Electronic Supplementary Material (ESI) for Catalysis Science & Technology.

Supporting Information:

A General and Expedient Amination of Alcohols Catalysed by a single-cite (NN)Co(II)-Bidentate Complex under Solventless Conditions

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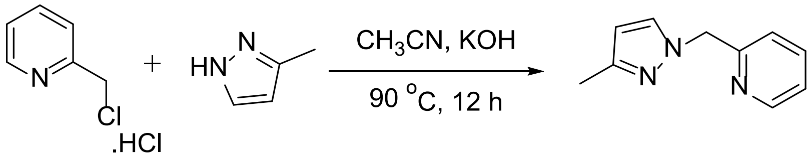
1. General Information

All catalytic experiments were conducted in flame-dried glassware under an atmosphere of nitrogen. The reagents were commercially obtained and used as received. All solvents were reagent grade or better. Toluene was refluxed over sodium/benzophenone, followed by being distilled an under-argon atmosphere and stored over sodium. Chemicals used in catalysis reactions were used without additional purification. Thin layer chromatography (TLC) was performed using silica gel precoated aluminium foil which was visualized with UV light at 254 nm or under iodine. Column chromatography was performed with SiO_2 (Silicycle Siliaflash F60 (230- 400 mesh). Fourier-transformed infrared (FT-IR) measurements were carried out with a Shimadzu IR Affinity-1S spectrophotometer with KBr pellets. The UV−Visible absorption spectra were recorded with a UV-Visible spectrophotometer (Jasco V-770) with $BaSO_4$ as a reference, equipped with a diffuse reflectance accessory. ^1H NMR (400 MHz), ^{13}C NMR (101 MHz) spectra were recorded on the Bruker AVANCE NEO 400 MHz spectrometer. Deuterated chloroform ($CDCl_3$) was used as the solvent, and chemical shift values (δ) are reported in parts per million relatives to the residual signals of this solvent [δ 7.27 for 1H (chloroform-d), δ 77.0 for $^{13}C\{^1H\}$ (chloroform-d). Abbreviations used in the NMR follow-up experiments: s, singlet; d, doublet; dd, doublet of doublet; t, triplet; tt, a triplet of triplet; td, a triplet of doublet; q, quartet; br, broad; m, multiplet. Mass spectra were obtained on GCMS-QP 5000 instruments with ionization voltages of 70 eV. High-resolution mass spectra (HRMS) were recorded by Electrospray ionisation (ESI) technique on an Agilent Mass Spectrometer (6200 series TOF/6500 series Q-TOF B.08.00) by infusing sample directly into the source using manual method. The detection of gases (H_2, $m/z = 2$) was determined using an online MS with an OmniStar™ Gas Analysis System GSD 320 (Pfeiffer) quadrupole mass spectrometer apparatus. The GC-MS Analysis was recorded on an Agilent 7890B GC system equipped with a 5977B MSD Mass analyser. Single crystal X-ray diffraction data were collected on a Bruker AXS SMART APEX CCD diffractometer using graphite monochromated MoKa ($\lambda = 0.7107$ Å) radiation at 100(2) K and the intensities were measured using ω scan with a scan width of 0.8°. A total of 606 frames per set were collected in different settings keeping the sample to a detector distance of 6.054 cm. Crystal data were reduced by SAINTPLUS, and an empirical absorption correction was applied using the package SADABS available in the Bruker software package. All the crystal structures were solved by direct methods using SHELXS-97[S1] and refined by full-matrix least squares method using SHELXL-97 as well as Olex 2.0.[S2]

2. Experimental Section

2.1 Synthesis of 2-((3-methyl-1H-pyrazol-1-yl)methyl)pyridine (NNPy^{Me} (L$_1$))

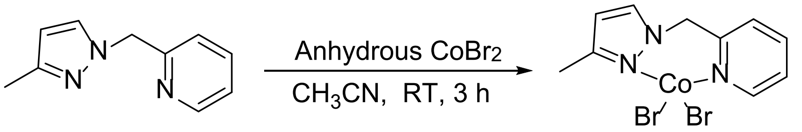


Scheme S1. Synthesis of ligand **L$_1$**

To a solution of 2-(chloromethyl)pyridine hydrochloride (0.6 g, 3.6 mmol) in acetonitrile (12 mL), 3-methyl pyrazole (0.326 g, 3.9 mmol) and potassium hydroxide (0.22 g, 3.9 mmol) was added. The reaction mixture refluxed for 12 h at 90 °C under N_2 atmosphere. After completion of the reaction, the reaction mixture was cooled to room temperature and the solvent was removed by rotavapor under vacuum. The resulting product was extracted using dichloromethane: water. The organic layer was dried over Na_2SO_4 afforded orange oil. Yield (0.565 g, 91%).

IR (KBr): ν = 3419.79, 2947.23, 2522.89, 1641.42, 1452.40, 1111.00, 1029.99, 599.86. ^{1}H NMR (400MHz, CDCl$_3$): δ 8.55(d, 1H), 7.63(t, 1H), 7.18(t, 1H), 6.80(d, 1H), 5.88(s, 1H), 5.35(s, 2H), 2.26(s, 3H). ^{13}C NMR (400MHz, CDCl$_3$): δ 156.90, 149.18, 139.03, 137.17, 130.87, 122.68, 121.66, 121.12, 105.83, 104.22, 57.08, 13.54. GC-MS (CHCl$_3$) m/z calcd for $C_{10}H_{11}N_3$: 173.10 found: 173.10.

2.2 Synthesis of bi-dentate (NN)Py^{Me}CoBr$_2$ bidentate complex.

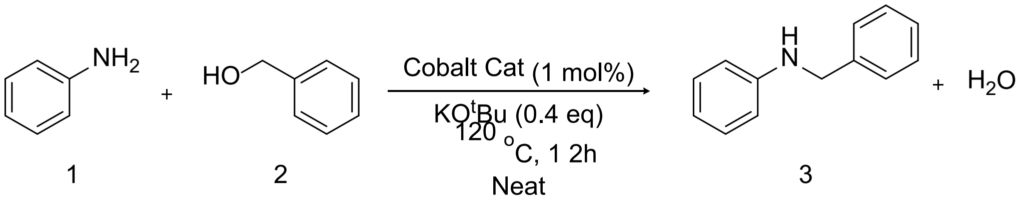


Scheme S2. Synthesis of Complex **I**

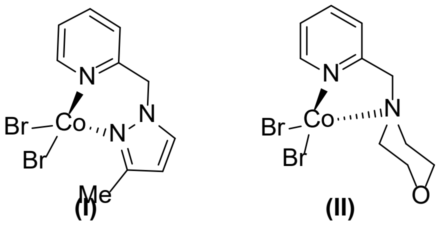
To an acetonitrile (3 mL) solution of ligand **L$_1$** (0.1 g, 5.7 mmol), anhydrous CoBr$_2$ (0.126 g, 5.7 mmol) in acetonitrile (3 mL) was added drop-wise. The reaction mixture was stirred for 3 h at room temperature. The resulting precipitate was filtered and dried. The precipitate was dissolved in methanol followed by diffusion of ether at room temperature afforded the blue color crystals of Co-L$_1$ in 2 days. Yield (0.131 g, 90%). IR (KBr): ν = 3444.87, 1635.44, 1444.68, 1311.59, 1111.00, 866.04, 765.74.

2.3 Optimization conditions

Table S1: Screening of Cobalt bidentate complex.[a]

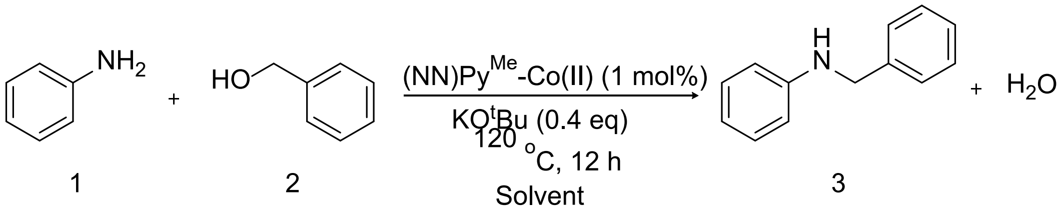


Entry	Catalyst	Yield of 3 (%)
1	[Co-II]	57
2	**[Co-I]**	**89**
3	-	20



Reaction conditions: **1** (0.5 mmol), **2** (0.55 mmol), Cobalt catalyst (1 mol%) and KO^{t}Bu (0.2 mmol) heated in neat condition at 120 °C (oil-bath temperature). [a]Isolated yield.

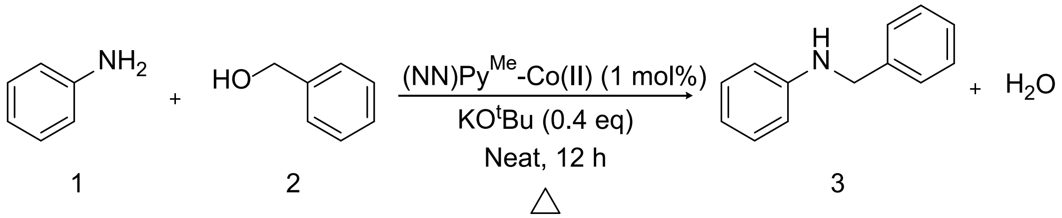
Table S2. Screening of solvent.[a]



Entry	Solvent	Yield of 3 (%)
1	**Neat**	**89**
2	Toluene	42
3	CH_3CN	27
4	THF	20
5	1,4 Dioxane	34
6	n-octane	53

Reaction conditions: **1** (0.5 mmol), **2** (0.55 mmol), (NN)Py^{Me}-Co(II) (1 mol%) and KO^{t}Bu (0.2 mmol) using 1 ml of solvent heated at 120 °C. [a]Isolated yield.

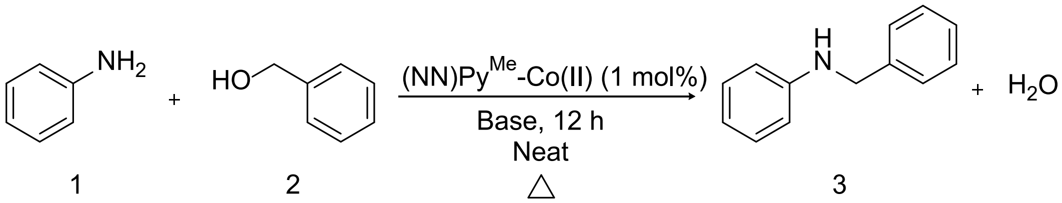
Table S3. Screening of temperature.^{a}



Entry	Temperature (°C)	Yield of 3 (%)
1	RT	NR
2	40 °C	NR
3	80 °C	NR
4	100 °C	45
5	**120 °C**	**89**

Reaction conditions: **1** (0.5 mmol), **2** (0.55 mmol), (NN)Py^{Me}-Co(II) (1 mol%) and KO^{t}Bu (0.2 mmol) heated in neat condition at different (oil-bath) temperatures. ^{a}Isolated yield.

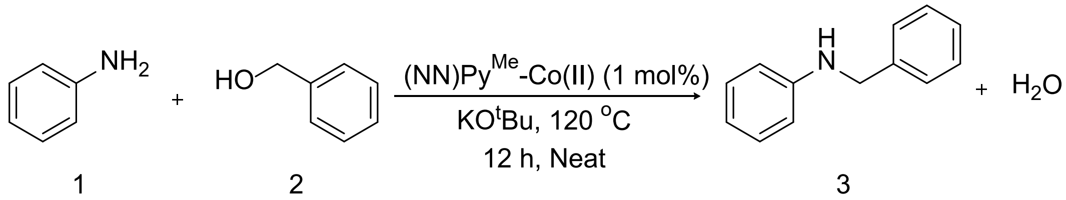
Table S4. Screening of Base.^{a}



Entry	Base	Yield of 3 (%)
1	**KO^{t}Bu**	**89**
2	KOH	34
3	K$_2$CO$_3$	52
4	NaO^{t}Bu	45
5	KH	NR
6	-	NR

Reaction conditions: **1** (0.5 mmol), **2** (0.55 mmol), (NN)Py^{Me}-Co(II) (1 mol%) and Base (0.2 mmol) heated in neat condition at 120 °C (oil-bath) temperatures. ^{a}Isolated yield.

Table S5. Screening of Base amount.[a]



Entry	KO^{t}Bu(eq)	Yield of 3 (%)
1	10 mol%	34
2	20 mol%	55
3	**40 mol%**	**89**
5	-	30

Reaction conditions: **1** (0.5 mmol), **2** (0.55 mmol), (NN)Py^{Me}-Co(II) (1 mol%) and Bases heated in neat condition at 120 °C (oil-bath) temperatures. [a]Isolated yield.

2.4 (NN)Py^{Me}CoBr$_2$ bidentate complex catalyzed *N*-alkylation of aniline with various benzyl alcohol

In an oven-dried screw cap reaction tube (15 mL), Aniline (0.5 mmol), benzyl alcohol derivates (0.55 mmol), [Co-I] (1 mol%), KO^{t}Bu (40 mol%) were added under argon flow in solventless condition. The tube was sealed tightly using Teflon and the reaction mixture was stirred with a magnetic stirring bar at 120 °C (oil-bath temperature) for 12 h. After completion of the reaction, the crude mixture was diluted with methanol and passed through a celite filter and followed by the preparation of slurry by adding little silica with the removal of the solvent under a vacuum. Finally, the crude mixture was purified by silica gel column chromatography (230 - 400 mesh size) using petroleum ether and ethyl acetate as an eluent to give the *N*-alkylated product. Yields were calculated for isolated pure products

2.5 (NN)Py^{Me}CoBr$_2$ bidentate complex catalyzed *N*-alkylation of benzyl alcohol with various aniline

In an oven-dried screw cap reaction tube (15 mL), benzyl alcohol derivates (0.5 mmol), aniline derivatives (0.55 mmol), [Cat-I] (1 mol%), KO^{t}Bu (40 mol%) were added under argon flow in solventless condition. The tube was sealed tightly using Teflon and the reaction mixture was stirred with a magnetic stirring bar at 120 °C (oil-bath temperature) for 12 h. After completion of the reaction, the crude mixture was diluted with methanol and passed through a celite filter and followed by the preparation of slurry by adding little silica with the removal of the solvent under a vacuum. Finally, the crude mixture was purified by silica gel column chromatography (230 - 400 mesh size) using petroleum ether and ethyl acetate as an eluent to give the *N*-alkylated product. Yields were calculated for isolated pure products.

2.6 (NN)Py^{Me}CoBr$_2$ bidentate complex catalyzed *N*-alkylation of aniline with an aliphatic alcohol

In an oven-dried screw cap reaction tube (15 mL), Aniline (0.5 mmol), aliphatic alcohol derivates (0.55 mmol), [Cat-I] (2 mol%), KO^{t}Bu (50 mol%) were added under argon flow in solventless condition. The tube was sealed tightly using Teflon and the reaction mixture was stirred with a magnetic stirring bar at 120 ^{o}C (oil-bath temperature) for 12 h. After completion of the reaction, the crude mixture was diluted with methanol and passed through a celite filter and followed by the preparation of slurry by adding little silica with the removal of the solvent under a vacuum. Finally, the crude mixture was purified by silica gel column chromatography (230 - 400 mesh size) using petroleum ether and ethyl acetate as an eluent to give the *N*-alkylated product. Yields were calculated for isolated pure products

2.7 (NN)Py^{Me}CoBr$_2$ bidentate complex catalyzed *N*-alkylation of biphenyl methanol with various aniline

In an oven-dried screw cap reaction tube (15 mL), biphenyl methanol (0.6 mmol), aniline derivatives (0.5 mmol), [Cat-I] (1.5 mol%), KO^{t}Bu (50 mol%) were added under argon flow in toluene solvent (1 mL). The tube was sealed tightly using Teflon and the reaction mixture was stirred with a magnetic stirring bar at 140 ^{o}C (oil-bath temperature) for 24 h. After completion of the reaction, the crude mixture was diluted with methanol and passed through a celite filter and followed by the preparation of slurry by adding little silica with the removal of the solvent under a vacuum. Finally, the crude mixture was purified by silica gel column chromatography (230 - 400 mesh size) using petroleum ether and ethyl acetate as an eluent to give the *N*-alkylated product. Yields were calculated for isolated pure products.

2.8 $(NN)Py^{Me}CoBr_2$ bidentate complex catalyzed *N*-alkylation of diamine with benzyl alcohol

In an oven-dried screw cap reaction tube (15 mL), benzyl alcohol (1mmol, 2mmol respectively), diamine (0.5 mmol), [Cat-I] (1 mol%), KO^{t}Bu (50 mol%) were added under argon flow in neat condition. The tube was sealed tightly using Teflon and the reaction mixture was stirred with a magnetic stirring bar at 120 °C (oil-bath temperature) for 12 h. After completion of the reaction, the crude mixture was diluted with methanol and pass through a celite filter and followed by preparation of slurry by adding little silica with removal of solvent under vacuum. Finally, the crude mixture was purified by silica gel column chromatography (230- 400 mesh size) using petroleum ether and ethyl acetate as an eluent to give the *N*-alkylated product. Yields were calculated for isolated pure products.

3. Characterization $(NN)Py^{Me}CoBr_2$ Bidentate Complex (II)

3.1 FT-IR analysis

The FT-IR spectra of ligand (L1) exhibit a characteristic (C=N) stretching vibration band at 1641.42 cm^{-1} respectively. The corresponding $(NN)Py^{Me}CoBr_2$ complexes show the C=N stretching vibration band at 1635.44 cm^{-1} respectively. After complex formation, the shift of C=N stretching frequency to the lower wave number is due to the reduction of the electron density at the nitrogen centre in the ligands. Therefore, the shift of C=N stretching frequency found in all Co-complexes confirms the successful coordination of nitrogen atoms of ligand to the cobalt (II) centre (Figures S1 and S2).

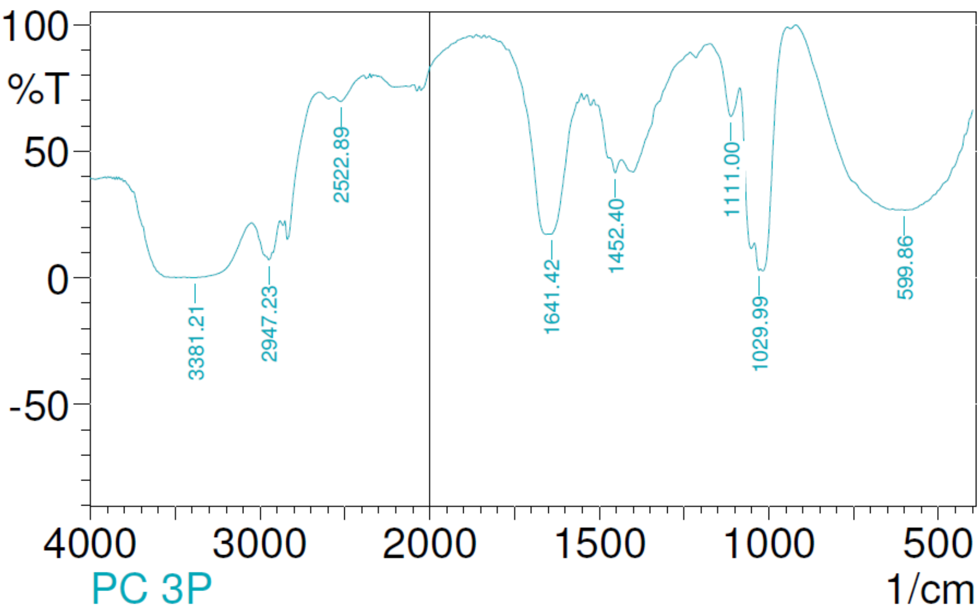


Figure S1. FT-IR Spectrum of ligand L2.

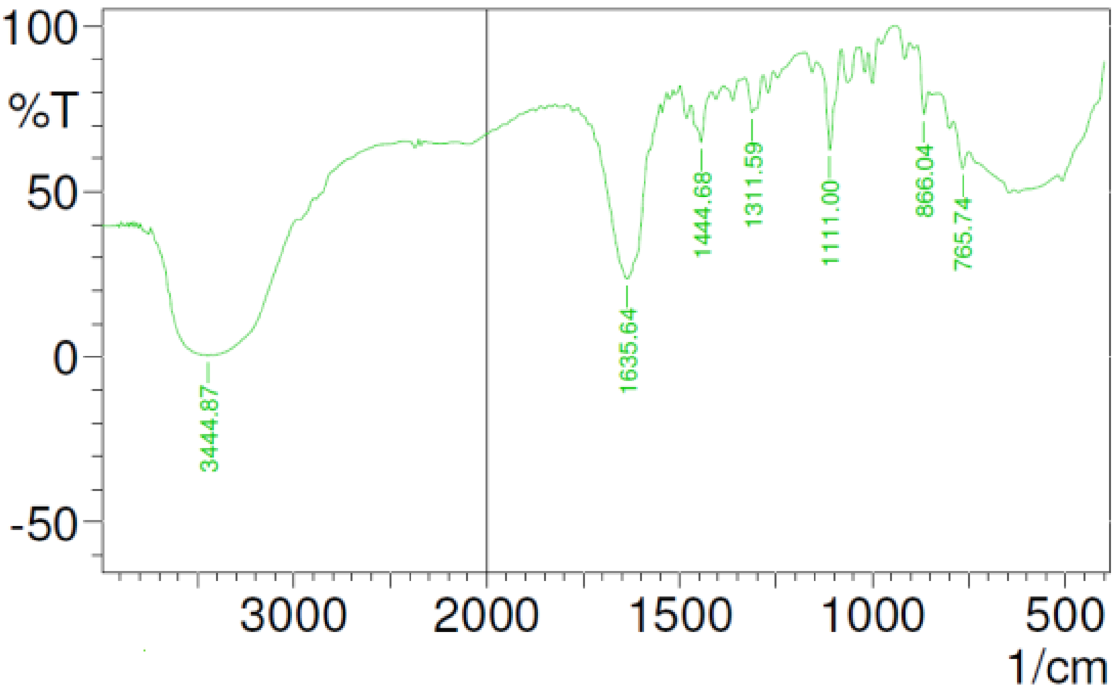


Figure S2. FT-IR Spectrum of Complex (II).

3.2 Absorption spectra analysis

The UV-visible absorption spectra for ligands and corresponding metal complexes were recorded in acetonitrile (1x10^{-5} M) at 298 K, as shown in Figure S3. The free ligand (NN)Py^{Me} displays the absorption bands at 212 nm and 258 nm. The Cat 1 complexes ((NN)^{PyMe}$CoBr_2$) exhibit the absorption band at 256, 296, 584, and 656 nm. Both the free ligand and its complex exhibit characteristic absorption bands in the range of 212-256 nm, and 256-296 nm could be attributed to π-π^* and n-π^* transitions. Complex (NN)Py^{Me}CoBr$_2$ exhibit low energy (longer wavelength) absorption bands at 584 nm and 656 nm were assigned to $^4A_2(F)\rightarrow{}^4T_1(P)$ and $^4A_2(F)\rightarrow{}^4T_1(F)$ transitions, respectively. Therefore, the absorption spectra analysis confirms the coordination of the ligand with the Co^{2+} metal center (Figure S3).

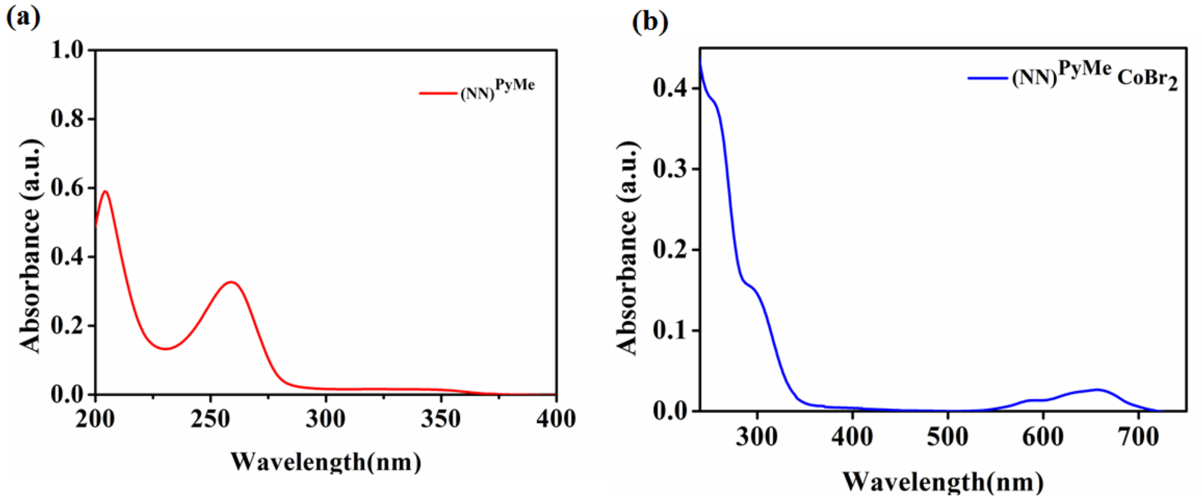


Figure S3. UV-Visible absorption spectra, (a) Free ligand (NN)Py^{Me} and (b) complex (NN)Py^{Me}CoBr$_2$ in CH_3CN ($1x10^{-5}$ M) at 298 K.

3.3 NMR analysis

^{1}H and ^{13}C NMR spectrum of free ligands (L1) were recorded in Deuterated chloroform ($CDCl_3$). ^{1}H NMR spectra of ligand L2 exhibits aromatic protons are resonated between 8.55 to 5.88 ppm and aliphatic (–CH_3) protons present at 2.26 and (–CH_2) 5.35 ppm.^{13}C NMR spectrum of free ligand (L1) exhibits the aromatic ring (Ar-C) carbons range between 157.94 to 104.11ppm and aliphatic (-CH_2) carbons range between 66.86 to 53.73 ppm and methyl (-CH_3) carbons present at 13.54 to 11.04 ppm (Figure S4).

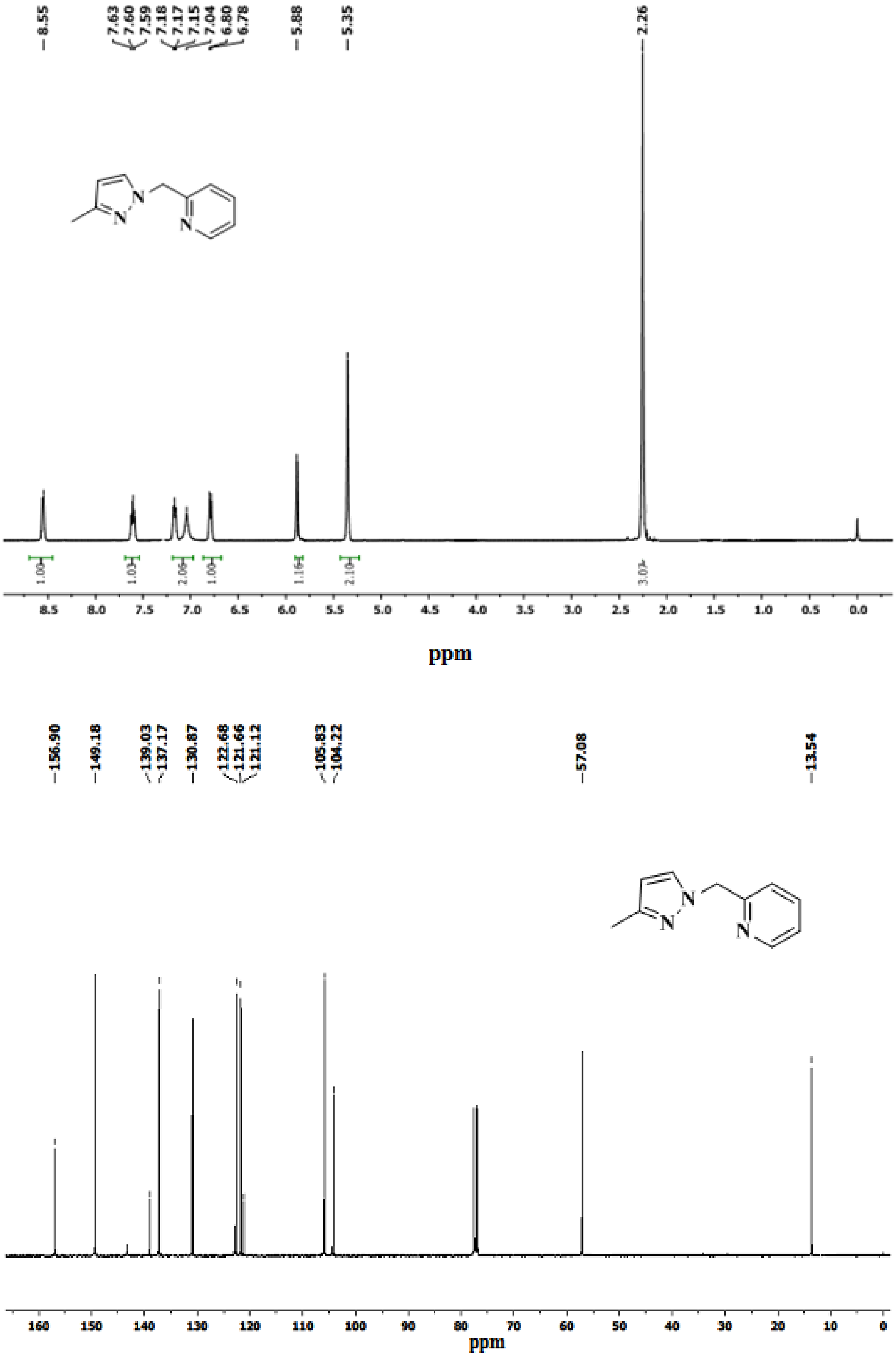


Figure S4. ^{1}H and ^{13}C NMR spectrum of L1

3.4 Mass analysis

The mass spectrum of free ligands (L1) was recorded in chloroform (Figure S5) and the Complex was recorded in Acetonitrile (Figure S6).

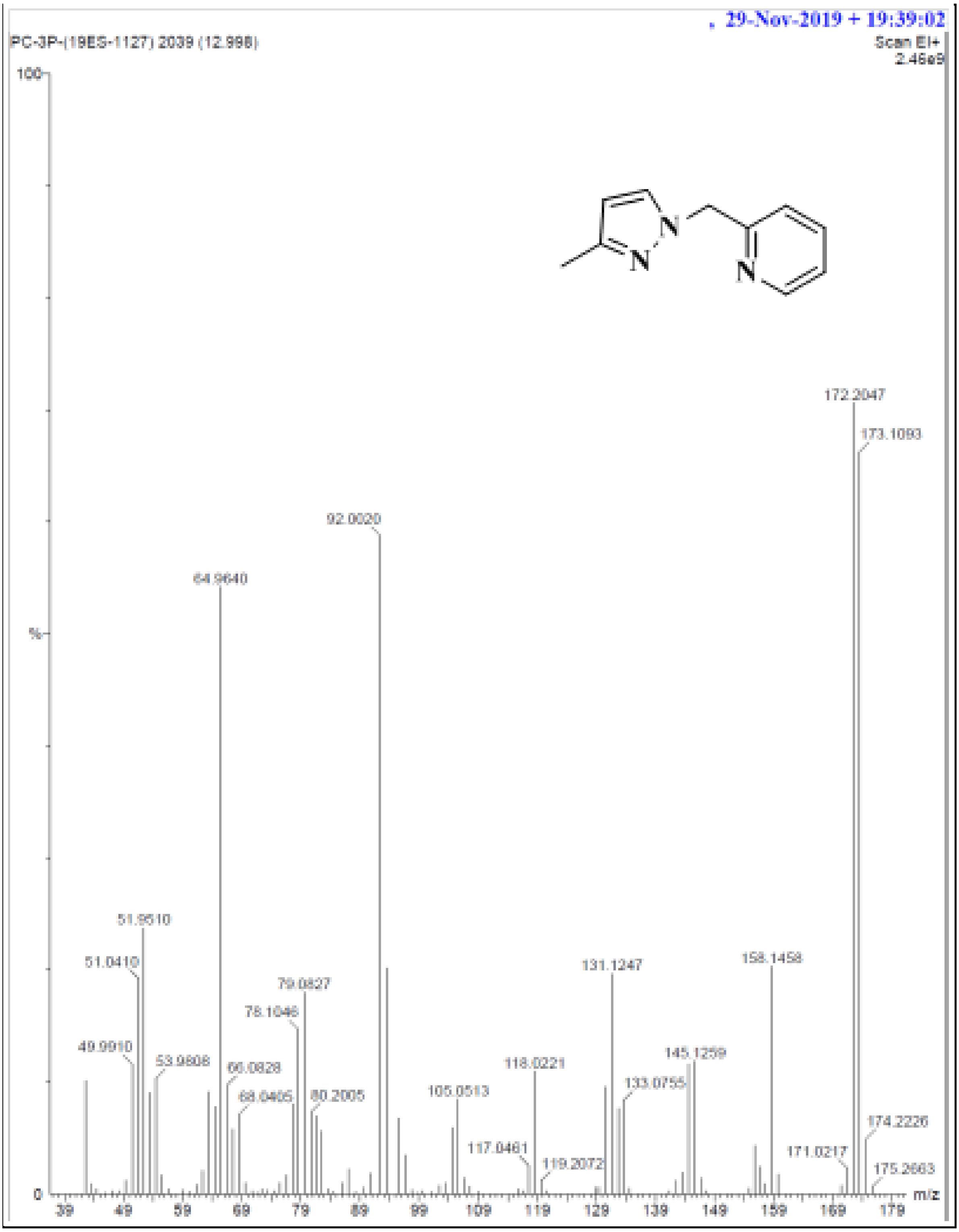


Figure S5. Mass spectrum of L1

Compound Details

Cpd. 1: C10 H11 Br2 Co N3

Name	Formula	RT	RI	Mass	Score	Algorithm	Lib/DB
	C10 H11 Br2 Co N3	0.549		389.8658	97.03	FBF	

Species	m/z	Score (Lib)	Num Spectra	Score (DB)	Score (Tgt)	Diff (ppm)
(M+NH4)+ (M+Na)+ (M+K)+	407.8995 412.8551 428.8289				97.03	1.65

Compound Spectra

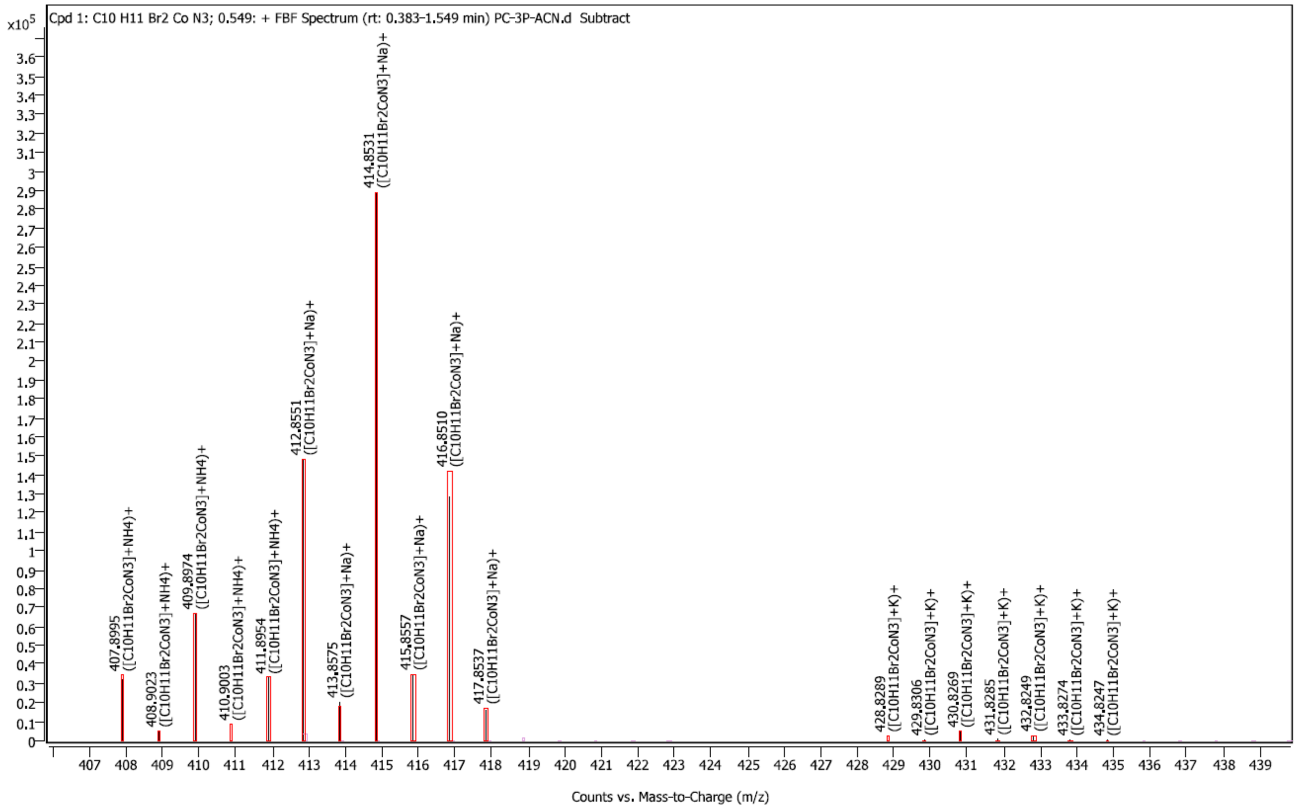


Figure S6. ESI-MS of Co-complex (II)

3.5 X-ray analysis

Reaction of L1 with $CoBr_2$ afforded the mono-nuclear tetra-coordinated complex $(NN)Py^{Me}CoBr_2$. The crystals of $(NN)Py^{Me}CoBr_2$ suitable for single crystal X-ray crystallography were obtained by vapour diffusion of diethyl ether into methanol solution of complex at room temperature afforded blue color crystals. Complex $(NN)^{PyMe}CoBr_2$ crystallizes in the triclinic system in the space group *P-1*. The crystallographic data are provided in Table S1. The crystal structure analysis divulges that, the Co(II) center in $(NN)Py^{Me}CoBr_2$ is displayed four coordinated, distorted tetrahedral structures with two nitrogen donor atoms of ligand (L1) and two bromide ions (Figure S6). The relevant bond angles of Co(II) centre are in the range of 110.51(13)° – 117.5(3)°. Selected bond length of Co(1)-N(2), Co(1)-N(1), Co(1)-Br(2) and Co(1)-Br(1) are found at 2.03(4), 2.00(4), 2.35(10) and 2.35(10) respectively. The bong angle of N(1)-Co(1)-N(2), N(2)-Co(1)-Br(2), N(1)-Co(1)-Br(2), N(2)-Co(1)-Br(1) and N(1)-Co(1)-Br(1) are found at 92.28(17) °, 110.72(13) °, 113.33(12), 116.66(12) and 115.51(12), respectively (Figure S7).

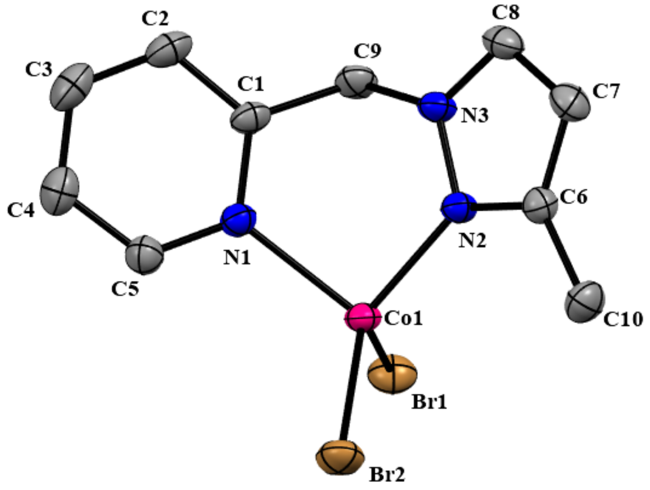


Figure S7. Single crystal X-ray structure of (NN)$Py^{Me}CoBr_2$.

Table S1. Crystal data and structure refinement for complex (NN)$Py^{Me}CoBr_2$

(NN)$Py^{Me}CoBr_2$ **(Complex I)**	
Empirical formula	$C_{10}H_{11}Br_2CoN_3$
Formula weight	391.97
Temperature	273.15 K
Wavelength	0.610 Å
Crystal system	Triclinic
Space group	*P-1*
Unit cell dimensions	a = 7.941(2) Å b = 8.311(2) Å c = 10.803(3) Å
Volume	654.1(3) $Å^3$
Z	2
Density	0.990 Mg/m3
Absorption coefficient	4.063 mm^{-1}
Theta range for data collection	5.242 to 55.188°
Reflections collected	3031

Refinement method	Full-matrix least-squares F^2
Data / restraints / parameters	3031 / 0 / 146
Final R indices [I>2sigma(I)]	R1 = 0.0447, wR2 = 0.1679

Table S2. Selected bond lengths [Å] and bond angles [°] for complex $(NN)^{PyMe}CoBr_2$

Co(1)-N(1)	2.0499 (19)	N(2)-Co(1)-Br(1)	116.66(12)
Co(1)-N(2)	2.0060 (18)	Br(1)-Co(1)-Br(2)	112.60(4)
Co(1)-Br(1)	2.3638 (6)	C(6)-N(1)-C(5)	104.7(4)
Co(1)-Br(2)	2.3636 (6)	C(6)-N(1)-Co(1)	137.0(5)
N(1)-C(1)	1.353(3)	C(5)-N(1)-Co(1)	118.0(3)
N(1)-C(5)	1.340(3)	C(3)-N(2)-C(11)	120.3(4)
N(2)-C(6)	1.343 (3)	C(3)-N(2)-Co(1)	119.2(4)
N(3)-C(8)	1.341 (3)	C(1)-N(1)-Co(1)	115.46(18)
N(1)-Co(1)-N(2)	92.28(17)	C(4)-N(1)-Co(1)	111.83(17)
N(1)-Co(1)-Br(2)	113.33(12)	C(10)-N(2)-C(6)	119.6(2)
N(2)-Co(1)-Br(2)	110.72(13)	C(10)-N(2)-Co(1)	127.9(2)
N(1)-Co(1)-Br(1)	115.51(12)		

3.6 Magnetic moment calculation and determination of the number of unpaired electrons in the complex (Evans Method)

Evans' method of ^{1}H-NMR was performed to determine the number of unpaired electrons (spin state) in complex I at room temperature. A WILMAD® coaxial insert (with a sealed capillary) tube containing only $CDCl_3$ solvent (with 0.1% TMS) was inserted into the normal NMR tubes containing the complex I (4.0 mM, with 0.1% TMS). We have calculated the chemical shift value of the TMS peak in the presence of complex I with respect to that of the TMS peak in the outer NMR tube. The magnetic moment was calculated using the given equation,

$$\mu_{eff} = 0.0618 *(\Delta\nu * T/2*f*M)^{1/2} \text{ BM}$$

Where f = oscillator frequency (MHz)

T= absolute temperature

M= molar concentration of complex

$\Delta\nu = 0.025*400 = 10$ Hz

$\mu_{eff} = 1.88$ BM

1 unpaired electron

$\Delta\nu$= difference in frequency (Hz)

between the two TMS signals

The calculated magnetic moment of complex I was determined to be 1.88 BM in $CDCl_3$ at RT, suggesting 1 unpaired electron in Co^{2+} centre of complex I (Figure S8).

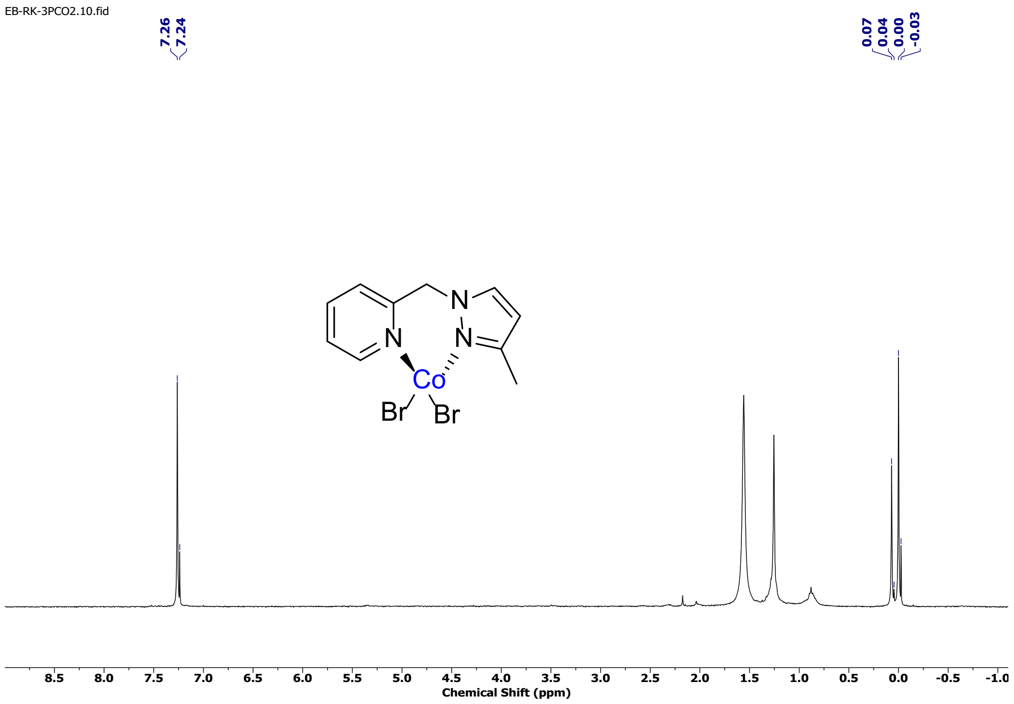


Figure S8. ^{1}H-NMR (400 MHz) spectra of isolated complex (4 mM) in $CDCl_3$ (0.1 % TMS).

3.7 Characterization of the catalyst after the catalytic reaction:

A detailed characterization of the catalyst after the catalytic reaction was performed using UV-Vis spectroscopy (Figure S9) and Powder XRD analyses (Figure S10).

3.7.1 Analysis of $(NN)^{PyMe}$Cobalt Catalyst using UV-Vis Spectroscopy

The UV-visible absorption spectra of the metal complex in acetonitrile were measured at different stages of the reaction. The initial spectrum of the metal complex (0.01 M) was obtained at room temperature (298 K). Then, benzyl alcohol and aniline were added in stoichiometric amounts and the spectrum was recorded again. The spectra in the visible region showed no significant changes, while the spectra in the UV region exhibited a noticeable shift. The reaction was further promoted by adding base (KO^{t}Bu) and the spectrum showed a remarkable shift in both regions at room temperature. Finally, the reaction mixture was refluxed at 120 ^{o}C for 1 hr and the final spectrum was obtained. The UV-visible spectra of the reaction mixture after the first and third cycles show no significant difference, implying that the catalyst generated in situ retains its activity throughout the reaction. This demonstrates the reusability of the cobalt-based homogeneous catalytic system for this reaction.

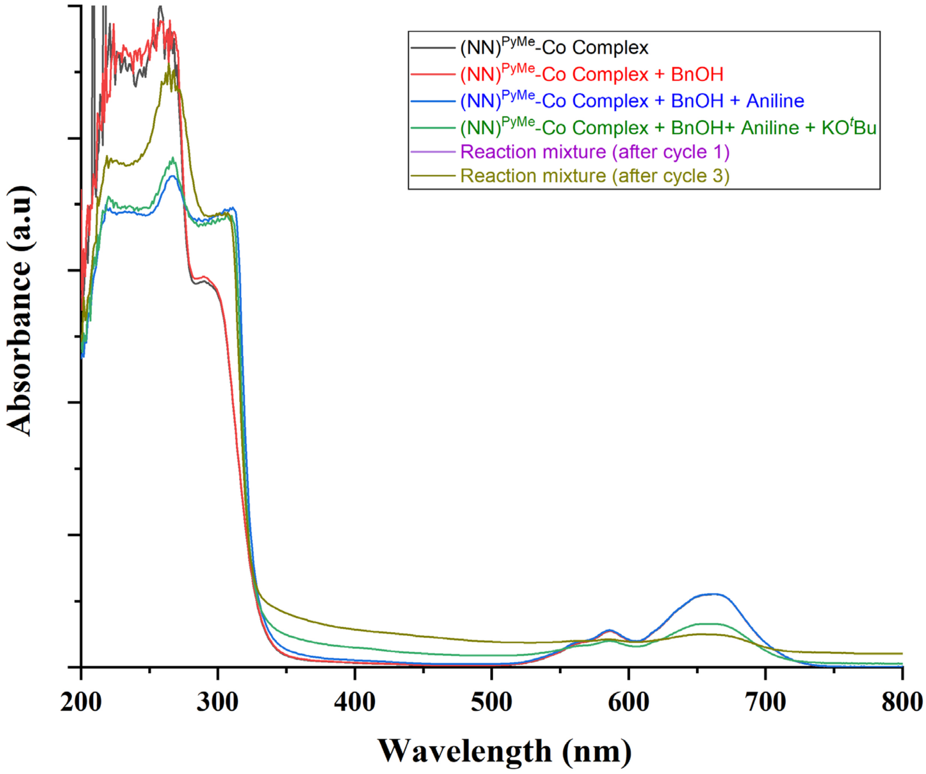


Figure S9. Analysis of (NN)Py^{Me}Cobalt Complex using UV-Vis Spectroscopy.

3.7.2. Analysis of (NN)^{PyMe}Cobalt Catalyst using Powder XRD

The Powder XRD technique was used to compare the (NN)Py^{Me}Cobalt complex with the $CoBr_2$ and the catalyst after the reaction. The powder patterns of the three samples were recorded at room temperature (298 K) and matched with the theoretical patterns from the Single Crystal XRD data. The results showed that the (NN)Py^{Me}Cobalt complex had a good agreement with the theoretically stimulated pattern (CIF) of the Single Crystal XRD, confirming its structure and purity. However, the catalyst exhibited a significant shift in the 2θ values after the reaction, indicating a structural change. The catalyst after the 3rd cycle of the reusability test was obtained by removal of the volatiles under vacuum and washing with pentane (2 x 1 mL), a dark brown powder was isolated and analyzed by Powder XRD. The PXRD patterns of the first and the third cycles are similar, which confirms the activity and reusability of the present cobalt catalyst for the *N*-alkylation reaction. This demonstrates the stability of the cobalt-based homogeneous catalytic system.

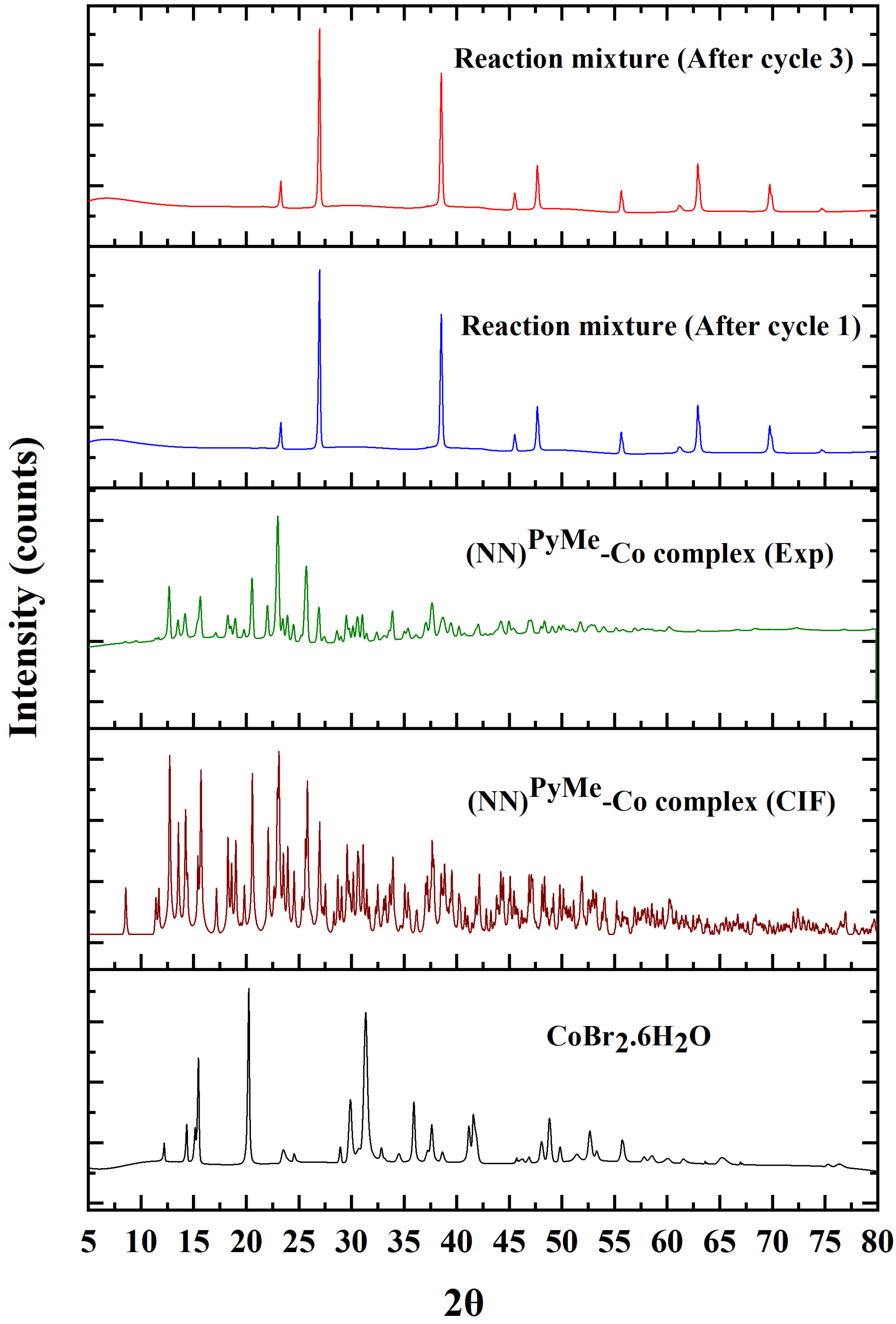
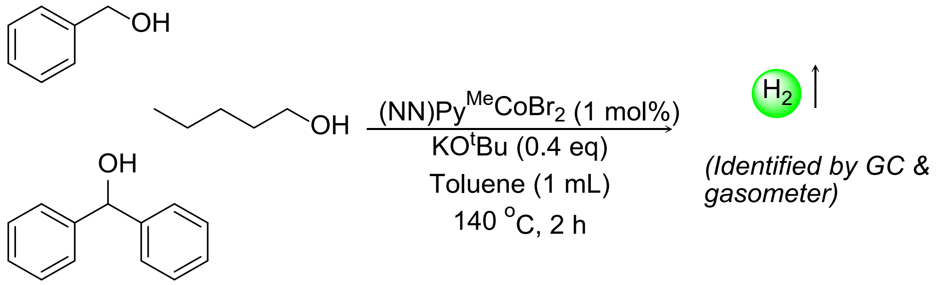


Figure S10. Powder XRD Pattern of $(NN)Py^{Me}$Cobalt Complex at RT (298K).

4. Mechanistic Investigation

4.1 H_2 detection

In an oven-dried screw cap reaction tube (15 mL), primary and secondary alcohol (0.5 mmol), KO^{t}Bu (0.2 mmol), Cat-(I) catalyst (1 mol%) and toluene (1 mL) were added in a gentle stream of argon. Then the reaction mixture was stirred with a magnetic stirring bar at 140 °C for 2 h. After completion of the reaction, the crude mixture was cooled to room temperature followed by the sample submitted for gasometer analysis for detection of H_2 gas (Figure S11).



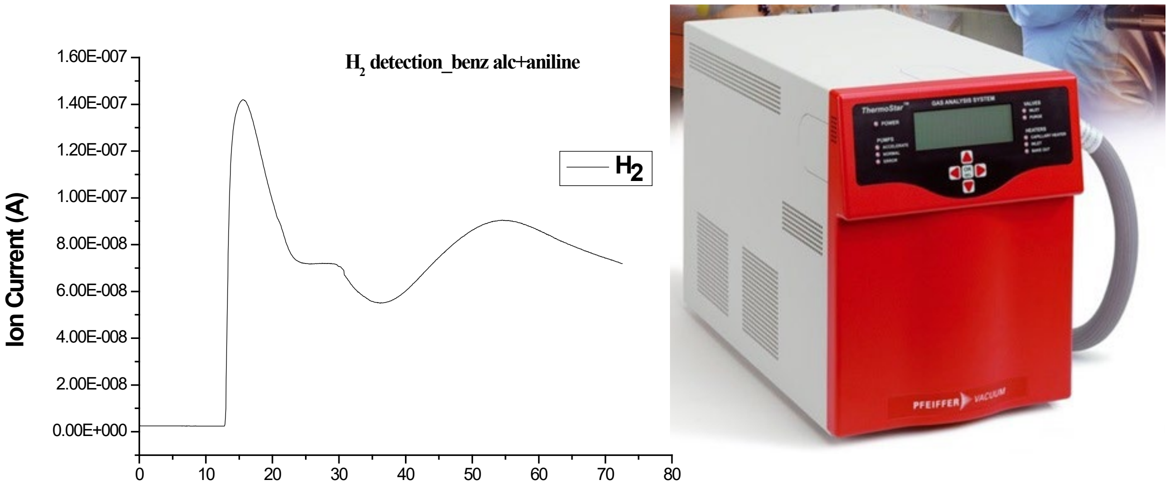


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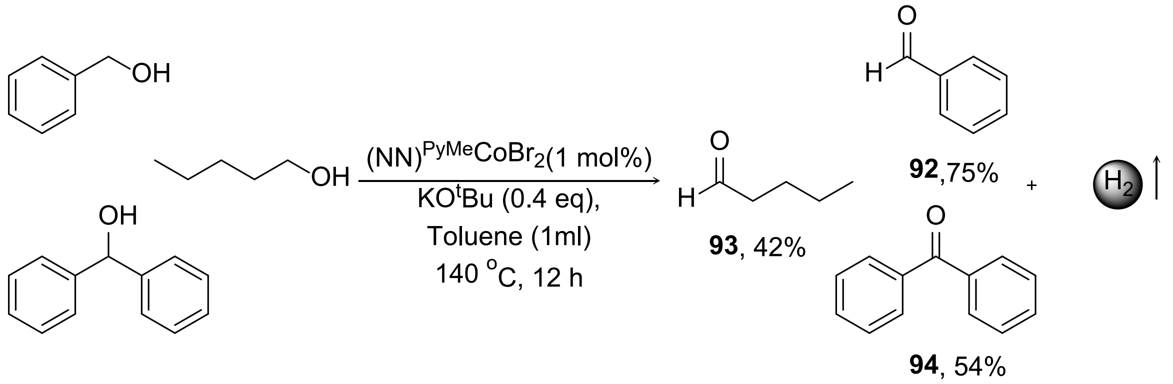
Figure S11. Gasometer analysis for the detection of hydrogen.

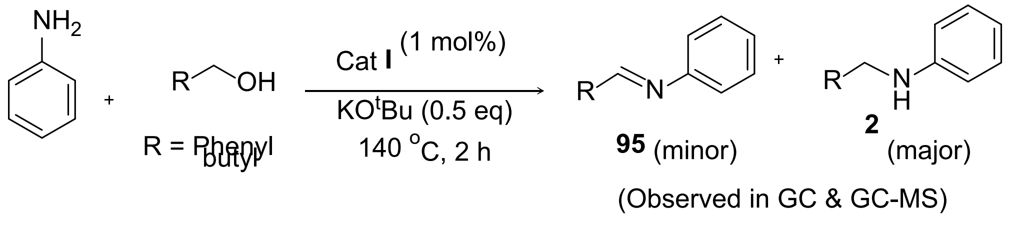
4.2 Determination of dehydrogenative product

In an oven-dried screw cap reaction tube (15 mL), primary and secondary alcohol (0.5 mmol), KO^{t}Bu (0.2 mmol), Cat-I catalyst (1 mol%) and toluene (1 mL) were added in a gentle stream of argon. Then the reaction mixture was stirred with a magnetic stirring bar at 140 °C for 12 h. After completion of the reaction, the crude mixture was filtered through a celite filter and washed with ethyl acetate, followed by the solvent being removed under vacuum and finally the residue was purified by silica gel column chromatography (230–400 mesh size) using petroleum-ether and ethyl acetate as an eluent to give the corresponding carbonyl product in the range of 42-75% yield.



4.3 Detection of intermediate aldimine

In an oven dried screw cap reaction tube (15 mL), Aniline (0.5 mmol) primary alcohol (0.55 mmol), KO^tBu (0.2 mmol), and Cat-(I) catalyst (1 mol%) were added in a gentle stream of argon. Then the reaction mixture was stirred with a magnetic stirring bar at 140 °C for 2 h. Subsequently, the sample was cooled to room temperature and filtered through celite filter and submitted to GC and GC-MS analysis. The corresponding imine intermediate (minor), and *N*-alkylated product (major) were identified from the reaction mixture.



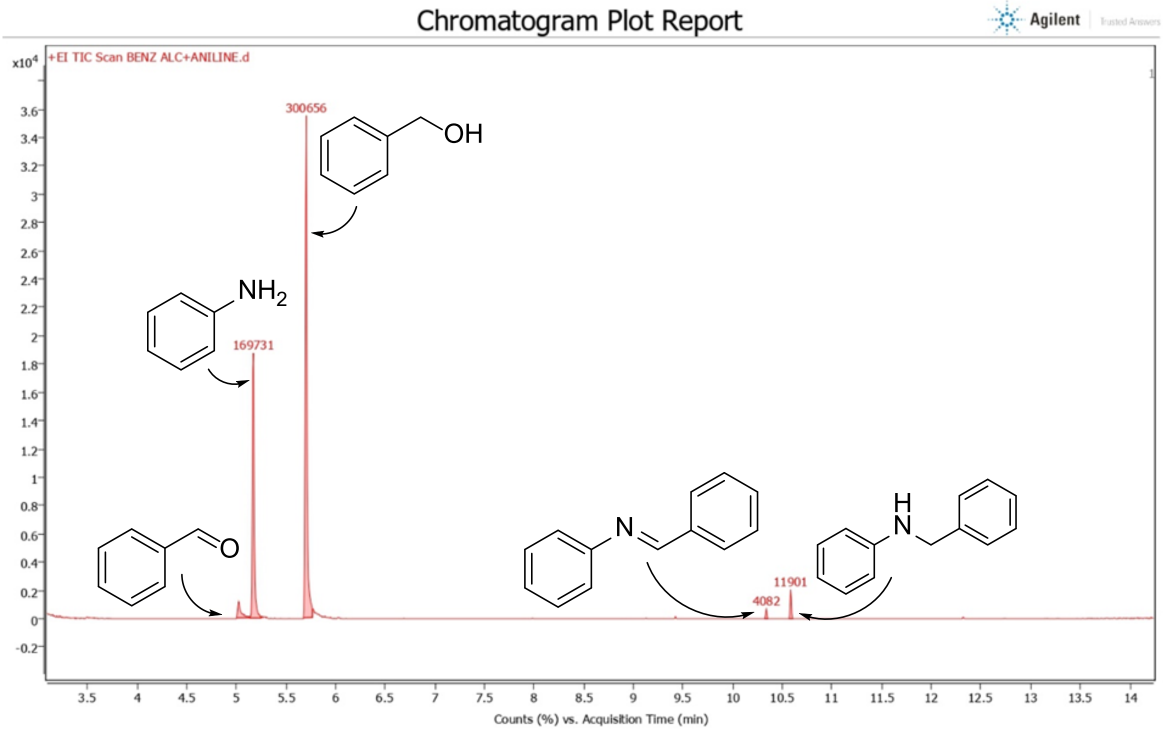
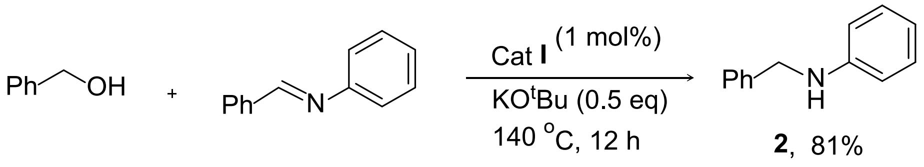


Figure S12. GC-MS analysis for the detection of intermediate aldimine

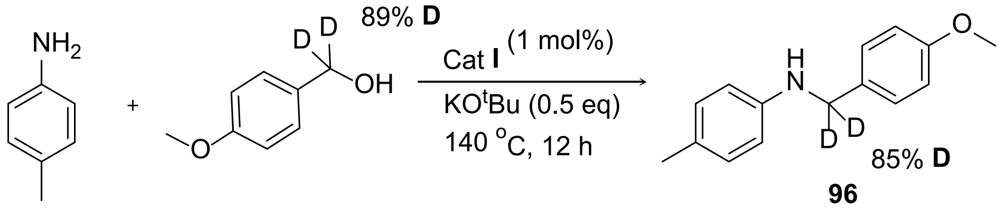
4.4 Hydrogenation of intermediate aldimine

In an oven dried screw cap reaction tube (15 mL), Benzyl alcohol (0.75 mmol), N,1-diphenylmethanimine (0.5 mmol), KO^{t}Bu (0.25 mmol), Cat-(I) catalyst (1 mol%) were added in a gentle stream of argon. Then the reaction mixture was stirred with a magnetic stirring bar at 140 °C for 12 h. After completion of the reaction the crude mixture was filtered through celite filter and washed with methanol, followed by the solvent was removed under vacuum and finally the residue was purified by silica gel column chromatography (230-400 mesh size) using petroleum-ether and ethyl acetate as an eluent to give the hydrogenated product in 81% yield.



4.5 Dueterium labelling experiments

To an oven-dried 15 mL screw-capped vial, Toluidine (0.5 mmol), 4-methoxybenzyl (deuterated) alcohol (0.55 mmol), KO^{t}Bu (0.5 mmol), Cat-(I) catalyst (1 mol%) were added under a gentle stream of argon. Then the reaction mixture was stirred for 12 h at 140 °C. After completion of the reaction, the crude mixture was filtered through a celite pad and washed with methanol followed by solvent was removed under vacuum. The residue was purified by column chromatography on silica gel (eluent: pet ether) to afford the 85% yield of N-alkylated deuterated product.



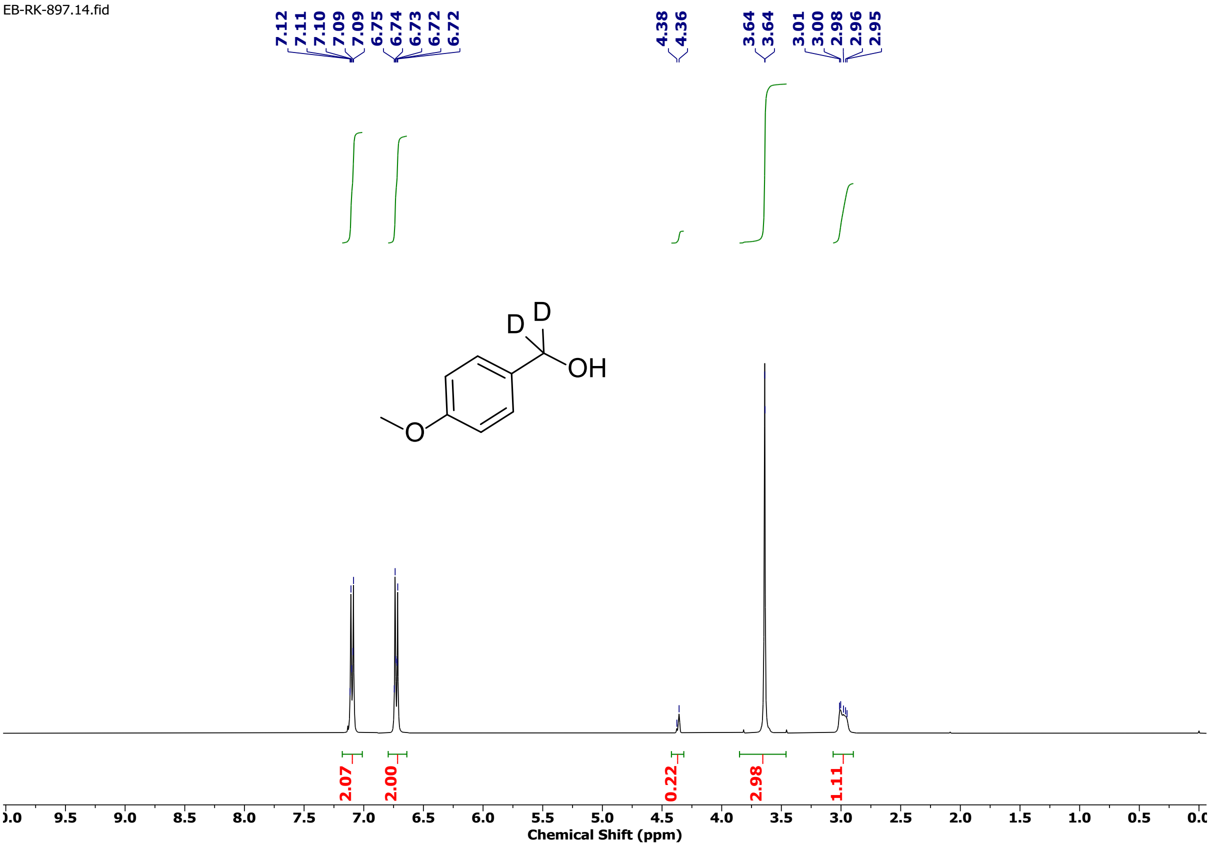


Figure S13. ^{1}H NMR of 4-methoxybenzyl (deuterated) alcohol

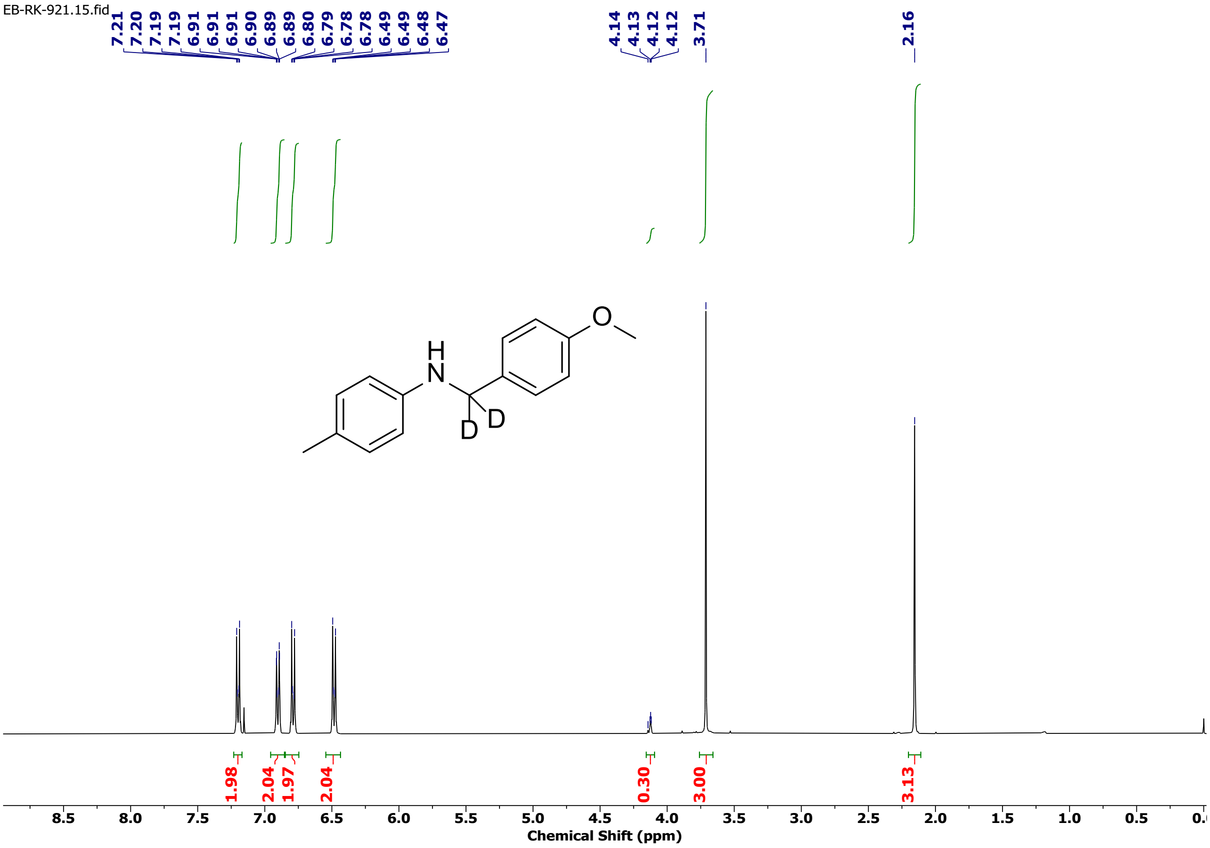
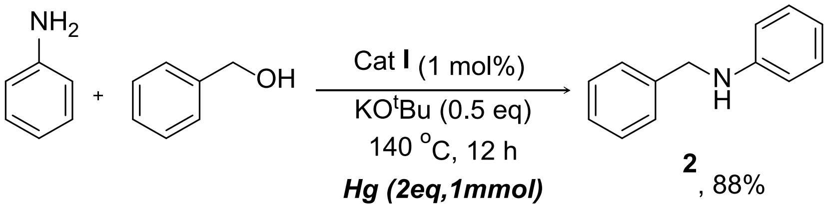


Figure S14. ^{1}H NMR of N-alkylated deuterated product

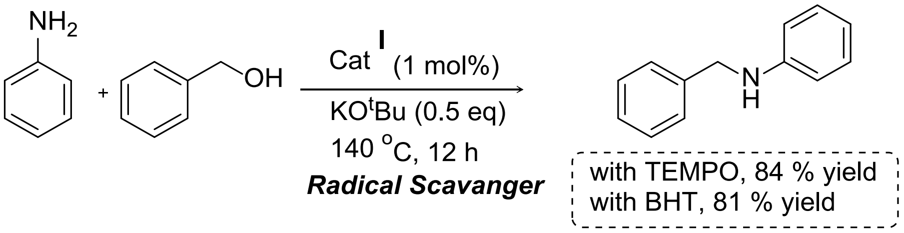
4.6 Mercury Test/ Homogenous test

To an oven-dried 15 mL screw-capped reaction tube, benzyl alcohol (0.55 mmol), aniline (0.5 mmol), KO^{t}Bu (0.5 mmol), Co- (I) catalyst (1 mol%), and mercury (2eq, 1mmol) were added under a gentle stream of argon. Then the reaction mixture was stirred for 12 h at 140 °C. After completion of the reaction, the crude mixture was cooled to room temperature followed by being filtered through a celite pad with several washings (3 x 3 mL methanol) and concentrated *in vacuo*. The residue was purified by column chromatography on silica gel (eluent: pet ether/ ethyl acetate) to afford the desired product in 88% yield.



4.7 Radical trapping experiments

To an oven-dried 15 mL screw-capped reaction tube, benzyl alcohol (0.55 mmol), aniline (0.5 mmol), KO^{t}Bu (0.5 mmol), Cat-(I) catalyst (1 mol%), and TEMPO/BHT (1 eq) were added under a gentle stream of argon. Then the reaction mixture was stirred for 12 h at 140 °C. After completion of the reaction the crude mixture was cooled to room temperature followed by filtered through a celite pad with several washings (3 x 3 mL methanol) and concentrated *in vacuo*. The residue was purified by column chromatography on silica gel (eluent: pet ether/ ethyl acetate) to afford the desired product in 84/ 81% yield.



4.8 Recyclability of the catalyst

Catalytic efficiency was assessed by determining ^{1}H NMR yields in each cycle. For example, in cycle 1, *p*-toluidine (0.2 mmol), benzyl alcohol (0.25 mmol), KO^{t}Bu (40 mmol%), [Co-I] (1 mol%) were heated at 120 °C (silicone oil-bath temperature) under an argon atmosphere in a reaction tube. After 12 h, the yield of the *N*-alkylated product (*N*-benzyl-4-methylaniline, **3**) was analyzed (95% yield by ^{1}H NMR using dibromomethane as an internal standard). After 1st cycle, to that same reaction mixture was added *p*-toluidine (0.2 mmol), benzyl alcohol (0.25 mmol), KO^{t}Bu (40 mmol%) and continued the heating for a further 12 h (2nd cycle yield is 63%). Thus, this procedure was repeated thrice (without additional the (NN)Py^{Me}cobalt complex **I**), and the yield of the *N*-alkylated amine **3** was analyzed for each cycle (3rd cycle yield is 46%).

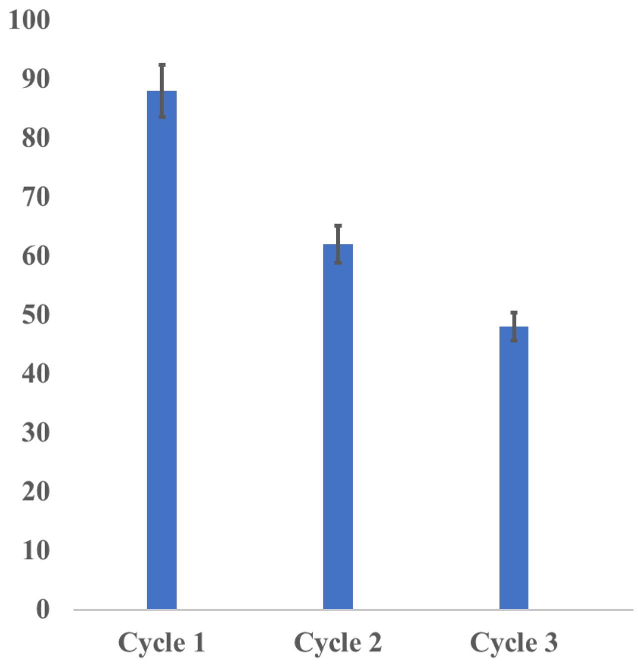
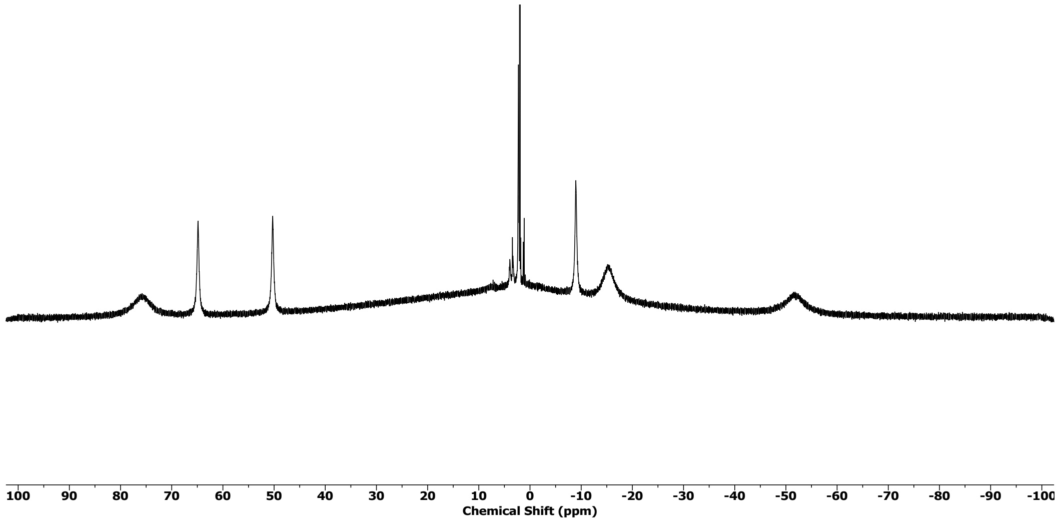


Figure S15. Reusable cobalt-based heterogeneous catalyst *N*-alkylation reaction.

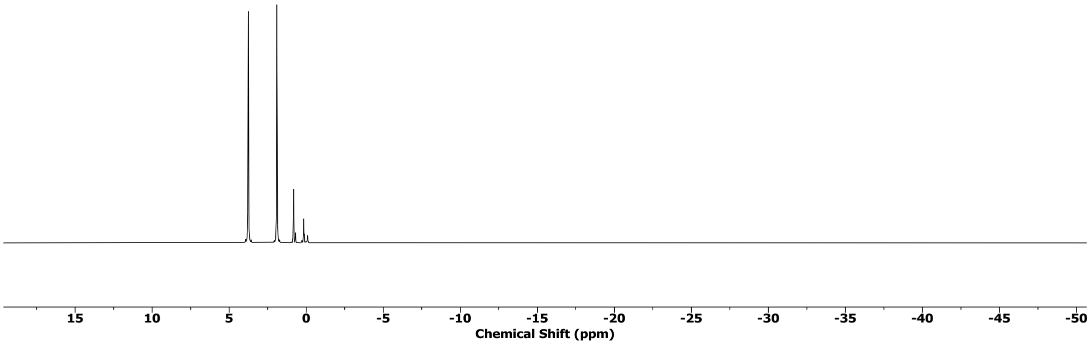
Various reports describe that the Co-hydride complex is an important intermediate in the dehydrogenation and related reactions (C-C and C-N formation) using amine and alcohol as alkylating agents *via* the borrowing hydrogenation strategy (Ref: *Chem. Rev*. **2019**, *119*, 2876 by Q.Liu and workers, *Chem. Rev*. **2019**, *119*, 2681 by S. Schneider, *Coord. Chem. Rev*. **2022**, *451*, 214257 by S. Kundu). Recently, our research group also contributed to cobalt catalysis, *Catal. Sci. Technol*. **2018**, *8*, 3469; *Chem. Commun*. **2018**, *54*, 90; *Catal. Sci. Technol*. **2018**, *8*, 428; *Synthesis* **2017**, *49*, 3957. Plausibly, we predict the *in situ* formation of a Co-H intermediate from alcohol; however, it is very challenging to isolate due to its highly unstable nature. The Chirik group reported similar cobalt-hydride species using bis(silylene)pyridine Cobalt(III) precatalysts using strong reducing agents like $NaHBEt_3$ and $LiHBEt_3$ (*Organometallics* **2020**, *39*, 2763). Using the same reaction procedure, several reactions were performed for the isolation and characterization of Co-H species with our catalytic system, using NNPyMe-Co(II) bi-dentate complex and $LiHBEt_3$ as a hydride donor. The detailed experiments are as follows.

Experiment 1. Characterization of NN^{PyMe}-Co(II) complex after reaction with $LiHBEt_3$

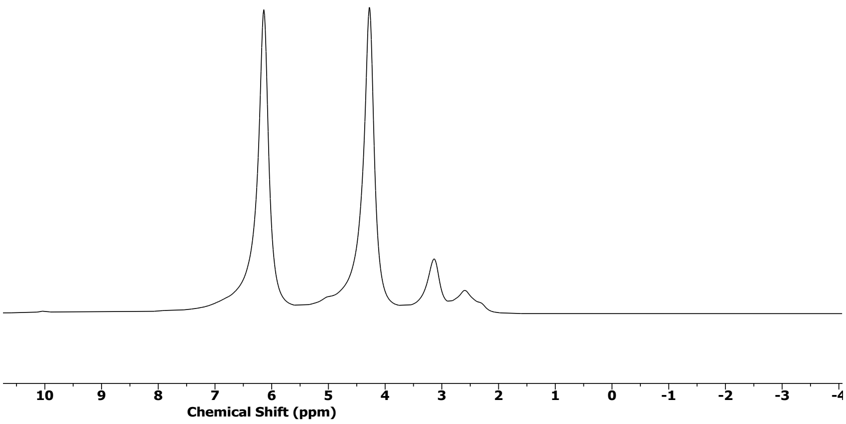
Step A. The long-range ^1H NMR of NN^{PyMe}-Co(II) complex in Acetonitrile (D3).



Step B. The ^1H NMR of $LiHBEt_3$ in Acetonitrile (D3).

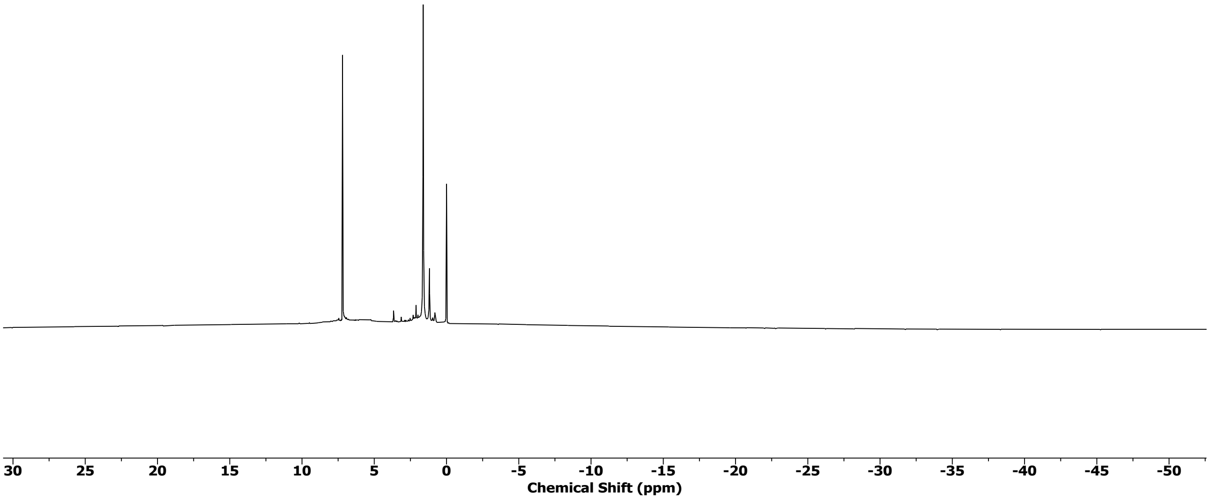


Step C. $LiHBEt_3$ (0.2000 mmol, 0.20 mL of a 1.0 M solution in toluene) was added to acetonitrile solution of NN^{PyMe}-Co(II) complex (0.1 mmol, 40 mg) at -90 °C. in 5 mL scintillation vial in a nitrogen filled glovebox. the resulting brown solution was let to stir at room temperature for 30 minutes and filtered through celite. Removal of the volatiles under vacuum and washing with pentane (2 x 1 mL) afforded a dark brown powder that was analyzed using ^1H NMR.



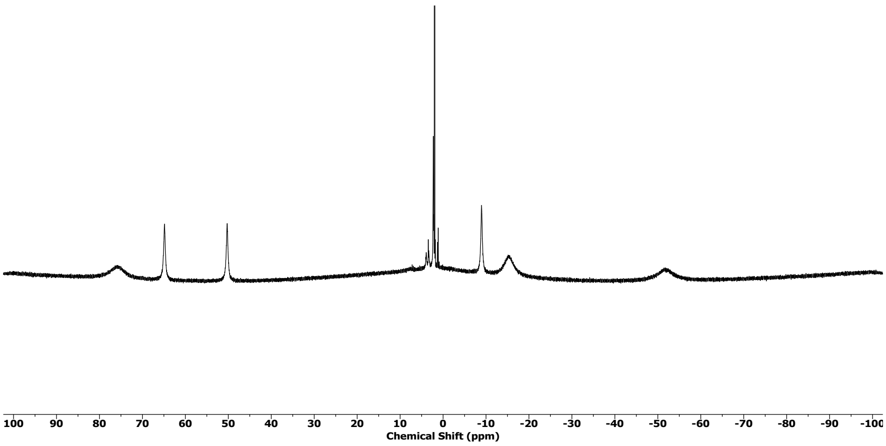
Experiment 2. *In Situ* analysis of NN^{PyMe}-Co(II) complex in presence of $NaBH_4$.

$NaBH_4$ (0.2 mmol, 7.5 mg) was added to acetonitrile solution of NN^{PyMe}-Co(II) complex (0.1 mmol, 40 mg) at -90 °C. in 5 mL scintillation vial in a nitrogen filled glovebox. The resulting dark green solution was let to stir at room temperature for 30 minutes and analyzed using ^{1}H NMR.

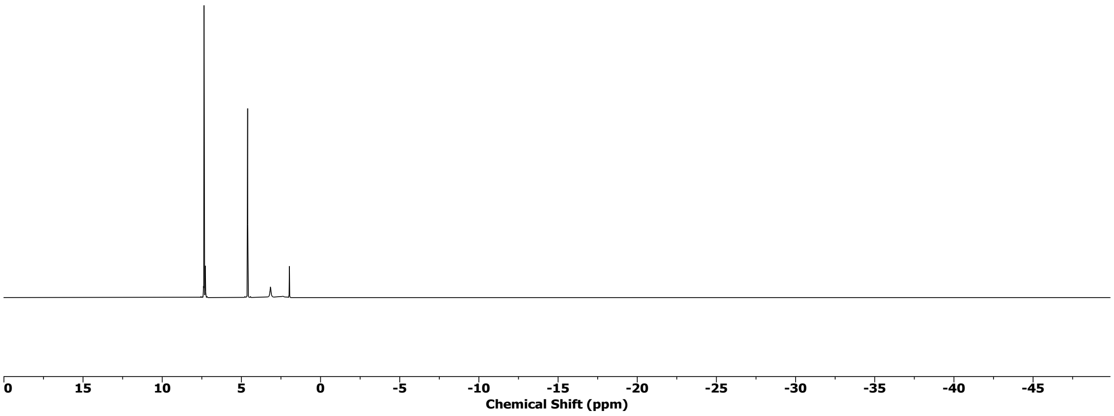


Experiment 3. Sequencial Analysis of NN^{PyMe}-Co(II) complex at standard reaction conditions.

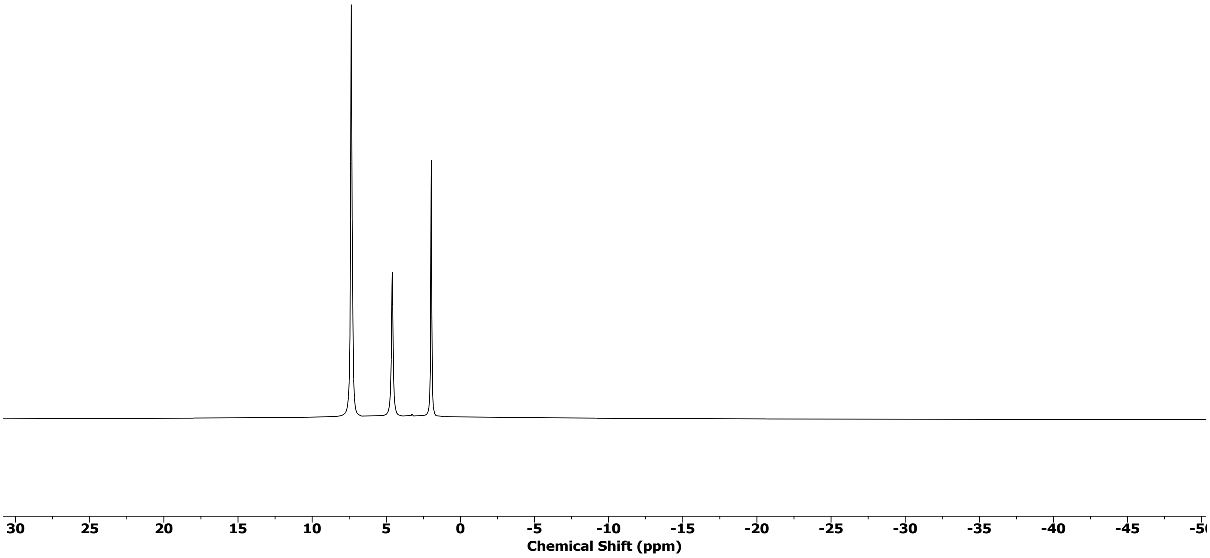
Step A. The long range ^{1}H NMR of NN^{PyMe}-Co(II) (0.1mmol, 40 mg) complex in Acetonitrile (D3).



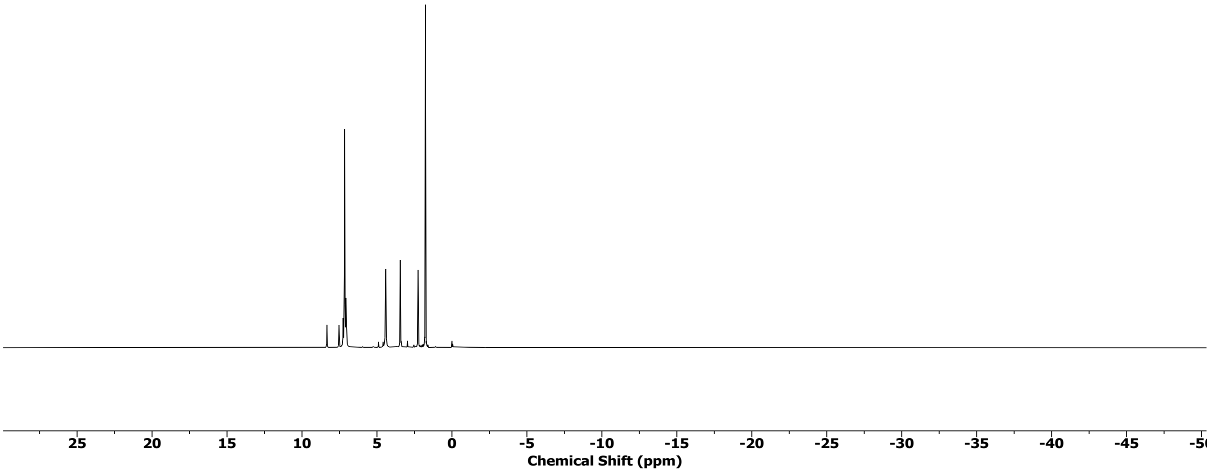
Step B. The addition of stoichiometric amount of benzyl alcohol (10μl, 0.1 mmol) to the acetonitrile (D3) solution of NN^{PyMe}-Co(II) complex (20 mg, 0.05 mmol) at room temperature.



Step C. Further addition of KOH (0.1 mmol, 5.6 mg) as a base to the solution at room temperature.



Step D. The resulting blue solution was kept for stir at 120 ^{o}C for 5 hr and filtered through celite afforded dark green solution analysed by NMR spectroscopy.



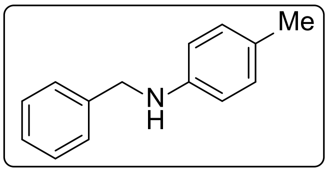
We attempted to isolate and characterize the Co-H species using NMR spectroscopy, following the method of Chirik et al. However, we did not observe any peaks corresponding to Co-H proton in any of the spectra recorded. This indicates that our attempts were unsuccessful. We propose two possible reasons for this outcome: (1) Chirik et al. used a pincer complex, which is much more stable than the bidentate system we employed. The use of $LiHBEt_3$ as a hydride donor might have decomposed our catalyst system. (2) The Co(II) species is paramagnetic, which makes the NMR characterization of the cobalt complex challenging.

5. References

S1. Dolomanov, O. V.; Bourhis, L. J.; Gildea, R. J.; Howard, J. A. K.; Puschmann, H. OLEX2: A Complete Structure Solution, Refinement and Analysis Program. *J. Appl. Cryst.* **2009**, 42, 339-341.

S2. G. M. Sheldrick. Crystal Structure Refinement with SHELXL. *Acta Cryst.* **2015**, C71, 3-8.

6. Characterization Data

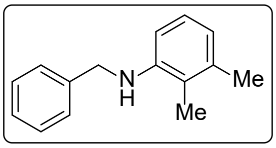


N-benzyl-4-methylaniline (3)

86mg, 88% isolated yield, Pale brown liquid.

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.33 – 7.02 (m, 5H), 6.89 (d, J = 8.3 Hz, 2H), 6.46 (d, J = 8.5 Hz, 2H), 4.19 (s, 2H), 3.85 (d, J = 135.0 Hz, 1H), 2.18 (s, 3H). 13C NMR (101 MHz, CDCl3) δ 145.97, 139.73, 129.84, 128.68, 127.59, 127.24, 126.83, 113.10, 48.72, 20.50.

HRMS (ESI): m/z Calcd for $C_{14}H_{16}N$ $[M-H]^+$: 198.1277; Found:198.1278.

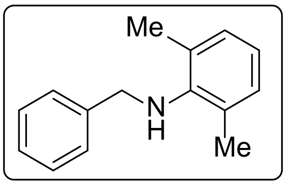


N-benzyl-2,3-dimethylaniline (4)

75mg, 71% isolated yield, Pale brown liquid.

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.37 – 7.09 (m, 5H), 6.91 (t, J = 7.8 Hz, 1H), 6.52 (d, J = 7.5 Hz, 1H), 6.42 (d, J = 8.1 Hz, 1H), 4.26 (s, 2H), 3.76 (s, 1H), 2.20 (s, 3H), 1.98 (s, 3H).^{13}C NMR (101 MHz, $CDCl_3$) δ 146.08, 139.71, 136.61, 128.72, 127.65, 127.28, 126.29, 120.37, 119.91, 119.50, 108.67, 108.18, 48.72, 20.81, 20.71, 12.72, 12.59.

HRMS (ESI): m/z Calcd for C15H18N+ $[M-H]^+$: 212.1434; Found: 212.1439.

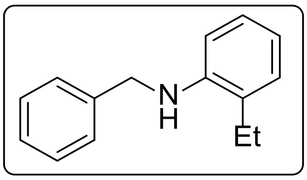


N-benzyl-2,6-dimethylaniline (5)

80mg, 76% isolated yield, Brown liquid.

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.34 – 7.17 (m, 5H), 6.87 (d, J = 7.4 Hz, 1H), 6.45 – 6.35 (m, 2H), 4.27 (s, 2H), 3.71 (s, 1H), 2.18 (s, 3H), 2.03 (s, 3H).^{13}C NMR (101 MHz, $CDCl_3$) δ 146.04, 139.64, 136.85, 129.99, 128.72, 127.70, 127.32, 119.02, 117.90, 110.90, 77.42, 76.79, 48.43, 21.62, 17.18.

HRMS (ESI): m/z Calcd for $C_{15}H_{18}N$ $[M-H]^+$: 212.1434; Found: 212.1436.

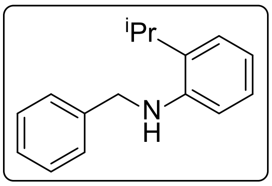


N-benzyl-2-ethylaniline (6)

76mg, 72% isolated yield, Colourless liquid.

^{1}H NMR (400 MHz, CDCl$_3$) δ 7.33 – 7.15 (m, 5H), 7.06 – 6.97 (m, 2H), 6.64 (t, J = 7.4 Hz, 1H), 6.54 (d, J = 7.9 Hz, 1H), 4.28 (s, 2H), 3.89 (s, 1H), 2.43 (q, J = 7.5 Hz, 2H), 1.18 (t, J = 7.5 Hz, 3H). ^{13}C NMR (101 MHz, CDCl$_3$) δ 145.50, 139.63, 128.73, 127.90, 127.63, 127.59, 127.30, 127.09, 117.43, 110.37, 77.43, 76.79, 48.41, 23.96, 12.93.

HRMS (ESI): m/z Calcd for $C_{15}H_{18}N$ [M-H]$^+$: 212.1434; Found: 212.1438.

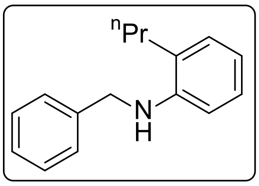


N-benzyl-2-isopropylaniline (7)

71mg, 63% isolated yield, Colourless liquid.

^{1}H NMR (400 MHz, CDCl$_3$) δ 7.34 – 7.16 (m, 5H), 7.10 (d, J = 9.0 Hz, 1H), 7.02 (t, J = 7.7 Hz, 1H), 6.68 (t, J = 7.5 Hz, 1H), 6.57 (d, J = 8.1 Hz, 1H), 4.30 (s, 2H), 4.21 – 3.72 (m, 1H), 2.82 (p, J = 6.8 Hz, 1H), 1.20 (d, J = 6.8 Hz, 6H). ^{13}C NMR (101 MHz, CDCl$_3$) δ 143.70, 138.56, 131.14, 127.64, 126.53, 126.21, 125.72, 123.88, 116.52, 47.52, 26.21, 21.28.

HRMS (ESI): m/z Calcd for $C_{16}H_{20}N$ [M-H]$^+$: 226.1590; Found: 226.1591.

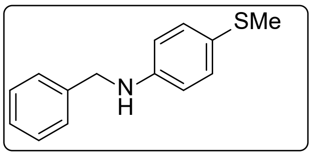


N-benzyl-2-propylaniline (8)

90mg, 80% isolated yield, Colourless liquid.

^{1}H NMR (400 MHz, CDCl$_3$) δ 7.33 – 7.12 (m, 5H), 7.00 (dd, J = 11.6, 6.9 Hz, 2H), 6.62 (t, J = 6.9 Hz, 1H), 6.54 (d, J = 8.0 Hz, 1H), 4.29 (s, 2H), 3.93 (s, 1H), 2.46 – 2.31 (m, 2H), 1.68 – 1.53 (m, 2H), 0.92 (t, J = 7.3 Hz, 3H). ^{13}C NMR (101 MHz, CDCl$_3$) δ 145.58, 139.66, 129.08, 128.72, 127.52, 127.26, 127.11, 117.29, 110.53, 77.41, 76.77, 48.42, 33.34, 21.71, 14.31.

HRMS (ESI): m/z Calcd for $C_{16}H_{20}N$ [M-H]$^+$: 226.1590; Found: 226.1594.

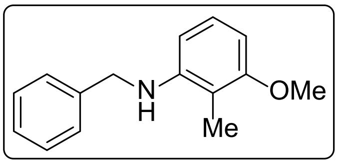


N-benzyl-4-(methylthio) aniline (9)

54mg, 48% isolated yield, Colourless liquid.

^{1}H NMR (400 MHz, CDCl$_3$) δ 7.28 – 7.15 (m, 5H), 7.12 (s, 1H), 7.10 (s, 1H), 6.48 (d, J = 8.7 Hz, 2H), 4.21 (s, 2H), 3.98 (s, 1H), 2.30 (s, 3H).^{13}C NMR (101 MHz, CDCl$_3$) δ 147.01, 139.20, 131.50, 128.73, 127.50, 127.36, 113.54, 77.46, 76.82, 48.33, 19.16.

HRMS (ESI): m/z Calcd for $C_{14}H_{16}NS$ [M-H]$^+$: 230.0998; Found: 230.0996.

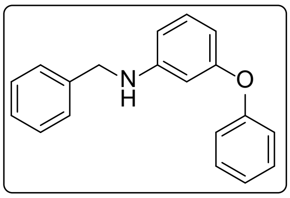


N-benzyl-3-methoxy-2-methylaniline (10)

62mg, 54% isolated yield, Colourless liquid

^{1}H NMR (400 MHz, CDCl$_3$) δ 7.36 – 7.15 (m, 5H), 6.96 (t, J = 8.2 Hz, 1H), 6.26 (dd, J = 14.8, 8.2 Hz, 2H), 4.29 (s, 2H), 3.83 (s, 1H), 3.72 (s, 3H), 1.97 (s, 3H).^{13}C NMR (101 MHz, CDCl$_3$) δ 157.75, 147.12, 139.66, 128.69, 127.54, 127.25, 126.82, 103.98, 100.78, 77.40, 76.77, 55.71, 48.61, 8.75.

HRMS (ESI): m/z Calcd for $C_{15}H_{18}NO$ [M-H]$^+$: 228.1383; Found: 228.1385.

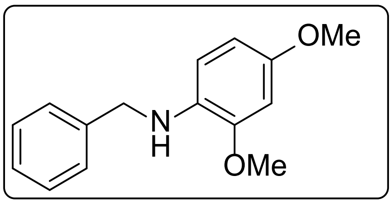


N-benzyl-3-phenoxyaniline (11)

78mg, 57% isolated yield,

^{1}H NMR (400 MHz, CDCl$_3$) δ 7.26 – 7.11 (m, 7H), 7.04 – 6.94 (m, 2H), 6.91 (d, J = 7.8 Hz, 2H), 6.26 (t, J = 9.7 Hz, 2H), 6.20 (s, 1H), 4.17 (s, 2H), 3.96 (s, 1H).^{13}C NMR (101 MHz, CDCl$_3$) δ 158.47, 157.22, 149.71, 139.07, 130.91 – 127.08 (m), 123.12, 119.02, 107.98, 103.36 (d, J = 21.8 Hz), 78.32 – 76.06 (m), 48.31.

HRMS (ESI): m/z Calcd for $C_{19}H_{18}NO$ [M-H]$^+$: 276.1383; Found: 276.1385.

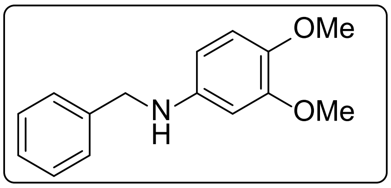


N-benzyl-2,4-dimethoxyaniline (12)

98mg, 81% isolated yield, Colourless liquid.

^{1}H NMR (400 MHz, CDCl$_3$) δ 7.32 – 7.11 (m, 5H), 6.45 – 6.35 (m, 2H), 6.28 (dd, J = 8.5, 2.6 Hz, 1H), 4.21 (s, 2H), 3.72 (s, 3H), 3.64 (s, 3H).^{13}C NMR (101 MHz, CDCl$_3$) δ 152.03, 147.95, 139.89, 132.58, 128.59, 127.60, 127.11, 110.41, 103.75, 99.23, 77.44, 76.81, 55.82, 55.51, 48.86.

HRMS (ESI): m/z Calcd for $C_{15}H_{18}NO_2$ [M-H]$^+$: 244.1332; Found: 244.1335.

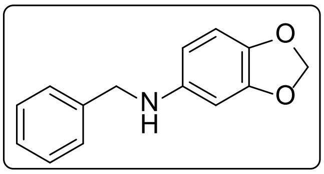


N-benzyl-3,4-dimethoxyaniline (13)

75mg, 62% isolated yield, Colourless liquid.

^{1}H NMR (400 MHz, CDCl$_3$) δ 7.32 – 7.14 (m, 5H), 6.65 (d, J = 8.5 Hz, 1H), 6.19 (d, J = 2.6 Hz, 1H), 6.08 (dd, J = 8.5, 2.6 Hz, 1H), 4.19 (s, 2H), 3.71 (d, J = 2.6 Hz, 6H).^{13}C NMR (101 MHz, CDCl$_3$) δ 150.03, 143.13, 141.69, 139.60, 128.65, 127.61, 127.26, 113.28, 103.62, 99.04, 77.43, 76.80, 56.73, 55.73, 49.22.

HRMS (ESI): m/z Calcd for $C_{15}H_{18}NO_2$ [M-H]$^+$: 244.1332; Found: 244.1334.

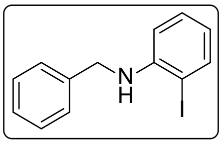


N-benzylbenzo[d][1,3]dioxol-5-amine (14)

69mg, 61% isolated yield, colourless liquid.

^{1}H NMR (400 MHz, CDCl$_3$) δ 7.32 – 7.15 (m, 5H), 6.57 (d, J = 8.3 Hz, 1H), 6.18 (d, J = 2.3 Hz, 1H), 5.99 (dd, J = 8.3, 2.3 Hz, 1H), 5.75 (s, 2H), 4.17 (s, 2H), 3.62 (s, 1H).^{13}C NMR (101 MHz, CDCl$_3$) δ 148.36, 143.94, 139.42, 128.66, 127.56, 127.28, 108.66, 104.47, 100.60, 96.05, 77.39, 76.75, 49.29.

HRMS (ESI): m/z Calcd for $C_{14}H_{14}NO_2$ [M-H]$^+$: 228.1019; Found: 228.1021.

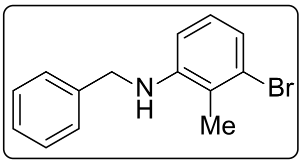


N-benzyl-2-iodoaniline (15)

116mg, 75% isolated yield, colourless liquid

^{1}H NMR (400 MHz, CDCl$_3$) δ 7.60 (d, J = 7.8 Hz, 1H), 7.32 – 7.15 (m, 5H), 7.07 (t, J = 7.7 Hz, 1H), 6.46 (d, J = 7.1 Hz, 1H), 6.37 (t, J = 8.2 Hz, 1H), 4.57 (s, 1H), 4.32 (s, 2H).^{13}C NMR (101 MHz, CDCl$_3$) δ 147.09, 139.04, 138.66, 129.48, 128.76, 127.23, 119.04, 118.74, 111.13, 85.34, 48.38.

HRMS (ESI): m/z Calcd for $C_{13}H_{13}IN$ [M-H]$^+$: 310.0087; Found: 310.0088.

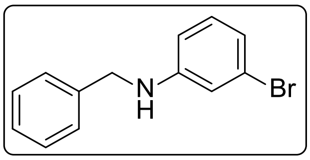


N-benzyl-3-bromo-2-methylaniline (16)

67mg, 58% isolated yield, colourless liquid

^{1}H NMR (400 MHz, CDCl3) δ 7.35 – 7.12 (m, 5H), 6.90 (t, J = 8.1 Hz, 1H), 6.70 (d, J = 7.6 Hz, 1H), 6.42 (d, J = 8.1 Hz, 1H), 4.28 (s, 2H), 3.93 (s, 1H), 2.15 (s, 3H). ^{13}C NMR (101 MHz, CDCl3) δ 145.97, 139.73, 129.84, 128.68, 127.59, 127.24, 126.83, 113.10, 48.72, 20.50.

HRMS (ESI): m/z Calcd for $C_{14}H_{14}BrN$ [M-H]$^+$: 275.0310; Found: 275.0318.

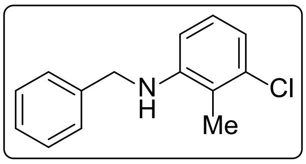


N-benzyl-3-bromoaniline (17)

113mg, 87% isolated yield, Colourless liquid.

^{1}H NMR (400 MHz, CDCl$_3$) δ 7.42 – 7.33 (m, 5H), 7.02 (t, J = 8.0 Hz, 1H), 6.84 (d, J = 8.7 Hz, 1H), 6.79 (t, J = 2.1 Hz, 1H), 6.54 (d, J = 10.5 Hz, 1H), 4.31 (s, 2H), 4.12 (s, 1H).^{13}C NMR (101 MHz, CDCl$_3$) δ 138.73, 130.54, 129.30, 128.77, 127.51, 123.31, 120.36, 117.72, 112.99, 111.55, 48.11.

HRMS (ESI): m/z Calcd for $C_{13}H_{13}BrN$ [M-H]$^+$: 262.0226; Found: 262.0228.

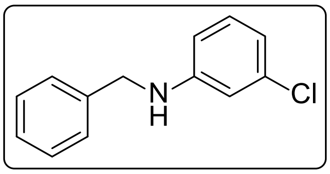


N-benzyl-3-chloro-2-methylaniline (18)

72mg, 62% isolated yield, Colourless liquid.

^{1}H NMR (400 MHz, CDCl$_3$) δ 7.35 – 7.12 (m, 5H), 6.90 (t, J = 8.1 Hz, 1H), 6.70 (d, J = 7.6 Hz, 1H), 6.42 (d, J = 8.1 Hz, 1H), 4.28 (s, 2H), 3.93 (s, 1H), 2.15 (s, 3H).^{13}C NMR (101 MHz, CDCl$_3$) δ 147.18, 138.95, 134.58, 128.79, 127.49, 127.27, 119.64, 118.21, 108.65.

HRMS (ESI): m/z Calcd for $C_{14}H_{15}ClN$ [M-H]$^+$: 232.0888; Found: 232.0891.



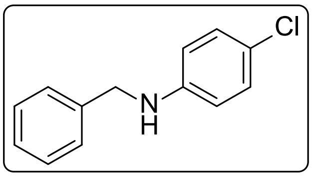
N-benzyl-3-chloroaniline (19)

82mg, 75% isolated yield, Colourless liquid.

^{1}H NMR (400 MHz, CDCl$_3$) δ 7.44 – 7.28 (m, 5H), 7.10 (t, J = 8.0 Hz, 1H), 6.72 (d, J = 7.9 Hz, 1H), 6.65 (t, J = 2.1 Hz, 1H), 6.52 (dd, J = 7.8, 2.7 Hz, 1H), 4.33 (s, 2H), 4.15 (s, 1H).

^{13}C NMR (101 MHz, CDCl$_3$) δ 149.29, 138.82, 135.08, 130.29, 128.80, 127.53, 117.46, 112.57, 111.20, 77.45, 76.82, 48.13.

HRMS (ESI): m/z Calcd for C13H13ClN [M-H]$^+$: 218.0731; Found: 218.0733.

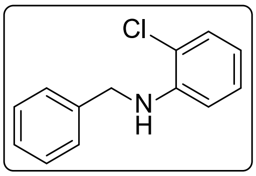


N-benzyl-4-chloroaniline (20)

97mg, 89% isolated yield, Colourless liquid.

^{1}H NMR (400 MHz, CDCl$_3$) δ 7.42 – 7.27 (m, 5H), 7.14 (d, J = 8.9 Hz, 2H), 6.57 (d, J = 8.9 Hz, 2H), 4.32 (s, 2H), 4.09 (s, 1H).^{13}C NMR (101 MHz, CDCl$_3$) δ 146.68, 138.98, 129.12, 128.75, 127.46, 127.42, 122.14, 113.98, 77.41, 76.78, 48.38.

HRMS (ESI): m/z Calcd for $C_{13}H_{13}ClN$ [M-H]$^+$: 218.0731; Found: 218.0733.

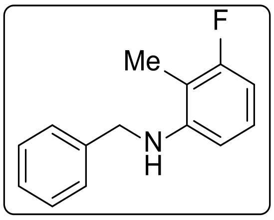


N-benzyl-2-chloroaniline (21)

75mg, 69% isolated yield, Colourless liquid.

^{1}H NMR (400 MHz, CDCl$_3$) δ 7.42 – 7.35 (m, 4H), 7.34 – 7.27 (m, 2H), 7.14 – 7.08 (m, 1H), 6.69 – 6.63 (m, 2H), 4.75 (s, 1H), 4.42 (s, 2H).^{13}C NMR (101 MHz, CDCl$_3$) δ 143.89, 138.78, 128.76, 127.84, 127.39, 127.31, 119.15, 117.45, 111.54, 77.39, 76.75, 47.88.

HRMS (ESI): m/z Calcd for $C_{13}H_{12}ClN$ [M-H]$^+$: 218.0731; Found: 218.0734.

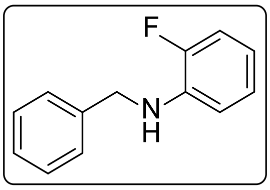


N-benzyl-3-fluoro-2-methylaniline (22)

51mg, 47% isolated yield, Colourless liquid

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.33 – 7.19 (m, 5H), 6.94 (q, J = 7.8 Hz, 1H), 6.39 (t, J = 8.8 Hz, 1H), 6.32 (d, J = 8.2 Hz, 1H), 4.30 (s, 2H), 3.90 (s, 1H), 1.99 (s, 3H). 13C NMR (101 MHz, CDCl3) δ 161.58, 159.19, 138.02, 127.70, 126.46, 126.37, 126.22, 126.11, 103.35, 103.12, 76.31, 75.67, 47.48, 7.24.

HRMS (ESI): m/z Calcd for $C_{14}H_{15}FN$ [M-H]$^+$: 216.1183; Found: 216.1188.

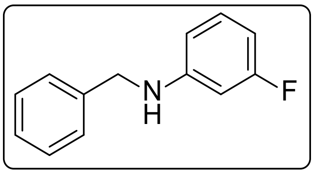


N-benzyl-2-fluoroaniline (23)

43mg, 43% isolated yield, Colourless liquid.

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.33 – 7.17 (m, 5H), 6.96 – 6.83 (m, 2H), 6.65 – 6.51 (m, 2H), 4.30 (s, 2H).^{13}C NMR (101 MHz, $CDCl_3$) δ 152.74, 150.37, 138.91, 128.71, 127.42, 124.58, 116.90, 114.49, 114.31, 112.35, 77.35, 76.71, 47.89.

HRMS (ESI): m/z Calcd for $C_{13}H_{13}FN$ [M-H]$^+$: 202.1027; Found: 202.1025.

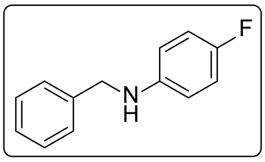


N-benzyl-3-fluoroaniline (24)

60mg, 60% isolated yield, Colourless liquid.

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.32 – 7.12 (m, 5H), 7.05 – 6.94 (m, 1H), 6.30 (td, J = 8.1, 2.0 Hz, 2H), 6.22 (dt, J = 11.6, 2.3 Hz, 1H), 4.20 (s, 2H), 4.06 (s, 1H).^{13}C NMR (101 MHz, $CDCl_3$) δ 165.37, 162.96, 149.98, 149.87, 138.86, 130.40, 130.29, 128.77, 127.51, 127.46, 108.79, 108.76, 104.11, 103.89, 99.70, 99.45, 77.41, 76.78, 48.22.

HRMS (ESI): m/z Calcd for $C_{13}H_{13}FN$ [M-H]$^+$: 202.1027; Found: 202.1029.

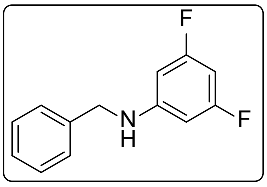


N-benzyl-4-fluoroaniline (25)

58mg, 58% isolated yield, Colourless liquid.

^{1}H NMR (400 MHz, CDCl$_3$) δ 7.30 – 7.10 (m, 5H), 6.84 – 6.73 (m, 2H), 6.45 (dd, J = 9.0, 4.4 Hz, 2H), 4.18 (s, 2H), 3.81 (s, 1H).^{13}C NMR (101 MHz, CDCl$_3$) δ 157.11, 154.77, 144.54, 144.52, 139.29, 128.72, 127.54, 127.36, 115.83, 115.60, 113.74, 113.67, 77.42, 76.78, 48.97.

HRMS (ESI): m/z Calcd for $C_{13}H_{13}FN$ [M-H]$^+$: 202.1027; Found: 202.1025.



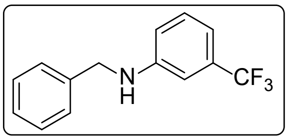
N-benzyl-3,5-difluoroaniline (26)

55mg, 51% isolated yield, Colourless liquid.

^{1}H NMR (400 MHz, CDCl$_3$) δ 7.32 – 7.14 (m, 3H), 6.10 – 5.97 (m, 2H), 4.20 (s, 2H).

^{13}C NMR (101 MHz, CDCl$_3$) δ 165.46, 165.30, 163.04, 162.88, 150.41, 150.28, 150.15, 138.23, 128.84, 127.63, 127.44, 95.72, 95.52, 95.44, 92.88, 92.62, 92.36, 48.09.

HRMS (ESI): m/z Calcd for $C_{13}H_{12}F_2N$ [M-H]$^+$: 220.0932; Found: 220.0935.

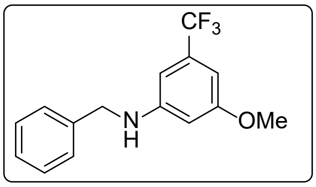


N-benzyl-3-(trifluoromethyl) aniline (27)

90mg, 72% isolated yield, Colourless liquid.

^{1}H NMR (400 MHz, CDCl$_3$) δ 7.27 – 7.14 (m, 5H), 7.11 (t, J = 7.9 Hz, 1H), 6.83 (d, J = 7.7 Hz, 1H), 6.72 (s, 1H), 6.61 (d, J = 10.4 Hz, 1H), 4.20 (s, 2H), 4.06 (s, 1H).^{13}C NMR (101 MHz, CDCl$_3$) δ 148.30, 138.65, 131.77, 131.45, 129.74, 128.84, 127.59, 127.58, 115.77, 115.75, 115.74, 114.00, 113.97, 109.18, 109.14, 77.43, 76.79, 48.15.

HRMS (ESI): m/z Calcd for $C_{14}H_{13}F_3N$ [M-H]$^+$: 252.0995; Found: 252.0995.

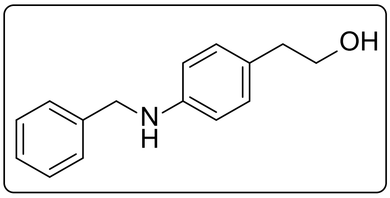


N-benzyl-3-methoxy-5-(trifluoromethyl) aniline (28)

90mg, 64% isolated yield, Colourless liquid.

^{1}H NMR (400 MHz, CDCl$_3$) δ 7.34 – 7.08 (m, 5H), 6.39 (s, 2H), 6.17 (d, J = 2.1 Hz, 1H), 4.21 (s, 2H), 3.65 (s, 3H).^{13}C NMR (101 MHz, CDCl$_3$) δ 161.02, 149.59, 138.55, 132.57, 128.80, 127.56, 127.54, 125.56, 122.85, 102.78, 99.40, 77.39, 76.76, 55.34, 48.17.

HRMS (ESI): m/z Calcd for $C_{15}H_{15}F_3NO$ [M-H]$^+$: 282.1100; Found: 282.1103.

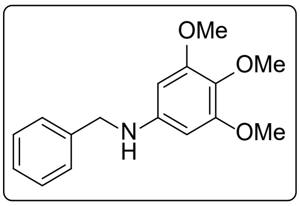


2-(4-(benzylamino) phenyl) ethan-1-ol (29)

76mg, 67% isolated yield,

^{1}H NMR (400 MHz, CDCl$_3$) δ 7.33 – 7.19 (m, 5H), 7.03 – 6.90 (m, 2H), 6.61 – 6.49 (m, 2H), 4.25 (s, 2H), 3.72 (t, J = 6.5 Hz, 2H), 2.69 (t, J = 6.5 Hz, 2H). 13C NMR (101 MHz, CDCl3) δ 162.20, 158.01, 148.01, 136.32, 127.73, 126.69, 110.55, 45.31, 33.84, 24.07.

HRMS (ESI): m/z Calcd for $C_{15}H_{18}NO$ [M-H]$^+$: 228.1383; Found: 228.1385.

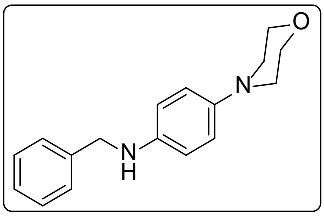


N-benzyl-3,4,5-trimethoxyaniline (30)

83mg, 61% isolated yield,

^{1}H NMR (400 MHz, CDCl$_3$) δ 7.33 – 7.16 (m, 5H), 5.80 (s, 2H), 4.21 (s, 2H), 3.69 (d, J = 7.8 Hz, 9H). 13C NMR (101 MHz, CDCl3) δ 150.03, 143.13, 141.68, 139.60, 128.66, 127.61, 127.26, 113.27, 103.62, 99.04, 77.43, 76.80, 56.74, 55.73, 49.22.

HRMS (ESI): m/z Calcd for $C_{16}H_{20}NO_3$ [M-H]$^+$: 274.1438; Found: 274.1440.

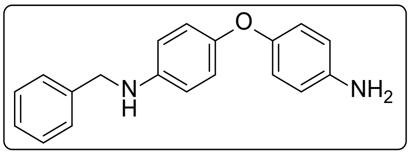


N-benzyl-4-morpholinoaniline (31)

68mg, 51% isolated yield,

^{1}H NMR (400 MHz, CDCl$_3$) δ 7.36 – 7.09 (m, 5H), 6.74 (d, J = 8.7 Hz, 2H), 6.53 (d, J = 8.4 Hz, 2H), 4.20 (s, 2H), 3.86 – 3.68 (m, 4H), 3.38 (s, 1H), 2.92 (s, 4H).^{13}C NMR (101 MHz,

$CDCl_3$) δ 142.59, 141.79, 138.65, 127.55, 126.50, 126.12, 117.34, 112.87, 66.07, 50.20, 47.96. HRMS (ESI): m/z Calcd for $C_{17}H_{21}N_2O$ $[M-H]^+$: 269.1648; Found: 269.1648.

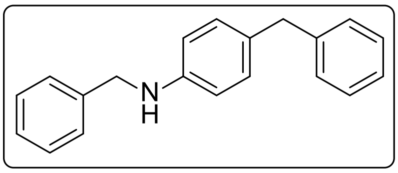


4-(4-aminophenoxy)-N-benzylaniline (32)

81mg, 56% isolated yield,

^1H NMR (400 MHz, $CDCl_3$) δ 7.33 – 7.12 (m, 5H), 6.79 – 6.65 (m, 4H), 6.58 – 6.43 (m, 4H), 4.18 (s, 2H), 3.51 (s, 3H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 150.88, 149.85, 144.04, 141.58, 139.53, 128.68, 127.61, 127.29, 119.72, 119.45, 116.32, 113.90, 77.44, 76.80, 49.04.

HRMS (ESI): m/z Calcd for $C_{19}H_{19}N_2O$ $[M-H]^+$: 291.1492; Found: 291.1496.

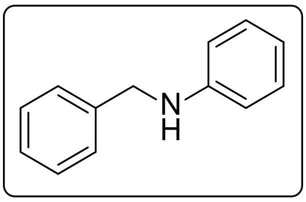


N,4-dibenzylaniline (33)

112mg, 82% isolated yield, Colourless liquid

^1H NMR (400 MHz, $CDCl_3$) δ 7.27 – 7.10 (m, 7H), 7.06 (d, J = 7.4 Hz, 3H), 6.88 (d, J = 8.1 Hz, 2H), 6.44 (d, J = 8.2 Hz, 2H), 4.15 (s, 2H), 3.75 (s, 3H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 146.53, 142.15, 139.65, 130.31, 129.86, 128.96, 128.75, 128.50, 127.67, 127.34, 125.96, 113.16, 48.67, 41.19.

HRMS (ESI): m/z Calcd for $C_{20}H_{20}N$ $[M-H]^+$: 274.1590; Found: 274.1594.

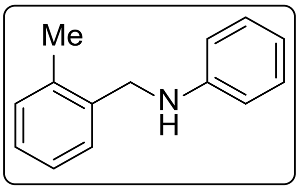


N-benzyl aniline (2)

80mg, 88% isolated yield, Colourless liquid

1H NMR (400 MHz, CDCl3) δ 7.43 – 7.33 (m, 4H), 7.30 (t, J = 6.9 Hz, 1H), 7.23 – 7.17 (m, 2H), 6.74 (t, J = 7.3 Hz, 1H), 6.66 (d, J = 7.6 Hz, 2H), 4.35 (s, 2H), 4.04 (s, 1H).13C NMR (101 MHz, CDCl3) δ 148.20, 139.48, 129.30, 128.67, 127.54, 127.26, 117.60, 112.89, 48.36.

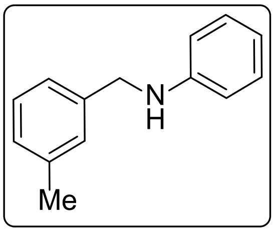
HRMS (ESI): m/z Calcd for $C_{13}H_{14}N$ $[M-H]^+$: 184.1121; Found: 184.1125.



N-(2-methylbenzyl) aniline (34)

58mg, 59% isolated yield, Colourless liquid.

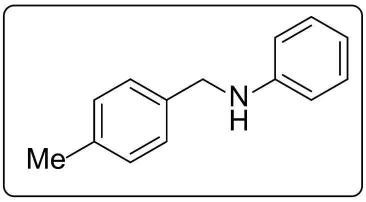
^{1}H NMR (400 MHz, $CDCl_3$) δ 7.22 (d, J = 6.9 Hz, 1H), 7.14 – 7.02 (m, 5H), 6.62 (t, J = 7.3 Hz, 1H), 6.51 (d, J = 8.5 Hz, 2H), 4.14 (s, 2H), 3.69 (s, 1H), 2.26 (s, 3H).^{13}C NMR (101 MHz, $CDCl_3$) δ 148.36, 137.08, 136.41, 130.49, 129.36, 128.33, 127.50, 126.24, 117.54, 112.77, 46.45, 19.01. HRMS (ESI): m/z Calcd for $C_{14}H_{16}N$ $[M-H]^+$: 198.1277; Found: 198.1270.



N-(3-methylbenzyl) aniline (35)

74mg, 76% isolated yield, Colourless liquid.

1H NMR (400 MHz, CDCl3) δ 7.23 (d, J = 7.6 Hz, 1H), 7.21 – 7.15 (m, 4H), 7.10 (d, J = 7.4 Hz, 1H), 6.72 (t, J = 7.3 Hz, 1H), 6.65 (d, J = 7.6 Hz, 2H), 4.29 (s, 2H), 3.99 (s, 1H), 2.36 (s, 3H).13C NMR (101 MHz, CDCl3) δ 148.21, 139.35, 138.34, 129.28, 128.56, 128.34, 128.03, 124.63, 117.59, 112.91, 48.42, 21.45. HRMS (ESI): m/z Calcd for $C_{14}H_{16}N$ $[M-H]^+$: 198.1277; Found: 198.1281.

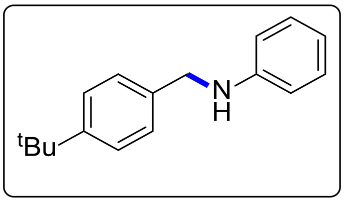


N-(4-methylbenzyl) aniline (36)

93mg, 95% isolated yield, Colourless liquid.

1H NMR (400 MHz, CDCl3) δ 7.29 (d, J = 7.9 Hz, 2H), 7.24 – 7.15 (m, 4H), 6.74 (t, J = 7.7 Hz, 1H), 6.66 (d, J = 7.8 Hz, 2H), 4.31 (s, 2H), 4.00 (s, 1H), 2.38 (s, 3H).13C NMR (101 MHz, CDCl3) δ 148.23, 136.91, 136.38, 129.34, 129.29, 127.57, 117.55, 112.89, 48.13, 21.14.

HRMS (ESI): m/z Calcd for $C_{14}H_{16}N$ $[M-H]^+$: 198.1277; Found: 198.1280.

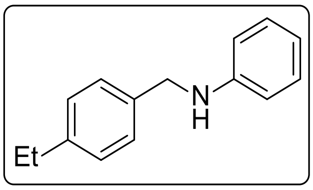


N-(4-(tert-butyl) benzyl) aniline (37)

68mg, 57 % isolated yield, Colourless liquid.

^{1}H NMR (400 MHz, CDCl$_3$) δ 7.39 (d, *J* = 8.4 Hz, 2H), 7.33 (d, *J* = 8.4 Hz, 2H), 7.23 – 7.16 (m, 2H), 6.74 (t, *J* = 6.9 Hz, 1H), 6.67 (d, *J* = 8.6 Hz, 2H), 4.31 (s, 2H), 3.99 (s, 1H), 1.34 (s, 9H).^{13}C NMR (101 MHz, CDCl$_3$) δ 150.27, 148.32, 136.40, 129.28, 127.41, 125.57, 117.51, 112.84, 77.37, 76.73, 48.04, 34.53, 31.41.

HRMS (ESI): m/z Calcd for $C_{17}H_{22}N$ [M-H]$^+$: 240.1747; Found: 240.1751.

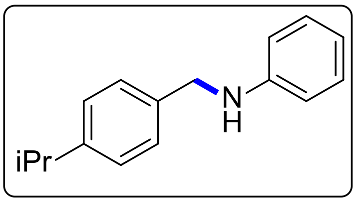


N-(4-ethylbenzyl) aniline (38)

75mg, 75% isolated yield, Colourless liquid.

1H NMR (400 MHz, CDCl3) δ 7.32 (d, J = 8.0 Hz, 2H), 7.23 – 7.17 (m, 4H), 6.74 (t, J = 7.3 Hz, 1H), 6.67 (d, J = 7.6 Hz, 2H), 4.31 (s, 2H), 3.99 (s, 1H), 2.68 (q, J = 7.6 Hz, 2H), 1.27 (t, J = 7.6 Hz, 3H).13C NMR (101 MHz, CDCl3) δ 148.29, 143.35, 136.65, 129.29, 128.16, 127.65, 117.52, 112.86, 77.38, 76.75, 48.15, 28.57, 15.67.

HRMS (ESI): m/z Calcd for $C_{15}H_{18}N$ [M-H]$^+$: 212.1434; Found: 212.1437.

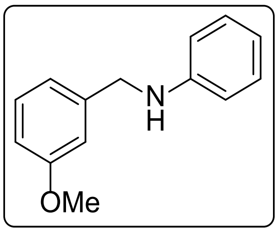


N-(4-isopropylbenzyl) aniline (39)

102mg, 91% isolated yield, Colourless liquid.

^{1}H NMR (400 MHz, CDCl$_3$) δ 7.30 (d, J = 8.1 Hz, 2H), 7.19 (dd, J = 17.2, 8.3 Hz, 4H), 6.72 (t, J = 7.3 Hz, 1H), 6.64 (d, J = 7.6 Hz, 2H), 4.28 (s, 2H), 3.95 (s, 1H), 2.91 (p, J = 6.9 Hz, 1H), 1.27 (d, J = 7.0 Hz, 6H).^{13}C NMR (101 MHz, CDCl$_3$) δ 148.38, 148.04, 136.86, 129.34, 127.73, 126.77, 117.56, 112.91, 77.47, 76.83, 48.19, 33.91, 24.14.

HRMS (ESI): m/z Calcd for $C_{16}H_{20}N^+$ [M-H]$^+$: 226.1590; Found: 226.1593.

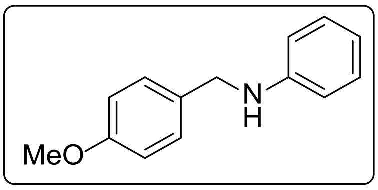


N-(3-methoxybenzyl) aniline (40)

84mg, 79% isolated yield, Colourless liquid.

^{1}H NMR (400 MHz, CDCl$_3$) δ 7.28 (t, J = 7.9 Hz, 1H), 7.23 – 7.17 (m, 2H), 7.01 – 6.93 (m, 2H), 6.85 (d, J = 8.2 Hz, 1H), 6.75 (t, J = 7.8 Hz, 1H), 6.66 (d, J = 7.6 Hz, 2H), 4.33 (s, 2H), 4.05 (s, 1H), 3.82 (s, 3H).^{13}C NMR (101 MHz, CDCl$_3$) δ 159.96, 148.19, 129.69, 129.30, 119.77, 117.63, 113.07, 112.91, 112.69, 77.40, 76.77, 55.24, 48.36.

HRMS (ESI): m/z Calcd for $C_{14}H_{16}NO$ [M-H]$^+$: 214.1226; Found: 214.1229.

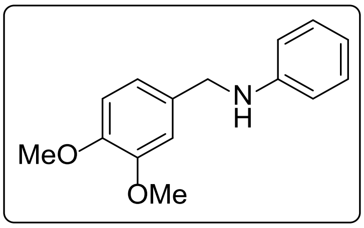


N-(4-methoxybenzyl) aniline (41)

91mg, 85% isolated yield, Colourless liquid.

^{1}H NMR (400 MHz, CDCl$_3$) δ 7.31 (d, J = 8.7 Hz, 2H), 7.22 – 7.16 (m, 2H), 6.90 (d, J = 8.7 Hz, 2H), 6.73 (t, J = 7.3 Hz, 1H), 6.65 (d, J = 7.6 Hz, 2H), 4.27 (s, 2H), 3.96 (s, 1H), 3.82 (s, 3H).^{13}C NMR (101 MHz, CDCl$_3$) δ 158.89, 148.24, 131.45, 129.28, 128.84, 117.53, 114.06, 112.87, 77.38, 76.74, 55.33, 47.83.

HRMS (ESI): m/z Calcd for $C_{14}H_{16}NO$ [M-H]$^+$: 214.1226; Found: 214.1232.

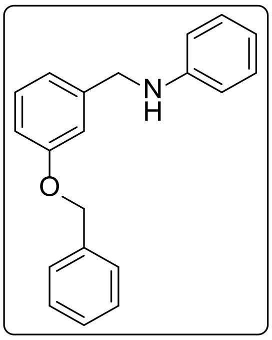


N-(3,4-dimethoxybenzyl) aniline (42)

71mg, 67% isolated yield, Colourless liquid.

^{1}H NMR (400 MHz, CDCl$_3$) δ 7.22 – 7.16 (m, 2H), 6.93 (d, J = 5.5 Hz, 2H), 6.85 (d, J = 8.6 Hz, 1H), 6.73 (t, J = 7.3 Hz, 1H), 6.66 (d, J = 7.6 Hz, 2H), 4.26 (s, 2H), 3.97 (s, 1H), 3.88 (d, J = 2.9 Hz, 6H).^{13}C NMR (101 MHz, CDCl$_3$) δ 149.20, 148.29, 131.99, 129.28, 119.73, 117.64, 112.92, 111.28, 110.88, 77.40, 76.76, 55.98, 55.90, 48.29.

HRMS (ESI): m/z Calcd for $C_{15}H_{18}NO_2$ [M-H]$^+$: 244.1332; Found: 244.1334.

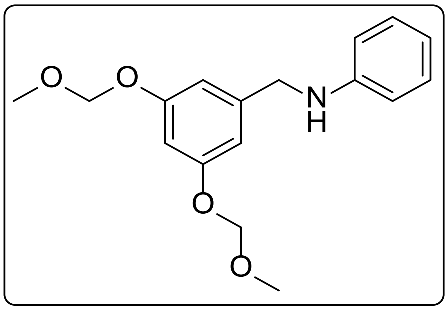


N-(3-(benzyloxy) benzyl) aniline (43)

102mg, 71% isolated yield, Colourless liquid.

^{1}H NMR (400 MHz, CDCl$_3$) δ 7.33 – 7.18 (m, 5H), 7.14 (t, J = 7.9 Hz, 1H), 7.09 – 7.03 (m, 2H), 6.93 – 6.83 (m, 2H), 6.77 (d, J = 8.2 Hz, 1H), 6.61 (t, J = 7.3 Hz, 1H), 6.51 (d, J = 7.6 Hz, 2H), 4.93 (s, 2H), 4.18 (s, 2H), 3.90 (s, 1H).^{13}C NMR (101 MHz, CDCl$_3$) δ 159.20, 148.19, 141.32, 137.03, 129.74, 129.32, 128.64, 128.02, 127.59, 120.05, 117.65, 114.02, 113.62, 112.93, 77.43, 76.80, 70.03, 48.33.

HRMS (ESI): m/z Calcd for $C_{20}H_{20}NO$ [M-H]$^+$: 290.1539; Found: 290.1547.

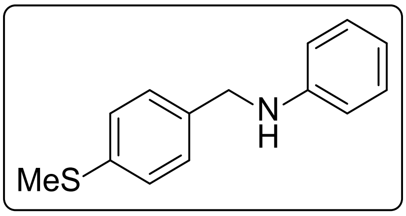


N-(3,5-bis(methoxy methoxy) benzyl) aniline (44)

104mg, 69% isolated yield, Colourless liquid.

^{1}H NMR (400 MHz, CDCl$_3$) δ 7.20 – 7.14 (m, 2H), 6.75 – 6.69 (m, 3H), 6.69 – 6.61 (m, 3H), 5.15 (s, 4H), 4.27 (s, 2H), 4.03 (s, 1H), 3.47 (s, 6H).^{13}C NMR (101 MHz, CDCl$_3$) δ 158.55, 148.08, 142.21, 129.24, 117.62, 112.92, 108.75, 103.63, 94.50, 77.37, 76.74, 56.10, 48.35.

HRMS (ESI): m/z Calcd for $C_{17}H_{22}NO_4$ [M-H]$^+$: 304.1543; Found: 304.1551.

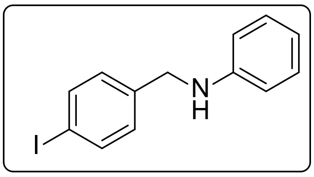


N-(4-(methylthio) benzyl) aniline (45)

69mg, 60% isolated yield, Colourless liquid.

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.23 – 7.12 (m, 4H), 7.12 – 7.04 (m, 2H), 6.63 (t, J = 7.3 Hz, 1H), 6.53 (d, J = 7.6 Hz, 2H), 4.19 (s, 2H), 3.91 (s, 1H), 2.38 (s, 3H).^{13}C NMR (101 MHz, $CDCl_3$) δ 148.09, 137.21, 136.48, 129.31, 128.06, 127.06, 117.67, 112.92, 77.41, 76.78, 47.89, 16.08.

HRMS (ESI): m/z Calcd for $C_{14}H_{16}NS$ $[M-H]^+$: 230.0998; Found: 230.1002.

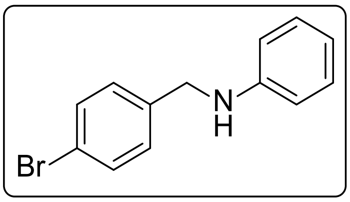


N-(4-iodobenzyl) aniline (46)

120mg, 78% isolated yield, Colourless liquid.

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.18 (d, J = 1.2 Hz, 4H), 7.06 (dd, J = 8.6, 7.4 Hz, 2H), 6.62 (t, J = 7.3 Hz, 1H), 6.49 (dd, J = 8.6, 1.0 Hz, 2H), 4.17 (s, 2H), 3.91 (s, 1H).^{13}C NMR (101 MHz, $CDCl_3$) δ 147.92, 138.11, 132.91, 129.38, 128.82, 128.77, 117.87, 112.97, 47.65.

HRMS (ESI): m/z Calcd for $C_{13}H_{13}IN$ $[M-H]^+$: 310.0087; Found: 310.0091.

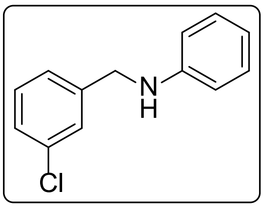


N-(4-bromobenzyl) aniline (47)

94mg, 72% isolated yield, Colourless liquid.

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.37 (d, J = 8.4 Hz, 2H), 7.16 (d, J = 8.4 Hz, 2H), 7.09 (t, J = 7.9 Hz, 2H), 6.65 (t, J = 7.3 Hz, 1H), 6.52 (d, J = 7.7 Hz, 2H), 4.21 (s, 2H), 4.03 (s, 1H).^{13}C NMR (101 MHz, $CDCl_3$) δ 147.79, 138.55, 131.73, 129.33, 129.08, 120.96, 117.88, 112.95, 77.38, 76.75, 47.70.

HRMS (ESI): m/z Calcd for $C_{13}H_{13}BrN$ $[M-H]^+$: 262.0226; Found: 262.0232.



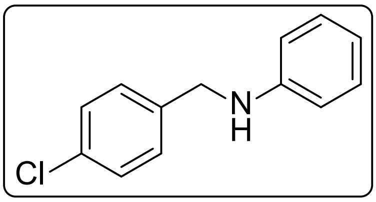
N-(3-chlorobenzyl) aniline (48)

81mg, 75% isolated yield, Colourless liquid.

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.25 (s, 1H), 7.14 (d, J = 2.2 Hz, 3H), 7.07 (dd, J = 8.6, 7.4 Hz, 2H), 6.63 (t, J = 7.3 Hz, 1H), 6.49 (dd, J = 8.6, 1.0 Hz, 2H), 4.18 (s, 2H), 3.93 (s, 1H).^{13}C NMR

(101 MHz, $CDCl_3$) δ 147.86, 141.84, 134.57, 129.97, 129.39, 127.42, 125.48, 117.91, 112.97, 47.80.

HRMS (ESI): m/z Calcd for C13H13ClN+ $[M-H]^+$: 218.0731; Found: 218.0733.

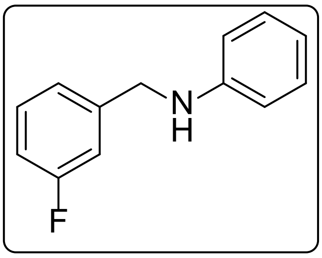


N-(4-chlorobenzyl) aniline (49)

81mg, 75% isolated yield, Colourless liquid

^{1}H NMR (400 MHz, CDCl3) δ 7.18 (d, J = 1.2 Hz, 4H), 7.06 (dd, J = 8.6, 7.4 Hz, 2H), 6.62 (t, J = 7.3 Hz, 1H), 6.49 (dd, J = 8.6, 1.0 Hz, 2H), 4.17 (s, 2H), 3.91 (s, 1H). 13C NMR (101 MHz, CDCl3) δ 147.92, 138.11, 132.91, 129.38, 128.82, 128.77, 117.87, 112.97, 47.65.

HRMS (ESI): m/z Calcd for $C_{13}H_{13}ClN$ $[M-H]^+$: 218.0731; Found: 218.0733.

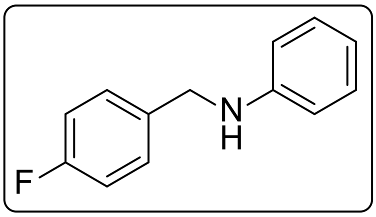


N-(3-fluorobenzyl) aniline (50)

41mg, 41% isolated yield, Colourless liquid.

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.36 – 7.28 (m, 1H), 7.23 – 7.14 (m, 3H), 7.11 (d, J = 9.8 Hz, 1H), 7.01 – 6.94 (m, 1H), 6.75 (t, J = 7.3 Hz, 1H), 6.64 (d, J = 7.7 Hz, 2H), 4.36 (s, 2H), 4.06 (s, 1H).^{13}C NMR (101 MHz, $CDCl_3$) δ 164.40, 161.96, 147.86, 142.42, 142.35, 130.17, 130.09, 129.33, 122.82, 122.79, 117.85, 114.29, 114.17, 114.08, 113.96, 47.82, 47.80.

HRMS (ESI): m/z Calcd for $C_{13}H_{13}FN$ $[M-H]^+$: 202.1027; Found: 202.1028.



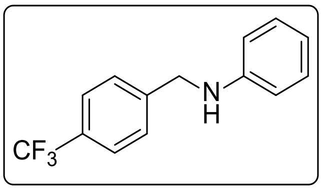
N-(4-fluorobenzyl) aniline (51)

63mg, 63% isolated yield, Colourless liquid

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.38 – 7.30 (m, 2H), 7.22 – 7.14 (m, 2H), 7.03 (t, J = 8.7 Hz, 2H), 6.74 (t, J = 7.3 Hz, 1H), 6.63 (d, J = 7.6 Hz, 2H), 4.31 (s, 2H), 4.14 (s, 1H).^{13}C NMR (101

MHz, $CDCl_3$) δ 163.29, 160.86, 147.88, 135.08, 135.05, 129.31, 129.08, 129.00, 117.82, 115.57, 115.35, 112.95, 47.68.

HRMS (ESI): m/z Calcd for $C_{13}H_{13}FN$ $[M-H]^+$: 202.1027; Found: 202.1031.



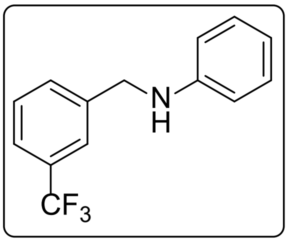
N-(4-(trifluoromethyl) benzyl) aniline (52)

56mg, 44% isolated yield,

^{1}H NMR (400 MHz, DCl_3) δ 7.60 (d, J = 8.1 Hz, 2H), 7.49 (d, J = 8.0 Hz, 2H), 7.22 – 7.15 (m, 2H), 6.75 (t, J = 7.3 Hz, 1H), 6.62 (d, J = 7.6 Hz, 2H), 4.42 (s, 2H), 4.25 (s, 1H).

^{13}C NMR (101 MHz, $CDCl_3$) δ 147.62, 143.72, 129.65, 129.36, 127.47, 125.64, 125.60, 125.56, 125.53, 122.85, 118.04, 112.96, 77.35, 76.72, 47.84.

HRMS (ESI): m/z Calcd for $C_{14}H_{13}F_3N$ $[M-H]^+$: 252.0995; Found: 252.0999.

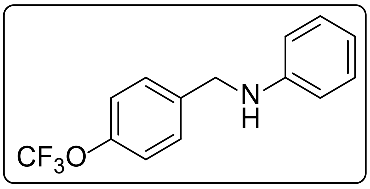


N-(3-(trifluoromethyl) benzyl) aniline (53)

85mg, 68 % isolated yield,

^{1}H NMR (400 MHz, CDCl3) δ 7.52 (s, 1H), 7.42 (t, J = 7.9 Hz, 2H), 7.32 (t, J = 7.7 Hz, 1H), 7.06 (t, J = 7.4 Hz, 2H), 6.64 (d, J = 8.4 Hz, 1H), 6.50 (d, J = 7.7 Hz, 2H), 4.25 (s, 2H), 3.95 (s, 1H).13C NMR (101 MHz, CD2Cl2) δ 145.90, 138.82, 129.24, 128.92, 128.78, 127.49, 127.24, 123.69, 122.24, 75.52, 74.89, 46.02.

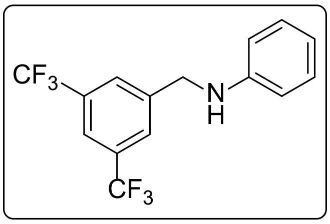
HRMS (ESI): m/z Calcd for $C_{14}H_{13}F_3N^+$ $[M-H]^+$: 252.0995; Found: 252.0996.



N-(4-(trifluoromethoxy) benzyl) aniline (54)

85mg, 63% isolated yield,

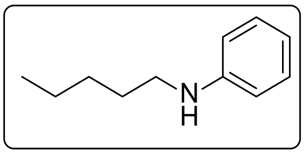
^{1}H NMR (400 MHz, CDCl$_3$) δ 7.28 (d, J = 8.7 Hz, 2H), 7.08 (dt, J = 7.4, 3.9 Hz, 4H), 6.64 (t, J = 7.3 Hz, 1H), 6.52 (d, J = 7.7 Hz, 2H), 4.23 (s, 2H), 3.92 (s, 1H). ^{13}C NMR (101 MHz, CDCl$_3$) δ 147.86, 138.31, 129.38, 128.72, 121.83, 121.21, 112.94, 77.41, 76.77, 47.58.
HRMS (ESI): m/z Calcd for $C_{14}H_{13}F_3NO$ $[M-H]^+$: 268.0944; Found: 268.0948.



N-(3,5-bis(trifluoromethyl)benzyl) aniline (55)

40mg, 25% isolated yield, Colourless liquid.

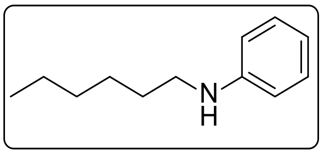
^{1}H NMR (400 MHz, CDCl$_3$) δ 7.84 (s, 2H), 7.79 (s, 1H), 7.19 (s, 2H), 6.78 (s, 1H), 6.61 (d, J = 9.6 Hz, 2H), 4.48 (s, 2H), 4.33 (s, 1H). ^{13}C NMR (101 MHz, CDCl$_3$) δ 147.25, 142.54, 132.10, 131.77, 129.45, 127.33, 124.69, 121.98, 121.25, 118.56, 113.06, 77.34, 76.71, 47.74.
HRMS (ESI): m/z Calcd for $C_{15}H_{12}F_6N$ $[M-H]^+$: 320.0868; Found: 320.0868.



N-pentylaniline (56)

32mg, 39% isolated yield, Dark brown liquid

^{1}H NMR (400 MHz, CDCl$_3$) δ 7.13 – 7.05 (m, 2H), 6.62 (tt, J = 7.3, 1.1 Hz, 1H), 6.56 – 6.49 (m, 2H), 3.03 (t, J = 7.2 Hz, 2H), 1.55 (dq, J = 10.6, 7.3 Hz, 2H), 1.34 – 1.24 (m, 4H), 0.87 – 0.80 (m, 3H). ^{13}C NMR (101 MHz, CDCl$_3$) δ 148.50, 129.23, 117.15, 112.76, 44.05, 29.36, 29.28, 22.52, 14.03.
HRMS (ESI): m/z Calcd for $C_{11}H_{18}N$ $[M-H]^+$: 164.1434; Found: 164.1435.

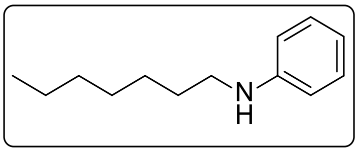


N-hexylaniline (57)

37mg, 42% isolated yield, Dark brown solid

^{1}H NMR (400 MHz, CDCl$_3$) δ 7.10 (dd, J = 8.6, 7.4 Hz, 2H), 6.66 – 6.58 (m, 1H), 6.54 (d, J = 7.5 Hz, 2H), 4.37 – 3.26 (m, 1H), 3.03 (t, J = 7.1 Hz, 2H), 1.54 (p, J = 7.0 Hz, 2H), 1.37 – 1.29 (m, 2H), 1.28 – 1.20 (m, 4H), 0.85 – 0.79 (m, 3H). ^{13}C NMR (101 MHz, CDCl$_3$) δ 148.50, 129.23, 117.15, 112.76, 44.07, 31.66, 29.55, 26.87, 22.63, 14.04.

HRMS (ESI): m/z Calcd for $C_{12}H_{20}N$ $[M-H]^+$: 178.1590; Found: 178.1591.

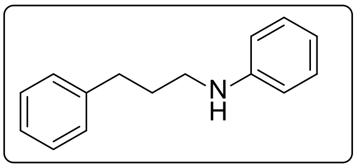


N-heptylaniline (58)

45mg, 47% isolated yield, Dark brown liquid

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.16 – 7.05 (m, 2H), 6.62 (tt, J = 7.4, 1.1 Hz, 1H), 6.58 – 6.50 (m, 2H), 3.03 (t, J = 7.1 Hz, 2H), 1.57 – 1.51 (m, 2H), 1.35 – 1.19 (m, 8H), 0.86 – 0.75 (m, 3H).^{13}C NMR (101 MHz, $CDCl_3$) δ 129.22, 117.18, 112.80, 44.10, 31.81, 29.59, 29.11, 27.14, 22.61, 14.06.

HRMS (ESI): m/z Calcd for C13H22N $[M-H]^+$: 192.1747; Found: 192.1746.

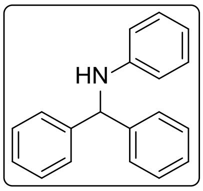


N-(3-phenylpropyl) aniline (59)

46mg, 44% isolated yield, Dark brown liquid

1H NMR (400 MHz, CDCl3) δ 7.26 – 7.20 (m, 2H), 7.15 – 7.07 (m, 5H), 6.62 (tt, J = 7.4, 1.1 Hz, 1H), 6.54 – 6.47 (m, 2H), 3.64 – 3.41 (m, 1H), 3.08 (t, J = 7.0 Hz, 2H), 2.71 – 2.64 (m, 2H), 1.89 (dq, J = 9.0, 7.2 Hz, 2H). 13C NMR (101 MHz, CDCl3) δ 147.10, 140.43, 127.99, 127.20, 127.17, 124.72, 115.98, 111.50, 42.17, 32.16, 29.83.

HRMS (ESI): m/z Calcd for C15H18N $[M-H]^+$: 212.1434; Found: 212.1435.

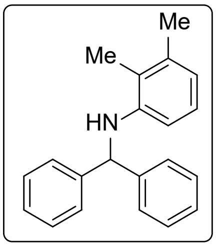


N-benzhydrylaniline (62)

110mg, 85% isolated yield, Pale yellow liquid.

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.30 – 7.19 (m, 8H), 7.18 – 7.10 (m, 2H), 7.05 – 6.98 (m, 2H), 6.60 (t, J = 7.3 Hz, 1H), 6.44 (d, J = 8.5 Hz, 2H), 5.40 (s, 1H), 4.13 (s, 1H).^{13}C NMR (101 MHz, $CDCl_3$) δ 147.43, 143.02, 129.20, 128.82, 127.53, 127.43, 117.74, 113.56, 77.43, 76.80, 63.12.

HRMS (ESI): m/z Calcd for $C_{19}H_{18}N$ $[M-H]^+$: 260.1434; Found: 260.1437.

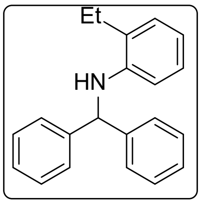


N-benzhydryl-2,3-dimethylaniline (63)

83mg, 58% isolated yield, Pale yellow liquid.

^{1}H NMR (400 MHz, CDCl$_3$) δ 7.34 (dt, J = 14.7, 7.3 Hz, 8H), 7.27 (s, 1H), 7.25 (d, J = 7.0 Hz, 1H), 6.88 (t, J = 7.8 Hz, 1H), 6.59 (d, J = 7.4 Hz, 1H), 6.32 (d, J = 8.1 Hz, 1H), 5.53 (s, 1H), 4.12 (s, 1H), 2.30 (s, 3H), 2.10 (s, 3H). 13C NMR (101 MHz, CDCl3) δ 153.74, 144.19, 142.91, 130.17, 128.84, 127.49, 127.37, 91.25, 63.78, 61.09, 55.76.

HRMS (ESI): m/z Calcd for $C_{21}H_{22}N$ [M-H]$^+$: 288.1747; Found: 288.1749.

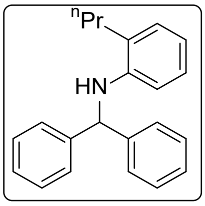


N-benzhydryl-2-ethylaniline (64)

103mg, 72% isolated yield, Colourless liquid.

^{1}H NMR (400 MHz, CDCl$_3$) δ 7.30 – 7.20 (m, 8H), 7.20 – 7.14 (m, 2H), 7.01 (d, J = 7.4 Hz, 1H), 6.90 (t, J = 7.7 Hz, 1H), 6.61 (t, J = 7.4 Hz, 1H), 6.35 (d, J = 8.1 Hz, 1H), 5.47 (s, 1H), 4.08 (s, 1H), 2.45 (q, J = 7.5 Hz, 2H), 1.19 (t, J = 7.5 Hz, 3H).^{13}C NMR (101 MHz, CDCl$_3$) δ 143.07, 128.81, 127.95 – 127.06 (m), 126.89, 117.58, 111.66, 62.96, 24.07, 12.87.

HRMS (ESI): m/z Calcd for $C_{21}H_{22}N$ [M-H]+: 288.1747; Found: 288.1748.



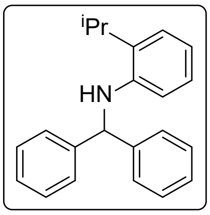
N-benzhydryl-2-propylaniline (65)

126mg, 84% isolated yield, Colourless liquid.

^{1}H NMR (400 MHz, CDCl$_3$) δ 7.34 – 7.27 (m, 7H), 7.22 (d, J = 5.6 Hz, 3H), 7.02 (d, J = 8.4 Hz, 1H), 6.93 (t, J = 7.1 Hz, 1H), 6.63 (t, J = 7.2 Hz, 1H), 6.39 (d, J = 7.8 Hz, 1H), 5.49 (s, 1H), 2.48 – 2.40 (m, 2H), 1.68 – 1.62 (m, 2H), 0.94 (t, J = 7.3 Hz, 3H).

13C NMR (101 MHz, CDCl3) δ 146.31, 145.94, 143.05, 142.09, 133.85, 130.24, 130.12, 128.44, 128.41, 125.91, 121.46, 121.38, 102.70, 43.82, 35.63, 28.94, 28.82.

HRMS (ESI): m/z Calcd for $C_{22}H_{24}N$ [M-H]$^+$: 302.1903; Found: 302.1906.

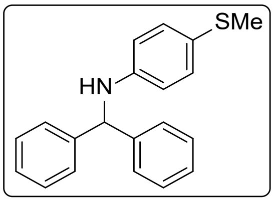


N-benzhydryl-2-isopropylaniline (66)

72mg, 48% isolated yield, Yellow liquid.

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.31 – 7.22 (m, 8H), 7.21 – 7.17 (m, 2H), 7.09 (d, J = 6.1 Hz, 1H), 6.93 – 6.86 (m, 1H), 6.65 (t, J = 7.5 Hz, 1H), 6.37 (d, J = 8.1 Hz, 1H), 5.46 (s, 1H), 2.82 (p, J = 6.7 Hz, 1H), 1.21 (s, 3H), 1.20 (s, 3H). 13C NMR (101 MHz, CDCl3) δ 143.61, 143.32, 142.13, 128.80, 127.52, 127.39, 118.25, 114.54, 67.13, 63.70, 51.21.

HRMS (ESI): m/z Calcd for $C_{22}H_{24}N$ [M-H]$^+$: 302.1903; Found: 302.1905.

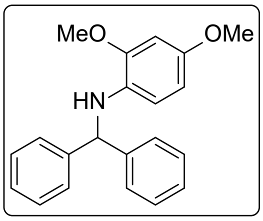


N-benzhydryl-4-(methylthio) aniline (67)

104mg, 68% isolated yield, Brown liquid.

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.50 – 7.39 (m, 8H), 7.36 (t, J = 6.8 Hz, 2H), 7.25 (d, J = 8.6 Hz, 2H), 6.59 (d, J = 8.7 Hz, 2H), 5.60 (s, 1H), 4.38 (s, 1H), 2.46 (s, 3H). 13C NMR (101 MHz, CDCl3) δ 146.16, 142.74, 131.18, 128.90, 127.56, 127.54, 124.83, 114.26, 63.13, 18.98.

HRMS (ESI): m/z Calcd for $C_{20}H_{20}NS$ [M-H]$^+$: 306.1311; Found: 306.1313.

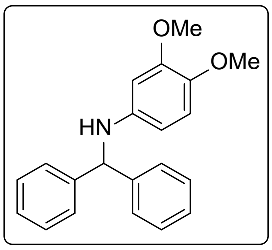


N-benzhydryl-2,4-dimethoxyaniline (68)

102mg, 64% isolated yield, Colourless liquid.

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.28 (d, J = 7.2 Hz, 4H), 7.22 (t, J = 7.5 Hz, 4H), 7.14 (t, J = 6.4 Hz, 2H), 6.55 (d, J = 8.6 Hz, 1H), 6.11 (d, J = 2.6 Hz, 1H), 5.93 (dd, J = 8.6, 2.6 Hz, 1H), 5.34 (s, 1H), 3.96 (s, 1H), 3.65 (s, 3H), 3.60 (s, 3H). 13C NMR (101 MHz, CDCl3) δ 143.61, 143.30, 142.12, 128.80, 127.52, 127.37, 118.25, 114.54, 67.14, 63.70, 51.22.

HRMS (ESI): m/z Calcd for $C_{21}H_{22}NO_2$ [M-H]$^+$: 320.1645; Found: 320.1648.

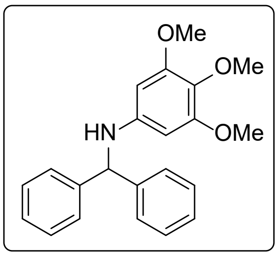


N-benzhydryl-3,4-dimethoxyaniline (69)

116mg, 73% isolated yield, Red solid.

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.28 (d, J = 7.2 Hz, 4H), 7.22 (t, J = 7.5 Hz, 4H), 7.14 (t, J = 6.4 Hz, 2H), 6.55 (d, J = 8.6 Hz, 1H), 6.11 (d, J = 2.6 Hz, 1H), 5.93 (dd, J = 8.6, 2.6 Hz, 1H), 5.34 (s, 1H), 3.96 (s, 1H), 3.65 (s, 3H), 3.60 (s, 3H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 149.80, 143.13, 128.78, 127.41, 127.38, 113.04, 104.39, 99.60, 63.96, 56.64, 55.60.

HRMS (ESI): m/z Calcd for $C_{21}H_{22}NO_2$ [M-H]$^+$: 320.1645; Found: 320.1646.

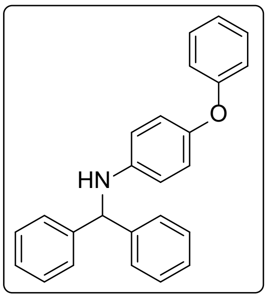


N-benzhydryl-3,4,5-trimethoxyaniline (70)

89mg, 51% isolated yield, Colourless liquid.

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.29 (dd, J = 8.4, 1.5 Hz, 4H), 7.25 – 7.19 (m, 4H), 7.17 – 7.12 (m, 2H), 5.68 (s, 2H), 5.36 (s, 1H), 4.10 (s, 1H), 3.63 (d, J = 0.8 Hz, 3H), 3.55 (s, 6H). 13C NMR (101 MHz, CDCl3) δ 153.74, 144.18, 142.91, 130.16, 128.84, 127.48, 127.37, 91.25, 63.79, 61.09, 55.76.

HRMS (ESI): m/z Calcd for $C_{22}H_{24}NO_3$ [M-H]$^+$: 350.1751; Found: 350.1753.



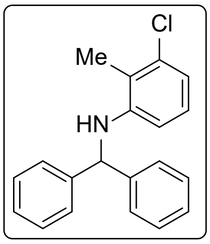
N-benzhydryl-4-phenoxyaniline (71)

126mg, 72% isolated yield, Colourless liquid.

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.24 – 7.10 (m, 12H), 6.98 – 6.89 (m, 2H), 6.84 (d, J = 7.8 Hz, 2H), 6.19 (dd, J = 18.4, 8.1 Hz, 2H), 6.09 (s, 1H), 5.36 (s, 1H), 4.17 (s, 1H). 13C NMR (101

MHz, CDCl3) δ 158.44, 157.02, 148.87, 142.67, 130.22, 129.71, 128.89, 127.55, 127.53, 123.18, 119.23, 108.65, 107.91, 104.00, 63.01.

HRMS (ESI): m/z Calcd for $C_{25}H_{22}NO$ $[M-H]^+$: 352.1696; Found: 352.1697.

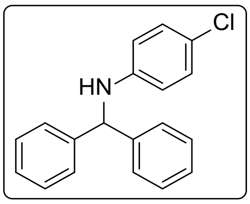


N-benzhydryl-3-chloro-2-methylaniline (72)

103mg, 67% isolated yield, Pale brown.

^1H NMR (400 MHz, $CDCl_3$) δ 7.29 – 7.22 (m, 8H), 7.21 – 7.16 (m, 2H), 6.79 (t, J = 8.1 Hz, 1H), 6.67 (d, J = 8.0 Hz, 1H), 6.24 (d, J = 7.9 Hz, 1H), 5.46 (s, 1H), 4.09 (s, 1H), 2.18 (s, 3H). 13C NMR (101 MHz, CDCl3) δ 146.33, 142.56, 134.44, 128.88, 127.55, 127.39, 127.11, 119.76, 118.35, 109.87, 63.00, 13.77.

HRMS (ESI): m/z Calcd for $C_{20}H_{19}ClN$ $[M-H]^+$: 308.1201; Found: 308.1203.

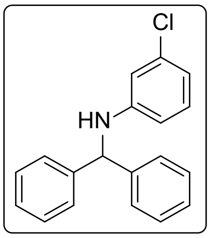


N-benzhydryl-4-chloroaniline (73)

127mg, 87% isolated yield, Brown liquid.

^1H NMR (400 MHz, $CDCl_3$) δ 7.33 (dd, J = 25.2, 4.8 Hz, 10H), 7.09 (s, 1H), 7.07 (s, 1H), 6.49 (d, J = 8.9 Hz, 2H), 5.48 (s, 1H), 4.28 (s, 1H).^{13}C NMR (101 MHz, $CDCl_3$) δ 145.81, 142.45, 128.97, 128.85, 128.77, 127.55, 127.48, 127.41, 114.60, 63.11.

HRMS (ESI): m/z Calcd for $C_{19}H_{17}ClN$ $[M-H]^+$: 294.1044; Found: 294.1044.



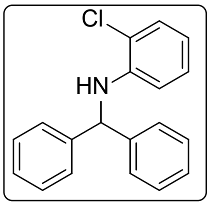
N-benzhydryl-3-chloroaniline (74)

91mg, 62% isolated yield, Pale yellow liquid.

^1H NMR (400 MHz, $CDCl_3$) δ 7.18 (dd, J = 23.9, 4.4 Hz, 10H), 6.88 (t, J = 8.1 Hz, 1H), 6.54 (d, J = 7.9 Hz, 1H), 6.41 (s, 1H), 6.28 (d, J = 11.0 Hz, 1H), 5.37 (s, 1H), 4.18 (s, 1H).^{13}C NMR

(101 MHz, $CDCl_3$) δ 148.39, 142.33, 134.87, 130.16, 128.89, 127.61, 127.45, 117.69, 113.40, 111.70, 62.87.

HRMS (ESI): m/z Calcd for $C_{19}H_{17}ClN$ [M-H]$^+$: 294.1044; Found: 294.1046.

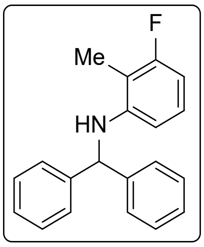


N-benzhydryl-2-chloroaniline (75)

85mg, 58% isolated yield, Pale yellow liquid.

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.39 (q, J = 7.9, 7.3 Hz, 8H), 7.31 (dd, J = 10.4, 8.0 Hz, 3H), 7.04 (t, J = 7.8 Hz, 1H), 6.67 (t, J = 7.6 Hz, 1H), 6.52 (d, J = 8.2 Hz, 1H), 5.60 (d, J = 4.4 Hz, 1H), 4.96 (s, 1H).^{13}C NMR (101 MHz, $CDCl_3$) δ 143.09, 142.33, 129.02, 128.87, 127.67, 127.55, 127.38, 117.63, 112.69, 62.64.

HRMS (ESI): m/z Calcd for $C_{19}H_{17}ClN$ [M-H]$^+$: 294.1044; Found: 294.1048.

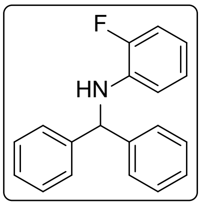


N-benzhydryl-3-fluoro-2-methylaniline (76)

86mg, 59% isolated yield, Colourless liquid.

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.41 – 7.34 (m, 8H), 7.33 – 7.28 (m, 2H), 6.93 (q, J = 8.0 Hz, 1H), 6.47 (t, J = 8.8 Hz, 1H), 6.25 (d, J = 8.2 Hz, 1H), 5.60 (s, 1H), 4.17 (s, 1H), 2.13 (s, 3H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 162.49, 160.10, 146.79, 142.67, 128.86, 127.52, 127.39, 127.11, 127.01, 108.80, 108.61, 107.07, 104.52, 104.28, 63.01, 8.46, 8.39.

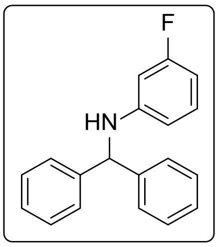
HRMS (ESI): m/z Calcd for $C_{20}H_{19}FN$ [M-H]$^+$: 292.1496; Found: 292.1498.



N-benzhydryl-2-fluoroaniline (77)

76mg, 55% isolated yield, Colourless liquid.

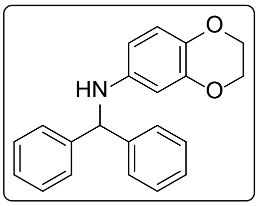
^{1}H NMR (400 MHz, $CDCl_3$) δ 7.30 – 7.19 (m, 8H), 7.16 (t, J = 7.0 Hz, 2H), 6.88 (dd, J = 11.2, 7.4 Hz, 1H), 6.75 (t, J = 7.7 Hz, 1H), 6.51 (q, J = 6.2 Hz, 1H), 6.39 (t, J = 7.7 Hz, 1H), 5.42 (d, J = 3.9 Hz, 1H), 4.41 (s, 1H). ^{13}C NMR (101 MHz, CDCl$_3$) δ 150.37, 142.48, 135.86, 135.74, 128.87, 127.57, 127.43, 124.52, 124.49, 117.10, 117.03, 114.43, 114.24, 113.43, 113.40, 62.73. HRMS (ESI): m/z Calcd for $C_{19}H_{17}FN$ $[M-H]^+$: 278.1340; Found: 278.1341.



N-benzhydryl-3-fluoroaniline (78)

90mg, 65% isolated yield, Pale yellow liquid.

^{1}H NMR (400 MHz, CDCl$_3$) δ 7.23 (q, J = 3.8, 2.6 Hz, 8H), 7.16 (dt, J = 8.5, 4.0 Hz, 2H), 6.96 – 6.88 (m, 1H), 6.30 – 6.24 (m, 1H), 6.21 (d, J = 9.8 Hz, 1H), 6.12 (d, J = 11.6 Hz, 1H), 5.38 (s, 1H), 4.24 (s, 1H). ^{13}C NMR (101 MHz, CDCl$_3$) δ 165.13, 162.72, 149.07, 148.96, 142.36, 130.23, 130.13, 128.87, 127.58, 127.43, 109.40, 109.38, 104.31, 104.09, 100.49, 100.23, 63.00. HRMS (ESI): m/z Calcd for $C_{19}H_{17}FN$ $[M-H]^+$: 278.1340; Found: 278.1343.

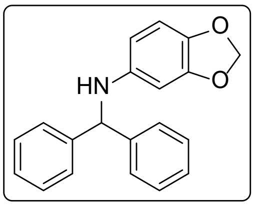


N-benzhydrylbenzo[d][1,3]dioxol-5-amine (79)

101mg, 64% isolated yield, Colourless liquid.

^{1}H NMR (400 MHz, CDCl$_3$) δ 7.24 – 7.18 (m, 6H), 7.16 – 7.08 (m, 4H), 6.54 – 6.50 (m, 1H), 5.99 – 5.93 (m, 2H), 5.27 (s, 1H), 3.98 – 3.92 (m, 4H). ^{13}C NMR (101 MHz, CDCl$_3$) □ 156.71, 155.96, 155.35, 148.62, 141.58, 141.36, 140.44, 140.25, 140.16, 139.40, 130.36, 120.11, 115.08, 90.15, 89.89, 89.64, 89.12.

HRMS (ESI): m/z Calcd for $C_{21}H_{20}NO_2$ $[M-H]^+$: 318.1489; Found: 318.1491.



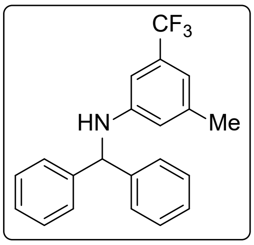
N-benzhydrylbenzo[d][1,3]dioxol-5-amine (80)

85mg, 56% isolated yield, Pale yellow liquid.

^{1}H NMR (400 MHz, CDCl$_3$) δ 7.28 – 7.20 (m, 8H), 7.18 – 7.13 (m, 2H), 6.49 (d, J = 8.3 Hz, 1H), 6.08 (s, 1H), 5.87 (d, J = 10.4 Hz, 1H), 5.71 (s, 2H), 5.31 (s, 1H), 3.95 (s, 1H). ^{13}C NMR

(101 MHz, $CDCl_3$) δ 148.17, 142.97, 139.73, 128.80, 127.43, 108.56, 105.24, 100.58, 96.56, 63.91.

HRMS (ESI): m/z Calcd for $C_{20}H_{18}NO_2$ $[M-H]^+$: 304.1332; Found: 304.1333.

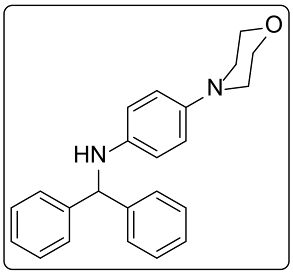


N-benzhydryl-3-methyl-5-(trifluoromethyl) aniline (81)

131mg, 77% isolated yield, Colourless liquid.

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.24 – 7.17 (m, 8H), 7.17 – 7.12 (m, 2H), 6.34 (d, J = 11.8 Hz, 2H), 6.06 (s, 1H), 5.39 (s, 1H), 4.33 (s, 1H), 3.54 (s, 3H). 13C NMR (101 MHz, CDCl3) δ 160.90, 148.72, 142.14, 128.93, 127.69, 127.41, 103.72, 103.68, 102.05, 99.47, 99.43, 62.94, 55.26.

HRMS (ESI): m/z Calcd for $C_{21}H_{19}F_3N$ $[M-H]^+$: 342.1464; Found: 342.1468.

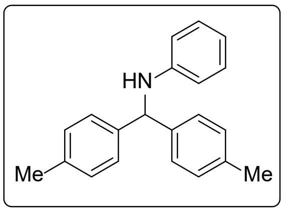


N-benzhydryl-4-morpholinoaniline (82)

82mg, 48% isolated yield, Colourless solid.

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.29 – 7.17 (m, 8H), 7.13 (t, J = 6.6 Hz, 2H), 6.64 (d, J = 8.5 Hz, 2H), 6.40 (d, J = 8.3 Hz, 2H), 5.33 (s, 1H), 3.70 (d, J = 3.8 Hz, 4H), 2.90 – 2.81 (m, 4H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 143.60, 143.30, 142.13, 128.80, 127.52, 127.38, 118.25, 114.54, 67.14, 63.70, 51.21.

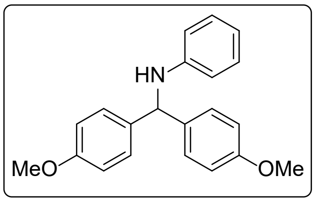
HRMS (ESI): m/z Calcd for $C_{23}H_{25}N_2O$ $[M-H]^+$: 345.1961; Found: 345.1963.



***N*-(di-p-tolylmethyl)aniline (83)**

88 mg, 62% isolated yield, Pale yellow liquid,

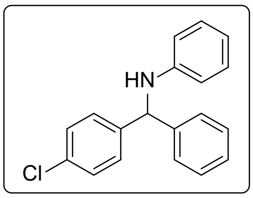
^{1}H NMR (400 MHz, $CDCl_3$) δ 7.18 - 7.14 (m, 4H) 7.06 - 6.99 (m, 6H) 6.63 - 6.60 (m, 1H) 6.48 - 6.44 (m, 2H) 5.35 (s, 1H) 4.11 (br. s., 1H) 2.24 (s, 6H) ppm. ^{13}C NMR (101 MHz, $CDCl_3$) δ 145.08, 143.08, 129.56, 128.66, 127.39, 127.24, 126.74, 113.52, 63.24, 20.34, ppm. HRMS (ESI): *m/z* Calcd for $C_{21}H_{20}N[M-H]^+$: 286.1590; Found: 286.1585.



N-(bis(4-methoxyphenyl)methyl)aniline (84)

108 mg, 68% isolated yield, Pale yellow liquid,

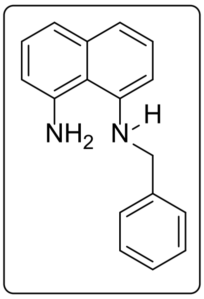
^{1}H NMR (400 MHz, $CDCl_3$) δ 7.24 (d, J=8.59 Hz, 4H) 7.10 - 7.06 (m, 2H) 6.86 - 6.82 (m, 4H) 6.73 - 6.67 (m, 1H) 6.52 (d, J=7.58 Hz, 2H) 5.40 (s, 1H) 4.16 (br. s., 1H) 3.76 (s, 6H) ppm. ^{13}C NMR (101 MHz, $CDCl_3$) δ 158.70, 147.39, 135.35, 129.04, 128.44, 128.08, 117.44, 113.99, 113.70, 113.41, 61.66, 55.20 ppm. HRMS (ESI): *m/z* Calcd for $C_{22}H_{20}O_2N[M-H]^+$: 318.1489; Found: 318.1486.



(S)-N-((4-chlorophenyl)(phenyl)methyl)aniline (85)

80 mg, 55% isolated yield, Pale yellow liquid

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.74 - 7.31 (m, 8H), 7.29 - 7.10 (m, 3H), 6.75 - 6.67 (m, 1H), 6.55 - 6.51 (m, 2H), 5.48 (br. s., 1H), 4.22 (br. s., 1H) ppm. ^{13}C NMR (101 MHz, $CDCl_3$) δ 147.34, 142.93, 129.09, 128.71, 128.17, 127.43, 127.33, 123.11, 120.91, 117.64, 113.47, 63.03 ppm. HRMS (EI): *m/z* Calcd for $C_{19}H_{15}NCl$ $[M-H]^+$: 292.0888; Found: 292.0878.

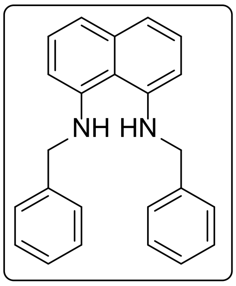


N1-benzylnaphthalene-1,8-diamine (86)

67mg, 54% isolated yield, Yellow liquid

^{1}H NMR (400 MHz, CDCl$_3$) δ 7.36 – 7.24 (m, 4H), 7.23 – 7.15 (m, 3H), 7.13 – 7.03 (m, 3H), 6.52 (d, *J* = 7.3 Hz, 1H), 6.43 (d, *J* = 7.3 Hz, 1H), 4.91 (s, 2H), 4.25 (s, 2H). ^{13}C NMR (101 MHz, CDCl$_3$) δ 146.45, 143.70, 139.20, 136.93, 128.82, 128.72, 128.55, 127.85, 127.69, 127.27, 126.75, 126.60, 125.97, 120.70, 118.54, 117.13, 113.07, 106.38, 77.29, 49.52.

HRMS (ESI): m/z Calcd for $C_{17}H_{17}N_2$ [M-H]$^+$: 249.1386; Found: 249.1388.

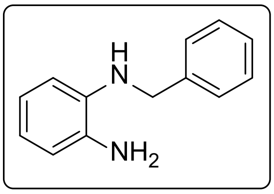


N1, N8-dibenzylnaphthalene-1,8-diamine (87)

93mg, 55% isolated yield, White solid

1H NMR (400 MHz, CDCl3) δ 7.21 – 7.08 (m, 14H), 6.52 (p, J = 4.4 Hz, 2H), 5.78 (s, 2H), 4.14 (s, 4H). 13C NMR (101 MHz, CDCl3) δ 146.14, 138.93, 136.92, 128.75, 127.95, 127.31, 126.35, 119.84, 117.37, 108.73, 77.33, 50.93.

HRMS (ESI): m/z Calcd for $C_{24}H_{23}N_2$ [M-H]$^+$: 339.1856; Found: 339.1857

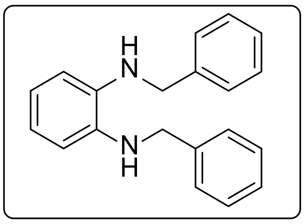


N1-benzylbenzene-1,2-diamine (88)

52mg, 53% isolated yield, Brown liquid.

^{1}H NMR (400 MHz, CDCl3) δ 7.45 – 7.27 (m, 5H), 6.81 (td, J = 7.5, 1.8 Hz, 1H), 6.77 – 6.64 (m, 3H), 4.32 (s, 2H), 3.38 (s, 3H). 13C NMR (101 MHz, CDCl3) δ 139.42, 137.75, 134.18, 128.63, 127.82, 127.29, 120.77, 118.85, 116.56, 112.00, 48.67.

HRMS (ESI): m/z Calcd for $C_{13}H_{15}N_2$ [M-H]$^+$: 199.1230; Found: 199.1234.



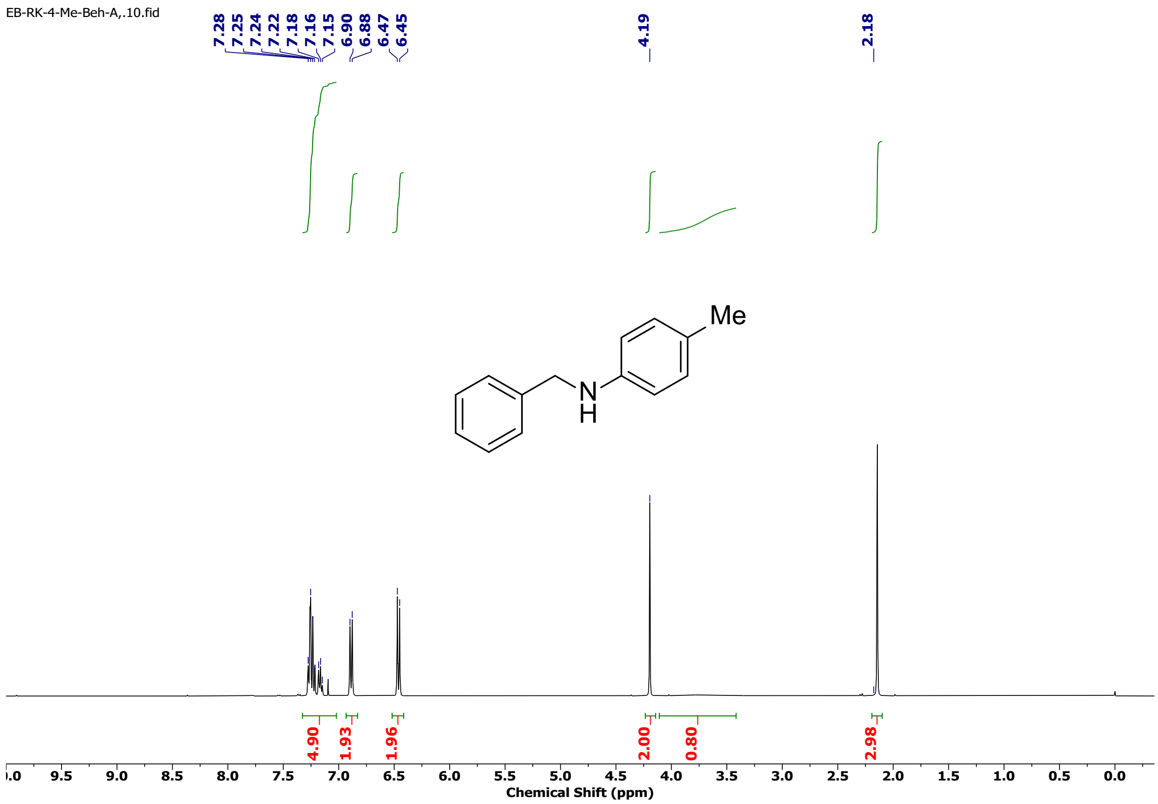
N1,N2-dibenzylbenzene-1,2-diamine (89)

88mg, 61% isolated yield, Yellow liquid

^{1}H NMR (400 MHz, CDCl3) δ 7.42 – 7.24 (m, 10H), 6.79 (dd, J = 5.8, 3.5 Hz, 2H), 6.72 (dd, J = 5.8, 3.5 Hz, 2H), 4.31 (s, 4H), 3.64 (s, 2H). 13C NMR (101 MHz, CDCl3) δ 139.43, 137.17, 128.64, 127.86, 127.29, 119.46, 112.00, 48.83.

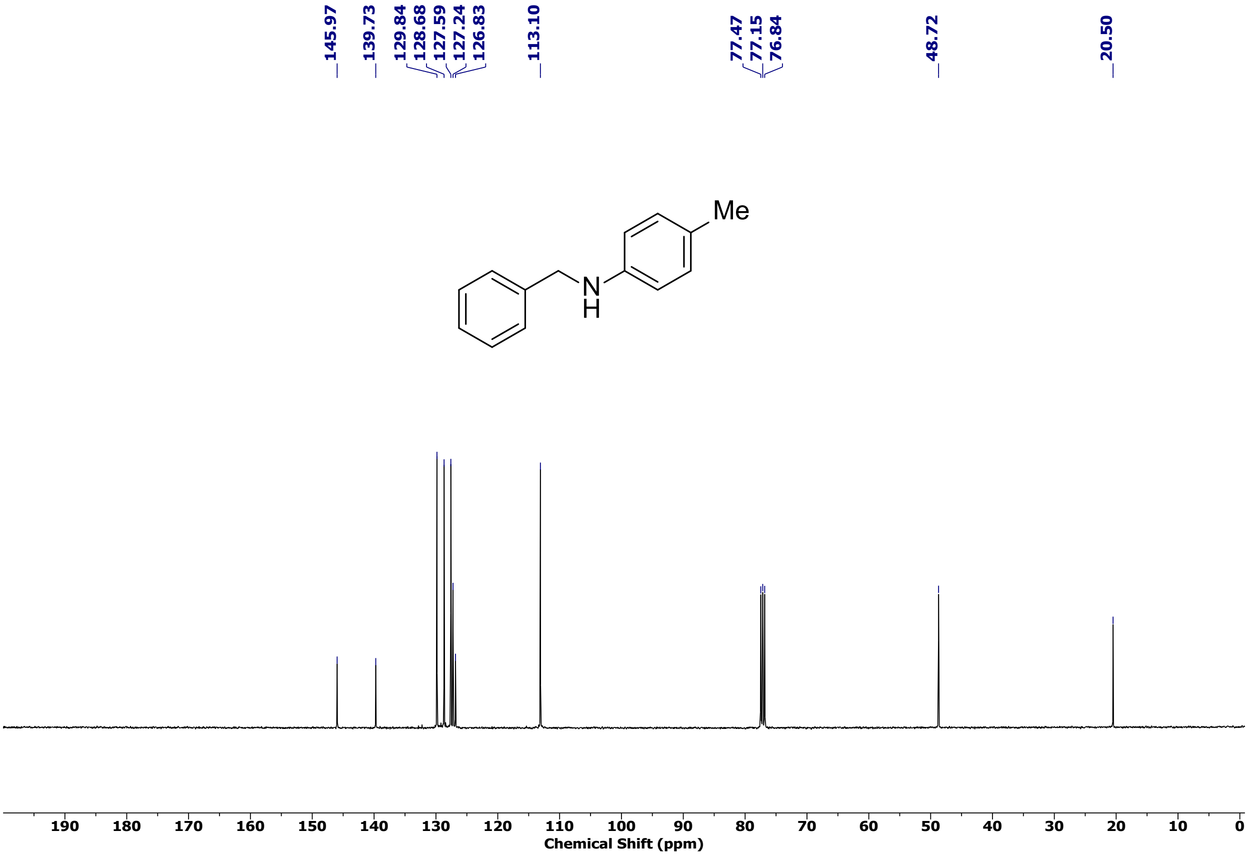
HRMS (ESI): m/z Calcd for $C_{20}H_{21}N_2$ $[M-H]^+$: 289.1699; Found: 289.1697.

8. Copy of ^{1}H and ^{13}C NMR Spectra

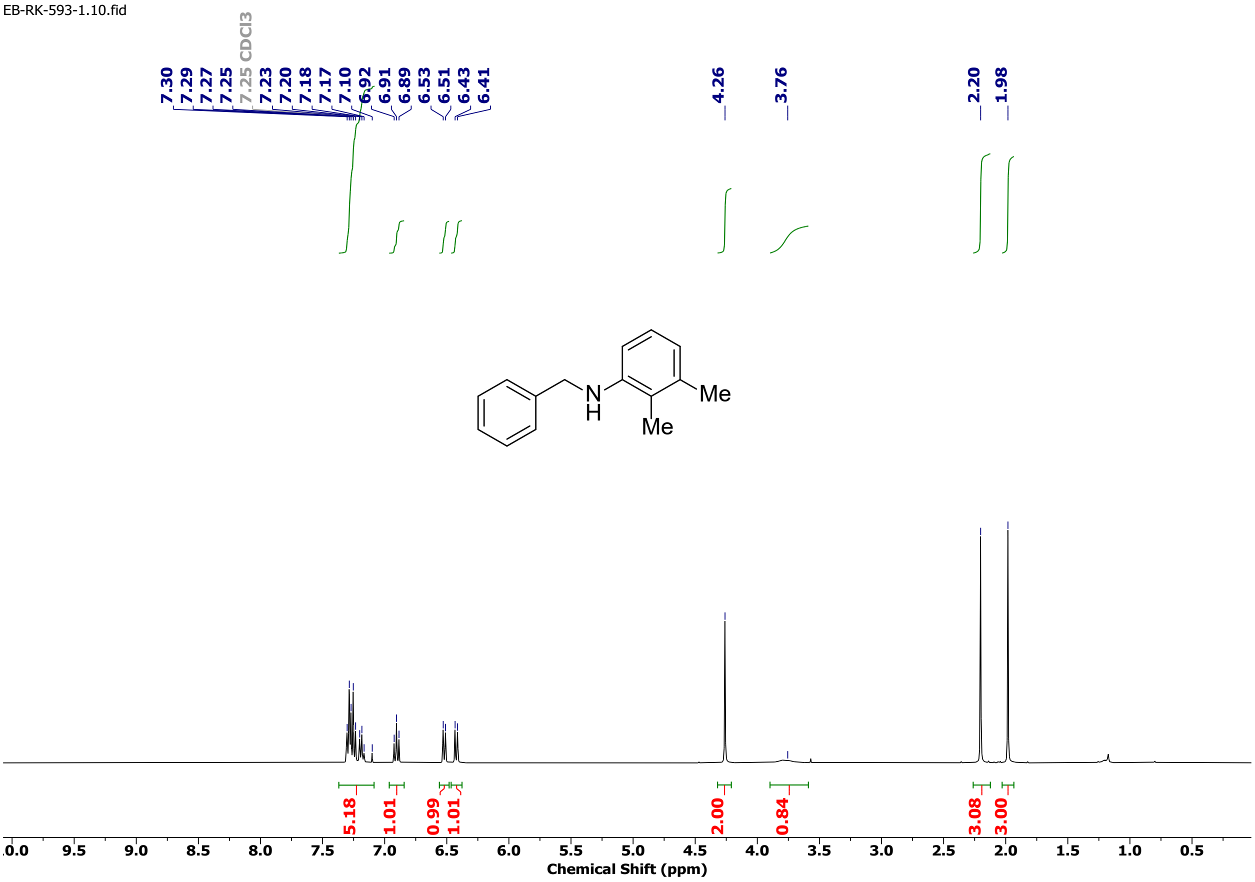


^{1}H

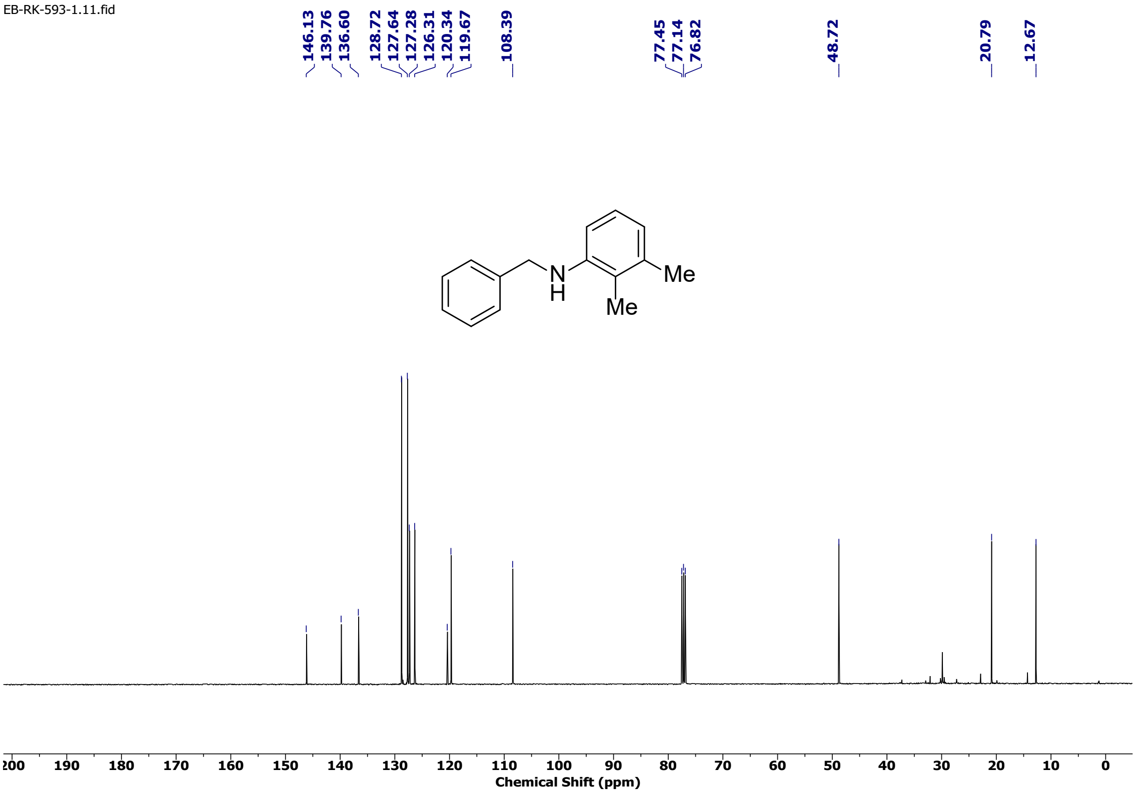
NMR of **3** (400 MHz, $CDCl_3$)



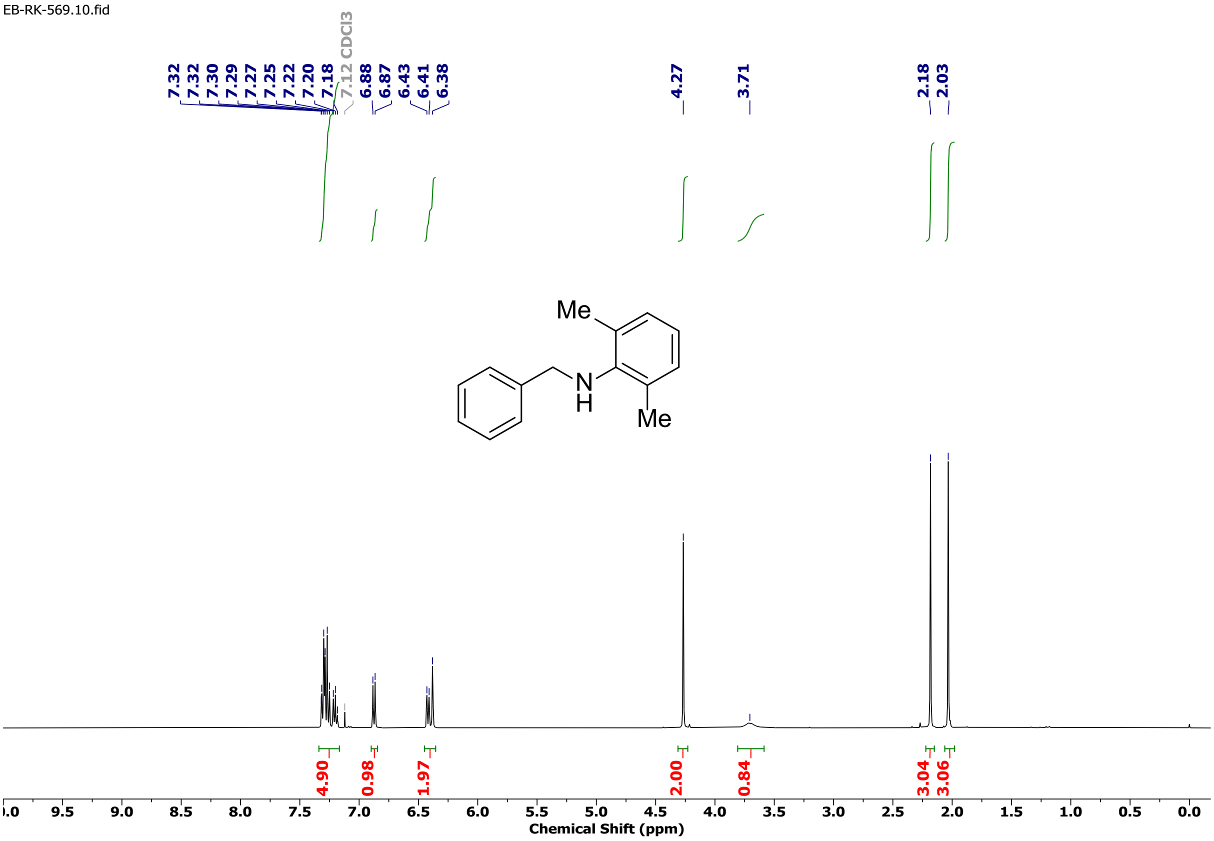
^{13}C NMR of **3** (100 MHz, $CDCl_3$)



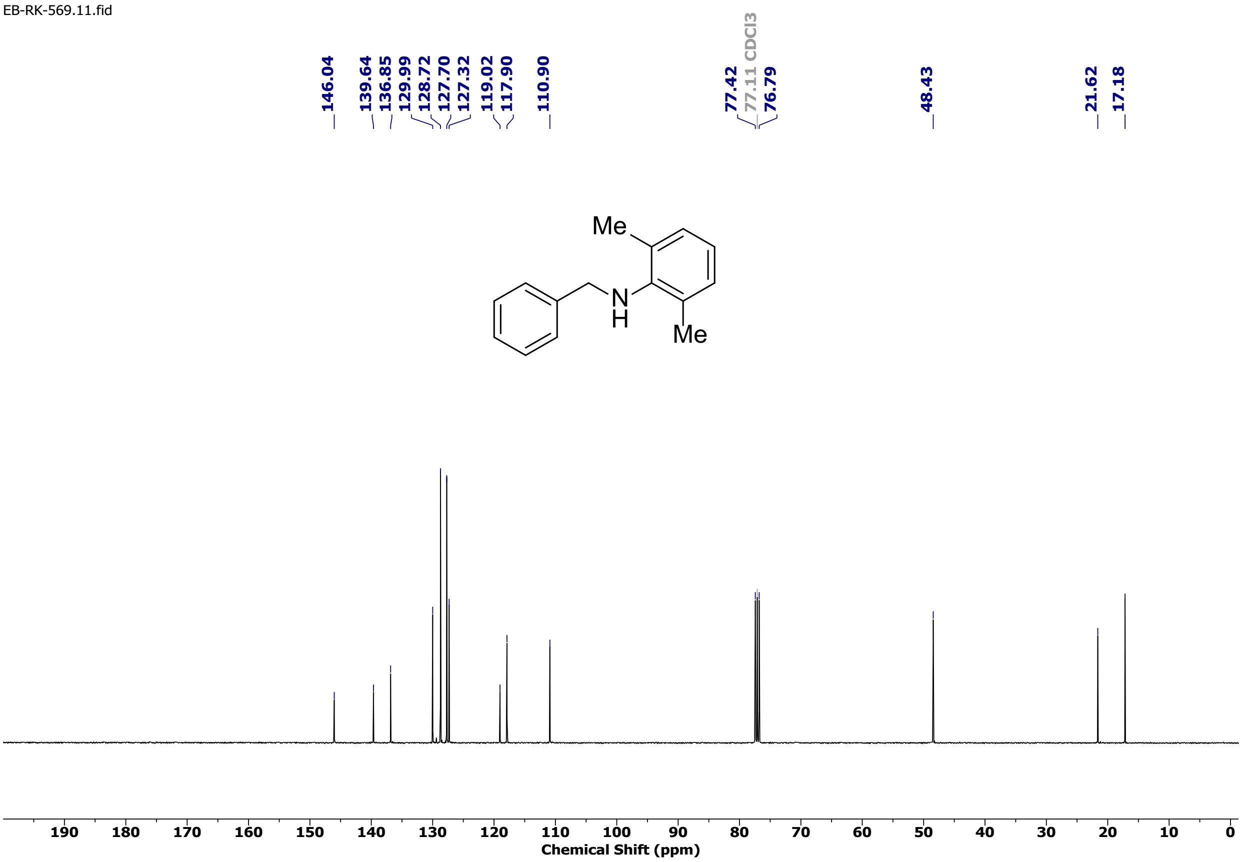
^{1}H NMR of **4** (400 MHz, $CDCl_3$)



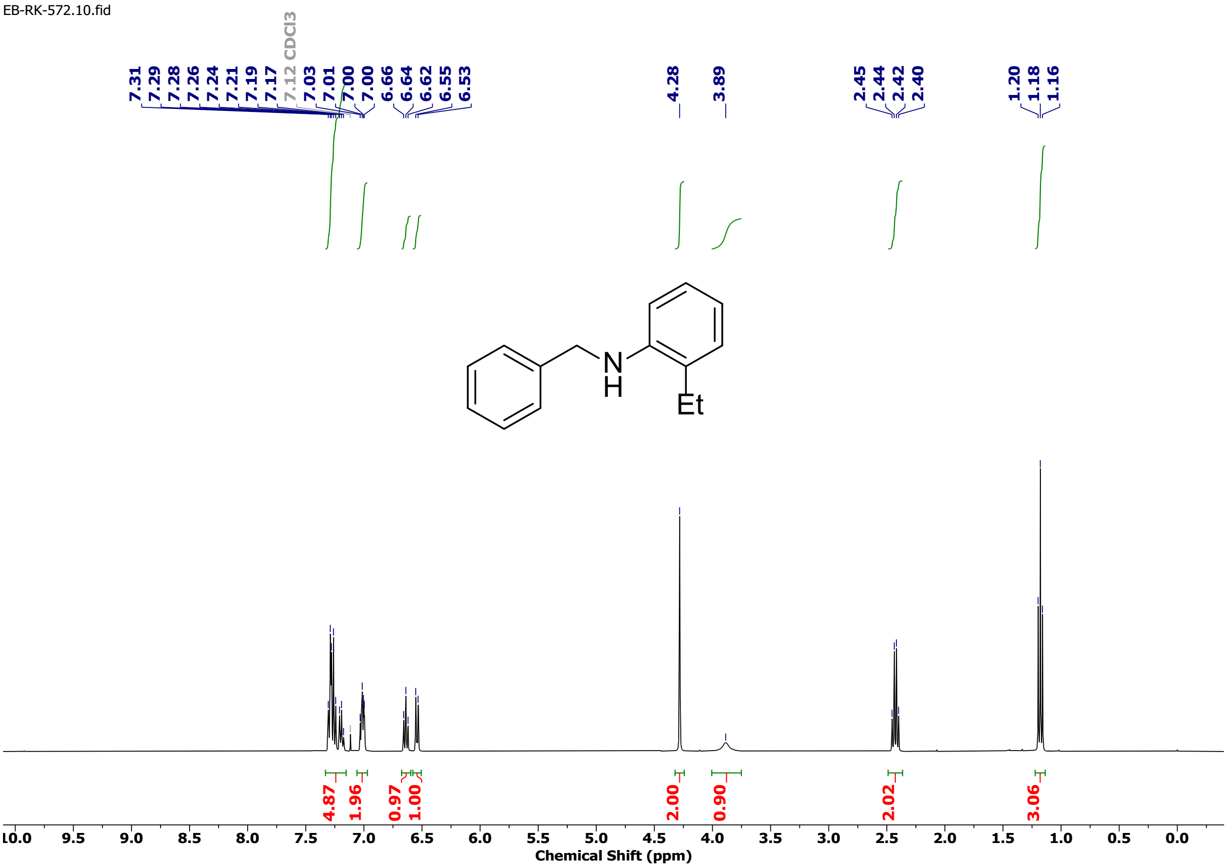
^{13}C NMR of **4** (100 MHz, $CDCl_3$)



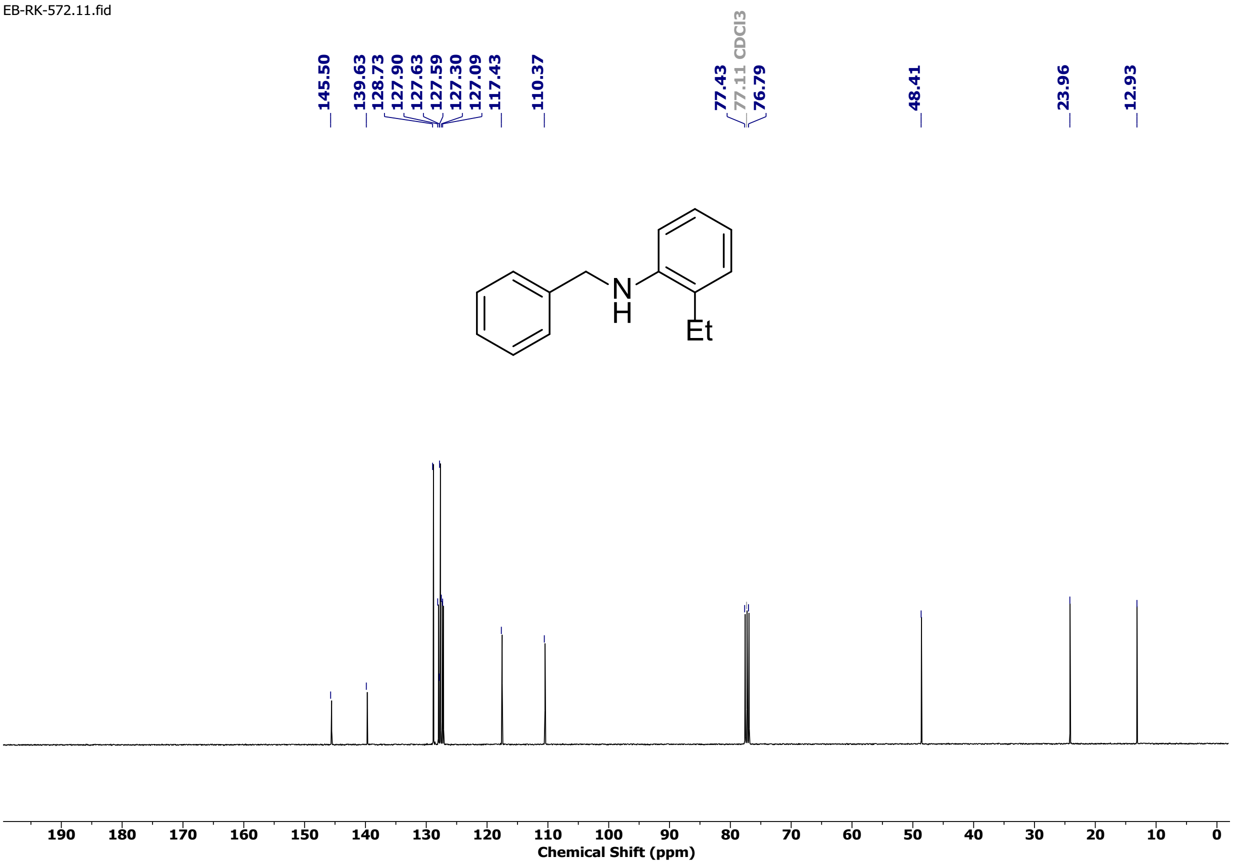
^{1}H NMR of **5** (400 MHz, CDCl$_3$)



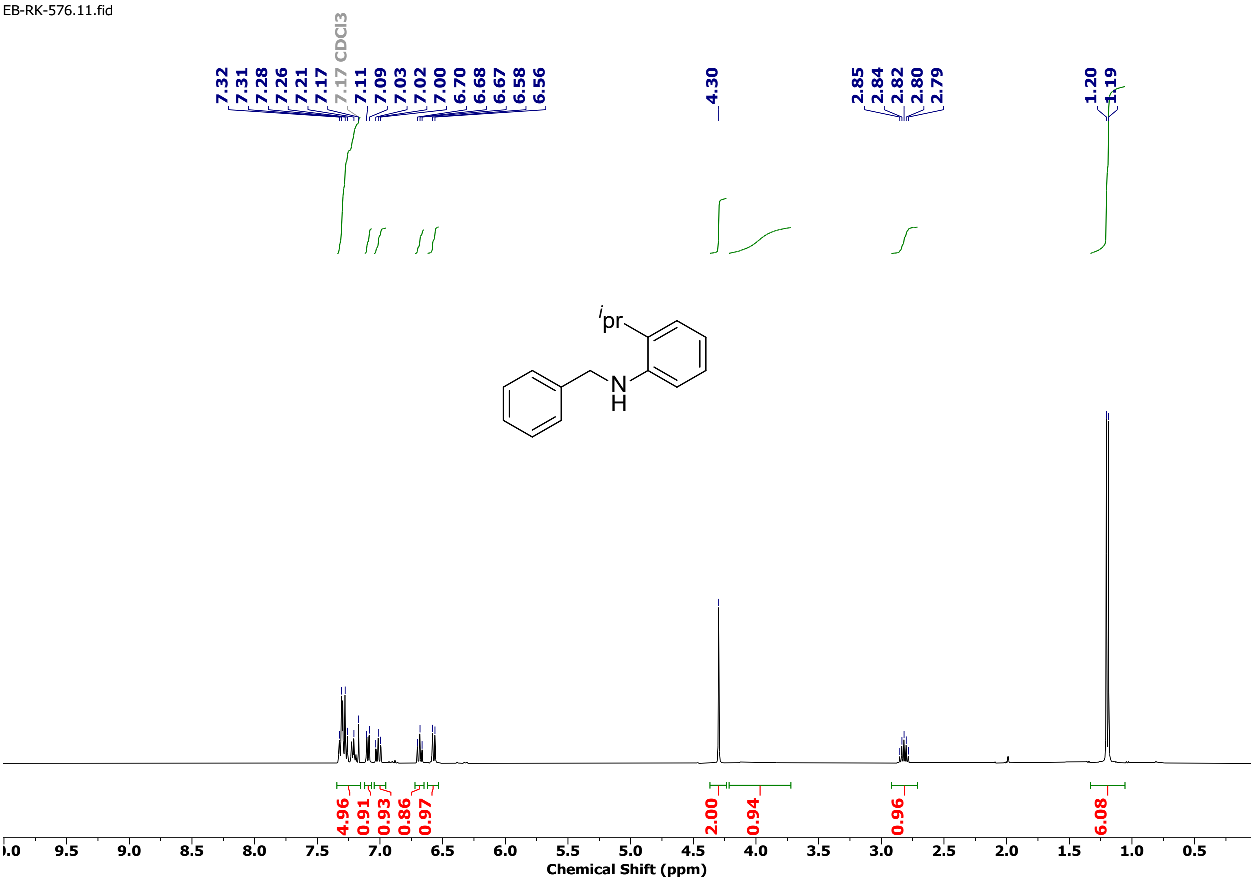
^{13}C NMR of **5** (100 MHz, CDCl$_3$)



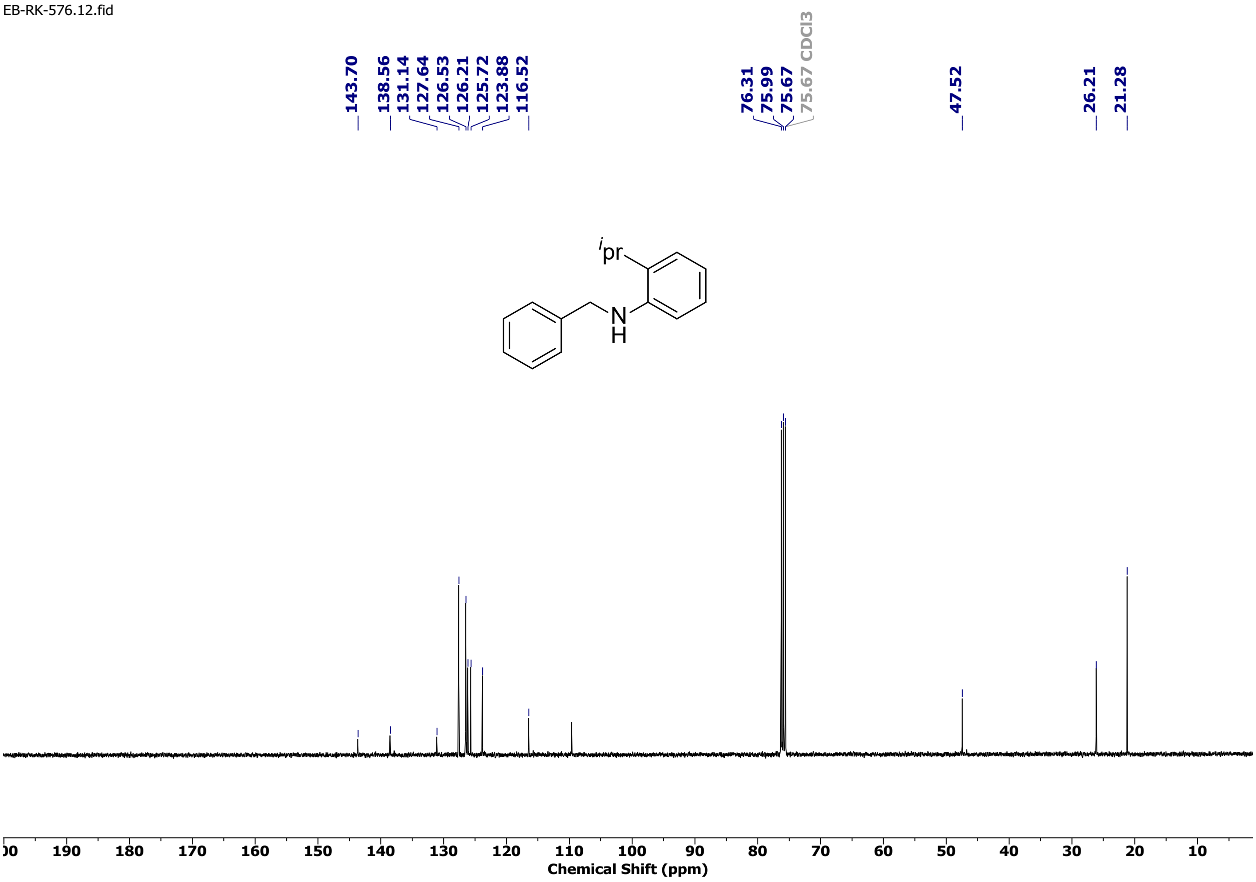
^{1}H NMR of **6** (400 MHz, CDCl$_3$)



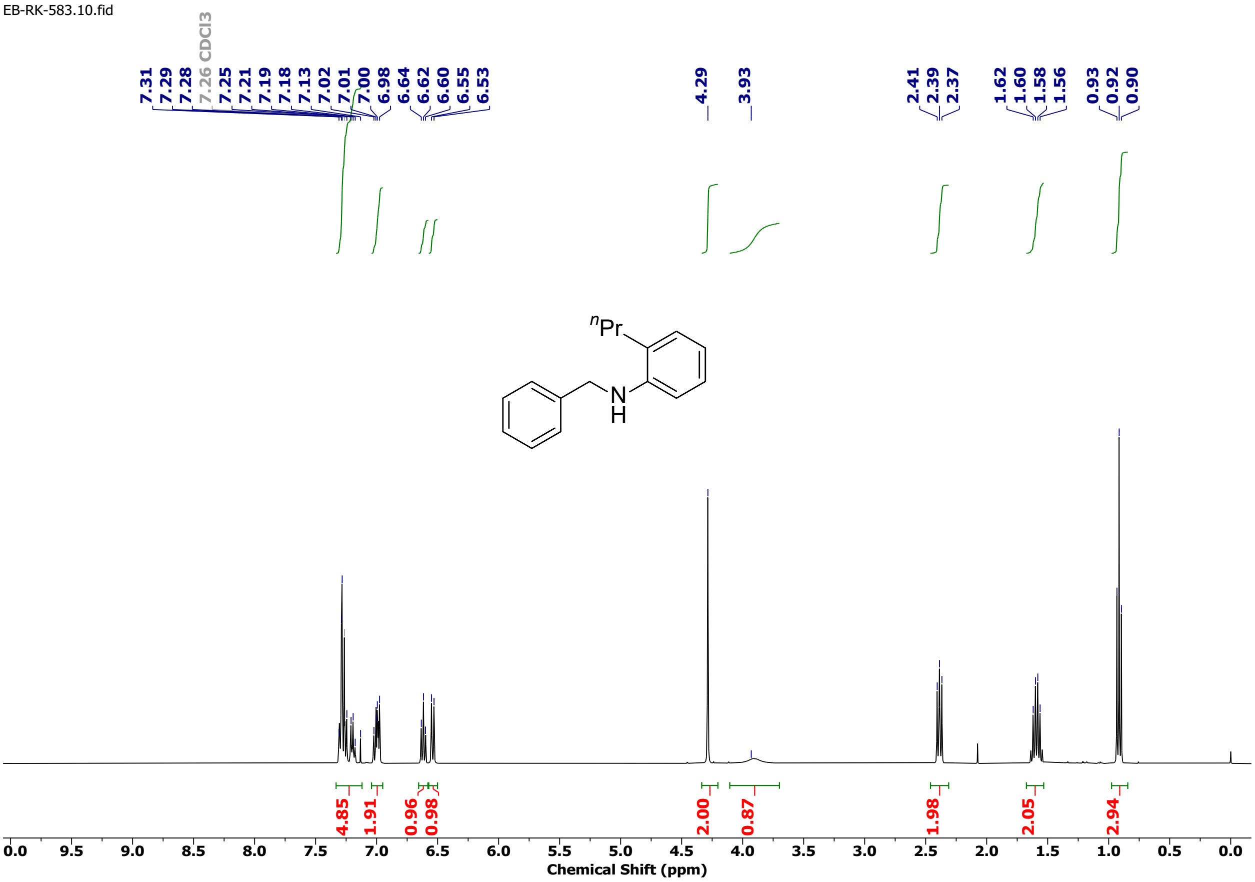
^{13}C NMR of **6** (100 MHz, CDCl$_3$)



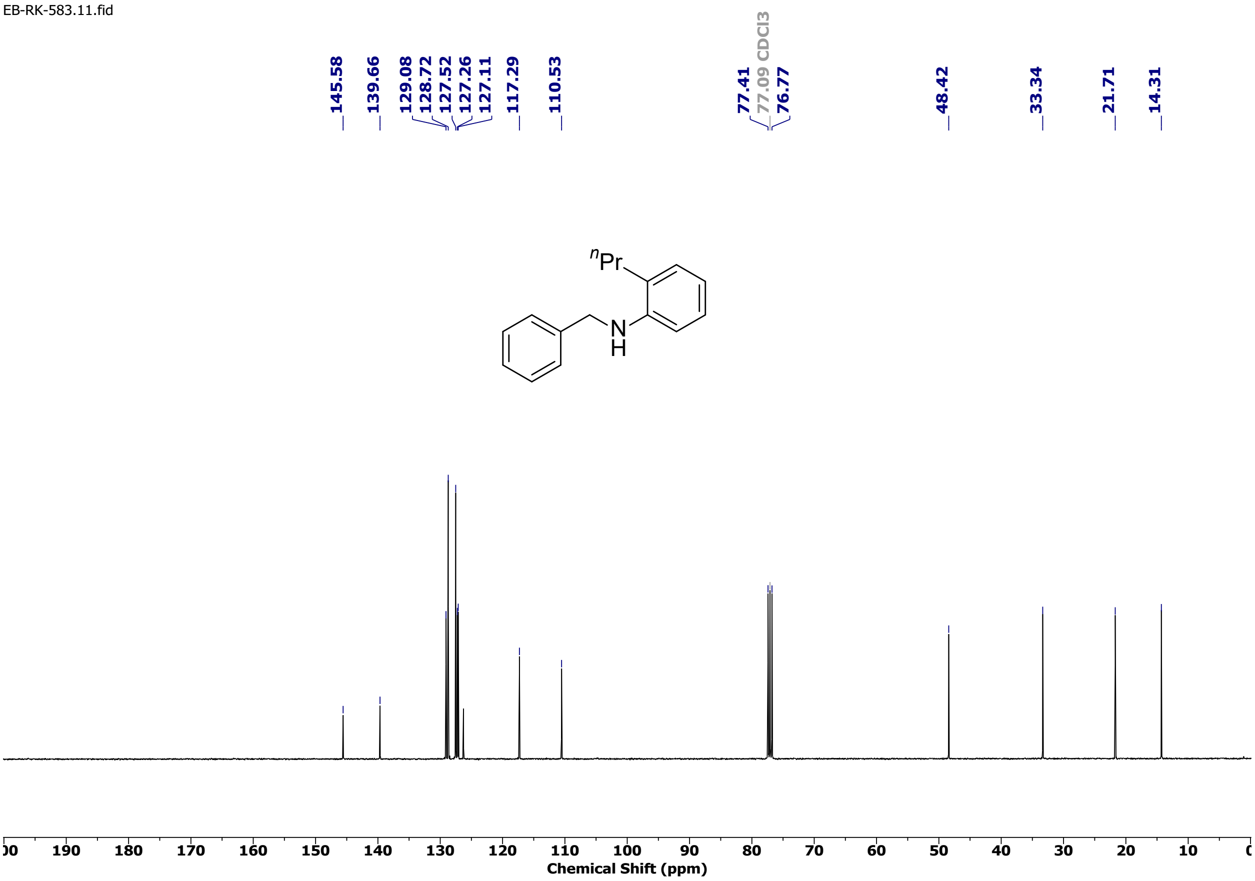
^{1}H NMR of **7** (400 MHz, CDCl$_3$)



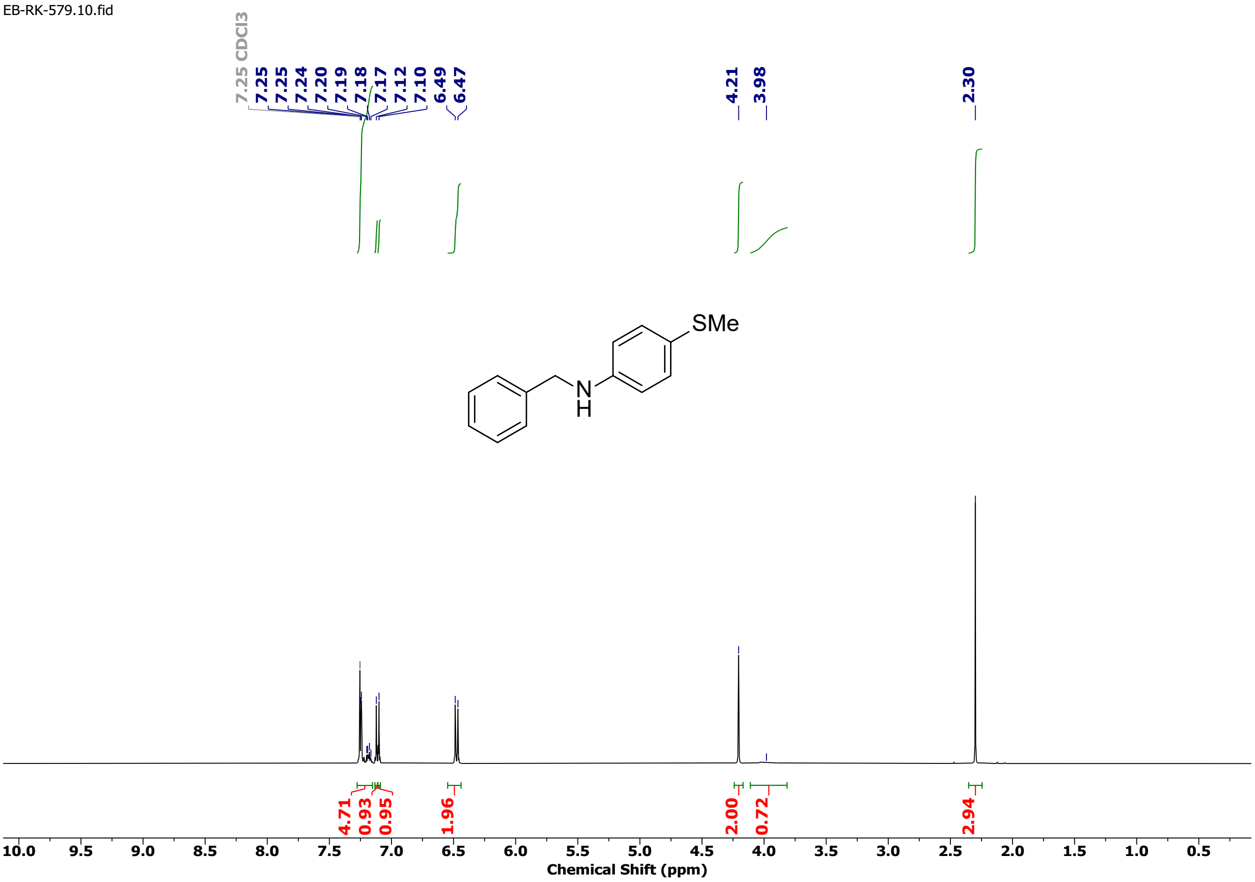
^{13}C NMR of **7** (100 MHz, CDCl$_3$)



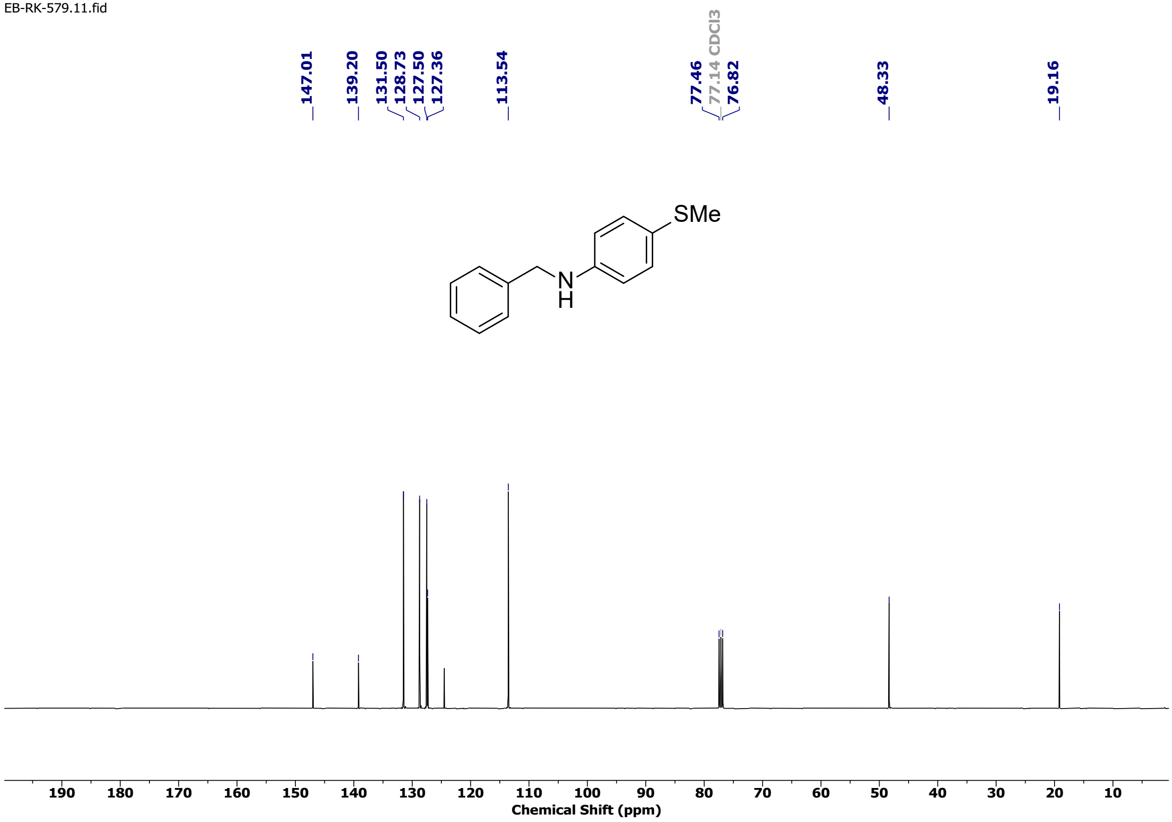
^{1}H NMR of **8** (400 MHz, CDCl$_3$)



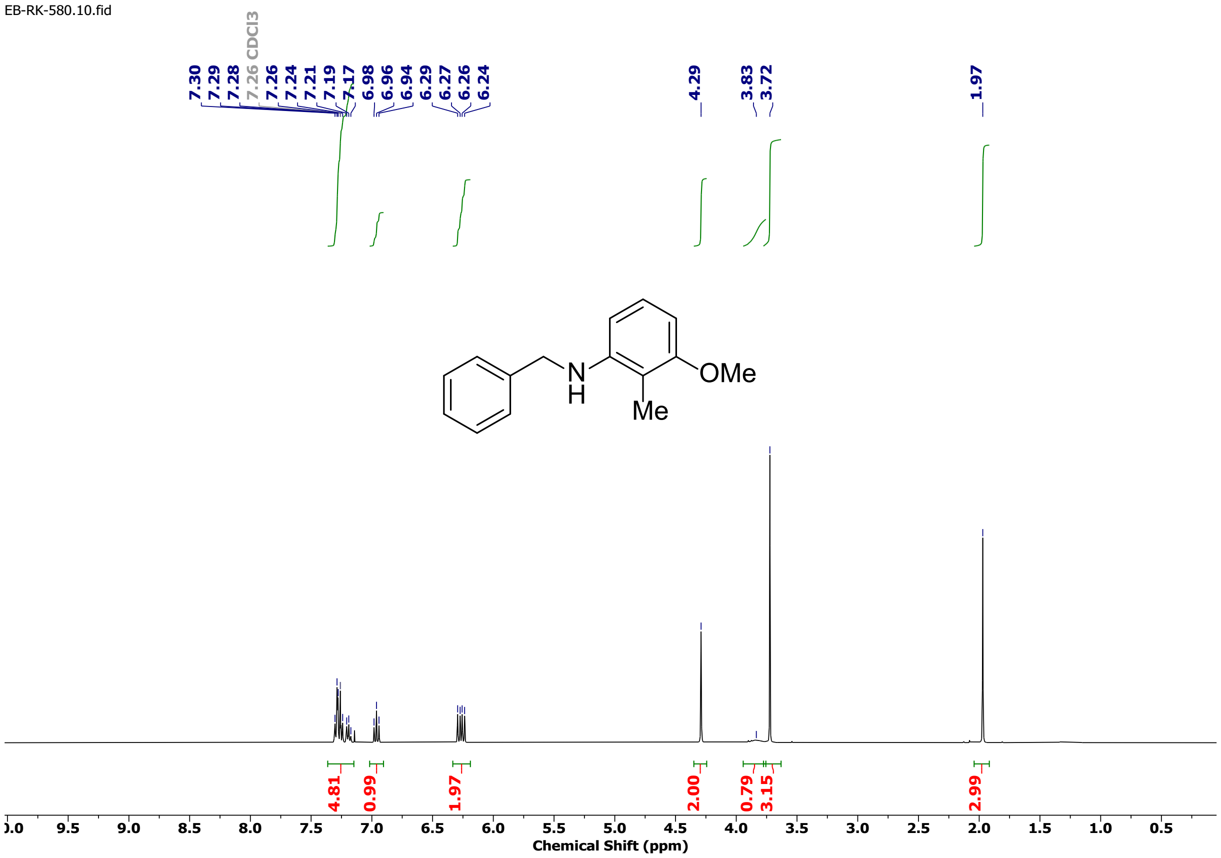
^{13}C NMR of **8** (100 MHz, CDCl$_3$)



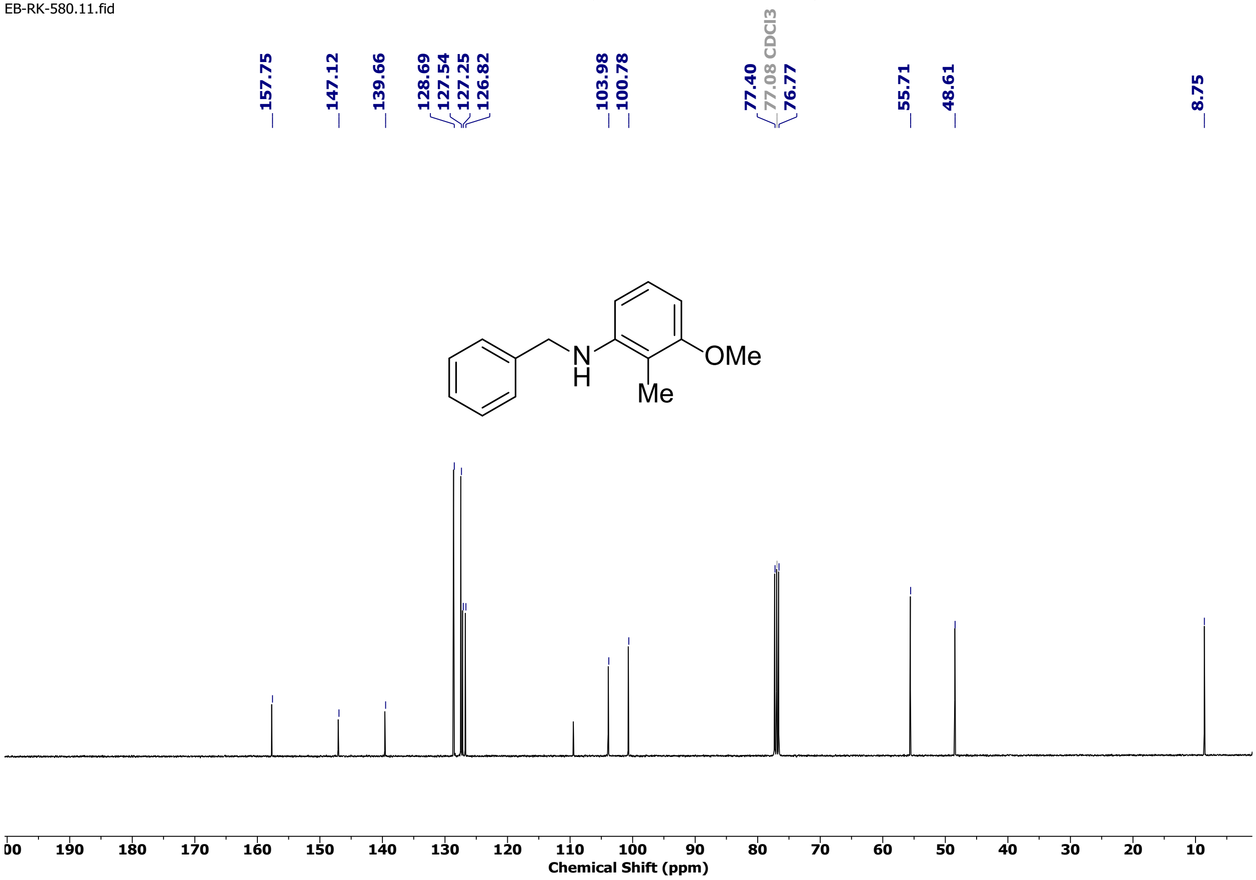
^{1}H NMR of **9** (400 MHz, CDCl$_3$)



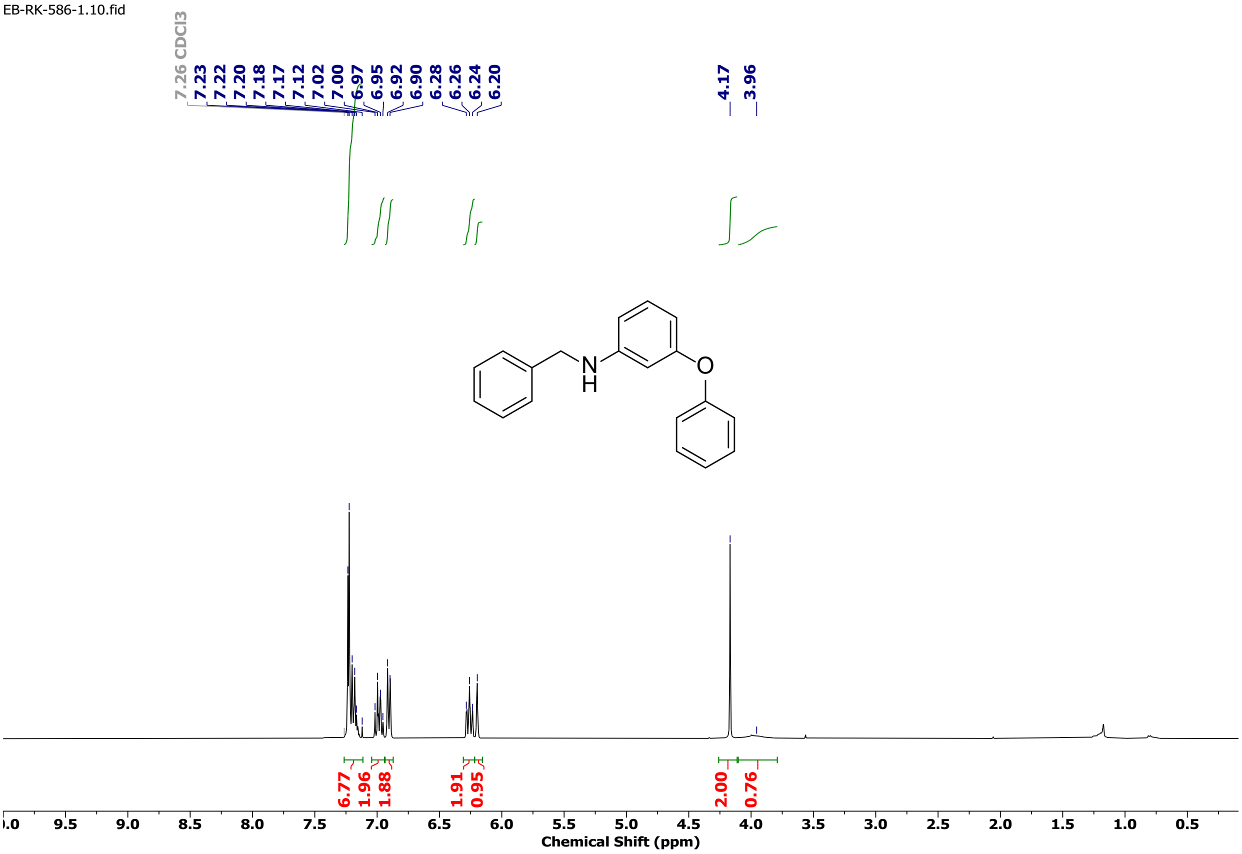
^{13}C NMR of **9** (100 MHz, CDCl$_3$)



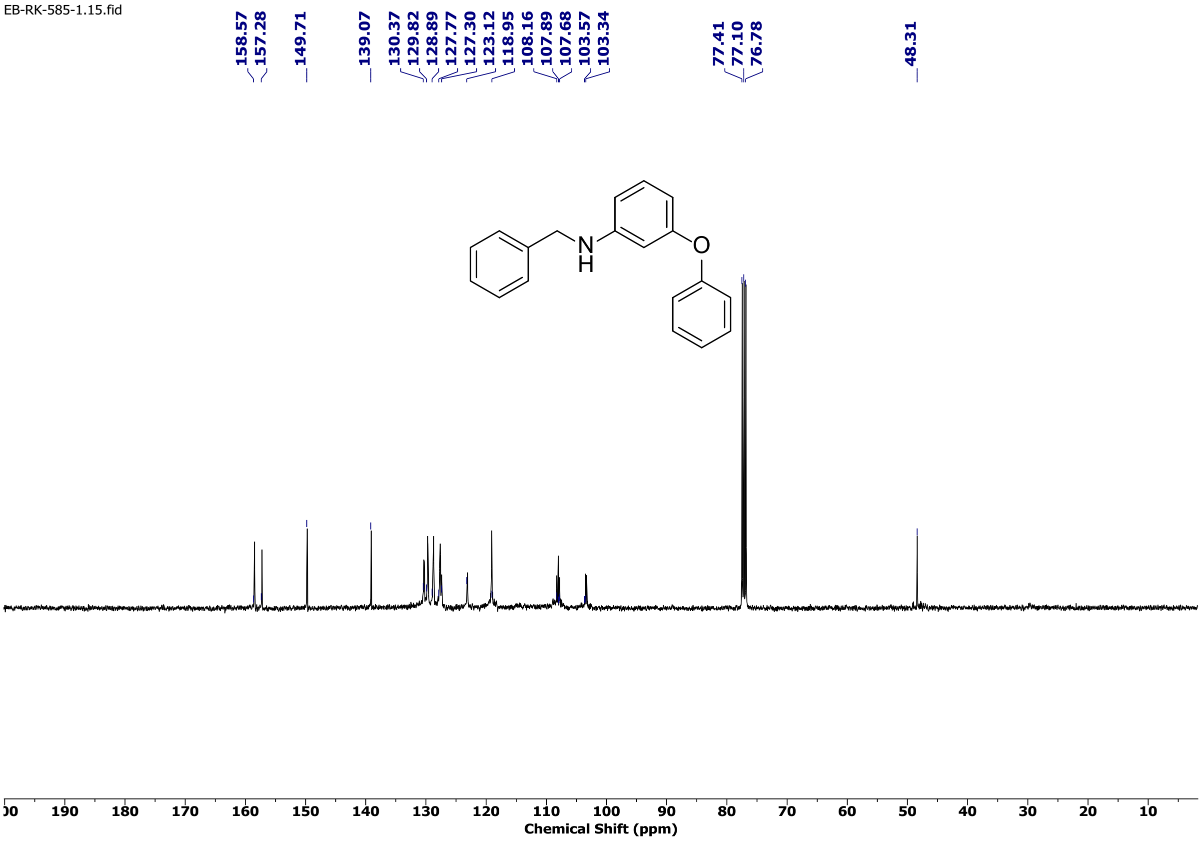
^{1}H NMR of **10** (400 MHz, $CDCl_3$)



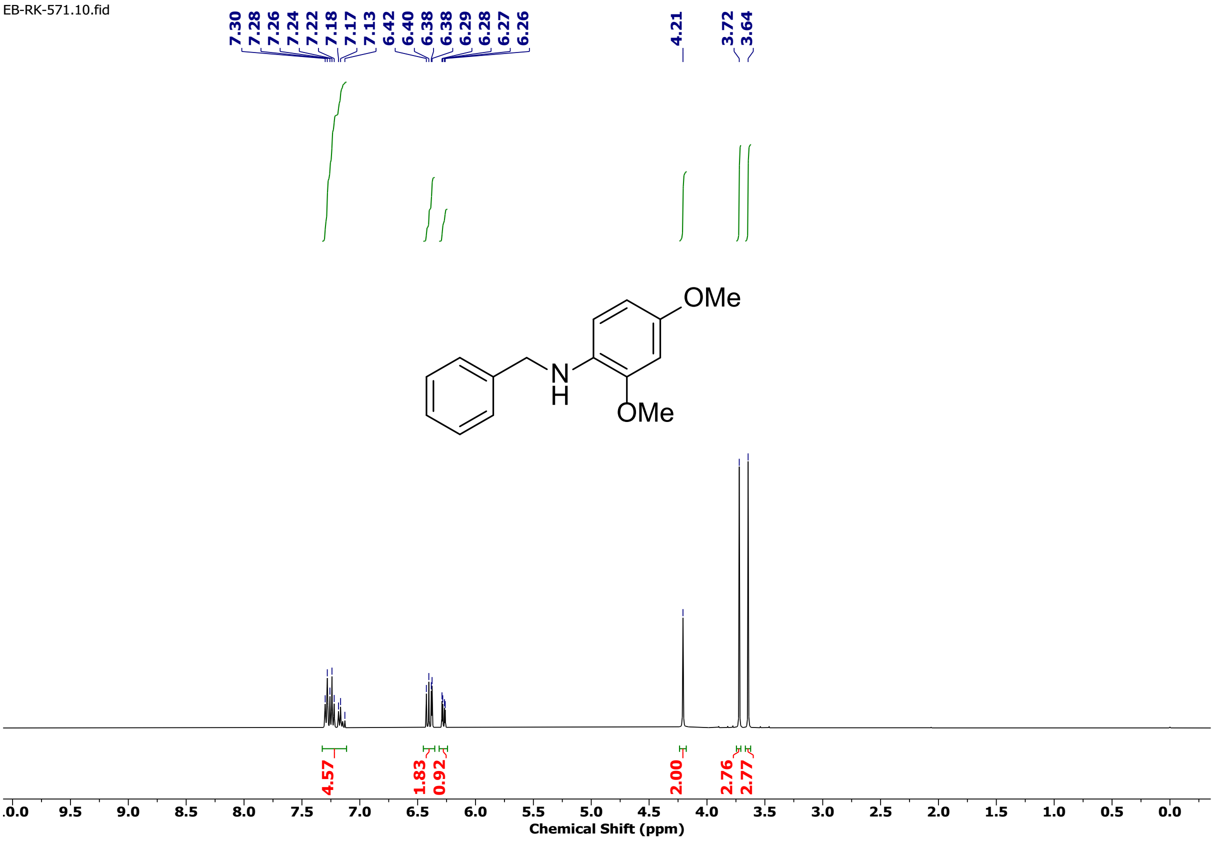
^{13}C NMR of **10** (100 MHz, $CDCl_3$)



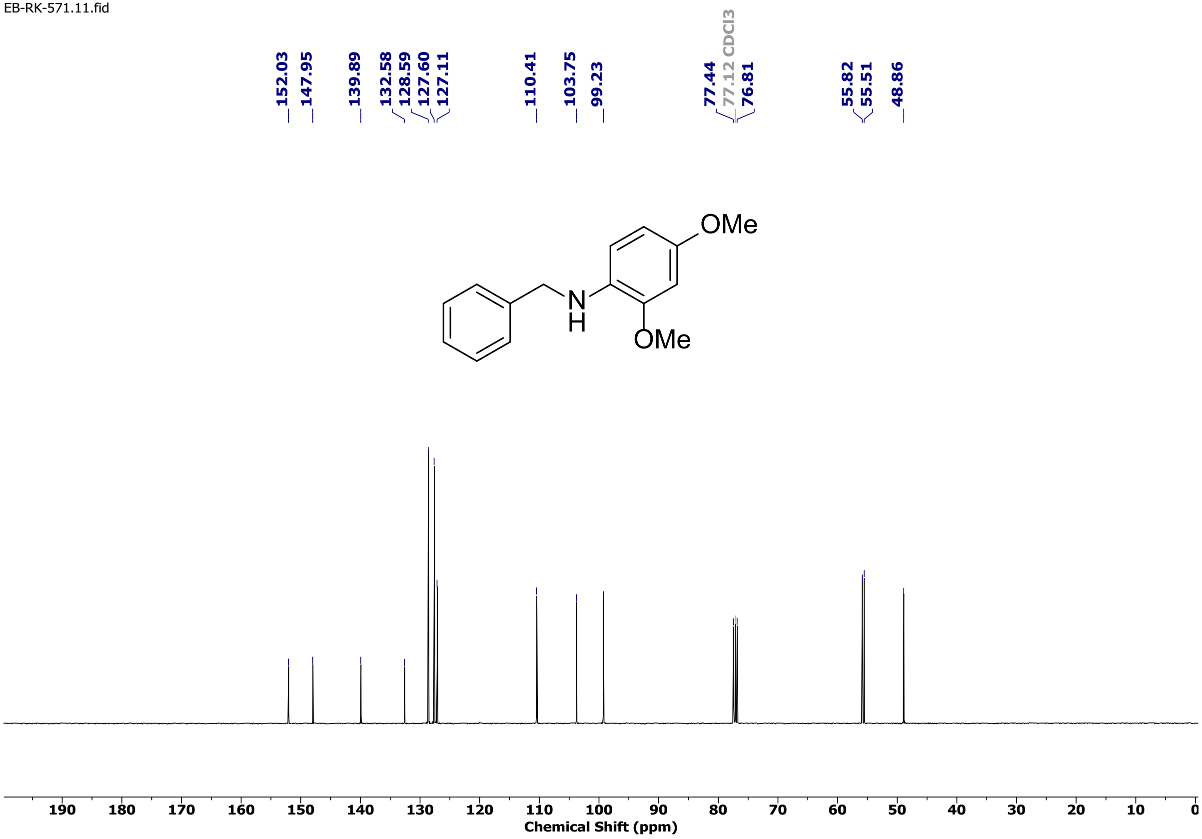
^{1}H NMR of **11** (400 MHz, $CDCl_3$)



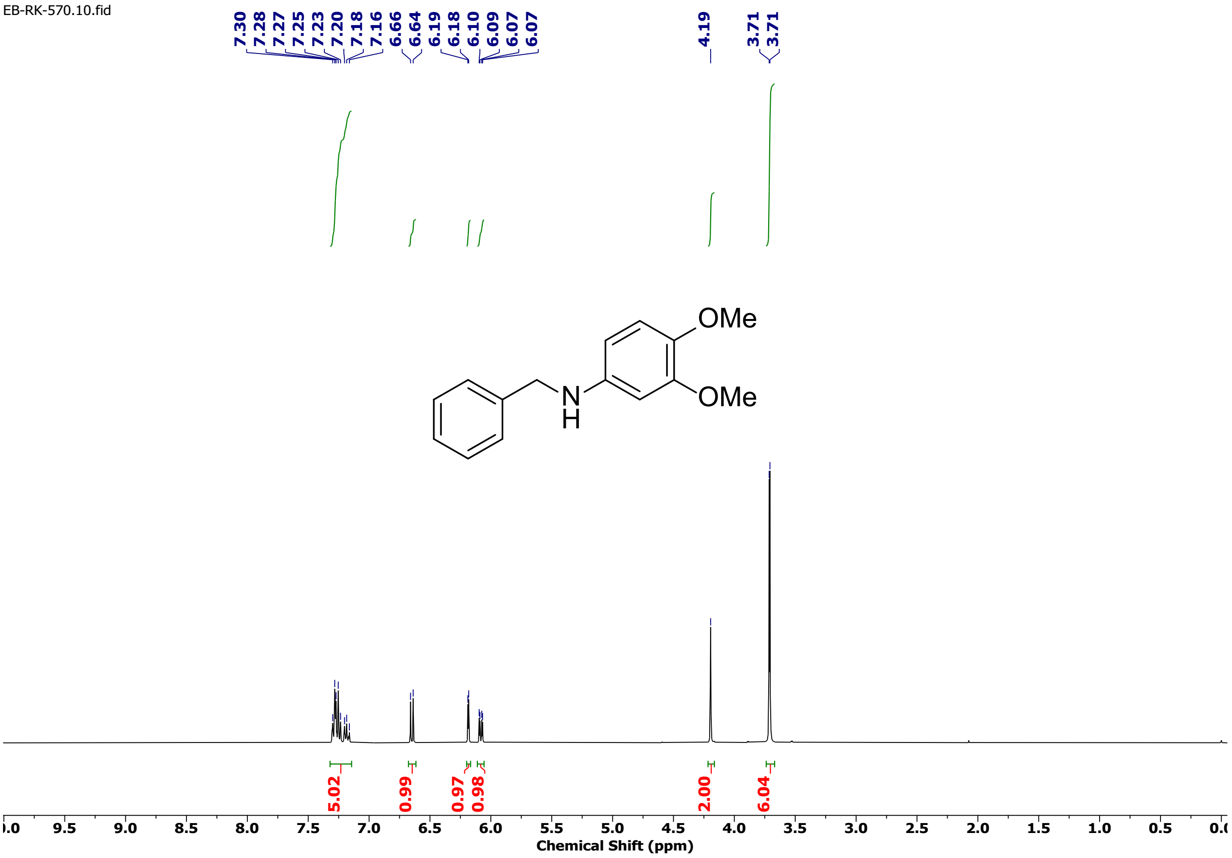
^{13}C NMR of **11** (100 MHz, $CDCl_3$)



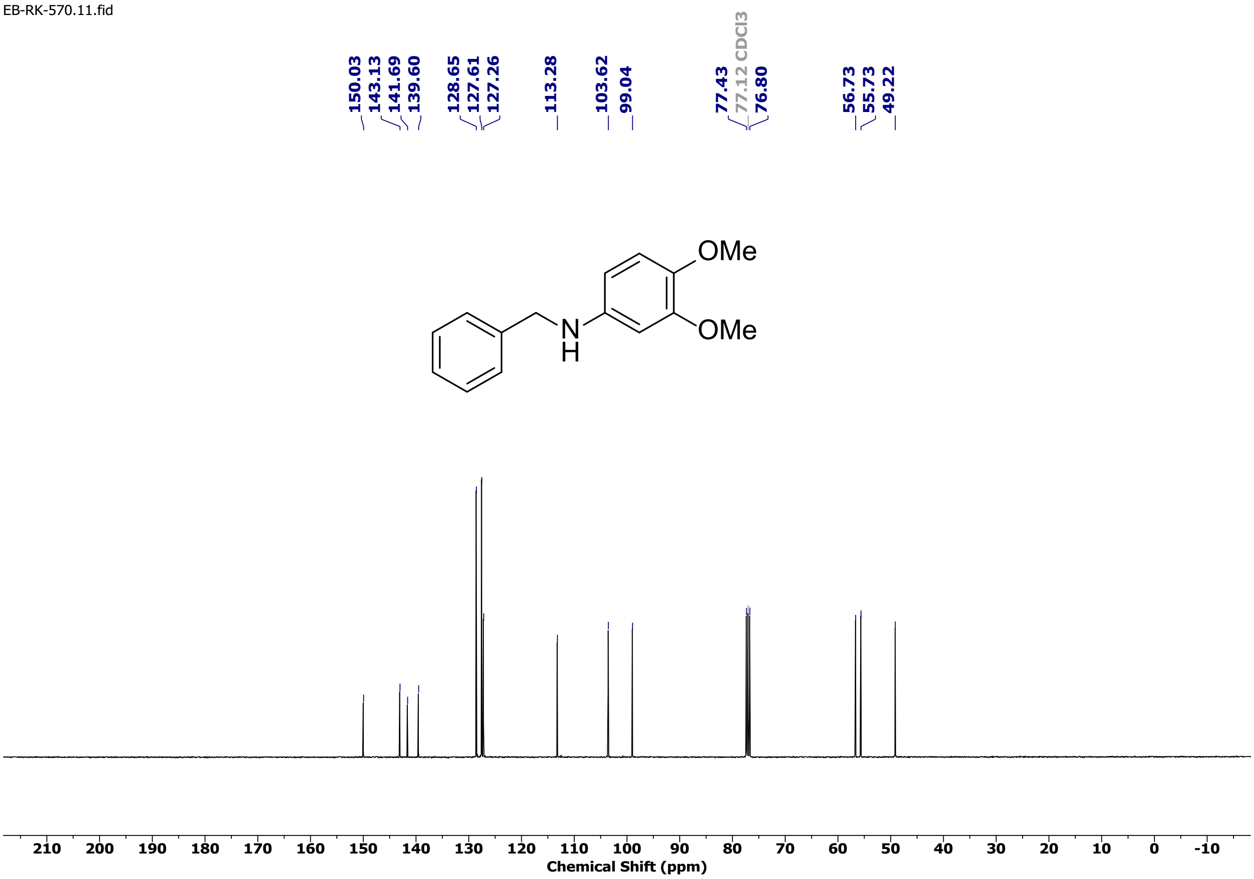
^{1}H NMR of **12** (400 MHz, CDCl$_3$)



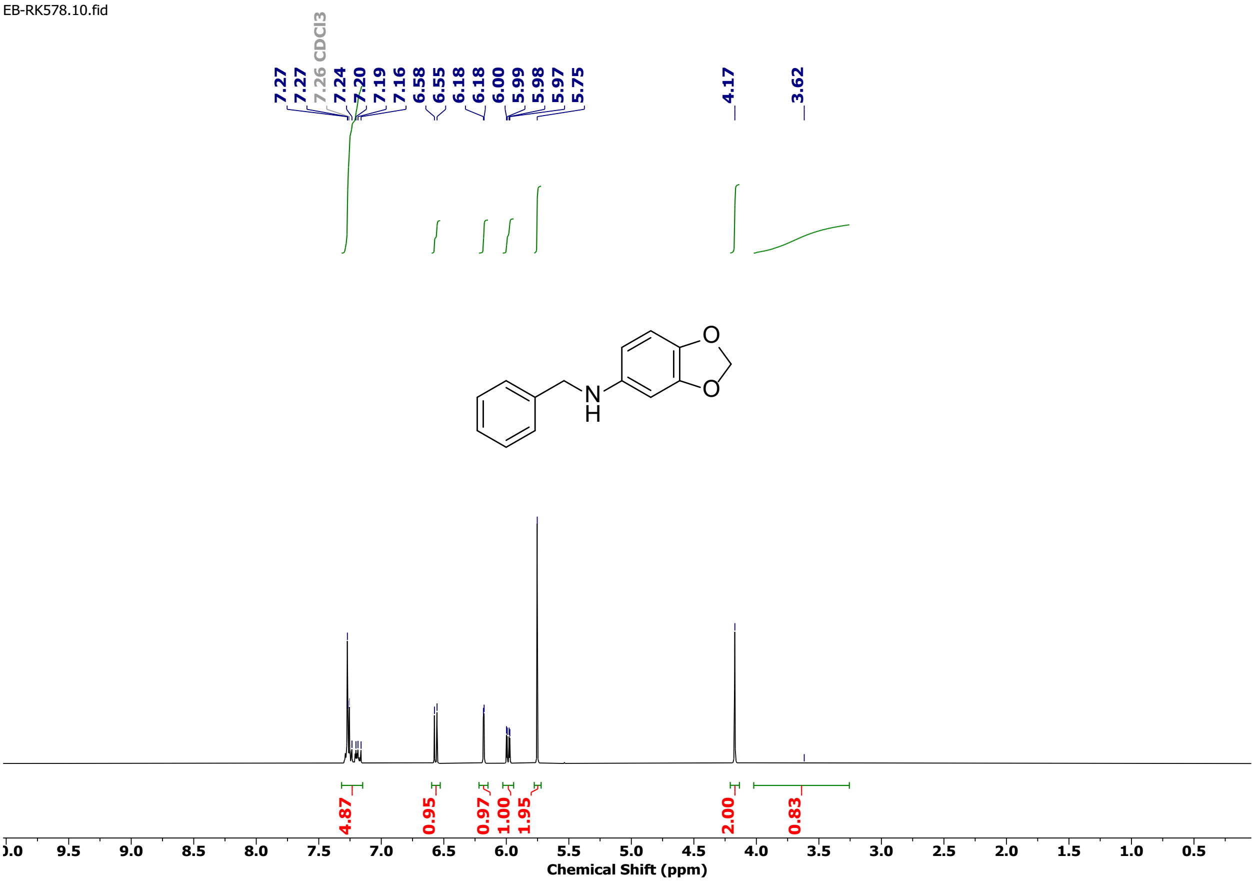
^{13}C NMR of **12** (100 MHz, CDCl$_3$)



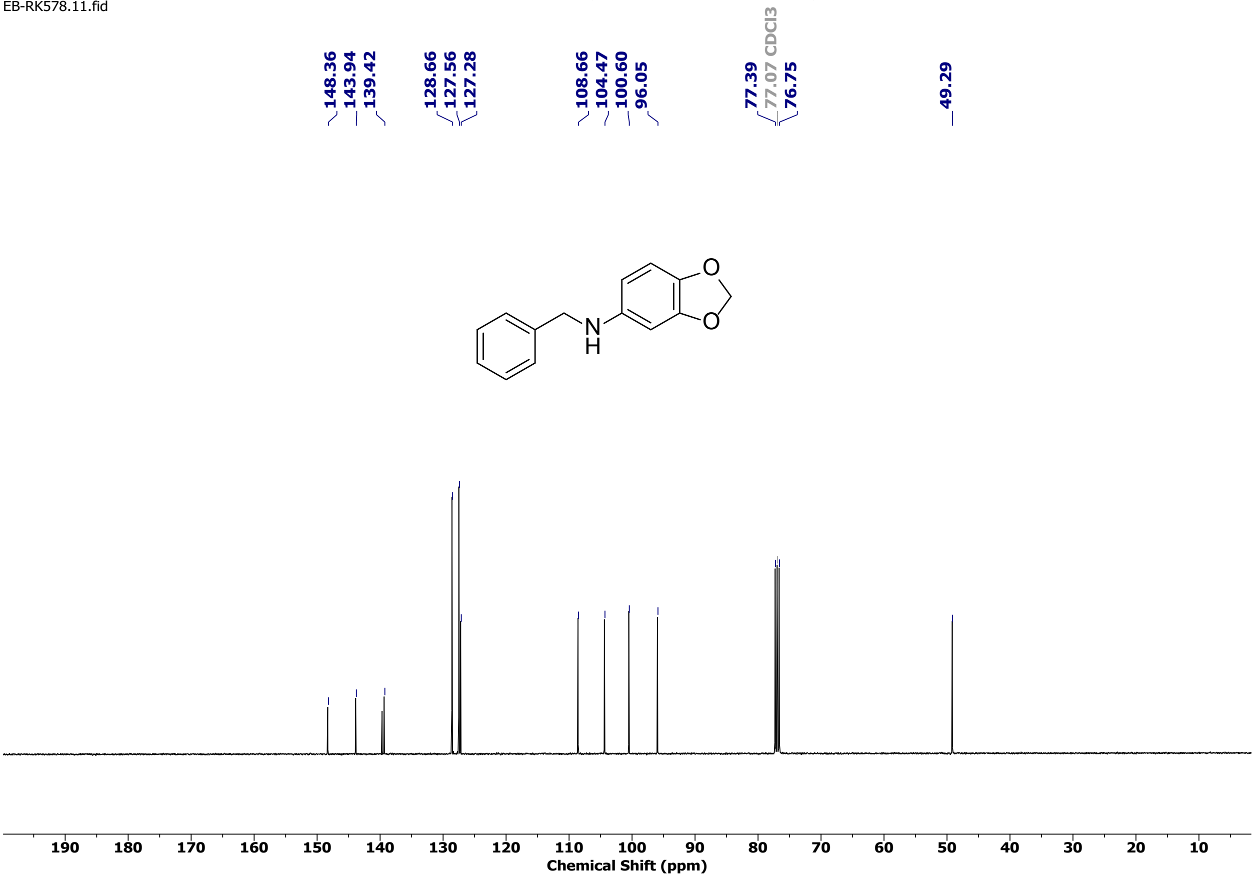
^{1}H NMR of **13** (400 MHz, $CDCl_3$)



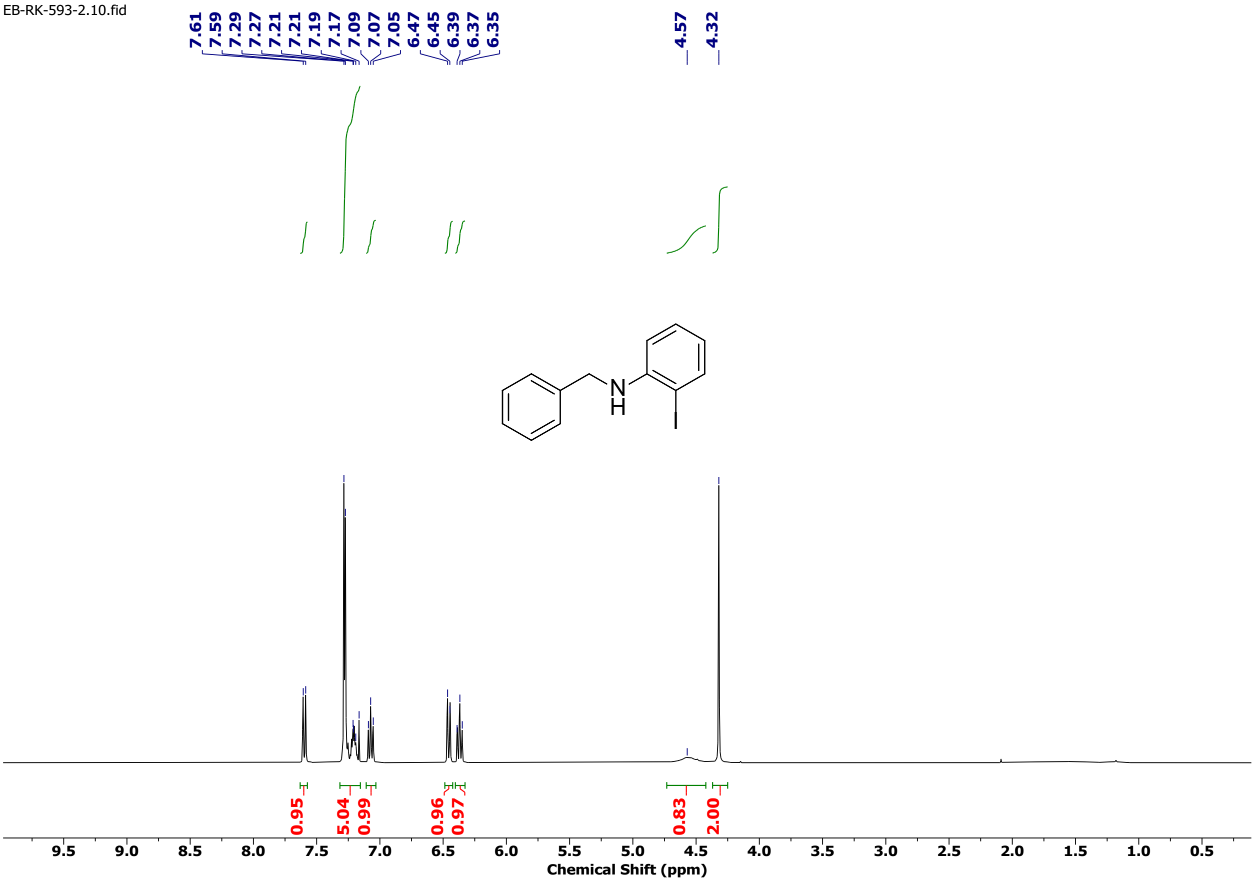
^{13}C NMR of **13** (100 MHz, $CDCl_3$)



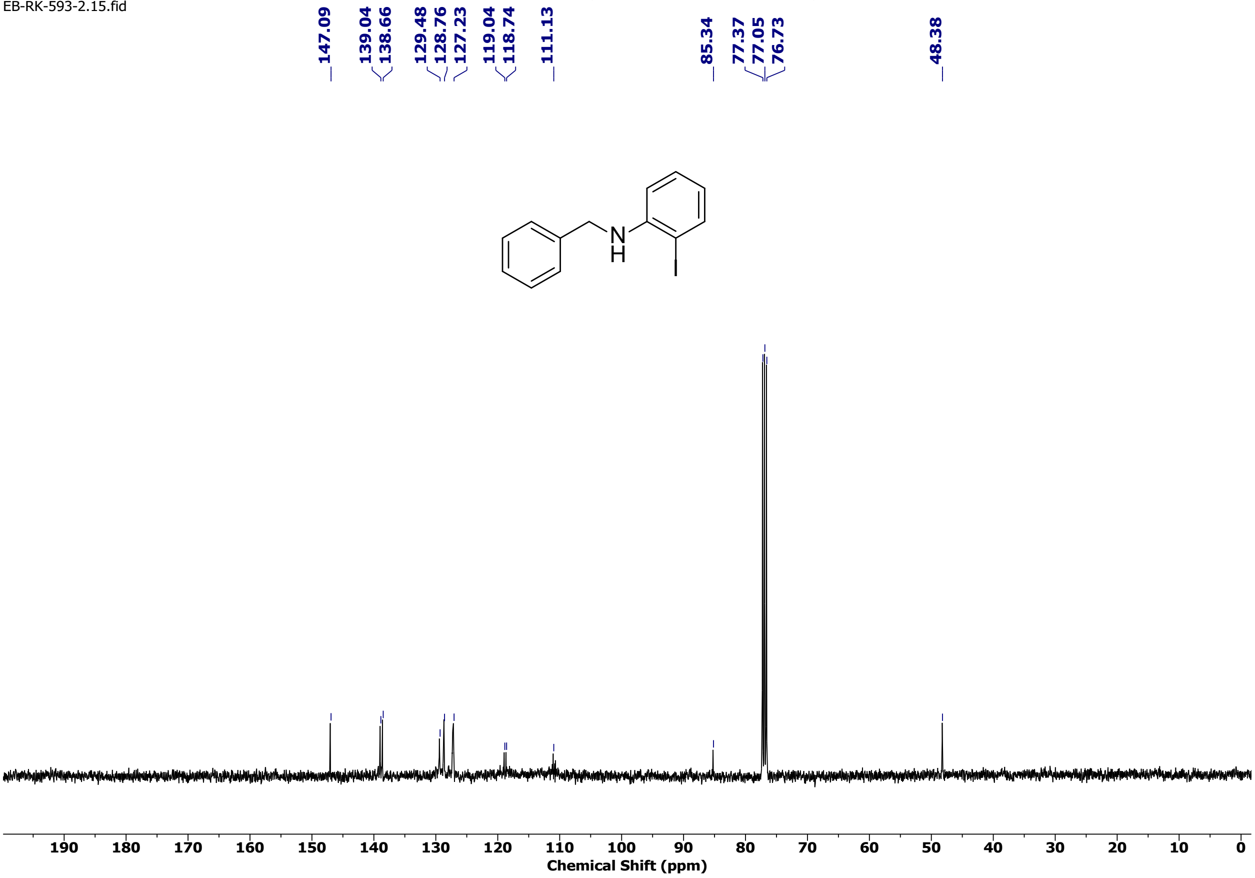
^{1}H NMR of **14** (400 MHz, $CDCl_3$)



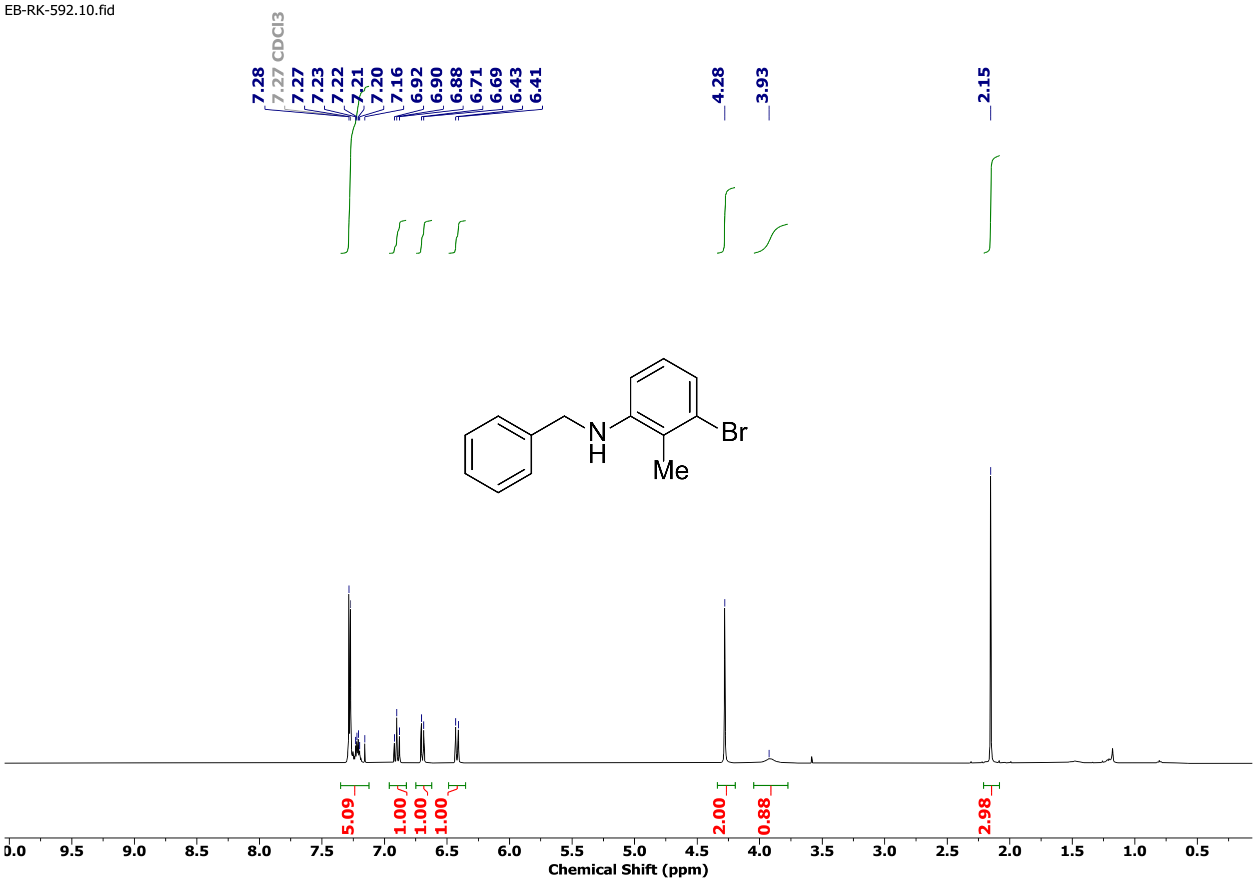
^{13}C NMR of **14** (100 MHz, $CDCl_3$)



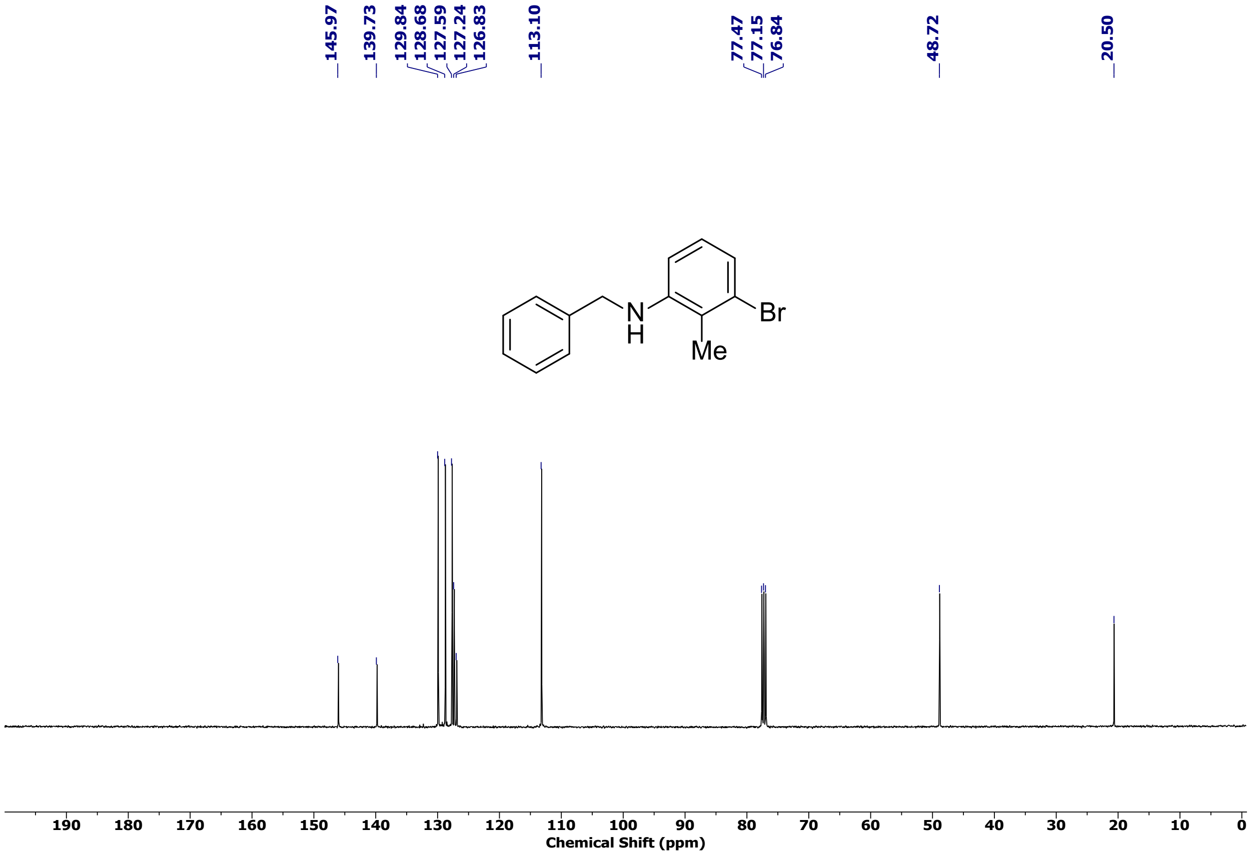
^{1}H NMR of **15** (400 MHz, $CDCl_3$)



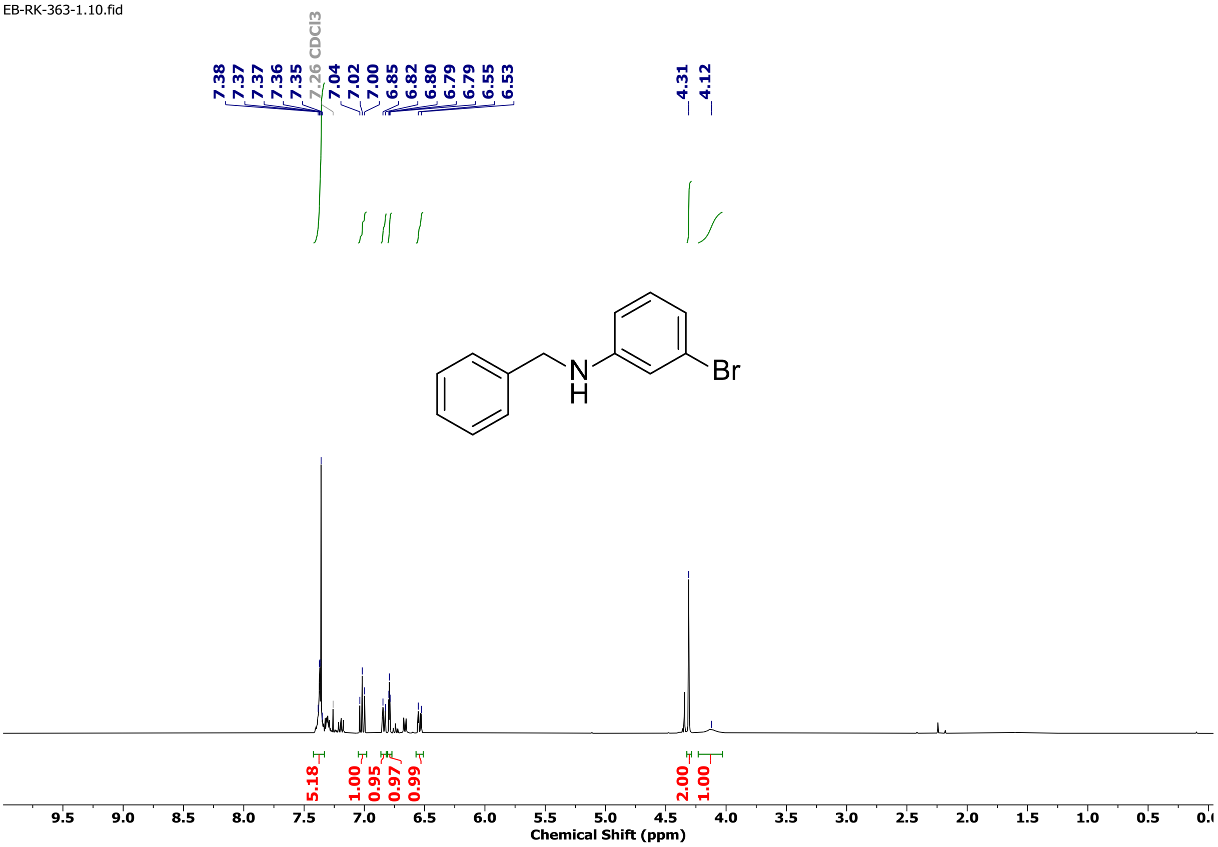
^{13}C NMR of **15** (100 MHz, $CDCl_3$)



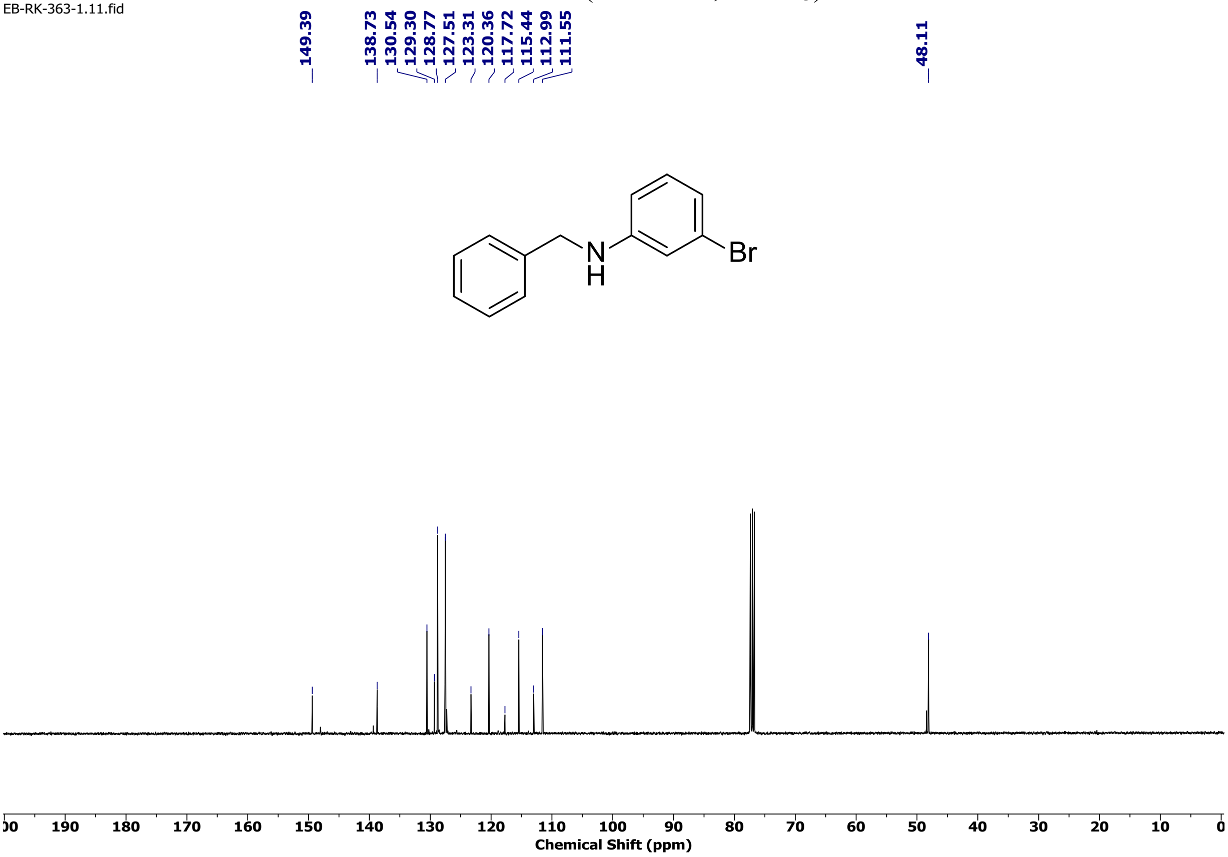
^{1}H NMR of **16** (400 MHz, $CDCl_3$)



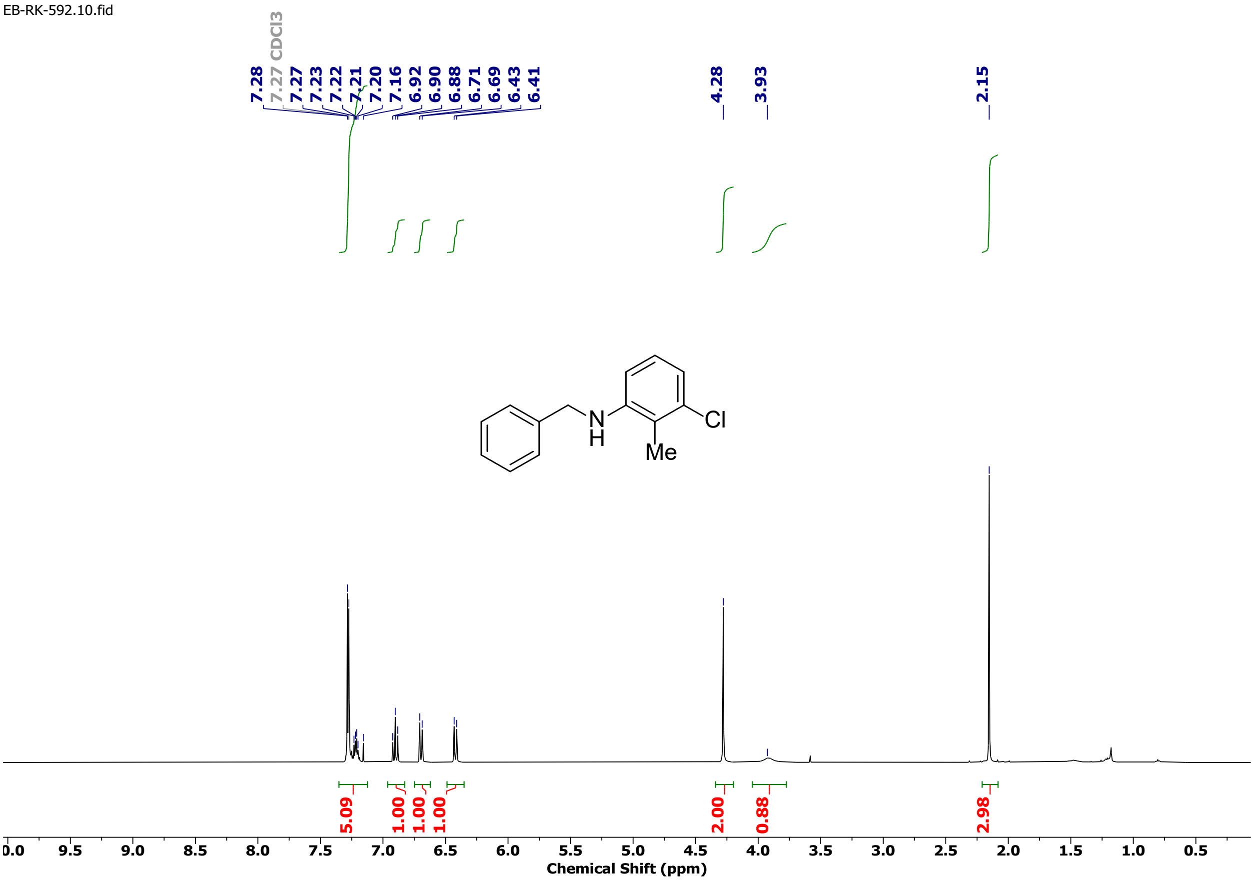
^{13}C NMR of **16**(100 MHz, $CDCl_3$)



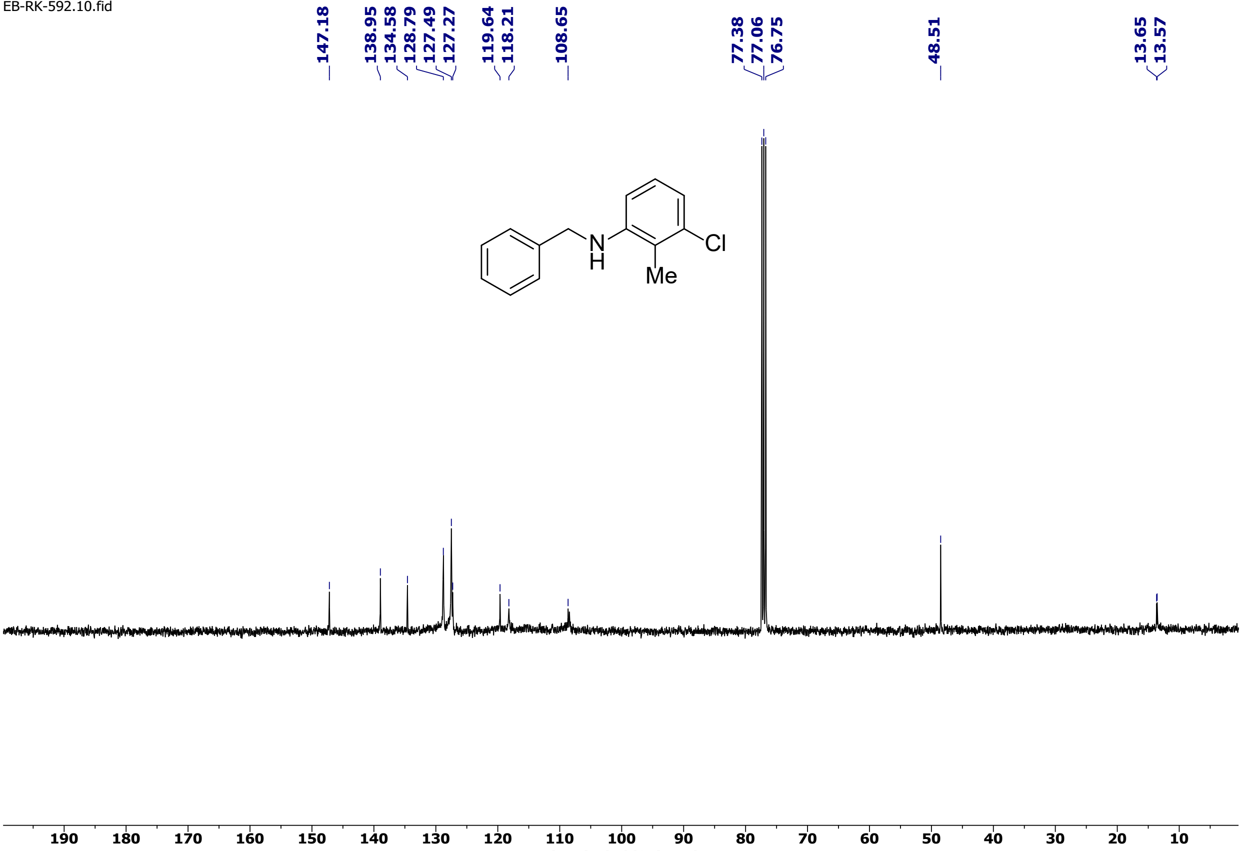
^{1}H NMR of **17** (400 MHz, $CDCl_3$)



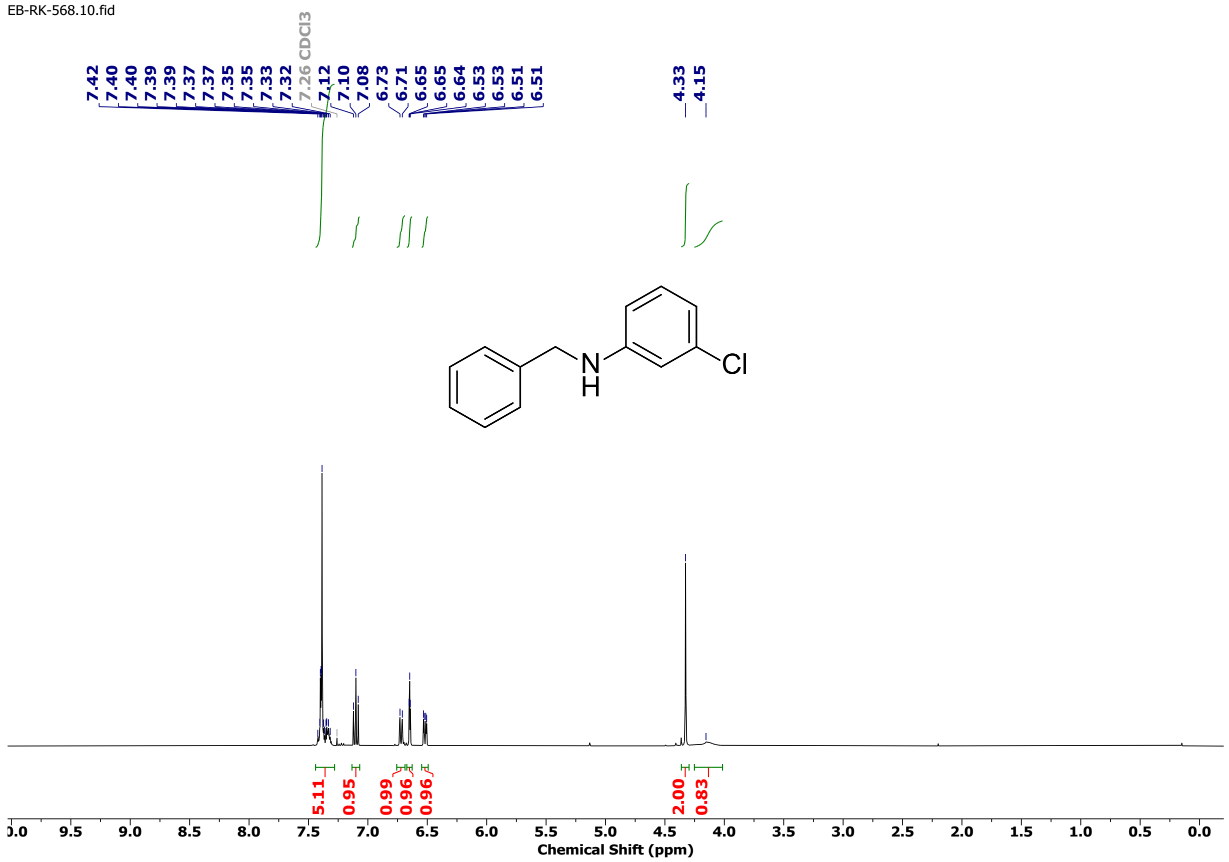
^{13}C NMR of **17** (100 MHz, $CDCl_3$)



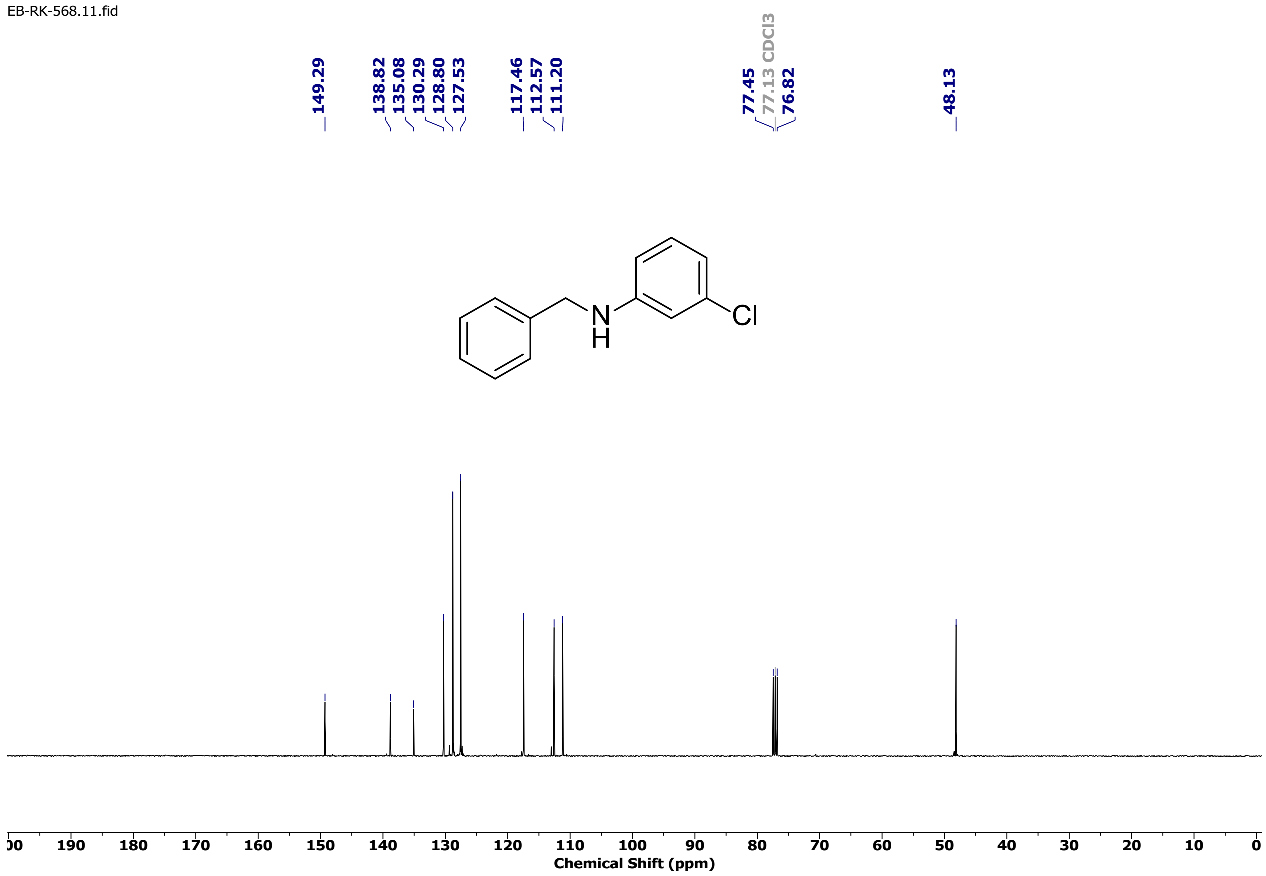
^{1}H NMR of **18** (400 MHz, $CDCl_3$)



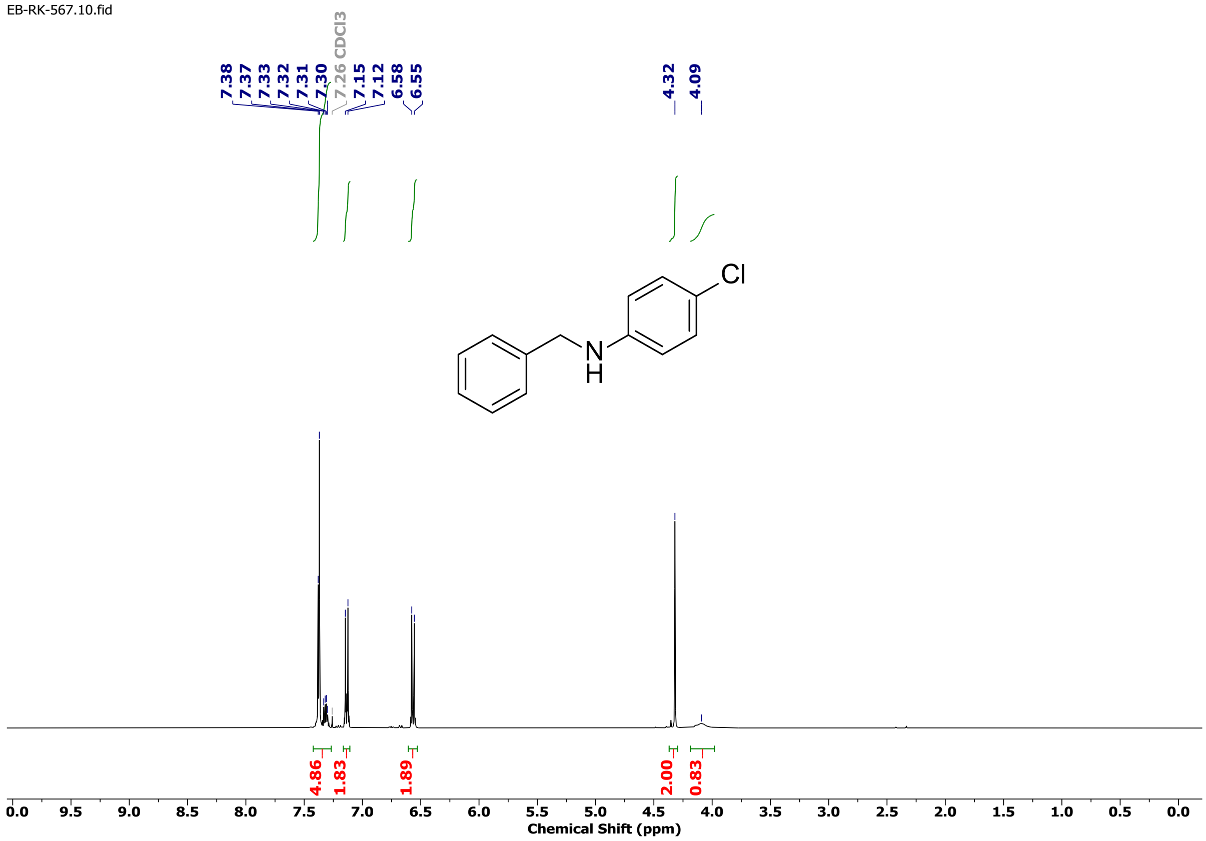
^{13}C NMR of **18** (100 MHz, $CDCl_3$)



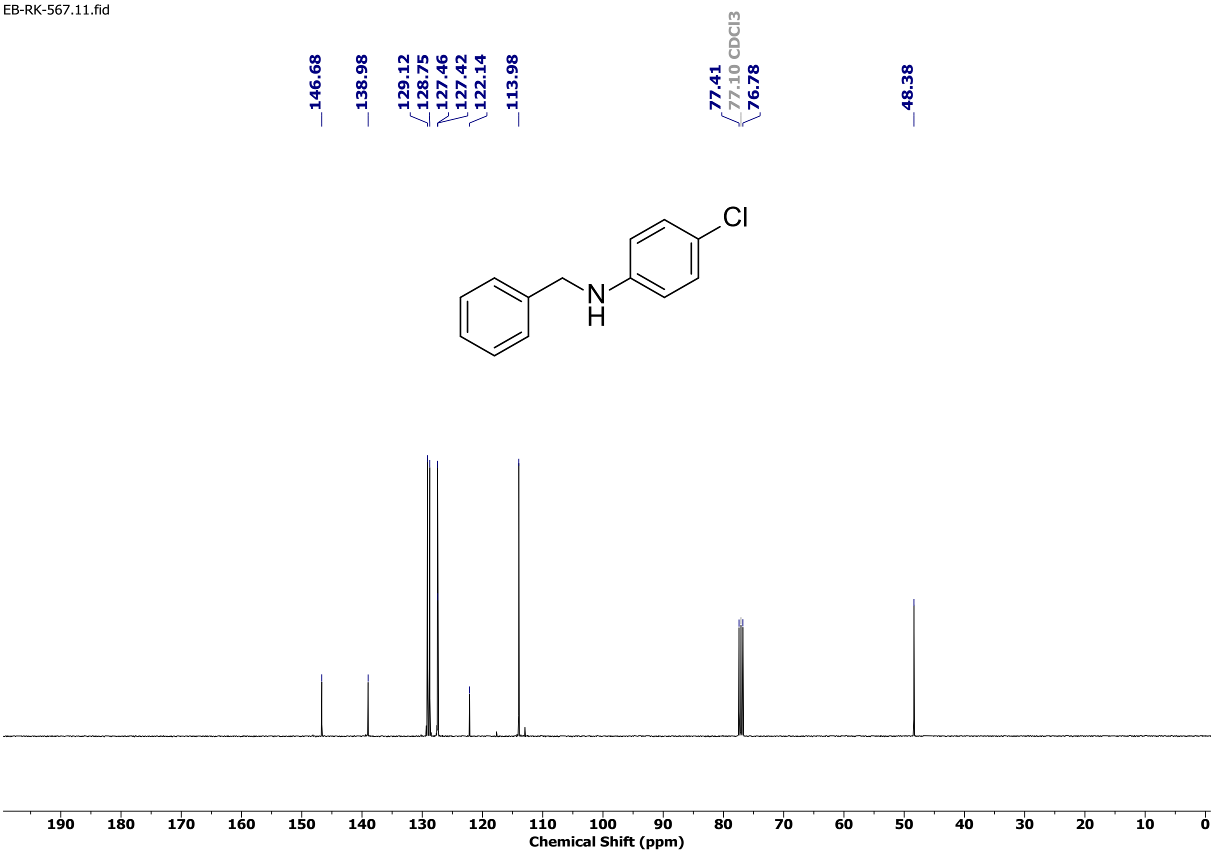
^{1}H NMR of **19** (400 MHz, $CDCl_3$)



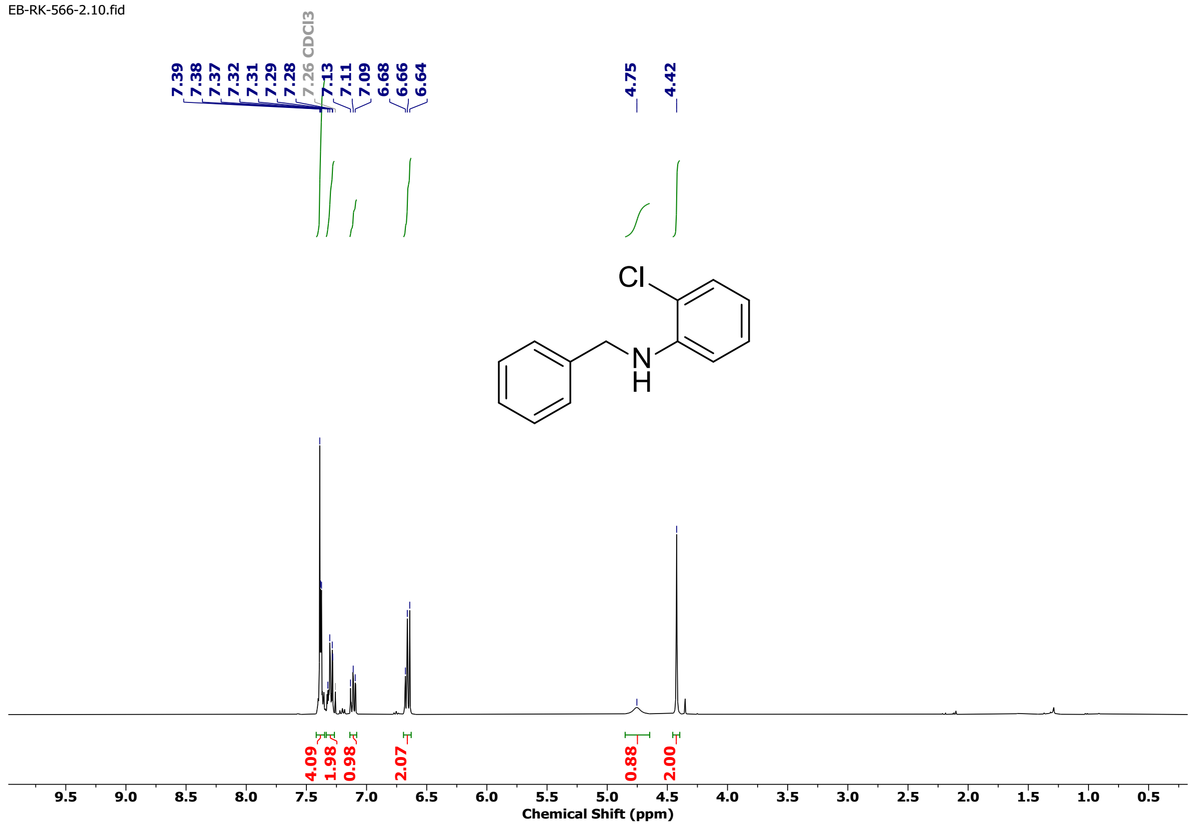
^{13}C NMR of **19** (100 MHz, $CDCl_3$)



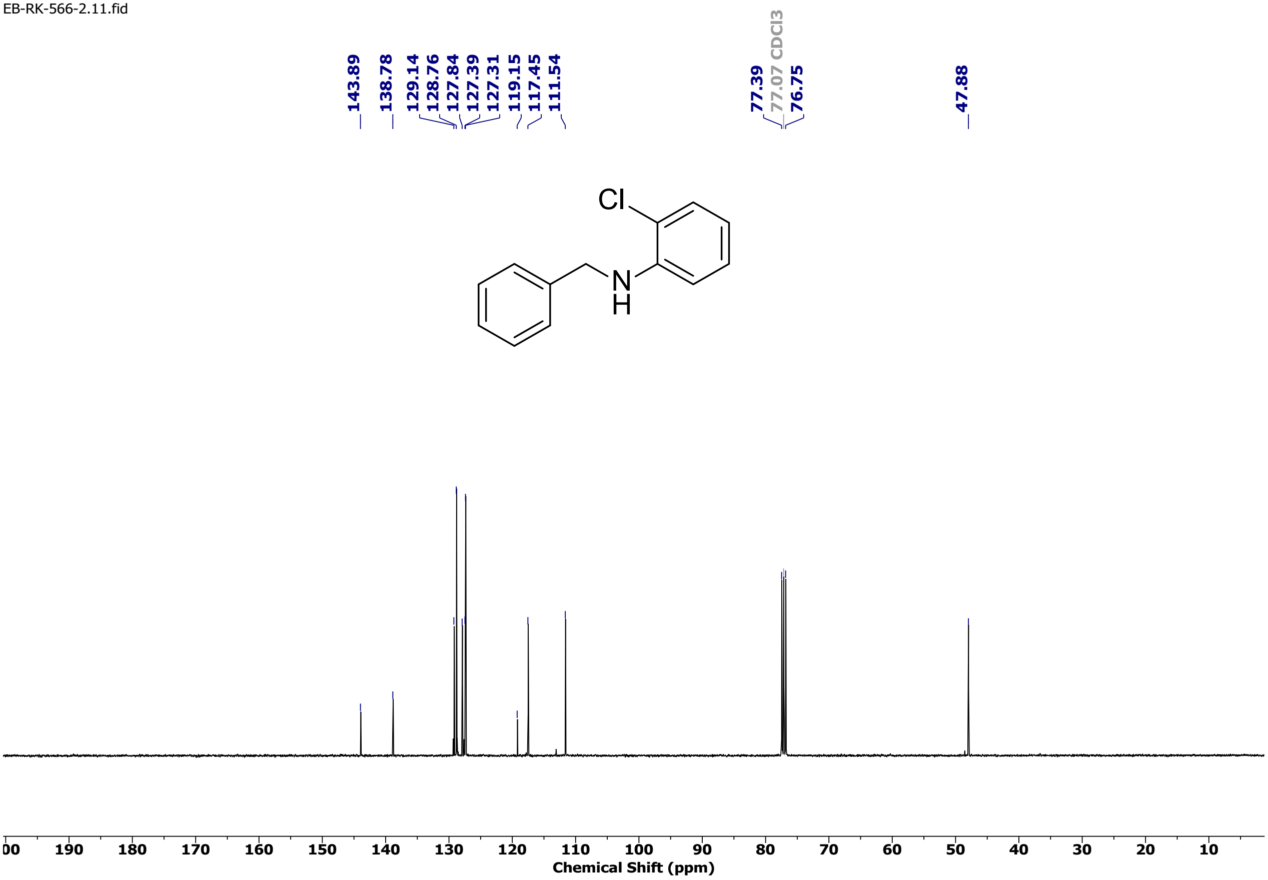
^{1}H NMR of **20** (400 MHz, CDCl$_3$)



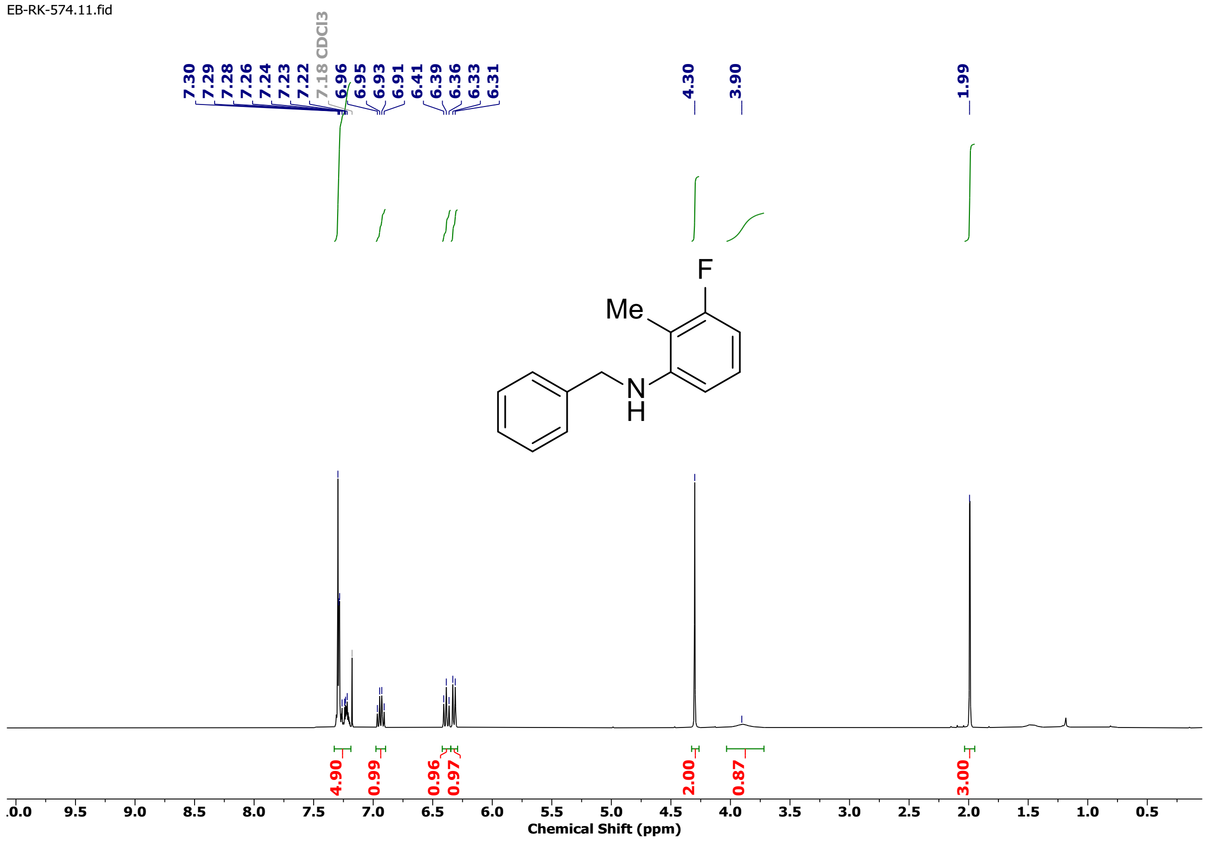
^{13}C NMR of **20** (100 MHz, CDCl$_3$)



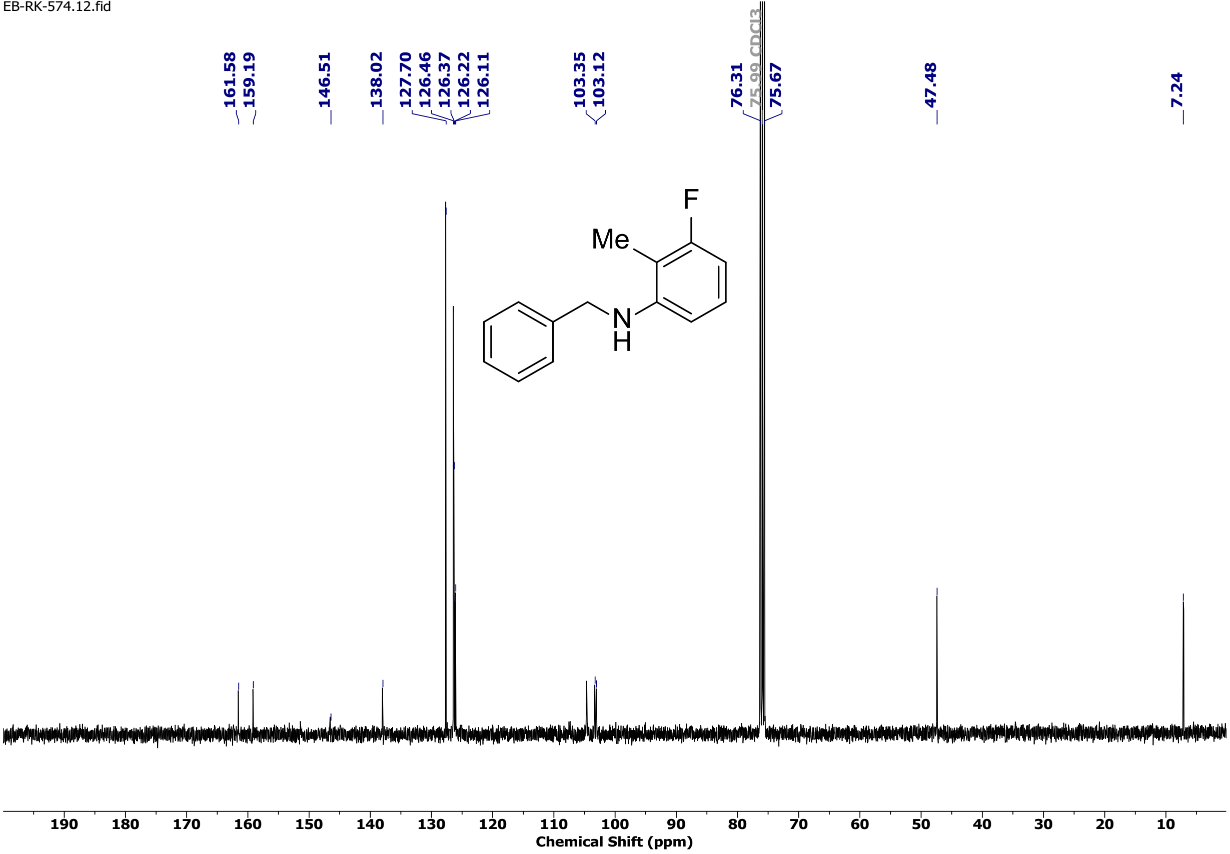
^{1}H NMR of **21** (400 MHz, CDCl$_3$)



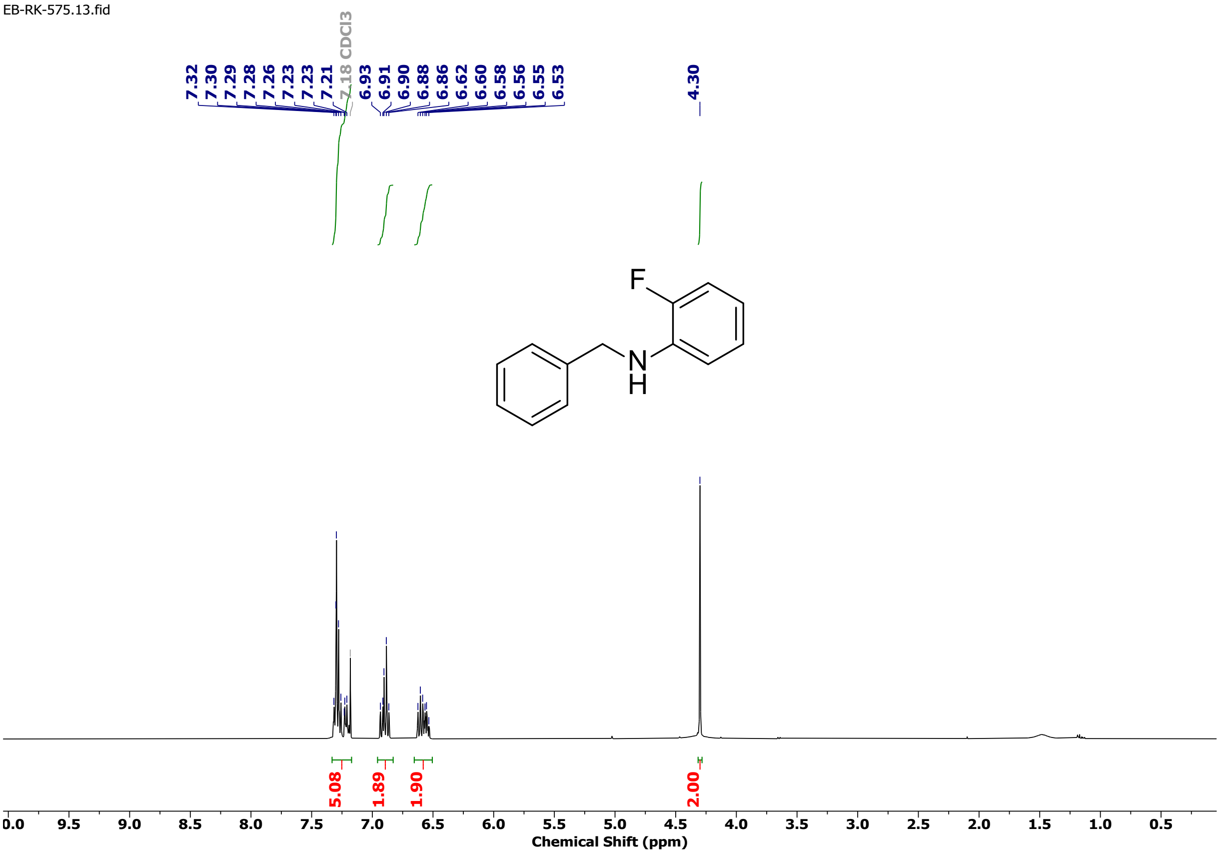
^{13}C NMR of **21** (100 MHz, CDCl$_3$)



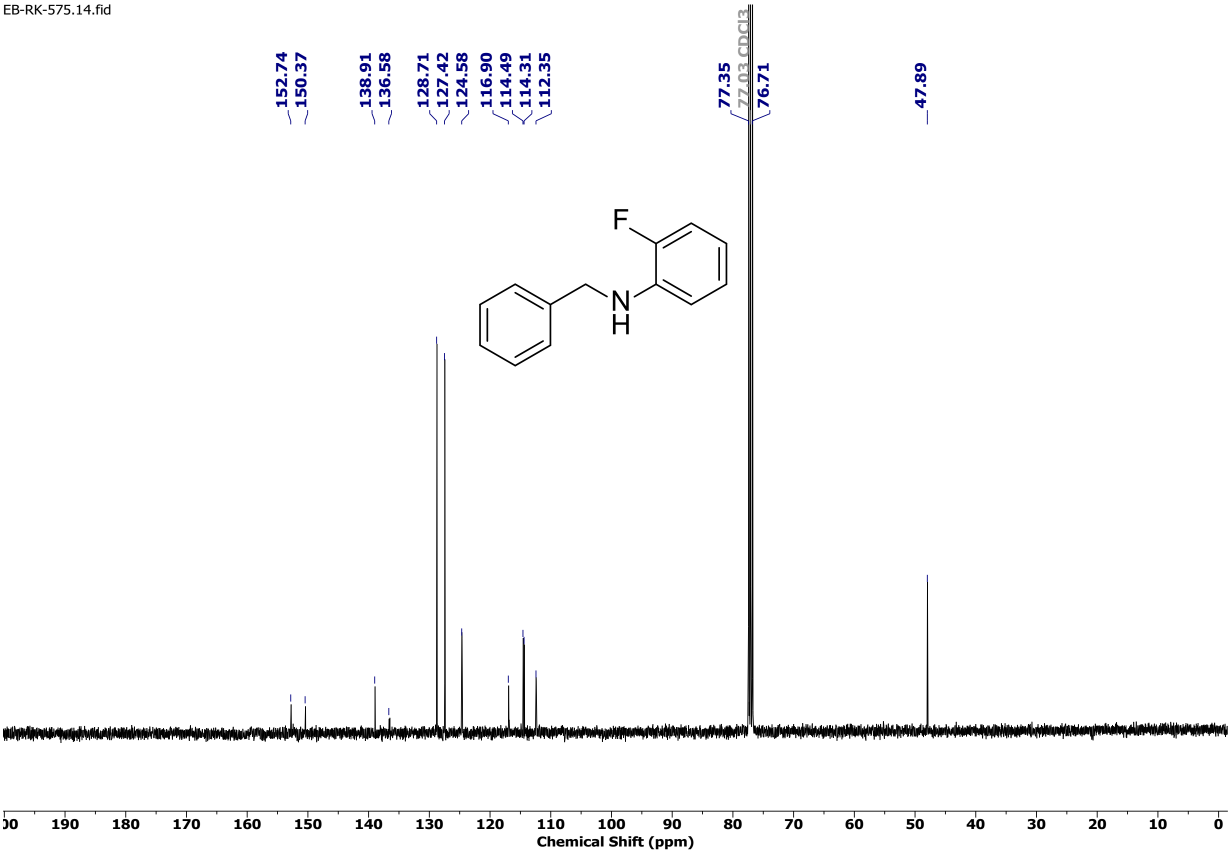
^{1}H NMR of **22** (400 MHz, CDCl$_3$)



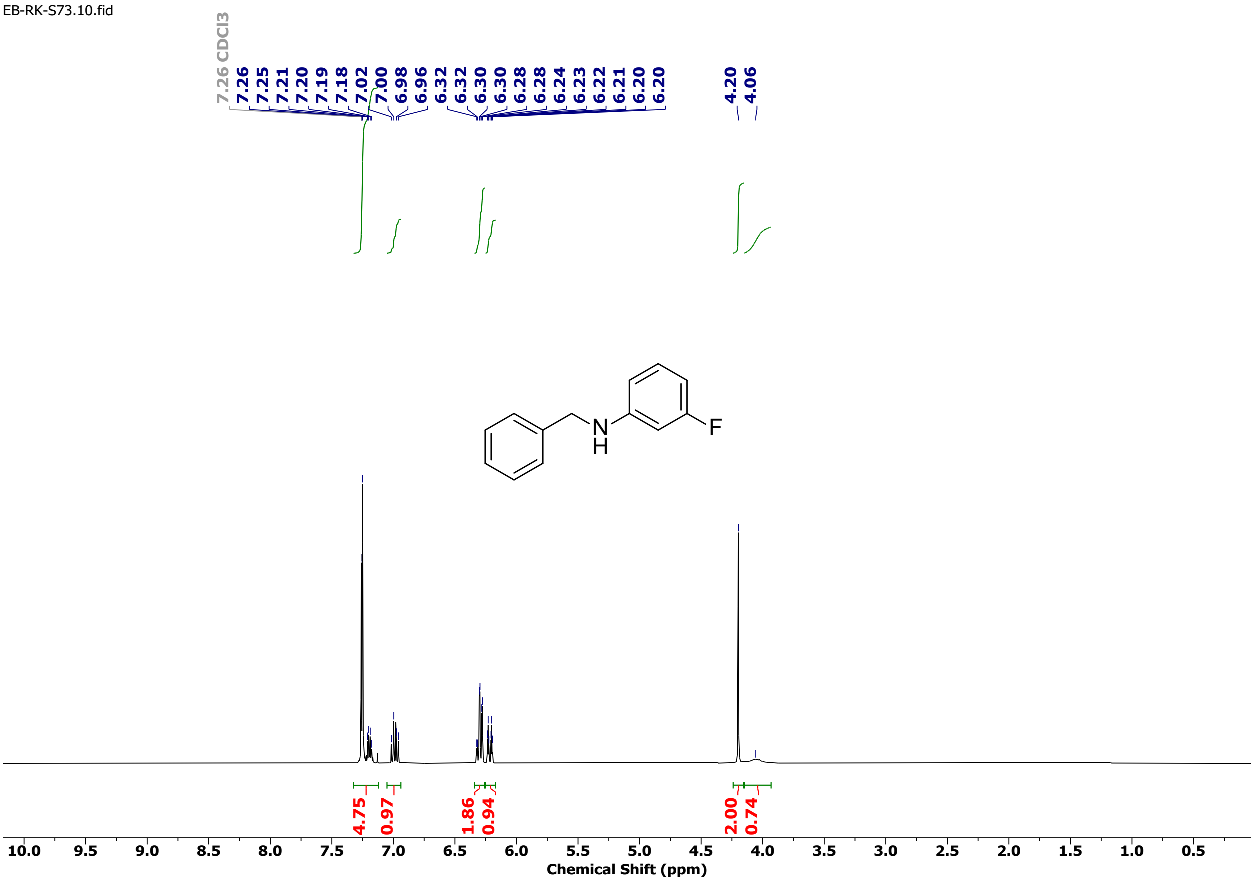
^{13}C NMR of **22** (100 MHz, CDCl$_3$)



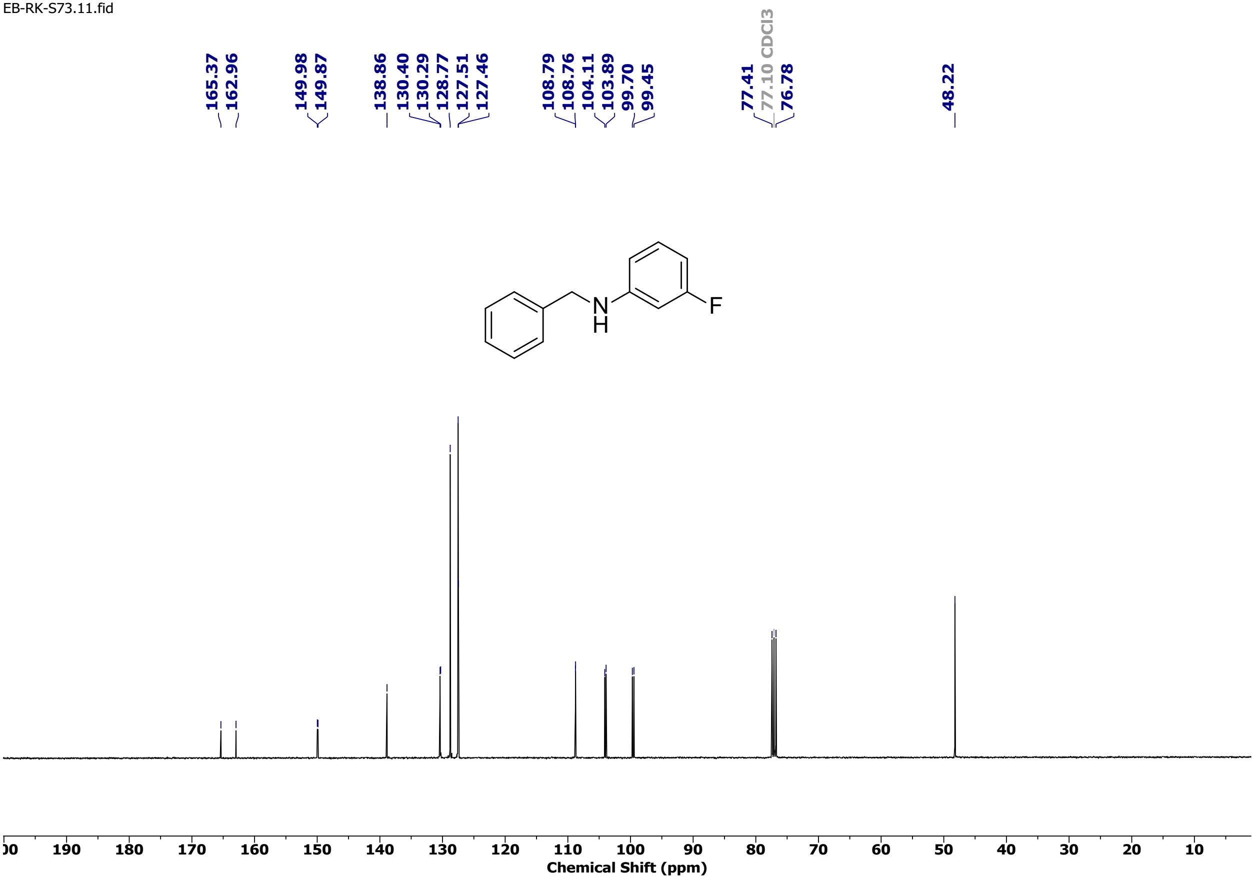
^{1}H NMR of **23** (400 MHz, $CDCl_3$)



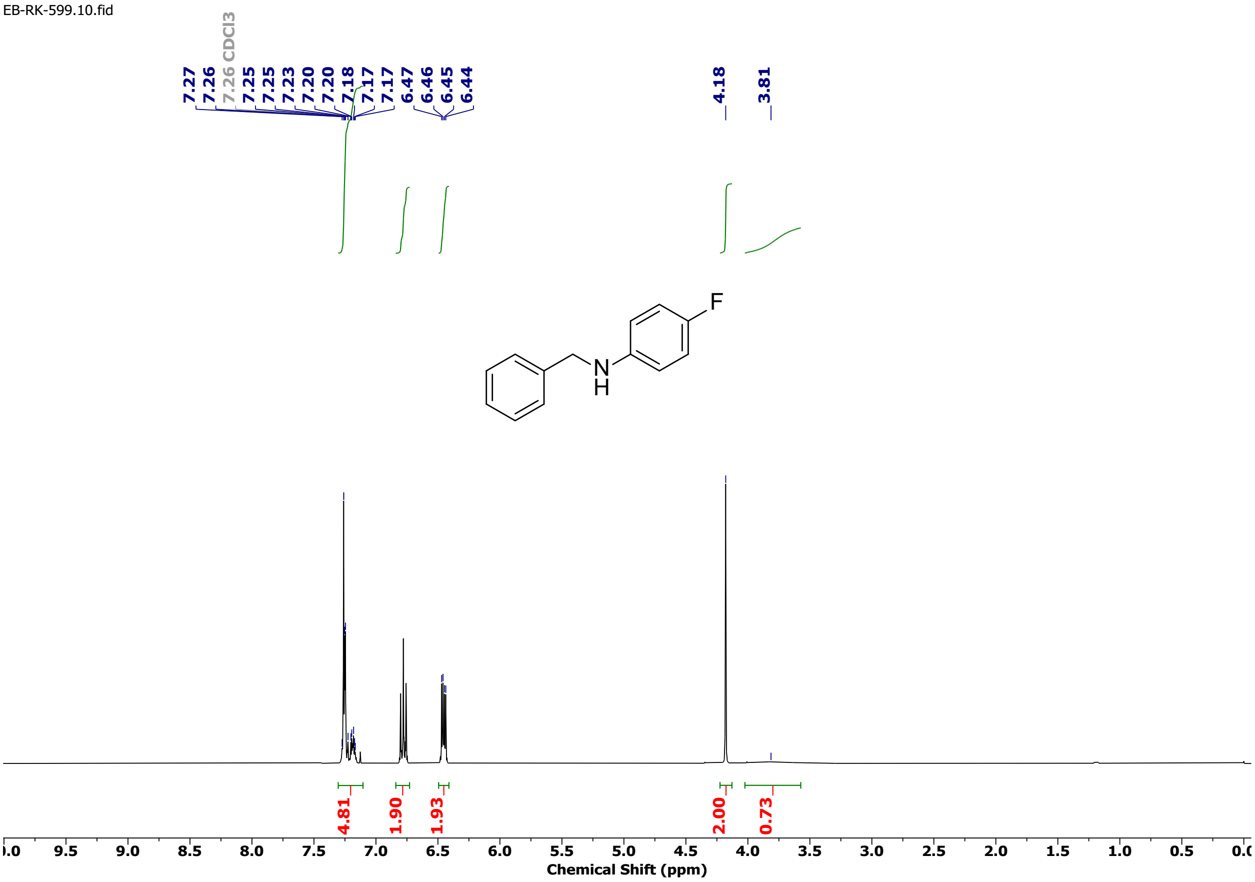
^{13}C NMR of **23** (100 MHz, $CDCl_3$)



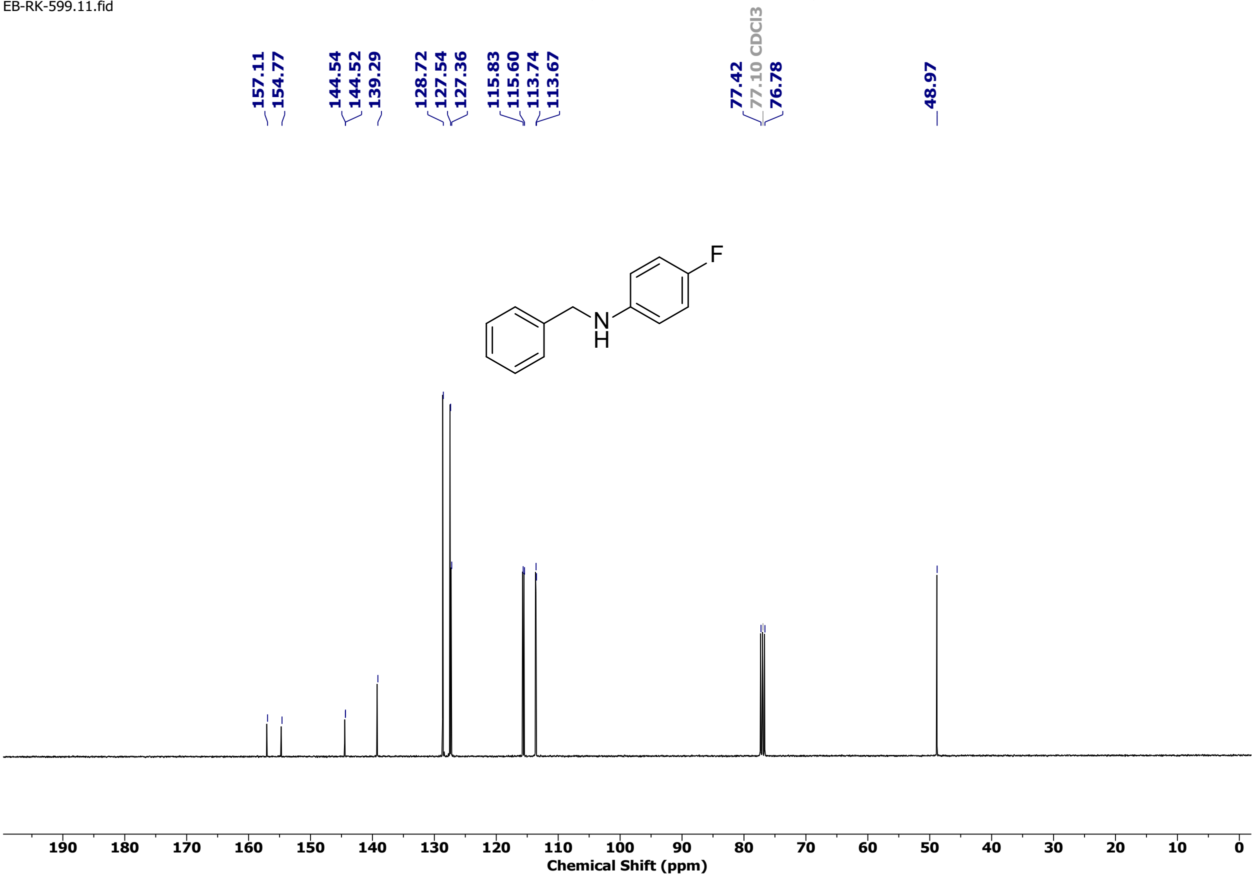
^{1}H NMR of **24** (400 MHz, $CDCl_3$)



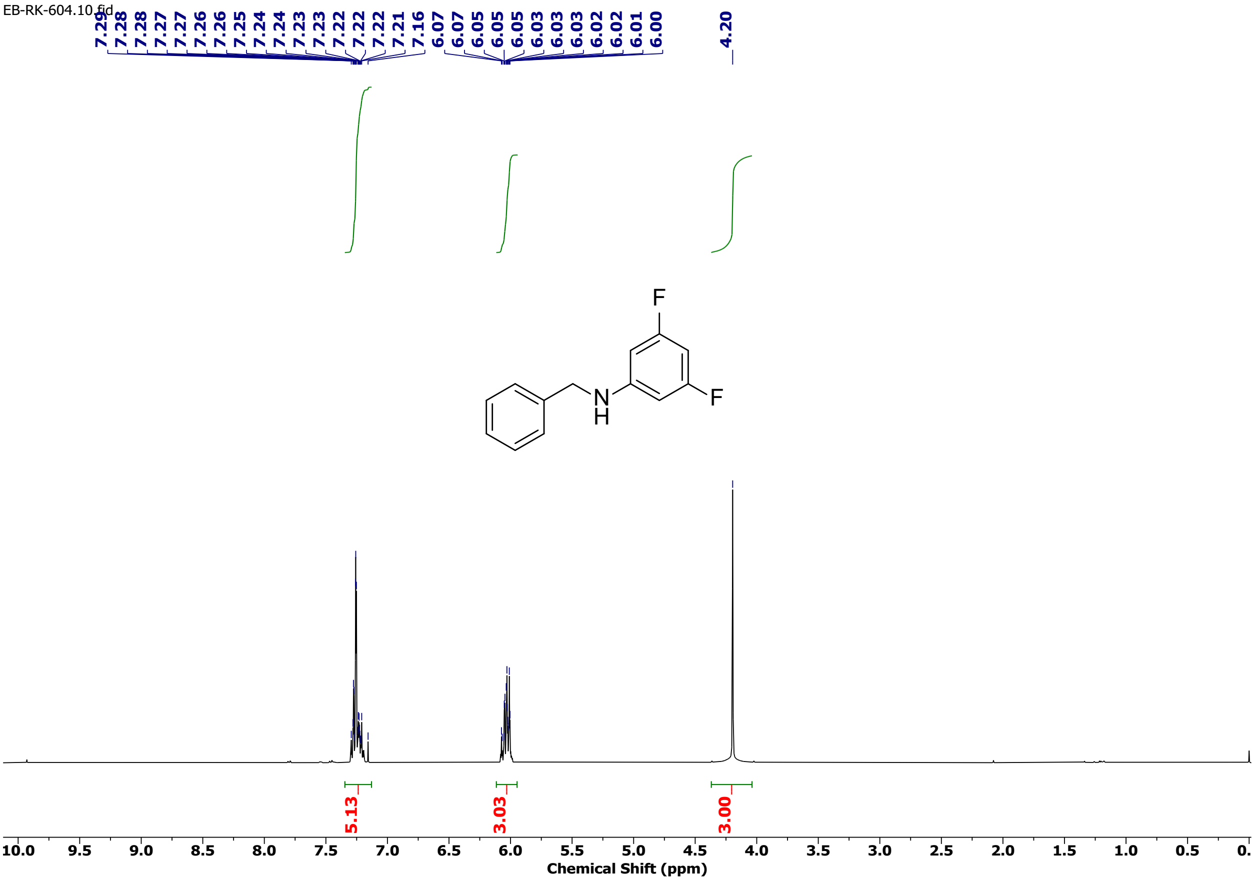
^{13}C NMR of **24** (100 MHz, $CDCl_3$)



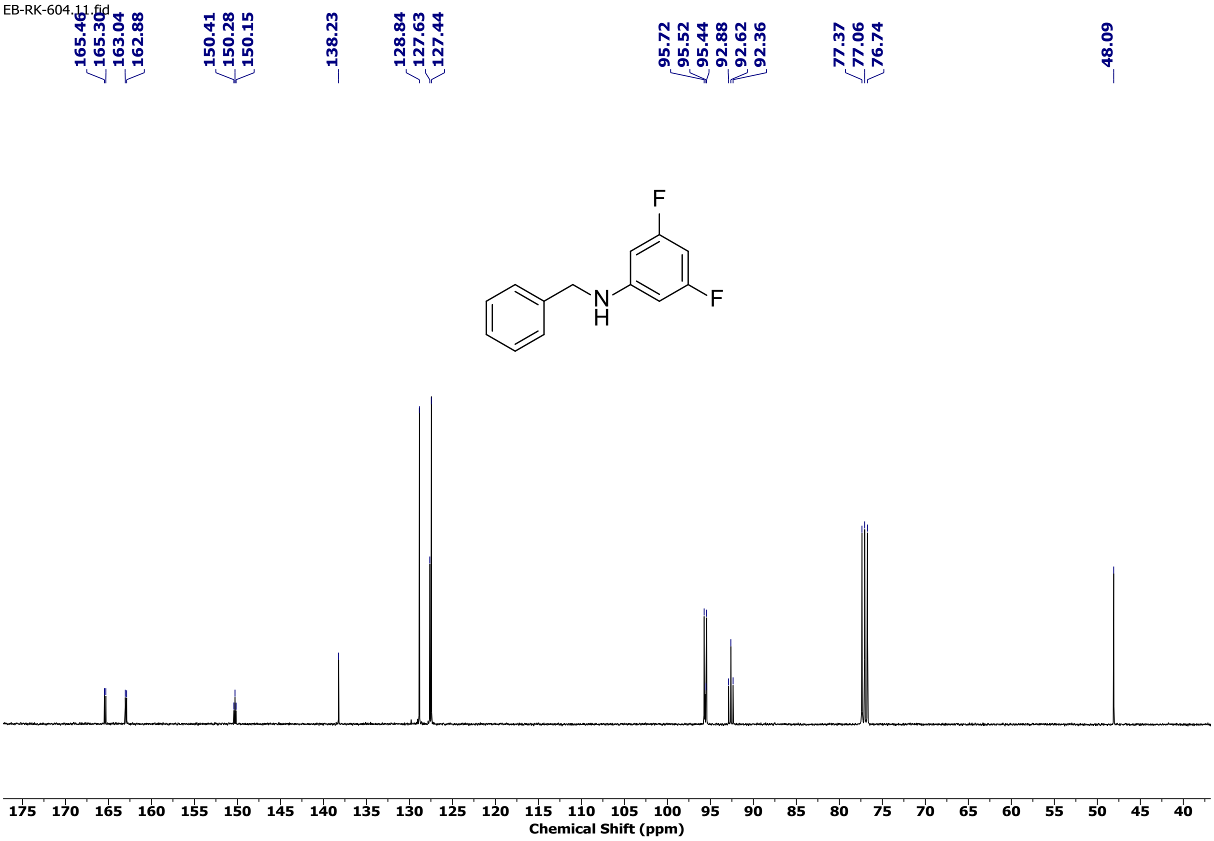
^{1}H NMR of **25** (400 MHz, CDCl$_3$)



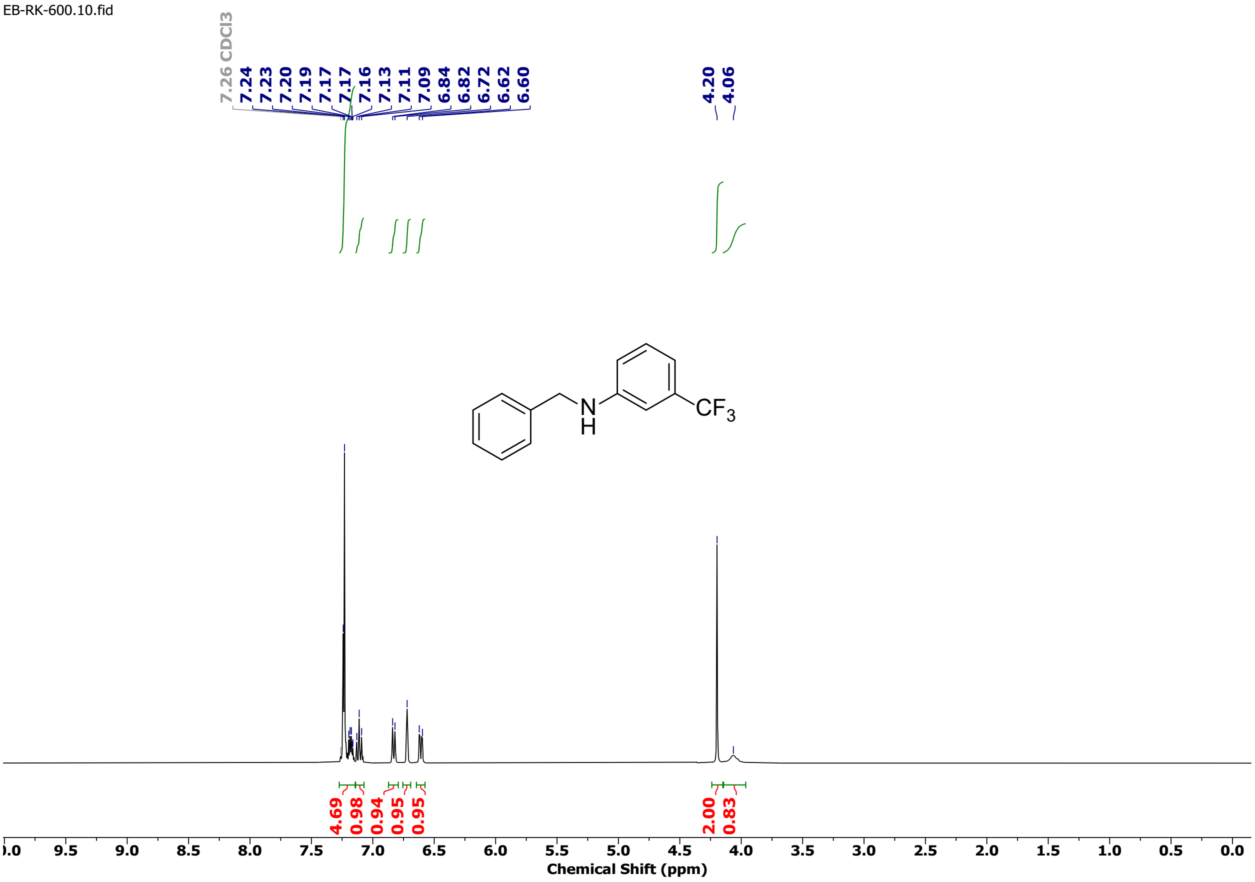
^{13}C NMR of **25** (100 MHz, CDCl$_3$)



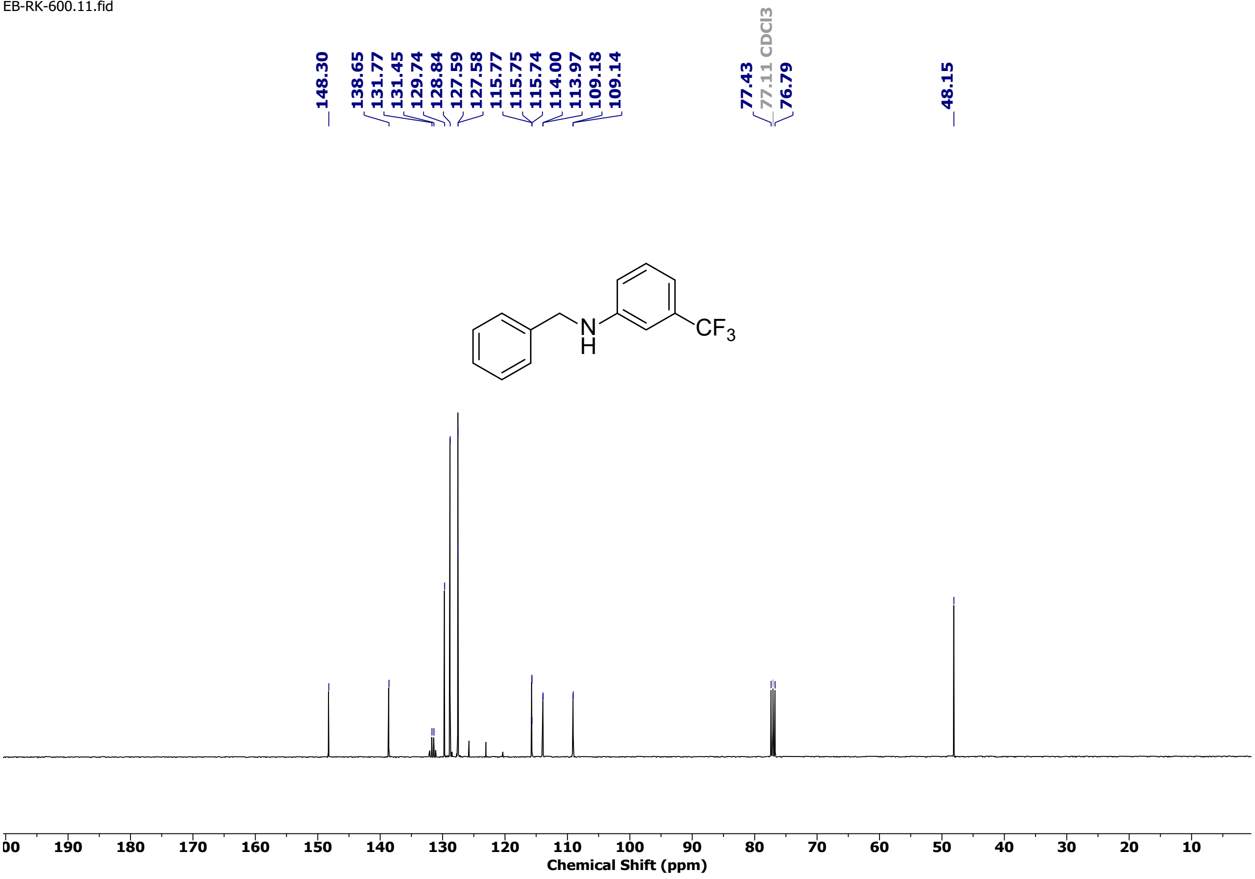
^{1}H NMR of **26** (400 MHz, $CDCl_3$))



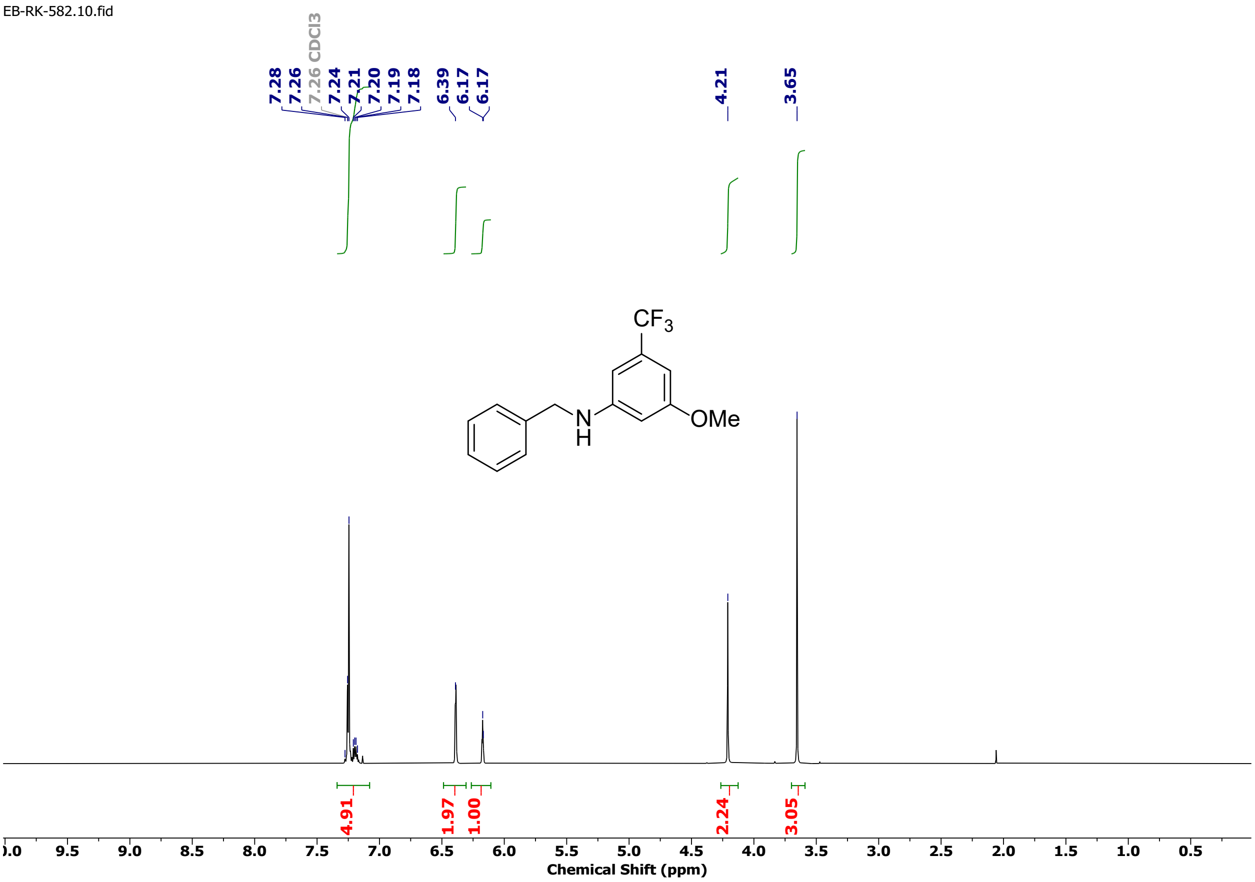
^{13}C NMR of **26** (100 MHz, $CDCl_3$)



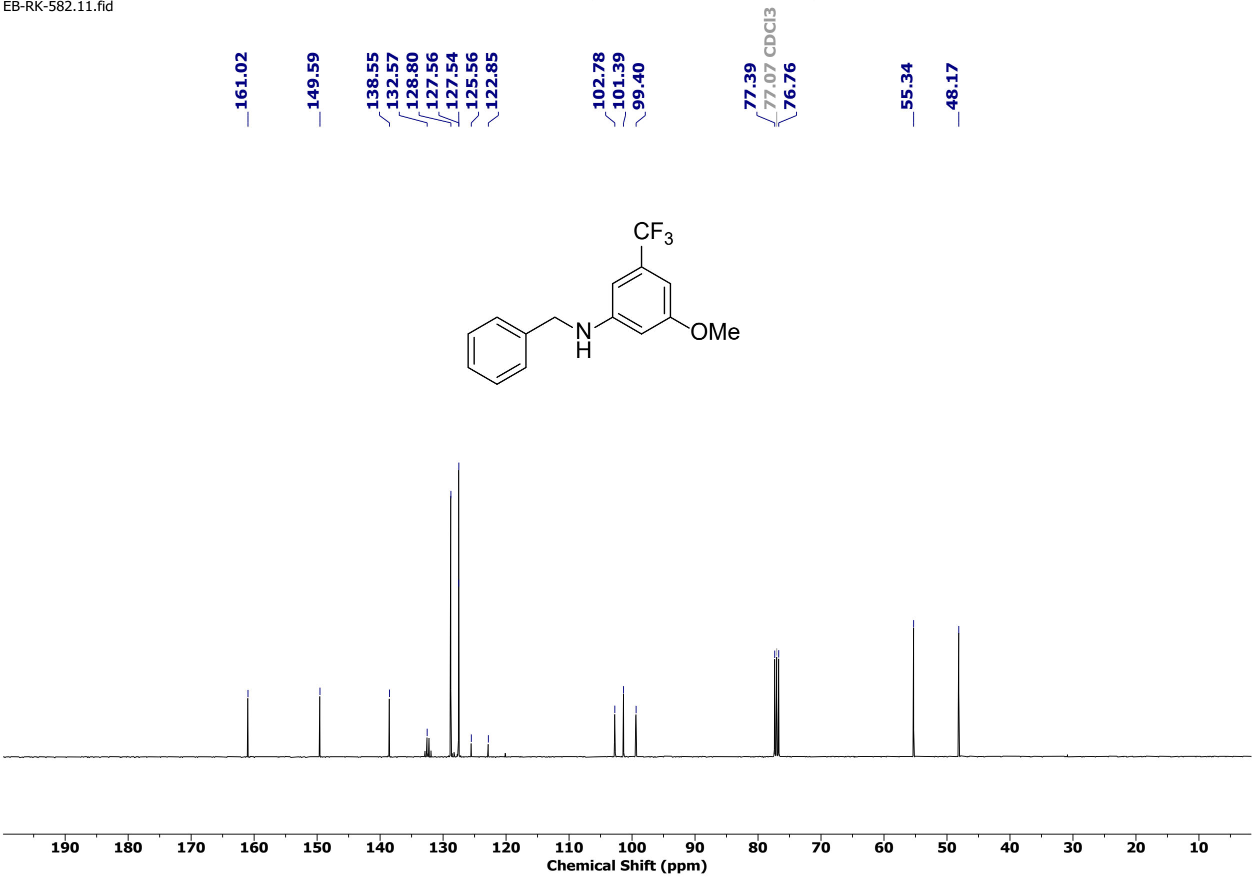
^{1}H NMR of **27** (400 MHz, CDCl$_3$)



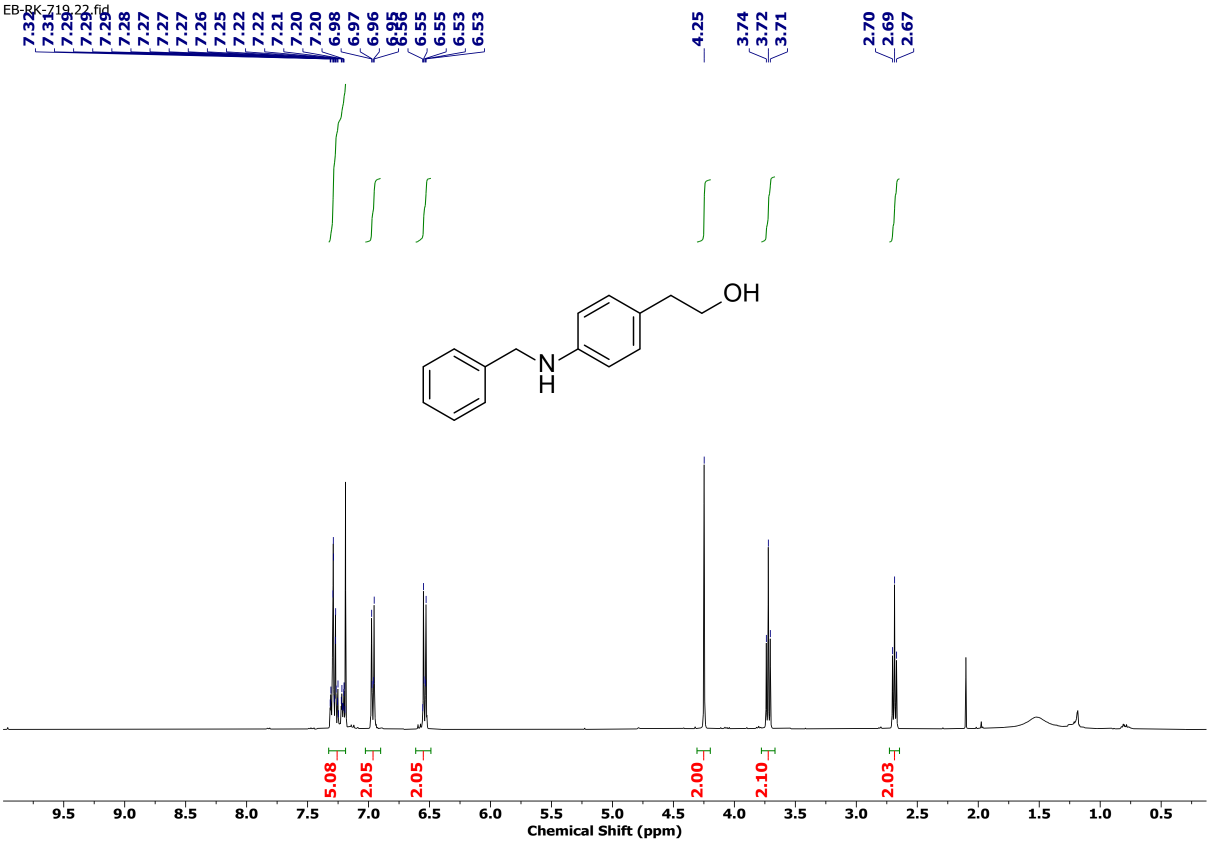
^{13}C NMR of **27** (100 MHz, CDCl$_3$)



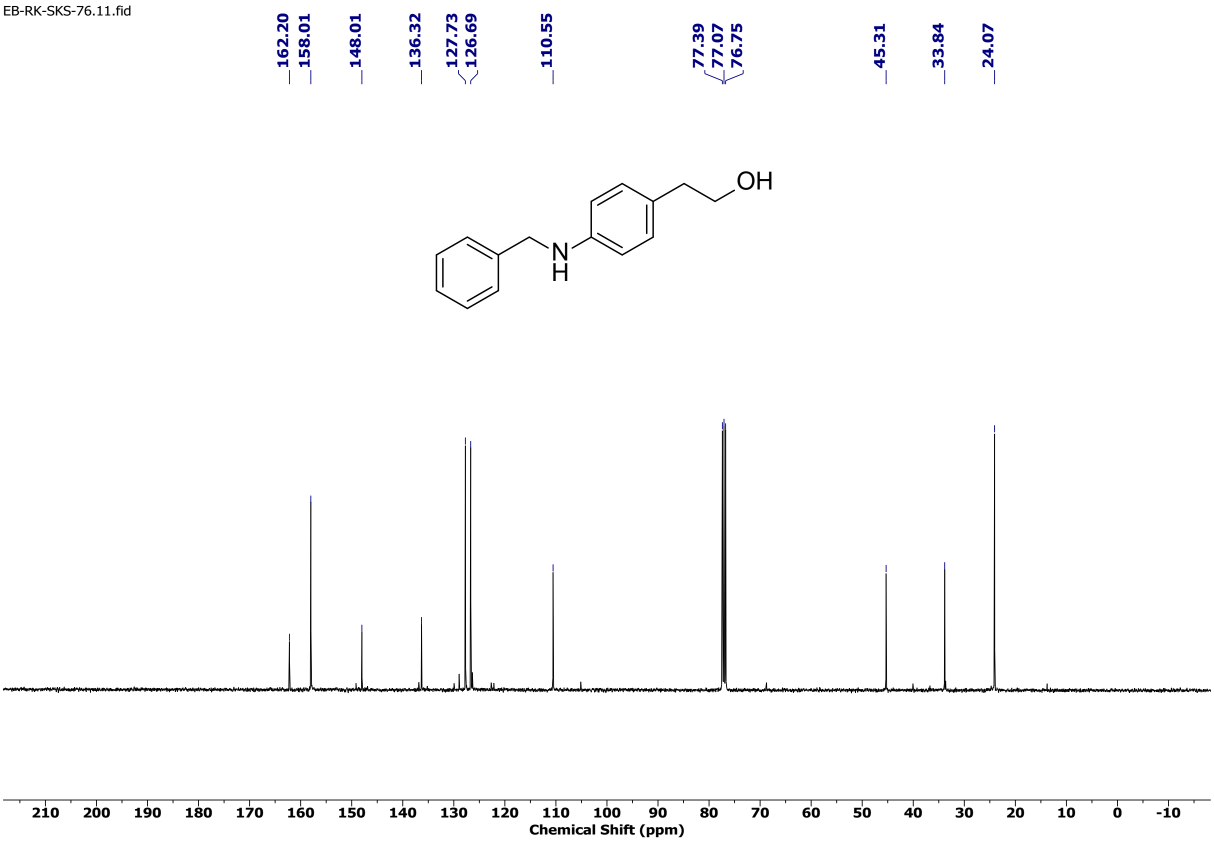
^{1}H NMR of **28** (400 MHz, CDCl$_3$)



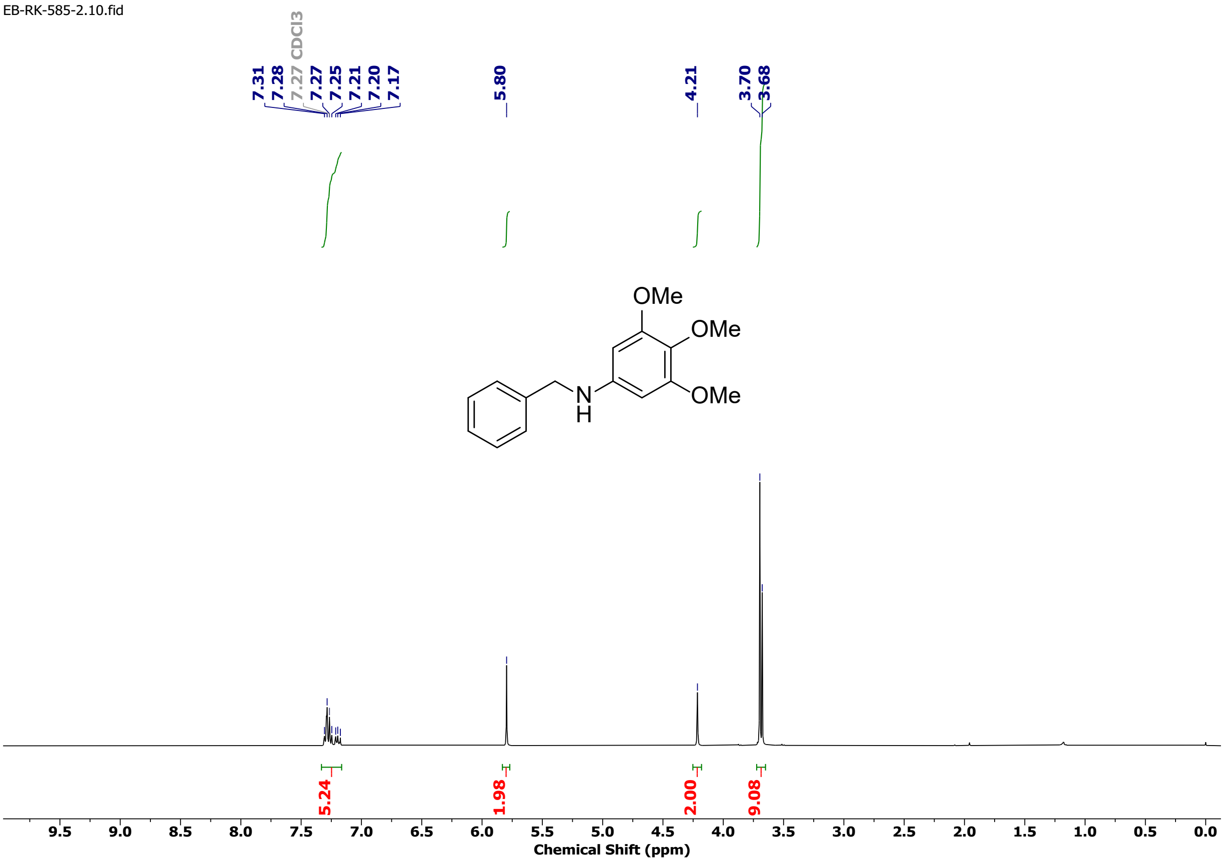
^{13}C NMR of **28** (100 MHz, CDCl$_3$)



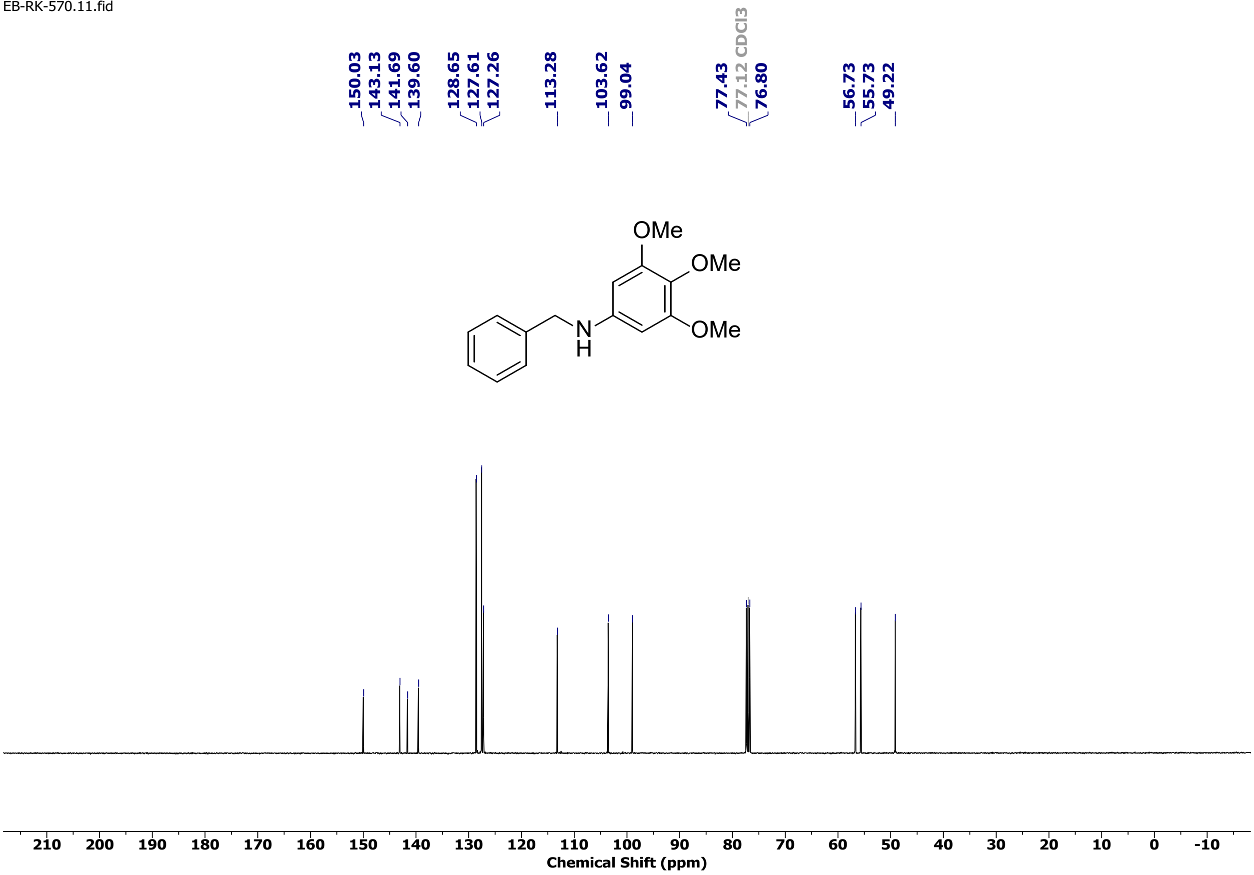
^{1}H NMR of **29** (400 MHz, CDCl$_3$)



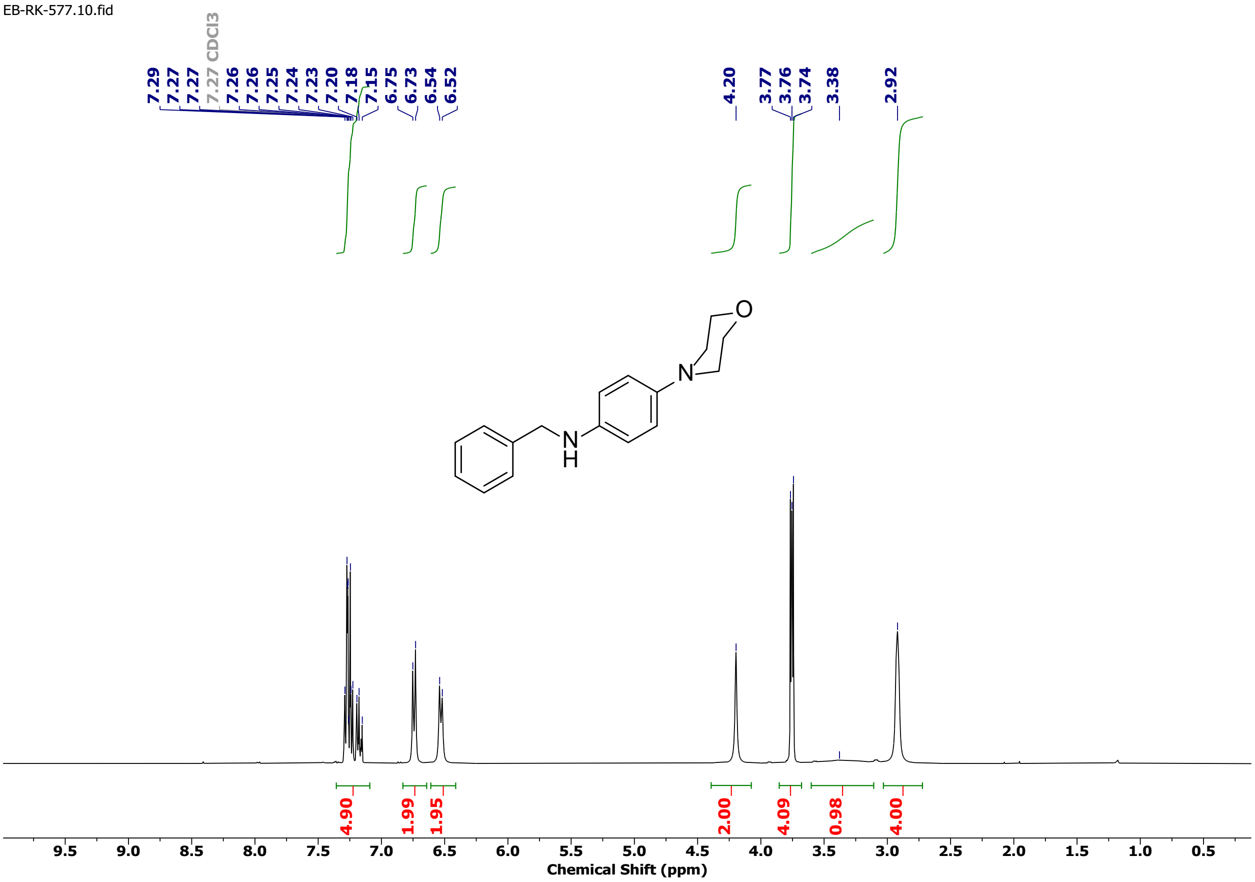
^{13}C NMR of **29** (100 MHz, CDCl$_3$)



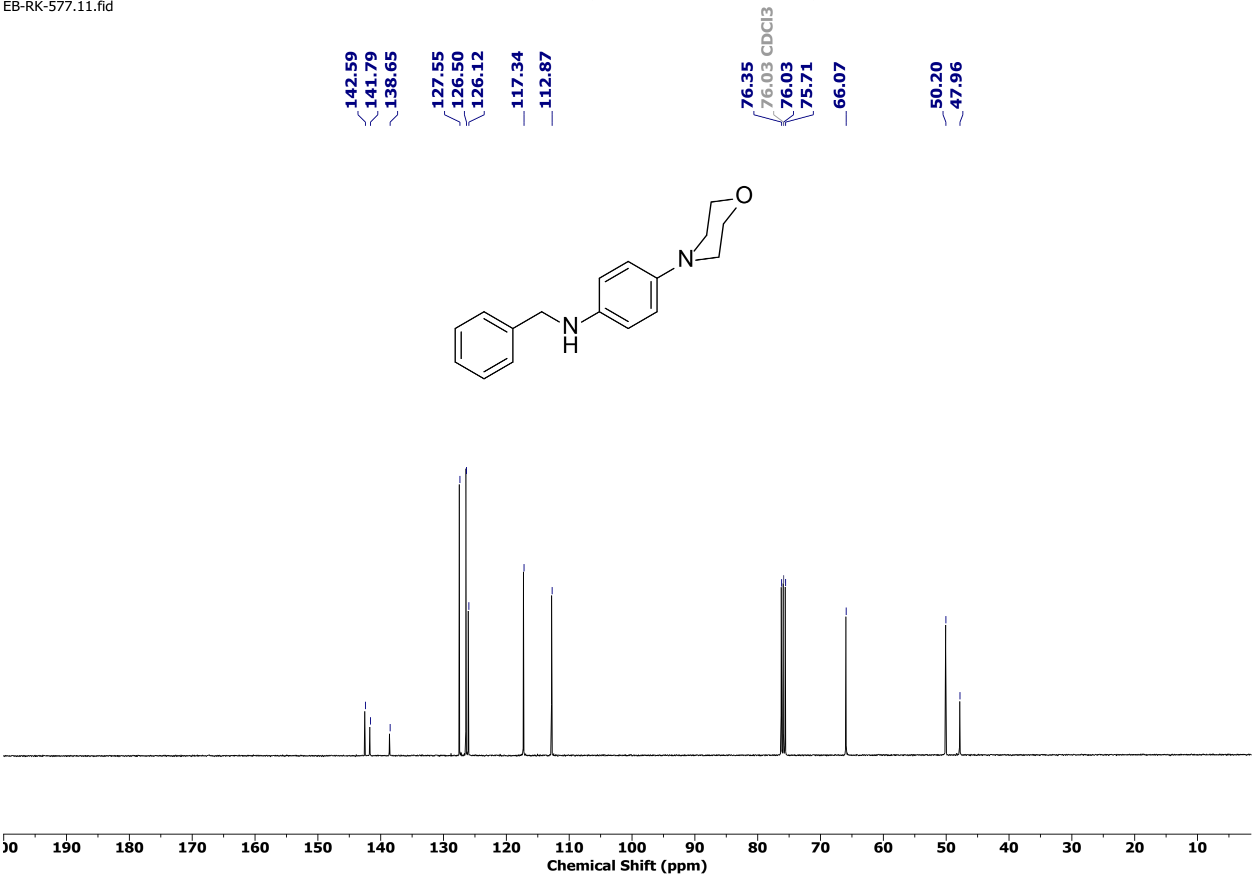
^{1}H NMR of **30** (400 MHz, CDCl$_3$)



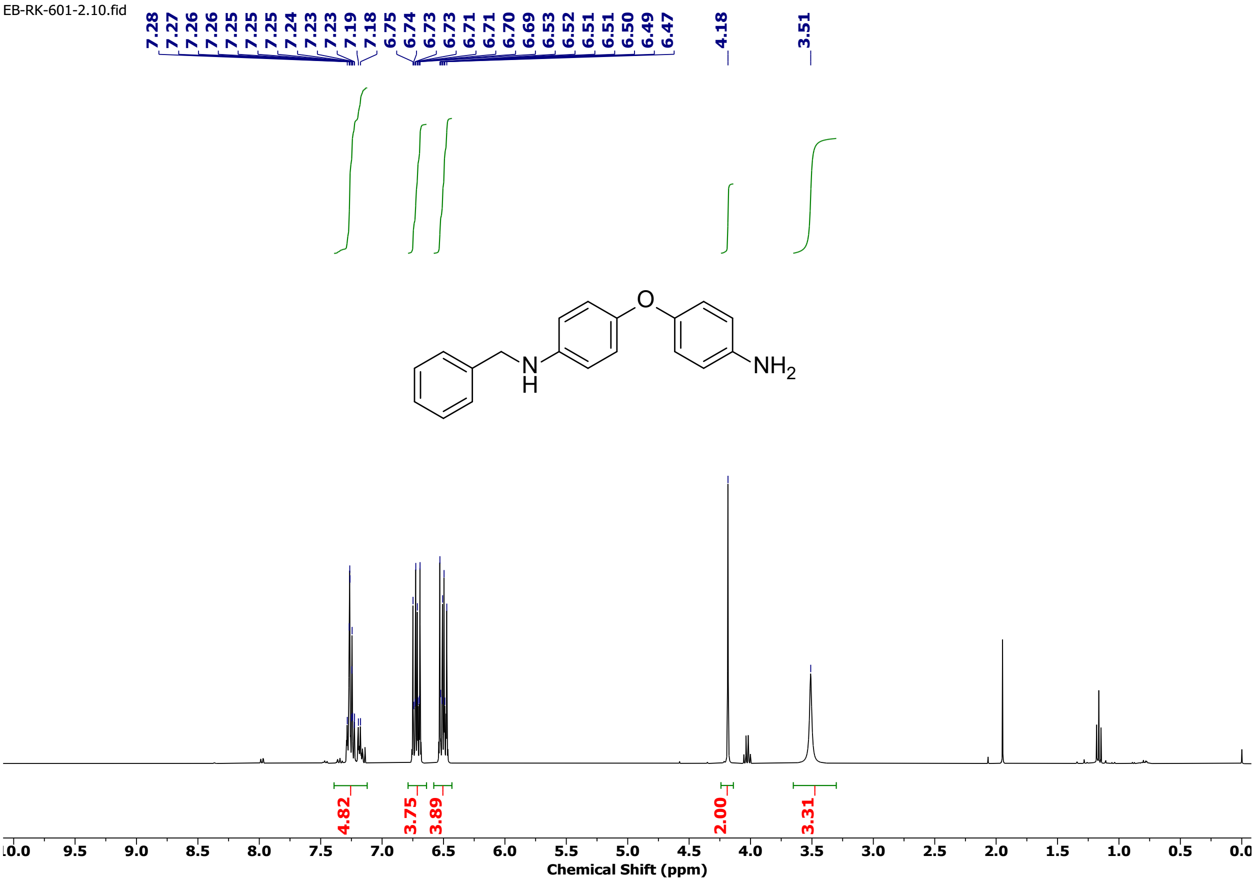
^{13}C NMR of **30** (100 MHz, CDCl$_3$)



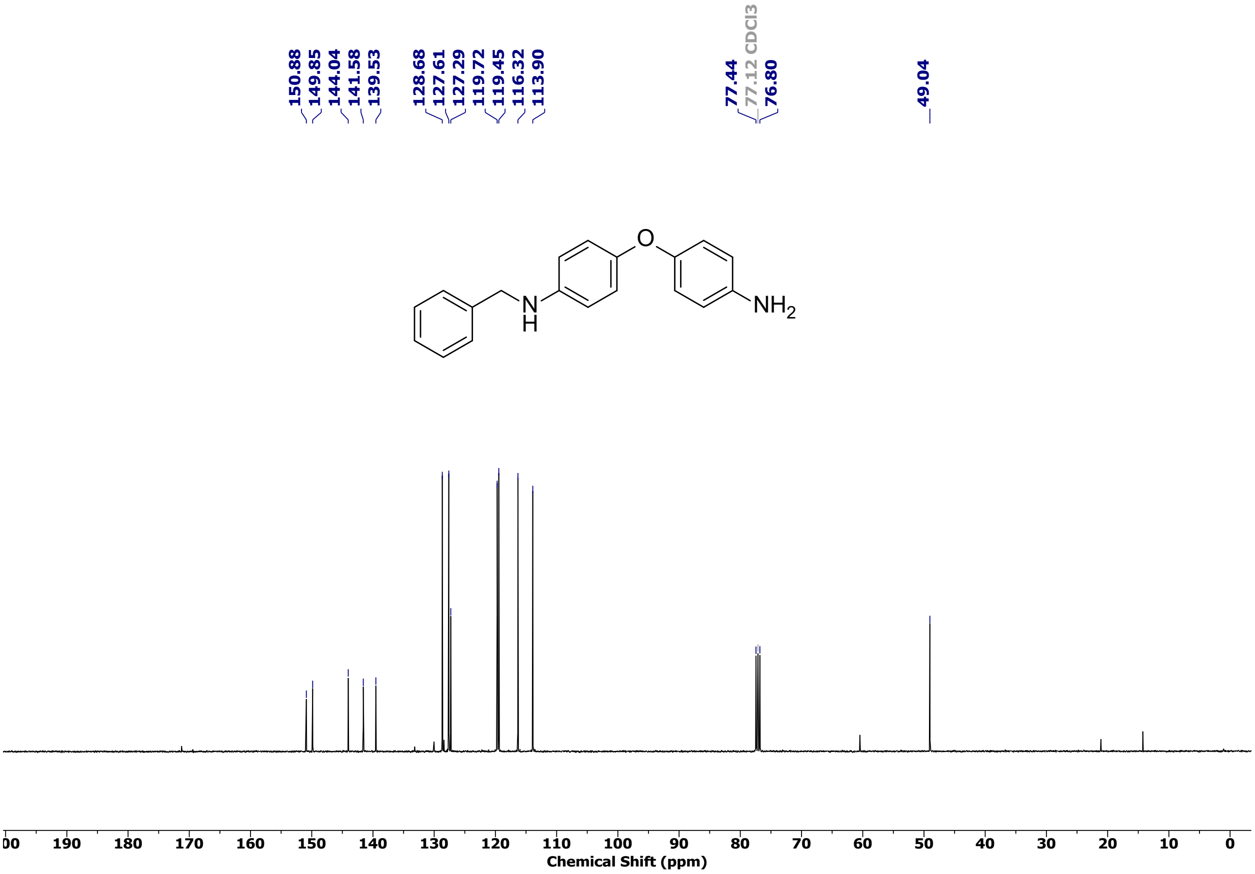
^{1}H NMR of **31** (400 MHz, CDCl$_3$)



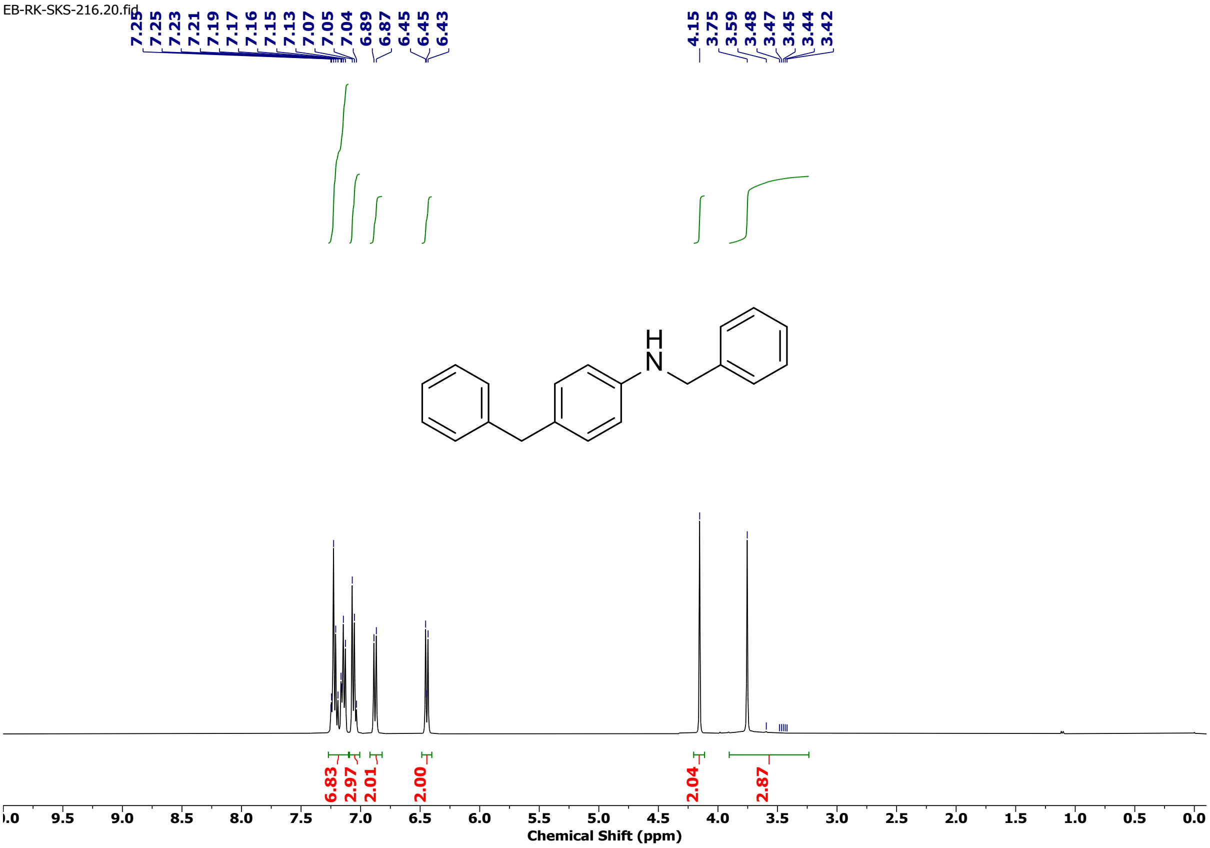
^{13}C NMR of **31** (100 MHz, CDCl$_3$)



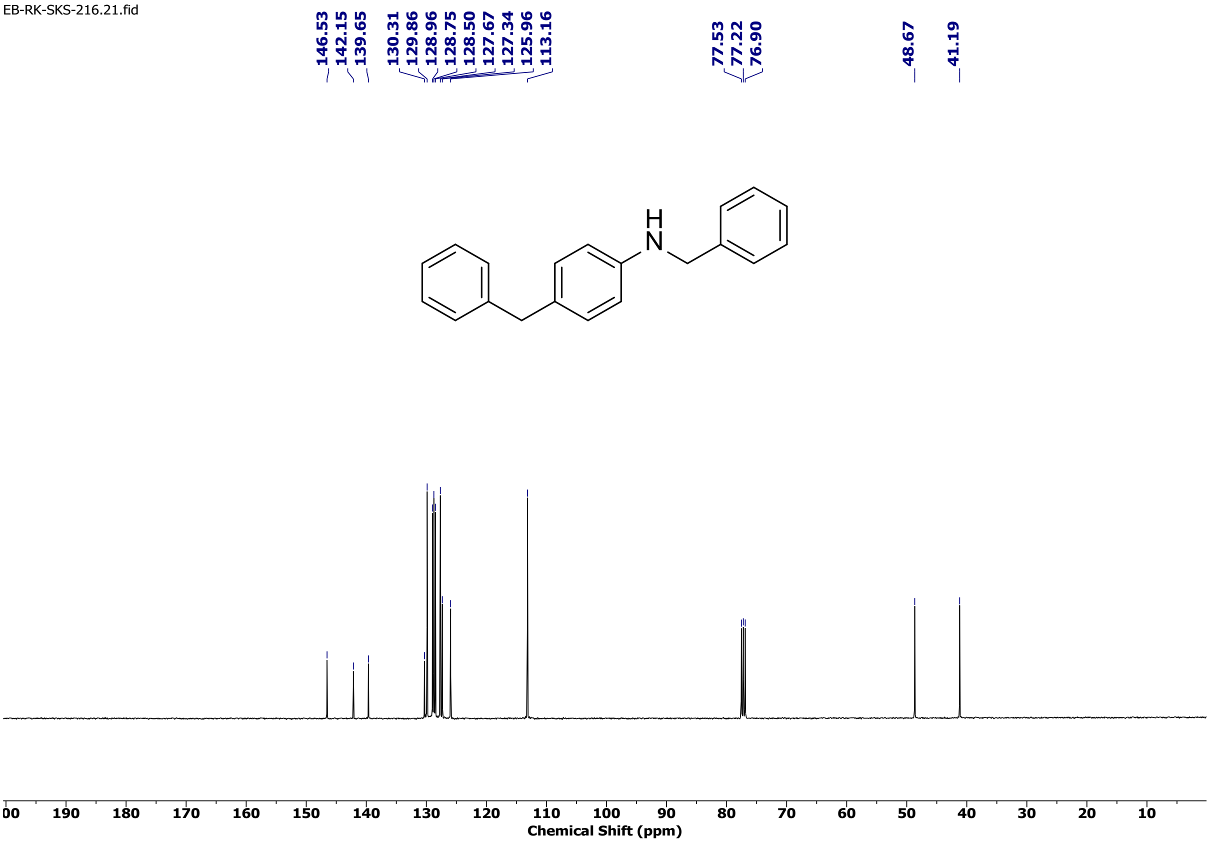
^{1}H NMR of **32** (400 MHz, $CDCl_3$)



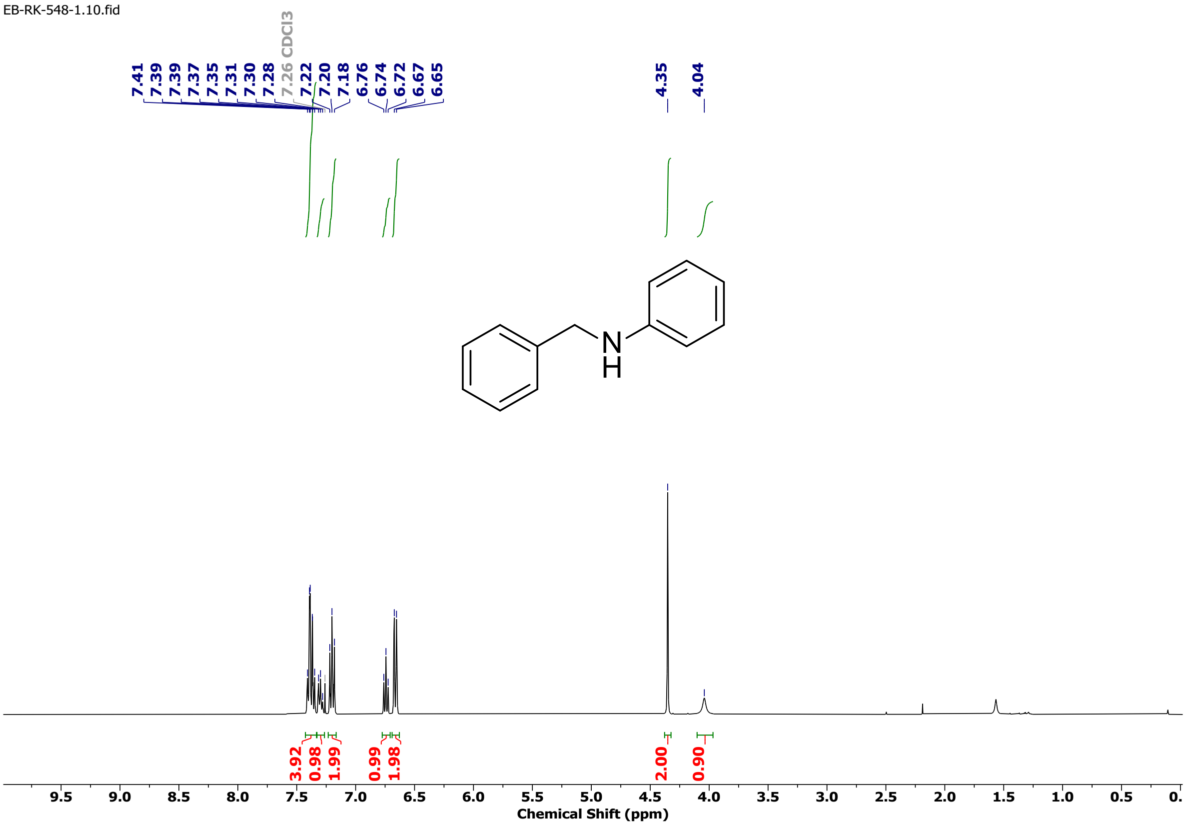
^{13}C NMR of **32** (100 MHz, $CDCl_3$)



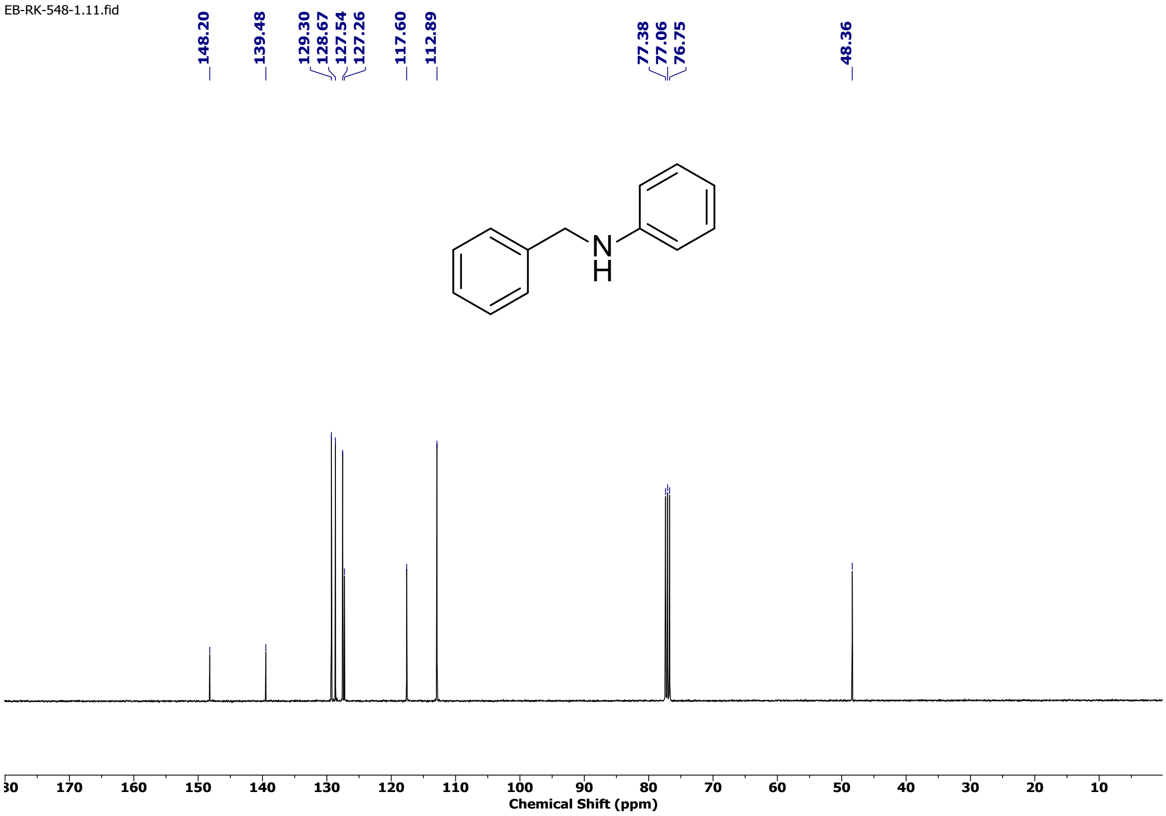
^{1}H NMR of **33** (400 MHz, $CDCl_3$)



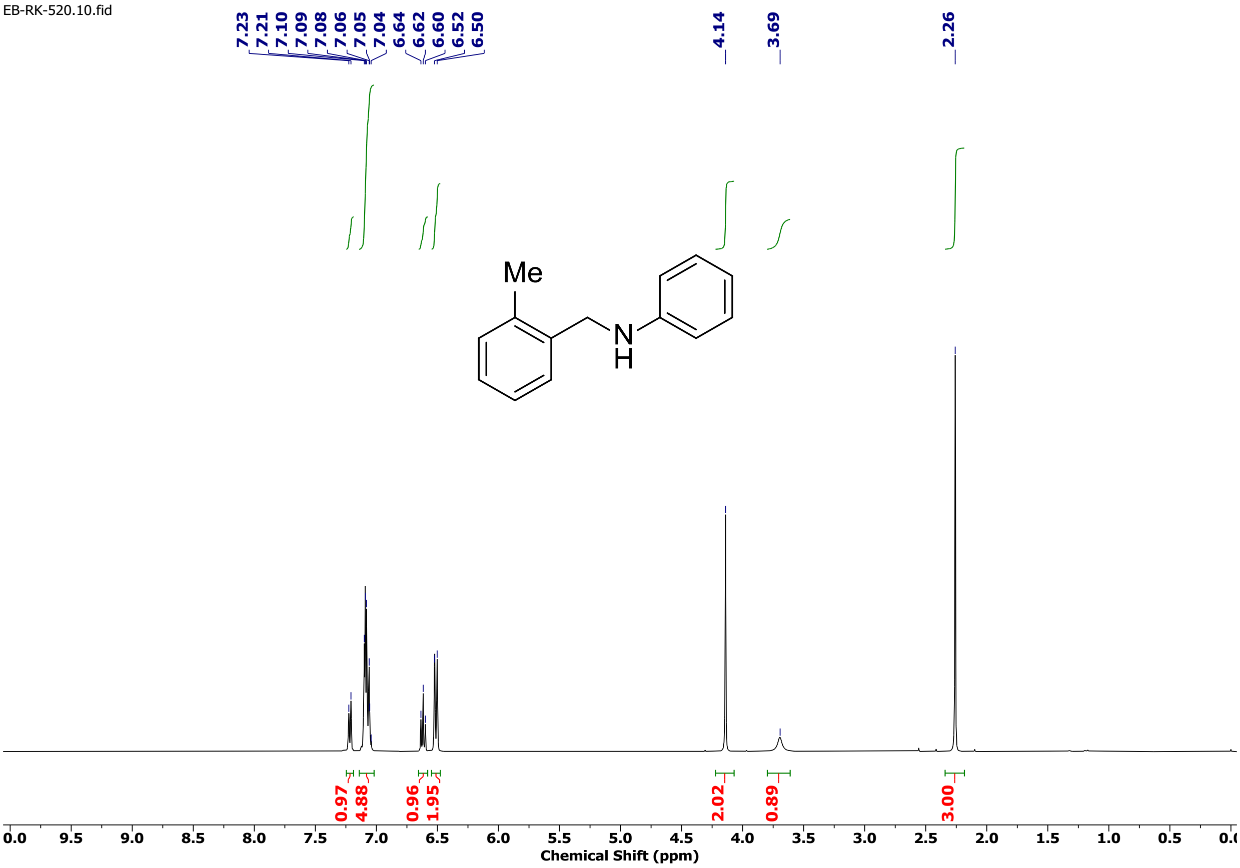
^{13}C NMR of **33** (100 MHz, $CDCl_3$)



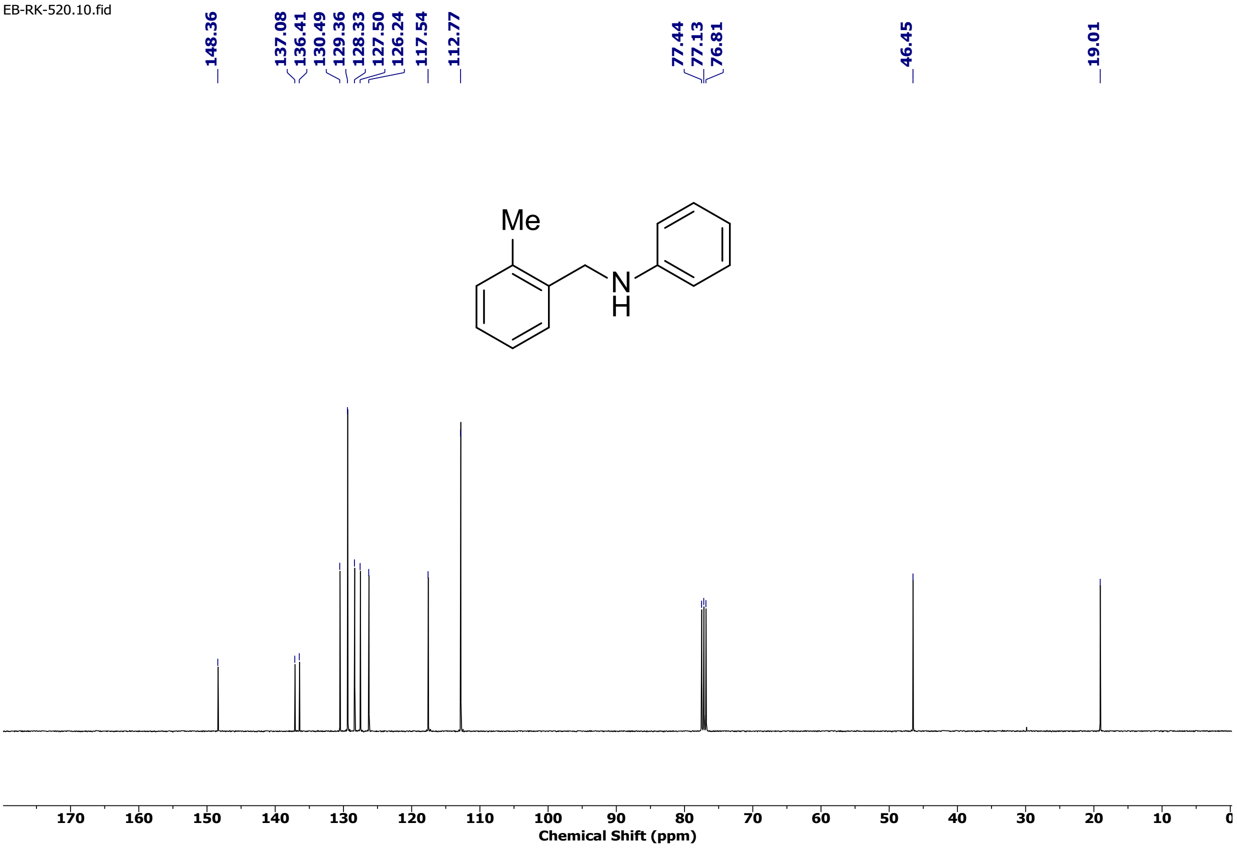
^{1}H NMR of **2** (400 MHz, CDCl$_3$)



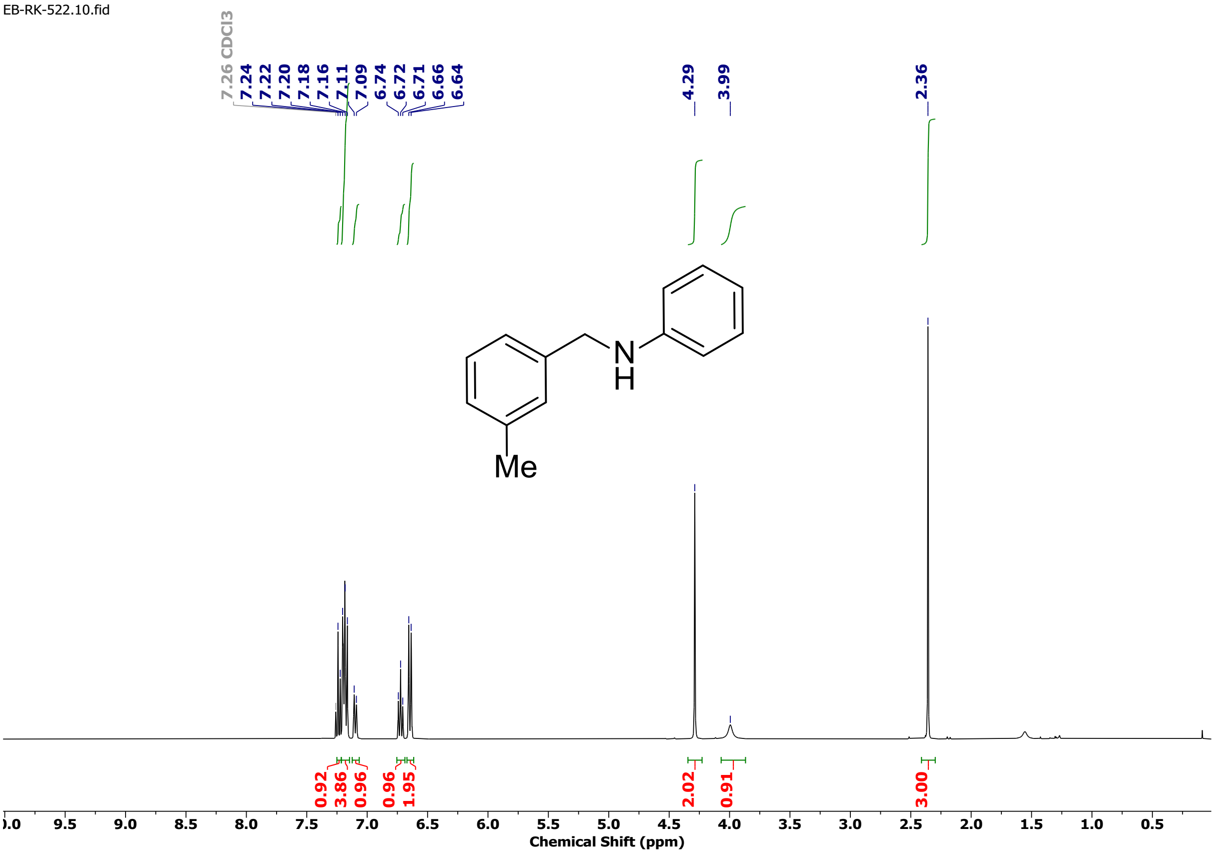
^{13}C NMR of **2** (100 MHz, CDCl$_3$)



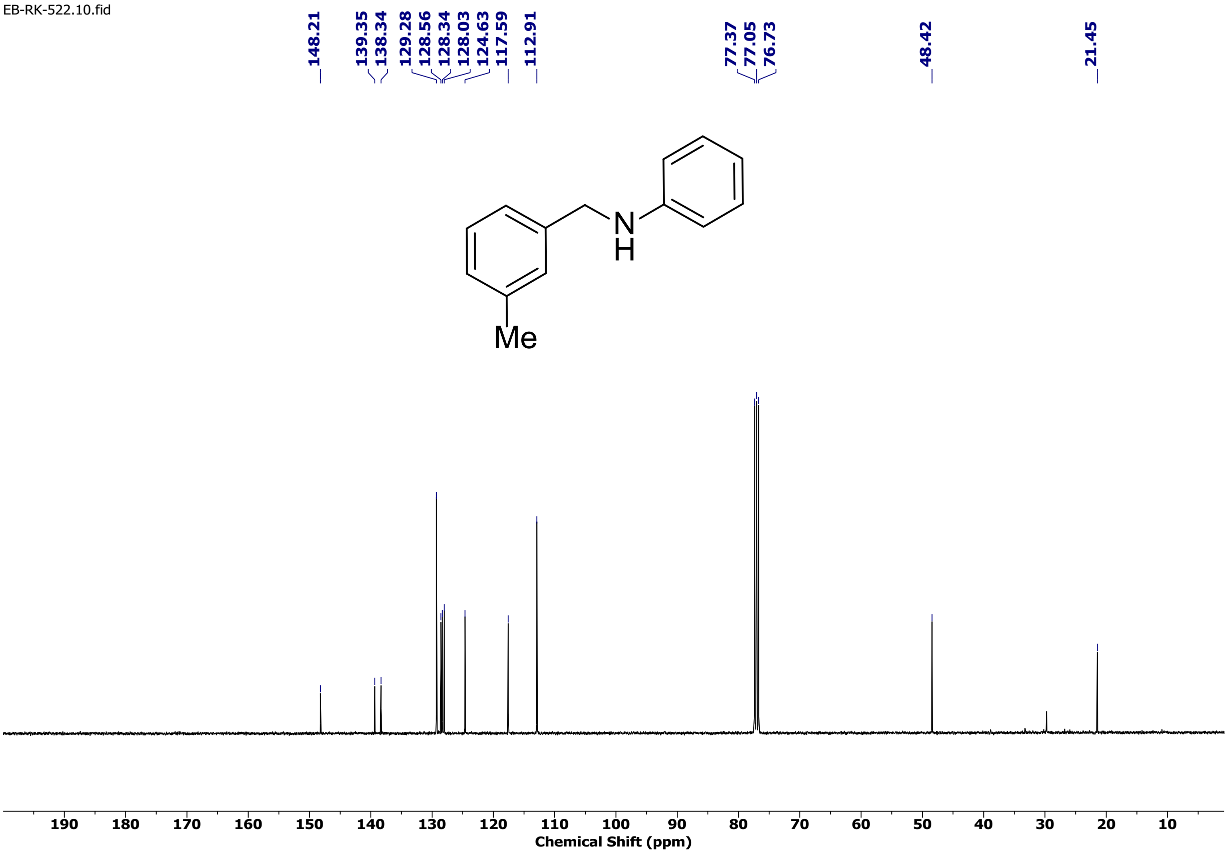
^{1}H NMR of **34** (400 MHz, CDCl$_3$)



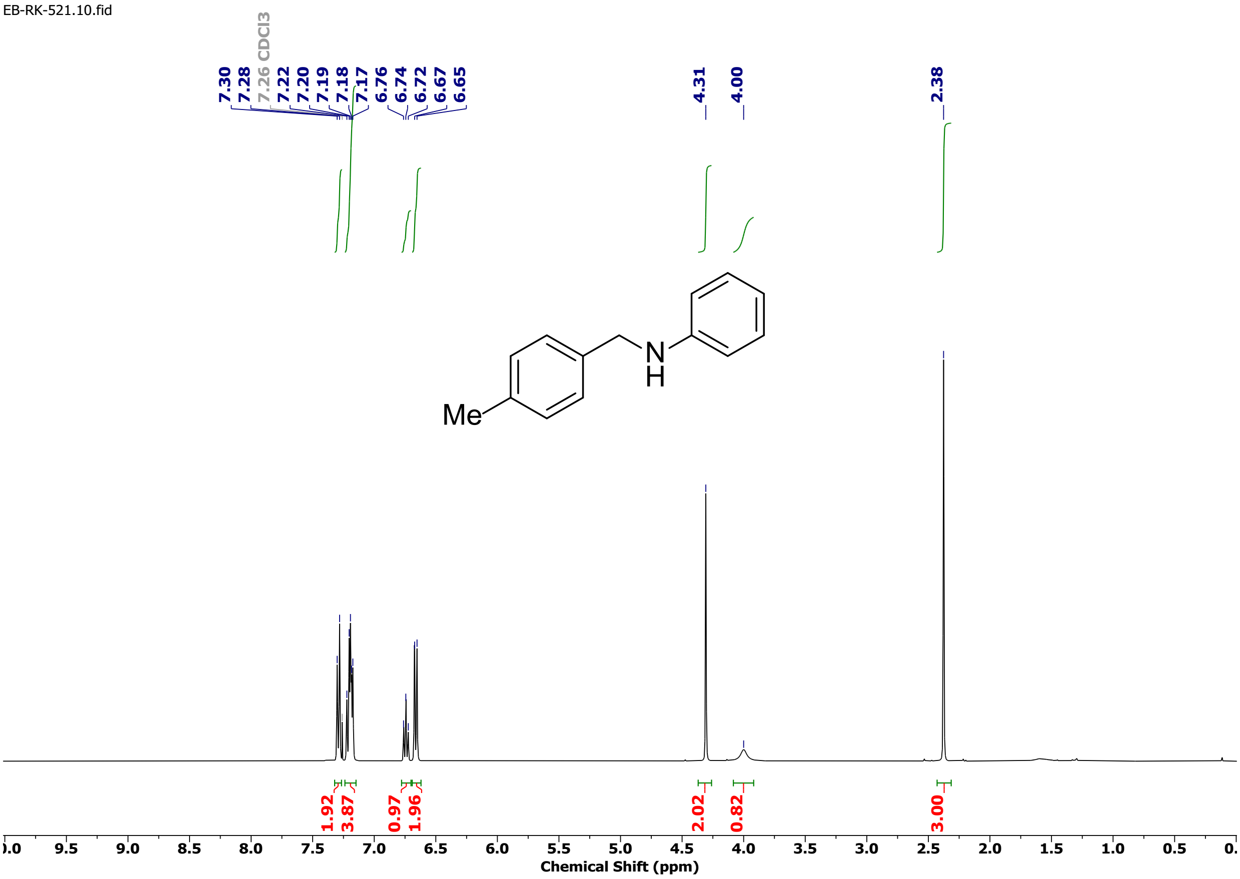
^{13}C NMR of **34** (100 MHz, CDCl$_3$)



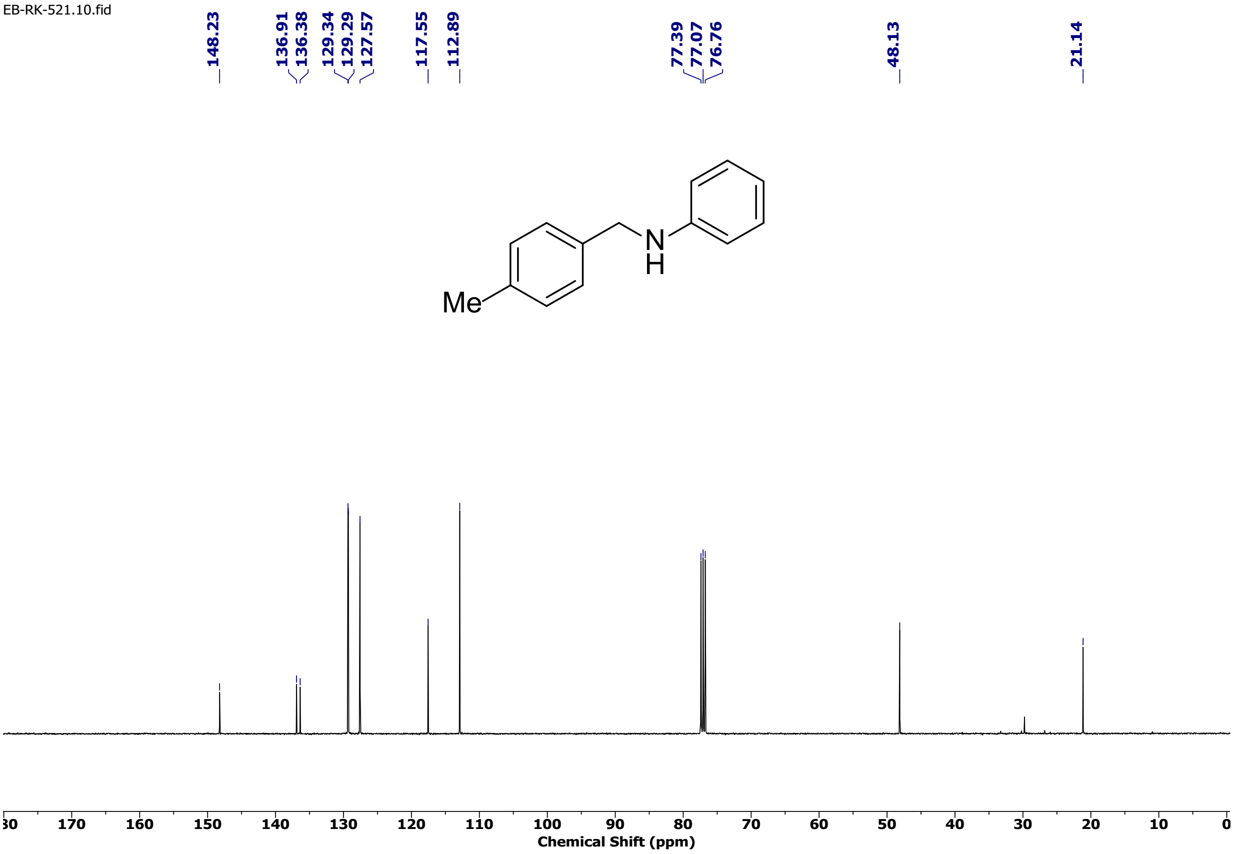
^{1}H NMR of **35** (400 MHz, CDCl$_3$)



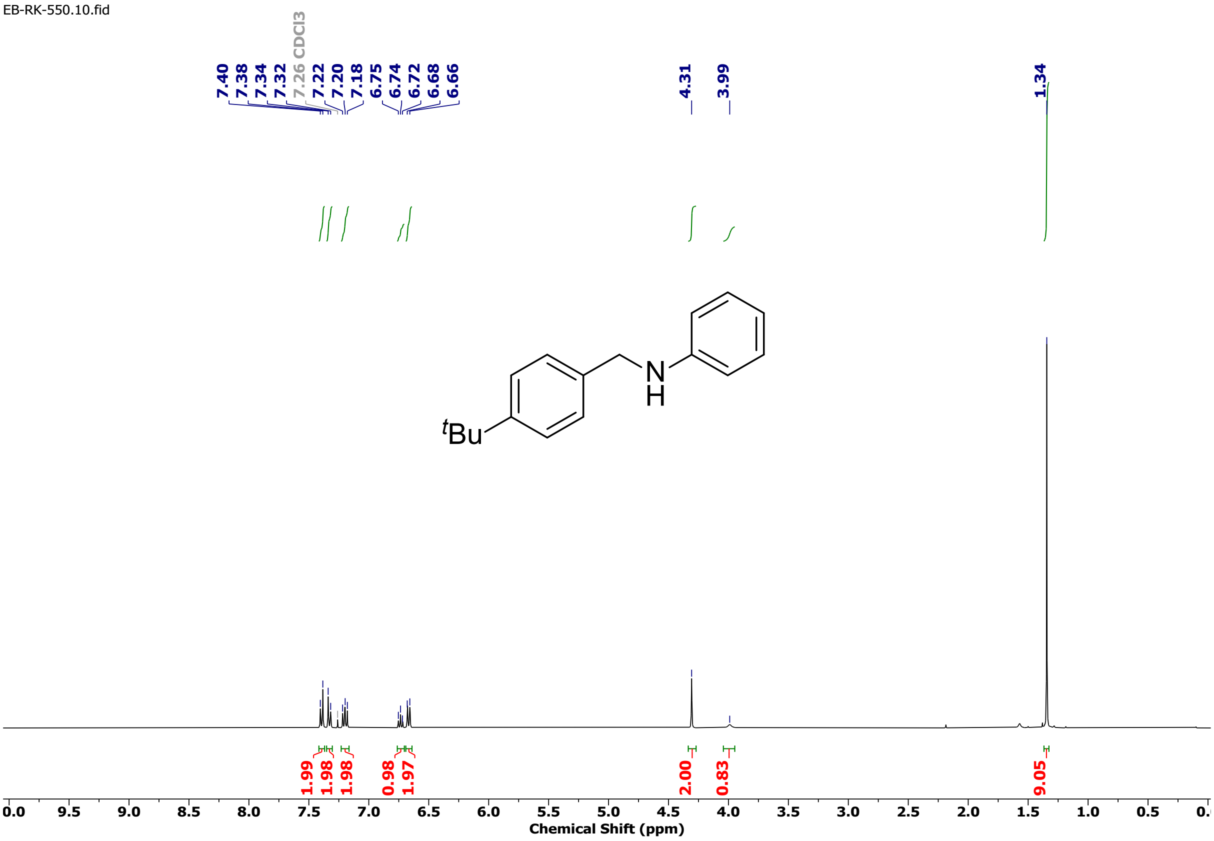
^{13}C NMR of **35** (100 MHz, CDCl$_3$)



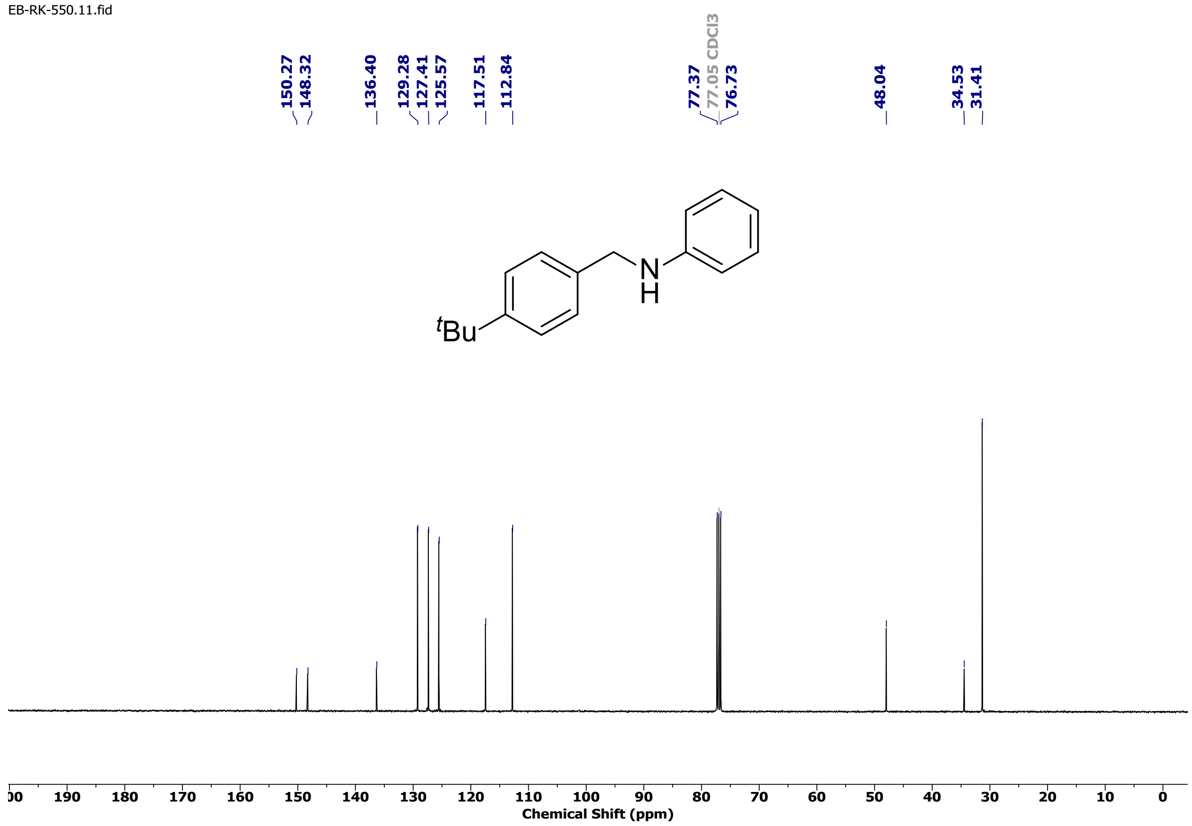
^{1}H NMR of **36** (400 MHz, CDCl$_3$)



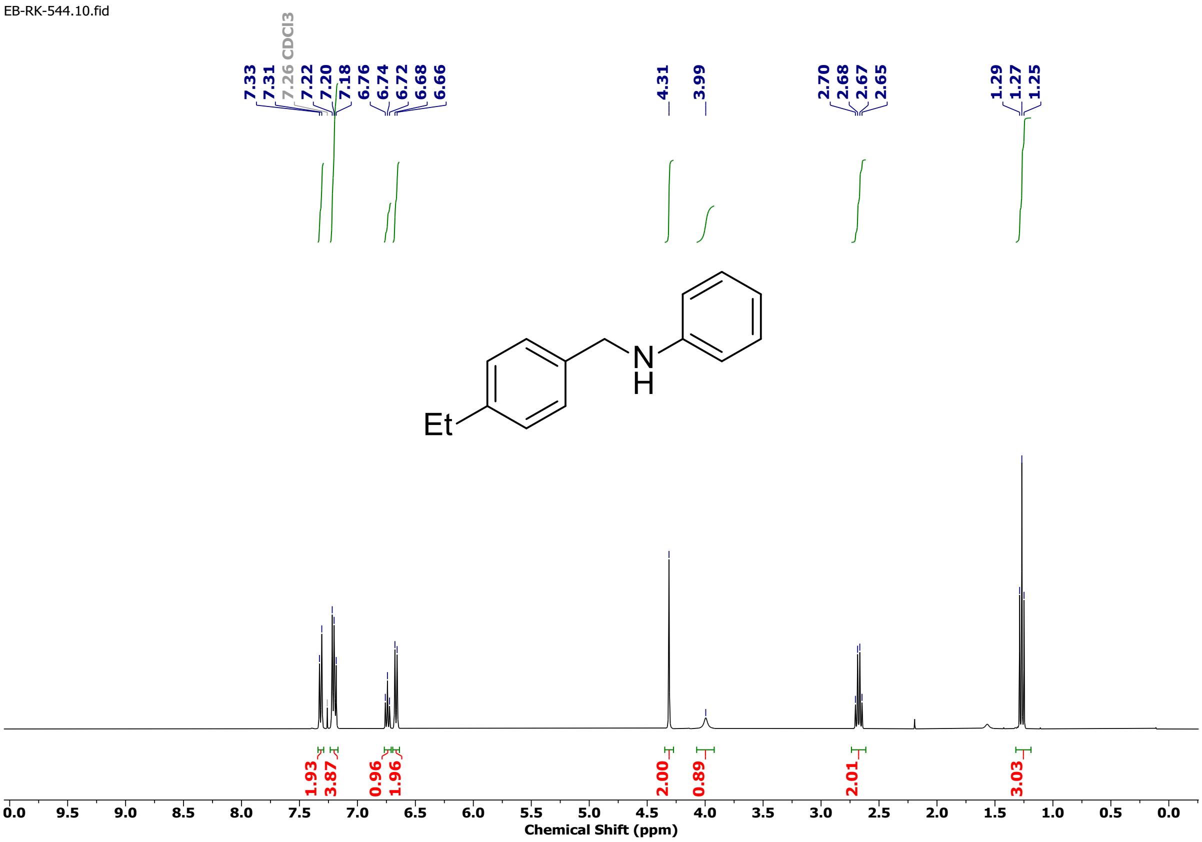
^{13}C NMR of **36** (100 MHz, CDCl$_3$)



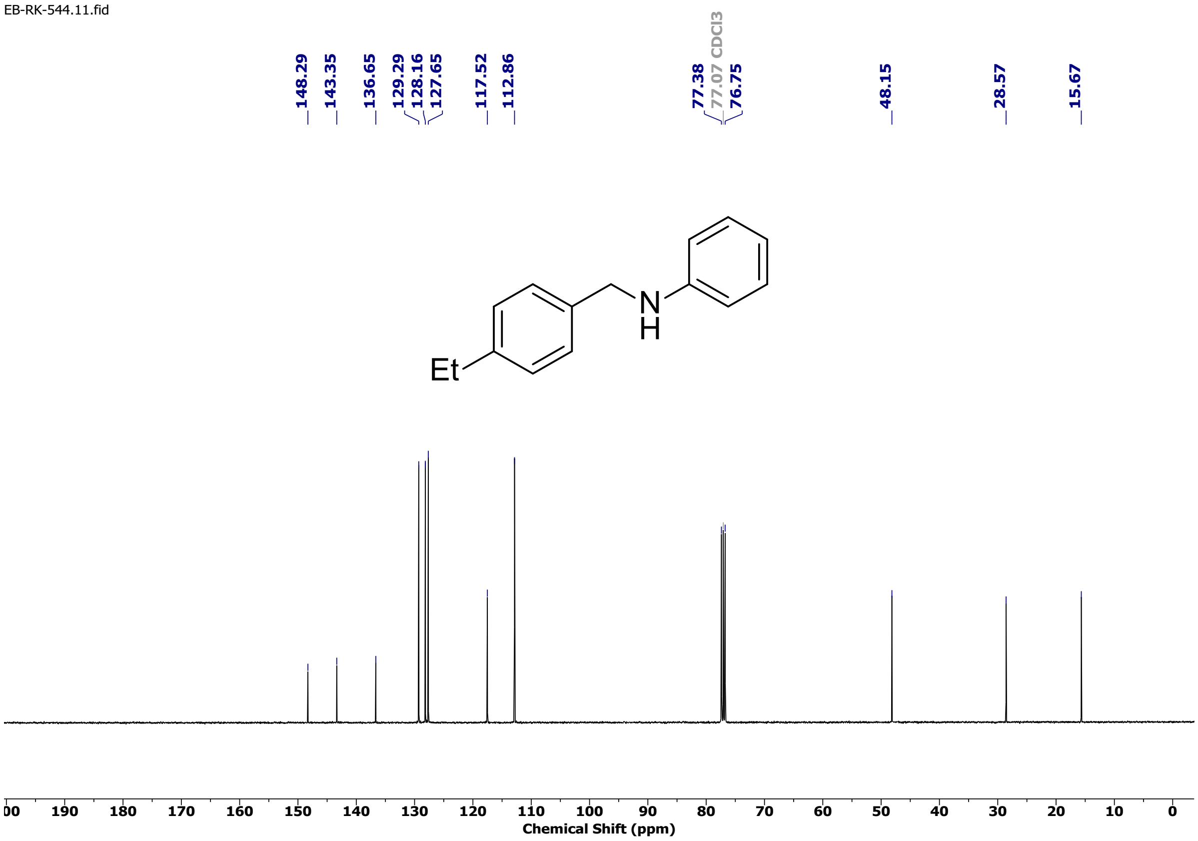
^{1}H NMR of **37** (400 MHz, CDCl$_3$)



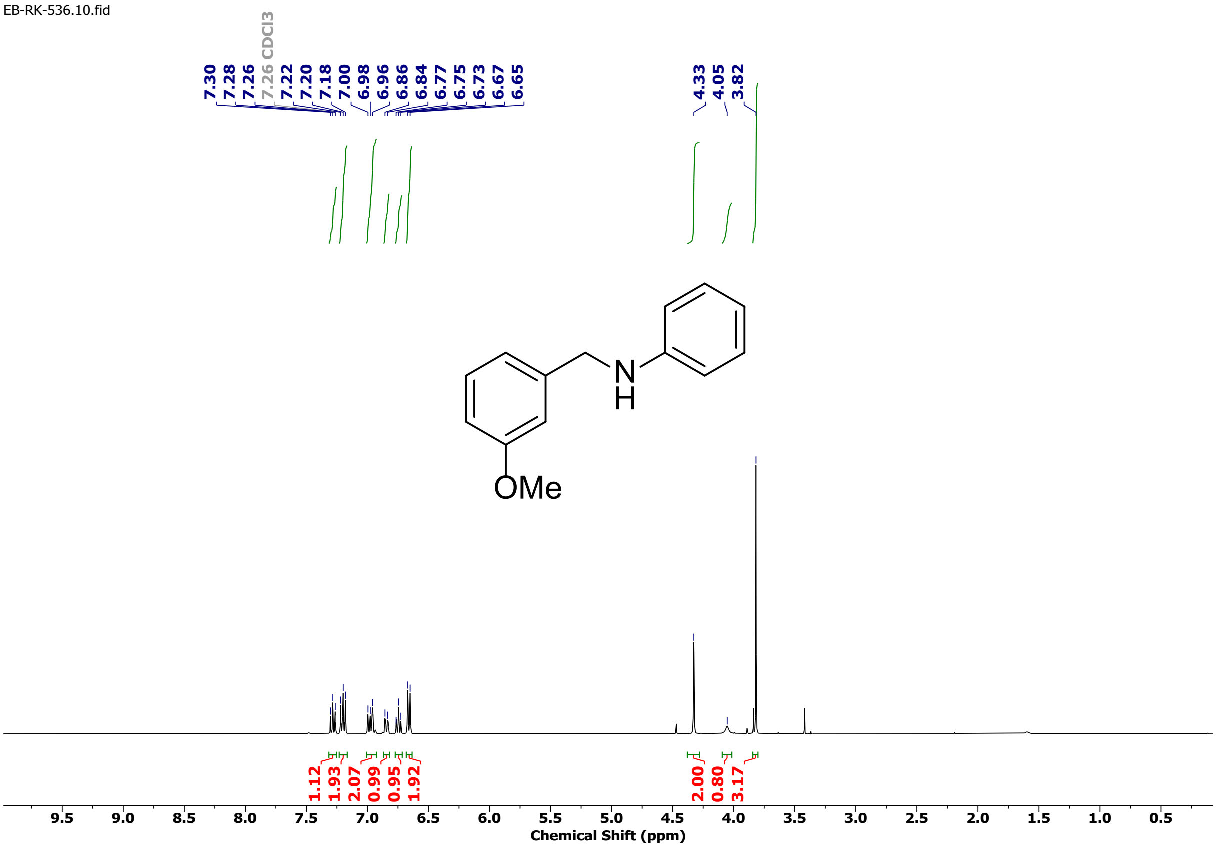
^{13}C NMR of **37** (100 MHz, CDCl$_3$)



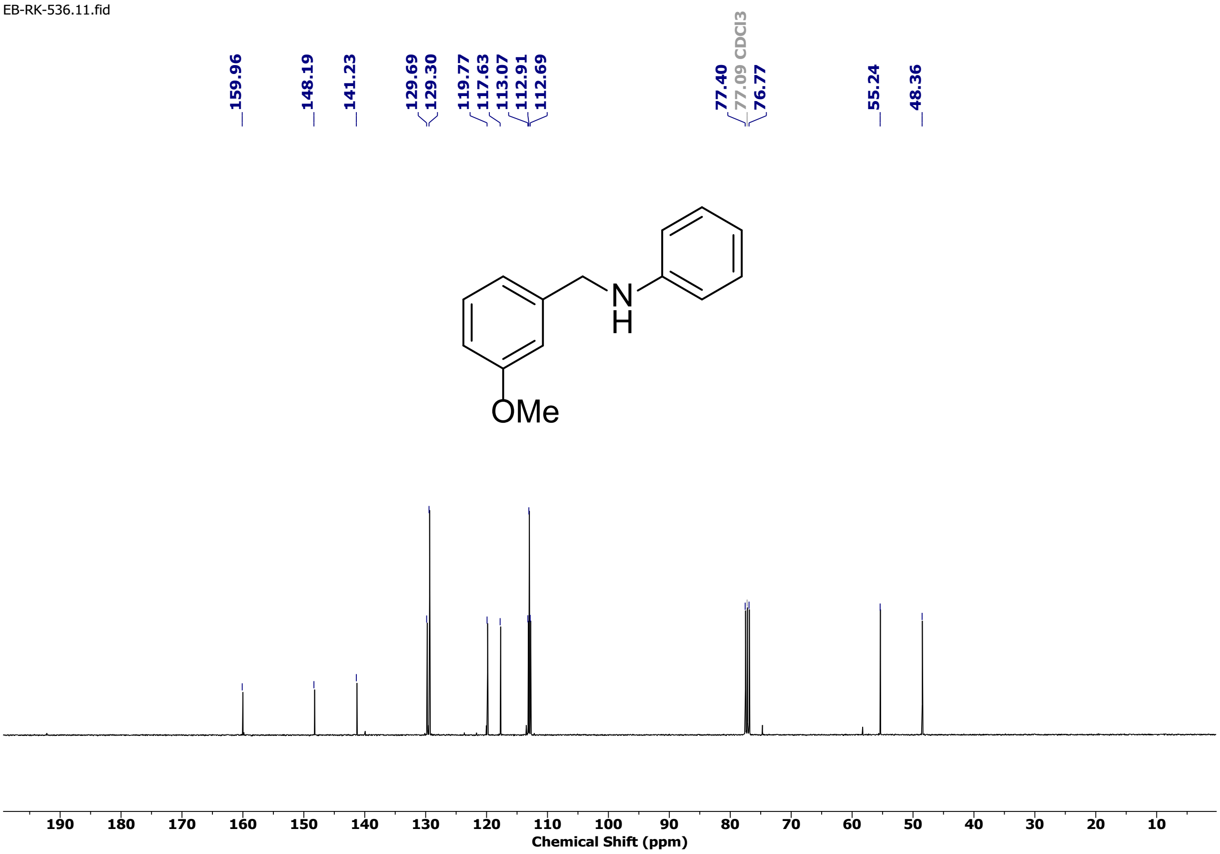
^{1}H NMR of **38** (400 MHz, CDCl$_3$)



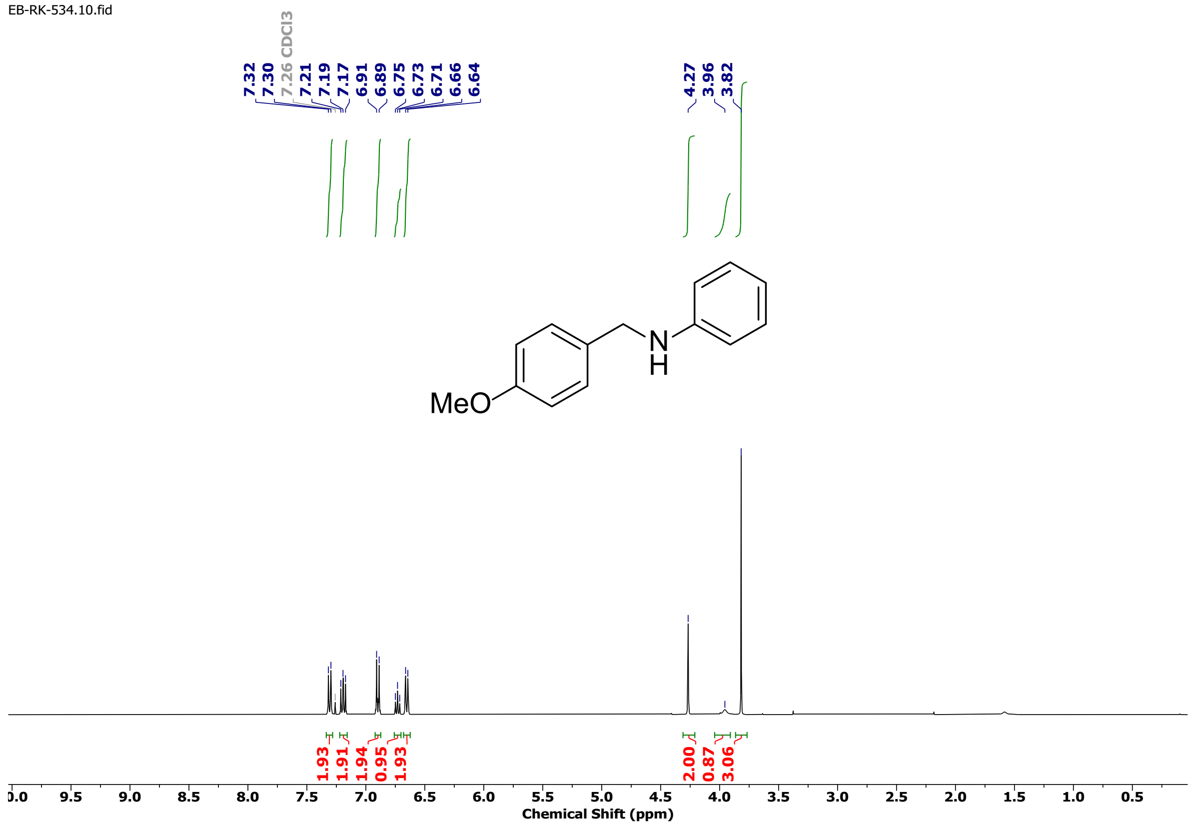
^{13}C NMR of **38** (100 MHz, CDCl$_3$)



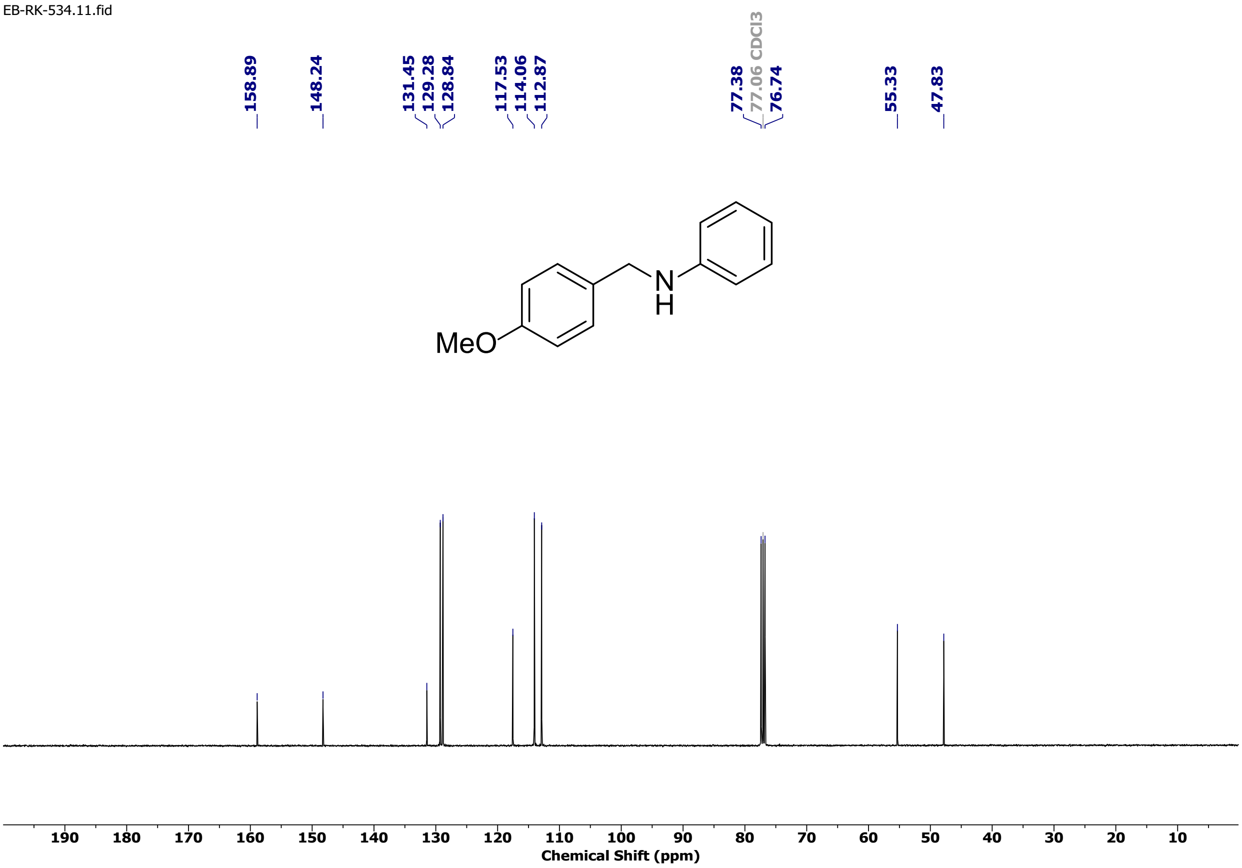
^{1}H NMR of **40** (400 MHz, CDCl$_3$)



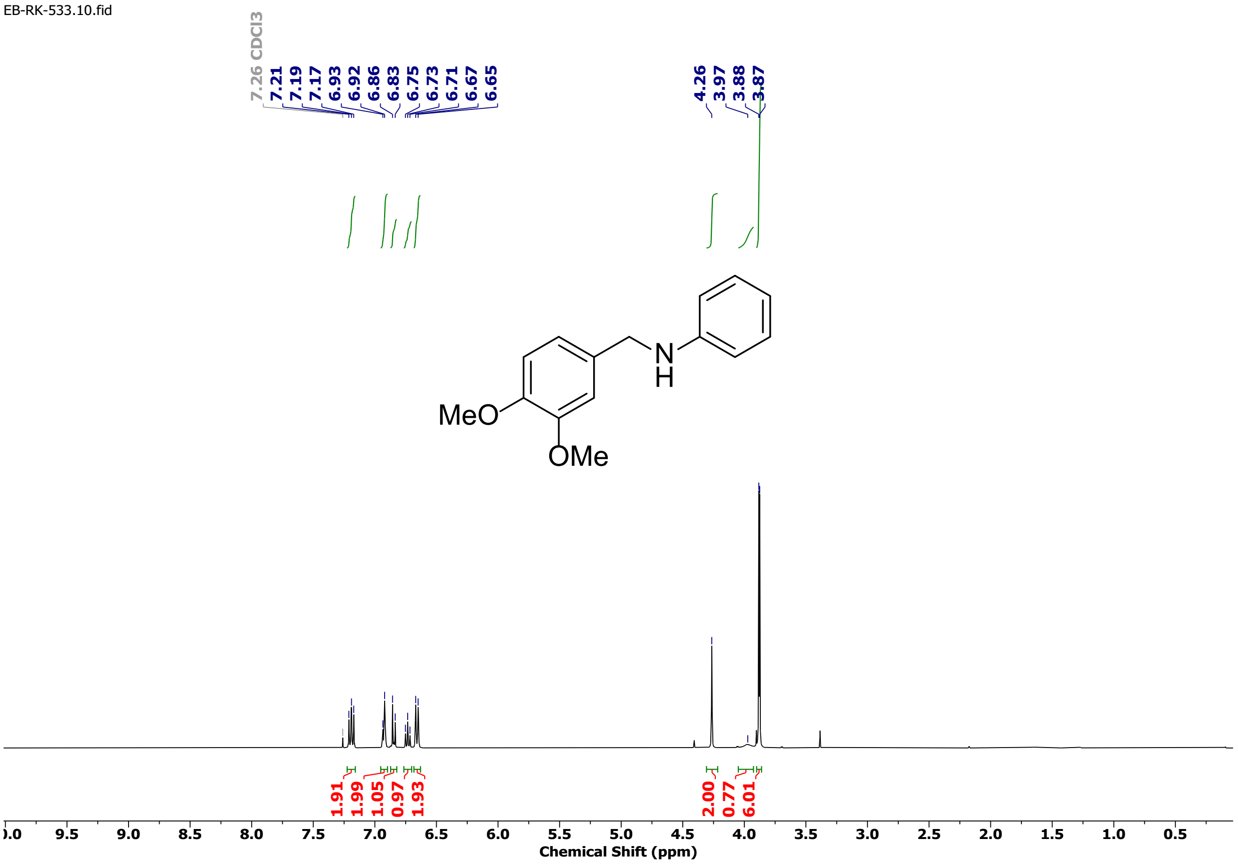
^{13}C NMR of **40** (100 MHz, CDCl$_3$)



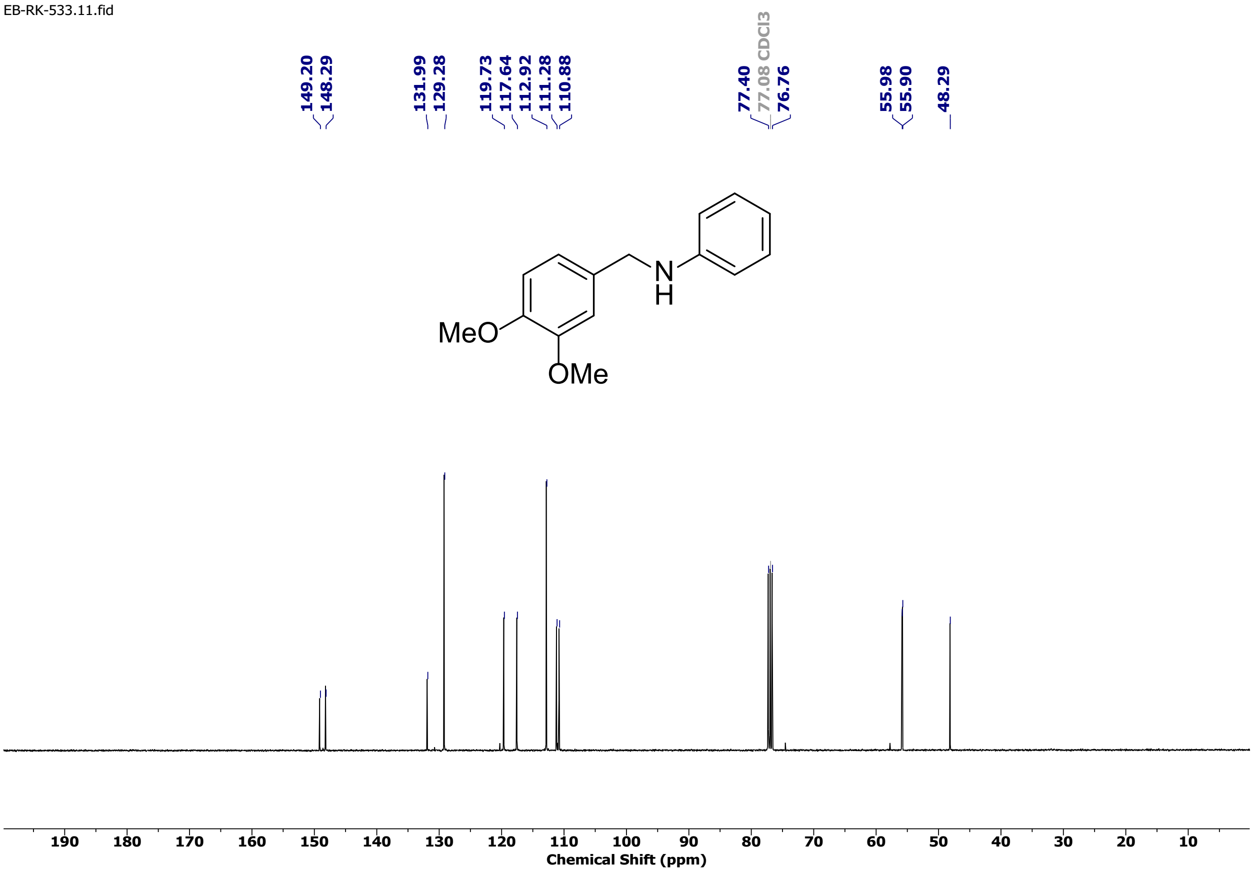
^{1}H NMR of **41** (400 MHz, CDCl$_3$)



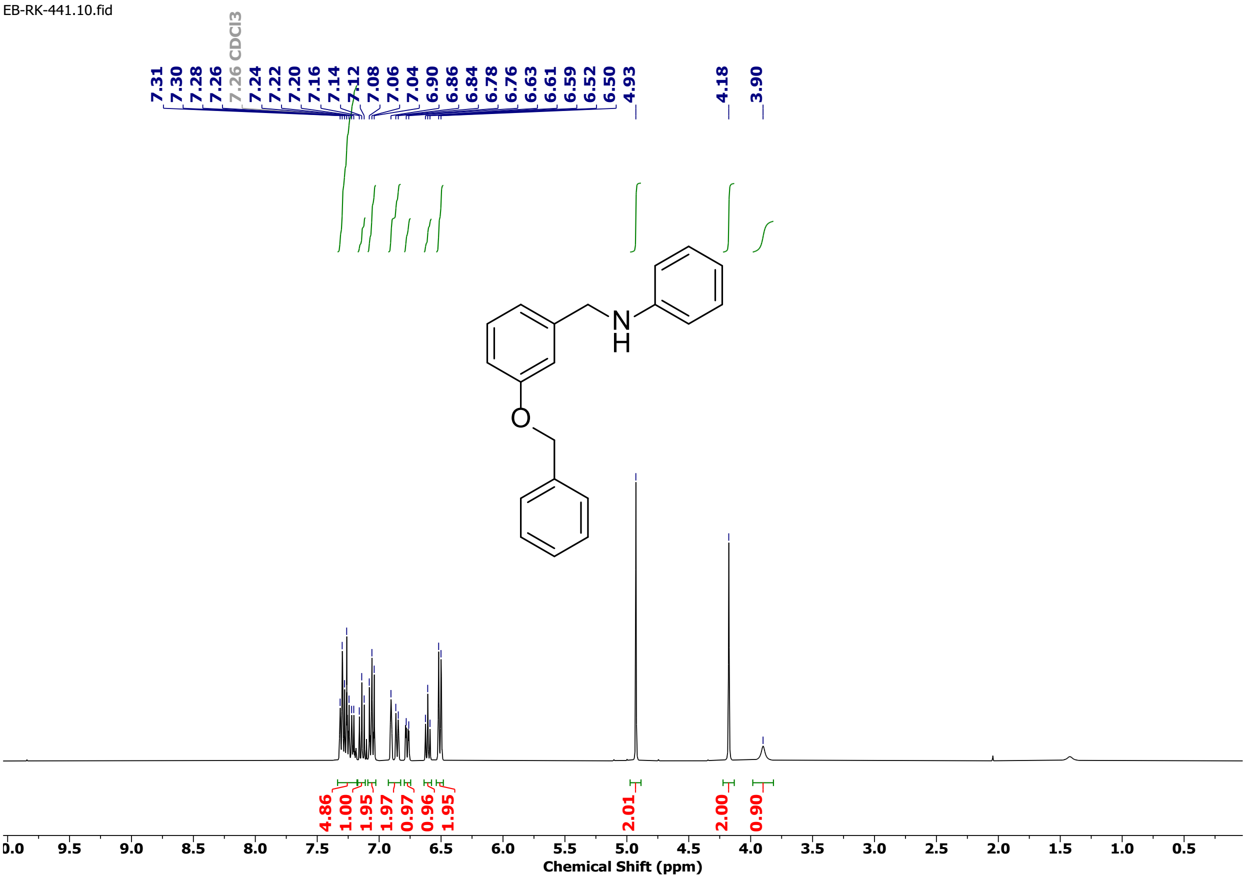
^{13}C NMR of **41** (100 MHz, CDCl$_3$)



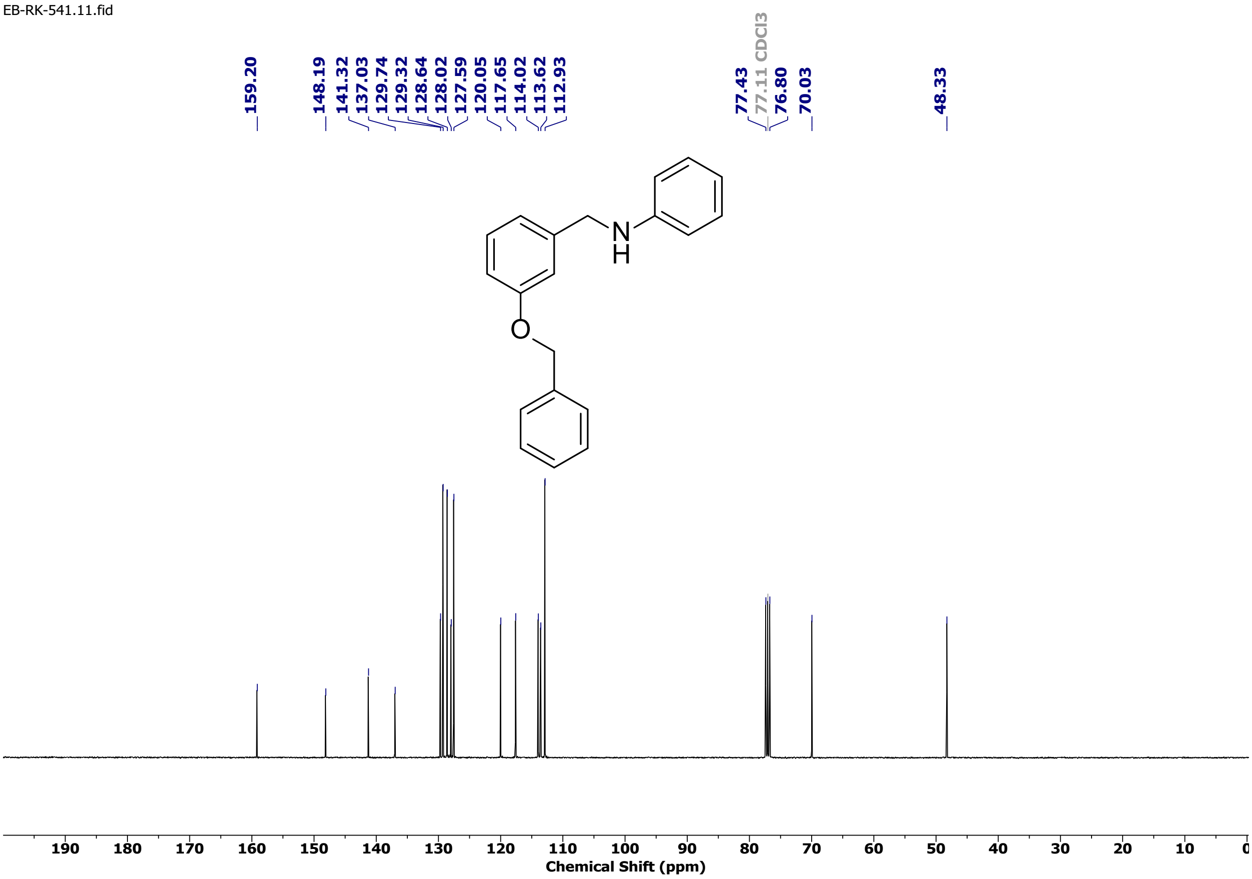
^{1}H NMR of **42** (400 MHz, CDCl$_3$)



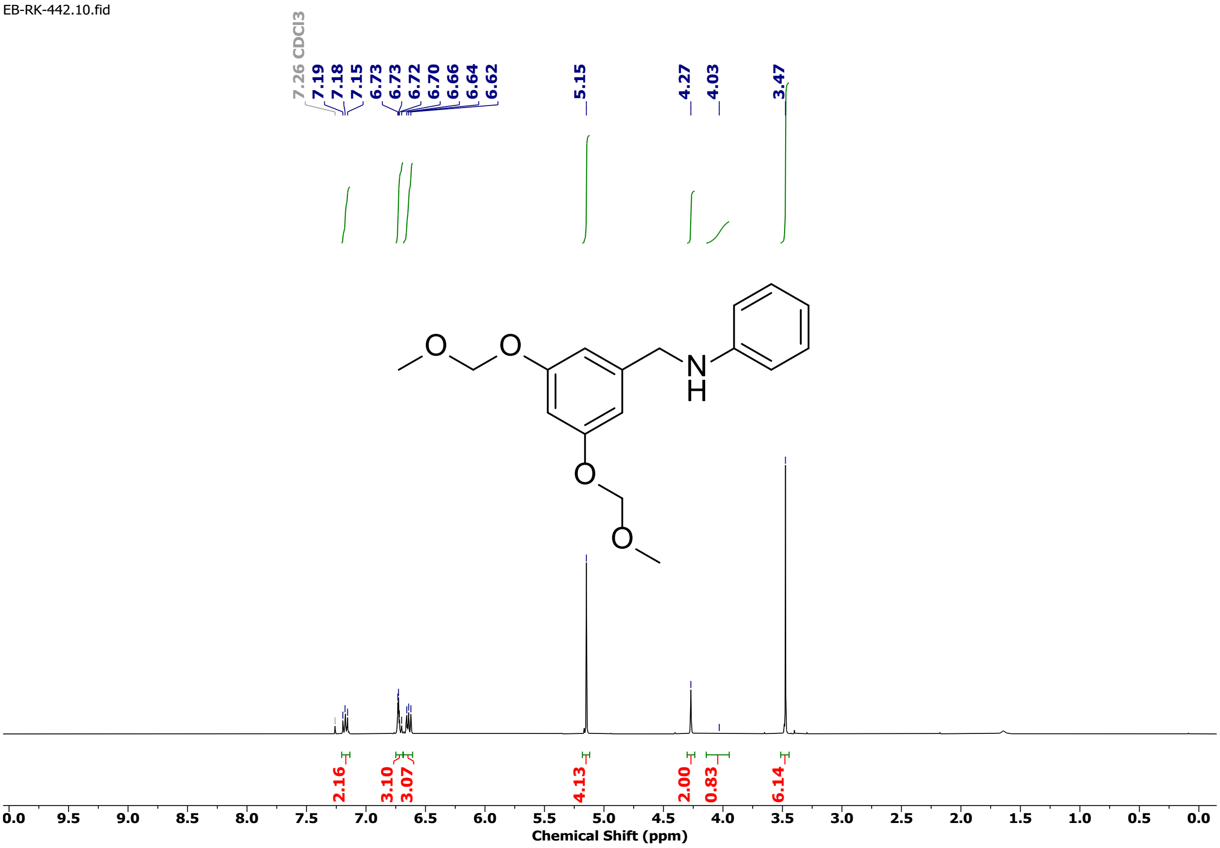
^{13}C NMR of **42** (100 MHz, CDCl$_3$)



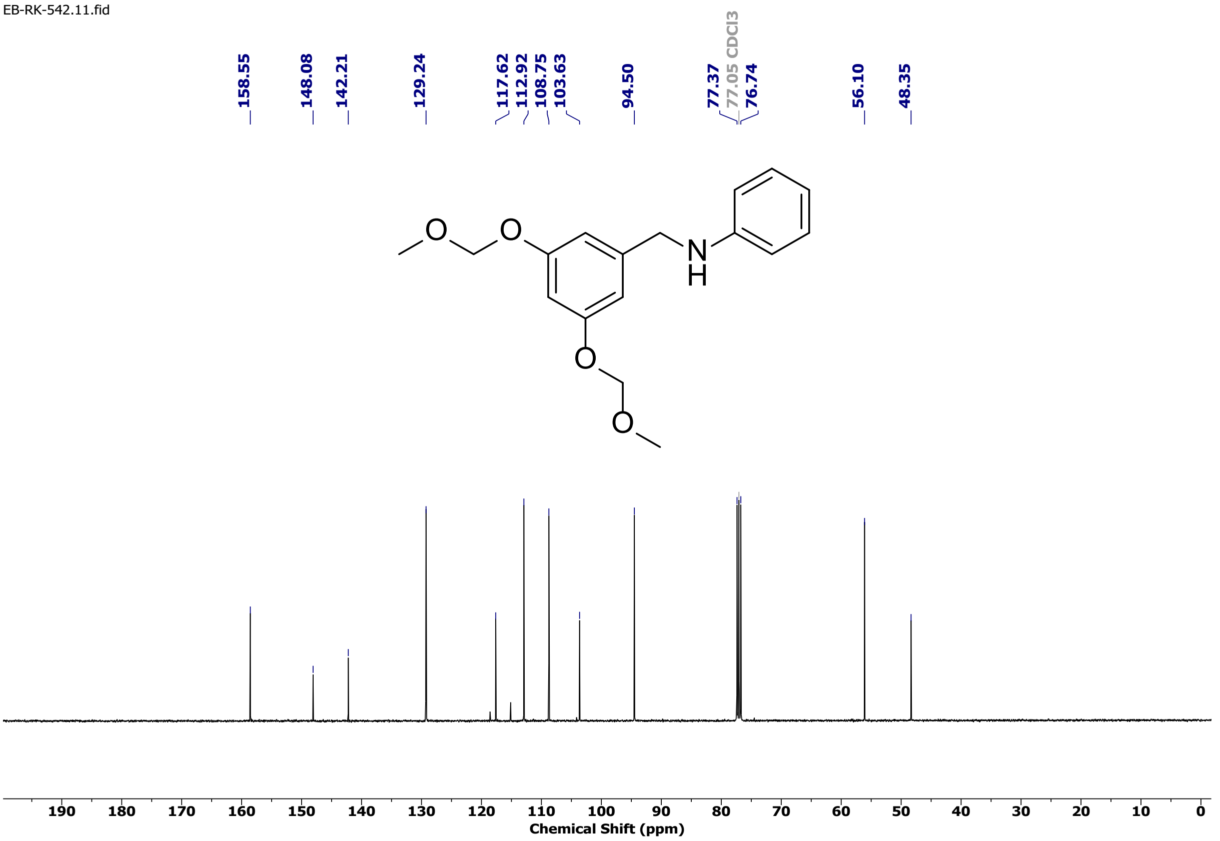
^{1}H NMR of **43** (400 MHz, CDCl$_3$)



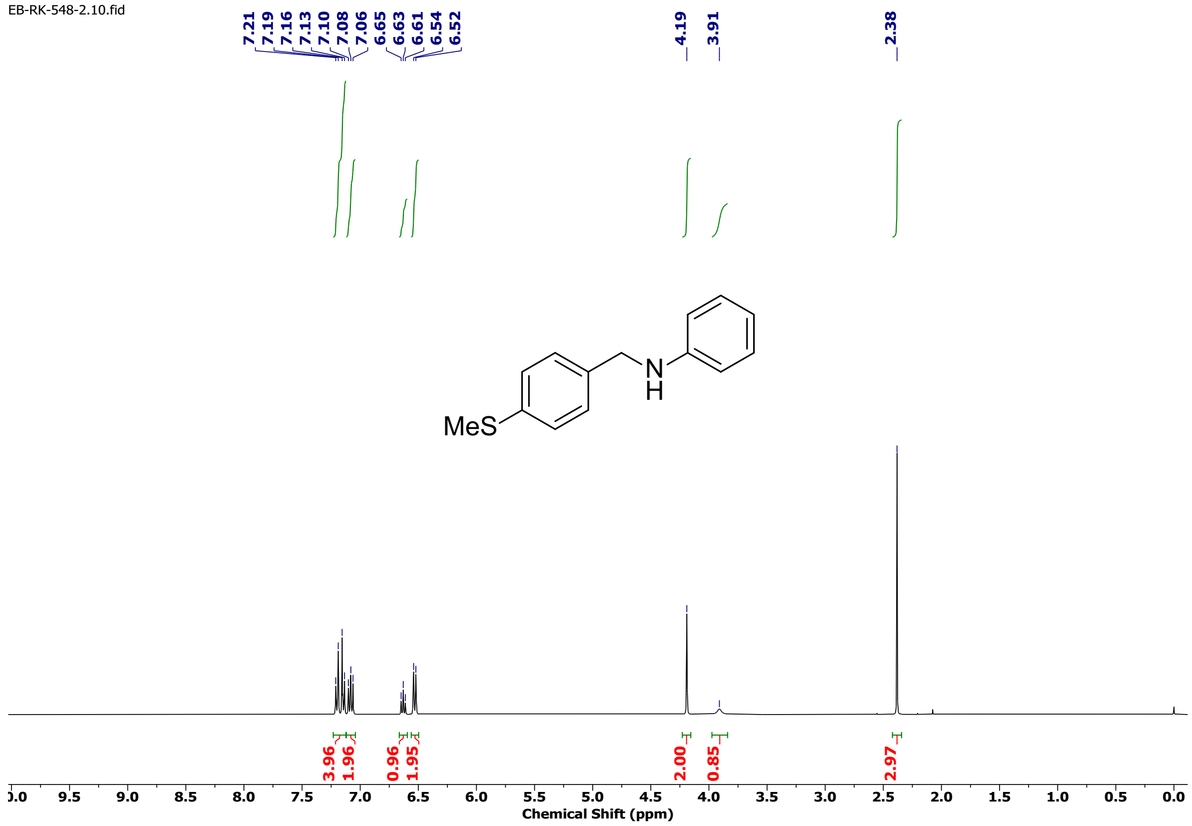
^{13}C NMR of **43** (100 MHz, CDCl$_3$)



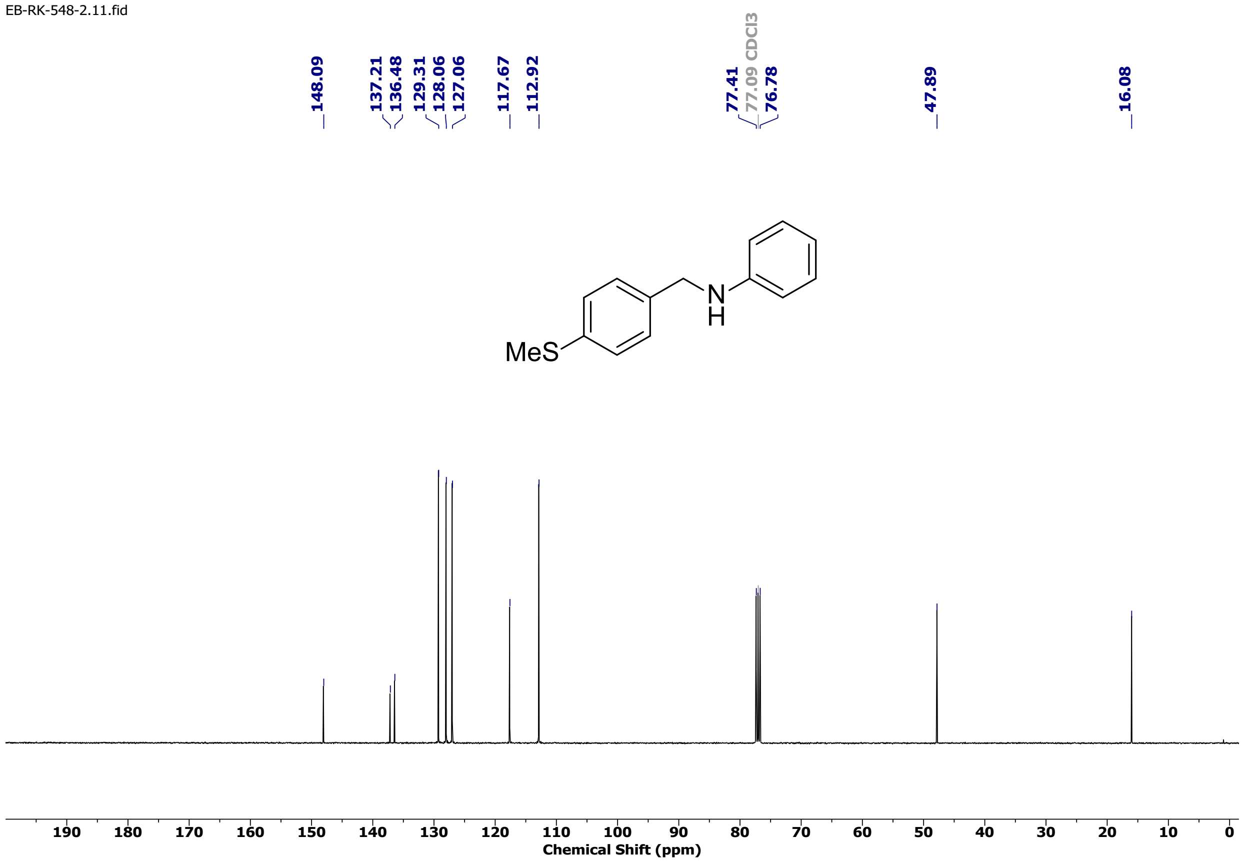
^{1}H NMR of **44** (400 MHz, $CDCl_3$)



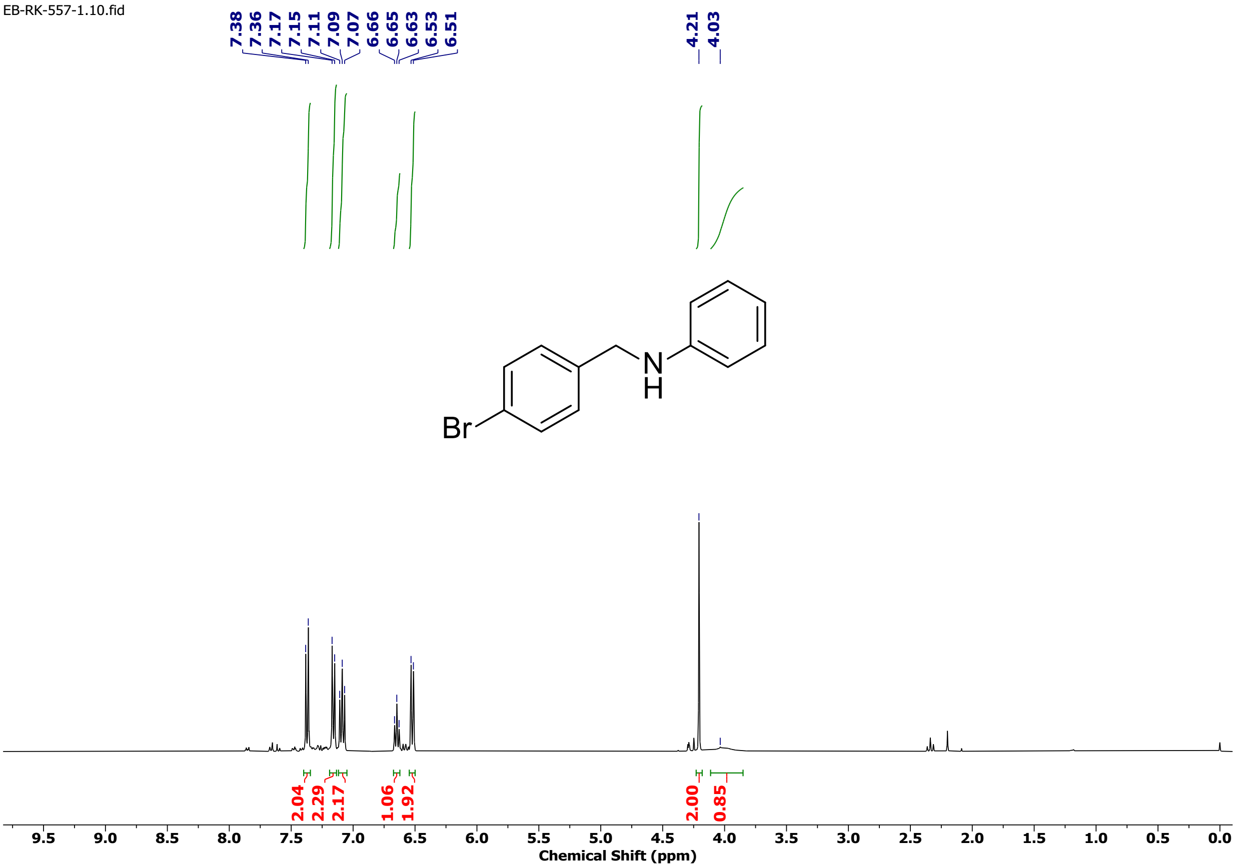
^{13}C NMR of **44** (100 MHz, $CDCl_3$)



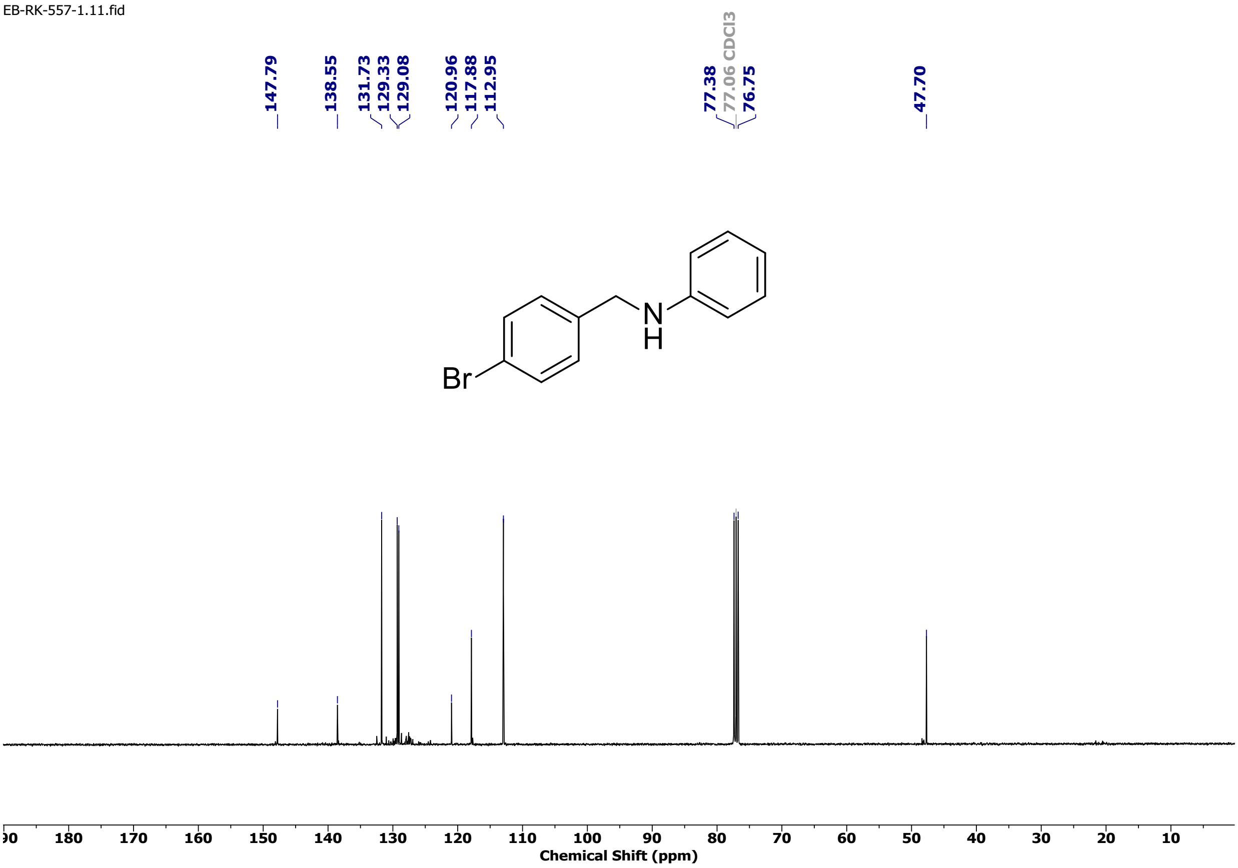
^{1}H NMR of **45** (400 MHz, CDCl$_3$)



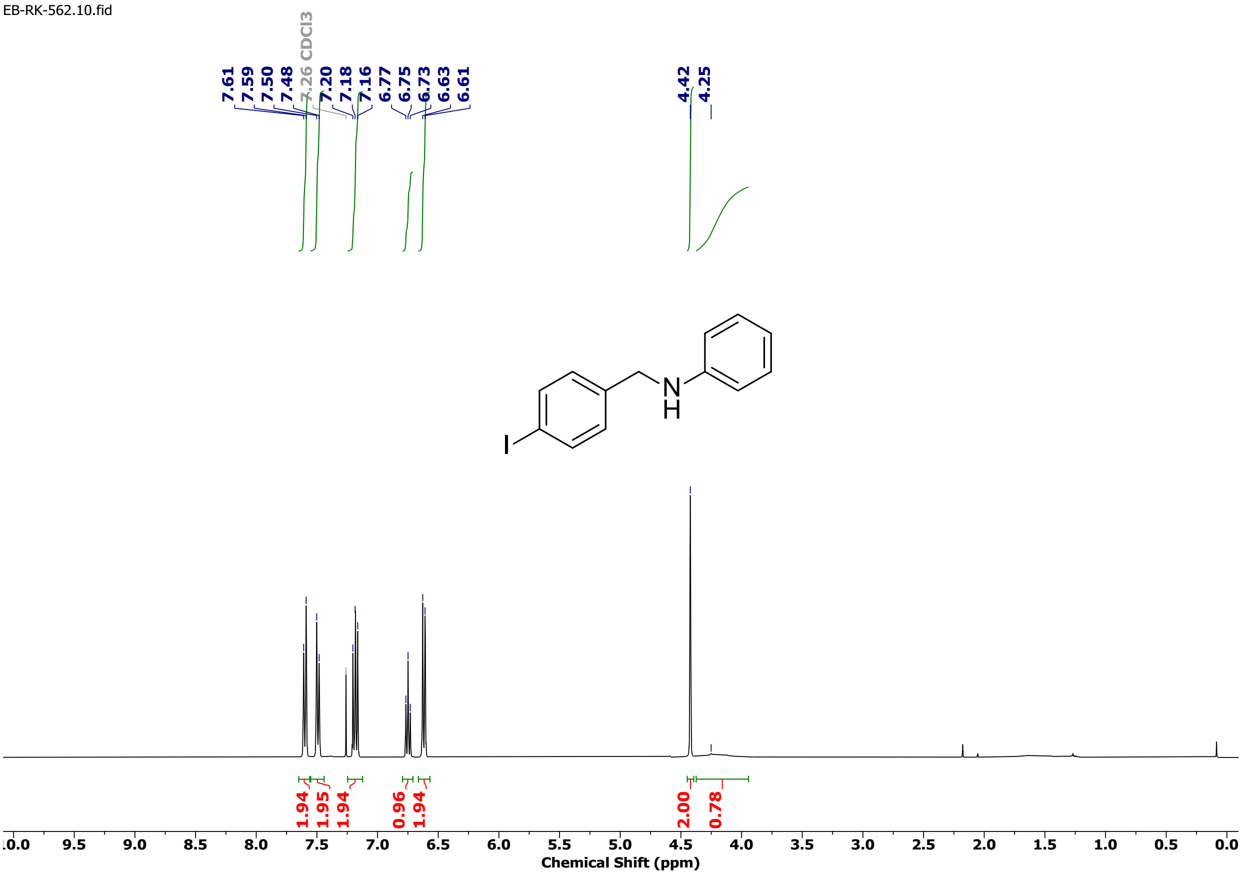
^{13}C NMR of **45** (100 MHz, CDCl$_3$)



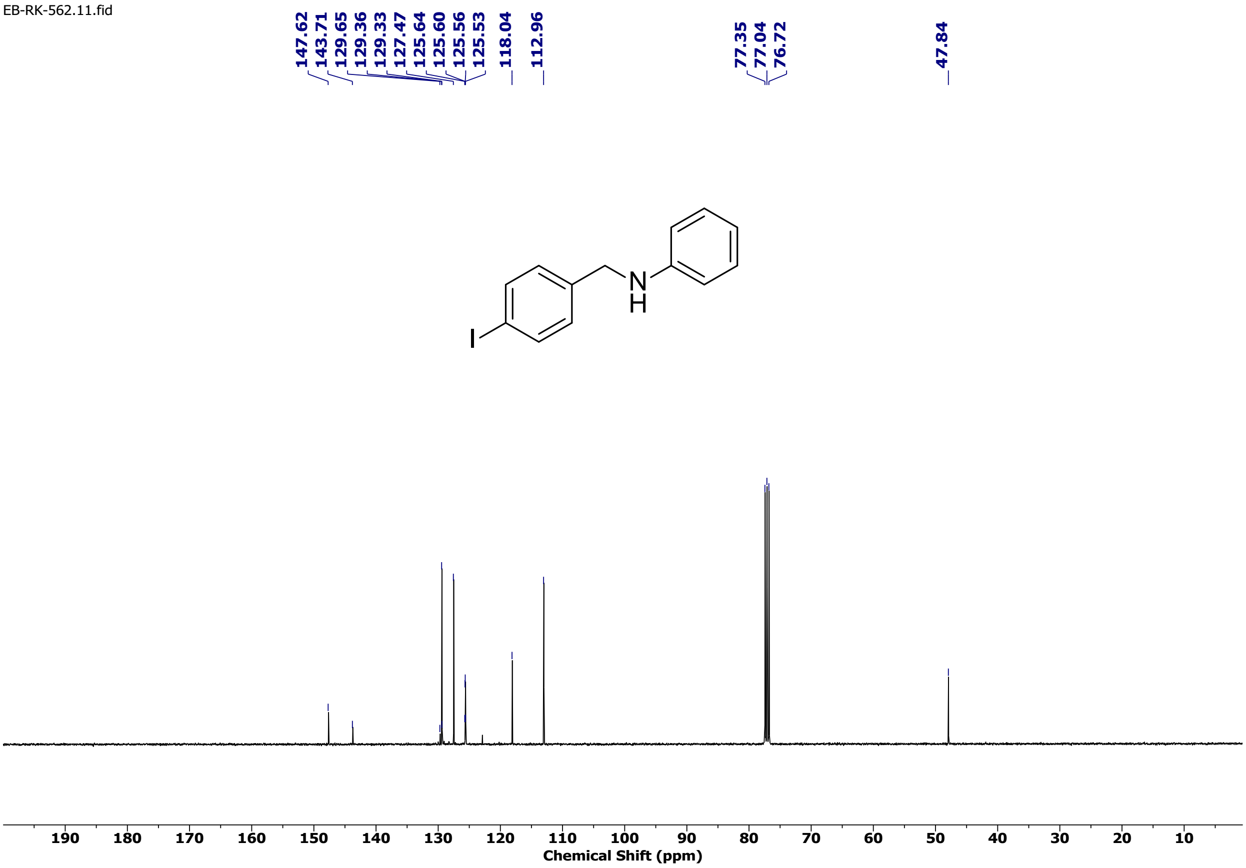
^{1}H NMR of **46** (400 MHz, $CDCl_3$)



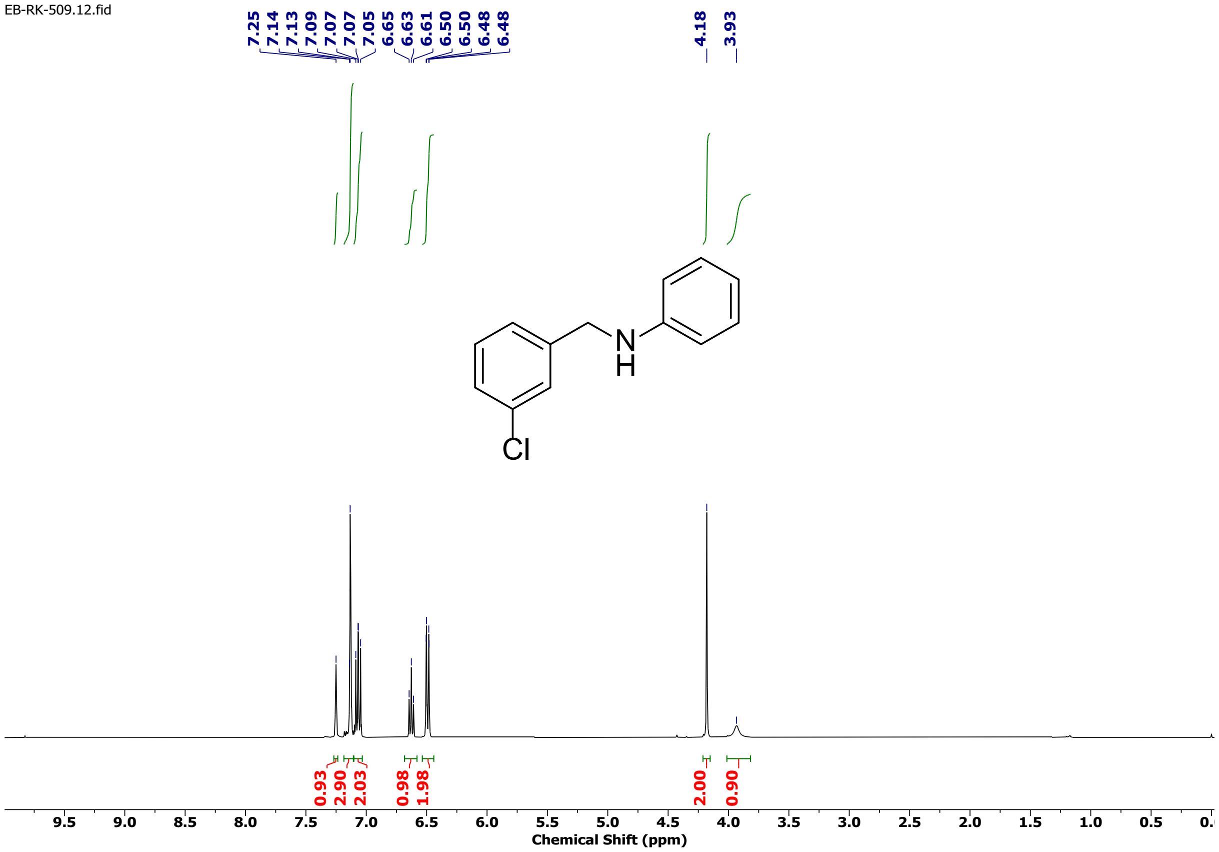
^{13}C NMR of **46** (100 MHz, $CDCl_3$)



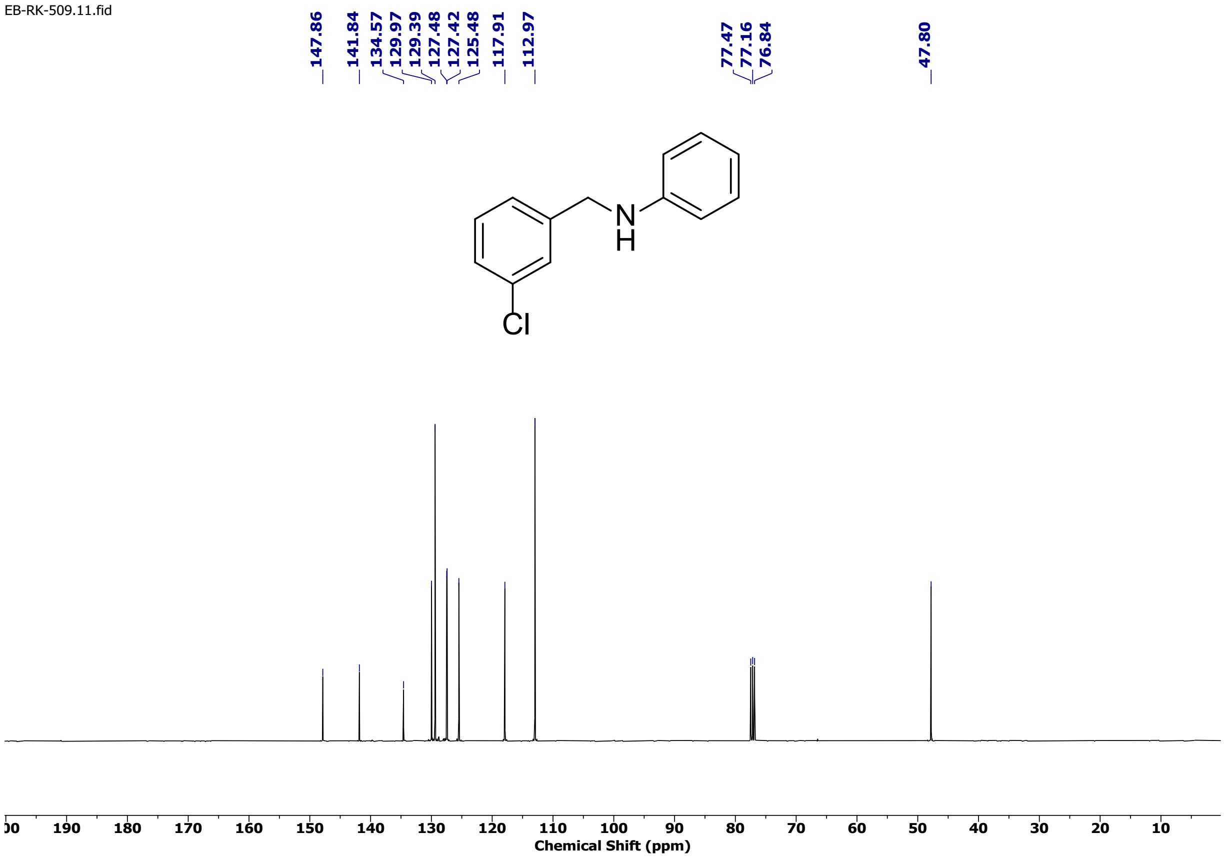
^{1}H NMR of **47** (400 MHz, $CDCl_3$)



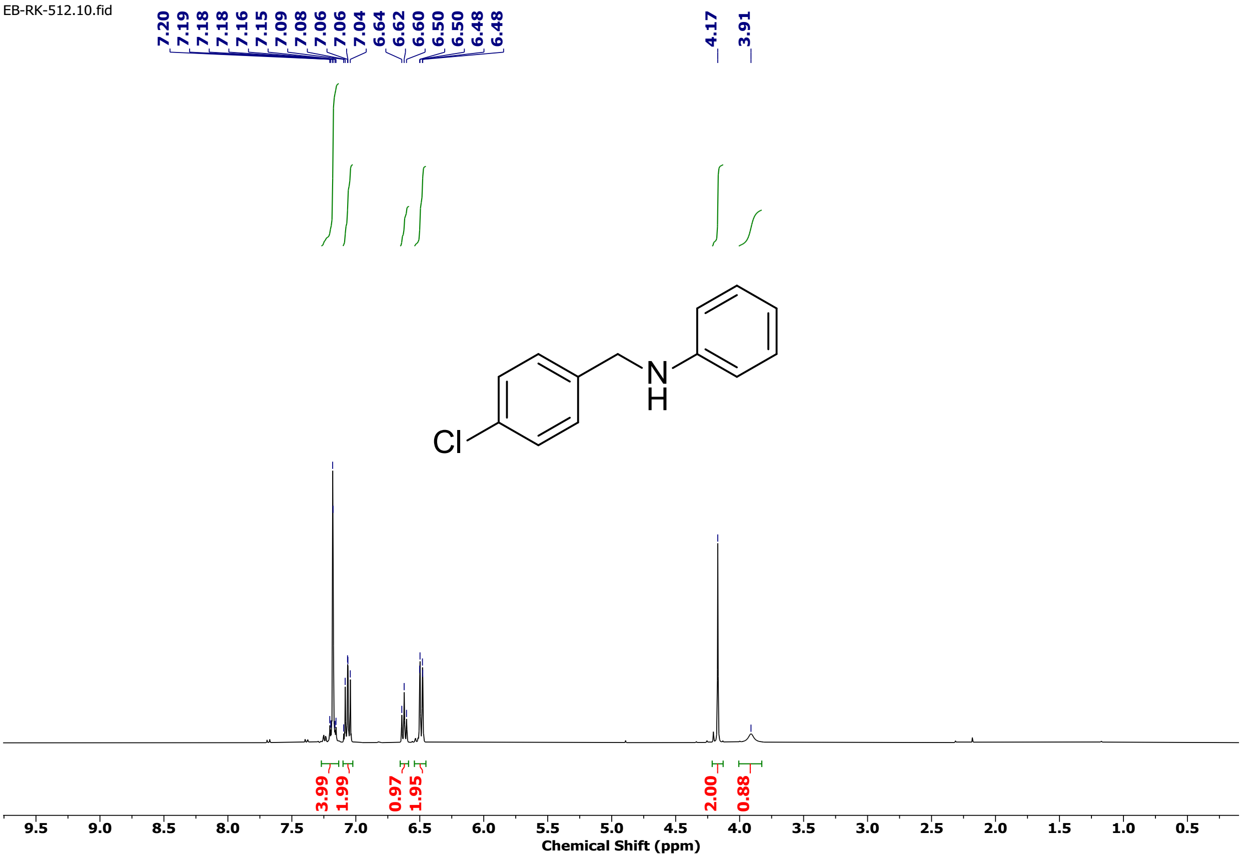
^{13}C NMR of **47** (100 MHz, $CDCl_3$)



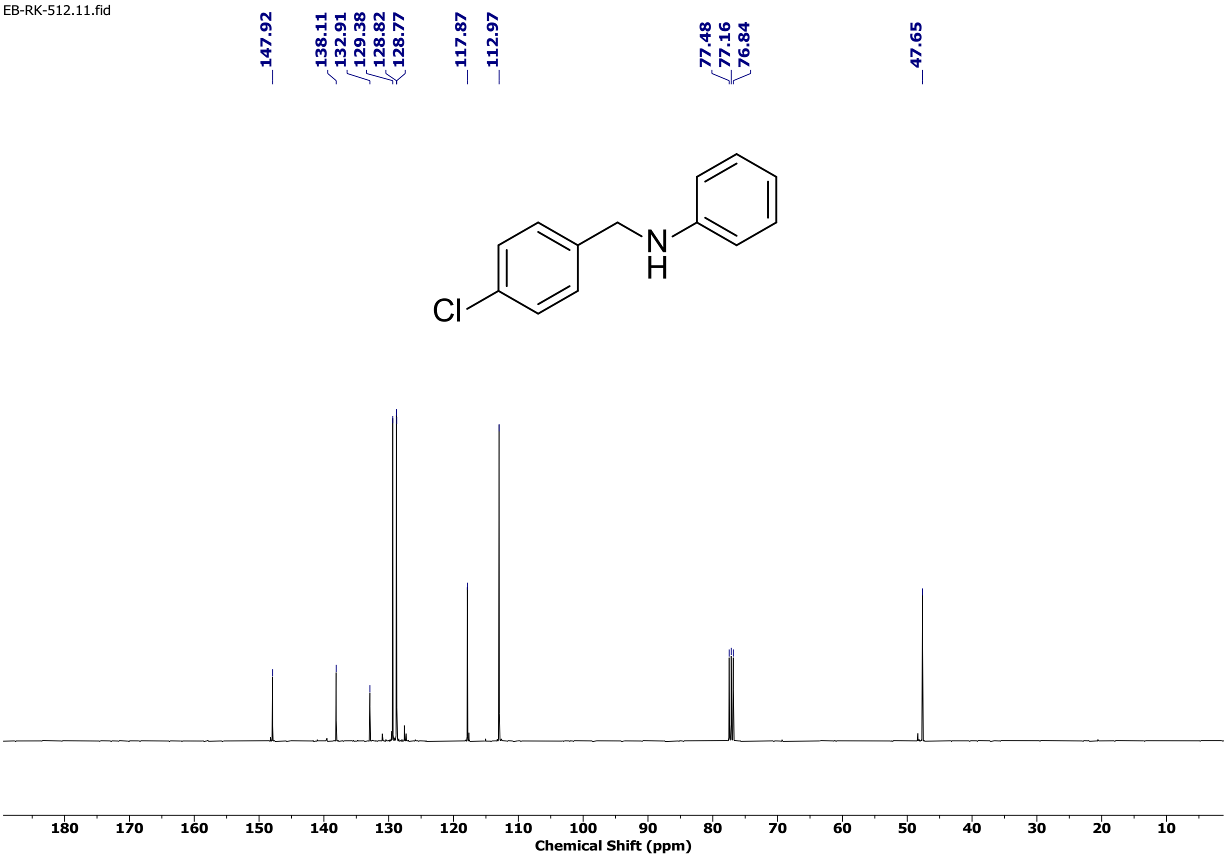
^{1}H NMR of **48** (400 MHz, $CDCl_3$)



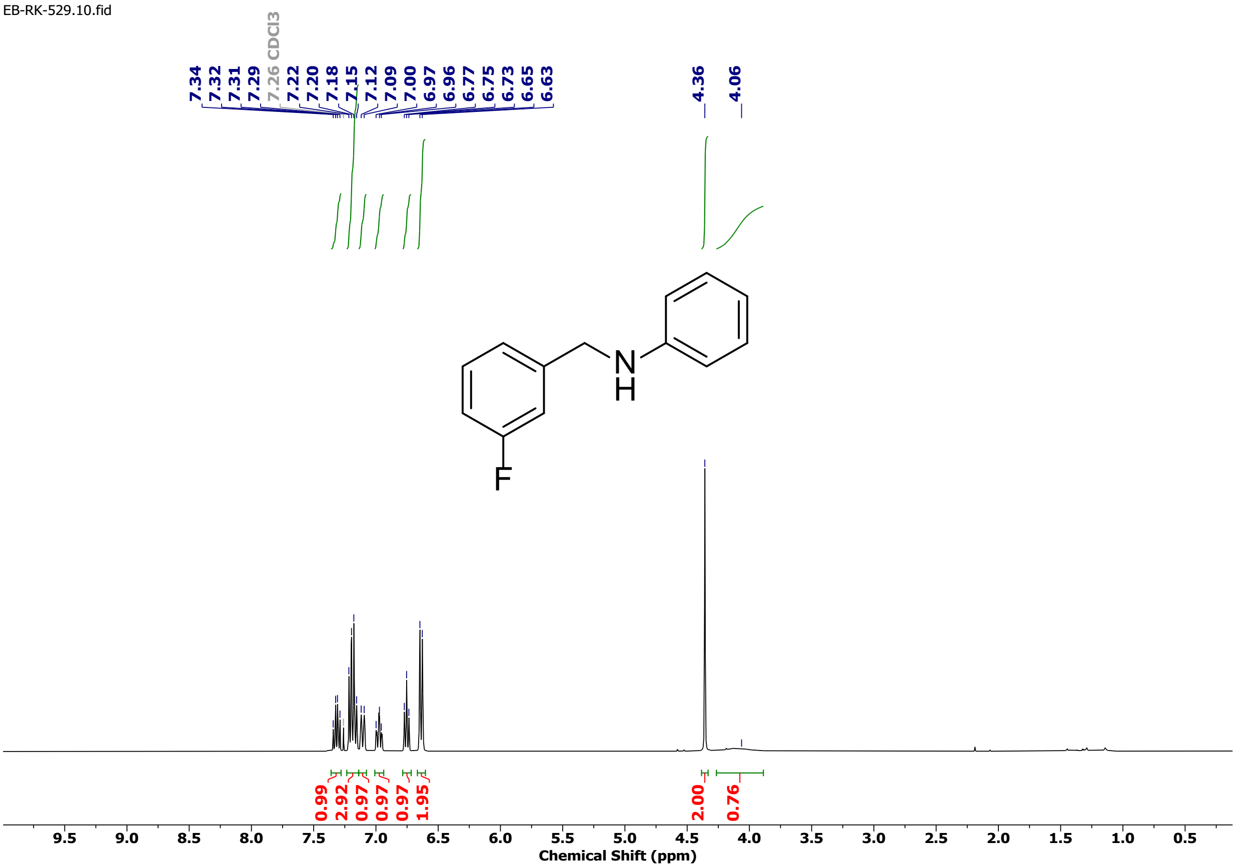
^{13}C NMR of **48** (100 MHz, $CDCl_3$)



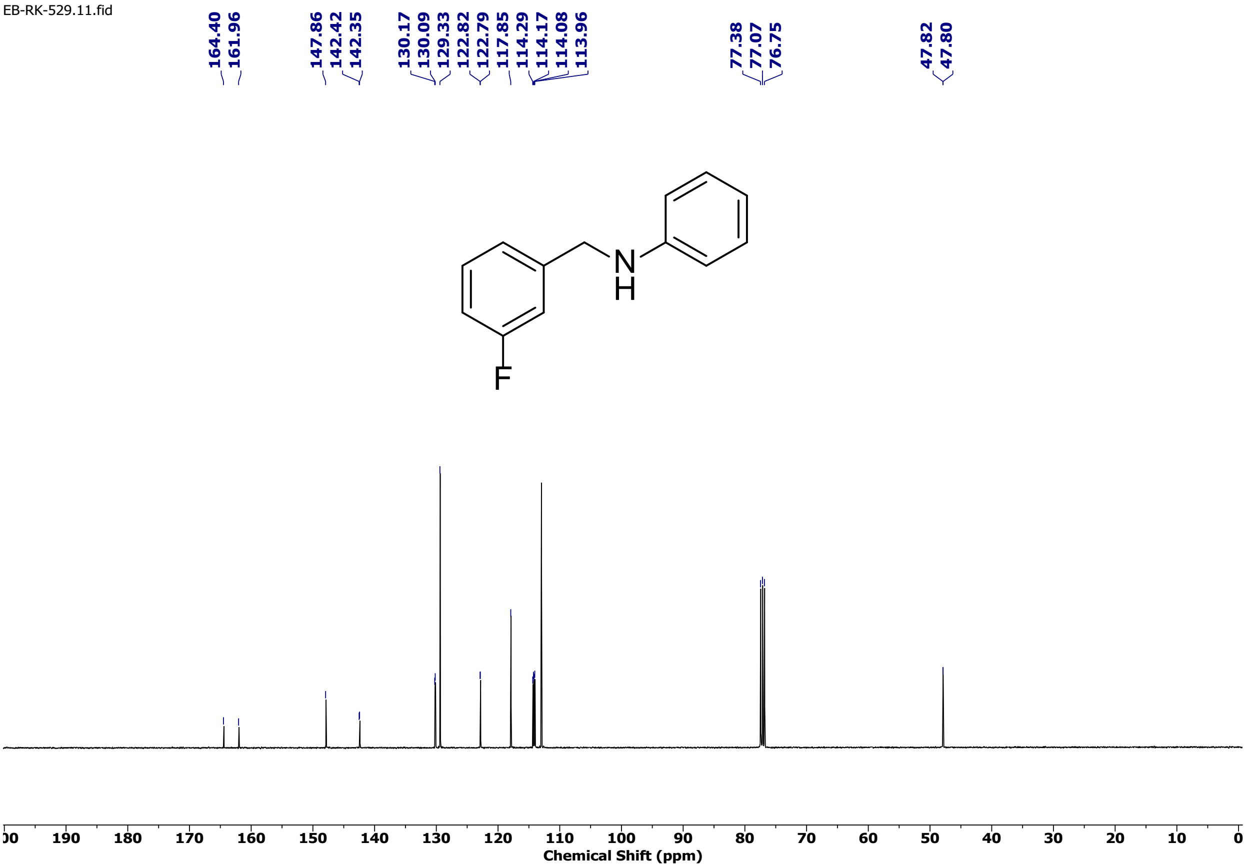
^{1}H NMR of **49** (400 MHz, CDCl$_3$)



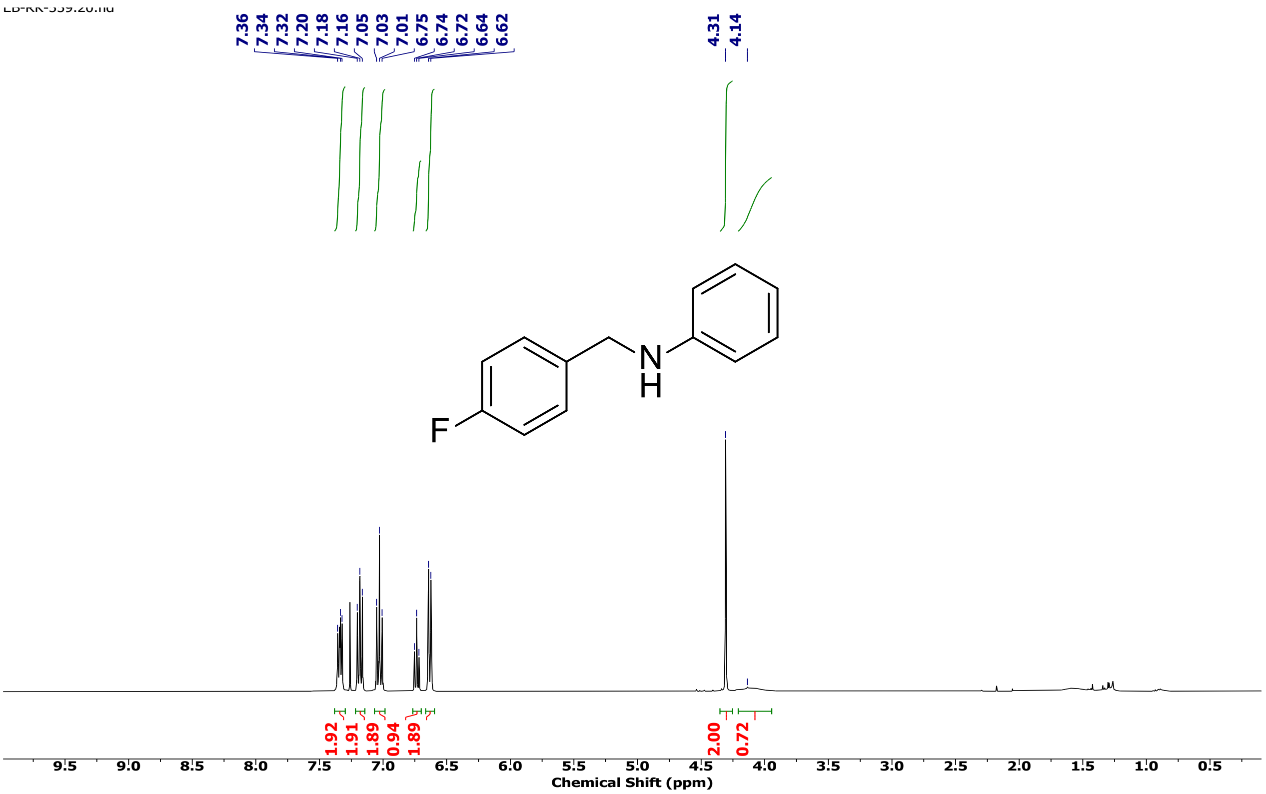
^{13}C NMR of **49** (100 MHz, CDCl$_3$)



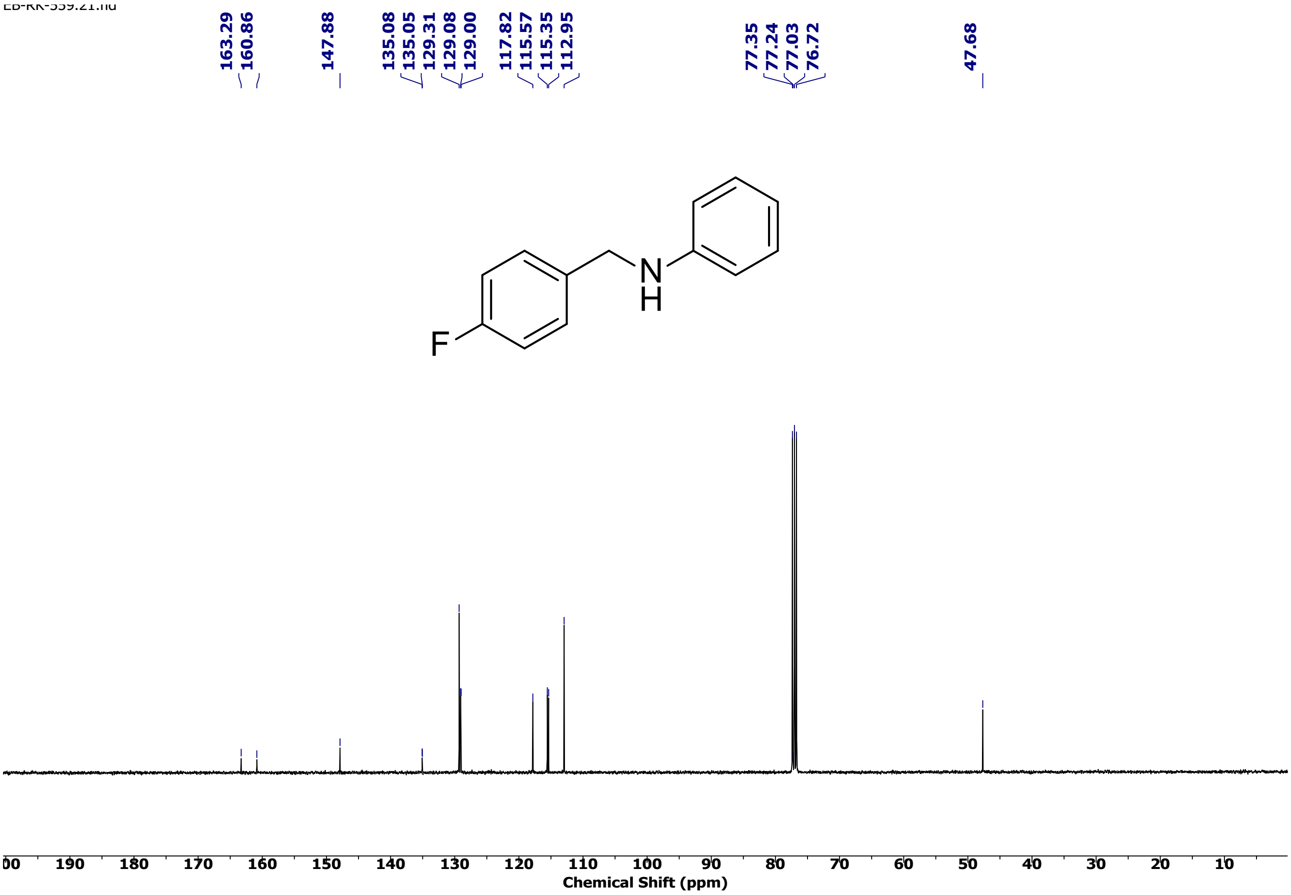
^{1}H NMR of **50** (400 MHz, CDCl$_3$)



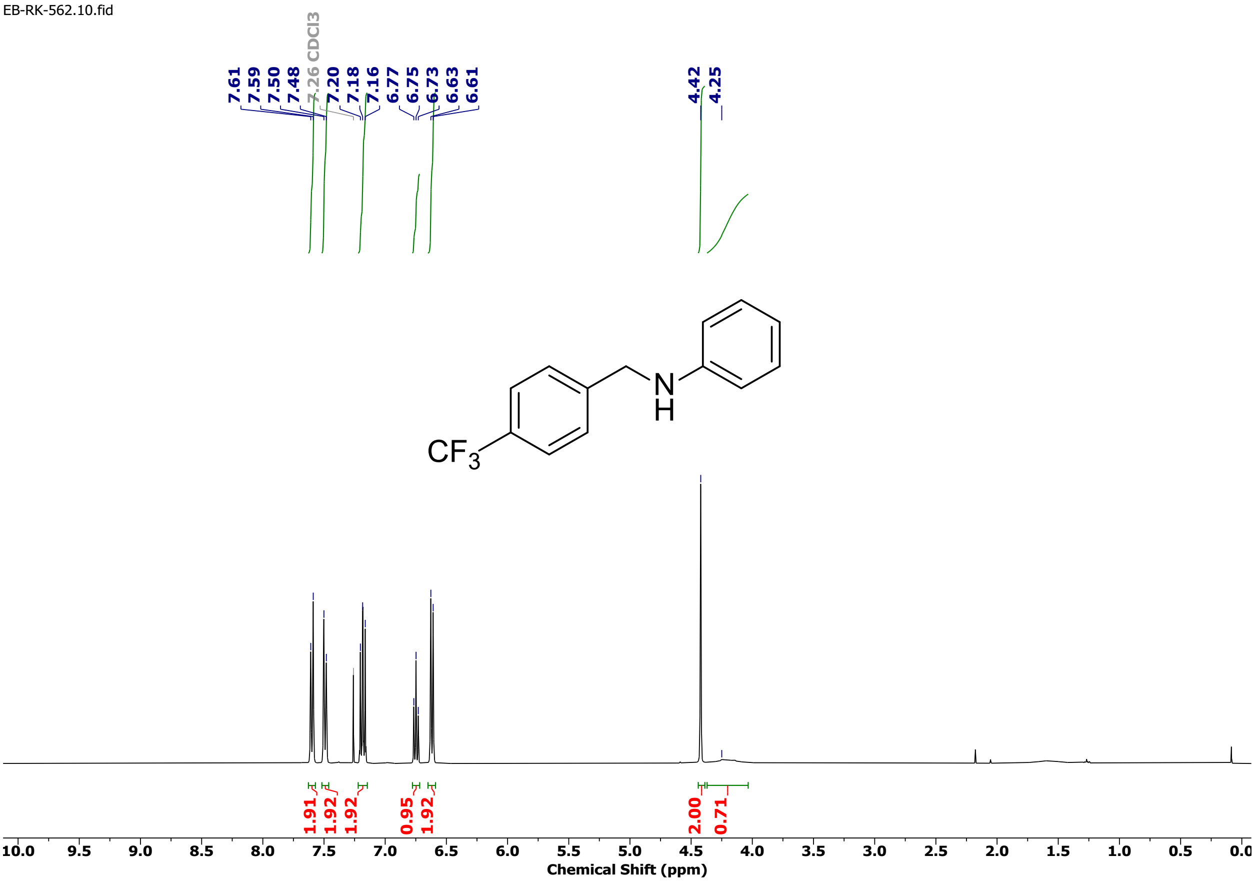
^{13}C NMR of **50** (100 MHz, CDCl$_3$)



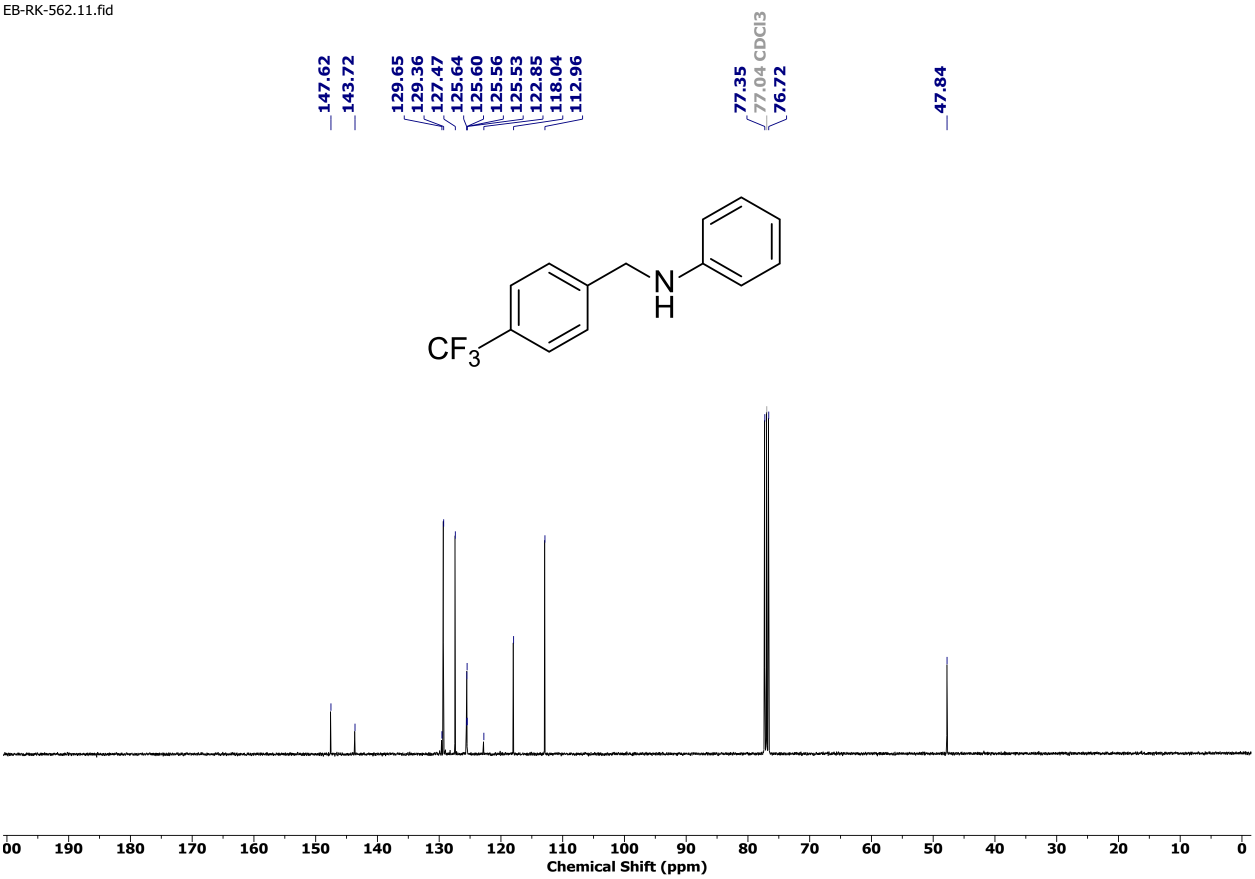
^{1}H NMR of **51** (400 MHz, $CDCl_3$)



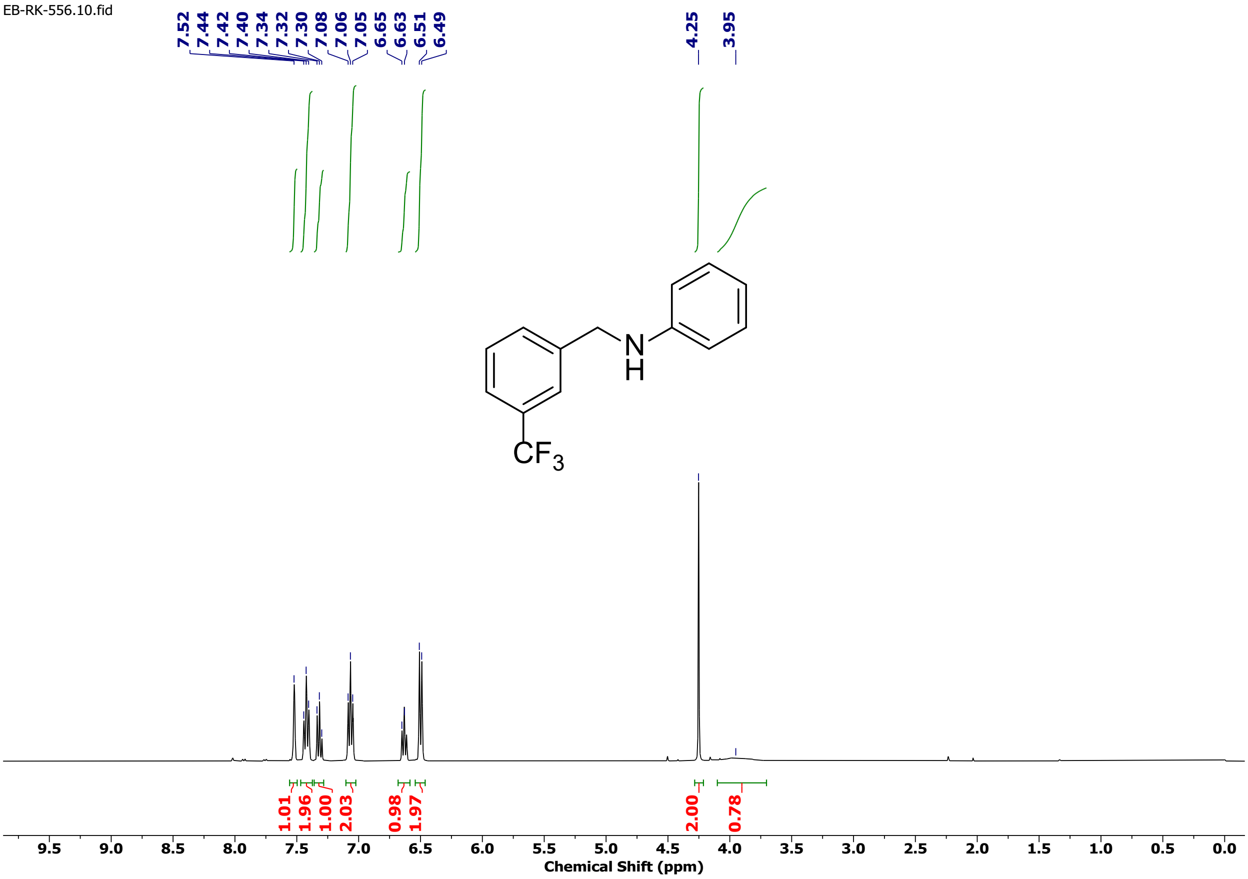
^{13}C NMR of **51** (100 MHz, $CDCl_3$)



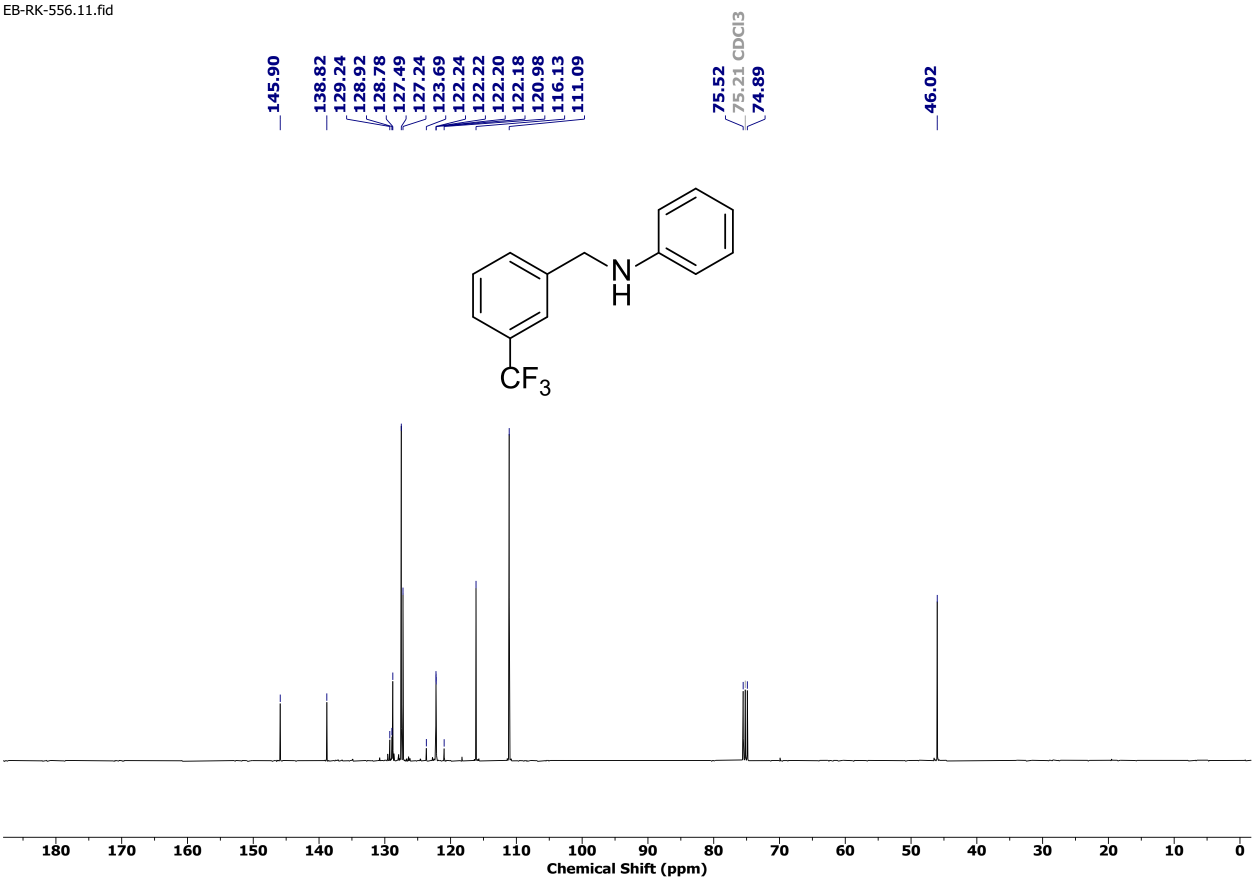
^{1}H NMR of **52** (400 MHz, CDCl$_3$)



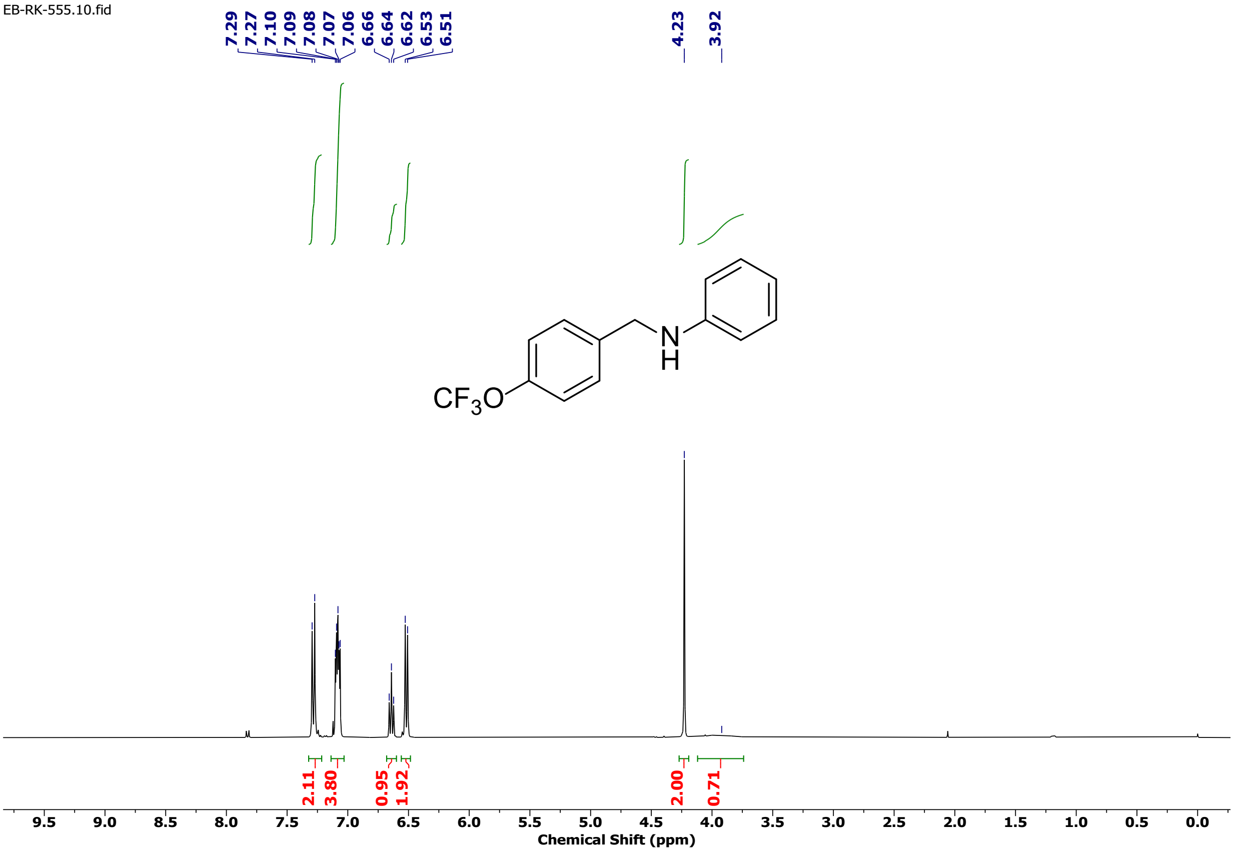
^{13}C NMR of **52** (100 MHz, CDCl$_3$)



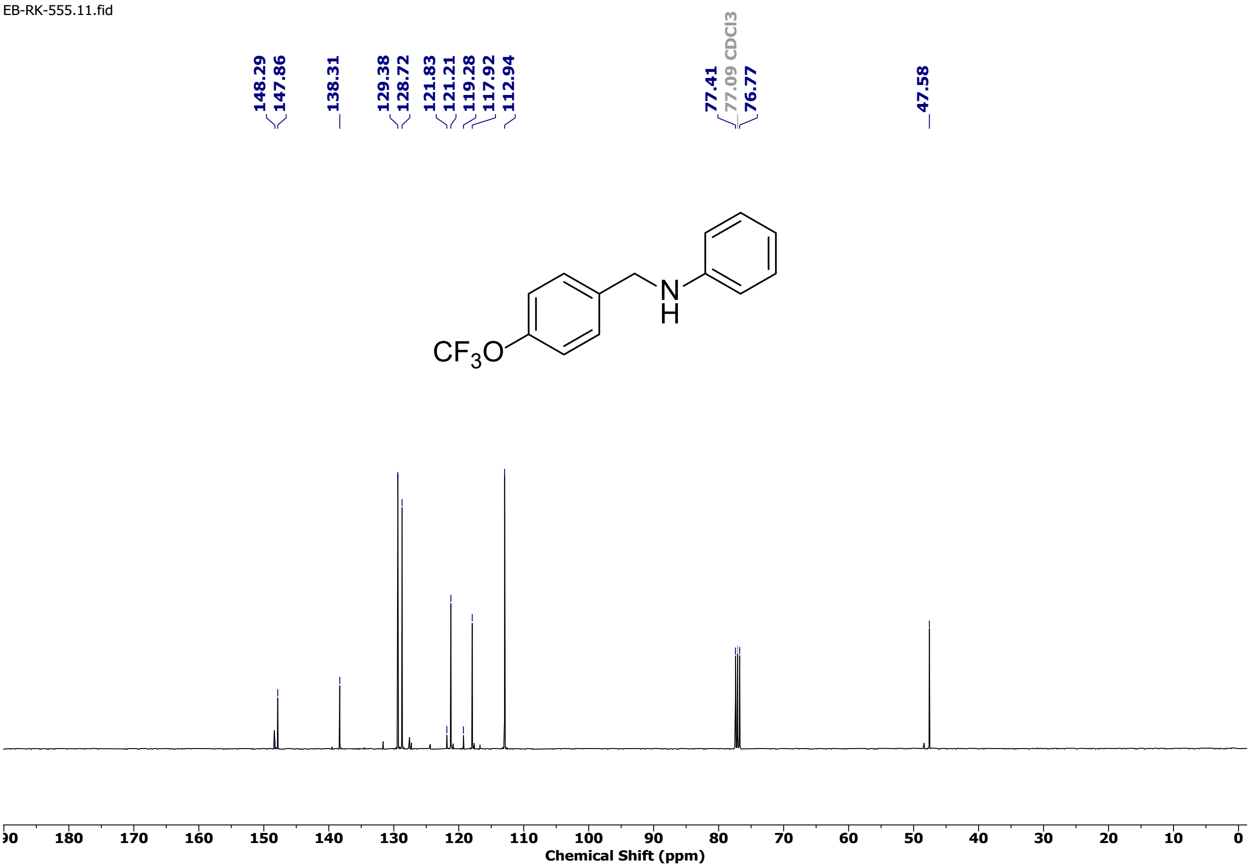
^{1}H NMR of **53** (400 MHz, CDCl$_3$)



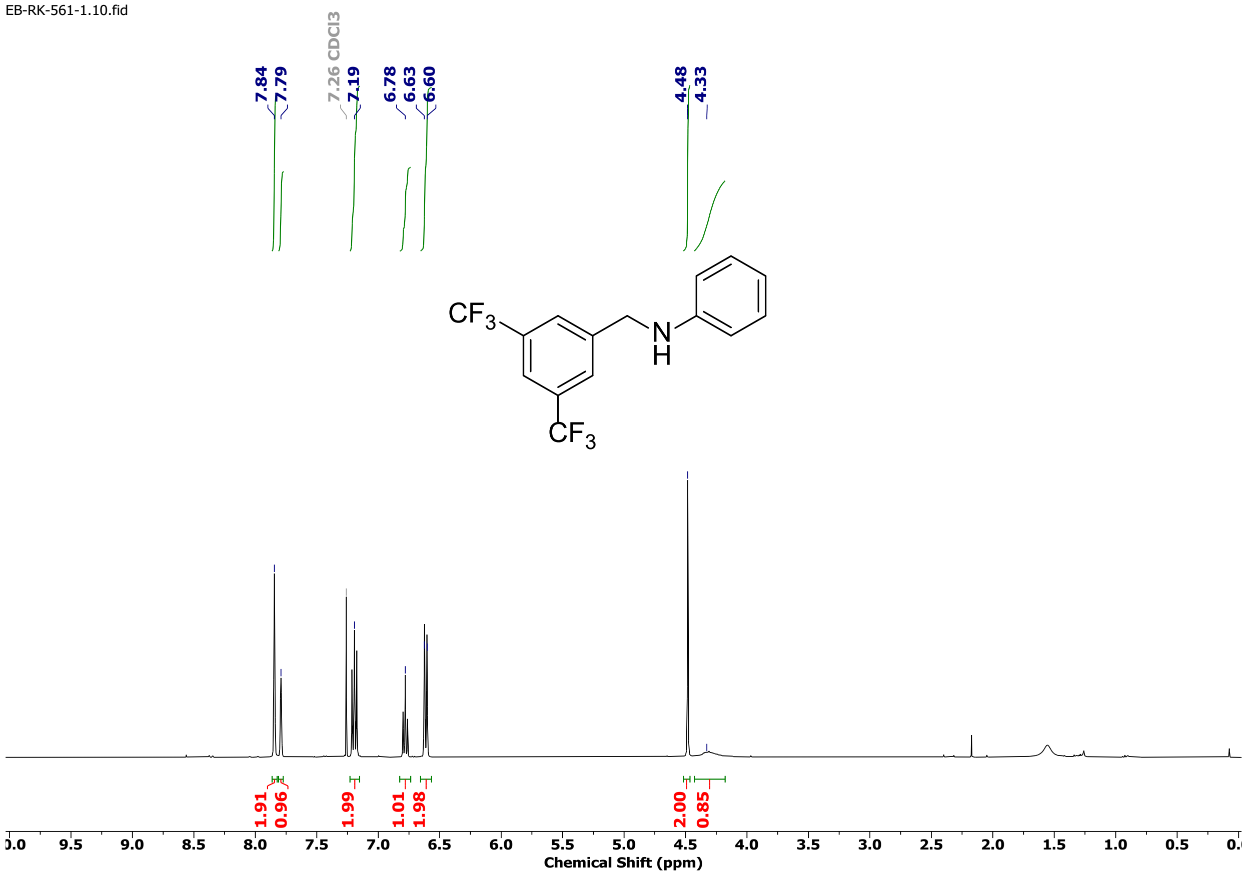
^{13}C NMR of **53** (100 MHz, CDCl$_3$)



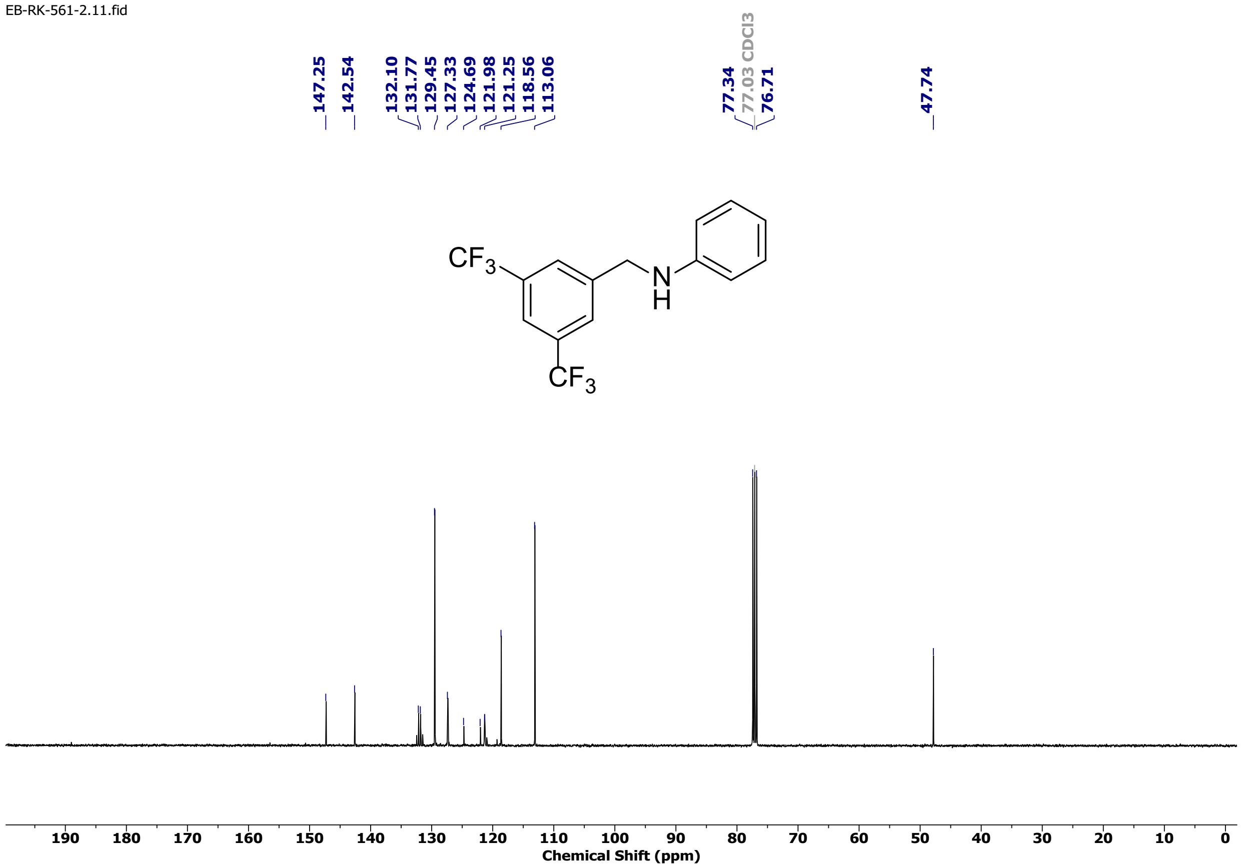
^{1}H NMR of **54** (400 MHz, CDCl$_3$)



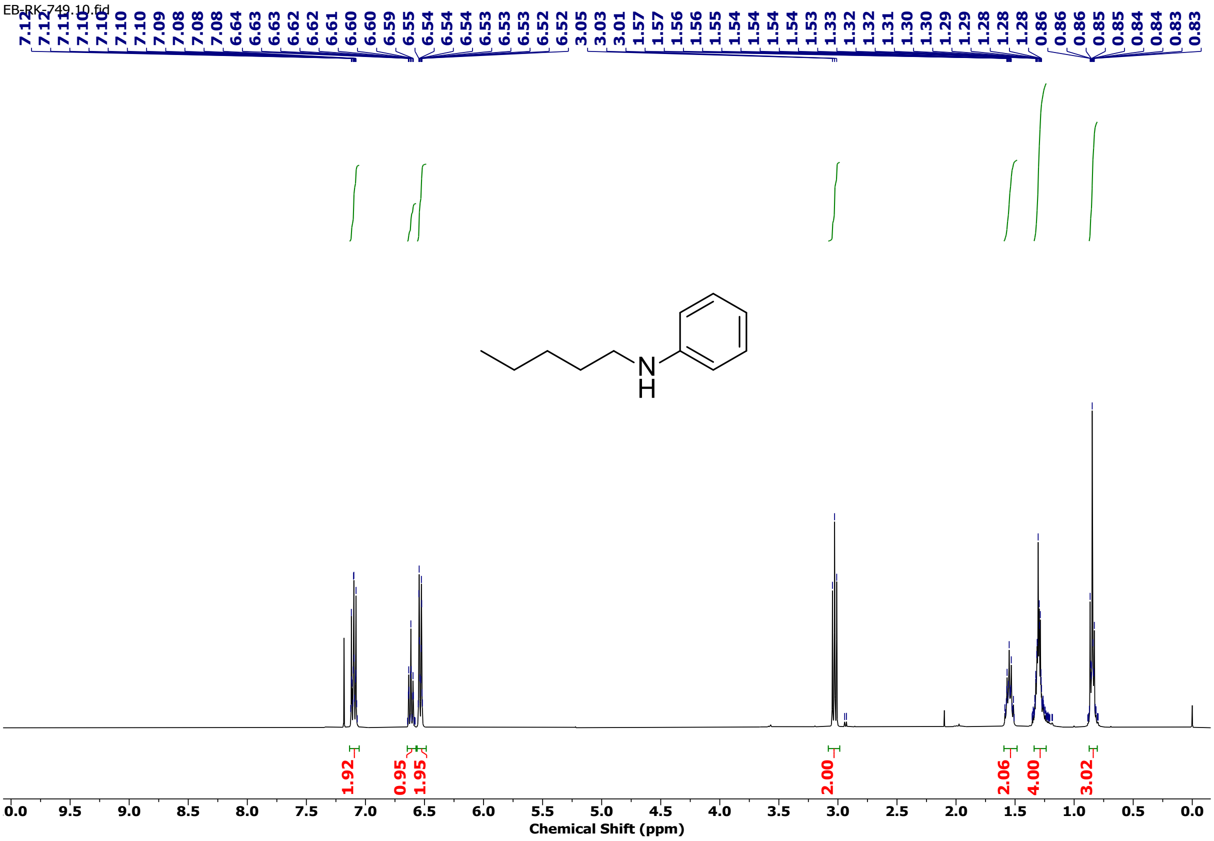
^{13}C NMR of **54** (100 MHz, CDCl$_3$)



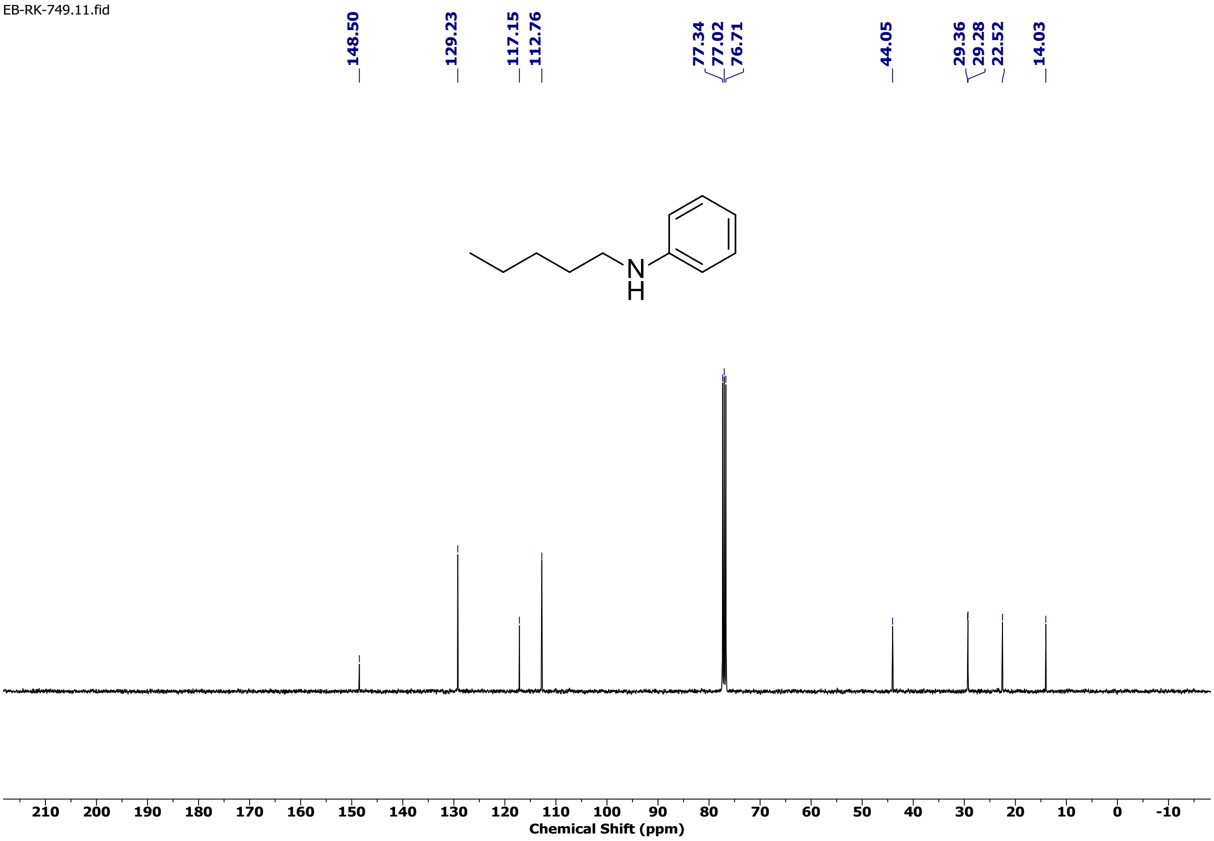
^{1}H NMR of **55** (400 MHz, CDCl$_3$)



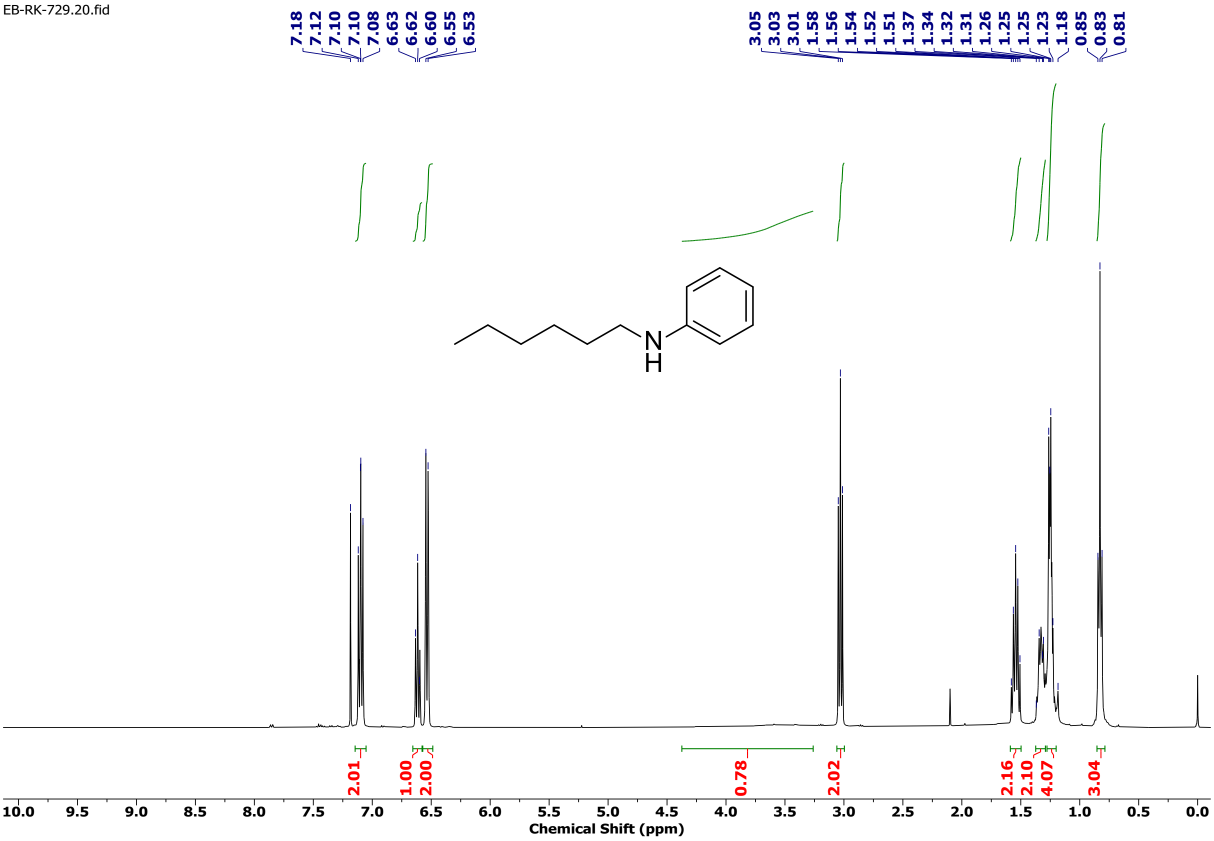
^{13}C NMR of **55** (100 MHz, CDCl$_3$)



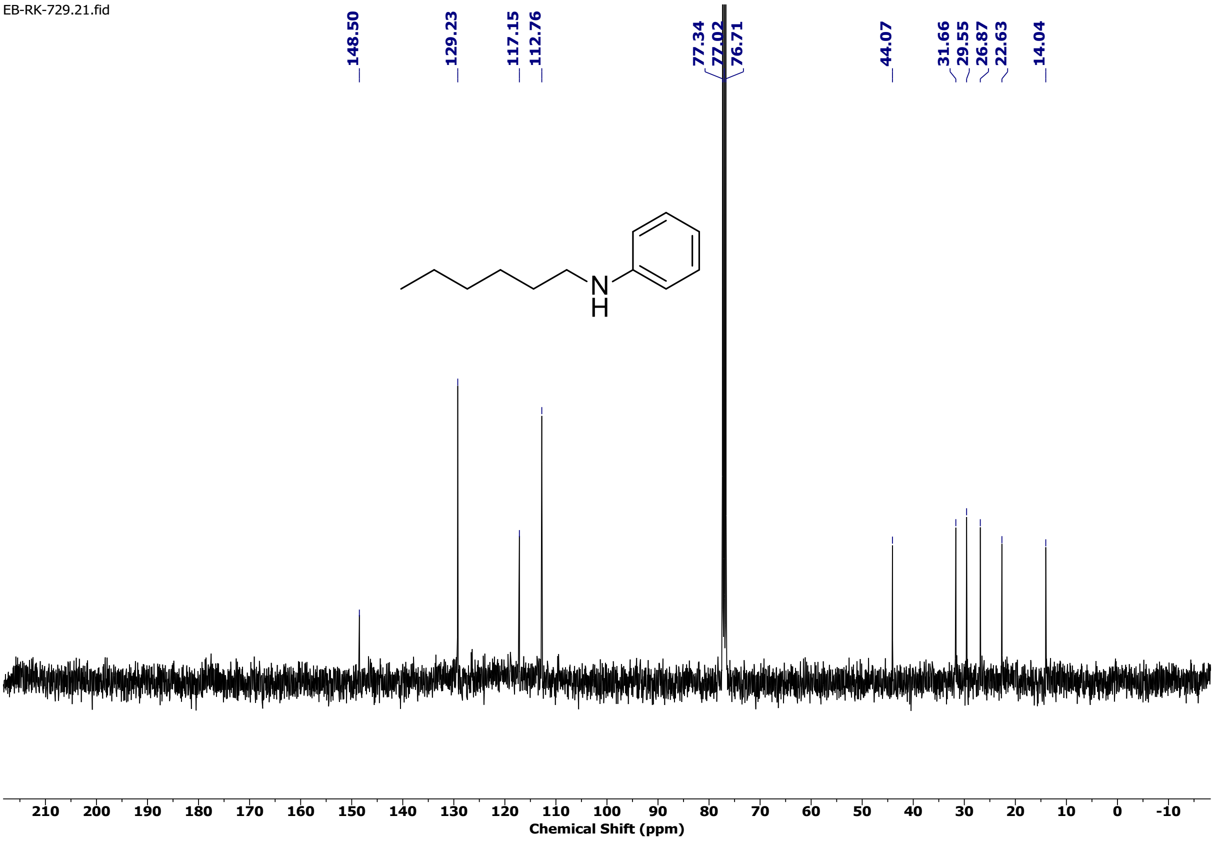
^{1}H NMR of **56** (400 MHz, CDCl$_3$)



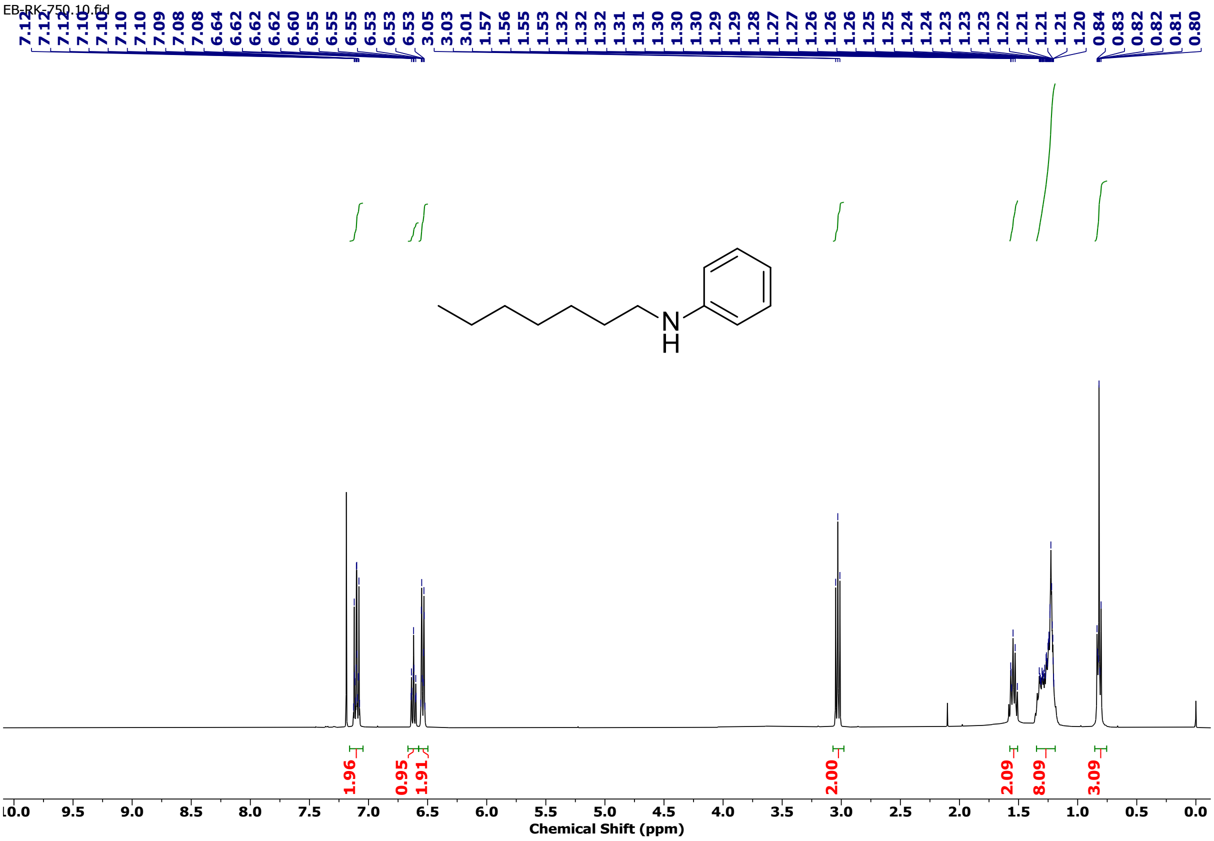
^{13}C NMR of **56** (100 MHz, CDCl$_3$)



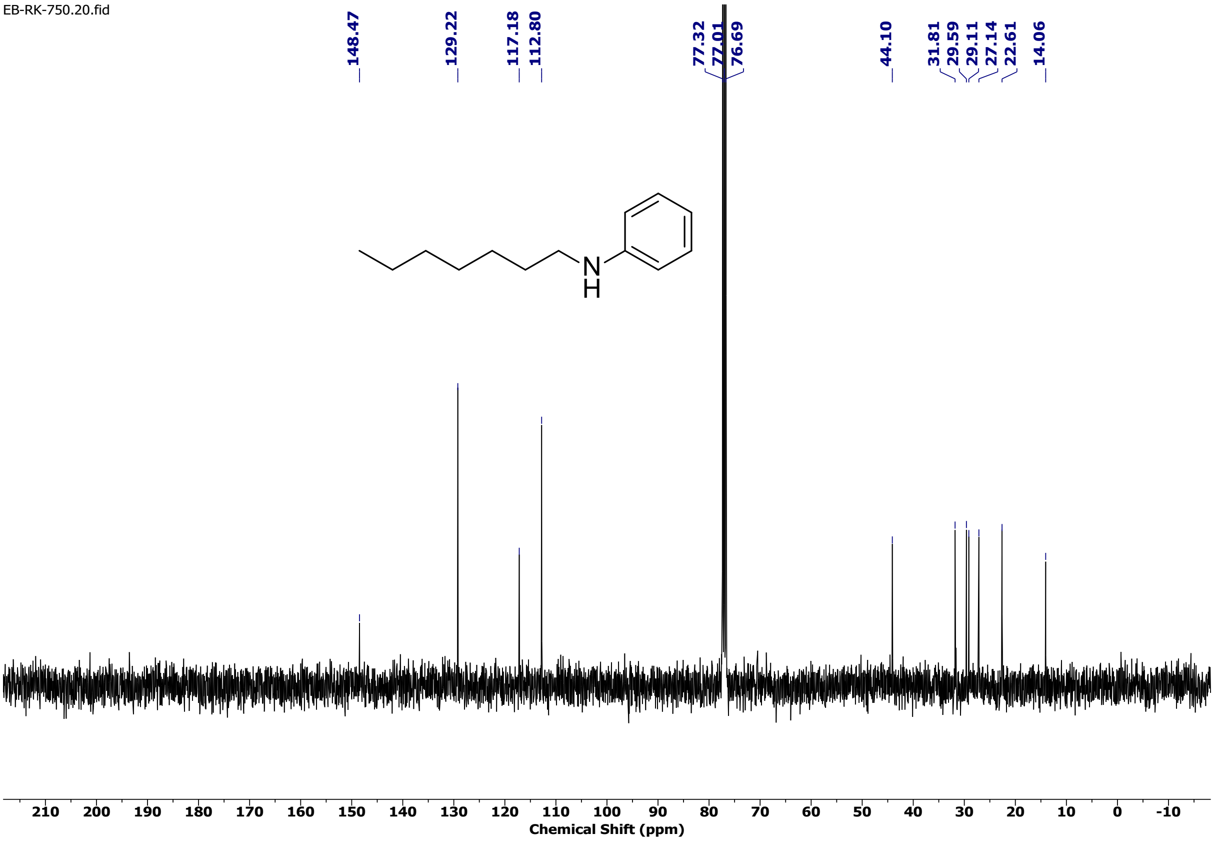
^{1}H NMR of **57** (400 MHz, $CDCl_3$)



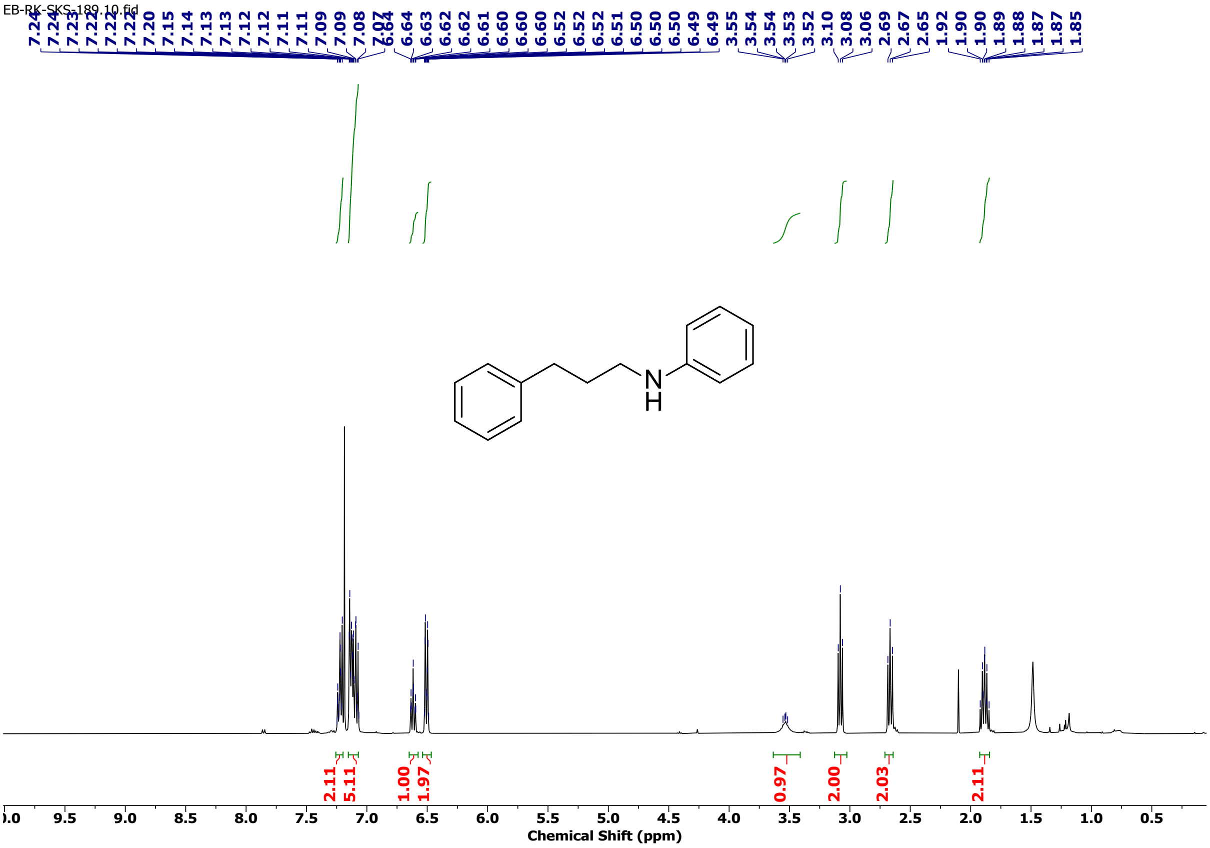
^{13}C NMR of **57** (100 MHz, CDCl



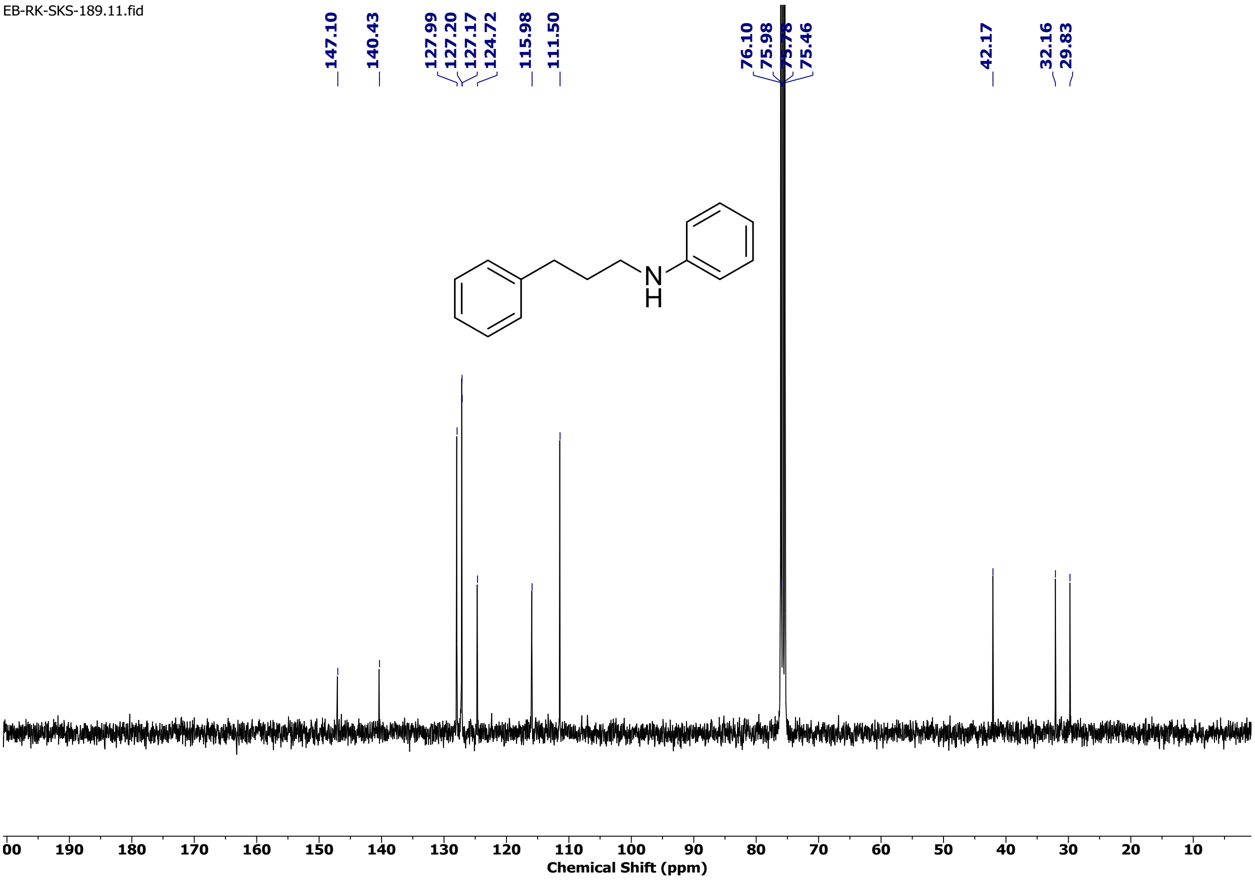
^{1}H NMR of **58** (400 MHz, CDCl$_3$)



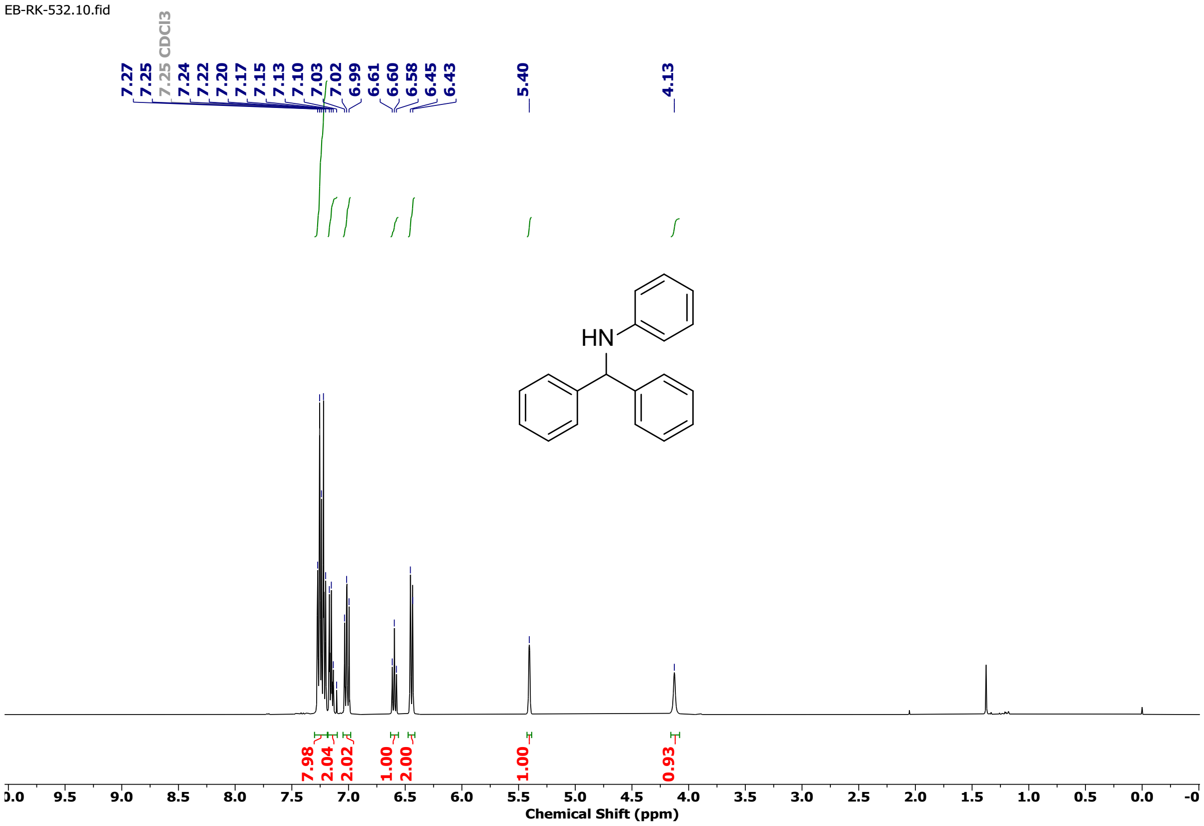
^{13}C NMR of **58** (100 MHz, CDCl$_3$)



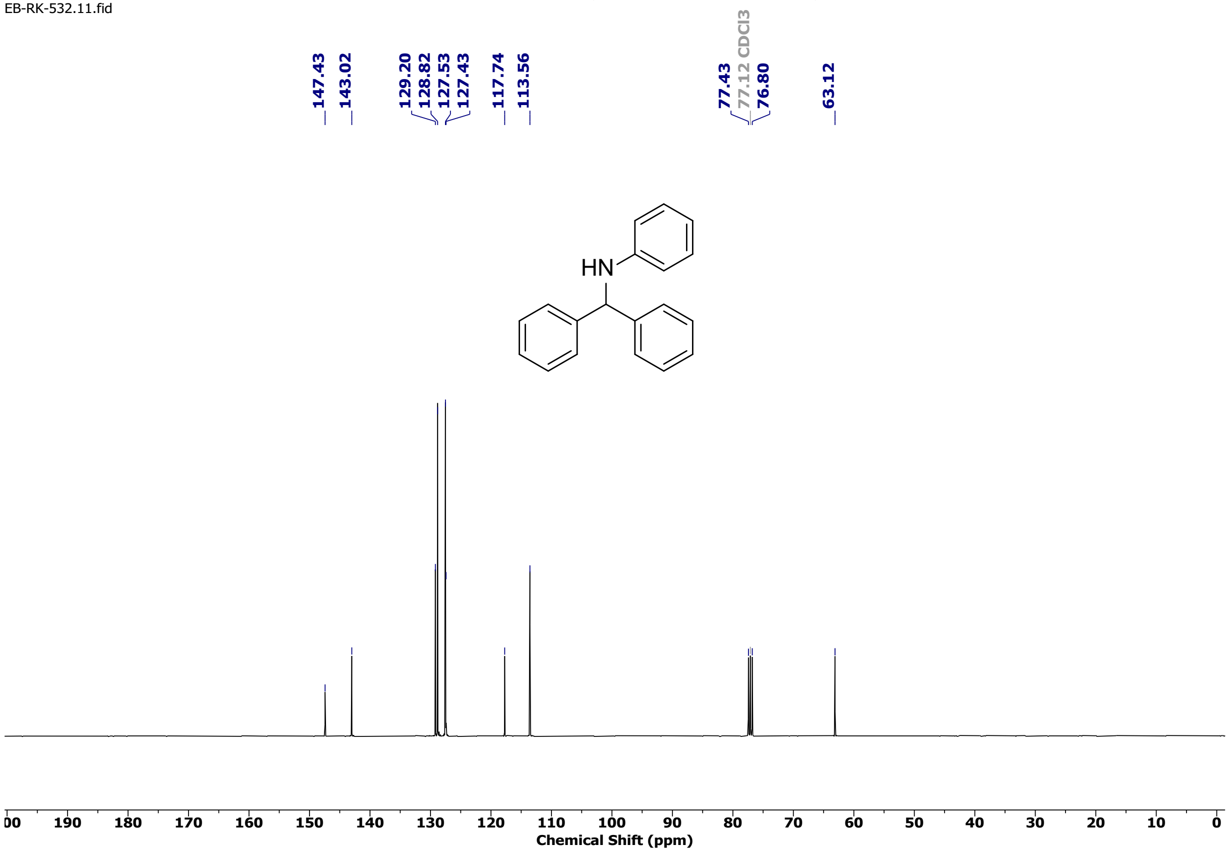
^{1}H NMR of **59** (400 MHz, CDCl$_3$)



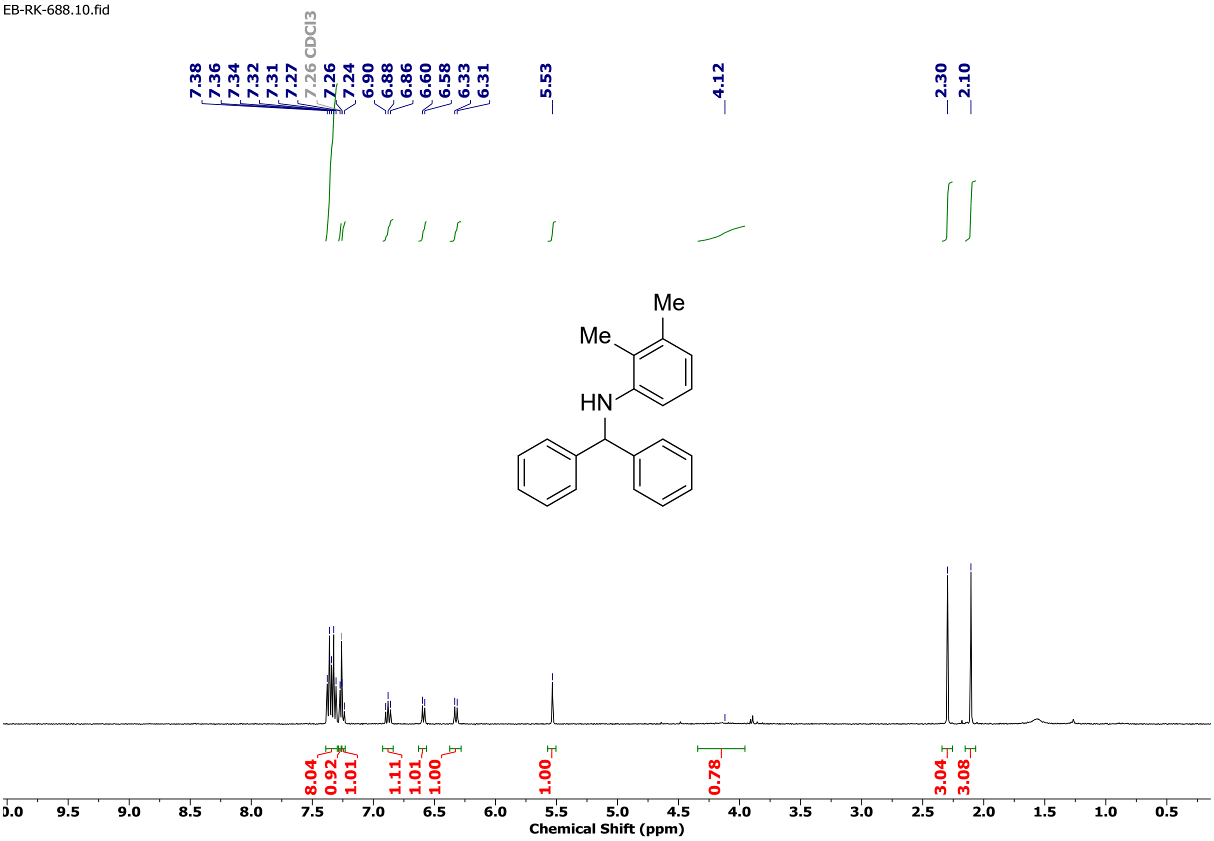
^{13}C NMR of **59** (100 MHz, CDCl$_3$)



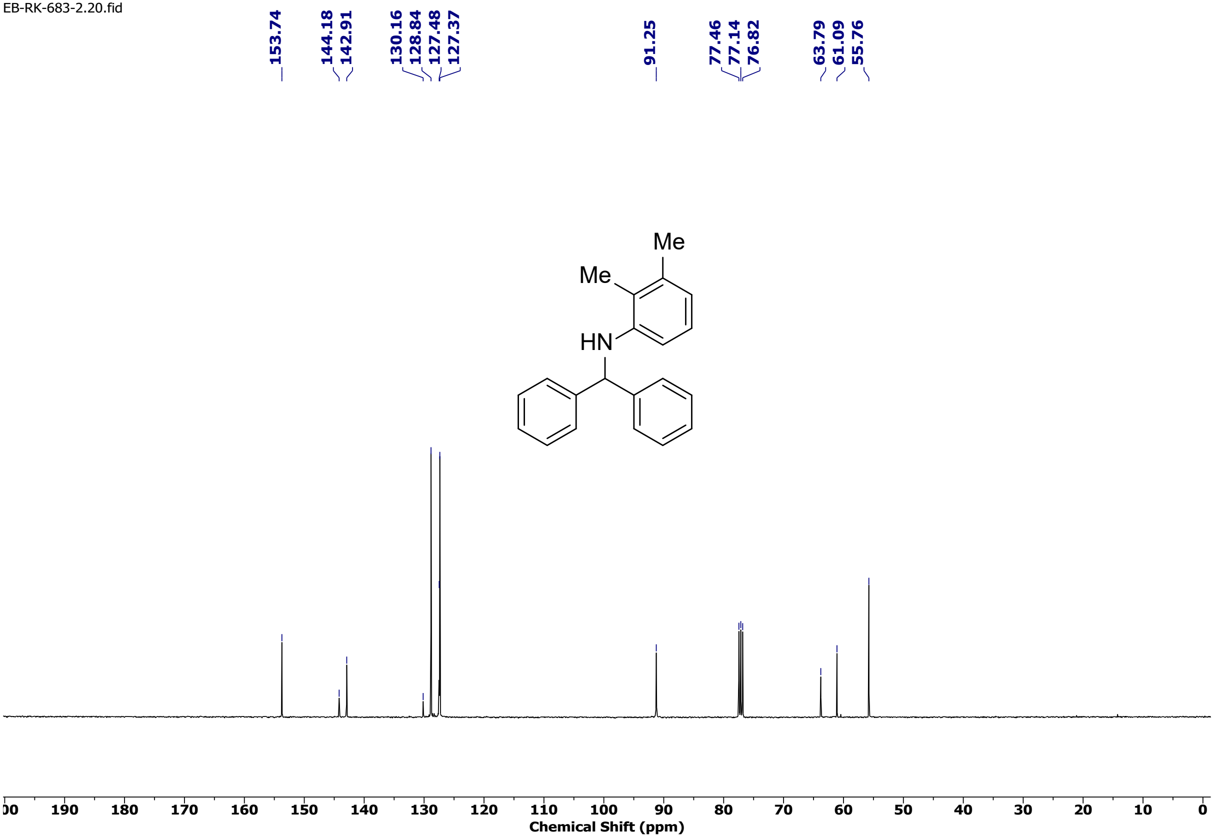
^{1}H NMR of **62** (400 MHz, $CDCl_3$)



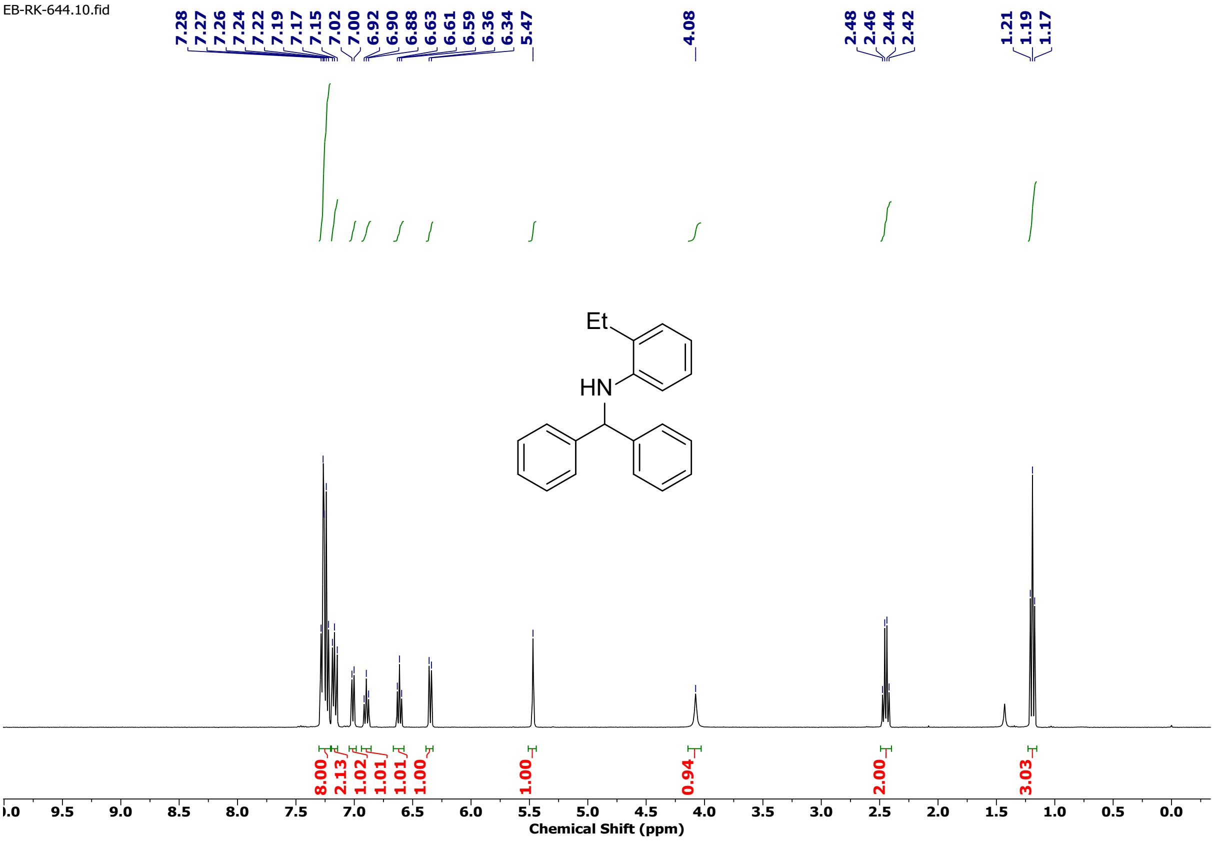
^{13}C NMR of **62** (100 MHz, $CDCl_3$)



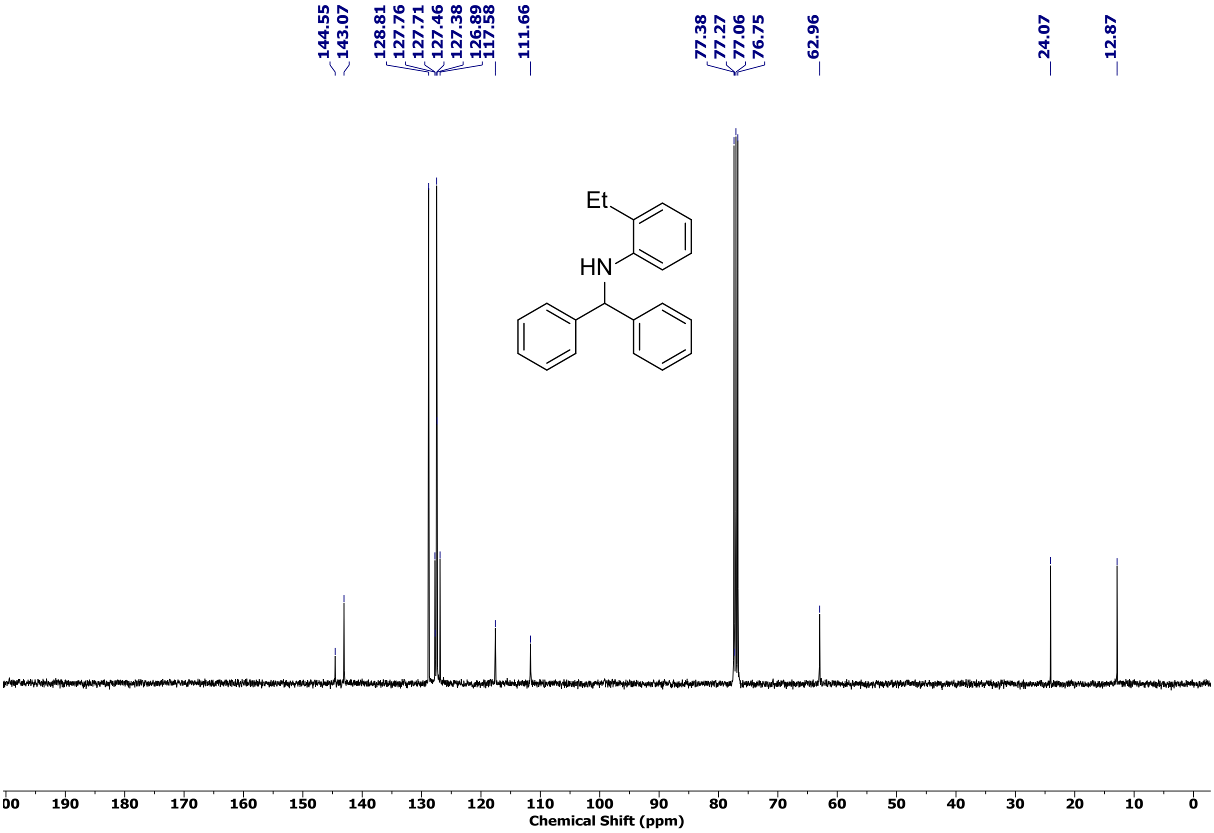
^{1}H NMR of **63** (400 MHz, $CDCl_3$)



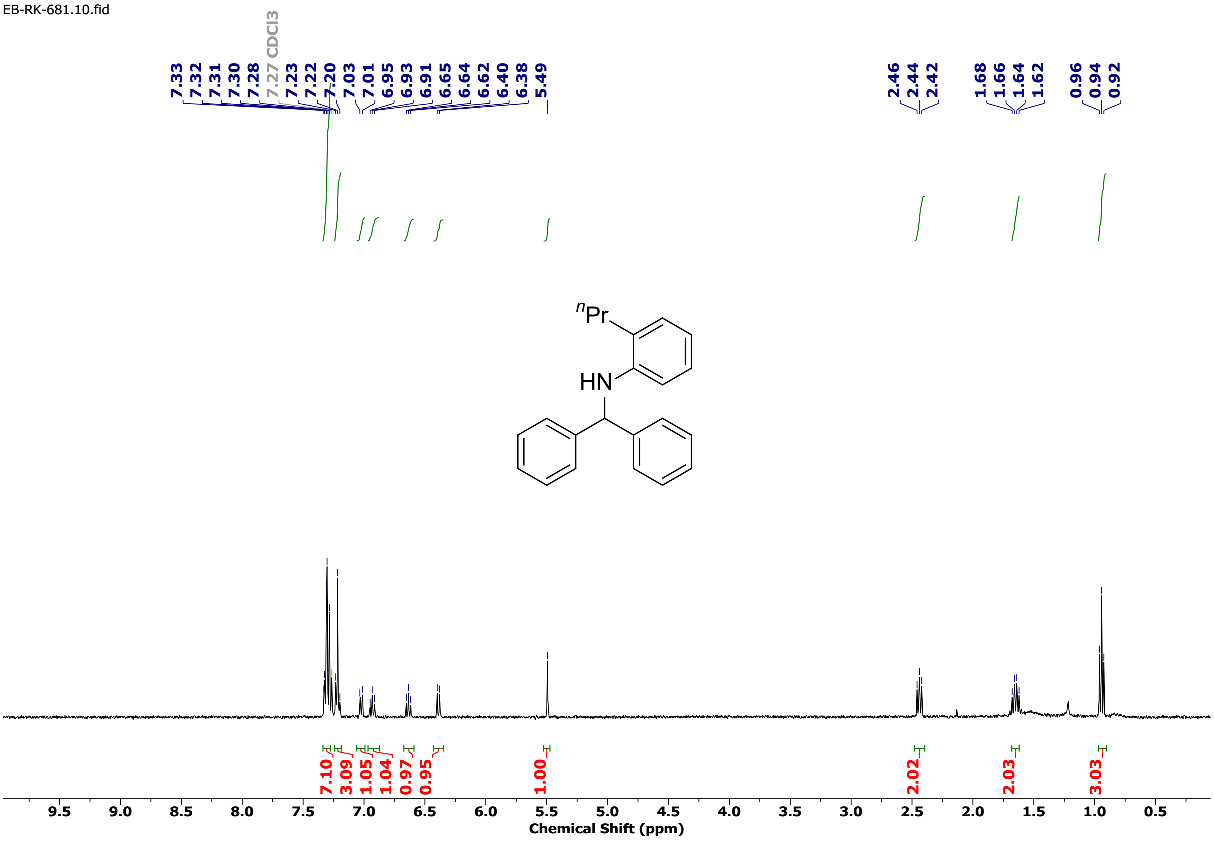
^{13}C NMR of **63** (100 MHz, $CDCl_3$)



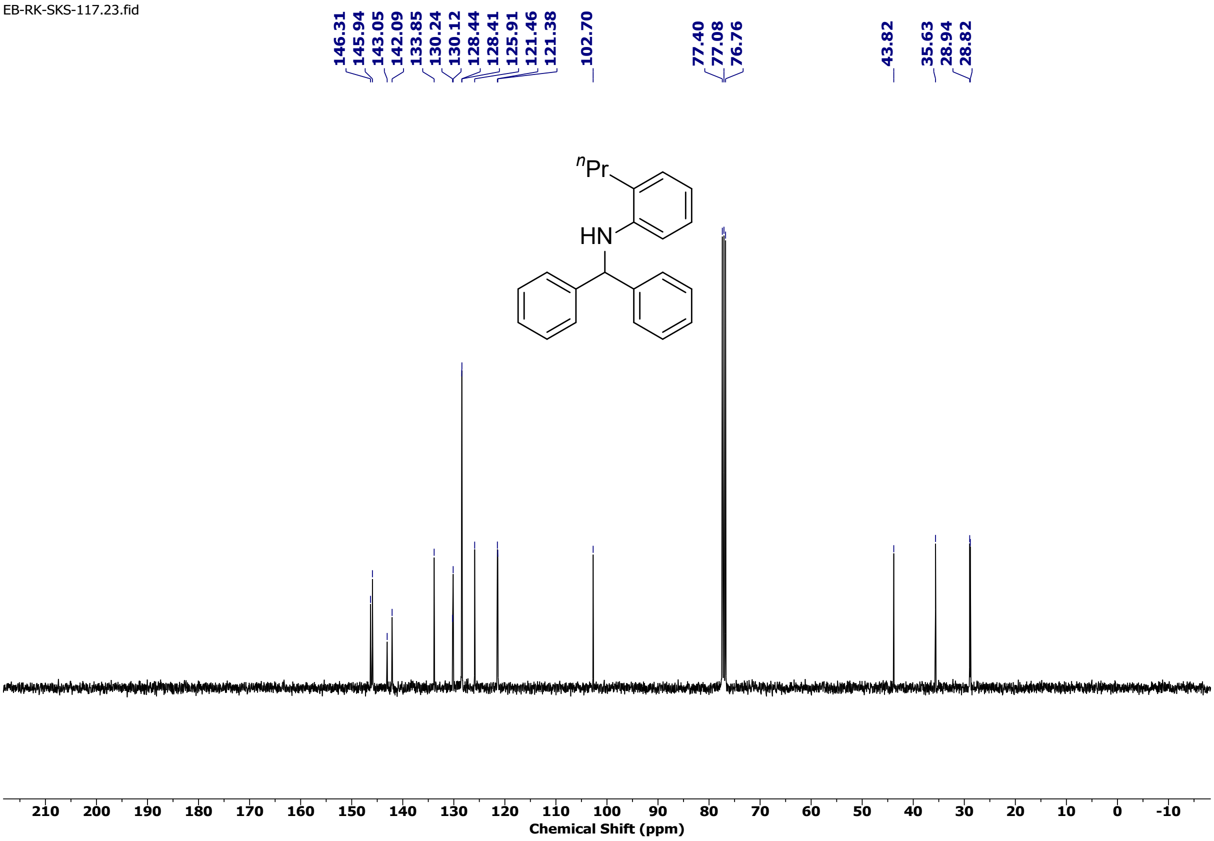
^{1}H NMR of **64** (400 MHz, CDCl$_3$)



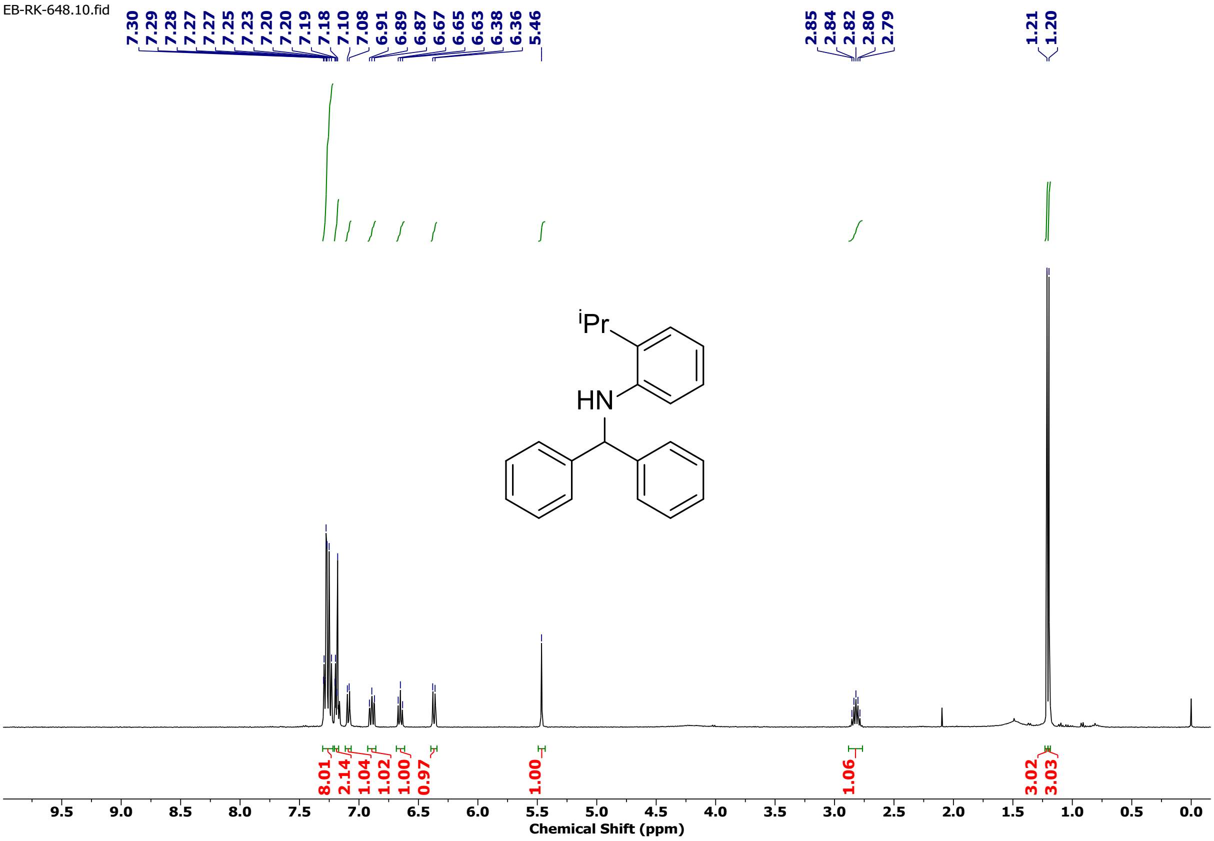
^{13}C NMR of **64** (100 MHz, CDCl$_3$)



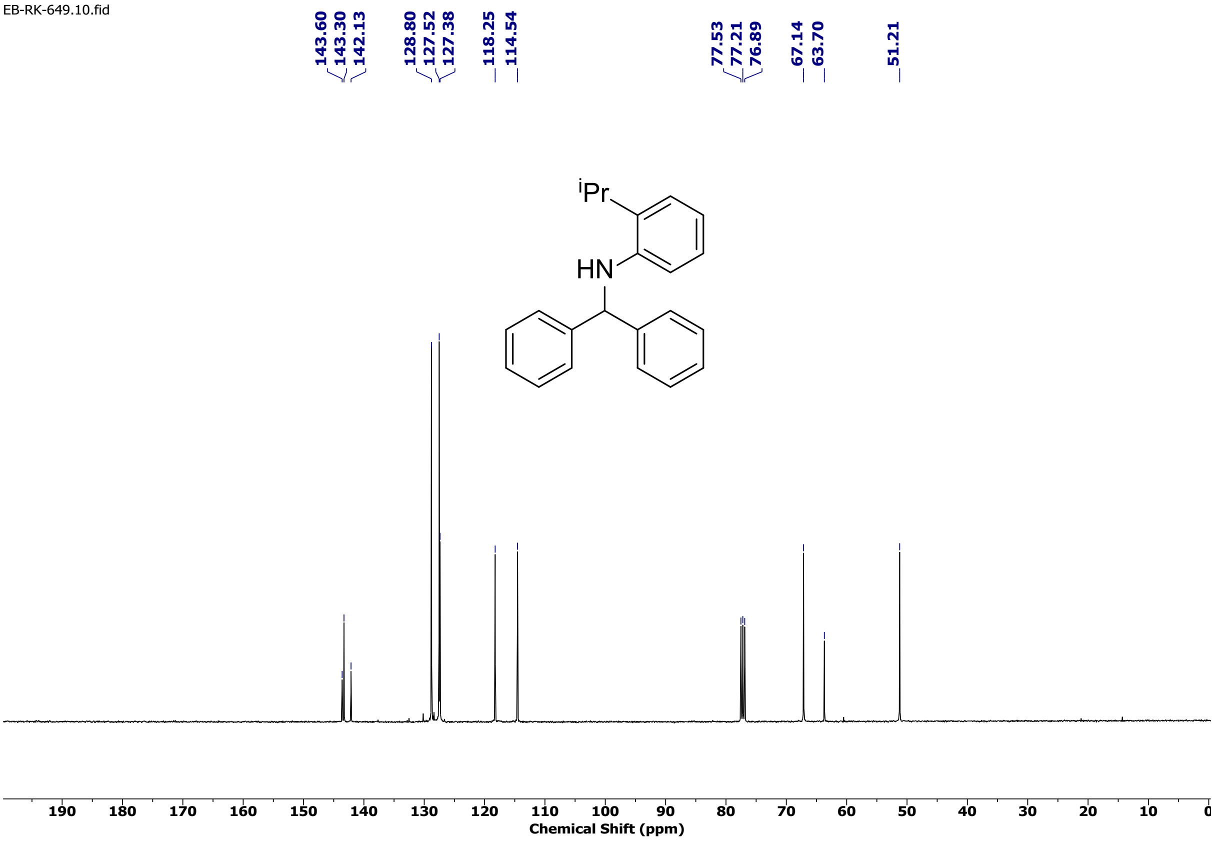
^{1}H NMR of **65** (400 MHz, CDCl$_3$)



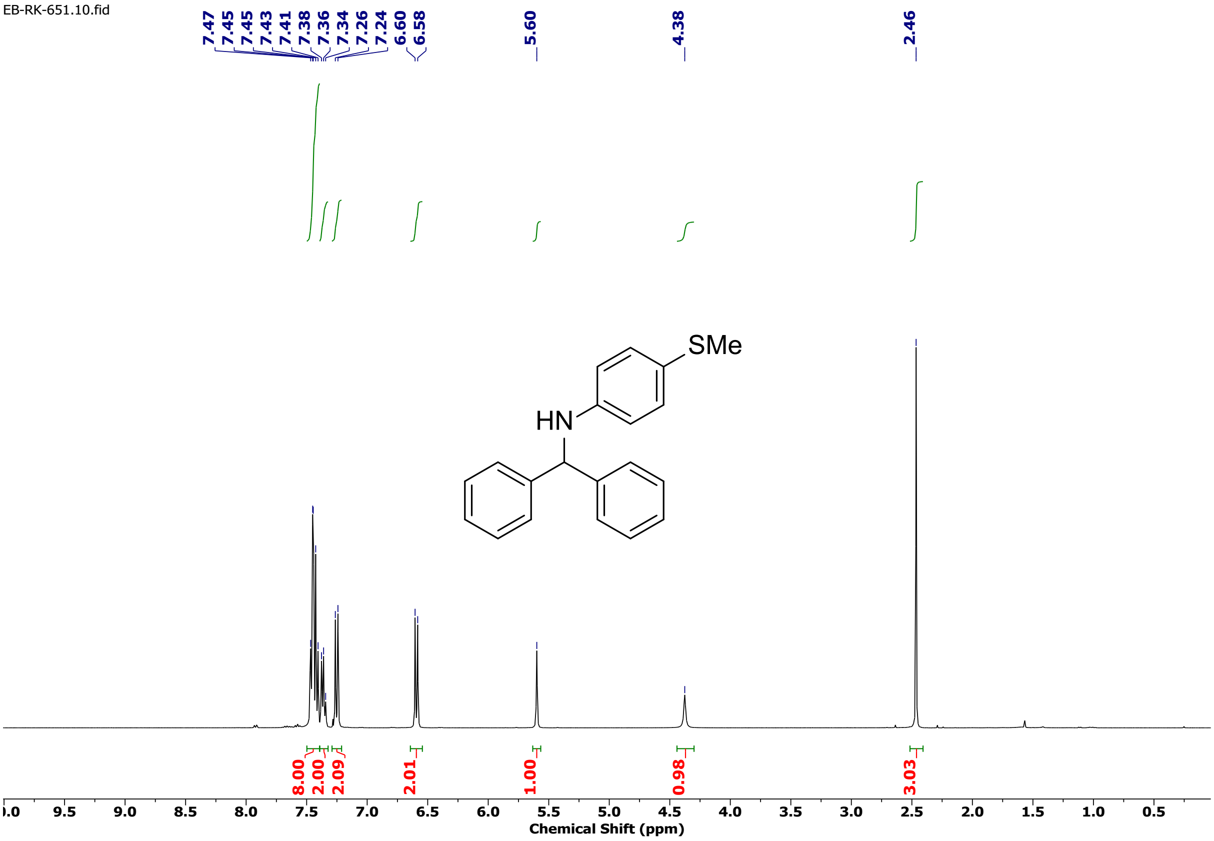
^{13}C NMR of **65** (100 MHz, CDCl$_3$)



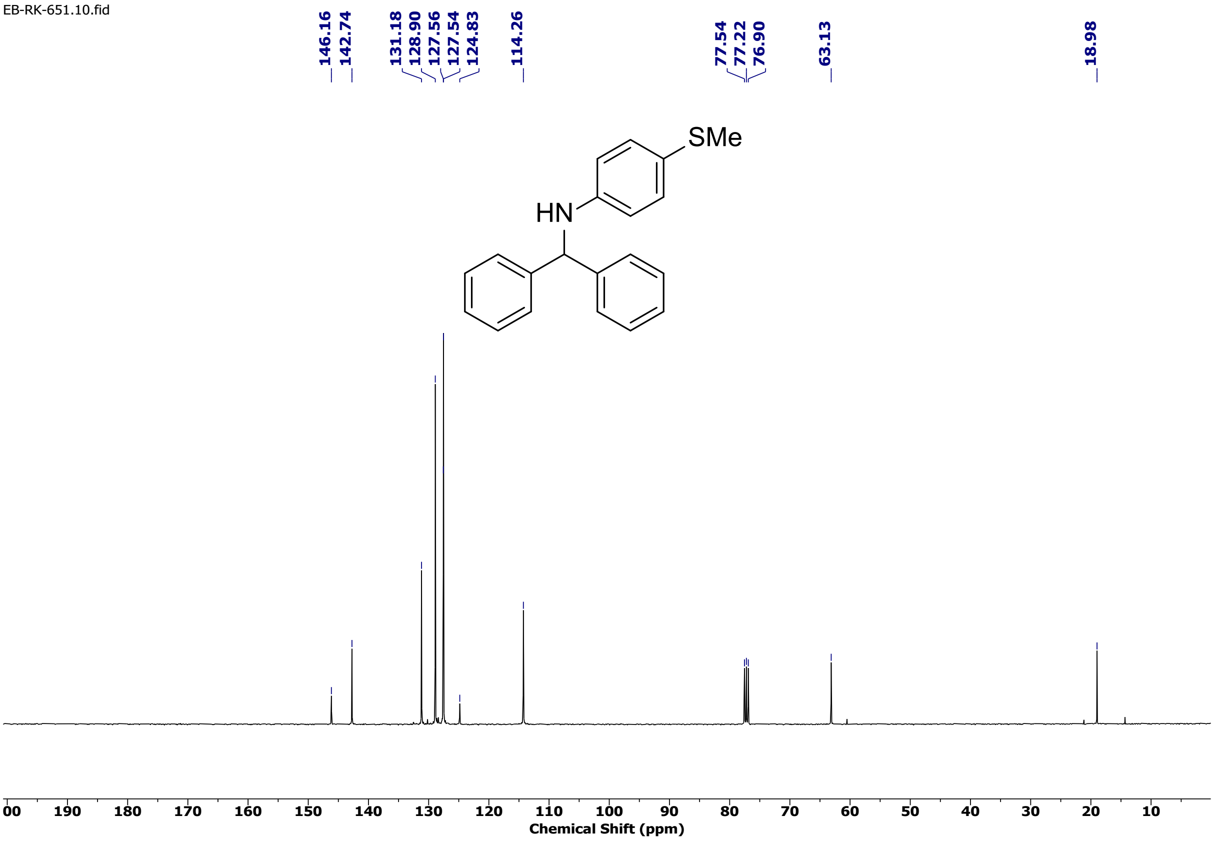
^{1}H NMR of **66**(400 MHz, $CDCl_3$)



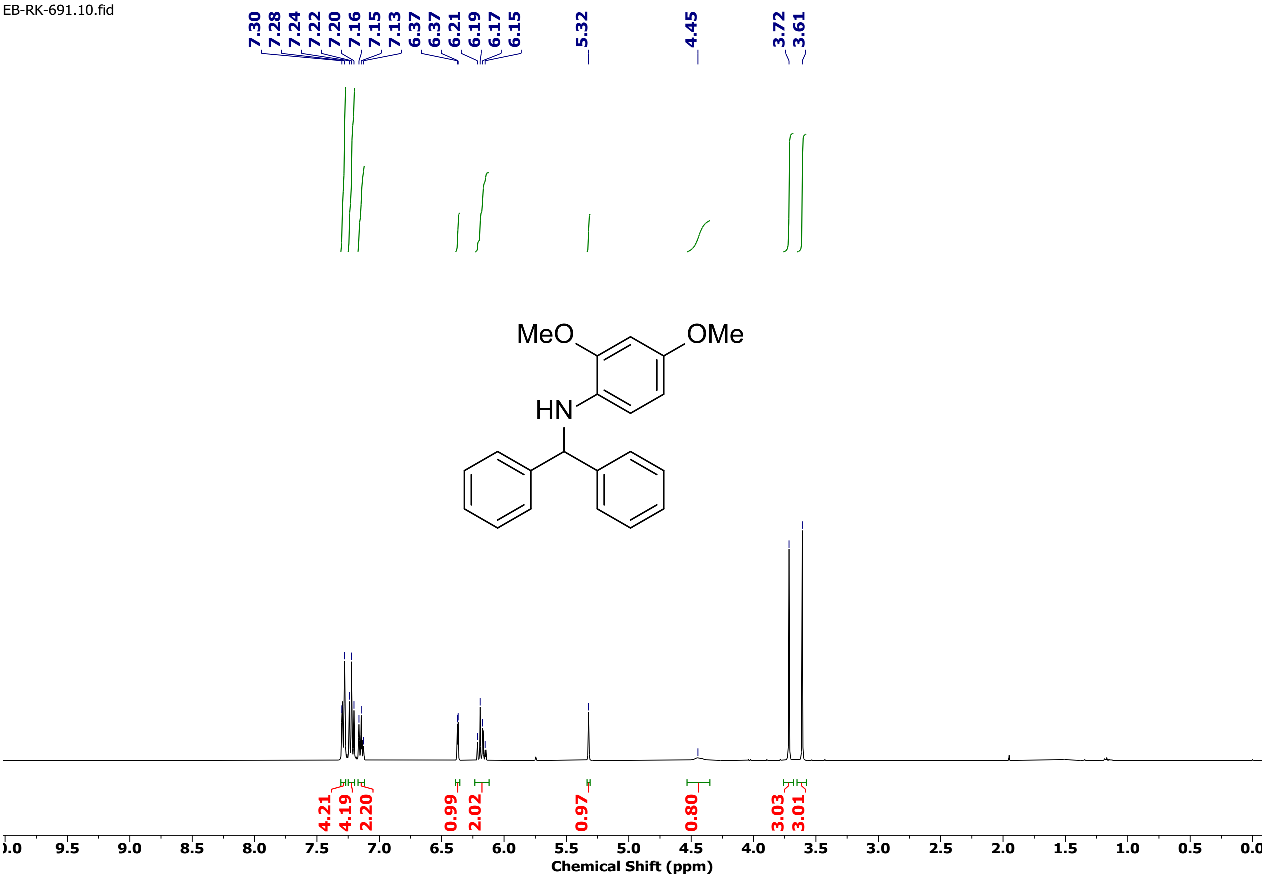
^{13}C NMR of **66** (100 MHz, $CDCl_3$)



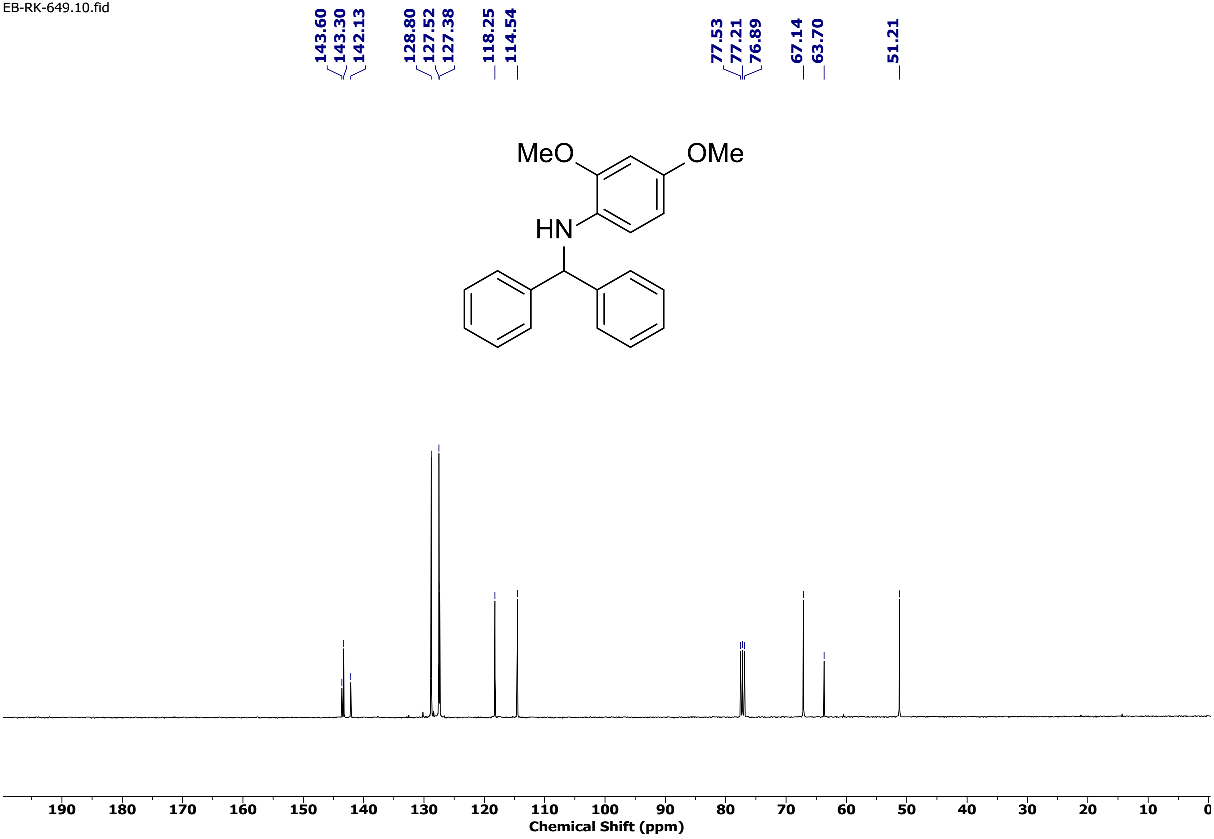
^{1}H NMR of **67** (400 MHz, CDCl$_3$)



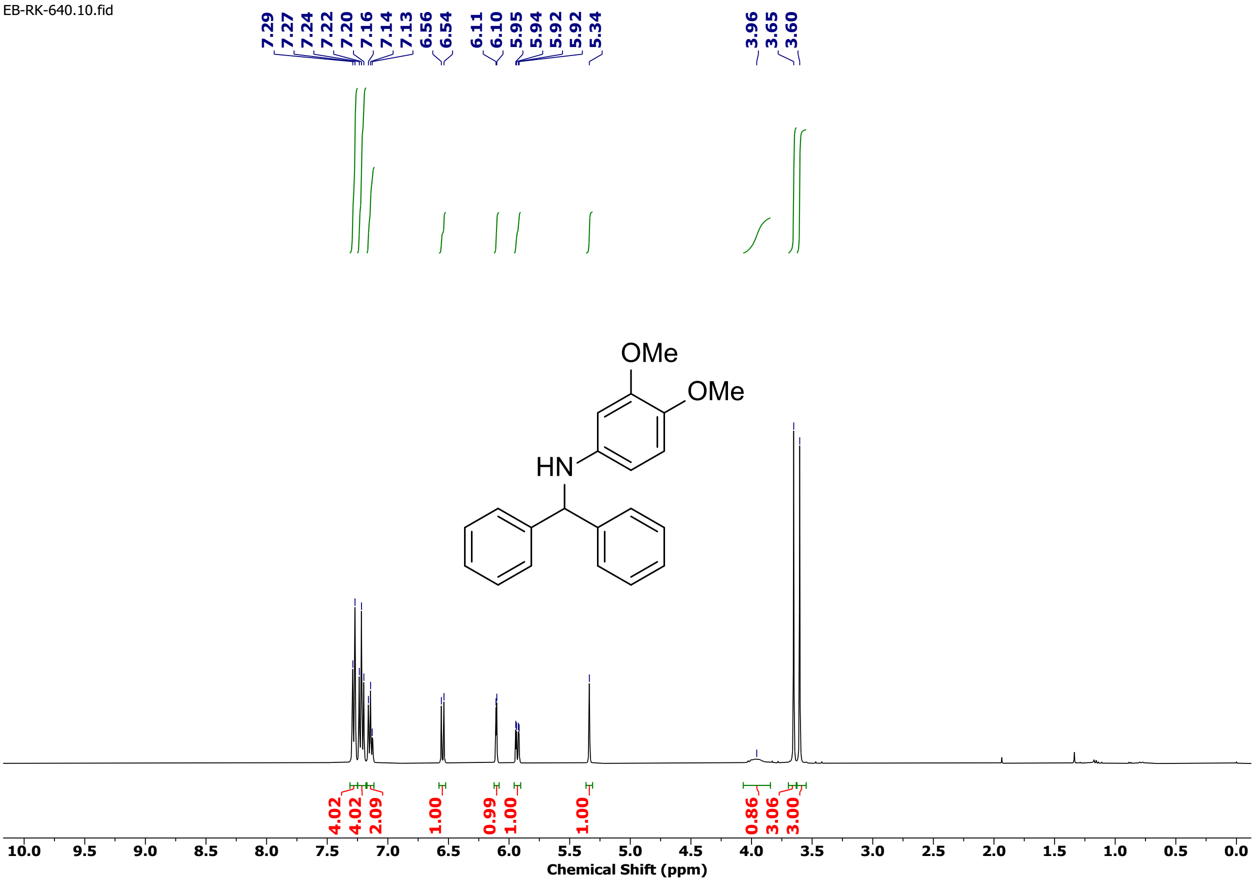
^{13}C NMR of **67** (100 MHz, CDCl$_3$)



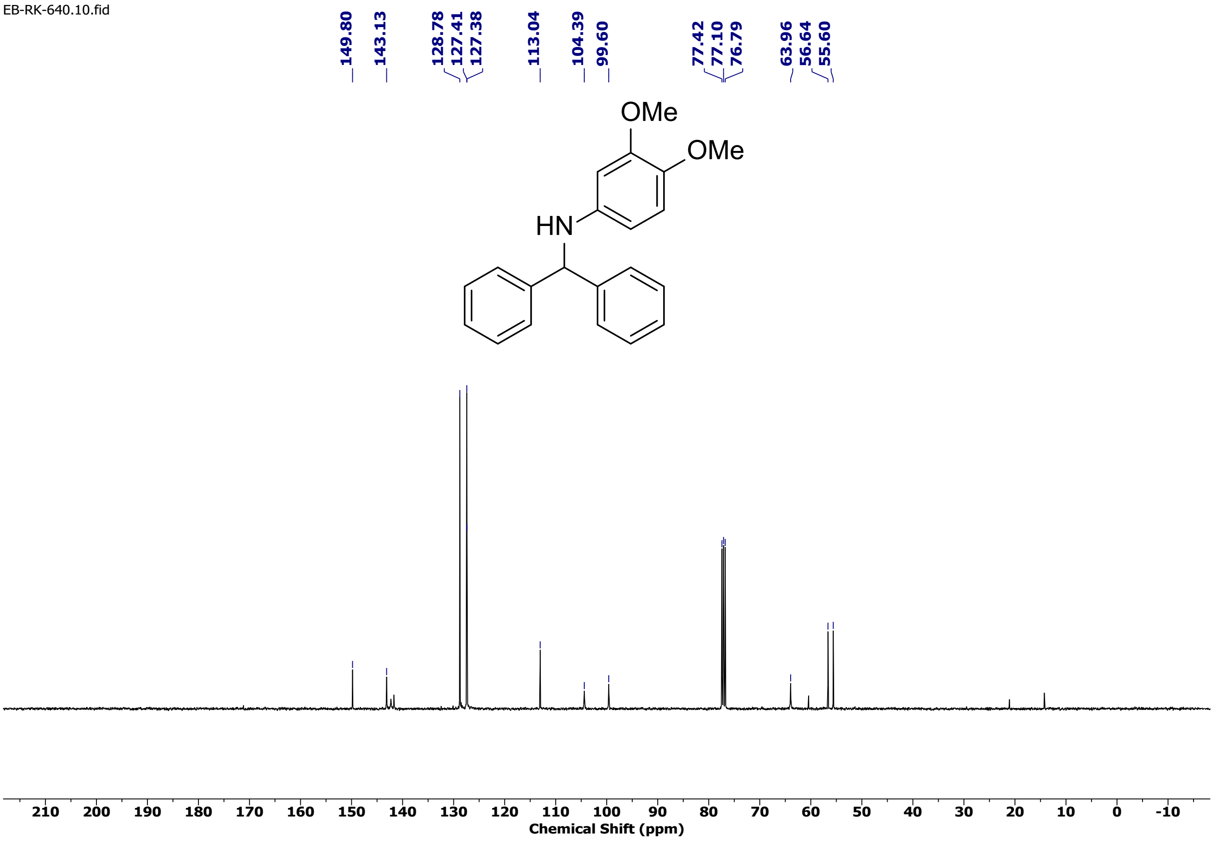
^{1}H NMR of **68** (400 MHz, CDCl$_3$)



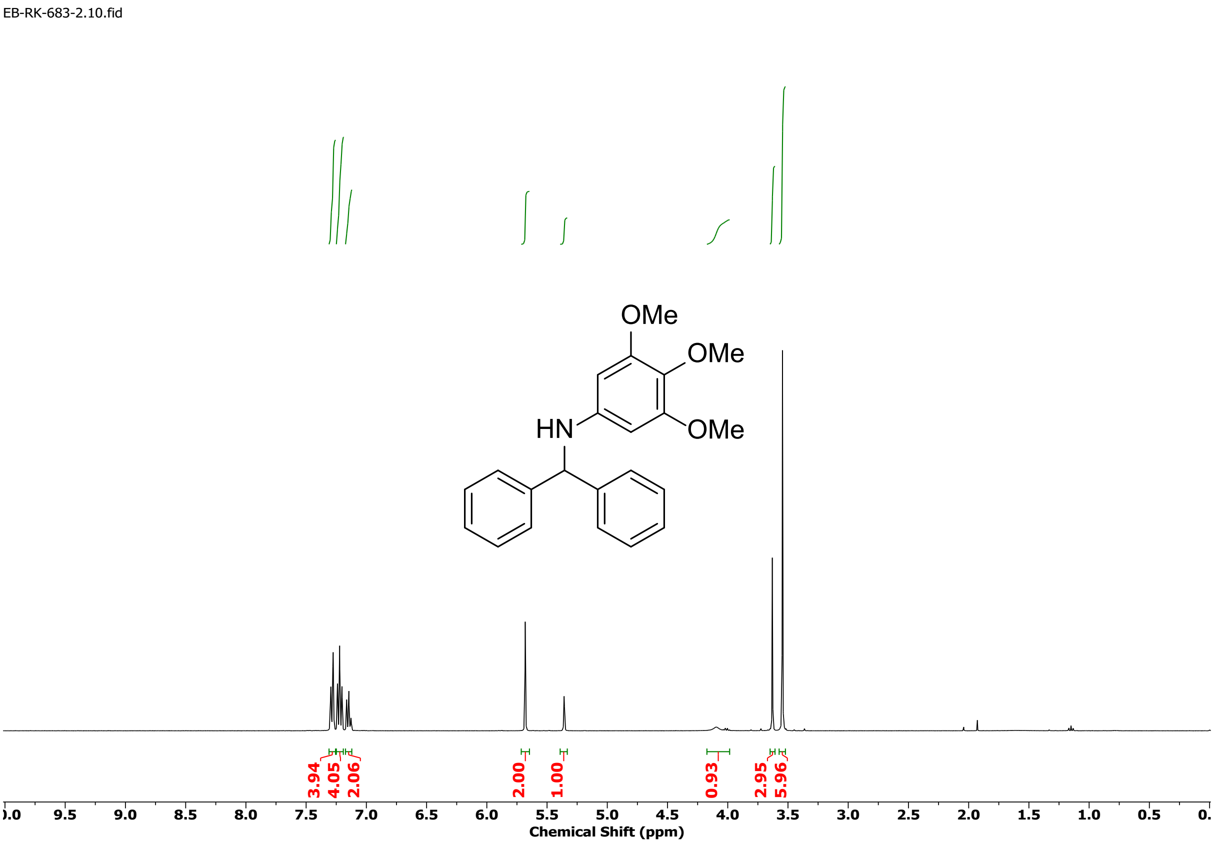
^{13}C NMR of **68** (100 MHz, CDCl$_3$)



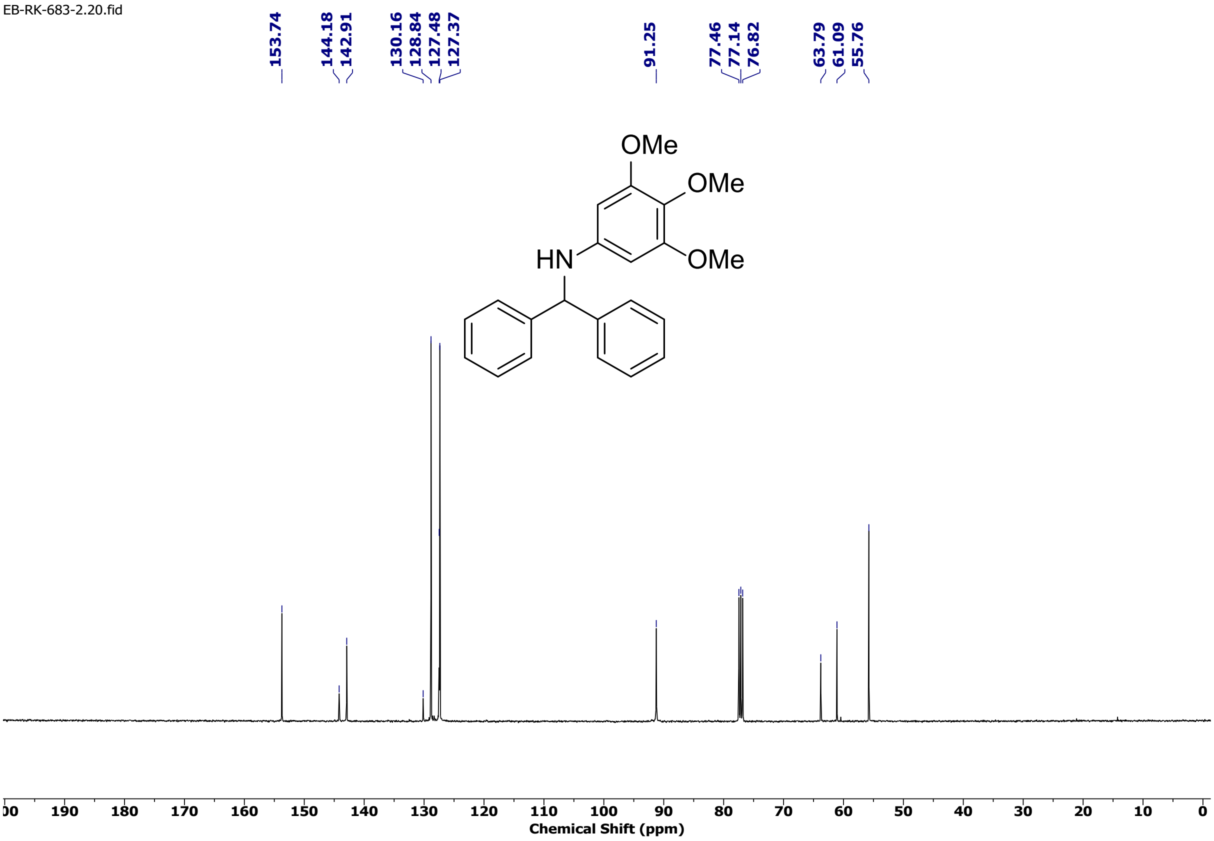
^{1}H NMR of **69** (400 MHz, CDCl$_3$)



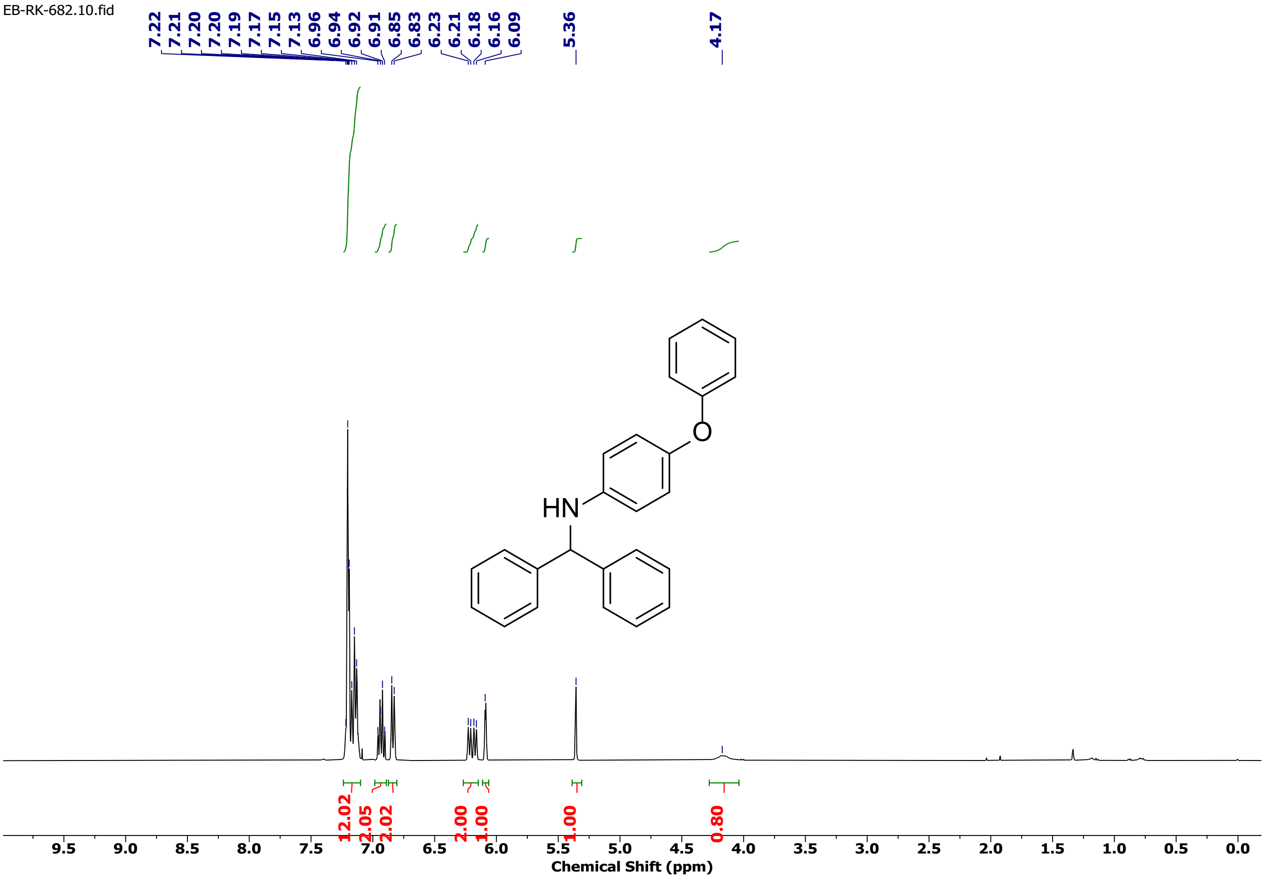
^{13}C NMR of **69** (100 MHz, CDCl$_3$)



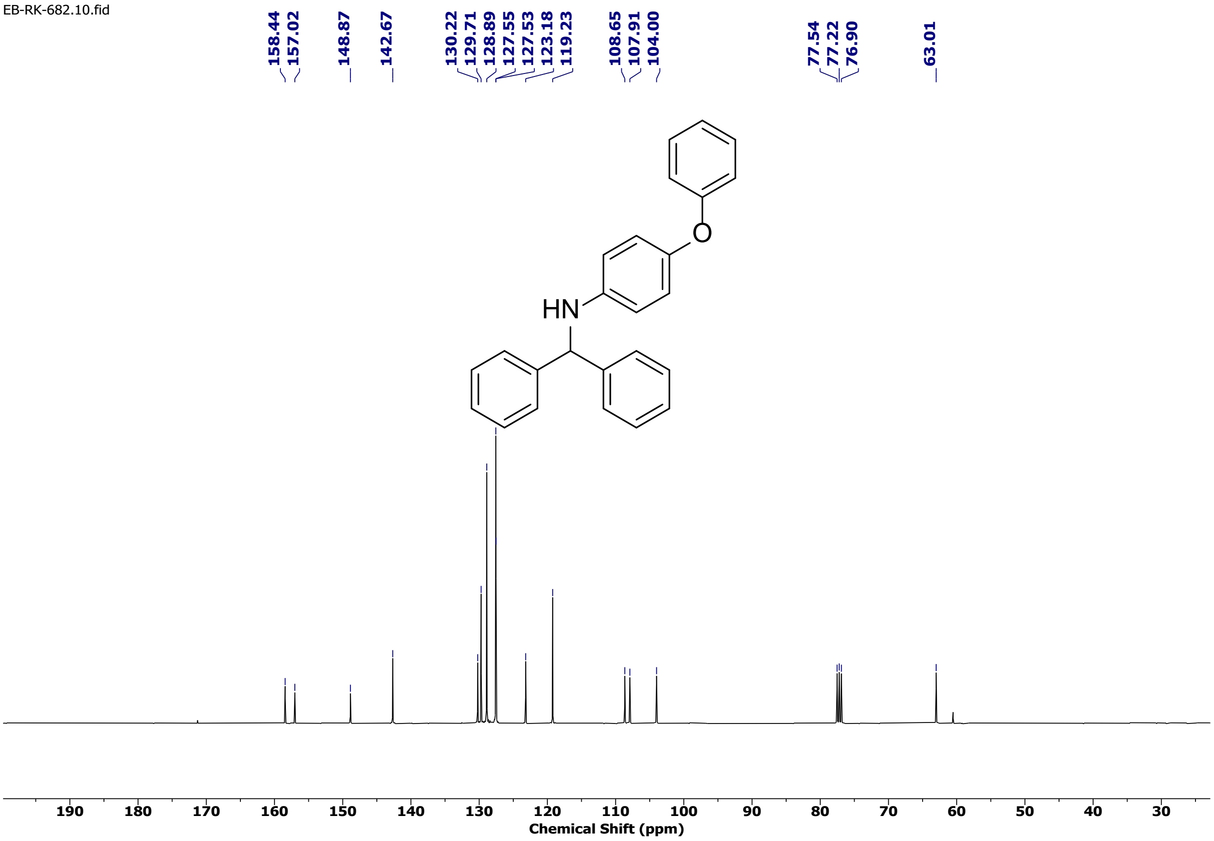
^{1}H NMR of **70** (400 MHz, $CDCl_3$)



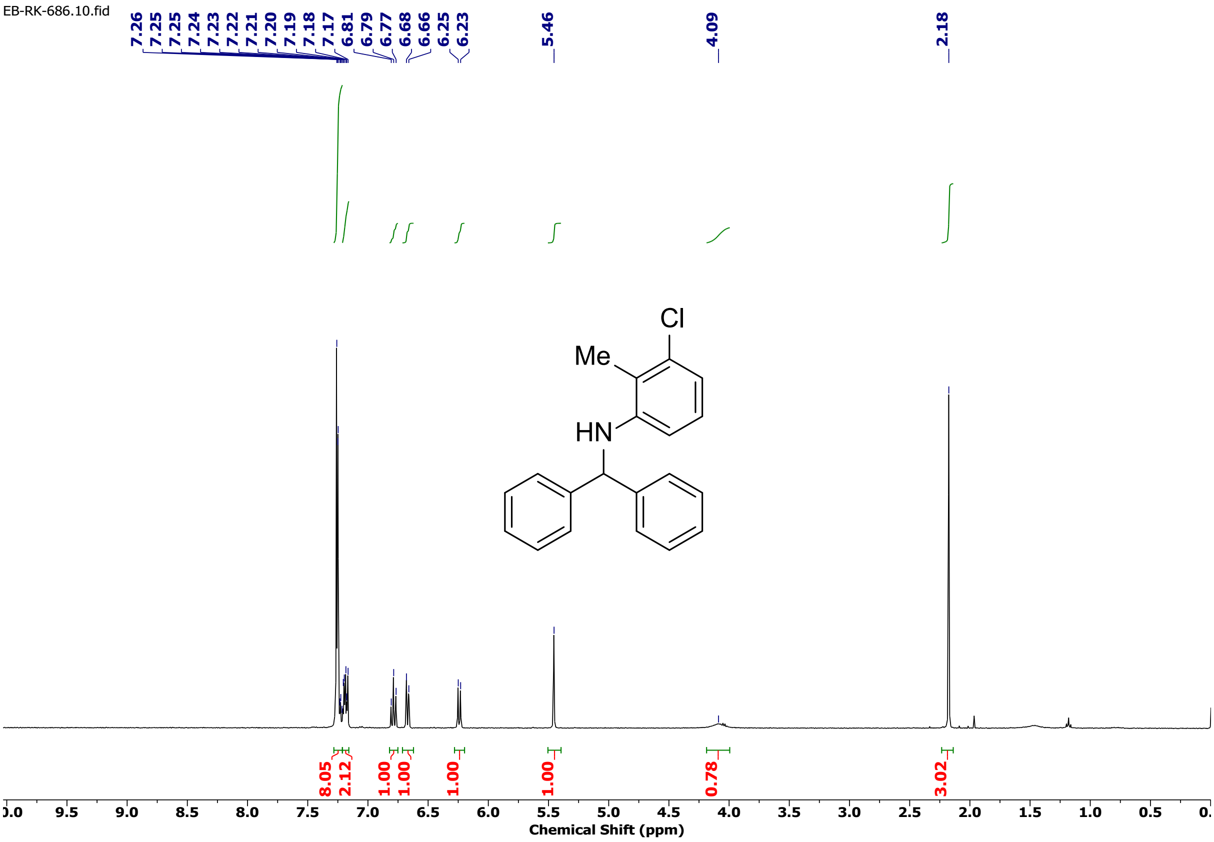
^{13}C NMR of **70** (100 MHz, $CDCl_3$)



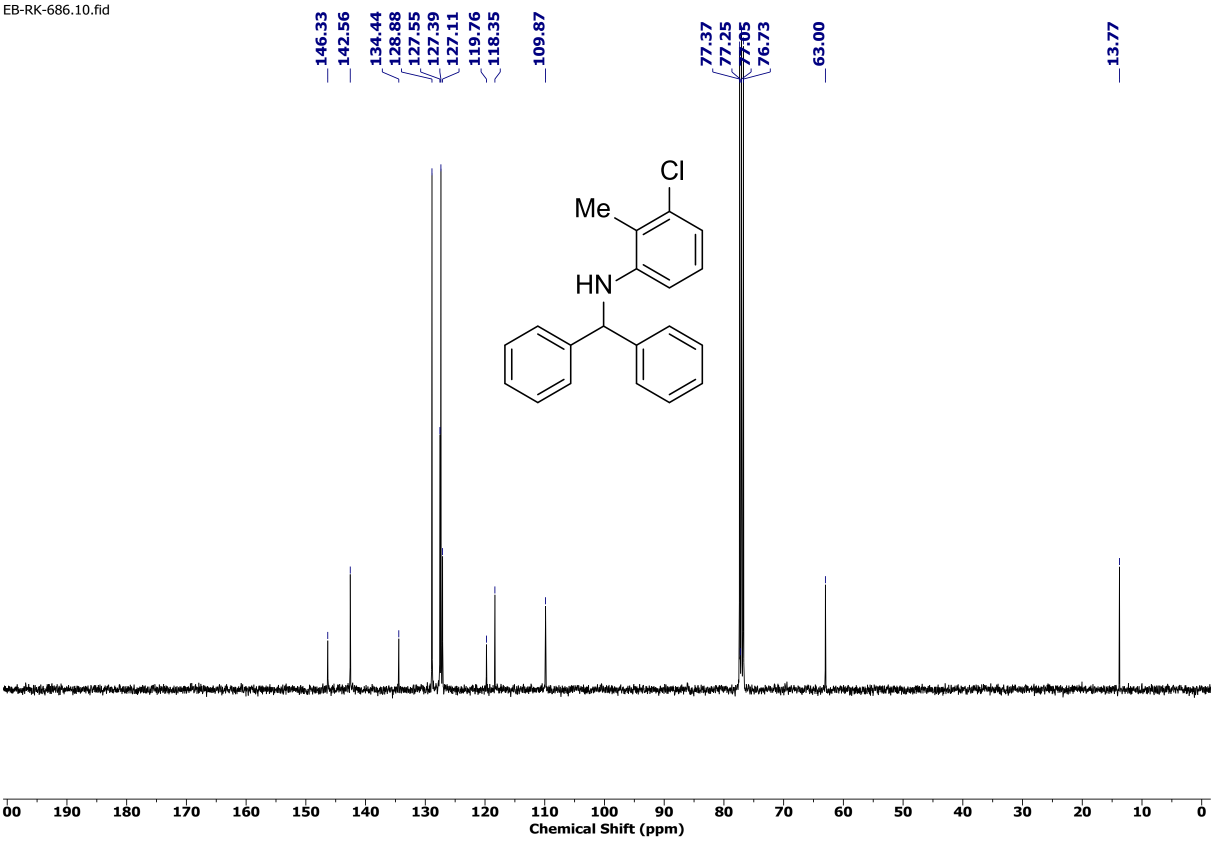
^{1}H NMR of **71** (400 MHz, CDCl$_3$)



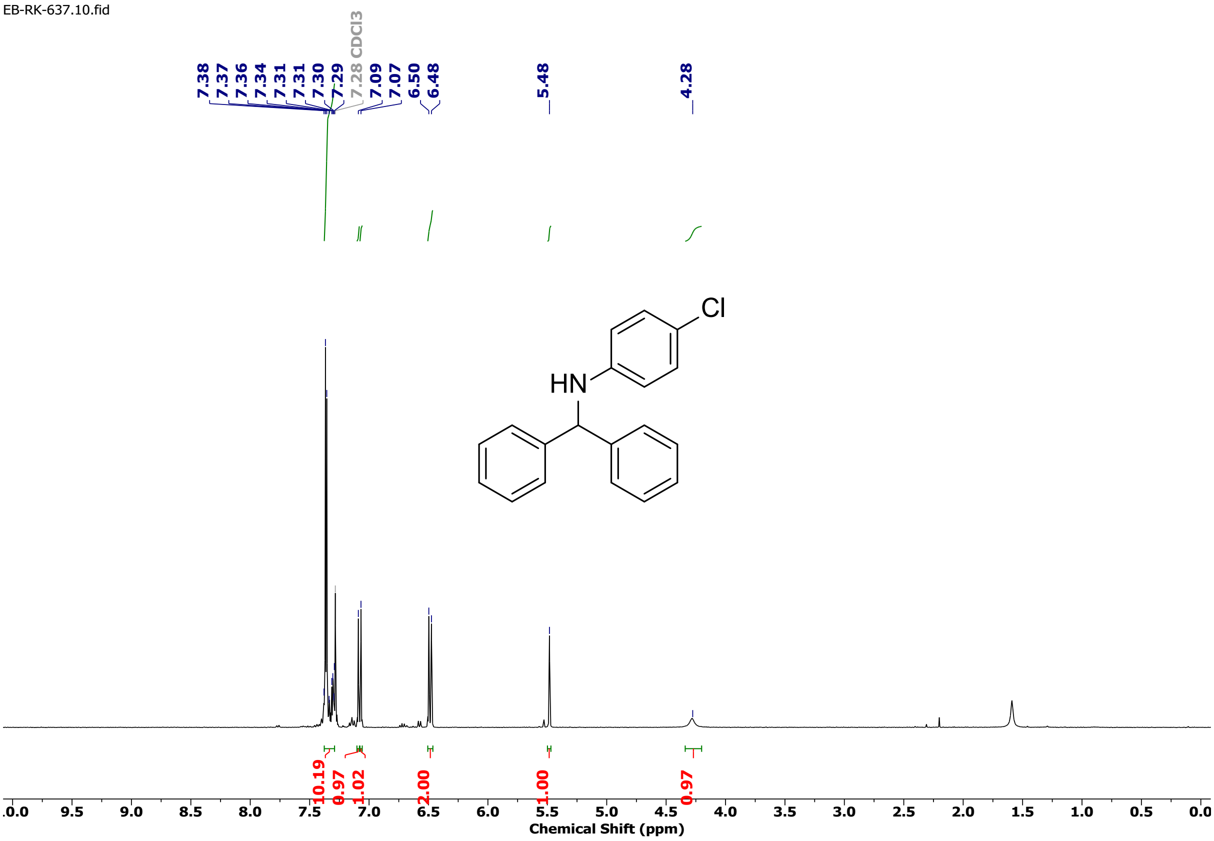
^{13}C NMR of **71** (100 MHz, CDCl$_3$)



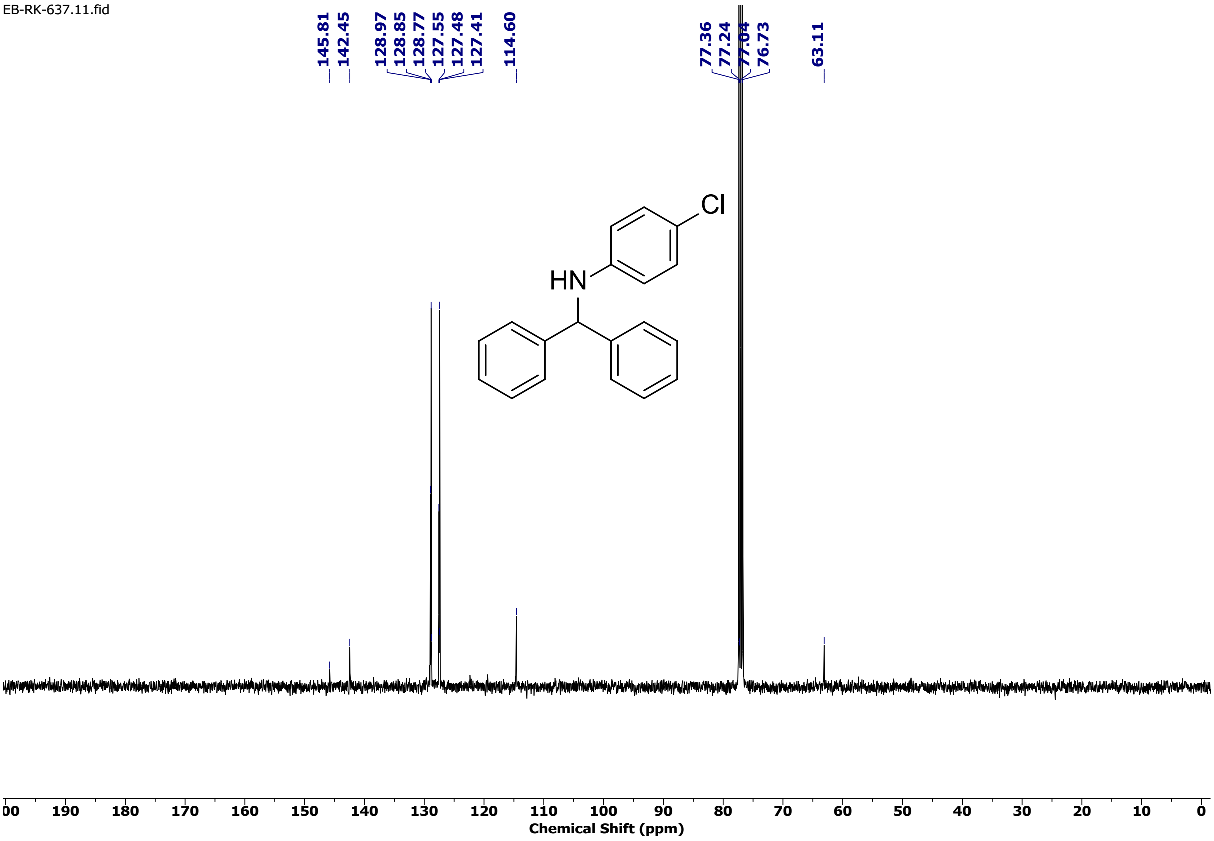
^{1}H NMR of **72** (400 MHz, CDCl$_3$)



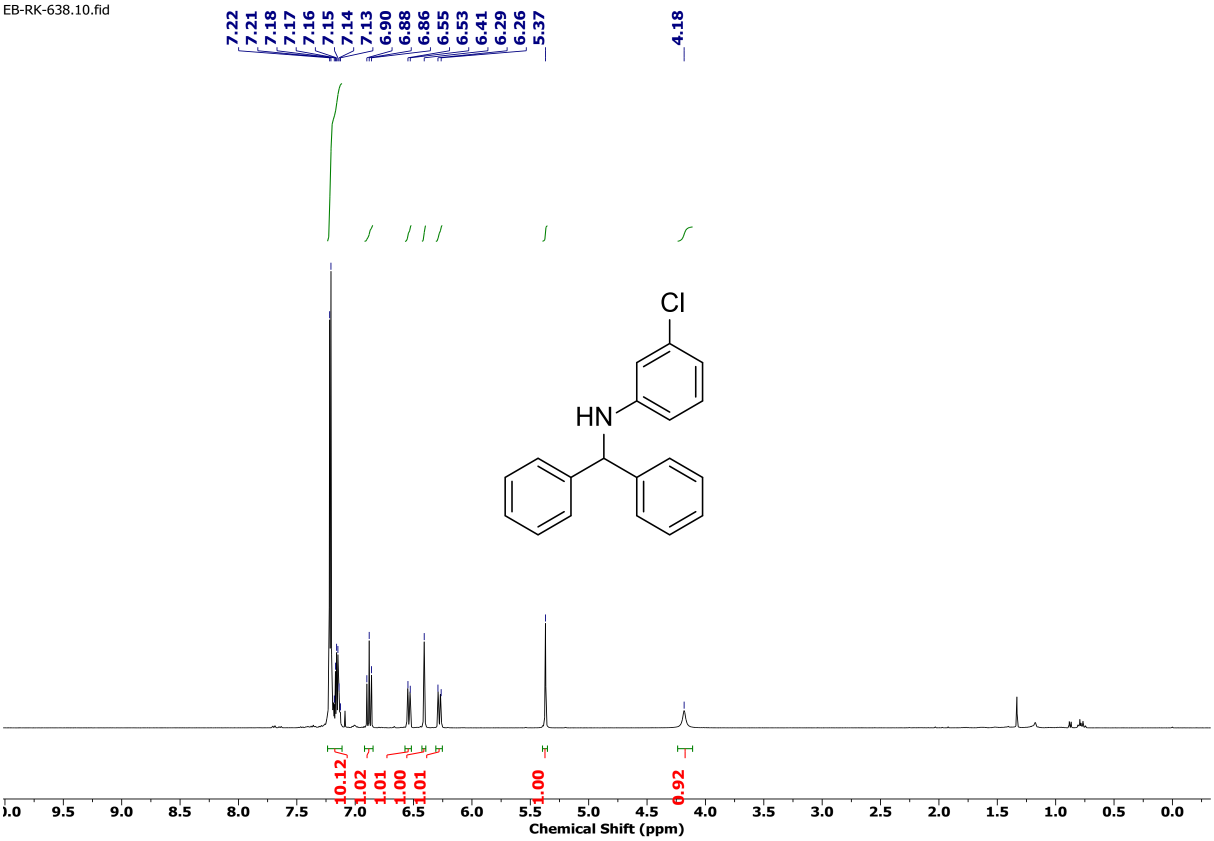
^{13}C NMR of **72** (100 MHz, CDCl$_3$)



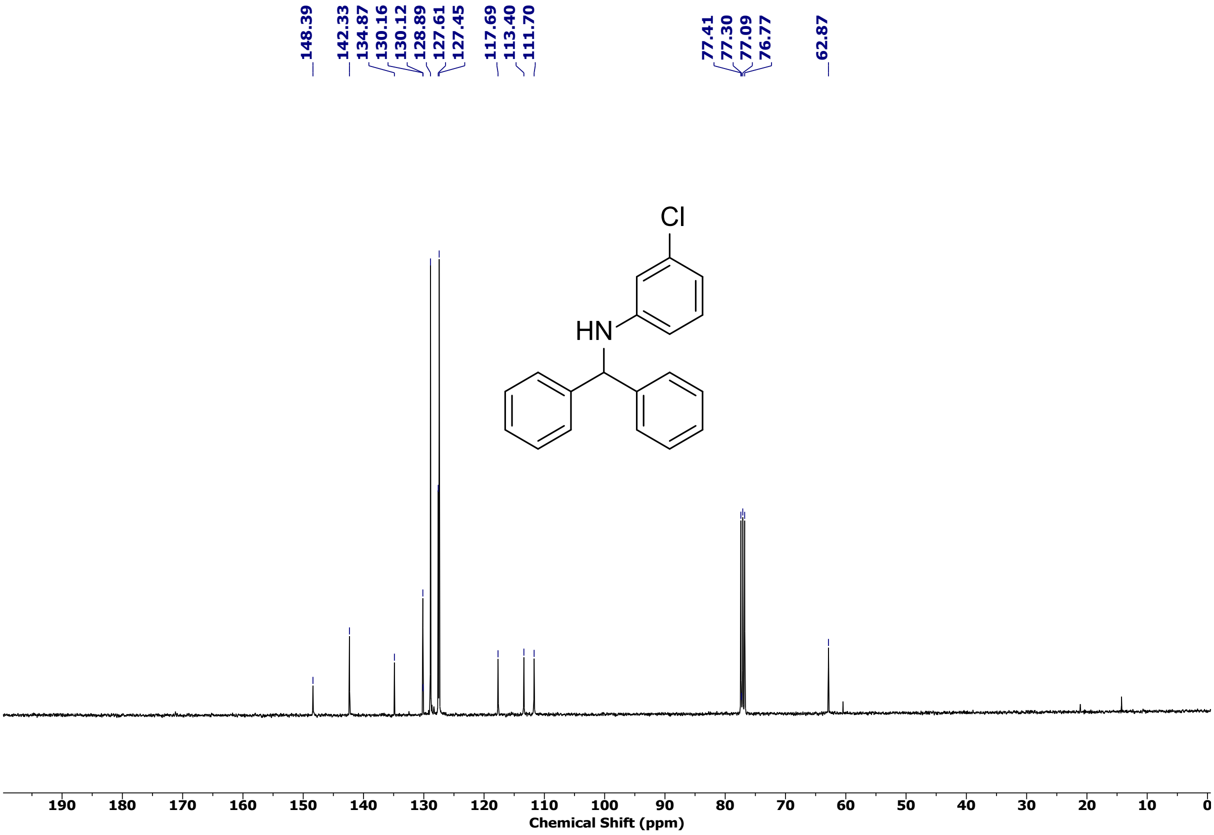
^{1}H NMR of **73** (400 MHz, CDCl$_3$)



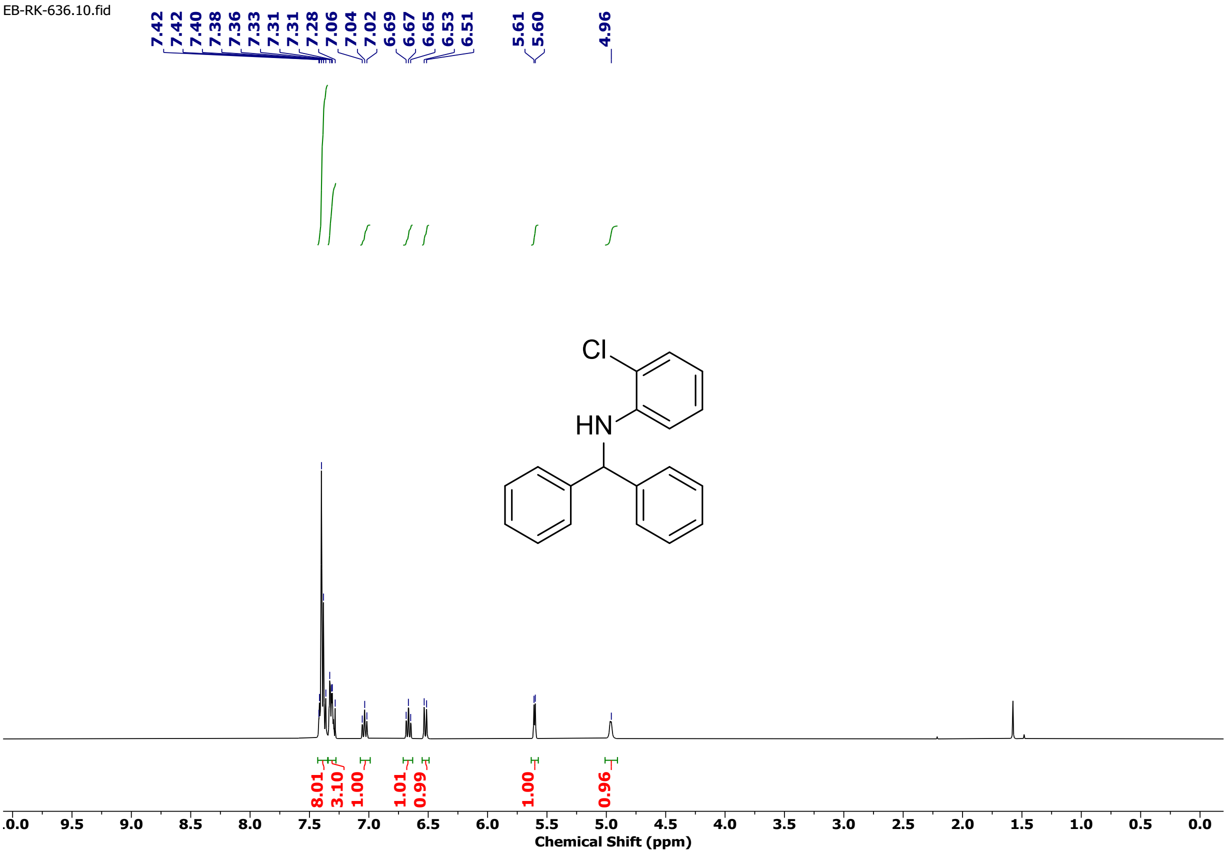
^{13}C NMR of **73** (100 MHz, CDCl$_3$)



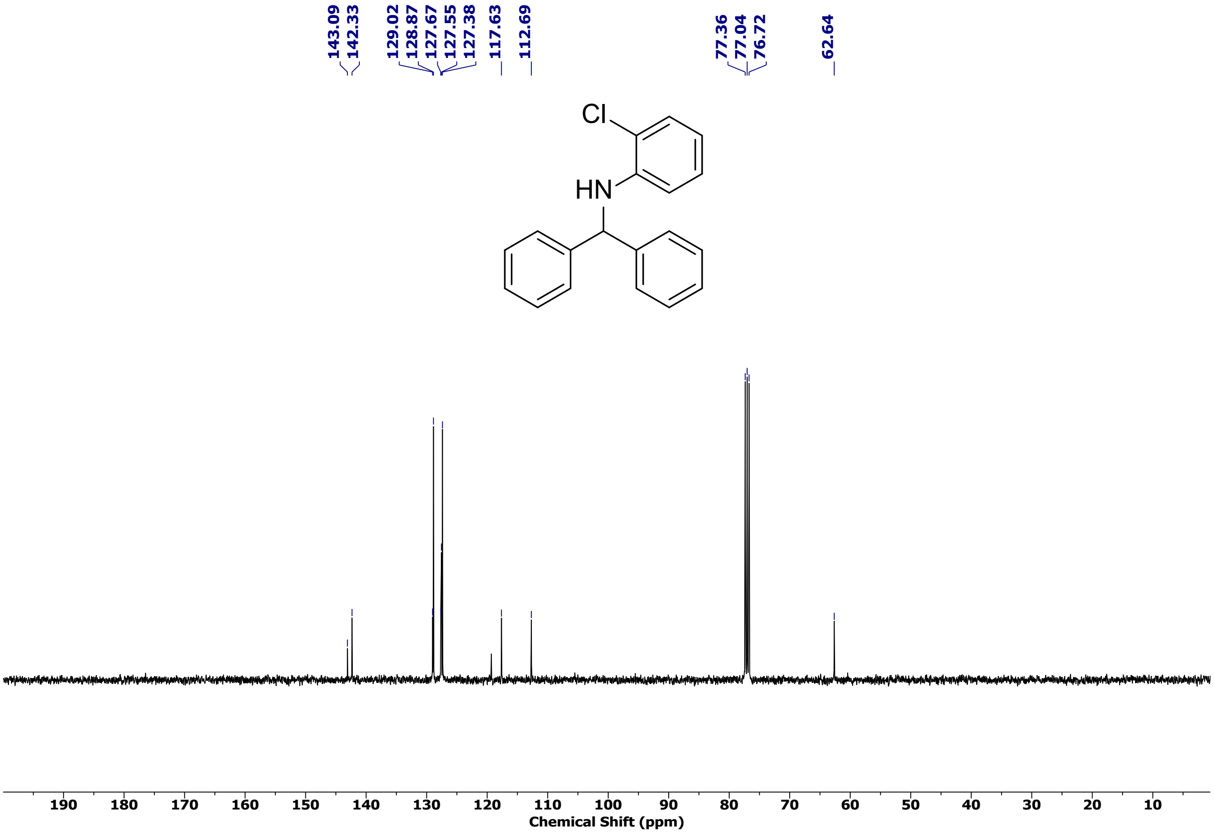
^{1}H NMR of **74** (400 MHz, CDCl$_3$)



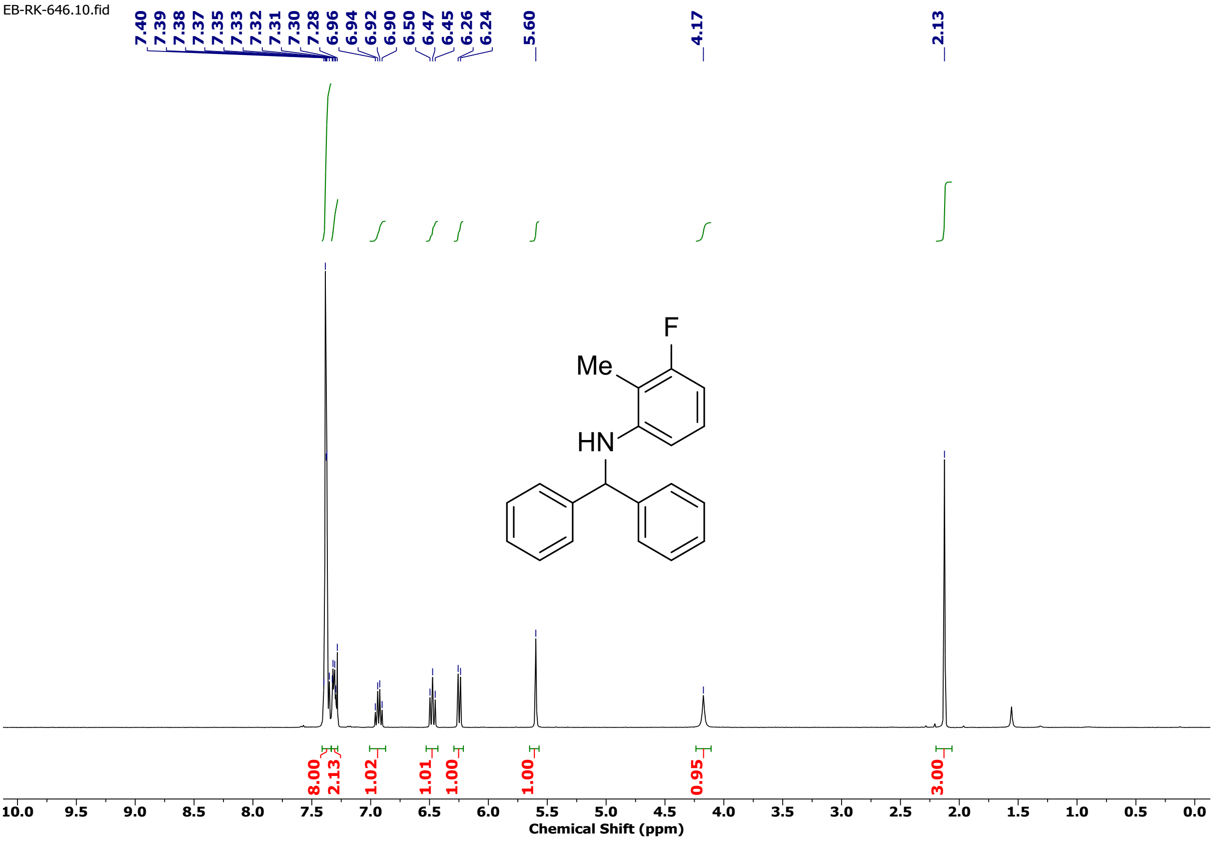
^{13}C NMR of **74** (100 MHz, CDCl$_3$)



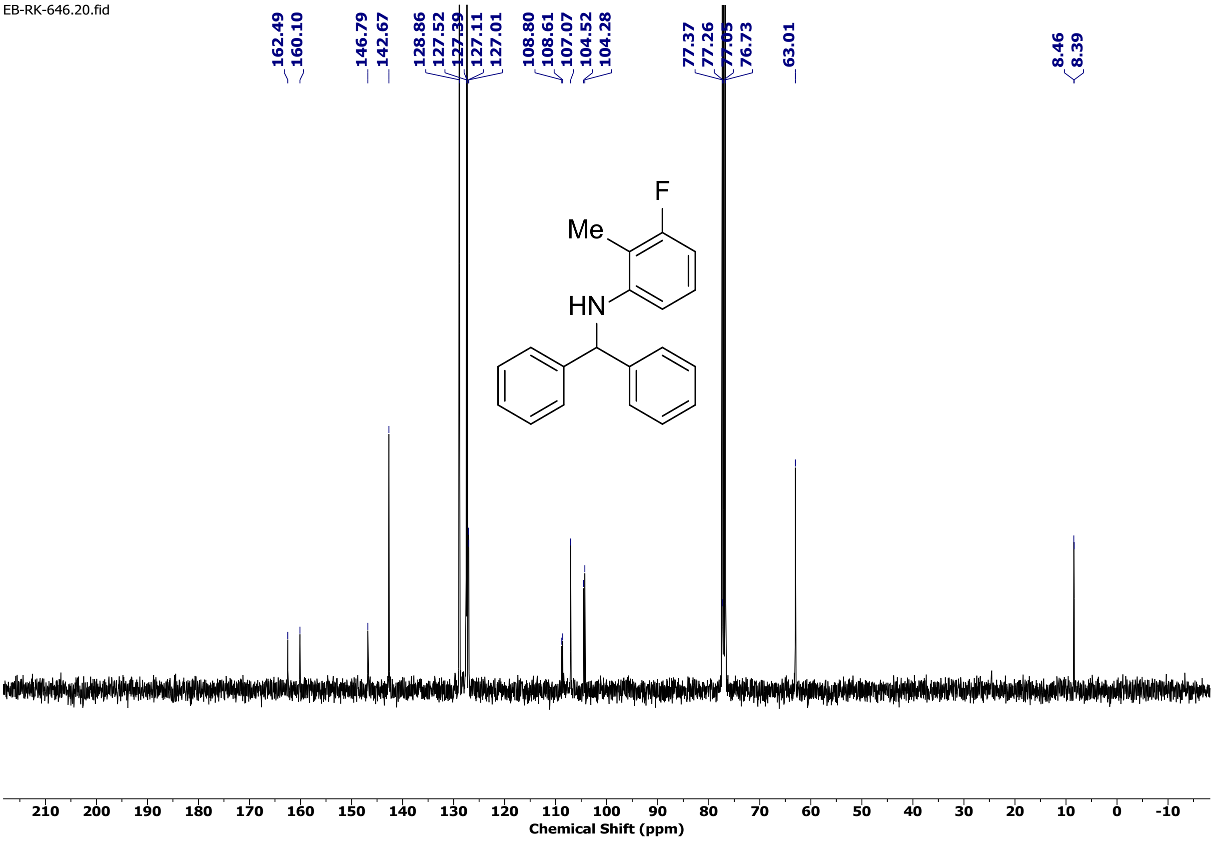
^{1}H NMR of **75** (400 MHz, CDCl$_3$)



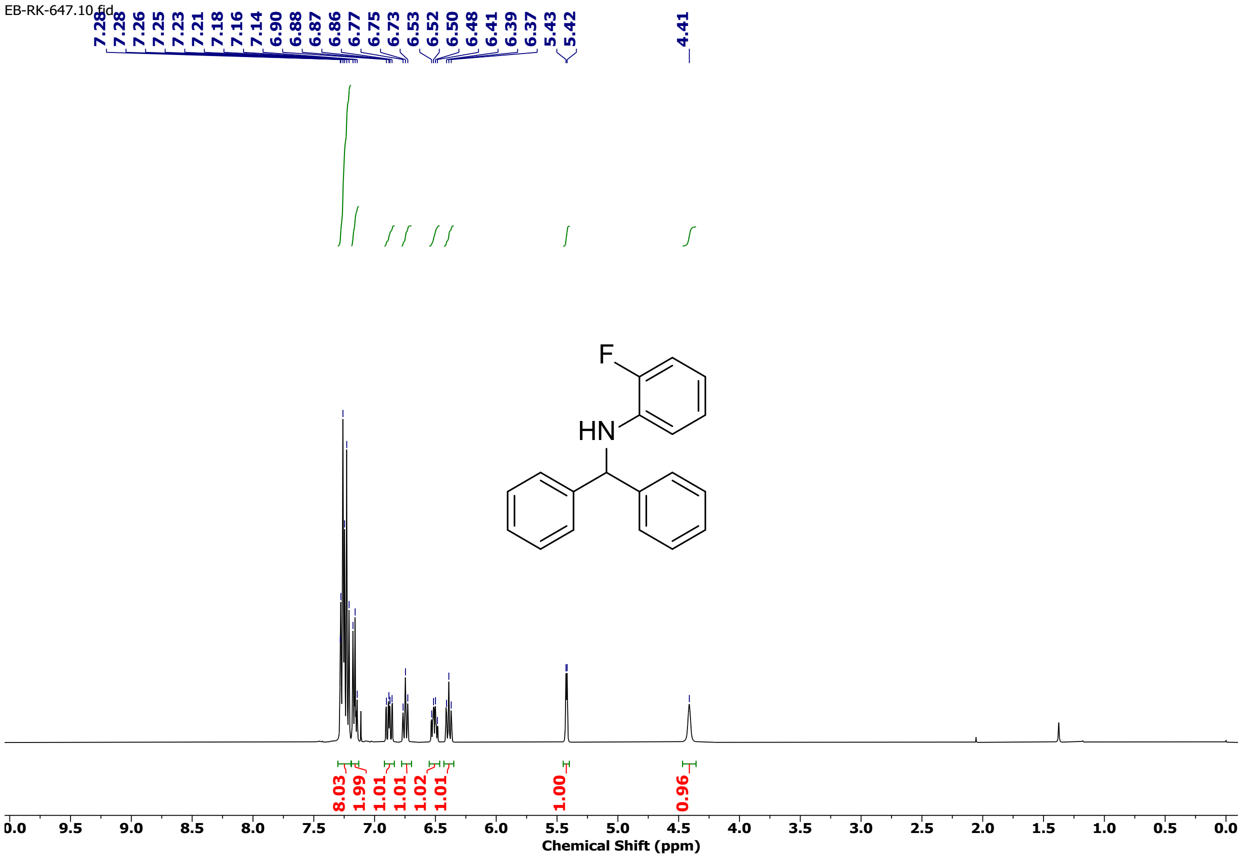
^{13}C NMR of **75** (100 MHz, CDCl$_3$)



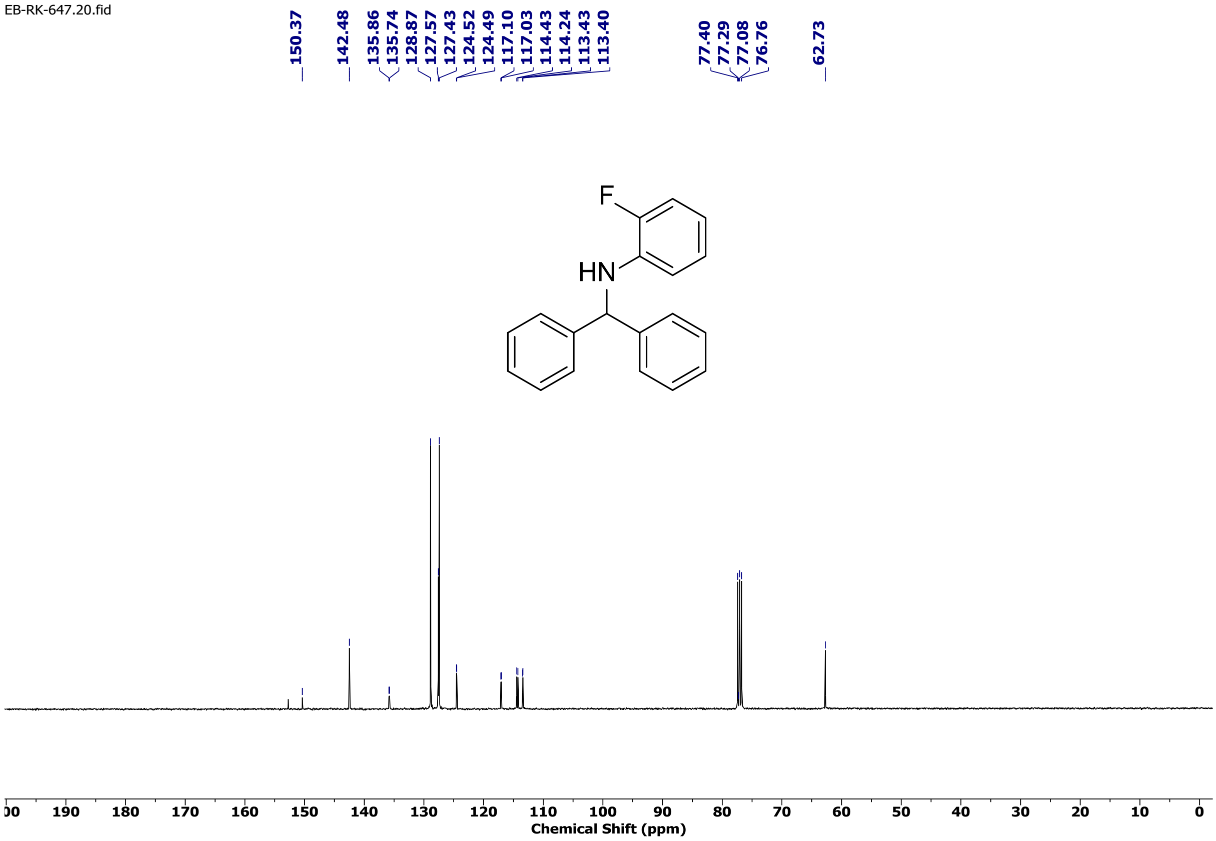
^{1}H NMR of **76**(400 MHz, CDCl$_3$)



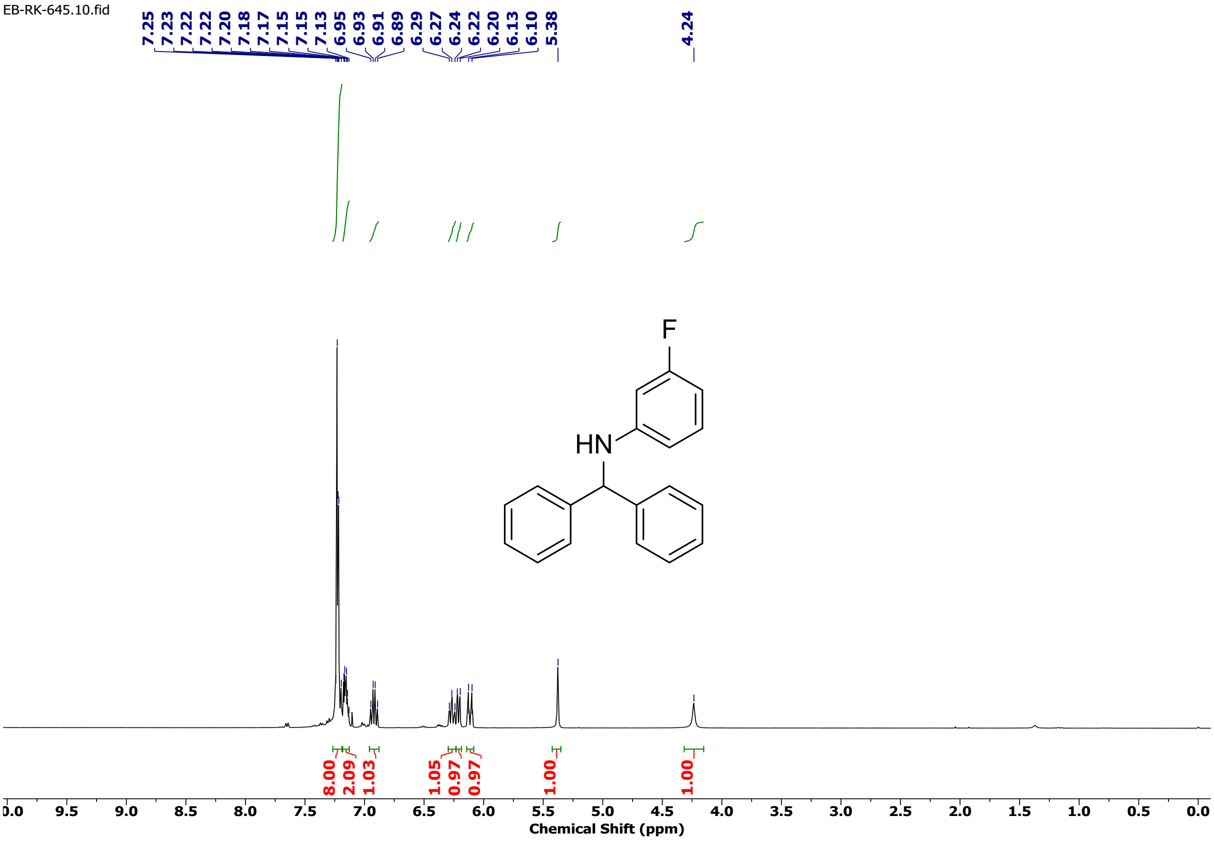
^{13}C NMR of **76** (100 MHz, CDCl$_3$)



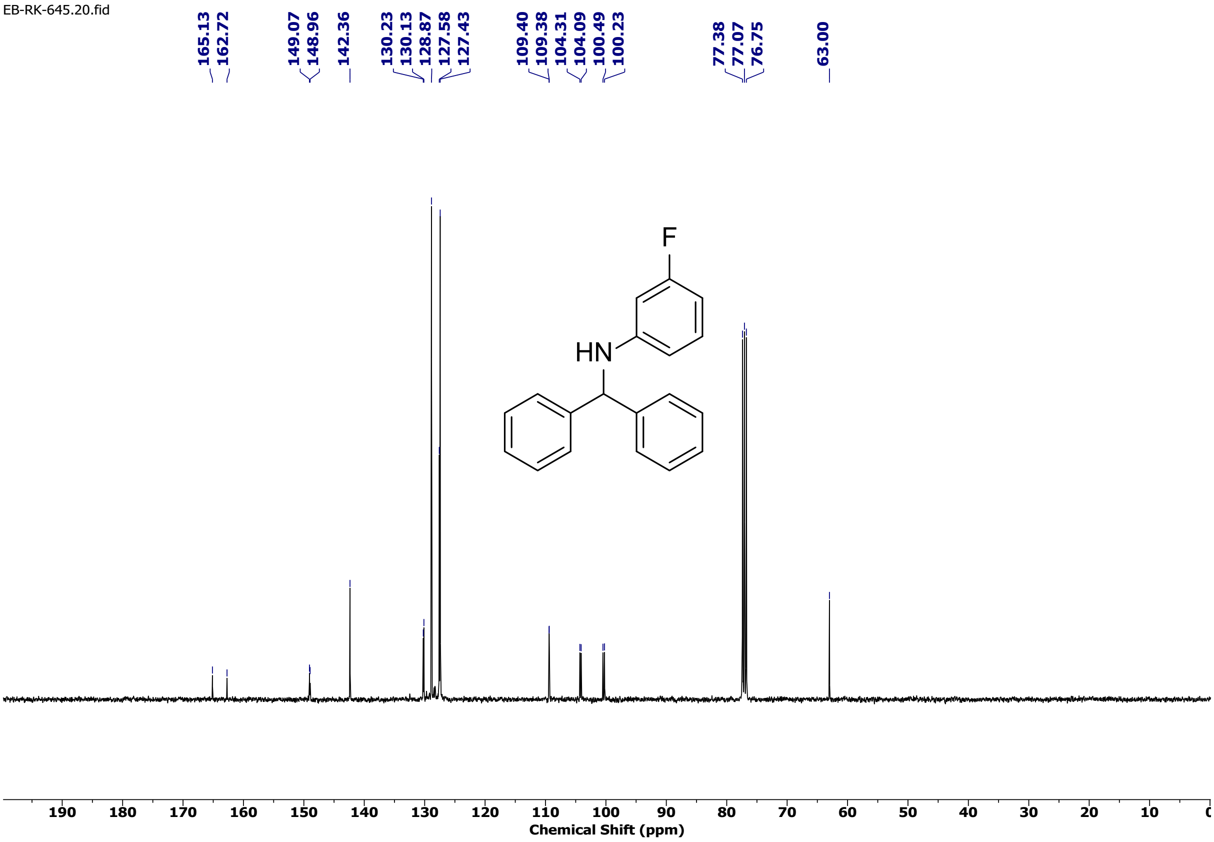
^{1}H NMR of **77** (400 MHz, CDCl$_3$)



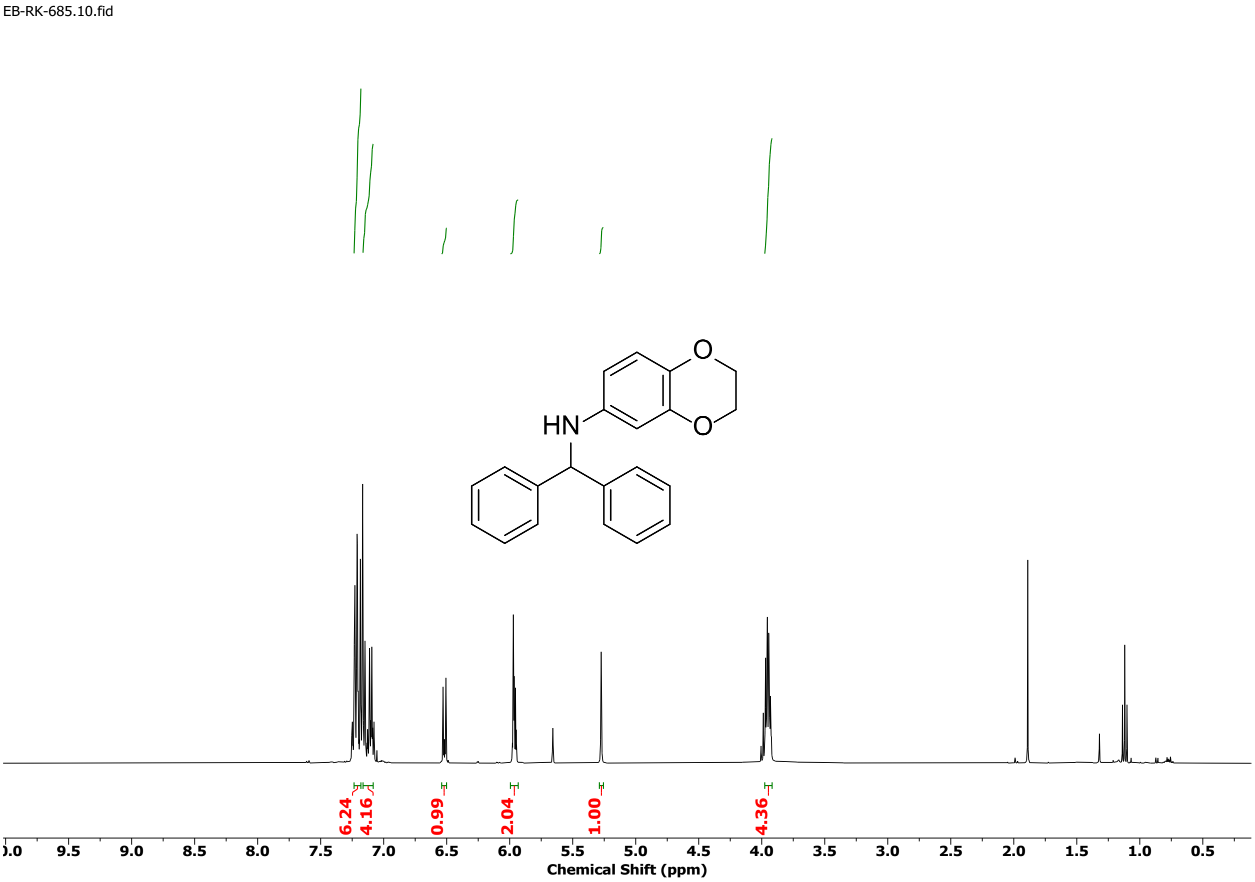
^{13}C NMR of **77** (100 MHz, CDCl$_3$)



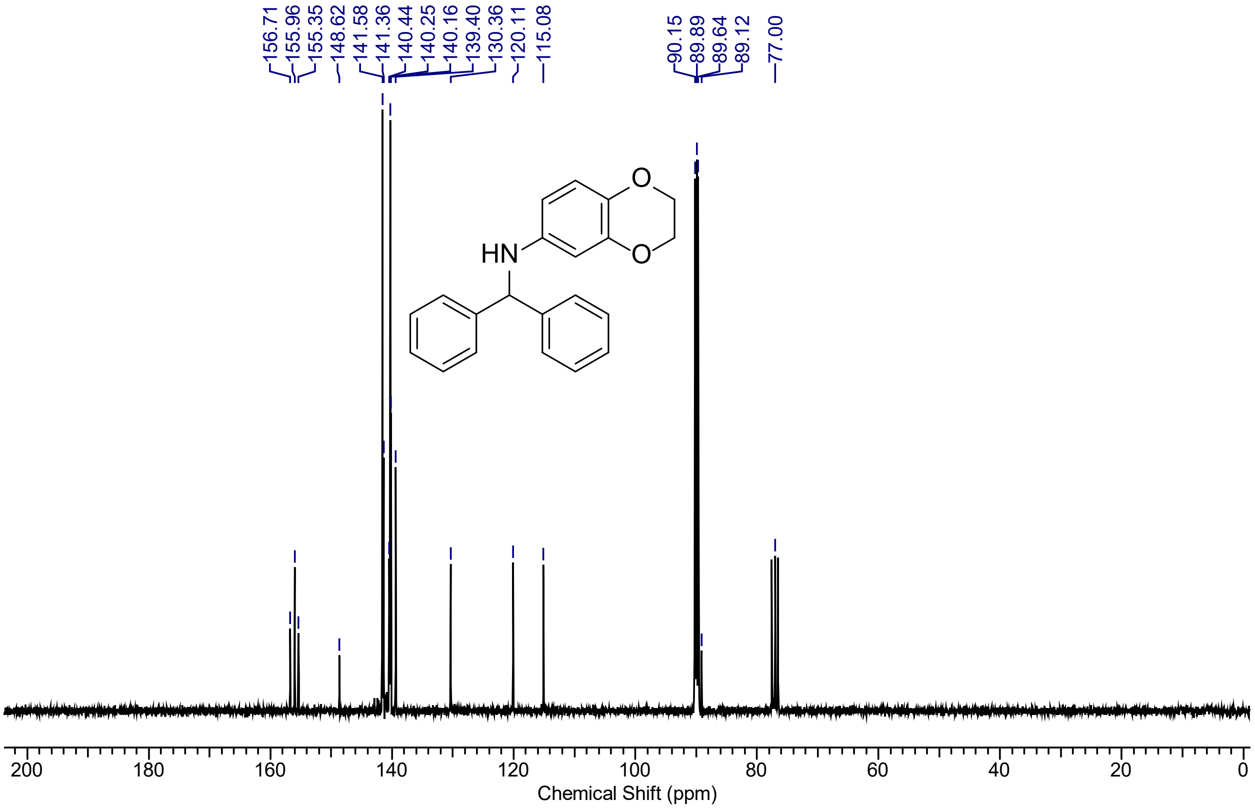
^{1}H NMR of **78** (400 MHz, CDCl$_3$)



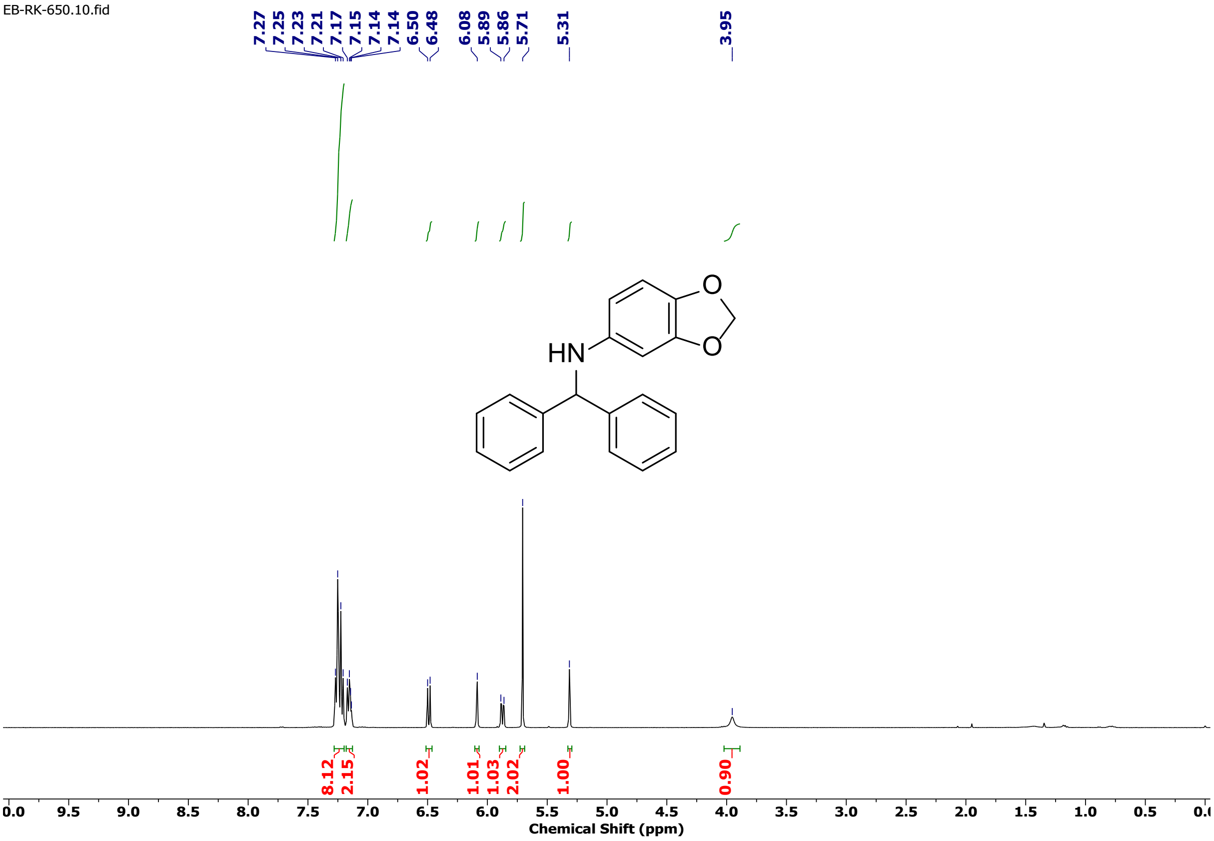
^{13}C NMR of **78** (100 MHz, CDCl$_3$)



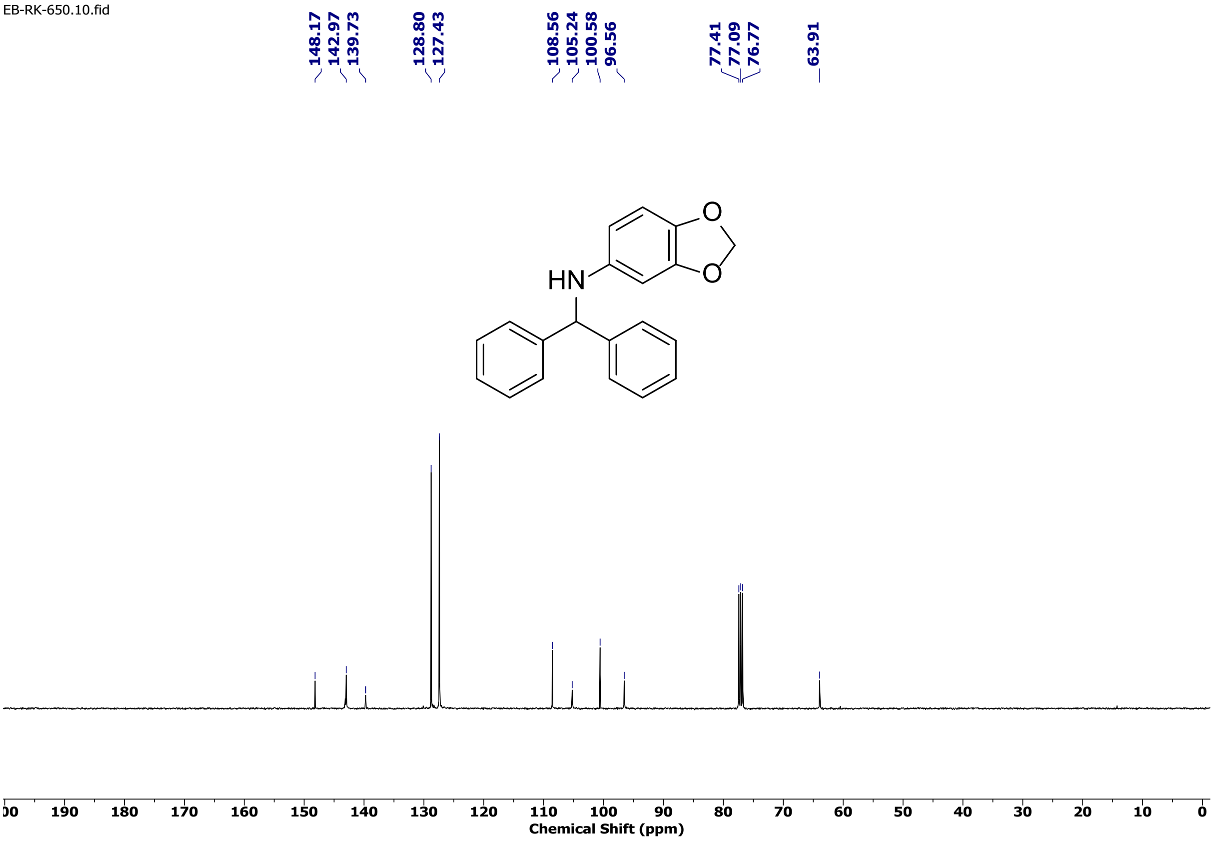
^{1}H NMR of **79** (400 MHz, CDCl$_3$)



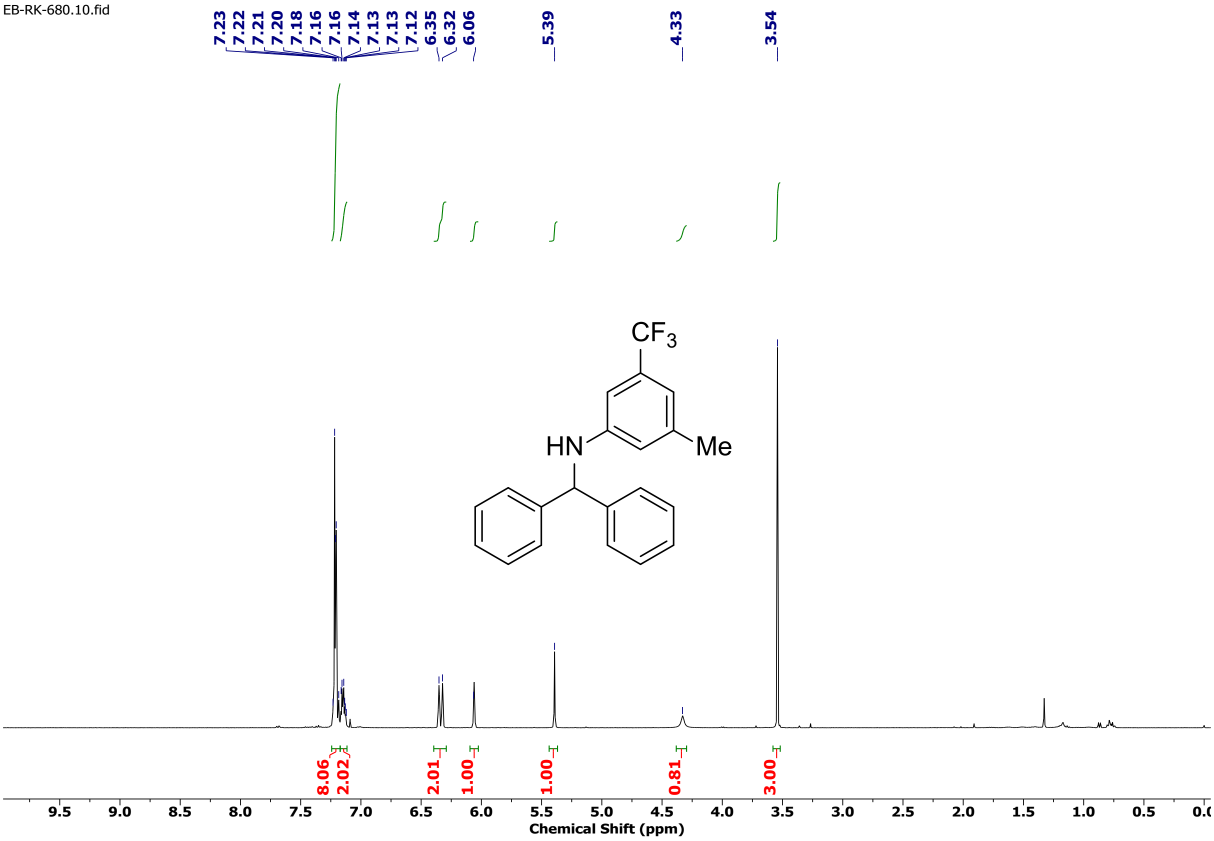
^{13}C NMR of **79** (100 MHz, CDCl$_3$)



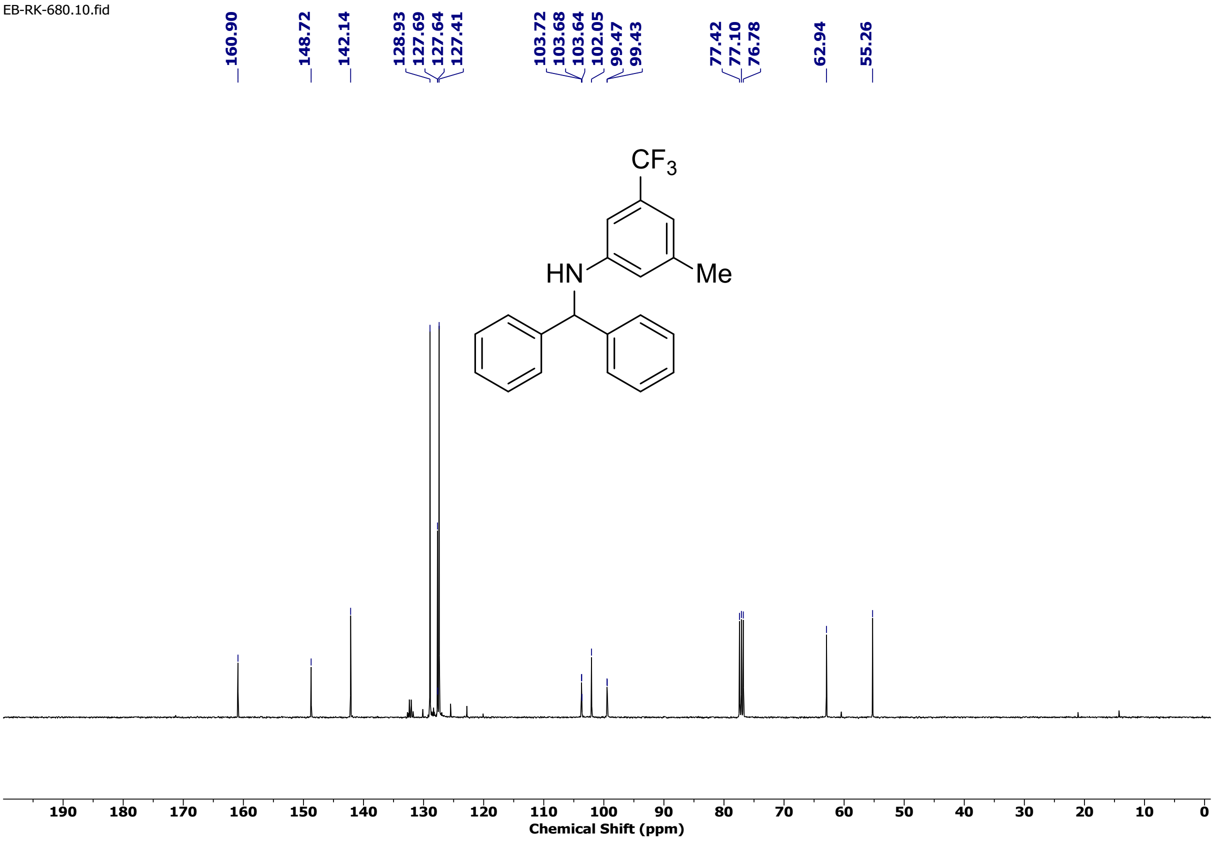
^{1}H NMR of **80** (400 MHz, CDCl$_3$)



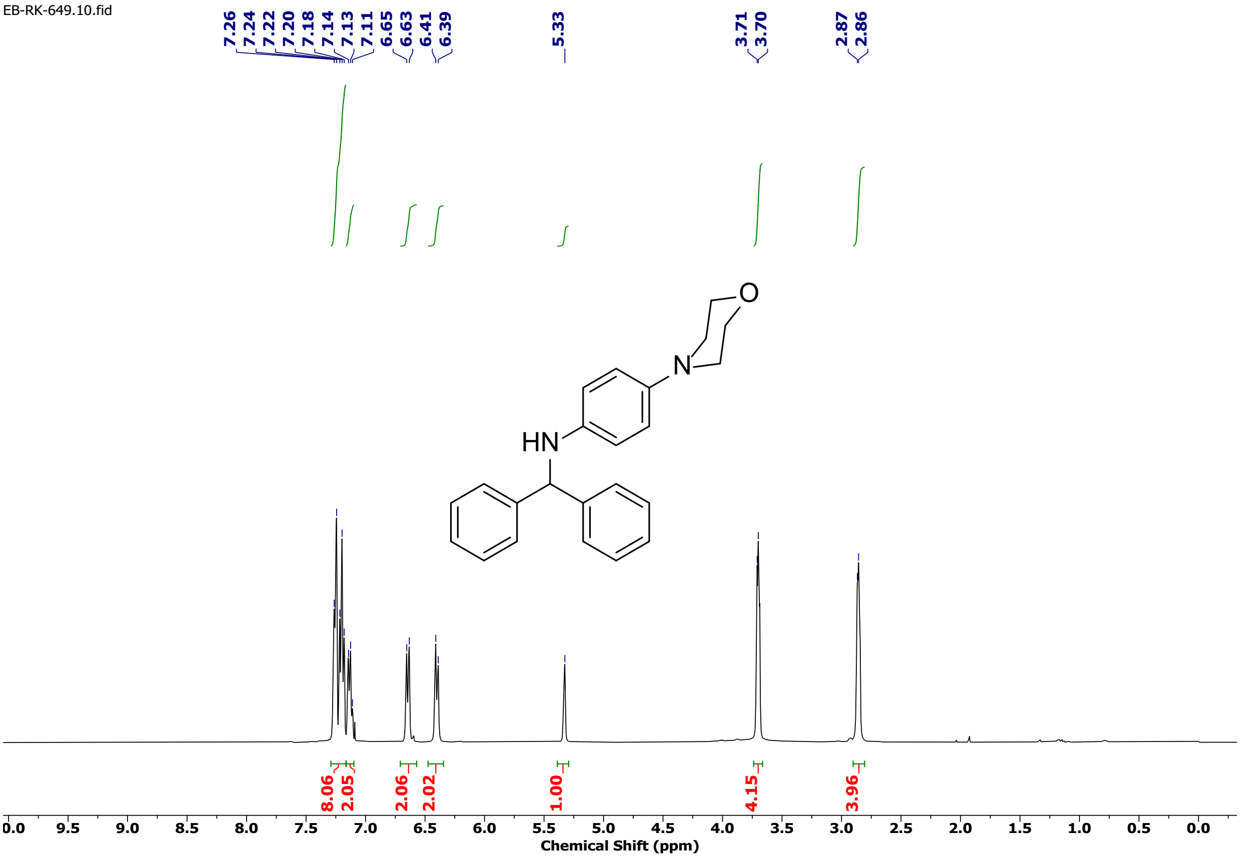
^{13}C NMR of **80** (100 MHz, CDCl$_3$)



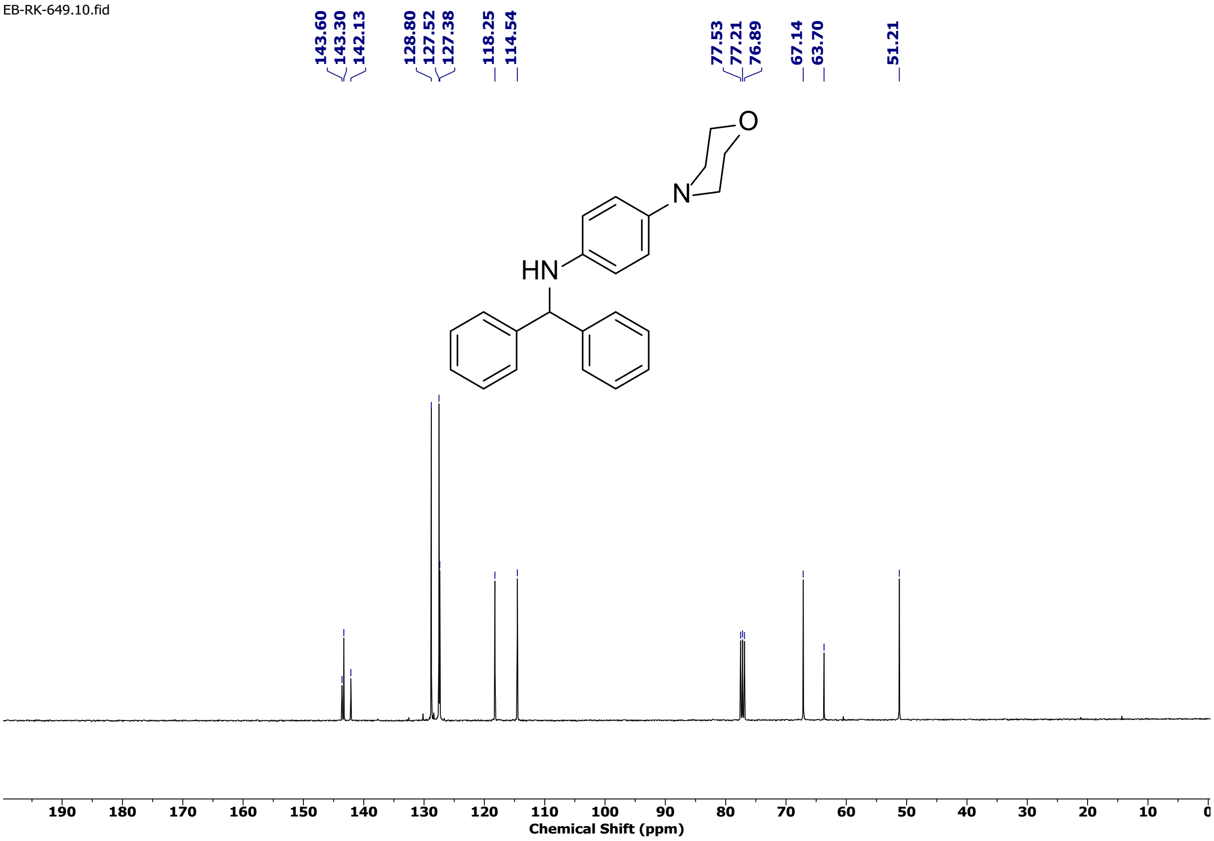
^{1}H NMR of **81** (400 MHz, $CDCl_3$)



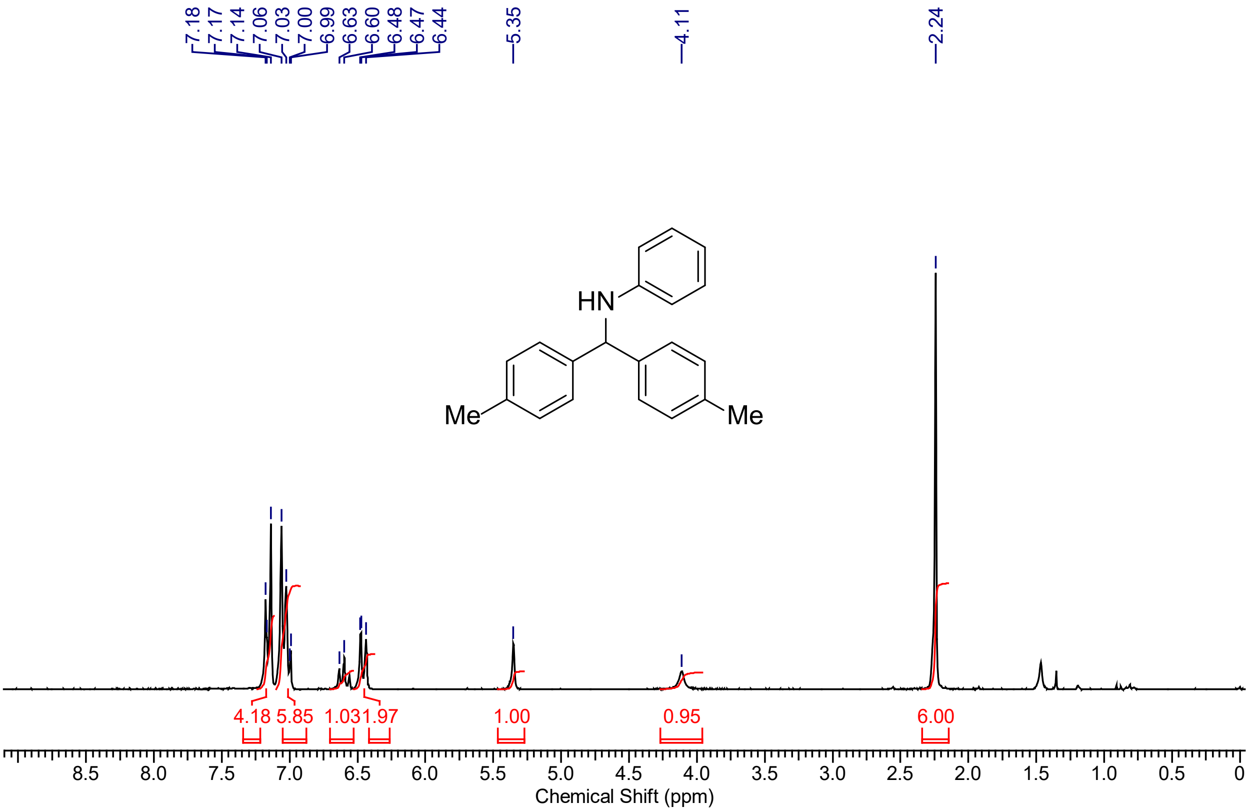
^{13}C NMR of **81** (100 MHz, $CDCl_3$)



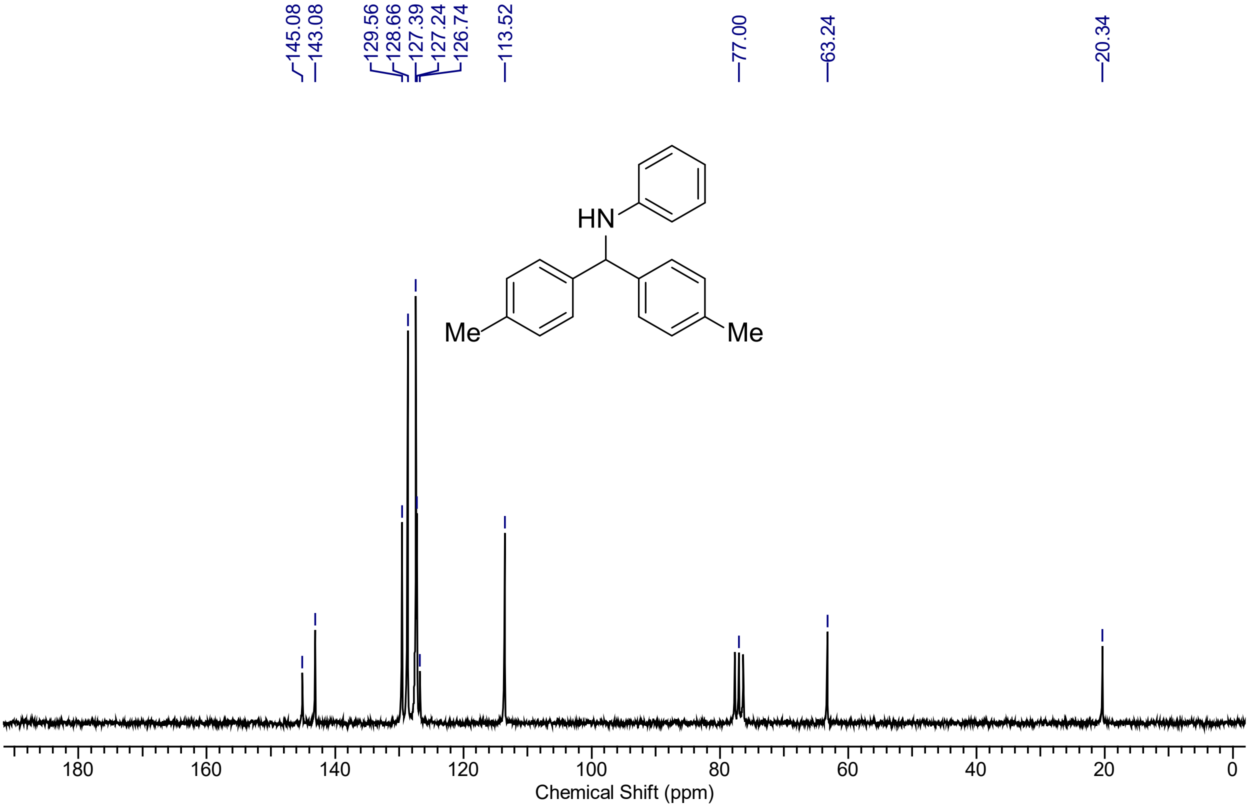
^{1}H NMR of **82** (400 MHz, CDCl$_3$)



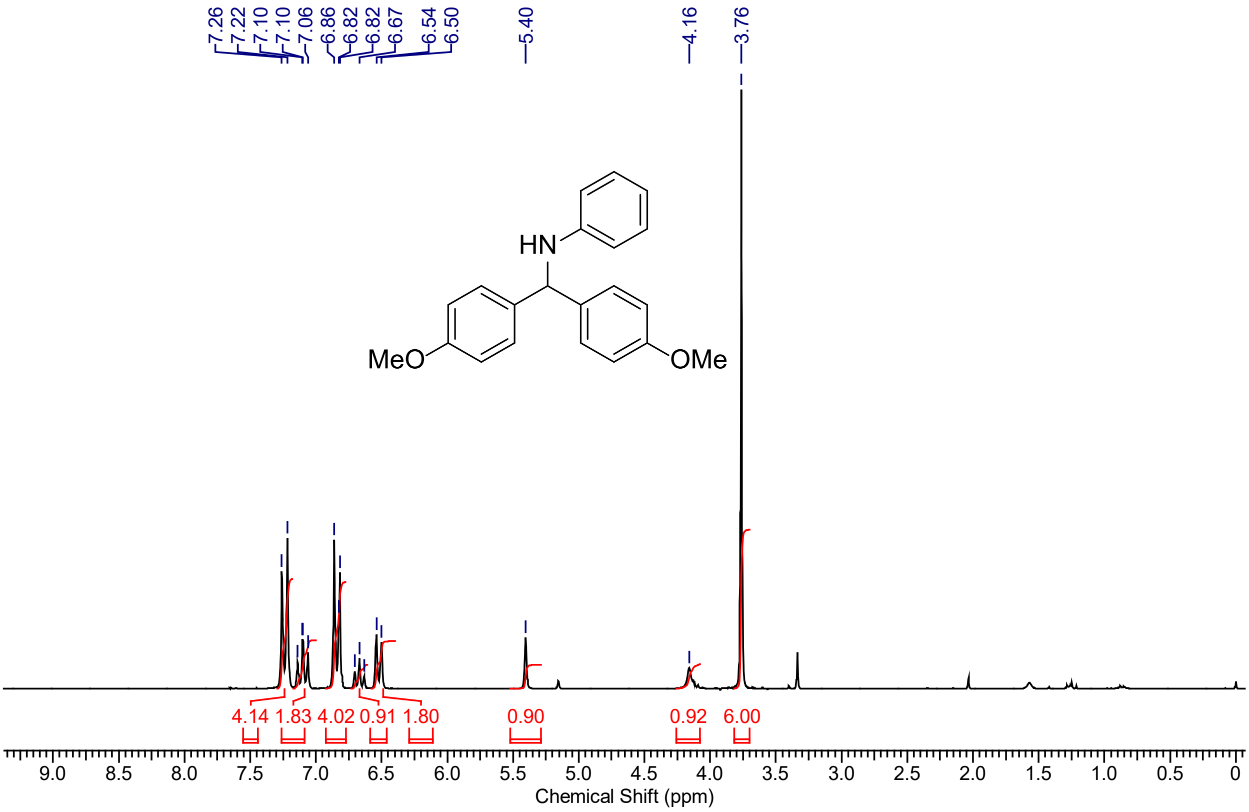
^{13}C NMR of **82** (100 MHz, CDCl$_3$)



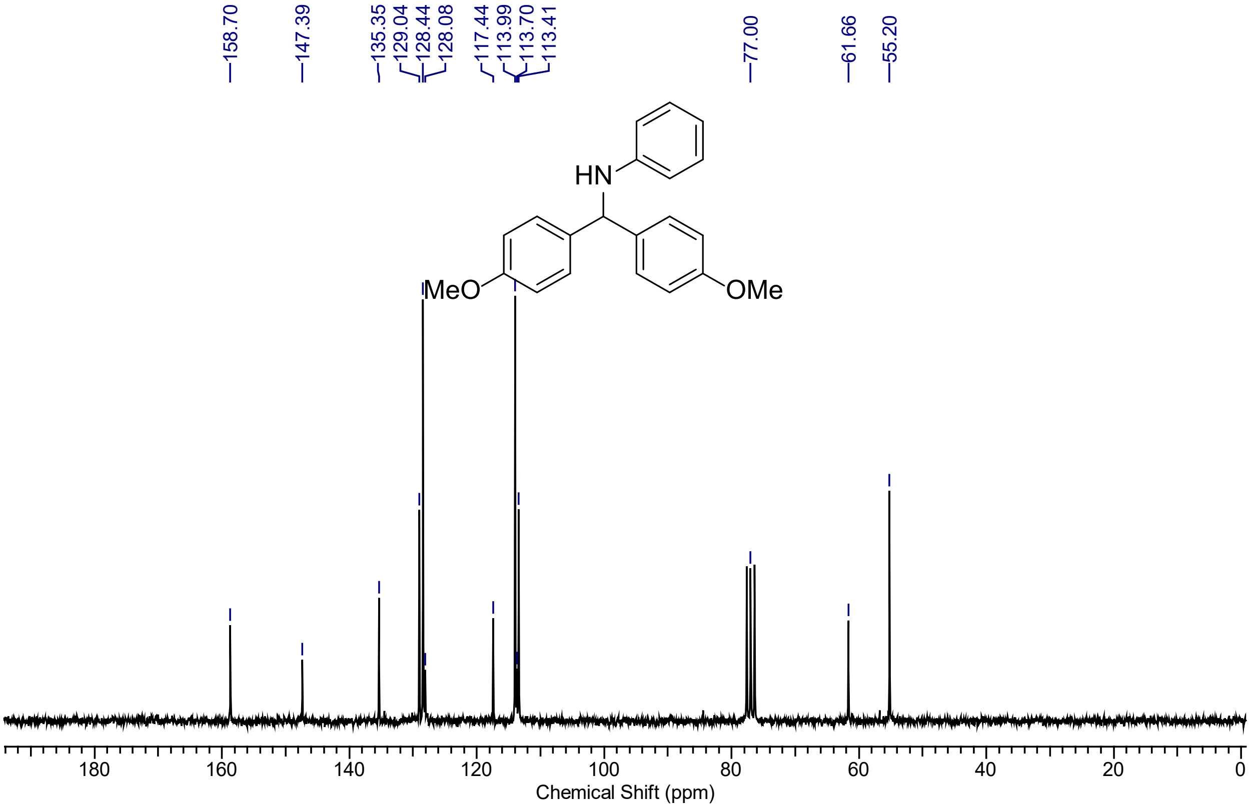
^{1}H NMR of **83** (400 MHz, CDCl$_3$)



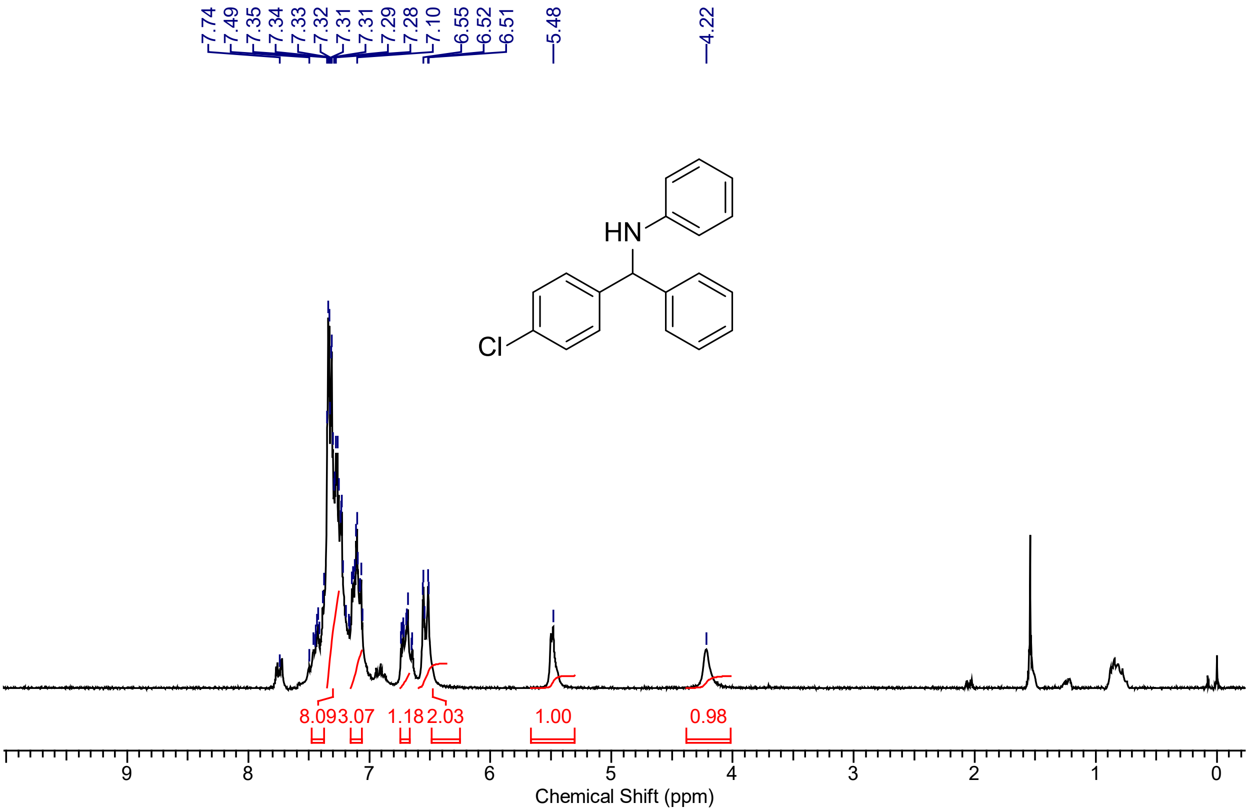
^{13}C NMR of **83** (100 MHz, CDCl$_3$)



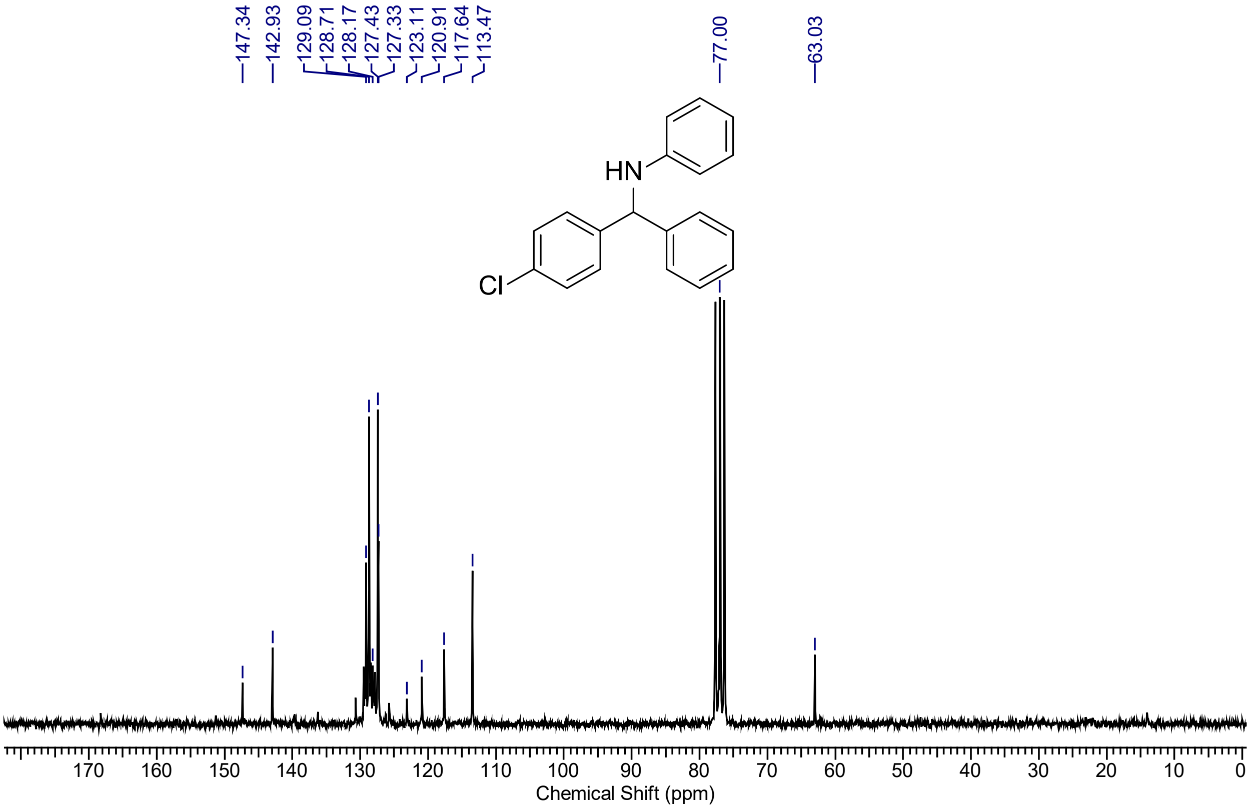
^{1}H NMR of **84** (400 MHz, CDCl$_3$)



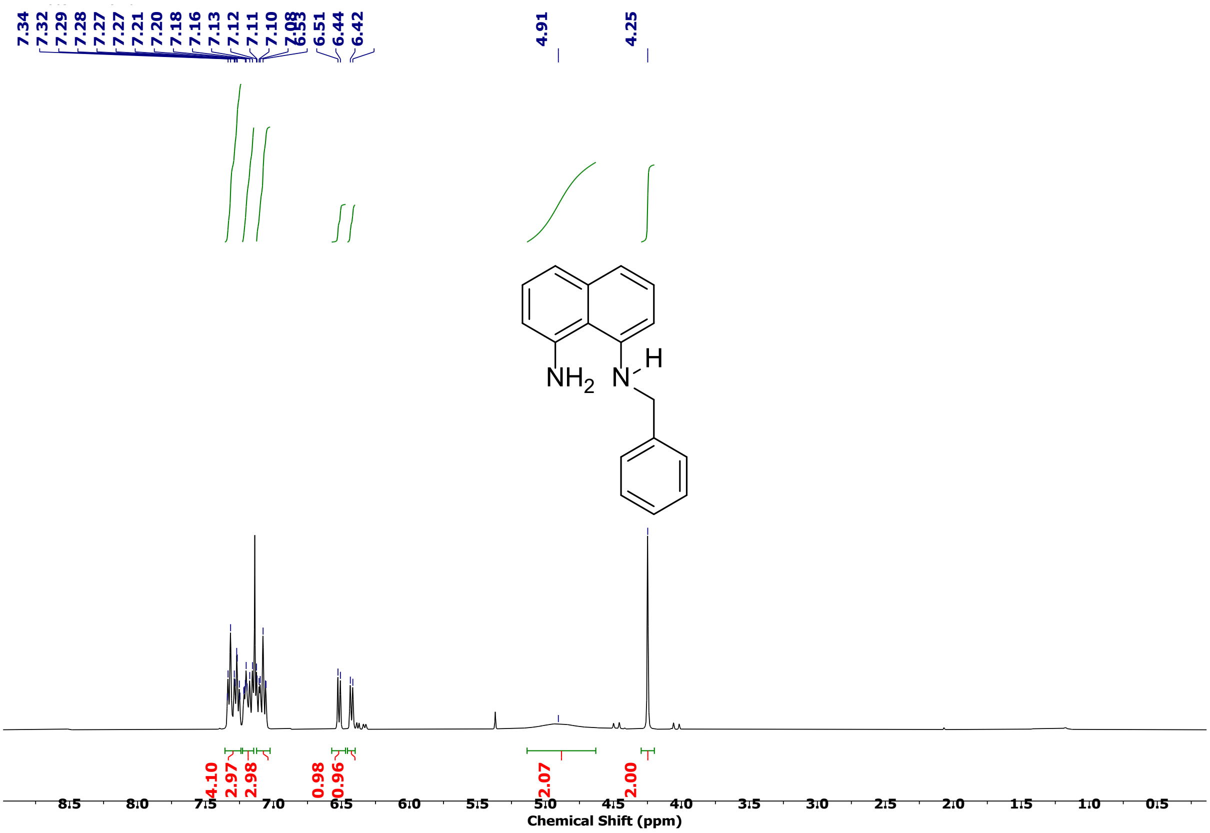
^{13}C NMR of **84** (100 MHz, CDCl$_3$)



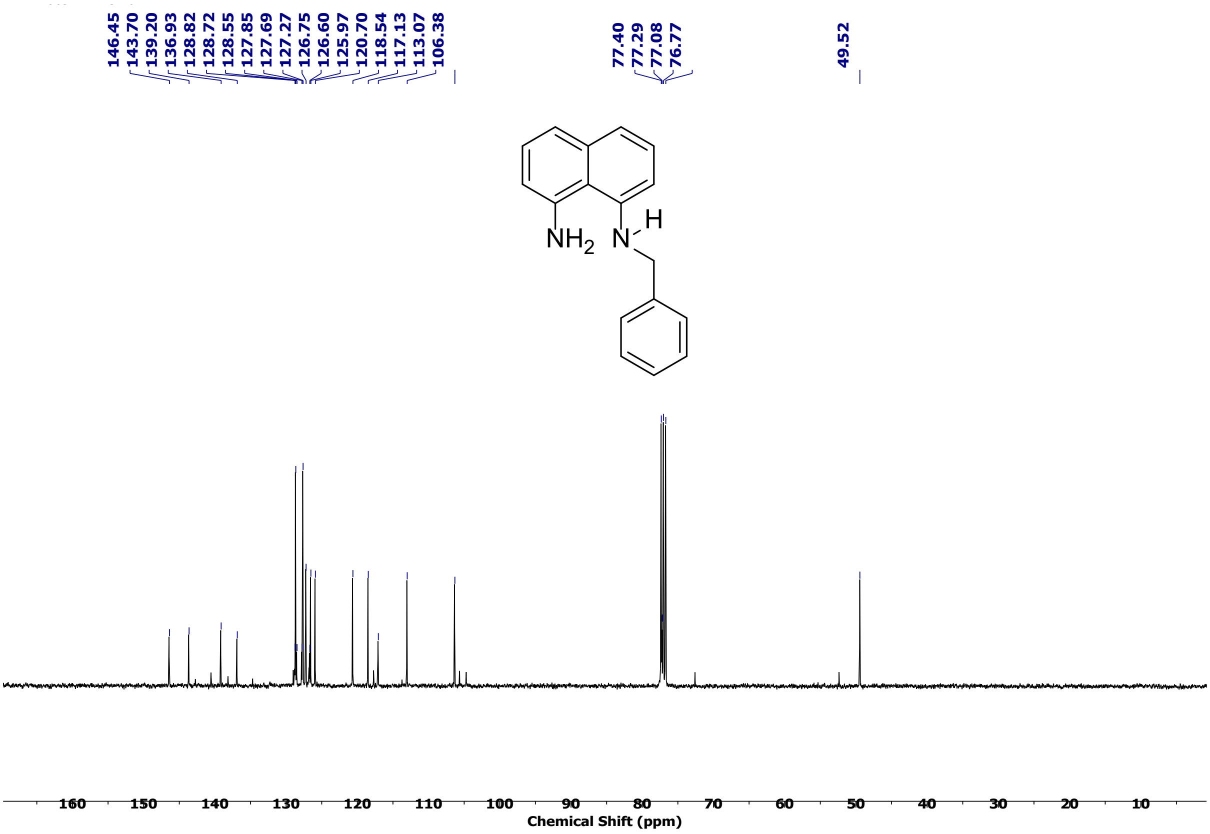
^{1}H NMR of **85** (400 MHz, CDCl$_3$)



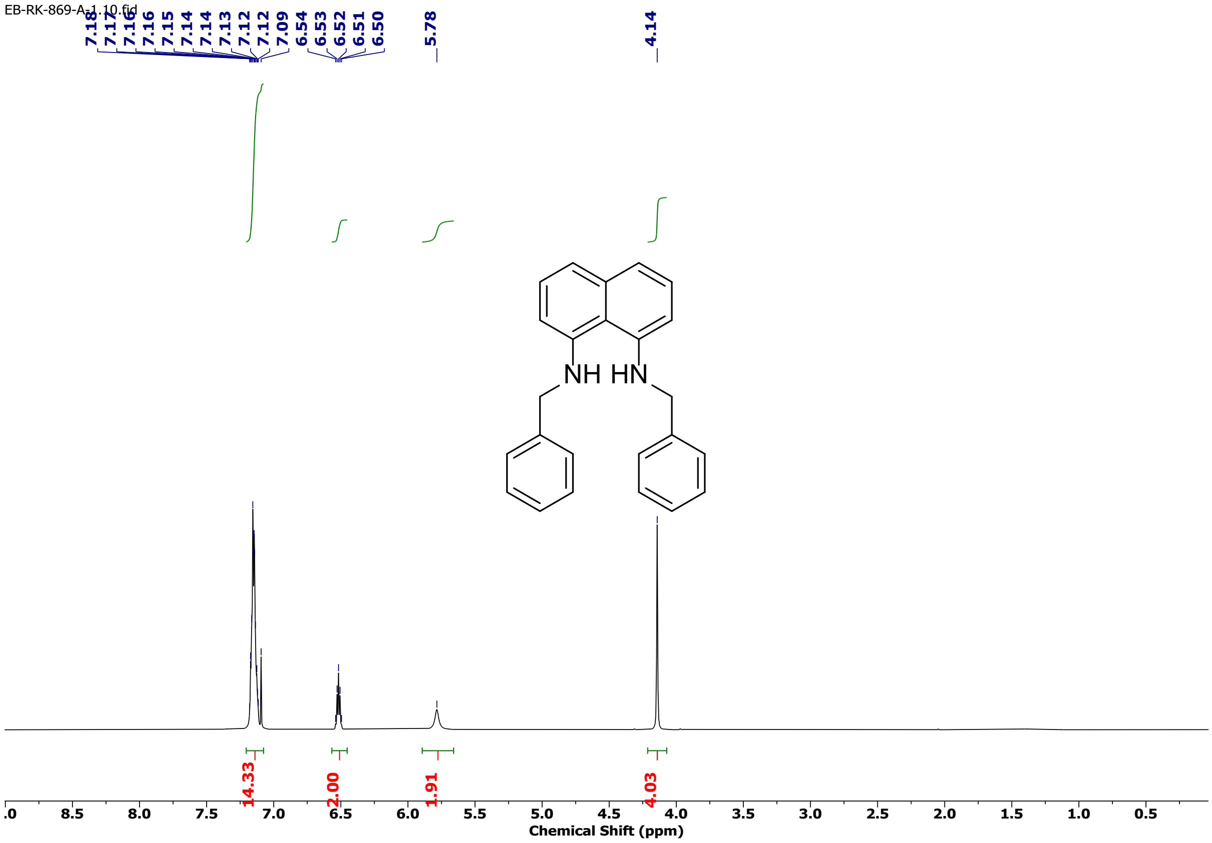
^{13}C NMR of **85** (100 MHz, CDCl$_3$)



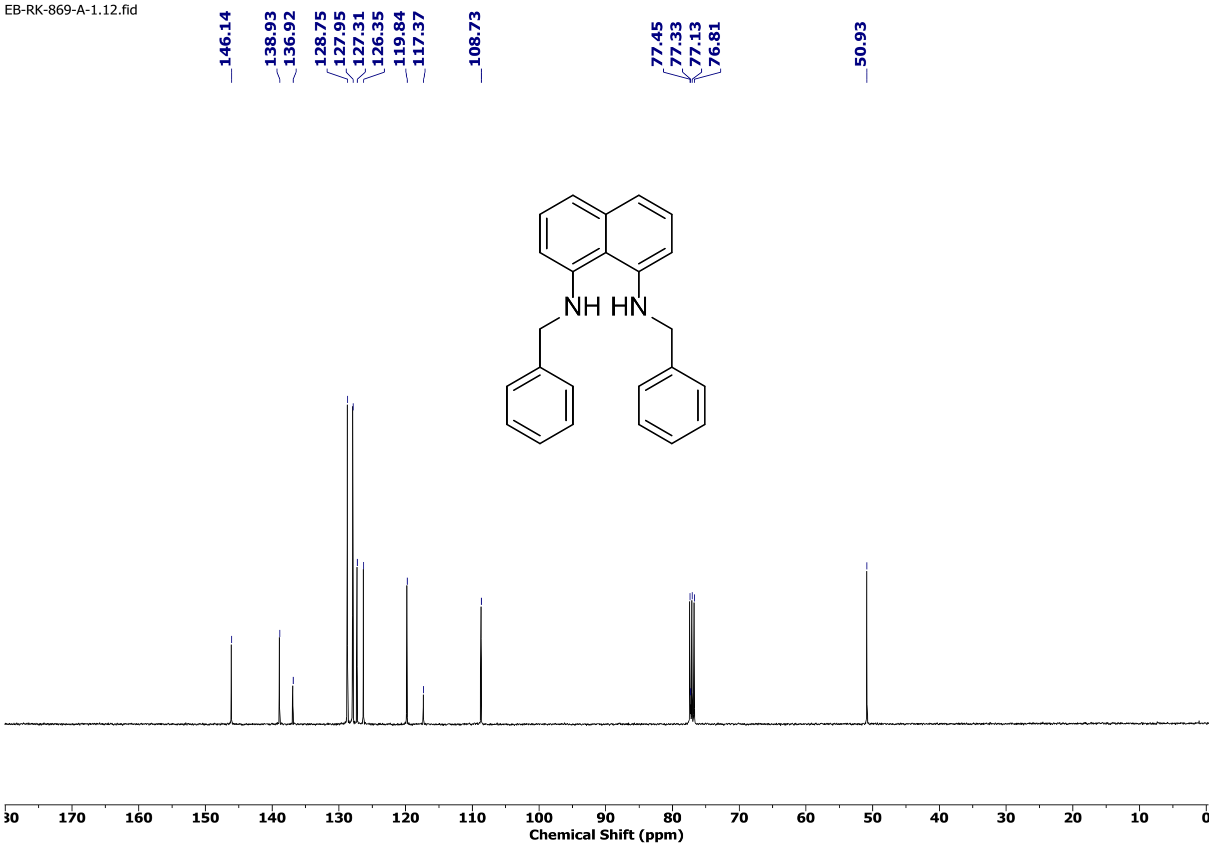
^{1}H NMR of **86** (400 MHz, $CDCl_3$)



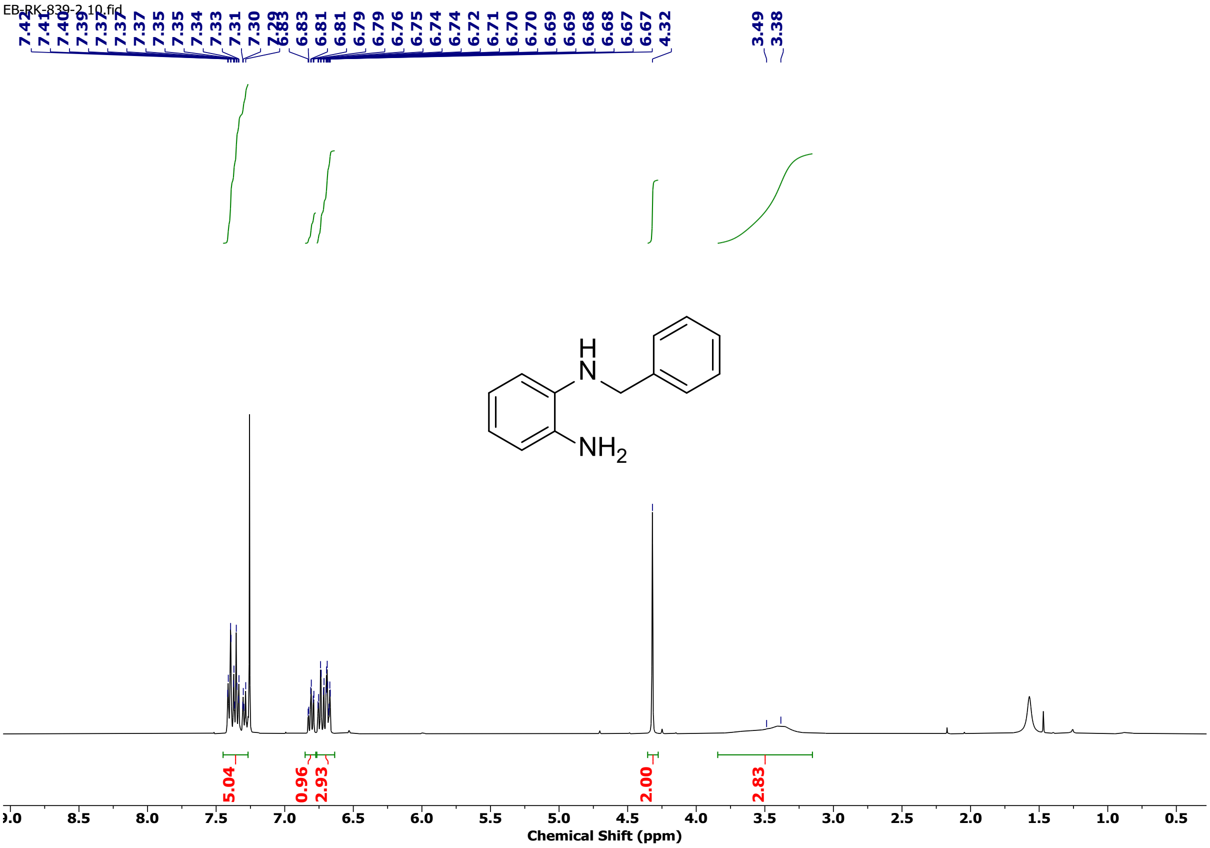
^{13}C NMR of **86** (100 MHz, $CDCl_3$)



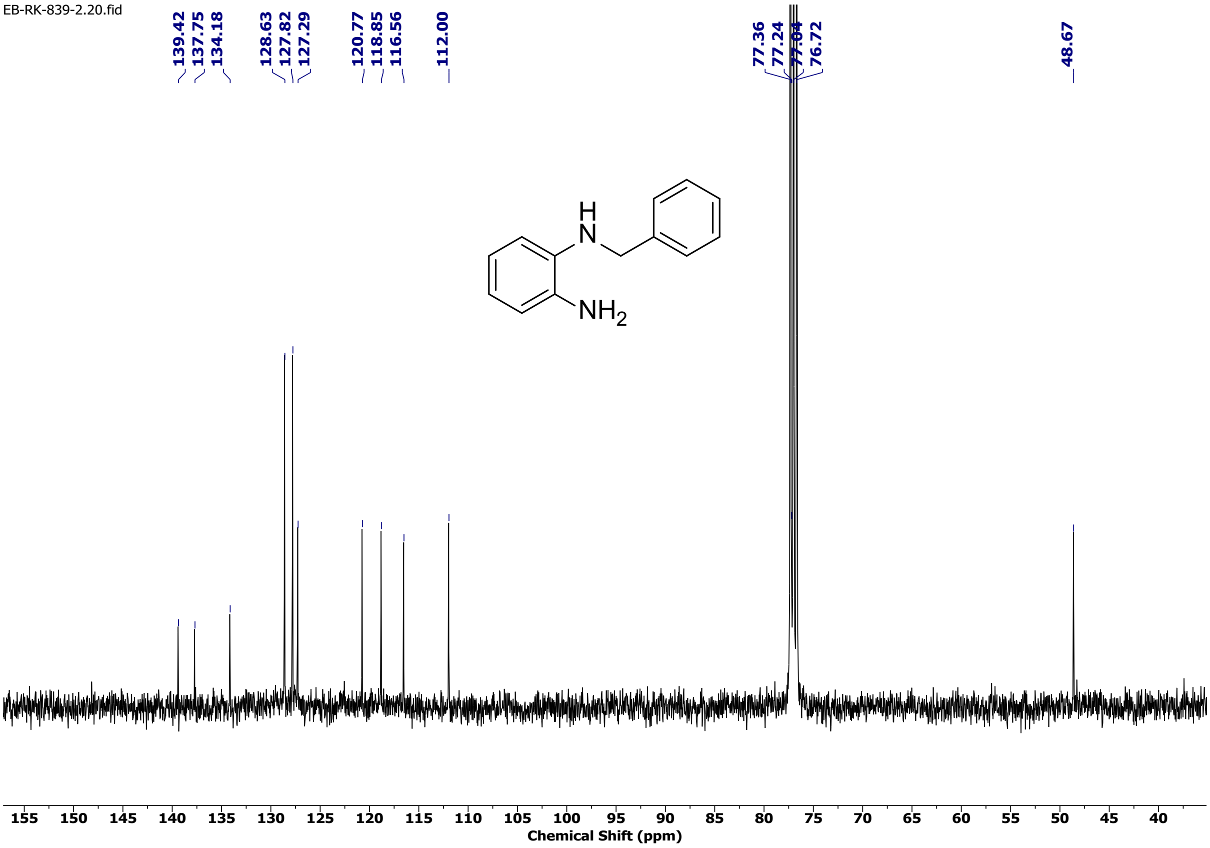
^{1}H NMR of **87** (400 MHz, CDCl$_3$)



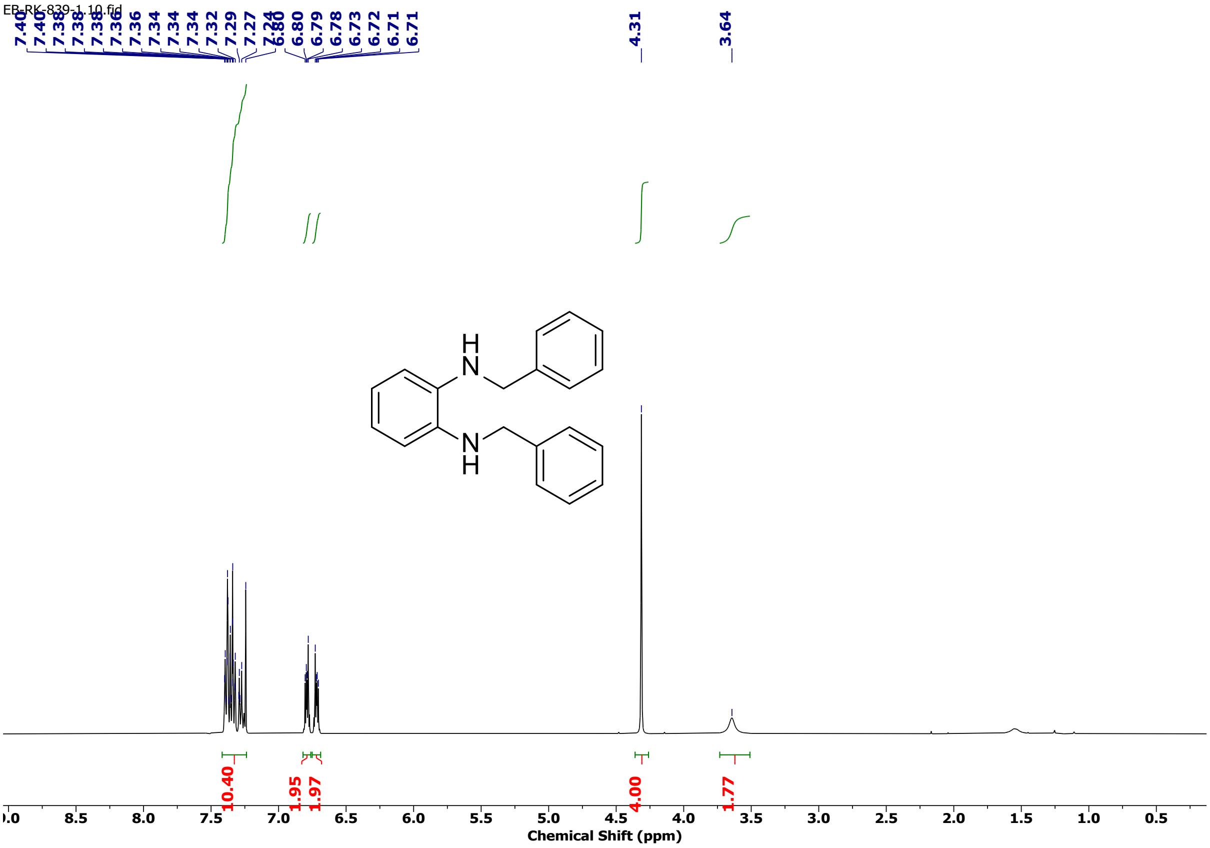
^{13}C NMR of **87** (100 MHz, CDCl$_3$)



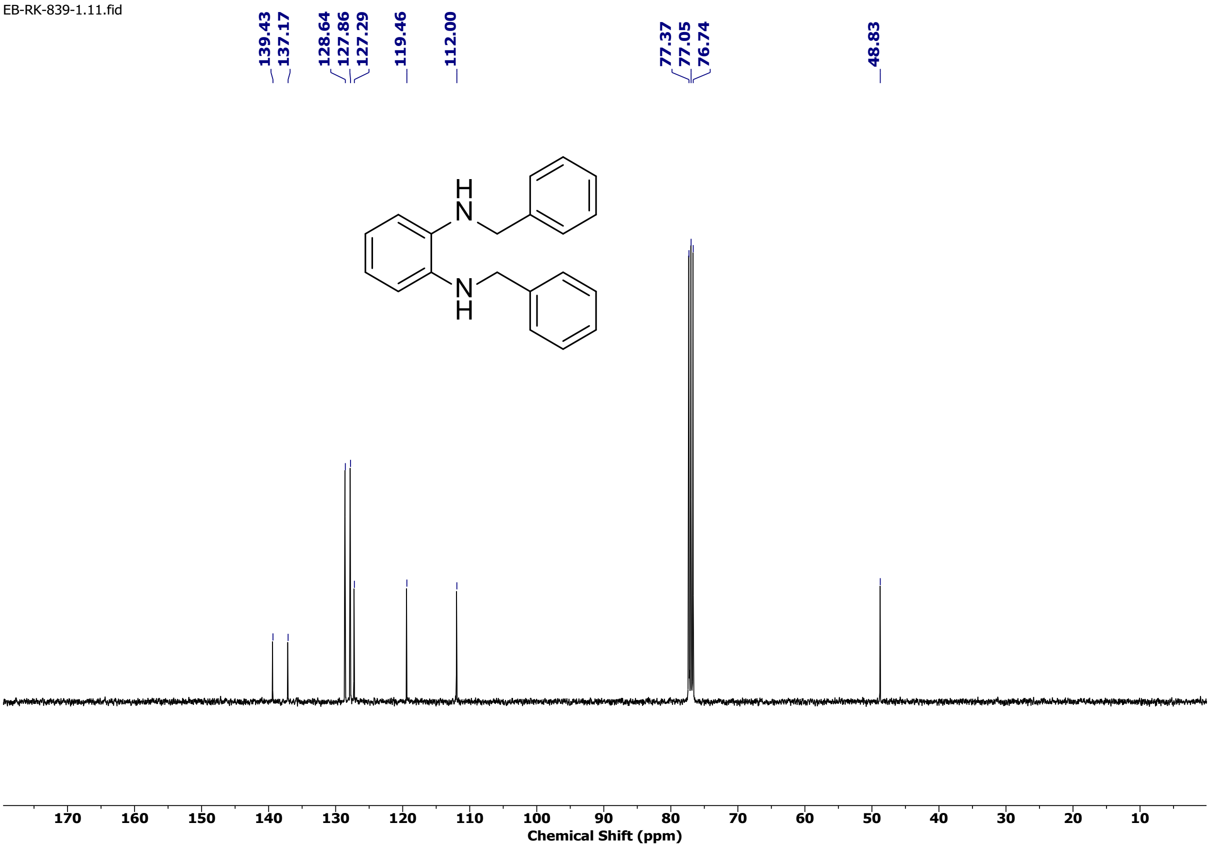
^{1}H NMR of **88** (400 MHz, CDCl$_3$)



^{13}C NMR of **88** (100 MHz, CDCl$_3$)



^{1}H NMR of **89** (400 MHz, $CDCl_3$)



^{13}C NMR of **89** (100 MHz, $CDCl_3$)