Supporting Information

Chromium Catalyzed Acceptorless Dehydrogenative (Cross)Coupling of Primary Amines to Secondary Imines

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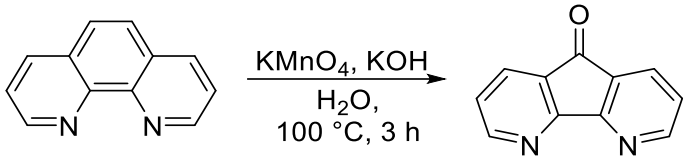
Table of Contents

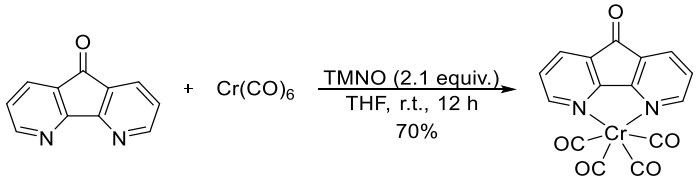
1. Procedures for the synthesis of ligand and complex

1.1 Synthesis of 4,5-diazafluoren-9-one (4,5-DAFO)

4,5-diazafluoren-9-one was synthesised as reported in literature with slight changes in the synthetic procedure. The ^{1}H and ^{13}C NMR spectra are in accord with literature data.[1] 1,10-phenanthroline monohydrate (10 g, 0.055 mol) and KOH (1 equiv., 10 g, 0.178 mol) were dissolved in distilled water (750 mL) and heated to 90 °C. As soon the solution becomes clear, a hot solution of $KMnO_4$ (2.87 equiv., 25 g, 0.158 mol) in distilled water (400 mL) was added dropwise over 2 h with constant stirring. When the addition was over, the mixture was allowed to stir further for 10 min and then filtered hot. After MnO_2 residues were filtered, the solution was allowed to cool at room temperature. From the orange crude filtrate, the organic part was extracted using chloroform (3 x 100 mL). The solvent was removed by rotary evaporator. The obtained crude product was then purified over silica gel (60-100 mesh size) using DCM as eluent. The compound was then dried over rotary evaporator to get pale yellow coloured crystalline powder (Yield = 56%).



1.2 Synthesis of Cr(CO)$_4$DAFO complex (Cr-1a)



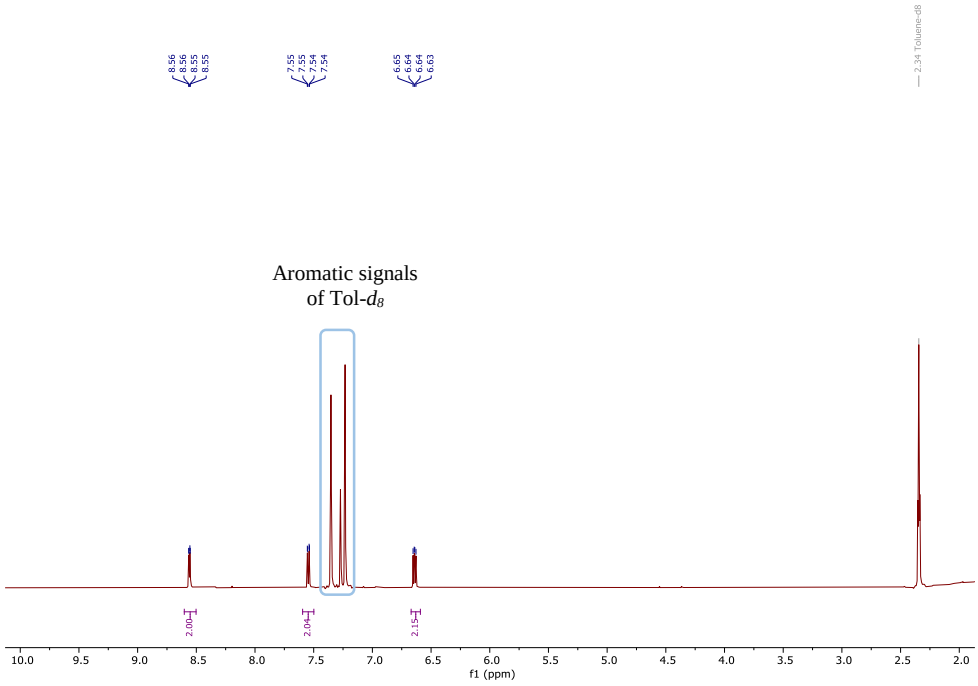


Figure S1: ^{1}H NMR spectrum of **Cr-1a** in tol-d_8 room temperature.

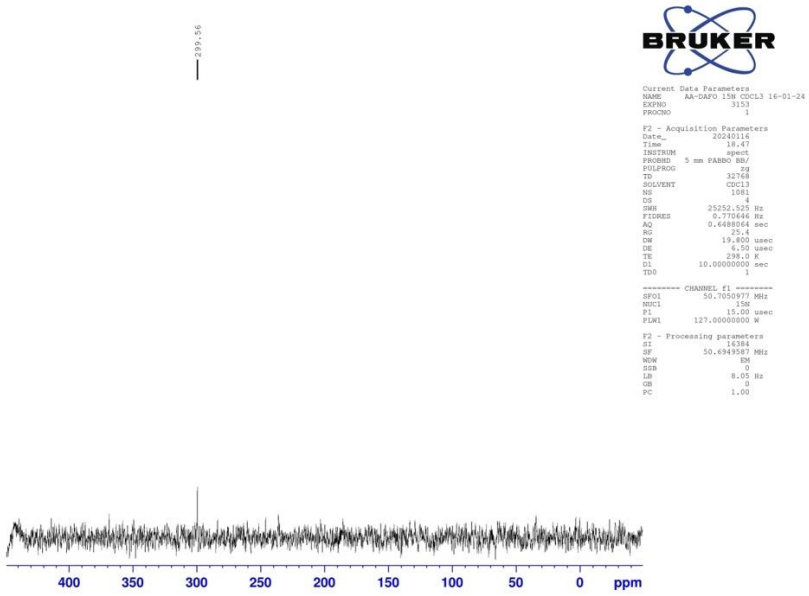


Figure S2: ^{15}N NMR spectrum of 4,5-DAFO in tol-d_8 at room temperature.

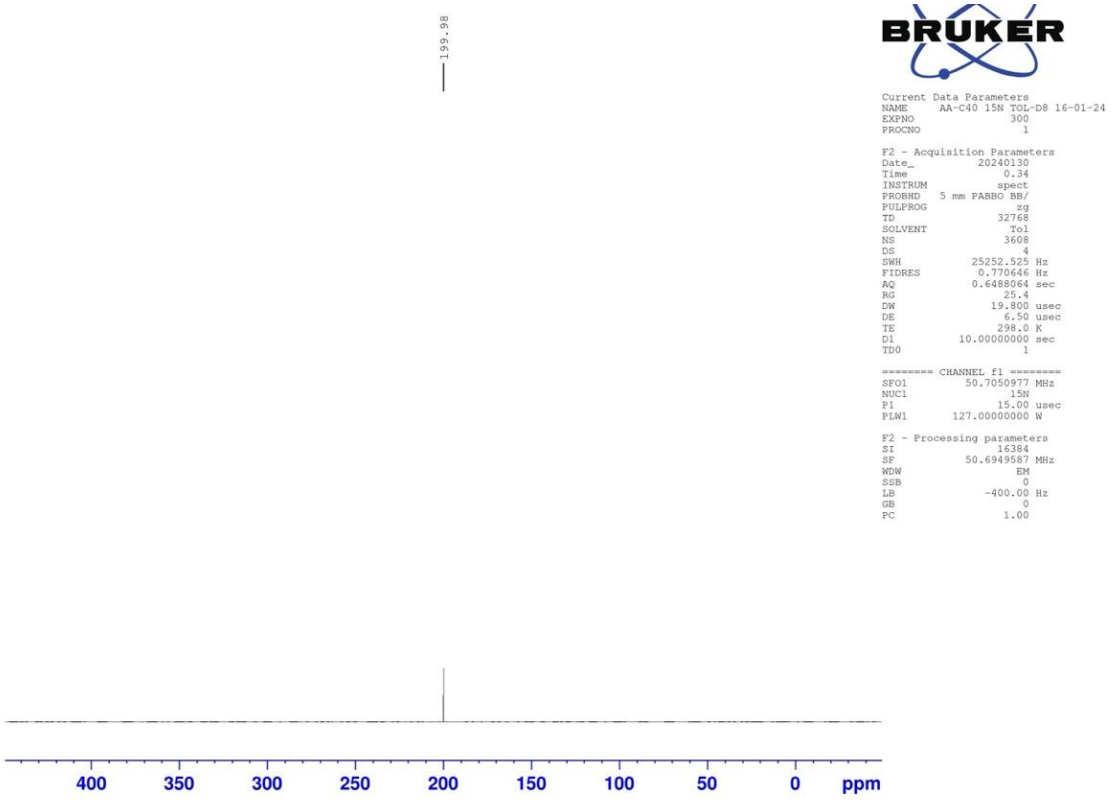


Figure S3: ^{15}N NMR spectrum of **Cr-1a** in tol-d_8 at room temperature.

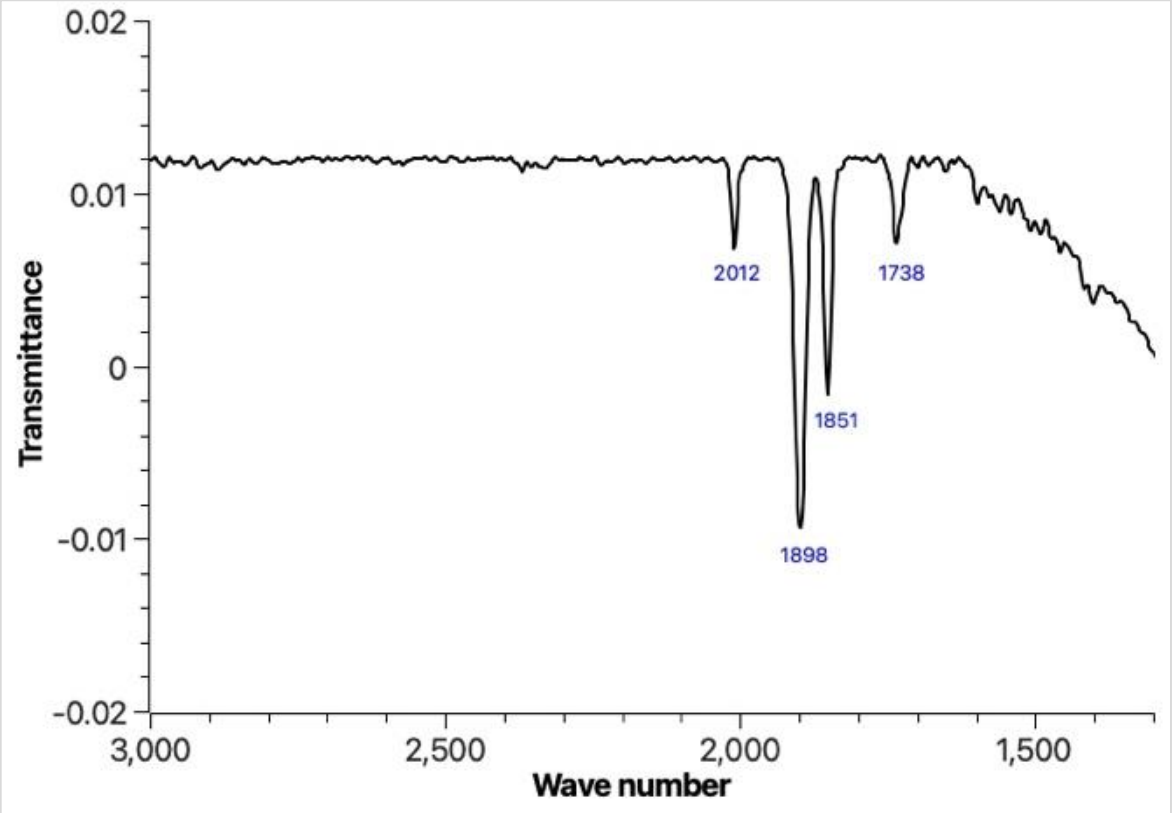


Figure S4: IR-ATR spectrum of **Cr-1a** in toluene.

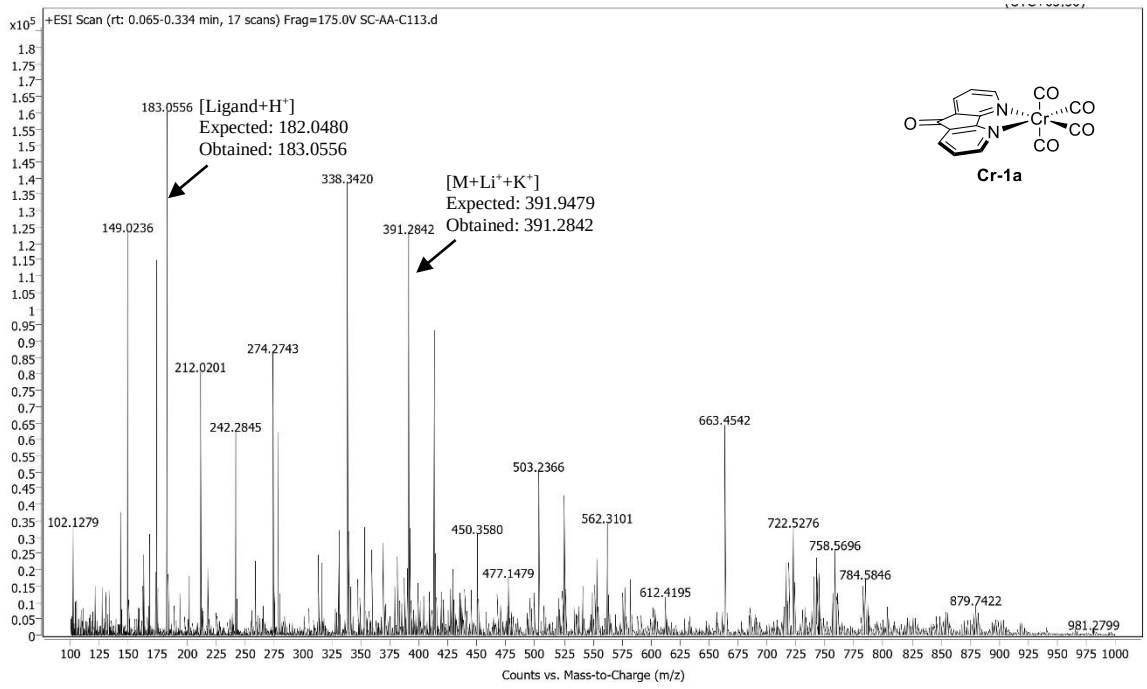


Figure S5: HRMS (ESI) spectrum of complex **Cr-1a** in acetonitrile.

2. X-Ray crystallographic studies

Dark red plate shaped single crystals of **Cr-1a** and **Cr-1a·DAFO** were grown by slow evaporation from a benzene-d6 and diethyl ether solutions, respectively. A suitable crystal was selected and the diffraction data was collected on a Bruker APEX-II CCD diffractometer at 150 K using Mo Kα radiation (λ = 0.71073 Å). The structures of **Cr-1a** and **Cr-1a·DAFO** were solved using the intrinsic phasing method and refined by full-matrix least-squares on F^2 (SHELX-2014) with ShelXT[2] and Olex2[3] structure solution program. The absorption correction was done using the multi-scan method (SADABS). Crystallographic data files for **Cr-1a** and **Cr-1a·DAFO** have been deposited to the Cambridge Crystallographic Data Centre. **CCDC number: 2431020 and 2426705**.

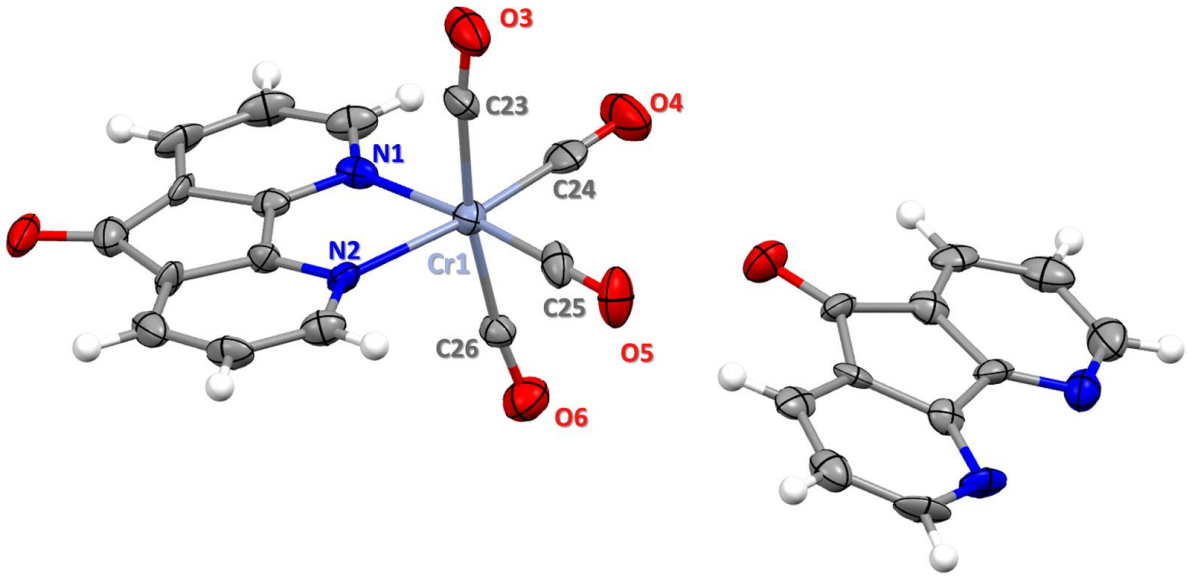


Figure S6: Molecular structure of **Cr-1a·DAFO**.
Selected bond distances (Å) and bond angles (°): Cr1-N1 2.174(6), Cr1-N2 2.171(7), Cr1-C23 1.891(10), Cr1-C24 1.819(10), Cr1-C25 1.850(10), Cr1-C26 1.868(9), O3-C23 1.147(10), O4-C24 1.174(10), O5-C25 1.155(10), O6-C26 1.163(9), N2-Cr1-N1 80.0(3), O3-C23-Cr1 172.4(8), O4-C24-Cr1 177.0(8), O5-C25-Cr1 178.4(8), O6-C26-Cr1 172.3(8). Thermal ellipsoids are drawn at the 30% probability level.

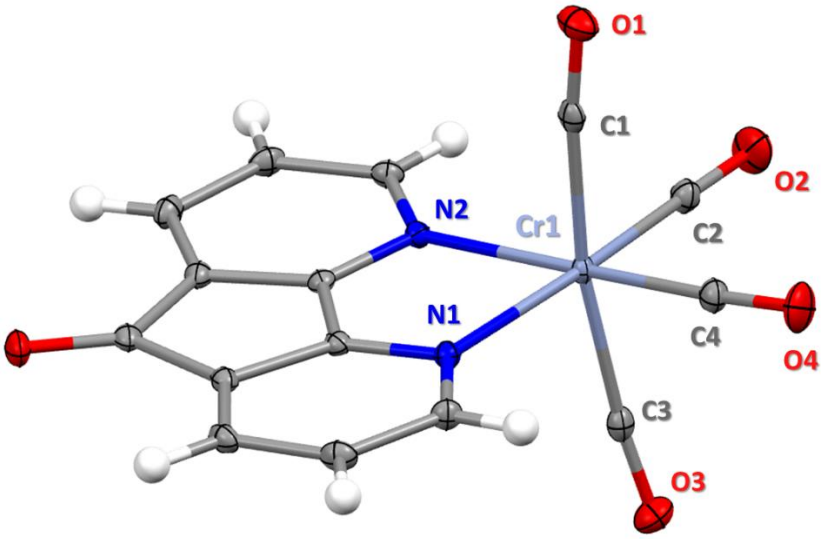


Figure S7: Molecular structure of **Cr-1a**.
Selected bond distances (Å) and bond angles (°): Cr1-N1 2.1608(14), Cr1-N2 2.1759(14), Cr1-C1 1.8950(19), Cr1-C2 1.8405(18), Cr1-C3 1.9152(19), Cr1-C4 1.8289(18), O1-C1 1.150(2), O2-C2 1.153(2), O3-C3 1.140(2), O4-C4 1.162(2), N2-Cr1-N1 80.19(5), O1-C1-Cr1 173.17(15), O2-C2-Cr1 178.03(18), O3-C3-Cr1 173.77(15), O4-C4-Cr1 176.89(16). Thermal ellipsoids are drawn at the 30% probability level.

Table S1. Crystal data and structure refinement for **Cr-1a**

Identification code	**Cr-1a·DAFO**	**Cr-1a**
Empirical formula	$C_{26}H_{12}CrN_4O_6$	$C_{15}H_6CrN_2O_5$
Formula weight	528.40	346.22
Temperature/K	150	150
Crystal system	Monoclinic	monoclinic
Space group	$P2_1/c$	P2/n
a/Å	11.339(6)	6.9252(11)
b/Å	29.542(16)	12.898(2)
c/Å	6.845(4)	15.288(3)
α/°	90	90
β/°	100.381(14)	90.937(5)
γ/°	90	90
Volume/$Å^3$	2255(2)	1365.3(4)
Z	4	4
$\rho_{calc}g/cm^3$	1.556	1.684
μ/mm^{-1}	0.560	0.867
F(000)	1072.0	696.0
Crystal size/mm^3	0.313 × 0.233 × 0.123	0.572 × 0.238 × 0.136
Radiation	MoKα (λ = 0.71073)	MoKα (λ = 0.71073)
2Θ range for data collection/°	3.652 to 51	4.132 to 51.498

Index ranges	$-13 \leq h \leq 12$, $-35 \leq k \leq 35$, $-8 \leq l \leq 8$	$-8 \leq h \leq 7$, $-15 \leq k \leq 15$, $-18 \leq l \leq 18$
Reflections collected	33135	21604
Independent reflections	4203 [R_{int} = 0.4557, R_{sigma} = 0.2846]	2605 [R_{int} = 0.0319, R_{sigma} = 0.0162]
Data/restraints/parameters	4203/0/334	2605/0/208
Goodness-of-fit on F^2	1.034	1.082
Final R indexes [I>=2σ (I)]	R_1 = 0.1030, wR_2 = 0.1395	R_1 = 0.0272, wR_2 = 0.0717
Final R indexes [all data]	R_1 = 0.2638, wR_2 = 0.1915	R_1 = 0.0298, wR_2 = 0.0736
Largest diff. peak/hole / e $Å^{-3}$	0.47/-0.60	0.34/-0.42

Crystallographic Alerts Level A from CheckCIF with the Author Responses

Datablock: mo_cr_dafo_red_0m

RINTA01_ALERT_3_A The value of Rint is greater than 0.25

Rint given 0.456
Author Response: The data quality is poor due to air sensitivity of crystal, probably causing it to degrade over time. The crystal diffracted extremely weakly. Multiple attempts were made to grow better diffracting crystals, but the problem persists. However, we can still unambiguously confirm the metal ligand connectivity and the overall structure of the complex.

PLAT020_ALERT_3_A The Value of Rint is Greater Than 0.12 ..... 0.456 Report
Author Response: The data quality is poor due to air sensitivity of crystal, probably causing it to degrade over time. The crystal diffracted extremely weakly. Multiple attempts were made to grow better diffracting crystals, but the problem persists. However, we can still unambiguously confirm the metal ligand connectivity and the overall structure of the complex.

3. Analysing the stability of the Cr-1a complex in various solvents

In order to understand the stability of complex **Cr-1a** in various solvents (DCM, CH_3CN, MeOH, acetone, MeOH), the solution of the complex was taken out of the glove box and kept outside for a while. The catalyst starts decomposing stating the instability of the catalyst in solution. The complex is stable in toluene and benzene and THF only under inert atmosphere. An exemplary solution of the catalyst was prepared in acetonitrile, which soon started to decompose within 15 minutes as obvious from the colour change (**Figure S8**). The solution was characterised via ^{1}H NMR, which showed signals for the free DAFO ligand and the complex mixture.

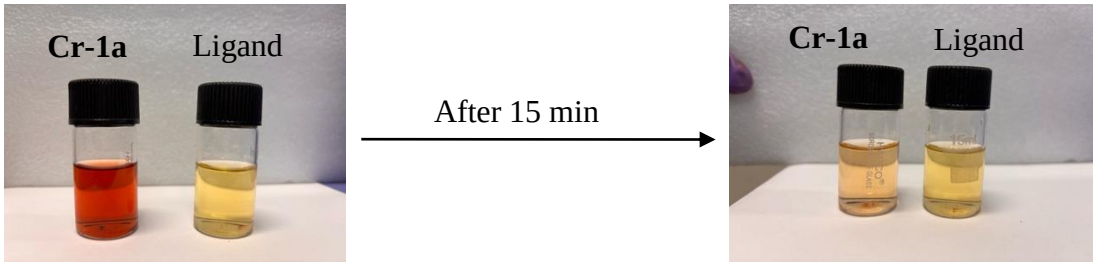


Figure S8: Changes in colour of the complex **Cr-1a** kept in CH_3CN in solution outside glove box.

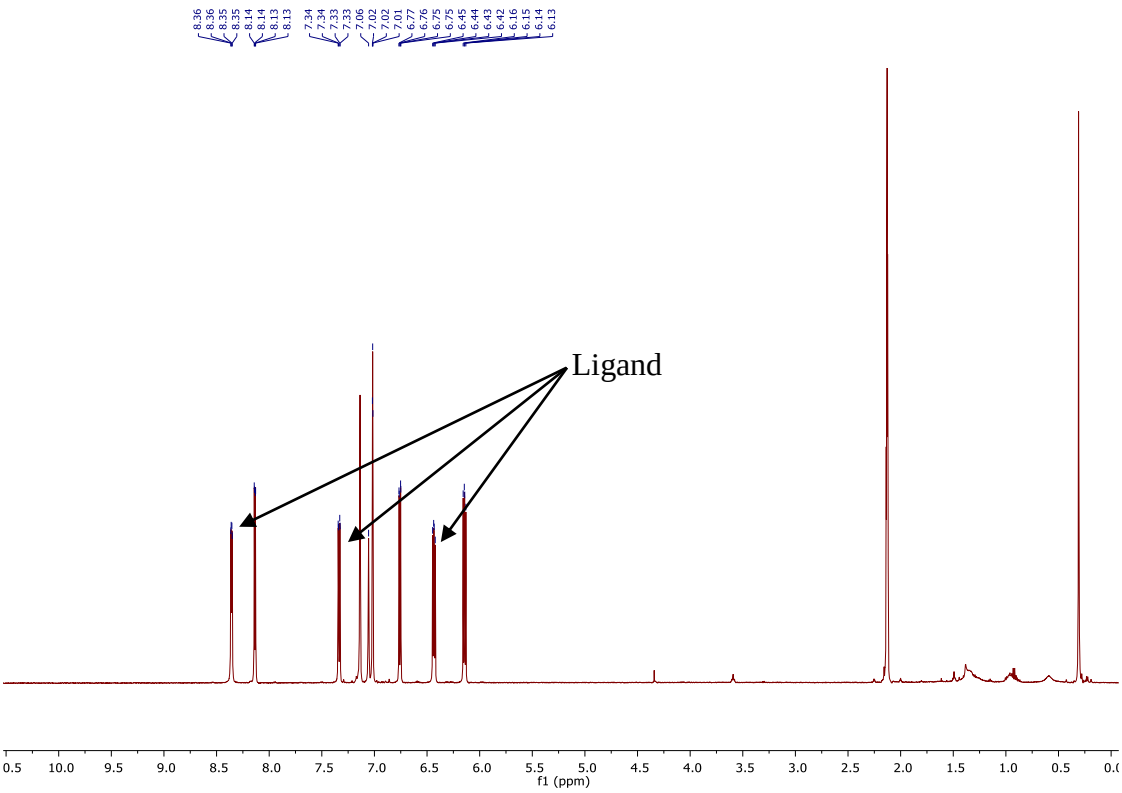


Figure S9: ^{1}H NMR (298 K, Tol-d8) spectrum of **Cr-1a** dissolved in acetonitrile taken after 15 min in solution state showing mixture of complex and ligand peaks.

4. Thermal stability of the Cr-1a complex

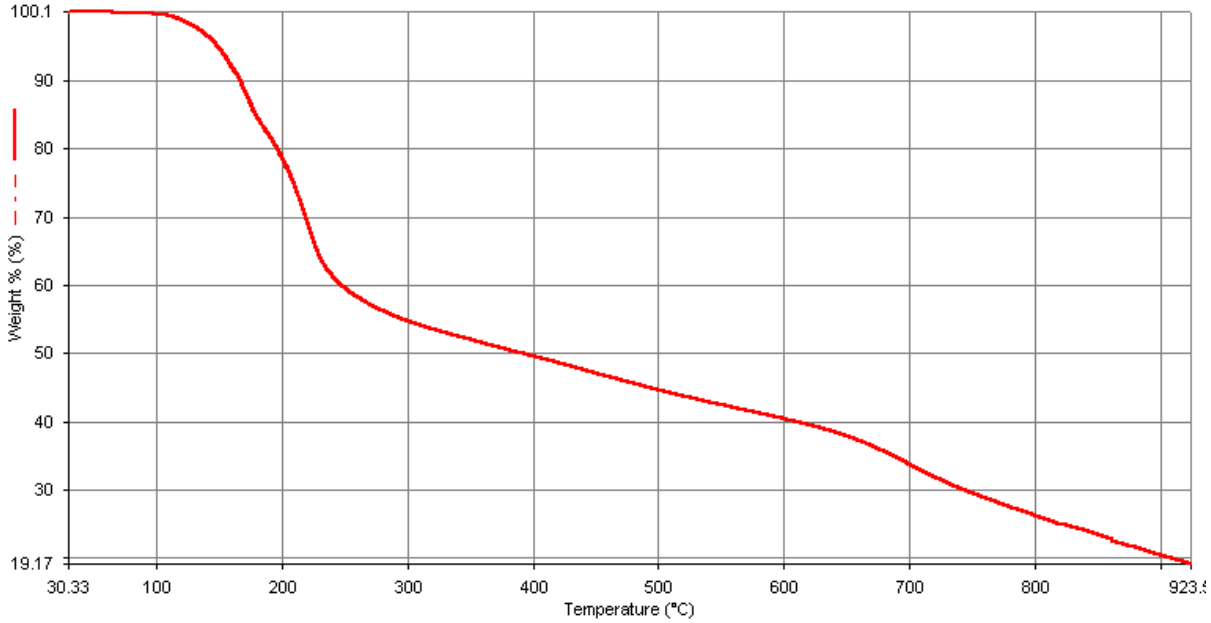


Figure S10: TGA plot of **Cr-1a**.

The TGA (Thermogravimetric analysis) curve of **Cr-1a** indicates the elimination of the moisture or volatile solvent at temperatures ranging from 100 to 200 °C. Gradual weight loss is observed from 200 – 400 °C, which could correspond to stepwise removal of the ligands from the complex. However, major decomposition is observed in the temperature range of 400 °C to 800 °C, where there is a significant weight loss (23.38%). Hence, the catalyst is stable upto 200 °C (Figure S10).

From the DSC (Differential Scanning Calorimetry) plot, upto ~800 °C, the curve shows relative stability with gradual downward trend. However, after 800 °C, significant heat absorption is observed suggesting a phase transition such as melting. (Figure S11).

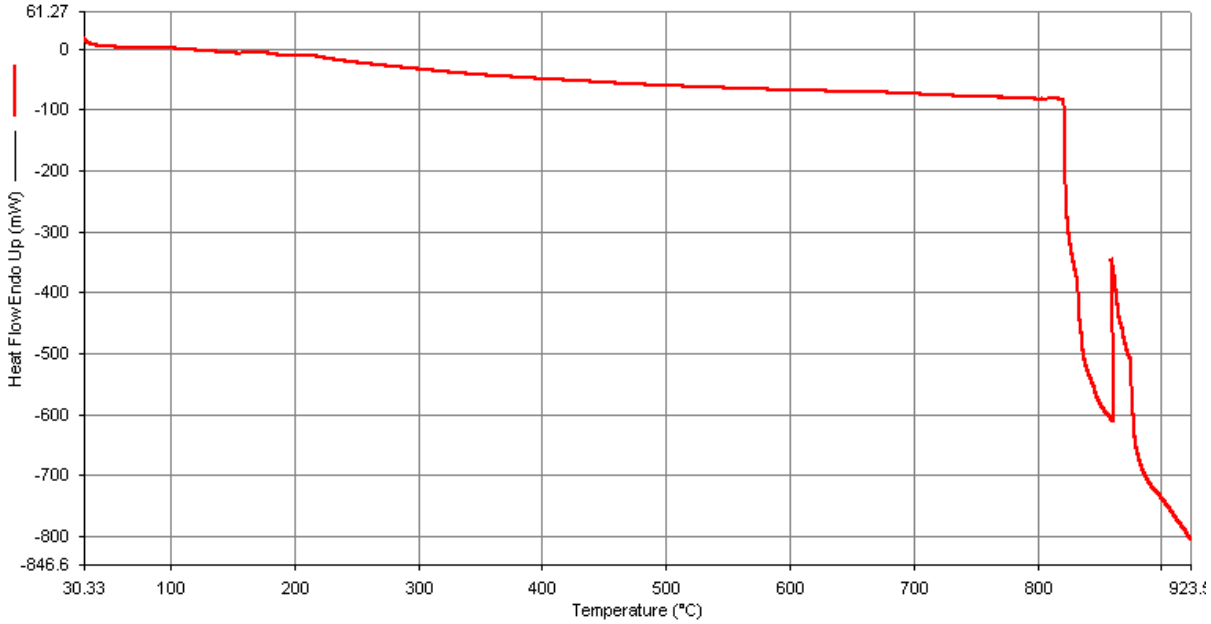


Figure S11: DSC plot of **Cr-1a**.

5. Analysing the stability of the Cr-1a with 5 equiv. of benzylamine at elevated temperature.

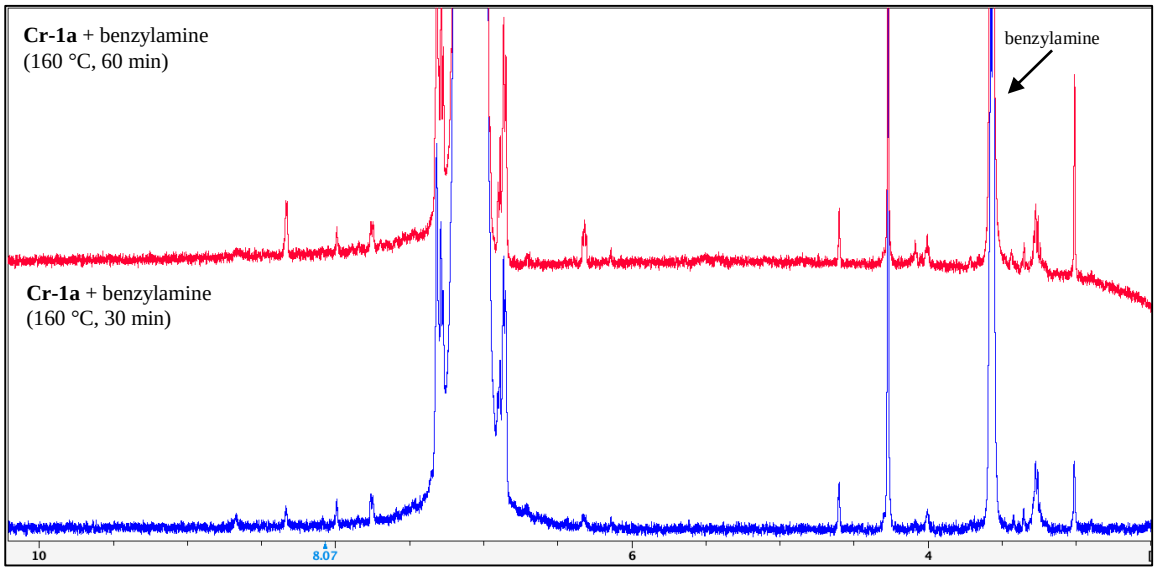


Figure S12: ^{1}H NMR spectra of the reaction mixture of **Cr-1a** and 5 equiv. benzylamine in benzene-d_6 at 160 °C after mentioned intervals.

6. Synthesis of Cr-2, Cr-3, Cr-4, Cr-5, Cr-6, Cr-7 and Cr-8:

Complexes (**C-2, C-3, C-4, C-5, C-7, C-7, C-8**) were synthesized by following the literature protocols.[4-7]

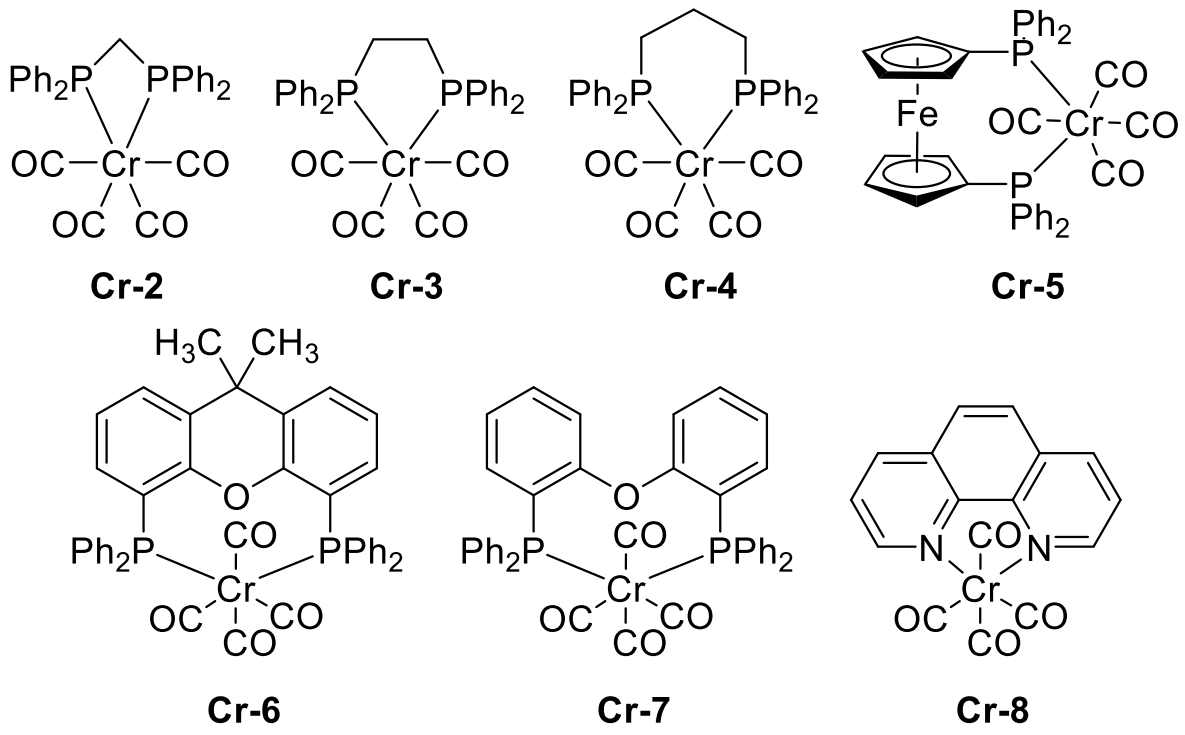


Figure S13: Chromium complexes tested for acceptorless dehydrogenation of primary amines to secondary imines.

7. H_2 detection experiments

7.1 Qualitative analysis of the evolved gas using Gas Chromatography for homocoupling reactions

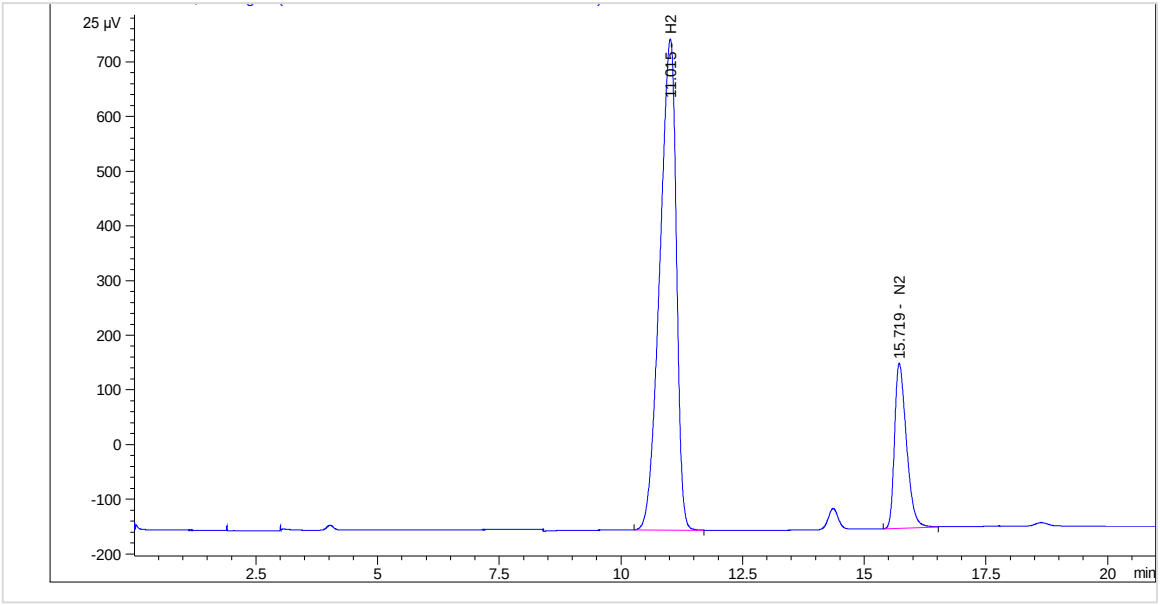


Figure S14: H_2 detection via GC-TCD for the chromium catalysed dehydrogenative coupling of benzylamine (1 mmol).

7.2 Qualitative analysis of the evolved gas using Gas Chromatography for cross-coupling reactions

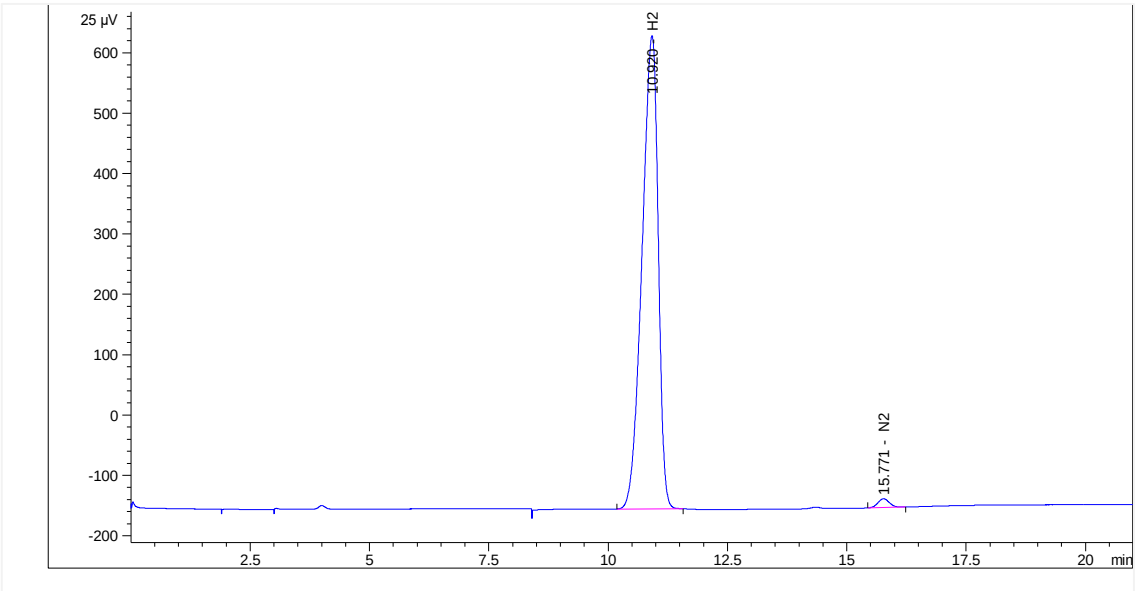


Figure S15: H_2 detection via GC-TCD for the chromium catalysed dehydrogenative cross-coupling of benzylamine (1 mmol) and aniline (2 mmol).

7.3 Hydrogenation of styrene using Pd/C and H_2 gas (evolved during dehydrogenation of benzylamine)

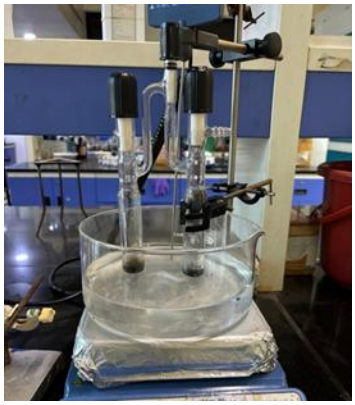


Figure. S16: Experimental bridge-shaped Schlenk tube setup for hydrogenation of styrene using Pd/C and generated H_2 from amine dehydrogenation.

Inside glovebox, in one chamber of a bridged Schlenk tube was taken benzylamine (1 mmol), **Cr-1a** (10 mol%) and toluene (2 mL). while in the other chamber was added styrene (1 mmol) and Pd/C in methanol (1mL). The 1st chamber was allowed to stir at 140 °C for 24 h for the amine dehydrogenation. Soon after the completion of the reaction, the Schlenk tube was allowed to cool down and the middle cap was opened slightly and the generated gas was allowed to pass from the 1st chamber to 2nd chamber. The 2nd chamber was allowed to stir at room temperature for the next 6 h. The conversion of styrene to ethyl benzene was confirmed via ^{1}H NMR.

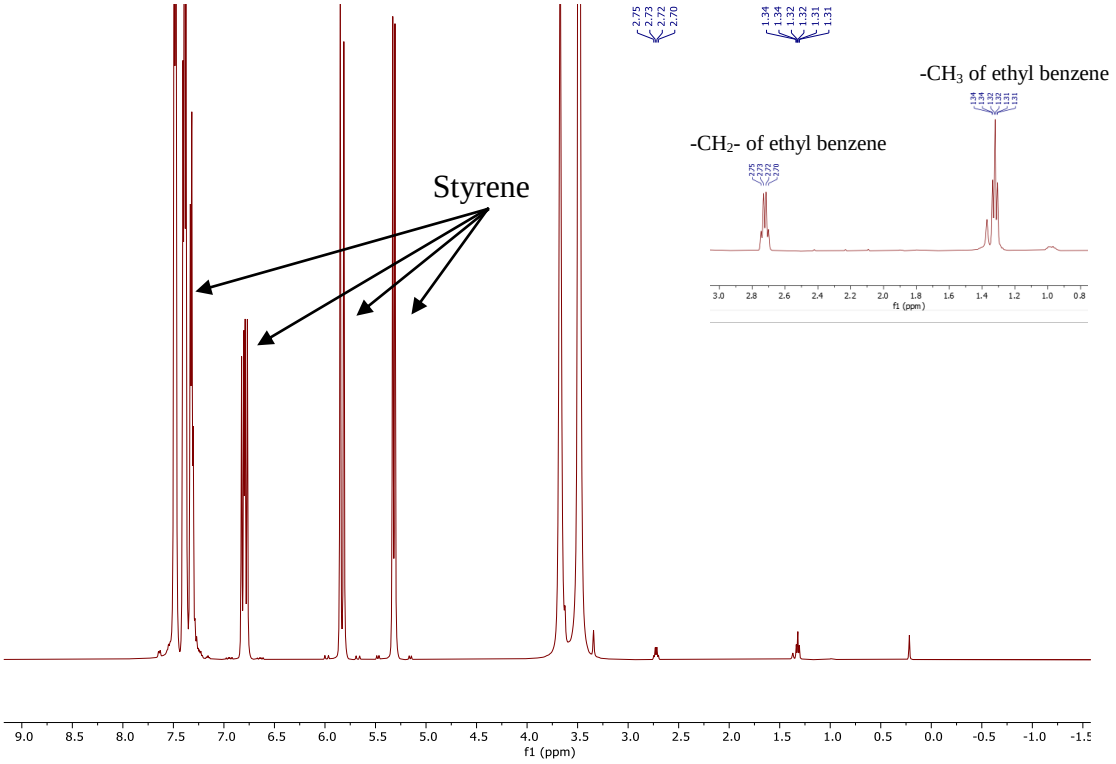


Figure S17: ^{1}H NMR (298 K, $CDCl_3$) spectrum of styrene hydrogenation using Pd/C and H_2, released from dehydrogenation of benzylamine.

8. Experiment for detection of NH_3 gas

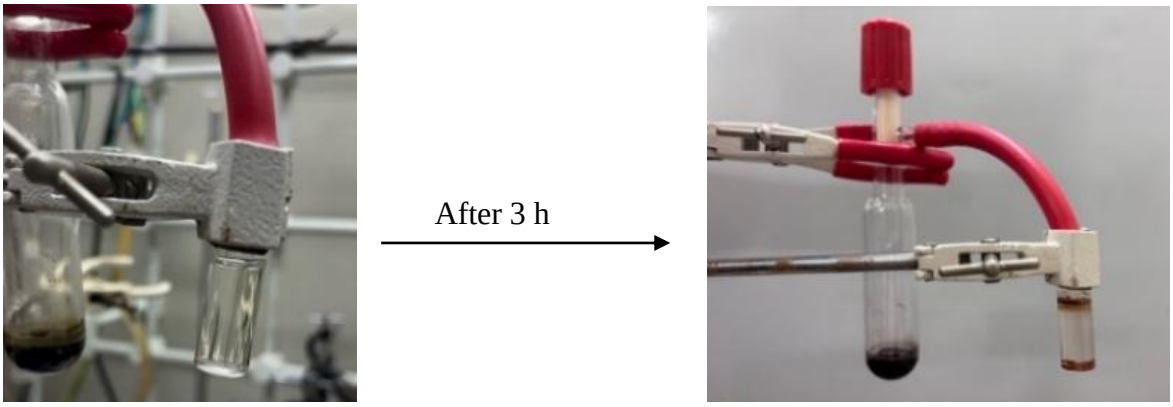
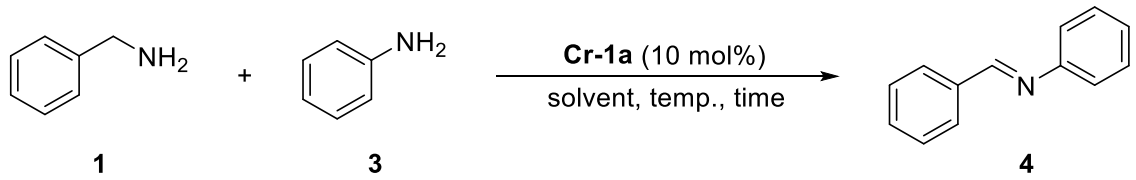


Figure S18: Detection of NH_3 using Nessler's reagent.

Inside glovebox, benzylamine (1 mmol, 109.2 µL) was added to a mixture of **Cr-1a** (10 mol%) in toluene (1.5 mL). The Schlenk tube was sealed and taken out of the glovebox and allowed to stir at 140 °C for 24 h. The Schlenk was cooled down and connected to a 5 mL vial containing Nessler's reagent using a fitting pipe. The Schlenk tube was then opened slightly, and the setup was left as it is. After 3 h, brown precipitate of $HgO.Hg(NH_2)I$ was observed, indicating the presence of NH_3.

9.Optimisation table for the cross-coupling of benzylamine with aniline

Table S2: Optimisation table for **Cr-1a** catalyzed cross-coupling of benzylamine with aniline.

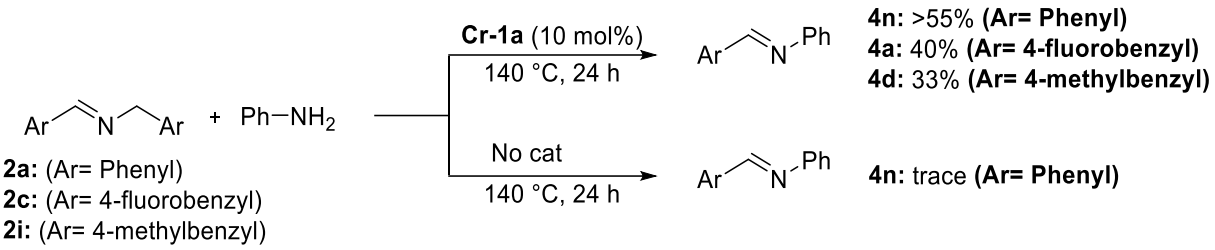


1 **3** **4**

Entry	Solvent (ml)	Base (mol%)	Temp. (°C)	time (hr)	Conversion[a]	yield[b]
1	Toluene (1.5)	NaOH (10)	140	24	neg	neg
2	Toluene (1.5)	KOtBu (10)	140	24	neg	neg
3	Toluene (1.5)	-	120	24	10	neg
4	1,4-dioxane(1.5)	-	120	24	5	5
5	Acetonitrile (1.5)	-	120	24	8	5
6	1,4-dioxane(1.5)	-	140	48	58	16
7	Acetonitrile (1.5)	-	140	48	14	2
8	Toluene (1.5)	-	140	48	75	69

Reaction condition: benzyl amine (0.3 mmol), aniline (0.6 mmol) Yields were determined by ^1H NMR analysis using 1,1,2,2-tetrachloroethane as internal standard.

10. Reaction of substituted *N*-benzylidenebenzylamine with aniline



Scheme S1: Reaction of *N*-benzylidenebenzylamine derivative with aniline in the presence and absence of complex **Cr-1a**.

10.1 In the absence of complex Cr-1a

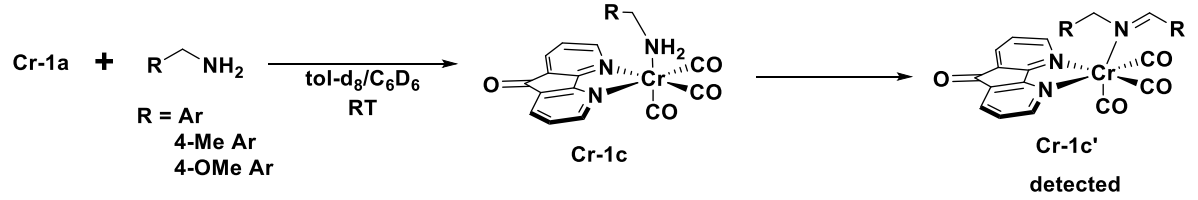
In a Schlenk tube under the nitrogen atmosphere, *N*-benzylidenebenzylamine (1 mmol, 188.2 µL) and aniline (2 equiv., 2 mmol, 182.6 µL) were mixed using a pipette in 2 mL of toluene. The Schlenk tube was then sealed properly and brought out of the glove box and allowed to stir at 140 °C for 24 h. After the completion of the reaction, it was allowed to cool down to room temp. and opened carefully in the fume hood. Trace amount of cross-coupled product was observed in ^{1}H NMR spectrum.

10.2 In the presence of complex Cr-1a

Under the nitrogen atmosphere, a mixture of **Cr-1a** (10 mol%) in toluene (2 mL) was taken. To the reaction mixture, *N*-benzylidenebenzylamine derivative (1 mmol) and aniline (2 equiv., 2 mmol, 182.6 µL) were added using a pipette. The Schlenk tube was then sealed properly and brought out of the glove box and allowed to stir at 140 °C for 24 h. After the completion of the reaction, it was allowed to cool down to room temp. and opened carefully in the fume hood. The cross-coupled product was observed in ^{1}H NMR.

11. Stoichiometric reaction of Cr-1a with primary amines and secondary imines

11.1 Stoichiometric reaction of Cr-1a with primary amines



Scheme S2: Stoichiometric reaction of **Cr-1a** with aryl amines at room temperature.

11.2 Spectra for stoichiometric reaction of Cr-1a with various aryl amines

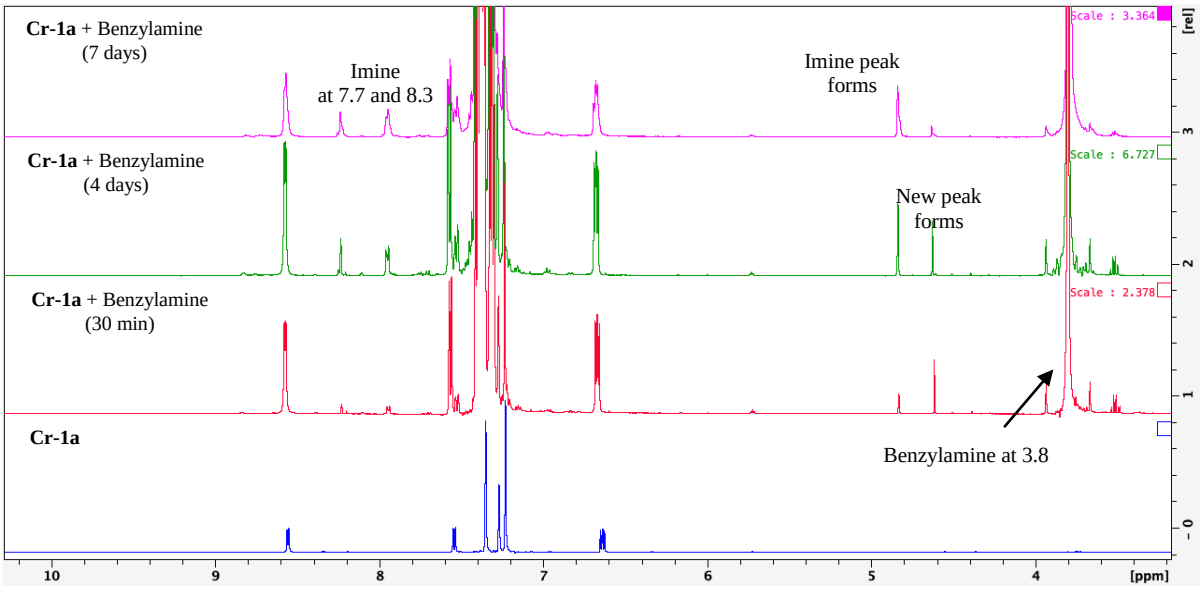


Figure S19: ^{1}H NMR spectra of the reaction mixture of **Cr-1a** and 5 equiv. benzylamine in tol-d_8 after various intervals at room temperature in toluene-d_8 (J-Young NMR tube).

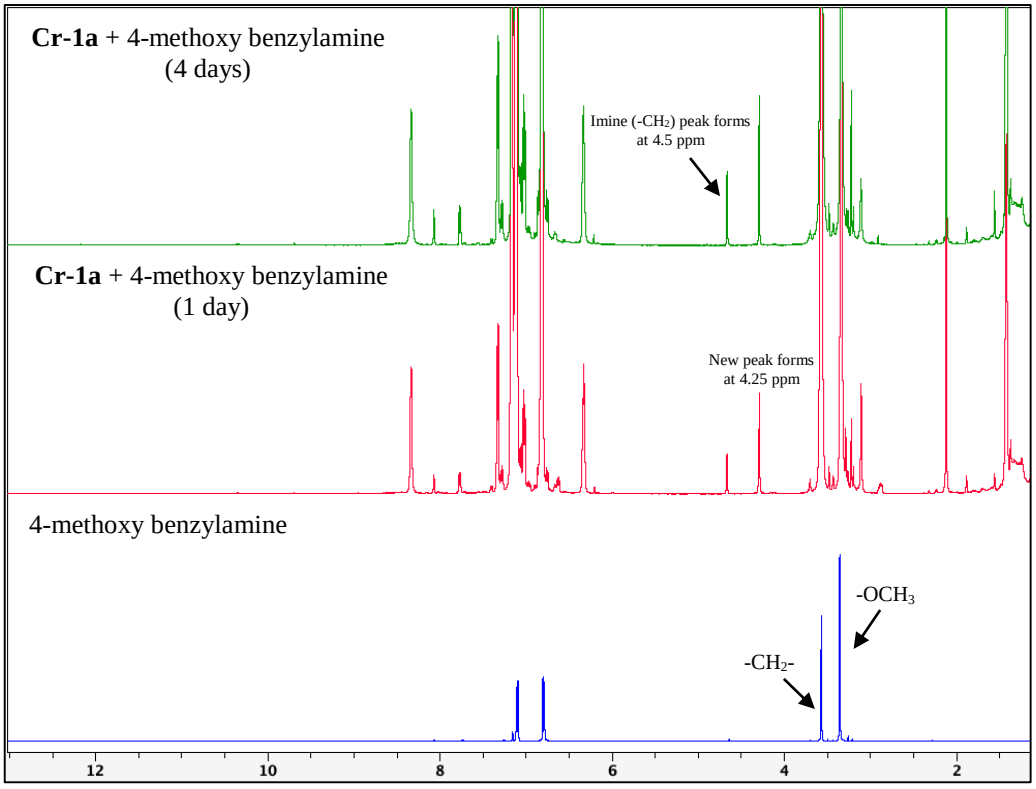


Figure S20: ^{1}H NMR spectra of the reaction mixture of **Cr-1a** and 5 equiv. 4-methoxy benzylamine in benzene-d_6 after various time intervals at room temperature (reactions were conducted inside glove box in a 15 mL vial, aliquot taken for NMR studies).

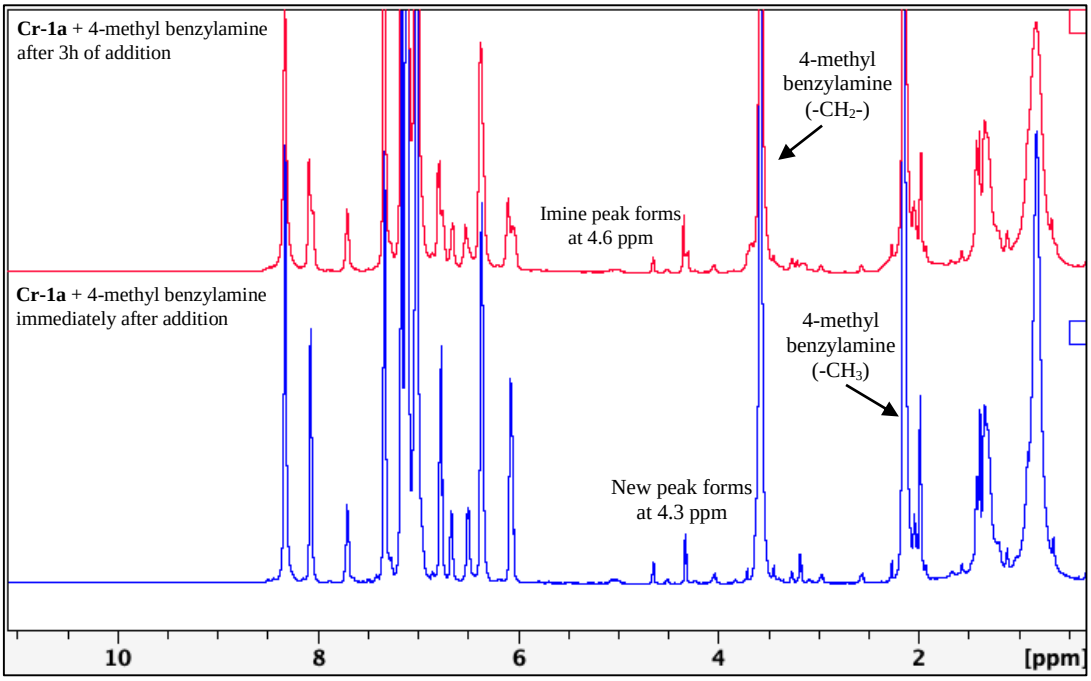


Figure S21: ^{1}H NMR spectra of the reaction mixture of **Cr-1a** and 1 equiv. 4-methyl benzylamine in benzene-d_6 soon after the addition and after 3 h, at room temperature (reactions were conducted inside glove box in a 15 mL vial).

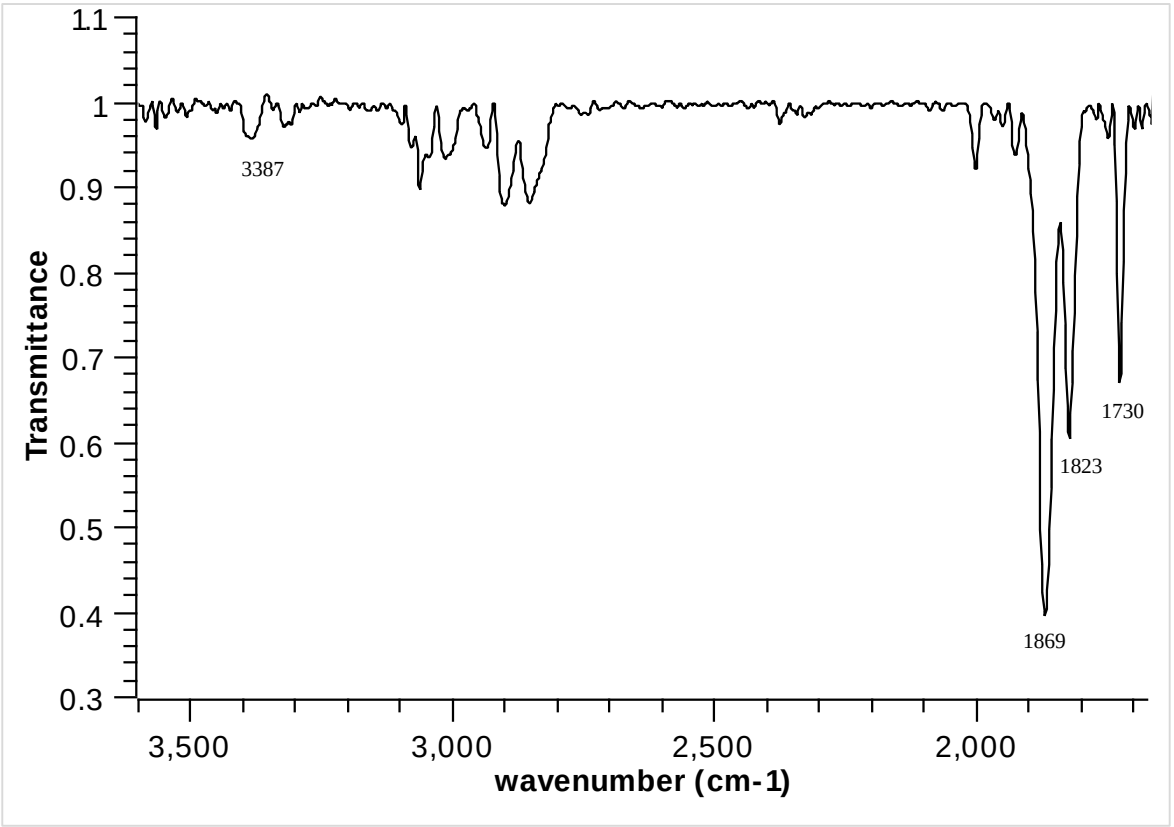


Figure S22: IR spectrum of the stoichiometric reaction between **Cr-1a** and 5 equiv. benzylamine (reaction carried out at room temperature).

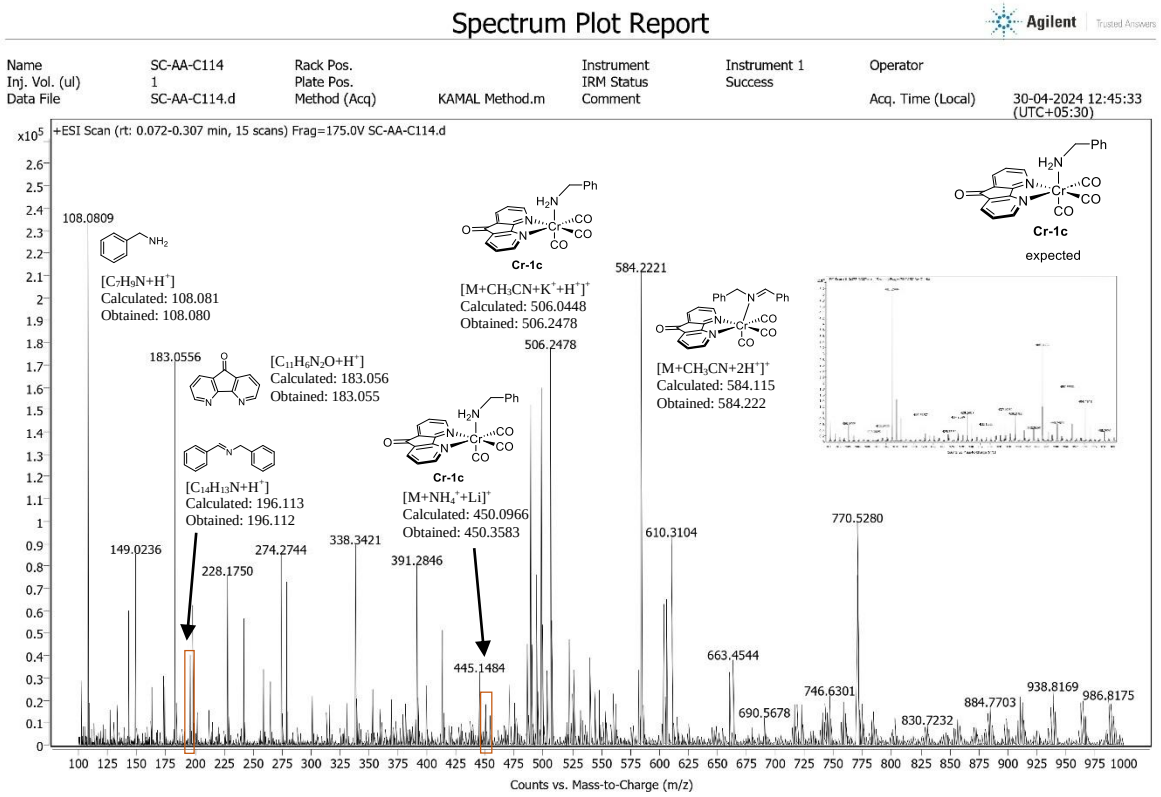


Figure S23: HRMS (ESI) spectrum of the reaction mixture of **Cr-1a** and 5 equiv. of benzylamine.

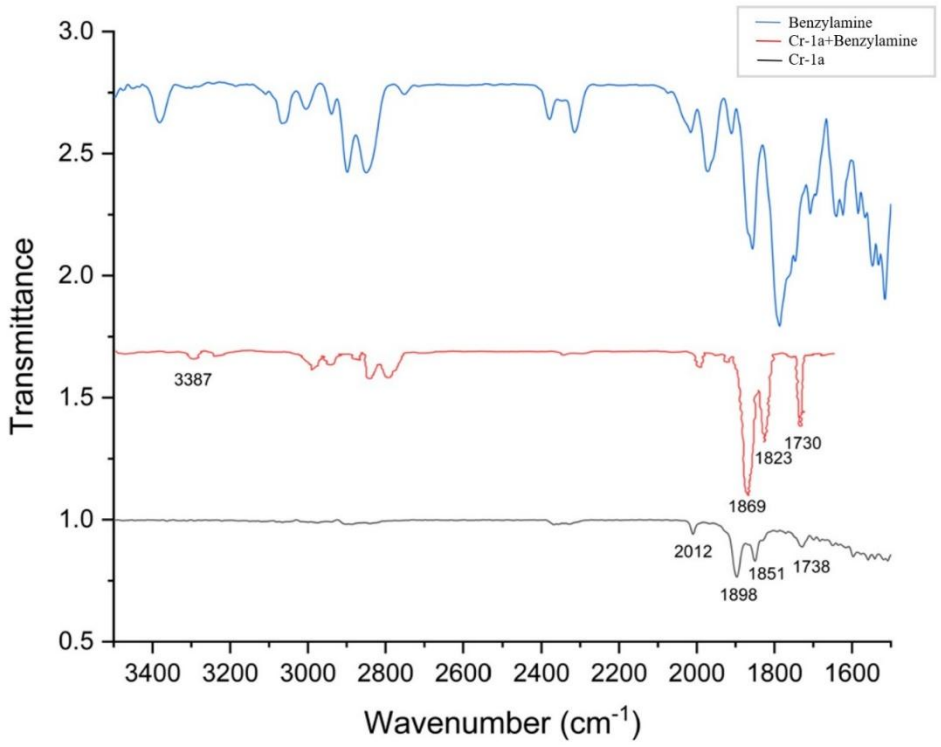
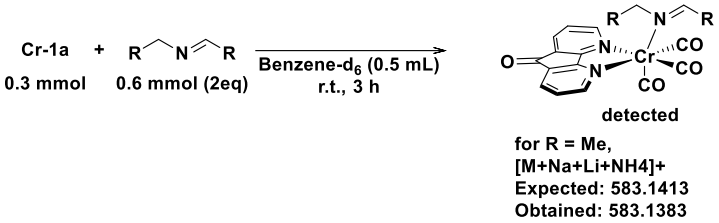


Figure S24: Stacked IR spectrum of **Cr-1a, Cr-1a**+benzylamine, and benzylamine.

12. Reaction of Cr-1a with substituted benzylidenebenzylamine



Scheme S3: Reaction of **Cr-1a** with secondary imines in stoichiometric amount.

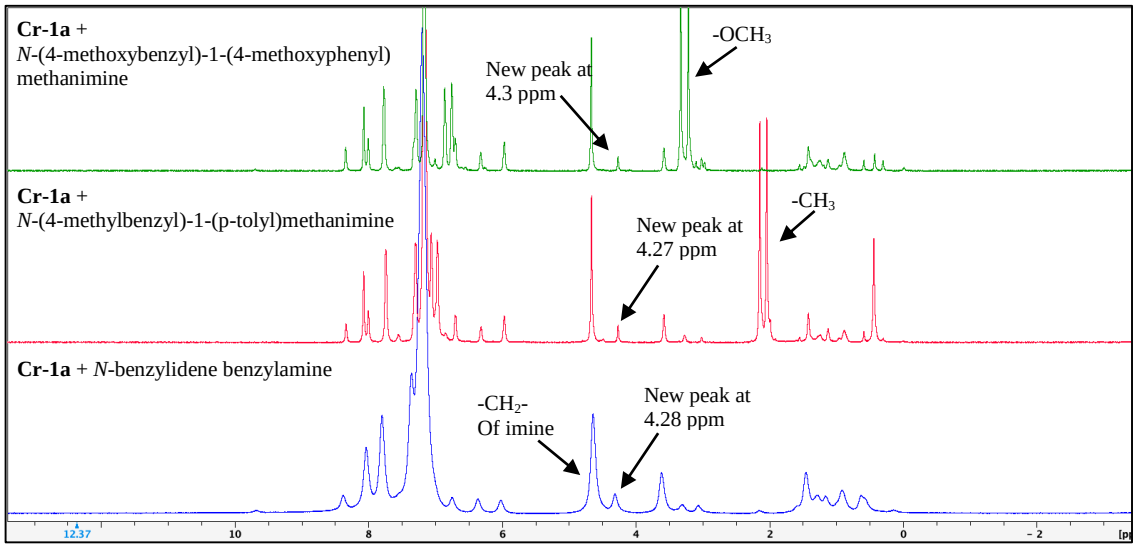


Figure S25: ^{1}H NMR spectra of the reaction mixture of **Cr-1a** and 2 equiv. of secondary imines in benzene-d_6 after 3 h of addition, at room temperature (reactions were carried out inside glove box in a 15 mL vial).

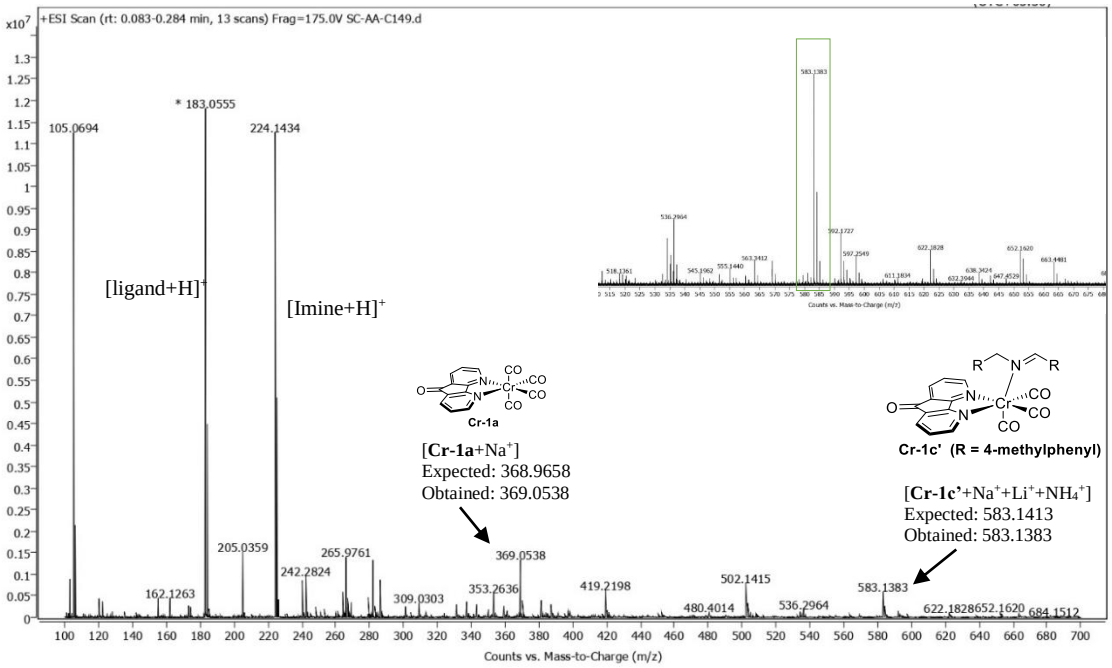


Figure S26: HRMS (ESI) spectrum of the reaction mixture of **Cr-1a** and N-(4-methylbenzyl)-1-(p-tolyl)methanimine (secondary imine, where R represents 4-methylphenyl group, expected complex).

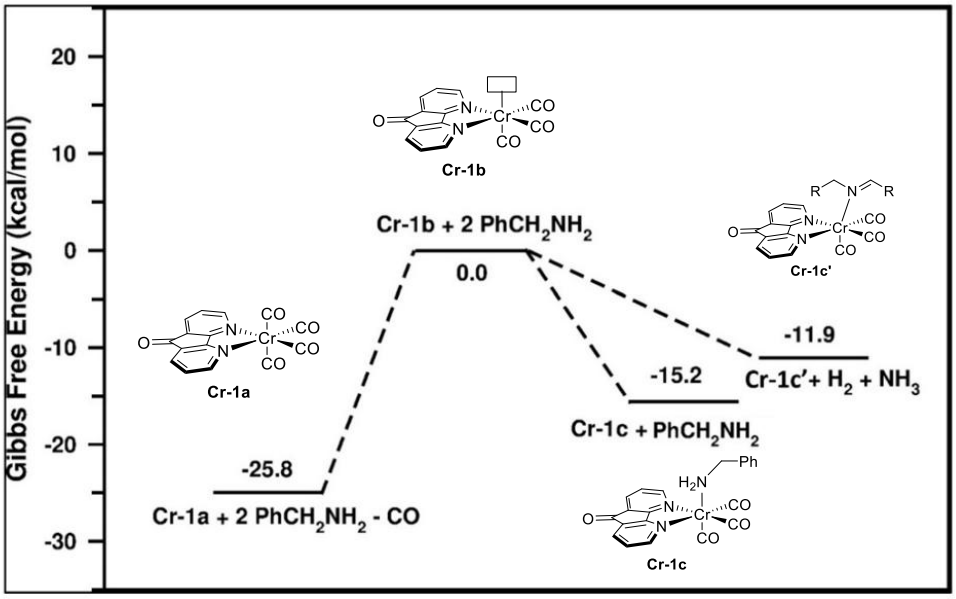


Figure S27: Gibbs free energy profile (in kcal mol^{-1}) for the reaction of **Cr-1a** with *N*-benzylidenebenzylamine using the B3LYP-D3/BS1 level of theory.

DFT calculation was performed to check the stability of **Cr-1c'** compared to **Cr-1c** and the corresponding Gibbs free energy diagram is shown in Figure S17. (Details on the computational method is provided in Section 14 of SI). The energy difference between **Cr-1c** and **Cr1c'** is only 3.3 kcal/mol which shows the probability of their coexistence at room temperature, with lower energy one more populated.

13. XPS Analysis of the dried reaction mixture Cr-1a and benzylamine

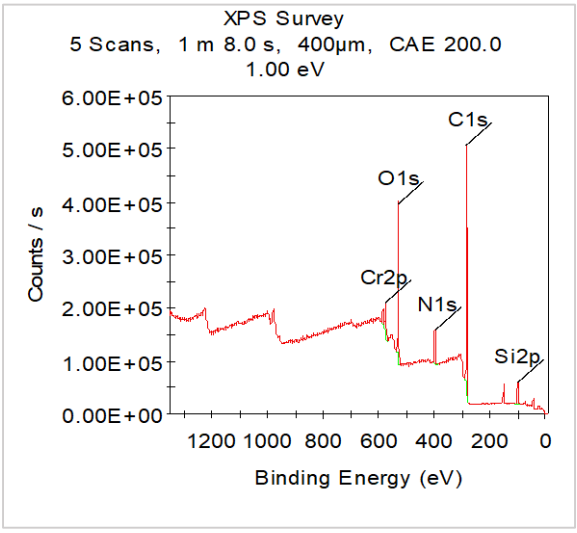
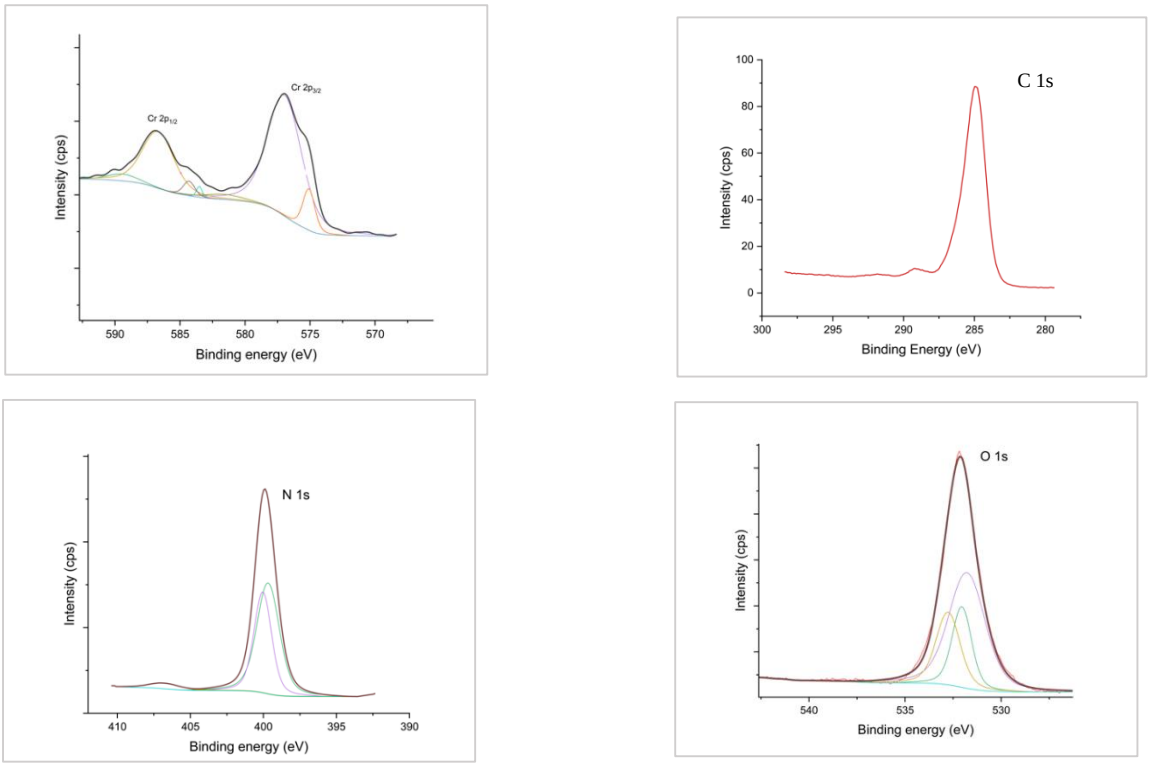


Figure S28: XPS spectrum of stoichiometric reaction of **Cr-1a** with benzylamine (2 equiv.).

As shown in Figure S28, the XPS spectra of the dried reaction mixture of the stoichiometric reaction between **Cr-1a** and 2 equiv. of benzylamine establish Cr 2p, N 1s, C 1s, O 1s. The deconvoluted peaks in the region Cr $2p_{3/2}$ at 575.04 eV and 576.9 eV predicts the presence of Cr(0) and Cr(III).[8] The

deconvoluted peaks of C 1s spectrum at 284.98 eV and 289.18 eV correspond to C-C, C-H bonds, and C=O (aromatic) of the DAFO respectively. The peaks for N 1s at 399.68 and 400.08 are expected to correspond N of the 4,5-DAFO and of the amine. The binding energy locations of 532.18 eV confirms the presence of O of -C=O- group of DAFO.[9]



Core-level XPS spectra of Cr 2p, C 1s, N 1s, O 1s

14. ^{1}H and ^{13}C NMR data of the imine products:

For homo-coupled products: The products **2a**, **2b**, **2c**, **2f**, **2g**, **2h**, **2i**, **2j**, **2l**, **2o** were isolated by column chromatography using neutral alumina (Al_2O_3) as stationary phase and n-hexane as eluent and the isolated products were characterised by ^{1}H and ^{13}C NMR technique. Crude NMR of compounds **2d**, **2e**, **2k**, **2m**, **2n**, **2p**, **2q** contain reaction mixture, solvents and grease peaks, which we were not able to remove (see exemplary NMR 2d, where grease peak is highlighted). The yield of the desired products from the reaction mixture were analysed using 1,1,2,2-tetrachloroethane as an internal standard.

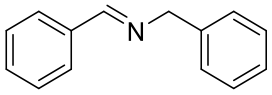
Cross-coupled products: The products **4e**, **4f**, **4h**, **4i**, **4n** were isolated by column chromatography using neutral alumina (Al_2O_3) as stationary phase and n-hexane as eluent and the isolated products were characterised by ^{1}H and ^{13}C NMR technique.

For the rest of the compounds **4a**, **4b**, **4c**, **4d**, **4g**, **4j**, **4k**, **4l**, **4m**; the crude NMR revealed presence of homo and cross-coupled product mixtures, which could not be separated

out. The conversion and selectivity towards cross-coupled product was confirmed using 1,1,2,2-tetrachloroethane as an internal standard. Few representative crude NMR spectra of **4c**, **4g**, and **4k** are added in the supporting file.

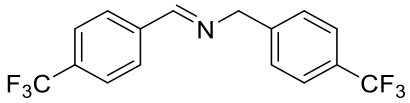
14.1 ^{1}H and ^{13}C NMR data of the isolated compounds:

***N*-benzyl-1-phenylmethanimine**[10] **(2a)**



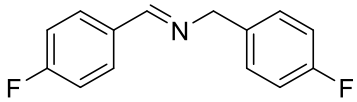
Pale yellow liquid **(**26 mg, 87%) **^{1}H NMR** (500 MHz, Chloroform-*d*) δ 8.3 (s, 1H), 7.8 – 7.7 (m, 2H), 7.3 (dd, *J* = 5.2, 1.9 Hz, 3H), 7.3 (d, *J* = 4.4 Hz, 4H), 7.2 (tt, *J* = 9.8, 4.7 Hz, 1H), 4.7 (s, 2H). **^{13}C NMR** (126 MHz, Chloroform-d) δ 162.1, 139.4, 136.2, 130.8, 129.1, 128.7, 128.6, 128.4, 128.1, 127.1, 65.1.

***N*-(4-(trifluoromethyl)benzyl)-1-(4-(trifluoromethyl)phenyl)methanimine**[10] **(2b)**



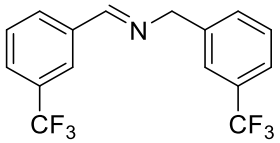
Light-brown-oily liquid (40 mg, 76%) **^{1}H NMR** (500 MHz, Chloroform-*d*) δ 8.5 (s, 1H), 7.9 (d, *J* = 8.0 Hz, 2H), 7.7 (d, *J* = 8.1 Hz, 2H), 7.6 (d, *J* = 8.1 Hz, 3H), 7.5 (d, *J* = 8.0 Hz, 2H), 4.9 (s, 2H). **^{13}C NMR** (126 MHz, Chloroform-*d*) δ 161.1, 143.1, 139.0, 132.6 (q, *J* = 32.4 Hz), 129.4 (q, *J* = 32.5 Hz), 128.5, 128.1, 123.2, 122.9, 120.9, 64.4. **^{19}F NMR** (471 MHz, Chloroform-d) δ -62.6 (d, J = 176.2 Hz).

***N*-(4-fluorobenzyl)-1-(4-fluorophenyl)methanimine**[10] **(2c)**



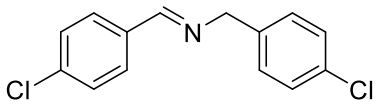
Brown-oily liquid (25 mg, 71%) **^{1}H NMR** (500 MHz, Chloroform-*d*) δ 8.4 (s, 1H), 7.8 (dd, *J* = 8.3, 5.6 Hz, 2H), 7.4 – 7.3 (m, 2H), 7.1 (t, *J* = 8.5 Hz, 2H), 7.1 (t, *J* = 8.5 Hz, 2H), 4.8 (s, 2H). **^{13}C NMR** (126 MHz, Chloroform-d) δ 165.4, 160.5, 135.0, 132.4, 130.2 (d, *J* = 8.7 Hz), 129.5 (d, *J* = 8.1 Hz), 115.8, 115.7, 115.4, 115.2, 64.2.

***N*-(3-(trifluoromethyl)benzyl)-1-(3-(trifluoromethyl)phenyl)methanimine**[11] **(2d)**



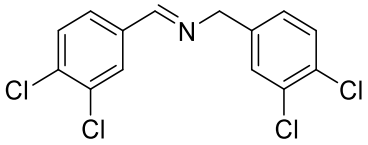
Light-yellow oily liquid **^{1}H NMR** (500 MHz, Chloroform-d) δ 8.5 (s, 1H), 8.1 (s, 1H), 8.0 (d, J = 7.7 Hz, 1H), 7.7 (d, J = 7.8 Hz, 1H), 7.6 (s, 1H), 7.6 – 7.6 (m, 3H), 7.5 (t, J = 7.6 Hz, 1H), 4.9 (s, 2H).

***N*-(4-chlorobenzyl)-1-(4-chlorophenyl)methanimine**[11] **(2f)**



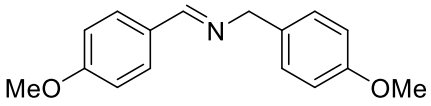
Light-brown solid (15 mg, 38%) **^{1}H NMR** (500 MHz, Chloroform-*d*) δ 8.3 (s, 1H), 7.8 – 7.7 (m, 2H), 7.4 – 7.4 (m, 2H), 7.4 – 7.3 (m, 2H), 7.3 – 7.2 (m, 3H), 4.8 (s, 2H). **^{13}C NMR** (126 MHz, Chloroform-*d*) δ 160.9, 137.6, 136.9, 134.5, 132.9, 129.5, 129.3, 129.0, 128.7, 64.2.

***N*-(3,4-dichlorobenzyl)-1-(3,4-dichlorophenyl)methanimine[12] (2g)**



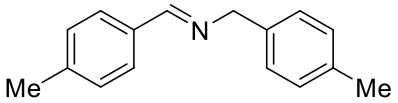
Brown-oily liquid (37 mg, 75%) **^{1}H NMR** (500 MHz, Chloroform-d) δ 8.3 (s, 1H), 7.9 (d, *J* = 1.9 Hz, 1H), 7.6 – 7.6 (m, 1H), 7.5 (d, *J* = 8.2 Hz, 1H), 7.5 – 7.4 (m, 2H), 7.2 (dd, *J* = 8.0, 1.9 Hz, 1H), 4.8 (s, 2H). **^{13}C NMR** (126 MHz, Chloroform-*d*) δ 160.0, 139.2, 135.7, 135.1, 133.2, 132.6, 131.1, 130.7, 130.5, 129.8 (d, *J* = 1.4 Hz), 127.4, 127.2, 63.6.

***N*-(4-methoxybenzyl)-1-(4-methoxyphenyl)methanimine[13] (2h)**



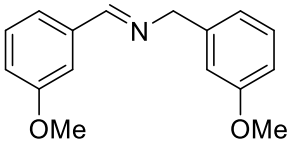
Yellow-oily liquid (14 mg, 36%) **^{1}H NMR** (500 MHz, Chloroform-*d*) δ 8.3 (s, 1H), 7.8 – 7.7 (m, 2H), 7.3 – 7.2 (m, 2H), 7.0 – 6.9 (m, 2H), 6.9 – 6.9 (m, 2H), 4.8 (s, 2H), 3.9 (s, 3H), 3.8 (s, 3H). **^{13}C NMR** (126 MHz, Chloroform-*d*) δ 161.7, 160.9, 158.7, 131.7, 129.8, 129.2, 114.0, 64.4, 55.3.

***N*-(4-methylbenzyl)-1-(p-tolyl)methanimine[12] (2i)**



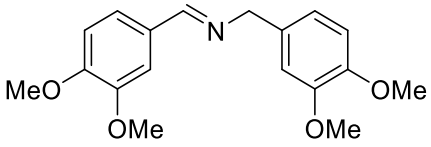
Light-brown solid (13mg, 38%) **^{1}H NMR** (500 MHz, Chloroform-*d*) δ 8.4 (s, 1H), 7.7 (d, *J* = 7.6 Hz, 2H), 7.2 (t, *J* = 4.7 Hz, 4H), 7.2 (d, *J* = 7.7 Hz, 2H), 4.8 (s, 2H), 2.4 (s, 3H), 2.4 (s, 3H). **^{13}C NMR** (126 MHz, Chloroform-*d*) δ 161.7, 141.0, 136.5, 136.4, 133.7, 129.3, 129.2, 128.3, 128.0, 64.8, 21.5, 21.1.

***N*-(3-methoxybenzyl)-1-(3-methoxyphenyl)methanimine[12] (2j)**



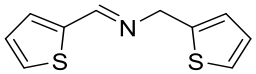
Brown-oily liquid (13 mg, 35%) **^{1}H NMR** (500 MHz, Chloroform-*d*) δ 8.7 (d, *J* = 1.8 Hz, 1H), 8.0 (dd, *J* = 7.7, 1.6 Hz, 1H), 7.3 (ddd, *J* = 7.3, 4.8, 1.9 Hz, 2H), 7.3 – 7.3 (m, 1H), 7.2 (d, *J* = 3.4 Hz, 4H), 4.9 (s, 2H), 2.6 (s, 3H), 2.4 (s, 3H). **^{13}C NMR** (126 MHz, Chloroform-*d*) δ 160.6, 137.8, 137.7, 136.2, 134.3, 130.9, 130.3, 130.2, 128.3, 127.7, 127.1, 126.2, 126.1, 63.4, 19.4 (d, *J* = 12.6 Hz).

***N*-(3,4-dimethoxybenzyl)-1-(3,4-dimethoxyphenyl)methanimine[10] (2l)**



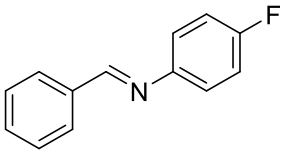
Light-brown solid (19 mg, 40%) **^{1}H NMR** (500 MHz, Chloroform-*d*) δ 8.3 (s, 1H), 7.5 (d, *J* = 1.9 Hz, 1H), 7.2 (dd, *J* = 8.2, 2.0 Hz, 1H), 6.8 (dd, *J* = 18.4, 10.0 Hz, 4H), 4.7 (s, 2H), 3.9 (s, 3H), 3.9 (s, 3H), 3.9 (s, 3H), 3.8 (s, 3H). **^{13}C NMR** (126 MHz, Chloroform-*d*) δ 161.3, 151.4, 149.3, 149.0, 148.1, 132.0, 129.4, 123.3, 120.2, 111.5, 111.2, 110.4, 108.8, 64.7, 55.9.

1-(thiophen-2-yl)-N-(thiophen-2-ylmethyl)methanimine[14] (2o)



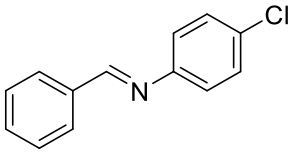
Brown-oily liquid (11 mg, 36%) **^{1}H NMR** (500 MHz, Chloroform-*d*) δ 8.3 (d, *J* = 1.5 Hz, 1H), 7.3 (dd, *J* = 5.0, 1.2 Hz, 1H), 7.3 (dd, *J* = 3.6, 1.2 Hz, 1H), 7.2 (dd, *J* = 4.9, 1.4 Hz, 1H), 7.0 (dd, *J* = 5.0, 3.6 Hz, 1H), 6.9 (ddd, *J* = 6.4, 4.2, 2.9 Hz, 2H), 4.9 (s, 2H).**^{13}C NMR** (126 MHz, Chloroform-*d*) δ 155.4, 142.2, 141.6, 131.0, 129.4, 127.4, 126.9, 125.3, 124.9, 58.5

***N*-(4-fluorophenyl)-1-phenylmethanimine[13] (4e)**



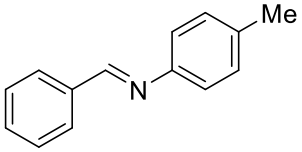
Light-brown solid (56 mg, 94%) **^{1}H NMR** (500 MHz, Chloroform-d) δ 8.5 (s, 1H), 8.0 – 7.9 (m, 2H), 7.5 (dt, *J* = 5.4, 2.6 Hz, 3H), 7.3 – 7.2 (m, 2H), 7.1 – 7.1 (m, 2H). **^{13}C NMR** (126 MHz, Chloroform-*d*) δ 162.3, 160.4, 160.2 (d, *J* = 1.7 Hz), 148.2 (d, *J* = 2.8 Hz), 136.2, 131.5, 128.9, 122.4 (d, *J* = 8.2 Hz), 116.0 (d, *J* = 22.4 Hz).

***N*-(4-chlorophenyl)-1-phenylmethanimine[15] (4f)**



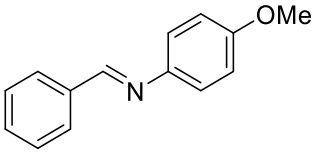
Brown solid (47 mg, 73%) **^{1}H NMR** (500 MHz, Chloroform-d) δ 8.5 (s, 1H), 8.0 – 7.9 (m, 2H), 7.5 (d, *J* = 7.3 Hz, 3H), 7.4 (d, *J* = 8.7 Hz, 2H), 7.2 (d, *J* = 8.6 Hz, 2H). **^{13}C NMR** (126 MHz, Chloroform-d) δ 160.8, 150.6, 136.1, 131.7, 131.5, 129.3, 129.0, 128.9, 122.3.

1-phenyl-*N*-(p-tolyl)methanimine[11] (4h)



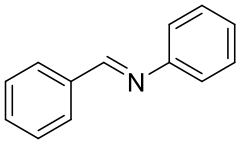
Brown-oily liquid (46 mg, 79%) **^{1}H NMR** (500 MHz, Chloroform-d) δ 8.6 (s, 1H), 8.1 (dd, *J* = 6.9, 3.1 Hz, 2H), 7.6 – 7.5 (m, 3H), 7.4 – 7.3 (m, 4H), 2.6 – 2.5 (m, 3H). **^{13}C NMR** (126 MHz, Chloroform-d) δ 159.2, 149.3, 136.3, 135.6, 131.0, 129.7, 128.6, 128.6, 120.8, 20.9.

***N*-(4-methoxyphenyl)-1-phenylmethanimine[10] (4i)**



Dark yellow-oily liquid (46 mg, 72%) **^{1}H NMR** (500 MHz, Chloroform-*d*) δ 8.5 (s, 1H), 7.9 (dd, *J* = 6.5, 3.1 Hz, 2H), 7.5 – 7.5 (m, 3H), 7.3 – 7.3 (m, 2H), 7.0 – 6.9 (m, 2H), 3.9 (s, 3H). **^{13}C NMR** (126 MHz, Chloroform-*d*) δ 158.4, 144.9, 136.5, 131.1, 128.8, 128.6, 122.3, 114.4, 55.5.

***N*,1-diphenylmethanimine[10] (4n)**

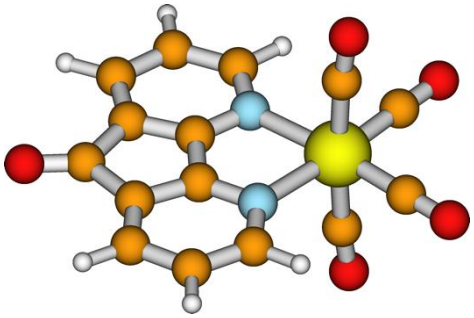
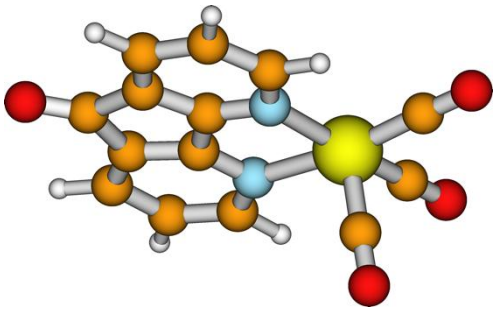


Yellow-oily liquid (41 mg, 75%) **^{1}H NMR** (500 MHz, Chloroform-*d*) δ 8.5 (s, 1H), 8.0 (dd, *J* = 6.6, 2.9 Hz, 2H), 7.5 (dd, *J* = 5.0, 2.0 Hz, 3H), 7.5 (dd, *J* = 8.9, 6.8 Hz, 2H), 7.3 – 7.3 (m, 3H). **^{13}C NMR** (126 MHz, Chloroform-*d*) δ 160.4, 152.2, 136.3, 131.5, 129.3, 128.9, 128.9, 126.0, 121.0.

15. Computational Studies

The Electronic structure calculations were performed using the hybrid functional B3LYP including dispersion corrections[16] to account for the van der Waal's interactions in the system. Double zeta basis set SDD[17] with effective core potential[18] was employed for Cr and the remaining atoms were treated with 6-31G+(d,p) basis sets. (This combination of basis set is referred as BS1). Solvent (Toluene) effects have been included in our calculations using the conductor-like polarizable continuum model (CPCM) with refractive index=1.497 and the dielectric constant=2.4)[19,20]. All stationary states were identified by harmonic vibrational frequency analysis. The Nudged elastic band (NEB) method in combination with TS finding algorithm was employed for locating the transition state. This method will also give minimum energy path (MEP) that connects forward and backward minima. All calculations were performed using ORCA version 5.0.3[21] and the computed electronic energy including the zeropoint energy corrections, Gibbs free energy (at 298.15 K and 1 atm) and frequencies along with the coordinates (in angstroms) of the identified stationary states are provided below.

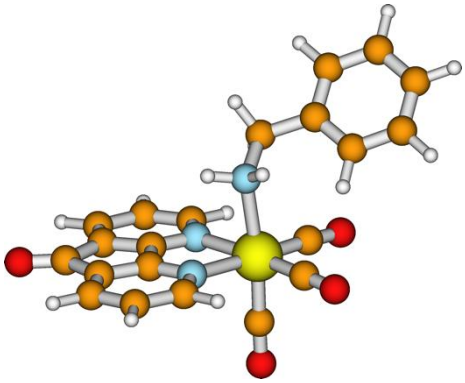
Table S3: Summary of the electronic structure calculation using B3LYP-D3/BS1 level of theory.

Cr-1a	**Cr-1b**
	
Totalthermal energy= -1146.20 Eh Final Gibbs free energy= -1146.27 Eh	Total thermal energy= -1032.88 Eh Final Gibbs free energy= -1032.95 Eh
Cr 1.423074 1.201952 0.240387 N 0.407618 3.139267 0.079178 N -0.658765 0.524365 0.130559 C -1.316028 -0.659723 0.145829 C -2.711254 -0.744182 0.062057 C -3.511733 0.411329 -0.041971 C -2.837626 1.626651 -0.059593 C -1.446992 1.589823 0.028694 C 0.764210 4.445416 0.044815 C -0.176302 5.477853 -0.059440 C -1.557646 5.207429 -0.133036 C -1.924230 3.867490 -0.098427 C -0.902189 2.925011 0.003166 C -3.233309 3.093375 -0.145372 O -4.356054 3.549949 -0.230762 C 3.121419 1.933711 0.317165	Cr 1.365717 1.064251 0.056406 N 0.399595 3.015557 0.002070 N -0.707727 0.425792 -0.085377 C -1.381746 -0.749838 -0.132755 C -2.780205 -0.809978 -0.118237 C -3.566699 0.359617 -0.077025 C -2.876539 1.566362 -0.037581 C -1.485427 1.504294 -0.044697 C 0.782702 4.315873 0.030547 C -0.141443 5.366676 0.073847 C -1.530563 5.124954 0.070889 C -1.924857 3.791956 0.032404 C -0.917930 2.830880 -0.000051 C -3.249914 3.041575 0.013712 O -4.366784 3.518397 0.035035 C 3.043443 1.750691 0.404988

C	1.617777	1.073177	-1.661691
C	2.110913	-0.512634	0.366371
O	4.200847	2.375255	0.365047
O	1.820023	0.957240	-2.796469
O	2.558026	-1.587980	0.444594
H	1.826388	4.657506	0.103221
H	0.179833	6.502128	-0.082131
H	-2.285981	6.008254	-0.212183
H	-4.593303	0.345024	-0.104121
H	-3.172675	-1.725577	0.080939
H	-0.703802	-1.551330	0.228385
C	1.361723	1.252281	2.155332
O	1.408879	1.238790	3.312826

C	1.794138	0.947047	-1.694616
C	2.009948	-0.645869	0.313849
O	4.118911	2.164987	0.615801
O	2.079538	0.867339	-2.829047
O	2.440428	-1.724514	0.468452
H	1.850947	4.503430	0.030313
H	0.232288	6.384551	0.100526
H	-2.244169	5.942363	0.099694
H	-4.650963	0.309015	-0.071220
H	-3.257522	-1.783434	-0.149288
H	-0.778637	-1.650552	-0.167588

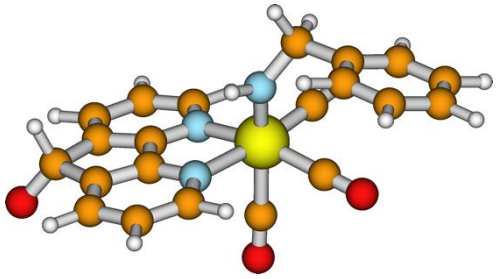
Cr-1c



Total thermal energy= -1359.53 Eh
Final Gibbs free energy= -1359.61 Eh

Cr	1.609687	1.084317	-0.299439
N	0.688704	3.012206	0.182008
N	-0.456527	0.435883	0.001737
C	-1.158718	-0.722373	-0.081321
C	-2.545240	-0.777880	0.101352
C	-3.295849	0.382102	0.385853
C	-2.578024	1.568898	0.478776
C	-1.199113	1.503873	0.283555
C	1.077602	4.309380	0.254660
C	0.180518	5.351031	0.518724
C	-1.194217	5.103700	0.713425
C	-1.596342	3.775123	0.635858
C	-0.612826	2.819930	0.382113
C	-2.919092	3.030378	0.728935
O	-4.017190	3.503115	0.949683

Cr-1d



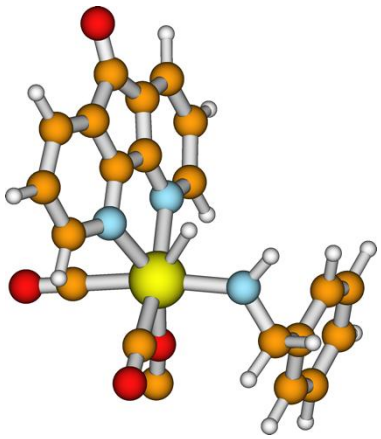
Total thermal energy= -1359.45 Eh
Final Gibbs free energy= -1359.53 Eh

Cr	0.380729	0.174300	-0.867892
N	-0.914187	1.801833	-1.283407
N	-1.458409	-0.728699	-0.137989
C	-1.863451	-1.913745	0.359049
C	-3.199744	-2.140338	0.716914
C	-4.172601	-1.131876	0.580024
C	-3.761278	0.103857	0.085441
C	-2.414032	0.203043	-0.250569
C	-0.804303	3.016749	-1.865565
C	-1.906929	3.867970	-1.983562
C	-3.177914	3.491919	-1.503153
C	-3.296922	2.252437	-0.883381
C	-2.135827	1.486274	-0.824725
C	-4.499312	1.454322	-0.247383
O	-5.606598	1.363773	-0.983685
C	1.861201	1.168124	-1.426306

C	3.287849	1.804624	-0.540981
C	1.307708	1.370456	-2.089628
C	2.213051	-0.602021	-0.712291
O	4.343148	2.269880	-0.761097
O	1.132084	1.550470	-3.236100
O	2.603431	-1.668126	-1.019703
H	2.131999	4.503803	0.089076
H	0.561570	6.365831	0.560138
H	-1.891961	5.912791	0.904334
H	-4.372172	0.340403	0.518800
H	-3.041500	-1.738629	0.015086
H	-0.585513	-1.614784	-0.309370
N	1.747686	0.849714	1.887723
H	1.913124	-0.127291	2.126571
C	2.698203	1.702296	2.645293
C	4.074288	1.090434	2.795198
C	4.913211	1.568668	3.813603
C	6.199991	1.054347	3.983097
C	6.664739	0.037616	3.140896
C	5.832547	-0.450901	2.131533
C	4.548738	0.075972	1.954425
H	0.808947	1.046724	2.230458
H	2.771920	2.659426	2.117629
H	2.304548	1.916233	3.646680
H	3.930020	-0.299609	1.148511
H	6.835236	1.440107	4.775641
H	4.554173	2.350515	4.479455
H	6.181266	-1.237503	1.468418
H	7.663549	-0.368471	3.273038

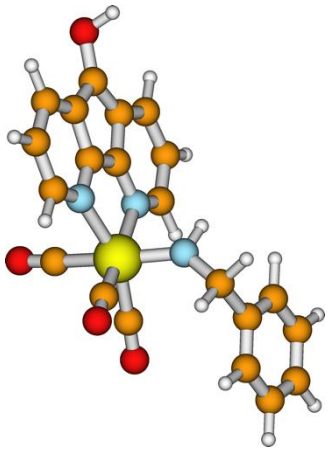
C	-0.295740	-0.432420	-2.666514
C	1.492512	-1.385871	-1.094814
O	2.794147	1.775795	-1.748049
O	-0.727595	-0.795733	-3.660918
O	2.165829	-2.303545	-1.253700
H	0.172538	3.297026	-2.243024
H	-1.767161	4.828016	-2.469857
H	-4.034064	4.149254	-1.627702
H	-5.209352	-1.321358	0.844119
H	-3.475331	-3.118321	1.098857
H	-1.109243	-2.687880	0.459452
N	0.816754	0.244895	0.915472
H	0.118346	-0.132956	1.556517
C	2.064834	0.530278	1.629659
C	3.025676	-0.641867	1.582552
C	2.722941	-1.834929	2.254303
C	3.571851	-2.938427	2.155854
C	4.738439	-2.859639	1.385281
C	5.051341	-1.671022	0.721267
C	4.195908	-0.568733	0.818247
H	-4.638469	1.942881	0.761483
H	2.540642	1.403920	1.176449
H	1.823234	0.779295	2.670262
H	4.435036	0.350665	0.290427
H	3.326224	-3.858365	2.678985
H	1.817328	-1.900148	2.852947
H	5.954680	-1.601900	0.121893
H	5.398277	-3.718854	1.306742

Cr-1d’



Total thermal energy= -1359.47 Eh
Final Gibbs free energy= -1359.55 Eh

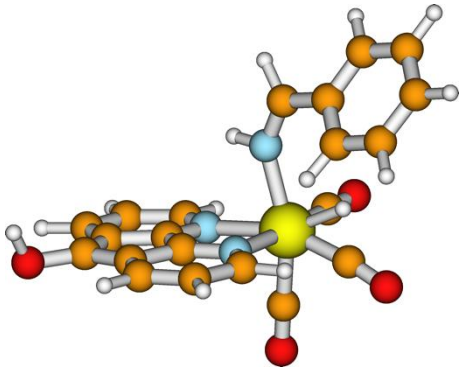
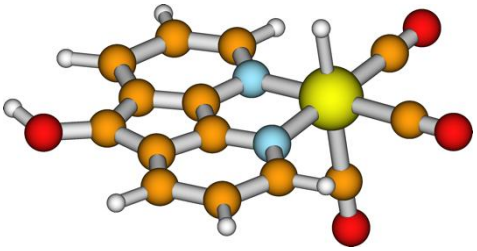
Cr-1e



Total thermal energy= -1359.48 Eh
Final Gibbs free energy= -1359.56 Eh

Cr	0.069543	-1.022135	-1.138787
N	-0.379786	1.039511	-0.608453
N	-2.120327	-1.195001	-0.763427
C	-3.048985	-2.173111	-0.750233
C	-4.379918	-1.932693	-0.385959
C	-4.808601	-0.649612	0.009347
C	-3.842926	0.351802	0.011609
C	-2.555362	-0.000572	-0.389785
C	0.324152	2.185748	-0.453202
C	-0.264956	3.370687	0.003687
C	-1.639231	3.435400	0.310063
C	-2.365189	2.262980	0.134243
C	-1.671278	1.140434	-0.315692
C	-3.803702	1.831571	0.366488
O	-4.721519	2.523361	0.760852
C	1.536315	-0.461048	-2.068420
C	-0.608032	-0.913553	-2.921732
C	0.378686	-2.847849	-1.387189
O	2.414802	-0.063802	-2.763620
O	-0.965558	-0.825895	-4.019985
O	0.586555	-3.982837	-1.517941
H	1.382831	2.140492	-0.683025
H	0.359661	4.249716	0.120523
H	-2.097479	4.351865	0.667064
H	-5.838221	-0.463247	0.297150
H	-5.080486	-2.761315	-0.399782
H	-2.714205	-3.164600	-1.037201
N	0.111336	-1.331937	0.865853
H	-0.184737	-0.475747	1.336294
C	1.306013	-1.806856	1.568746
C	2.484313	-0.859226	1.414753
C	2.444132	0.412776	2.011318
C	3.435918	1.357767	1.752077
C	4.493056	1.049135	0.884017
C	4.556468	-0.216295	0.297540
C	3.558940	-1.162286	0.566905
H	1.087558	-1.936007	2.641792
H	1.583679	-2.795499	1.182423
H	3.604313	-2.145434	0.102923
H	3.392231	2.337183	2.222655
H	1.614487	0.665167	2.668673
H	5.372451	-0.462232	-0.375106
H	5.260696	1.788309	0.672755
H	1.732369	-0.845136	-0.890210

Cr	1.425691	0.588706	0.166203
N	0.850168	2.689732	0.371152
N	-0.673185	0.266400	0.061528
C	-1.521576	-0.761657	-0.085889
C	-2.922516	-0.563521	-0.030652
C	-3.492152	0.696112	0.166623
C	-2.630103	1.804547	0.327707
C	-1.226276	1.478397	0.261749
C	1.414163	3.891488	0.519319
C	0.621199	5.054002	0.715669
C	-0.771685	5.005734	0.755874
C	-1.406833	3.747879	0.598489
C	-0.492041	2.650490	0.410749
C	-2.723408	3.207911	0.551350
O	-3.909751	3.930933	0.617844
C	3.258961	0.610425	-0.351825
C	1.143402	1.011606	-1.771281
C	1.682989	-1.267085	0.155752
O	4.369957	0.539426	-0.651491
O	0.941900	1.331978	-2.851269
O	1.873000	-2.409131	0.188639
H	2.497882	3.942352	0.487245
H	1.130942	6.005904	0.828563
H	-1.343895	5.918431	0.898467
H	-4.572698	0.807883	0.190107
H	-3.562286	-1.431658	-0.153960
H	-1.095553	-1.745109	-0.248543
N	1.910238	0.807359	1.926498
H	1.655045	1.712740	2.321848
C	2.798402	0.095310	2.838280
C	4.194886	0.693269	2.865573
C	4.391249	2.043303	3.192080
C	5.673001	2.597055	3.183792
C	6.778320	1.804032	2.851887
C	6.591554	0.456551	2.533095
C	5.304901	-0.092313	2.536635
H	2.357716	0.129887	3.845369
H	2.858703	-0.954765	2.543019
H	5.160510	-1.136489	2.271038
H	5.810759	3.644804	3.436302
H	3.539332	2.667512	3.451661
H	7.443176	-0.165286	2.271201
H	7.775807	2.234109	2.843519
H	-4.132106	4.109695	1.542732

Cr-1f	Cr-1g
	
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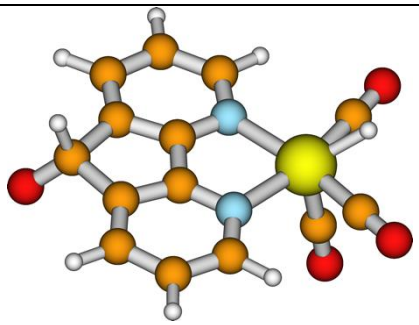
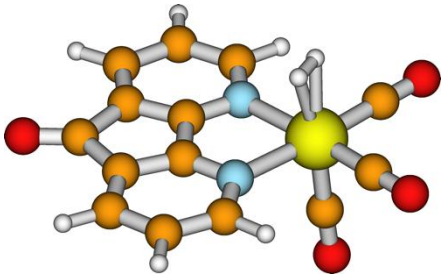
Cr	2.094774	1.711514	-0.268792
N	0.630972	3.311535	-0.360875
N	0.431616	0.626600	0.649827
C	0.146442	-0.602167	1.096736
C	-1.127080	-0.917860	1.638817
C	-2.153266	0.021842	1.721126
C	-1.901984	1.327694	1.233534
C	-0.567308	1.522946	0.723315
C	0.569715	4.579674	-0.789394
C	-0.608827	5.351152	-0.617406
C	-1.752947	4.837002	-0.005877
C	-1.724034	3.499401	0.459044
C	-0.466832	2.825055	0.240688
C	-2.595706	2.562795	1.079405
C	3.468786	2.744644	-1.004924
C	1.405345	1.441749	-2.023482
C	2.889639	0.120172	-0.689174
O	4.347561	3.347093	-1.463951
O	1.000168	1.294548	-3.090791
O	3.311909	-0.920274	-1.057771
H	1.447453	4.984962	-1.281379
H	-0.606116	6.373041	-0.983694
H	-2.640699	5.455008	0.096459
H	-3.118613	-0.258969	2.133693
H	-1.293407	-1.932031	1.988794
H	0.923169	-1.356825	1.023808
N	2.430469	2.631294	1.585643
H	1.997191	3.553483	1.540692
C	3.118956	2.490393	2.664811
C	3.850799	1.282067	3.050032
C	5.045225	1.426213	3.777291

Cr	1.655016	1.212928	-0.293575
N	0.692374	3.134882	-0.237672
N	-0.231363	0.535797	0.487086
C	-0.808592	-0.615098	0.867348
C	-2.132356	-0.637373	1.371775
C	-2.911005	0.515182	1.485515
C	-2.343381	1.749249	1.086492
C	-0.990992	1.640813	0.601975
C	0.977469	4.412765	-0.535113
C	0.026467	5.442346	-0.325738
C	-1.249285	5.192185	0.181845
C	-1.592883	3.856362	0.500673
C	-0.542257	2.905086	0.246469
C	-2.696471	3.127933	1.028156
C	3.167785	2.183944	-0.836681
C	1.443423	0.858333	-2.086574
C	2.123282	-0.586817	-0.184102
O	4.102398	2.785436	-1.151606
O	1.278052	0.642485	-3.208538
O	2.414348	-1.704201	-0.099569
H	1.961248	4.632862	-0.933198
H	0.315453	6.457127	-0.580148
H	-1.949071	6.010958	0.324224
H	-3.924014	0.451764	1.873059
H	-2.543775	-1.596464	1.670012
H	-0.226580	-1.525554	0.784637
O	-3.941453	3.659435	1.344761
H	-3.959173	3.920567	2.276842
H	3.071766	0.745178	0.275606

C	5.797782	0.302966	4.121715
C	5.346477	-0.974524	3.771725
C	4.135578	-1.127140	3.086381
C	3.385975	-0.006508	2.733198
H	3.197982	3.336899	3.351786
H	2.423638	-0.120620	2.251702
H	6.729312	0.422080	4.666736
H	5.391532	2.419602	4.050359
H	3.768943	-2.119124	2.840409
H	5.929817	-1.848999	4.044556
O	-3.931537	2.802336	1.385370
H	-4.045612	2.832145	2.345947
H	3.283959	0.697802	0.359813

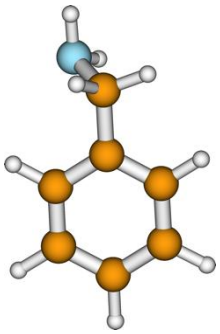
Cr-1h	**Cr-1i**
	
Total thermal energy= -1033.99 Eh Final Gibbs free energy= -1034.06 Eh	Total thermal energy= -1034.06 Eh Final Gibbs free energy= -1034.13 Eh

Cr	1.902717	-0.808182	-0.511859	Cr	1.833359	-0.762298	-0.389946
N	0.934237	1.102100	-0.378616	N	0.784733	1.157008	-0.406053
N	0.023368	-1.465912	0.288006	N	-0.137977	-1.416282	0.294323
C	-0.547089	-2.649211	0.615246	C	-0.728526	-2.585439	0.640594
C	-1.845490	-2.715832	1.129728	C	-2.060165	-2.654716	1.067456
C	-2.615913	-1.553318	1.332233	C	-2.868849	-1.502287	1.142323
C	-2.039834	-0.329249	1.002352	C	-2.264920	-0.302599	0.781319
C	-0.749168	-0.388366	0.488811	C	-0.932236	-0.352781	0.379008
C	1.235865	2.383379	-0.693102	C	1.074782	2.444049	-0.714624
C	0.336142	3.426759	-0.450029	C	0.144259	3.479762	-0.564826
C	-0.931347	3.186607	0.116030	C	-1.168069	3.229372	-0.114444
C	-1.257119	1.871564	0.437728	C	-1.471459	1.906512	0.188533
C	-0.283573	0.921096	0.153907	C	-0.459572	0.963279	0.022696
C	-2.530485	1.169143	1.048763	C	-2.695748	1.154080	0.690170
C	3.341397	0.138865	-1.200276	C	3.441631	-0.055877	-0.964709
C	1.579629	-1.232483	-2.277272	C	1.404566	-1.126575	-2.146526
C	2.444336	-2.607699	-0.354216	C	2.579313	-2.444828	-0.241099
O	4.239603	0.745467	-1.612251	O	4.462705	0.369644	-1.348351
O	1.356710	-1.485919	-3.379612	O	1.162202	-1.378042	-3.259983

O	2.774892	-3.707518	-0.247986
H	2.207555	2.572899	-1.133952
H	0.632586	4.434875	-0.721119
H	-1.627320	4.003564	0.285551
H	-3.626581	-1.619822	1.725376
H	-2.253253	-3.692278	1.370327
H	0.041998	-3.545993	0.462137
O	-3.691459	1.429016	0.450605
H	-2.487304	1.434692	2.145067
H	3.434899	-1.018241	-0.091577

O	3.058108	-3.510496	-0.163917
H	2.080392	2.639067	-1.071524
H	0.447892	4.489668	-0.818907
H	-1.891333	4.031679	-0.008808
H	-3.903145	-1.558830	1.466311
H	-2.469051	-3.623722	1.332802
H	-0.110002	-3.474347	0.579496
O	-3.786209	1.617428	0.959845
H	1.976989	-0.628973	1.463065
H	2.496333	-0.103456	1.205777

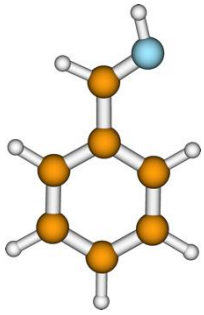
Benzylamine



Total thermal energy= -326.60 Eh
Final Gibbs free energy= -326.64 Eh

C	-2.108893	0.895026	-0.200055
C	-3.439530	0.784391	0.222656
C	-1.387197	-0.278709	-0.469645
C	-4.044650	-0.469963	0.367810
C	-3.318669	-1.631567	0.093731
C	-1.985834	-1.531614	-0.325503
C	-1.457556	2.252000	-0.364965
N	-0.240860	2.361384	0.459491
H	0.202177	3.265492	0.312378
H	-0.483056	2.305991	1.446715
H	-1.152462	2.385807	-1.410547
H	-2.204933	3.030951	-0.147477
H	-4.007567	1.686166	0.439653
H	-0.351070	-0.202142	-0.786907
H	-1.415159	-2.431036	-0.540719
H	-3.784013	-2.606846	0.206325
H	-5.078118	-0.536709	0.696761

Benzenemethanimine

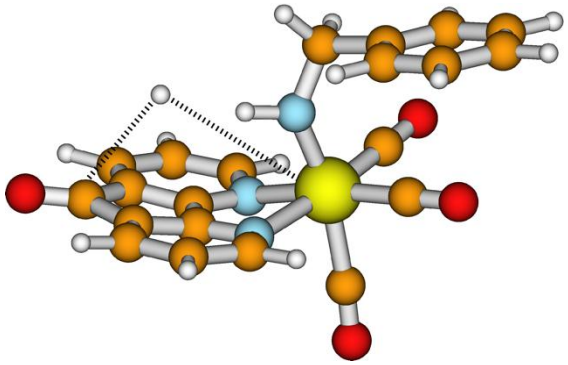


Total thermal energy= -325.41 Eh
Final Gibbs free energy= -325.45 Eh

C	-2.078380	0.863258	-0.147614
C	-3.478628	0.776161	-0.094200
C	-1.313445	-0.316047	-0.103752
C	-4.109376	-0.466888	0.001992
C	-3.341932	-1.634369	0.045496
C	-1.942932	-1.555297	-0.007576
C	-1.447664	2.191993	-0.248846
N	-0.178041	2.360075	-0.298755
H	0.048922	3.353886	-0.367185
H	-2.153237	3.033728	-0.278484
H	-4.072454	1.686518	-0.128434
H	-0.231646	-0.243470	-0.145958
H	-1.346951	-2.462838	0.026390
H	-3.828855	-2.602515	0.120680
H	-5.193211	-0.523935	0.042737

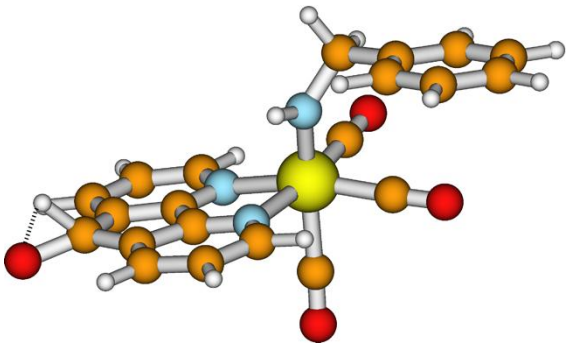
TS1

TS2



Total thermal energy= -1359.40 Eh
Final Gibbs free energy= -1359.48 Eh
Imaginary frequency= -413.75 cm^{-1}

Cr	0.374737	-0.112685	-1.293633
N	-0.905655	1.559189	-1.749045
N	-1.525213	-1.029762	-0.697311
C	-1.918039	-2.172453	-0.090285
C	-3.125464	-2.258981	0.611720
C	-3.950376	-1.129985	0.780904
C	-3.519905	0.049812	0.188073
C	-2.362676	-0.006371	-0.591400
C	-0.714157	2.849529	-2.110686
C	-1.651796	3.844726	-1.817310
C	-2.806814	3.557470	-1.066097
C	-2.974894	2.239275	-0.660191
C	-2.040165	1.302592	-1.103381
C	-3.979455	1.496385	0.202166
O	-4.989795	1.947788	0.712186
C	1.915897	0.848383	-1.751956
C	-0.155411	-0.768628	-3.122040
C	1.572932	-1.603280	-1.244868
O	2.875987	1.444216	-2.008716
O	-0.535690	-1.134371	-4.138223
O	2.332699	-2.468669	-1.300659
H	0.210480	3.078750	-2.628277
H	-1.453446	4.858338	-2.148636
H	-3.502910	4.340216	-0.782421
H	-4.848227	-1.175227	1.389041
H	-3.396873	-3.205733	1.066540
H	-1.243086	-3.018309	-0.164460
N	0.449292	0.330277	0.485964
H	-0.461290	0.507769	0.978234
C	1.533607	0.672329	1.407826
C	2.537345	-0.454827	1.515182
C	2.153857	-1.667336	2.108339
C	3.045979	-2.737562	2.174165



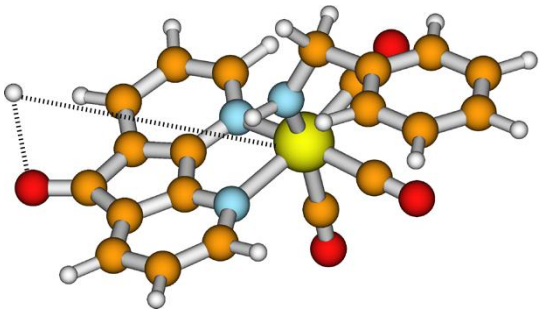
Total thermal energy= -1359.40 Eh
Final Gibbs free energy= -1359.48 Eh
Imaginary Frequency= -1647.15 cm^{-1}

Cr	0.453672	0.325361	-1.131274
N	-0.961012	1.884077	-1.464238
N	-1.278966	-0.741823	-0.344149
C	-1.582093	-1.930243	0.197189
C	-2.881935	-2.207584	0.677306
C	-3.900866	-1.249625	0.641012
C	-3.597766	0.012422	0.098553
C	-2.277816	0.150397	-0.404934
C	-0.975520	3.136392	-1.954311
C	-2.144893	3.922798	-1.910308
C	-3.335264	3.453523	-1.338878
C	-3.338482	2.155868	-0.802011
C	-2.117468	1.442691	-0.941826
C	-4.278320	1.300803	-0.067165
O	-5.697743	1.509177	0.011539
C	1.808941	1.476977	-1.721767
C	-0.287950	-0.362645	-2.862383
C	1.739543	-1.053888	-1.458988
O	2.660723	2.183717	-2.061107
O	-0.768490	-0.795770	-3.805877
O	2.543547	-1.848293	-1.679272
H	-0.056218	3.513789	-2.387479
H	-2.104200	4.920382	-2.335440
H	-4.221227	4.081040	-1.314408
H	-4.889790	-1.478678	1.027154
H	-3.078578	-3.192933	1.087665
H	-0.788489	-2.668900	0.246232
N	0.947217	0.370625	0.637027
H	0.258076	-0.015593	1.283373
C	2.212052	0.598682	1.330648
C	2.990274	-0.689181	1.535726
C	2.418654	-1.766926	2.228308
C	3.115797	-2.967472	2.373167

C	4.337675	-2.607249	1.648359
C	4.729189	-1.399924	1.064569
C	3.831162	-0.329088	0.998467
H	-1.758617	1.449833	1.664073
H	2.042058	1.580912	1.060581
H	1.097148	0.892624	2.389050
H	4.133829	0.605115	0.533109
H	2.736528	-3.673020	2.632294
H	1.148962	-1.768299	2.510571
H	5.729183	-1.291892	0.653802
H	5.031409	-3.441875	1.694380

C	4.398122	-3.104335	1.827498
C	4.978586	-2.031599	1.146104
C	4.274303	-0.831862	0.998651
H	-4.762096	1.774496	0.916846
H	2.819507	1.302188	0.756541
H	1.993143	1.064514	2.301863
H	4.719809	-0.005509	0.450410
H	2.660087	-3.796077	2.908079
H	1.421866	-1.670394	2.652042
H	5.972288	-2.130406	0.718295
H	4.938975	-4.040184	1.934587

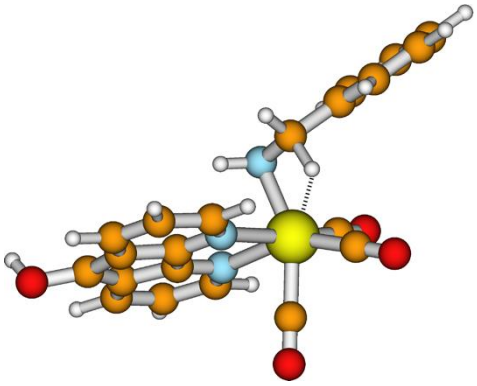
TS3



Total thermal energy= -1359.37 Eh
Final Gibbs free energy= -1359.45 Eh
Imaginary Frequency= -597.81 cm^{-1}

Cr	0.410460	0.064923	-0.943703
N	-0.846259	1.715369	-1.392994
N	-1.495723	-0.861962	-0.348500
C	-1.935022	-1.991021	0.255704
C	-3.272545	-2.139584	0.648167
C	-4.217877	-1.115139	0.447661
C	-3.772145	0.050398	-0.178721
C	-2.420981	0.067641	-0.559565
C	-0.688044	3.024853	-1.739928
C	-1.766329	3.912274	-1.771701
C	-3.087761	3.497012	-1.489683
C	-3.251194	2.134026	-1.198526
C	-2.097567	1.350988	-1.127212
C	-4.353846	1.378194	-0.585550
O	-5.457337	1.869127	-0.304279
C	1.917562	1.054011	-1.423567
C	-0.154153	-0.533221	-2.781343
C	1.536956	-1.496710	-1.105170

TS4

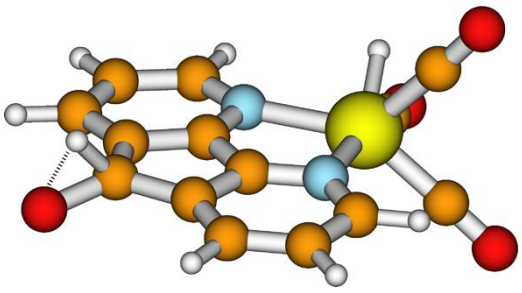


Total thermal energy= -1359.44 Eh
Final Gibbs free energy= -1359.52 Eh
Imaginary Frequency= -4862.53 cm^{-1}

Cr	0.576388	-0.142279	-1.180836
N	-0.698162	1.752338	-1.117160
N	-1.479096	-1.061174	-0.656146
C	-2.010725	-2.258697	-0.396864
C	-3.376594	-2.403109	-0.032249
C	-4.229532	-1.308277	0.073880
C	-3.705171	-0.020411	-0.196123
C	-2.307123	0.000146	-0.565222
C	-0.511318	3.064747	-1.280724
C	-1.584902	3.977322	-1.116835
C	-2.866062	3.554904	-0.767614
C	-3.092177	2.171719	-0.572268
C	-1.934547	1.330686	-0.789100
C	-4.168797	1.320303	-0.204600
C	2.119656	0.904298	-1.337981
C	-0.101591	0.167456	-2.999186
C	1.488336	-1.587012	-2.072748
O	3.048765	1.586603	-1.399810

O	2.866521	1.657264	-1.703980
O	-0.517814	-0.890037	-3.805766
O	2.221248	-2.412278	-1.223346
H	0.319504	3.349389	-1.971785
H	-1.565279	4.948692	-2.022480
H	-3.929487	4.175421	-1.544115
H	-5.243424	-1.229162	0.784807
H	-3.570212	-3.063726	1.132742
H	-1.199881	-2.769242	0.431637
N	0.740438	0.124162	0.863671
H	0.010389	-0.260861	1.464351
C	1.941286	0.426007	1.647860
C	2.936109	-0.718338	1.629960
C	2.625112	-1.937615	2.249017
C	3.510907	-3.013809	2.179230
C	4.722249	-2.881795	1.489287
C	5.042158	-1.667562	0.877122
C	4.150021	-0.592412	0.945010
H	2.415167	1.321110	1.236028
H	1.640616	0.648233	2.678995
H	4.396441	0.347430	0.458301
H	3.259243	-3.954200	2.661532
H	1.684405	-2.044093	2.784207
H	5.980539	-1.557043	0.341201
H	5.411215	-3.719629	1.433440
H	-4.895664	3.732914	0.581983
O	-0.511323	0.323512	-4.057796
O	2.050574	-2.415604	-2.641679
H	0.484652	3.402233	-1.544673
H	-1.383273	5.033307	-1.266348
H	-3.665502	4.282352	-0.653873
H	-5.268927	-1.447606	0.357388
H	-3.749587	-3.402595	0.169107
H	-1.355175	-3.120823	-0.469423
N	0.692785	0.340783	0.864683
H	-0.290842	0.369498	1.139560
C	1.173488	-0.969778	1.087307
C	2.627284	-1.109097	1.479855
C	3.413893	0.011983	1.761077
C	4.752828	-0.147497	2.130574
C	5.310660	-1.426246	2.227369
C	4.522591	-2.550873	1.954546
C	3.187438	-2.390924	1.581312
H	0.508599	-1.611585	1.681463
H	2.576489	-3.264667	1.363403
H	5.359022	0.727898	2.346074
H	2.967016	0.997133	1.685103
H	4.948175	-3.547557	2.030345
H	6.350896	-1.548294	2.515343
O	-5.485891	1.695818	0.031874
H	-5.516684	2.325613	0.766200
H	1.133470	-1.606547	0.072797

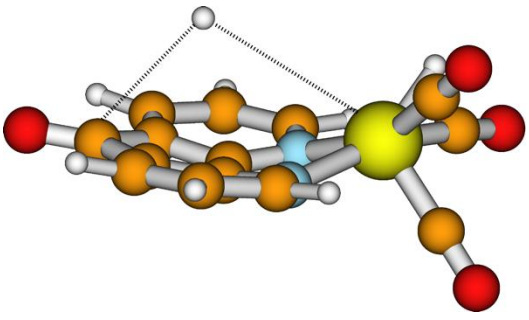
TS5



Total thermal energy= -1033.94 Eh
Final Gibbs free energy= -1034.00 Eh
Imaginary Frequency= -1641.43 cm^{-1}

Cr	1.747053	-0.778837	-0.855944
N	0.981761	1.138606	-0.332905
N	-0.063984	-1.477792	0.001567
C	-0.701699	-2.650412	0.179544
C	-2.008780	-2.696215	0.707335

TS6



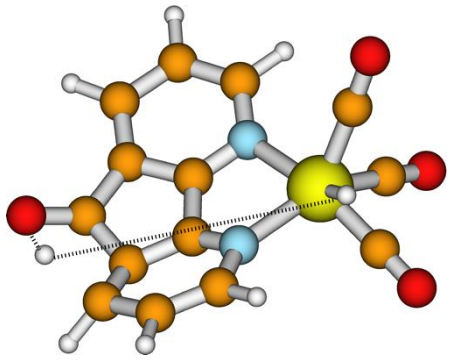
Total thermal energy= -1033.93 Eh
Final Gibbs free energy= -1033.99 Eh
Imaginary Frequency= -544.66 cm^{-1}

Cr	1.697159	-0.732156	-0.545981
N	0.672586	1.116514	-0.781993
N	-0.292752	-1.452511	-0.270249
C	-0.787344	-2.625844	0.193746

C	-2.705105	-1.535032	1.072267
C	-2.057600	-0.298899	0.904130
C	-0.750864	-0.380725	0.359179
C	1.318383	2.434851	-0.483357
C	0.429373	3.466447	-0.119012
C	-0.835141	3.202453	0.426260
C	-1.205692	1.858853	0.608812
C	-0.234484	0.914506	0.190761
C	-2.349770	1.118314	1.154414
C	3.000610	-0.073706	-2.006923
C	1.740057	-2.215535	-2.069218
C	2.766038	-1.939071	0.167806
O	3.798967	0.367603	-2.730422
O	1.728107	-3.069056	-2.844483
O	3.386848	-2.635804	0.847548
H	2.294462	2.650181	-0.903975
H	0.746748	4.492190	-0.275171
H	-1.501853	4.017784	0.691017
H	-3.715998	-1.598973	1.464021
H	-2.480486	-3.666878	0.819445
H	-0.173003	-3.552671	-0.107672
O	-3.655081	1.665566	1.389597
H	-2.683766	1.402366	2.263986
H	3.184899	-0.160113	-0.518606

C	-2.019464	-2.697383	0.850692
C	-2.744373	-1.530480	1.155037
C	-2.214958	-0.326654	0.704920
C	-1.069340	-0.385609	-0.090190
C	1.086842	2.407388	-0.821729
C	0.279336	3.458708	-0.379658
C	-0.975005	3.209626	0.208272
C	-1.395055	1.886049	0.247712
C	-0.576784	0.929891	-0.355219
C	-2.521636	1.140558	0.939118
C	3.151202	0.103231	-1.252986
C	1.849889	-1.717449	-2.106441
C	2.476419	-2.234967	0.311658
O	4.034980	0.666449	-1.776924
O	1.930564	-2.319989	-3.087371
O	2.957590	-3.129189	0.855668
H	2.090986	2.589455	-1.187363
H	0.666495	4.470066	-0.437130
H	-1.554319	4.010773	0.656440
H	-3.641984	-1.571533	1.764141
H	-2.373180	-3.665365	1.187930
H	-0.174182	-3.507702	0.045027
O	-3.487210	1.617321	1.507398
H	-0.194982	0.483936	2.393841
H	3.128519	-0.193134	0.071633

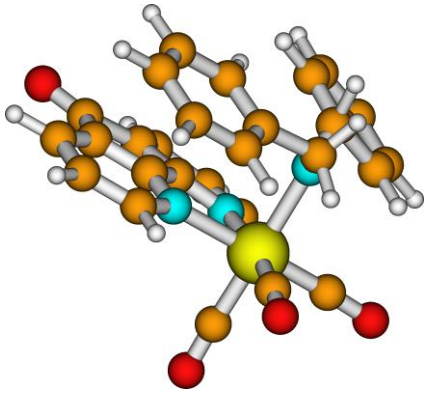
TS7



Total thermal energy= -1033.94 Eh
Final Gibbs free energy= -1034.00 Eh
Imaginary frequency= 1930.76 cm^{-1}

Cr	1.653117	-0.914328	-0.887968

Cr-1c'



Total thermal energy= -1628.46 Eh
Final Gibbs free energy= -1628.55 Eh

Cr	2.560913	3.318658	-0.881213

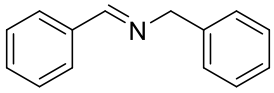
N	0.774215	1.054261	-0.890506
N	-0.017421	-1.399623	0.244022
C	-0.479212	-2.394584	1.120898
C	-1.686057	-2.298750	1.779843
C	-2.635543	-1.203483	1.614086
C	-2.168870	-0.290570	0.578852
C	-0.891084	-0.422490	0.049544
C	1.143328	2.347052	-1.115226
C	0.308752	3.405084	-0.752035
C	-0.937531	3.195560	-0.119496
C	-1.337254	1.872405	0.069542
C	-0.436782	0.886590	-0.383964
C	-2.400065	1.098661	0.767679
C	3.304671	-0.237298	-0.374767
C	2.332207	-0.622726	-2.624136
C	2.016420	-2.676638	-1.244690
O	4.313678	0.190317	-0.006126
O	2.720671	-0.466264	-3.699847
O	2.228894	-3.802046	-1.457671
H	2.120320	2.507445	-1.555882
H	0.656116	4.417577	-0.929732
H	-1.529013	4.035410	0.229663
H	-3.689237	-1.482392	1.674672
H	-1.943558	-3.120642	2.443427
H	0.194636	-3.228110	1.277336
O	-3.105217	1.350584	1.831764
H	-2.951285	0.169172	2.340760
H	2.441106	-1.970173	0.019958

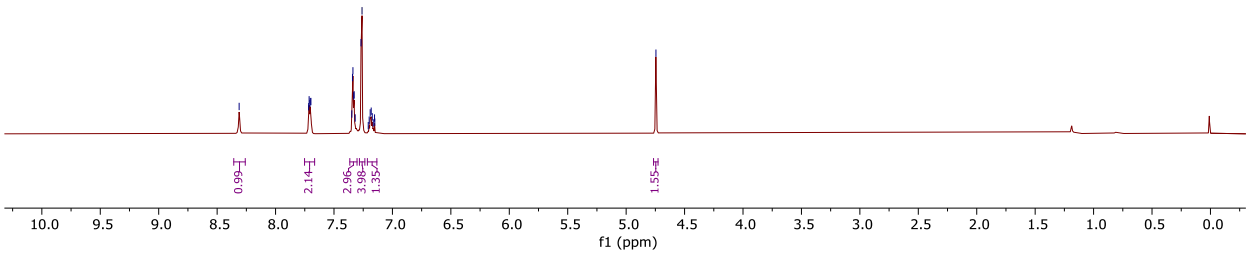
N	0.552230	4.219343	-0.898557
N	1.445678	1.801701	0.217680
C	1.678294	0.538476	0.650046
C	0.693799	-0.239765	1.265626
C	-0.613428	0.250847	1.462288
C	-0.859596	1.539705	1.006177
C	0.202728	2.227372	0.418033
C	-0.069161	5.239741	-1.537393
C	-1.436000	5.498350	-1.397016
C	-2.256032	4.686500	-0.587672
C	-1.629619	3.619323	0.044258
C	-0.256993	3.467843	-0.157476
C	-2.091487	2.415869	0.849253
C	3.397522	4.637817	-1.855711
C	2.173166	2.480730	-2.474572
C	4.112604	2.330897	-0.890473
O	3.959036	5.429094	-2.518406
O	1.971555	1.956722	-3.503889
O	5.082416	1.671662	-0.980900
H	0.553940	5.858813	-2.170095
H	-1.861289	6.339607	-1.932869
H	-3.320595	4.875854	-0.492499
H	-1.382781	-0.360603	1.923049
H	0.953528	-1.241359	1.589099
H	2.678366	0.154266	0.492152
N	3.007822	4.283681	1.043890
C	3.983568	3.569921	1.898302
C	3.396190	2.394030	2.649980
C	4.132294	1.208442	2.761076
C	3.657996	0.144686	3.535415
C	2.433692	0.253805	4.199253
C	1.685632	1.430648	4.080551
C	2.166250	2.493327	3.314267
H	4.407651	4.272705	2.629123
H	1.573028	3.397899	3.221690
H	4.241139	-0.768878	3.610867
H	5.078008	1.117401	2.233265
H	0.725341	1.518099	4.580745
H	2.059088	-0.573018	4.795821
O	-3.216706	2.186471	1.252805
C	2.555115	5.359782	1.581812
C	1.656292	6.360871	0.969478
C	2.083424	7.131283	-0.121373
C	0.428698	6.650967	1.585016
C	1.280034	8.168883	-0.600723
C	0.044253	8.435808	-0.004485

C	-0.382387	7.671232	1.087152
H	4.800928	3.232376	1.262371
H	2.877097	5.612255	2.599403
H	3.040731	6.924960	-0.584446
H	0.106044	6.068397	2.443785
H	-1.341830	7.874269	1.553830
H	-0.581637	9.238355	-0.383866
H	1.620352	8.763879	-1.443214

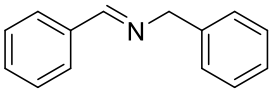
16. Spectra of the isolated compounds

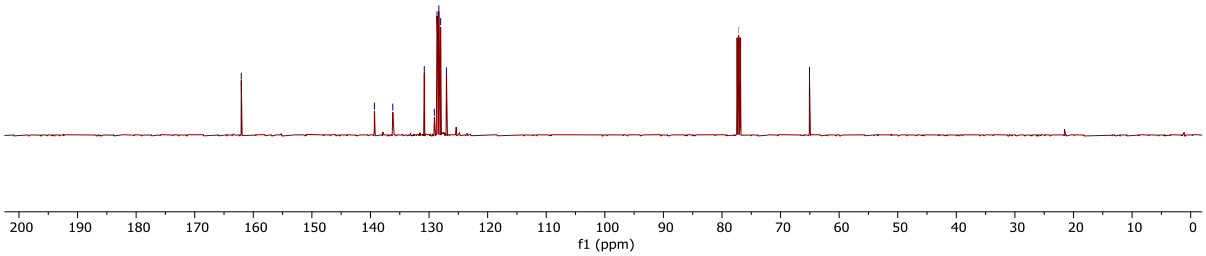
^{1}H NMR of 2a (500 MHz, $CDCl_3$):



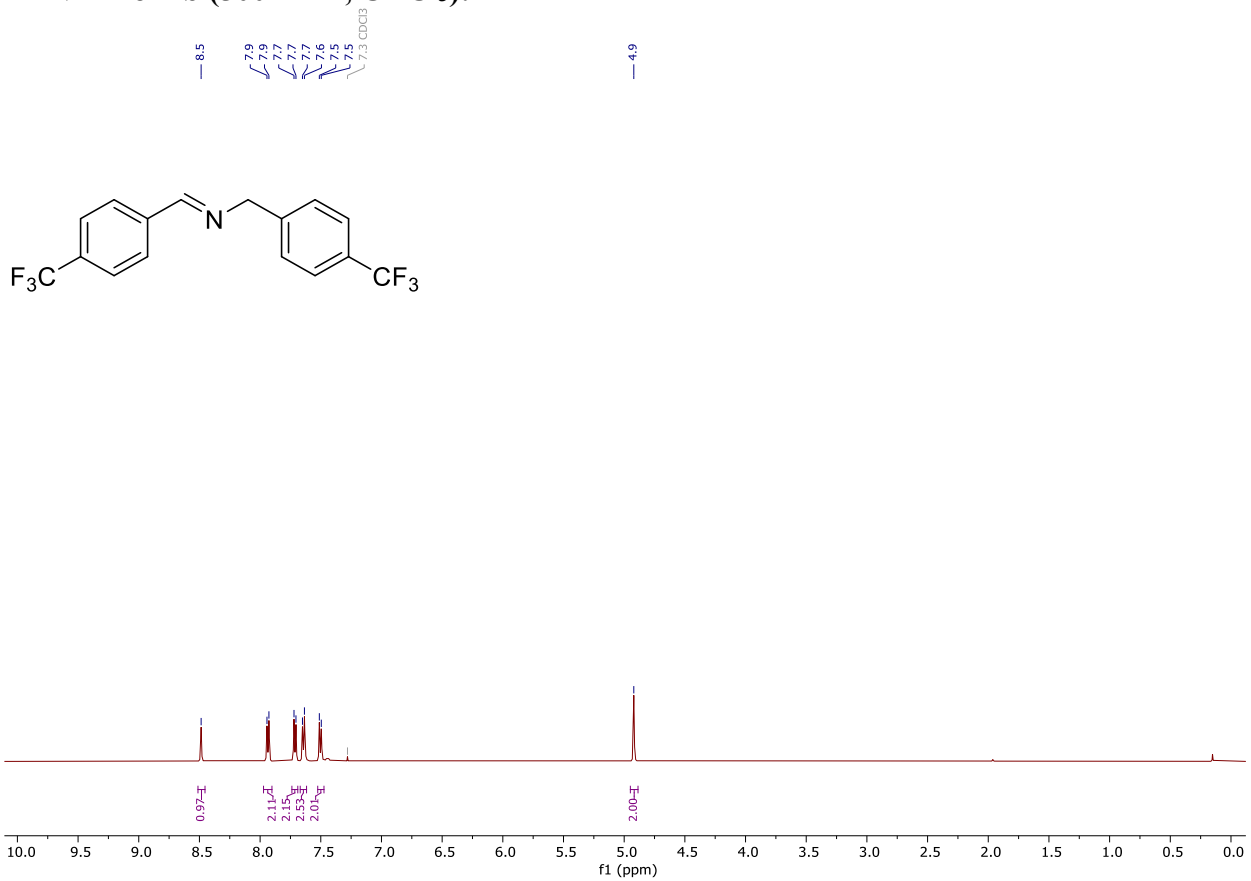


^{13}C{^{1}H} NMR of 2a (126 MHz, $CDCl_3$):

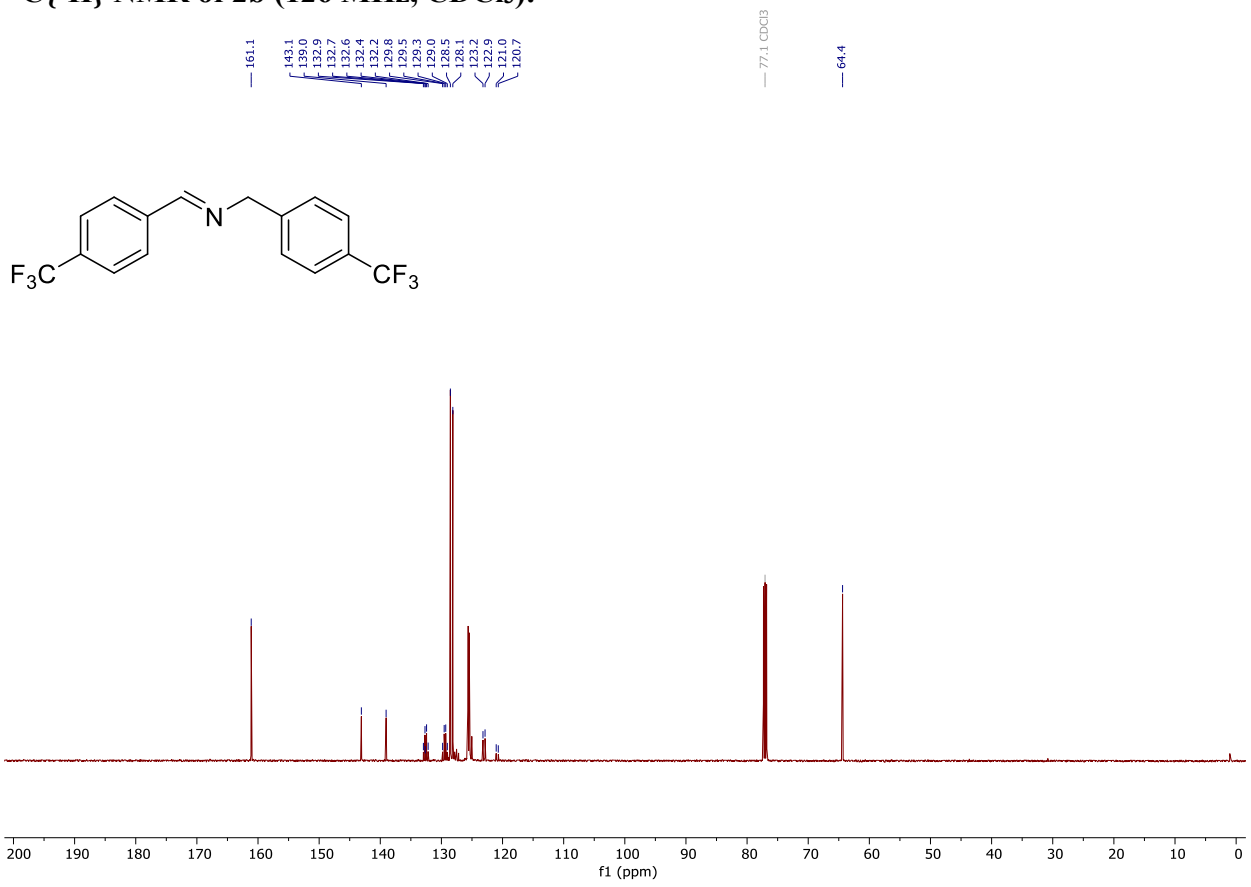




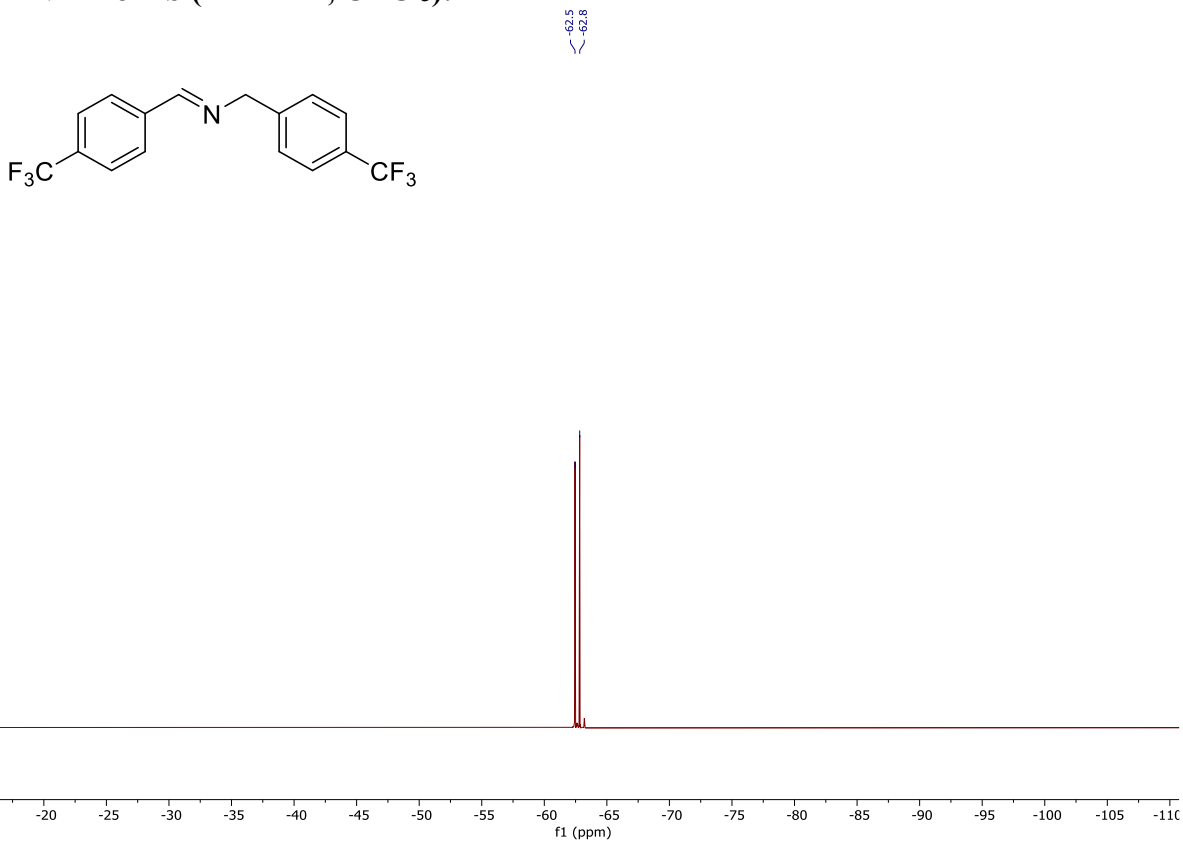
^{1}H NMR of 2b (500 MHz, $CDCl_3$):



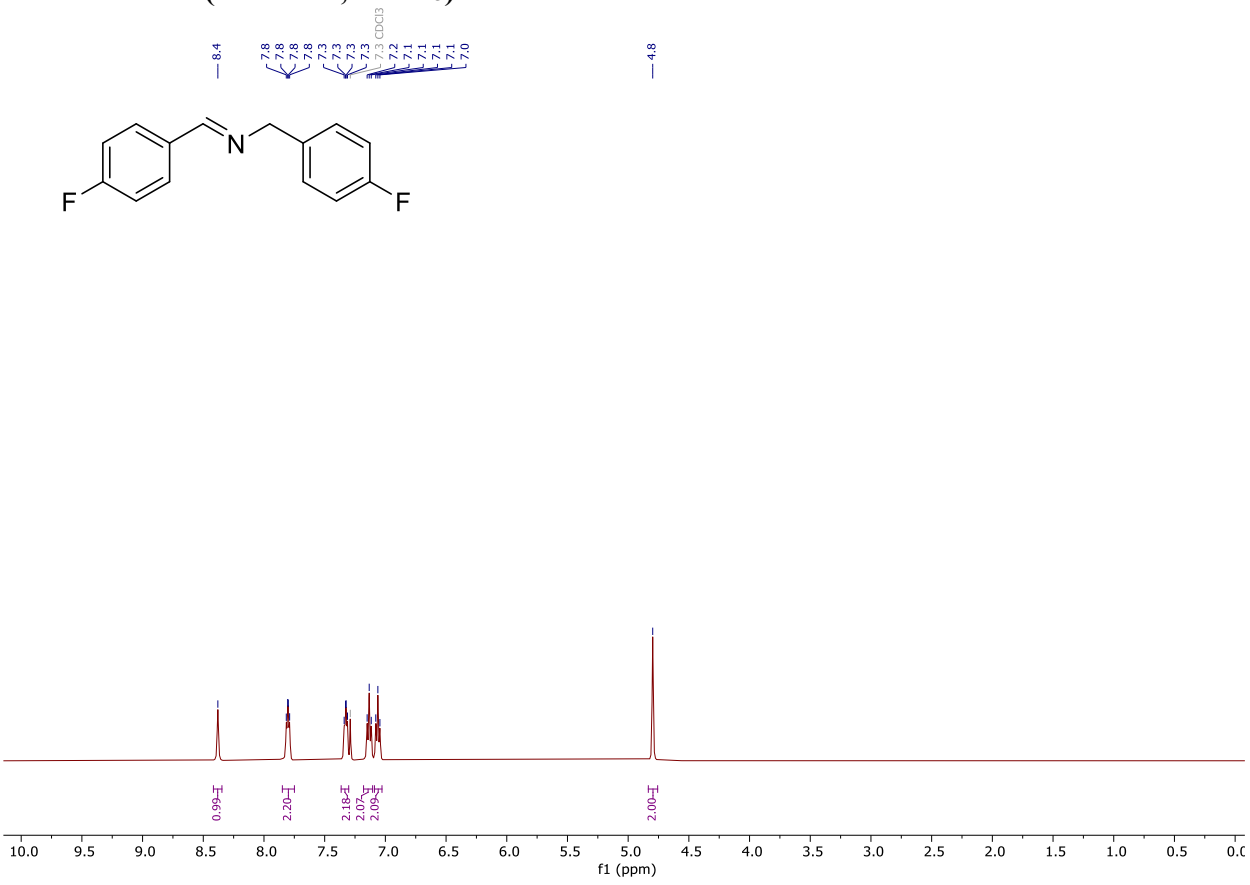
^{13}C{^{1}H} NMR of 2b (126 MHz, $CDCl_3$):



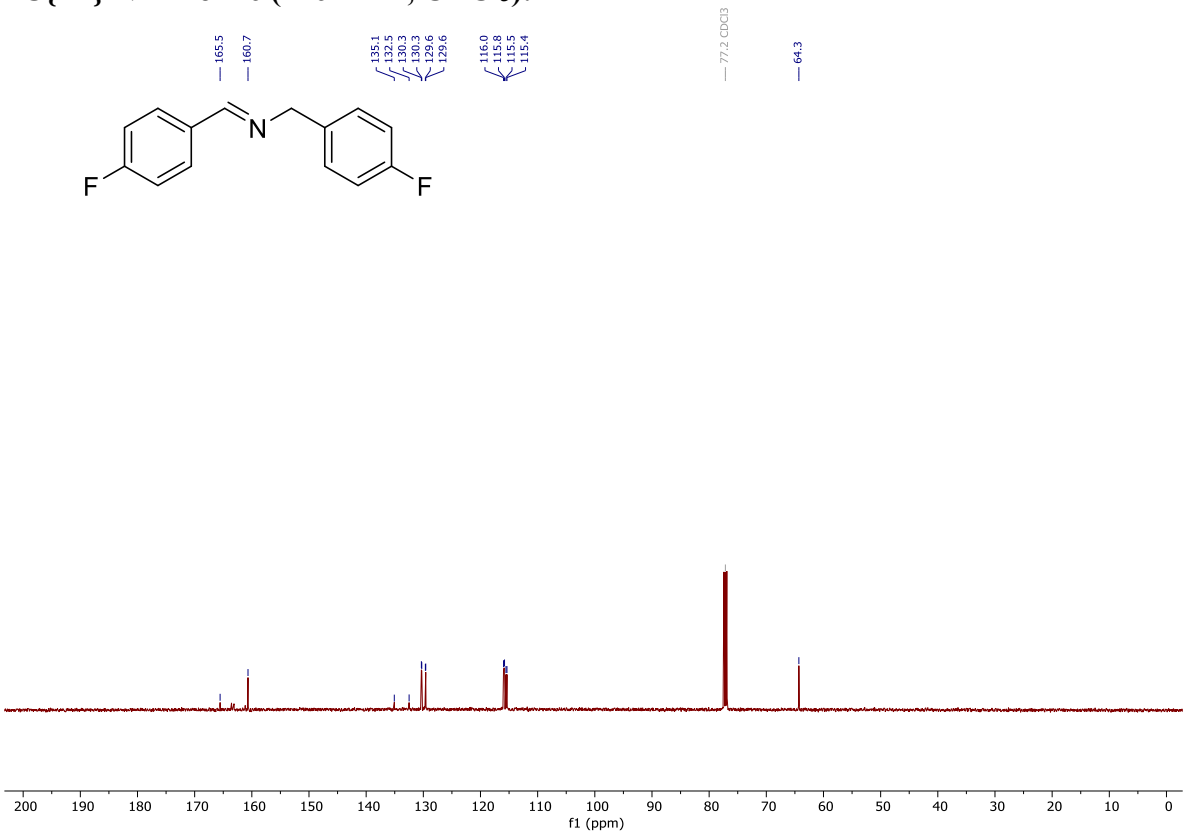
^{19}F NMR of 2b (471 MHz, $CDCl_3$):



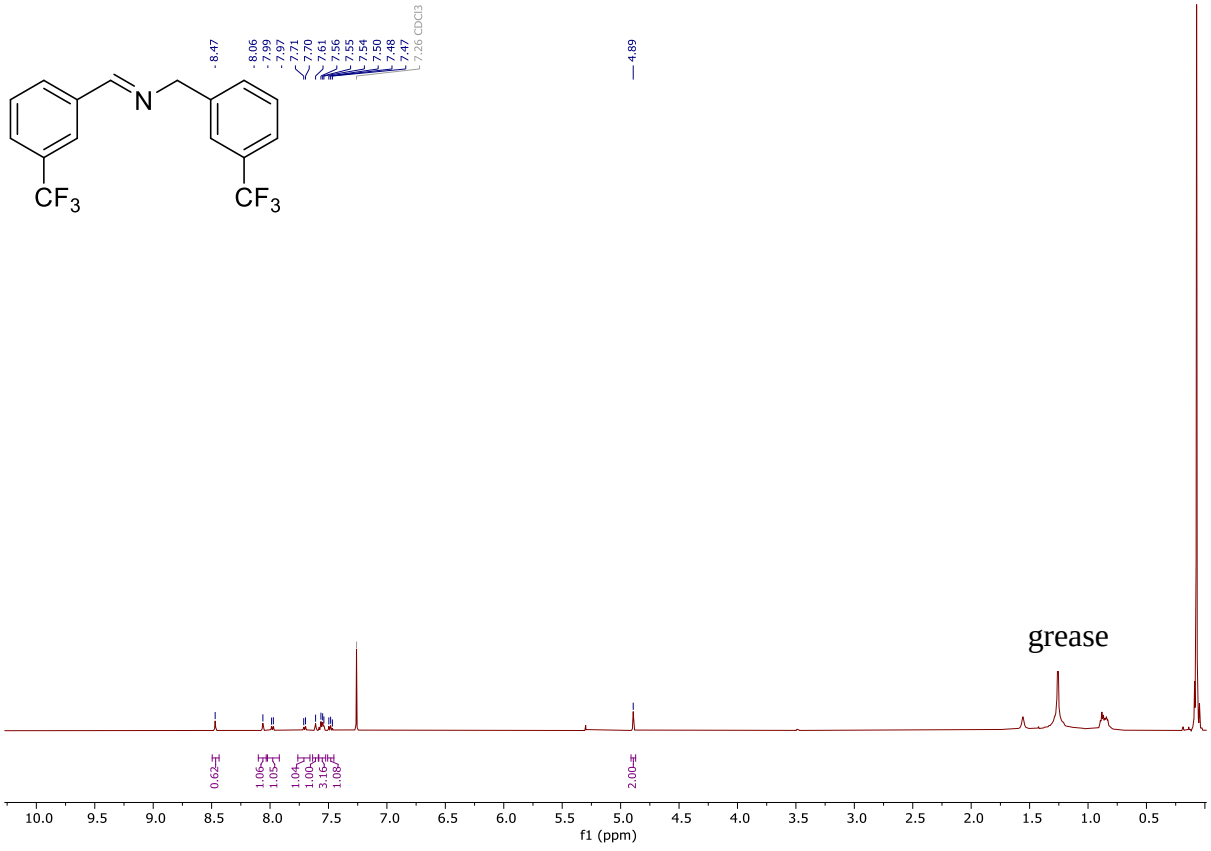
^{1}H NMR of 2c (500 MHz, $CDCl_3$):



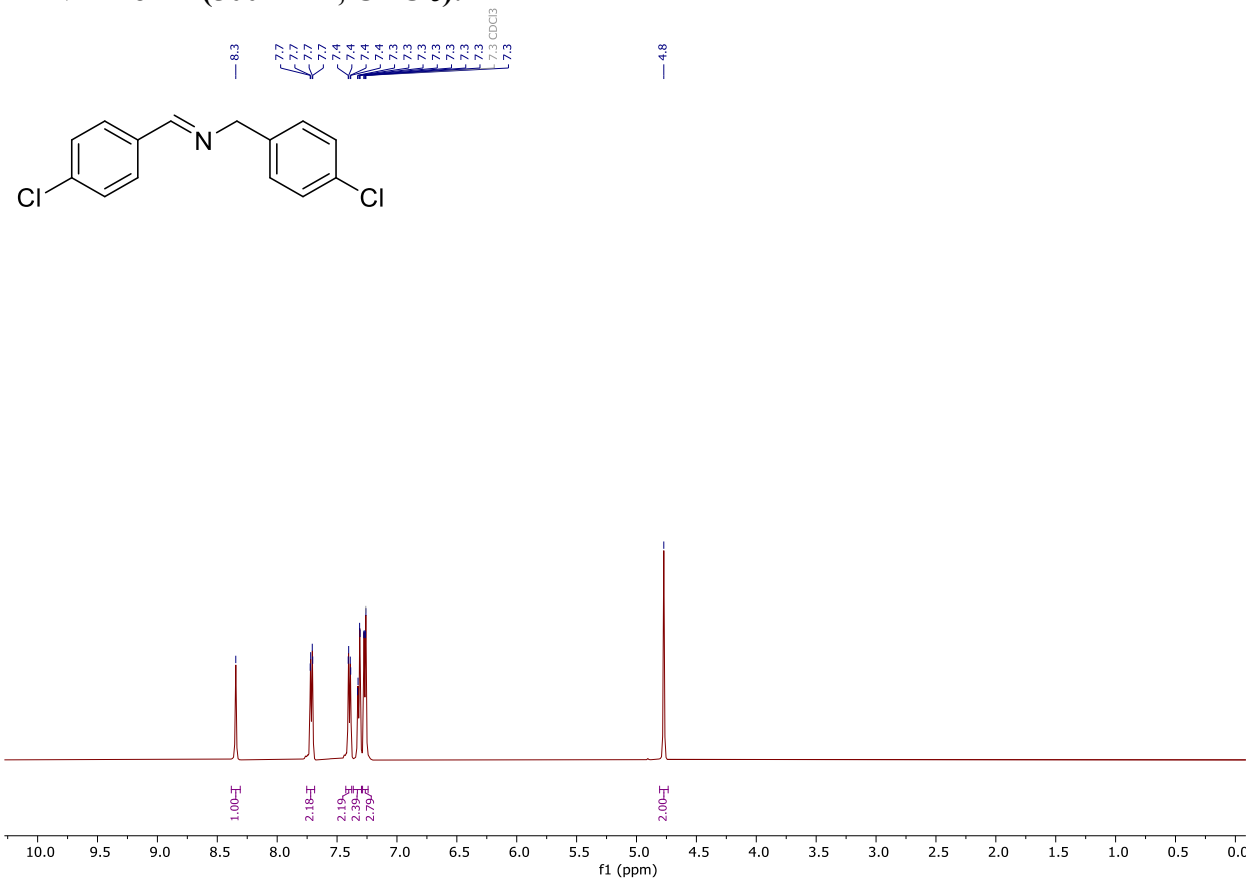
$^{13}C\{^{1}H\}$ NMR of 2c (126 MHz, $CDCl_3$):



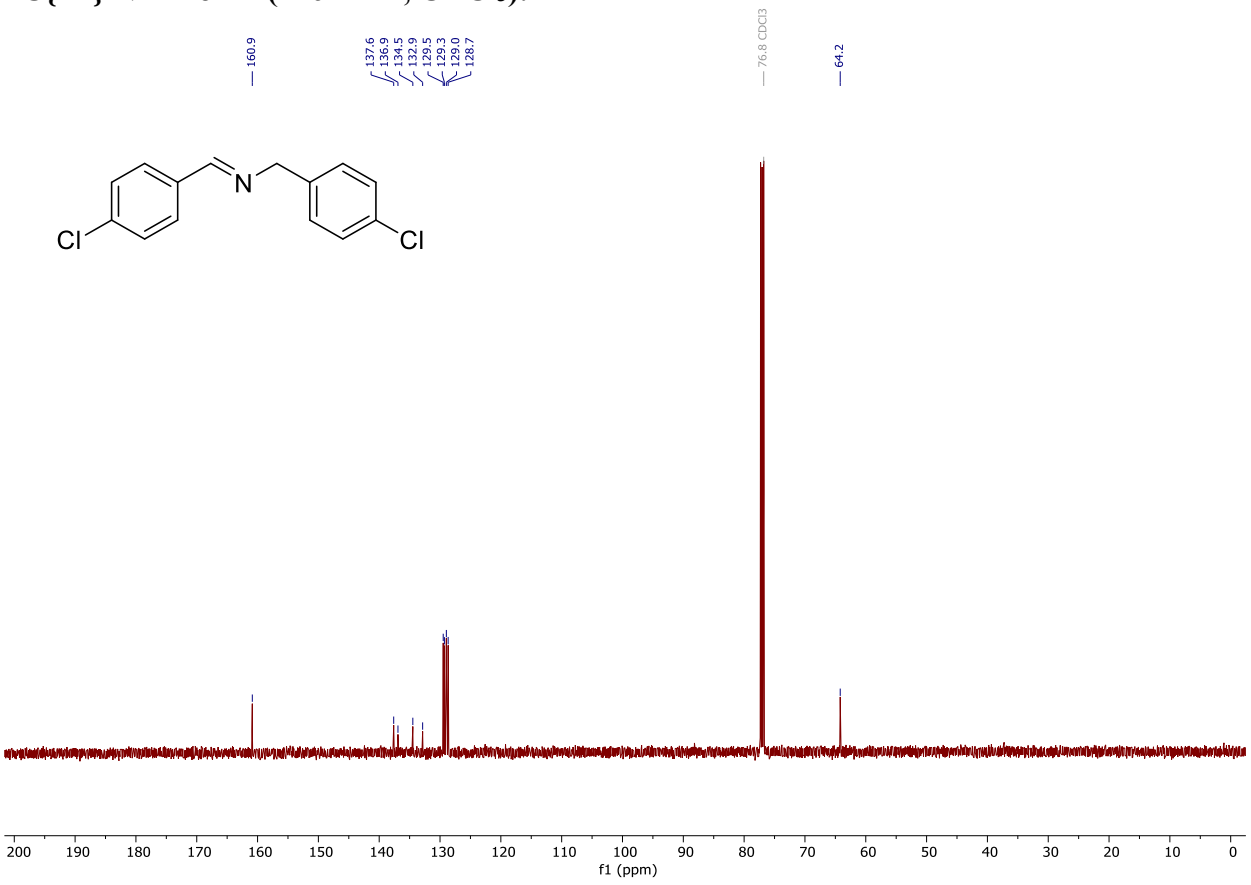
^{1}H NMR of 2d (500 MHz, $CDCl_3$):



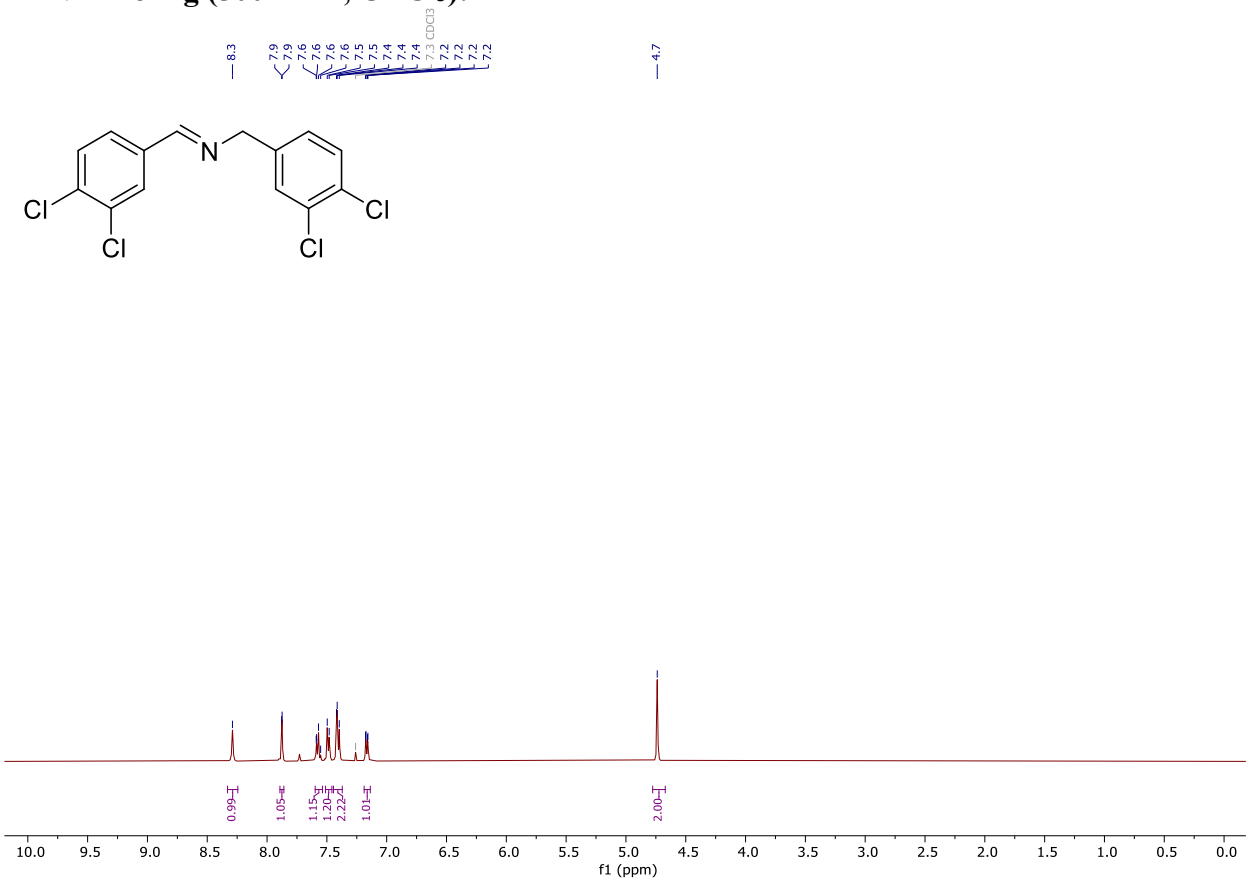
^{1}H NMR of 2f (500 MHz, $CDCl_3$):



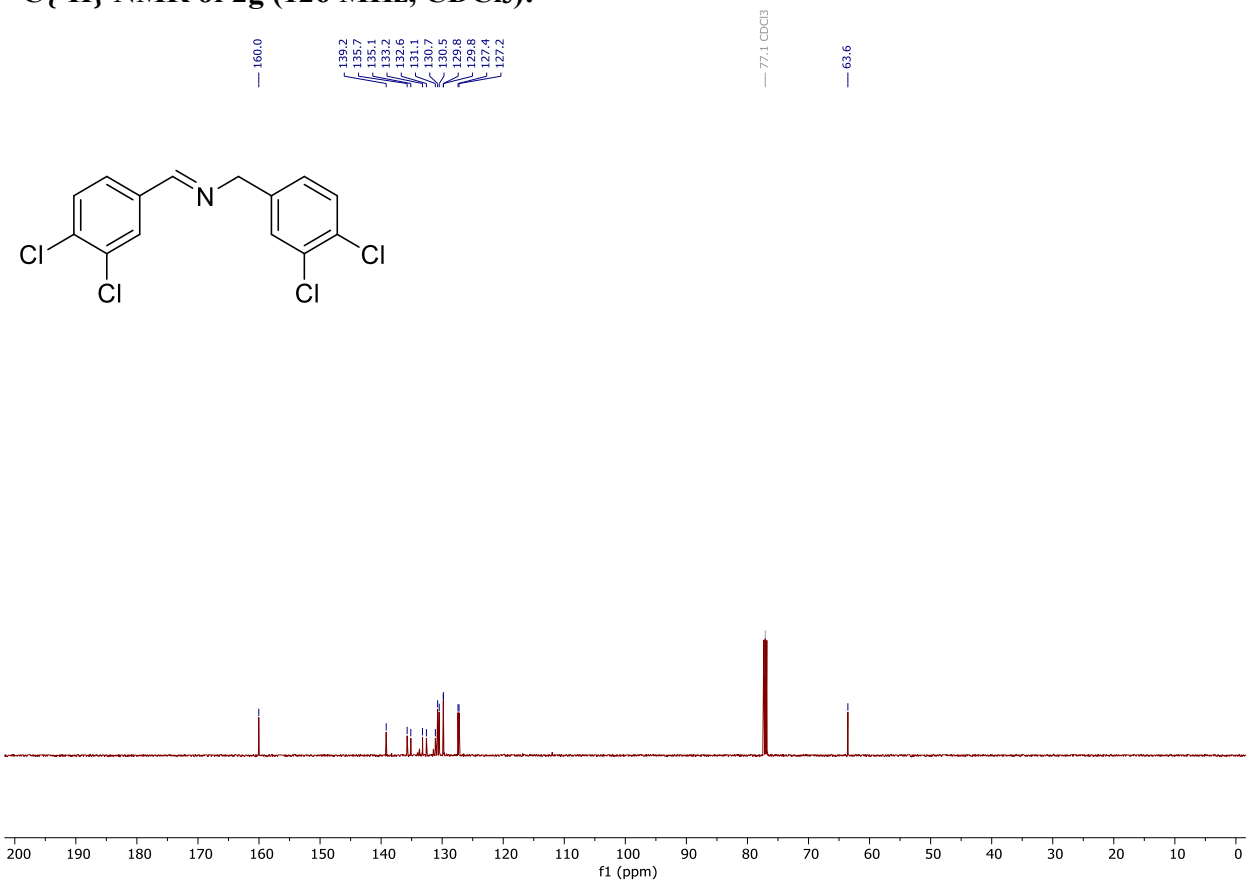
^{13}C{^{1}H} NMR of 2f (126 MHz, $CDCl_3$):



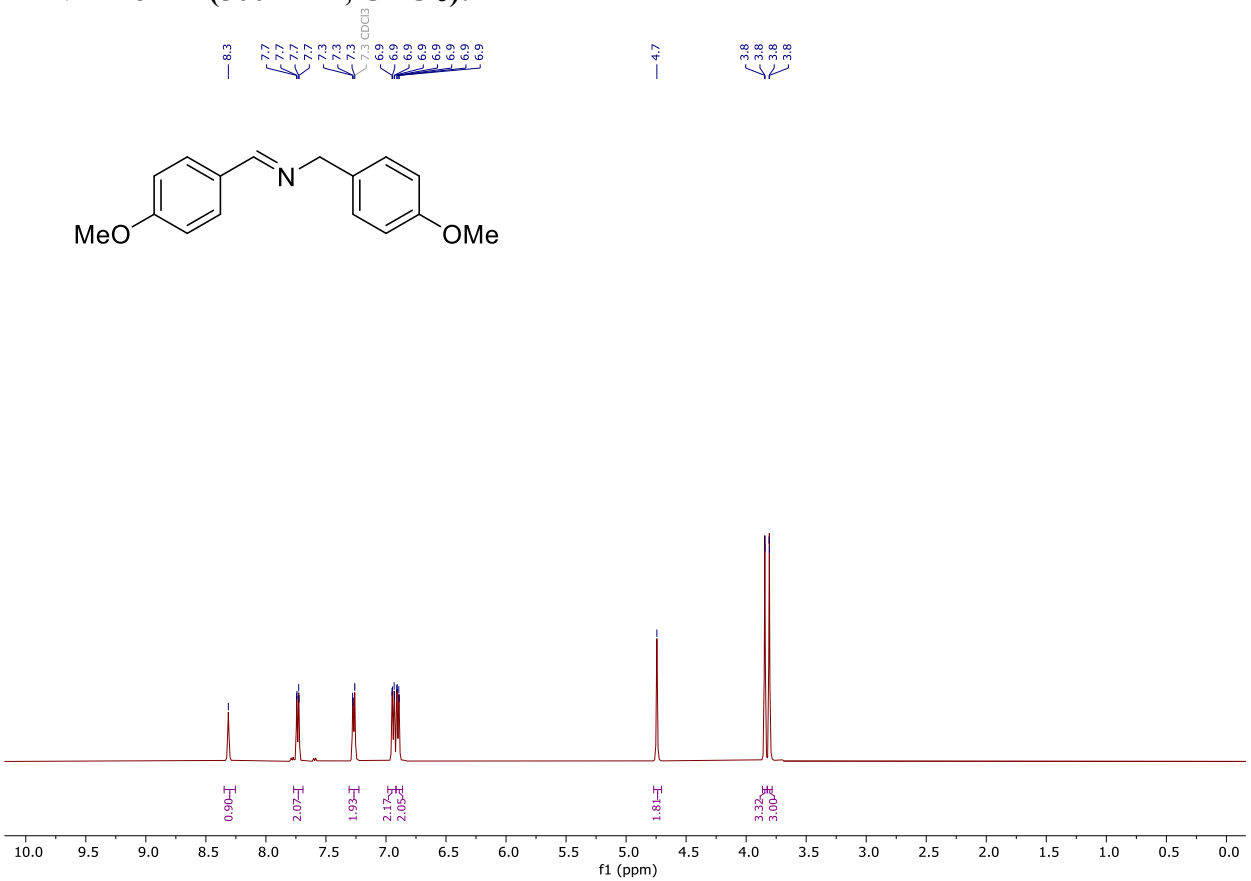
^{1}H NMR of 2g (500 MHz, $CDCl_3$):



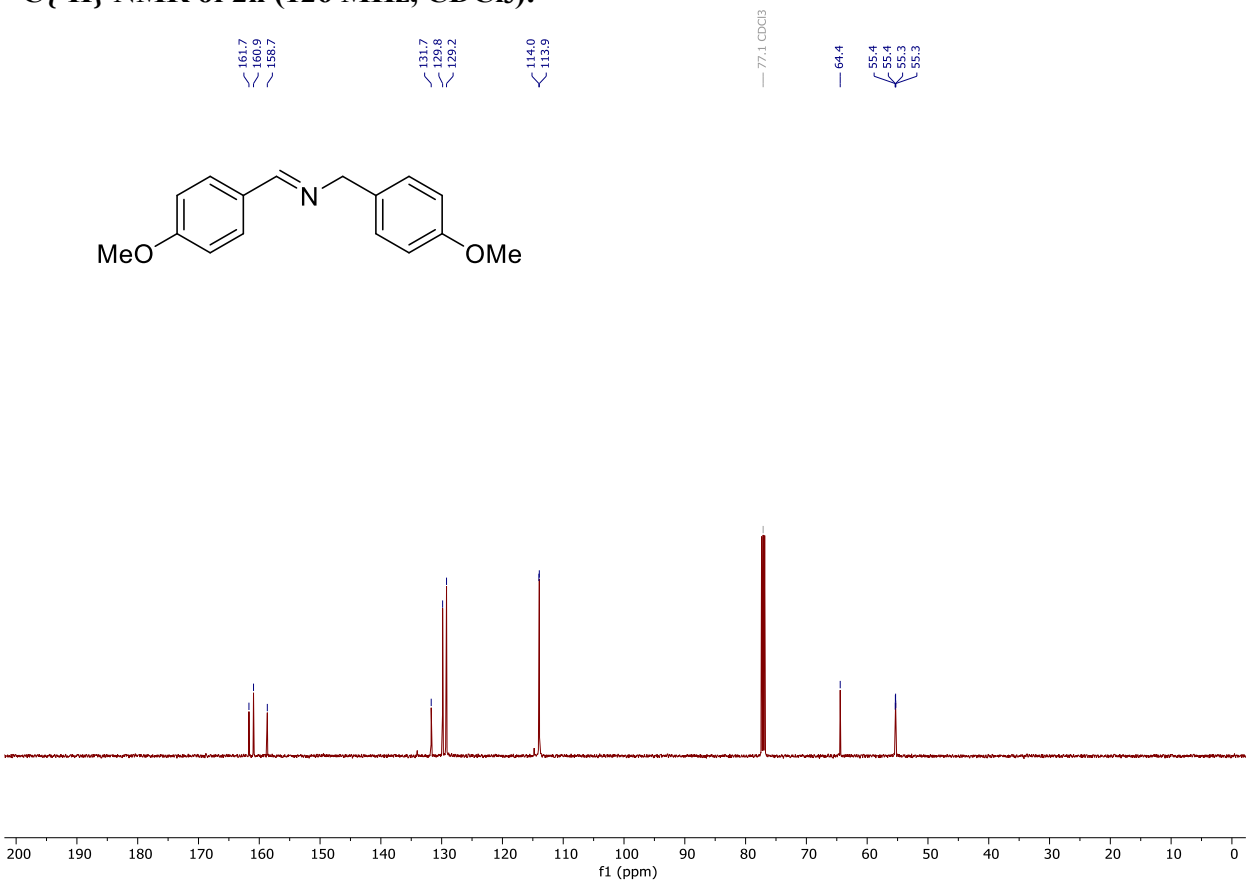
^{13}C{^{1}H} NMR of 2g (126 MHz, $CDCl_3$):



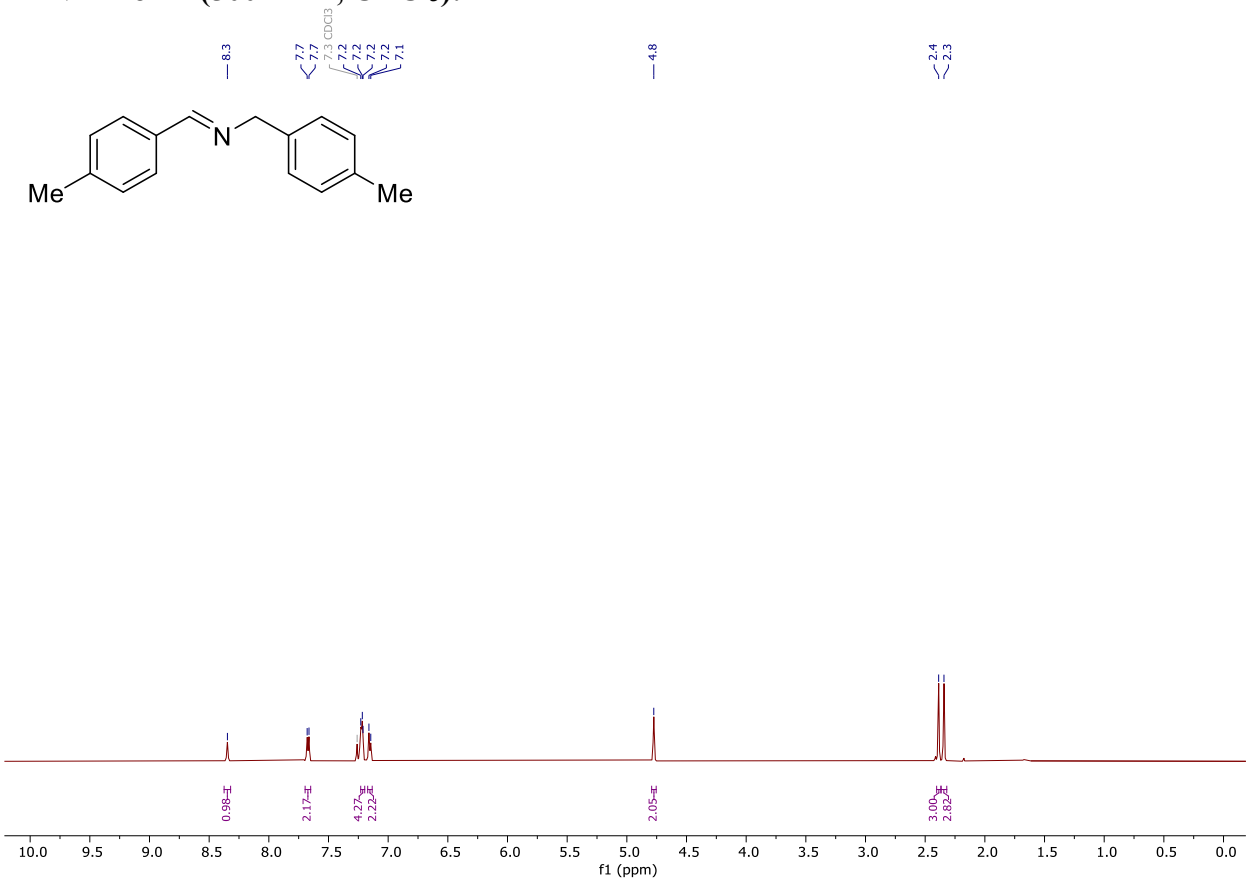
^{1}H NMR of 2h (500 MHz, $CDCl_3$):



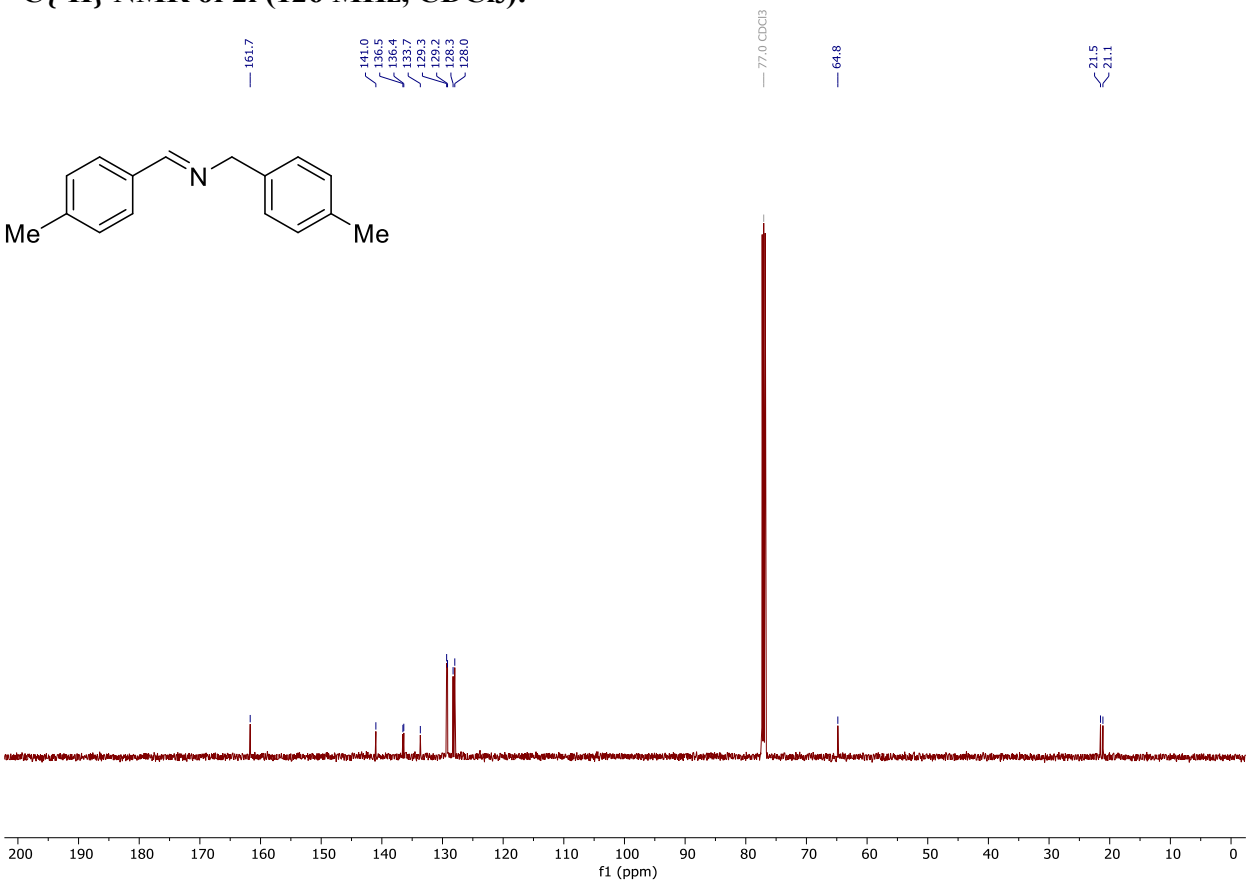
^{13}C{^{1}H} NMR of 2h (126 MHz, $CDCl_3$):



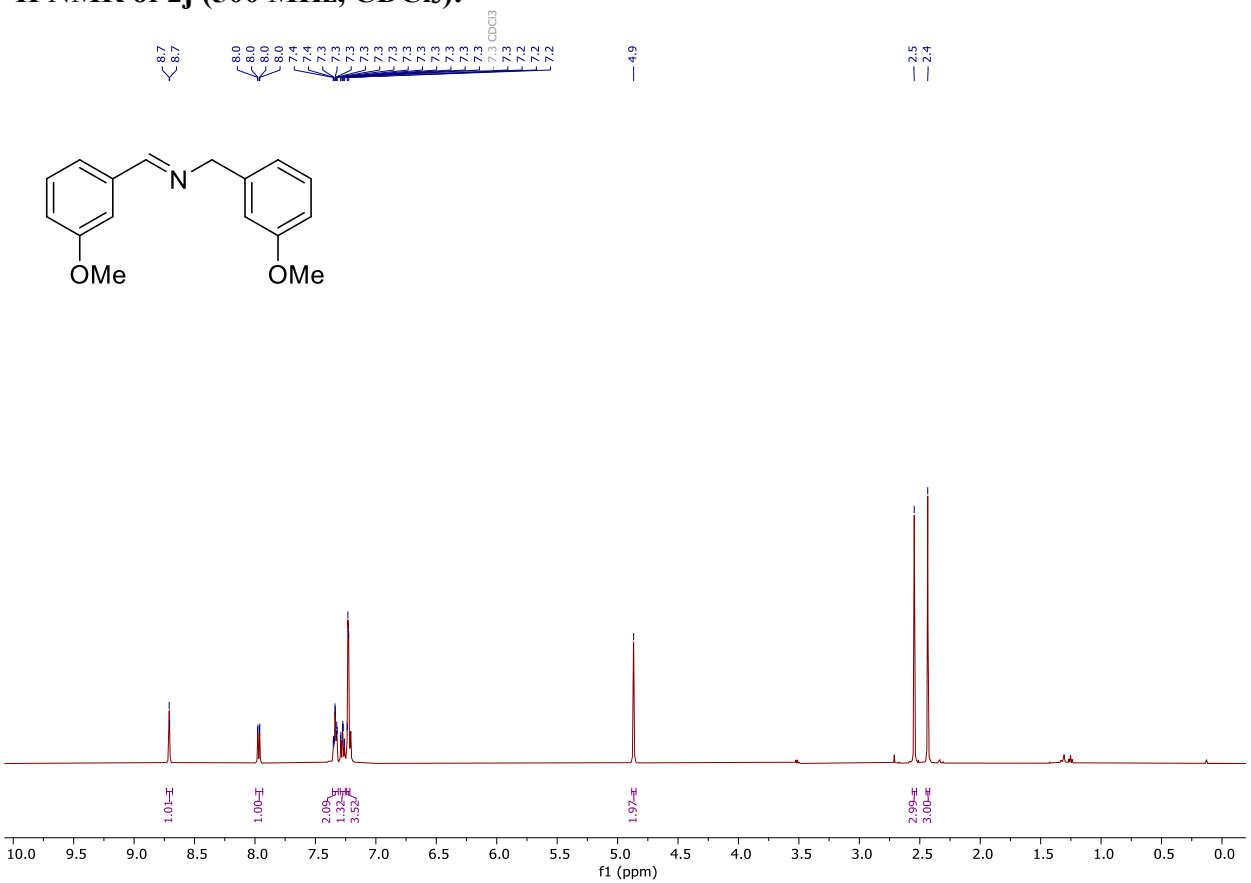
^{1}H NMR of 2i (500 MHz, $CDCl_3$):



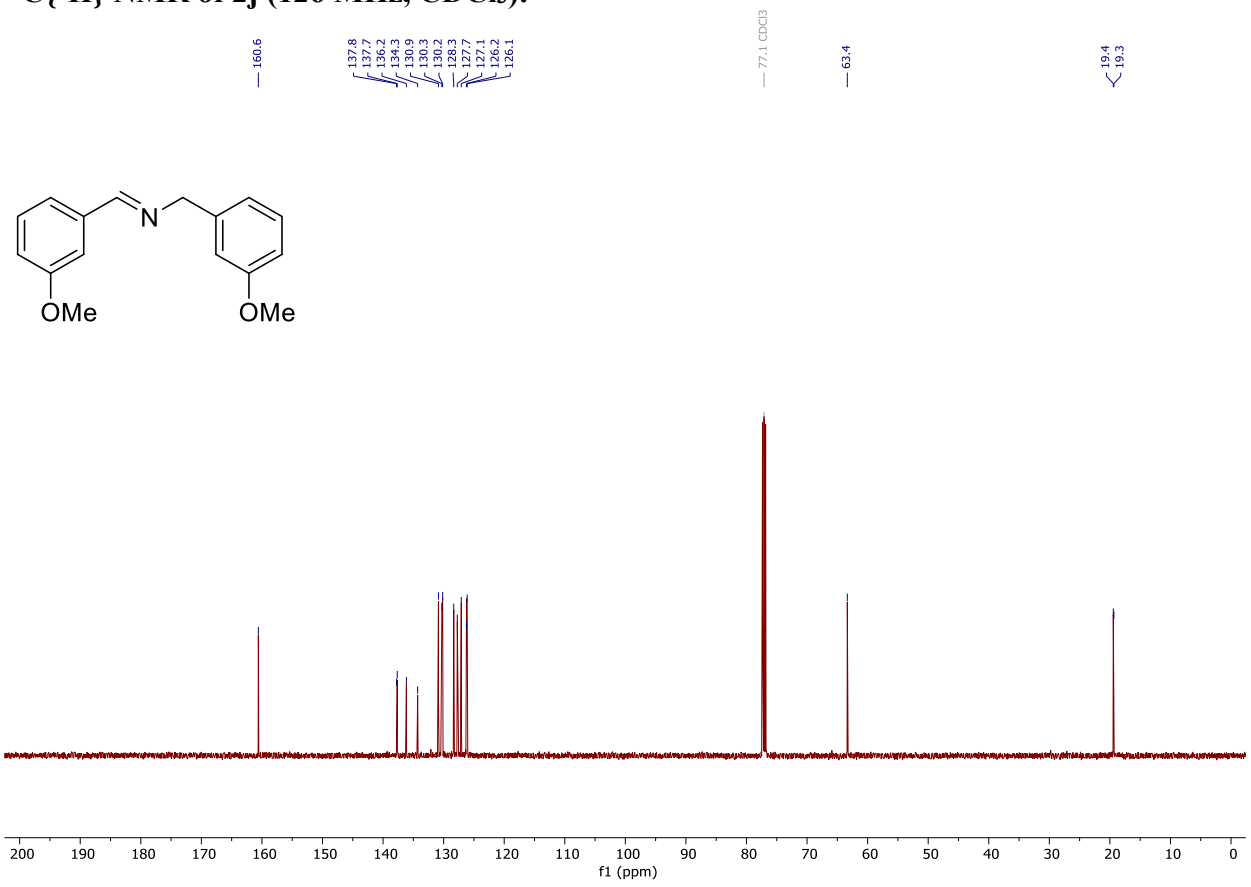
^{13}C{^{1}H} NMR of 2i (126 MHz, $CDCl_3$):



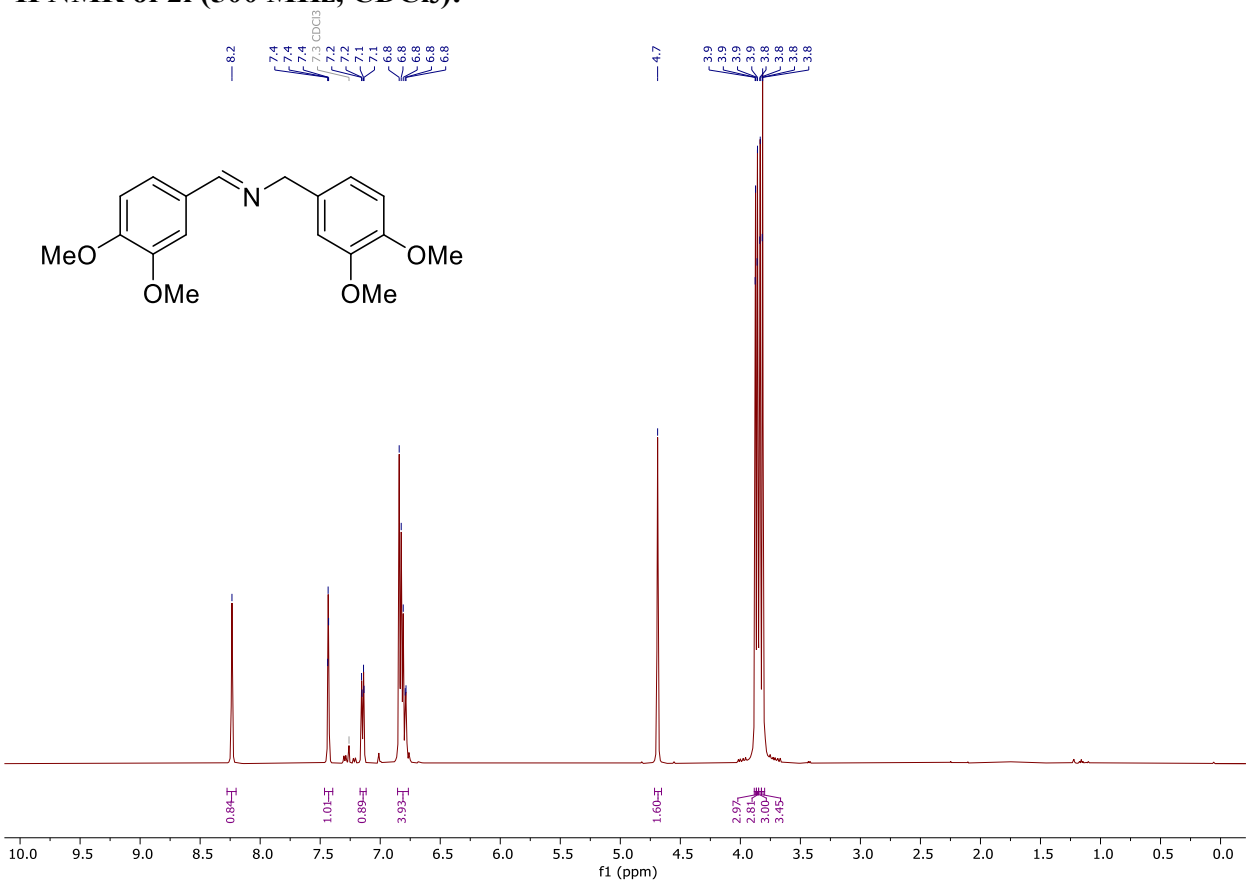
^{1}H NMR of 2j (500 MHz, $CDCl_3$):



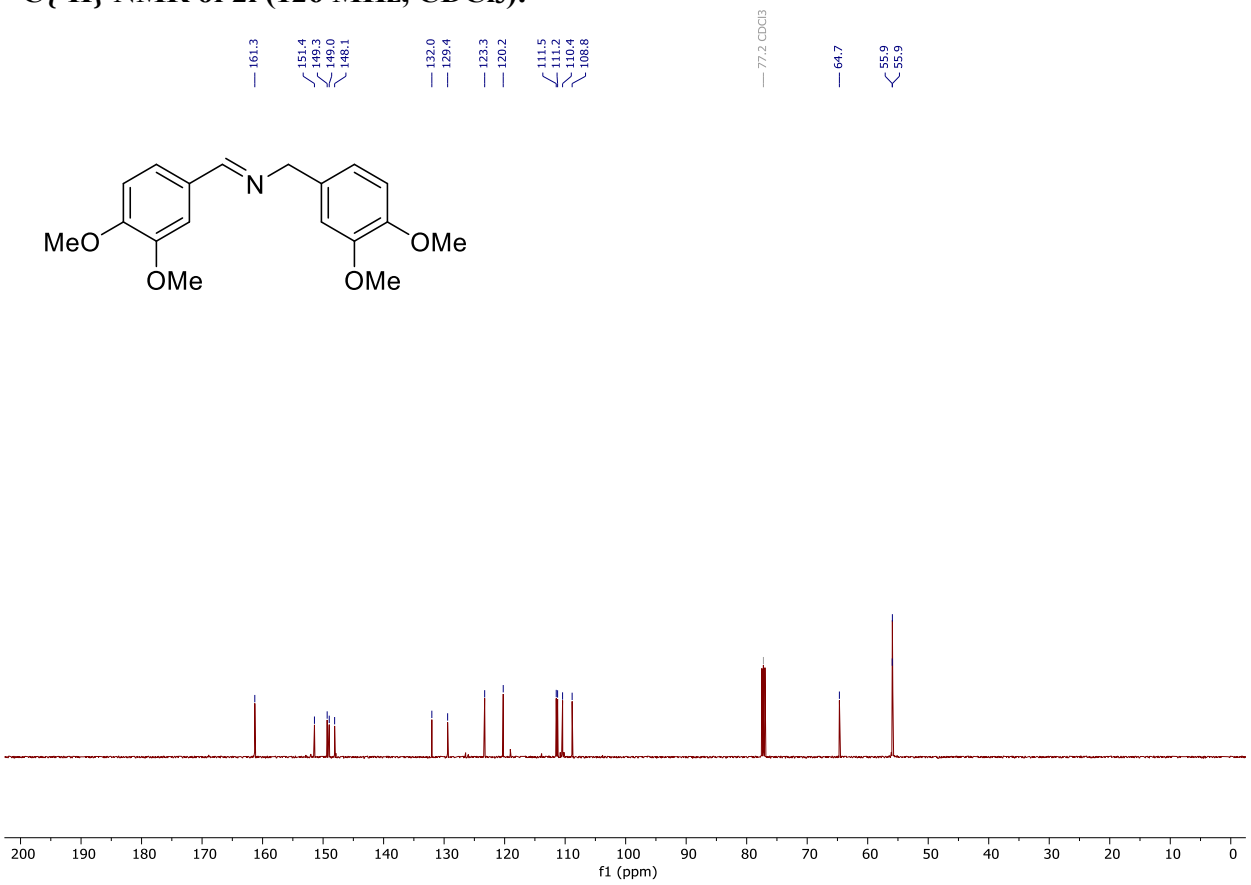
^{13}C{^{1}H} NMR of 2j (126 MHz, $CDCl_3$):



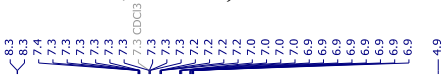
^{1}H NMR of 2l (500 MHz, $CDCl_3$):

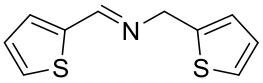


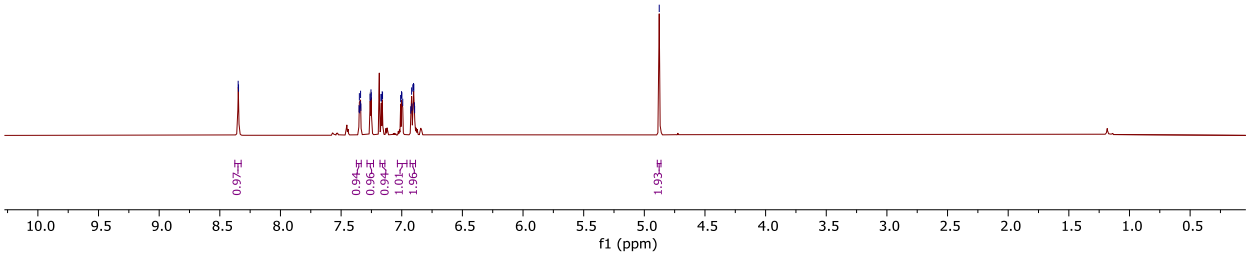
^{13}C{^{1}H} NMR of 2l (126 MHz, $CDCl_3$):



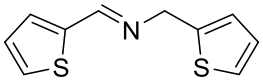
^{1}H NMR of 2o (500 MHz, $CDCl_3$):

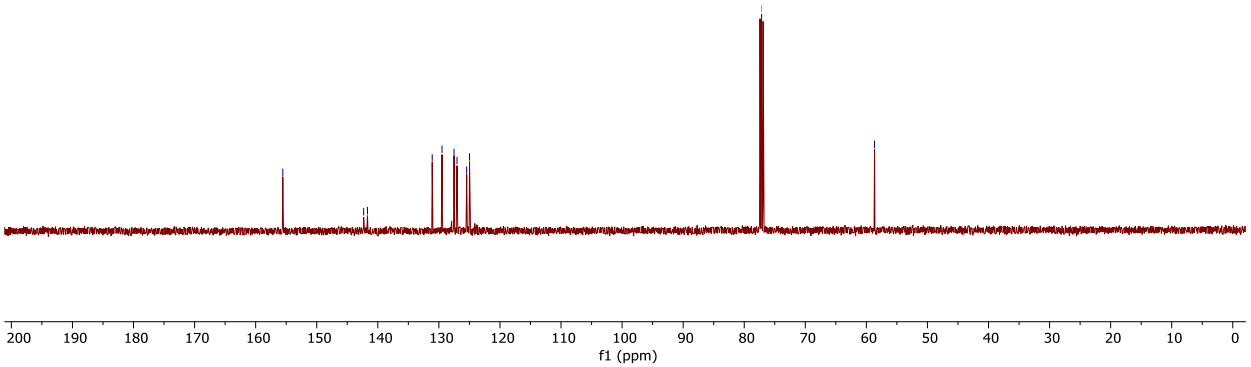




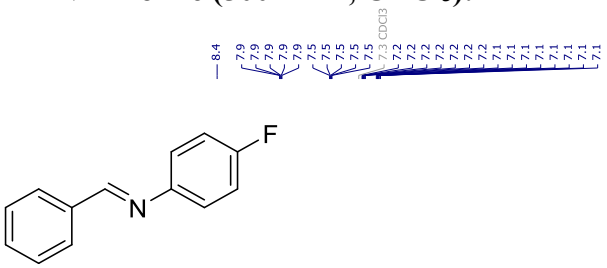


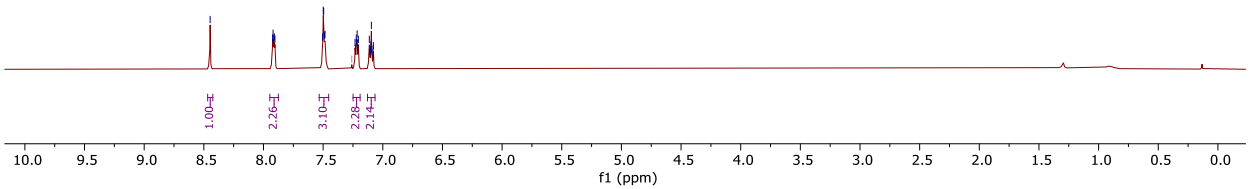
^{13}C{^{1}H} NMR of 2o (126 MHz, $CDCl_3$):



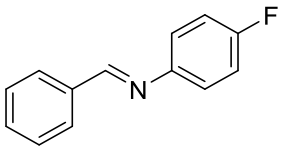


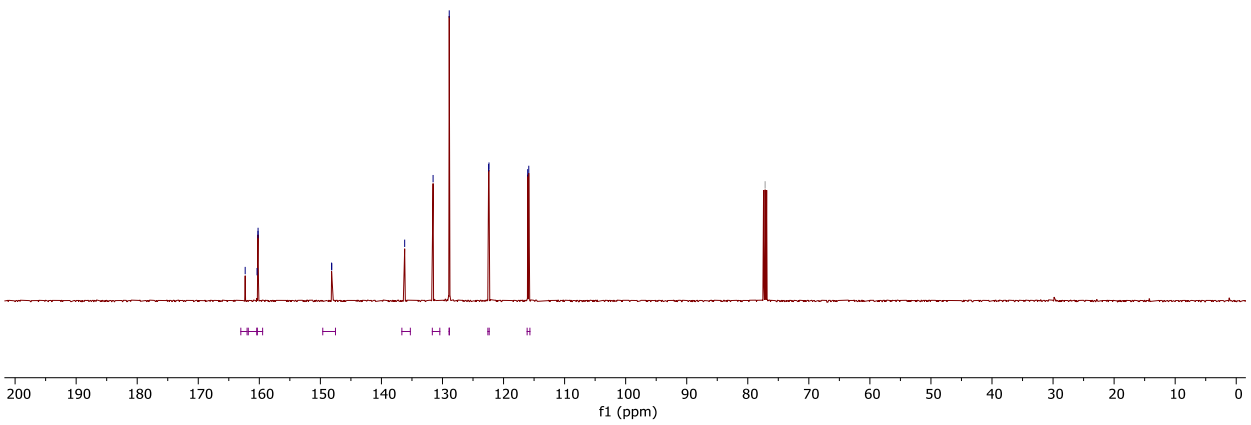
^{1}H NMR of 4e (500 MHz, $CDCl_3$):



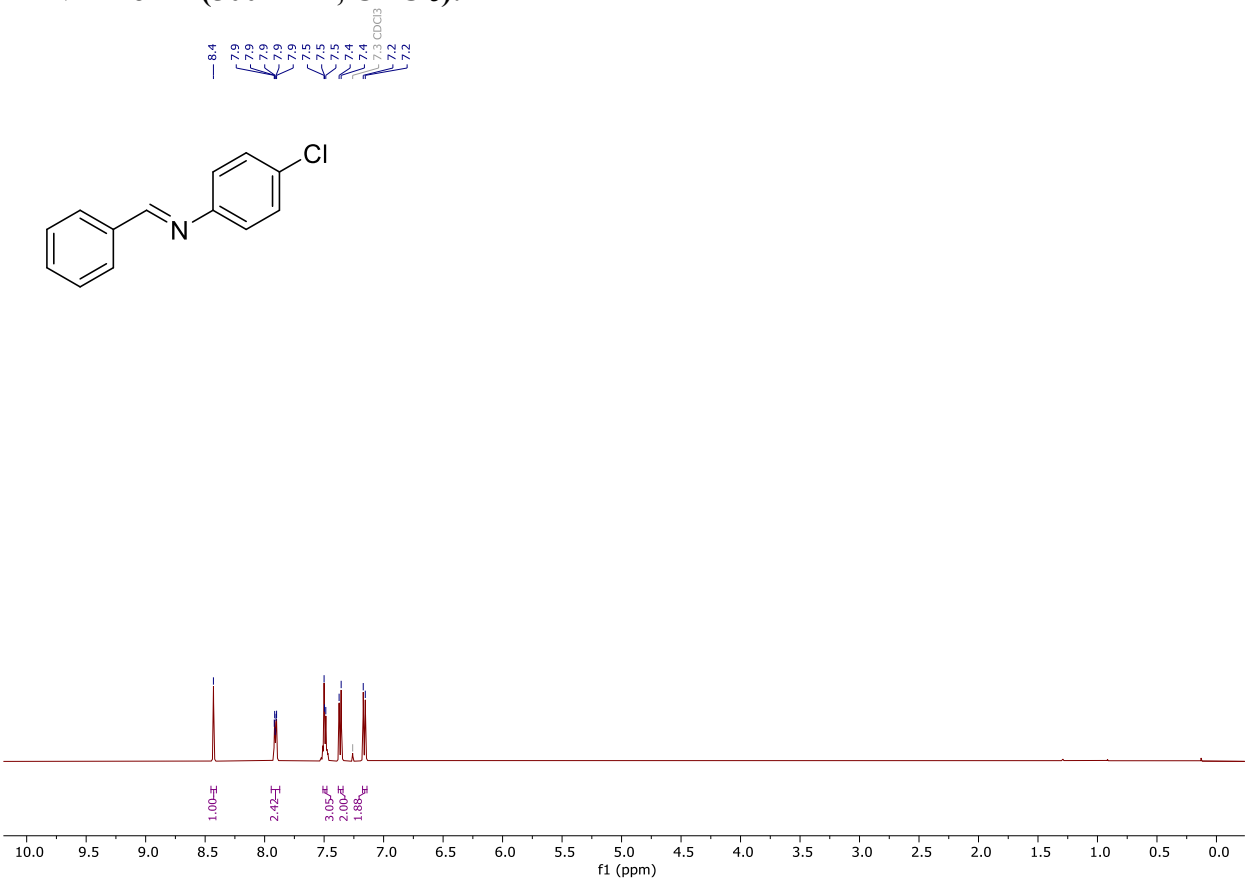


^{13}C{^{1}H} NMR of 4e (126 MHz, $CDCl_3$):

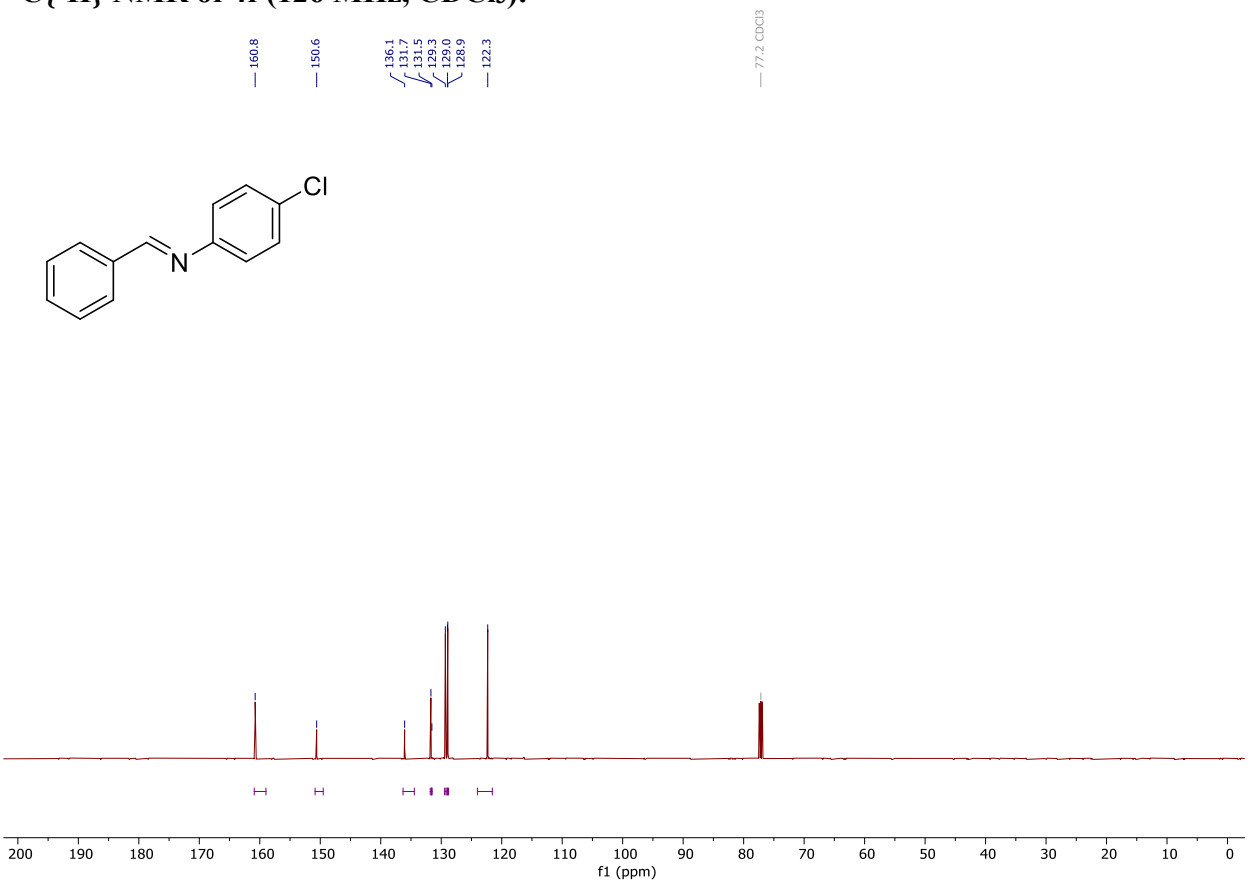




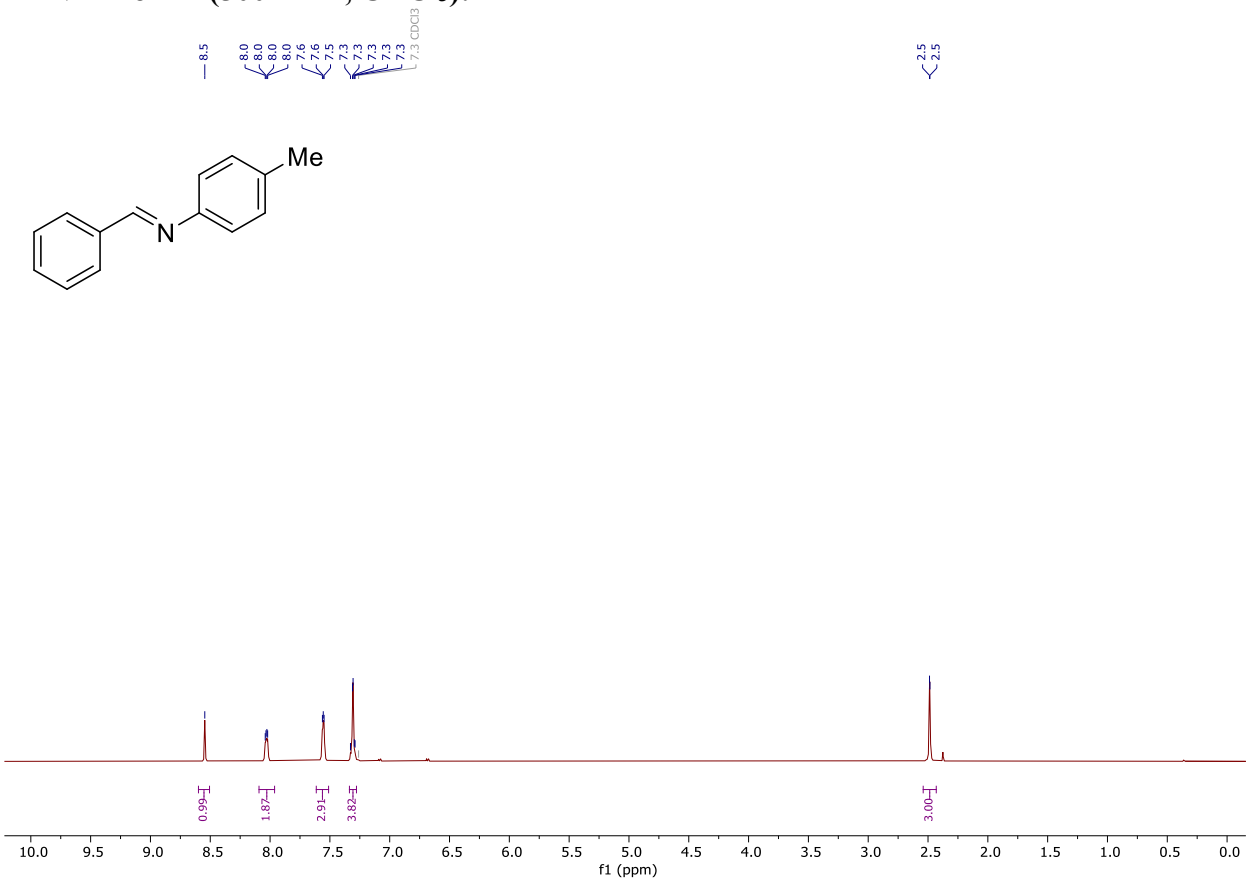
^{1}H NMR of 4f (500 MHz, $CDCl_3$):



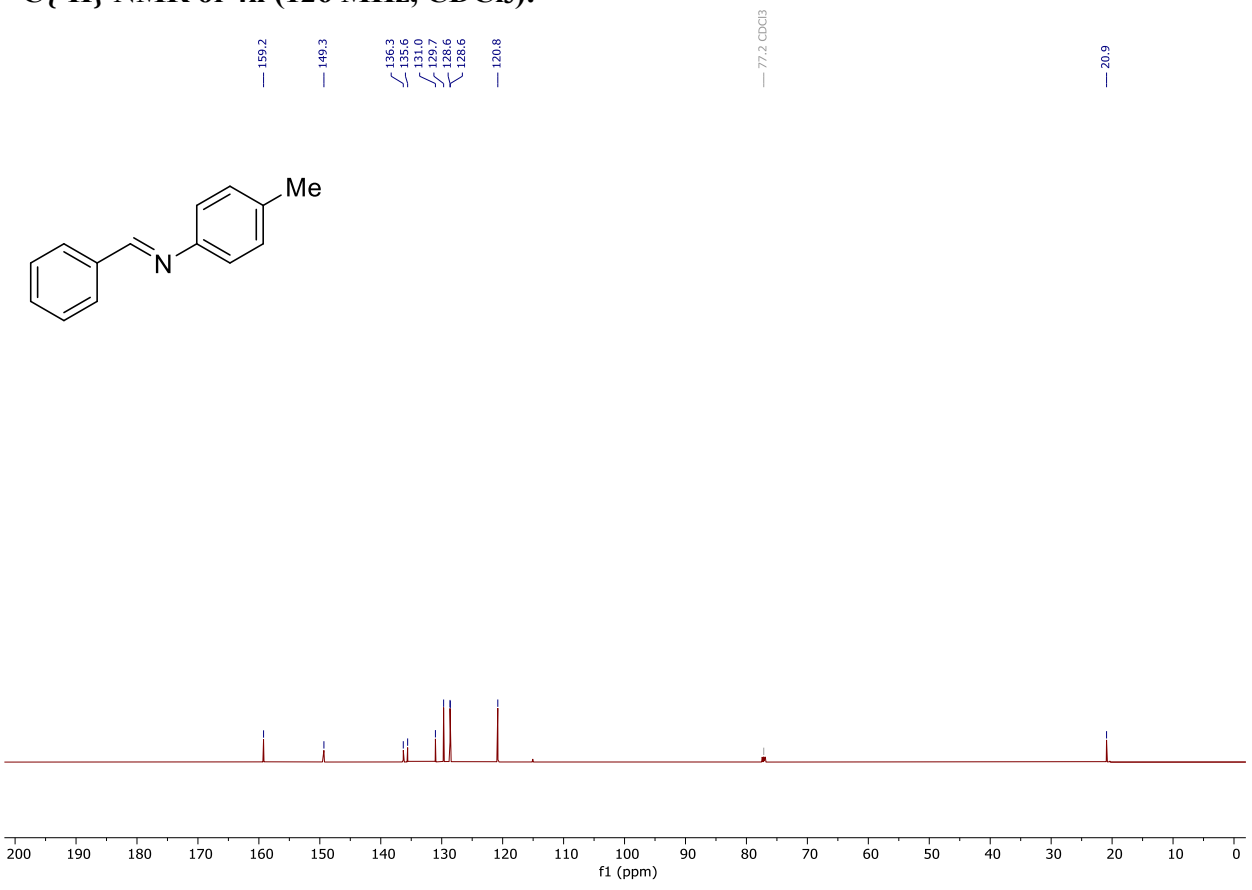
^{13}C{^{1}H} NMR of 4f (126 MHz, $CDCl_3$):



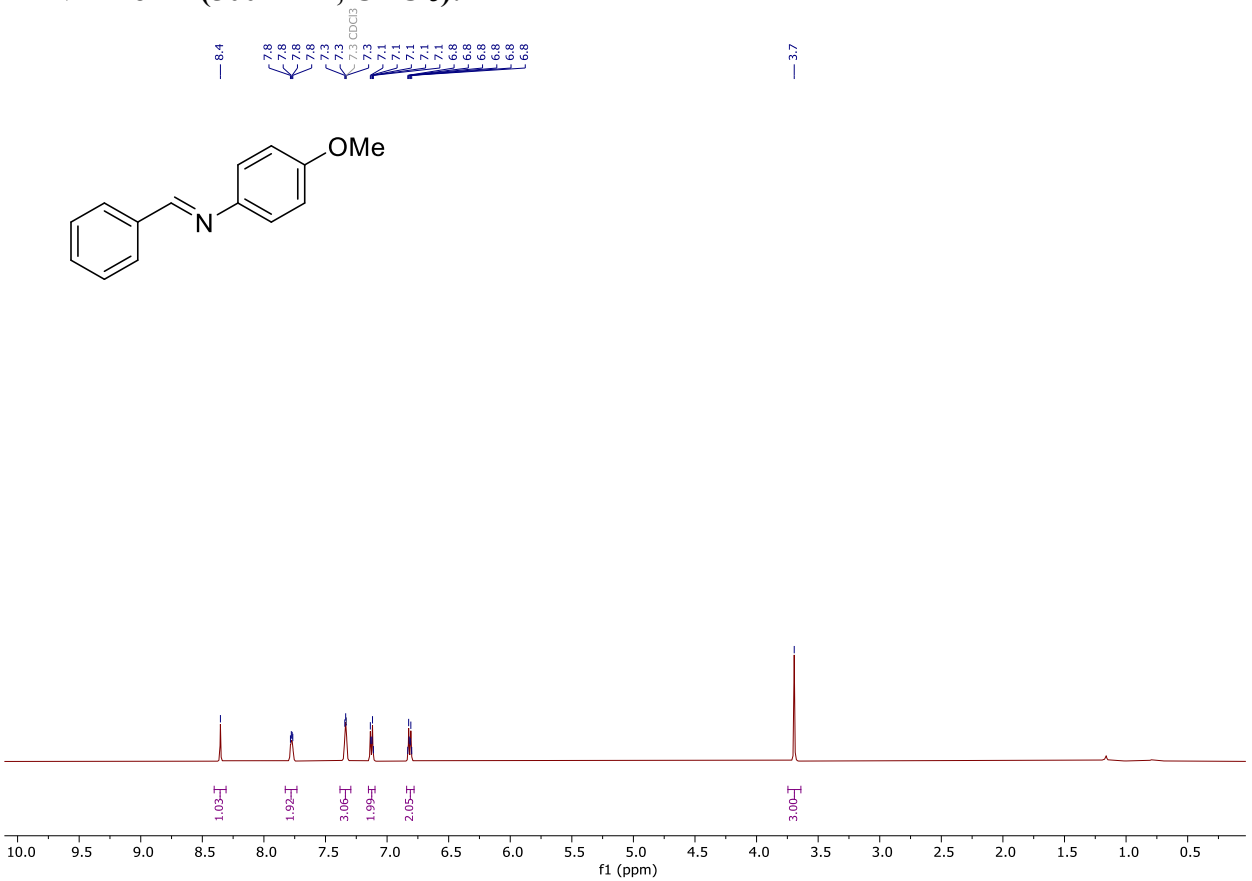
^{1}H NMR of 4h (500 MHz, $CDCl_3$):



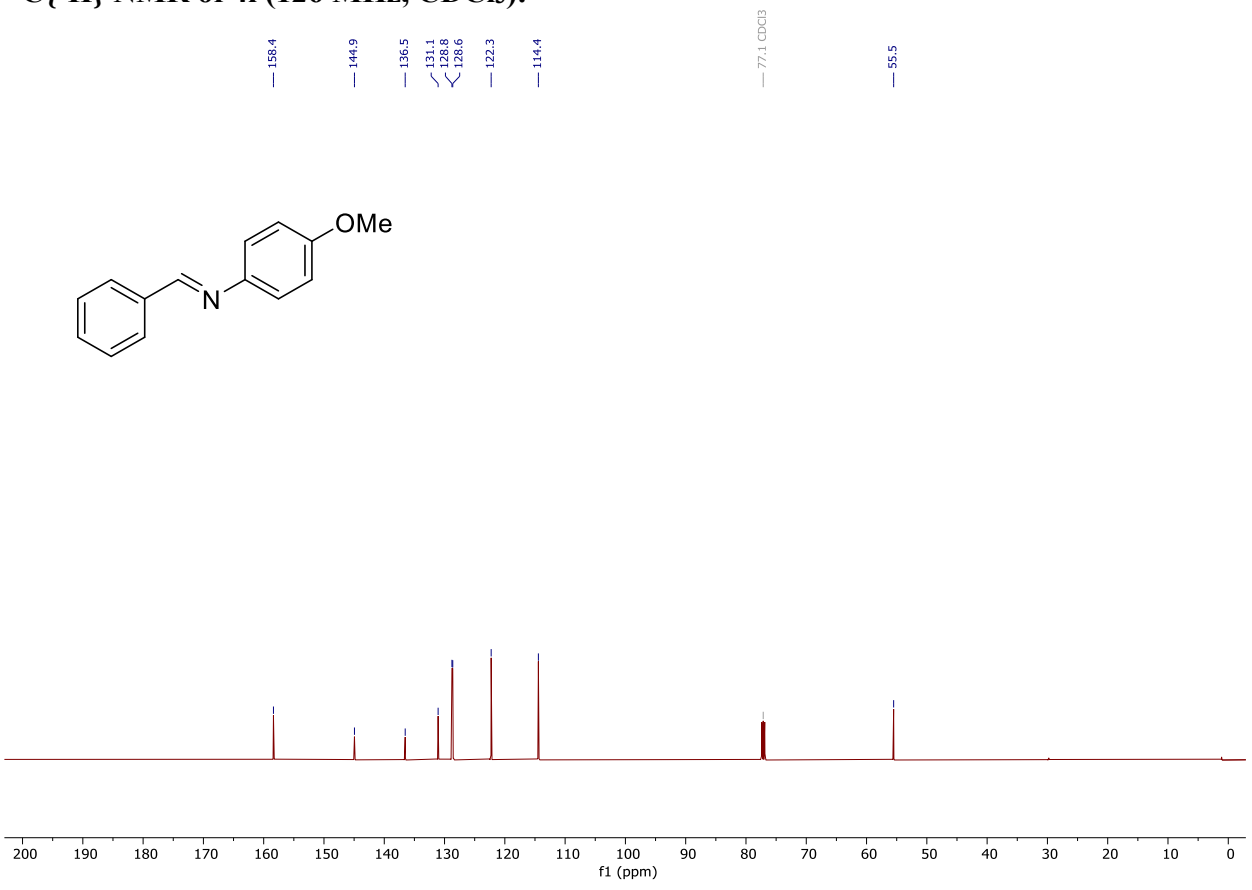
^{13}C{^{1}H} NMR of 4h (126 MHz, $CDCl_3$):



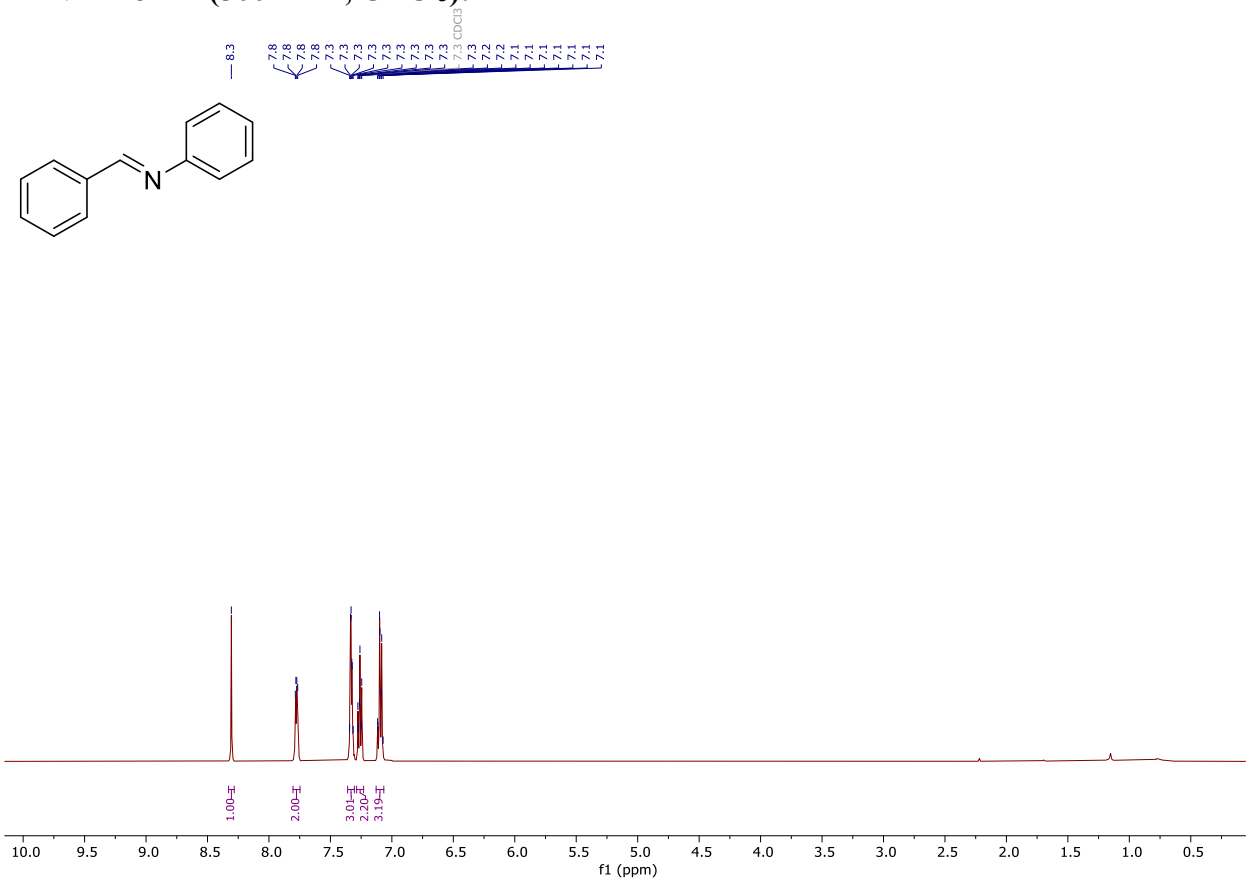
^{1}H NMR of 4i (500 MHz, $CDCl_3$):



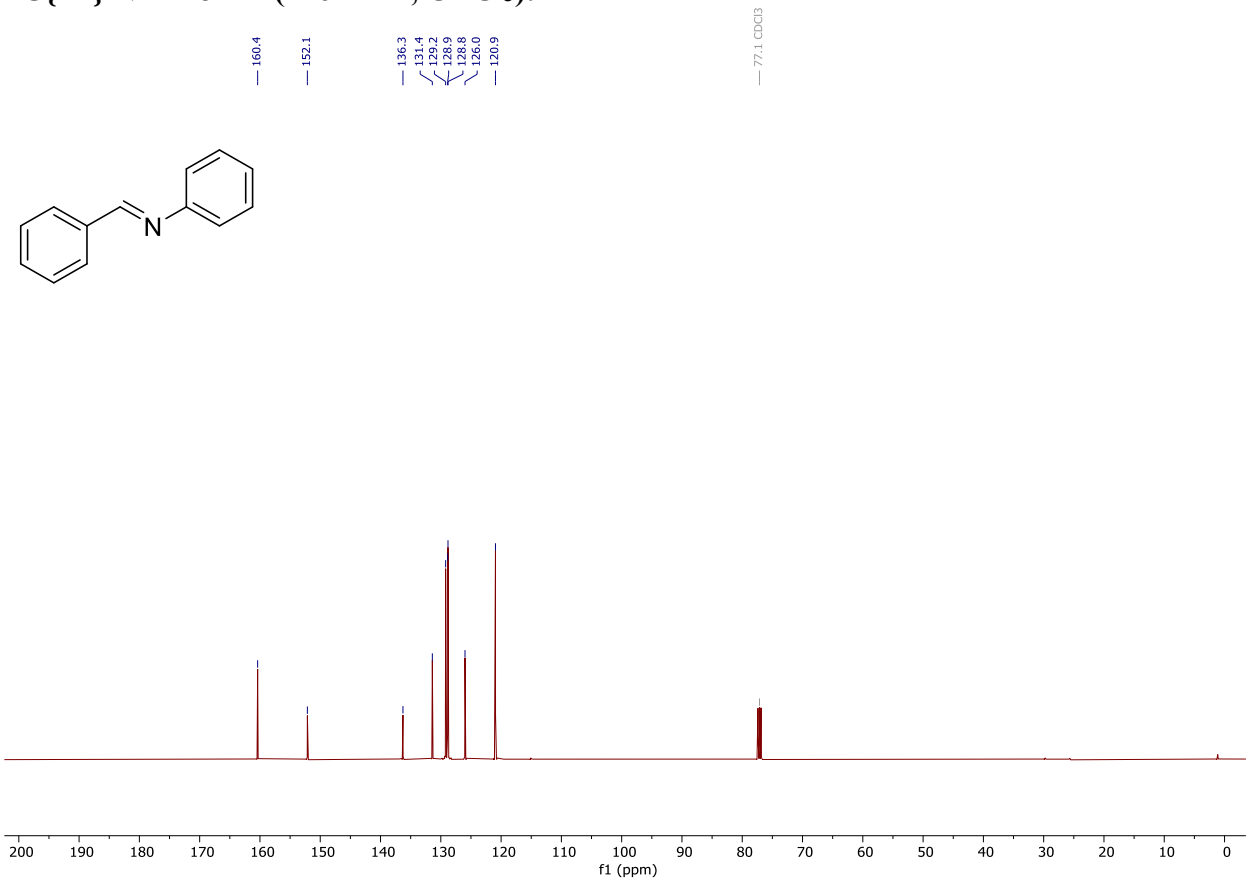
^{13}C{^{1}H} NMR of 4i (126 MHz, $CDCl_3$):



^{1}H NMR of 4n (500 MHz, $CDCl_3$):

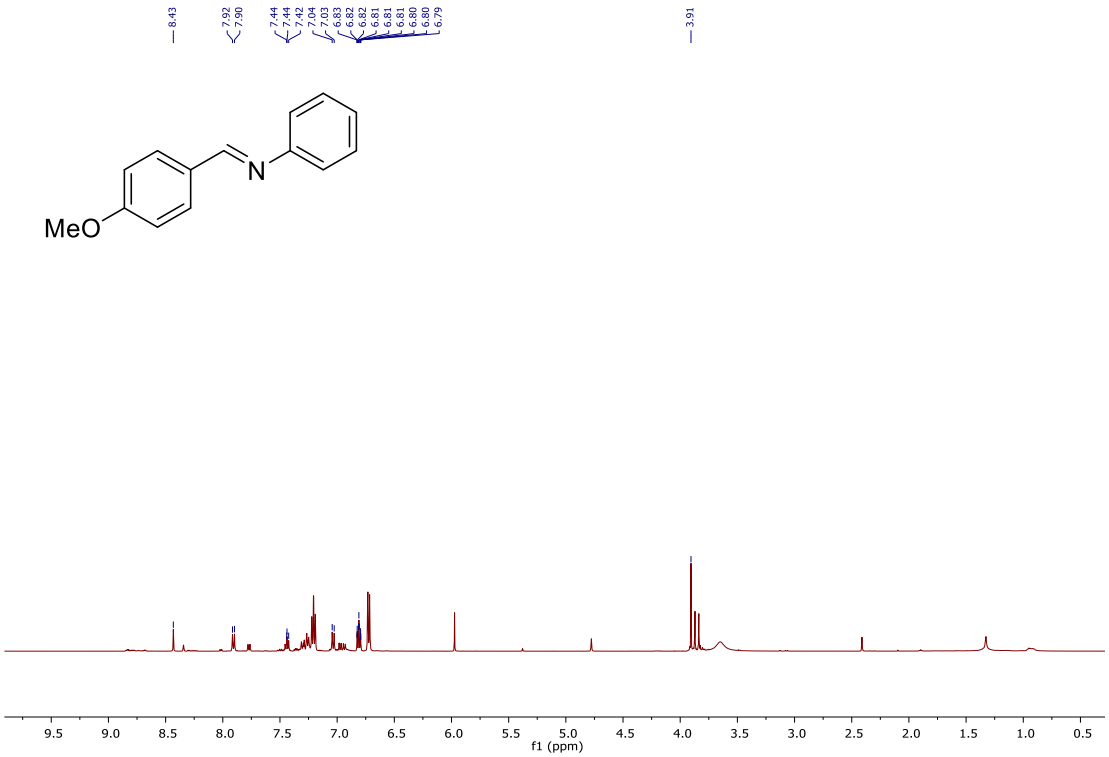


^{13}C{^{1}H} NMR of 4n (126 MHz, $CDCl_3$):

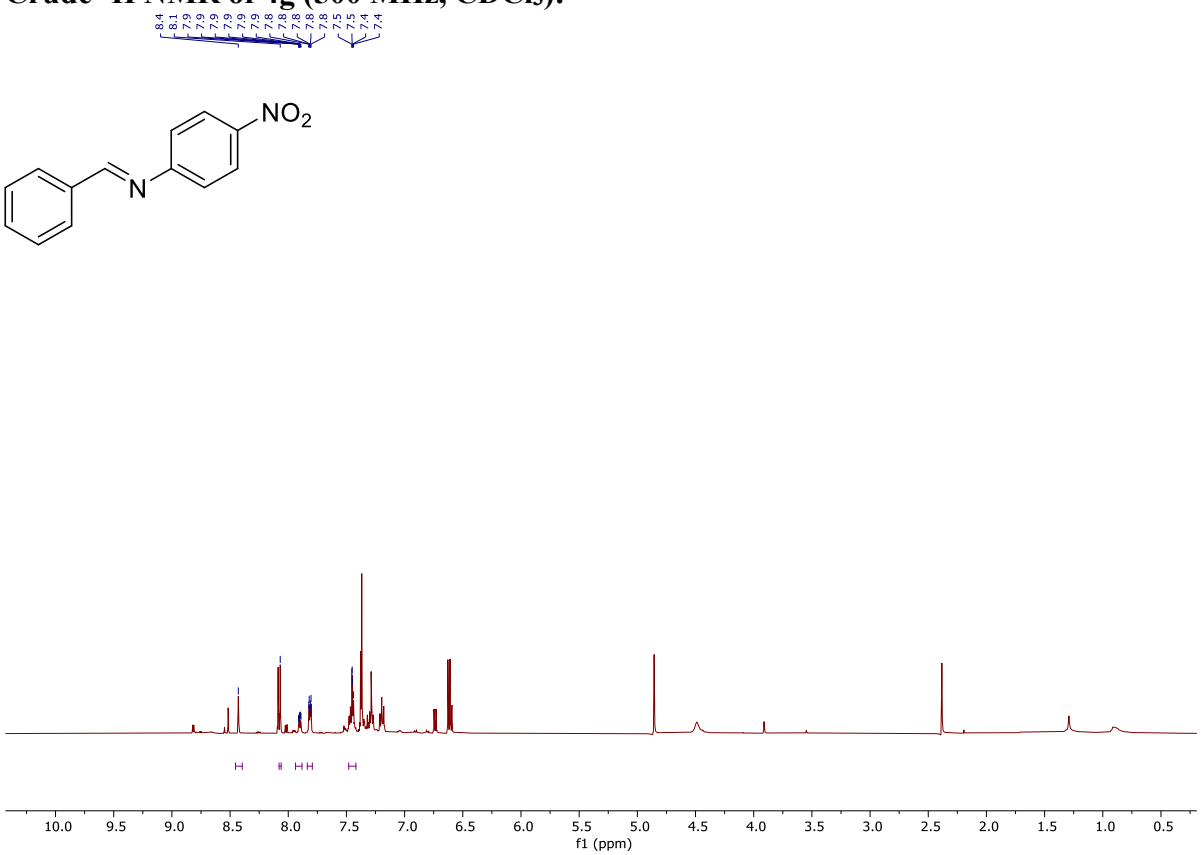


17. Selected crude ^{1}H NMR of cross-coupled reaction mixture (containing homo-coupled mixture)

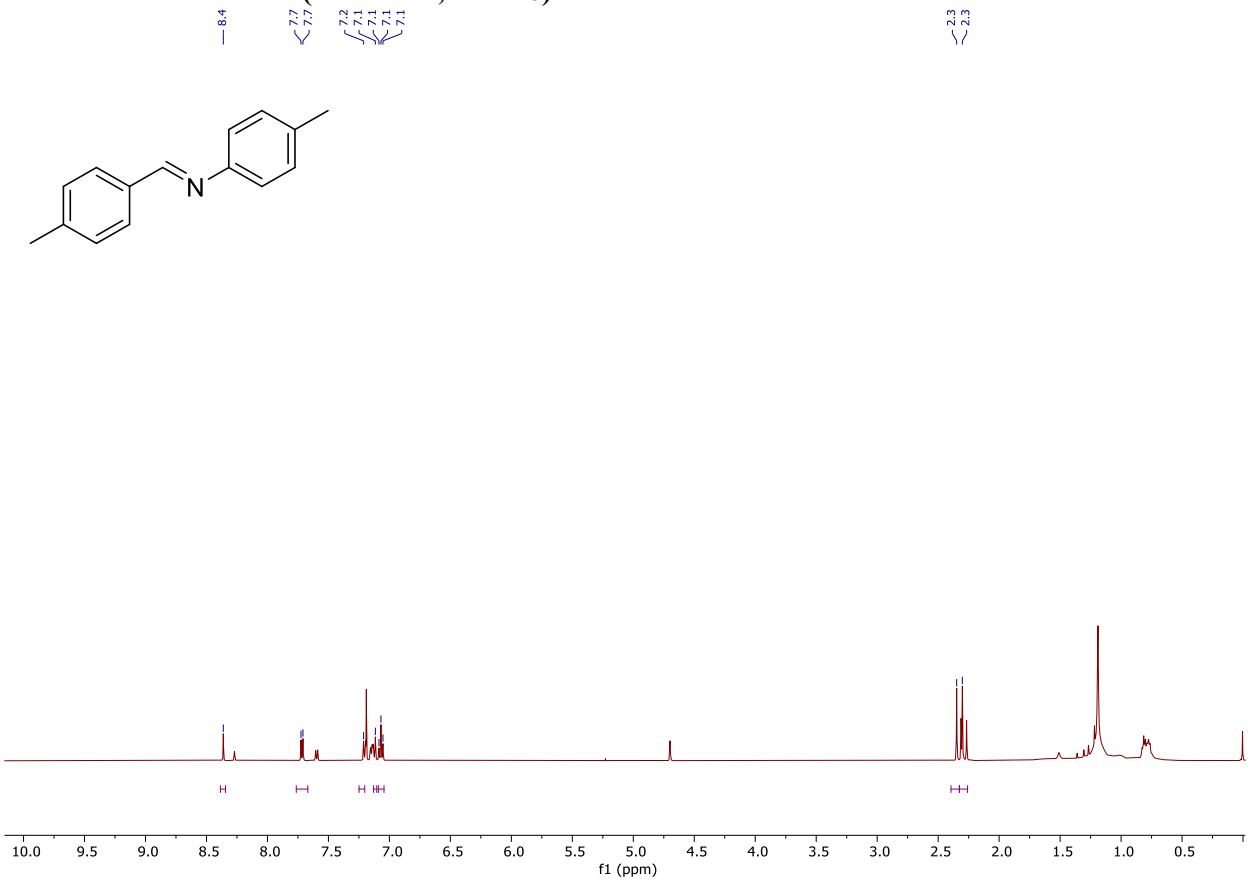
Crude ^{1}H NMR of 4c (500 MHz, $CDCl_3$):



Crude ^{1}H NMR of 4g (500 MHz, $CDCl_3$):



Crude ^{1}H NMR of 4k (500 MHz, $CDCl_3$):



18. References

1 B. Ramezani, G. H. Shahverdizadeh, L. Edjlali, F. Ramezani and M. Babazadeh, *Chemistry Select*, 2020, **42**, 13081 - 13090.

2 O.V. Dolomanov, L.J. Bourhis, R.J. Gildea, J.A.K. Howard and H. Puschmann, *J. Appl. Cryst.*, 2009, **42,** 339-341.

3 G.M. Sheldrick, *Acta Cryst.*, 2015, **C71**, 3-8.

4 Z. Ozer and S. Ozkar, *Turk. J. Chem.* 1999, **23**, 9– 14.

5 A. C. Ohs, A. L. Rheingold, M. J. Shaw and C. Nataro, *Organometallics*, 2004, **23**, 4655–4660.

6 J. Berstler, A. Lopez, D. Ménard, W. G. Dougherty, W. S. Kassel, A. Hansen, A. Daryaei, P. Ashitey, M. J. Shaw, N. Fey, and C. Nataro, *J. Organomet. Chem.* 2012, **712**, 37−45.

7 Y. Kim, S. Ryu, W. Cho, M. Kim, M. H. Park and Y. Kim, *Inorg. Chem.*, 2019, **58**, 5922– 5931.

8 M. C. Biesinger, B. P. Payne, A. P. Grosvenor, L. W.M. Lau, A. R. Gerson and R. S. C. Smart, *Appl. Surf. Sci.*, 2011, **7**, 2717-2730.

9 E. Desimoni and B. Brunetti, *Chemosensors*, 2015, **3**, 70-117.

10 A. T. Murray, R. King, J. V. Donnelly, M. J. Dowley, F. Tuna, D. Sells, M. P. John and D. R. Carbery, *ChemCatChem*, 2016, **8**, 510-514.

11 R. D. Patil and S. Adimurthy, *Adv. Synth. Catal.*, 2011, **10**, 1695-1700.

12 W. Zhao, C. Yang, X. Zhang, Y. Deng, C. Han, Z. Ma, L. Wang and L. Ye, *ChemSusChem*, 2020, **1**, 116-120.

13 D. Riemer, W. Schilling, A. Goetz, Y. Zhang, S. Gehrke, I. Tkach, O. Hollóczki and O. S. Das, *ACS Catal.*, 2018, **8**, 11679-11687.

14 L. Liu, S. Zhang, X. Fu, and C. Yan, *Chem. Commun*., 2011, **47**, 10148-10150.

15 T. Schwob and R. Kempe, *Angew. Chem. Int. Ed.*, 2016, **55**, 15175-15179.

16 S. Grimme, J. Antony, S. Ehrlich and H. Krieg, *J. Chem. Phys.*, 2010, **15**, 154104.

17 M. Xiang, N. Li, B. R. King and H. F. Schaefer, *New J. Chem.*, 2014, **38**, 1433–1440.

18 P. J. Hay and W. R. Wadt, *J. Chem. Phys.*, 1985, **1**, 270–283.

19 V. Barone and M. Cossi, *J. Phys. Chem. A*, 1998, **102**, 1995−2001.

20 M. Cossi, N. Rega, G. Scalmani and V. Barone, *J. Comput. Chem.*, 2003, **24**, 669−681.

21 S. Kostera, B. Wyrzykiewicz, P. Pawluć and B. Marciniec, *Dalton Trans.*, 2017, **35**, 11552-11555.