Supporting Information

For

Nickel-Catalysed Direct C2-Arylation of N-Heterocyclic Carbenes

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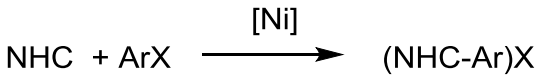
Contents:

Experimental

Materials and Methods: Unless otherwise stated, all syntheses and manipulations were carried out under an inert gas atmosphere (Ar or N_2) using standard *Schlenk* techniques or a glove-box (LABMasterPro, MBraun). Solvents were dried over appropriate drying agents, distilled and stored over molecular sieve prior to use. Deuterated solvents were dried over appropriate drying agents, distilled, and stored inside a glove box. NMR spectra were recorded on a Bruker Avance II 500 or a Bruker Avance III 500 HD spectrometer. ESI mass spectra were recorded with a Bruker Esquire 3000 spectrometer. Melting points were measured with a Büchi B-545 Melting Point apparatus. IPr (**1a**),[1] SIPr (**1b**),[2] Me_2-IPr (**1c**),[3] $Ni(cod)_2$,[4] $(IPr)_2NiCl$ (**9**),[5] $[(IPr)Ni(\mu\text{-}Cl)]_2$ (**10**-Cl),[6] and $[(IPr)Ni(\mu\text{-}Br)]_2$ (**10**-Br)[7] were prepared according to literature methods. Iodobenzene, aryl bromides, aryl chlorides, phenyl triflate were purchased from commercial suppliers and used as received without further purification.

General procedure for the C2-arylation of NHCs: To a Schlenk flask containing a mixture of NHC (1 to 1.5 mmol) and nickel precatalyst was added 20 mL of a dried and degased organic solvent. The resulting solution was stirred at rt for five minutes. The desired aryl electrophile was added in one portion and the reaction mixture was refluxed for an appropriate time. The product formed was filtred through a G4 frit, washed with 10 mL toluene, and dried under vacuum.

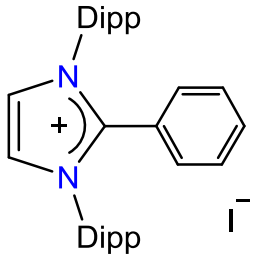
Table S1. Reactions of NHCs with ArX to C2-arylated imidazolium salts (NHC-Ar)X.



Entry	NHC	Ar	X	[Ni] (mol%)	Solvent	Time (h)	Temp. (ºC)	(NHC-Ar)X Yield (%)
1	IPr	Ph	I	$Ni(cod)_2$ (5)	*o*-xylene	2	140	65
2	**IPr**	**Ph**	**Br**	**$Ni(cod)_2$ (5)**	***o*-xylene**	**2**	**140**	**75**
3	IPr	Ph	Br	$Ni(cod)_2$ (5)	THF	3	66	67
4	IPr	Ph	Br	$Ni(cod)_2$ (5)	1,4-dioxane	4	104	66
5	IPr	Ph	Br	$Ni(cod)_2$ (2)	*o*-xylene	2	140	53
6	IPr	Ph	Cl	$Ni(cod)_2$ (5)	*o*-xylene	4	140	7
7	IPr	Ph	Cl	$(IPr)_2Ni$ (2.5)	*o*-xylene	5	140	12
8	IPr	Ph	Cl	$[(IPr)Ni(\mu\text{-}Cl)]_2$ (2.5)	*o*-xylene	3	140	12
9	IPr	Ph	OTf	$Ni(cod)_2$ (5)	*o*-xylene	4	140	16
10	IPr	4-anisyl	Cl	$Ni(cod)_2$ (5)	*o*-xylene	2	140	17

11	SIPr	Ph	Br	$Ni(cod)_2$ (5)	*o*-xylene	2	140	45
12	Me_2-IPr	Ph	Br	$Ni(cod)_2$ (5)	*o*-xylene	2	140	79
13	IPr	Ph	Br	$[(IPr)Ni(\mu\text{-}Cl)]_2$ (2.5)	*o*-xylene	3	140	75
14	IPr	Ph	Br	$[(IPr)Ni(\mu\text{-}Br)]_2$ (2.5)	*o*-xylene	2	140	77
15	IPr	4-tolyl	Br	$Ni(cod)_2$ (5)	*o*-xylene	3	140	75
16	IPr	3-tolyl	Br	$Ni(cod)_2$ (5)	*o*-xylene	4	140	74
17	IPr	2-tolyl	Br	$Ni(cod)_2$ (5)	*o*-xylene	8	140	n.c.
18	IPr	2-tolyl	Br	$[(IPr)Ni(\mu\text{-}Br)]_2$ (2.5)	*o*-xylene	6	140	n.c
19	IPr	4-anisyl	Br	$Ni(cod)_2$ (5)	*o*-xylene	2	140	87
20	IPr	3-anisyl	Br	$Ni(cod)_2$ (5)	*o*-xylene	2	140	61
21	IPr	2-anisyl	Br	$Ni(cod)_2$ (5)	*o*-xylene	4	140	n.c.
22	IPr	4-Me(O)C-C_6H_4	Br	$Ni(cod)_2$ (5)	*o*-xylene	3	140	75
23	IPr	3-Me(O)C-C_6H_4	Br	$Ni(cod)_2$ (5)	*o*-xylene	2	140	71
24	IPr	4-Me_2N-C_6H_4	Br	$Ni(cod)_2$ (5)	*o*-xylene	2	140	71
25	IPr	3-MeO(O)C-C_6H_4	Br	$Ni(cod)_2$ (5)	*o*-xylene	1	140	69
26	IPr	2-MeO(O)C-C_6H_4	Br	$Ni(cod)_2$ (5)	*o*-xylene	4	140	n.c.
27	IPr	4-EtO(O)C-C_6H_4	Br	$Ni(cod)_2$ (5)	*o*-xylene	2	140	56
28	IPr	4-O_2N-C_6H_4	Br	$Ni(cod)_2$ (5)	*o*-xylene	4	140	n.c.
29	IPr	2-O_2N-C_6H_4	Br	$Ni(cod)_2$ (5)	*o*-xylene	4	140	n.c.
30	IPr	3,5-$(F_3C)_2$-C_6H_3	Br	$Ni(cod)_2$ (5)	*o*-xylene	3	140	n.c.

Synthesis of (IPrPh)I (2)[8]



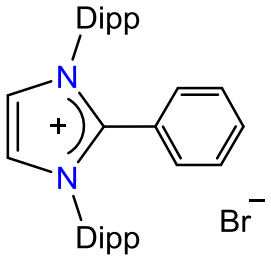
Method: To a 20 mL *o*-xylene solution of IPr (0.51 g, 1.31 mmmol) and $Ni(cod)_2$ (17 mg, 5 mol%) was added iodobenzene (0.15 mL, 1.34 mmol). The resulting brown solution was refluxed for 2 h. The coupling product **2** formed as a white solid, which was separated by filtration, washed with 10 mL toluene, and dried under vacuum.

Yield: 0.50 g, 65%

^{1}H NMR (500 MHz, $CDCl_3$, 25 ºC): δ 1.01 (d, $^3J_{H,H}$ = 6.21 Hz, 12H, $CH(CH_3)_2$), 1.33 (d, $^3J_{H,H}$ = 6.19 Hz, 12H, $CH(CH_3)_2$), 2.48 (sep, 4H, $CH(CH_3)_2$), 6.94 (d, $^3J_{H,H}$ = 7.38 Hz, 2H, *o*-C_6H_5), 7.22 (t, $^3J_{H,H}$ = 7.95 Hz, 2H, *m*-C_6H_5), 7.31 (d, $^3J_{H,H}$ = 7.51 Hz, 4H, *m*-C_6H_3), 7.39 (t, $^3J_{H,H}$ = 7.04 Hz, 1H, *p*-C_6H_5), 7.56 (t, $^3J_{H,H}$ = 6.57 Hz, 2H, *p*-C_6H_3), 8.32 (s, 2H, NC*H*) ppm.

^{13}C NMR (125 MHz, $CDCl_3$, 25 ºC): δ 22.76 ($CH(CH_3)_2$), 25.78 ($CH(CH_3)_2$), 29.55 ($CH(CH_3)_2$), 120.82, 125.47 (*m*-C_6H_3) , 127.51 (NCH), 129.31 (*m*-C_6H_5), 130.10 (*o*-C_6H_5), 132.47 (*p*-C_6H_3), 132.82 (*p*-C_6H_5), 144.98 ppm.

Synthesis of (IPrPh)Br (3a):



To a 20 mL *o*-xylene solution of IPr (1.00 g, 2.57 mmol) and $Ni(cod)_2$ (35 mg, 0.13 mmol, 5 mol%) was added bromobenzene (0.30 mL, 2.87 mmol). The resulting brown solution was refluxed for 2 h. The

coupling product **3a** formed as a white solid, which was separated by filtration, washed with 10 mL toluene, and dried under vacuum.

Yield: 1.05 g (75%).

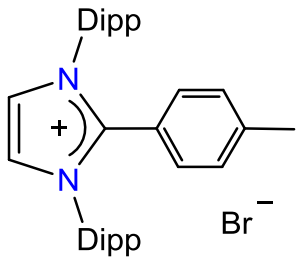
^{1}H NMR (500 MHz, $CDCl_3$, 25 ºC): δ 1.00 (d, $^{3}J_{H,H}$ = 6.68 Hz, 12H, CH(CH_3)$_2$), 1.33 (d, $^{3}J_{H,H}$ = 6.59 Hz, 12H, CH(CH_3)$_2$), 2.48 (sep, $^{3}J_{H,H}$ = 6.02 Hz, 4H, CH(CH$_3$)$_2$), 6.94 (d, $^{3}J_{H,H}$ = 7.97 Hz, 2H, *o*-C$_6H_5$), 7.21 (t, $^{3}J_{H,H}$ = 7.65 Hz, 2H, *m*-C$_6H_5$), 7.30 (d, $^{3}J_{H,H}$ = 7.82 Hz, 4H, *m*-C$_6H_3$), 7.38 (t, $^{3}J_{H,H}$ = 7.53 Hz, 1H, *p*-C$_6H_5$), 7.55 (t, $^{3}J_{H,H}$ = 7.78 Hz, 2H, *p*-C$_6H_3$), 8.38 (s, 2H, NCH) ppm.

^{13}C NMR (125 MHz, $CDCl_3$25 ºC): δ 22.62 (CH(*C*H$_3$)$_2$), 25.62 (CH(*C*H$_3$)$_2$), 29.37 (*C*H(CH$_3$)$_2$), 120.76, 125.26 (*m*-*C*$_6$H$_3$) , 127.63 (N*C*H), 129.17 (*m*-*C*$_6$H$_5$), 130.02 (*o*-*C*$_6$H$_5$), 132.37 (*p*-*C*$_6$H$_3$), 132.59 (*p*-*C*$_6$H$_5$), 144.86 ppm.

ESI-MS m/z: 465.4 [M-Br]$^{+}$.

Mp.: 283 °C (dec.).

Synthesis of {(IPr-(4-tolyl)}Br (3b)



Method: *o*-xylene, 3h

Reagents: IPr **(**0.5 g, 1.29 mmol), 4-bromotoluene (0.2 mL, 1.62 mmol), Ni(cod)$_2$ (17 mg, 5 mol%).

Yield: 0.54 g, 75%.

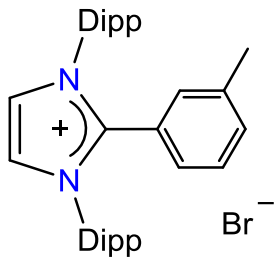
^{1}H NMR (500 MHz, $CDCl_3$, 25 ºC): δ 1.01 (d, $^{3}J_{H,H}$ = 6.73 Hz, 12H, CH(CH_3)$_2$), 1.32 (d, $^{3}J_{H,H}$ = 6.63 Hz, 12H, CH(CH_3)$_2$), 2.24 (s, 3H, CH_3), 2.48 (sep, $^{3}J_{H,H}$ = 6.75 Hz, 4H, CH(CH$_3$)$_2$), 6.82 (d, ^{3}J = 7.98 Hz, 2H, C$_6H_4$), 7.01 (d, $^{3}J_{H,H}$ = 8.05 Hz, 2H, C$_6H_4$), 7.31 (d, $^{3}J_{H,H}$ = 7.80 Hz, 4H, *m*-C$_6H_3$), 7.56 (t, $^{3}J_{H,H}$ = 7.80 Hz, 2H, *p*-C$_6H_3$), 8.20 (s, 2H, NCH) ppm.

^{13}C NMR (125 MHz, $CDCl_3$, 25 ºC): δ 21.58, 22.78 (CH(*C*H$_3$)$_2$), 25.69 (CH(*C*H$_3$)$_2$), 29.51 (*C*H(CH$_3$)$_2$), 29.85, 125.40 (*m*-*C*$_6$H$_3$) , 127.21 (N*C*H), 129.16 (*C*$_6$H$_4$), 130.02 (*C*$_6$H$_4$), 130.28 (*p*-*C*$_6$H$_3$), 132.33, 145.05 (*C*$_6$H$_3$, *C*$_6$H$_4$) ppm.

ESI-MS m/z: 479.4 [M-Br]$^{+}$.

Mp.: 276 °C (dec.).

Synthesis of {(IPr-(3-tolyl)}Br (3c)



Method: *o*-xylene, 4h

Reagents: IPr **(**0.5 g, 1.29 mmol), 3-bromotoluene (0.2 mL, 1.62 mmol), $Ni(cod)_2$ (18 mg, 5 mol%).

Yield: 0.53 g, 74%

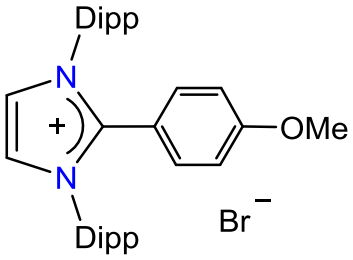
^{1}H NMR (500 MHz, $CDCl_3$, 25 ºC): δ 1.03 (d, $^3J_{H,H}$ = 6.77 Hz, 12H, $CH(CH_3)_2$), 1.34 (d, $^3J_{H,H}$ = 6.68 Hz, 12H, $CH(CH_3)_2$), 2.10 (s, 3H, CH_3), 2.49 (sep, $^3J_{H,H}$ = 6.72 Hz, 4H, $CH(CH_3)_2$), 6.73 (d, $^3J_{H,H}$ = 7.95 Hz, 1H, C_6H_4), 6.80 (s, 1H, *o*-C_6H_4), 7.09 (t, $^3J_{H,H}$ = 7.77 Hz, 1H, *m*-C_6H_4), 7.18 (d, $^3J_{H,H}$ = 7.66 Hz, 1H, C_6H_4), 7.31 (d, $^3J_{H,H}$ = 7.82 Hz, 4H, *m*-C_6H_3), 7.55 (t, $^3J_{H,H}$ = 7.84 Hz, 2H, *p*-C_6H_3), 8.13 (s, 2H, NC*H*) ppm.

^{13}C NMR (125 MHz, $CDCl_3$, 25 ºC): δ 20.87 (CH_3), 22.47 ($CH(CH_3)_2$), 25.51 ($CH(CH_3)_2$), 29.21 ($CH(CH_3)_2$), 125.00 (*p*-C_6H_3) , 126.03 (N*C*H), 127.82 (C_6H_4), 128.84, 129.73 (*m*-C_6H_4), 130.01 (*o*-C_6H_4), 131.98 (*m*-C_6H_3), 133.04 (C_6H_4), 139.13, 144.74 (C_6H_3, C_6H_4) ppm.

Mp.: 262 °C (dec.).

ESI-MS m/z: 479.4 $[M\text{-}Br]^+$

Synthesis of {(IPr-(4-anisyl)}Br (3d)



Method: *o*-xylene, 2h

Reagents: IPr **(**0.5 g, 1.29 mmol), 4-bromoanisole (0.2 mL, 1.60 mmol), $Ni(cod)_2$ (18 mg, 5 mol%).

Yield: 0.64 g, 87%

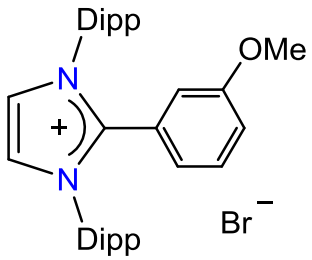
^{1}H NMR (500 MHz, $CDCl_3$, 25 ºC): δ 1.02 (d, $^3J_{H,H}$ = 6.76 Hz, 12H, CH(CH_3)$_2$), 1.33 (d, $^3J_{H,H}$ = 6.66 Hz, 12H, CH(CH_3)$_2$), 2.49 (sep, $^3J_{H,H}$ = 6.79 Hz, 4H, CH(CH$_3$)$_2$), 3.72 (s, 3H, OCH_3), 6.68 (d, $^3J_{H,H}$ = 8.71 Hz, 2H, C$_6H_4$), 6.86 (d, $^3J_{H,H}$ = 8.74 Hz, 2H, C$_6H_4$), 7.33 (d, $^3J_{H,H}$ = 7.78 Hz, 4H, *m*-C$_6H_3$), 7.57 (t, $^3J_{H,H}$ = 7.84 Hz, 2H, *p*-C$_6H_3$), 8.04 (s, 2H, NCH) ppm.

^{13}C NMR (126 MHz, $CDCl_3$25 ºC): δ 20.69, 22.69 (CH(*C*H$_3$)$_2$), 25.41 (CH(*C*H$_3$)$_2$), 29.38 (*C*H(CH$_3$)$_2$), 55.59 (*C*H$_3$), 114.71 (*C*$_6$H$_4$), 124.67, 125.35 (*p*-*C*$_6$H$_3$), 126.58, 130.92 (*m*-*C*$_6$H$_3$), 132.22 (*C*$_6$H$_4$), 144.93 ppm.

Mp.: 246 °C (dec.).

ESI-MS m/z: 495.4 [M-Br]$^+$

Synthesis of {(IPr-(3-anisyl)}Br (3e)



Method: *o*-xylene, 2h

Reagents: IPr **(**0.5 g, 1.29 mmol), 3-bromoanisole (0.2 mL, 1.60 mmol), Ni(cod)$_2$ (18 mg, 5 mol%).

Yield: 0.45 g, 74%

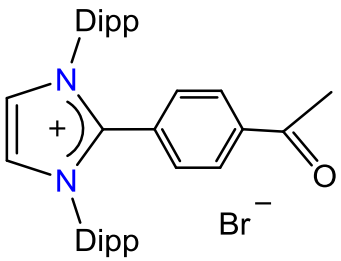
^{1}H NMR (500 MHz, $CDCl_3$, 25 ºC): δ 1.01 (d, $^3J_{H,H}$ = 6.77 Hz, 12H, CH(CH_3)$_2$), 1.33 (d, $^3J_{H,H}$ = 6.67 Hz, 12H, CH(CH_3)$_2$), 2.49 (sep, $^3J_{H,H}$ = 6.63 Hz, 4H, CH(CH$_3$)$_2$), 3.43 (s, 3H, OCH_3), 6.40 (s, 1H, *o*-C$_6H_4$) 6.51 (d, $^3J_{H,H}$ = 7.94 Hz, 1H, C$_6H_4$), 6.89 (d, $^3J_{H,H}$ = 8.29 Hz, 1H, C$_6H_4$), 7.10 (t, $^3J_{H,H}$ = 8.12 Hz, 1H, *m*-C$_6H_4$), 7.32 (d, $^3J_{H,H}$ = 7.80 Hz, 4H, *m*-C$_6H_3$), 7.57 (t, $^3J_{H,H}$ = 7.81 Hz, 2H, *p*-C$_6H_3$), 8.31 (s, 2H, NCH) ppm.

^{13}C NMR (125 MHz, $CDCl_3$, 25 ºC): δ 22.68 (CH(*C*H$_3$)$_2$), 25.61 (CH(*C*H$_3$)$_2$), 29.51 (*C*H(CH$_3$)$_2$), 55.55 (*C*H$_3$), 114.39 (*m*-*C*$_6$H$_4$), 118.76 (*C*$_6$H$_4$), 121.41 (*C*$_6$H$_4$), 125.33 (*p*-*C*$_6$H$_3$), 127.54, 130.23 (*m*-*C*$_6$H$_3$), 132.21 (*m*-*C*$_6$H$_4$), 144.86, 159.69, 164.44 ppm.

Mp.: 218 °C (dec.).

ESI-MS m/z: 495.4 [M-Br]$^+$.

Synthesis of {(IPr-(4-acetylphenyl)}Br (3f)



Method: *o*-xylene, 3h

Reagents: IPr **(**0.5 g, 1.29 mmol), 4-bromoacetophenone (0.26 g, 1.33 mmol), $Ni(cod)_2$ (18 mg, 5 mol%).

Yield: 0.57 g, 75%

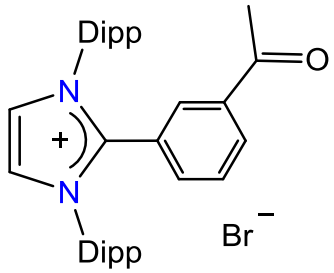
^{1}H NMR (500 MHz, $CDCl_3$) δ [ppm]: 0.99 (d, $^3J_{H,H}$ = 6.8 Hz, 12H, $CH(CH_3)_2$), 1.33 (d, $^3J_{H,H}$ = 6.67 Hz, 12H, $CH(CH_3)_2$), 2.44 (m, 4H, $CH(CH_3)_2$), 2.50 (s, 3H, $COCH_3$), 7.04 (d, $^3J_{H,H}$ = 7.9 Hz, 2H, C_6H_4), 7.31 (d, $^3J_{H,H}$ = 7.80 Hz, 4H, *m*-C_6H_3), 7.57 (t, $^3J_{H,H}$ = 8.3 Hz, 2H, *p*-C_6H_3), 7.75 (d, $^3J_{H,H}$ = 8.3 Hz, 2H, C_6H_4), 8.79 (s, 2H, NC*H*) ppm.

^{13}C NMR (125 MHz, $CDCl_3$) δ [ppm]: δ 22.78 ($CH(CH_3)_2$), 23.94, 24.91 ($CH(CH_3)_2$), 25.71, 26.76 ($COCH_3$), 29.32, 29.53 ($CH(CH_3)_2$), 124.93, 125.51 (*p*-C_6H_3), 129.64, 129.95 (*m*-C_6H_3), 132.61 (*m*-C_6H_4), 144.85, 145.13 ppm.

Mp.: 232 °C (dec.).

ESI-MS m/z: 507.4 $[M\text{-}Br]^+$.

Synthesis of {(IPr-(3-acetylphenyl)}Br (3g)



Method: *o*-xylene, 2h

Reagents: IPr **(**0.5 g, 1.29 mmol), 3-bromoacetophenone (0.18 mL, 1.35 mmol), $Ni(cod)_2$ (18 mg, 5 mol%).

Yield: 0.55 g, 71%

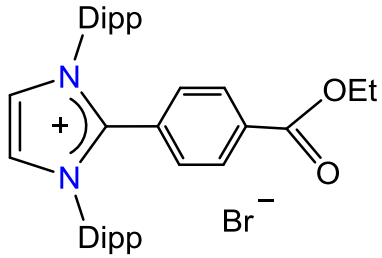
^{1}H NMR (500 MHz, $CDCl_3$, 25 ºC): δ 1.01 (d, $^{3}J_{H,H}$ = 6.8 Hz, 12H, $CH(CH_3)_2$), 1.33 (d, $^{3}J_{H,H}$ = 6.67 Hz, 12H, $CH(CH_3)_2$), 2.33 (s, 3H, $COCH_3$) , 2.45 (sep, $^{3}J_{H,H}$ = 6.7 Hz, 4H, $CH(CH_3)_2$), 7.09 (d, $^{3}J_{H,H}$ = 7.1 Hz, 1H, C_6H_4), 7.31 (d, $^{3}J_{H,H}$ = 7.8 Hz, 4H, *p*-C_6H_3), 7.36 (t, $^{3}J_{H,H}$ = 7.2 Hz, 1H, C_6H_4), 7.56 (t, $^{3}J_{H,H}$ = 7.9 Hz, 2H, *m*-C_6H_3), 7.59 (s, 1H, *o*-C_6H_4), 7.94 (d, $^{3}J_{H,H}$ = 7.7 Hz, 1H, C_6H_4), 8.76 (s, 2H, NC*H*).

^{13}C NMR (125 MHz, $CDCl_3$, 25 ºC): δ 22.63 ($CH(CH_3)_2$), 25.81 ($CH(CH_3)_2$), 29.32 ($COCH_3$); 29.57 ($CH(CH_3)_2$), 121.63, 124.92, 125.52 (*p*-C_6H_3), 128.42, 129.14, 129.93 (*m*-C_6H_3), 132.26, 132.55, 132.79 (*m*-C_6H_4), 137.51, 144.88, 145.12, 195.23 ppm.

Mp.: 232 °C (dec.).

ESI-MS m/z: 507.4 $[M\text{-}Br]^+$.

Synthesis of {(IPr(4-(EtO(O)C)-C_6H_4)}Br (3h)



Method: *o*-xylene, 2h

Reagents: IPr **(**0.52 g, 1.33 mmol), ethyl-4-bromobenzoate (0.33 mL, 1.54 mmol), $Ni(cod)_2$ (18 mg, 5 mol%).

Yield: 0.46 g, 56%

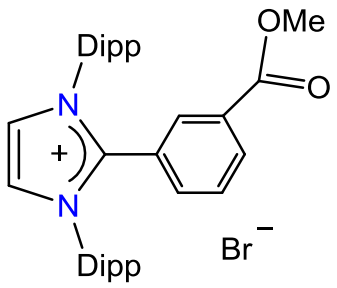
^{1}H NMR (500 MHz, $CDCl_3$, 25 ºC): δ 0.99 (d, $^{3}J_{H,H}$ = 6.9 Hz, 12H, $CH(CH_3)_2$), 1.33 (d, $^{3}J_{H,H}$ = 6.7 Hz, 12H, $CH(CH_3)_2$), 2.44 (s, $^{3}J_{H,H}$ = 7.3 Hz , 4H, $CH(CH_3)_2$), 4.30 (q, $^{3}J_{H,H}$ = 7.2 Hz, 4H, OCH_2CH_3), 7.01 (d, $^{3}J_{H,H}$ = 8.4 Hz, 2H, C_6H_4), 7.30 (d, $^{3}J_{H,H}$ = 7.9 Hz, 4H, *m*-C_6H_3), 7.56 (t, $^{3}J_{H,H}$ = 7.9 Hz, 2H, *p*-C_6H_3), 7.85 (d, $^{3}J_{H,H}$ = 8.5 Hz, 2H, C_6H_4), 8.81 (s, 2H, NC*H*) ppm.

^{13}C NMR (125 MHz, $CDCl_3$, 25 ºC): δ 14.92, 23.42 ($CH(CH_3)_2$), 25.56 ($CH(CH_3)_2$), 26.37, 29.97 ($CH(CH_3)_2$), 30.17, 62.79 (OCH_2CH_3), 125.57 (C_6H_3), 126.11, 129.51 (N*C*H), 129.98 (C_6H_4), 130.70 (C_6H_4), 133.18 (C_6H_3), 145.52, 145.79 (C_6H_3, C_6H_4) ppm.

Mp.: 275 °C

ESI-MS m/z: 537.4 $[M\text{-}Br]^+$.

Synthesis of {(IPr-(3-(MeO(O)C)C_6H_4)}Br (3i)



Method: *o*-xylene, 1h

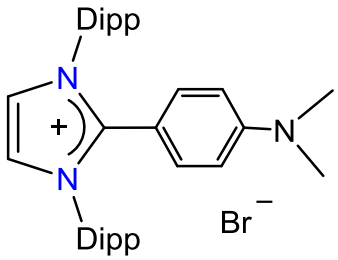
Reagents: IPr **(**0.5 g, 1.29 mmol), methyl-3-bromobenzoate (0.32 g, 1.48 mmol), $Ni(cod)_2$ (18 mg, 5 mol%).

Yield: 0.53 g, 69%

^{1}H NMR (500 MHz, $CDCl_3$, 25 ºC): δ 1.02 (d, $^3J_{H,H}$ = 6.8 Hz, 12H, $CH(CH_3)_2$), 1.33 (d, $^3J_{H,H}$ = 6.67 Hz, 12H, $CH(CH_3)_2$), 2.12 (s, 3H, CO_2CH_3) , 2.37 (sep, $^3J_{H,H}$ = 6.7 Hz, 4H, $CH(CH_3)_2$), 7.41 (d, $^3J_{H,H}$ = 7.8 Hz, 4H, *p*-C_6H_3), 7.55 (t, $^3J_{H,H}$ = 7.9 Hz, 2H, *m*-C_6H_3), 8.24 (s, 2H, NC*H*) ppm.

ESI-MS m/z: 523.4 $[M\text{-}Br]^+$.

Synthesis of {(IPr-(4-Me_2N-C_6H_4)}Br (3j)



Method: *o*-xylene, 2h

Reagents: IPr **(**0.51 g, 1.31 mmol), 4-bromo-N,N-dimethylaniline (0.28 g, 1.48 mmol), $Ni(cod)_2$ (18 mg, 5 mol%).

Yield: 0.55 g, 71%

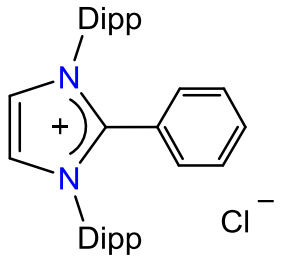
^{1}H NMR (500 MHz, $CDCl_3$, 25 ºC): δ 0.98 (d, $^3J_{H,H}$ = 6.21 Hz, 12H, $CH(CH_3)_2$), 1.28 (d, $^3J_{H,H}$ = 6.19 Hz, 12H, $CH(CH_3)_2$), 2.47 (sep, 4H, $CH(CH_3)_2$), 2.88 (s, 6H, $N(CH_3)_2$), 6.28 (d, $^3J_{H,H}$ = 9.04 Hz, 2H, C_6H_4), 6.66 (d, $^3J_{H,H}$ = 9.03 Hz, 2H, C_6H_4), 7.31 (d, $^3J_{H,H}$ = 7.80 Hz, 4H, *m*-C_6H_3), 7.55 (t, $^3J_{H,H}$ = 7.79Hz, 2H, *p*-C_6H_3), 8.18 (s, 2H, NC*H*) ppm.

^{13}C NMR (125 MHz, $CDCl_3$, 25 ºC): δ 22.83 ($CH(CH_3)_2$), 25.36 ($CH(CH_3)_2$), 29.35 ($CH(CH_3)_2$), 39.84 ($N(CH_3)_2$), 67.20, 105.99, 111.06 (C_6H_4), 125.38 (C_6H_3), 126.32 (NCH), 130.23 (C_6H_4), 131.06 (C_6H_3), 132.01, 144.96, 145.93, 151.96 ppm.

Mp.: 266 °C (dec.).

ESI-MS m/z: 508.4 $[M\text{-}Br]^+$

Synthesis of (IPrPh)Cl (4)



Method: o-xylene, 4h

Reagents: IPr **(**0.51 g, 1.31 mmol), PhCl (0.14 mL, 1.38 mmol), $Ni(cod)_2$ (18 mg, 5 mol%).

Yield: 0.05 g, 7%

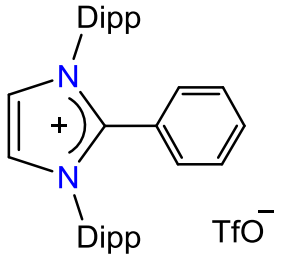
^{1}H NMR (500 MHz, $CDCl_3$, 25 ºC): δ 0.97 (d, $^3J_{H,H}$ = 6.8 Hz, 12H, $CH(CH_3)_2$), 1.30 (d, $^3J_{H,H}$ = 6.9 Hz, 12H, $CH(CH_3)_2$), 2.44 (sep, $^3J_{H,H}$ = 6.6 Hz, 4H, $CH(CH_3)_2$), 6.91 (d, $^3J_{H,H}$ = 8.5 Hz, 2H, *o*-C_6H_5), 7.19 (t, $^3J_{H,H}$ = 8.0 Hz, 2H, *m*-C_6H_5), 7.28 (d, $^3J_{H,H}$ = 7.8 Hz, 4H, *m*-C_6H_3), 7.35 (t, $^3J_{H,H}$ = 7.6 Hz, 1H, *p*-C_6H_5), 7.53 (t, $^3J_{H,H}$ = 8.9 Hz, 2H, *p*-C_6H_3), 8.70 (s, 2H, NCH) pp,.

^{13}C NMR (125 MHz, $CDCl_3$, 25 ºC): δ 22.72 ($CH(CH_3)_2$), 25.66 ($CH(CH_3)_2$), 29.46 ($CH(CH_3)_2$), 124.87, 125.32 (*m*-C_6H_3) , 128.22 (NCH), 129.25 (*m*-C_6H_5), 130.27 (*o*-C_6H_5), 132.26 (*p*-C_6H_3), 132.60 (*p*-C_6H_5), 144.93, 145.16 ppm.

Mp.: 203 °C (dec.)

ESI-MS m/z: 465.4 $[M\text{-}Cl]^+$

Synthesis of (IPrPh)OTf (5)



Method: o-xylene, 2h

Reagents: IPr (0.5 g, 1.29 mmmol), PhOTf (0.25 g, 1.54 mmol), $Ni(cod)_2$ (19 mg, 5 mol%).

Yield: 0.12 g, 16%

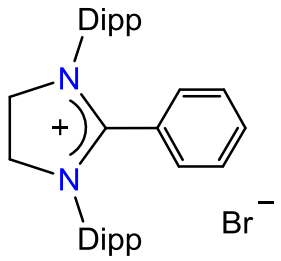
^{1}H NMR (500 MHz, $CDCl_3$, 25 ºC): δ 1.00 (d, $^3J_{H,H}$ = 6.9 Hz, 12H, $CH(CH_3)_2$), 1.28 (d, $^3J_{H,H}$ = 6.8 Hz, 12H, $CH(CH_3)_2$), 2.42 (sep, $^3J_{H,H}$ = 6.9 Hz, 4H, $CH(CH_3)_2$), 6.92 (d, $^3J_{H,H}$ = 8.5 Hz, 1H, *o*-C_6H_5), 7.21 (t, $^3J_{H,H}$ = 8.0 Hz, 2H, *m*-C_6H_5), 7.29 (d, $^3J_{H,H}$ = 7.9 Hz, 4H, *m*-C_6H_3), 7.30 (t, $^3J_{H,H}$ = 7.6 Hz, 1H, *p*-C_6H_5), 7.55 (t, $^3J_{H,H}$ = 7.9 Hz, 2H, *p*-C_6H_3), 8.16 (s, 2H, NC*H*) ppm.

^{13}C NMR (125 MHz, $CDCl_3$, 25 ºC): δ 22.75 ($CH(CH_3)_2$), 25.45 ($CH(CH_3)_2$), 29.49 ($CH(CH_3)_2$), 120.85, 125.37 (*m*-C_6H_3), 127.40 (N*C*H), 129.23, 129.33 (*m*-C_6H_5), 132.37 (*p*-C_6H_3), 132.76 (*p*-C_6H_5), 144.92 ppm.

Mp.: 228-229 °C (dec.)

ESI-MS m/z: 465.4 $[M\text{-}OTf]^+$

Synthesis of (SIPrPh)Br (6a)



Method: *o*-xylene, 2h

Reagents: SIPr (0.5 g, 1.29 mmmol), PhBr (0.14 mL, 1.29 mmol), $Ni(cod)_2$ (18 mg, 5 mol%).

Yield: 0.32 g, 45%

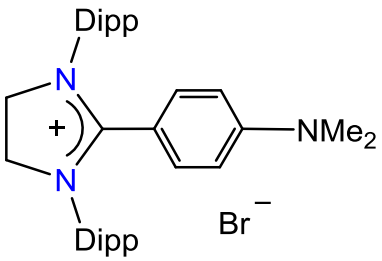
^{1}H NMR (500 MHz, $CDCl_3$, 25 ºC): δ 0.99 (d, $^3J_{H,H}$ = 6.67 Hz, 12H, $CH(CH_3)_2$), 1.42 (d, $^3J_{H,H}$ = 6.61 Hz, 12H, $CH(CH_3)_2$), 3.06 (sep, $^3J_{H,H}$ = 6.55 Hz, 4H, $CH(CH_3)_2$), 4.94 (s, 4H, NCH_2), 7.02 (d, $^3J_{H,H}$ = 7.85 Hz, 2H, *o*-C_6H_5), 7.16 (t, $^3J_{H,H}$ = 7.67 Hz, 2H, *m*-C_6H_5), 7.19 (d, $^3J_{H,H}$ = 7.77 Hz, 4H, *m*-C_6H_3), 7.37 (t, $^3J_{H,H}$ = 7.30 Hz, 1H, *p*-C_6H_5), 7.41 (t, $^3J_{H,H}$ = 7.47 Hz, 2H, *p*-C_6H_3) ppm.

^{13}C NMR (125 MHz, $CDCl_3$, 25 ºC): δ 23.34 ($CH(CH_3)_2$), 26.25 ($CH(CH_3)_2$), 29.35 ($CH(CH_3)_2$), 55.18 (NCH_2), 121.42, 125.60 (C_6H_3), 128.90 (C_6H_5), 129.52 (C_6H_5), 131.14, 131.34 (C_6H_3), 133.88 (C_6H_5), 145.74, 166.19 ppm.

Mp.: 296 °C (dec.).

ESI-MS m/z: 467.4 $[M\text{-}Br]^+$

Synthesis of {SIPr-(4-Me_2N-C_6H_4)}Br (6b)



Method: *o*-xylene, 2h

Reagents: SIPr (0.51 g, 1.31 mmmol), 4-bromo-N,N-dimethylaniline (0.27 g, 1.35 mmol), $Ni(cod)_2$ (18 mg, 5 mol%).

Yield: 0.52 g, 68%

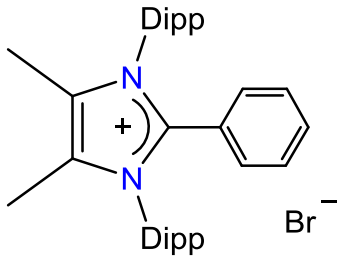
^{1}H NMR (500 MHz, $CDCl_3$, 25 ºC): δ 0.99 (d, $^3J_{H,H}$ = 6.5 Hz, 12H, $CH(CH_3)_2$), 1.40 (d, $^3J_{H,H}$ = 6.5 Hz, 12H, $CH(CH_3)_2$), 2.90 (s, 6H, $N(CH_3)_2$), 3.03 (sep, $^3J_{H,H}$ = 7.2 Hz, 4H, $CH(CH_3)_2$), 4.72 (s, 4H, NCH_2), 6.22 (d, $^3J_{H,H}$ = 8.8 Hz, 2H, C_6H_4), 6.80 (d, $^3J_{H,H}$ = 8.8 Hz, 2H, C_6H_4), 7.22 (d, $^3J_{H,H}$ = 7.6 Hz, 4H, *m*-C_6H_3), 7.42 (t, $^3J_{H,H}$ = 7.5 Hz, 2H, *p*-C_6H_3) ppm.

^{13}C NMR (125 MHz, $CDCl_3$, 25 ºC): δ 23.43 ($CH(CH_3)_2$), 25.80 ($CH(CH_3)_2$), 29.27 ($CH(CH_3)_2$), 39.88 (NCH_3), 54.61 (NCH_2),105.84, 110.41 (C_6H_4), 125.60 (C_6H_3), 130.89 (C_6H_3), 131.76 (C_6H_4), 132.77, 145.64, 153.06, 165.95 ppm.

Mp.: 292-293 °C

ESI-MS m/z: 510.5 $[M-Br]^+$.

Synthesis of {(Me_2-IPr)-Ph}Br (7a)



Method: *o*-xylene, 2h

Reagents: Me_2-IPr (0.51 g, 1.22 mmmol), PhBr (0.15 mL, 1.43 mmol), $Ni(cod)_2$ (18 mg, 5 mol%).

Yield: 0.55 g, 79%

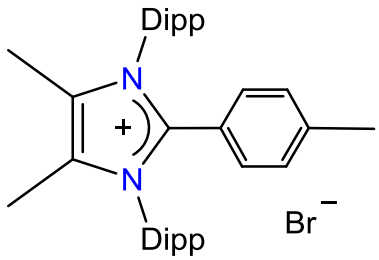
^{1}H NMR (500 MHz, $CDCl_3$, 25 ºC): δ 0.98 (d, $^{3}J_{H,H}$ = 6.7 Hz, 12H, $CH(CH_3)_2$), 1.30 (d, $^{3}J_{H,H}$ = 6.6 Hz, 12H, $CH(CH_3)_2$), 2.42 (sept, $^{3}J_{H,H}$ = 5 Hz, 4H, $CH(CH_3)_2$), 2.43 (s, 6H, CH_3), 6.95 (d, $^{3}J_{H,H}$ = 8.1 Hz, 2H, *o*-C_6H_5), 7.15 (t, $^{3}J_{H,H}$ = 7.4 Hz, 2H, *m*-C_6H_5), 7.35 (t, $^{3}J_{H,H}$ = 8.2 Hz, 1H, *p*-C_6H_5), 7.37 (d, $^{3}J_{H,H}$ = 7.8 Hz, 4H, *m*-C_6H_3), 7.61 (t, $^{3}J_{H,H}$ = 7.78 Hz, 2H, *p*-C_6H_3) ppm.

^{13}C NMR (125 MHz, $CDCl_3$, 25 ºC): δ 10.83, 23.43, 25.11, 29.22, 126.01, 129.05, 130.56, 132.47, 132.65, 145.34 ppm.

Mp: 311-314°C dec.

ESI-MS m/z: 493.4 $[M\text{-}Br]^+$.

Synthesis of {(Me_2-IPr)-4-tolyl}Br (7b)



Method: *o*-xylene, 2h

Reagents: Me_2-IPr (0.50 g, 1.20 mmmol), 4-bromotoluene (0.16 mL, 1.43 mmol), $Ni(cod)_2$ (20 mg, 5 mol%).

Yield: 0.61 g, 86%

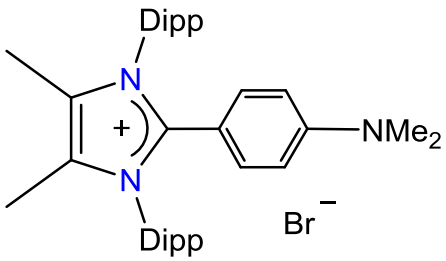
^{1}H NMR (500 MHz, $CDCl_3$, 25 ºC): δ 0.97 (d, $^{3}J_{H,H}$ = 6.6 Hz, 12H, $CH(CH_3)_2$), 1.29 (d, $^{3}J_{H,H}$ = 6.6 Hz, 12H, $CH(CH_3)_2$), 2.21 (s, 3H, Ar-CH_3), 2.39 (m, 4H, $CH(CH_3)_2$), 2.41 (s, 6H, CH_3), 6.80 (d, $^{3}J_{H,H}$ = 8.2 Hz, 2H, C_6H_4), 6.93 (d, $^{3}J_{H,H}$ = 8.0 Hz, 2H, C_6H_4), 7.36 (d, $^{3}J_{H,H}$ = 7.7 Hz, 4H, *m*-C_6H_3), 7.62 (t, $^{3}J_{H,H}$ = 7.8 Hz, 2H, *p*-C_6H_3) ppm.

^{13}C NMR (125 MHz, $CDCl_3$, 25 ºC): δ 10.84, 21.48, 23.42, 24.96, 29.21, 118.48, 125.99, 128.83, 129.72, 130.33, 132.58, 143.48, 145.27 ppm.

Mp: 296-297 °C dec.

ESI-MS m/z: 507.5 $[M\text{-}Br]^+$.

Synthesis of {(Me_2-IPr)-(4-Me_2N-C_6H_4)}Br (7c)



Method: *o*-xylene, 2h

Reagents: Me_2-IPr (0.51 g, 1.22 mmmol), 4-bromo-N,N-dimethylaniline (0.25 g, 1.25 mmol), $Ni(cod)_2$ (18 mg, 5 mol%).

Yield: 0.52 g, 68%

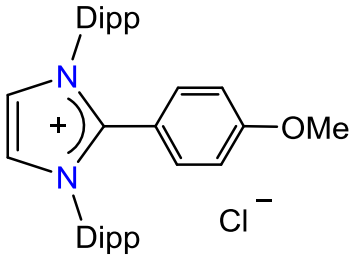
^{1}H NMR (500 MHz, $CDCl_3$, 25 ºC): δ 0.96 (d, $^3J_{H,H}$ = 5.3 Hz, 12H, $CH(CH_3)_2$), 1.28 (d, $^3J_{H,H}$ = 5.1 Hz, 12H, $CH(CH_3)_2$), 2.25 (s, 6H, Ar-CH_3), 2.40 (m, 4H, $CH(CH_3)_2$), 2.89 (s, 6H, CH_3), 6.20 (d, $^3J_{H,H}$ = 8.3 Hz, 2H, C_6H_4), 6.63 (d, $^3J_{H,H}$ = 8.0 Hz, 2H, C_6H_4), 7.40 (d, $^3J_{H,H}$ = 7.7 Hz, 4H, *m*-C_6H_3), 7.65 (t, $^3J_{H,H}$ = 7.8 Hz, 2H, *p*-C_6H_3) ppm.

^{13}C NMR (125 MHz, $CDCl_3$, 25 ºC): δ 10.36, 23.44, 24.62, 29.21, 39.83, 106.50, 128.38, 129.66, 129.97, 132.46, 144.57, 145.22, 151.72 ppm.

Mp: 313-315 °C dec.

ESI-MS m/z: 536. 5 $[M-Br]^+$.

Synthesis of {(IPr-(4-MeO-C_6H_4)}Cl (8)



Method: *o*-xylene, 2h

Reagents: IPr **(**0.5 g, 1.29 mmol), 4-chloroanisole (0.16 mL, 1.29 mmol), $Ni(cod)_2$ (18 mg, 5 mol%).

Yield: 0.12 g, 17%

^{1}H NMR (500 MHz, $CDCl_3$, 25 ºC): δ 0.98 (d, $^3J_{H,H}$ = 6.86 Hz, 12H, CH(CH_3)$_2$), 1.30 (d, $^3J_{H,H}$ = 6.78 Hz, 12H, CH(CH_3)$_2$), 2.45 (sep, $^3J_{H,H}$ = 6.87 Hz, 4H, CH(CH$_3$)$_2$), 3.71 (s, 3H, OCH_3), 6.64 (d, $^3J_{H,H}$ = 9.09 Hz, 2H, C_6H_4), 6.82 (d, $^3J_{H,H}$ = 9.09 Hz, 2H, C_6H_4), 7.30 (d, $^3J_{H,H}$ = 7.84 Hz, 4H, *m*-C_6H_3), 7.54 (t, $^3J_{H,H}$ = 7.84 Hz, 2H, *p*-C_6H_3), 8.62 (s, 2H, NCH) ppm.

^{13}C NMR (125 MHz, $CDCl_3$, 25 ºC): δ 22.81(CH(*C*H$_3$)$_2$), 25.56(CH(*C*H$_3$)$_2$), 29.42(*C*H(CH$_3$)$_2$), 55.67 (*C*H$_3$), 112.75, 114.72 (*C*$_6$H$_4$), 125.36 (*m*-*C*$_6$H$_3$), 127.77 (N*C*H), 130.57, 130.98 (*C*$_6$H$_4$), 132.17 (*p*-*C*$_6$H$_3$), 140.47, 144.97, 162.48 ppm.

Mp.: 283 °C (dec.)

ESI-MS m/z: 495.4 $[M\text{-}Cl]^+$

Stoichiometric Reactions

*(1) Reaction of IPr, Ni(cod)$_2$, and PhBr to [2{IPr-(Ph)}]NiBr$_4$ (**14**-H)*

To a 10 mL toluene solution of IPr (109 g, 0.26 mmol) and Ni(cod)$_2$ (75 mg, 0.26 mmol) was added PhBr (40 mg, 0.26 mmol). The resulting brown solution was stirred at room temperature (rt), which resulted in a green solution after 10 minutes. A greenish crystalline solid was formed, which was isolated by filtration and dried under vacuum to obtain **14**-H. Yield: 47 mg.

^{1}H NMR (500 MHz, $CDCl_3$, 25 ºC): δ 0.97 (br, 12H, CH(CH_3)$_2$), 1.37 (br, 12H, CH(CH_3)$_2$), 2.52 (br, 4H, CH(CH$_3$)$_2$), 6.92 (br, 2H, C_6H_5), 7.19 (br, 5H, C_6H_3, C_6H_5), 7.34 (br, 2H, C_6H_5), 7.51 (br, 2H, C_6H_3), 9.13 (br, 2H, NCH) ppm.

*(2) Reaction of IPr, Ni(cod)$_2$, and 4-Bromotoluene to [2{IPr-(4-tolyl)}]NiBr$_4$ (**14**-Me)*

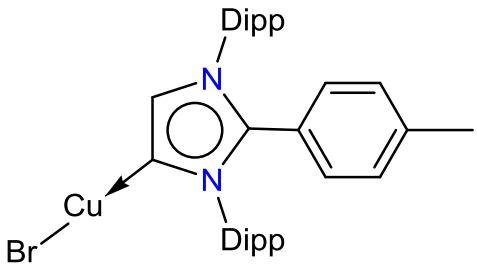
To a 10 mL toluene solution of IPr (101 mg, 0.26 mmol) and Ni(cod)$_2$ (71 mg, 0.26 mmol) was added 4-bromotoluene (44 mg, 0.26 mmol) and the resulting solution was stirred at room temperature for 0.5h. Compound [2{IPr-(4-tolyl)}]NiBr$_4$ (**14**-Me) was precipitated out as a light green solid, which was separated by filtration. The mother liquor was stored at 6 ºC overnight to obtain suitable single crystals of [2{IPr-(4-tolyl)}]NiBr$_4$ (**14**-Me) for X-ray diffraction analyses (Figure S4). Yield of **14**-Me: 56 mg.

^{1}H NMR (500 MHz, $CDCl_3$, 25 ºC): δ 1.08 (br, 12H, CH(CH_3)$_2$), 1.64 (br, 12H, CH(CH_3)$_2$), 2.36 (s 3H, C6H$_4$CH_3), 2.72 (br, 4H, CH(CH$_3$)$_2$), 7.03 (br, 2H, C_6H_4), 7.18 (br, 2H, C_6H_4), 7.36 (br, 4H, C_6H_3), 7.58 (br, 2H, C_6H_3), 9.51 (br, 2H, NCH) ppm.

Benzene soluble part contains 4,4'-dimethylbiphenyl[9]

^{1}H NMR (500 MHz, C_6DCl_3, 25 ºC): δ 2.16 (s, 6H, CH_3), 7.07 (d, J = 7.8 Hz, C_6H_4), 7.46 (d, J = 8.0 Hz, C_6H_4) ppm.

Synthesis of {(aIPr-(4-tolyl)}CuBr (22)



To a flask containing {IPr-(4-anisyl)}Br (0.50g, 0.90 mmol), LiHMDS (0.17 g, 1.02 mmol) and CuBr (0.0.13 g, 0.90 mmol) was added 20 mL of THF at -10 °C. The resulting light brown suspension was stirred overnight at room temperature. Filtration through a plug of Celite afforded a light yellow solution. The volatiles were removed under vacuum to obtain **22** as a off-white solid.

Yield: 80%, 0.45 g.

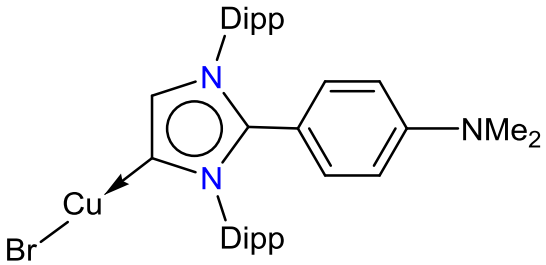
^{1}HNMR (500 MHz, $CDCl_3$, 25ºC): δ 0.96 (d, $^{3}J_{H,H}$ = 6.9 Hz, 6H, $CH(CH_3)_2$), 0.99 (d, $^{3}J_{H,H}$ = 6.9 Hz, 6H, $CH(CH_3)_2$), 1.23 (d, $^{3}J_{H,H}$ = 6.8 Hz, 6H, $CH(CH_3)_2$), 1.39 (d, $^{3}J_{H,H}$ = 6.8 Hz, 6H, $CH(CH_3)_2$), 2.17 (s, 3H, CH_3), 2.55 (m, 4H, $CH(CH_3)_2$, 6.73 (d, $^{3}J_{H,H}$ = 8.2 Hz, 2H, C_6H_4), 6.87 (s, 1H, NC*H*), 6.89 (d, $^{3}J_{H,H}$ = 4.3 Hz, 2H, C_6H_4), 7.19 (d, $^{3}J_{H,H}$ = 7.8 Hz, 2H, *m*-C_6H_3), 7.24 (d, $^{3}J_{H,H}$ = 7.8 Hz, 2H, *m*-C_6H_3), 7.41 (t, $^{3}J_{H,H}$ = 7.7 Hz, 1H, *p*-C_6H_3), 7.46 (t, $^{3}J_{H,H}$ = 7.8 Hz, 1H, *p*-C_6H_3) ppm.

^{13}C NMR (125 MHz, $CDCl_3$, 25ºC): δ 21.36 (CH_3), 22.70 ($CH(CH_3)_2$), 22.76 ($CH(CH_3)_2$), 25.79 ($CH(CH_3)_2$), 26.03 ($CH(CH_3)_2$), 28.96 ($CH(CH_3)_2$), 68.16, 120.41, 124.59 (C_6H_3), 124.77 (C_6H_3), 128.91 (C_6H_4), 129.25 (C_6H_4), 129.88, 130.50 (C_6H_3), 131.01 (C_6H_3), 131.80, 135.66, 141.29, 144.28, 145.23, 160.34 ppm.

Mp.: 178-179 °C (dec.)

ESI-MS m/z: 582.4 $[M+CH_3CN]^+$.

Synthesis of {(aIPr-(4-Me_2N-C_6H_4)}CuBr (23)



Yield: 62%

To a flask containing (IPr-4-NMe_2-C_6H_4)Br (0.231g, 0.392 mmol), KHMDS (0.105 g, 0.526 mmol) and CuBr (0.058 g, 0.404 mmol) was added 15 mL of THF at -10 °C. The resulting light brown suspension was stirred overnight at room temperature. Filtration through a plug of Celite afforded a light yellow solution. The volatiles were removed under vacuum to obtain **23** as a light yellow solid (0.158 g, 0.243 mmol, 62%).

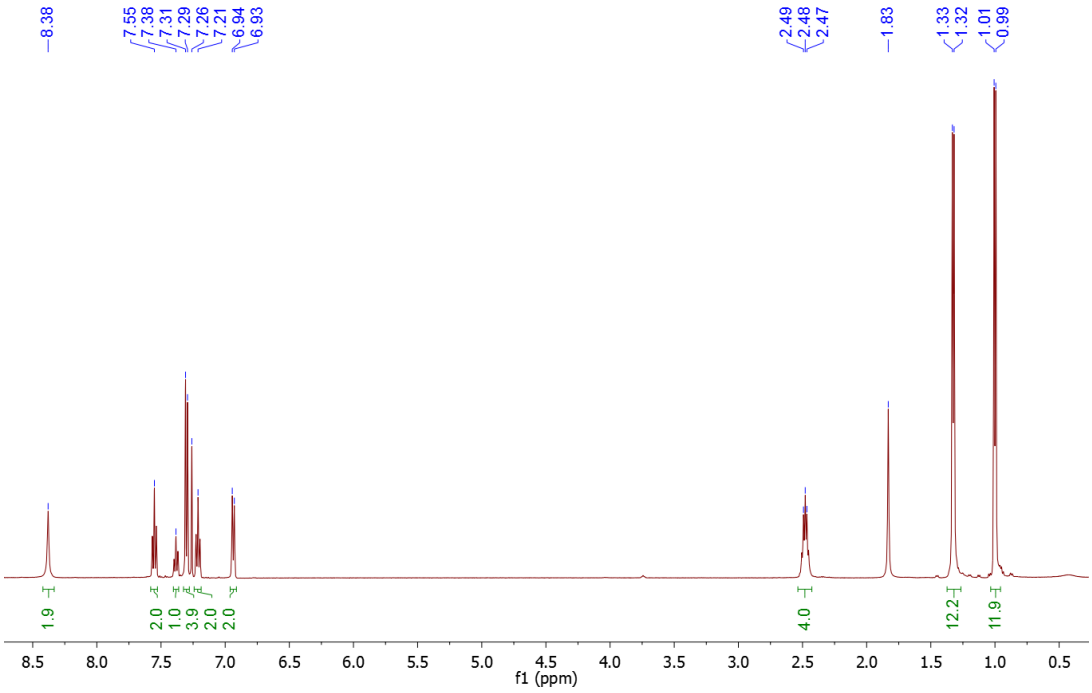
^{1}H NMR (500 MHz, $CDCl_3$, 25ºC): δ 0.97 (d, $^3J_{H,H}$ = 6.9 Hz, 6H, $CH(CH_3)_2$), 1.00 (d, $^3J_{H,H}$ = 6.9 Hz, 6H, $CH(CH_3)_2$), 1.23 (d, $^3J_{H,H}$ = 6.7 Hz, 6H, $CH(CH_3)_2$), 1.38 (d, $^3J_{H,H}$ = 6.7 Hz, 6H, $CH(CH_3)_2$), 2.59 (m, 4H, $CH(CH_3)_2$), 2.83 (s, 6H, $N(CH_3)_2$), 6.24 (d, $^3J_{H,H}$ = 8.9 Hz, 2H, C_6H_4), 6.64 (d, $^3J_{H,H}$ = 8.8 Hz, 2H, C_6H_4), 6.80 (s, 1H, NC*H*), 7.21 (d, $^3J_{H,H}$ = 7.7 Hz, 2H, *m*-C_6H_3), 7.24 (d, $^3J_{H,H}$ = 7.7 Hz, 2H, *m*-C_6H_3), 7.42 (t, $^3J_{H,H}$ = 7.7 Hz, 1H, *p*-C_6H_3), 7.46 (t, $^3J_{H,H}$ = 7.8 Hz, 1H, *p*-C_6H_3) ppm.

^{13}C NMR (125 MHz, $CDCl_3$, 25ºC): δ 22.82 ($CH(CH_3)_2$), 25.62 ($CH(CH_3)_2$), 25.82 ($CH(CH_3)_2$), 28.91 ($CH(CH_3)_2$), 39.83 ($N(CH_3)_2$), 68.14, 109.61, 110.83 (C_6H_4), 124.57 (C_6H_3), 124.74 (C_6H_3), 129.29 (NCH), 130.03 (C_6H_3)), 130.20 (C_6H_3), 130.70, 132.98, 136.31, 144.95, 150.86 ppm.

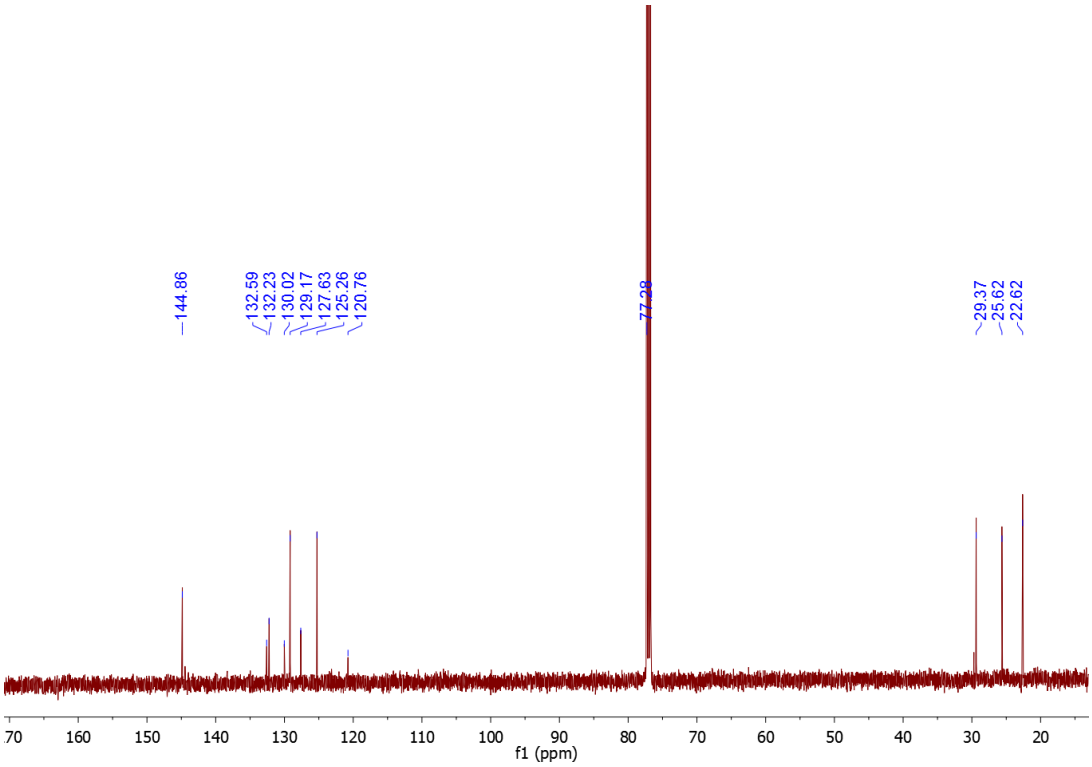
Mp.: 188-189 °C

ESI-MS m/z: 611.4 $[M+CH_3CN]^+$.

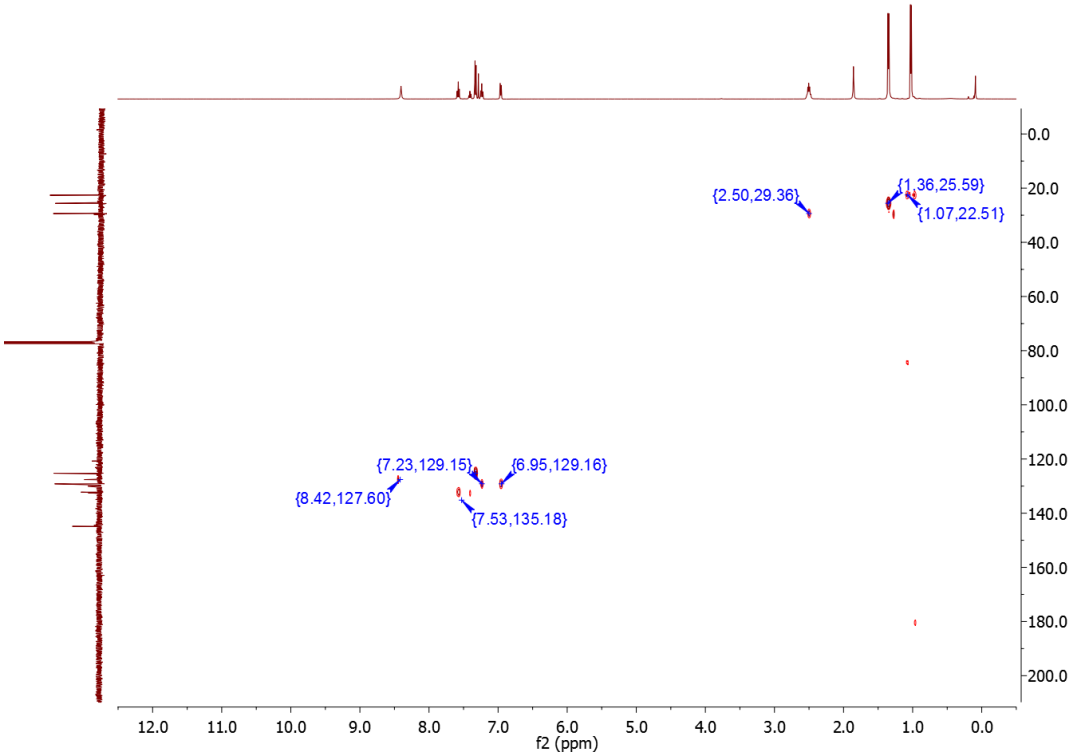
Plots of NMR Spectra



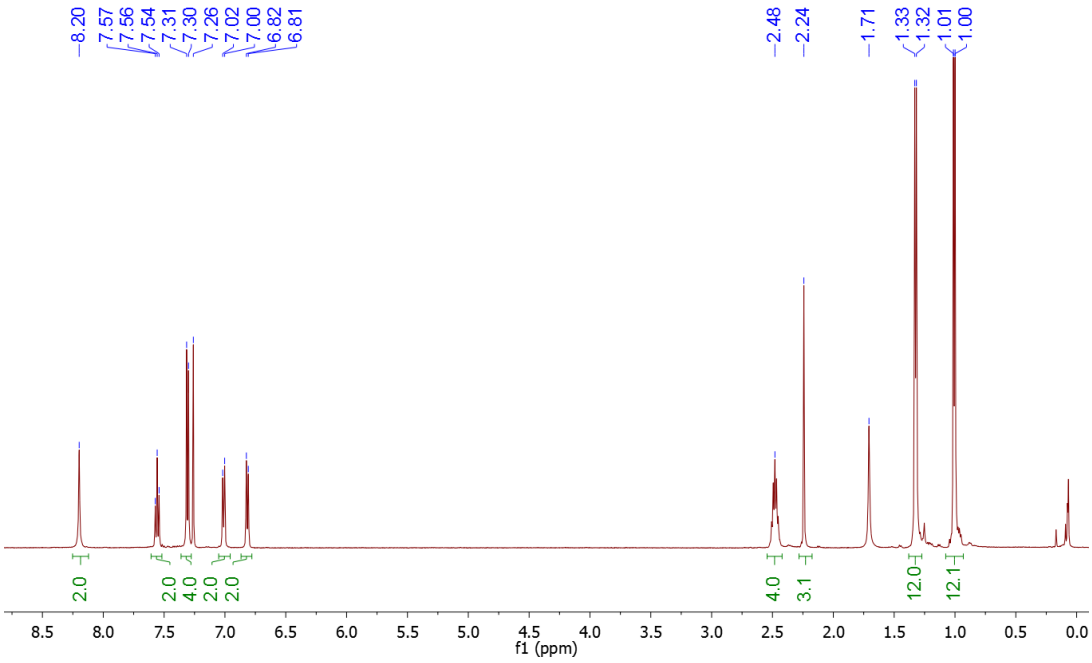
Plot P1. ^{1}H NMR spectrum of (IPrPh)Br (**3a**).



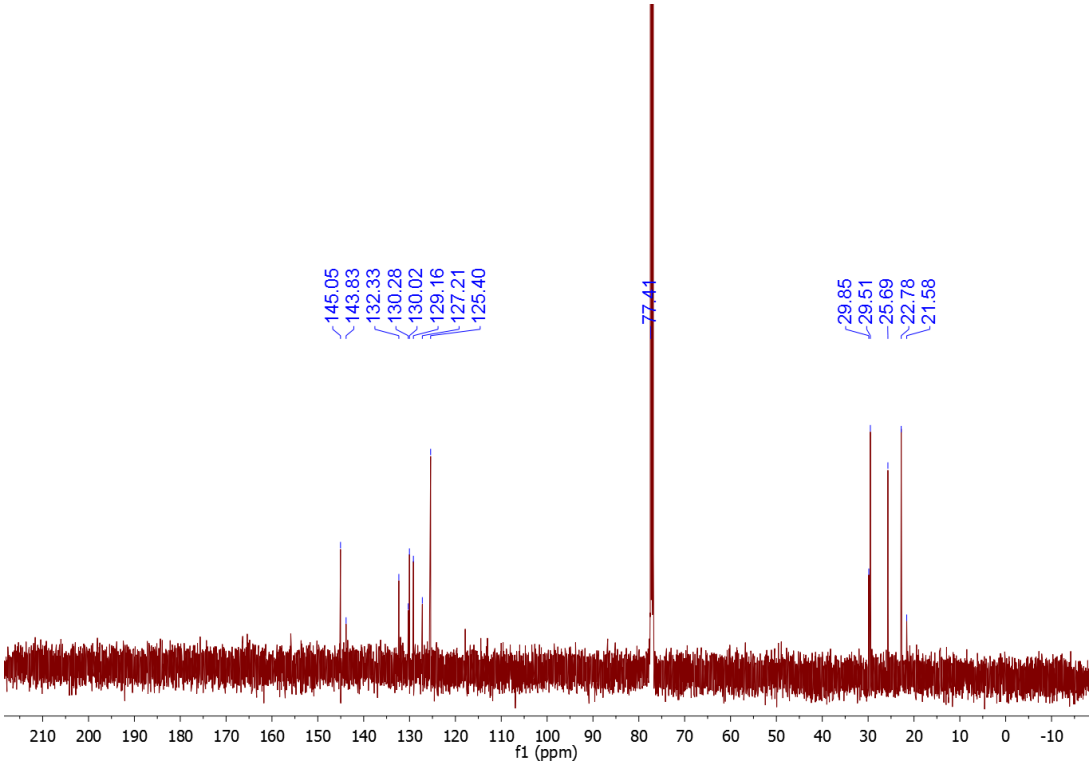
Plot P2. ^{13}C{^{1}H} NMR spectrum of (IPrPh)Br (**3a**).



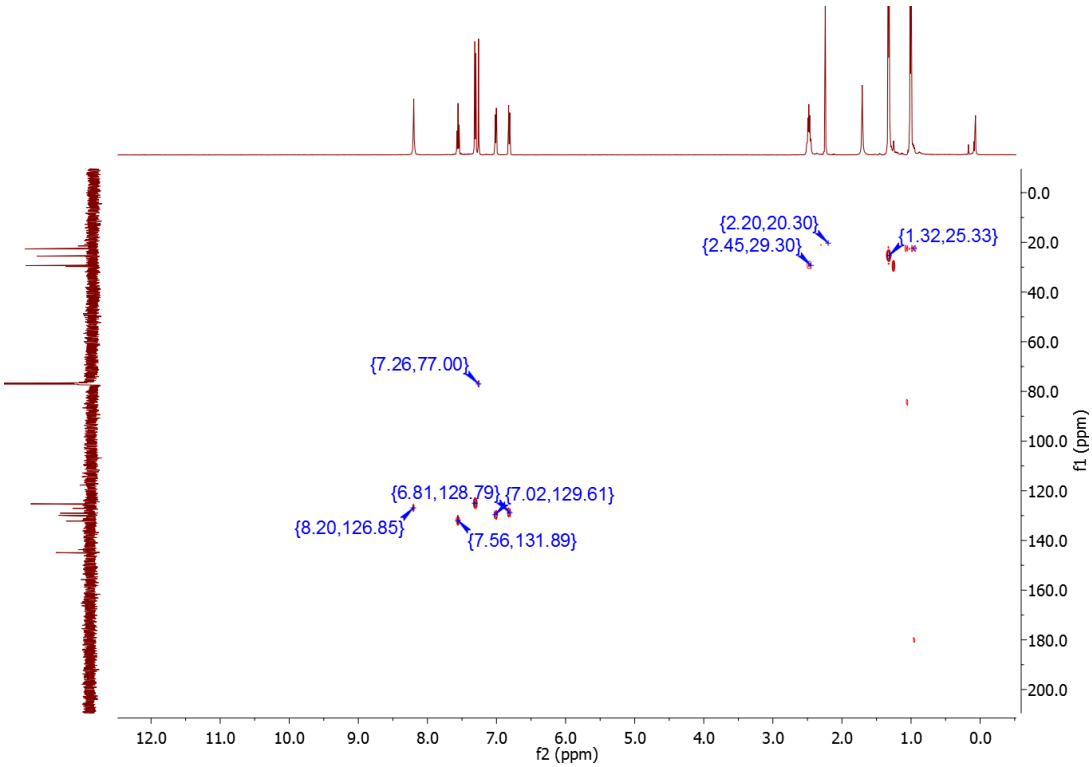
Plot P3. ^{1}H-^{13}C HMQC NMR spectrum of (IPrPh)Br (**3a**).



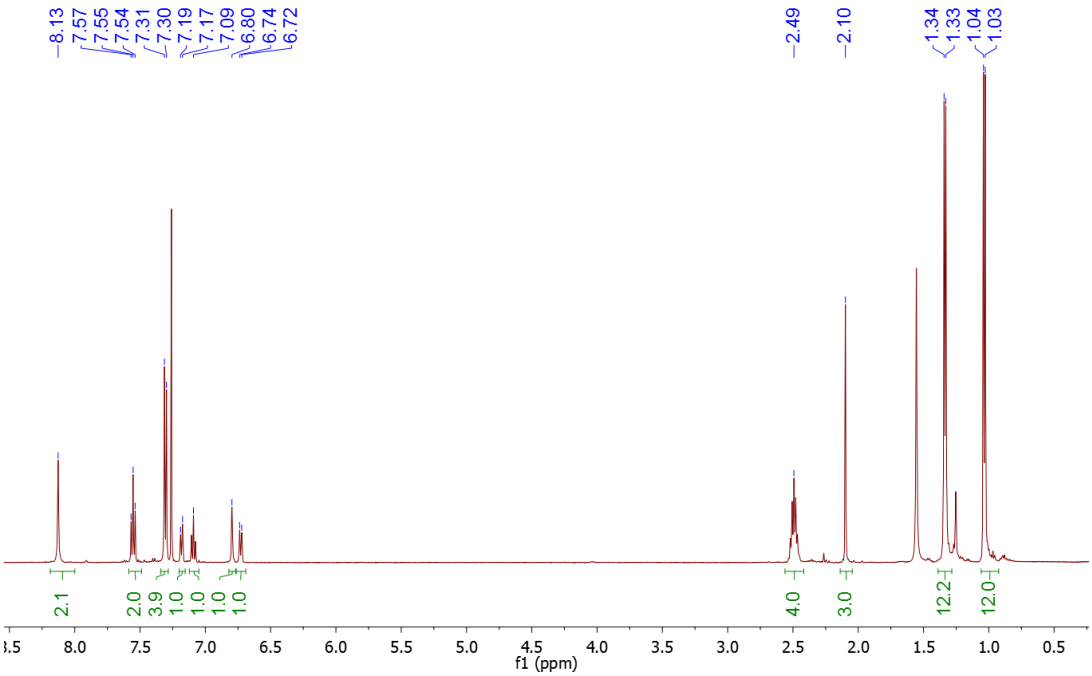
Plot P4. ^{1}H NMR spectrum of {IPr-(4-tolyl)}Br (**3b**).



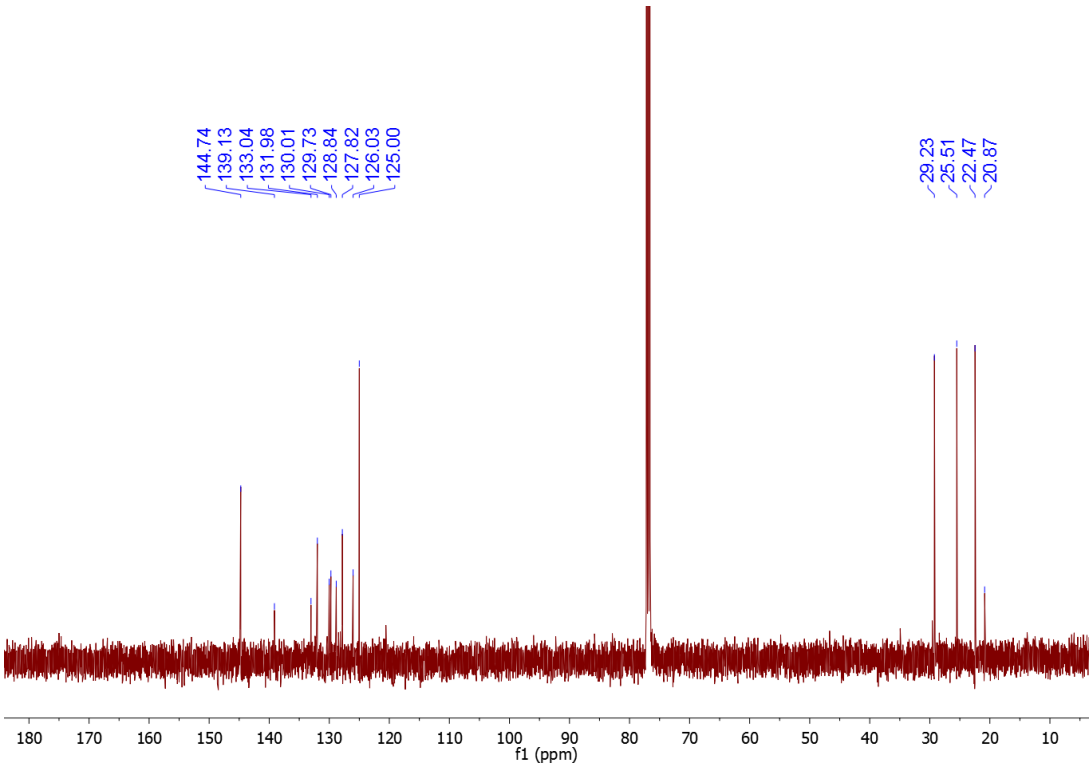
Plot P5. $^{13}C\{^{1}H\}$ NMR spectrum of {IPr-(4-tolyl)}Br (**3b**).



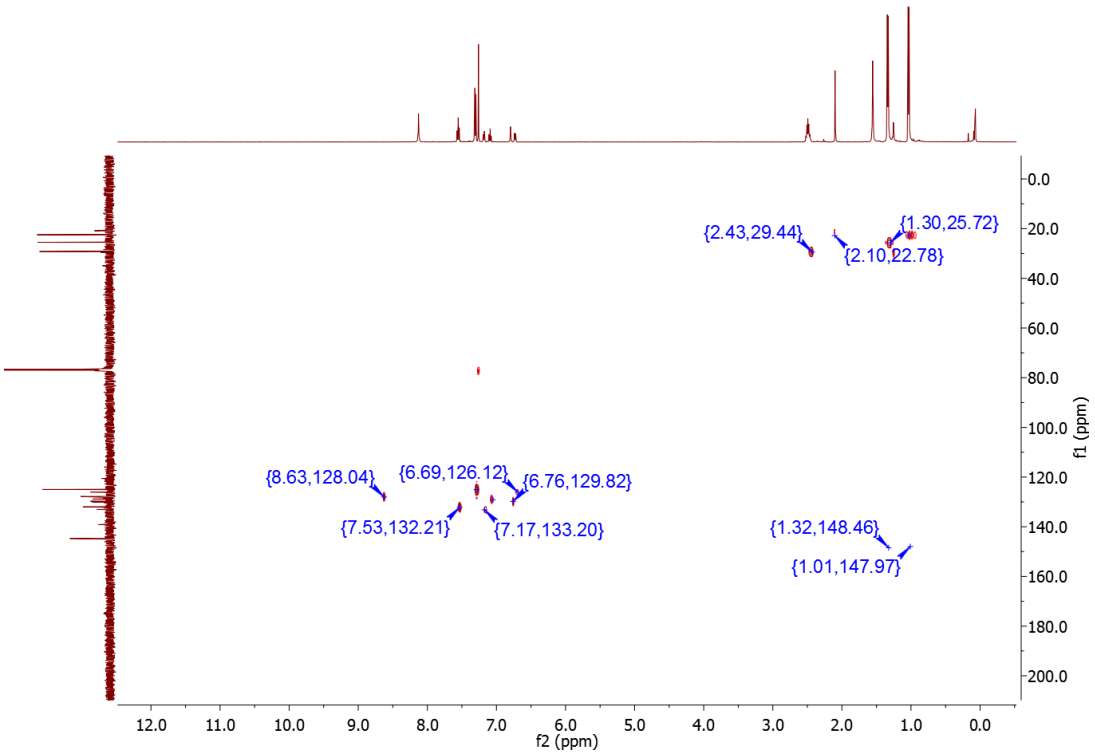
Plot P6. ^{1}H-^{13}C HMQC NMR spectrum of {IPr-(4-tolyl)}Br (**3b**).



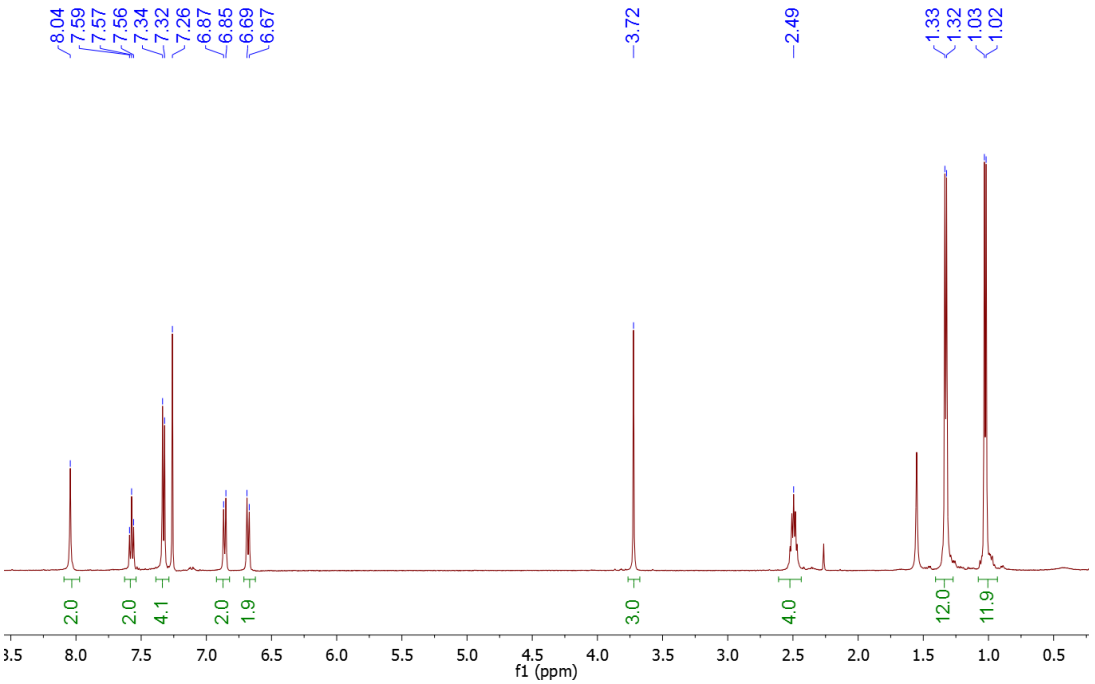
Plot P7. ^{1}H NMR spectrum of {IPr-(3-tolyl)}Br (**3c**).



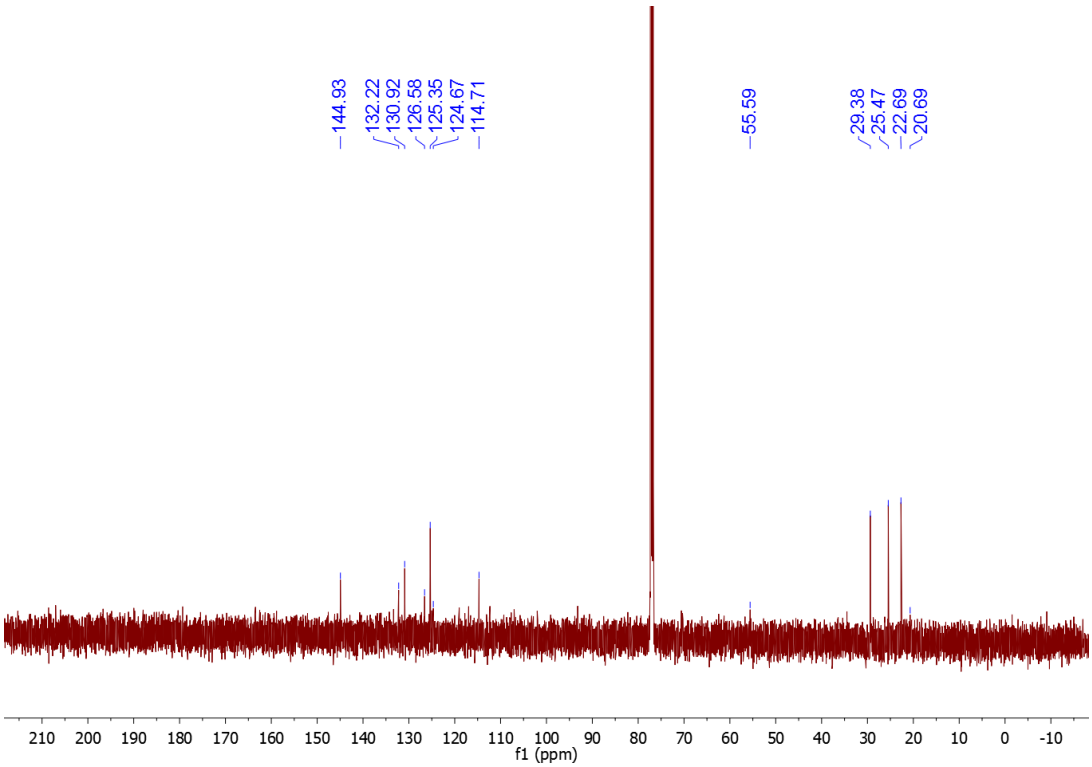
Plot P8. ^{13}C{^{1}H} NMR spectrum of {IPr-(3-tolyl)}Br (**3c**).



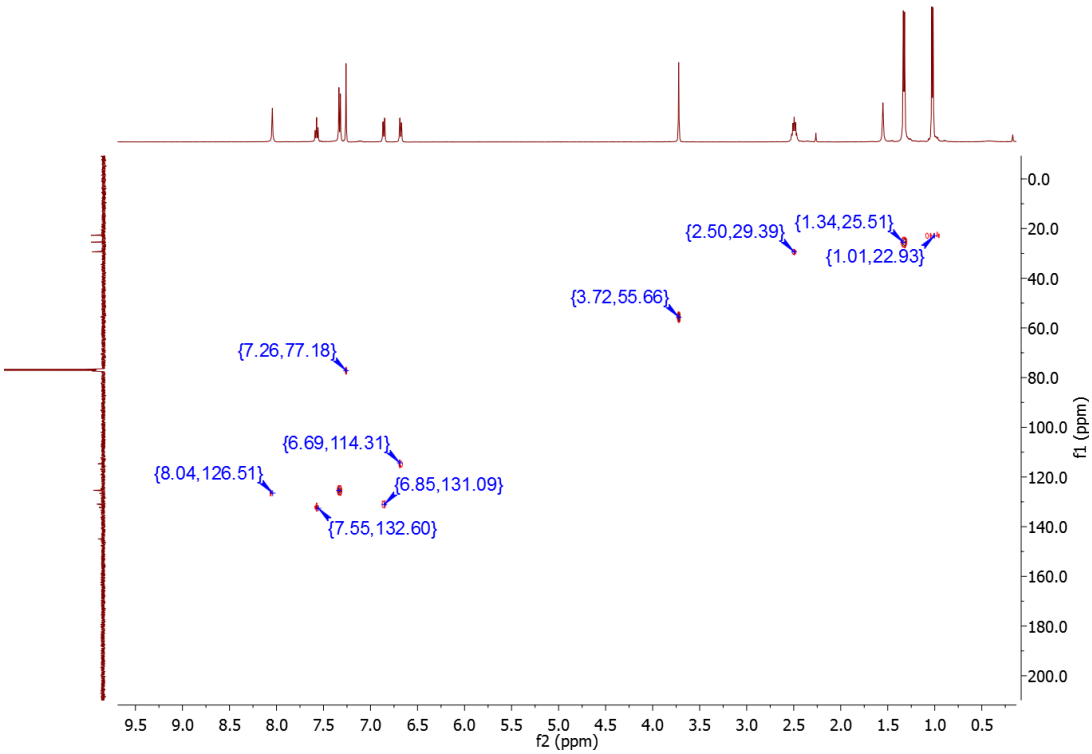
Plot P9. ^{1}H-^{13}C HMQC NMR spectrum of {IPr-(3-tolyl)}Br (**3c**).



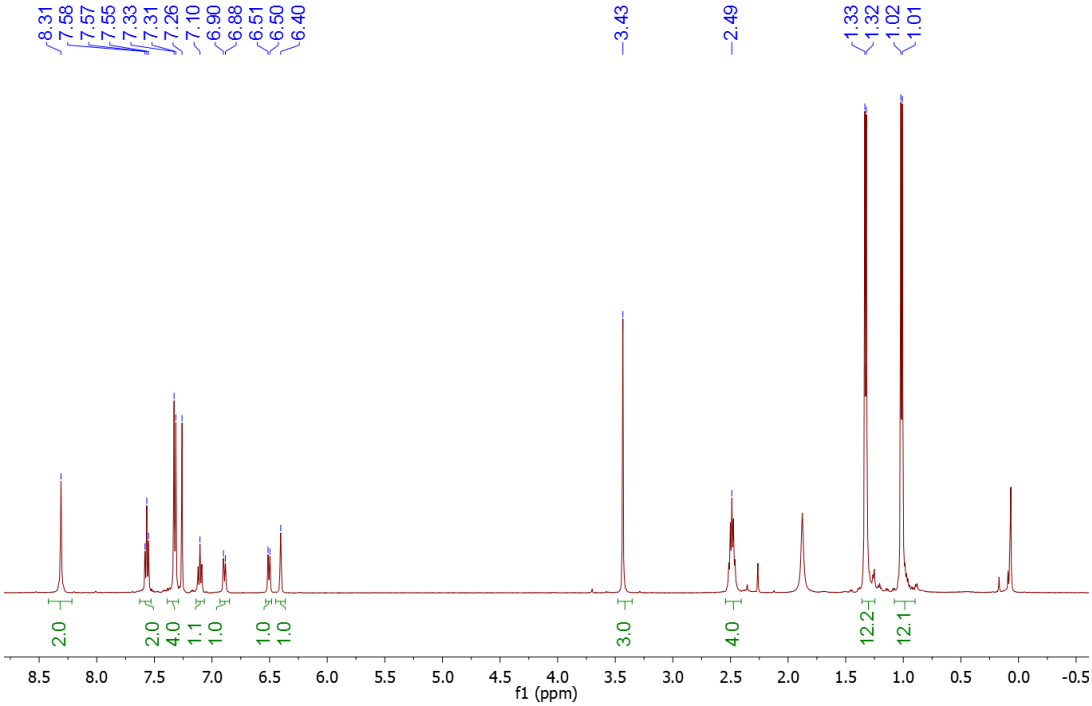
Plot P10. ^{1}H NMR spectrum of {IPr-(4-anisyl)}Br (**3d**).



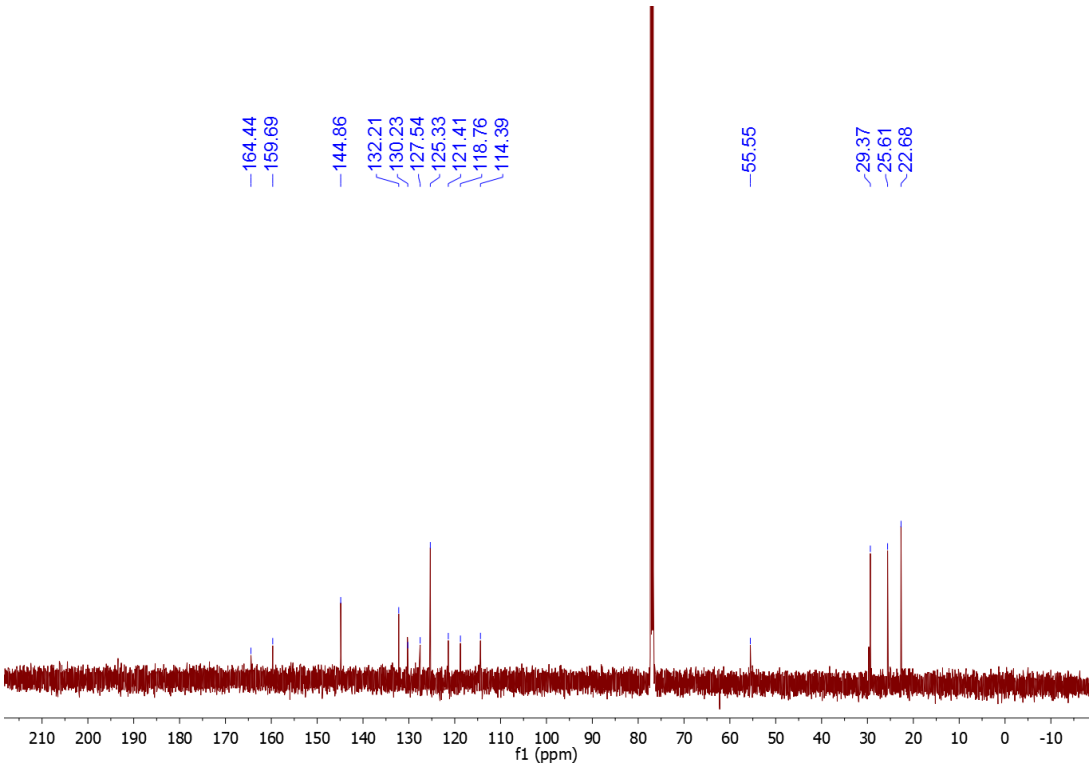
Plot P11. $^{13}C\{^{1}H\}$ NMR spectrum of {IPr-(4-anisyl)}Br (**3d**).



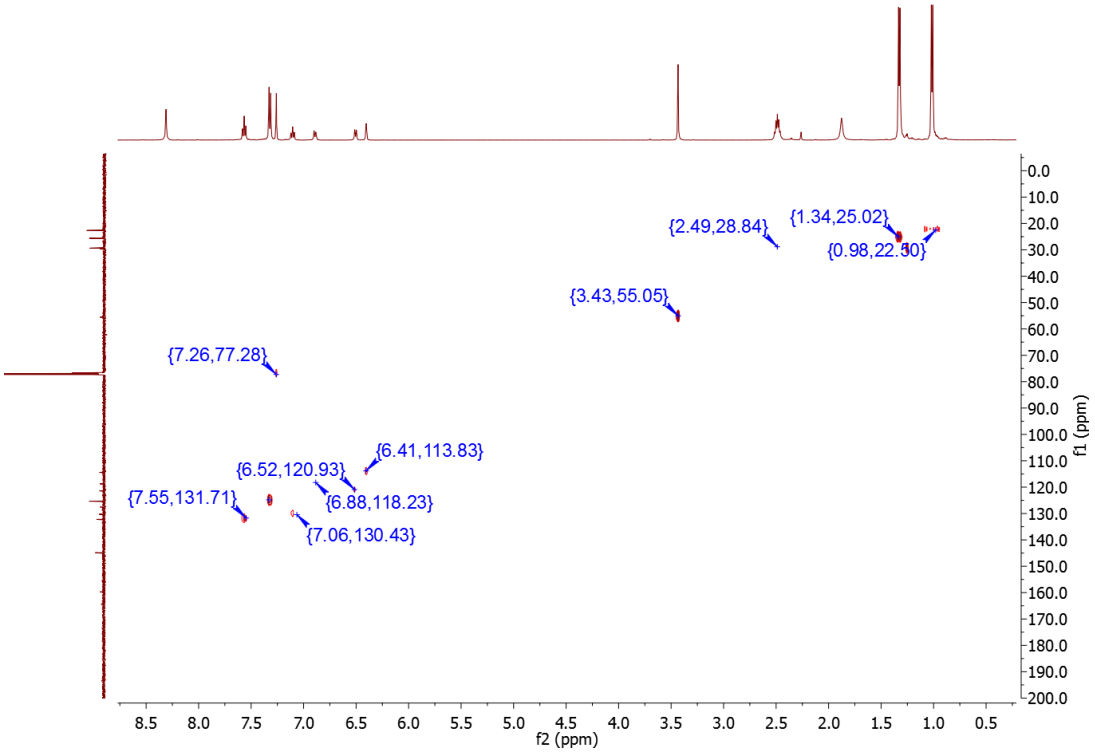
Plot P12. ^{1}H-^{13}C HMQC NMR spectrum of {IPr-(4-anisyl)}Br (**3d**).



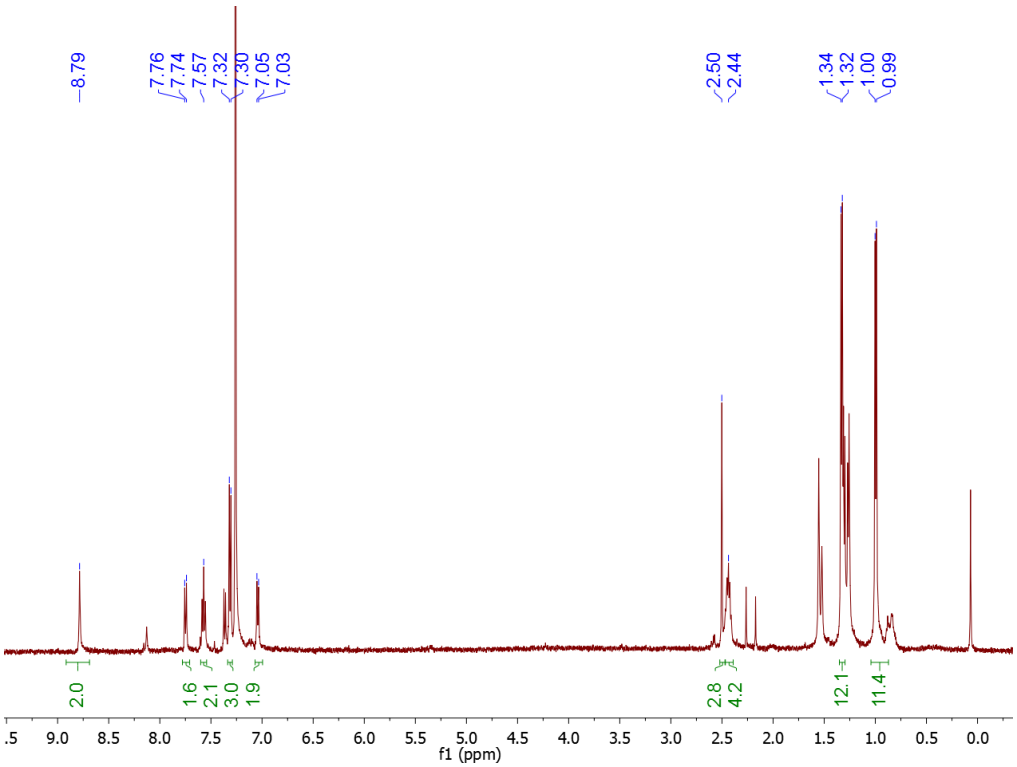
Plot P13. ^{1}H NMR spectrum of {IPr-(3-anisyl)}Br (**3e**).



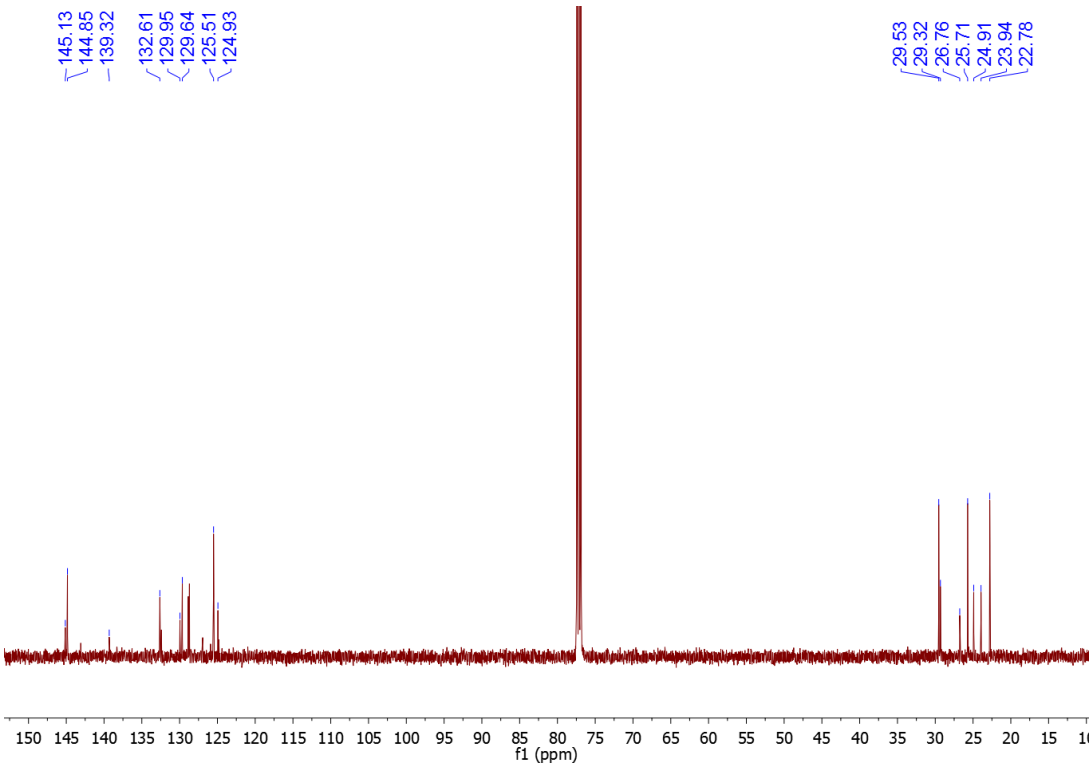
Plot P14. ^{13}C{^{1}H} NMR spectrum of {IPr-(3-anisyl)}Br (**3e**).



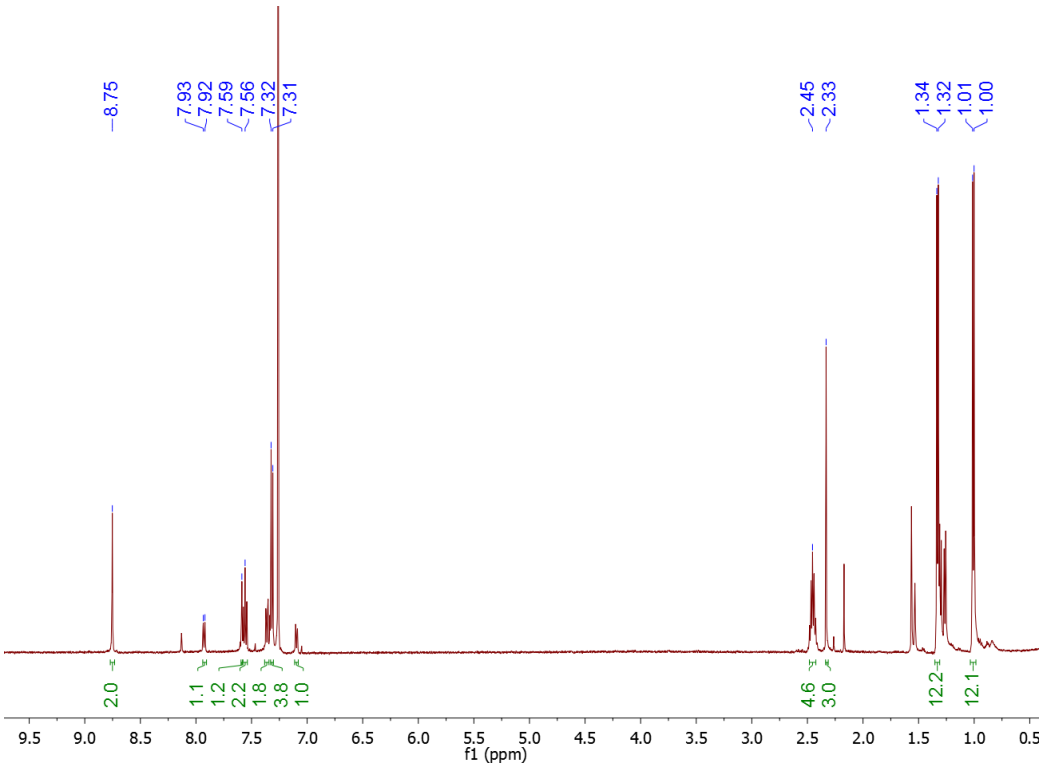
Plot P15. ^{1}H-^{13}C HMQC NMR spectrum of {IPr-(3-anisyl)}Br (**3e**).



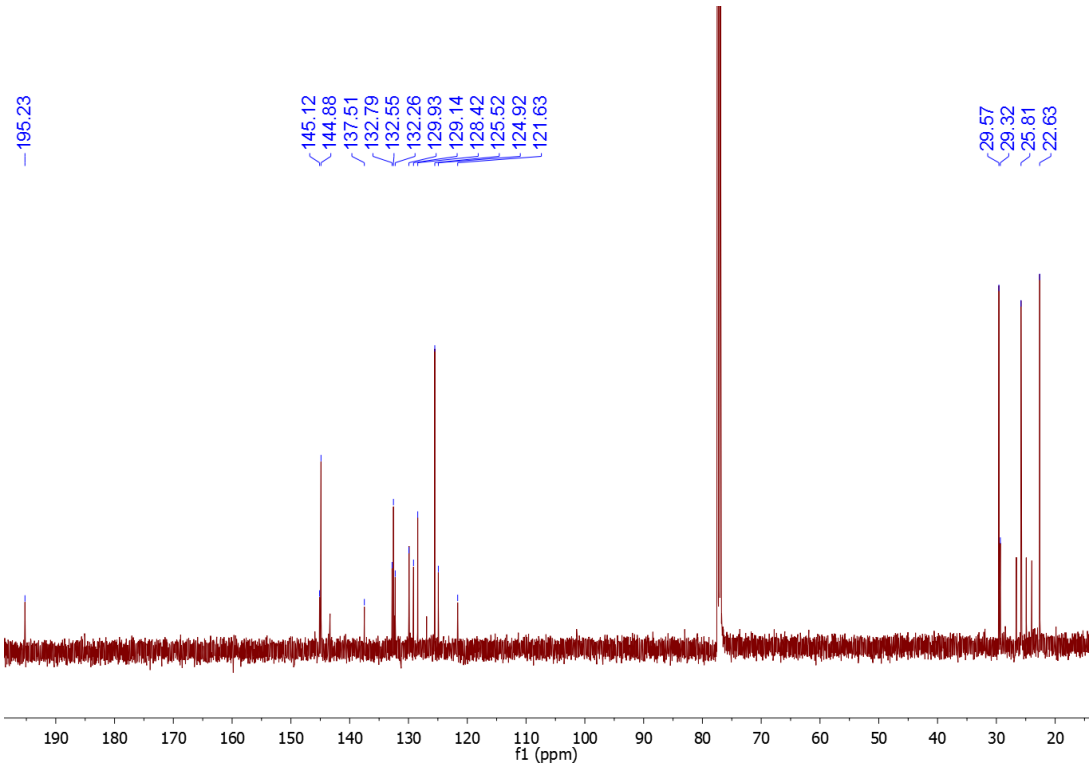
Plot P16. ^{1}H NMR spectrum of {IPr-(4-acetylphenyl)}Br (**3f**).



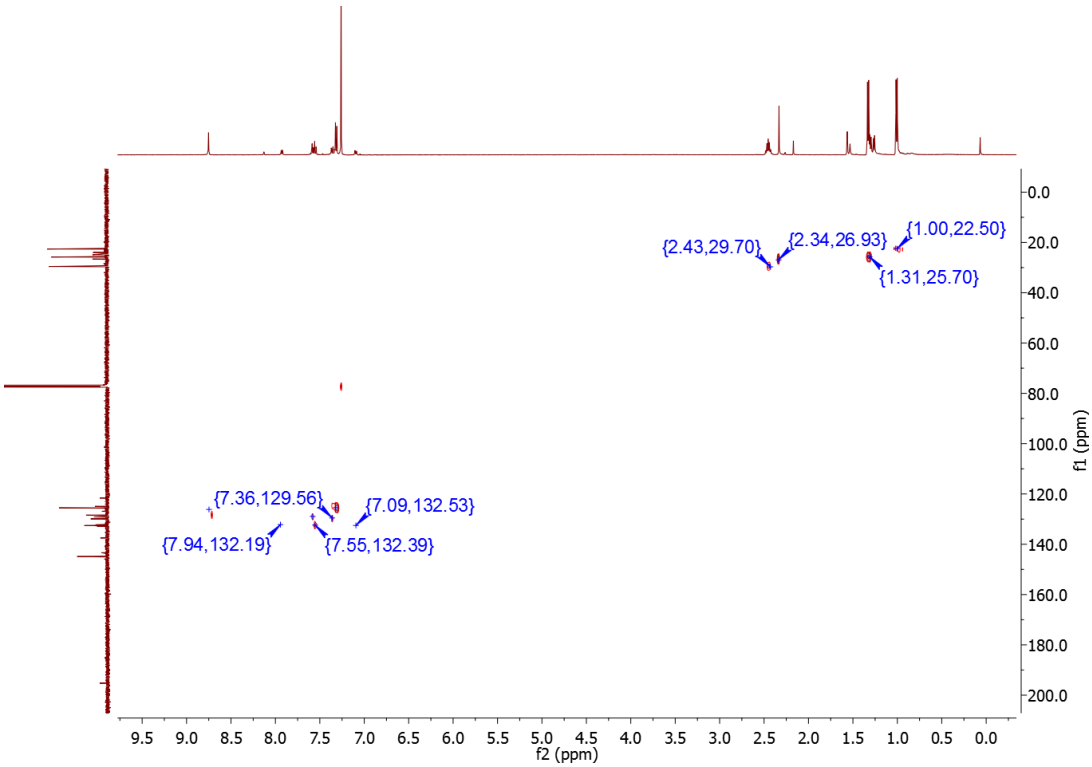
Plot P17. $^{13}C\{^{1}H\}$ NMR spectrum of {IPr-(4-acetylphenyl)}Br (**3f**).



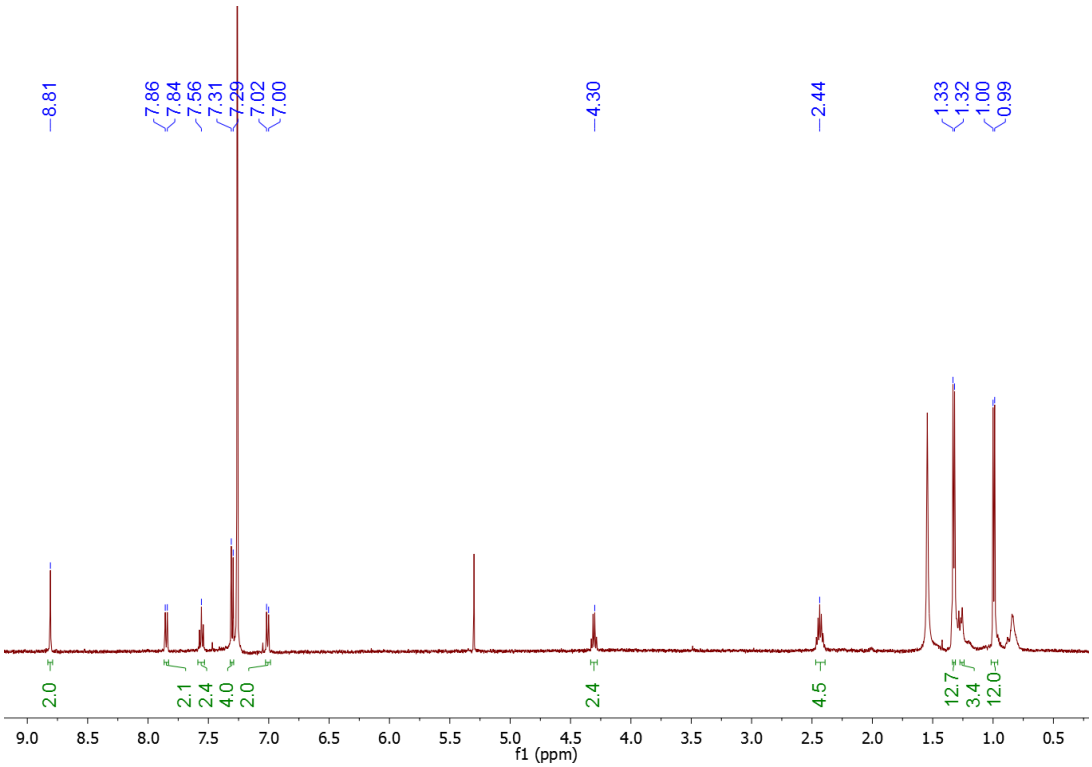
Plot P18. ^{1}H NMR spectrum of {IPr-(3-acetylphenyl)}Br (**3g**).



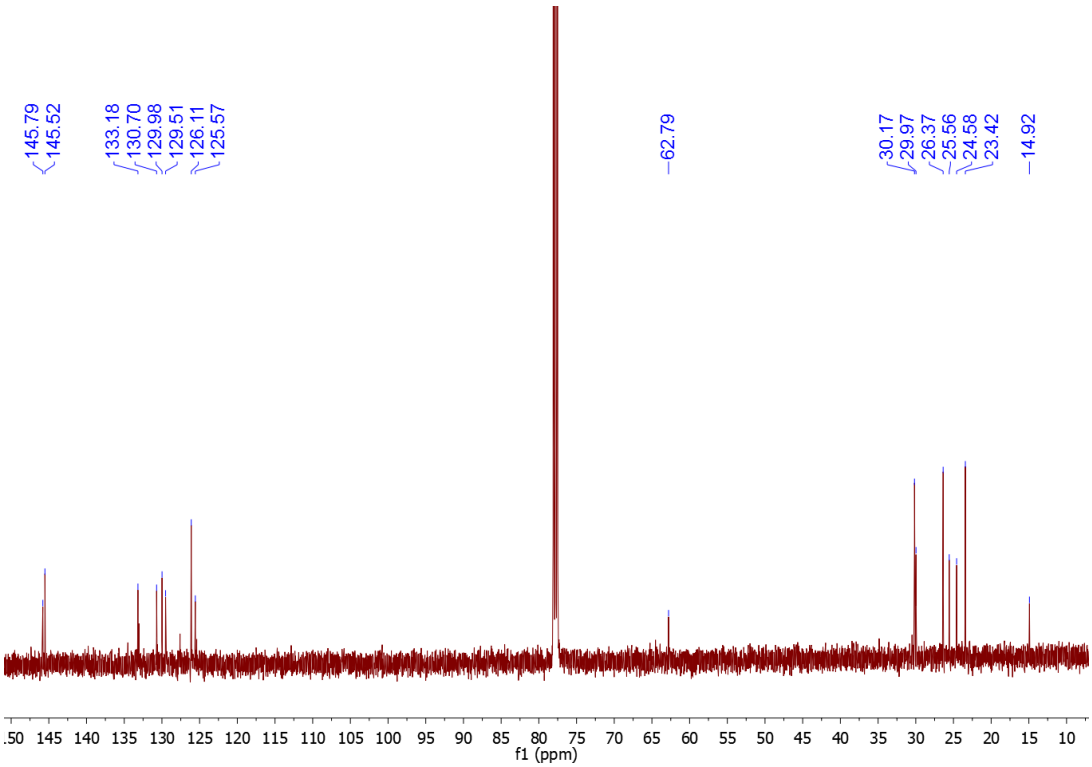
Plot P19. $^{13}C\{^{1}H\}$ NMR spectrum of {IPr-(3-acetylphenyl)}Br (**3g**).



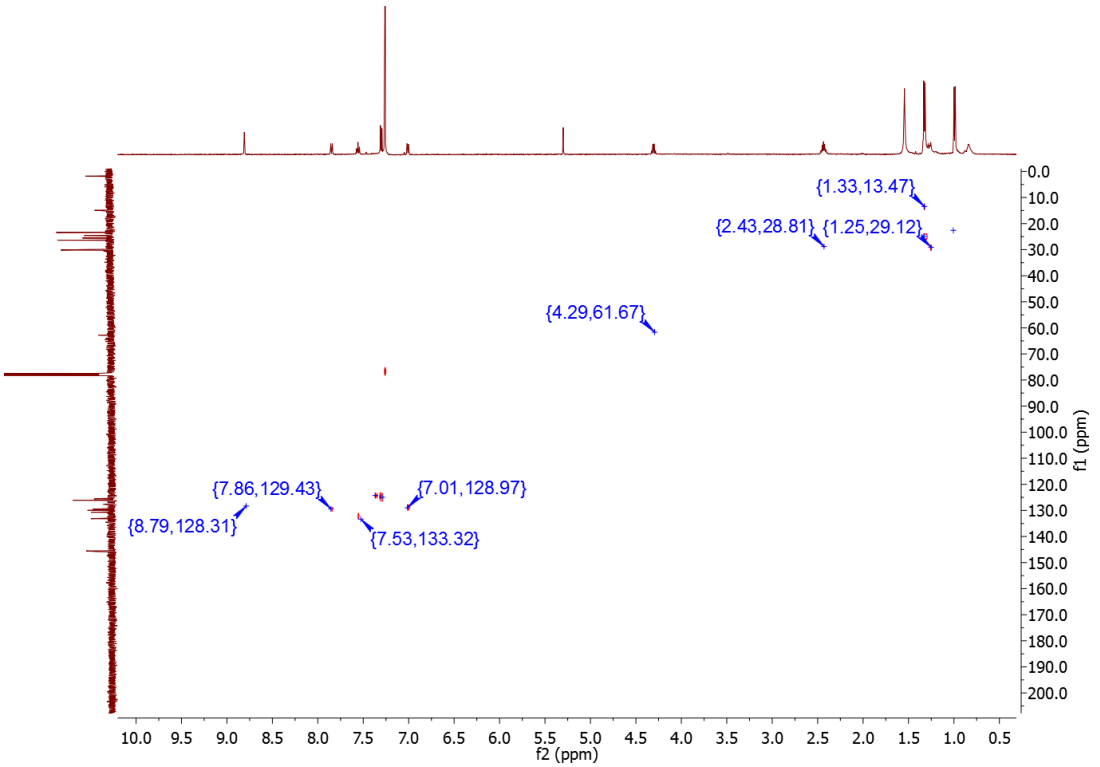
Plot P20. ^{1}H-^{13}C HMQC NMR spectrum of {IPr-(3-acetyl)}Br (**3g**).



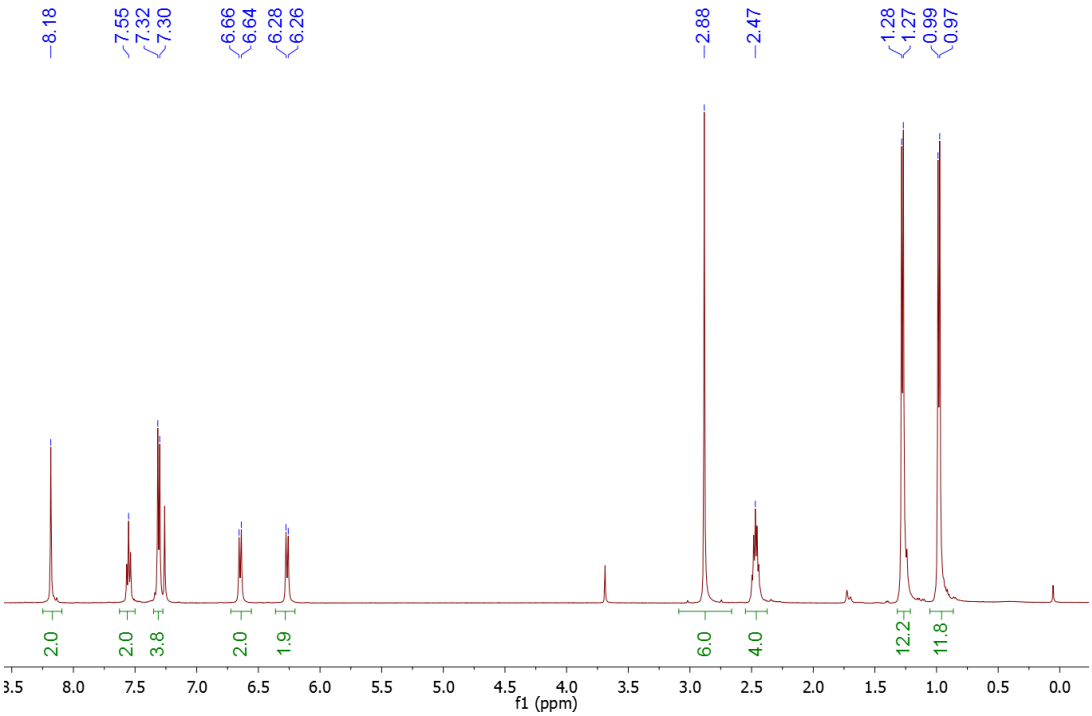
Plot P21. ^{1}H NMR spectrum of {IPr-(4-EtO(O)C-C_6H_4)}Br (**3h**).



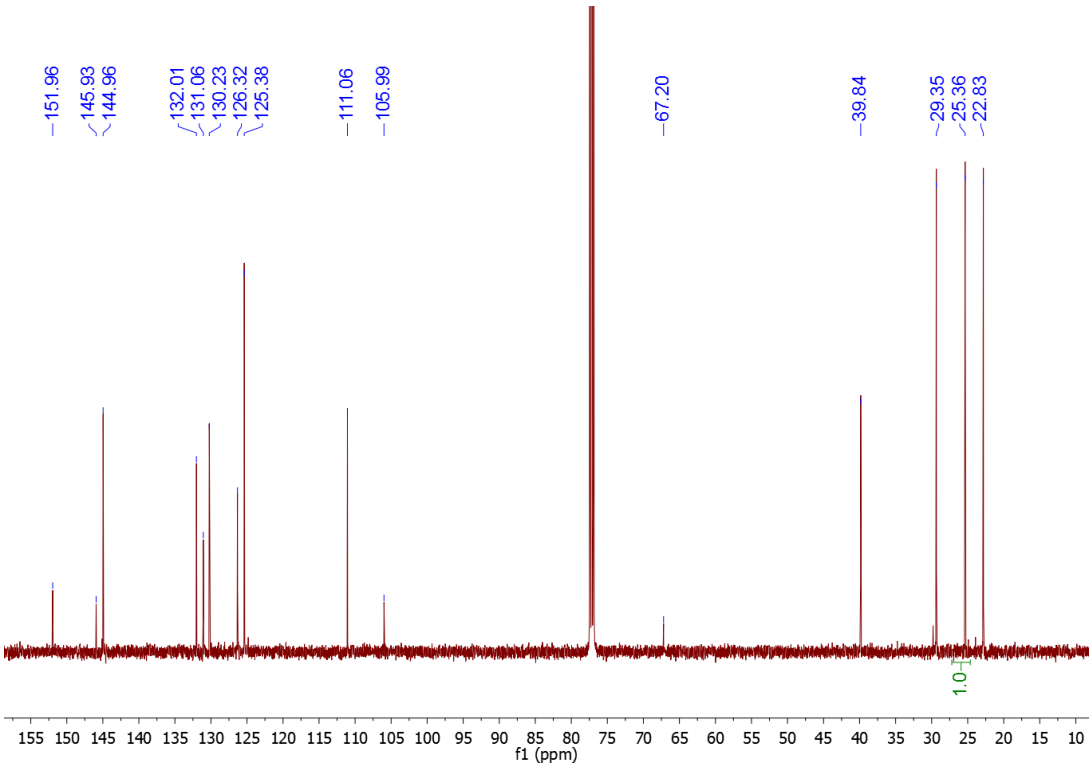
Plot P22. ^{13}C{^{1}H} NMR spectrum of {IPr-(4-EtO(O)C-C_6H_4)}Br (**3h**).



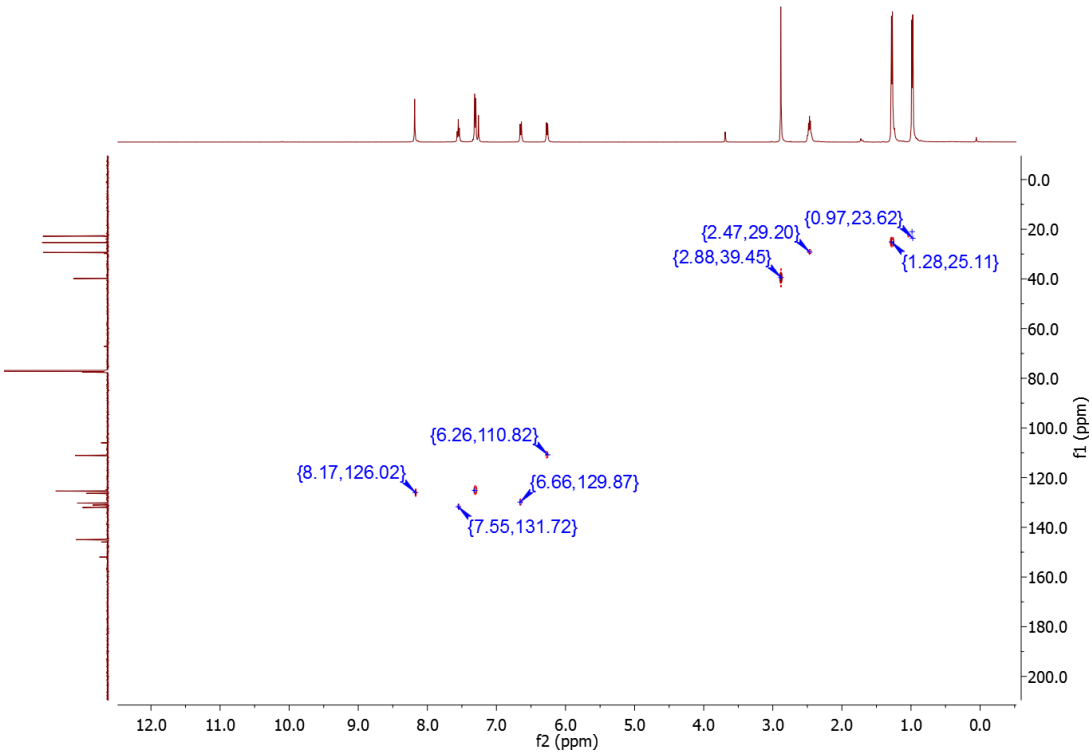
Plot P23. ^{1}H-^{13}C HMQC NMR spectrum of {IPr-(4-EtO(O)C-C_6H_4)}Br (**3h**).



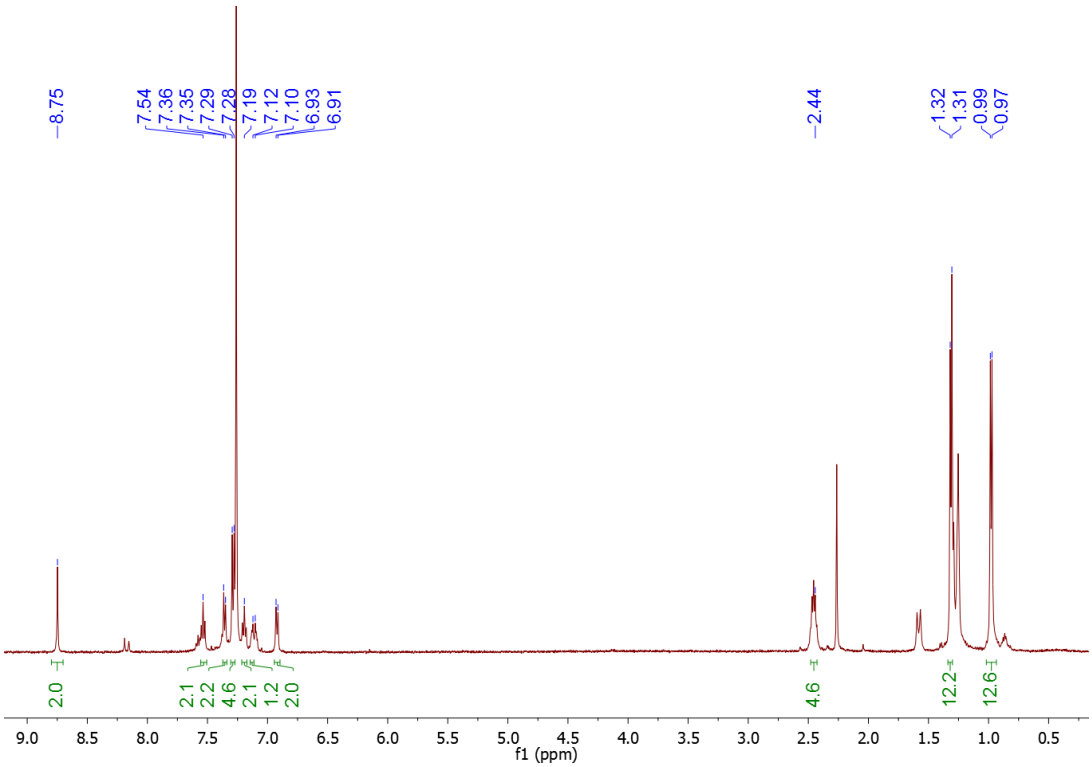
Plot P24. ^{1}H NMR spectrum of {IPr-(4-Me_2N-C_6H_4)}Br (**3j**).



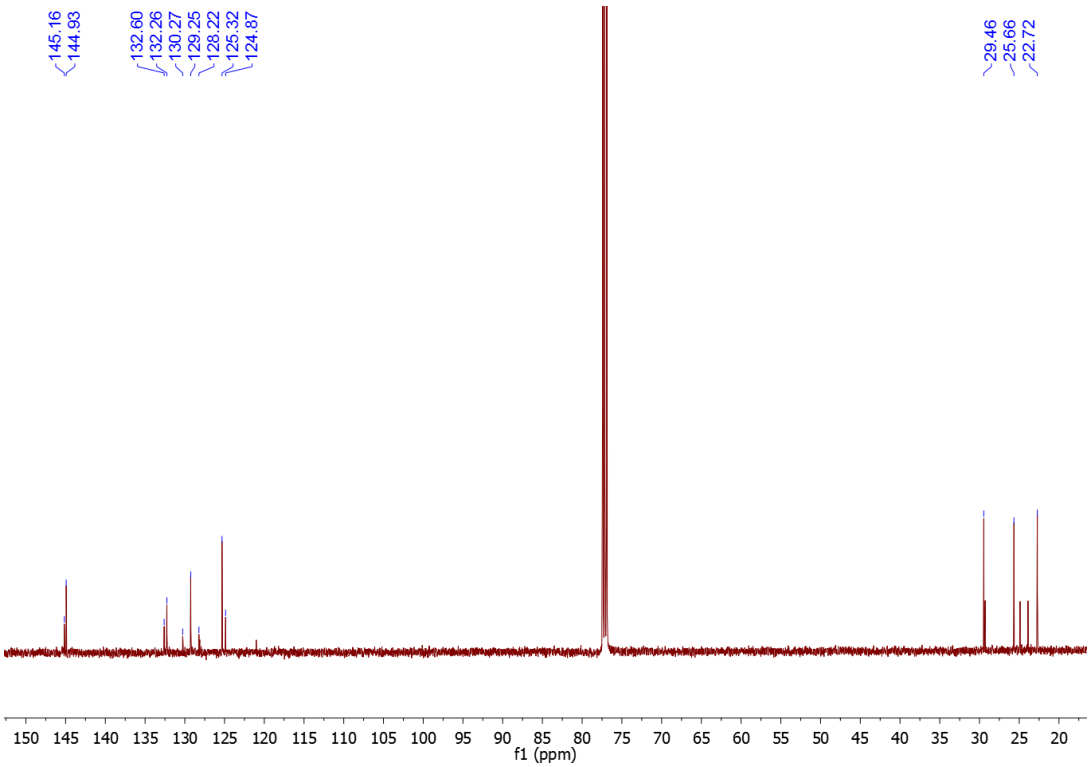
Plot P25. $^{13}C\{^{1}H\}$ NMR spectrum of {IPr-(4-Me_2N-C_6H_4)}Br (**3j**).



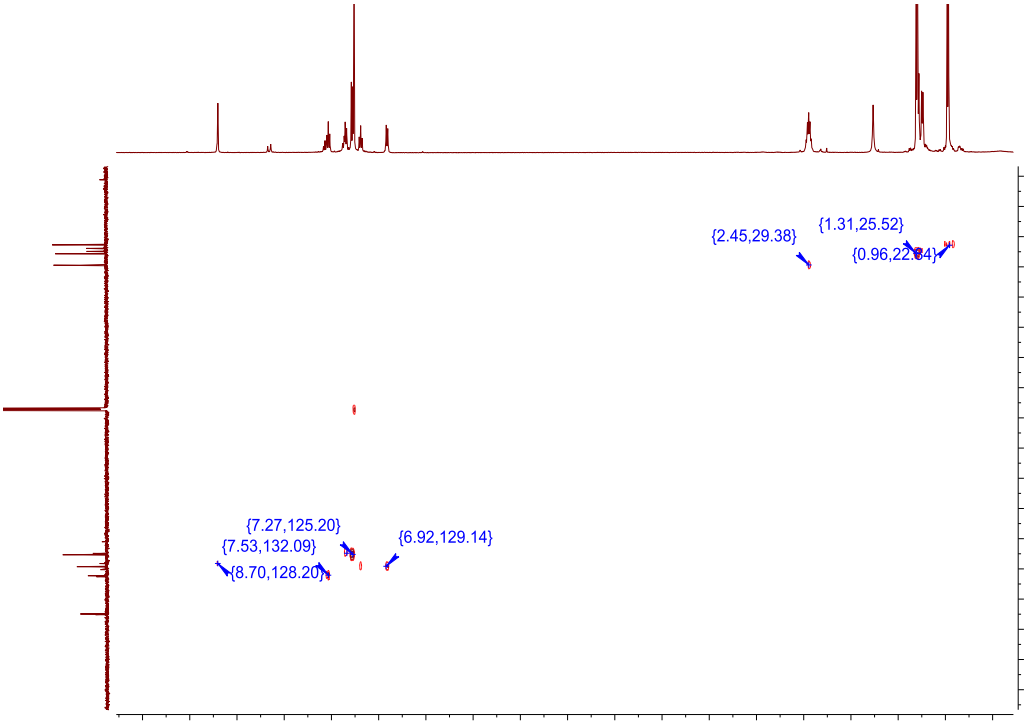
Plot P26. ^{1}H-^{13}C HMQC NMR spectrum of {IPr-(4-Me_2N-C_6H_4)}Br (**3j**).



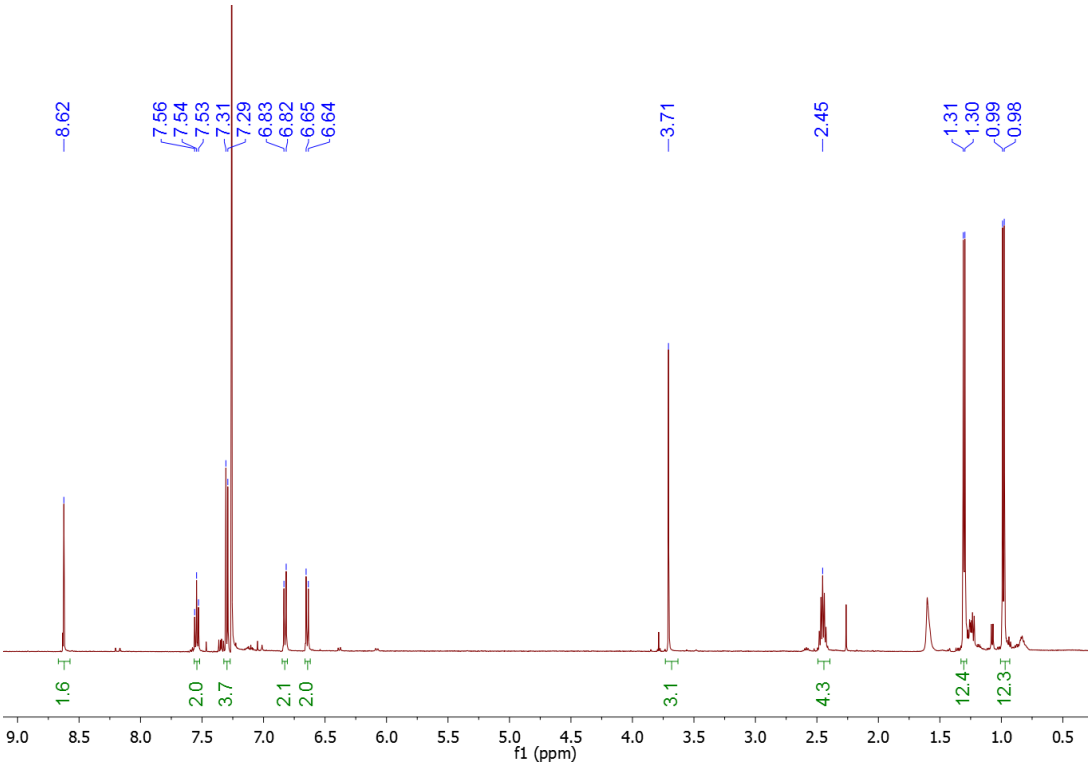
Plot P27. ^{1}H NMR spectrum of (IPrPh)Cl (**4a**).



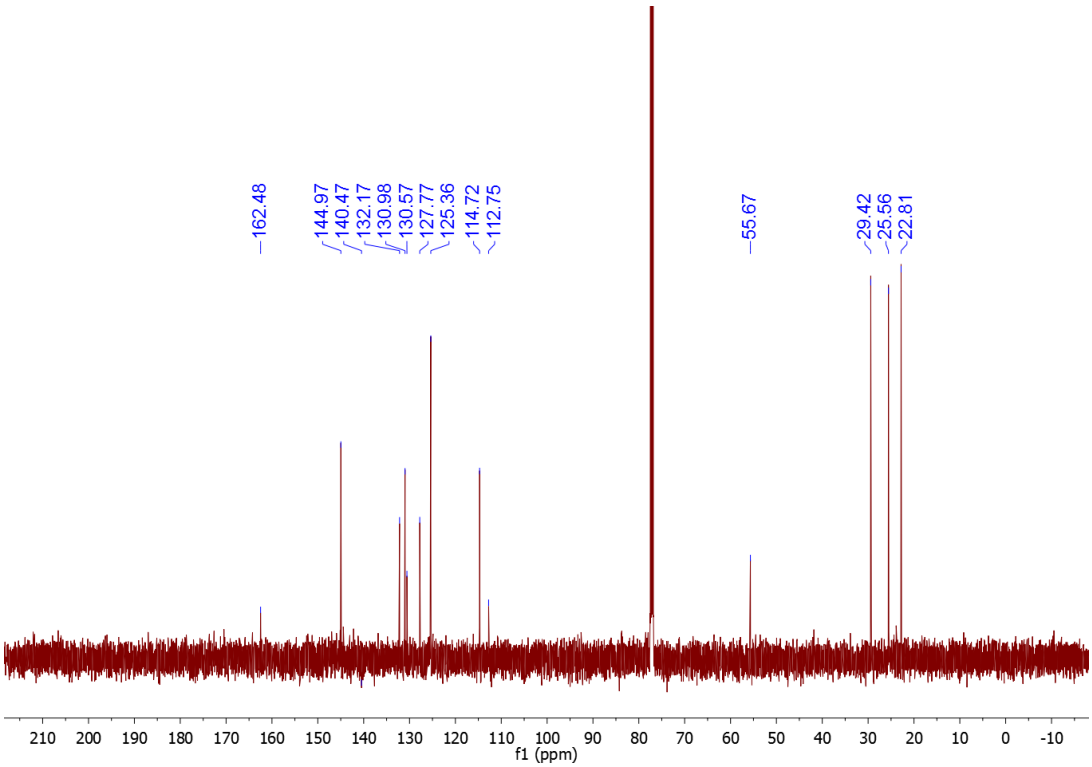
Plot P28. ^{13}C{^{1}H} NMR spectrum of (IPrPh)Cl (**4**).



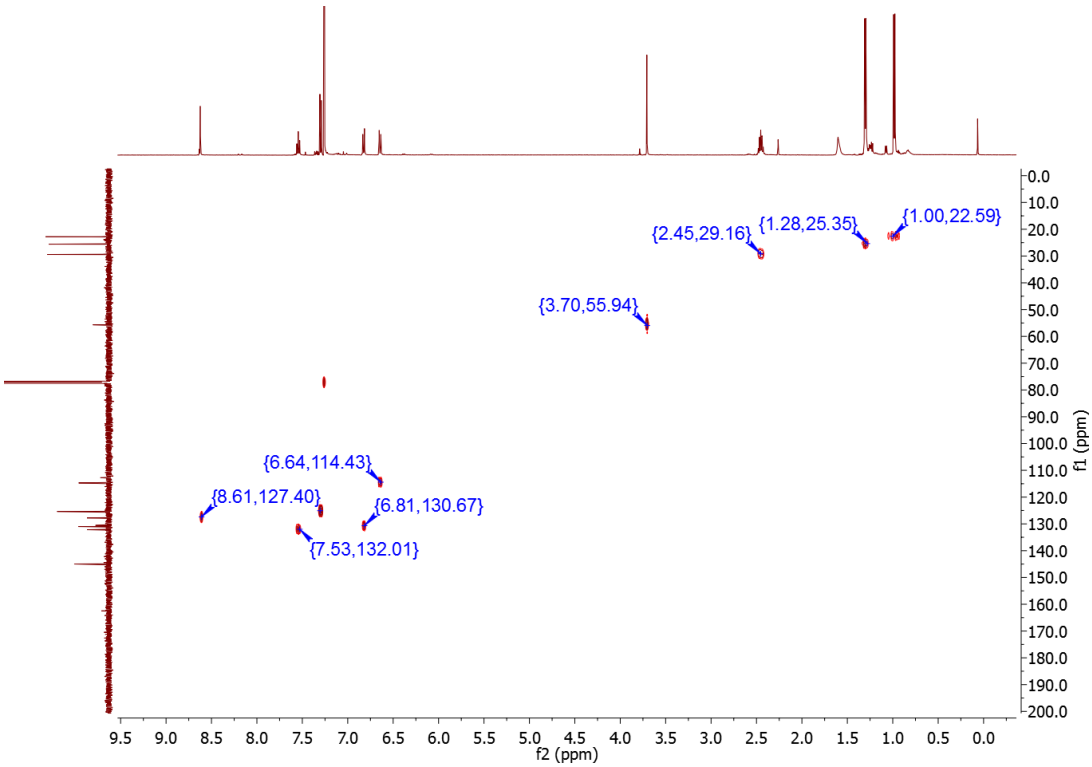
Plot P29. ^{1}H-^{13}C HMQC NMR spectrum of (IPrPh)Cl (**4**).



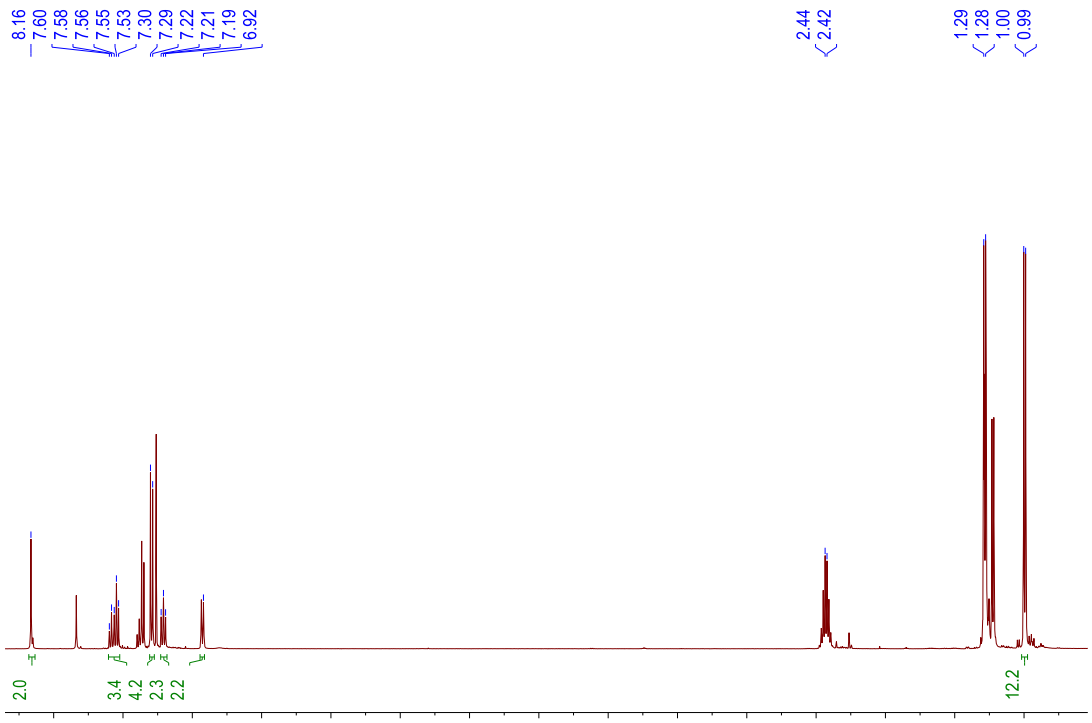
Plot P30. ^{1}H NMR spectrum of {IPr-(4-anisyl)}Cl (**8**).



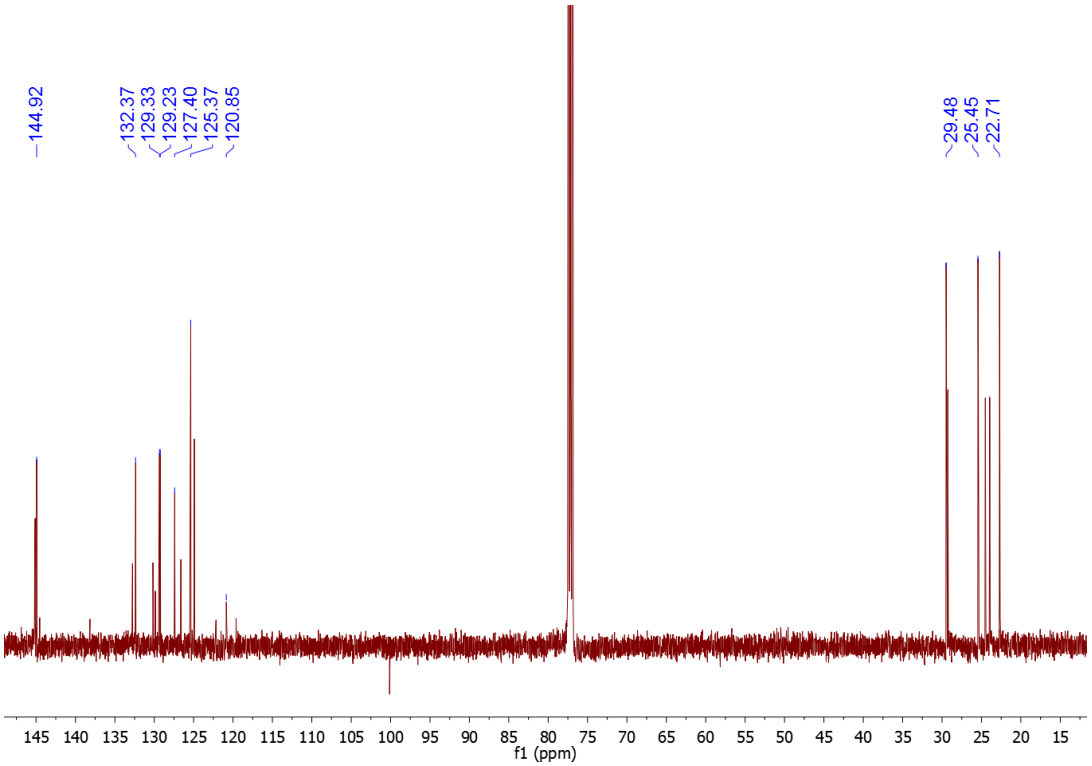
Plot P31. $^{13}C\{^{1}H\}$ NMR spectrum of {IPr-(4-anisyl)}Cl (**8**).



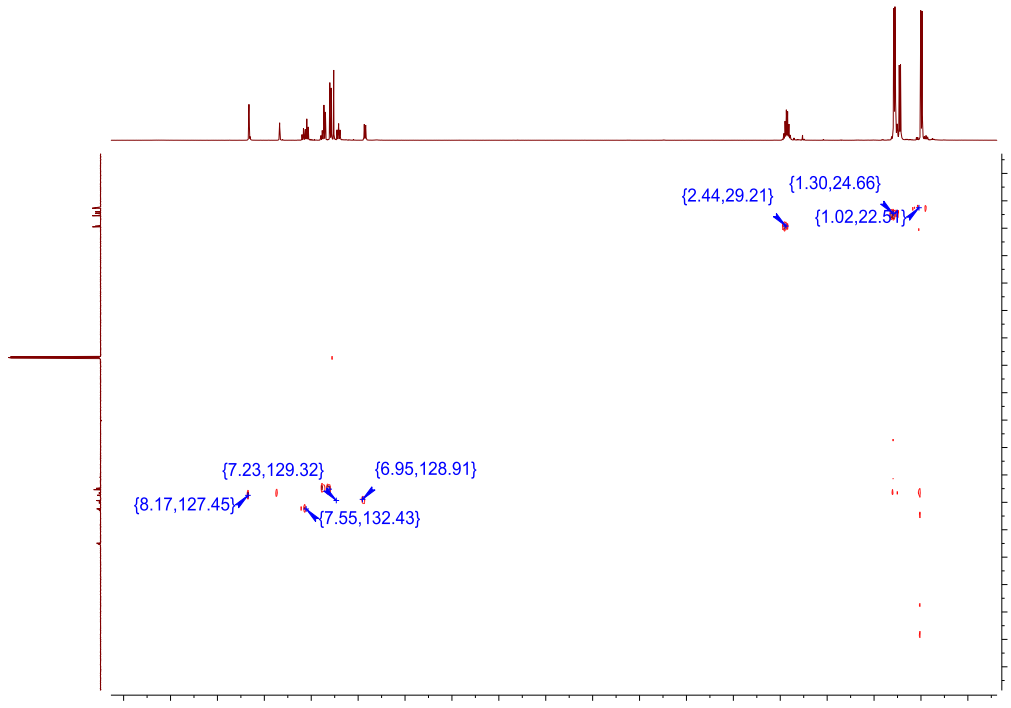
Plot P32. ^{1}H-^{13}C HMQC NMR spectrum of {IPr-(4-anisyl)}Cl (**8**).



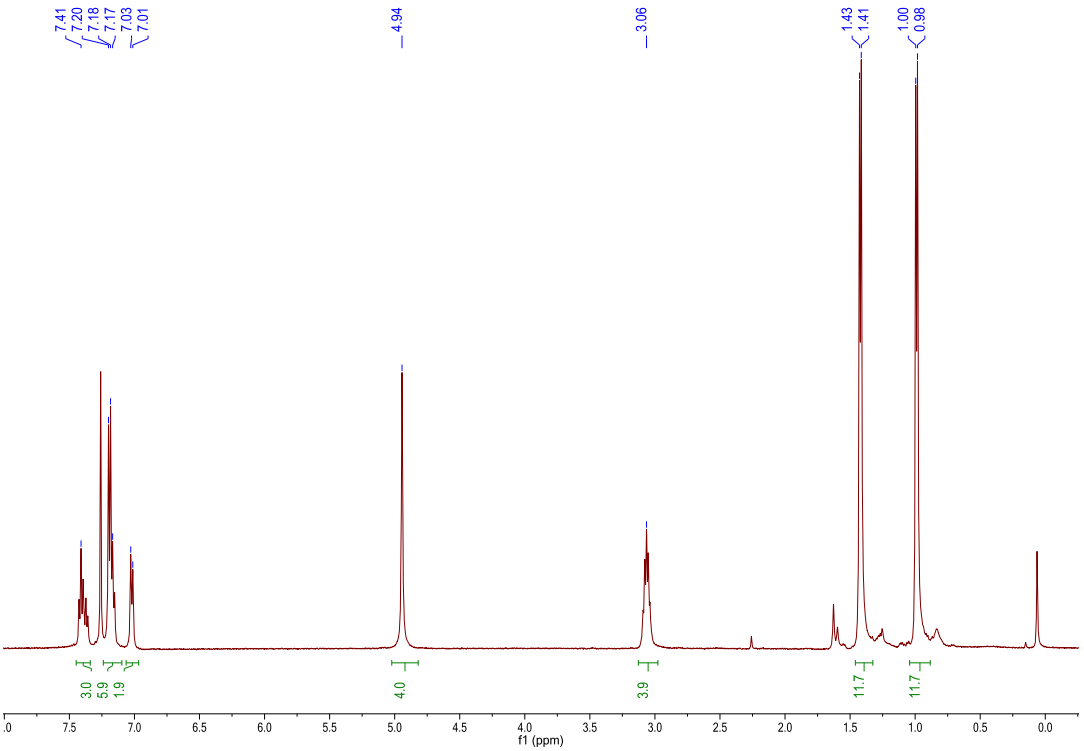
Plot P33. ^{1}H NMR spectrum of (IPrPh)OTf (**5**).



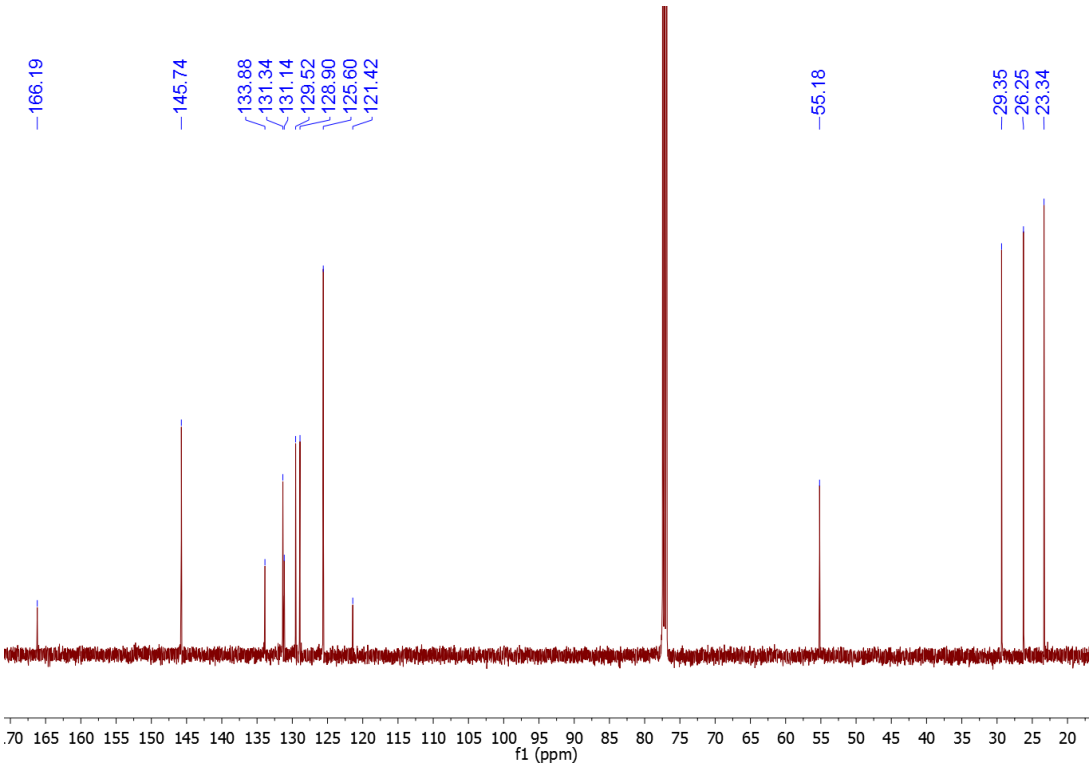
Plot P34. ^{13}C{^{1}H} NMR spectrum of (IPrPh)OTf (**5**).



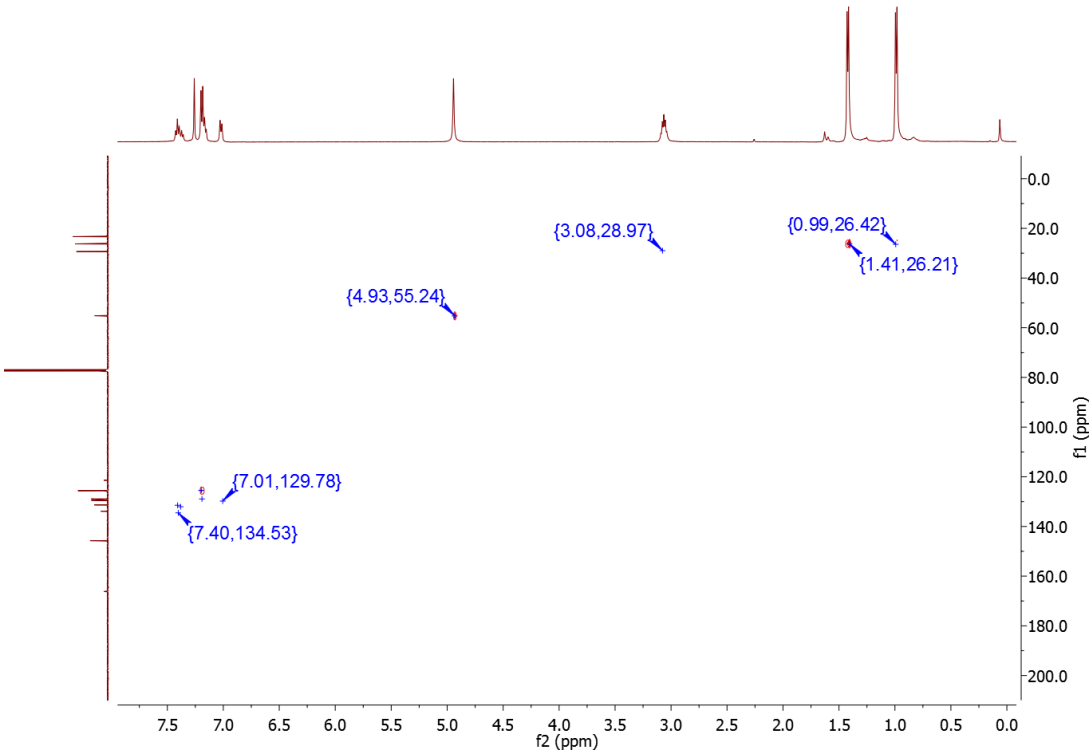
Plot P35. ^{1}H-^{13}C HMQC NMR spectrum of (IPrPh)OTf (**5**).



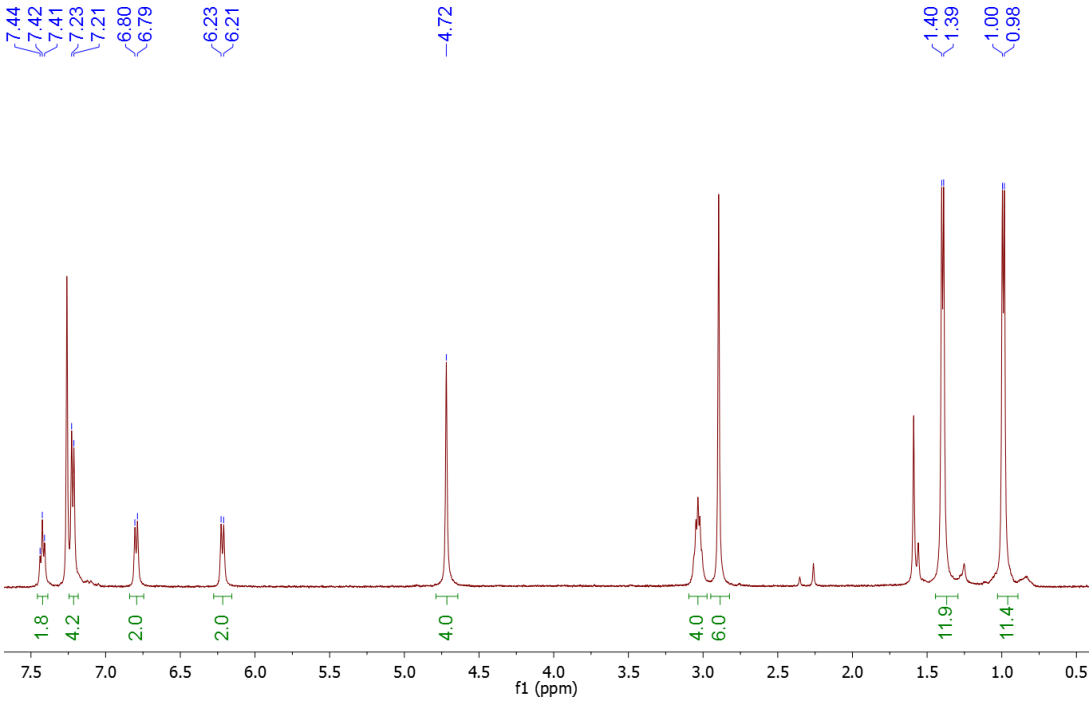
Plot P36. ^{1}H NMR spectrum of (SIPrPh)Br (**6a**).



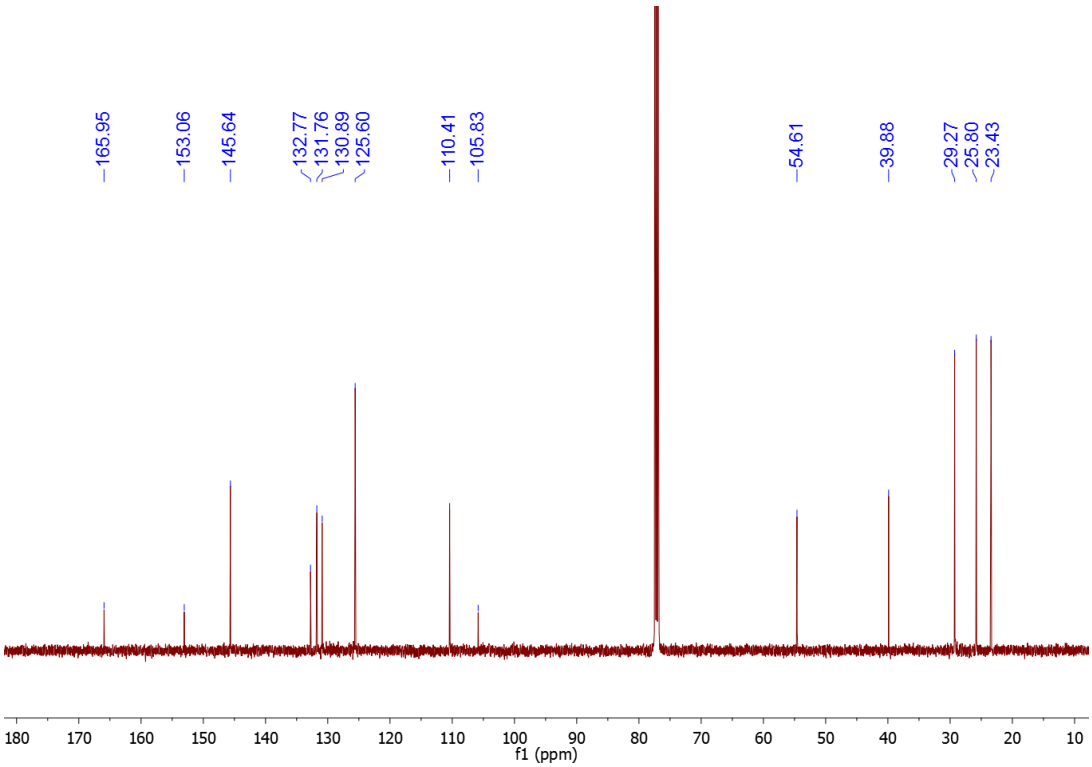
Plot P37. $^{13}C\{^{1}H\}$ NMR spectrum of (SIPrPh)Br (**6a**).



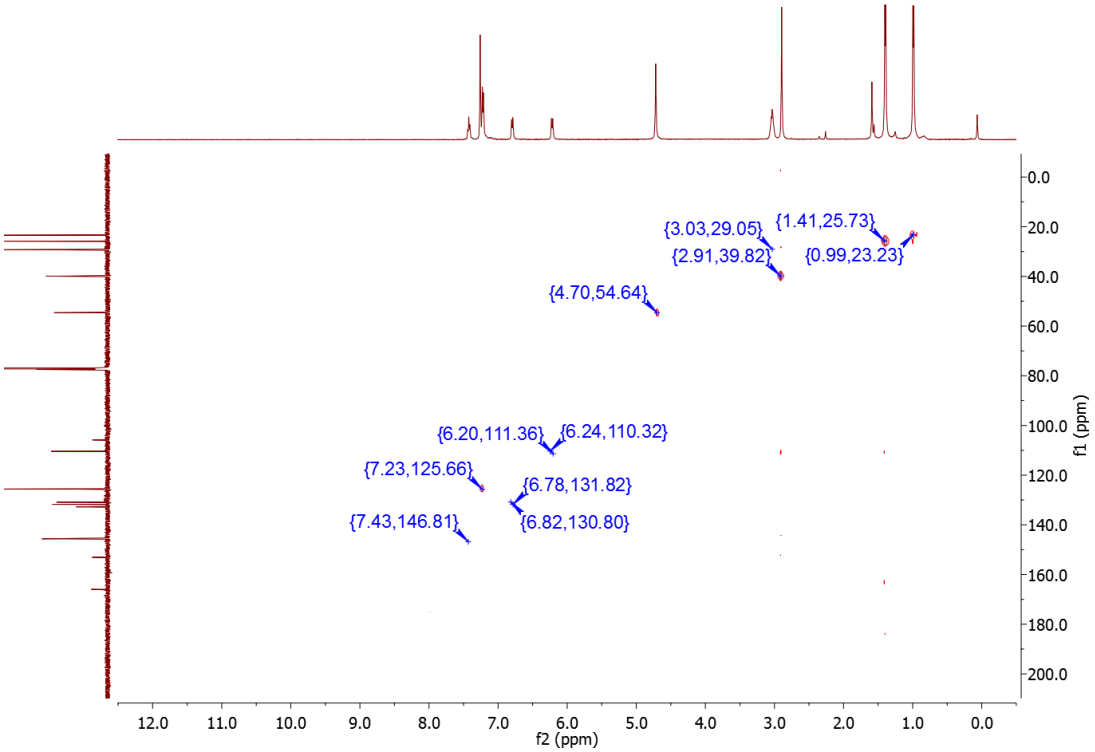
Plot P38. ^{1}H-^{13}C HMQC NMR spectrum of (SIPrPh)Br (**6a**).



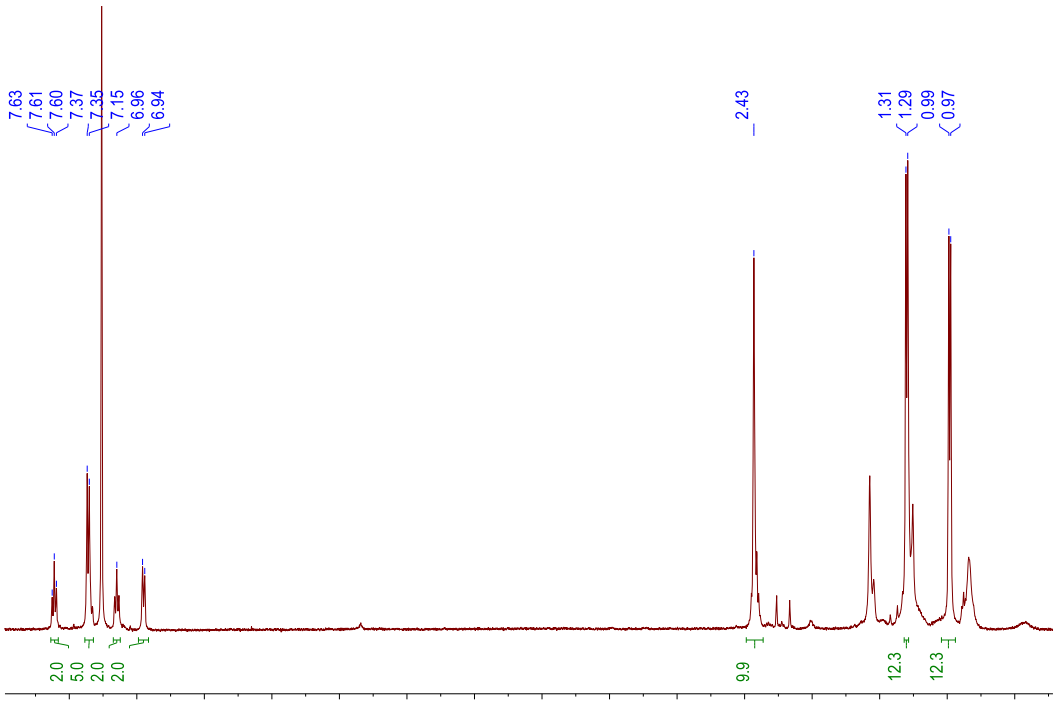
Plot P39. ^{1}H NMR spectrum of {SIPr(4-Me_2N-C_6H_4)}Br (**6b**).



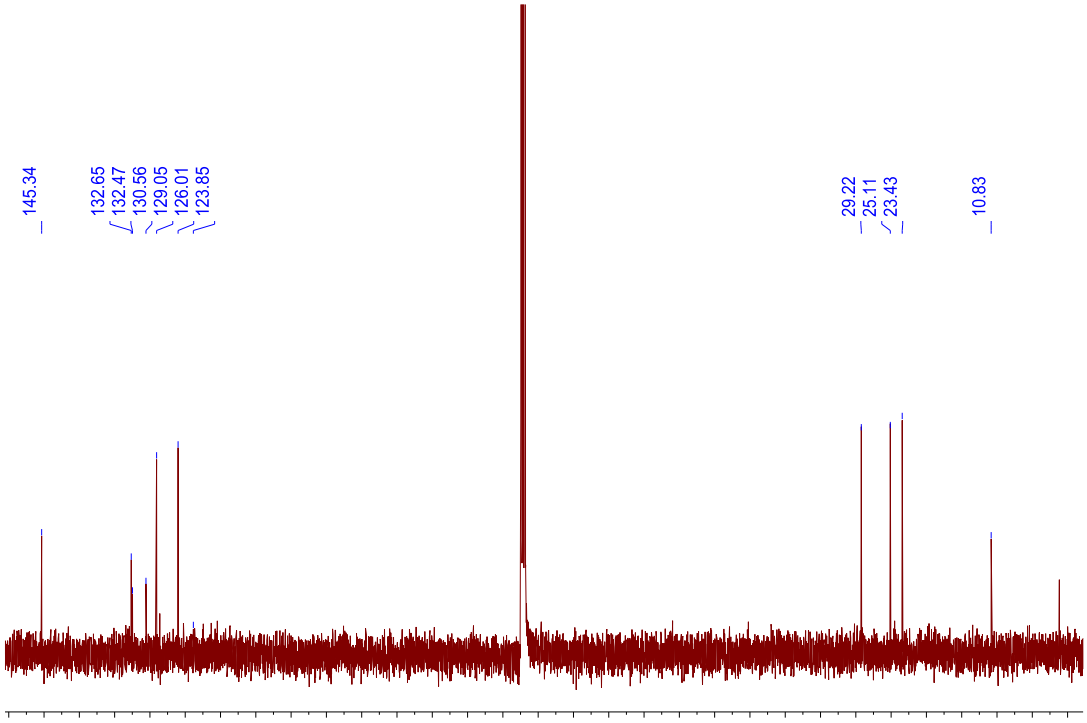
Plot P40. $^{13}C\{^{1}H\}$ NMR spectrum of {SIPr(4-Me_2N-C_6H_4)}Br (**6b**).



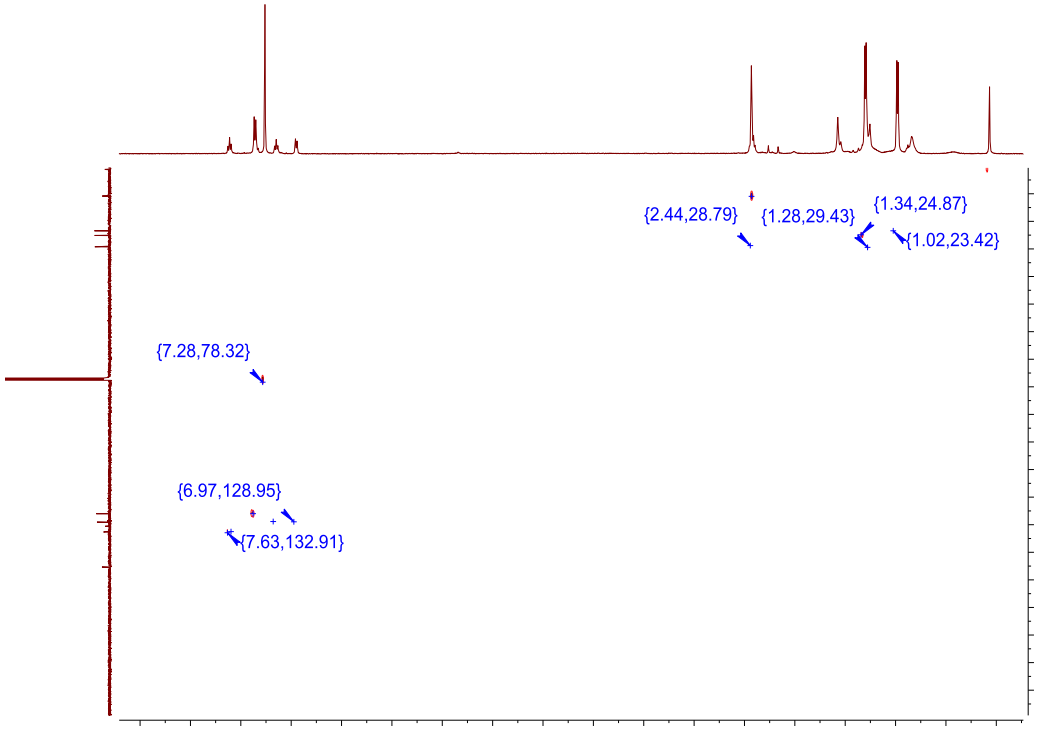
Plot P41. ^{1}H-^{13}C HMQC NMR spectrum of {SIPr(4-Me_2N-C_6H_4)}Br (**6b**).



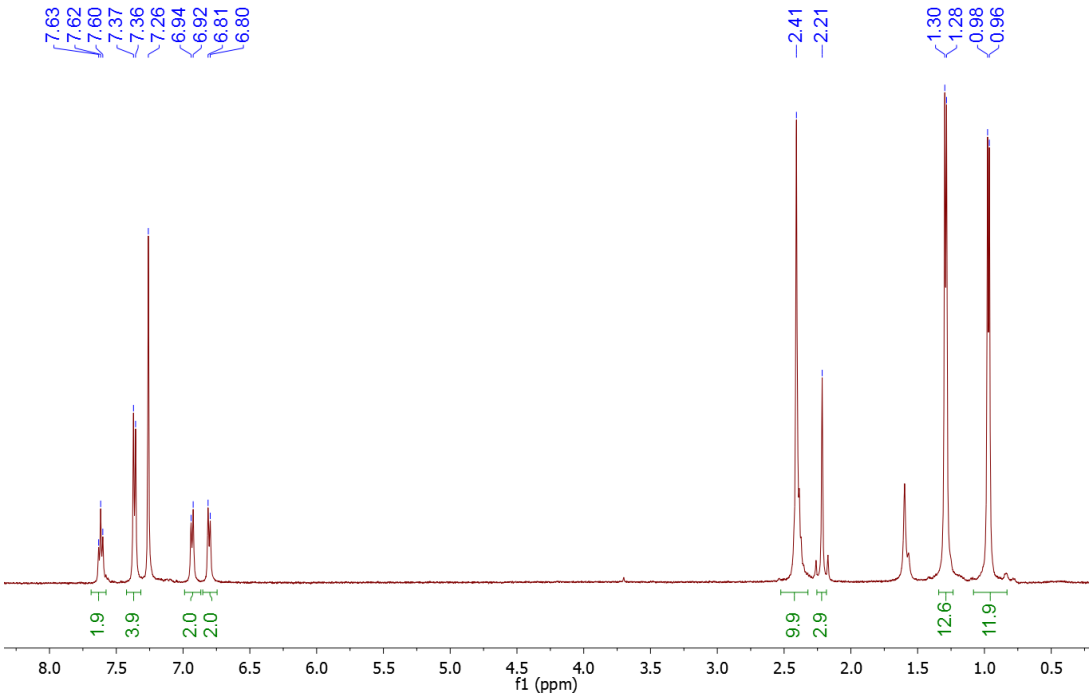
Plot P42. ^{1}H NMR spectrum of {(Me_2-IPr)Ph}Br (**7a**).



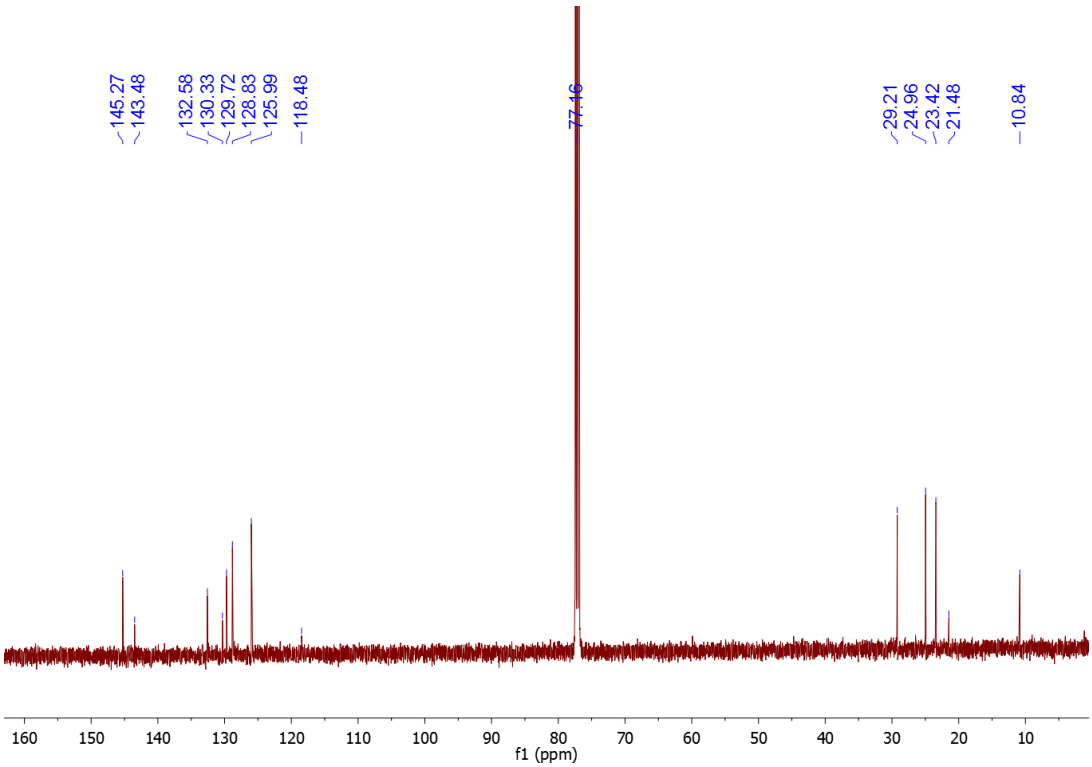
Plot P43. $^{13}C\{^{1}H\}$ NMR spectrum of {(Me_2-IPr)Ph}Br (**7a**).



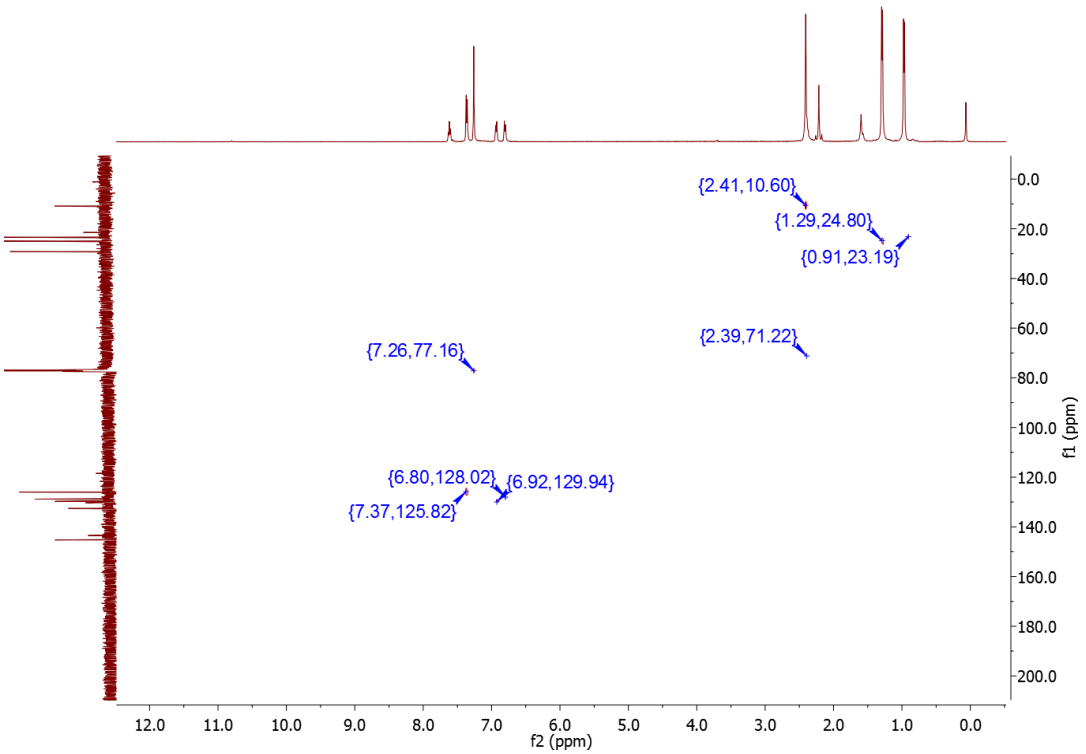
Plot P44. ^{1}H-^{13}C HMQC NMR spectrum of {(Me_2-IPr)Ph}Br (**7a**).



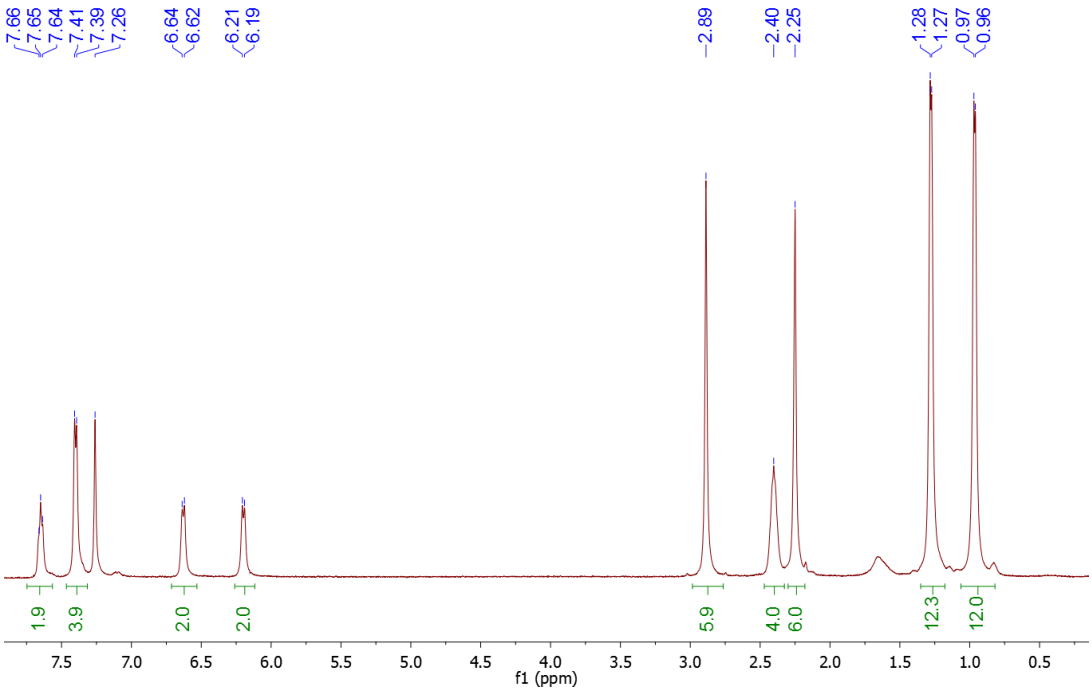
Plot P45. ^{1}H NMR spectrum of {(Me$_2$-IPr)-4-tolyl}Br (**7b**).



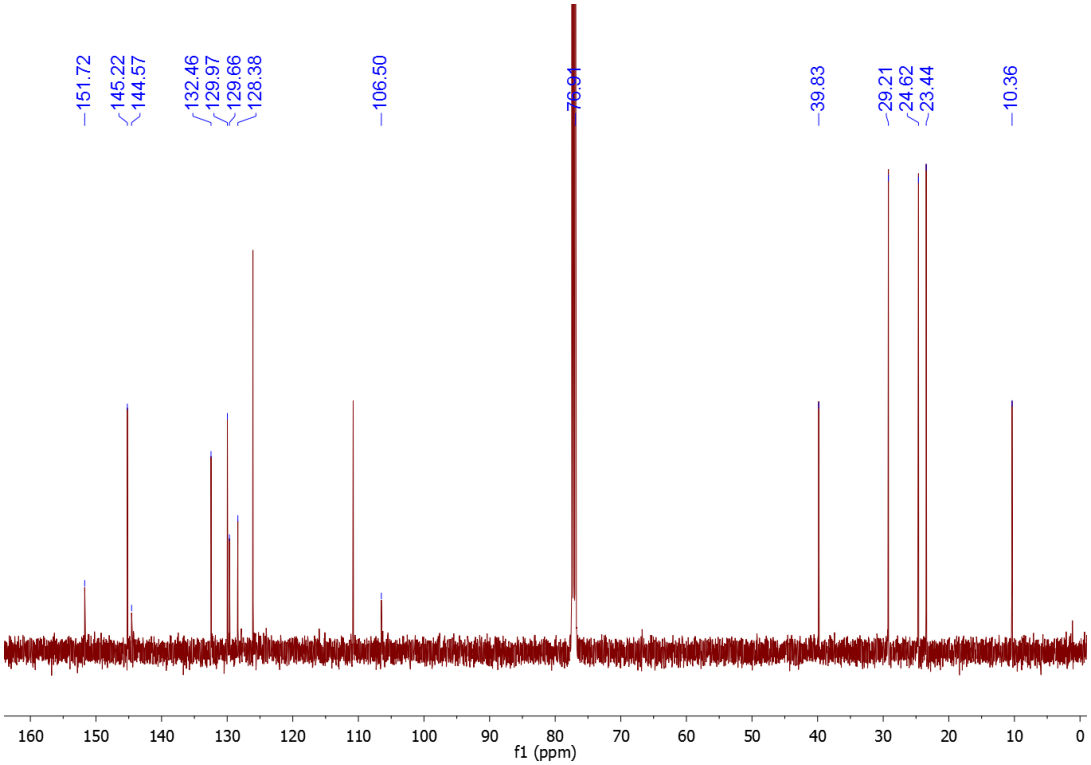
Plot P46. ^{13}C{^{1}H} NMR spectrum of {(Me$_2$-IPr)-4-tolyl}Br (**7b**).



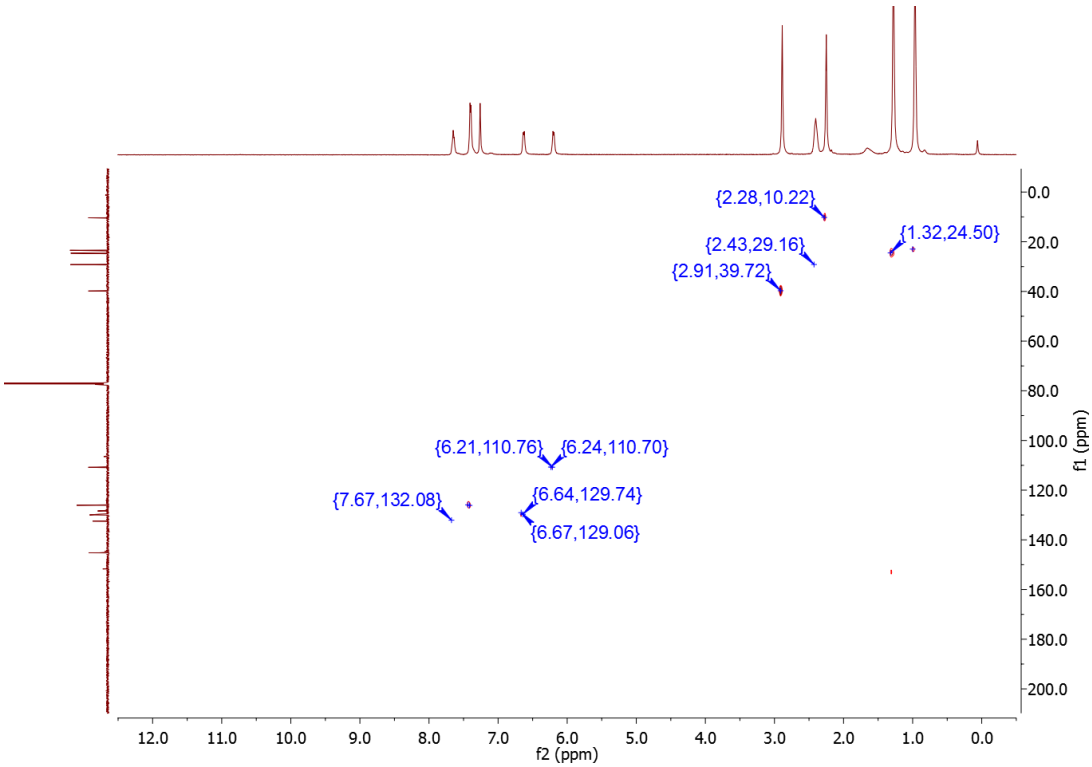
Plot P47. ^{1}H-^{13}C HMQC NMR spectrum of {(Me_2-IPr)-4-tolyl}Br (**7b**).



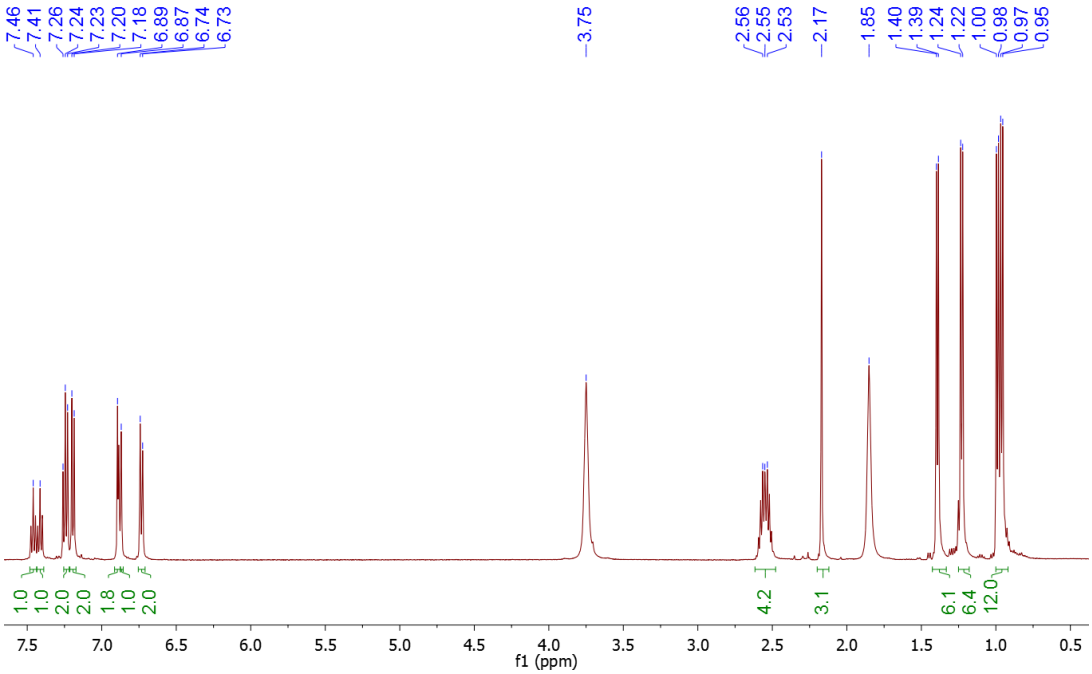
Plot P48. ^{1}H NMR spectrum of {(Me_2-IPr)-(4-Me_2N-C_6H_4)}Br (**7c**).



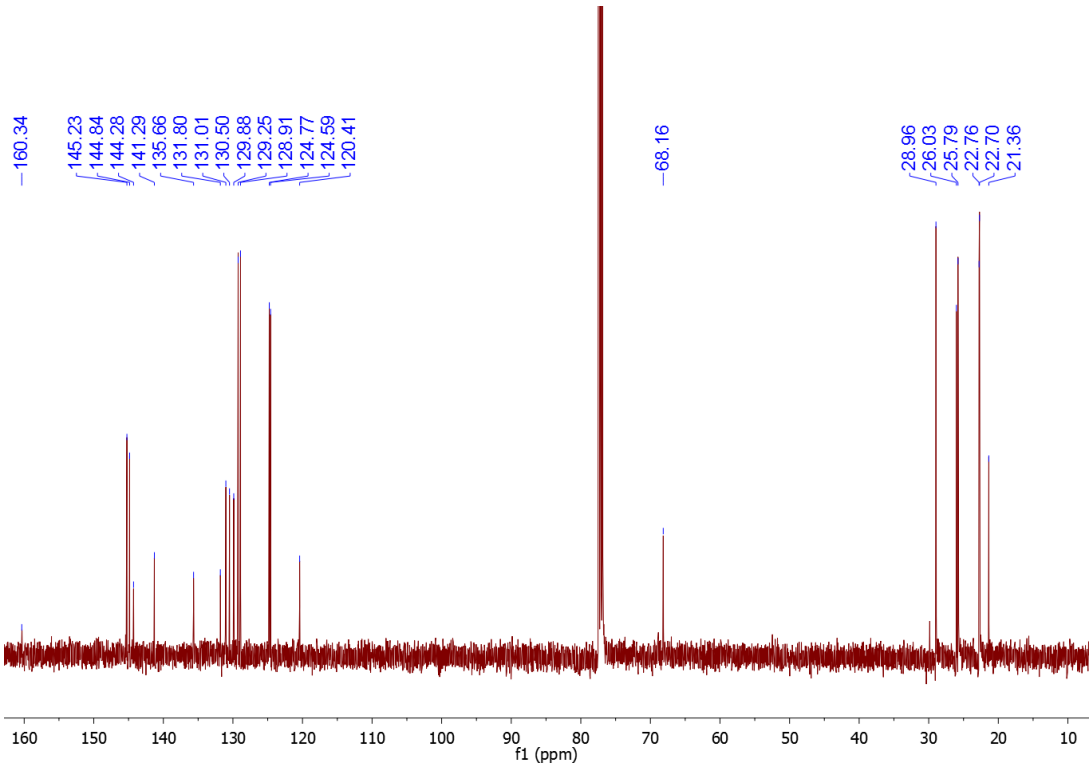
Plot P49. $^{13}C\{^{1}H\}$ NMR spectrum of {(Me_2-IPr)-(4-Me_2N-C_6H_4)}Br (**7c**).



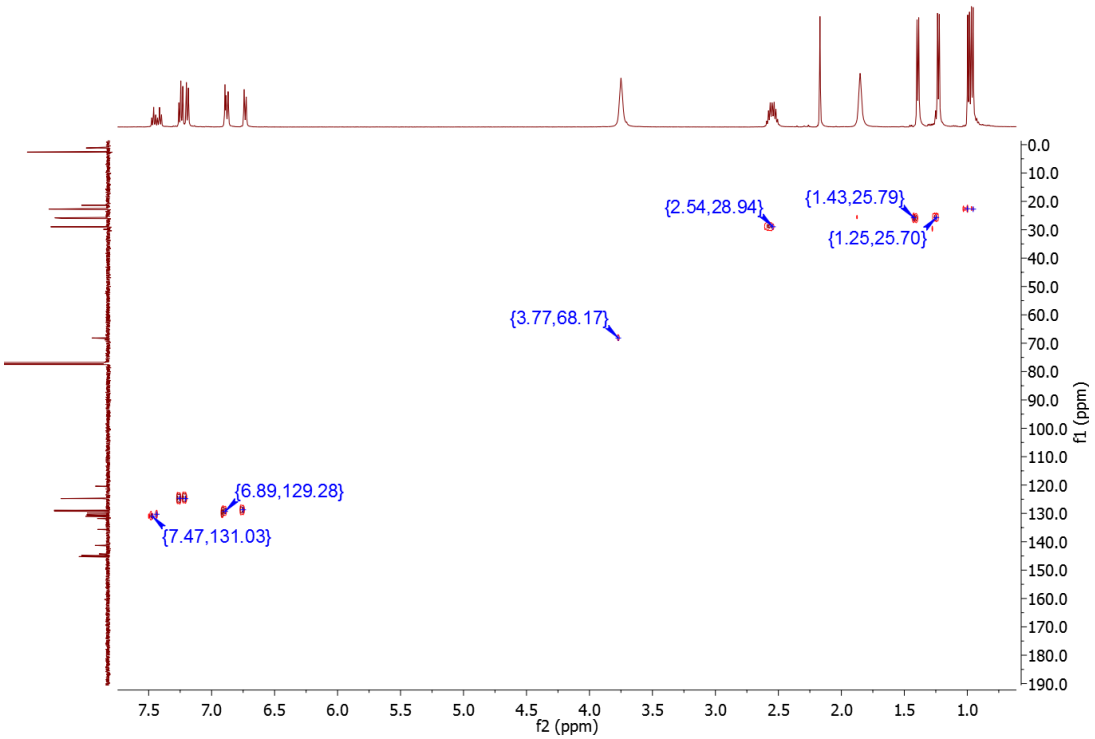
Plot P50. ^{1}H-^{13}C HMQC NMR spectrum of {(Me_2-IPr)-(4-Me_2N-C_6H_4)}Br (**7c**).



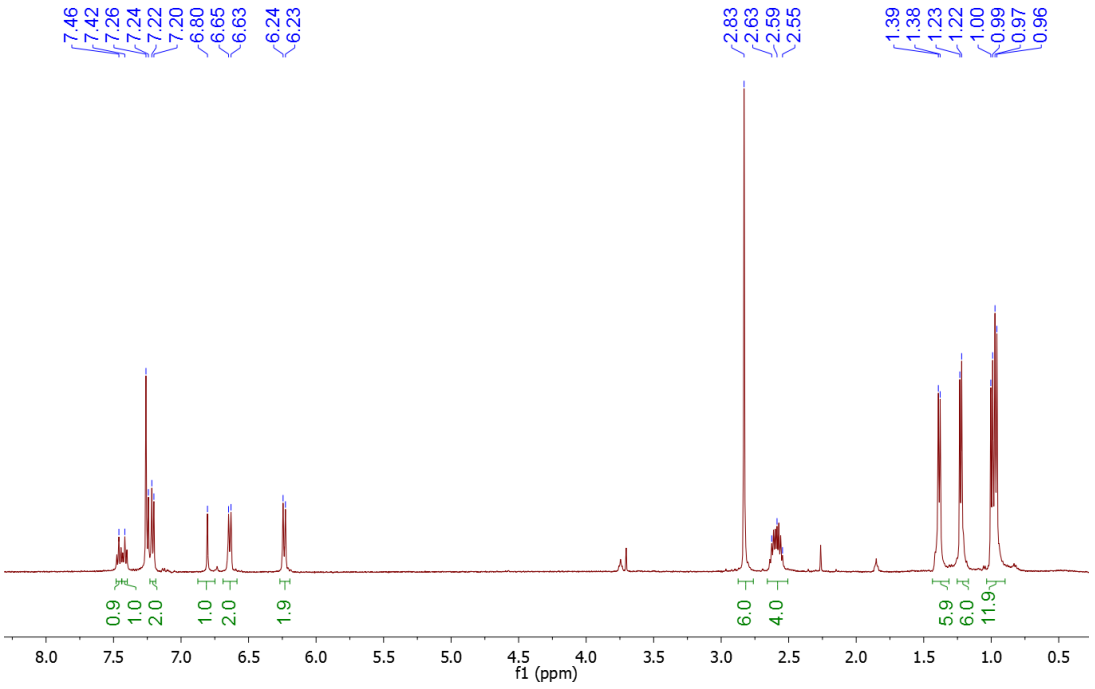
Plot P51. ^{1}H NMR spectrum of (aIPr$^{4\text{-tolyl}}$)CuBr (**22**).



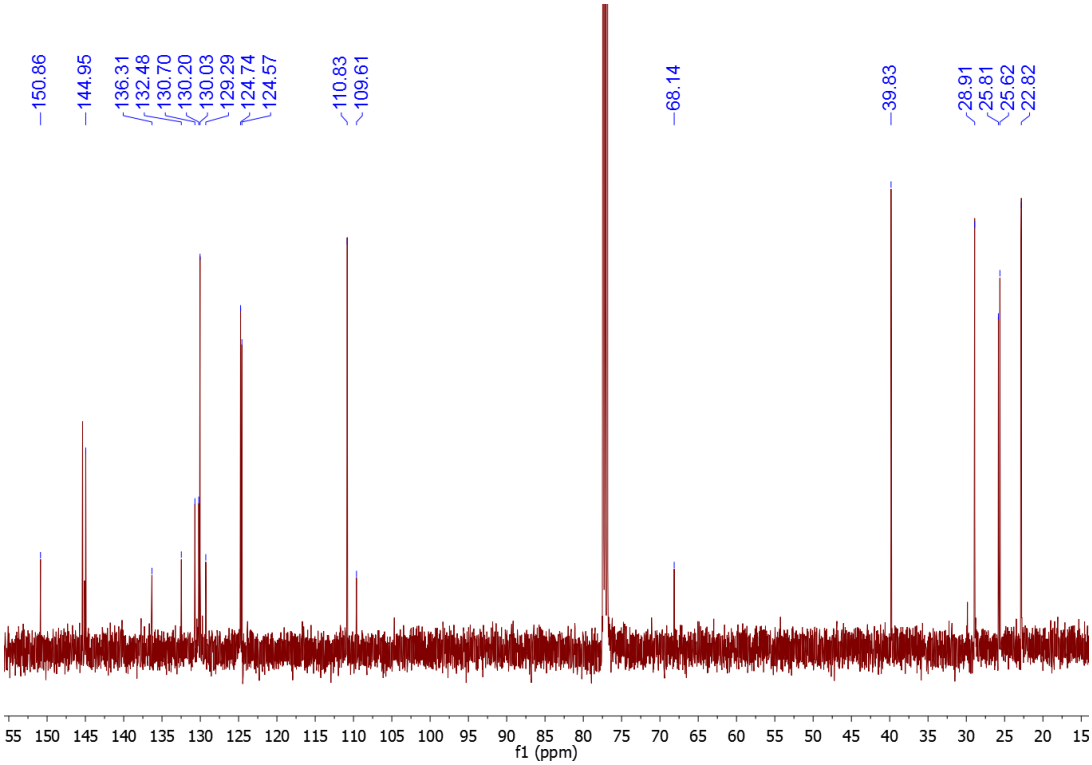
Plot P52. ^{13}C{^{1}H} NMR spectrum of (aIPr$^{4\text{-tolyl}}$)CuBr (**22**).



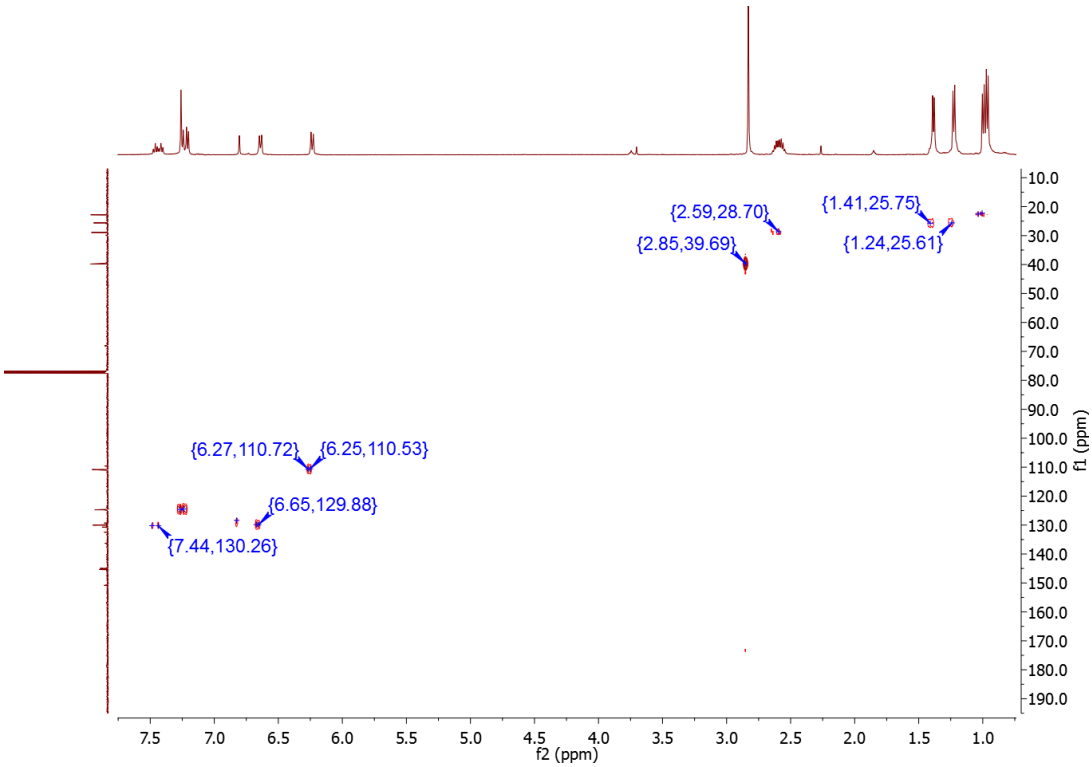
Plot P53. ^{1}H-^{13}C HMQC NMR spectrum of (aIPr$^{4\text{-tolyl}}$)CuBr (**22**).



Plot P54. ^{1}H NMR spectrum of {aIPr(4-Me_2N-C_6H_4)}CuBr (**23**).



Plot P55. $^{13}C\{^{1}H\}$ NMR spectrum of {aIPr(4-Me_2N-C_6H_4)}CuBr (**23**).



Plot P56. ^{1}H-^{13}C HMQC NMR spectrum of {aIPr(4-Me_2N-C_6H_4)}CuBr (**23**).

DFT calculations

Computational methods. Density Functional Theory (DFT) calculations were carried out using B3LYP functional,[10] plus D3 dispersion correction energy terms designed by Grimme *et al.*[11] (B3LYP-D3) available in Gaussian 09 suite quantum chemical programs (revision D1).[12] structures were fully optimized in gas phase. The standard 6-31G(d) basis set were used for lighter atoms and the basis set with Stuttggart-Dresden relativistic pseudopotential (SDD)[13] was used for Ni atom. The solvent effects were described by the universal continuum-dielectric solvation model SMD.[14] The stationary points was confirmed by calculation of the frequency calculations. The intermediates have only real frequencies, while the transition states have one imaginary frequency. The intrinsic reaction coordinate (IRC)[15] calculations were performed at the same level of theory of optimization and frequency calculations to further authenticate the transition states. Quoted Gibbs free energy values have zero-point energy vibrational (ZPE), thermal, entropic corrections at 298.15 K, unless otherwise specified.

CARTESIAN COORDINATES

15M

B3LYP-D3/BSI SCF energy (a. u.) : -978.5470075

Ni	1.583360	-0.013212	0.127040
N	4.386569	1.080608	0.132785
N	4.384957	-1.068563	0.138912
C	3.543875	0.008520	0.171359
C	5.714493	0.683442	0.073751
H	6.527253	1.392423	0.035847
C	5.712589	-0.673549	0.079196
H	6.525144	-1.382770	0.037106
C	3.953618	-2.461221	0.169142
H	4.308227	-2.946333	1.084251
H	2.863737	-2.490556	0.141661
H	4.348306	-2.992922	-0.701920
C	3.950896	2.472701	0.144935
H	2.861561	2.497188	0.095411
H	4.285409	2.966020	1.063225
H	4.361670	2.999044	-0.721857
Ni	-1.607368	0.006656	-0.093296
H	-4.395575	3.002547	1.018783
C	-3.937211	2.470965	0.179290

H	-4.228255	2.953455	-0.759640
H	-2.851589	2.506527	0.274550
N	-4.360980	1.076316	0.186689
C	-3.515338	0.003938	0.094997
N	-4.361739	-1.071955	0.119113
C	-3.936039	-2.463547	0.037036
H	-4.275144	-2.909195	-0.903652
H	-4.348085	-3.029573	0.878143
H	-2.847088	-2.499212	0.076804
H	-6.498253	-1.389354	0.256417
C	-5.687221	-0.678311	0.217134
C	-5.686871	0.677868	0.259190
H	-6.497657	1.385705	0.339482
Br	-0.007296	-1.948246	-0.198908
Br	-0.006586	1.941414	-0.251323

16M

B3LYP-D3/BSI SCF energy (a. u.) : -1223.605815

Ni	1.259867	-1.130541	-1.315292
N	-1.459168	-1.158261	-2.494639
N	-1.248530	-2.605360	-0.919327
C	-0.546188	-1.667068	-1.615558
C	-2.698902	-1.754222	-2.336740
H	-3.556943	-1.465285	-2.923270
C	-2.563570	-2.668644	-1.341042
H	-3.284746	-3.323155	-0.877813
C	-0.672866	-3.462901	0.113288
H	-1.436881	-3.675981	0.863423
H	-0.315249	-4.397791	-0.328720
H	0.154656	-2.939231	0.594549
C	-1.160909	-0.159036	-3.510670
H	-0.191912	0.283122	-3.276614

H	-1.117457	-0.623922	-4.501089
H	-1.924931	0.621393	-3.497556
17	1.859623	0.161166	0.779782
H	2.937888	2.433032	-1.606498
C	1.858032	2.500260	-1.751280
H	1.624425	3.282696	-2.476981
H	1.510533	1.533451	-2.119775
N	1.187897	2.810674	-0.493912
C	1.098723	1.952732	0.566398
N	0.408953	2.674640	1.501854
C	0.004720	2.184662	2.816274
H	0.523608	1.248877	3.022068
H	-1.074530	2.004673	2.830062
H	0.265559	2.925171	3.577667
H	-0.470717	4.644536	1.632513
C	0.083545	3.936032	1.036902
C	0.577787	4.023361	-0.224234
H	0.553217	4.829456	-0.941058
C	-2.948538	0.474108	0.402239
C	-1.950705	-0.181165	1.112364
C	-2.328234	-1.189891	2.004880
C	-3.672587	-1.534992	2.156080
H	-3.957155	-2.317929	2.853662
H	-5.702001	-1.127853	1.534612
C	-4.653686	-0.865890	1.418517
C	-4.297752	0.154819	0.533096
H	-5.051374	0.688942	-0.035585
H	-1.547347	-1.690219	2.569543
H	-0.902224	0.060308	0.975919
Br	3.545941	-0.538829	-1.046494
Br	-2.436684	1.934135	-0.810977

Br	1.365617	-1.348353	2.591307

TS16-17M

B3LYP-D3/BSI SCF energy (a. u.) : -1223.599824

Ni	0.522704	-0.850340	0.973988
N	3.416531	-0.127819	1.152108
N	3.089316	-1.843606	-0.099447
C	2.427972	-0.931587	0.666623
C	4.662873	-0.529131	0.699332
H	5.570929	-0.013978	0.972446
C	4.454553	-1.614494	-0.090665
H	5.146463	-2.234280	-0.639966
C	2.441637	-2.922977	-0.840003
H	2.725018	-2.866577	-1.894710
H	2.738590	-3.892316	-0.428990
H	1.359209	-2.809357	-0.761728
C	3.184938	1.023106	2.013169
H	2.125214	1.042636	2.271581
H	3.783884	0.938681	2.924826
H	3.437148	1.947452	1.486407
Ni	-1.863083	-1.047050	0.092685
H	-2.537366	1.055938	2.770738
C	-1.988609	1.735730	2.116835
H	-1.982185	2.742841	2.539132
H	-0.964777	1.371200	2.023685
N	-2.610803	1.785186	0.797804
C	-2.636216	0.738525	-0.081384
N	-3.311995	1.245230	-1.158713
C	-3.640097	0.497995	-2.369256
H	-3.071281	-0.431811	-2.376896
H	-3.377012	1.093732	-3.248301

H	-4.710253	0.268719	-2.391491
H	-4.239529	3.126067	-1.690537
C	-3.696851	2.558974	-0.950140
C	-3.251158	2.900010	0.286265
H	-3.325459	3.825373	0.835997
C	1.465617	2.095673	-1.011649
C	0.653531	1.085897	-1.516958
C	1.219000	0.152420	-2.392595
C	2.567215	0.241339	-2.741852
H	3.000902	-0.489304	-3.418911
H	4.412280	1.333236	-2.482078
C	3.360830	1.263873	-2.217203
C	2.812320	2.208104	-1.344313
H	3.419213	3.009460	-0.936561
H	0.593711	-0.655061	-2.760515
H	-0.386744	0.997934	-1.224301
Br	-1.180792	-1.668943	2.468243
Br	0.694471	3.399059	0.240024
Br	-1.356366	-2.492041	-1.783587

17M

B3LYP-D3/BSI SCF energy (a. u.) : -1223.602689

Ni	0.616141	-0.475649	0.195889
N	3.537624	-0.454704	0.880454
N	3.030454	-2.223942	-0.221839
C	2.488059	-1.078333	0.276051
C	4.708737	-1.185834	0.750666
H	5.646127	-0.856205	1.171921
C	4.387191	-2.306587	0.054472
H	4.987722	-3.150994	-0.247354
C	2.276546	-3.238681	-0.949410
H	2.555701	-3.232234	-2.008155

H	2.480458	-4.225548	-0.524759
H	1.210802	-3.025312	-0.852979
C	3.437314	0.835589	1.550352
H	2.391718	1.009973	1.807314
H	4.036160	0.821115	2.464951
H	3.785075	1.638443	0.893732
Ni	-1.867038	-0.838291	0.648379
H	-2.480983	2.958930	2.133066
C	-1.989733	2.605056	1.221389
H	-1.520657	3.447734	0.705731
H	-1.229584	1.875466	1.493894
N	-2.965127	1.967687	0.342226
C	-3.027394	0.627534	0.064056
N	-4.113471	0.527664	-0.763162
C	-4.643422	-0.719463	-1.307739
H	-3.897128	-1.504729	-1.189261
H	-4.865767	-0.586908	-2.370557
H	-5.558069	-1.002843	-0.777106
H	-5.576304	1.876218	-1.611502
C	-4.706284	1.759727	-0.983602
C	-3.980203	2.669951	-0.287449
H	-4.087319	3.739247	-0.188311
C	1.507183	1.899089	-1.304219
C	0.319844	1.143009	-1.319585
C	0.291947	-0.033586	-2.103231
C	1.432070	-0.421765	-2.832012
H	1.393965	-1.322708	-3.436400
H	3.476496	0.037656	-3.328040
C	2.592517	0.339424	-2.773321
C	2.640453	1.514042	-1.998586
H	3.544597	2.111530	-1.955891

H	-0.636020	-0.588999	-2.194668
H	-0.596729	1.538785	-0.898922
Br	-0.271908	-0.377946	2.542610
Br	1.532280	3.558238	-0.263216
Br	-1.628099	-2.892872	-0.643307

TS17M-18M

B3LYP-D3/BSI SCF energy (a. u.) : -1223.565302

Ni	-1.921122	0.192298	-0.253744
N	-4.429013	-1.328671	-0.923837
N	-2.963455	-2.583909	0.017773
C	-3.178946	-1.298680	-0.376580
C	-4.976536	-2.602833	-0.872840
H	-5.954172	-2.829483	-1.269681
C	-4.050057	-3.393196	-0.271726
H	-4.066608	-4.444210	-0.027462
C	-1.747603	-3.027741	0.698656
H	-1.833936	-2.887225	1.779014
H	-1.577686	-4.083615	0.474323
H	-0.904325	-2.437492	0.342368
C	-5.064879	-0.186377	-1.563926
H	-4.487851	0.706736	-1.320285
H	-5.083485	-0.316857	-2.650827
H	-6.088664	-0.070656	-1.194509
Ni	1.677372	-0.064163	0.300404
H	2.587549	0.509257	-3.302008
C	3.155553	1.063851	-2.551041
H	3.855168	1.748704	-3.037147
H	2.459698	1.628715	-1.932350
N	3.909142	0.143640	-1.701352
C	3.452170	-0.393128	-0.535493
N	4.461682	-1.210821	-0.127778

C	4.466224	-1.995756	1.104155
H	3.497021	-1.894545	1.592144
H	5.250188	-1.630540	1.774553
H	4.647999	-3.048382	0.867994
H	6.418124	-1.766945	-0.863901
C	5.521018	-1.188118	-1.020489
C	5.169374	-0.335072	-2.016284
H	5.696068	-0.026270	-2.906013
C	-1.046245	2.657068	0.752177
C	-1.683907	1.609339	1.430365
C	-3.100174	1.559465	1.372603
C	-3.812364	2.540185	0.657556
H	-4.898210	2.504807	0.637588
H	-3.690530	4.313965	-0.561873
C	-3.132840	3.558888	-0.012232
C	-1.727310	3.614692	0.022336
H	-1.191856	4.400151	-0.504443
H	-3.633483	0.798559	1.935776
H	-1.115530	0.938515	2.074000
Br	0.017050	-0.391152	-1.676919
Br	1.294481	2.358906	0.605299
Br	0.992188	-1.223130	2.358169

18M

B3LYP-D3/BSI SCF energy (a. u.) : -1223.640665

Ni	-1.503019	-0.008572	0.014287
N	-3.052805	2.087493	-1.279705
N	-3.491539	1.917494	0.820561
C	-2.729165	1.382652	-0.165552
C	-4.011645	3.051156	-0.994232
H	-4.392368	3.724358	-1.746316
C	-4.288788	2.941197	0.330303

H	-4.964771	3.495689	0.962301
C	-3.486764	1.423088	2.193870
H	-4.039244	0.481868	2.251283
H	-2.454105	1.250608	2.503957
H	-3.943704	2.171827	2.844225
C	-2.443300	1.888359	-2.587646
H	-1.703999	1.091329	-2.500701
H	-3.205692	1.606493	-3.320249
H	-1.940877	2.804793	-2.910403
Ni	1.994701	-0.200195	0.594566
H	4.704454	2.529594	-1.481793
C	3.779702	2.051092	-1.151557
H	3.758374	2.012140	-0.061640
H	2.913766	2.613514	-1.508591
N	3.744722	0.684281	-1.671666
C	3.080836	-0.342313	-1.082030
N	3.318763	-1.410956	-1.884292
C	2.808096	-2.759100	-1.641899
H	2.817399	-2.957405	-0.570154
H	3.454715	-3.477182	-2.151099
H	1.781810	-2.851063	-2.003760
H	4.411010	-1.769539	-3.717160
C	4.105600	-1.055400	-2.968402
C	4.373390	0.269775	-2.833703
H	4.958877	0.941041	-3.442447
C	-2.982222	-1.177725	-0.057346
C	-3.743982	-1.347736	-1.224122
C	-4.797743	-2.267113	-1.274413
C	-5.126425	-3.019800	-0.145262
H	-5.948177	-3.730647	-0.179742
H	-4.628103	-3.440578	1.912430

C	-4.387316	-2.852927	1.029021
C	-3.326403	-1.942198	1.071148
H	-2.739401	-1.848256	1.981563
H	-5.364761	-2.389863	-2.195080
H	-3.509803	-0.762591	-2.110891
Br	0.401523	1.680126	0.020274
Br	3.541356	0.273980	2.343149
Br	0.105414	-1.841446	0.422663

19M

B3LYP-D3/BSI SCF energy (a. u.) : -807.5677828

C	-1.920465	-0.000045	-0.000088
N	-2.747388	0.219005	1.051004
C	-4.077831	0.135491	0.665576
C	-4.078001	-0.135428	-0.665219
N	-2.747638	-0.219011	-1.050944
C	1.920465	-0.000045	0.000081
N	2.747662	-0.219001	1.050920
C	4.078016	-0.135453	0.665156
C	4.077815	0.135515	-0.665629
N	2.747363	0.219001	-1.051032
Ni	0.000000	0.000019	0.000018
C	2.268613	-0.461219	2.405922
C	2.268089	0.461077	-2.405956
C	-2.268145	0.461085	2.405939
C	-2.268558	-0.461245	-2.405932
H	1.991443	0.483268	2.883984
H	1.397057	-1.116771	2.351812
H	3.056423	-0.949885	2.983827
H	3.055704	0.949946	-2.983955
H	1.991072	-0.483473	-2.883987
H	1.396389	1.116436	-2.351772

H	-1.396455	1.116459	2.351777
H	-3.055780	0.949939	2.983923
H	-1.991124	-0.483462	2.883971
H	-1.397014	-1.116811	-2.351797
H	-3.056361	-0.949899	-2.983857
H	-1.991360	0.483236	-2.883990
H	4.889871	-0.271835	1.362286
H	4.889503	0.271904	-1.362956
H	-4.889535	0.271861	1.362888
H	-4.889840	-0.271789	-1.362372
Br	0.000002	2.402666	0.000011
Br	0.000000	-2.402609	0.000018

20M

B3LYP-D3/BSI SCF energy (a. u.) : -1025.775114

C	-1.919797	-0.237892	0.069035
N	-2.799794	-0.549327	-0.919517
C	-4.111712	-0.441833	-0.479447
C	-4.052890	-0.054942	0.820093
N	-2.706707	0.073226	1.132654
C	1.918835	-0.247968	-0.066034
N	2.714543	0.062593	-1.123213
C	4.057918	-0.072050	-0.801492
C	4.105911	-0.462716	0.497372
N	2.790461	-0.565848	0.927891
Ni	-0.000556	-0.245500	-0.003716
C	2.194381	0.410624	-2.438987
C	2.380074	-0.957336	2.269897
C	-2.400780	-0.938943	-2.265465
C	-2.175947	0.414725	2.445873
C	0.004337	1.672698	-0.002426
C	0.687379	2.413940	0.983276

C	0.684723	3.812623	0.994372
C	0.011710	4.522121	-0.002907
C	-0.664985	3.815763	-0.999945
C	-0.674899	2.417110	-0.988394
H	1.859266	-0.489354	-2.963323
H	1.351959	1.093150	-2.312463
H	2.980696	0.901770	-3.017325
H	3.112389	-1.656080	2.681853
H	2.305597	-0.080352	2.921986
H	1.411631	-1.454794	2.198766
H	-1.430726	-1.434460	-2.203379
H	-3.135122	-1.639168	-2.671290
H	-2.334134	-0.061376	-2.917619
H	-1.331609	1.094147	2.315709
H	-2.956169	0.907195	3.031293
H	-1.840992	-0.488400	2.964882
H	1.241928	1.884686	1.756526
H	1.218096	4.348695	1.777373
H	0.014526	5.609334	-0.003097
H	-1.195535	4.354335	-1.783148
H	-1.232044	1.890442	-1.761547
Br	-0.007969	-2.753251	-0.008363
H	4.843722	0.112799	-1.517215
H	4.942365	-0.676230	1.144425
H	-4.953630	-0.649923	-1.121161
H	-4.832797	0.131318	1.541879

TS20M-21M

B3LYP-D3/BSI SCF energy (a. u.) : -1025.726258

C	-2.072305	-0.089151	-0.119134
N	-2.787913	0.604921	-1.054697

N	-3.039367	-0.607388	0.692968
C	-4.312937	-0.253992	0.272265
H	-5.202761	-0.569569	0.795108
C	-4.155293	0.507979	-0.839196
H	-4.879573	0.978168	-1.486569
Ni	-0.110423	-0.332210	-0.018653
C	1.698635	0.068988	-0.043903
N	2.709454	-0.216767	0.891991
N	2.380892	0.021597	-1.286868
C	3.916844	-0.446219	0.249018
C	3.714788	-0.321661	-1.081091
H	4.818574	-0.659143	0.803312
H	4.401456	-0.434636	-1.906474
C	0.852834	1.504851	0.237084
C	1.011440	2.545855	-0.702012
C	0.355200	1.850448	1.516109
C	0.640978	3.853771	-0.403752
H	1.459627	2.320446	-1.665332
C	-0.030090	3.158997	1.809553
H	0.231011	1.084548	2.274516
C	0.106721	4.166048	0.851545
H	0.778218	4.636796	-1.145888
H	-0.439821	3.391304	2.789543
H	-0.180189	5.187631	1.085867
Br	0.122830	-2.734300	-0.048392
C	1.679557	-0.326521	-2.515554
H	0.779780	0.287313	-2.612408
H	2.338010	-0.131132	-3.368201
H	1.371007	-1.378299	-2.502950
C	2.452939	-0.491383	2.288213
H	2.335615	0.434551	2.866701

H	1.544096	-1.097026	2.370725
H	3.291028	-1.058577	2.700774
C	-2.767124	-1.391656	1.891030
H	-2.849070	-0.763956	2.785512
H	-3.483345	-2.215220	1.958806
H	-1.760676	-1.802693	1.809329
C	-2.180008	1.291264	-2.184503
H	-2.829896	2.110184	-2.505141
H	-1.218845	1.698036	-1.867942
H	-2.025971	0.601420	-3.021072

21M

B3LYP-D3/BSI SCF energy (a. u.) : -1025.732505

C	2.052033	-0.399101	0.058661
N	2.889704	0.299858	0.881285
N	2.884758	-1.276948	-0.570183
C	4.198343	-1.134646	-0.147032
H	5.000502	-1.741861	-0.537827
C	4.201280	-0.140995	0.777457
H	5.003505	0.280602	1.363605
Ni	0.085475	-0.207997	-0.054825
C	-1.805852	0.570984	-0.141919
N	-2.746376	0.052723	-1.090906
N	-2.526813	0.588032	1.100451
C	-3.843435	-0.442338	-0.388286
C	-3.724400	-0.119517	0.910966
H	-4.645495	-0.947562	-0.905723
H	-4.396062	-0.299907	1.736539
C	-0.947959	1.748245	-0.449400
C	-0.907433	2.873074	0.415707
C	0.028401	1.673048	-1.483837

C	0.035390	3.872391	0.250373
H	-1.670490	2.953011	1.183747
C	0.994231	2.692810	-1.627569
H	-0.032643	0.908100	-2.252820
C	1.008937	3.775225	-0.765680
H	0.013699	4.747205	0.895496
H	1.725005	2.617656	-2.428120
H	1.751587	4.559853	-0.882869
Br	-0.656303	-2.446873	0.425871
C	-1.822021	0.419291	2.370867
H	-0.944008	1.068699	2.395136
H	-2.493660	0.710885	3.185587
H	-1.490120	-0.616622	2.506681
C	-2.349962	-0.485612	-2.377558
H	-2.008964	0.312669	-3.045027
H	-1.554944	-1.234946	-2.257568
H	-3.218551	-0.961293	-2.840127
C	2.454077	-2.213043	-1.601383
H	2.671370	-1.811885	-2.597715
H	2.977559	-3.164195	-1.471744
H	1.382433	-2.378065	-1.485742
C	2.435309	1.321278	1.813896
H	3.211786	2.082713	1.929261
H	1.534383	1.786977	1.412111
H	2.209890	0.880214	2.790636

Details of X-Ray Diffraction Analysis

Suitable crystals were selected, coated with paratone-*N* oil, mounted on a glass fiber and transferred onto the goniometer of the diffractometer into a nitrogen gas cold stream solidifying the oil. The crystal data were collected on a Rigaku Supernova diffractometer using mirror-monochromated radiation. The structures were solved by Direct Methods and refined by full-matrix least-squares cycles using SHELX-97.[16] Compound **26** contains three molecules of toluene per asymmetric unit; two of them are disordered over two sites near an inversion center. These three toluene molecules were restrained to be same and the atoms were constrained to have same displacement parameters.

Crystal and refinement details, as well as CCDC numbers are provided in Table S2 and S3. CCDC 1559107 (**3a**), 1559108 (**3b**), 1559109 (**3j**), 1559110 (**14**-Me), and 1559111 (**26**), contain the supplementary crystallographic data for this paper. These data can be obtained free of charge from The Cambridge Crystallographic Data Centre via www.ccdc.ac.uk/data_request/cif.

Table S2. Crystal data and structure refinement for **3a**, **3b**, and **3j**.

	Compound **3a**	Compound **3b**	Compound **3j**
Empirical formula	$C_{33}H_{41}BrN_2$	$C_{34}H_{43}BrN_2$	$C_{35}H_{46}N_3Br$
Formula weight	545.59	559.61	588.66
Temperature/K	220.0(1)	100.0(1)	100.0(1)
Crystal system	monoclinic	triclinic	monoclinic
Space group	C2/c	Pī	$P2_1/c$
a/Å	30.08483(19)	12.65346(19)	9.07979(11)
b/Å	8.95600(6)	15.1670(2)	26.6494(4)
c/Å	22.48986(13)	18.3140(3)	13.52664(16)
α/°	90	110.1753(14)	90
β/°	95.3846(6)	102.3785(13)	95.0975(11)
γ/°	90	96.7444(12)	90
Volume/Å^3	6032.92(7)	3151.39(9)	3260.11(7)
Z	8	4	4
ρ_{calc}mg/mm^3	1.201	1.179	1.199
μ/mm^{-1}	2.008	1.933	1.287
F(000)	2304.0	1184.0	1248.0
Crystal size/mm^3	0.36 × 0.294 × 0.216	0.161 × 0.066 × 0.023	0.218 × 0.187 × 0.125
Radiation	Cu Kα / 1.54184 Å	Cu Kα / 1.54184 Å	Mo Kα / 0.71073 Å
2Θ range for data collection	5.9 to 144.7°	5.3 to 145.1°	3.1 to 60.2°
Index ranges	$-37 \le h \le 37$, $-11 \le k \le 10$, $-27 \le l \le 27$	$-15 \le h \le 15$, $-18 \le k \le 18$, $-22 \le l \le 22$	$-12 \le h \le 12$, $-37 \le k \le 37$, $-19 \le l \le 19$
Reflections collected	54009	61446	188113
Independent reflections	5945[R(int) = 0.0248]	12465[R(int) = 0.0372]	9564[R(int) = 0.0403]
Data/restraints/parameters	5945/0/333	12465/0/689	9564/0/362
Goodness-of-fit on F^2	1.049	1.079	1.080
Final R indexes [I>=2σ (I)]	R_1 = 0.0302, wR_2 = 0.0791	R_1 = 0.0447, wR_2 = 0.1301	R_1 = 0.0290, wR_2 = 0.0705
Final R indexes [all data]	R_1 = 0.0307, wR_2 = 0.0795	R_1 = 0.0512, wR_2 = 0.1354	R_1 = 0.0330, wR_2 = 0.0722
Largest diff. peak/hole / e Å^{-3}	0.35/-0.54	0.80/-1.44	0.45/-0.48

Table S3. Crystal data and structure refinement for **14**-Me and **23**.

	Compound **14**-Me	Compound **23**
Empirical formula	$C_{68}H_{86}Br_4N_4Ni$	$C_{49}H_{61}BrCuN_3$
Formula weight	1337.75	835.45
Temperature/K	100.0(1)	100.0(1)
Crystal system	monoclinic	triclinic
Space group	I2/a	Pī
a/Å	22.2529(4)	12.2492(2)
b/Å	17.8637(4)	12.9626(2)
c/Å	18.7897(3)	15.7524(3)
α/°	90	82.7553(15)
β/°	103.2084(18)	77.8500(15)
γ/°	90	65.2414(18)
Volume/Å^3	7271.7(2)	2218.39(8)
Z	4	2
ρ_{calc}mg/mm^3	1.222	1.251
μ/mm^{-1}	2.502	1.428
F(000)	2760.0	880.0
Crystal size/mm^3	0.296 × 0.12 × 0.019	0.433 × 0.26 × 0.109
Radiation	Mo Kα / 0.71073 Å	MoKα / 0.71073 Å
2Θ range for data collection	3.2 to 60.2°	3.5 to 60.2°
Index ranges	$-31 \le h \le 31$, $-25 \le k \le 25$, $-26 \le l \le 26$	$-17 \le h \le 17$, $-18 \le k \le 18$, $-22 \le l \le 22$
Reflections collected	83727	100993
Independent reflections	10702[R(int) = 0.0597]	13038[R(int) = 0.0416]
Data/restraints/parameters	10702/0/357	13038/45/479
Goodness-of-fit on F^2	1.049	1.044
Final R indexes [I>=2σ (I)]	R_1 = 0.0390, wR_2 = 0.0909	R_1 = 0.0495, wR_2 = 0.1332
Final R indexes [all data]	R_1 = 0.0570, wR_2 = 0.0963	R_1 = 0.0614, wR_2 = 0.1403
Largest diff. peak/hole / e Å^{-3}	0.68/-0.57	1.03/-1.05

Compound 3a:

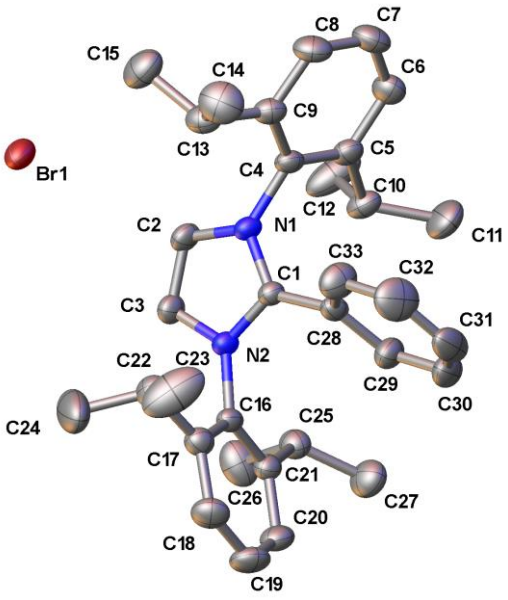


Figure S1. Molecular structure of (IPrPh)Br (**3a**).

Bond lengths for 3a

Atom	Atom	Length/Å	Atom	Atom	Length/Å
N1	C1	1.3436(16)	C13	C15	1.534(2)
N1	C2	1.3831(18)	C16	C17	1.3970(19)
N1	C4	1.4565(17)	C16	C21	1.398(2)
N2	C1	1.3441(18)	C17	C18	1.394(2)
N2	C3	1.3858(17)	C17	C22	1.515(2)
N2	C16	1.4552(16)	C18	C19	1.378(3)
C1	C28	1.4663(18)	C19	C20	1.377(2)
C2	C3	1.350(2)	C20	C21	1.396(2)
C4	C5	1.401(2)	C21	C25	1.520(2)
C4	C9	1.398(2)	C22	C23	1.512(3)
C5	C6	1.394(2)	C22	C24	1.526(3)
C5	C10	1.518(2)	C25	C26	1.527(2)
C6	C7	1.384(2)	C25	C27	1.531(2)
C7	C8	1.376(3)	C28	C29	1.386(2)

C8	C9	1.395(2)	C28	C33	1.381(2)
C9	C13	1.520(2)	C29	C30	1.383(2)
C10	C11	1.524(2)	C30	C31	1.366(3)
C10	C12	1.521(2)	C31	C32	1.380(3)
C13	C14	1.526(2)	C32	C33	1.392(3)

Bond angles for 3a

Atom	Atom	Atom	Angle/°	Atom	Atom	Atom	Angle/°
C1	N1	C2	109.04(11)	C14	C13	C15	110.18(15)
C1	N1	C4	123.84(11)	C17	C16	N2	117.11(12)
C2	N1	C4	126.26(11)	C17	C16	C21	123.83(12)
C1	N2	C3	108.92(11)	C21	C16	N2	118.96(12)
C1	N2	C16	123.05(11)	C16	C17	C22	122.90(13)
C3	N2	C16	127.65(11)	C18	C17	C16	116.67(14)
N1	C1	N2	107.62(11)	C18	C17	C22	120.36(14)
N1	C1	C28	127.16(12)	C19	C18	C17	120.88(15)
N2	C1	C28	125.21(11)	C20	C19	C18	121.11(14)
C3	C2	N1	107.24(12)	C19	C20	C21	120.72(15)
C2	C3	N2	107.18(12)	C16	C21	C25	122.80(13)
C5	C4	N1	117.14(12)	C20	C21	C16	116.68(13)
C9	C4	N1	119.23(12)	C20	C21	C25	120.49(13)
C9	C4	C5	123.63(13)	C17	C22	C24	108.29(15)
C4	C5	C10	122.67(13)	C23	C22	C17	113.00(15)
C6	C5	C4	117.06(14)	C23	C22	C24	112.5(2)
C6	C5	C10	120.16(14)	C21	C25	C26	109.90(13)
C7	C6	C5	120.49(15)	C21	C25	C27	111.93(14)
C8	C7	C6	121.05(15)	C26	C25	C27	110.49(15)
C7	C8	C9	121.11(15)	C29	C28	C1	119.79(13)
C4	C9	C13	123.68(13)	C33	C28	C1	120.21(14)

C8	C9	C4	116.63(14)	C33	C28	C29	119.95(14)
C8	C9	C13	119.63(14)	C30	C29	C28	120.44(17)
C5	C10	C11	112.53(15)	C31	C30	C29	119.63(18)
C5	C10	C12	109.51(12)	C30	C31	C32	120.53(16)
C12	C10	C11	110.20(16)	C31	C32	C33	120.27(19)
C9	C13	C14	111.86(15)	C28	C33	C32	119.16(18)
C9	C13	C15	109.93(13)				

Crystallographic details of 3b:

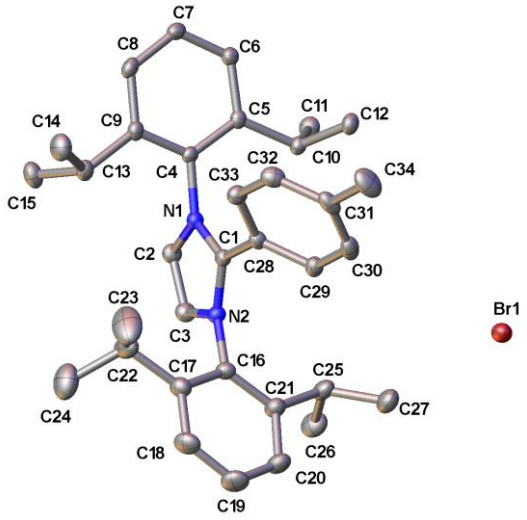


Figure S2. Molecular structure of (IPr(4-tolyl))Br (**3b**).

Bond lengths for 3b.

Atom	Atom	Length/Å	Atom	Atom	Length/Å
N1	C1	1.350(2)	N3	C35	1.344(3)
N1	C2	1.385(3)	N3	C36	1.383(3)
N1	C4	1.452(2)	N3	C38	1.457(2)
N2	C1	1.352(3)	N4	C35	1.350(3)
N2	C3	1.388(3)	N4	C37	1.386(3)
N2	C16	1.454(2)	N4	C50	1.450(3)

C1	C28	1.463(3)	C35	C62	1.466(3)
C2	C3	1.347(3)	C36	C37	1.356(3)
C4	C5	1.398(3)	C38	C39	1.393(3)
C4	C9	1.408(3)	C38	C43	1.405(3)
C5	C6	1.395(3)	C39	C40	1.398(3)
C5	C10	1.520(3)	C39	C44	1.517(3)
C6	C7	1.387(3)	C40	C41	1.383(3)
C7	C8	1.387(3)	C41	C42	1.388(3)
C8	C9	1.394(3)	C42	C43	1.395(3)
C9	C13	1.521(3)	C43	C47	1.522(3)
C10	C11	1.535(3)	C44	C45	1.540(4)
C10	C12	1.533(3)	C44	C46	1.529(3)
C13	C14	1.538(3)	C47	C48	1.528(3)
C13	C15	1.533(3)	C47	C49	1.524(4)
C16	C17	1.404(3)	C50	C51	1.402(3)
C16	C21	1.397(3)	C50	C55	1.396(3)
C17	C18	1.403(3)	C51	C52	1.400(3)
C17	C22	1.511(3)	C51	C56	1.520(3)
C18	C19	1.375(4)	C52	C53	1.387(3)
C19	C20	1.388(3)	C53	C54	1.380(3)
C20	C21	1.399(3)	C54	C55	1.394(3)
C21	C25	1.519(3)	C55	C59	1.523(3)
C22	C23	1.499(4)	C56	C57	1.532(3)
C22	C24	1.555(4)	C56	C58	1.524(3)
C25	C26	1.534(3)	C59	C60	1.533(3)
C25	C27	1.541(3)	C59	C61	1.535(3)
C28	C29	1.399(3)	C62	C63	1.397(3)
C28	C33	1.398(3)	C62	C67	1.400(3)
C29	C30	1.392(3)	C63	C64	1.381(3)
C30	C31	1.390(3)	C64	C65	1.402(3)
C31	C32	1.392(3)	C65	C66	1.389(3)

C31	C34	1.508(3)	C65	C68	1.503(3)
C32	C33	1.386(3)	C66	C67	1.385(3)

Bond angles for 3b.

Atom	Atom	Atom	Angle/°	Atom	Atom	Atom	Angle/°
C1	N1	C2	109.40(16)	C35	N3	C36	109.76(17)
C1	N1	C4	127.12(16)	C35	N3	C38	126.84(17)
C2	N1	C4	123.47(16)	C36	N3	C38	123.39(17)
C1	N2	C3	109.15(16)	C35	N4	C37	109.50(17)
C1	N2	C16	126.60(16)	C35	N4	C50	125.81(17)
C3	N2	C16	122.39(17)	C37	N4	C50	124.67(17)
N1	C1	N2	106.89(16)	N3	C35	N4	106.81(17)
N1	C1	C28	126.50(17)	N3	C35	C62	127.61(18)
N2	C1	C28	126.41(17)	N4	C35	C62	125.57(18)
C3	C2	N1	107.24(17)	C37	C36	N3	107.06(19)
C5	C4	N1	118.75(16)	C36	C37	N4	106.87(18)
C5	C4	C9	123.62(17)	C39	C38	N3	117.45(17)
C9	C4	N1	117.60(17)	C39	C38	C43	123.73(18)
C4	C5	C10	123.22(17)	C43	C38	N3	118.77(17)
C6	C5	C4	117.00(17)	C38	C39	C40	117.43(19)
C6	C5	C10	119.78(18)	C38	C39	C44	123.09(19)
C2	C3	N2	107.31(17)	C40	C39	C44	119.46(19)
C7	C6	C5	120.95(19)	C41	C40	C39	120.4(2)
C6	C7	C8	120.59(18)	C40	C41	C42	120.7(2)
C7	C8	C9	121.11(18)	C41	C42	C43	121.3(2)
C4	C9	C13	122.71(18)	C38	C43	C47	122.06(19)
C8	C9	C4	116.68(18)	C42	C43	C38	116.40(19)
C8	C9	C13	120.61(18)	C42	C43	C47	121.49(19)
C5	C10	C11	110.31(16)	C39	C44	C45	109.45(19)

C5	C10	C12	110.42(16)	C39	C44	C46	111.7(2)
C12	C10	C11	110.44(17)	C46	C44	C45	111.3(2)
C9	C13	C14	112.02(18)	C43	C47	C48	113.1(2)
C9	C13	C15	110.82(16)	C43	C47	C49	111.2(2)
C15	C13	C14	110.33(18)	C49	C47	C48	108.8(2)
C17	C16	N2	116.97(18)	C51	C50	N4	117.28(18)
C21	C16	N2	119.42(18)	C55	C50	N4	118.76(18)
C21	C16	C17	123.45(19)	C55	C50	C51	123.95(19)
C16	C17	C22	123.30(19)	C50	C51	C56	122.29(19)
C18	C17	C16	116.7(2)	C52	C51	C50	116.5(2)
C18	C17	C22	120.0(2)	C52	C51	C56	121.15(19)
C19	C18	C17	121.3(2)	C53	C52	C51	120.5(2)
C18	C19	C20	120.4(2)	C54	C53	C52	121.3(2)
C19	C20	C21	121.1(2)	C53	C54	C55	120.5(2)
C16	C21	C20	116.9(2)	C50	C55	C59	123.09(19)
C16	C21	C25	123.22(18)	C54	C55	C50	117.1(2)
C20	C21	C25	119.82(19)	C54	C55	C59	119.8(2)
C17	C22	C24	111.3(2)	C51	C56	C57	111.7(2)
C23	C22	C17	111.9(2)	C51	C56	C58	111.6(2)
C23	C22	C24	110.0(2)	C58	C56	C57	110.2(2)
C21	C25	C26	110.5(2)	C55	C59	C60	111.03(19)
C21	C25	C27	111.88(18)	C55	C59	C61	110.5(2)
C26	C25	C27	110.24(19)	C60	C59	C61	110.9(2)
C29	C28	C1	119.14(18)	C63	C62	C35	120.62(18)
C33	C28	C1	121.41(18)	C63	C62	C67	119.2(2)
C33	C28	C29	119.37(18)	C67	C62	C35	120.13(18)
C30	C29	C28	120.2(2)	C64	C63	C62	120.25(19)
C31	C30	C29	120.5(2)	C63	C64	C65	121.2(2)
C30	C31	C32	118.89(19)	C64	C65	C68	120.8(2)
C30	C31	C34	120.5(2)	C66	C65	C64	117.8(2)
C32	C31	C34	120.6(2)	C66	C65	C68	121.4(2)

C33	C32	C31	121.4(2)	C67	C66	C65	121.9(2)
C32	C33	C28	119.62(19)	C66	C67	C62	119.6(2)

Crystallographic details of {(IPr)(4-Me_2N-C_6H_4)}Br (3j):

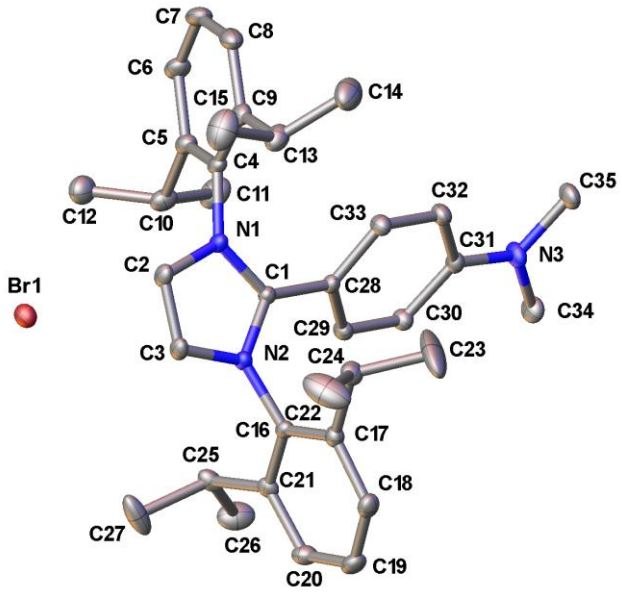


Figure S3. Molecular structure of {(IPr)(4-Me_2N-C_6H_4)}Br (**3j**).

Bond lengths for 3j

Atom	Atom	Length/Å	Atom	Atom	Length/Å
N1	C1	1.3484(15)	C13	C14	1.532(2)
N1	C2	1.3853(15)	C13	C15	1.531(2)
N1	C4	1.4496(15)	C16	C17	1.4039(16)
N2	C1	1.3523(14)	C16	C21	1.4008(16)
N2	C3	1.3872(15)	C17	C18	1.3975(17)
N2	C16	1.4516(14)	C17	C22	1.5210(18)
N3	C31	1.3645(15)	C18	C19	1.3829(19)
N3	C34	1.4572(17)	C19	C20	1.3860(19)
N3	C35	1.4532(17)	C20	C21	1.3963(17)

C1	C28	1.4581(16)	C21	C25	1.5201(17)
C2	C3	1.3514(17)	C22	C23	1.511(2)
C4	C5	1.3950(18)	C22	C24	1.518(2)
C4	C9	1.4007(17)	C25	C26	1.5283(19)
C5	C6	1.3982(17)	C25	C27	1.5289(19)
C5	C10	1.5189(18)	C28	C29	1.3989(16)
C6	C7	1.386(2)	C28	C33	1.4008(16)
C7	C8	1.382(2)	C29	C30	1.3805(16)
C8	C9	1.3953(18)	C30	C31	1.4134(17)
C9	C13	1.5191(19)	C31	C32	1.4146(17)
C10	C11	1.530(2)	C32	C33	1.3842(17)
C10	C12	1.531(2)			

Bond angles for 3j.

Atom	Atom	Atom	Angle/°	Atom	Atom	Atom	Angle/°
C1	N1	C2	109.65(10)	C9	C13	C15	110.90(12)
C1	N1	C4	128.21(10)	C15	C13	C14	110.33(13)
C2	N1	C4	122.03(10)	C17	C16	N2	117.10(10)
C1	N2	C3	109.24(10)	C21	C16	N2	119.11(10)
C1	N2	C16	127.40(10)	C21	C16	C17	123.49(11)
C3	N2	C16	121.63(10)	C16	C17	C22	122.98(11)
C31	N3	C34	120.40(11)	C18	C17	C16	116.91(11)
C31	N3	C35	120.62(11)	C18	C17	C22	120.10(11)
C35	N3	C34	118.73(10)	C19	C18	C17	120.83(12)
N1	C1	N2	106.83(10)	C18	C19	C20	120.95(12)
N1	C1	C28	126.54(10)	C19	C20	C21	120.71(12)
N2	C1	C28	126.60(10)	C16	C21	C25	122.68(11)
C3	C2	N1	107.00(10)	C20	C21	C16	117.07(11)
C2	C3	N2	107.29(10)	C20	C21	C25	120.17(11)

C5	C4	N1	118.25(11)	C23	C22	C17	111.00(12)
C5	C4	C9	123.76(11)	C23	C22	C24	110.67(17)
C9	C4	N1	117.78(11)	C24	C22	C17	111.70(12)
C4	C5	C6	116.90(12)	C21	C25	C26	111.98(12)
C4	C5	C10	123.24(11)	C21	C25	C27	110.25(10)
C6	C5	C10	119.85(12)	C26	C25	C27	110.35(13)
C7	C6	C5	120.74(13)	C29	C28	C1	120.35(10)
C8	C7	C6	120.80(13)	C29	C28	C33	118.09(11)
C7	C8	C9	120.87(13)	C33	C28	C1	121.51(10)
C4	C9	C13	122.79(12)	C30	C29	C28	121.26(11)
C8	C9	C4	116.87(12)	C29	C30	C31	121.18(11)
C8	C9	C13	120.34(12)	N3	C31	C30	121.10(11)
C5	C10	C11	109.74(12)	N3	C31	C32	121.74(11)
C5	C10	C12	111.46(11)	C30	C31	C32	117.16(11)
C11	C10	C12	111.05(12)	C33	C32	C31	121.06(11)
C9	C13	C14	111.80(13)	C32	C33	C28	121.14(11)

Crystallographic details of {2(IPr-4-tolyl)] $NiBr_4$ (14-Me):

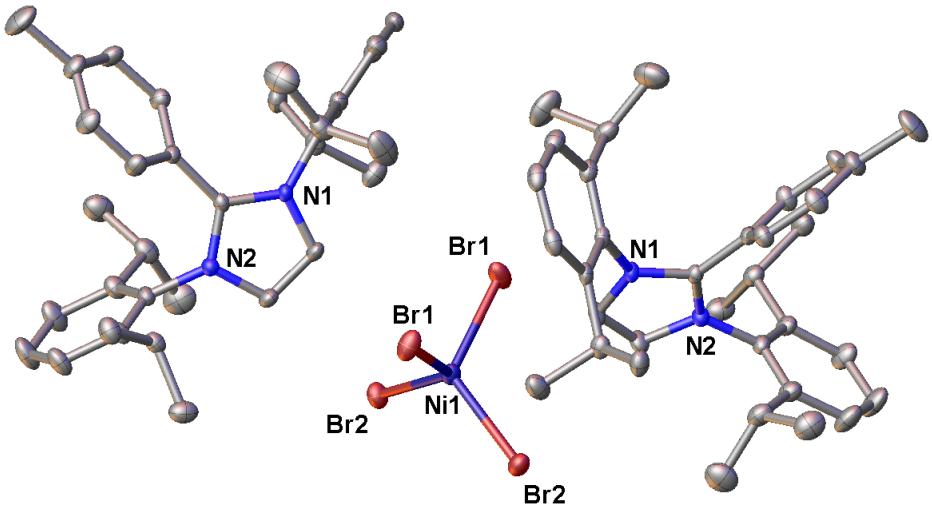


Figure S4. Molecular structure of {2(IPr-4-tolyl)] $NiBr_4$ (**14**-Me).

Bond lengths for 14-Me.

Atom	Atom	Length/Å	Atom	Atom	Length/Å
Br1	Ni1	2.3944(3)	C13	C14	1.531(3)
Br2	Ni1	2.4010(3)	C13	C15	1.532(3)
Ni1	Br1[1]	2.3944(3)	C16	C17	1.398(3)
Ni1	Br2[1]	2.4010(3)	C16	C21	1.403(3)
N1	C1	1.348(2)	C17	C18	1.402(3)
N1	C2	1.381(3)	C17	C22	1.513(3)
N1	C4	1.447(3)	C18	C19	1.381(3)
N2	C1	1.344(3)	C19	C20	1.382(4)
N2	C3	1.393(3)	C20	C21	1.389(3)
N2	C16	1.447(3)	C21	C25	1.525(3)
C1	C28	1.463(3)	C22	C23	1.537(3)
C2	C3	1.345(3)	C22	C24	1.536(3)
C4	C5	1.396(3)	C25	C26	1.525(4)
C4	C9	1.406(3)	C25	C27	1.528(4)
C5	C6	1.399(3)	C28	C29	1.396(3)
C5	C10	1.517(3)	C28	C33	1.391(3)
C6	C7	1.389(3)	C29	C30	1.379(3)
C7	C8	1.381(3)	C30	C31	1.391(3)
C8	C9	1.394(3)	C31	C32	1.393(3)
C9	C13	1.523(3)	C31	C34	1.511(3)
C10	C11	1.527(4)	C32	C33	1.387(3)
C10	C12	1.527(4)			

Bond angles for 14-Me.

Atom	Atom	Atom	Angle/°	Atom	Atom	Atom	Angle/°
Br1	Ni1	Br1[1]	103.60(2)	C9	C13	C14	112.32(19)

Br1[1]	Ni1	Br2	99.886(8)	C9	C13	C15	111.11(18)
Br1	Ni1	Br2	119.812(8)	C14	C13	C15	110.44(19)
Br1[1]	Ni1	Br2[1]	119.809(8)	C17	C16	N2	119.58(19)
Br1	Ni1	Br2[1]	99.888(8)	C17	C16	C21	123.58(19)
Br2[1]	Ni1	Br2	114.53(2)	C21	C16	N2	116.79(19)
C1	N1	C2	109.39(17)	C16	C17	C18	116.7(2)
C1	N1	C4	127.69(17)	C16	C17	C22	122.82(19)
C2	N1	C4	122.74(16)	C18	C17	C22	120.5(2)
C1	N2	C3	109.10(17)	C19	C18	C17	121.2(2)
C1	N2	C16	124.85(17)	C18	C19	C20	120.1(2)
C3	N2	C16	124.25(18)	C19	C20	C21	121.7(2)
N1	C1	C28	127.82(18)	C16	C21	C25	123.0(2)
N2	C1	N1	107.12(17)	C20	C21	C16	116.7(2)
N2	C1	C28	125.00(18)	C20	C21	C25	120.3(2)
C3	C2	N1	107.35(18)	C17	C22	C23	111.52(19)
C2	C3	N2	107.04(19)	C17	C22	C24	110.30(19)
C5	C4	N1	119.10(18)	C24	C22	C23	109.64(19)
C5	C4	C9	124.39(19)	C21	C25	C26	113.2(2)
C9	C4	N1	116.38(19)	C21	C25	C27	110.0(2)
C4	C5	C6	116.2(2)	C26	C25	C27	110.1(2)
C4	C5	C10	123.37(19)	C29	C28	C1	118.51(19)
C6	C5	C10	120.4(2)	C33	C28	C1	122.33(19)
C7	C6	C5	120.9(2)	C33	C28	C29	119.14(19)
C8	C7	C6	121.2(2)	C30	C29	C28	120.2(2)
C7	C8	C9	120.6(2)	C29	C30	C31	121.4(2)
C4	C9	C13	123.12(19)	C30	C31	C32	117.9(2)
C8	C9	C4	116.7(2)	C30	C31	C34	120.9(2)
C8	C9	C13	120.12(19)	C32	C31	C34	121.2(2)
C5	C10	C11	111.2(2)	C33	C32	C31	121.4(2)
C5	C10	C12	111.1(2)	C32	C33	C28	119.9(2)
C11	C10	C12	111.6(2)				

Crystallographic details of {(aIPr)(4-Me_2N-C_6H_4)}CuBr (**23**).

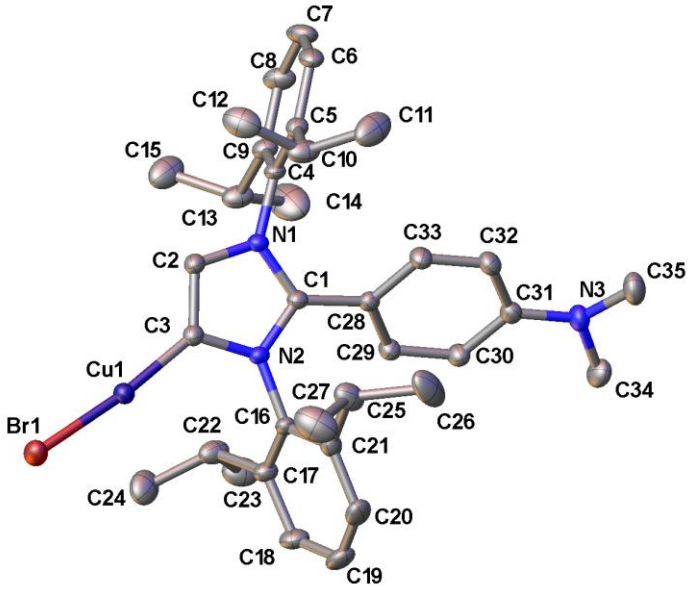


Figure S5. Molecular structure of {(aIPr)(4-Me_2N-C_6H_4)}CuBr (**23**).

Bond lengths for 23.

Atom	Atom	Length/Å	Atom	Atom	Length/Å
Br1	Cu1	2.2438(4)	C21	C25	1.507(4)
Cu1	C3	1.886(2)	C22	C23	1.538(4)
N1	C1	1.347(3)	C22	C24	1.520(4)
N1	C2	1.385(3)	C25	C26	1.537(4)
N1	C4	1.441(3)	C25	C27	1.536(5)
N2	C1	1.348(3)	C28	C29	1.392(3)
N2	C3	1.409(3)	C28	C33	1.402(3)
N2	C16	1.444(3)	C29	C30	1.384(3)
N3	C31	1.368(3)	C30	C31	1.413(3)
N3	C34	1.448(4)	C31	C32	1.404(4)
N3	C35	1.452(4)	C32	C33	1.378(3)
C1	C28	1.458(3)	C36	C37	1.385(5)
C2	C3	1.371(3)	C36	C41	1.378(5)

C4	C5	1.403(3)	C36	C42	1.504(4)
C4	C9	1.401(3)	C37	C38	1.385(5)
C5	C6	1.396(3)	C38	C39	1.373(5)
C5	C10	1.513(4)	C39	C40	1.365(5)
C6	C7	1.385(4)	C40	C41	1.388(5)
C7	C8	1.386(4)	C43	C44	1.455(12)
C8	C9	1.396(3)	C43	C48	1.409(10)
C9	C13	1.516(3)	C43	C49	1.493(11)
C10	C11	1.536(4)	C44	C45	1.367(10)
C10	C12	1.529(4)	C45	C46	1.394(12)
C13	C14	1.515(4)	C46	C47	1.311(12)
C13	C15	1.526(4)	C47	C48	1.377(10)
C16	C17	1.400(3)	C50	C51	1.465(10)
C16	C21	1.397(3)	C50	C55	1.420(10)
C17	C18	1.396(3)	C50	C56	1.412(10)
C17	C22	1.517(3)	C51	C52	1.260(9)
C18	C19	1.380(4)	C52	C53	1.462(9)
C19	C20	1.375(4)	C53	C54	1.250(10)
C20	C21	1.396(4)	C54	C55	1.348(9)

Bond angles for 23.

Atom	Atom	Atom	Angle/°	Atom	Atom	Atom	Angle/°
C3	Cu1	Br1	174.31(7)	C16	C21	C25	123.2(2)
C1	N1	C2	108.70(18)	C20	C21	C16	116.9(2)
C1	N1	C4	127.16(19)	C20	C21	C25	119.9(2)
C2	N1	C4	123.99(18)	C17	C22	C23	111.8(2)
C1	N2	C3	111.89(18)	C17	C22	C24	109.9(2)
C1	N2	C16	123.52(19)	C24	C22	C23	110.2(2)
C3	N2	C16	124.29(18)	C21	C25	C26	111.5(3)

C31	N3	C34	119.7(2)	C21	C25	C27	109.7(2)
C31	N3	C35	119.7(2)	C27	C25	C26	111.0(3)
C34	N3	C35	116.7(2)	C29	C28	C1	121.0(2)
N1	C1	N2	106.51(19)	C29	C28	C33	117.6(2)
N1	C1	C28	127.2(2)	C33	C28	C1	121.3(2)
N2	C1	C28	126.2(2)	C30	C29	C28	121.5(2)
C3	C2	N1	109.97(19)	C29	C30	C31	121.0(2)
N2	C3	Cu1	127.41(16)	N3	C31	C30	120.9(2)
C2	C3	Cu1	129.57(18)	N3	C31	C32	121.9(2)
C2	C3	N2	102.92(19)	C32	C31	C30	117.1(2)
C5	C4	N1	118.1(2)	C33	C32	C31	121.2(2)
C9	C4	N1	118.22(19)	C32	C33	C28	121.5(2)
C9	C4	C5	123.6(2)	C37	C36	C42	121.1(3)
C4	C5	C10	122.7(2)	C41	C36	C37	117.4(3)
C6	C5	C4	117.0(2)	C41	C36	C42	121.5(3)
C6	C5	C10	120.2(2)	C36	C37	C38	121.5(3)
C7	C6	C5	120.8(2)	C39	C38	C37	120.3(4)
C6	C7	C8	120.7(2)	C40	C39	C38	118.8(3)
C7	C8	C9	121.1(2)	C39	C40	C41	121.0(4)
C4	C9	C13	122.8(2)	C36	C41	C40	121.0(3)
C8	C9	C4	116.8(2)	C44	C43	C49	116.7(7)
C8	C9	C13	120.4(2)	C48	C43	C44	115.4(8)
C5	C10	C11	112.5(3)	C48	C43	C49	127.9(9)
C5	C10	C12	109.5(2)	C45	C44	C43	120.1(8)
C12	C10	C11	110.0(2)	C44	C45	C46	119.6(10)
C9	C13	C15	110.7(2)	C47	C46	C45	122.5(11)
C14	C13	C9	111.4(3)	C46	C47	C48	119.9(10)
C14	C13	C15	111.4(3)	C47	C48	C43	122.4(9)
C17	C16	N2	118.75(19)	C55	C50	C51	108.1(6)
C21	C16	N2	118.0(2)	C56	C50	C51	133.5(7)
C21	C16	C17	123.2(2)	C56	C50	C55	116.6(7)

C16	C17	C22	123.0(2)	C52	C51	C50	123.0(8)
C18	C17	C16	117.1(2)	C51	C52	C53	122.8(8)
C18	C17	C22	119.9(2)	C54	C53	C52	114.4(8)
C19	C18	C17	121.0(3)	C53	C54	C55	123.8(8)
C20	C19	C18	120.6(2)	C54	C55	C50	124.7(8)
C19	C20	C21	121.3(2)				

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