Supporting Information for

# Efficient and chemoselective imine synthesis catalyzed by a well-defined $PN^3$- manganese (II) pincer system

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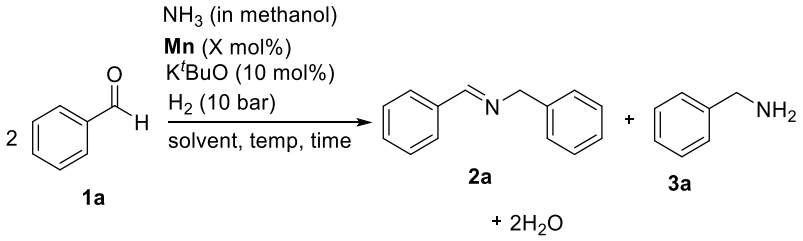
## 1. General information.

All manipulation of air- and/or moisture-sensitive compounds were carried out under an atmosphere of purified argon in a vacuum atmospheres glovebox or using standard Schenk techniques. All solvents were distilled under Ar from appropriate drying agents. Unless otherwise stated, commercial reagents were used as received without purification. Column chromatography was performed on silica gel (60–120mesh). NMR spectra were recorded on Bruker Advance 400, Bruker Avance-500, or Bruker Avance-600 NMR spectrometers in deuterated solvents. $^{1}$H NMR chemical shifts were referenced to the residual hydrogen signals of the deuterated solvents, and the $^{13}$C NMR chemical shifts were referenced tothe $^{13}$C signals of the deuterated solvents. Data are reported as follows: chemical shift, multiplicity (s = singlet, d = doublet, t = triplet, q = quartet, p = pentet, s = sextet, h = heptet, m =multiplet, br = broad), coupling constants (Hz) and integration. Gas chromatography was performed on Agilent 5975C GC inert XL EI/CI MSD with Triple-Axis MS Detector. The X-ray diffraction data were collected using Bruker-AXS KAPPA-APEXII CCD diffractometer (CuKα, λ= 1.54178 Å). Indexing was performed using APEX2 (Difference Vectors method). Data integration and reduction were performed using SaintPlus 6.01. Absorption correction was performed by multi-scan method implemented in SADABS. Space groups were determinedusing XPREP implemented in APEX2. Structures were solved using SHELXS-97 (direct methods) and refined using SHELXL-97 (fullmatrix least-squares on F2). Elemental analyses were conducted by Flash 2000-Thermo Scientific CHNO Analyzer. Synthesis of PN$^{3}$P*$^{t}$Bu$_2$ ligand was prepared according to the previous report.[1] Catalysts **Mn1** and **Mn2** were prepared according to our previous report.[2]

## 2. Experimental methods:

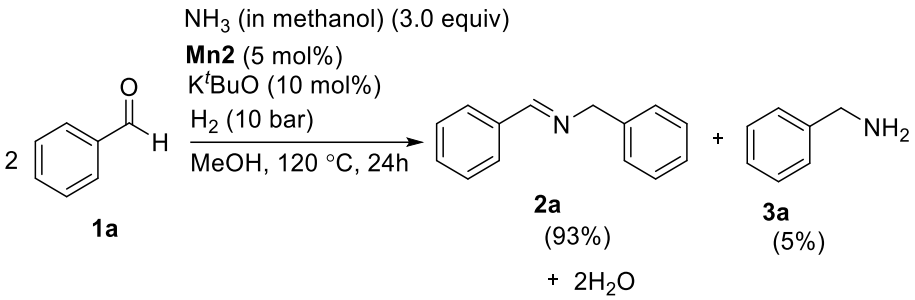
**Table S1. Optimization of the reaction conditions for reductive amination of benzaldehyde**




| entry | **Mn** (X mol%) | Solvent | T (°C) | conv. (%) | Yield (**2a**,**3a**)[b] |
|---|---|---|---|---|---|
| 1 | **Mn1** (3) | Methanol | 120 | 75 | 71,10 |
| 2 | **Mn1** (3) | Toluene | 120 | 70 | 68,2 |
| 3 | **Mn2** (5) | Methanol | 120 | 100 | 93, 5 |
| 4 | **Mn2** (5) | Toluene | 120 | 75 | 71,2 |
| 5 | **Mn2**(5) | MeOH | 100 | 90 | 82,5 |
| 6 | **Mn2**(5) | MeOH | 90 | 90 | 80,7 |
| 7 | **Mn2**(5) | MeOH | 80 | 88 | 78,6 |

[a]For the reaction, benzaldehyde (2.0 mmol), $NH_3$ in methanol (3.0 equiv), **Mn** (3~5 mol %), K$^t$BuO (10 mol%), $H_2$ (10 bar). [b]Determined by GC-MS using mesitylene as the internal standard and NMR yields using $CH_2Br_2$ as an internal standard. [c]48h. [d]bibenzylamin*e* (35%) was formed and confirmed by GC-MS. [e]$H_2$(35bar).

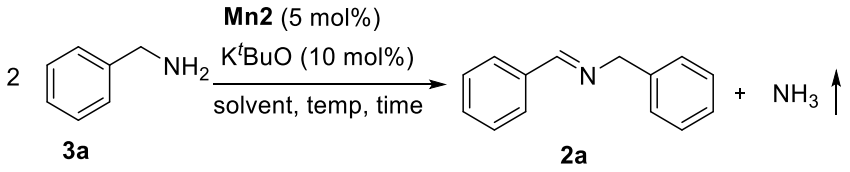
**Table S2. Deviation from the standard reaction conditions**




| Entry | Deviation in reaction conditions | Yield (**2a**, **3a** %)[b] |
|---|---|---|
| 1 | without **Mn2** | 10, - |
| 2 | without K$^t$BuO | 20, - |
| 3 | without $H_2$ | trace |
| 4 | $NH_3$ gas | 80, 10 |
| 5 | 48 h | 94,- |
| 6 | 5 bar $H_2$ pressure | 70, 3 |
| 7 | without solvent | 80, 5 |

[a]For the reaction, benzaldehyde (2.0 mmol), $NH_3$ in methanol (3.0 equiv), **Mn2** (5 mol %), K$^t$BuO (10 mol%), $H_2$ (10 bar). [b]Determined by GC-MS using mesitylene as the internal standard and NMR yields using $CH_2Br_2$ as an internal standard.

**Table S3. Optimization of the reaction conditions for oxidative coupling of benzylamine**




| Entry | Solvent | Temp (°C) | Time (h) | conv. (%) | Yield (**2a**, %)[b] |
|---|---|---|---|---|---|
| 1 | Methanol | 120 | 15 | 100 | 95 |
| 2 | Methanol | 100 | 15 | 100 | 95 |
| 3 | Methanol | 80 | 15 | 100 | 95 |
| 4 | Ethanol | 80 | 24 | 80 | 75 |

| | | | | | |
|---|---|---|---|---|---|
| 5 | $^{i}$PrOH | 80 | 24 | 80 | 78 |
| 6 | Toluene | 80 | 24 | 100 | 90 |
| 7 | Toluene | 80 | 15 | 100 | 90 |
| 8 | Toluene | 60 | 15 | 60 | 55 |
| 9 | THF | 80 | 15 | 60 | 57 |
| 10 | No solvent | 80 | 15 | 80 | 76 |
| 11 | No solvent | 80 | 48 | 80 | 78 |

[a]For the reaction, benzylamine (2.0 mmol), **Mn2** (3 mol %), K$^{t}$BuO (6 mol%). [b]Determined by GC-MS using mesitylene as internal standard and NMR yields using $CH_2Br_2$ as an internal standard.

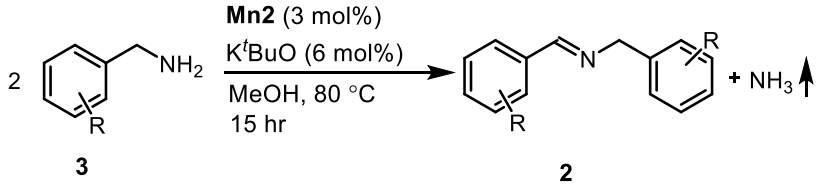
**S3-1. Typical procedure for the reductive amination of aldehydes to imines:**

To a mixture of aldehydes (2.0 mmol) and $NH_3$ in methanol (3.0 equiv.) in methanol solvent was added **Mn2** (5 mol%), K$^{t}$BuO (10 mol%) in a Parr high-pressure reactor. The autoclave was purged three times with hydrogen, and then the solution was pressurized with 10 bar of $H_2$ and heated at 120 °C (oil bath temperature) for 24~48 h. The reaction mixture was then cooled down in an ice bath for 30 min before releasing $H_2$ pressure. For quantitative GC analysis, mesitylene was added and injected into GC. After completion of the reaction, the solvent was evaporated and the resulting residue was purified by a base-washed silica gel column (adding 2% $Et_3N$ into the mixture of petroleum ether and ethyl acetate) or by column chromatography on a neutral alumina column to afford the corresponding imines.

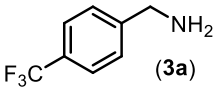
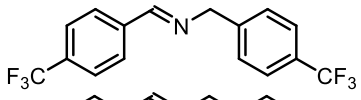
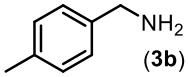
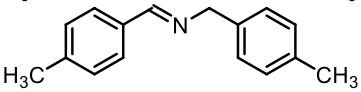
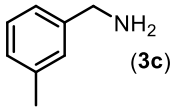
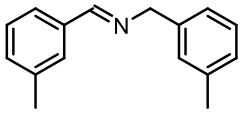
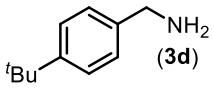
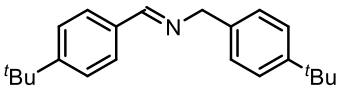
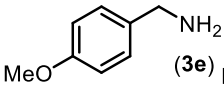
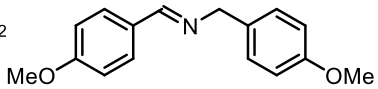
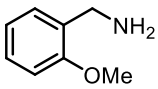
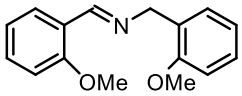
**S3-2. Typical procedure dehydrogenative homocoupling of amines:**

To a mixture of benzylamine in toluene was added **Mn2** (5 mol%), K$^{t}$BuO (10 mol%) in a glass reaction tube and heated at 80 °C (oil bath temperature) for 15 h. The reaction mixture was then cooled down and tolune solvent was evaporated. For quantitative GC analysis, mesitylene was added and injected into GC. After completion of the reaction, the solvent was evaporated and the resulting residue was purified by a base-washed silica gel column (adding 2% $Et_3N$ into the mixture of petroleum ether and ethyl acetate) or by column chromatography on a neutral alumina column to afford the corresponding imines.

**Table S4. Substrate Scope for the reductive homocoupling of amines**

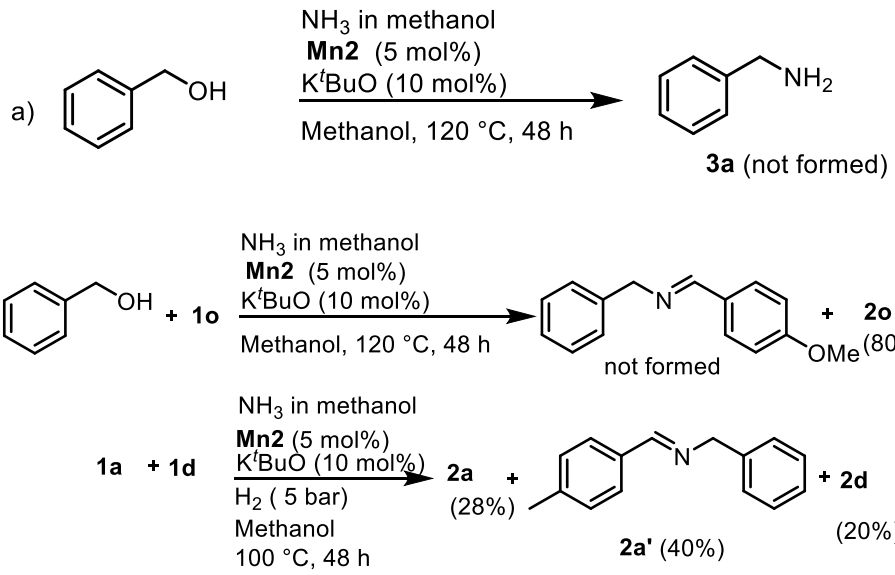



**3** **2**

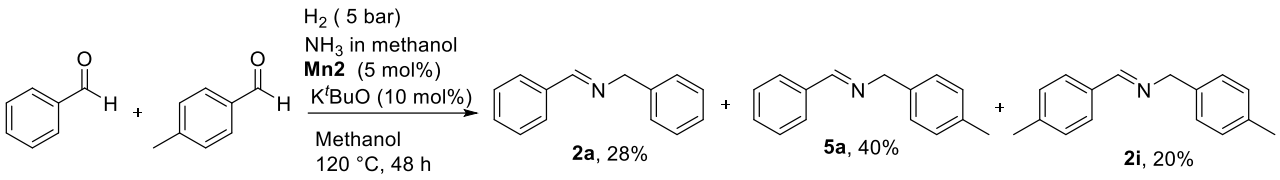
| entry | substrate | product | yield (%)[b] |
|---|---|---|---|
| 1 |  (**3a**) |  | **2k** 89 |
| 2 |  (**3b**) |  | **2l** 95 |
| 3 |  (**3c**) |  | **2m** 89 |
| 4 |  (**3d**) |  | **2n** 95 |
| 5 |  (**3e**) |  | **2o** 87 |
| 6 |  (**3f**) |  | **2p** 85 |

[a]For the reaction, amine (2.0 mmol), $NH_3$ in methanol (3.0 equiv.), **Mn2** (3 mol%), K$^t$BuO (6 mol%) in methanol (1.0 mL). [b]Isolated yields.

**S3-3. Control experiments**

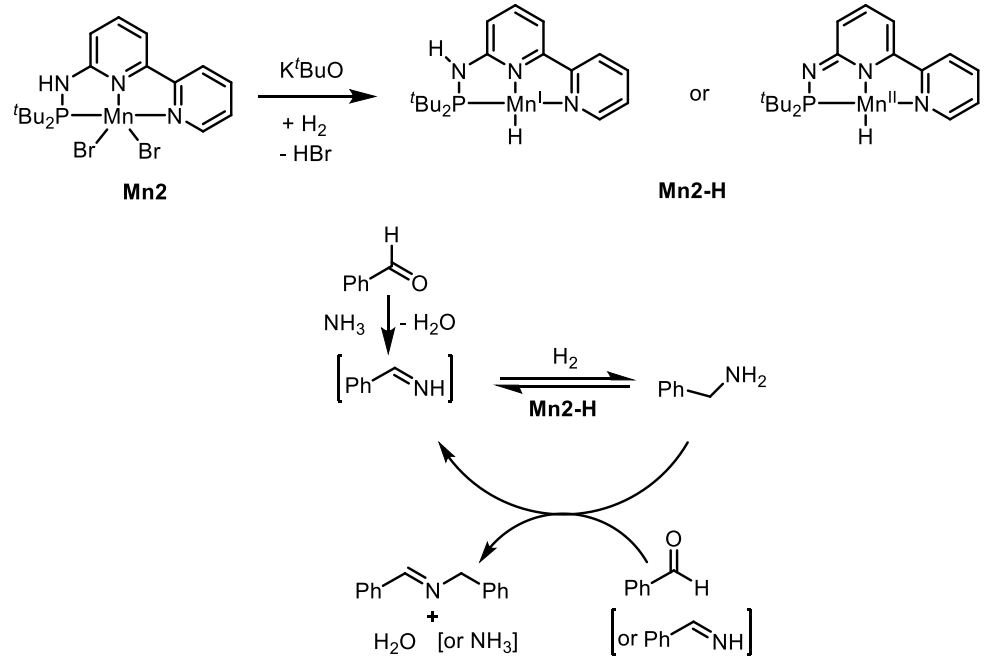


**S3-4. Synthetic procedure for the reductive amination of benzaldehyde and *p*-tolualdehydes to imines:**



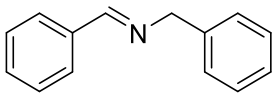

To a mixture of benzaldehyde (1.0 mmol) and *p*-tolualdehyde (1.0 mmol) in methanol was added $NH_3$ in methanol (3.0 equiv.), **Mn2** (20 mg, 0.047 mmol) and K$^t$BuO (10.5 mg, 0.1 mmol) in a Parr high-pressure reactor. The autoclave was purged three times with hydrogen, and then the solution was pressurized with 10 bar of $H_2$ and heated at 120 °C (oil bath temperature) for 48 h. The reaction mixture was then cooled down in an ice bath for 15 min before releasing $H_2$ pressure. After completion of the reaction, the solvent was evaporated and the resulting residue was purified by a base-washed silica gel column (adding 2% $Et_3N$ into the mixture of petroleum ether and ethyl acetate) or by column chromatography on a neutral alumina column to afford the corresponding mixture of imine products **2a** (28%), **5a** (40%) and **2i** (20%).

**S4. A Plausible reaction mechanism**




**4. Synthesis and Product characterization**.

***N*-benzylidenebenzylamine (2a)**:



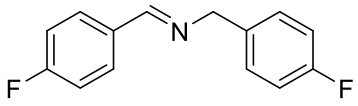
According to typical procedure **3A**, a mixture of benzaldehyde (100 mg, 0.94 mmol) and $NH_3$ in methanol (2.82 mmol) in methnaol was added **Mn2** (12.7 mg, 0.028 mmol), K$^t$BuO (11.0 mg, 0.094 mmol). The product was obtained as a white solid (151.0 mg, 85%).

$^1$H NMR ($CDCl_3$, 600 MHz): $\delta$=8.43 (s, 1H), 7.84-7.82 (m, 2H), 7.46-7.45 (m, 3H), 7.39-7.38 (m, 4H), 7.33-7.29 (m, 1H),4.87 (s, 2H).

$^{13}$C NMR ($CDCl_3$, 151 MHz): $\delta$=162.1, 139.4, 136.3, 130.9, 128.7, 128.6, 128.4, 128.1, 127.1, 65.2.

The characterization of the product was compared with the reported one.[1]

***N*-(4-fluorobenzyl)-1-(4-fluorophenyl)methanimine (2b)**:

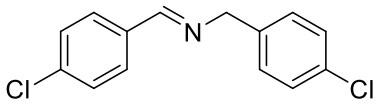



According to typical procedure **3A**, a mixture of 4-fluorobenzaldehyde (100 mg, 0.80 mmol) and $NH_3$ in methanol (2.40 mmol) in methanol was added **Mn2** (17.2 mg, 0.04 mmol) and K$^t$BuO (9.0 mg, 0.080 mmol) The product was obtained as a white solid (168.0 mg, 90%).

$^1$HNMR ($CDCl_3$, 600 MHz): $\delta$=8.36 (s, 1H), 7.82-7.79 (m, 2H), 7.35-7.32 (m, 2H), 7.15-7.05 (m, 4H), 4.79 (s, 2H).

$^{13}$C NMR ($CDCl_3$, 151 MHz): $\delta$=165.3, 163.7, 162.9, 161.3, 160.6, 135.1 (d, *J* = 3.2 Hz), 132.5 (d, *J* = 3.2 Hz), 130.2 (d, *J* = 8.6 Hz), 129.6 (d, *J* = 8.0 Hz), 115.8 (d, *J* = 22.2 Hz), 115.4 (d, *J* = 21.3 Hz), 64.2.
The characterization of the product was compared with the reported one.[3]

***N*-(4-chlorobenzyl)-1-(4-chlorophenyl)methanimine (2c)**:

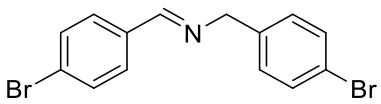



According to typical procedure **3A**, a mixture of 4-chlorobenzaldehyde (100 mg, 0.71 mmol) and $NH_3$ in methanol (2.13 mmol) in methanol was added **Mn2** (15.5 mg, 0.035 mmol) and K$^t$BuO (8.0 mg, 0.070 mmol). The product was obtained as a white solid (173.0 mg, 92%).

$^1$HNMR ($CDCl_3$, 600 MHz): $\delta$=8.34 (s, 1H), 7.74-7.72 (m, 2H), 7.42-7.40 (m, 2H), 7.35-7.33 (m, 2H), 7.29-7.28 (m, 2H), 4.78 (s, 2H).

$^{13}$C NMR ($CDCl_3$, 151 MHz): $\delta$=160.8, 137.7, 136.9, 134.6, 132.9, 129.5, 129.3, 129.0, 128.7, 64.2.
The characterization of the product was compared with the reported one.[1]

***N*-(4-bromobenzyl)-1-(4-bromophenyl)methanimine (2d)**:

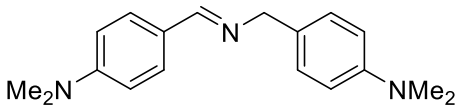



According to typical procedure **3A**, a mixture of 4-bromobenzaldehyde (100 mg, 0.54 mmol) and $NH_3$ in methanol (1.62 mmol) in methnaol was added **Mn2** (12.0 mg, 0.027 mmol) and K$^t$BuO (6.0 mg, 0.054 mmol). The product was obtained as a white solid (173.0 mg, 91%).

$^1$HNMR ($CDCl_3$, 600 MHz): $\delta$=8.32 (s, 1H), 7.65-7.64 (m, 2H), 7.56-7.55 (m, 2H), 7.48-7.46 (m, 2H), 7.22-7.21 (m, 2H), 4.74 (s, 2H).

$^{13}$C NMR ($CDCl_3$, 151 MHz): $\delta$=161.1, 138.2, 135.0, 132.0, 131.7, 129.8, 129.8, 125.5, 121.0, 64.3.
The characterization of the product was compared with the reported one.[3]

**4-(((4-(dimethylamino)benzyl)imino)methyl)-*N*,*N*-dimethylaniline (2f)**:

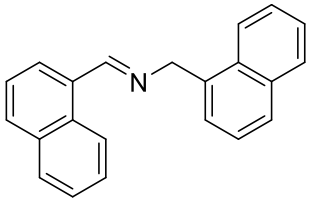



According to typical procedure **3A**, a mixture of 4-(dimethylamino)benzaldehyde (100 mg, 0.67 mmol) and $NH_3$ in methanol (2.01 mmol) in methanol was added **Mn2** (14.5 mg, 0.033 mmol) and K$^t$BuO (7.5 mg, 0.067 mmol).The product was obtained as a white solid (143.0 mg, 76%).

$^1$H NMR ($CDCl_3$, 500 MHz): $\delta$=8.26 (s, 1H), 7.68-7.67 (m, 2H), 7.26-7.22 (m, 2H), 6.77-6.70 (m, 4H), 4.72 (s, 2H), 3.02 (s, 6H), 2.94 (s, 6H).

$^{13}$C NMR ($CDCl_3$, 126 MHz): $\delta$=161.3, 152.1, 149.9, 129.7, 129.0, 128.1, 124.7, 113.0, 111.7, 64.6, 41.0, 40.3.
The characterization of the product was compared with the reported one.[6]

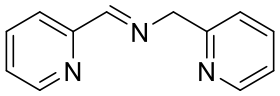
**1-(naphthalen-2-yl)-*N*-(naphthalen-2-ylmethyl)methanimine (2g)**:




According to typical procedure **3A**, a mixture of 1-napthaldehyde (100 mg, 0.64 mmol) and $NH_3$ in methanol (2.01 mmol) in methnaol was added **Mn2** (13.8 mg, 0.032 mmol) and K$^t$BuO (7.5 mg, 0.064 mmol). The product was obtained as a white solid (143.0 mg, 76%).

$^1$H NMR ($CDCl_3$, 600 MHz): $\delta$=8.61 (s, 1H), 8.11-8.09 (m, 2H), 7.92-7.83 (m, 7H), 7.55-7.45 (m, 5H), 5.06 (s, 2H).
$^{13}$C NMR ($CDCl_3$, 151 MHz): $\delta$=162.4, 137.0, 135.0, 134.0, 133.8, 133.3, 132.8, 130.4, 128.8, 128.7, 128.3, 128.1, 128.0, 127.9, 127.4, 126.7, 126.6, 126.2, 125.8, 124.1, 65.4.
The characterization of the product was compared with the reported one.[7]

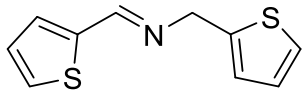
**1-(pyridin-3-yl)-*N*-(pyridin-3-ylmethyl)methanimine (2h)**:



According to typical procedure **3A**, a mixture of 2-pyridinecarboxyaldehyde (100 mg, 0.93 mmol) and $NH_3$ in methanol (2.70 mmol) in methanol (5.0 ml) was added **Mn2** (20.0 mg, 0.019 mmol) and K$^t$BuO (10.4 mg, 0.093 mmol). The product was obtained as a white solid (129.0 mg, 68%).

$^1$HNMR ($CDCl_3$, 500 MHz): $\delta$=8.77 (s, 1H), 8.51-8.50 (m, 1H), 8.48-8.47 (m, 1H), 8.39-8.37 (m, 1H), 8.31-8.30 (m, 1H), 8.00-7.98 (m, 1H), 7.54-7.52 (m, 1H), 7.20-7.18 (m, 1H), 7.14-7.11 (m, 1H), 4.68 (s, 2H).
$^{13}$C NMR ($CDCl_3$, 126 MHz): $\delta$=159.6, 151.6, 150.1, 149.1, 148.4, 135.3, 134.4, 134.2, 131.2, 123.5, 123.3, 62.2.
The characterization of the product was compared with the reported one.[7]

**(*E*)-1-(thiophen-2-yl)-N-(thiophen-2-ylmethyl)methanimine (2i):**

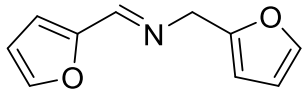


According to typical procedure **3A**, a mixture of Furfural (100 mg, 0.89 mmol) and $NH_3$ in methanol (2.7 mmol) in methanol (5.0 ml) was added **Mn2** (19.7 mg, 0.044 mmol) and K$^t$BuO (10.0 mg, 0.089 mmol). The product was obtained as a yellow solid (126.0 mg, 68%).

$^1$H NMR (500 MHz, $CDCl_3$) δ= 8.42 (s, 1H, CH), 7.42 (d, *J* = 5.0 Hz, 1H, ArH), 7.34-7.33 (m, 1H, ArH), 7.24 (d, *J* = 5.0 Hz, 1H, ArH), 7.08 (t, *J* = 4.3 Hz, 1H, ArH), 7.00-6.98 (m, 2H, ArH), 4.95 (s, 2H, $CH_2$).

The characterization of the product was compared with the reported one.[1]

**(*E*)-1-(furan-2-yl)-N-(furan-2-ylmethyl)methanimine (2j):**

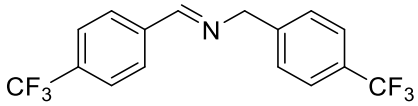


According to typical procedure **3A**, a mixture of Furfural (100 mg, 1.04 mmol) and $NH_3$ in methanol (3.0 mmol) in methanol (5.0 ml) was added **Mn2** (22.0 mg, 0.052 mmol) and K$^t$BuO (11.0 mg, 0.10 mmol). The product was obtained as a brown oil (160.0 mg, 88%).

$^1$H NMR (500 MHz, $CDCl_3$) $\delta$=8.11 (s, 1H, CH), 7.51 (s, 1H, ArH), 7.38 (s, 1H), 6.78 (d, *J* = 3.3 Hz, 1H), 6.47 (dd, *J* = 3.3, 1.7 Hz, 1H), 6.34-6.33 (m, 1H), 6.27 (d, *J* = 3.1 Hz, 1H), 4.75 (s, 2H).

The characterization of the product was compared with the reported one.[8]

***N*-(4-trifluoromethylbenzylidene)-4-(trifluoromethyl)benzylamine (2k)**:



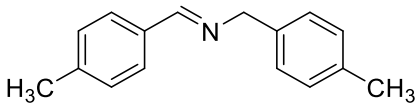
According to typical procedure **3B**, a mixture of 4-trifluoromethylbenzylamine (100 mg, 0.57 mmol) in

toluene was added **Mn2** (7.3 mg, 0.017 mmol) and K$^t$BuO (4.0 mg, 0.034 mmol). The product was obtained as a white solid (173.0 mg, 91%).

$^1$H NMR ($CDCl_3$, 500 MHz): $\delta$=8.47 (s, 1H), 7.93 (d, $J$ = 8.1 Hz, 2H), 7.71 (d, $J$ = 8.1 Hz, 2H), 7.64 (d, $J$ = 8.1 Hz, 2H), 7.50 (d, $J$ = 8.1 Hz, 2H), 4.91 (s, 2H).

$^{13}$C NMR ($CDCl_3$, 126 MHz): $\delta$=161.2, 143.3, 139.2, 132.7 (q, $J$ = 32.6 Hz), 129.6 (q, $J$ = 32.3 Hz), 128.7, 128.3, 125.8 (q, $J$ = 3.8 Hz), 125.6 (q, $J$ = 3.8 Hz), 124.3 (q, $J$ = 272 Hz), 123.9 (q, $J$ = 272 Hz), 64.5.
The characterization of the product was compared with the reported one.[5,6]

***N*-(4-methylbenzylidene)-4-methylbenzylamine (2l)**:

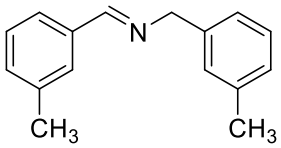



According to typical procedure **3B**, a mixture of 4-methylbenzylamine (100 mg, 0.83 mmol) in toluene was added **Mn2** (10.7 mg, 0.024 mmol) and K$^t$BuO (5.6 mg, 0.040 mmol). The product was obtained as a white solid (180.0 mg, 95%).

$^1$H NMR($CDCl_3$, 500 MHz): $\delta$=8.42 (s, 1H), 7.75 (d, $J$ = 8.1 Hz, 2H), 7.31-7.28 (m, 4H), 7.23 (d, $J$ = 7.9 Hz, 2H), 4.85 (s, 2H), 2.46 (s, 3H), 2.42 (s, 3H).

$^{13}$C NMR ($CDCl_3$, 126 MHz): $\delta$=161.8, 141.1, 136.6, 136.5, 133.8, 129.4, 129.3, 128.4, 128.1, 65.0, 21.7, 21.3.
The characterization of the product was compared with the reported one.[1]

***N*-(3-methylbenzyl)-1-(*m*-tolyl)methanimine (2m)**:

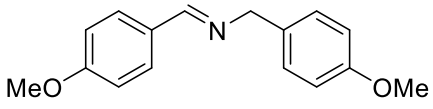



According to typical procedure **3B**, a mixture of 3-methylbenzylamine (100 mg, 0.83 mmol) in toluene was added **Mn** (10.7 mg, 0.024 mmol) and K$^t$BuO (5.6 mg, 0.040 mmol). The product was obtained as a white solid (180.0 mg, 95%).

$^1$H NMR($CDCl_3$, 600 MHz): $\delta$=8.43 (s, 1H), 7.75 (br, 1H), 7.64-7.63 (m, 1H), 7.40-7.37 (m, 2H), 7.34-7.31 (m, 2H), 7.25-7.22 (m, 2H), 7.17-7.16 (m, 1H), 4.87 (s, 2H), 2.46 (s, 3H), 2.44 (s, 3H).

$^{13}$C NMR ($CDCl_3$, 151 MHz): $\delta$=162.1, 139.3, 138.4, 138.1, 136.2, 131.6, 128.8, 128.6, 128.5, 128.5, 127.8, 125.9, 125.2, 65.2, 21.5, 21.3.
The characterization of the product was compared with the reported one.[1]

***N*-(4-methoxybenzyl)-1-(4-methoxyphenyl)methanimine (2o)**:[1]



According to typical procedure **3B**, a mixture of 4-methoxybenzylamine (100 mg, 0.73 mmol) in toluene was added **Mn2** (9.5 mg, 0.021 mmol) and K$^t$BuO (5.0 mg, 0.043 mmol). The product was obtained as a white solid (164.0 mg, 87%).

$^1$H NMR (CDCl3, 600 MHz): $\delta$=8.32 (s, 1H), 7.76-7.74 (m, 2H), 7.29-7.28 (m, 2H), 6.96-6.90 (m, 4H), 4.75 (s, 2H), 3.84 (s, 3H), 3.81 (s, 3H).

$^{13}$C NMR (CDCl3, 151 MHz): $\delta$=161.7, 160.9, 158.7, 131.8, 129.9, 129.2, 128.3, 114.0, 113.9, 64.5, 55.4, 55.3.

The characterization of the product was compared with the reported one.[1]

## 5. References.


(1) Liu, L.; Zhang, S.; Fu, X.; Yan, C.-H. *Chem. Commun.,* 2011, ***47***, 10148-10150.

(2) S. S. Gholap, A. Al Dakhil, P. Chakraborty, H. Li, I. Dutta, P. K. Das and K.-W. Huang, *Chem. Commun.*, 2021, **57**, 11815-11818.

(3) Chen, B.; Shang, S.; Wang, L.; Zhang, Y.; Gao, S. *Chem. Commun.,* 2016, ***52***, 481-484.

(4) Wendlandt, A. E.; Stahl, S. S. *Org. Lett.,* 2012, ***14***, 2850-2853.

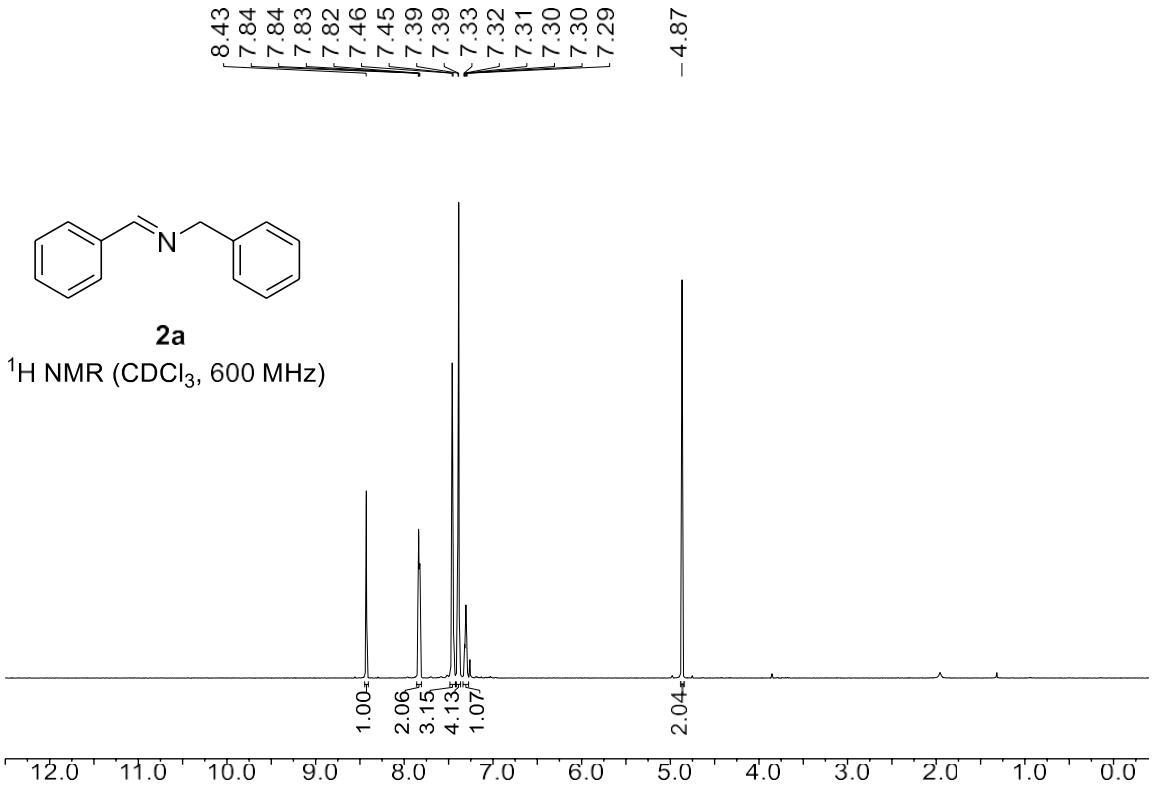
(5) Murray, A. T.; King, R.; Donnelly, J. V. G.; Dowley, M. J. H.; Tuna, F.; Sells, D.; John, M. P.; Carbery, D. R. *ChemCatChem,* 2016, ***8***, 510-514.

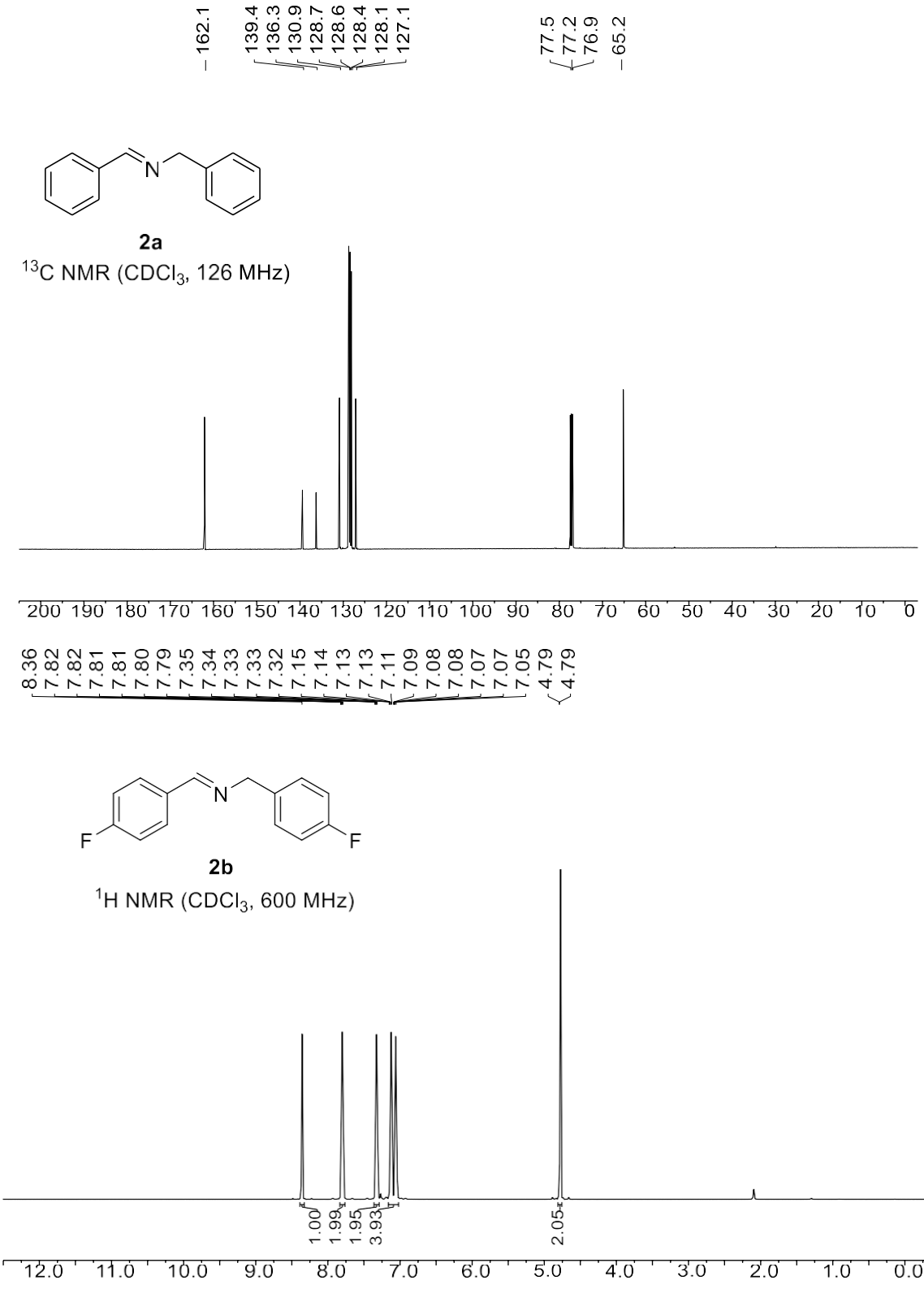
(6) Chakraborty, S.; Milstein, D. *ACS Catal.,* 2017, ***7***, 3968-3972.

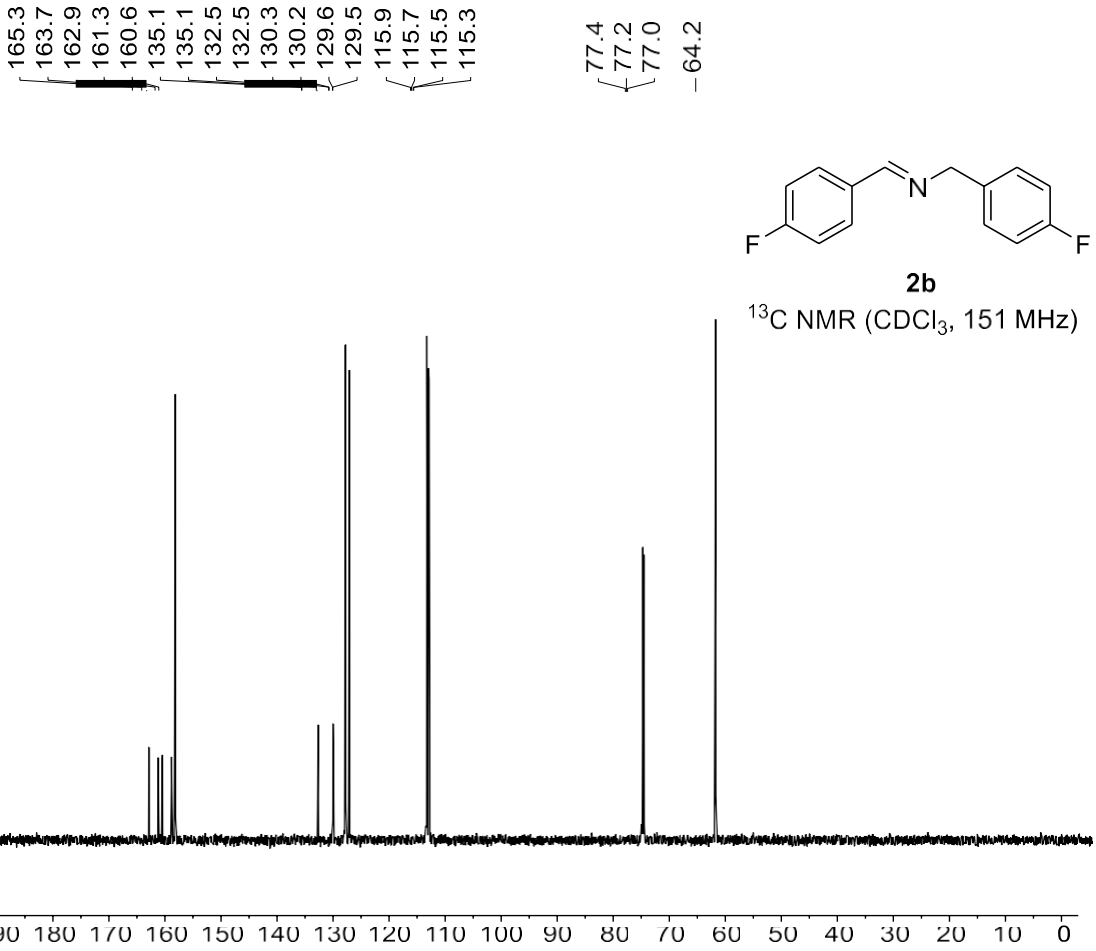
(7) Beeby, A.; Parker, D.; Williams, J. A. G. *J. Chem. Soc., Perkin Trans.* 1996, ***2,*** 1565-1579.

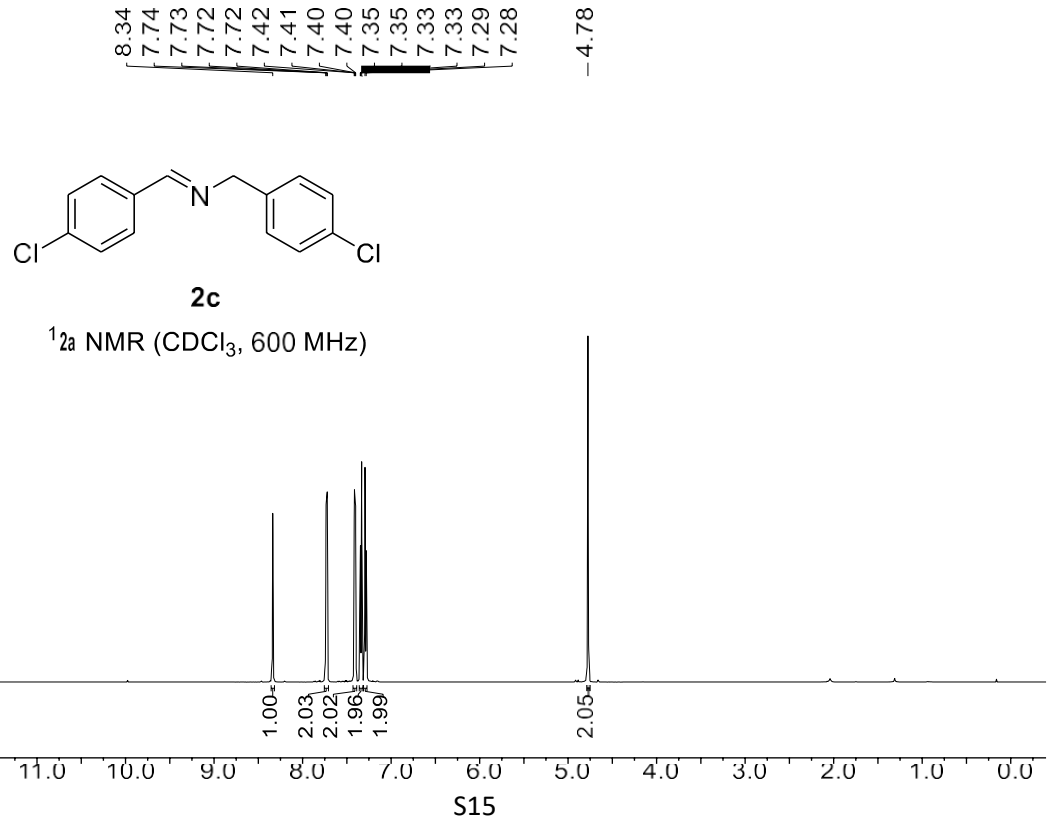
(8) J. Wang, Y. Zhai, Y. Wang, H. Yu, W. Zhao and Y. Wei, *Dalton Trans.*, 2018, **47**, 13323-13327.

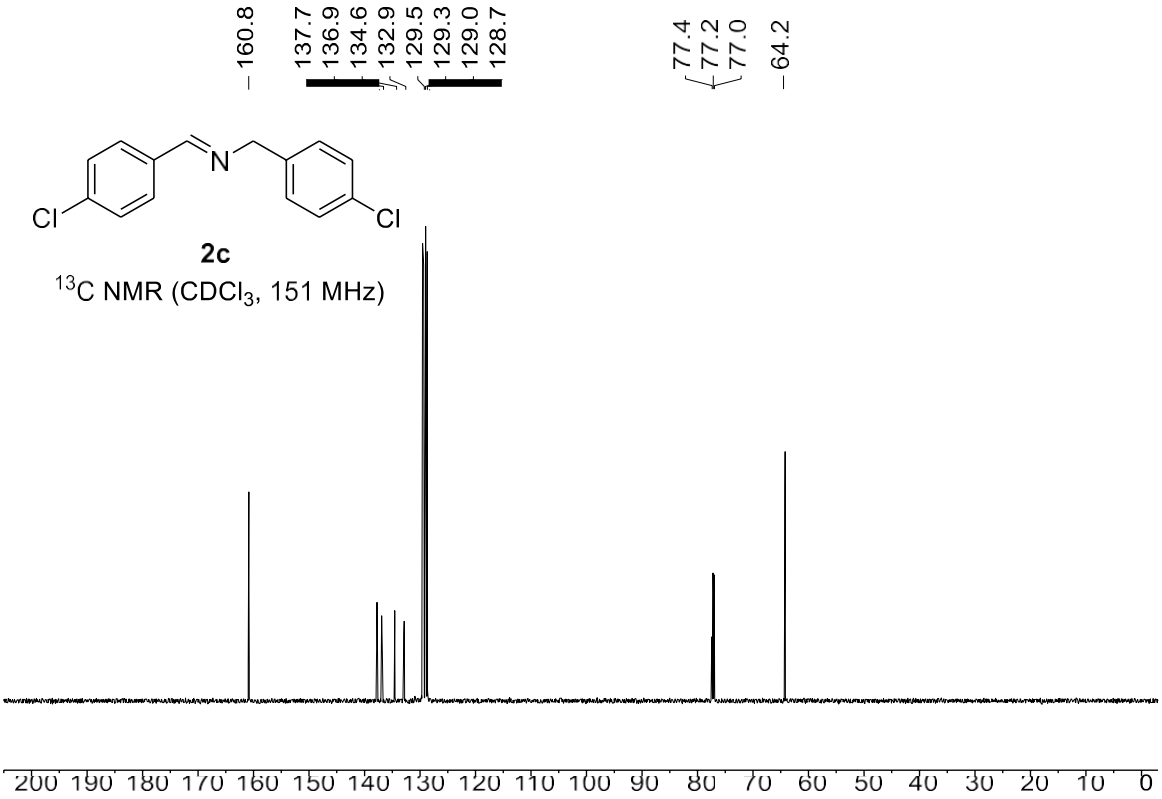
## 6. $^{1}$H-NMR and $^{13}$C-NMR spectras of imine products isolated.

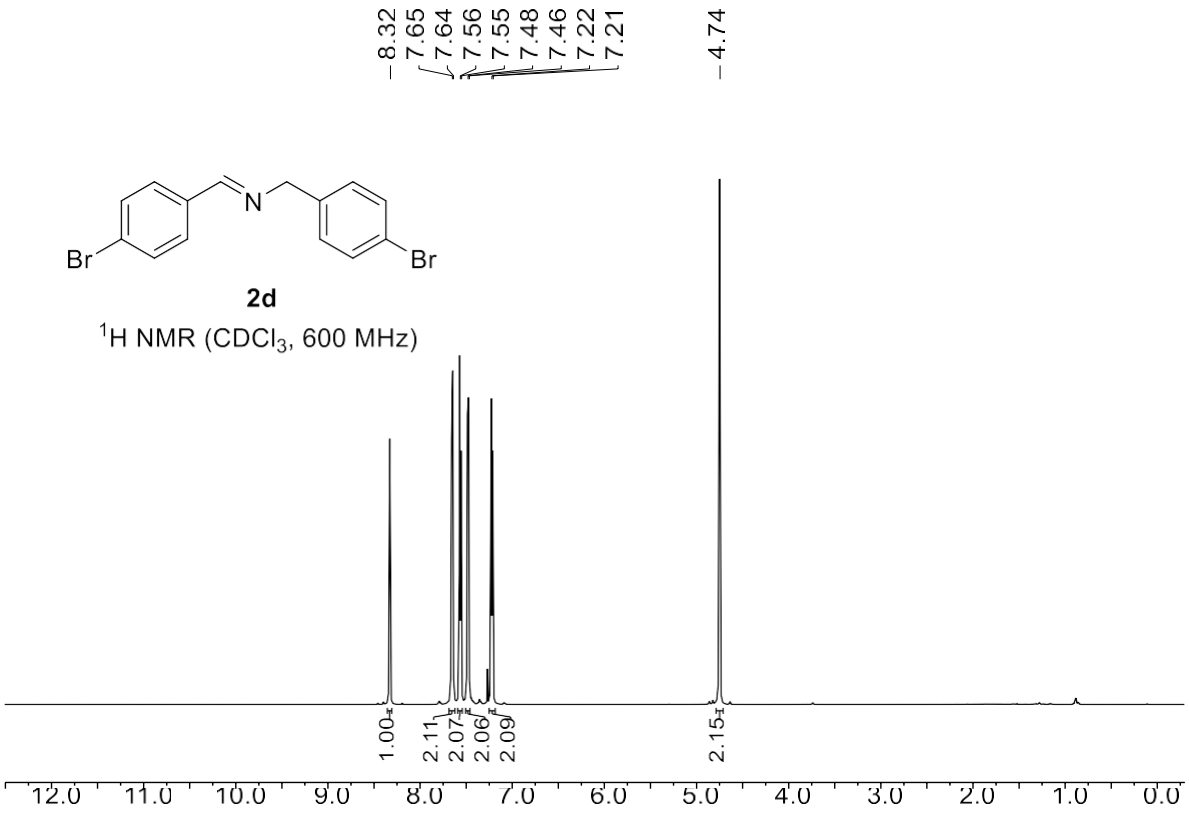


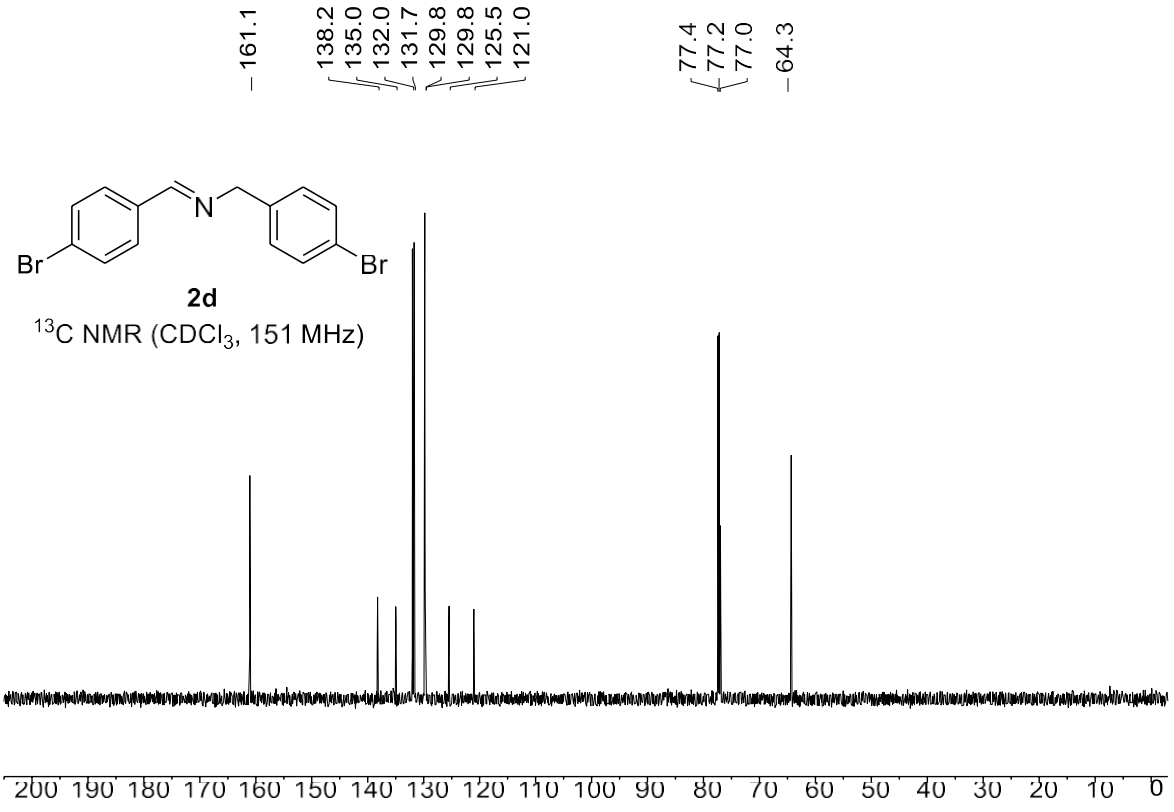

162.1
139.4
136.3
130.9
128.7
128.6
128.4
128.1
127.1
77.5
77.2
76.9
65.2
N
2a
13C NMR (CDCl3, 126 MHz)
200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0
8.36
7.82
7.82
7.81
7.81
7.80
7.79
7.35
7.34
7.33
7.33
7.32
7.15
7.14
7.13
7.13
7.11
7.09
7.08
7.08
7.07
7.07
7.05
4.79
4.79
N
F
F
2b
1H NMR (CDCl3, 600 MHz)
1.00
1.99
1.95
3.93
2.05
12.0 11.0 10.0 9.0 8.0 7.0 6.0 5.0 4.0 3.0 2.0 1.0 0.0

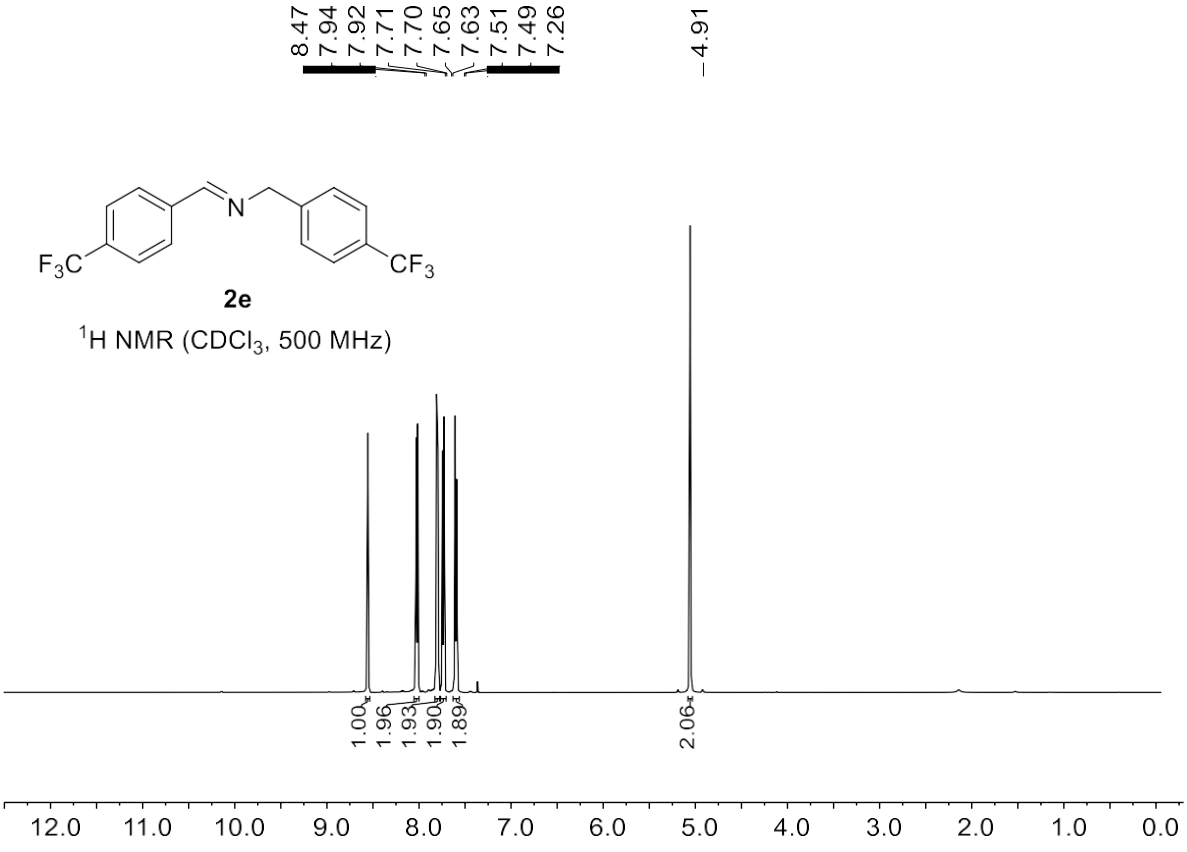

165.3
163.7
162.9
161.3
160.6
135.1
135.1
132.5
132.5
130.3
130.2
129.6
129.5
115.9
115.7
115.5
115.3
77.4
77.2
77.0
64.2
N
F
F
2b
13C NMR (CDCl3, 151 MHz)
200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0

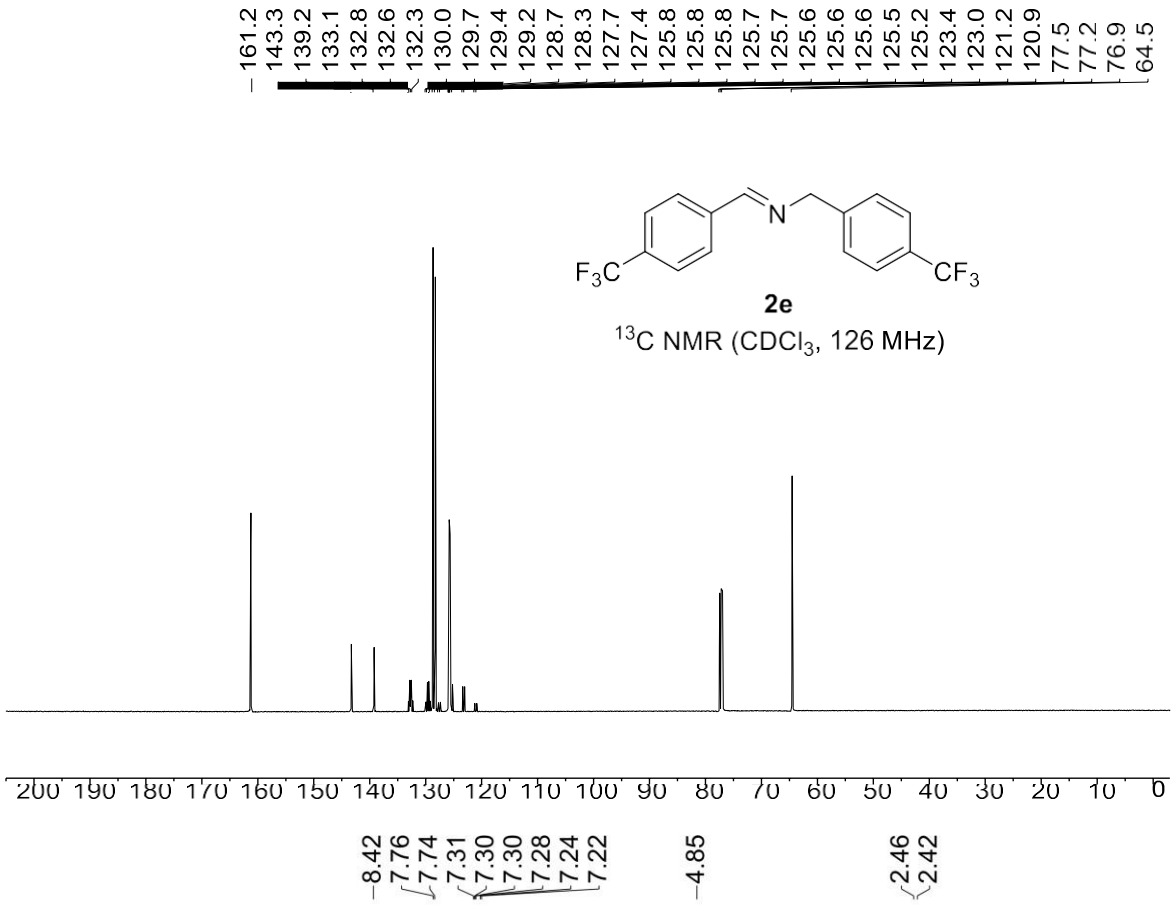

8.34
7.74
7.73
7.72
7.72
7.42
7.41
7.40
7.40
7.35
7.35
7.33
7.33
7.29
7.28
4.78
N
Cl
Cl
2c
12a NMR (CDCl3, 600 MHz)
1.00
2.03
2.02
1.96
1.99
2.05
12.0 11.0 10.0 9.0 8.0 7.0 6.0 5.0 4.0 3.0 2.0 1.0 0.0

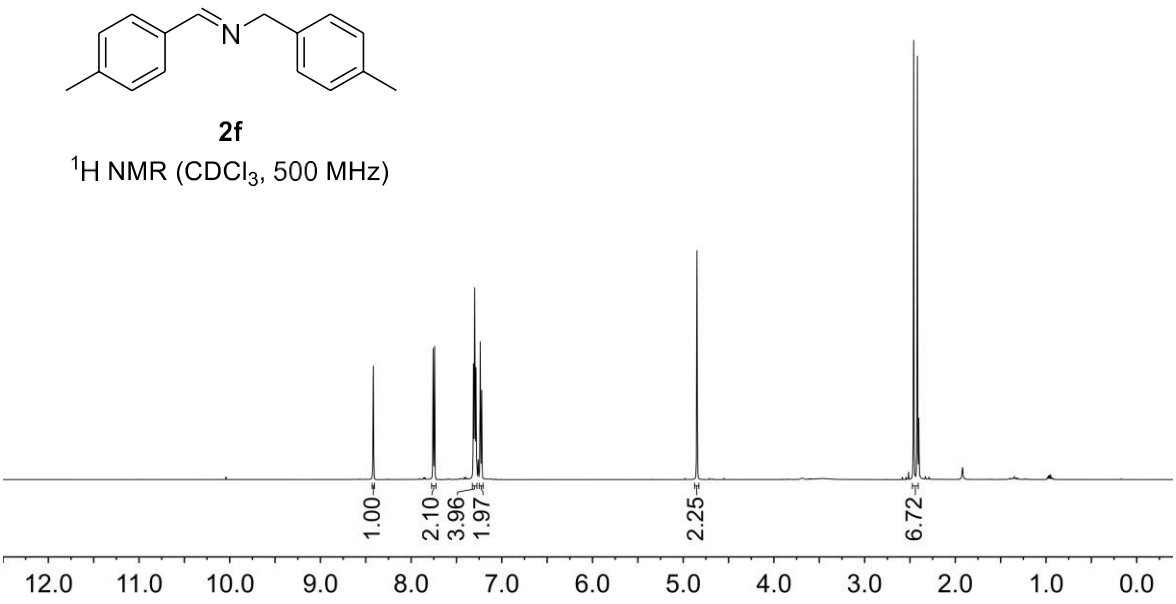

160.8
137.7
136.9
134.6
132.9
129.5
129.3
129.0
128.7
77.4
77.2
77.0
64.2
N
Cl
Cl
2c
13C NMR (CDCl3, 151 MHz)
200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0

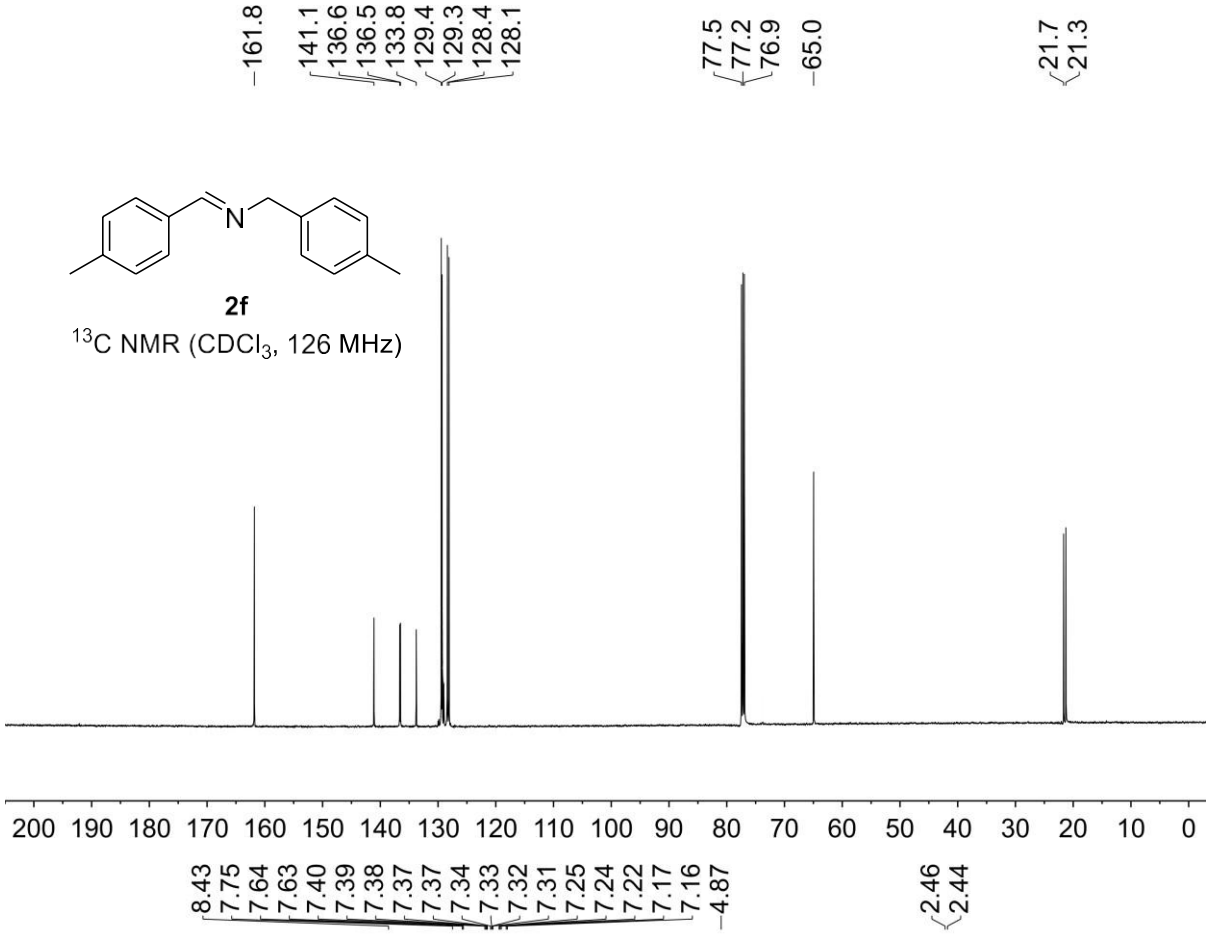

8.32
7.65
7.64
7.56
7.55
7.48
7.46
7.22
7.21
4.74
N
Br
Br
2d
1H NMR (CDCl3, 600 MHz)
1.00
2.11
2.07
2.06
2.09
2.15
12.0 11.0 10.0 9.0 8.0 7.0 6.0 5.0 4.0 3.0 2.0 1.0 0.0


161.1
138.2
135.0
132.0
131.7
129.8
129.8
125.5
121.0
77.4
77.2
77.0
64.3
N
Br
Br
2d
13C NMR (CDCl3, 151 MHz)
200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0


8.47
7.94
7.92
7.71
7.70
7.65
7.63
7.51
7.49
7.26
4.91
N
F3C
CF3
2e
1H NMR (CDCl3, 500 MHz)
1.00
1.96
1.93
1.90
1.89
2.06
12.0 11.0 10.0 9.0 8.0 7.0 6.0 5.0 4.0 3.0 2.0 1.0 0.0


161.2
143.3
139.2
133.1
132.8
132.6
132.3
130.0
129.7
129.4
129.2
128.7
128.3
127.7
127.4
125.8
125.8
125.8
125.7
125.7
125.6
125.6
125.6
125.5
125.2
123.4
123.0
121.2
120.9
77.5
77.2
76.9
64.5
N
F3C
CF3
2e
13C NMR (CDCl3, 126 MHz)
200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0
8.42
7.76
7.74
7.31
7.30
7.30
7.28
7.24
7.22
4.85
2.46
2.42


N
2f
1H NMR (CDCl3, 500 MHz)
1.00
2.10
3.96
1.97
2.25
6.72
12.0 11.0 10.0 9.0 8.0 7.0 6.0 5.0 4.0 3.0 2.0 1.0 0.0


161.8
141.1
136.6
136.5
133.8
129.4
129.3
128.4
128.1
77.5
77.2
76.9
65.0
21.7
21.3
N
2f
13C NMR (CDCl3, 126 MHz)
200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0


8.43
7.75
7.64
7.63
7.40
7.39
7.38
7.37
7.37
7.34
7.33
7.32
7.31
7.25
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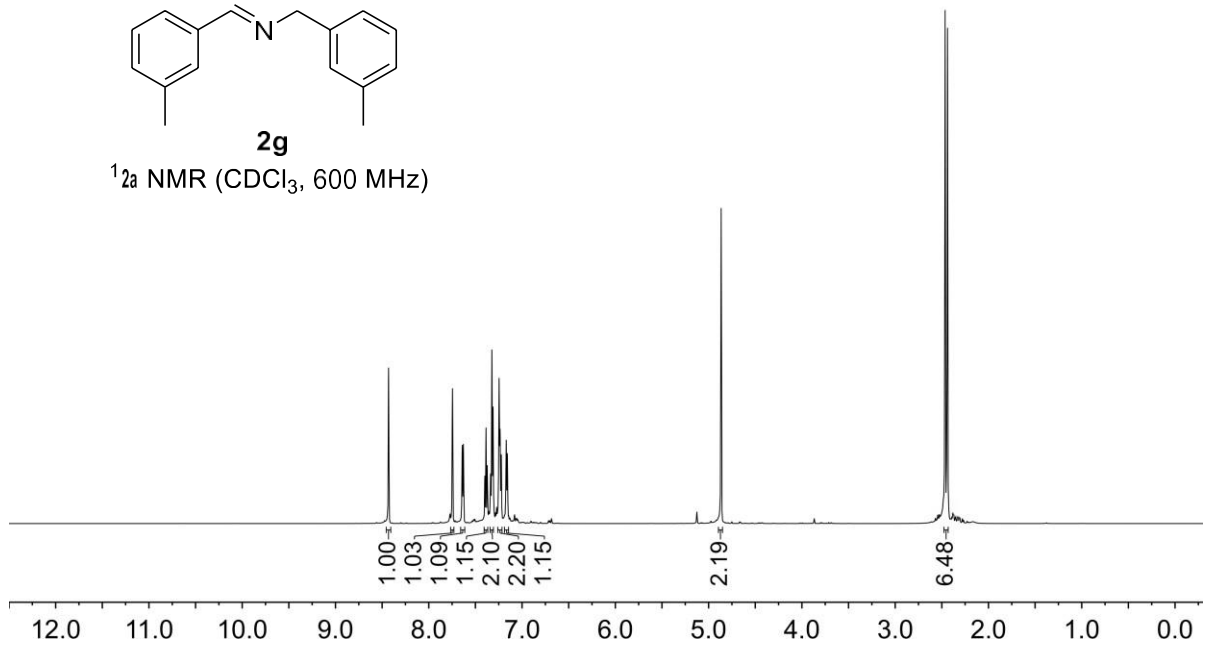
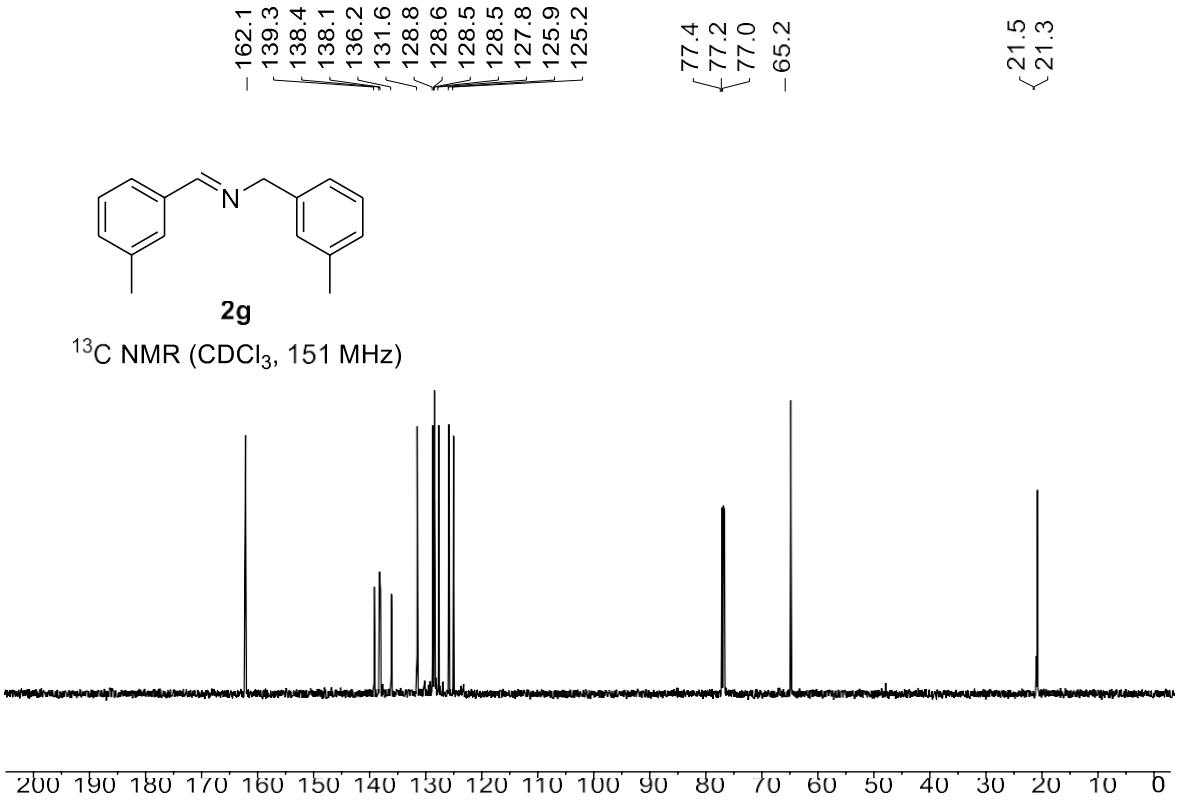
7.22
7.17
7.16
4.87
2.46
2.44


N
2g
12a NMR (CDCl3, 600 MHz)
1.00
1.03
1.09
1.15
2.10
2.20
1.15
2.19
6.48
12.0 11.0 10.0 9.0 8.0 7.0 6.0 5.0 4.0 3.0 2.0 1.0 0.0


162.1
139.3
138.4
138.1
136.2
131.6
128.8
128.6
128.5
128.5
127.8
125.9
125.2
77.4
77.2
77.0
65.2
21.5
21.3
N
2g
13C NMR (CDCl3, 151 MHz)
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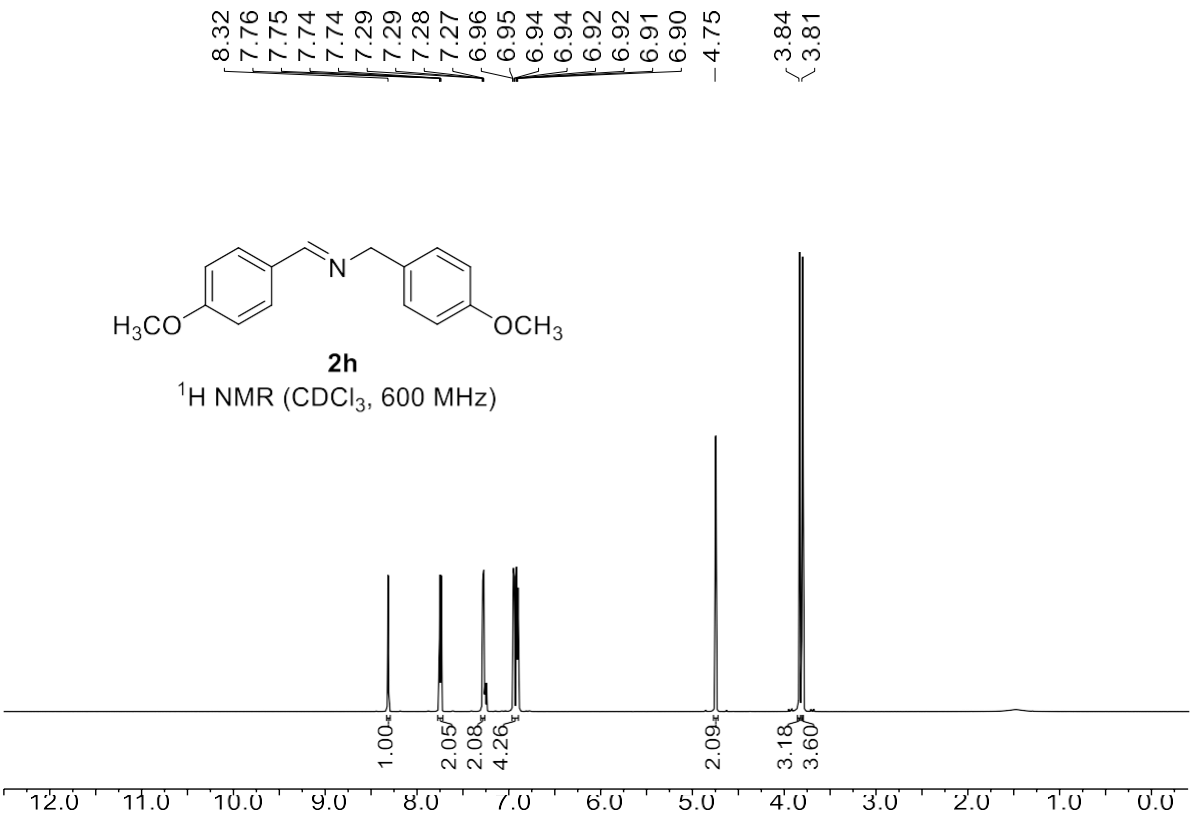
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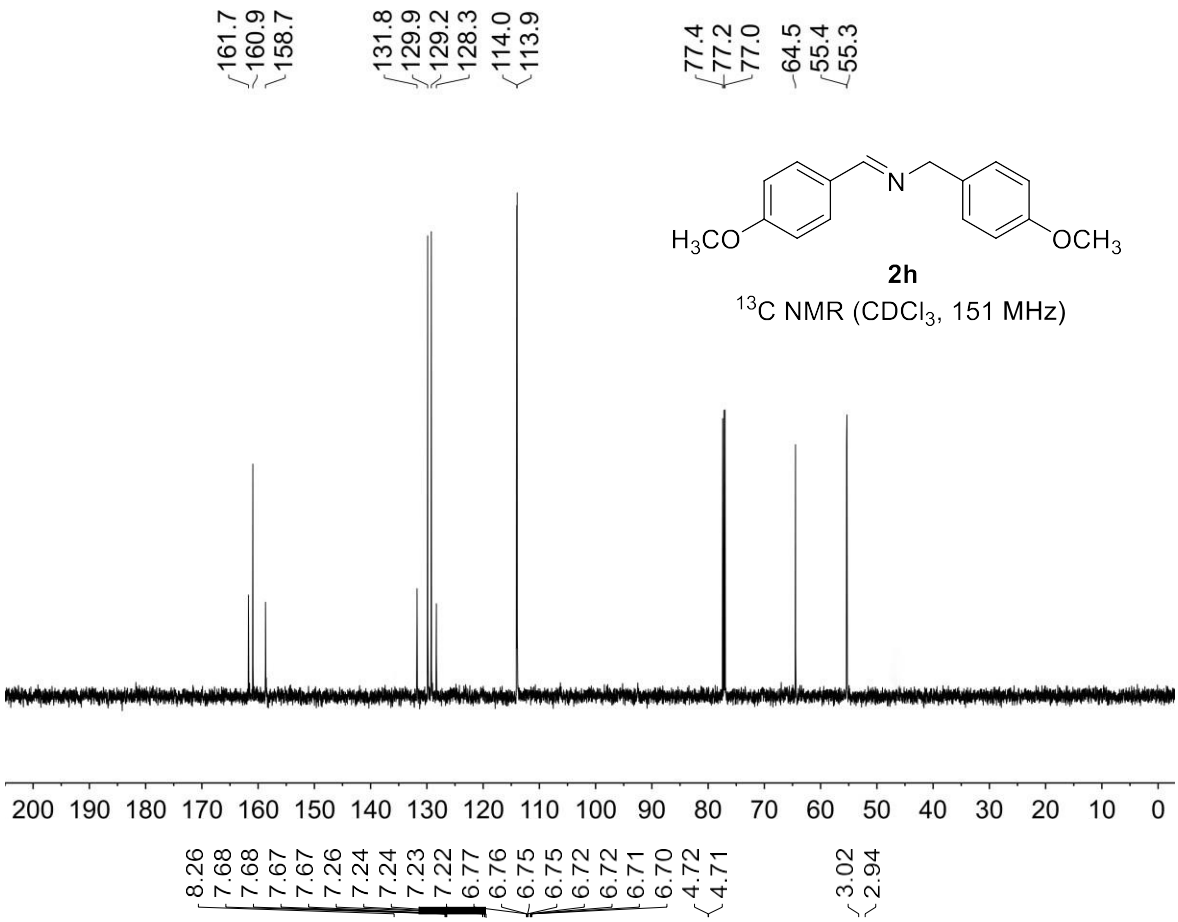
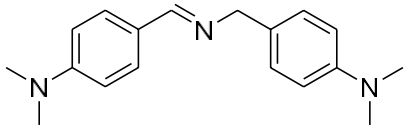
7.74
7.29
7.29
7.28
7.27
6.96
6.95
6.94
6.94
6.92
6.92
6.91
6.90
4.75
3.84
3.81
N
H3CO
OCH3
2h
1H NMR (CDCl3, 600 MHz)
1.00
2.05
2.08
4.26
2.09
3.18
3.60
12.0 11.0 10.0 9.0 8.0 7.0 6.0 5.0 4.0 3.0 2.0 1.0 0.0




**2h**

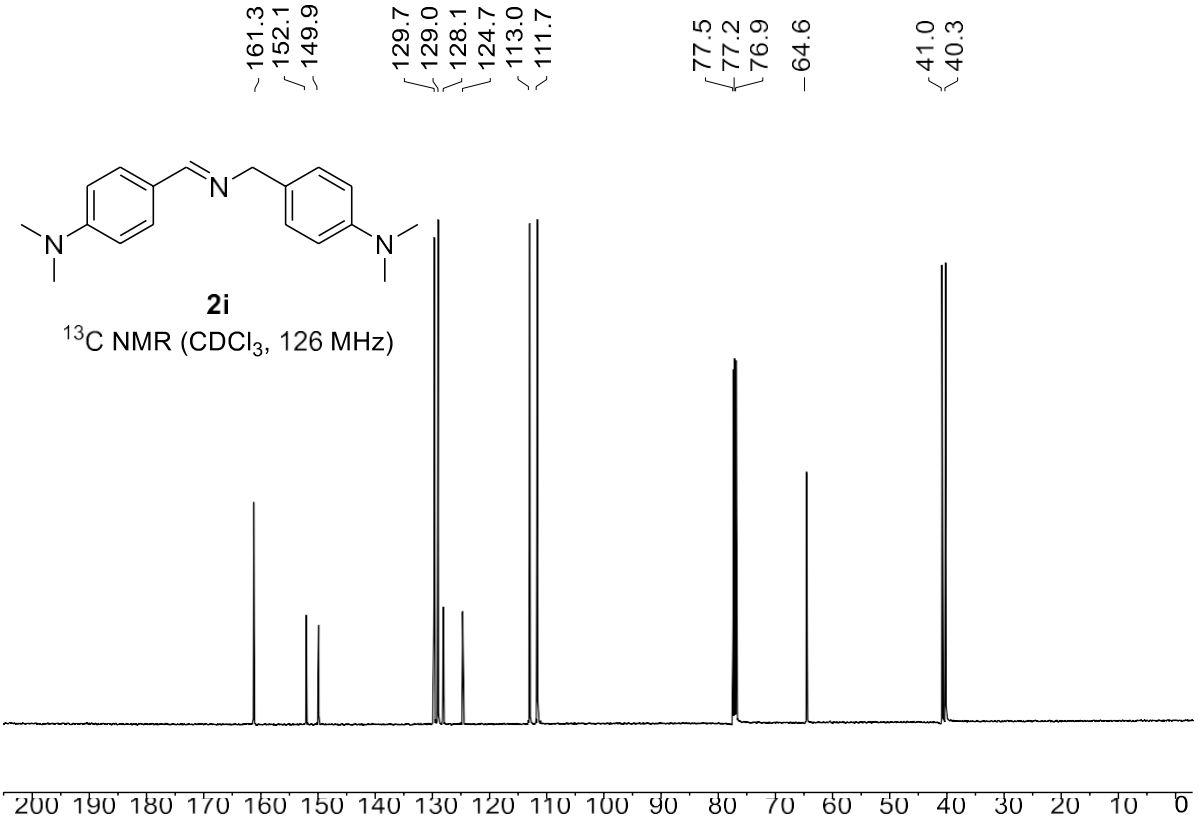
$^{13}$C NMR ($CDCl_3$, 151 MHz)



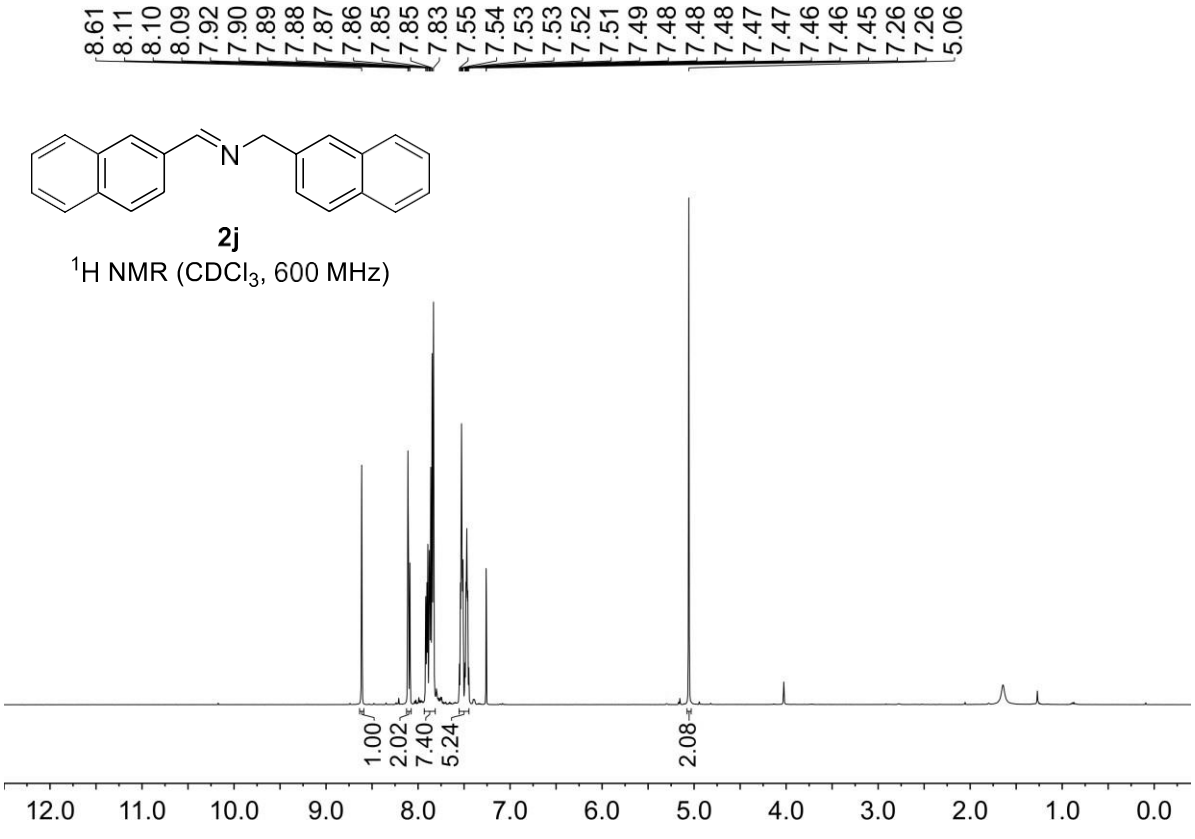

**2i**

$^{1}$H NMR ($CDCl_3$, 500 MHz)



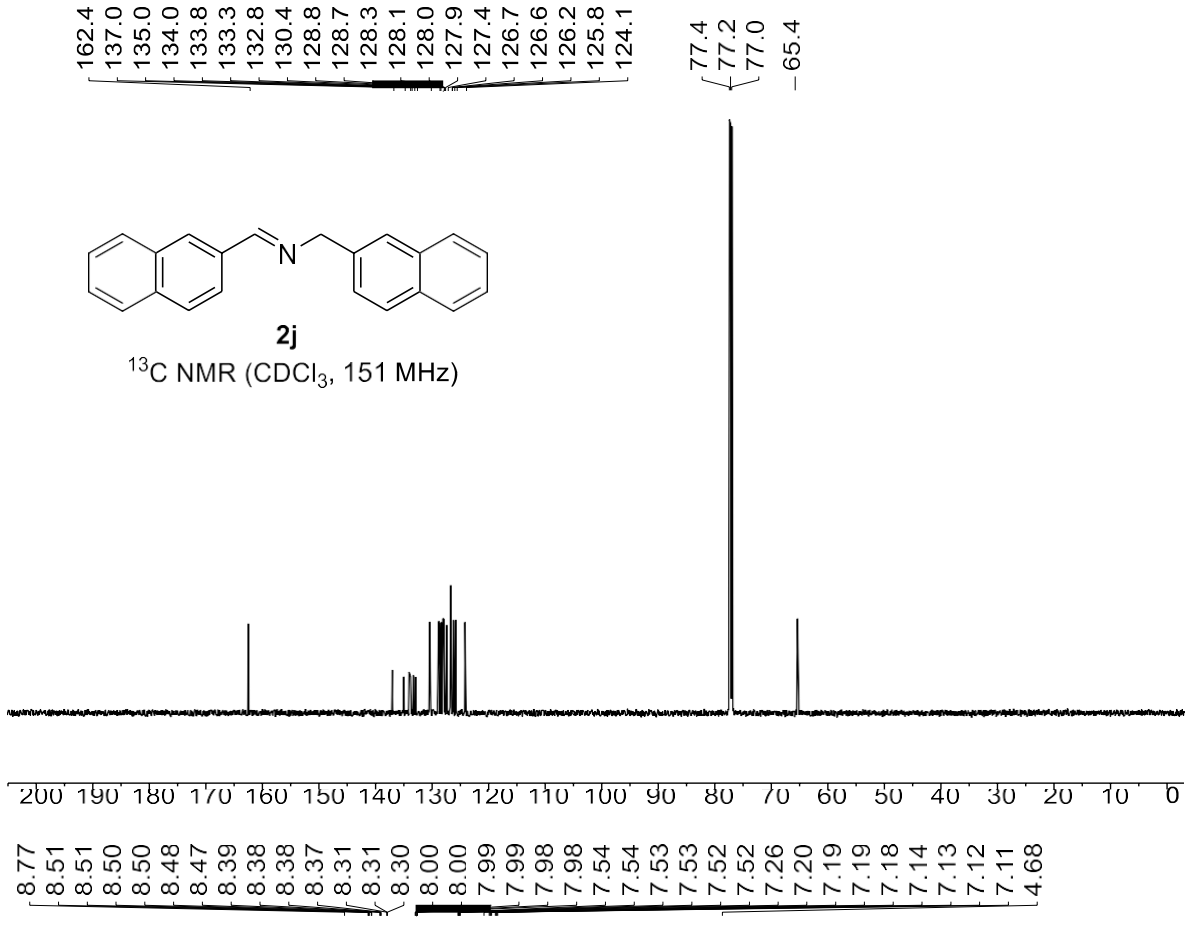

**2i**

$^{13}$C NMR ($CDCl_3$, 126 MHz)



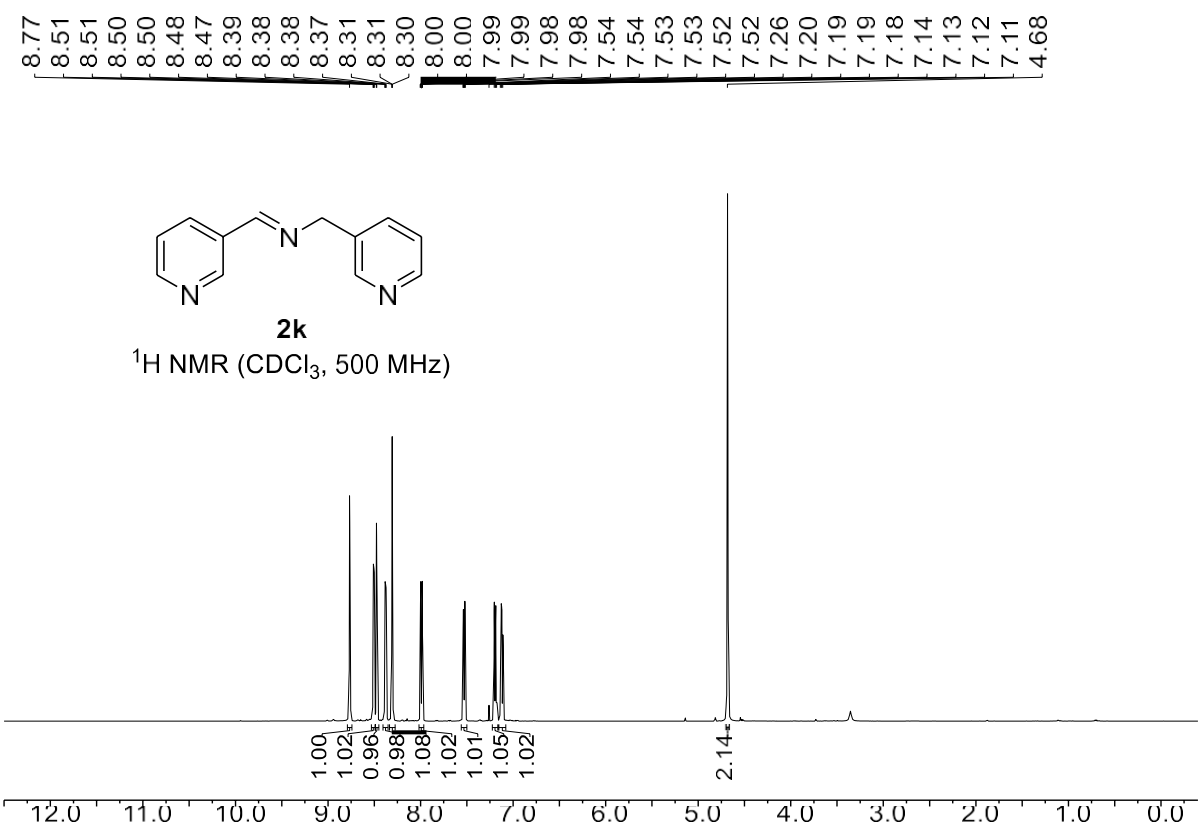

**2j**

$^{1}$H NMR ($CDCl_3$, 600 MHz)



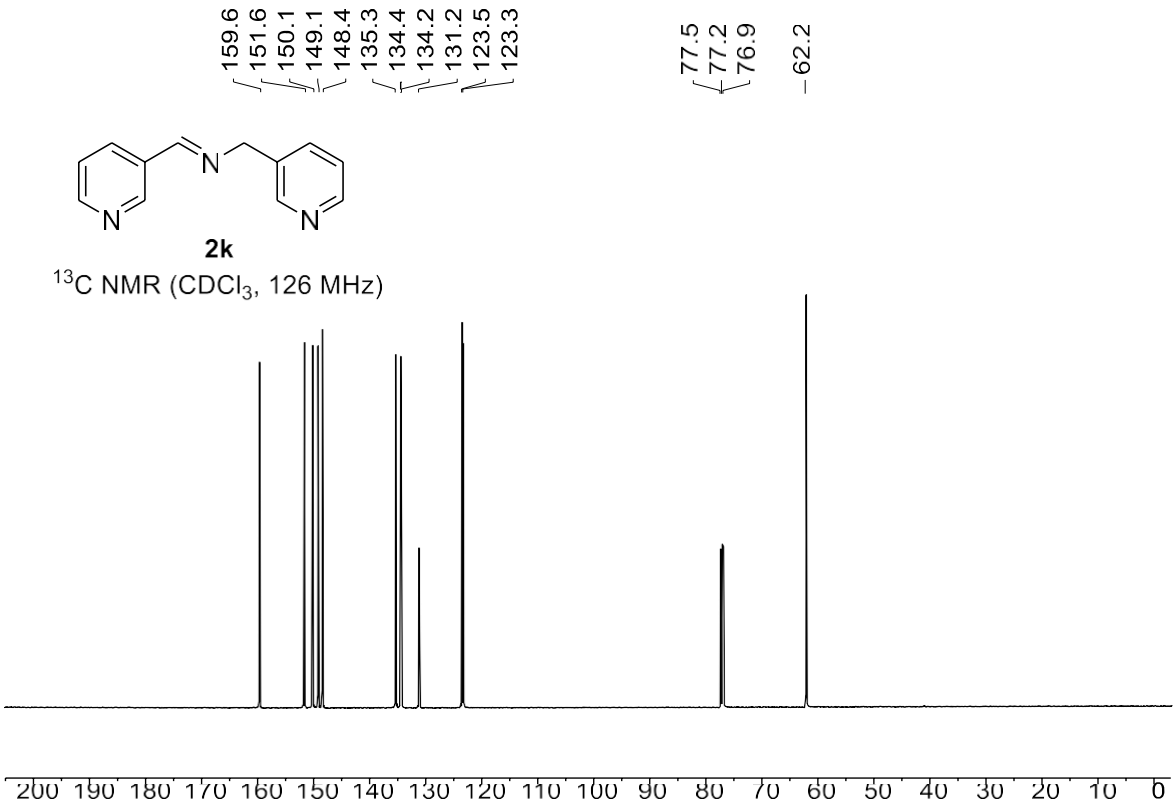

**2j**

$^{13}$C NMR ($CDCl_3$, 151 MHz)




**2k**

$^{1}$H NMR ($CDCl_3$, 500 MHz)


159.6
151.6
150.1
149.1
148.4
135.3
134.4
134.2
131.2
123.5
123.3
77.5
77.2
76.9
62.2
N
N
N
2k
13C NMR (CDCl3, 126 MHz)
200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0