Supporting information of

"Ni(I)-Ni(III) Cycle in Buchwald-Hartwig Amination of Aryl Bromide Mediated by NHC-ligated Ni(I) Complexes"

Takahiro Inatomi, Yukino Fukahori, Yuji Yamada, Shinji Kanegawa, Yuji Koga, and Kouki Matsubara*

Department of Chemistry, Fukuoka University. Nanakuma 8-19-1, Fukuoka 814-0180, Japan.

Contents

S-1. General experimental details

All experiments were carried out under an inert gas atmosphere using standard Schlenk techniques and glove box (MBraun UniLab) as otherwise noted. THF, Toluene, hexane, benzene-d_6 were distilled from benzophenone ketyl and stored under a nitrogen atmosphere. Organic reagents used for coupling reactions were distilled just before use. Other reagents were used as receive. bis(4-methoxyphenyl)amine[1], N-(p-tolyl)-[1,1'-biphenyl]-4-amine[2], 4-fluoro-N-phenylaniline[1], N-(p-tolyl)naphthalen-1-amine[3] were prepared according to the literature methods. N-Heterocyclic carbene (IPr) was prepared according to the literature methods.[4] Nickel dimer : $[(\mu\text{-X})(\text{IPr})\text{Ni}]_2$ (X = Cl, Br)(**1a,b**) was prepared according to the literature methods.[5] Column chromatography of organic product was carried out using slica gel (Kanto Kagaku, silica gel 60N (spherical, neutral)). The ^{1}H NMR spectra were taken with a Bruker Avance-III400 Y plus 400 MHz spectrometer at room temperature. Chemical shifts (δ) were recorded in ppm from the solvent signal. The magnetic properties of the materials were investigated using a Quantum Design MPMS-5S superconducting quantum interference device (SQUID) magnetometer. The elemental analysis was carried out with YANACO CHN Corder MT-5, AUTO-SAMPLER, using aluminum pan, where the samples were held in a glove box. The UV-Vis measurements were taken with a Lambda 35 UV-Vis spectrometer using either a 10 mm quartz cell. The X-band EPR measurements were collected with a Bruker EMX Plus spectrometer equipped with a continuous flow N_2 cryostat. EPR simulation was conducted using PHI program.

S-2. Preparation of monomeric nickel(I) halide complexes [NiX(bpy)(IPr)] (2a, b) (X = Cl, Br)

Synthesis of [NiCl(bpy)(IPr)] (**2a**)

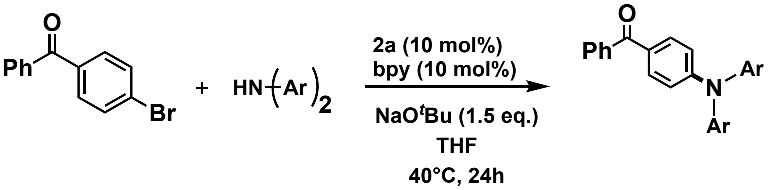
The Ni(I) complex **2a** was prepared according to the similar method with a literature.[6] In a glove box, [(μ-Cl)(IPr)Ni]$_2$ (**1-Cl**) (30 mg, 0.030 mmol), 2,2'-bipyridyl (9.5 mg, 0.061 mmol), and THF (1.0 mL) were added to a 5 mL screw-capped tube. After the compounds were dissolved, hexane (1.5 mL) was slowly added to the solution and cooled to -30ºC. Dark purple crystals of **2a** were obtained, after removal of the liquid and washing with small amount of cold hexane (60 mg, 0.094 mmol, 95% yield). ^{1}H NMR (C_6D_6): δ 0.81~1.59 (bs), 6.17 (bs), 6.77 (bs). Elemental analysis calcd (%) for $C_{37}H_{44}ClN_4Ni$: C, 69.55; H, 6.94; N, 8.77. Found: C, 69.18; H, 6.97; N, 8.44.

Synthesis of [NiBr(bpy)(IPr)] (**2b**)

The Ni(I) complex **2b** was prepared according to the similar method with literature.[6] In a glove box, [(μ-Br)(IPr)Ni]$_2$ (**1-Br**) (110 mg, 0.104 mmol), 2,2'-bipyridyl (40.7 mg, 0.261 mmol), and THF (15 mL) were added to a 25 mL screw-capped tube. After the compounds were dissolved, hexane (23 mL) was slowly added to the solution and cooled to -30ºC. Dark purple crystals of **2b** were obtained, after removal of the liquid and washing with cold hexane (132 mg, 0.193 mmol, 93% yield). ^{1}H NMR (C_6D_6): δ 1.39 (bs), 6.32 (bs), 6.77 (bs). Elemental analysis calcd (%) for $C_{37}H_{44}BrN_4Ni\cdot 2THF\cdot 1bpy$: C, 67.15; H, 6.97; N, 8.54; found: C, 67.25; H, 7.18; N, 8.45.

S-3. Buchwald-Hartwig amination to yield triarylamines

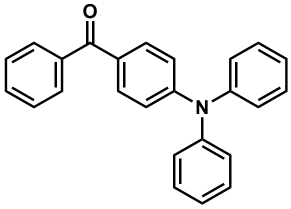
S-3-1. General procedure for amination reaction of 4-bromobenzophenone with aromatic amines.



In a glovebox, a Schlenk tube was charged with **2a** (31.9 mg, 0.05 mmol), 2,2'bipyridyl (15.6 mg, 0.10 mmol), aromatic amine (0.60 mmol), NaO^{t}Bu (71.1 mg, 0.75 mmol), 4-bromobenzophenone (130.6 mg, 0.50 mmol), and THF (0.2 mL). The reaction mixture was stirred at 40~80ºC for 24~48 h. After addition of water, the organic layer was extracted with CH_2Cl_2 for three times. The combined organic layer was washed with brine, dried over Na_2SO_4, and concentrated under reduced pressure. The residue was purified by column chromatography using silica gel eluted with dichloromethane/hexane (1/3) to obtain corresponding triarylamine.

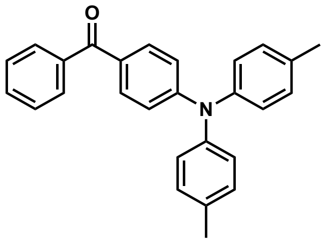
S-3-2. Characterization of triarylamines.

(4-(diphenylamino)phenyl)(phenyl)methanone)



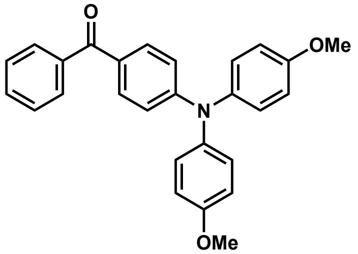
This reaction was conducted with diphenylamine and the reaction condition was 40ºC/24 h. The title compound was isolated as a yellow oil in 95% yield. (CAS No. 16911-33-4) ^{1}H NMR ($CDCl_3$): δ 7.77 (m, 3H), 7.69 (t, *J* = 8.6 Hz, 3H), 7.64-7.44 (m, 5H), 7.33 (t, *J* = 7.9 Hz, 4H), 7.18 (d, *J* = 7.4 Hz, 3H), 7.14 (t, *J* = 7.3 Hz, 2H), 7.01 (d, *J* = 8.9 Hz, 2H).

(4-(di-*p*-tolylamino)phenyl)(phenyl)methanone)



This reaction was conducted with di-*p*-tolylamine and the reaction condition was 40ºC/24 h. The title compound was isolated as a yellow oil in 91% yield. (4-(di-*p*-tolylamino)phenyl)(phenyl)methanone): (CAS No. 245442-58-4) ^{1}H NMR ($CDCl_3$): δ7.76 (d, *J* = 7.4 Hz, 2 H, *Benzoyl*), 7.68 (d, *J* = 8.9 Hz, 2 H, *Benzoyl*), 7.55 (t, *J* = 7.4 Hz, 1 H, *Benzoyl*), 7.46 (t, *J* = 7.3 Hz, 2 H, *Benzoyl*), 7.14 (d, *J* = 8.3 Hz, 4H, *tolyl*), 7.08 (d, *J* = 8.6 Hz, 4H, *tolyl*), 6.95 (d, *J* = 8.9 Hz, 2H, *Benzoyl*), 2.34 (s, 6H, -CH_3). ^{13}C NMR ($CDCl_3$): δ 195.2 (*C*=O), 152.3 (*Benzoyl*), 143.9 (*Tolyl*), 138.7 (*Benzoyl*), 134.6 (*Tolyl*), 132.0 (*Benzoyl*), 131.5 (*Benzoyl*), 130.3 (*Tolyl*), 129.6 (*Benzoyl*), 128.7 (*Benzoyl*), 128.1 (*Tolyl*), 126.2 (*Tolyl*), 118.3 (*Benzoyl*), 20.9 (-CH_3).

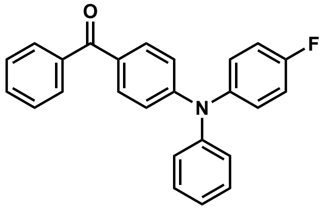
(4-(bis(4-methoxyphenyl)amino)phenyl)(phenyl)methanone



This reaction was conducted with bis(4-methoxyphenyl)amine and the reaction condition was 40°C/24 h. The title compound was isolated as a yellow oil in 91% yield. ^{1}H NMR ($CDCl_3$): δ 7.74 (d, *J* = 6.4 Hz, 2H, *Benzoyl*), 7.67 (d, *J* = 9.0 Hz, 2H, *Benzoyl*), 7.53 (t, *J* = 6.4 Hz, 1H, *Benzoyl*), 7.44 (t, *J* = 7.2 Hz, 2H, *Benzoyl*), 7.14 (d, *J* = 9.0 Hz, 4H, *Anisyl*), 6.88-6.84 (m, 6H), 3.81 (s, 6H, -*OMe*). ^{13}C NMR ($CDCl_3$): δ 195.1 (*C*=O), 157.1 (*Anisyl*), 152.8 (*Benzoyl*), 139.3 (*Anisyl*), 138.8 (*Benzoyl*), 132.1 (*Benzoyl*), 131.5 (*Benzoyl*), 129.6 (*Benzoyl*), 128.1 (*Benzoyl*), 127.9 (*Anisyl*), 116.7 (*Benzoyl*), 115.0 (*Anisyl*), 55.5 (-O*Me*).

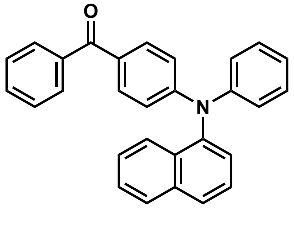
Elemental analysis calcd (%) for $C_{27}H_{23}NO_3$: C, 79.20; H, 5.66; N, 3.42; found: C, 78.96; H, 5.82; N, 3.26.

(4-((4-fluorophenyl)(phenyl)amino)phenyl)(phenyl)methanone



This reaction was conducted with 4-fluoro-N-phenylaniline and the reaction condition was 80ºC/48 h. The title compound was isolated as a yellow oil in 91% yield. ^{1}H NMR ($CDCl_3$): δ 7.77 (d, *J* = 7.0 Hz, 2H, *Benzoyl*), 7.72 (d, *J* = 8.8 Hz, 2H, *Benzoyl*), 7.55 (t, *J* = 7.4 Hz, 1H, *Benzoyl*), 7.46 (t, *J* = 6.8 Hz, 2H, *Ph*), 7.33 (t, *J* = 7.9 Hz, 2H, *Ph*), 7.19-7.12 (m, 5H), 7.04 (t, *J* = 8.6 Hz, 2H, *Ph*), 6.98 (d, *J* = 8.8 Hz , 2H, *Benzoyl*). ^{19}F NMR ($CDCl_3$): δ -116.93. ^{13}C NMR ($CDCl_3$): δ 195.1 (*C*=O), 161.1 (*Ph*, $^1J_{C\text{-}F}$ = 243.6 Hz), 151.9 (*Benzoyl*), 146.4 (*Ph*), 142.5 (*Ph*, $^4J_{C\text{-}F}$ = 3.1 Hz), 138.4 (*Benzoyl*), 132.0 (*Benzoyl*), 131.7 (*Benzoyl*), 129.7 (*Benzoyl*), 129.6 (*Ph*), 129.5 (*Benzoyl*), 128.1 (*Benzoyl*), 128.0 (*Ph,* $^3J_{C\text{-}F}$ = 8.2 Hz), 125.6 (*Benzoyl*), 124.7 (*Ph*), 119.0 (*Ph*), 116.7 (*Ph*, $^2J_{C\text{-}F}$ = 22.5 Hz). Elemental analysis calcd (%) for $C_{25}H_{18}FNO$: C, 81.72; H, 4.94; N, 3.81; found: C, 81.70; H, 5.01; N, 3.78.

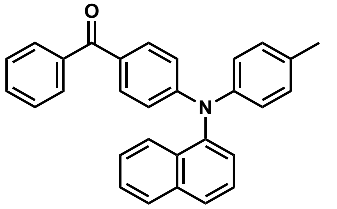
(4-(naphthalen-1-yl(phenyl)amino)phenyl)(phenyl)methanone



This reaction was conducted with N-phenylnaphthalen-1-amine and the reaction condition was 80ºC/48 h. The title compound was isolated as a yellow oil in 79% yield. ^{1}H NMR

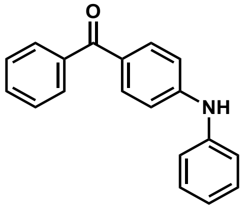
($CDCl_3$): δ 7.90 (t, *J* = 8.0 Hz, 2H, *Benzoyl*), 7.81 (d, *J* = 8.4 Hz, 1H, *Napthyl*), 7.73 (d, *J* = 7.2 Hz, 2H, *Benzoyl*), 7.67 (d, *J* = 8.7 Hz, 2H, *Benzoyl*), 7.50-7.36 (m, 7H), 7.28-7.21 (m, 4H), 7.06 (t, *J* = 7.0 Hz, 1H, *Benzoyl*), 6.88 (d, *J* = 9.0 Hz , 2H, *Benzoyl*). ^{13}C NMR ($CDCl_3$): δ 195.1 (*C*=O), 152.3 (*Benzoyl*), 146.6 (*Ph*), 142.1 (*Naphthyl*), 138.5 (*Benzoyl*), 135.2 (*Naphthyl*), 132.1 (*Benzoyl*), 131.9 (*Benzoyl*), 131.5 (*Benzoyl*), 130.9 (*Benzoyl*), 129.5 (*Ph*), 129.4 (*Naphthyl*), 128.8 (*Naphthyl*), 128.5(*Ph*), 128.0 (*Naphthyl*), 127.5(*Ph*), 127.4 (*Naphthyl*), 126.8 (*Naphthyl*), 126.4 (*Naphthyl*), 126.3(*Ph*), 124.3 (*Benzoyl*), 124.1 (*Naphthyl*), 123.7 (*Naphthyl*), 117.7 (*Benzoyl*). Elemental analysis calcd (%) for $C_{29}H_{21}NO\cdot 0.5H_2O$: C, 85.27; H, 5.43; N, 3.43; found: C, 85.20; H, 5.35; N, 3.14.

(4-(naphthalen-1-yl(p-tolyl)amino)phenyl)(phenyl)methanone



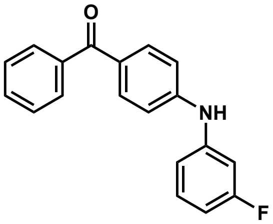
This reaction was conducted with N-(p-tolyl)naphthalen-1-amine and the reaction condition was 80ºC/48 h. The title compound was isolated as a yellow oil in 72% yield. ^{1}H NMR ($CDCl_3$): δ 7.91 (t, *J* = 7.3 Hz, 2H, *Benzoyl*), 7.82 (d, *J* = 7.7 Hz, 1H, *Naphthyl*), 7.73 (d, *J* = 8.2 Hz, 2H, *tolyl*), 7.65 (d, *J* = 9.5 Hz, 2H, *Benzoyl*), 7.53-7.47 (m, 3H), 7.44-7.37 (m, 4H), 7.15 (d, *J* = 8.6 Hz, 2H, *tolyl*), 7.10 (d, *J* = 8.2 Hz , 2H, *tolyl*), 6.81 (d, *J* = 8.6 Hz, 2H, *Benzoyl*), 2.31 (s, 3H, *tolyl*). ^{13}C NMR ($CDCl_3$): δ 195.4 (*C*=O), 152.7 (*Benzoyl*), 143.9 (*tolyl*), 142.3 (*Naphthyl*), 138.7 (*Benzoyl*), 135.3 (*tolyl*), 134.3 (*Naphthyl*), 132.2 (*Benzoyl*), 131.5 (*Benzoyl*), 131.0 (*Benzoyl*), 130.2 (*Benzoyl*), 129.6 (*tolyl*), 128.6 (*Naphthyl*), 128.4 (*Naphthyl*), 128.1 (*tolyl*), 127.4 (*Naphthyl*), 127.3 (*Naphthyl*), 126.8 (*Naphthyl*), 126.4 (*Naphthyl*), 124.8 (*Benzoyl*), 123.9 (*tolyl*), 117.1 (*Benzoyl*), 20.9 (-CH_3). Elemental analysis calcd (%) for $C_{30}H_{23}NO\cdot 0.3H_2O$: C, 85.89; H, 5.69; N, 3.34; found: C, 86.00; H, 5.55; N, 3.32.

phenyl(4-(phenylamino)phenyl)methanone



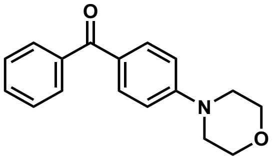
This reaction was conducted with aniline and the reaction condition was 60ºC/48 h. The title compound was isolated as a pale yellow solid in 96% yield. (CAS No. 4058-17-7) ^{1}H NMR (CDCl$_3$): δ 7.77 (dd, *J* = 6.7 Hz, 4H, *Benzoyl*), 7.55 (t, *J* = 7.5 Hz, 1H, *Benzoyl*), 7.47 (t, *J* = 7.4 Hz, 2H, *Benzoyl*), 7.35 (t, *J* = 7.9 Hz, 2H, *Ph*), 7.20 (d, *J* = 7.7 Hz, 2H, *Ph*), 7.09 (t, *J* = 7.4 Hz, 1H, *Ph*), 7.02 (d, *J* = 9.1 Hz, 2H, *Benzoyl*), 6.11 (brs, 1H, -N*H*). ^{13}C NMR (CDCl$_3$): δ 195.2 (*C*=O), 148.2 (*Benzoyl*), 140.6 (*Ph*), 138.7 (*Benzoyl*), 132.7 (*Benzoyl*), 131.6 (*Benzoyl*), 129.6 (*Benzoyl*), 129.5 (*Benzoyl*), 128.8 (*Benzoyl*), 128.1 (*Benzoyl*), 123.4 (*Ph*), 120.7 (*Ph*), 114.4 (*Benzoyl*).

(4-((3-fluorophenyl)amino)phenyl)(phenyl)methanone



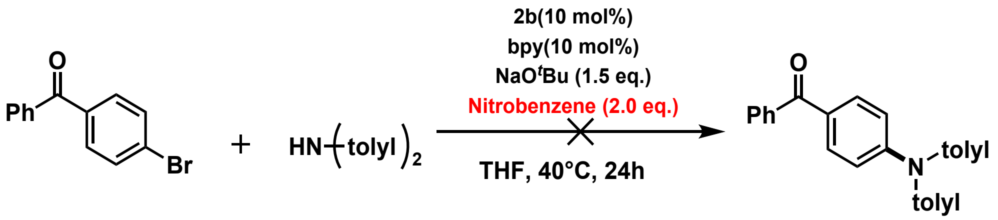
This reaction was conducted with aniline and the reaction condition was 60ºC/48 h. The title compound was isolated as a pale yellow solid in 94% yield. ^{1}H NMR (CDCl$_3$): δ 7.78 (m, 4H), 7.56 (t, *J* = 7.5 Hz, 1H, *Benzoyl*), 7.48 (t, *J* = 7.4 Hz, 2H *Benzoyl*), 7.27 (m, 1H), 7.07 (d, *J* = 7.7 Hz, 2H, *Benzoyl*), 6.93 (m, 2H), 6.74 (m, 1H) 6.22 (brs, 1H, -N*H*). ^{19}F NMR (CDCl$_3$): δ -111.54. ^{13}C NMR (CDCl$_3$): δ 195.2 (*C*=O), 164.8 (*Ph*, $^1J_{C\text{-}F}$ = 243.7 Hz), 147.0 (*Benzoyl*), 142.8 (*Ph*, $^3J_{C\text{-}F}$ = 10.7 Hz), 138.5 (*Benzoyl*), 132.6 (*Benzoyl*), 131.8 (*Benzoyl*), 130.7 (*Ph*, $^3J_{C\text{-}F}$ = 9.7 Hz), 129.6 (*Benzoyl*), 128.2 (*Benzoyl*), 115.3 (*Benzoyl*), 115.2 (*Ph*, $^4J_{C\text{-}F}$ = 2.8 Hz), 109.6 (*Ph*, $^2J_{C\text{-}F}$ = 24.4 Hz), 106.8 (*Ph*, $^2J_{C\text{-}F}$ = 21.1 Hz). Elemental analysis calcd (%) for $C_{19}H_{14}FNO$: C, 78.33; H, 4.84; N, 4.81; found: C, 78.08; H, 4.81; N, 4.75.

(4-morpholinophenyl)(phenyl)methanone



This reaction was conducted with aniline and the reaction condition was 80ºC/48 h. The title compound was isolated as a pale yellow solid in 61% yield. (CAS No. 24758-49-4) ^{1}H NMR (CDCl$_3$): δ 7.80 (d, *J* = 9.0 Hz, 2H, *Benzoyl*), 7.74 (d, *J* = 7.7 Hz, 2H, *Benzoyl*), 7.54 (t, *J* = 7.4 Hz, 1H, *Benzoyl*), 7.46 (t, *J* = 7.4 Hz, 2H, *Benzoyl*), 6.89 (d, *J* = 8.9 Hz, 2H, *Benzoyl*), 3.86 (t, *J* = 4.9 Hz, 4H, *Morpholyl*), 3.32 (t, *J* = 5.0 Hz, 4H, *Morpholyl*). ^{13}C NMR (CDCl$_3$): δ 195.2 (*C*=O), 154.0 (*Benzoyl*), 138.7 (*Benzoyl*), 132.4 (*Benzoyl*), 131.6 (*Benzoyl*), 129.6 (*Benzoyl*), 128.1 (*Benzoyl*), 127.8 (*Benzoyl*), 113.2 (*Benzoyl*), 66.6 (*Morpholyl*), 47.6 (*Morpholyl*).

S-4. Ni(I)/NHC catalyzed amination in the presence of nitrobenzene



In a glovebox, a 20 mL Schlenk tube was charged with **2b** (34.0 mg, 0.05 mmol), 2,2'-bipyridyl (8.0 mg, 0.05 mmol), di(*p*-tolyl)amine (0.60 mmol), NaO^{t}Bu (71.1 mg, 0.75 mmol), 4-bromobenzophenone (130.6 mg, 0.50 mmol), nitrobenzene (51.2 μL, 1.0 mmol), and THF (0.2 mL). The reaction mixture was stirred at 40°C for 24 h. In ^{1}H NMR spectra of the crude mixture, the corresponding product, 4-N,N-di(p-tolyl)aminobenzophenone were not detected at all as shown in Figure S1.

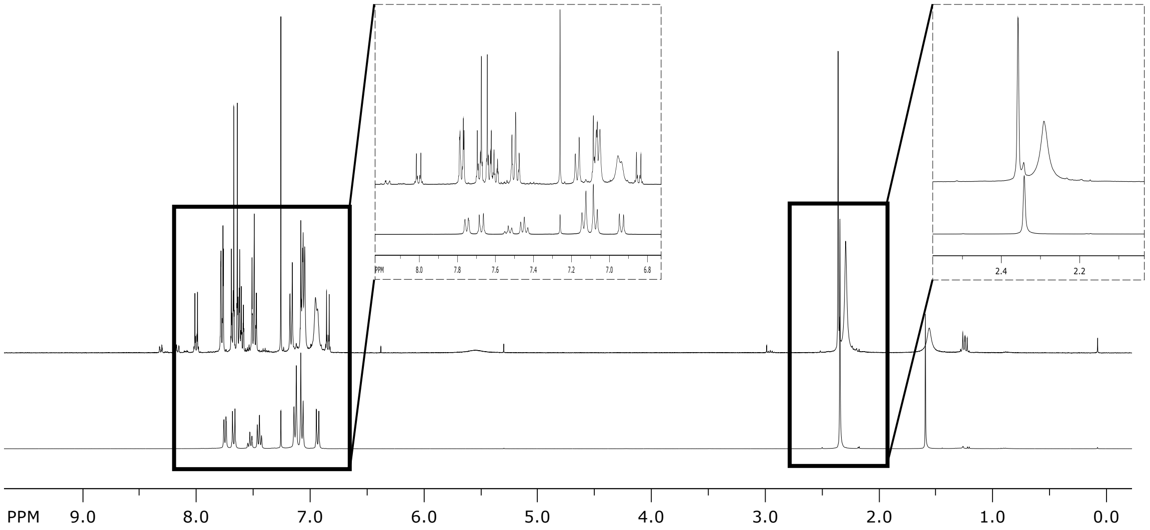
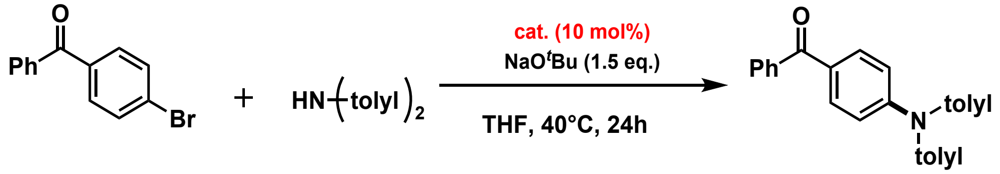


Figure S1. ^{1}H NMR spectra of the crude mixture (top) and an authentic sample of 4-N,N-di(p-tolyl)aminobenzophenone (bottom).

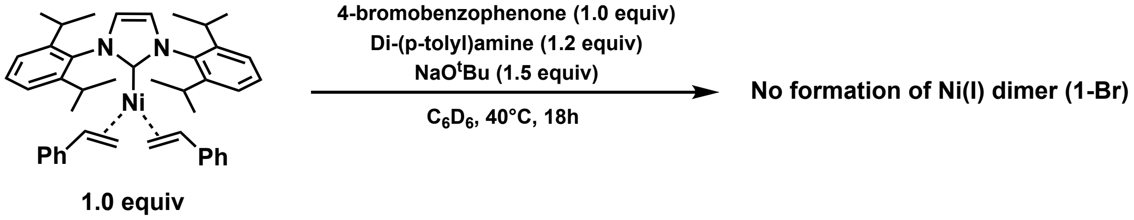
S-5. [Ni(styrene)$_2$(IPr)] catalyzed amination with 4-bromobenzophenone



Catalyst: 2b 91%
: Ni(styrene)$_2$(IPr) 88%

In a glovebox, a 20 mL Schlenk tube was charged with **2b** (34.0 mg, 0.05 mmol) or Ni(0)(styrene)$_2$(IPr) (32.8 mg, 0.05 mmol), 2,2'-bipyridyl (8.0 mg, 0.05 mmol), di(*p*-tolyl)amine (0.60 mmol), NaO^{t}Bu (71.1 mg, 0.75 mmol), 4-bromobenzophenone (130.6 mg, 0.50 mmol), and THF (0.2 mL). The reaction mixture was stirred at 40°C for 24 h. After addition of water, the organic layer was extracted with AcOEt for three times. The combined organic layer was washed with brine and dried over Na_2SO_4, filtered and concentrated in vacuo. The residue was purified with silica-gel column chromatography eluted with dichloromethane/hexane (1/3) to obtain the corresponding product, 4-N,N-di(p-tolyl)aminobenzophenone as a yellow oil in 91% (by **2b**) or 88% yield (by Ni(0)).

The result suggested that the active key compound seems to be the same under these conditions with Ni(I) and Ni(0). However, the ^{1}H NMR spectra of both the crude mixtures after the catalytic reaction in the presence of Ni(0) and Ni(I) complexes were completely different from each other (Figure S2).



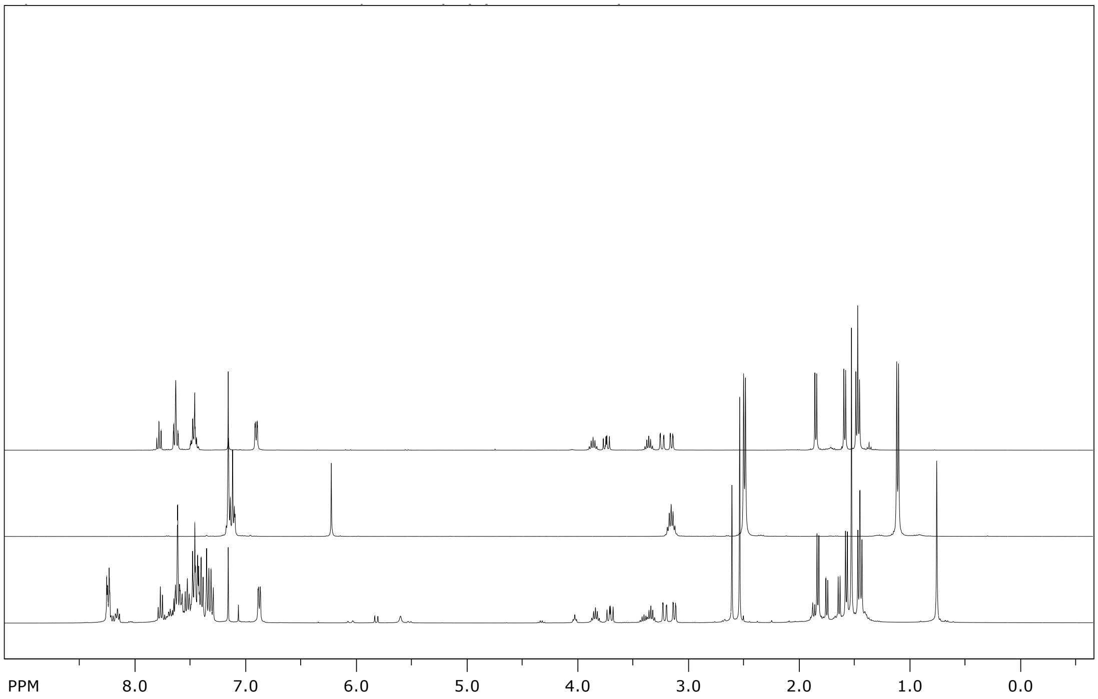


Figure S2. Stacked ^{1}H NMR spectra of [Ni(styrene)$_2$(IPr)] (top), [Ni(μ-Br)(IPr)]$_2$ (midle), and reaction mixture (bottom)

S-6. Stoichiometric reaction of Ni(I) complex (1a, 2a) with diarylamines

S-6-1. Stoichiometric reaction of Ni(I) complex 2a with diarylamines

In a glovebox, complex **2a** (100 mg, 0.16 mmol), diarylamine (0.16 mmol) and NaO^{t}Bu (34.0 mg, 0.35 mmol) were placed in a 20 mL Schlenk tube in THF (2 mL). The suspension was stirred for 1 hour at room temperature to give a dark purple solution. The volatiles were removed under reduced pressure, the residue was extracted into THF, filtered through celite and evaporated to dryness. The residue was washed with hexane to give **3a-b** as a black solid.

Complex **3a**

The title compound was isolated as a black solid in 24% yield. Elemental analysis calcd (%) for $C_{49}H_{54}N_5Ni\cdot0.5Et_2O$: C, 75.74; H, 7.35; N, 8.66. Found: C, 75.74; H, 7.35; N, 8.66.

Complex **3b**

The title compound was isolated as a black solid in 12% yield. Elemental analysis calcd (%) for $C_{51}H_{58}N_5Ni\cdot0.3THF$: C, 76.30; H, 7.42; N, 8.50. Found: C, 76.30; H, 7.44; N, 7.78.

S-6-2. Stoichiometric reaction of Ni(I) complex 1a with diarylamines

In a glovebox, dimer **1a** (50.0 mg, 0.052 mmol), diphenylamine (35.1 mg, 0.207 mmol), and NaO*ᵗ*Bu (24.0 mg, 0.249 mmol) were placed in a 20 mL Schlenk tube in toluene (2 mL). The suspension was stirred for 10 minutes at room temperature to give a dark blue solution. The volatiles were removed under reduced pressure, the residue extracted into toluene and evaporated to dryness. The residue was washed with hexane to give **4** as a purple solid (53.2 mg, 83 % yield).Elemental analysis calcd. (%) for $C_{39}H_{46}N_3Ni{\cdot}Et_2O$: C, 74.89; H, 8.19; N, 6.09. Found: C, 74.63; H, 8.24; N, 6.54.

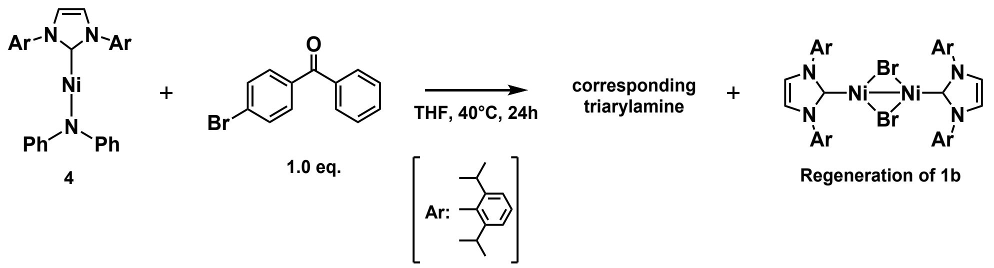
S-7. Stoichiometric reaction of Ni(I) amide complexes (3a, 4) with 4-bromobenzophene

S-7-1. Using complex 3a as a substrate

In a glovebox, a Schlenk tube was charged with **3a** (50 mg, 0.065 mmol), 2,2'-bipyridyl (51 mg, 0.33 mmol), 4-bromobenzophenone (17 mg, 0.065 mmol), and THF (1.0 mL). The reaction mixture was stirred at 40ºC for 24 h. After addition of water, the organic layer was extracted with CH_2Cl_2 for three times. The combined organic layer was washed with brine and dried over Na_2SO_4, and concentrated under reduced pressure. The residue was purified by column chromatography using silica gel eluted with dichloromethane/hexane (1/3) to obtain corresponding triarylamine (16.3 mg, 0.047 mmol, 72 % yield).

S-7-2. Using complex 4 as a substrate

The complex **4** (30 mg, 0.049 mmol), 4-bromobenzophenone (13 mg, 0.049 mmol), and THF (0.2 mL) were treated, being similar to the above method to obtain the corresponding triarylamine (12.0 mg, 0.034 mmol, 70 % yield). By ^1H NMR analysis, we detected that dimer complex(1-Br) was regenerated.



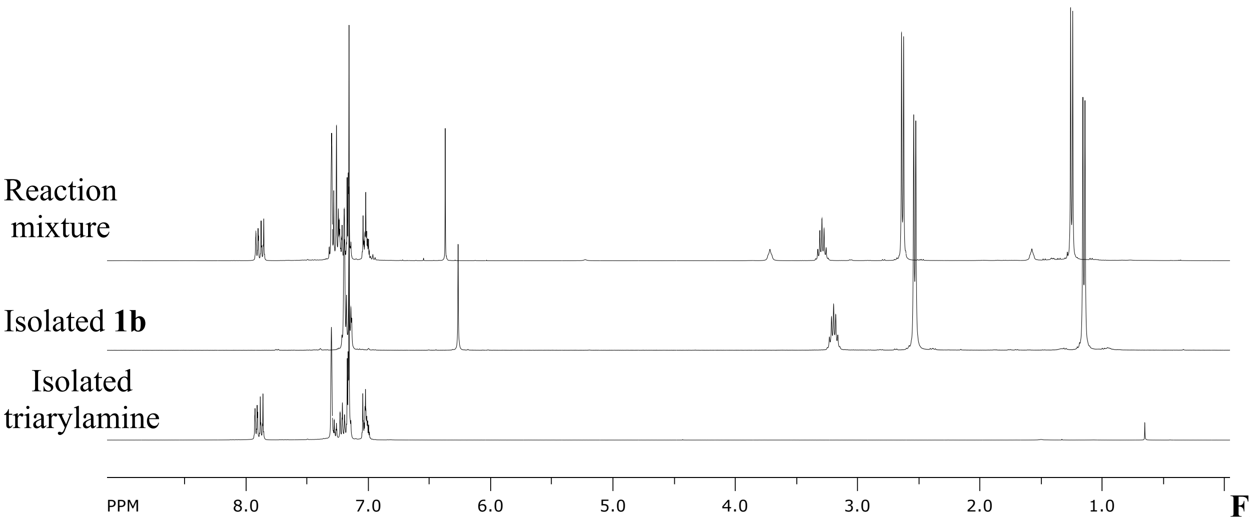


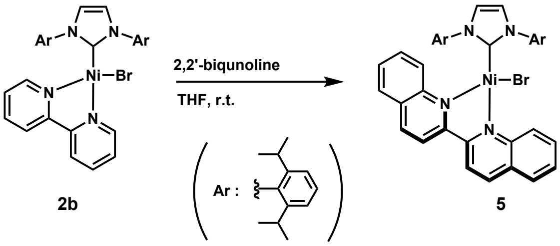
Figure S3. Comparison of the ^{1}H NMR spectra (400 MHz, C_6D_6) for the reaction mixture (top) from **4** and 4-bromobenzophenone, isolated **1b** (middle) and isolated 4-N,N-diphenylaminobenzophenone (bottom), strongly suggesting that the Ni(I) dimer **1b** regenerated from **4** in the reaction with the aryl bromide, accompanied with formation of the triarylamine.

S-8. Catalytic reaction of diphenylamine with 4-bromobenzophenone using 3a as catalysts.

In a glovebox, a Schlenk tube was charged with **3a** (38.6 mg, 0.050 mmol), 4-bromobenzophenone (130.6 mg, 0.50 mmol), diphenylamine (101.5 mg, 0.60 mmol), 2,2’-bipyridyl (46.9 mg, 0.30 mmol), NaO*ᵗ*Bu (71.1 mg, 0.74 mmol), and THF (0.2 mL). The reaction mixture was stirred at 40ºC for 24 h. After addition of water, the organic layer was extracted with CH_2Cl_2 for three times. The combined organic layer was washed with brine, dried over Na_2SO_4, and concentrated under reduced pressure. The residue was purified by column chromatography using silica gel eluted with dichloromethane/hexane (1/3) to obtain corresponding triarylamine (82.8 mg, 0.237 mmol, 47 % yield).

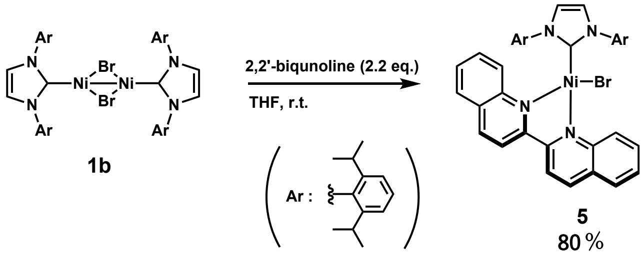
S-9. Ligand exchange reactions of 2a or 3a with 2,2'-biquinoline at room temperature.

S-9-1. Analysis of UV-Vis spectroscopy in the reaction of complex 2b with 2,2'-biquinoline to form complex 5.



In a glove box, a quartz cell was charged with a solution of complex **2b** in THF (200 μM; 1.0 mL, 2.0 μM) and a solution of 2,2'-biquinoline in THF (200 μM; 1.0 mL, 2.0 μM).

S-9-2. Preparation of complex 5.



The Ni(I) complex **5** was prepared according to the similar method with a literature.[3] In a glove box, [(μ-Br)(IPr)Ni]$_2$ (**1b**) (80 mg, 0.076 mmol), 2,2'-biquinoline (42.8 mg, 0.167 mmol, 2.2 eq.), and THF (1.0 mL) were added to a Schlenk tube. After the compounds were dissolved, hexane (2.0 mL) was slowly added to the solution and cooled to -30ºC. The obtained dark-blue crystals of **5** were washed with small amount of cold hexane and dried (95.1 mg, 80% yield). ^{1}H NMR (C_6D_6): δ 14.34 (bs), 11.54 (bs), 6.55 (bs), 5.99 (bs), 1.72 (bs), -0.25 (bs). Elemental analysis calcd (%) for $C_{45}H_{48}BrN_4Ni$: C, 68.98; H, 6.18; N, 7.15. Found: C, 68.24; H, 6.32; N, 6.95.

Because the complex **5** was pooly characterized, we observed EPR spectrum of **5** in THF glass at 90 K, which was compared with that of **2b** (Figure S4). Because these complexes have similar bidentate ligands, bipyridine and biquinoline, the spectra were also similar, as expeced.

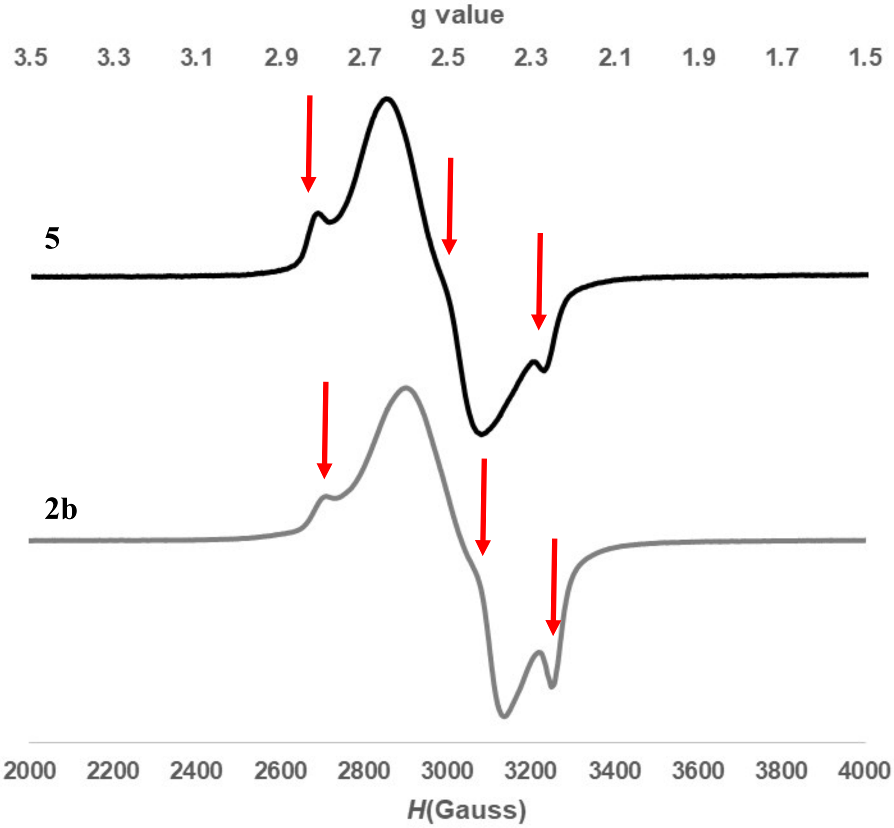


Figure S4. EPR spectra of **5** (top: $g_x = 2.505$, $g_y = 2.27$, $g_x = 2.085$) and **2b** (bottom: $g_x = 2.484$, $g_y = 2.229$, $g_x = 2.07$) in THF glass at 90 K (-183 °C).

S-10. Continuous wave X-band electron paramagnetic resonance (CW X-band EPR) spectroscopy.

CW X-band EPR spectrum was recorded on a Bruker EMX Plus spectrometer equipped with a continuous flow N_2 cryostat. The EPR spectrum was recorded under nonsaturating conditions using the microwave frequency of 9.414 GHz, field modulation of 100 kHz, modulation amplitude of 4 G, microwave power of 0.11 mW, respectively. The EPR spectrum was simulated with the PHI program[7], which is based on the following spin Hamiltonian of $S = 1/2$ system:

$$\hat{H}_{\text{spin}} = g\mu_{\text{B}}\vec{S}\vec{H}$$

where g is the g tensor, μ_{B} is the Bohr magneton, S is the electronic spin and H is the magnetic field.

The best simulation was reproduced by the superimposition of Ni(I) and Ni(III) species. The spin Hamiltonian parameters were determined to be as follows; $g_{x,y} = 2.098$ and $g_z = 2.530$, $W_{x,y} = 0.11$ and $W_z = 0.22$ GHz for Ni(I) species and $g_x = 2.560$, $g_y = 2.309$ and $g_z = 2.009$, $W_x = 0.25$, $W_y = 0.14$ and $W_z = 0.05$ GHz for Ni(III) species, where W is the linewidth (Figure S5). The integral ratios of these simulated spectra have also been determined as shown in Figure S6.

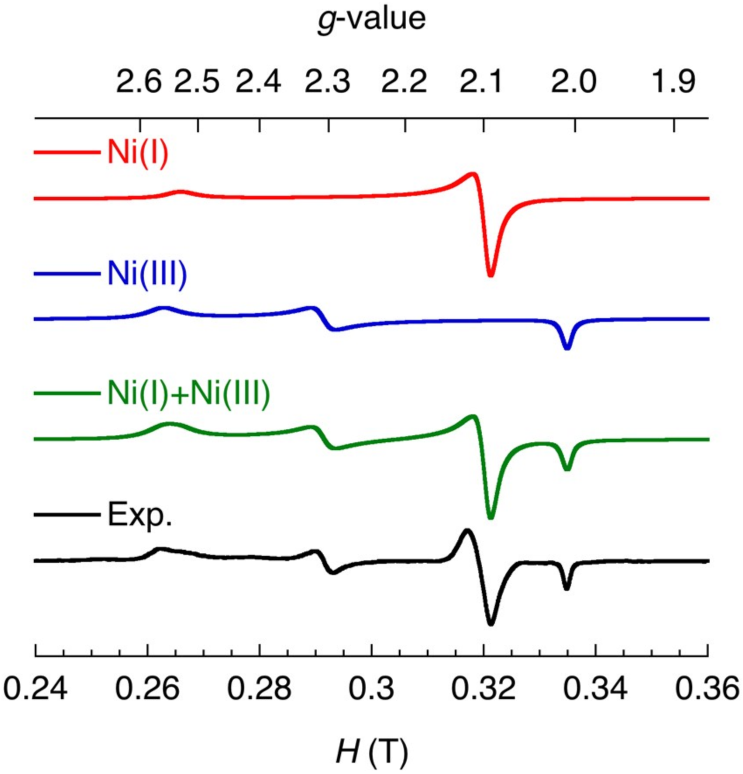


Figure S5. X-band EPR spectrum for the reaction mixture of **4** with 1 equiv of 4-bromoanisole (THF glass, at –178ºC) (black), which can be reproduced by those indicated with computer simulation of proposed compounds, mononuclear Ni(I) intermediate (red, axial: $g_{x,y}$ = 2.098 and g_z = 2.530, $W_{x,y}$ = 0.11 and W_z = 0.22 GHz) and Ni(III) product (blue, rhombic: g_x = 2.560, g_y = 2.309 and g_z = 2.009, W_x = 0.25, W_y = 0.14 and W_z = 0.05 GHz) The green represents a data simulated to the two components simultaneously.

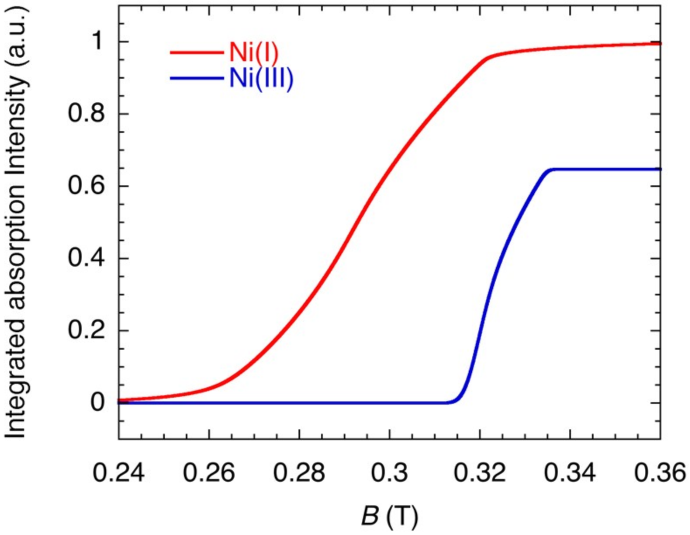


Figure S6. Integrated absporbtion intensity vs. B(T), calculated using the simulated spectra of Ni(I) and Ni(III). It shows the ratio of the two compounds to some extent. Because the intensity of EPR varies to some extent according to the transition probability (Boltzmann distribution) at a certain temperature inherent in these Ni (I) and Ni (III) complexes, the integral ratio of the EPR signal is not necessarily the ratio of the amounts of these compounds.

S-11. Computational details.

All the calculations were performed using the GAUSSIAN 09 package.[8] The geometry optimization was performed using the density functional theory (DFT) without symmetry restriction. The subsequent harmonic vibrational analyses were carried out to confirm the nature of the stationary points, yielding no imaginary frequency for the minima.

The dissociation energy of **3a** to **4** with bpy was obtained using the dispersion-corrected B3LYP functional[9] with Becke–Johnson damping[10] (B3LYP-D3BJ) and applying the standard basis set of 6-31G(d,p) to all atoms (Figure S7). We also corrected the basis set superposition error (BSSE) by a counterpoise method[11] for more accurate estimation.

For the EPR parameter calculation, more expensive basis sets were utilized because of sensitive dependence on basis set. The B3LYP functional and 6-31G(d) basis set for all atoms were applied in the full geometry optimization, and the single-point calculation for g values at the obtained structure was performed with def2-TZVPP, which was reported to show the relatively good agreement with experimental data of Ni(I) complex.[10] In order to confirm the functional dependency, another famous functional, BP86, was also applied to the geometry optimization and sequential EPR parameter calculation with the basis set of 6-31G(d) and showed similar tendency with B3LYP one (Table S1). Furthermore, complex stability of the possible candidates for reaction intermediate, i.e. Ni(III) complexes having square planar (SP) or pyramidal (Th) coordination was examined by estimation of Gibbs free energies at the condition of 298.15 K and 1 atm. In order to confirm the complex stability more accurately, the relative Gibbs free energies were calculated at B3LYP-D3BJ/6-31G(d,p) (Figure S8).

All the computation was carried out using the computer facilities at Research Institute for Information Technology, Kyushu University.

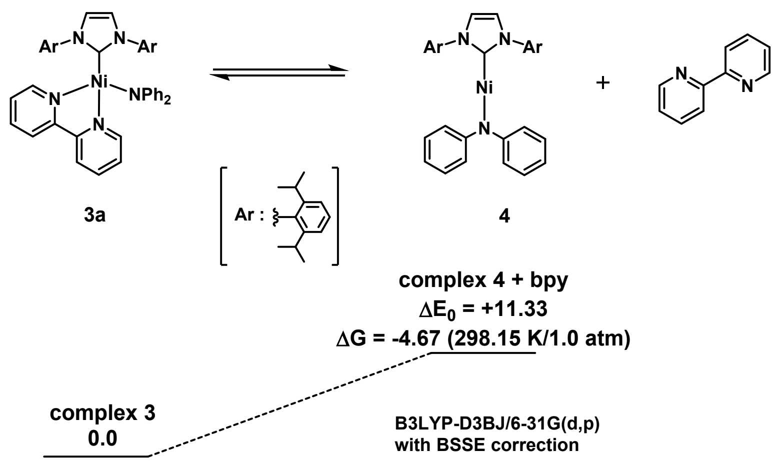


Figure S7. Dissociative energy including ZPE correction (*ΔE₀*) and Gibbs energy (*ΔG*) in kcal/mol from **3a** to **4** with bpy calculated with B3LYP-D3BJ/6-31G(d,p) level, including BSSE correction.

Table S1. Calculated *g* values ($g_1 > g_2 > g_3$) of complex **4** and its complexes coordinated by 4-bromoanisole reactant and THF solvent, and possible candidates for reaction intermediate, which are Ni(III) complexes having square planar (SP) or pyramidal (Th) coordination.

	B3LYP/def2-TZVPP[a]			BP86/6-31G		
	g_1	g_2	g_3	g_1	g_2	g_3
4	2.696	2.547	2.245	2.684	2.264	2.093
4-BrAn	2.614	2.517	2.191	2.224	2.199	2.089
4-THF	2.515	2.324	2.134	2.399	2.281	2.026
Ni(III)_SP (S = 1/2)	2.032	2.018	2.009	2.215	2.060	2.033
Ni(III)_Th (S = 1/2)	2.376	2.326	2.159	2.210	2.144	2.024
Ni(III)_SP (S = 3/2)	3.465	3.325	3.115	2.986	2.763	2.645

[a] Single point calculation at the structure optimized with B3LYP/6-31G.

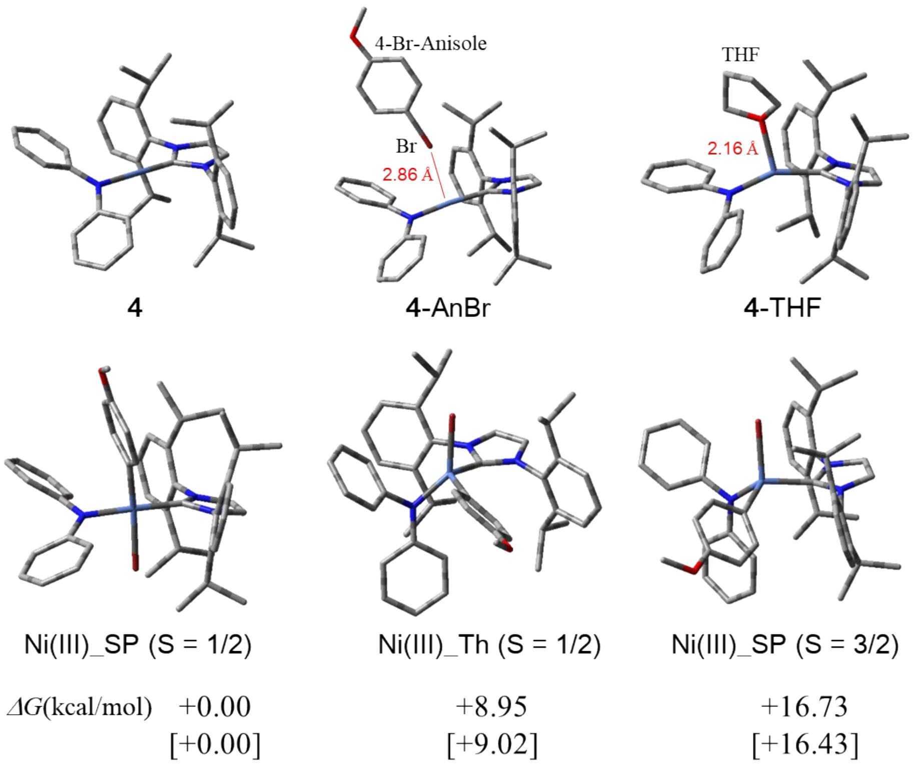


Figure S8. Optimized structures of complex **4** and its complexes coordinated by 4-bromoanisole reactant and THF solvent, and possible candidates of Ni(III) for reaction intermediate calculated at B3LYP/6-31G(d) level. Relative Gibbs free energies (ΔG) were also estimated at the condition of 298.15 K and 1 atm. The values in brackets indicates the relative Gibbs free energies calculated at the B3LYP-D3BJ/6-31G(d) level.

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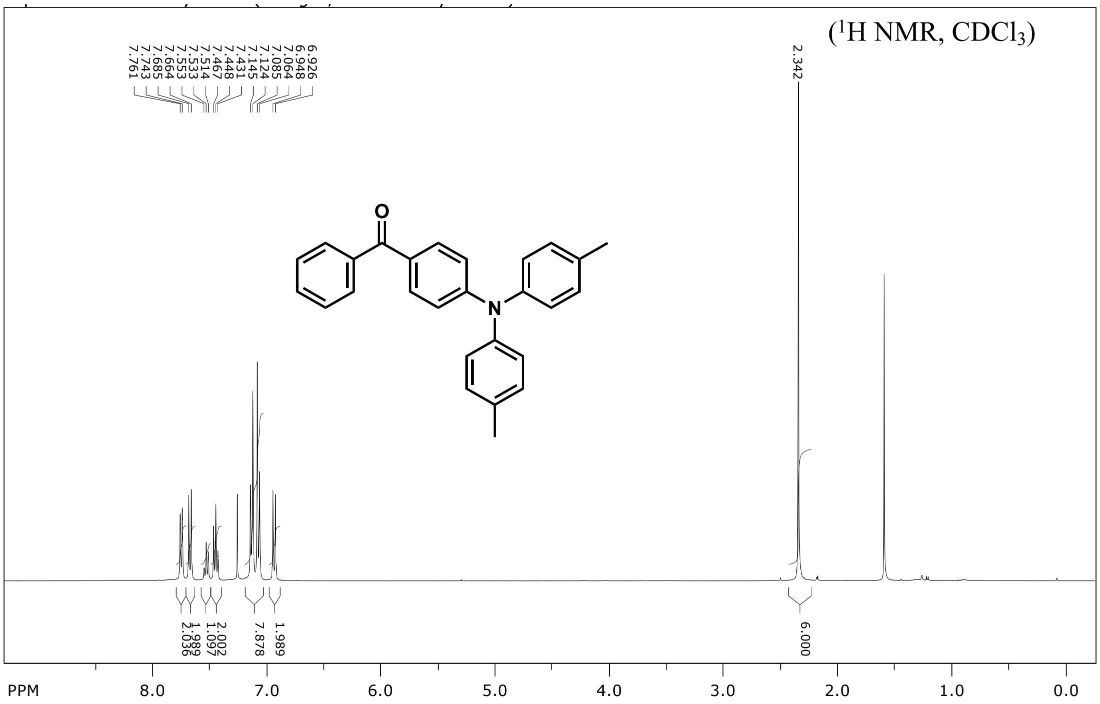
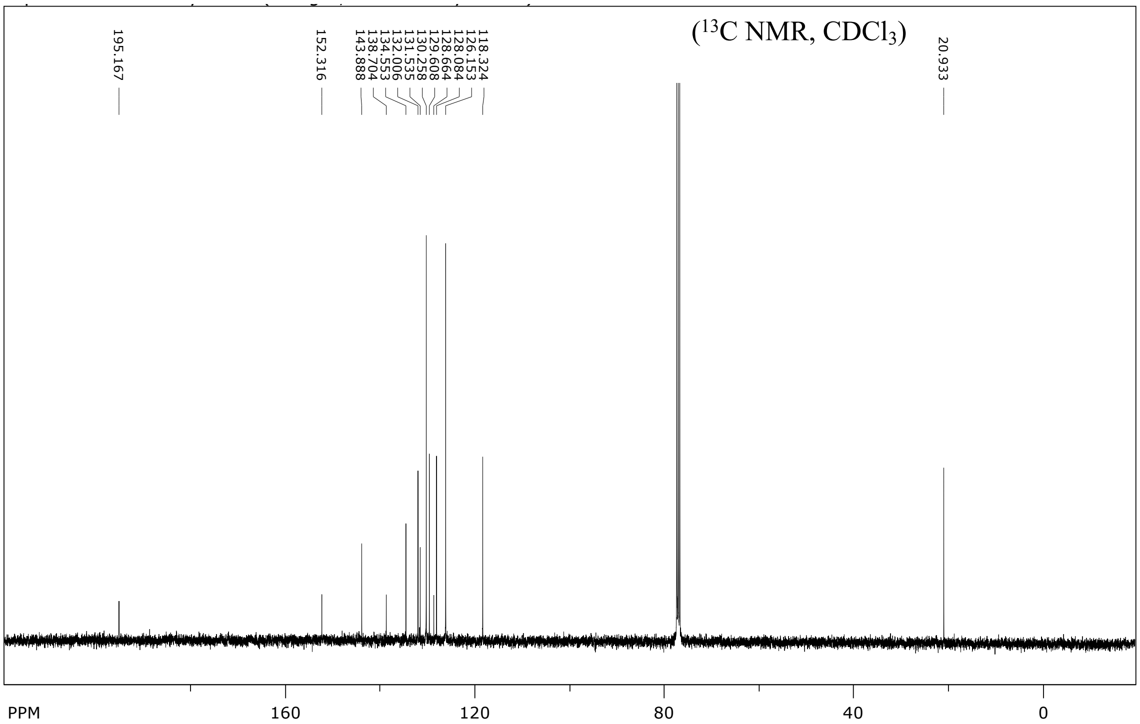
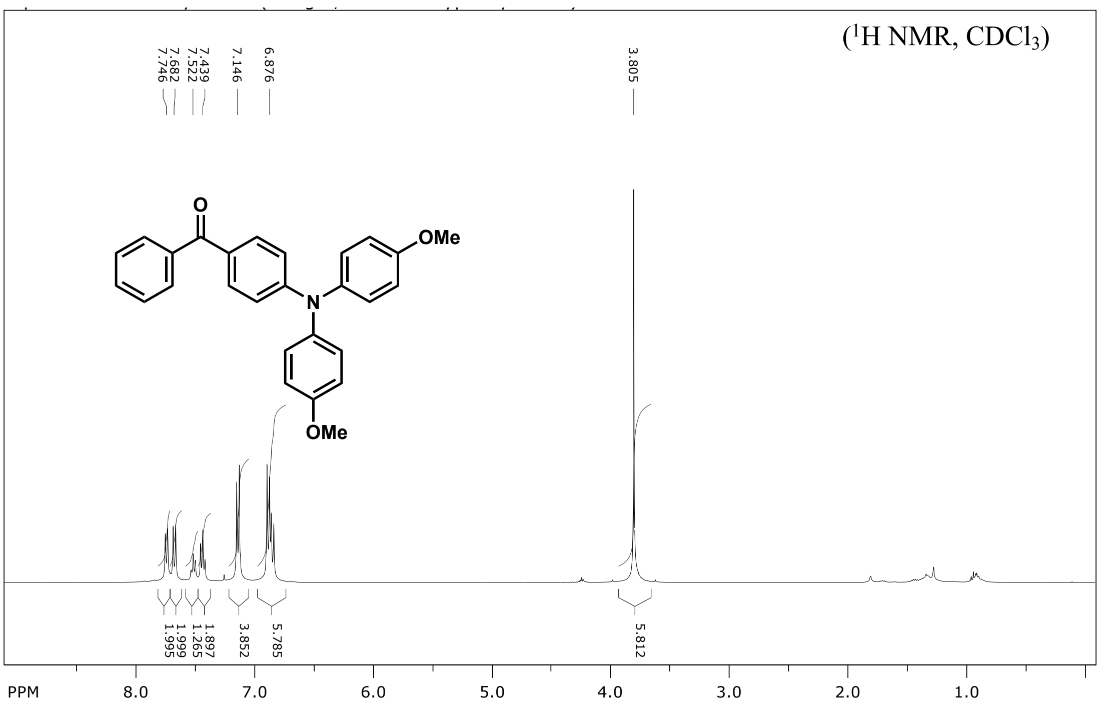
Spectra for the Isolated Compounds.



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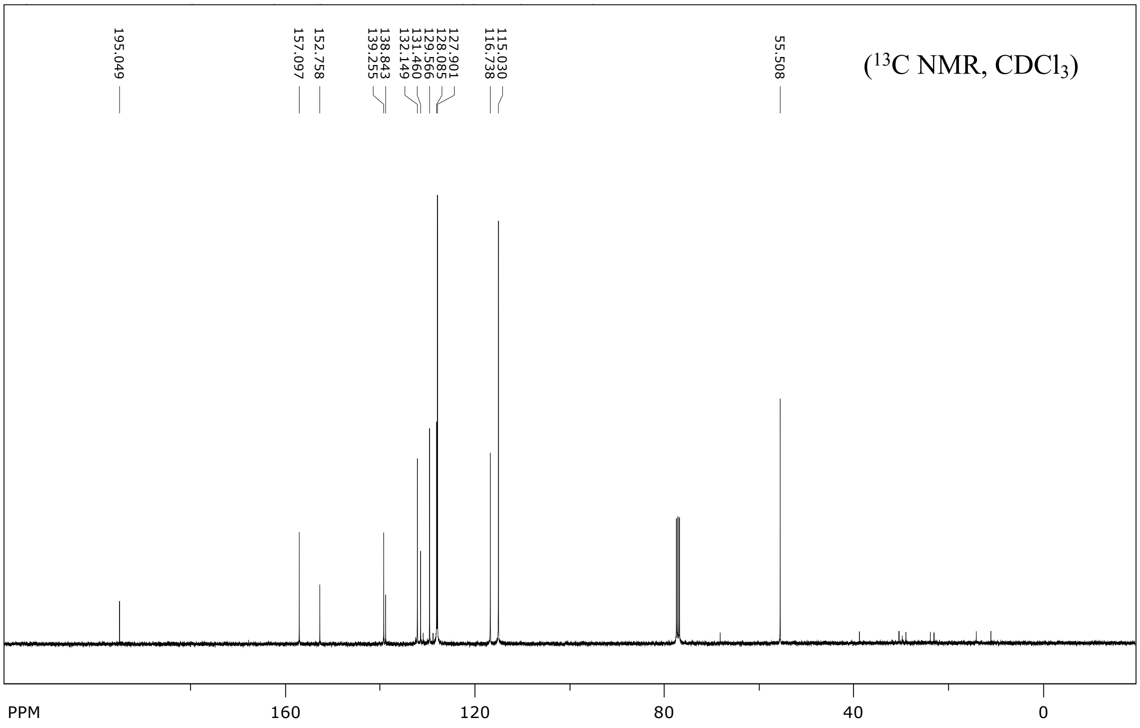
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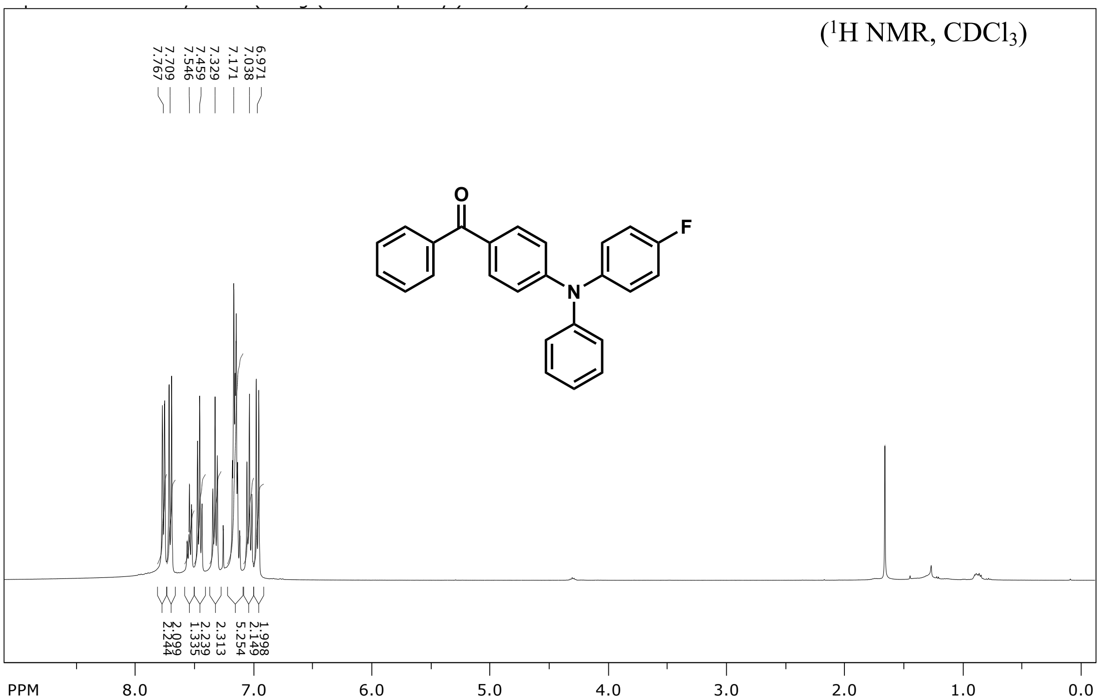
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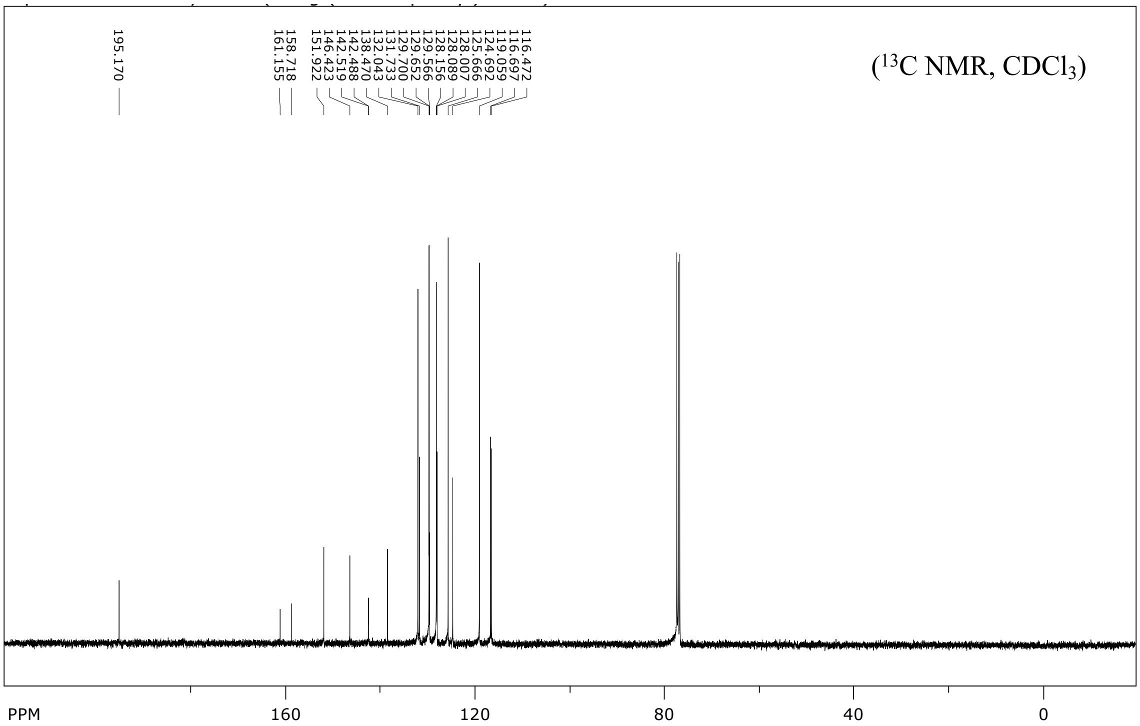
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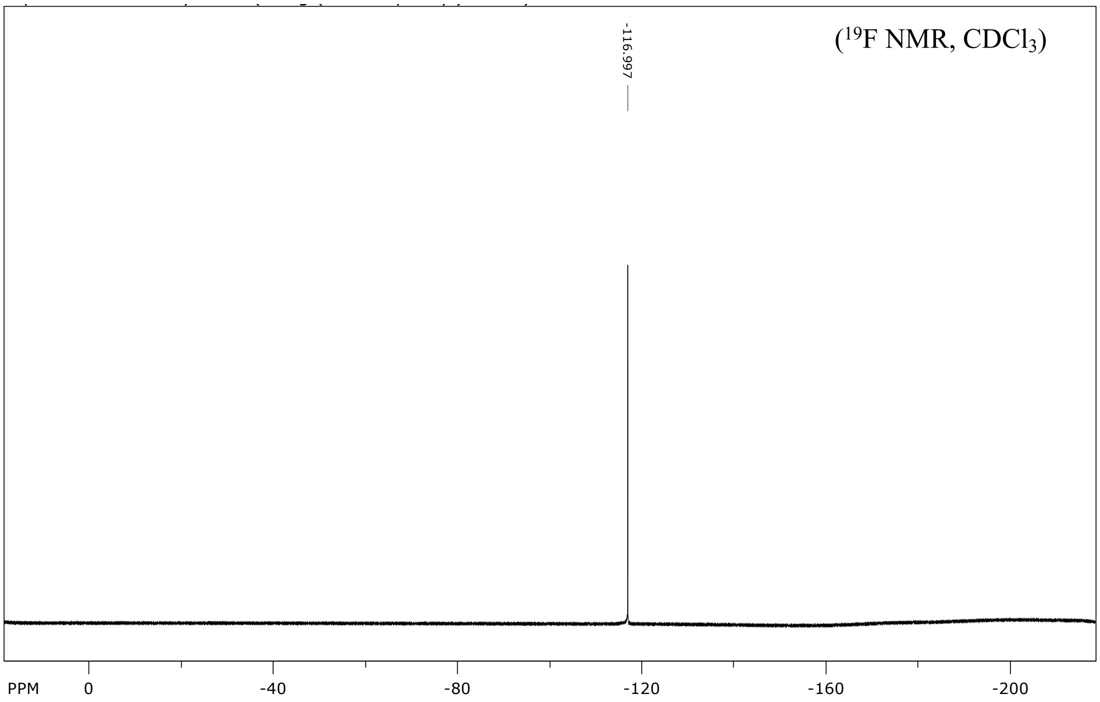

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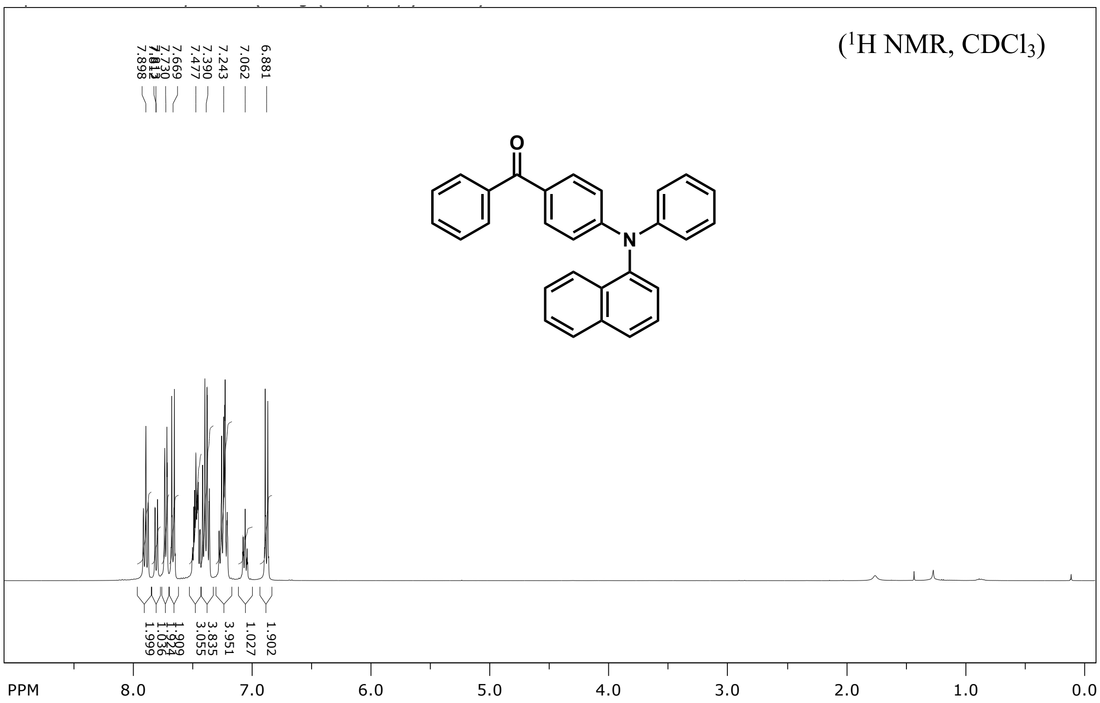
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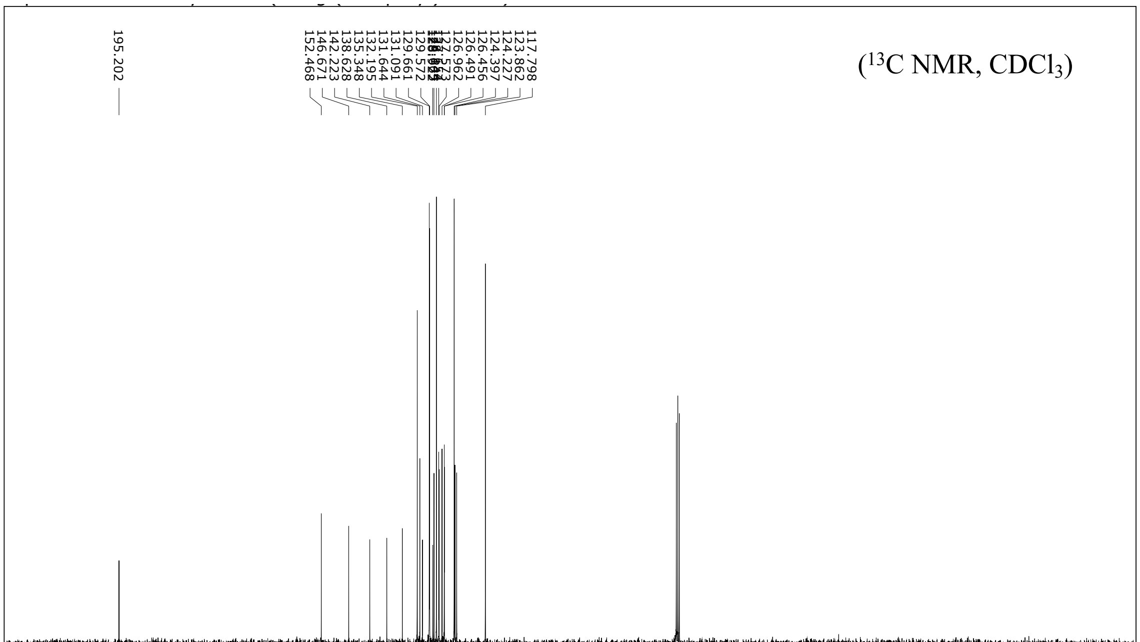
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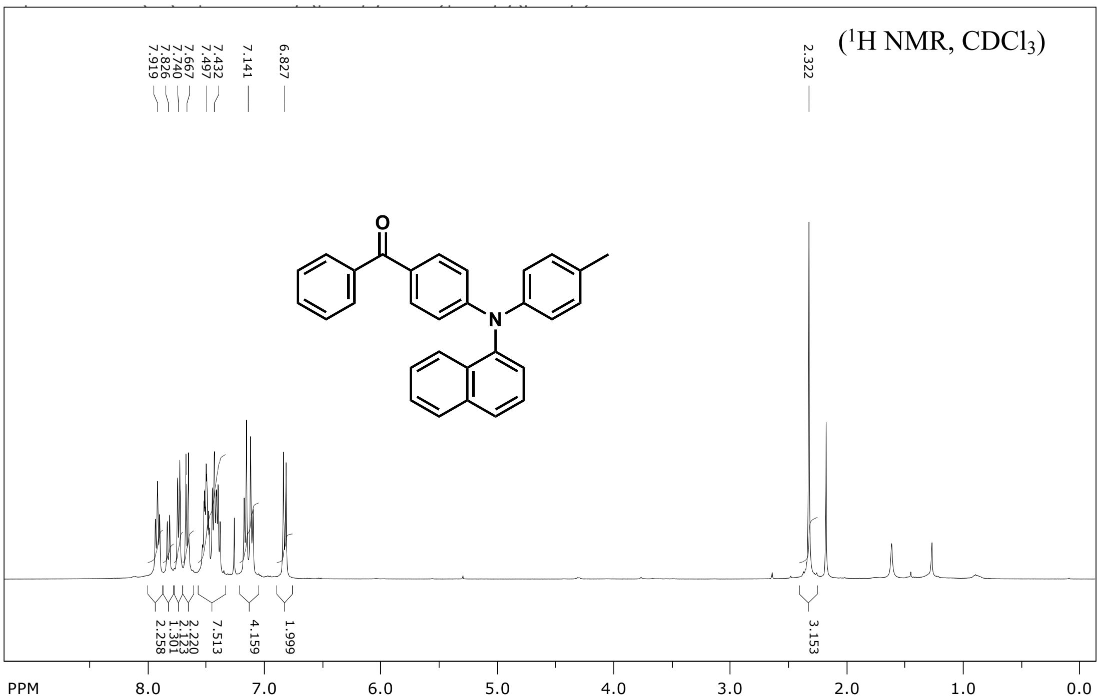
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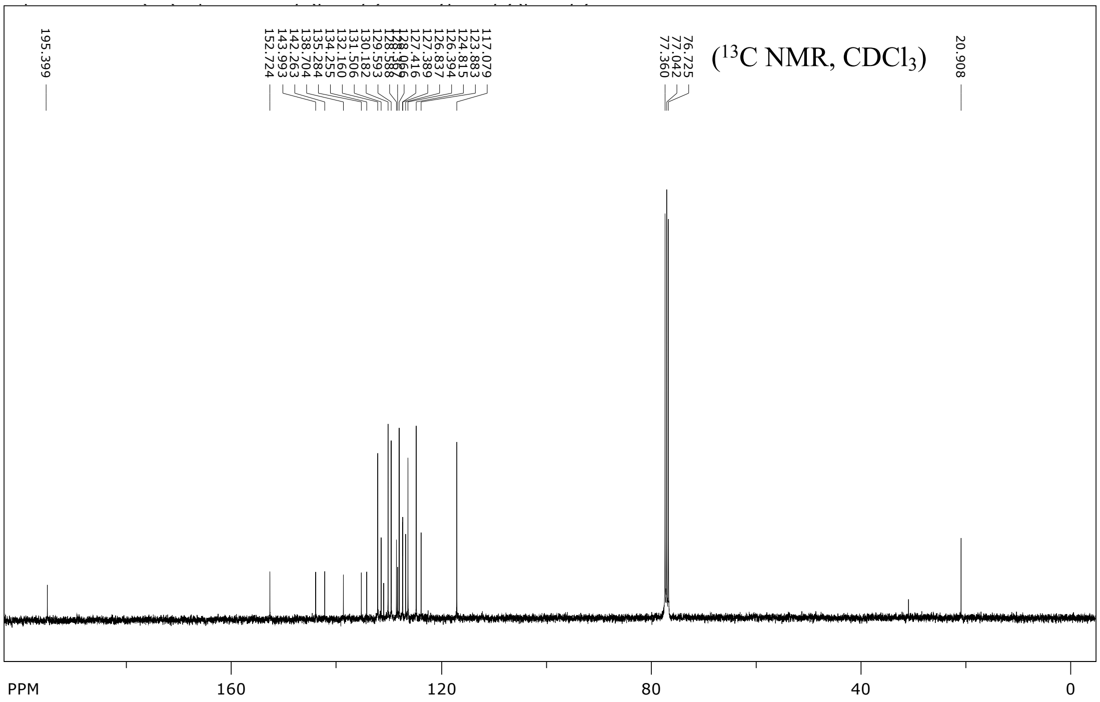
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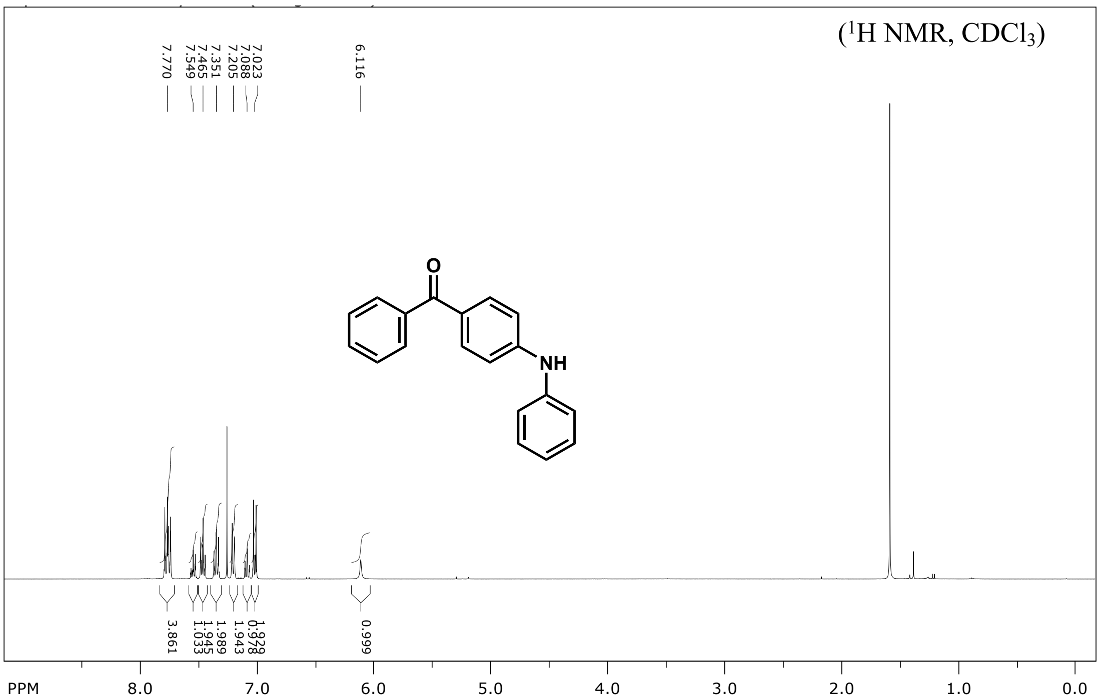
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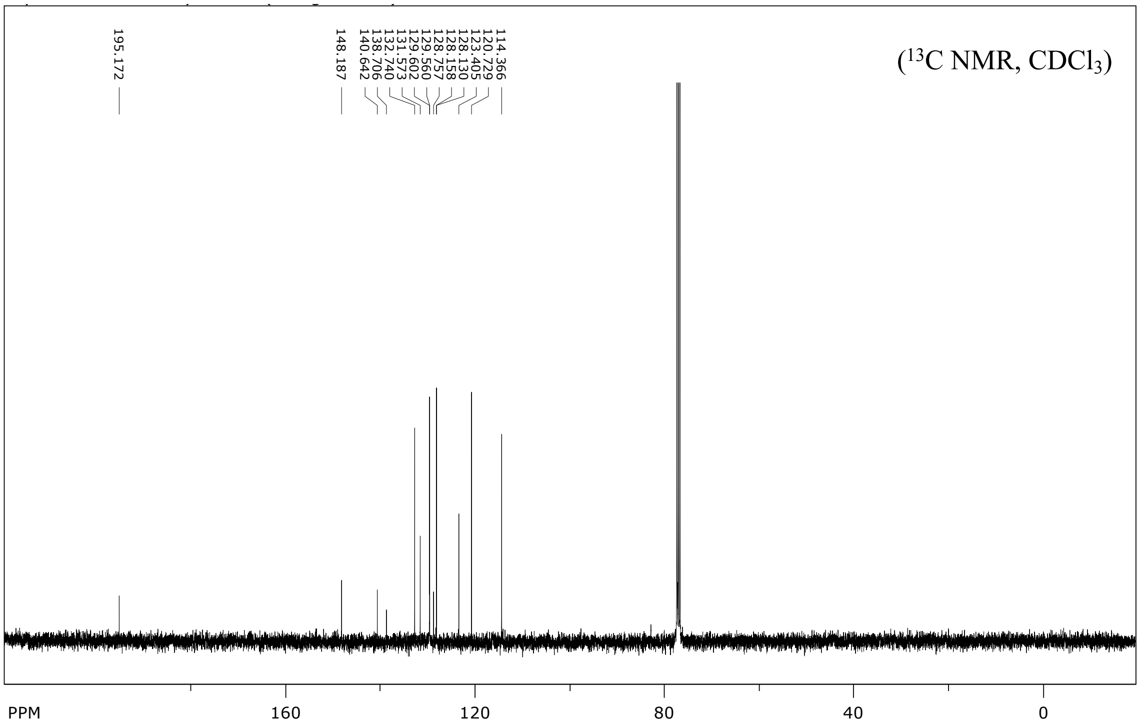
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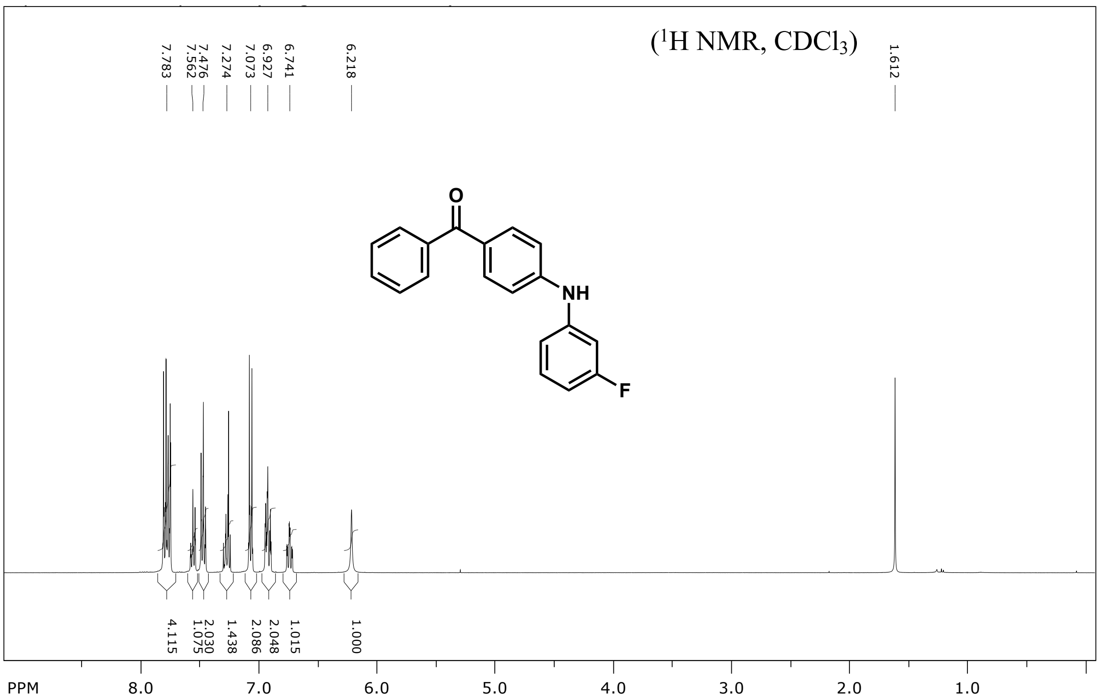
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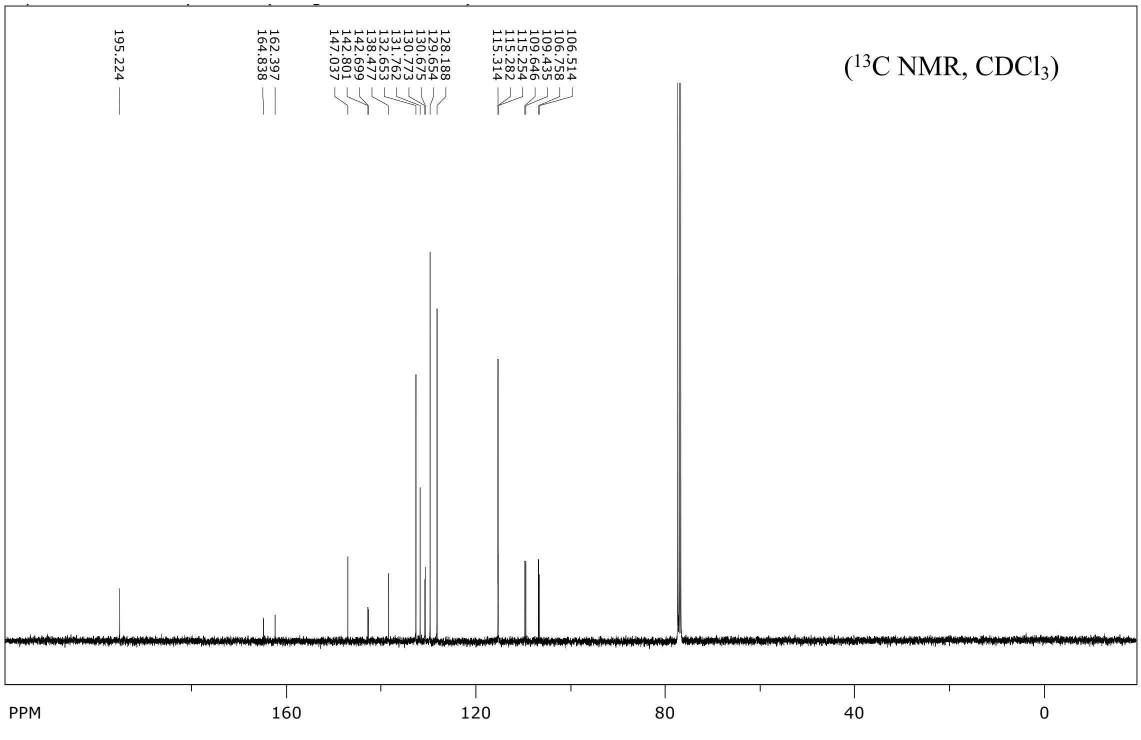
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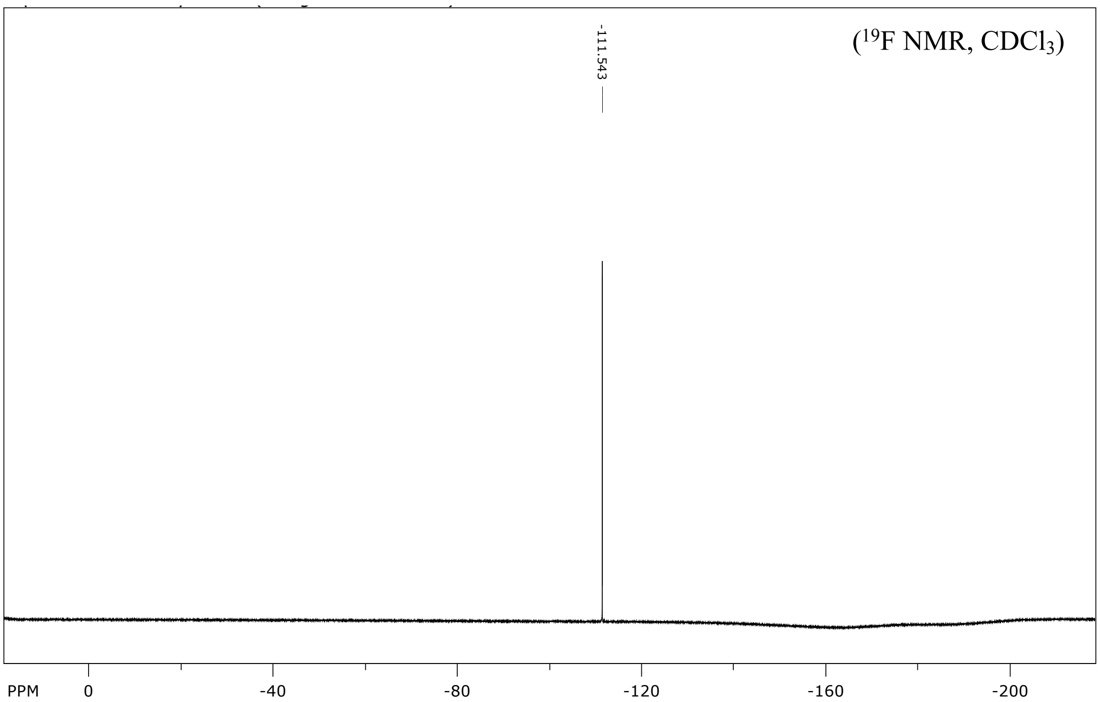

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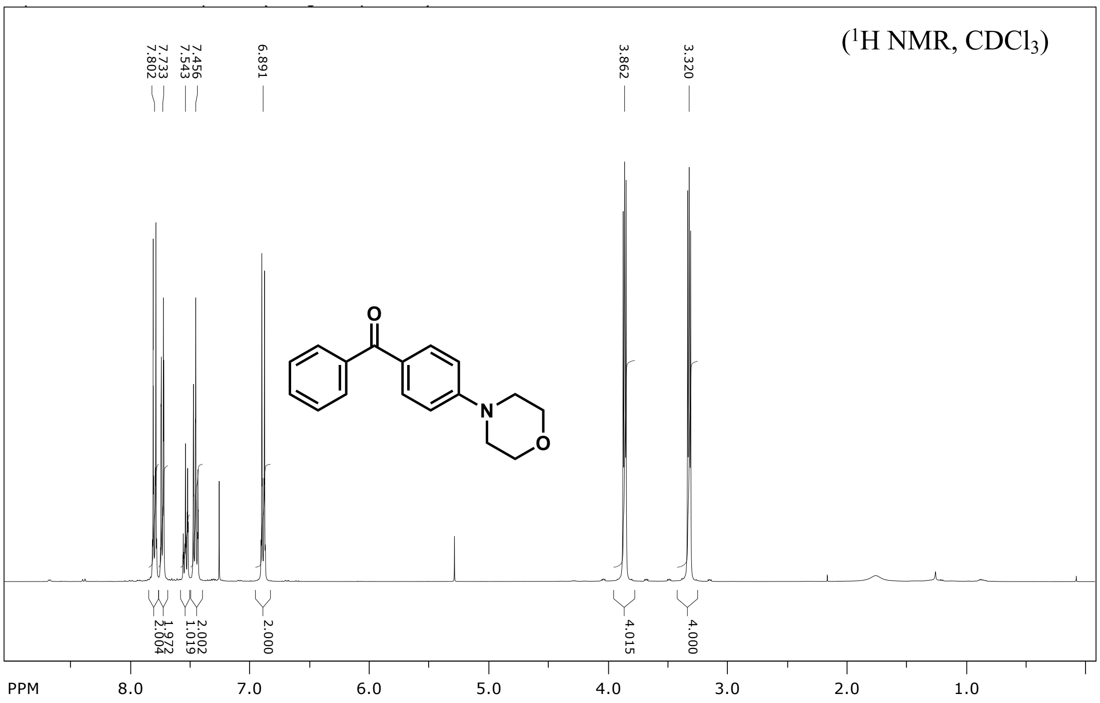
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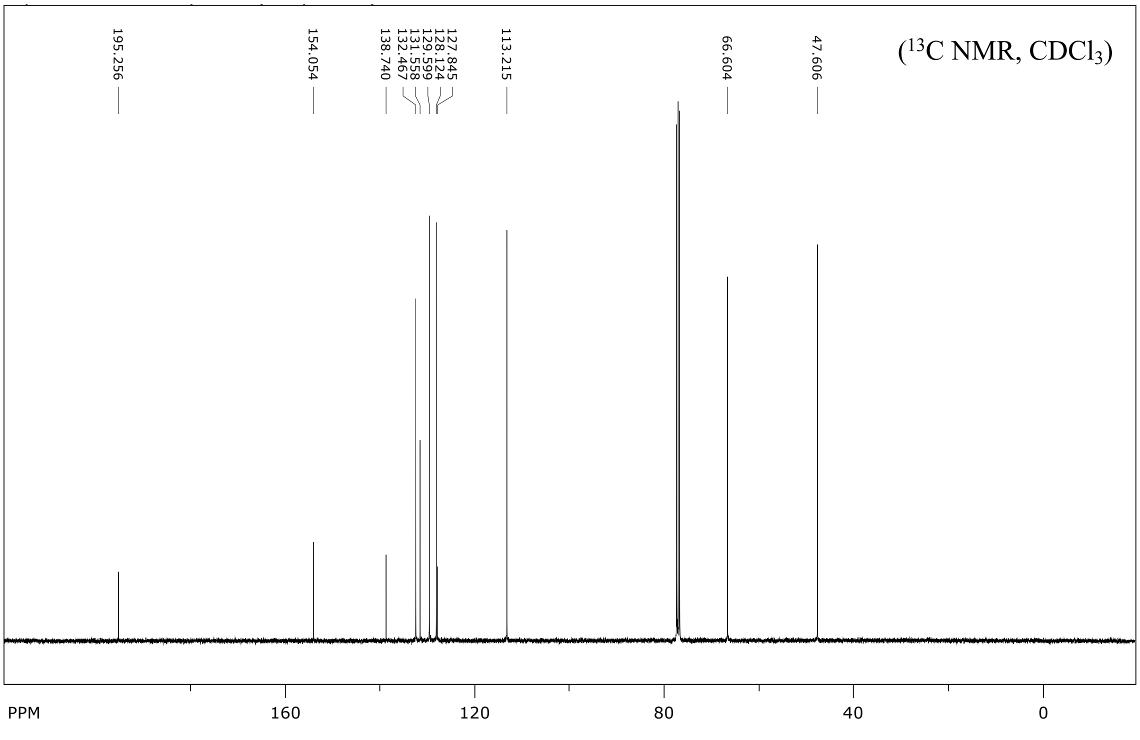
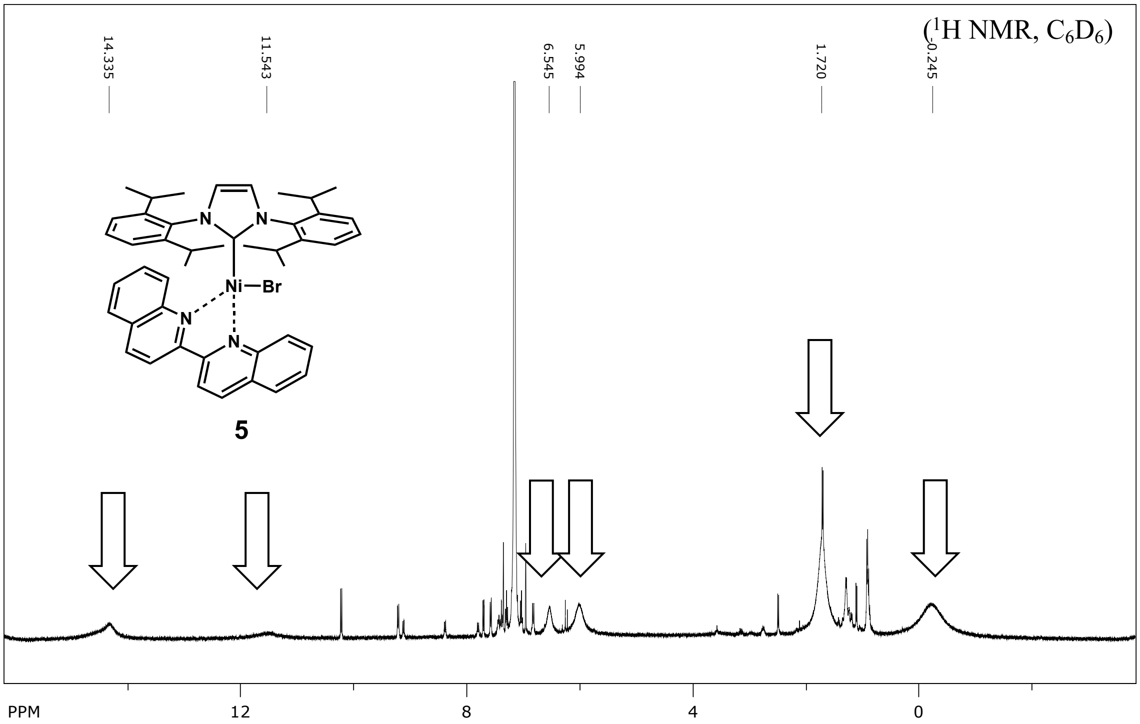
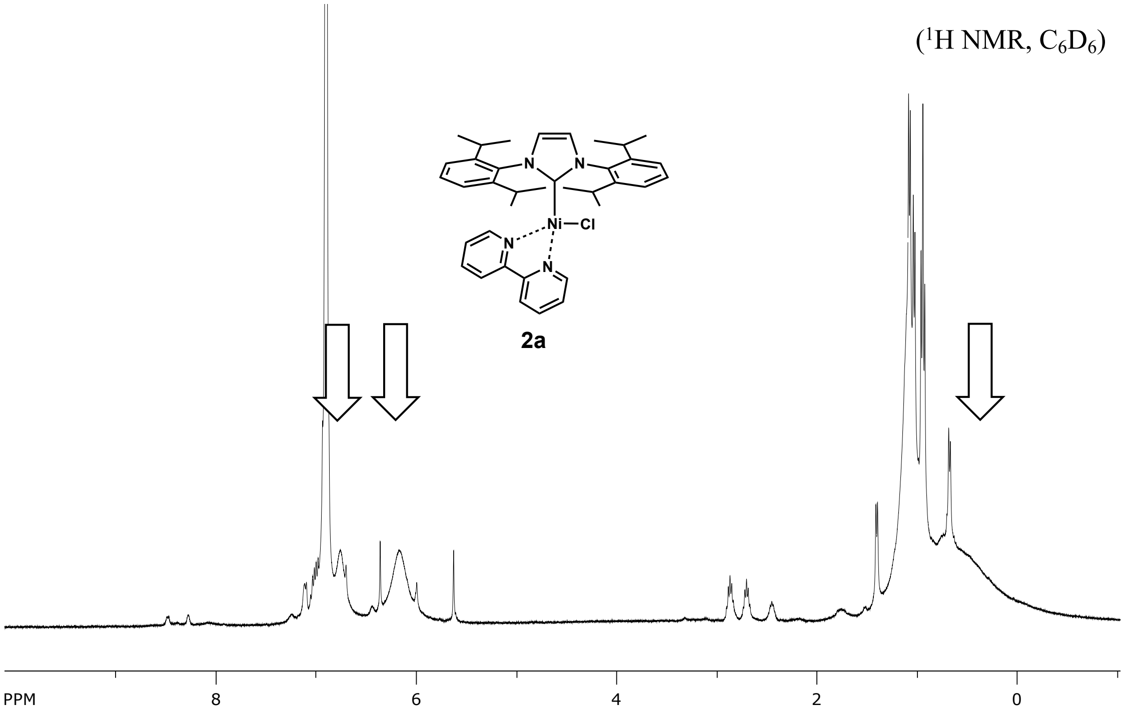
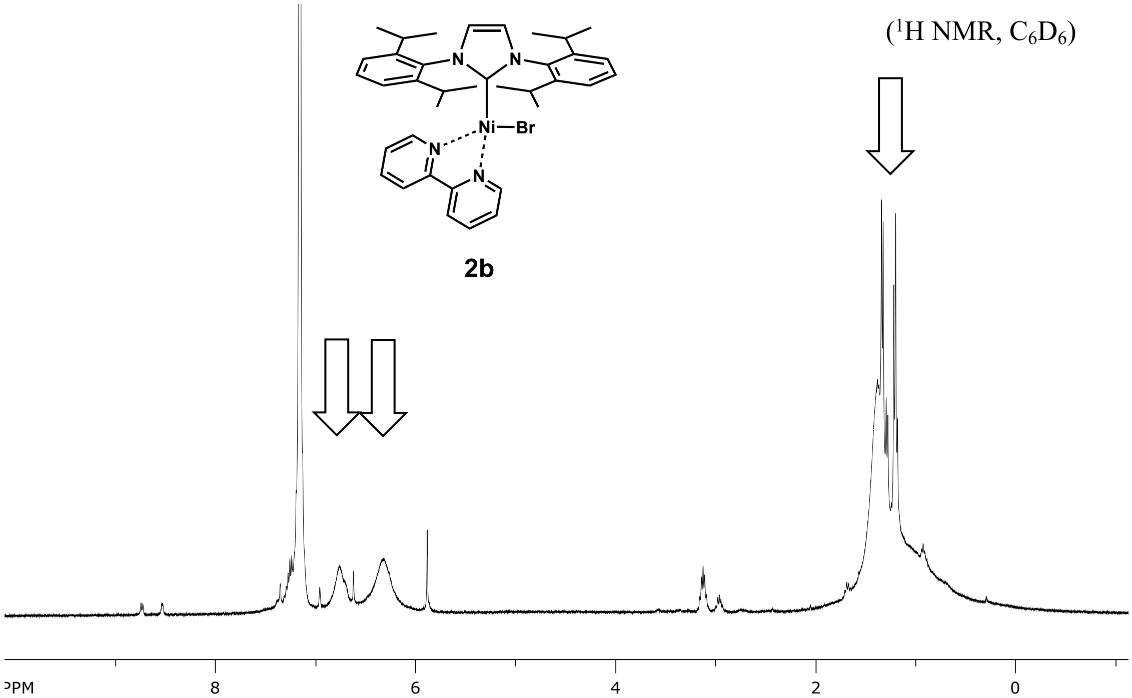
2.0
1.0


(¹³C NMR, CDCl₃)
195.256
154.054
138.740
132.467
131.558
129.599
128.124
127.845
113.215
66.604
47.606
PPM
160
120
80
40
0


(^{1}H NMR, C_6D_6)
14.335
11.543
6.545
5.994
1.720
-0.245
N
N
Ni
Br
N
N
5
PPM
12
8
4
0


(^{1}H NMR, C_6D_6)
N
N
Ni
Cl
N
N
2a
PPM
8
6
4
2
0


(¹H NMR, C₆D₆)
N
N
Ni
Br
N
N
2b
PPM
8
6
4
2
0