

Supporting Information

Excited-state Palladium-Catalysed Reductive Alkylation of Imines: Scope and Mechanism

Rajesh Kancherla,^{†a} Krishnamoorthy Muralirajan^{†a} and Magnus Rueping^{*a}

*^aKAUST Catalysis Center, KCC, King Abdullah University of Science and Technology,
KAUST, Thuwal 23955-6900, Saudi Arabia.*

[†] These authors contributed equally to this work.

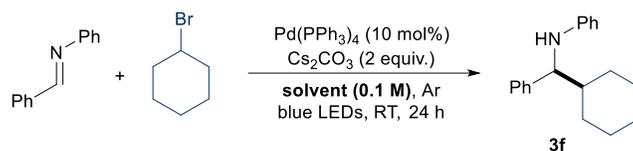
1. General information

Reagent Information. Unless otherwise stated, all reactions were carried out under argon atmosphere in screw cap reaction tubes. All the reagents and solvents were bought from Sigma Aldrich and Alfa Aesar in a sure-seal bottle and were used as received. Palladium catalysts were obtained from Sigma Aldrich and Strem chemicals. For column chromatography, silica gel (100–200 mesh) from Aldrich was used. A gradient elution using petroleum ether/ethyl acetate was performed based on Merck aluminium TLC sheets (silica gel 60 F₂₅₄). Organic solutions were concentrated under reduced pressure on a Büchi rotary evaporator.

Analytical Information. All isolated compounds are characterized by ¹H NMR, ¹³C NMR spectroscopy and gas chromatography-mass spectrometry (GC-MS), and high-resolution mass spectra (HRMS). Copies of the ¹H NMR, ¹³C NMR can be found in the supporting information. ¹H NMR spectra were recorded in deuterated solvents either on a Bruker Avance-II 500 (500 and 126 MHz) or 400 (400 and 101 MHz) instrument and are internally referenced to residual protic solvent signals. The ¹H NMR spectra are reported as δ /ppm downfield from tetramethylsilane (multiplicity, number of protons, assignment, coupling constant *J*/Hz). All ¹H NMR experiments are reported as follows unless otherwise stated: chemical shift (δ ppm), integration, multiplicity (s = singlet, d = doublet, t = triplet, q = quartet, m = multiplet, dd = doublet of doublets and dt = doublet of triplets, respectively), and coupling constants (Hz). ¹³C NMR spectra were recorded in deuterated solvents on Bruker Avance-II spectrometers at 101 or 126 MHz, with the central peak of the deuterated solvent as the internal standard. Chemical shifts (δ) are given in parts per million (ppm), and coupling constants (*J*) are given in Hertz (Hz) rounded to the nearest 0.1 Hz. The ¹³C NMR spectra are reported as δ /ppm and were obtained with ¹H decoupling (note: CDCl₃ referenced at δ 7.26 ppm for ¹H NMR, 77.16 ppm for ¹³C NMR). All GCMS analysis was done by Agilent 7890A GC system connected with 5975C inert XL EI/CI MSD (with triple-axis detector). High-resolution mass spectra (HRMS) analysis was performed using Bruker micro Time-of-Flight (TOF)-MS equipped with an ESI source. Luminescence intensities were recorded using a fluoromax-4 spectrophotometer from Horiba Scientific. Linear absorption spectra were collected on an Agilent 8453 Spectrophotometer.

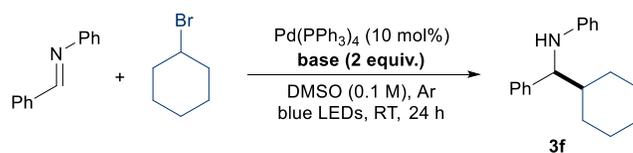
All reaction mixtures were irradiated with 34 W Kessil KSH150B blue light from a 4 cm distance. The emission maximum of the light source used is 425 nm. Regular fans are employed to maintain the temperature at room temperature (32 ± 2 °C).

2. Optimization details for reductive alkylation of imines:

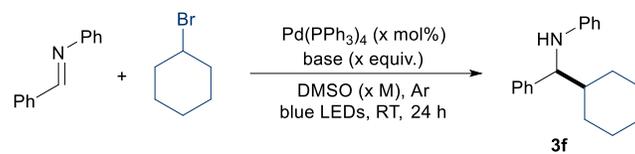


Entry	Solvent variation ^[a]	Yield 3f , (%) ^[b]
1	DMSO	53
2	MeOH	40
3	DMF	36
4	CH ₃ CN	34
5	1,4-dioxane	28
6	Toluene	7
7	DCE	2

^[a]Reaction condition: Imine (0.1 mmol), bromocyclohexane (0.2 mmol), solvent (1 mL), 34 W blue LEDs, Ar, 24 h, room temperature (T = 32 ± 2 °C). ^[b]Yields determined by GC-FID analysis using internal standard.



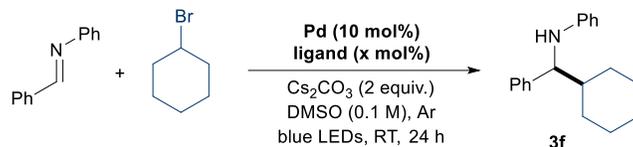
Entry	Base variation	Yield 3f , (%)
1	Cs ₂ CO ₃	53
2	CsOAc	43
3	K ₃ PO ₄	43
4	K ₂ CO ₃	40
5	Na ₂ CO ₃	30
6	TEA	26
7	KOAc	18
8	K ₂ HPO ₄	15



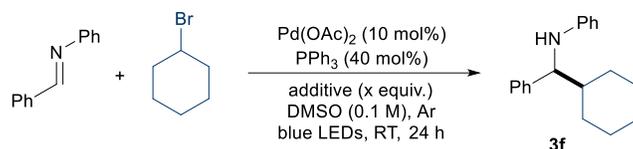
Entry	Miscellaneous variation	Yield 3f , (%)
1	Cs ₂ CO ₃ (2 equiv)	54
2	Cs ₂ CO ₃ (3 equiv)	55
3	DMSO (0.5 mL)	54
4	DMSO (1 mL)	53
5	DMSO (1.5 mL)	55
6	Pd(PPh ₃) ₄ (5 mol%)	30
7	Pd(PPh ₃) ₄ (10 mol%)	53
8	Pd(PPh ₃) ₄ (15 mol%)	81



Entry	PPh ₃ loading	Yield 3f , (%)
1	5 mol%	44
2	10 mol%	68
3	15 mol%	72
4	20 mol%	80
5	25 mol%	83
6	30 mol%	84
7	35 mol%	88
8	40 mol%	89
9	45 mol%	91
10	50 mol%	80



Entry	Pd and ligand variation	Yield 3f , (%)
1	PdCl ₂ (10 mol%), PPh ₃ (40 mol%)	48
2	PdCl ₂ (10 mol%), PPh ₃ (60 mol%)	69
3	Pd(PPh ₃) ₂ Cl ₂ (10 mol%), PPh ₃ (40 mol%)	67
4	Pd(PPh ₃) ₂ Cl ₂ (10 mol%), Xant-phos (20 mol%)	28
5	Pd(OAc) ₂ (10 mol%), PPh ₃ (60 mol%)	70
6	Pd(OAc) ₂ (10 mol%), PPh ₃ (70 mol%)	75
7	Pd(OAc) ₂ (10 mol%), PPh ₃ (80 mol%)	83
8	Pd(OAc) ₂ (10 mol%), PPh ₃ (90 mol%)	88
9	Pd(OAc) ₂ (10 mol%), PPh ₃ (100 mol%)	93 (85)

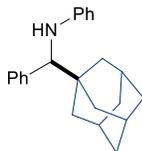


Entry	Pd(OAc) ₂ loading	Yield 3f , (%)
1	TEA (4 equiv.), Na ₂ CO ₃ (1 equiv.)	46
2	Tributyl amine (4 equiv.)	29
3	Piperidine (4 equiv.)	37
4	Zn powder (3 equiv.)	34

3. General procedure for the synthesis of compounds **3a-r**, and **4a-x**

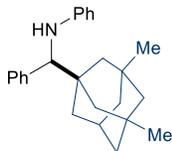
A clean, oven-dried screw cap reaction tube equipped with a PTFE-coated stir-bar was charged with imine (0.2 mmol), Pd(OAc)₂ (10 mol%, 0.02 mmol, 4.5 mg), PPh₃ (100 mol%, 0.2 mmol, 52.5 mg), Cs₂CO₃ (2 equiv, 0.4 mmol, 130 mg, added inside glove box), and alkyl bromide (2 equiv., 0.4 mmol), capped with Teflon septum and parafilm. The reaction tube was then purged with argon followed by the addition of anhydrous DMSO (0.1 M, 2 mL) under argon. The reaction tube was then stirred well for 10 min to generate yellow color which is then irradiated using 34 W blue LEDs while stirring at RT (under fan cooling). After 48 hours, the reaction mixture was treated with water and then extracted with ethyl acetate (3 x 10 mL). The organic layer was collected, dried over anhydrous Na₂SO₄, and concentrated *in vacuo*. The residue was purified by column chromatography using silica gel (100-200 mesh size) and hexane or EtOAc/petether as the eluent. Note that although in case of bromocyclohexane an yield of 85% (**3f**) was obtained in 24 h, we still see that some amount of imine remains. In case of majority of alkyl bromides, most of

the imine were found unreacted in 24 h, and so we have chosen to extend the reaction time to 48 h for performing the scope.



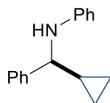
***N*-(adamantan-1-yl)(phenyl)methyl)aniline (3a):** The title compound was prepared according to the general procedure from *N*-benzylideneaniline (36.2 mg, 0.2 mmol) and 1-bromoadamantane (86 mg, 0.4 mmol). Pure product was obtained as white solid in 82% (52 mg) yield after column chromatography of the crude reaction mixture (silica gel, gradient 2% EtOAc/hexane).

¹H NMR (400 MHz, CDCl₃) δ 7.34 – 7.21 (m, 5H), 7.07 (t, *J* = 7.9 Hz, 2H), 6.61 (t, *J* = 7.1 Hz, 1H), 6.53 (d, *J* = 8.1 Hz, 2H), 4.38 (s, 1H), 3.92 (s, 1H), 2.03 (s, 3H), 1.76 (t, *J* = 11.8 Hz, 6H), 1.63 (d, *J* = 12.3 Hz, 3H), 1.54 (d, *J* = 12.1 Hz, 3H). **¹³C NMR (101 MHz, CDCl₃)** δ 148.01, 140.37, 129.12, 128.79, 127.71, 126.85, 116.88, 113.23, 68.08, 39.40, 37.07, 36.62, 28.57. **HRMS (ESI-TOF)** *m/z* calcd. for C₂₃H₂₇N (M+Na)⁺ 340.2041, found 340.2055. **GCMS (EI)** *m/z* calcd. for C₂₃H₂₇N [M⁺] 317.2, found 317.2, 182.1, 135.1, 104.0, 77.0.



***N*-(3,5-dimethyladamantan-1-yl)(phenyl)methyl)aniline (3b):** The title compound was prepared according to the general procedure from *N*-benzylideneaniline (36.2 mg, 0.2 mmol) and 1-bromo-3,5-dimethyladamantane (79.5 μL, 0.4 mmol). Pure product was obtained as yellow oil in 75% (52 mg) yield after column chromatography of the crude reaction mixture (silica gel, gradient 2% EtOAc/hexane).

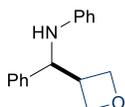
¹H NMR (500 MHz, CDCl₃) δ 7.29 – 7.19 (m, 5H), 7.03 (t, *J* = 7.9 Hz, 2H), 6.57 (t, *J* = 7.3 Hz, 1H), 6.48 (d, *J* = 8.0 Hz, 2H), 4.33 (s, 1H), 3.92 (s, 1H), 2.07 (p, *J* = 3.2 Hz, 1H), 1.55 – 1.52 (m, 2H), 1.37 – 1.24 (m, 6H), 1.16 – 1.04 (m, 4H), 0.81 (s, 6H). **¹³C NMR (101 MHz, CDCl₃)** δ 147.91, 140.41, 129.13, 128.78, 127.75, 126.84, 116.91, 113.21, 67.56, 51.17, 45.84, 45.49, 43.28, 38.51, 38.05, 31.30, 30.83, 29.56. **HRMS (ESI-TOF)** *m/z* calcd. for C₂₅H₃₁N (M+Na)⁺ 368.2354, found 368.2359. **GCMS (EI)** *m/z* calcd. for C₂₅H₃₁N [M⁺] 345.2, found 345.2, 182.1, 163.2, 121.1, 104.1, 91.1.



***N*-(cyclopropyl(phenyl)methyl)aniline (3c):** The title compound was prepared according to the general procedure from *N*-benzylideneaniline (36.2 mg, 0.2 mmol) and bromocyclopropane (32

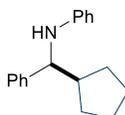
μL , 0.4 mmol) for 72 h. Pure product was obtained as yellow oil in 51% (22.7 mg) yield after column chromatography of the crude reaction mixture (silica gel, gradient 1% EtOAc/hexane).

^1H NMR (400 MHz, CDCl_3) δ 7.41 (d, $J = 7.0$ Hz, 2H), 7.34 (t, $J = 7.7$ Hz, 2H), 7.27 – 7.24 (m, 1H), 7.08 (t, $J = 8$ Hz, 2H), 6.64 (t, $J = 7.3$ Hz, 1H), 6.48 (d, $J = 7.5$ Hz, 2H), 4.39 (s, 1H), 3.67 (d, $J = 8.3$ Hz, 1H), 1.24 – 1.15 (m, 1H), 0.67 – 0.53 (m, 2H), 0.49 (dq, $J = 9.9, 4.9$ Hz, 1H), 0.39 (dq, $J = 9.5, 4.9$ Hz, 1H). **^{13}C NMR (101 MHz, CDCl_3)** δ 147.73, 143.41, 129.15, 128.64, 127.14, 126.57, 117.35, 113.50, 63.05, 19.85, 4.31, 3.64. **GCMS (EI)** m/z calcd. for $\text{C}_{16}\text{H}_{17}\text{N}$ [M^+] 223.1, found 223.1, 182.1, 131.1, 116.0, 91.0, 77.0. The analytical data correspond with those reported in the literature.¹



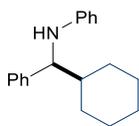
***N*-(oxetan-3-yl(phenyl)methyl)aniline (3d)**: The title compound was prepared according to the general procedure from *N*-benzylideneaniline (36.2 mg, 0.2 mmol) and 3-bromooxetane (33.2 μL , 0.4 mmol) for 72 h. Pure product was obtained as white solid in 70% (33.5 mg) yield after column chromatography of the crude reaction mixture (silica gel, gradient 30% EtOAc/Pet.ether).

^1H NMR (400 MHz, CDCl_3) δ 7.36 – 7.30 (m, 4H), 7.28 – 7.22 (m, 1H), 7.11 (t, $J = 7.6$ Hz, 2H), 6.68 (t, $J = 7.3$ Hz, 1H), 6.58 (d, $J = 8$ Hz, 2H), 4.85 (t, $J = 6.8$ Hz, 2H), 4.71 (d, $J = 8.9$ Hz, 1H), 4.69 – 4.62 (m, 2H), 4.55 (t, $J = 6.2$ Hz, 1H), 4.24 (s, 1H), 3.32 – 3.23 (m, 1H). **^{13}C NMR (101 MHz, CDCl_3)** δ 147.08, 141.28, 129.29, 128.95, 127.68, 126.51, 117.93, 113.74, 74.96, 74.22, 60.63, 41.95. **HRMS (ESI-TOF)** m/z calcd. for $\text{C}_{16}\text{H}_{17}\text{NO}$ ($\text{M}+\text{Na}$)⁺ 262.1202, found 262.1179. **GCMS (EI)** m/z calcd. for $\text{C}_{16}\text{H}_{17}\text{NO}$ [M^+] 239.1, found 239.1, 182.1, 117.1, 104.0, 91.0, 77.0.



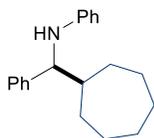
***N*-(cyclopentyl(phenyl)methyl)aniline (3e)**: The title compound was prepared according to the general procedure from *N*-benzylideneaniline (36.2 mg, 0.2 mmol) and bromocyclopentane (43 μL , 0.4 mmol). Pure product was obtained as yellow oil in 75% (37.6 mg) yield after column chromatography of the crude reaction mixture (silica gel, gradient 1% EtOAc/hexane).

^1H NMR (400 MHz, CDCl_3) δ 7.42 – 7.30 (m, 4H), 7.24 (t, $J = 7.1$ Hz, 1H), 7.10 (t, $J = 7.2$ Hz, 2H), 6.65 (t, $J = 7.3$ Hz, 1H), 6.55 (d, $J = 7.5$ Hz, 2H), 4.23 (s, 1H), 4.12 (d, $J = 8.4$ Hz, 1H), 2.20 (q, $J = 8.3, 7.6$ Hz, 1H), 1.93 (dtd, $J = 11.8, 7.5, 4.1$ Hz, 1H), 1.78 – 1.41 (m, 6H), 1.40 – 1.26 (m, 1H). **^{13}C NMR (101 MHz, CDCl_3)** δ 147.74, 144.04, 129.13, 128.40, 127.04, 126.89, 117.09, 113.33, 63.15, 47.89, 30.25, 30.07, 25.34, 25.30. **GCMS (EI)** m/z calcd. for $\text{C}_{18}\text{H}_{21}\text{N}$ [M^+] 251.1, found 251.2, 182.1, 117.1, 104.0, 91.1, 77.0. The analytical data correspond with those reported in the literature.¹



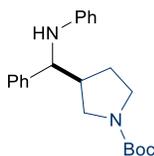
***N*-(cyclohexyl(phenyl)methyl)aniline (3f):** The title compound was prepared according to the general procedure from *N*-benzylideneaniline (36.2 mg, 0.2 mmol) and bromocyclohexane (49.3 μ L, 0.4 mmol). Pure product was obtained as yellow oil in 85% (45 mg) yield after column chromatography of the crude reaction mixture (silica gel, gradient 1% EtOAc/hexane).

^1H NMR (400 MHz, CDCl_3) δ 7.35 – 7.30 (m, 4H), 7.28 – 7.19 (m, 1H), 7.12 – 7.07 (m, 2H), 6.64 (t, $J = 7.3$ Hz, 1H), 6.54 (d, $J = 7.4$ Hz, 2H), 4.17 (s, 1H), 4.15 (d, $J = 6.3$ Hz, 1H), 1.93 (d, $J = 11.9$ Hz, 1H), 1.86 – 1.65 (m, 4H), 1.58 (m, 1H), 1.33 – 1.01 (m, 5H). **^{13}C NMR (101 MHz, CDCl_3)** δ 147.88, 142.76, 129.15, 128.29, 127.34, 126.84, 117.03, 113.27, 63.51, 45.02, 30.36, 29.58, 26.55, 26.51, 26.48. **GCMS (EI)** m/z calcd. for $\text{C}_{19}\text{H}_{23}\text{N}$ [M^+] 265.1, found 265.1, 183.1, 181.9, 104.0, 91.0, 77.0. The analytical data correspond with those reported in the literature.²



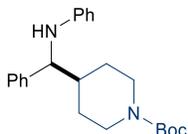
***N*-(cycloheptyl(phenyl)methyl)aniline (3g):** The title compound was prepared according to the general procedure from *N*-benzylideneaniline (36.2 mg, 0.2 mmol) and bromocycloheptane (55 μ L, 0.4 mmol). Pure product was obtained as yellow oil in 82% (45.8 mg) yield after column chromatography of the crude reaction mixture (silica gel, gradient 1% EtOAc/hexane).

^1H NMR (400 MHz, CDCl_3) δ 7.37 – 7.28 (m, 4H), 7.25 – 7.21 (m, 1H), 7.09 (t, $J = 7.7$ Hz, 2H), 6.63 (t, $J = 7.3$ Hz, 1H), 6.51 (d, $J = 8.0$ Hz, 2H), 4.26 (d, $J = 5.4$ Hz, 1H), 4.12 (s, 1H), 1.96 – 1.88 (m, 1H), 1.85 – 1.65 (m, 4H), 1.65 – 1.27 (m, 8H). **^{13}C NMR (101 MHz, CDCl_3)** δ 147.96, 142.97, 129.17, 128.31, 127.25, 126.75, 117.02, 113.25, 63.82, 46.51, 32.37, 29.51, 28.40, 28.14, 27.11, 27.10. **HRMS (ESI-TOF)** m/z calcd. for $\text{C}_{20}\text{H}_{25}\text{N}$ ($\text{M}+\text{Na}$)⁺ 302.1879, found 302.1862. **GCMS (EI)** m/z calcd. for $\text{C}_{20}\text{H}_{25}\text{N}$ [M^+] 279.2, found 279.1, 182.1, 104.1, 91.1, 77.1, 55.1.



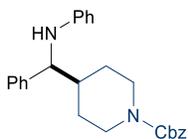
Tert-butyl 3-(phenyl(phenylamino)methyl)pyrrolidine-1-carboxylate (3h): The title compound was prepared according to the general procedure from *N*-benzylideneaniline (36.2 mg, 0.2 mmol) and 1-Boc-3-bromopyrrolidine (100 mg, 0.4 mmol). Pure product was obtained as yellow oil in 85% (59.8 mg) yield after column chromatography of the crude reaction mixture (silica gel, gradient 15% EtOAc/Pet.ether).

¹H NMR (400 MHz, CDCl₃) δ 7.32 – 7.31 (m, 4H), 7.25 – 7.21 (m, 1H), 7.06 (q, *J* = 7.1, 6.5 Hz, 2H), 6.65 – 6.63 (m, 1H), 6.54 – 6.48 (m, 2H), 4.23 – 4.18 (m, 2H), 3.74 – 3.65 (m, 1H), 3.51 – 3.42 (m, 1H), 3.27 – 3.19 (m, 2H), 2.46 (h, *J* = 8.3 Hz, 1H), 1.69 – 1.58 (m, 2H), 1.46 (s, 9H). **¹³C NMR (101 MHz, CDCl₃)** δ 154.65, 146.95, 142.36, 129.24, 128.78, 127.54, 126.79, 117.78, 113.63, 79.50, 61.43, 61.16, 50.20, 49.38, 46.63, 45.75, 45.45, 29.82, 29.53, 29.02, 28.68. d.r. (1:1.2). **HRMS (ESI-TOF)** *m/z* calcd. for C₂₂H₂₈N₂O₂ (M+Na)⁺ 375.2048, found 375.2089. **GCMS (EI)** *m/z* calcd. for C₂₂H₂₈N₂O₂ [M⁺] 352.2, found 281.1, 252.1, 207.0, 182.1, 159.1, 130.0, 104.0, 91.9, 77.0.



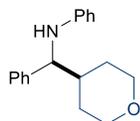
Tert-butyl 4-(phenyl(phenylamino)methyl)piperidine-1-carboxylate (3i): The title compound was prepared according to the general procedure from *N*-benzylideneaniline (36.2 mg, 0.2 mmol) and 1-Boc-4-bromopiperidine (105.6 mg, 0.4 mmol). Pure product was obtained as yellow solid in 82% (60 mg) yield after column chromatography of the crude reaction mixture (silica gel, gradient 15% EtOAc/Pet.ether).

¹H NMR (500 MHz, CDCl₃) δ 7.35 – 7.19 (m, 5H), 7.08 (t, *J* = 7.3 Hz, 2H), 6.64 (t, *J* = 7.3 Hz, 1H), 6.53 (d, *J* = 7.9 Hz, 2H), 4.11 – 4.17 (m, 4H), 2.75 – 2.50 (m, 2H), 1.98 – 1.70 (m, 2H), 1.46 (s, 10H), 1.35 – 1.20 (m, 2H). **¹³C NMR (126 MHz, CDCl₃)** δ 154.82, 147.31, 141.86, 129.20, 128.55, 127.24, 127.21, 117.54, 113.55, 79.55, 62.91, 43.99, 43.39, 29.45, 28.92, 28.56. **HRMS (ESI-TOF)** *m/z* calcd. for C₂₃H₃₀N₂O₂ (M+Na)⁺ 389.2205, found 389.2258. **GCMS (EI)** *m/z* calcd. for C₂₃H₃₀N₂O₂ [M⁺] 366.2, found 366.1, 266.1, 207.1, 182.1, 104.0, 77.0, 57.0.



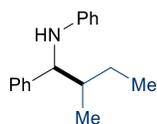
Benzyl 4-(phenyl(phenylamino)methyl)piperidine-1-carboxylate (3j): The title compound was prepared according to the general procedure from *N*-benzylideneaniline (36.2 mg, 0.2 mmol) and 4-bromo-*N*-Z-piperidine (119.2 mg, 0.4 mmol). Pure product was obtained as yellow oil in 78% (62.5 mg) yield after column chromatography of the crude reaction mixture (silica gel, gradient 20% EtOAc/Pet.ether).

¹H NMR (500 MHz, CDCl₃) δ 7.48 – 7.20 (m, 10H), 7.09 (t, *J* = 7.7 Hz, 2H), 6.65 (t, *J* = 7.3 Hz, 1H), 6.53 (d, *J* = 7.9 Hz, 2H), 5.14 (s, 2H), 4.45 – 3.95 (m, 4H), 2.72 (bs, 2H), 1.99 – 1.75 (m, 2H), 1.54 – 1.18 (m, 3H). **¹³C NMR (126 MHz, CDCl₃)** δ 155.25, 147.38, 141.77, 136.92, 129.21, 128.58, 128.07, 127.96, 127.29, 127.17, 117.51, 113.48, 67.14, 62.73, 44.25, 44.15, 43.26, 29.33, 28.79. **HRMS (ESI-TOF)** *m/z* calcd. for C₂₆H₂₈N₂O₂ (M+Na)⁺ 423.2048, found 423.2073. **GCMS (EI)** *m/z* calcd. for C₂₆H₂₈N₂O₂ [M⁺] 400.2, found 400.2, 182.1, 104.0, 91.0, 77.0, 65.0.



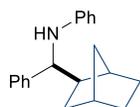
***N*-(phenyl(tetrahydro-2H-pyran-4-yl)methyl)aniline (3k):** The title compound was prepared according to the general procedure from *N*-benzylideneaniline (36.2 mg, 0.2 mmol) and 4-bromo-tetrahydropyran (45 μ L, 0.4 mmol). Pure product was obtained as yellow solid in 93% (49.7 mg) yield after column chromatography of the crude reaction mixture (silica gel, gradient 12% EtOAc/Pet.ether).

^1H NMR (400 MHz, CDCl_3) δ 7.35 – 7.30 (m, 4H), 7.26 – 7.22 (m, 1H), 7.10 (t, J = 8 Hz, 2H), 6.65 (t, J = 7.3 Hz, 1H), 6.54 (d, J = 7.6 Hz, 2H), 4.15 (d, J = 6.8 Hz, 2H), 4.04 (dd, J = 11.4, 3.6 Hz, 1H), 3.96 (dd, J = 11.6, 2.9 Hz, 1H), 3.35 (dtd, J = 19.8, 11.8, 2.3 Hz, 2H), 1.95 – 1.78 (m, 2H), 1.49 (dtd, J = 23.5, 11.9, 4.5 Hz, 2H), 1.39 – 1.26 (m, 1H). **^{13}C NMR (101 MHz, CDCl_3)** δ 147.52, 141.93, 129.21, 128.53, 127.20, 117.40, 113.40, 68.11, 67.99, 63.04, 42.36, 30.38, 29.89. **HRMS (ESI-TOF) m/z** calcd. for $\text{C}_{18}\text{H}_{21}\text{NO}$ ($\text{M}+\text{Na}$) $^+$ 290.1521, found 290.1520. **GCMS (EI) m/z** calcd. for $\text{C}_{18}\text{H}_{21}\text{NO}$ [M^+] 267.1, found 267.1, 182.1, 117.1, 104.0, 91.1, 77.1.



***N*-(2-methyl-1-phenylbutyl)aniline (3l):** The title compound was prepared according to the general procedure from *N*-benzylideneaniline (36.2 mg, 0.2 mmol) and 2-bromobutane (43.7 μ L, 0.4 mmol). Pure product was obtained as yellow oil in 73% (35 mg) yield after column chromatography of the crude reaction mixture (silica gel, gradient 1% EtOAc/hexane).

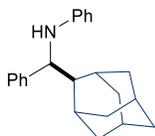
^1H NMR (400 MHz, CDCl_3) δ 7.37 – 7.29 (m, 8H), 7.27 – 7.21 (m, 2H), 7.13 – 7.07 (m, 4H), 6.65 (tdd, J = 7.3, 2.5, 1.2 Hz, 2H), 6.53 (d, J = 7.9 Hz, 4H), 4.35 (d, J = 4.8 Hz, 1H), 4.25 (d, J = 5.8 Hz, 1H), 4.13 (s, 2H), 1.89 – 1.78 (m, 2H), 1.71 – 1.47 (m, 2H), 1.35 – 1.14 (m, 2H), 1.01 – 0.88 (m, 12H). **^{13}C NMR (101 MHz, CDCl_3)** δ 147.85, 143.07, 142.45, 129.17, 128.35, 128.28, 127.43, 127.10, 126.85, 126.72, 117.07, 117.06, 113.28, 113.27, 62.66, 61.56, 41.98, 41.64, 26.96, 25.47, 16.22, 14.53, 12.16, 11.92. d.r. (1:1). **GCMS (EI) m/z** calcd. for $\text{C}_{17}\text{H}_{21}\text{N}$ [M^+] 239.1, found 239.1, 182.1, 104.0, 91.0, 77.0. The analytical data correspond with those reported in the literature.³



***N*-(((1R,2R,4S)-bicyclo[2.2.1]heptan-2-yl)(phenyl)methyl)aniline (3m):** The title compound was prepared according to the general procedure from *N*-benzylideneaniline (36.2 mg, 0.2 mmol)

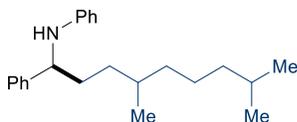
and exo-2-bromonorbornane (51.4 μL , 0.4 mmol). Pure product was obtained as brown oil in 83% (46 mg) yield after column chromatography of the crude reaction mixture (silica gel, gradient 1% EtOAc/hexane).

^1H NMR (400 MHz, CDCl_3) δ 7.42 – 7.28 (m, 8H), 7.28 – 7.19 (m, 2H), 7.14 – 7.04 (m, 4H), 6.63 (m, 2H), 6.54 (m, 4H), 4.24 – 4.07 (m, 2H), 3.90 (d, $J = 10.3$ Hz, 1H), 3.84 (d, $J = 10.1$ Hz, 1H), 2.51 (d, $J = 4.2$ Hz, 1H), 2.34 (d, $J = 4.3$ Hz, 1H), 2.24 (t, $J = 4.3$ Hz, 1H), 1.89 (d, $J = 4.2$ Hz, 1H), 1.81 (td, $J = 9.3, 5.5$ Hz, 1H), 1.74 – 1.37 (m, 8H), 1.35 – 0.98 (m, 9H). **^{13}C NMR (101 MHz, CDCl_3)** δ 148.02, 147.73, 144.37, 142.91, 129.16, 129.11, 128.47, 128.36, 127.73, 127.30, 126.99, 126.96, 117.14, 117.05, 113.34, 113.25, 63.90, 62.47, 50.60, 50.22, 39.25, 38.60, 37.15, 36.74, 36.71, 36.14, 35.70, 35.28, 30.44, 30.22, 28.98, 28.75. d.r. (1:1.2). **HRMS (ESI-TOF)** m/z calcd. for $\text{C}_{20}\text{H}_{23}\text{N}$ ($\text{M}+\text{Na}$) $^+$ 300.1723, found 300.1721. **GCMS (EI)** m/z calcd. for $\text{C}_{20}\text{H}_{23}\text{N}$ [M^+] 277.1, found 277.1, 182.1, 117.0, 104.0, 91.0, 77.0.



***N*-(((1r,3r,5r,7r)-adamantan-2-yl)(phenyl)methyl)aniline (3n)**: The title compound was prepared according to the general procedure from *N*-benzylideneaniline (36.2 mg, 0.2 mmol) and 2-bromoadamantane (86 mg, 0.4 mmol). Pure product was obtained as white solid in 62% (39.3 mg) yield after column chromatography of the crude reaction mixture (silica gel, gradient 2% EtOAc/hexane).

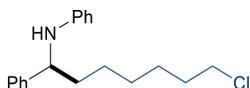
^1H NMR (400 MHz, CDCl_3) δ 7.38 (d, $J = 7.1$ Hz, 2H), 7.32 (t, $J = 7.5$ Hz, 2H), 7.22 (t, $J = 7.2$ Hz, 1H), 7.09 (t, $J = 7.8$ Hz, 2H), 6.66 – 6.58 (m, 3H), 4.59 (d, $J = 10.7$ Hz, 1H), 4.09 (s, 1H), 2.34 (s, 1H), 2.11 – 1.98 (m, 3H), 1.95 – 1.72 (m, 7H), 1.65 – 1.51 (m, 3H), 1.34 (s, 1H). **^{13}C NMR (101 MHz, CDCl_3)** δ 147.89, 143.65, 129.16, 128.48, 127.15, 126.92, 116.92, 113.18, 58.30, 51.67, 39.21, 39.19, 38.22, 32.23, 32.03, 29.17, 28.83, 28.11, 27.86. **HRMS (ESI-TOF)** m/z calcd. for $\text{C}_{23}\text{H}_{27}\text{N}$ ($\text{M}+\text{Na}$) $^+$ 340.2041, found 340.2061. **GCMS (EI)** m/z calcd. for $\text{C}_{23}\text{H}_{27}\text{N}$ [M^+] 317.2, found 317.2, 182.1, 167.1, 152.1, 128.1, 104.0.



***N*-(4,8-dimethyl-1-phenylnonyl)aniline (3o)**: The title compound was prepared according to the general procedure from *N*-benzylideneaniline (36.2 mg, 0.2 mmol) and 1-bromo-3,7-dimethyloctane (83 μL , 0.4 mmol). Pure product was obtained as yellow oil in 42% (27 mg) yield after column chromatography of the crude reaction mixture (silica gel, gradient 1% EtOAc/hexane).

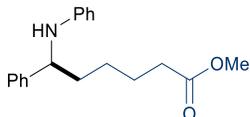
^1H NMR (400 MHz, CDCl_3) δ 7.38 – 7.32 (m, 4H), 7.27 – 7.22 (m, 1H), 7.10 (t, $J = 7.8$ Hz, 2H), 6.66 (t, $J = 7.3$ Hz, 1H), 6.54 (d, $J = 8.0$ Hz, 2H), 4.29 (td, $J = 7.1, 6.6, 1.9$ Hz, 1H), 4.08 (s, 1H),

1.90 – 1.72 (m, 2H), 1.60 – 1.07 (m, 10H), 0.87 – 0.90 (m, 9H). ^{13}C NMR (101 MHz, CDCl_3) δ 147.64, 144.56, 144.46, 129.21, 128.65, 126.98, 126.96, 126.53, 126.47, 117.23, 113.35, 58.78, 58.73, 39.40, 37.24, 37.13, 36.68, 36.57, 33.77, 33.69, 32.88, 32.85, 28.08, 24.84, 22.84, 22.74, 19.79, 19.73. d.r. (1:1). HRMS (ESI-TOF) m/z calcd. for $\text{C}_{23}\text{H}_{33}\text{N}$ ($\text{M}+\text{Na}$) $^+$ 346.2511, found 346.2539. GCMS (EI) m/z calcd. for $\text{C}_{23}\text{H}_{33}\text{N}$ [M^+] 323.2, found 323.2, 280.1, 194.1, 182.1, 167.0, 152.0, 117.0.



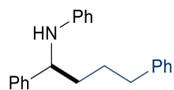
***N*-(7-chloro-1-phenylheptyl)aniline (3p)**: The title compound was prepared according to the general procedure from *N*-benzylideneaniline (36.2 mg, 0.2 mmol) and 1-bromo-6-chlorohexane (59.7 μL , 0.4 mmol). Pure product was obtained as yellow oil in 35% (21 mg) yield after column chromatography of the crude reaction mixture (silica gel, gradient 1% EtOAc/hexane).

^1H NMR (400 MHz, CDCl_3) δ 7.37 – 7.31 (m, 4H), 7.26 – 7.22 (m, 1H), 7.10 (t, $J = 7.7$ Hz, 2H), 6.65 (t, $J = 7.3$ Hz, 1H), 6.53 (d, $J = 8.0$ Hz, 2H), 4.32 (t, $J = 6.8$ Hz, 1H), 4.16 – 4.07 (m, 1H), 3.53 (t, $J = 6.7$ Hz, 2H), 1.87 – 1.72 (m, 4H), 1.48 – 1.33 (m, 6H). ^{13}C NMR (101 MHz, CDCl_3) δ 147.54, 144.28, 129.21, 128.67, 127.03, 126.48, 117.28, 113.34, 58.28, 45.17, 38.91, 32.61, 28.87, 26.83, 26.29. HRMS (ESI-TOF) m/z calcd. for $\text{C}_{19}\text{H}_{24}\text{ClN}$ ($\text{M}+\text{Na}$) $^+$ 324.1495, found 324.1520. GCMS (EI) m/z calcd. for $\text{C}_{19}\text{H}_{24}\text{ClN}$ [M^+] 301.1, found 301.1, 194.1, 182.1, 167.1, 152.1, 128.1, 117.1.



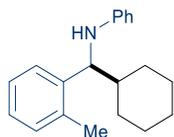
Methyl 6-phenyl-6-(phenylamino)hexanoate (3q): The title compound was prepared according to the general procedure from *N*-benzylideneaniline (36.2 mg, 0.2 mmol) and methyl 5-bromopentanoate (57.2 μL , 0.4 mmol). Pure product was obtained as yellow oil in 44% (26 mg) yield after column chromatography of the crude reaction mixture (silica gel, gradient 14% EtOAc/hexane).

^1H NMR (500 MHz, CDCl_3) δ 7.35 – 7.30 (m, 4H), 7.25 – 7.21 (m, 1H), 7.09 (t, $J = 8.0$ Hz, 2H), 6.64 (td, $J = 7.3, 1.2$ Hz, 1H), 6.52 (d, $J = 8.0$ Hz, 2H), 4.31 (t, $J = 6.8$ Hz, 1H), 4.09 (s, 1H), 3.66 (s, 3H), 2.31 (t, $J = 7.5$ Hz, 2H), 1.88 – 1.76 (m, 2H), 1.67 (p, $J = 7.6$ Hz, 2H), 1.52 – 1.32 (m, 2H). ^{13}C NMR (126 MHz, CDCl_3) δ 174.07, 147.46, 144.10, 129.20, 128.69, 127.06, 126.46, 117.31, 113.35, 58.12, 51.63, 38.61, 33.97, 25.98, 24.89. GCMS (EI) m/z calcd. for $\text{C}_{19}\text{H}_{23}\text{NO}_2$ [M^+] 297.1, found 297.1, 266.1, 194.1, 182.1, 167.1, 129.1, 117.1. The analytical data correspond with those reported in the literature.⁴



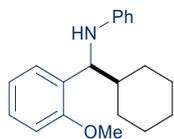
***N*-(1,4-diphenylbutyl)aniline (3r):** The title compound was prepared according to the general procedure from *N*-benzylideneaniline (36.2 mg, 0.2 mmol) and 1-bromo-3-phenylpropane (60.8 μ L, 0.4 mmol). Pure product was obtained as yellow oil in 50% (30 mg) yield after column chromatography of the crude reaction mixture (silica gel, gradient 4% EtOAc/hexane).

^1H NMR (500 MHz, CDCl_3) δ 7.40 – 7.30 (m, 6H), 7.28 – 7.17 (m, 4H), 7.12 (t, $J = 7.7$ Hz, 2H), 6.67 (t, $J = 7.3$ Hz, 1H), 6.54 (d, $J = 8.0$ Hz, 2H), 4.36 (t, $J = 6.6$ Hz, 1H), 4.06 (s, 1H), 2.67 (td, $J = 7.4, 2.8$ Hz, 2H), 1.93 – 1.66 (m, 4H). **^{13}C NMR (126 MHz, CDCl_3)** δ 147.49, 144.13, 142.06, 129.20, 128.68, 128.52, 128.47, 127.04, 126.50, 125.98, 117.29, 113.34, 58.23, 38.41, 35.76, 28.13. **GCMS (EI)** m/z calcd. for $\text{C}_{22}\text{H}_{23}\text{N}$ [M^+] 301.1, found 301.1, 208.1, 194.1, 182.1, 167.1, 152.1, 131.1. The analytical data correspond with those reported in the literature.²



***N*-(cyclohexyl(*o*-tolyl)methyl)aniline (4a):** The title compound was prepared according to the general procedure from *N*-phenyl-1-(*o*-tolyl)methanimine (39 mg, 0.2 mmol) and bromocyclohexane (49.3 μ L, 0.4 mmol). Pure product was obtained as white solid in 70% (39 mg) yield after column chromatography of the crude reaction mixture (silica gel, gradient 5% EtOAc/Pet.ether).

^1H NMR (500 MHz, CDCl_3) δ 7.29 (d, $J = 6.7$ Hz, 1H), 7.17 – 7.05 (m, 5H), 6.61 (t, $J = 7.0$ Hz, 1H), 6.46 (d, $J = 8.0$ Hz, 2H), 4.39 (d, $J = 6.1$ Hz, 1H), 4.13 (s, 1H), 2.46 (s, 3H), 1.93 (d, $J = 12.1$ Hz, 1H), 1.81 – 1.54 (m, 5H), 1.29 – 1.08 (m, 5H). **^{13}C NMR (126 MHz, CDCl_3)** δ 148.02, 141.05, 135.33, 130.61, 129.22, 126.48, 126.45, 126.15, 116.97, 113.02, 59.30, 44.40, 30.81, 28.85, 26.73, 26.62, 26.61, 19.72. **HRMS (ESI-TOF)** m/z calcd. for $\text{C}_{20}\text{H}_{25}\text{N}$ ($\text{M}+\text{Na}$)⁺ 302.1885, found 302.1908. **GCMS (EI)** m/z calcd. for $\text{C}_{20}\text{H}_{25}\text{N}$ [M^+] 279.2, found 279.2, 196.2, 180.1, 104.1, 91.1, 77.1.



***N*-(cyclohexyl(2-methoxyphenyl)methyl)aniline (4b):** The title compound was prepared according to the general procedure from 1-(2-methoxyphenyl)-*N*-phenylmethanimine (42.2 mg, 0.2 mmol) and bromocyclohexane (49.3 μ L, 0.4 mmol). Pure product was obtained as white solid

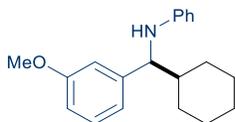
in 72% (42.5 mg) yield after column chromatography of the crude reaction mixture (silica gel, gradient 5% EtOAc/Pet.ether).

¹H NMR (500 MHz, CDCl₃) δ 7.22 – 7.16 (m, 2H), 7.06 (t, *J* = 8 Hz, 2H), 6.89 – 6.86 (m, 2H), 6.59 (t, *J* = 7.3 Hz, 1H), 6.54 (d, *J* = 7.4 Hz, 2H), 4.53 (d, *J* = 7.3 Hz, 1H), 4.29 (s, 1H), 3.89 (s, 3H), 2.00 (d, *J* = 12.6 Hz, 1H), 1.80 – 1.64 (m, 4H), 1.46 (d, *J* = 12.0 Hz, 1H), 1.27 – 1.03 (m, 5H). **¹³C NMR (126 MHz, CDCl₃)** δ 157.43, 148.22, 130.87, 129.14, 128.25, 127.64, 120.56, 116.70, 113.12, 110.60, 57.83, 55.50, 43.45, 30.49, 29.84, 26.68, 26.56, 26.51. **HRMS (ESI-TOF)** *m/z* calcd. for C₂₀H₂₅NO (M+Na)⁺ 318.1834, found 318.1861. **GCMS (EI)** *m/z* calcd. for C₂₀H₂₅NO [M⁺] 295.1, found 295.2, 212.1, 196.1, 180.1, 121.1, 115.1, 104.1, 91.1, 77.1.



***N*-(cyclohexyl(2-fluorophenyl)methyl)aniline (4c)**: The title compound was prepared according to the general procedure from 1-(2-fluorophenyl)-*N*-phenylmethanimine (39.8 mg, 0.2 mmol) and bromocyclohexane (49.3 μL, 0.4 mmol). Pure product was obtained as white solid in 77% (43.6 mg) yield after column chromatography of the crude reaction mixture (silica gel, gradient 5% EtOAc/Pet.ether).

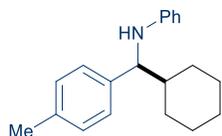
¹H NMR (500 MHz, CDCl₃) δ 7.29 – 7.24 (m, 1H), 7.10 – 7.06 (m, 3H), 7.02 (d, *J* = 10.0 Hz, 1H), 6.91 (td, *J* = 8.4, 2.6 Hz, 1H), 6.64 (t, *J* = 7.3 Hz, 1H), 6.49 (d, *J* = 8.0 Hz, 2H), 4.14 (s, 1H), 4.12 (d, *J* = 6.1 Hz, 1H), 1.88 (d, *J* = 12.8 Hz, 1H), 1.81 – 1.72 (m, 2H), 1.68 – 1.61 (m, 2H), 1.55 (d, *J* = 13.0 Hz, 1H), 1.29 – 1.02 (m, 5H). **¹³C NMR (126 MHz, CDCl₃)** δ 163.16 (d, *J* = 245.6 Hz), 147.60, 145.87 (d, *J* = 6.1 Hz), 129.73 (d, *J* = 8.2 Hz), 129.23, 123.05 (d, *J* = 2.8 Hz), 117.35, 114.10 (d, *J* = 21.3 Hz), 113.80 (d, *J* = 21.3 Hz), 113.27, 63.21, 44.94, 30.32, 29.47, 26.49, 26.45, 26.43. **¹⁹F NMR (471 MHz, CDCl₃)** δ -113.43. **HRMS (ESI-TOF)** *m/z* calcd. for C₁₉H₂₂FN (M+Na)⁺ 306.1628, found 306.1608. **GCMS (EI)** *m/z* calcd. for C₁₉H₂₂FN [M⁺] 283.1, found 283.1, 200.2, 185.1, 180.1, 170.1, 152.1, 146.1, 133.1.



***N*-(cyclohexyl(3-methoxyphenyl)methyl)aniline (4d)**: The title compound was prepared according to the general procedure from 1-(3-methoxyphenyl)-*N*-phenylmethanimine (42.2 mg, 0.2 mmol) and bromocyclohexane (49.3 μL, 0.4 mmol). Pure product was obtained as yellow oil in 78% (46 mg) yield after column chromatography of the crude reaction mixture (silica gel, gradient 5% EtOAc/Pet.ether).

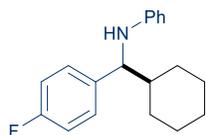
¹H NMR (500 MHz, CDCl₃) δ 7.22 (t, *J* = 7.9 Hz, 1H), 7.07 (t, *J* = 7.9 Hz, 2H), 6.90 (d, *J* = 7.6 Hz, 1H), 6.86 (s, 1H), 6.76 (dd, *J* = 8.2, 2.6 Hz, 1H), 6.61 (t, *J* = 7.3 Hz, 1H), 6.51 (d, *J* = 8.4 Hz,

2H), 4.14 (s, 1H), 4.09 (d, $J = 6.3$ Hz, 1H), 3.79 (s, 3H), 1.90 (d, $J = 12.5$ Hz, 1H), 1.80 – 1.61 (m, 4H), 1.55 (d, $J = 12.5$ Hz, 1H), 1.28 – 1.02 (m, 5H). ^{13}C NMR (126 MHz, CDCl_3) δ 159.70, 147.93, 144.72, 129.23, 129.16, 119.87, 117.06, 113.32, 113.28, 111.73, 63.54, 55.26, 44.98, 30.42, 29.61, 26.55, 26.52, 26.49. HRMS (ESI-TOF) m/z calcd. for $\text{C}_{20}\text{H}_{25}\text{NO}$ ($\text{M}+\text{Na}$) $^+$ 318.1834, found 318.1851. GCMS (EI) m/z calcd. for $\text{C}_{20}\text{H}_{25}\text{NO}$ [M^+] 295.1, found 295.2, 212.1, 168.1, 121.1, 104.1, 91.1, 77.1.



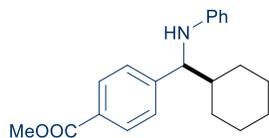
***N*-(cyclohexyl(*p*-tolyl)methyl)aniline (4e):** The title compound was prepared according to the general procedure from *N*-phenyl-1-(*p*-tolyl)methanimine (39 mg, 0.2 mmol) and bromocyclohexane (49.3 μL , 0.4 mmol). Pure product was obtained as yellow oil in 69% (38.5 mg) yield after column chromatography of the crude reaction mixture (silica gel, gradient 5% EtOAc/Pet.ether).

^1H NMR (400 MHz, CDCl_3) δ 7.19 (d, $J = 7.9$ Hz, 2H), 7.09 (dd, $J = 20.0, 7.8$ Hz, 4H), 6.61 (t, $J = 7.3$ Hz, 1H), 6.52 (d, $J = 8.0$ Hz, 2H), 4.15 (s, 1H), 4.11 (d, $J = 6.3$ Hz, 1H), 2.33 (s, 3H), 1.94 – 1.89 (m, 1H), 1.80 – 1.55 (m, 5H), 1.29 – 1.01 (m, 5H). ^{13}C NMR (101 MHz, CDCl_3) δ 147.98, 139.69, 136.29, 129.15, 129.01, 127.23, 116.94, 113.27, 63.21, 45.04, 30.35, 29.62, 26.57, 26.53, 26.49, 21.21. GCMS (EI) m/z calcd. for $\text{C}_{20}\text{H}_{25}\text{N}$ [M^+] 279.2, found 279.1, 196.1, 180.1, 165.1, 152.1, 128.1. The analytical data correspond with those reported in the literature.⁵



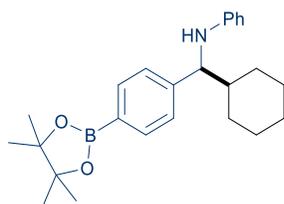
***N*-(cyclohexyl(4-fluorophenyl)methyl)aniline (4f):** The title compound was prepared according to the general procedure from 1-(4-fluorophenyl)-*N*-phenylmethanimine (39.8 mg, 0.2 mmol) and bromocyclohexane (49.3 μL , 0.4 mmol). Pure product was obtained as yellow oil in 67% (38 mg) yield after column chromatography of the crude reaction mixture (silica gel, gradient 5% EtOAc/Pet.ether).

^1H NMR (500 MHz, CDCl_3) δ 7.28 – 7.23 (m, 2H), 7.08 (t, $J = 7.5$ Hz, 2H), 6.99 (t, $J = 8.7$ Hz, 2H), 6.63 (t, $J = 7.3$ Hz, 1H), 6.48 (d, $J = 8.0$ Hz, 2H), 4.13 (s, 1H), 4.11 (d, $J = 6.2$ Hz, 1H), 1.88 (d, $J = 12.5$ Hz, 1H), 1.81 – 1.59 (m, 4H), 1.54 (d, $J = 13.4$ Hz, 1H), 1.26 – 0.99 (m, 5H). ^{13}C NMR (126 MHz, CDCl_3) δ 161.86 (d, $J = 244.3$ Hz), 147.68, 138.37 (d, $J = 3.2$ Hz), 129.20, 128.71 (d, $J = 7.9$ Hz), 117.25, 115.15 (d, $J = 21.3$ Hz), 113.30, 62.91, 45.08, 30.23, 29.56, 26.52, 26.47, 26.43. ^{19}F NMR (471 MHz, CDCl_3) δ -116.41. GCMS (EI) m/z calcd. for $\text{C}_{19}\text{H}_{22}\text{FN}$ [M^+] 283.1, found 283.1, 200.2, 185.1, 170.1, 152.1, 146.1, 133.1. The analytical data correspond with those reported in the literature.⁶



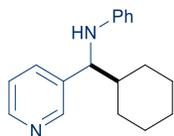
Methyl 4-(cyclohexyl(phenylamino)methyl)benzoate (4g): The title compound was prepared according to the general procedure from methyl-4-((phenylimino)methyl)benzoate (47.8 mg, 0.2 mmol) and bromocyclohexane (49.3 μ L, 0.4 mmol). Pure product was obtained as yellow solid in 94% (60.8 mg) yield after column chromatography of the crude reaction mixture (silica gel, gradient 5% EtOAc/Pet.ether).

^1H NMR (500 MHz, CDCl_3) δ 7.99 (d, J = 8.4 Hz, 2H), 7.39 (d, J = 8.1 Hz, 2H), 7.07 (t, J = 7.9 Hz, 2H), 6.63 (t, J = 7.3 Hz, 1H), 6.48 (d, J = 8.7 Hz, 2H), 4.20 (s, 1H), 4.18 (s, 1H), 3.90 (s, 3H), 1.87 (d, J = 11.8 Hz, 1H), 1.79 – 1.64 (m, 4H), 1.54 (d, J = 13.9 Hz, 1H), 1.26 – 1.02 (m, 5H). **^{13}C NMR (126 MHz, CDCl_3)** δ 167.14, 148.47, 147.49, 129.70, 129.19, 128.90, 127.38, 117.37, 113.26, 63.40, 52.10, 44.88, 30.28, 29.44, 26.44, 26.42, 26.39. **GCMS (EI)** m/z calcd. for $\text{C}_{21}\text{H}_{25}\text{NO}_2$ [M^+] 323.1, found 323.2, 292.1, 240.2, 209.1, 181.1, 149.1, 141.1. The analytical data correspond with those reported in the literature.⁵



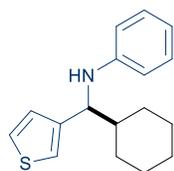
***N*-(cyclohexyl(4-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)phenyl)methyl)aniline (4h):** The title compound was prepared according to the general procedure from *N*-phenyl-1-(4-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)phenyl)methanimine (61.4 mg, 0.2 mmol) and bromocyclohexane (49.3 μ L, 0.4 mmol). Pure product was obtained as yellow solid in 74% (58 mg) yield after column chromatography of the crude reaction mixture (silica gel, gradient 8% EtOAc/Pet.ether).

^1H NMR (400 MHz, CDCl_3) δ 7.75 (d, J = 7.7 Hz, 2H), 7.30 (d, J = 7.7 Hz, 2H), 7.03 (t, J = 7.1 Hz, 2H), 6.59 (t, J = 7.3 Hz, 1H), 6.48 (d, J = 8.0 Hz, 2H), 4.17 (s, 1H), 4.13 (d, J = 6.2 Hz, 1H), 1.87 (d, J = 11.6 Hz, 1H), 1.80 – 1.47 (m, 5H), 1.33 (s, 12H), 1.24 – 0.98 (m, 5H). **^{13}C NMR (101 MHz, CDCl_3)** δ 147.80, 146.24, 134.83, 129.16, 126.83, 117.10, 113.31, 83.81, 63.64, 44.98, 30.35, 29.54, 26.52, 26.47, 25.06, 24.99. The carbon directly attached to boron atoms is not detected due to quadrupolar broadening. **HRMS (ESI-TOF)** m/z calcd. for $\text{C}_{25}\text{H}_{34}\text{BNO}_2$ ($\text{M}+\text{Na}^+$) 414.2580, found 414.2588. **GCMS (EI)** m/z calcd. for $\text{C}_{25}\text{H}_{34}\text{BNO}_2$ [M^+] 391.2, found 391.3, 308.2, 208.1, 146.6, 104.1, 77.1.



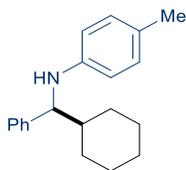
***N*-(cyclohexyl(pyridin-3-yl)methyl)aniline (4i)**: The title compound was prepared according to the general procedure from *N*-phenyl-1-(pyridin-3-yl)methanimine (37.6 mg, 0.2 mmol) and bromocyclohexane (49.3 μ L, 0.4 mmol). Pure product was obtained as white solid in 42% (22.3 mg) yield after column chromatography of the crude reaction mixture (silica gel, gradient 37% EtOAc/Pet.ether).

^1H NMR (500 MHz, CDCl_3) δ 8.58 (s, 1H), 8.48 (d, $J = 6.4$ Hz, 1H), 7.61 (dt, $J = 7.9, 2.0$ Hz, 1H), 7.21 (dd, $J = 7.8, 4.8$ Hz, 1H), 7.09 – 7.05 (m, 2H), 6.64 (t, $J = 7.4$ Hz, 1H), 6.48 (d, $J = 8.0$ Hz, 2H), 4.18 (bs, 2H), 1.89 (d, $J = 12.7$ Hz, 1H), 1.80 – 1.65 (m, 4H), 1.56 (d, $J = 12.8$ Hz, 1H), 1.27 – 1.00 (m, 5H). **^{13}C NMR (126 MHz, CDCl_3)** δ 149.46, 148.46, 147.26, 138.08, 134.75, 129.25, 123.43, 117.54, 113.28, 61.28, 44.79, 30.06, 29.45, 26.38, 26.32, 26.28. **HRMS (ESI-TOF)** m/z calcd. for $\text{C}_{18}\text{H}_{22}\text{N}_2$ ($\text{M}+\text{Na}$) $^+$ 289.1675, found 289.1667. **GCMS (EI)** m/z calcd. for $\text{C}_{18}\text{H}_{22}\text{N}_2$ [M^+] 266.1, found 266.1, 207.1, 183.2, 174.1, 166.1, 154.1, 130.1.



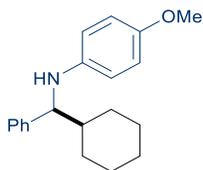
***N*-(cyclohexyl(thiophen-3-yl)methyl)aniline (4j)**: The title compound was prepared according to the general procedure from *N*-phenyl-1-(thiophen-3-yl)methanimine (37.4 mg, 0.2 mmol) and bromocyclohexane (49.3 μ L, 0.4 mmol). Pure product was obtained as yellow solid in 69% (37.4 mg) yield after column chromatography of the crude reaction mixture (silica gel, gradient 4% EtOAc/Pet.ether).

^1H NMR (500 MHz, CDCl_3) δ 7.16 (d, $J = 5.1$ Hz, 1H), 7.13 (t, $J = 7.7$ Hz, 2H), 6.95 – 6.93 (m, 2H), 6.68 (t, $J = 7.3$ Hz, 1H), 6.61 (d, $J = 8.0$ Hz, 2H), 4.45 (d, $J = 6.2$ Hz, 1H), 4.08 (s, 1H), 1.97 – 1.93 (m, 1H), 1.87 – 1.64 (m, 5H), 1.32 – 1.07 (m, 5H). **^{13}C NMR (126 MHz, CDCl_3)** δ 148.12, 147.72, 129.24, 126.62, 124.31, 123.64, 117.64, 113.43, 59.57, 45.40, 30.14, 29.60, 26.50, 26.41, 26.36. **HRMS (ESI-TOF)** m/z calcd. for $\text{C}_{17}\text{H}_{21}\text{NS}$ ($\text{M}+\text{Na}$) $^+$ 294.1292, found 294.1295. **GCMS (EI)** m/z calcd. for $\text{C}_{17}\text{H}_{21}\text{NS}$ [M^+] 271.1, found 271.1, 188.1, 179.1, 154.1, 135.0, 128.1.



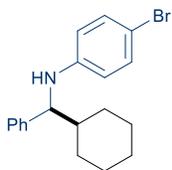
***N*-(cyclohexyl(phenyl)methyl)-4-methylaniline (4k):** The title compound was prepared according to the general procedure from 1-phenyl-*N*-(*p*-tolyl)methanimine (39 mg, 0.2 mmol) and bromocyclohexane (49.3 μ L, 0.4 mmol). Pure product was obtained as yellow solid in 63% (35.2 mg) yield after column chromatography of the crude reaction mixture (silica gel, gradient 4% EtOAc/Pet.ether).

^1H NMR (500 MHz, CDCl_3) δ 7.33 – 7.31 (m, 4H), 7.23 (h, $J = 4.1$ Hz, 1H), 6.90 (d, $J = 8.1$ Hz, 2H), 6.45 (d, $J = 8.4$ Hz, 2H), 4.12 (d, $J = 6.2$ Hz, 1H), 4.06 (s, 1H), 2.19 (s, 3H), 1.91 (d, $J = 12.9$ Hz, 1H), 1.81 – 1.63 (m, 4H), 1.57 (d, $J = 12.7$ Hz, 1H) 1.28 – 1.03 (m, 5H). **^{13}C NMR (126 MHz, CDCl_3)** δ 145.65, 142.98, 129.67, 128.27, 127.35, 126.77, 126.12, 113.36, 63.76, 45.05, 30.37, 29.54, 26.57, 26.53, 26.50, 20.43. **GCMS (EI)** m/z calcd. for $\text{C}_{20}\text{H}_{25}\text{N}$ [M^+] 279.2, found 279.1, 196.1, 180.1, 165.1, 152.1, 141.1. The analytical data correspond with those reported in the literature.⁷



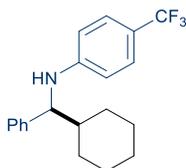
***N*-(cyclohexyl(phenyl)methyl)-4-methoxyaniline (4l):** The title compound was prepared according to the general procedure from *N*-(4-methoxyphenyl)-1-phenylmethanimine (42.3 mg, 0.2 mmol) and bromocyclohexane (49.3 μ L, 0.4 mmol). Pure product was obtained as brown oil in 66% (39 mg) yield after column chromatography of the crude reaction mixture (silica gel, gradient 3% EtOAc/Pet.ether).

^1H NMR (400 MHz, CDCl_3) δ 7.34 – 7.30 (m, 4H), 7.27 – 7.21 (m, 1H), 6.70 (d, $J = 8.9$ Hz, 2H), 6.48 (d, $J = 8.9$ Hz, 2H), 4.08 (d, $J = 6.2$ Hz, 1H), 3.94 (s, 1H), 3.70 (s, 3H), 1.93 (d, $J = 11.9$ Hz, 1H), 1.82 – 1.63 (m, 4H), 1.57 (d, $J = 12.3$ Hz, 1H), 1.30 – 1.00 (m, 5H). **^{13}C NMR (101 MHz, CDCl_3)** δ 151.75, 142.99, 142.21, 128.24, 127.38, 126.77, 114.84, 114.41, 64.39, 55.84, 45.05, 30.31, 29.62, 26.55, 26.52, 26.48. **GCMS (EI)** m/z calcd. for $\text{C}_{20}\text{H}_{25}\text{NO}$ [M^+] 295.1, found 295.1, 212.2, 197.1, 168.1, 134.1, 122.1, 108.1. The analytical data correspond with those reported in the literature.⁸



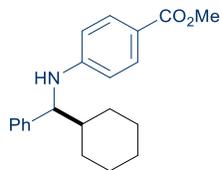
4-Bromo-*N*-(cyclohexyl(phenyl)methyl)aniline (4m): The title compound was prepared according to the general procedure from *N*-(4-bromophenyl)-1-phenylmethanimine (52 mg, 0.2 mmol) and bromocyclohexane (49.3 μ L, 0.4 mmol). Pure product was obtained as yellow oil in 54% (37.1 mg) yield after column chromatography of the crude reaction mixture (silica gel, gradient 3% EtOAc/Pet.ether).

^1H NMR (400 MHz, CDCl_3) δ 7.32 – 7.20 (m, 5H), 7.13 (d, J = 8.8 Hz, 2H), 6.37 (d, J = 8.8 Hz, 2H), 4.19 (s, 1H), 4.06 (d, J = 6.3 Hz, 1H), 1.88 (d, J = 11.9 Hz, 1H), 1.79 – 1.60 (m, 4H), 1.55 – 1.50 (m, 1H), 1.30 – 0.96 (m, 5H). **^{13}C NMR (101 MHz, CDCl_3)** δ 146.78, 142.13, 131.83, 128.39, 127.27, 127.05, 114.87, 108.62, 63.56, 44.91, 30.29, 29.59, 26.50, 26.45, 26.42. **GCMS (EI) m/z** calcd. for $\text{C}_{19}\text{H}_{22}\text{BrN}$ [M^+] 343.0, found 345.1, 343.1, 262.1, 260.1, 182.0, 180.1, 171.1, 155.0, 115.1, 104.1. The analytical data correspond with those reported in the literature.⁹



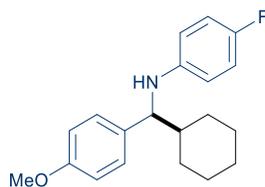
***N*-(cyclohexyl(phenyl)methyl)-4-(trifluoromethyl)aniline (4n):** The title compound was prepared according to the general procedure from 1-phenyl-*N*-(4-(trifluoromethyl)phenyl)methanimine (49.8 mg, 0.2 mmol) and bromocyclohexane (49.3 μ L, 0.4 mmol). Pure product was obtained as yellow oil in 70% (46.6 mg) yield after column chromatography of the crude reaction mixture (silica gel, gradient 4% EtOAc/Pet.ether).

^1H NMR (500 MHz, CDCl_3) δ 7.34 – 7.23 (m, 7H), 6.52 (d, J = 8.5 Hz, 2H), 4.50 (s, 1H), 4.16 (d, J = 6.4 Hz, 1H), 1.91 (d, J = 12.3 Hz, 1H), 1.81 – 1.64 (m, 4H), 1.54 (d, J = 14.4 Hz, 1H), 1.30 – 1.02 (m, 5H). **^{13}C NMR (126 MHz, CDCl_3)** δ 150.24, 141.79, 128.50, 127.23, 127.21, 126.55 (q, J = 3.78 Hz), 125.12 (q, $J_{\text{C-F}}$ = 270.9 Hz), 118.57 (q, J = 32.76 Hz), 112.44, 63.23, 44.83, 30.29, 29.60, 26.46, 26.41, 26.38. **^{19}F NMR (471 MHz, CDCl_3)** δ -61.03. **HRMS (ESI-TOF) m/z** calcd. for $\text{C}_{20}\text{H}_{22}\text{F}_3\text{N}$ ($\text{M}+\text{Na}$)⁺ 356.1602, found 356.1625. **GCMS (EI) m/z** calcd. for $\text{C}_{20}\text{H}_{22}\text{F}_3\text{N}$ [M^+] 333.1, found 333.2, 314.2, 250.0, 231.1, 180.1, 172.0.



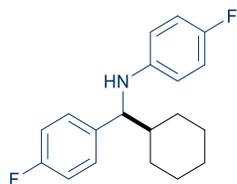
Methyl 4-((cyclohexyl(phenyl)methyl)amino)benzoate (4o): The title compound was prepared according to the general procedure from methyl-4-(benzylideneamino)benzoate (47.8 mg, 0.2 mmol) and bromocyclohexane (49.3 μ L, 0.4 mmol). Pure product was obtained as white solid in 83% (53.7 mg) yield after column chromatography of the crude reaction mixture (silica gel, gradient 15% EtOAc/Pet.ether).

^1H NMR (500 MHz, CDCl_3) δ 7.76 (d, J = 8.8 Hz, 2H), 7.32 – 7.20 (m, 5H), 6.47 (d, J = 8.8 Hz, 2H), 4.64 (s, 1H), 4.18 (t, J = 6.0 Hz, 1H), 3.81 (s, 3H), 1.90 (d, J = 12.8 Hz, 1H), 1.80 – 1.64 (m, 4H), 1.53 (d, J = 12.8 Hz, 1H), 1.27 – 0.99 (m, 5H). **^{13}C NMR (126 MHz, CDCl_3)** δ 167.40, 151.55, 141.72, 131.47, 128.46, 127.20, 127.17, 118.23, 112.18, 63.06, 51.57, 44.75, 30.25, 29.59, 26.43, 26.37, 26.34. **HRMS (ESI-TOF)** m/z calcd. for $\text{C}_{21}\text{H}_{25}\text{NO}_2$ ($\text{M}+\text{Na}$) $^+$ 346.1783, found 346.1832. **GCMS (EI)** m/z calcd. for $\text{C}_{21}\text{H}_{25}\text{NO}_2$ [M^+] 323.1, found 323.2, 292.2, 240.1, 181.1, 135.1, 91.1, 77.1.



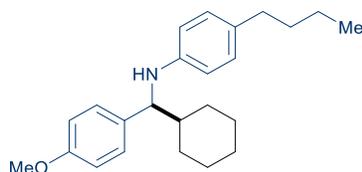
***N*-(cyclohexyl(4-methoxyphenyl)methyl)-4-fluoroaniline (4p):** The title compound was prepared according to the general procedure from *N*-(4-fluorophenyl)-1-(4-methoxyphenyl)methanimine (45.8 mg, 0.2 mmol) and bromocyclohexane (49.3 μ L, 0.4 mmol). Pure product was obtained as yellow oil in 51% (32 mg) yield after column chromatography of the crude reaction mixture (silica gel, gradient 5% EtOAc/Pet.ether).

^1H NMR (500 MHz, CDCl_3) δ 7.17 (d, J = 8.7 Hz, 2H), 6.84 (d, J = 8.6 Hz, 2H), 6.76 (t, J = 8.8 Hz, 2H), 6.43 – 6.39 (m, 2H), 4.00 – 3.98 (m, 2H), 3.78 (s, 3H), 1.91 – 1.86 (m, 1H), 1.79 – 1.69 (m, 2H), 1.68 – 1.51 (m, 3H), 1.28 – 0.96 (m, 5H). **^{13}C NMR (126 MHz, CDCl_3)** δ 158.56, 155.59 (d, J = 234.3 Hz), 144.32, 134.48, 128.30, 115.53 (d, J = 22.1 Hz), 114.03 (d, J = 7.4 Hz), 113.73, 63.61, 55.31, 45.13, 30.19, 29.77, 26.56, 26.50, 26.46. **^{19}F NMR (471 MHz, CDCl_3)** δ -128.86. **GCMS (EI)** m/z calcd. for $\text{C}_{20}\text{H}_{24}\text{FNO}$ [M^+] 313.1, found 313.2, 230.1, 202.2, 186.1, 134.1, 121.1, 111.1, 95.1, 77.1. The analytical data correspond with those reported in the literature.¹⁰



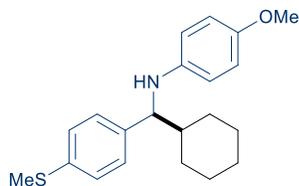
***N*-(cyclohexyl(4-fluorophenyl)methyl)-4-fluoroaniline (4q):** The title compound was prepared according to the general procedure from *N*-1-bis(4-fluorophenyl)methanimine (43.4 mg, 0.2 mmol) and bromocyclohexane (49.3 μ L, 0.4 mmol). Pure product was obtained as yellow oil in 58% (35 mg) yield after column chromatography of the crude reaction mixture (silica gel, gradient 5% EtOAc/Pet.ether).

^1H NMR (500 MHz, CDCl_3) δ 7.25 – 7.22 (m, 2H), 6.99 (t, J = 8.7 Hz, 2H), 6.80 – 6.75 (t, J = 8.7 Hz, 2H), 6.42 – 6.37 (m, 2H), 4.04 (s, 1H), 4.03 (s, 1H), 1.89 – 1.86 (m, 1H), 1.81 – 1.71 (m, 2H), 1.69 – 1.57 (m, 2H), 1.53 (m, 1H), 1.28 – 0.97 (m, 5H). **^{13}C NMR (126 MHz, CDCl_3)** δ 161.89 (d, J = 244.6 Hz), 155.71 (d, J = 234.6 Hz), 144.04 (d, J = 2.0 Hz), 138.14 (d, J = 3.1 Hz), 128.72 (d, J = 7.8 Hz), 115.60 (d, J = 22.1 Hz), 115.21 (d, J = 21.3 Hz), 114.04 (d, J = 7.3 Hz), 63.58, 45.06, 30.16, 29.61, 26.49, 26.44, 26.40. **HRMS (ESI-TOF)** m/z calcd. for $\text{C}_{19}\text{H}_{21}\text{F}_2\text{N}$ ($\text{M}+\text{Na}$) $^+$ 324.1540, found 324.1563. **GCMS (EI)** m/z calcd. for $\text{C}_{19}\text{H}_{21}\text{F}_2\text{N}$ [M^+] 301.1, found 301.1, 218.1, 170.0, 146.1, 133.0, 122.0, 109.0.



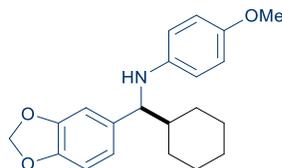
4-Butyl-*N*-(cyclohexyl(4-methoxyphenyl)methyl)aniline (4r): The title compound was prepared according to the general procedure from *N*-(4-butylphenyl)-1-(4-methoxyphenyl)methanimine (53.4 mg, 0.2 mmol) and bromocyclohexane (49.3 μ L, 0.4 mmol). Pure product was obtained as yellow oil in 50% (35 mg) yield after column chromatography of the crude reaction mixture (silica gel, gradient 1% EtOAc/Pet.ether).

^1H NMR (400 MHz, CDCl_3) δ 7.22 (d, J = 8.6 Hz, 2H), 6.90 (d, J = 8.4 Hz, 2H), 6.86 (d, J = 8.6 Hz, 2H), 6.45 (d, J = 8.4 Hz, 2H), 4.06 (d, J = 6.1 Hz, 1H), 4.03 (s, 1H), 3.80 (s, 3H), 2.45 (t, J = 8 Hz, 2H), 1.90 (d, J = 12.5 Hz, 1H), 1.80 – 1.48 (m, 7H), 1.33 (h, J = 7.3 Hz, 2H), 1.27 – 0.99 (m, 5H), 0.91 (t, J = 7.3 Hz, 3H). **^{13}C NMR (101 MHz, CDCl_3)** δ 158.40, 145.90, 135.00, 131.31, 129.00, 128.29, 113.63, 113.25, 63.17, 55.28, 45.17, 34.79, 34.09, 30.25, 29.69, 26.58, 26.54, 26.50, 22.48, 14.12. **HRMS (ESI-TOF)** m/z calcd. for $\text{C}_{24}\text{H}_{33}\text{NO}$ ($\text{M}+\text{Na}$) $^+$ 374.2460, found 374.2489. **GCMS (EI)** m/z calcd. for $\text{C}_{24}\text{H}_{33}\text{NO}$ [M^+] 351.2, found 351.3, 268.1, 238.2, 225.1, 210.1, 160.1, 121.1, 106.1.



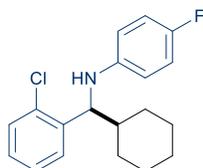
***N*-(cyclohexyl(4-(methylthio)phenyl)methyl)-4-methoxyaniline (4s):** The title compound was prepared according to the general procedure from *N*-(4-methoxyphenyl)-1-(4-(methylthio)phenyl)methanimine (51.4 mg, 0.2 mmol) and bromocyclohexane (49.3 μ L, 0.4 mmol). Pure product was obtained as brown oil in 54% (36.8 mg) yield after column chromatography of the crude reaction mixture (silica gel, gradient 13% EtOAc/Pet.ether).

^1H NMR (500 MHz, CDCl_3) δ 7.23 – 7.18 (m, 4H), 6.68 (d, J = 8.9 Hz, 2H), 6.45 (d, J = 8.9 Hz, 2H), 4.02 (d, J = 6.1 Hz, 1H), 3.89 (s, 1H), 3.69 (s, 3H), 2.47 (s, 3H), 1.88 (d, J = 12.8 Hz, 1H), 1.79 – 1.70 (m, 2H), 1.68 – 1.54 (m, 3H), 1.27 – 0.99 (m, 5H). **^{13}C NMR (126 MHz, CDCl_3)** δ 151.82, 142.10, 140.06, 136.32, 127.92, 126.62, 114.85, 114.43, 63.94, 55.85, 45.03, 30.20, 29.60, 26.53, 26.49, 26.45, 16.02. **GCMS (EI)** m/z calcd. for $\text{C}_{21}\text{H}_{27}\text{NOS}$ [M^+] 341.1, found 341.2, 258.1, 243.1, 218.1, 137.1, 122.0, 108.1, 77.1. The analytical data correspond with those reported in the literature.¹⁰



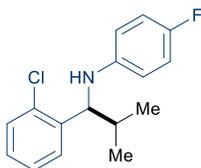
***N*-(benzo[d][1,3]dioxol-5-yl(cyclohexyl)methyl)-4-methoxyaniline (4t):** The title compound was prepared according to the general procedure from 1-(benzo[d][1,3]dioxol-5-yl)-*N*-(4-methoxyphenyl)methanimine (51 mg, 0.2 mmol) and bromocyclohexane (49.3 μ L, 0.4 mmol). Pure product was obtained as brown oil in 51% (34.6 mg) yield after column chromatography of the crude reaction mixture (silica gel, gradient 10% EtOAc/Pet.ether).

^1H NMR (500 MHz, CDCl_3) δ 6.79 (s, 1H), 6.74 (s, 2H), 6.69 (d, J = 8.9 Hz, 2H), 6.46 (d, J = 8.9 Hz, 2H), 5.92 (dd, J = 9.1, 1.5 Hz, 2H), 3.95 (d, J = 6.2 Hz, 1H), 3.85 (s, 1H), 3.69 (s, 3H), 1.90 (d, J = 12.3 Hz, 1H), 1.79 – 1.71 (m, 2H), 1.68 – 1.64 (m, 1H), 1.61 – 1.51 (m, 2H), 1.28 – 0.97 (m, 5H). **^{13}C NMR (126 MHz, CDCl_3)** δ 151.83, 147.77, 146.34, 142.16, 137.17, 120.60, 114.86, 114.44, 107.96, 107.53, 100.94, 64.20, 55.88, 45.16, 30.26, 29.81, 26.56, 26.51, 26.47. **GCMS (EI)** m/z calcd. for $\text{C}_{21}\text{H}_{25}\text{NO}_3$ [M^+] 339.1, found 339.2, 256.1, 216.1, 135.1, 108.1, 77.1. The analytical data correspond with those reported in the literature.¹⁰



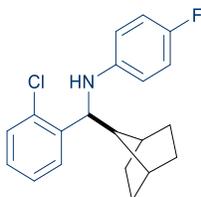
***N*-(2-chlorophenyl)(cyclohexyl)methyl)-4-fluoroaniline (4u):** The title compound was prepared according to the general procedure from 1-(2-chlorophenyl)-*N*-(4-fluorophenyl)methanimine (46.7 mg, 0.2 mmol) and bromocyclohexane (49.3 μ L, 0.4 mmol). Pure product was obtained as brown oil in 93% (59 mg) yield after column chromatography of the crude reaction mixture (silica gel, gradient 3% EtOAc/Pet.ether).

^1H NMR (400 MHz, CDCl_3) δ 7.37 (d, $J = 7.5$ Hz, 1H), 7.32 (d, $J = 7.4$ Hz, 1H), 7.26 – 7.14 (m, 2H), 6.81 (t, $J = 8.7$ Hz, 2H), 6.46 – 6.41 (m, 2H), 4.62 (d, $J = 6.4$ Hz, 1H), 4.12 (s, 1H), 1.94 (d, $J = 12.3$ Hz, 1H), 1.83 – 1.69 (m, 4H), 1.57 – 1.53 (m, 1H), 1.31 – 1.07 (m, 5H). **^{13}C NMR (101 MHz, CDCl_3)** δ 155.70 (d, $J = 234.6$ Hz), 143.77, 140.03, 133.69, 129.71, 128.35, 128.05, 126.97, 115.64 (d, $J = 22.3$ Hz), 113.83 (d, $J = 7.3$ Hz), 59.99, 43.85, 30.29, 28.93, 26.55, 26.50, 26.44. **HRMS (ESI-TOF)** m/z calcd. for $\text{C}_{19}\text{H}_{21}\text{ClFN}$ ($\text{M}+\text{Na}$) $^+$ 340.1244, found 340.1262. **GCMS (EI)** m/z calcd. for $\text{C}_{19}\text{H}_{21}\text{ClFN}$ [M^+] 317.1, found 317.1, 234.1, 198.1, 170.1, 151.1, 122.1, 95.1.



***N*-(1-(2-chlorophenyl)-2-methylpropyl)-4-fluoroaniline (4v):** The title compound was prepared according to the general procedure from 1-(2-chlorophenyl)-*N*-(4-fluorophenyl)methanimine (46.7 mg, 0.2 mmol) and 2-bromopropane (18.7 μ L, 0.4 mmol). Pure product was obtained as brown oil in 76% (42.2 mg) yield after column chromatography of the crude reaction mixture (silica gel, gradient 4% EtOAc/Pet.ether).

^1H NMR (400 MHz, CDCl_3) δ 7.36 (dd, $J = 7.4, 1.9$ Hz, 1H), 7.31 (dd, $J = 7.3, 2.2$ Hz, 1H), 7.17 (pd, $J = 7.3, 1.8$ Hz, 2H), 6.79 (t, $J = 8.7$ Hz, 2H), 6.41 (dd, $J = 8.9, 4.3$ Hz, 2H), 4.59 (d, $J = 5.9$ Hz, 1H), 4.07 (s, 1H), 2.18 – 2.06 (m, 1H), 1.01 (d, $J = 6.9$ Hz, 6H). **^{13}C NMR (101 MHz, CDCl_3)** δ 155.77 (d, $J = 234.7$ Hz), 143.72, 140.17, 133.62, 129.80, 128.23, 128.14, 127.00, 115.68 (d, $J = 22.3$ Hz), 113.91 (d, $J = 7.3$ Hz), 60.37, 33.68, 20.11, 17.92. **HRMS (ESI-TOF)** m/z calcd. for $\text{C}_{16}\text{H}_{17}\text{ClFN}$ ($\text{M}+\text{Na}$) $^+$ 300.0931, found 300.0942. **GCMS (EI)** m/z calcd. for $\text{C}_{16}\text{H}_{17}\text{ClFN}$ [M^+] 277.1, found 277.1, 199.0, 183.0, 171.0, 152.0, 139.0, 133.0.



***N*-(bicyclo[2.2.1]heptan-7-yl(2-chlorophenyl)methyl)-4-fluoroaniline (4w):** The title compound was prepared according to the general procedure from 1-(2-chlorophenyl)-*N*-(4-

fluorophenyl)methanimine (46.7 mg, 0.2 mmol) and 7-bromobicyclo[2.2.1]heptane (50.8 μ L, 0.4 mmol) for 72 h. Pure product was obtained as yellow oil in 71% (46.8 mg) yield after column chromatography of the crude reaction mixture (silica gel, gradient 3% EtOAc/Pet.ether).

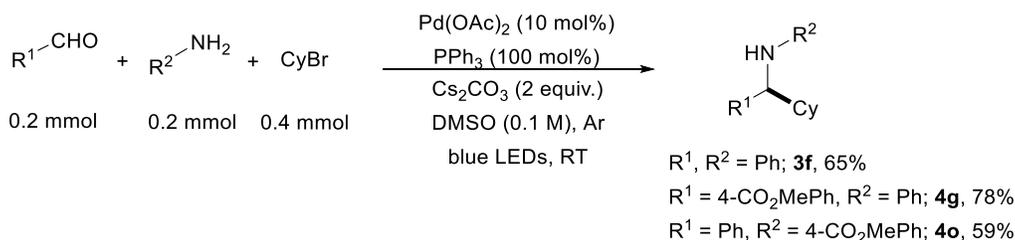
^1H NMR (400 MHz, CDCl_3) δ 7.39 (d, J = 7.8 Hz, 1H), 7.32 (d, J = 7.9 Hz, 1H), 7.21 (t, J = 7.5 Hz, 1H), 7.13 (td, J = 7.6, 1.8 Hz, 1H), 6.78 (t, J = 8.7 Hz, 2H), 6.49 – 6.44 (m, 2H), 4.57 (d, J = 10.1 Hz, 1H), 4.18 (s, 1H), 2.37 (t, J = 4.3 Hz, 1H), 2.18 – 2.04 (m, 1H), 1.89 – 1.77 (m, 2H), 1.71 – 1.59 (m, 2H), 1.52 – 1.43 (m, 1H), 1.37 – 1.13 (m, 4H). **^{13}C NMR (101 MHz, CDCl_3)** δ 155.81 (d, J = 234.7 Hz), 143.57, 141.82, 133.17, 129.73, 128.63, 128.16, 127.47, 115.65 (d, J = 22.3 Hz), 114.05 (d, J = 7.3 Hz), 58.68, 38.43, 37.82, 30.77, 29.85, 28.24, 27.59. **HRMS (ESI-TOF)** m/z calcd. for $\text{C}_{20}\text{H}_{21}\text{ClFN}$ ($\text{M}+\text{Na}$) $^+$ 352.1244, found 352.1263. **GCMS (EI)** m/z calcd. for $\text{C}_{20}\text{H}_{21}\text{ClFN}$ [M^+] 329.1, found 329.1, 234.1, 219.1, 198.0, 177.0, 151.0, 122.0.



Ethyl 2-cyclohexyl-2-(*p*-tolylamino)acetate (4x): The title compound was prepared according to the general procedure from ethy-2-(*p*-tolylimino)acetate (38.2 mg, 0.2 mmol) and bromocyclohexane (49.3 μ L, 0.4 mmol). Pure product was obtained as yellow oil in 30% (16.5 mg) yield after column chromatography of the crude reaction mixture (silica gel, gradient 10% EtOAc/Pet.ether).

^1H NMR (400 MHz, CDCl_3) δ 6.97 (d, J = 8.1 Hz, 2H), 6.56 (d, J = 8.3 Hz, 2H), 4.16 (q, J = 7.1 Hz, 2H), 3.82 (d, J = 6.0 Hz, 1H), 2.22 (s, 3H), 1.87 – 1.65 (m, 6H), 1.28 – 1.09 (m, 9H). **^{13}C NMR (101 MHz, CDCl_3)** δ 173.94, 145.19, 129.89, 127.58, 113.96, 62.67, 60.89, 41.43, 29.75, 29.36, 26.35, 26.25, 26.21, 20.53, 14.46. **GCMS (EI)** m/z calcd. for $\text{C}_{17}\text{H}_{25}\text{NO}_2$ [M^+] 275.1, found 275, 202, 106. The analytical data correspond with those reported in the literature.¹¹

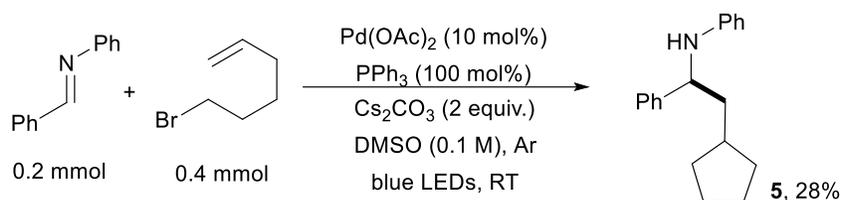
Three-component reaction



A clean, oven-dried screw cap reaction tube equipped with a PTFE-coated stir-bar was charged with aldehyde (0.2 mmol), aniline (0.2 mmol), Pd(OAc)₂ (10 mol%, 0.02 mmol, 4.5 mg), PPh₃ (100 mol%, 0.2 mmol, 52.5 mg), Cs₂CO₃ (2 equiv, 0.4 mmol, 130 mg), and alkyl bromide (2 equiv., 0.4 mmol), capped with Teflon septum and parafilm. The reaction tube was then purged with argon followed by the addition of anhydrous DMSO (0.1 M, 2 mL) under argon. The reaction tube was then stirred well for 10 min to generate a yellow color. The reaction is then irradiated using 34 W blue LEDs while stirring at RT (under fan cooling). After 48 hours, the reaction mixture was treated with water and then extracted with ethyl acetate (3 x 10 mL). The organic layer was collected, dried over anhydrous Na₂SO₄, and concentrated *in vacuo*. The residue was purified by column chromatography using silica gel (100-200 mesh size) and EtOAc/petether as the eluent.

Radical clock experiment

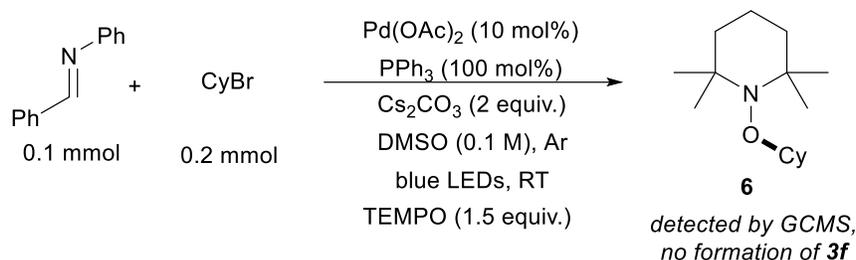
Following the general procedure, radical clock experiment with 6-bromohex-1-ene were carried out which showed the formation of radical rearranged products **5** exclusively, confirming the radical reactivity of metal alkyl species.



***N*-(2-cyclopentyl-1-phenylethyl)aniline (5):** The title compound was prepared according to the general procedure from *N*-benzylideneaniline (36.2 mg, 0.2 mmol) and 6-bromo-1-hexene (53.3 μ L, 0.4 mmol). Pure product was obtained as yellow oil in 28% (14.8 mg) yield after column chromatography of the crude reaction mixture (silica gel, gradient 1% EtOAc/hexane).

¹H NMR (400 MHz, CDCl₃) δ 7.37 – 7.30 (m, 4H), 7.24 (q, J = 7.1, 6.5 Hz, 1H), 7.09 (t, J = 7.6 Hz, 2H), 6.64 (t, J = 7.3 Hz, 1H), 6.53 (d, J = 7.9 Hz, 2H), 4.34 (t, J = 6.7 Hz, 1H), 4.10 (s, 1H), 1.88 – 1.76 (m, 5H), 1.69 – 1.48 (m, 4H), 1.24 – 1.12 (m, 2H). **¹³C NMR (101 MHz, CDCl₃)** δ 147.62, 144.75, 129.22, 128.68, 126.96, 126.46, 117.18, 113.31, 57.76, 45.87, 37.18, 33.01, 25.32, 25.10. **HRMS (ESI-TOF)** m/z calcd. for C₁₉H₂₃N (M+Na)⁺ 288.1728, found 288.1730. **GCMS (EI)** m/z calcd. for C₁₉H₂₃N [M⁺] 265.1, found 265.1, 182.1, 167.1, 152.0, 128.0, 115.0, 104.0.

TEMPO trapping experiment



TEMPO radical trapping experiment was conducted to support the proposed light-mediated inner shear electron transfer oxidative addition mechanism. A clean, oven-dried screw cap reaction tube equipped with a PTFE-coated stir-bar was charged with *N*-benzylideneaniline (36.2 mg, 0.2 mmol), bromocyclohexane (49.3 μ L, 0.4 mmol), Pd(OAc)₂ (10 mol%, 0.02 mmol, 4.5 mg), PPh₃ (100 mol%, 0.2 mmol, 52.5 mg), TEMPO (46.8 mg, 0.3 mmol), and Cs₂CO₃ (2 equiv, 0.4 mmol, 130 mg), capped with Teflon septum and parafilm. The reaction tube was then purged with argon followed by the addition of anhydrous DMSO (0.1 M, 2 mL) under argon. The reaction tube was then stirred well for 10 min to generate yellow color which is then irradiated using 34 W blue LEDs while stirring at RT (under fan cooling). After 48 hours, the reaction mixture was treated with water and then extracted with ethyl acetate (3 x 10 mL). The organic layer was collected, and then subjected to GCMS. The GC-MS of the crude reaction mixture did not show the formation of product **3f**, while a TEMPO-alkyl adduct was observed.

Steady-state Stern-Volmer quenching experiments

Emission spectra were collected on a fluoromax-4 Spectrophotometer with excitation and emission slit widths of 5 nm. Quenching experiments were carried out using a 0.4 mM solution of Pd(PPh₃)₄ in DMF and variable concentrations of bromocyclohexane dispensed in DMF (4, 8, 12, 16, 20 mM). The samples were prepared in 2 mL quartz cuvettes, equipped with PTFE stoppers, and sealed with parafilm inside a nitrogen-filled glove box, removed from the glove box and an emission spectrum was collected. Samples were excited at 380 nm and the intensity of emission was monitored at 630 nm expressed as the ratio I_0/I , where I_0 is the emission intensity of [Pd] at 630 nm in the absence of a quencher and I is the observed intensity, as a function of the quencher concentration was measured. Fluorescence emission spectra and Stern-Volmer plot are given in the Figures below.

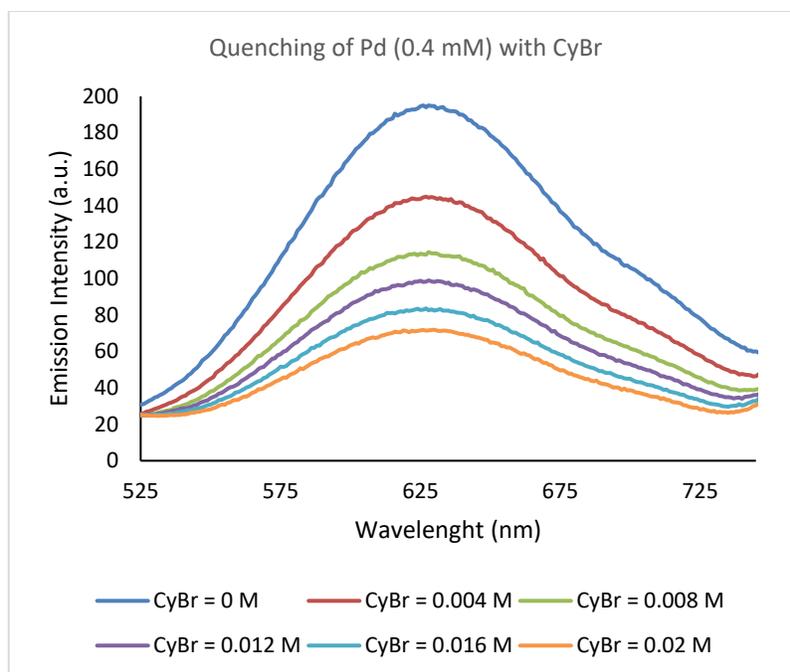


Figure S1. Emission spectra of Pd(PPh₃)₄ (0.4 mM) at different concentrations of bromocyclohexane ($\lambda_{\text{ex}}=380\text{nm}$).

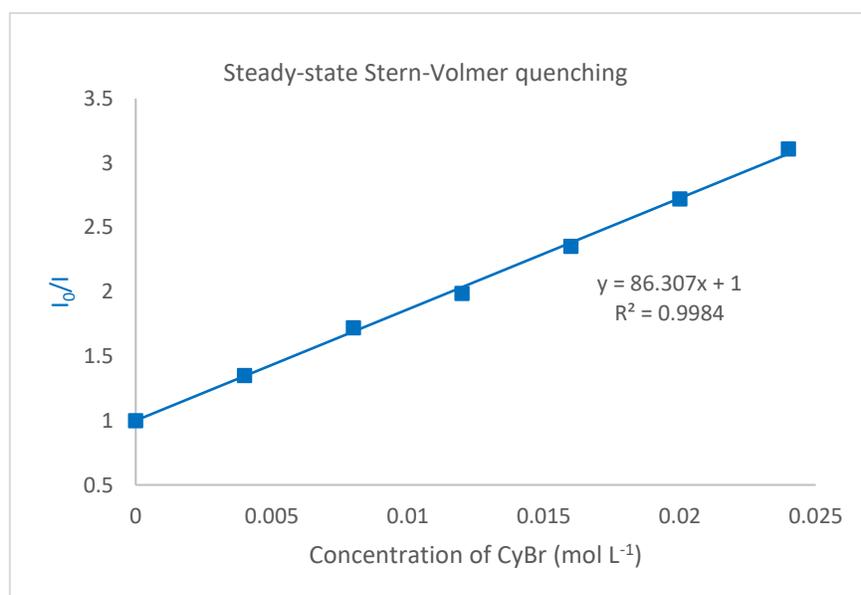


Figure S2. The Stern-Volmer plot of Pd(PPh₃)₄ (0.4 mM) at different concentrations of bromocyclohexane.

Photoluminescence lifetime (Time-resolved Stern-Volmer quenching) experiments

Time-resolved Stern-Volmer quenching experiments were carried out using a 0.4 mM solution of Pd(PPh₃)₄ in DMF and variable concentrations of bromocyclohexane dispensed in DMF (4, 8, 12, 16, 20 mM). The samples were prepared in 2 mL quartz cuvettes, equipped with screw cap PTFE stoppers, and sealed with parafilm inside the argon-filled glove-box. The intensity of the emission peak at 630 nm is expressed as the ratio k_{obs}/k_0 , where k_0 is the decay of Pd(PPh₃)₄ at 630 nm in the absence of bromocyclohexane and k_{obs} is the observed decay, as a function of the bromocyclohexane concentration was measured. An Argon saturated 0.4 mM solution in DMF was used for the determination of the photoluminescence lifetimes of the Pd(PPh₃)₄. Photoluminescence decay traces were acquired based on time-correlated single-photon-counting (TCSPC) techniques using a fluoromax-4 spectrophotometer from Horiba Scientific. A 372 nm diode laser was used as the excitation source. The photoluminescence signals were obtained using an automated motorized monochromator. Time-resolved emission data were fit to a single exponential decay to extract the observed rate constant (k_{obs}). Phosphorescence emission spectra and Stern-Volmer plots for each component are given in below.

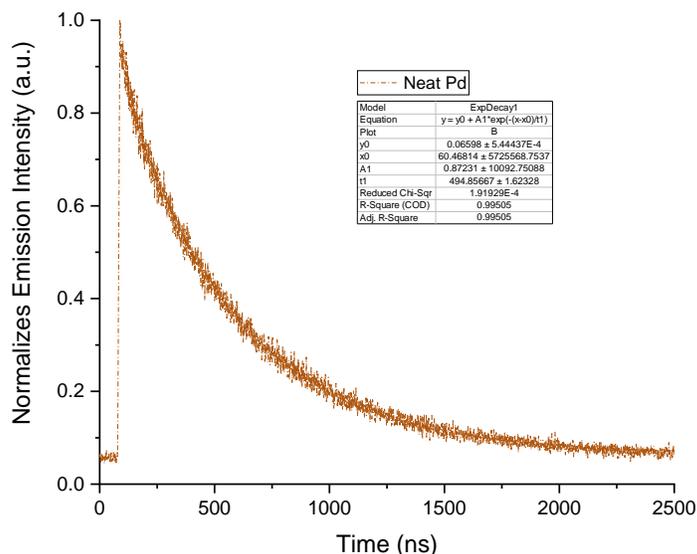


Figure S3. Phosphorescence lifetime of Pd(PPh₃)₄ in DMF (0.4 mM). Spectroscopic experiments were performed one single time. The excited-state *Pd(PPh₃)₄ exhibits a long lived triplet state with a life time of $\tau_0 = 494.85 \pm 1.62$ ns.

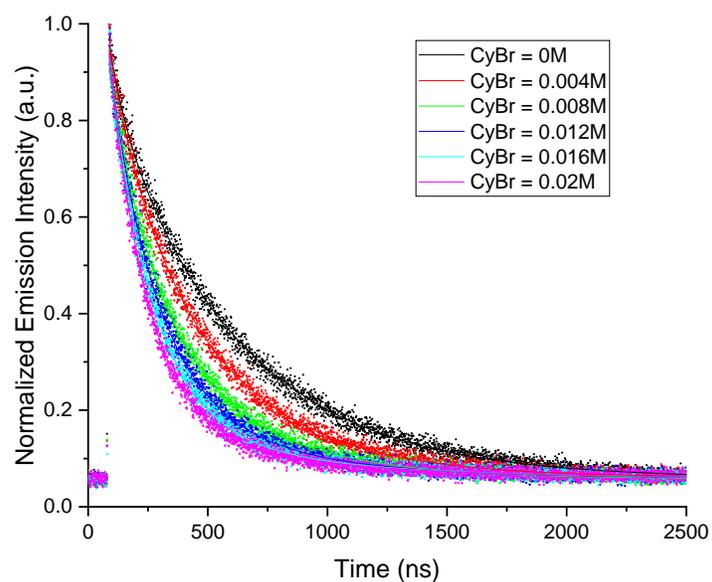


Figure S4. Phosphorescence lifetimes of Pd(PPh₃)₄ (0.4 mM) at different concentrations of bromocyclohexane. Spectroscopic experiments were performed one single time.

Concentration [M]	k_{obs}	k_{obs}/k_0
0	2.229465011	1
0.004	2.989996608	1.341127397
0.008	3.774240627	1.69289072
0.012	4.462542534	2.001620349
0.016	5.210638498	2.337169892
0.02	5.998940947	2.690753574

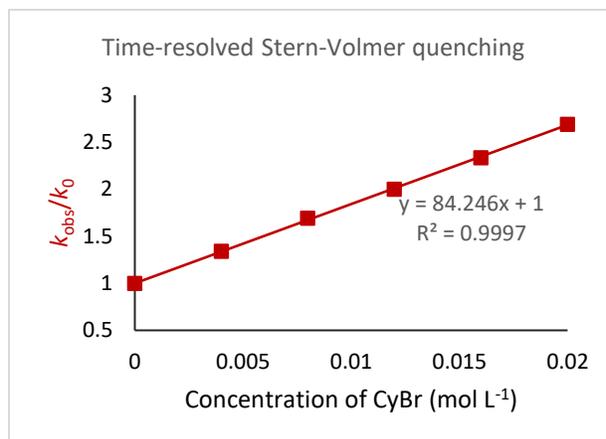


Figure S5. Time-resolved Stern-Volmer quenching plot of Pd(PPh₃)₄ in DMF (0.4 mM) at different concentrations of concentrations of bromocyclohexane.¹²

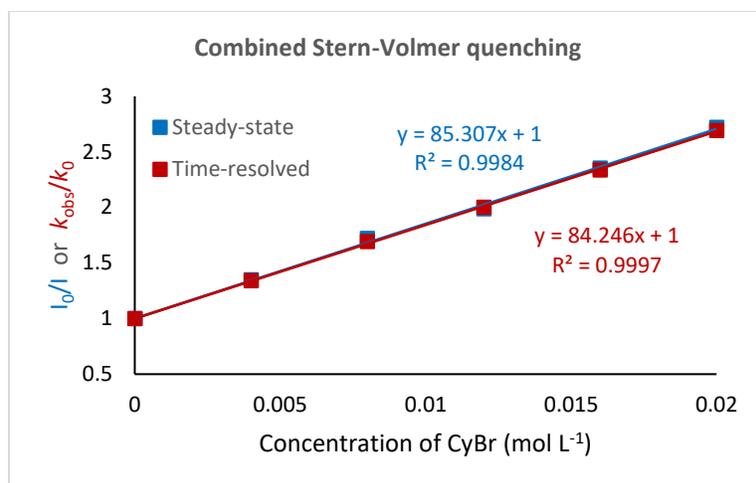


Figure S6. Combined steady-state and time-resolved Stern-Volmer quenching plot of Pd(PPh₃)₄ in DMF (0.4 mM) at different concentrations of concentrations of bromocyclohexane.¹²

Concentration [M]	k_{obs}	$k = 1/t_1 - 1/t_0 \text{ } \mu\text{s}$	$k = 1/t_1 - 1/t_0 * 10^6 \text{ s}$
0	2.229465011	0	0
0.004	2.989996608	0.760531597	760531.597
0.008	3.774240627	1.544775616	1544775.616
0.012	4.462542534	2.233077523	2233077.523
0.016	5.210638498	2.981173487	2981173.487
0.02	5.998940947	3.769475936	3769475.936

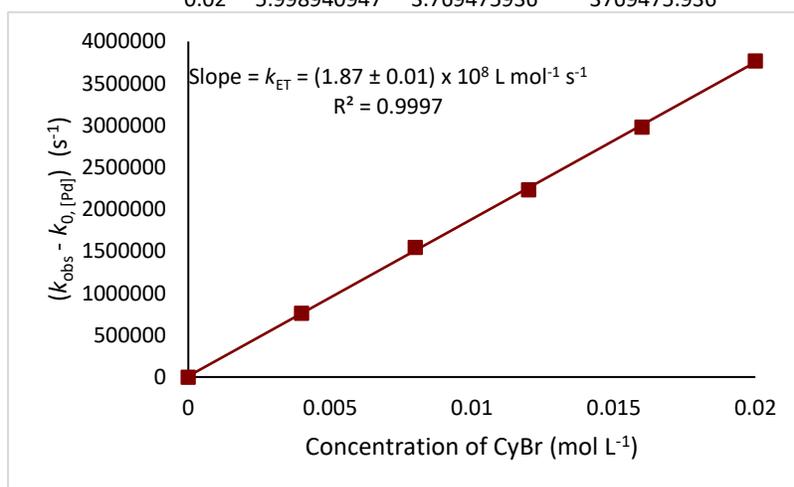


Figure S7. A Plot of the observed rate constant (k_{obs}) of *Pd(PPh₃)₄ (0.4 mM) corrected by its intrinsic ground state recovery rate (k_0) vs. different concentrations of bromocyclohexane to determine the electron transfer rate constant (k_{ET}) between Pd and bromocyclohexane. Data were collected by the use of phosphorescence lifetime measurements.¹²

Mechanistic discussion:

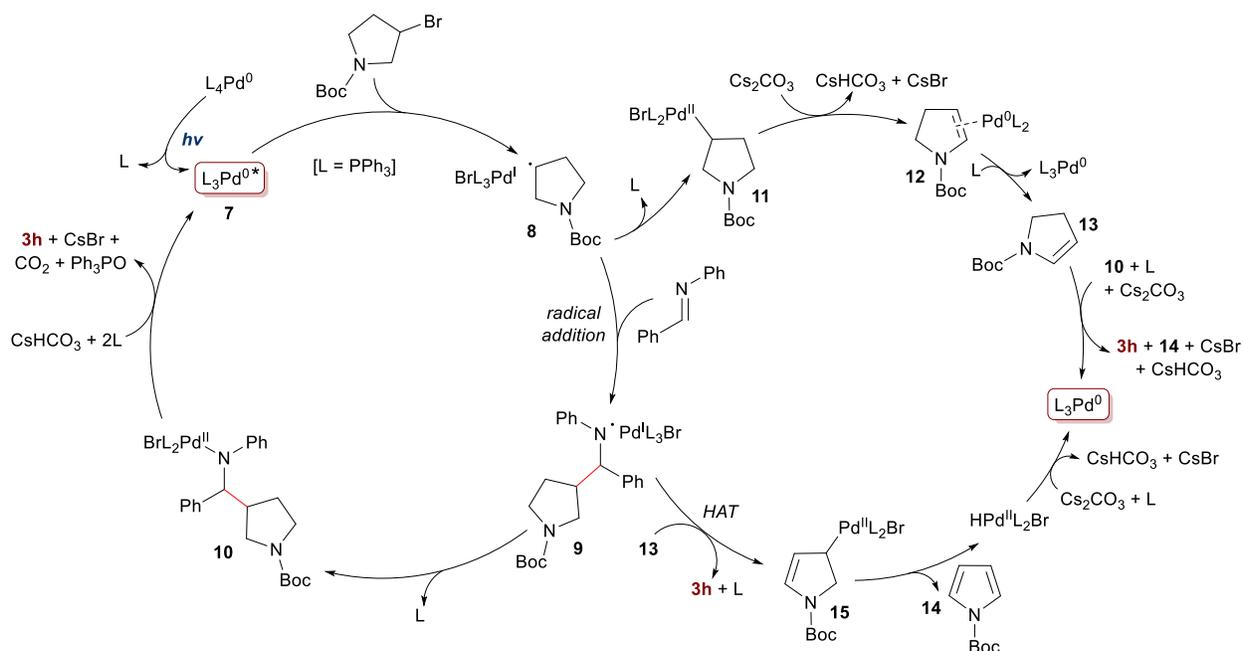


Figure S8. Alternate pathways for the Pd^{II} reduction.

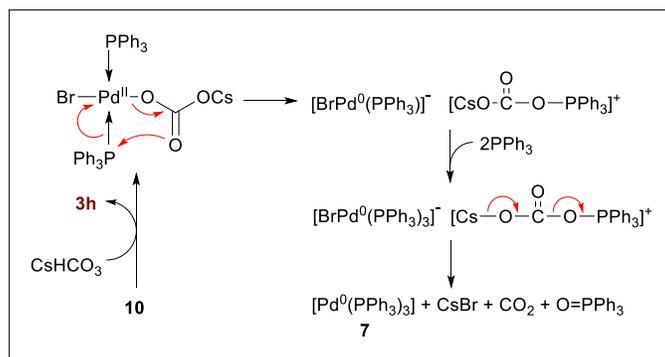


Figure S9. Balanced equation from intermediate **10** to **7**, resulting in product formation and Pd^{II} reduction.

A plausible reaction mechanism proceeding via the inner-sphere ET pathway is proposed (Figure 2f, and S8). The in situ generated Pd(PPh₃)₄ complex undergoes excitation in the presence of visible light resulting in the triplet state *Pd⁰L₃ (**7**) that provides open coordination site for the alkyl bromide association. This results in the inner sphere electron transfer furnishing hybrid alkyl radical Pd^I intermediate. The alkyl radical then adds to the imine resulting in an *N*-centered radical intermediate **9** which undergoes radical recombination with Pd^I forming a Pd^{II} intermediate **10** with the release of PPh₃. To realize the product formation and the regeneration of Pd⁰ from intermediate **10**, hydrogen and oxygen are required which made us investigate their source. We initially tested the reaction using DMSO-d₆ as a solvent which did not result in any deuterium incorporated alkylation product **3f** which confirmed that the DMSO is not acting as a source of

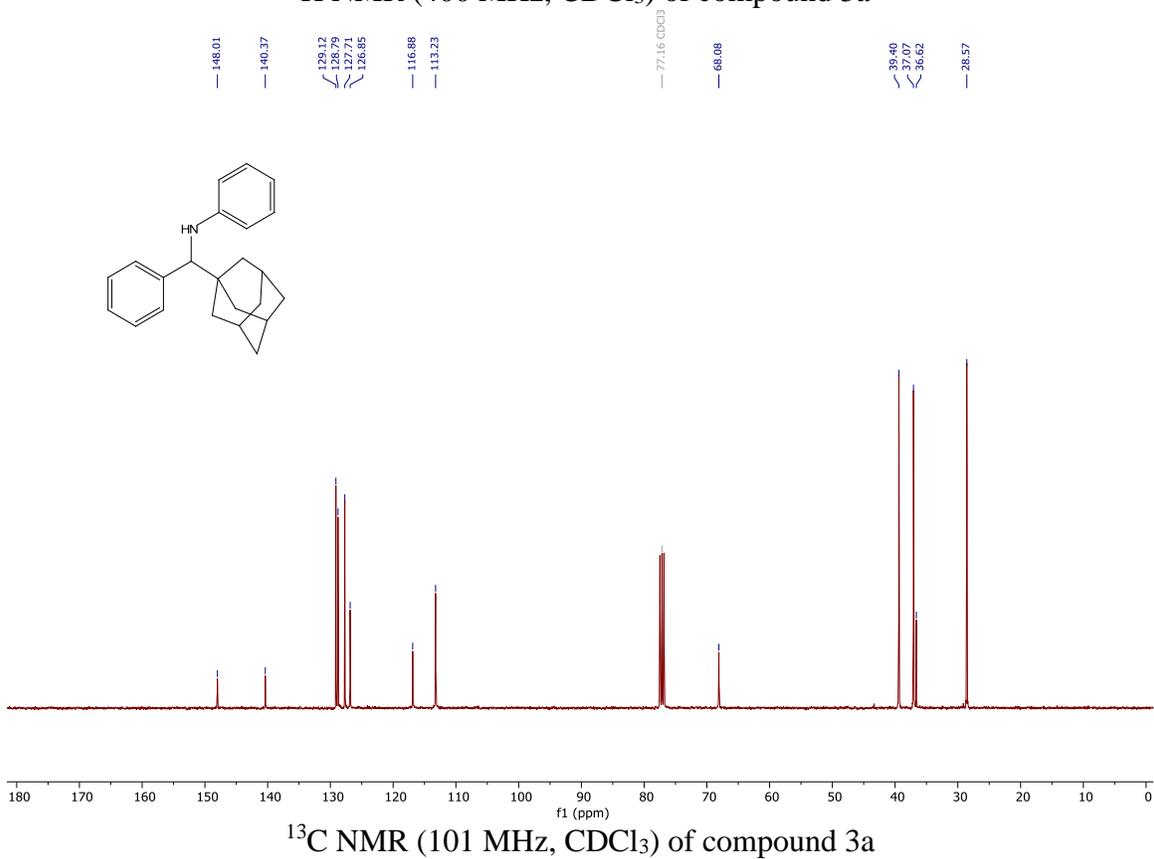
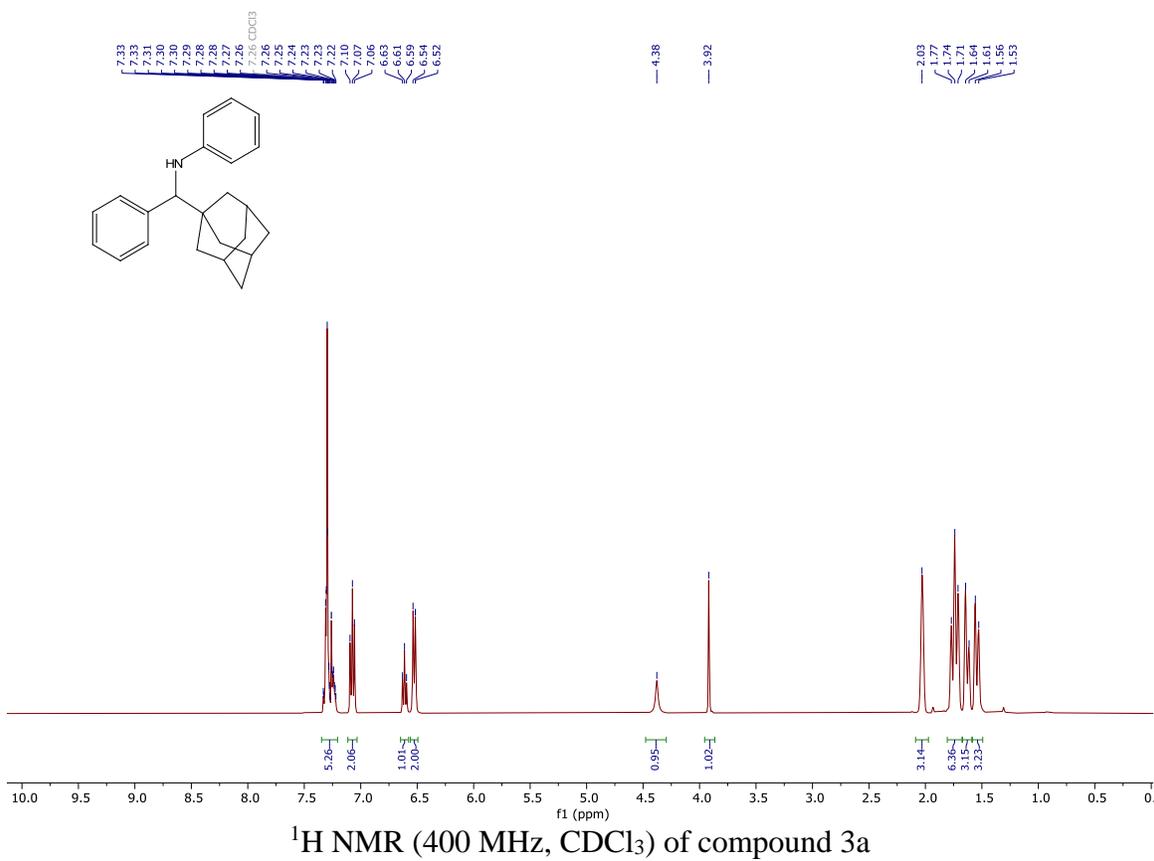
hydrogen. Besides, the formation of triphenylphosphine oxide is observed even in solvents without oxygen (CH₃CN, Toluene), making us conclude that the DMSO being used in the reaction is acting as the source of neither hydrogen nor oxygen. This helped us to identify the CsHCO₃ being generated in the reaction as the source of hydrogen and oxygen, which facilitates the release of hydroalkylation product **3** and Pd⁰ from intermediate **10** along with the generation of triphenylphosphine oxide which is observed in comparable yields to the amine **3** formed (Figure 2f, S8 and S9).

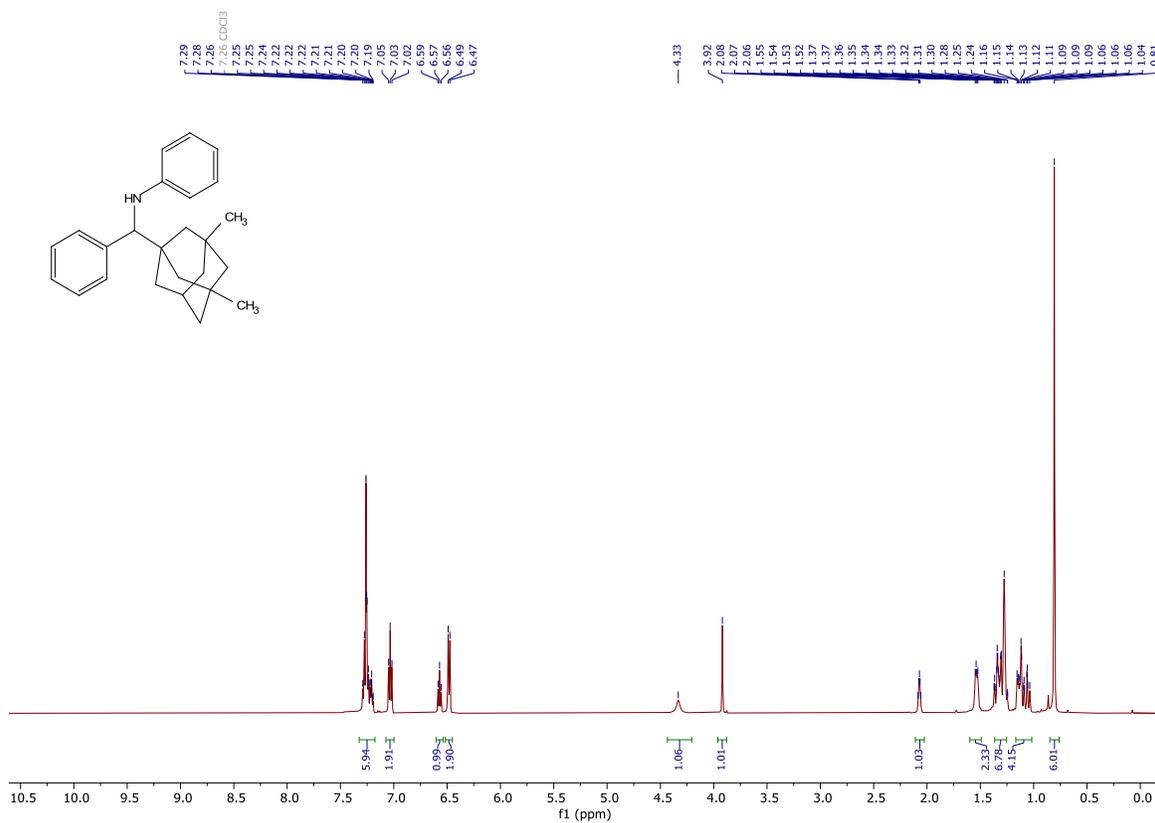
Besides, hybrid alkyl radical Pd^I intermediate **8** also can undergo radical recombination to give Pd^{II} intermediate **11** followed by the β-hydride elimination resulting in the release of olefination intermediate **13** and Pd⁰.¹³ Intermediate **10** in the presence of Cs₂CO₃ could also release the hydroalkylation product **3** along with the reduction of Pd^{II} to Pd⁰ via Pd^{II}-mediated allylic C–H bond activation followed by β-hydride elimination from intermediate **13** to give oxidized substrate **14**.¹⁴ Both compounds **13** and **14** have been identified under the standard reaction conditions. Alongside, it is conceivable that a hydrogen atom transfer (HAT) mechanism might also be operative,¹⁵ where the *N*-centered radical intermediate **9** can undergo intermolecular HAT with olefination intermediate **13** resulting in the formation of hydroalkylation product **3** along with the release of Pd^{II}-intermediate **15** that undergoes β-hydride elimination to release **14** and reduced Pd⁰.

The reduction of Pd^{II} by dehydrogenation to produce **14** is not a representative process for this reaction. However, we included this as an alternate pathway, which will be applicable for the alkyl bromides that can undergo a series of β-hydride elimination events. Since we use 100 mol% of PPh₃, we believe that the catalysis and the reduction of Pd^{II} to Pd⁰ are facilitated mainly by the excess phosphine used. Alongside, examples where the alkyl bromides can undergo a series of β-hydride elimination events, this alternate pathway proposed can also be considered. We could see the diene in case of **3h**, and **3j** which is easy to analyze. In the case of **3i** we could not identify the diene due to the fragmentation. However in the case of bromocyclohexane, we could see the formation of cyclohexene, but identifying the diene/triene in this particular case is difficult due to the solvent interference.

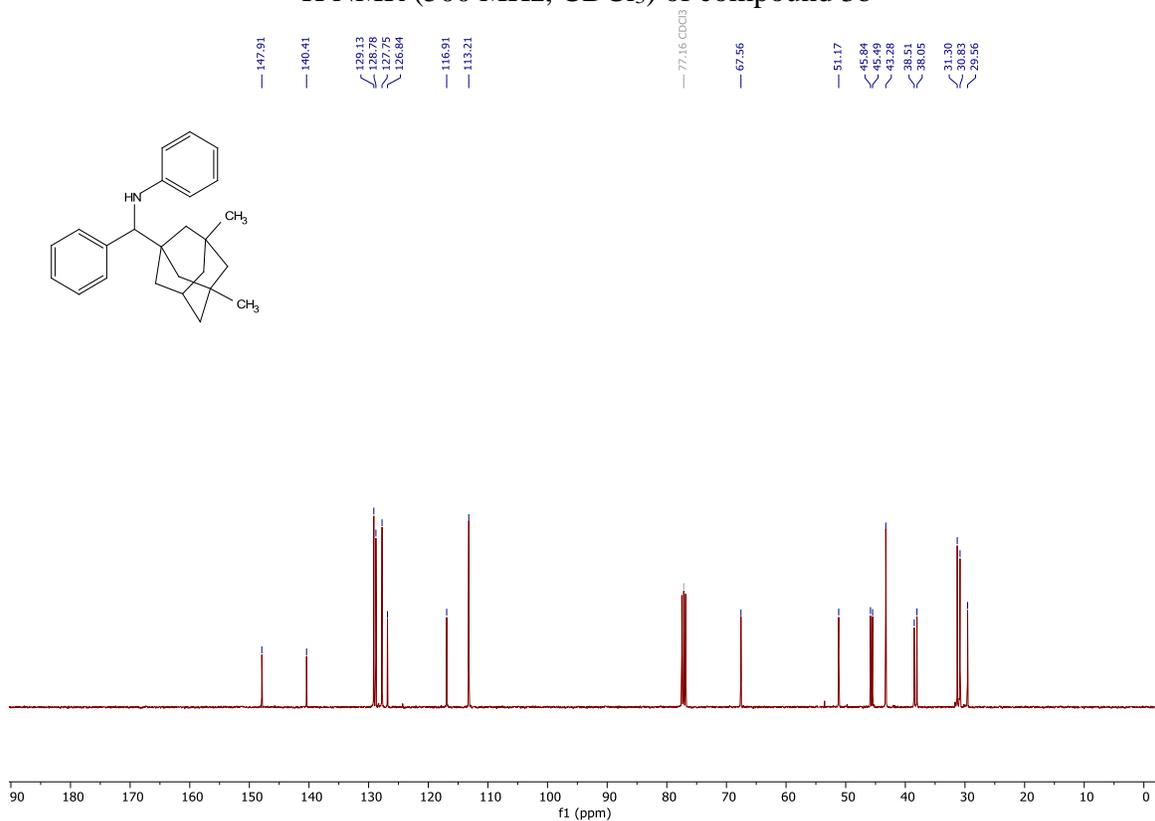
References

1. Y. Du, J. Hou, Q. Lu, W. Hao, W. Yu and J. Chang, *New J. Chem.*, 2021, **45**, 16223–16226.
2. J. Jia, Q. Lefebvre and M. Rueping, *Org. Chem. Front.*, 2020, **7**, 602–608.
3. M. Hatano, S. Suzuki and K. Ishihara, *J. Am. Chem. Soc.*, 2006, **128**, 9998–9999.
4. M. Yus, R. Torregrosa and I. M. Pastor, *Molecules* 2004, **9**, 330–348.
5. N. R. Patel, C. B. Kelly, A. P. Siegenfeld and G. A. Molander, *ACS Catal.*, 2017, **7**, 1766–1770.
6. S. Pillitteri, P. Ranjan, L. G. Voskressensky, E. V. Van der Eycken, and U. K. Sharma, *Mol Catal.*, 2021, **514**, 111841.
7. X.-K. Qi, L. Guo, L.-J. Yao, H. Gao, C. Yang, and W. Xia, *Org. Lett.* 2021, **23**, 4473–4477.
8. A. V. Malkov, K. Vranková, S. Stoncius, and P. Kocovský, *J. Org. Chem.*, 2009, **74**, 5839–5849.
9. J. Safaei-Ghomi, A. Kakavand-Qalenoie, M. A. Ghasemzadeh, and M. Salavati-Niasari, *Turk. J. Chem.*, 2012, **36**, 852–859.
10. X. Wang, B. Zhu, J. Dong, H. Tian, Y. Liu, H. Song and Q. Wang, : *Chem. Commun.*, 2021, **57**, 5028–5031.
11. C. Wang, M. Guo, R. Qi, Q. Shang, Q. Liu, S. Wang, L. Zhao, R. Wang, and Z. Xu, *Angew. Chem. Int. Ed.* 2018, **57**, 15841–15846.
12. (a) R. Kancherla, K. Muralirajan, B. Maity, S. Karuthedath, G. S. Kumar, F. Laquai, L. Cavallo and M. Rueping, *Nat. Commun.*, 2022, **13**, 2737; (b) S. Mukherjee, T. Patra and F. Glorius, *ACS Catal.*, 2018, **8**, 5842–5846; (c) M. Teders, C. Henkel, L. Anhäuser, F. Strieth-Kalthoff, A. Gómez-Suárez, R. Kleinmans, A. Kahnt, A. Rentmeister, D. Guldi and F. Glorius, *Nat. Chem.*, 2018, **10**, 981–988; (d) H. Yue, C. Zhu, R. Kancherla, F. Liu and M. Rueping, *Angew. Chem. Int. Ed.*, 2020, **59**, 5738–5746; (e) L. Huang, C. Zhu, L. Yi, H. Yue, R. Kancherla and M. Rueping, *Angew. Chem. Int. Ed.*, 2020, **59**, 457–464.
13. W.-M. Cheng, R. Shang and Y. Fu, *Nat. Commun.*, 2018, **9**, 5215.
14. A. V. Iosub and S. S. Stahl, *J. Am. Chem. Soc.*, 2015, **137**, 3454–3457.
15. W. Jin and S. Yu, *Org. Lett.*, 2021, **23**, 6931–6935.

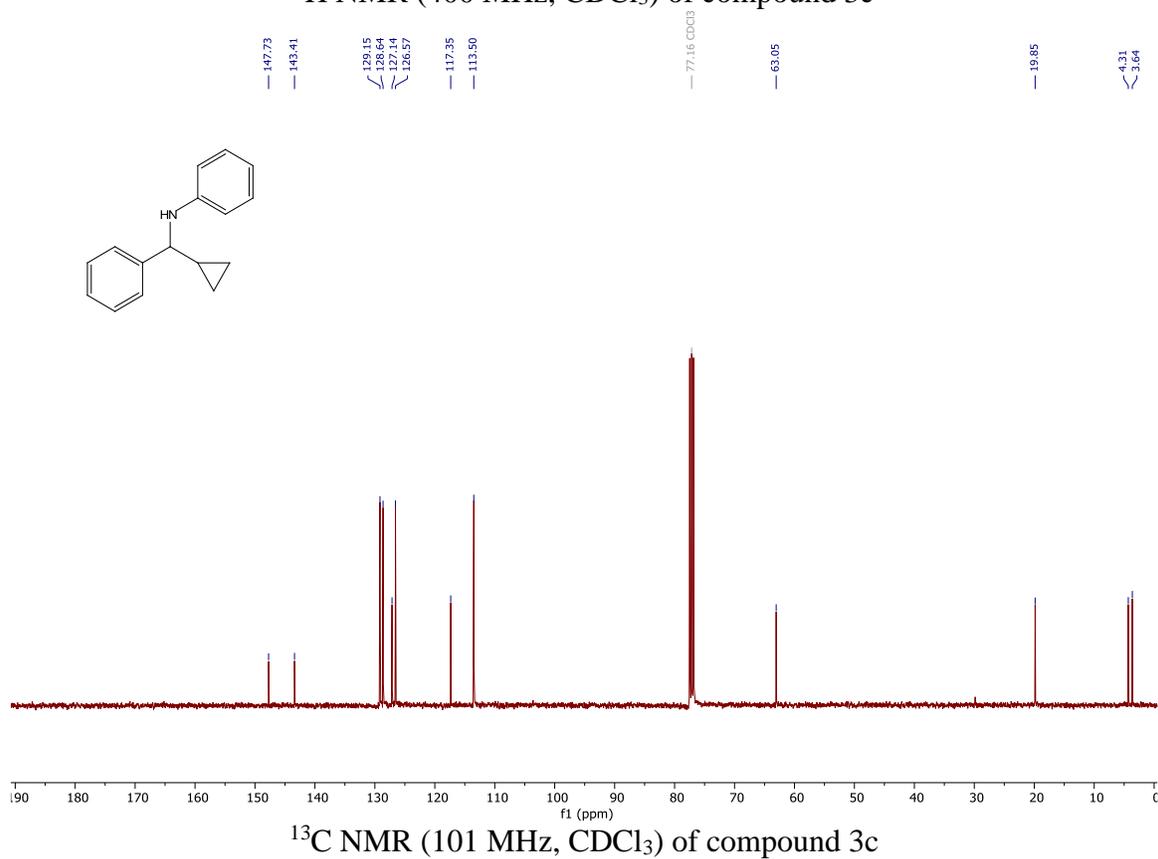
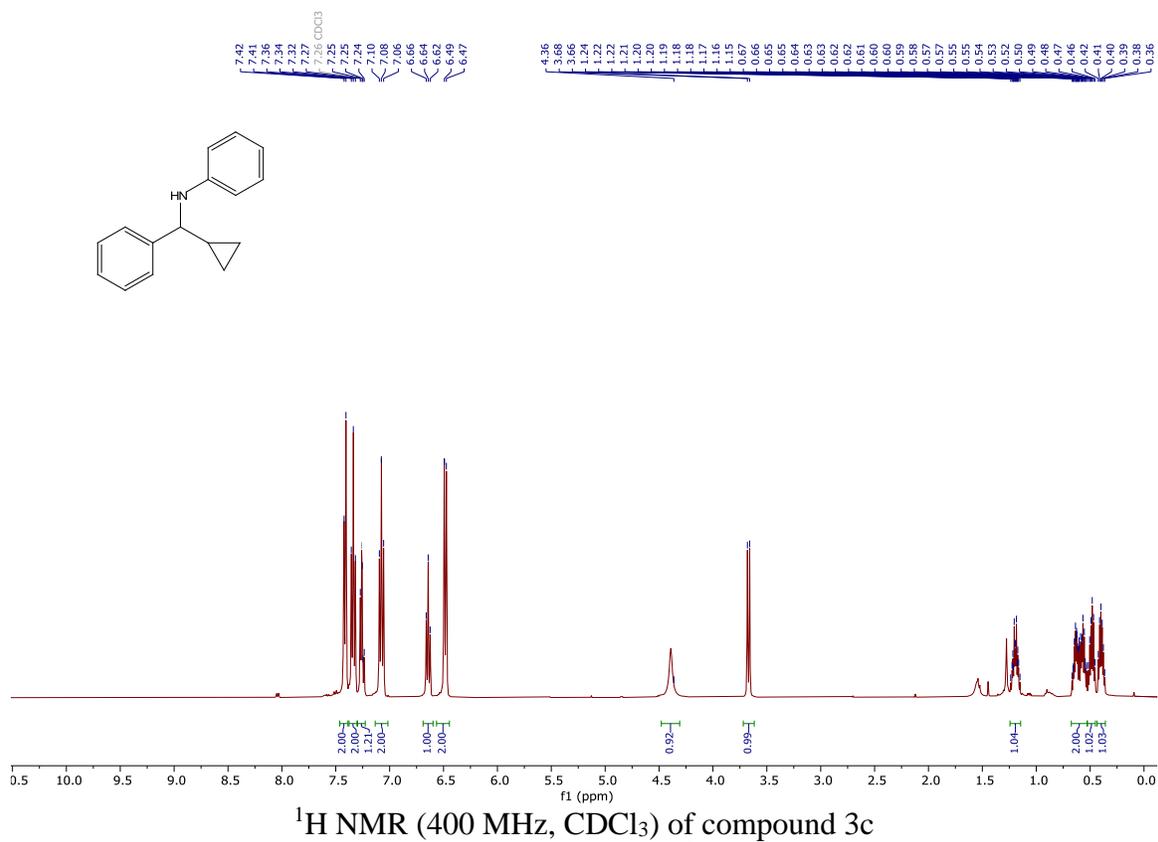


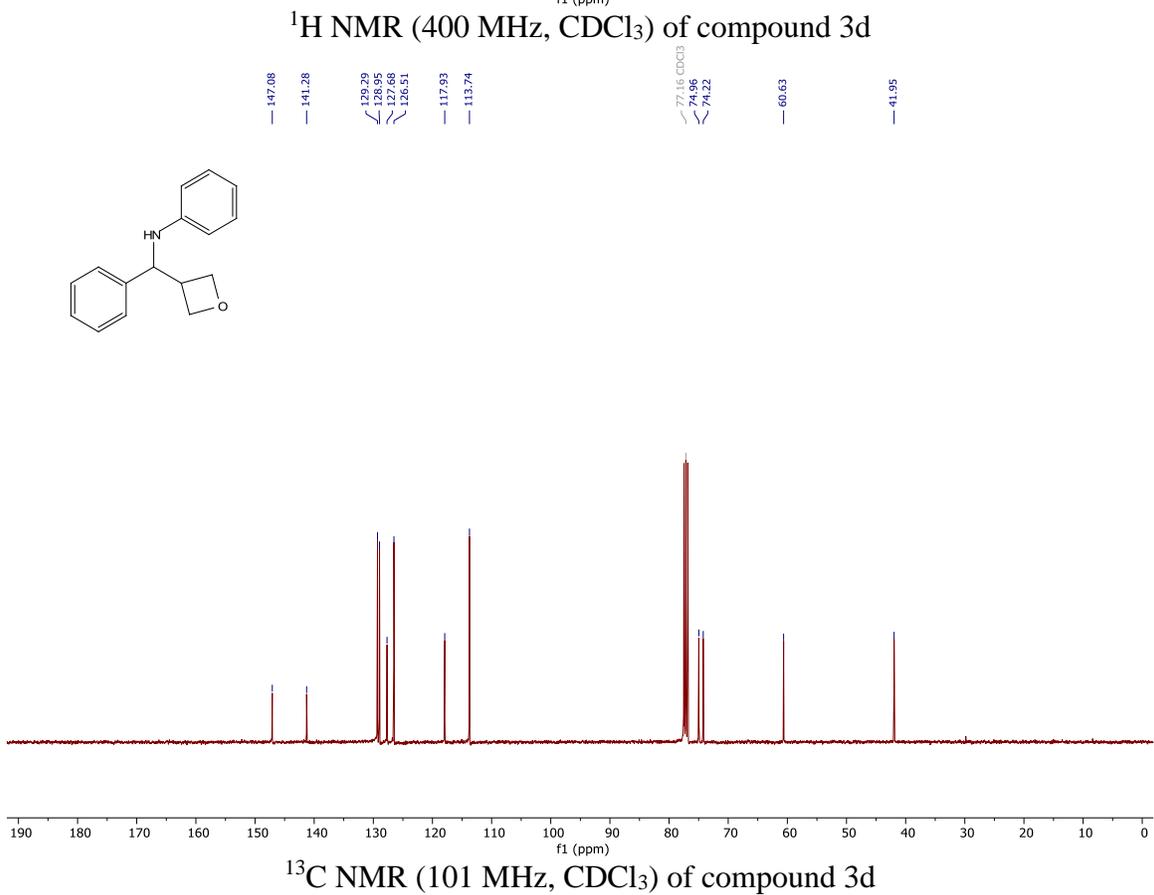
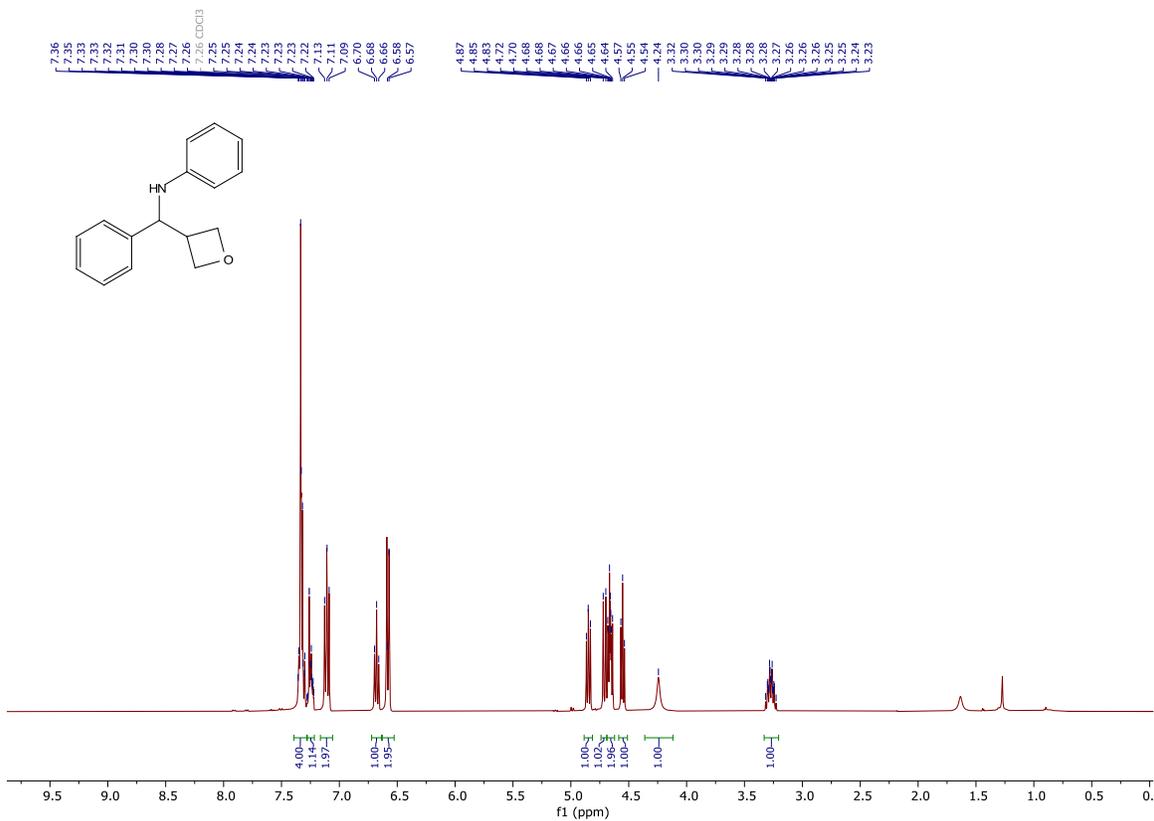


¹H NMR (500 MHz, CDCl₃) of compound 3b

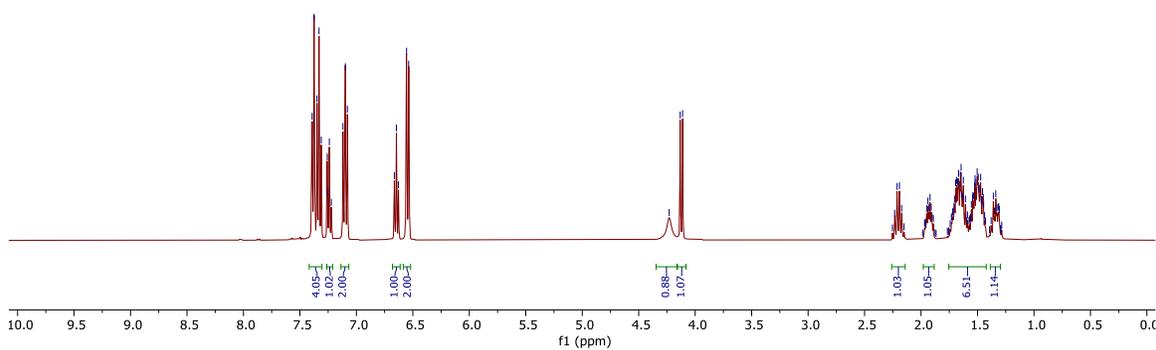
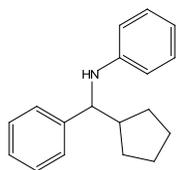


¹³C NMR (101 MHz, CDCl₃) of compound 3b

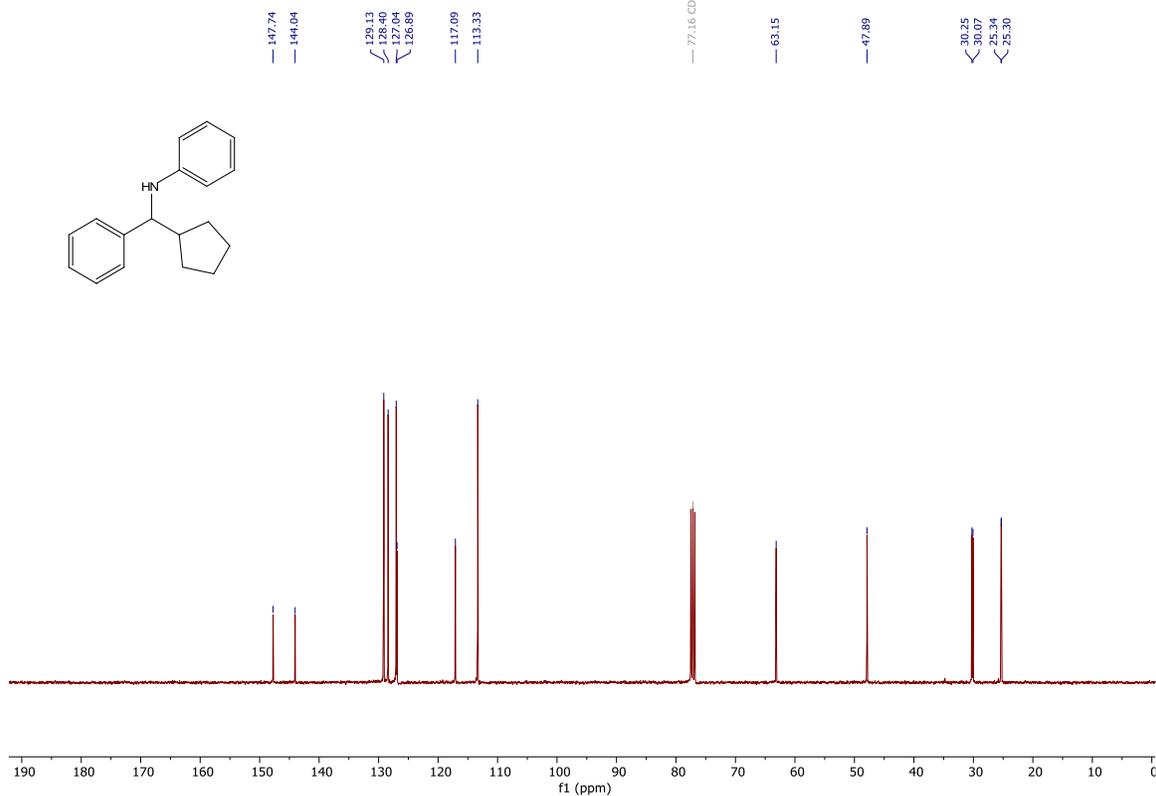
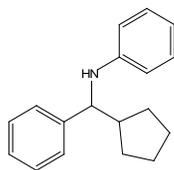




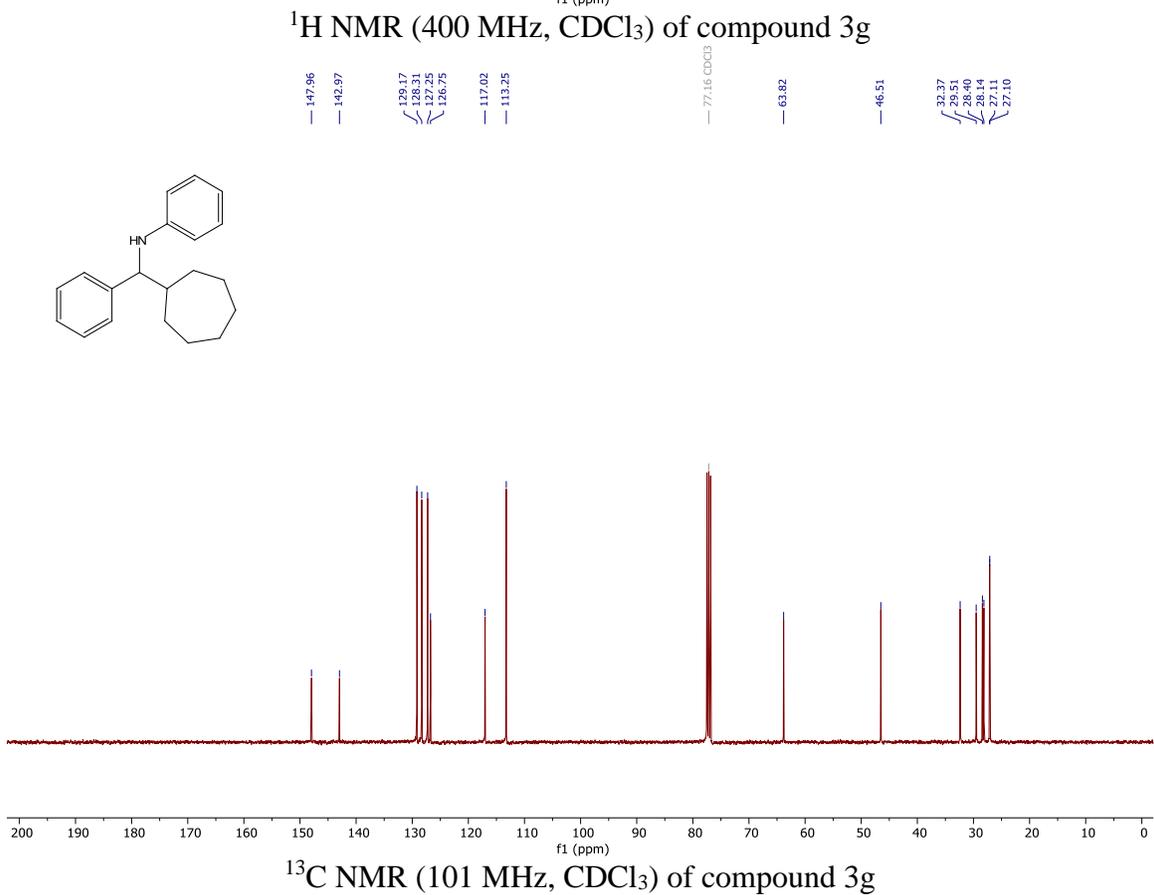
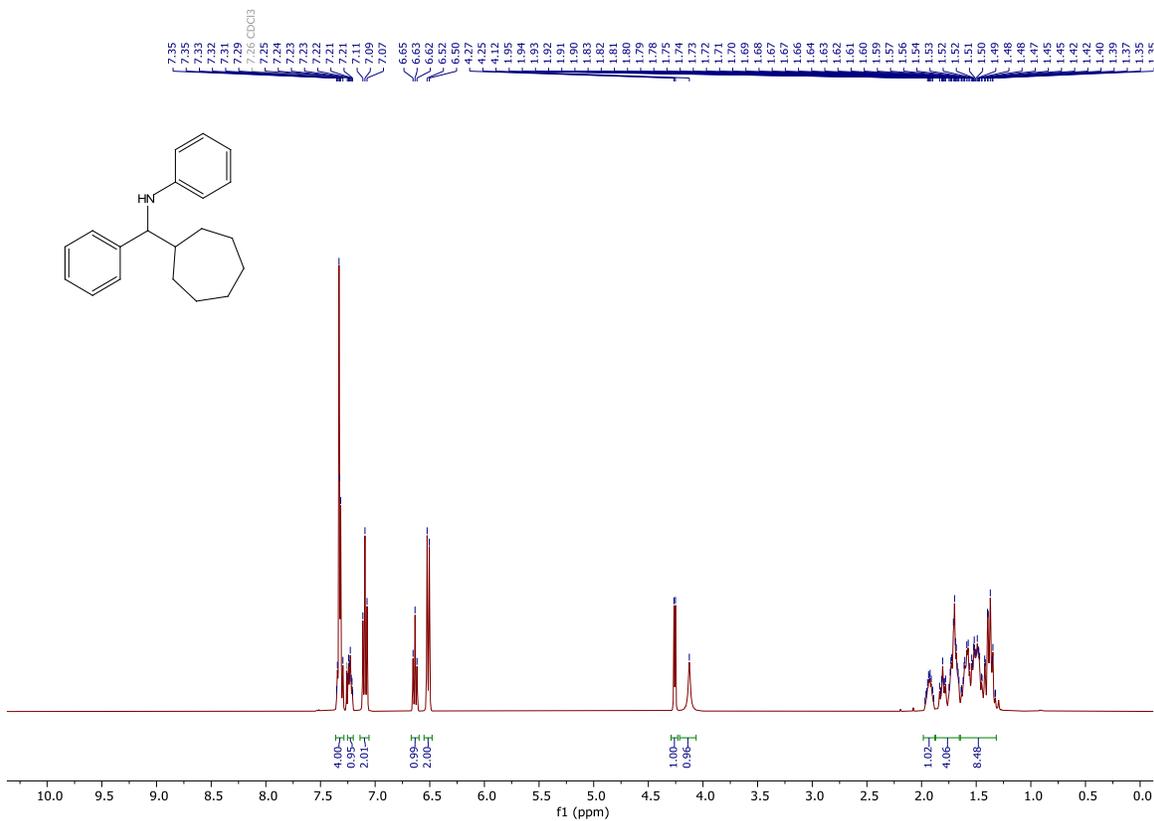
7.39
7.38
7.35
7.34
7.31
7.26 CDCl₃
7.26
7.25
7.24
7.22
7.21
7.12
7.10
7.08
6.96
6.95
6.83
6.56
6.54
4.23
4.13
2.25
2.23
2.21
2.19
2.17
2.16
1.97
1.96
1.95
1.94
1.93
1.92
1.91
1.90
1.89
1.87
1.74
1.73
1.72
1.72
1.71
1.71
1.69
1.68
1.68
1.68
1.67
1.66
1.65
1.65
1.64
1.63
1.63
1.61
1.60
1.59
1.59
1.58
1.57
1.56
1.55
1.54
1.54
1.53
1.53
1.52
1.52
1.51
1.50
1.49
1.49
1.48
1.47
1.46
1.45
1.45
1.44
1.44
1.38
1.38
1.36
1.35
1.34
1.34
1.33
1.33
1.31
1.31
1.29

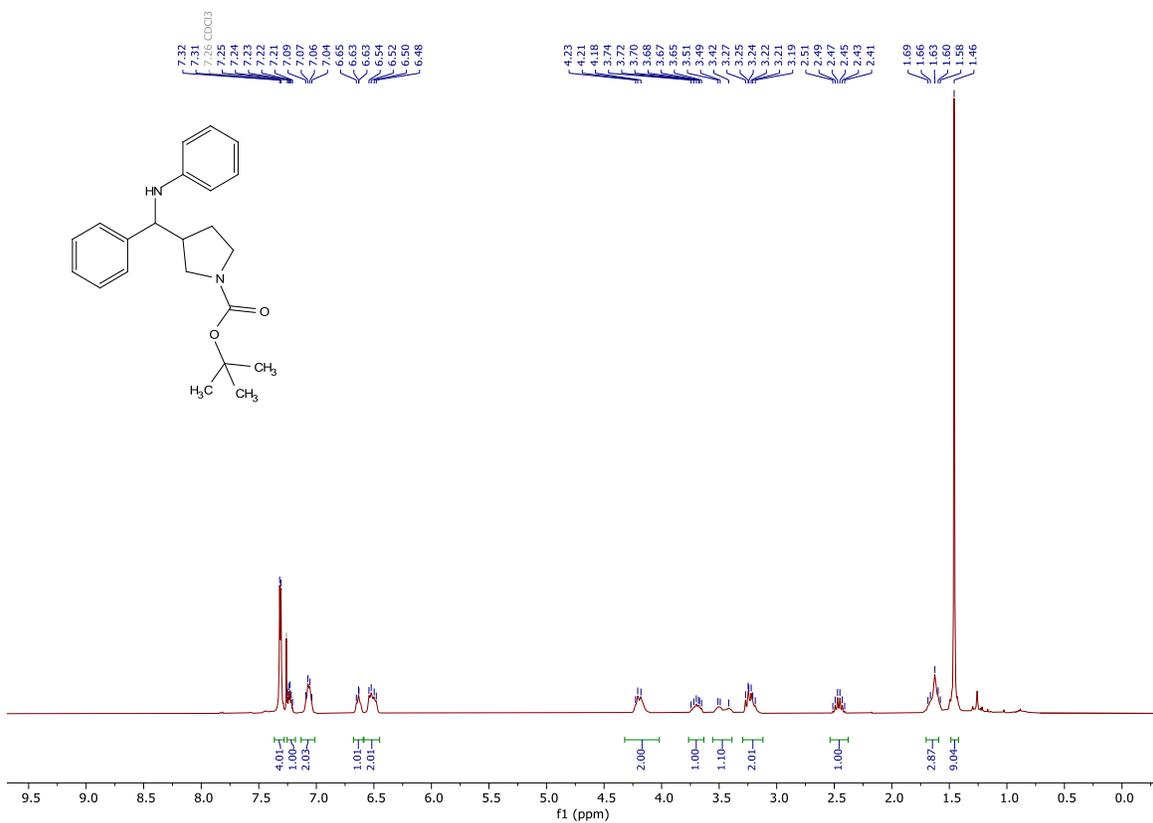


¹H NMR (400 MHz, CDCl₃) of compound 3e

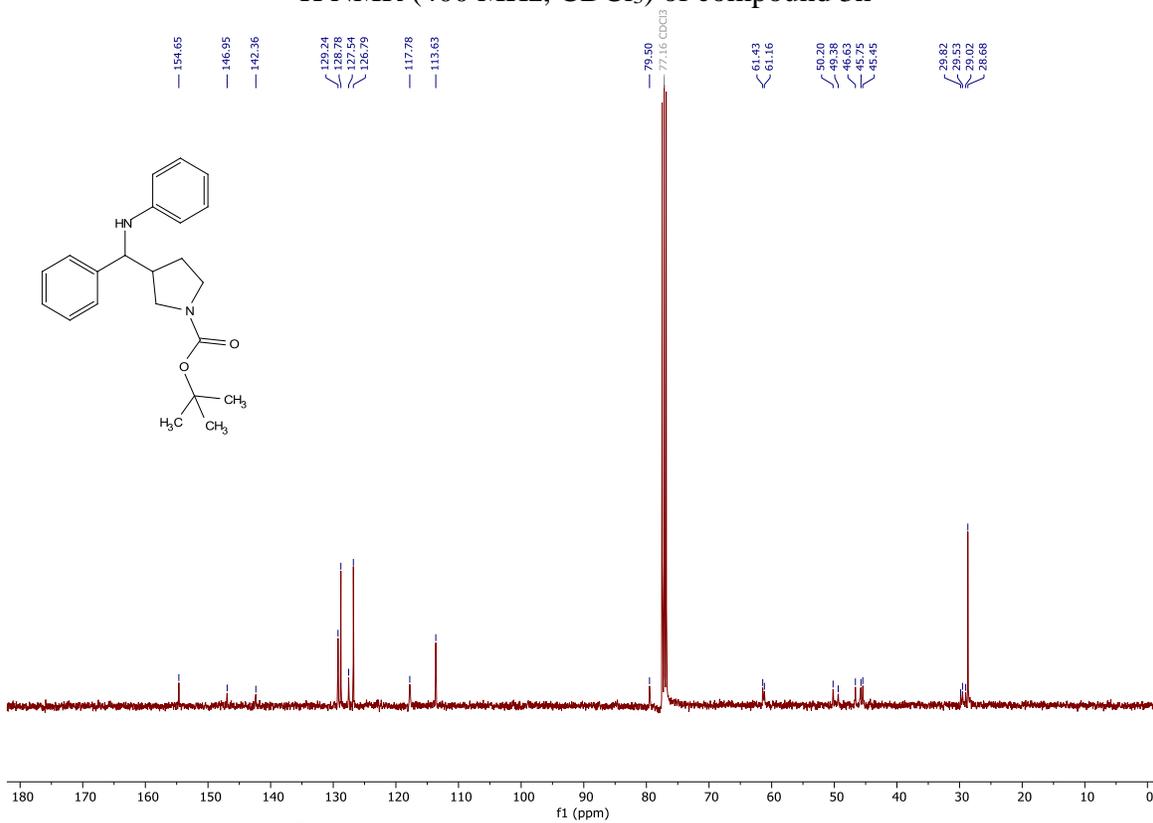


¹³C NMR (101 MHz, CDCl₃) of compound 3e

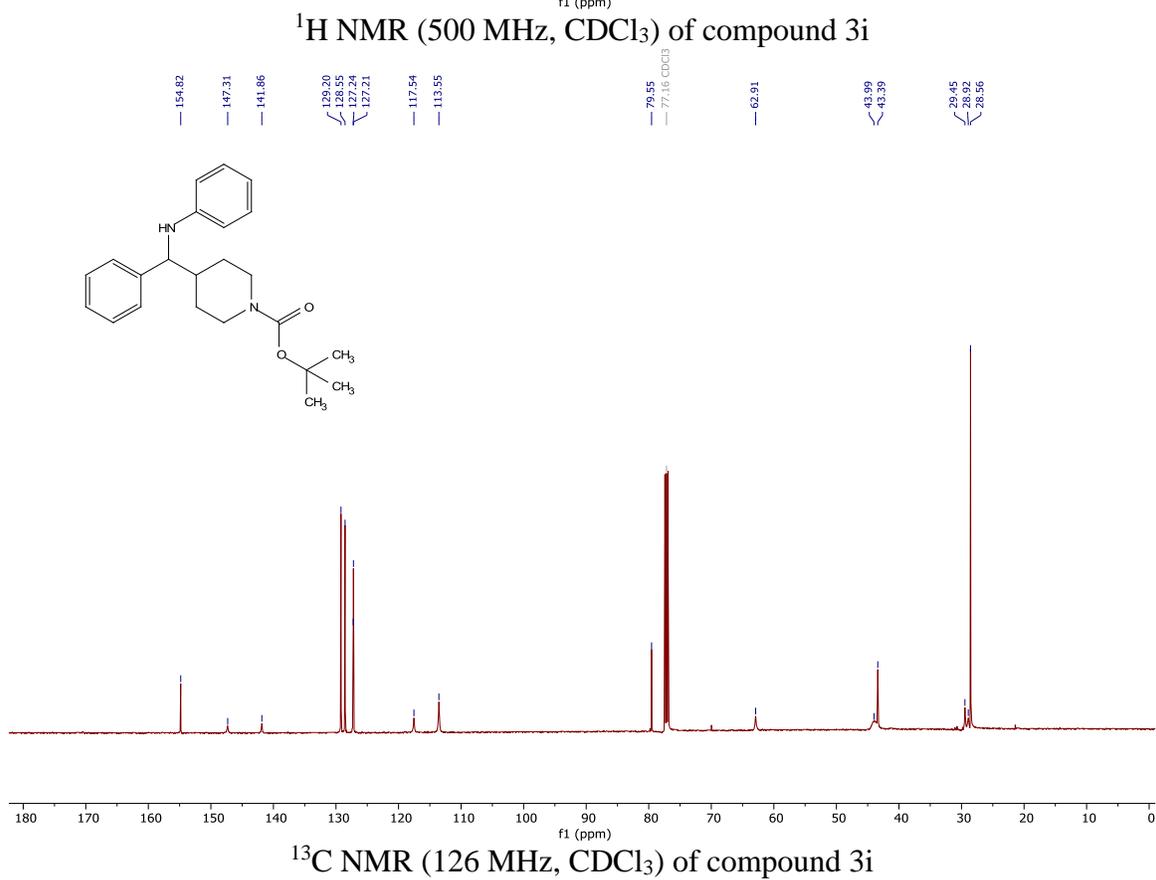
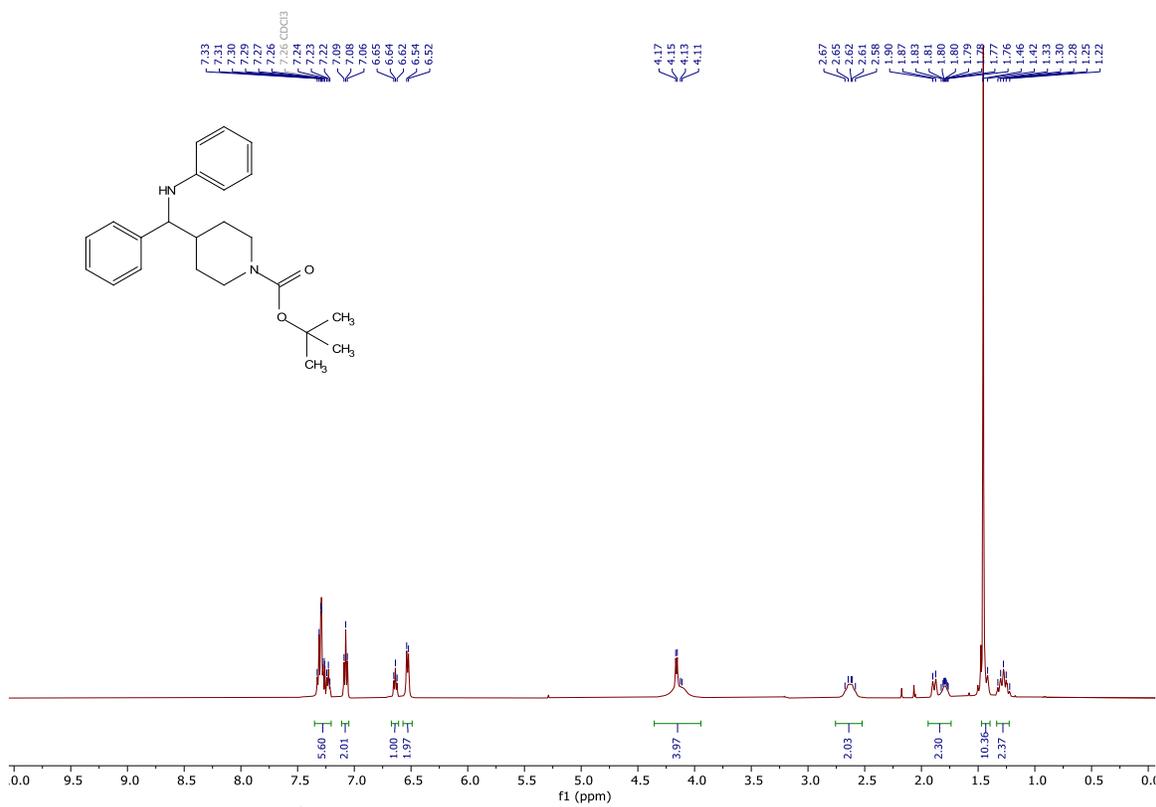


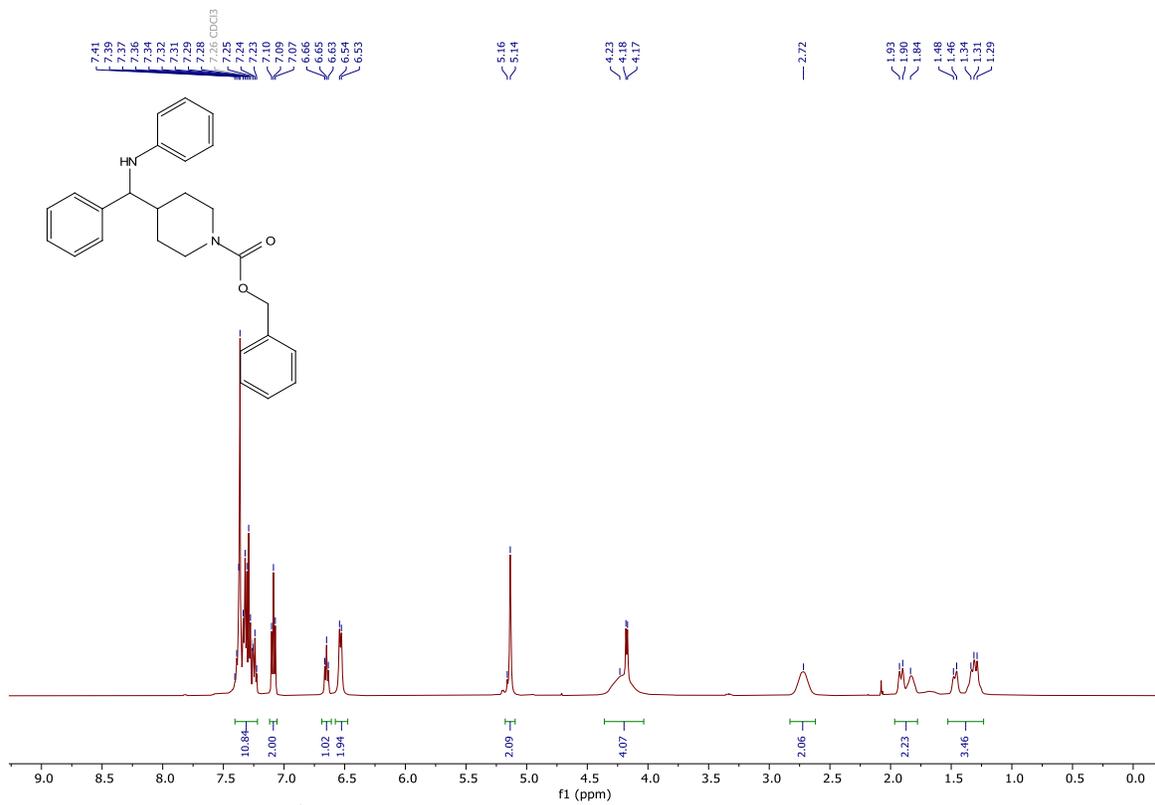


¹H NMR (400 MHz, CDCl₃) of compound 3h

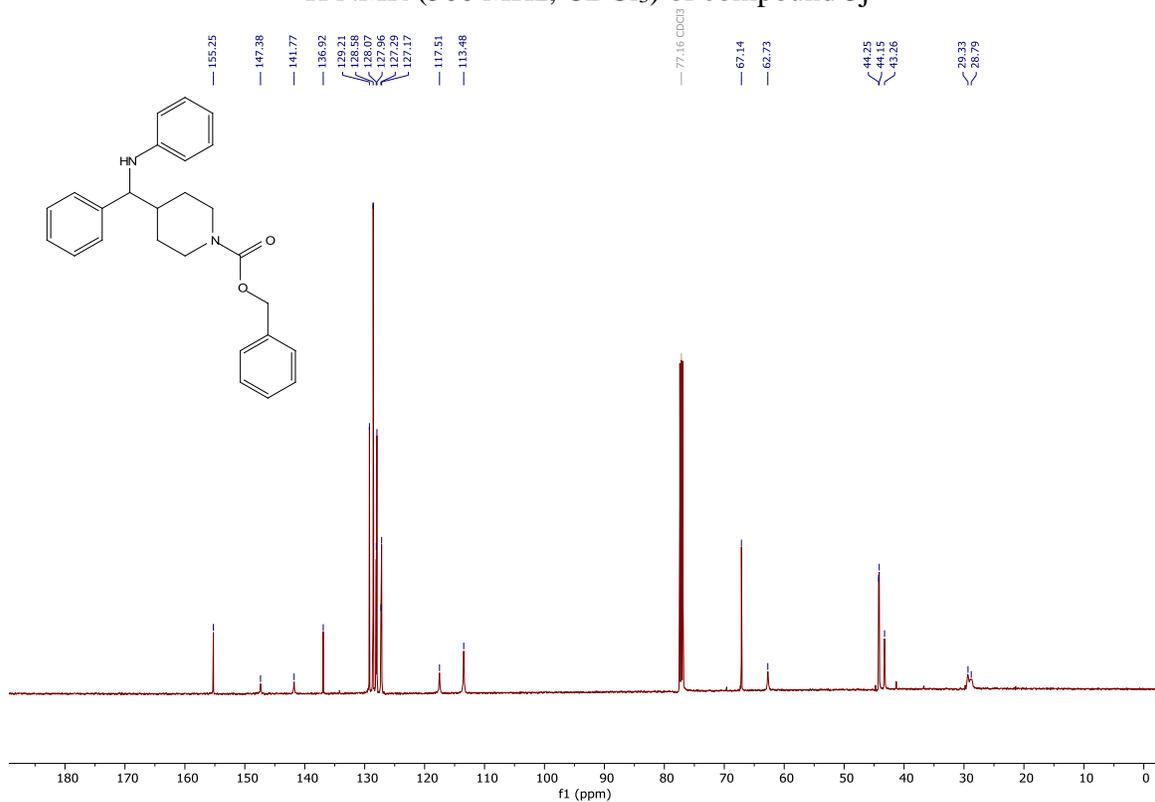


¹³C NMR (101 MHz, CDCl₃) of compound 3h

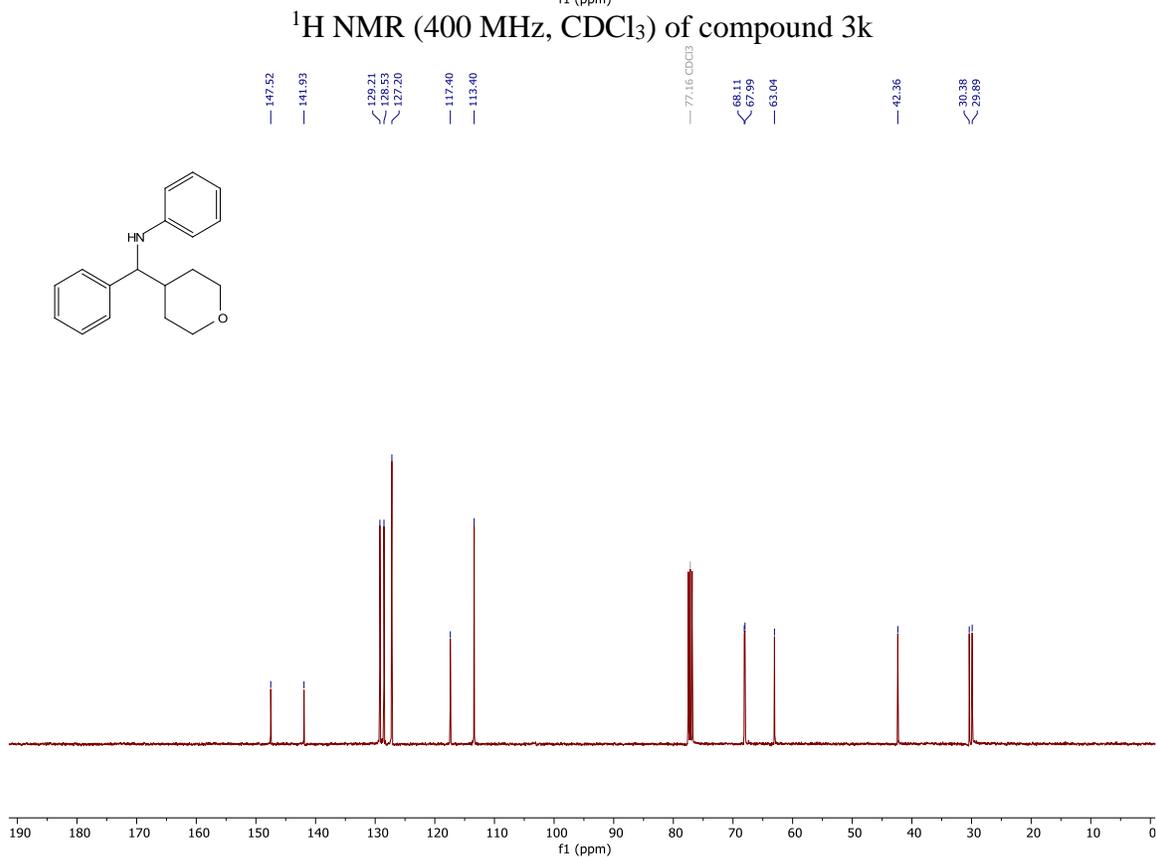
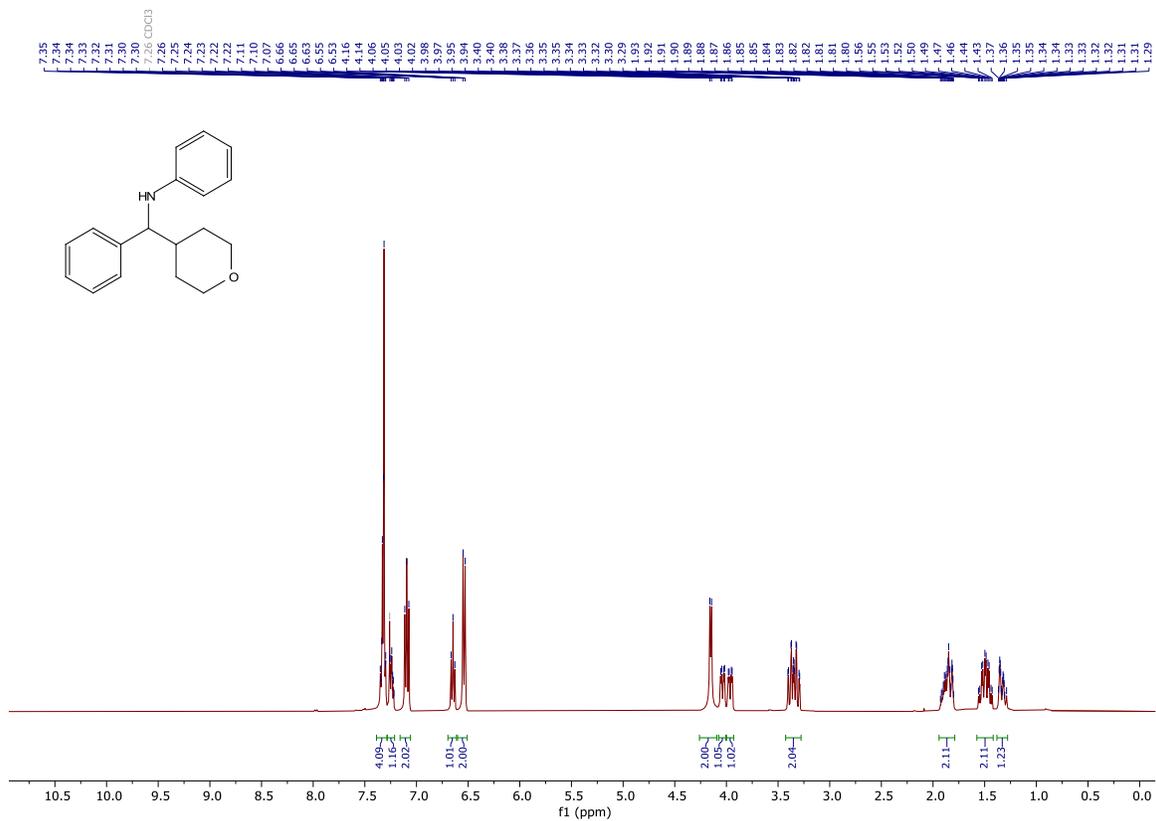


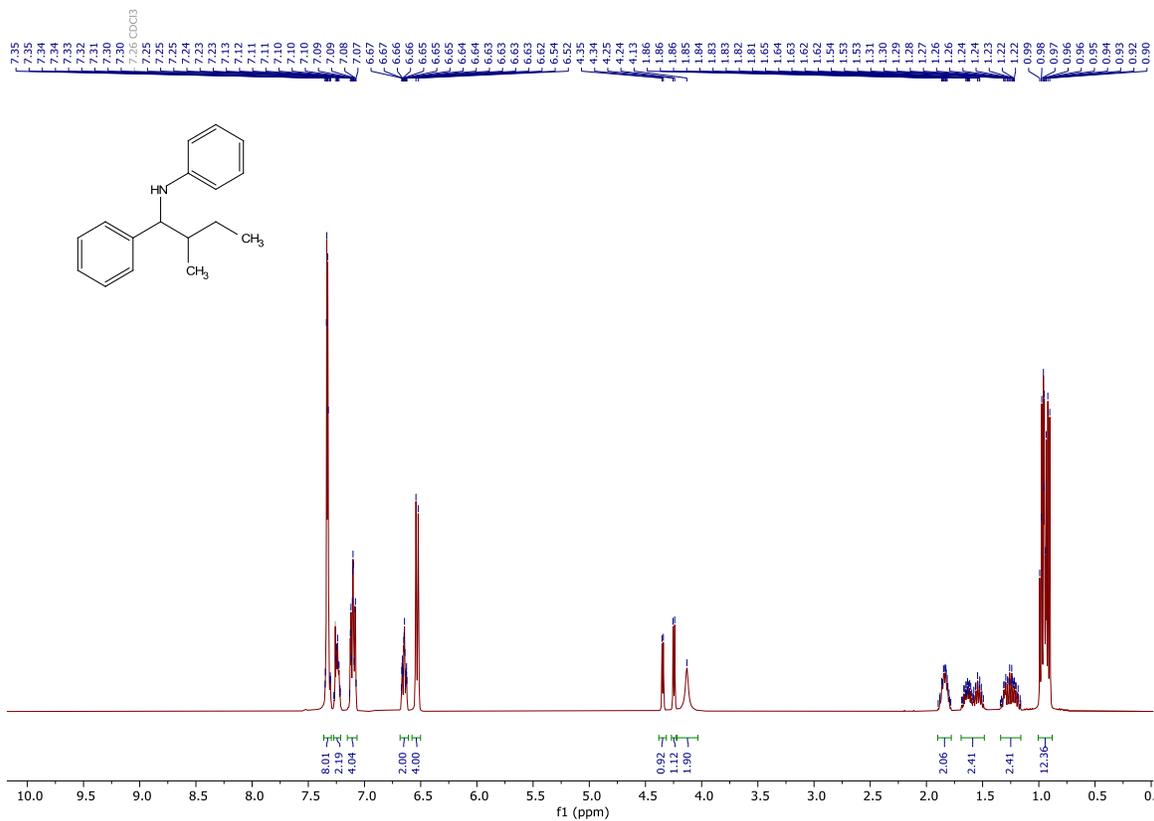


¹H NMR (500 MHz, CDCl₃) of compound 3j

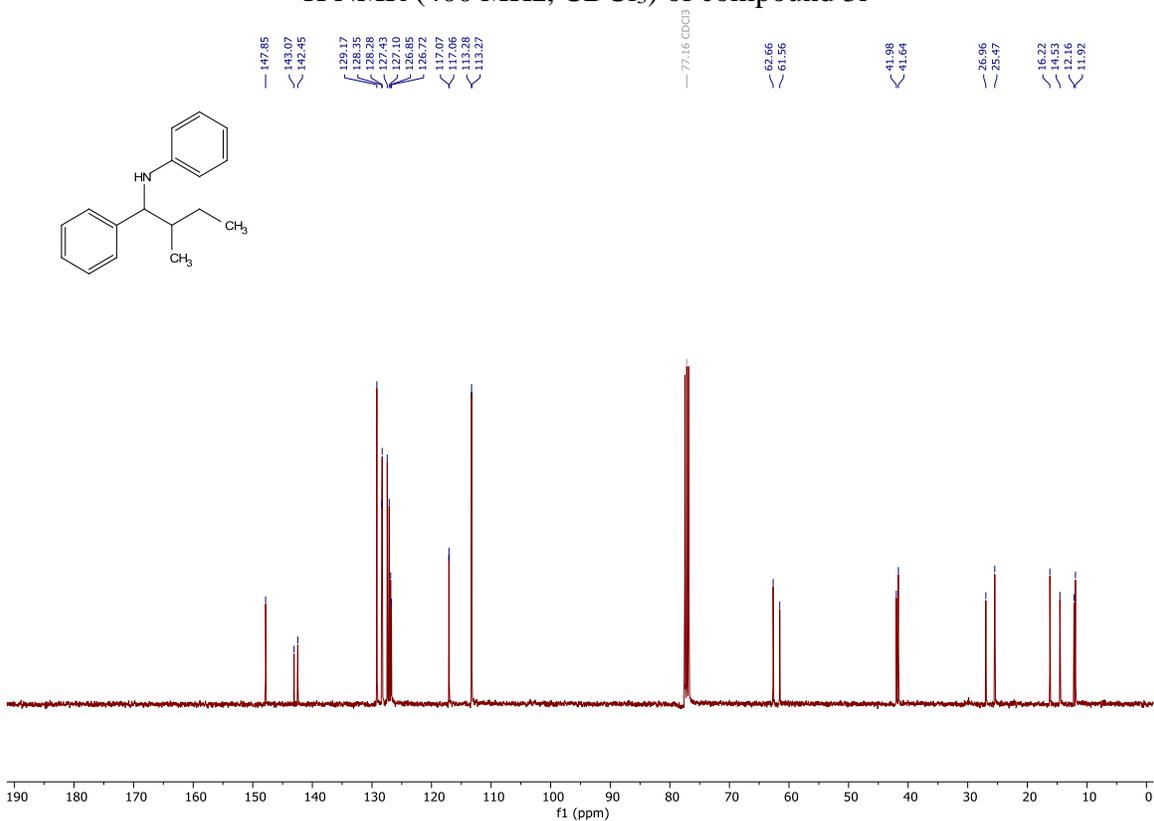


¹³C NMR (126 MHz, CDCl₃) of compound 3j

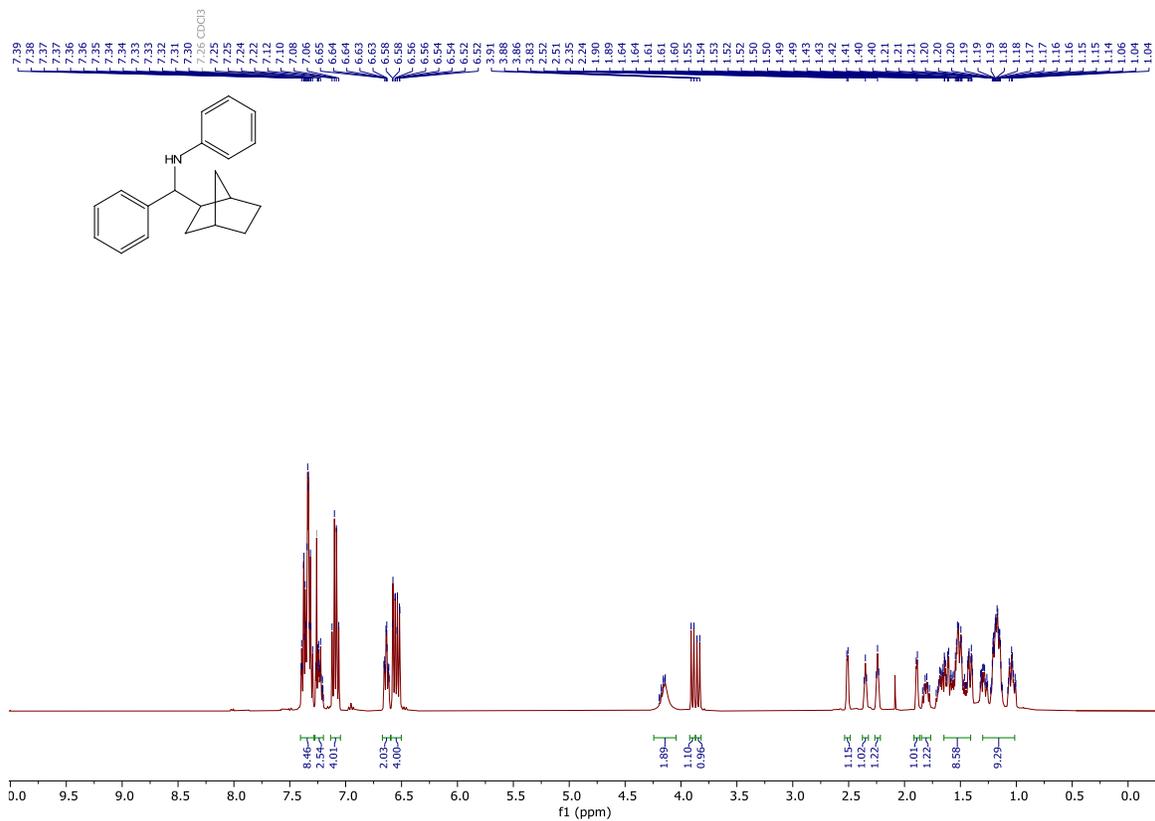




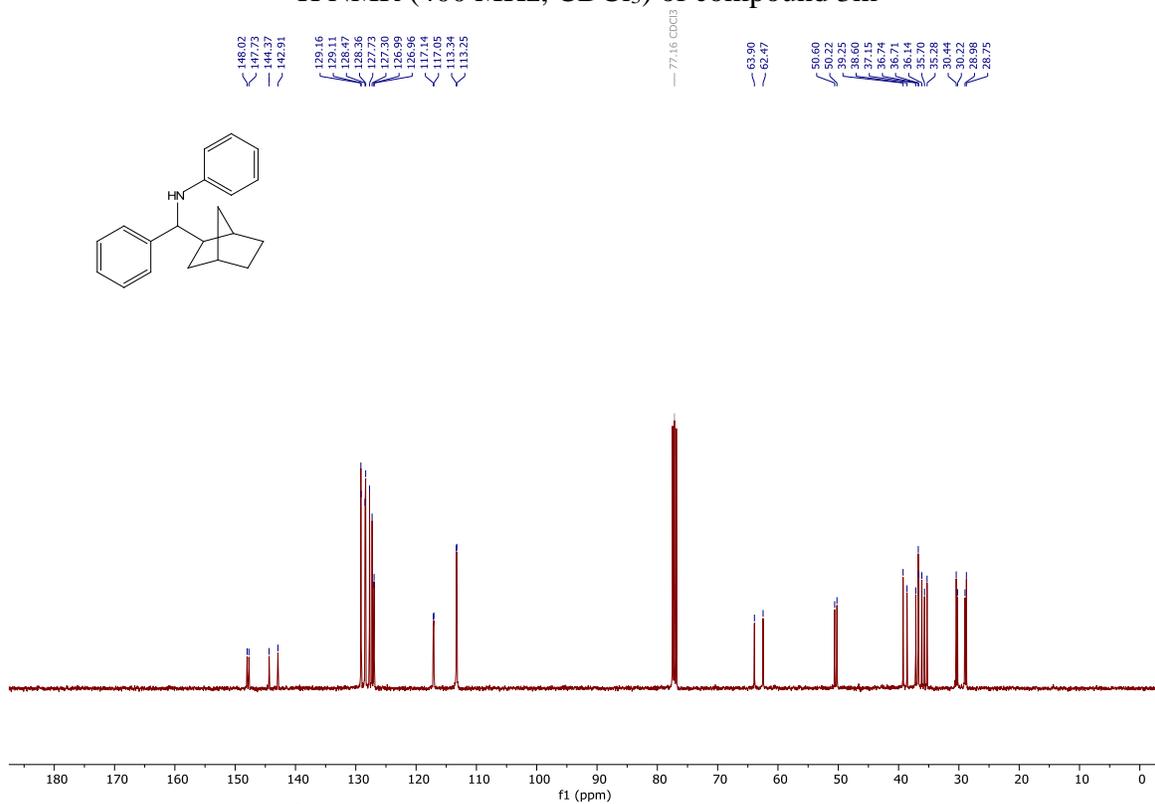
¹H NMR (400 MHz, CDCl₃) of compound 31



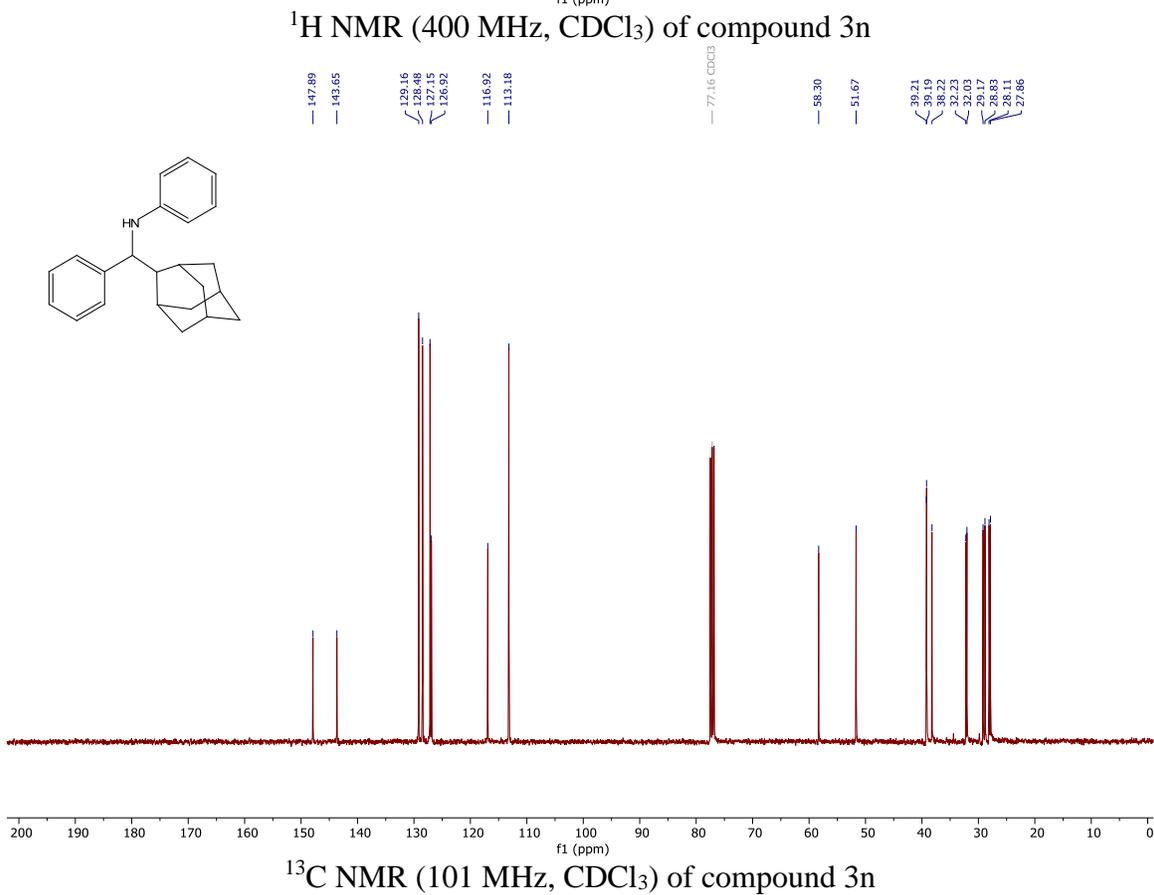
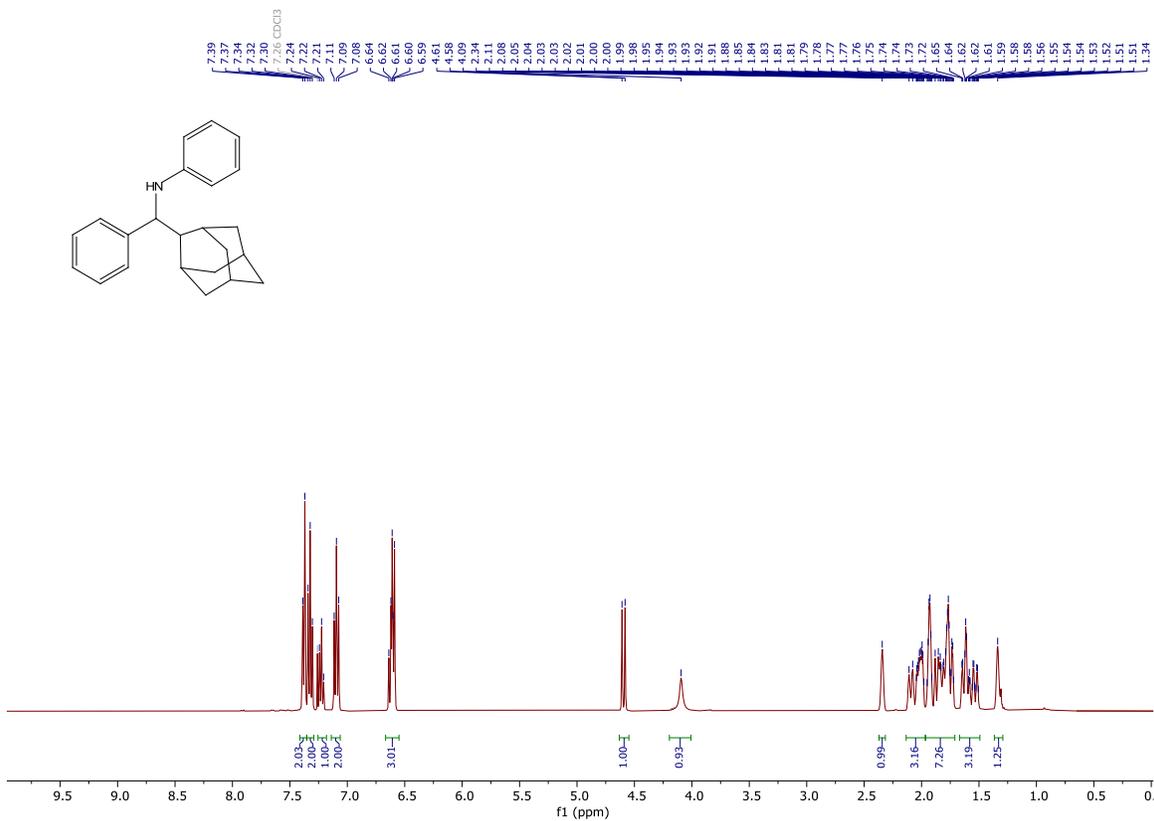
¹³C NMR (101 MHz, CDCl₃) of compound 31

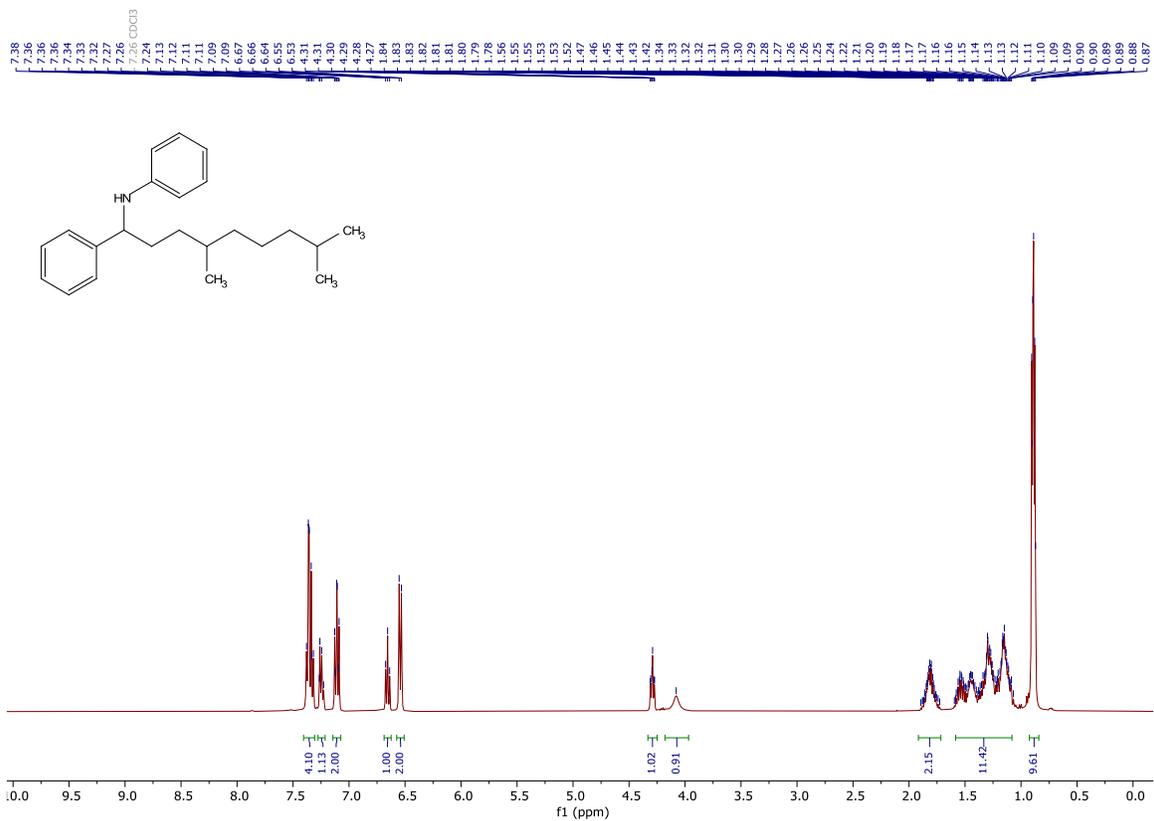


¹H NMR (400 MHz, CDCl₃) of compound 3m

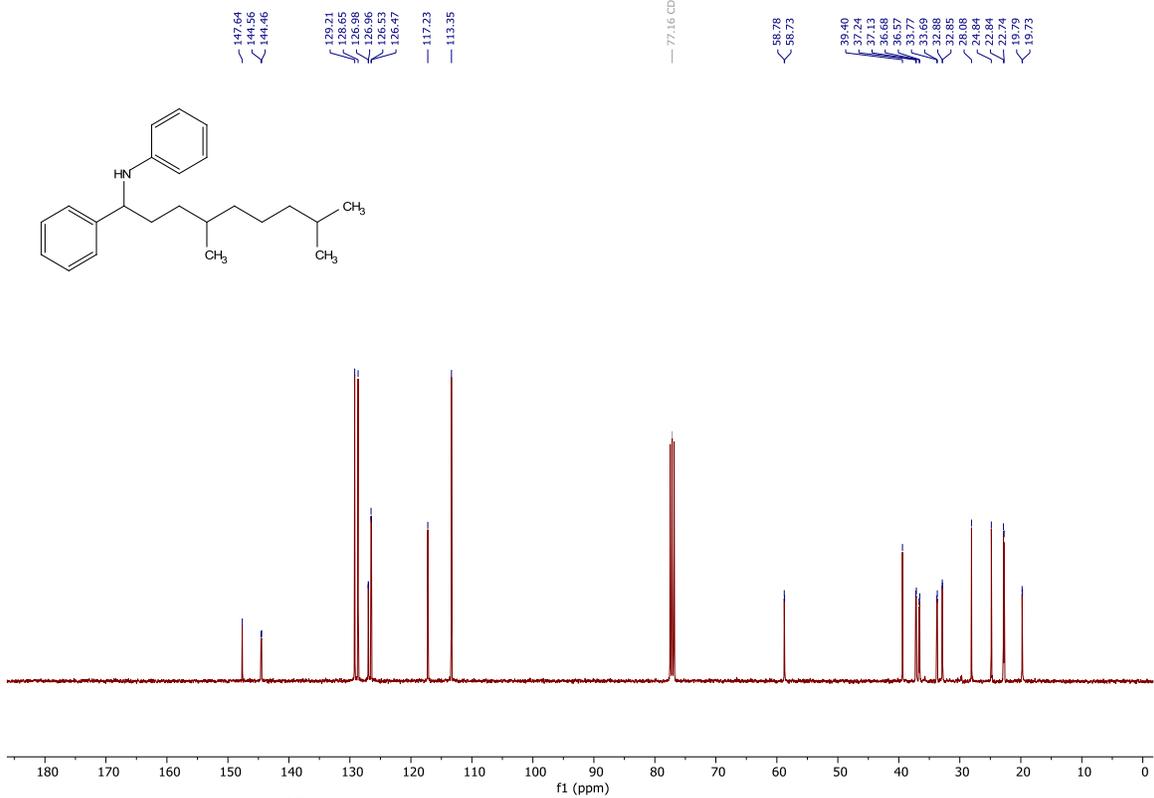


¹³C NMR (101 MHz, CDCl₃) of compound 3m

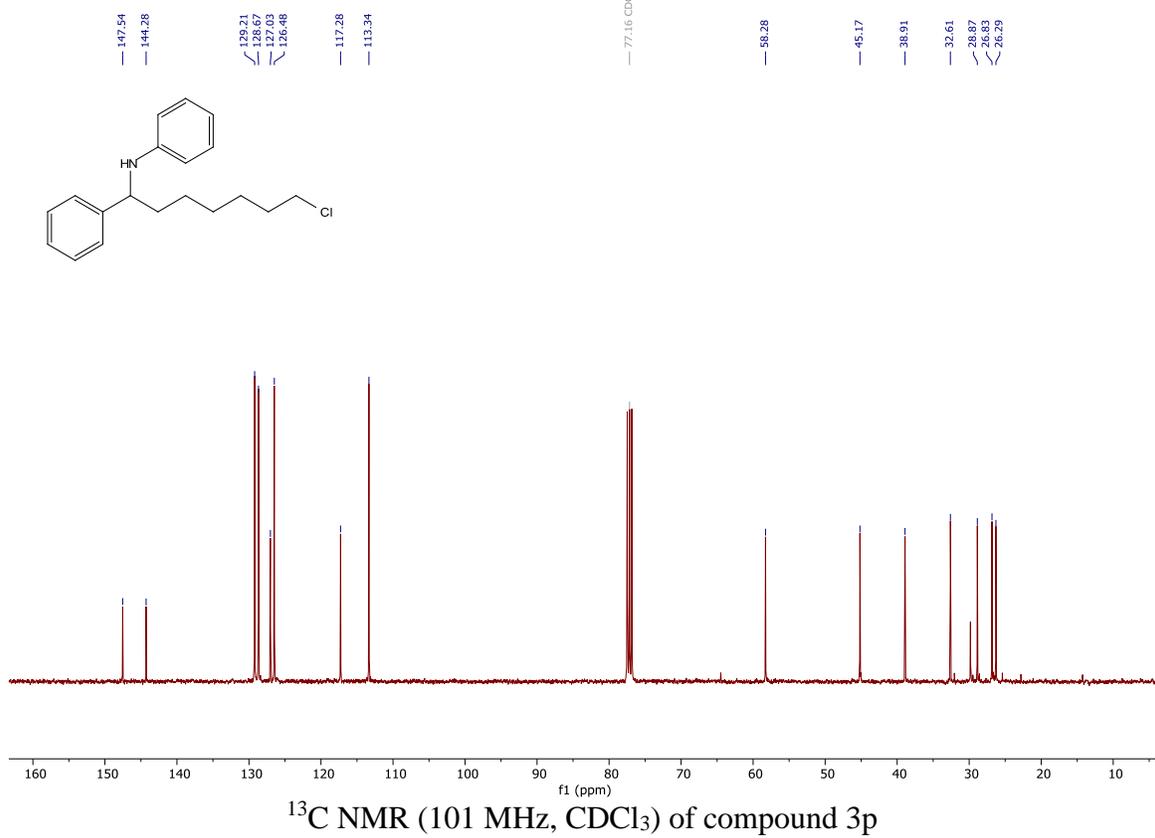
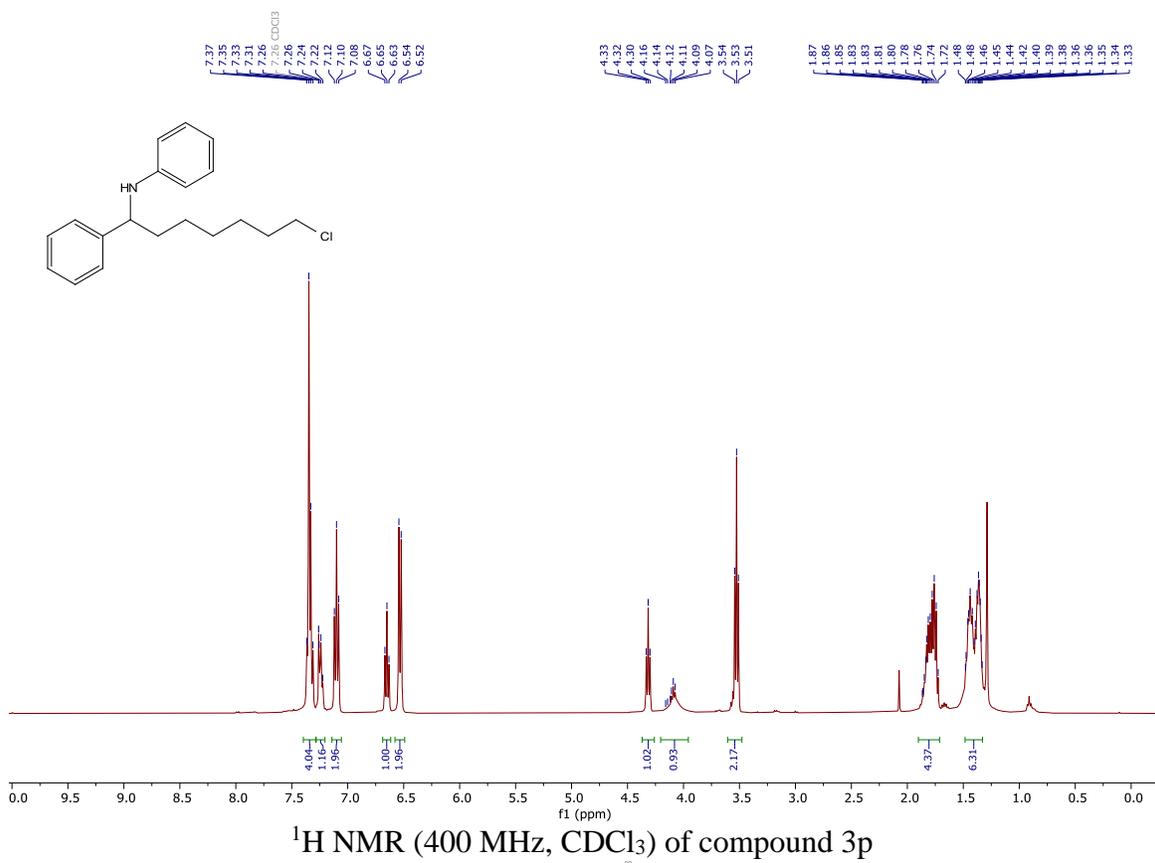


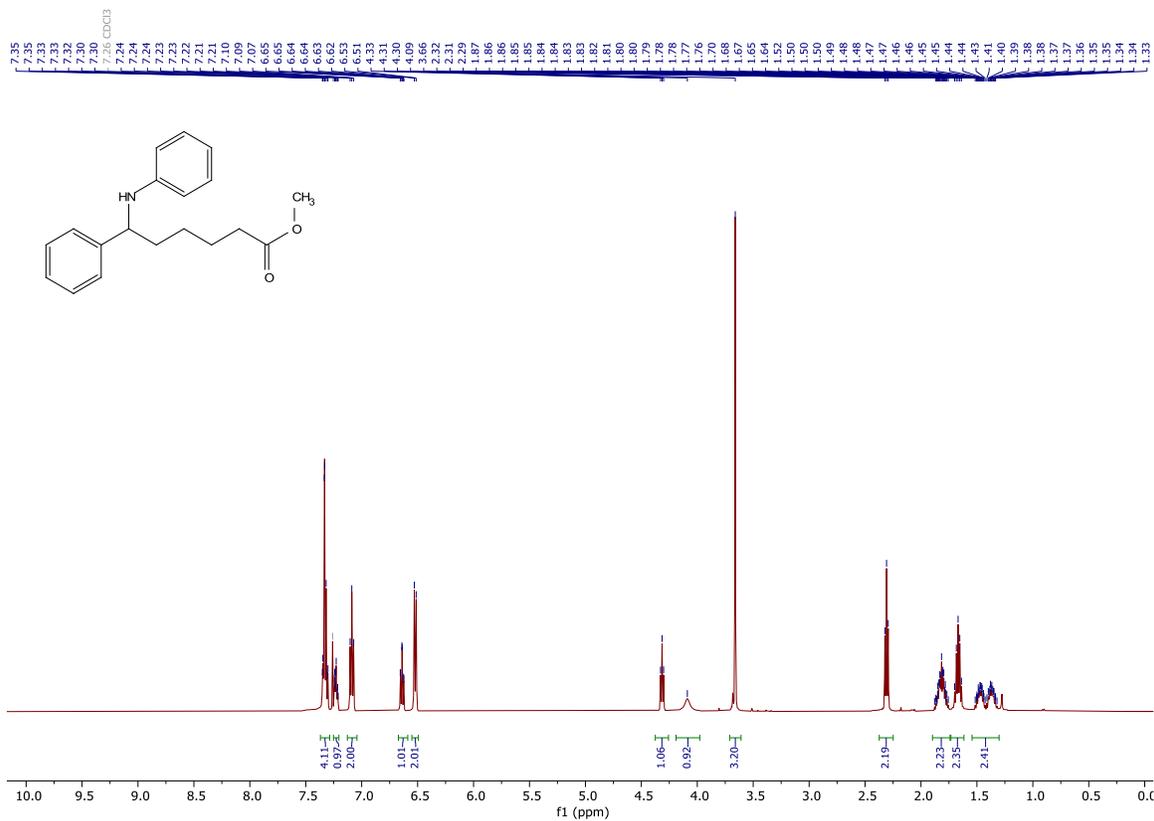


¹H NMR (400 MHz, CDCl₃) of compound 3o

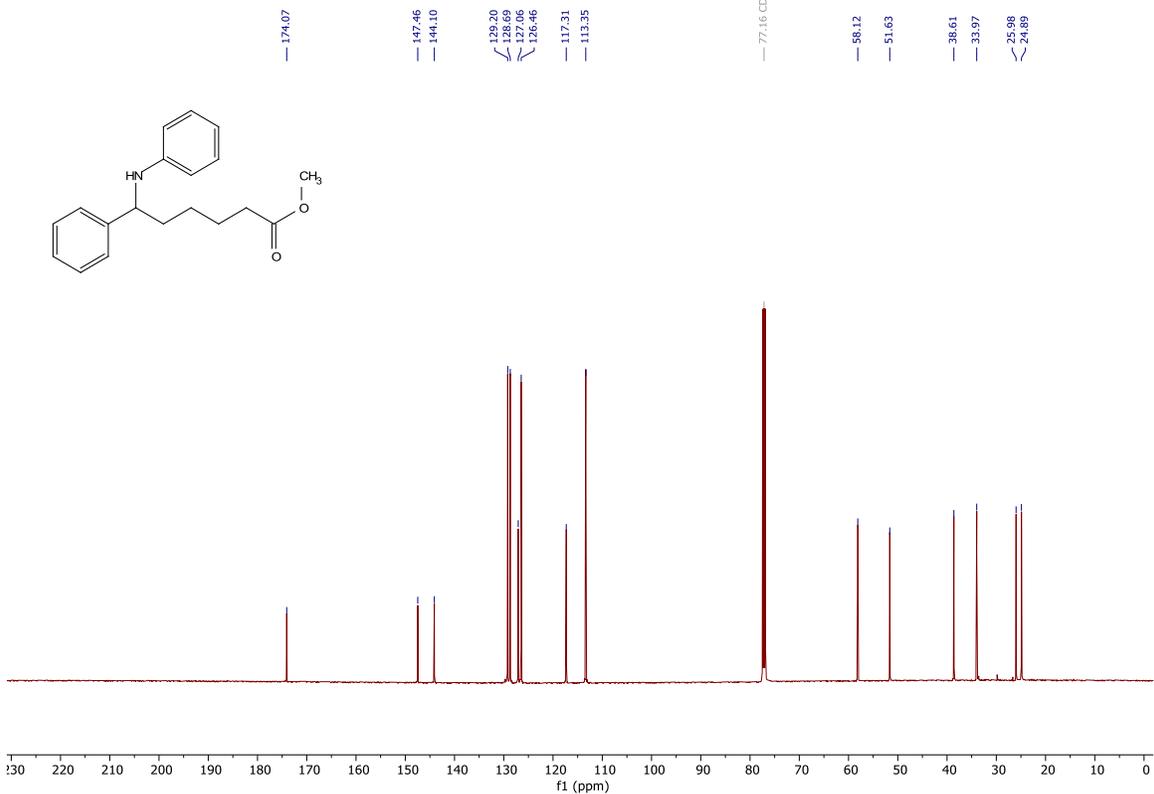


¹³C NMR (101 MHz, CDCl₃) of compound 3o

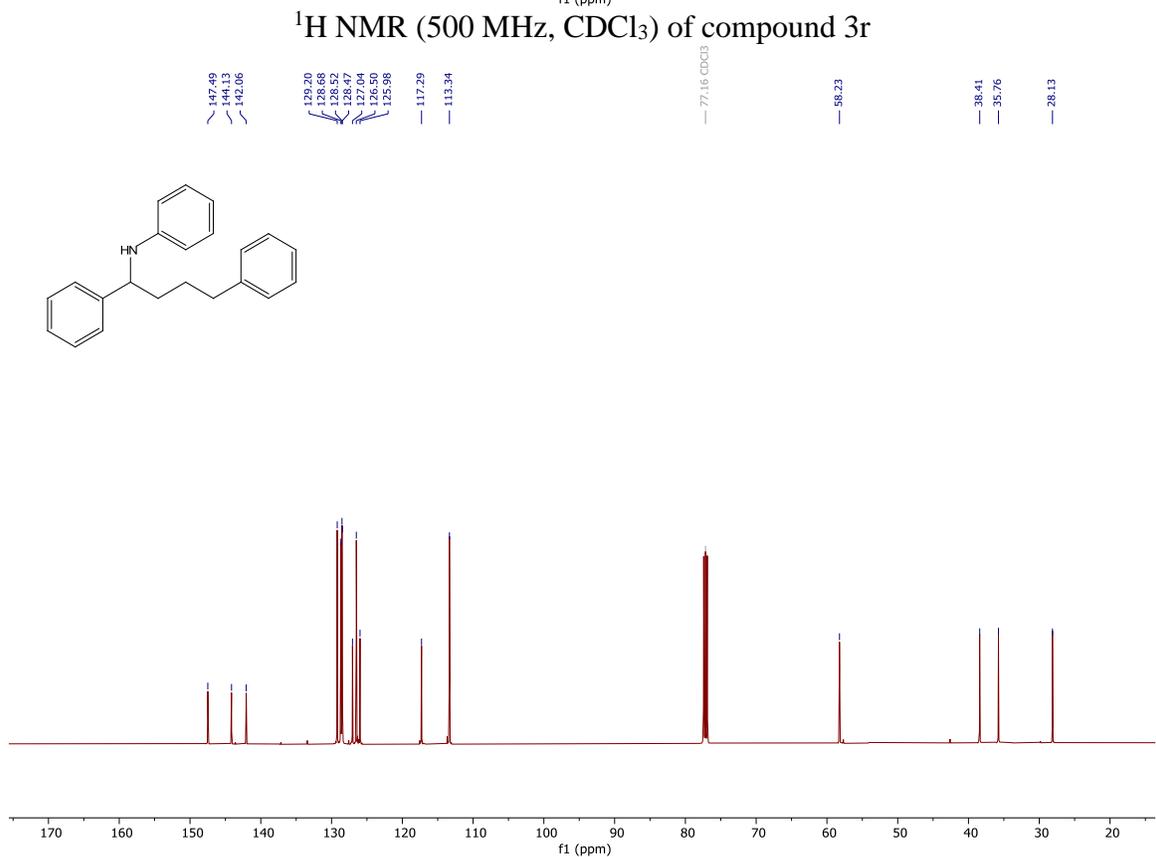
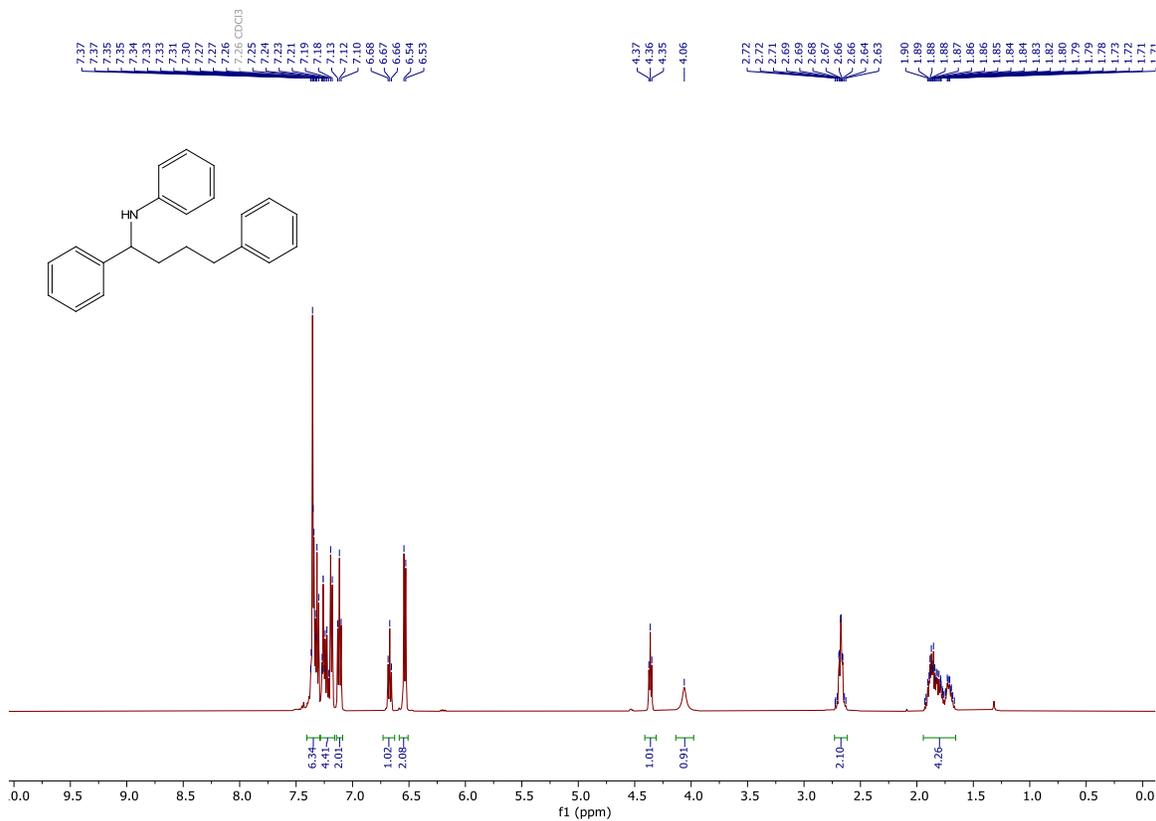


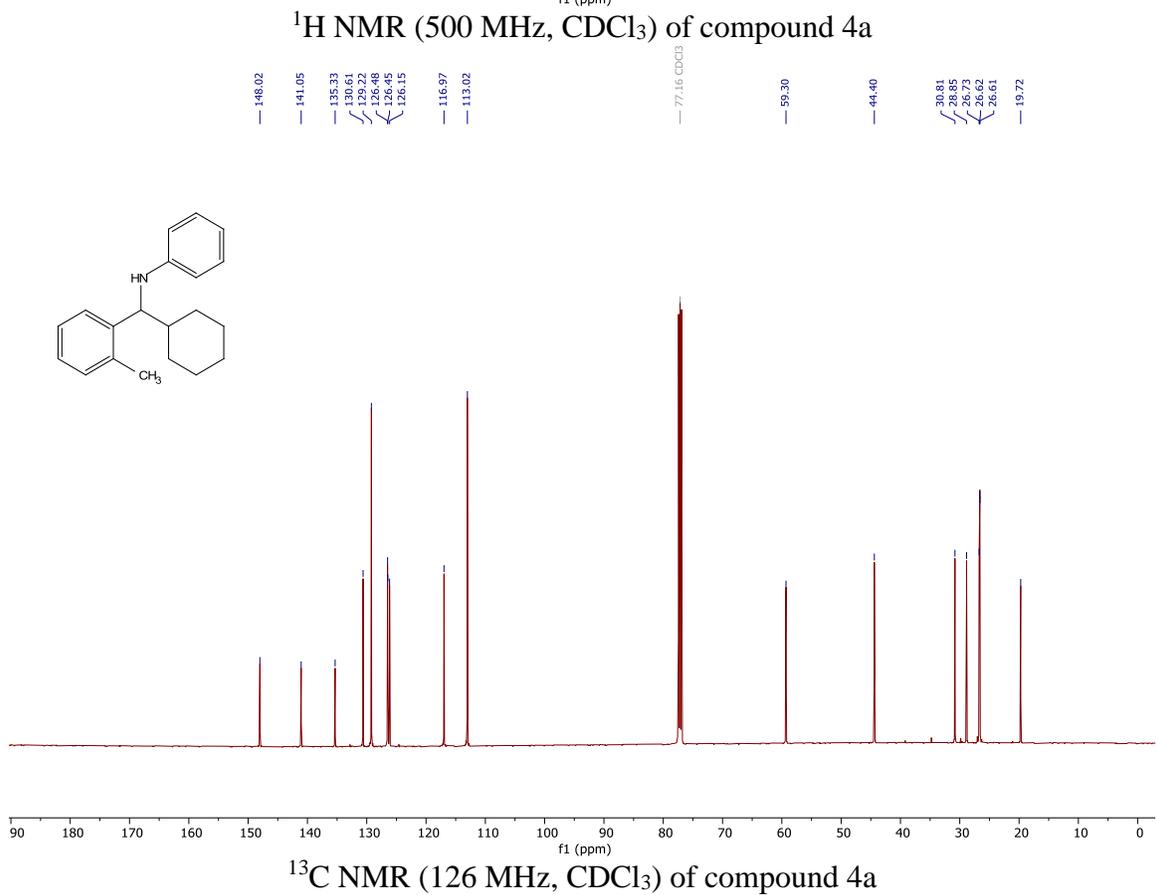
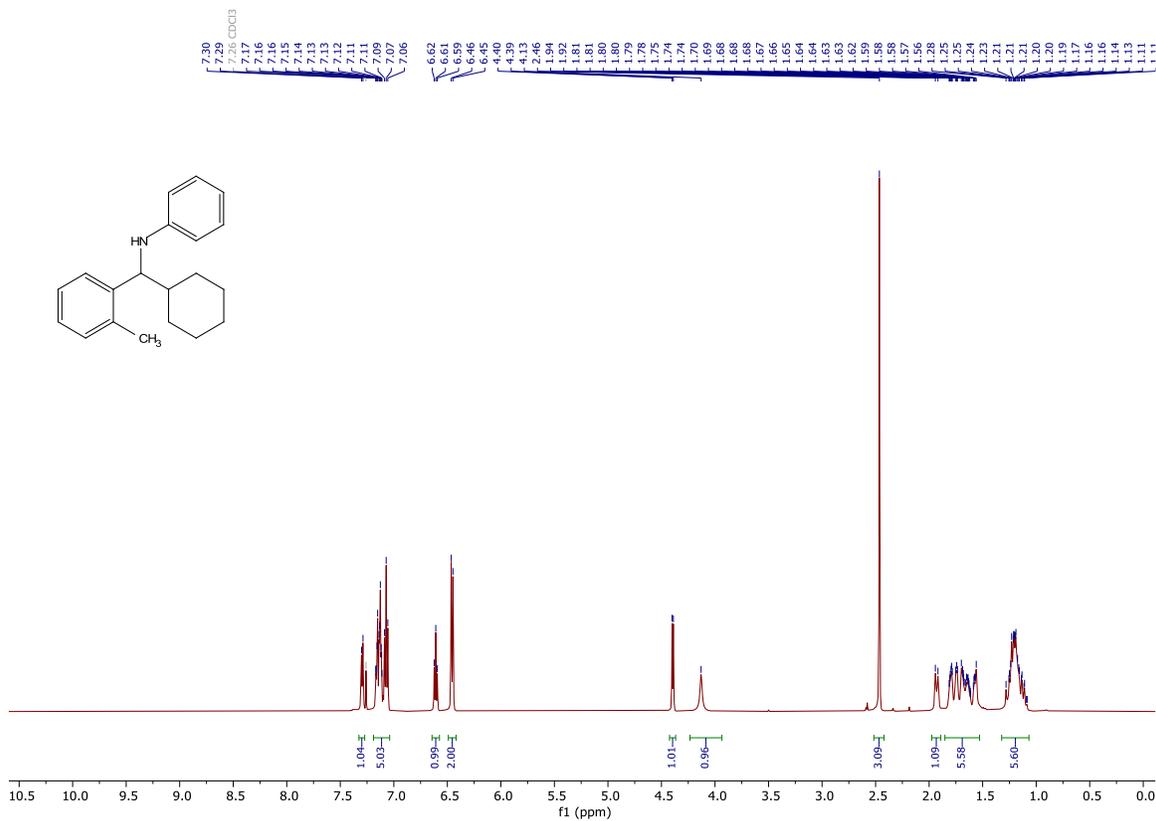


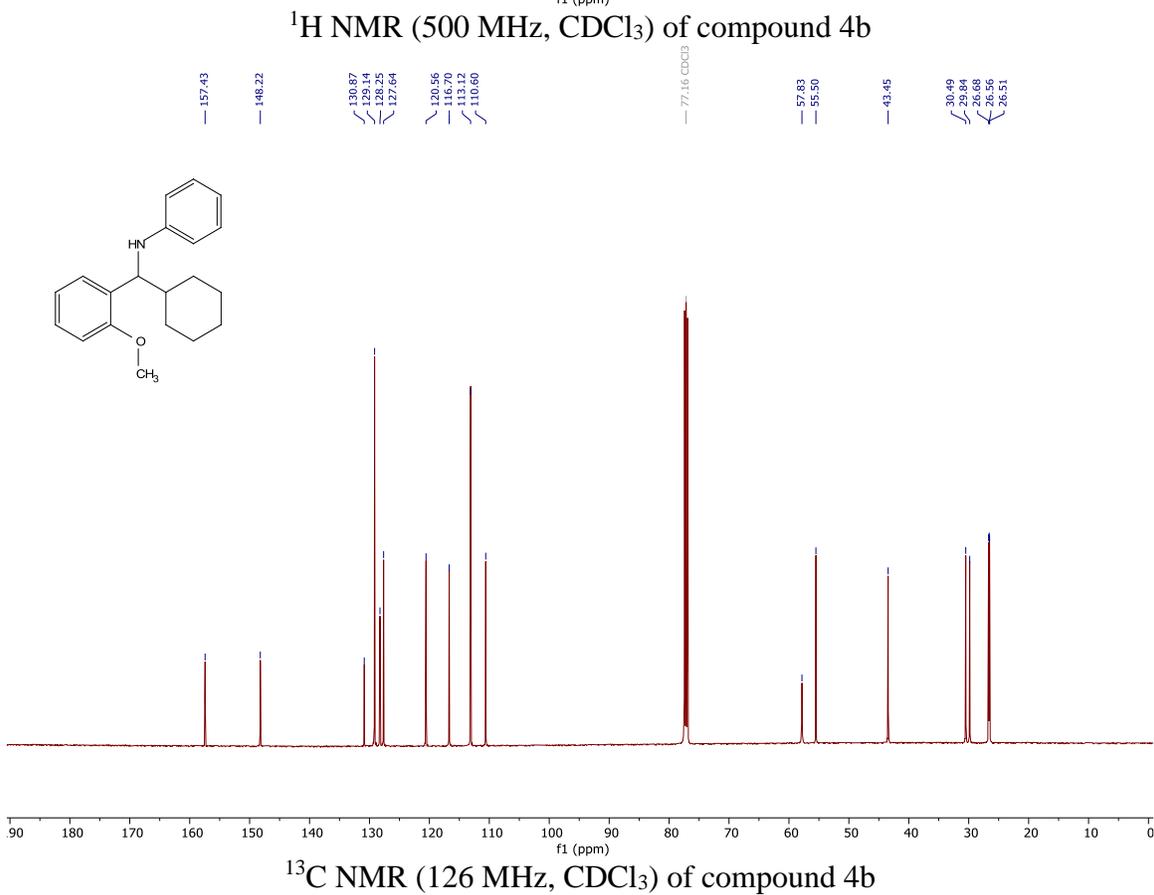
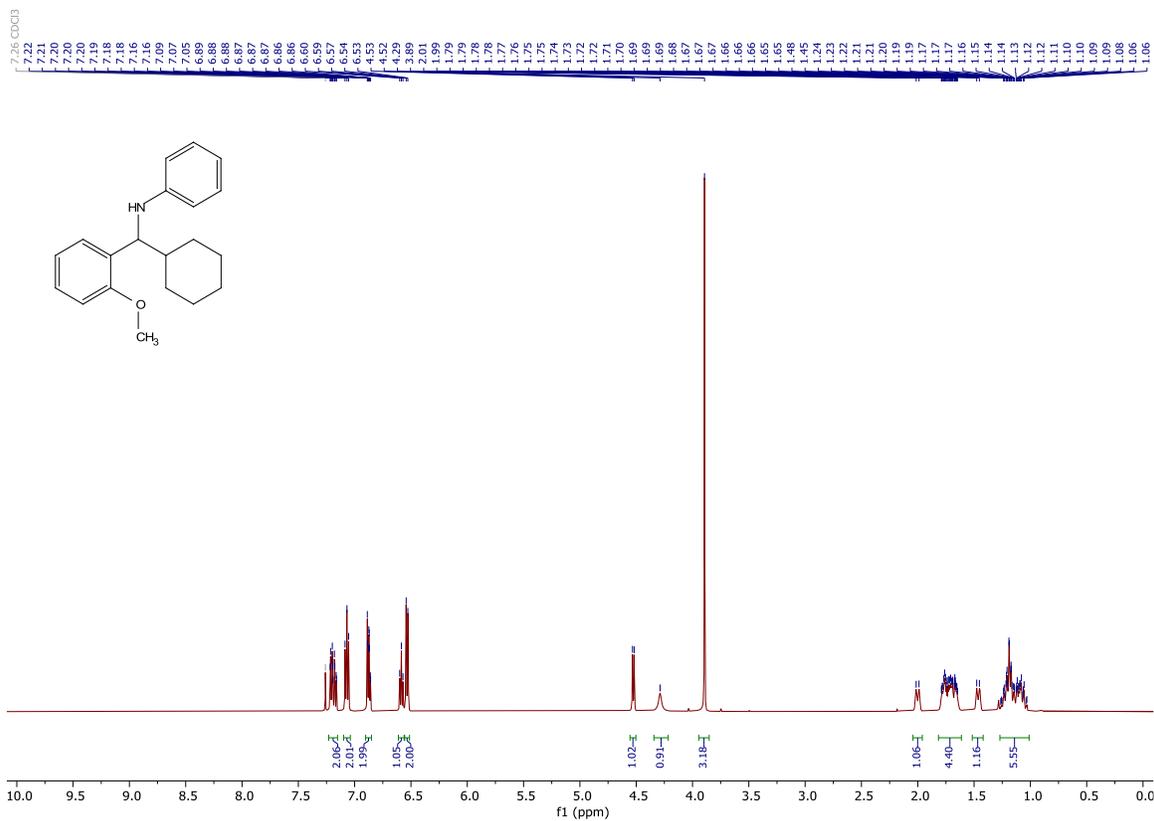
¹H NMR (500 MHz, CDCl₃) of compound 3q

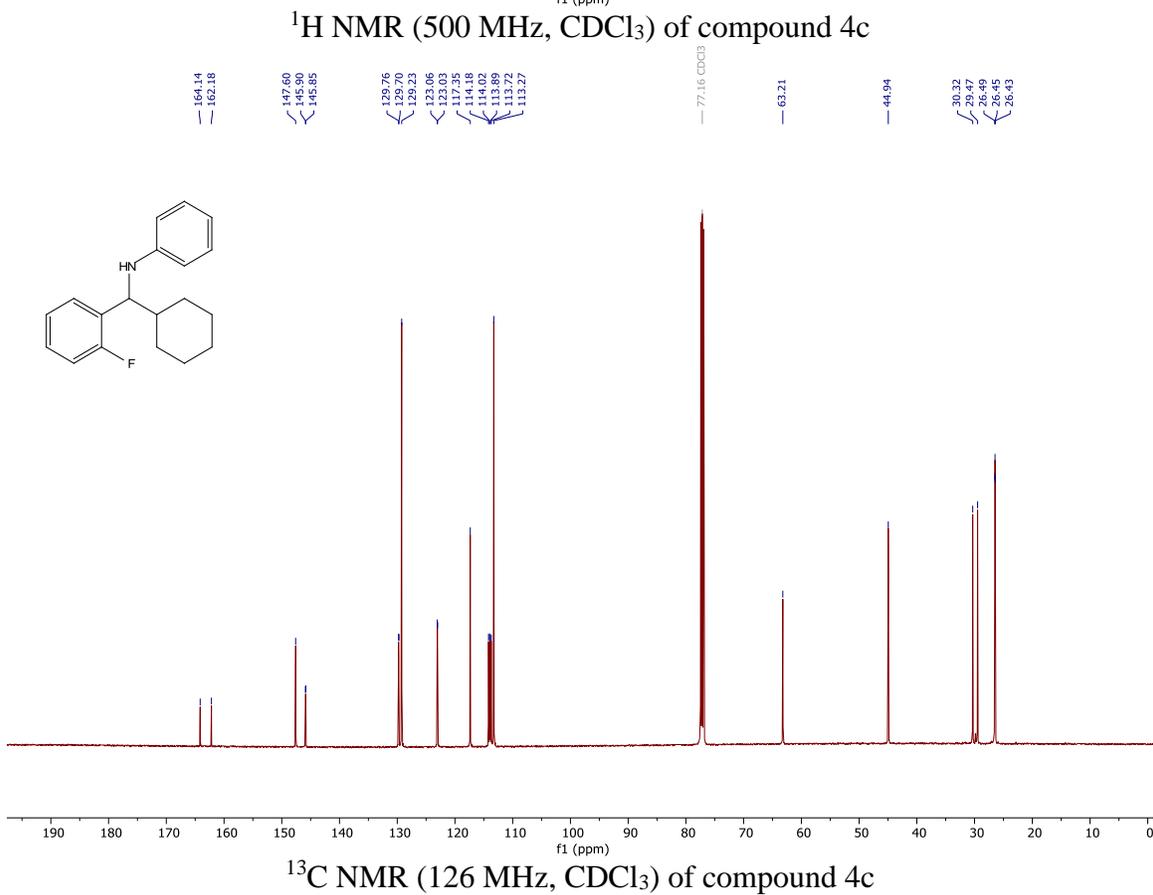
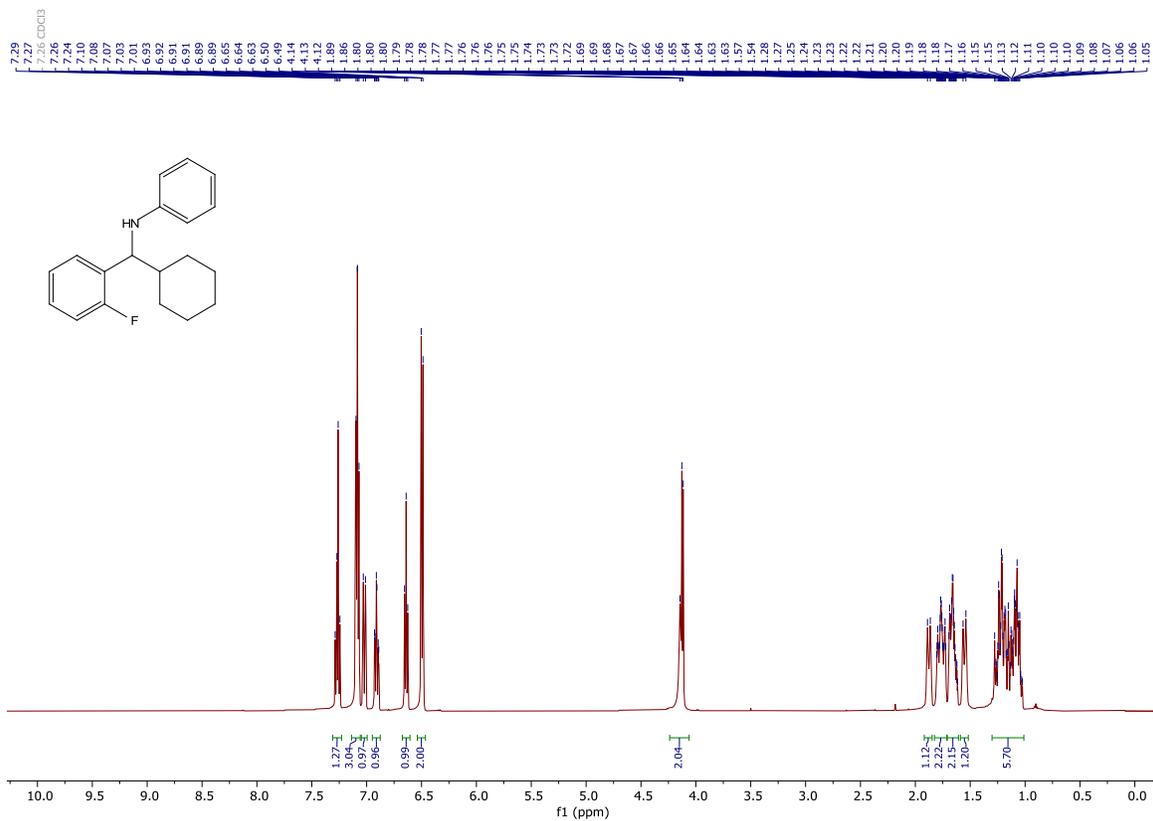


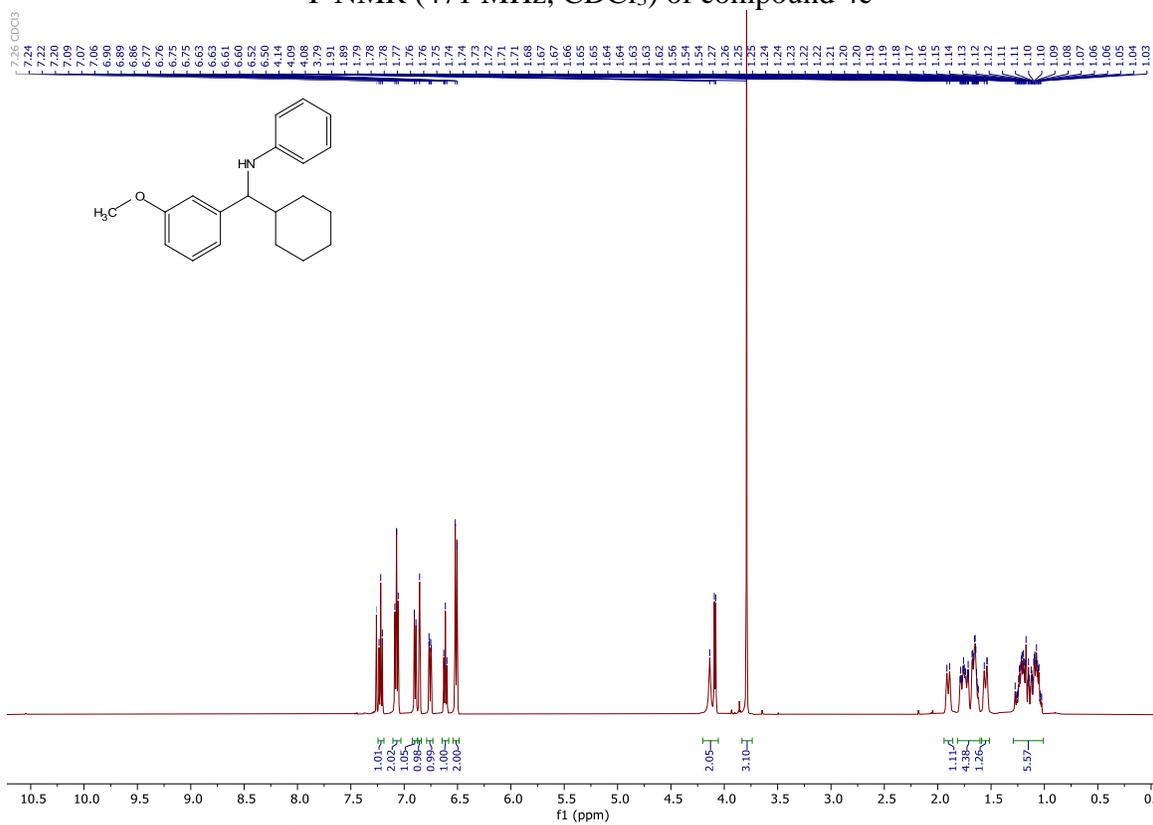
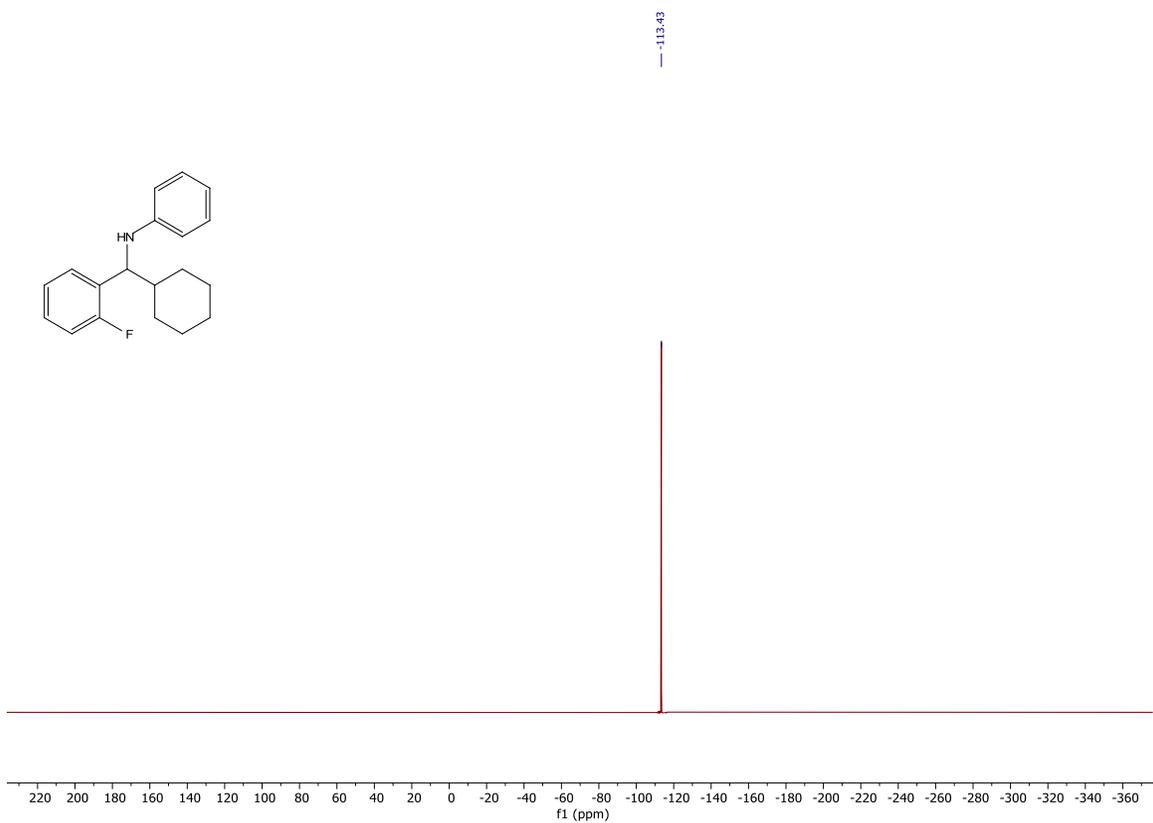
¹³C NMR (126 MHz, CDCl₃) of compound 3q

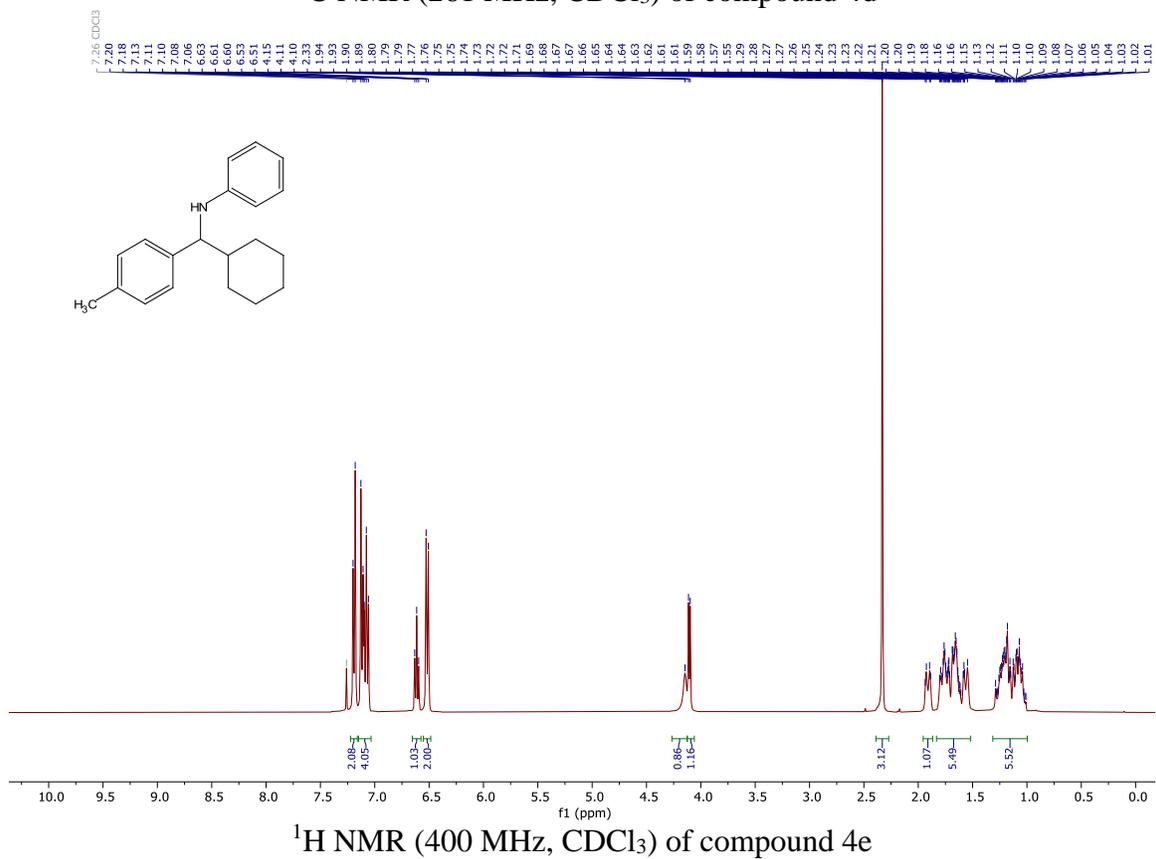
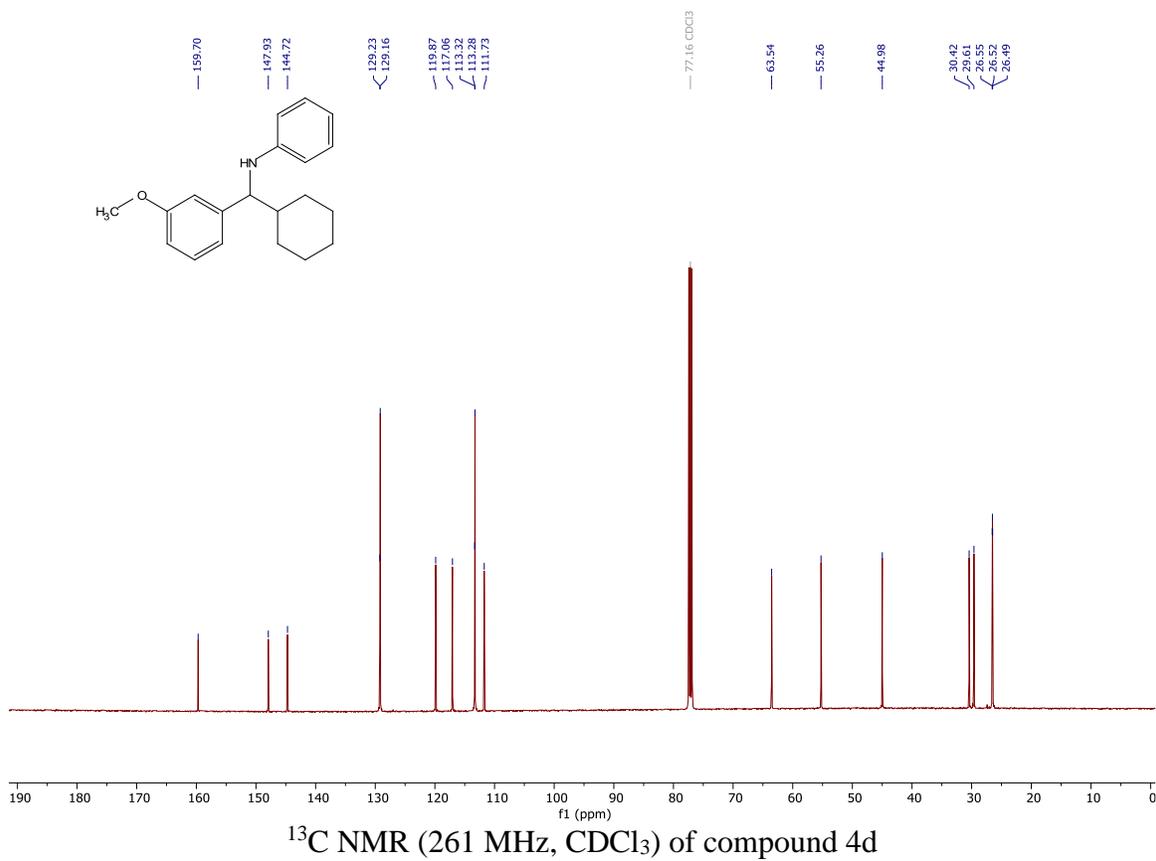


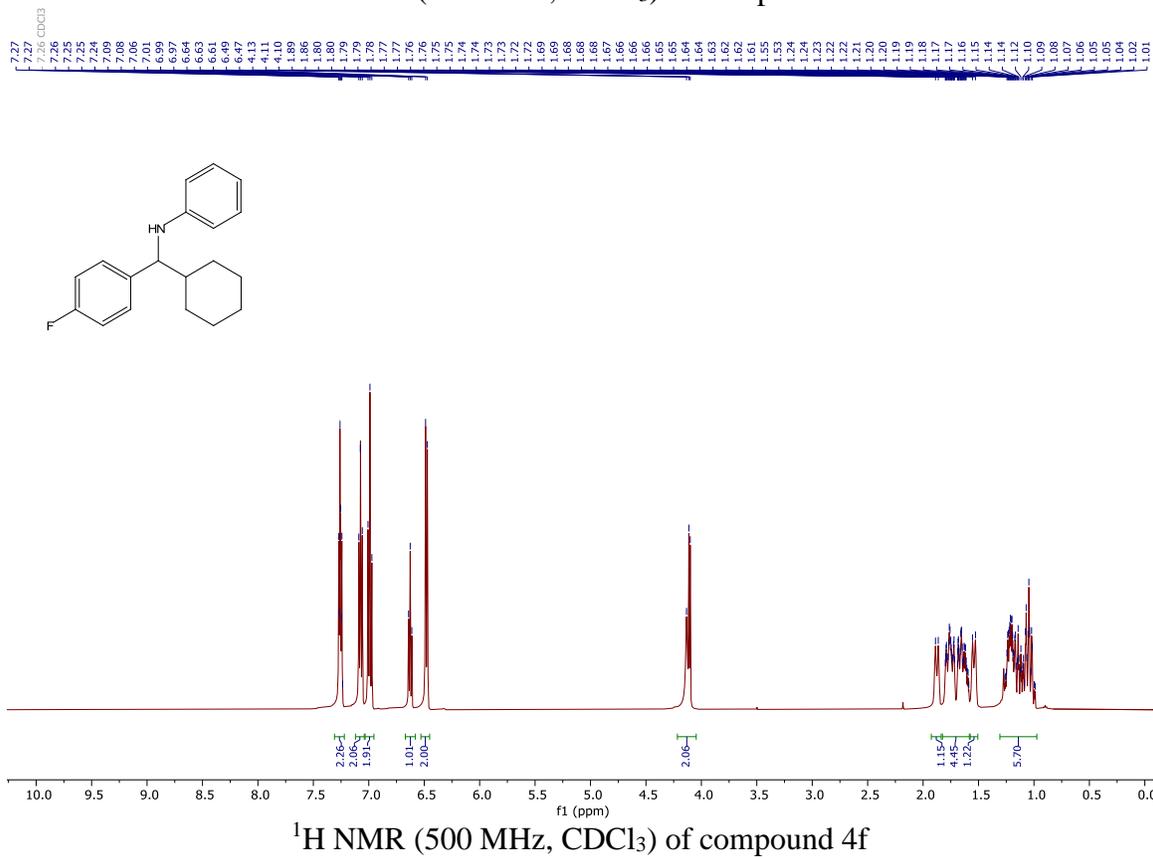
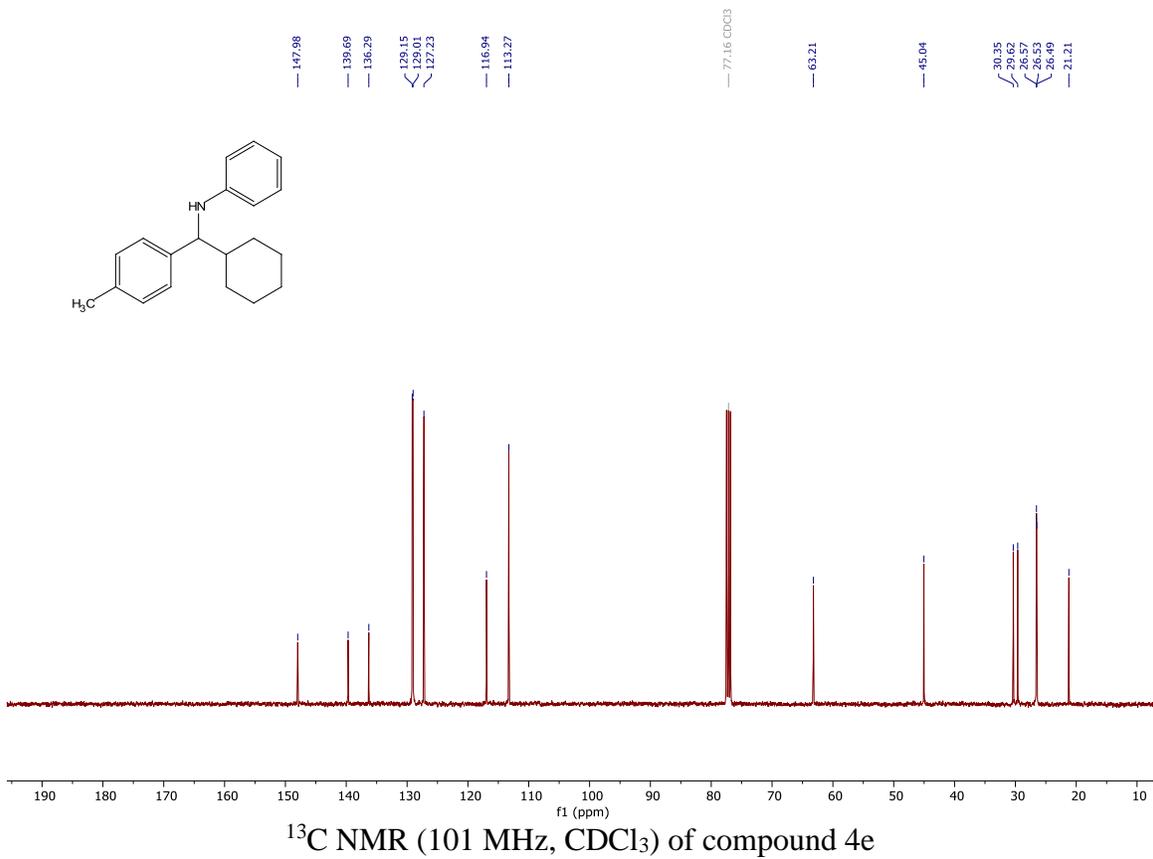


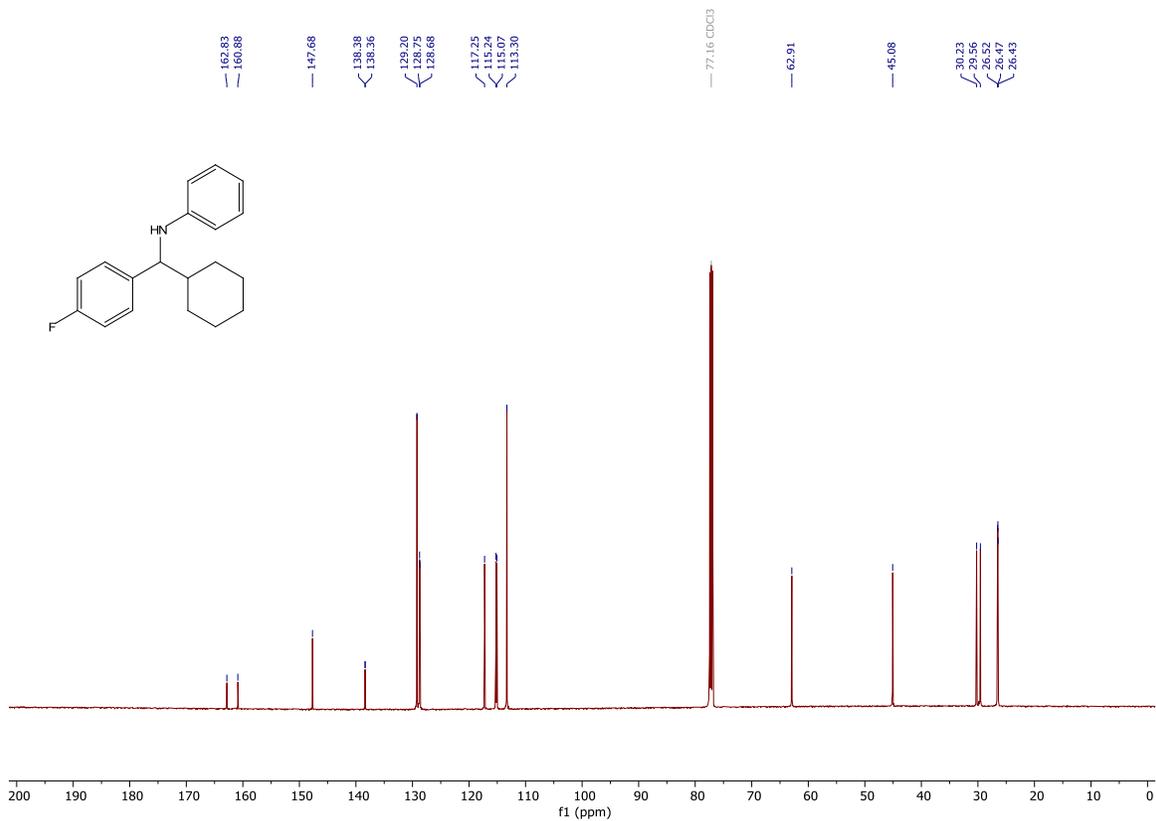




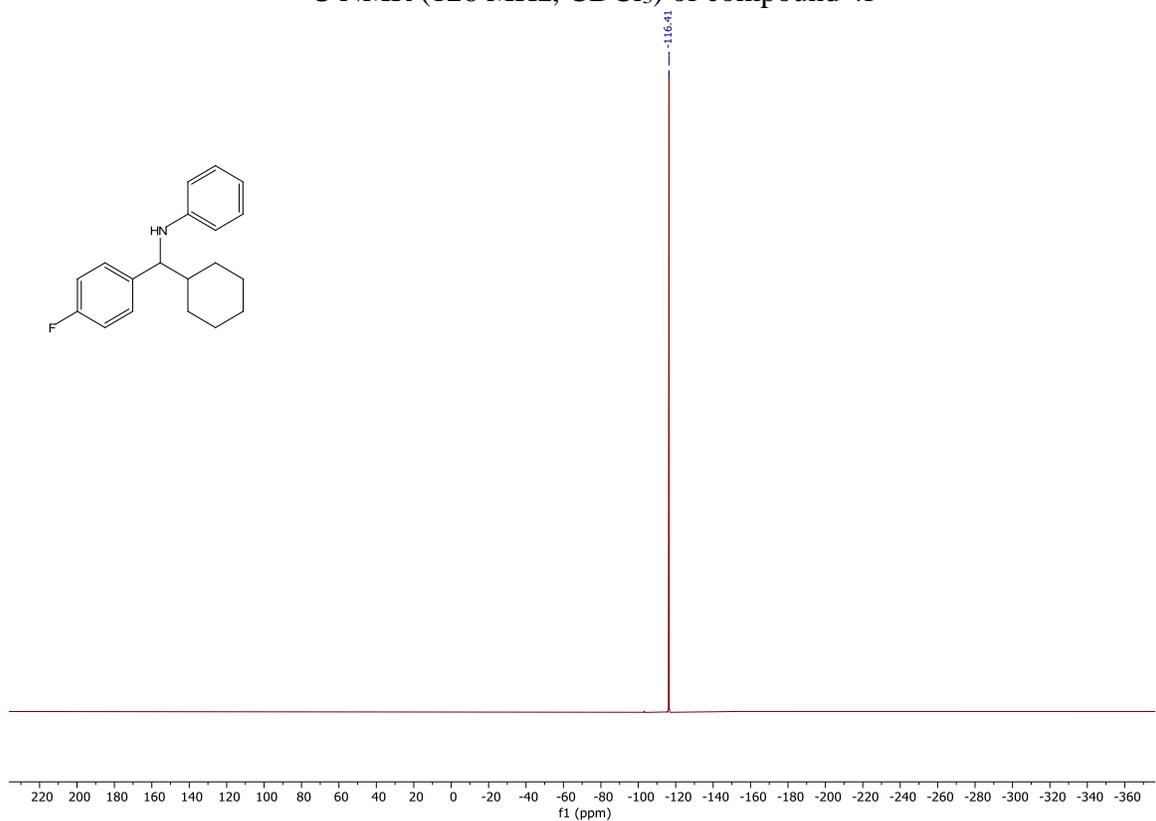




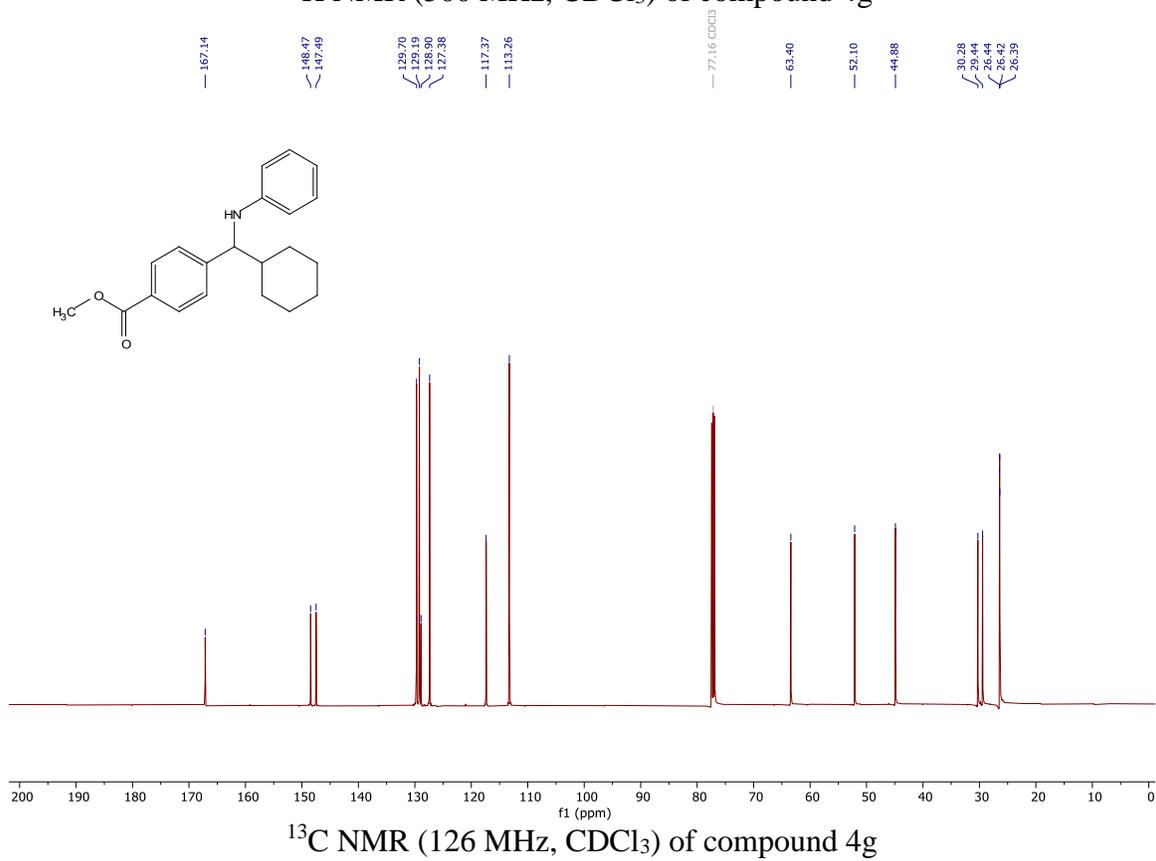
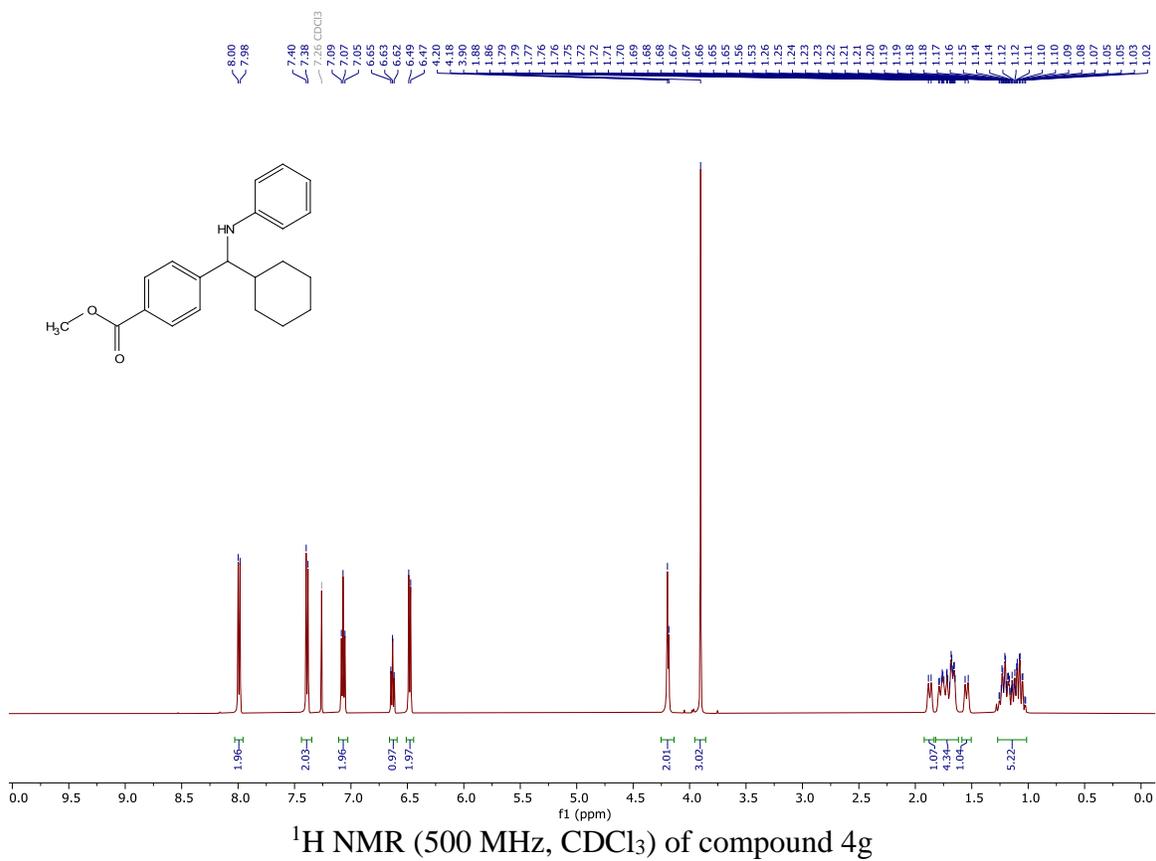


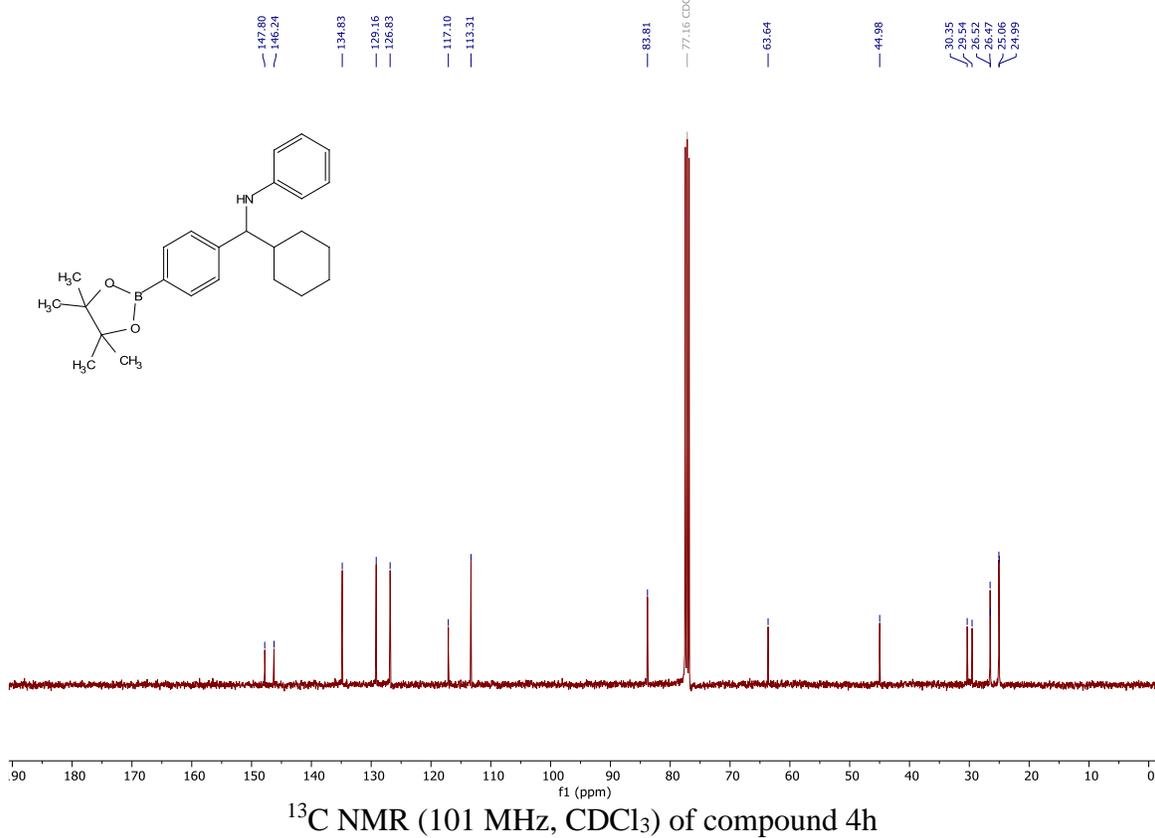
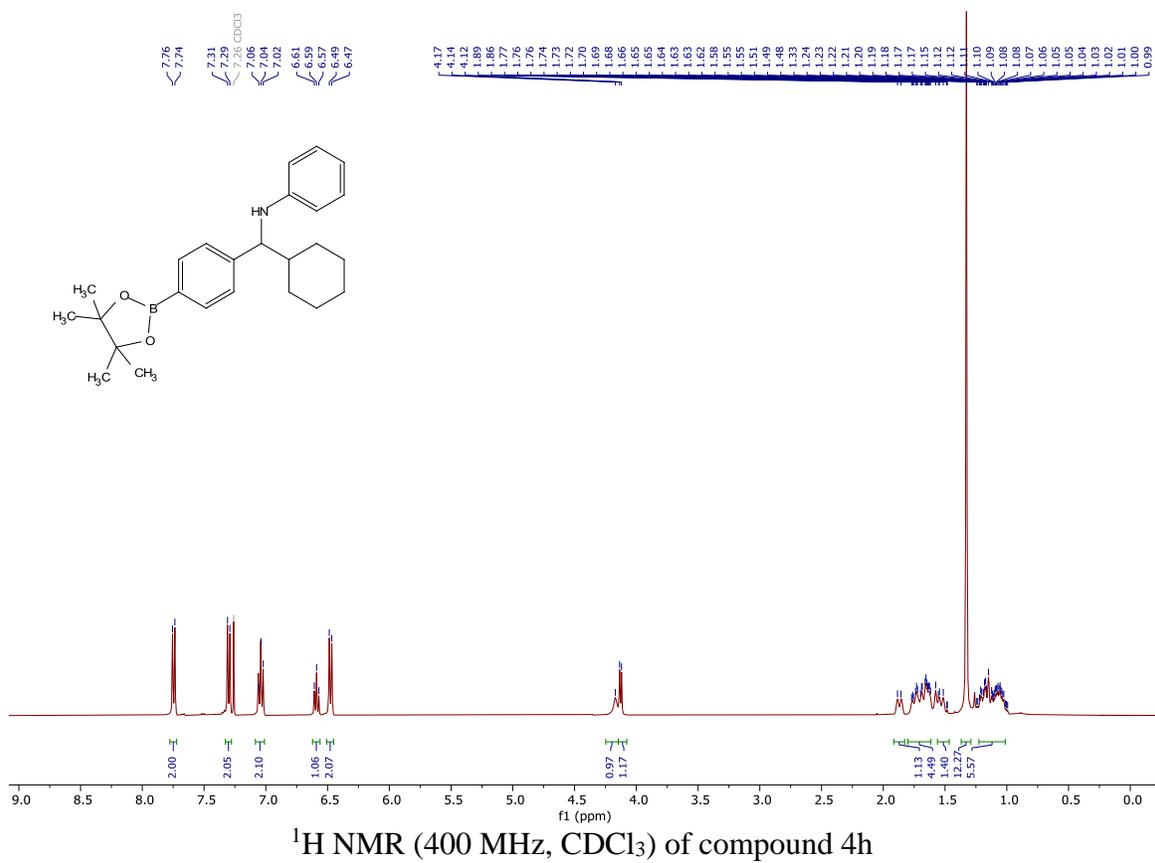


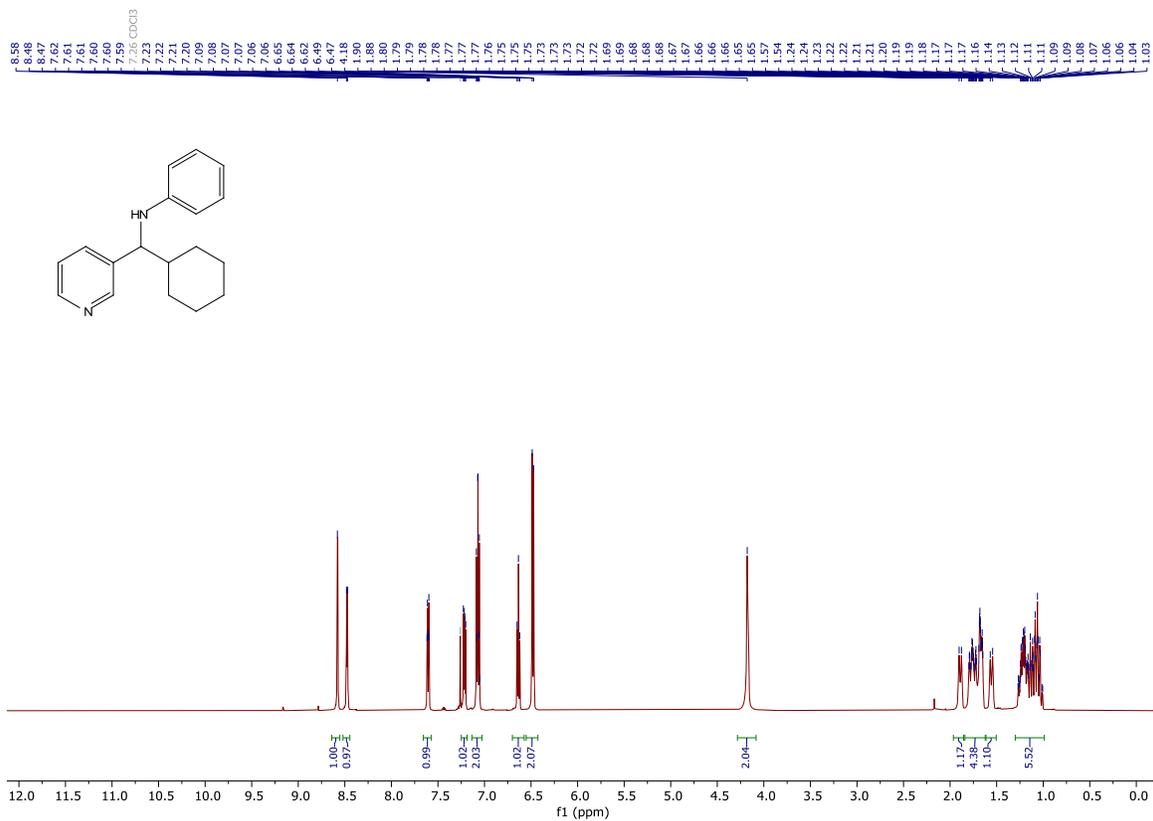
¹³C NMR (126 MHz, CDCl₃) of compound 4f



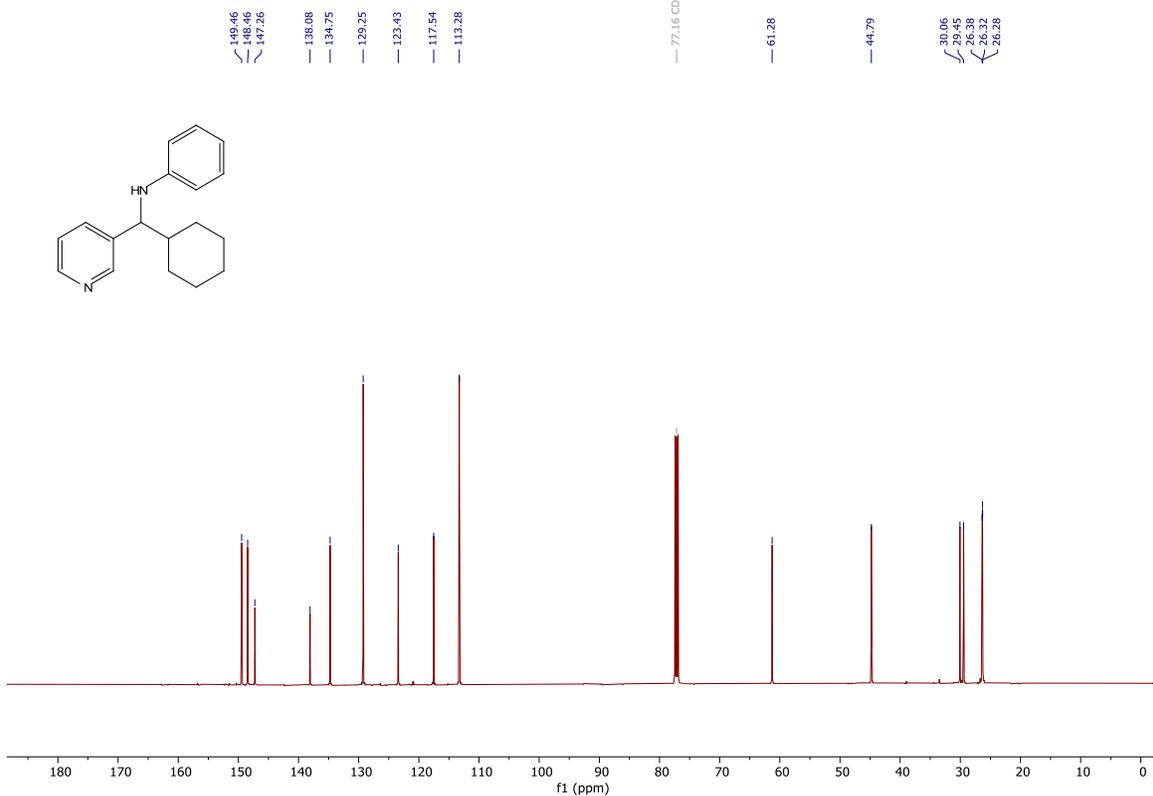
¹⁹F NMR (471 MHz, CDCl₃) of compound 4f





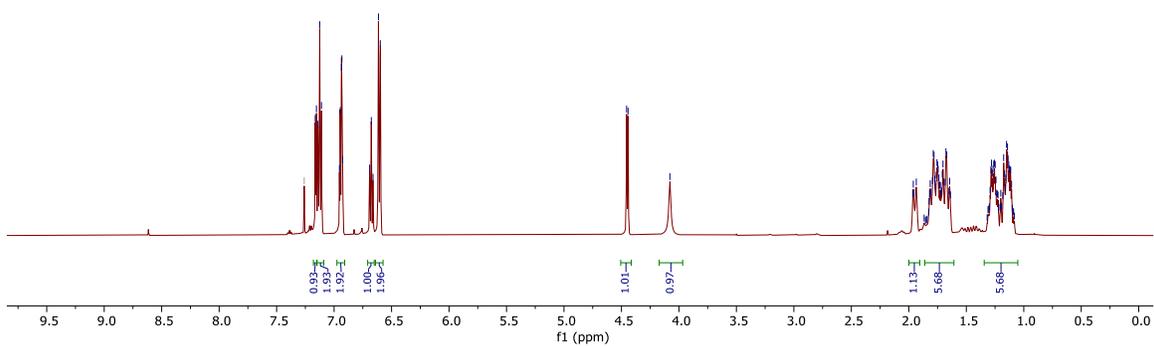
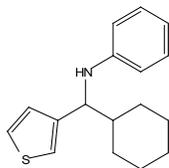


^1H NMR (500 MHz, CDCl_3) of compound 4i



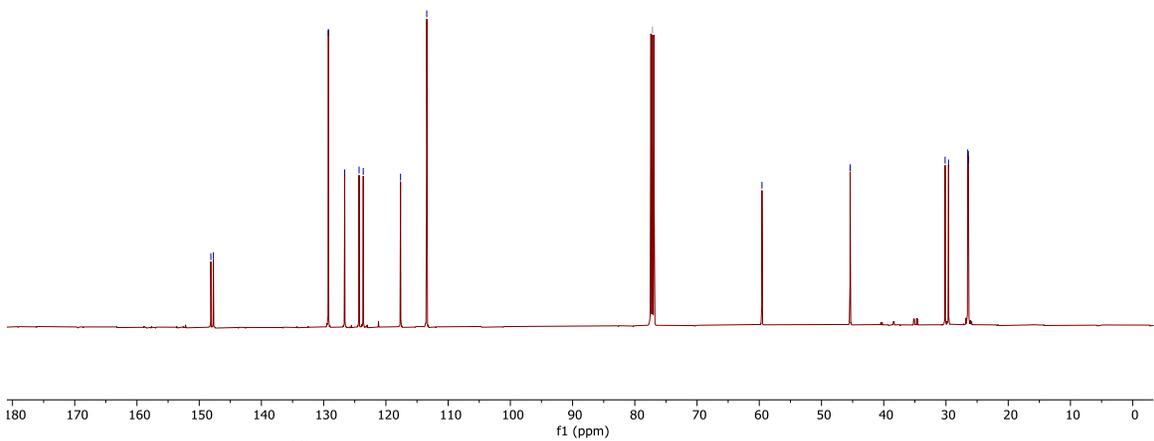
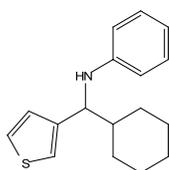
^{13}C NMR (126 MHz, CDCl_3) of compound 4i

7.26 CDCl₃
 7.16
 7.15
 7.14
 7.13
 7.11
 6.95
 6.94
 6.83
 6.83
 6.69
 6.68
 6.66
 6.60
 6.60
 4.46
 4.44
 4.08
 1.97
 1.95
 1.94
 1.83
 1.82
 1.82
 1.81
 1.79
 1.79
 1.78
 1.77
 1.77
 1.76
 1.76
 1.75
 1.74
 1.74
 1.73
 1.73
 1.72
 1.72
 1.71
 1.71
 1.70
 1.70
 1.68
 1.67
 1.65
 1.64
 1.64
 1.31
 1.31
 1.30
 1.29
 1.28
 1.28
 1.27
 1.27
 1.26
 1.25
 1.25
 1.24
 1.24
 1.23
 1.23
 1.22
 1.22
 1.21
 1.21
 1.20
 1.19
 1.18
 1.17
 1.17
 1.16
 1.16
 1.15
 1.15
 1.14
 1.14
 1.13
 1.13
 1.12
 1.12
 1.11
 1.11
 1.10
 1.09
 1.08

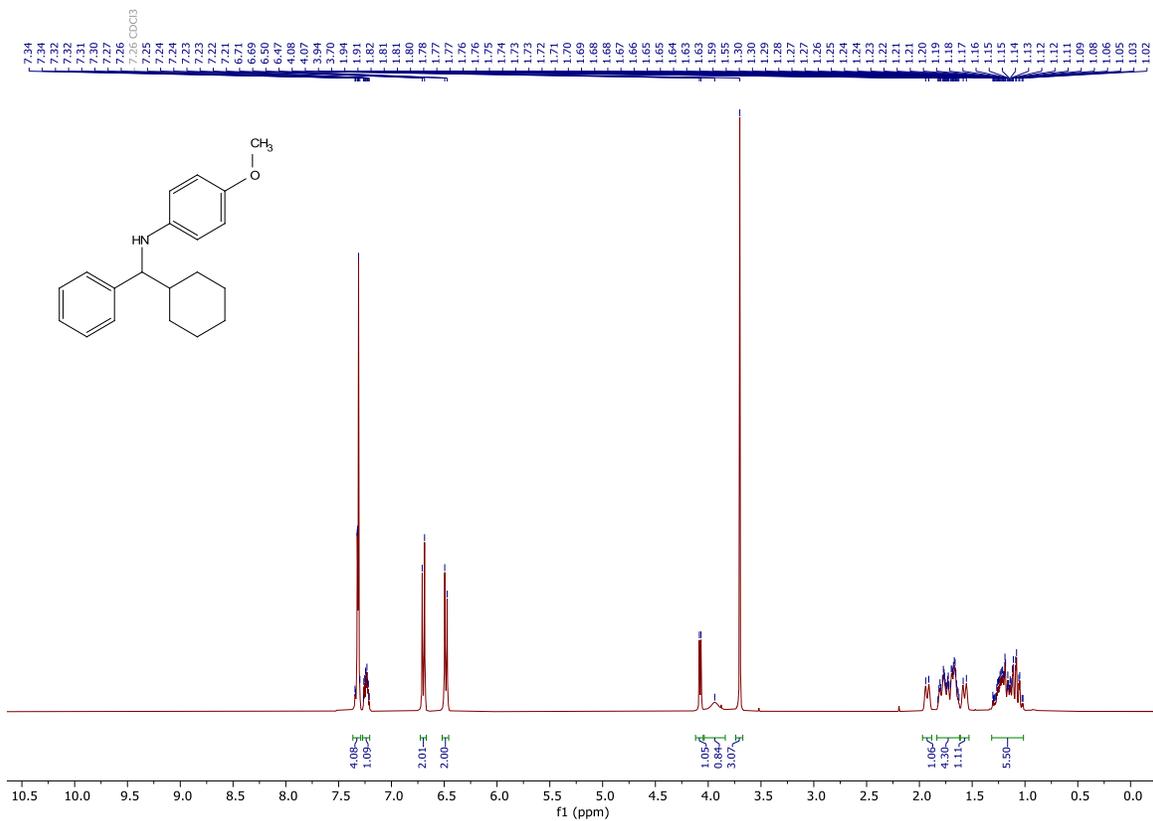


¹H NMR (500 MHz, CDCl₃) of compound 4j

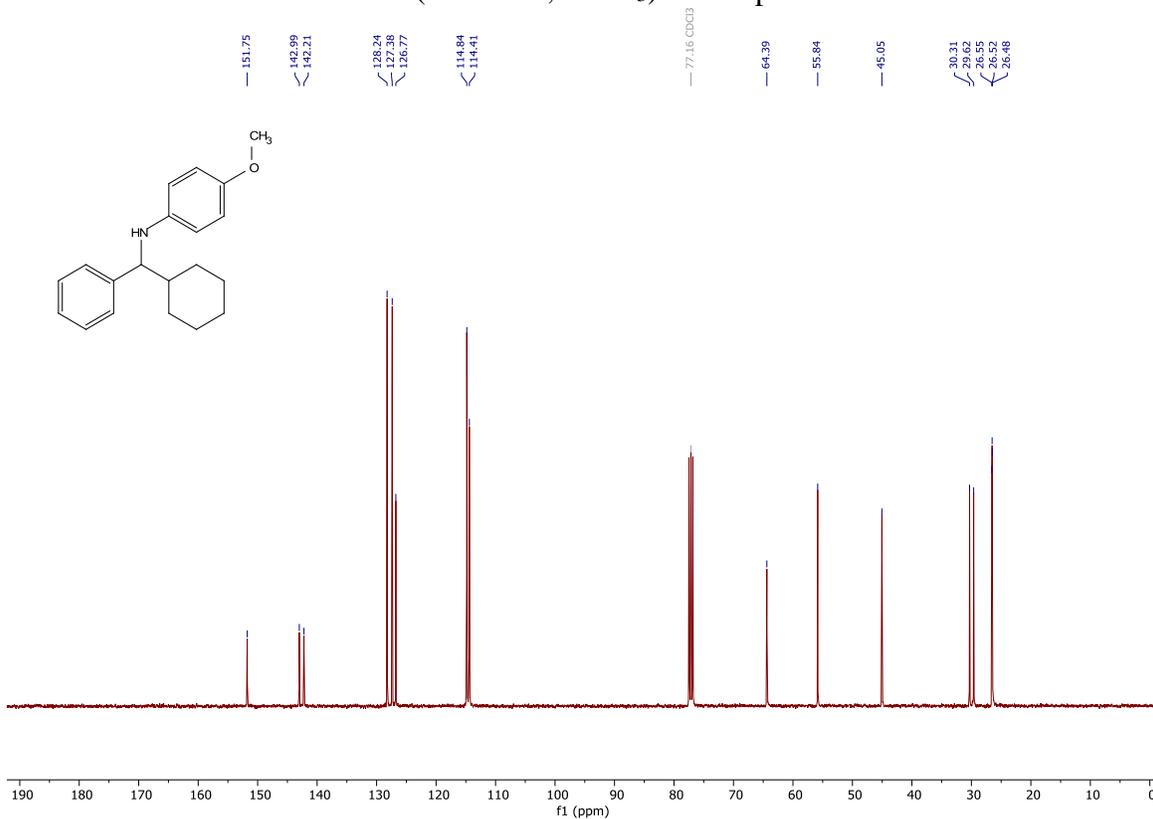
148.12
 147.72
 129.24
 126.62
 124.31
 123.64
 117.64
 113.43
 77.16 CDCl₃
 59.57
 45.40
 30.14
 29.60
 26.50
 26.41
 26.36



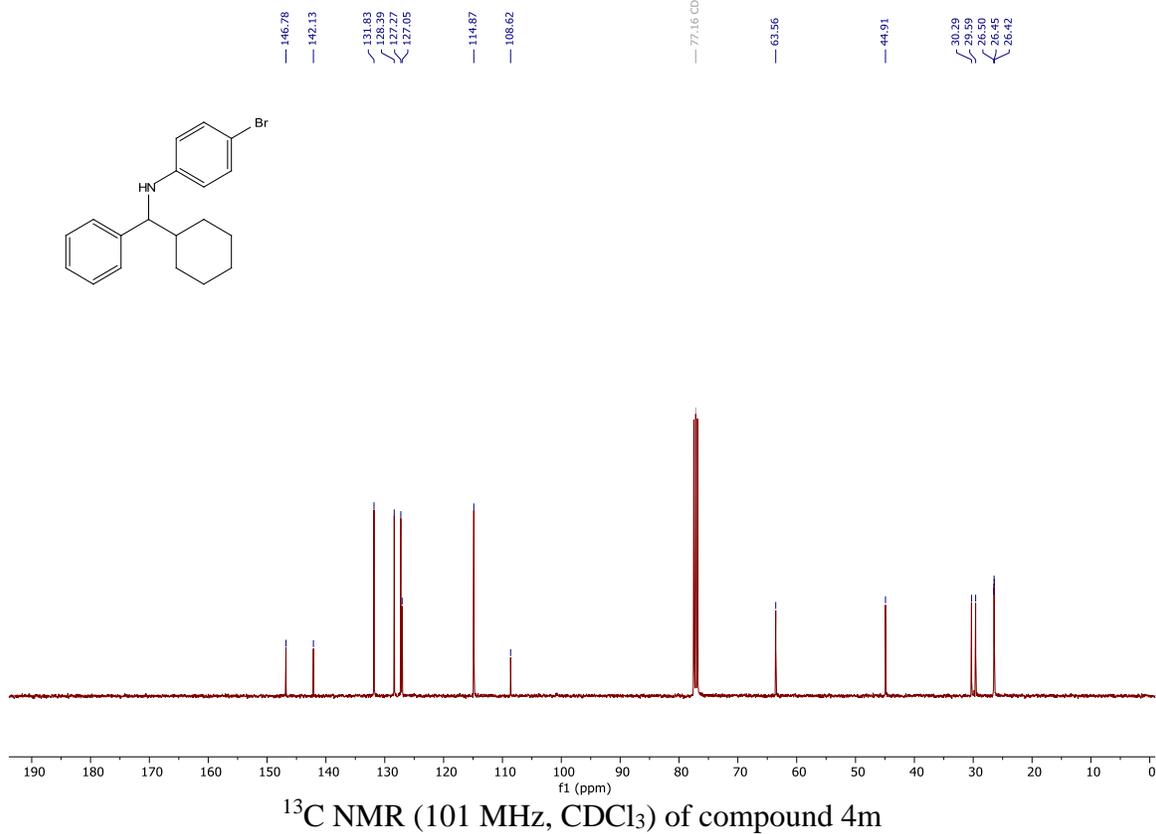
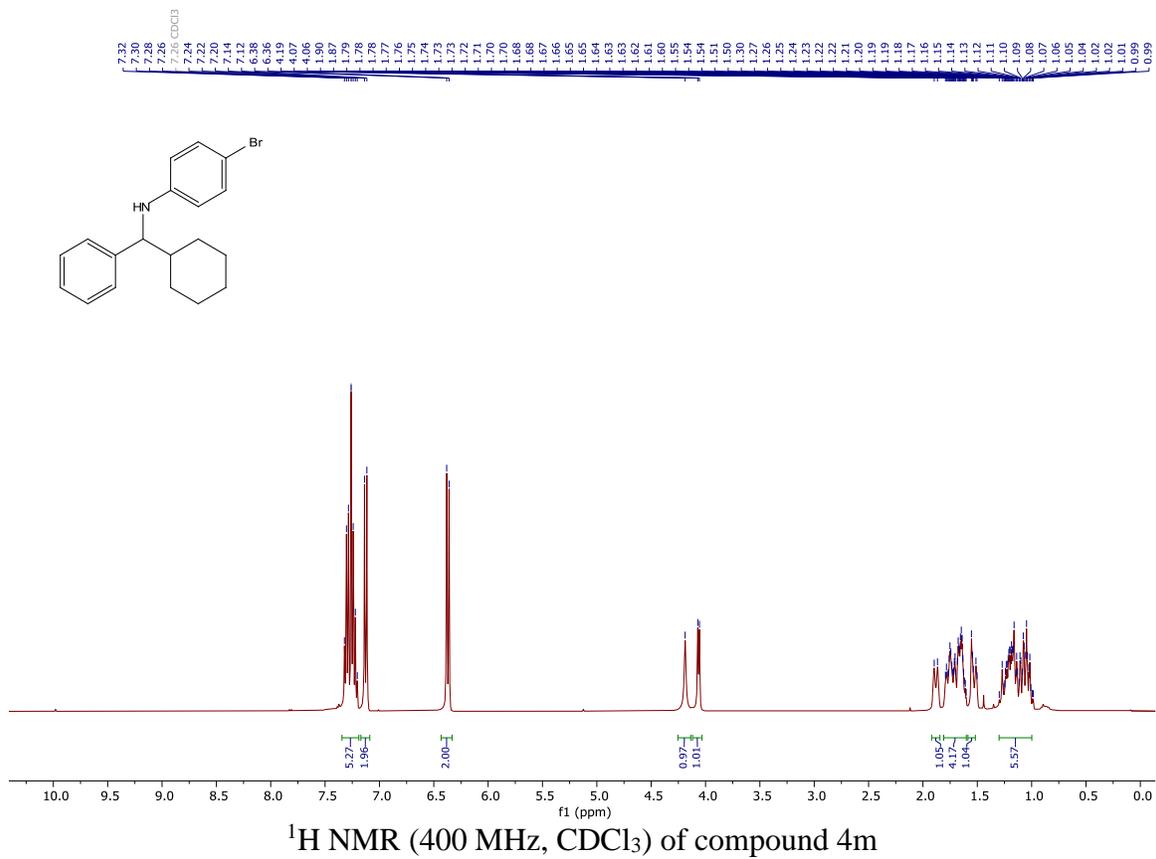
¹³C NMR (126 MHz, CDCl₃) of compound 4j

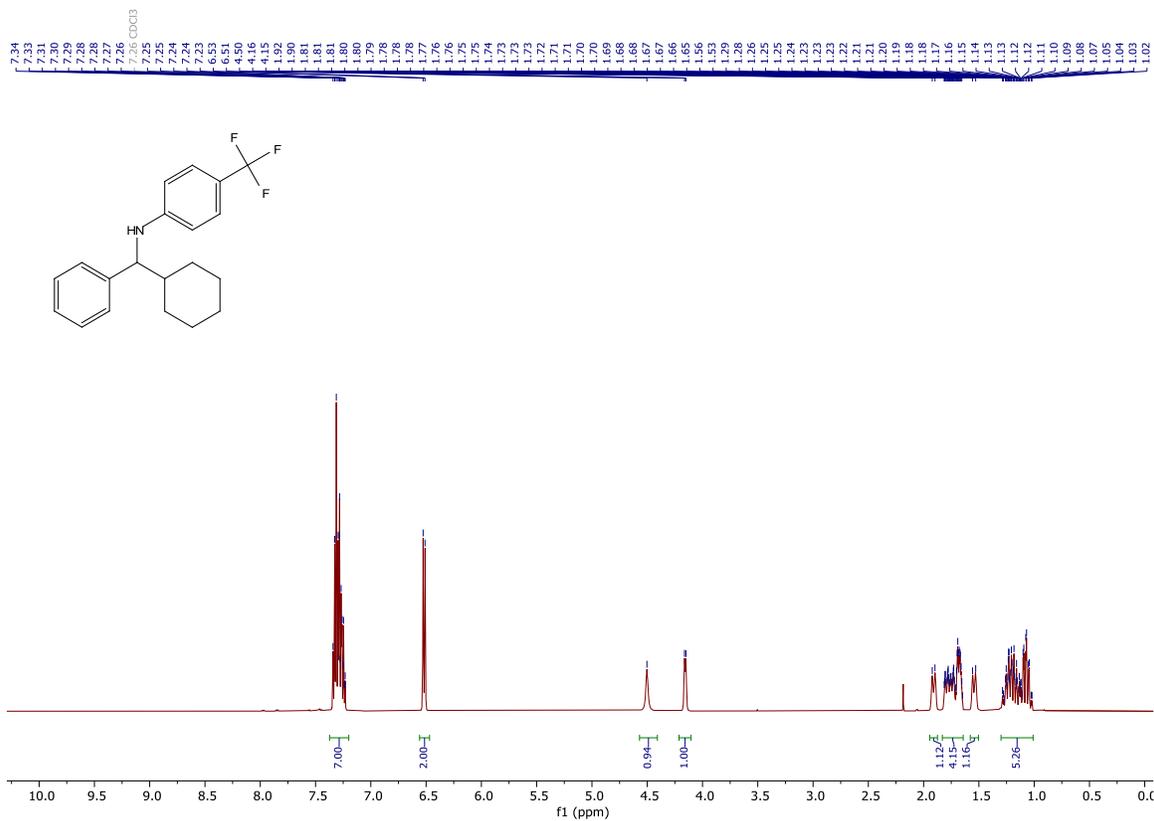


¹H NMR (400 MHz, CDCl₃) of compound 41

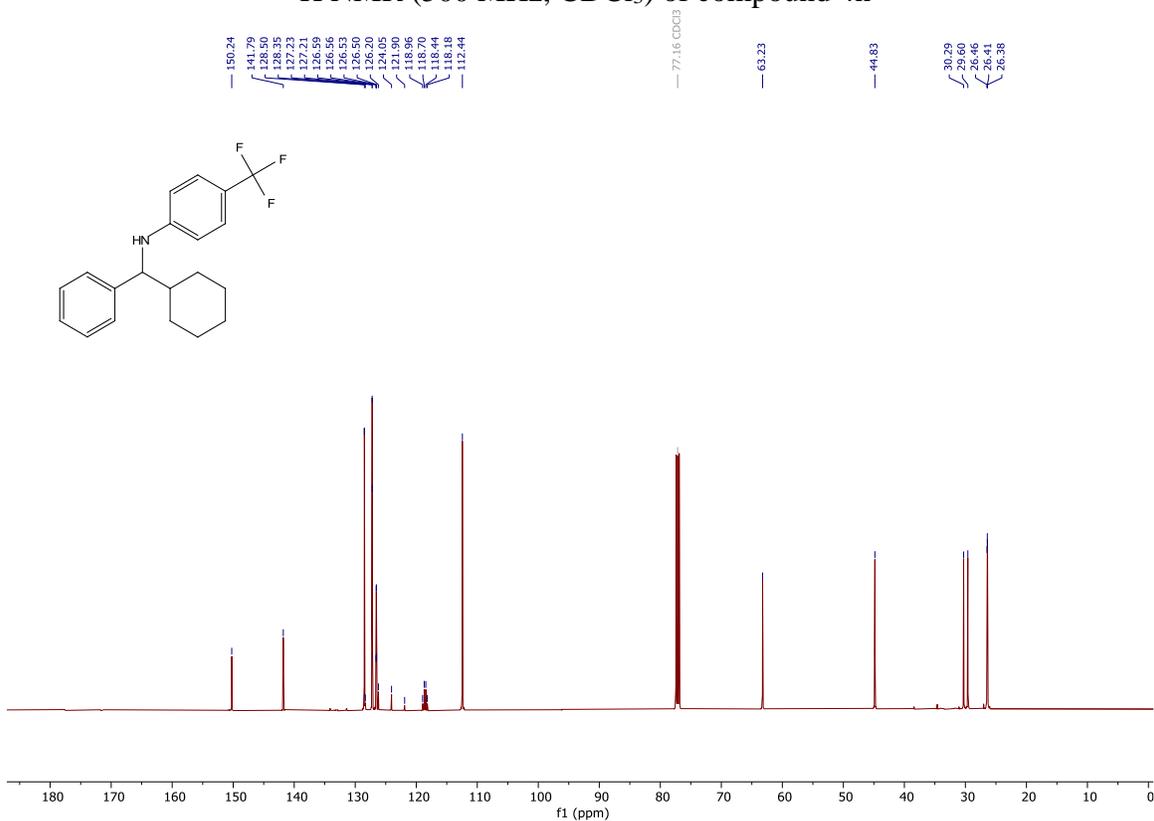


¹³C NMR (101 MHz, CDCl₃) of compound 41

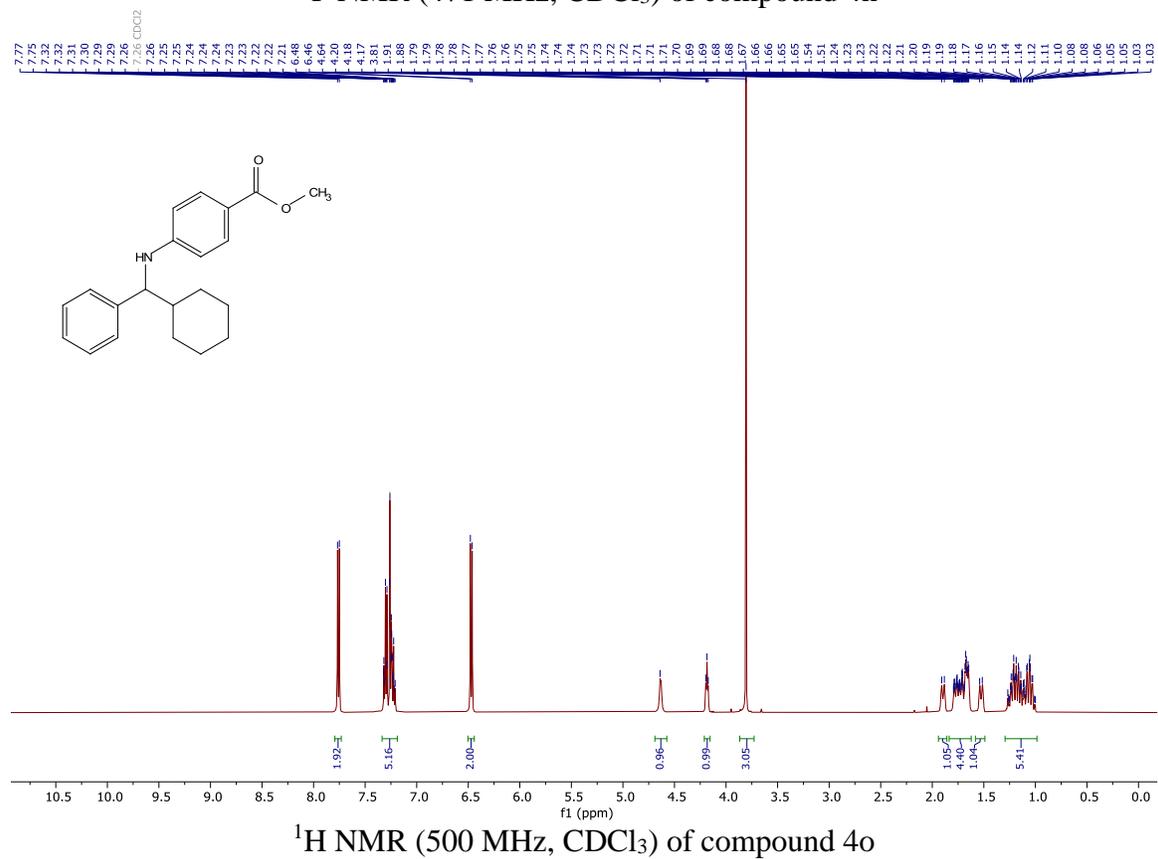
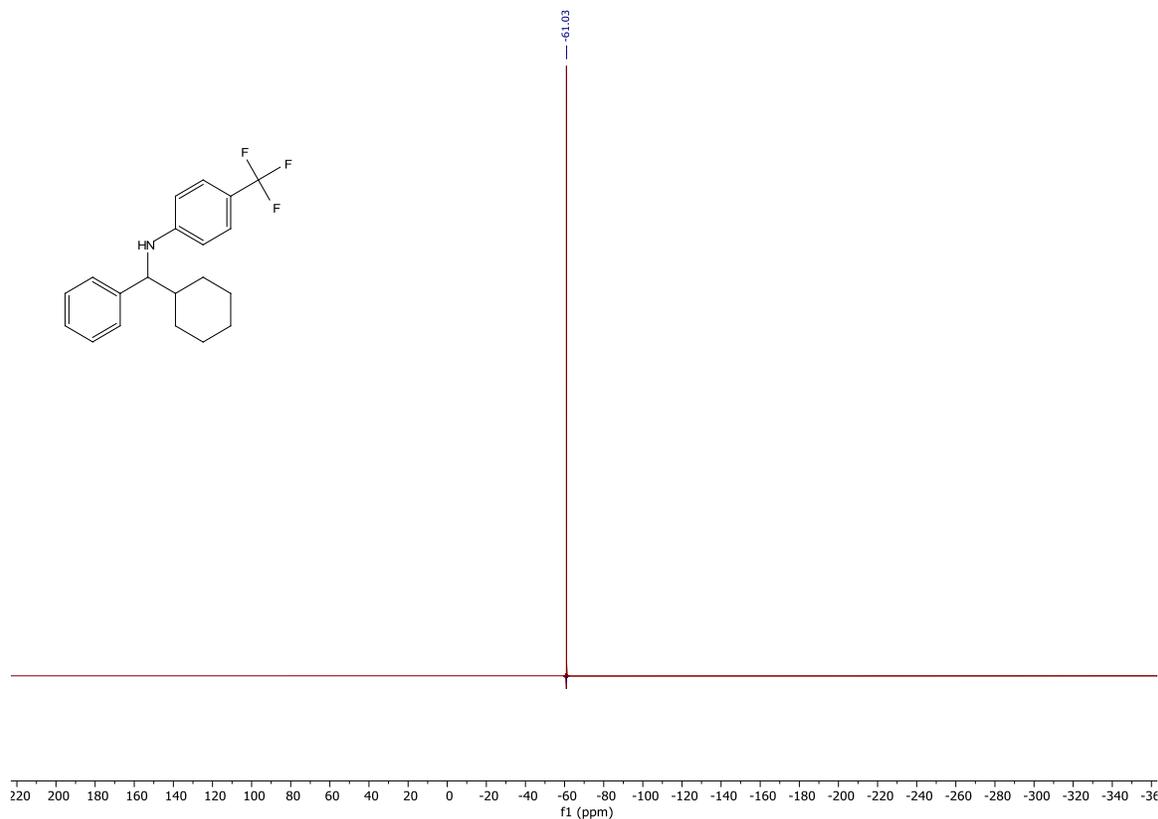


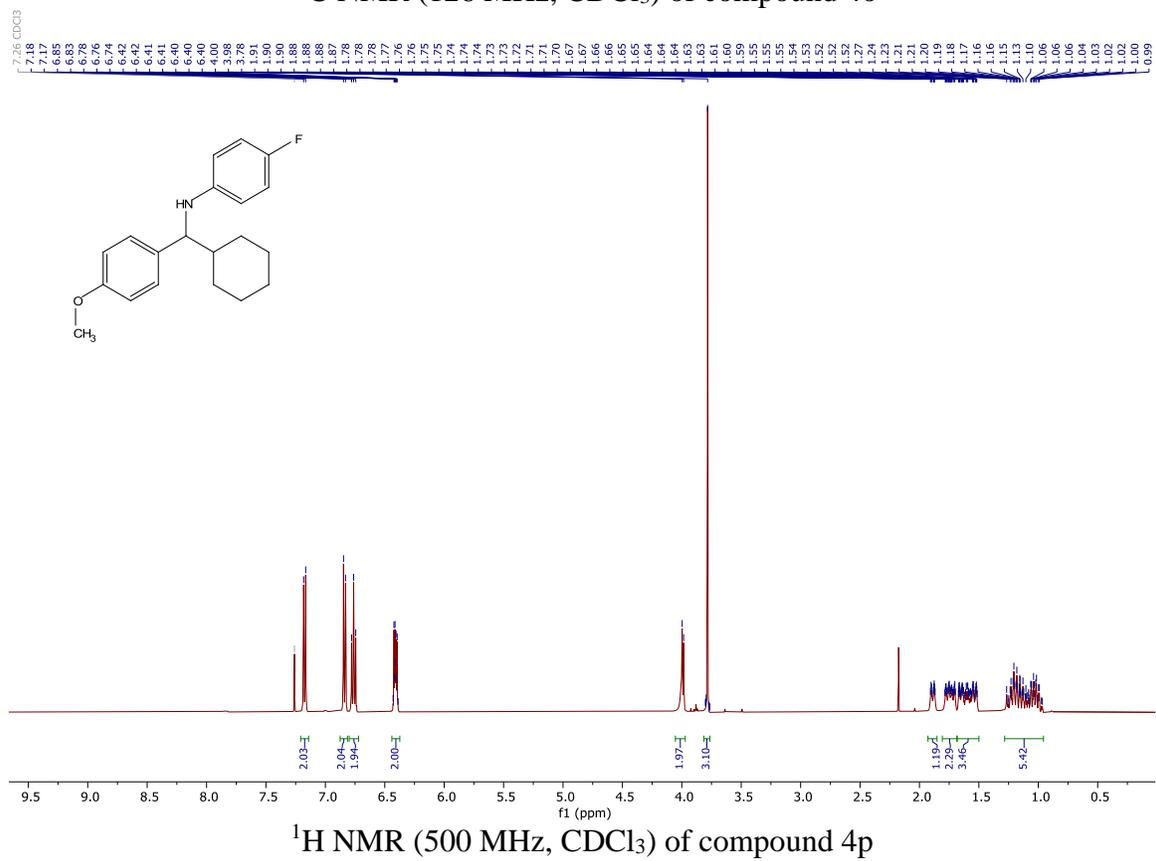
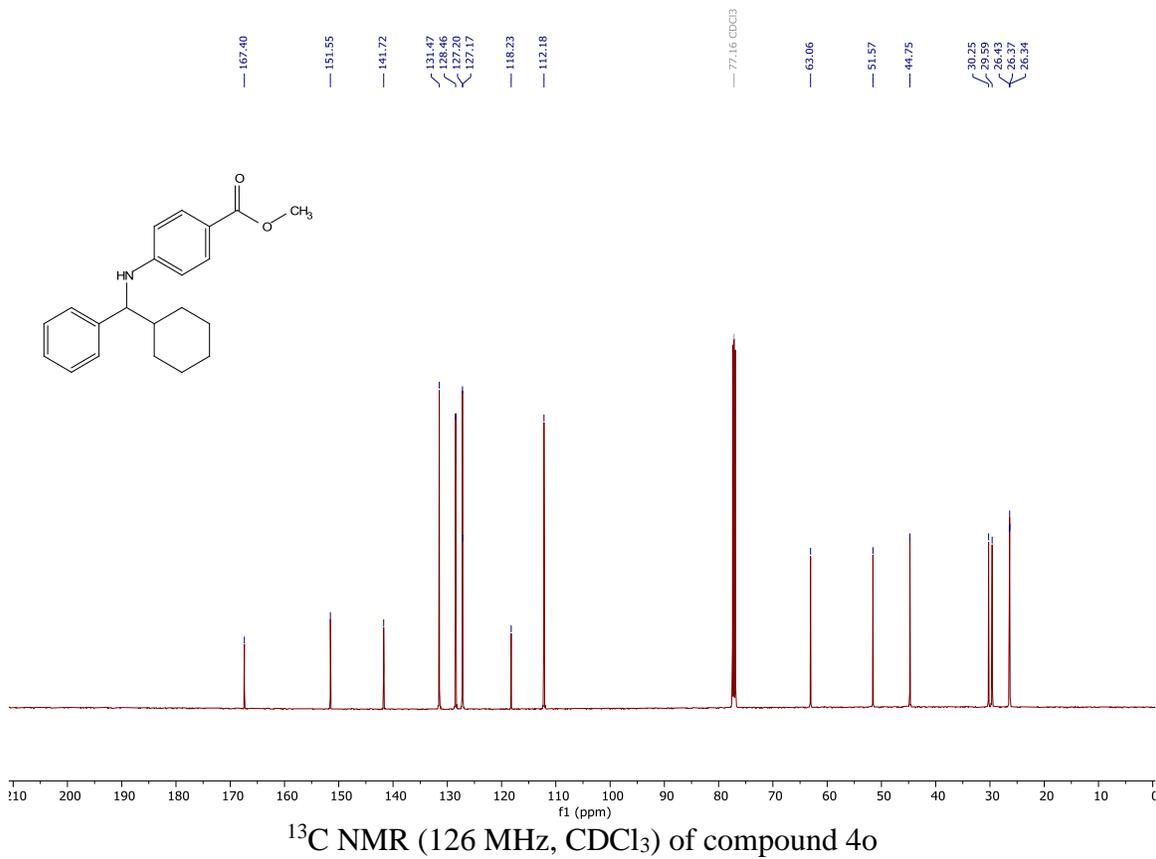


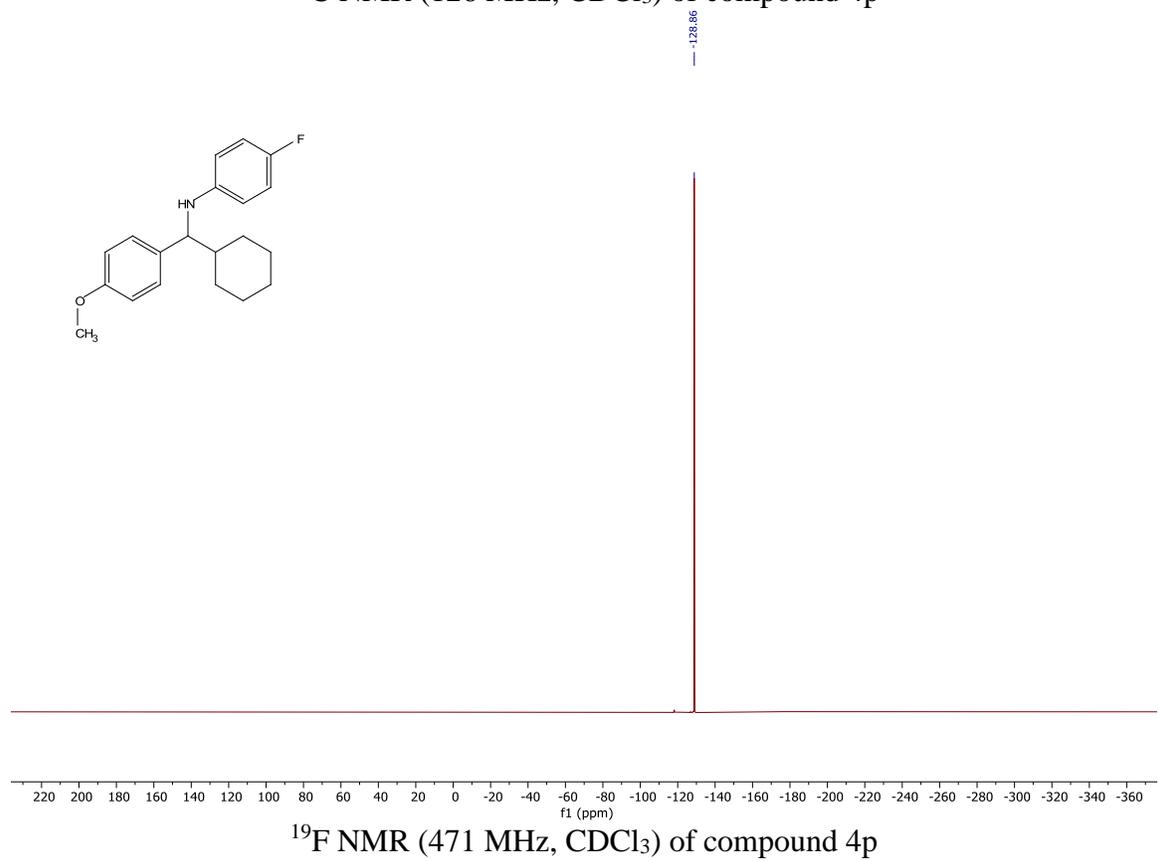
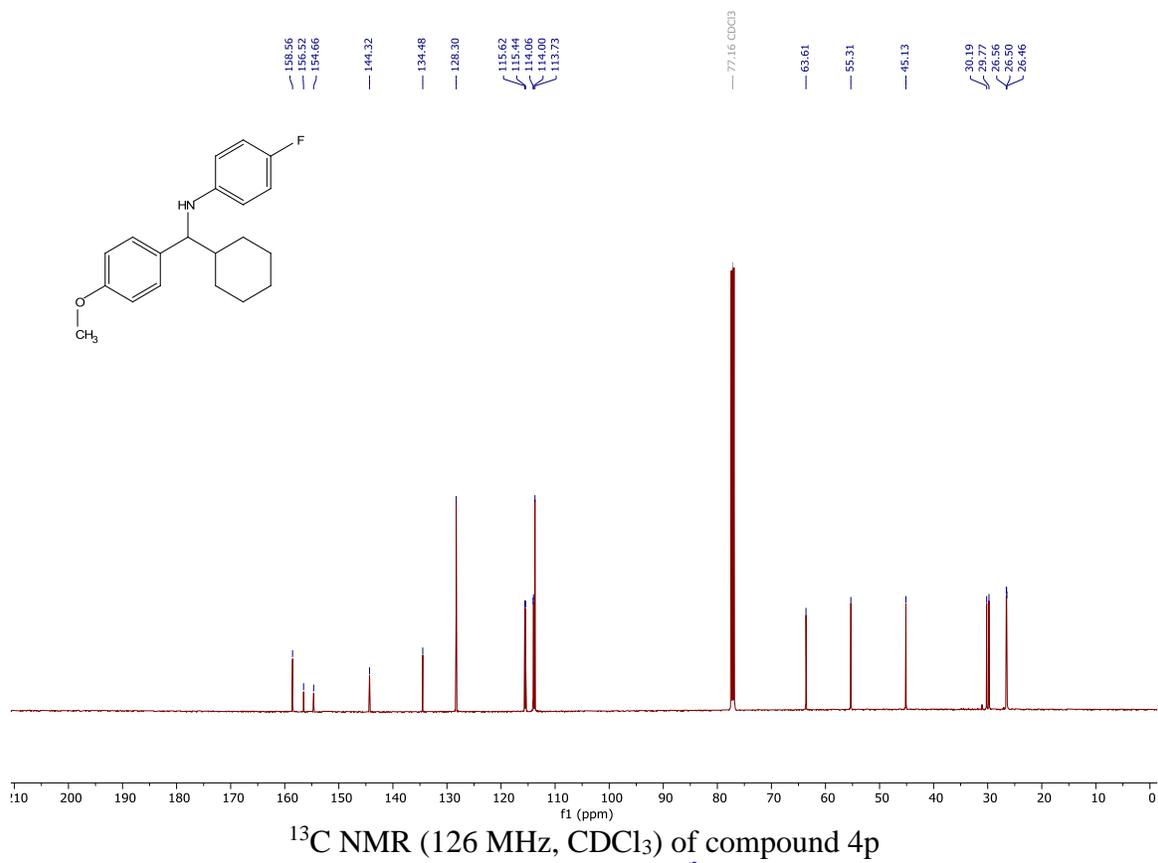
^1H NMR (500 MHz, CDCl_3) of compound 4n

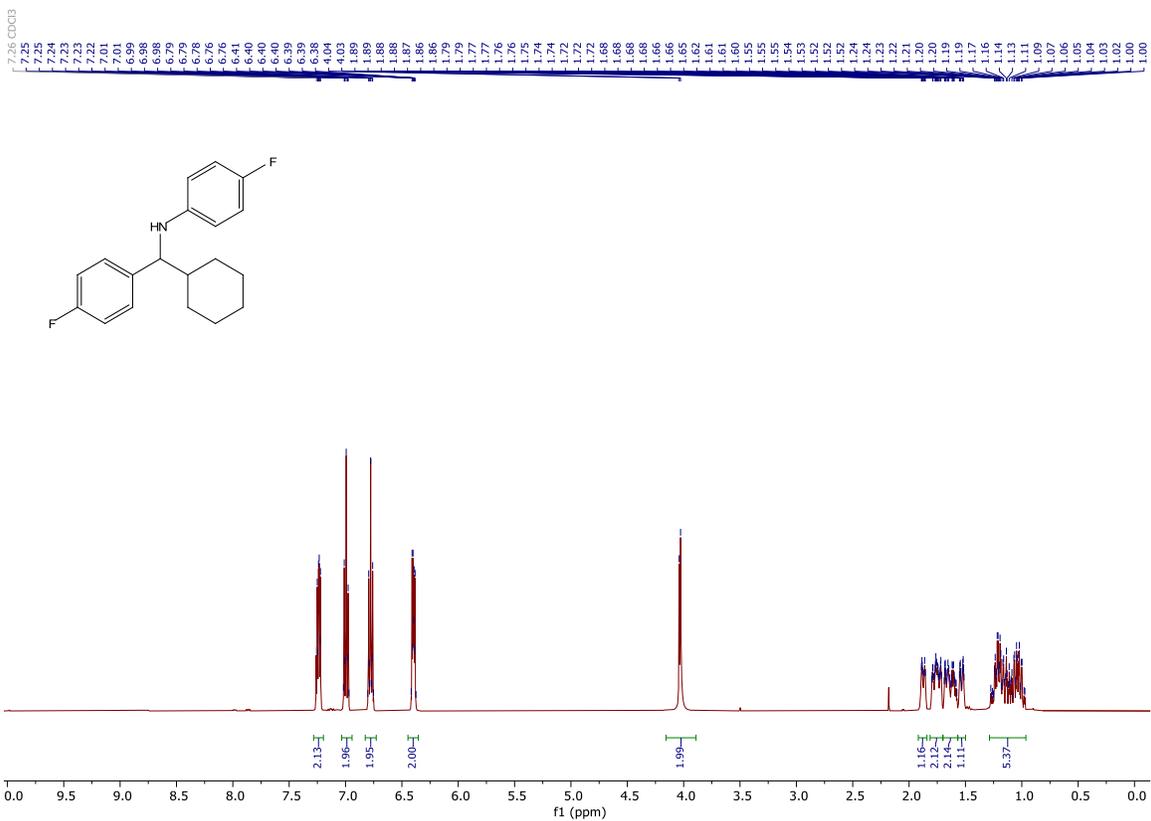


^{13}C NMR (126 MHz, CDCl_3) of compound 4n

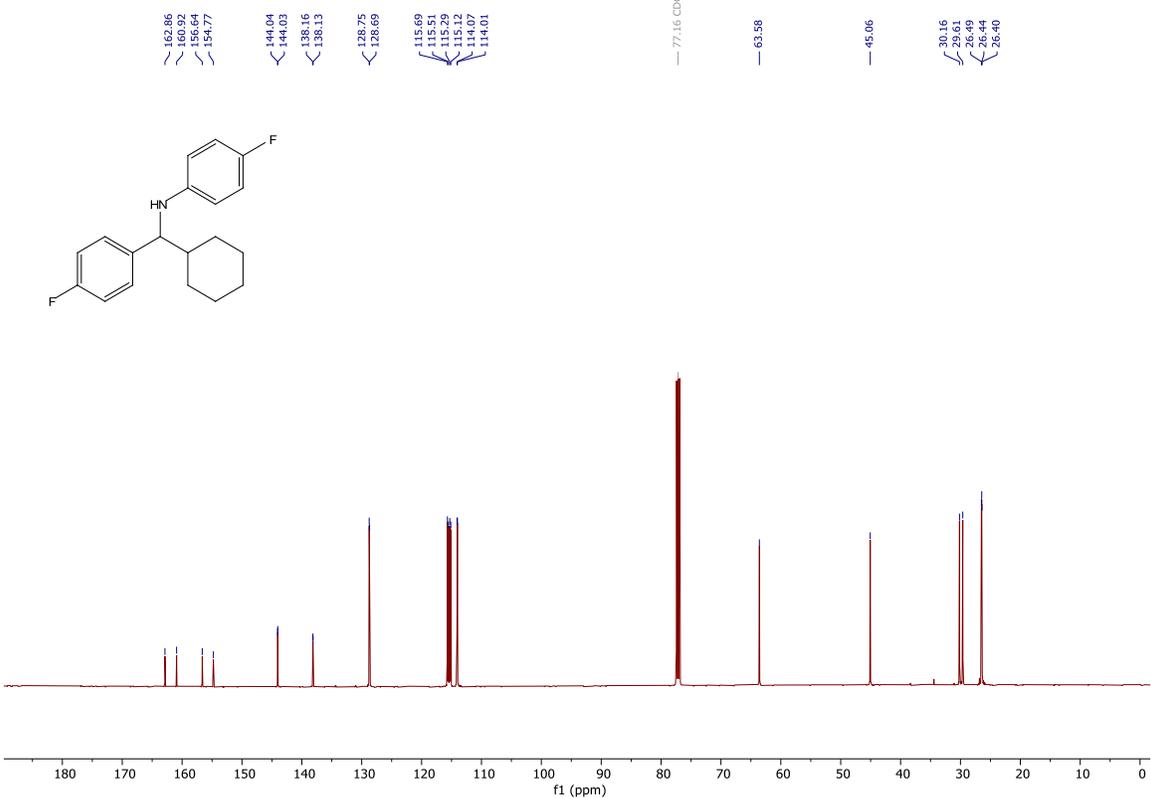








¹H NMR (500 MHz, CDCl₃) of compound 4q



¹³C NMR (126 MHz, CDCl₃) of compound 4q

