# Nickel-Mediated Oxidative Fluorination for PET with Aqueous [\^^\{18\}F<br>)] Fluoride 

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## Supporting Information

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

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## Materials and Methods

All air- and moisture-insensitive reactions were carried out under an ambient atmosphere, magnetically stirred, and monitored by thin layer chromatography (TLC) using EMD TLC plates pre-coated with $250 \mu \mathrm{~m}$ thickness silica gel 60 F 254 plates and visualized by fluorescence quenching under UV light. Flash chromatography was performed on Dynamic Adsorbents Silica Gel $40-63 \mu \mathrm{~m}$ 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 $3 \AA$ 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 $\mathrm{CaH}_{2}$ and vacuum-distilled. Acetonitrile and acetonitrile- $d_{3}$ were dried over $\mathrm{P}_{2} \mathrm{O}_{5}$ and vacuumdistilled. Pyridine and tetramethylethylenediamine (TMEDA) were dried over $\mathrm{CaH}_{2}$ and distilled. DMSO was distilled from sodium triphenylmethanide and stored over $3 \AA$ sieves. ${ }^{3}$ Acetone was distilled over $\mathrm{B}_{2} \mathrm{O}_{3}$. MeOH was degassed at $-30^{\circ} \mathrm{C}$ under dynamic vacuum ( $10^{-4} \mathrm{Torr}$ ) for one hour and stored over $3 \AA$ sieves. Anhydrous DMF and dioxane bottles equipped with a SureSeal ${ }^{\mathrm{TM}}$ were purchased from Sigma Aldrich®. 18 -Crown- 6 was sublimed. KF was ground finely and dried at $200^{\circ} \mathrm{C}$ under dynamic vacuum ( $10^{-4}$ Torr) before use. $\mathrm{Ni}(\mathrm{COD})_{2}$ and all other chemicals were used as received. All deutrated solvents were purchased from Cambridge Isotope Laboratories. $\mathrm{Ni}(\mathrm{COD})_{2}$ and 18 -crown-6 were purchased from Strem Chemicals. (Diacetoxyiodo)benzene, potassium fluoride, 4-methoxypyridine, pyrrolidine, $p$-toluenesulfonic acid, $p$-methoxybenzenesulfonamide, and F-TEDA- $\mathrm{BF}_{4}$ (Selectfluor ${ }^{\circledR}$ ) 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 ${ }^{1} \mathrm{H}$ acquisitions, a Varian Unity/Inova 500 spectrometer operating at 500 MHz and 125 MHz for ${ }^{1} \mathrm{H}$ and ${ }^{13} \mathrm{C}$ acquisitions, respectively, a Varian Mercury 400 spectrometer operating at 375 MHz and 101 MHz for ${ }^{19} \mathrm{~F}$ and ${ }^{13} \mathrm{C}$ acquisitions, respectively, or a Varian Mercury 300 spectrometer operating at 100 MHz for ${ }^{11} \mathrm{~B}$ acquisitions. Chemical shifts were referenced to the residual proton solvent peaks $\left({ }^{1} \mathrm{H}: \mathrm{CDCl}_{3}, \delta 7.26 ; \mathrm{C}_{6} \mathrm{D}_{6}, \delta 7.16 ; \mathrm{CD}_{2} \mathrm{Cl}_{2}, \delta 5.32 ; \mathrm{D}_{2} \mathrm{O}, \delta 4.79\right.$; $\left.\left(\mathrm{CD}_{3}\right)_{2} \mathrm{SO}, \delta 2.50 ; \mathrm{CD}_{3} \mathrm{CN}, \delta 1.94\right)$, solvent ${ }^{13} \mathrm{C}$ signals $\left(\mathrm{CDCl}_{3}, \delta 77.16 ; \mathrm{C}_{6} \mathrm{D}_{6}, \delta 128.06 ; \mathrm{CD}_{2} \mathrm{Cl}_{2}\right.$, $\left.\delta 53.84 ; \mathrm{CD}_{3} \mathrm{CN}, \delta 1.32,\left(\mathrm{CD}_{3}\right)_{2} \mathrm{SO}, \delta 39.52\right),{ }^{4}$ dissolved or external neat $\mathrm{PhF}\left({ }^{19} \mathrm{~F}, \delta-113.15\right.$ relative to $\mathrm{CFCl}_{3}$ ) or dissolved 3-nitrofluorobenzene ( -112.0 ppm ). Signals are listed in ppm, and multiplicity identified as $\mathrm{s}=$ singlet, $\mathrm{br}=$ broad, $\mathrm{d}=$ doublet, $\mathrm{t}=$ triplet, $\mathrm{q}=$ quartet, quin $=$ quintet, sep $=$ septet, $\mathrm{m}=$ multiplet; coupling constants in Hz; integration. Concentration under reduced pressure was performed by rotary evaporation at $25-30^{\circ} \mathrm{C}$ 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) ${ }^{5}$



All manipulations were carried out in a dry box under a $\mathrm{N}_{2}$ atmosphere. To (diacetoxyiodo)benzene ( $3.00 \mathrm{~g}, 9.31 \mathrm{mmol}, 1.00$ equiv) dissolved in $\mathrm{CH}_{2} \mathrm{Cl}_{2}(100 \mathrm{~mL}$ ) in a round-bottom flask was added TMSOTf ( $4.14 \mathrm{~g}, 18.6 \mathrm{mmol}, 2.00$ equiv) drop-wise over 1 minute at $23{ }^{\circ} \mathrm{C}$. 4-Methoxypyridine ( $2.03 \mathrm{~g}, 18.6 \mathrm{mmol}, 2.00$ equiv) in $\mathrm{CH}_{2} \mathrm{Cl}_{2}(15 \mathrm{~mL})$ 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 $100 \mathrm{~mL}^{\text {of }} \mathrm{Et}_{2} \mathrm{O}$ to precipitate a white solid while stirring vigorously, and the resulting solid was collected on a frit. The solid was washed with $\mathrm{Et}_{2} \mathrm{O}(3 \times 10 \mathrm{~mL})$ and subsequently dried under vacuum to afford 6.52 g of the title compound as a colorless solid ( $97 \%$ ).

NMR Spectroscopy: ${ }^{1} \mathrm{H}$ NMR ( $500 \mathrm{MHz}, \mathrm{CD}_{3} \mathrm{CN}, 23^{\circ} \mathrm{C}, \delta$ ): $8.77(\mathrm{~d}, J=7.5 \mathrm{~Hz}, 4 \mathrm{H}), 8.60(\mathrm{~d}, J=$ $8.5 \mathrm{~Hz}, 2 \mathrm{H}), 7.79(\mathrm{t}, J=7.5 \mathrm{~Hz}, 1 \mathrm{H}), 7.64(\mathrm{t}, J=8.5 \mathrm{~Hz}, 2 \mathrm{H}), 7.19(\mathrm{~d}, J=7.5 \mathrm{~Hz}, 4 \mathrm{H}), 3.99(\mathrm{~s}$, $3 \mathrm{H}) .{ }^{13} \mathrm{C}$ NMR ( $125 \mathrm{MHz}, \mathrm{CD}_{3} \mathrm{CN}, 23^{\circ} \mathrm{C}, \delta$ ): 172.1, 149.9, 136.1, 135.7, 134.2, 125.7, 121.9 (q, $J=319 \mathrm{~Hz}$, triflate), 115.3, 58.5. ${ }^{19} \mathrm{~F}$ NMR ( $375 \mathrm{MHz}, \mathrm{CD}_{3} \mathrm{CN}, 23^{\circ} \mathrm{C}, 8$ ): -77.5 . Anal: calcd for $\mathrm{C}_{20} \mathrm{H}_{19} \mathrm{~F}_{6} \mathrm{IN}_{2} \mathrm{O}_{8} \mathrm{~S}_{2}$ : C, 33.34; H, 2.66; N, 3.89; found: C, 33.05; H, 2.59; N, 3.73.

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



Under air, to 2-bromopyridine ( $4.54 \mathrm{~g}, 28.7 \mathrm{mmol}, 1.00$ equiv) in DME- $\mathrm{H}_{2} \mathrm{O}(1: 1,100 \mathrm{~mL}$ ) at 23 ${ }^{\circ} \mathrm{C}$ was added $\mathrm{K}_{2} \mathrm{CO}_{3}$ ( $5.96 \mathrm{~g}, 43.1 \mathrm{mmol}$, 1.50 equiv), 2-aminophenylboronic acid pinacol ester $(6.30 \mathrm{~g}, 28.7 \mathrm{mmol}, 1.00$ equiv), and tetrakis(triphenylphosphine)palladium ( $1.66 \mathrm{~g}, 1.44 \mathrm{mmol}$,
$5.00 \mathrm{~mol} \%$ ). The reaction mixture was stirred at $100^{\circ} \mathrm{C}$ for 3.0 h . After cooling to $23^{\circ} \mathrm{C}$, the phases were separated and the aqueous phase was extracted with $\operatorname{EtOAc}(3 \times 50 \mathrm{~mL})$. The combined organic phases were washed with brine $(100 \mathrm{~mL})$ and dried $\left(\mathrm{Na}_{2} \mathrm{SO}_{4}\right)$. The filtrate was concentrated in vacuo and the residue was purified by chromatography on silica gel eluting with hexanes/EtOAc $4: 1$ ( $\mathrm{v} / \mathrm{v}$ ) to afford 4.20 g of the title compound as a red-brown oil ( $86 \%$ ).
$\mathrm{R}_{f}=0.38$ (hexanes/EtOAc 3:1 (v/v)). NMR Spectroscopy: ${ }^{1} \mathrm{H}$ NMR ( $500 \mathrm{MHz}, \mathrm{CDCl}_{3}, 23{ }^{\circ} \mathrm{C}, \delta$ ): $8.61-8.60(\mathrm{~m}, 1 \mathrm{H}), 7.78-7.75(\mathrm{~m}, 1 \mathrm{H}), 7.65(\mathrm{~d}, J=7.9 \mathrm{~Hz}, 1 \mathrm{H}), 7.51(\mathrm{dd}, J=7.6 \mathrm{~Hz}, 1.4 \mathrm{~Hz}, 1 \mathrm{H})$, 7.19-7.16 (m, 2H), 6.80-6.76 (m, 2H), 5.72 (br s, 2H). ${ }^{13} \mathrm{C}$ NMR ( $125 \mathrm{MHz}, \mathrm{CDCl}_{3}, 23{ }^{\circ} \mathrm{C}, \delta$ ): $159.5,147.9,146.6,136.9,129.9,129.4,122.2,122.2,121.0,117.6,117.2$. These spectroscopic data correspond to previously reported data. ${ }^{6}$

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



To 2-(2-pyridinyl)aniline (S1) ( $851 \mathrm{mg}, 5.00 \mathrm{mmol}, 1.00$ equiv) in $\mathrm{CH}_{2} \mathrm{Cl}_{2}(10 \mathrm{~mL})$ at $0{ }^{\circ} \mathrm{C}$ was added pyridine ( $1.60 \mathrm{~mL}, 20.0 \mathrm{mmol}, 4.00$ equiv) and 2 -nitrobenzenesulfonyl chloride ( 2.20 g , $10.0 \mathrm{mmol}, 2.00$ equiv). The reaction mixture was warmed to $23^{\circ} \mathrm{C}$ and stirred for 2.0 hr before the addition of water $(10 \mathrm{~mL})$. The phases were separated and the aqueous layer was extracted with $\mathrm{CH}_{2} \mathrm{Cl}_{2}(3 \times 8 \mathrm{~mL})$. The combined organic phases were washed with brine ( 30 mL ) and dried $\left(\mathrm{Na}_{2} \mathrm{SO}_{4}\right)$. 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\%).
$\mathrm{R}_{f}=0.12$ (hexanes/EtOAc 7:3 (v/v)). Melting Point: 91-94 ${ }^{\circ} \mathrm{C}$. NMR Spectroscopy: ${ }^{1} \mathrm{H}$ NMR ( $500 \mathrm{MHz}, \mathrm{CDCl}_{3}, 23^{\circ} \mathrm{C}, \delta$ ): 8.73 (d, $J=5.0 \mathrm{~Hz}, 1 \mathrm{H}$ ), 7.94 (dd, $J=7.5 \mathrm{~Hz}, 2.0 \mathrm{~Hz}, 1 \mathrm{H}$ ), 7.82 (dd, $J=8.0 \mathrm{~Hz}, 1.0 \mathrm{~Hz}, 1 \mathrm{H}), 7.74$ (ddd, $J=7.5 \mathrm{~Hz}, 7.5 \mathrm{~Hz}, 2.0 \mathrm{~Hz}, 1 \mathrm{H}), 7.63-7.52$ (m, 5H), 7.38 (ddd, $J=7.5 \mathrm{~Hz}, 7.5 \mathrm{~Hz}, 1.5 \mathrm{~Hz}, 1 \mathrm{H}), 7.27-7.24(\mathrm{~m}, 1 \mathrm{H}), 7.18$ (ddd, $J=7.5 \mathrm{~Hz}, 7.5 \mathrm{~Hz}, 1.0 \mathrm{~Hz}, 1 \mathrm{H})$. ${ }^{13} \mathrm{C}$ NMR ( $125 \mathrm{MHz}, \mathrm{CDCl}_{3}, 23{ }^{\circ} \mathrm{C}, \delta$ ): 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 $(\mathrm{m} / \mathrm{z})$ : Calcd for $\left[\mathrm{C}_{17} \mathrm{H}_{13} \mathrm{~N}_{3} \mathrm{O}_{4} \mathrm{~S}+\mathrm{H}\right]$, 356.06995. Found, 356.07008. These spectroscopic data correspond to previously reported data. ${ }^{7}$

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



To silver(I) oxide ( $4.99 \mathrm{~g}, 21.5 \mathrm{mmol}, 0.500$ equiv) in $\mathrm{CH}_{3} \mathrm{CN}(200 \mathrm{~mL})$ at $23^{\circ} \mathrm{C}$ was added 2-(2-pyridinyl)phenyl-2-nitrobenzenesulfonanilide ( $\mathbf{S 2}$ ) ( $15.3 \mathrm{~g}, 43.1 \mathrm{mmol}, 1.00$ equiv). After stirring for 12 h at $65^{\circ} \mathrm{C}$, the resulting light gray solid was collected on a frit and dried in vacuo to afford 18.3 g of the title compound as a light gray solid ( $92 \%$ ).

Anal: calcd for $\mathrm{C}_{17} \mathrm{H}_{12} \mathrm{AgN}_{3} \mathrm{O}_{4} \mathrm{~S}: \mathrm{C}, 44.17$; $\mathrm{H}, 2.62$; $\mathrm{N}, 9.09$; found: C, $44.06 ; \mathrm{H}, 2.66 ; \mathrm{N}, 9.00$. ${ }^{1} \mathrm{H}$ and ${ }^{13} \mathrm{C}$ NMR spectra were not obtained due to low solubility.

## Synthesis of aryl and alkenyl nickel complexes (1a-11)

## Synthesis of nickel aryl bromide complex $7 \mathrm{a}^{8}$



To a solution of TMEDA ( $83.0 \mathrm{mg}, 0.107 \mathrm{~mL}, 0.717 \mathrm{mmol}, 1.00$ equiv) and 4-bromobiphenyl ( $167 \mathrm{mg}, 0.717 \mathrm{mmol}, 1.00$ equiv) in toluene $(4 \mathrm{~mL})$ was added $\mathrm{Ni}(\mathrm{COD})_{2}(200 \mathrm{mg}, 0.717 \mathrm{mmol}$, 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 $(3 \times 5 \mathrm{~mL})$ and dried in vacuo to afford 288 mg of the title compound as an orange solid (99\%).

NMR Spectroscopy: ${ }^{1} \mathrm{H}$ NMR ( $\left.500 \mathrm{MHz}, \mathrm{CD}_{2} \mathrm{Cl}_{2}, \delta\right): 7.59(\mathrm{~d}, J=8.0 \mathrm{~Hz}, 2 \mathrm{H}), 7.52(\mathrm{~d}, J=7.5 \mathrm{~Hz}$, $1 \mathrm{H}), 7.38-7.35(\mathrm{~m}, 2 \mathrm{H}), 7.24-7.21(\mathrm{~m}, 1 \mathrm{H}), 7.10(\mathrm{~d}, J=7.7 \mathrm{~Hz}, 2 \mathrm{H}), 2.56-2.26(\mathrm{br}, 16 \mathrm{H}) .{ }^{13} \mathrm{C}$ NMR ( $125 \mathrm{MHz}, \mathrm{CD}_{2} \mathrm{Cl}_{2}, \delta$ ): 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 ${ }^{1} \mathrm{H}$ and ${ }^{13} \mathrm{C}$ NMR spectra was previously reported for a similar nickel complex. ${ }^{8 \mathrm{a}}$ Anal: calcd for $\mathrm{C}_{18} \mathrm{H}_{25} \mathrm{BrN}_{2} \mathrm{Ni}$ : C, $52.99 ; \mathrm{H}, 6.18$; 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) ( $0.227 \mathrm{~g}, 0.490 \mathrm{mmol}, 1.00$ equiv) and nickel aryl bromide complex 7 a ( $0.200 \mathrm{~g}, 0.490 \mathrm{mmol}, 1.00$ equiv) in a 20 mL vial was added a toluene solution ( 4 mL ) that contained pyridine ( $78.0 \mathrm{mg}, 79.0 \mu \mathrm{~L}, 0.980 \mathrm{mmol}, 2.00$ equiv) at $23{ }^{\circ} \mathrm{C}$, followed by addition of acetonitrile ( 1 mL ). After stirring for 1 min at 23 , the solution was filtered through a glass frit, and the filtered cake was extracted further with dichloromethane $(3 \times 5 \mathrm{~mL})$. 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 $\mathrm{CH}_{2} \mathrm{Cl}_{2}(3 \mathrm{~mL})$ 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: ${ }^{1} \mathrm{H}$ NMR ( $500 \mathrm{MHz}, \mathrm{CDCl}_{3}, \delta$ ): 9.17 (d, $J=5.4 \mathrm{~Hz}, 2 \mathrm{H}$ ), $8.25(\mathrm{~d}, J=5.4 \mathrm{~Hz}$, $1 \mathrm{H}), 7.57-7.47(\mathrm{~m}, 6 \mathrm{H}), 7.43-7.36(\mathrm{~m}, 3 \mathrm{H}), 7.32-7.28(\mathrm{~m}, 3 \mathrm{H}), 7.21-6.97(\mathrm{~m}, 10 \mathrm{H}), 6.61-6.59$ (m, 1H). ${ }^{13} \mathrm{C}$ NMR ( $125 \mathrm{MHz}, \mathrm{CDCl}_{3}, \delta$ ): 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 $\mathrm{C}_{34} \mathrm{H}_{26} \mathrm{~N}_{4} \mathrm{NiO}_{4} \mathrm{~S}: \mathrm{C}, 63.28 ; \mathrm{H}, 4.06$; N , 8.68; found: C, 63.02; H, 4.31; N, 8.48.

## Synthesis of nickel aryl bromide complex 7b



To a solution of TMEDA ( $104 \mathrm{mg}, 0.133 \mathrm{~mL}, 0.896 \mathrm{mmol}, 1.00$ equiv) and 2-bromofluorene ( 220 $\mathrm{mg}, 0.896 \mathrm{mmol}, 1.00$ equiv) in toluene ( 4 mL ) was added $\mathrm{Ni}(\mathrm{COD})_{2}(250 \mathrm{mg}, 0.896 \mathrm{mmol}, 1.00$ 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 $\times 5 \mathrm{~mL}$ ) and dried in vacuo to afford 348 mg of the title compound as a pink solid $(92 \%)$.
${ }^{1} \mathrm{H}$ NMR ( $\left.500 \mathrm{MHz}, \mathrm{CD}_{2} \mathrm{Cl}_{2}, \delta\right): 7.73(\mathrm{~s}, 1 \mathrm{H}), 7.62(\mathrm{~d}, J=6.4 \mathrm{~Hz}, 1 \mathrm{H}), 7.53(\mathrm{~d}, J=6.4 \mathrm{~Hz}, 1 \mathrm{H})$, 7.45 (d, $J=6.4 \mathrm{~Hz}, 1 \mathrm{H}), 7.31-7.26(\mathrm{~m}, 2 \mathrm{H}), 7.18-7.15(\mathrm{~m}, 1 \mathrm{H}), 3.78(\mathrm{br} \mathrm{s}, 2 \mathrm{H}), 2.55-2.23$ (br, 16 H ). ${ }^{13} \mathrm{C}$ NMR ( $125 \mathrm{MHz}, \mathrm{CD}_{2} \mathrm{Cl}_{2}, \delta$ ): 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 $\mathrm{C}_{19} \mathrm{H}_{25} \mathrm{BrN}_{2} \mathrm{Ni}^{\text {: }}$ 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



7b


95\%


1b

To (2-(2-pyridinyl)phenyl-2-nitrobenzenesulfonamide)silver(I) (8) ( $110 \mathrm{mg}, 0.238 \mathrm{mmol}, 1.00$ equiv) and nickel aryl bromide complex $7 \mathbf{b}$ ( $100 \mathrm{mg}, 0.238 \mathrm{mmol}, 1.00$ equiv) in a 20 mL vial was added a toluene solution $(4 \mathrm{~mL})$ that contained pyridine ( $37.7 \mathrm{mg}, 38.4 \mu \mathrm{~L}, 0.476 \mathrm{mmol}, 2.00$ equiv) at $23^{\circ} \mathrm{C}$, followed by addition of acetonitrile ( 0.5 mL ). After stirring for 1 min at 23 , the solution was filtered through a glass frit, and the filtered cake was extracted further with dichloromethane $(3 \times 3 \mathrm{~mL})$. 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 $\mathrm{CH}_{2} \mathrm{Cl}_{2}(2 \mathrm{~mL})$ and layering with pentane ( 20 mL ) to afford 0.148 g of the title compound as a yellow solid ( $95 \%$ ).
$\mathrm{R}_{f}=0.53$ (hexanes/EtOAc 1:2 (v/v)). NMR Spectroscopy: ${ }^{1} \mathrm{H}$ NMR ( $500 \mathrm{MHz}, \mathrm{CDCl}_{3}, 23^{\circ} \mathrm{C}, \delta$ ): $9.18(\mathrm{~d}, J=5.3 \mathrm{~Hz}, 2 \mathrm{H}), 8.24(\mathrm{~d}, J=6.4 \mathrm{~Hz}, 1 \mathrm{H}), 7.65(\mathrm{~s}, 1 \mathrm{H}), 7.58-7.46(\mathrm{~m}, 6 \mathrm{H}), 7.40-7.37(\mathrm{~m}$, 2H), 7.29-7.21 (m, 3H), 7.16-7.07 (m, 6H), 7.02-6.97 (m, 2H), 6.57-6.54 (m, $J=6.3,1 \mathrm{H}), 3.72-$ $3.58(\mathrm{~m}, 2 \mathrm{H}) .{ }^{13} \mathrm{C}$ NMR ( $125 \mathrm{MHz}, \mathrm{CDCl}_{3}, 23{ }^{\circ} \mathrm{C}, \delta$ ): $156.0,155.2,152.6,151.4,147.0,142.6$, $142.2,141.3,141.0,137.1,137.1,136.7,136.6,135.6,133.0,131.8,131.6,130.4,130.2,129.9$, 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 $\mathrm{C}_{35} \mathrm{H}_{26} \mathrm{~N}_{4} \mathrm{NiO}_{4} \mathrm{~S} \cdot\left(\mathrm{CH}_{2} \mathrm{Cl}_{2}\right)_{0.1}$ : 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 ( $122 \mathrm{mg}, 0.157 \mathrm{~mL}, 1.05 \mathrm{mmol}, 1.00$ equiv) and tert-butyl 5-bromoindole-1-carboxylate ( $311 \mathrm{mg}, 1.05 \mathrm{mmol}, 1.00$ equiv) in toluene ( 5 mL ) was added $\mathrm{Ni}(\mathrm{COD})_{2}$ ( $293 \mathrm{mg}, 1.05 \mathrm{mmol}, 1.00$ 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 ( $3 \times 5 \mathrm{~mL}$ ) and dried in vacuo to afford 491 mg of the title compound as a peach solid (99\%).
${ }^{1} \mathrm{H}$ NMR ( $600 \mathrm{MHz}, \mathrm{CD}_{2} \mathrm{Cl}_{2}, \delta$ ): $7.64(\mathrm{~d}, J=7.4 \mathrm{~Hz}, 1 \mathrm{H}), 7.55(\mathrm{~s}, 1 \mathrm{H}), 7.48(\mathrm{~d}, J=8.6 \mathrm{~Hz}, 1 \mathrm{H})$, $7.36(\mathrm{~d}, J=3.3 \mathrm{~Hz}, 1 \mathrm{H}), 6.38(\mathrm{~d}, J=3.6 \mathrm{~Hz}, 1 \mathrm{H}), 2.56-2.21(\mathrm{br}, 16 \mathrm{H}) .{ }^{13} \mathrm{C}$ NMR ( 125 MHz , $\left.\mathrm{CD}_{2} \mathrm{Cl}_{2}, \delta\right): 150.3,132.9,129.3,129.0,128.5,124.2,111.8,106.4,83.1,61.4$ (br), 57.3 (br), 49.3 (br), 48.4 (br), 28.0. Anal: calcd for $\mathrm{C}_{19} \mathrm{H}_{30} \mathrm{BrN}_{3} \mathrm{NiO}_{2}: \mathrm{C}, 48.44 ; \mathrm{H}, 6.42$; $\mathrm{N}, 8.92$; found: C, 48.14; H, 6.22; N, 8.84.

## Synthesis of nickel aryl complex 1c



7c


93\%


1c

To (2-(2-pyridinyl)phenyl-2-nitrobenzenesulfonamide)silver(I) (8) ( $98.0 \mathrm{mg}, 0.212 \mathrm{mmol}, 1.00$ equiv) and nickel aryl bromide complex 7 c ( $100 \mathrm{mg}, 0.212 \mathrm{mmol}, 1.00$ equiv) in a 20 mL vial was added a toluene solution ( 3 mL ) that contained pyridine ( $33.6 \mathrm{mg}, 34.2 \mu \mathrm{~L}, 0.425 \mathrm{mmol}, 2.00$ equiv) at $23^{\circ} \mathrm{C}$, followed by addition of acetonitrile $(0.5 \mathrm{~mL})$. After stirring for 1 min at 23 , the solution was filtered through a glass frit, and the filtered cake was extracted further with
dichloromethane $(3 \times 3 \mathrm{~mL})$. 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 $\mathrm{CH}_{2} \mathrm{Cl}_{2}(2 \mathrm{~mL})$ and layering with pentane ( 20 mL ) to afford 140 mg of the title compound as a yellow solid (93\%).
$\mathrm{R}_{f}=0.53$ (hexanes/EtOAc 1:2 (v/v)). NMR Spectroscopy: ${ }^{1} \mathrm{H}$ NMR ( $500 \mathrm{MHz}, \mathrm{CDCl}_{3}, 23^{\circ} \mathrm{C}, \delta$ ): 9.10 (d, $J=4.3 \mathrm{~Hz}, 2 \mathrm{H}), 8.16$ (d, $J=5.3 \mathrm{~Hz}, 1 \mathrm{H}), 7.59-7.39$ (m, 6H), 7.33-7.29 (m, 2H), 7.21$7.18(\mathrm{~m}, 2 \mathrm{H}), 7.09-7.00(\mathrm{~m}, 5 \mathrm{H}), 6.93-6.91(\mathrm{~m}, 2 \mathrm{H}), 6.48-6.47(\mathrm{~m}, 1 \mathrm{H}), 6.23(\mathrm{~d}, J=4.3,1 \mathrm{H})$, 1.50 (s, 9H). ${ }^{13} \mathrm{C}$ NMR ( $125 \mathrm{MHz}, \mathrm{CDCl}_{3}, 23{ }^{\circ} \mathrm{C}, \delta$ ): 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 $\mathrm{C}_{35} \mathrm{H}_{31} \mathrm{~N}_{5} \mathrm{NiO}_{6} \mathrm{~S}$ $\left(\mathrm{CH}_{2} \mathrm{Cl}_{2}\right)_{0.1}: \mathrm{C}, 58.81 ; \mathrm{H}, 4.39 ; \mathrm{N}, 9.77$; found: C, $58.49 ; \mathrm{H}, 4.39 ; \mathrm{N}, 9.81$. X-ray quality crystals were obtained from $2 \mathrm{~mL} \mathrm{CH}_{2} \mathrm{Cl}_{2}$ solution that contained 10.0 mg of the title compound slowly layered with 8.0 mL pentane at $23^{\circ} \mathrm{C}$. For crystallography data, see X-ray section.

## Synthesis of nickel aryl bromide complex 7d



To a solution of TMEDA ( $83.0 \mathrm{mg}, 0.107 \mathrm{~mL}, 0.717 \mathrm{mmol}, 1.00$ equiv) and 4bromobenzophenone ( $187 \mathrm{mg}, 0.717 \mathrm{mmol}, 1.00$ equiv) in toluene ( 4 mL ) was added $\mathrm{Ni}(\mathrm{COD})_{2}$ ( $200 \mathrm{mg}, 0.717 \mathrm{mmol}, 1.00$ 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 ( $3 \times 5 \mathrm{~mL}$ ) and dried in vacuo to afford 305 mg of the title compound as an orange solid ( $98 \%$ ).
${ }^{1} \mathrm{H}$ NMR ( $600 \mathrm{MHz}, \mathrm{CD}_{2} \mathrm{Cl}_{2}, \delta$ ): 7.77 (d, $J=7.5 \mathrm{~Hz}, 2 \mathrm{H}$ ), $7.70(\mathrm{~d}, J=6.4 \mathrm{~Hz}, 2 \mathrm{H}), 7.56-7.52$ (m, $1 \mathrm{H}), 7.46-7.43(\mathrm{~m}, 2 \mathrm{H}), 7.24(\mathrm{~d}, J=7.5 \mathrm{~Hz}, 2 \mathrm{H}), 2.56-2.22(\mathrm{br}, 16 \mathrm{H}) .{ }^{13} \mathrm{C}$ NMR ( 125 MHz , $\mathrm{CD}_{2} \mathrm{Cl}_{2}, \delta$ ): 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 $\mathrm{C}_{19} \mathrm{H}_{25} \mathrm{BrN}_{2} \mathrm{NiO}$ (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


45\%


To (2-(2-pyridinyl)phenyl-2-nitrobenzenesulfonamide)silver(I) (8) ( $212 \mathrm{mg}, 0.459 \mathrm{mmol}, 1.00$ equiv) and nickel aryl bromide complex $7 \mathbf{d}(200 \mathrm{mg}, 0.459 \mathrm{mmol}, 1.00$ equiv) in a 20 mL vial was added a toluene solution $(4 \mathrm{~mL})$ that contained pyridine $(78.0 \mathrm{mg}, 79.0 \mu \mathrm{~L}, 0.980 \mathrm{mmol}, 2.00$ equiv) at $23{ }^{\circ} \mathrm{C}$, followed by addition of acetonitrile ( 1.0 mL ). After stirring for 1 min at 23 , the solution was filtered through a glass frit, and the filtered cake was extracted further with dichloromethane $(3 \times 5 \mathrm{~mL})$. 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 $\mathrm{CH}_{2} \mathrm{Cl}_{2}(2 \mathrm{~mL})$ and layering with pentane ( 20 mL ) to afford 138 mg of the title compound as a yellow solid (45\%).
$\mathrm{R}_{f}=0.41$ (hexanes/EtOAc 1:2 (v/v)). NMR Spectroscopy: ${ }^{1} \mathrm{H}$ NMR ( $500 \mathrm{MHz}, \mathrm{CD}_{2} \mathrm{Cl}_{2}, 23{ }^{\circ} \mathrm{C}$, §): 9.13 (d, $J=5.3 \mathrm{~Hz}, 2 \mathrm{H}), 8.17$ (d, $J=5.3 \mathrm{~Hz}, 1 \mathrm{H}), 7.69(\mathrm{~d}, J=7.6 \mathrm{~Hz}, 2 \mathrm{H}), 7.66-7.56(\mathrm{~m}, 5 \mathrm{H})$, $7.52-7.49(\mathrm{~m}, 1 \mathrm{H}), 7.41-7.35(\mathrm{~m}, 5 \mathrm{H}), 7.26-7.23(\mathrm{~m}, 2 \mathrm{H}), 7.19-7.16(\mathrm{~m}, 4 \mathrm{H}), 7.08(\mathrm{~d}, J=8.3$ $\mathrm{Hz}, 1 \mathrm{H}), 7.02(\mathrm{br} \mathrm{s}, 2 \mathrm{H}), 6.67-6.64(\mathrm{~m}, 1 \mathrm{H}) .{ }^{13} \mathrm{C}$ NMR ( $125 \mathrm{MHz}, \mathrm{CD}_{2} \mathrm{Cl}_{2}, 23{ }^{\circ} \mathrm{C}, \delta$ ): 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 $\mathrm{C}_{35} \mathrm{H}_{26} \mathrm{~N}_{4} \mathrm{NiO}_{5} \mathrm{~S}\left(\mathrm{CH}_{2} \mathrm{Cl}_{2}\right)_{0.15}$ : C, $61.53 ; \mathrm{H}, 3.86 ; \mathrm{N}, 8.17$; found: C, 61.19; H, 4.20; N, 8.58.

## Synthesis of nickel aryl bromide complex 7e



To a solution of TMEDA ( $83.0 \mathrm{mg}, 0.107 \mathrm{~mL}, 0.717 \mathrm{mmol}, 1.00$ equiv) and 1 -bromo-2cyclohexylbenzene ( $171 \mathrm{mg}, 0.717 \mathrm{mmol}, 1.00$ equiv) in toluene $(4 \mathrm{~mL})$ was added $\mathrm{Ni}(\mathrm{COD})_{2}$
( $200 \mathrm{mg}, 0.717 \mathrm{mmol}, 1.00$ 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 ( $3 \times 5 \mathrm{~mL}$ ) and dried in vacuo to afford 208 mg of the title compound as a pink solid (70\%).
${ }^{1} \mathrm{H}$ NMR ( $600 \mathrm{MHz}, \mathrm{CD}_{2} \mathrm{Cl}_{2}, \delta$ ): $7.37(\mathrm{~d}, J=7.5 \mathrm{~Hz}, 2 \mathrm{H}), 6.68-6.62(\mathrm{~m}, 3 \mathrm{H}), 5.55-5.45(\mathrm{~m}, 1 \mathrm{H})$, $2.75-2.23(\mathrm{br}, 16 \mathrm{H}), 2.05-1.73(\mathrm{~m}, 8 \mathrm{H}), 2.05-1.73(\mathrm{~m}, 8 \mathrm{H}), 1.48-1.41(\mathrm{~m}, 1 \mathrm{H}), 1.15(\mathrm{br} \mathrm{s}, 1 \mathrm{H})$. ${ }^{13} \mathrm{C}$ NMR ( $125 \mathrm{MHz}, \mathrm{CD}_{2} \mathrm{Cl}_{2}, \delta$ ): 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 $\mathrm{C}_{18} \mathrm{H}_{31} \mathrm{BrN}_{2} \mathrm{Ni}$ : C, 52.21; H, 7.55; N, 6.77; found: C, 51.87; H, 7.43; N, 6.73.

## Synthesis of nickel aryl complex 1e


$7 e$

$1 \mathbf{1 e}$

To (2-(2-pyridinyl)phenyl-2-nitrobenzenesulfonamide)silver(I) (8) ( $223 \mathrm{mg}, 0.483 \mathrm{mmol}, 1.00$ equiv) and nickel aryl bromide complex 7 e ( $200 \mathrm{mg}, 0.483 \mathrm{mmol}, 1.00$ equiv) in a 20 mL vial was added a toluene solution ( 4 mL ) that contained pyridine ( $76.0 \mathrm{mg}, 78.0 \mu \mathrm{~L}, 0.966 \mathrm{mmol}, 2.00$ equiv) at $23^{\circ} \mathrm{C}$, followed by addition of acetonitrile $(1.0 \mathrm{~mL})$. After stirring for 1 min at 23 , the solution was filtered through a glass frit, and the filtered cake was extracted further with dichloromethane $(3 \times 5 \mathrm{~mL})$. 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 $\mathrm{CH}_{2} \mathrm{Cl}_{2}(2 \mathrm{~mL})$ and layering with pentane ( 20 mL ) to afford 146 mg of the title compound as a yellow solid (46\%).
$\mathrm{R}_{f}=0.66$ (hexanes/EtOAc 1:2 (v/v)). NMR Spectroscopy: ${ }^{1} \mathrm{H}$ NMR ( $500 \mathrm{MHz}, \mathrm{CDCl}_{3}, 23^{\circ} \mathrm{C}, \delta$ ): 9.09 (d, $J=5.3 \mathrm{~Hz}, 2 \mathrm{H}), 8.33(\mathrm{~d}, J=5.3 \mathrm{~Hz}, 1 \mathrm{H}), 8.18(\mathrm{~d}, J=7.5 \mathrm{~Hz}, 1 \mathrm{H}), 7.62-7.46(\mathrm{~m}, 4 \mathrm{H})$, $7.40-7.37(\mathrm{~m}, 1 \mathrm{H}), 7.29-7.26(\mathrm{~m}, 1 \mathrm{H}), 7.15-7.09(\mathrm{~m}, 5 \mathrm{H}), 7.00-6.93(\mathrm{~m}, 3 \mathrm{H}), 6.73-6.70(\mathrm{~m}, 1 \mathrm{H})$, 6.59-6.56 (m, 1H), 6.49 (d, $J=7.4,1 \mathrm{H}), 4.86-4.82(\mathrm{~m}, 1 \mathrm{H}), 1.73-1.01(\mathrm{~m}, 10 \mathrm{H}) .{ }^{13} \mathrm{C}$ NMR (125, $\left.\mathrm{CDCl}_{3}, 23{ }^{\circ} \mathrm{C}, \delta\right): 156.2,156.1,153.1,151.8,151.2,147.0,141.2,137.0,136.6,135.4$, $134.2,131.8,130.3,130.1,129.8,128.9,128.6,125.1,124.1,124.0,123.0,122.7,122.5,121.7$, 49.0, 35.5, 34.5, 27.4, 26.9, 26.4. Anal: calcd for $\mathrm{C}_{34} \mathrm{H}_{32} \mathrm{~N}_{4} \mathrm{NiO}_{4} \mathrm{~S}\left(\mathrm{CH}_{2} \mathrm{Cl}_{2}\right)_{0.1}: \mathrm{C}, 62.07 ; \mathrm{H}, 4.92$; N, 8.49; found: C, 61.91; H, 4.92; N, 8.69.

## 4-bromophenethyl benzoate (S3)



To a mixture of 2-(4-bromophenyl)ethanol $\left(1.00 \mathrm{~g}, 4.97 \mathrm{mmol}, 1.00\right.$ equiv) and $\mathrm{Et}_{3} \mathrm{~N}(0.763 \mathrm{ml}$, $0.554 \mathrm{~g}, 5.47 \mathrm{mmol}, 1.10$ equiv) in a round-bottom flask in THF ( 20 ml ) was added benzoyl chloride ( $0.589 \mathrm{~mL}, 0.713 \mathrm{~g}, 5.07 \mathrm{mmol}, 1.02$ equiv). The reaction mixture was stirring for 4 h at $23{ }^{\circ} \mathrm{C}$ and concentrated in vacuo. The residue was purified by chromatography on silica gel eluting with hexanes/EtOAc $1: 1(\mathrm{v} / \mathrm{v})$ to afford 1.50 g of the title compound as a colorless solid (99\%).
$\mathrm{R}_{f}=0.70$ (hexanes/EtOAc 1:1 (v/v)). NMR Spectroscopy: ${ }^{1} \mathrm{H}$ NMR ( $500 \mathrm{MHz}, \mathrm{CDCl}_{3}, 23^{\circ} \mathrm{C}, \delta$ ): $8.00(\mathrm{~d}, J=7.2 \mathrm{~Hz}, 1 \mathrm{H}), 7.58-7.54(\mathrm{~m}, 1 \mathrm{H}), 7.45-7.42(\mathrm{~m}, 4 \mathrm{H}), 7.16(\mathrm{~d}, J=8.4 \mathrm{~Hz}, 2 \mathrm{H}), 4.51(\mathrm{t}$, $J=6.4 \mathrm{~Hz}, 2 \mathrm{H}), 3.04(\mathrm{t}, J=6.4 \mathrm{~Hz}, 2 \mathrm{H}) .{ }^{13} \mathrm{C}$ NMR ( $\left.125 \mathrm{MHz}, \mathrm{CDCl}_{3}, 23^{\circ} \mathrm{C}, \delta\right): 166.6,137.1$, 133.1, 131.8, 130.8, 130.3, 129.7, 128.5, 120.6, 65.2, 34.8. HRMS-FIA (m/z): calcd for $\mathrm{C}_{15} \mathrm{H}_{13} \mathrm{BrO}_{2}\left[\mathrm{M}+\mathrm{Na}^{+}, 326.9991\right.$; found, 327.0007.

## Synthesis of nickel aryl bromide complex $7 f$



To a solution of TMEDA ( $83 \mathrm{mg}, 0.107 \mathrm{~mL}, 0.717 \mathrm{mmol}, 1.00$ equiv) and 4-bromophenethyl benzoate ( $219 \mathrm{mg}, 0.717 \mathrm{mmol}, 1.00$ equiv) in toluene ( 4 mL ) was added $\mathrm{Ni}(\mathrm{COD})_{2}(200 \mathrm{mg}$, $0.717 \mathrm{mmol}, 1.00$ 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 $(3 \times 5 \mathrm{~mL})$ and dried in vacuo to afford 208 mg of the title compound as an orange-pink solid ( $90 \%$ ).
${ }^{1} \mathrm{H}$ NMR ( $600 \mathrm{MHz}, \mathrm{CD}_{2} \mathrm{Cl}_{2}, \delta$ ): $7.98(\mathrm{~d}, J=6.9 \mathrm{~Hz}, 2 \mathrm{H}), 7.57-7.55(\mathrm{~m}, 1 \mathrm{H}), 7.45-7.42(\mathrm{~m}, 4 \mathrm{H})$, $6.77(\mathrm{~d}, J=5.5 \mathrm{~Hz}, 2 \mathrm{H}), 4.41(\mathrm{t}, J=6.2 \mathrm{~Hz}, 2 \mathrm{H}), 2.90(\mathrm{t}, J=6.2 \mathrm{~Hz}, 2 \mathrm{H}), 2.53-2.15(\mathrm{br}, 16 \mathrm{H}) .$. ${ }^{13} \mathrm{C}$ NMR ( $125 \mathrm{MHz}, \mathrm{CD}_{2} \mathrm{Cl}_{2}, \delta$ ): 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 $\mathrm{C}_{21} \mathrm{H}_{29} \mathrm{BrN}_{2} \mathrm{NiO}_{2}$ : C, 52.54; H , 6.09; N, 5.84; found: C, 52.81; H, 5.95; N, 5.53.

## Synthesis of nickel aryl complex if



7f


$$
51 \%
$$


$1 f$

To (2-(2-pyridinyl)phenyl-2-nitrobenzenesulfonamide)silver(I) (8) (193 mg, $0.417 \mathrm{mmol}, 1.00$ equiv) and nickel aryl bromide complex $7 \mathbf{7 f}(200 \mathrm{mg}, 0.417 \mathrm{mmol}, 1.00$ equiv) in a 20 mL vial was added a toluene solution ( 4 mL ) that contained pyridine ( $65.9 \mathrm{mg}, 67.1 \mu \mathrm{~L}, 0.833 \mathrm{mmol}, 2.00$ equiv) at $23^{\circ} \mathrm{C}$, followed by addition of acetonitrile ( 1.0 mL ). After stirring for 1 min at 23 , the solution was filtered through a glass frit, and the filtered cake was extracted further with dichloromethane $(3 \times 5 \mathrm{~mL})$. 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 ( $51 \%$ ).
$\mathrm{R}_{f}=0.52$ (hexanes/EtOAc 1:2 (v/v)). NMR Spectroscopy: ${ }^{1} \mathrm{H}$ NMR ( $400 \mathrm{MHz}, \mathrm{CDCl}_{3}, 23^{\circ} \mathrm{C}, \delta$ ): $9.13(\mathrm{~d}, J=5.6 \mathrm{~Hz}, 2 \mathrm{H}), 8.17(\mathrm{~d}, J=5.2 \mathrm{~Hz}, 1 \mathrm{H}), 7.94(\mathrm{~d}, J=8.0 \mathrm{~Hz}, 2 \mathrm{H}), 7.55-7.45(\mathrm{~m}, 5 \mathrm{H})$, $7.41-7.28(\mathrm{~m}, 6 \mathrm{H}), 7.17-7.07(\mathrm{~m}, 5 \mathrm{H}), 7.01-6.97(\mathrm{~m}, 2 \mathrm{H}), 6.68(\mathrm{~d}, J=7.6,2 \mathrm{H}), 6.57-6.54(\mathrm{~m}$, $1 \mathrm{H}), 4.32(\mathrm{t}, J=7.2 \mathrm{~Hz}, 2 \mathrm{H}), 2.81(\mathrm{t}, J=7.2 \mathrm{~Hz}, 2 \mathrm{H}) .{ }^{13} \mathrm{C}$ NMR ( $125 \mathrm{MHz} \mathrm{CDCl}{ }_{3} 23^{\circ} \mathrm{C}, \delta$ ): 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 $\mathrm{C}_{37} \mathrm{H}_{30} \mathrm{~N}_{4} \mathrm{NiO}_{6} \mathrm{~S}: \mathrm{C}, 61.94 ; \mathrm{H}, 4.21$; 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 ( $3.50 \mathrm{~g}, 9.20 \mathrm{mmol}, 1.00$ equiv) ${ }^{9}$ in a roundbottom flask in MeOH ( 70 ml ) was added copper(II) bromide ( $11.0 \mathrm{~g}, 49.2 \mathrm{mmol}, 5.00$ equiv) in $\mathrm{H}_{2} \mathrm{O}(70 \mathrm{~mL})$ in one portion. The reaction mixture was stirred at reflux for 3 d . The reaction
mixture was cooled to $23{ }^{\circ} \mathrm{C}$ and subsequently poured into $\mathrm{H}_{2} \mathrm{O}(200 \mathrm{~mL})$. The colorless precipitate was collected on a frit, followed by washing with water $(3 \times 30 \mathrm{~mL}) . \mathrm{CH}_{2} \mathrm{Cl}_{2}(100$ mL ) was added to the solid and the solution was filtered though a pad of Celite. The filtrate was concentrated, triturated with $\mathrm{Et}_{2} \mathrm{O}(3 \times 5 \mathrm{~mL})$ and dried to afford 2.60 g of the title compound as a colorless solid ( $85 \%$ yield).
NMR Spectroscopy: ${ }^{1} \mathrm{H}$ NMR ( $\left.500 \mathrm{MHz}, \mathrm{CDCl}_{3}, 23^{\circ} \mathrm{C}, \delta\right): 7.28(\mathrm{~d}, J=8.6 \mathrm{~Hz}, 1 \mathrm{H}), 7.26(\mathrm{~s}, 1 \mathrm{H})$, $7.17(\mathrm{~d}, J=8.6 \mathrm{~Hz}, 1 \mathrm{H}), 2.92-2.90(\mathrm{~m}, 2 \mathrm{H}), 2.56-2.50(\mathrm{~m}, 2 \mathrm{H}), 2.28-2.23(\mathrm{~m}, 1 \mathrm{H}), 2.21-1.98(\mathrm{~m}$, $4 \mathrm{H}), 1.69-1.41(\mathrm{~m}, 6 \mathrm{H}), 0.93(\mathrm{~s}, 3 \mathrm{H}) .{ }^{13} \mathrm{C}$ NMR ( $125 \mathrm{MHz}, \mathrm{CDCl}_{3}, 23^{\circ} \mathrm{C}, \delta$ ): 220.7, 139.0, 138.9, $131.8,128.8,127.3,119.7,50.5,48.0,44.2,38.0,35.9,31.6,29.3,26.4,25.8,21.7,13.9$. HRMSFIA ( $\mathrm{m} / \mathrm{z}$ ): calcd for $\mathrm{C}_{18} \mathrm{H}_{21} \mathrm{BrO}[\mathrm{M}+\mathrm{Na}]^{+}, 333.0849$; found, 333.0861 .

## Synthesis of nickel aryl bromide complex 7 g





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

NMR Spectroscopy: ${ }^{1} \mathrm{H}$ NMR ( $600 \mathrm{MHz}, \mathrm{CD}_{2} \mathrm{Cl}_{2}, \delta$ ): $7.21(\mathrm{~d}, J=8.2 \mathrm{~Hz}, 1 \mathrm{H}$ ), $7.16(\mathrm{~s}, 1 \mathrm{H}), 6.73$ (d, $J=6.9 \mathrm{~Hz}, 1 \mathrm{H}$ ), 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). ${ }^{13} \mathrm{C}$ NMR ( $125 \mathrm{MHz}, \mathrm{CD}_{2} \mathrm{Cl}_{2}, \delta$ ): 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 $\mathrm{C}_{24} \mathrm{H}_{37} \mathrm{BrN}_{2} \mathrm{NiO}: \mathrm{C}, 56.73 ; \mathrm{H}, 7.34$; N, 5.51 ; found: C, $52.92 ; \mathrm{H}, 6.91$; 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 $\mathbf{1 g}$ (see below). HRMS-FIA ( $\mathrm{m} / \mathrm{z}$ ): calcd for $\mathrm{C}_{24} \mathrm{H}_{37} \mathrm{~N}_{2} \mathrm{NiO}[\mathrm{M}-\mathrm{Br}]^{+}, 427.2259$; found, 427.2263.

## Synthesis of nickel aryl complex 1 g



7g


51\%


To (2-(2-pyridinyl)phenyl-2-nitrobenzenesulfonamide)silver(I) (8) (193 mg, $0.417 \mathrm{mmol}, 1.00$ equiv) and nickel aryl bromide complex $7 \mathbf{g}(200 \mathrm{mg}, 0.417 \mathrm{mmol}, 1.00$ equiv) in a 20 mL vial was added a toluene solution ( 4 mL ) that contained pyridine $(65.9 \mathrm{mg}, 67.1 \mu \mathrm{~L}, 0.833 \mathrm{mmol}, 2.00$ equiv) at $23^{\circ} \mathrm{C}$, followed by addition of acetonitrile $(1.0 \mathrm{~mL})$. After stirring for 1 min at 23 , the solution was filtered through a glass frit, and the filtered cake was extracted further with dichloromethane $(3 \times 5 \mathrm{~mL})$. 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 $\mathrm{CH}_{2} \mathrm{Cl}_{2}(2 \mathrm{~mL})$ and layering with pentane ( 20 mL ) to afford 152 mg of the title compound as a yellow solid ( $51 \%$ ).
$\mathrm{R}_{f}=0.35$ (hexanes/EtOAc 1:2 (v/v)). NMR Spectroscopy: ${ }^{1} \mathrm{H}$ NMR ( $500 \mathrm{MHz}, \mathrm{CDCl}_{3}, 23{ }^{\circ} \mathrm{C}, \delta$ ): $9.14(\mathrm{~d}, J=4.9 \mathrm{~Hz}, 2 \mathrm{H}), 8.28-8.26(\mathrm{~m}, 1 \mathrm{H}), 7.54-7.45(\mathrm{~m}, 4 \mathrm{H}), 7.36-7.28(\mathrm{~m}, 2 \mathrm{H}), 7.16-6.97(\mathrm{~m}$, $9 \mathrm{H}), 6.66-6.62(\mathrm{~m}, 2 \mathrm{H}), 2.77-2.60(\mathrm{~m}, 2 \mathrm{H}), 2.47-2.41(\mathrm{~m}, 2 \mathrm{H}), 2.21-1.85(\mathrm{~m}, 6 \mathrm{H}), 1.55-1.27$ $(4 \mathrm{H}), 0.82(\mathrm{~m}, 3 \mathrm{H}) .{ }^{13} \mathrm{C} \operatorname{NMR}\left(125 \mathrm{MHz} \mathrm{CDCl}_{3}, 23{ }^{\circ} \mathrm{C}, \delta\right): 221.3,156.0,152.7,152.7,151.5$, $150.7,150.6,147.0,141.3,137.0,136.6,135.9,135.8,135.7,133.9,133.8,133.7,133.1,132.9$, $131.6,131.3,130.5,130.4,130.1,129.7,128.8,128.4,128.3,124.4,124.2,124.1,122.8,122.7$, $122.7,122.6,121.7,50.7,48.2,44.2,44.2,38.4,38.3,36.0,31.8,29.5,29.5,26.9,25.6,25.6,21.7$, 14.0. Anal: calcd for $\mathrm{C}_{40} \mathrm{H}_{38} \mathrm{~N}_{4} \mathrm{NiO}_{5} \mathrm{~S}\left(\mathrm{CH}_{2} \mathrm{Cl}_{2}\right)_{0.1}$ : C, $63.88 ; \mathrm{H}, 5.11$; 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 ( $1.00 \mathrm{~g}, 4.97 \mathrm{mmol}, 1.00$ equiv) and $\mathrm{K}_{2} \mathrm{CO}_{3}(3.44 \mathrm{~g}, 24.9$
mmol, 5.00 equiv) in THF ( 10 mL ) in an oven-dried round-bottom flask fitted with a reflux condenser under a $\mathrm{N}_{2}$ atmosphere at $23{ }^{\circ} \mathrm{C}$ was added (bromomethyl)cyclopropane ( $1.01 \mathrm{~g}, 0.724$ $\mathrm{mL}, 7.46 \mathrm{mmol}, 1.50$ equiv). The reaction mixture was warmed in an oil heating bath at a temperature of $70^{\circ} \mathrm{C}$ and heated at reflux with vigorous stirring for 40 hours. The reaction mixture was cooled to $23^{\circ} \mathrm{C}$ and poured into $\mathrm{H}_{2} \mathrm{O}(30 \mathrm{~mL})$ in a separatory funnel. $\mathrm{CHCl}_{3}(30 \mathrm{~mL})$ was added, the funnel was shaken and the organic phase collected. The aqueous phase was then extracted with $\mathrm{CHCl}_{3}(2 \times 30 \mathrm{~mL})$. The combined organic phases were washed with brine ( 30 mL ), dried with $\mathrm{Na}_{2} \mathrm{SO}_{4}$, 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).
$\mathrm{R}_{f}=0.30$ (hexanes/EtOAc 19:1 (v/v)). NMR Spectroscopy: ${ }^{1} \mathrm{H}$ NMR ( $600 \mathrm{MHz}, \mathrm{CDCl}_{3}, 23^{\circ} \mathrm{C}$, §): 10.45 ( $\mathrm{s}, 1 \mathrm{H}$ ), $7.91(\mathrm{~d}, J=2.5 \mathrm{~Hz}, 1 \mathrm{H}), 7.58(\mathrm{dd}, J=8.9,2.6 \mathrm{~Hz}, 1 \mathrm{H}), 6.84(\mathrm{~d}, J=8.9 \mathrm{~Hz}, 1 \mathrm{H})$, $3.91(\mathrm{~d}, J=7.2 \mathrm{~Hz}, 2 \mathrm{H}), 1.32-1.26(\mathrm{~m}, 1 \mathrm{H}), 0.71-0.63(\mathrm{~m}, 2 \mathrm{H}), 0.41-0.34(\mathrm{~m}, 2 \mathrm{H}) .{ }^{13} \mathrm{C}$ NMR ( $125 \mathrm{MHz}, \mathrm{CDCl}_{3}, 23^{\circ} \mathrm{C}, \delta$ ): 188.7, 160.5, 138.3, 130.9, 126.5, 115.0, 113.5, 73.9, 10.1, 3.4. HRMS-FIA ( $\mathrm{m} / \mathrm{z}$ ): calcd for $\mathrm{C}_{11} \mathrm{H}_{11} \mathrm{BrNaO}_{2}[\mathrm{M}+\mathrm{Na}]^{+}$, 276.9840; found, 276.9820 .

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



To 5-bromo-2-(cyclopropylmethoxy)benzaldehyde ( $\mathbf{S 5}$ ) ( $3.10 \mathrm{~g}, 12.2 \mathrm{mmol}, 1.00$ equiv) and LiCl $\left(0.541 \mathrm{~g}, 12.8 \mathrm{mmol}, 1.05\right.$ equiv) in $\mathrm{MeCN}(45 \mathrm{~mL})$ in a round-bottom flask under a $\mathrm{N}_{2}$ atmosphere at $0^{\circ} \mathrm{C}$ was added triethyl phosphonoacetate $(3.00 \mathrm{~g}, 2.68 \mathrm{~mL}, 13.4 \mathrm{mmol}, 1.10$ equiv) and 1,8-diazabicycloundec-7-ene (DBU) ( $2.04 \mathrm{~g}, 2.02 \mathrm{~mL}, 13.4 \mathrm{mmol}, 1.10$ equiv). Upon the addition of DBU, the reaction mixture turned yellow. The reaction mixture was warmed to 23 ${ }^{\circ} \mathrm{C}$ and stirred for 15 hours. The reaction mixture was poured into $\mathrm{H}_{2} \mathrm{O}(75 \mathrm{~mL})$ in a separatory funnel. $\mathrm{CHCl}_{3}(75 \mathrm{~mL})$ was added and the funnel was shaken and the organic phase collected. The aqueous phase was extracted from with $\mathrm{CHCl}_{3}(2 \times 50 \mathrm{~mL})$. All organic phases were combined and washed with brine ( 50 mL ), dried with $\mathrm{Na}_{2} \mathrm{SO}_{4}$, and concentrated in vacuo. The residue was purified by chromatography on silica gel, eluting with $5-10 \%$ EtOAc in hexanes ( $\mathrm{v} / \mathrm{v}$ ) to afford 3.89 g of the title compound as a colorless solid ( $98 \%$ yield).
$\mathrm{R}_{f}=0.25$ (hexanes/EtOAc 19:1 (v/v)). NMR Spectroscopy: ${ }^{1} \mathrm{H}$ NMR ( $500 \mathrm{MHz}, \mathrm{CDCl}_{3}, 2{ }^{\circ}{ }^{\circ} \mathrm{C}$, ס): 7.93 (d, $J=16.1 \mathrm{~Hz}, 1 \mathrm{H}$ ), $7.60(\mathrm{~d}, J=2.4 \mathrm{~Hz}, 1 \mathrm{H}), 7.37$ (dd, $J=8.8,2.5 \mathrm{~Hz}, 1 \mathrm{H}), 6.74(\mathrm{~d}, 8.8$ $\mathrm{Hz}, 1 \mathrm{H}), 6.53(\mathrm{~d}, J=16.1 \mathrm{~Hz}, 1 \mathrm{H}), 4.26(\mathrm{q}, J=6.8 \mathrm{~Hz}, 2 \mathrm{H}), 3.84(\mathrm{~d}, J=6.8 \mathrm{~Hz}, 2 \mathrm{H}), 1.34-1.25$ $(\mathrm{m}, 4 \mathrm{H}), 0.70-0.61(\mathrm{~m}, 2 \mathrm{H}), 0.40-0.31(\mathrm{~m}, 2 \mathrm{H}) .{ }^{13} \mathrm{C}$ NMR ( $125 \mathrm{MHz}, \mathrm{CDCl}_{3}, 23{ }^{\circ} \mathrm{C}, \delta$ ): 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
$(\mathrm{m} / \mathrm{z})$ : calcd for $\mathrm{C}_{15} \mathrm{H}_{18} \mathrm{BrO}_{3}[\mathrm{M}+\mathrm{H}]^{+}, 325.0439$; 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, $11.6 \mathrm{mmol}, 1.00$ equiv) in $\mathrm{PhMe}(30 \mathrm{~mL})$ in a flame-dried round-bottom flask under a $\mathrm{N}_{2}$ atmosphere at $-78{ }^{\circ} \mathrm{C}$ was added a 1.0 M solution of diisobutylaluminum hydride (DIBAL-H) in PhMe ( $26 \mathrm{~mL}, 26$ mmol, 2.2 equiv) in 6 portions dropwise every 10 minutes for 1 hour. The reaction was warmed to $0^{\circ} \mathrm{C}$ over 2 hours and then warmed to $23^{\circ} \mathrm{C}$ and stirred at this temperature for 1 hour. The reaction mixture was poured onto a concentrated aqueous Rochelle's salt (potassium sodium tartrate) solution ( 400 mL ). EtOAc ( 400 mL ) was added and the mixture was stirred for 3 hour until two liquid phases separated cleanly. The phases were partitioned and the aqueous phase was extracted from with EtOAc ( 300 mL ). The organic phases were combined and washed with brine ( 200 mL ), dried with $\mathrm{Na}_{2} \mathrm{SO}_{4}$, and concentrated in vacuo. The residue was purified by chromatography on silica gel, eluting with a gradient of $10-25 \%$ EtOAc in hexanes ( $\mathrm{v} / \mathrm{v}$ ) to afford 2.77 g of the title compound as a colorless solid ( $84 \%$ yield).
$\mathrm{R}_{f}=0.15$ (hexanes/EtOAc 6:1 (v/v)). NMR Spectroscopy: ${ }^{1} \mathrm{H}$ NMR ( $500 \mathrm{MHz}, \mathrm{CDCl}_{3}, 23^{\circ} \mathrm{C}, \delta$ ): $7.53(\mathrm{~d}, J=2.4 \mathrm{~Hz}, 1 \mathrm{H}), 7.26(\mathrm{dd}, J=8.8,2.4 \mathrm{~Hz}, 1 \mathrm{H}), 6.88(\mathrm{~d}, J=16.1 \mathrm{~Hz}, 1 \mathrm{H}), 6.69(\mathrm{~d}, J=8.8$ $\mathrm{Hz}, 1 \mathrm{H}), 6.39$ (dt, $J=16.1,5.9 \mathrm{~Hz}, 1 \mathrm{H}), 4.33$ (br dd, $J=4.6,4.6 \mathrm{~Hz}, 2 \mathrm{H}), 3.79$ (d, $J=6.8 \mathrm{~Hz}, 2 \mathrm{H}$ ), $1.71(\mathrm{brt}, J=5.1 \mathrm{~Hz}, 1 \mathrm{H}), 1.31-1.23(\mathrm{~m}, 1 \mathrm{H}), 0.68-0.58(\mathrm{~m}, 2 \mathrm{H}), 0.38-0.30(\mathrm{~m}, 2 \mathrm{H}) .{ }^{13} \mathrm{C}$ NMR ( $125 \mathrm{MHz}, \mathrm{CDCl}_{3}, 23{ }^{\circ} \mathrm{C}, \delta$ ): 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 $\mathrm{C}_{13} \mathrm{H}_{15} \mathrm{BrNaO}_{2}[\mathrm{M}+\mathrm{Na}]^{+}$, 305.0153; found, 305.0123.
((1S,2S)-2-(5-bromo-2-(cyclopropylmethoxy)phenyl)cyclopropyl)methanol (S8)


Following a published procedure for asymmetric allylic cyclopropanation: ${ }^{10}$ To dimethoxyethane (DME) ( $1.39 \mathrm{~g}, 1.60 \mathrm{~mL}, 15.4 \mathrm{mmol}, 1.90$ equiv) in $\mathrm{CH}_{2} \mathrm{Cl}_{2}(50 \mathrm{~mL})$ in a flame-dried round-
bottom flask under a $\mathrm{N}_{2}$ atmosphere cooled in an ethyleneglycol/ $\mathrm{CO}_{2}$ bath at $-15^{\circ} \mathrm{C}$ was added diethylzinc ( $2.01 \mathrm{~g}, 1.67 \mathrm{~mL}, 16.3 \mathrm{mmol}, 2.00$ equiv), while maintaining the bath temperature between -15 and $-10^{\circ} \mathrm{C} . \mathrm{CH}_{2} \mathrm{I}_{2}(8.70 \mathrm{~g}, 2.62 \mathrm{~mL}, 32.5 \mathrm{mmol}, 4.00$ equiv) was added dropwise over 20 minutes at $-15^{\circ} \mathrm{C}$. The reaction mixture was stirred at $-15^{\circ} \mathrm{C}$ for 10 minutes. A solution of ( $4 R, 5 R$ )-2-butyl- $N, N, N^{\prime}, N^{\prime}$-tetramethyl-1,3,2-dioxaborolane-4,5-dicarboxamide ( $2.63 \mathrm{~g}, 2.46$ $\mathrm{mL}, 9.75 \mathrm{mmol}, 1.20$ equiv) in $\mathrm{CH}_{2} \mathrm{Cl}_{2}(10 \mathrm{~mL})$ from a separate flame-dried round-bottom flask under a $\mathrm{N}_{2}$ atmosphere was added over 5 minutes via syringe. A solution of ( $E$ )-3-(5-bromo-2-(cyclopropylmethoxy)phenyl)prop-2-en-1-ol (S7) ( $2.30 \mathrm{~g}, 8.12 \mathrm{mmol}, 1.00$ equiv) in $\mathrm{CH}_{2} \mathrm{Cl}_{2}$ ( 10 mL ) from a separate flame-dried round-bottom flask under a $\mathrm{N}_{2}$ atmosphere was added over 5 minutes via syringe. The reaction mixture was allowed to warm to $23^{\circ} \mathrm{C}$ and stirred for 20 hours. Saturated aqueous $\mathrm{NH}_{4} \mathrm{Cl}$ solution ( 10 mL ) and $1 \mathrm{M} \mathrm{HCl}(50 \mathrm{~mL})$ 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 $(100 \mathrm{~mL})$. The combined organic phases were transferred to an Erlenmeyer flask. 2 M NaOH solution ( 60 mL ) and $30 \% \mathrm{H}_{2} \mathrm{O}_{2}$ 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 $\mathrm{HCl}(75 \mathrm{~mL})$, saturated aqueous $\mathrm{Na}_{2} \mathrm{CO}_{3}$ solution ( 75 mL ), saturated aqueous $\mathrm{NaHCO}_{3}$ solution ( 75 mL ) and brine $(75 \mathrm{~mL}$ ). The organic phase was dried with $\mathrm{MgSO}_{4}$, and concentrated in vacuo. The residue was purified by chromatography on silica gel, eluting with a gradient of $10-30 \%$ EtOAc in hexanes ( $\mathrm{v} / \mathrm{v}$ ) 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- $N, N, N^{\prime}, N^{\prime}$ 'tetramethyl-1,3,2-dioxaborolane-4,5-dicarboxamide. Absolute stereochemistry was assigned by analogy. ${ }^{10}$
$\mathrm{R}_{f}=0.20$ (hexanes/EtOAc 6:1 (v/v)). NMR Spectroscopy: ${ }^{1} \mathrm{H}$ NMR ( $500 \mathrm{MHz}, \mathrm{CDCl}_{3}, 23^{\circ} \mathrm{C}, \delta$ ): 7.24 (dd, $J=8.8,2.4 \mathrm{~Hz}, 1 \mathrm{H}), 7.09(\mathrm{~d}, J=2.4 \mathrm{~Hz}, 1 \mathrm{H}), 6.65(\mathrm{~d}, J=8.8 \mathrm{~Hz}, 1 \mathrm{H}), 3.95(\mathrm{ddd}, J=$ $10.7,8.8,4.9 \mathrm{~Hz}, 1 \mathrm{H}), 3.82(\mathrm{~d}, J=7.3 \mathrm{~Hz}, 2 \mathrm{H}), 3.19(\mathrm{ddd}, J=10.7,10.7,2.0,1 \mathrm{H}), 2.40(\mathrm{dd}, J=$ $8.5,2.0 \mathrm{~Hz}, 1 \mathrm{H}), 1.86(\mathrm{ddd}, J=8.5,5.0,5.0 \mathrm{~Hz}, 1 \mathrm{H}) 1.34-1.27(\mathrm{~m}, 1 \mathrm{H}), 1.20-1.15(\mathrm{~m}, 1 \mathrm{H})$, $1.14-1.09(\mathrm{~m}, 1 \mathrm{H}), 0.86(\mathrm{ddd}, J=9.0,5.0,5.0 \mathrm{~Hz}, 1 \mathrm{H}), 0.71-0.65(\mathrm{~m}, 2 \mathrm{H}), 0.40-0.34(\mathrm{~m}, 2 \mathrm{H})$. ${ }^{13} \mathrm{C}$ NMR ( $125 \mathrm{MHz}, \mathrm{CDCl}_{3}, 23{ }^{\circ} \mathrm{C}, \delta$ ): 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 $\mathrm{C}_{14} \mathrm{H}_{17} \mathrm{BrNaO}_{2}[\mathrm{M}+\mathrm{Na}]^{+}, 319.0310$; found, 319.0327.

Figure S1: Enantiodiscriminating HPLC trace of S8


HPLC method: Chiracel ODH column with 5\% isopropanol/hexanes eluent for racemic $\mathbf{S 8}$ and enantioenriched S8. Percent of total integration listed for each peak.

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


To ((1S,2S)-2-(5-bromo-2-(cyclopropylmethoxy)phenyl)cyclopropyl)methanol (S8) ( $2.15 \mathrm{~g}, 7.23$ mmol, 1.00 equiv) in $\mathrm{CH}_{2} \mathrm{Cl}_{2}(30 \mathrm{~mL})$ in an oven-dried round-bottom flask under a $\mathrm{N}_{2}$ atmosphere at $0^{\circ} \mathrm{C}$ was added $\mathrm{Et}_{3} \mathrm{~N}(2.20 \mathrm{~g}, 3.03 \mathrm{~mL}, 21.7 \mathrm{mmol}, 3.00$ equiv $)$ and $\mathrm{MsCl}(1.66 \mathrm{~g}$, $1.13 \mathrm{~mL}, 14.5 \mathrm{mmol}, 2.00$ equiv). The reaction mixture was stirred at $0^{\circ} \mathrm{C}$ for 2 hours. The reaction mixture turned yellow and a precipitate formed. The reaction mixture was poured into a separatory funnel with saturated $\mathrm{NH}_{4} \mathrm{Cl}$ solution $(40 \mathrm{~mL})$. The funnel was shaken and the organic phase collected. The aqueous phase was extracted from with diethyl ether ( $3 \times 75 \mathrm{~mL}$ ). The organic phases were combined and washed with saturated $\mathrm{NaHCO}_{3}(100 \mathrm{~mL})$ and brine $(100 \mathrm{~mL})$, dried with $\mathrm{MgSO}_{4}$, and concentrated in vacuo. The residue was dissolved in DMF ( 30 mL ) and $\mathrm{NaN}_{3}\left(1.88 \mathrm{~g}, 28.9 \mathrm{mmol}, 4.00\right.$ equiv) was added. The reaction mixture was heated at $60^{\circ} \mathrm{C}$ for 1 hour. The reaction mixture was cooled and poured into 60 mL of water. The reaction mixture was extracted from with diethyl ether $(3 \times 75 \mathrm{~mL})$. The combined organic phases were washed with brine ( 100 mL ), dried with $\mathrm{MgSO}_{4}$, and concentrated in vacuo. The residue was purified by chromatography on silica gel, eluting with a gradient of 5-10\% EtOAc in hexanes ( $\mathrm{v} / \mathrm{v}$ ) to afford 1.95 g of the title compound as a colorless oil ( $84 \%$ yield).
$\mathrm{R}_{f}=0.60$ (hexanes/EtOAc 19:1 (v/v)). NMR Spectroscopy: ${ }^{1} \mathrm{H}$ NMR ( $500 \mathrm{MHz}, \mathrm{CDCl}_{3}, 23{ }^{\circ} \mathrm{C}$, ס): $7.21(\mathrm{dd}, J=8.7,2.3 \mathrm{~Hz}, 1 \mathrm{H}), 6.96(\mathrm{~d}, J=2.3 \mathrm{~Hz}, 1 \mathrm{H}), 6.66(\mathrm{~d}, J=8.7 \mathrm{~Hz}, 1 \mathrm{H}), 3.84-3.78(\mathrm{~m}$,
$2 \mathrm{H}), 3.40(\mathrm{dd}, J=12.8,6.4,1 \mathrm{H}), 3.24(\mathrm{dd}, J=12.8,7.1 \mathrm{~Hz}, 1 \mathrm{H}), 2.11$ (ddd, $J=8.7,5.0,5.0 \mathrm{~Hz}$, $1 \mathrm{H}), 1.38-1.32(\mathrm{~m}, 1 \mathrm{H}), 1.31-1.25(\mathrm{~m}, 1 \mathrm{H}), 1.08-1.04(\mathrm{~m}, 1 \mathrm{H}), 0.98-0.94(\mathrm{~m}, 1 \mathrm{H}), 0.68-0.58(\mathrm{~m}$, $2 \mathrm{H}), 0.40-0.31(\mathrm{~m}, 2 \mathrm{H}) .{ }^{13} \mathrm{C}$ NMR ( $\left.125 \mathrm{MHz}, \mathrm{CDCl}_{3}, 23^{\circ} \mathrm{C}, \delta\right): 156.9,132.8,129.5,128.8,113.4$, 112.9, 73.3, 55.3, 20.8, 16.2, 12.8, 10.4, 3.3, 3.2. HRMS-FIA (m/z): calcd for $\mathrm{C}_{14} \mathrm{H}_{16} \mathrm{BrN}_{3} \mathrm{NaO}$ [M $+\mathrm{Na}]^{+}, 344.0374$; found, 344.0363.

## $t$-Butyl (((1S,2S)-2-(5-bromo-2-(cyclopropylmethoxy)phenyl)cyclopropyl)methyl) carbamate $(S 10){ }^{9}$



To 2-((1S,2S)-2-(azidomethyl)cyclopropyl)-4-bromo-1-(cyclopropylmethoxy)benzene (S9) (1.90 g, $5.90 \mathrm{mmol}, 1.00$ equiv) in a round-bottom flask open to air in a $2: 1$ solution of dioxane: $\mathrm{H}_{2} \mathrm{O}$ $(45 \mathrm{~mL})$ cooled to $0^{\circ} \mathrm{C}$ was added $\operatorname{tin}(\mathrm{II})$ chloride $(5.59 \mathrm{~g}, 29.5 \mathrm{mmol}, 5.00$ equiv). The reaction mixture was allowed to warm to $23^{\circ} \mathrm{C}$ and stirred for 15 hours. Saturated aqueous $\mathrm{NaHCO}_{3}$ solution ( 50 mL ) was carefully added. The addition was accompanied by foaming. $\mathrm{H}_{2} \mathrm{O}(15 \mathrm{~mL})$ was added followed by $\mathrm{Boc}_{2} \mathrm{O}(3.86 \mathrm{~g}, 4.11 \mathrm{~mL}, 17.7 \mathrm{mmol}, 3.00$ equiv $)$. The reaction mixture was stirred for 3 hours and then transferred to a separatory funnel. The reaction mixture was extracted from with EtOAc $(3 \times 75 \mathrm{~mL})$. The combined organic phases were washed with brine ( 75 mL ), dried with $\mathrm{Na}_{2} \mathrm{SO}_{4}$, 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).
$\mathrm{R}_{f}=0.25$ (hexanes/EtOAc 19:1 (v/v)). NMR Spectroscopy: ${ }^{1} \mathrm{H}$ NMR ( $500 \mathrm{MHz}, \mathrm{CDCl}_{3}, 23{ }^{\circ} \mathrm{C}$, ס): 7.23 (dd, $J=8.3,2.4 \mathrm{~Hz}, 1 \mathrm{H}), 7.06$ (br d, $J=2.0 \mathrm{~Hz}, 1 \mathrm{H}), 6.66(\mathrm{~d}, J=8.8 \mathrm{~Hz}, 1 \mathrm{H}), 5.27$ (br, $1 \mathrm{H}), 3.97$ (dd, $J=9.5,7.1 \mathrm{~Hz}, 1 \mathrm{H}$ ), $3.72-3.66$ (m, 2H), 2.66 (br dd, $J=10.0,10.0,1 \mathrm{H}), 1.83$ (ddd, $J=6.6,6.6,4.9 \mathrm{~Hz}, 1 \mathrm{H}), 1.43(\mathrm{br}, 10 \mathrm{H}), 1.06-0.99(\mathrm{br} \mathrm{m}, 2 \mathrm{H}), 0.83-0.80(\mathrm{br} \mathrm{m}, 1 \mathrm{H}), 0.67(\mathrm{br} \mathrm{m}$, 2 H ), 0.38 (br m, 2H). ${ }^{13} \mathrm{C}$ NMR ( $125 \mathrm{MHz}, \mathrm{CDCl}_{3}, 23^{\circ} \mathrm{C}, \delta$ ): 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 ( $\mathrm{m} / \mathrm{z}$ ): calcd for $\mathrm{C}_{19} \mathrm{H}_{26} \mathrm{BrNNaO}_{3}\left[\mathrm{M}+\mathrm{Na}^{+}, 418.0988\right.$; 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 ( $41.6 \mathrm{mg}, 53.7 \mu \mathrm{~L}, 0.358 \mathrm{mmol}, 1.00$ equiv) and $t$-butyl ( ( $(1 \mathrm{~S}, 2 \mathrm{~S})$-2-(5-bromo-2-(cyclopropylmethoxy)phenyl)cyclopropyl)methyl) carbamate (S10) ( $0.142 \mathrm{~g}, 0.358$ $\mathrm{mmol}, 1.00$ equiv) in toluene ( 3 mL ) was added $\mathrm{Ni}(\mathrm{COD})_{2}(0.100 \mathrm{~g}, 0.358 \mathrm{mmol}, 1.00$ equiv), and the mixture was stirred at room temperature for 45 min . Pentane $(16 \mathrm{~mL})$ was added to the mixtures and the resulting solid was collected on a frit. The solid was washed with pentane ( $3 \times 5$ mL ) and dried in vacuo to afford 0.183 g of the title compound as a peach solid $(89 \%)$.
Reliable ${ }^{1} \mathrm{H}$ NMR and ${ }^{13} \mathrm{C}$ NMR data could not be obtained due to the instability of $\mathbf{7 h}$ in most organic solvents. However, some representative peaks were observed in $\mathrm{CD}_{2} \mathrm{Cl}_{2}$. NMR Spectroscopy: ${ }^{1} \mathrm{H}$ NMR ( $\left.500 \mathrm{MHz}, \mathrm{CD}_{2} \mathrm{Cl}_{2}, 23^{\circ} \mathrm{C}, \delta\right): 7.15(\mathrm{~d}, J=7.8 \mathrm{~Hz}, 1 \mathrm{H}), 7.02(\mathrm{~s}, 1 \mathrm{H}), 6.47$ (d, $J=7.8 \mathrm{~Hz}, 1 \mathrm{H}), 5.43(\mathrm{br}, 1 \mathrm{H}), 3.86(\mathrm{br} \mathrm{s}, 1 \mathrm{H}), 3.62(\mathrm{br} \mathrm{s}, 1 \mathrm{H}), 2.52-2.19$ (br, 18H), 1.41 (s, 9 H ), 0.61 (br m, 2H), 0.33 (br s, 2H). ${ }^{13} \mathrm{C}$ NMR ( $125 \mathrm{MHz}, \mathrm{CD}_{2} \mathrm{Cl}_{2}, 23{ }^{\circ} \mathrm{C}, \delta$ ): 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 $\mathrm{C}_{25} \mathrm{H}_{42} \mathrm{BrN}_{3} \mathrm{NiO}_{3}$ : C, 52.57; H, 7.41; N, 7.36; found: C, 50.08; H, 7.03; N, 7.10. Numerous attempts (recrystallization using different solvents) were made to obtain satisfactory elemental analysis data but none of them was successful. However, this material is of sufficient purity for use in the preparation of analytically pure $\mathbf{1 h}$ in the next step. HRMS-FIA ( $\mathrm{m} / \mathrm{z}$ ): calcd for $\mathrm{C}_{25} \mathrm{H}_{42} \mathrm{~N}_{3} \mathrm{NiO}_{3}[\mathrm{M}-\mathrm{Br}]^{+}$, 490.2574; found, 490.2590.

## Synthesis of nickel aryl complex 1h



7h


 $38 \%$


1h

To (2-(2-pyridinyl)phenyl-2-nitrobenzenesulfonamide)silver(I) (8) ( $0.113 \mathrm{~g}, 0.245 \mathrm{mmol}, 1.00$ equiv) and nickel aryl bromide complex $7 \mathrm{~h}(0.140 \mathrm{~g}, 0.245 \mathrm{mmol}, 1.00$ equiv) in a 20 mL vial was added a toluene solution ( 3 mL ) that contained pyridine ( $38.8 \mathrm{mg}, 39.5 \mu \mathrm{~L}, 0.490 \mathrm{mmol}, 2.00$ equiv) at $23^{\circ} \mathrm{C}$, followed by addition of acetonitrile ( 0.5 mL ). After stirring for 1 min at 23 , the solution was filtered through a glass frit, and the filtered cake was extracted further with dichloromethane $(3 \times 5 \mathrm{~mL})$. 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 $\mathrm{CH}_{2} \mathrm{Cl}_{2}(2 \mathrm{~mL})$ and layering with pentane ( 20 mL ) to afford 75.0 mg of the title compound as a yellow solid (38\%).
$\mathrm{R}_{f}=0.47$ (hexanes/EtOAc 1:2 (v/v)). NMR Spectroscopy: ${ }^{1} \mathrm{H}$ NMR ( $500 \mathrm{MHz}, \mathrm{CD}_{2} \mathrm{Cl}_{2}, 23{ }^{\circ} \mathrm{C}$, ס): 9.09 (d, $J=3.4 \mathrm{~Hz}, 2 \mathrm{H}), 8.15(\mathrm{dd}, J=8.9,6.0 \mathrm{~Hz}, 1 \mathrm{H}), 7.61-7.63(\mathrm{~m}, 3 \mathrm{H}), 7.39-7.32(\mathrm{~m}, 3 \mathrm{H})$, 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$6.31(\mathrm{~m}, 1 \mathrm{H}), 5.29(\mathrm{br}, 1 \mathrm{H}), 3.75(\mathrm{br} \mathrm{s}, 1 \mathrm{H}), 3.56-3.48(\mathrm{~m}, 1 \mathrm{H}), 2.57-2.52(\mathrm{br} \mathrm{m}, 1 \mathrm{H}), 2.58-2.50$ (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$0.24(\mathrm{~m}, 2 \mathrm{H}) .{ }^{13} \mathrm{C}$ NMR ( $\left.125 \mathrm{MHz}, \mathrm{CD}_{2} \mathrm{Cl}_{2}, 23^{\circ} \mathrm{C}, \delta\right): 155.4,152.7,151.7,141.5,137.7,137.1$, 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 ${ }^{1} \mathrm{H}$ NMR spectrum. Reliable ${ }^{13} \mathrm{C}$ NMR data were not obtained due to the decomposition of $\mathbf{1 h}$ in the solvent over time. Anal: calcd for $\mathrm{C}_{41} \mathrm{H}_{43} \mathrm{~N}_{5} \mathrm{NiO}_{7} \mathrm{~S}$ : C, 60.90 ; $\mathrm{H}, 5.36$; N, 8.66; found: C, 60.21 ; H , 5.57; N, 8.66. HRMS-FIA ( $\mathrm{m} / \mathrm{z}$ ): calcd for $\mathrm{C}_{36} \mathrm{H}_{39} \mathrm{~N}_{4} \mathrm{NiO}_{7} \mathrm{~S}[\mathrm{M}-\text { pyridine }+\mathrm{H}]^{+}, 729.1887$; 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-4,5dihydroxyphenylalanine methyl ester ( $8.00 \mathrm{~g}, 20.5 \mathrm{mmol}, 1.00$ equiv) and $\mathrm{Et}_{3} \mathrm{~N}(5.72 \mathrm{ml}, 4.15 \mathrm{~g}$, $164 \mathrm{mmol}, 2.00$ equiv) in a round-bottom flask in $\mathrm{PhMe}(100 \mathrm{ml})$ was added $\mathrm{Boc}_{2} \mathrm{O}(3.86 \mathrm{~g}, 4.11$ $\mathrm{mL}, 17.7 \mathrm{mmol}, 3.00$ equiv) in one portion. The reaction mixture was stirring under nitrogen atmosphere at $80^{\circ} \mathrm{C}$ for 9 h . The reaction mixture was cooled to $23^{\circ} \mathrm{C}$ and was concentrated in vacuo. The residue was purified by chromatography on silica gel, eluting with a gradient of $30 \%$ EtOAc in hexanes ( $\mathrm{v} / \mathrm{v}$ ) to afford 11.5 g of the title compound as a light yellow solid ( $95 \%$ yield).
$\mathrm{R}_{f}=0.53$ (hexanes/EtOAc 2:1 (v/v)). NMR Spectroscopy: ${ }^{1} \mathrm{H}$ NMR ( $500 \mathrm{MHz}, \mathrm{CDCl}_{3}, 23^{\circ} \mathrm{C}, \delta$ ): $7.46(\mathrm{~s}, 1 \mathrm{H}), 7.11(\mathrm{~s}, 1 \mathrm{H}), 5.10(\mathrm{~d}, J=8.4 \mathrm{~Hz}, 1 \mathrm{H}), 4.61-4.57(\mathrm{~m}, 1 \mathrm{H}), 3.68(\mathrm{~s}, 3 \mathrm{H}), 3.25-3.20(\mathrm{~m}$, $1 \mathrm{H}), 3.11-3.06(\mathrm{~m}, 1 \mathrm{H}), 1.51(\mathrm{~s}, 18 \mathrm{H}), 1.37(\mathrm{~s}, 9 \mathrm{H}) .{ }^{13} \mathrm{C}$ NMR ( $125 \mathrm{MHz}, \mathrm{CDCl}_{3}, 23{ }^{\circ} \mathrm{C}, \delta$ ): $172.2,155.0,150.3,141.8,141.7,134.6,127.2,125.3,120.8,84.3,84.1,80.1,53.3,52.5,38.2$, 28.3, 27.6, 27.5. HRMS-FIA ( $\mathrm{m} / \mathrm{z}$ ): calcd for $\mathrm{C}_{25} \mathrm{H}_{36} \mathrm{BrNO}_{10}[\mathrm{M}+\mathrm{Na}]^{+}$, 612.1415; found, 612.1413.

## Synthesis of nickel aryl bromide complex 7i



To a solution of TMEDA ( $125 \mathrm{mg}, 0.161 \mathrm{~mL}, 1.08 \mathrm{mmol}, 1.00$ equiv) and $N$-(tert-butoxycarbonyl)-3,4-di(tert-butoxycarbonyloxy)-6-bromo-L-phenylalaninemethyl ester (S11) ( $635 \mathrm{mg}, 1.08 \mathrm{mmol}, 1.00$ equiv) in toluene $(8 \mathrm{~mL})$ was added $\mathrm{Ni}(\mathrm{COD})_{2}(300 \mathrm{mg}, 1.08 \mathrm{mmol}$, 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 $(3 \times 5 \mathrm{~mL})$ and dried in vacuo to afford 735 mg of the title compound as a red solid ( $92 \%$ ).
NMR Spectroscopy: ${ }^{1} \mathrm{H}$ NMR ( $500 \mathrm{MHz}, \mathrm{CD}_{3} \mathrm{CN} 23{ }^{\circ} \mathrm{C}, \delta$ ): $7.39(\mathrm{~s}, 1 \mathrm{H}), 6.73(\mathrm{~s}, 1 \mathrm{H}), 5.50(\mathrm{br} \mathrm{s}$,
$1 \mathrm{H}), 4.51(\mathrm{br} \mathrm{s}, 1 \mathrm{H}), 3.84(\mathrm{~s}, 3 \mathrm{H}), 3.80-3.70(\mathrm{~m}, 1 \mathrm{H}), 2.63-2.22(\mathrm{br}, 18 \mathrm{H}), 1.54(\mathrm{~s}, 9 \mathrm{H}), 1.50(\mathrm{~s}$, 9 H ), 1.35 ( $\mathrm{s}, 9 \mathrm{H}$ ). ${ }^{13} \mathrm{C}$ NMR ( $125 \mathrm{MHz}, \mathrm{CD}_{3} \mathrm{CN} 23{ }^{\circ} \mathrm{C}, \delta$ ): 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 ${ }^{1} \mathrm{H}$ NMR spectrum. Anal: calcd for $\mathrm{C}_{31} \mathrm{H}_{52} \mathrm{BrN}_{3} \mathrm{NiO}_{10}(\mathrm{PhMe})_{0.2}$ : 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


$7 i$

$1 i$

To (2-(2-pyridinyl)phenyl-2-nitrobenzenesulfonamide)silver(I) (7) (302 mg, $0.650 \mathrm{mmol}, 1.00$ equiv) and nickel aryl bromide complex $7 \mathbf{i}(500 \mathrm{mg}, 0.650 \mathrm{mmol}, 1.00$ equiv) in a round-bottom flask was added a toluene solution ( 8 mL ) that contained pyridine ( $103 \mathrm{mg}, 105 \mu \mathrm{~L}, 1.31 \mathrm{mmol}$, 2.00 equiv) at $23^{\circ} \mathrm{C}$, followed by addition of acetonitrile ( 2.0 mL ). After stirring for 1 min at 23 , the solution was filtered through a glass frit, and the filtered cake was extracted further with dichloromethane $(3 \times 5 \mathrm{~mL})$. The combined filtrate was concentrated in vacuo and the resulting residue was purified by chromatography on silica gel eluting with hexanes/EtOAc $1: 3(\mathrm{v} / \mathrm{v})(0.5 \%$ $\mathrm{Et}_{3} \mathrm{~N}$ ) to afford 260 mg of the title compound as a yellow solid (40\%).
$\mathrm{R}_{f}=0.40$ (hexanes/EtOAc 1:2 (v/v)). NMR Spectroscopy: ${ }^{1} \mathrm{H}$ NMR ( $500 \mathrm{MHz}, \mathrm{CD}_{2} \mathrm{Cl}_{2}, 23{ }^{\circ} \mathrm{C}$, ס): 9.04 (d, $J=4.9 \mathrm{~Hz}, 2 \mathrm{H}), 8.32(\mathrm{~d}, J=5.4 \mathrm{~Hz}, 0.4 \mathrm{H}), 8.26(\mathrm{~d}, J=5.4 \mathrm{~Hz}, 0.6 \mathrm{H}), 8.05(\mathrm{~s}, 1 \mathrm{H})$, $7.66-7.32(\mathrm{~m}, 7 \mathrm{H}), 7.27-7.15(\mathrm{~m}, 5 \mathrm{H}), 7.08-7.01(\mathrm{~m}, 4 \mathrm{H}), 6.73-6.63(\mathrm{~m}, 1 \mathrm{H}), 6.40(\mathrm{~s}, 0.6 \mathrm{H})$, $6.32(\mathrm{~s}, 0.4 \mathrm{H}), 4.35-4.22(\mathrm{~m}, 1 \mathrm{H}), 4.07-3.93(\mathrm{~m}, 1 \mathrm{H}), 3.88-3.80(\mathrm{~m}, 2 \mathrm{H}), 3.54-3.41(\mathrm{~m}, 3 \mathrm{H})$, $1.59(\mathrm{~s}, 5 \mathrm{H}), 1.58(\mathrm{~s}, 5 \mathrm{H}), 1.44(\mathrm{~s}, 9 \mathrm{H}), 1.31(\mathrm{~s}, 8 \mathrm{H}) .{ }^{13} \mathrm{C}$ NMR ( $125 \mathrm{MHz} \mathrm{CD}{ }_{2} \mathrm{Cl}_{2}, 23{ }^{\circ} \mathrm{C}, \delta$ ): $173.2,156.2,155.3,154.5,151.8,151.5,151.4,147.2,140.8,140.7,139.7,139.5,139.3,138.3$, $138.0,137.6,137.5,136.6,136.3,135.8,132.0,130.9,130.8,130.2,129.1,129.1,128.6,127.9$, $127.8,124.8,124.7,124.6,123.6,123.0,122.7,122.5,119.4,119.2,83.5,83.4,79.8,54.6,52.3$, 40.8, 28.4, 28.1, 27.9, 27.7. Note: Conformational isomers were observed in the ${ }^{1} \mathrm{H}$ NMR spectrum, which is possibly due to slow rotation about bonds as seen for similar complexes. ${ }^{12}$ Anal: calcd for $\mathrm{C}_{47} \mathrm{H}_{53} \mathrm{~N}_{5} \mathrm{NiO}_{14} \mathrm{~S}$ : C, 56.30; H, 5.33 ; N, 6.98 ; found: C, $55.98 ; \mathrm{H}, 5.18 ; \mathrm{N}, 6.90$. HRMS-FIA (m/z): calcd for $\mathrm{C}_{42} \mathrm{H}_{49} \mathrm{~N}_{4} \mathrm{NiO}_{14} \mathrm{~S}$ [M - pyridine +H$]^{+}$, 923.2314; found, 923.2276.

## Synthesis of nickel aryl bromide complex 7j



7j

To a solution of TMEDA ( $83.0 \mathrm{mg}, 0.107 \mathrm{~mL}, 0.717 \mathrm{mmol}, 1.00$ equiv) and 3-bromobenzamide ( $143 \mathrm{mg}, 0.717 \mathrm{mmol}, 1.00$ equiv) in toluene ( 4 mL ) was added $\mathrm{Ni}(\mathrm{COD})_{2}(200 \mathrm{mg}, 0.717 \mathrm{mmol}$, 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 $(3 \times 5 \mathrm{~mL})$ and dried in vacuo to afford 225 mg of the title compound as a pink solid ( $84 \%$ ).
${ }^{1} \mathrm{H}$ NMR ( $600 \mathrm{MHz}, \mathrm{CD}_{2} \mathrm{Cl}_{2}, \delta$ ): $7.97(\mathrm{~s}, 1 \mathrm{H}), 7.71(\mathrm{~d}, J=7.5 \mathrm{~Hz}, 1 \mathrm{H}), 7.07(\mathrm{~d}, J=7.5 \mathrm{~Hz}, 1 \mathrm{H})$, $6.90-6.88(\mathrm{~m}, 1 \mathrm{H}), 6.10(\mathrm{br} \mathrm{s}, 1 \mathrm{H}), 5.32(\mathrm{br} \mathrm{s}, 1 \mathrm{H}), 2.56-2.20(\mathrm{br}, 16 \mathrm{H}) .{ }^{13} \mathrm{C}$ NMR spectra were not obtained due to low solubility. Anal: calcd for $\mathrm{C}_{13} \mathrm{H}_{22} \mathrm{BrN}_{3} \mathrm{NiO}: \mathrm{C}, 41.64 ; \mathrm{H}, 5.91 ; \mathrm{N}, 11.21$; found: C, 41.36; $\mathrm{H}, 5.78$; $\mathrm{N}, 10.95$.

## Synthesis of nickel aryl complex $\mathbf{1 j}$



To (2-(2-pyridinyl)phenyl-2-nitrobenzenesulfonamide)silver(I) (8) ( $247 \mathrm{mg}, 0.533 \mathrm{mmol}, 1.00$ equiv) and nickel aryl bromide complex $7 \mathbf{j}$ ( $200 \mathrm{mg}, 0.533 \mathrm{mmol}, 1.00$ equiv) in a 20 mL vial was added a toluene solution ( 4 mL ) that contained pyridine $(84.0 \mathrm{mg}, 86.0 \mu \mathrm{~L}, 1.07 \mathrm{mmol}, 2.00$ equiv) at $23{ }^{\circ} \mathrm{C}$, followed by addition of acetonitrile ( 1.0 mL ). After stirring for 1 min at 23 , the solution was filtered through a glass frit, and the filtered cake was extracted further with dichloromethane $(3 \times 5 \mathrm{~mL})$. 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 $\mathrm{CH}_{2} \mathrm{Cl}_{2}(2 \mathrm{~mL})$ and layering with pentane ( 20 mL ) to afford 154 mg of the title compound as a yellow solid (47\%).
$\mathrm{R}_{f}=0.26$ (EtOAc). NMR Spectroscopy: ${ }^{1} \mathrm{H}$ NMR ( $\left.500 \mathrm{MHz}, \mathrm{CD}_{2} \mathrm{Cl}_{2}, 23{ }^{\circ} \mathrm{C}, \delta\right): 9.13$ (d, $J=4.9$ $\mathrm{Hz}, 2 \mathrm{H}), 8.15(\mathrm{~d}, J=5.4 \mathrm{~Hz}, 1 \mathrm{H}), 7.86(\mathrm{~s}, 1 \mathrm{H}), 7.78(\mathrm{~d}, J=7.2 \mathrm{~Hz}, 1 \mathrm{H}), 7.63-7.56(\mathrm{~m}, 3 \mathrm{H})$, $7.42-7.32(\mathrm{~m}, 3 \mathrm{H}), 7.23-7.17(\mathrm{~m}, 4 \mathrm{H}), 7.08-7.02(\mathrm{~m}, 4 \mathrm{H}), 6.87-6.84(\mathrm{~m}, 1 \mathrm{H}), 6.64-6.61(\mathrm{~m}, 1 \mathrm{H})$, $5.94(\mathrm{br} \mathrm{s}, 1 \mathrm{H}), 5.32(\mathrm{br} \mathrm{s}, 1 \mathrm{H}) .{ }^{13} \mathrm{C}$ NMR ( $125 \mathrm{MHz} \mathrm{CD}{ }_{2} \mathrm{Cl}_{2}, 23^{\circ} \mathrm{C}, \delta$ ): 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 $\mathrm{C}_{29} \mathrm{H}_{23} \mathrm{~N}_{5} \mathrm{NiO}_{5} \mathrm{~S}\left(\mathrm{CH}_{2} \mathrm{Cl}_{2}\right)_{0.25}: \mathrm{C}$, 55.46; H, 3.74; N, 11.05; found: C, 55.22; H, 3.82; N, 11.28.

## 4-bromobenzoic acid succinimidyl ester (S12)



To 4-bromobenzoic acid ( $5.00 \mathrm{~g}, 24.9 \mathrm{mmol}, 1.00$ equiv) and $N$-hydroxysuccinimide ( $3.66 \mathrm{~g}, 31.8$ 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) ( $6.77 \mathrm{~g}, 32.8 \mathrm{mmol}, 1.32$ equiv) dropwise over 5 min at $23^{\circ} \mathrm{C}$. The reaction mixture was stirring at $23^{\circ} \mathrm{C}$ 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 ( $86 \%$ ).
$\mathrm{R}_{f}=0.25$ (hexanes/EtOAc 2:1 (v/v)). NMR Spectroscopy: ${ }^{1} \mathrm{H}$ NMR ( $500 \mathrm{MHz}, \mathrm{CDCl}_{3}, 23^{\circ} \mathrm{C}, \delta$ ): $7.99(\mathrm{~d}, J=8.7 \mathrm{~Hz}, 2 \mathrm{H}), 7.67(\mathrm{~d}, J=8.7 \mathrm{~Hz}, 1 \mathrm{H}), 2.90(\mathrm{~s}, 4 \mathrm{H}) .{ }^{13} \mathrm{C}$ NMR ( $125 \mathrm{MHz}, \mathrm{CDCl}_{3}, 23$ $\left.{ }^{\circ} \mathrm{C}, \delta\right): 169.2,161.5,132.5,132.1,130.6,124.2,25.8$. These spectroscopic data correspond to the reported data. ${ }^{13}$

## Synthesis of nickel aryl bromide complex 7k



To a solution of TMEDA ( $83.0 \mathrm{mg}, 0.107 \mathrm{~mL}, 0.717 \mathrm{mmol}, 1.00$ equiv) and 4-bromobenzoic acid succinimidyl ester (S12) ( $214 \mathrm{mg}, 0.717 \mathrm{mmol}, 1.00$ equiv) in toluene ( 4 mL ) was added $\mathrm{Ni}(\mathrm{COD})_{2}(200 \mathrm{mg}, 0.717 \mathrm{mmol}, 1.00$ 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 ( $3 \times 5 \mathrm{~mL}$ ) and dried in vacuo to afford 300 mg of the title compound as an orange solid ( $89 \%$ ).
${ }^{1} \mathrm{H}$ NMR ( $500 \mathrm{MHz}, \mathrm{CD}_{2} \mathrm{Cl}_{2}, \delta$ ): $7.86(\mathrm{~d}, J=8.2 \mathrm{~Hz}, 2 \mathrm{H}), 7.49(\mathrm{~d}, J=6.9 \mathrm{~Hz}, 2 \mathrm{H}), 2.83$ (br s, 4H), 2.57-2.22 (br, 16H). ${ }^{13} \mathrm{C}$ NMR ( $125 \mathrm{MHz}, \mathrm{CD}_{2} \mathrm{Cl}_{2}, \delta$ ): 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 $\mathrm{C}_{17} \mathrm{H}_{24} \mathrm{BrN}_{3} \mathrm{NiO}_{4}$ : C, 43.17; H, 5.11; N, 8.88; found: C, 43.65; H, 4.54; N, 7.48.

## Synthesis of nickel aryl complex 1 k



7k
 $51 \%$


1k

To (2-(2-pyridinyl)phenyl-2-nitrobenzenesulfonamide)silver(I) (8) (195 mg, $0.423 \mathrm{mmol}, 1.00$ equiv) and nickel aryl bromide complex $7 \mathbf{k}$ ( $200 \mathrm{mg}, 0.423 \mathrm{mmol}, 1.00$ equiv) in a 20 mL vial was added a toluene solution ( 4 mL ) that contained pyridine ( $66.9 \mathrm{mg}, 68.1 \mu \mathrm{~L}, 0.833 \mathrm{mmol}, 2.00$ equiv) at $23^{\circ} \mathrm{C}$, followed by addition of acetonitrile ( 1.0 mL ). After stirring for 1 min at 23 , the solution was filtered through a glass frit, and the filtered cake was extracted further with dichloromethane ( $3 \times 5 \mathrm{~mL}$ ). 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 ( $51 \%$ ).
$\mathrm{R}_{f}=0.47$ (hexanes/EtOAc 1:6 (v/v)). NMR Spectroscopy: ${ }^{1} \mathrm{H}$ NMR ( $500 \mathrm{MHz}, \mathrm{CDCl}_{3}, 23^{\circ} \mathrm{C}, \delta$ ): 9.10 (d, $J=5.2 \mathrm{~Hz}, 2 \mathrm{H}), 8.05$ (d, $J=5.6 \mathrm{~Hz}, 1 \mathrm{H}), 7.7(\mathrm{~d}, J=7.9 \mathrm{~Hz}, 2 \mathrm{H}), 7.58-7.54$ (m, 3H), $7.47-7.32(\mathrm{~m}, 5 \mathrm{H}), 7.19-7.11(\mathrm{~m}, 4 \mathrm{H}), 7.05-6.97(\mathrm{~m}, 3 \mathrm{H}), 6.63-6.61(\mathrm{~m}, 1 \mathrm{H}), 2.81(\mathrm{~s}, 4 \mathrm{H}) .{ }^{13} \mathrm{C}$ NMR ( $125 \mathrm{MHz} \mathrm{CDCl}_{3}, 23^{\circ} \mathrm{C}$, $\delta$ ): 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 $\mathrm{C}_{33} \mathrm{H}_{25} \mathrm{~N}_{5} \mathrm{NiO}_{8} \mathrm{~S}$ : C, 55.80 ; H, 3.55; N, 9.86; found: C, 55.53; H, 3.50; N, 9.61.

## Synthesis of nickel alkenyl bromide complex 71



71

To a solution of TMEDA ( $83.0 \mathrm{mg}, 0.107 \mathrm{~mL}, 0.717 \mathrm{mmol}, 1.00$ equiv) and bromotriphenylethylene ( $240 \mathrm{mg}, 0.717 \mathrm{mmol}, 1.00$ equiv) in toluene ( 4 mL ) was added $\mathrm{Ni}(\mathrm{COD})_{2}(200 \mathrm{mg}, 0.717 \mathrm{mmol}, 1.00$ equiv), and the mixture was stirred at room temperature for 40 min . Pentane ( 16 mL ) was added to the mixtures and the resulting solid was collected on a frit. The solid was washed with pentane ( $3 \times 5 \mathrm{~mL}$ ) and dried in vacuo to afford 305 mg of the title compound as a pink solid ( $86 \%$ ). ${ }^{1} \mathrm{H}$ NMR ( $\left.500 \mathrm{MHz}, \mathrm{C}_{6} \mathrm{D}_{6}, \delta\right): 9.41(\mathrm{~d}, J=7.2 \mathrm{~Hz}, 2 \mathrm{H}), 8.20(\mathrm{~d}$, $J=7.2 \mathrm{~Hz}, 2 \mathrm{H}), 7.51-7.48(\mathrm{~m}, 2 \mathrm{H}), 7.32-7.29(\mathrm{~m}, 1 \mathrm{H}), 7.01-6.98(\mathrm{~m}, 2 \mathrm{H}), 6.91-6.88(\mathrm{~m}, 1 \mathrm{H})$, 1.89 (br, 16H). ${ }^{13} \mathrm{C}$ NMR ( $125 \mathrm{MHz}, \mathrm{C}_{6} \mathrm{D}_{6}, \delta$ ): 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 11 in the next step. HRMS-FIA ( $\mathrm{m} / \mathrm{z}$ ): calcd for $\mathrm{C}_{26} \mathrm{H}_{31} \mathrm{~N}_{2} \mathrm{Ni}[\mathrm{M}-\mathrm{Br}]^{+}$, 429.1841; found, 429.1845.

## Synthesis of nickel alkenyl complex 11



To (2-(2-pyridinyl)phenyl-2-nitrobenzenesulfonamide)silver(I) (8) ( $93.0 \mathrm{mg}, 0.417 \mathrm{mmol}, 1.00$ equiv) and nickel alkenyl bromide complex $7 \mathbf{7 l}(0.100 \mathrm{mg}, 0.417 \mathrm{mmol}, 1.00$ equiv) in a 20 mL vial was added a toluene solution ( 3 mL ) that contained pyridine ( $32.0 \mathrm{mg}, 32.5 \mu \mathrm{~L}, 0.833 \mathrm{mmol}$, 2.00 equiv) at $23^{\circ} \mathrm{C}$, followed by addition of acetonitrile ( 0.5 mL ). After stirring for 1 min at 23 , the solution was filtered through a glass frit, and the filtered cake was extracted further with
dichloromethane $(3 \times 5 \mathrm{~mL})$. 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 $\mathrm{CH}_{2} \mathrm{Cl}_{2}(2 \mathrm{~mL})$ and layering with pentane ( 20 mL ) to afford 78.0 mg of the title compound as a yellow solid ( $52 \%$ ).
$\mathrm{R}_{f}=0.66$ (hexanes/EtOAc 1:2 (v/v)). NMR Spectroscopy: ${ }^{1} \mathrm{H}$ NMR ( $500 \mathrm{MHz}, \mathrm{CDCl}_{3}, 23^{\circ} \mathrm{C}, \delta$ ): $9.85(\mathrm{~d}, J=7.5 \mathrm{~Hz}, 1 \mathrm{H}), 8.77-8.60(\mathrm{~m}, 3 \mathrm{H}), 7.80(\mathrm{~d}, J=7.3 \mathrm{~Hz}, 1 \mathrm{H}), 7.74-7.70(\mathrm{~m}, 1 \mathrm{H}), 7.49-$ $7.30(\mathrm{~m}, 6 \mathrm{H}), 7.24-6.82(\mathrm{~m}, 15 \mathrm{H}), 6.69-6.59(\mathrm{~m}, 4 \mathrm{H}), 6.40(\mathrm{~d}, J=7.1 \mathrm{~Hz}, 1 \mathrm{H}), .{ }^{13} \mathrm{C}$ NMR ( 125 $\left.\mathrm{MHz}, \mathrm{CDCl}_{3}, 23^{\circ} \mathrm{C}, \delta\right): 160.7,156.7,156.5,154.6,152.3,152.0,151.9,151.6,148.0,147.9$, $147.3,146.9,145.2,143.7,143.2,142.4,141.8,141.0,137.4,136.8,136.5,136.2,135.9,135.8$, 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 ${ }^{13} \mathrm{C}$ peaks than could be expected, possibly due to slow rotation about bonds as seen for similar complexes. ${ }^{9}$ Anal: calcd for $\mathrm{C}_{42} \mathrm{H}_{32} \mathrm{~N}_{4} \mathrm{NiO}_{4} \mathrm{~S}\left(\mathrm{CH}_{2} \mathrm{Cl}_{2}\right)_{0.15}$ : C, $66.59 ; \mathrm{H}, 4.28$; $\mathrm{N}, 7.37$; found: $\mathrm{C}, 66.71$; $\mathrm{H}, 4.24$; $\mathrm{N}, 7.51$. HRMS-FIA ( $\mathrm{m} / \mathrm{z}$ ): calcd for $\mathrm{C}_{37} \mathrm{H}_{27} \mathrm{~N}_{3} \mathrm{NaNiO}_{4} \mathrm{~S}[\mathrm{M}-\text { pyridine }+\mathrm{H}]^{+}, 668.1149$; 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. $\mathbf{2 b}$ and $\mathbf{2 j}$ were purchased from Matrix Scientific and Aldrich, respectively. $\mathbf{2 c},{ }^{14} \mathbf{2 d},{ }^{15} \mathbf{2 g},{ }^{9} \mathbf{2 h},{ }^{9} \mathbf{2 i},{ }^{15}$ and $\mathbf{2 k}{ }^{16}$ were synthesized based on reported procedures. 2e, 2f, and $\mathbf{2 l}$ were synthesized by electrophilic fluorination of $\mathbf{1 e}, \mathbf{1 f}$, and $\mathbf{1 1}$ with Selectfluor®.

## 4-Flurobiphenyl (2a)



In a glove box under a $\mathrm{N}_{2}$ atmosphere, nickel aryl complex $\mathbf{1 a}(40 \mathrm{mg}, 0.062 \mathrm{mmol}, 1.0$ equiv), tetrabutylammonium difluorotriphenylsilicate (TBAT) ( $50 \mathrm{mg}, 0.093 \mathrm{mmol}, 1.5$ equiv), and oxidant 6 ( $69 \mathrm{mg}, 0.093 \mathrm{mmol}, 1.5$ equiv) were placed in a 20 mL vial. The vial was taken out of the glove box, and immersed in an ice bath at $0^{\circ} \mathrm{C}$ for 5 minutes. To the reaction mixture was added quickly pre-cooled acetonitrile $(4 \mathrm{~mL})$ at $0^{\circ} \mathrm{C}$ in one portion and the solution was stirred for 1 min at $0^{\circ} \mathrm{C}$. After warming to $23^{\circ} \mathrm{C}$, the solution was concentrated in vacuo and the residue was purified by chromatography on silica gel eluting with hexane/EtOAc 99:1 (v/v) to afford 6.9 mg of the title compound as a white solid ( $65 \%$ yield).
$\mathrm{R}_{f}=0.60$ (hexanes/EtOAc 19:1 (v/v)). ${ }^{1} \mathrm{H}-\mathrm{NMR}\left(500 \mathrm{MHz}, \mathrm{CDCl}_{3}, 23^{\circ} \mathrm{C}, \delta\right): \delta 7.56-7.54(\mathrm{~m}$, 4H), 7.45-7.42 (m, 2H), 7.36-7.33 (m, 1H), 7.15-7.11 (m, 2H). ${ }^{13} \mathrm{C}-\mathrm{NMR}\left(125 \mathrm{MHz}, \mathrm{CDCl}_{3}, 23\right.$ $\left.{ }^{\circ} \mathrm{C}, \delta\right): 162.7$ (d, $J=244 \mathrm{~Hz}$ ), 140.5, 137.6, 129.0, 128.9 (d, $J=8.5 \mathrm{~Hz}$ ), 127.5, 127.3, 115.8 (d, $J$ $=21 \mathrm{~Hz}) ;{ }^{19} \mathrm{~F}$-NMR ( $375 \mathrm{MHz}, \mathrm{CDCl}_{3}, 23{ }^{\circ} \mathrm{C}$ ): $\delta-116.2$. These spectroscopic data correspond to previously reported data. ${ }^{12}$

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



Nickel aryl complex 1e ( $50 \mathrm{mg}, 0.077 \mathrm{mmol}, 1.0$ equiv) and 1-chloromethyl-4-fluoro-1,4diazoniabicyclo[2.2.2]octane bis(tetrafluoroborate) (Selectfluor ${ }^{\circledR}$ ) ( $33 \mathrm{mg}, 0.092 \mathrm{mmol}, 1.5$ equiv) were placed in a 20 mL vial. To the reaction mixture was added acetonitrile ( 4 mL ) at 23 ${ }^{\circ} \mathrm{C}$ in one portion and the solution was stirred for 1 min at $23^{\circ} \mathrm{C}$. The solution was concentrated in vacuo and the residue is purified by chromatography on silica gel eluting with pentane to afford 8.1 mg of the title compound and cyclohexylbenzene as a $1: 2$ mixture (a colorless oil, $22 \%$ yield based on 1-cyclohexyl-2-fluorobenzene). Due to the difficulty of purification of the title compound and its volatility, ${ }^{17}$ the above mixture was used without further purification for identifying [ $\left.{ }^{18} \mathrm{~F}\right] 2 \mathrm{e}$ by HPLC analysis.
$\mathrm{R}_{f}=0.67$ (pentane). NMR Spectroscopy: Selected ${ }^{1} \mathrm{H}$ NMR ( $400 \mathrm{MHz}, \mathrm{CDCl}_{3}, 23{ }^{\circ} \mathrm{C}, \delta$ ): 7.07$7.03(\mathrm{~m}, 1 \mathrm{H}), 2.94-2.89(\mathrm{~m}, 1 \mathrm{H}) .{ }^{19} \mathrm{~F}$ NMR ( $\left.375 \mathrm{MHz}, \mathrm{CD}_{3} \mathrm{CN}, 23{ }^{\circ} \mathrm{C}, \delta\right):-120.0$. These spectroscopic data correspond to previously reported data. ${ }^{17}$

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



1f


55\%

$2 f$

Nickel aryl complex $1 f\left(30 \mathrm{mg}, 0.042 \mathrm{mmol}, 1.0\right.$ equiv) and Selectfluor ${ }^{\circledR}$ ( $18 \mathrm{mg}, 0.050 \mathrm{mmol}$, 1.2 equiv) were placed in a 20 mL vial. To the reaction mixture was added quickly acetonitrile ( 3 mL ) at $23^{\circ} \mathrm{C}$ in one portion and the solution was stirred for 1 min at $23^{\circ} \mathrm{C}$. The solution was subsequently concentrated in vacuo and the residue is purified by chromatography on silica gel eluting with hexane/EtOAc $4: 1(\mathrm{v} / \mathrm{v})$ to afford 5.6 mg of the title compound as a colorless solid
(55\% yield).
$\mathrm{R}_{f}=0.47$ (hexanes/EtOAc 4:1 (v/v)). NMR Spectroscopy: ${ }^{1} \mathrm{H}$ NMR ( $500 \mathrm{MHz}, \mathrm{CDCl}_{3}, 23^{\circ} \mathrm{C}, \delta$ ): 7.00 (d, $J=7.5 \mathrm{~Hz}, 2 \mathrm{H}), 7.57-7.54(\mathrm{~m}, 1 \mathrm{H}), 7.45-7.42(\mathrm{~m}, 2 \mathrm{H}), 7.26-7.23$ (m, 2H), 7.02-6.99 (m, $2 \mathrm{H}), 5.51(\mathrm{t}, J=6.5 \mathrm{~Hz}, 2 \mathrm{H}), 3.06(\mathrm{t}, J=6.5 \mathrm{~Hz}, 2 \mathrm{H}) .{ }^{13} \mathrm{C}$ NMR ( $\left.125 \mathrm{MHz}, \mathrm{CDCl}_{3}, 23{ }^{\circ} \mathrm{C}, \delta\right)$ : $166.6,161.9(\mathrm{~d}, J=243 \mathrm{~Hz}), 133.7(\mathrm{~d}, J=2.9 \mathrm{~Hz}), 133.1(\mathrm{~s}), 130.5(\mathrm{~s}), 130.4(\mathrm{~d}, J=27 \mathrm{~Hz})$, 129.7, 128.5, $115.5(\mathrm{~d}, J=22 \mathrm{~Hz}), 65.5,34.6 .{ }^{19} \mathrm{~F}$ NMR ( $375 \mathrm{MHz}, \mathrm{CDCl}_{3}, 23{ }^{\circ} \mathrm{C}, \delta$ ): -116.8 . HRMS-FIA (m/z): calcd for $\mathrm{C}_{15} \mathrm{H}_{13} \mathrm{FO}_{2}[\mathrm{M}+\mathrm{H}]^{+}, 245.0972$; found, 245.0982.

## $N$-(tert-butoxycarbonyl)-3,4-di(tert-butoxycarbonyloxy)-6-trimethylstannyl-Lphenylalaninemethyl ester (S13)



S11
S13

To $\quad N$-(tert-butoxycarbonyl)-3,4-di(tert-butoxycarbonyloxy)-6-bromo-L-phenylalaninemethyl ester (S11) ( $1.00 \mathrm{~g}, 1.69 \mathrm{mmol}, 1.00$ equiv) in dioxane $(20 \mathrm{~mL})$ at $23^{\circ} \mathrm{C}$ was added lithium chloride ( $0.359 \mathrm{~g}, 8.47 \mathrm{mmol}, 5.0$ equiv), tetrakis(triphenylphosphine)palladium ( $0.391 \mathrm{~g}, 0.339$ $\mathrm{mmol}, 20.0 \mathrm{~mol} \%$ ) and bis(trimethyltin) ( $1.11 \mathrm{~g}, 3.39 \mathrm{mmol}, 2.00$ equiv). After stirring for 5 hr at $100{ }^{\circ} \mathrm{C}$, the reaction mixture was cooled to $23^{\circ} \mathrm{C}$ and concentrated in vacuo. The residue was purified by chromatography on silica gel, eluting with hexanes/EtOAc 5:1 (v/v), to afford 420 mg of the title compound as a colorless oil ( $37 \%$ yield).
$\mathrm{R}_{f}=0.55$ (hexane/EtOAc 3:1 (v/v)). NMR Spectroscopy: ${ }^{1} \mathrm{H}$ NMR ( $500 \mathrm{MHz}, \mathrm{CDCl}_{3}, 23^{\circ} \mathrm{C}, \delta$ ): $7.26(\mathrm{br} \mathrm{s}, 1 \mathrm{H}), 7.08(\mathrm{br} \mathrm{s}, 1 \mathrm{H}), 4.89(\mathrm{~d}, J=7.6 \mathrm{~Hz}, 1 \mathrm{H}), 4.53-4.48(\mathrm{~m}, 1 \mathrm{H}), 3.70(\mathrm{~s}, 3 \mathrm{H}), 3.10-$ $3.00(\mathrm{~m}, 2 \mathrm{H}), 1.54(\mathrm{~s}, 9 \mathrm{H}), 1.53(\mathrm{~s}, 9 \mathrm{H}), 1.39(\mathrm{~s}, 9 \mathrm{H}), 0.35(\mathrm{~s}, 9 \mathrm{H}) .{ }^{13} \mathrm{C}$ NMR ( $125 \mathrm{MHz}, \mathrm{CDCl}_{3}$, $\left.23{ }^{\circ} \mathrm{C}, \delta\right): 172.7,155.2,150.9,150.8,142.7,141.7,141.5,141.0,130.4,123.4,110.8,83.8,80.2$, 54.5, 52.5, 40.4, 28.3, 27.7, 27.7, -7.7. HRMS-FIA (m/z): calcd for $\mathrm{C}_{28} \mathrm{H}_{45} \mathrm{NO}_{10} \mathrm{Sn}[\mathrm{M}+\mathrm{H}]^{+}$, 676.2144; found, 676.2171.

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



To $N$-Boc- $O$-Boc-6-trimethylstannyl-DOPA methyl ester (S13) (142 $\mathrm{mg}, 0.211 \mathrm{mmol}, 1.00$ equiv)
in acetone ( 4 mL ) at $23^{\circ} \mathrm{C}$ was added silver oxide ( $2.45 \mathrm{mg}, 0.0106 \mathrm{mmol}, 5.0 \mathrm{~mol} \%$ ), sodium bicarbonate ( $35.5 \mathrm{mg}, 0.422 \mathrm{mmol}, 2.0$ equiv), sodium trifluoromethanesulfonate ( $36.3 \mathrm{mg}, 0.211$ $\mathrm{mmol}, 1.0$ equiv) and Selectfluor® ( $112 \mathrm{mg}, 0.317 \mathrm{mmol}, 1.50$ equiv). The reaction mixture was stirred for 5 hr at $65^{\circ} \mathrm{C}$ in a sealed vial. After cooling to $23^{\circ} \mathrm{C}$, the reaction mixture was filtered through a pad of celite, eluting with $\mathrm{CH}_{2} \mathrm{Cl}_{2}$ and the filtrate was concentrated in vacuo. The residue was purified by chromatography on silica gel, eluting with hexane/EtOAc $4: 1(\mathrm{v} / \mathrm{v})$, to afford 45.0 mg of the title compound as a colorless solid ( $40 \%$ yield).
$\mathrm{R}_{f}=0.37$ (hexane/EtOAc 3:1 (v/v)). NMR Spectroscopy: ${ }^{1} \mathrm{H}$ NMR ( $500 \mathrm{MHz}, \mathrm{CDCl}_{3}, 23^{\circ} \mathrm{C}, \delta$ ): $7.05(\mathrm{~d}, J=6.9 \mathrm{~Hz}, 1 \mathrm{H}), 7.02(\mathrm{~d}, J=9.6 \mathrm{~Hz}, 1 \mathrm{H}), 5.07(\mathrm{~d}, J=7.7 \mathrm{~Hz}, 1 \mathrm{H}), 4.57-4.53(\mathrm{~m}, 1 \mathrm{H})$, $3.71(\mathrm{~s}, 3 \mathrm{H}), 3.18-3.04(\mathrm{~m}, 2 \mathrm{H}), 1.54(\mathrm{~s}, 9 \mathrm{H}), 1.53(\mathrm{~s}, 9 \mathrm{H}), 1.41(\mathrm{~s}, 9 \mathrm{H}) .{ }^{13} \mathrm{C}$ NMR ( 125 MHz , $\left.\mathrm{CDCl}_{3}, 23^{\circ} \mathrm{C}, \delta\right): 172.0,158.2(\mathrm{~d}, J=246 \mathrm{~Hz}), 155.1,150.8,150.4,142.1(\mathrm{~d}, J=12 \mathrm{~Hz}), 138.6$, $125.4(\mathrm{~d}, J=5.6 \mathrm{~Hz}), 121.5(\mathrm{~d}, J=18 \mathrm{~Hz}), 110.8(\mathrm{~d}, J=28 \mathrm{~Hz}), 84.4,84.1,80.2,53.5,52.6,31.7$, 28.4, 27.7, 27.7. ${ }^{19} \mathrm{~F}$ NMR ( $375 \mathrm{MHz}, \mathrm{CDCl}_{3}, 23{ }^{\circ} \mathrm{C}, \delta$ ): -117.6 . Mass HRMS-FIA ( $\mathrm{m} / \mathrm{z}$ ): calcd for $\mathrm{C}_{25} \mathrm{H}_{36} \mathrm{FNO}_{10}[\mathrm{M}+\mathrm{Na}]^{+}$, 552.2215; found, 552.2214.

## I-Fluoro-1,2,2-triphenylethylene (21)



Nickel aryl complex 11 ( $30 \mathrm{mg}, 0.040 \mathrm{mmol}, 1.0$ equiv) and Selectfluor® ( $17 \mathrm{mg}, 0.048 \mathrm{mmol}$, 1.2 equiv) were placed in a 20 mL vial. To the reaction mixture was added quickly acetonitrile ( 3 mL ) at $23^{\circ} \mathrm{C}$ in one portion and the solution was stirred for 1 min at $23^{\circ} \mathrm{C}$. The solution was subsequently concentrated in vacuo and the residue is purified by chromatography on silica gel eluting with $\mathrm{Et}_{2} \mathrm{O} / \mathrm{CH}_{2} \mathrm{Cl}_{2} 2: 1(\mathrm{v} / \mathrm{v})$ to afford 4.0 mg of the title compound as a colorless solid (36\% yield).
$\mathrm{R}_{f}=0.88\left(\mathrm{Et}_{2} \mathrm{O} / \mathrm{CH}_{2} \mathrm{Cl}_{2} 2: 1(\mathrm{v} / \mathrm{v})\right)$. NMR Spectroscopy: ${ }^{1} \mathrm{H}$ NMR ( $\left.500 \mathrm{MHz}, \mathrm{CDCl}_{3}, 23{ }^{\circ} \mathrm{C}, \delta\right)$ : 7.39-6.95 (m, 15H). ${ }^{13} \mathrm{C}$ NMR ( $125 \mathrm{MHz}, \mathrm{CDCl}_{3}, 23^{\circ} \mathrm{C}, \delta$ ): $130.8(\mathrm{~d}, J=2.8 \mathrm{~Hz}), 130.1(\mathrm{~d}, J=$ $3.4 \mathrm{~Hz}), 130.8(\mathrm{~d}, J=2.8 \mathrm{~Hz}), 129.2(\mathrm{~d}, J=4.6 \mathrm{~Hz}), 128.7$, 128.3, 128.2, 128.1, 128.1, 128.0, 127.7, 127.6, 127.5, 127.1. ${ }^{19} \mathrm{~F}$ NMR ( $375 \mathrm{MHz}, \mathrm{CDCl}_{3}, 23{ }^{\circ} \mathrm{C}, \delta$ ): -101.2. These spectroscopic data correspond to previously reported data. ${ }^{18}$

## Radiochemistry

## General methods

No-carrier-added $\left[{ }^{18} \mathrm{~F}\right] f l u o r i d e$ was produced from water $97 \%$ enriched in ${ }^{18} \mathrm{O}$ (ISOFLEX, USA) by the nuclear reaction ${ }^{18} \mathrm{O}(\mathrm{p}, \mathrm{n})^{18} \mathrm{~F}$ using a Siemens Eclipse HP cyclotron and a silver-bodied target at Massachusetts General Hospital Athinoula A. Martinos Center for Biomedical Imaging. The produced $\left[{ }^{18} \mathrm{~F}\right]$ fluoride in water was transferred from the cyclotron target by helium push. An Agilent Eclipse XDB-C18, $5 \mu \mathrm{~m}, 4.6 \times 150 \mathrm{~mm}$ HPLC column was used for analysis. Analytical HPLC used the following mobile phases: $0.1 \% \mathrm{CF}_{3} \mathrm{CO}_{2} \mathrm{H}$ in water (A) $0.1 \% \mathrm{CF}_{3} \mathrm{CO}_{2} \mathrm{H}$ in acetonitrile (B). Program: 5\% (B) and $95 \%$ (A) for 10 minutes. In the HPLC analysis of the ${ }^{18} \mathrm{~F}$ labeled compounds, isotopically unmodified ( ${ }^{19} \mathrm{~F}$-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 $\mathrm{P}_{2} \mathrm{O}_{5}$. 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 $\left[{ }^{18} \mathrm{~F}\right] f l u o r i d e$ solution $(20-50 \mu \mathrm{~L}, 2-5 \mathrm{mCi})$ obtained from a cyclotron was added to an acetonitrile solution ( $2.0-5.0 \mathrm{~mL}$ ) of 20 mg of $18-\mathrm{cr}-6$. The resulting solution (200$500 \mu \mathrm{l}$ ) was added quickly to a septum-capped vial containing 1.0 mg nickel complex $\mathbf{1}$ and 1.0 equiv of $\mathbf{6}$ (relative to $\mathbf{1}$ ). 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 [ $\left.{ }^{18} \mathrm{~F}\right] f l u o r i d e$ relative to nickel complex ${ }^{19}$

Method to calculate the number of $\left.{ }^{18} \mathrm{~F}\right] f l u o r i d e ~ a t o m s ~ t h a t ~ e x h i b i t ~ r a d i o a c t i v i t y ~ o f ~ 1.0 ~ C i: ~$
N (atoms) $\times \lambda\left(\mathrm{s}^{-1}\right)=1.0 \mathrm{Ci}=3.7 \times 10^{10}(\mathrm{~Bq})$
$\mathrm{N}=3.7 \times 10^{10} / \lambda\left(\lambda\right.$ is the decay constant in $\left.\left(\mathrm{s}^{-1}\right): \lambda\left({ }^{[18} \mathrm{F}\right] f l u o r i d e\right)$ is $\left.1.5 \times 10^{-4} \mathrm{~s}^{-1}\right)$
Typical radioactivity for a reaction: 0.5 mCi

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

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

Mole of $\left[{ }^{18} \mathrm{~F}\right] f l u o r i d e: ~ 1.3 \times 10^{11} / 6.02 \times 10^{23}=0.21 \mathrm{pmol}$
Reaction conditions: For the aqueous solutions of [ $\left.{ }^{18} \mathrm{~F}\right]$ fluoride $(2-5 \mu \mathrm{l}, 100-500 \mu \mathrm{Ci}$; $500 \mu \mathrm{Ci}$ in $5 \mu \mathrm{l}$ water corresponds to a concentration of 42 nM in $\left.\left[{ }^{18} \mathrm{~F}\right]\right)$.

## 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 ${ }^{18} \mathrm{~F}$ 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 (\%) | ${ }^{18} \mathrm{~F}$ in solution (\%) | RCY (\%) | Average RCY (\%) |
| :---: | :---: | :---: | :---: | :---: | :---: |
| 1 | $\left[{ }^{18} \mathrm{~F}\right] 2 \mathrm{a}$ | 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 | $\left[{ }^{18} \mathrm{~F}\right] 2 \mathrm{~b}$ | 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 | $\left[{ }^{18} \mathrm{~F}\right] 2 \mathrm{c}$ | 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 | $\left[{ }^{18} \mathrm{~F}\right] 2 \mathrm{~d}$ | 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 | $\left[{ }^{18} \mathrm{~F}\right] 2 \mathrm{e}$ | 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 | $\left[{ }^{18} \mathrm{~F}\right] 2 \mathrm{f}$ | 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 | $\left[{ }^{18} \mathrm{~F}\right] 2 \mathrm{~g}$ | 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 | $\left[{ }^{18} \mathrm{~F}\right] 2 \mathrm{~h}$ | 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 | $\left[{ }^{18} \mathrm{~F}\right] 2 \mathrm{i}$ | 41 | 68 | 28 | 15 |
| :---: | :---: | :---: | :---: | :---: | :---: |
| 52 |  | 14 | 76 | 11 |  |
| 53 |  | 17 | 59 | 10 |  |
| 54 |  | 13 | 64 | 8 |  |
| 55 | $\left[{ }^{18} \mathrm{~F}\right] 2 \mathrm{j}$ | 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 | $\left[{ }^{18} \mathrm{~F}\right] 2 \mathrm{k}$ | 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 | $\left[{ }^{18} \mathrm{~F}\right] 21$ | 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 60 mm on the horizontal axis of the following radio TLC scans).

## Figure S3. Example Radio TLC Scan of $\left[{ }^{18}\right.$ F $] \mathbf{2 a}$



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

## Figure S4. Example Radio TLC Scan of $\left[{ }^{18} \mathrm{~F}\right] 2 \mathrm{~b}$



Entry 7 of Table S1. Percent of total integration listed for $\left[{ }^{[8} \mathbf{F}\right] \mathbf{2 b}$

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


Entry 14 of Table S1. Percent of total integration listed for $\left[{ }^{18} \mathbf{F}\right] \mathbf{2 c}$
Figure S6. Example Radio TLC Scan of $\left[{ }^{18}\right.$ F] 2 d


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

## Figure S7. Example Radio TLC Scan of $\left[{ }^{18} \mathrm{~F}\right] 2 \mathrm{e}$



Entry 25 of Table S1. Percent of total integration listed for $\left[{ }^{18} \mathbf{F}\right] 2 \mathbf{e}$
Figure S8. Example Radio TLC Scan of $\left[{ }^{18} \mathrm{~F}\right] 2 f$


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

Figure S9. Example Radio TLC Scan of $\left[{ }^{18}\right.$ F $] 2 \mathrm{~g}$


Entry 39 of Table S1. Percent of total integration listed for $\left[{ }^{18} \mathbf{F}\right] \mathbf{2 g}$
Figure S10. Example Radio TLC Scan of [ ${ }^{18}$ F] 2 h


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

## Figure S11. Example Radio TLC Scan of $\left[{ }^{18} \mathrm{~F}\right] 2 \mathrm{i}$



Entry 53 of Table S1. Percent of total integration listed for $\left[{ }^{18} \mathbf{F}\right] 2 \mathbf{i}$
Figure S12. Example Radio TLC Scan of $\left[{ }^{[18} \mathrm{F}\right] 2 \mathrm{j}$


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

Figure S13. Example Radio TLC Scan of [ ${ }^{18}$ F] ${ }^{1} \mathrm{k}$


Entry 63 of Table S1. Percent of total integration listed for $\left[{ }^{18} \mathbf{F}\right] \mathbf{2 k}$
Figure S14. Example Radio TLC Scan of $\left[{ }^{18} \mathrm{~F}\right] 21$


Entry 71 of Table S1. Percent of total integration listed for $\left[{ }^{18} \mathbf{F}\right] \mathbf{2 1}$

## Characterization of ${ }^{18} \mathbf{F}$-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, $5 \mu \mathrm{~m}$, $4.6 \times 150 \mathrm{~mm}$ HPLC column was used for analytical HPLC analysis. Analytical HPLC used the following mobile phases: $0.1 \% \mathrm{CF}_{3} \mathrm{CO}_{2} \mathrm{H}$ in water (A) $0.1 \% \mathrm{CF}_{3} \mathrm{CO}_{2} \mathrm{H}$ in acetonitrile (B). Program: $95 \%$ (A) and $5 \%$ (B) for 10 minutes. Note: radioactivity chromatographs have been offset ( -0.125 min ) to account for the delay volume (time) between the UV diode array detector and the radioactivity detector.

Figure S15. Characterization of $\left[{ }^{18} \mathrm{~F}\right] \mathbf{2 a}$


280 nm UV trace (top) of authentic sample (2a), radioactivity trace of the reaction mixture (middle) containing [ ${ }^{18} \mathbf{F} \mathbf{~} \mathbf{2 a}$, 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 $\left[{ }^{18} \mathrm{~F}\right] 2 \mathrm{~b}$


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

Figure S17. Characterization of $\left[{ }^{18} \mathrm{~F}\right] 2 \mathrm{c}$


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

## Figure S18. Characterization of $\left[{ }^{18} \mathrm{~F}\right] 2 \mathrm{~d}$



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

## Figure S19. Characterization of $\left[{ }^{18} \mathrm{~F}\right] 2 \mathrm{e}$



254 nm UV trace (top) of authentic sample ( $\mathbf{2 e}$ and cyclohexylbenzene as a $1: 2$ mixture), radioactivity trace of the reaction mixture (middle) containing [ $\left.{ }^{18} \mathbf{F}\right] 2 \mathbf{e}$, 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 $\left[{ }^{18} \mathrm{~F}\right] 2 \mathrm{f}$


280 nm UV trace (top) of authentic sample ( $\mathbf{2 f}$ ), radioactivity trace of the reaction mixture (middle) containing [ ${ }^{18} \mathbf{F}$ ]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 $\left[{ }^{18} \mathrm{~F}\right] 2 \mathrm{~g}$



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

Figure S22. Characterization of $\left[{ }^{18} \mathrm{~F}\right] 2 \mathrm{~h}$


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

Figure S23. Characterization of $\left[{ }^{18} \mathrm{~F}\right] 2 \mathrm{i}$


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

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



280 nm UV trace (top) of authentic sample ( $\mathbf{2} \mathbf{j}$ ), radioactivity trace of the reaction mixture (middle) containing [ ${ }^{18} \mathbf{F}$ ] $\mathbf{2}$ j, 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 $\left[{ }^{18} \mathbf{F}\right] 2 \mathrm{k}$


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

Figure S26. Characterization of $\left[{ }^{18} \mathrm{~F}\right] 21$


280 nm UV trace (top) of authentic sample (21), radioactivity trace of the reaction mixture (middle) containing [ ${ }^{18} \mathbf{F}$ ]2l, and 280 nm UV trace (bottom) of the reaction mixture. Note: radioactivity chromatographs have been offset $(-0.125 \mathrm{~min})$ to account for the delay volume (time) between the diode array detector and the radioactivity detector.

## Determination of specific activity of $\left[{ }^{18} \mathrm{~F}\right] 2 \mathrm{~g}$

Specific activity of $\left[{ }^{18} \mathbf{F}\right] \mathbf{2 g}$ 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 $\mathbf{2 g}$. For $595 \mu \mathrm{Ci}$ of $\left.{ }^{[18} \mathbf{F}\right] 2 \mathrm{~g}$ a UV absorbance of 9.7 was measured corresponding to 0.56 nmol for a specific activity of $1.1 \mathrm{Ci} / \mu \mathrm{mol}(41 \mathrm{GBq} / \mu \mathrm{mol})$ 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 $\mathbf{2 g}$ (see Tables S1 and Figures S11).

Table S2. Data for standard curve of UV absorbance vs amount of $\mathbf{2 g}$

| $\mathrm{nmol} \mathbf{2 g}$ | 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, $\lambda=0.71073 \AA$ ), and equipped with an Oxford Cryosystems nitrogen flow apparatus. The collection method involved $0.5^{\circ}$ scans in $\omega$ at $28^{\circ}$ in $2 \theta$. Data integration down to $0.82 \AA$ 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 $\mathbf{5 0 \%}$ probability ellipsoids.


Table S3. Experimental details

|  | $\mathbf{1 c}$ |
| :--- | :--- |
| Crystal data | $\mathrm{C}_{75} \mathrm{H}_{74} \mathrm{~N}_{10} \mathrm{Ni}_{2} \mathrm{O}_{12} \mathrm{~S}_{2}$ |
| Chemical formula |  |


| $M_{\mathrm{r}}$ | 1488.98 |
| :---: | :---: |
| Crystal system, space group | Monoclinic, $P 2{ }_{1} / c$ |
| Temperature (K) | 100 |
| $a, b, c(\AA)$ | 14.5704 (11), 15.7185 (12), 30.632 (2) |
| $\beta\left({ }^{\circ}\right)$ | 96.597 (1) |
| $V\left(\AA^{3}\right)$ | 6969.0 (9) |
| Z | 4 |
| Radiation type | Mo $K \alpha$ |
| $\mu\left(\mathrm{mm}^{-1}\right)$ | 0.67 |
| Crystal size (mm) | $0.32 \times 0.26 \times 0.24$ |
| Data collection |  |
| Diffractometer | Bruker D8 goniometer with CCD area detector diffractometer |
| Absorption correction | Multi-scan <br> SADABS |
| $T_{\text {min }}, T_{\text {max }}$ | 0.814, 0.856 |
| No. of measured, independent and observed $[I>2 \sigma(I)]$ reflections | 77361, 13259, 8722 |
| $R_{\text {int }}$ | 0.107 |
| $(\sin \theta / \lambda)_{\text {max }}\left(\AA^{-1}\right)$ | 0.611 |
| Refinement |  |
| $R\left[F^{2}>2 \sigma\left(F^{2}\right)\right], w R\left(F^{2}\right), S$ | 0.061, 0.163, 1.01 |
| No. of reflections | 13259 |
| No. of parameters | 936 |
| No. of restraints | 62 |
| H -atom treatment | H -atom parameters constrained |
| $\Delta \rho_{\text {max }}, \Delta \rho_{\text {min }}\left(\mathrm{e} \AA^{-3}\right)$ | 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 ( $\left(\mathrm{A},{ }^{\circ}\right.$ )

| 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) |
| $\mathrm{C} 2 \mathrm{P}-\mathrm{H} 2 \mathrm{PA}$ | 0.9900 | C94-H94 | 0.9500 |
| $\mathrm{C} 2 \mathrm{P}-\mathrm{H} 2 \mathrm{~PB}$ | 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) | $\mathrm{C} 1-\mathrm{N} 1$ | 1.357 (5) |
| C1S—H1SA | 0.9800 | $\mathrm{C} 1-\mathrm{C} 2$ | 1.374 (6) |
| C1S-H1SB | 0.9800 | $\mathrm{C} 1-\mathrm{H} 1$ | 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) | C29-06 | 1.202 (5) |
| C71-C76 | 1.405 (6) | C29-05 | 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) |
| $\mathrm{C} 2 \mathrm{P}-\mathrm{C} 1 \mathrm{P}-\mathrm{H} 1 \mathrm{PA}$ | 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) |
| $\mathrm{C} 2 \mathrm{P}-\mathrm{C} 1 \mathrm{P}-\mathrm{H} 1 \mathrm{PC}$ | 109.5 | O9-N8-C67 | 119.4 (4) |
| H1PA - C1P-H1PC | 109.5 | O10-N8-C67 | 116.5 (4) |
| $\mathrm{H} 1 \mathrm{~PB}-\mathrm{C} 1 \mathrm{P}-\mathrm{H} 1 \mathrm{PC}$ | 109.5 | C79-N9-C78 | 122.0 (4) |
| C3P-C2P-C1P | 147.5 (14) | C79-N9-C71 | 130.1 (4) |
| $\mathrm{C} 3 \mathrm{P}-\mathrm{C} 2 \mathrm{P}-\mathrm{H} 2 \mathrm{PA}$ | 99.9 | C78-N9-C71 | 107.9 (3) |
| $\mathrm{C} 1 \mathrm{P}-\mathrm{C} 2 \mathrm{P}-\mathrm{H} 2 \mathrm{PA}$ | 99.9 | C95-N10-C91 | 118.5 (4) |
| $\mathrm{C} 3 \mathrm{P}-\mathrm{C} 2 \mathrm{P}-\mathrm{H} 2 \mathrm{~PB}$ | 99.9 | C95-N10-Ni2 | 120.1 (3) |
| $\mathrm{C} 1 \mathrm{P}-\mathrm{C} 2 \mathrm{P}-\mathrm{H} 2 \mathrm{~PB}$ | 99.9 | C91-N10-Ni2 | 121.1 (3) |
| $\mathrm{H} 2 \mathrm{PA}-\mathrm{C} 2 \mathrm{P}-\mathrm{H} 2 \mathrm{~PB}$ | 104.2 | C79-O11-C80 | 121.0 (3) |
| $\mathrm{C} 4 \mathrm{P}-\mathrm{C} 3 \mathrm{P}-\mathrm{C} 2 \mathrm{P}$ | 133.8 (14) | O7-S2-O8 | 117.58 (19) |


| $\mathrm{C} 4 \mathrm{P}-\mathrm{C} 3 \mathrm{P}-\mathrm{H} 3 \mathrm{PA}$ | 103.8 | O7-S2-N7 | 108.85 (18) |
| :---: | :---: | :---: | :---: |
| $\mathrm{C} 2 \mathrm{P}-\mathrm{C} 3 \mathrm{P}-\mathrm{H} 3 \mathrm{PA}$ | 103.8 | O8-S2-N7 | 112.83 (19) |
| $\mathrm{C} 4 \mathrm{P}-\mathrm{C} 3 \mathrm{P}-\mathrm{H} 3 \mathrm{~PB}$ | 103.8 | O7-S2-C62 | 107.04 (19) |
| $\mathrm{C} 2 \mathrm{P}-\mathrm{C} 3 \mathrm{P}-\mathrm{H} 3 \mathrm{~PB}$ | 103.8 | O8-S2-C62 | 104.47 (19) |
| H3PA $-\mathrm{C} 3 \mathrm{P}-\mathrm{H} 3 \mathrm{~PB}$ | 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) |
| $\mathrm{C} 5 \mathrm{P}-\mathrm{C} 4 \mathrm{P}-\mathrm{H} 4 \mathrm{PA}$ | 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 - $\mathrm{C} 4 \mathrm{P}-\mathrm{H} 4 \mathrm{~PB}$ | 103.2 | N6-Ni2-N7 | 89.41 (14) |
| $\mathrm{C} 4 \mathrm{P}-\mathrm{C} 5 \mathrm{P}-\mathrm{H} 5 \mathrm{PA}$ | 109.5 | $\mathrm{N} 1-\mathrm{C} 1-\mathrm{C} 2$ | 122.8 (4) |
| C4P-C5P-H5PB | 109.5 | $\mathrm{N} 1-\mathrm{C} 1-\mathrm{H} 1$ | 118.6 |
| H5PA - C5P-H5PB | 109.5 | C2- $\mathrm{C} 1-\mathrm{H} 1$ | 118.6 |
| C4P-C5P-H5PC | 109.5 | $\mathrm{C} 1-\mathrm{C} 2-\mathrm{C} 3$ | 118.6 (4) |
| H5PA - $\mathrm{C} 5 \mathrm{P}-\mathrm{H} 5 \mathrm{PC}$ | 109.5 | $\mathrm{C} 1-\mathrm{C} 2-\mathrm{H} 2$ | 120.7 |
| H5PB-C5P- H5PC | 109.5 | C3-C2-H2 | 120.7 |
| C3S-C2S-C1S | 168.7 (17) | C4-C3-C2 | 119.2 (4) |
| $\mathrm{C} 3 \mathrm{~S}-\mathrm{C} 2 \mathrm{~S}-\mathrm{H} 2 \mathrm{SA}$ | 93.5 | C4-C3-H3 | 120.4 |
| $\mathrm{C} 1 \mathrm{~S}-\mathrm{C} 2 \mathrm{~S}-\mathrm{H} 2 \mathrm{SA}$ | 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 |
| $\mathrm{C} 2 \mathrm{~S}-\mathrm{C} 3 \mathrm{~S}-\mathrm{C} 4 \mathrm{~S}$ | 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- C 11 | 119.2 (4) |
| C4S-C3S-H3SB | 103.7 | C7-C6-C5 | 120.2 (4) |
| H3SA-C3S-H3SB | 105.4 | C11-C6-C5 | 120.6 (4) |


| C3S-C4S-C5S | 141.1 (15) | C8-C7-C6 | 121.2 (4) |
| :---: | :---: | :---: | :---: |
| C3S-C4S-H4SA | 101.7 | C8- $\mathrm{C} 7-\mathrm{H} 7$ | 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 | $\mathrm{C} 11-\mathrm{C} 10-\mathrm{H} 10$ | 119.6 |
| C54-C53-C52 | 118.9 (5) | C10-C11-C6 | 119.0 (4) |
| C54- $\mathrm{C} 53-\mathrm{H} 53$ | 120.5 | C10- $\mathrm{C} 11-\mathrm{N} 2$ | 120.7 (4) |
| C52-C53-H53 | 120.5 | C6- $\mathrm{C} 11-\mathrm{N} 2$ | 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- $\mathrm{C} 57-\mathrm{H} 57$ | 119.5 | C16-C15-H15 | 120.2 |
| C57-C58-C59 | 120.2 (5) | C15-C16-C17 | 118.5 (4) |
| C57-C58-H58 | 119.9 | C15-C16-H16 | 120.7 |


| C59-C58-H58 | 119.9 | C17-C16-H16 | 120.7 |
| :---: | :---: | :---: | :---: |
| C60-C59-C58 | 119.7 (5) | C16-C17-C12 | 122.7 (4) |
| C60-C59-H59 | 120.1 | C16-C17-N3 | 114.4 (4) |
| C58-C59-H59 | 120.1 | C12-C17-N3 | 122.9 (4) |
| C59-C60-C61 | 120.7 (4) | C22-C21-C26 | 120.9 (4) |
| C59-C60-H60 | 119.6 | C22-C21-N4 | 132.2 (4) |
| C61-C60-H60 | 119.6 | C26-C21-N4 | 106.9 (4) |
| C60-C61-C56 | 120.0 (4) | C23-C22-C21 | 117.6 (4) |
| C60-C61-N7 | 121.4 (4) | $\mathrm{C} 23-\mathrm{C} 22-\mathrm{H} 22$ | 121.2 |
| C56-C61-N7 | 118.5 (4) | $\mathrm{C} 21-\mathrm{C} 22-\mathrm{H} 22$ | 121.2 |
| C67-C62-C63 | 116.8 (4) | C22-C23-C24 | 123.3 (4) |
| C67-C62-S2 | 126.1 (3) | $\mathrm{C} 22-\mathrm{C} 23-\mathrm{H} 23$ | 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- $667-\mathrm{C} 62$ | 123.0 (4) | C27-C28-N4 | 109.9 (4) |
| C66-C67-N8 | 115.2 (4) | C27-C28-H28 | 125.0 |
| C62-C67-N8 | 121.8 (4) | N4-C28-H28 | 125.0 |
| C72-C71-C76 | 121.0 (4) | O6-C29-O5 | 127.8 (4) |


| C72-C71-N9 | 131.6 (4) | O6-C29-N4 | 122.4 (4) |
| :---: | :---: | :---: | :---: |
| C76-C71-N9 | 107.3 (3) | O5-C29-N4 | 109.8 (4) |
| C73-C72-C71 | 117.2 (4) | C33-C30-O5 | 109.0 (4) |
| C73-C72-H72 | 121.4 | C33-C30-C32 | 112.2 (5) |
| C71-C72-H72 | 121.4 | O5-C30-C32 | 101.1 (4) |
| C72-C73-C74 | 123.5 (4) | C33-C30-C31 | 110.8 (5) |
| C72-C73-H73 | 118.3 | O5-C30-C31 | 109.6 (4) |
| C74-C73-H73 | 118.3 | C32-C30-C31 | 113.6 (4) |
| C75-C74-C73 | 117.8 (4) | C30-C31-H31A | 109.5 |
| C75-C74-Ni2 | 126.3 (3) | C30-C31-H31B | 109.5 |
| C73-C74-Ni2 | 115.9 (3) | H31A-C31-H31B | 109.5 |
| C74-C75-C76 | 120.1 (4) | C30-C31-H31C | 109.5 |
| C74-C75-H75 | 119.9 | H31A-C31-H31C | 109.5 |
| C76-C75-H75 | 119.9 | H31B-C31-H31C | 109.5 |
| C75-C76-C71 | 120.2 (4) | C30-C32-H32A | 109.5 |
| C75-C76-C77 | 133.0 (4) | C30-C32-H32B | 109.5 |
| C71-C76-C77 | 106.8 (4) | H32A-C32-H32B | 109.5 |
| C78-C77-C76 | 108.2 (4) | C30-C32-H32C | 109.5 |
| C78-C77-H77 | 125.9 | H32A-C32-H32C | 109.5 |
| C76-C77-H77 | 125.9 | H32B-C32-H32C | 109.5 |
| C77-C78-N9 | 109.9 (4) | C30-C33-H33A | 109.5 |
| C77-C78-H78 | 125.1 | C30-C33-H33B | 109.5 |
| N9-C78-H78 | 125.1 | H33A-C33-H33B | 109.5 |
| O12-C79-O11 | 127.8 (4) | C30-C33-H33C | 109.5 |
| O12-C79-N9 | 122.5 (4) | H33A-C33-H33C | 109.5 |
| O11-C79-N9 | 109.7 (4) | H33B-C33-H33C | 109.5 |
| O11-C80-C82 | 108.8 (4) | N5-C41-C42 | 122.4 (4) |
| O11-C80-C83 | 110.5 (4) | N5-C41-H41 | 118.8 |
| C82-C80-C83 | 112.9 (4) | C42- $\mathrm{C} 41-\mathrm{H} 41$ | 118.8 |


| O11-C80-C81 | 101.3 (3) | C43-C42-C41 | 119.3 (5) |
| :---: | :---: | :---: | :---: |
| C82-C80-C81 | 110.7 (4) | C43-C42-H42 | 120.4 |
| C83-C80-C81 | 112.0 (4) | C41-C42-H42 | 120.4 |
| C80-C81-H81A | 109.5 | C44-C43-C42 | 118.5 (5) |
| C80-C81-H81B | 109.5 | C44-C43-H43 | 120.7 |
| H81A-C81-H81B | 109.5 | C42-C43-H43 | 120.7 |
| C80-C81-H81C | 109.5 | C43-C44-C45 | 119.3 (5) |
| H81A-C81-H81C | 109.5 | C43-C44-H44 | 120.3 |
| H81B-C81-H81C | 109.5 | C45-C44-H44 | 120.3 |
| C80-C82-H82A | 109.5 | N5-C45-C44 | 122.8 (5) |
| C80-C82-H82B | 109.5 | N5-C45-H45 | 118.6 |
| H82A-C82-H82B | 109.5 | C44-C45-H45 | 118.6 |
| C80-C82-H82C | 109.5 | C5-N1-C1 | 118.7 (4) |
| H82A-C82-H82C | 109.5 | C5-N1-Ni1 | 122.5 (3) |
| H82B-C82-H82C | 109.5 | C1—N1—Ni1 | 118.6 (3) |
| C80-C83-H83A | 109.5 | C11-N2-S1 | 118.5 (3) |
| C80-C83-H83B | 109.5 | C11-N2-Ni1 | 107.8 (3) |
| H83A-C83-H83B | 109.5 | S1-N2-Ni1 | 128.6 (2) |
| C80-C83-H83C | 109.5 | O3-N3-O4 | 124.1 (4) |
| H83A-C83-H83C | 109.5 | O3-N3-C17 | 118.9 (4) |
| H83B-C83-H83C | 109.5 | O4-N3-C17 | 116.9 (4) |
| N10-C91-C92 | 121.9 (5) | C29-N4-C28 | 122.0 (4) |
| N10-C91-H91 | 119.1 | C29-N4-C21 | 129.6 (4) |
| C92-C91-H91 | 119.1 | C28-N4-C21 | 108.2 (3) |
| C93-C92-C91 | 119.5 (5) | C45-N5-C41 | 117.5 (4) |
| C93-C92-H92 | 120.3 | C45-N5-Ni1 | 122.4 (3) |
| C91-C92-H92 | 120.3 | C41-N5-Ni1 | 120.1 (3) |
| C94-C93-C92 | 118.6 (5) | C29-O5-C30 | 121.4 (4) |
| C94-C93-H93 | 120.7 | $\mathrm{O} 2-\mathrm{S} 1-\mathrm{O} 1$ | 117.78 (19) |


| C92-C93-H93 | 120.7 | O2-S1-N2 | 112.58 (19) |
| :---: | :---: | :---: | :---: |
| C93-C94-C95 | 120.0 (5) | O1-S1-N2 | 108.63 (18) |
| C93-C94-H94 | 120.0 | $\mathrm{O} 2-\mathrm{S} 1-\mathrm{C} 12$ | 104.50 (19) |
| C95-C94-H94 | 120.0 | $\mathrm{O} 1-\mathrm{S} 1-\mathrm{C} 12$ | 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) |
| $\mathrm{C} 1 \mathrm{P}-\mathrm{C} 2 \mathrm{P}-\mathrm{C} 3 \mathrm{P}-\mathrm{C} 4 \mathrm{P}$ | 17 (3) | C61-N7-Ni2-N6 | 62.1 (3) |
| $\mathrm{C} 2 \mathrm{P}-\mathrm{C} 3 \mathrm{P}-\mathrm{C} 4 \mathrm{P}-\mathrm{C} 5 \mathrm{P}$ | 19 (6) | S2-N7-Ni2-N6 | -93.0 (3) |
| C1S-C2S-C3S-C4S | -25 (8) | $\mathrm{N} 1-\mathrm{C} 1-\mathrm{C} 2-\mathrm{C} 3$ | -0.5 (7) |
| $\mathrm{C} 2 \mathrm{~S}-\mathrm{C} 3 \mathrm{~S}-\mathrm{C} 4 \mathrm{~S}-\mathrm{C} 5 \mathrm{~S}$ | 21 (3) | C1-C2-C3-C4 | -1.2(7) |
| N6-C51-C52-C53 | -1.1(7) | $\mathrm{C} 2-\mathrm{C} 3-\mathrm{C} 4-\mathrm{C} 5$ | 1.1 (7) |
| C51-C52-C53-C54 | -1.1 (7) | C3-C4-C5-N1 | 0.5 (6) |
| C52-C53-C54-C55 | 1.3 (7) | C3-C4-C5-C6 | -177.5 (4) |
| C53-C54-C55-N6 | 0.6 (7) | N1-C5-C6-C7 | -139.7 (4) |
| C53-C54-C55-C56 | -178.8 (4) | C4-C5-C6-C7 | 38.4 (6) |
| N6-C55-C56-C57 | -142.2 (4) | N1-C5-C6-C11 | 38.9 (6) |
| C54-C55-C56-C57 | 37.3 (6) | C4-C5-C6-C11 | -143.0 (4) |
| N6-C55-C56-C61 | 39.5 (6) | C11-C6-C7-C8 | -0.7 (7) |
| C54-C55-C56-C61 | -141.0 (4) | C5-C6-C7-C8 | 177.9 (5) |
| C61-C56-C57-C58 | -1.3 (7) | C6-C7-C8-C9 | -1.1 (8) |
| C55-C56-C57-C58 | -179.7 (4) | C7-C8-C9-C10 | 1.6 (8) |
| C56-C57-C58-C59 | -0.6 (8) | C8-C9-C10-C11 | -0.4 (8) |
| C57-C58-C59-C60 | 1.8 (8) | C9-C10-C11-C6 | -1.4 (7) |


| C58-C59-C60-C61 | -1.1 (7) | C9-C10-C11-N2 | -175.8 (4) |
| :---: | :---: | :---: | :---: |
| C59-C60-C61-C56 | -0.9 (7) | C7-C6-C11-C10 | 2.0 (6) |
| C59-C60-C61-N7 | -176.7 (4) | C5-C6-C11-C10 | -176.6 (4) |
| C57-C56-C61-C60 | 2.1 (6) | C7-C6- ${ }^{\text {C11-N2 }}$ | 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) | S $1-\mathrm{C} 12-\mathrm{C} 13-\mathrm{C} 14$ | -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) | $\mathrm{S} 1-\mathrm{C} 12-\mathrm{C} 17-\mathrm{N} 3$ | -1.9 (6) |
| C63-C62-C67-N8 | 178.1 (4) | C26-C21-C22-C23 | 2.5 (6) |
| S2-C62-C67-N8 | -4.4 (6) | N4-C21-C22-C23 | -177.8 (4) |
| C76-C71-C72-C73 | 3.8 (6) | C21-C22-C23-C24 | -1.2 (7) |
| N9-C71-C72-C73 | -179.7 (4) | C22-C23-C24-C25 | -1.1(7) |
| C71-C72-C73-C74 | -1.5 (7) | C22-C23-C24-Ni1 | 176.3 (3) |
| C72-C73-C74-C75 | -1.8 (7) | C23-C24-C25-C26 | 2.1 (6) |
| C72-C73-C74-Ni2 | 178.0 (4) | Ni1-C24-C25-C26 | -175.1 (3) |
| C73-C74-C75-C76 | 2.7 (6) | C24-C25-C26-C21 | -0.8 (6) |
| Ni2-C74-C75-C76 | -177.0 (3) | C24-C25-C26-C27 | 178.9 (4) |
| C74-C75-C76-C71 | -0.4 (6) | C22-C21-C26-C25 | -1.6 (6) |
| C74-C75-C76-C77 | -178.2 (4) | N4-C21-C26-C25 | 178.6 (4) |
| C72-C71-C76-C75 | -3.0 (6) | C22-C21-C26-C27 | 178.7 (4) |
| N9-C71-C76-C75 | 179.8 (4) | N4-C21-C26-C27 | -1.1 (4) |


| C72-C71-C76-C77 | 175.3 (4) | C25-C26-C27-C28 | -179.6 (4) |
| :---: | :---: | :---: | :---: |
| N9-C71-C76-C77 | -2.0 (4) | C21-C26-C27-C28 | 0.1 (5) |
| C75-C76-C77-C78 | 179.4 (4) | C26-C27-C28-N4 | 1.0 (5) |
| C71-C76-C77-C78 | 1.5 (5) | N5-C41-C42-C43 | 0.9 (7) |
| C76-C77-C78-N9 | -0.4 (5) | C41-C42-C43-C44 | -1.7 (7) |
| N10-C91-C92-C93 | 0.8 (7) | C42-C43-C44-C45 | 1.2 (7) |
| C91-C92-C93-C94 | 1.2 (8) | C43-C44-C45-N5 | 0.3 (7) |
| C92-C93-C94-C95 | -1.8(7) | C4-C5-N1-C1 | -2.1 (6) |
| C93-C94-C95-N10 | 0.5 (7) | C6-C5-N1-C1 | 175.9 (4) |
| C52-C51-N6-C55 | 2.9 (7) | $\mathrm{C} 4-\mathrm{C} 5-\mathrm{N} 1-\mathrm{Ni} 1$ | 171.7 (3) |
| C52-C51-N6-Ni2 | -170.8 (4) | C6-C5-N1-Ni1 | -10.2 (5) |
| C54-C55-N6-C51 | -2.7 (6) | $\mathrm{C} 2-\mathrm{C} 1-\mathrm{N} 1-\mathrm{C} 5$ | 2.1 (6) |
| C56-C55-N6-C51 | 176.8 (4) | $\mathrm{C} 2-\mathrm{C} 1-\mathrm{N} 1-\mathrm{Ni} 1$ | -171.9 (3) |
| C54-C55-N6-Ni2 | 170.9 (3) | C10- $\mathrm{C} 11-\mathrm{N} 2-\mathrm{S} 1$ | -81.1 (5) |
| C56-C55-N6-Ni2 | -9.7 (5) | C6- $\mathrm{C} 11-\mathrm{N} 2-\mathrm{S} 1$ | 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- $\mathrm{C} 11-\mathrm{N} 2-\mathrm{Ni} 1$ | -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) | $\mathrm{C} 26-\mathrm{C} 21-\mathrm{N} 4-\mathrm{C} 29$ | 176.2 (4) |


| C72-C71-N9-C79 | 2.0 (7) | C22-C21-N4-C28 | -178.0 (4) |
| :---: | :---: | :---: | :---: |
| C76-C71-N9-C79 | 178.9 (4) | C26-C21-N4-C28 | 1.7 (5) |
| C72-C71-N9-C78 | -175.1 (4) | C44-C45-N5-C41 | -1.1 (6) |
| C76-C71-N9-C78 | 1.8 (4) | C44-C45-N5-Ni1 | -179.3 (3) |
| C94-C95-N10-C91 | 1.5 (6) | C42-C41-N5-C45 | 0.5 (6) |
| C94-C95-N10-Ni2 | 174.4 (3) | C42-C41-N5-Ni1 | 178.7 (3) |
| C92-C91-N10-C95 | -2.2 (7) | O6-C29-O5-C30 | 0.7 (7) |
| C92-C91-N10-Ni2 | -175.0 (4) | N4-C29-O5-C30 | -179.0 (4) |
| O12-C79-O11-C80 | 8.2 (7) | C33-C30-O5-C29 | -67.3 (6) |
| N9-C79-O11-C80 | -171.5 (3) | C32-C30-O5-C29 | 174.3 (4) |
| C82-C80-O11-C79 | 56.7 (5) | C31-C30-O5-C29 | 54.2 (6) |
| C83-C80-O11-C79 | -67.8 (5) | C11-N2-S1-O2 | 35.0 (4) |
| C81-C80-O11-C79 | 173.4 (4) | Ni1-N2-S1-O2 | -173.4 (2) |
| C61-N7-S2-O7 | 171.8 (3) | C11-N2-S1-O1 | 167.3 (3) |
| Ni2-N7-S2-O7 | -35.0 (3) | Ni1-N2-S1-O1 | -41.1 (3) |
| C61-N7-S2-O8 | 39.4 (4) | C11-N2-S1-C12 | -78.5 (3) |
| Ni2-N7-S2-O8 | -167.4 (2) | Ni1-N2-S1-C12 | 73.1 (3) |
| C61-N7-S2-C62 | -73.8 (3) | $\mathrm{C} 13-\mathrm{C} 12-\mathrm{S} 1-\mathrm{O} 2$ | -28.6 (4) |
| Ni2-N7-S2-C62 | 79.4 (3) | $\mathrm{C} 17-\mathrm{C} 12-\mathrm{S} 1-\mathrm{O} 2$ | 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- $\mathrm{C} 12-\mathrm{S} 1-\mathrm{O} 1$ | 26.7 (4) |
| C67-C62-S2-O8 | 150.9 (4) | $\mathrm{C} 13-\mathrm{C} 12-\mathrm{S} 1-\mathrm{N} 2$ | 90.4 (4) |
| C63-C62-S2-O8 | -31.6 (4) | C17- $\mathrm{C} 12-\mathrm{S} 1-\mathrm{N} 2$ | -88.8 (4) |
| C67-C62-S2-N7 | -90.2 (4) | C45-N5-Ni1-C24 | -92.6 (4) |
| C63-C62-S2-N7 | 87.3 (4) | $\mathrm{C} 41-\mathrm{N} 5-\mathrm{Ni} 1-\mathrm{C} 24$ | 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) | $\mathrm{C} 23-\mathrm{C} 24-\mathrm{Ni} 1-\mathrm{N} 2$ | 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) | $\mathrm{C} 1-\mathrm{N} 1-\mathrm{Ni} 1-\mathrm{N} 2$ | 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



${ }^{13} \mathrm{C}$ NMR $\left(\mathrm{CD}_{3} \mathrm{CN}, 23{ }^{\circ} \mathrm{C}\right)$ of 6

${ }^{1} \mathrm{H}$ NMR $\left(\mathrm{CD}_{2} \mathrm{Cl}_{2}, 23{ }^{\circ} \mathrm{C}\right)$ of $\mathbf{7 a}$

${ }^{13} \mathrm{C}$ NMR $\left(\mathrm{CD}_{2} \mathrm{Cl}_{2}, 23{ }^{\circ} \mathrm{C}\right)$ of $\mathbf{7 a}$

${ }^{1} \mathrm{H}$ NMR $\left(\mathrm{CDCl}_{3}, 23{ }^{\circ} \mathrm{C}\right)$ of $\mathbf{1 a}$

${ }^{1} \mathrm{H} \operatorname{NMR}\left(\mathrm{CDCl}_{3}, 23^{\circ} \mathrm{C}\right)$ of $\mathbf{1 a}$

${ }^{1} \mathrm{H}$ NMR $\left(\mathrm{CD}_{2} \mathrm{Cl}_{2}, 23^{\circ} \mathrm{C}\right)$ of $\mathbf{7 b}$

${ }^{13} \mathrm{C}$ NMR $\left(\mathrm{CD}_{2} \mathrm{Cl}_{2}, 23{ }^{\circ} \mathrm{C}\right)$ of $\mathbf{7 b}$

${ }^{1} \mathrm{H}$ NMR $\left(\mathrm{CDCl}_{3}, 23^{\circ} \mathrm{C}\right)$ of $\mathbf{1 b}$


${ }^{13} \mathrm{C}$ NMR $\left(\mathrm{CDCl}_{3}, 23{ }^{\circ} \mathrm{C}\right)$ of $\mathbf{1 b}$

${ }^{1} \mathrm{H}$ NMR $\left(\mathrm{CD}_{2} \mathrm{Cl}_{2}, 23{ }^{\circ} \mathrm{C}\right)$ of $\mathbf{7 c}$

${ }^{13} \mathrm{C}$ NMR $\left(\mathrm{CD}_{2} \mathrm{Cl}_{2}, 23{ }^{\circ} \mathrm{C}\right)$ of $\mathbf{7 c}$

${ }^{1} \mathrm{H}$ NMR $\left(\mathrm{CDCl}_{3}, 23^{\circ} \mathrm{C}\right)$ of $\mathbf{1 c}$

${ }^{13} \mathrm{C}$ NMR $\left(\mathrm{CDCl}_{3}, 23{ }^{\circ} \mathrm{C}\right)$ of $\mathbf{1 c}$


${ }^{1} \mathrm{H}$ NMR $\left(\mathrm{CD}_{2} \mathrm{Cl}_{2}, 23{ }^{\circ} \mathrm{C}\right)$ of $\mathbf{7 d}$


${ }^{13} \mathrm{C}$ NMR $\left(\mathrm{CD}_{2} \mathrm{Cl}_{2}, 23{ }^{\circ} \mathrm{C}\right)$ of $7 \mathbf{d}$

${ }^{1} \mathrm{H}$ NMR $\left(\mathrm{CDCl}_{3}, 23{ }^{\circ} \mathrm{C}\right)$ of $\mathbf{1 d}$

${ }^{13} \mathrm{C}$ NMR $\left(\mathrm{CDCl}_{3}, 23{ }^{\circ} \mathrm{C}\right)$ of $\mathbf{1 d}$


${ }^{1} \mathrm{H}$ NMR $\left(\mathrm{CD}_{2} \mathrm{Cl}_{2}, 23{ }^{\circ} \mathrm{C}\right)$ of $\mathbf{7 e}$


${ }^{13} \mathrm{C}$ NMR $\left(\mathrm{CD}_{2} \mathrm{Cl}_{2}, 23{ }^{\circ} \mathrm{C}\right)$ of $\mathbf{7 e}$

${ }^{1} \mathrm{H}$ NMR $\left(\mathrm{CDCl}_{3}, 23^{\circ} \mathrm{C}\right)$ of $\mathbf{1 e}$


${ }^{13} \mathrm{C}$ NMR $\left(\mathrm{CDCl}_{3}, 23{ }^{\circ} \mathrm{C}\right)$ of $\mathbf{1 e}$

${ }^{1} \mathrm{H}$ NMR $\left(\mathrm{CDCl}_{3}, 23^{\circ} \mathrm{C}\right)$ of $\mathbf{S 3}$


${ }^{13} \mathrm{C}$ NMR $\left(\mathrm{CDCl}_{3}, 23{ }^{\circ} \mathrm{C}\right)$ of $\mathbf{S 3}$


${ }^{1} \mathrm{H}$ NMR $\left(\mathrm{CD}_{2} \mathrm{Cl}_{2}, 23{ }^{\circ} \mathrm{C}\right)$ of $7 \mathbf{f}$

${ }^{13} \mathrm{C}$ NMR $\left(\mathrm{CD}_{2} \mathrm{Cl}_{2}, 23{ }^{\circ} \mathrm{C}\right)$ of $\mathbf{7 f}$

${ }^{1} \mathrm{H}$ NMR $\left(\mathrm{CDCl}_{3}, 23^{\circ} \mathrm{C}\right)$ of $\mathbf{1 f}$

${ }^{13} \mathrm{C}$ NMR $\left(\mathrm{CDCl}_{3}, 23{ }^{\circ} \mathrm{C}\right)$ of $\mathbf{1 f}$

${ }^{1} \mathrm{H}$ NMR $\left(\mathrm{CDCl}_{3}, 23^{\circ} \mathrm{C}\right)$ of $\mathbf{S 4}$


${ }^{13} \mathrm{C}$ NMR $\left(\mathrm{CDCl}_{3}, 23{ }^{\circ} \mathrm{C}\right)$ of $\mathbf{S 4}$

${ }^{1} \mathrm{H}$ NMR $\left(\mathrm{CD}_{2} \mathrm{Cl}_{2}, 23{ }^{\circ} \mathrm{C}\right)$ of $\mathbf{7 g}$
${ }^{13} \mathrm{C}$ NMR $\left(\mathrm{CD}_{2} \mathrm{Cl}_{2}, 23{ }^{\circ} \mathrm{C}\right)$ of $\mathbf{7 g}$


${ }^{1} \mathrm{H}$ NMR $\left(\mathrm{CDCl}_{3}, 23^{\circ} \mathrm{C}\right)$ of $\mathbf{1 g}$


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${ }^{13} \mathrm{C}$ NMR $\left(\mathrm{CDCl}_{3}, 23{ }^{\circ} \mathrm{C}\right)$ of $\mathbf{1 g}$

${ }^{1} \mathrm{H}$ NMR $\left(\mathrm{CD}_{2} \mathrm{Cl}_{2}, 23{ }^{\circ} \mathrm{C}\right)$ of $\mathbf{7 h}$

${ }^{13} \mathrm{C}$ NMR $\left(\mathrm{CD}_{2} \mathrm{Cl}_{2}, 23{ }^{\circ} \mathrm{C}\right)$ of $\mathbf{7 h}$

${ }^{1} \mathrm{H}$ NMR $\left(\mathrm{CD}_{2} \mathrm{Cl}_{2}, 23{ }^{\circ} \mathrm{C}\right)$ of $\mathbf{1 h}$


${ }^{13} \mathrm{C}$ NMR $\left(\mathrm{CD}_{2} \mathrm{Cl}_{2}, 23{ }^{\circ} \mathrm{C}\right)$ of $\mathbf{1 h}$

${ }^{1} \mathrm{H}$ NMR $\left(\mathrm{CDCl}_{3}, 23^{\circ} \mathrm{C}\right)$ of $\mathbf{S 1 1}$

${ }^{13} \mathrm{C}$ NMR $\left(\mathrm{CDCl}_{3}, 23{ }^{\circ} \mathrm{C}\right)$ of $\mathbf{S 1 1}$

${ }^{1} \mathrm{H}$ NMR $\left(\mathrm{CD}_{3} \mathrm{CN}, 23^{\circ} \mathrm{C}\right)$ of $\mathbf{7 i}$

${ }^{13} \mathrm{C}$ NMR $\left(\mathrm{CD}_{3} \mathrm{CN}, 23^{\circ} \mathrm{C}\right)$ of $\mathbf{7 i}$

${ }^{1} \mathrm{H}$ NMR $\left(\mathrm{CD}_{2} \mathrm{Cl}_{2}, 23^{\circ} \mathrm{C}\right)$ of $\mathbf{1 i}$

${ }^{13} \mathrm{C}$ NMR $\left(\mathrm{CD}_{2} \mathrm{Cl}_{2}, 23{ }^{\circ} \mathrm{C}\right)$ of $\mathbf{1 i}$

${ }^{1} \mathrm{H}$ NMR $\left(\mathrm{CD}_{2} \mathrm{Cl}_{2}, 23{ }^{\circ} \mathrm{C}\right)$ of $\mathbf{7} \mathbf{j}$

${ }^{1} \mathrm{H} \operatorname{NMR}\left(\mathrm{CD}_{2} \mathrm{Cl}_{2}, 23{ }^{\circ} \mathrm{C}\right)$ of $\mathbf{1} \mathbf{j}$

${ }^{13} \mathrm{C}$ NMR $\left(\mathrm{CD}_{2} \mathrm{Cl}_{2}, 23{ }^{\circ} \mathrm{C}\right)$ of $\mathbf{1} \mathbf{j}$

${ }^{1} \mathrm{H} \operatorname{NMR}\left(\mathrm{CDCl}_{3}, 23{ }^{\circ} \mathrm{C}\right)$ of $\mathbf{S 1 2}$


${ }^{13} \mathrm{C}$ NMR $\left(\mathrm{CDCl}_{3}, 23{ }^{\circ} \mathrm{C}\right)$ of $\mathbf{S 1 2}$


${ }^{1} \mathrm{H}$ NMR $\left(\mathrm{CD}_{2} \mathrm{Cl}_{2}, 23{ }^{\circ} \mathrm{C}\right)$ of $\mathbf{7 k}$


${ }^{13} \mathrm{C}$ NMR $\left(\mathrm{CD}_{2} \mathrm{Cl}_{2}, 23{ }^{\circ} \mathrm{C}\right)$ of $\mathbf{7 k}$

${ }^{1} \mathrm{H} \operatorname{NMR}\left(\mathrm{CDCl}_{3}, 23{ }^{\circ} \mathrm{C}\right)$ of $\mathbf{1 k}$


${ }^{13} \mathrm{C}$ NMR $\left(\mathrm{CDCl}_{3}, 23{ }^{\circ} \mathrm{C}\right)$ of $\mathbf{1 k}$

${ }^{1} \mathrm{H}$ NMR $\left(\mathrm{C}_{6} \mathrm{D}_{6}, 23{ }^{\circ} \mathrm{C}\right)$ of 71

${ }^{13} \mathrm{C}$ NMR $\left(\mathrm{C}_{6} \mathrm{D}_{6}, 23{ }^{\circ} \mathrm{C}\right)$ of $7 \mathbf{l}$


${ }^{1} \mathrm{H}$ NMR $\left(\mathrm{CDCl}_{3}, 23^{\circ} \mathrm{C}\right)$ of $\mathbf{1 1}$

${ }^{13} \mathrm{C}$ NMR $\left(\mathrm{CDCl}_{3}, 23{ }^{\circ} \mathrm{C}\right)$ of $\mathbf{1 1}$

${ }^{1} \mathrm{H}$ NMR $\left(\mathrm{CDCl}_{3}, 23^{\circ} \mathrm{C}\right)$ of $\mathbf{2 f}$


${ }^{13} \mathrm{C}$ NMR $\left(\mathrm{CDCl}_{3}, 23{ }^{\circ} \mathrm{C}\right)$ of $\mathbf{1 1}$


$-90$
${ }^{19} \mathrm{~F}$ NMR $\left(\mathrm{CDCl}_{3}, 23{ }^{\circ} \mathrm{C}\right)$ of $\mathbf{2 f}$

${ }^{1} \mathrm{H}$ NMR $\left(\mathrm{CDCl}_{3}, 23{ }^{\circ} \mathrm{C}\right)$ of $\mathbf{S 1 3}$


$\stackrel{⿷_{0}^{2}}{2}$ $\stackrel{\circ}{\sim}$
9
60
©
100
$\stackrel{\circ}{-}$
$\stackrel{\circ}{\sim}$
${ }^{13} \mathrm{C}$ NMR $\left(\mathrm{CDCl}_{3}, 23{ }^{\circ} \mathrm{C}\right)$ of $\mathbf{S 1 3}$

${ }^{1} \mathrm{H}$ NMR $\left(\mathrm{CDCl}_{3}, 23^{\circ} \mathrm{C}\right)$ of $\mathbf{2 i}$




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08T-
$-170$
$-160$
$-150$
$-140$
$-130$
$-120$
$-110$
$-100$

운
${ }^{19} \mathrm{~F}$ NMR $\left(\mathrm{CDCl}_{3}, 23{ }^{\circ} \mathrm{C}\right)$ of $\mathbf{2 f}$


${ }^{1} \mathrm{H}$ NMR $\left(\mathrm{CDCl}_{3}, 23^{\circ} \mathrm{C}\right)$ of $\mathbf{2 1}$

${ }^{13} \mathrm{C}$ NMR $\left(\mathrm{CDCl}_{3}, 23{ }^{\circ} \mathrm{C}\right)$ of 21


${ }^{19} \mathrm{~F}$ NMR $\left(\mathrm{CDCl}_{3}, 23{ }^{\circ} \mathrm{C}\right)$ of $\mathbf{2 l}$

## References

(1) Still, W. C.; Kahn, M.; Mitra, A. J. Org. Chem. 1978, 43, 2925.
(2) Pangborn, A. B.; Giardello, M. A.; Grubbs, R. H.; Rosen, R. K.; Timmers, F. J. Organometallics 1996, 15, 1518.
(3) Matthews, W. S.; Bares, J. E.; Bartmess, J. E.; Bordwell, F. G.; Cornforth, F. J.; Drucker, G. E.; Margolin, Z.; McCallum, R. J.; McCollum, G. J.; Vanier, N. R. J. Am. Chem. Soc. 1975, 97, 7006.
(4) Fulmer, G. R.; Miller, A. J. M.; Sherden, N. H.; Gottlieb, H. E.; Nudelman, A.; Stoltz, B. M.;

Bercaw, J. E.; Goldberg, K. I. Organometallics 2010, 29, 2176.
(5) R. Weiss, J. Seubert, Angew. Chem., Int. Ed. 1994, 33, 891.
(6) Rebstock, A. S.; Mongin, F.; Trecourt, F.; Queguiner, G. Org. Biomol. Chem. 2003, 1, 3064.
(7) Furuya, T.; Ritter, T. J. Am. Chem. Soc. 2008, 130, 10060.
(8) (a) Marshall, W. J.; Grushin, V. V. Can. J. Chem. 2005, 83, 640. (b) Higgs, A. T.; Zinn, P. J.;

Simmons, S. J.; Sanford, M. S. Organometallics 2009, 28, 6142. (c) Higgs, A. T.; Zinn, P. J.;
Sanford, M. S. Organometallics 2010, 29, 5446.
(9) Lee, E.; Kamlet, A. S.; Powers, D. C.; Neumann, C. N.; Boursalian, G. B.; Furuya, T.; Choi, D. C.; Hooker, J. M.; Ritter, T. Science 2011, 334, 639.
(10) A. B. Charette, H. Juteau, H. Lebel, C. Molinaro, J. Am. Chem. Soc. 1998, 120, 11943.
(11) Kirschbaum, S.; Waldmann, H. J. Org. Chem. 1998, 63, 4936.
(12)Furuya, T.; Kaiser, H. M.; Ritter, T. Angew. Chem. Int. Ed. 2008, 47, 5993.
(13) Sotgiu, G.; Galeotti, M.; Samori, C.; Bongini, A.; Mazzanti, A. Chem. Eur. J. 2011, 17, 7947.
(14) Furuya, T.; Ritter, T. Org. Lett. 2009, 11, 2860.
(15) Tang, P. P.; Wang, W. K.; Ritter, T. J. Am. Chem. Soc. 2011, 133, 11482.
(16) Dissoki, S.; Hagooly, A.; Elmachily, S.; Mishani, E. J. Label. Compd. Radiopharm. 2011, 54, 693.
(17) Noel, T.; Maimone, T. J.; Buchwald, S. L. Angew. Chem. Int. Ed.2011, 50, 8900.
(18) DesMarteau, D. D.; Xu, Z.-Q.;Witz, M. J. Org. Chem. 1992, 57, 629.
(19) Saha, G. B. Basics of PET Imaging: Physics, Chemistry, and Regulations, 2nd ed.; Springer: New York, 2010; pp 5-10.

