Supporting Information

for

Hybrid silylene-Pd catalyst: efficient C-N cross-coupling of sterically bulky amines and chiral amines

Sandeep H. Kaulage,[a]‡ Nasrina Parvin,[a] ‡ Kishor V. Khopade,[b] and Shabana Khan*[a]

[a]*Department of Chemistry, Indian Institute of Science Education and Research Pune, Dr. Homi Bhabha Road, Pashan, Pune - 411008, India*

[b]*Polymer Science and Engineering division, CSIR-National Chemical Laboratory, Dr. Homi Bhabha Road, Pashan, Pune – 411008, India; Academy of Scientific and Innovative Research (AcSIR), Sector 19, Kamla Nehru Nagar, Ghaziabad 201002, Uttar Pradesh, India.*

*Email: shabana@iiserpune.ac.in.

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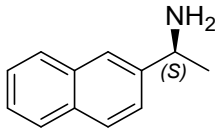
S1. Experimental Procedures

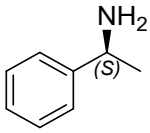
All experiments were carried out under an inert gas atmosphere of dinitrogen (N_2) using standard Schlenk techniques and in a dinitrogen-filled MBRAUN MB 150-G1 glove box. The solvents used were purified by an MBRAUN solvent purification system (MB SPS-800). 2,6-bis[bis(phenyl)methyl]-4-methylaniline[1] and 2,6-bis[bis(4-tert-butylphenyl) methyl]-4-methylaniline[2a] were prepared by literature methods. PNGe[2b], PNSn[2b], PNP[2c] and IPr[2d] ligands were prepared as per reported procedure. DPEPhos was purchased from Sigma Aldrich and used as it is. All chemicals purchased from Aldrich were used without further purification. ^{1}H, ^{13}C, and ^{19}F NMR spectra were recorded in $CDCl_3$ using a Bruker 400 MHz; all NMR spectra were reported in ppm units with external standard trimethyl silane (δ 0 ppm) or $CDCl_3$ (δ 7.26 ppm). Multiplicities are given as: brs (broad singlet), s (singlet), d (doublet), t (triplet), q (quartet), dd (doublets of doublet), dt (doublets of triplet), td (triplets of doublet) or m (multiplet). Mass spectra were recorded using AB Sciex, 4800 plus MALDI TOF/TOF. HRMS (ESI, APCI) were performed on a Fourier Transform ion cyclotron resonance mass spectrometer. Analytical thin-layer chromatography (TLC) was conducted with TLC plates (Silica gel 60 F_{254}) and visualization on TLC was achieved by UV light. Column chromatography was performed on silica gel 200-300 mesh with freshly distilled solvents. Analytical chiral HPLC was performed on an Agilent Technologies 1260 Infinity instrument with Chiralpak AD-H column (250mm X 4.6mm X 5 μm). Gradient: Isocratic; Flow rate: 1ml/min; Injection volume: 10 μL; UV detection: 254 nm; Column temp.: ambient; Retention times: RT's may vary by ±1.0 min. Toluene and THF were refluxed over Na/benzophenone and distilled under an argon atmosphere. Solvents used for column chromatography were of technical grade and used after distillation.

The purity of chiral amines:

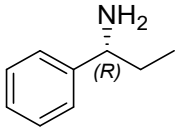
All reagents were obtained commercially and used without further purification. The optical purity of all starting amino compounds is shown below.



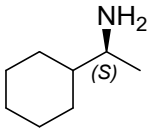
99% Purity, 98% ee



99% Purity, 98% ee



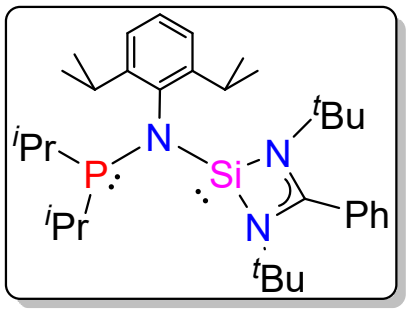
99% Purity, 98% ee



99% Purity, 98% ee

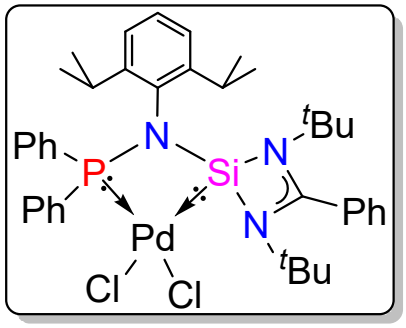
I) Synthesis of ligand L2 and complex 1-3

a) Synthesis of L2:



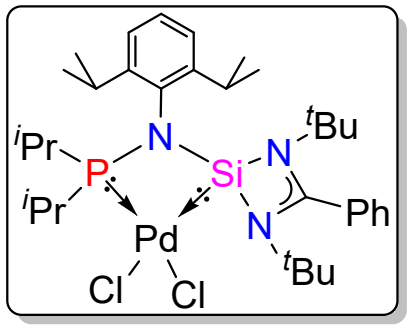
A 100 mL Schlenk flask was charged with chlorosilylene[3] (0.295 g, 1 mmol) and LiN(P^{i}Pr$_2$)(2,6-^{i}Pr$_2$C$_6$H$_3$) (0.373 g, 1 mmol) followed by the addition of toluene (30 mL) at room temperature, and stirred for 12 h. The resulting solution was filtered off, and the solvent was removed to yield a white crystalline solid. Single crystals suitable for X-ray analysis were grown in toluene at room temperature. M. P.: 130˚C. Yield: 90 % (0.496 g). **^{1}H NMR (400 MHz, C$_6$D$_6$):** δ 7.33 (d, J = 7.5 Hz, 2H), 7.25 (d, J = 7.4 Hz, 1H), 7.07 (d, J = 8.2 Hz, 1H), 7.04 – 6.93 (m, 2H), 6.93 – 6.85 (m, 2H), 4.43 – 3.68 (m, 2H), 2.92 – 2.58 (m, 2H), 1.48 (d, J = 6.9 Hz, 12H), 1.42 (s, 12H), 1.15 (s, 18H). **^{13}C NMR (101 MHz, C$_6$D$_6$):** δ 175.93 (s), 147.47 (s), 139.72 (d, J = 1.3 Hz), 130.80 (d, J = 28.2 Hz), 128.86 (s), 127.72 (s), 122.80 (s), 116.18 (s), 54.51 (s), 31.36 (d, J = 2.4 Hz), 27.74 (s), 24.99 (s), 23.18 (s), 21.62 (d, J = 15.8 Hz). **^{31}P NMR (162 MHz, C$_6$D$_6$):** δ -39.17 (s). **^{29}Si NMR (80 MHz, C$_6$D$_6$):** δ -67.47 (d, J = 14.0 Hz). **HRMS (ESI):** calculated for $C_{33}H_{54}N_3PSi$ $[M]^+$ *m/z* 551.3825, found 551.3269. **MALDI *m/z* (C$_{33}$H$_{54}$N$_3$PSi):** 551.85 $[M]^+$.

b) Synthesis of 1:



A 100 mL Schlenk flask was charged with **L1**[4] (0.310 g, 0.5 mmol) and $PdCl_2(ACN)_2$ (0.130 g, 0.5 mmol) followed by the addition of THF (30 mL) at room temperature and stirred for 3 h. The resulting solution was filtered off, and the solvent was reduced to 3 mL and kept for crystallization at 0° C. M. P.: 210-212˚C. Yield: 62 % (0.493 g). **^{1}H NMR (400 MHz, $CDCl_3$)**: NMR integration is not done due to broadening in the ^{1}H spectra. **^{13}C NMR (101 MHz, $CDCl_3$):** δ 179.7, 146.0, 143.4, 135.1, 135.0, 132.0, 131.6, 130.7, 130.5, 130.1, 128.8, 128.6, 128.5, 128.2, 128.0, 127.7, 126.5, 125.2, 125.1, 122.5, 77.2, 67.8, 56.6, 31.9, 31.2, 30.7, 28.8, 28.2, 28.0, 25.4, 23.4, 21.6, 0.8. **^{31}P NMR (162 MHz, $CDCl_3$):** δ 58.04 (s). **^{29}Si NMR (80 MHz, $CDCl_3$)**: δ -28.82 (d, J = 21.5 Hz). **HRMS (ESI):** calculated for $C_{39}H_{50}Cl_2N_3PPdSi$ $[M]^+$ *m/z* 795.1924, found 795.5019. **MALDI *m/z* ($C_{39}H_{50}Cl_2N_3PPdSi$):** 797.18 $[M]^+$.

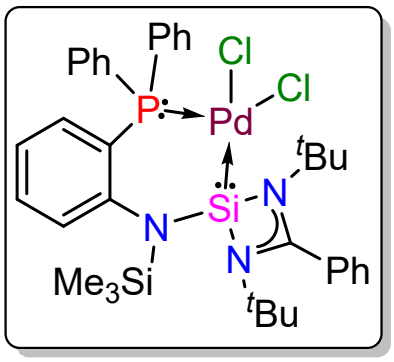
c) Synthesis of 2:



A 100 mL Schlenk flask was charged with **L2** (0.275 g, 0.5 mmol) and $PdCl_2(ACN)_2$ (0.130 g, 0.5 mmol) followed by the addition of THF (30 mL) at room temperature and stirred for 3 h. The resulting solution was filtered off, and the solvent was reduced to 3 mL and kept for crystallization at 0° C. M. P.: 227-230˚C. Yield: 58 % (0.420 g). **^{1}H NMR (400 MHz, $CDCl_3$)**: NMR integration is not done due to broadening in the ^{1}H spectra. **^{13}C NMR (101 MHz, $CDCl_3$):** δ 180.1, 146.0, 134.5, 131.9, 131.5, 131.1, 130.2, 129.5, 128.7, 128.4, 128.2, 128.0, 127.2, 125.7, 125.5, 122.8, 68.1, 57.0, 32.2, 31.5, 31.1, 28.8, 28.3, 27.9, 25.7, 23.6, 22.6, 21.7, 17.0, 1.1. **^{29}Si NMR (80 MHz, $CDCl_3$):** δ -30.17 (d, J = 17.1 Hz). **^{31}P NMR (162 MHz, $CDCl_3$):** δ 95.70 (s). **HRMS**

(ESI): calculated for $C_{33}H_{54}Cl_2N_3PPdSi$ $[M]^+$ *m/z* 727.2237, found 727.5298. **MALDI *m/z* ($C_{33}H_{54}Cl_2N_3PPdSi$):** 729.15$[M]^+$.

d) Synthesis of 3:



A 100 mL Schlenk flask was charged with **L3**[5] (0.304 g, 0.5 mmol) and $PdCl_2(ACN)_2$ (0.130 g, 0.5 mmol) followed by the addition of toluene (30 mL) at room temperature and stirred for 12 h. The resulting solution was filtered off, and the solvent was removed to yield a pale yellow solid. Single crystals suitable for X-ray analysis were grown in DCM-Pentane (2:1) at 0° C. M. P.: 278-281˚C. Yield: 48 % (0.375 g). **^{1}H NMR (400 MHz, $CDCl_3$):** δ 8.08 (d, J = 7.4 Hz, 1H), 7.57 – 7.31 (m, 15H), 7.05 – 6.95 (m, 2H), 6.65 – 6.54 (m, 2H), 1.14 (s, 9H), 1.07 (s, 9H), 0.04 (s, 9H). **^{13}C NMR (101 MHz, $CDCl_3$):** δ 177.18 (s), 150.38 (s), 134.55(s), 133.09 (s), 131.87 (s), 131.38 (s), 129.53 (s), 129.22 (d, J = 11.9 Hz), 128.35 (s), 128.13 (s), 127.81 (s), 126.69 (s), 125.34(s), 124.11 (s), 31.08 (d, J = 7.6 Hz), 4.17 (s). **^{31}P NMR (162 MHz, $CDCl_3$):** δ 18.55 (s). **^{29}Si NMR (80 MHz, $CDCl_3$):** δ 16.66 (d, J = 19.6 Hz), 11.47 (s). **HRMS (ESI):** calculated for $C_{36}H_{46}Cl_2N_3PPdSi_2$ $[M\text{-}TMSCl]^+$ *m/z* 783.1380, found 674.1420. **MALDI *m/z* ($C_{36}H_{46}Cl_2N_3PPdSi_2$):** 784.14$[M]^+$.

II) General procedure C-N coupling

A general methodology for C-N cross-coupling reactions with microwave method (A):

In a glovebox, a microwave tube equipped with a magnetic stir bar was charged with 2.8 eq. NaO^{t}Bu, 2 mol% of $Pd(dba)_2$ and 2 mol% **L1/L2** ligand. 2 mL toluene, 1.2 equiv. amine, and 1 equiv. aromatic halide were added using the Schlenk line. The reaction mixture was stirred for 60 min at 150 °C in a microwave. The crude product was purified by column chromatography to afford the corresponding product. Enantiomeric excess (% ee) was determined by HPLC analysis using chiral stationary phases as indicated for each substrate.

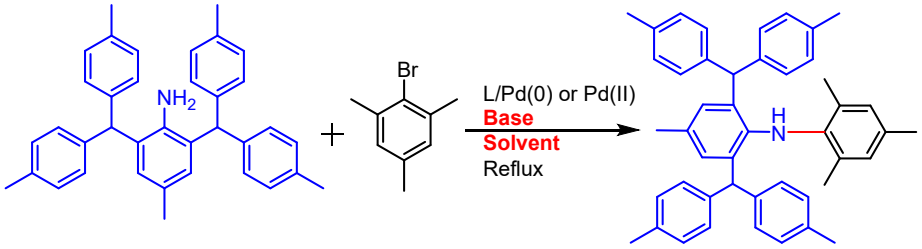
A general methodology for C-N cross-coupling reactions using conventional method (B):

2 mL toluene was added into the mixture of ligand **L1** (0.012 mmol) and $Pd(dba)_2$ (0.012 mmol) in a 100 mL Schlenk flask and stirred at room temperature for 1 h. 0.625 mmol of aryl halide was added, and 1.75 mmol of NaO^{t}Bu and 0.625 mmol of bulky primary aniline were added into this and stirred for 24 h at 100 °C. All the additions were done in an inert atmosphere. The reaction mixture was cooled to room temperature and extracted in ethyl acetate. Sodium sulfate was added as a drying agent. The resulting solution was dried *in vacuo* and purified by column chromatography (n-hexane: ethyl acetate) to afford the expected product. Products obtained as solids were dried under a high vacuum. Analytical thin-layer chromatography was performed on pre-coated silica plates. All the compounds were characterized by NMR spectroscopy and mass spectrometry.

S2. Optimization of reaction condition

I) Conventional method

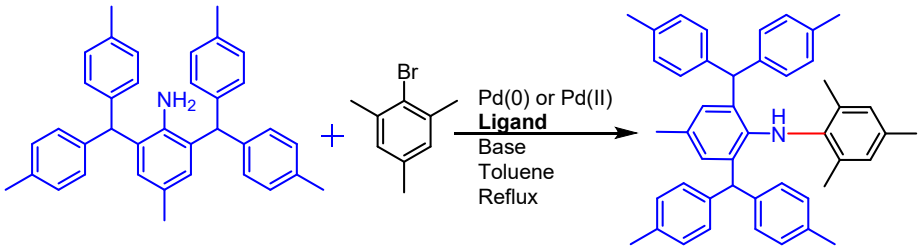
Table S1: Optimization of catalyst, base and solvent for the C-N cross-coupling of a sterically bulky aniline[a]



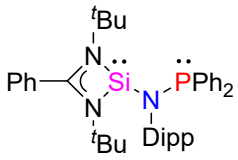
Entry	Ligand	Solvent	Base	Isolated Yield %
1	L1	Toluene	Cs_2CO_3	10
2	L1	Toluene	NaOH	NR
3	L1	Toluene	K_2CO_3	NR
4	L1	Toluene	LiO^{t}Bu	70
5	L1	Toluene	KO^{t}Bu	93
6	**L1**	**Toluene**	**NaO^{t}Bu**	**99**
7	L1	THF	NaO^{t}Bu	56
8	L1	Benzene	NaO^{t}Bu	94
9	L1	1,4-dioxane	NaO^{t}Bu	95

[a]Reaction conditions: aryl amine (0.5 mmol, 1equiv.), aryl bromide (0.5 mmol, 1 equiv.), base (1.4 mmol, 2.8 equiv.), ligand (0.01 mmol, 2 mol%), [Pd] (0.01 mmol, 2 mol%), solvent (2 mL), and 24 h. All are isolated yields.

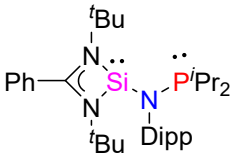
Table S2: Ligand and catalyst 1, 2, and 3 effect on the C-N cross-coupling of a sterically bulky aniline[a]



Entry	Ligand	Solvent	Base	Isolated Yield %
1	**L1**	**Toluene**	**NaO^{t}Bu**	**>99**
2	**L2**	**Toluene**	**NaO^{t}Bu**	**>99**
3	L3	Toluene	NaO^{t}Bu	90
4	L4	Toluene	NaO^{t}Bu	70
5	L5	Toluene	NaO^{t}Bu	63
6	L6	Toluene	NaO^{t}Bu	60
7	L7	Toluene	NaO^{t}Bu	91
8	L8	Toluene	NaO^{t}Bu	94
9	L9	Toluene	NaO^{t}Bu	75
10	1	Toluene	NaO^{t}Bu	69
11	2	Toluene	NaO^{t}Bu	73
12	3	Toluene	NaO^{t}Bu	58



L1



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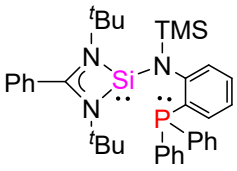

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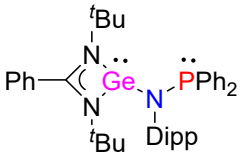

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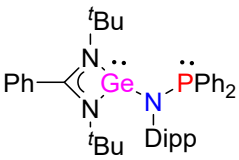

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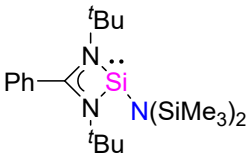

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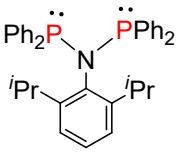

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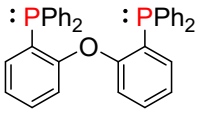

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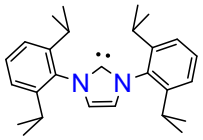

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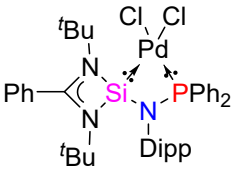

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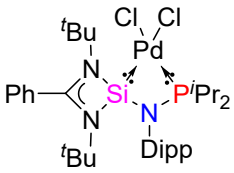

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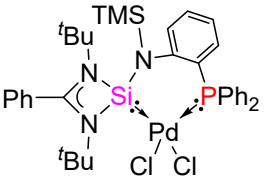
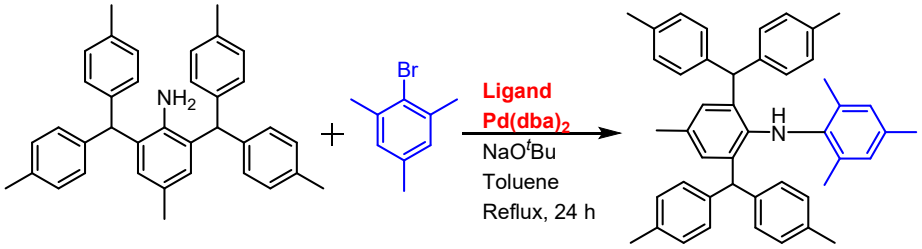


3

[a]Reaction conditions: aryl amine (0.5 mmol, 1equiv.), aryl bromide (0.5 mmol, 1 equiv.), NaO^{t}Bu (1.4 mmol, 2.8 equiv.), ligand (0.01 mmol, 2 mol%), [Pd] (0.01 mmol, 2 mol%), toluene (2 mL), 100 ^{o}C and 24 h. All are isolated yields (average of two runs).

Table S3: Effect of the catalyst loading on the C-N cross-coupling of a sterically bulky aniline[a]



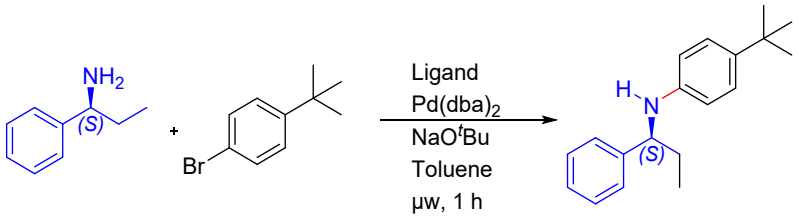
Entry	Ligand Mol%	$Pd(dba)_2$ Mol%	Time (h)	Isolated Yields
1	1	1	12	75
2	1	1	20	90
3	2	2	12	85
4	**2**	**2**	**20**	**>99**
5[¥]	5	-	20	0
6[Φ]	-	5	20	15

[a]Recation Condition: Aryl amine (0.5 mmol, 1equiv.), aryl bromide (0.5 mmol, 1 equiv.), NaO^{t}Bu (1.4 mmol, 2.8 equiv.), ligand (0.01 mmol, 2 mol%), [Pd] (0.01 mmol, 2 mol%), toluene (2 mL), 100^{o}C and 24 h. All are isolated yields (average of two runs). [¥]Blank reaction without Pd source. [Φ]Blank reaction with only Pd source.

II) Microwave method

Table S4: Optimization table for microwave-assisted C-N cross-coupling reactions[$]

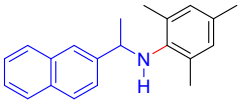
Screening of microwave-assisted reaction[6] conditions for the coupling of (*S*)-1-phenylpropan-1-amine and 1-bromo-4-(tert-butyl)benzene using **L2**/Pd(dba)$_2$.



Entry	Mol% Pd	Mol% Ligand	Temp (°C)	Time (Min)	Isolated Yield[#] %
1	1	1	150	180	55
2	1	1	150	60	55
3	**2**	**2**	**150**	**60**	**69**
4	-	5	150	60	NR
5	5	-	150	60	19

[$]Reaction conditions: aryl amine= (*S*)-1-phenylpropan-1-amine (1 equiv.), aryl bromide= 1-bromo-4-(tert-butyl)benzene (1 equiv.), **L2**/Pd(dba)$_2$ (2 mol%), NaO^{t}Bu (2.8 equiv.), toluene, μw. [#]Isolated yields (average of two runs). NR : No reaction.

III) List of Racemic compounds prepared for HPLC



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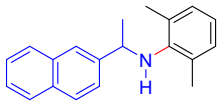
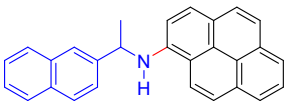
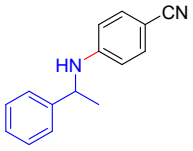


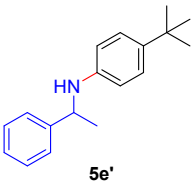
5b'



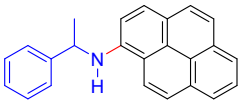
5c'



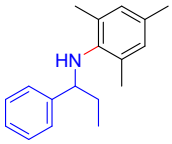
5d'



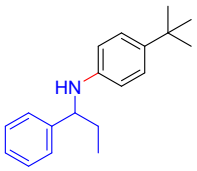
5e'



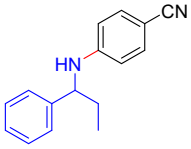
5f'



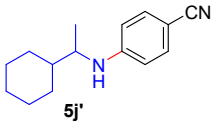
5g'



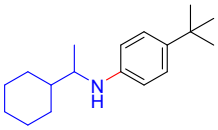
5h'



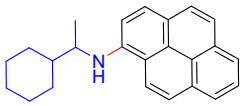
5i'



5j'



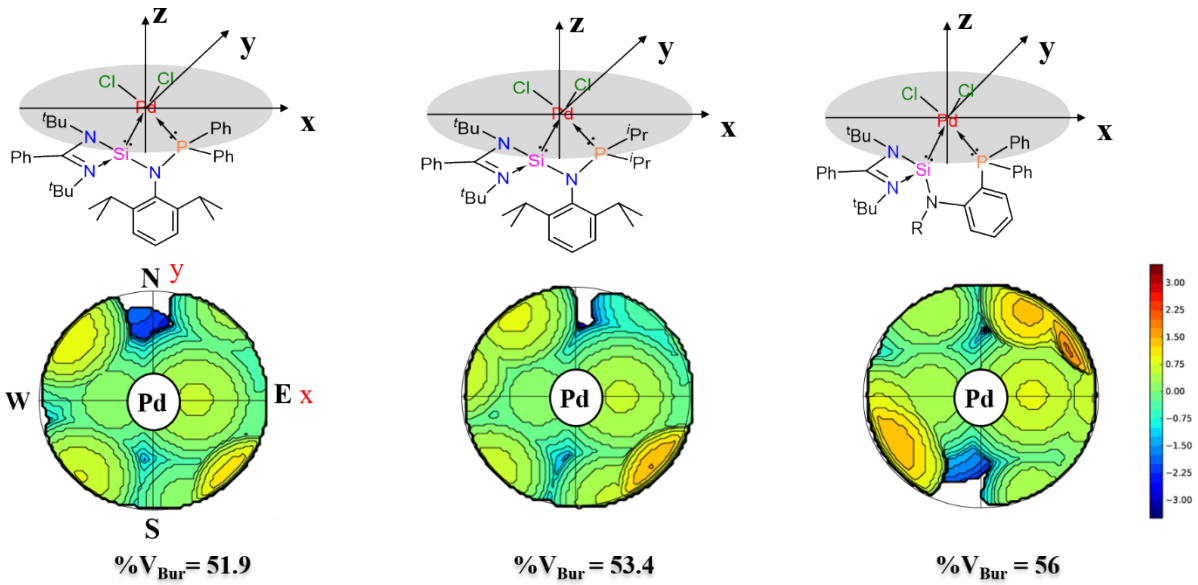
5k'



5l'

S3. Calculations of percentage buried volume and bite angle comparison

To gain insight into steric and electronic factors of 1, 2, and 3, we have performed bite angle[7] measurements from X-ray analysis, and Steric maps measurement from SambVca 2.1.[8] Percentage buried volume are mentioned below in the table.[9]



$\%V_{Bur}$= 51.9 $\%V_{Bur}$ = 53.4 $\%V_{Bur}$ = 56

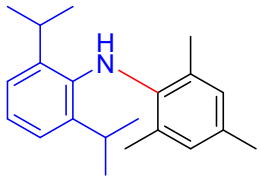
Catalyst	% V_{bur}	Bite angle	SW	NW	NE	SE
1	51.9	69.36(4)	52.1	48.8	49.0	56.6
2	53.4	69.16(2)	51.2	55.8	45.9	60.7
3	56.0	87.73(2)	53.0	52.5	63.9	54.7

Figure S1: Topographical steric maps of Pd(II) complexes **1** to **3** [SiNP(Pd)Cl_2] showing $\%V_{bur}$ per quadrant.

S4. Analytical data of products

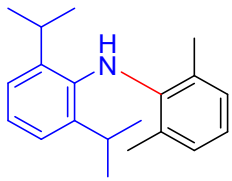
I) NMR spectra of bulky amine substrates

(4a) *N*-(2,6-diisopropylphenyl)-2,4,6-trimethylaniline



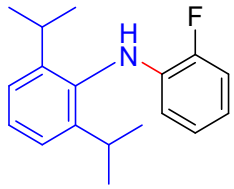
Titled compound prepared according to **General procedure B**. The crude product was purified by column chromatography (0-2% EtOAc in hexane) to provide the aminated product as a white solid in 90% yield (160 mg). **^{1}H NMR (400 MHz, $CDCl_3$):** δ 1.15 (*d*, 12H, *J*= 6.9 Hz, CH*Me*$_2$), 2.00 (*s*, 6H, C*H*$_3$), 2.27 (*s*, 3H, C*H*$_3$), 3.13-3.30 (*m*, 2H, C*H*Me$_2$), 4.74 (*s*, 1H, N*H*), 6.80 (*s*, 2H, Ph), 7.14 (*s*, 3H, Ph) **^{13}C{^{1}H} NMR (100.613 MHz, $CDCl_3$):** δ 19.38, 20.54, 23.56, 28.08, 123.34, 124.27, 126.43, 129.18, 130.15, 139.28, 140.55, 143.47 ppm. **HRMS (ESI):** calculated for $C_{21}H_{29}N$ $[M+H]^+$ *m/z* 296.2378, found 296.2379.

(4b) *N*-(2,6-diisopropylphenyl)-2,6-dimethylaniline



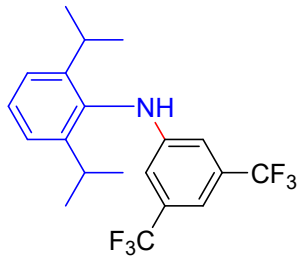
Titled compound prepared according to **General procedure B**. The crude product was purified by column chromatography (0-2% EtOAc in hexane) to provide the aminated product as an off-white solid in 86% yield (210 mg). **^{1}H NMR (400 MHz, $CDCl_3$):** δ 1.16 (*d*, 12H, *J*= 6.9 Hz, CH*Me*$_2$), 2.02 (*s*, 6H, C*H*$_3$), 3.14-3.24 (*m*, 2H, C*H*Me$_2$), 4.83 (*s*, 1H, N*H*), 6.76 (*t*, 1H, *J*= 7.4 Hz, Ph), 6.97 (*d*, 2H, *J*= 7.4 Hz, Ph), 7.12-7.21 (*m*, 3H, Ph) **^{13}C{^{1}H} NMR (100.613 MHz, $CDCl_3$):** δ 19.48, 23.59, 28.18, 29.85, 119.72, 123.37, 124.95, 125.75, 129.64, 138.92, 143.26, 144.28. **HRMS (ESI):** calculated for $C_{20}H_{27}N$ $[M+H]^+$ *m/z* 282.2215, found 282.2219.

(4c) *N*-(2-fluorophenyl)-2,6-diisopropylaniline



Titled compound prepared according to **General procedure B**. The crude product was purified by column chromatography (5% EtOAc in hexane) to provide the aminated product as a yellow syrup in 96% yield (156 mg)**. ^{1}H NMR (400 MHz, $CDCl_3$)**: δ 1.18 (*d*, 12H, *J*= 6.9 Hz, CHMe_2), 3.16-3.26 (*m*, 2H, C*H*Me$_2$), 5.34 (*s*, 1H, N*H*), 6.20-6.24 (*m*, 1H, Ph), 6.63-6.69 (*m*, 1H, Ph), 6.85-6.89 (*m*, 1H, Ph), 7.05-7.10 (*m*, 1H, Ph), 7.26-7.29 (*m*, 2H, Ph), 7.33-7.37 (*m*, 1H, Ph) **^{13}C{^{1}H} NMR (100.613 MHz, $CDCl_3$):** δ 14.22, 23.94, 28.29, 29.80, 113.20, 114.58, 114.76, 117.06, 117.13, 124.00, 124.49, 127.69, 128.21, 134.22, 136.46, 136.57, 147.83, 149.94, 152.31 ppm. **^{19}F{^{1}H} NMR (376.66 MHz, CDCl3):** δ -137.41 ppm. **MALDI *m/z* ($C_{18}H_{22}FN$):** 271.81 $[M]^+$.

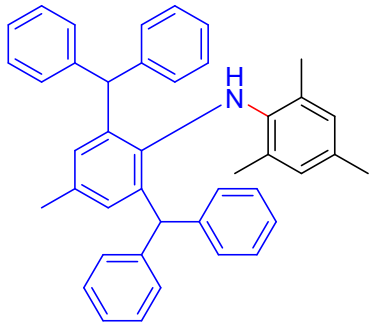
(4d) *N*-(3,5-bis(trifluoromethyl)phenyl)-2,6-diisopropylaniline



Titled compound prepared according to **General procedure B**. The crude product was purified by column chromatography (10% EtOAc in hexane) to provide the aminated product as a yellow syrup in 97% yield (228 mg)**. ^{1}H NMR (400 MHz, $CDCl_3$):** δ 1.17 (*d*, 12H, *J*= 6.9 Hz, CHMe_2), 3.06-3.16 (*m*, 2H, C*H*Me$_2$), 5.53 (*s*, 1H, N*H*), 6.85 (*s*, 2H, Ph), 7.19 (*s*, 1H, Ph), 7.28-7.29 (*m*, 2H, Ph), 7.37-7.41 (*m*, 1H, Ph) **^{13}C{^{1}H} NMR (100.613 MHz, $CDCl_3$):** δ 23.79, 28.35,

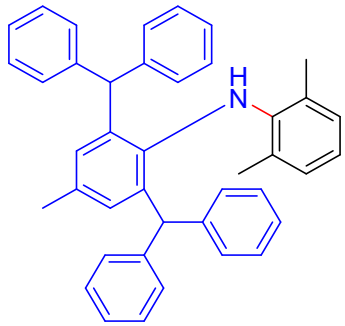
29.71, 124.40, 128.50, 132.35, 132.70, 147.40, 148.93 ppm. **$^{19}F\{^{1}H\}$ NMR (376.66 MHz, CDCl3):** δ -63.21 ppm.**MALDI *m/z* ($C_{20}H_{21}NF_6$):** 392.27 $(M+3H)^+$.

(4e) 2,6-dibenzhydryl-*N*-mesityl-4-methylaniline



Titled compound prepared according to **General procedure B**. The crude product was purified by column chromatography (2% EtOAc in hexane) to provide the aminated product as a white crystalline solid in 85% yield (284 mg). **^{1}H NMR (400 MHz, $CDCl_3$):** δ 1.44 (*s*, 6H, CH_3), 2.12 (*s*, 3H, CH_3), 2.24 (*s*, 3H, CH_3), 4.11 (*s*, 1H, N*H*), 5.51 (*s*, 2H, $CHPh_2$), 6.47 (*s*, 2H, Ph), 6.70 (*m*, 2H, Ph), 6.90 (*d*, 8H, *J*= 6.7 Hz, Ph), 7.16-7.26 (*m*, 12H, Ph) ppm. **$^{13}C\{^{1}H\}$ NMR (100.613 MHz, $CDCl_3$):** δ 18.45, 20.46, 21.41, 52.23, 125.88, 126.18, 128.18, 128.95, 129.10, 129.48, 129.55, 131.71, 137.52, 138.47, 138.73, 143.58 ppm. **MALDI *m/z* ($C_{42}H_{39}N$):** 557.54 $[M]^+$.

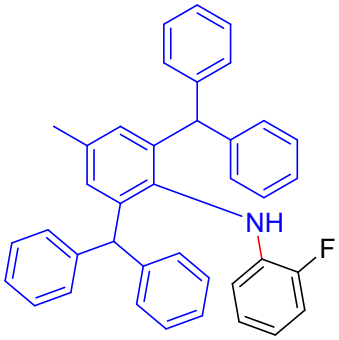
(4f) 2,6-dibenzhydryl-*N*-(2,6-dimethylphenyl)-4-methylaniline



Titled compound prepared according to **General procedure B**. The crude product was purified by column chromatography (5% EtOAc in hexane) to provide the aminated product as a white powder in 99% yield (322 mg). **^{1}H NMR (400 MHz, $CDCl_3$):** δ 1.46 (*s*, 6H, CH_3), 2.14 (*s*,

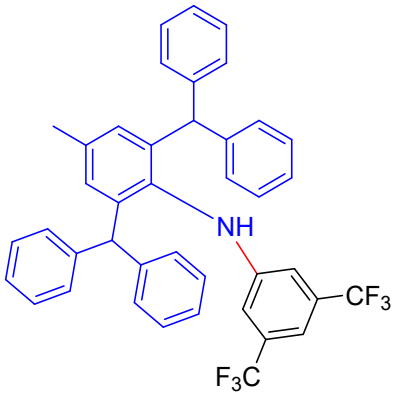
3H, CH_3), 4.19 (*s*, 1H, N*H*), 5.52 (*s*, 2H, CHPh_2), 6.50 (*s*, 2H, Ph), 6.68-6.77 (*m*, 1H, Ph), 6.91 (*d*, 8H, *J*=7.1 Hz, Ph), 7.15-7.30 (*m*, 12H, Ph) ppm. **^{13}C{^{1}H} NMR (100.613 MHz, $CDCl_3$):** δ 18.49, 21.43, 29.71, 52.30, 119.57, 125.46, 126.23, 128.22, 128.98, 129.04, 129.46, 132.27, 137.20, 138.97, 141.29, 143.54 ppm. **MALDI *m/z* ($C_{41}H_{37}N$):** 543.41 $[M]^+$.

(4g) 2,6-dibenzhydryl-*N*-(2-fluorophenyl)-4-methylaniline



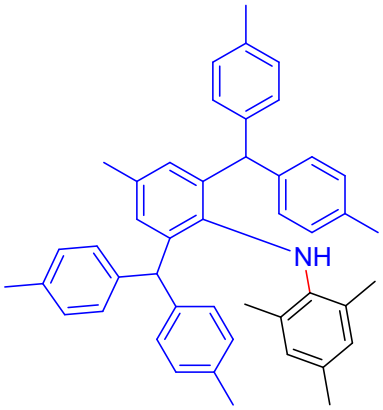
Titled compound prepared according to **General procedure B**. The crude product was purified by column chromatography (10% EtOAc in hexane) to provide the aminated product as a white solid in 98% yield (313 mg). **^{1}H NMR (400 MHz, $CDCl_3$):** δ 2.19 (*s*, 3H, CH_3), 4.73 (*s*, 1H, N*H*), 5.60 (*s*, 2H, CHPh_2), 6.28-6.41 (*m*, 1H, Ph), 6.59-6.68 (*m*, 1H, Ph), 6.72 (*s*, 2H, Ph), 6.79-6.87 (*m*, 1H, Ph), 6.92-7.04 (*m*, 8H, Ph), 7.14-7.23 (*m*, 13H, Ph) **^{13}C{^{1}H} NMR (100.613 MHz, $CDCl_3$):** δ 21.75, 51.82, 112.92, 114.75, 114.93, 117.32, 117.38, 124.60, 126.21, 128.33, 129.38, 129.89, 134.12, 136.64, 143.34, 144.22 **^{19}F{^{1}H} NMR (376.66 MHz, $CDCl_3$):** δ -136.75 (s) **MALDI *m/z* ($C_{39}H_{32}FN$):** 533.45$[M]^+$.

(4h) 2,6-dibenzhydryl-*N*-(3,5-bis(trifluoromethyl)phenyl)-4-methylaniline



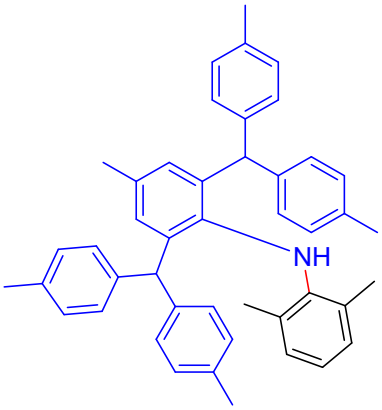
Titled compound prepared according to **General procedure B**. The crude product was purified by column chromatography (15% EtOAc in hexane) to provide the aminated product as an off-white solid in 95% yield (371 mg). **^{1}H NMR (400 MHz, $CDCl_3$):** δ 2.20 (*s*, 3H, CH_3), 4.82 (*s*, 1H, N*H*), 5.45 (*s*, 2H, CHPh_2), 6.64 (*s*, 2H, Ph), 6.70 (*s*, 2H, Ph), 6.90-6.92 (*m*, 8H, Ph), 7.09-7.24 (*m*, 13H, Ph) **^{13}C{^{1}H} NMR (100.613 MHz, $CDCl_3$):** δ 21.72, 52.12, 126.48, 128.42, 129.16, 130.09, 132.92, 137.65, 142.70, 143,94, 147.98 **^{19}F{^{1}H} NMR (376.66 MHz, $CDCl_3$):** δ -63.08 (s) **MALDI *m/z* ($C_{41}H_{31}NF_6$):** 651.35 $[M]^+$.

(4i) *N*-(2,6-bis(di-*p*-tolylmethyl)-4-methylphenyl)-2,4,6-trimethylaniline



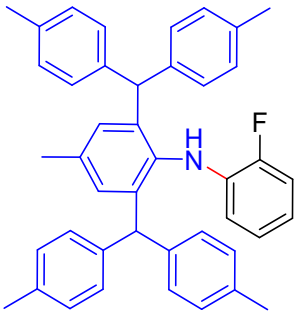
Titled compound prepared according to **General procedure B**. The crude product was purified by column chromatography (5% EtOAc in hexane) to provide the aminated product as white needles in a 99% yield (364 mg). **^{1}H NMR (400 MHz, $CDCl_3$):** δ 1.52 (*s*, 6H, CH_3), 2.16 (*s*, 3H, CH_3), 2.26 (*s*, 3H, CH_3), 2.35 (*s*, 12H, CH_3), 4.20 (*s*, 1H, N*H*), 5.48 (*s*, 2H, CHPh_2), 6.54 (*s*, 2H, Ph), 6.73 (*s*, 2H, Ph), 6.81 (*d*, 8H, *J*= 8.0 Hz, Ph), 7.06 (*d*, 8H, *J*= 7.8 MHz, Ph) **^{13}C{^{1}H} NMR (100.613 MHz, $CDCl_3$):** δ 18.62, 20.53, 21.12, 21.50, 51.43, 126.08, 128.89, 128.99, 129.36, 129.58, 131.63, 135.52, 137.67, 138.79, 139.07, 140.94 **MALDI *m/z* ($C_{46}H_{47}N$):** 613.46 $[M]^+$.

(4j) 2,6-bis(di-*p*-tolylmethyl)-*N*-(2,6-dimethylphenyl)-4-methylaniline



Titled compound prepared according to **General procedure B**. The crude product was purified by column chromatography (5% EtOAc in hexane) to provide the aminated product as an off-white solid in 96% yield (345 mg) **^{1}H NMR (400 MHz, $CDCl_3$):** δ 1.49 (*s*, 6H, CH_3), 2.15 (*s*, 3H, CH_3), 2.33 (*s*, 12H, CH_3), 4.24 (*s*, 1H, N*H*), 5.45 (*s*, 2H, CHPh_2), 6.52 (*s*, 2H, Ph), 6.66-6.73 (*m*, 1H, Ph), 6.78 (*d*, 8H, *J* = 7.7 Hz, Ph), 6.90 (*d*, 2H, *J* = 7.2 Hz, Ph), 7.04 (*d*, 8H, *J*= 7.5 Hz, Ph) **^{13}C{^{1}H} NMR (100.613 MHz, $CDCl_3$):** δ 18.67, 21.13, 21.47, 29.80, 51.50, 119.49, 125.61, 128.93, 129.02, 129.34, 132.20, 135.58, 137.31, 139.30, 140.88, 141.61 **MALDI *m/z* ($C_{45}H_{45}N$):** 599.47 $[M]^+$.

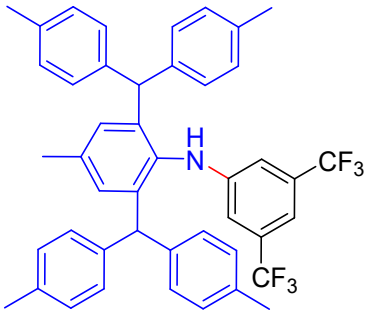
(4k) 2,6-bis(di-*p*-tolylmethyl)-*N*-(2-fluorophenyl)-4-methylaniline



Titled compound prepared according to **General procedure B**. The crude product was purified by column chromatography (12% EtOAc in hexane) to provide the aminated product as a white microcrystalline solid in 96% yield (339 mg). **^{1}H NMR (400 MHz, $CDCl_3$):** δ 2.20 (*s*, 3H, CH_3), 2.31 (*s*, 12H, CH_3), 4.80 (*s*, 1H, N*H*), 5.53 (*s*, 2H, CHPh_2), 6.75 (*s*, 2H, Ph), 6.85-6.87 (*m*, 9H, Ph), 7.02-7.04 (*m*, 11H, Ph) **^{13}C{^{1}H} NMR (100.613 MHz, $CDCl_3$):** δ 21.03, 21.69,

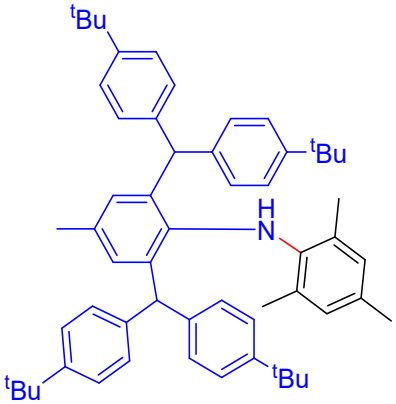
50.92, 113.01, 114.61, 114.78, 124.48, 128.30, 128.91, 129.15, 129.60, 130.13, 133.99, 135.58, 140.58, 144.28. **$^{19}F\{^{1}H\}$ NMR (376.66 MHz, $CDCl_3$):** δ -136.78 (s) **MALDI *m/z* ($C_{43}H_{40}FN$):** 590.57 $[M+H]^+$.

(4l) *N*-(3,5-bis(trifluoromethyl)phenyl)-2,6-bis(di-*p*-tolylmethyl)-4-methylaniline



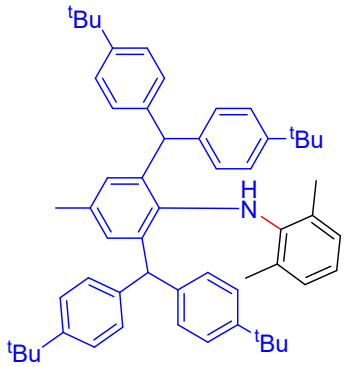
Titled compound prepared according to **General procedure B**. The crude product was purified by column chromatography (20% EtOAc in hexane) to provide the aminated product as a brownish solid in 95% yield (402 mg). **^{1}H NMR (400 MHz, $CDCl_3$):** δ 2.24 (*s*, 3H, CH_3), 2.32 (*s*, 12H, CH_3), 4.90 (*s*, 1H, N*H*), 5.40 (*s*, 2H, CHPh_2), 6.66 (*s*, 2H, Ph), 6.75 (*s*, 2H, Ph), 6.82 (*d*, 8H, *J*= 8.0 Hz, Ph), 7.04 (*d*, 8H, *J*= 7.9 Hz, Ph), 7.15 (*s*, 1H, Ph) **$^{13}C\{^{1}H\}$ NMR (100.613 MHz, $CDCl_3$):** δ 20.97, 21.73, 51.32, 128.99, 129.07, 129.91, 132.87, 135.89, 137.44, 139.93, 144.08, 148.12. **$^{19}F\{^{1}H\}$ NMR (376.66 MHz, $CDCl_3$):** δ -63.16 (s) **MALDI *m/z* ($C_{45}H_{39}NF_6$):** 707.44 $[M]^+$.

(4m) 2,6-bis(bis(4-(*tert*-butyl)phenyl)methyl)-*N*-mesityl-4-methylaniline



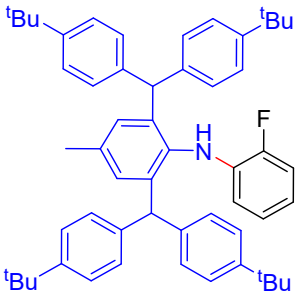
Titled compound prepared according to **General procedure B**. The crude product was purified by column chromatography (5% EtOAc in hexane) to provide the aminated product as a white powder in 99% yield (464 mg). **^{1}H NMR (400 MHz, $CDCl_3$):** δ 1.22 (*s*, 36H, CH_3), 1.31 (*s*, 6H, CH_3), 2.11 (*s*, 3H, CH_3), 2.19 (*s*, 3H, CH_3), 4.03 (*s*, 1H, N*H*), 5.34 (*s*, 2H, CHPh_2), 6.45 (*s*, 2H, Ph), 6.62 (*s*, 2H, Ph), 6.79 (*dd*, 8H, *J*= 8.3, 1.9 Hz, Ph), 7.20 (*dd*, 8H, *J*= 8.3, 1.9 Hz, Ph) **^{13}C{^{1}H} NMR (100.613 MHz, $CDCl_3$):** δ 18.26, 20.56, 21.47, 31.49, 34.50, 51.54, 125.01, 125.85, 128.67, 128.83, 129.16, 129.40, 131.28, 137.42, 138.58, 138.80, 140.69, 148.79 **MALDI *m/z* ($C_{58}H_{71}N$):** 782.71 $[M]^+$.

(4n) 2,6-bis(bis(4-(*tert*-butyl)phenyl)methyl)-*N*-(2,6-dimethylphenyl)-4-methylaniline



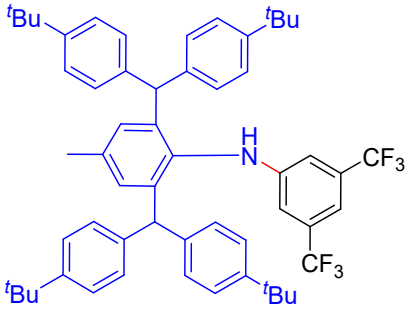
Titled compound prepared according to **General procedure B**. The crude product was purified by column chromatography (5% EtOAc in hexane) to provide the aminated product as a yellow solid in 98% yield (450 mg). **^{1}H NMR (400 MHz, $CDCl_3$):** δ 1.30 (*s*, 36H, CH_3), 1.58 (*s*, 6H, CH_3), 2.24 (*s*, 3H, CH_3), 4.94 (*s*, 1H, N*H*), 5.59 (*s*, 2H, CHPh_2), 6.55-6.62 (*m*, 1H, Ph), 6.72-6.76 (*m*, 1H, Ph) 6.82 (*s*, 2H, Ph), 6.92 (*d*, 8H, *J*= 7.7, Ph), 6.97-7.03 (*m*, 1H, Ph), 7.23 (*d*, 8H, *J*= 7.9 Hz, Ph) **^{13}C{^{1}H} NMR (100.613 MHz, $CDCl_3$):** δ 21.70, 31.38, 34.33, 50.68, 124.99, 128.89, 129.57, 134.02, 136.31, 140.37, 144.41, 148.70 **MALDI *m/z* ($C_{57}H_{69}N$):** 767.83 $[M]^+$.

(4o) 2,6-bis(bis(4-(*tert*-butyl)phenyl)methyl)-*N*-(2-fluorophenyl)-4-methylaniline



Titled compound prepared according to **General procedure B**. The crude product was purified by column chromatography (10 % EtOAc in hexane) to provide the aminated product as a pale yellowish solid in 80 % yield (363 mg). **^{1}H NMR (400 MHz, $CDCl_3$):** δ 1.27 (*s*, 36H, CH_3), 2.23 (*s*, 3H, CH_3), 4.92 (*s*, 1H, N*H*), 5.57 (*s*, 2H, CHPh_2), 6.19 (*s*, 1H, ArF), 6.71 (*s*, 1H, ArF), 6.80 (*s*, 2H, Ph), 6.89 (*d*, 2H, *J*= 7.4 Hz, Ph), 6.79 (*dd*, 8H, *J*= 8.3, 1.9 Hz, Ph), 7.23 (*d*, 8H, *J*= 7.4 Hz, Ph) **^{13}C{^{1}H} NMR (100.613 MHz, $CDCl_3$):** δ 21.78, 31.47, 34.41, 50.75, 125.08, 128.98, 129.65, 134.09, 136.40, 140.45, 144.50, 148.78. **^{19}F{^{1}H} NMR (376.66 MHz, $CDCl_3$):** δ -137.14 (s) **MALDI: *m/z* ($C_{55}H_{67}NF$):** 758.68 $[M]^+$.

(4p) 2,6-bis(bis(4-(*tert*-butyl)phenyl)methyl)-*N*-(3,5-bis(trifluoromethyl)phenyl)-4-methylaniline

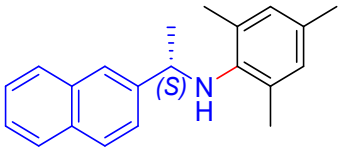


Titled compound prepared according to **General procedure B**. The crude product was purified by column chromatography (0-2 % EtOAc in hexane) to provide the aminated product as an off-white colored solid in 95 % yield (510 mg). **^{1}H NMR (400 MHz, $CDCl_3$):** δ 2.24 (*s*, 3H, CH_3), 2.32 (*s*, 12H, CH_3), 4.90 (*s*, 1H, N*H*), 5.40 (*s*, 2H, CHPh_2), 6.66 (*s*, 2H, Ph), 6.75 (*s*, 2H, Ph), 6.82 (*d*, 8H, *J*= 8.0 Hz, Ph), 7.04 (*d*, 8H, *J*= 7.9 Hz, Ph), 7.15 (*s*, 1H, Ph) **^{13}C{^{1}H} NMR**

(100.613 MHz, $CDCl_3$): δ 21.83, 31.41, 34.43, 51.16, 125.25, 128.81, 130.12, 132.98, 137.50, 139.96, 144.14, 148.40, 149.12 **$^{19}F\{^1H\}$ NMR (376.66 MHz, $CDCl_3$):** δ -63.03 (s) **MALDI *m/z* ($C_{57}H_{63}NF_6$):** 876.86 $[M]^+$.

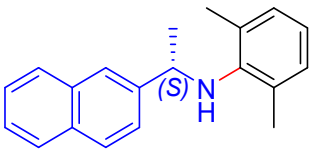
II) NMR spectra of Chiral substrates

(5a) (*S*)-2,4,6-trimethyl-*N*-(1-(naphthalen-2-yl)ethyl)aniline



Titled compound prepared according to **General procedure A**. The crude product was purified by column chromatography (2 % EtOAc in hexane) to provide the aminated product as a yellow solid in L1: 56 %, L2: 62% yield. **^1H NMR (400 MHz, $CDCl_3$):** δ 8.06 (dd, J = 6.3, 3.5 Hz, 1H), 7.91 – 7.86 (m, 1H), 7.77 (dd, J = 15.5, 7.6 Hz, 2H), 7.56 – 7.46 (m, 3H), 6.82 (s, 2H), 5.11 (q, J = 6.7 Hz, 1H), 3.37 (brs, 1H), 2.25 (s, 3H), 2.22 (s, 6H), 1.60 (d, J = 6.7 Hz, 3H). **^{13}C NMR (101 MHz, $CDCl_3$):** δ 143.49 (s), 142.79 (s), 134.31 (s), 131.24 (s), 131.09 (s), 130.02 (s), 129.48 (s), 129.28 (s), 127.78 (s), 126.33 (s), 126.08 (s), 125.87 (s), 123.59 (s), 123.00 (s), 53.70 (s), 24.40 (s), 20.97 (s), 19.48 (s). **HRMS (ESI):** calculated for $C_{21}H_{23}N$ $[M+H]^+$ *m/z* 289.1830, found 289.1828. **HPLC analysis:** (AD-H, 0.5 % IPA in Hexane, 1 mL/min, 254 nm) indicated ee with **L1** 91 % & with **L2** >99 %.

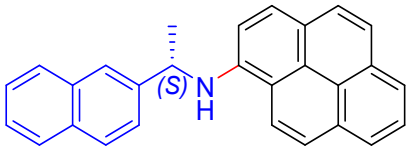
(5b) (*S*)-2,6-dimethyl-*N*-(1-(naphthalen-2-yl)ethyl)aniline



Titled compound prepared according to **General procedure A**. The crude product was purified by column chromatography (2 % EtOAc in hexane) to provide the aminated product as a pale-yellow solid in L1: 53 %, L2: 55% yield. **^1H NMR (400 MHz, $CDCl_3$):** δ 8.07 – 7.98 (m, 1H),

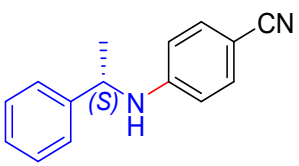
7.91 – 7.83 (m, 1H), 7.79 (d, J = 8.2 Hz, 1H), 7.73 (d, J = 7.1 Hz, 1H), 7.55 – 7.40 (m, 3H), 6.98 (d, J = 7.4 Hz, 2H), 6.80 (t, J = 7.5 Hz, 1H), 5.19 (q, J = 6.7 Hz, 1H), 3.53 (s, 1H), 2.24 (s, 6H), 1.61 (d, J = 6.6 Hz, 3H). **^{13}C NMR (101 MHz, $CDCl_3$):** δ 145.42 (s), 141.98 (s), 133.67 (s), 130.57 (s), 128.78 (s), 128.65 (s), 128.43 (s), 127.98 (s), 127.21 (s), 125.72 (s), 125.44 (s), 125.26 (s), 122.88 (s), 122.29 (s), 121.02 (s), 52.72 (s), 29.53 (s), 23.87 (s), 18.99 (s). **HRMS (ESI):** calculated for $C_{20}H_{21}N$ $[M+H]^+$ *m/z* 276.1752, found 276.1742. **HPLC analysis:** (AD-H, 0.5 % IPA in Hexane, 1 mL/min, 254 nm) indicated ee with **L1** 88 % & with **L2** >99 %.

(5c) (*S*)-*N*-(1-(naphthalen-2-yl)ethyl)pyren-1-amine



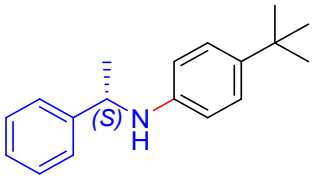
Titled compound prepared according to **General procedure A**. The crude product was purified by column chromatography (2 % EtOAc in hexane) to provide the aminated product as a yellow solid in L1: 60 %, L2: 54% yield. **^{1}H NMR (400 MHz, $CDCl_3$):** δ 8.25 (d, J = 5.1 Hz, 1H), 8.16 (d, J = 9.1 Hz, 1H), 8.11 – 7.98 (m, 2H), 7.95 (d, J = 7.8 Hz, 2H), 7.80 – 7.69 (m, 5H), 7.63 – 7.52 (m, 2H), 7.36 (t, J = 7.7 Hz, 1H), 7.00 (s, 1H), 5.65 (s, 1H), 1.91 (d, J = 6.3 Hz, 3H). **^{13}C NMR (101 MHz, $CDCl_3$):** δ 134.31 (s), 130.97 (s), 129.38 (s), 127.89 (s), 126.79 – 125.08 (m), 122.64 (s), 23.87 (s), 14.28 (s). **HRMS (ESI):** calculated for $C_{28}H_{21}N$ $[M+H]^+$ *m/z* 371.1674, found 371.1669. **HPLC analysis:** (AD-H, 0.5 % IPA in Hexane, 1 mL/min, 254 nm) indicated ee with **L1** 81 % & with **L2** 99 %.

(5d) (*R*)-4-((1-phenylethyl)amino)benzonitrile



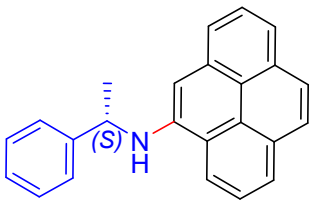
Titled compound prepared according to **General procedure A**. The crude product was purified by column chromatography (20 % EtOAc in hexane) to provide the aminated product as an off-white solid in L1: 49 %, L2: 58% yield. **^{1}H NMR (400 MHz, $CDCl_3$):** δ 7.20 (m, 6H), 7.16 – 7.10 (m, 1H), 6.37 (d, J = 8.7 Hz, 2H), 4.70 (s, 1H), 4.46 – 4.32 (m, 1H), 1.43 (d, J = 6.8 Hz, 3H). **^{13}C NMR (101 MHz, $CDCl_3$):** δ 150.33 (s), 143.63 (s), 133.37 (s), 128.74 (s), 127.18 (s), 125.52 (s), 120.46 (s), 112.78 (s), 98.32 (s), 52.94 (s), 24.52 (s). **HRMS (ESI):** calculated for $C_{15}H_{14}N_2$ $[M+H]^+$ *m/z* 223.1235, found 223.1225. **HPLC analysis:** (AD-H, 3 % IPA in Hexane, 1 mL/min, 254 nm) indicated ee with **L1** 90 % & with **L2** 95 %.

(5e) (*S*)-4-(*tert*-butyl)-*N*-(1-phenylethyl)aniline



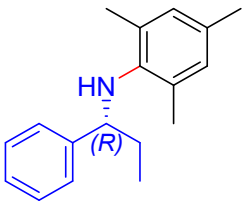
Titled compound prepared according to **General procedure A**. The crude product was purified by column chromatography (2 % EtOAc in hexane) to provide the aminated product as a yellow syrup in L1: 57 %, L2: 53% yield. **^{1}H NMR (400 MHz, $CDCl_3$):** δ 7.31 – 7.28 (m, 2H), 7.23 (t, J = 7.6 Hz, 2H), 7.16 – 7.11 (m, 1H), 7.03 (d, J = 8.6 Hz, 2H), 6.38 (d, J = 8.6 Hz, 2H), 4.36 (q, J = 6.7 Hz, 1H), 3.84 (s, 1H), 1.41 (d, J = 6.7 Hz, 3H), 1.15 (s, 9H). **^{13}C NMR (101 MHz, $CDCl_3$):** δ 145.7, 145.2, 140.0, 128.7, 126.9, 126.0, 113.0, 53.9, 33.9, 31.6, 25.2. **HRMS (ESI):** calculated for $C_{18}H_{23}N$ $[M+H]^+$ *m/z* 254.1908, found 254.1901. **HPLC analysis:** (AD-H, 3 % IPA in Hexane, 1 mL/min, 254 nm) indicated ee with **L1** 85 % & with **L2** 98 %.

(5f) (*R*)-*N*-(1-phenylethyl)pyren-4-amine



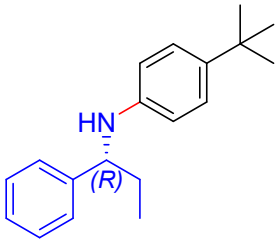
Titled compound prepared according to **General procedure A**. The crude product was purified by column chromatography (5 % EtOAc in hexane) to provide the aminated product as an off-white solid in L1: 42 %, L2: 60% yield. **^{1}H NMR (400 MHz, $CDCl_3$):** δ 8.04 – 7.84 (m, 4H), 7.71 (m, 5H), 7.33 (d, J = 7.5 Hz, 2H), 7.20 (t, J = 7.4 Hz, 2H), 7.13 (d, J = 8.9 Hz, 1H), 7.01 (m, 1H), 4.74 (s, 1H), 1.65 (d, J = 6.4 Hz, 3H). **^{13}C NMR (101 MHz, $CDCl_3$):** δ 147.62 (s), 145.37 (s), 136.86 (s), 132.28 (s), 131.91 – 131.16 (m), 128.83 (s), 127.27 (s), 126.08 (s), 124.56 – 123.30 (m), 119.47 (s), 111.05 (s), 54.17 (s), 28.08 (s), 26.46 (d, J = 20.7 Hz), 25.02 (s). **HRMS (ESI):** calculated for $C_{24}H_{19}N$ $[M+H]^+$ *m/z* 321.1517, found 321.1519. **HPLC analysis:** (AD-H, 100 % Hexane, 1 mL/min, 230 nm) indicated ee with **L1** 95 % & with **L2** >99 %.

(5g) (*S*)-2,4,6-trimethyl-*N*-(1-phenylpropyl)aniline



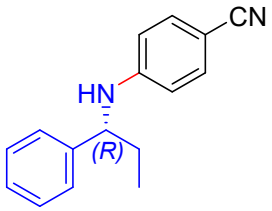
Titled compound prepared according to **General procedure A**. The crude product was purified by column chromatography (2 % EtOAc in hexane) to provide the aminated product as a yellow solid in L1: 52 %, L2: 56% yield. **^{1}H NMR (400 MHz, $CDCl_3$):** δ 7.31 – 7.26 (m, 2H), 7.24 – 7.18 (m, 3H), 6.75 (s, 2H), 3.96 (dd, J = 8.7, 5.6 Hz, 1H), 3.17 (s, 1H), 2.20 (s, 3H), 2.12 (s, 6H), 1.33 – 1.20 (m, 2H), 0.87 (t, J = 7.4 Hz, 3H). **^{13}C NMR (101 MHz, $CDCl_3$):** δ 143.74 (s), 142.12 (s), 132.69 (s), 130.46 (s), 129.17 (s), 128.40 – 127.42 (m), 126.68 (d, J = 9.7 Hz), 63.52 (s), 31.61 (s), 29.35 (s), 20.35 (s), 18.69 (s), 11.04 (s). **HRMS (ESI):** calculated for $C_{18}H_{23}N$ $[M+H]^+$ *m/z* 253.1830, found 253.1832. **HPLC analysis:** (AD-H, 1.5 % IPA in Hexane, 1 mL/min, 254 nm) indicated ee with **L1** 70 % & with **L2** 75 %.

(5h) (*R*)-4-(*tert*-butyl)-*N*-(1-phenylpropyl)aniline



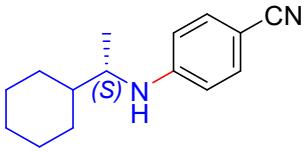
Titled compound prepared according to **General procedure A**. The crude product was purified by column chromatography (2 % EtOAc in hexane) to provide the aminated product as a yellow syrup in L1: 62 %, L2: 69% yield. **^{1}H NMR (400 MHz, $CDCl_3$):** δ 7.58 (m, 2H), 7.53 (m, 2H), 7.45 (m, 1H), 7.40 – 7.33 (m, 2H), 6.81 – 6.52 (m, 1H), 4.43 (t, J = 6.0 Hz, 1H), 4.20 (s, 1H), 2.03 (td, J = 7.0, 4.2 Hz, 2H), 1.49 (s, 9H), 1.17 (m, 4.8 Hz, 3H). **^{13}C NMR (101 MHz, $CDCl_3$):** δ 145.31 (s), 144.35 (s), 139.76 (s), 128.53 (s), 126.89 (s), 126.56 (s), 125.90 (s), 112.97 (s), 60.08 (s), 33.81 (s), 31.82 (s), 31.62 (s), 10.94 (s). **HRMS (ESI):** calculated for $C_{19}H_{25}N$ $[M+H]^+$ *m/z* 268.2065, found 268.2064. **HPLC analysis:** (AD-H, 3 % IPA in Hexane, 1 mL/min, 254 nm) indicated ee with **L1** 64% & with **L2** 86 %.

(5i) (*S*)-4-((1-phenylpropyl)amino)benzonitrile



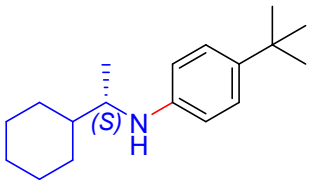
Titled compound prepared according to **General procedure A**. The crude product was purified by column chromatography (20 % EtOAc in hexane) to provide the aminated product as a white solid in L1: 66 %, L2: 68% yield. **^{1}H NMR (400 MHz, $CDCl_3$):** δ 7.31 – 7.06 (m, 7H), 6.41 (d, J = 8.7 Hz, 2H), 4.82 (s, 1H), 4.17 (t, J = 6.7 Hz, 1H), 1.77 (m, 2H), 0.88 (t, J = 7.4 Hz, 3H). **^{13}C NMR (101 MHz, $CDCl_3$):** δ 150.74 (s), 142.44 (s), 133.46 (s), 128.69 (s), 127.30 (s), 126.30 (s), 120.70 (s), 112.84 (s), 98.15 (s), 59.22 (s), 31.33 (s), 10.79 (s). **HRMS (ESI):** calculated for $C_{16}H_{16}N_2$ $[M+H]^+$ *m/z* 237.1391, found 237.1382. **HPLC analysis:** (AD-H, 3 % IPA in Hexane, 1 mL/min, 254 nm) indicated ee with **L1** 80 % & with **L2** 92 %.

(5j) (*S*)-4-((1-cyclohexylethyl)amino)benzonitrile



Titled compound prepared according to **General procedure A**. The crude product was purified by column chromatography (20 % EtOAc in hexane) to provide the aminated product as a yellow semi-solid in L1: 73 %, L2: 69 % yield. **^{1}H NMR (400 MHz, $CDCl_3$):** δ 7.34 (d, J = 8.7 Hz, 2H), 6.51 (d, J = 8.7 Hz, 2H), 4.32 (m, 1H), 3.32 (m, 1H), 1.81 – 1.60 (m, 5H), 1.40 (m, 1H), 1.25 – 1.14 (m, 3H), 1.11 (d, J = 6.6 Hz, 3H), 0.99 (dd, J = 19.6, 7.2 Hz, 2H). **^{13}C NMR (101 MHz, $CDCl_3$):** δ 151.45 (s), 133.91 (s), 121.14 (s), 112.42 (s), 97.35 (s), 52.89 (s), 43.12 (s), 29.82 (s), 28.76 (s), 26.82 – 26.29 (m), 17.48 (s). **HRMS (ESI):** calculated for $C_{15}H_{20}N$ $[M+H]^+$ *m/z* 229.1704, found 229.1710. **HPLC analysis:** (AD-H, 3 % IPA in Hexane, 1 mL/min, 254 nm) indicated ee with **L1** 61 % & with **L2** 79 %.

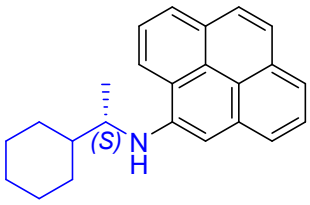
(5k) (*S*)-4-(*tert*-butyl)-*N*-(1-cyclohexylethyl)aniline



Titled compound prepared according to **General procedure A**. The crude product was purified by column chromatography (2 % EtOAc in hexane) to provide the aminated product as a yellow syrup in L1: 69 %, L2: 62 % yield. **^{1}H NMR (400 MHz, $CDCl_3$):** δ 7.13 – 7.04 (m, 2H), 6.43 (dd, J = 8.4, 1.4 Hz, 2H), 3.32 – 3.07 (m, 2H), 1.67 (ddd, J = 44.3, 31.2, 13.1 Hz, 5H), 1.33 (dd, J = 21.0, 9.7 Hz, 1H), 1.19 (s,9H), 1.16 – 1.05 (m, 3H), 1.01 (dd, J = 6.5, 1.3 Hz, 3H), 0.96 (m, 2H). **^{13}C NMR (101 MHz, $CDCl_3$):** δ 141.32 (s), 138.10 (s), 124.96 (s), 121.72 (s), 111.49 (s), 52.09 (s), 42.00 (s), 32.72 (s), 30.55 (s), 28.76 (s), 27.41 (s), 26.28 – 25.15 (m), 21.41 (s), 16.48 (s). **HRMS (ESI):** calculated for $C_{18}H_{29}N$ $[M+H]^+$ *m/z* 260.2378, found

260.2374. **HPLC analysis:** (AD-H, 0.5 % IPA in Hexane, 1 mL/min, 254 nm) indicated ee with **L1** 99 % & with **L2** 99 %.

(5l) (*S*)-*N*-(1-cyclohexylethyl)pyren-4-amine



Titled compound prepared according to **General procedure A**. The crude product was purified by column chromatography (2 % EtOAc in hexane) to provide the aminated product as a pale yellowish semi-solid in L1: 58 %, L2: 65% yield. **^{1}H NMR (400 MHz, $CDCl_3$):** δ 8.11 – 7.99 (m, 3H), 7.98 – 7.87 (m, 4H), 7.77 (d, J = 8.8 Hz, 1H), 7.34 (d, J = 8.4 Hz, 1H), 3.77 (m, 1H), 2.00 (d, J = 12.5 Hz, 1H), 1.92 – 1.80 (m, 3H), 1.79 – 1.62 (m, 2H), 1.32 (d, J = 4.7 Hz, 3H),1.30 (m, 2H) 1.28 – 1.15 (m, 3H). **^{13}C NMR (101 MHz, $CDCl_3$):** δ 132.85 (s), 132.56 – 132.34 (m), 131.79 (s), 131.36 (s), 127.62 (s), 126.07 (s), 125.18 (s), 123.59 (s), 123.03 (s), 119.78 (s), 118.94 (s), 42.92 (s), 30.22 (s), 28.60 (s), 26.75 (d, J = 9.6 Hz), 26.51 (s), 22.72 (s), 17.29 (s), 14.40 (s). **HRMS (ESI):** calculated for $C_{24}H_{25}N$ $[M+H]^+$ *m/z* 328.2065, found 328.2076. **HPLC analysis:** (AD-H, 1.5 % IPA in Hexane, 1 mL/min, 254 nm) indicated ee with **L1** 73 % & with **L2** 87 %.

S5. Refinment data of single crystal X-ray diffraction

Single crystals of suitable size, coated with paraffin oil were mounted for all the complexes, substrates and ligand. Crystal data for all the compounds were collected on a Bruker Smart Apex Duo diffractometer at 100K/150 K using Mo Kα radiation (λ = 0.71073 Å) or CuKα (λ = 1.54178). Collected data were integrated by using SAINT and then absorption correction was done by multi-scan method using SADABS program. All the structures were solved by direct methods and refined by full-matrix least-squares methods against F^2 (SHELXL-2014/7). The data were corrected for disordered electron density through the SQUEEZE procedure, as implemented in PLATON. Crystallographic Information File (CIF) for the structures has been deposited to the Cambridge Crystallographic Data centre as supplementary publication no: CCDC no:

L2 (2193639); 1 (2193662); 2 (2193663); 3 (2203939); 4f (2193666) 4i (2193667); 5c (2193664); 5h (2193665).

L2

Table S5a: Crystal data and structure refinement for L2 (CCDC:2193639)

Identification code	**L2**
Empirical formula	$C_{33}H_{54}N_3PSi$
Formula weight	551.85
Temperature/K	150(2)
Crystal system	triclinic
Space group	P-1
a/Å	10.461(10)
b/Å	10.611(10)
c/Å	16.467(16)
α/°	83.31(3)
β/°	87.04(3)
γ/°	67.44(2)
Volume/Å^3	1676(3)
Z	2
ρ_{calc}g/cm^3	1.093
μ/mm^{-1}	0.142
F(000)	604.0
Crystal size/mm^3	0.431 × 0.321 × 0.215
Radiation	MoKα (λ = 0.71073)
2Θ range for data collection/°	4.18 to 56.806
Index ranges	$-13 \leq h \leq 13$, $-14 \leq k \leq 14$, $-22 \leq l \leq 22$
Reflections collected	89242
Independent reflections	8352 [R_{int} = 0.1013, R_{sigma} = 0.0529]
Data/restraints/parameters	8352/0/357
Goodness-of-fit on F^2	1.032
Final R indexes [I>=2σ (I)]	R_1 = 0.0447, wR_2 = 0.0914
Final R indexes [all data]	R_1 = 0.0694, wR_2 = 0.0998
Largest diff. peak/hole / e Å^{-3}	0.31/-0.34

1

Table S5b: Crystal data and structure refinement for 1 (CCDC: 2193662)

Identification code	**1**
Empirical formula	$C_{39}H_{50}Cl_2N_3PPdSi$
Formula weight	797.18
Temperature/K	150(2)
Crystal system	monoclinic
Space group	$P2_1/n$
a/Å	11.721(2)
b/Å	14.864(3)
c/Å	21.818(5)
α/°	90
β/°	98.244(6)
γ/°	90
Volume/Å^3	3761.9(13)
Z	4
ρ_{calc}g/cm^3	1.408
μ/mm^{-1}	0.742
F(000)	1656.0
Crystal size/mm^3	0.431 × 0.285 × 0.251
Radiation	MoKα (λ = 0.71073)
2Θ range for data collection/°	4.218 to 56.718
Index ranges	$-15 \leq h \leq 15$, $-19 \leq k \leq 19$, $-29 \leq l \leq 29$
Reflections collected	160554
Independent reflections	9403 [R_{int} = 0.1096, R_{sigma} = 0.0425]
Data/restraints/parameters	9403/0/434
Goodness-of-fit on F^2	1.044
Final R indexes [I>=2σ (I)]	R_1 = 0.0365, wR_2 = 0.0744
Final R indexes [all data]	R_1 = 0.0566, wR_2 = 0.0820
Largest diff. peak/hole / e Å^{-3}	0.59/-0.76

2

Table S5c: Crystal data and structure refinement for 2(CCDC: 2193663).

Identification code	2
Empirical formula	$C_{33}H_{54}Cl_2N_3PPdSi$
Formula weight	729.15
Temperature/K	100(2)
Crystal system	monoclinic
Space group	$P2_1$
a/Å	11.502(2)
b/Å	12.782(3)
c/Å	12.058(2)
α/°	90.00(3)
β/°	94.41(3)
γ/°	90.00(3)
Volume/Å^3	1767.5(6)
Z	2
ρ_{calc}g/cm^3	1.370
μ/mm^{-1}	0.782
F(000)	764.0
Crystal size/mm^3	0.512 × 0.321 × 0.158
Radiation	MoKα (λ = 0.71073)
2Θ range for data collection/°	4.652 to 56.838
Index ranges	$-15 \leq h \leq 15$, $-17 \leq k \leq 17$, $-16 \leq l \leq 16$
Reflections collected	63801
Independent reflections	8840 [R_{int} = 0.0821, R_{sigma} = 0.0519]
Data/restraints/parameters	8840/1/385
Goodness-of-fit on F^2	1.048
Final R indexes [I>=2σ (I)]	R_1 = 0.0351, wR_2 = 0.0768
Final R indexes [all data]	R_1 = 0.0422, wR_2 = 0.0795
Largest diff. peak/hole / e Å^{-3}	0.72/-0.82
Flack parameter	0.06(3)

3

Table S5d: Crystal data and structure refinement for 3(CCDC: 2203939).

Identification code	3
Empirical formula	$C_{37}H_{48}Cl_4N_3PPdSi_2$
Formula weight	870.13
Temperature/K	293(2)
Crystal system	monoclinic
Space group	C2/c
a/Å	25.422(4)
b/Å	11.0674(13)
c/Å	33.751(4)
α/°	90
β/°	109.835(6)
γ/°	90
Volume/Å^3	8933(2)
Z	8
ρ_{calc}g/cm^3	1.294
μ/mm^{-1}	0.772
F(000)	3584.0
Crystal size/mm^3	0.27 × 0.1 × 0.09
Radiation	MoKα (λ = 0.71073)
2Θ range for data collection/°	5.106 to 50.202
Index ranges	$-30 \leq h \leq 30$, $-13 \leq k \leq 13$, $-40 \leq l \leq 40$
Reflections collected	125014
Independent reflections	7861 [R_{int} = 0.2289, R_{sigma} = 0.1392]
Data/restraints/parameters	7861/0/442
Goodness-of-fit on F^2	1.048
Final R indexes [I>=2σ (I)]	R_1 = 0.0738, wR_2 = 0.1011
Final R indexes [all data]	R_1 = 0.1432, wR_2 = 0.1192
Largest diff. peak/hole / e Å^{-3}	0.57/-0.64

4f

Table S5e:Crystal data and structure refinement for 4f (CCDC:2193666).

Identification code	4f
Empirical formula	$C_{41}H_{37}N$
Formula weight	543.71
Temperature/K	150.15
Crystal system	monoclinic
Space group	$P2_1/n$
a/Å	10.939(2)
b/Å	26.563(6)
c/Å	11.124(2)
α/°	90
β/°	112.526(6)
γ/°	90
Volume/Å^3	2985.7(11)
Z	4
ρ_{calc}g/cm^3	1.210
μ/mm^{-1}	0.069
F(000)	1160.0
Crystal size/mm^3	0.315 × 0.278 × 0.169
Radiation	MoKα (λ = 0.71073)
2Θ range for data collection/°	4.25 to 56.82
Index ranges	$-14 \leq h \leq 14$, $-35 \leq k \leq 35$, $-14 \leq l \leq 14$
Reflections collected	105287
Independent reflections	7440 [R_{int} = 0.1577, R_{sigma} = 0.0732]
Data/restraints/parameters	7440/0/382
Goodness-of-fit on F^2	1.024
Final R indexes [I>=2σ (I)]	R_1 = 0.0548, wR_2 = 0.1123
Final R indexes [all data]	R_1 = 0.1117, wR_2 = 0.1368
Largest diff. peak/hole / e Å^{-3}	0.67/-0.32

4i

Table S5f: Crystal data and structure refinement for 4i (CCDC:2193667)

Identification code	4i
Empirical formula	$C_{46}H_{47}N$
Formula weight	613.84
Temperature/K	150(2)
Crystal system	monoclinic
Space group	$P2_1/n$
a/Å	12.506(4)
b/Å	23.229(8)
c/Å	13.297(4)
α/°	90
β/°	114.039(11)
γ/°	90
Volume/Å^3	3528(2)
Z	4
ρ_{calc}g/cm^3	1.156
μ/mm^{-1}	0.066
F(000)	1320.0
Crystal size/mm^3	0.268 × 0.265 × 0.144
Radiation	MoKα (λ = 0.71073)
2Θ range for data collection/°	3.784 to 56.768
Index ranges	$-16 \leq h \leq 16$, $-31 \leq k \leq 30$, $-17 \leq l \leq 13$
Reflections collected	51581
Independent reflections	8793 [R_{int} = 0.1240, R_{sigma} = 0.1053]
Data/restraints/parameters	8793/0/432
Goodness-of-fit on F^2	1.007
Final R indexes [I>=2σ (I)]	R_1 = 0.0644, wR_2 = 0.1364
Final R indexes [all data]	R_1 = 0.1468, wR_2 = 0.1720
Largest diff. peak/hole / e Å^{-3}	0.23/-0.26

5c

Table S5g: Crystal data and structure refinement for 5c(CCDC:2193664).

Identification code	5c
Empirical formula	$C_{28}H_{21}N$
Formula weight	371.46
Temperature/K	150.15
Crystal system	orthorhombic
Space group	$P2_12_12_1$
a/Å	8.6857(15)
b/Å	12.012(2)
c/Å	37.160(6)
α/°	90
β/°	90
γ/°	90
Volume/Å^3	3877.1(11)
Z	8
ρ_{calc}g/cm^3	1.273
μ/mm^{-1}	0.558
F(000)	1568.0
Crystal size/mm^3	0.341 × 0.268 × 0.186
Radiation	CuKα (λ = 1.54178)
2Θ range for data collection/°	4.756 to 155.666
Index ranges	$-10 \leq h \leq 10$, $-14 \leq k \leq 15$, $-46 \leq l \leq 45$
Reflections collected	64151
Independent reflections	7843 [R_{int} = 0.1220, R_{sigma} = 0.0588]
Data/restraints/parameters	7843/0/526
Goodness-of-fit on F^2	1.151
Final R indexes [I>=2σ (I)]	R_1 = 0.0737, wR_2 = 0.1242
Final R indexes [all data]	R_1 = 0.0955, wR_2 = 0.1351
Largest diff. peak/hole / e Å^{-3}	0.24/-0.25
Flack parameter	-0.6(4)

5h

Table S5h: Crystal data and structure refinement for 5h(CCDC:2193665).

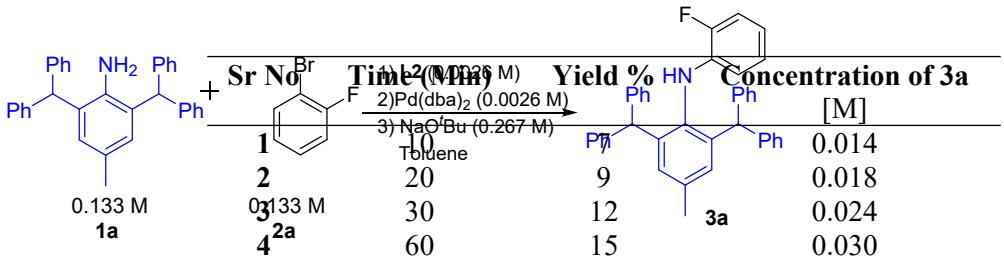
Identification code	5h
Empirical formula	$C_{19}H_{25}N$
Formula weight	267.40
Temperature/K	150.15
Crystal system	monoclinic
Space group	C2
a/Å	23.428(3)
b/Å	5.9565(8)
c/Å	23.648(3)
α/°	90
β/°	101.376(6)
γ/°	90
Volume/Å^3	3235.2(7)
Z	8
ρ_{calc}g/cm^3	1.098
μ/mm^{-1}	0.469
F(000)	1168.0
Crystal size/mm^3	0.315 × 0.219 × 0.169
Radiation	CuKα (λ = 1.54178)
2Θ range for data collection/°	3.812 to 151.31
Index ranges	$-28 \leq h \leq 27$, $-7 \leq k \leq 7$, $-29 \leq l \leq 29$
Reflections collected	61573
Independent reflections	6625 [R_{int} = 0.0854, R_{sigma} = 0.0379]
Data/restraints/parameters	6625/1/427
Goodness-of-fit on F^2	1.039
Final R indexes [I>=2σ (I)]	R_1 = 0.0395, wR_2 = 0.0830
Final R indexes [all data]	R_1 = 0.0499, wR_2 = 0.0891
Largest diff. peak/hole / e Å^{-3}	0.15/-0.14
Flack parameter	-0.1(3)

S6. Kinetic Experiments

I) Procedure for Standard Kinetic Experiments

In the standard rate measurements, a Schlenk tube was charged with ligand and metal precursor (**L2**/$Pd(dba)_2$) (5 mg, 2 mol%), NaO^{t}Bu (0.038 g, 0.4 mmol), aryl halide **2a** (22 µL, 0.2 mmol), Ar-NH_2 **1a** (0.088 g, 0.2 mmol), and 1.5 mL toluene was added as a reaction solvent. The Schlenk tube containing the reaction mixture was heated at 100 °C in a preheated oil bath, at regular interval of time (10, 20, 30, 60, 90, 120, 150 mins etc.) and after completion, the reaction solvent was completely evaporated in a vacuum. The total reaction mixture was dissolved in 0.6 mL of $CDCl_3$ and internal standard 1,4-dioxane (8 µL, 0.1 mmol) was added to the reaction tube. Then this reaction mixture was passed through a PTFE filter (25 mm, 0.22 µM), and reaction progress was monitored by ^{1}H NMR spectroscopy at regular intervals of time. (See Table S9 in the supporting information). The data of the concentration of product [M] *vs* time (min) plot was drawn with "Origin pro-8.5" (Figure S2). The rate was determined by initial rate method. The slope of the linear fitting represents the reaction rate.

Table S8: Concentrations of product **3a** at different time intervals



Sr No	Time (Min)	Yield %	Concentration of 3a [M]
1	10	7	0.014
2	20	9	0.018
3	30	12	0.024
4	60	15	0.030
5	90	16	0.032
6	120	18	0.036
7	150	21	0.042
8	180	26	0.052
9	210	28	0.056
10	240	34	0.068

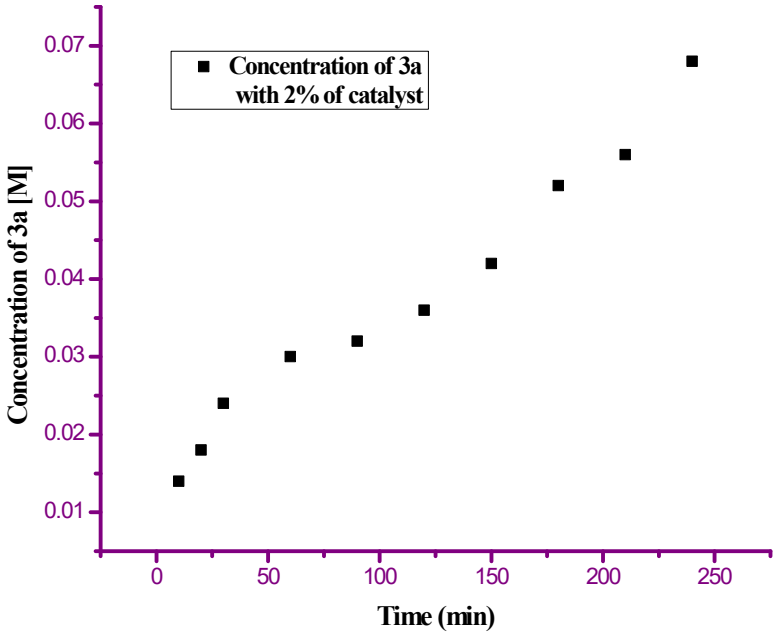


Figure S2: Time dependent formation of **3a**, employing 0.0026 M catalyst loading (2 mol%)

II) Procedure for Rate Order Determination

The rate order of the amination reaction with various components was determined by the initial rate method. The data of the concentration of the product vs time (min) plot was fitted linear with Origin Pro 8.5. The slope of the linear fitting represents the reaction rate. The order of the reaction was then determined by plotting $\log_{10}$(rate) vs $\log_{10}$(canc.) for a particular component.

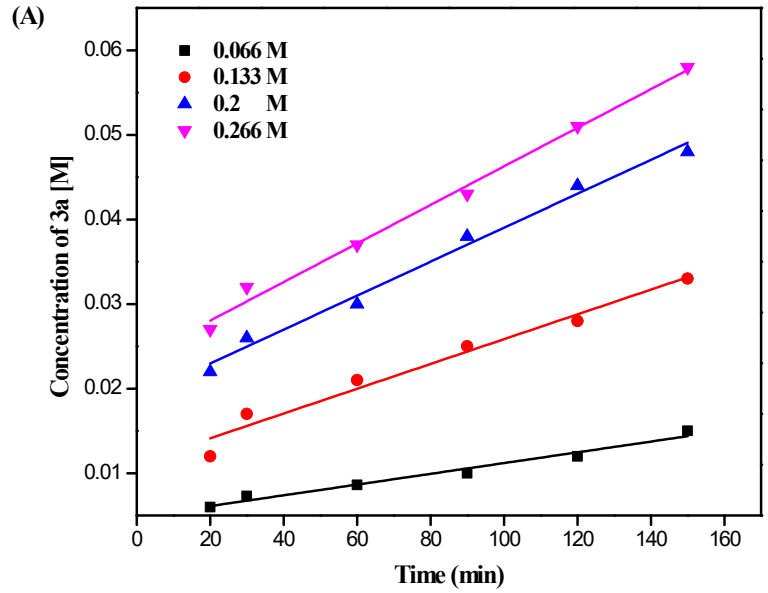
a) Representative procedure: rate determination with respect to amine

To determine the order of the amination reaction on Ar*-NH_2, initial rate at different initial concentration of amine were determined. The final data was obtained by averaging the results of two independent experiments for same initial concentration. In standard experiment, a Schlenk tube was charged with ligand and metal precursor (**L2**/$Pd(dba)_2$) (5 mg, 2 mol%), NaO^{t}Bu (0.038 g, 0.4 mmol), aryl halide **2a** (22 µL, 0.2 mmol), Ar-NH_2 **1a** (0.088 g, 0.2 mmol), and 1.5 mL toluene was added as a reaction solvent. The Schlenk tube containing the reaction mixture was heated at 100 ^{o}C in a preheated oil bath, at regular interval of time (10, 20, 30, 60,

90, and 120 mins) and after completion, the reaction solvent was completely evaporated in a vacuum. The total reaction mixture was dissolved in 0.6 mL of $CDCl_3$ and internal standard 1,4-dioxane (8 µL, 0.1 mmol) was added to the reaction tube. Then this reaction mixture was passed through a PTFE filter (25 mm, 0.22 µm), The concentration of **3a** obtained in each sample is determined with respect to internal standard " 1,4-dioxane ".

Table S9: Rate of amination reaction at different initial concentration of amine (**1a**)

Experiment	Amount of **1a** (g)	Initial Conc. of **1a** [M]	Initial Rate [$Mmin^{-1}$] x 10^{-4}	R^2
1	0.044	0.066	0.635 ± 0.048	0.9712
2	0.088	0.133	1.460 ± 0.127	0.9630
3	0.132	0.2	2.007 ± 0.107	0.9859
4	0.176	0.266	2.280 ± 0.098	0.9907



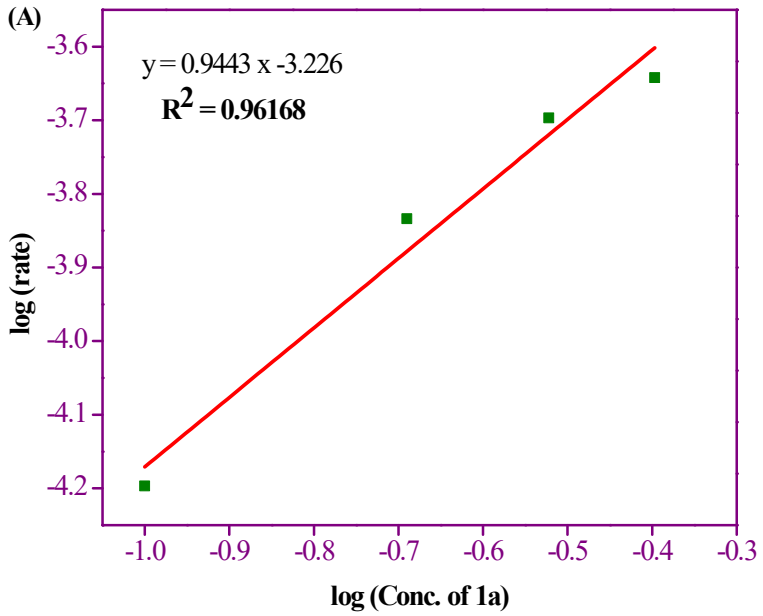


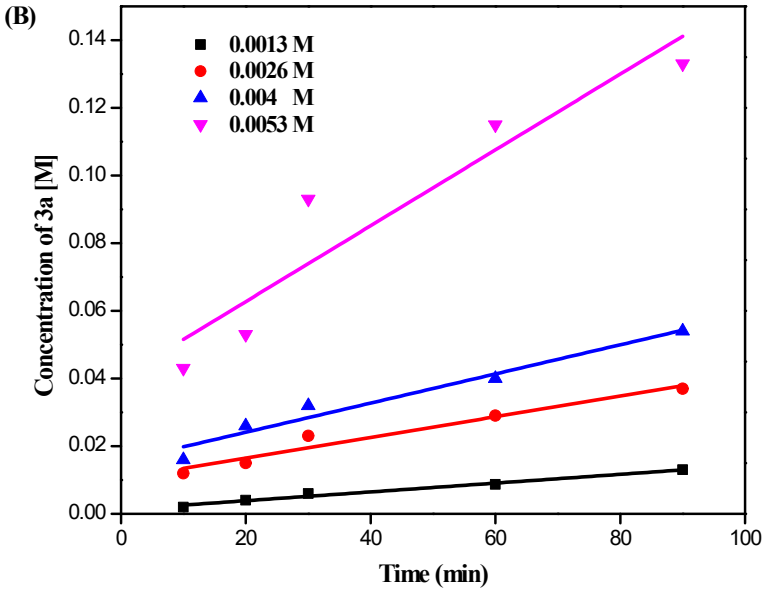
Figure S3: (A) Time-dependent formation of **3a** at different initial concentrations of **1a** (A') Plot of $\log_{10}$(Conc. of **1a**) *vs*. $\log_{10}$(rate).

b) Representative procedure: rate determination with respect to catalyst

To determine the order of the amination reaction on catalyst loading initial rate at different initial concentration of amine were determined. The final data was obtained by averaging the results of two independent experiments for same initial concentration. In standard experiment, a Schlenk tube was charged with ligand and metal precursor (**L2**/$Pd(dba)_2$) (5 mg, 2 mol%), NaO^{t}Bu (0.038 g, 0.4 mmol), aryl halide **2a** (22 µL, 0.2 mmol), Ar-NH_2 **1a** (0.088 g, 0.2 mmol), and 1.5 mL toluene was added as a reaction solvent. The Schlenk tube containing the reaction mixture was heated at 100 ^{o}C in a preheated oil bath, at regular interval of time (10, 20, 30, 60, and 90 mins) and after completion, the reaction solvent was completely evaporated in a vacuum. The total reaction mixture was dissolved in 0.6 mL of $CDCl_3$ and internal standard 1,4-dioxane (8 µL, 0.1 mmol) was added to the reaction tube. Then this reaction mixture was passed through a PTFE filter (25 mm, 0.22 µm), The concentration of **3a** obtained in each sample is determined with respect to internal standard "1, 4-dioxane".

Table S10: Rate of amination reaction at different initial concentrations of catalyst

Experiment	Amount of catalyst (g)	Initial Conc. of catalyst [M]	Initial Rate [$Mmin^{-1}$] x 10^{-4}	R^2
1	0.003	0.0013	1.020 ± 0.0845	0.9731
2	0.006	0.0026	2.451 ± 0.0738	0.9964
3	0.009	0.004	3.393 ± 0.383	0.9508
4	0.012	0.0053	9.208 ± 0.877	0.9646



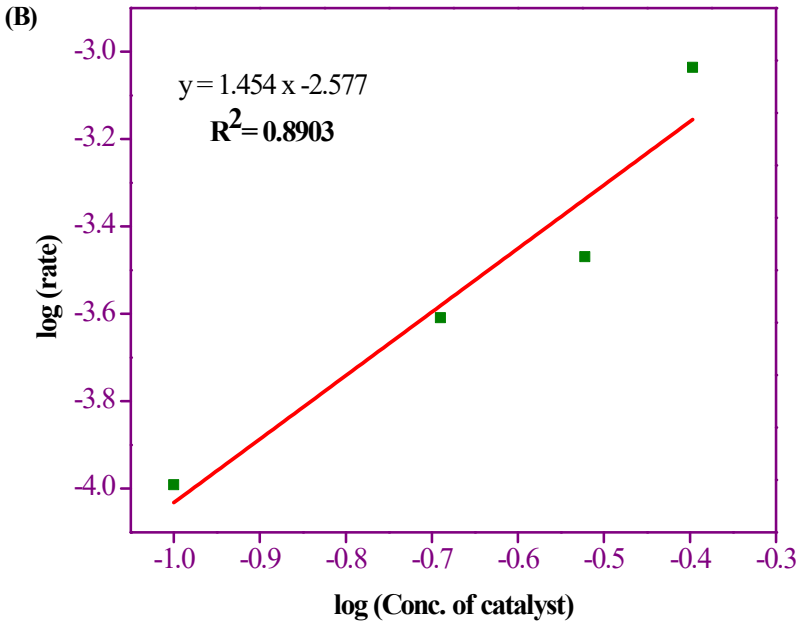


Figure S4: (B) Time-dependent formation of **3a** at different initial concentrations of catalyst (B') Plot of $\log_{10}$(Conc. of **catalyst**) *vs*. $\log_{10}$(rate).

a) Representative procedure: rate determination with respect to aryl bromide

To determine the order of the amination reaction on aryl bromide, initial rate at different initial concentration of amine were determined. The final data was obtained by averaging the results of two independent experiments for same initial concentration. In standard experiment, a Schlenk tube was charged with ligand and metal precursor (**L2**/$Pd(dba)_2$) (5 mg, 2 mol%), NaO^tBu (0.038 g, 0.4 mmol), aryl halide **2a** (22 µL, 0.2 mmol), Ar-NH_2 **1a** (0.088 g, 0.2 mmol), and 1.5 mL toluene was added as a reaction solvent. The Schlenk tube containing the reaction mixture was heated at 100 ^oC in a preheated oil bath, at regular interval of time (10, 20, 30, 60, and 90 mins) and after completion, the reaction solvent was completely evaporated in a vacuum. The total reaction mixture was dissolved in 0.6 mL of $CDCl_3$ and internal standard 1,4-dioxane (8 µL, 0.1 mmol) was added to the reaction tube. Then this reaction mixture was passed through a PTFE filter (25 mm, 0.22 µm), The concentration of **2a** obtained in each sample is determined with respect to internal standard " 1,4-dioxane".

Table S11: Rate of Amination reaction at different initial concentrations of aryl bromide (**2a**)

Experiment	Amount of **2a** (g)	Initial Conc. of **2a** [M]	Initial Rate [$Mmin^{-1}$] x 10^{-4}	R^2
1	0.0126	0.066	1.156 ± 0.118	0.9592
2	0.0253	0.133	1.799 ± 0.164	0.9674
3	0.0380	0.2	2.289 ± 0.243	0.9562
4	0.0506	0.266	2.355 ± 0.104	0.9921

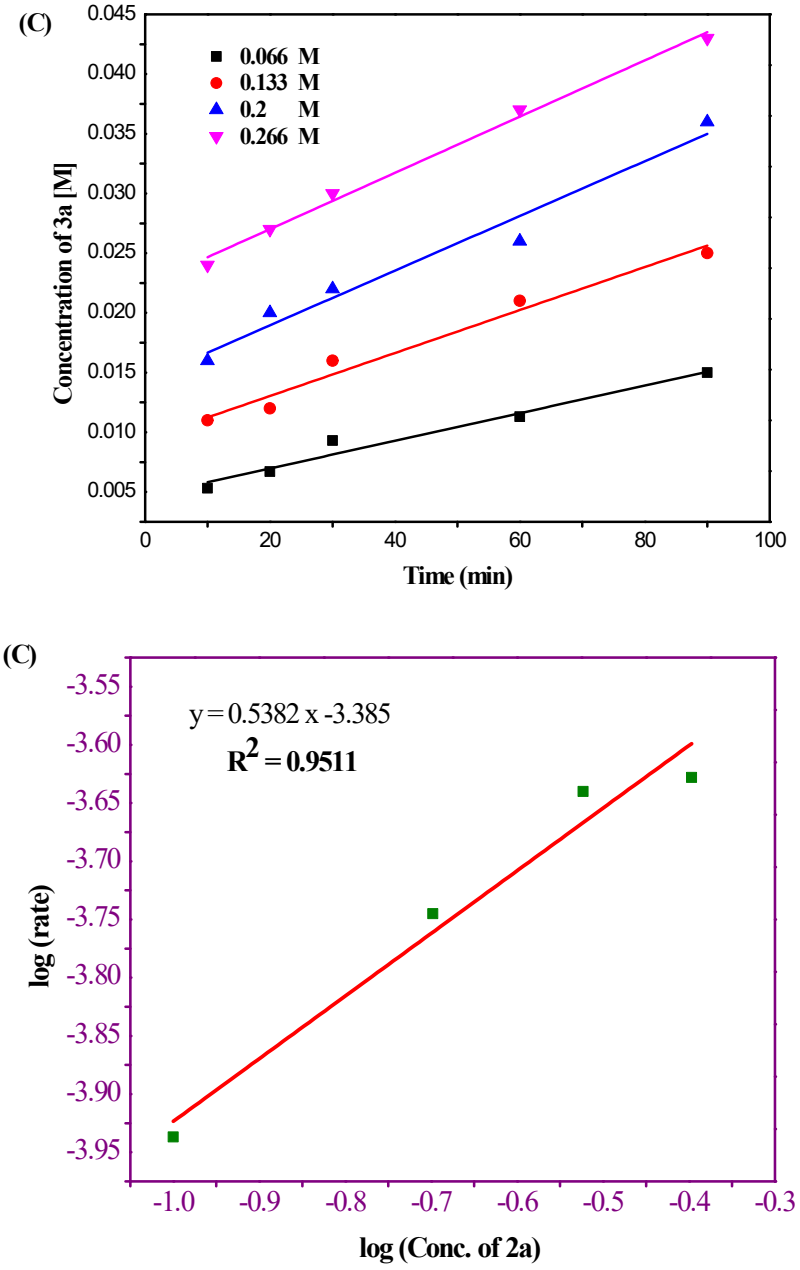
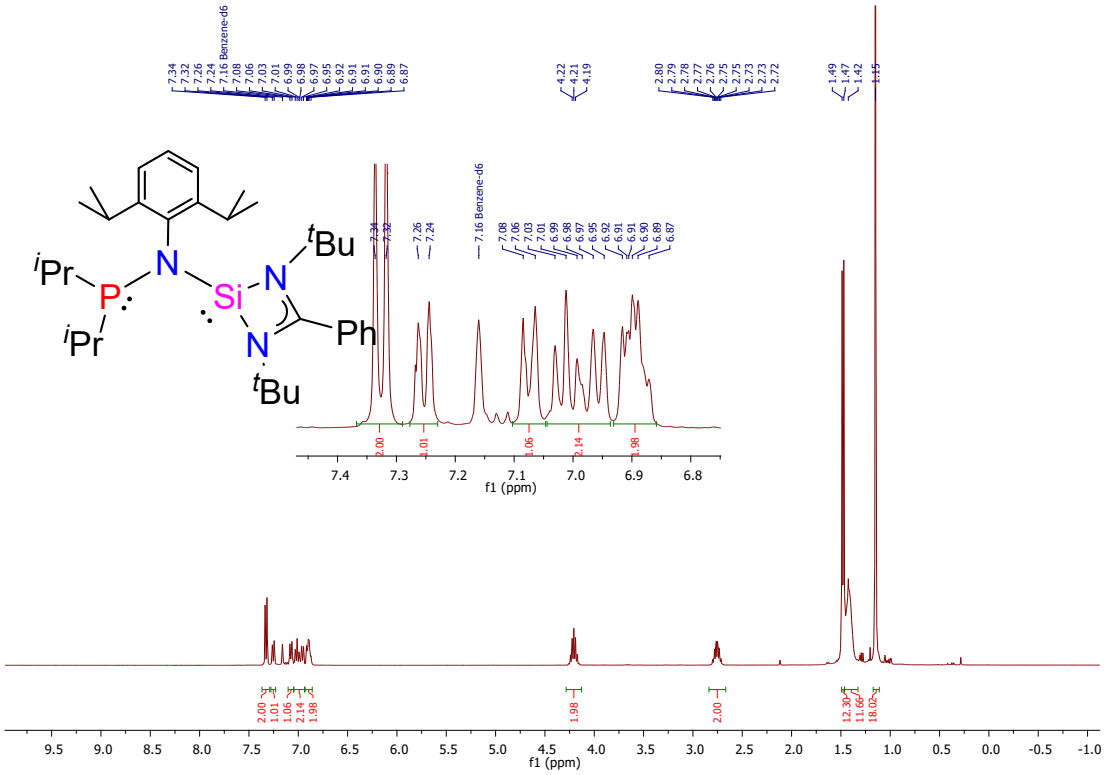
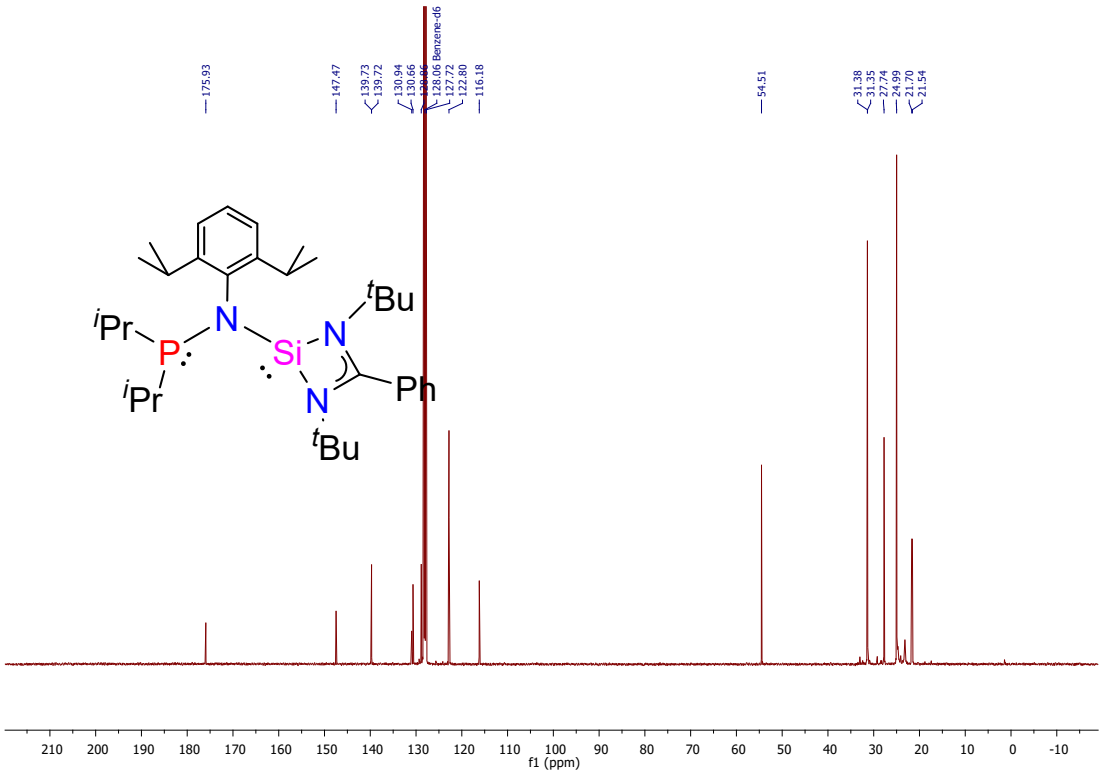


Figure S5: (C) Time-dependent formation of **3a** at different initial concentrations of **2a** (C') Plot of $\log_{10}$(Conc. of **2a**) *vs*. $\log_{10}$(rate).

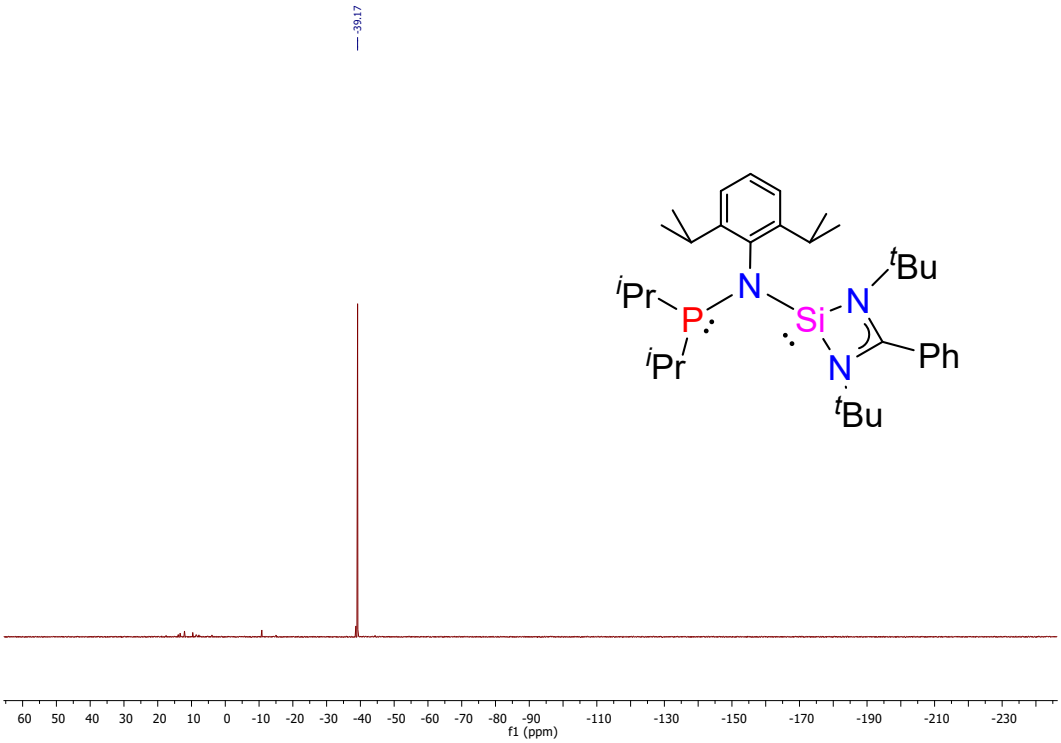
S7. NMR Spectra



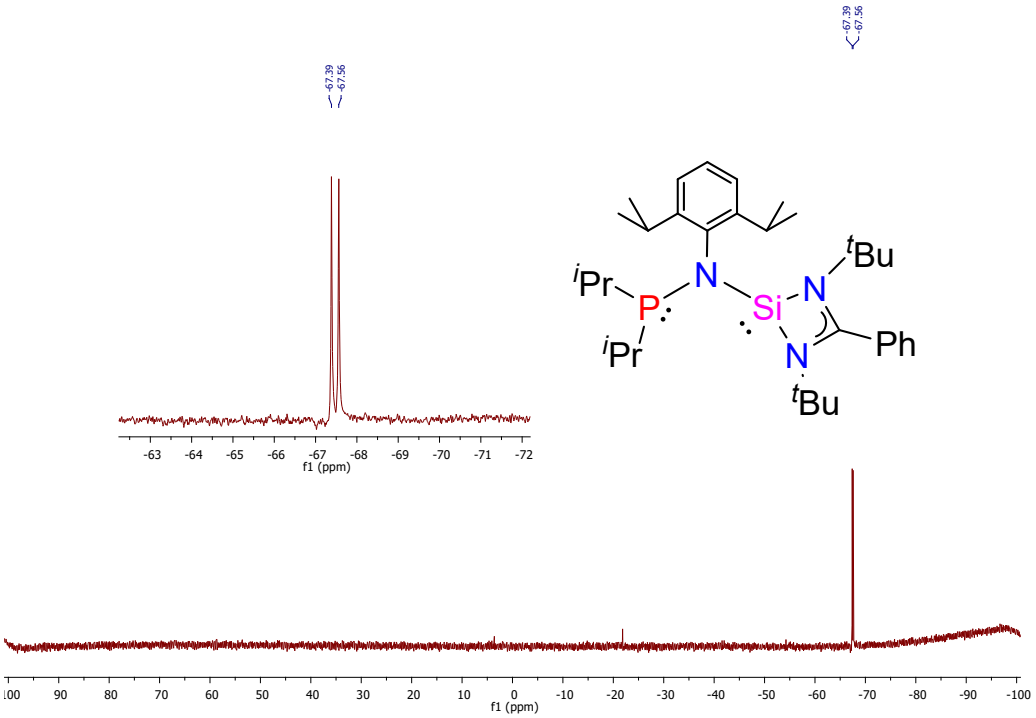
^{1}H NMR of L2



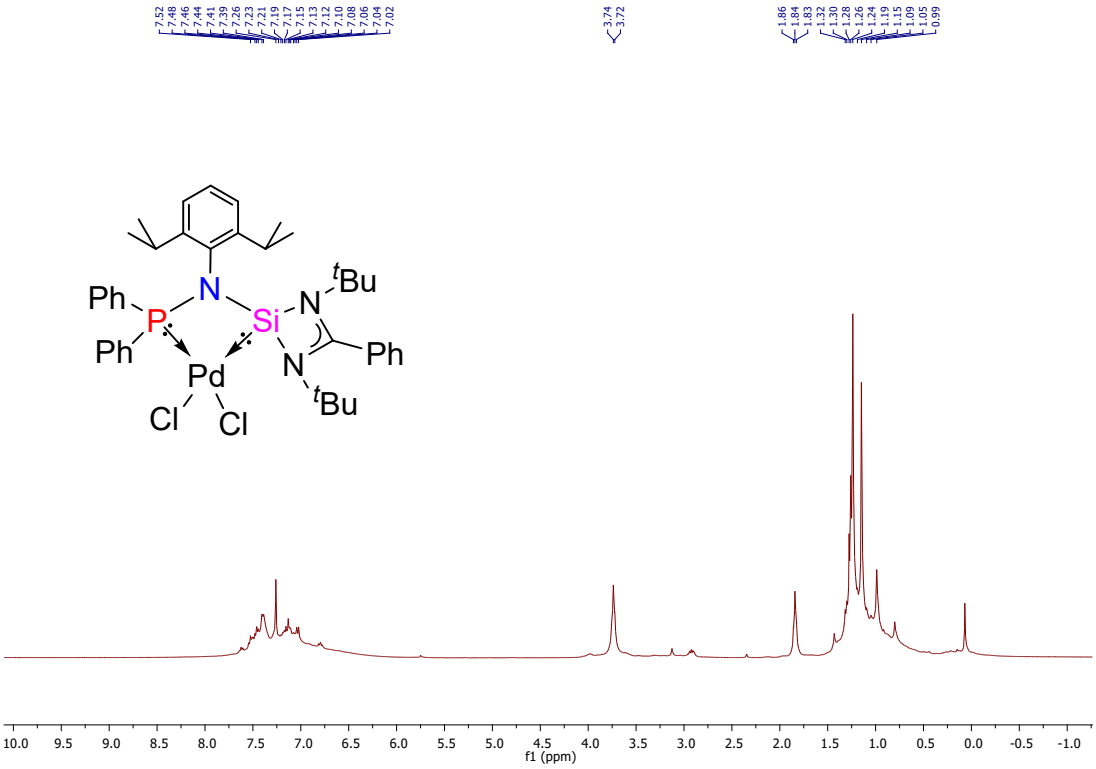
$^{13}C\{^1H\}$ NMR of L2



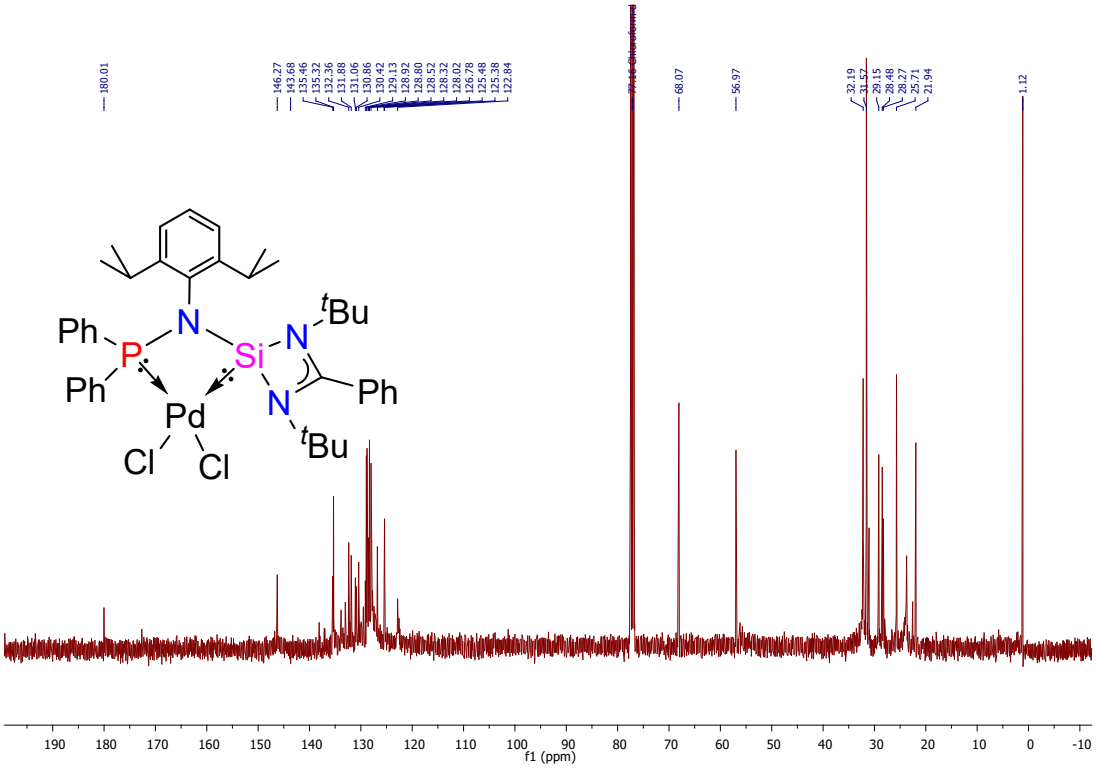
$^{31}P\{^1H\}$ NMR of L2



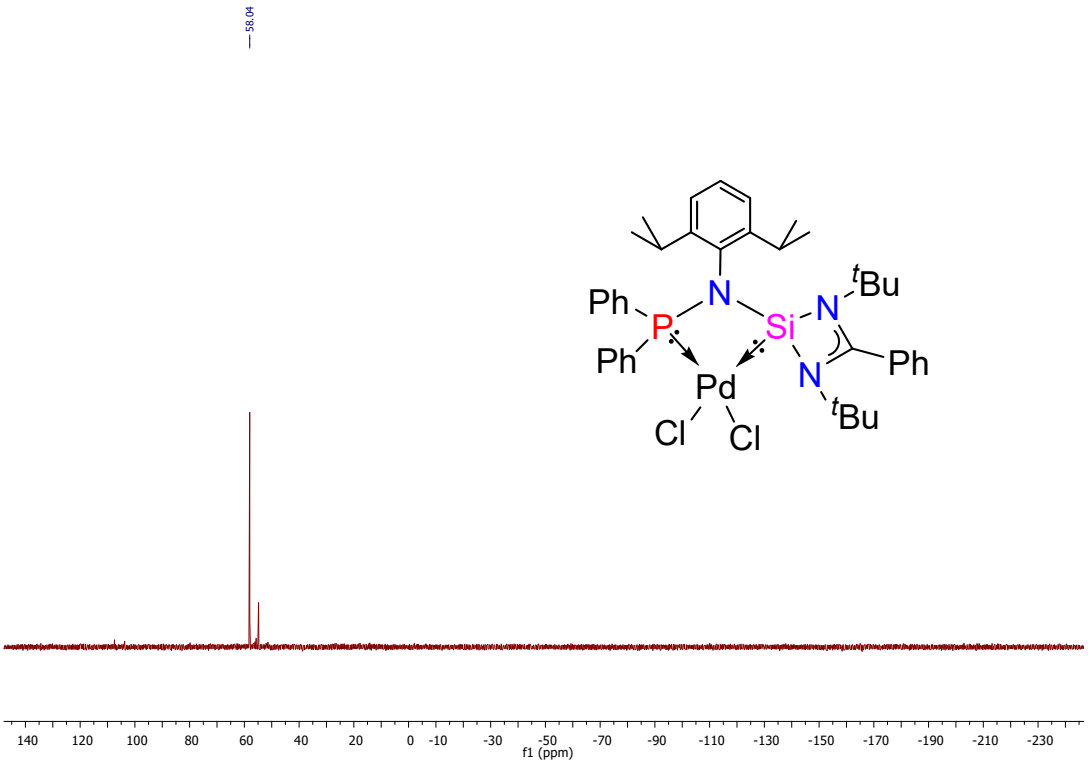
$^{29}Si\{^1H\}$ NMR of L_2



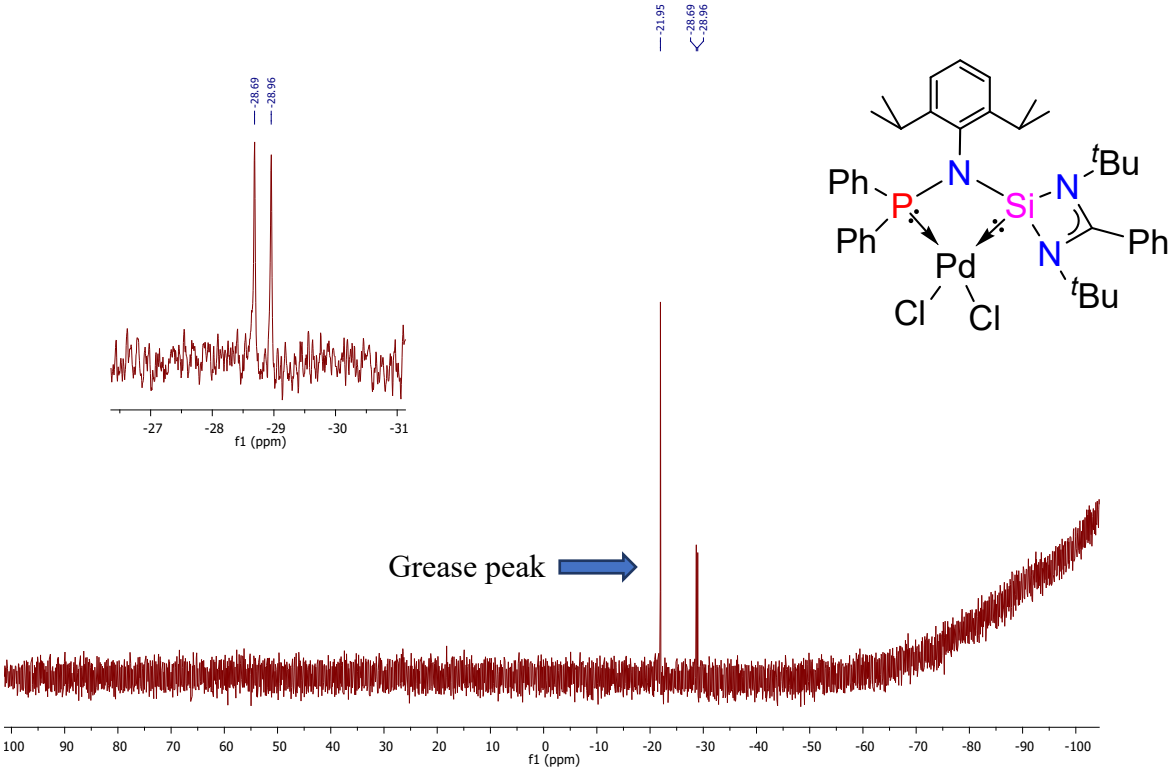
^{1}H NMR of 1



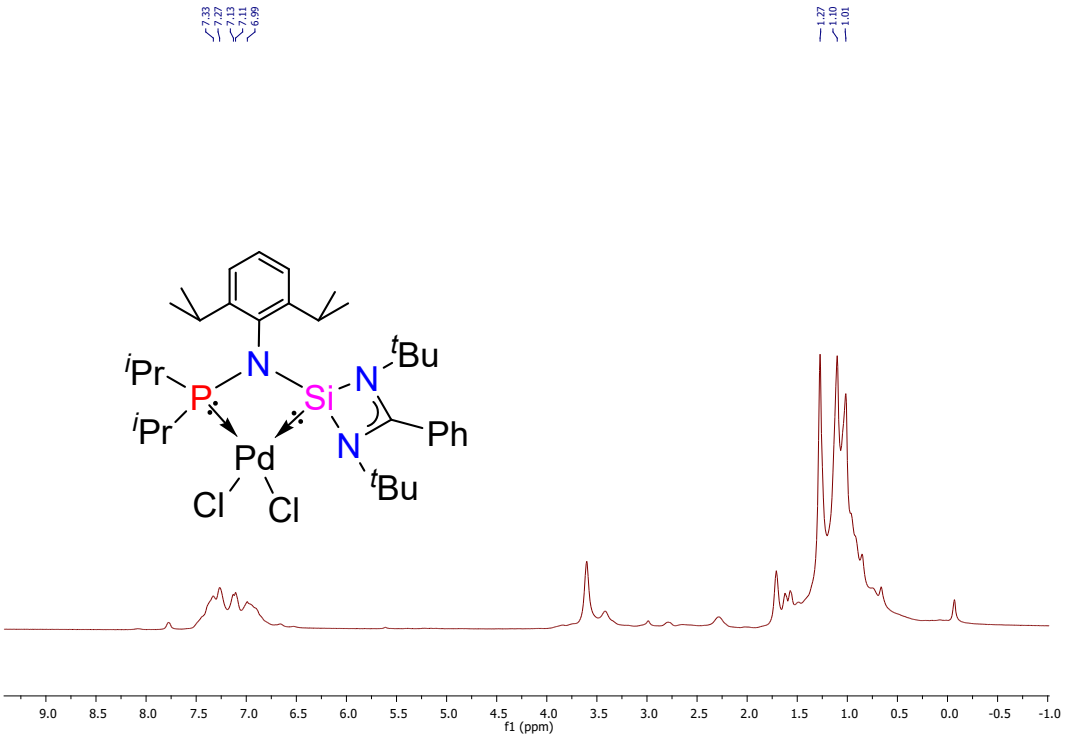
^{13}C{^{1}H} NMR of 1



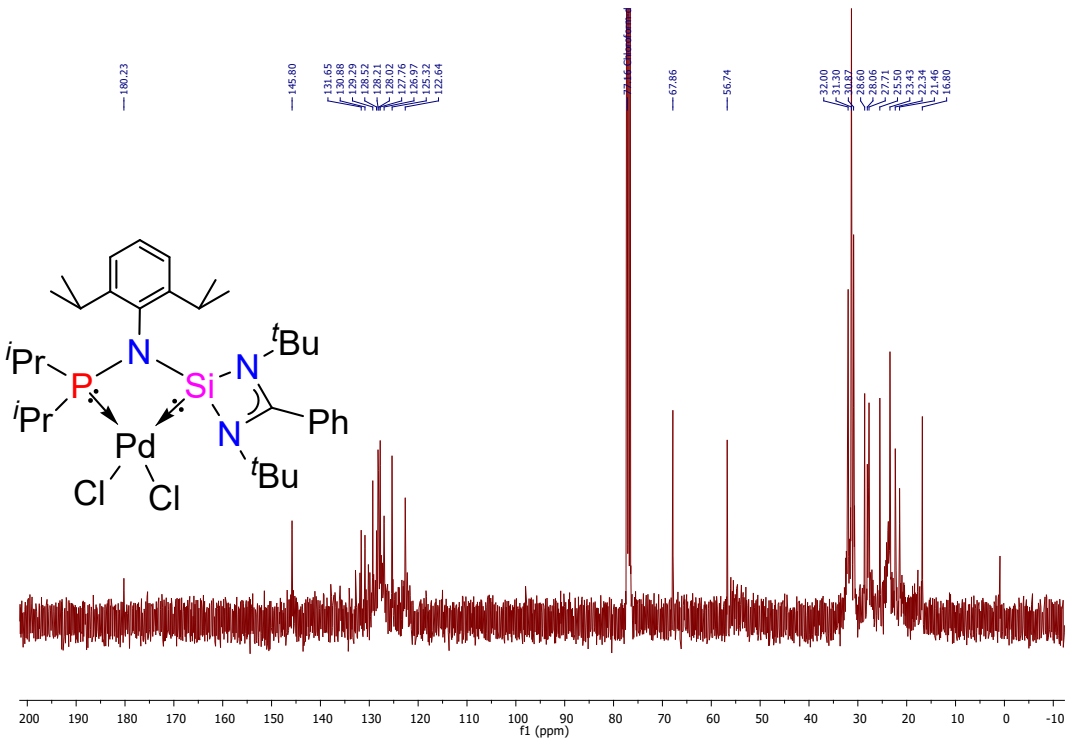
$^{31}P\{^{1}H\}$ NMR of 1



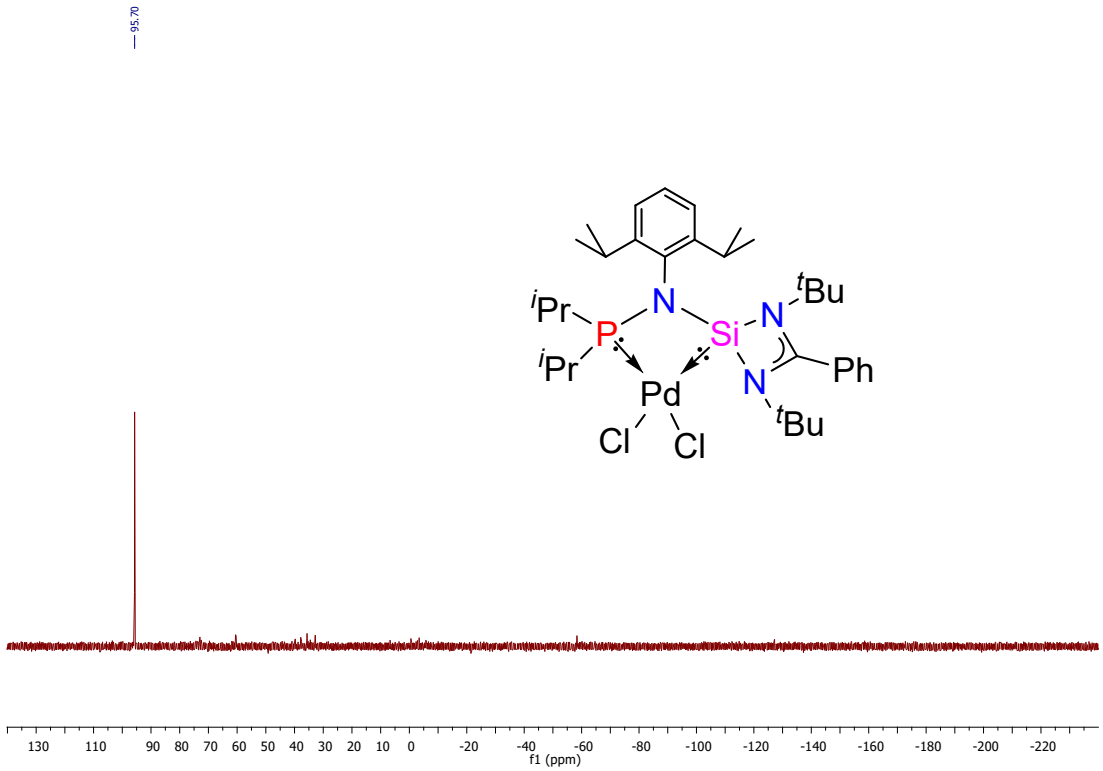
$^{29}Si\{^{1}H\}$ NMR of 1



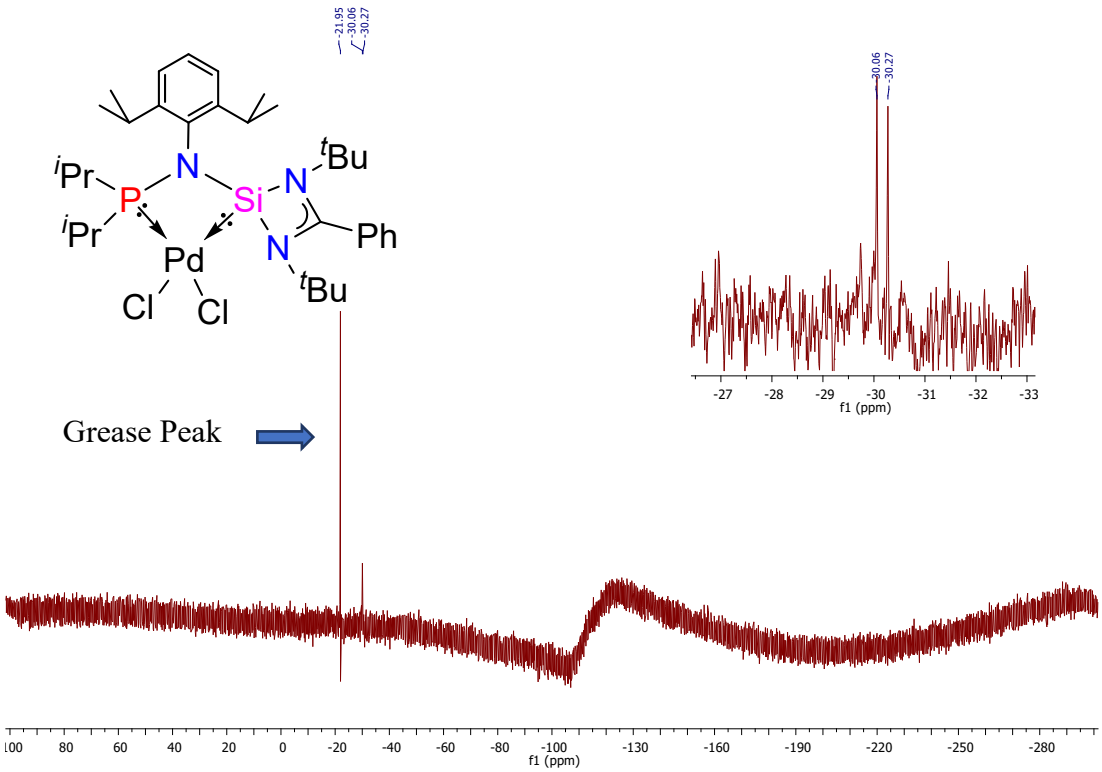
^{1}H NMR of 2



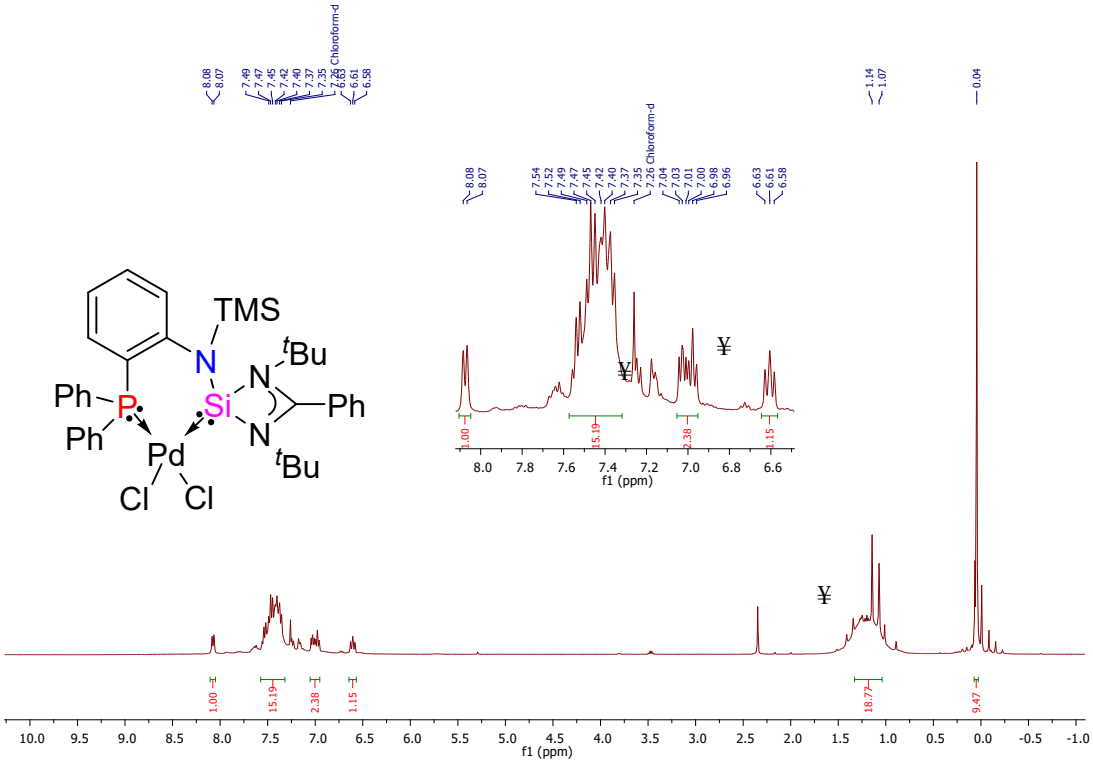
^{13}C{^{1}H} NMR of 2



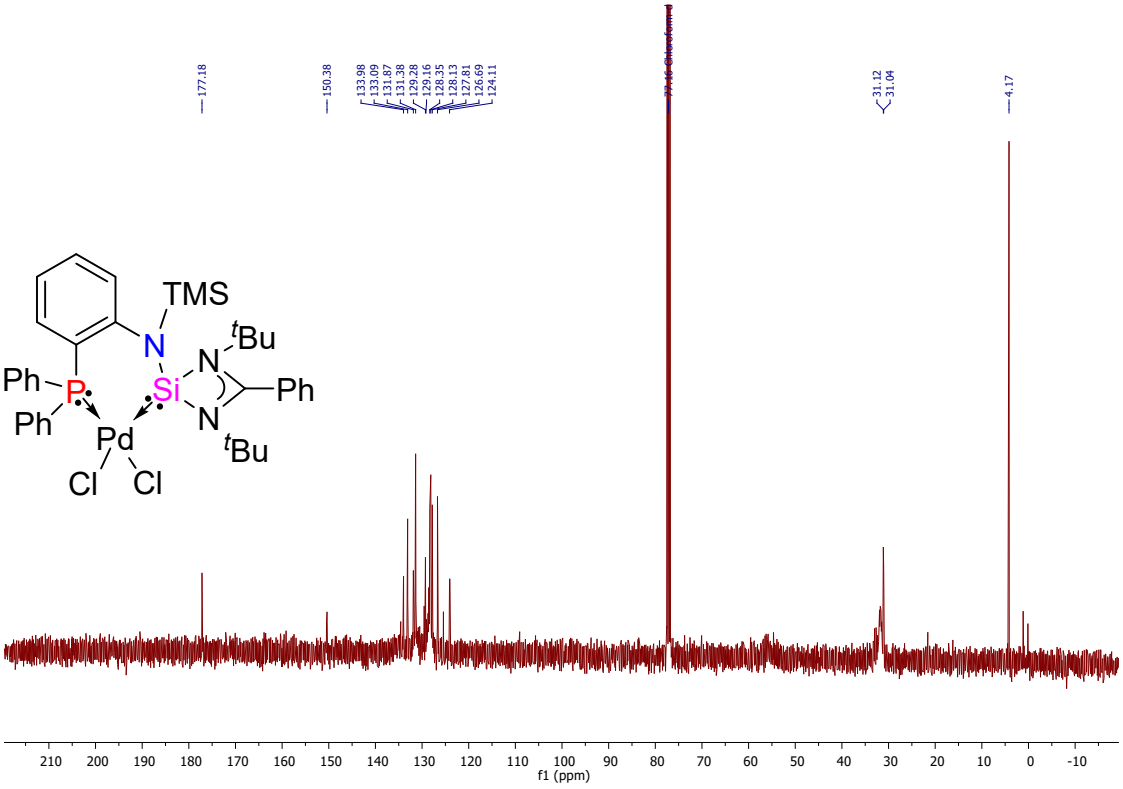
$^{31}P\{^{1}H\}$ NMR of 2



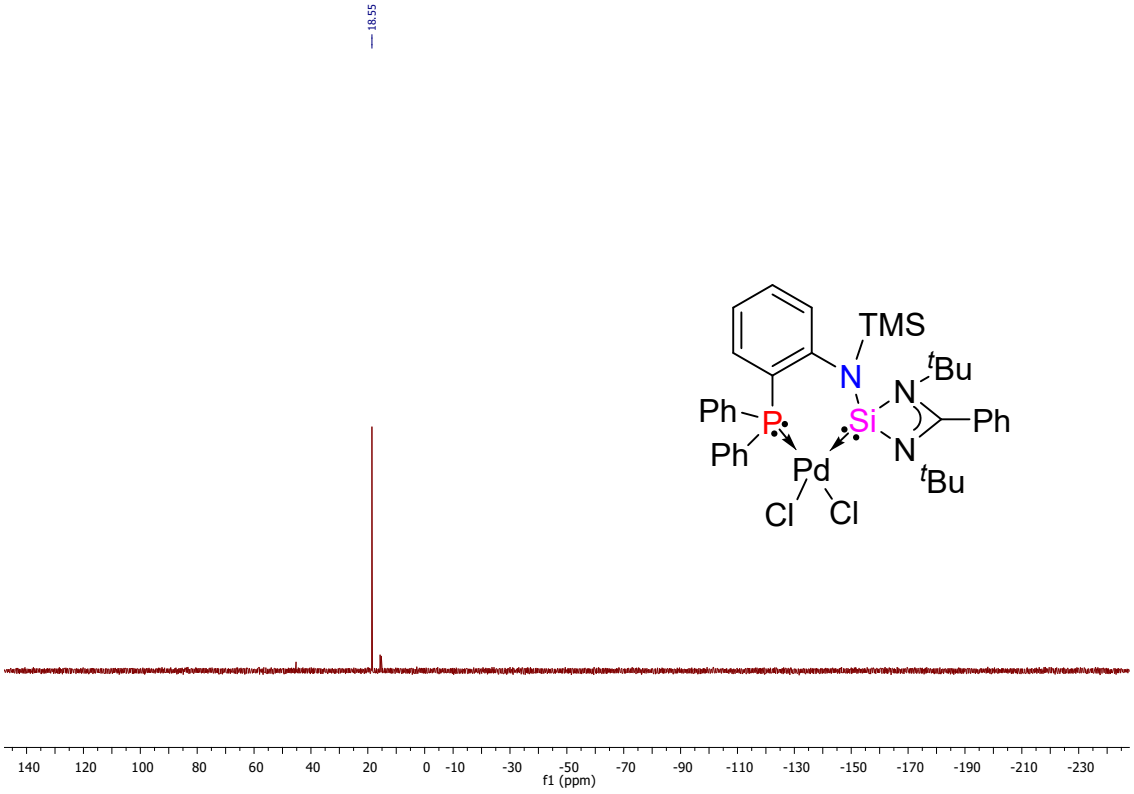
$^{29}Si\{^{1}H\}$ NMR of 2



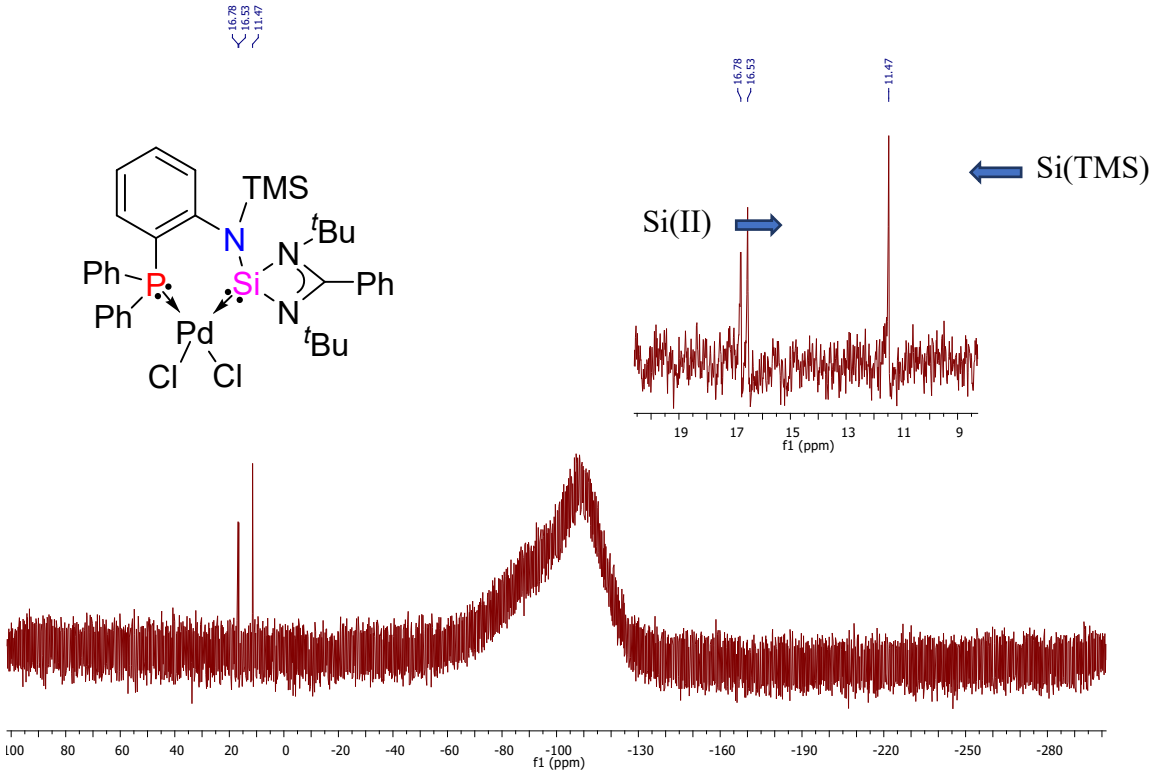
^{1}H NMR of 3 (¥ =Toluene)



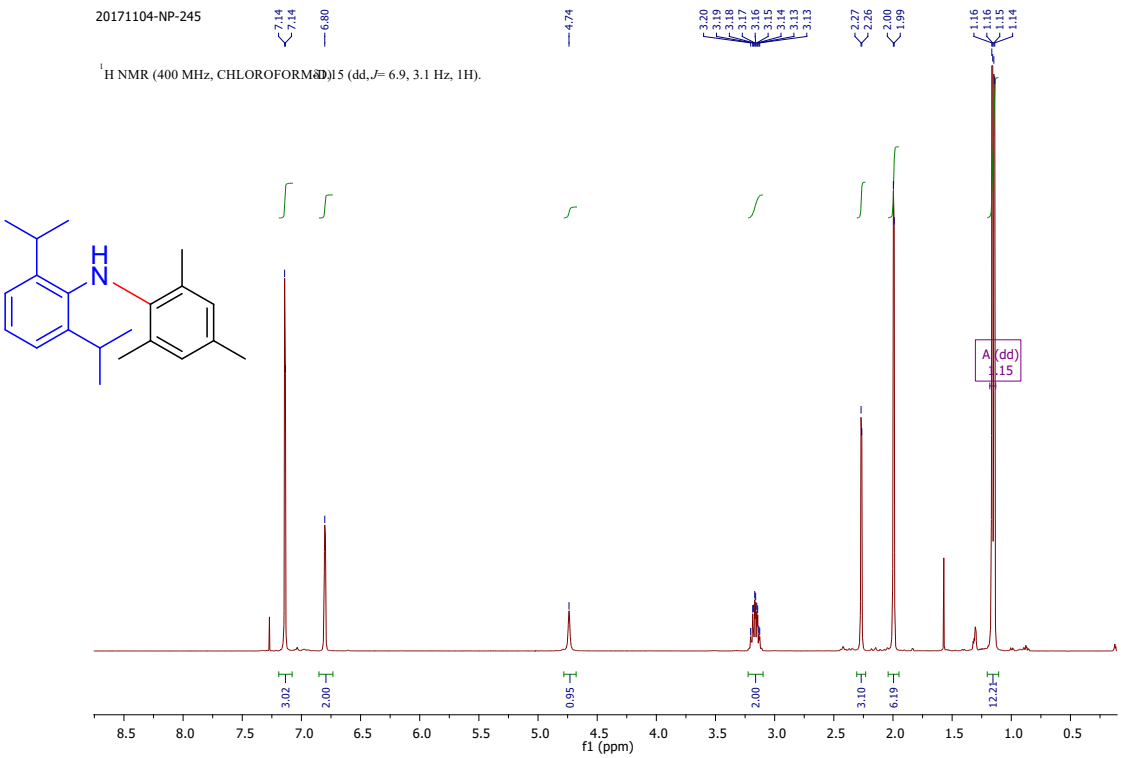
^{13}C{^{1}H} NMR of 3



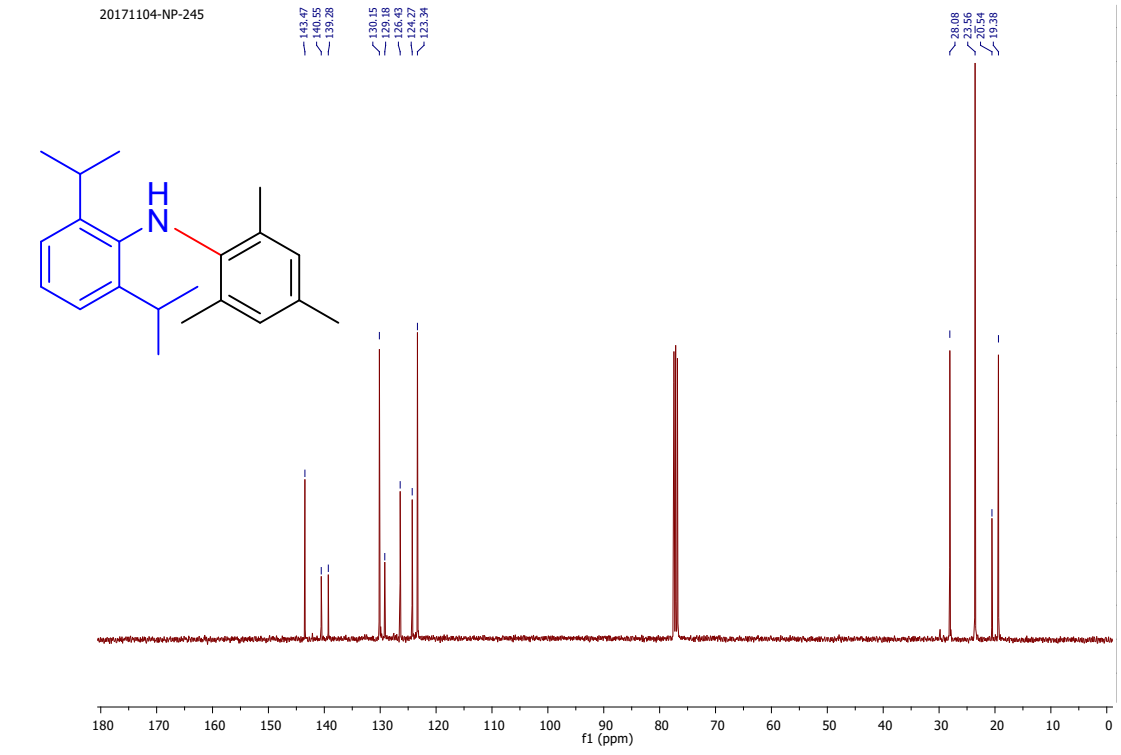
$^{31}P\{^{1}H\}$ NMR of 3



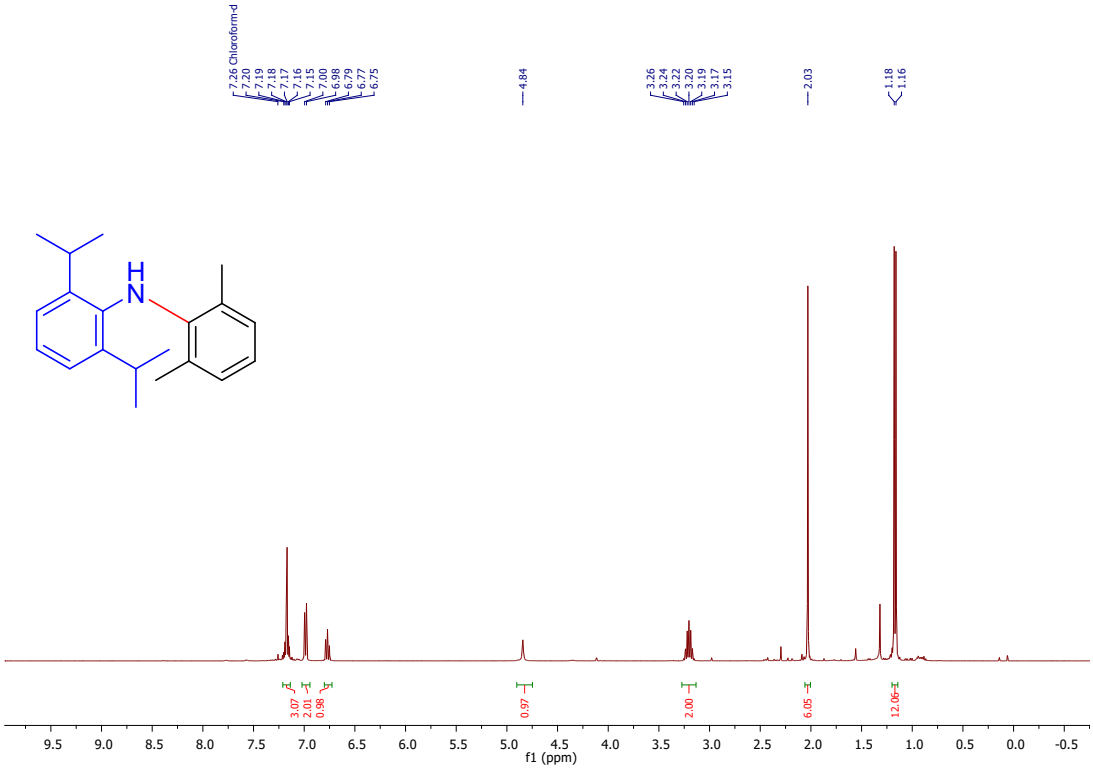
$^{29}Si\{^{1}H\}$ NMR of 3



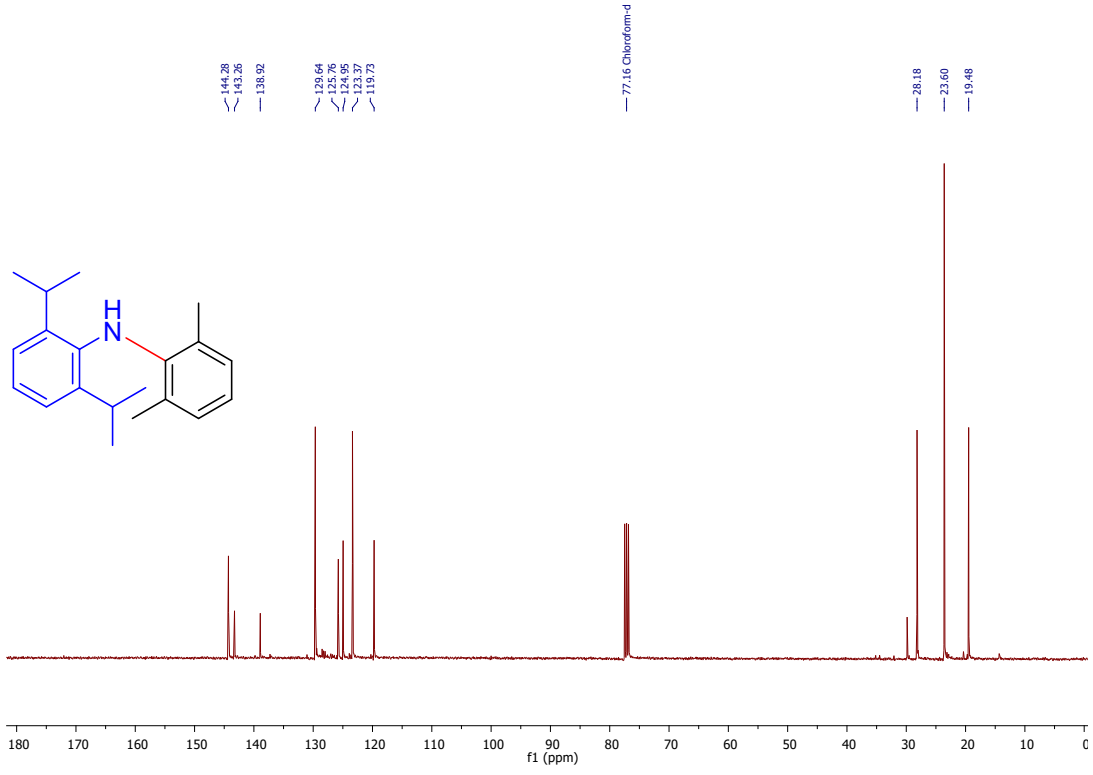
^{1}H NMR of 4a



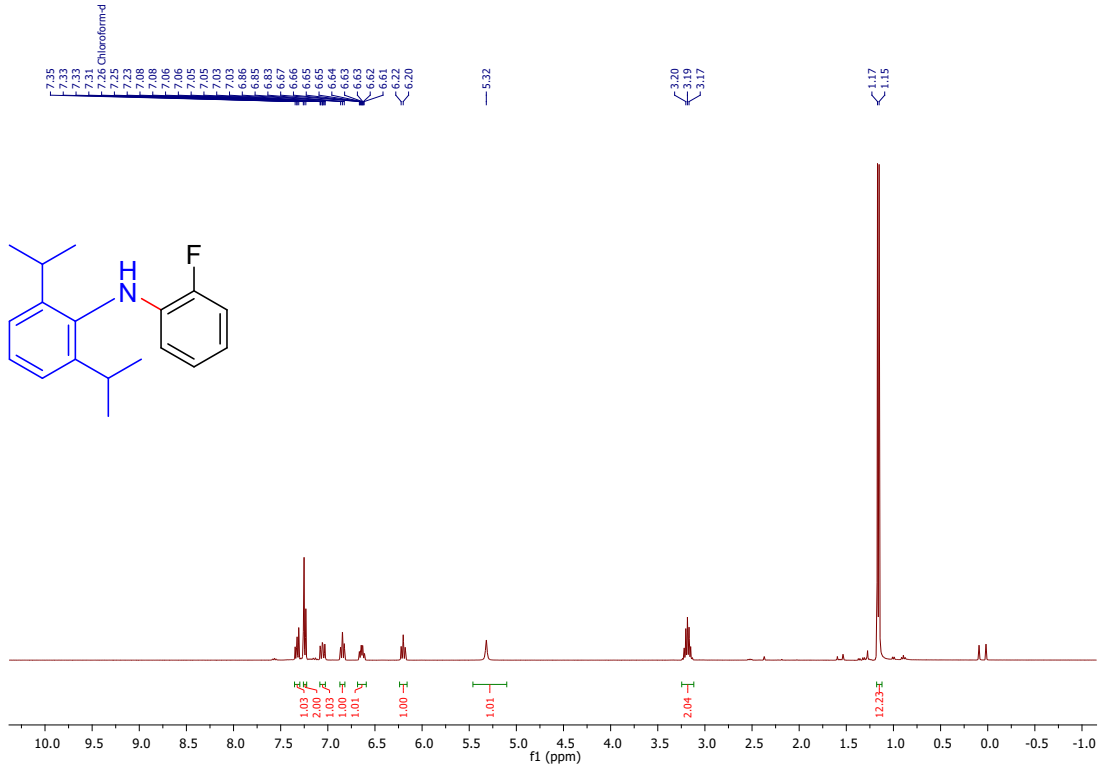
^{13}C{^{1}H} NMR of 4a



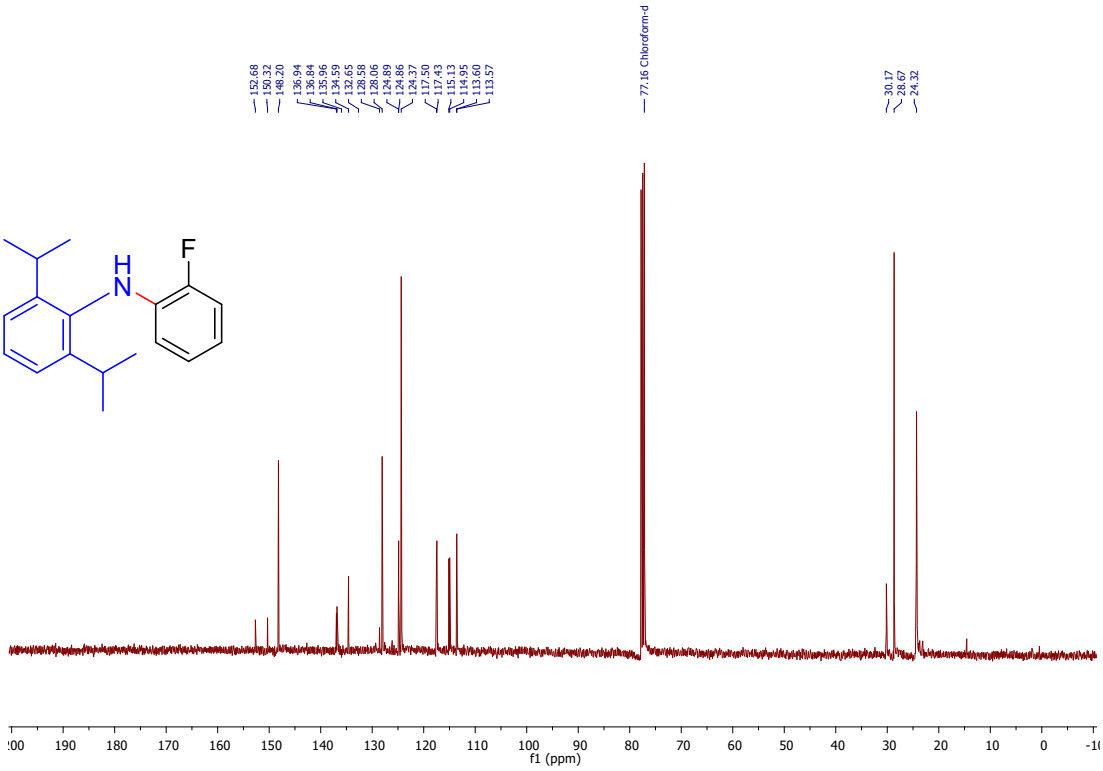
^{1}H NMR of 4b



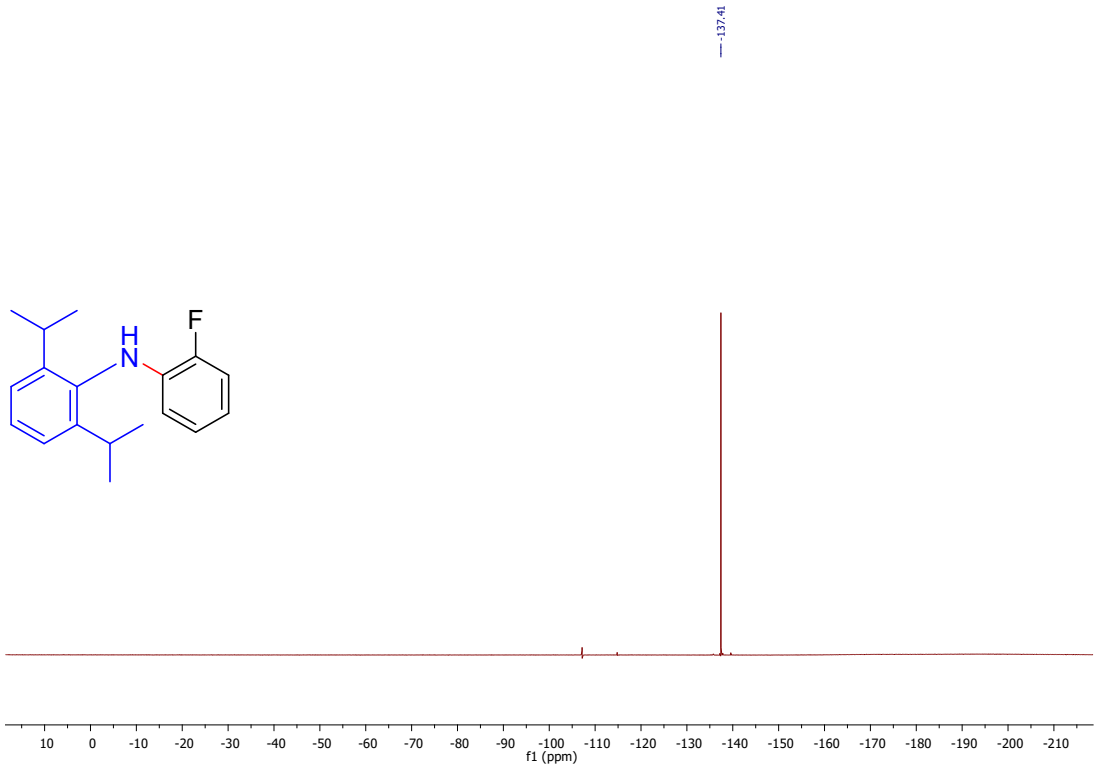
^{13}C{^{1}H} NMR of 4b



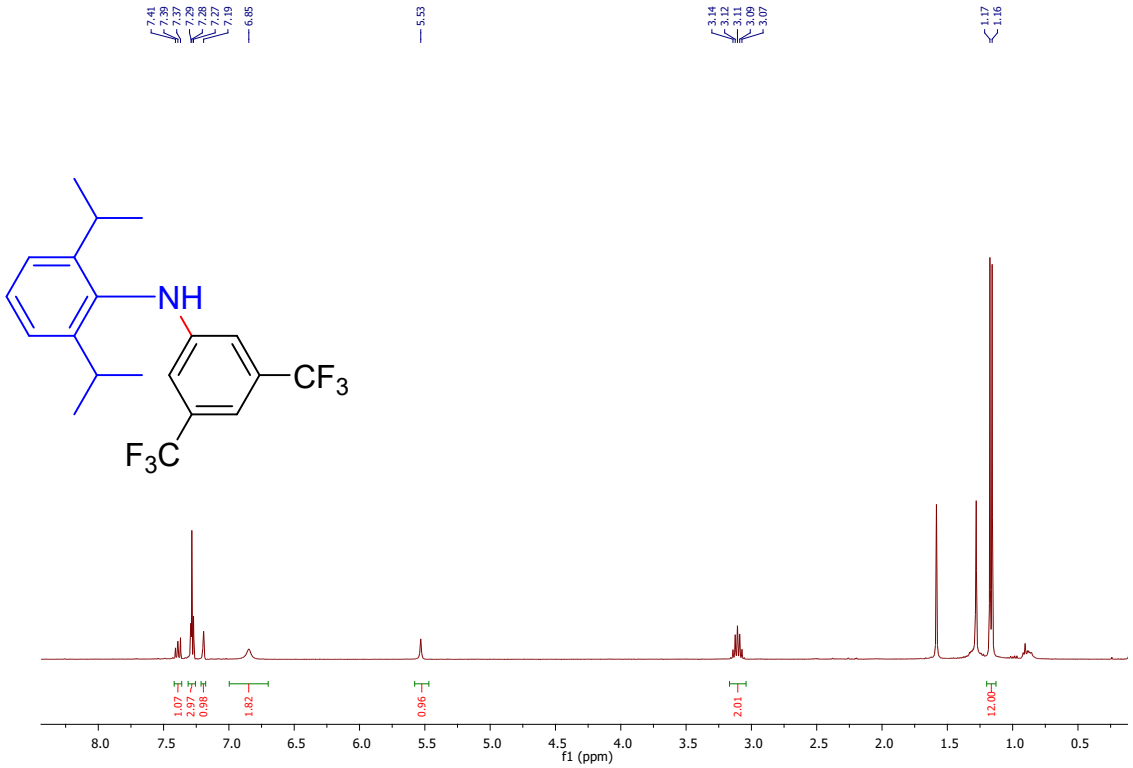
^{1}H NMR of 4c



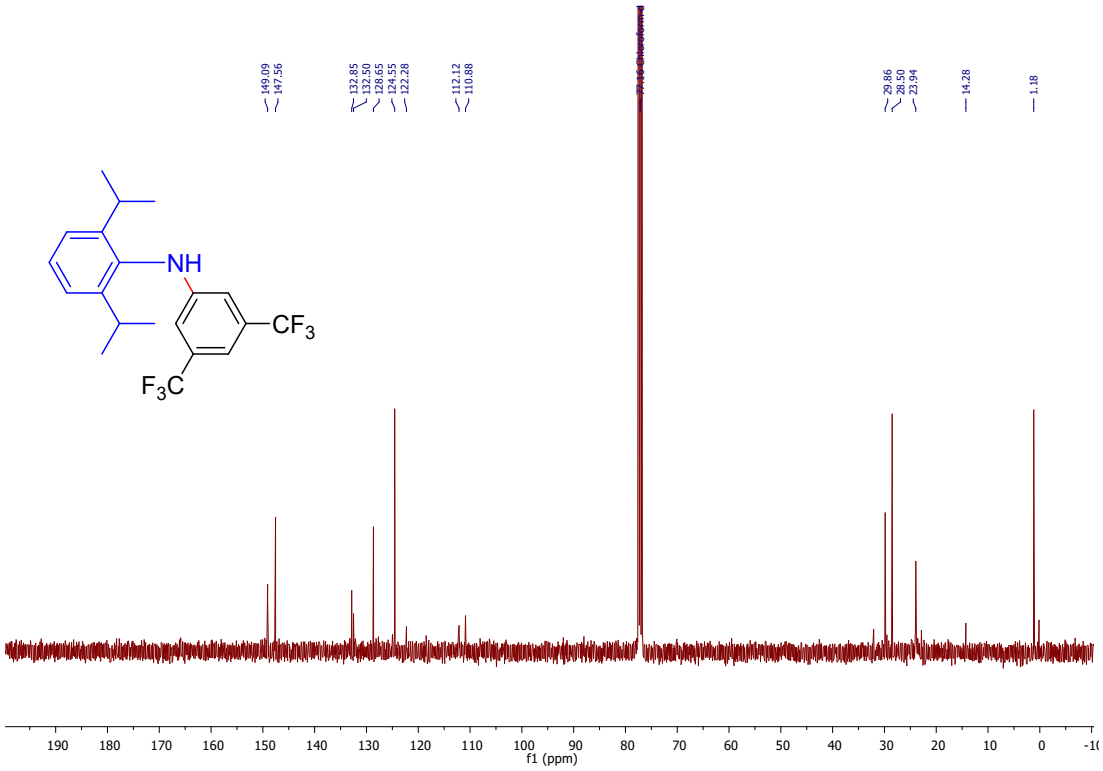
^{13}C{^{1}H} NMR of 4c



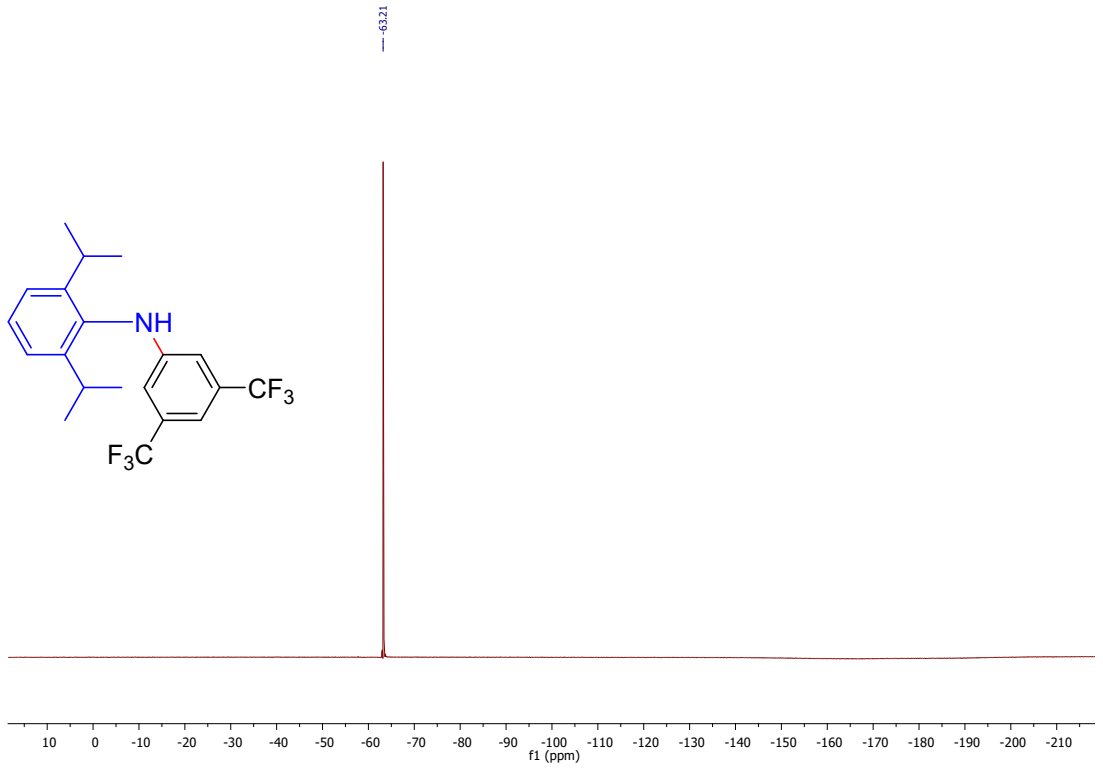
$^{19}F\{^{1}H\}$ NMR of 4c



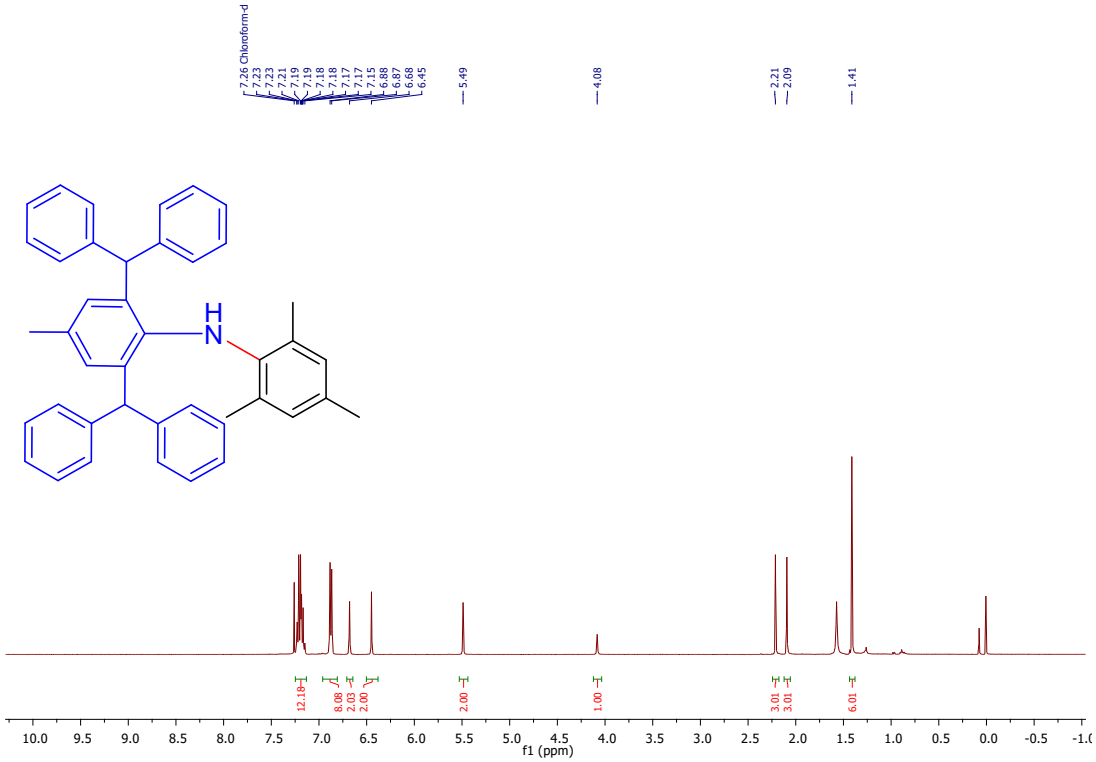
^{1}H NMR of 4d



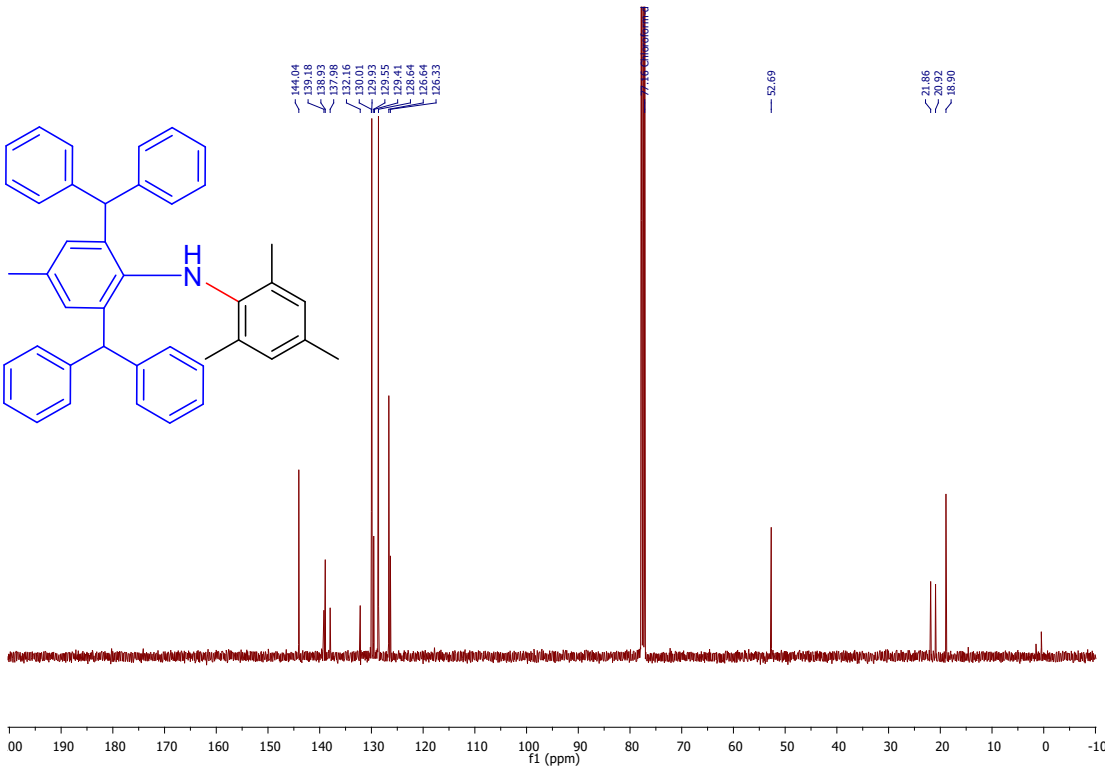
$^{13}C\{^{1}H\}$ NMR of 4d



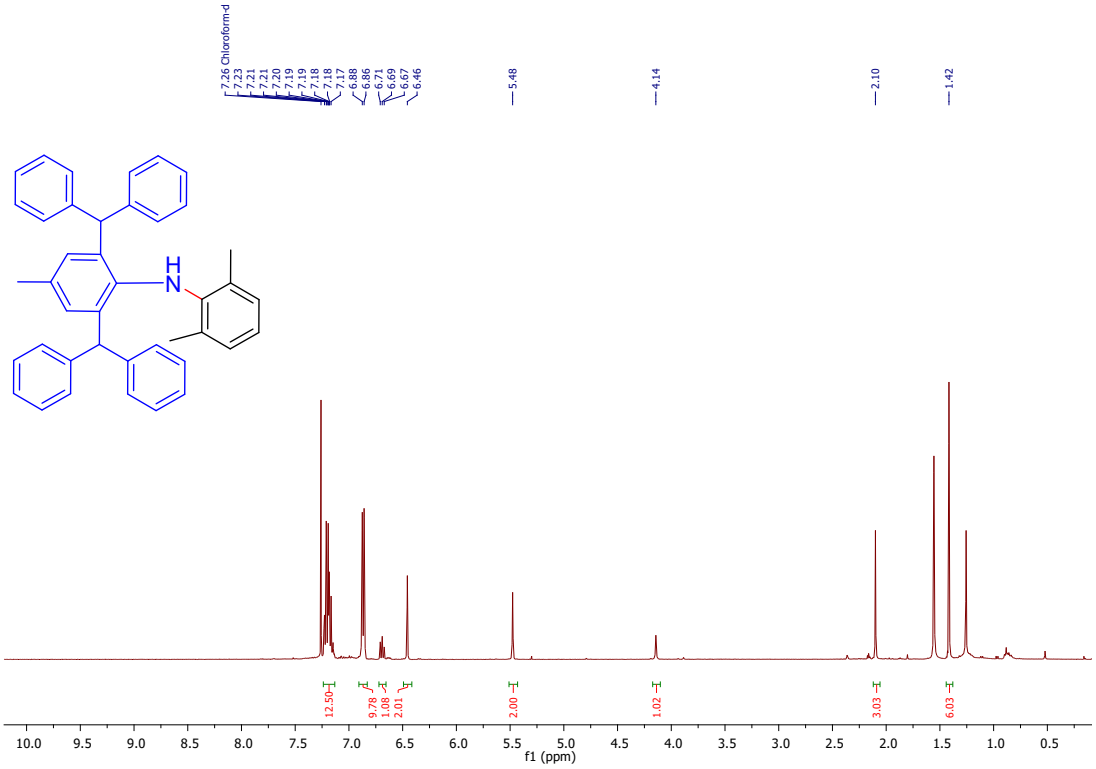
$^{19}F\{^{1}H\}$ NMR of 4d



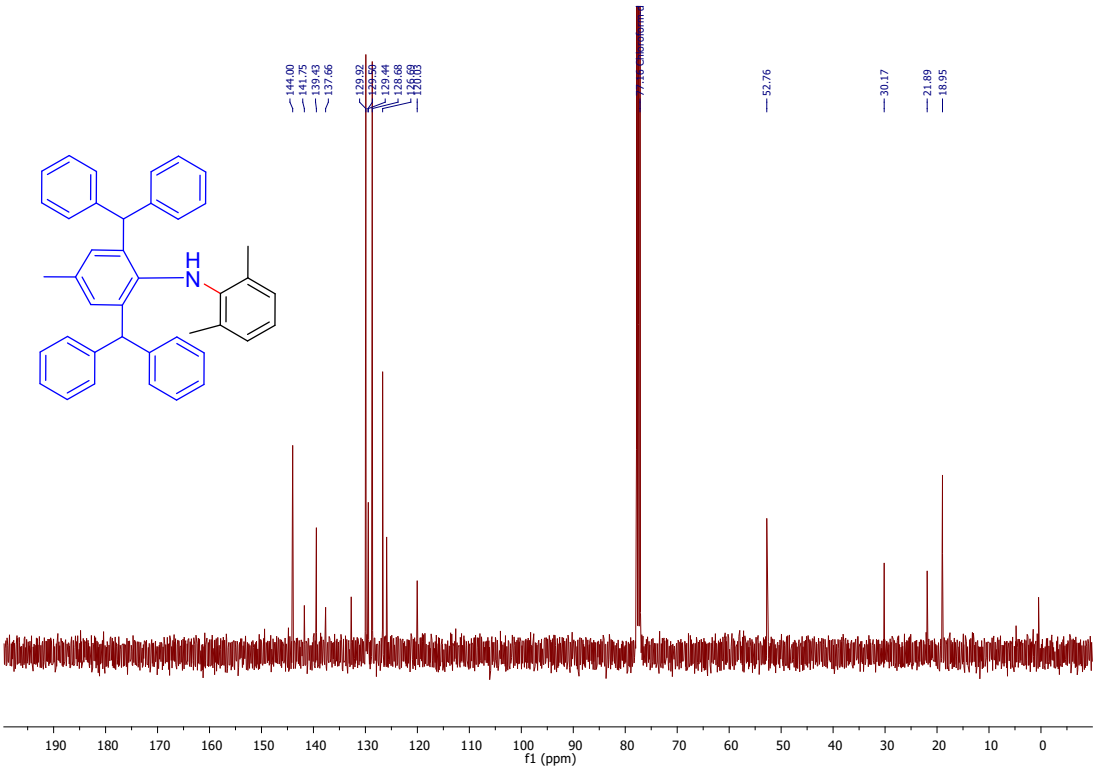
^{1}H NMR of 4e



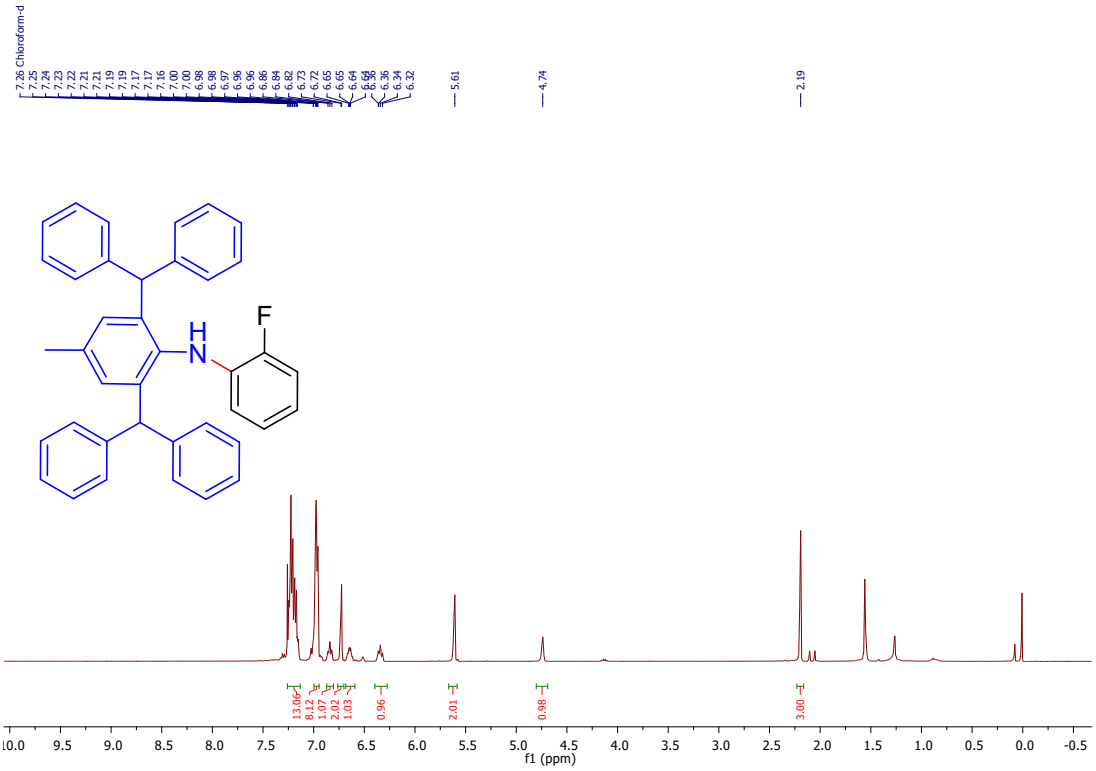
^{13}C{^{1}H} NMR of 4e



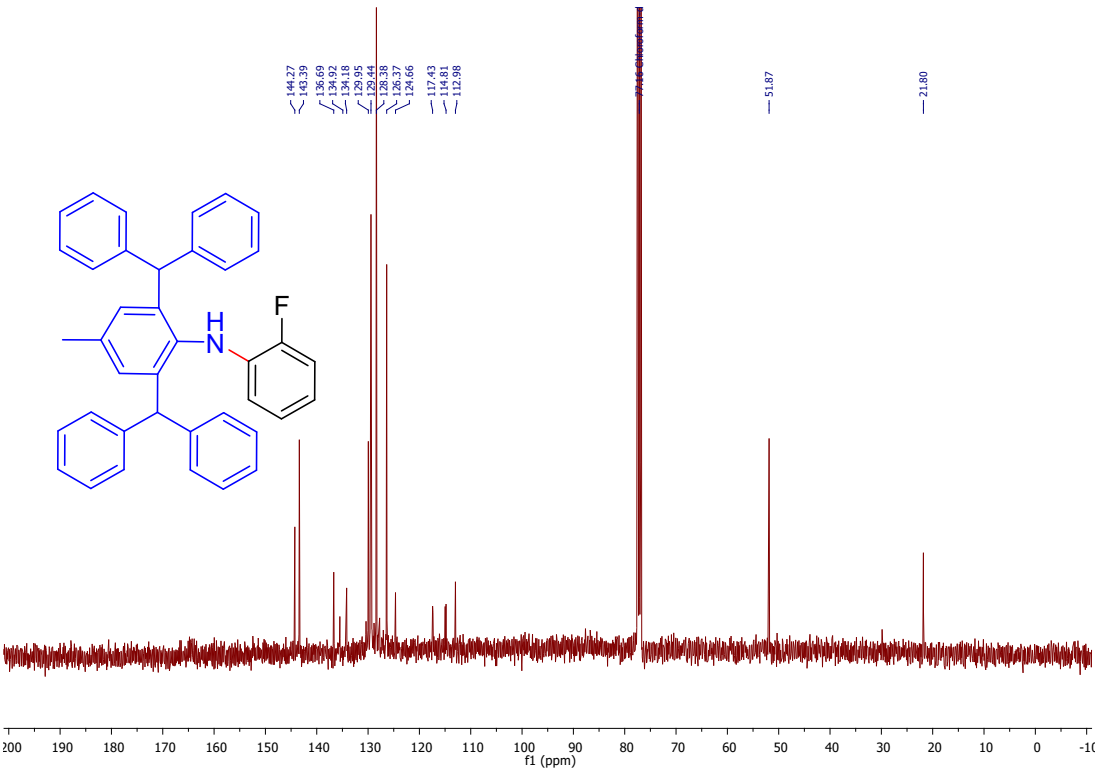
^{1}H NMR of 4f



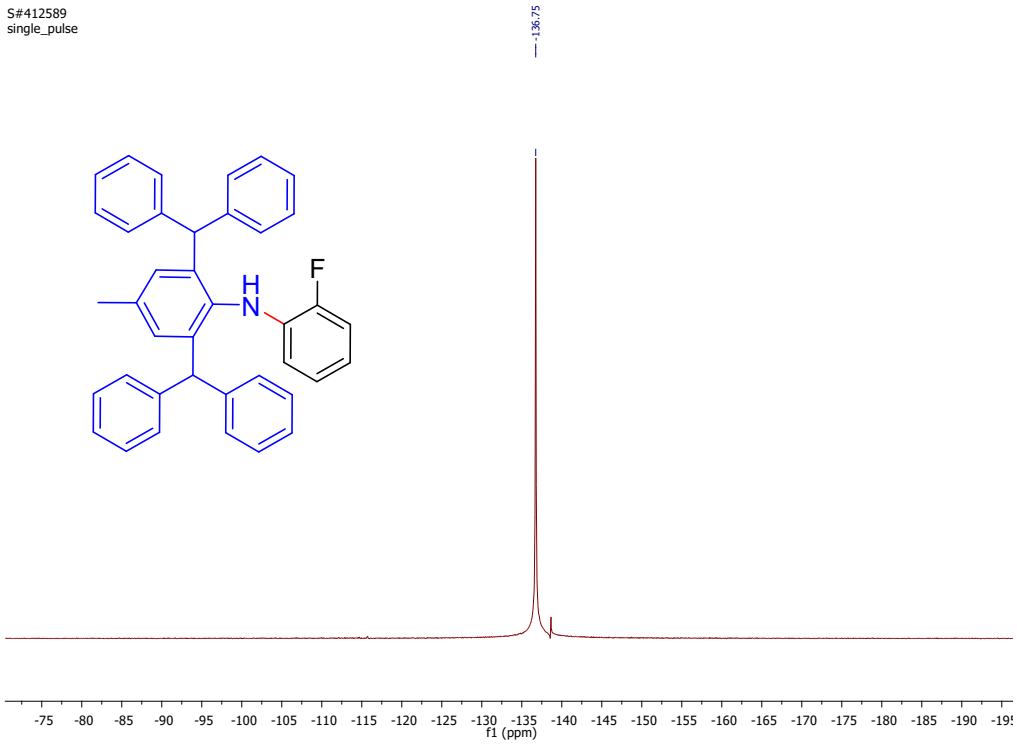
^{13}C{^{1}H} NMR of 4f


7.26 Chloroform-d
7.25
7.24
7.23
7.22
7.21
7.21
7.19
7.19
7.17
7.17
7.16
7.00
7.00
6.98
6.98
6.97
6.96
6.96
6.86
6.84
6.82
6.72
6.72
6.65
6.65
6.64
6.64
6.36
6.34
6.32
5.61
4.74
2.19
H
N
F
13.06
8.12
1.07
2.02
1.03
0.96
2.01
0.98
3.00
f1 (ppm)

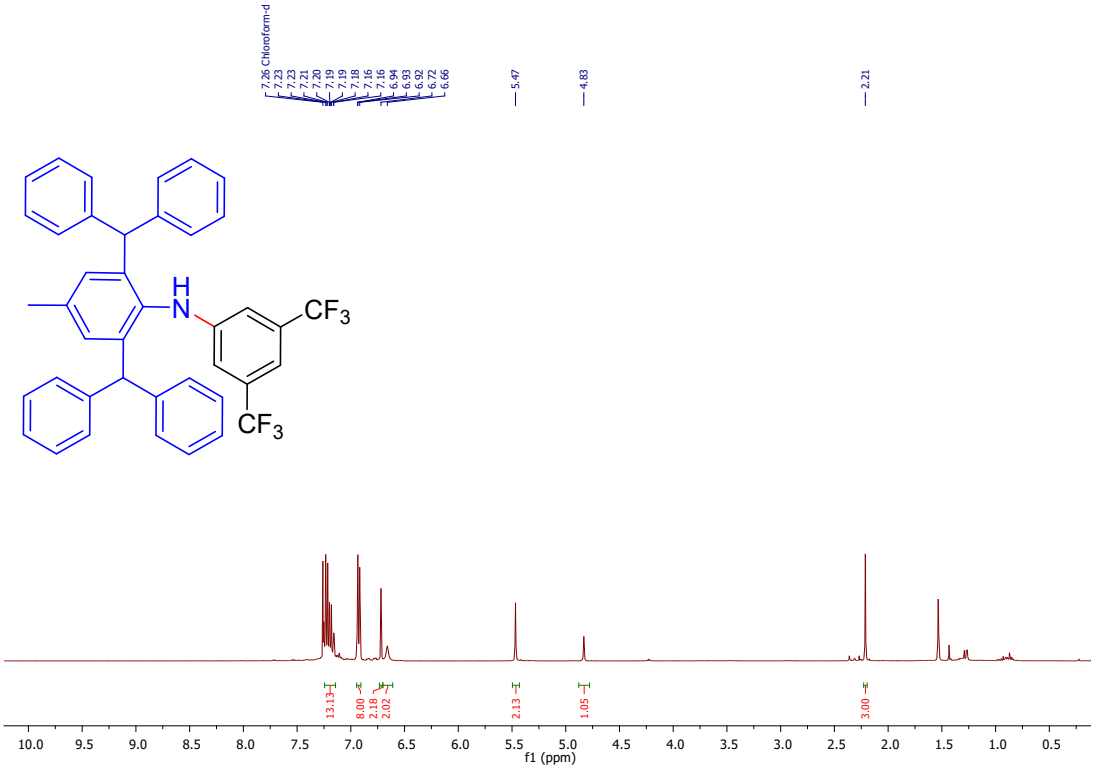
^{1}H NMR of 4g


144.27
143.39
136.69
134.92
134.18
129.95
129.44
128.38
126.37
124.66
117.43
114.81
112.98
77.16 Chloroform-d
51.87
21.80
H
N
F
f1 (ppm)

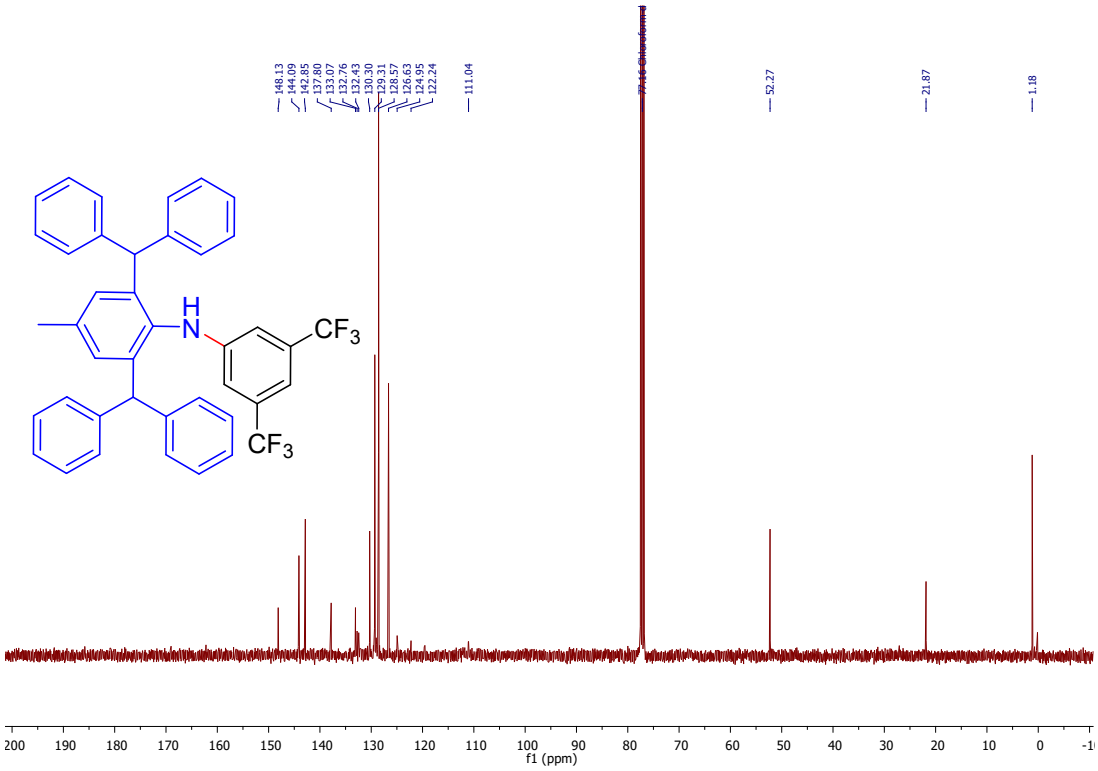
$^{13}C\{^{1}H\}$ NMR of 4g



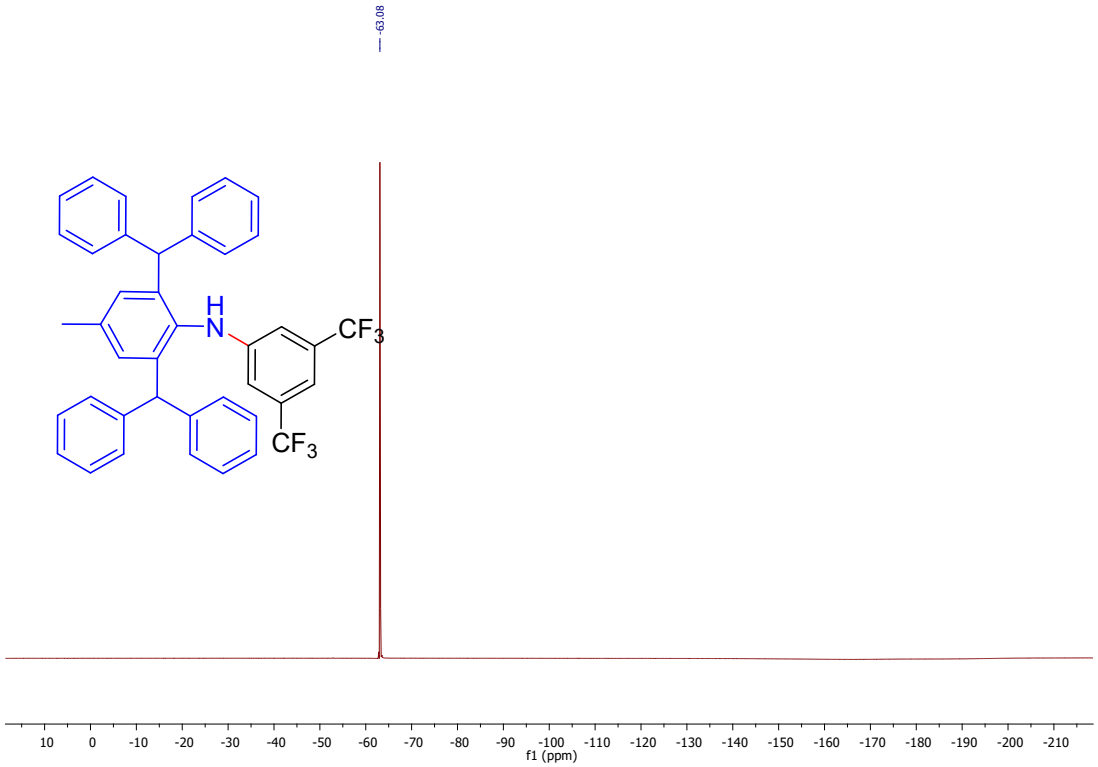
$^{19}F\{^{1}H\}$ NMR of 4g



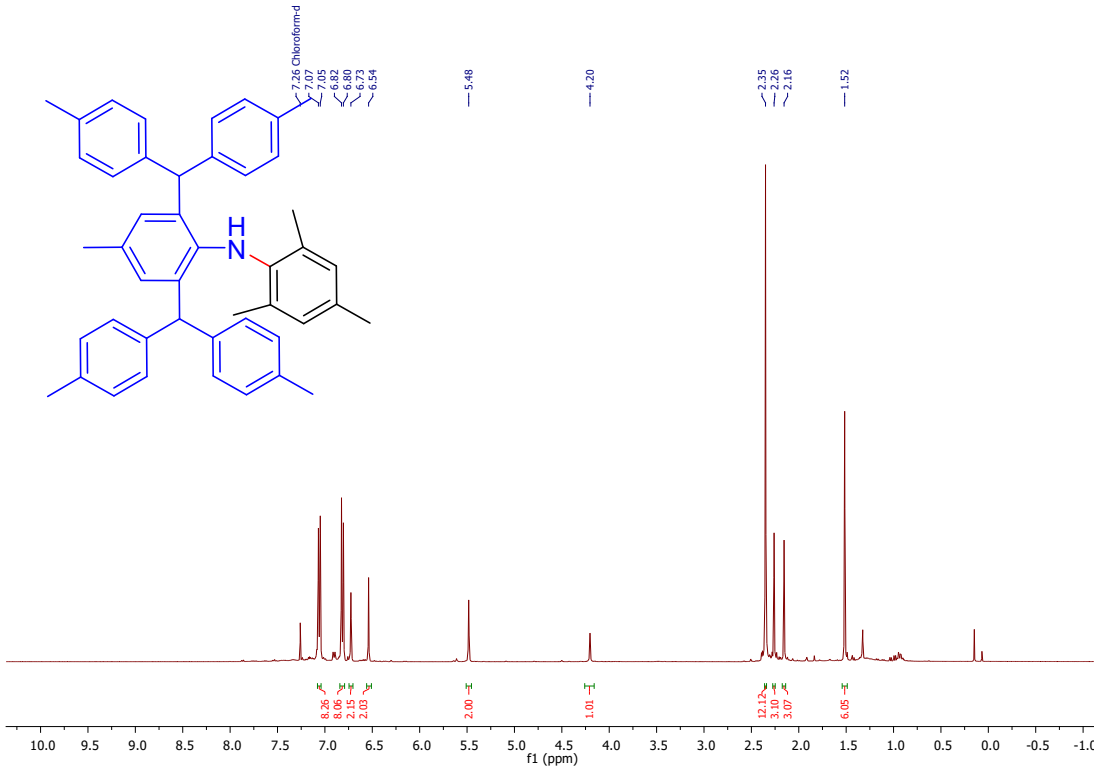
^{1}H NMR of 4h



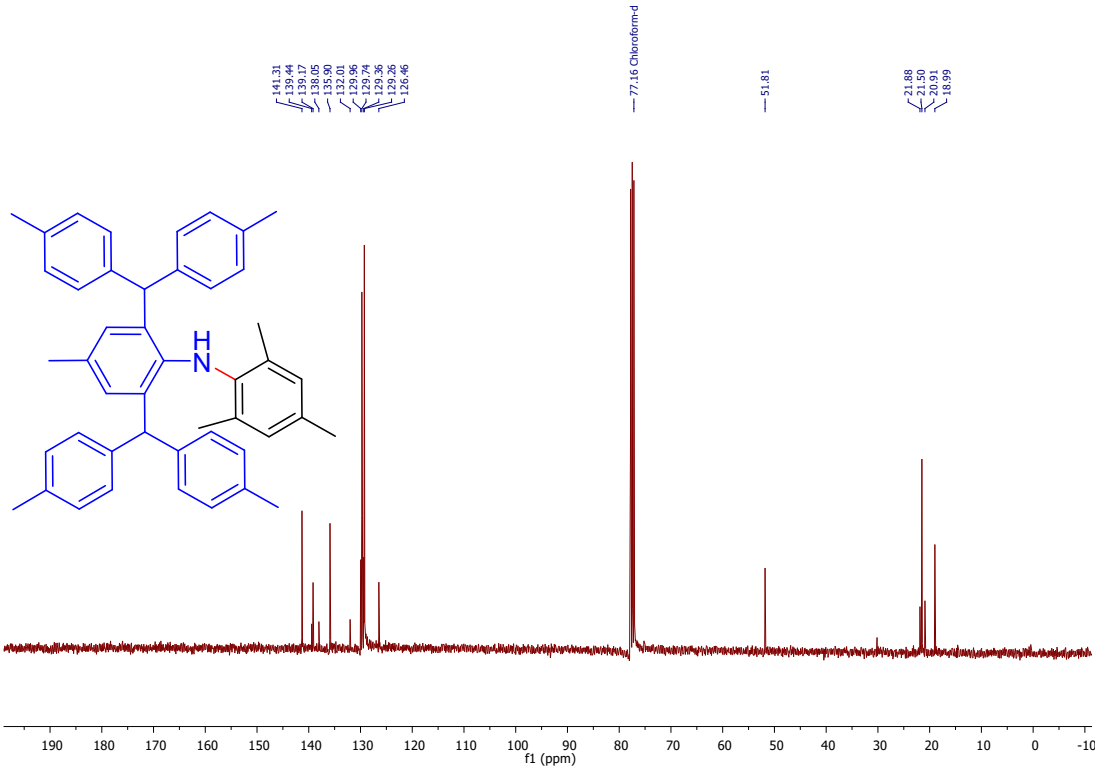
$^{13}C\{^{1}H\}$ NMR of 4h



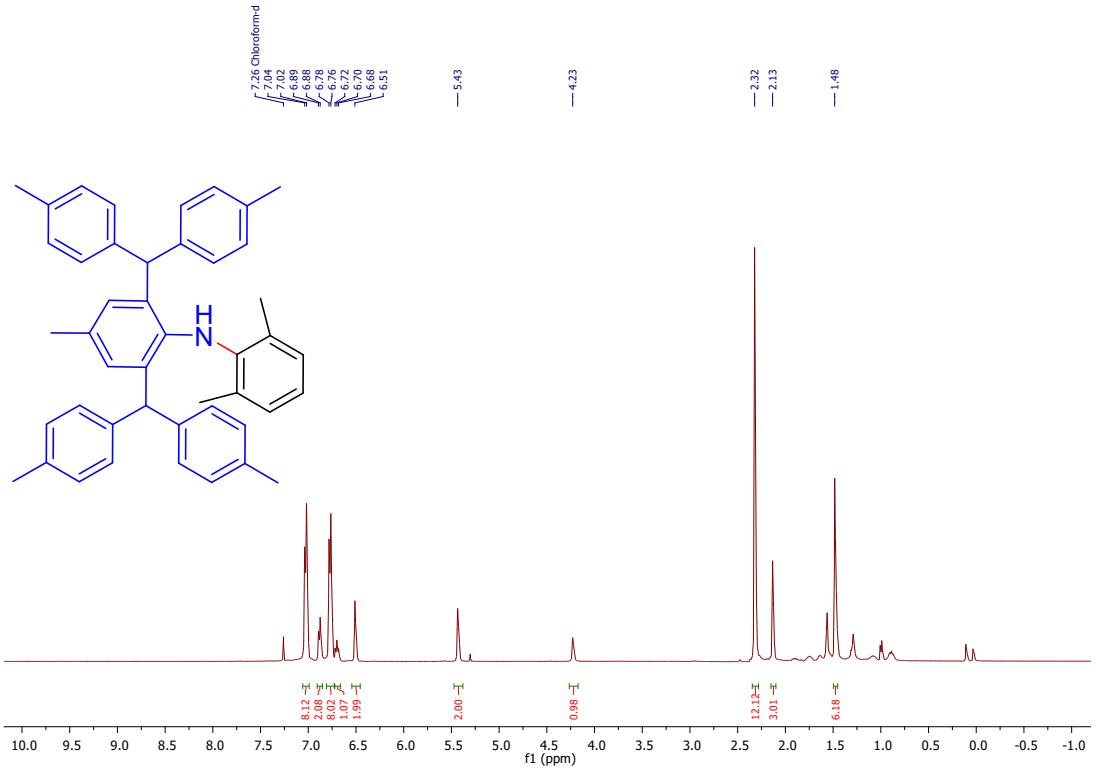
$^{19}F\{^{1}H\}$ NMR of 4h



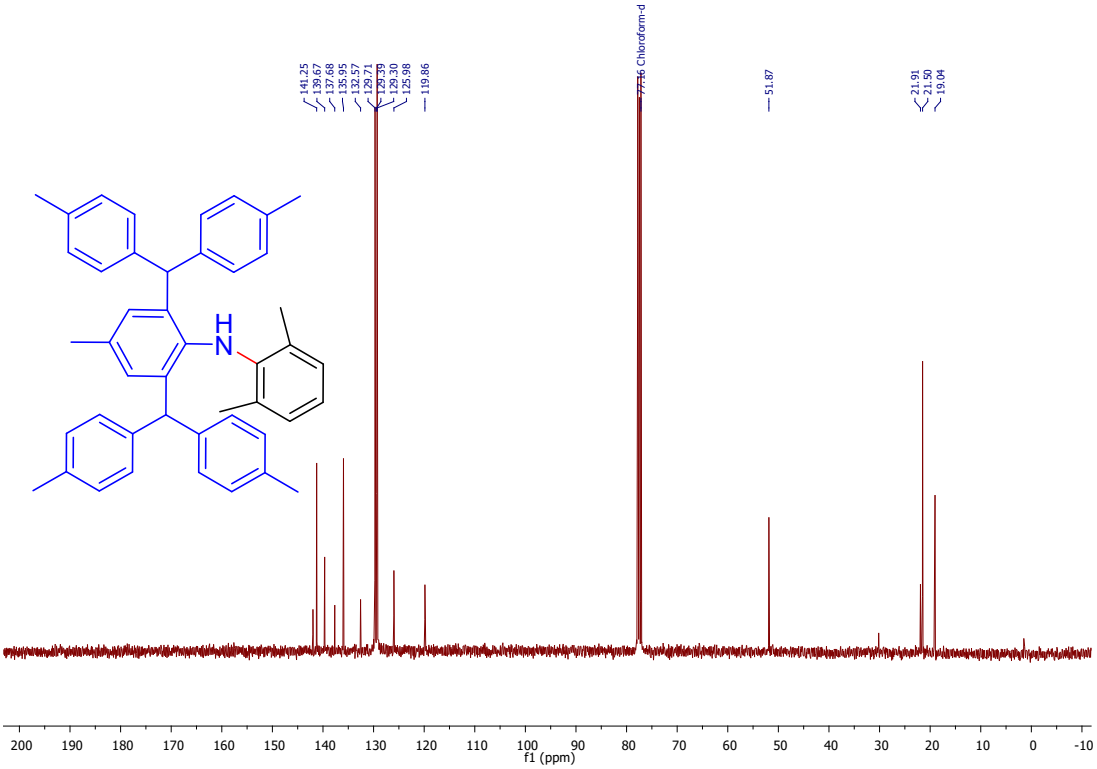
^{1}H NMR of 4i



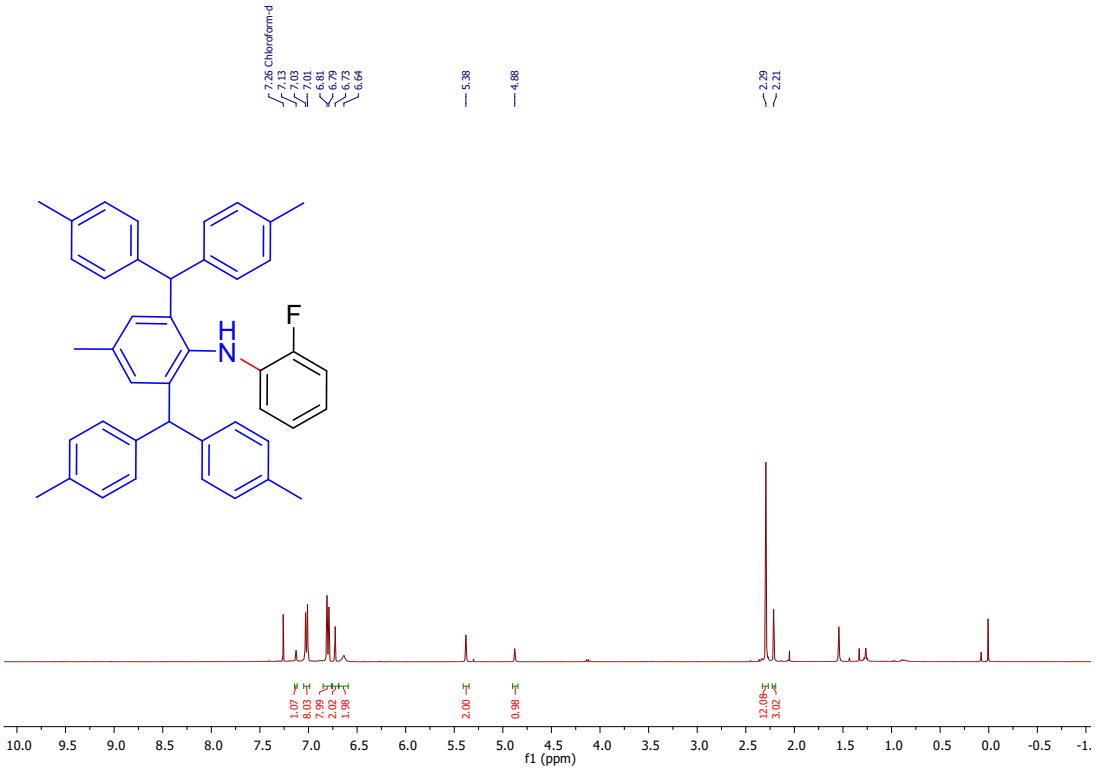
$^{13}C\{^{1}H\}$ NMR of 4i



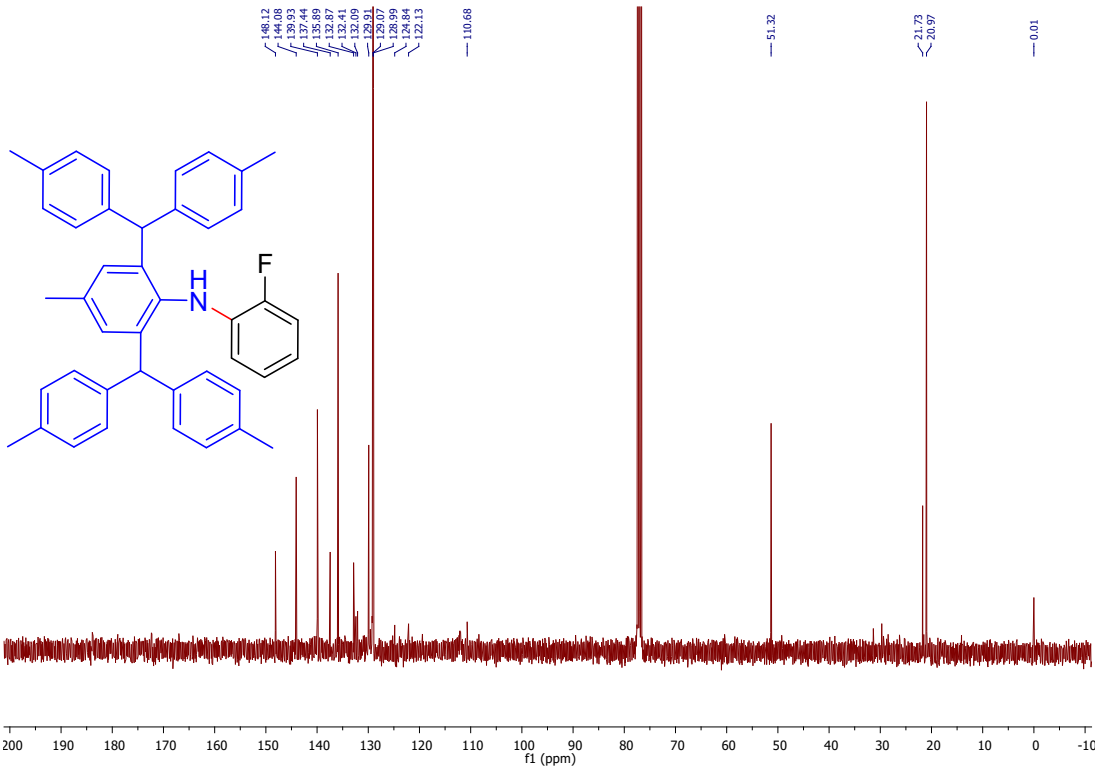
^{1}H NMR of 4j



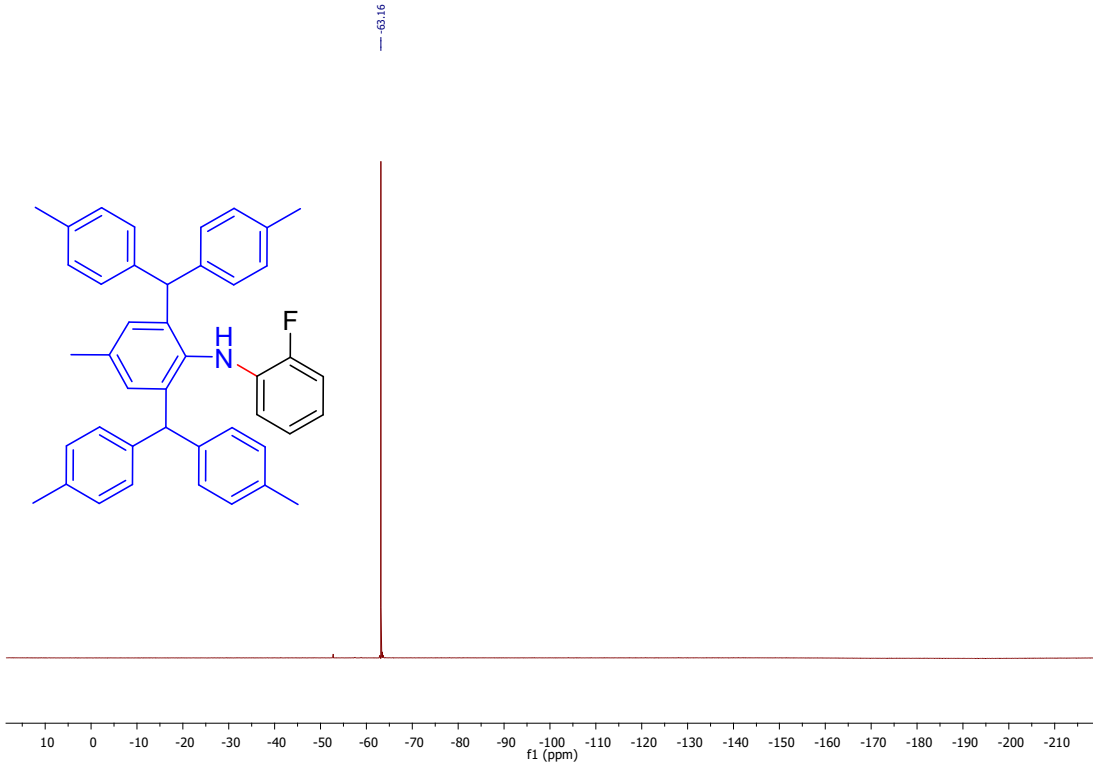
$^{13}C\{^{1}H\}$ NMR of 4j



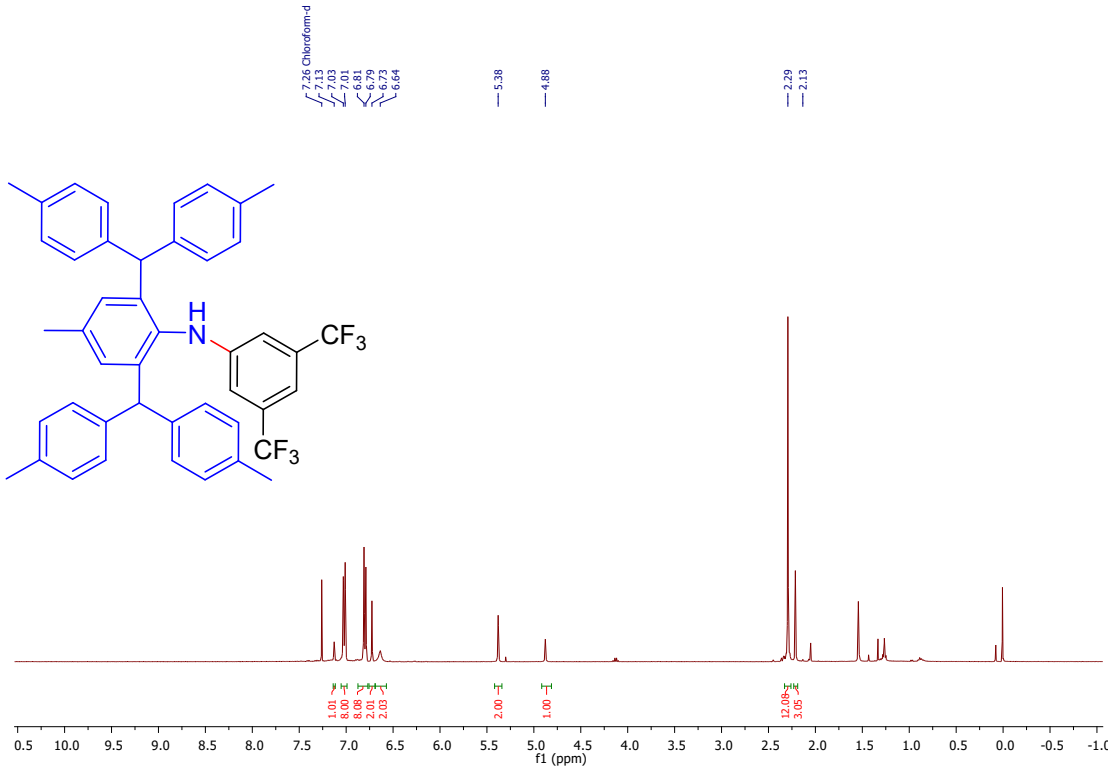
^{1}H NMR of 4k



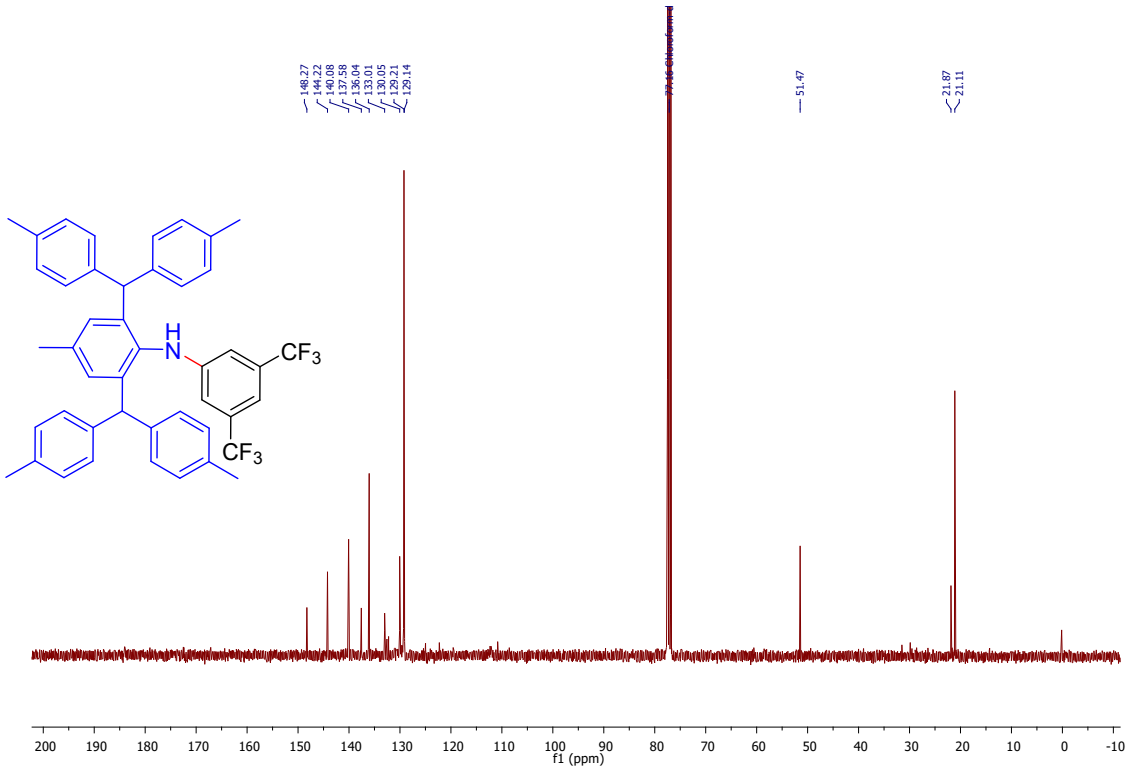
$^{13}C\{^{1}H\}$ NMR of 4k



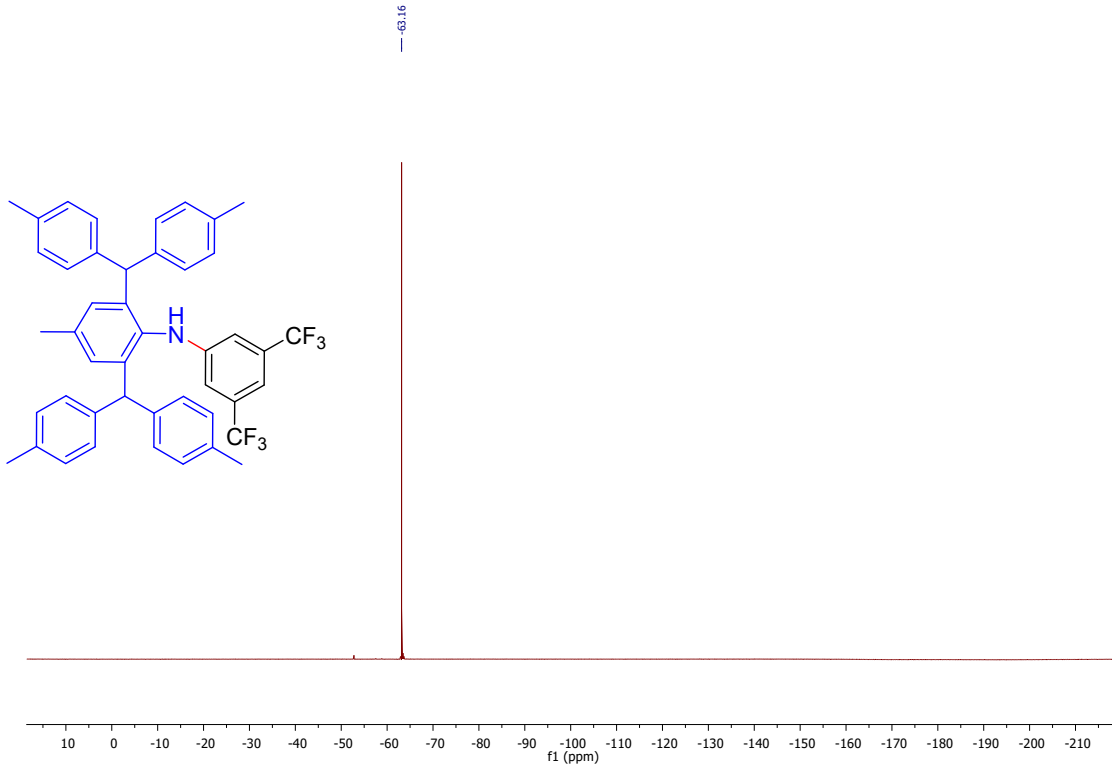
$^{19}F\{^{1}H\}$ NMR of 4k



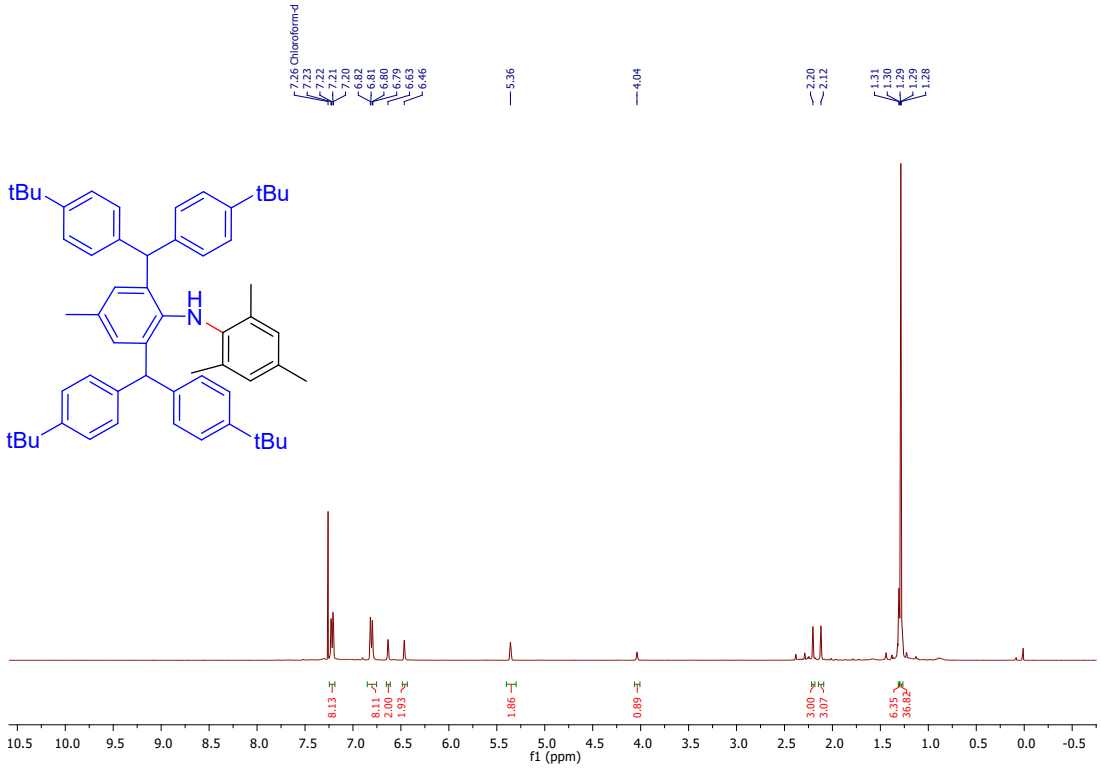
^{1}H NMR of 4l



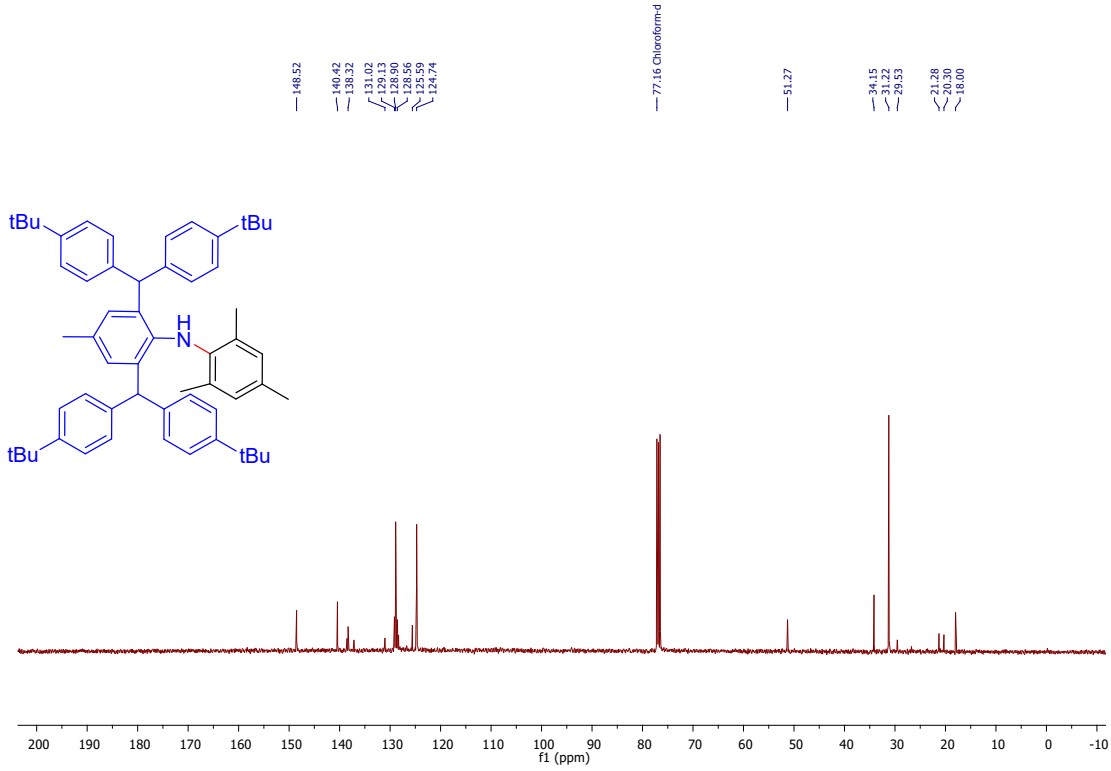
$^{13}C\{^{1}H\}$ NMR of 4l



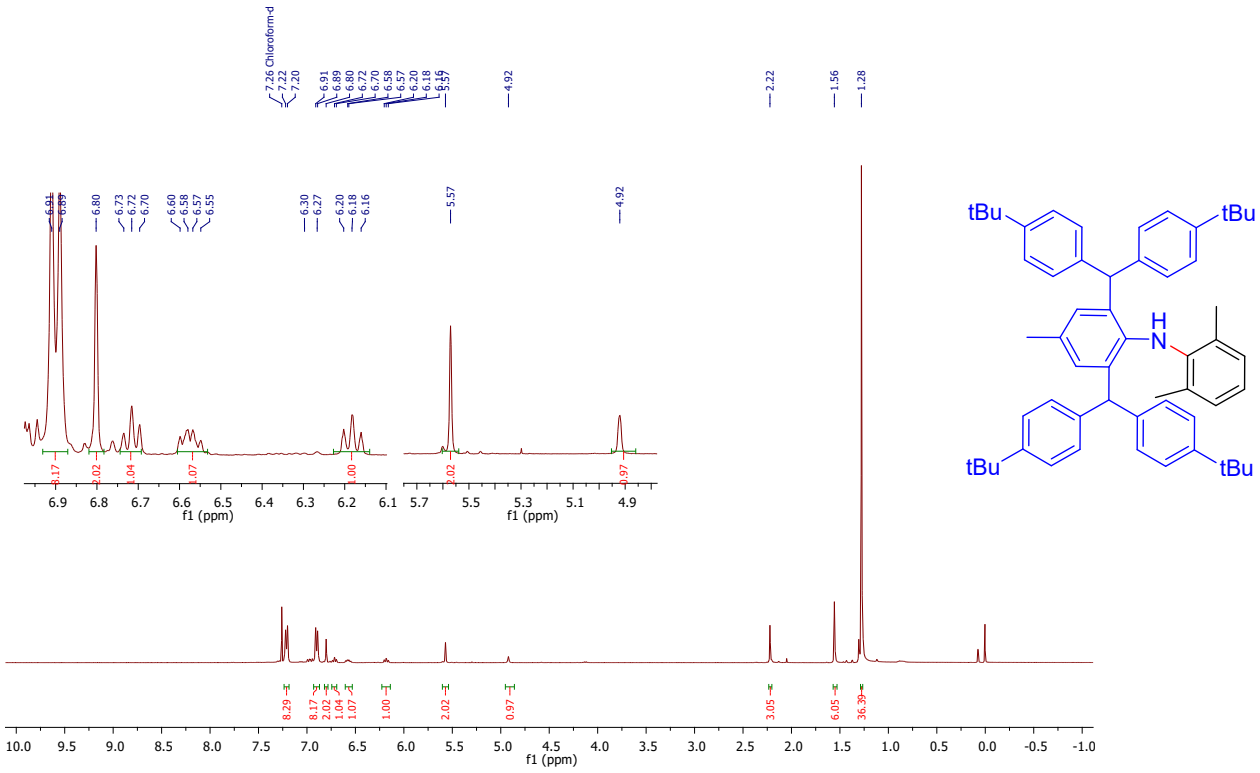
$^{19}F\{^{1}H\}$ NMR of 4l



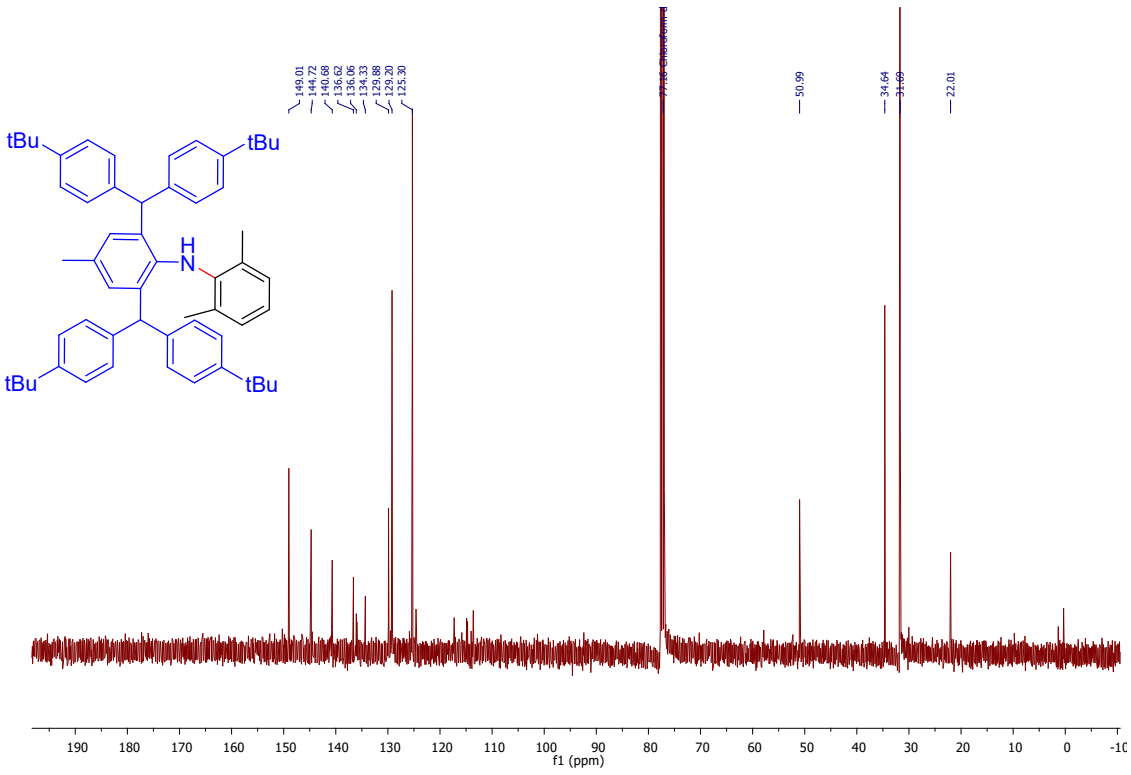
^{1}H NMR of 4m



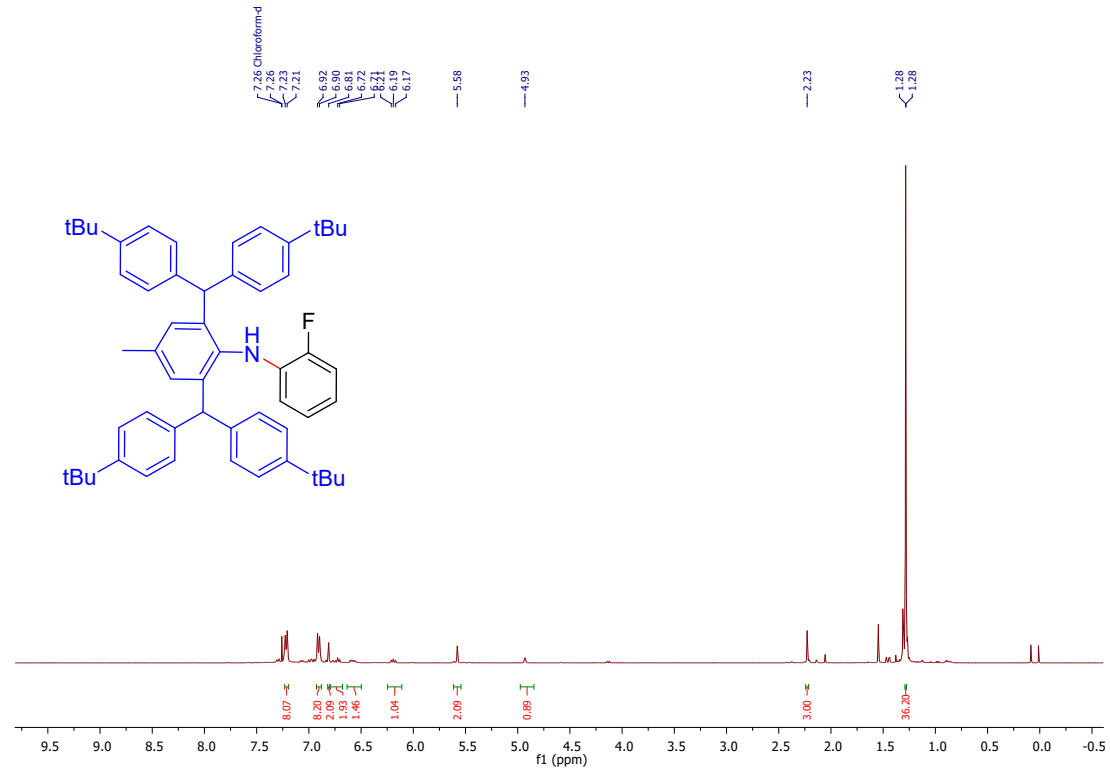
^{13}C{^{1}H} NMR of 4m



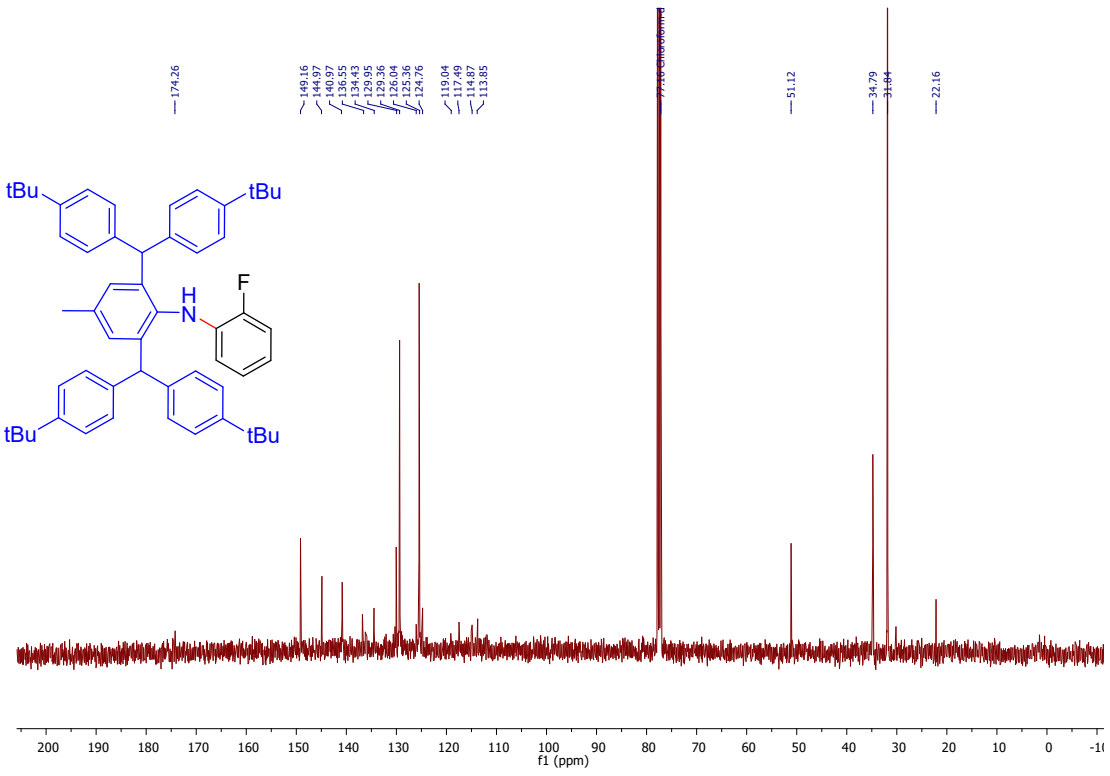
^{1}H NMR of 4n



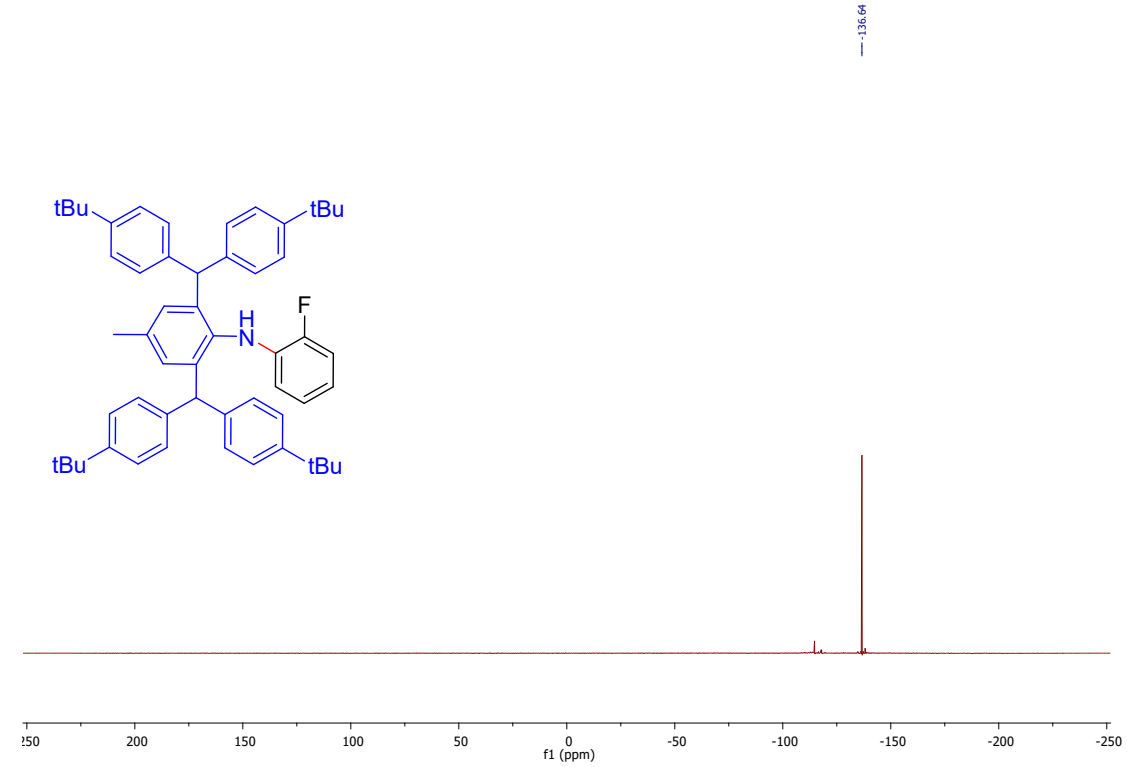
^{13}C{^{1}H} NMR of 4n



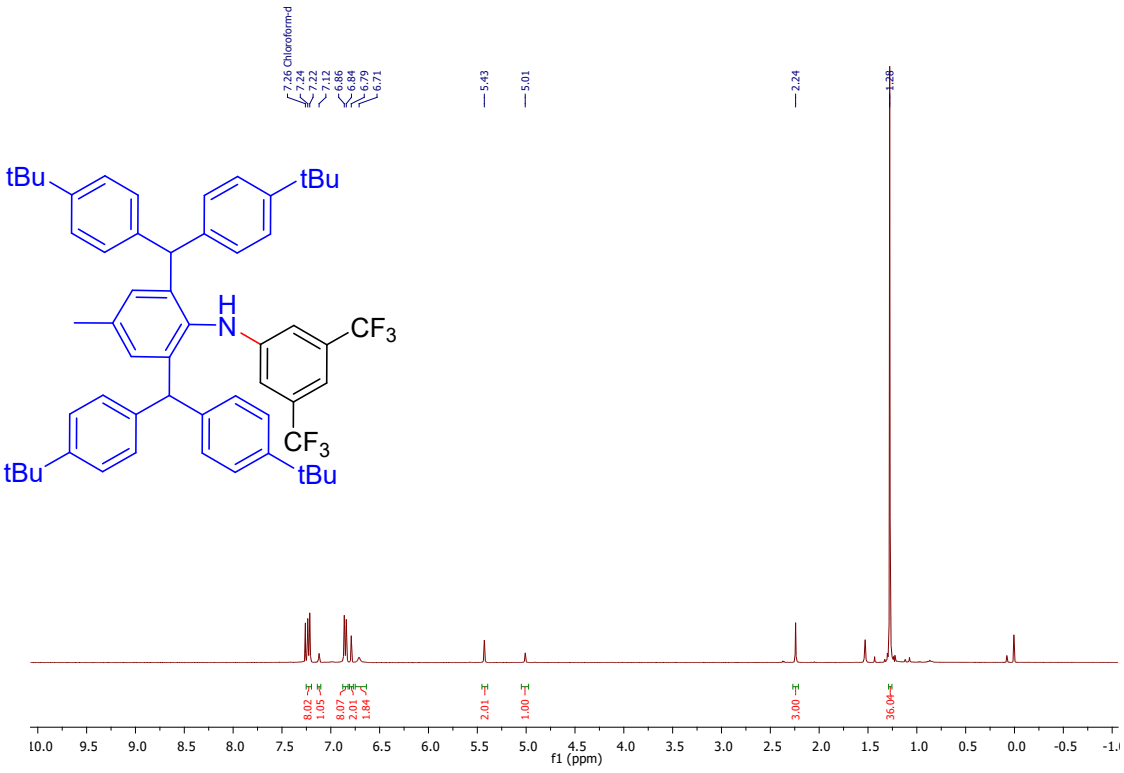
^{1}H NMR of 4o



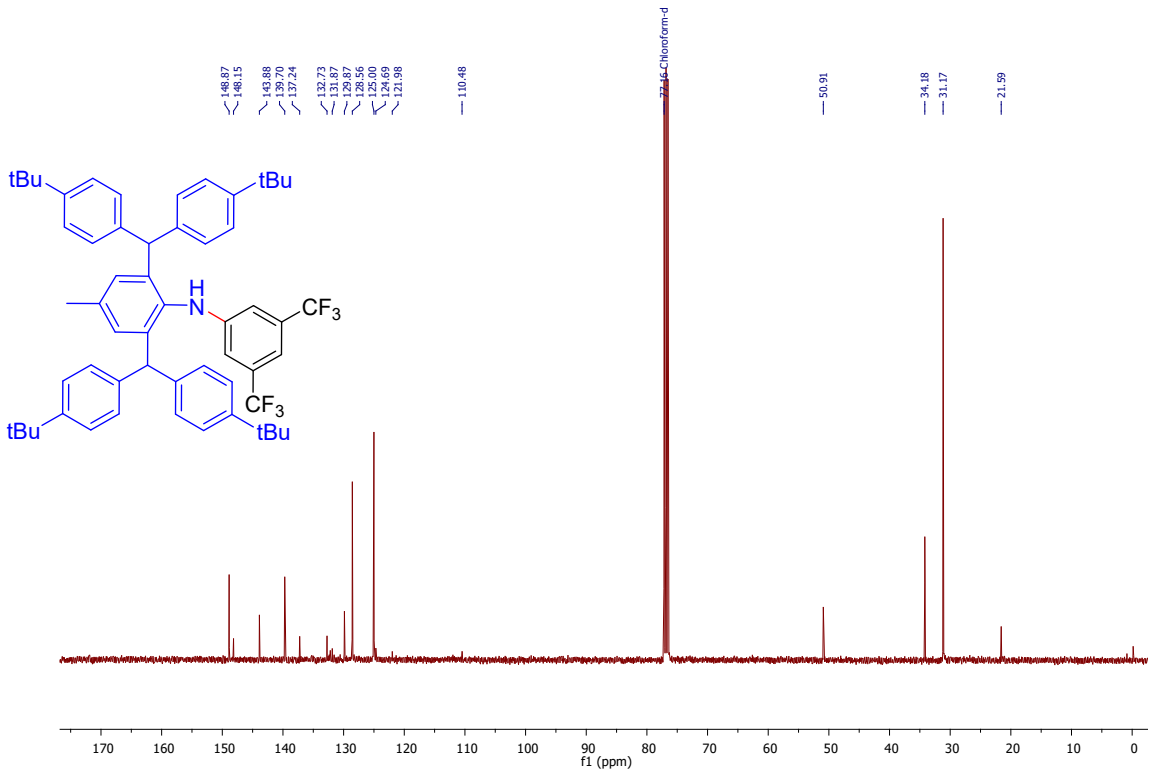
^{13}C{^{1}H} NMR of 4o



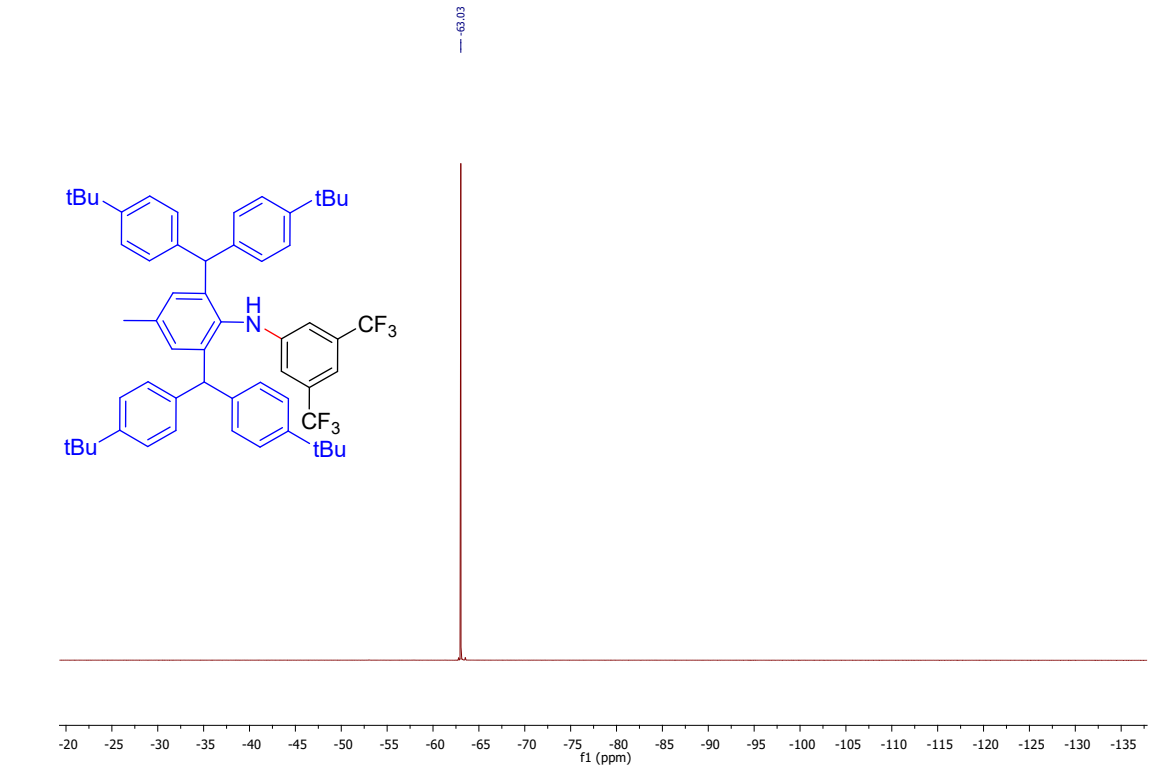
$^{19}F\{^{1}H\}$ NMR of 4o



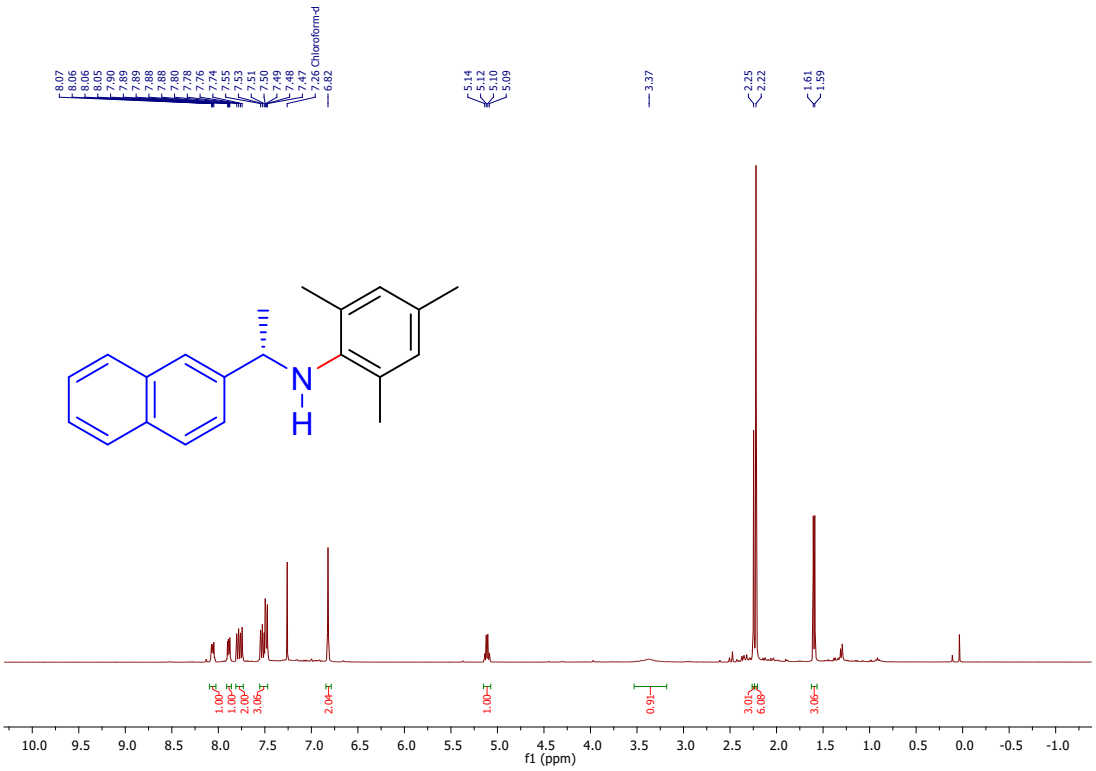
^{1}H NMR of 4p



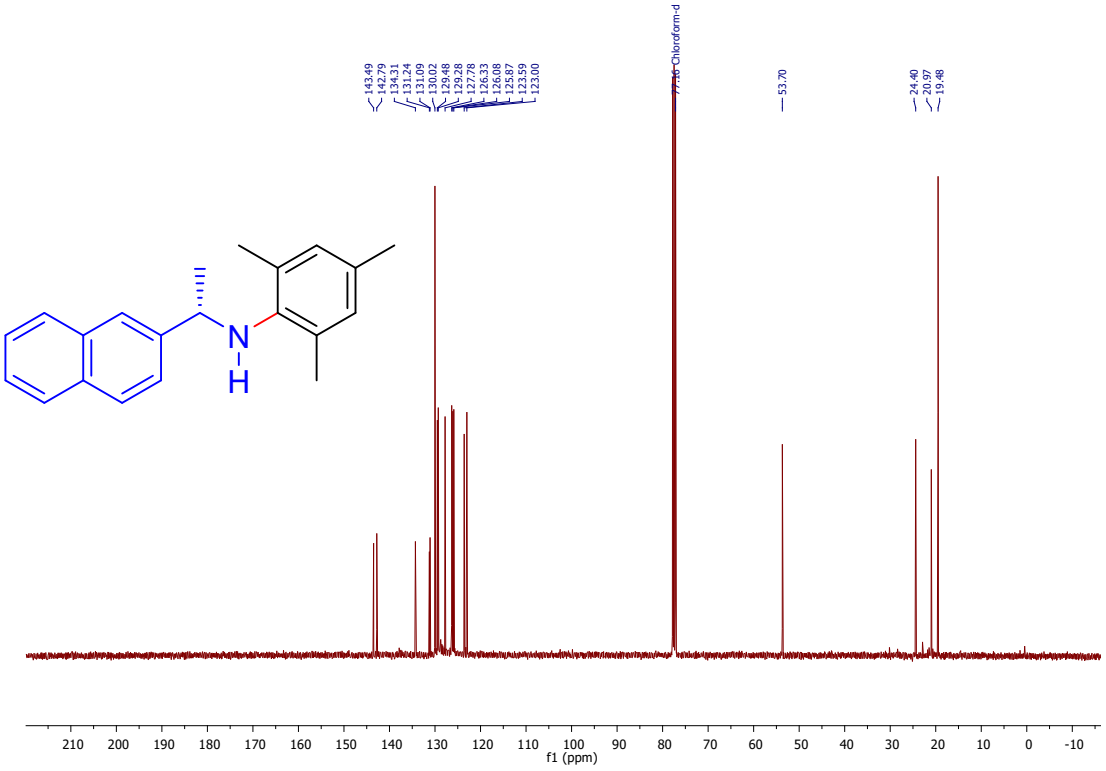
$^{13}C\{^{1}H\}$ NMR of 4p



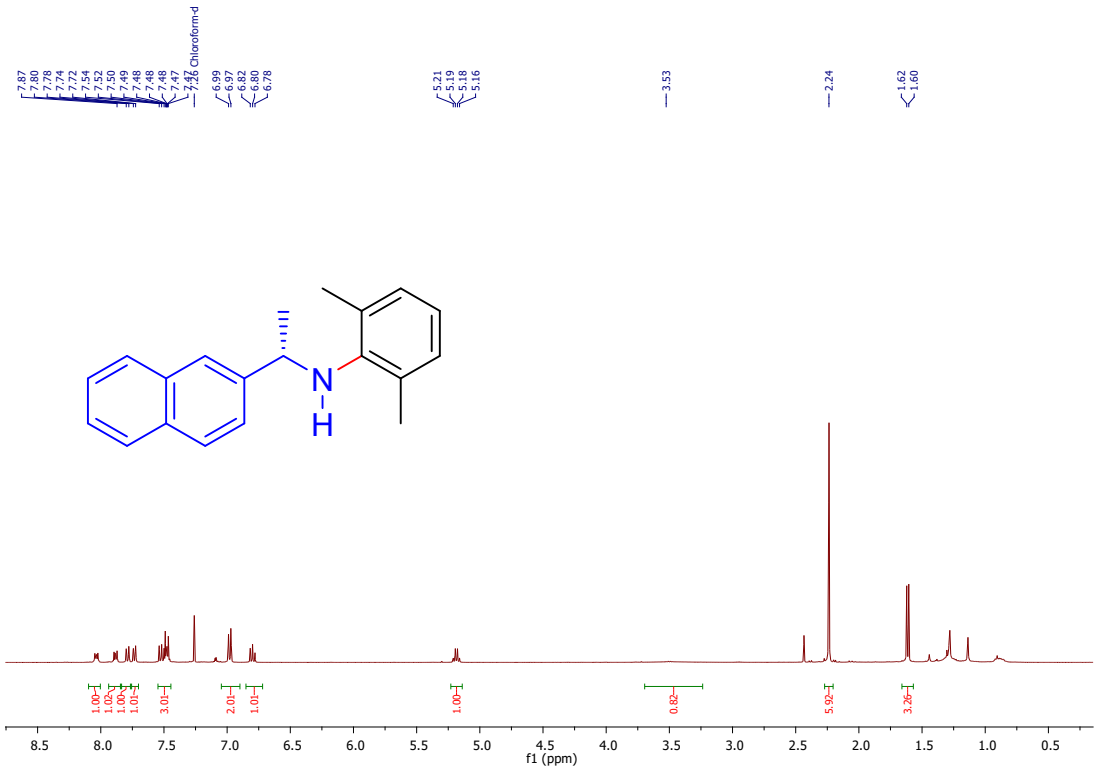
$^{19}F\{^{1}H\}$ NMR of 4p



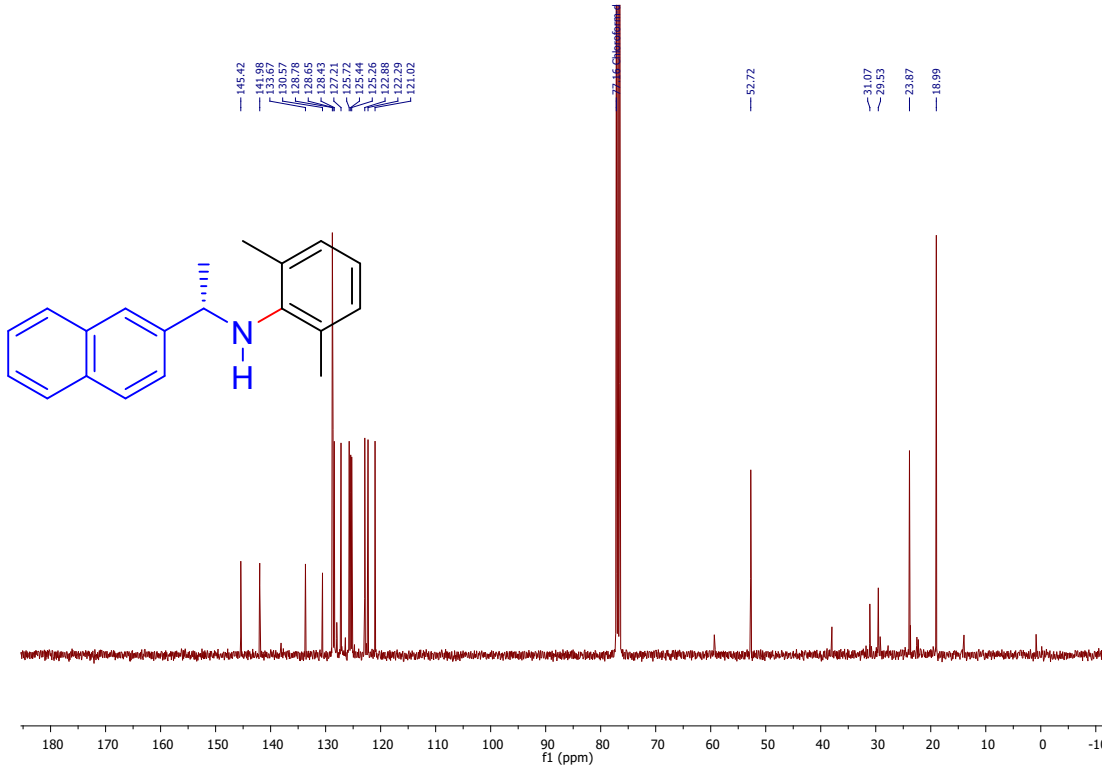
^{1}H NMR of 5a



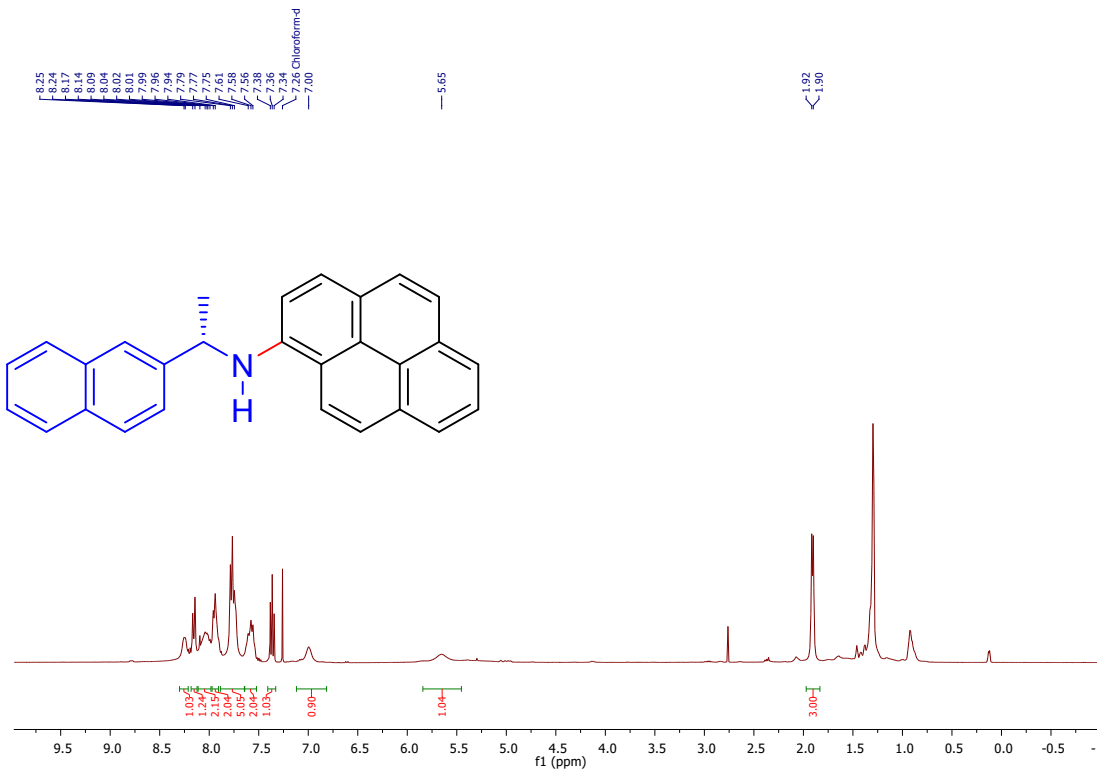
^{13}C{^{1}H} NMR of 5a



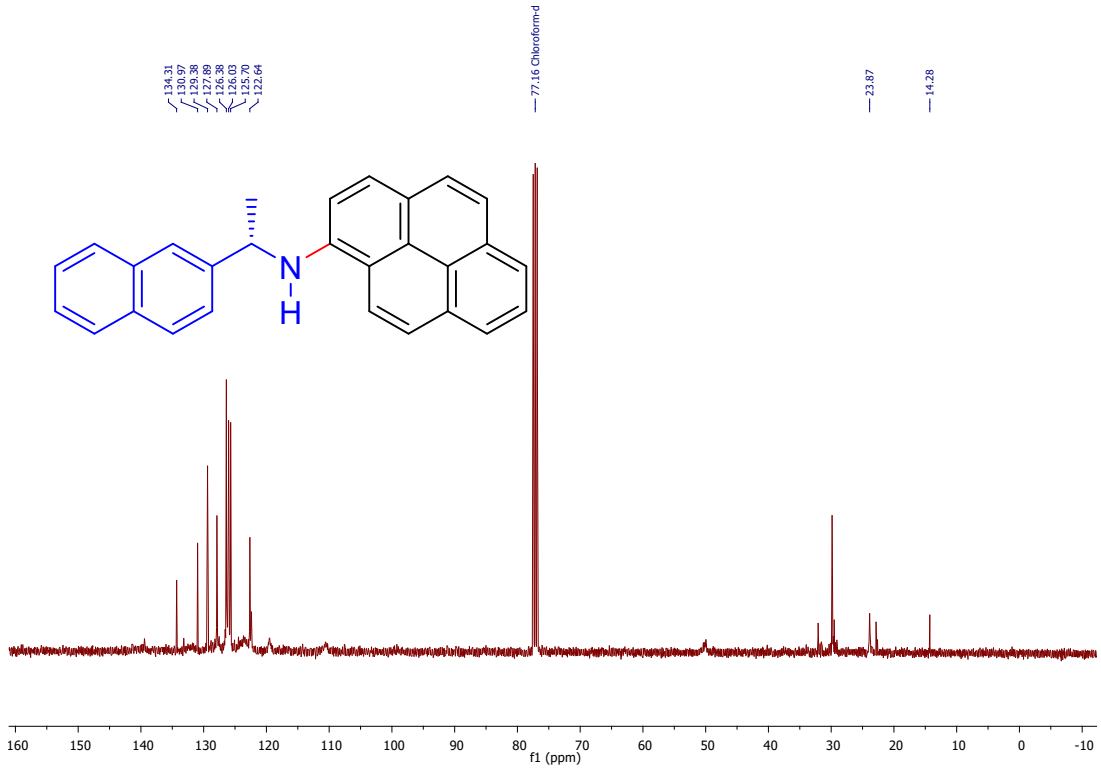
^{1}H NMR of 5b



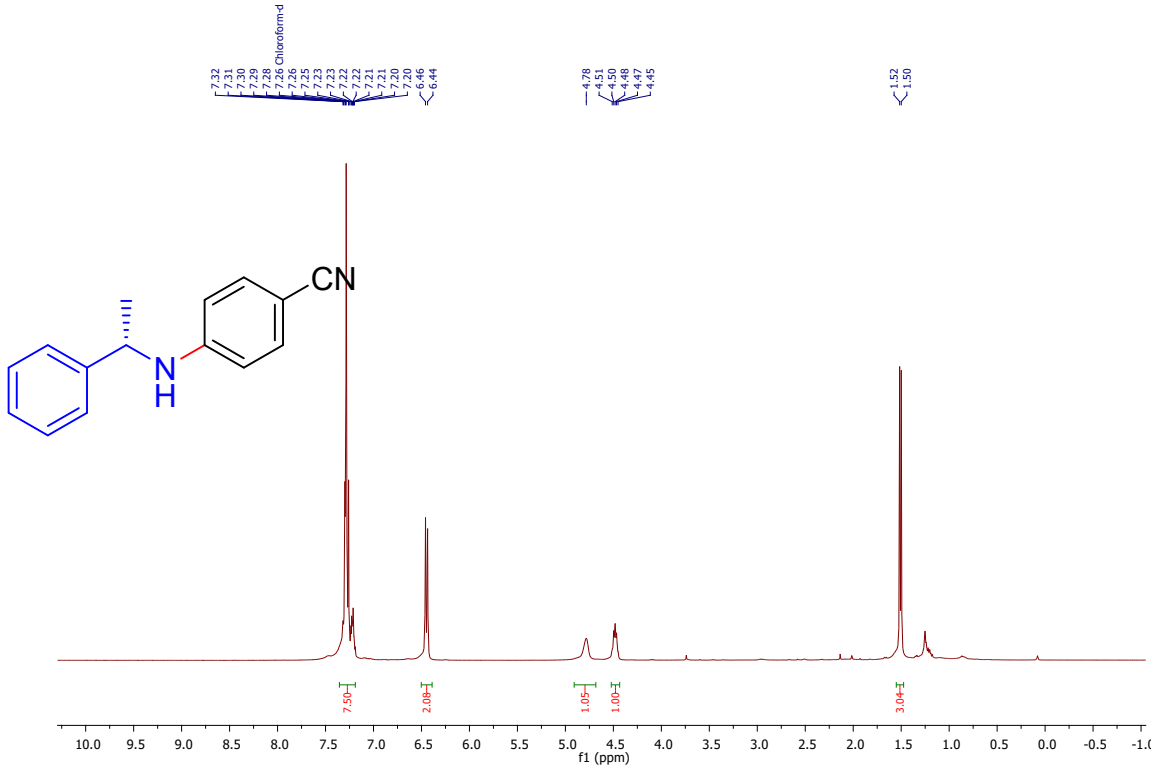
^{13}C{^{1}H} NMR of 5b



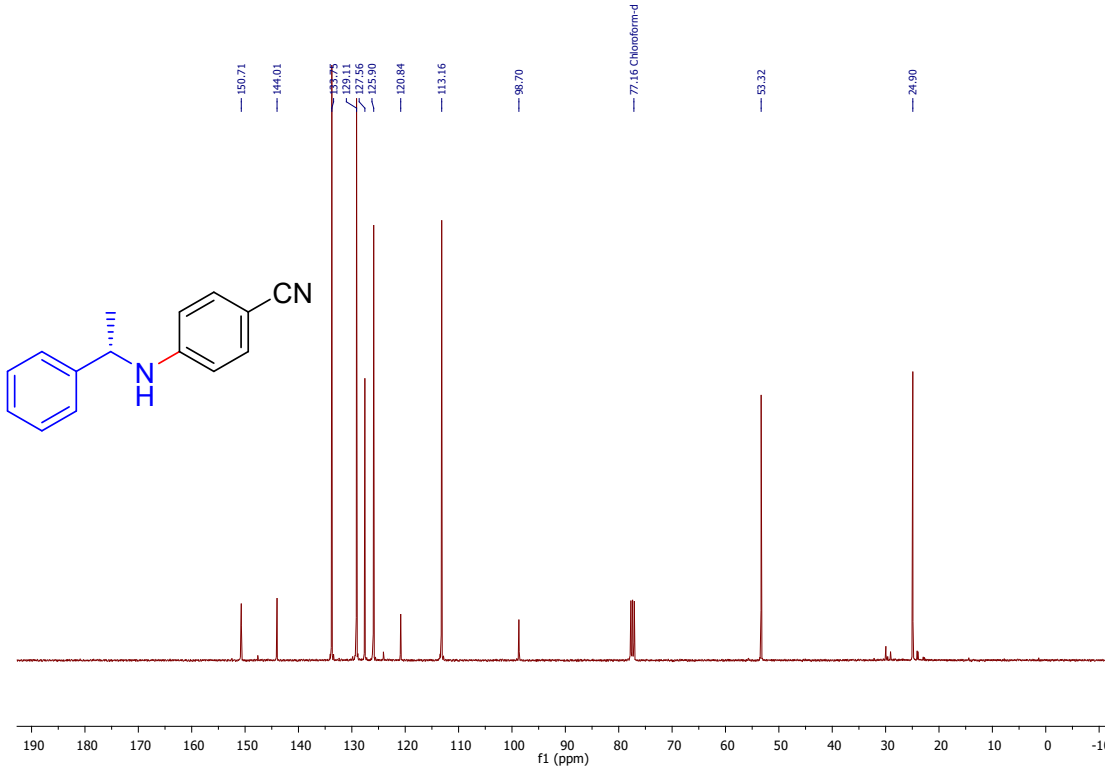
^{1}H NMR of 5c



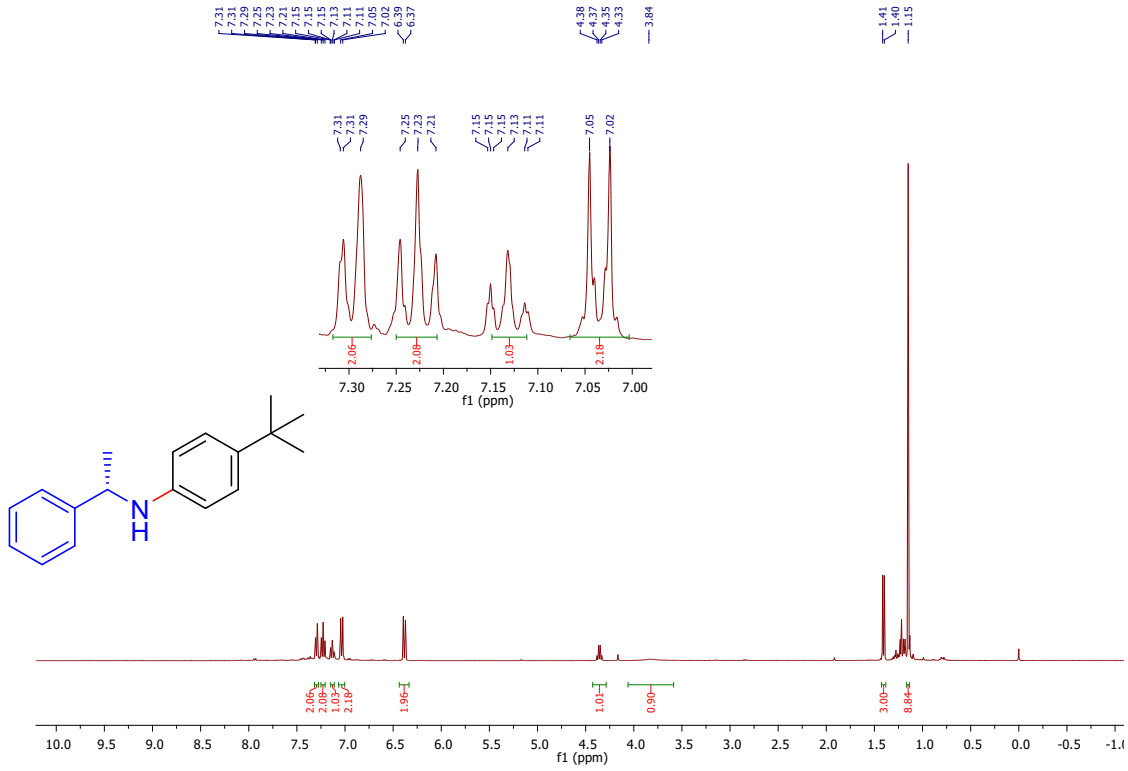
^{13}C{^{1}H} NMR of 5c



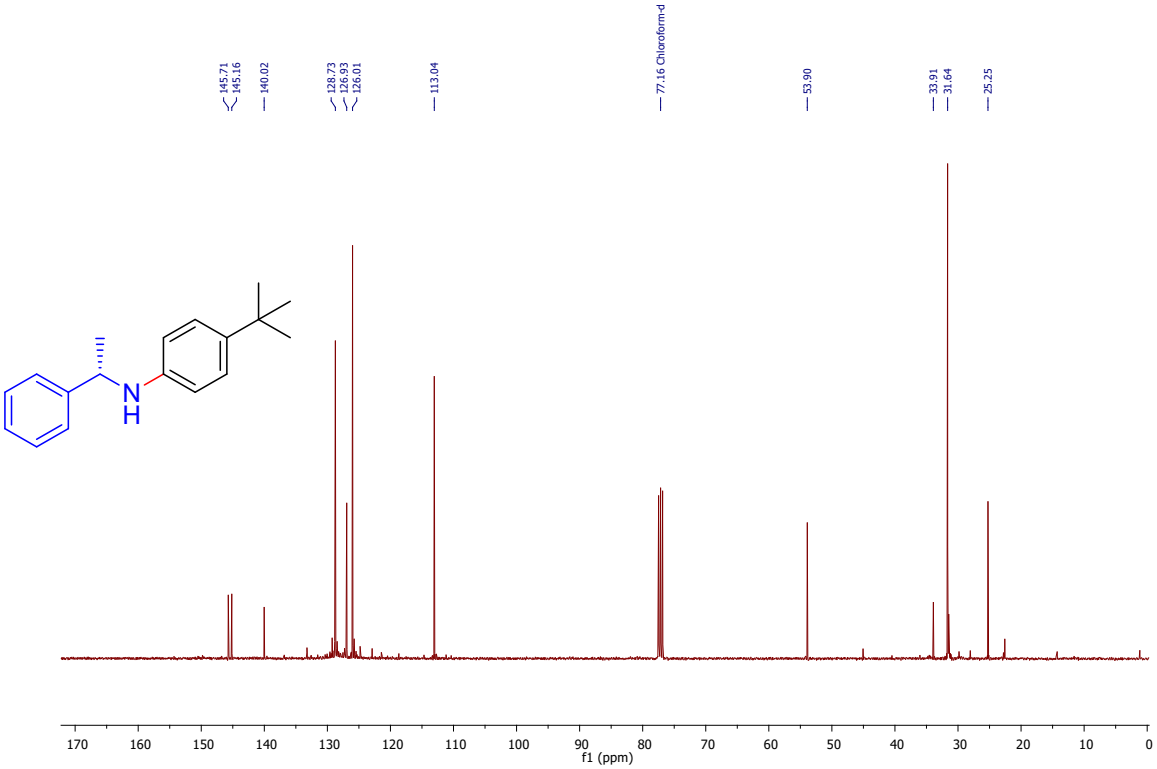
^{1}H NMR of 5d



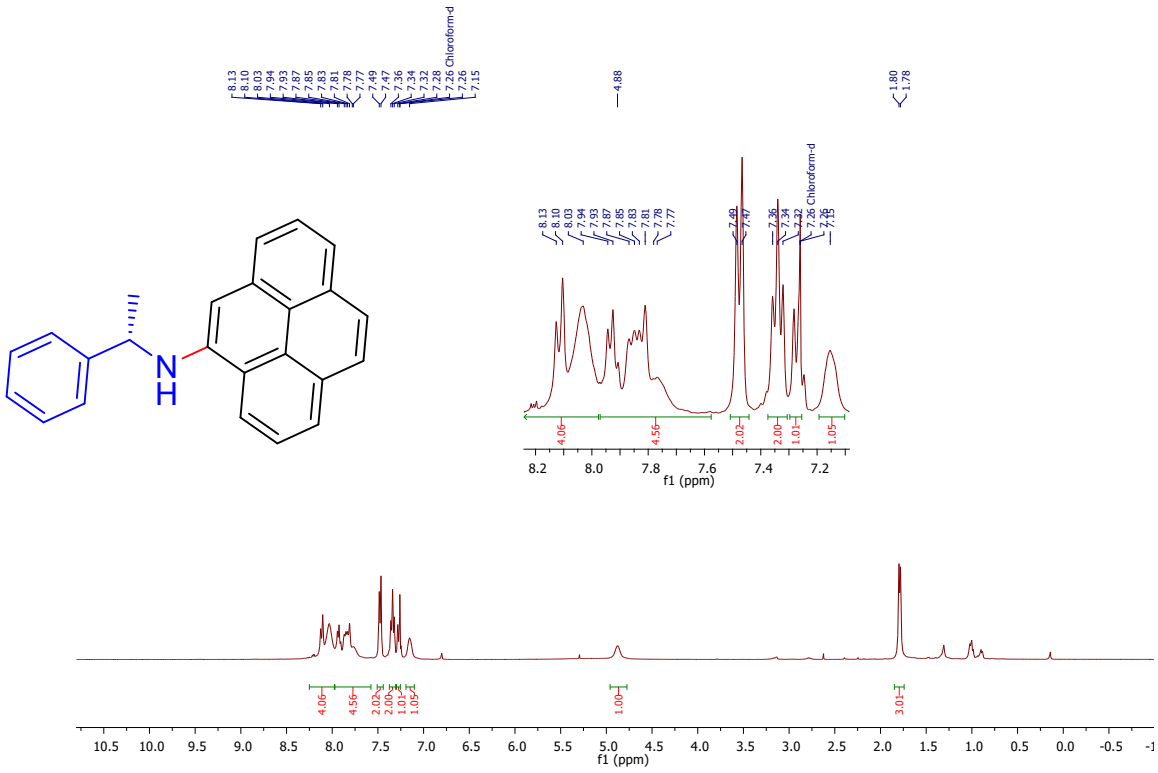
^{13}C{^{1}H} NMR of 5d



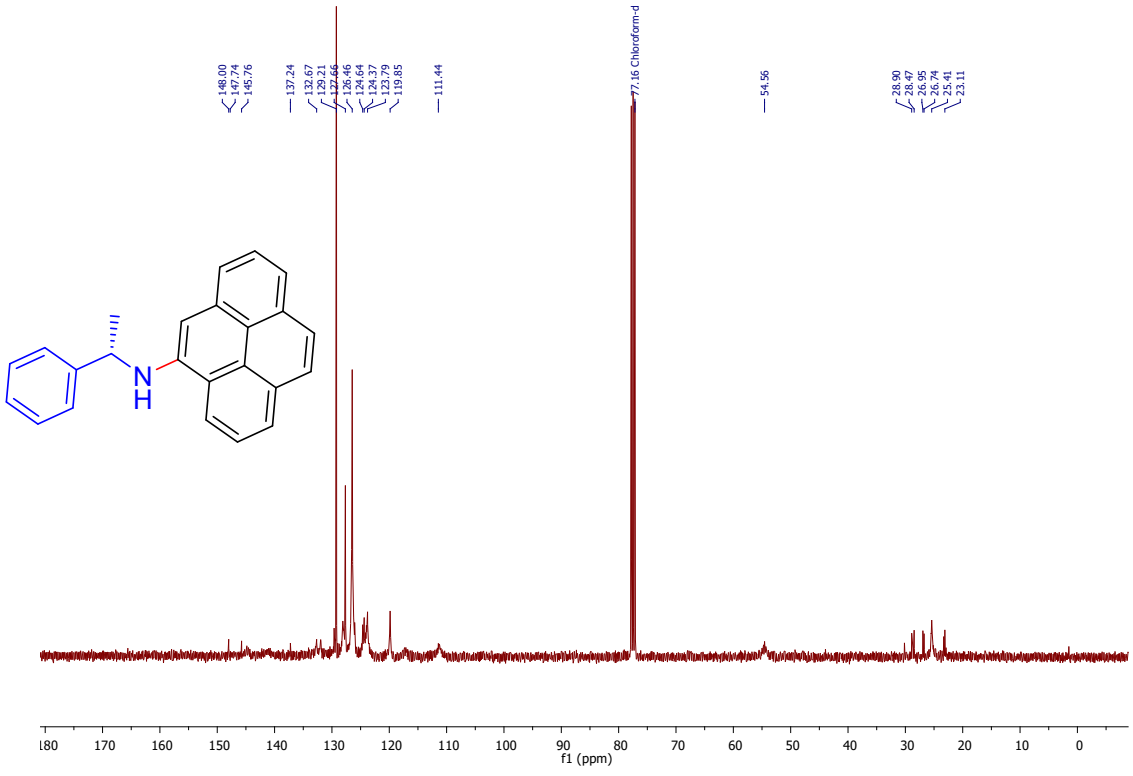
^{1}H NMR of 5e



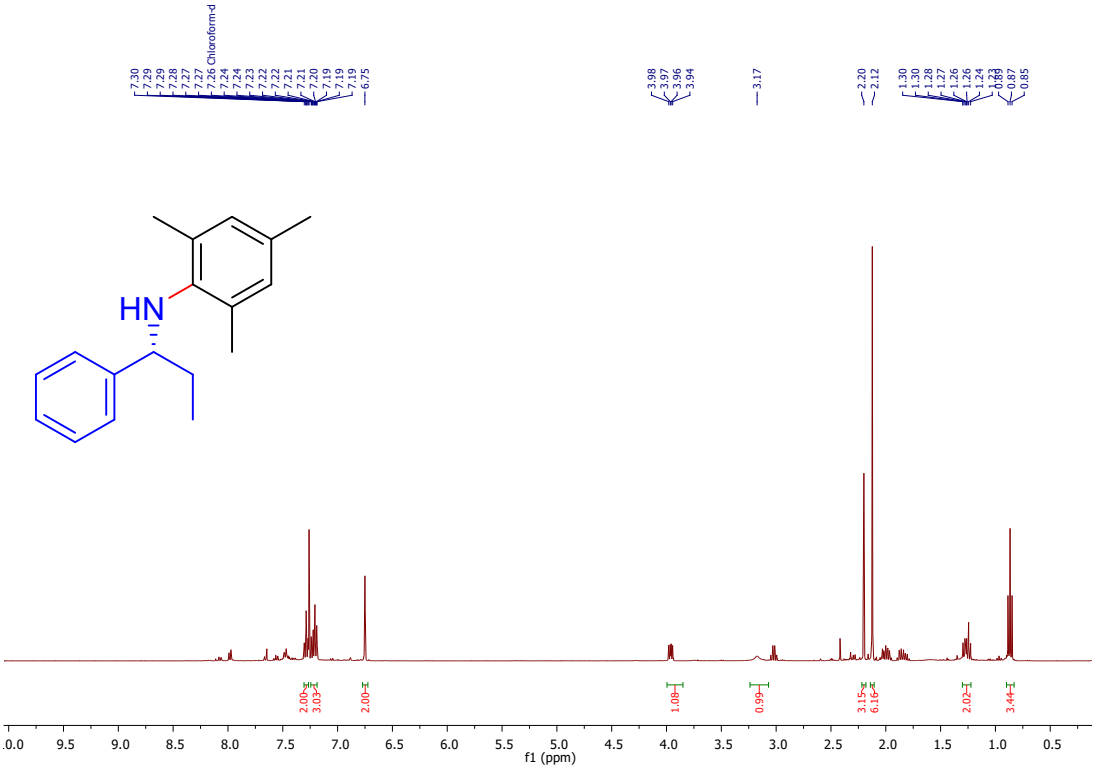
^{13}C{^{1}H} NMR of 5e



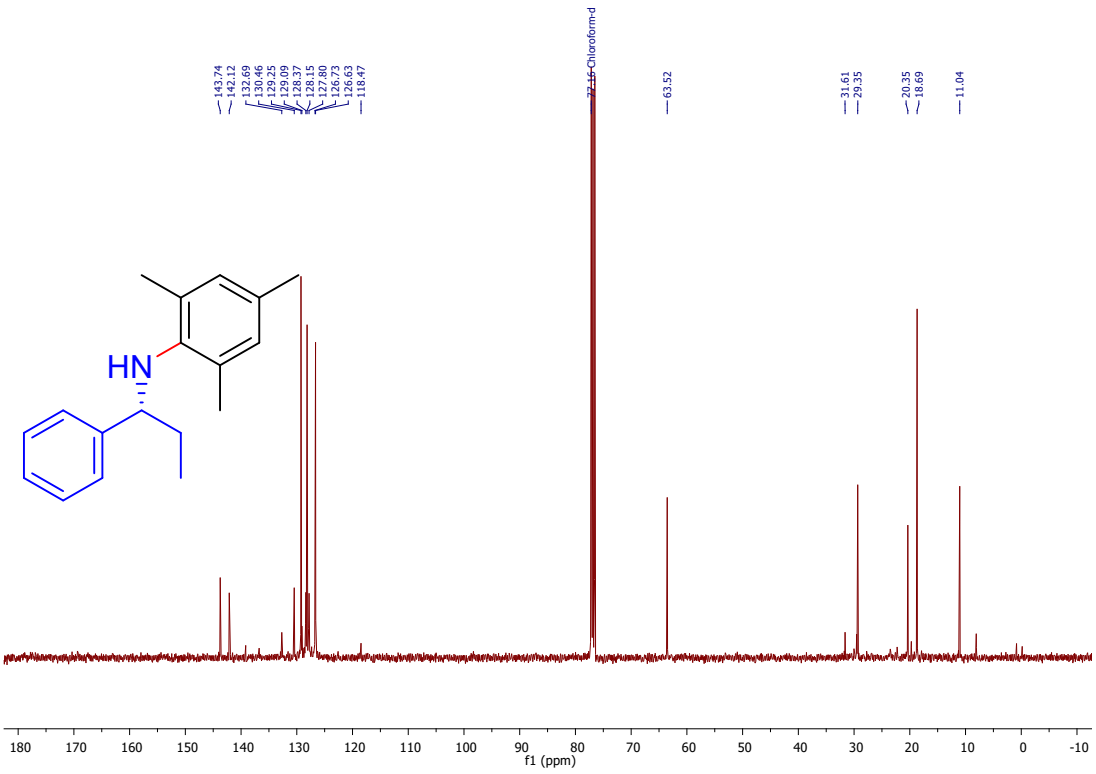
^{1}H NMR of 5f



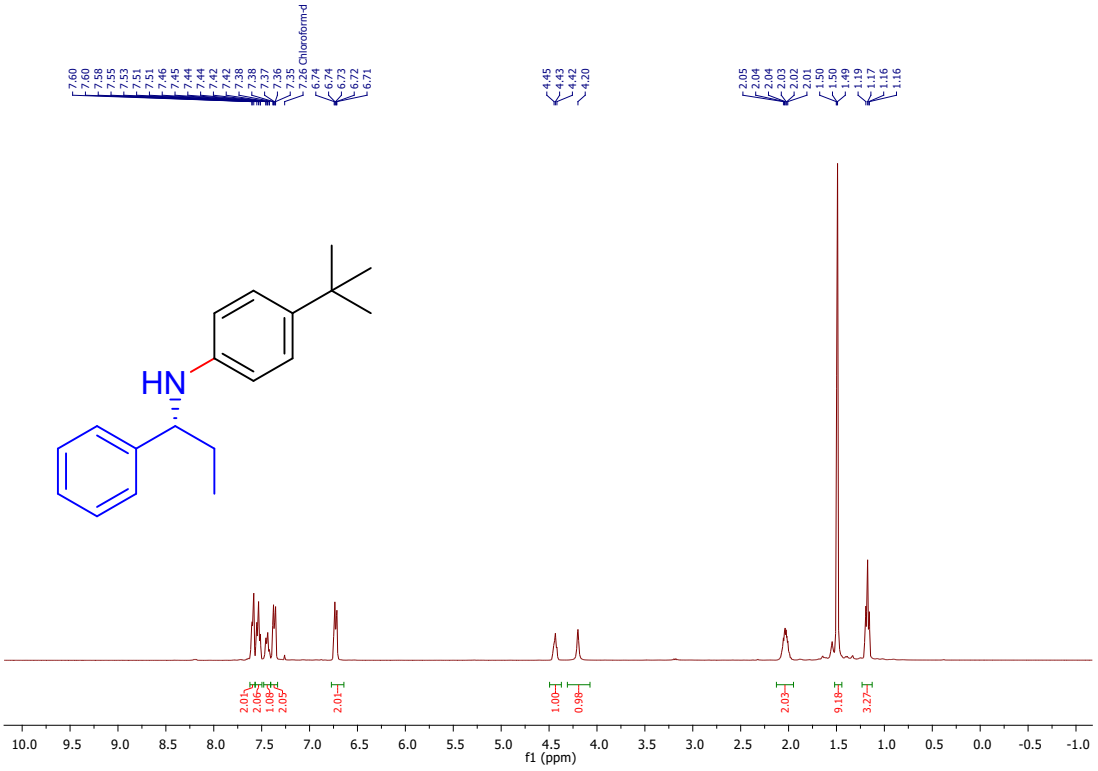
^{13}C{^{1}H} NMR of 5f



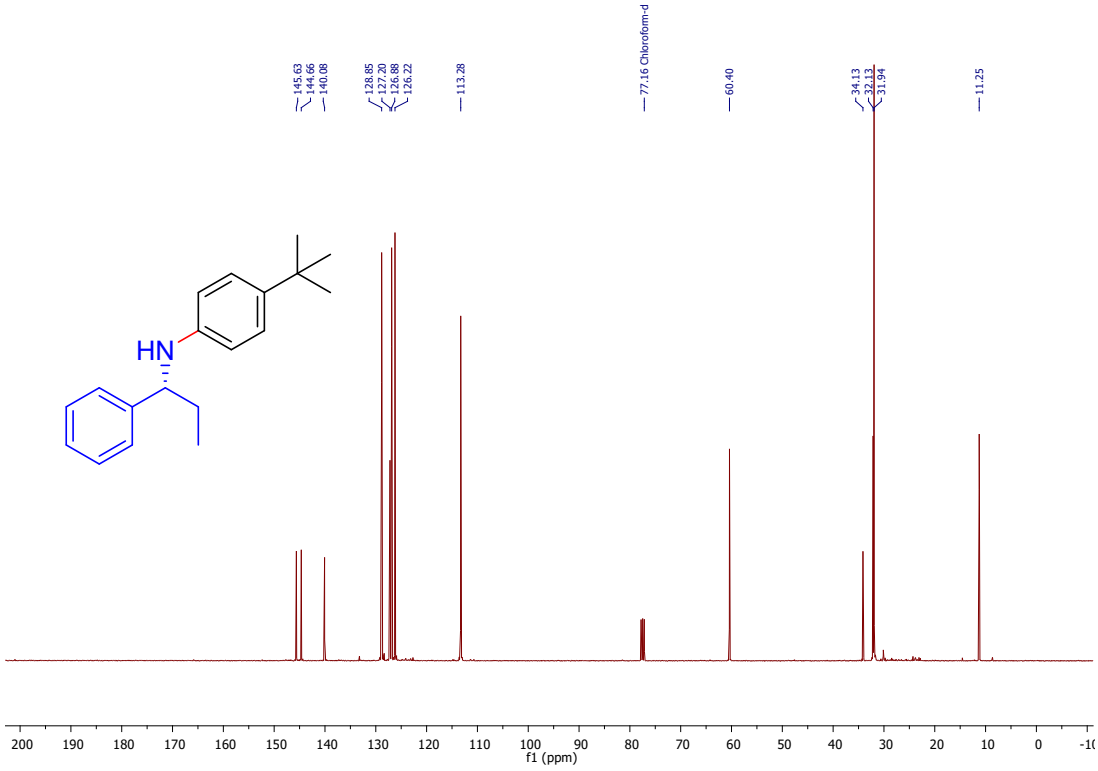
^{1}H NMR of 5g



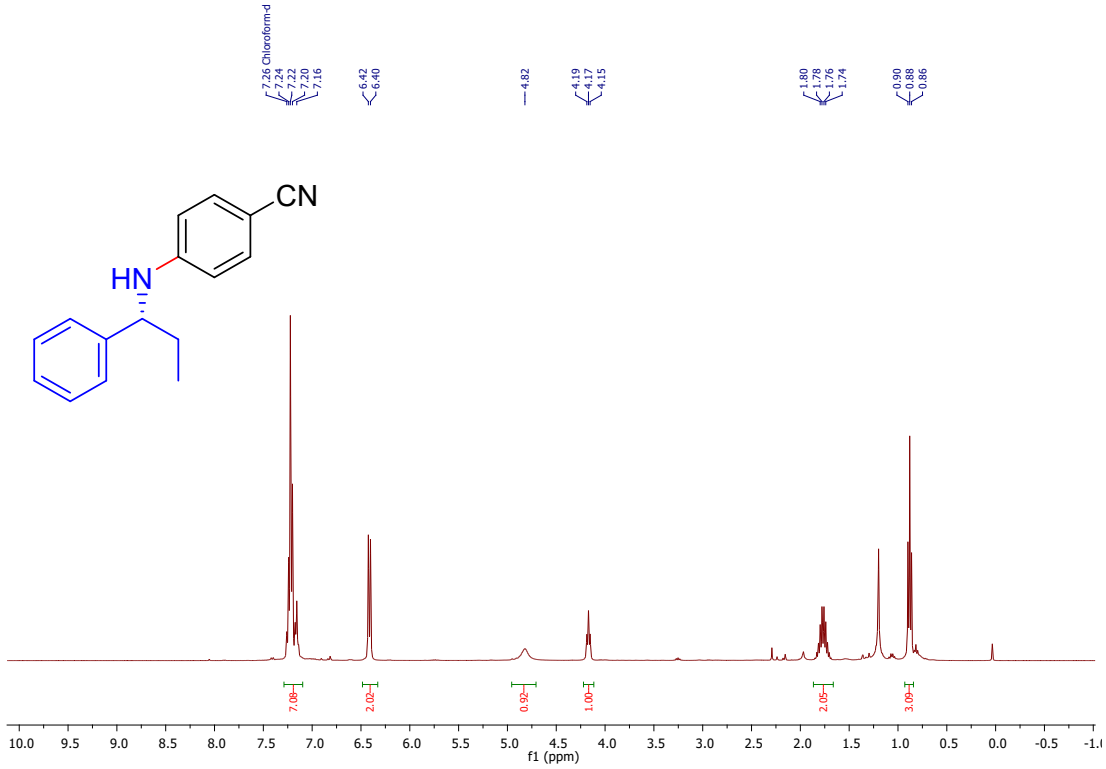
^{13}C{^{1}H} NMR of 5g



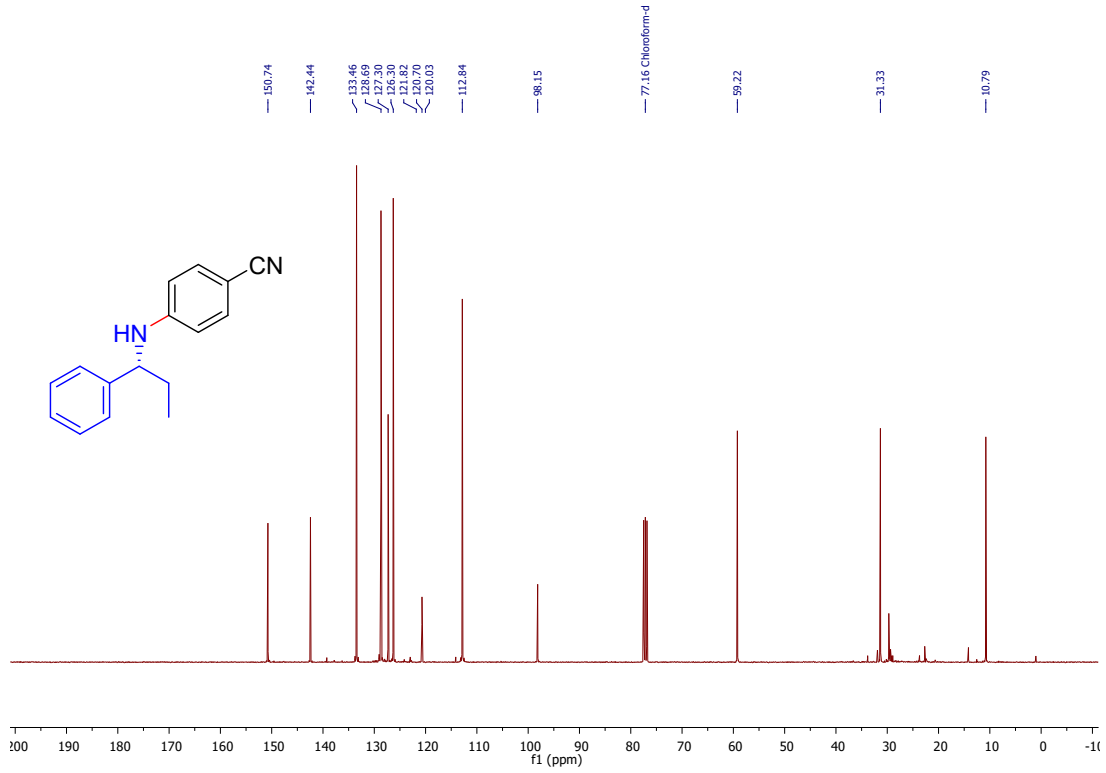
^{1}H NMR of 5h



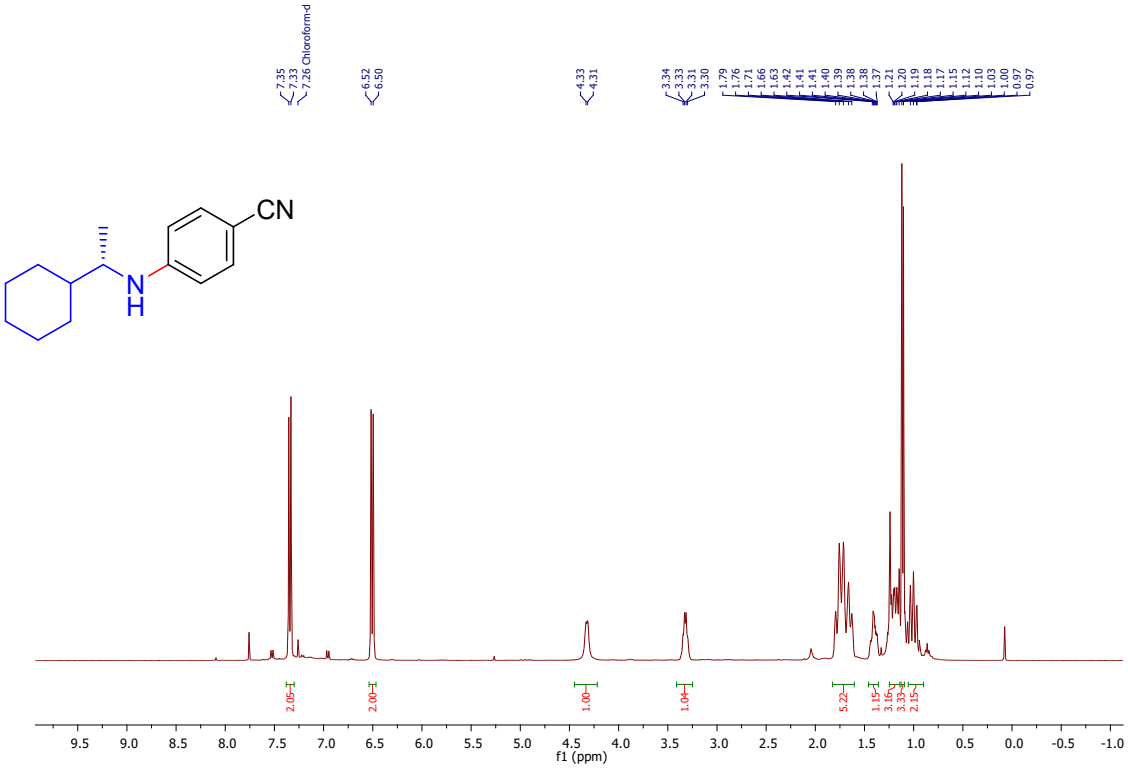
^{13}C{^{1}H} NMR of 5h



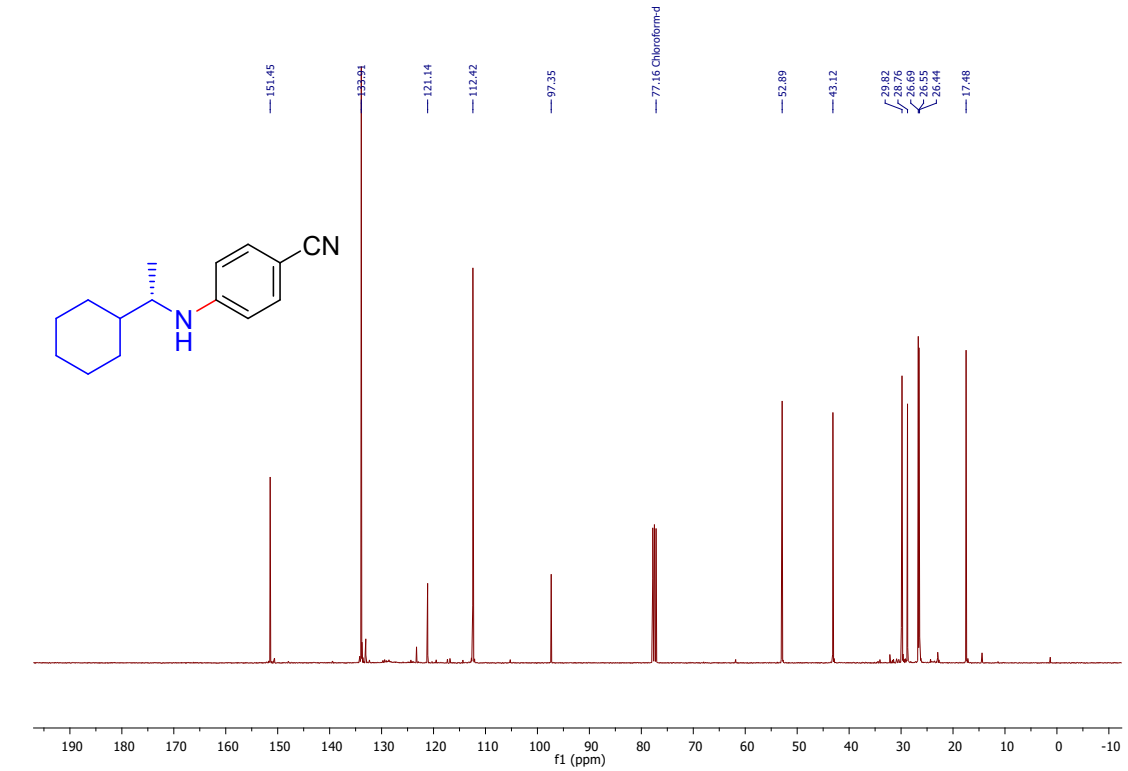
^{1}H NMR of 5i



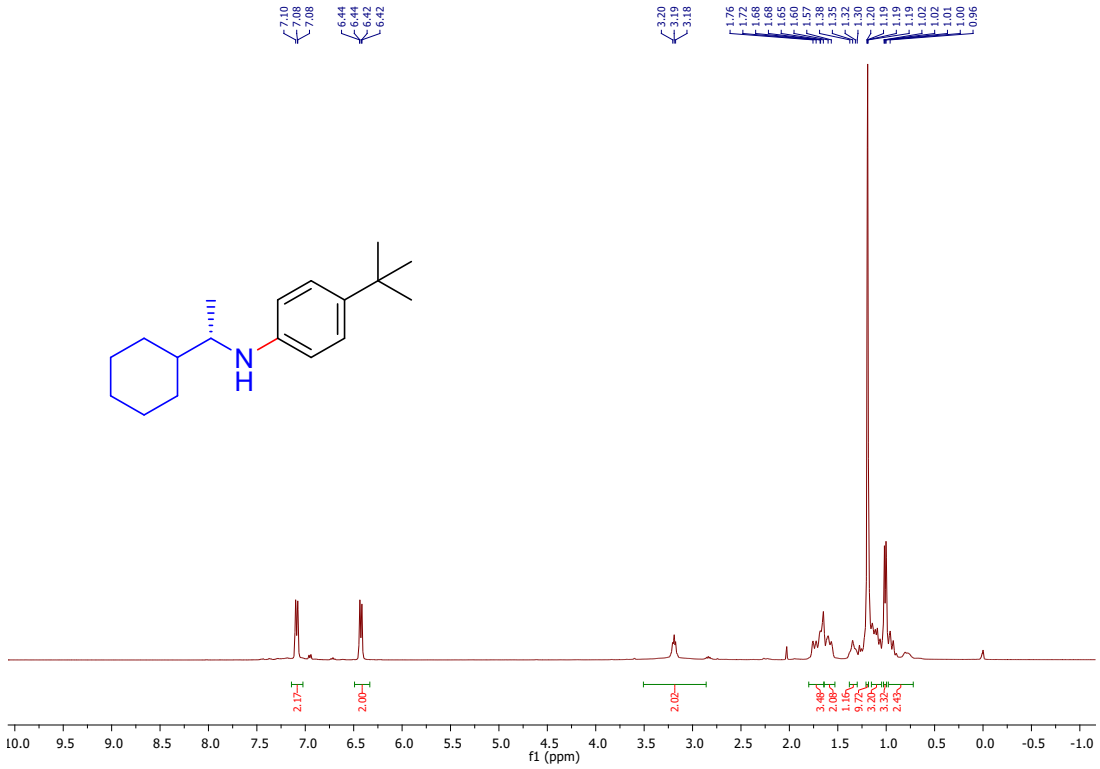
^{13}C{^{1}H} NMR of 5i



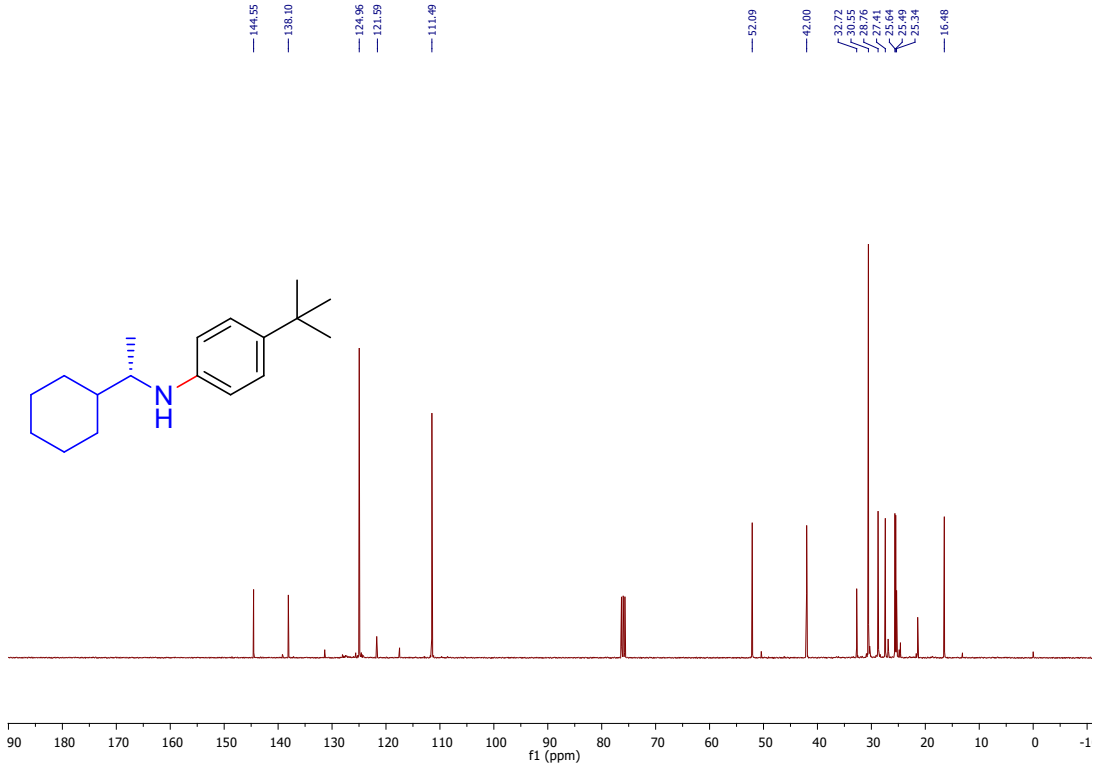
^{1}H NMR of 5j



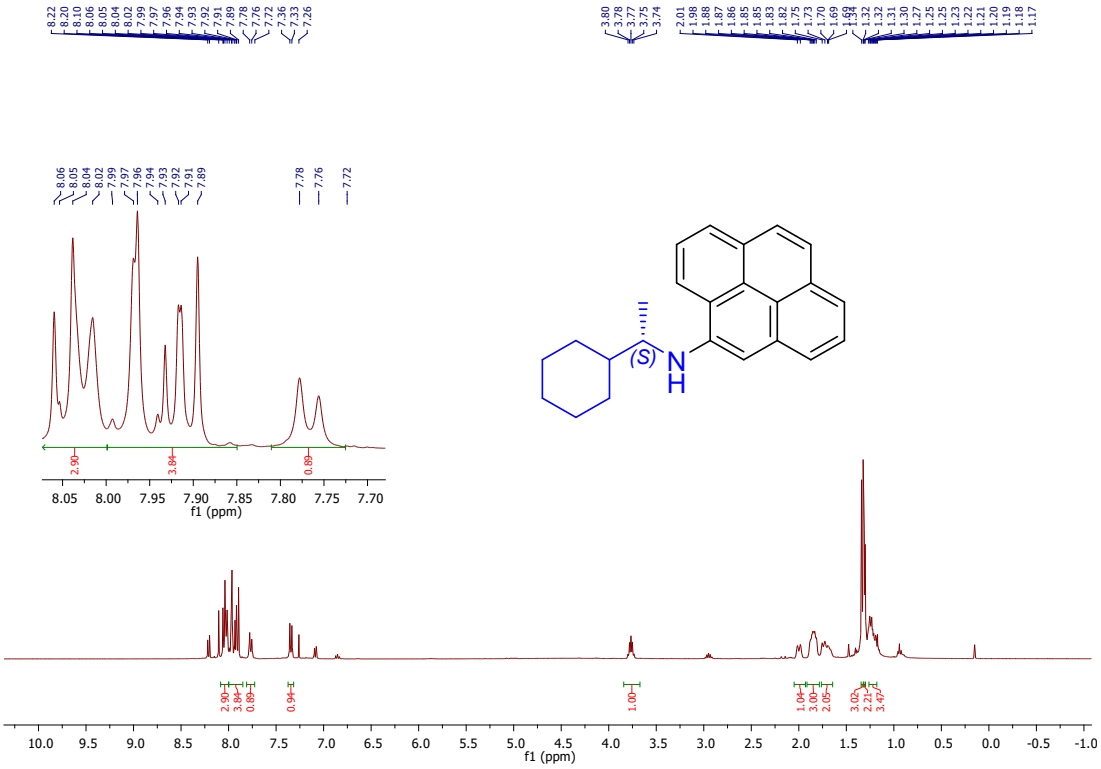
^{13}C{^{1}H} NMR of 5j



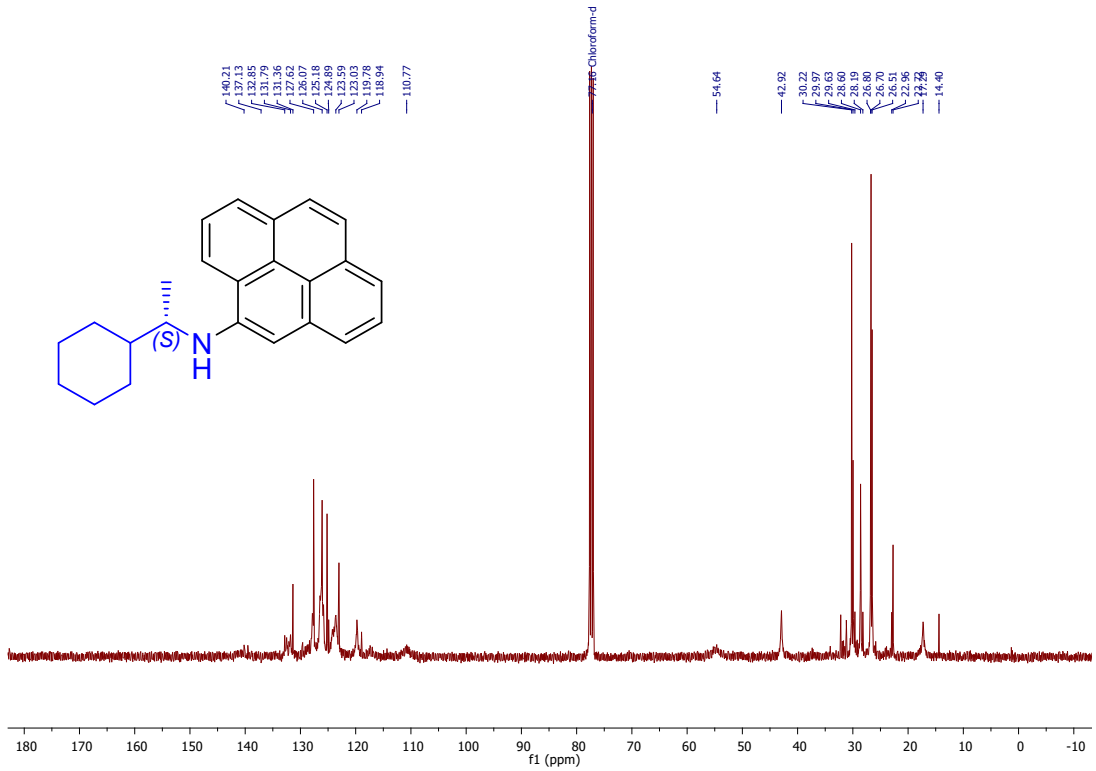
^{1}H NMR of 5k



^{13}C{^{1}H} NMR of 5k



^{1}H NMR of 5l



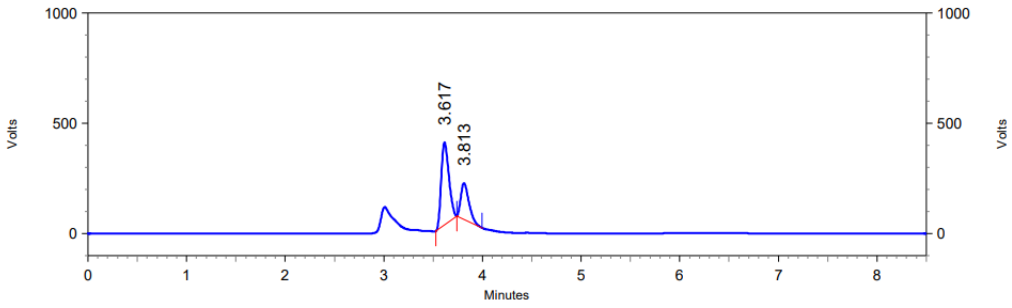
^{13}C{^{1}H} NMR of 5l

S8. HPLC Data

HPLC: Column: Chiral Pak AD-H (250 mm × 4.6 mm × 5 µm); Eluent: n-Hexane: Isopropyl Alcohol (Ratio specified with particular chromatogram); Gradient: Isocratic; Flow rate: 1ml/min; Injection volume: 10 µL; UV detection: 254 nm; Column temp.: ambient; Retention time may vary by ±1.0 min.

I) Ligand effect on ee% with microwave method:

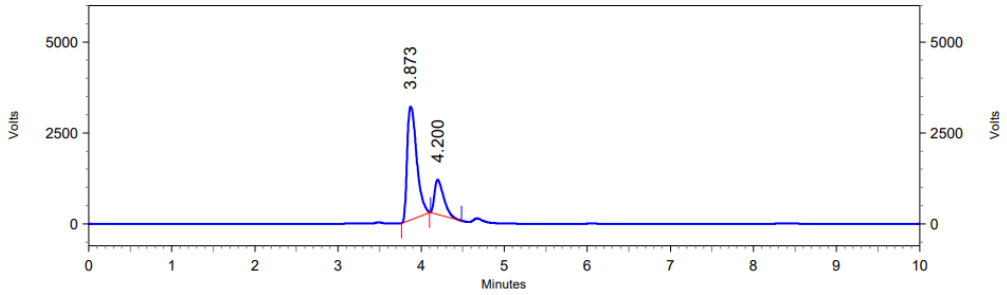
1) IPr



VWD: Signal A, 254 nm Results

Retention Time	Area	Area %
3.617	33801649	68.17
3.813	15782514	31.83
Totals	49584163	100.00

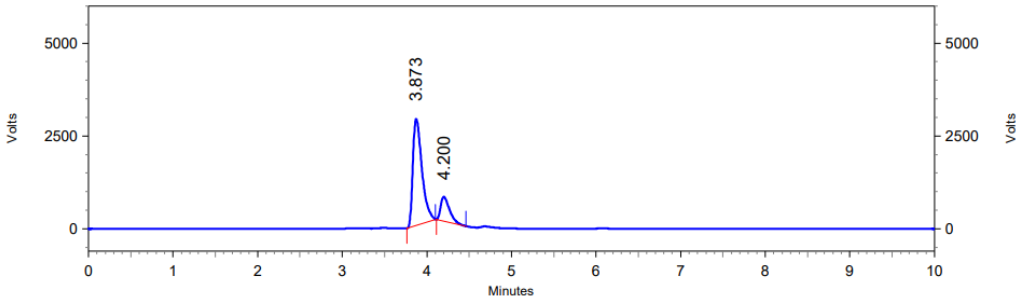
2) DPEPhos



VWD: Signal A, 254 nm
Results

Retention Time	Area	Area %
3.873	415727416	76.91
4.200	124791925	23.09
Totals	540519341	100.00

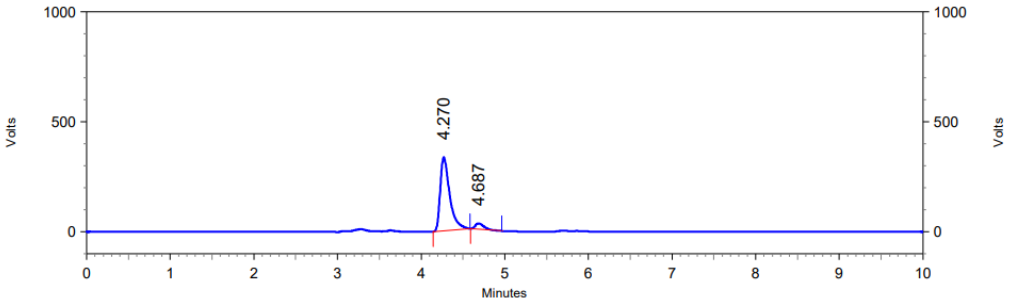
3) L1



VWD: Signal A, 254 nm
Results

Retention Time	Area	Area %
3.873	359243258	81.74
4.200	80226176	18.26
Totals	439469434	100.00

4) L2

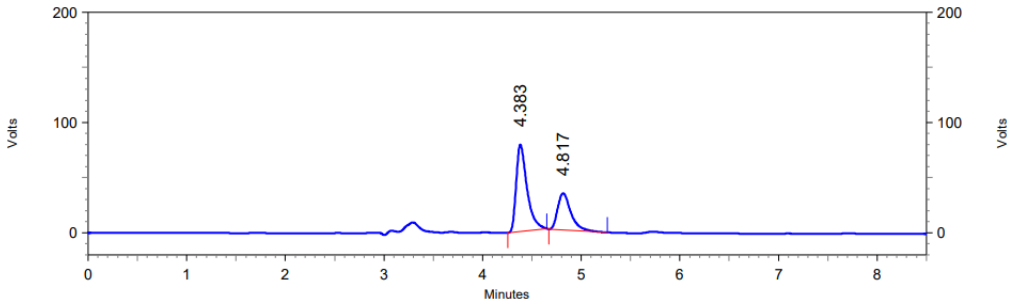


VWD: Signal A, 254 nm Results

Retention Time	Area	Area %
4.270	44134846	93.04
4.687	3300156	6.96

Totals	47435002	100.00

5) PNP(DIPP)



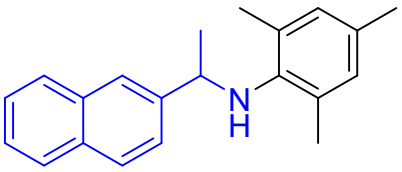
VWD: Signal A, 254 nm Results

Retention Time	Area	Area %
4.383	10139694	66.13
4.817	5193883	33.87

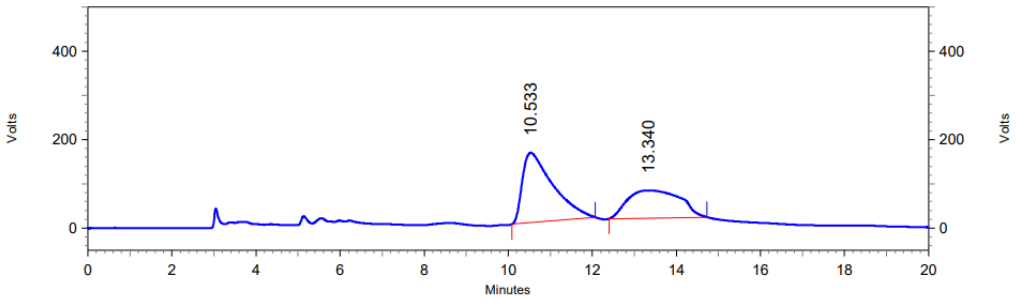
Totals	15333577	100.00

II) HPLC chromatogram for substrates 5a – 5l

5a)



Racemic

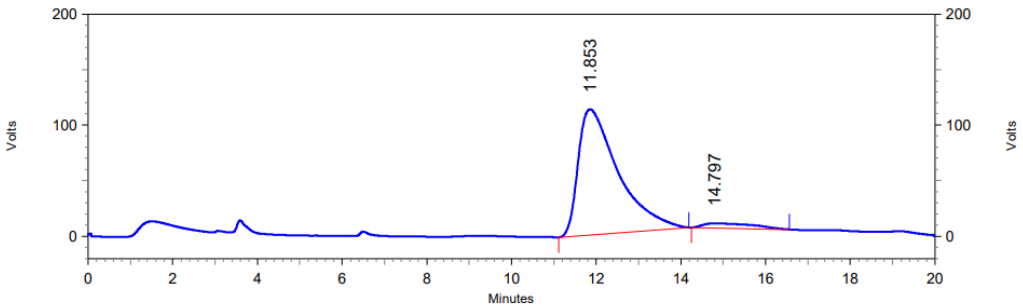


VWD: Signal A, 254 nm Results

Retention Time	Area	Area %
10.533	134259012	59.44
13.340	91602257	40.56

Totals	225861269	100.00

L1

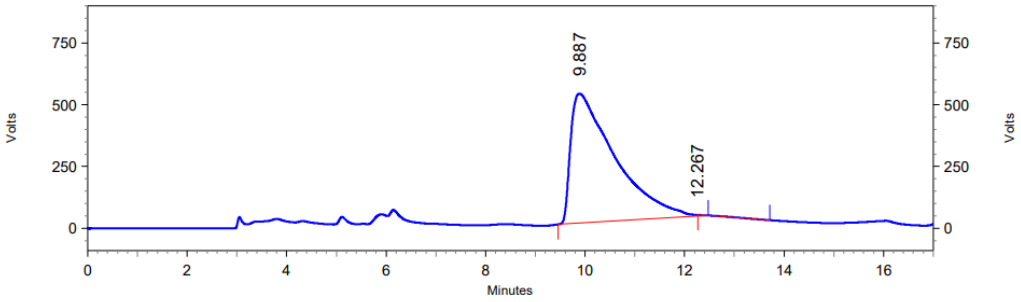


VWD: Signal A, 254 nm Results

Retention Time	Area	Area %
11.853	123838773	95.42
14.797	5945854	4.58

Totals	129784627	100.00

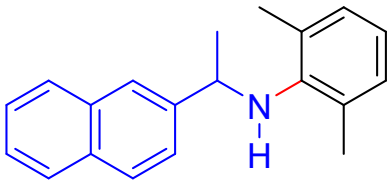
L2



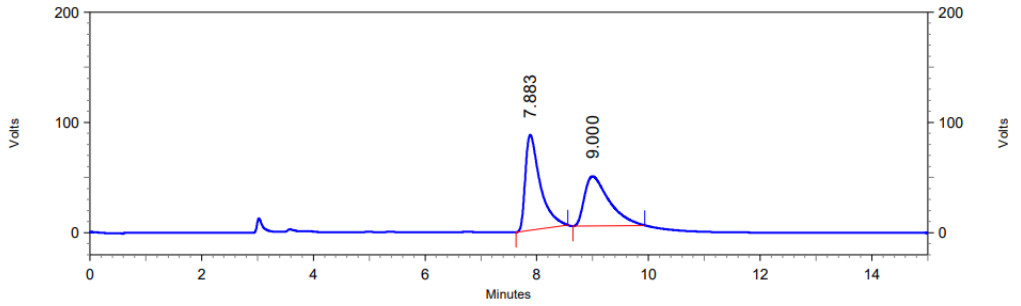
VWD: Signal A,
254 nm Results

Retention Time	Area	Area %	Height	Height %
9.887	541686123	99.78	8793630	100.00
12.267	1200209	0.22	0	0.00
Totals	542886332	100.00	8793630	100.00

5b)



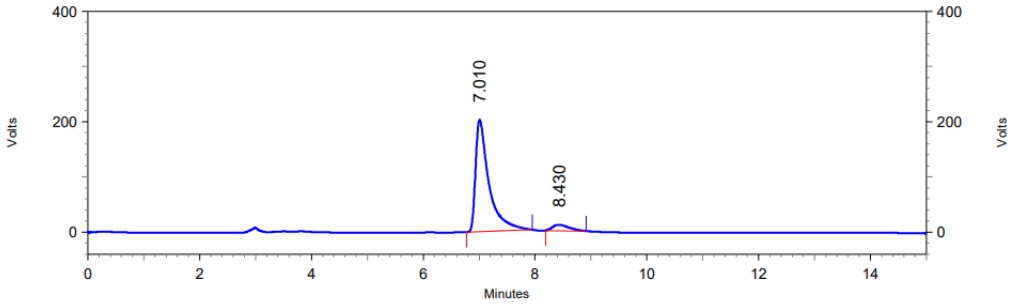
Racemic



VWD: Signal A, 254 nm Results

Retention Time	Area	Area %
7.883	26852383	53.69
9.000	23161041	46.31
Totals	50013424	100.00

L1

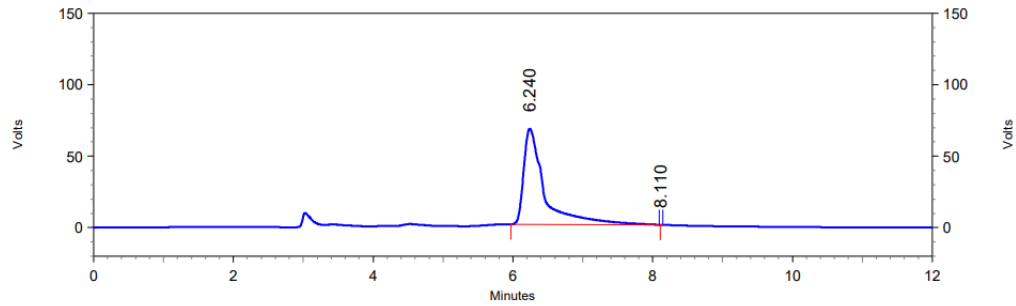


VWD: Signal A, 254 nm Results

Retention Time	Area	Area %
7.010	56931215	93.99
8.430	3637223	6.01

Totals	60568438	100.00

L2

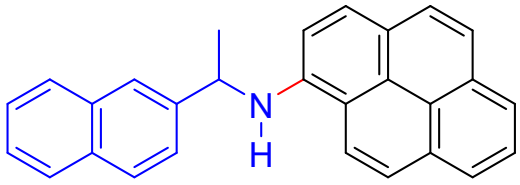


VWD: Signal A, 254 nm Results

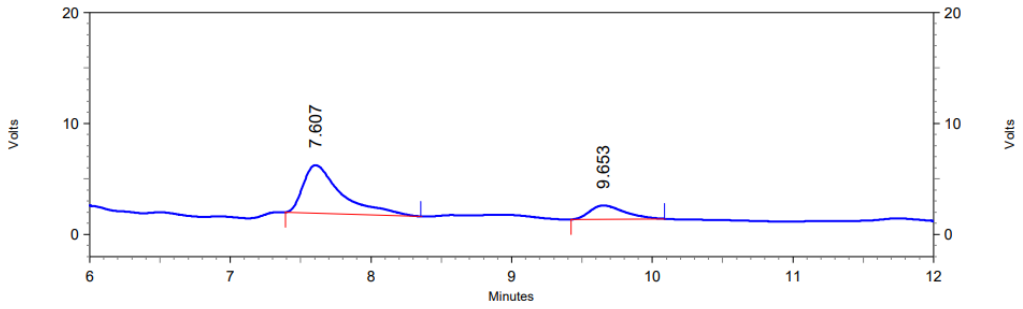
Retention Time	Area	Area %
6.240	23075542	100.00
8.110	5	0.00

Totals	23075547	100.00

5c)



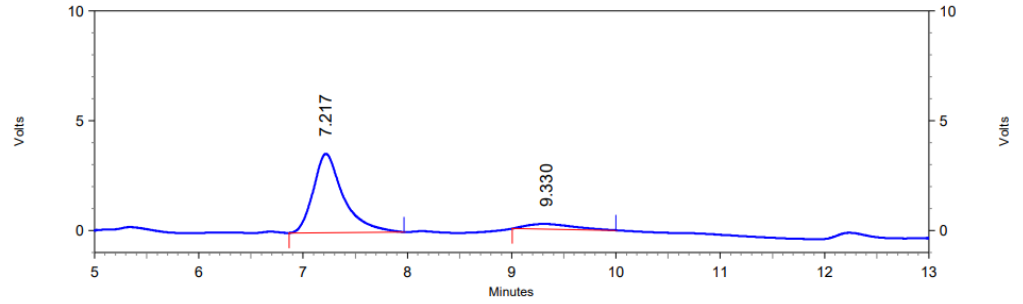
Racemic



VWD: Signal A, 254 nm Results

Retention Time	Area	Area %
7.607	1376954	79.61
9.653	352586	20.39
Totals	1729540	100.00

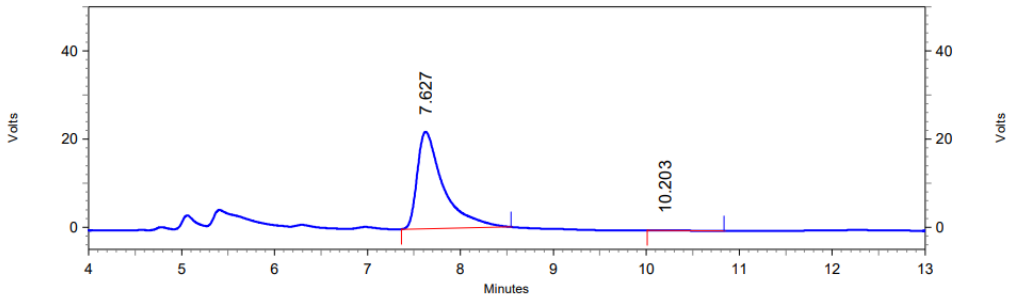
L1



VWD: Signal A, 254 nm Results

Retention Time	Area	Area %
7.217	1202282	90.65
9.330	124017	9.35
Totals	1326299	100.00

L2

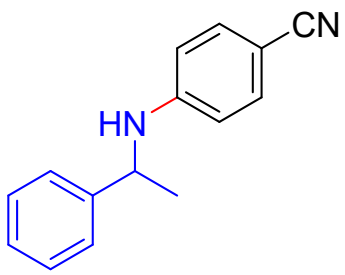


VWD: Signal A, 254 nm Results

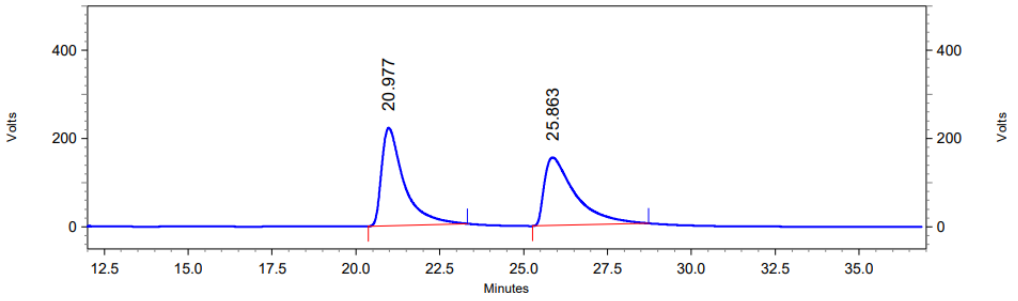
Retention Time	Area	Area %
7.627	7193883	99.72
10.203	19848	0.28

Totals	7213731	100.00

5d)



Racemic

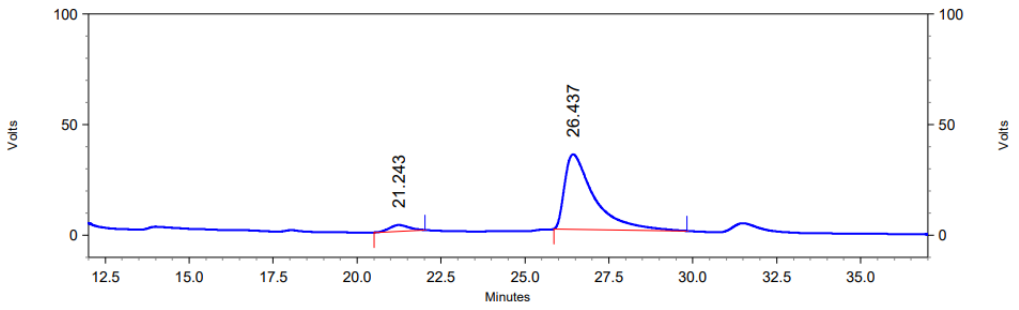


VWD: Signal A, 254 nm Results

Retention Time	Area	Area %
20.977	172649448	51.05
25.863	165572386	48.95

Totals	338221834	100.00

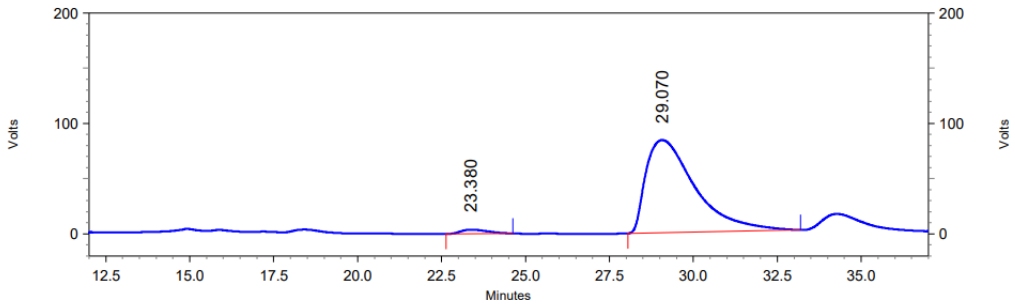
L1



VWD: Signal A, 254 nm Results

Retention Time	Area	Area %
21.243	1886988	5.16
26.437	34689578	94.84
Totals	36576566	100.00

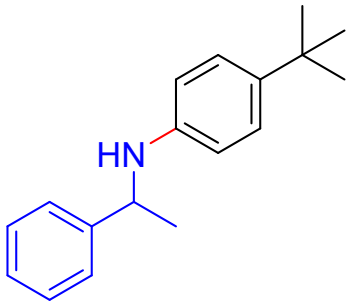
L2



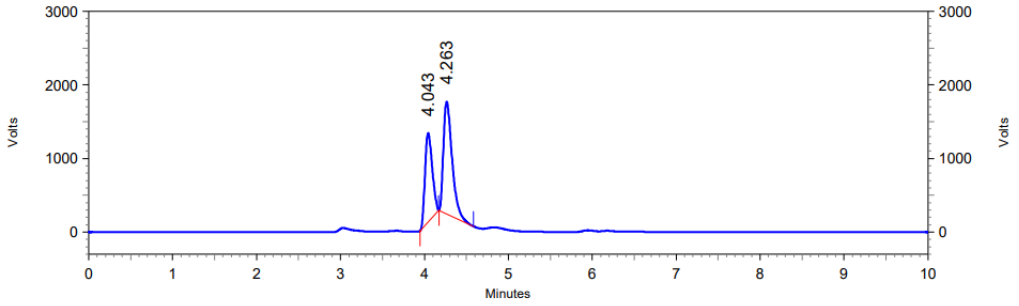
VWD: Signal A, 254 nm Results

Retention Time	Area	Area %
23.380	3500052	2.37
29.070	143990419	97.63
Totals	147490471	100.00

5e)



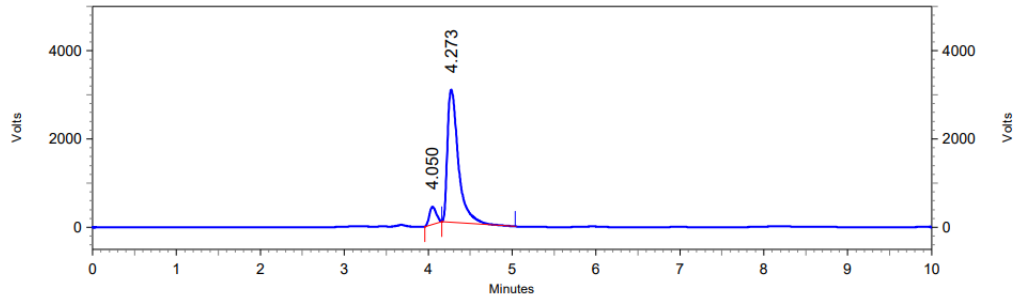
Racemic



VWD: Signal A, 254 nm Results

Retention Time	Area	Area %
4.043	121049064	39.65
4.263	184266536	60.35
Totals	305315600	100.00

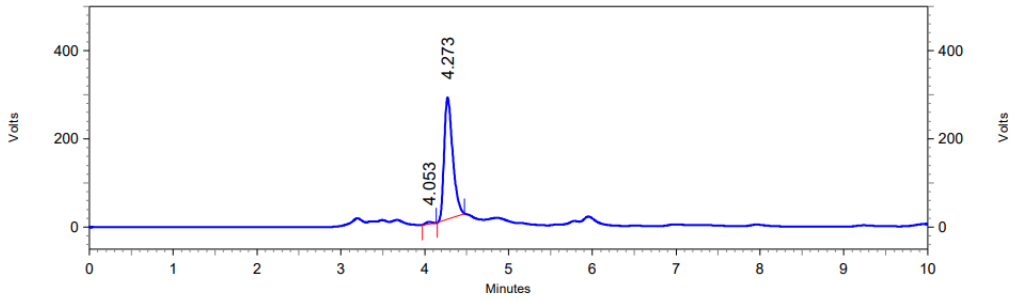
L1



VWD: Signal A, 254 nm Results

Retention Time	Area	Area %
4.050	37782763	7.64
4.273	456791225	92.36
Totals	494573988	100.00

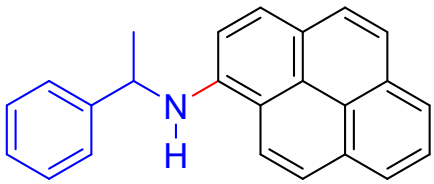
L2



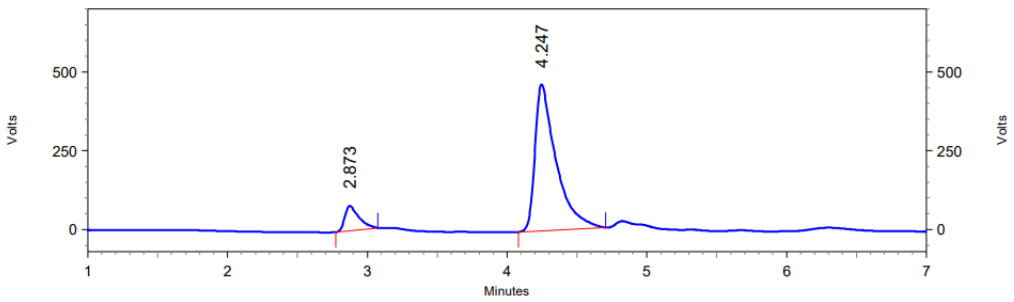
VWD: Signal A, 254 nm Results

Retention Time	Area	Area %
4.053	381322	1.15
4.273	32829292	98.85
Totals	33210614	100.00

5f)



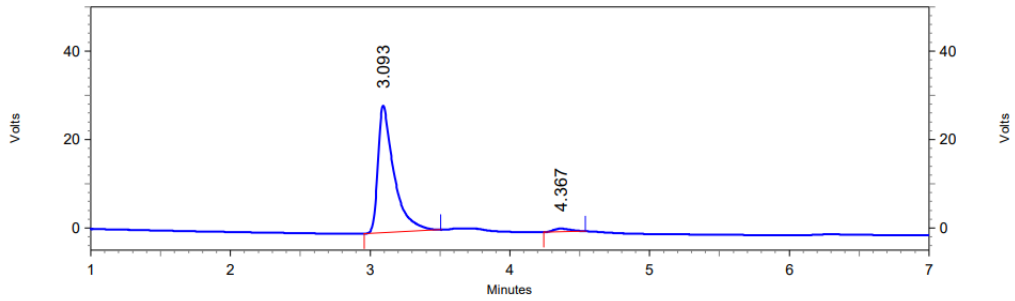
Racemic



VWD: Signal A, 230 nm Results

Retention Time	Area	Area %
2.873	9261795	10.17
4.247	81797329	89.83
Totals	91059124	100.00

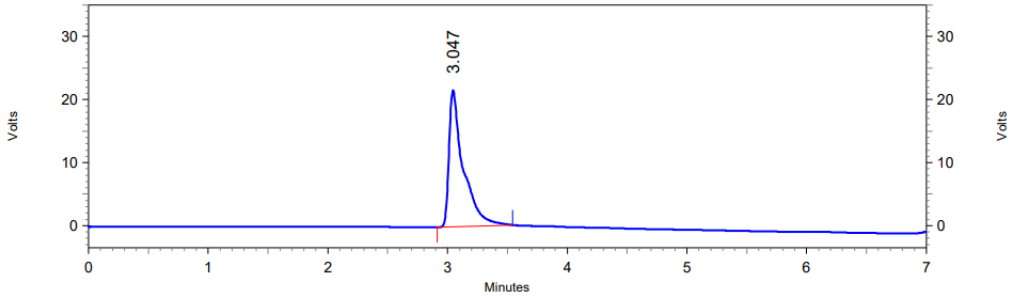
L1



VWD: Signal A, 230 nm Results

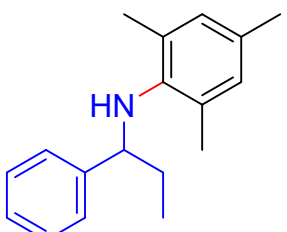
Retention Time	Area	Area %
3.093	3846037	97.40
4.367	102760	2.60
Totals	3948797	100.00

L2



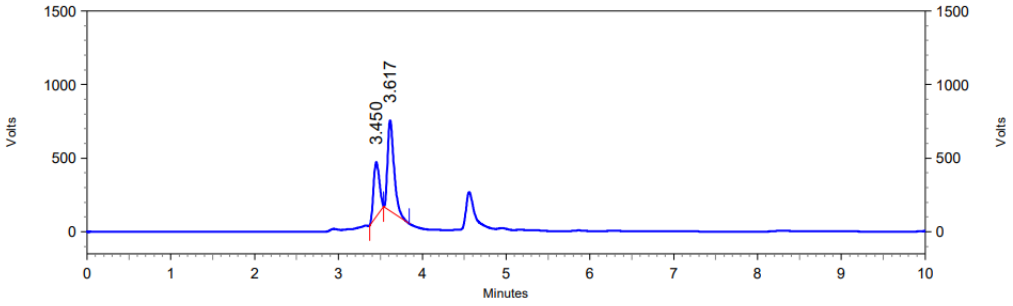
VWD: Signal A, 230 nm Results

Retention Time	Area	Area %	Height	Height %
3.047	3013716	100.00	362722	100.00
Totals	3013716	100.00	362722	100.00



5g)

Racemic

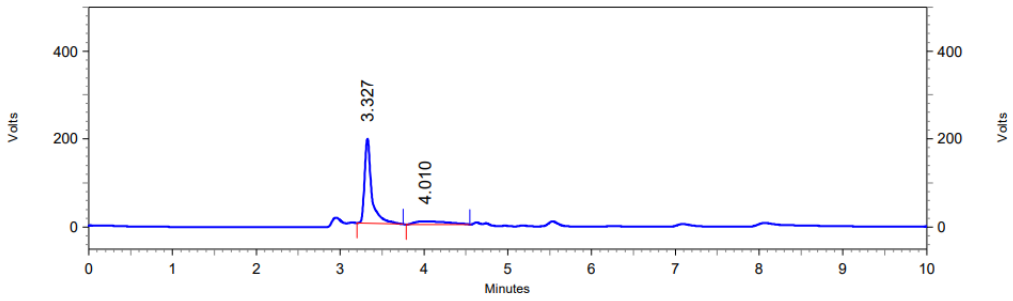


VWD: Signal A, 254 nm Results

Retention Time	Area	Area %
3.450	30158112	35.31
3.617	55256616	64.69

Totals	85414728	100.00

L1

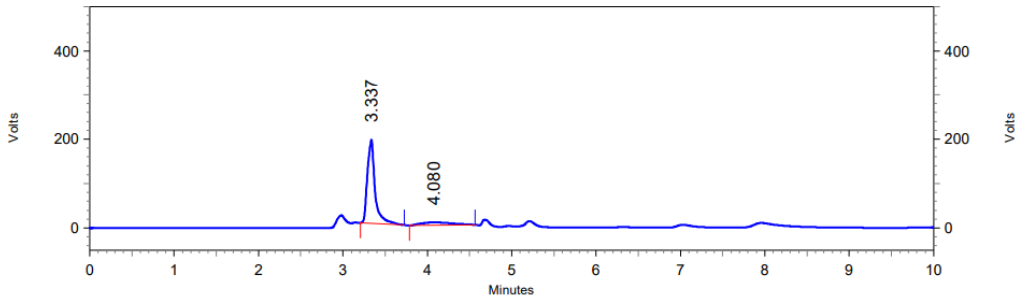


VWD: Signal A, 254 nm Results

Retention Time	Area	Area %
3.327	18980255	85.14
4.010	3311944	14.86

Totals	22292199	100.00

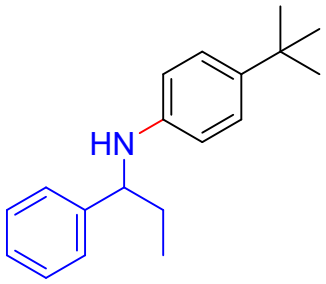
L2



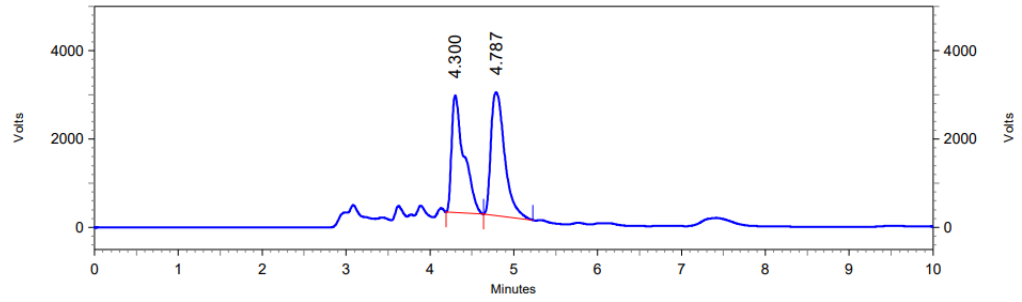
VWD: Signal A, 254 nm Results

Retention Time	Area	Area %
3.337	19878135	87.41
4.080	2862233	12.59
Totals	22740368	100.00

5h)



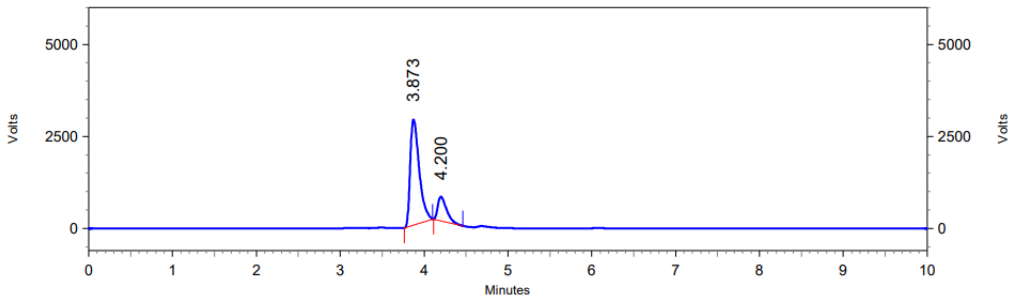
Racemic



VWD: Signal A, 254 nm Results

Retention Time	Area	Area %
4.300	454308814	45.98
4.787	533763283	54.02
Totals	988072097	100.00

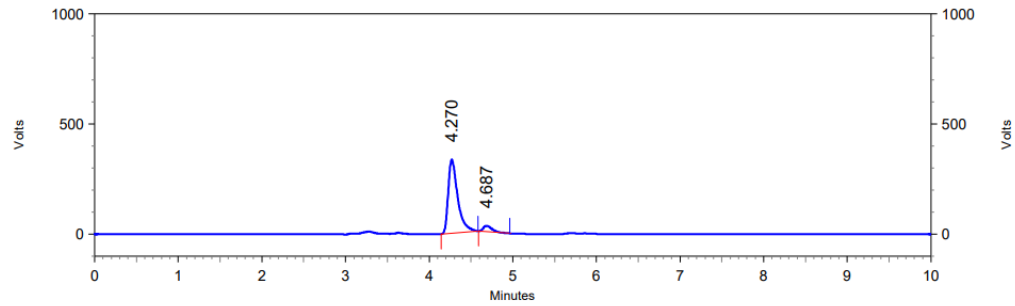
L1



VWD: Signal A, 254 nm Results

Retention Time	Area	Area %
3.873	359243258	81.74
4.200	80226176	18.26
Totals	439469434	100.00

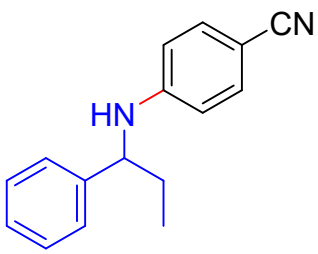
L2



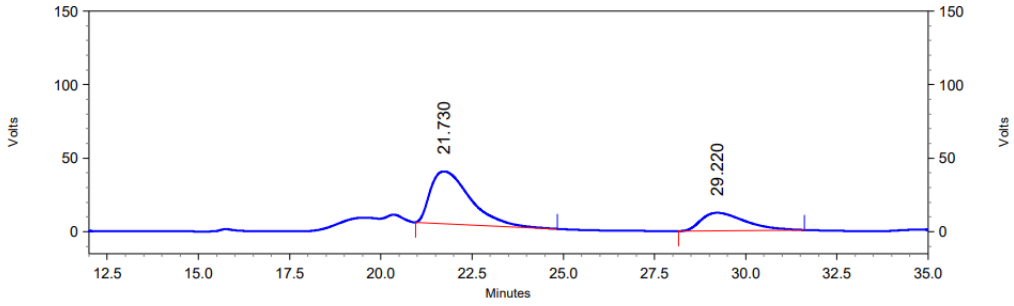
VWD: Signal A, 254 nm Results

Retention Time	Area	Area %
4.270	44134846	93.04
4.687	3300156	6.96
Totals	47435002	100.00

5i)



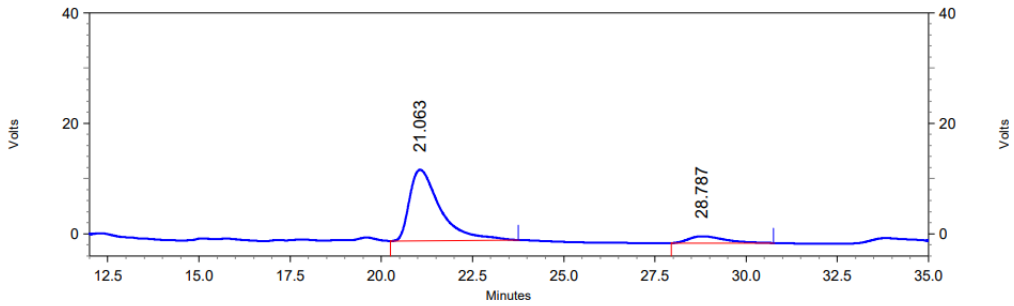
Racemic



VWD: Signal A, 254 nm Results

Retention Time	Area	Area %
21.730	45156591	72.57
29.220	17067476	27.43
Totals	62224067	100.00

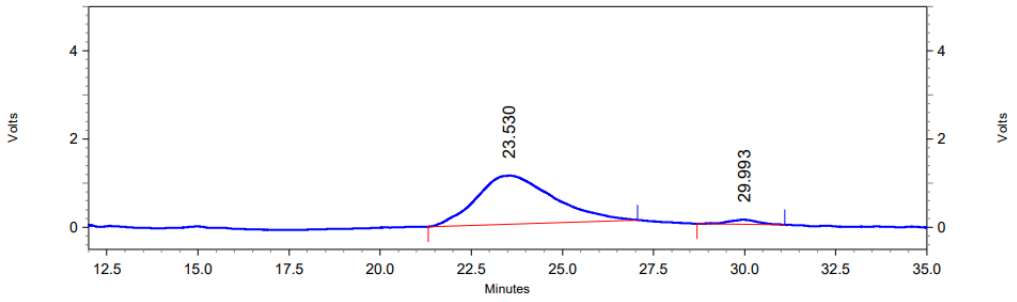
L1



VWD: Signal A, 254 nm Results

Retention Time	Area	Area %
21.063	12573633	89.88
28.787	1415779	10.12
Totals	13989412	100.00

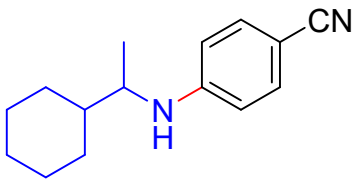
L2



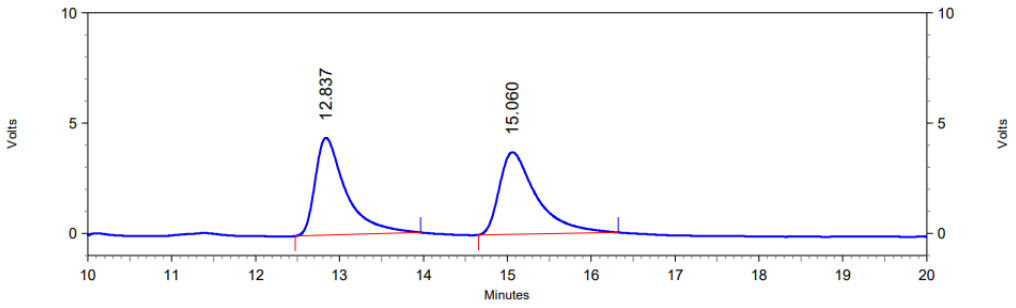
VWD: Signal A, 254 nm Results

Retention Time	Area	Area %
23.530	2712458	96.18
29.993	107601	3.82
Totals	2820059	100.00

5j)



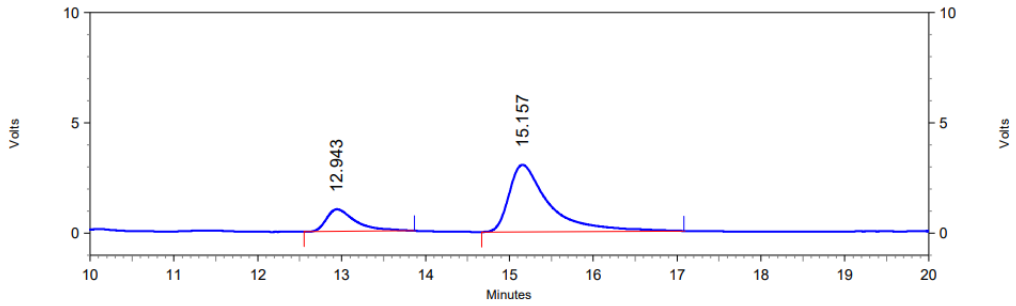
Racemic



VWD: Signal A, 254 nm
Results

Retention Time	Area	Area %
12.837	1885887	49.64
15.060	1913535	50.36
Totals	3799422	100.00

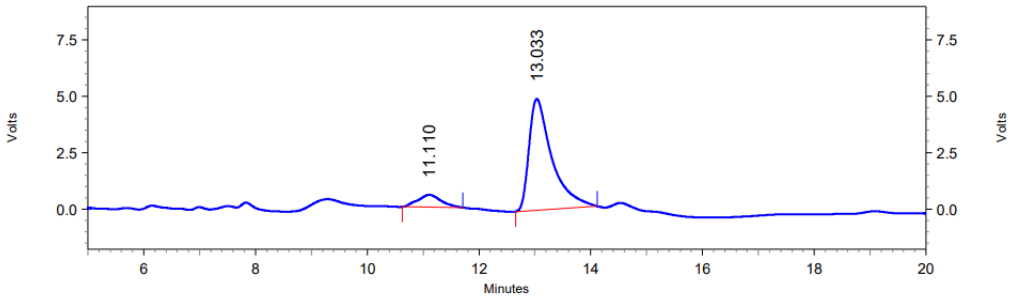
L1



VWD: Signal A, 254 nm
Results

Retention Time	Area	Area %
12.943	412565	19.69
15.157	1682521	80.31
Totals	2095086	100.00

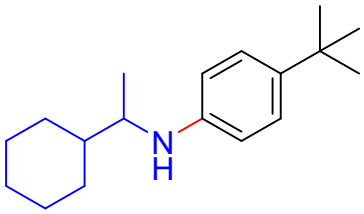
L2



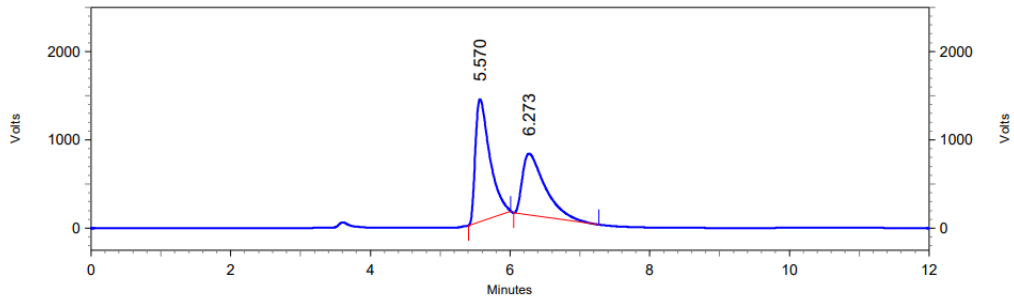
VWD: Signal A, 254 nm Results

Retention Time	Area	Area %
11.110	271263	10.35
13.033	2349577	89.65
Totals	2620840	100.00

5k)



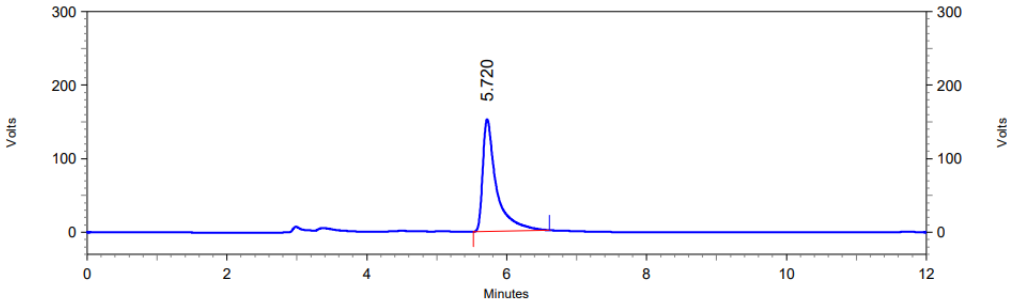
Racemic



VWD: Signal A, 254 nm Results

Retention Time	Area	Area %
5.570	334954824	55.82
6.273	265108345	44.18
Totals	600063169	100.00

L1

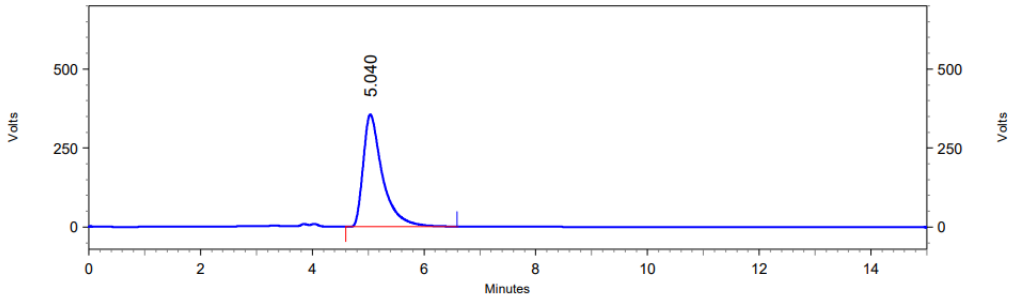


VWD: Signal A, 254 nm Results

Retention Time	Area	Area %
5.720	34710778	100.00

Totals	34710778	100.00

L2

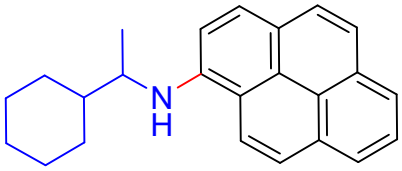


VWD: Signal A, 254 nm Results

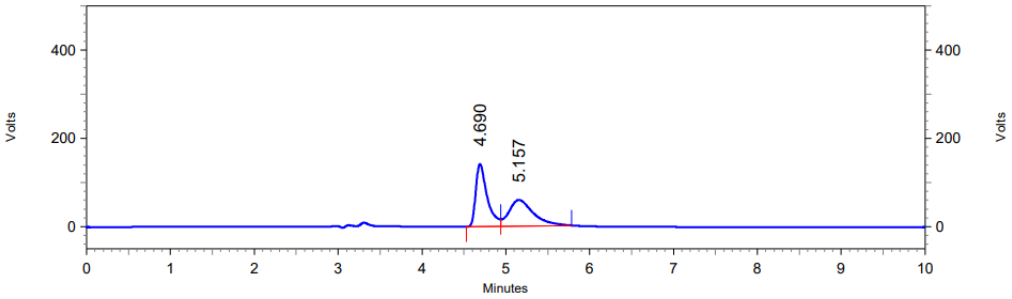
Retention Time	Area	Area %
5.040	143219782	100.00

Totals	143219782	100.00

5l)



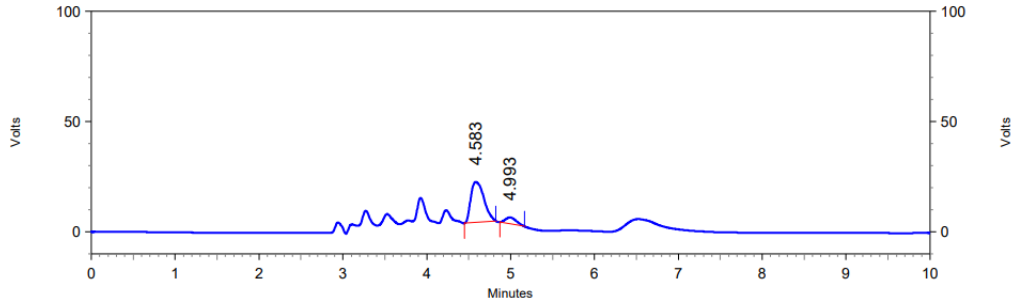
Racemic



VWD: Signal A, 254 nm
Results

Retention Time	Area	Area %
4.690	22657336	52.94
5.157	20144316	47.06
Totals	42801652	100.00

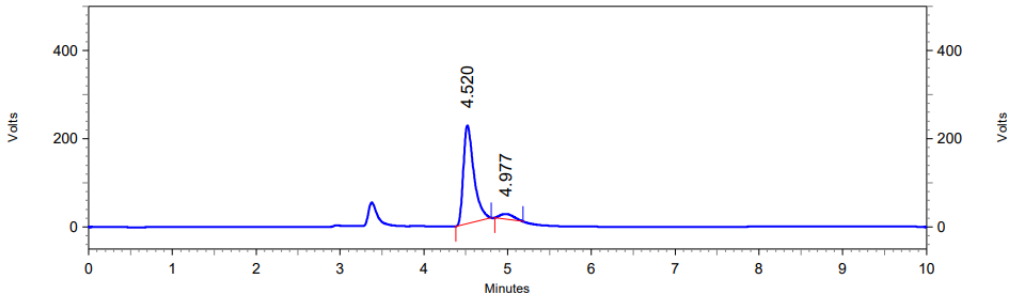
L1



VWD: Signal A, 254 nm Results

Retention Time	Area	Area %	Height	Height %
4.583	3373211	88.32	308670	86.29
4.993	446091	11.68	49054	13.71
Totals	3819302	100.00	357724	100.00

L2



VWD: Signal A, 254 nm
Results

Retention Time	Area	Area %
4.520	32579288	93.34
4.977	2323071	6.66
Totals	34902359	100.00

S9. References

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