Supporting Information

Mechanistic Studies of Hydride Transfer to Imines from a Highly Active and Chemoselective Manganate Catalyst

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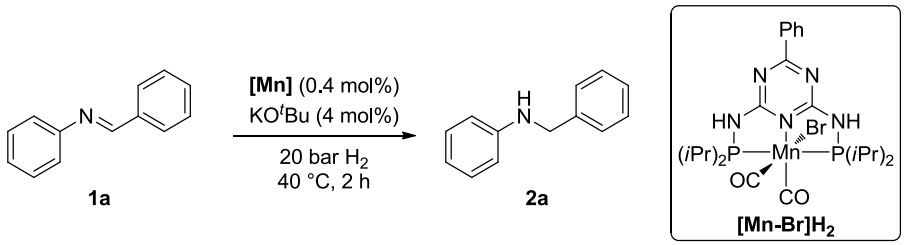
1 General Considerations

All reactions were carried out under nitrogen or argon atmosphere using standard Schlenk or glove box techniques. Solvents were purified by distillation (pentane, Et_2O, CH_2Cl_2). Dry solvents were distilled over sodium benzophenone or over CaH_2 (2-methyl-thf) or were obtained from Acros. Dry solvents were stored over molecular sieves (3 Å). Chemicals were purchased from commercial vendors and used without further purification if not noted otherwise. Imines were purchased from commercial vendors, or were synthesized according to literature procedures[1, 2] and purified using distillation, recrystallization or sublimation. NMR spectra were collected on a Varian INOVA 300 (300 MHz for ^{1}H, 75 MHz for ^{13}C), a Varian INOVA 400 (400 MHz for ^{1}H, 101 MHz for ^{13}C, 162 MHz for ^{31}P), or a Bruker Avance III HD 500 (500 MHz for ^{1}H, 125.7 MHz for ^{13}C, 202 MHz for ^{31}P). Chemical shifts are reported in ppm relative to the residual solvent signal [$CDCl_3$: 7.26 ppm (^{1}H); 77.16 ppm (^{13}C). CD_2Cl_2: 5.32 ppm (^{1}H); 53.84 ppm (^{13}C). thf_{D8}: 3.58 ppm, 1.72 ppm (^{1}H); 67.2 ppm, 25.3 ppm (^{13}C)]. Coupling constants (*J*) are reported in Hz (coupling patterns: s = singulet, d = doublet, t = triplet, q = quartet, hept = heptet, bs = broad singulet, m = multiplet). ^{13}C NMR spectra were measured ^{1}H decoupled. GC analyses were carried out on an Agilent 6850 network system with an Optima 17 column (30 m x 320 µm, 0.25 µm) and GC/MS analyses were conducted on an Agilent 7890A GC system equipped with a HP 5MS column (30 m x 320 µm x 0.25 µm) and a 5975C inert MSD detector (EI, 70 eV). Elemental analyses were carried out on an Elementar Unicube. Melting points were measured on a Stuart Scientific Melting Point Apparatus SMP3. UV-vis measurements were conducted on an Agilent Cary 60 UV-Vis. IR spectra were collected on a Shimadzu IRTracer-100 with KBr pellets. The pellets of the compounds were prepared in a glove box with dry KBr and subsequently measured under air. Macherey Nagel silica gel 60 (40–63 µm particle size) was used for column chromatography. All organic compounds were characterized by ^{1}H and ^{13}C NMR analysis. Unknown compounds or compounds with incomplete spectroscopic literature data were further analyzed via elemental analysis. The ligands were synthesized according to literature procedures[3] and the precatalysts were also synthesized similar to literature procedures[4], in thf under reflux for 1.5 h and subsequent removal of the solvent. Hydrogenations were conducted in PARR Instrument stainless steel autoclaves N-MT5 300 mL equipped with heating mantles and temperature controllers. X-ray crystal structure analysis was performed on a STOE STADIVARI [λ(Mo-Kα) = 0.71073 Å] equipped with an Oxford Cryostream low temperature unit. Structure solution and refinement was accomplished with OlexSys 2[5], SHELXL-2014[6], WinGX[7], and Mercury 3.9[8].

2 Hydrogenation of Imines

2.1 Parameter Screening

N-benzylideneaniline (**1a**) was chosen as the model substrate for the imine hydrogenation reaction (Scheme S 1).



Scheme S 1. Starting conditions for the imine hydrogenation with *N*-benzylidenaniline (**1a**).

General screening procedure: Under nitrogen atmosphere in a glove box screw-vials were charged with magnetic stir bars, base, Mn precatalyst, **1a** (1.00 mmol, 1.00 eq.), and solvent (2 mL). The vials were placed in an autoclave, which was sealed and purged three times with hydrogen, before adjusting the pressure to 20 bar. The reactions were stirred and heated to the desired temperature. After the reaction, hydrogen was released, 1 mL H_2O, 100 µL dodecane as internal standard, and 7 mL Et_2O were added to each vial and the mixtures were homogenized. A sample of the organic phase was dried over Na_2SO_4 and analyzed via GC.

Screenings are listed in Table S 1–Table S 5.

Table S 1. Solvent screening.[a]

Entry	Solvent	Yield of **2a** [%][b]
1	thf	61
2	1,4-dioxane	23
3	toluene	12
4	2-methyl-2-butanol	0
5	diglyme	20
6	dimethoxyethane	0
7	2-methyl-thf	33

[a] **1a** (1.0 mmol), KO^{t}Bu (4 mol%), **[Mn-Br]H_2** (0.4 mol%), solvent (2 mL), 40 °C, 20 bar H_2, 2 h. [b] Determined by GC with dodecane as internal standard.

Table S 2. Base screening.[a]

Entry	Base	Yield of **2a** [%][b]
1	LiO^tBu	0
2	NaO^tBu	8
3	KO^tBu	61
4	NaHMDS[c]	3
5	KHMDS[d]	12
6	Cs_2CO_3	0
7	KOH	0
8	NaOH	0
9	KH	13

[a] **1a** (1.0 mmol), Base (4 mol%), **[Mn-Br]H$_2$** (0.4 mol%), thf (2 mL), 40 °C, 20 bar H_2, 2h. [b] Determined by GC with dodecane as internal standard. [c] Sodium bis(trimethylsilyl)amide. [d] Potassium bis-(trimethylsilyl)amide.

Table S 3. Base amount screening.[a]

Entry	Base amount [eq. with respect to the precatalyst]	Yield of **2a** [%][b]
1	1	0
2	2	0
3	5	16
4	8	54
5	10	61
6	12	54

[a] **1a** (1.0 mmol), KO^tBu, **[Mn-Br]H$_2$** (0.4 mol%), thf (2 mL), 40 °C, 20 bar H_2, 2 h. [b] Determined by GC with dodecane as internal standard.

Table S 4. Precatalyst screening.[a]

Entry	Precatalyst	Yield of **2a** [%][b]
1	R = Ph, X = N	37
2	R = 4-F_3C-C_6H_4, X = N	11
3	R = NH-cyclopropyl, X = N	20
4	R = NEt_2, X = N	14
5	R = Me, X = N	28
6	R = H, X = CH	2
7	$PN_5P[MnCl_2]$	0
8	$[Mn(CO)_5Br]$	1

[a] **1a** (1.0 mmol), KO^tBu (1.6 mol%), precatalyst (0.2 mol%), thf (2 mL), 40 °C, 20 bar H_2, 2 h. [b] Determined by GC with dodecane as internal standard.

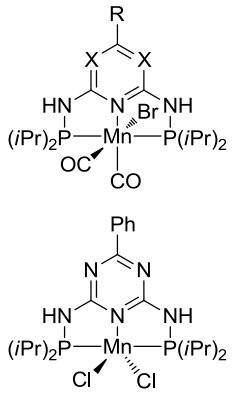


Table S 5. Screening of the catalyst loading at 40 °C and 50 °C.[a]

Entry	Catalyst Loading [mol%]	Temperature [°C]	Yield of **2a** [%][b]
1	0.4	40	95
2	0.3	40	69
3	0.05	40	0
4	0.4	50	>99
5	0.3	50	79
6	0.05	50	0

[a] **1a** (1.0 mmol), KO^{t}Bu (10 eq. with respect to **[Mn-Br]H$_2$**), **[Mn-Br]H$_2$**, thf (2 mL), 20 bar H_2, 4 h.
[b] Determined by GC with dodecane as internal standard.

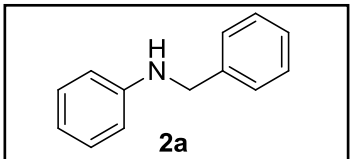
2.2 Substrate Synthesis

2.2.1. Aldimine Reduction

General procedure for aldimine reduction: Under nitrogen atmosphere in a glove box screw-vials were charged with magnetic stir bars, KO^{t}Bu (4 mol%), **[Mn-Br]H$_2$** (0.4 mol%), imine **1** (1.00 mmol, 1.00 eq.), and thf (2 mL). The vials were placed in an autoclave, which was sealed and purged three times with hydrogen, before adjusting the pressure to 20 bar. The reactions were stirred and heated to 50 °C. After 4 h, the hydrogen was released, 1 mL H_2O and 7 mL Et_2O were added to each vial, and the mixtures were homogenized. The mixture was dried with Na_2SO_4, filtered, washed with Et_2O or CH_2Cl_2, and the solvent was removed under reduced pressure. The product was isolated via a short silica column.

_N_-benzylaniline (2a)

According to the general procedure with *N*-benzylideneaniline (**1a**) (181 mg, 1.00 mmol, 1.00 eq.). Purification by column chromatography (silica gel, pentane/diethylether, 9:1).



2a
Chemical Formula: $C_{13}H_{13}N$
Molecular Weight: 183.25

Yield: 98 % (982 µmol, 180 mg) yellowish solid.

Upscaling: According to the general procedure with *N*-benzylideneaniline (**1a**) (3.62 g, 20.0 mmol, 1.00 eq.) and 20 mL thf. Purification by column chromatography (silica gel, pentane/diethylether, 9:1).

Yield: 98 % (19.6 mmol, 3.59 g) yellowish solid.

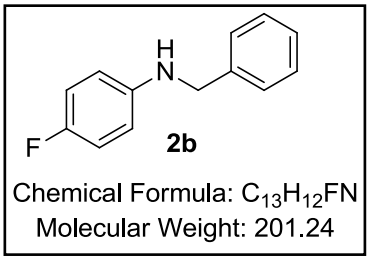
^{1}H NMR (500 MHz, $CDCl_3$): δ 7.43 – 7.36 (m, 4H), 7.34 – 7.28 (m, 1H), 7.24 – 7.18 (m, 2H), 6.76 (t, *J* = 7.3 Hz, 1H), 6.67 (d, *J* = 7.8 Hz, 2H), 4.36 (s, 2H), 4.07 (s, 1H).

^{13}C NMR (126 MHz, $CDCl_3$): δ 148.2, 139.5, 129.4, 128.8, 127.6, 127.4, 117.7, 113.0, 48.4.

The spectroscopic data correspond to those reported in literature.[9]

N-benzyl-4-fluoroaniline (2b)

According to the general procedure with *N*-benzylidene-4-fluoroaniline (**1b**) (199 mg, 1.00 mmol, 1.00 eq.). Purification by column chromatography (silica gel, pentane/diethylether, 9:1).



Yield: 95 % (954 µmol, 192 mg) yellowish solid.

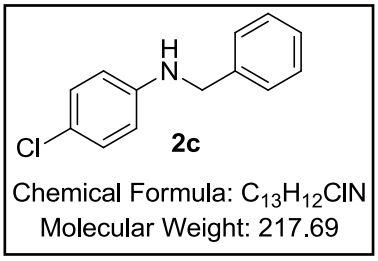
^{1}H NMR (500 MHz, $CDCl_3$): δ 7.42 – 7.35 (m, 4H), 7.35 – 7.28 (m, 1H), 6.95 – 6.87 (m, 2H), 6.62 – 6.55 (m, 2H), 4.31 (s, 2H), 3.95 (bs, 1H).

^{13}C NMR (126 MHz, $CDCl_3$): δ 156.0 (d, *J* = 235.0 Hz), 144.6 (d, *J* = 1.8 Hz), 139.4, 128.8, 127.6, 127.4, 115.8 (d, *J* = 22.3 Hz), 113.7 (d, *J* = 7.4 Hz), 49.0.

The spectroscopic data correspond to those reported in literature.[9]

N-benzyl-4-chloroaniline (2c)

According to the general procedure with *N*-benzylidene-4-chloroaniline (**1c**) (215 mg, 1.00 mmol, 1.00 eq.). Purification by column chromatography (silica gel, pentane/diethylether, 9:1).



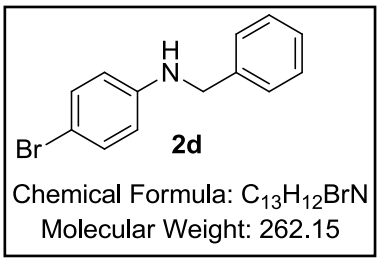
Yield: 98 % (983 µmol, 214 mg) orange solid.

^{1}H NMR (500 MHz, $CDCl_3$): δ 7.40 – 7.33 (m, 4H), 7.33 – 7.27 (m, 1H), 7.15 – 7.09 (m, 2H), 6.58 – 6.53 (m, 2H), 4.31 (s, 2H), 4.09 (s, 1H).

^{13}C NMR (126 MHz, $CDCl_3$): δ 146.7, 139.0, 129.2, 128.8, 127.5, 127.5, 122.2, 114.0, 48.5.

The spectroscopic data correspond to those reported in literature.[9]

_N_-benzyl-4-bromoaniline (2d)



According to the general procedure with *N*-benzylidene-4-bromoaniline (**1d**) (260 mg, 1.00 mmol, 1.00 eq.). Purification by column chromatography (silica gel, pentane/diethylether, 9:1).

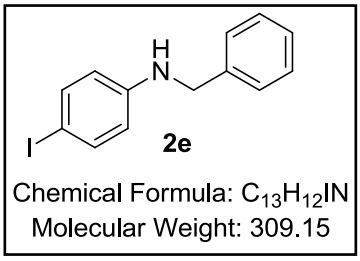
Yield: 96 % (957 µmol, 251 mg) yellow solid.

^{1}H NMR (500 MHz, $CDCl_3$): δ 7.38-7.31 (m, 4H), 7.31 – 7.26 (m, 1H), 7.24 (d, *J* = 8.7 Hz, 2H), 6.50 (d, *J* = 8.7 Hz, 2H), 4.29 (s, 2H), 4.23 (bs, 1H).

^{13}C NMR (126 MHz, $CDCl_3$): δ 147.0, 138.9, 132.1, 128.8, 127.6, 127.5, 114.6, 109.4, 48.4.

The spectroscopic data correspond to those reported in literature.[10]

_N_-benzyl-4-iodoaniline (2e)



According to the general procedure with *N*-benzylidene-4-iodoaniline (**1e**) (307 mg, 1.00 mmol, 1.00 eq.). Purification by column chromatography (silica gel, pentane/diethylether, 9:1).

Yield: 99 % (987 µmol, 305 mg) yellowish oil.

Upscaling: According to the general procedure with *N*-benzylidene-4-iodoaniline (**1e**) (6.14 g, 20.0 mmol, 1.00 eq.) and 20 mL thf. Purification by column chromatography (silica gel, pentane/diethylether, 95:5).

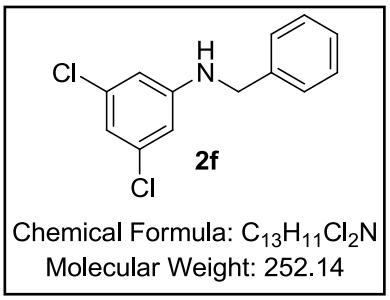
Yield: 98 % (19.5 mmol, 6.04 g) yellowish oil.

^{1}H NMR (300 MHz, $CDCl_3$): δ 7.44 – 7.38 (m, 2H), 7.37 – 7.32 (m, 4H), 7.32 – 7.26 (m, 1H), 6.45 – 6.40 (m, 2H), 4.30 (s, 2H), 4.19 (s, 1H).

^{13}C NMR (75 MHz, $CDCl_3$): δ 147.7, 138.9, 137.9, 128.8, 127.5, 115.2, 78.3, 48.2.

The spectroscopic data correspond to those reported in literature.[11]

_N_-benzyl-3,5-dichloroaniline (2f)



According to the general procedure with *N*-benzylidene-3,5-dichloroaniline (**1f**) (250 mg, 1.00 mmol, 1.00 eq.). Purification by column chromatography (silica gel, pentane/diethylether, 9:1).

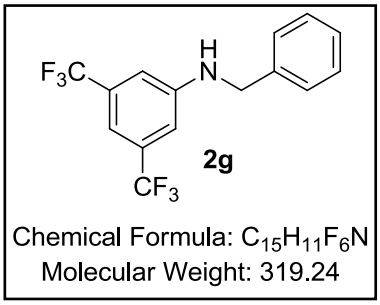
Yield: 94 % (940 µmol, 237 mg) yellow oil.

^{1}H NMR (500 MHz, $CDCl_3$): δ 7.40 – 7.28 (m, 5H), 6.69 (t, *J* = 1.7 Hz, 1H), 6.49 (d, *J* = 1.7 Hz, 2H), 4.32 (bs, 1H), 4.29 (s, 2H).

^{13}C NMR (126 MHz, $CDCl_3$): δ 149.5, 138.0, 135.5, 128.9, 127.7, 127.5, 117.4, 111.1, 48.0.

The spectroscopic data correspond to those reported in literature.[12]

_N_-benzyl-3,5-bis(trifluoromethyl)aniline (2g)



According to the general procedure with *N*-benzylidene-3,5-bis(trifluoromethyl)aniline (**1g**) (317 mg, 1.00 mmol, 1.00 eq.). Purification by column chromatography (silica gel, pentane/diethylether, 9:1).

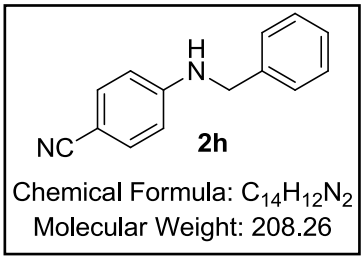
Yield: 95 % (952 µmol, 304 mg) yellow oil.

^{1}H NMR (500 MHz, $CDCl_3$): δ 7.43 – 7.29 (m, 5H), 7.18 (s, 1H), 6.98 (s, 2H), 4.50 (bs, 1H), 4.38 (s, 2H).

^{13}C NMR (126 MHz, $CDCl_3$): δ 148.7, 137.7, 132.6 (q, *J* = 32.7 Hz), 129.1, 128.0, 127.7, 123.7 (q, *J* = 273 Hz), 112.1, 110.6, 48.2.

The spectroscopic data correspond to those reported in literature.[13]

4-(benzylamino)benzonitrile (2h)



According to the general procedure with 4-(benzylideneamino)benzonitrile (**1h**) (206 mg, 1.00 mmol, 1.00 eq.). Purification by column chromatography (silica gel, pentane/diethylether, 8:2).

Yield: 94 % (941 µmol, 196 mg) yellowish solid.

Upscaling: According to the general procedure with 4-(benzylideneamino)benzonitrile (**1g**) (4.12 g, 20.0 mmol, 1.00 eq.) and 20 mL thf. Purification by column chromatography (silica gel, pentane/diethylether, 8:2).

Yield: 90 % (18.0 mmol, 3.75 g) yellowish solid.

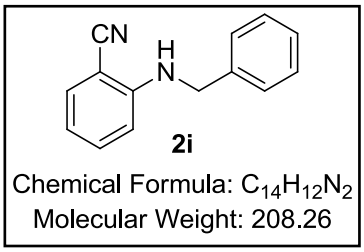
^{1}H NMR (500 MHz, $CDCl_3$): δ 7.41 (d, *J* = 8.8 Hz, 2H), 7.39 – 7.28 (m, 5H), 6.59 (d, *J* = 8.8 Hz, 2H), 4.69 (bs, 1H), 4.38 (s, 2H).

^{13}C NMR (126 MHz, $CDCl_3$): δ 151.2, 137.9, 133.8, 129.0, 127.8, 127.4, 120.5, 112.5, 99.1, 47.6.

The spectroscopic data correspond to those reported in literature.[14]

2-(benzylamino)benzonitrile (2i)

According to the general procedure with 2-(benzylideneamino)benzonitrile (**1i**) (206 mg, 1.00 mmol, 1.00 eq.). Purification by column chromatography (silica gel, pentane/diethylether, 9:1).



2i
Chemical Formula: $C_{14}H_{12}N_2$
Molecular Weight: 208.26

Yield: 86 % (864 µmol, 180 mg) yellow solid.

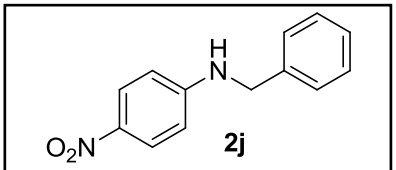
^{1}H NMR (500 MHz, $CDCl_3$): δ 7.42 (dd, *J* = 7.7, 1.4 Hz, 1H), 7.39 – 7.28 (m, 6H), 6.69 (td, *J* = 7.7, 0.7 Hz, 1H), 6.64 (d, *J* = 8.5 Hz, 1H), 5.04 (bs, 1H), 4.44 (d, *J* = 5.6 Hz, 2H).

^{13}C NMR (126 MHz, $CDCl_3$): δ 150.2, 137.8, 134.4, 132.9, 129.0, 127.8, 127.3, 118.0, 117.0, 111.1, 96.0, 47.6.

The spectroscopic data correspond to those reported in literature.[15]

***N*-benzyl-4-nitroaniline (2j)**

According to the general procedure with *N*-benzylidene-4-nitroaniline (**1j**) (226 mg, 1.00 mmol, 1.00 eq.) with 0.6 mol% **[Mn-Br]H$_2$** and a reaction time of 16 h. Purification by column chromatography (silica gel, pentane/CH_2Cl_2, 9:1).



2j
Chemical Formula: $C_{13}H_{12}N_2O_2$
Molecular Weight: 228.25

Yield: 85 % (854 µmol, 195 mg) orange solid.

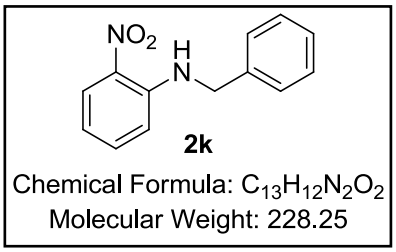
^{1}H NMR (500 MHz, $CDCl_3$): δ 8.13 – 8.04 (m, 2H), 7.43 – 7.29 (m, 5H), 6.62 – 6.52 (m, 2H), 4.91 (s, 1H), 4.44 (s, 2H).

^{13}C NMR (126 MHz, $CDCl_3$): δ 153.2, 138.4, 137.5, 129.1, 128.0, 127.5, 126.5, 111.5, 47.8.

The spectroscopic data correspond to those reported in literature.[16]

_N_-benzyl-2-nitroaniline (2k)

According to the general procedure with *N*-benzylidene-2-nitroaniline (**1k**) (226 mg, 1.00 mmol, 1.00 eq.) with 0.6 mol% **[Mn-Br]H$_2$** and a reaction time of 18 h. Purification by column chromatography (silica gel, pentane/diethylether, 8:2).



2k
Chemical Formula: $C_{13}H_{12}N_2O_2$
Molecular Weight: 228.25

Yield: 81 % (806 µmol, 184 mg) orange oil.

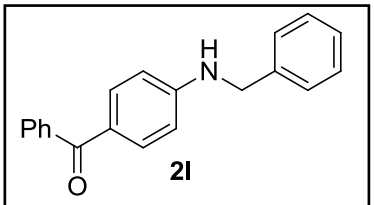
^{1}H NMR (500 MHz, $CDCl_3$): δ 8.44 (bs, 1H), 8.20 (dd, *J* = 8.6, 1.5 Hz, 1H), 7.44 – 7.33 (m, 5H), 7.33 – 7.28 (m, 1H), 6.82 (d, *J* = 8.6 Hz, 1H), 6.72 – 6.63 (m, 1H), 4.56 (d, *J* = 5.7 Hz, 2H).

^{13}C NMR (126 MHz, $CDCl_3$): δ 145.4, 137.5, 136.4, 132.4, 129.1, 127.8, 127.2, 127.0, 115.9, 114.3, 47.2.

The spectroscopic data correspond to those reported in literature.[17]

(4-(benzylamino)phenyl)(phenyl)methanone (2l)

According to the general procedure with (4-(benzylideneamino)phenyl)(phenyl)methanone (**1l**) (285 mg, 1.00 mmol, 1.00 eq.). Purification by column chromatography (silica gel, pentane/diethylether, 8:2).



2l
Chemical Formula: $C_{20}H_{17}NO$
Molecular Weight: 287.36

Yield: 77 % (773 µmol, 222 mg) brightly-yellow solid.

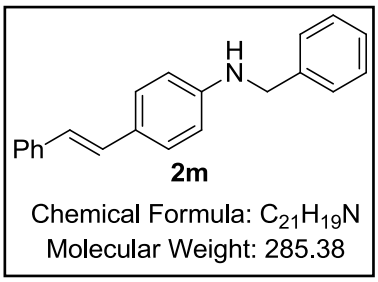
^{1}H NMR (500 MHz, $CDCl_3$): δ 7.82 – 7.63 (m, 4H), 7.58 – 7.20 (m, 8H), 6.63 (d, *J* = 7.9 Hz, 2H), 4.72 (bs, 1H), 4.42 (s, 2H).

^{13}C NMR (126 MHz, $CDCl_3$): δ 195.3, 152.0, 139.2, 138.3, 133.1, 131.4, 129.6, 128.9, 128.1, 127.7, 127.5, 126.5, 111.6, 47.7.

The spectroscopic data correspond to those reported in literature.[18]

_N_-benzyl-4-styrylaniline (2m)

According to the general procedure with *N*-benzylidene-4-((*E*)-styryl)aniline (**1m**) (283 mg, 1.00 mmol, 1.00 eq.) and 0.6 mol% **[Mn-Br]H$_2$**. Purification by column chromatography (silica gel, pentane/diethylether, 9:1).



Yield: 94 % (943 µmol, 269 mg) orange-yellow solid.

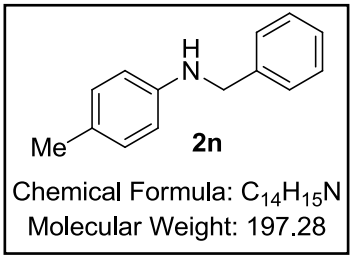
^{1}H NMR (500 MHz, $CDCl_3$): δ 7.49 (d, *J* = 7.5 Hz, 2H), 7.42 – 7.28 (m, 9H), 7.22 (t, *J* = 7.3 Hz, 1H), 7.05 (d, *J* = 16.3 Hz, 1H), 6.92 (d, *J* = 16.3 Hz, 1H), 6.65 (d, *J* = 8.6 Hz, 2H), 4.38 (s, 2H), 4.30 (s, 1H).

^{13}C NMR (126 MHz, $CDCl_3$): δ 147.8, 139.2, 138.2, 128.9, 128.8, 128.7, 127.9, 127.6, 127.5, 127.2, 126.9, 126.2, 124.8, 113.1, 48.4.

The spectroscopic data correspond to those reported in literature.[19]

_N_-benzyl-4-methylaniline (2n)

According to the general procedure with *N*-benzylidene-4-methylaniline (**1n**) (195 mg, 1.00 mmol, 1.00 eq.). Purification by column chromatography (silica gel, pentane/diethylether, 9:1).



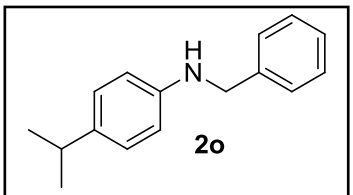
Yield: 85 % (847 µmol, 167 mg) yellowish oil.

^{1}H NMR (500 MHz, $CDCl_3$): δ 7.47 – 7.37 (m, 4H), 7.37 – 7.30 (m, 1H), 7.07 (d, *J* = 7.1 Hz, 2H), 6.63 (d, *J* = 6.8 Hz, 2H), 4.37 (s, 2H), 3.95 (bs, 1H), 2.32 (s, 3H).

^{13}C NMR (126 MHz, $CDCl_3$): δ 146.0, 139.8, 129.8, 128.7, 127.6, 127.2, 126.8, 113.1, 48.7, 20.5.

The spectroscopic data correspond to those reported in literature.[9]

***N*-benzyl-4-isopropylaniline (2o)**



Chemical Formula: $C_{16}H_{19}N$
Molecular Weight: 225.33

According to the general procedure with *N*-benzylidene-4-isopropylaniline (**1o**) (223 mg, 1.00 mmol, 1.00 eq.). Purification by column chromatography (silica gel, pentane/diethylether, 9:1).

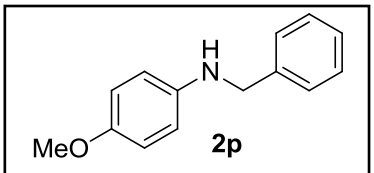
Yield: 93 % (932 µmol, 210 mg) orange oil.

^{1}H NMR (500 MHz, $CDCl_3$): δ 7.47 – 7.37 (m, 4H), 7.37 – 7.31 (m, 1H), 7.12 (d, *J* = 8.3 Hz, 2H), 6.66 (d, *J* = 8.4 Hz, 2H), 4.36 (s, 2H), 4.03 (s, 1H), 2.88 (hept, *J* = 6.9 Hz, 1H), 1.28 (d, *J* = 6.9 Hz, 6H).

^{13}C NMR (126 MHz, $CDCl_3$): δ 146.3, 139.8, 138.2, 128.7, 127.7, 127.3, 127.2, 113.0, 48.8, 33.3, 24.4.

The spectroscopic data correspond to those reported in literature.[20]

***N*-benzyl-4-methoxyaniline (2p)**



Chemical Formula: $C_{14}H_{15}NO$
Molecular Weight: 213.28

According to the general procedure with *N*-benzylidene-4-methoxyaniline (**1p**) (211 mg, 1.00 mmol, 1.00 eq.) and 0.6 mol% **[Mn-Br]H$_2$**. Purification by column chromatography (silica gel, pentane/diethylether, 9:1).

Yield: 94 % (942 µmol, 201 mg) yellowish solid.

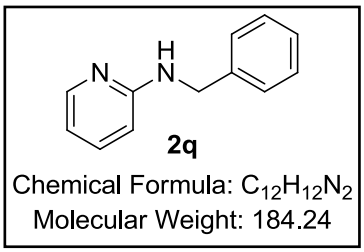
^{1}H NMR (500 MHz, $CDCl_3$): δ 7.44 – 7.36 (m, 4H), 7.36 – 7.29 (m, 1H), 6.85 – 6.80 (m, 2H), 6.67 – 6.62 (m, 2H), 4.32 (s, 2H), 3.87 (bs, 1H), 3.78 (s, 3H).

^{13}C NMR (126 MHz, $CDCl_3$): δ 152.2, 142.5, 139.7, 128.7, 127.6, 127.2, 115.0, 114.2, 55.8, 49.3.

The spectroscopic data correspond to those reported in literature.[9]

_N_-benzylpyridin-2-amine (2q)

According to the general procedure with *N*-benzylidenepyridin-2-amine (**1q**) (182 mg, 1.00 mmol, 1.00 eq.). Purification by column chromatography (silica gel, pentane/diethylether, 7:3).



2q

Chemical Formula: $C_{12}H_{12}N_2$
Molecular Weight: 184.24

Yield: 92 % (923 µmol, 170 mg) white solid.

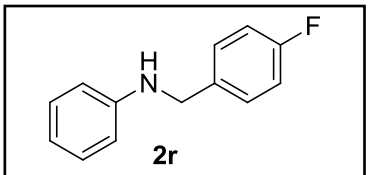
^{1}H NMR (500 MHz, $CDCl_3$): δ 8.11 (dd, *J* = 5.0, 0.9 Hz, 1H), 7.44 – 7.32 (m, 5H), 7.32 – 7.26 (m, 1H), 6.60 (ddd, *J* = 7.0, 5.1, 0.6 Hz, 1H), 6.39 (d, *J* = 8.4 Hz, 1H), 5.03 (bs, 1H), 4.52 (d, *J* = 5.8 Hz, 2H).

^{13}C NMR (126 MHz, $CDCl_3$): δ 158.7, 148.2, 139.3, 137.6, 128.8, 127.5, 127.4, 113.2, 106.9, 46.4.

The spectroscopic data correspond to those reported in literature.[13]

_N_-(4-fluorobenzyl)aniline (2r)

According to the general procedure with *N*-(4-fluorobenzylidene)aniline (**1r**) (199 mg, 1.00 mmol, 1.00 eq.) and 0.6 mol% **[Mn-Br]H$_2$**. Purification by column chromatography (silica gel, pentane/diethylether, 8:2).



2r

Chemical Formula: $C_{13}H_{12}FN$
Molecular Weight: 201.24

Yield: 93 % (934 µmol, 188 mg) yellowish oil.

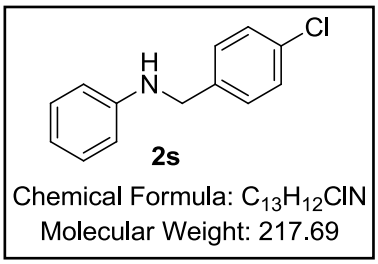
^{1}H NMR (500 MHz, $CDCl_3$): δ 7.34 (dd, *J* = 7.8, 5.7 Hz, 2H), 7.22 – 7.16 (m, 2H), 7.07 – 7.00 (m, 2H), 6.75 (td, *J* = 7.3, 0.8 Hz, 1H), 6.67 – 6.61 (m, 2H), 4.31 (s, 2H), 4.16 (bs, 1H).

^{13}C NMR (126 MHz, $CDCl_3$): δ 163.2, 161.2, 147.9, 135.1, 129.4, 129.2, 129.1, 118.0, 115.7, 115.5, 113.1, 47.8.

The spectroscopic data correspond to those reported in literature.[20]

_N_-(4-chlorobenzyl)aniline (2s)

According to the general procedure with _N_-(4-chlorobenzylidene)aniline (**1s**) (215 mg, 1.00 mmol, 1.00 eq.). Purification by column chromatography (silica gel, pentane/diethylether, 9:1).



2s
Chemical Formula: $C_{13}H_{12}ClN$
Molecular Weight: 217.69

Yield: 95 % (946 µmol, 206 mg) yellowish oil.

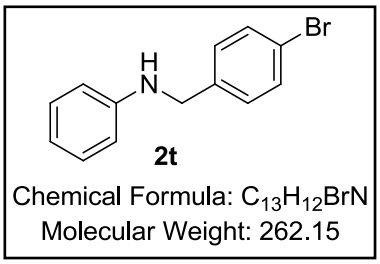
^{1}H NMR (300 MHz, $CDCl_3$): δ 7.32 (d, *J* = 2.4 Hz, 4H), 7.25 – 7.14 (m, 2H), 6.76 (t, *J* = 7.3 Hz, 1H), 6.63 (d, *J* = 6.8 Hz, 2H), 4.32 (s, 2H), 4.10 (bs, 1H).

^{13}C NMR (75 MHz, $CDCl_3$): δ 147.9, 138.1, 132.9, 129.4, 128.8, 128.8, 117.9, 113.0, 47.7.

The spectroscopic data correspond to those reported in literature.[19]

_N_-(4-bromobenzyl)aniline (2t)

According to the general procedure with _N_-(4-bromobenzylidene)aniline (**1t**) (260 mg, 1.00 mmol, 1.00 eq.). Purification by column chromatography (silica gel, pentane/diethylether, 9:1).



2t
Chemical Formula: $C_{13}H_{12}BrN$
Molecular Weight: 262.15

Yield: 94 % (942 µmol, 247 mg) yellow oil.

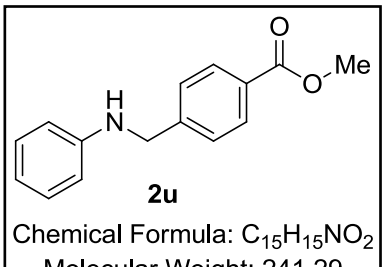
^{1}H NMR (500 MHz, $CDCl_3$): δ 7.53 (d, *J* = 8.3 Hz, 2H), 7.31 (d, *J* = 8.3 Hz, 1H), 7.27 (t, *J* = 7.7 Hz, 2H), 6.83 (t, *J* = 7.3 Hz, 1H), 6.68 (d, *J* = 8.3 Hz, 2H), 4.34 (s, 2H), 4.12 (s, 1H).

^{13}C NMR (126 MHz, $CDCl_3$): δ 147.8, 138.6, 131.7, 129.4, 129.1, 120.9, 117.8, 112.9, 47.6.

The spectroscopic data correspond to those reported in literature.[19]

methyl-4-((phenylamino)methyl)benzoate (2u)

According to the general procedure with methyl-4-((phenylimino)methyl)benzoate (**1u**) (239 mg, 1.00 mmol, 1.00 eq.). Purification by column chromatography (silica gel, pentane/diethylether, 9:1).



2u
Chemical Formula: $C_{15}H_{15}NO_2$
Molecular Weight: 241.29

Yield: 74 % (738 µmol, 178 mg) yellow oil.

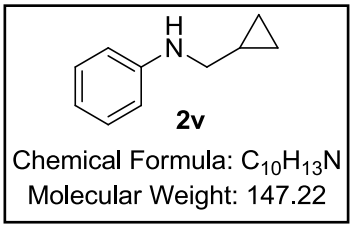
^{1}H NMR (500 MHz, $CDCl_3$): δ 8.04 – 7.99 (m, 2H), 7.45 (d, *J* = 8.1 Hz, 2H), 7.21 – 7.14 (m, 2H), 6.77 – 6.71 (m, 1H), 6.65 – 6.59 (m, 2H), 4.41 (s, 2H), 4.24 (bs, 1H), 3.92 (s, 3H).

^{13}C NMR (126 MHz, $CDCl_3$): δ 167.1, 147.8, 145.1, 130.1, 129.4, 129.2, 127.3, 118.0, 113.0, 52.2, 48.1.

The spectroscopic data correspond to those reported in literature.[14]

N-(cyclopropylmethyl)aniline (2v)

According to the general procedure with *N*-(cyclopropylmethylene)aniline (**1v**) (145 mg, 1.00 mmol, 1.00 eq.). Purification by column chromatography (silica gel, pentane/diethylether, 98:2).



2v
Chemical Formula: $C_{10}H_{13}N$
Molecular Weight: 147.22

Yield: 81 % (808 µmol, 119 mg) yellow-orange oil.

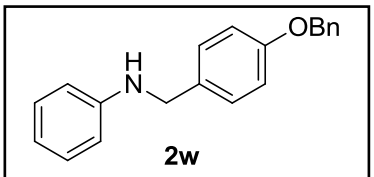
^{1}H NMR (500 MHz, $CDCl_3$): δ 7.22 – 7.15 (m, 2H), 6.71 (t, *J* = 7.3 Hz, 1H), 6.67 – 6.60 (m, 2H), 4.03 (bs, 1H), 2.96 (d, *J* = 6.9 Hz, 2H), 1.16 – 1.06 (m, 1H), 0.58 – 0.53 (m, 2H), 0.27 – 0.22 (m, 2H).

^{13}C NMR (126 MHz, $CDCl_3$): δ 148.6, 129.4, 117.4, 112.9, 49.2, 11.0, 3.58.

The spectroscopic data correspond to those reported in literature.[21]

N-(4-(benzyloxy)benzyl)aniline (2w)

According to the general procedure with *N*-(4-(benzyloxy)benzylidene)aniline (**1w**) (287 mg, 1.00 mmol, 1.00 eq.). Purification by column chromatography (silica gel, pentane/diethylether, 9:1).



2w
Chemical Formula: $C_{20}H_{19}NO$
Molecular Weight: 289.37

Yield: 97 % (968 µmol, 280 mg) white solid.

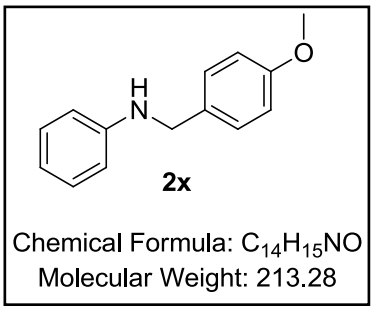
^{1}H NMR (500 MHz, $CDCl_3$): δ 7.50 – 7.45 (m, 2H), 7.45 – 7.39 (m, 2H), 7.39 – 7.30 (m, 3H), 7.25 – 7.18 (m, 2H), 7.02 – 6.96 (m, 2H), 6.76 (t, *J* = 7.3 Hz, 1H), 6.70-6.65 (m, 2H), 5.09 (s, 2H), 4.28 (s, 2H), 4.04 (bs, 1H).

^{13}C NMR (126 MHz, $CDCl_3$): δ 158.2, 148.2, 137.1, 131.8, 129.4, 129.0, 128.7, 128.1, 127.6, 117.7, 115.1, 113.0, 70.1, 47.9.

The spectroscopic data correspond to those reported in literature.[22]

N-(4-(methoxybenzyl)aniline (2x)

According to the general procedure with *N*-(4-(methoxybenzylidene)aniline (**1x**) (211 mg, 1.00 mmol, 1.00 eq.) and 0.6 mol% **[Mn-Br]H$_2$**. Purification by column chromatography (silica gel, pentane/diethylether, 9:1).



2x

Chemical Formula: $C_{14}H_{15}NO$
Molecular Weight: 213.28

Yield: 91 % (910 µmol, 194 mg) yellowish solid.

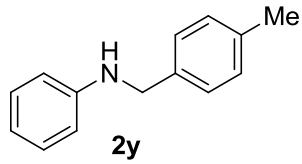
^{1}H NMR (500 MHz, $CDCl_3$): δ 7.30 (d, *J* = 8.6 Hz, 2H), 7.19 (t, *J* = 7.8 Hz, 2H), 6.89 (d, *J* = 8.5 Hz, 2H), 6.73 (t, *J* = 7.3 Hz, 1H), 6.66 (d, *J* = 7.7 Hz, 2H), 4.26 (s, 2H), 4.10 (bs, 1H), 3.81 (s, 3H).

^{13}C NMR (126 MHz, $CDCl_3$): δ 159.0, 148.2, 131.4, 129.4, 129.0, 117.7, 114.1, 113.1, 55.4, 48.0.

The spectroscopic data correspond to those reported in literature.[20]

N-(4-methylbenzyl)aniline (2y)

According to the general procedure with *N*-(4-methylbenzylidene)aniline (**1y**) (195 mg, 1.00 mmol, 1.00 eq.). Purification by column chromatography (silica gel, pentane/diethylether, 9:1).



2y

Chemical Formula: $C_{14}H_{15}N$
Molecular Weight: 197.28

Yield: 86 % (862 µmol, 170 mg) white solid.

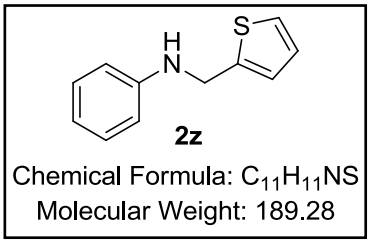
^{1}H NMR (300 MHz, $CDCl_3$): δ 7.33 – 7.26 (m, 2H), 7.26 – 7.14 (m, 4H), 6.81 – 6.71 (m, 1H), 6.71 – 6.62 (m, 2H), 4.29 (s, 2H), 3.98 (bs, 1H), 2.39 (s, 3H).

^{13}C NMR (75 MHz, $CDCl_3$): δ 148.3, 136.9, 136.4, 129.4, 129.3, 127.6, 117.5, 112.9, 48.1, 21.2.

The spectroscopic data correspond to those reported in literature.[20]

_N_-(thiophen-2-ylmethyl)aniline (2z)

According to the general procedure with _N_-(thiophen-2-ylmethylene)aniline (**1z**) (187 mg, 1.00 mmol, 1.00 eq.) and 0.6 mol% **[Mn-Br]H$_2$**. Purification by column chromatography (silica gel, pentane/diethylether, 9:1).



2z

Chemical Formula: $C_{11}H_{11}NS$
Molecular Weight: 189.28

Yield: 93 % (925 µmol, 175 mg) orange oil.

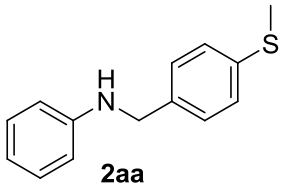
^{1}H NMR (500 MHz, $CDCl_3$): δ 7.26 – 7.19 (m, 3H), 7.07 – 7.02 (m, 1H), 7.02 – 6.98 (m, 1H), 6.82 – 6.75 (m, 1H), 6.71 (d, J = 7.8 Hz, 2H), 4.54 (s, 2H), 4.13 (s, 1H).

^{13}C NMR (126 MHz, $CDCl_3$) δ 147.7, 143.0, 129.4, 127.0, 125.2, 124.7, 118.2, 113.3, 43.6.

The spectroscopic data correspond to those reported in literature.[19]

_N_-(4-(methylthio)benzyl)aniline (2aa)

According to the general procedure with _N_-(4-(methylthio)benzylidene)aniline (**1aa**) (227 mg, 1.00 mmol, 1.00 eq.). Purification by column chromatography (silica gel, pentane/diethylether, 95:5).



2aa

Chemical Formula: $C_{14}H_{15}NS$
Molecular Weight: 229.34

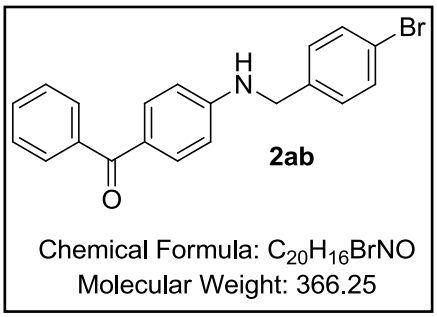
Yield: 97 % (972 µmol, 223 mg) yellow solid.

^{1}H NMR (500 MHz, $CDCl_3$): δ 7.30 (d, J = 8.2 Hz, 2H), 7.24 (d, J = 8.2 Hz, 2H), 7.18 (t, J = 7.9 Hz, 2H), 6.73 (t, J = 7.3 Hz, 1H), 6.64 (d, J = 8.0 Hz, 2H), 4.49 – 4.03 (m, 3H), 2.48 (s, 3H).

^{13}C NMR (126 MHz, $CDCl_3$): δ 148.0, 137.3, 136.4, 129.4, 128.2, 127.1, 117.9, 113.2, 48.1, 16.1.

The spectroscopic data correspond to those reported in literature.[20]

(4-((4-bromobenzyl)amino)phenyl)(phenyl)methanone (2ab)



According to the general procedure with (4-((4-bromobenzylidene)amino)phenyl)(phenyl)methanone (**1ab**) (364 mg, 1.00 mmol, 1.00 eq.). Purification by column chromatography (silica gel, pentane/diethylether, 6:4).

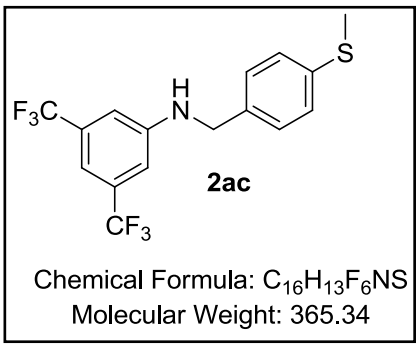
Yield: 93 % (926 µmol, 339 mg) white solid.

^{1}H NMR (500 MHz, CD_2Cl_2): δ 7.72 – 7.66 (m, 4H), 7.56 – 7.51 (m, 1H), 7.51 – 7.43 (m, 4H), 7.28 – 7.23 (m, 2H), 6.66 – 6.58 (m, 2H), 4.89 (t, *J* = 5.4 Hz, 1H), 4.39 (d, *J* = 5.8 Hz, 2H).

^{13}C NMR (126 MHz, CD_2Cl_2): δ 195.2, 152.2, 139.6, 138.3, 133.2, 132.3, 131.8, 129.9, 129.5, 128.6, 127.0, 121.5, 112.1, 47.3.

Elemental analysis – Anal. Calcd for $C_{20}H_{16}BrNO$: C, 65.59; H, 4.40; N, 3.82. Found: C, 65.54; H, 4.32; N, 3.71.

***N*-(4-(methylthio)benzyl)-3,5-bis(trifluoromethyl)aniline (2ac)**



According to the general procedure with *N*-(4-(methylthio)benzylidene)-3,5-bis(trifluoromethyl)aniline (**1ac**) (363 mg, 1.00 mmol, 1.00 eq.). Purification by column chromatography (silica gel, pentane/diethylether, 9:1).

Yield: 97 % (969 µmol, 354 mg) yellow solid.

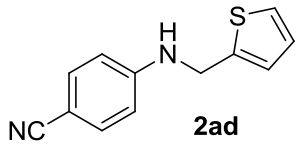
^{1}H NMR (500 MHz, CD_2Cl_2): δ 7.29 (d, *J* = 8.5 Hz, 2H), 7.27 – 7.23 (m, 2H), 7.17 (s, 1H), 7.00 (s, 2H), 4.64 (s, 1H), 4.35 (d, *J* = 5.6 Hz, 2H), 2.48 (s, 3H).

^{13}C NMR (126 MHz, CD_2Cl_2): δ 149.3, 138.7, 135.1, 132.7 (q, *J* = 32.6 Hz), 128.5, 127.2, 124.2 (q, *J* = 272.5 Hz), 112.66 – 112.42 (m), 110.8 – 110.5 (m), 47.9, 16.0.

Elemental analysis – Anal. Calcd for $C_{16}H_{13}F_6NS$: C, 52.60; H, 3.59; N, 3.83. Found: C, 52.95; H, 3.72; N, 3.81.

4-((thiophen-2-ylmethyl)amino)benzonitrile (2ad)

According to the general procedure with 4-((thiophen-2-ylmethylene)amino)benzonitrile (**1ad**) (212 mg, 1.00 mmol, 1.00 eq.). Purification by column chromatography (silica gel, pentane/diethylether, 8:2).



2ad

Chemical Formula: $C_{12}H_{10}N_2S$
Molecular Weight: 214.29

Yield: 96 % (961 µmol, 206 mg) yellow solid.

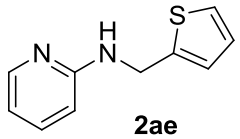
^{1}H NMR (500 MHz, $CDCl_3$): δ 7.44 – 7.39 (m, 2H), 7.24 (dd, *J* = 5.1, 1.1 Hz, 1H), 7.04 – 7.00 (m, 1H), 6.98 (dd, *J* = 5.0, 3.5 Hz, 1H), 6.66 – 6.60 (m, 2H), 4.84 (s, 1H), 4.55 (s, 2H).

^{13}C NMR (126 MHz, $CDCl_3$): δ 150.6, 141.1, 133.7, 127.1, 125.6, 125.1, 120.4, 112.7, 99.5, 42.6.

The spectroscopic data correspond to those reported in literature.[23]

***N*-(thiophen-2-ylmethyl)pyridin-2-amine (2ae)**

According to the general procedure with *N*-(thiophen-2-ylmethylene)pyridin-2-amine (**1ae**) (188 mg, 1.00 mmol, 1.00 eq.). Purification by column chromatography (silica gel, pentane/diethylether, 7:3).



2ae

Chemical Formula: $C_{10}H_{10}N_2S$
Molecular Weight: 190.26

Yield: 73 % (731 µmol, 139 mg) white-yellowish solid.

^{1}H NMR (500 MHz, $CDCl_3$): δ 8.12 (d, *J* = 4.8 Hz, 1H), 7.47 – 7.37 (m, 1H), 7.20 (dd, *J* = 5.1, 1.1 Hz, 1H), 7.03 – 6.99 (m, 1H), 6.96 (dd, *J* = 5.0, 3.5 Hz, 1H), 6.62 (dd, *J* = 6.7, 5.5 Hz, 1H), 6.43 (d, *J* = 8.4 Hz, 1H), 4.94 (bs, 1H), 4.70 (d, *J* = 5.8 Hz, 2H).

^{13}C NMR (126 MHz, $CDCl_3$): δ 158.2, 148.2, 142.7, 137.6, 126.9, 125.3, 124.8, 113.6, 107.5, 41.4.

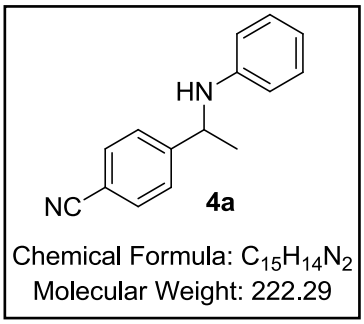
The spectroscopic data correspond to those reported in literature.[10]

2.2.2. Ketimine Reduction

General procedure for ketimine reduction: Under nitrogen atmosphere in a glove box screw-vials were charged with magnetic stir bars, KO^{t}Bu (5 eq. with respect to **[Mn-Br]H$_2$**),

[Mn-Br]H$_2$, ketimine (**3**) (1.00 mmol, 1.00 eq.), and thf (2 mL). The vials were placed in an autoclave, which was sealed and purged three times with hydrogen, before adjusting the pressure to 20 bar. The reactions were heated to 50 °C and stirred for 18 h. After the reaction, the hydrogen was released, 1 mL H_2O and 7 mL Et_2O were added to each vial, and the mixtures were homogenized. Subsequently, the liquid phase was dried with Na_2SO_4, filtered, washed with Et_2O or CH_2Cl_2 and the solvent was removed under reduced pressure. The product was isolated by column chromatography.

4-(1-(phenylamino)ethyl)benzonitrile (4a)



According to the general procedure with 4-(1-(phenylimino)ethyl)benzonitrile (**3a**) (220 mg, 1.00 mmol, 1.00 eq.) and 3 mol% **[Mn-Br]H$_2$**. Purification by column chromatography (silica gel, pentane/diethylether, 8:2).

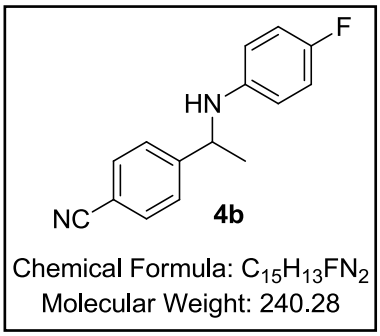
Yield: 73 % (729 µmol, 162 mg) white solid.

^{1}H NMR (500 MHz, $CDCl_3$): δ 7.61 (d, *J* = 8.3 Hz, 2H), 7.50 (d, *J* = 8.2 Hz, 2H), 7.16 – 7.06 (m, 2H), 6.70 (t, *J* = 7.3 Hz, 1H), 6.46 (d, *J* = 7.8 Hz, 2H), 4.52 (q, *J* = 6.8 Hz, 1H), 4.24 (bs, 1H), 1.53 (d, *J* = 6.8 Hz, 3H).

^{13}C NMR (126 MHz, $CDCl_3$): δ 151.1, 146.5, 132.7, 129.3, 126.8, 119.1, 118.1, 113.5, 110.8, 53.6, 25.0.

The spectroscopic data correspond to those reported in literature.[24]

4-(1-((4-fluorophenyl)amino)ethyl)benzonitrile (4b)



According to the general procedure with 4-(1-((4-fluorophenyl)imino)ethyl)benzonitrile (**3b**) (238 mg, 1.00 mmol, 1.00 eq.) and 3 mol% **[Mn-Br]H$_2$**. Purification by column chromatography (silica gel, pentane/diethylether, 8:2).

Yield: 71 % (712 µmol, 171 mg) white solid.

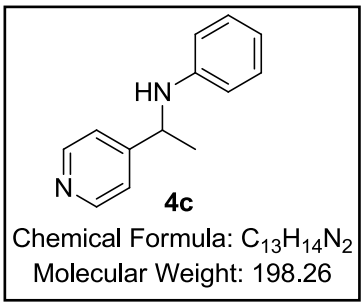
^{1}H NMR (500 MHz, $CDCl_3$): δ 7.61 (d, *J* = 8.3 Hz, 2H), 7.47 (d, *J* = 8.2 Hz, 2H), 6.84 – 6.75 (m, 2H), 6.42 – 6.32 (m, 2H), 4.45 (q, *J* = 6.8 Hz, 1H), 4.07 (bs, 1H), 1.51 (d, *J* = 6.8 Hz, 3H).

^{13}C NMR (126 MHz, $CDCl_3$): δ 157.0, 155.1, 150.9, 142.9, 132.8, 126.8, 119.0, 115.9, 115.7, 114.3, 114.2, 111.0, 54.2, 25.0.

The spectroscopic data correspond to those reported in literature.[25]

N-(1-(pyridin-4-yl)ethyl)aniline (4c)

According to the general procedure with *N*-(1-(pyridin-4-yl)ethylidene)aniline (**3c**) (196 mg, 1.00 mmol, 1.00 eq.) and 3 mol% **[Mn-Br]H$_2$**. Purification by column chromatography (silica gel, diethylether).



4c
Chemical Formula: $C_{13}H_{14}N_2$
Molecular Weight: 198.26

Yield: 79 % (787 µmol, 156 mg) white solid.

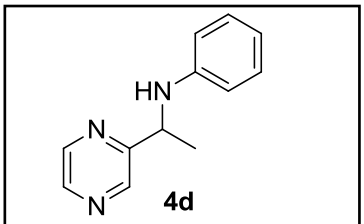
^{1}H NMR (500 MHz, $CDCl_3$): δ 8.55 (s, 2H), 7.31 (s, 2H), 7.10 (t, *J* = 7.9 Hz, 2H), 6.68 (t, *J* = 7.3 Hz, 1H), 6.46 (d, *J* = 7.9 Hz, 2H), 4.46 (q, *J* = 6.5 Hz, 1H), 4.08 (s, 1H), 1.52 (d, *J* = 6.8 Hz, 3H).

^{13}C NMR (126 MHz, $CDCl_3$): δ 154.6, 150.2, 146.7, 129.3, 121.3, 117.9, 113.3, 52.8, 24.6.

Elemental analysis – Anal. Calcd for $C_{13}H_{14}N_2$: C, 78.75; H, 7.12; N, 14.13. Found: C, 78.88; H, 6.83; N, 14.03.

N-(1-(pyrazin-2-yl)ethyl)aniline (4d)

According to the general procedure with *N*-(1-(pyrazin-2-yl)ethylidene)aniline (**3d**) (197 mg, 1.00 mmol, 1.00 eq.) and 1 mol% **[Mn-Br]H$_2$**. Purification by column chromatography (silica gel, pentane/diethylether, 4:6).



4d
Chemical Formula: $C_{12}H_{13}N_3$
Molecular Weight: 199.25

Yield: 85 % (853 µmol, 170 mg) brownish solid.

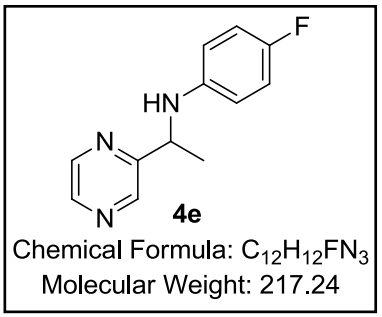
^{1}H NMR (500 MHz, $CDCl_3$): δ 8.66 (s, 1H), 8.53 (s, 1H), 8.48 – 8.43 (m, 1H), 7.13 (t, *J* = 7.8 Hz, 2H), 6.70 (t, *J* = 7.3 Hz, 1H), 6.58 (d, *J* = 8.0 Hz, 2H), 5.00 – 4.01 (bs, 1H), 4.70 (q, *J* = 6.8 Hz, 1H), 1.59 (d, *J* = 6.8 Hz, 3H).

^{13}C NMR (126 MHz, $CDCl_3$): δ 159.1, 146.5, 144.2, 143.4, 143.2, 129.4, 118.3, 113.8, 53.1, 22.9.

Elemental analysis – Anal. Calcd for $C_{12}H_{13}N_3$: C, 72.33; H, 6.58; N, 21.09. Found: C, 72.35; H, 6.44; N, 20.96.

4-fluoro-*N*-(1-(pyrazin-2-yl)ethyl)aniline (4e)

According to the general procedure with 4-fluoro-*N*-(1-(pyrazin-2-yl)ethylidene)aniline (**3e**) (215 mg, 1.00 mmol, 1.00 eq.) and 2 mol% **[Mn-Br]H$_2$**. Purification by column chromatography (silica gel, pentane/diethylether, 1:2).



4e
Chemical Formula: $C_{12}H_{12}FN_3$
Molecular Weight: 217.24

Yield: 81 % (806 µmol, 175 mg) orange oil.

^{1}H NMR (500 MHz, $CDCl_3$): δ 8.62 (s, 1H), 8.52 (s, 1H), 8.48 – 8.42 (m, 1H), 6.86 – 6.79 (m, 2H), 6.53 – 6.46 (m, 2H), 4.67 – 4.56 (m, 1H), 4.29 (s, 1H), 1.56 (d, *J* = 6.8 Hz, 3H).

^{13}C NMR (126 MHz, $CDCl_3$): δ 159.1, 157.1, 155.2, 144.2, 143.5, 143.1, 143.1, 143.1, 116.0, 115.8, 114.6, 114.5, 53.6, 23.0.

Elemental analysis – Anal. Calcd for $C_{12}H_{12}FN_3$: C, 66.34; H, 5.57; N, 19.34. Found: C, 65.96; H, 5.43; N, 19.49.

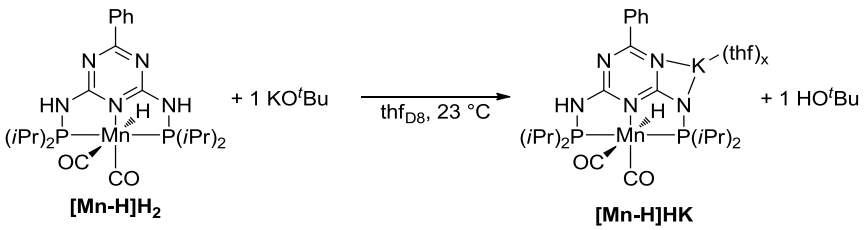
3 Mechanistic Investigations

3.1 Reaction Intermediates

3.1.1. Activation of the Manganese Complexes

[Mn-H]H$_2$ with 1 eq. KO^{t}Bu

[Mn-H]H$_2$ (20 µmol, 1.0 eq.) and KO^{t}Bu (20 µmol, 1.0 eq.) were stirred in thf$_{D8}$ (500 µL) for 1 minute. The red mixture immediately turned dark red and was transferred to an NMR tube.



[Mn-H]H$_2$ **[Mn-H]HK**

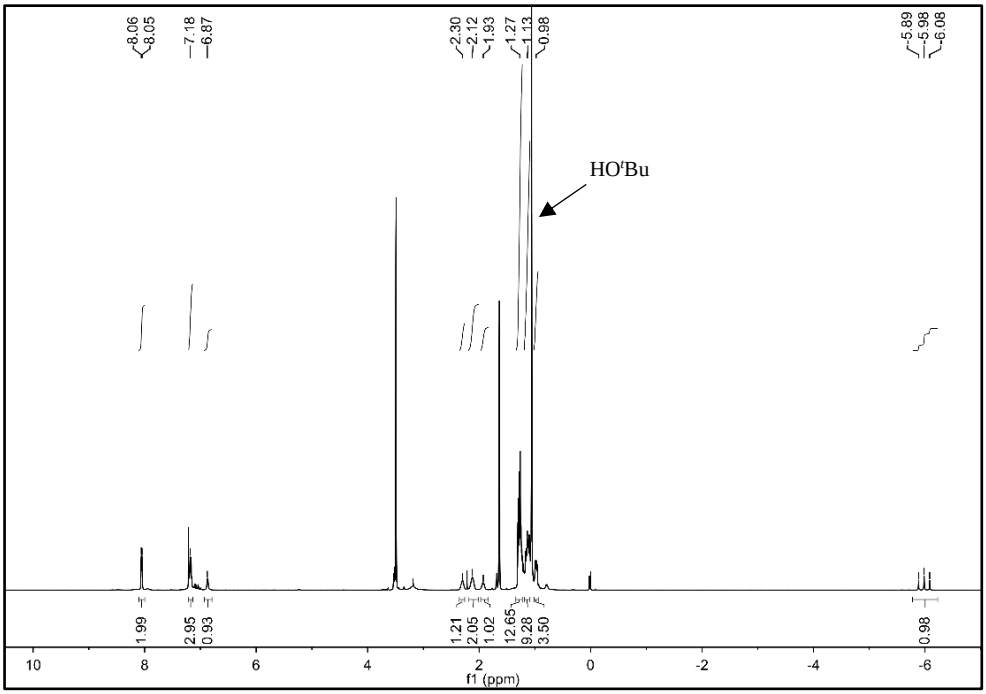


Figure S 1. ^{1}H NMR spectrum of the reaction of complex **[Mn-H]H$_2$** and 1 eq. KO^{t}Bu in thf$_{D8}$.

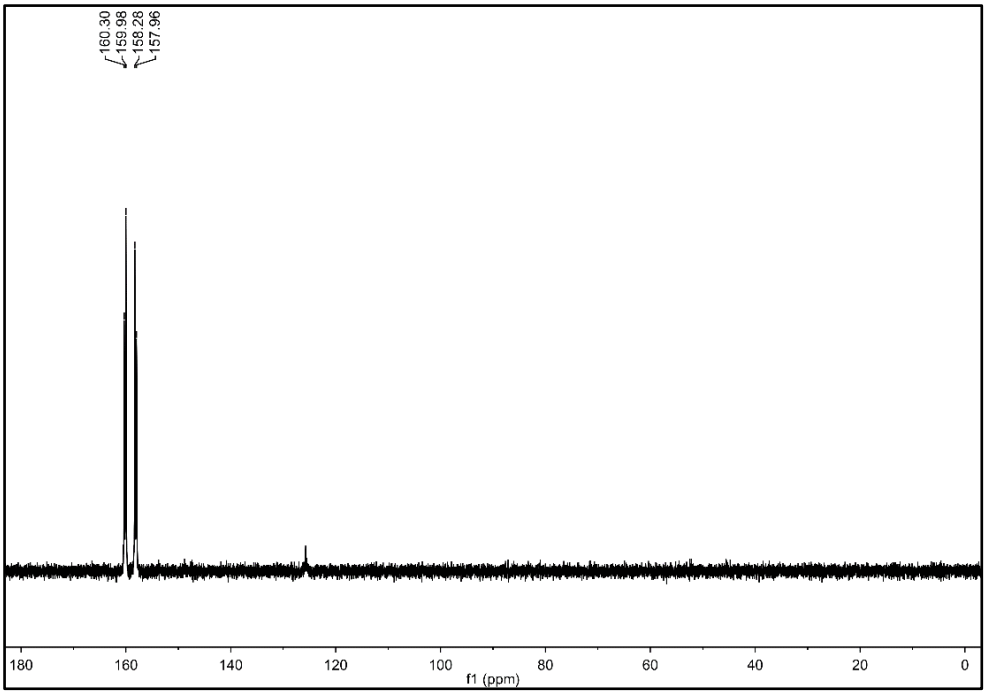


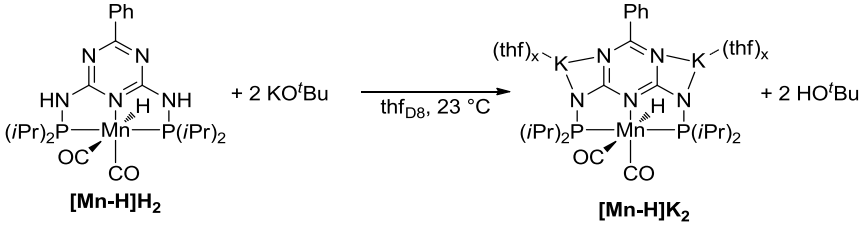
Figure S 2. ^{31}P NMR spectrum of the reaction of complex **[Mn-H]H$_2$** and 1 eq. KO^{t}Bu in thf$_{D8}$.

^{1}H NMR (500 MHz, thf$_{D8}$): δ 8.05 (d, *J* = 7.1 Hz, 2H), 7.18 (m, 3H), 6.87 (s, 1H), 2.30 (m, 1H), 2.12 (m, 2H), 1.93 (m, 1H), 1.27 (m, 12H), 1.13 (m, 9H), 0.98 (m, 3H), -5.98 (t, *J* = 49.5 Hz, 1H). ^{31}P NMR (202 MHz, thf$_{D8}$): δ 160.14 (d, *J* = 65.3 Hz), 158.12 (d, *J* = 64.6 Hz).

Only one NH (^{1}H NMR: 6.87 ppm) proton is left and both phosphorus atoms (^{31}P NMR: 160.3–158.0 ppm) and the adjacent isopropyl groups (^{1}H NMR: three signals of C*H*: 2.30–1.93 ppm) are magnetically not equivalent, consistent with the proposed structure for **[Mn-H]HK** (^{1}H, ^{31}P NMR: Figure S 1 and Figure S 2). Furthermore, it can be concluded that the reaction of **[Mn-H]H$_2$** with KO^{t}Bu is a quantitative and fast reaction.

[Mn-H]H$_2$ with 2 eq. KO^{t}Bu

[Mn-H]H$_2$ (20 µmol, 1.0 eq.) and KO^{t}Bu (40 µmol, 2.0 eq.) were stirred in thf$_{D8}$ (500 µL) for 1 minute. The red mixture immediately turned dark red and was transferred to an NMR tube.



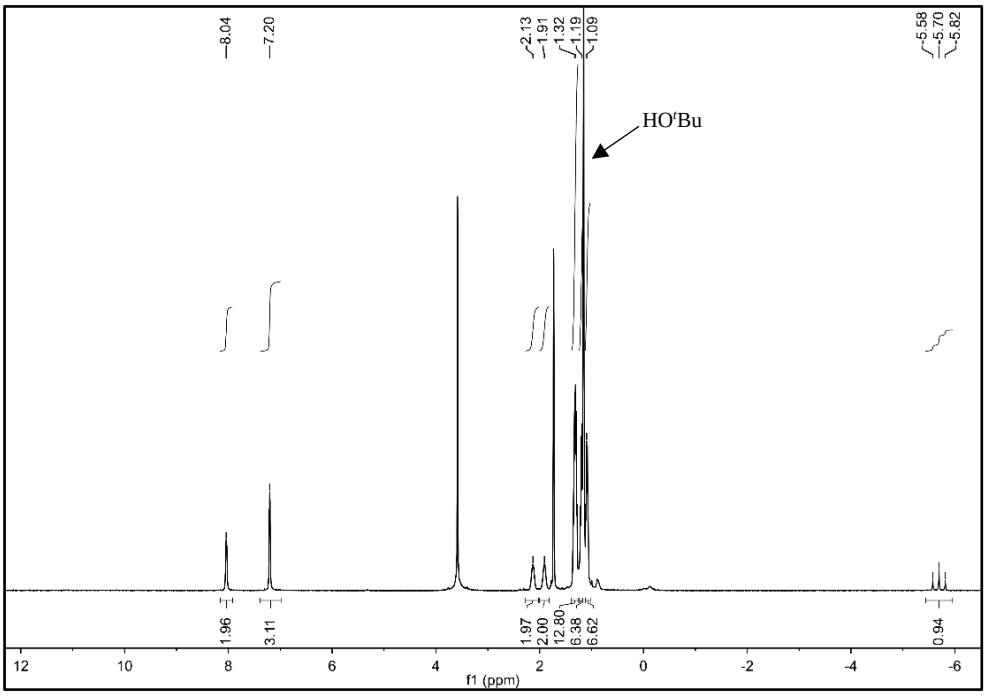


Figure S 3. ^{1}H NMR spectrum of the reaction of **[Mn-H]H$_2$** and 2 eq. KO^{t}Bu in thf$_{D8}$.

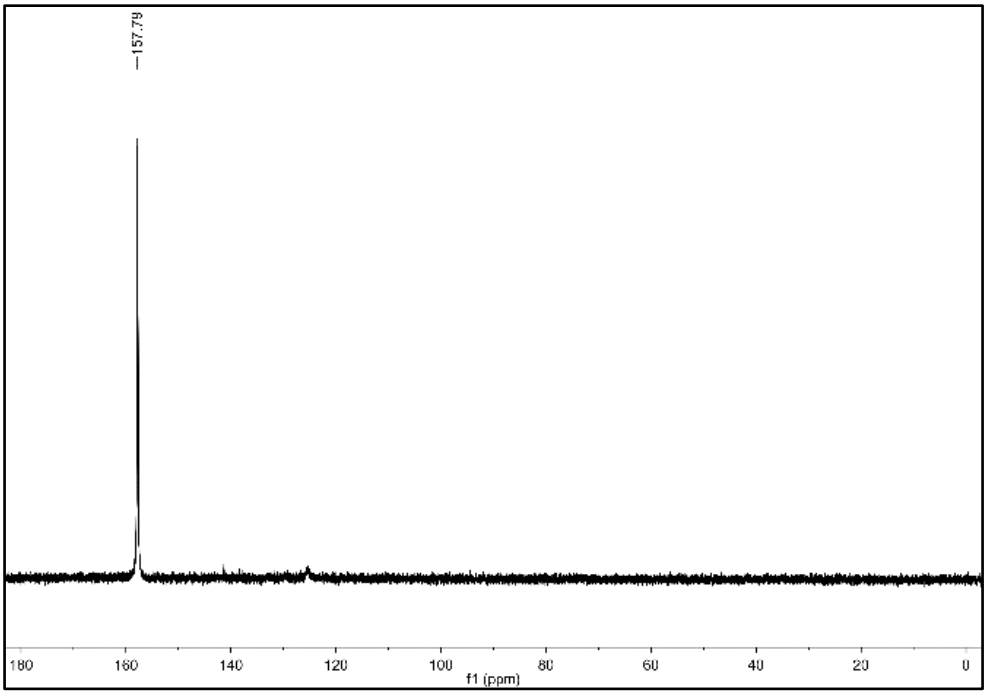


Figure S 4. ^{31}P NMR spectrum of the reaction of **[Mn-H]H$_2$** and 2 eq. KO^{t}Bu in thf$_{D8}$.

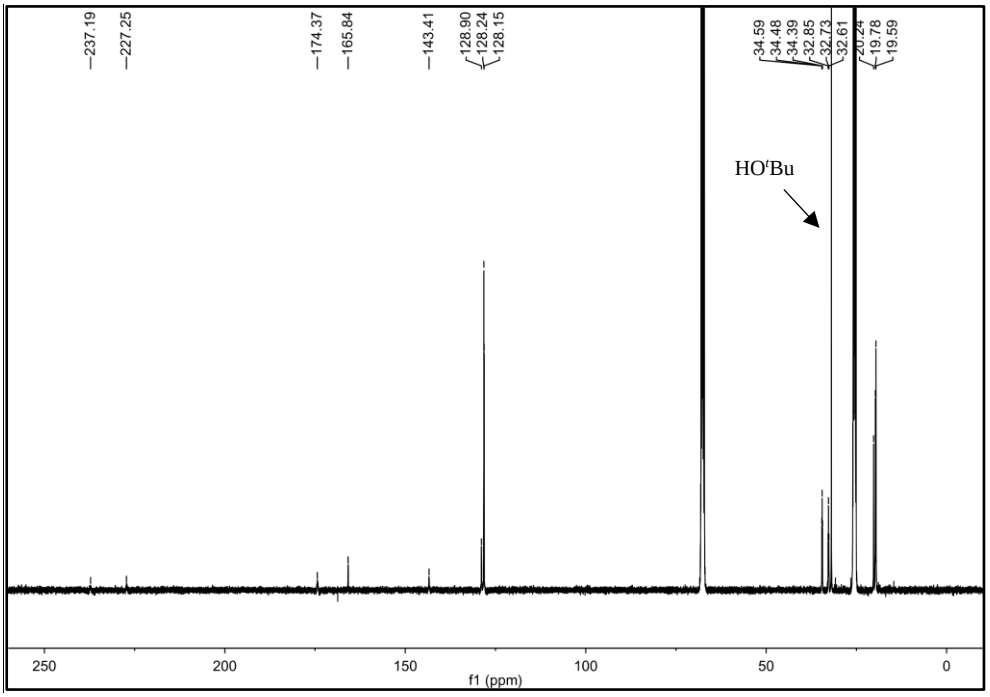


Figure S 5. ^{13}C NMR spectrum of the reaction of **[Mn-H]H$_2$** and 2 eq. KO^{t}Bu in thf$_{D8}$.

^{1}H NMR (400 MHz, thf$_{D8}$): δ 8.04 (m, 2H), 7.20 (m, 3H), 2.13 (m, 2H), 1.91 (m, 2H), 1.32 (m, 12H), 1.19 (m, 6H), 1.09 (m, 6H), -5.70 (t, *J* = 48.0 Hz, 1H). ^{13}C NMR (101 MHz, thf$_{D8}$): δ 237.2 (m), 227.3(m), 174.4, 165.9, 143.4, 128.9, 128.2, 128.2, 34.5 (t, *J* = 10.1), 32.7 (t, *J* = 12.4 Hz), 20.2, 19.8, 19.6 (m). ^{31}P NMR (202 MHz, thf$_{D8}$): δ 157.8 (s).

It can be stated from the ^{1}H and ^{31}P NMR spectra (Figure S 3 and Figure S 4), that no NH proton is left and that both phosphorus atoms (^{31}P NMR: 157.8 ppm) and the adjacent isopropyl groups (^{1}H NMR: two signals of C*H*: 2.13, 1.91 ppm) are magnetically equivalent, consistent with the proposed structure of **[Mn-H]K$_2$**. Furthermore, it can be concluded that the reaction of **[Mn-H]H$_2$** with 2 eq. KO^{t}Bu is also a quantitative and fast reaction.

[Mn-H]H$_2$ with 10 eq. KO^{t}Bu

[Mn-H]H$_2$ (20 µmol, 1.0 eq.) and KO^{t}Bu (200 µmol, 10.0 eq.) were stirred in thf$_{D8}$ (500 µL) for 1 minute. The red mixture immediately turned dark red and was transferred to an NMR tube.

No further deprotonation takes place (^{1}H: Figure S 6, ^{31}P: Figure S 7) in comparison to **[Mn-H]K$_2$**.

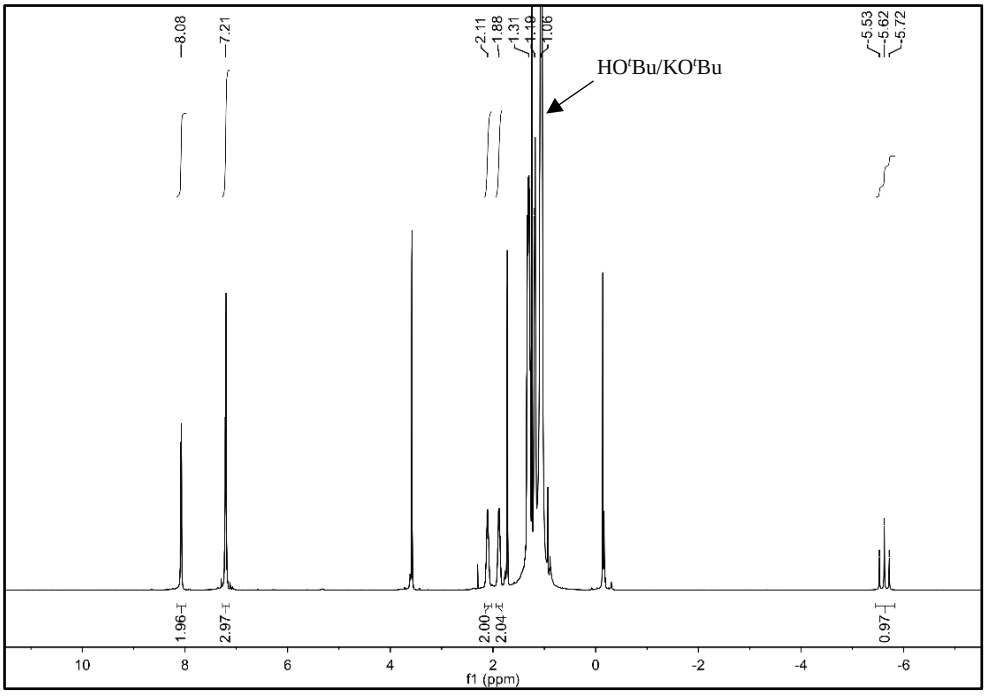


Figure S 6. ^{1}H NMR spectrum of the reaction of complex **[Mn-H]H$_2$** and 10 eq. KO^{t}Bu in thf$_{D8}$.

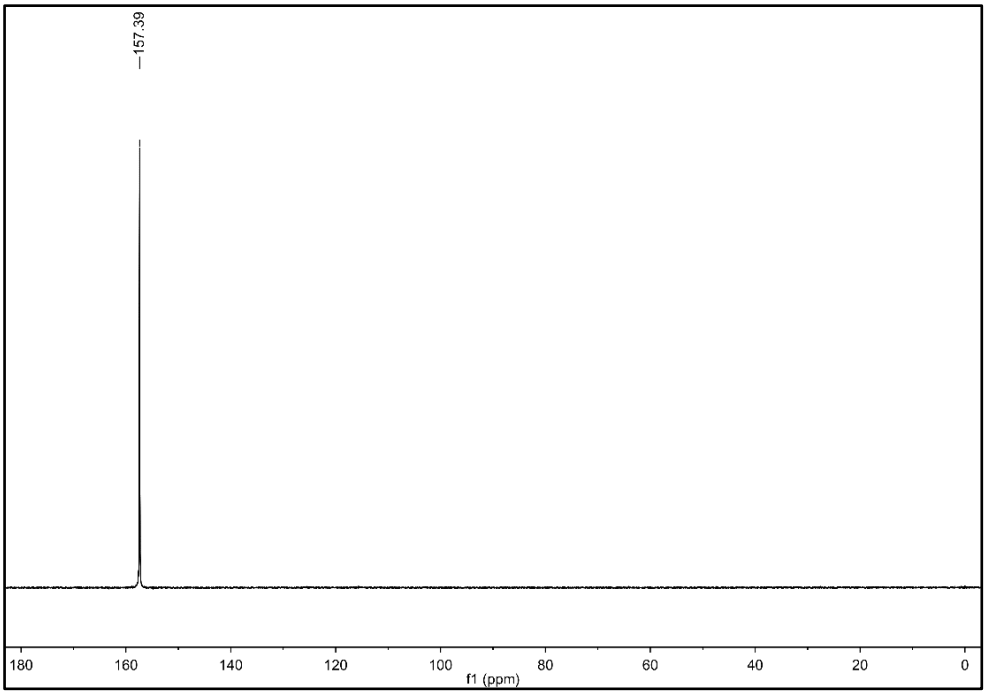


Figure S 7. ^{31}P NMR spectrum of the reaction of complex **[Mn-H]H$_2$** and 10 eq. KO^{t}Bu in thf$_{D8}$.

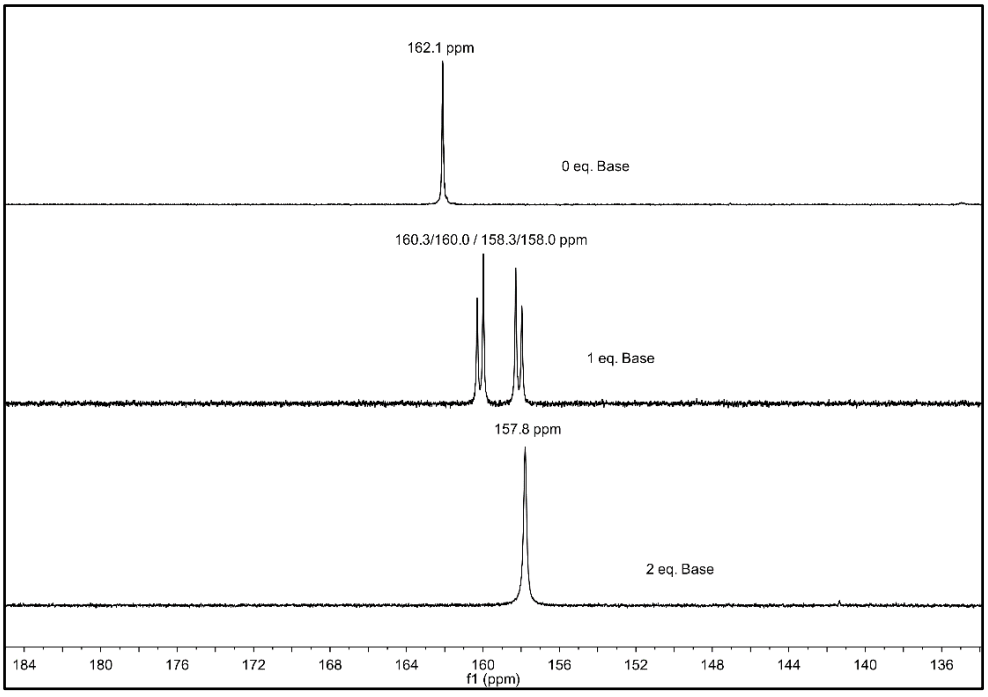
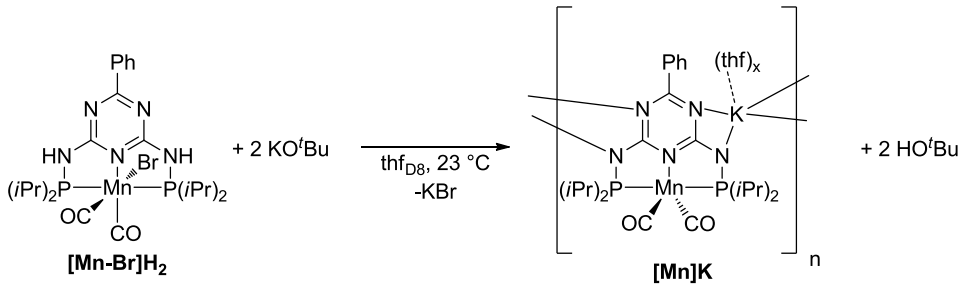


Figure S 8. Comparison of ^{31}P NMR spectra for the reactions of **[Mn-H]H$_2$** with 0, 1 and 2 eq. of KO^{t}Bu.

[Mn-Br]H$_2$ with 2 eq. KO^{t}Bu

[Mn-Br]H$_2$ (20 µmol, 1.0 eq.) and KO^{t}Bu (40 µmol, 2.0 eq.) were stirred in thf$_{D8}$ (500 µL) for 1 minute. The yellow mixture immediately turned dark green and was transferred to an NMR tube.



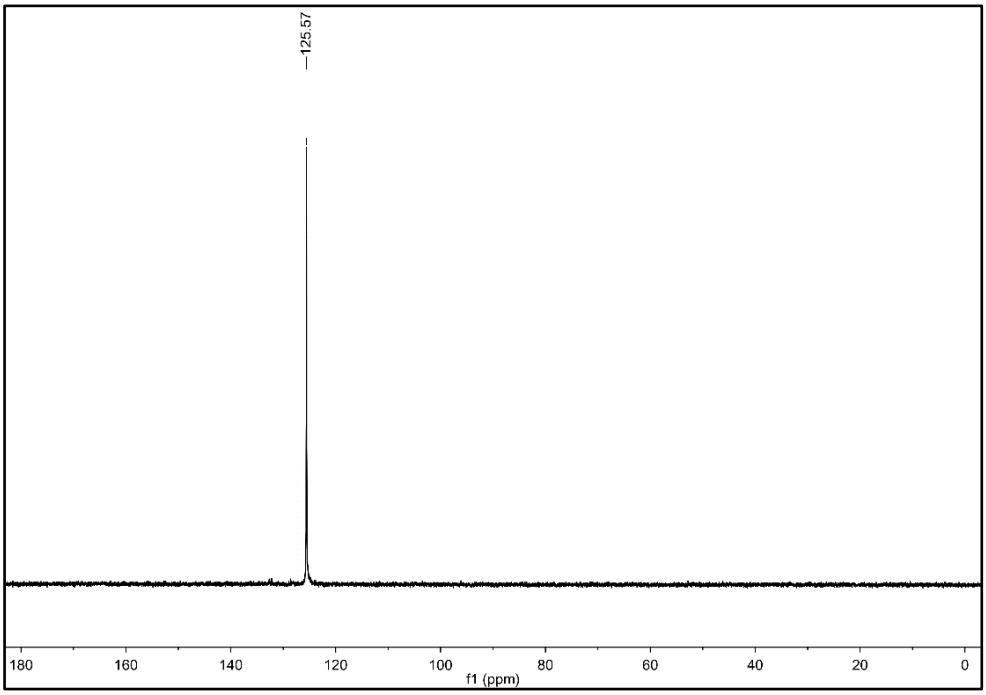


Figure S 9. ^{31}P NMR spectrum of the reaction of complex **[Mn-Br]H$_2$** with 2 eq. KO^{t}Bu in thf$_{D8}$.

Considering that complex **[Mn]K** is a coordination polymer, it precipitates quickly. Obtaining an analyzable ^{1}H NMR spectrum is not easily possible in thf.

Therefore, complex **[Mn]K** was synthesized by mixing complex **[Mn-Br]H$_2$** (305 mg, 500 µmol, 1.0 eq.) and KO^{t}Bu (118 mg, 1.05 mmol, 2.1 eq.) in 2 mL thf, which was let to precipitate over night. The solvent was filtered off, the residue was washed with thf twice to remove remaining KO^{t}Bu and HO^{t}Bu and the remaining solvent was removed in vacuum to obtain a green powder. A few mg of the powder were dissolved in DMSO$_{D6}$ to measure ^{1}H and ^{31}P NMR.

In the ^{1}H NMR spectrum (Figure S 10) no NH proton signal is present and the CH-proton signals of the isopropyl groups are magnetically equivalent resulting in only one peak at 2.21 ppm. In the ^{31}P NMR spectrum (Figure S 11) there is also only one peak, consistent with the spectrum in thf_{D8} (Figure S 9), indicating the magnetic equivalence of the two phosphorus atoms. The results support the postulated structure of **[Mn]K**.

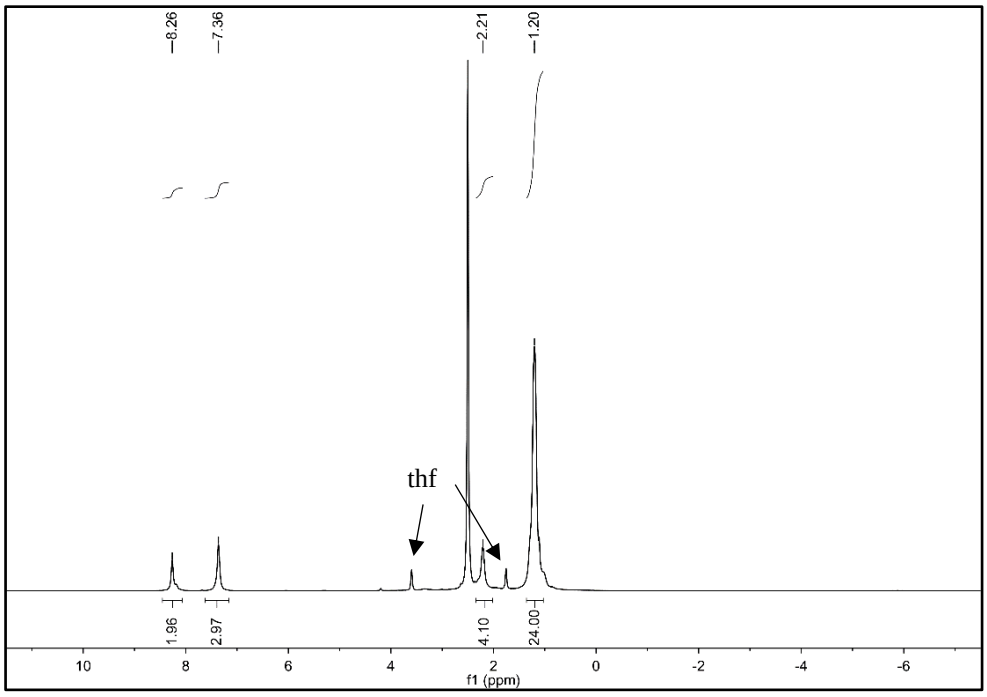


Figure S 10. ^{1}H NMR spectrum of **[Mn]K** in $DMSO_{D6}$.

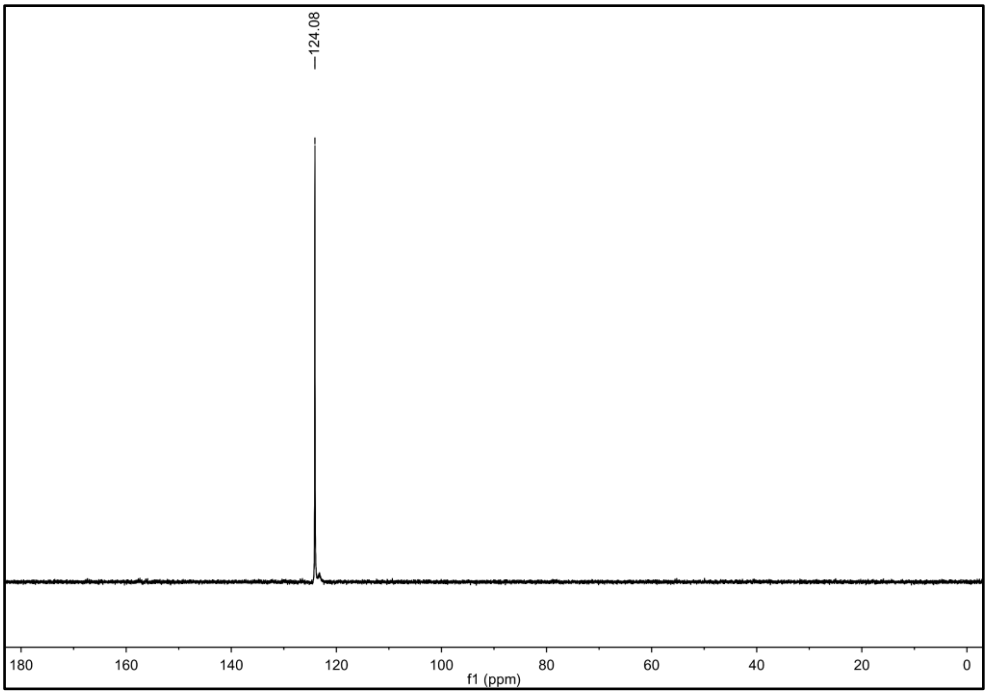


Figure S 11. ^{31}P NMR spectrum of **[Mn]K** in $DMSO_{D6}$.

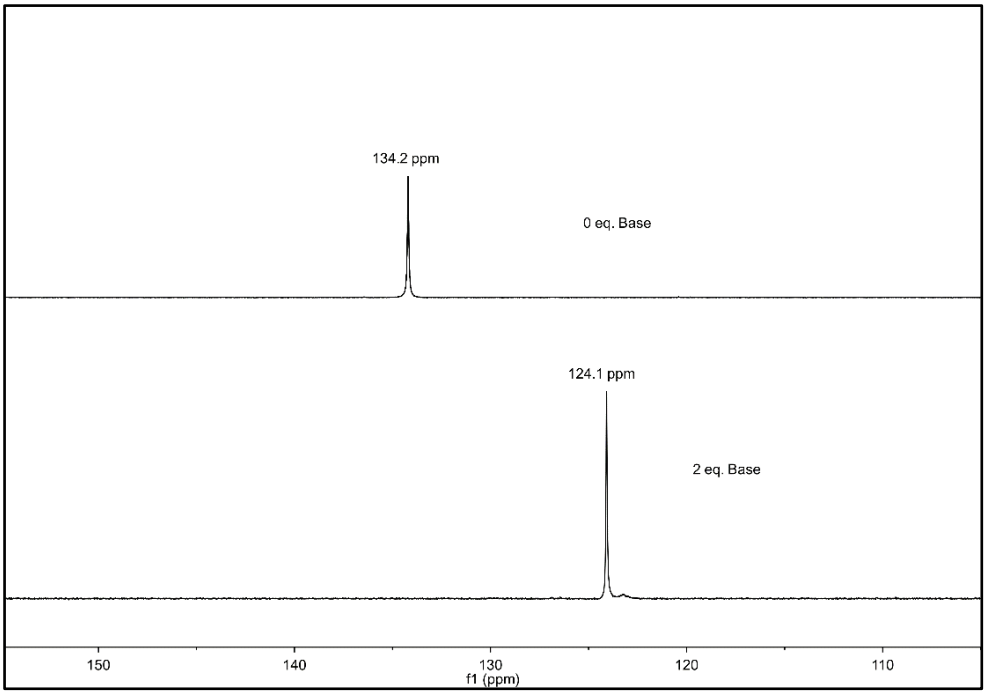


Figure S 12. Comparison of ^{31}P NMR spectra of complex **[Mn-Br]H$_2$** with and without KO^{t}Bu measured in $DMSO_{D6}$.

^{1}H NMR (500 MHz, $DMSO_{D6}$): δ 8.45 – 8.07 (m, 2H), 7.36 (s, 3H), 2.21 (bs, 4H), 1.36 – 1.03 (m, 24H). ^{31}P NMR (202 MHz, $DMSO_{D6}$): δ 124.1 (s).

3.1.2. Syntheses of [Mn]K, [Mn-H]HK and [Mn-H]K_2

3.1.2.1. [Mn]K

[Mn-H]H_2 (95.0 mg, 179 µmol, 1.0 eq.) and imine **1a** (48.6 mg, 268 µmol, 1.5 eq.) were dissolved in thf (210µL) and KO^{t}Bu (0.2 M in thf; 1.79 mL, 358 µmol, 2.0 eq.) was added dropwise while stirring. The dark red mixture was heated to 50 °C over night. After that, the flask was cooled down to -24 °C for 10 h, the solvent was subsequently filtered off and the solid was washed three times with 5 mL of thf. The powder was dried under vacuum and the product was obtained as a dark green powder.

Yield: 41 % (74.0 µmol, 42.0 mg) dark green powder.

^{1}H NMR (400 MHz, DMSO): δ 8.27 (s, 2H), 7.37 (s, 3H), 2.20 (bs, 4H), 1.41 – 1.07 (m, 24H). ^{31}P NMR (202 MHz, DMSO): δ 123.9. ^{13}C NMR (101 MHz, DMSO): δ 235.2, 176.2, 168.7, 140.0, 129.4, 127.8, 127.3, 27.6 (t, *J* = 12.6 Hz), 18.6, 18.5, 17.9, 17.7. Melting point: 287 °C (Decomposition). Elemental analysis – Anal. Calcd for $C_{23}H_{33}KMnN_5O_2P_2$: C, 48.68; H, 5.86; N, 12.34. Found: C, 47.40; H, 6.00; N, 11.82.

3.1.2.2. [Mn-H]HK

[Mn-H]H_2 (53.1 mg, 100 µmol, 1.0 eq.) was dissolved in 4 mL thf and KH (4.01 mg, 100 µmol, 1.0 eq.) was added. The mixture was stirred for 10 minutes at room temperature and the solvent was subsequently removed under vacuum while keeping the temperature below 0 °C. The product was obtained as a glassy solid, which was scratched with a spatula to yield an orange powder and was further dried under vacuum.

Yield: 62 % (61.5 µmol, 35 mg)

^{1}H NMR (400 MHz, thf_{D8}): δ 8.14 (d, *J* = 6.9 Hz, 2H), 7.39 – 7.20 (m, 3H), 6.95 (s, 1H), 2.38 (s, 1H), 2.21 (s, 2H), 2.02 (s, 1H), 1.43 – 1.30 (m, 12H), 1.29 – 1.13 (m, 9H), 1.12 – 1.02 (m, 3H), -5.90 (t, *J* = 49.6 Hz, 1H). ^{31}P NMR (202 MHz, thf_{D8}): δ 160.2 (d, *J* = 65.0 Hz), 158.2 (d, *J* = 66.9 Hz). ^{13}C NMR (126 MHz, thf_{D8}): δ 234.6, 225.2, 174.1, 169.9, 167.2, 140.6, 130.5, 128.6, 128.5, 34.1 (m), 32.6 (m), 19.7 (m), 19.2. Melting Point: 95 °C (Decomposition). Elemental analysis – Anal. Calcd for $C_{23}H_{35}KMnN_5O_2P_2$: C, 48.50; H, 6.19; N, 12.30. Found: C, 48.36; H, 6.85; N, 11.86.

3.1.2.3. [Mn-H]K_2

[Mn-H]H_2 (53.1 mg, 100 µmol, 1.0 eq.) was dissolved in 4 mL thf and KH (8.02 mg, 200 µmol, 2.0 eq.) was added. The mixture was stirred for 30 minutes at room temperature and the solvent was subsequently removed under vacuum while keeping the temperature below 0 °C. The product was obtained as a glassy solid, which was scratched with a spatula to yield an orange powder and was further dried under vacuum.

Yield: 54 % (54.4 µmol, 37 mg)

^{1}H NMR (500 MHz, thf_{D8}): δ 8.26 – 7.75 (m, 2H), 7.40 – 7.00 (m, 3H), 2.24 – 2.04 (m, 2H), 1.95 – 1.84 (m, 2H), 1.36 – 1.27 (m, 12H), 1.25 – 1.14 (m, 6H), 1.14 – 1.02 (m, 6H), -5.71 (t, *J* = 48.1 Hz, 1H). ^{31}P NMR (202 MHz, thf_{D8}): δ 157.8 (s). ^{13}C NMR (126 MHz, thf_{D8}): δ 237.3, 227.3, 174.5, 165.7, 143.6, 128.8, 128.2, 128.1, 34.5 (t, *J* = 10.1 Hz), 32.8 (t, *J* = 12.1 Hz), 20.2, 19.8, 19.6, 19.6 (m).Melting Point: 142 °C (Decomposition). Elemental analysis – Anal. Calcd for $C_{23}H_{34}K_2MnN_5O_2P_2$ (+thf): C, 47.71; H, 6.23; N, 10.30. Found: C, 46.37; H, 6.18; N, 10.43.

3.1.3. Crystals for X-Ray Crystal Analysis

[Mn-Br]H_2 (50 mg, 81.9 µmol, 1.0 eq.) was dissolved in 4 mL thf and KO^{t}Bu (164 mM; 1.00 mL, 164 µmol, 2.0 eq.) was added dropwise while stirring. The solution immediately turned from yellow to dark green. The crystals were collected in a glove box after several days.

The same crystals were obtained by NMR experiments like shown in Table S 14.

Both crystal fractions showed the same structure obtained by X-ray crystallography.

3.1.4. Investigation of a Hypothetical Amide Complex

K•**2a** (produced with KH and **2a** in thf over night with subsequent removal of the solvent under vacuum) (23.2 mg, 105 µmol, 3.0 eq.) and **[Mn-Br]H_2** (21.4 mg, 35 µmol, 1.0 eq.) were dissolved in thf_{D8} while stirring. The solution turned dark red and was subsequently transferred to an NMR tube.

A C*H* signal of the imine (8.50 ppm) and the hydride signal (-5.61 ppm) appear in the ^{1}H NMR spectrum (Figure S 13). The ^{31}P NMR spectrum (Figure S 14) shows that as a main product **[Mn-H]K_2** was produced according to the shift of the signal at 157 ppm. There is no evidence of an amide complex in a reasonable amount.

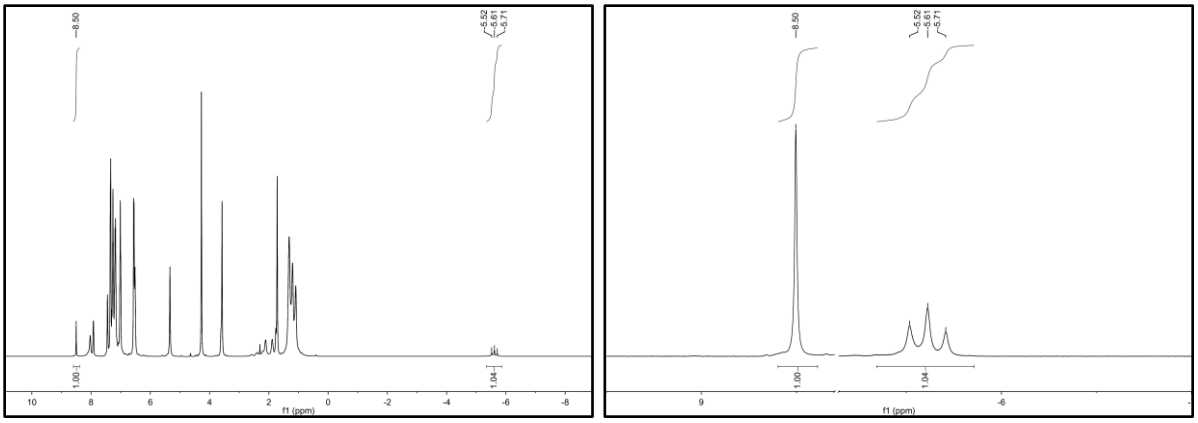


Figure S 13. ^{1}H NMR spectrum of the reaction of K•**2a** with complex **[Mn-Br]H$_2$**.

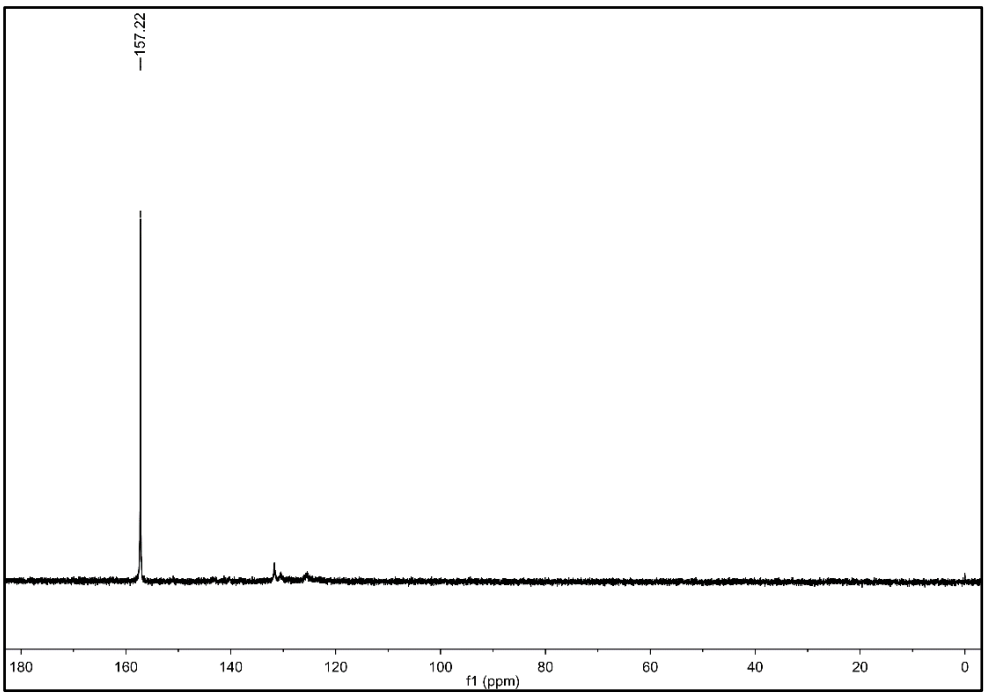


Figure S 14. ^{31}P NMR spectrum of the reaction of K•**2a** with complex **[Mn-Br]H$_2$**.

In another experiment the activated complex **[Mn]K** (preparation as shown in 3.1.1) (30 mg, 43.6 µmol, 1.0 eq.; calculated as 1:1 mixture with KBr) was mixed with K•**2a** (46.4 mg, 219 µmol, 5.0 eq.) in thf$_{D8}$. The mixture turned dark red and was transferred to an NMR tube after 5 minutes of stirring. The observations (Figure S 15) are the same as for the experiment with the bromide complex **[Mn-Br]H$_2$** above (Figure S 14).

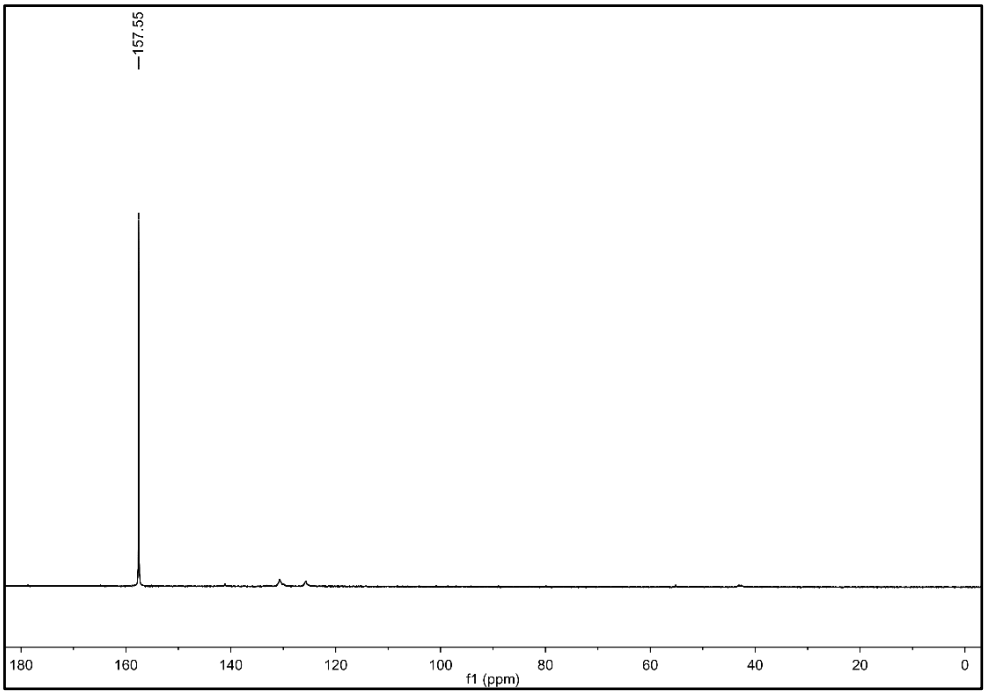


Figure S 15. ^{31}P NMR spectrum of the mixture of complex **[Mn]K** and K•**2a** in thf_{D8}.

3.1.5. Time-dependent Stability of [Mn-H]H_2 and [Mn-H]K_2

Stability of [Mn-H]H_2

A stock solution of **[Mn-H]H_2** in thf_{D8} (0.15 M) was stored at room temperature for 3 months and was measured subsequently via NMR (Figure S 16 and Figure S 17). No degradation of the complex is observable.

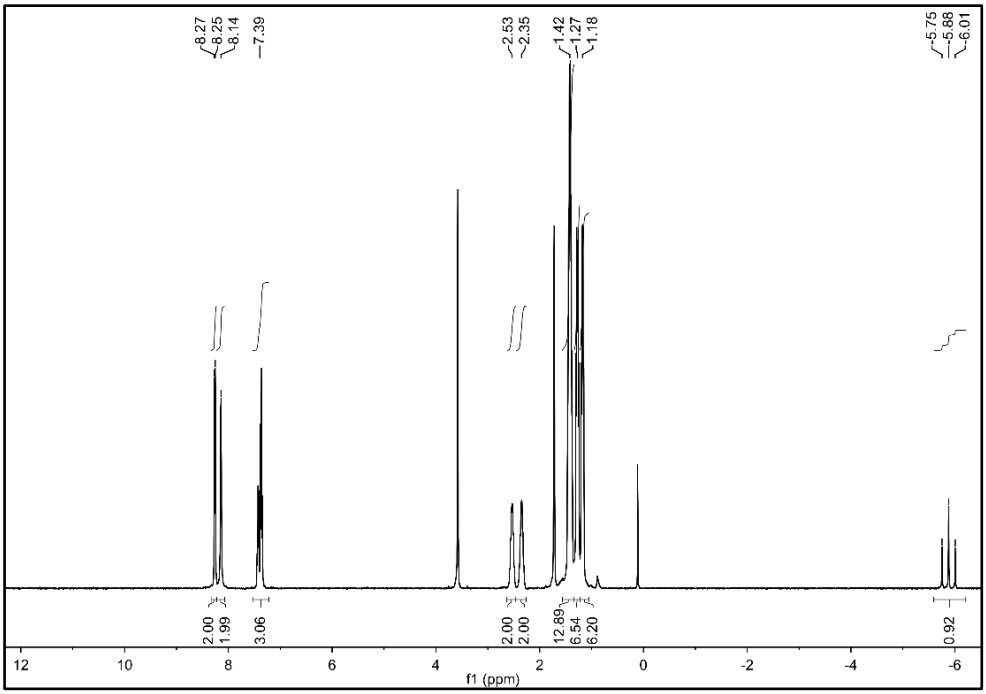


Figure S 16. ^{1}H NMR spectrum of a stock solution of **[Mn-H]H$_2$** in thf$_{D8}$ which was stored at room temperature for 3 months.

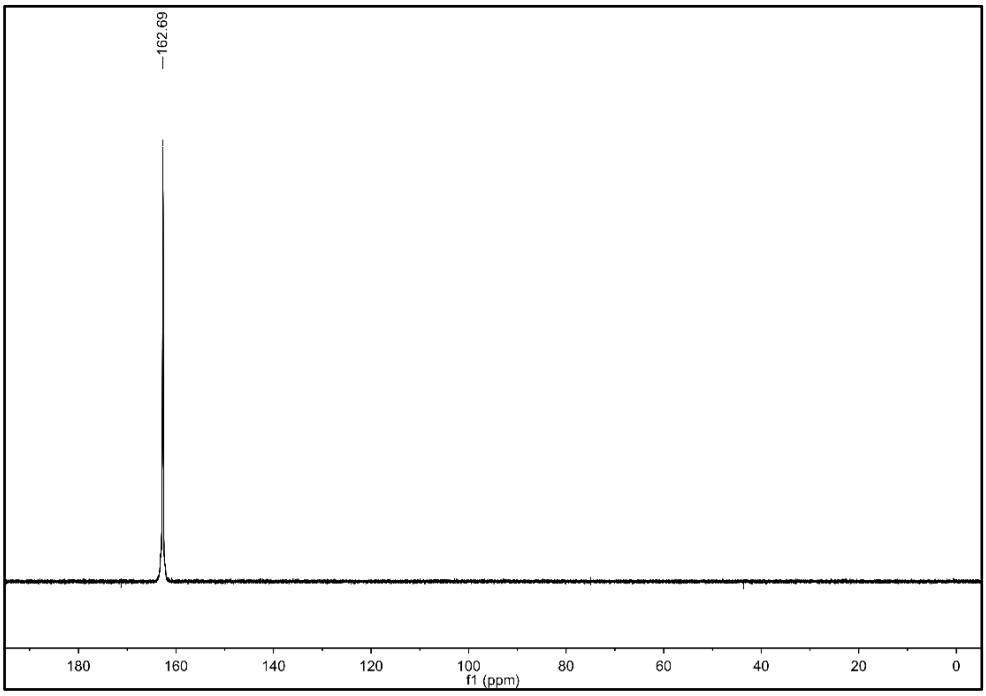


Figure S 17. ^{31}P NMR spectrum of a stock solution of **[Mn-H]H$_2$** in thf$_{D8}$ which was stored at room temperature for 3 months.

Stability of [Mn-H]K_2

KO^tBu (30 µmol, 2.0 eq.) was added to a solution of **[Mn-H]H_2** (15 µmol, 1.0 eq.) in thf_{D8} (500 µL in total) at rt. The mixture immediately turned to a dark red color and was transferred to a Young NMR tube. A ^1H NMR spectrum was measured to make sure that double deprotonation took place. The solution was stored for 3 days at room temperature and an ^1H NMR spectrum was measured again (Figure S 18). The complex did not decompose over time.

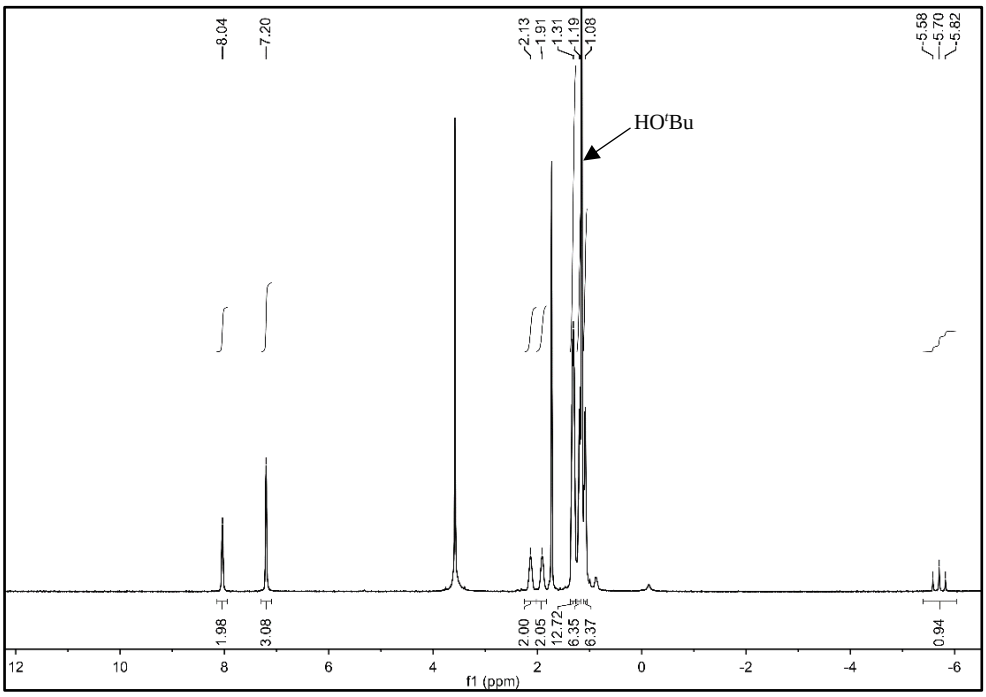


Figure S 18. ^1H NMR spectrum of **[Mn-H]K_2** after 3 days at room temperature in thf_{D8}.

3.2 Stoichiometric Hydride Transfer Reactions

3.2.1. General Procedure

A Young NMR tube was charged with thf_{D8} solutions of hydride complex **[Mn-H]H_2** and imine and the NMR spectrometer was shimmed herewith for ^1H NMR spectra. The tube was subsequently cooled down with liquid nitrogen and KO^tBu (solution in thf_{D8}) was added, resulting in a total volume of 700 µL thf_{D8}. Shortly after melting, the mixture was homogenized and cooled down with liquid nitrogen again. Directly before introducing the tube into the NMR it was brought to room temperature and the measurement was started at 23 °C.

3.2.2. Experimental Probing of the Catalytic Cycle

[Mn-H]H$_2$ (30 µmol, 1.0 eq.), **1a** (60 µmol, 2.0 eq.) and KO^{t}Bu (60 µmol, 2.0 eq.) were dissolved in thf$_{D8}$ (700 µL) in a Young NMR tube and inserted into an NMR spectrometer at 23 °C. The reaction was monitored via ^{1}H NMR for 5 h. After four days at 23 °C the reaction progress was checked with ^{1}H NMR, subsequently transferred into an autoclave and the tube was washed with 500 µL thf$_{D8}$. The autoclave was purged three times with H_2, before the pressure was adjusted to 20 bar H_2. The reaction was stirred over night at 40 °C. Afterwards, the solution was transferred to an NMR tube.

It can be asserted from the ^{1}H NMR spectra in Figure S 19 that the hydride (e.g. Mn-*H* -5.71 ppm) and partially **1a** (e.g. N=C*H* 8.51 ppm) is consumed under production of amine **2a** (e.g. C*H*$_2$ 4.28 ppm). The shift of the acidic hydrogen atoms (HO^{t}Bu between about 3.5 and 7 ppm), produced at the beginning of the reaction by deprotonation of complex **[Mn-H]H$_2$**, can most likely be attributed to 1 eq. KO^{t}Bu reproduced in the reaction. The sharp bend of the shift of the acidic protons is due to a change of the time intervals of the measurements.

After 4 days (Figure S 20) almost all the hydride was transferred (Mn-*H* -5.71 ppm). As expected, the result is a mixture of **1a** (e.g. N=C*H* 8.51 ppm) and **2a** (e.g. C*H*$_2$ 4.28 ppm).

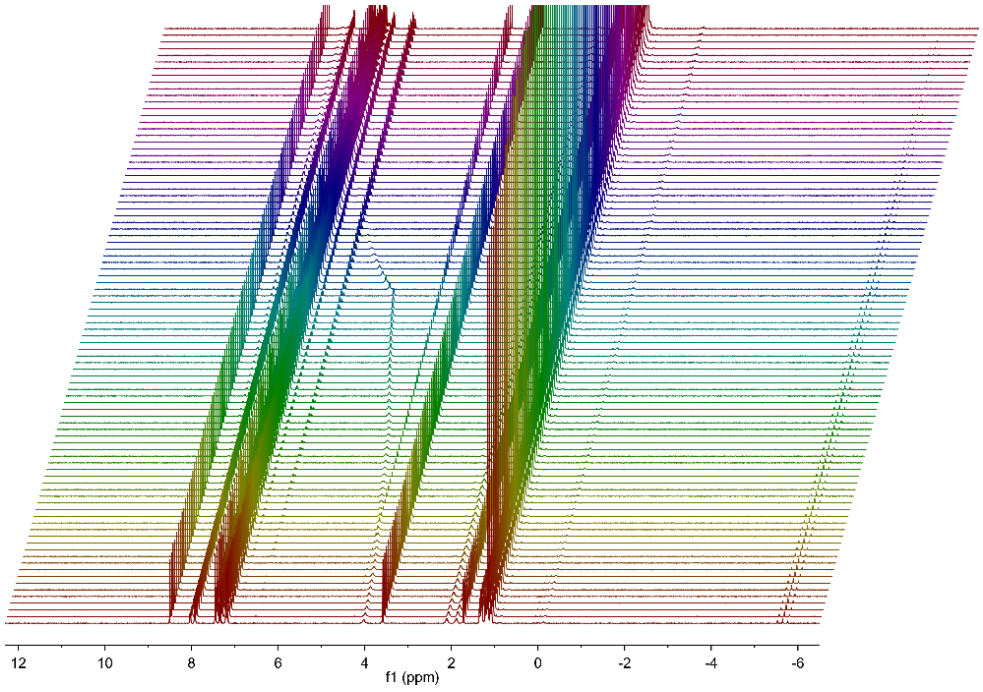


Figure S 19. ^{1}H NMR experiment with **[Mn-H]H$_2$**, **1a** and KO^{t}Bu in thf$_{D8}$.

After one night of stirring with 20 bar H_2 at 40 °C the double deprotonated complex **[Mn-H]K$_2$** is fully regenerated as can be concluded from ^{1}H NMR (8.03, 7.20, 2.12, 1.89, 1.31, 1.19, 1.08, -5.70 ppm) (Figure S 21) and ^{31}P NMR (157.8 ppm) (Figure S 22). **1a** was completely transformed into amine **2a** (7.35, 7.26, 7.19, 7.01, 6.52, 5.33, 4.28 ppm). The stoichiometry of **[Mn-H]K$_2$** and **2a** is still 1:2. The acidic protons of HO^{t}Bu were shifted upfield, most likely due to consumption of KO^{t}Bu and re-formation of HO^{t}Bu (3.5 ppm, Figure S 22). Herewith, the catalytic cycle is closed.

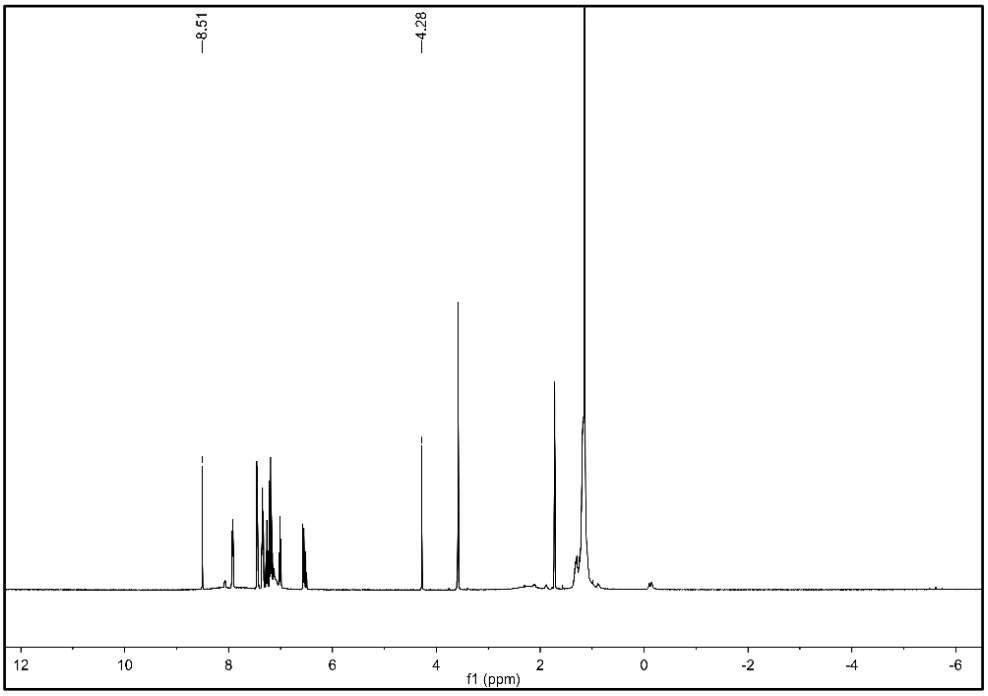


Figure S 20. ^{1}H NMR spectrum of the reaction mixture after 4 days at rt.

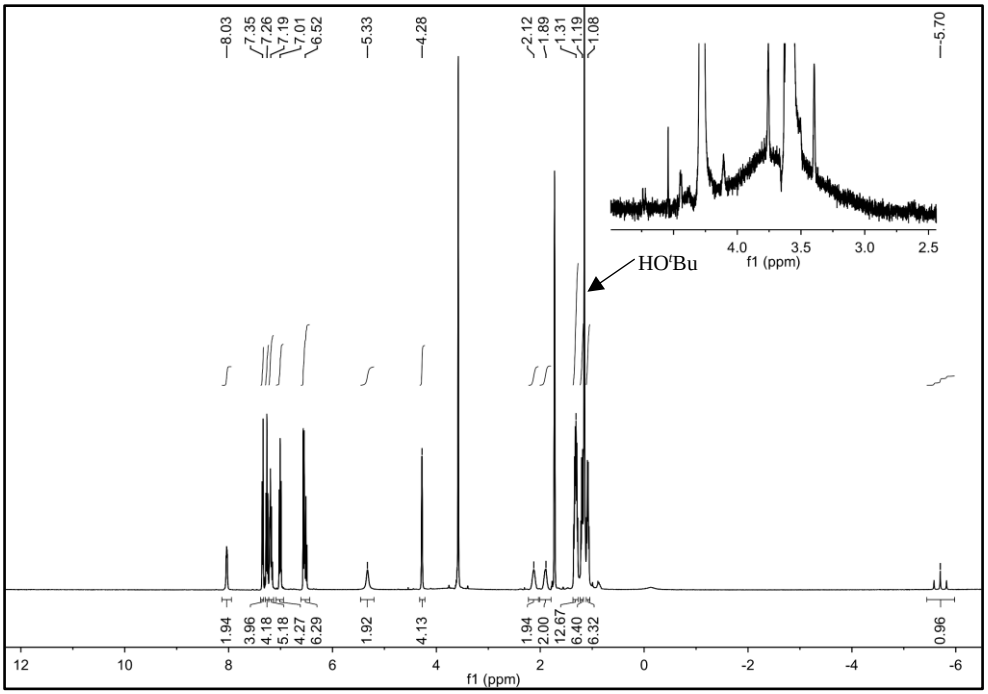


Figure S 21. ^{1}H NMR spectrum of the reaction mixture after 1 d of stirring at 40 °C with 20 bar H_2.

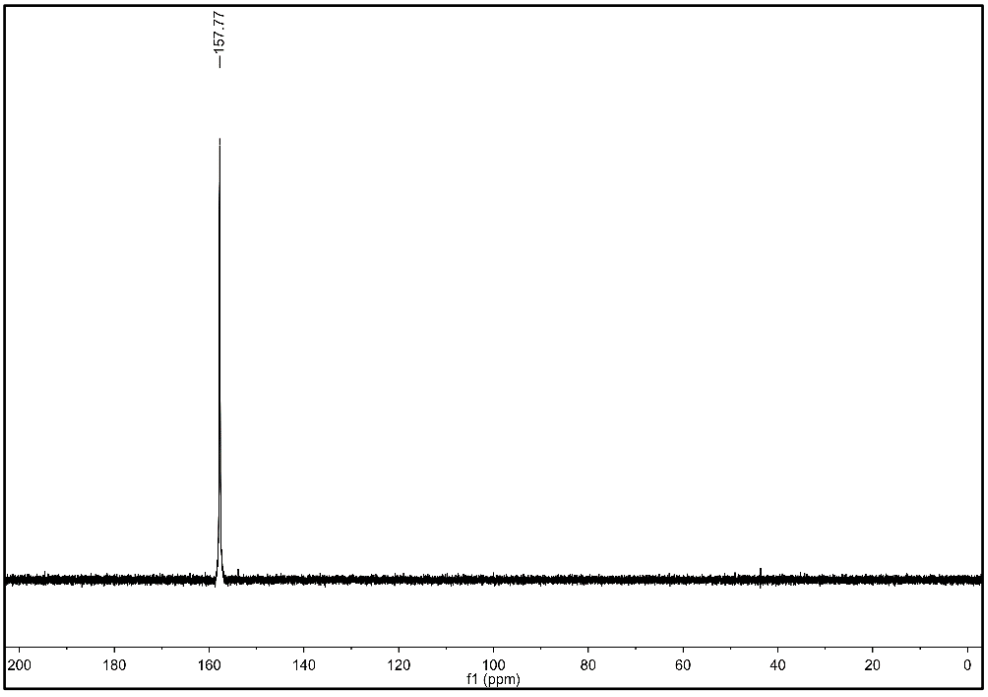


Figure S 22. ^{31}P NMR spectrum of the reaction mixture after 1 d of stirring at 40 °C with 20 bar H_2.

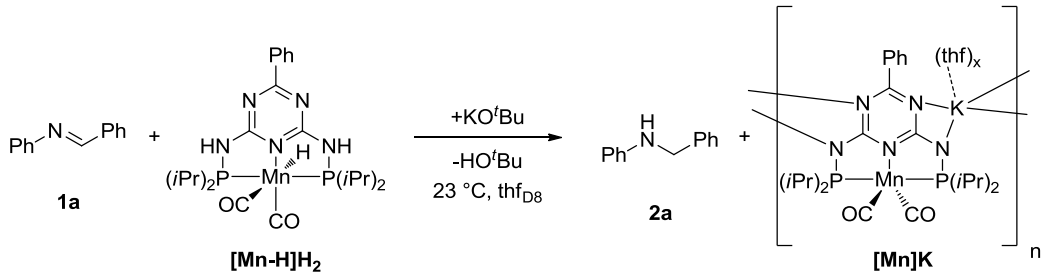
3.2.3. Partial Reaction Orders

The dependency of the reaction between **[Mn-H]H$_2$** and **1a** on the reactant concentrations was investigated by ^{1}H NMR experiments according to the general procedure (3.2.1).

3.2.3.1. Base Concentration

The dependency of the reaction rate on the base concentration was investigated as it is shown in Table S 6. From 0 to 1 eq. of base no reaction was observed. The initial reaction rate grows drastically from 1–2 eq. of base and stagnates thereafter.

Table S 6. Variation of the amount of KO^{t}Bu in the reaction of **[Mn-H]H$_2$** and **1a** and correspondent initial rates (r_i).[a]



Equivalents KO^{t}Bu[b]	r_i $[\frac{\mu mol}{mL*h}]$[c]	R^2
0	0	/
1	0.44 ± 0.09	0.319
2	8.28 ± 0.17	0.983
3[d]	8.37 ± 0.08	0.996
4	9.12 ± 0.25	0.971

[a] **[Mn-H]H$_2$** (30 µmol), **1a** (30 µmol), KO^{t}Bu, thf$_{D8}$ (700 µL), 23 °C. [b] With respect to **[Mn-H]H$_2$**. [c] Initial rate of the consumption of **1a**. [d] Calculated by the production of amine.

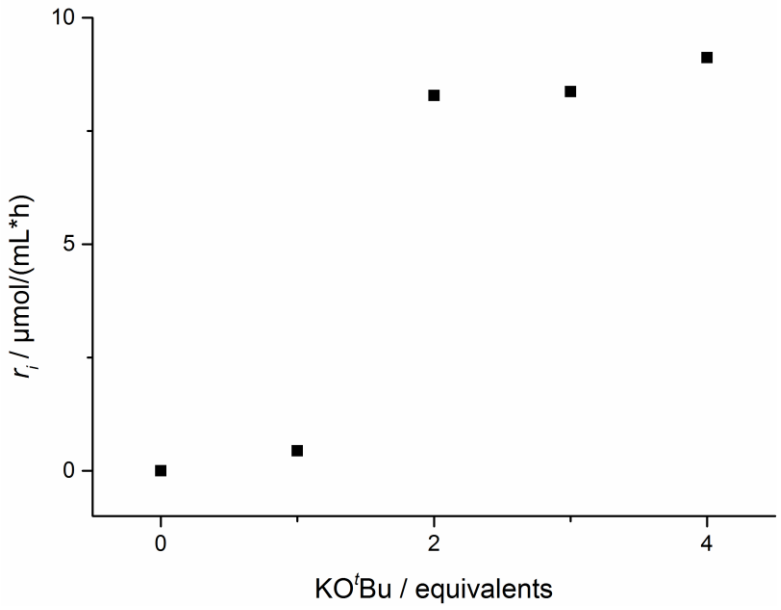
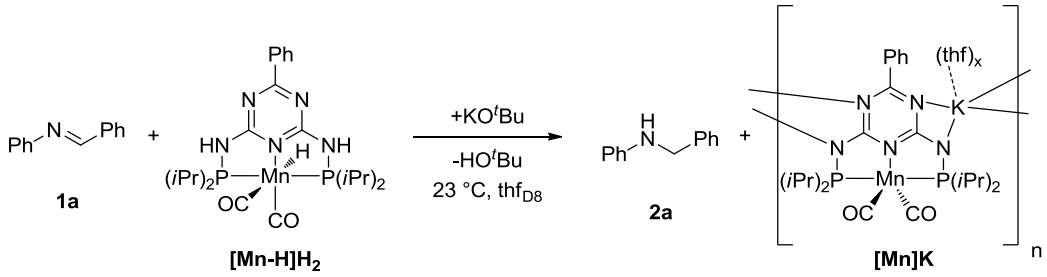


Figure S 23. Dependency of r_i on the concentration of KO^{t}Bu.

3.2.3.2. HO^{t}Bu Concentration

HO^{t}Bu is produced immediately after the addition of KO^{t}Bu because of the deprotonation of hydride complex **[Mn-H]H$_2$**. 1 eq. of **[Mn-H]H$_2$** with 2 eq. of KO^{t}Bu yields 2 eq. of HO^{t}Bu (Entry 1, Table S 7).

Table S 7. Variation of the amount of HO^{t}Bu in the reaction of **[Mn-H]H$_2$** and **1a**.[a]



Equivalents HO^{t}Bu[b]	r_i $[\frac{\mu mol}{mL*h}]$[c]	R^2
2	8.28 ± 0.17	0.983
4	8.29 ± 0.19	0.979

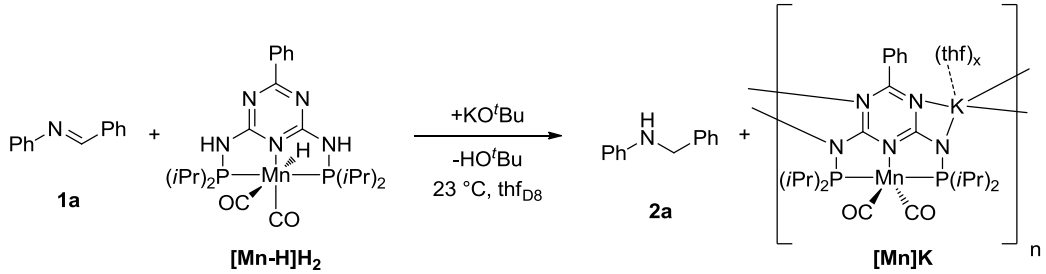
[a] **[Mn-H]H$_2$** (30 µmol), **1a** (30 µmol), KO^{t}Bu (60 µmol), thf$_{D8}$ (700 µL), 23 °C. [b] With respect to **[Mn-H]H$_2$**. [c] Initial rate of the consumption of **1a**.

Considering the results shown in Table S 7, HO^{t}Bu has no influence on the reaction rate.

3.2.3.3. Imine Concentration

The dependency of the reduction of imine **1a** on the concentration of **1a** was determined (Table S 8).

Table S 8. Variation of the imine (**1a**) concentration.[a]



Equivalents **1a**[b]	r_i $[\frac{\mu mol}{mL*h}]$[c]	R^2
0.5	4.38 ± 0.12	0.969
1	8.28 ± 0.17	0.983
2	16.6 ± 0.4	0.989

[a] **[Mn-H]H2** (30 µmol), **1a**, KO^{t}Bu (60 µmol), thf$_{D8}$ (700 µL), 23 °C. [b] With respect to **[Mn-H]H2**. [c] Initial rate of the consumption of **1a**.

Considering following equation:

$$r = \ k * [A]^a * [B]^b \ ... \tag{1}$$

r is the reaction rate, *[A]*, *[B]* are the concentrations of the components, and ^{a} and ^{b} are the partial reaction orders with respect to the components. The variables expect for *[A]* and ^{a} can be combined to constant *k'* when the concentration of only one component (A) is varied (r_i is the initial rate).

$$r_i = \ k' * [A]^a \tag{2}$$

It follows:

$$\ln(r_i) = \ln(k') + a * \ln([A]) \tag{3}$$

This is a linear equation for the variation of the concentration of only one component at once. By plotting $\ln(r_i)$ against $\ln([A])$ the reaction order a with respect to this component follows as the slope of the line.

Table S 9. $\ln(r_i)$ and $\ln([A])$ (A is **1a**)

$\ln(r_i)$	$\ln([A])$
1.477 ± 0.027	3.065
2.114 ± 0.021	3.758
2.809 ± 0.024	4.451

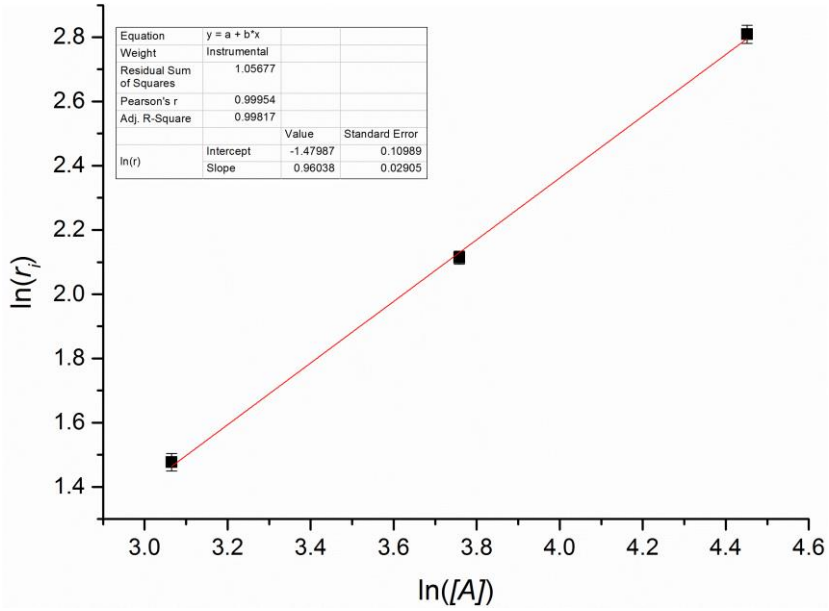


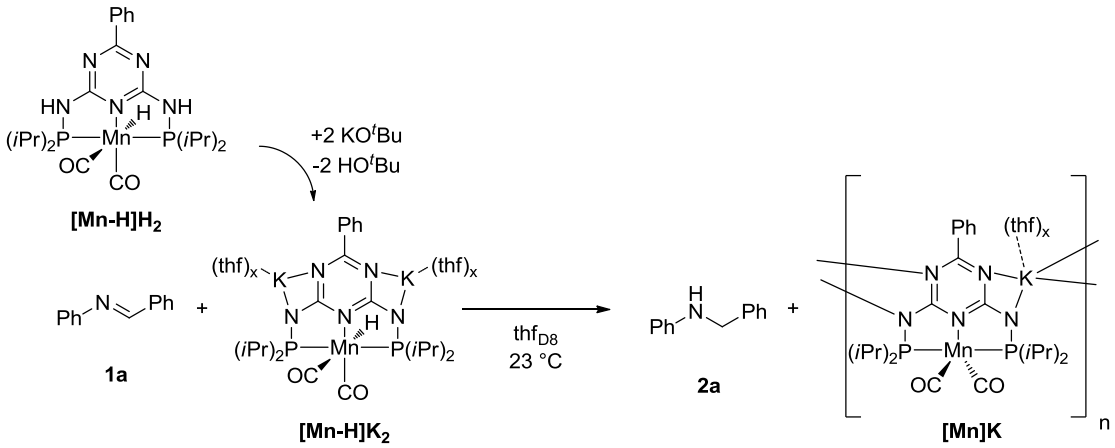
Figure S 24. $\ln(r_i)$ against $\ln([A])$.

The partial reaction order with respect to imine **1a** which equals the slope in Figure S 24 is $a = 0.960 \pm 0.029$. Therefore, the reaction order with respect to **1a** is 1. With $R^2 = 0.999$ (R = Pearson Correlation Coefficient) a good linear correlation was observed.

3.2.3.4. Concentration of [Mn-H]K_2

The dependency of the reduction of imine **1a** on the concentration of **[Mn-H]K_2** was determined (Table S 10). **[Mn-H]K_2** was produced by adding 2 eq. of KO^{t}Bu to 1 eq. of **[Mn-H]H_2**.

Table S 10. Variation of the amount of **[Mn-H]K$_2$** in the hydrogenation of **1a**.[a]



Equivalents **[Mn-H]K$_2$**[b]	r_i $[\frac{\mu mol}{mL*h}]$[c]	R^2
0.5	4.07 ± 0.12	0.969
1	8.28 ± 0.17	0.983
2	17.96 ± 0.25	0.989

[a] **1a** (30 µmol), **[Mn-H]H$_2$**, KO^{t}Bu (2 eq. with respect to **[Mn-H]H$_2$**), thf$_{D8}$ (700 µL), 23 °C. [b] With respect to **1a**. [c] Initial rate of the consumption of **1a**.

Table S 11. Values of ln(r_i) and ln($[B]$) (B = **[Mn-H]K$_2$**).

ln(r_i)	ln([B])
1.404 ± 0.059	3.065
2.114 ± 0.021	3.758
2.888 ± 0.013	4.451

The reaction order with respect to **[Mn-H]K$_2$** which equals the slope in Figure S 25 is a = 1.10 ± 0.03. Thus, the partial reaction order can be assumed as 1. With R^2 = 0.9995 a linear good correlation was observed.

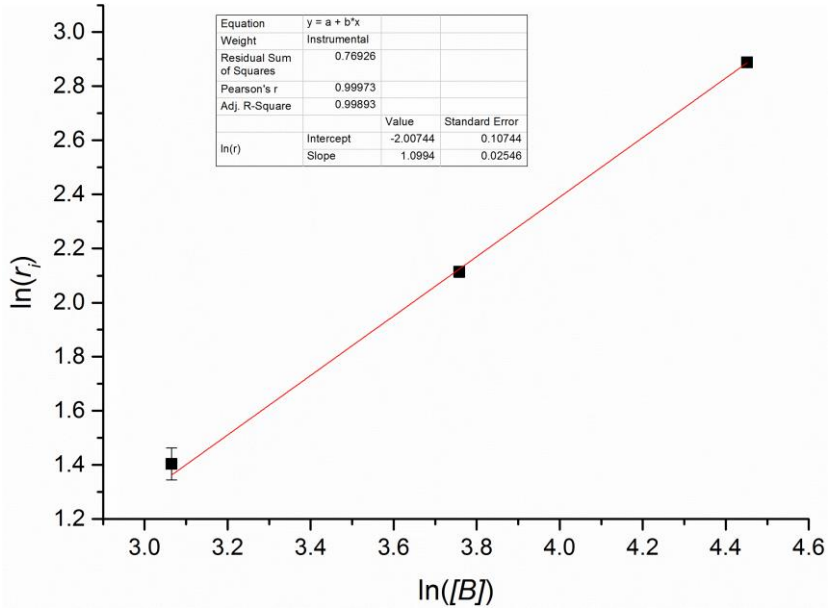


Figure S 25. Plot of $\ln(r_i)$ against $\ln([B])$.

3.2.4. Reaction Constant *k* and Reaction Order

Under the evidence-based assumption that the reaction order is 2 (1 with respect to **1a** and 1 with respect to **[Mn-H]K$_2$**) the reaction order *k* was calculated. The data of an equimolar reaction between **1a** and **[Mn-H]K$_2$** was used.

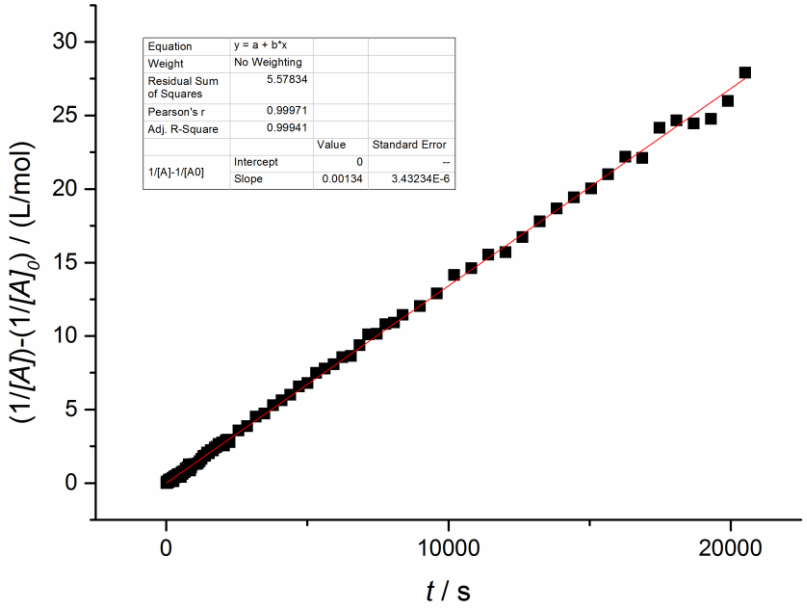


Figure S 26. Plotting of $\frac{1}{[A]} - \frac{1}{[A]_0}$ against *t*. *A* is **1a**.

Equation (4) is a linear equation shown in Figure S 26:

$$\frac{1}{[A]} - \frac{1}{[A]_0} = k * t \quad (4)$$

[A] is the concentration of **1a** during the reaction and *[A]₀* is the concentration of **1a** at $t = 0$.

As it can be seen from Figure S 26 the plot for a reaction order of 2 produces an almost perfectly straight line with $R^2 = 0.999$. Furthermore, the reaction constant k at 23 °C for the reaction between **1a** and **[Mn-H]K₂** was calculated as:

$$k = (1.34 * 10^{-3} \pm 3.43 * 10^{-6}) \frac{L}{mol * s} \quad (5)$$

3.2.5. Reaction under CO Atmosphere

In order to evaluate if CO has an influence on the reaction rate, a reaction was carried out analogous to 3.2.1 with an equimolar ratio of **[Mn-H]H₂** (30 µmol, 1.0 eq.) and **1a** (30 µmol, 1.0 eq.) but after adding KO^{t}Bu (60 µmol, 2 eq.) and cooling down the NMR tube with liquid nitrogen it was evacuated and purged with CO three times. The CO pressure was adjusted to 0.5 bar overpressure, the NMR was then heated up to room temperature and immediately inserted into the NMR.

Table S 12. CO experiment for the stoichiometric reduction of **1a** with **[Mn-H]H₂**.[a]

CO [bar]	r_i [$\frac{\mu mol}{mL*h}$][b]	R^2
0	8.28 ± 0.17	0.983
1.5	7.56 ± 0.14	0.989

[a] **[Mn-H]H₂** (30 µmol), **1a** (30 µmol), KO^{t}Bu (60 µmol), thf_{D8} (700 µL), 23 °C.
[b] Initial rate of the consumption of **1a**.

According to the results, CO does not have an essential influence on the reaction rate (Table S 12). The difference between the experiment with and without CO can be explained with the fact, that the first points in time could not be used for the regression line (Figure S 27), probably because of equilibrium effects due to the CO overpressure.

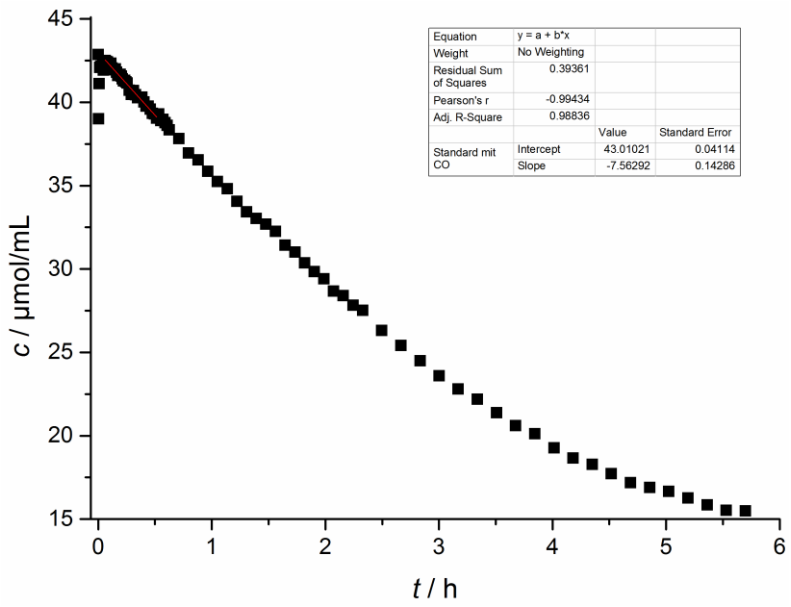


Figure S 27. Consumption of **1a** in the reaction of **1a** and **[Mn-H]K$_2$** under CO atmosphere.

3.2.6. Alkali Metal Ion Testing

LiO^tBu, NaO^tBu and KO^tBu were tested as bases in the stoichiometric reaction of **1a** and **[Mn-H]H$_2$**. The reactions were conducted according to the general procedure (3.2.1) at 50 °C with **[Mn-H]H$_2$** (30 µmol, 1.0 eq.), **1a** (30 µmol, 1.0 eq.) and base (60 µmol, 2.0 eq.).

The initial rates are listed in Table S 13.

Table S 13. Initial rates of the amine production in the reaction between **1a** and **[Mn-H]H$_2$**.

	LiO^tBu	NaO^tBu	KO^tBu
Initial rate $[\frac{mM}{h}]$	0.68 ± 0.01	5.50 ± 0.05	48.1 ± 1.07

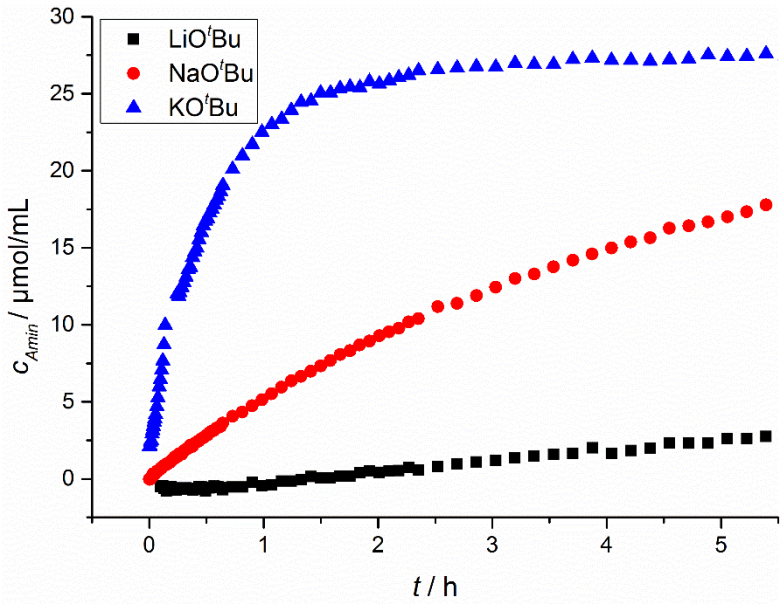


Figure S 28. Comparison between the intial rates of the amine (**2a**) production in the stoichiometric reaction between **[Mn-H]H$_2$** and **1a** employing KO^{t}Bu, NaO^{t}Bu or LiO^{t}Bu as the base.

3.2.7. Hammett Study

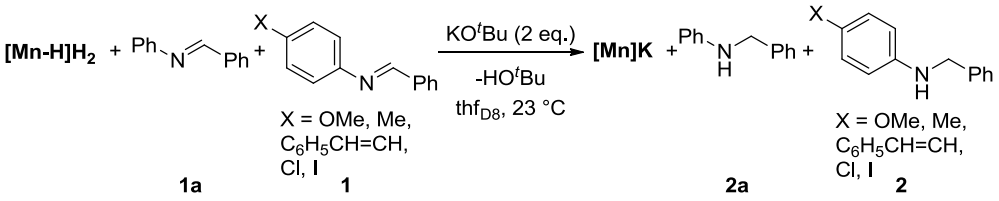
Competition experiments between standard imine **1a** and other imines **1** with various functional groups were carried out in order to gain further insight into the electronic structure of the intermediates which are involved in the rate-determining step (Hammett study [26, 27]).

With a first-order dependency on imine **1a** (see 3.2.3.3) and the assumption that the reaction order is the same for different imines, following equation applies:

$$\ln\left(\frac{X_0}{X}\right) = \frac{k_X}{k_H} * \ln\left(\frac{H_0}{H}\right) \quad (6)$$

X_0 is the initial concentration of a substrate **1** with a functional group other than H, X is the corresponding concentration during the reaction, H_0 is the initial concentration of standard imine **1a** and H is the corresponding concentration during the reaction. k_X is the reaction constant for the reaction with the substituted imine **1** and k_H is the reaction constant for **1a**. By plotting $\ln\left(\frac{X_0}{X}\right)$ against $\ln\left(\frac{H_0}{H}\right)\frac{k_X}{k_H} = k_{rel}$ can be obtained as the slope of the line. Subsequent plotting of k_{rel} against different σ-values[26,28] allows the gathering of information if anions, cations or radicals are involved in the rate-determining step.

Table S 14. Values obtained from competition experiments with substrates with different functional groups and values obtained from plotting log(k_{rel}) against different σ-values[26, 28].[a]



Functional Group (X)	R^2	k_{rel}	log(k_{rel})	σ^{26}	$\sigma^{+\,26}$	$\sigma^{\bullet\,28}$	$\sigma^{-\,26}$
OMe	0.993	0.0780 ± 0.0007	-1.108 ± 0.004	-0.27	-0.78	0.24	-0.26
Me	0.997	0.183 ± 0.001	-0.738 ± 0.002	-0.17	-0.31	0.11	-0.17
C_6H_5-CH=CH	0.979	15.36 ± 0.30	1.186 ± 0.008	-0.07	-1.00	/ [b]	0.13
Cl	0.981	23.25 ± 0.46	1.366 ± 0.009	0.23	0.11	0.12	0.19
I	0.923	56.84 ± 2.30	1.755 ± 0.018	0.18	0.14	/ [b]	0.27
R^2				0.61	0.01	0.11	0.94

[a] **[Mn-H]H2** (30 µmol, 1.0 eq.), **1a** (15 µmol, 0.5 eq.), **1** (15 µmol, 0.5 eq.) KO^{t}Bu (60 µmol, 2.0 eq.), thf_{D8} (700 µL), 23 °C. [b] No data available in literature.

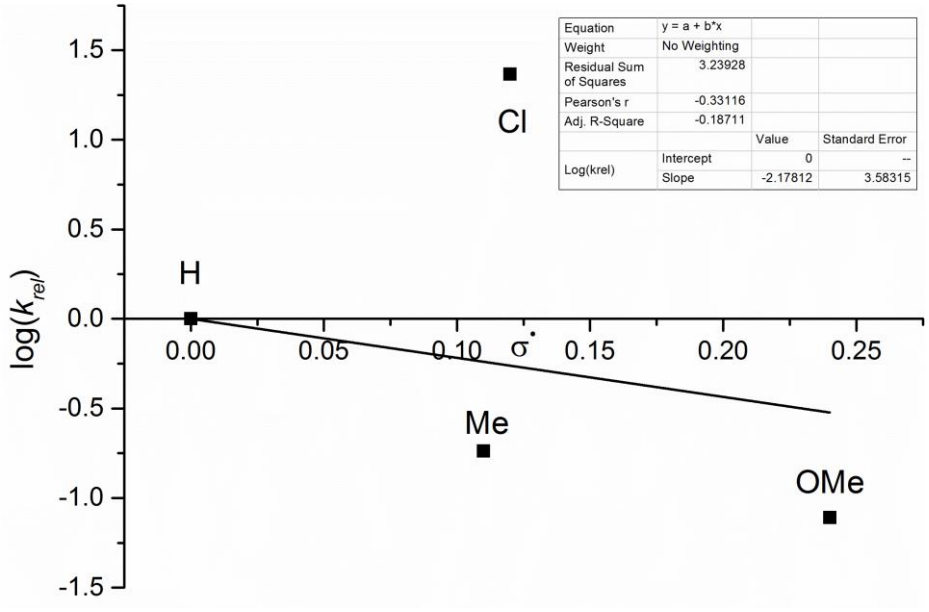


Figure S 29. Hammett plot with σ-values for radical reactions[28].

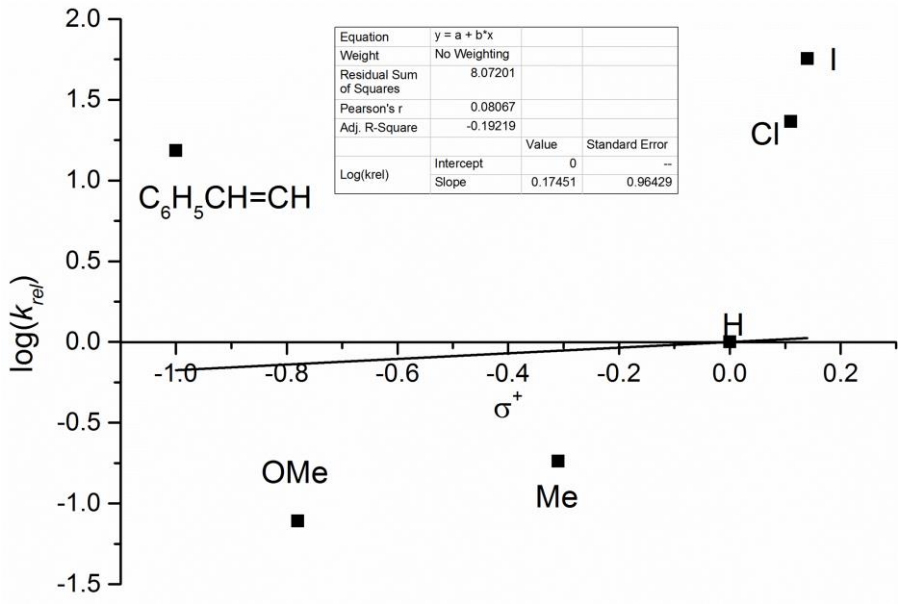


Figure S 30. Hammett plot with σ-values optimized for reactions with an evolving positive charge in conjugation with the substituent[26].

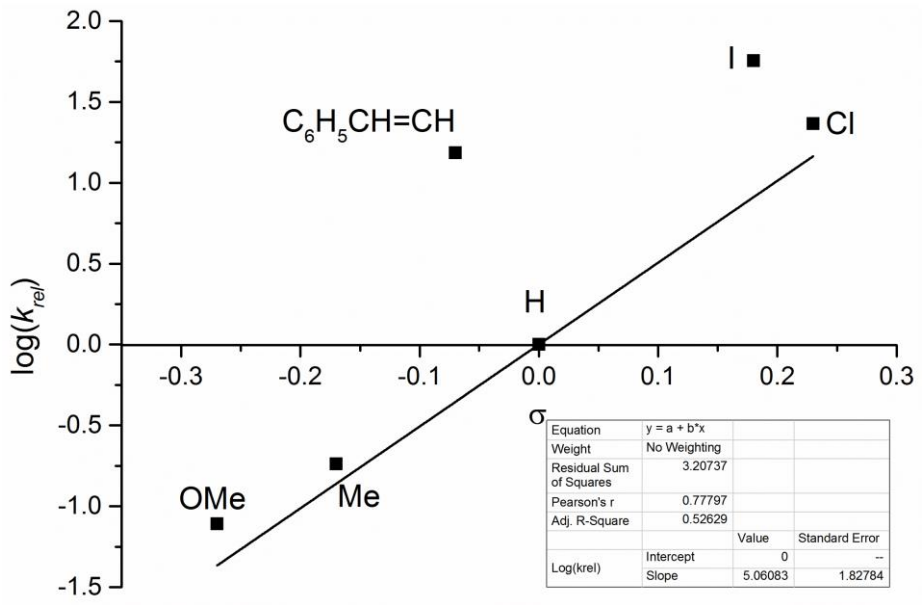


Figure S 31. Hammett plot with standard σ-values[26].

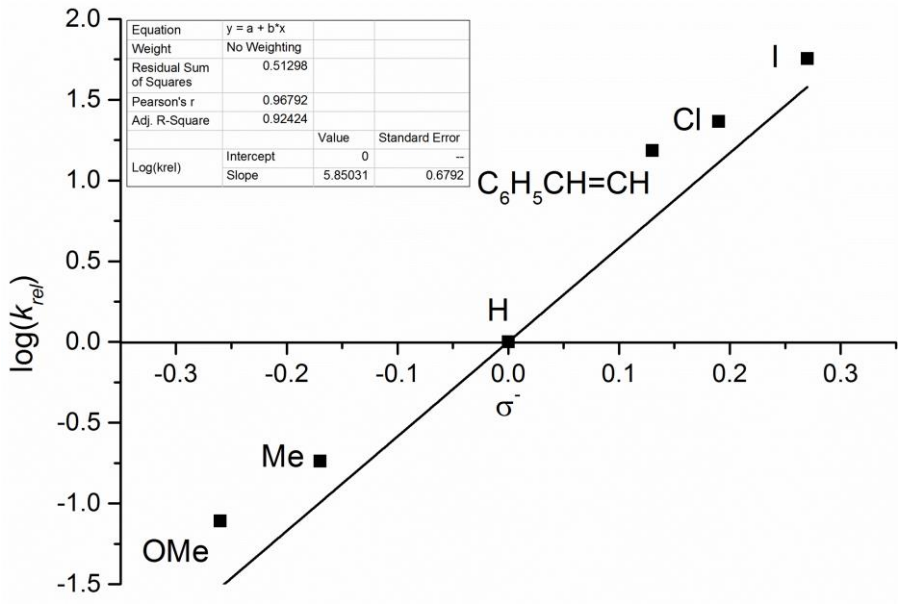


Figure S 32. Hammett plot with sigma σ⁻–values (values for a reaction with an evolving negative charge in conjugation with the substituent).

Plotting of $\ln\left(\frac{X_0}{X}\right)$ against $\ln\left(\frac{H_0}{H}\right)$ yielded lines with high R^2-values, indicating good linear dependencies (Table S 14). The Hammett plots (Figure S 29 –Figure S 32) show, that the only fitting σ-values are the σ⁻-values, optimized for reactions in which a negative charge is built up which is resonance-stabilized by the substituent. The slope, which is the reaction constant ρ = 5.85, is relatively high, indicating that a strong negative charge is built up during the rate-determining step. It can be concluded, that there are most likely no radical or cationic intermediates present during the rate determining step and a strong negative charge is built up, which is delocalized over the substituent, consistent with a hydride transfer, producing a transiently negative charge on the nitrogen atom at the former imine.

3.3 Hydrogenation Experiments

3.3.1. Crown Ether Addition

According to the general procedure for hydrogenation reactions (2.2.1) an autoclave was charged with **1a** (181 mg, 1.00 mmol. 1.0 eq.), KO^{t}Bu (0.16 M in thf; 250 µL, 40 µmol, 4 mol%), **[Mn-Br]H$_2$** (0.008 M in thf, 500 µL, 4 µmol, 0.4 mol%), 18-crown-6 (0.16 M in thf; 250 µL, 40 µmol, 4 mol%) and 1 mL thf. The reaction was stirred for 4 h at 50 °C. After the

reaction, 1 mL H_2O, 100 µL dodecan and 7 mL Et_2O were added, the mixture homogenized, and a sample for GC analysis was dried over Na_2SO_4.

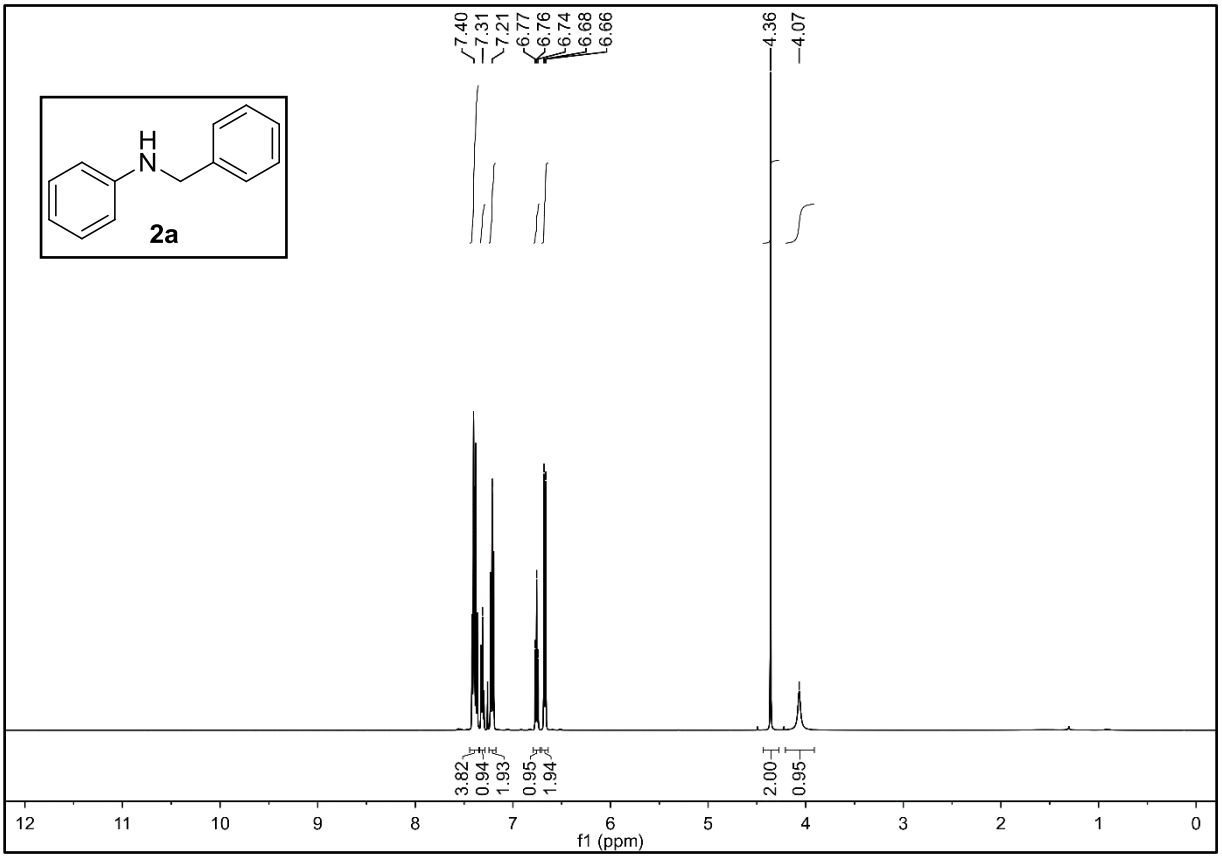
Yield of **2a** (determined by GC): 38 %.

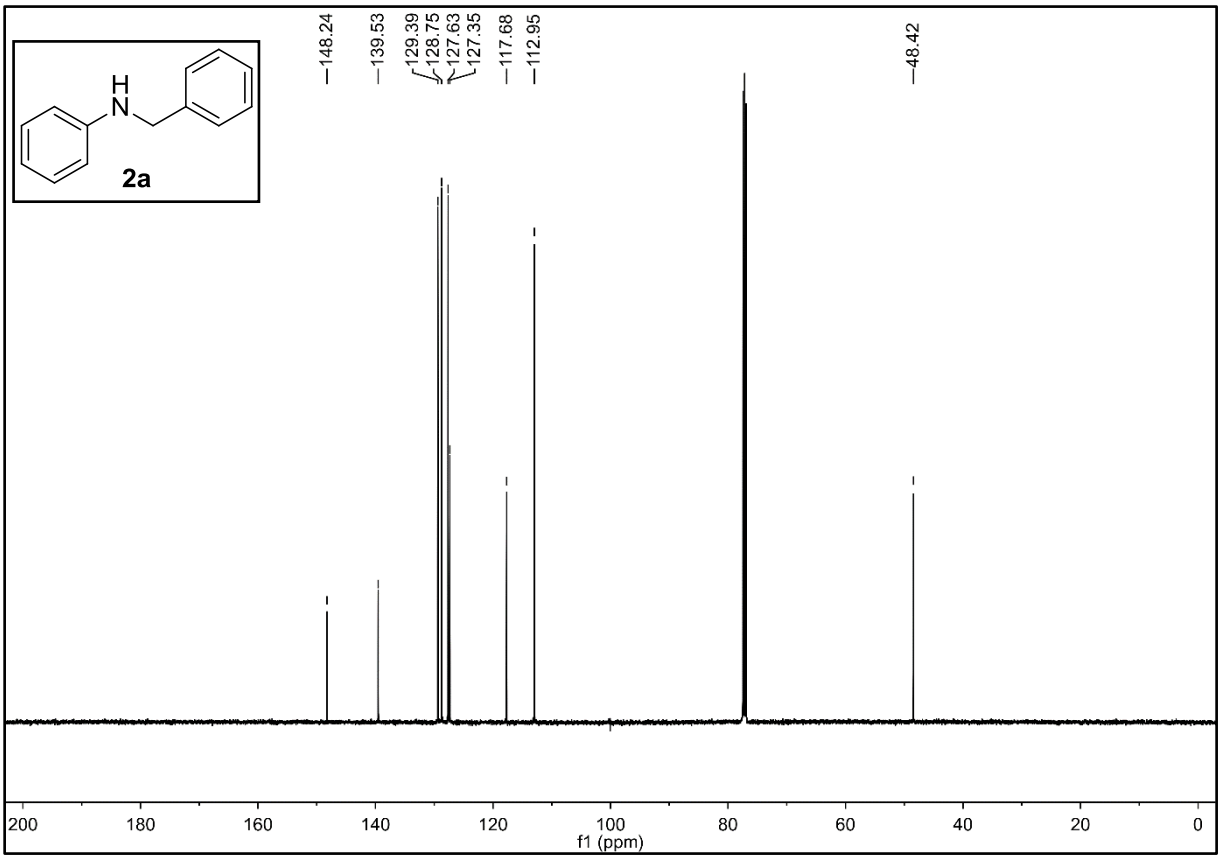
3.3.1. Hydrogenation with [Mn-H]K_2 and HOtBu

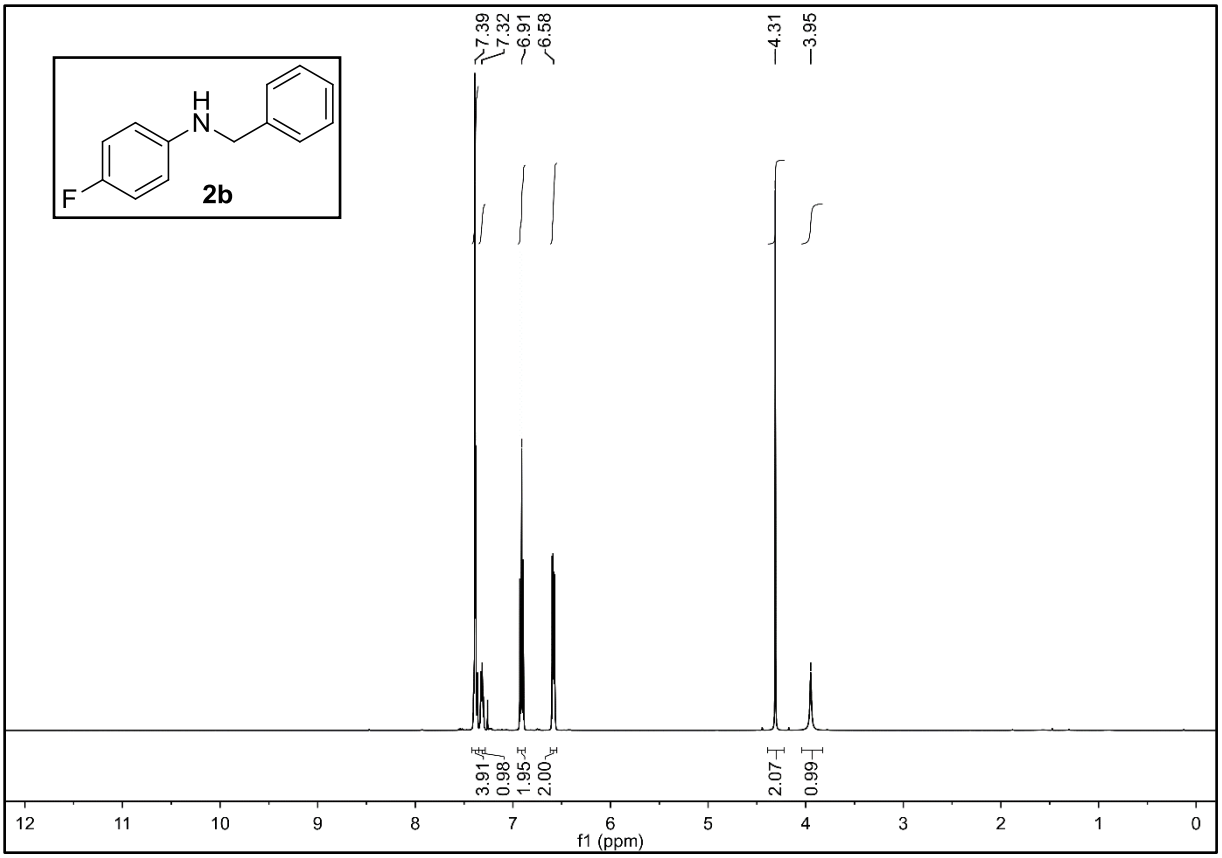
An autoclave was charged with **1a** (181 mg, 1.00 mmol. 1.0 eq.) **[Mn-H]K_2** (0.004 M in thf, 1.00 mL, 4 µmol, 0.4 mol%), HO^{t}Bu (0.04 M in thf; 100 µL, 4 µmol, 0.4 mol%) and 900 µL thf. The reaction was stirred for 24 h at 50 °C. After the reaction, 1 mL H_2O, 100 µL dodecan and 7 mL Et_2O were added, the mixture homogenized, and a sample for GC analysis was dried over Na_2SO_4.

Yield of **2a** (determined by GC): 28 %.

4 NMR Spectra



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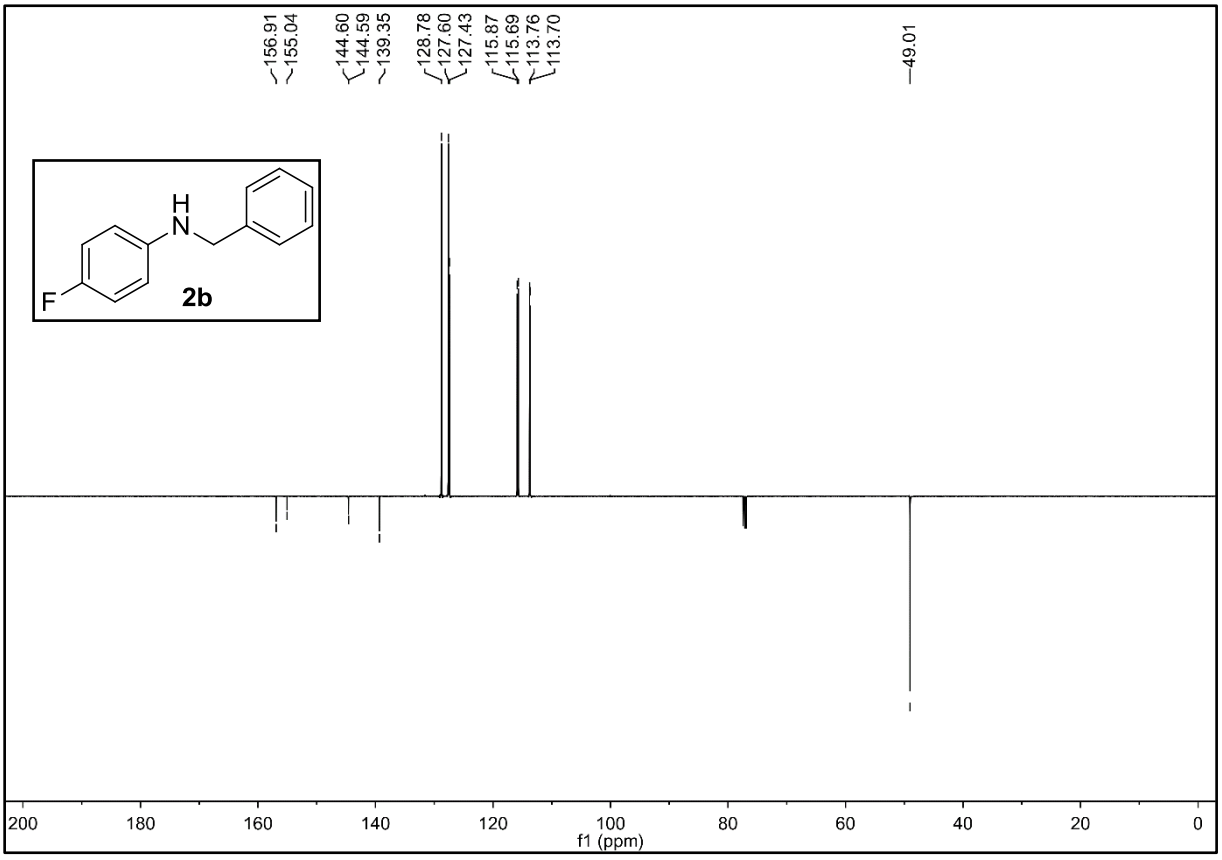
7.32
6.91
6.58
4.31
3.95
3.91
0.98
1.95
2.00
2.07
0.99
2b
f1 (ppm)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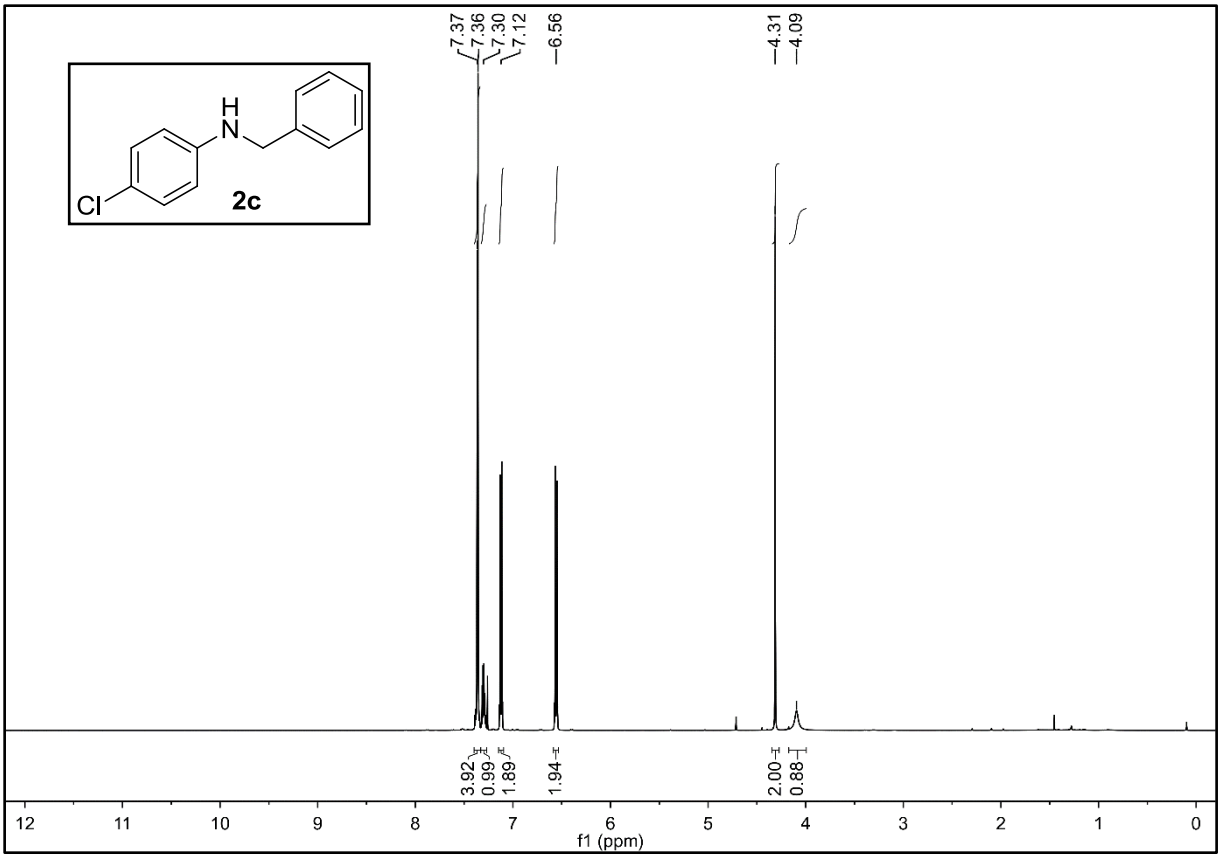
155.04
144.60
144.59
139.35
128.78
127.60
127.43
115.87
115.69
113.76
113.70
49.01
2b
f1 (ppm)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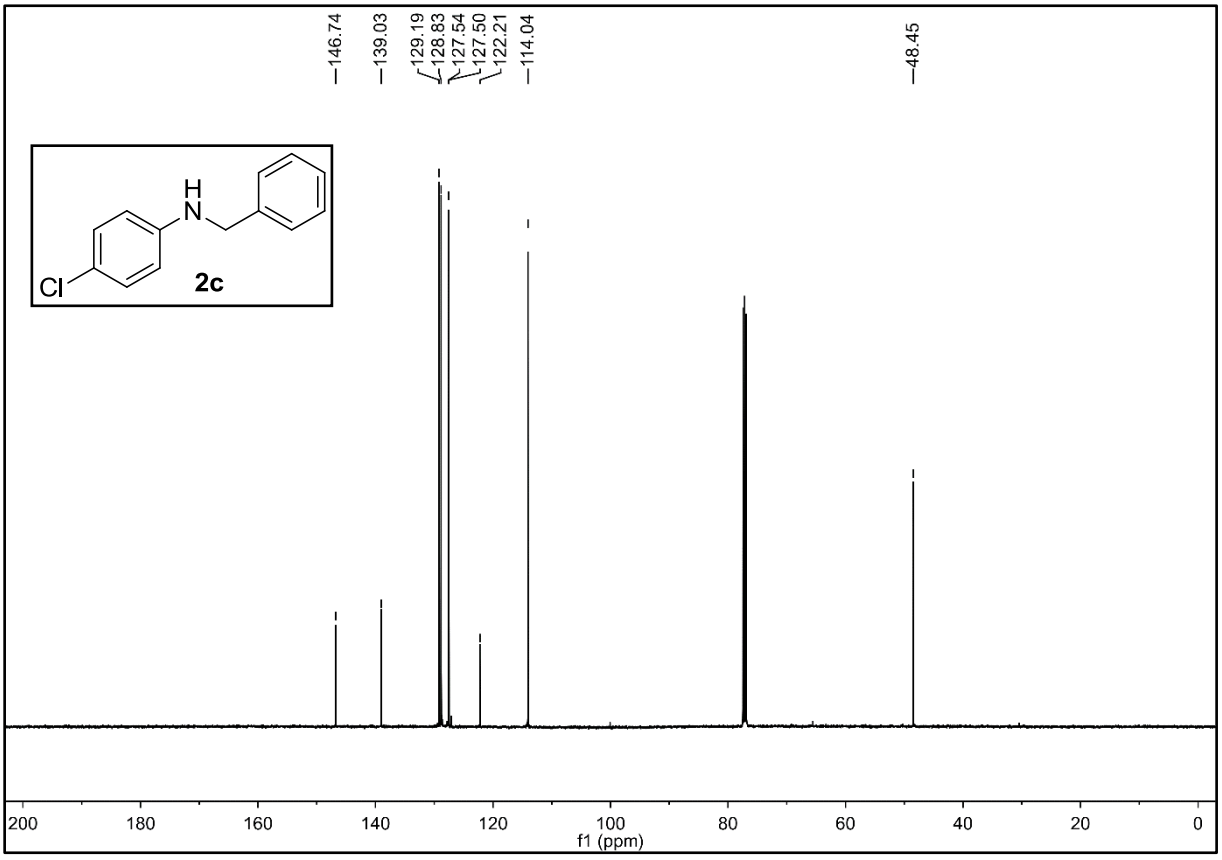
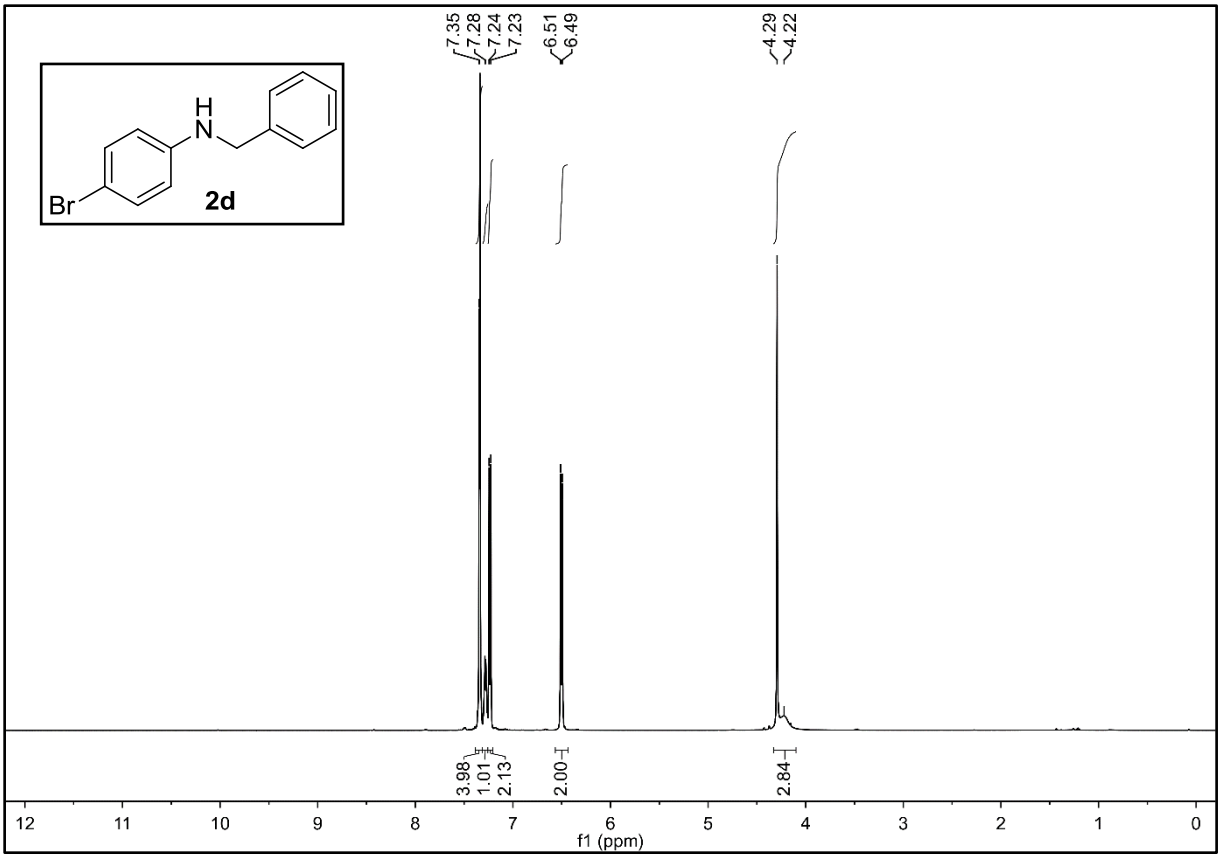
7.36
7.30
7.12
6.56
4.31
4.09
H
N
Cl
2c
3.92
0.99
1.89
1.94
2.00
0.88
12
11
10
9
8
7
6
5
4
3
2
1
0
f1 (ppm)


146.74
139.03
129.19
128.83
127.54
127.50
122.21
114.04
48.45
H
N
Cl
2c
200
180
160
140
120
100
80
60
40
20
0
f1 (ppm)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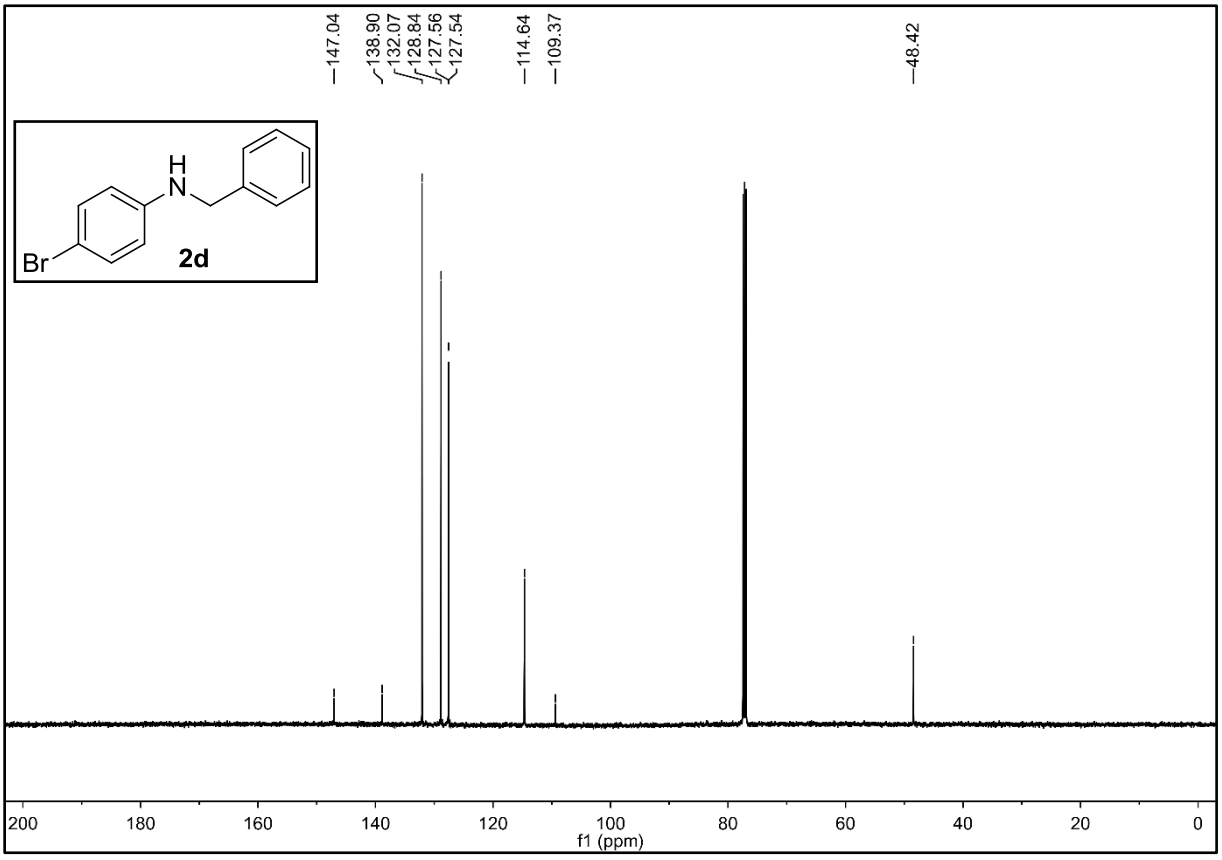
7.28
7.24
7.23
6.51
6.49
4.29
4.22
H
N
Br
2d
3.98
1.01
2.13
2.00
2.84
12
11
10
9
8
7
6
5
4
3
2
1
0
f1 (ppm)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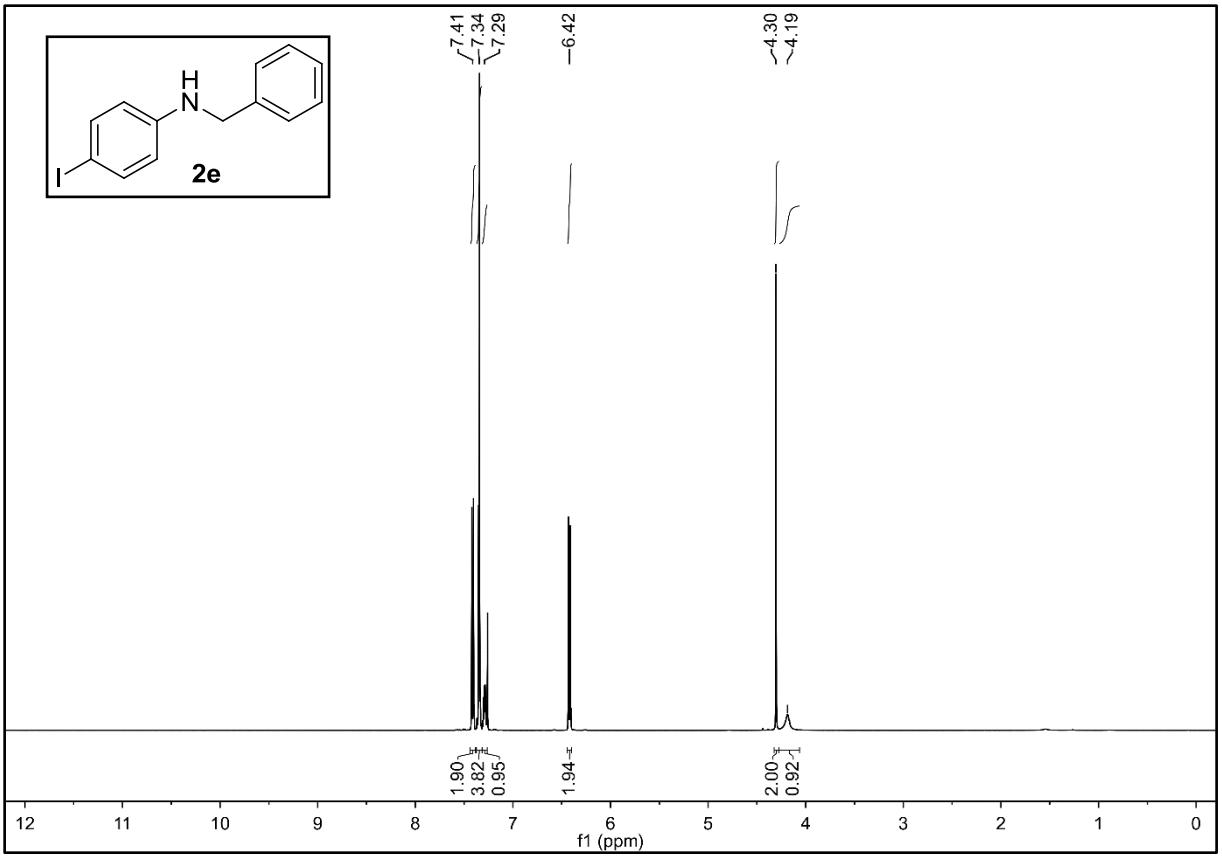
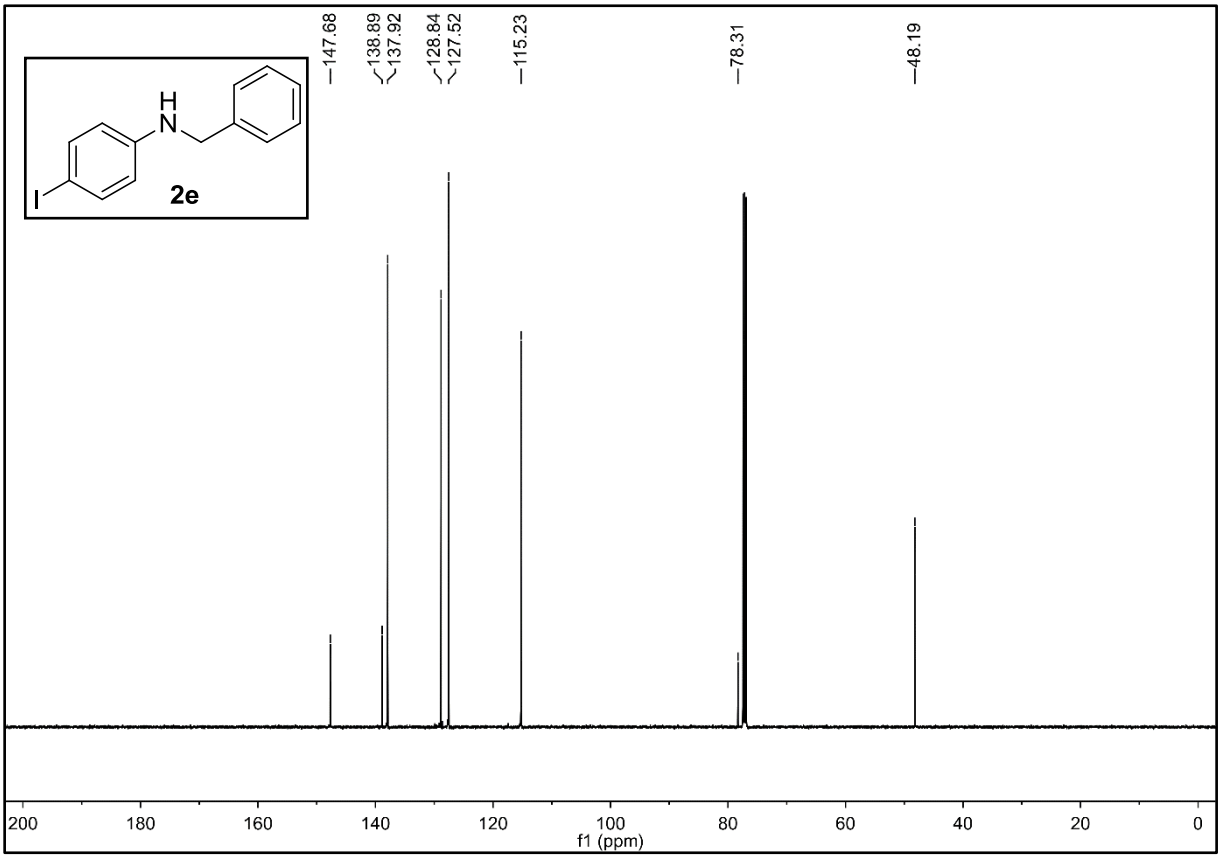
138.90
132.07
128.84
127.56
127.54
114.64
109.37
48.42
H
N
Br
2d
200
180
160
140
120
100
80
60
40
20
0
f1 (ppm)


7.41
7.34
7.29
6.42
4.30
4.19
1.90
3.82
0.95
1.94
2.00
0.92
2e
f1 (ppm)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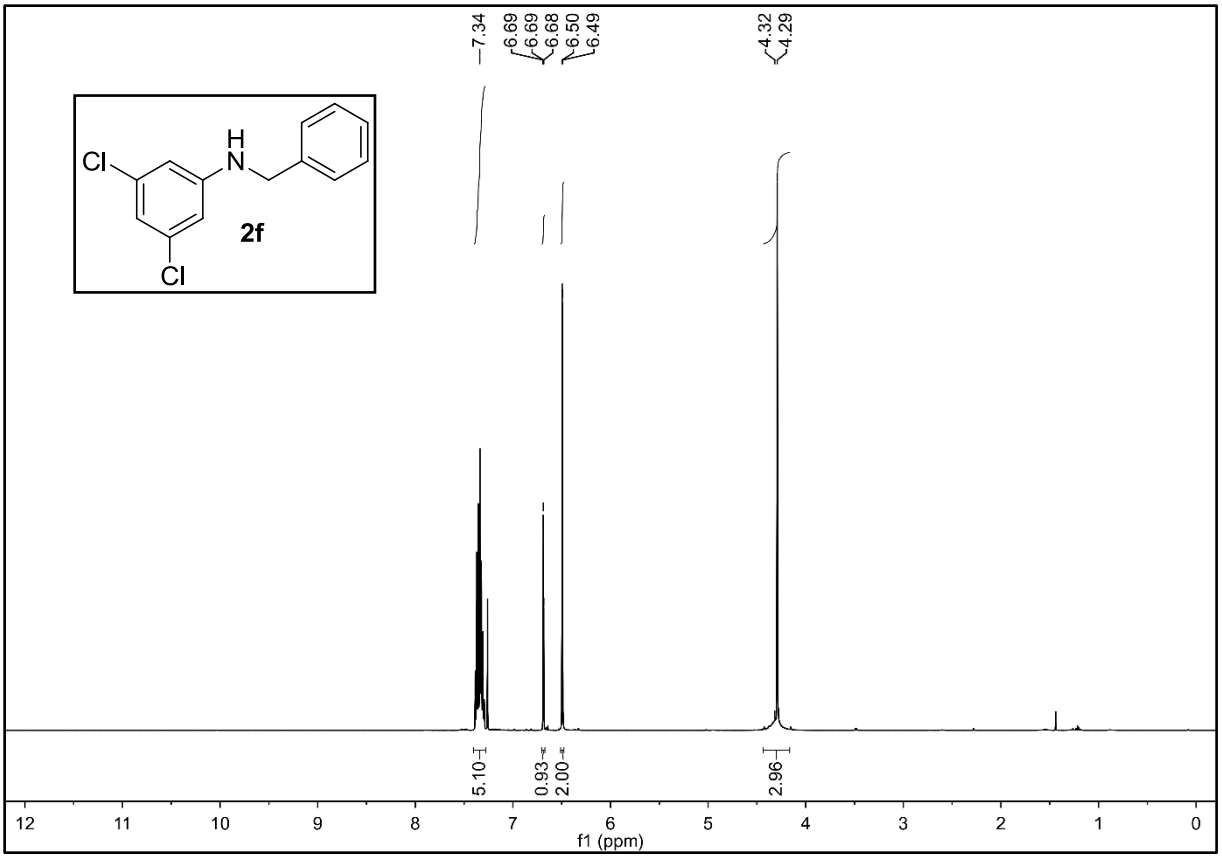
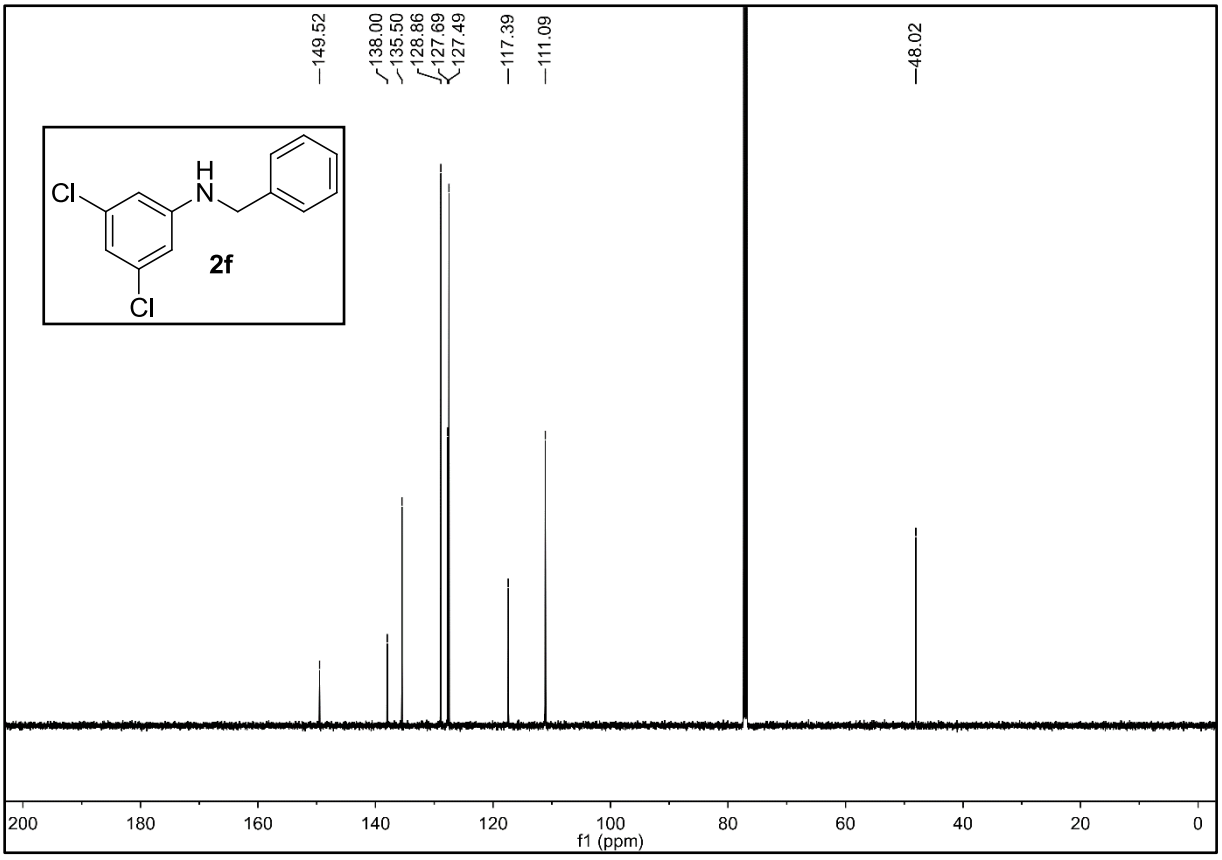
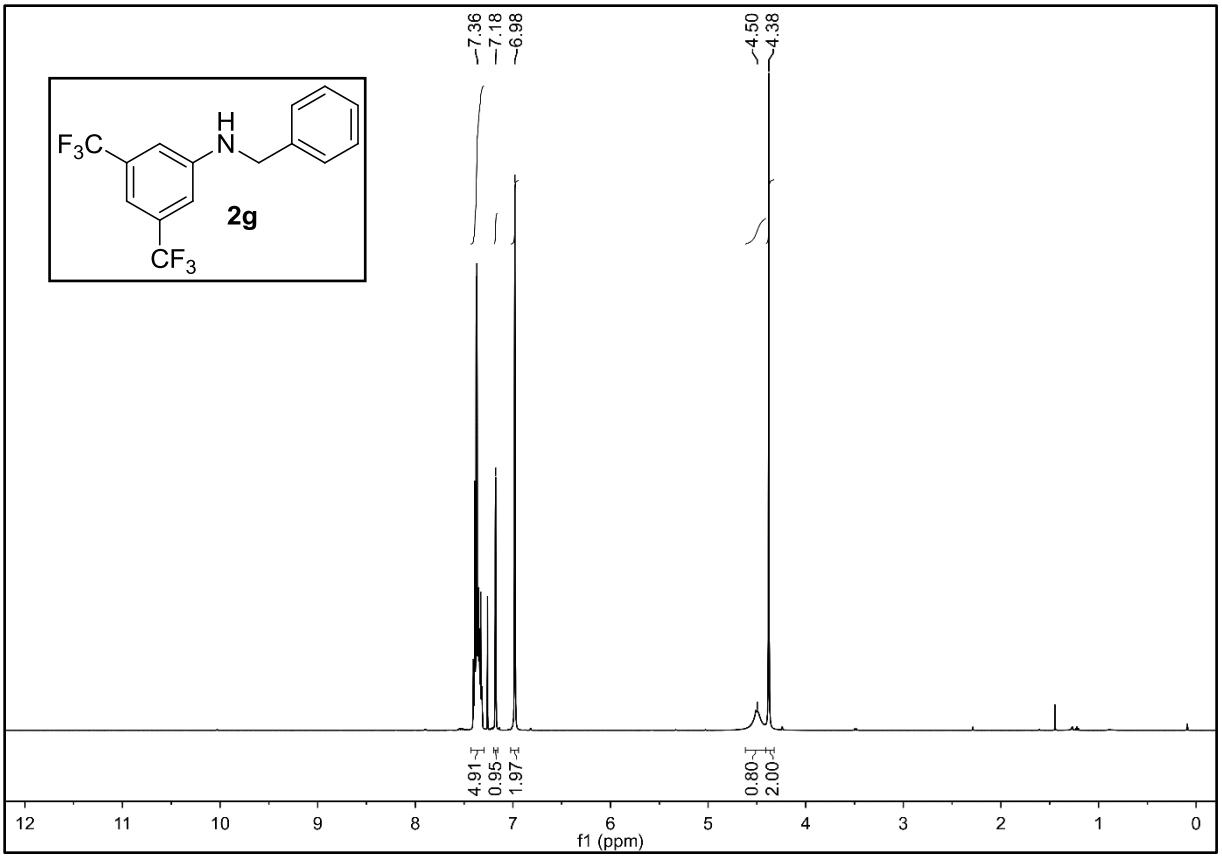
127.52
115.23
78.31
48.19
2e
f1 (ppm)


7.34
6.69
6.69
6.68
6.50
6.49
4.32
4.29
Cl
H
N
Cl
2f
5.10
0.93
2.00
2.96
12
11
10
9
8
7
6
5
4
3
2
1
0
f1 (ppm)


149.52
138.00
135.50
128.86
127.69
127.49
117.39
111.09
48.02
Cl
H
N
Cl
2f
200
180
160
140
120
100
80
60
40
20
0
f1 (ppm)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N
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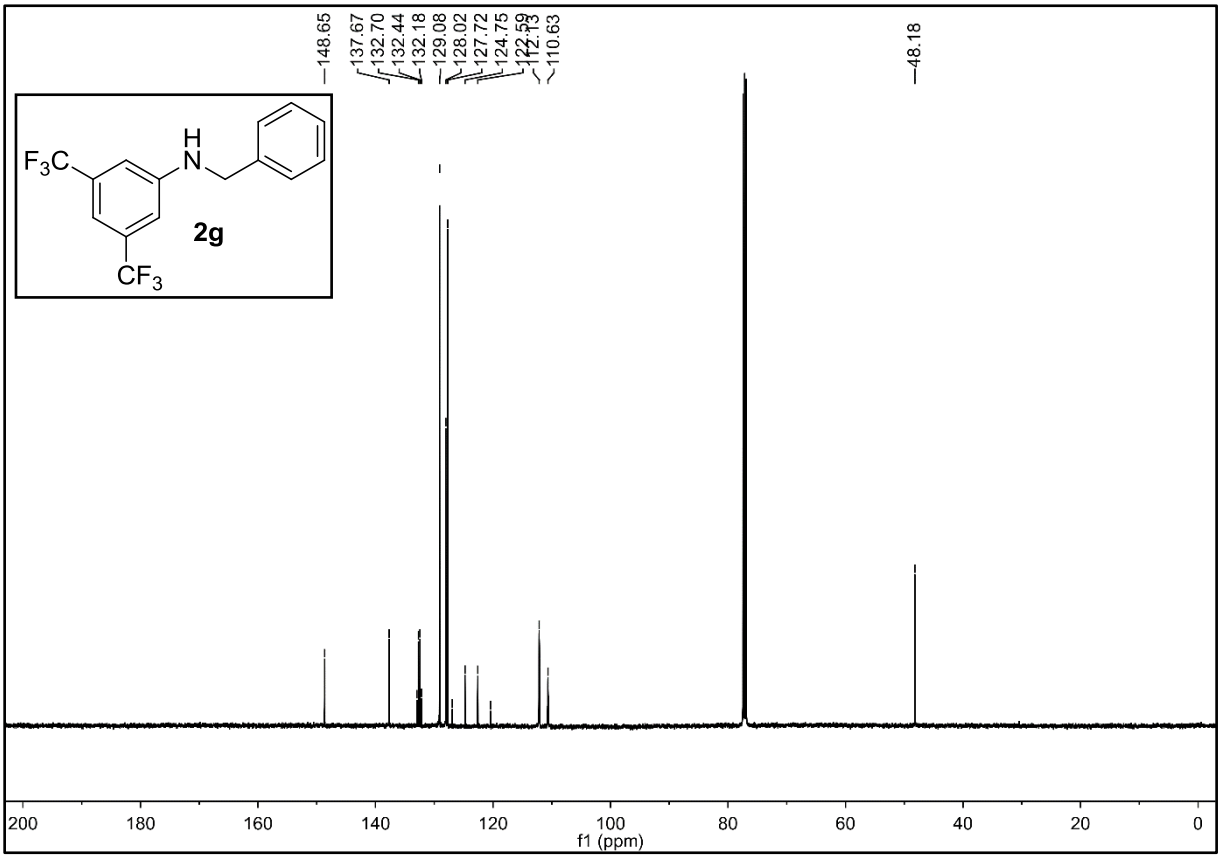
11
10
9
8
7
6
5
4
3
2
1
0
f1 (ppm)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110.63
48.18
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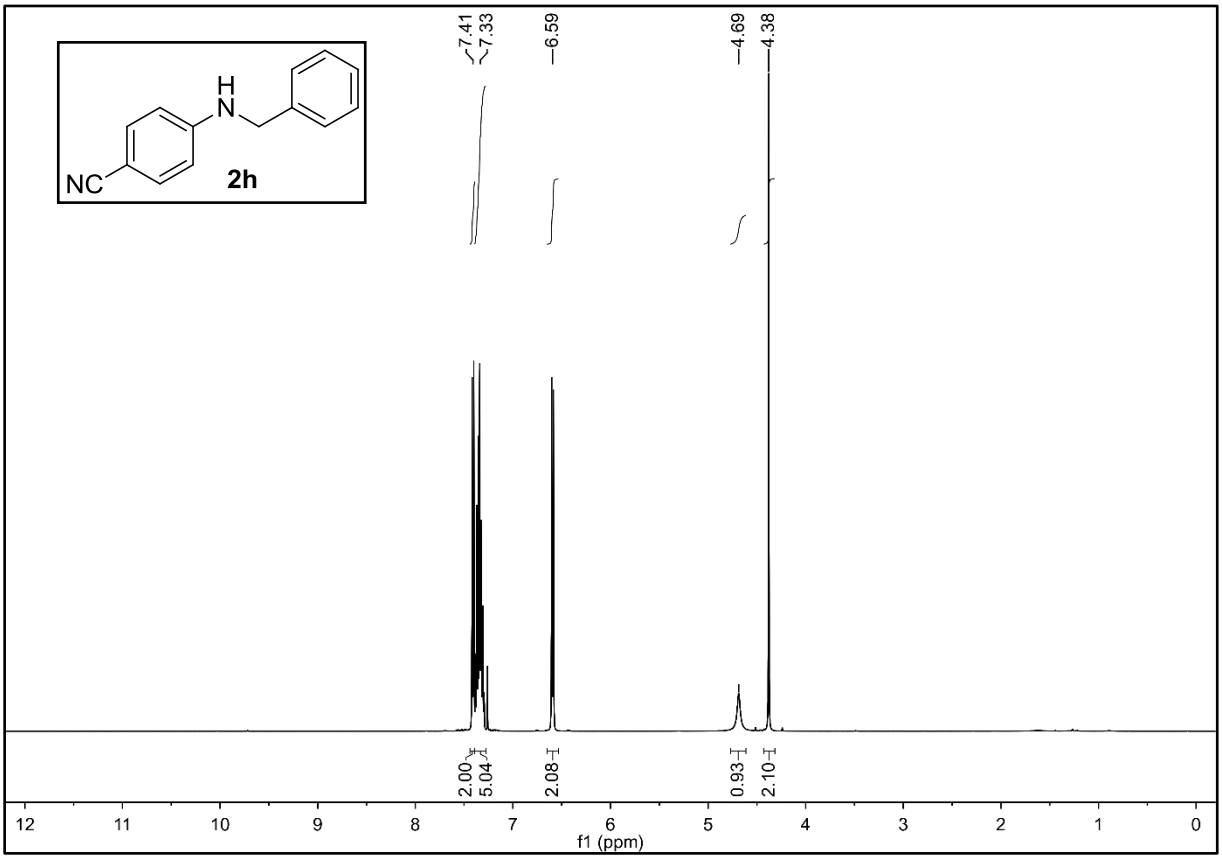
F3C
CF3
H
N
200
180
160
140
120
100
80
60
40
20
0
f1 (ppm)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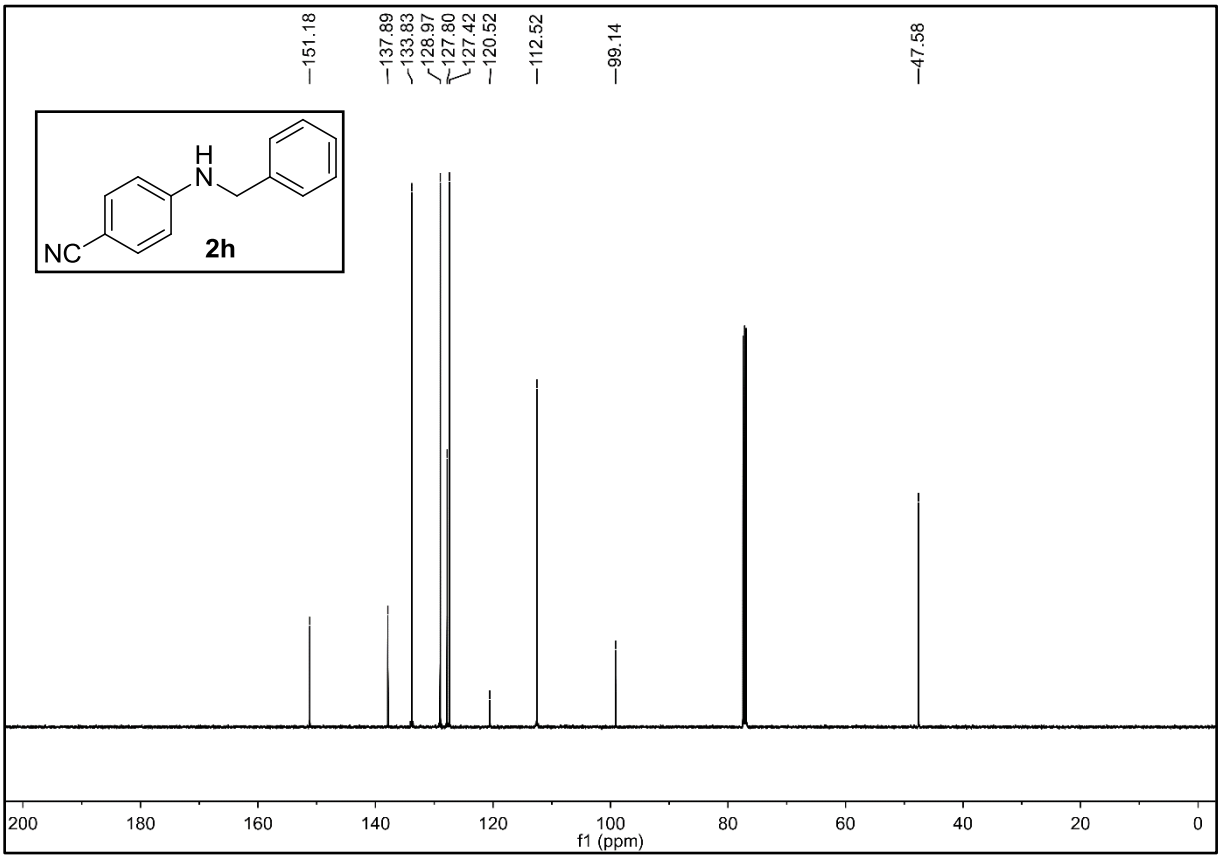
4.38
2.00
5.04
2.08
0.93
2.10
12
11
10
9
8
7
6
5
4
3
2
1
0
f1 (ppm)
NC
2h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127.42
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99.14
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180
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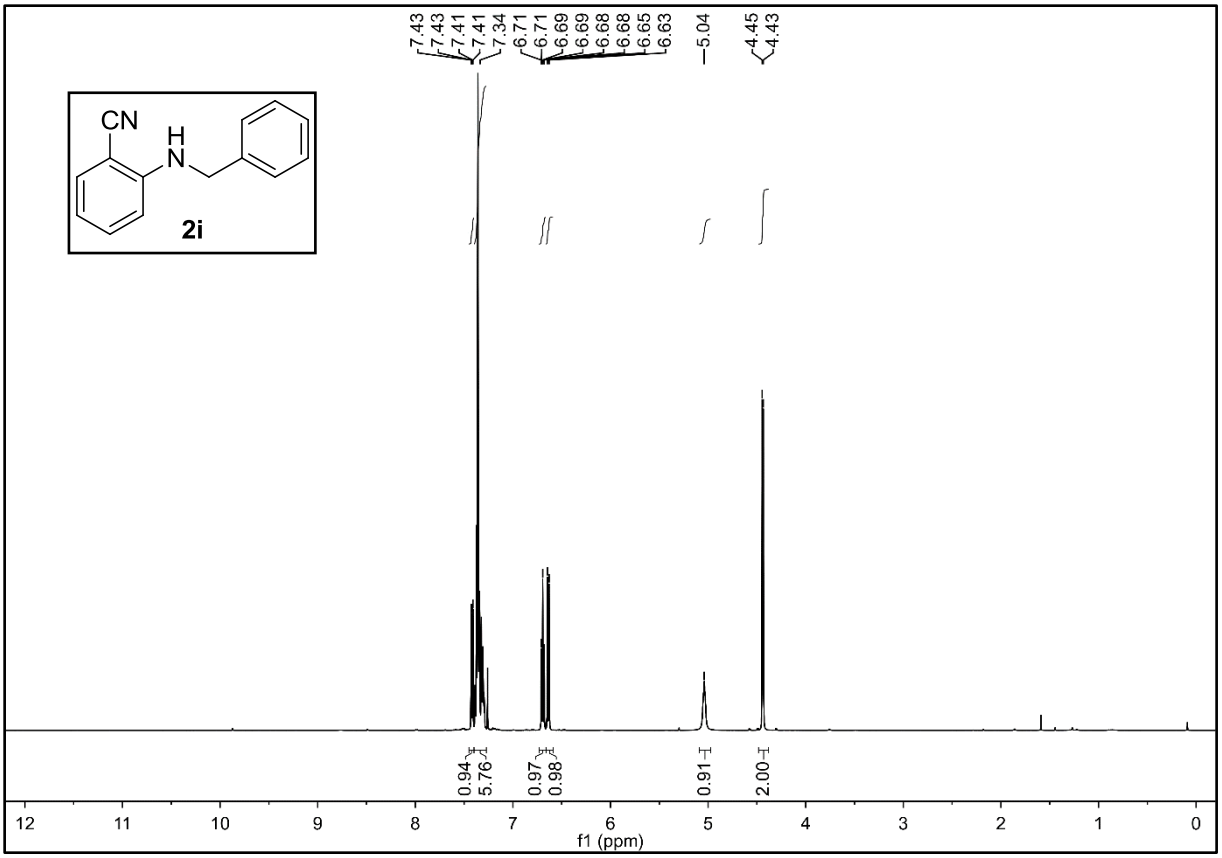
140
120
100
80
60
40
20
0
f1 (ppm)
NC
2h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6.71
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6.69
6.68
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6.65
6.63
5.04
4.45
4.43
CN
H
N
2i
0.94
5.76
0.97
0.98
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10
9
8
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6
5
4
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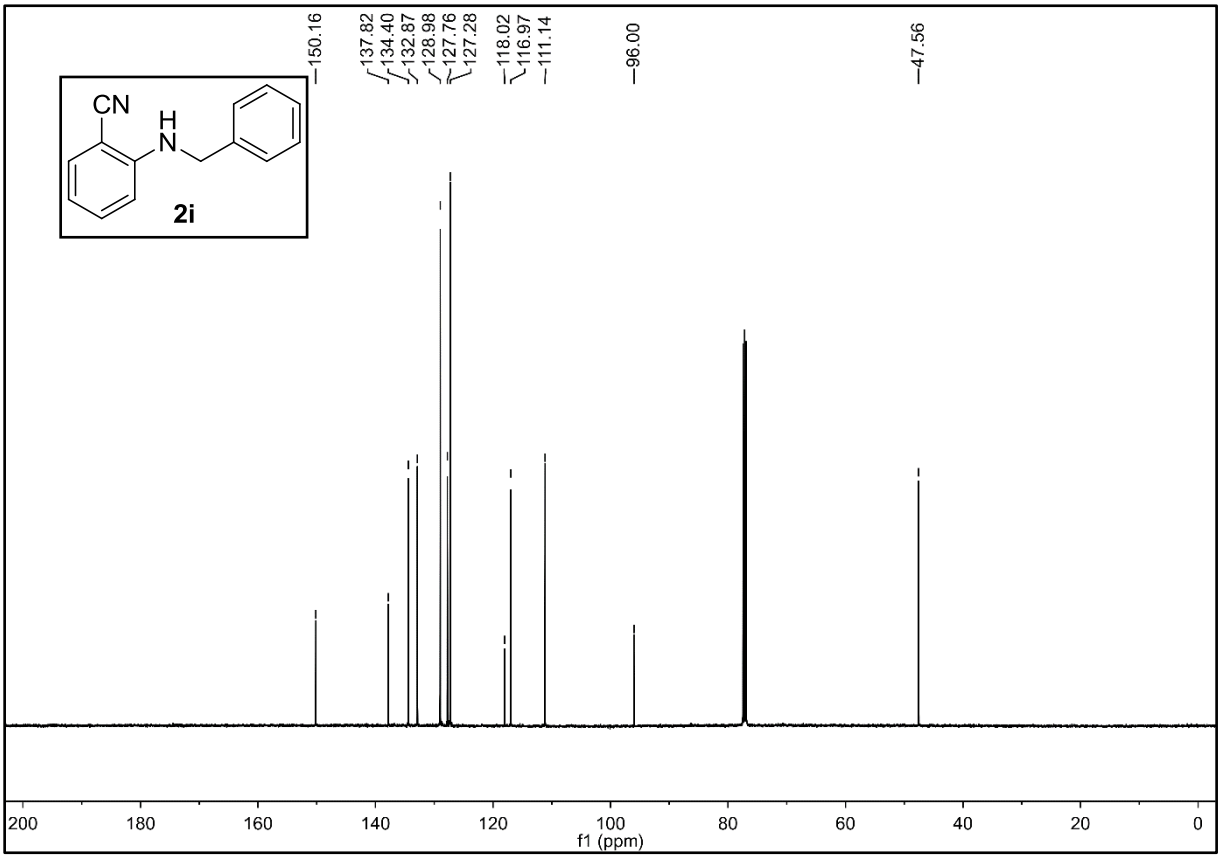
2
1
0
f1 (ppm)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118.02
116.97
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H
N
2i
200
180
160
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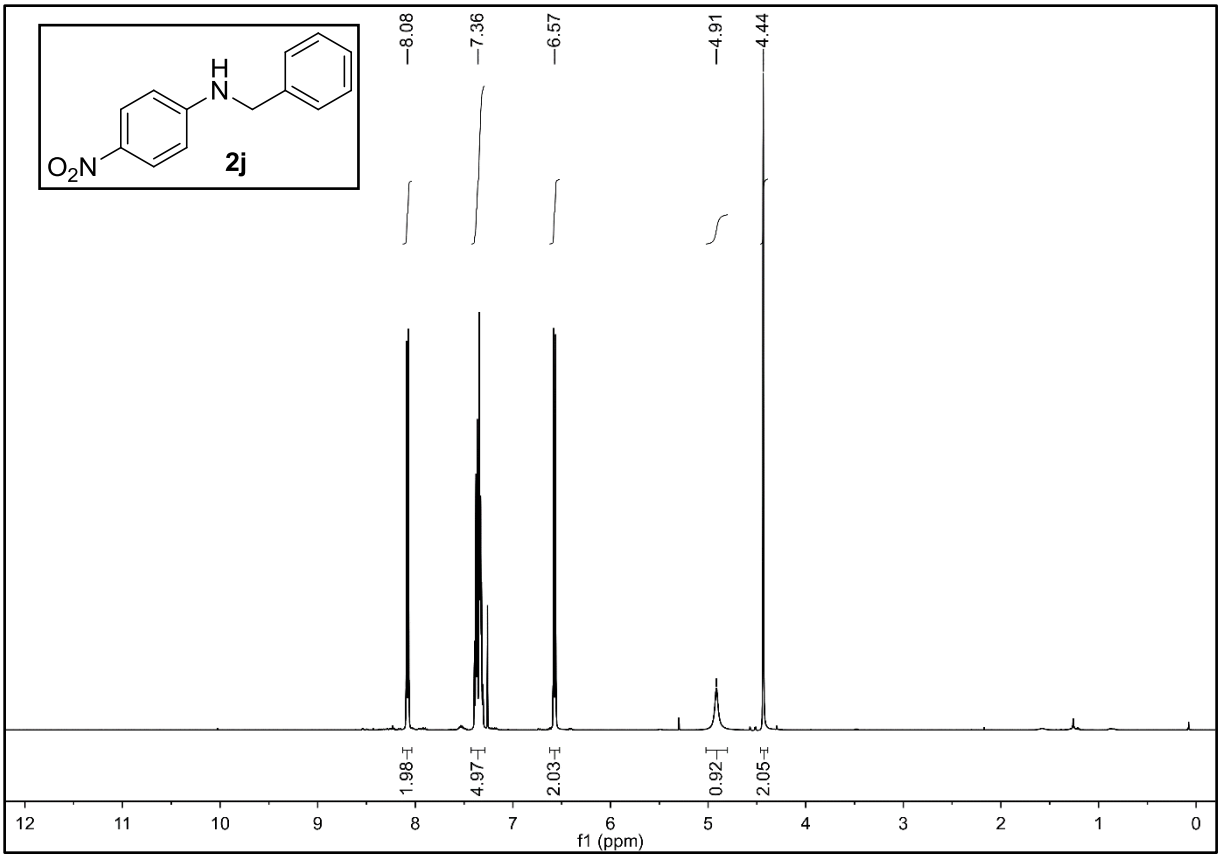
100
80
60
40
20
0
f1 (ppm)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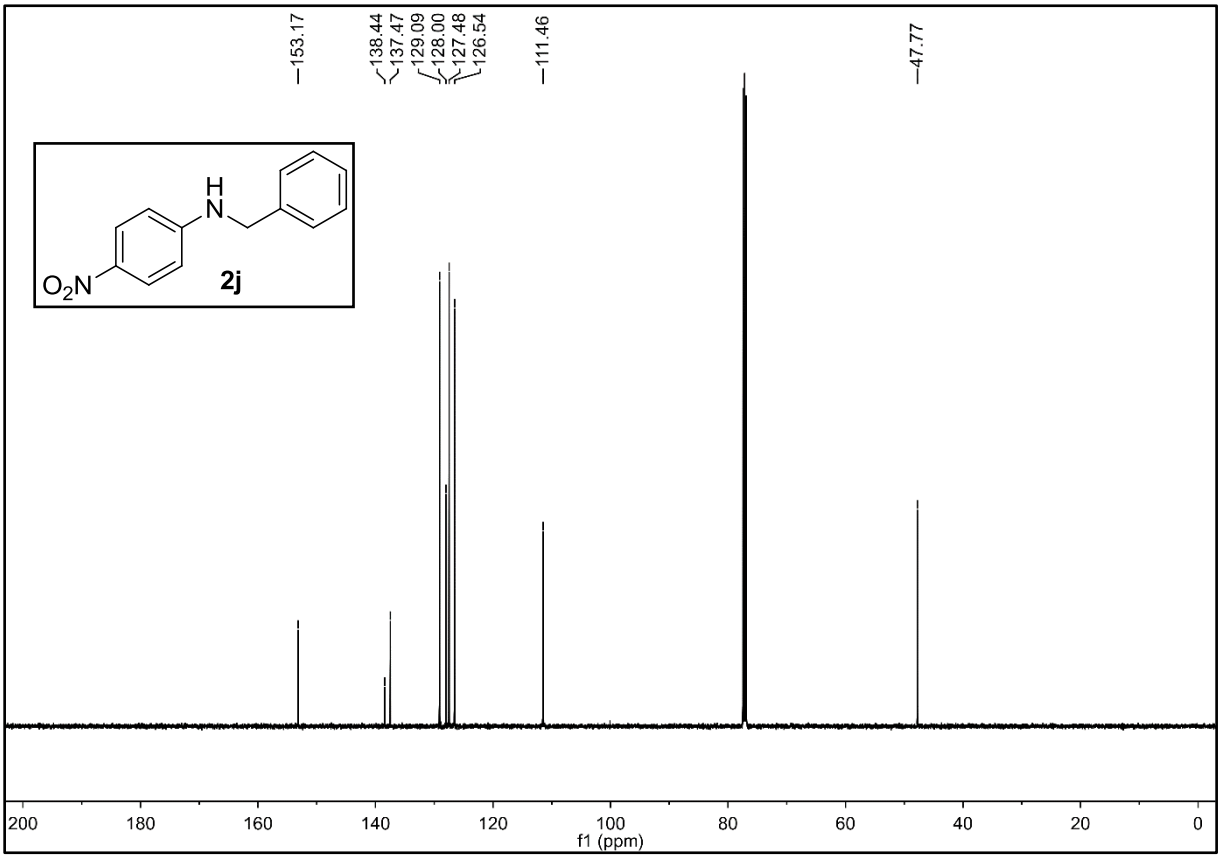
4.97
2.03
0.92
2.05
2j
f1 (ppm)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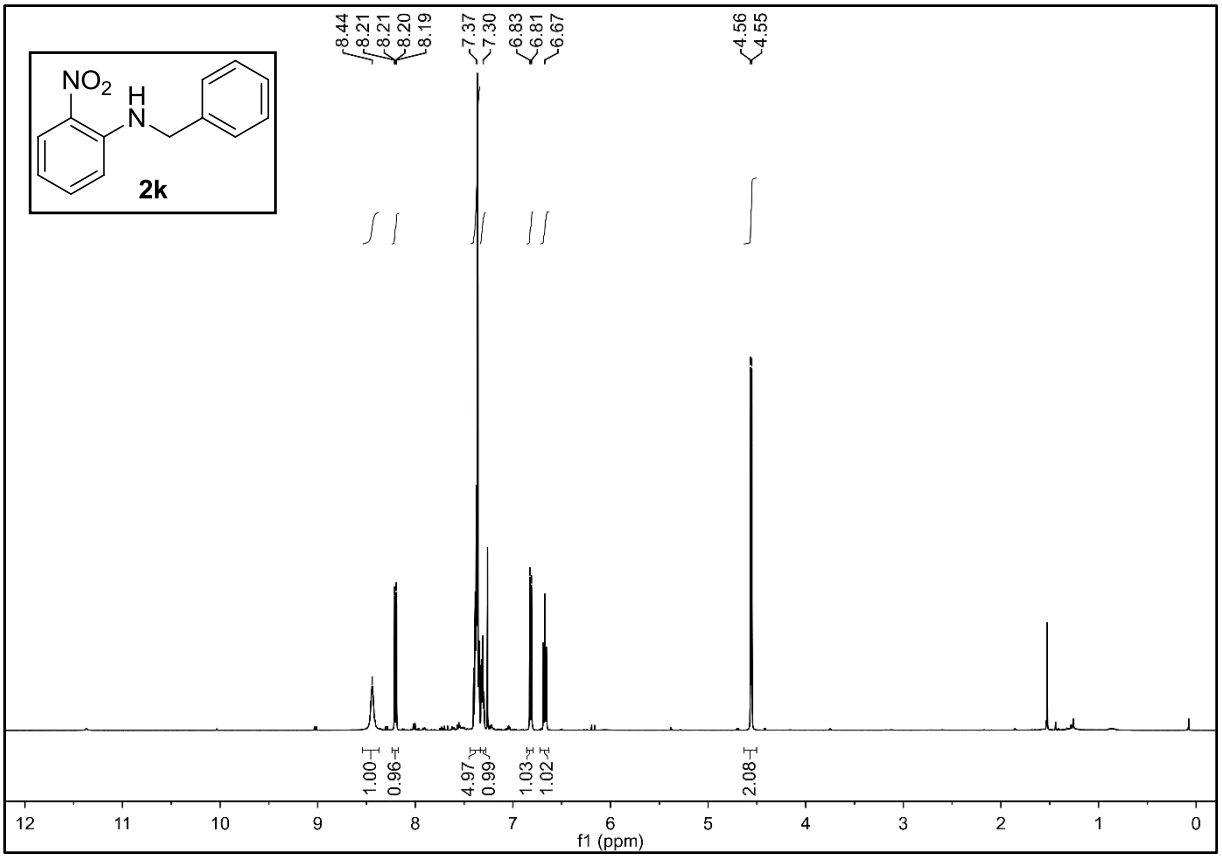
47.77
2j
f1 (ppm)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8.21
8.20
8.19
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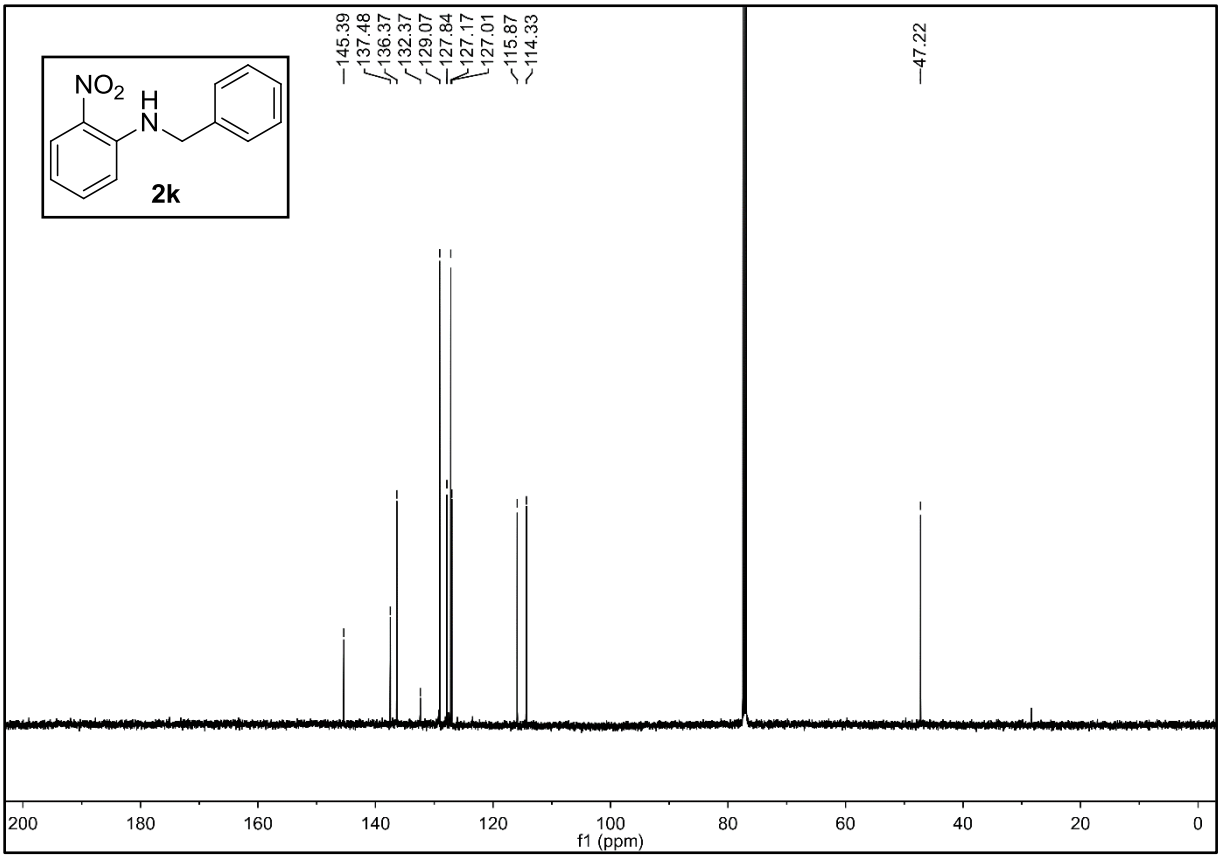
6.83
6.81
6.67
4.56
4.55
NO2
H
N
2k
1.00
0.96
4.97
0.99
1.03
1.02
2.08
12
11
10
9
8
7
6
5
4
3
2
1
0
f1 (ppm)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129.07
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114.33
47.22
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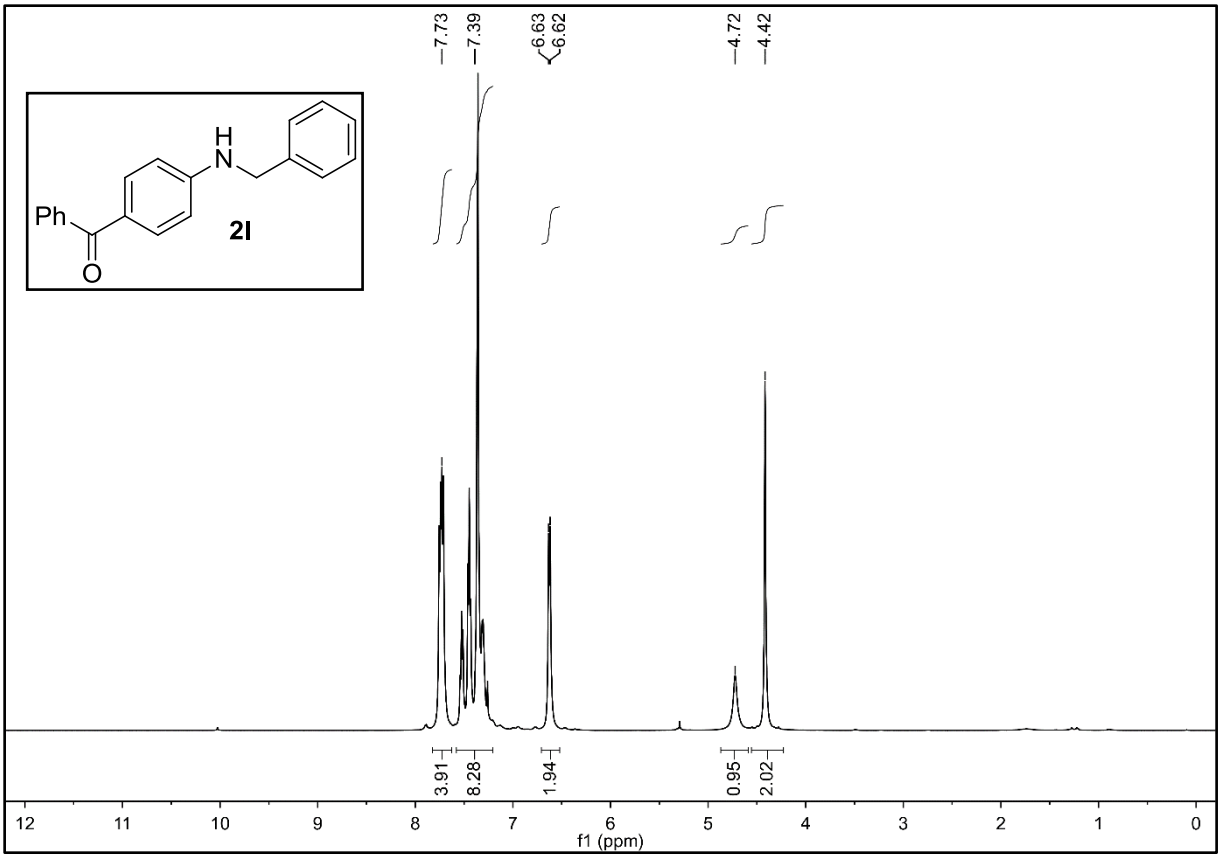
H
N
2k
200
180
160
140
120
100
80
60
40
20
0
f1 (ppm)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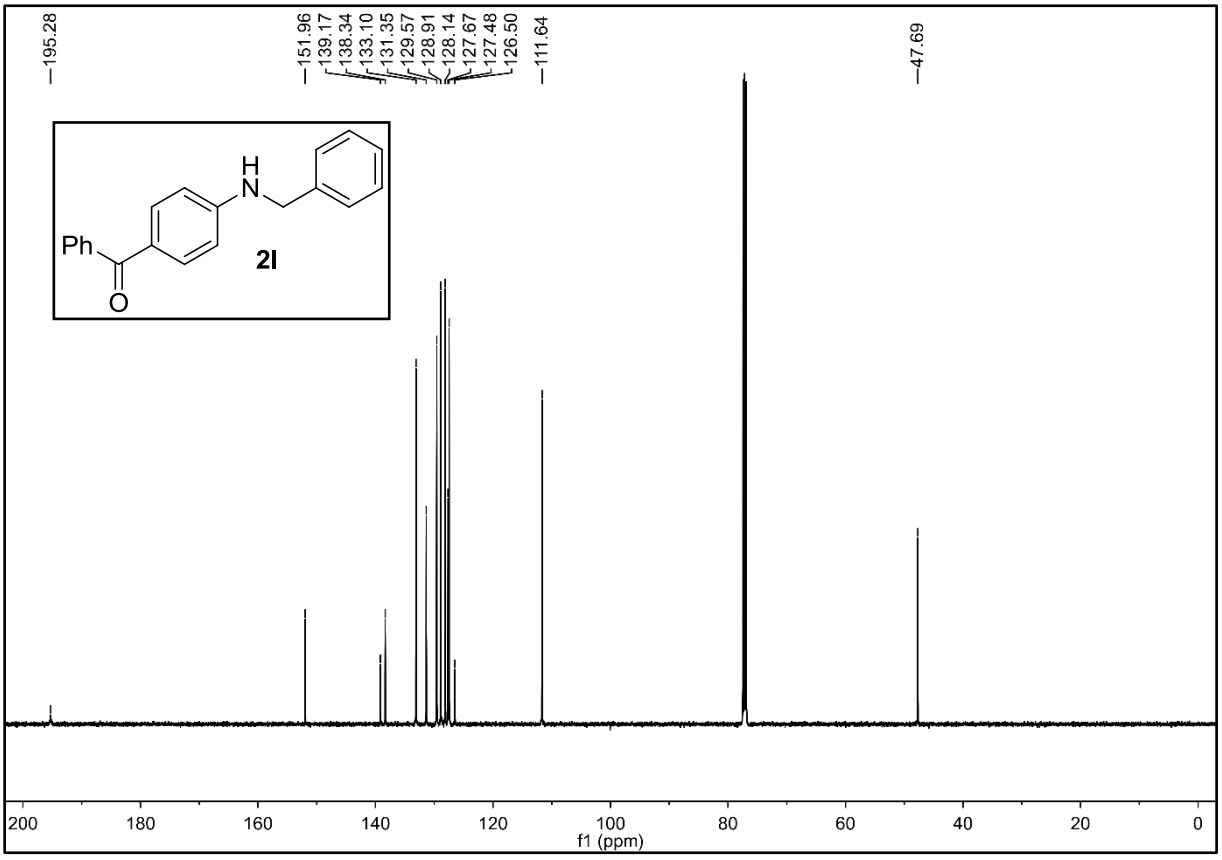
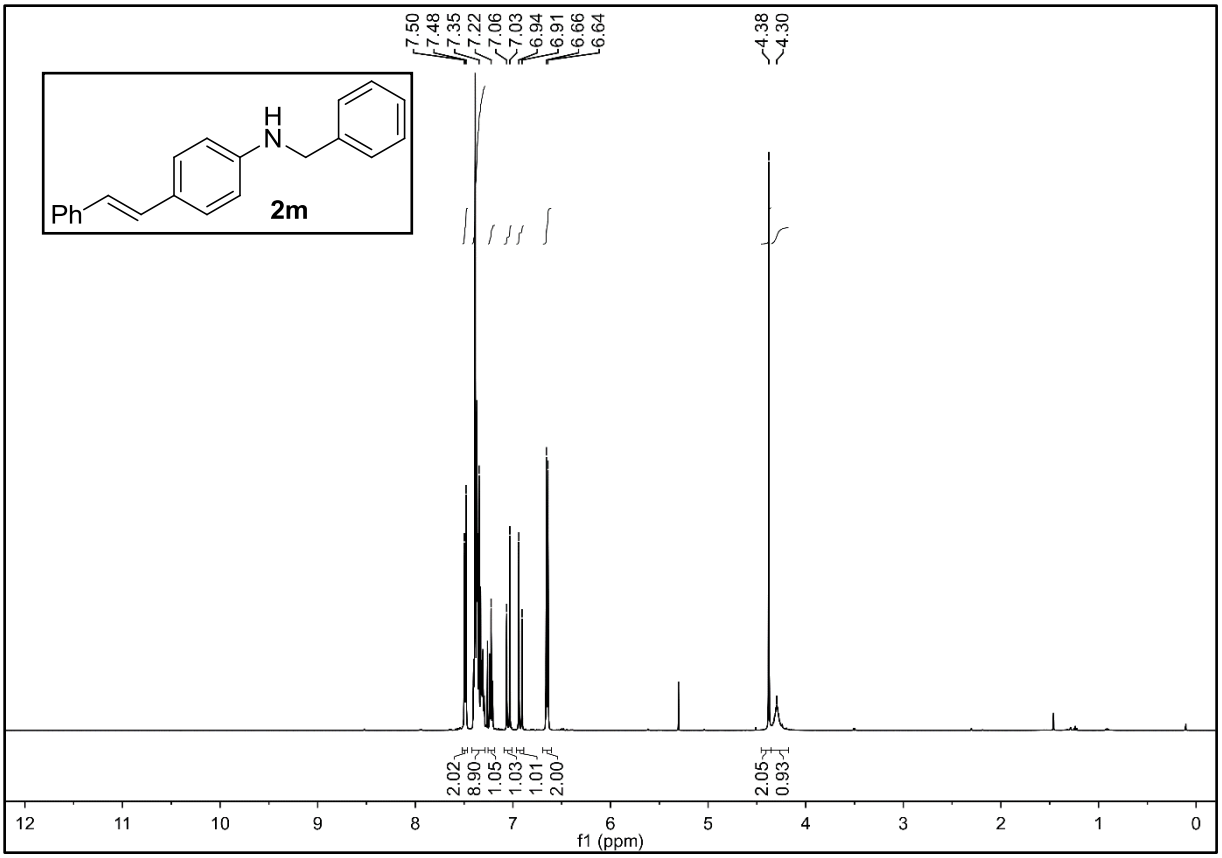
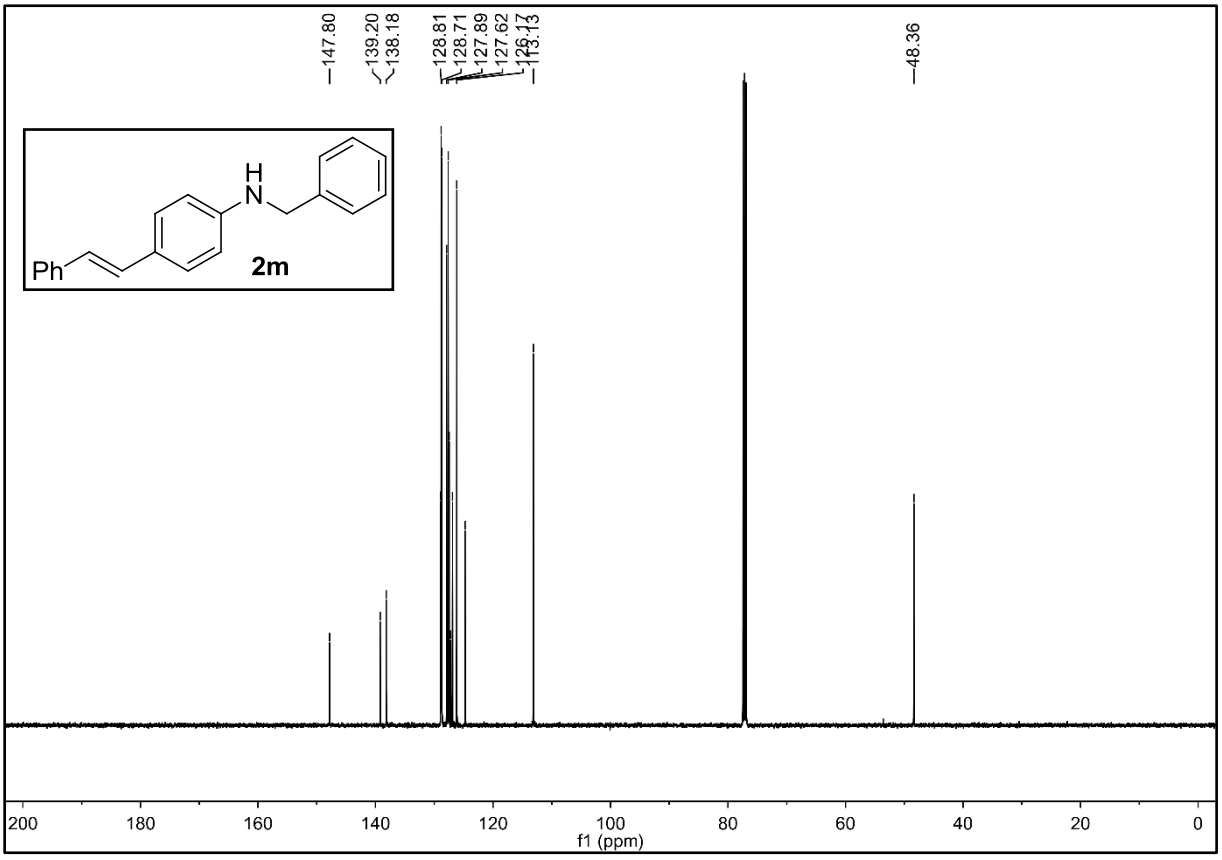
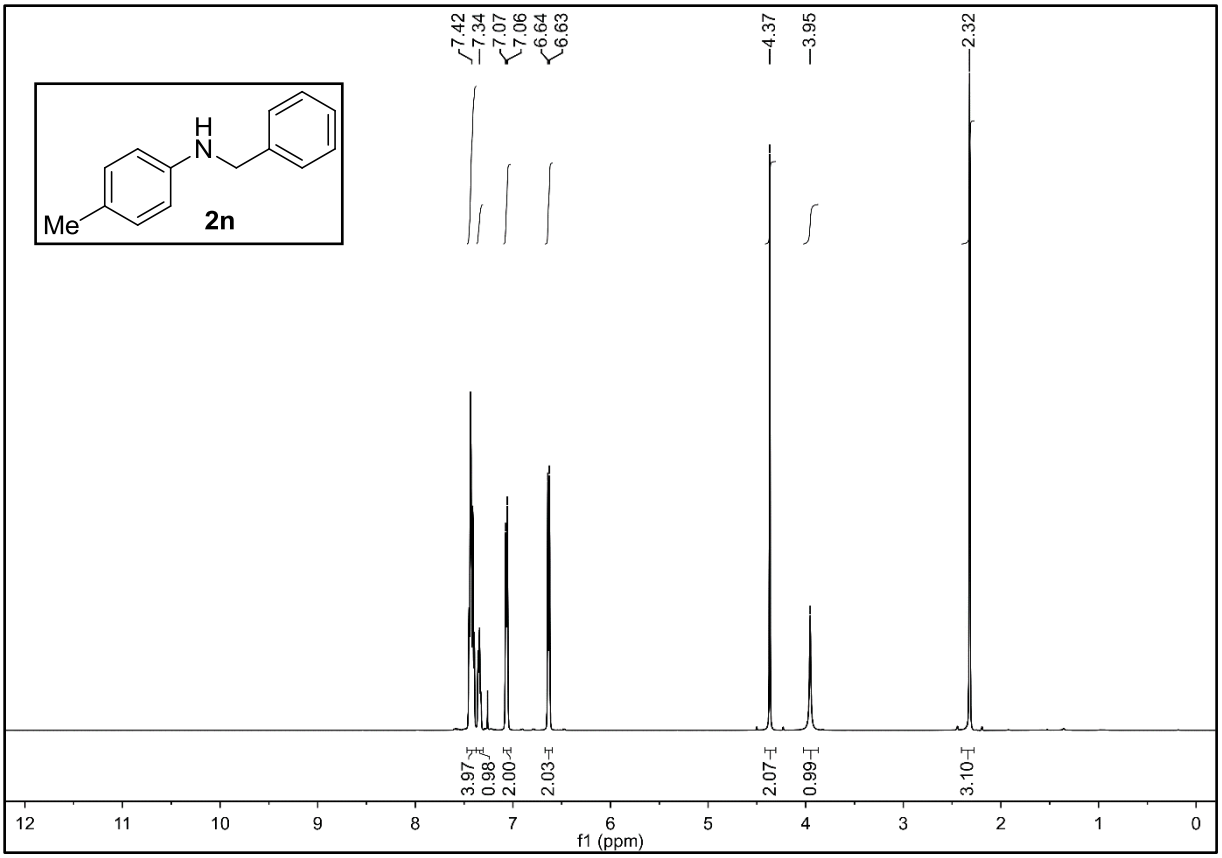
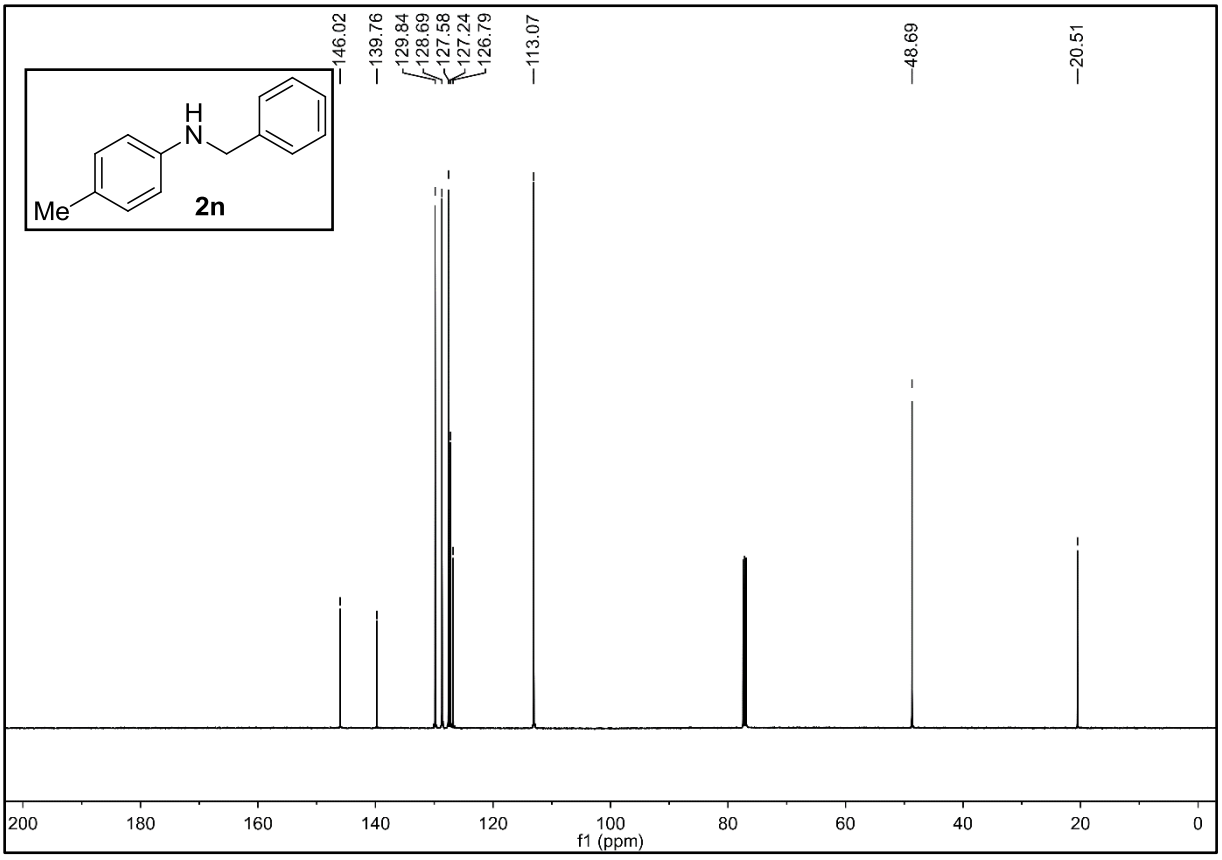
6.62
4.72
4.42
H
N
Ph
O
2l
3.91
8.28
1.94
0.95
2.02
f1 (ppm)

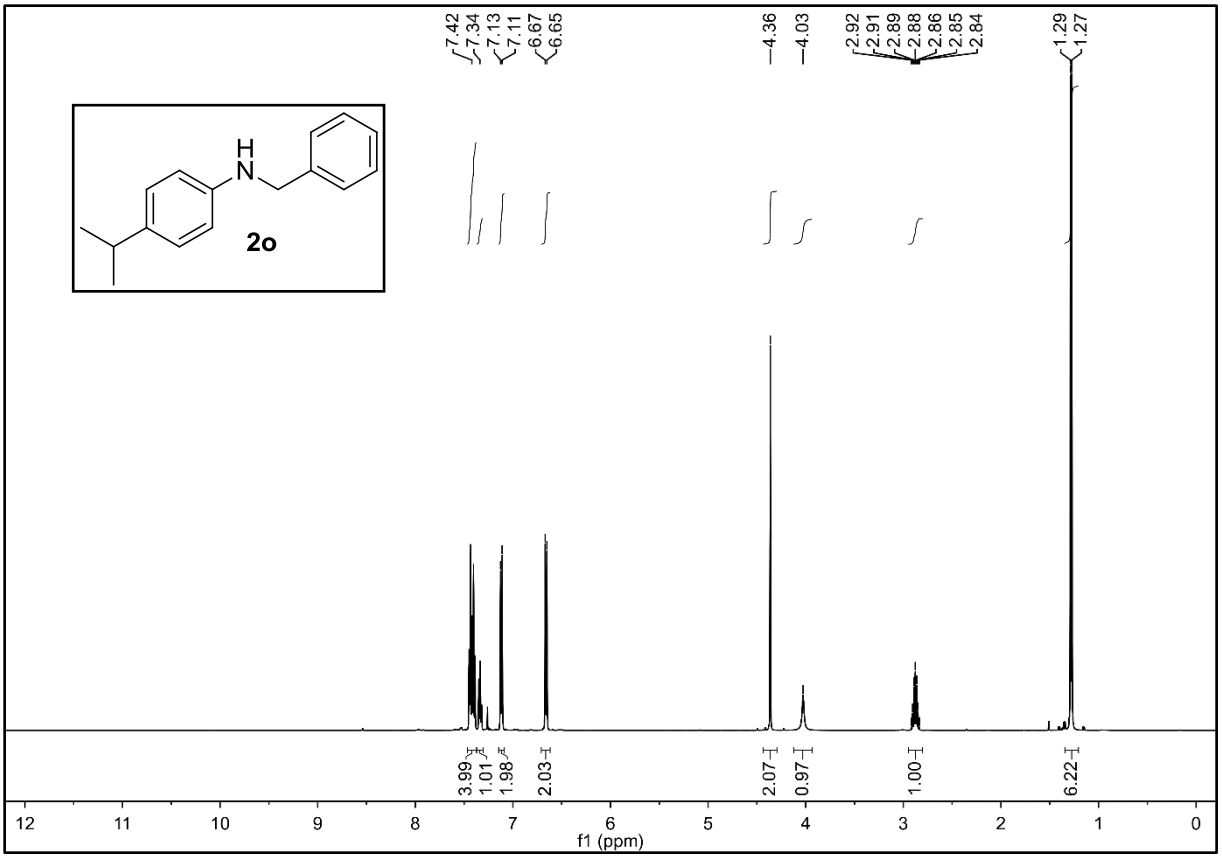

195.28
151.96
139.17
138.34
133.10
131.35
129.57
128.91
128.14
127.67
127.48
126.50
111.64
47.69
H
N
Ph
O
2l
f1 (ppm)

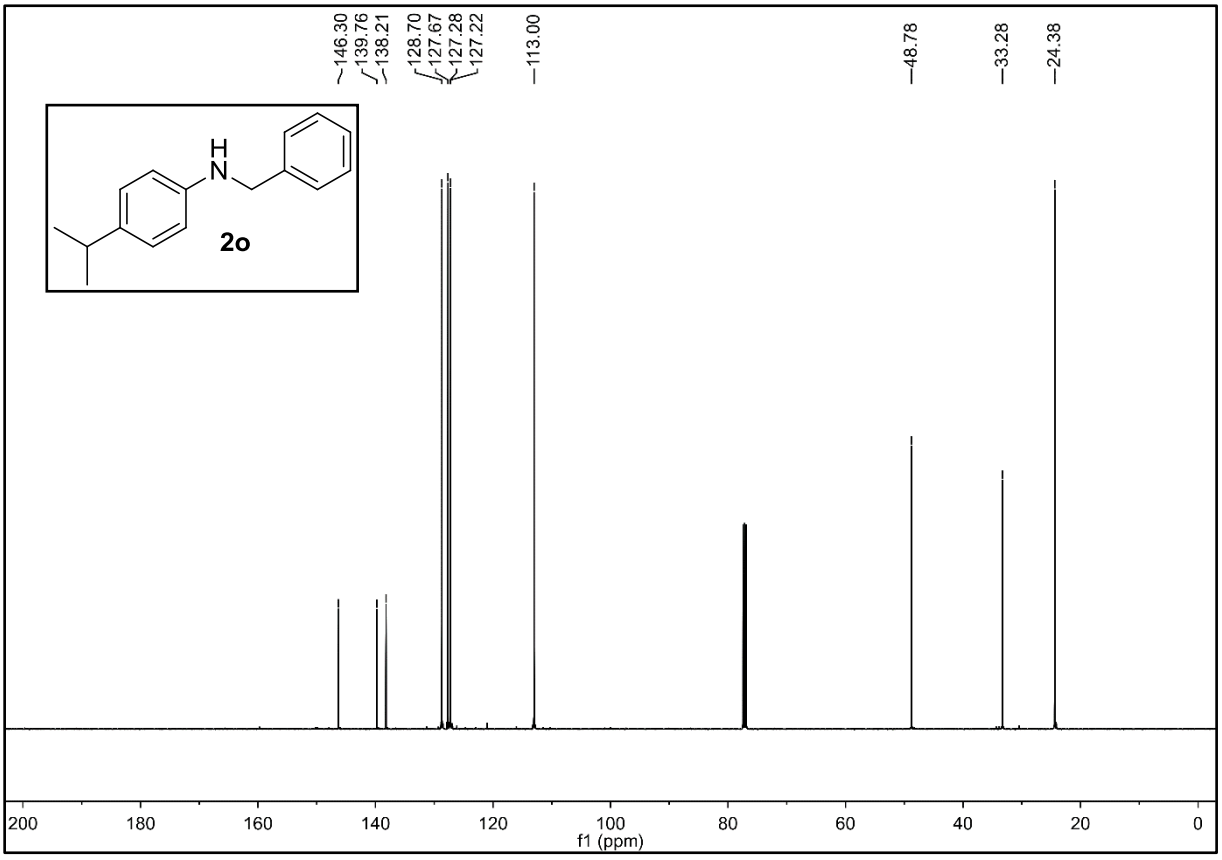

7.50
7.48
7.35
7.22
7.06
7.03
6.94
6.91
6.66
6.64
4.38
4.30
H
N
Ph
2m
2.02
8.90
1.05
1.03
1.01
2.00
2.05
0.93
12
11
10
9
8
7
6
5
4
3
2
1
0
f1 (ppm)

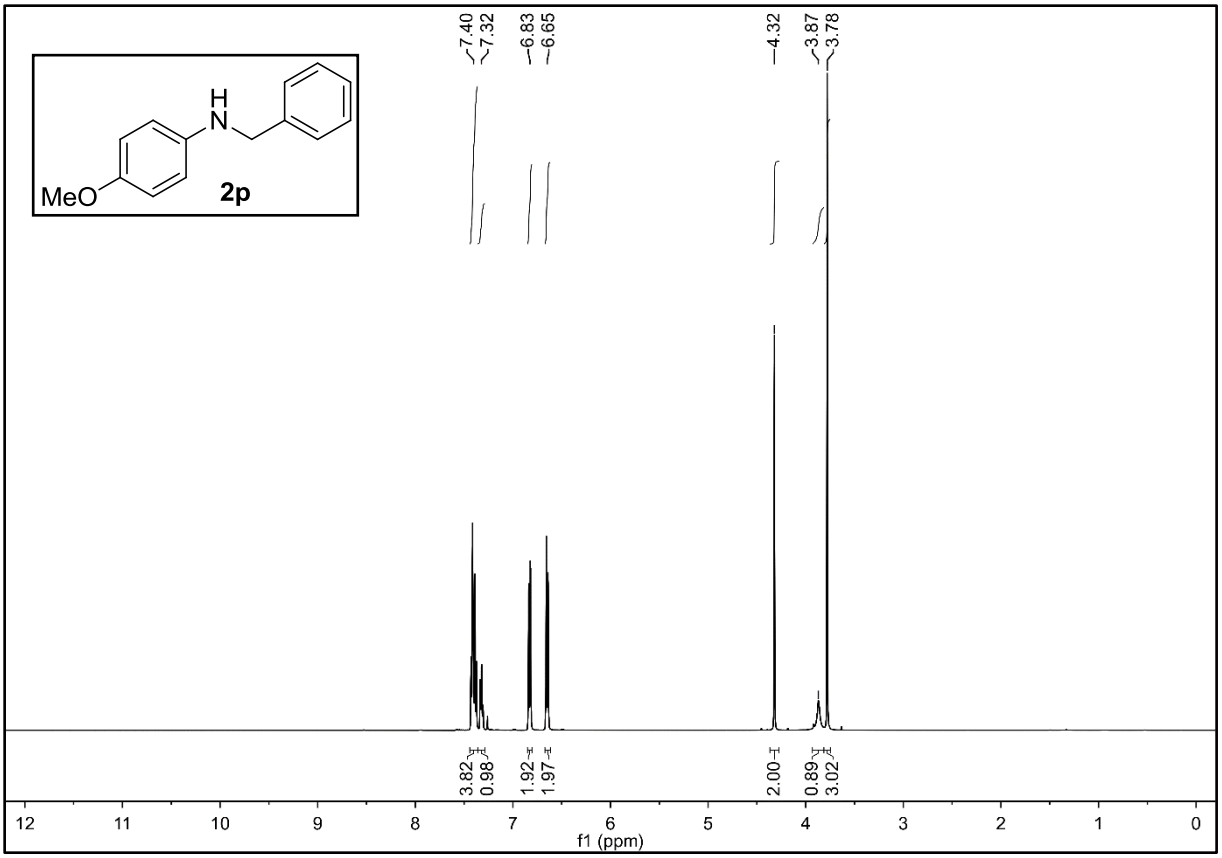

147.80
139.20
138.18
128.81
128.71
127.89
127.62
126.17
113.13
48.36
H
N
Ph
2m
200
180
160
140
120
100
80
60
40
20
0
f1 (ppm)

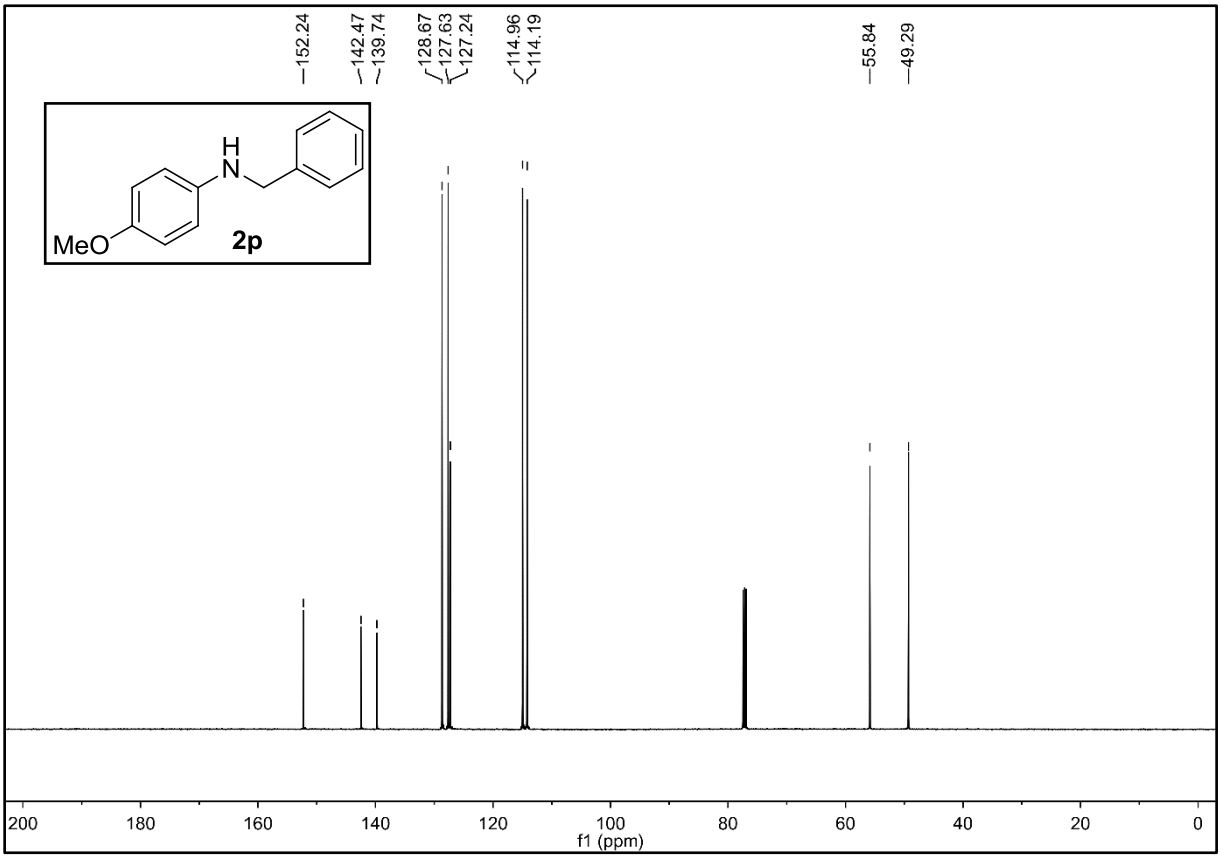

7.42
7.34
7.07
7.06
6.64
6.63
4.37
3.95
2.32
3.97
0.98
2.00
2.03
2.07
0.99
3.10
H
N
Me
2n
12
11
10
9
8
7
6
5
4
3
2
1
0
f1 (ppm)

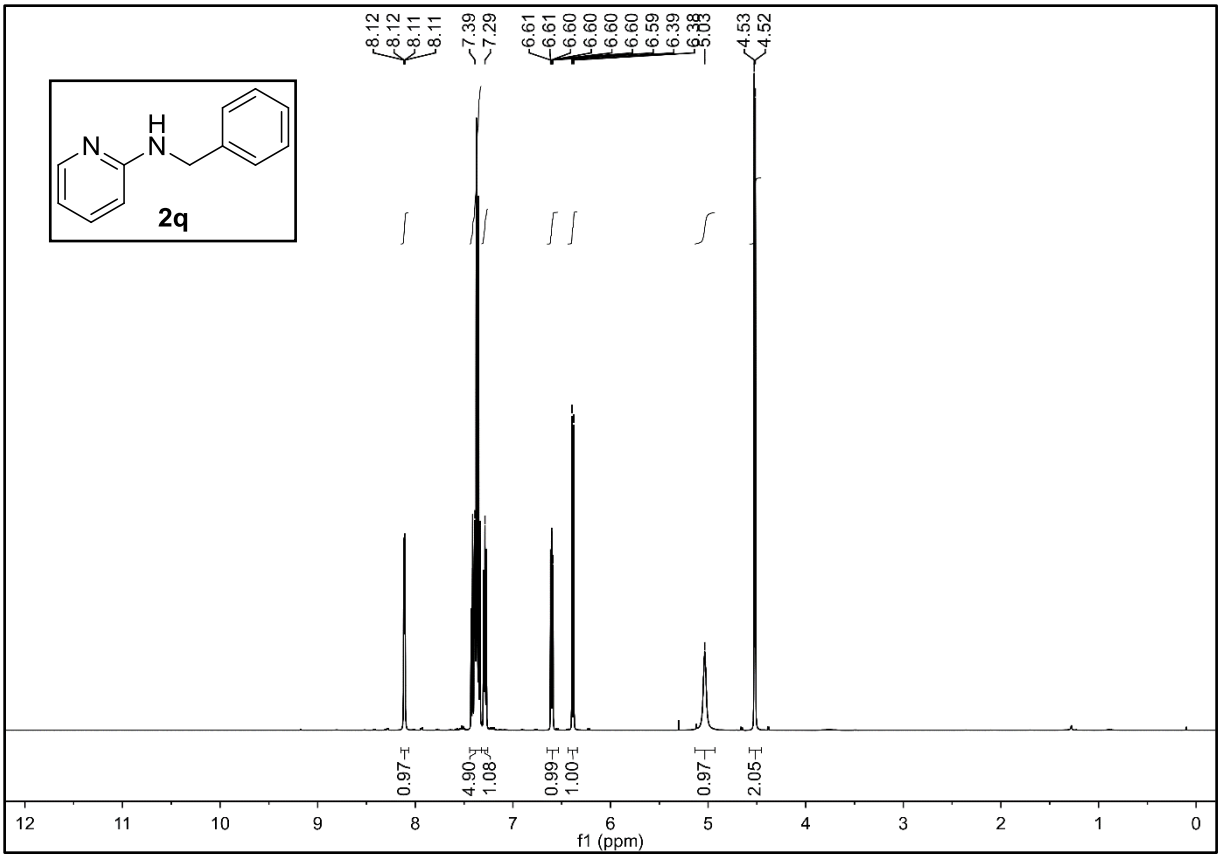

146.02
139.76
129.84
128.69
127.58
127.24
126.79
113.07
48.69
20.51
H
N
Me
2n
200
180
160
140
120
100
80
60
40
20
0
f1 (ppm)

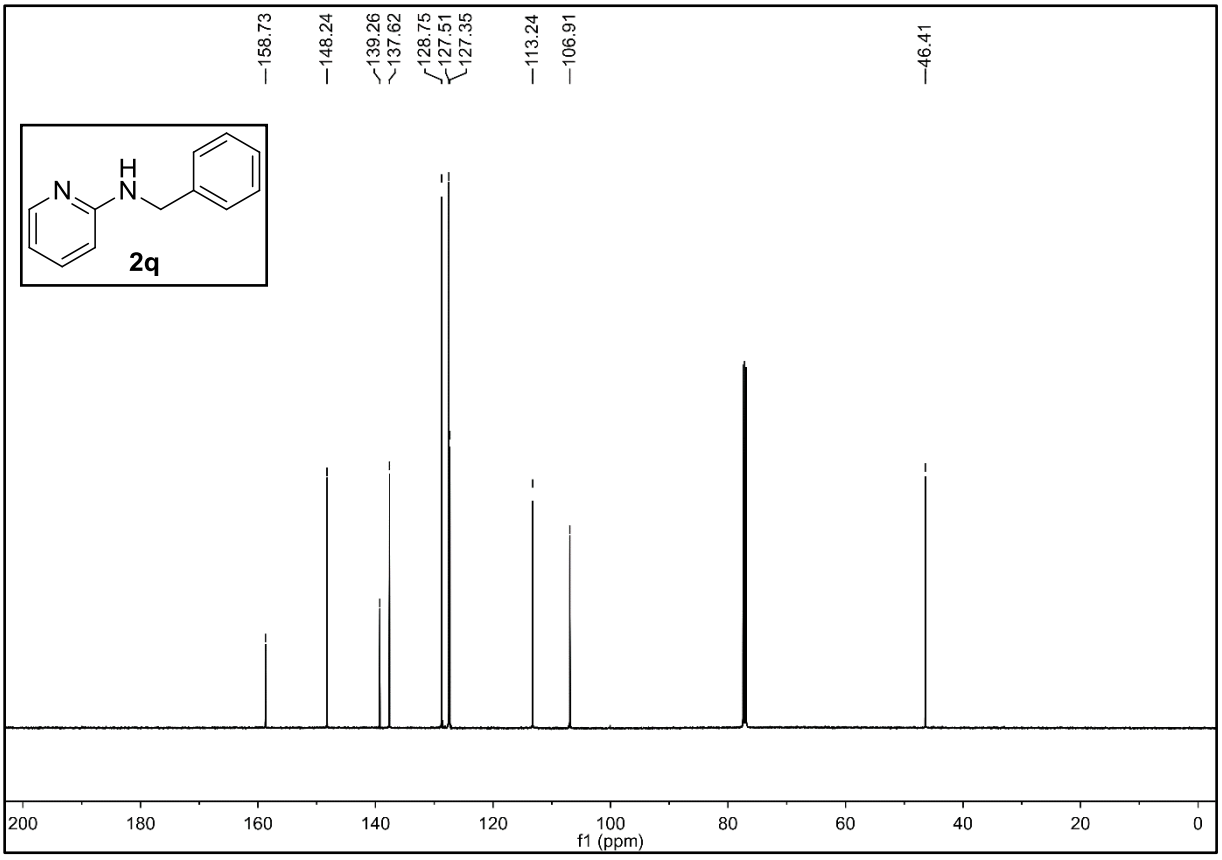

7.42
7.34
7.13
7.11
6.67
6.65
4.36
4.03
2.92
2.91
2.89
2.88
2.86
2.85
2.84
1.29
1.27
H
N
2o
3.99
1.01
1.98
2.03
2.07
0.97
1.00
6.22
12
11
10
9
8
7
6
5
4
3
2
1
0
f1 (ppm)

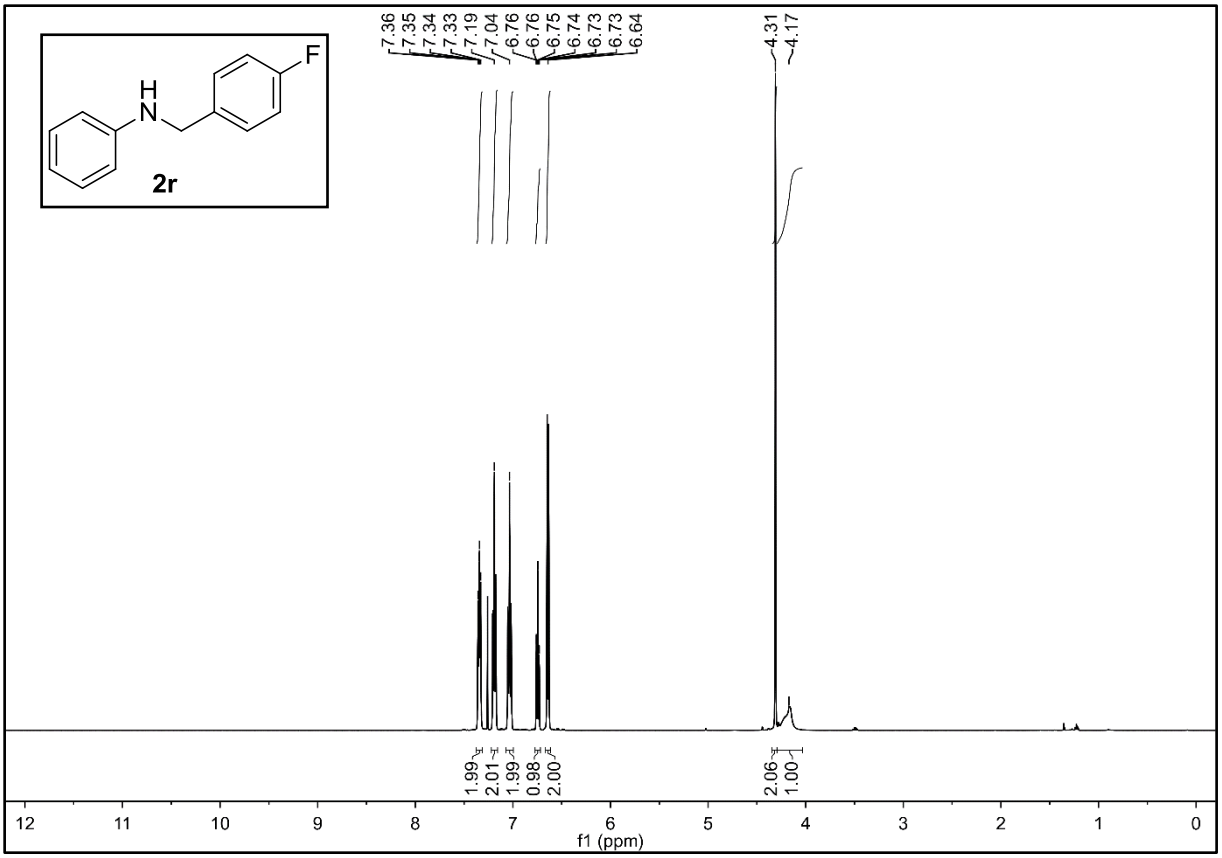

146.30
139.76
138.21
128.70
127.67
127.28
127.22
113.00
48.78
33.28
24.38
H
N
2o
200
180
160
140
120
100
80
60
40
20
0
f1 (ppm)

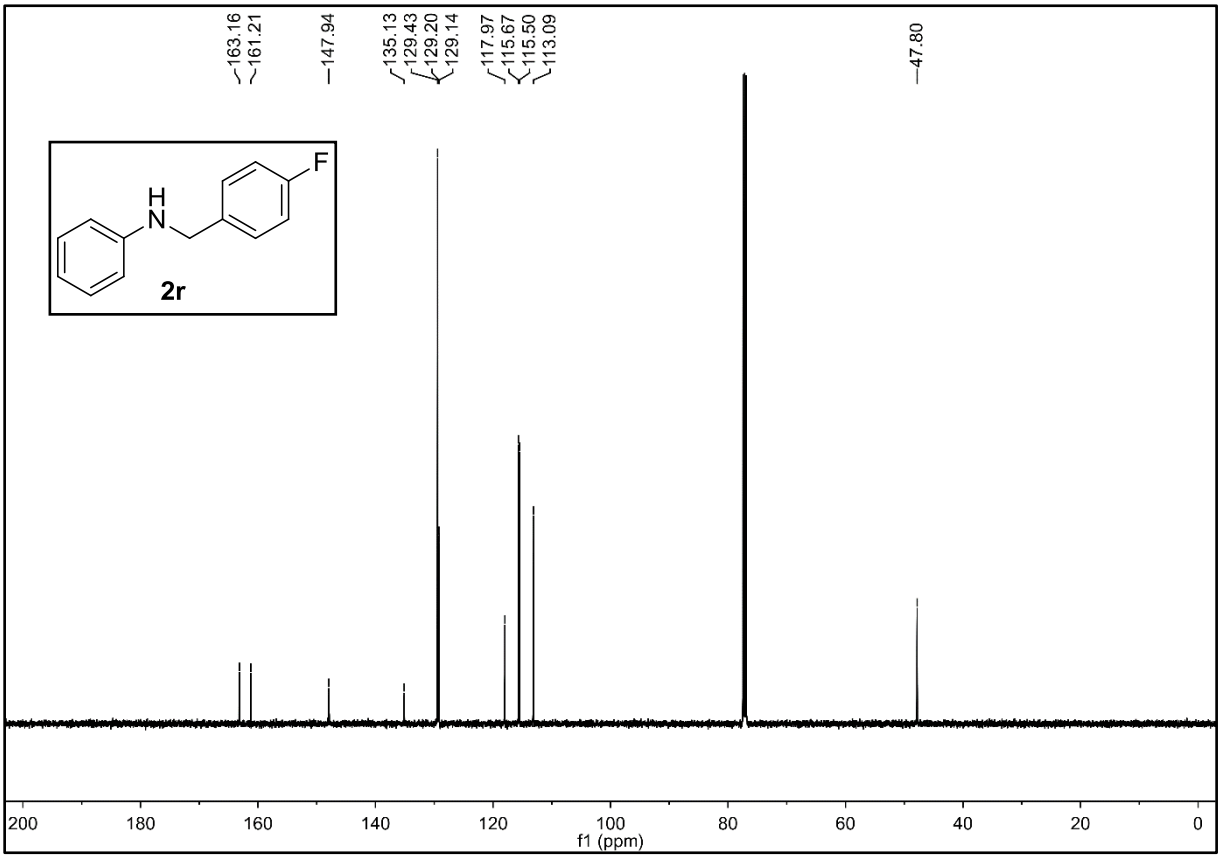

7.40
7.32
6.83
6.65
4.32
3.87
3.78
3.82
0.98
1.92
1.97
2.00
0.89
3.02
MeO
2p
f1 (ppm)

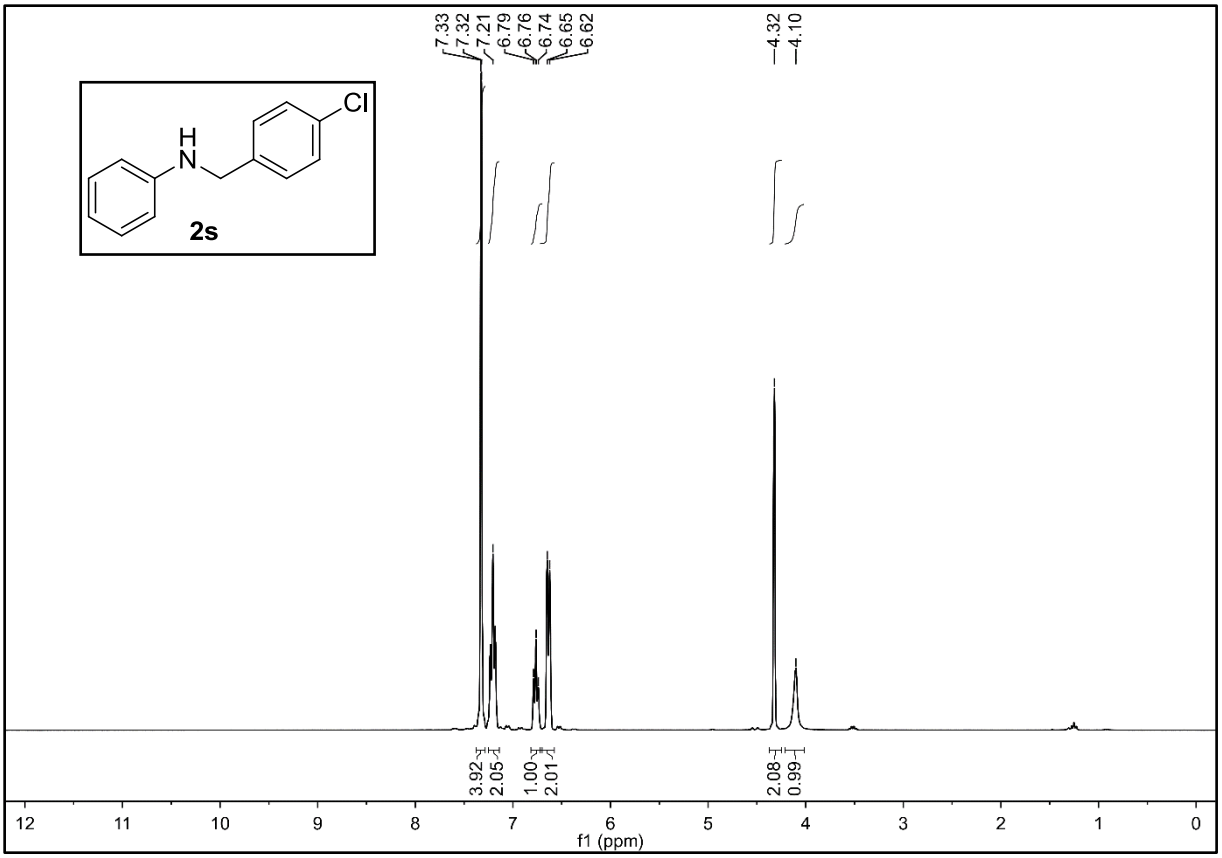

152.24
142.47
139.74
128.67
127.63
127.24
114.96
114.19
55.84
49.29
MeO
2p
f1 (ppm)

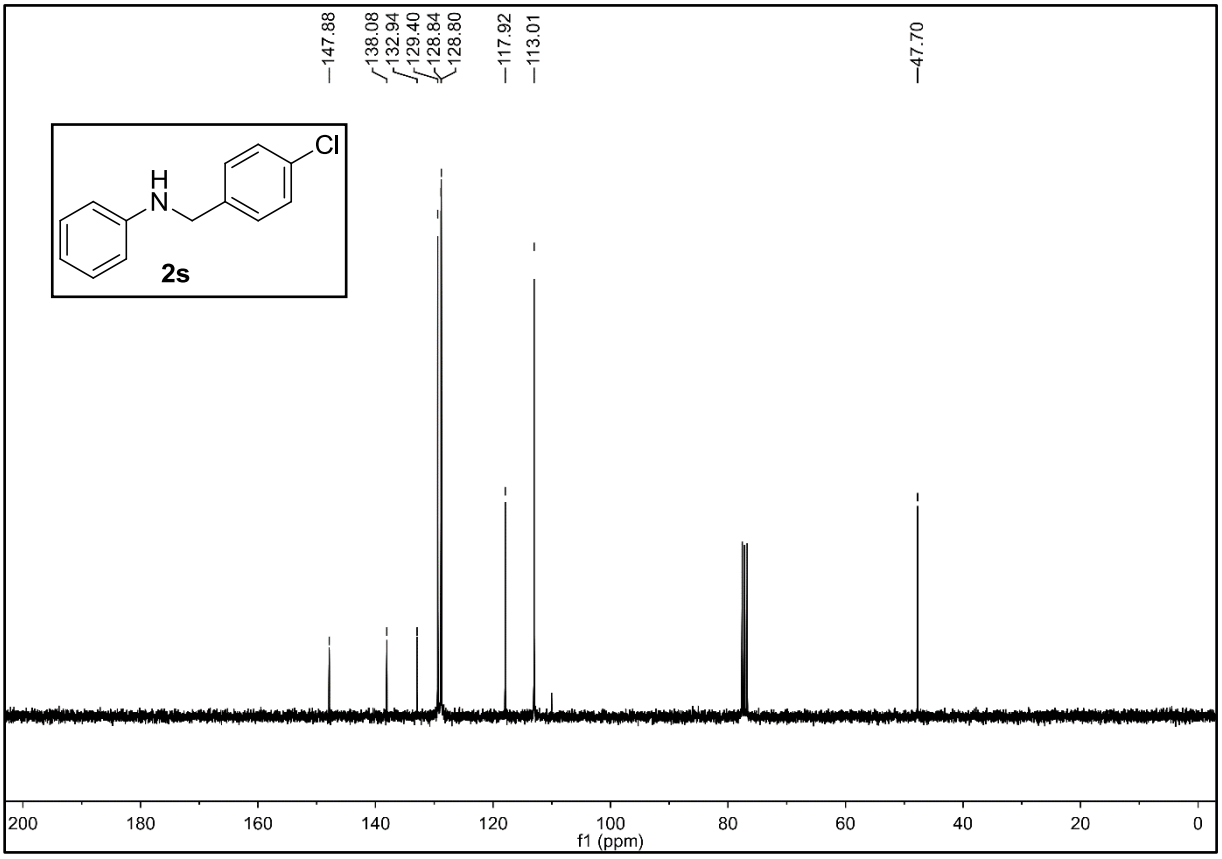

8.12
8.12
8.11
8.11
7.39
7.29
6.61
6.61
6.60
6.60
6.60
6.60
6.59
6.39
6.38
5.03
4.53
4.52
2q
0.97
4.90
1.08
0.99
1.00
0.97
2.05
12
11
10
9
8
7
6
5
4
3
2
1
0
f1 (ppm)

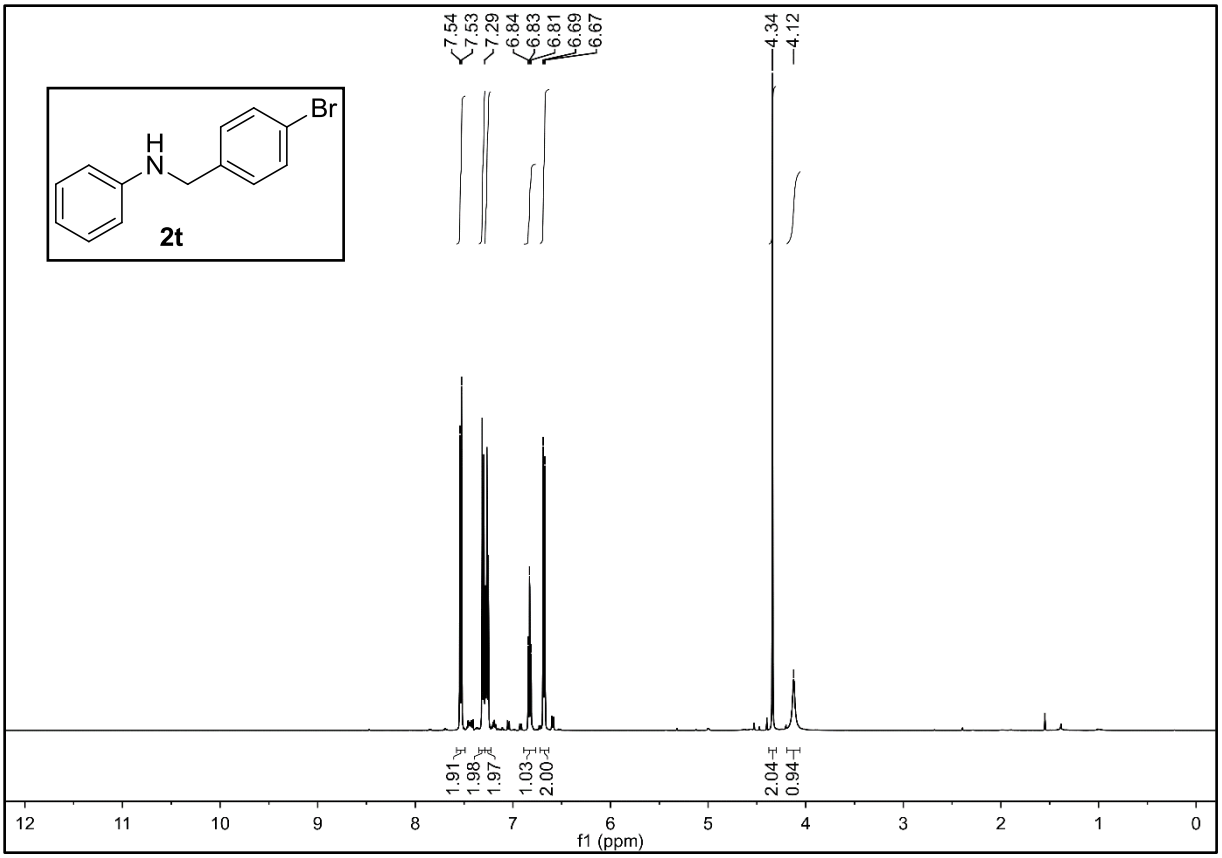

158.73
148.24
139.26
137.62
128.75
127.51
127.35
113.24
106.91
46.41
2q
200
180
160
140
120
100
80
60
40
20
0
f1 (ppm)

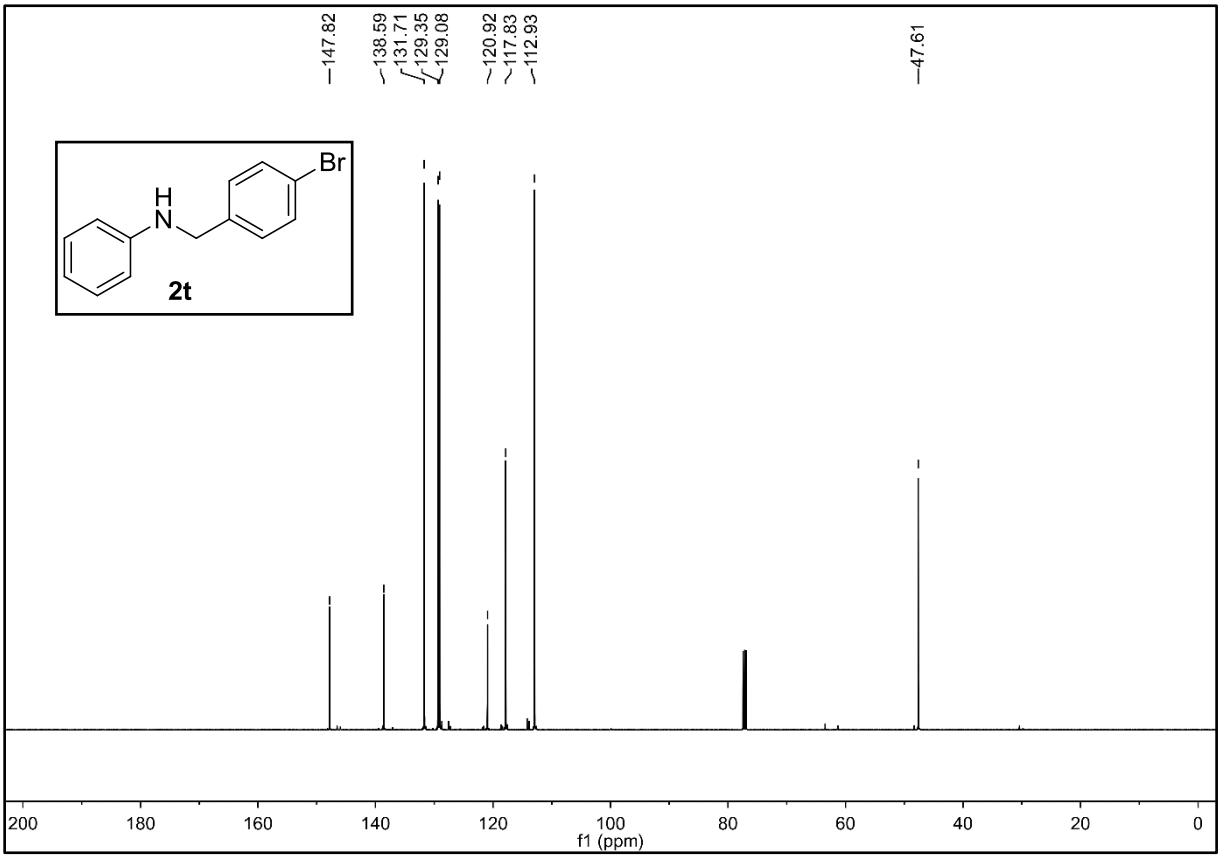

7.36
7.35
7.34
7.33
7.19
7.04
6.76
6.76
6.75
6.74
6.73
6.73
6.64
4.31
4.17
1.99
2.01
1.99
0.98
2.00
2.06
1.00
F
H
N
2r
12
11
10
9
8
7
6
5
4
3
2
1
0
f1 (ppm)

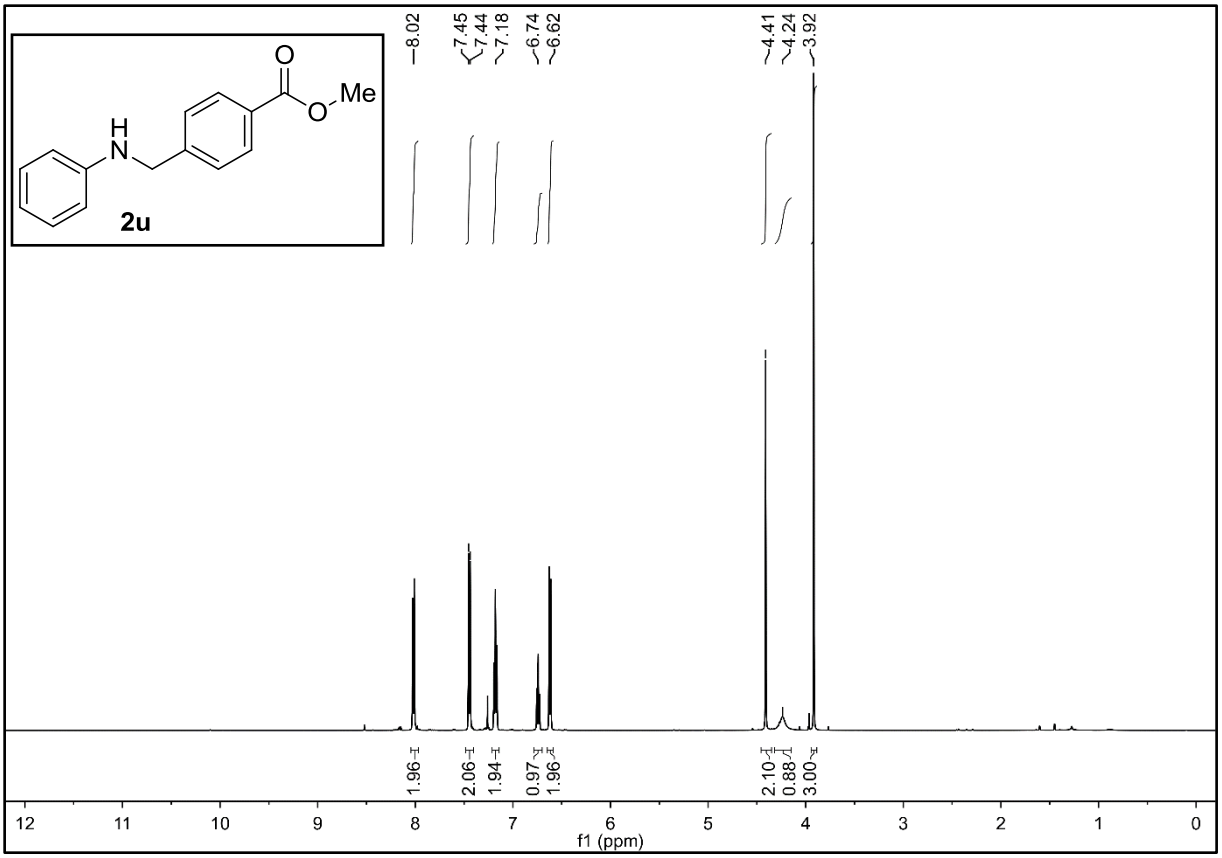

163.16
161.21
147.94
135.13
129.43
129.20
129.14
117.97
115.67
115.50
113.09
47.80
F
H
N
2r
200
180
160
140
120
100
80
60
40
20
0
f1 (ppm)

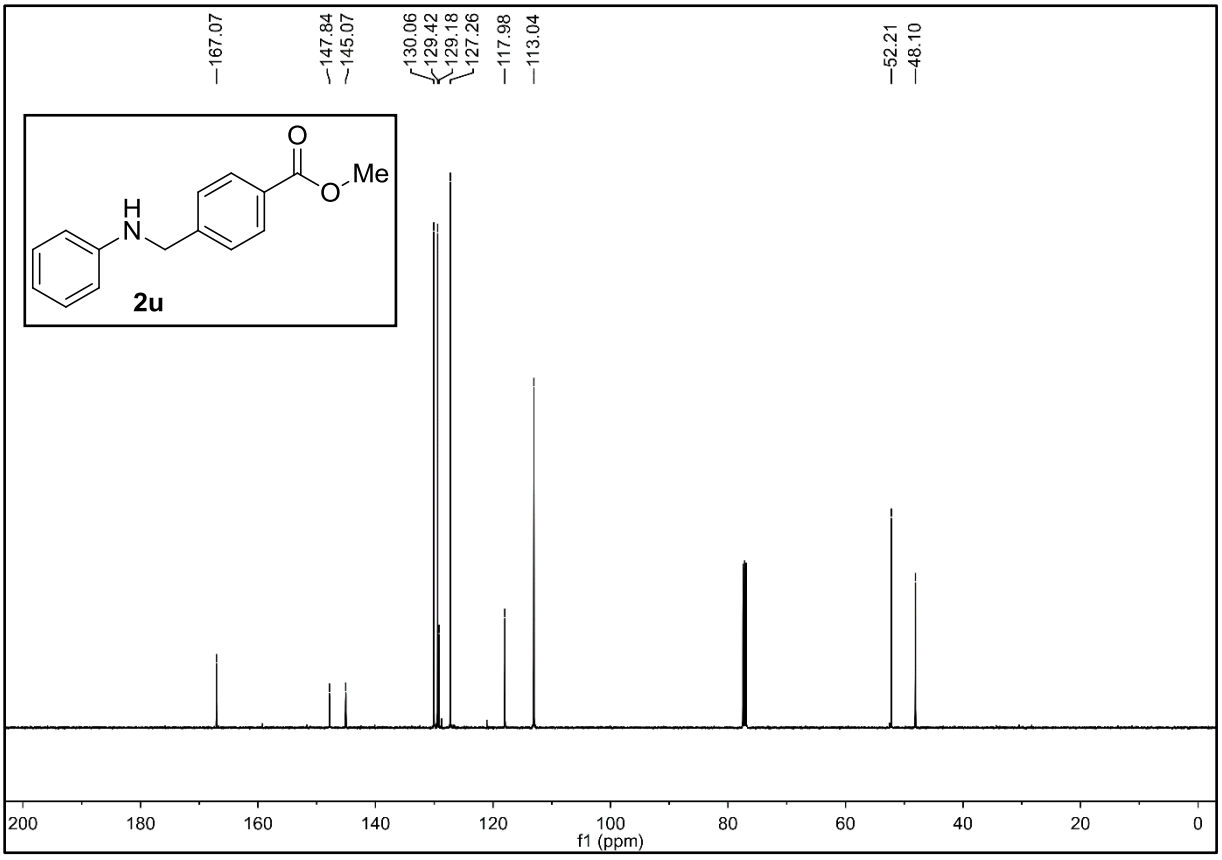

7.33
7.32
7.21
6.79
6.76
6.74
6.65
6.62
4.32
4.10
Cl
H
N
2s
3.92
2.05
1.00
2.01
2.08
0.99
12
11
10
9
8
7
6
5
4
3
2
1
0
f1 (ppm)

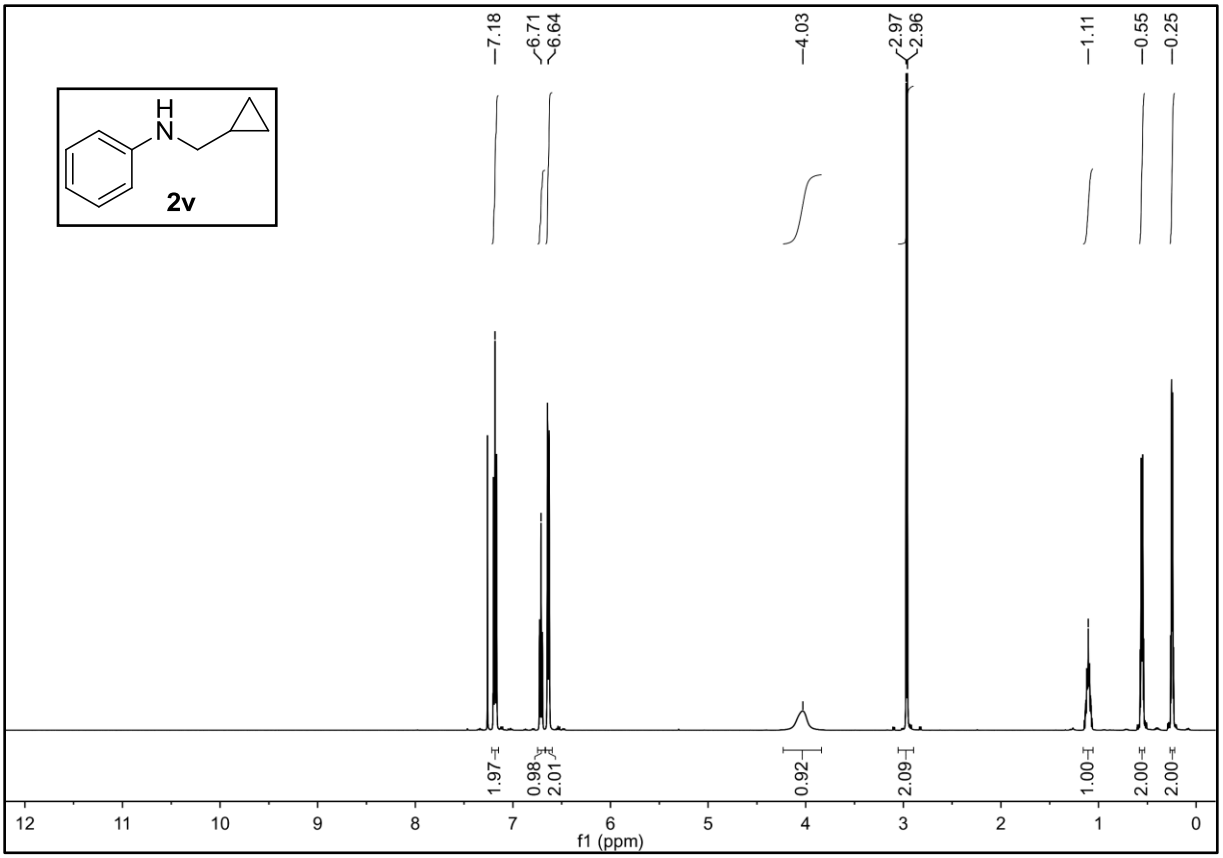

147.88
138.08
132.94
129.40
128.84
128.80
117.92
113.01
47.70
Cl
H
N
2s
200
180
160
140
120
100
80
60
40
20
0
f1 (ppm)

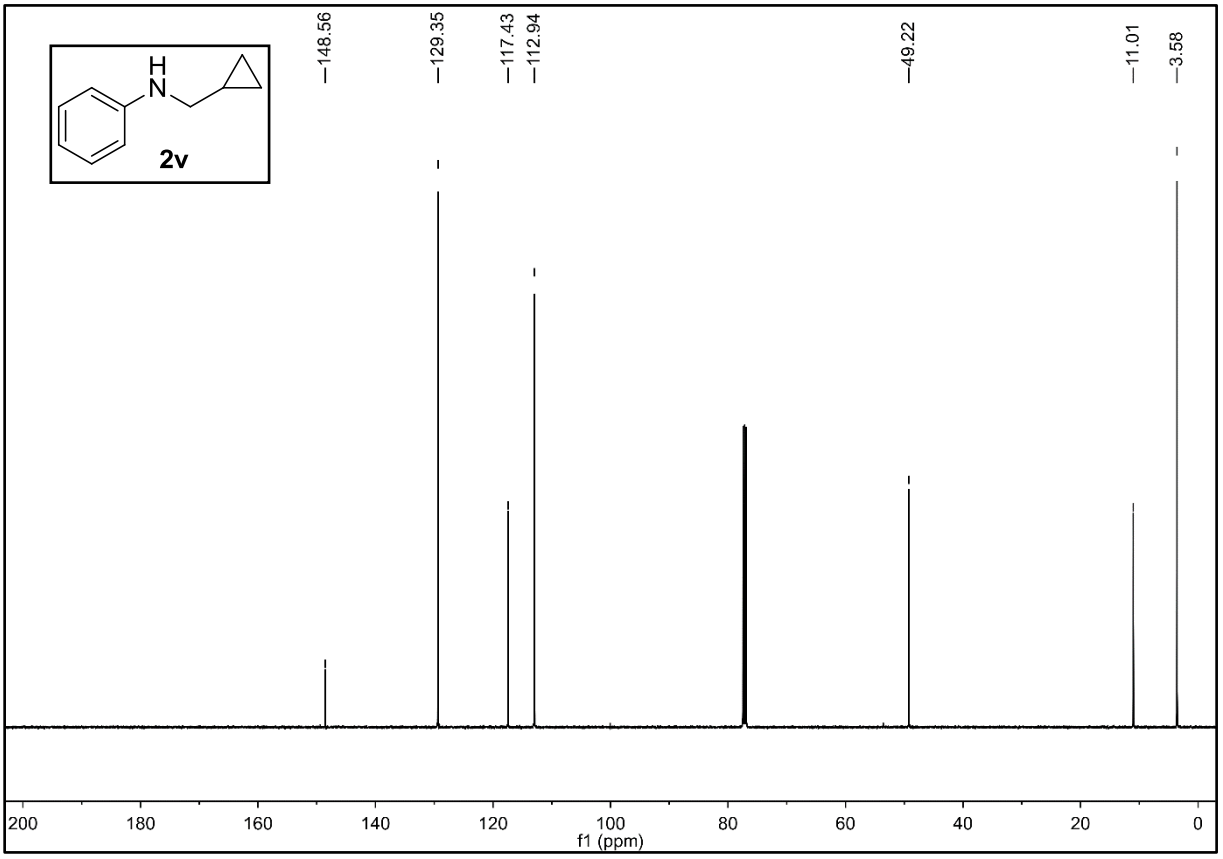

7.54
7.53
7.29
6.84
6.83
6.81
6.69
6.67
4.34
4.12
Br
H
N
2t
1.91
1.98
1.97
1.03
2.00
2.04
0.94
12
11
10
9
8
7
6
5
4
3
2
1
0
f1 (ppm)

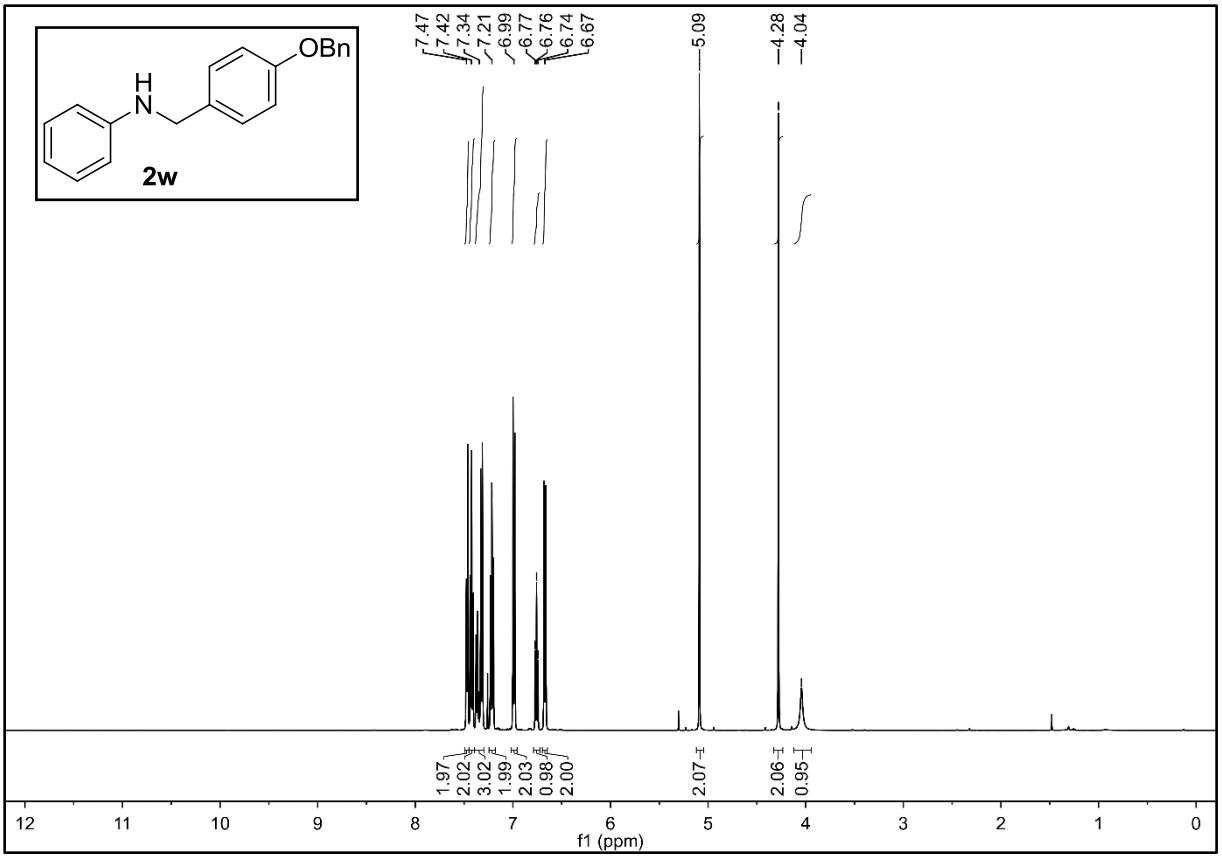

147.82
138.59
131.71
129.35
129.08
120.92
117.83
112.93
47.61
Br
H
N
2t
200
180
160
140
120
100
80
60
40
20
0
f1 (ppm)

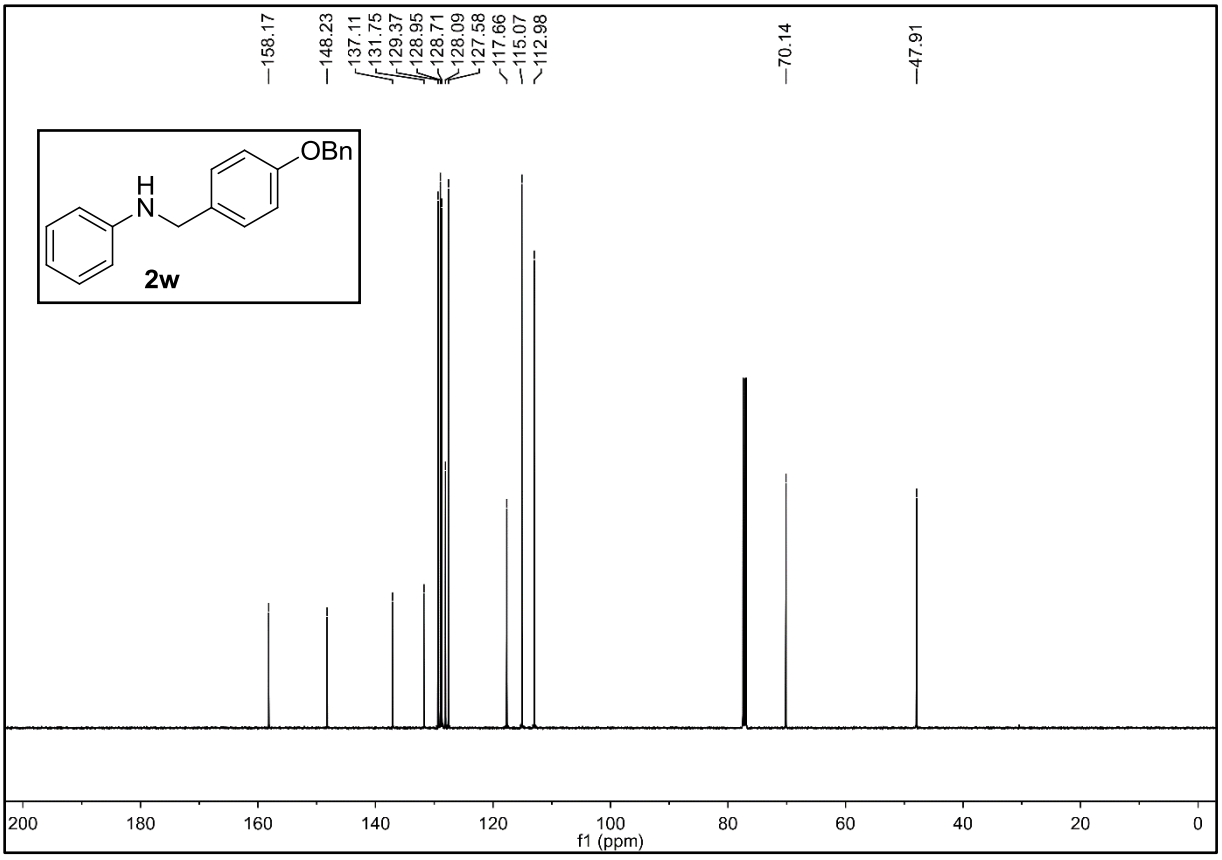

8.02
7.45
7.44
7.18
6.74
6.62
4.41
4.24
3.92
1.96
2.06
1.94
0.97
1.96
2.10
0.88
3.00
O
Me
O
H
N
2u
12
11
10
9
8
7
6
5
4
3
2
1
0
f1 (ppm)

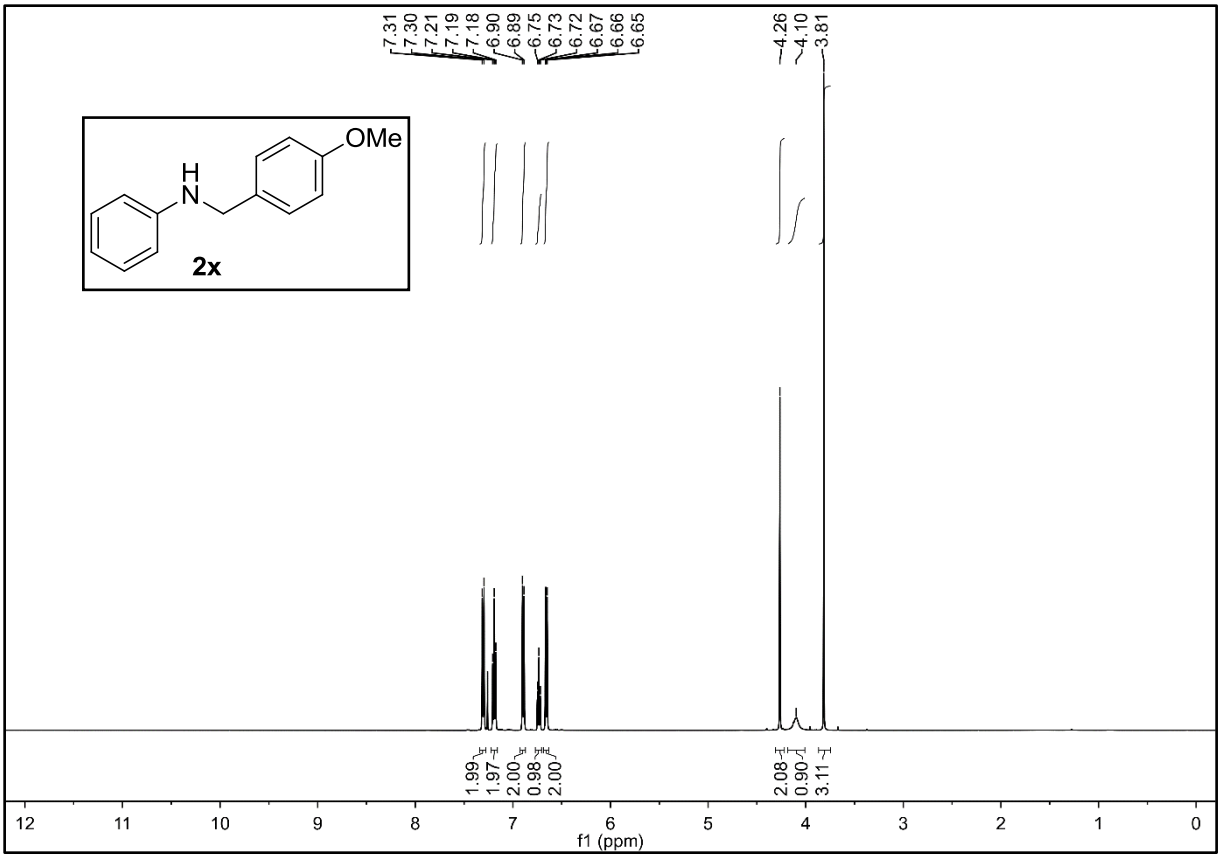

167.07
147.84
145.07
130.06
129.42
129.18
127.26
117.98
113.04
52.21
48.10
O
Me
O
H
N
2u
200
180
160
140
120
100
80
60
40
20
0
f1 (ppm)

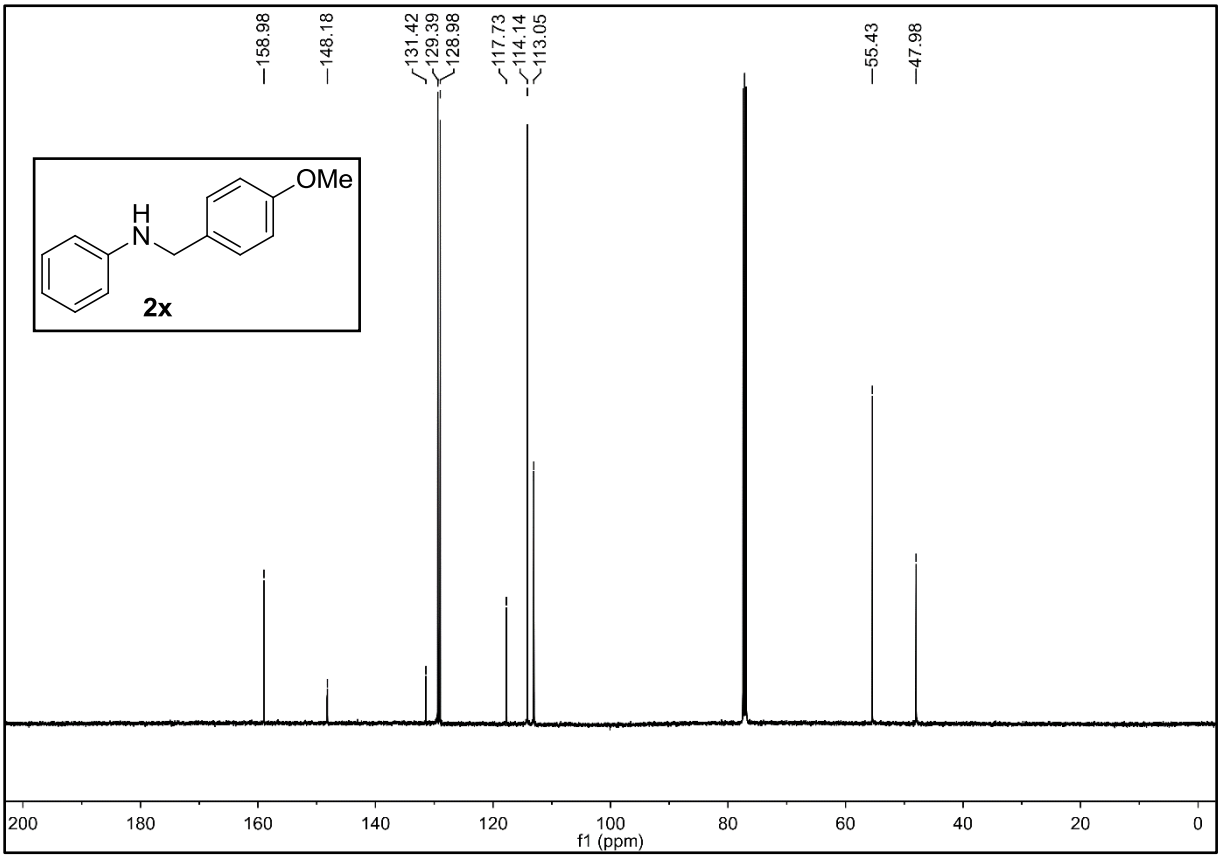

7.18
6.71
6.64
4.03
2.97
2.96
1.11
0.55
0.25
2v
1.97
0.98
2.01
0.92
2.09
1.00
2.00
2.00
f1 (ppm)

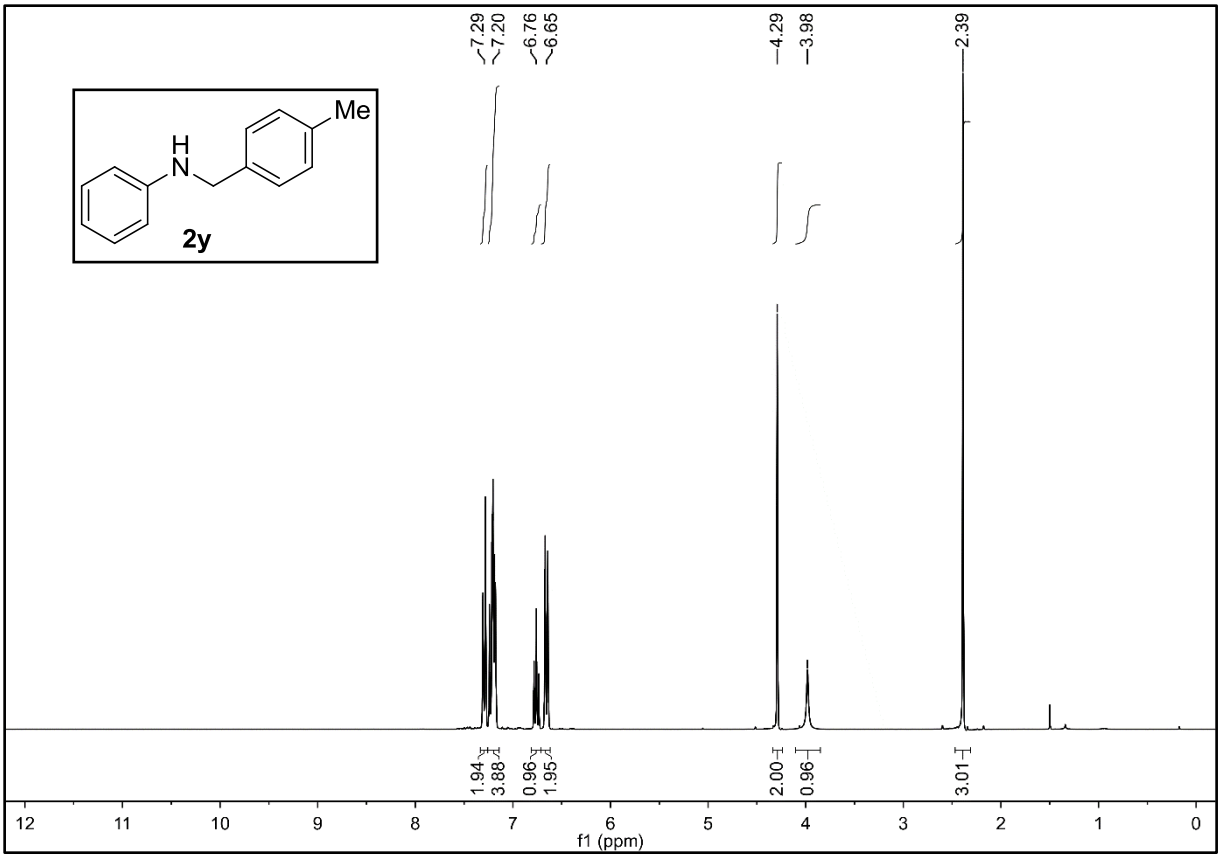

148.56
129.35
117.43
112.94
49.22
11.01
3.58
2v
f1 (ppm)

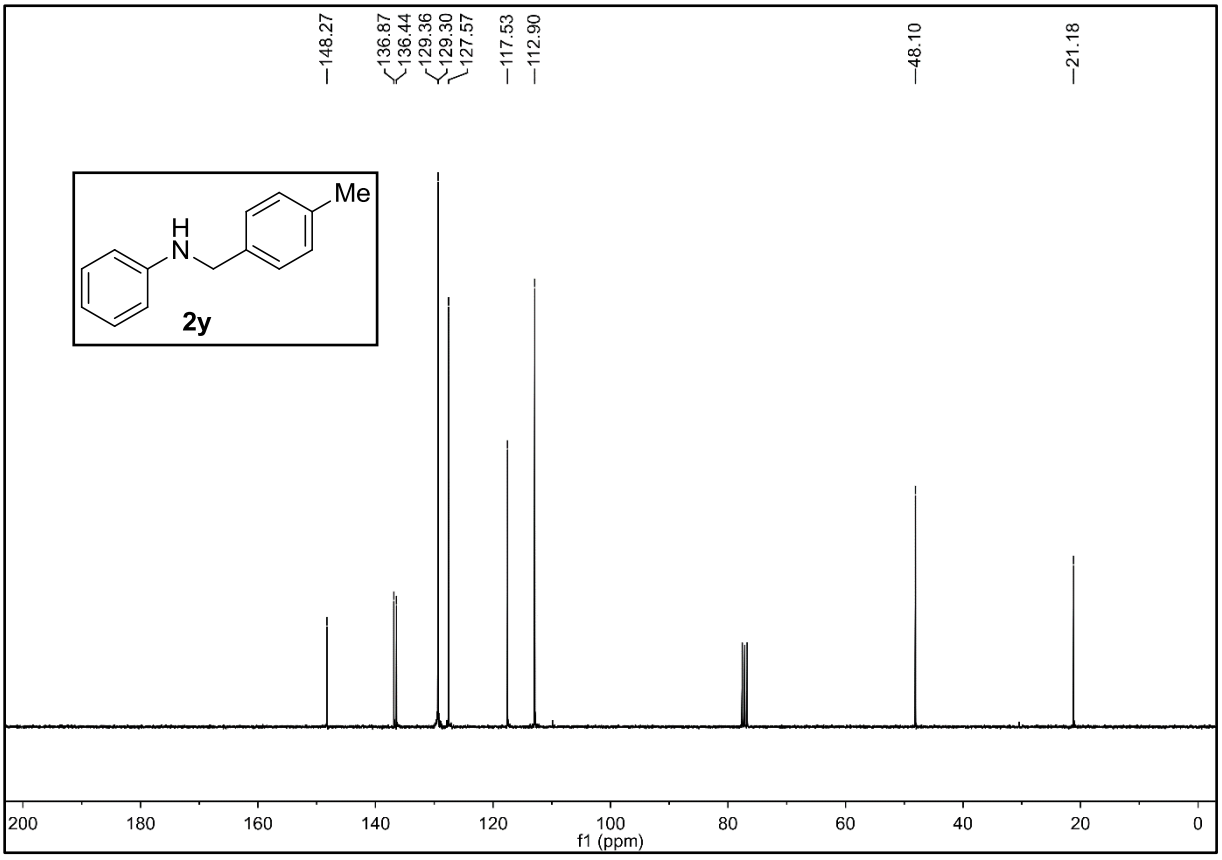

OBn
H
N
2w
7.47
7.42
7.34
7.21
6.99
6.77
6.76
6.74
6.67
5.09
4.28
4.04
1.97
2.02
3.02
1.99
2.03
0.98
2.00
2.07
2.06
0.95
12
11
10
9
8
7
6
5
4
3
2
1
0
f1 (ppm)

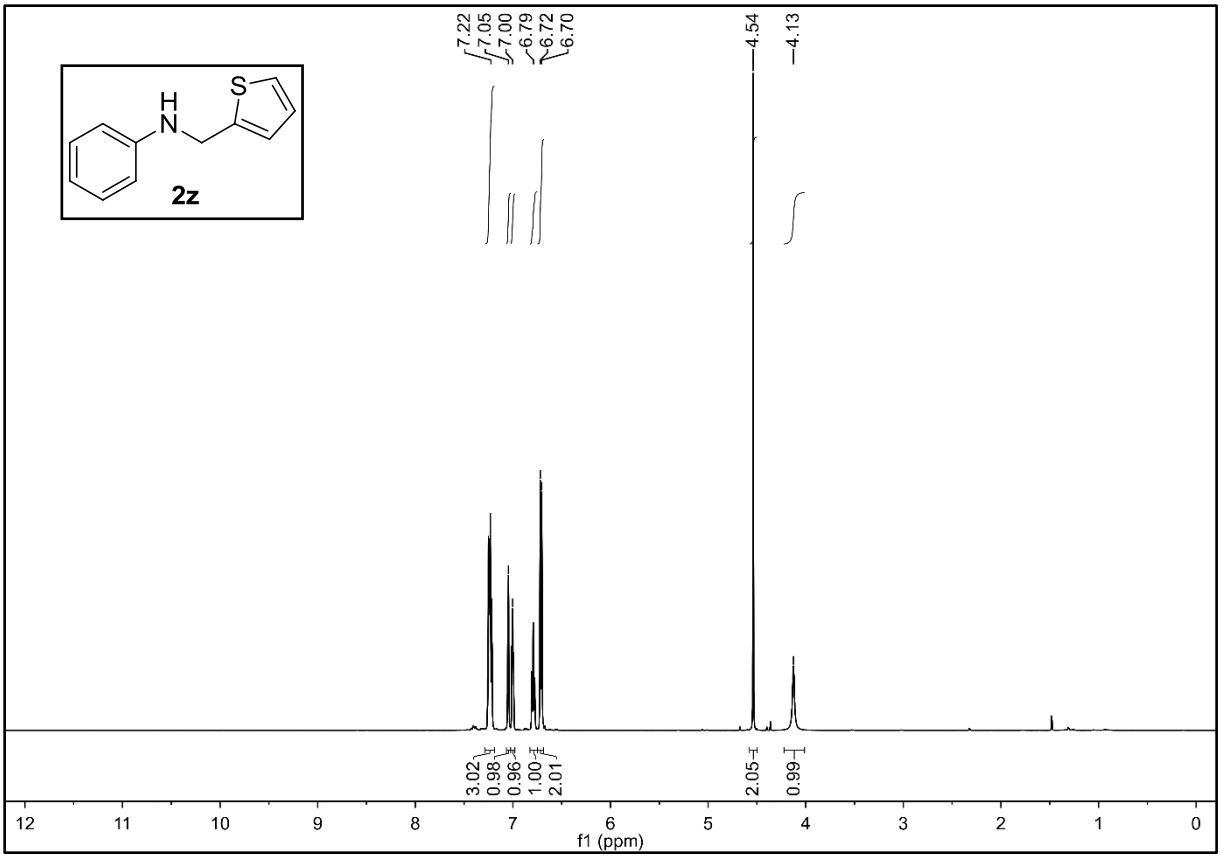

OBn
H
N
2w
158.17
148.23
137.11
131.75
129.37
128.95
128.71
128.09
127.58
117.66
115.07
112.98
70.14
47.91
200
180
160
140
120
100
80
60
40
20
0
f1 (ppm)

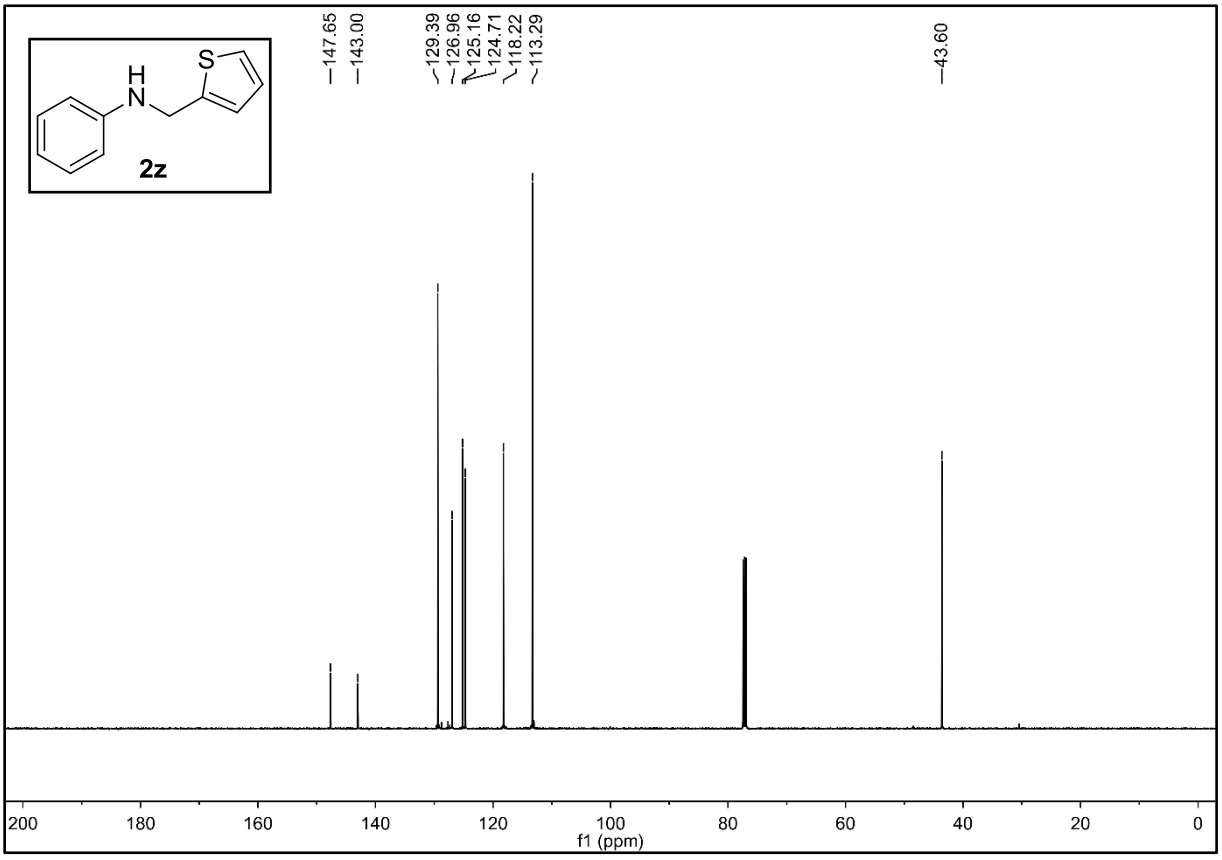

7.31
7.30
7.21
7.19
7.18
6.90
6.89
6.75
6.73
6.72
6.67
6.66
6.65
4.26
4.10
3.81
OMe
H
N
2x
1.99
1.97
2.00
0.98
2.00
2.08
0.90
3.11
12
11
10
9
8
7
6
5
4
3
2
1
0
f1 (ppm)

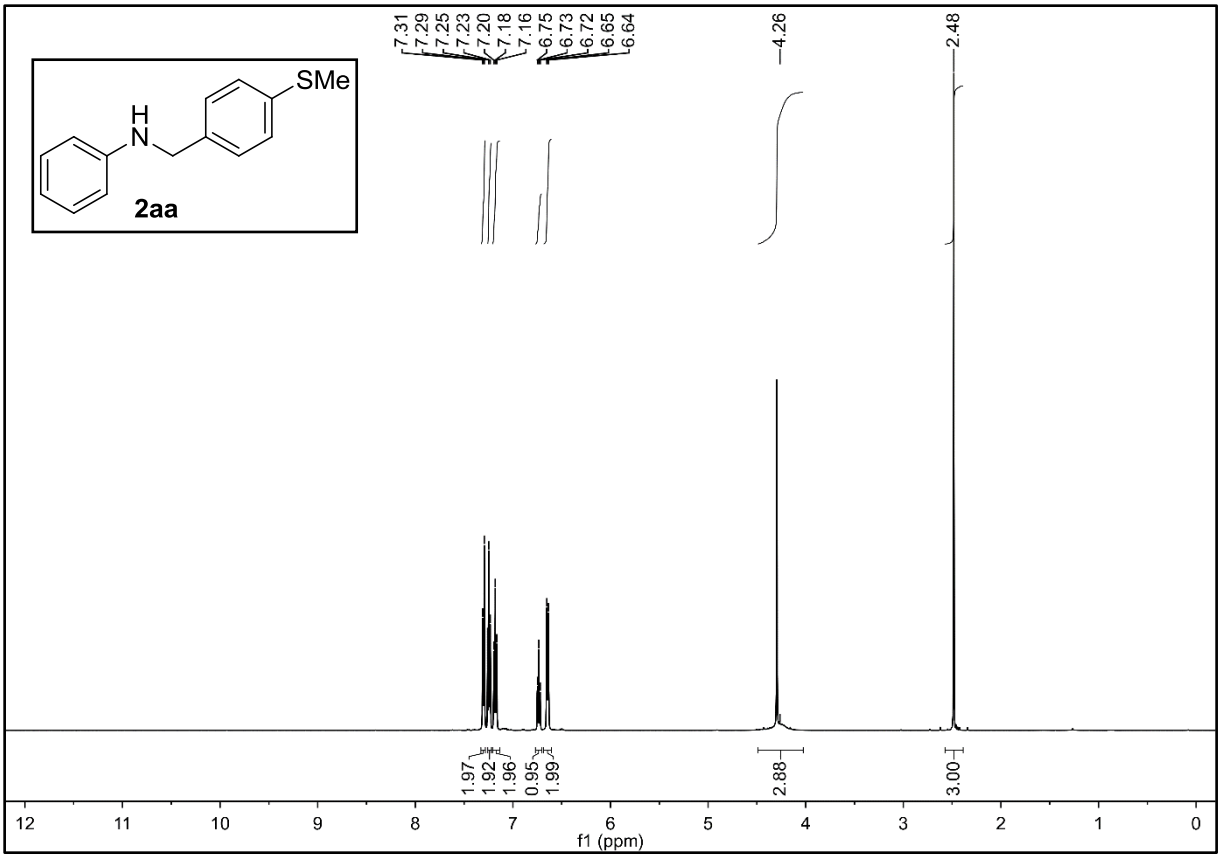

158.98
148.18
131.42
129.39
128.98
117.73
114.14
113.05
55.43
47.98
OMe
H
N
2x
200
180
160
140
120
100
80
60
40
20
0
f1 (ppm)

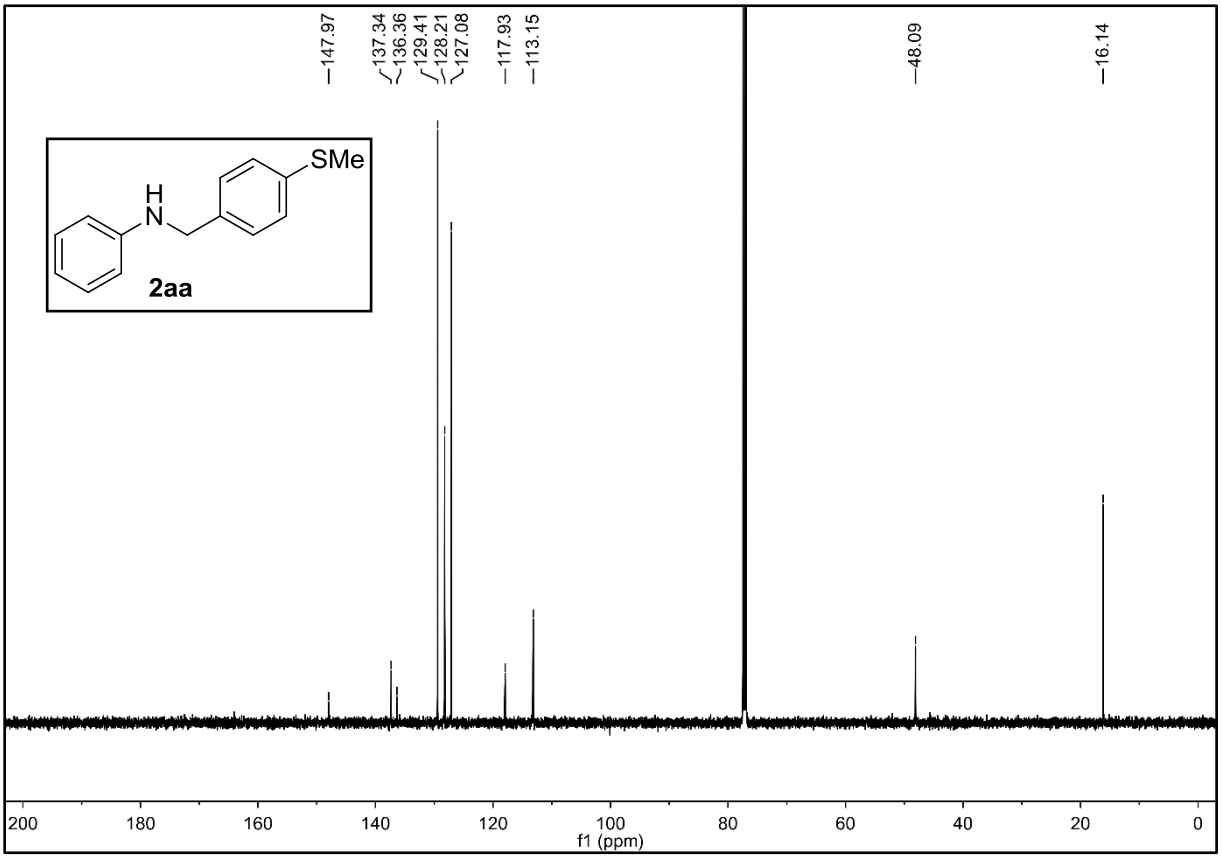

7.29
7.20
6.76
6.65
4.29
3.98
2.39
Me
H
N
2y
1.94
3.88
0.96
1.95
2.00
0.96
3.01
12
11
10
9
8
7
6
5
4
3
2
1
0
f1 (ppm)

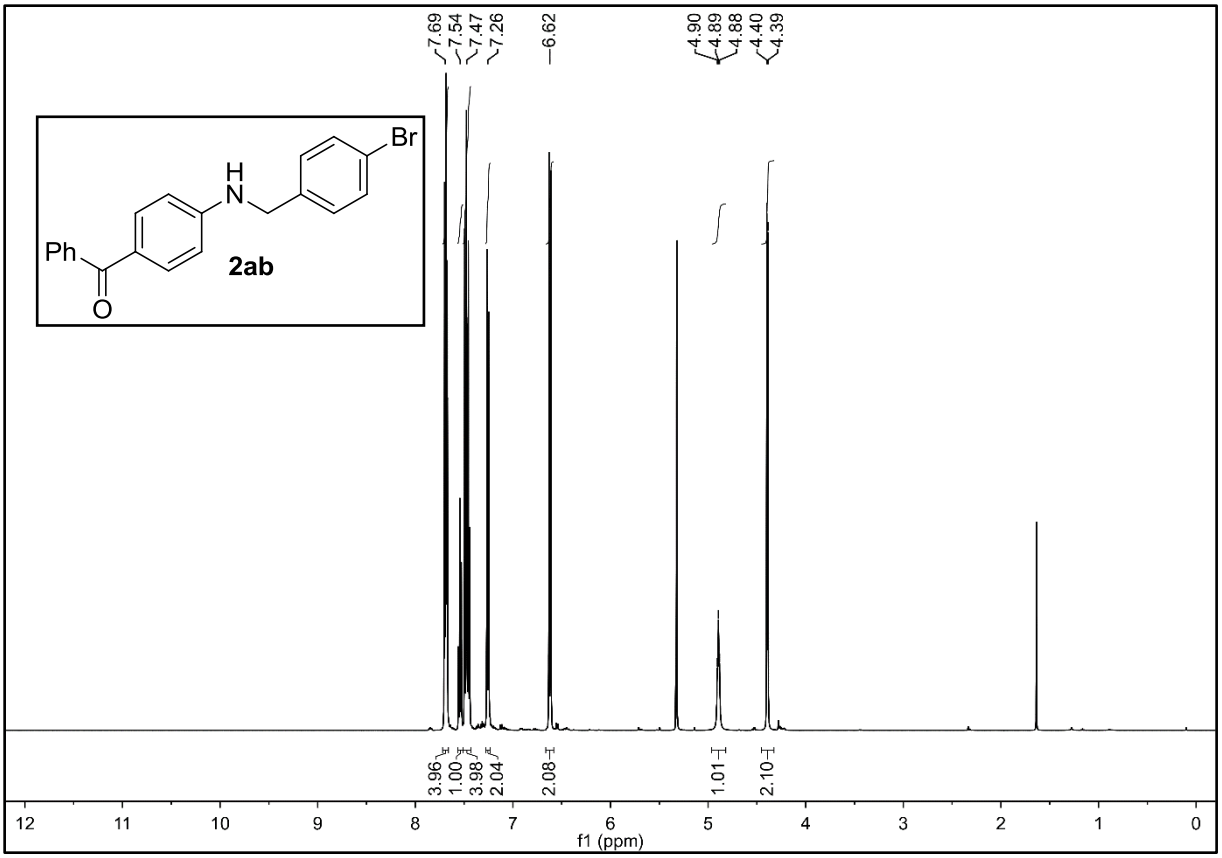

148.27
136.87
136.44
129.36
129.30
127.57
117.53
112.90
48.10
21.18
Me
H
N
2y
200
180
160
140
120
100
80
60
40
20
0
f1 (ppm)

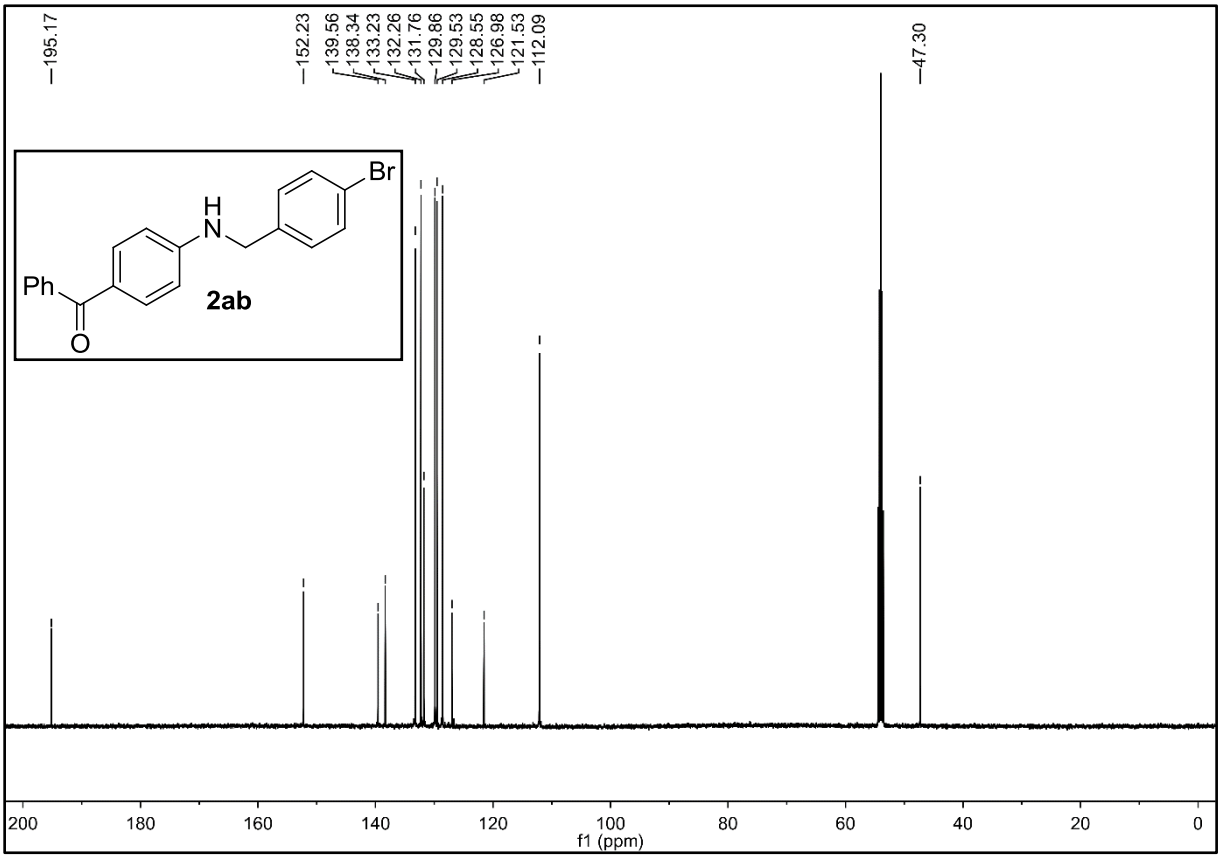

7.22
7.05
7.00
6.79
6.72
6.70
4.54
4.13
2z
3.02
0.98
0.96
1.00
2.01
2.05
0.99
12
11
10
9
8
7
6
5
4
3
2
1
0
f1 (ppm)


147.65
143.00
129.39
126.96
125.16
124.71
118.22
113.29
43.60
2z
200
180
160
140
120
100
80
60
40
20
0
f1 (ppm)


7.31
7.29
7.25
7.23
7.20
7.18
7.16
6.75
6.73
6.72
6.65
6.64
4.26
2.48
SMe
H
N
2aa
1.97
1.92
1.96
0.95
1.99
2.88
3.00
12
11
10
9
8
7
6
5
4
3
2
1
0
f1 (ppm)


147.97
137.34
136.36
129.41
128.21
127.08
117.93
113.15
48.09
16.14
SMe
H
N
2aa
200
180
160
140
120
100
80
60
40
20
0
f1 (ppm)


7.69
7.54
7.47
7.26
6.62
4.90
4.89
4.88
4.40
4.39
Br
H
N
Ph
O
2ab
3.96
1.00
3.98
2.04
2.08
1.01
2.10
12
11
10
9
8
7
6
5
4
3
2
1
0
f1 (ppm)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152.23
139.56
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132.26
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129.86
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112.09
47.30
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Ph
O
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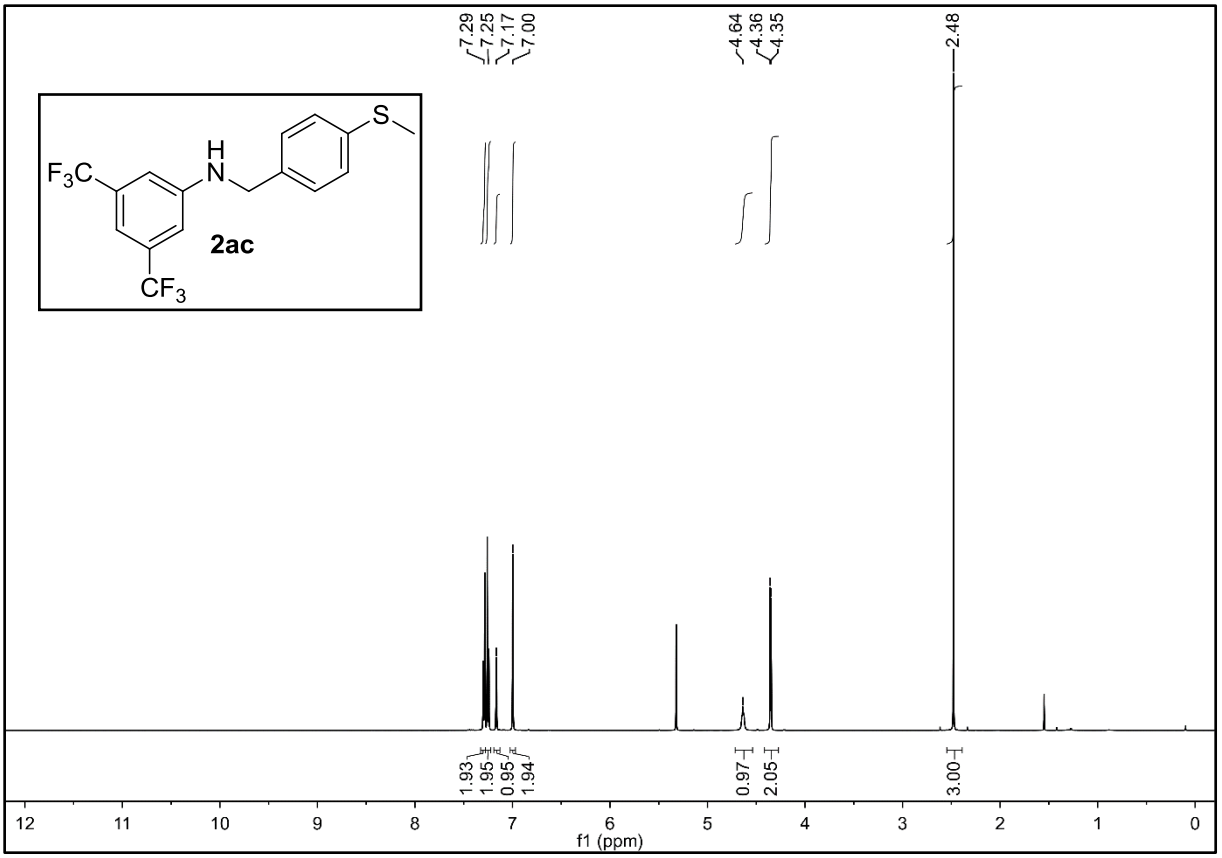
f1 (ppm)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7.17
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4.35
2.48
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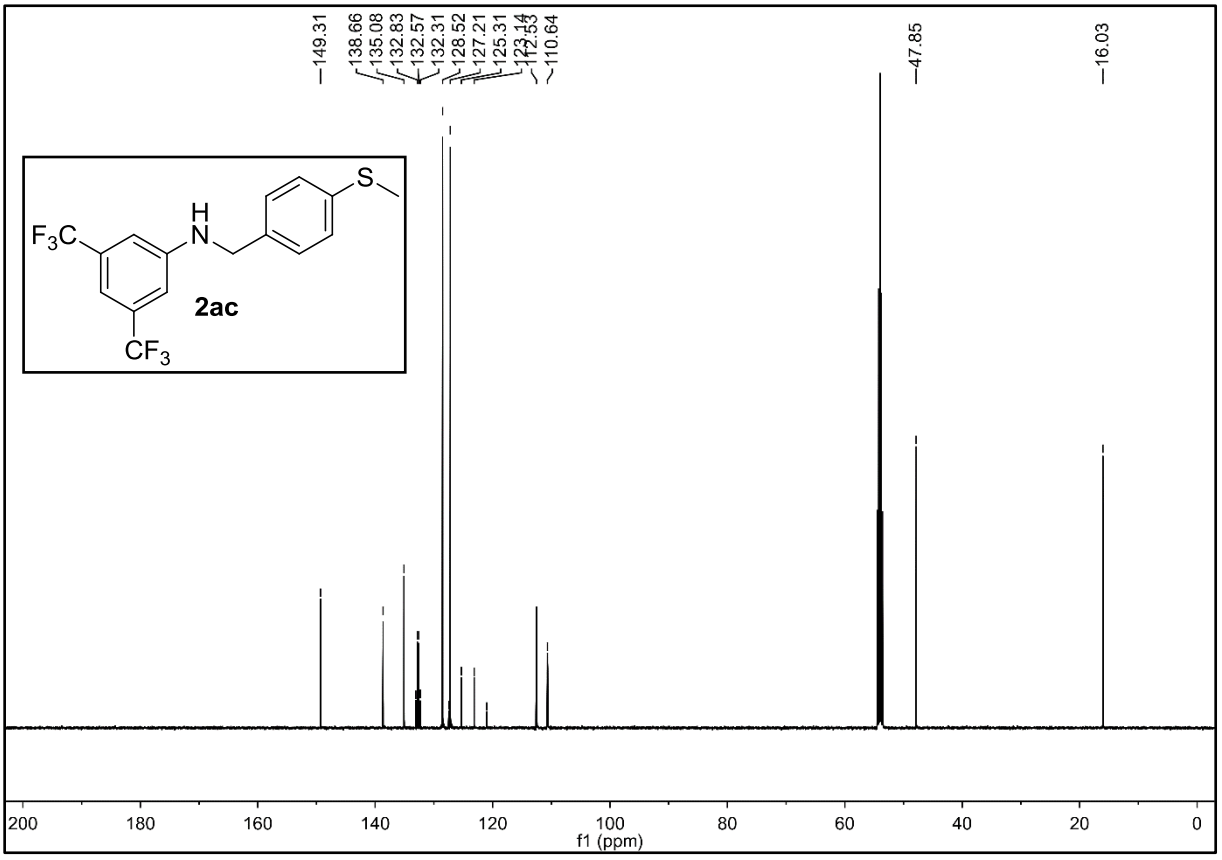
0.95
1.94
0.97
2.05
3.00
2ac
f1 (ppm)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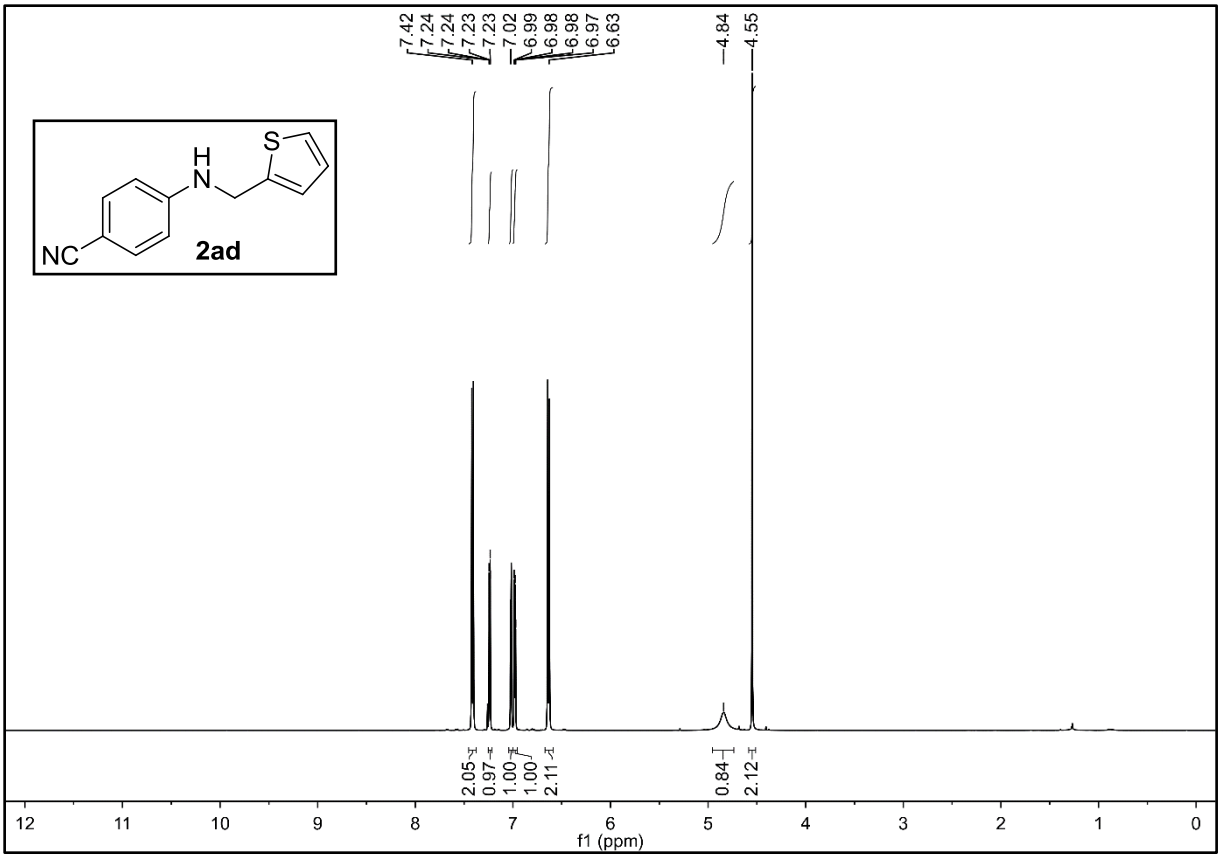
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7.02
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6.98
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4.55
2.05
0.97
1.00
1.00
2.11
0.84
2.12
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S
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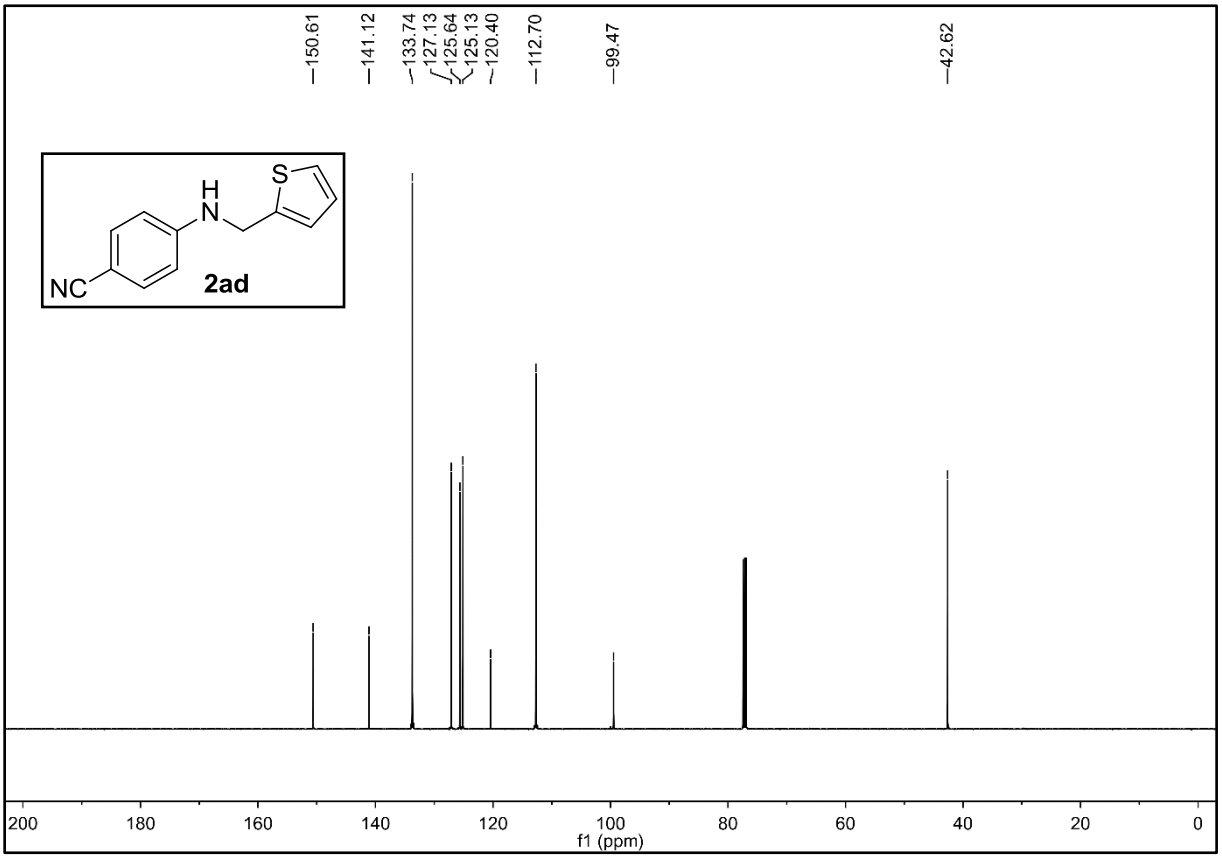
f1 (ppm)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141.12
133.74
127.13
125.64
125.13
120.40
112.70
99.47
42.62
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N
S
NC
2ad
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180
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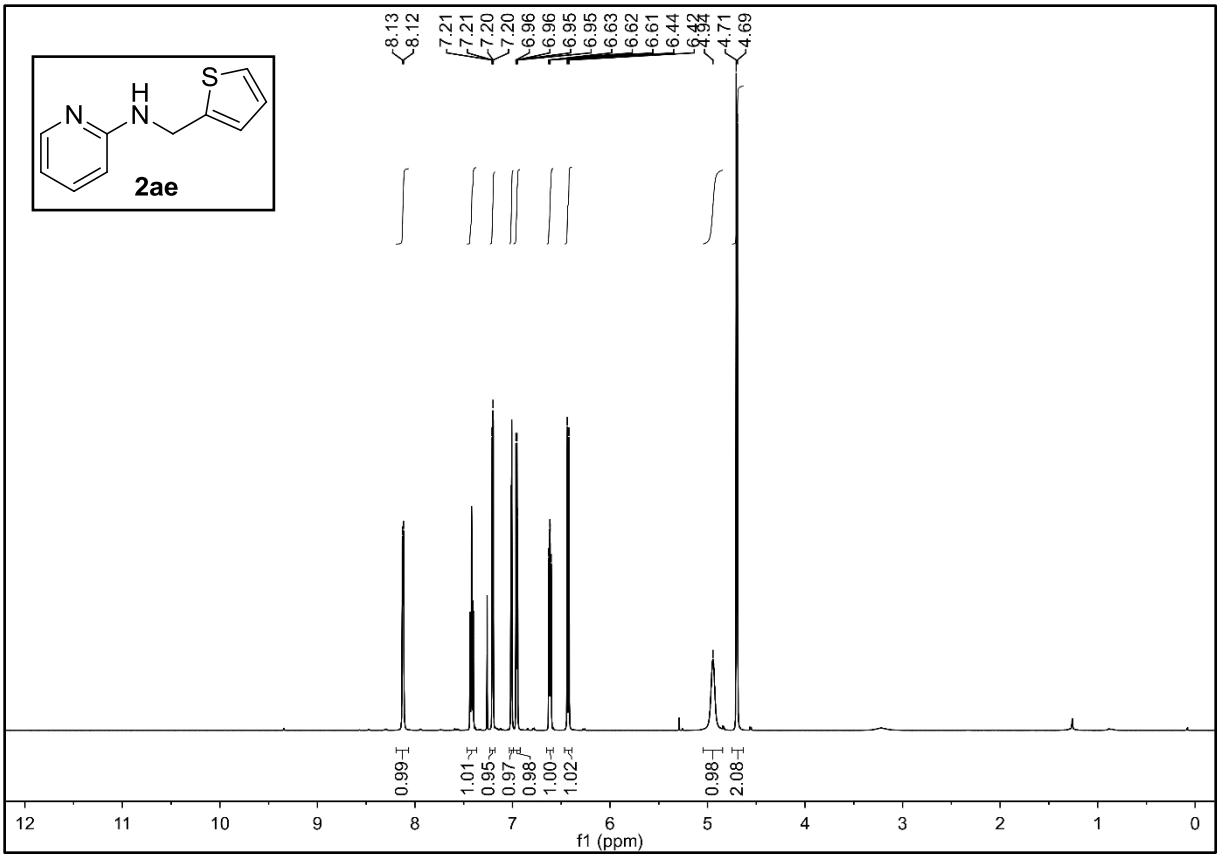
140
120
100
80
60
40
20
0
f1 (ppm)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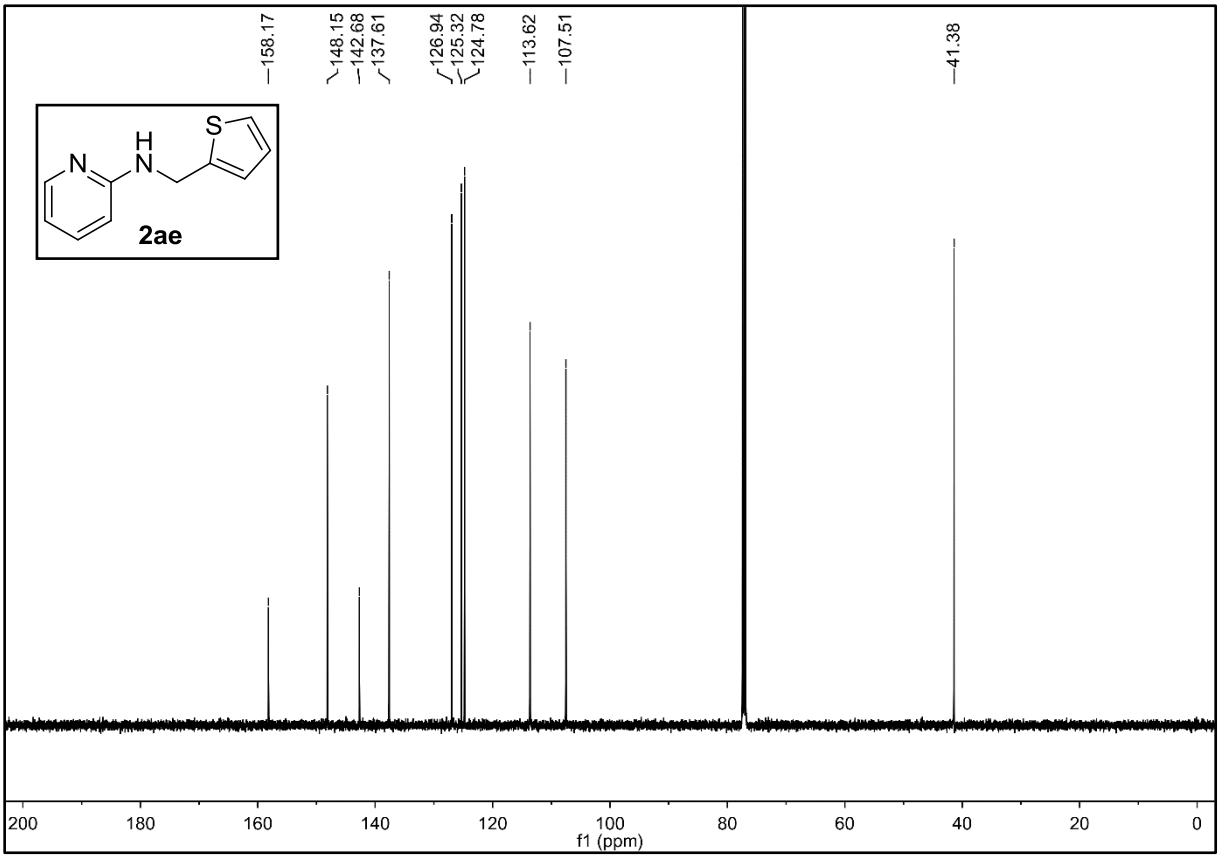
8.12
7.21
7.21
7.20
7.20
6.96
6.96
6.95
6.95
6.63
6.62
6.61
6.44
6.42
4.94
4.71
4.69
0.99
1.01
0.95
0.97
0.98
1.00
1.02
0.98
2.08
12
11
10
9
8
7
6
5
4
3
2
1
0
f1 (ppm)
2ae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142.68
137.61
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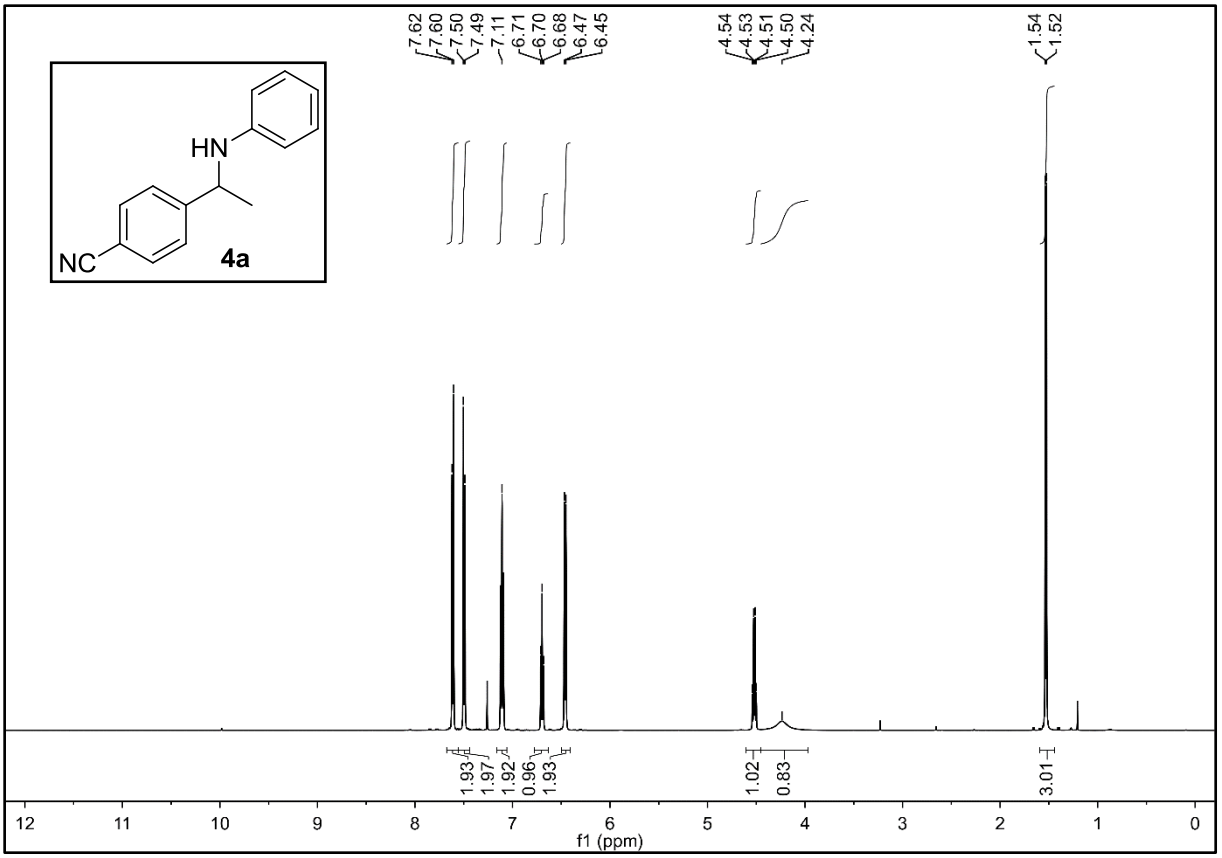
125.32
124.78
113.62
107.51
41.38
200
180
160
140
120
100
80
60
40
20
0
f1 (ppm)
2ae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6.70
6.68
6.47
6.45
4.54
4.53
4.51
4.50
4.24
1.54
1.52
HN
NC
4a
1.93
1.97
1.92
0.96
1.93
1.02
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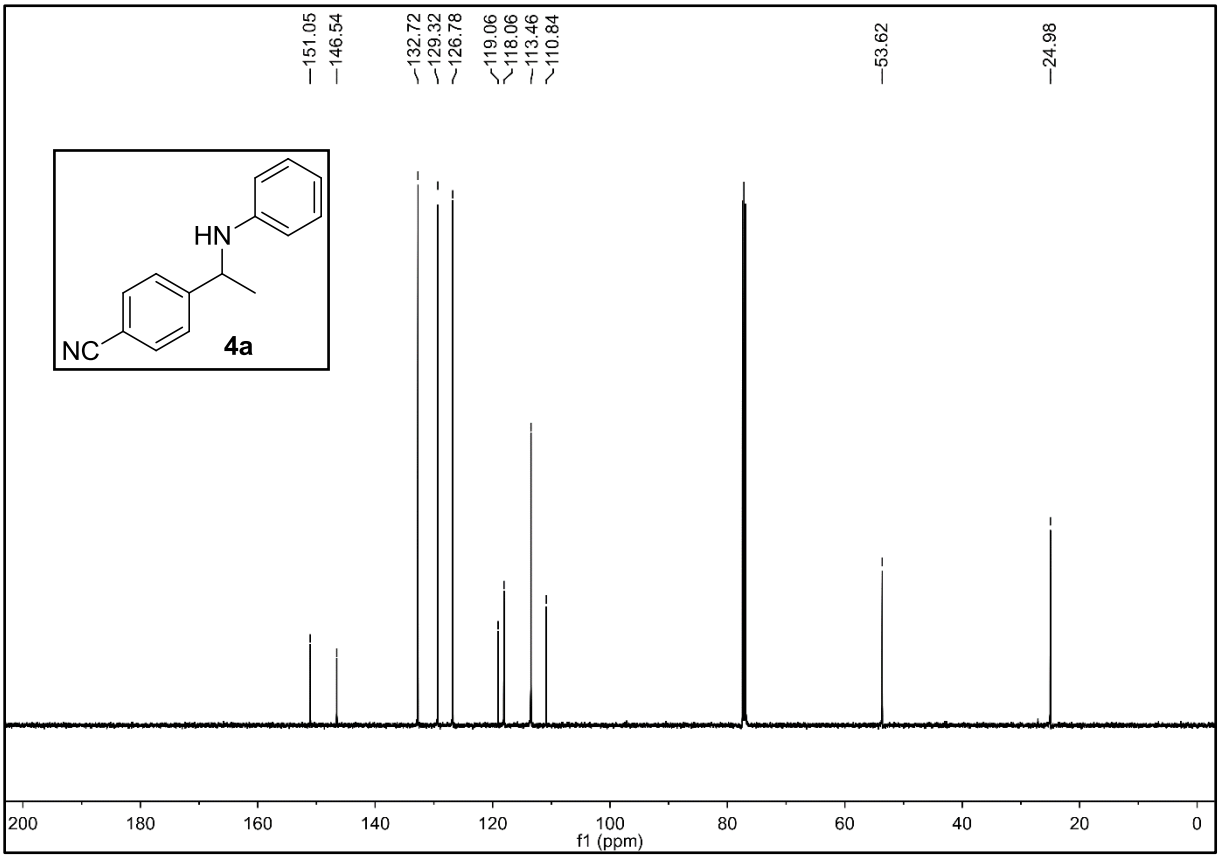
12
11
10
9
8
7
6
5
4
3
2
1
0
f1 (ppm)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132.72
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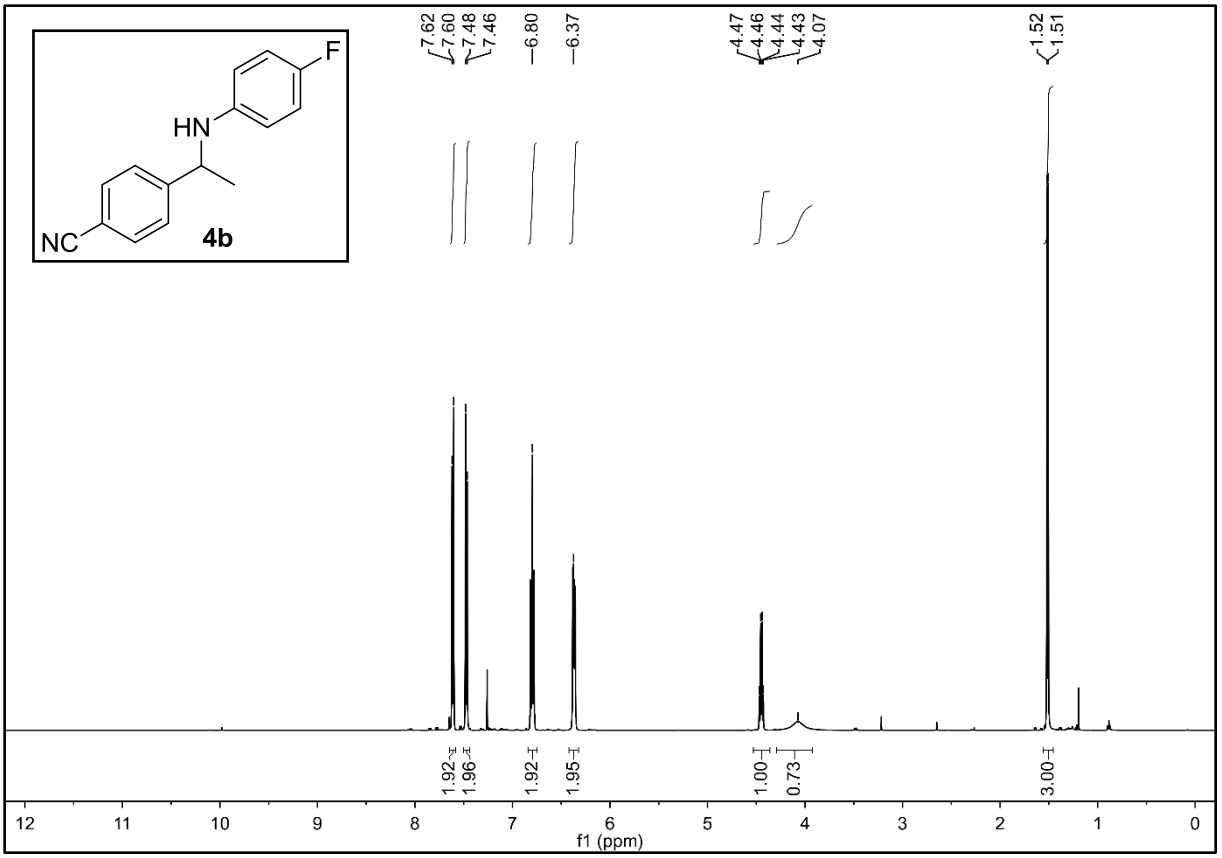
126.78
119.06
118.06
113.46
110.84
53.62
24.98
HN
NC
4a
200
180
160
140
120
100
80
60
40
20
0
f1 (ppm)


F
HN
NC
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7.62
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6.80
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4.47
4.46
4.44
4.43
4.07
1.52
1.51
1.92
1.96
1.92
1.95
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9
8
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5
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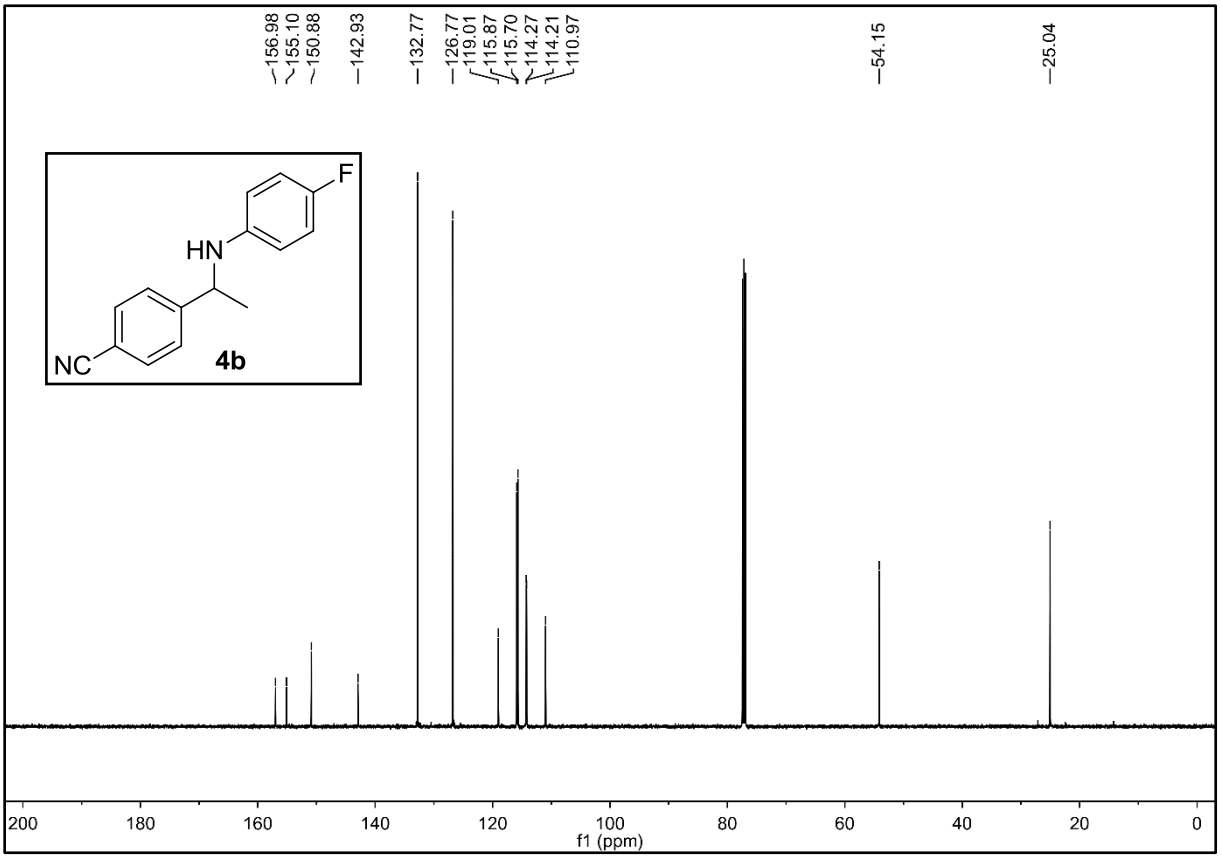
0
f1 (ppm)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132.77
126.77
119.01
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110.97
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4b
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100
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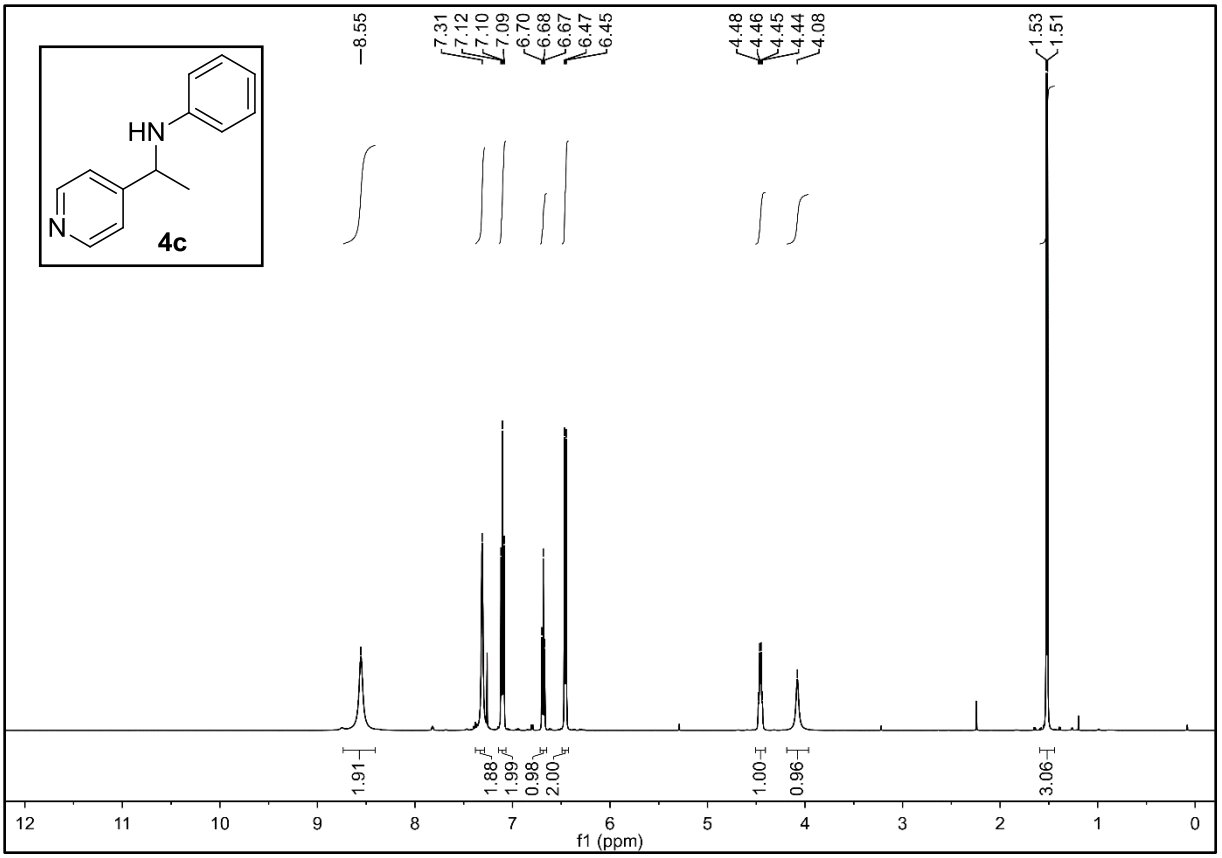
f1 (ppm)


HN
N
4c
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7.31
7.12
7.10
7.09
6.70
6.68
6.67
6.47
6.45
4.48
4.46
4.45
4.44
4.08
1.53
1.51
1.91
1.88
1.99
0.98
2.00
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3.06
12
11
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7
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4
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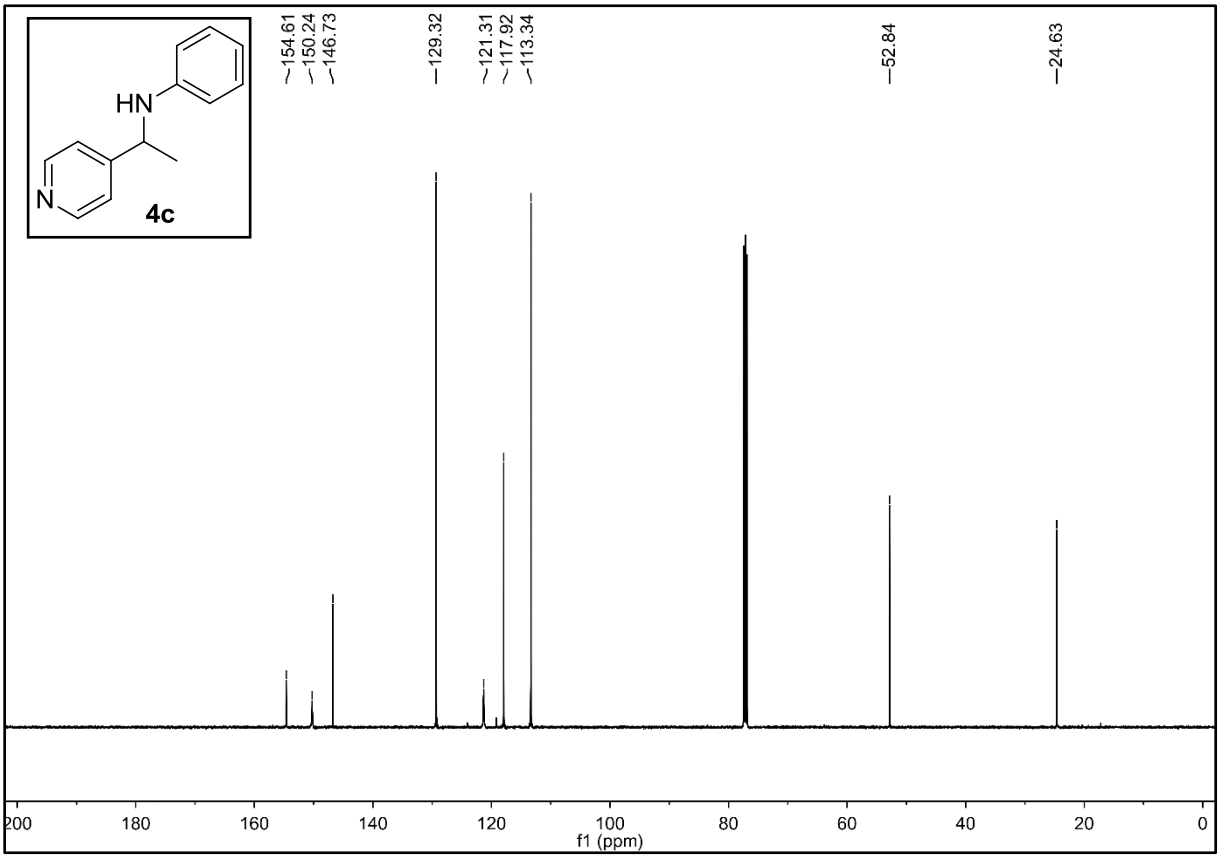
2
1
0
f1 (ppm)


HN
N
4c
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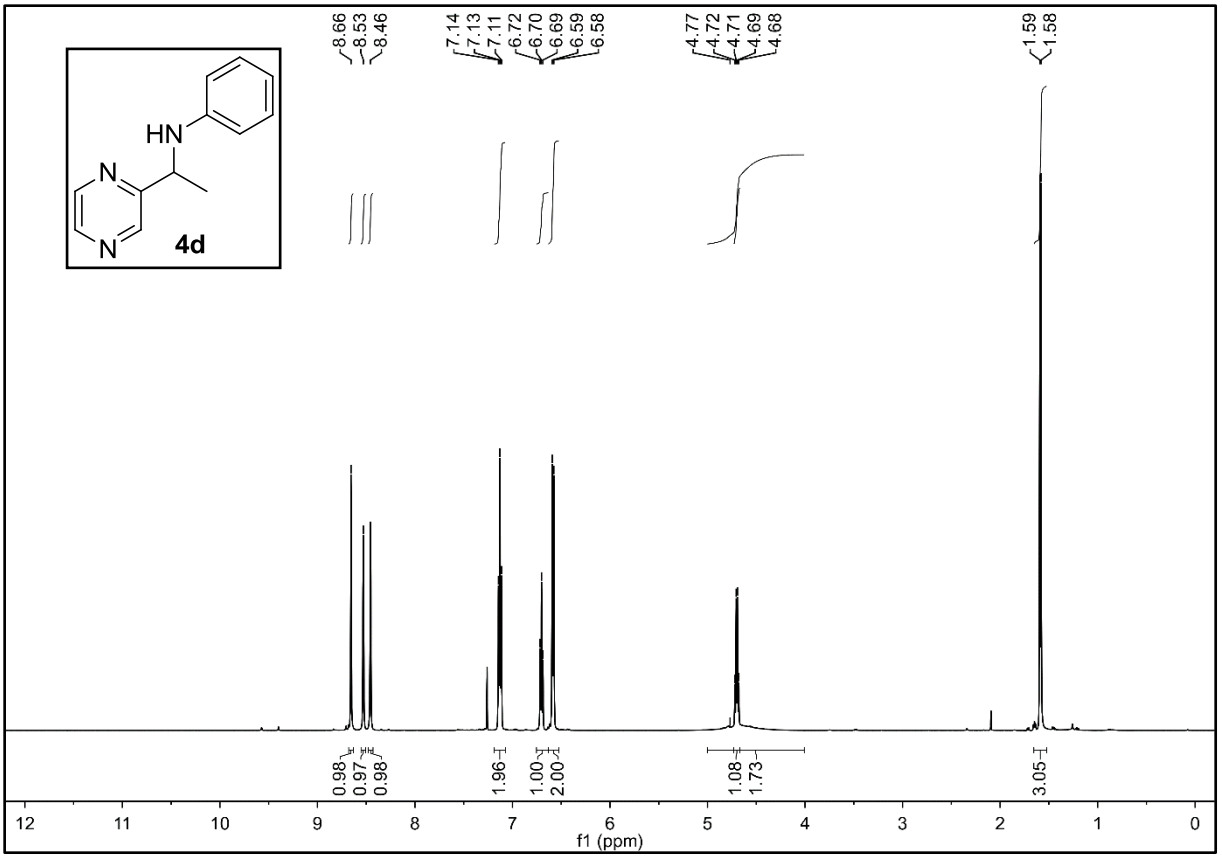
146.73
129.32
121.31
117.92
113.34
52.84
24.63
200
180
160
140
120
100
80
60
40
20
0
f1 (ppm)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N
N
4d
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6.72
6.70
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6.58
4.77
4.72
4.71
4.69
4.68
1.59
1.58
0.98
0.97
0.98
1.96
1.00
2.00
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12
11
10
9
8
7
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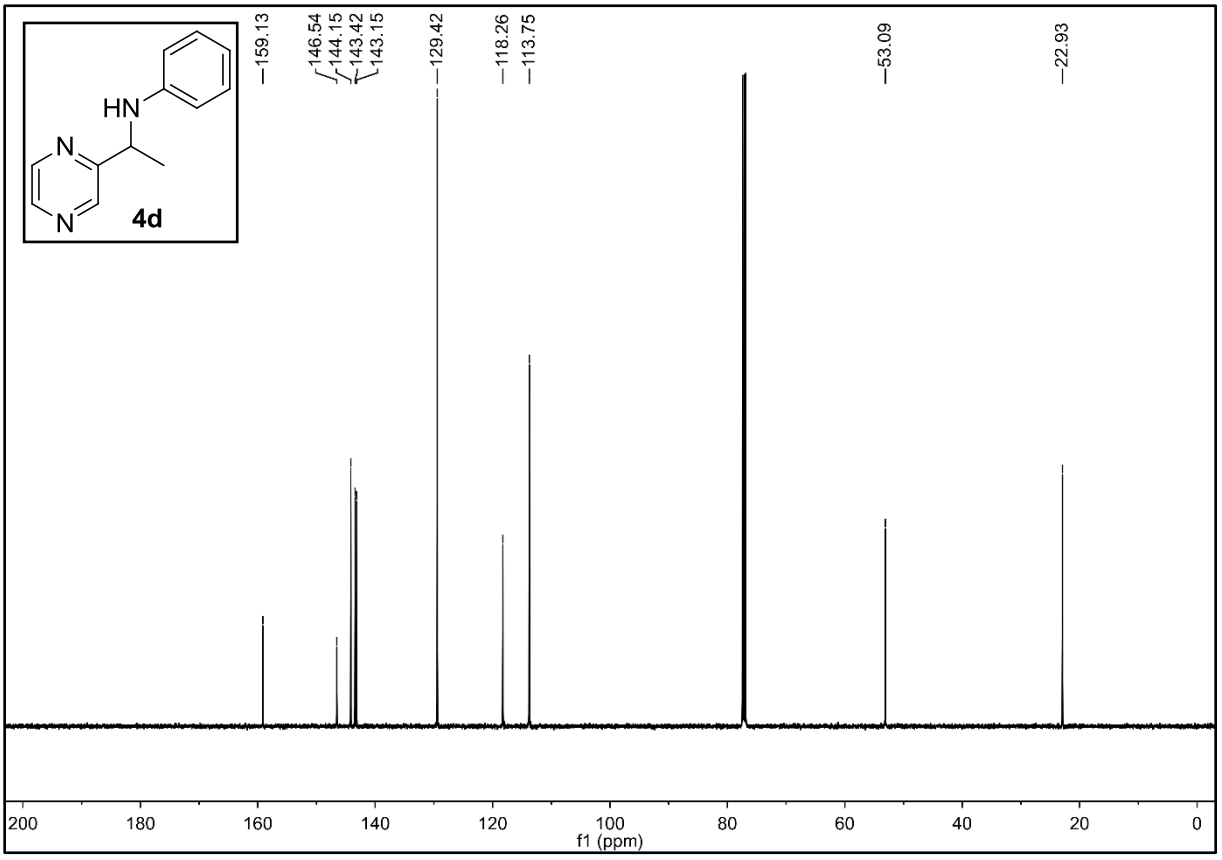
5
4
3
2
1
0
f1 (ppm)


HN
N
N
4d
159.13
146.54
144.15
143.42
143.15
129.42
118.26
113.75
53.09
22.93
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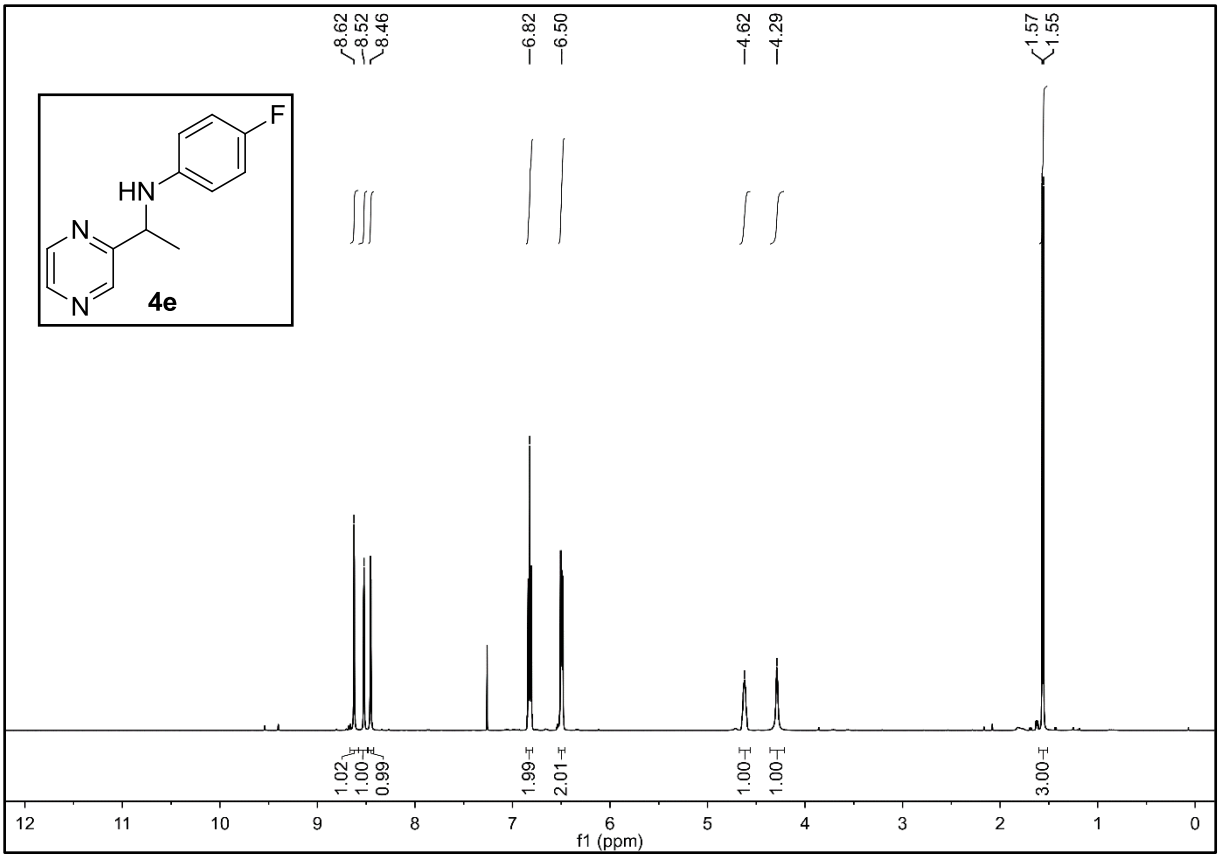
180
160
140
120
100
80
60
40
20
0
f1 (ppm)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N
4e
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1.00
0.99
1.99
2.01
1.00
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2
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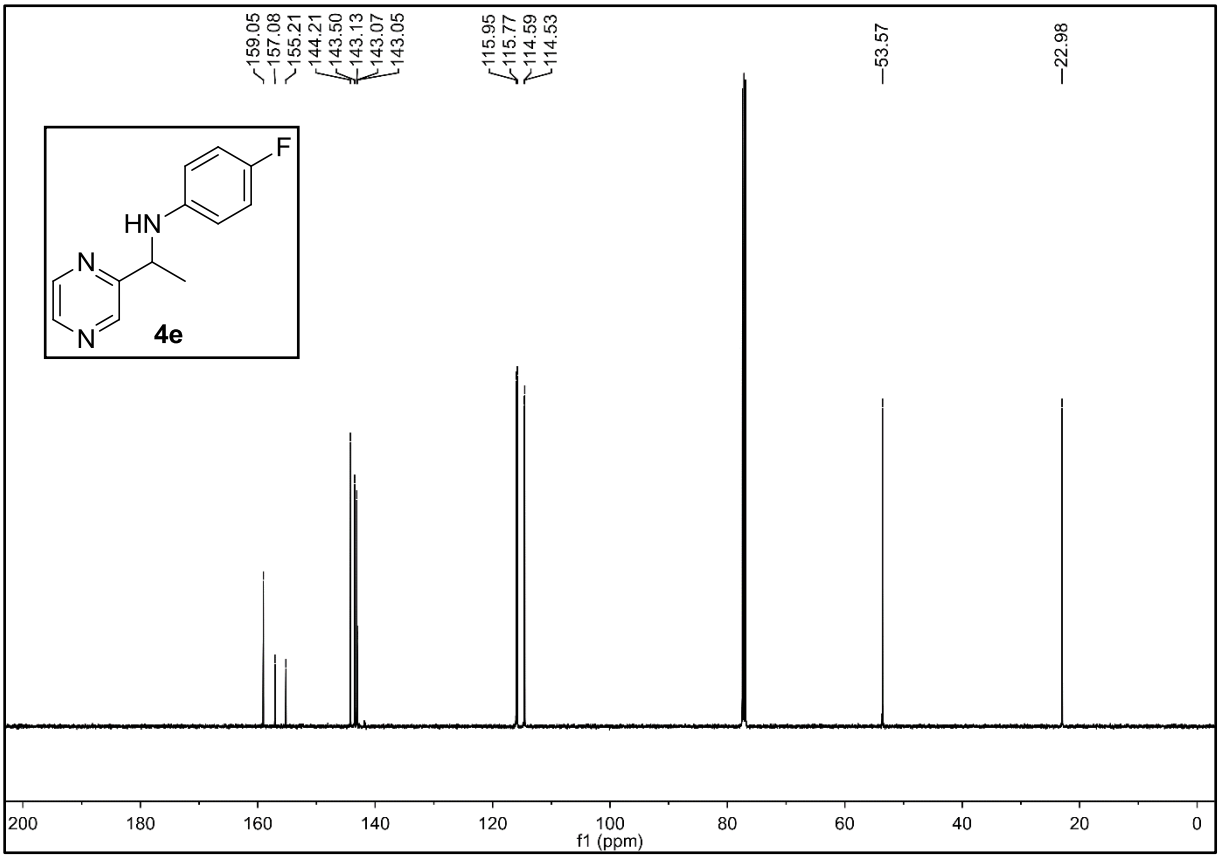
0
f1 (ppm)


159.05
157.08
155.21
144.21
143.50
143.13
143.07
143.05
115.95
115.77
114.59
114.53
53.57
22.98
F
HN
N
N
4e
200
180
160
140
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100
80
60
40
20
0
f1 (ppm)

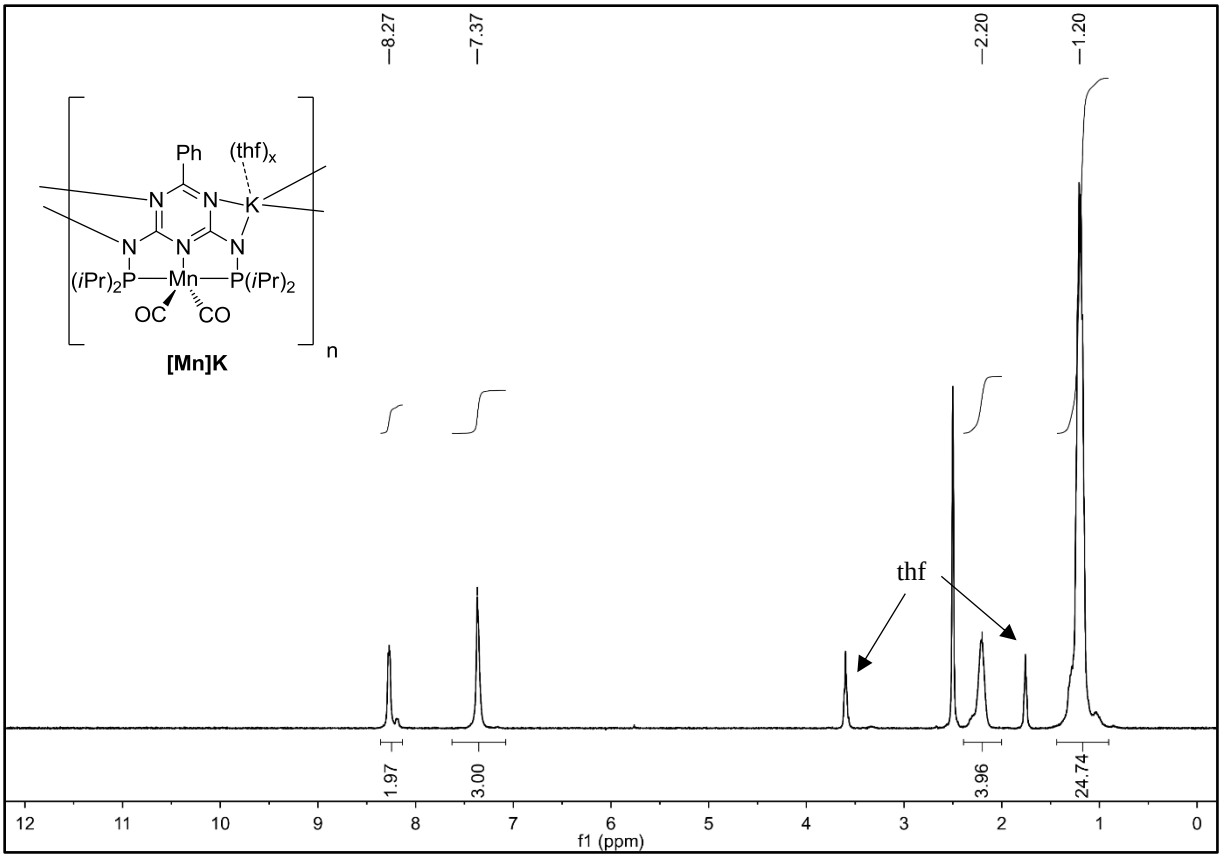


Figure S 33. ^{1}H NMR of **[Mn]K** in DMSO.

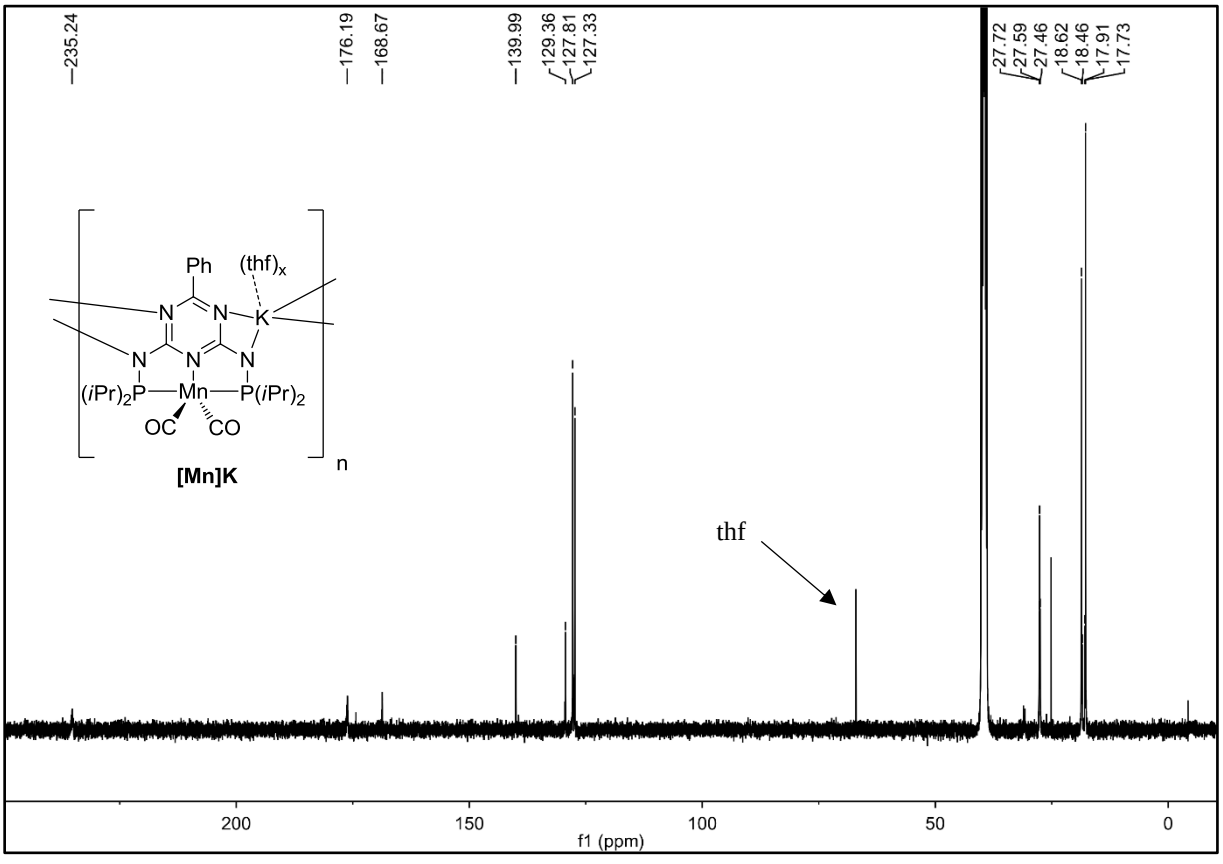


Figure S 34. ^{13}C NMR of **[Mn]K** in DMSO.

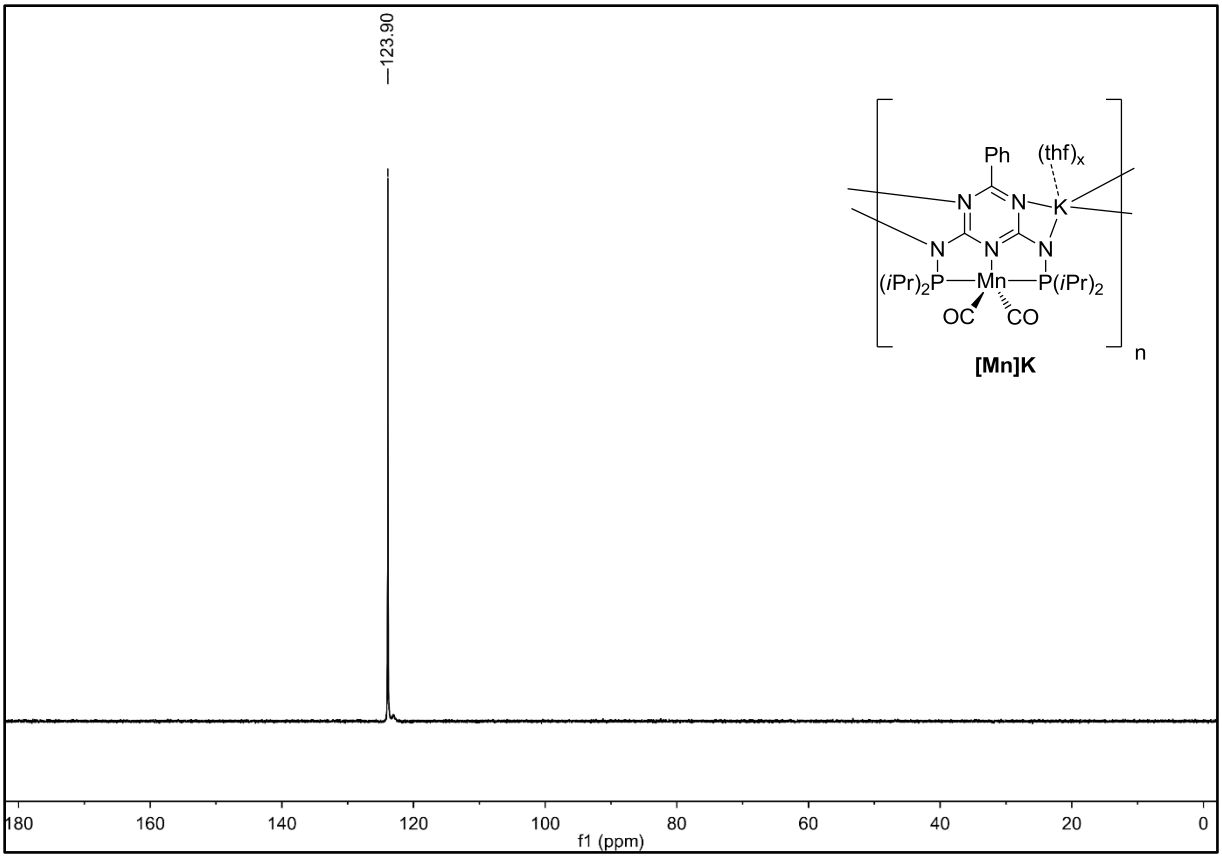


Figure S 35. ^{31}P NMR of **[Mn]K** in DMSO.

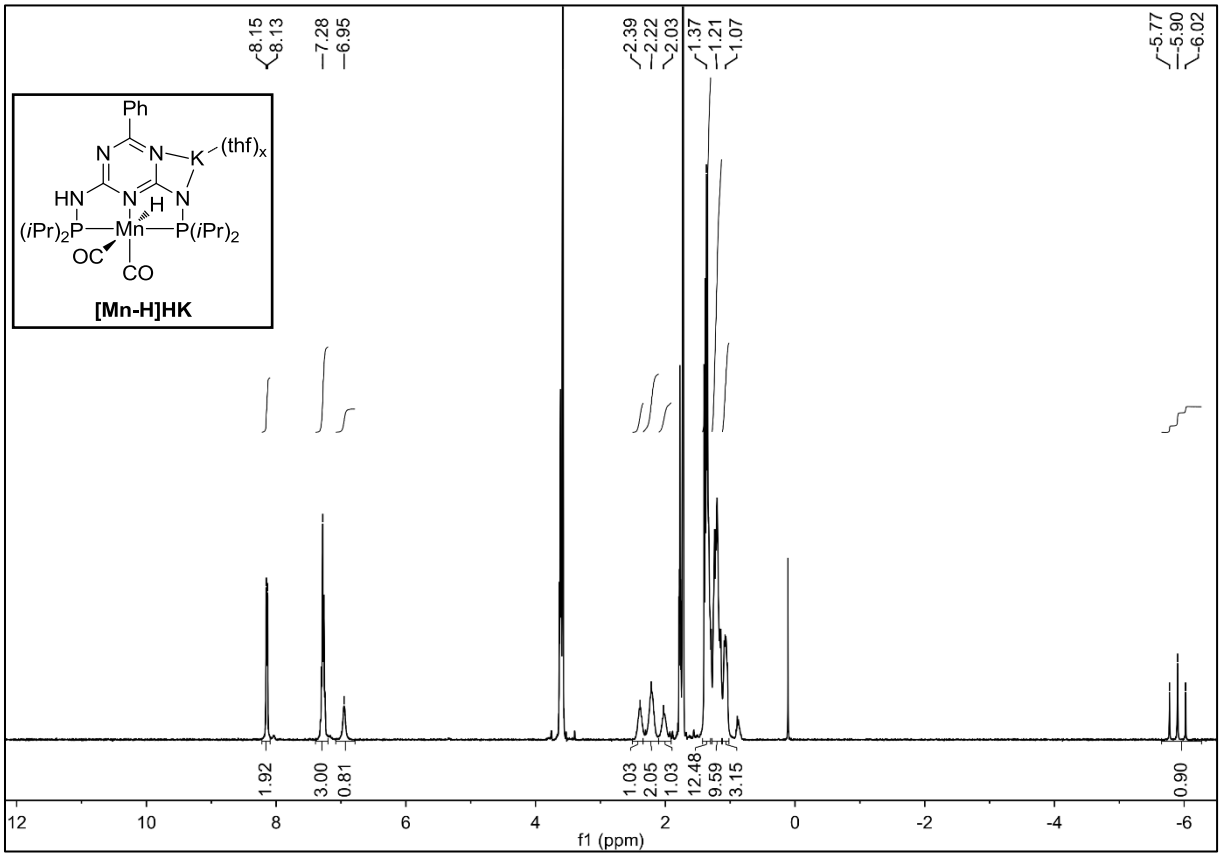


Figure S 36. ^{1}H NMR of **[Mn-H]HK** in thf_{D8}.

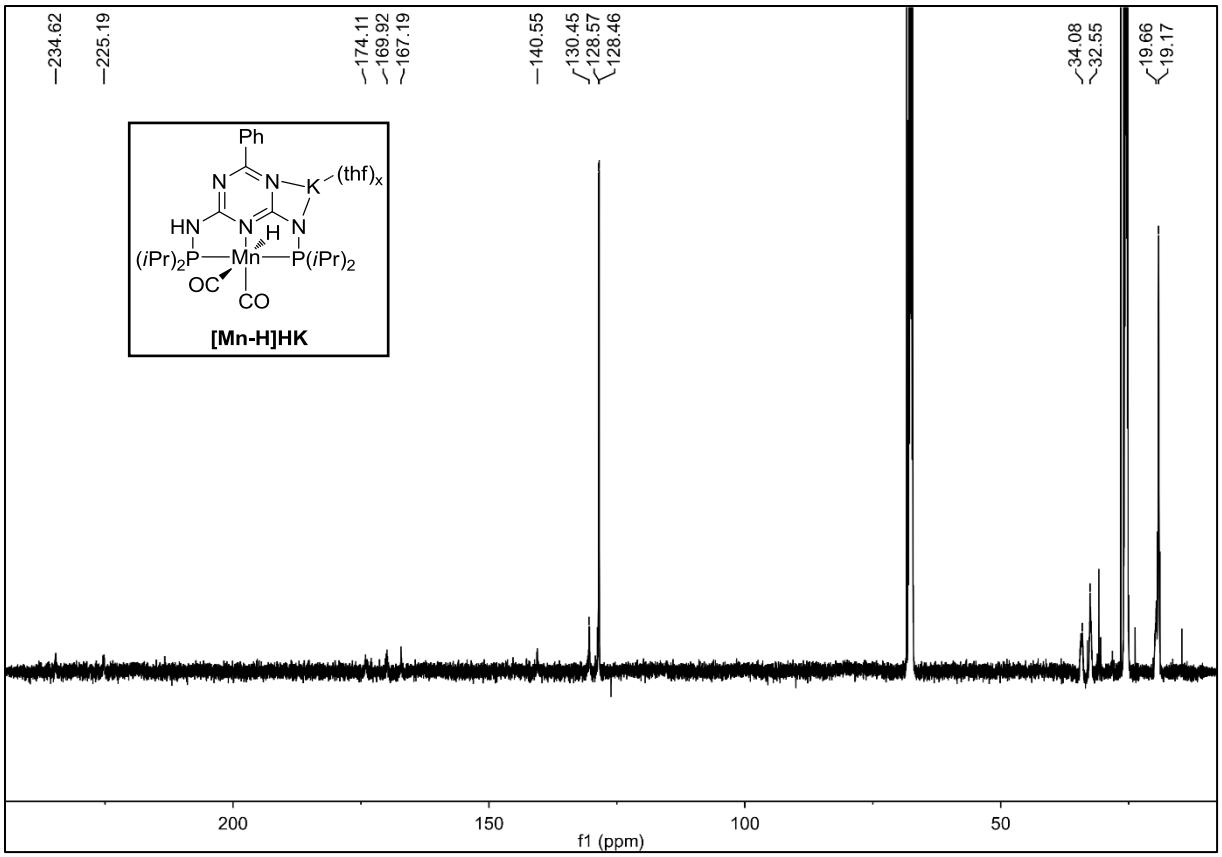


Figure S 37. ^{13}C NMR of **[Mn-H]HK** in thf_{D8}.

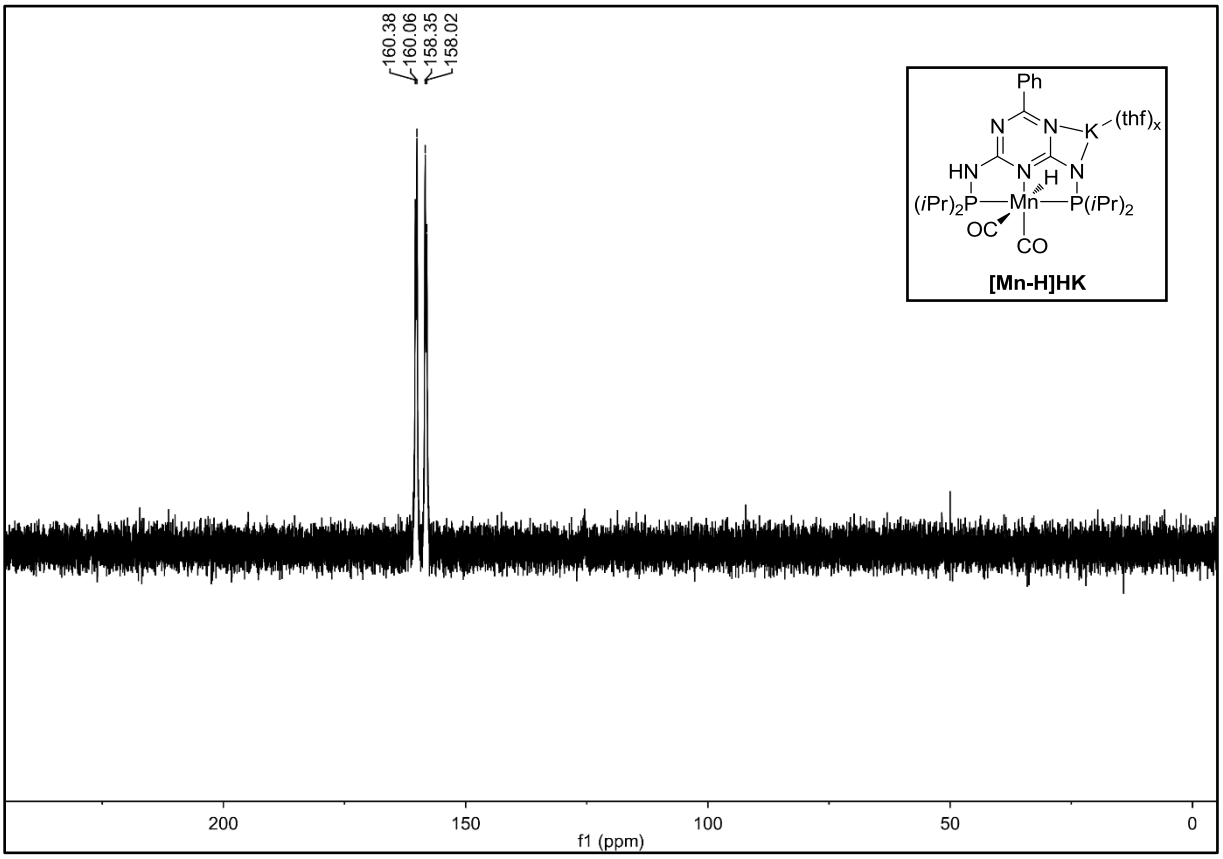


Figure S 38. ^{31}P NMR of **[Mn-H]HK** in thf_{D8}.

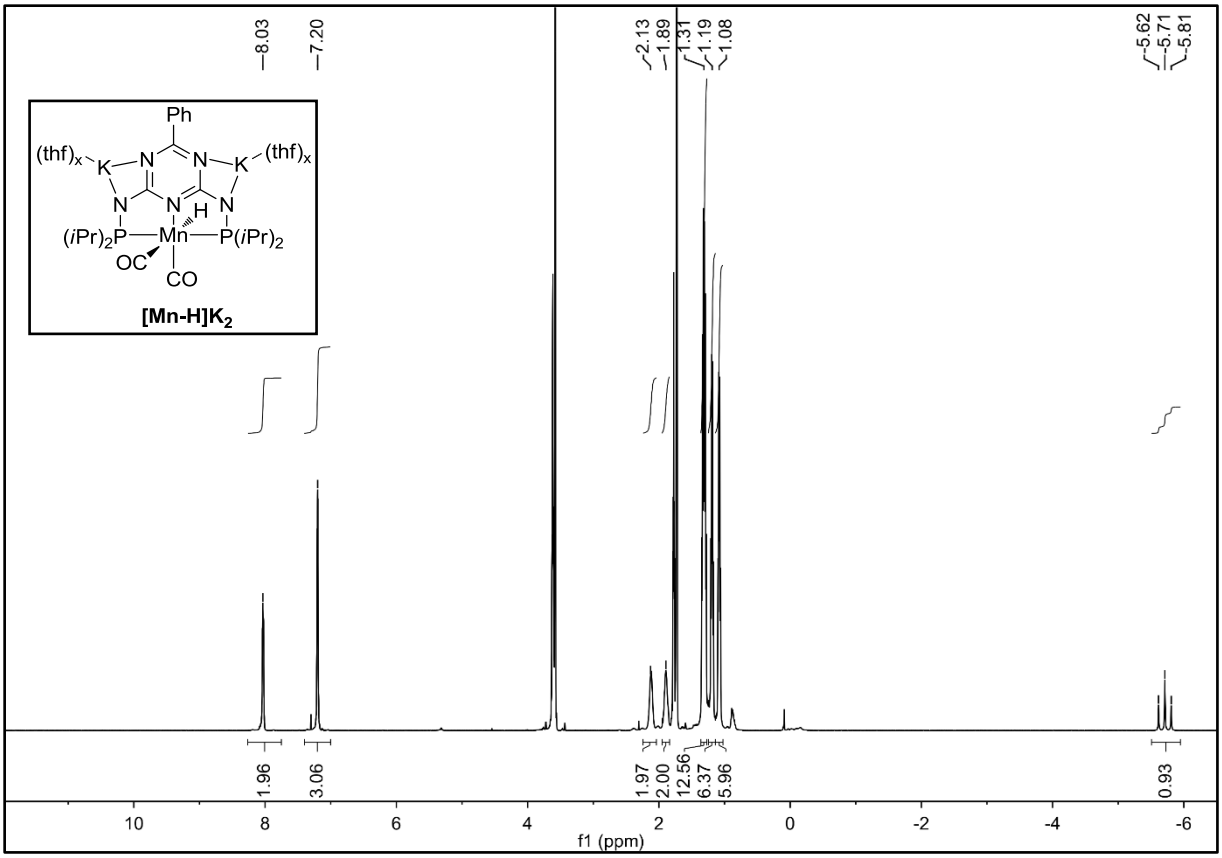


Figure S 39. ^{1}H NMR of **[Mn-H]K$_2$** in thf$_{D8}$.

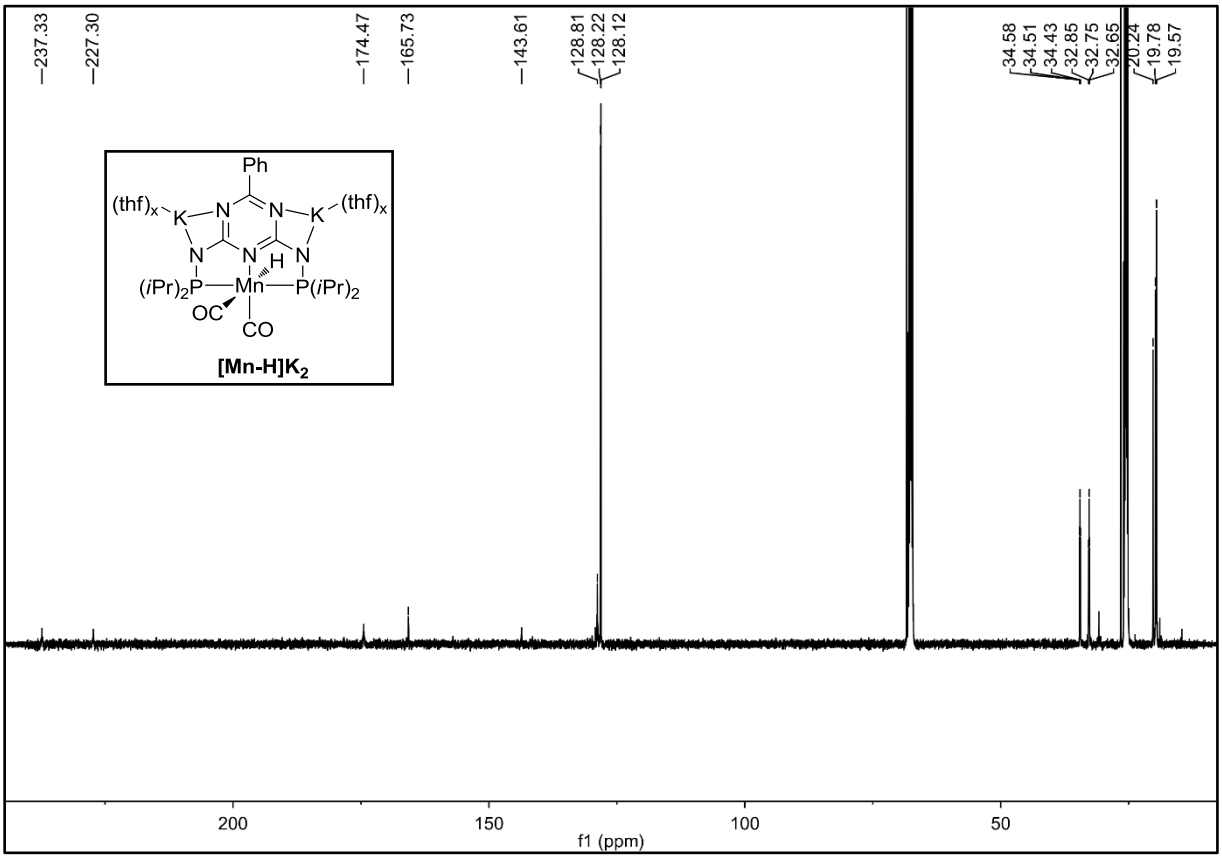


Figure S 40. ^{13}C NMR of **[Mn-H]K$_2$** in thf$_{D8}$.

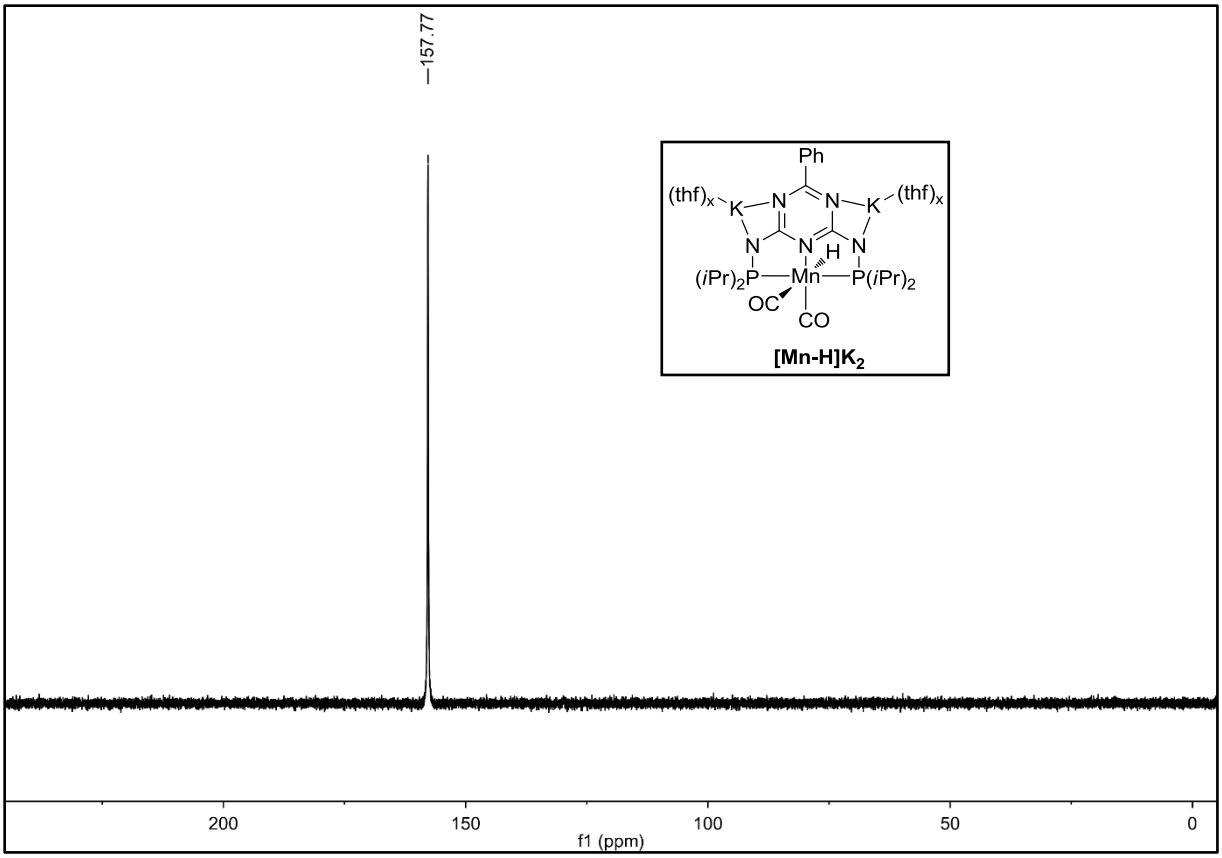


Figure S 41. ^{31}P NMR of **[Mn-H]K$_2$** in thf$_{D8}$.

5 UV-vis Data

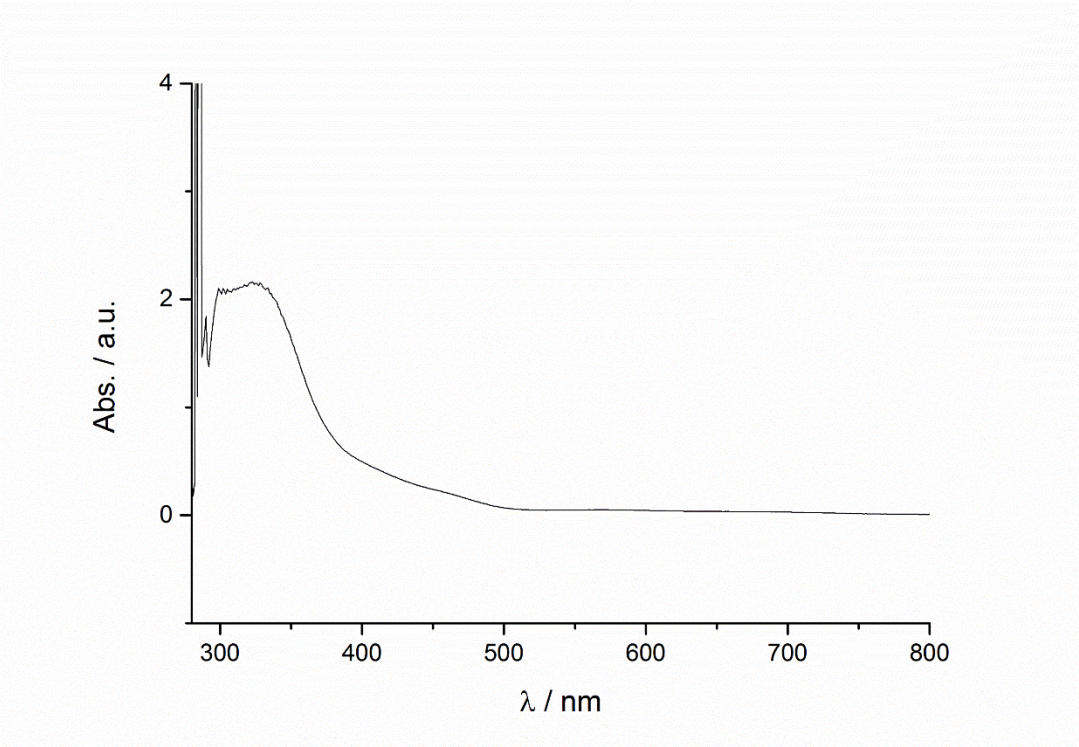


Figure S 42. UV-vis spectrum of [**Mn]K**.

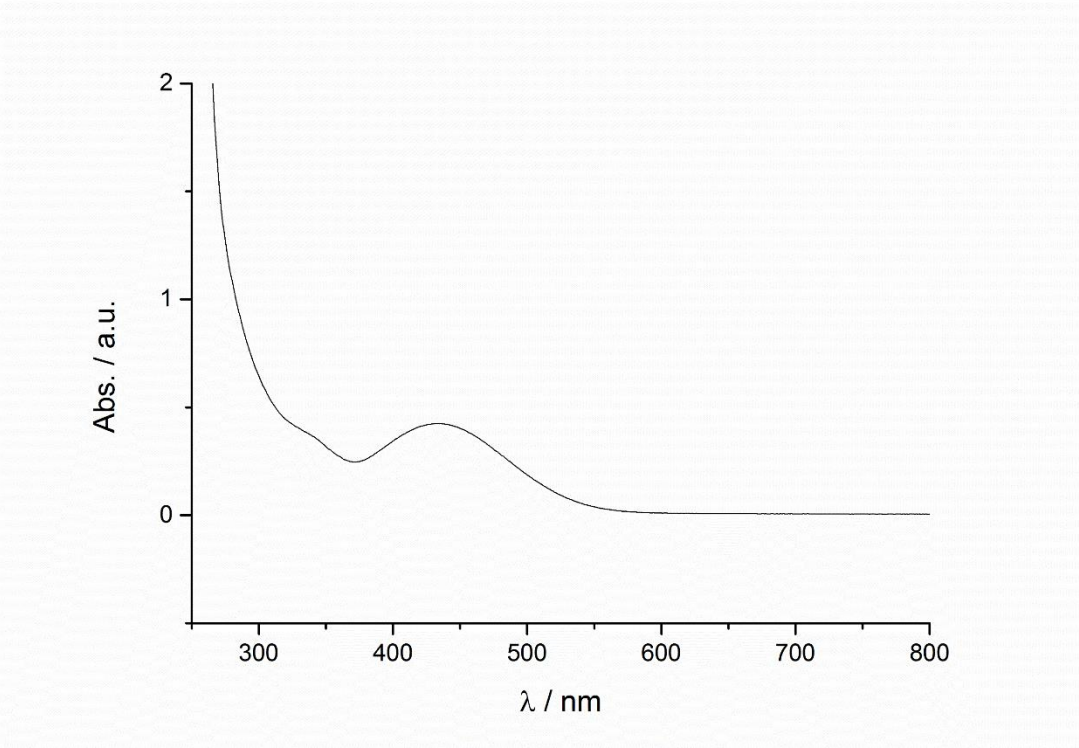


Figure S 43. UV-vis spectrum of **[Mn-H]HK**.

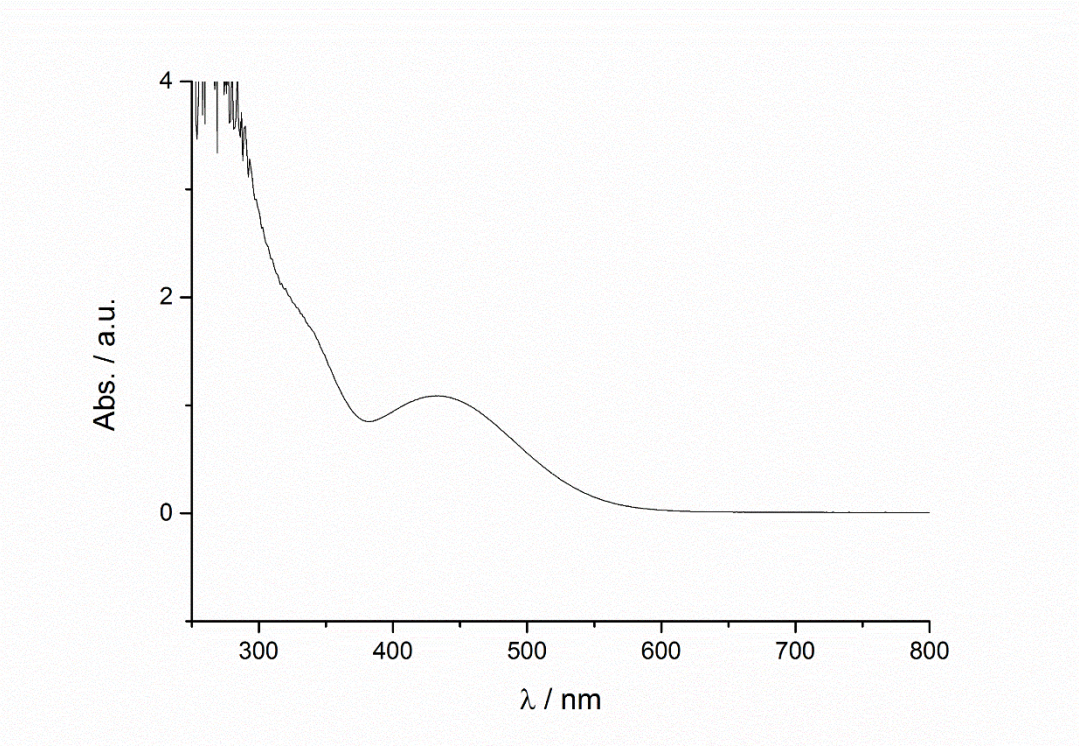


Figure S 44: UV-vis spectrum of **[Mn-H]K$_2$**.

6 IR Data

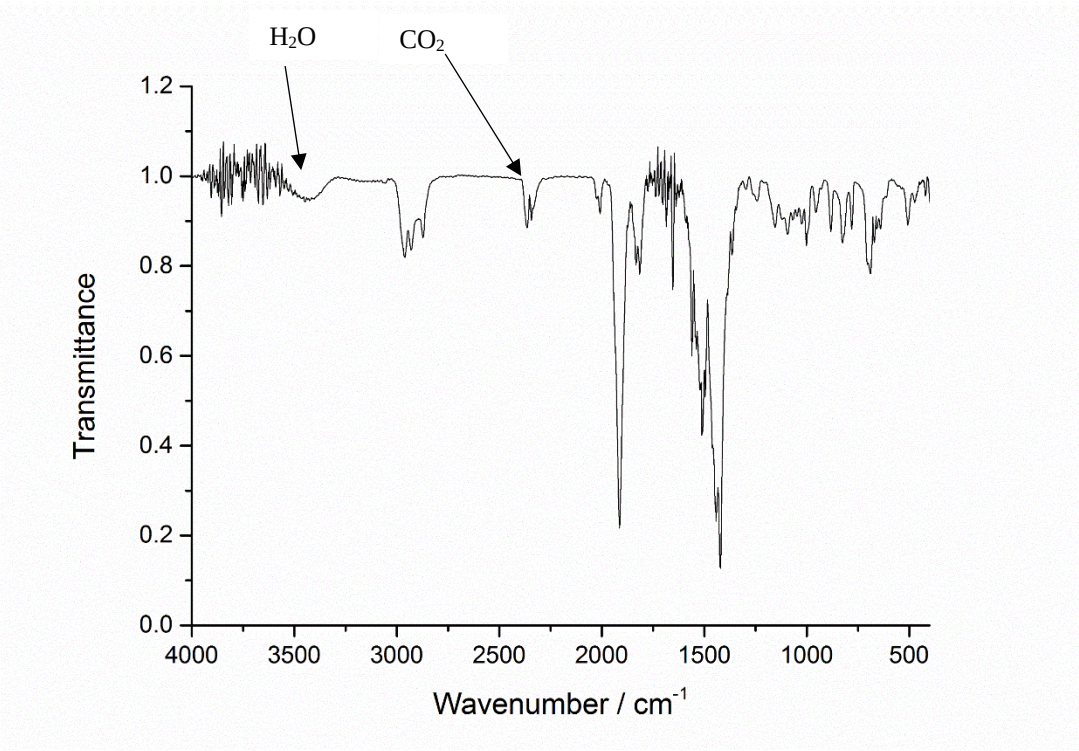


Figure S 45. IR spectrum of **[Mn]K**.

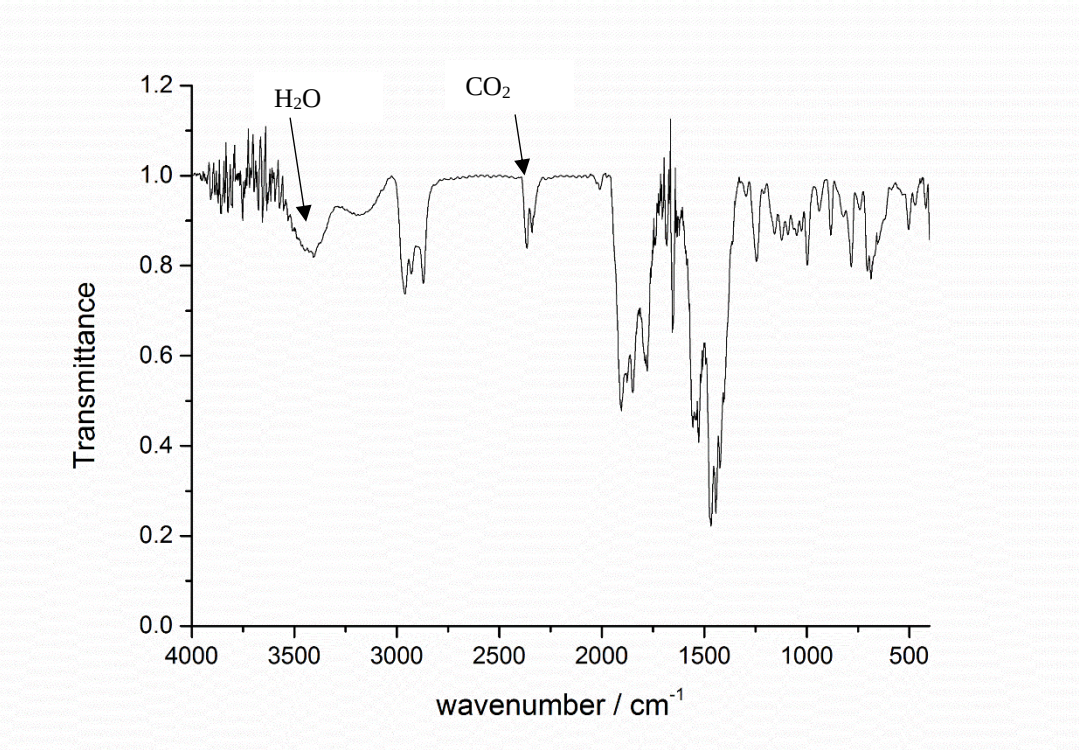


Figure S 46.IR spectrum of **[Mn-H]HK.**

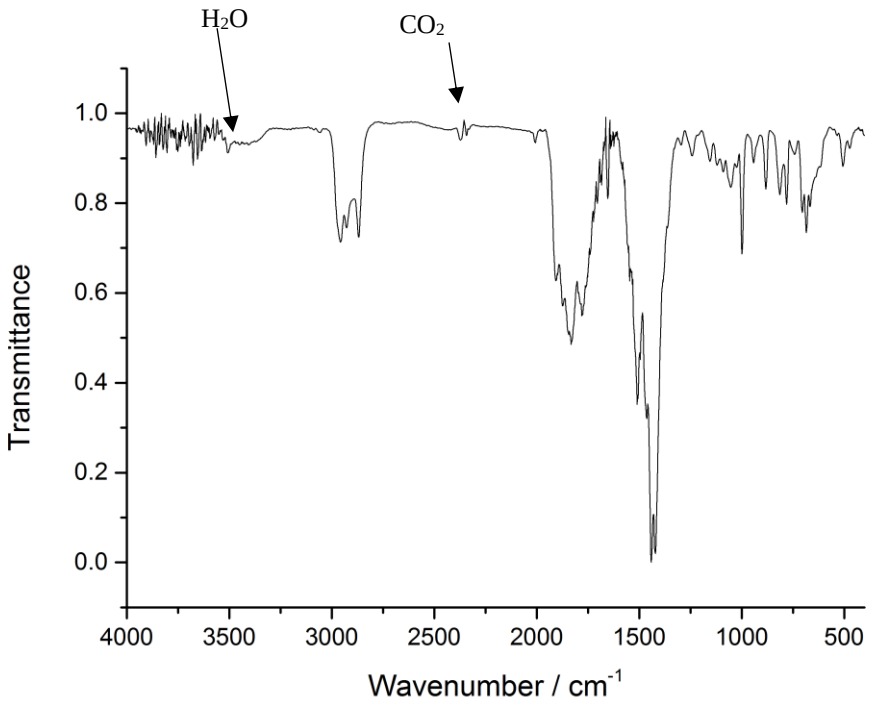
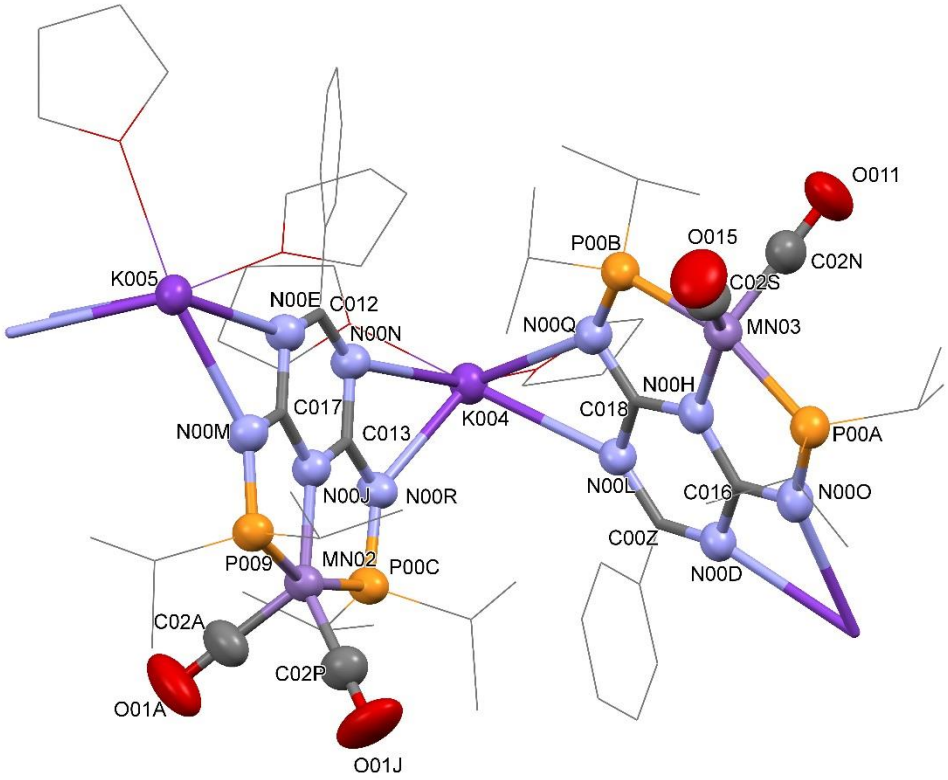


Figure S 47. IR spectrum of **[Mn-H]K$_2$**.

7 Crystallographic Data



checkCIF/PLATON (basic structural check) for [Mn]K

Structure factors have been supplied for datablock(s) sv493_1a1_m_p21n_sx
THIS REPORT IS FOR GUIDANCE ONLY. IF USED AS PART OF A REVIEW PROCEDURE FOR PUBLICATION, IT SHOULD NOT REPLACE THE EXPERTISE OF AN EXPERIENCED CRYSTALLOGRAPHIC REFEREE.

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No syntax errors found.                    CIF dictionary
Please wait while processing ....          Interpreting this report
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Structure factor report

Datablock: sv493_1a1_m_p21n_sx

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Bond precision:          C-C = 0.0093 A                  Wavelength=0.71073
Cell:        a=12.840(3)        b=45.110(9)        c=20.490(4)
             alpha=90           beta=96.90(3)      gamma=90
Temperature: 133 K
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	Calculated	Reported
Volume	11782(4)	11782(4)
Space group	P 21/n	P 1 21/n 1
Hall group	-P 2yn	-P 2yn
Moiety formula	C93 H147 K3 Mn3 N15 O12 P6, C4 H8 O [+ solvent]	0.25(C93 H147 K3 Mn3 N15 O12 P6), 0.25(C4 H8 O)
Sum formula	C97 H155 K3 Mn3 N15 O13 P6 [+ solvent]	C24.25 H38.75 K0.75 Mn0.75 N3.75 O3.25 P1.50
Mr	2207.31	551.82

Dx,g cm-3	1.244	1.244
Z	4	16
Mu (mm-1)	0.564	0.564
F000	4672.0	4672.0
F000'	4682.31	
h,k,lmax	17,60,27	17,59,27
Nref	30347	28052
Tmin,Tmax	0.972,0.990	0.983,0.994
Tmin'	0.944	

Correction method= # Reported T Limits: Tmin=0.983 Tmax=0.994 AbsCorr = NONE

Data completeness= 0.924 Theta(max)= 28.662

R(reflections)= 0.0983(15175) wR2(reflections)= 0.3280(28052)

S = 1.060 Npar= 1305

The following ALERTS were generated. Each ALERT has the format
test-name_ALERT_alert-type_alert-level.
Click on the hyperlinks for more details of the test.

Alert level B

PLAT973_ALERT_2_B Check Calcd Positive Resid. Density on Mn01 1.74 eA-3
And 2 other PLAT973 Alerts
PLAT973_ALERT_2_B Check Calcd Positive Resid. Density on Mn02 1.67 eA-3
PLAT973_ALERT_2_B Check Calcd Positive Resid. Density on Mn03 1.56 eA-3

Alert level C

ABSTY03_ALERT_1_C The _exptl_absorpt_correction_type has been given as none.
However values have been given for Tmin and Tmax. Remove
these if an absorption correction has not been applied.
From the CIF: _exptl_absorpt_correction_T_min 0.983
From the CIF: _exptl_absorpt_correction_T_max 0.994
PLAT084_ALERT_3_C High wR2 Value (i.e. > 0.25) ..... 0.33 Report
PLAT094_ALERT_2_C Ratio of Maximum / Minimum Residual Density .... 2.01 Report
PLAT220_ALERT_2_C Non-Solvent Resd 1 C Ueq(max)/Ueq(min) Range 6.0 Ratio
PLAT222_ALERT_3_C Non-Solv. Resd 1 H Uiso(max)/Uiso(min) Range 5.1 Ratio
PLAT241_ALERT_2_C High 'MainMol' Ueq as Compared to Neighbors of C038 Check
And 7 other PLAT241 Alerts
PLAT241_ALERT_2_C High 'MainMol' Ueq as Compared to Neighbors of C03C Check
PLAT241_ALERT_2_C High 'MainMol' Ueq as Compared to Neighbors of C03F Check
PLAT241_ALERT_2_C High 'MainMol' Ueq as Compared to Neighbors of C03I Check
PLAT241_ALERT_2_C High 'MainMol' Ueq as Compared to Neighbors of C03J Check
PLAT241_ALERT_2_C High 'MainMol' Ueq as Compared to Neighbors of C03K Check
PLAT241_ALERT_2_C High 'MainMol' Ueq as Compared to Neighbors of C03O Check
PLAT241_ALERT_2_C High 'MainMol' Ueq as Compared to Neighbors of C03R Check
PLAT242_ALERT_2_C Low 'MainMol' Ueq as Compared to Neighbors of O00U Check
And 4 other PLAT242 Alerts
PLAT242_ALERT_2_C Low 'MainMol' Ueq as Compared to Neighbors of O00W Check
PLAT242_ALERT_2_C Low 'MainMol' Ueq as Compared to Neighbors of C02W Check
PLAT242_ALERT_2_C Low 'MainMol' Ueq as Compared to Neighbors of C032 Check
PLAT242_ALERT_2_C Low 'MainMol' Ueq as Compared to Neighbors of C036 Check
PLAT260_ALERT_2_C Large Average Ueq of Residue Including O02U 0.124 Check
PLAT341_ALERT_3_C Low Bond Precision on C-C Bonds ..... 0.00929 Ang.
PLAT360_ALERT_2_C Short C(sp3)-C(sp3) Bond C03B - C03N . 1.40 Ang.
And 5 other PLAT360 Alerts
PLAT360_ALERT_2_C Short C(sp3)-C(sp3) Bond C03B - C03O . 1.43 Ang.
PLAT360_ALERT_2_C Short C(sp3)-C(sp3) Bond C03F - C03H . 1.42 Ang.
PLAT360_ALERT_2_C Short C(sp3)-C(sp3) Bond C03H - C03R . 1.42 Ang.
PLAT360_ALERT_2_C Short C(sp3)-C(sp3) Bond C03D - C03M . 1.40 Ang.
PLAT360_ALERT_2_C Short C(sp3)-C(sp3) Bond C03G - C03L . 1.43 Ang.
PLAT410_ALERT_2_C Short Intra H...H Contact H03M ..H23D . 1.93 Ang.
x,y,z = 1_555 Check
PLAT911_ALERT_3_C Missing FCF Refl Between Thmin & STh/L= 0.600 302 Report
PLAT973_ALERT_2_C Check Calcd Positive Resid. Density on K006 1.26 eA-3
PLAT973_ALERT_2_C Check Calcd Positive Resid. Density on K004 1.23 eA-3
PLAT977_ALERT_2_C Check Negative Difference Density on H23A -0.31 eA-3
And 3 other PLAT977 Alerts
PLAT977_ALERT_2_C Check Negative Difference Density on Hz -0.38 eA-3
PLAT977_ALERT_2_C Check Negative Difference Density on H7CA -0.32 eA-3
PLAT977_ALERT_2_C Check Negative Difference Density on H1CA -0.34 eA-3
PLAT978_ALERT_2_C Number C-C Bonds with Positive Residual Density. 0 Info

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Alert level G

PLAT002_ALERT_2_G Number of Distance or Angle Restraints on AtSite 11 Note

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PLAT003_ALERT_2_G Number of Uiso or Uij Restrained non-H Atoms ...         18 Report
PLAT004_ALERT_5_G Polymeric Structure Found with Maximum Dimension          1 Info
PLAT042_ALERT_1_G Calc. and Reported MoietyFormula Strings  Differ     Please Check
PLAT045_ALERT_1_G Calculated and Reported Z Differ by a Factor ...       0.25 Check
PLAT072_ALERT_2_G SHELXL First  Parameter in WGHT  Unusually Large       0.20 Report
PLAT176_ALERT_4_G The CIF-Embedded .res File Contains SADI Records         13 Report
PLAT178_ALERT_4_G The CIF-Embedded .res File Contains SIMU Records          4 Report
PLAT180_ALERT_4_G Check Cell Rounding: # of Values Ending with 0 =          4 Note
PLAT301_ALERT_3_G Main Residue  Disorder ..............(Resd  1  )         4% Note
PLAT398_ALERT_2_G Deviating  C-O-C    Angle From 120 for O02U           103.9 Degree
PLAT605_ALERT_4_G Largest Solvent Accessible VOID in the Structure       134 A**3
PLAT720_ALERT_4_G Number of Unusual/Non-Standard Labels ..........       288 Note
PLAT794_ALERT_5_G Tentative Bond Valency for Mn01      (I)       .       1.02 Info
And 2 other PLAT794 Alerts
PLAT794_ALERT_5_G Tentative Bond Valency for Mn02      (I)       .       1.02 Info
PLAT794_ALERT_5_G Tentative Bond Valency for Mn03      (I)       .       1.03 Info
PLAT860_ALERT_3_G Number of Least-Squares Restraints .............       109 Note
PLAT868_ALERT_4_G ALERTS Due to the Use of _smtbx_masks Suppressed          ! Info
PLAT883_ALERT_1_G No Info/Value for _atom_sites_solution_primary .     Please Do !
PLAT910_ALERT_3_G Missing # of FCF Reflection(s) Below Theta(Min).          1 Note
PLAT912_ALERT_4_G Missing # of FCF Reflections Above STh/L=  0.600       1973 Note
```

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   0 ALERT level A = Most likely a serious problem - resolve or explain
   3 ALERT level B = A potentially serious problem, consider carefully
  35 ALERT level C = Check. Ensure it is not caused by an omission or oversight
  21 ALERT level G = General information/check it is not something unexpected

   4 ALERT type 1 CIF construction/syntax error, inconsistent or missing data
  37 ALERT type 2 Indicator that the structure model may be wrong or deficient
   7 ALERT type 3 Indicator that the structure quality may be low
   7 ALERT type 4 Improvement, methodology, query or suggestion
   4 ALERT type 5 Informative message, check
```

It is advisable to attempt to resolve as many as possible of the alerts in all categories. Often the minor alerts point to easily fixed oversights, errors and omissions in your CIF or refinement strategy, so attention to these fine details can be worthwhile. In order to resolve some of the more serious problems it may be necessary to carry out additional measurements or structure refinements. However, the purpose of your study may justify the reported deviations and the more serious of these should normally be commented upon in the discussion or experimental section of a paper or in the "special_details" fields of the CIF. checkCIF was carefully designed to identify outliers and unusual parameters, but every test has its limitations and alerts that are not important in a particular case may appear. Conversely, the absence of alerts does not guarantee there are no aspects of the results needing attention. It is up to the individual to critically assess their own results and, if necessary, seek expert advice.

Publication of your CIF in IUCr journals

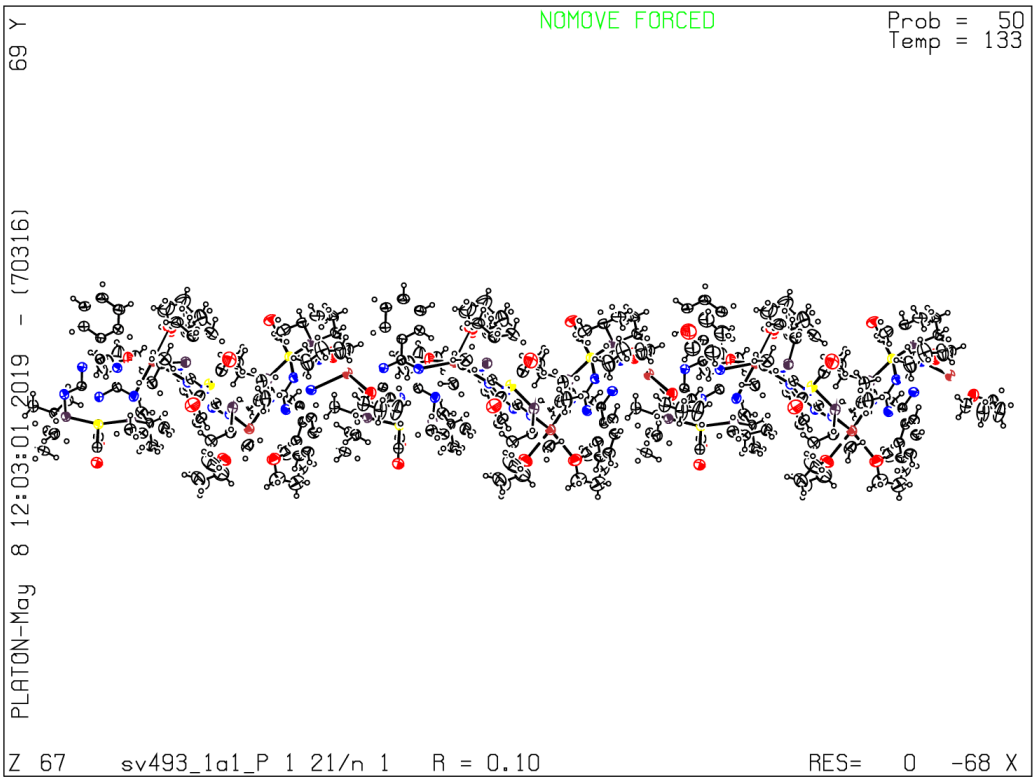
A basic structural check has been run on your CIF. These basic checks will be run on all CIFs submitted for publication in IUCr journals (*Acta Crystallographica*, *Journal of Applied Crystallography*, *Journal of Synchrotron Radiation*); however, if you intend to submit to *Acta Crystallographica Section C* or *E* or *IUCrData*, you should make sure that full publication checks are run on the final version of your CIF prior to submission.

Publication of your CIF in other journals

Please refer to the *Notes for Authors* of the relevant journal for any special instructions relating to CIF submission.

PLATON version of 03/05/2019; check.def file version of 29/04/2019

Datablock sv493_1a1_m_p21n_sx - ellipsoid plot



8 References

[1] Lai, P. S.; Dubland, J. A.; Sarwar, M. G.; Chudzinski, M. G.; Taylor, M. S. *Tetrahedron* **2011**, *67*, 7586-7592.

[2] Perrone, S.; Salomone, A.; Caroli, A.; Falcicchio, A.; Citti, C.; Cannazza, G.; Troisi, L. *Eur. J. Org. Chem.* **2014**, 5932-5938.

[3] Freitag, F.; Irrgang, T.; Kempe, R. *Chem. Eur. J.* **2017**, *23*, 12110-12113.

[4] Kallmeier, F.; Irrgang, T.; Dietel, T.; Kempe, R. *Angew. Chem. Int. Ed.* **2016**, *55*, 11806-11809.

[5] Dolomanov, O. V.; Bourhis, L. J.; Gildea, R. J.; Howard, J. A. K.; Puschmann, *J. Appl. Cryst.* **2009**, *42*, 339-341.

[6] Sheldrick, G. M. *Acta Cryst.* **2015**, *C71*, 3–8.

[7] Farrugia, L. J. *J. Appl. Cryst.* **2012**, *45*, 849–854.

[8] Macrae, C. F.; Bruno, I. J.; Chisholm, J. A.; Edgington, P. R.; McCabe, P.; Pidcock, E.; Rodriguez-Monge, L.; Taylor, R.; van de Streek, J.; Wood, P. A. *J. Appl. Cryst.* **2008**, *41*, 466-470.

[9] Yamane, Y.; Liu, X.; Hamasaki, A.; Ishida, T.; Haruta, M.; Yokoyama, T.; Tokunaga, M. *Org. Lett.* **2009**, *11*, 5162–5165.

[10] Elangovan, S.; Neumann, J.; Sortais, J.; Junge, K.; Darcel, C.; Beller, M. *Nat. Commun.* **2016**, *7*, 12641.

[11] Thakur, M. S.; Nayal, O. S.; Sharma, A.; Rana, R.; Kumar, N.; Maurya, S. K. *Eur. J. Org. Chem.***2018**, 6729–6732.

[12] Abdukader, A.; Jin, H.; Cheng, Y.; Zhu, C. *Tetrahedron Lett.* **2014**, *55*, 4172–4174.

[13] Landge, V. G.; Mondal, A.; Kumar, V.; Nandakumar, A.; Balaraman, E. *Org. Biomol. Chem.* **2018**, *16*, 8175-8180.

[14] Kawahara, R.; Fujita, K.; Yamaguchi, R. *Adv. Synth. Catal.* **2011**, *353*, 1161 – 1168.

[15] Zhou, Y.; Zhou, H.; Liu, S.; Pi, D.; Shen, G. *Tetrahedron* **2017**, *73*, 3898-3904.

[16] Fernandes, A.; Royo, B. *ChemCatChem* **2017**, *9*, 3912 –3917.

[17] Likhar, P.; Arundhathi, R.; Kantam, M.; Prathima, P. *Eur. J. Org. Chem.* **2009**, 5383–5389.

[18] Yang, C.; Fu, Y.; Huang, Y.; Yi, J.; Guo, Q; Liu, L. *Angew. Chem. Int. Ed.* **2009**, *48*, 7398 –7401.

[19] Fertig, R.; Irrgang, T.; Freitag, F.; Zander, J.; Kempe, R. *ACS Catal.* **2018**, *8*, 8525−8530.

[20] Rösler, S.; Ertl, M.; Irrgang, T.; Kempe, R. *Angew.Chem. Int. Ed.* **2015**, *54*, 15046–15050.

[21] Wong, C.; McBurney, R.; Binding, S.; Peterson, M.; Gonçales, V.; Gooding, J.; Messerle, B. *Green Chem.* **2017**, *19*, 3142-3151.

[22] Woo, L.; Wood, P.; Bubert, C.; Thomas, M.; Purohit, A.; Potter, B. *ChemMedChem* **2013**, *8*, 779 – 799.

[23] MacQueen, P.; Stradiotto, M. *Synlett* **2017**, *28*, 1652-1656.

[24] Villa-Marcos, B.; Tang, W.; Wu, X.; Xiao, J. *Org. Biomol. Chem.* **2013**, *11*, 6934–6939.

[25] Aziz, J.; Brion, J.; Hamze, A.; Alami, M. *Adv. Synth. Catal.* **2013**, *355*, 2417 – 2429.

[26] Hansch, C.; Leo, A.; Taft, R. *Chem. Rev.* **1991**, *91*, 165-195.

[27] Keinicke, L.; Fristrup, P.; Norrby, P.-O.; Madsen, R. *J. Am. Chem. Soc.* **2005**, *127*, 15756–15761.

[28] Creary, X.; Mehrsheikh-Mohammadi, M.; McDonald, S. *J. Org. Chem.* **1987**, *52*, 3254-3263.