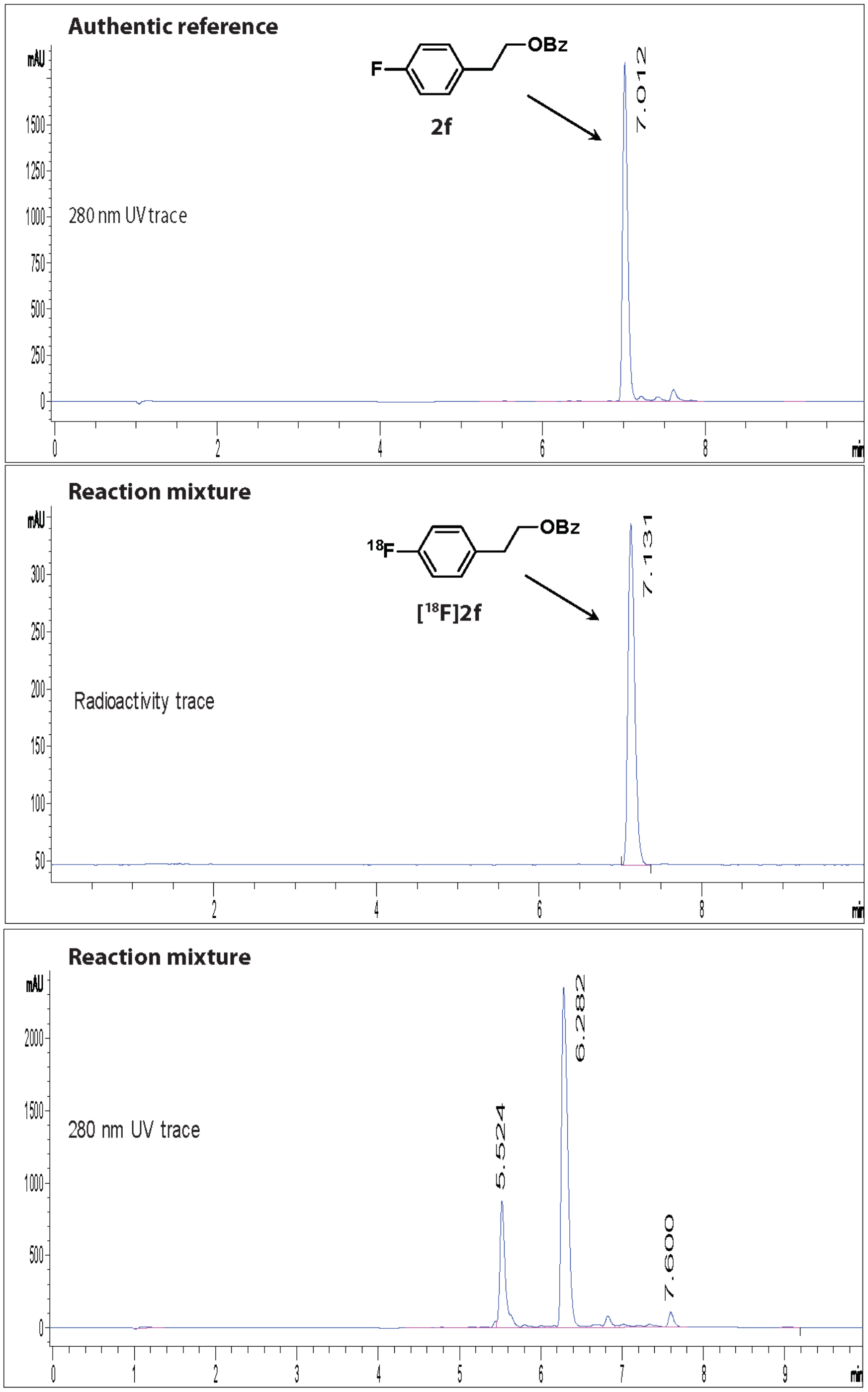
280 nm UV trace (top) of authentic sample (**2d**), radioactivity trace of the reaction mixture (middle) containing **[$^{18}$F]2d**, and 280 nm UV trace (bottom) of the reaction mixture. Note: radioactivity chromatographs have been offset (–0.125 min) to account for the delay volume (time) between the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

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



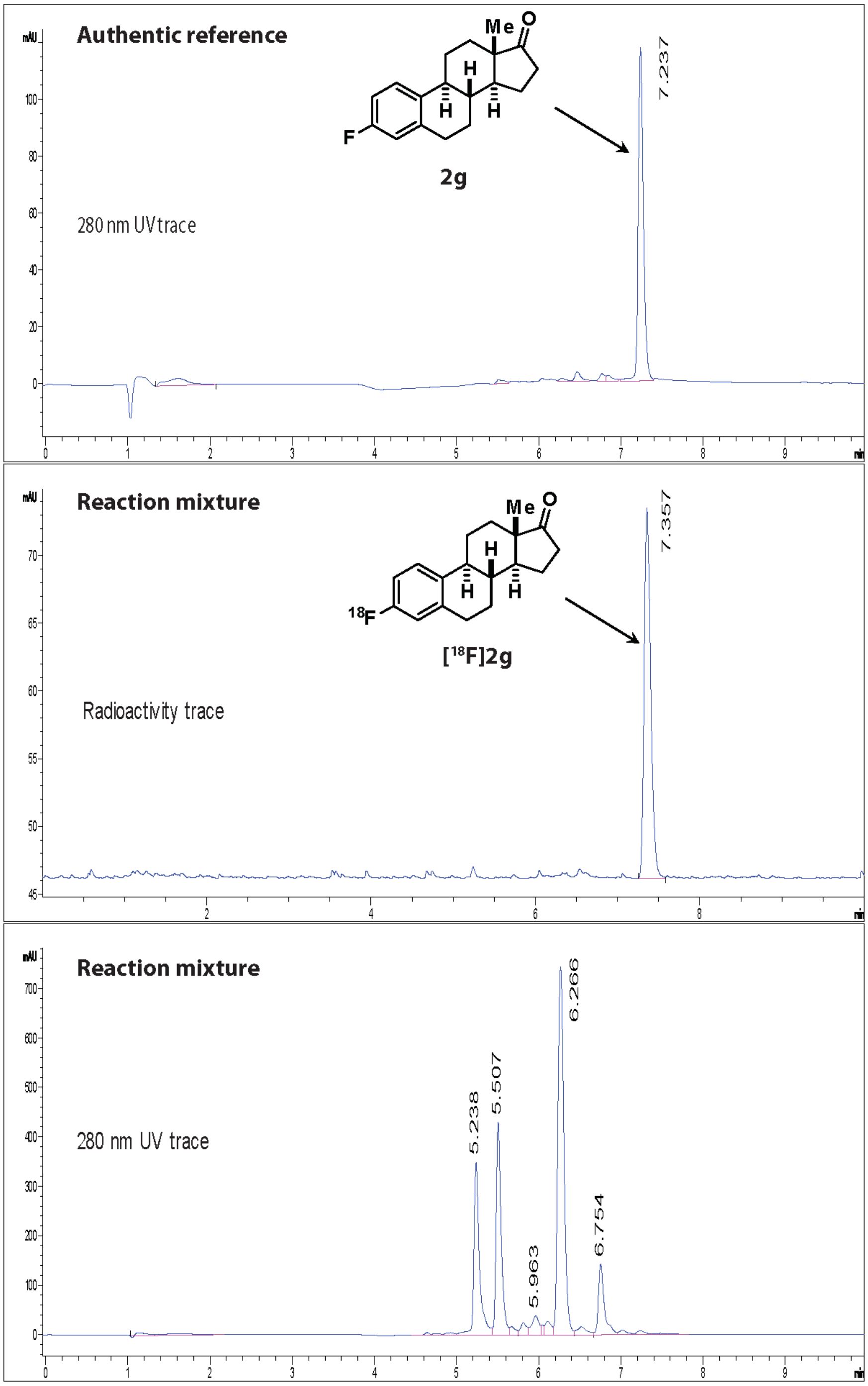
254 nm UV trace (top) of authentic sample (**2e** and cyclohexylbenzene as a 1:2 mixture), radioactivity trace of the reaction mixture (middle) containing **$[^{18}F]$2e**, and 254 nm UV trace (bottom) of the reaction mixture. Note: radioactivity chromatographs have been offset (–0.125 min) to account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

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



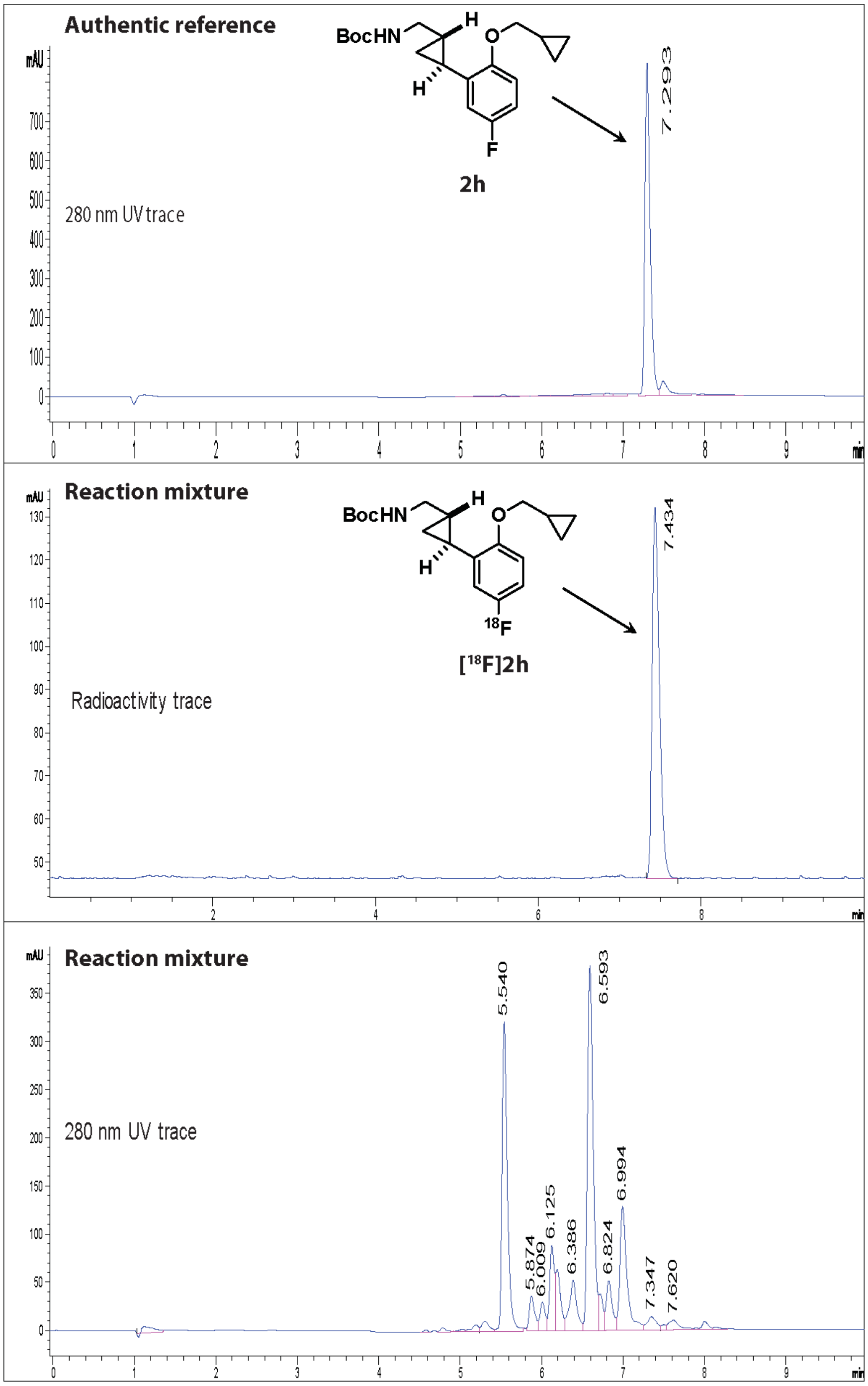
280 nm UV trace (top) of authentic sample (**2f**), radioactivity trace of the reaction mixture (middle) containing **[$^{18}$F]2f**, and 280 nm UV trace (bottom) of the reaction mixture. Note: radioactivity chromatographs have been offset (–0.125 min) to account for the delay volume (time) between the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

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



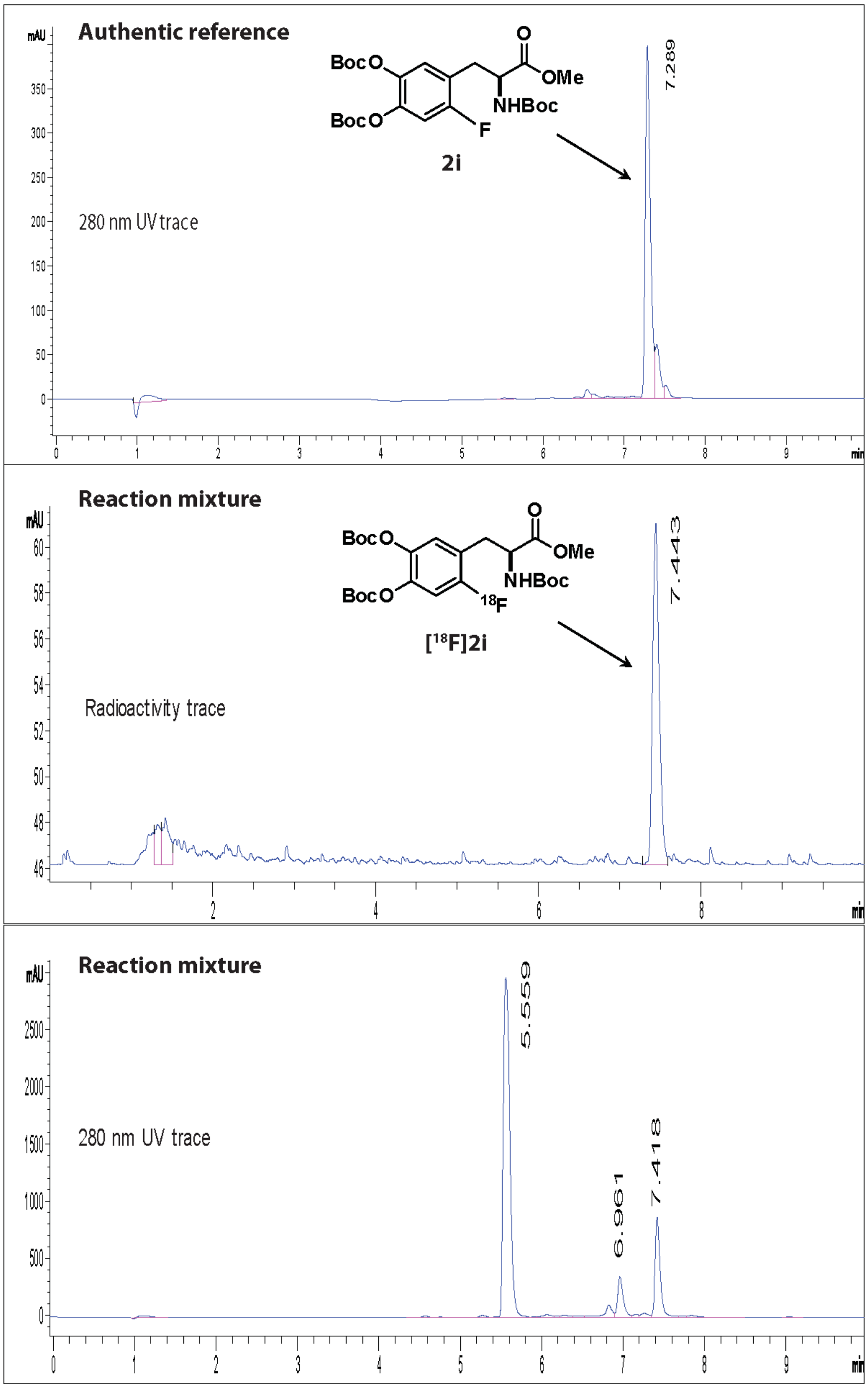
280 nm UV trace (top) of authentic sample (**2g**), radioactivity trace of the reaction mixture (middle) containing **[$^{18}$F]2g**, and 280 nm UV trace (bottom) of the reaction mixture. Note: radioactivity chromatographs have been offset (–0.125 min) to account for the delay volume (time) between the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

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



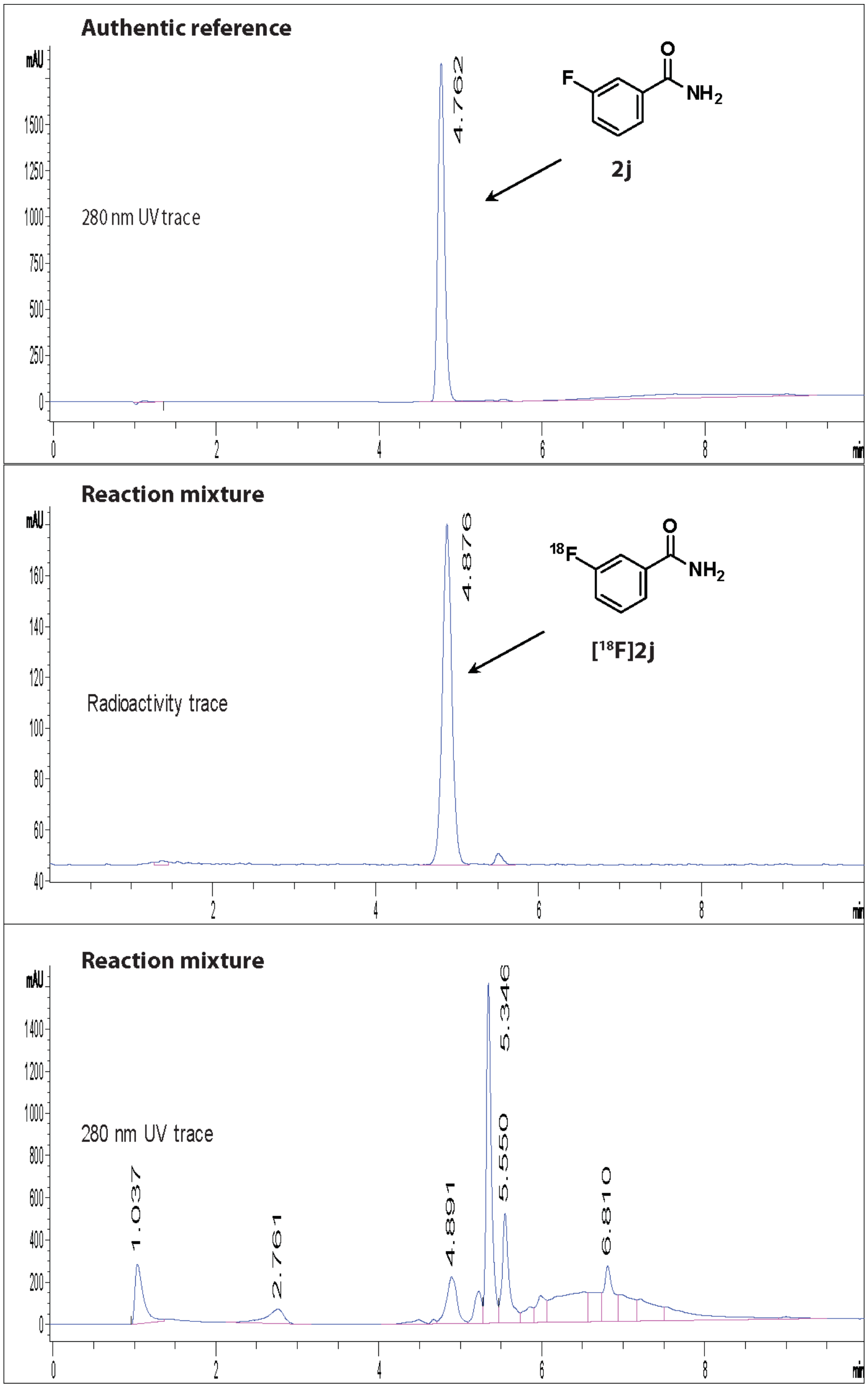
280 nm UV trace (top) of authentic sample (**2h**), radioactivity trace of the reaction mixture (middle) containing **[$^{18}$F]2h**, and 280 nm UV trace (bottom) of the reaction mixture. Note: radioactivity chromatographs been been offset (–0.125 min) to account for the delay volume (time) between the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

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



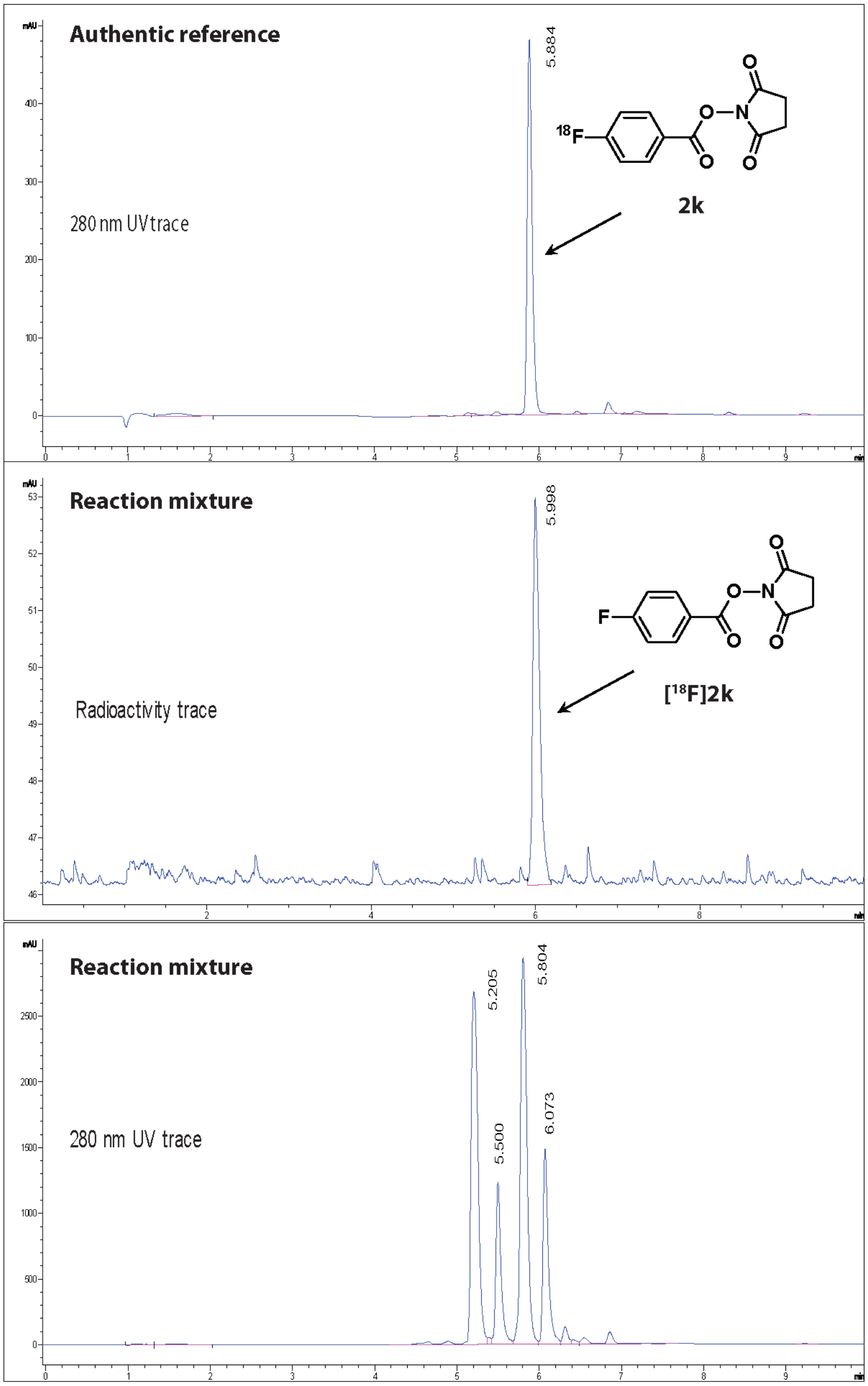
280 nm UV trace (top) of authentic sample (**2i**), radioactivity trace of the reaction mixture (middle) containing **[$^{18}$F]2i**, and 280 nm UV trace (bottom) of the reaction mixture. Note: radioactivity chromatographs have been offset (–0.125 min) to account for the delay volume (time) between the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

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



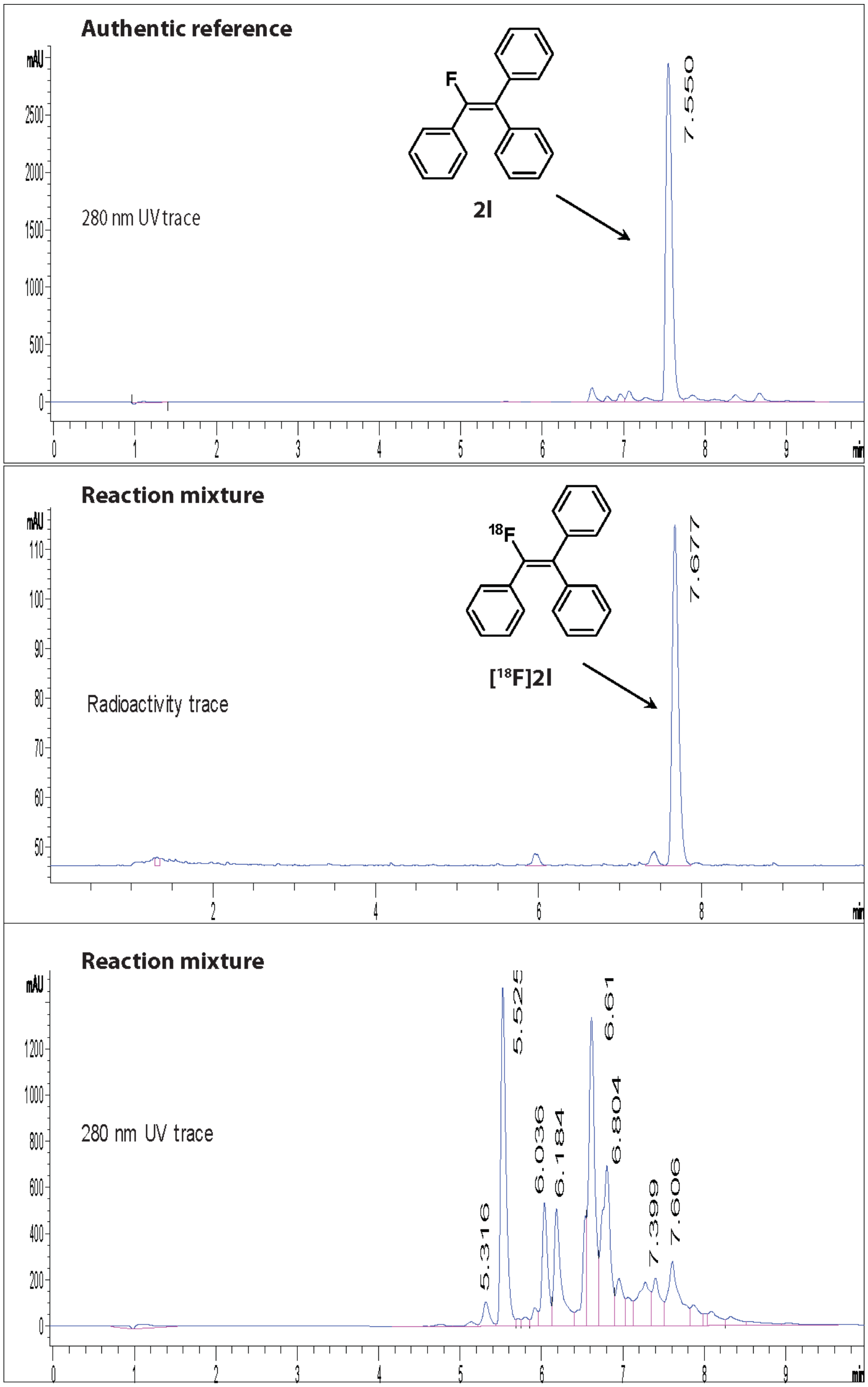
280 nm UV trace (top) of authentic sample (**2j**), radioactivity trace of the reaction mixture (middle) containing **[$^{18}$F]2j**, and 280 nm UV trace (bottom) of the reaction mixture. Note: radioactivity chromatographs have been offset (–0.125 min) to account for the delay volume (time) between the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



280 nm UV trace (top) of authentic sample (**2l**), radioactivity trace of the reaction mixture (middle) containing **[$^{18}$F]2l**, 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.

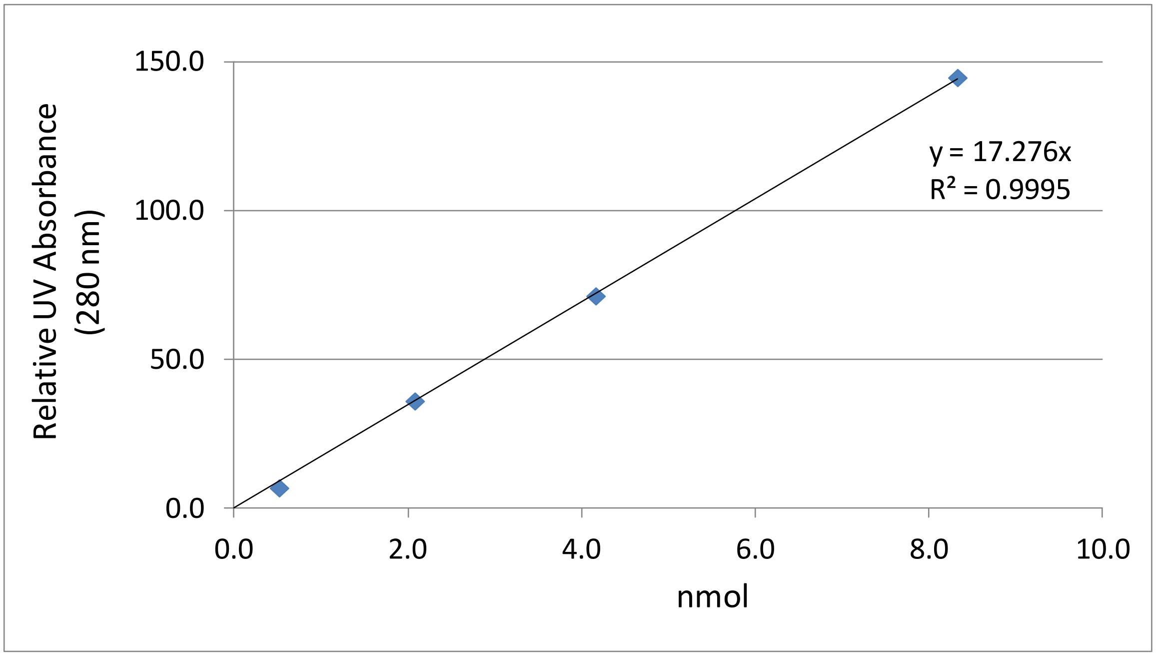
### Determination of specific activity of [$^{18}$F]2g

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 ($\mathrm{Mo}_{\mathrm{K}\alpha}$ radiation, $\lambda$=0.71073 Å), and equipped with an Oxford Cryosystems nitrogen flow apparatus. The collection method involved 0.5° scans in $\omega$ at 28° in $2\theta$. 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 again $F^2$ 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.**

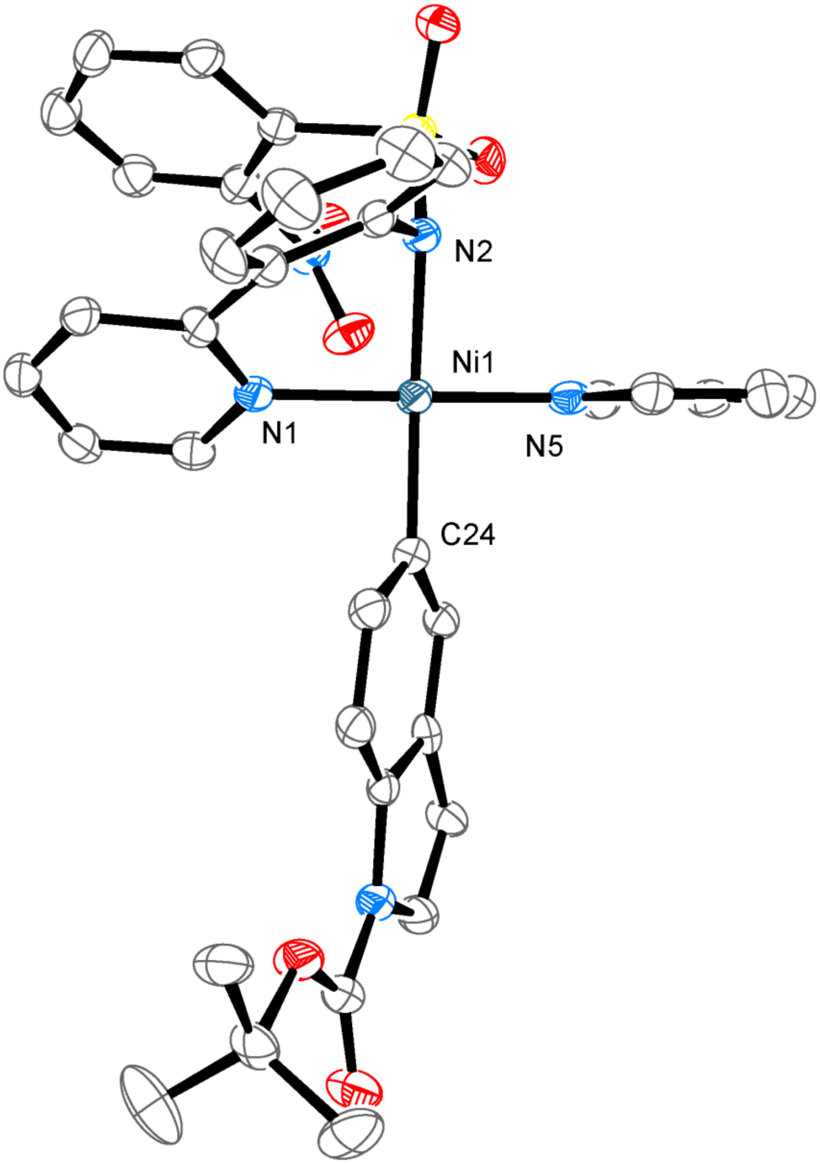


**Table S3. Experimental details**

| | **1c** |
|---|---|
| Crystal data | |
| Chemical formula | $C_{75}H_{74}N_{10}Ni_2O_{12}S_2$ |

| | |
|---|---|
| $M_r$ | 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<br>*SADABS* |
| $T_{min}$, $T_{max}$ | 0.814, 0.856 |
| No. of measured, independent and observed [$I > 2\sigma(I)$] reflections | 77361, 13259, 8722 |
| $R_{int}$ | 0.107 |
| $(\sin \theta/\lambda)_{max}$ (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 |
| $\Delta\rho_{max}$, $\Delta\rho_{min}$ (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, º)**

| | | | |
|---|---|---|---|
| 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) |

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| 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 |

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| 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) |

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| 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 |

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| 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) |

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| 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) |

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| 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) |

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| 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) |

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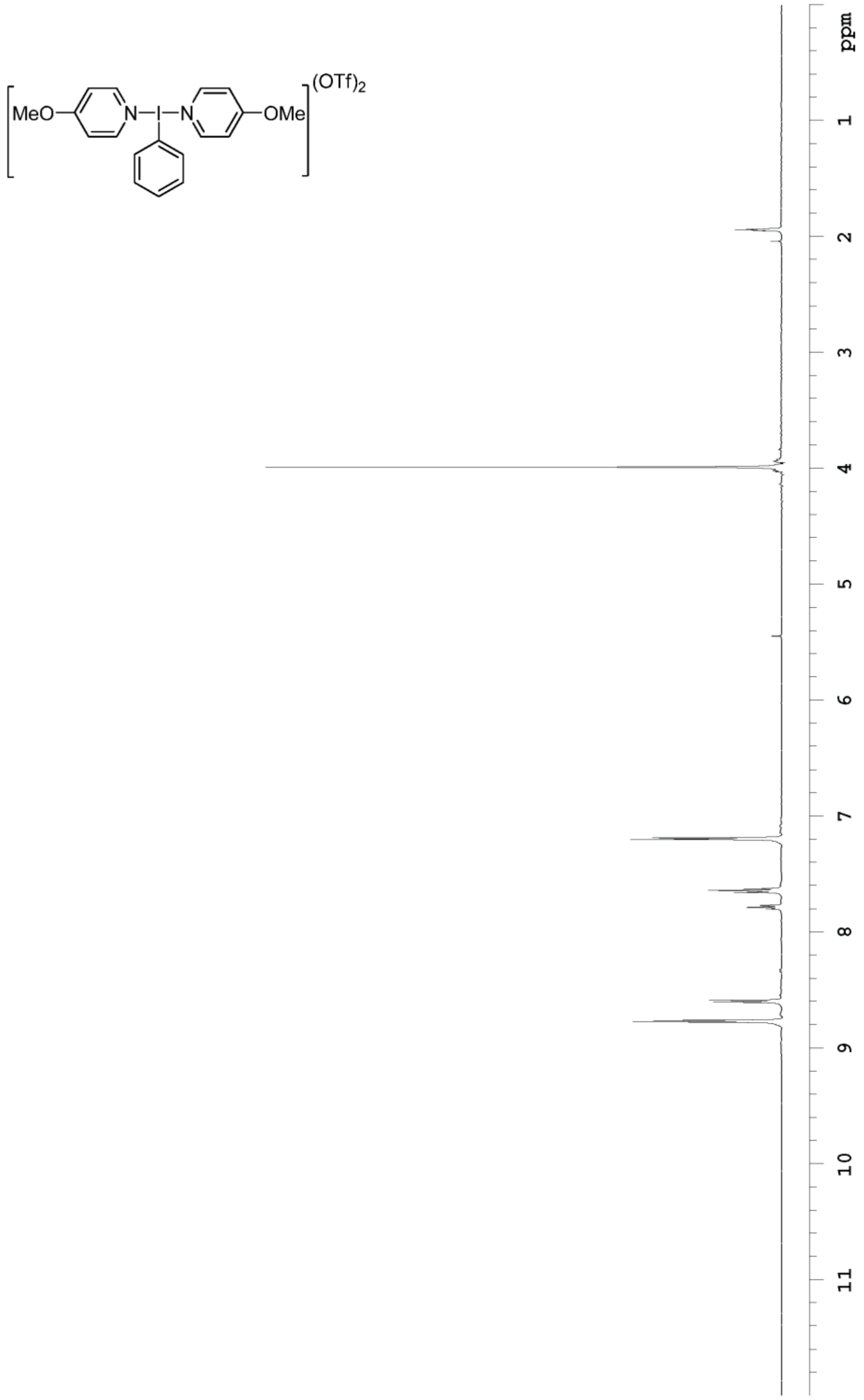
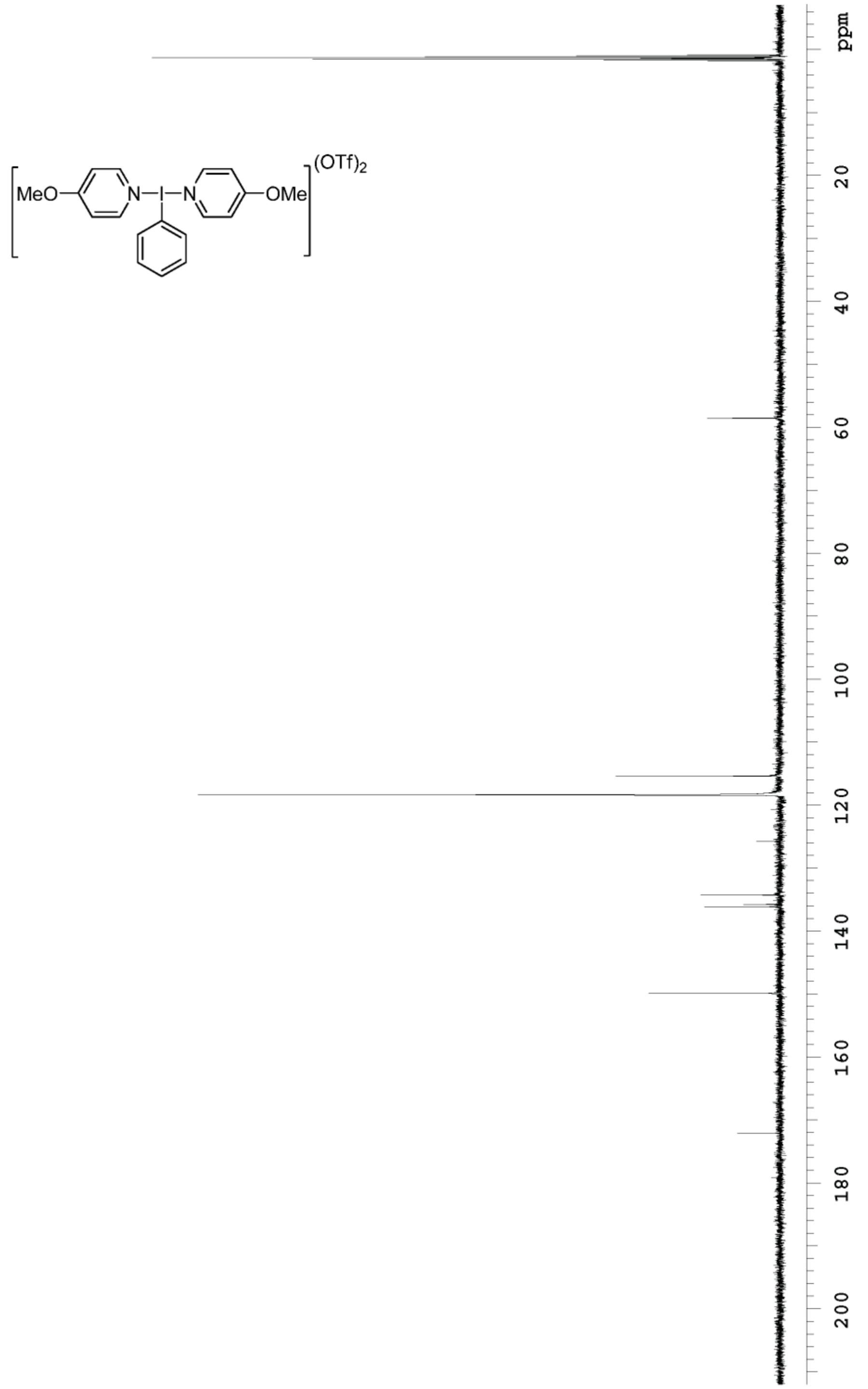
| C72—C71—N9—C79 | 2.0 (7) | C22—C21—N4—C28 | -178.0 (4) |
| C76—C71—N9—C79 | 178.9 (4) | C26—C21—N4—C28 | 1.7 (5) |
| C72—C71—N9—C78 | -175.1 (4) | C44—C45—N5—C41 | -1.1 (6) |
| C76—C71—N9—C78 | 1.8 (4) | C44—C45—N5—Ni1 | -179.3 (3) |
| C94—C95—N10—C91 | 1.5 (6) | C42—C41—N5—C45 | 0.5 (6) |
| C94—C95—N10—Ni2 | 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) |

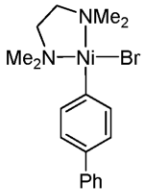
## Spectroscopic Data

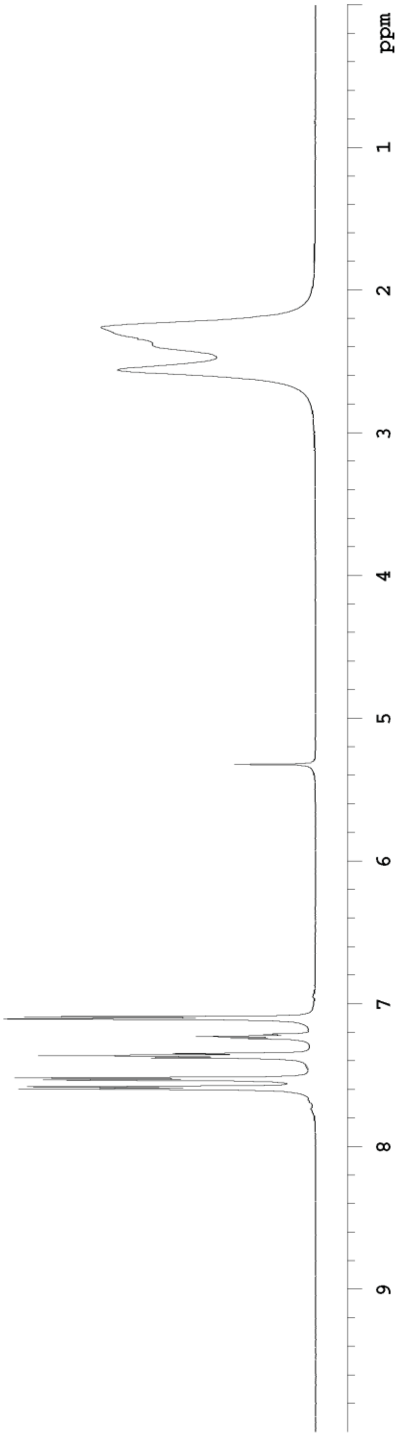


$^1$H NMR (CD$_3$CN, 23 ºC) of **6**

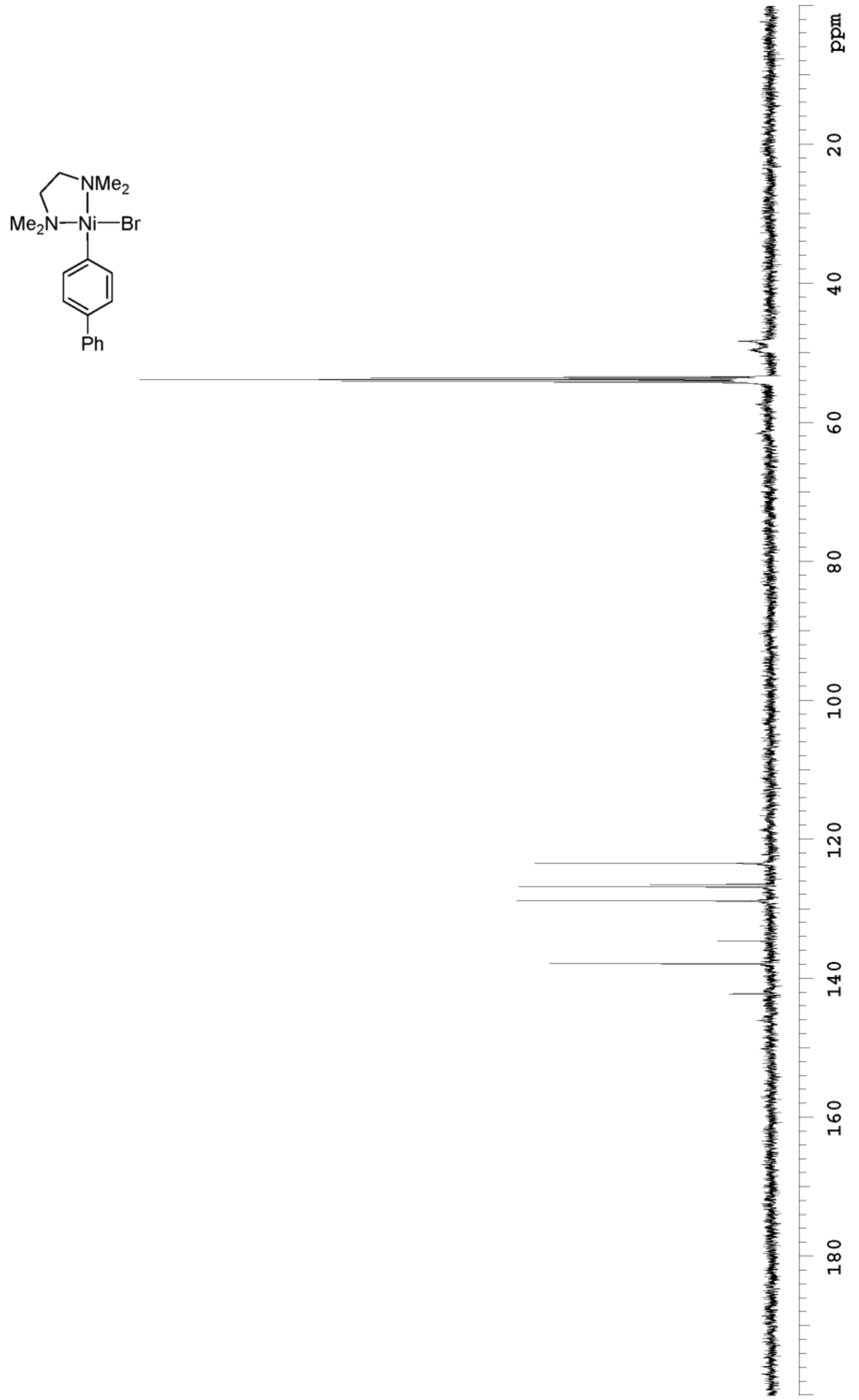


$^{13}$C NMR (CD$_3$CN, 23 ºC) of **6**





$^1$H NMR ($CD_2Cl_2$, 23 ºC) of **7a**



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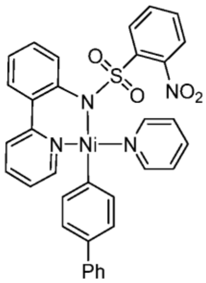
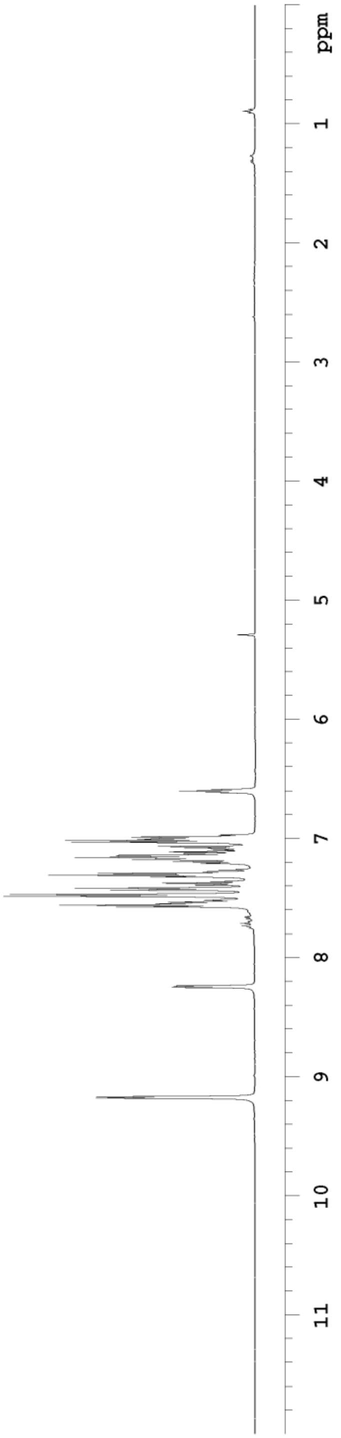
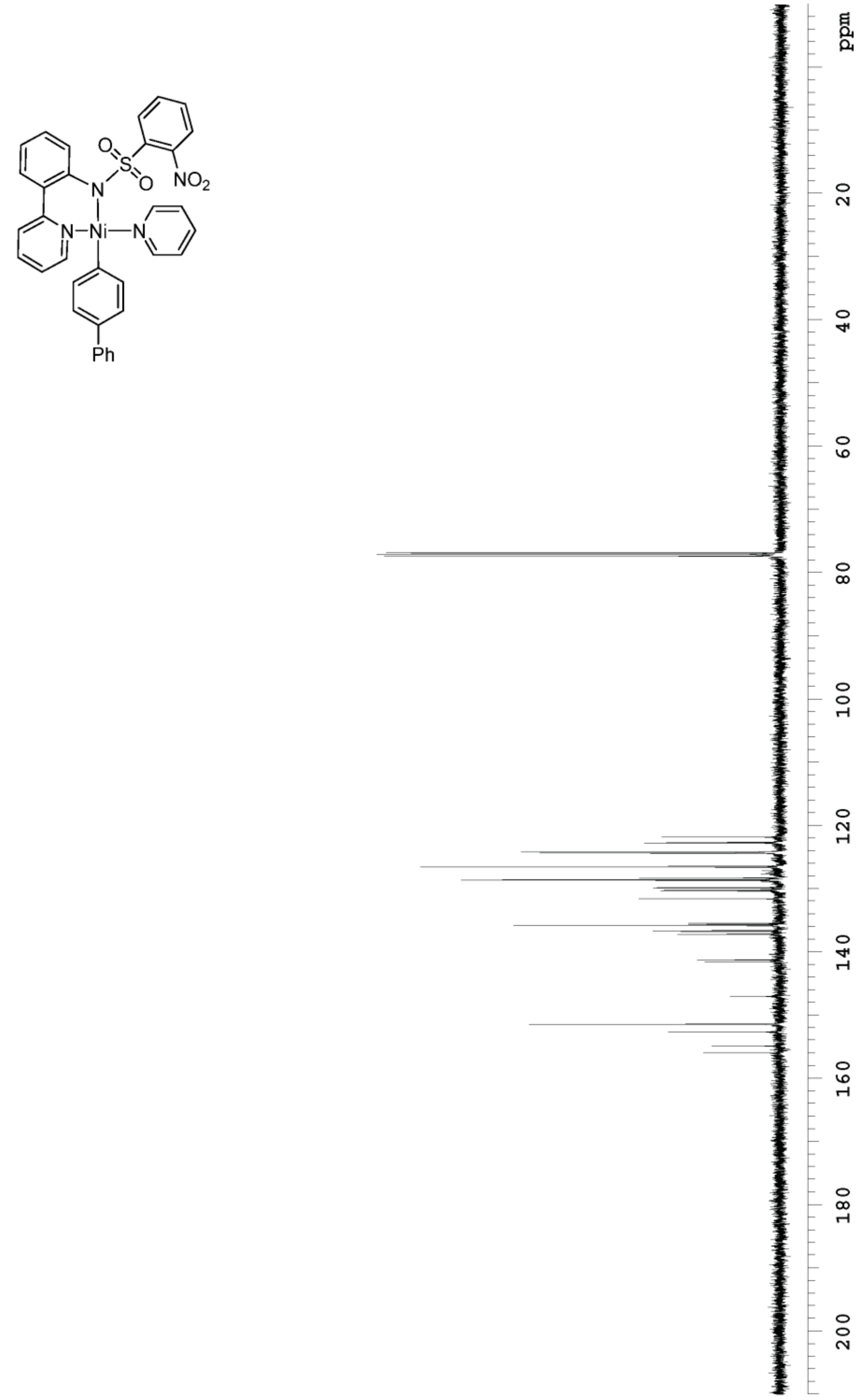
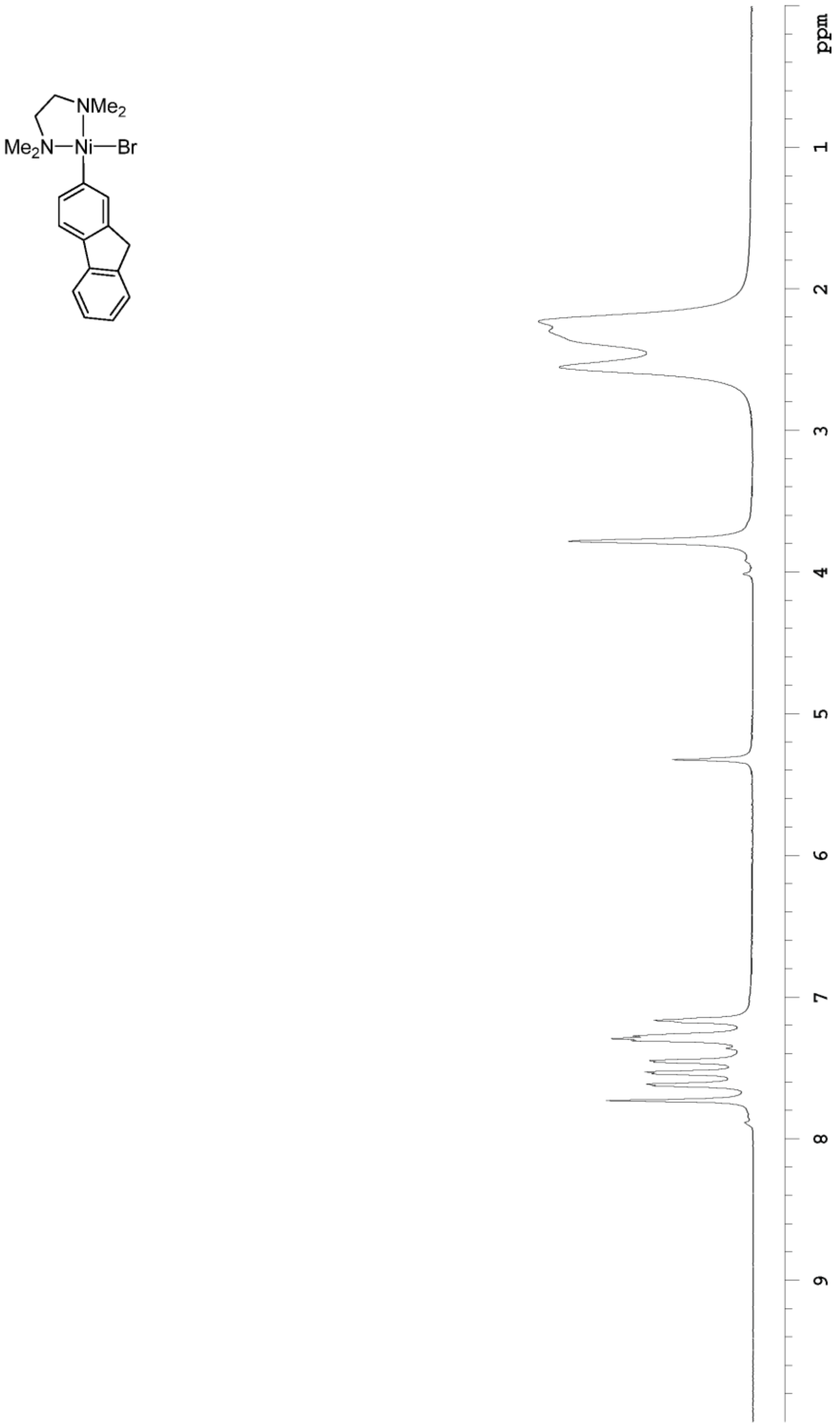




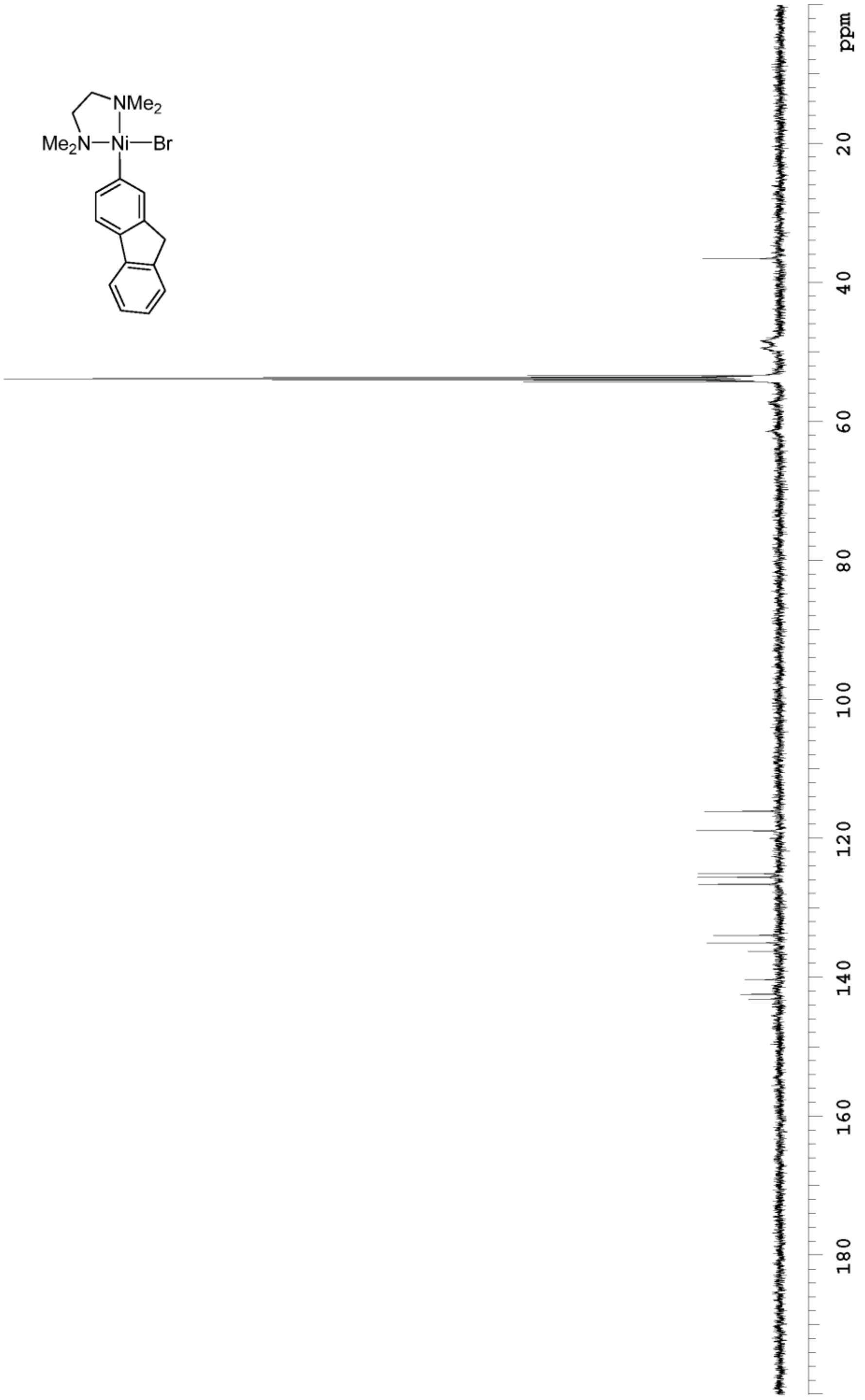
$^1$H NMR (CDCl$_3$, 23 ºC) of **1a**



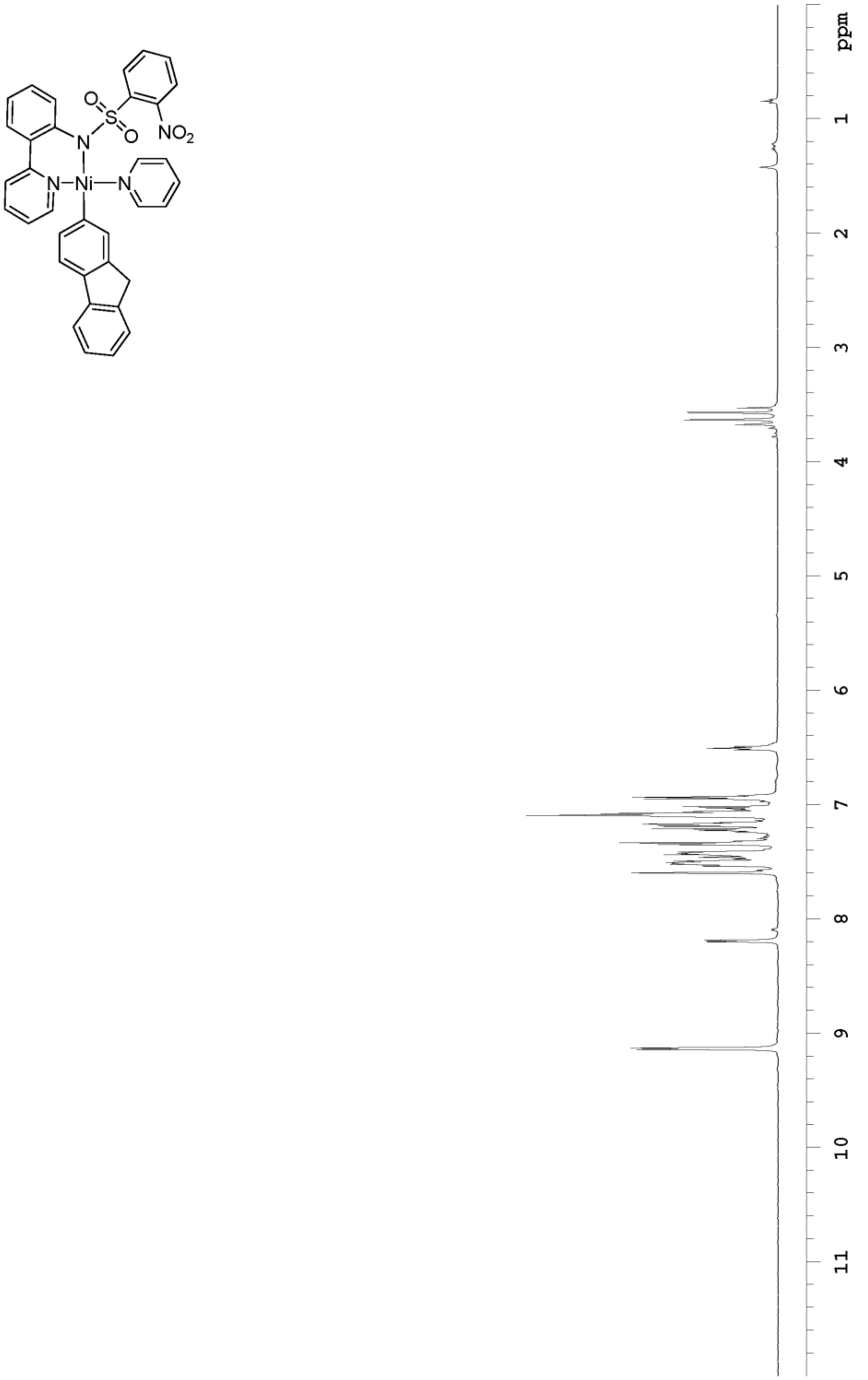
$^1$H NMR (CDCl$_3$, 23 ºC) of **1a**



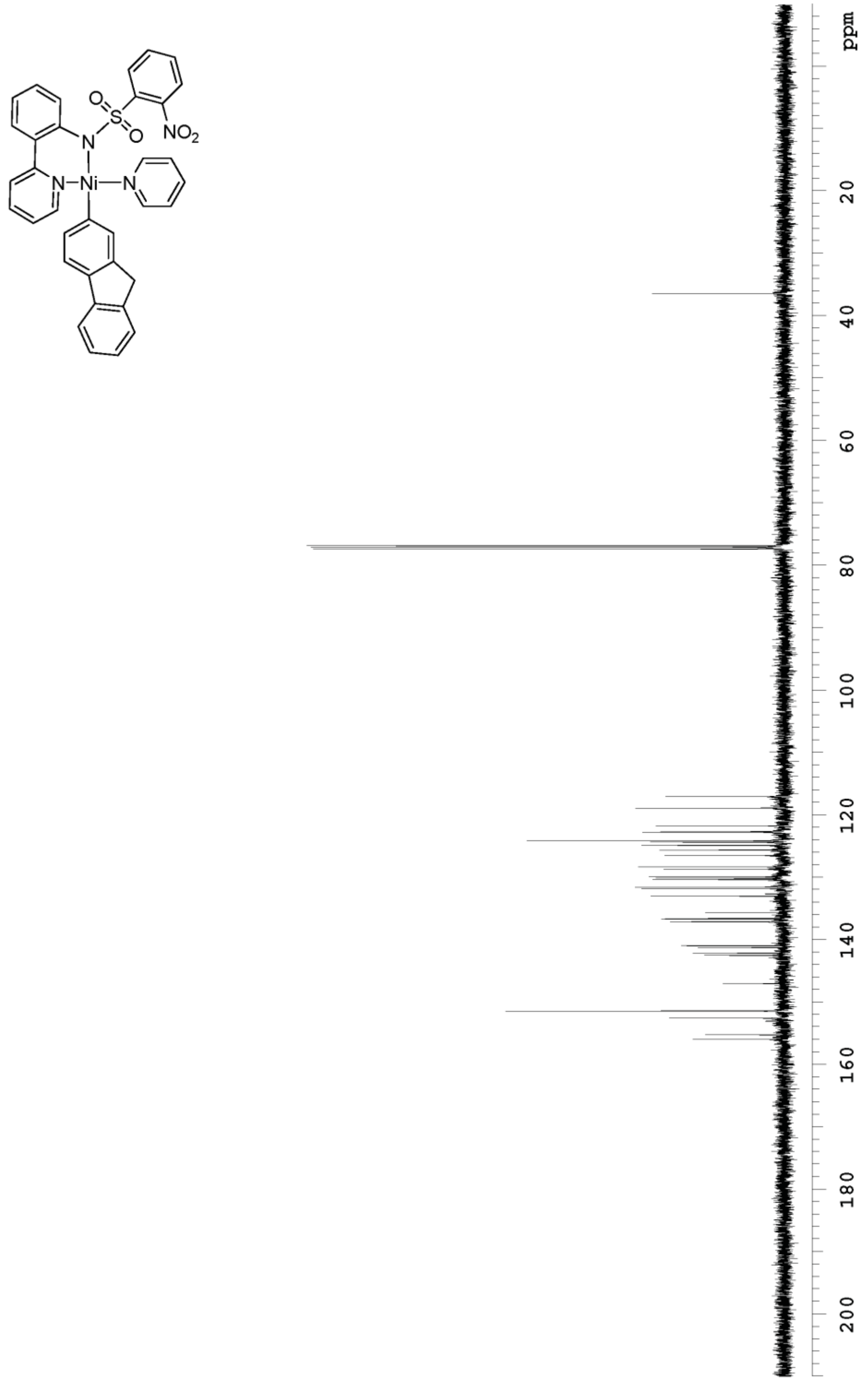
$^1$H NMR ($CD_2Cl_2$, 23 ºC) of **7b**



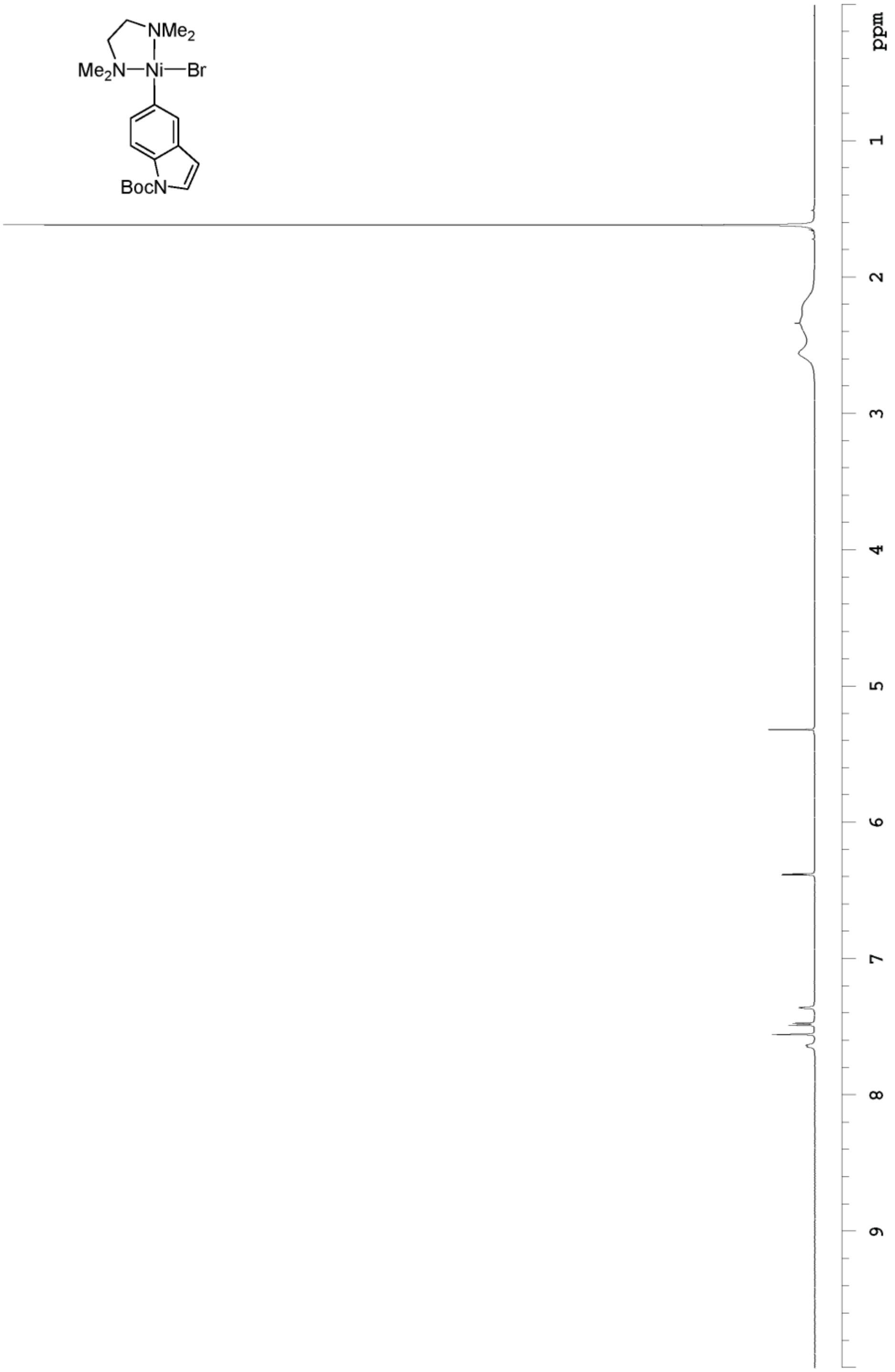
$^{13}$C NMR ($CD_2Cl_2$, 23 ºC) of **7b**



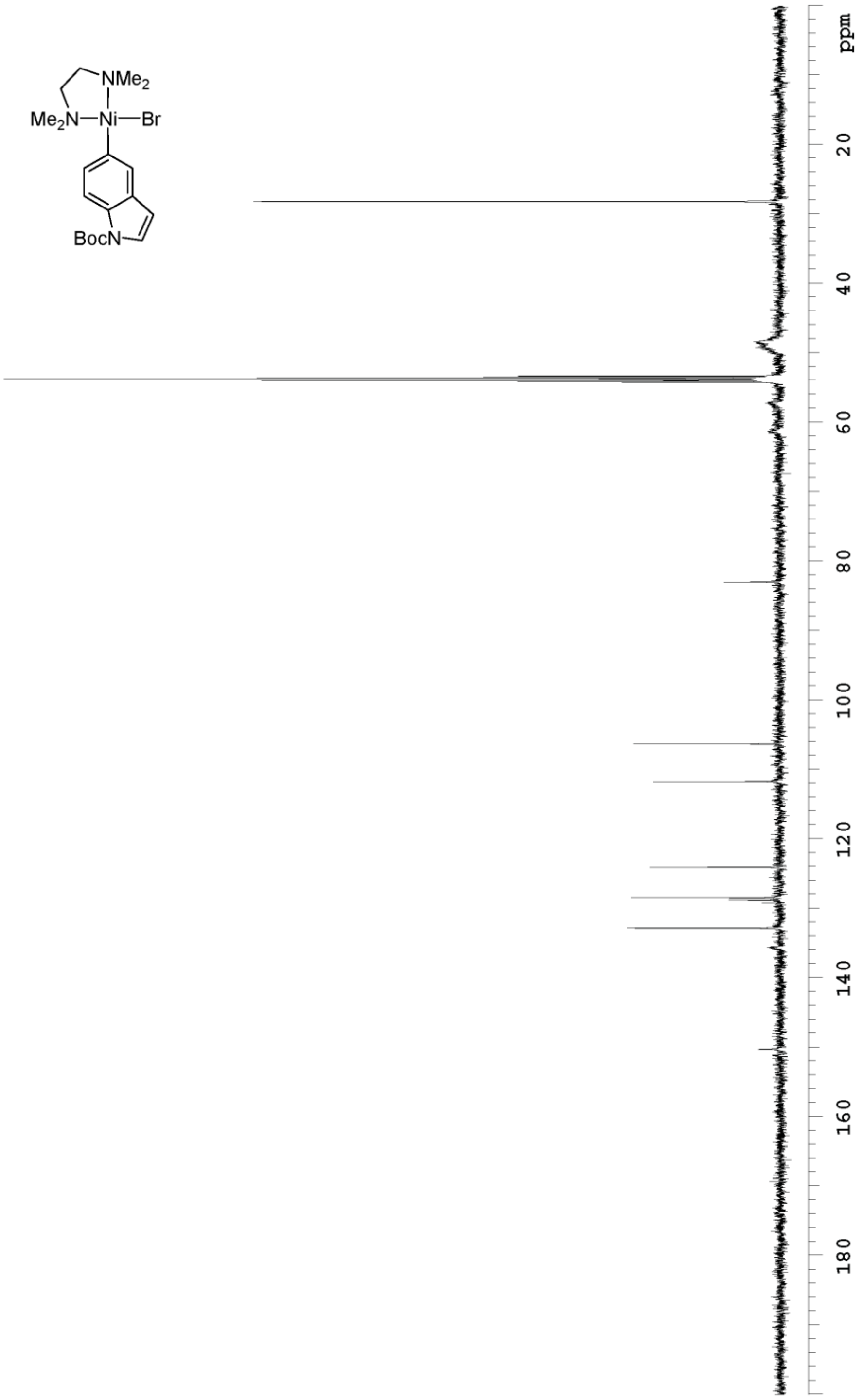
$^1$H NMR (CDCl$_3$, 23 ºC) of **1b**



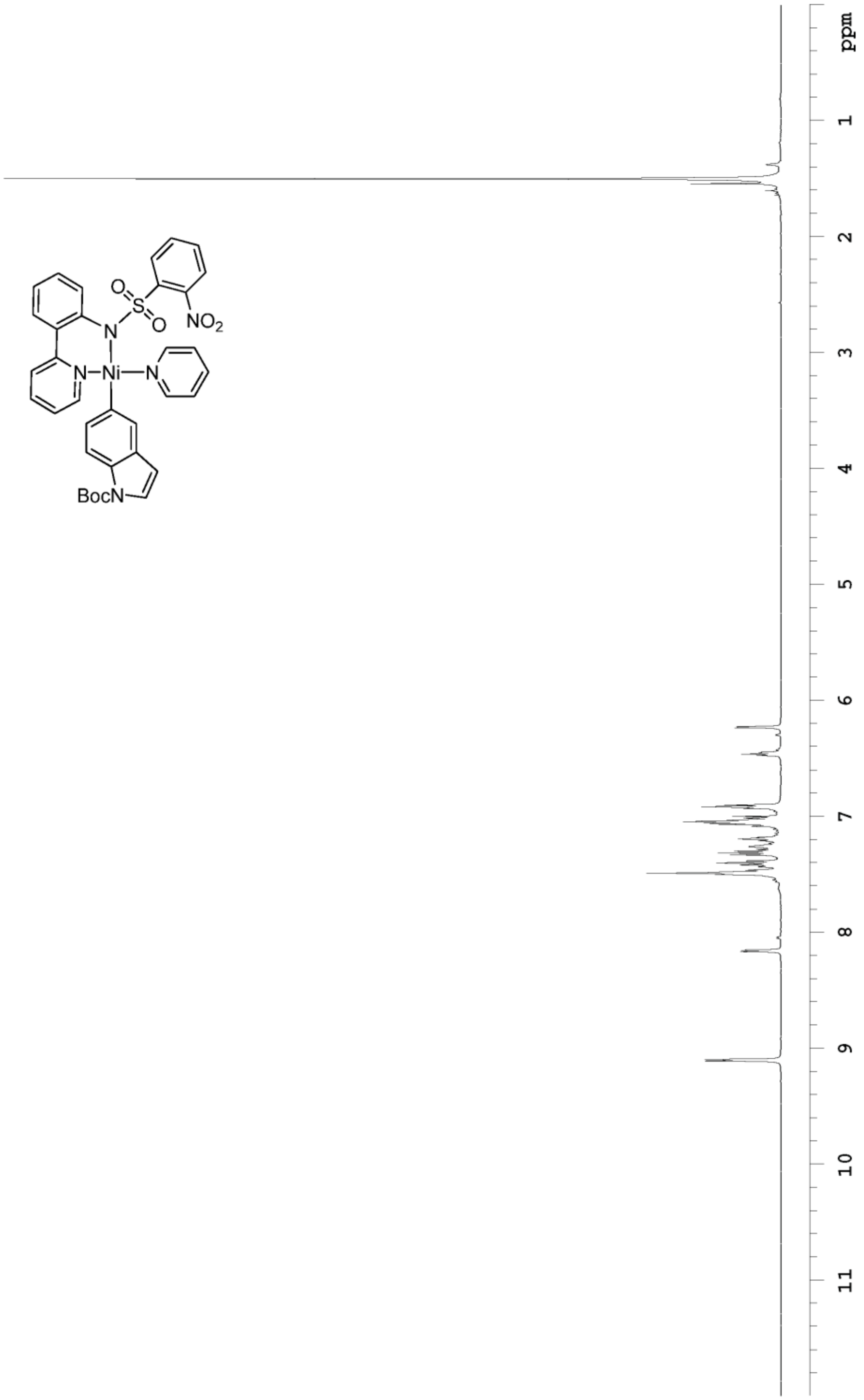
$^{13}$C NMR (CDCl$_3$, 23 ºC) of **1b**



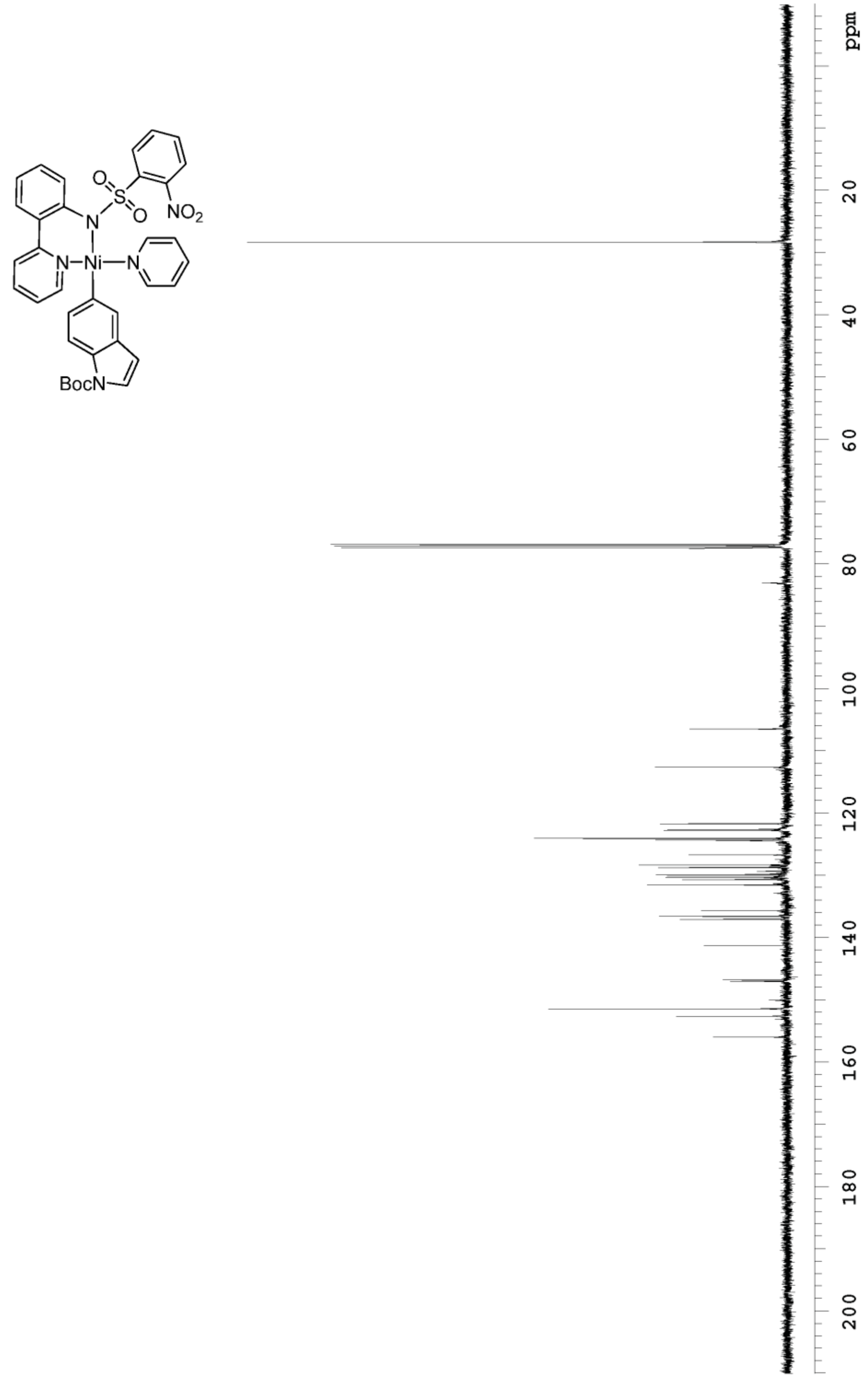
$^1$H NMR ($CD_2Cl_2$, 23 ºC) of **7c**



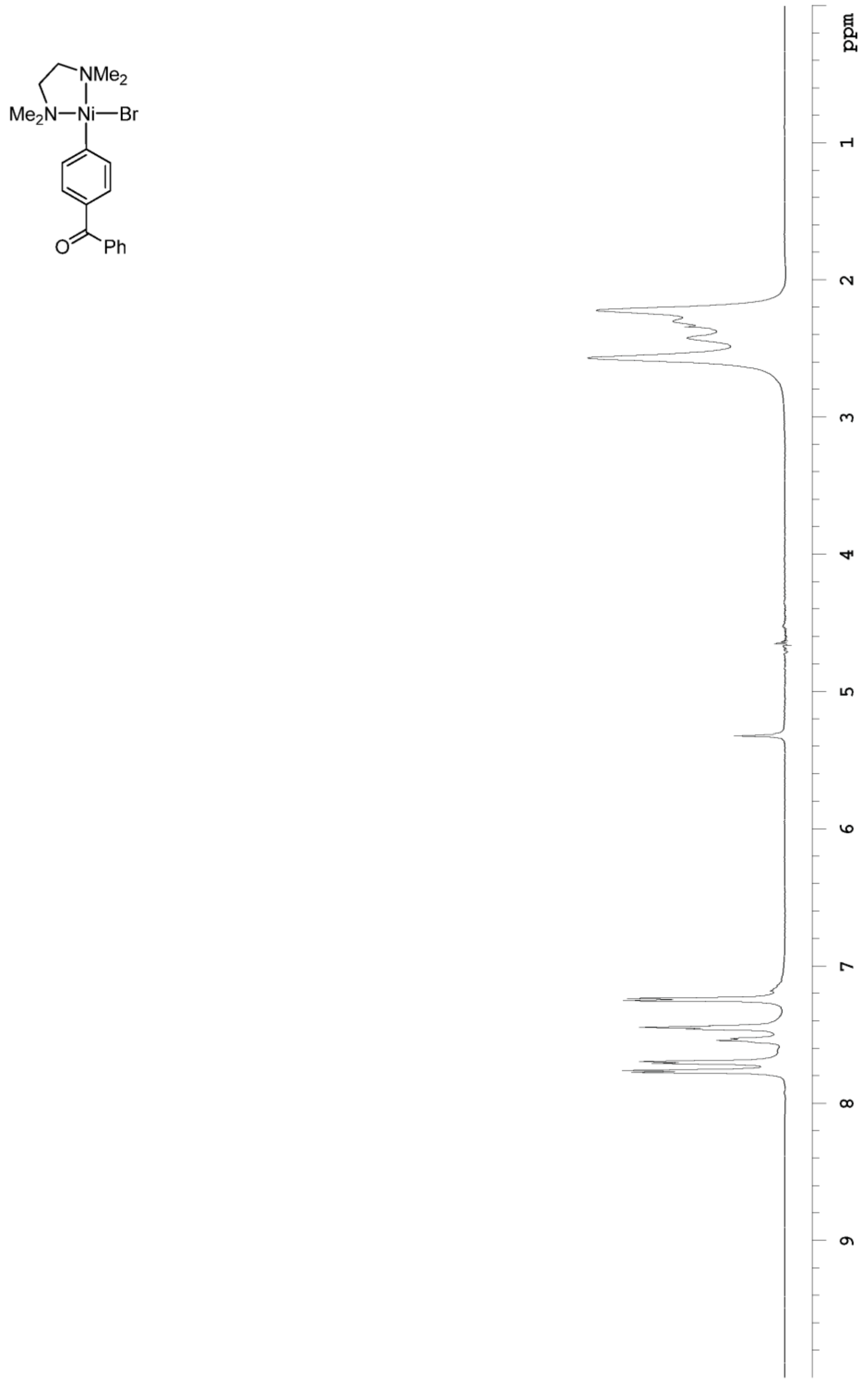
$^{13}$C NMR ($CD_2Cl_2$, 23 ºC) of **7c**



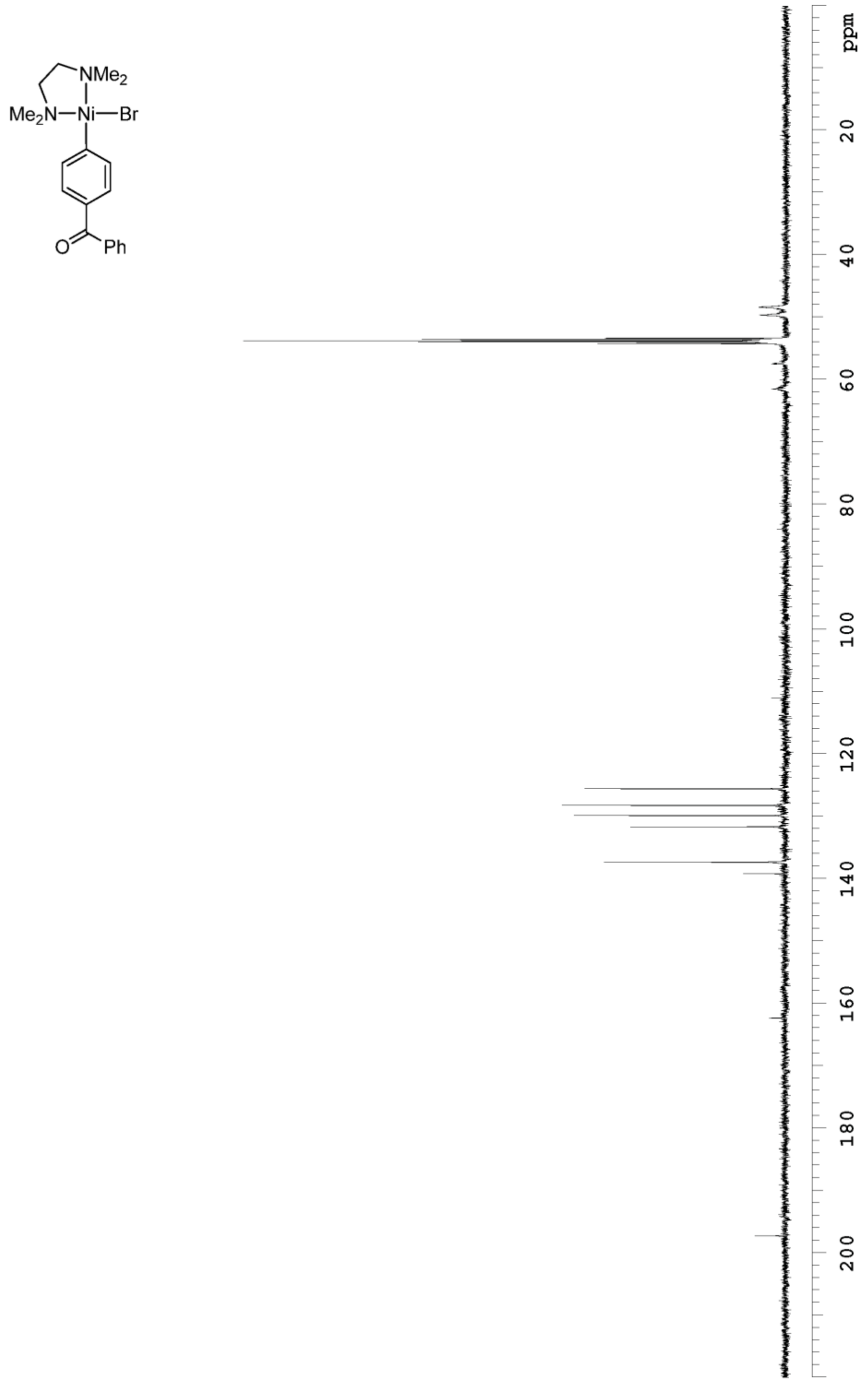
$^1$H NMR (CDCl$_3$, 23 ºC) of **1c**



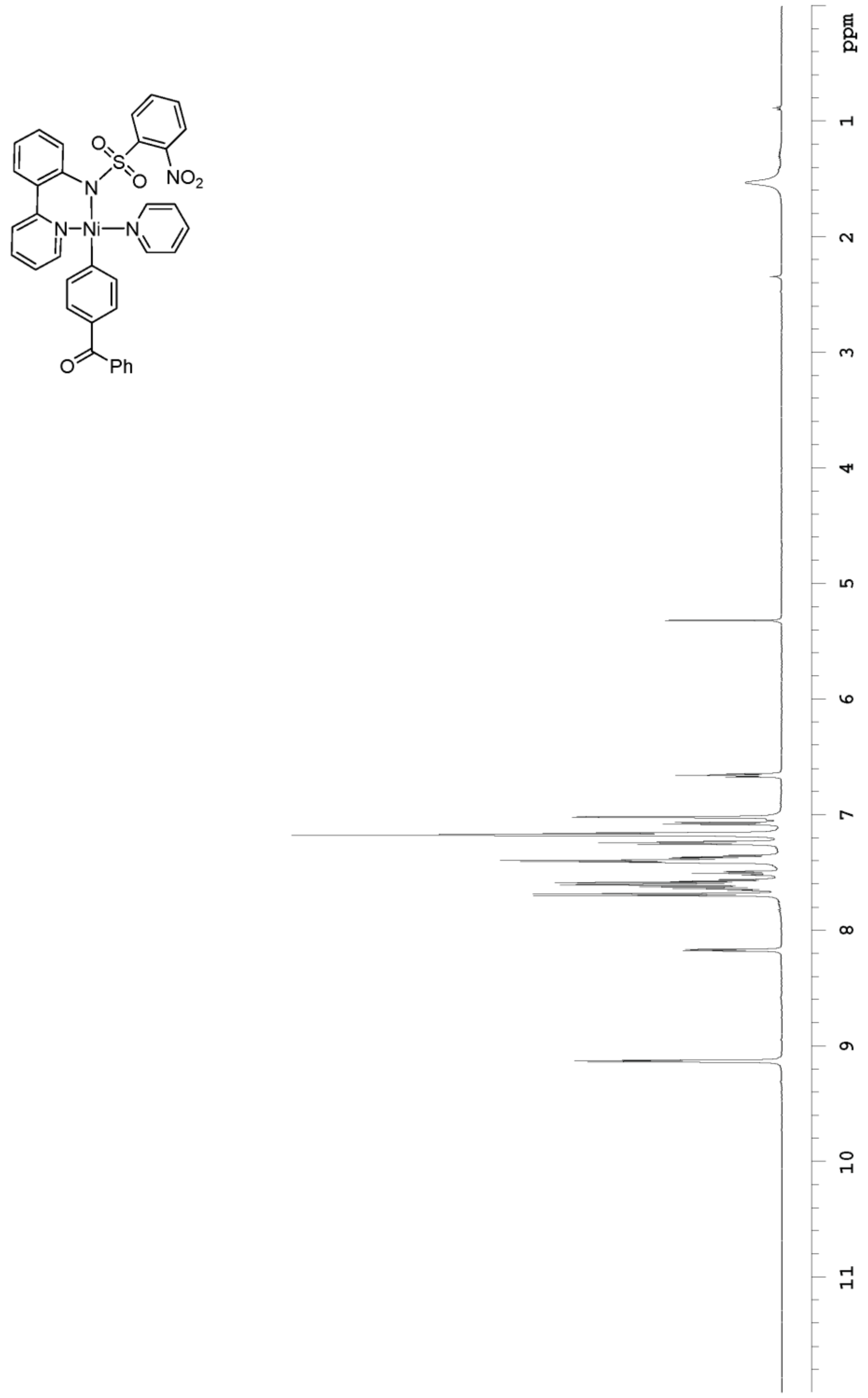
$^{13}$C NMR (CDCl$_3$, 23 ºC) of **1c**



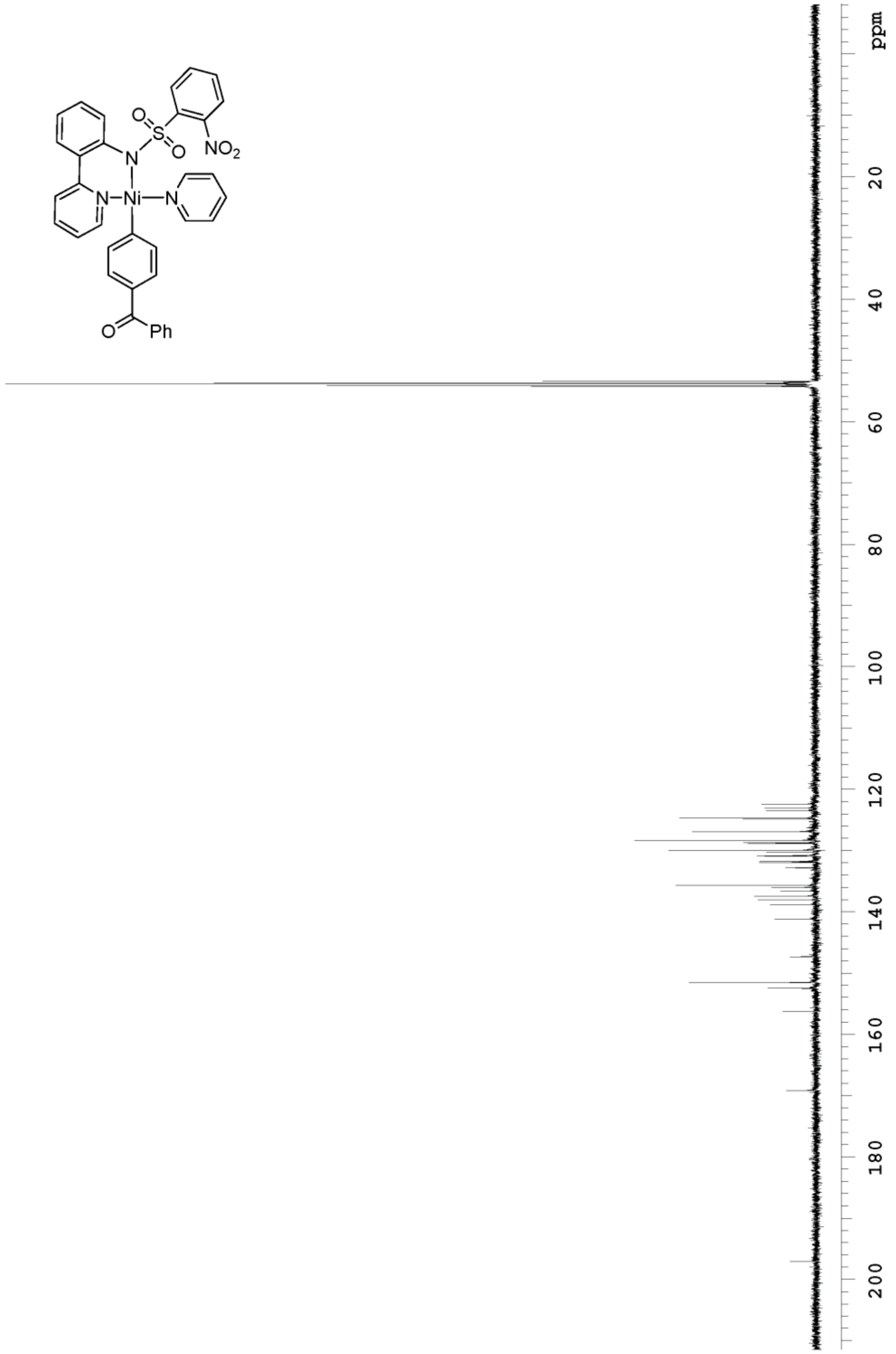
$^1$H NMR ($CD_2Cl_2$, 23 ºC) of **7d**



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



$^1$H NMR (CDCl$_3$, 23 ºC) of **1d**



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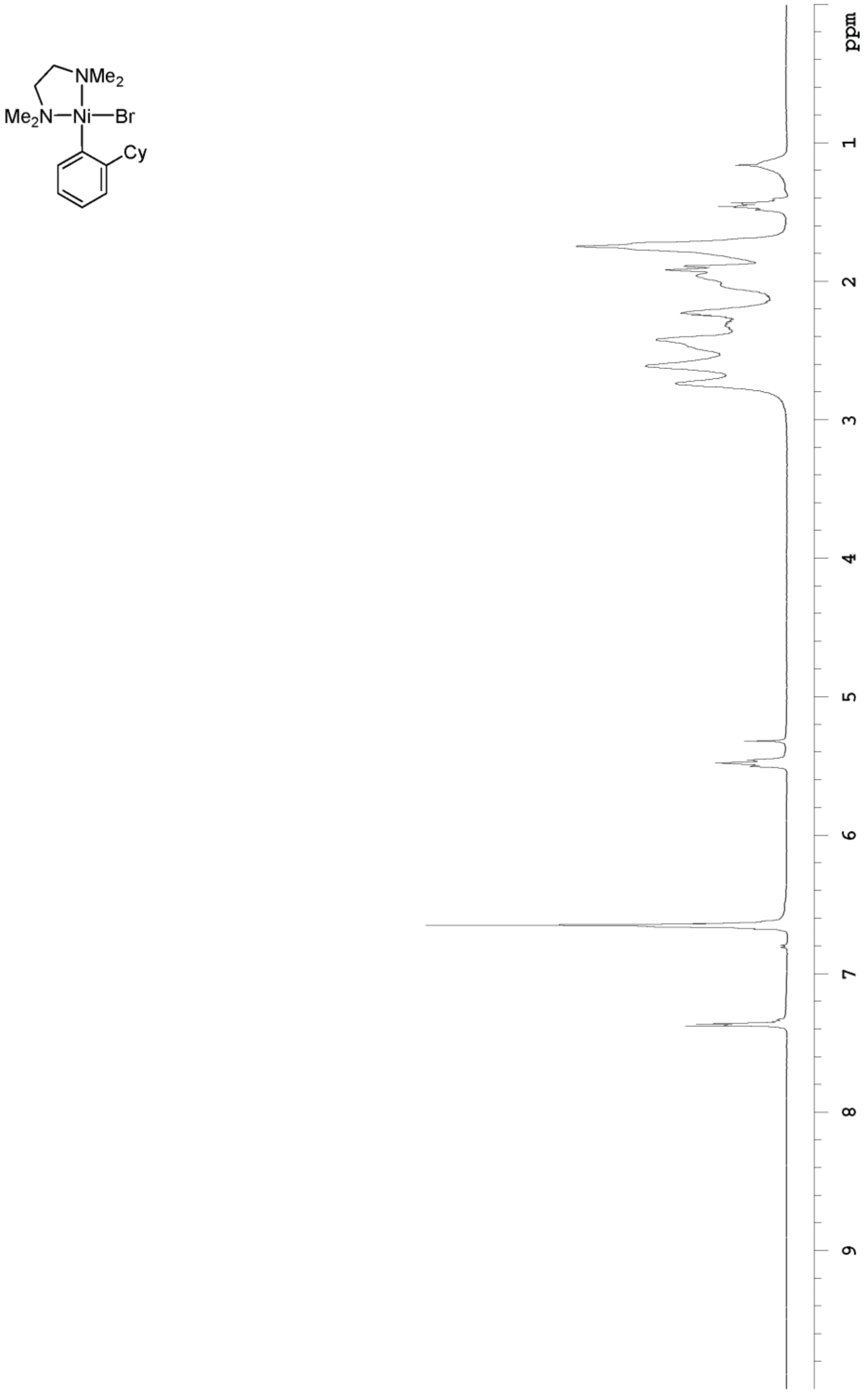

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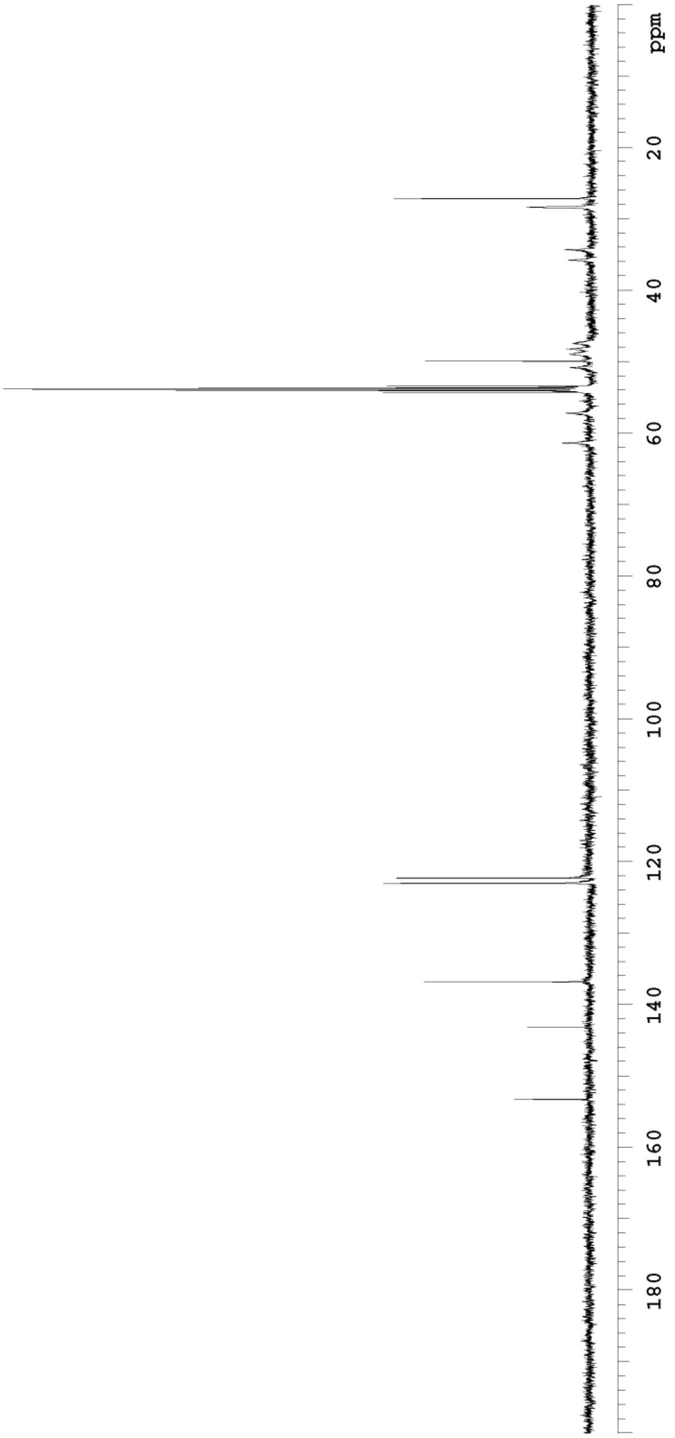

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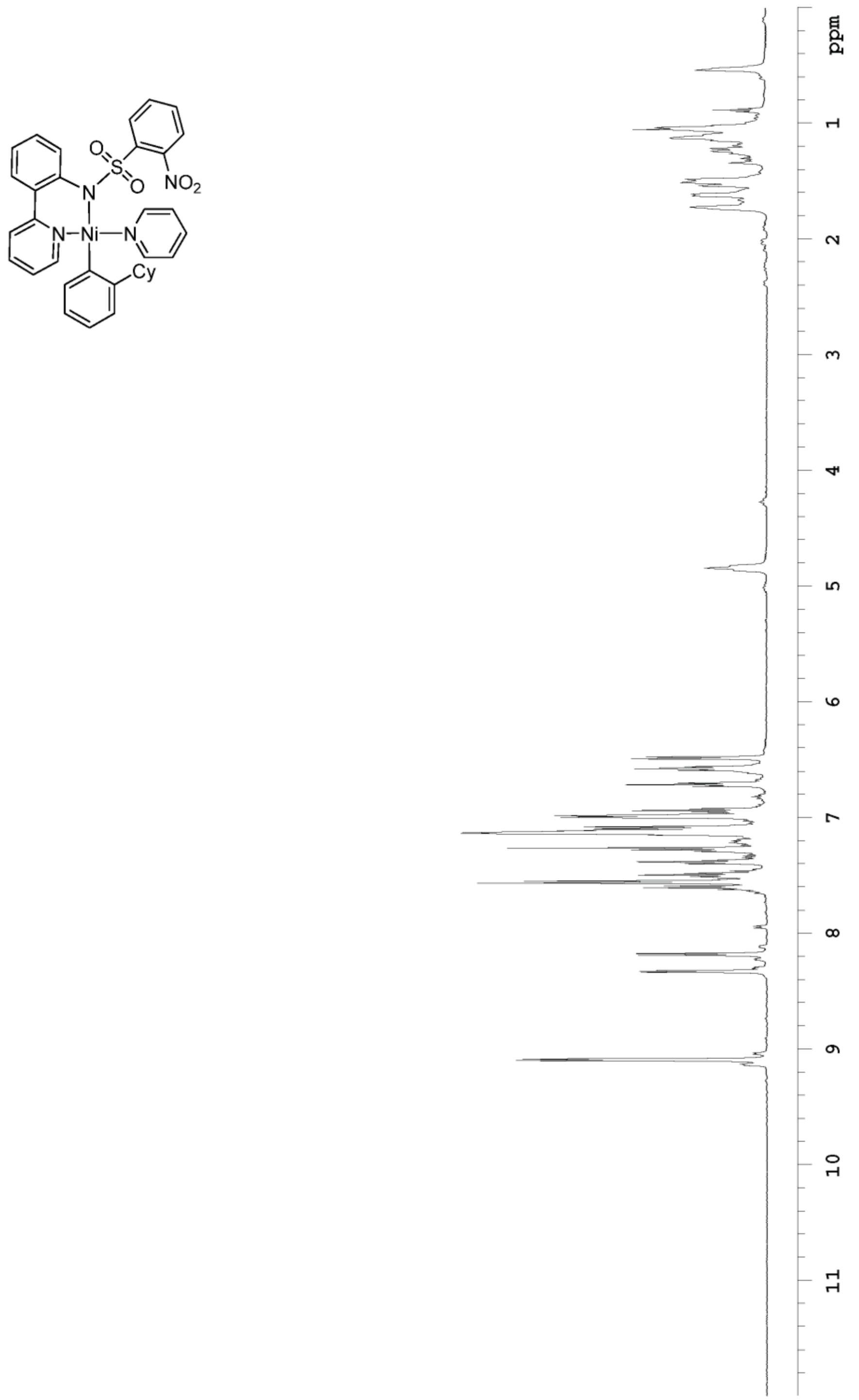

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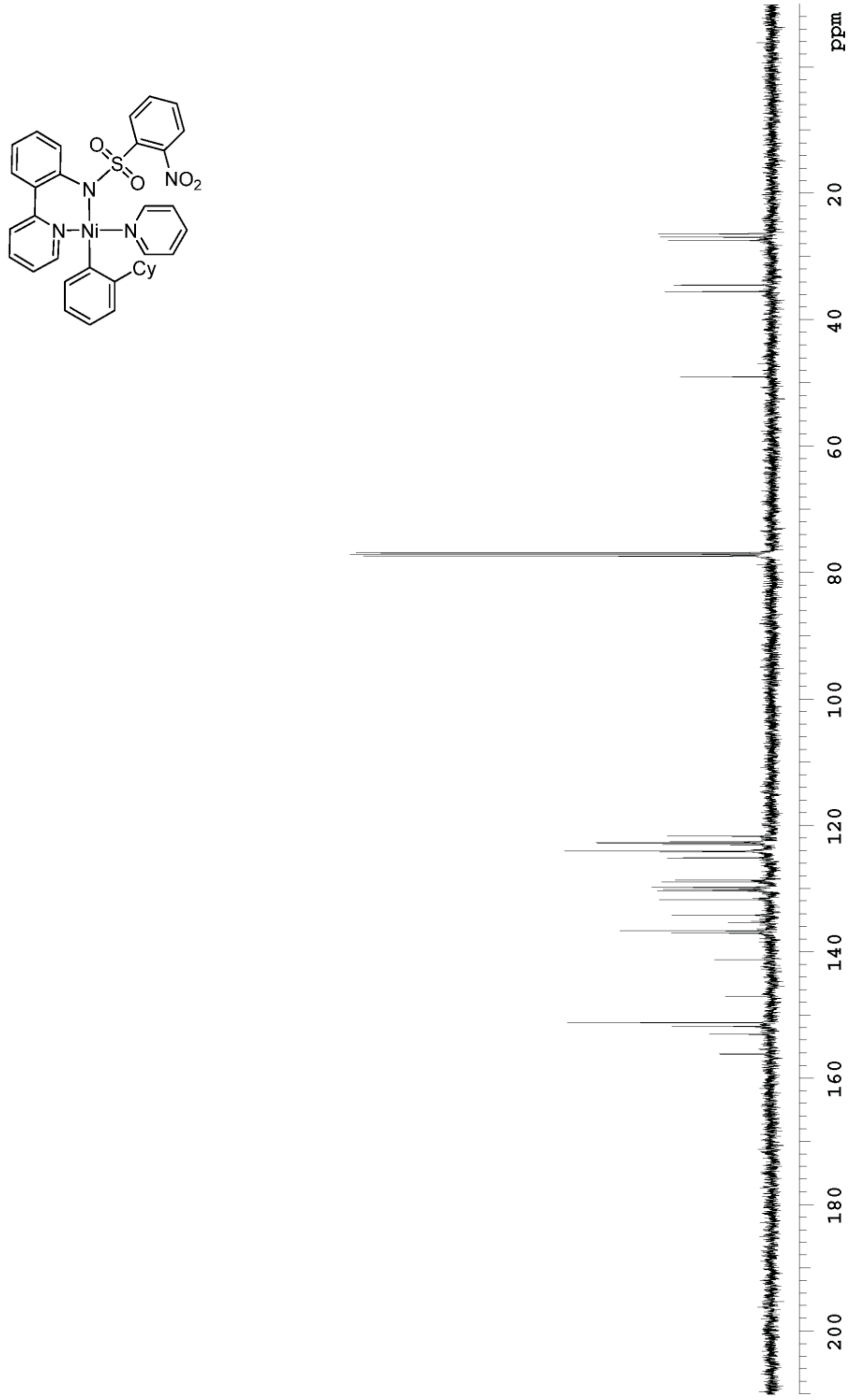

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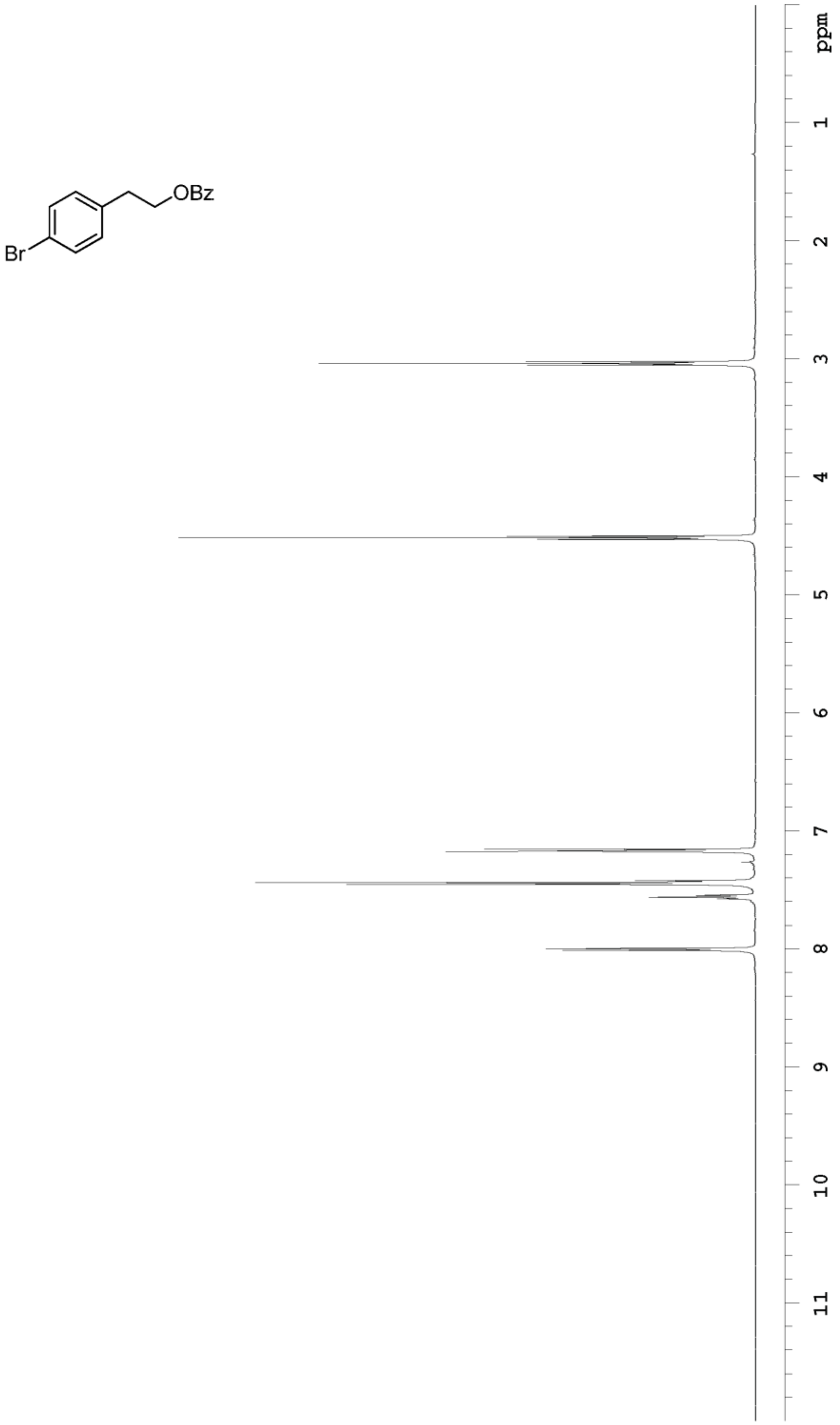
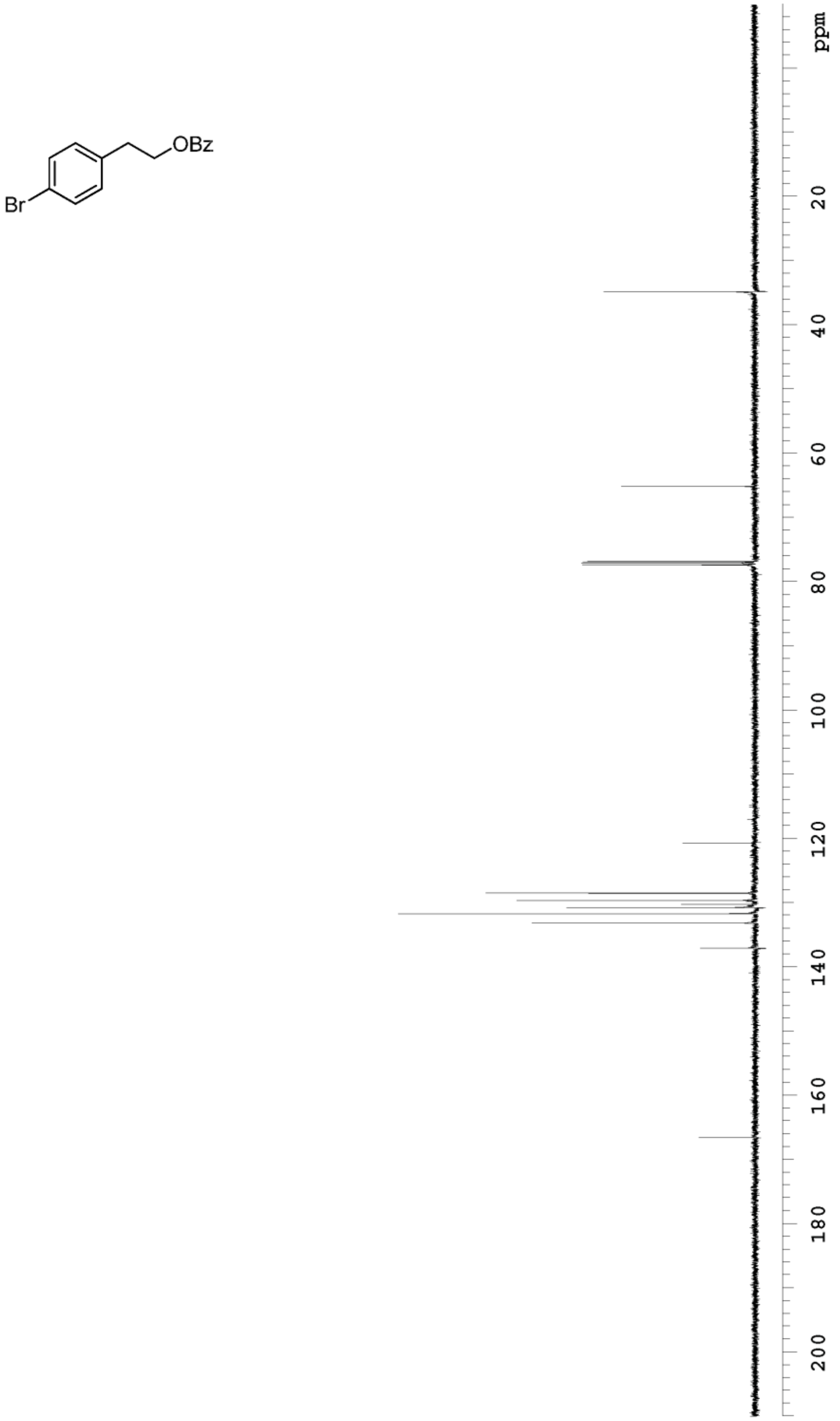
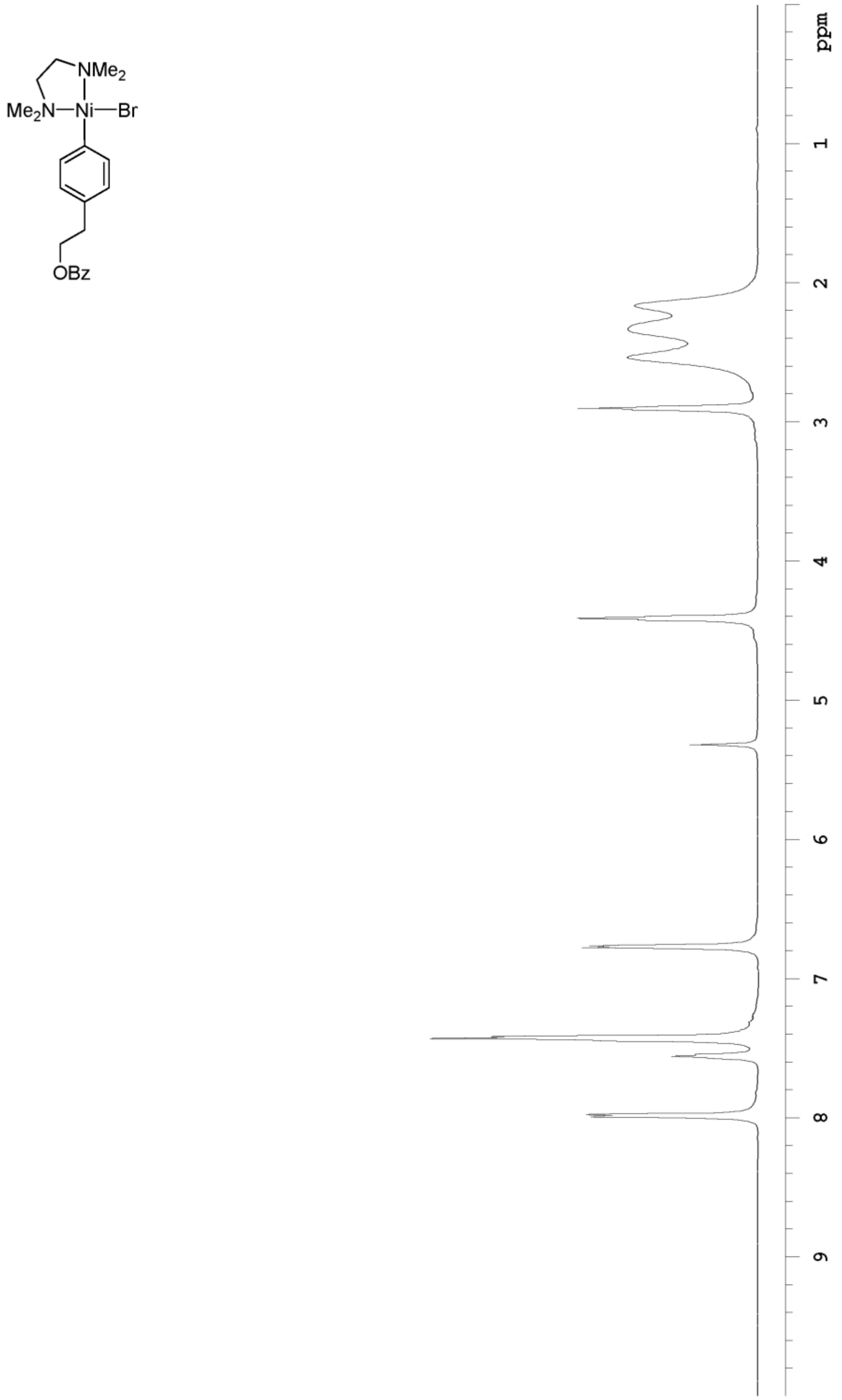


$^1$H NMR (CDCl$_3$, 23 ºC) of **S3**



$^{13}$C NMR (CDCl$_3$, 23 ºC) of **S3**



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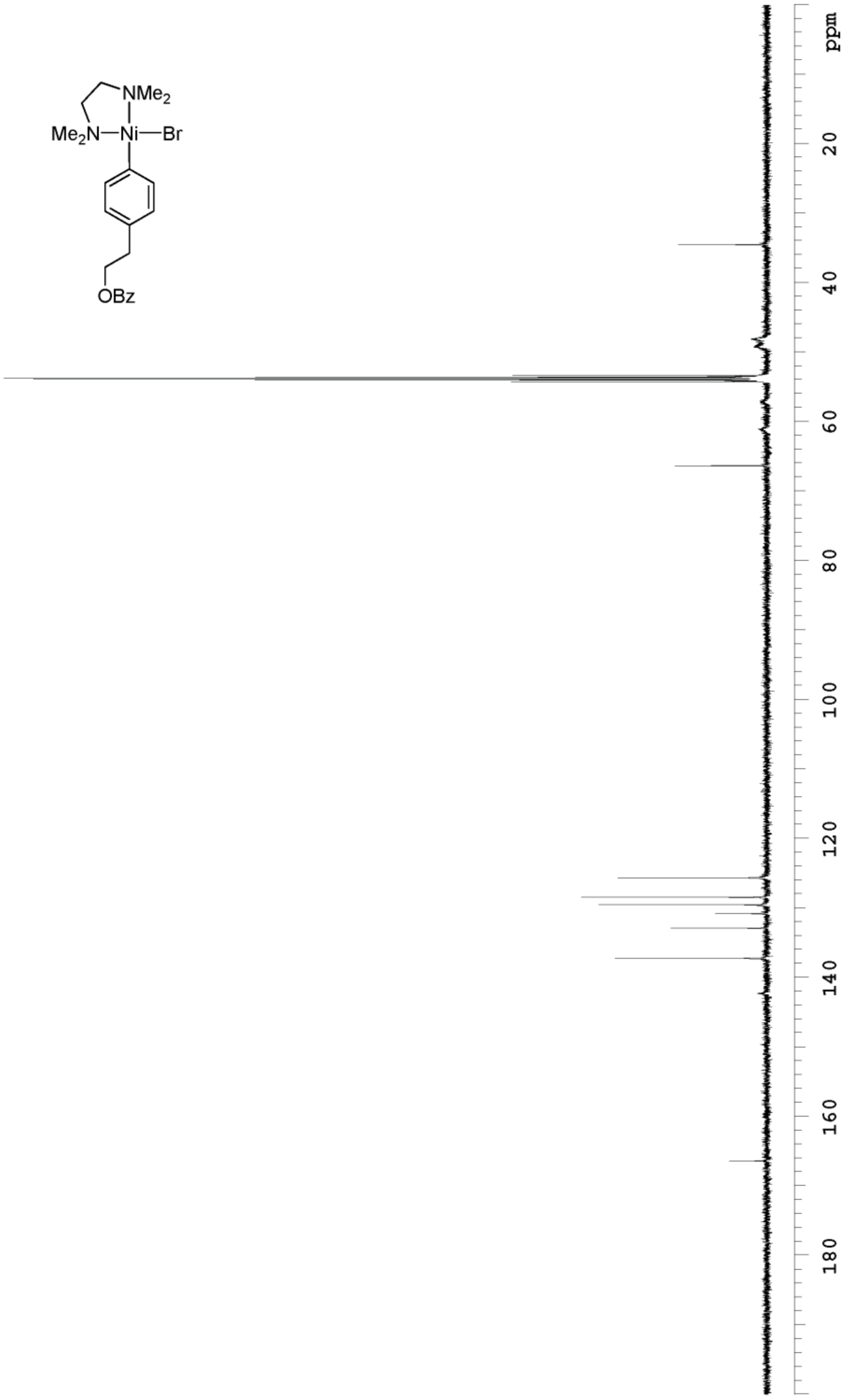

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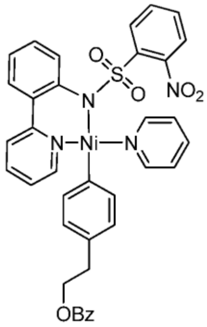

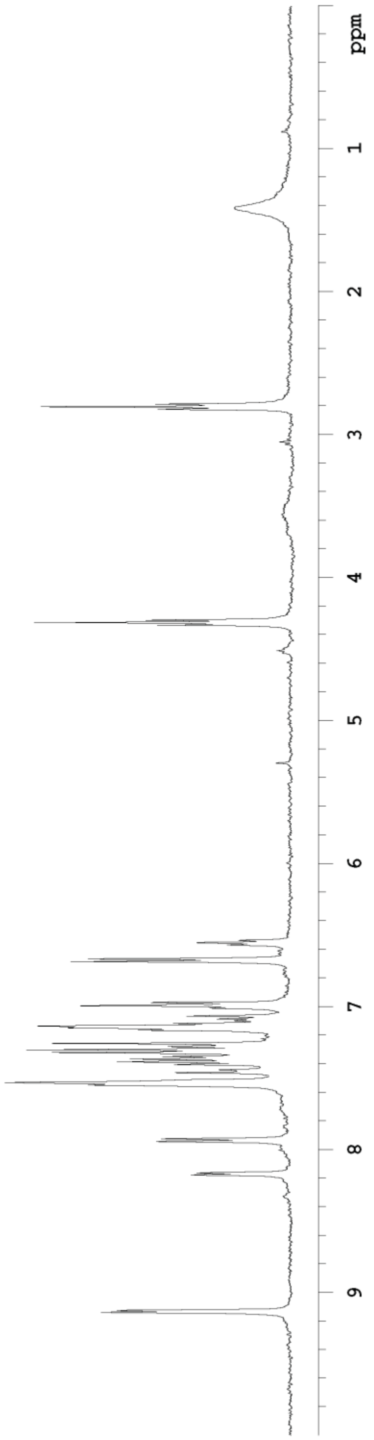

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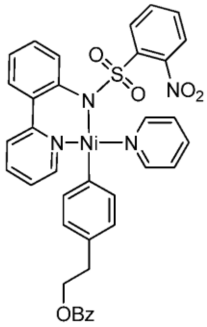

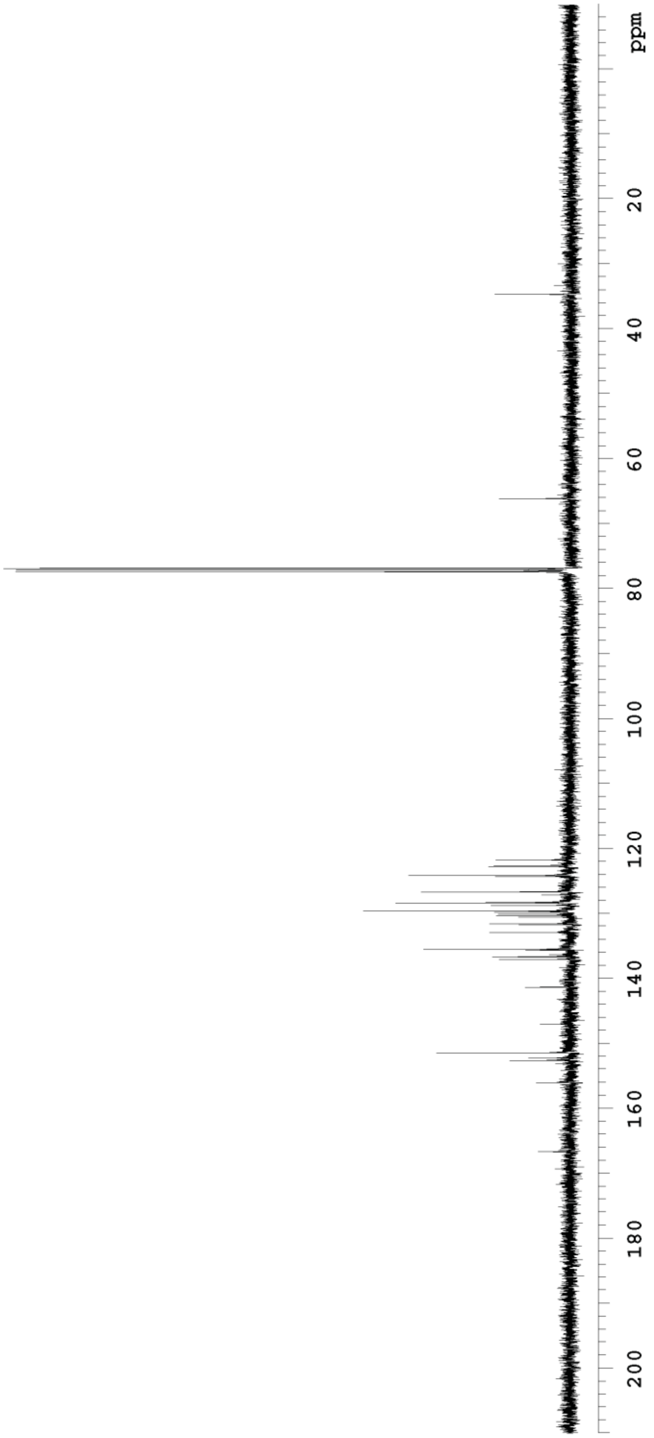

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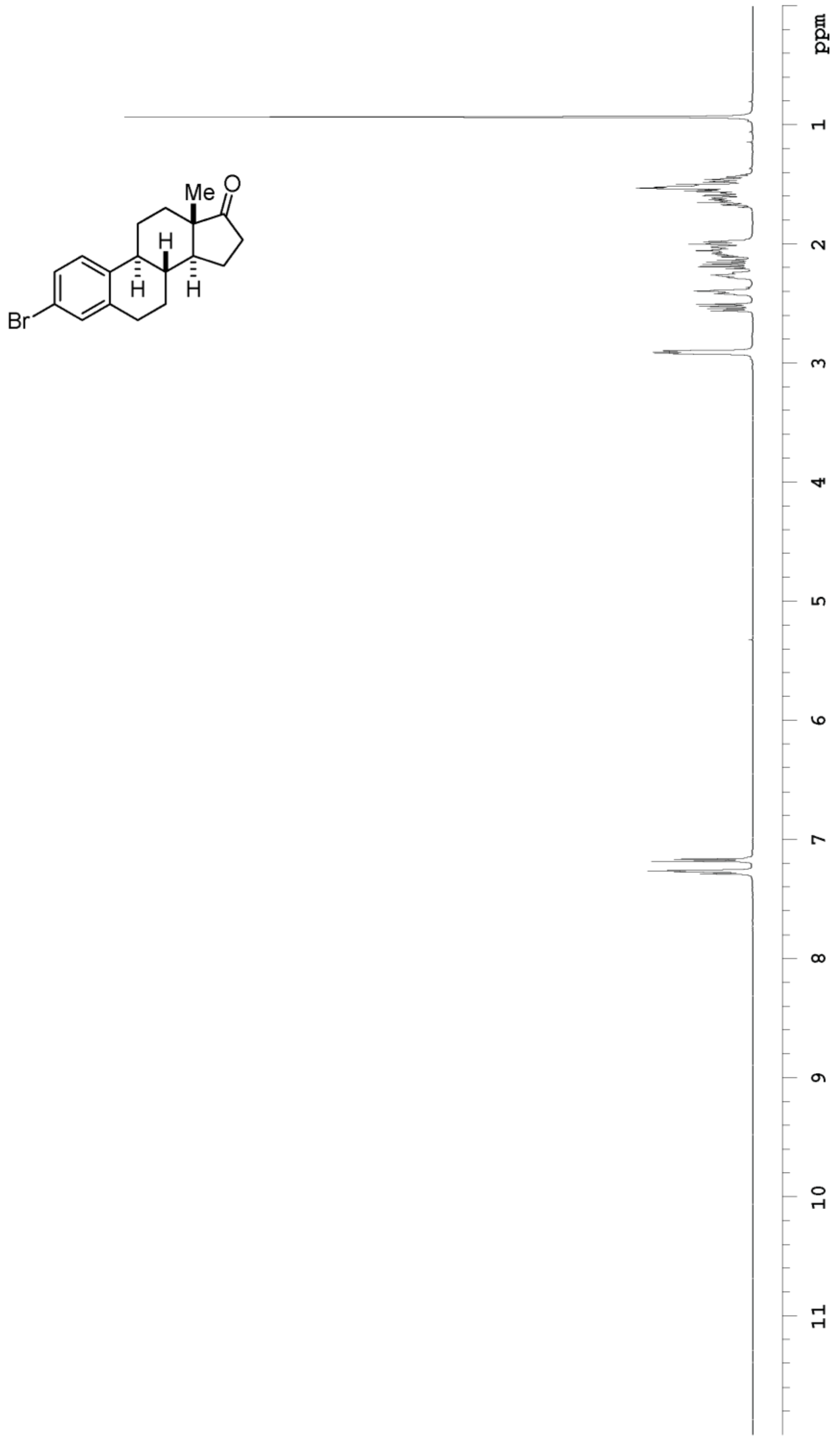

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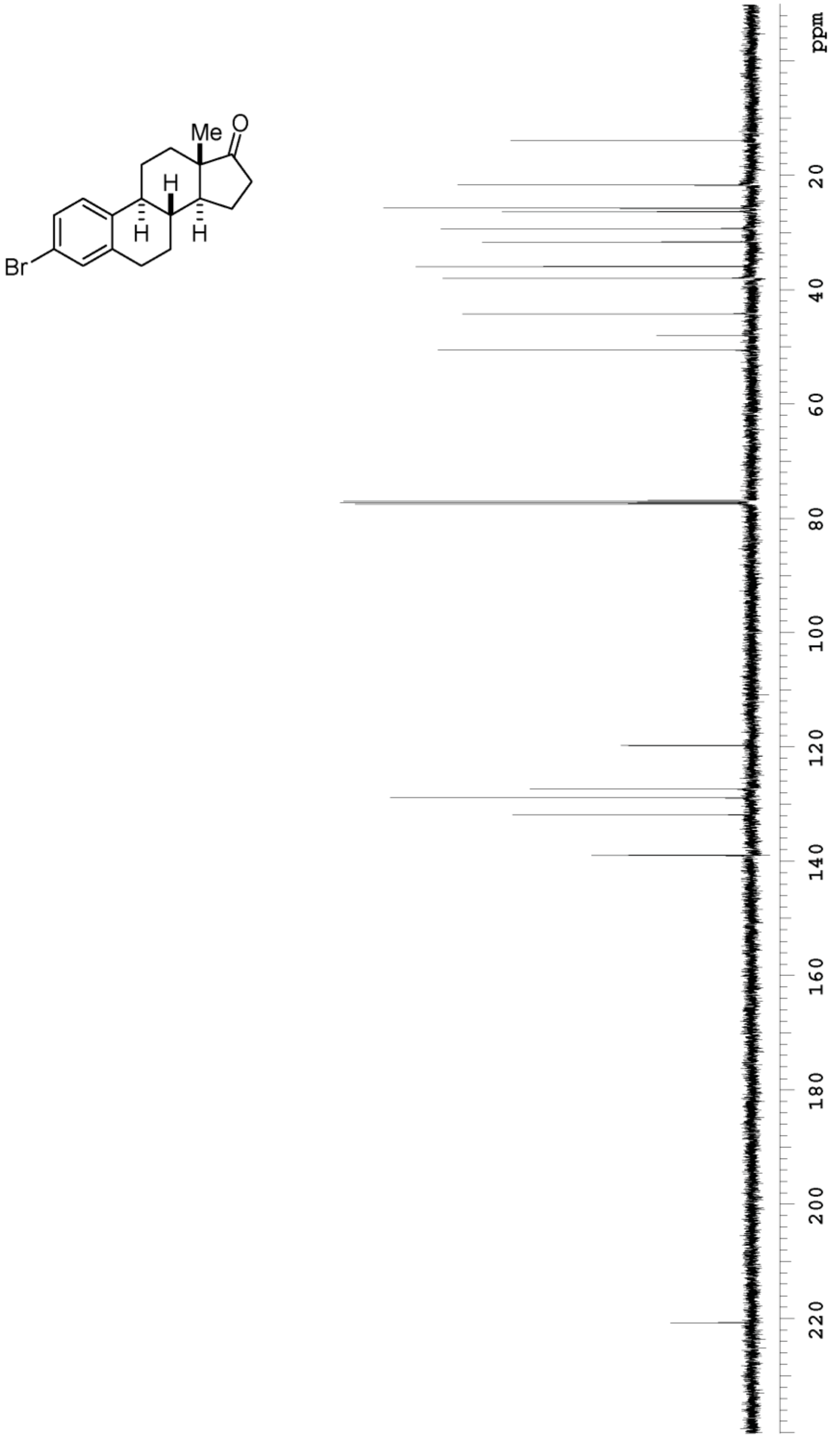
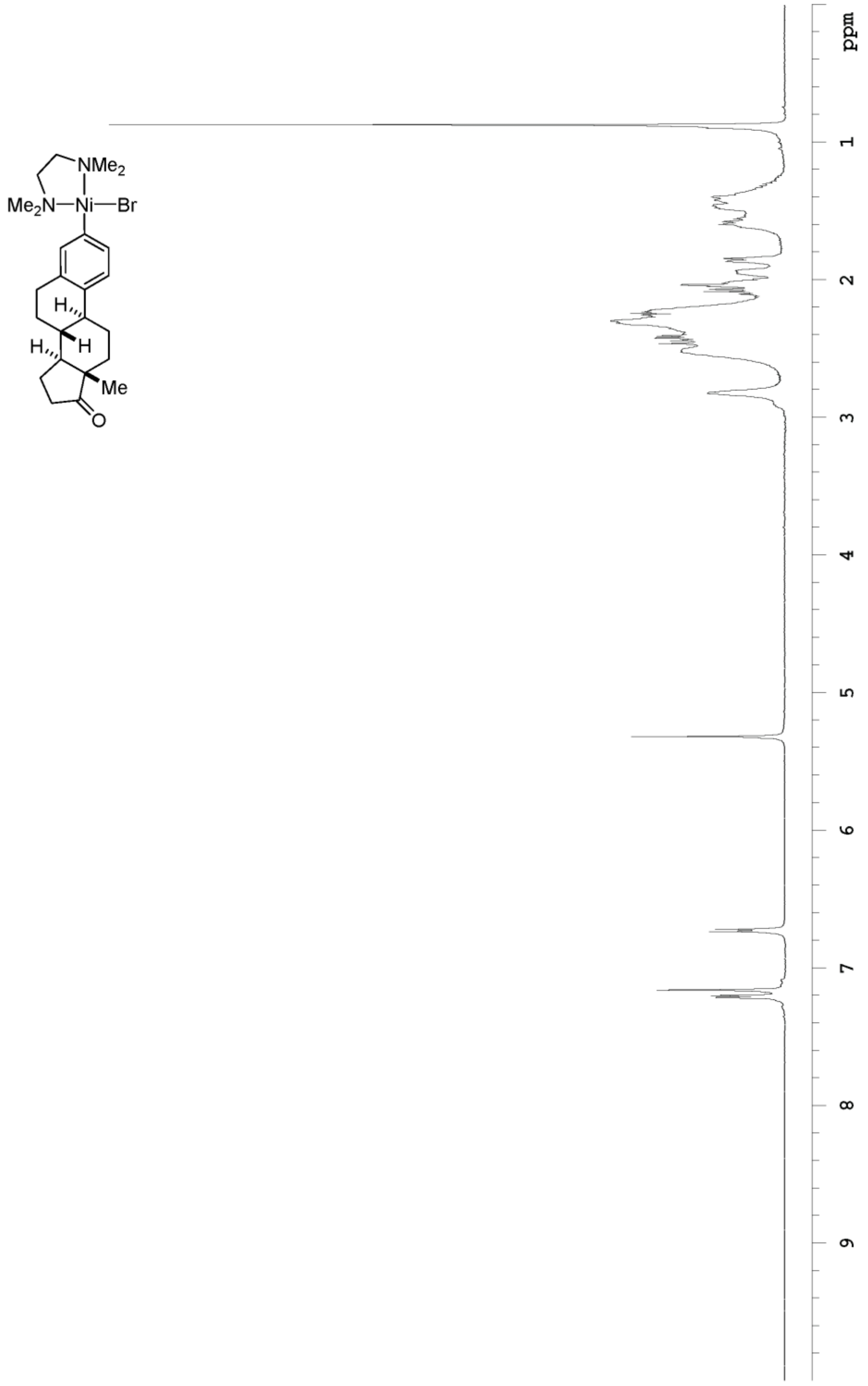
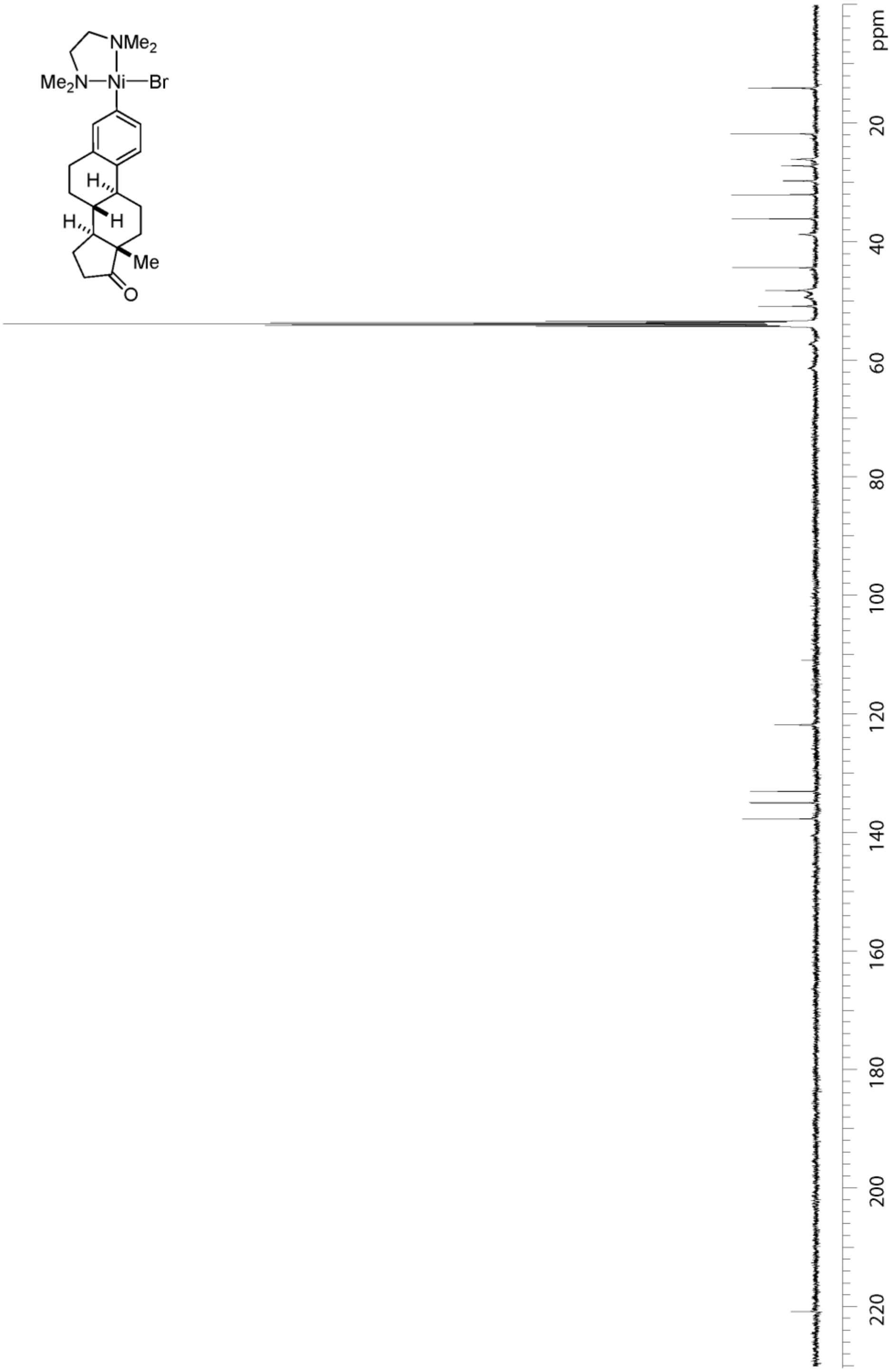


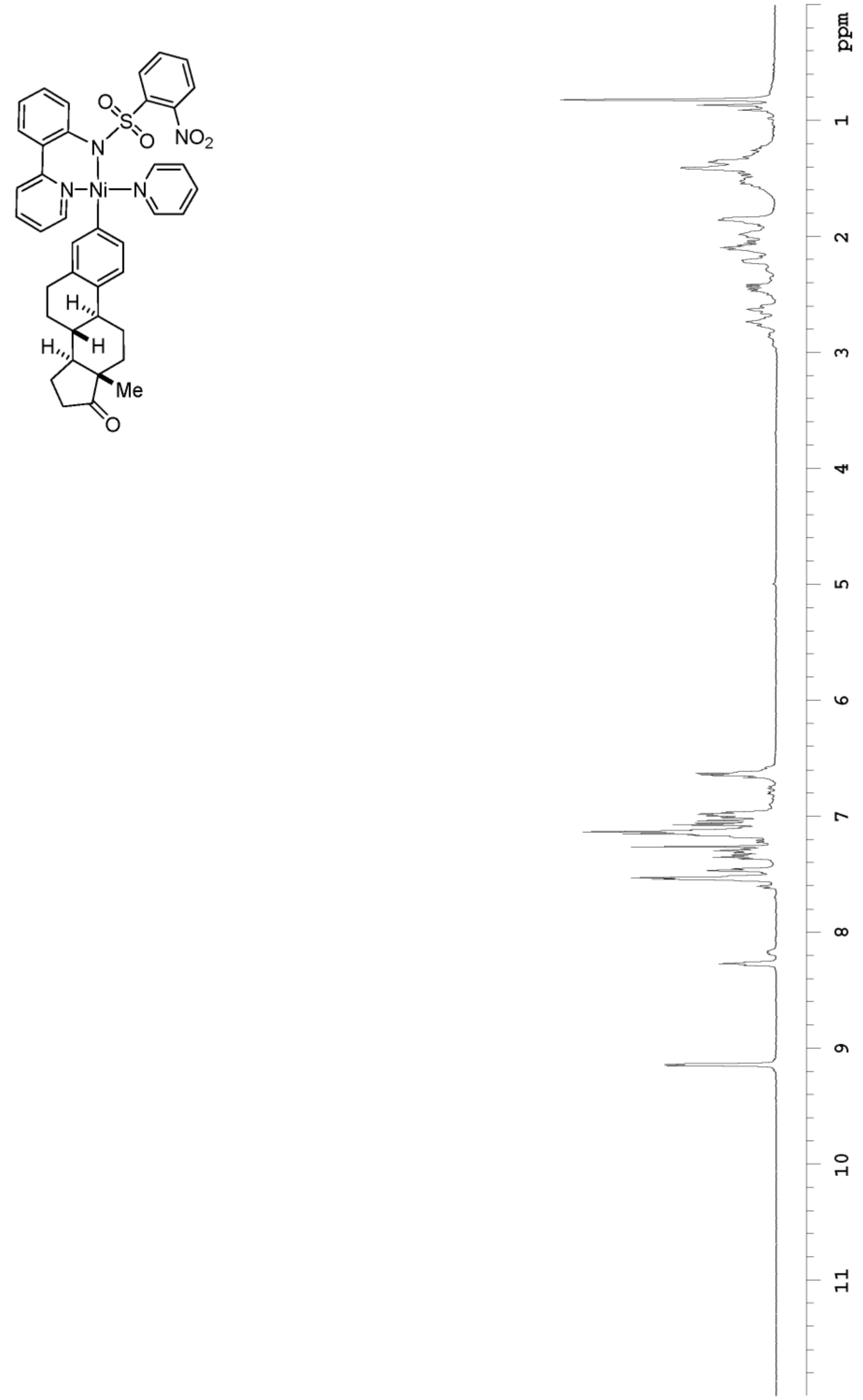
$^{13}$C NMR (CDCl$_3$, 23 ºC) of **S4**



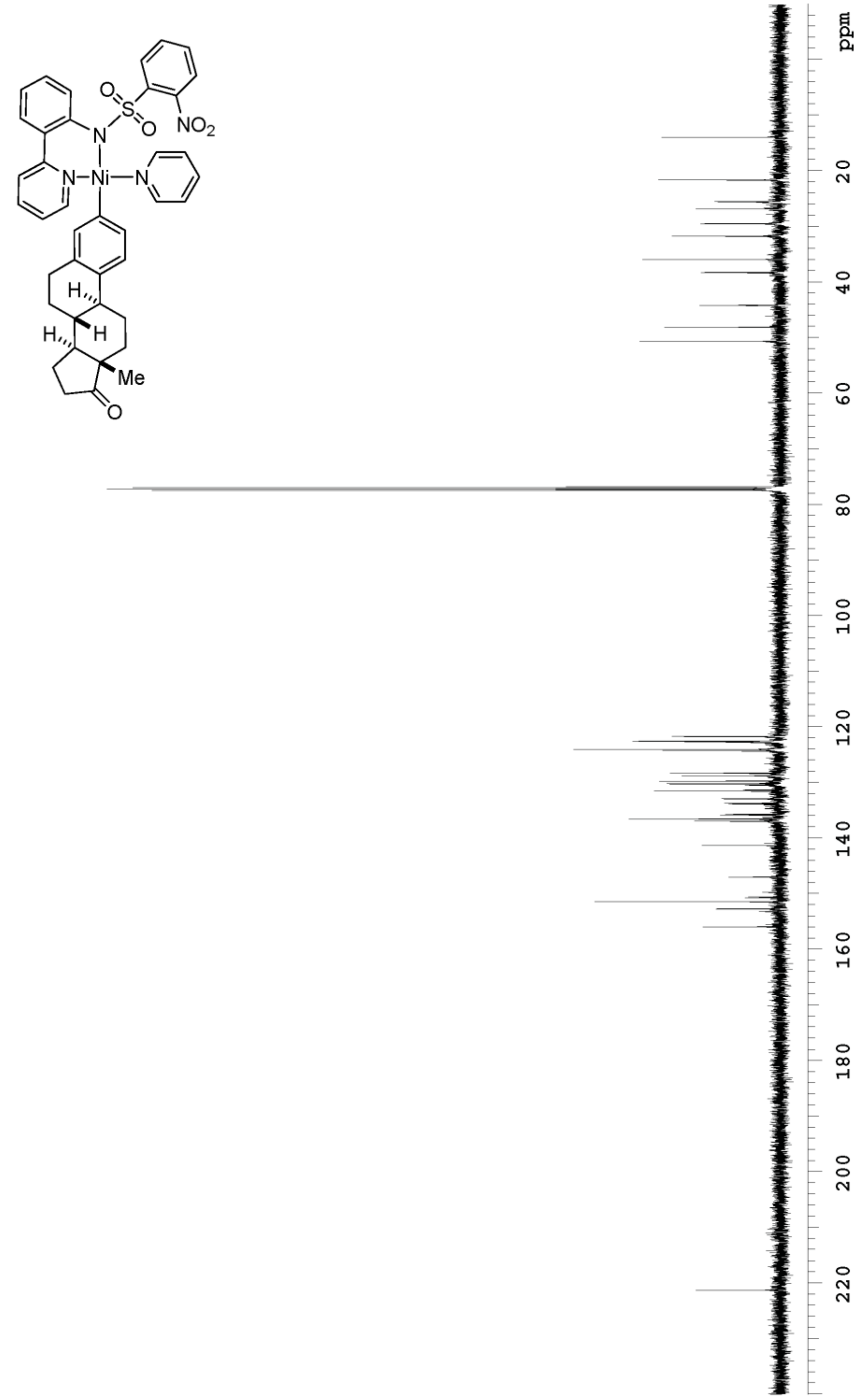
$^{1}$H NMR ($CD_2Cl_2$, 23 ºC) of **7g**



$^{13}$C NMR ($CD_2Cl_2$, 23 ºC) of **7g**



$^1$H NMR (CDCl$_3$, 23 ºC) of **1g**



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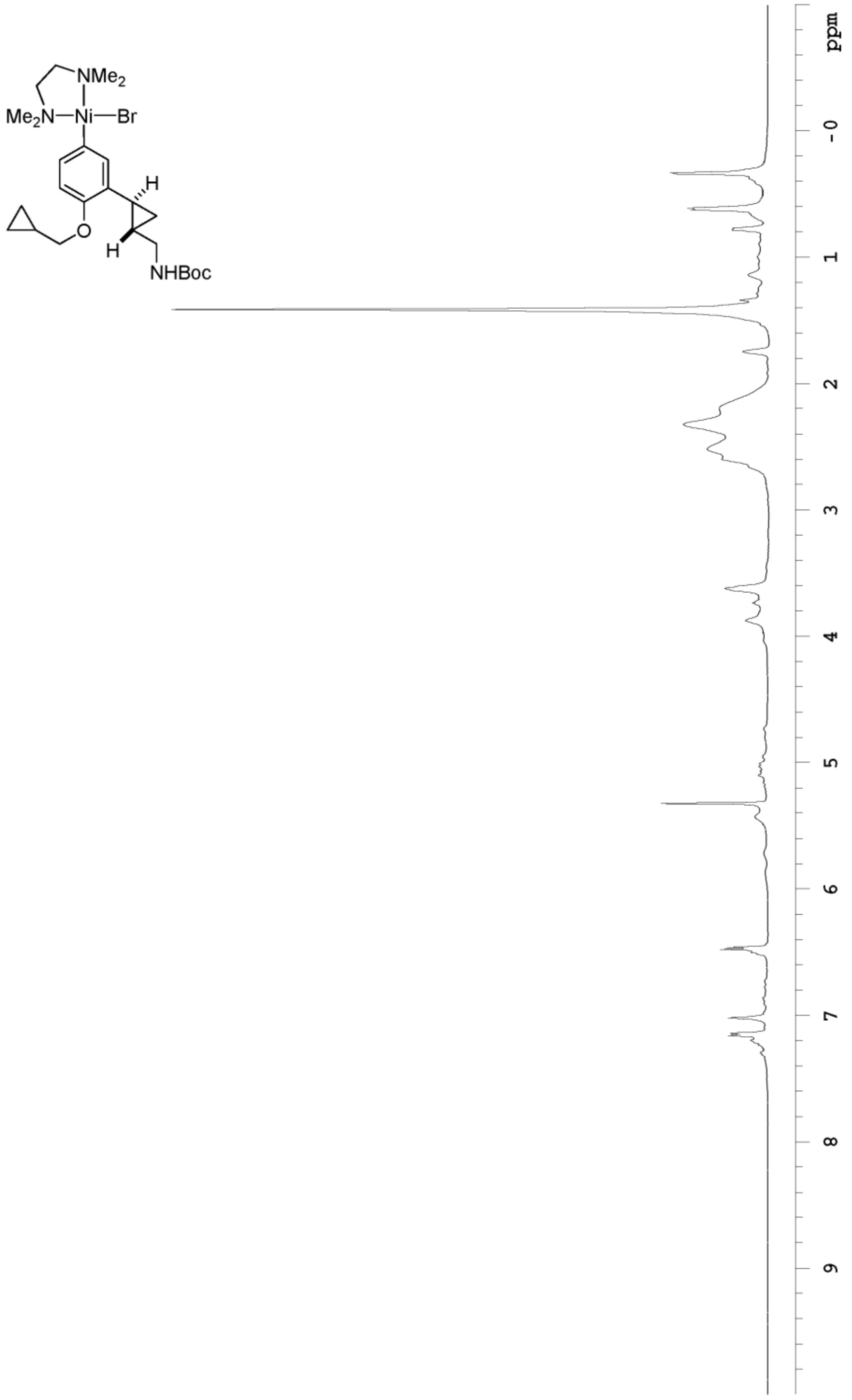

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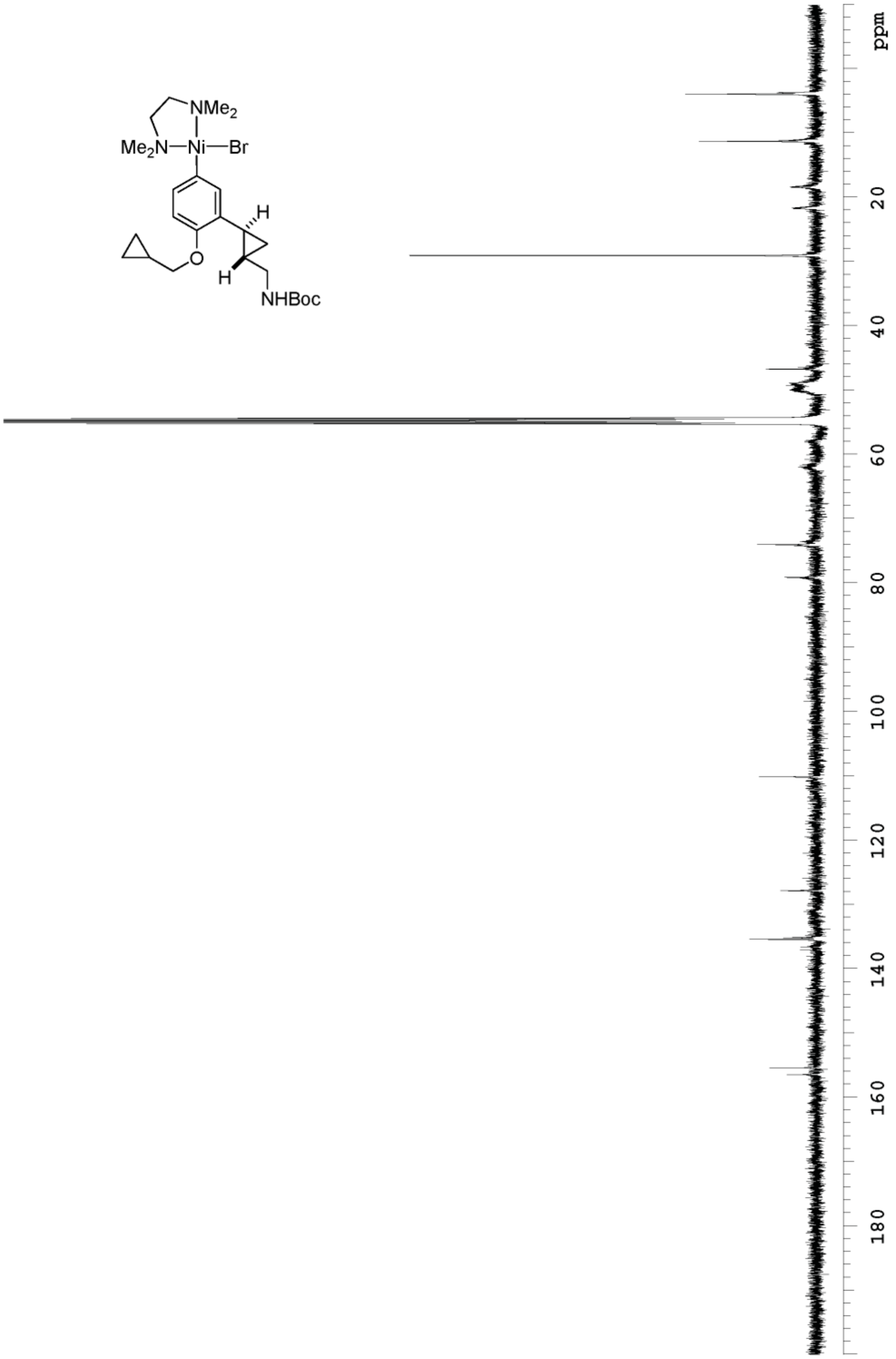

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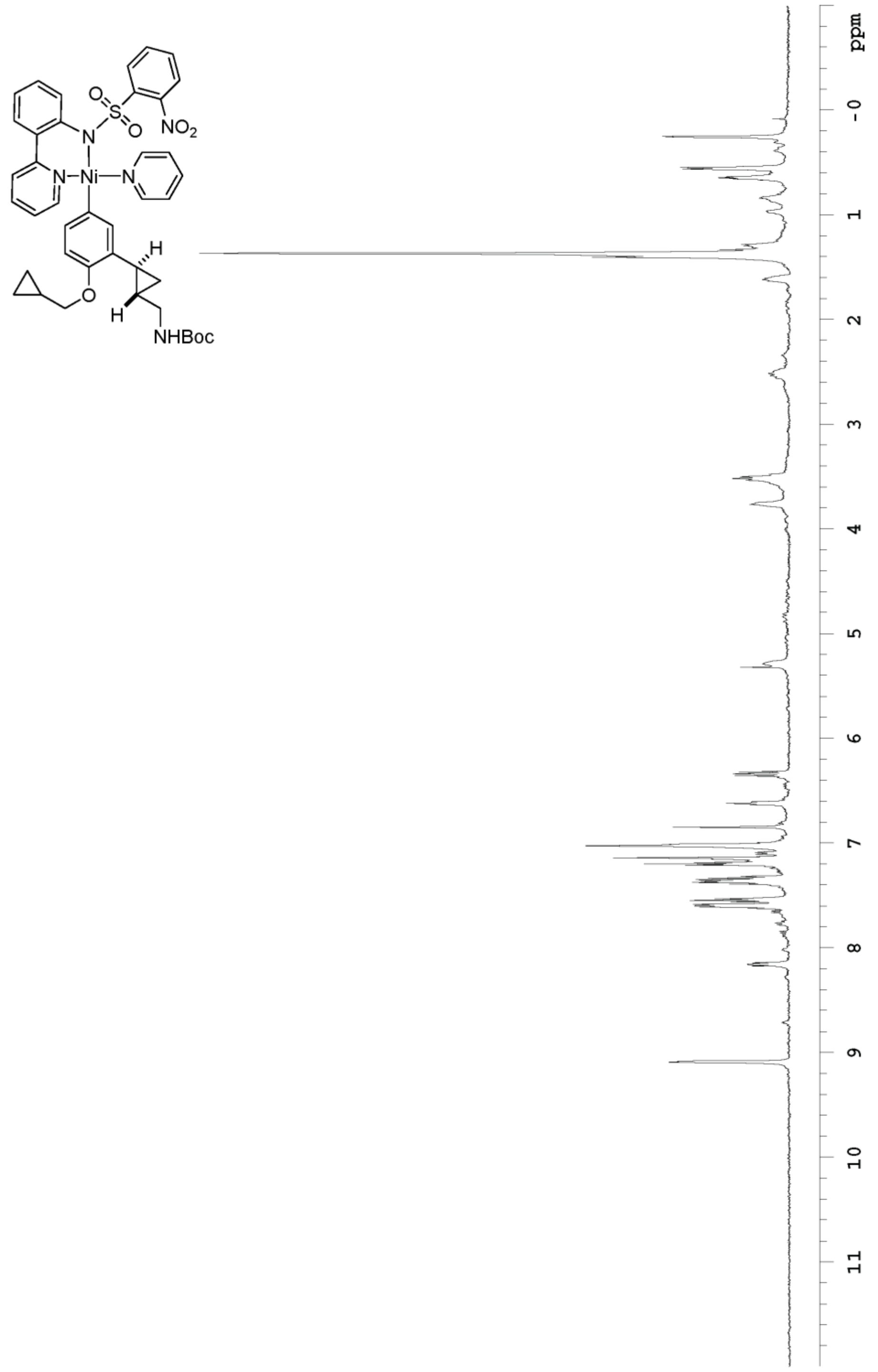

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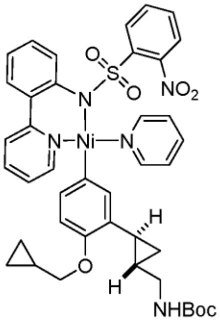

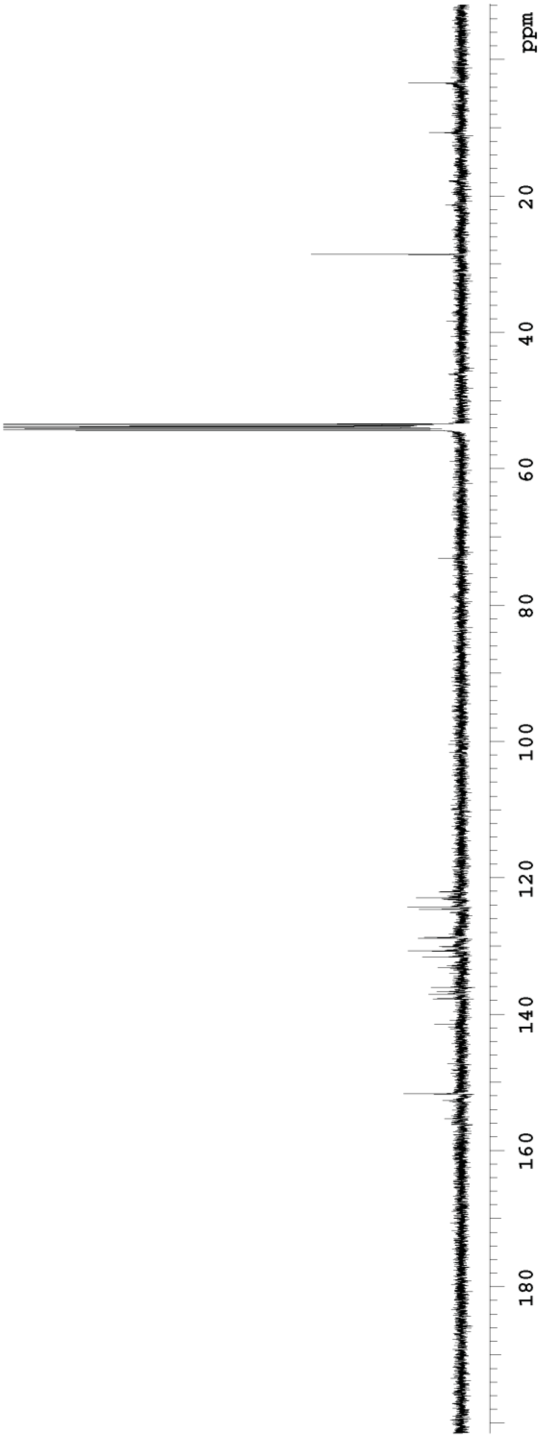

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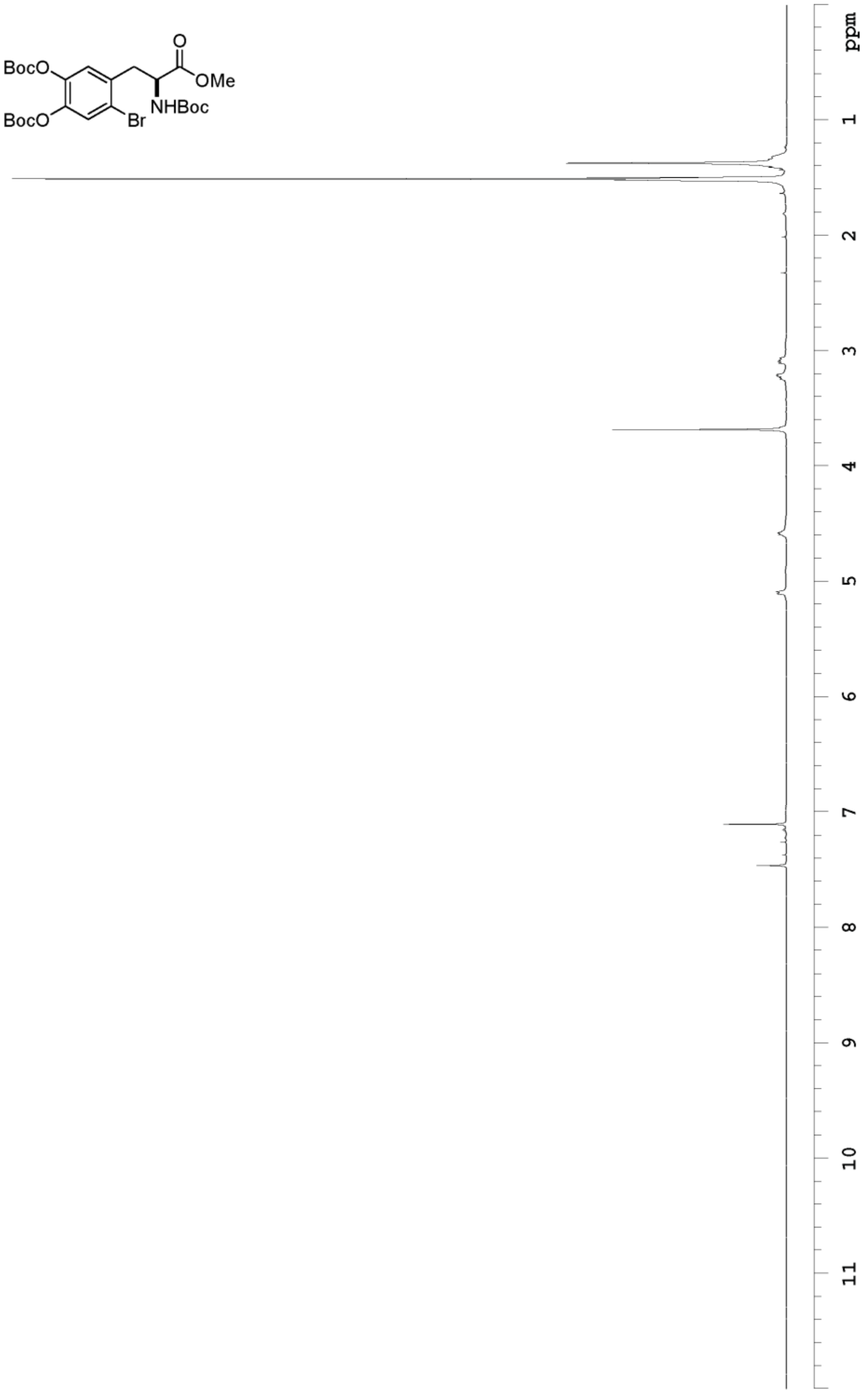
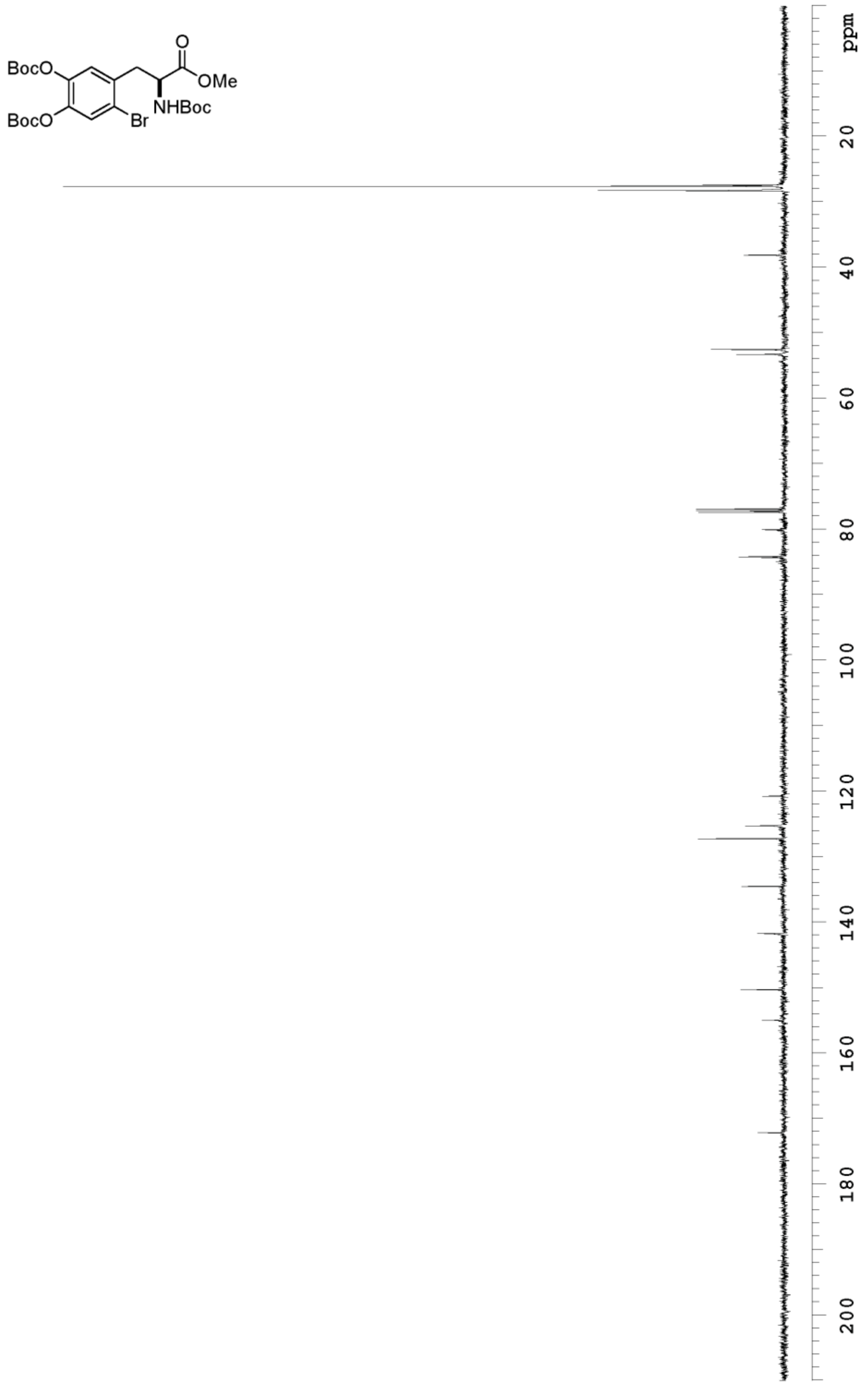


$^1$H NMR (CDCl$_3$, 23 ºC) of **S11**



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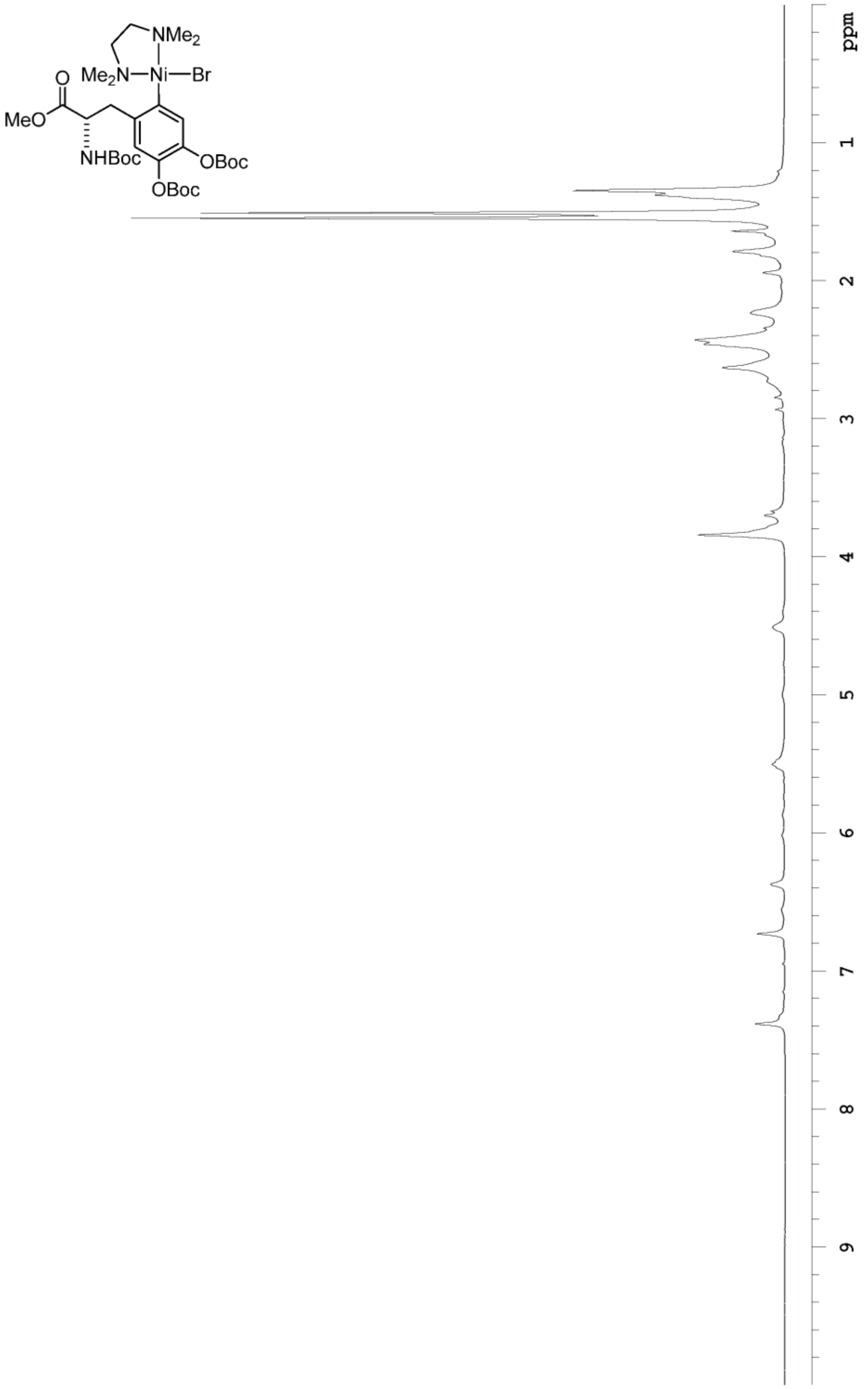
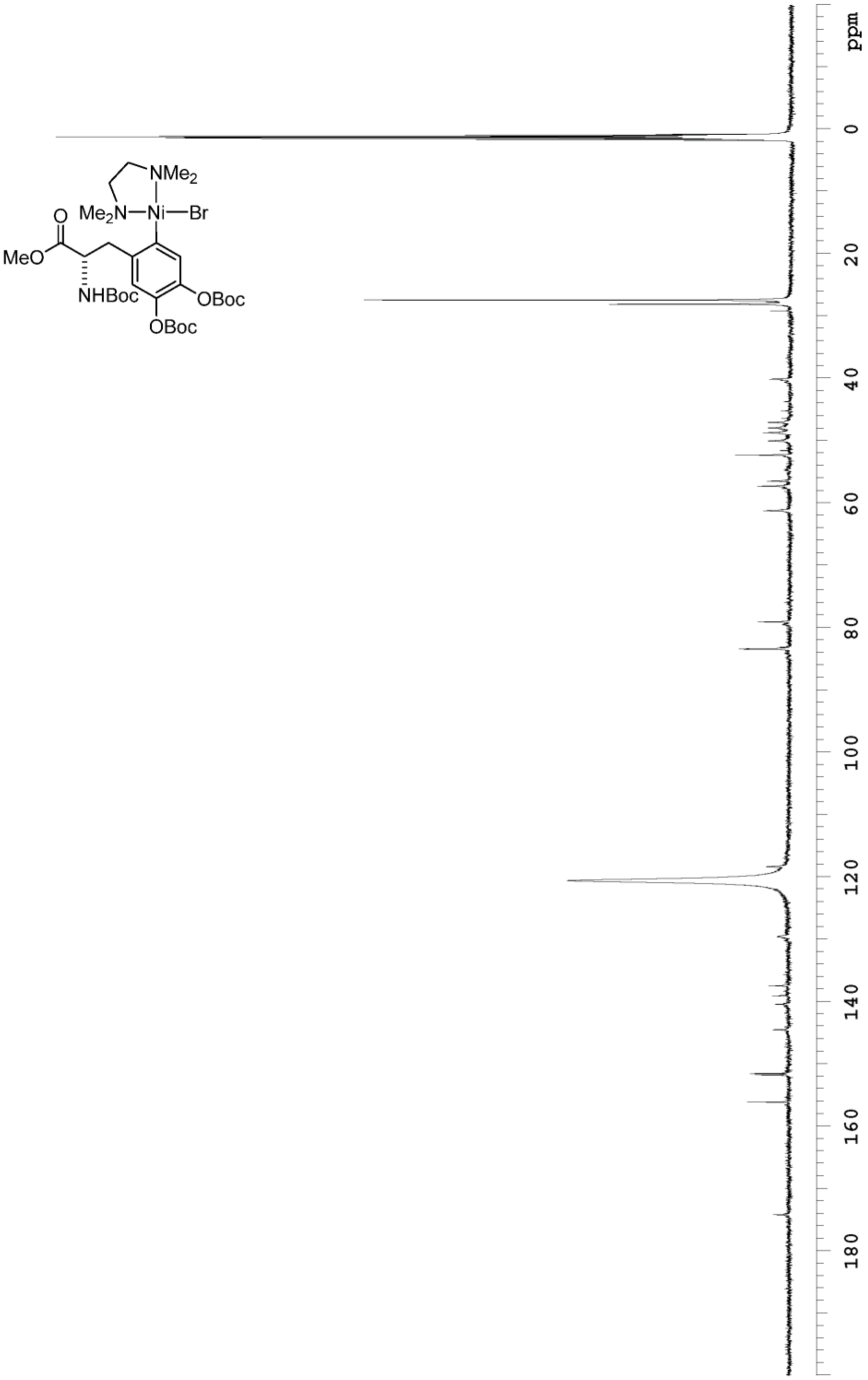
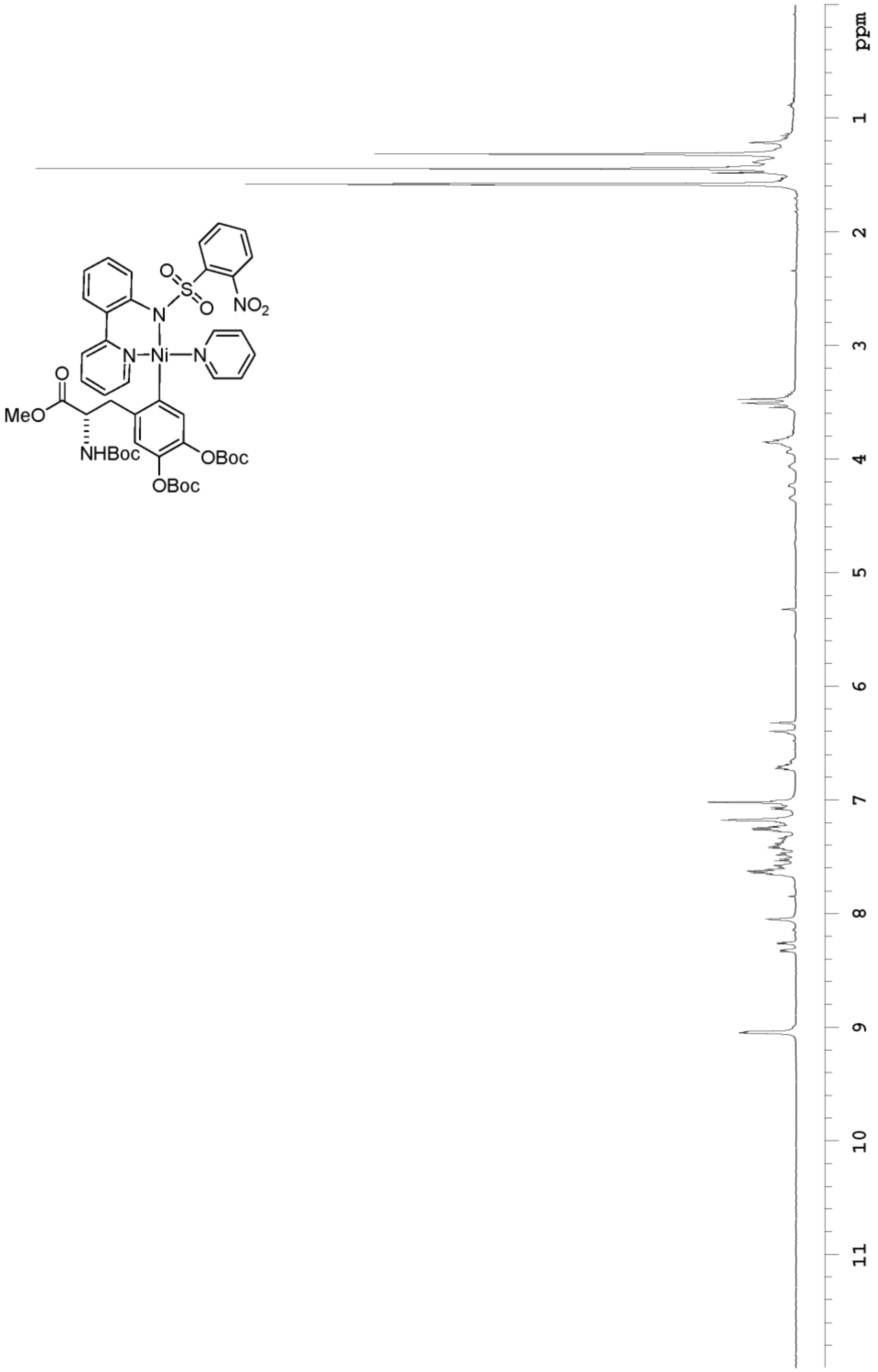


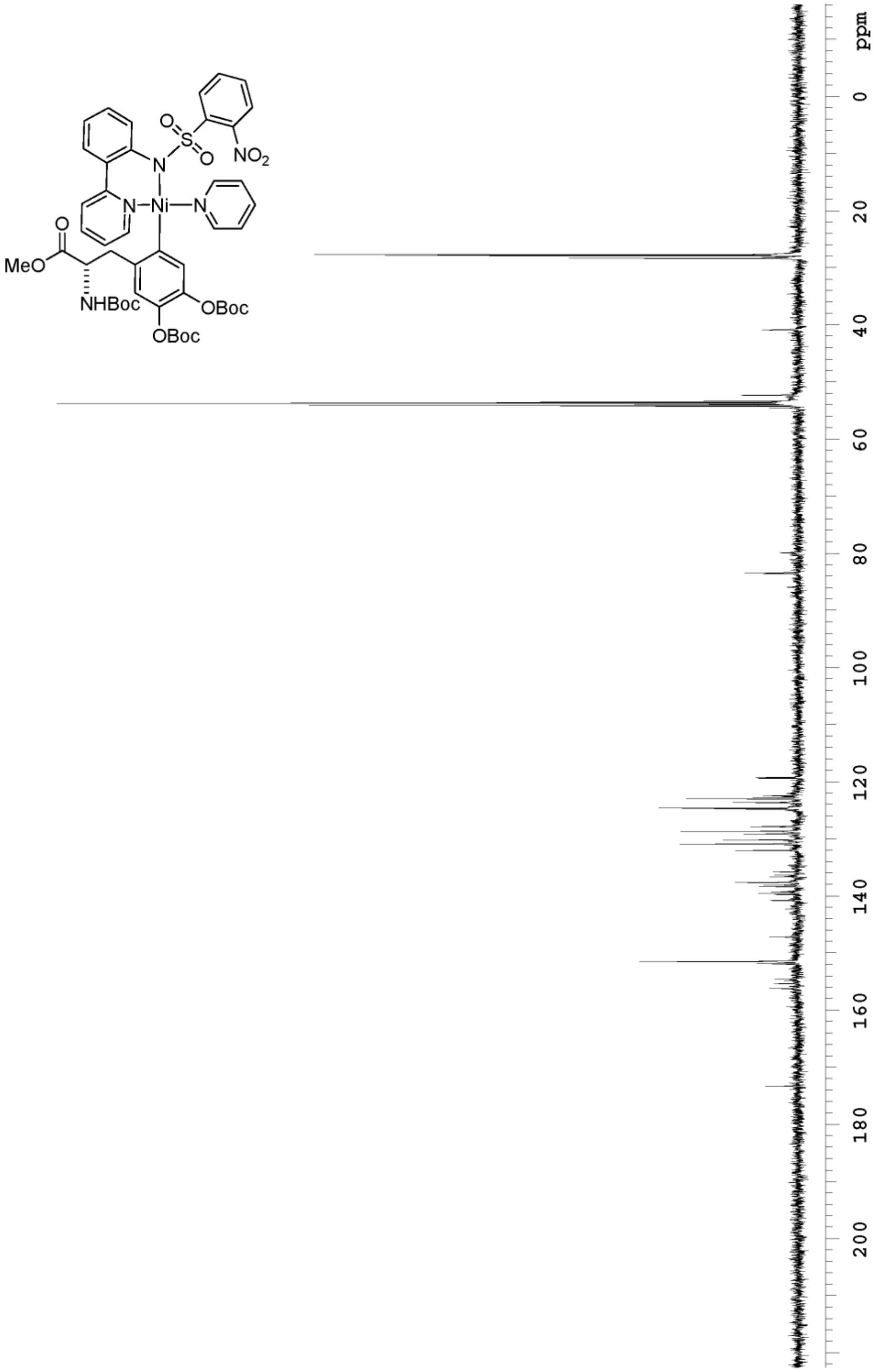
$^1$H NMR (CD$_3$CN, 23 ºC) of **7i**



$^{13}$C NMR (CD$_3$CN, 23 ºC) of **7i**



$^1$H NMR ($CD_2Cl_2$, 23 ºC) of **1i**



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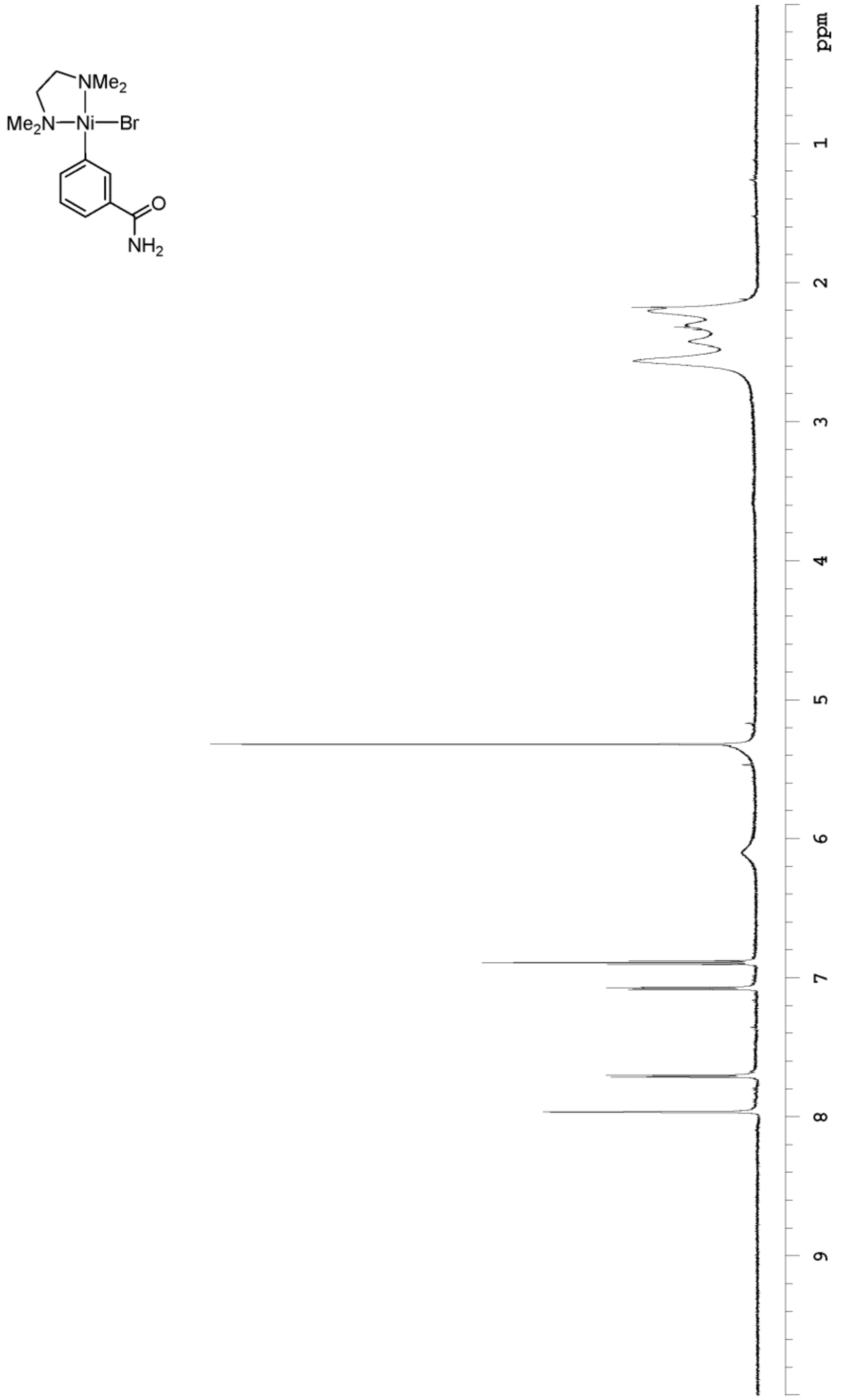

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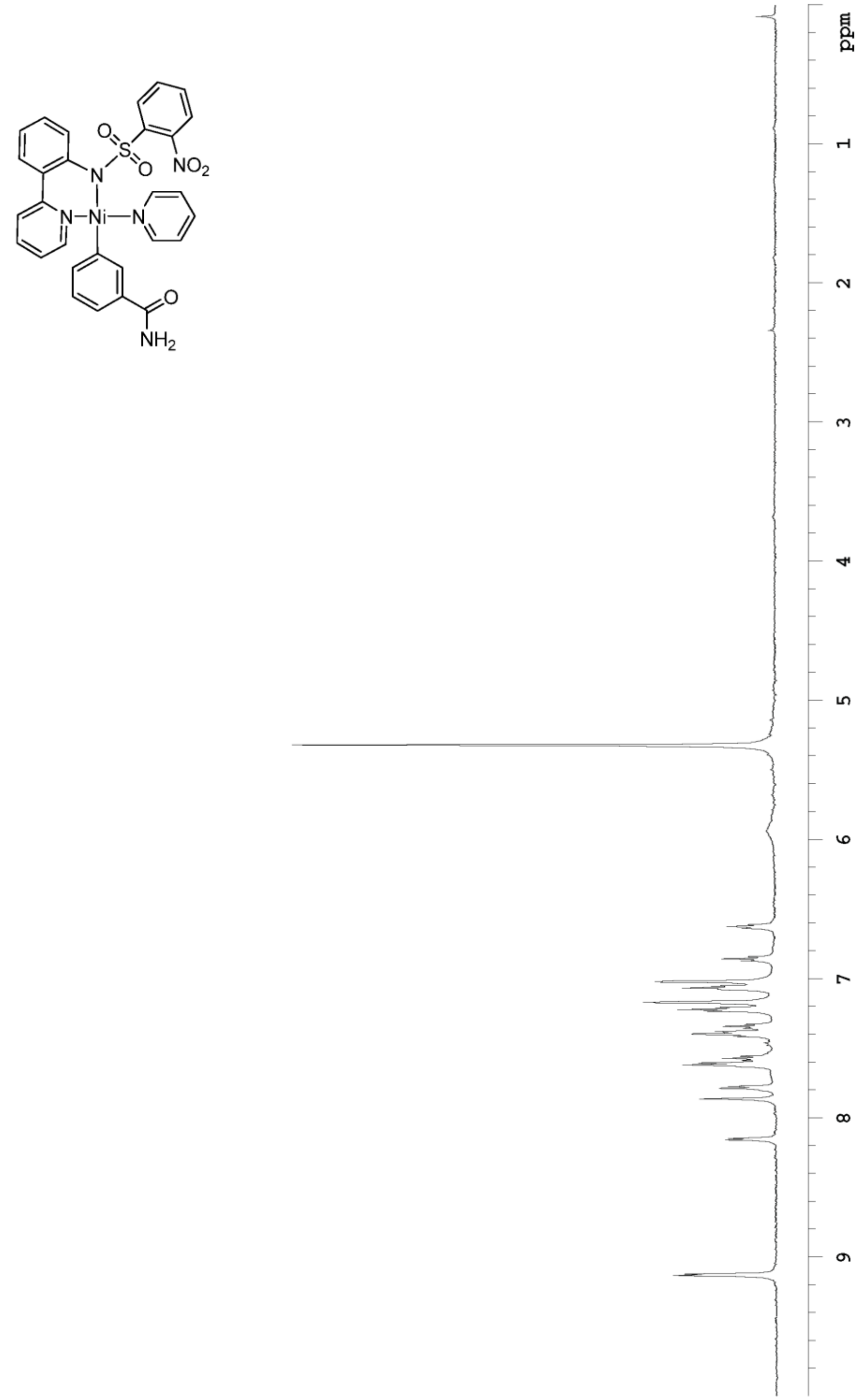

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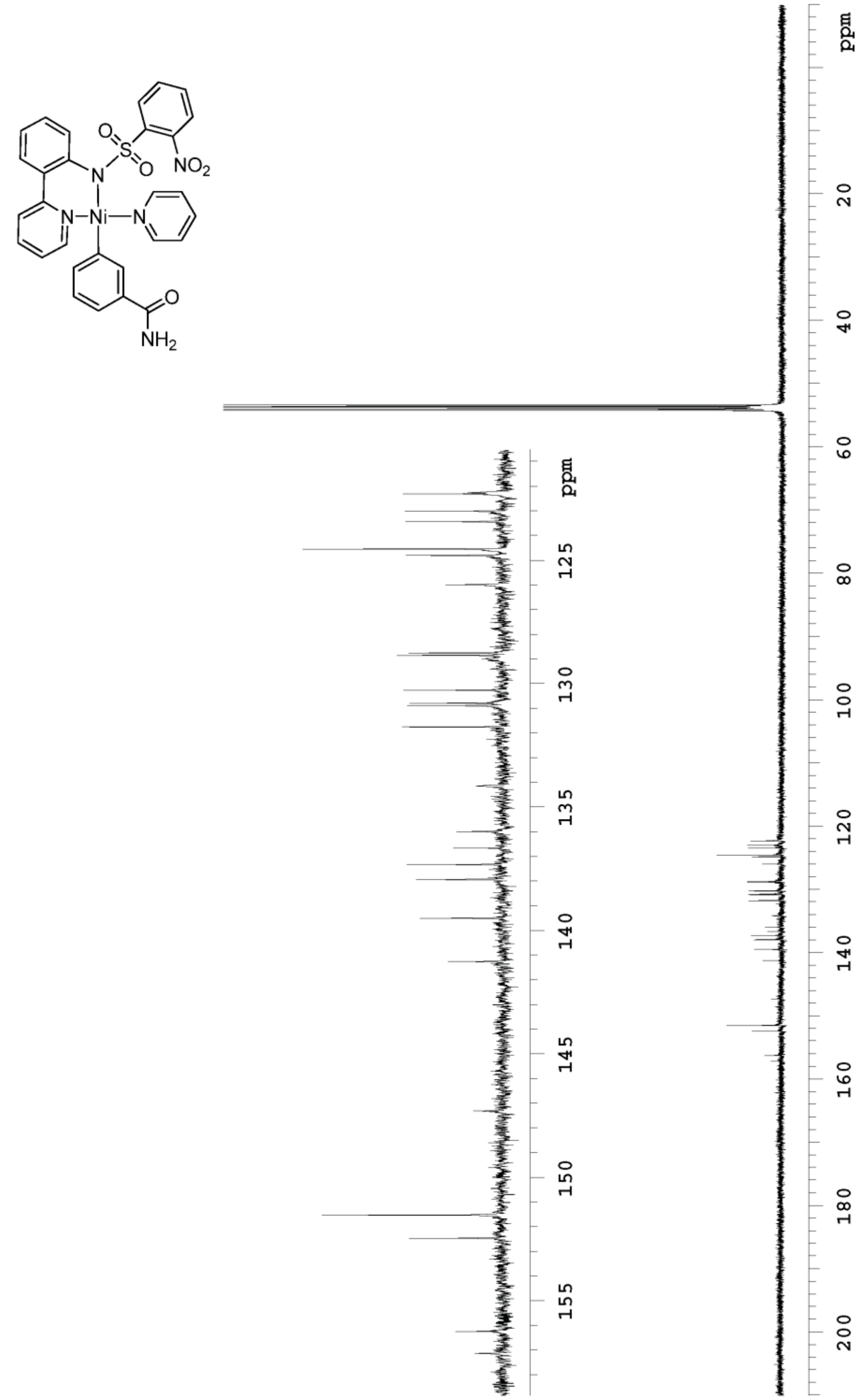

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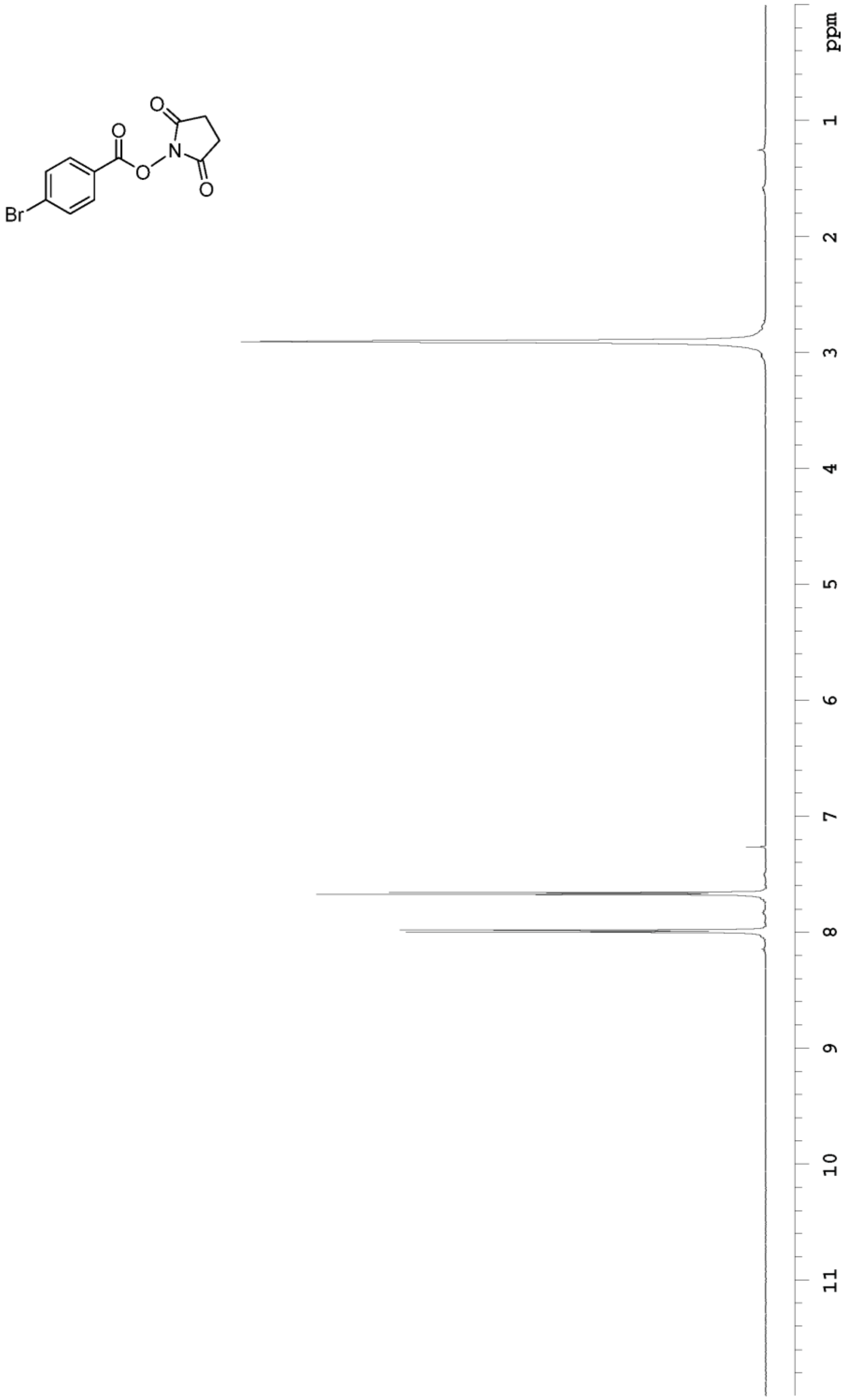
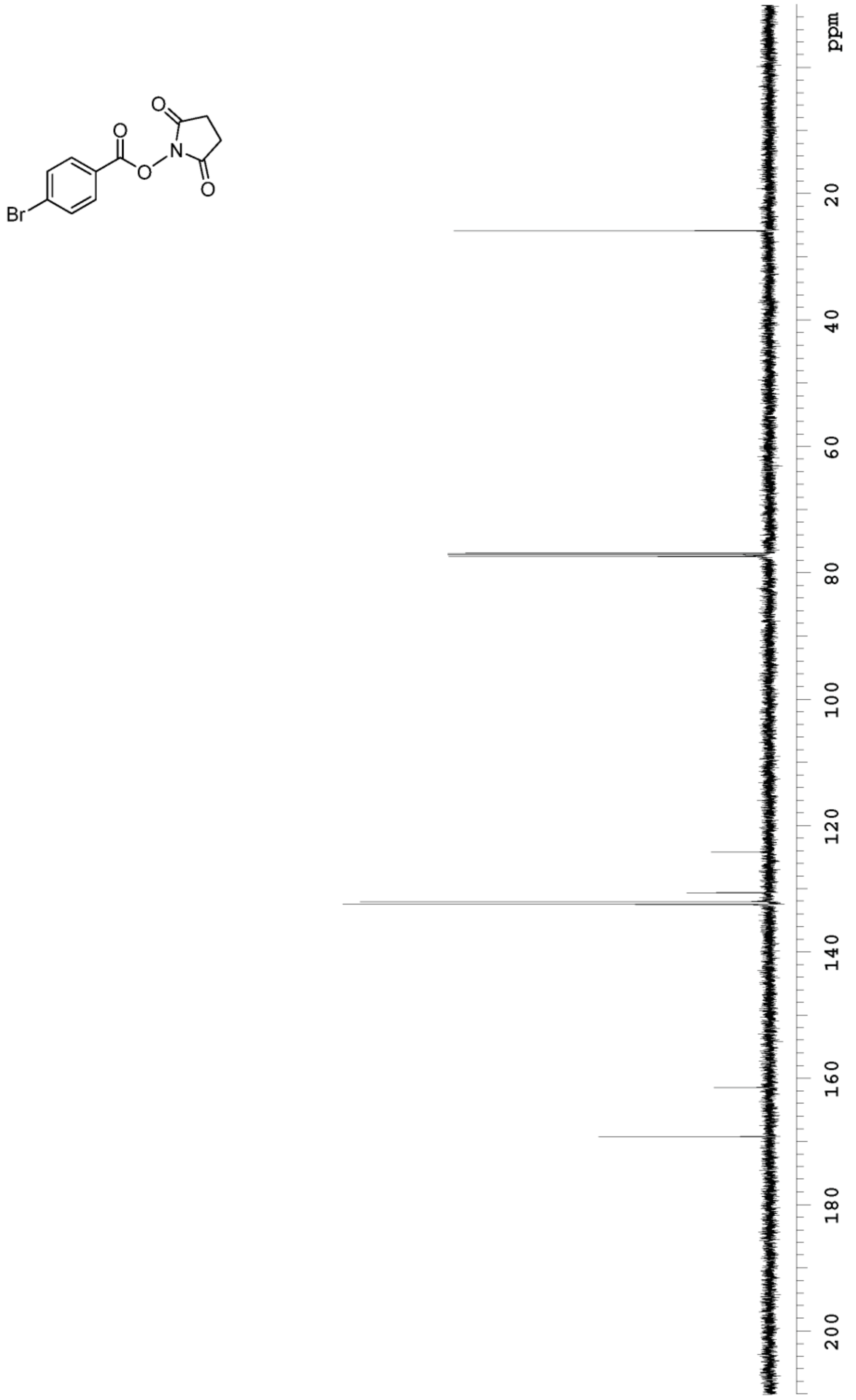
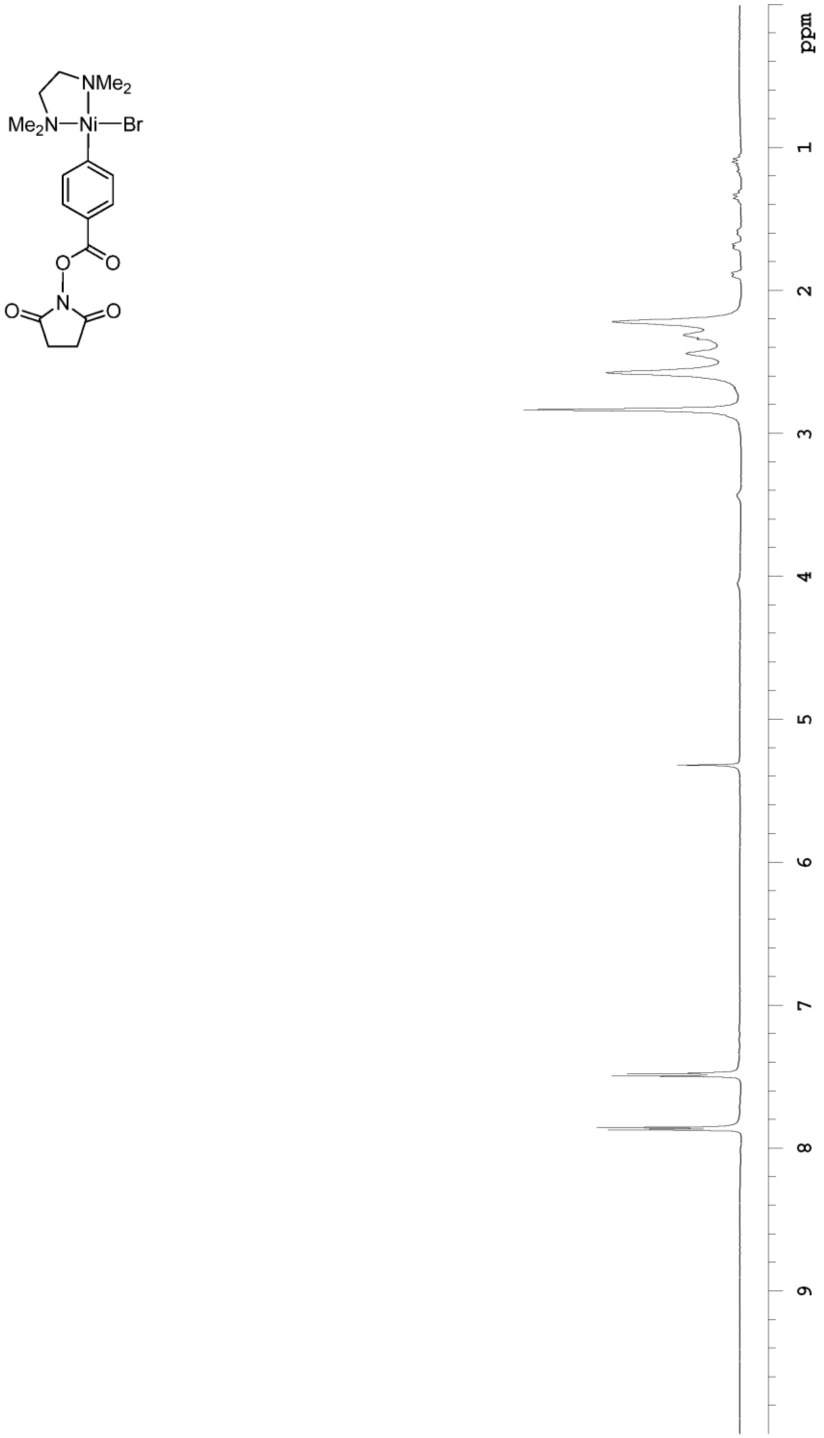


$^1$H NMR (CDCl$_3$, 23 ºC) of **S12**



$^{13}C$ NMR ($CDCl_3$, 23 ºC) of **S12**



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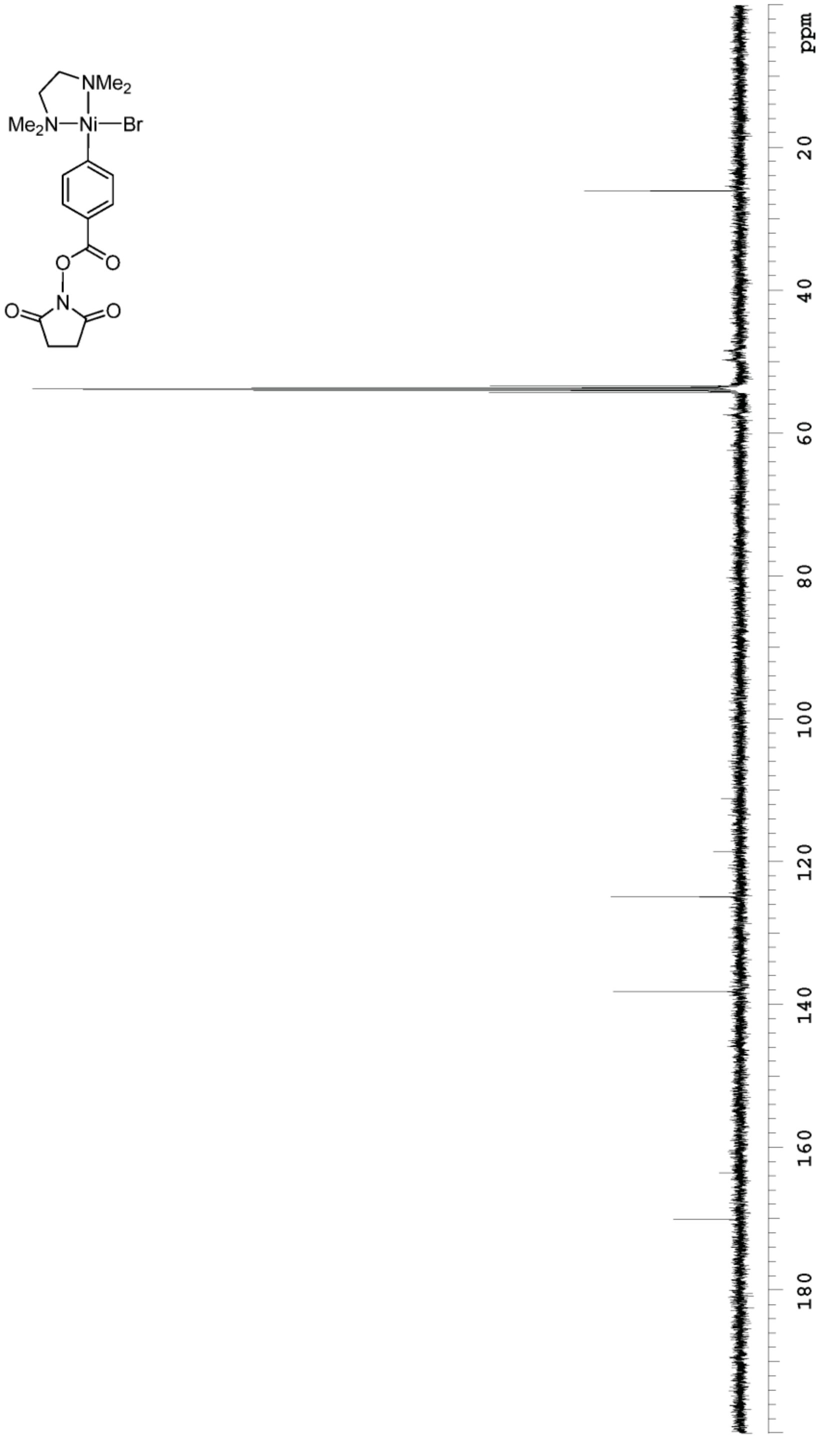
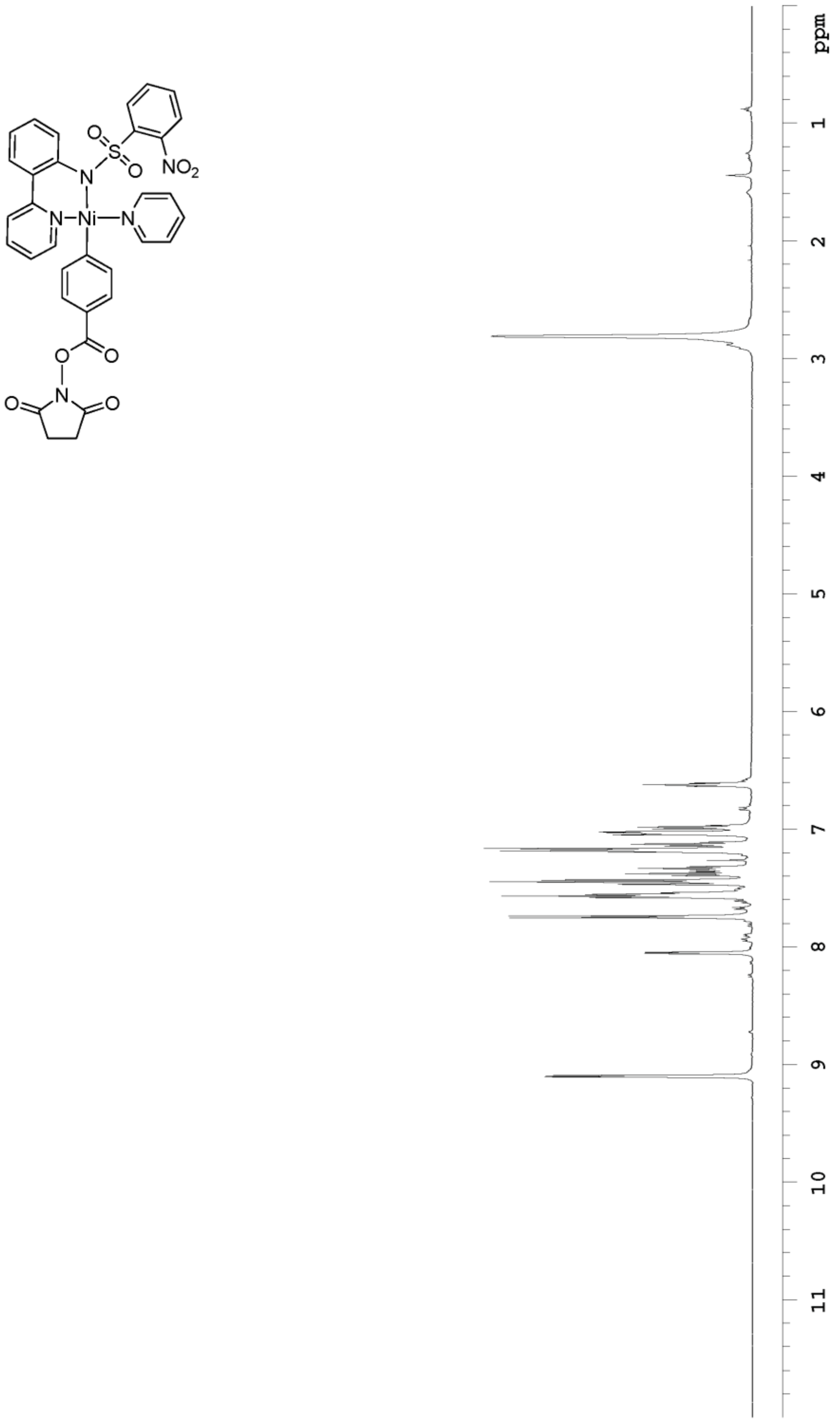
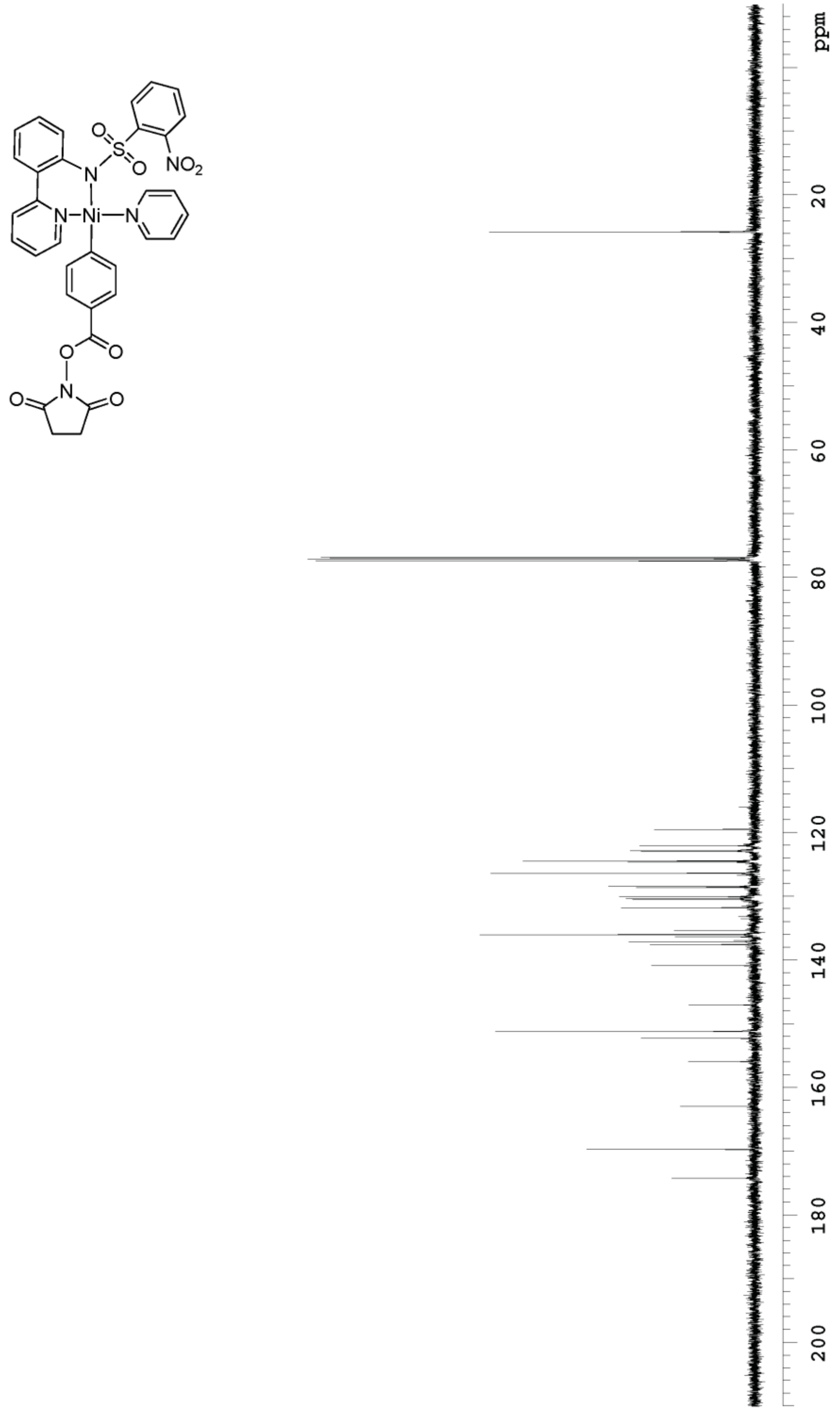


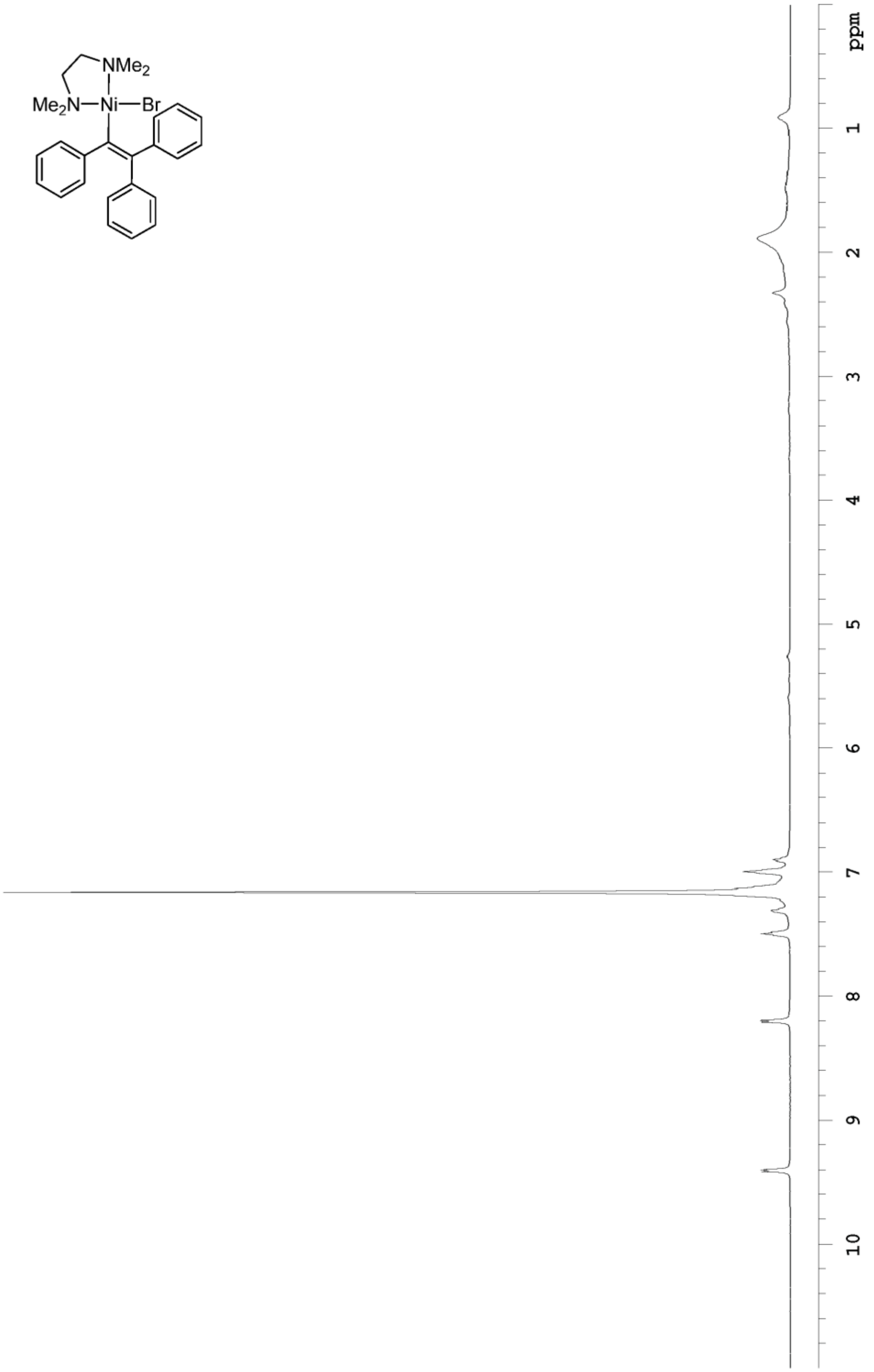
$^{13}$C NMR ($CD_2Cl_2$, 23 ºC) of **7k**



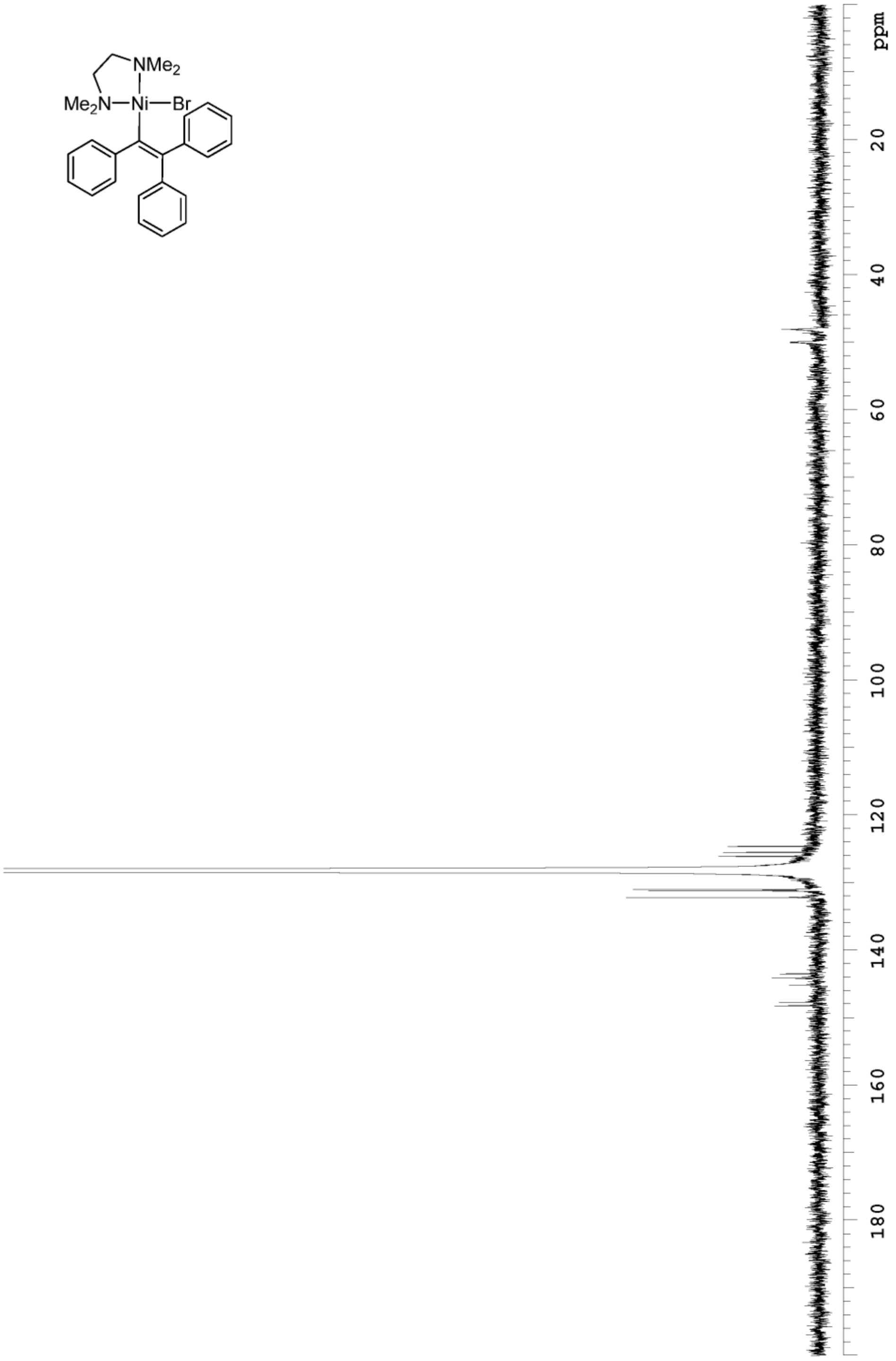
$^1$H NMR ($CDCl_3$, 23 ºC) of **1k**



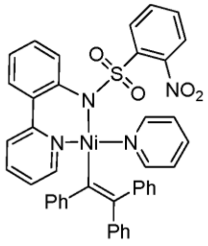
$^{13}$C NMR (CDCl$_3$, 23 ºC) of **1k**

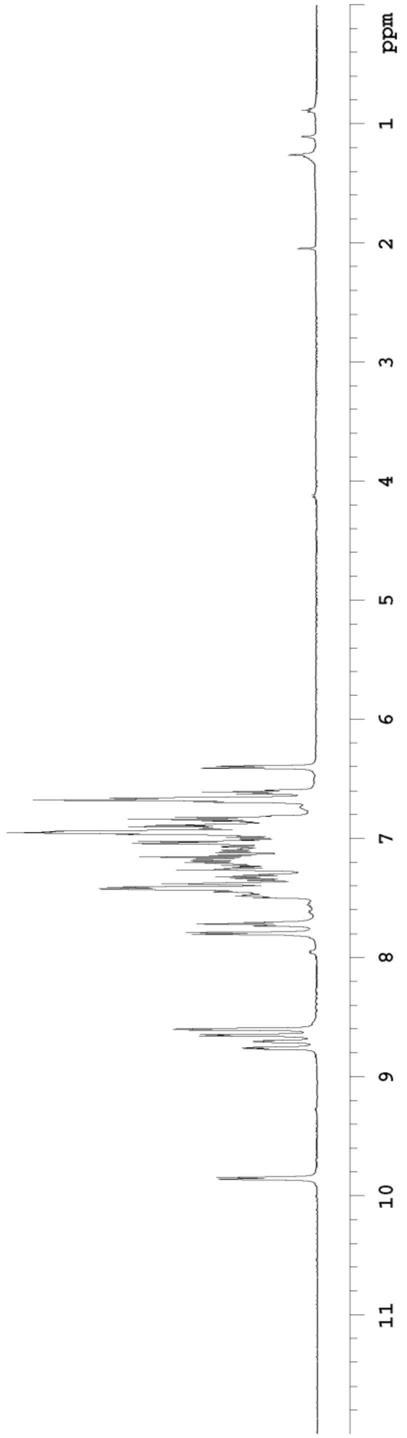


$^1$H NMR ($C_6D_6$, 23 ºC) of **7l**

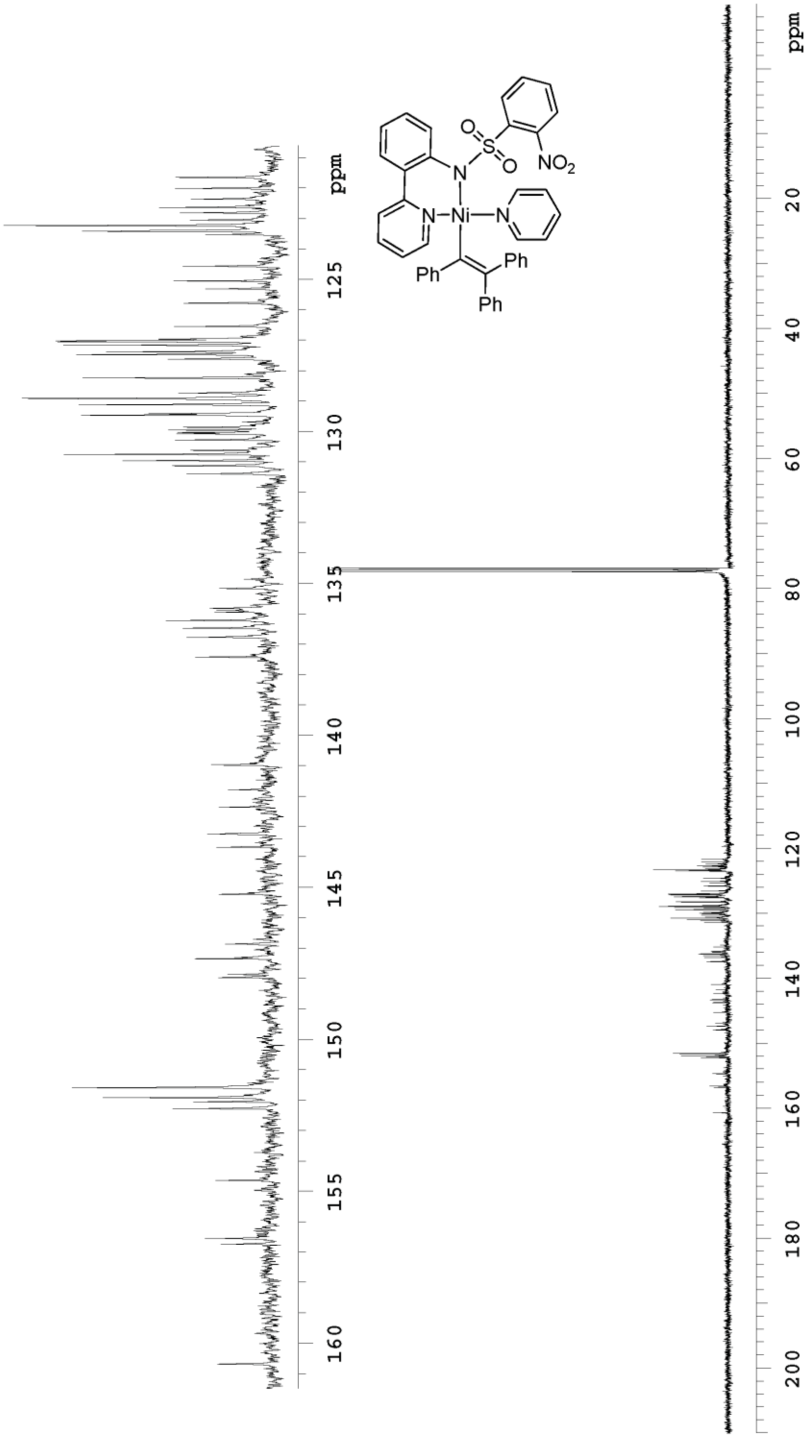


$^{13}$C NMR ($C_6D_6$, 23 ºC) of **7l**





$^1$H NMR (CDCl$_3$, 23 ºC) of **1l**



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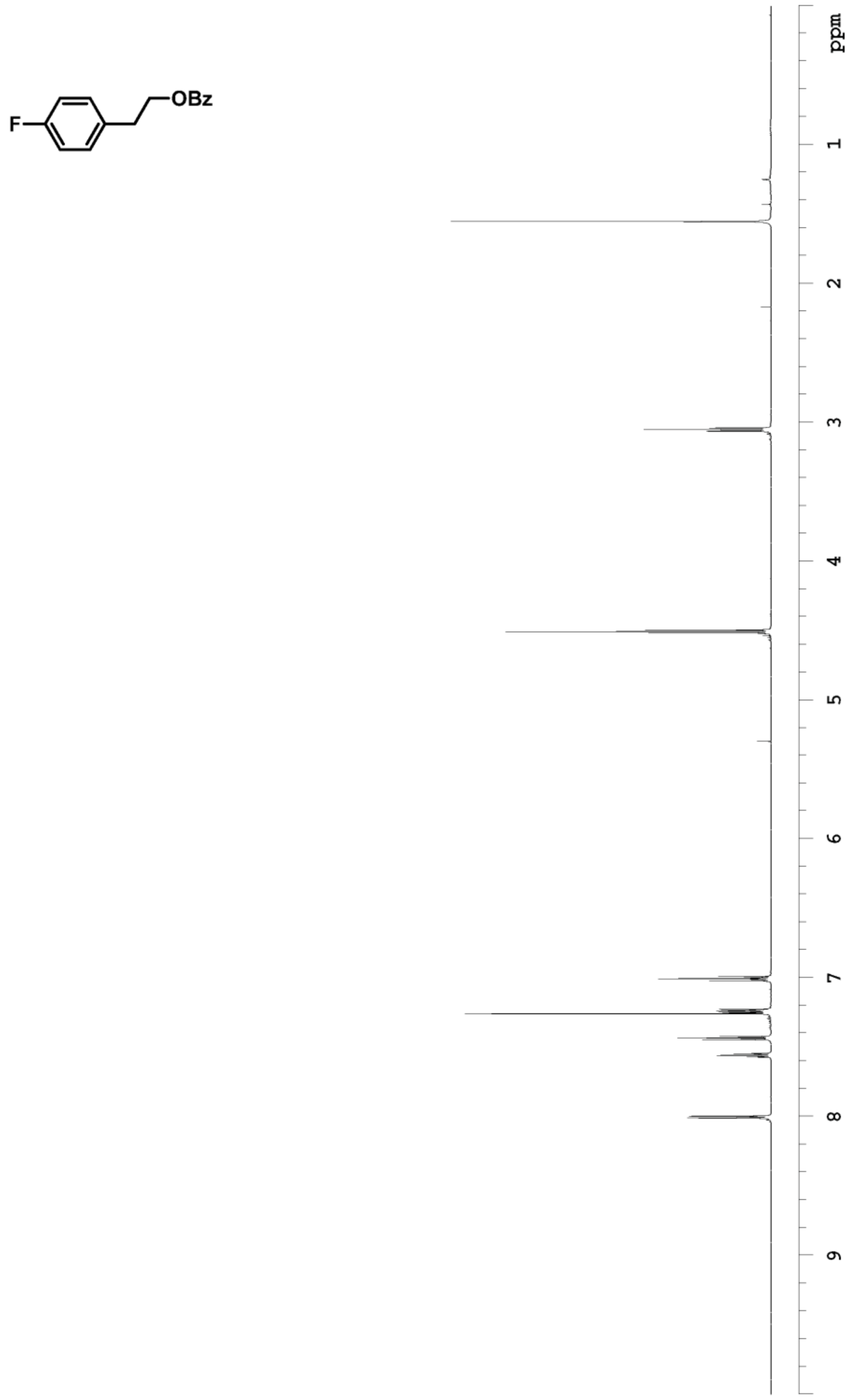
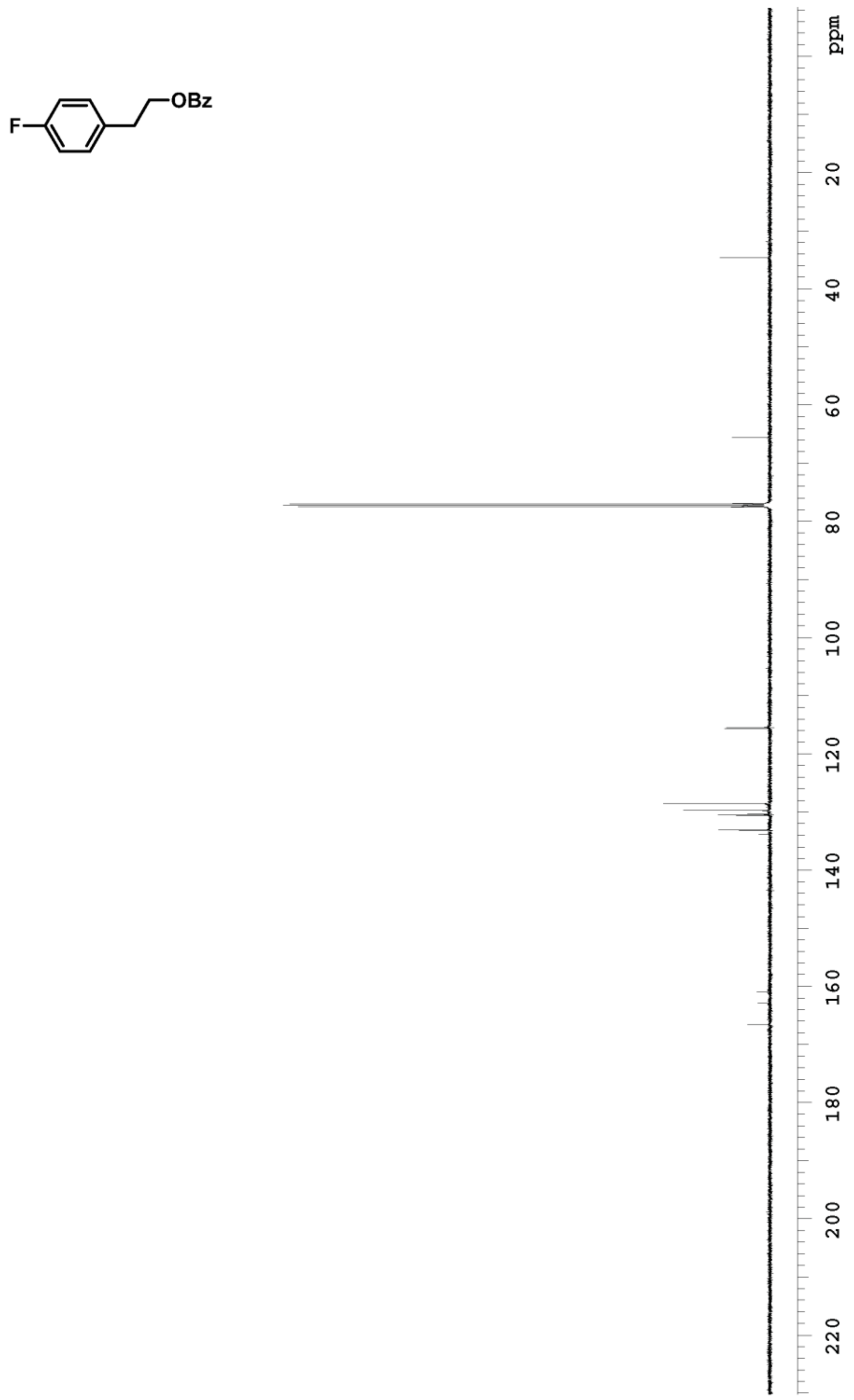
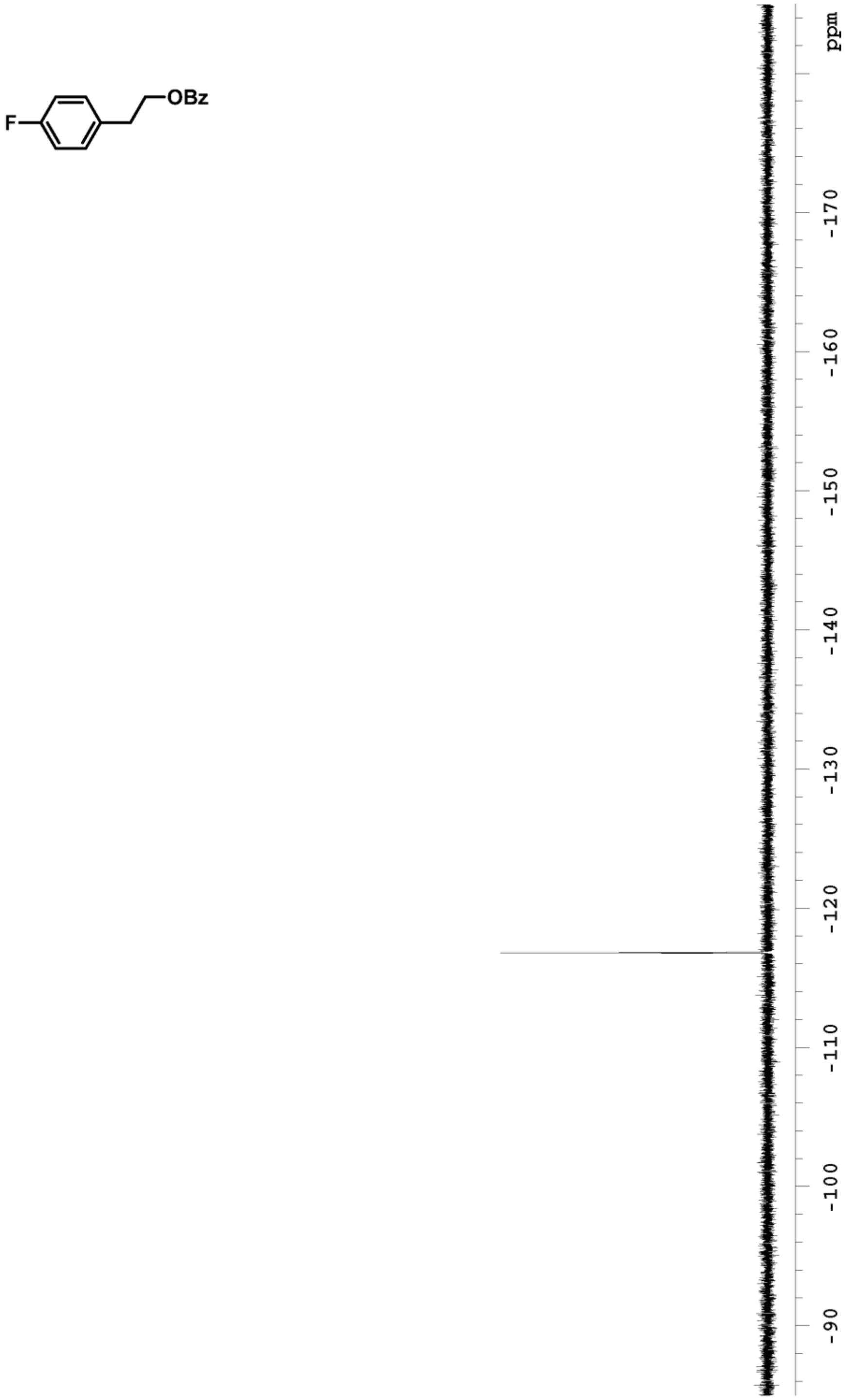


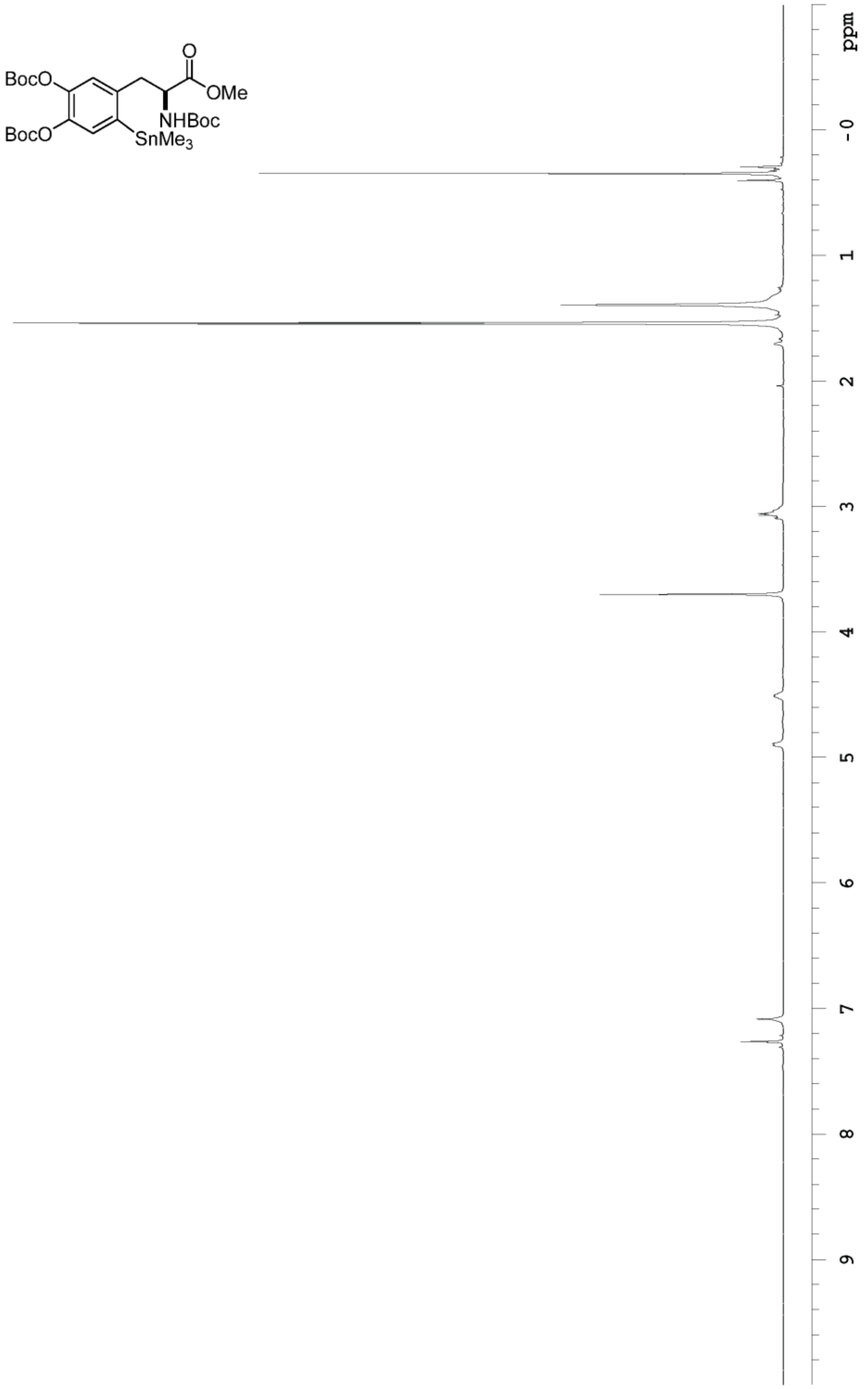
$^{1}$H NMR (CDCl$_3$, 23 ºC) of **2f**



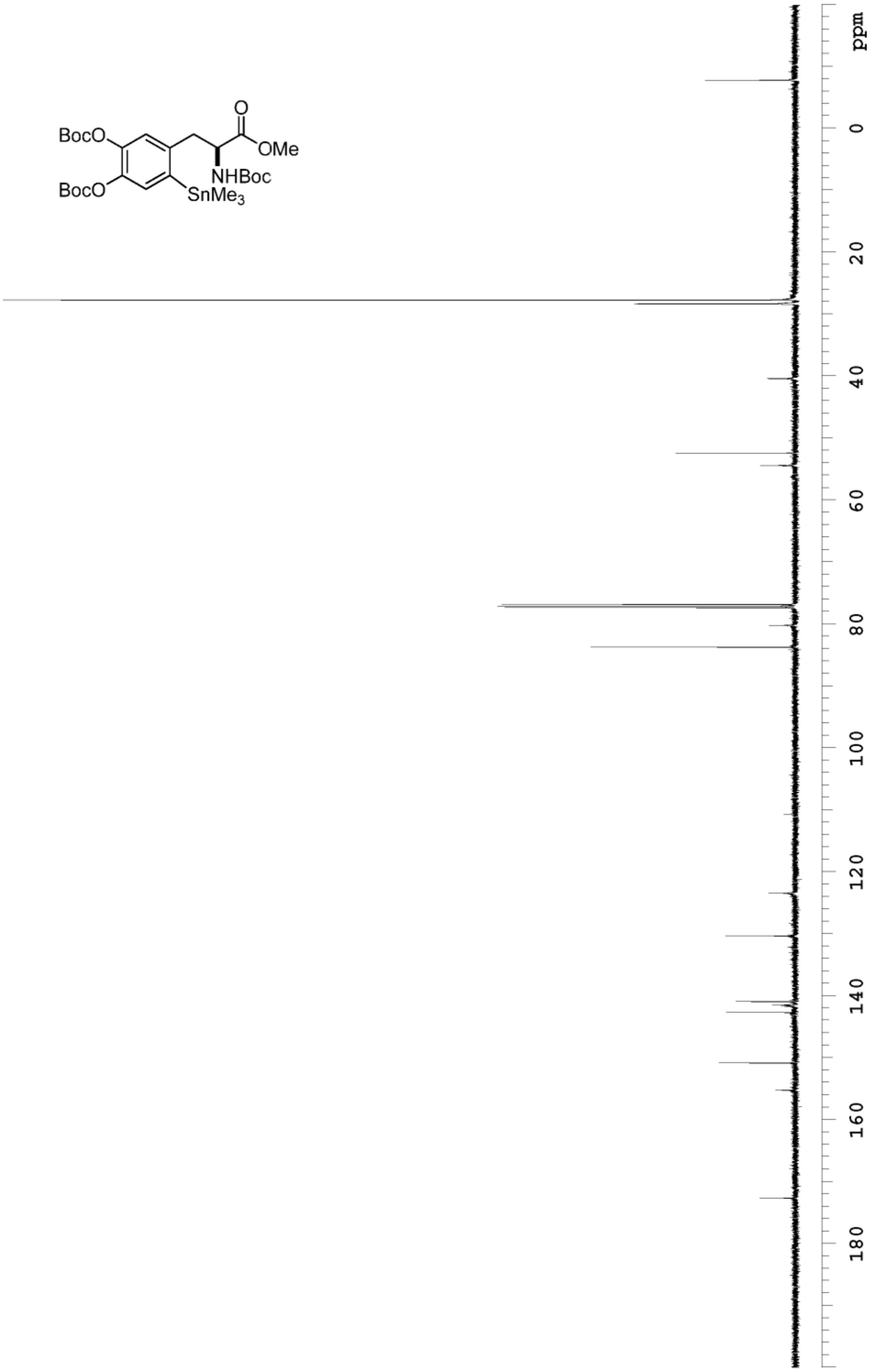
$^{13}$C NMR (CDCl$_3$, 23 ºC) of **1l**



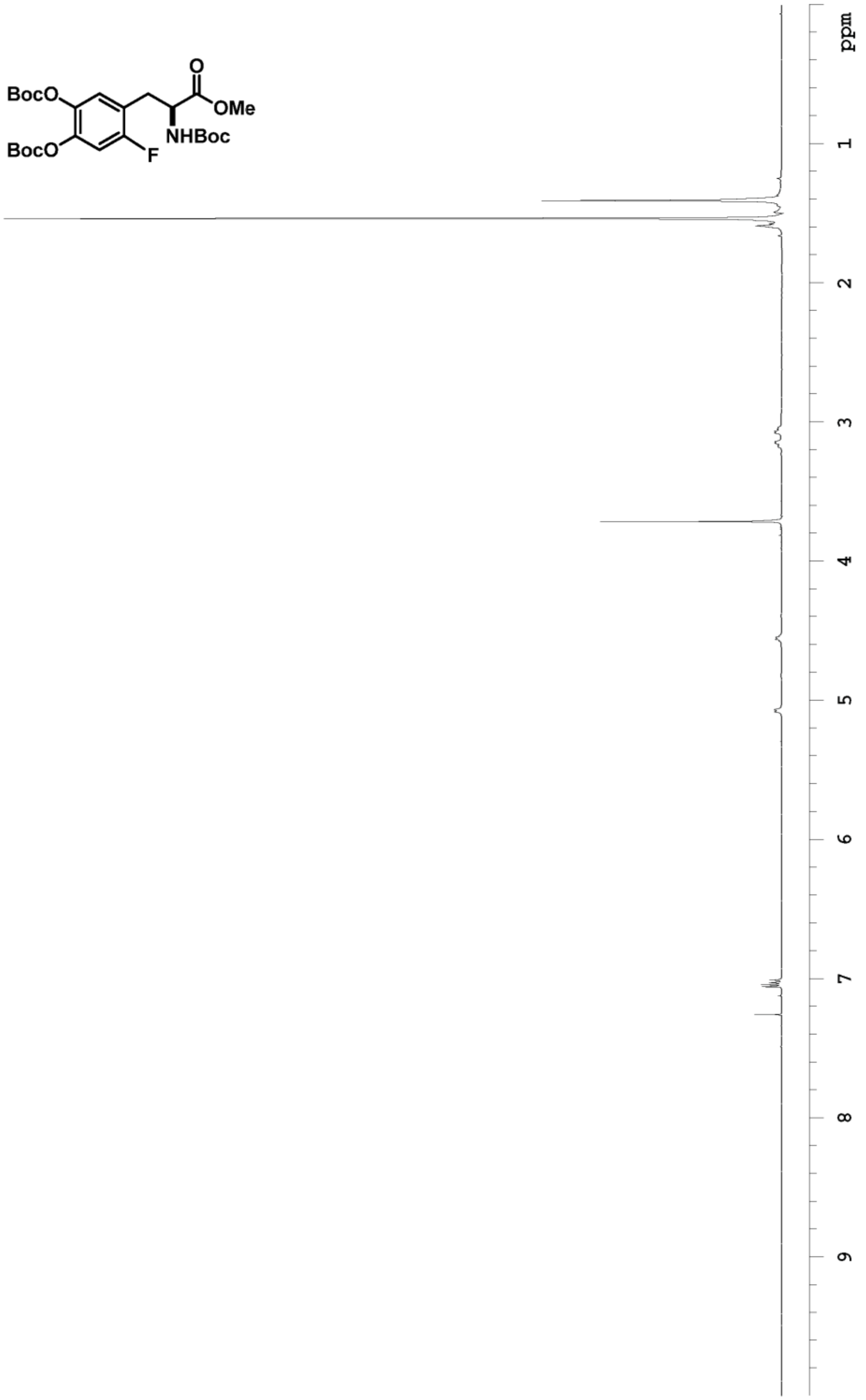
$^{19}$F NMR (CDCl$_3$, 23 ºC) of **2f**



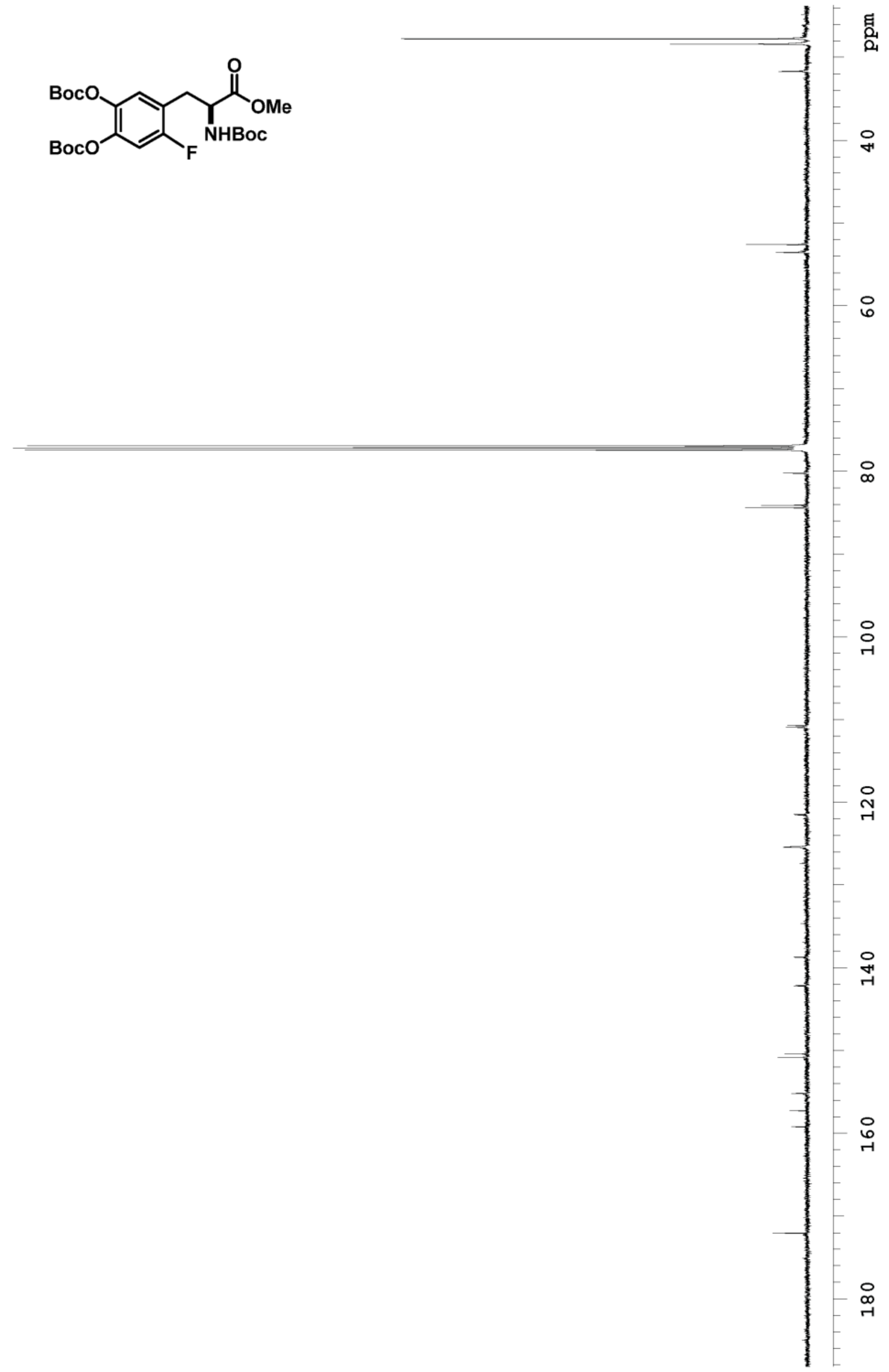
$^1$H NMR (CDCl$_3$, 23 ºC) of **S13**



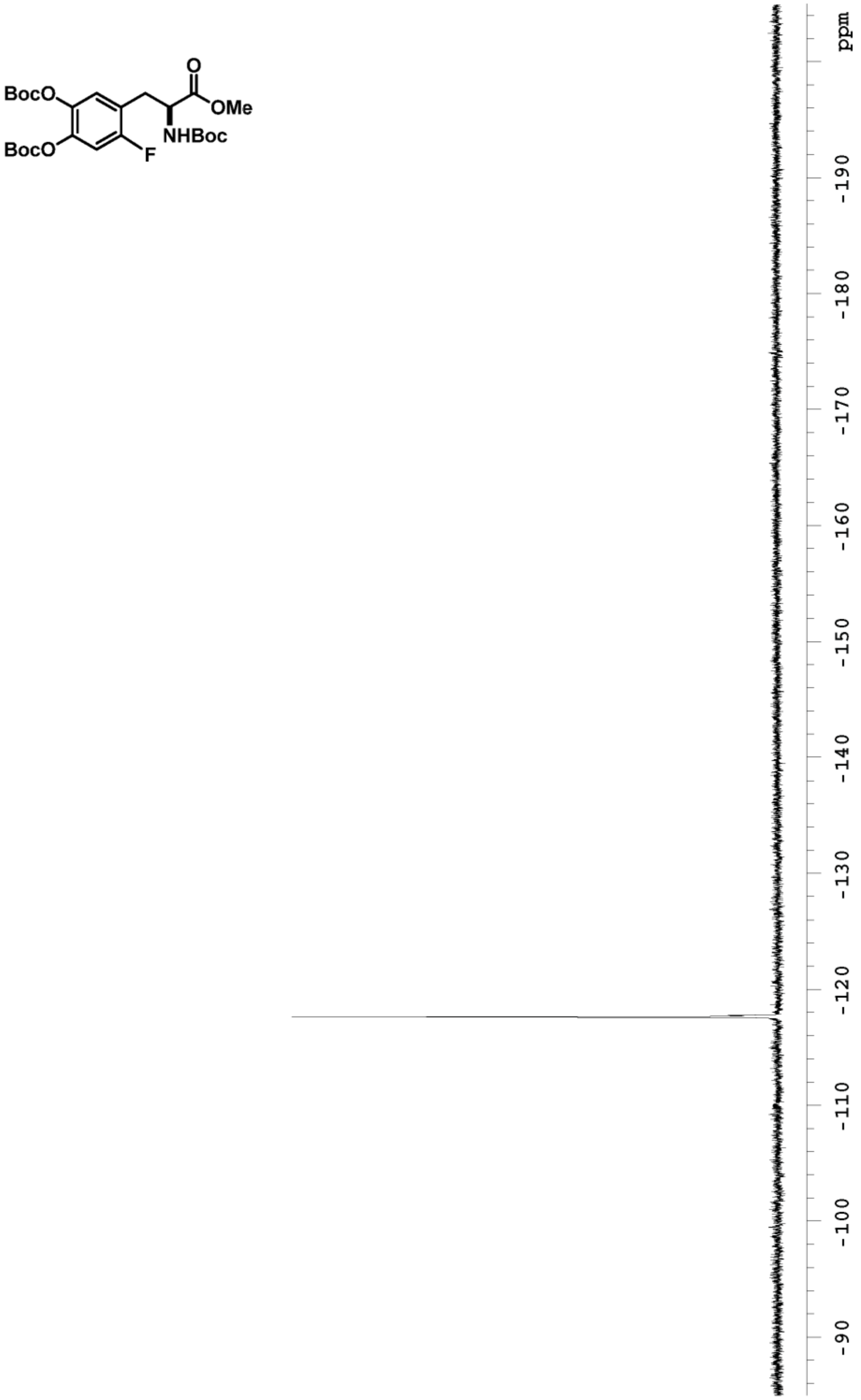
$^{13}$C NMR (CDCl$_3$, 23 ºC) of **S13**



$^1$H NMR (CDCl$_3$, 23 ºC) of **2i**



$^{13}$C NMR (CDCl$_3$, 23 ºC) of **2i**



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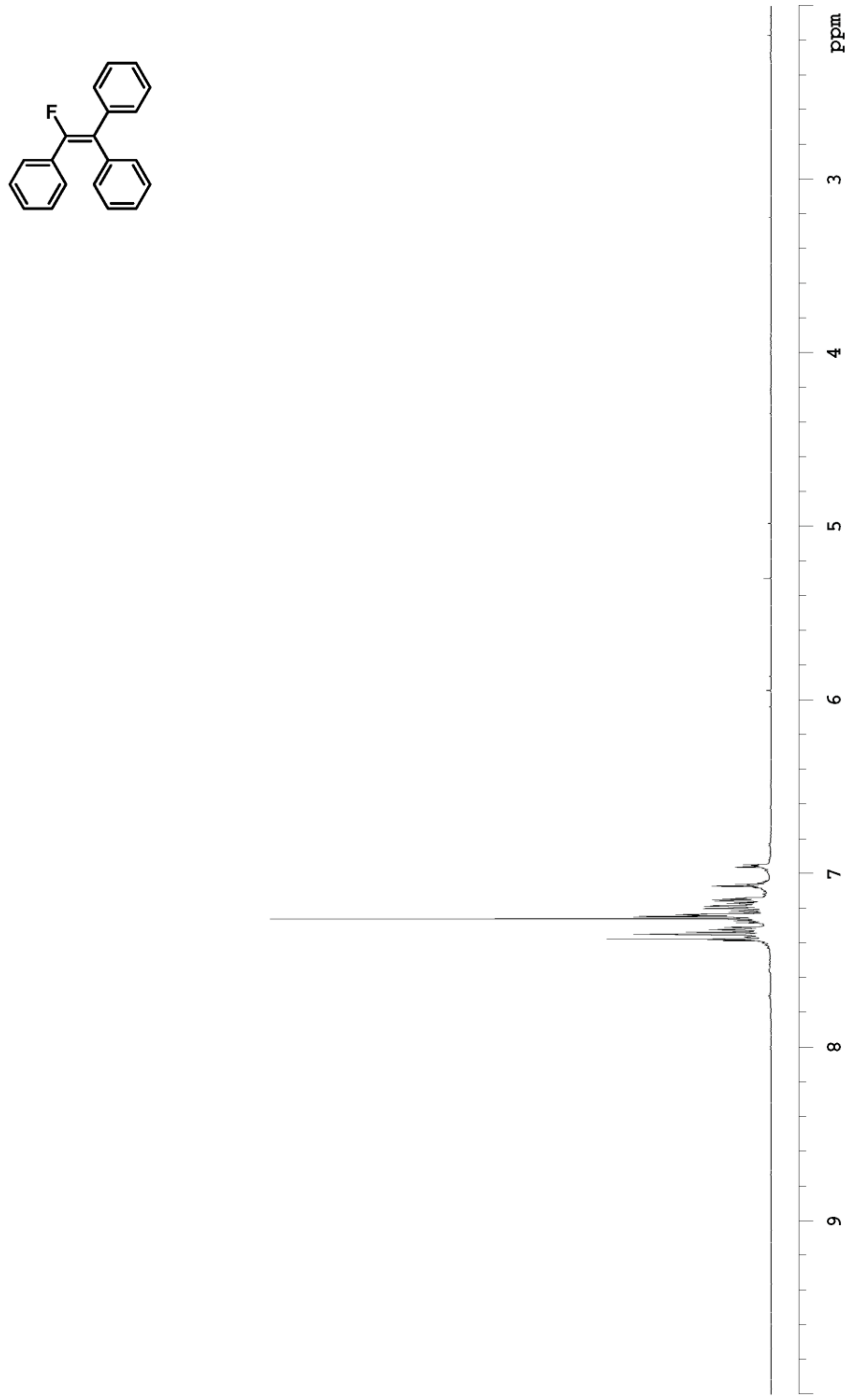
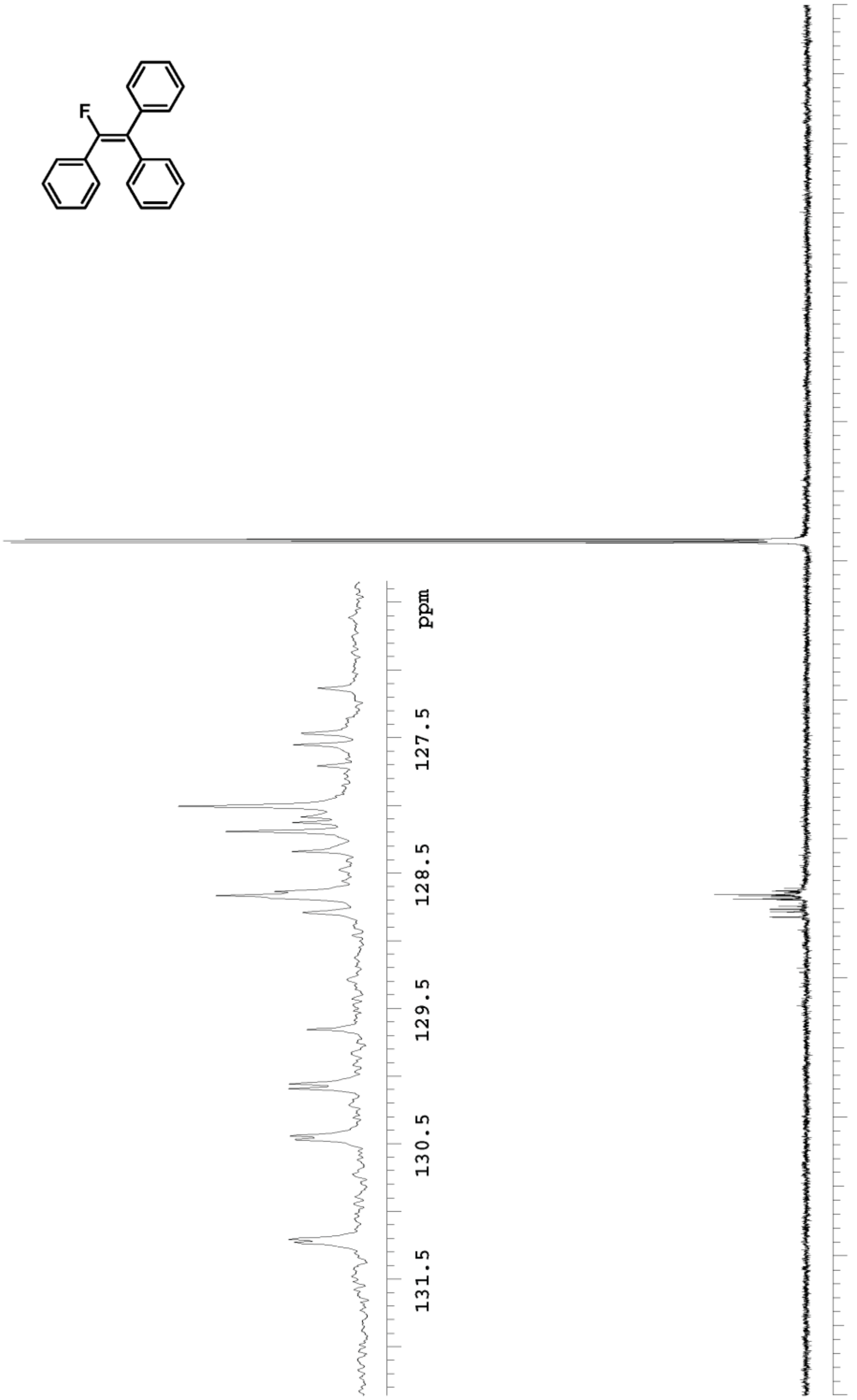
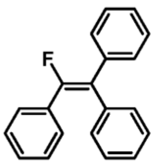
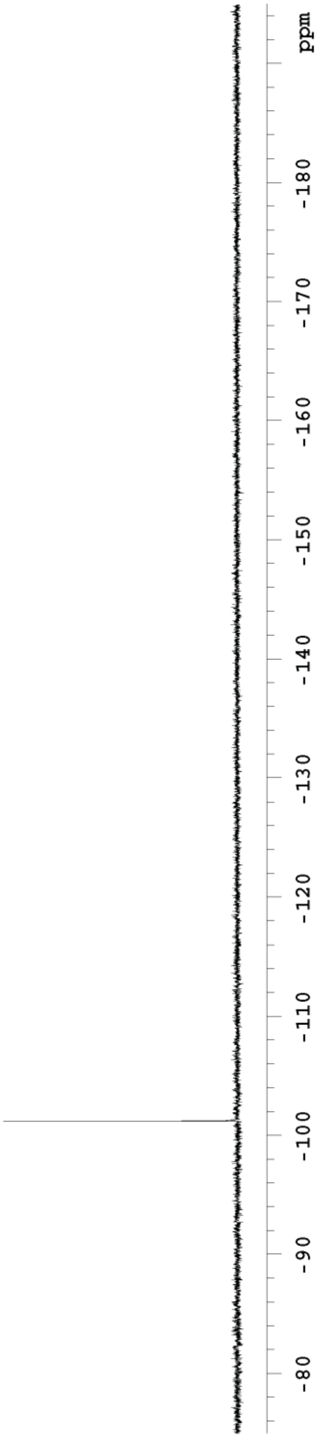


$^1$H NMR (CDCl$_3$, 23 ºC) of **2l**



$^{13}$C NMR (CDCl$_3$, 23 ºC) of **2l**





$^{19}$F NMR (CDCl$_3$, 23 ºC) of **2l**

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