Supplementary Information (SI) for Chemical Communications.

Boron Appended Ru-NHC Catalyzed Selective Deoxygenative Hydrogenation of Tertiary Amides and Desulfurization of Thioamides

Raju Sharma,[a] Gowtham Kenguva,[b] Rambabu Dandela [b] and Prosenjit Daw*[a]

[a] Department of Chemical Sciences, Indian Institute of Science Education and Research Berhampur, Transit Campus, (Govt. ITI Building), Engg. School Junction, Berhampur 760010, Odisha, India

[b] Department of Industrial and Engineering Chemistry, Institute of Chemical Technology, Indian Oil Odisha Campus, Samantpuri, Bhubaneswar 751013, Odisha, India

Corresponding Author

Email: pdaw@iiserbpr.ac.in

Contents:

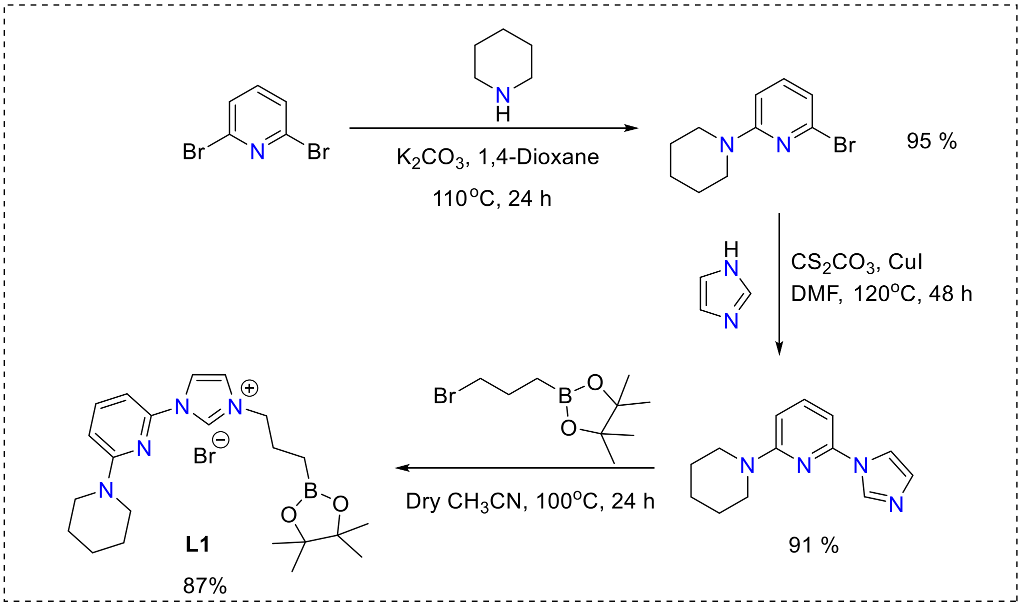
1. General experimental details 3
2. Synthetic Procedure of Ligand L1-L3 5
3. Synthetic Procedure of Metal Complexes 1-3, 1-PF_6 and 1-BF_4 9
  3.1. Synthetic procedure of Complex 1 9
  3.2. Synthetic procedure of complex 1-PF_6 10
  3.3. Synthetic procedure of complex 2 11
  3.4. Synthetic procedure of complex 3 12
  3.5. Synthetic procedure of complex 1-BF_4 13
Table S1. Optimization Table for Tertiary Amide Hydrogenation[a] 14
4. General Procedure for Synthesis of Tertiary Amides 15
5. General Procedure for Synthesis of Amide (4w) 17
Table S2. Optimization Table for Tertiary Thioamide Hydrogenation[a] 19
6. General Procedure for Synthesis of Tertiary Thioamides 19
7. General Procedure for Synthesis of Primary Thioamides 21
8. Typical Procedure for Catalytic Deoxygenative Reduction of Tertiary Amides 24
9. Characterization of Amine Products Derived from Tertiary Amides 24
10. Typical Procedure for Catalytic Desulfurization of Tertiary Thioamides 29
11. Characterization of Amine Products Derived from Tertiary Thioamides 29
12. Typical Procedure for Catalytic Desulfurizative Hydrogenation of Primary Thioamides 31
13. Characterization of Nitrile Products Derived from Primary Thioamides 31
14. Control Experiments 33
  14.1. Evaluating the role of appended Lewis basic arm 33
  14.2. Evaluating the role of appended Lewis acidic boron arm 34
    14.2.1. Catalytic reaction of amide 4a using complex 3 34
    14.2.2. Catalytic reaction of amide 4a using complex 3 and external $Ph(CH_2)_2Bpin$ 35
    14.2.3. Catalytic reaction of amide 4a using only $Ph(CH_2)_2Bpin$ 37
  14.3. Catalytic hydrogenation of acetophenone using complex 1 38
15. Homogeneity test using mercury drop experiment 41
16. Mechanistic Studies 42
  16.1. Generation of [Ru-H] species using complex 1 42

16.2. Stoichiometric reaction of in-situ generated Ru-H intermediate with amide 4a 44
16.3. Catalytic reaction of in-situ generated Ru-H intermediate (A) with amide 4a using a fewer equiv. of $PhSiH_3$ 46
16.4. Variable Temperature (VT) NMR study for the detection of appended boron-substrate interaction in complex 1 47
16.4.1. Variable Temperature (VT) NMR study of complex 1 and complex 1 +amide 4a 47
16.4.2. Variable Temperature (VT) NMR study using dimethylaminopyridine (DMAP) and complex 1 49
16.5. ESI-HRMS control experiment of stoichiometric reaction of a 1:1:1 mixture of complex 1, $PhSiH_3$ and 4a 51
16.6. Identification of siloxane by-product 52
17. ^{1}H NMR monitoring of 5a formation with progress of time 54
18. Spectroscopic data 55
19. Deoxygenative hydrogenation of secondary amide 137
20. Scale-up reaction of deoxygenative hydrogenation of 4a to 5a using complex 1 158
21. Dehydrogenation of benzylamine using complex 1 159
22. GC-TCD analysis of H_2 gas release during desulfurization of thioamide 8a to nitrile 9a using complex 1 160
23. Synthetic procedure and characterization data for 1,3-Diphenyldisiloxane 161
24. Deoxygenative hydrogenation of 4a to 5a using 1,3-diphenyldisiloxane (DPDS) as the hydride source 163
25. Variable Temperature (VT) NMR study for the interaction of appended boron in complex 1 with N,N-Dimethylacetamide (DMA) 166
26. ^{1}H NMR monitoring of N,N-Dimethylethanamine formation with the progress of time 169
27. Catalytic deoxygenative hydrogenation of N,N-dimethylacetamide using complex 1 170
28. Plausible Reaction Mechanism 172
29. X-Ray Crystallographic data 173
30. References 175

1. General experimental details

All the experiments were performed under a nitrogen-filled glove box atmosphere or by standard schlenk technique unless otherwise stated. All chemicals were purchased from commercial suppliers and used without further purification unless otherwise stated. All the solvents were pre-dried following the literature processes. ^{1}H, ^{13}C, and ^{11}B NMR spectra were recorded on 400 MHz FT-NMR Bruker AVANCE NEO Ascend 400 spectrometer. The chemical shifts (δ) for ^{1}H NMR are given in parts per million (ppm) referenced to the residual proton signal of the deuterated solvent ($CHCl_3$ at δ 7.26 ppm, C_6H_6 at 7.16 ppm, DMSO, ^{1}H; 2.50 ppm and ^{13}C; 39.52 ppm). Coupling constants are expressed in hertz (Hz). ^{13}C NMR spectra were referenced to the carbon signal of $CDCl_3$ (77.16 ppm). The following abbreviations are used to describe NMR signals: s = singlet, d = doublet, t = triplet, m = multiplet, dd = doublet of doublets, q = quartet. High-resolution mass Spectrometry (ESI-HRMS) was performed on Xevo G2-XS QT of Quadrupole Time of Flight Mass spectrometer waters. Elemental analysis was done using the UNICUBE CHNSO element analyzer. The single crystal data was collected on Bruker D8 quest diffractometer. IR spectra were recorded on Bruker TENSOR II FT-IR Spectrometer. The abbreviation br = broad in IR spectral data. The GCMS analysis of the crude reaction mixture was analyzed by GCMS-FID (TRACE 1610, TG-5MS column). Silver Oxide (Ag_2O) was purchased from Sigma-Aldrich and used as directly. $RuCl_3.3H_2O$ was purchased from Arora-Matthey. Dichloro(p-Cymene)ruthenium(II) dimer was prepared according to the procedure in the literature.[1] 2-(3-bromopropyl)-4,4,5,5-tetramethyl-1,3,2-dioxaborolane was prepared following the literature procedure.[2] 4,4,5,5-tetramethyl-2-phenethyl-1,3,2-dioxaborolane i.e $Ph(CH_2)_2Bpin$ was prepared according to literature procedure.[3]

2. Synthetic Procedure of Ligand L1-L3



Scheme S1: Synthesis of Ligand L1

Synthesis of 2-bromo-6-(piperidine-1-yl)pyridine[4]:

In a 100 mL round bottom flask equipped with a condenser, 2,6-dibromopyridine (2 g, 8.44 mmol) and potassium carbonate (1.75 g, 12.66 mmol) were taken under nitrogen atmosphere. 10 mL of dry 1,4-dioxane was added followed by the addition of 1.6 mL of piperidine (16.88 mmol) and heated the solution at 110° C for 24 h. After completion of the reaction, the solvent was evaporated under a vacuum and the crude product was isolated using silica column chromatography eluted with 20 % ethyl acetate/ hexane mixture to afford the desired product as a colorless oil (1.93 g, 95 %).

^{1}H NMR (400 MHz, CDCl$_3$) δ (ppm) = 7.31 – 7.28 (m, 1H), 6.71 (d, *J* = 7.4 Hz, 1H), 6.54 (d, *J* = 8.4 Hz, 1H), 3.55 (s, 4H), 1.68 (s, 6H).

^{13}C NMR (101 MHz, CDCl$_3$) δ (ppm) = 159.47, 140.24, 139.33, 115.18, 104.90, 46.14, 25.57, 24.72.

135-DEPT NMR (101 MHz, CDCl$_3$) δ (ppm) = 139.24, 114.88, 104.64, 45.94, 25.37, 24.52.

ESI-HRMS (m/z), [M+H]$^+$: Calc. 241.0340; Found 241.0349. (M= $C_{10}H_{13}N_2Br$)

Synthesis of 2-(1H-imidazol-1-yl)-6-(piperidin-1-yl)pyridine:

In a 50 mL sealed tube, cesium carbonate (2.7 g, 8.28 mmol), imidazole (0.28 g, 4.14 mmol) and copper iodide (0.315 g, 1.65 mmol) were added under nitrogen atmosphere. 8 mL of dry DMF was added followed by the addition of 2-bromo-6-(piperidine-1-yl)pyridine (1 g, 4.14 mmol) in 2 mL DMF, and the tube was sealed and heated at 120 ºC for 48 hours. After the completion of the reaction, the solvent was evaporated under reduced pressure and the crude product was purified using silica column chromatography eluted with 80 % ethyl acetate/ hexane mixture to afford the desired product as a pale brown liquid (862.15 mg, 91 %).

^{1}H NMR (400 MHz, CDCl$_3$) δ (ppm) = 8.29 (s, 1H), 7.57 (s, 1H), 7.52 (t, *J* = 8.0 Hz, 1H), 7.14 (s, 1H), 6.54 (dd, *J* = 9.3, 8.3 Hz, 2H), 3.59 (s, 4H), 1.66 (s, 6H).

^{13}C NMR (101 MHz, CDCl$_3$) δ (ppm) = 158.71, 147.71, 139.97, 135.14, 130.10, 116.30, 104.62, 99.19, 46.16, 25.55, 24.82.

ESI-HRMS (m/z), $[M+H]^+$: Calc. 229.1453; Found 229.1448. (M= $C_{13}H_{16}N_4$)

Synthesis of ligand L1:

To a mixture of 2-(1H-imidazol-1-yl)-6-(piperidin-1-yl)pyridine (150 mg, 0.657 mmol) and 2-(3-bromopropyl)-4,4,5,5-tetramethyl-1,3,2-dioxaborolane (180 mg, 0.722 mmol) under a nitrogen atmosphere was added 5 mL of dry acetonitrile and heated the solution at 100 ºC for 24 hours. The solution was completely evaporated which afforded an off-white foamy solid that was washed thoroughly with (5 x 5 mL) dry diethyl ether to afford a desired imidazolium salt **L1** as a white solid (272.45 mg, 87%).[5] The single crystal suitable for X-ray diffraction analysis of **L1** was grown by vapor diffusion of diethyl ether into a concentrated acetonitrile solution of **L1** at room temperature.

^{1}H NMR (400 MHz, CDCl$_3$) δ (ppm): 11.28 (s, 1H), 8.11 (s, 1H), 7.64 (t, *J* = 8.0 Hz, 1H), 7.42 (d, *J* = 8.2 Hz, 2H), 6.66 (d, *J* = 8.5 Hz, 1H), 4.54 (t, *J* = 7.0 Hz, 2H), 3.57 (s, 4H), 2.10 – 2.03 (m, 2H), 1.65 (s, 6H), 1.21 (s, 12H), 0.85 (t, *J* = 7.7 Hz, 2H).

^{13}C NMR (101 MHz, CDCl$_3$) δ (ppm): 158.23, 144.42, 141.16, 135.60, 121.91, 118.62, 107.72, 101.10, 83.59, 52.11, 46.09, 25.45, 25.27, 24.95, 24.59.

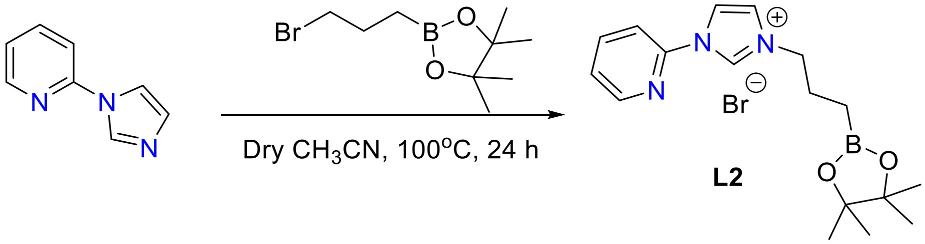
135-DEPT NMR (101 MHz, CDCl$_3$) δ (ppm) = 140.94, 135.39, 121.70, 118.41, 107.50, 100.88, 51.89, 45.87, 25.23, 25.06, 24.74, 24.38.

^{11}B NMR (128 MHz, CDCl$_3$) δ (ppm) = 33.69 (br).

ESI-HRMS (m/z), $[M-Br]^+$: Calc. 397.2775; Found 397.2788 . (M= $C_{22}H_{34}BBrN_4O_2$)

IR (ATR) ῡ (cm^{-1}) = 3036, 2926, 2854, 1617, 1556, 1534, 1495, 1444, 1374, 1318, 1282, 1226, 1203, 1141, 1127, 1089, 1027, 999, 971, 935, 855, 831, 785.

Anal. calcd. for $C_{22}H_{34}BBrN_4O_2$ (%): C, 55.37; H, 7.18; N, 11.74. found: C, 53.39; H, 7.14; N, 11.36.



Scheme S2: Synthesis of ligand L2

To a mixture of 2-(1H-imidazol-1-yl)pyridine (205 mg, 1.41 mmol) and 2-(3-bromopropyl)-4,4,5,5-tetramethyl-1,3,2-dioxaborolane (386.8 mg, 1.55 mmol) under a nitrogen atmosphere was added 5 mL of dry acetonitrile and heated the solution at 100 ºC for 24 hours. The solution was completely evaporated which afforded an off-white foamy solid that was washed thoroughly with (5 x 5 mL) dry diethyl ether to afford a desired imidazolium salt **L2** as a white solid (499.9 mg, 90%).

^{1}H NMR (400 MHz, $CDCl_3$) δ (ppm) = 11.71 (s, 1H), 8.63 (d, *J* = 8.2 Hz, 1H), 8.50 (d, *J* = 4.5 Hz, 1H), 8.32 (s, 1H), 8.05 (t, *J* = 7.8 Hz, 1H), 7.43 (s, 2H), 4.54 (t, *J* = 7.2 Hz, 2H), 2.15 – 2.07 (m, 2H), 1.22 (s, 12H), 0.88 (t, *J* = 7.8 Hz, 2H).

^{13}C NMR (101 MHz, $CDCl_3$) δ (ppm) = 148.99, 146.11, 140.89, 136.14, 125.26, 122.17, 118.89, 115.41, 83.69, 52.32, 25.22, 24.99.

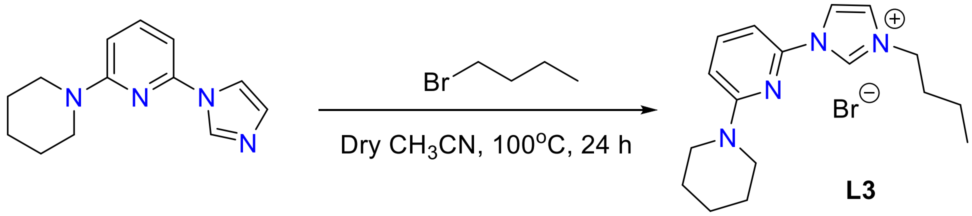
135-DEPT NMR (101 MHz, $CDCl_3$) δ (ppm) = 148.79, 140.69, 135.89, 125.07, 122.01, 118.73, 115.19, 52.15, 25.01, 24.78.

^{11}B NMR (128 MHz, $CDCl_3$) δ (ppm) = 33.35 (br).

ESI-HRMS (m/z), $[M-Br]^+$: Calc. 314.2040; Found 314.2045 (M= $C_{17}H_{25}BBrN_3O_2$)

IR (ATR) ῡ (cm^{-1}) = 2973, 1600, 1544, 1476, 1441, 1406, 1362, 1330, 1297, 1273, 1220, 1144, 1113, 1077, 995, 967, 884, 846, 775,733.

Anal. calcd. for $C_{17}H_{25}BBrN_3O_2$ (%): C, 51.81; H, 6.39; N, 10.66 found: C, 49.22; H, 6.18; N, 10.90.



Scheme S3: Synthesis of ligand L3

Synthesis of ligand L3:

In a 25 mL shlenck tube, 2-(1H-imidazol-1-yl)-6-(piperidin-1-yl)pyridine (150 mg, 0.657 mmol) and 5 mL of dry acetonitrile was added under a nitrogen atmosphere followed by the addition of 78 µL of butyl bromide (99 mg, 0.722 mmol) and heated the solution at 100 ºC for 24 hours. The solution was completely evaporated which afforded an off-white solid that was washed thoroughly with (5 x 5 mL) dry diethyl ether to afford a desired imidazolium salt **L3** as a white solid (216. 68 mg, 90%).

^{1}H NMR (400 MHz, CDCl$_3$) δ (ppm) = 11.47 (s, 1H), 8.08 (s, 1H), 7.67 (t, *J* = 7.5 Hz, 1H), 7.44 (d, *J* = 6.9 Hz, 1H), 7.37 (s, 1H), 6.69 (d, *J* = 8.5 Hz, 1H), 4.59 (s, 2H), 3.59 (s, 4H), 1.98 (br s, 2H), 1.65 (s, 6H), 1.45 (dd, *J* = 13.5, 6.8 Hz, 2H), 0.99 (t, *J* = 7.1 Hz, 3H).

^{13}C NMR (101 MHz, CDCl$_3$) δ (ppm) = 158.29, 144.39, 141.32, 136.15, 121.63, 118.76, 107.85, 101.32, 50.58, 46.19, 32.59, 25.52, 24.63, 19.77, 13.75.

135-DEPT NMR (101 MHz, CDCl$_3$) δ (ppm) = 140.92, 135.03, 122.09, 118.63, 108.00, 101.31, 50.08, 46.31, 32.15, 25.06, 24.12, 19.31, 13.35.

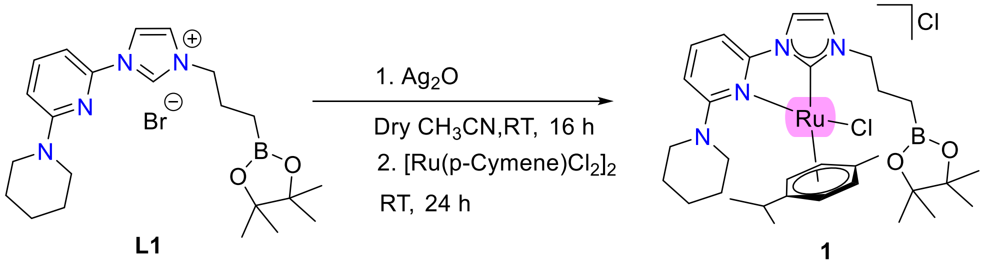
ESI-HRMS (m/z), [M-Br]$^+$: Calc. 285.2079; Found 285.2108 (M= $C_{17}H_{25}BrN_4$)

IR (ATR) ῡ (cm^{-1}) = 3052, 2934, 2859, 1617, 1555, 1531, 1504, 1445, 1358, 1251, 1199, 1178, 1121, 1091, 1022, 974, 932, 875, 857, 787, 772, 746.

Anal. calcd. for $C_{17}H_{25}BrN_4$ (%): C, 55.89; H, 6.90; N, 15.34 found: C, 55.39; H, 7.08; N, 14.62.

3. Synthetic Procedure of Metal Complexes 1-3, 1-PF$_6$ and 1-BF$_4$

3.1. Synthetic procedure of Complex 1



Scheme S4: Synthesis of metal complex 1

In a 25 mL oven dried shlenck tube, imidazolium salt **L1** (110 mg, 0.23 mmol), silver oxide (26.7 mg, 0.115 mmol) were added under a nitrogen atmosphere followed by the addition of 10 mL of dry acetonitrile. The solution was stirred at room temperature under dark for 16 hours after which [Ru(p-Cymene)Cl$_2$]$_2$ (70.4 mg, 0.115 mmol) was added directly under a nitrogen atmosphere and stirred the solution for an additional 24 hours. The solution was completely evaporated under a vacuum and 20 mL of dry THF was added and filtered the solution through celite. The filtrate was concentrated to 1 mL and 10 mL of dry diethyl ether was added which precipitated a light-yellow solid that was further washed with (5x 5 mL) diethyl ether to obtain the desired complex **1** as a light yellow solid (145.65 mg, 90%).

^{1}H NMR (400 MHz, CDCl$_3$) δ (ppm) = 8.50 (s, 1H), 8.03 (s, 2H), 7.38 (s, 1H), 7.06 (s, 1H), 6.17 (d, *J* = 5.0 Hz, 1H), 5.92 (s, 1H), 5.82 (d, *J* = 4.8 Hz, 1H), 5.32 (s, 1H), 4.42 (s, 1H), 4.24 (s, 1H), 3.33 (s, 2H), 2.21 (s, 5H), 2.09 (s, 1H), 1.91 (s, 2H), 1.76 (s, 6H), 1.28 (s, 12H), 0.97 (t, *J* = 6.8 Hz, 2H), 0.83 (dd, *J* = 14.9, 6.4 Hz, 6H).

^{13}C NMR (101 MHz, CDCl$_3$) δ (ppm) = 182.05, 169.12, 152.42, 143.33, 124.71, 113.15, 109.23, 94.39, 85.88, 83.67, 53.34, 31.21, 25.49, 25.44, 25.18, 25.06, 24.01, 22.84, 22.51, 19.10.

DEPT-135 NMR (101 MHz, CDCl$_3$) δ (ppm) = 142.66, 124.07, 112.98, 108.81, 94.13, 85.17, 52.93, 30.96, 25.20, 25.15, 24.91, 24.79, 23.75, 22.40, 22.01, 18.71.

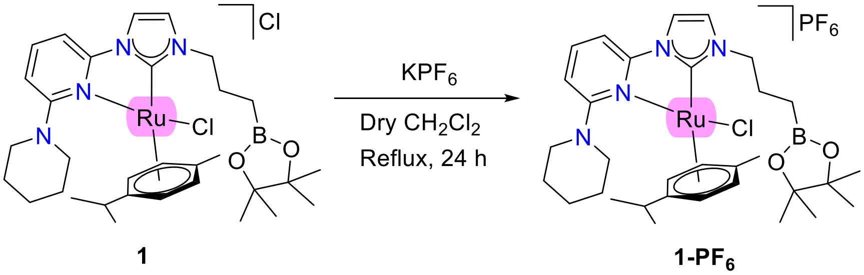
^{11}B NMR (128 MHz, CDCl$_3$) δ (ppm) = 33.26 (br).

ESI- HRMS (m/z), [**1**-Cl]$^+$: Calc. 667.2524; Found 667.2524 (**1**= $C_{32}H_{47}BCl_2N_4O_2Ru$)

IR (ATR) ῡ (cm^{-1}) = 3085, 2965, 2931, 1613, 1561, 1476, 1374, 1323, 1247, 1211, 1142, 1106, 1055, 1031, 967, 922, 845, 800, 740, 694, 674.

Anal. calcd. for $C_{32}H_{47}BCl_2N_4O_2Ru.CH_2Cl_2$ (%): C, 50.33; H, 6.27; N, 7.12 found: C, 50.02; H, 6.19; N, 7.33.

3.2. Synthetic procedure of complex 1-PF$_6$



Scheme S5: Synthesis of metal complex 1-PF$_6$

In a 25 mL oven-dried shlenck tube, complex 1 (100 mg, 0.142 mmol) and KPF6 (39.3 mg, 0.213 mmol) were added under a nitrogen atmosphere, followed by the addition of 10 mL of dry dichloromethane. The solution was heated at 50 ºC for 24 hours in an oil bath. During this time, the light yellowish solution turns to light brown. The solution was completely evaporated under the vacuum and 20 mL of dry THF was added to dissolve the residue and filtered the solution through celite. The filtrate was concentrated to 1 mL and 10 mL of dry diethyl ether was added which precipitated a brown solid that was further washed with (5x 5 mL) diethyl ether to obtain the desired complex **1-PF$_6$** as a light brown solid (99.45 mg, 86%). The single crystal suitable for X-ray diffraction analysis of **1-PF$_6$** was grown by vapor diffusion of diethyl ether into a concentrated THF solution of complex at 5 ºC.

^{1}H NMR (400 MHz, $CDCl_3$) δ (ppm) = 7.87 (t, *J* = 8.0 Hz, 1H), 7.65 (br s, 1H), 7.31 (br s, 1H), 7.23 (br s, 1H), 7.01 (d, *J* = 8.2 Hz, 1H), 6.09 (d, *J* = 6.1 Hz, 1H), 5.84 (d, *J* = 5.9 Hz, 1H), 5.77 (d, *J* = 6.1 Hz, 1H), 5.31 (d, *J* = 5.7 Hz, 1H), 4.41 – 4.34 (m, 1H), 4.28 – 4.21(m, 1H), 3.41 (t, *J* = 8 Hz, 2H), 2.17 (s, 3H), 2.15 – 2.04 (m, 3H), 1.90 (br s, 2H), 1.74 (br s, 4H), 1.59 (br s, 2H), 1.28 (s, 12H), 0.95 (t, *J* = 7.6 Hz, 2H), 0.84 (d, *J* = 6.9 Hz, 3H), 0.78 (d, *J* = 6.9 Hz, 3H).

^{13}C NMR (101 MHz, $CDCl_3$) δ (ppm) = 182.99, 169.38, 152.22, 142.12, 124.19, 117.39, 112.92, 105.80, 94.24, 85.13, 83.71, 52.81, 31.03, 25.39, 25.25, 25.12, 25.02, 24.03, 22.50, 21.82, 18.72.

DEPT 135-NMR (176 MHz, $CDCl_3$) δ (ppm) = 141.92, 123.99, 117.18, 112.71, 105.60, 52.60, 30.83, 25.04, 24.92, 24.81, 23.82, 22.30, 21.61, 18.51.

^{11}B NMR (128 MHz, $CDCl_3$) δ (ppm) = 33.98 (br).

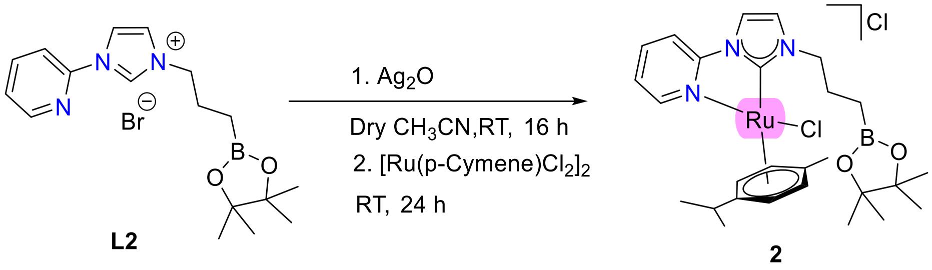
^{31}P NMR (162 MHz, $CDCl_3$) δ (ppm) = -144.31 (m).

^{19}F NMR (377 MHz, $CDCl_3$) δ (ppm) = -72.79 (d).

ESI-HRMS (m/z), [**M**-PF_6]$^+$: Calc. 667.2524; Found 667.2524. (M= $C_{32}H_{47}BClF_6N_4O_2PRu$)

Anal. calcd. for $C_{32}H_{47}BClF_6N_4O_2PRu$ (%): C, 47.33; H, 5.83; N, 6.90 found: C, 46.48; H, 6.00; N, 6.78.

3.3. Synthetic procedure of complex 2



Scheme 6: Synthesis of metal complex 2

In a 25 mL oven dried shlenck tube, imidazolium salt **L2** (100 mg, 0.253 mmol), silver oxide (29.3 mg, 0.126 mmol) were added under a nitrogen atmosphere followed by the addition of 10 mL of dry acetonitrile. The solution was stirred at RT under dark for 16 hours after which [Ru(p-Cymene)Cl_2]$_2$ (77.7 mg, 0.126 mmol) was added directly under a nitrogen atmosphere and stirred the solution for an additional 24 hours. The solution was completely evaporated under a vacuum and 20 mL of dry THF was added and filtered the solution using celite. The filtrate was concentrated to 1 mL and 10 mL of dry diethyl ether was added which precipitated a light yellow solid that was further washed with (5x 5 mL) diethyl ether to obtain the desired complex **2** as a light yellow solid (138.3 mg, 93%).

^{1}H NMR (400 MHz, DMSO) δ (ppm) = 9.34 (d, *J* = 5.5 Hz, 1H), 8.45 (s, 1H), 8.25 (t, *J* = 7.7 Hz, 1H), 8.16 (d, *J* = 8.2 Hz, 1H), 7.86 (s, 1H), 7.52 (t, *J* = 6.5 Hz, 1H), 6.34 (d, *J* = 6.1 Hz, 2H), 6.19 (d, *J* = 6.2 Hz, 1H), 5.71 (d, *J* = 5.8 Hz, 1H), 4.43 – 4.30 (m, 2H), 2.38-2.31 (m, 1H), 2.12 (s, 3H), 1.99 – 1.91 (m, 2H), 1.21 (s, 12H), 1.09 (t, *J* = 7.0 Hz, 2H), 0.83 (dd, *J* = 12.6, 6.8 Hz, 6H).

^{13}C NMR (101 MHz, DMSO) δ (ppm) = 182.98, 155.77, 151.28, 141.54, 125.04, 122.92, 116.91, 112.25, 90.94, 86.27, 82.92, 52.60, 30.39, 24.68, 24.62, 22.19, 21.74, 18.59.

135-DEPT NMR (101 MHz, DMSO) δ (ppm) = 155.55, 141.35, 124.84, 122.72, 116.68, 112.02, 90.74, 86.04, 52.39, 30.19, 24.46, 24.42, 21.97, 21.52, 18.38.

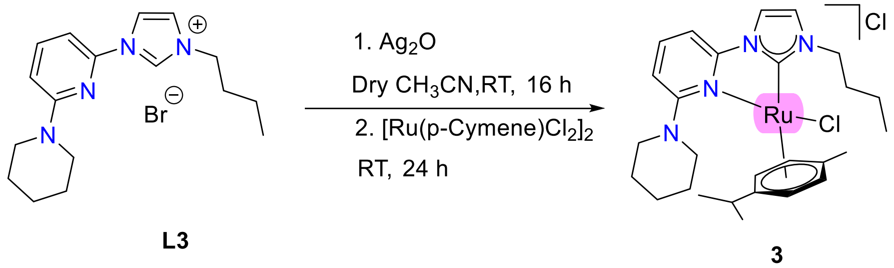
^{11}B NMR (128 MHz, DMSO) δ (ppm)= 31.98 (br).

HRMS (m/z), [**2**-Cl] $^+$: Calc. 584.1789; Found 584.1794. (**2**= $C_{27}H_{38}BCl_2N_3O_2Ru$)

IR (ATR) ῡ (cm^{-1}) = 3085, 2964, 1615, 1578, 1493, 1458, 1373, 1326, 1260, 1218, 1140, 1191, 1025, 967, 867, 800, 743, 680.

Anal. calcd. for $C_{27}H_{38}BCl_2N_3O_2Ru.2CH_2Cl_2$. Et_2O (%): C, 45.91; H, 6.07; N, 4.87 found: C, 46.39; H, 6.18; N, 4.88.

3.4. Synthetic procedure of complex 3



Scheme 7: Synthesis of metal complex 3

In a 25 mL oven dried shlenck tube, imidazolium salt **L3** (130 mg, 0.355 mmol), silver oxide (41.3 mg, 0.178 mmol) were added under a nitrogen atmosphere followed by the addition of 10 mL of dry acetonitrile. The solution was stirred at RT under dark for 16 hours after which [Ru(p-Cymene)$Cl_2]_2$ (109 mg, 0.178 mmol) was added directly under a nitrogen atmosphere and stirred the solution for an additional 24 hours. The solution was completely evaporated under a vacuum and 20 mL of dry THF was added and filtered the solution through celite. The filtrate was concentrated to 1 mL, and 10 mL of dry diethyl ether was added, which resulted in the precipitation of a light yellow solid that was further washed with (5x 5 mL) diethyl ether to obtain the desired complex **3** as a light yellow solid (194.3 mg, 92.5%).

^{1}H NMR (400 MHz, $CDCl_3$) δ (ppm) = 7.90 (s, 2H), 7.45 (d, *J* = 4.1 Hz, 1H), 7.32 (s, 1H), 7.01 (d, *J* = 7.4 Hz, 1H), 6.11 (d, *J* = 4.6 Hz, 1H), 5.88 (d, *J* = 4.2 Hz, 1H), 5.77 (d, *J* = 5.3 Hz, 1H), 5.30 (d, *J* = 4.1 Hz, 1H), 4.47 – 4.27 (m, 2H), 3.37 (s, 2H), 2.15 (s, 3H), 1.97 (t, *J* = 8 Hz, 2H), 1.89 (br, s, 1H), 1.74 (s, 6H), 1.51 – 1.44 (m, 2H), 1.27 (br s, 2H), 1.01 (t, *J* = 8.0 Hz, 3H), 0.85 (d, *J* = 6.4 Hz, 3H), 0.78 (d, *J* = 6.1 Hz, 3H).

^{13}C NMR (101 MHz, $CDCl_3$) δ (ppm) = 181.89, 168.37, 151.32, 141.24, 123.10, 116.79, 111.85, 105.19, 93.13, 84.12, 82.70, 64.98, 51.81, 50.14, 31.44, 30.03, 24.39, 24.12, 24.01, 22.98, 21.55, 20.70, 19.13, 17.68, 12.91.

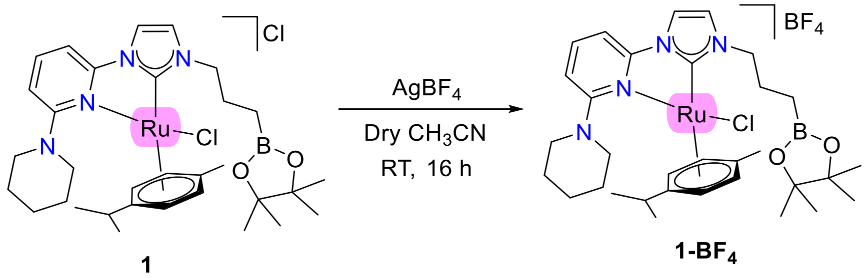
135-DEPT NMR (101 MHz, $CDCl_3$) δ (ppm) = 141.00, 122.90, 116.46, 111.65, 104.83, 92.93, 83.89, 51.60, 49.92, 31.23, 29.82, 24.18, 23.91, 23.80, 22.78, 21.34, 20.47, 18.92, 17.47, 12.70.

ESI-HRMS (m/z), [**3**-Cl]$^+$: Calc. 555.1829; Found 555.1846. (**3**= $C_{27}H_{38}Cl_2N_4Ru$)

IR (ATR) ῡ (cm^{-1}) = 3083, 2964, 1615, 1578, 1493, 1374, 1326, 1260, 1218, 1140, 1091, 1024, 967, 849, 799, 743, 680.

Anal. calcd. for $C_{27}H_{38}Cl_2N_4Ru$. CH_2Cl_2 (%): C, 49.78; H, 5.97; N, 8.29 found: C, 47.80; H, 6.32; N, 7.61.

3.5. Synthetic procedure of complex 1-BF_4



Scheme S8: Synthesis of metal complex 1-BF_4

In a 25 mL oven-dried shlenck tube, complex **1** (60 mg, 0.085 mmol) and $AgBF_4$ (24.93 mg, 0.128 mmol) were added under a nitrogen atmosphere, followed by the addition of 10 mL of dry acetonitrile. The solution was stirred for 16 hours at RT. During this time, the light yellowish solution turns to a yellowish-orange solution. The solution was completely evaporated under the vacuum and 20 mL of dry THF was added to dissolve the residue and filtered the solution through celite. The filtrate was completely evaporated and washed the obtained solid with (5x 5 mL) of dry diethylether to afford the desired complex **1-BF_4** as a light yellowish-orange solid (56.72 mg, 88%).

^1H NMR (400 MHz, $CDCl_3$) δ (ppm) = 7.90 (t, *J* = 8.0 Hz, 1H), 7.81 (d, *J* = 1.8 Hz, 1H), 7.39 (d, *J* = 7.9 Hz, 1H), 7.32 (d, *J* = 1.8 Hz, 1H), 7.02 (d, *J* = 8.2 Hz, 1H), 6.11 (d, *J* = 6.1 Hz, 1H), 5.86 (d, *J* = 5.9 Hz, 1H), 5.78 (d, *J* = 6.1 Hz, 1H), 5.32 (d, *J* = 5.7 Hz, 1H), 4.42 – 4.35 (m, 1H), 4.28 – 4.21 (m, 1H), 3.39 (s, 2H), 2.18 (s, 3H), 2.15-2.04 (m, 3H), 1.90 (s, 2H), 1.75 (s, 4H), 1.63 (s, 2H), 1.28 (s, 12H), 0.95 (t, *J* = 7.6 Hz, 2H), 0.85 (d, *J* = 6.9 Hz, 3H), 0.79 (d, *J* = 6.9 Hz, 3H).

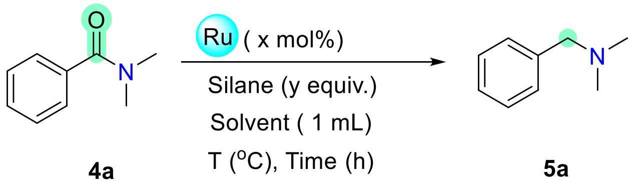
^{13}C NMR (101 MHz, $CDCl_3$) δ (ppm) = 182.71, 169.31, 152.30, 142.31, 124.15, 117.82, 112.93, 106.28, 94.15, 85.20, 83.69, 52.79, 31.03, 25.27, 25.13, 25.02, 24.02, 22.58, 21.88, 18.75.

^{11}B NMR (128 MHz, $CDCl_3$) δ (ppm) = 33.28 (br, s), -0.89 (s).

^{19}F NMR (377 MHz, $CDCl_3$) δ (ppm) = -152.66 (s), -152.71 (s).

ESI-HRMS (m/z), [**M**-BF_4^-]$^+$: Calc. 667.2524; Found 667.2499. (M= $C_{32}H_{47}B_2ClF_4N_4O_2Ru$)

Table S1. Optimization Table for Tertiary Amide Hydrogenation^a



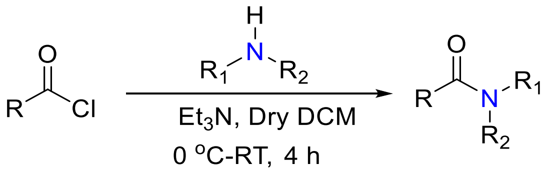
Sl. No.	[Ru] (mol %)	Silane (equiv.)	T (° C)	Time (h)	Solvent (mL)	Yield 5a (%)^b
1	1 (5)	1	60	24	Toluene	95
2	1 (2)	1	60	24	Toluene	94
3	1 (1)	1	60	24	Toluene	45
4	1 (1)	1	60	48	Toluene	65
5	1 (1)	1	80	24	Toluene	84
6	1 (1)	1	100	24	Toluene	85
7	1 (0.2)	1	100	48	Toluene	22
8	1 (1)	1	80	36	Toluene	85
9	**1 (1)**	**1.1**	**80**	**36**	**Toluene**	**97**
10	1 (1)	1.1	80	24	Toluene	88
11	1 (1)	1.1	60	36	Toluene	75
12	1 (1)	Ph_2SiH_2 (1.1)	80	36	Toluene	55
13	1 (1)	Et_3SiH (1.1)	80	36	Toluene	NR
14	1 (1)	1.1	80	36	Benzene	97
15	1 (1)	1.1	80	36	THF	61
16	1 (1)	1.1	80	36	1,4-dioxane	33
17	1 (1)	1.1	80	36	DCM	30
18	-	1.1	80	36	Toluene	NR
19	[Ru(p-Cymene)Cl_2]$_2$ (1)	1.1	80	36	Toluene	20

20[c]	1 (1)	1.1	80	36	Toluene	90
21	2 (1)	1.1	80	36	Toluene	90
22	3(1)	1.1	80	36	Toluene	38
23	1-PF_6 (1)	1.1	80	36	Toluene	94
24	1-BF_4(1)	1.1	80	36	Toluene	96

[a]Reaction conditions: **4a** (0.503 mmol, 1 equiv.), **[Ru]** (x mol %), **Silanes** (y equiv. w.r.t **4a**), Toluene (1 mL). [b]Yield was determined using ^1H NMR using mesitylene as internal standard. [c]In the presence of Hg (300 equiv. w.r.t. catalyst **1**). NR= No Reaction,

4. General Procedure for Synthesis of Tertiary Amides

Method A: Tertiary amides were prepared by using a slightly modified literature procedure.[6]

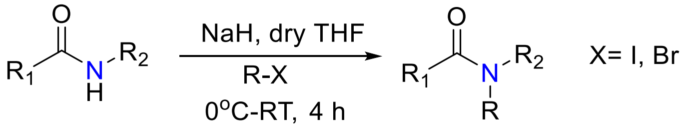


In a 100 mL oven dried round bottom flask, 10 mL of dry DCM was added followed by the addition of amine (3 equiv.) and Et_3N (3 equiv.) and cooled the solution to 0 ºC. Acyl chloride (1 equiv.) was added drop wise and allow the solution to warm to room temperature and stir for additional 4 hours. After completion of reaction, excess amine was evaporated under reduced pressure and the solution was extracted with DCM (3 x 20 mL). The organic layer was dried over anhydrous Na_2SO_4, and the filtrate was concentrated under reduced pressure.

For amides **4a-4e**, **4h**, **4o**, **and 4p:** Pure product was obtained after removing the solvents.

For amides **4f** and **4g**: Purified with silica gel column chromatography using ethyl acetate/ hexane mixture as the eluent.

Method B: Tertiary amides were prepared by using a slightly modified literature procedure.[7]



In a 100 mL round bottom flask, sodium hydride (2 equiv.) in 15 mL of dry THF was added under nitrogen atmosphere and cooled the solution to 0º C. Secondary amide (1 equiv.) was added in one portion and stirred the solution until H_2 gas evolution ceased. Alkyl or allyl halides (2 equiv.) was added dropwise and the solution was allowed to warm to room temperature and stirred for 4 hours. The solution was evaporated under vacuum and quenched with 20 mL water and extracted with DCM (3 x 20 mL). The organic layer was dried over anhydrous Na_2SO_4, and the filtrate was concentrated to obtain the desired amide in excellent yield.

For amides **4l, 4n**: Purified with silica gel column chromatography using ethyl acetate/ hexane mixture as the eluent.

Amide **4u** was prepared according to the known literature procedure.[8]

Amide **4w-4z** was prepared following the similar literature procedure[9] and slightly modified procedure for steps 2-3[6,7]

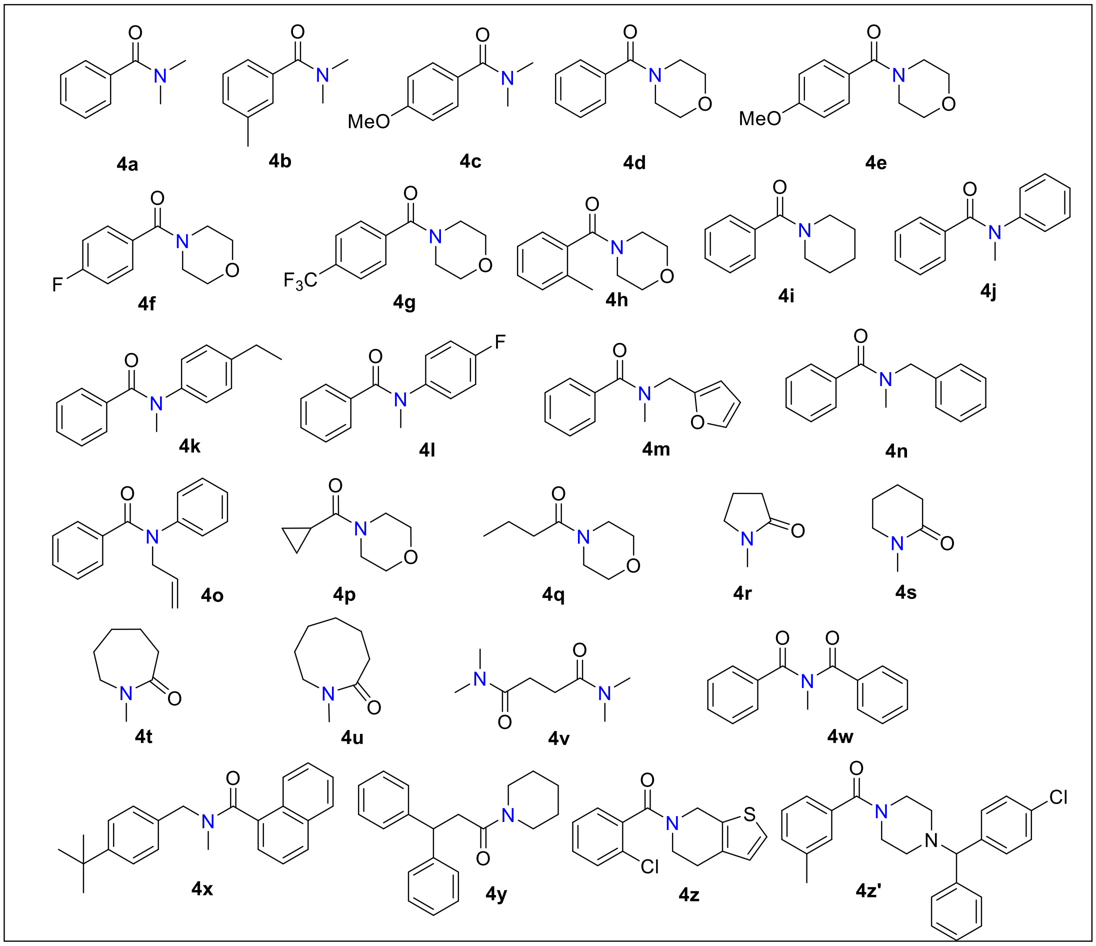
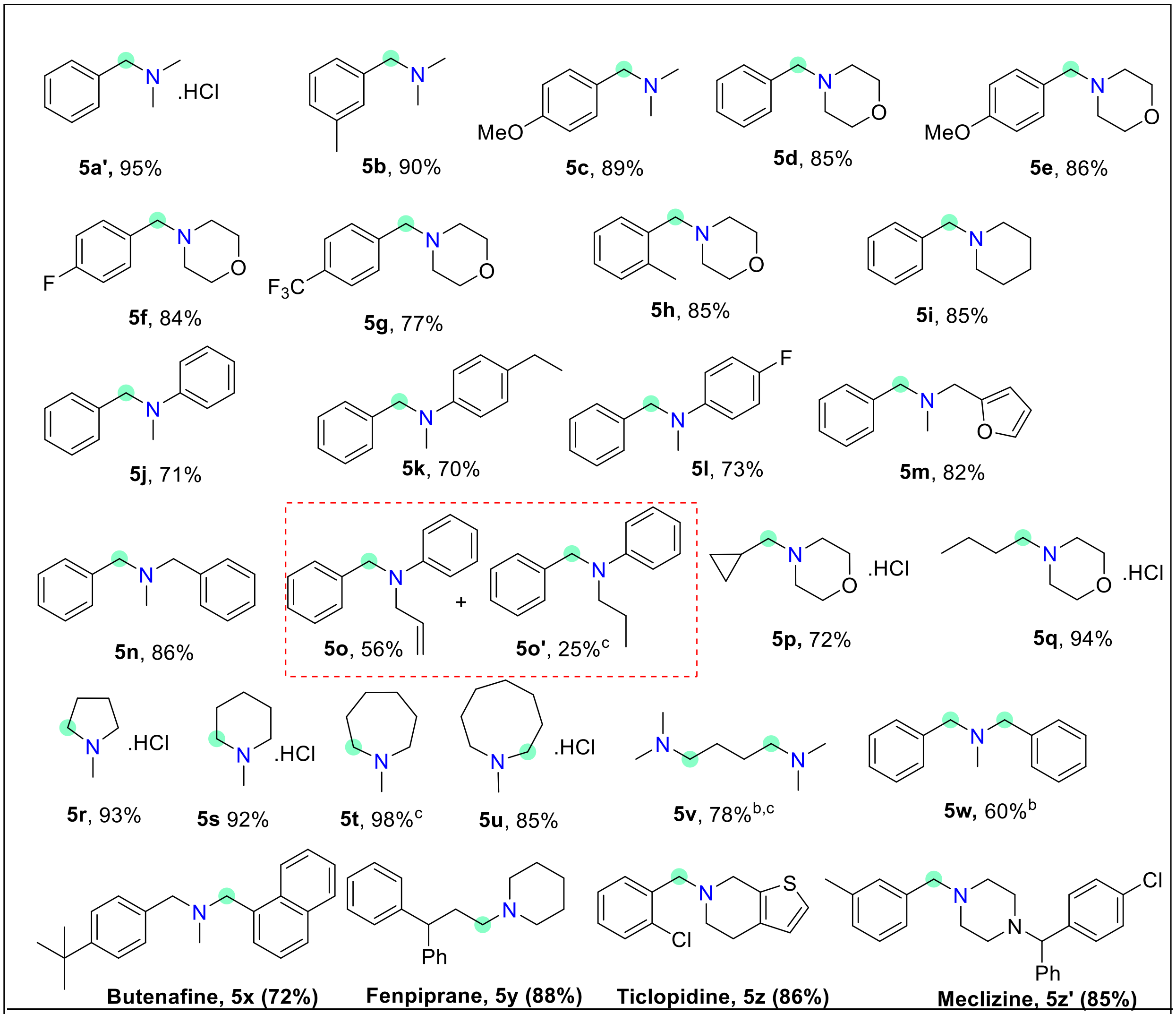


Figure S1A. List of tertiary amide substrates (**4a-4z'**)

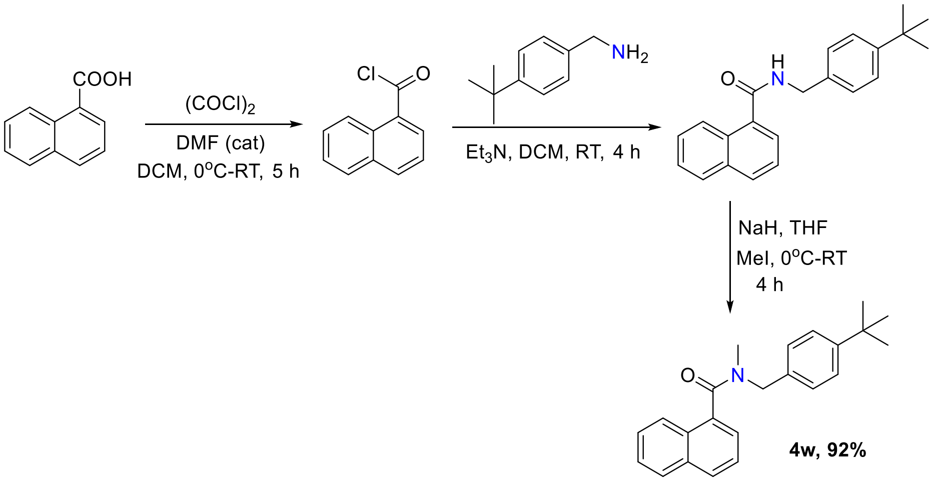


[a]Reaction conditions: Amide (0.503 mmol, 1 equiv.), 1 (1 mol %), $PhSiH_3$ (1.1 equiv. w.r.t amide), Toluene (1 mL), 36 h. bIsolated yields. [b]Reaction was performed using 2.2 equiv. of $PhSiH_3$, 120 ºC, 36 h. [c]NMR yield using mesitylene as the internal standard.

Figure S1B. List of tertiary amines derived from tertiary amides (**5a'-5z'**)

5. General Procedure for Synthesis of Amide (4w)

Amide **4w** was prepared following the known literature procedure[9] for step 1 and slightly modified procedure for steps 2-3[6,7]


4w, 92%

Step1:

In a 100 mL oven dried two neck round bottom flask, 1-napthoic acid (1 equiv., 4.64 mmol) was taken under N_2 atmosphere. 10 mL dry DCM was added and the solution was cooled to 0 ºC. Oxalyl chloride (2 equiv., 9.29 mmol) and four drops of DMF were added dropwise, and the solution was allowed to warm to room temperature and stirred for an additional 5 hours. After completion of the reaction, excess oxalyl chloride and the solvent were evaporated under reduced pressure. The oily liquid obtained was used in the next step without further purification.

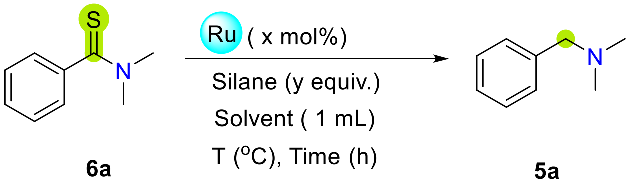
Step2:

In a 100 mL oven dried two neck round bottom flask, (4-(tert-butyl)phenyl)methanamine (1.5 equiv., 4.72 mmol) was taken under N_2 atmosphere. 8 mL dry DCM was added and the solution was cooled to 0 ºC. Triethyl amine (2 equiv., 6.29 mmol) was added dropwise and stirred the solution for 30 minutes, followed by the addition of 1-napthoyl chloride (1 equiv., 3.14 mmol) in 2 mL of dry DCM and allowing the solution to warm to room temperature and stir for additional 3.5 hours. After completion of reaction, solvent was evaporated under reduced pressure. The residue obtained was purified using silica gel column chromatography (40% EA/hexane mixture) to obtain the desired product N-(4-(tert-butyl)benzyl)-1-naphthamide as a white solid.

Step 3:

In a 100 mL oven dried two neck round bottom flask N-(4-(tert-butyl)benzyl)-1-naphthamide (1 equiv., 1.89 mmol) and NaH (2 equiv., 3.78 mmol) was taken under N_2 atmosphere. 10 mL dry THF was added, and the solution was cooled to 0 ºC and stirred for 30 minutes until the H_2 gas stopped. Methyl iodide (2 equiv., 3.78 mmol) was added dropwise and stirred the solution for 3.5 hours. After completion of reaction, solvent was evaporated under reduced pressure. The residue obtained was purified using silica gel column chromatography (30% EA/hexane mixture) to obtain the desired product N-(4-(tert-butyl)benzyl)-N-methyl-1-naphthamide as a white solid (92%).

Table S2. Optimization Table for Tertiary Thioamide Hydrogenation[a]

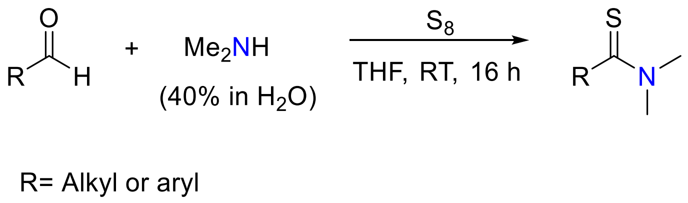


Sl. No.	[Ru] (mol %)	Silane (equiv.)	T (° C)	Time (h)	Solvent (mL)	Yield 5a (%)[b]
1	1 (1)	$PhSiH_3$ (1.1)	100	24	Toluene	99
2	1 (2)	$PhSiH_3$ (1.1)	80	24	Toluene	99
3	1 (1)	$PhSiH_3$ (1.1)	60	24	Toluene	98
4	1 (1)	$PhSiH_3$ (1.1)	RT	24	Toluene	ND
5	**1 (1)**	**$PhSiH_3$ (1.1)**	**60**	**12**	**Toluene**	**98**
6	1 (1)	$PhSiH_3$ (1.1)	60	6	Toluene	55
7	1 (1)	$PhSiH_3$ (1)	60	12	Toluene	90
8	1 (0.5)	$PhSiH_3$ (1.1)	60	12	Toluene	54
9	1 (1)	Et_3SiH (1.1)	60	12	Toluene	ND
10	1 (1)	$PhSiH_3$ (1.1)	60	12	Benzene	98
11	1 (1)	$PhSiH_3$ (1.1)	60	12	1,4-Dioxane	47
12	1 (1)	$PhSiH_3$ (1.1)	60	12	THF	18
13	3 (1)	$PhSiH_3$ (1.1)	60	12	Toluene	35
14	2 (1)	$PhSiH_3$ (1.1)	60	12	Toluene	91

[a]Reaction conditions: **6a** (0.503 mmol, 1 equiv.), **[Ru]** (x mol %), **Silanes** (y equiv. w.r.t 6a), Toluene (1 mL). [b]Yield was determined using ^1H NMR using mesitylene as internal standard.

6. General Procedure for Synthesis of Tertiary Thioamides

Tertiary thioamides (**6a-6g and 6n**) were prepared by using a known literature procedure.[10]

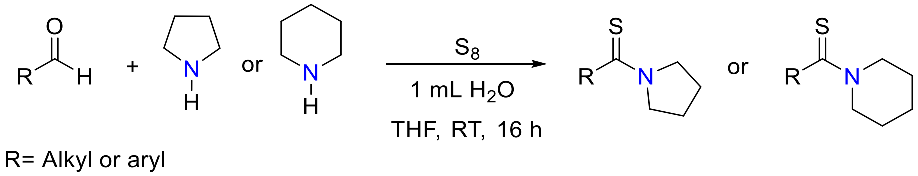


Method A:

In a 100 mL oven dried round bottom flask, elemental sulfur (2 equiv.) was taken. 3 mL of THF was added followed by the addition of dimethylamine (40% in H_2O, 5 equiv.) and aldehyde (1 equiv.). The solution was stirred for 16 hours at RT. The solvent and excess amines were removed under reduced pressure. The obtained crude residue was purified using silica gel column chromatography using mixture of ethyl acetate/ Hexane as the eluent.

Tertiary thioamides (**6h-6m**) were prepared by using a slightly modified literature procedure.[10]

Method B:



In a 100 mL oven dried round bottom flask, elemental sulfur (2 equiv.) was taken in 3 mL of THF and 1 mL of H_2O was added followed by the addition of pyrrolidine or piperidine (5 equiv.) and aldehyde (1 equiv.). The solution was stirred for 16 hours at RT. The solvent and excess amines were removed under reduced pressure. The obtained crude residue was purified using silica gel column chromatography using mixture of ethyl acetate/ Hexane as the eluent.

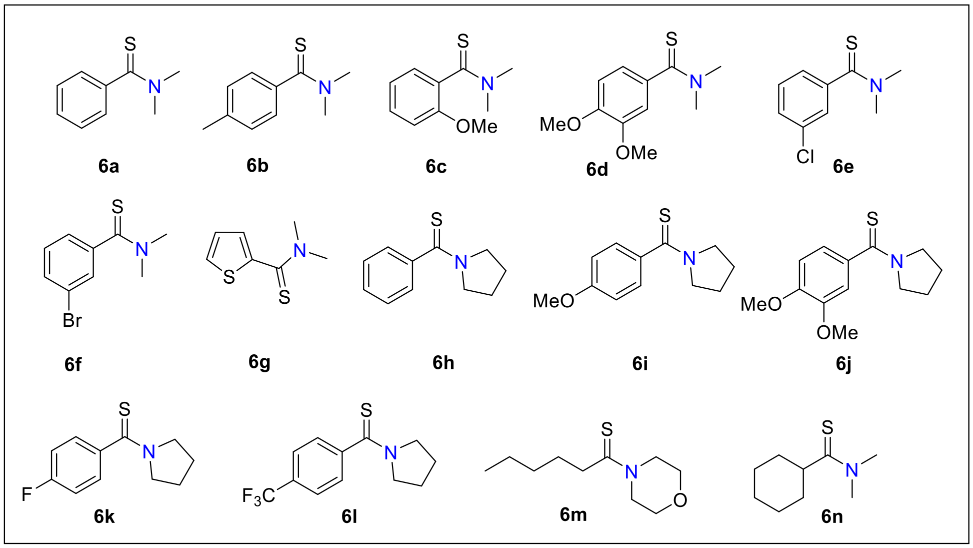
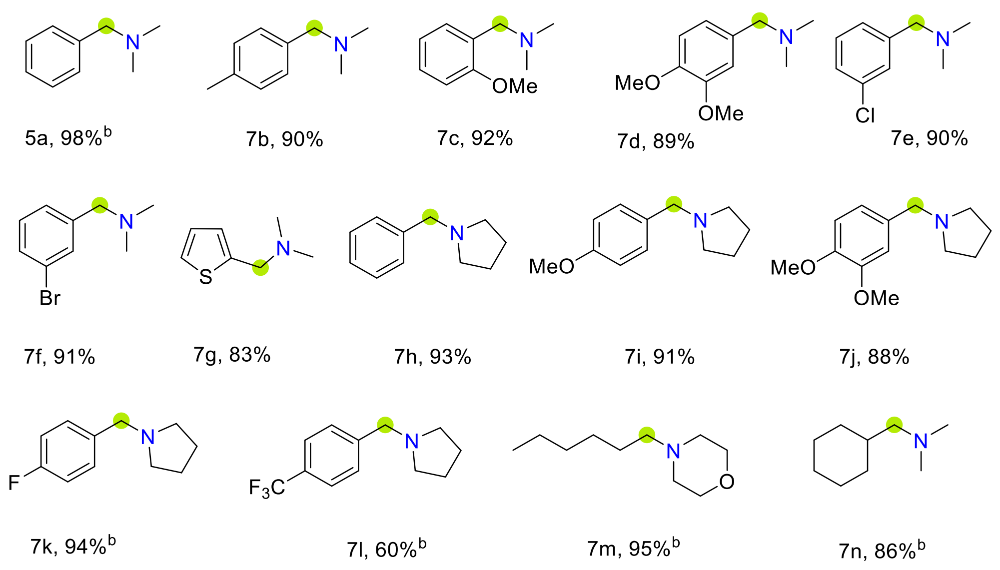


Figure S2A. List of tertiary thioamide substrates (**6a-6n**)

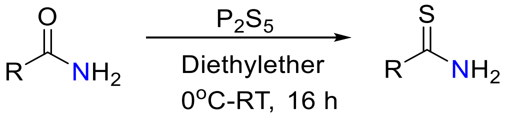


[a]Reaction conditions: (A) Tertiary thioamide (0.503 mmol, 1 equiv.), 1 (1 mol %), $PhSiH_3$ (1.1 equiv. w.r.t thioamide), Toluene (1 mL), 12 h.Isolated Yield. [b]NMR yield.

Figure S2B. List of tertiary amines derived from tertiary thioamides (**5a-7n**)

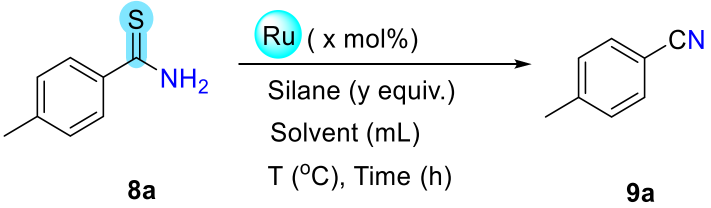
7. General Procedure for Synthesis of Primary Thioamides

Primary thioamides (**8a-8f**) were prepared by using a known literature procedure.[11]



In a 100 mL oven-dried round bottom flask, primary amide (1 equiv.) was taken. 40 mL of diethyl ether was added and cooled the solution to 0 ºC. P_2S_5 (0.5 equiv.) was added portion-wise, and the solution was allowed to warm to RT and stir for 16 hours. The solution was filtered through celite and washed thoroughly with diethyl ether and the filtrate obtained was evaporated under vacuum. The crude residue was purified using silica gel column chromatography using ethyl acetate/ Hexane as the eluent.

Table S3. Optimization Table for Primary Thioamide Hydrogenation[a]



Sl. No.	[Ru] (mol %)	Silane (equiv.)	T (° C)	Time (h)	Solvent (mL)	Yield 9a (%)[b]
1	1 (1)	$PhSiH_3$ (1)	100	12	Toluene	83
2	1 (1)	$PhSiH_3$ (1)	100	16	Toluene	94
3	1 (1)	$PhSiH_3$ (0.8)	100	16	Toluene	80
4	1 (1)	$PhSiH_3$ (1)	90	16	Toluene	63
5	1 (0.5)	$PhSiH_3$ (1)	100	16	Toluene	61
6	1 (1)	Ph_2SiH_2 (1)	100	16	Toluene	76
7	1 (1)	$PhSiH_3$ (1)	100	16	THF	51
8	1 (1)	$PhSiH_3$ (1)	100	16	1,4-Dioxane	62
9	1 (1)	$PhSiH_3$ (1)	100	16	DCM	37
10	3 (1)	$PhSiH_3$ (1)	100	16	Toluene	67

[a]Reaction conditions: **8a** (0.503 mmol, 1 equiv.), **[Ru]** (x mol %), **Silanes** (y equiv. w.r.t 8a), Toluene (1.5 mL). [b]Yield was determined using ^1H NMR using mesitylene as internal standard.

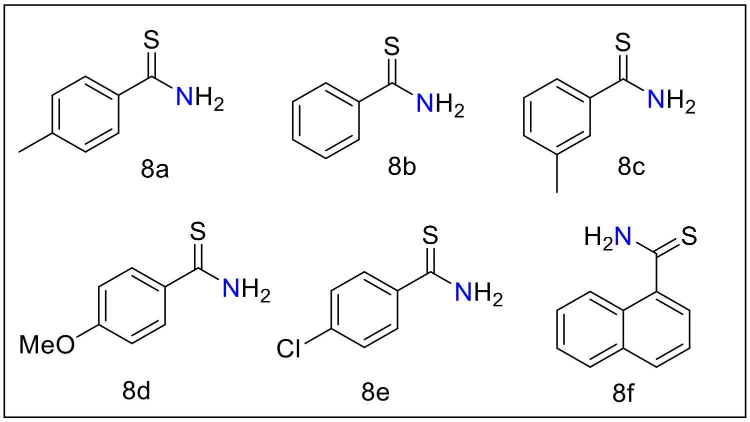
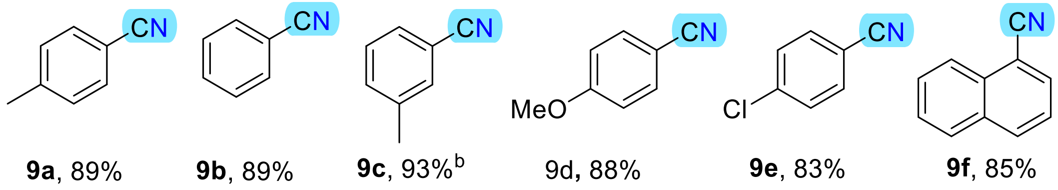


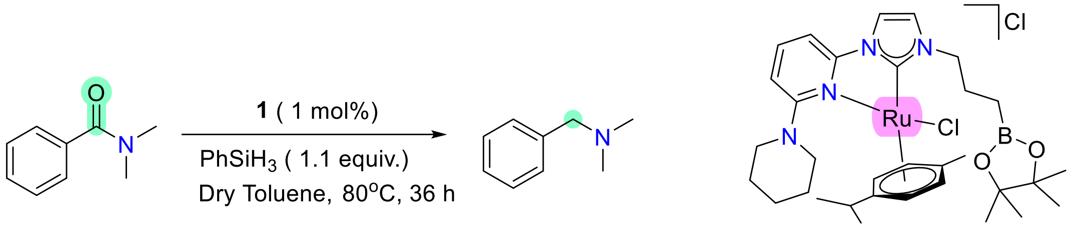
Figure S3A. List of primary thioamide substrates (8a-8f)



^{a}Primary thioamides (0.503 mmol, 1 equiv.), 1 (1 mol %), $PhSiH_3$ (1 equiv. w.r.t thioamide), Toluene (1.5 mL), 16 h. Isolated yields. ^{b}NMR yield using mesitylene as the internal standard.

Figure S3B. List of nitriles derived from primary thioamides (9a-9f)

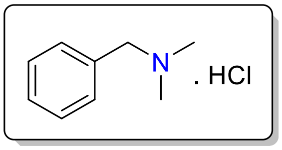
8. Typical Procedure for Catalytic Deoxygenative Reduction of Tertiary Amides



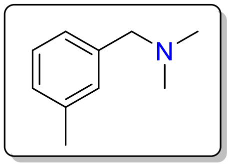
4a 5a 1

Inside a N$_2$ filled glove box, a 25 mL pressure tube equipped with a magnetic stirring bar was charged with **1** (3.53 mg, 1 mol%), **4a** (75 mg, 0.503 mmol). 1 mL of dry toluene was added followed by the addition of phenylsilane (59.9 mg, 0.553 mmol) and the closed vessel was heated at 80 °C for 36 hours. After completion of reaction, the solution was cooled down to room temperature and mesitylene (0.503 mmol) was added as internal standard and NMR yield was analyzed using ^{1}H NMR in CDCl$_3$ as the solvent. In all cases, the product peaks were integrated with respect to the -C*H*- peak of the internal standard mesitylene which was normalized to 3. The solution was passed through a small pad of celite and concentrated under reduced pressure. The residue was purified by column chromatography using silica/neutral alumina in EtOAc/ hexane mixture as the eluent. In the case of volatile amine compounds, the product was isolated as a hydrochloride salt using 2 M HCl in diethylether solution.

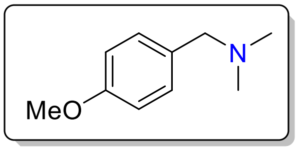
9. Characterization of Amine Products Derived from Tertiary Amides



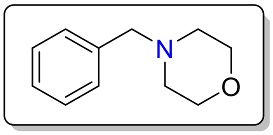
N,N-dimethyl-1-phenylmethanamine hydrochloride (5a′): white solid, 68.47 mg (95%). ^{1}H NMR (400 MHz, CDCl$_3$) δ (ppm) = 12.84 (s, 1H), 7.60 (s, 2H), 7.46 (s, 3H), 4.16 (d, *J* = 2.6 Hz, 2H), 2.75 (s, 6H); ^{13}C NMR (101 MHz, CDCl$_3$) δ (ppm) = 131.23, 130.44, 129.61, 128.49, 61.49, 42.44. ESI-HRMS (m/z) [M-Cl$^-$]$^+$, calcd. 136.1126; found 136.1123. (M= C$_9$H$_{14}$N)



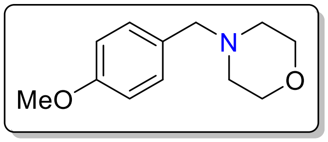
N,N-dimethyl-1-(m-tolyl)methanamine[12] (5b): Colorless liquid, 67.58 mg (90%). ^{1}H NMR (400 MHz, CDCl$_3$) δ (ppm) = 7.21 (t, *J* = 7.5 Hz, 1H), 7.14 (s, 1H), 7.08 (t, *J* = 6.6 Hz, 2H), 3.38 (s, 2H), 2.34 (s, 3H), 2.24 (s, 6H); ^{13}C NMR (101 MHz, CDCl$_3$) δ (ppm) = 129.97, 128.23, 127.93, 126.33, 64.57, 45.56, 21.35.



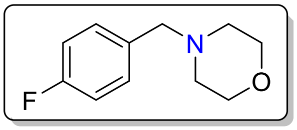
1-(4-methoxyphenyl)-N,N-dimethylmethanamine[12] (5c): Colorless liquid, 73.91 mg (89%). ^{1}H NMR (400 MHz, $CDCl_3$) δ (ppm) = 7.21 (d, *J* = 8.6 Hz, 2H), 6.85 (d, *J* = 8.6 Hz, 2H), 3.80 (s, 3H), 3.36 (s, 2H), 2.22 (s, 6H); ^{13}C NMR (101 MHz, $CDCl_3$) δ (ppm): 158.85, 131.09, 130.42, 113.74, 63.86, 55.39, 45.34.



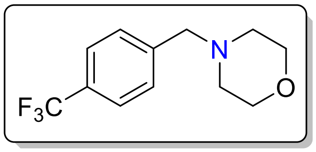
1-benzylmorpholine[13] (5d): Colorless liquid, 76.35 mg (85%). ^{1}H NMR (400 MHz, $CDCl_3$) δ (ppm) = 7.31 – 7.23 (m, 5H), 3.69 (t, *J* = 4.8 Hz, 4H), 3.48 (s, 2H), 2.43 (t, *J* = 4.0 Hz 4H); ^{13}C NMR (101 MHz, $CDCl_3$) δ (ppm) = 137.91, 129.35, 128.40, 127.29, 67.17, 63.62, 53.77. ESI-HRMS (m/z) $[M+H]^+$, calcd. 178.1232; found 178.1077. (M= $C_{11}H_{15}NO$)



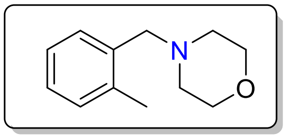
1-(4-methoxybenzyl)morpholine[14] (5e): Colorless liquid, 80.5 mg (86%). ^{1}H NMR (400 MHz, $CDCl_3$) δ (ppm) 7.23 (d, *J* = 8.5 Hz, 2H), 6.85 (d, *J* = 8.6 Hz, 2H), 3.80 (s, 3H), 3.70 (t, *J* = 4.0 Hz, 4H), 3.43 (s, 2H), 2.42(t, *J* = 40 Hz, 4H). ^{13}C NMR (101 MHz, $CDCl_3$) δ (ppm) = 158.94, 130.53, 129.88, 113.76, 67.17, 62.99, 55.40, 53.68.



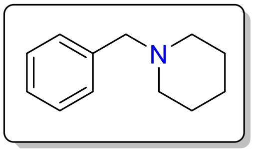
1-(4-fluorobenzyl)morpholine[15] (5f): Yellow liquid, 117.59 mg (84%). ^{1}H NMR (400 MHz, $CDCl_3$) δ (ppm) 7.21 (dd, *J* = 8.4, 5.7 Hz, 2H), 6.92 (t, *J* = 8 Hz, 2H), 3.63 (t, *J* = 4 Hz, 4H), 3.38 (s, 2H), 2.35 (t, *J* = 4 Hz, 4H). ^{13}C NMR (101 MHz, $CDCl_3$) δ (ppm) = 163.40, 160.96, 133.59, 130.79, 115.29, 115.08, 67.12, 62.75, 53.66. ^{19}F NMR (377 MHz, $CDCl_3$) δ (ppm) = -115.76 (s). ESI-HRMS (m/z) $[M+H]^+$, calcd. 196.1138; found 196.1001. (M= $C_{11}H_{14}FNO$)



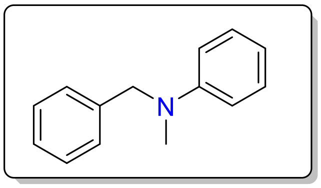
1-(4-(trifluoromethyl)benzyl)morpholine[16] (5g): Yellow liquid, 94.95 mg (77%). ^{1}H NMR (400 MHz, $CDCl_3$) δ (ppm) = 7.57 (d, *J* = 8.0 Hz, 2H), 7.46 (d, *J* = 8.0 Hz, 2H), 3.71 (t, *J* = 4 Hz, 4H), 3.54 (s, 2H), 2.44 (t, *J* = 4 Hz, 4H); ^{13}C NMR (101 MHz, $CDCl_3$) δ (ppm) = 142.33, 129.37, 125.36 (q), 67.12, 62.98, 53.77. ESI-HRMS (m/z) $[M+H]^+$, calcd. 246.1106; found 246.0919. (M= $C_{12}H_{14}F_3NO$)



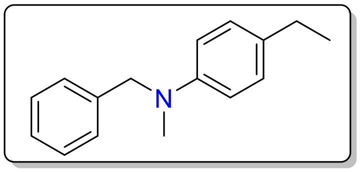
1-(2-methylbenzyl)morpholine (5h): Colorless liquid, 79.98 mg (83%). ^{1}H NMR (400 MHz, $CDCl_3$) δ (ppm) = 7.25 (d, *J* = 6.4 Hz, 1H), 7.19-7.11 (m, 3H), 3.68 (t, *J* = 4.0 Hz, 4H), 3.46 (s, 2H), 2.44 (s, 4H), 2.37 (s, 3H); ^{13}C NMR (101 MHz, $CDCl_3$) δ (ppm) = 137.75, 130.43, 130.06, 127.30, 125.59, 67.25, 61.42, 53.80, 19.35. ESI-HRMS (m/z) $[M+H]^+$, calcd. 192.1388; found 192.1402. (M= $C_{12}H_{17}NO$)



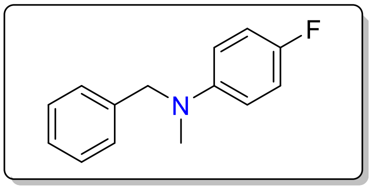
1-Benzylpiperidine[13] (5i): Colorless oil, 74.70 mg (85%). ^{1}H NMR (400 MHz, CDCl$_3$) δ (ppm) = 7.31 – 7.25 (m, 5H), 3.47 (s, 2H), 2.37 (br s, 4H), 1.60 – 1.54 (m, 4H), 1.45 – 1.39 (m, 2H); ^{13}C NMR (101 MHz, CDCl$_3$) δ (ppm) = 138.77, 135.83, 129.39, 128.23, 126.96, 64.05, 54.64, 26.13, 24.54. GC-MS (m/z), calcd. 175.13; found 175.15. (M= $C_{12}H_{17}N$)



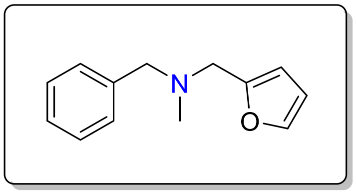
N-benzyl-N-methylaniline[13] (5j): Yellow liquid, 70.32 mg (71%). ^{1}H NMR (400 MHz, CDCl$_3$) δ (ppm) = 7.33 – 7.30 (m, 2H), 7.25 -7.20 (m, 5H), 6.77 – 6.70 (m, 3H), 4.54 (s, 2H), 3.02 (s, 3H); ^{13}C NMR (101 MHz, CDCl$_3$) δ (ppm) = 149.91, 139.18, 129.32, 128.70, 126.99, 126.88, 116.67, 112.50, 56.78, 38.64. ESI-HRMS (m/z) [M+H]$^+$, calcd. 198.1283; found 198.1167. (M= $C_{14}H_{15}N$)



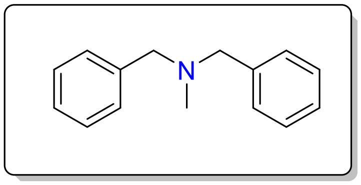
N-benzyl-4-ethyl-N-methylaniline[17] (5k): Yellow liquid, 79.65 mg (70%). ^{1}H NMR (400 MHz, CDCl$_3$) δ (ppm) = ^{1}H NMR (400 MHz, CDCl$_3$) δ (ppm) = 7.25 – 7.21 (m, 2H), 7.18 – 7.14 (m, 3H), 6.98 (d, *J* = 8.5 Hz, 2H), 6.64 (d, *J* = 8.1 Hz, 2H), 4.41 (s, 2H), 2.90 (s, 3H), 2.48 (q, *J* = 7.6 Hz, 2H), 1.12 (t, *J* = 7.6 Hz, 3H); ^{13}C NMR (101 MHz, CDCl$_3$) δ (ppm) = 148.13, 139.45, 132.55, 128.65, 127.00 (d), 112.84, 57.21, 38.79, 27.92, 16.02.



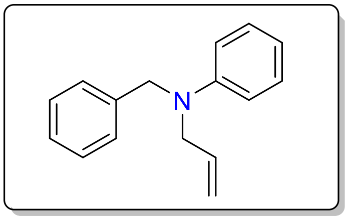
N-benzyl-4-fluoro-N-methylaniline[17] (5l): Yellow liquid, 78.56 mg (73%). ^{1}H NMR (400 MHz, CDCl$_3$) δ (ppm) = 7.33 – 7.30 (m, 2H), 7.26–7.21 (m, 3H), 6.94-6.88 (m, 2H), 6.69-6.66 (m, 2H), 4.46 (s, 2H), 2.96 (s, 3H); ^{13}C NMR (101 MHz, CDCl$_3$) δ (ppm) = 155.84, 153.50, 145.59, 137.89, 127.71, 126.11, 126.01, 114.74, 114.52, 112.86 (d), 56.69, 38.22. ^{19}F NMR (377 MHz, CDCl$_3$) δ (ppm) = -129.09. ESI-HRMS (m/z) [M+H]$^+$, calcd. 216.1189; found 216.1091. (M= $C_{14}H_{14}FN$)



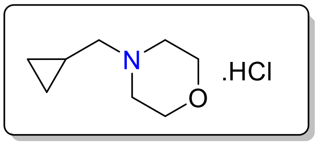
N-benzyl-1-(furan-2-yl)-N-methylmethanamine[18] (5m): Colorless viscous liquid, 82.78 mg (82%). ^{1}H NMR (400 MHz, CDCl$_3$) δ (ppm) = 7.41 (br s, 1H), 7.35-7.27 (m, 5H), 6.34 (m, 1H), 6.22 (d, *J* = 3.1 Hz, 1H), 3.59 (s, 2H), 3.55 (s, 2H), 2.25 (s, 3H); ^{13}C NMR (101 MHz, CDCl$_3$) δ (ppm) = 152.62, 142.16, 138.83, 129.26, 128.39, 127.18, 110.18, 108.68, 61.32, 53.40, 42.13. ESI-HRMS (m/z) [M+H]$^+$, calcd. 202.1232; found 202.1185. (M= $C_{13}H_{15}NO$)



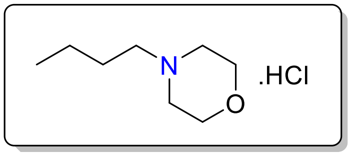
N-benzyl-N-methyl-1-phenylmethanamine[18] (5n): Colorless oil**,** 91.52 mg (86%). ^{1}H NMR (400 MHz, CDCl$_3$) δ (ppm) = 7.30 – 7.15 (m, 10H), 3.45 (s, 4H), 2.11 (s, 3H). ^{13}C NMR (101 MHz, CDCl$_3$) δ (ppm) = 139.49, 129.07, 128.36, 127.06, 62.01, 42.39. ESI-HRMS (m/z) [M+H]$^+$, calcd. 212.1439; found 212.1479. (M= $C_{15}H_{17}N$)



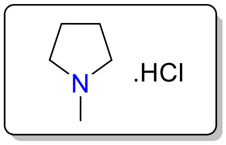
N-allyl-N-benzylaniline[19] (5o): Colorless viscous liquid, 62.78 mg (56%). ^{1}H NMR (400 MHz, CDCl$_3$) δ (ppm) = 7.31 – 7.22 (m, 5H), 7.18-7.14 (m, 2H) 6.71 – 6.65 (m, 3H), 5.90 – 5.82 (m, 1H), 5.20 – 5.15 (m, 2H), 4.53 (s, 2H), 3.99 (d, *J* = 4.8 Hz, 2H); ^{13}C NMR (101 MHz, CDCl$_3$) δ (ppm) = 149.10, 139.10, 133.80, 129.28, 128.72, 126.95, 126.74, 116.65, 116.47, 112.54, 54.10, 53.19. ESI-HRMS (m/z) [M+H]$^+$, calcd. 224.1439; found 224.1357. (M= $C_{16}H_{17}N$)



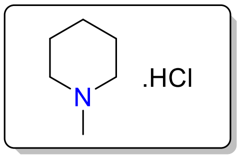
4-(cyclopropylmethyl)morpholine hydrochloride (5p): White solid, 51.23 mg (72%). ^{1}H NMR (400 MHz, CDCl$_3$) δ (ppm) = ^{1}H NMR (400 MHz, CDCl$_3$) δ (ppm) = 13.00 (s, 1H), 4.33 (t, *J* = 12.3 Hz, 2H), 3.98 (d, *J* = 10.9 Hz, 2H), 3.55 (d, *J* = 11.9 Hz, 2H), 2.91 (br s, 4H), 1.37-1.31 (m, 1H), 0.80 (q, *J* = 5.5 Hz, 2H), 0.45 (q, *J* = 5.2 Hz, 2H); ^{13}C NMR (101 MHz, CDCl$_3$) δ = (ppm) = 63.77, 62.49, 51.68, 5.13, 5.00. ESI-HRMS (m/z) [M-Cl$^-$]$^+$, calcd. 142.1232; found 142.1232. (M= $C_8H_{16}NO$)



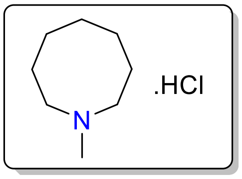
1-butylmorpholine hydrochloride (5q): White solid, 68.24 mg (94%). ^{1}H NMR (400 MHz, CDCl$_3$) δ (ppm) = 13.05 (s, 1H), 4.33 (t, *J* = 12.3 Hz, 2H), 3.96 (d, *J* = 11.7 Hz, 2H), 3.43 (d, *J* = 11.6 Hz, 2H), 2.95 – 2.84 (m, 4H), 1.90 (br s, 2H), 1.46 – 1.37 (m, 2H), 0.97 (t, *J* = 7.3 Hz, 3H). ^{13}C NMR (101 MHz, CDCl$_3$) δ (ppm) = 63.76, 58.04, 52.00, 25.23, 20.24, 13.65. ESI-HRMS (m/z) [M-Cl$^-$]$^+$, calcd. 144.1388; found 144.1421. (M= $C_8H_{18}NO$)



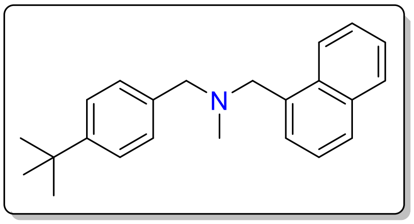
1-methylpyrrolidine hydrochloride (5r): White solid, 39.86 mg (93%). ^{1}H NMR (400 MHz, CDCl$_3$) δ (ppm) = 12.31 (s, 1H), 3.74 (br s, 2H), 2.83 (d, *J* = 4.6 Hz, 3H), 2.81-2.76 (m, 2H), 2.19 – 2.04 (m, 4H); ^{13}C NMR (101 MHz, CDCl$_3$) δ (ppm) = 55.45, 41.08, 23.82. ESI-HRMS (m/z) [M-Cl$^-$]$^+$, calcd. 86.0970; found 86.0692. (M= $C_5H_{12}N$)



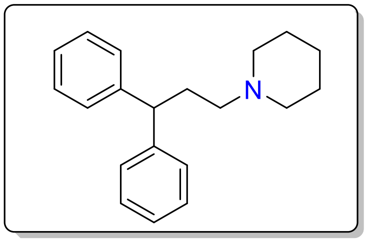
1-methylpiperidine hydrochloride (5s): White solid, 43.82 mg (92%). ^{1}H NMR (400 MHz, CDCl$_3$) δ (ppm) = 12.16 (s, 1H), 3.46 (d, *J* = 11.1 Hz, 2H), 2.73 (d, *J* = 4.4 Hz, 3H), 2.65 (dd, *J* = 21.8, 10.5 Hz, 2H), 2.23 (q, *J* = 12.9 Hz, 2H), 1.86 (t, *J* = 17.6 Hz, 3H), 1.43 – 1.32 (m, 1H); ^{13}C NMR (101 MHz, CDCl$_3$) δ (ppm) = 55.25, 44.08, 22.86, 21.65. ESI-HRMS (m/z) [M-Cl$^{-]+}$, calcd. 100.1126; found 100.0781. (M= $C_6H_{14}N$)



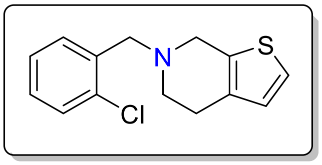
1-methylazocane hydrochloride (5u): White solid, 66.43 mg (85%). ^{1}H NMR (400 MHz, $CDCl_3$) δ (ppm) = 11.94 (s, 1H), 3.46 (br s, 2H), 2.99 (br s, 2H), 2.76 (s, 3H), 2.0 –1.54 (m, 10H); ^{13}C NMR (101 MHz, $CDCl_3$) δ (ppm) = 52.77, 43.25, 26.20, 24.24, 22.50. ESI-HRMS (m/z) $[M-Cl^-]^+$, calcd. 128.1439; found 128.1131. (M= $C_8H_{17}N$)



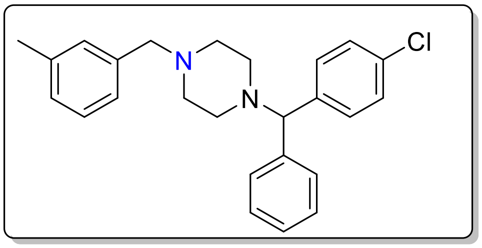
N-(4-(tert-butyl)benzyl)-N-methyl-1-(naphthalen-1-yl)methanamine (Butenafine)[20] (5x): Colorless oily liquid (115.13, 72%). ^{1}H NMR (400 MHz, $CDCl_3$) δ (ppm) = 8.41 (d, *J* = 8.0 Hz, 1H), 7.97 (d, *J* = 7.9 Hz, 1H), 7.90 (d, *J* = 8.2 Hz, 1H), 7.66 – 7.59 (m, 3H), 7.56 – 7.44 (m, 5H), 4.08 (s, 2H), 3.73 (s, 2H), 2.36 (s, 3H), 1.48 (s, 9H); ^{13}C NMR (101 MHz, $CDCl_3$) δ (ppm) = 149.93, 136.36, 135.13, 134.03, 132.68, 128.92, 128.47, 128.01, 127.50, 125.75, 125.65, 125.19 (d), 125.02, 62.14, 60.54, 42.48, 34.55, 31.55. ESI-HRMS (m/z) $[M+H]^+$, calcd. 318.2222; found 318.2265. (M= $C_{23}H_{27}N$)



1-(3,3-diphenylpropyl)piperidine (Fenpiprane)[21] (5y): Colourless oily liquid, 123.86 mg (88%).^{1}H NMR (400 MHz, $CDCl_3$) δ (ppm) = 7.29 – 7.14 (m, 10H), 3.97-3.94 (m, 1H), 2.36 (br s, 4H), 2.30 – 2.25 (m, 4H), 1.62 – 1.56 (m, 4H), 1.45 – 1.42 (m, 2H); ^{13}C NMR (101 MHz, $CDCl_3$) δ (ppm): 145.04, 128.55, 127.98, 126.24, 57.92, 54.80, 49.53, 32.83, 26.05, 24.55. ESI- HRMS (m/z) $[M+H]^+$, calcd. 280.2065; found 280.2083. (M= $C_{20}H_{25}N$)

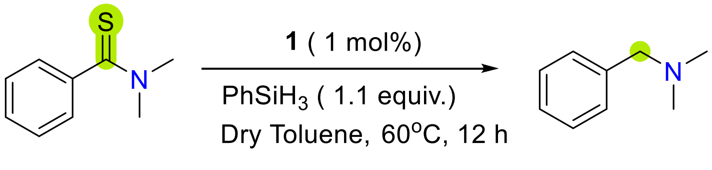


6-(2-chlorobenzyl)-4,5,6,7-tetrahydrothieno[2,3-c]pyridine (Ticlopidine)[21] (5z): Colorless oily liquid, 114.42 mg (86%).^{1}H NMR (400 MHz, $CDCl_3$) δ (ppm) = 7.50 (dd, *J* = 7.5, 1.7 Hz, 1H), 7.31 (dd, *J* = 7.7, 1.5 Hz, 1H), 7.21-7.12 (m, 2H), 7.01 (d, *J* = 5.1 Hz, 1H), 6.65 (d, *J* = 5.1 Hz, 1H), 3.78 (s, 2H), 3.59 (s, 2H), 2.85 – 2.80 (m, 4H); ^{13}C NMR (101 MHz, $CDCl_3$) δ (ppm) = 136.16, 134.37, 133.96, 133.52, 130.78, 129.57, 128.34, 126.85, 125.37, 122.76, 58.52, 53.19, 50.84, 25.61. ESI-HRMS (m/z) $[M+H]^+$, calcd. 264.0614; found 264.0623 (M= $C_{14}H_{14}ClNS$)



1-((4-chlorophenyl)(phenyl)methyl)-4-(3-methylbenzyl)piperazine (Meclizine)[21] (5z'): Off white solid, 167.37 mg (85%). ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.38-5.35 (m, 4H), 7.29 – 7.21 (m, 4H), 7.20 – 7.05 (m, 5H), 4.23 (s, 1H), 3.50 (s, 2H), 2.50-2.43 (m, 8H), 2.34 (s, 3H); ^{13}C NMR (101 MHz, $CDCl_3$) δ (ppm) = 142.29, 141.50, 137.84, 132.57, 130.11, 129.32, 128.70, 128.64, 128.15, 127.97, 127.90, 127.19, 126.49, 75.52, 63.14, 53.40, 51.83, 21.48. ESI-HRMS (m/z) $[M+H]^+$, calcd. 391.1941; found 391.1951 (M= $C_{25}H_{27}ClN_2$)

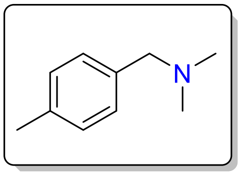
10. Typical Procedure for Catalytic Desulfurization of Tertiary Thioamides



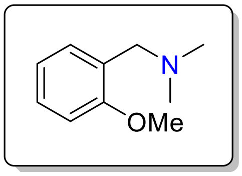
6a **5a**

Inside a N_2 filled glove box, a 25 mL pressure tube equipped with a magnetic stirring bar was charged with **1** (3.53 mg, 1 mol%), **6a** (83.2 mg, 0.503 mmol). 1 mL of dry toluene was added followed by the addition of phenylsilane (59.9 mg, 0.553 mmol) and the closed vessel was heated at 60 ºC for 12 hours. After completion of reaction, solution was cooled down to room temperature and mesitylene (0.503 mmol) was added as internal standard and product NMR yield was analyzed using ^{1}H NMR in $CDCl_3$ as the solvent. In all cases, the product peaks were integrated with respect to the -C*H*- peak of the internal standard mesitylene which was normalized to 3. The solution was passed through small pad of celite and concentrated under reduced pressure. The residue was purified by column chromatography using silica/neutral alumina in EtOAc/ hexane mixture as the eluent.

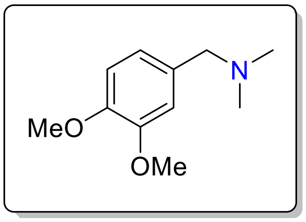
11. Characterization of Amine Products Derived from Tertiary Thioamides



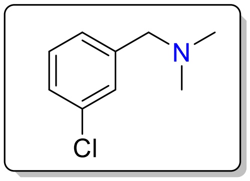
N,N-dimethyl-1-(p-tolyl)methanamine (7b): Colorless liquid, 67.86 mg (90%). ^{1}H NMR (400 MHz, $CDCl_3$) δ (ppm) = 7.21 (d, *J* = 7.4 Hz, 2H), 7.13 (d, *J* = 7.5 Hz, 2H), 3.45 (s, 2H), 2.34 (s, 3H), 2.26 (s, 6H); ^{13}C NMR (101 MHz, $CDCl_3$) δ (ppm) = 134.27, 129.46, 129.19, 127.88, 63.86, 45.02, 21.27.



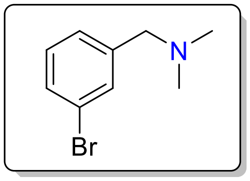
1-(2-methoxyphenyl)-N,N-dimethylmethanamine (7c): Colorless liquid, 76.68 mg, (92%).^{1}H NMR (400 MHz, $CDCl_3$) δ (ppm) = 7.38 – 7.33 (m, 2H), 7.02-6.94 (m, 2H), 3.90 (s, 3H), 3.62 (s, 2H), 2.39 (s, 6H); ^{13}C NMR (101 MHz, $CDCl_3$) δ (ppm) = 158.11, 131.49, 128.94, 120.45, 110.64, 57.60, 55.62, 45.12.



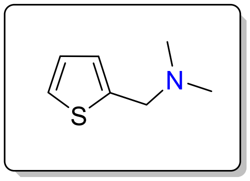
1-(3,4-dimethoxyphenyl)-N,N-dimethylmethanamine (7d): Colorless liquid, 87.49 mg, (89%).^{1}H NMR (400 MHz, CDCl$_3$) δ (ppm) = 6.92 (s, 1H), 6.80 (s, 2H), 3.87 (d, *J* = 8.2 Hz, 6H), 3.40 (s, 2H), 2.25 (s, 6H); ^{13}C NMR (101 MHz, CDCl$_3$) δ (ppm) = 149.09, 148.40, 121.50, 112.31, 110.85, 64.13, 56.02 (d), 45.15.



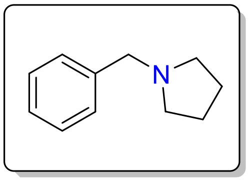
1-(3-chlorophenyl)-N,N-dimethylmethanamine (7e): Colorless liquid, 76.98 mg, (90%).^{1}H NMR (400 MHz, CDCl$_3$) δ (ppm) = 7.35 (s, 1H), 7.27 (d, *J* = 1.3 Hz, 3H), 3.51 (s, 2H), 2.32 (s, 6H); ^{13}C NMR (101 MHz, CDCl$_3$) δ (ppm) = 134.49, 129.91, 129.52, 127.96, 127.64, 63.37, 44.98.



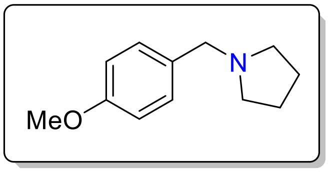
1-(3-bromophenyl)-N,N-dimethylmethanamine (7f): Colorless liquid, 97.63 mg, (91%). ^{1}H NMR (400 MHz, CDCl$_3$) δ (ppm) = 7.50 (s, 1H), 7.40 (d, *J* = 7.8 Hz, 1H), 7.27 (d, *J* = 7.4 Hz, 1H), 7.20 (t, *J* = 7.7 Hz, 1H), 3.43 (s, 2H), 2.27 (s, 6H); ^{13}C NMR (101 MHz, CDCl$_3$) δ (ppm) = 140.85, 132.22, 130.52, 130.04, 127.87, 122.63, 63.67, 45.30.



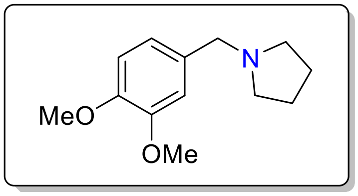
N,N-dimethyl-1-(thiophen-2-yl)methanamine (7g) : Colorless liquid, 58.87 mg, (83%).^{1}H NMR (400 MHz, CDCl$_3$) δ (ppm) = 7.25 (dd, *J* = 5.0, 1.3 Hz, 1H), 6.96-6.92 (m, 2H), 3.68 (s, 2H), 2.30 (s, 6H); ^{13}C NMR (101 MHz, CDCl$_3$) δ (ppm) = 126.61, 126.44, 125.33, 58.25, 44.99.



1-benzylpyrrolidine (7h): Colorless liquid, 75.62 mg, (93%).^{1}H NMR (400 MHz, CDCl$_3$) δ (ppm) = 7.32-7.21 (m, 5H), 3.61 (s, 2H), 2.51 (s, 4H), 1.76 (s, 4H); ^{13}C NMR (101 MHz, CDCl$_3$) δ (ppm) = 139.04, 129.13, 128.38, 127.12, 60.77, 54.22, 23.54.

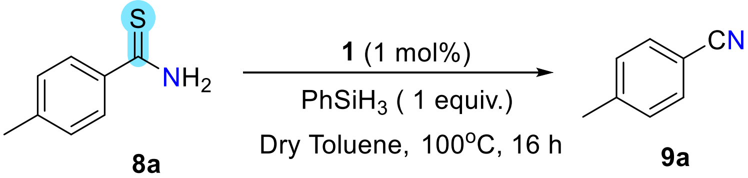


1-(4-methoxybenzyl)pyrrolidine (7i): Colorless liquid, 73.82 mg, (91%).^{1}H NMR (400 MHz, CDCl$_3$) δ 7.26 (d, *J* = 7.7 Hz, 2H), 6.85 (d, *J* = 7.6 Hz, 2H), 3.80 (s, 3H), 3.58 (s, 2H), 2.52 (s, 4H), 1.79 (s, 4H); ^{13}C NMR (101 MHz, CDCl$_3$) δ (ppm) = 158.79, 131.20, 130.28, 113.74, 60.07, 55.37, 54.09, 23.50.



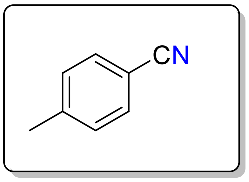
1-(3,4-dimethoxybenzyl)pyrrolidine (7j): Colorless liquid, 98.23 mg, (88%).^{1}H NMR (400 MHz, CDCl$_3$) δ (ppm) = 6.92(d, *J* = 9.0 Hz, 1H), 6.86-6.79 (m, 2H), 3.88 (d, *J* = 9.0 Hz, 6H), 3.57 (s, 2H), 2.52 (s, 4H), 1.81 – 1.78 (m, 4H); ^{13}C NMR (101 MHz, CDCl$_3$) δ (ppm) = 148.99, 148.18, 121.13, 112.28, 110.93, 60.62, 56.05 (d), 54.23, 23.57.

12. Typical Procedure for Catalytic Desulfurizative Hydrogenation of Primary Thioamides

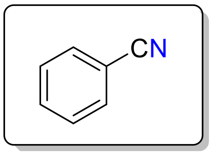


Inside a N_2 filled glove box, a 25 mL pressure tube equipped with a magnetic stirring bar was charged with **1** (3.53 mg, 1 mol%), **8a** (0.503 mmol). 1.5 mL of dry toluene was added followed by the addition of phenylsilane (54.43 mg, 0.503 mmol) and the closed vessel was heated at 100 ºC for 16 hours. After completion of reaction, solution was cooled down to room temperature. 0.5 mL of $CHCl_3$ and mesitylene (0.503 mmol) was added as internal standard and product NMR yield was analyzed using ^{1}H NMR in $CDCl_3$ as the solvent. In all cases, the product peaks were integrated with respect to the -C*H*- peak of the internal standard mesitylene which was normalized to 3. The residue was purified by column chromatography using neutral alumina in EtOAc/ hexane mixture as the eluent.

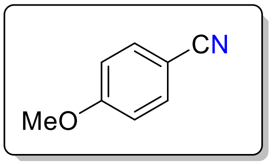
13. Characterization of Nitrile Products Derived from Primary Thioamides



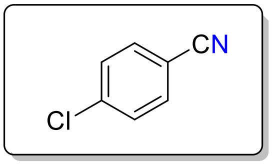
4-methylbenzonitrile[22] (9a): Beige solid, 52.63 mg, (89 %). ^{1}H NMR (400 MHz, $CDCl_3$) δ (ppm) = 7.67 (d, *J* = 8.2 Hz, 2H), 7.40 (d, *J* = 8.0 Hz, 2H), 2.55 (s, 3H); ^{13}C NMR (101 MHz, $CDCl_3$) δ (ppm) = 143.78, 132.11, 129.92, 119.23, 109.39, 21.90.



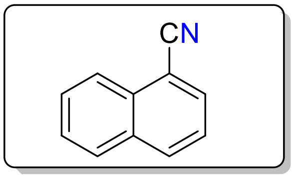
Benzonitrile[22] (9b): Colorless oil, 46.33 (89%). ^{1}H NMR (400 MHz, $CDCl_3$) δ (ppm) =7.67-7.58 (m, 3H), 7.49-7.45 (m, 2H); ^{13}C NMR (101 MHz, $CDCl_3$) δ (ppm) = 132.89, 132.28, 129.24, 118.96, 112.58.



4-methoxybenzonitrile[22] (9d): White Solid, 59.32 mg (88%). ^{1}H NMR (400 MHz, $CDCl_3$) δ (ppm) = 7.58 (d, *J* = 8.9 Hz, 2H), 6.95 (d, *J* = 8.9 Hz, 2H), 3.85 (s, 3H); ^{13}C NMR (101 MHz, $CDCl_3$) δ (ppm) = 162.96, 134.10, 119.34, 114.87, 104.09, 55.66.



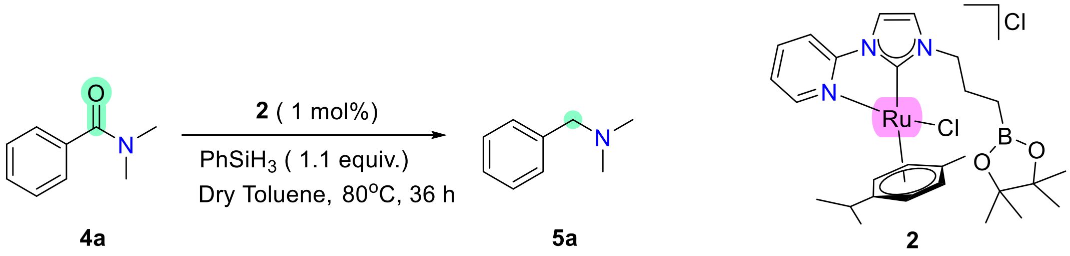
4-chlorobenzonitrile[22] (9e)**:** White Solid, 57.57 mg (83%). ^{1}H NMR (400 MHz, $CDCl_3$) δ (ppm) = ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.60 (d, *J* = 8.4 Hz, 2H), 7.47 (d, *J* = 8.5 Hz, 2H); ^{13}C NMR (101 MHz, $CDCl_3$) δ (ppm) = 139.71, 133.53, 129.85, 118.11, 110.95.



1-naphthonitrile[23] (9f): Pale Yellow liquid, 65.73 mg (85%). ^{1}H NMR (400 MHz, $CDCl_3$) δ (ppm) = 8.20 (dd, *J* = 8.0, 5.2 Hz, 1H), 8.06 – 8.02 (m, 1H), 7.88 (dd, *J* = 13.4, 7.8 Hz, 2H), 7.68 – 7.57 (m, 2H), 7.48 (dd, *J* = 14.4, 6.9 Hz, 1H); ^{13}C NMR (101 MHz, $CDCl_3$) δ (ppm) = 133.31, 132.92, 132.62, 132.33, 128.69, 128.61, 127.57, 125.10 (d), 124.94, 117.85, 110.15.

14. Control Experiments

14.1. Evaluating the role of appended Lewis basic arm



Inside a N_2 filled glove box, a 25 mL pressure tube equipped with a magnetic stirring bar was charged with **2** (3.12 mg, 1 mol%) and **4a** (75 mg, 0.503 mmol). 1 mL of dry toluene was added followed by the addition of phenylsilane (59.9 mg, 0.553 mmol) and the closed vessel was heated at 80º C for 36 hours. The solution was cooled to room temperature, and 70 µL of mesitylene (60.5 mg, 0.503 mmol) was added as an internal standard. The yield was analyzed using ^{1}H NMR in $CDCl_3$, which yielded 0.452 mmol (90%) of desired deoxygenated amine product **5a**.

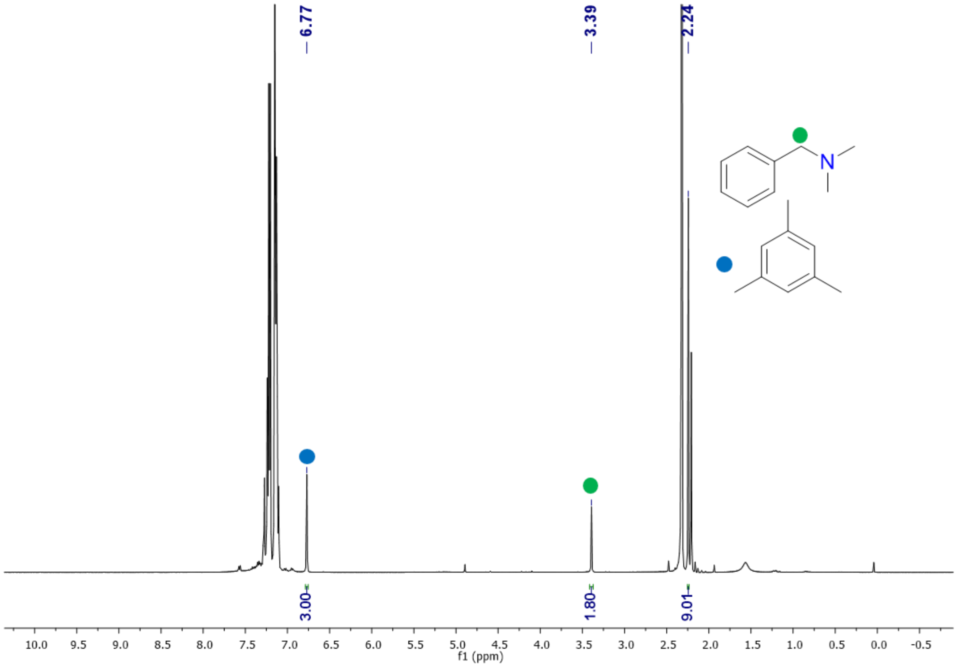
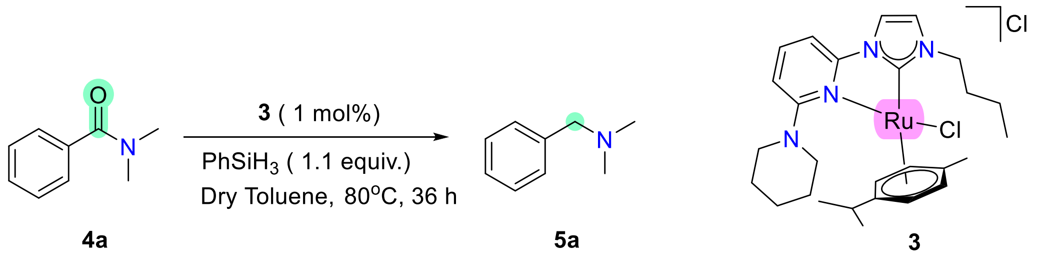


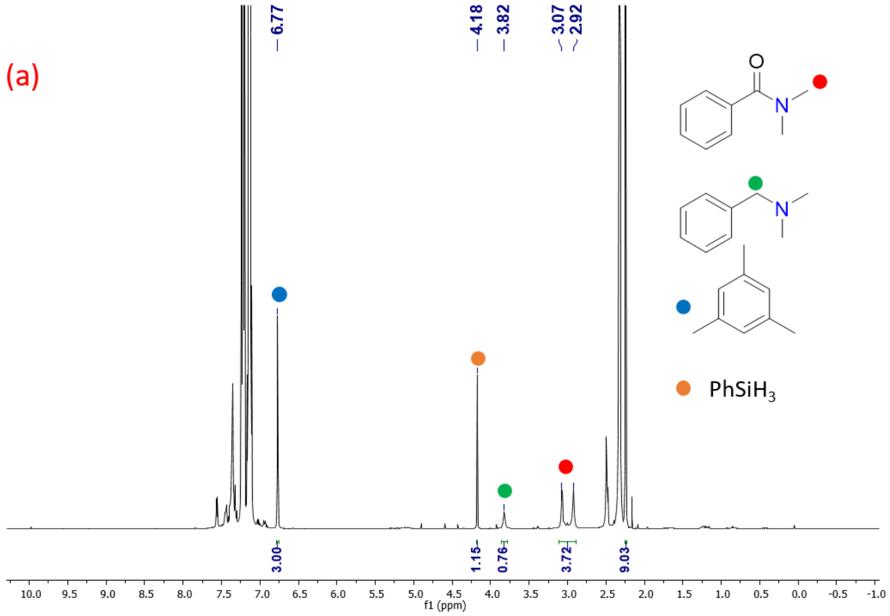
Figure S4. ^{1}H NMR spectrum of deoxygenative hydrogenation of **4a** catalyzed by complex **2** in $CDCl_3$ (Table S1, entry 21)

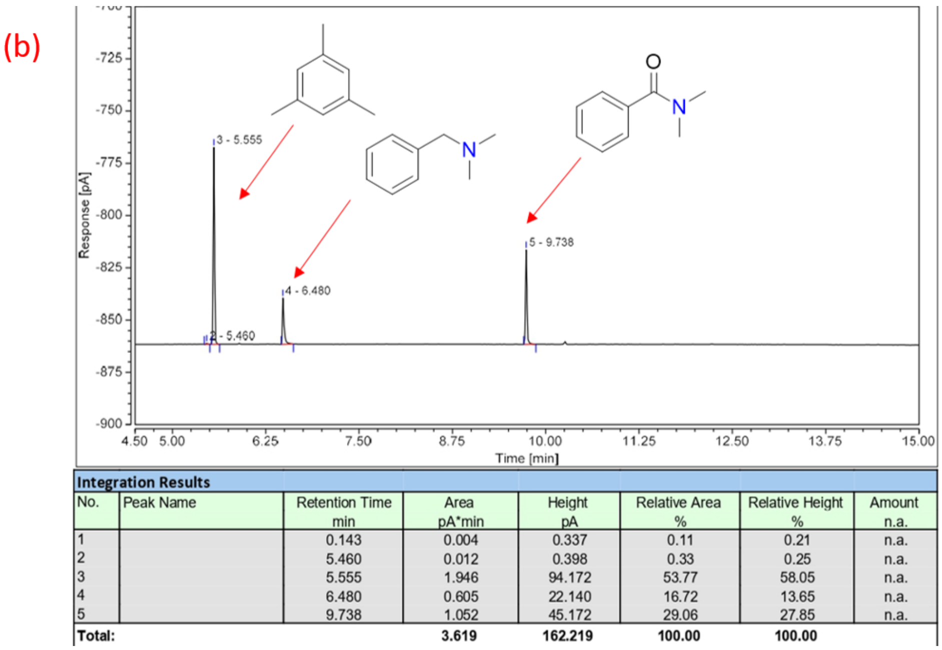
14.2. Evaluating the role of appended Lewis acidic boron arm

14.2.1. Catalytic reaction of amide 4a using complex 3



Inside a glove box, a 25 mL pressure tube equipped with a magnetic stirring bar was charged with **3** (2.97 mg, 1 mol%) and **4a** (75 mg, 0.503 mmol). 1 mL of dry toluene was added followed by the addition of phenylsilane (59.9 mg, 0.553 mmol) and the closed vessel was heated at 80 ºC for 36 hours. The solution was cooled to room temperature and 70 µL of mesitylene (60.5 mg, 0.503 mmol) was added as internal standard and yield was analyzed using ^{1}H NMR in CDCl$_{3,}$ which yielded 0.191 mmol (38%) of desired deoxygenated amine product **5a**.



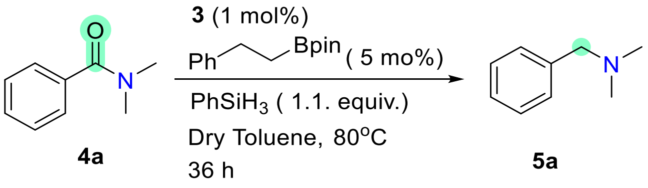


Integration Results

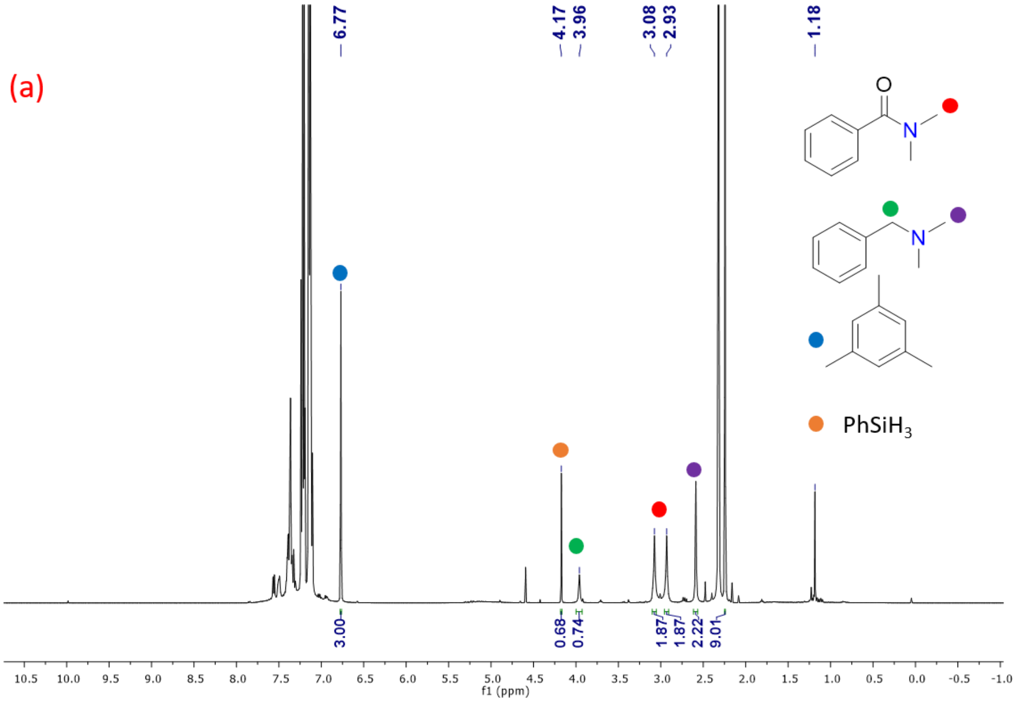
No.	Peak Name	Retention Time min	Area pA*min	Height pA	Relative Area %	Relative Height %	Amount n.a.
1		0.143	0.004	0.337	0.11	0.21	n.a.
2		5.460	0.012	0.398	0.33	0.25	n.a.
3		5.555	1.946	94.172	53.77	58.05	n.a.
4		6.480	0.605	22.140	16.72	13.65	n.a.
5		9.738	1.052	45.172	29.06	27.85	n.a.
Total:			**3.619**	**162.219**	**100.00**	**100.00**	

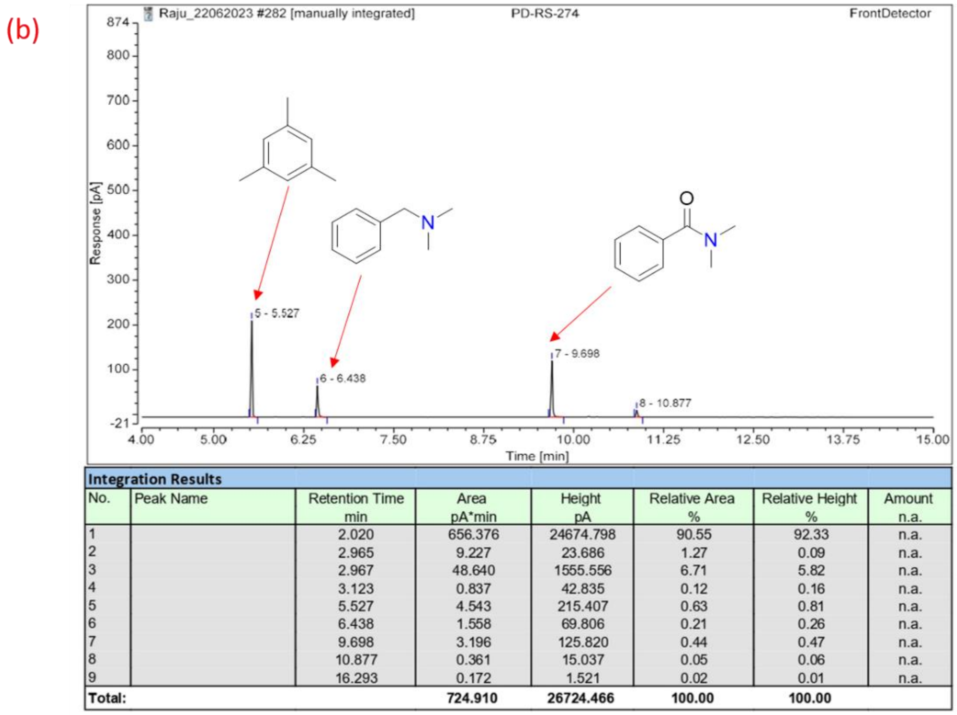
Figure S5. Deoxygenative hydrogenation of **4a** catalyzed by complex **3** (a) ^{1}H NMR in $CDCl_3$ (b) GC-MS spectrum (Table S1, entry 22)

14.2.2. Catalytic reaction of amide 4a using complex 3 and external Ph(CH$_2$)$_2$Bpin



A 25 mL pressure tube equipped with a magnetic stirring bar was charged with **3** (2.97 mg, 1 mol%), Ph(CH$_2$)$_2$Bpin (5.84 mg , 5 mol%) **4a** (75 mg, 0.503 mmol). 1 mL of dry toluene was added followed by the addition of phenylsilane (59.9 mg, 0.553 mmol) and the closed vessel was heated at 80 ºC for 36 hours. The solution was cooled to room temperature and 70 µL of mesitylene (60.5 mg, 0.503 mmol) was added as internal standard and yield was analyzed using ^{1}H NMR in $CDCl_3$ which yielded 0.186 mmol (37%) of desired deoxygenated amine product **5a**.



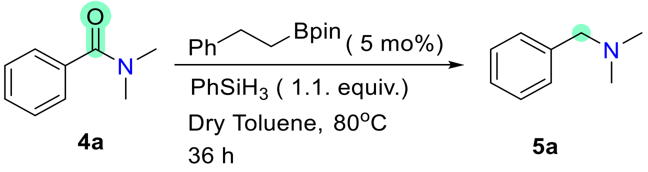


Integration Results

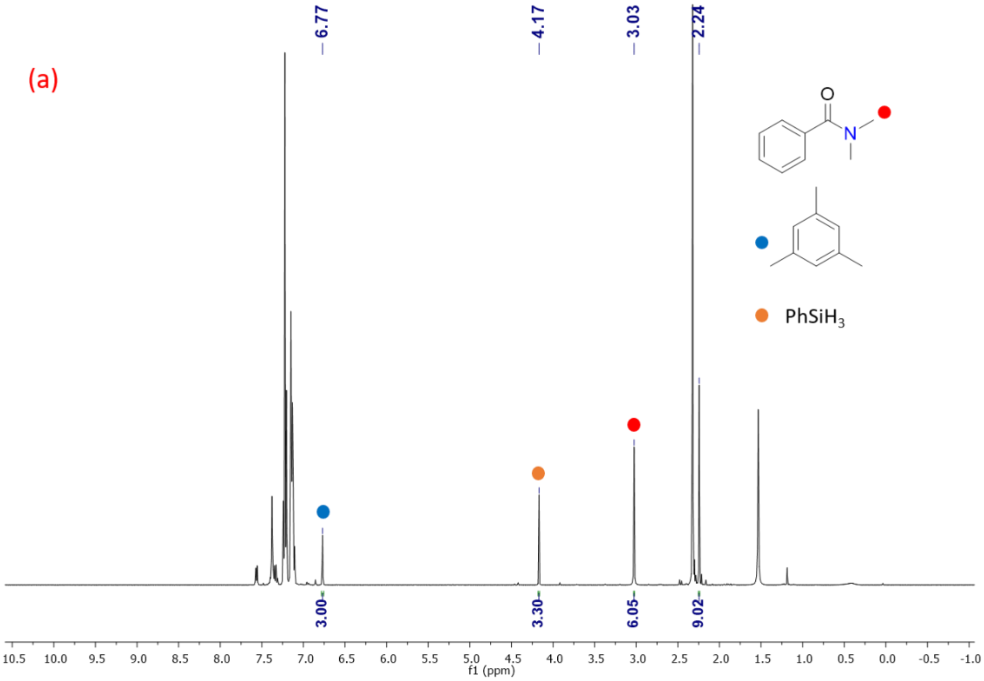
No.	Peak Name	Retention Time min	Area pA*min	Height pA	Relative Area %	Relative Height %	Amount n.a.
1		2.020	656.376	24674.798	90.55	92.33	n.a.
2		2.965	9.227	23.686	1.27	0.09	n.a.
3		2.967	48.640	1555.556	6.71	5.82	n.a.
4		3.123	0.837	42.835	0.12	0.16	n.a.
5		5.527	4.543	215.407	0.63	0.81	n.a.
6		6.438	1.558	69.806	0.21	0.26	n.a.
7		9.698	3.196	125.820	0.44	0.47	n.a.
8		10.877	0.361	15.037	0.05	0.06	n.a.
9		16.293	0.172	1.521	0.02	0.01	n.a.
Total:			**724.910**	**26724.466**	**100.00**	**100.00**	

Figure S6. Deoxygenative hydrogenation of **4a** catalyzed by complex **3** and external Ph$(CH_2)_2$Bpin (a) ^{1}H NMR in $CDCl_3$ (b) GC-MS spectrum

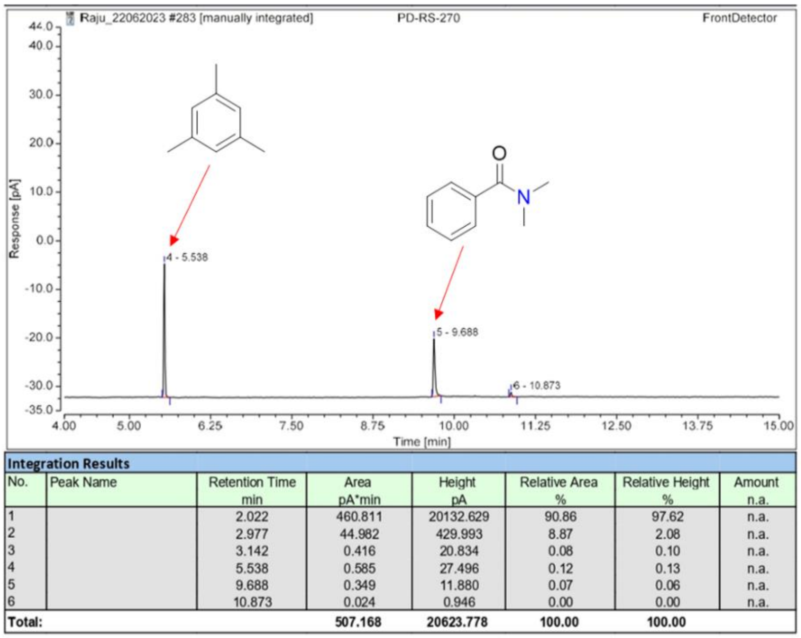
14.2.3. Catalytic reaction of amide 4a using only Ph(CH$_2$)$_2$Bpin



A 25 mL pressure tube equipped with a magnetic stirring bar was charged with Ph(CH$_2$)$_2$Bpin (5.84 mg, 5 mol%) and **4a** (75 mg, 0.503 mmol). 1 mL of dry toluene was added followed by the addition of phenylsilane (59.9 mg, 0.553 mmol) and the closed vessel was heated at 80 ºC for 36 hours. The solution was cooled to room temperature and 70 µL of mesitylene (60.5 mg, 0.503 mmol) was added as internal standard and yield was analyzed using ^{1}H NMR in CDCl$_3$, where no amine formation was detected.



(b)

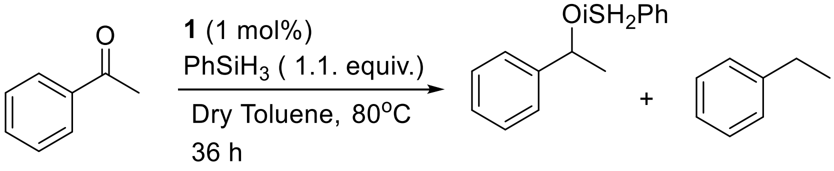


Integration Results

No.	Peak Name	Retention Time min	Area pA*min	Height pA	Relative Area %	Relative Height %	Amount n.a.
1		2.022	460.811	20132.629	90.86	97.62	n.a.
2		2.977	44.982	429.993	8.87	2.08	n.a.
3		3.142	0.416	20.834	0.08	0.10	n.a.
4		5.538	0.585	27.496	0.12	0.13	n.a.
5		9.688	0.349	11.880	0.07	0.06	n.a.
6		10.873	0.024	0.946	0.00	0.00	n.a.
Total:			**507.168**	**20623.778**	**100.00**	**100.00**	

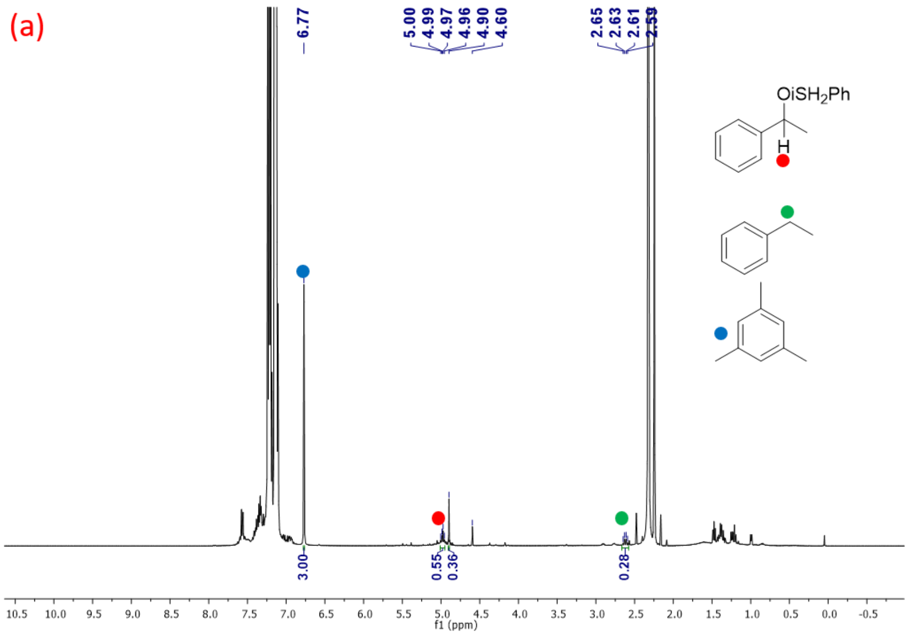
Figure S7. Deoxygenative hydrogenation of **4a** catalyzed by $Ph(CH_2)_2Bpin$ (a) ^1H NMR in $CDCl_3$ (b) GC-MS spectrum

14.3. Catalytic hydrogenation of acetophenone using complex 1

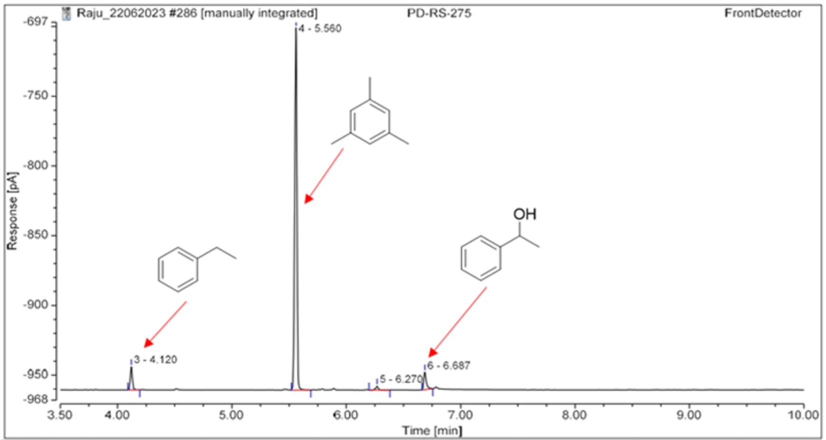


A 25 mL pressure tube equipped with a magnetic stirring bar was charged with complex **1** (3.5 mg, 1 mol%) and acetophenone (60.5 mg,0.503 mmol). 1 mL of dry toluene was added, followed by the addition of phenylsilane (59.9 mg, 0.553 mmol), and the closed vessel was heated at 80 ºC for 36 hours. The solution was cooled to room temperature and 70 µL of mesitylene (60.5 mg, 0.503 mmol) was added as internal standard and yield was analyzed using ^1H NMR in $CDCl_3$ which yielded 0.276 mmol (55%) of silylated product along with 0.07 mmol (14%) ethyl benzene as the deoxygenated product. This result further depicted that the boron arm in SCS of complex **1** might be involved in substrate deoxygenation during catalysis.

(a)



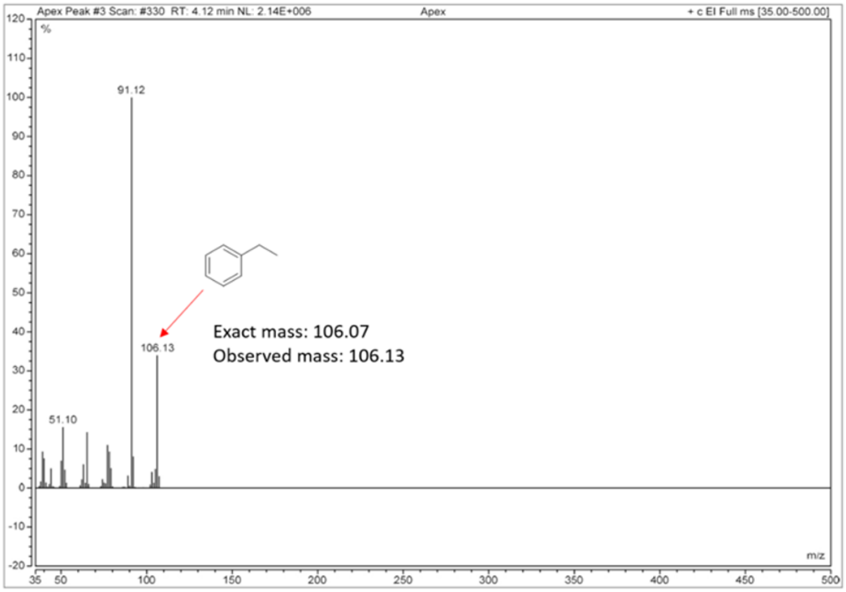
(b)



Integration Results

No.	Peak Name	Retention Time min	Area pA*min	Height pA	Relative Area %	Relative Height %	Amount n.a.
1		2.040	632.551	23349.738	57.36	87.16	n.a.
2		3.005	461.051	3044.133	41.81	11.36	n.a.
3		4.120	0.350	16.627	0.03	0.06	n.a.
4		5.560	5.623	259.740	0.51	0.97	n.a.
5		6.270	0.076	2.796	0.01	0.01	n.a.
6		6.687	0.324	12.502	0.03	0.05	n.a.
7		10.227	1.308	58.613	0.12	0.22	n.a.
8		11.455	0.447	17.903	0.04	0.07	n.a.
9		11.652	0.445	17.560	0.04	0.07	n.a.
10		16.913	0.188	3.269	0.02	0.01	n.a.
11		19.250	0.474	6.844	0.04	0.03	n.a.
Total:			1102.835	26789.726	100.00	100.00	

(c)



(d)

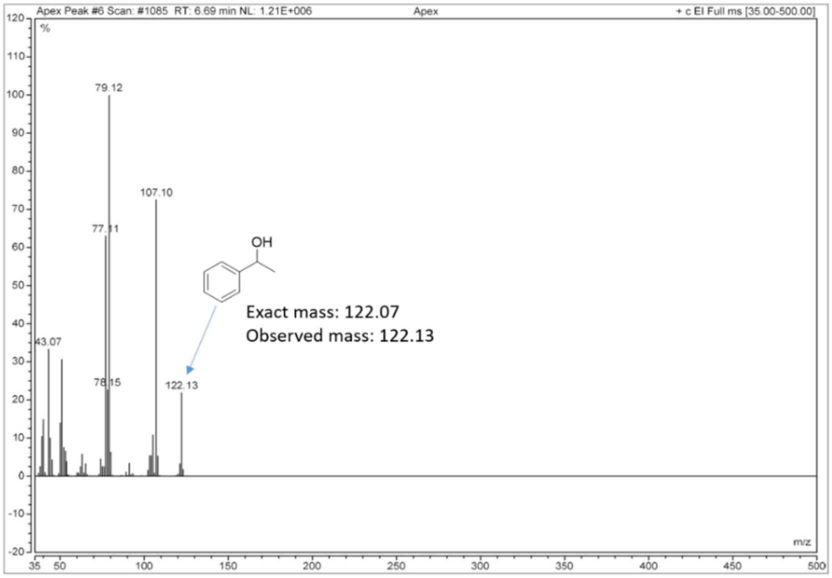
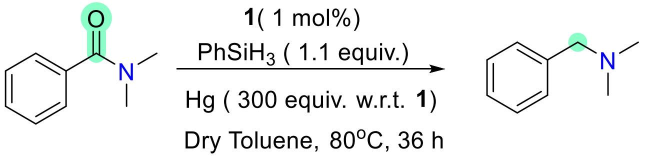


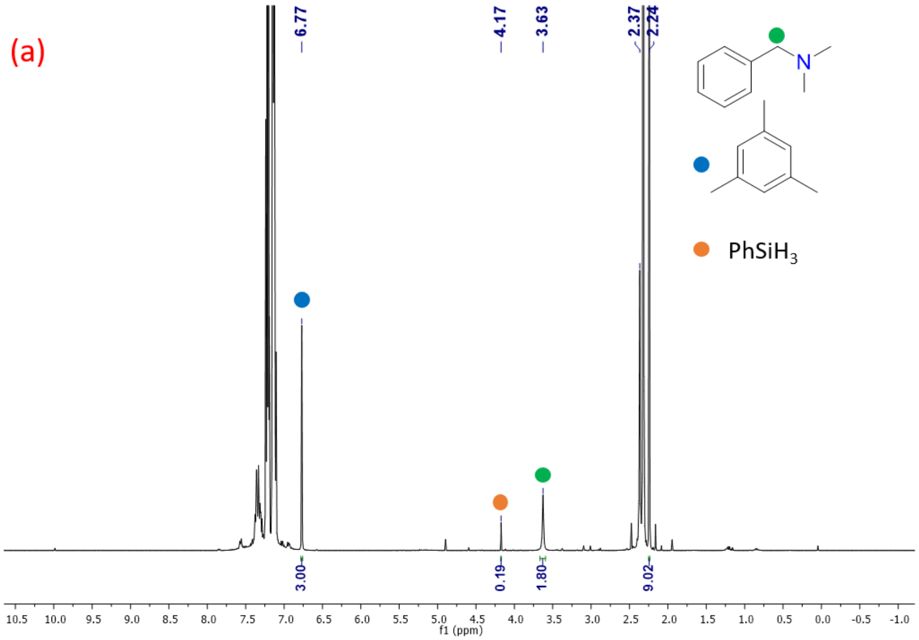
Figure S8. Deoxygenative hydrogenation of acetophenone catalyzed by complex **1** (a) ^{1}H NMR in $CDCl_3$ (b) GC-MS spectrum (b) Mass pattern for ethylbenzene (d) Mass pattern for 1-phenylethan-1-ol

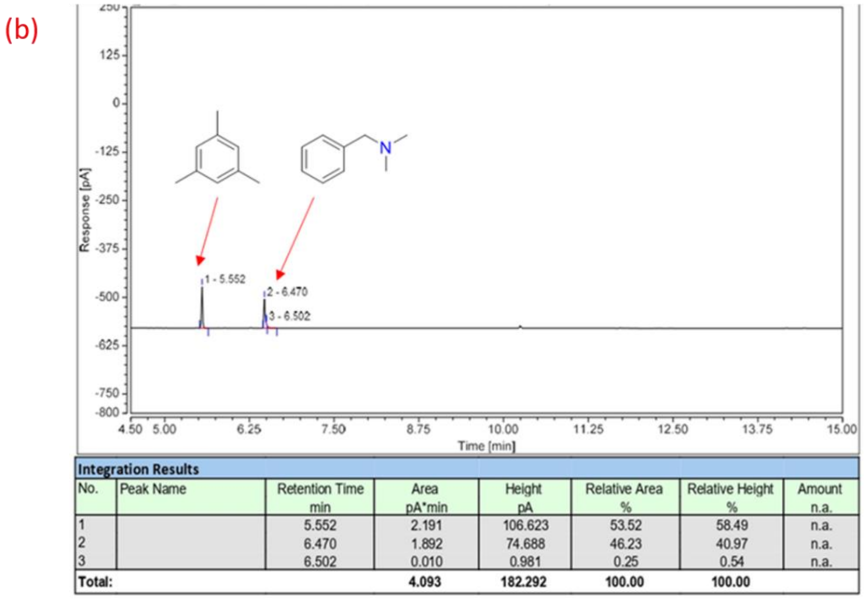
15. Homogeneity test using mercury drop experiment



4a **5a, 90%**

Inside a glove box, a 25 mL pressure tube equipped with a magnetic stirring bar was charged with catalyst **1** (3.53 mg, 1 mol%) and **4a** (0.503 mmol). 1 mL of dry toluene was added followed by the addition of mercury (302.7 mg, 300 equiv. w.r.t. **1**) and phenylsilane (0.553 mmol). The tube was sealed properly and brought out of the glove box and heated at 80 ºC for 36 hours. The solution was cooled to room temperature and mesitylene (0.503 mmol) was added as the internal standard and aliquot was analyzed using ^{1}H NMR in $CDCl_3$ which yielded 0.452 mmol (90%) of desired deoxygenated amine product **5a**. This result confirms the homogeneous behavior of catalyst **1** towards deoxygenative hydrogenation.





Integration Results

No.	Peak Name	Retention Time min	Area pA*min	Height pA	Relative Area %	Relative Height %	Amount n.a.
1		5.552	2.191	106.623	53.52	58.49	n.a.
2		6.470	1.892	74.688	46.23	40.97	n.a.
3		6.502	0.010	0.981	0.25	0.54	n.a.
Total:			**4.093**	**182.292**	**100.00**	**100.00**	

Figure S9. Deoxygenative hydrogenation of **4a** catalyzed by complex **1** in presence of Hg (a) ^{1}H NMR in $CDCl_3$ (b) GC-MS spectrum (Table S1, entry 20)

16. Mechanistic Studies

16.1. Generation of [Ru-H] species using complex 1

Inside a glove box, in a pre-dried NMR tube, 1:1 mixture of **1** (0.0163 mmol) and $PhSiH_3$ (0.0163 mmol) in 0.6 mL C_6D_6 or $CDCl_3$ was added and the tube was brought out of the glove box and heated for 1 hour at 50 ^{o}C and then subjected to ^{1}H NMR analysis to observe the [Ru-H] species.

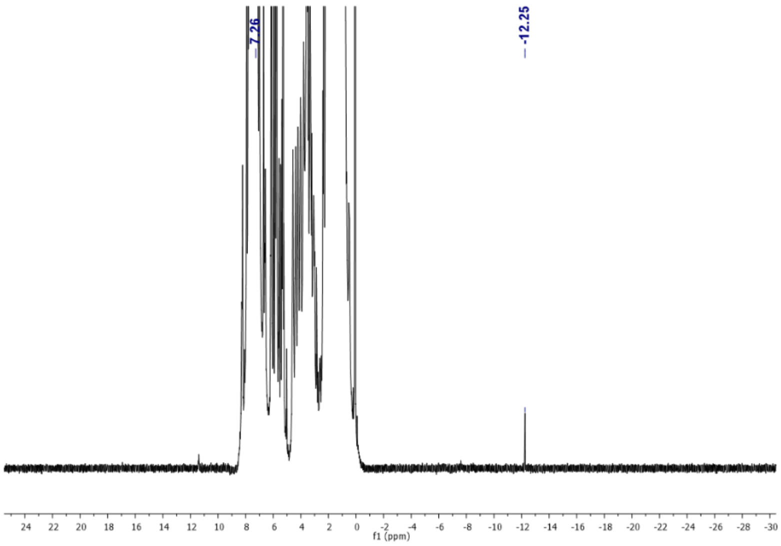


Figure S10. ^{1}H NMR spectrum for [**Ru-H**] species observed after reaction of **1** with $PhSiH_3$ in $CDCl_3$

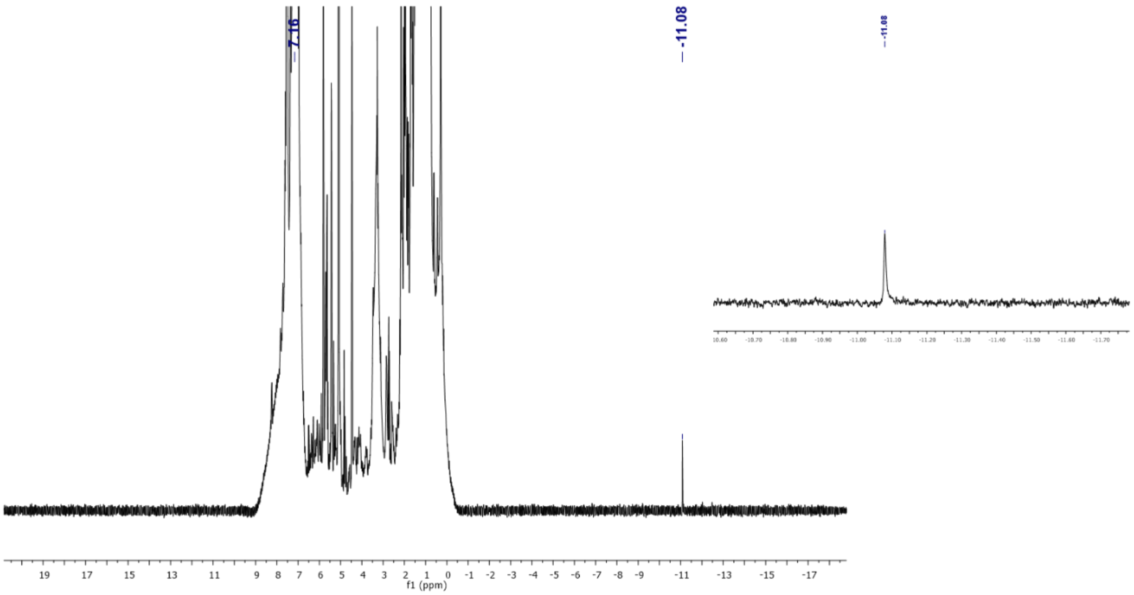


Figure S11. ^{1}H NMR spectrum for [**Ru-H**] species observed after reaction of **1** with $PhSiH_3$ in C_6D_6

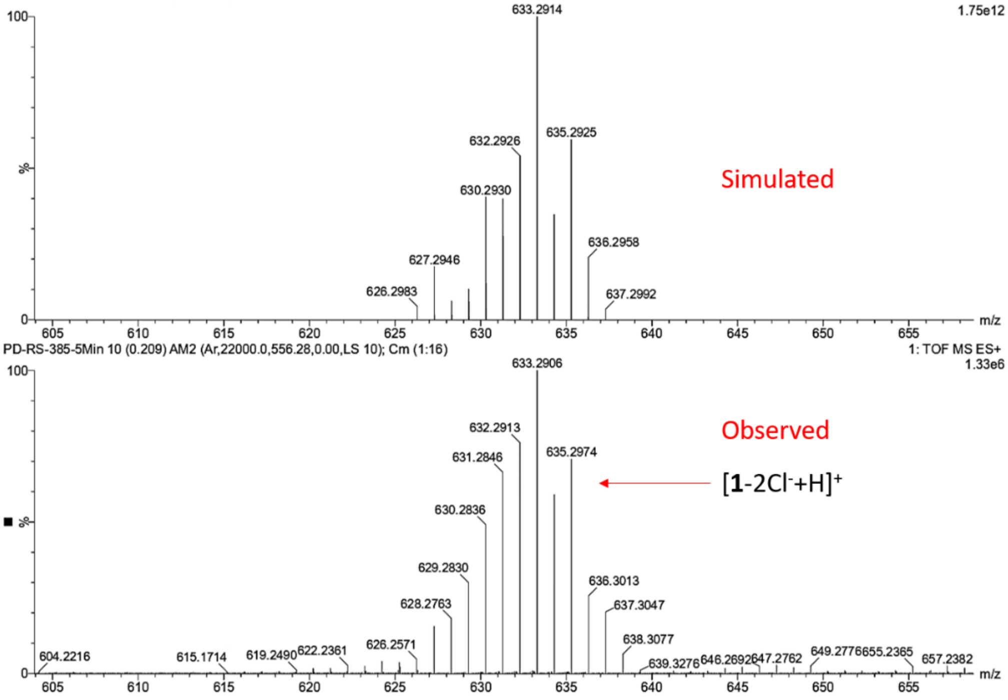
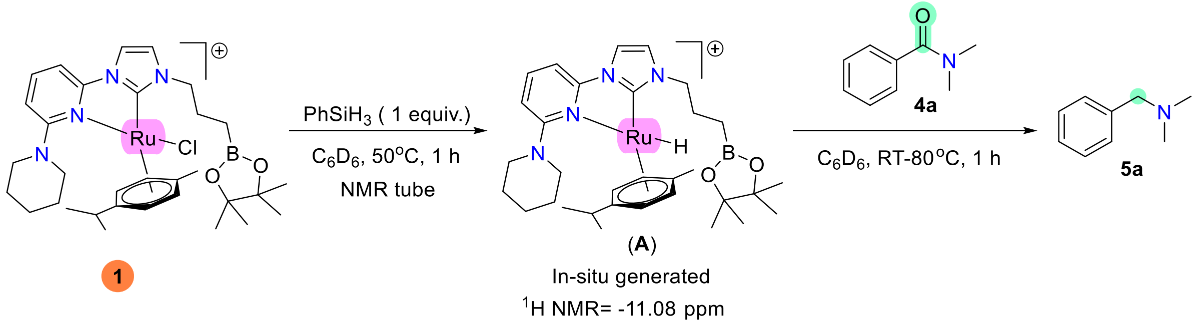
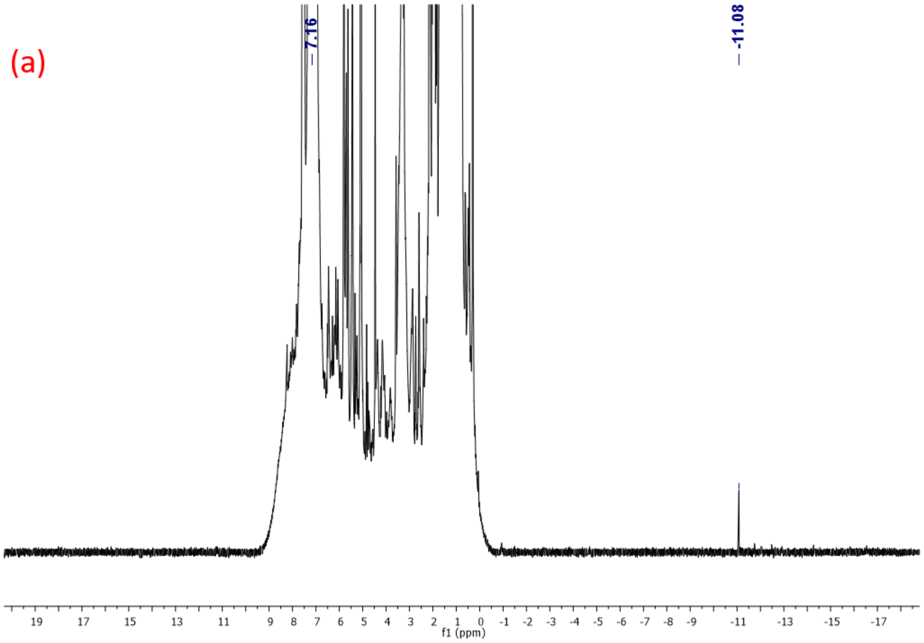


Figure S12. ESI-HRMS spectrum of Ru-H intermediate **(A)**

16.2. Stoichiometric reaction of in-situ generated Ru-H intermediate with amide 4a



Inside a glove box, in a pre-dried NMR tube, at first, a 1:1 mixture of **1** (0.017 mmol) and $PhSiH_3$ (0.017 mmol) in 0.6 mL C_6D_6 was added and the tube was brought out of the glove box and heated for 1 hour at 50 ºC and then subjected to ^1H NMR analysis which depicted a singlet peak at -11.08 ppm which corresponds to intermediate (**A**). The same tube was brought inside the glove box and amide **4a** (0.017 mmol) was added and ^1H NMR was analyzed first at RT, which showed a small amount of amine **5a** formation. Further, the solution was heated at 80 ºC for 1 hour and analyzed by ^1H NMR, where almost complete amine **5a** formation was observed.



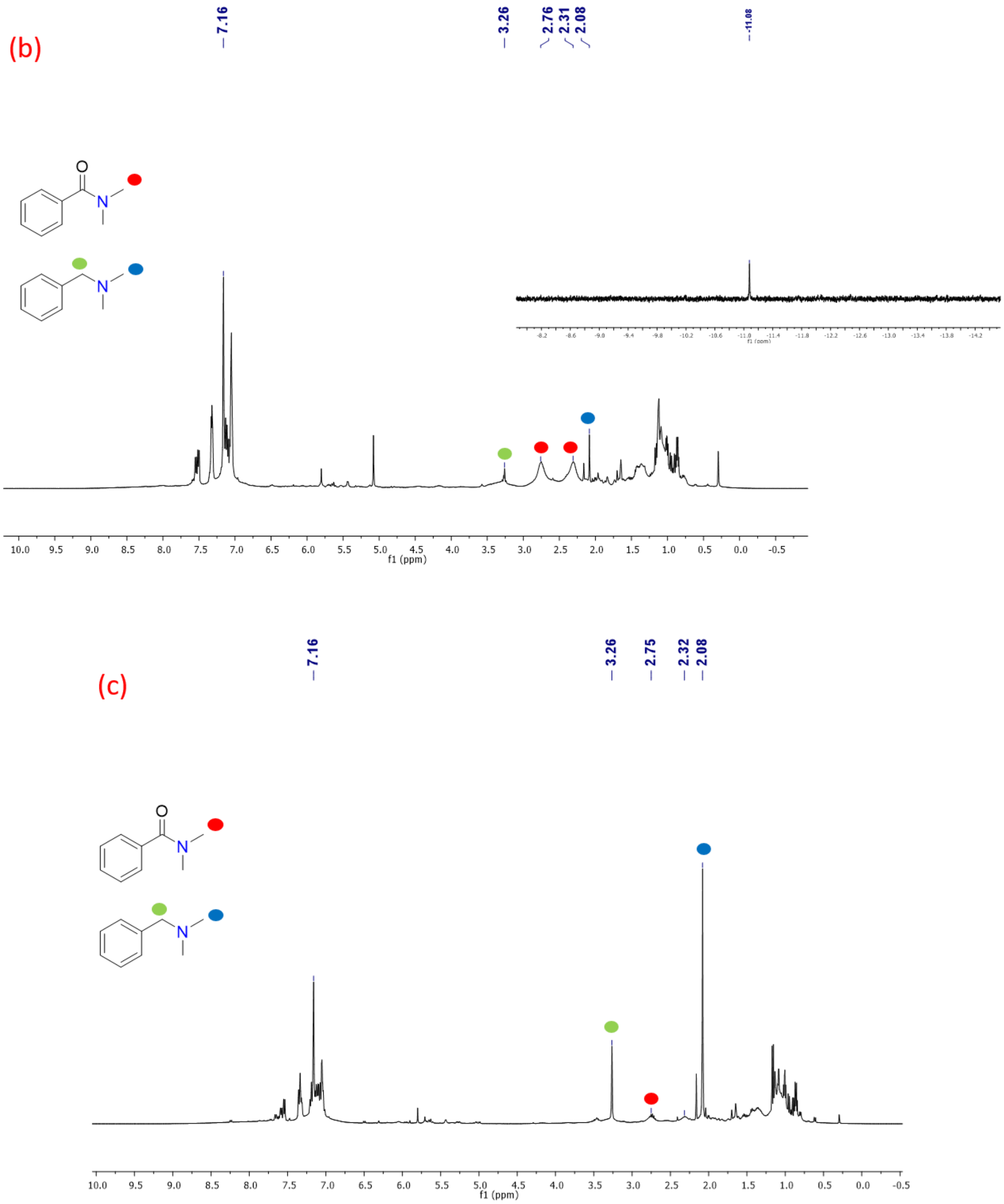
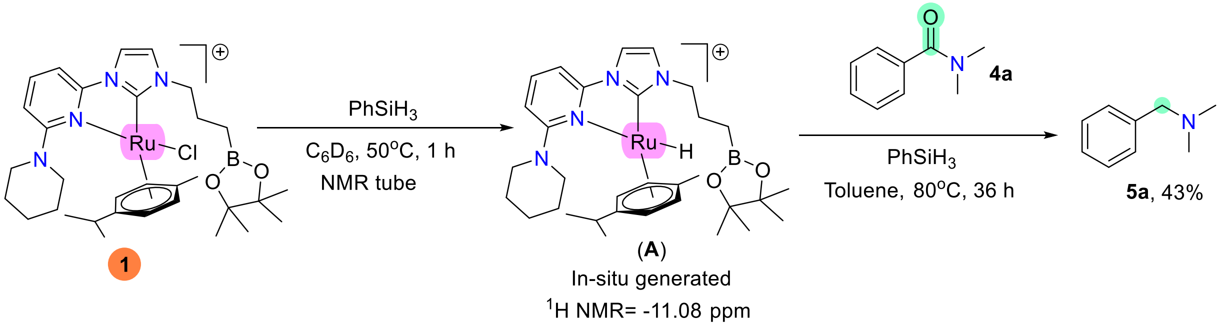


Figure S13. (a) ^{1}H NMR of 1:1 mixture of complex **1** and $PhSiH_3$ (b) After 1 equiv. of amide **4a** addition at RT (c) After heating the same solution at 80 ºC for 1 hour

16.3. Catalytic reaction of in-situ generated Ru-H intermediate (A) with amide 4a using a fewer equiv. of $PhSiH_3$



Inside a glove box, in a pre-dried NMR tube, at first, a 1:1 mixture of **1** (7.02 mg, 1 mol% w.r.t. amide **4a**) and $PhSiH_3$ (1.08 mg, 1 mol% w.r.t. amide **4a**) in 0.5 mL C_6D_6 was added and the tube was brought out of the glove box and heated for 1 hour at 50 ºC and then subjected to ^1H NMR analysis which depicted a singlet peak at -11.08 ppm which corresponds to intermediate (**A**). Inside a glove box, the in-situ generated intermediate (**A**) was transferred to a 25 mL pressure tube containing amide **4a** (149.19 mg, 1 equiv.), $PhSiH_3$ (54.11 mg, 0.5 equiv. w.r.t. **4a**) and dry toluene (0.5 mL). The tube was brought out of the glove box and heated at 80 ºC for 36 hours in an oil bath. Mesitylene (69.6 µL, 0.5 equiv. w.r.t. **4a**) was added and ^1H NMR was analyzed, where 43% NMR yield of amine **5a** formation was observed.

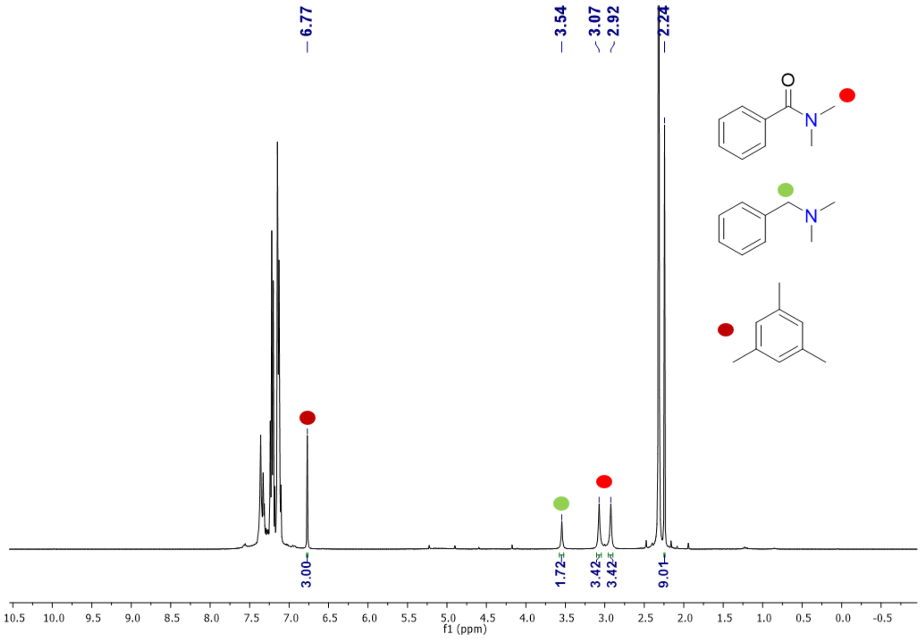
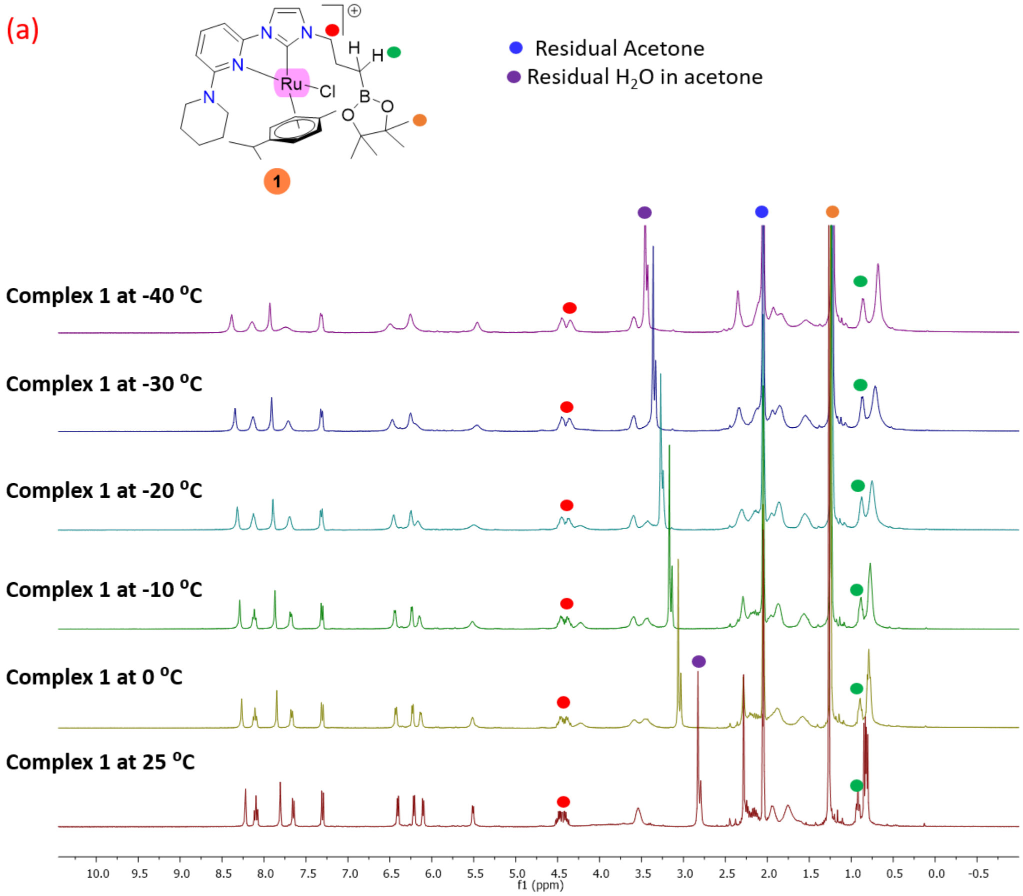


Figure S14. ^1H NMR spectrum of crude reaction mixture in $CDCl_3$ for deoxygenative hydrogenation of **4a** catalyzed by in-situ generated Ru-H intermediate (**A**) with a fewer equiv. of $PhSiH_3$

16.4. Variable Temperature (VT) NMR study for the detection of appended boron-substrate interaction in complex 1

16.4.1. Variable Temperature (VT) NMR study of complex 1 and complex 1 +amide 4a

In a pre-dried NMR tube, a 1:10 mixture of **1** (0.021 mmol)**, 4a** (0.213 mmol), and 0.6 mL acetone-d_6 was added and variable temperature NMR study was performed from 25 ^{o}C to -40 ^{o}C. However, no such significant shifting of protons of appended boron ^{1}H and ^{11}B was observed under the measured NMR temperature scale.



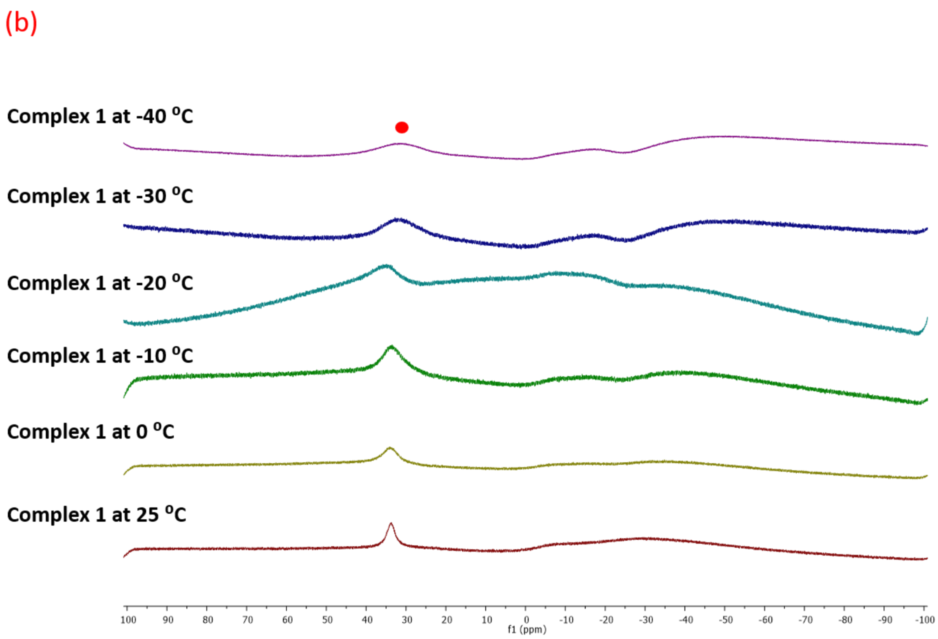
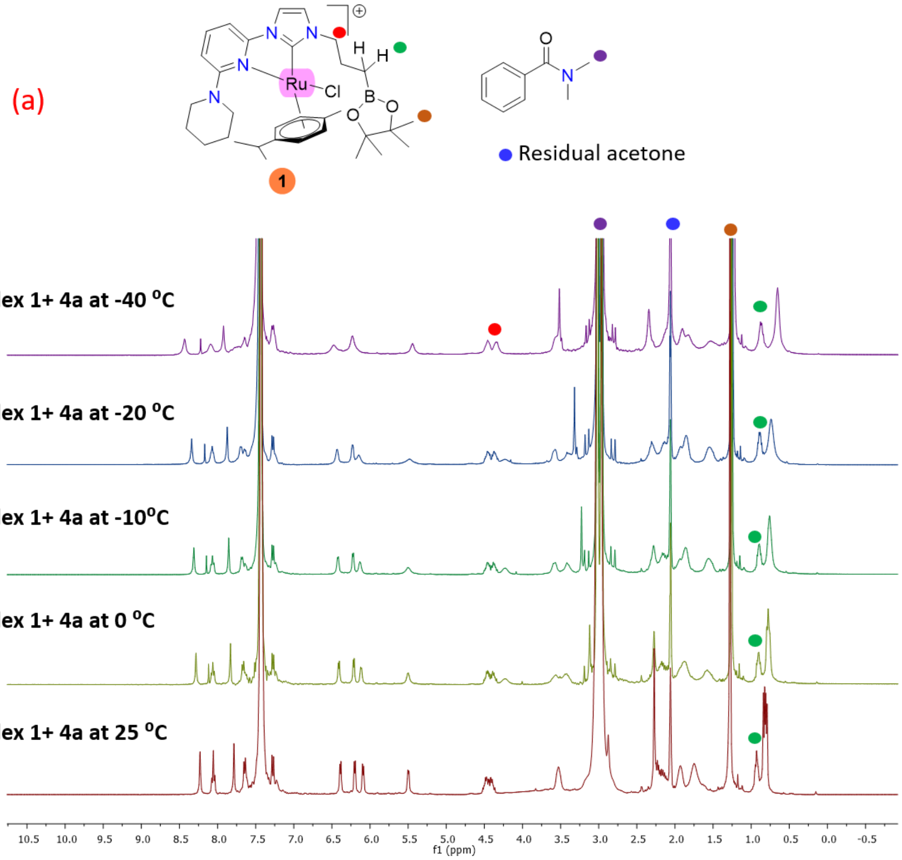


Figure S15. Variable temperature (VT) NMR of only complex **1** in acetone-d$_6$ (a) ^{1}H NMR spectrum measured from 25 °C to -40 °C (b) ^{11}B NMR spectrum measured from 25 °C to -40 °C



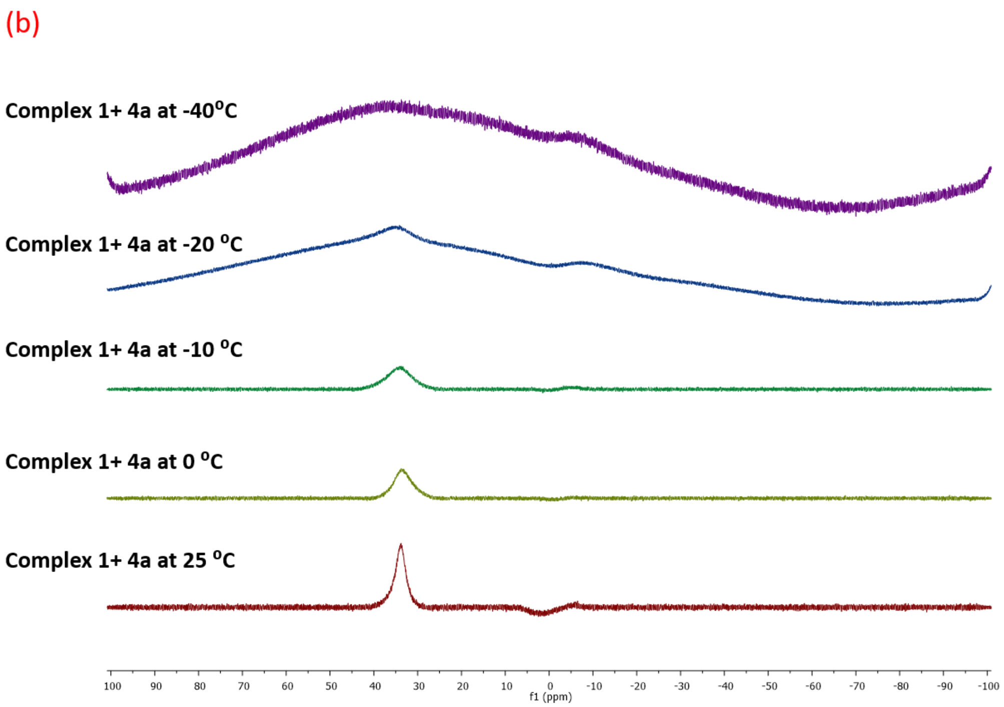
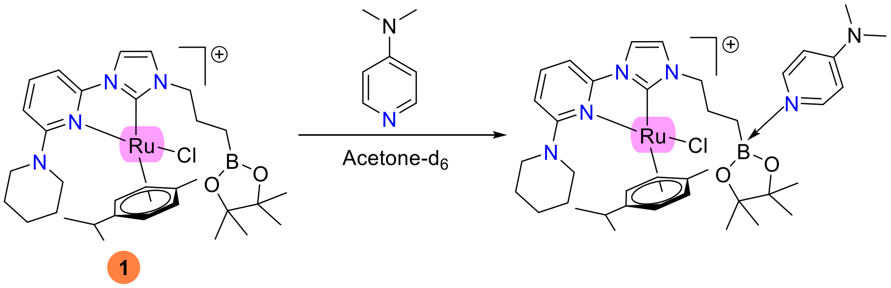


Figure S16. Variable temperature (VT) NMR of a mixture of complex **1** and amide **4a** in acetone-d$_6$ (a) ^{1}H NMR spectrum measured from 25 ºC to -40 ºC (b) ^{11}B NMR spectrum measured from 25 ºC to -40 ºC

16.4.2. Variable Temperature (VT) NMR study using dimethylaminopyridine (DMAP) and complex 1



In a pre-dried NMR tube, a 1:5 mixture of **1** (0.014 mmol)**,** dimethylaminopyridine (DMAP) (0.071mmol), and 0.6 mL acetone-d$_6$ was added and variable temperature NMR study was performed from 25 ºC to -40 ºC. The ^{1}H NMR analysis revealed a significant up-field shift (shielding) of methylene protons (-CH$_2$) adjacent to the –Bpin arm from 0.91 ppm to 0.47 ppm with a gradual decreasing the temperature from 25 ºC to -40 ºC. The ^{11}B NMR spectrum also showed a significant up-field shift of peak signal from 32.30 ppm to 12.80 ppm at -40 ºC. These results revealed the formation of adduct between appended boron of complex **1** and DMAP.[24]

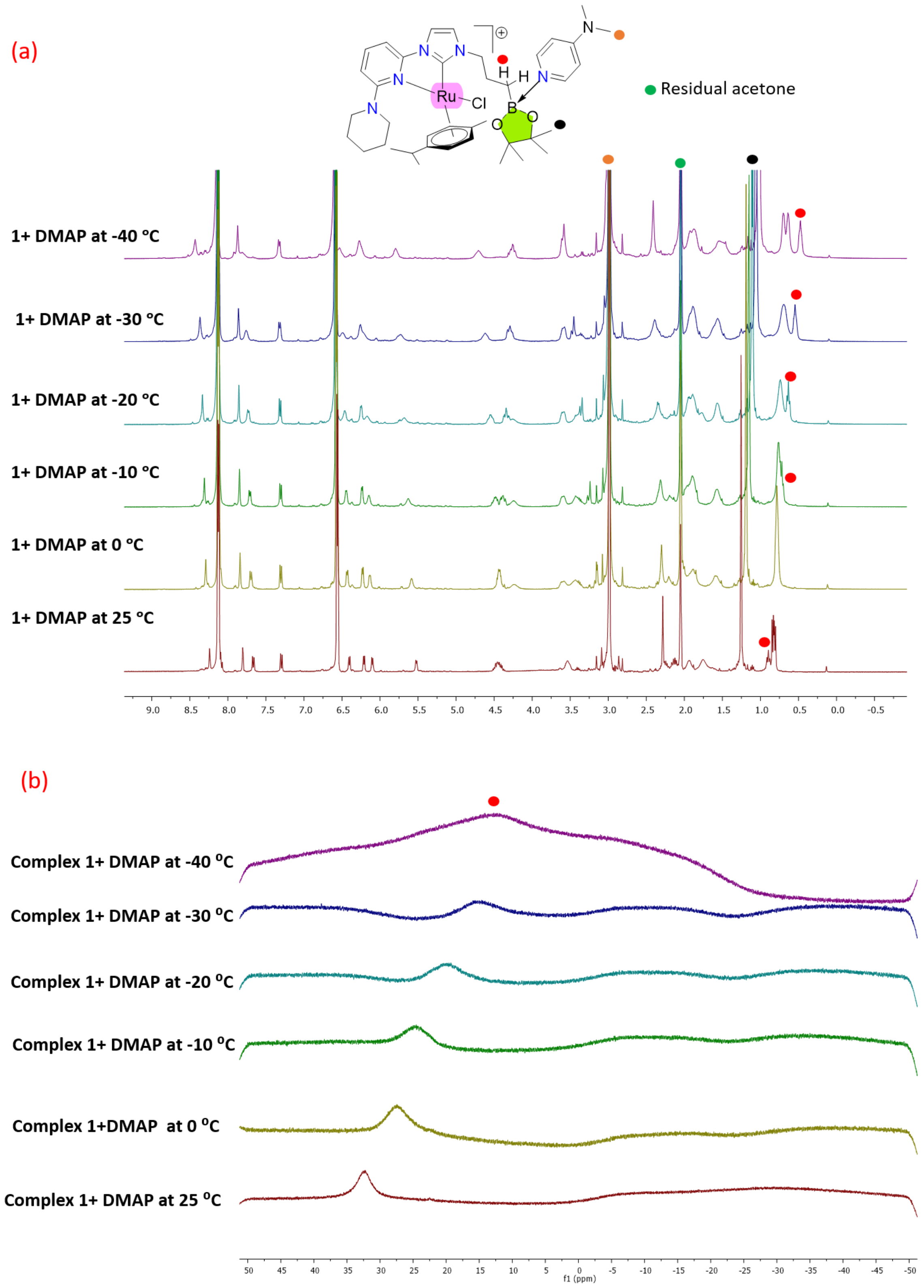
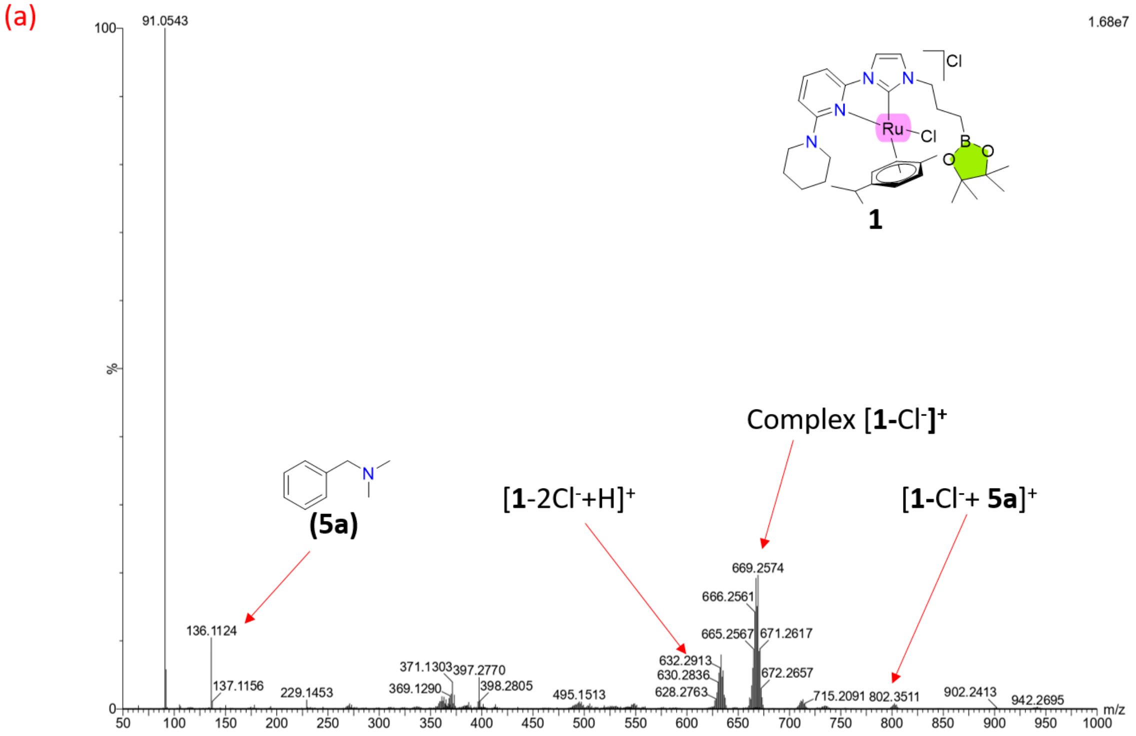


Figure S17. Variable temperature (VT) NMR of a mixture of complex **1** and DMAP in acetone-d$_6$ (a) ^{1}H NMR spectrum measured from 25 ºC to -40 ºC (b) ^{11}B NMR spectrum measured from 25 ºC to -40 ºC

16.5. ESI-HRMS control experiment of stoichiometric reaction of a 1:1:1 mixture of complex 1, $PhSiH_3$ and 4a

Inside a glove box, in a 10 mL pressure tube, a 1:1:1 mixture of **1** (10 mg, 0.014 mmol) and $PhSiH_3$ (1.54 mg, 0.014 mmol), amide **4a** (2.12 mg, 0.014 mmol) and 0.6 mL of dry toluene was added and the tube was brought out of the glove box and heated for 10 minutes at 60 ºC. A little aliquot was submitted for ESI-HRMS mass analysis. Mass analysis showed the complete formation of amine **5a** as a peak signal at $[M+H]^+$, *m/z* = 136.1124 [M= $C_9H_{13}N$] was observed along with the presence of active Ru-H intermediate (**A**) at [**1**-2Cl$^-$+H]$^+$ (*m/z* =633.2906) [**1**= $C_{32}H_{47}BCl_2N_4O_2Ru$]. Moreover, the presence of peak signal at [**1**-Cl$^-$+ **5a**]$^+$, (*m/z* = 802.3511) was also observed, which is assigned as amine **5a** coordinated Ru-complex **1**.



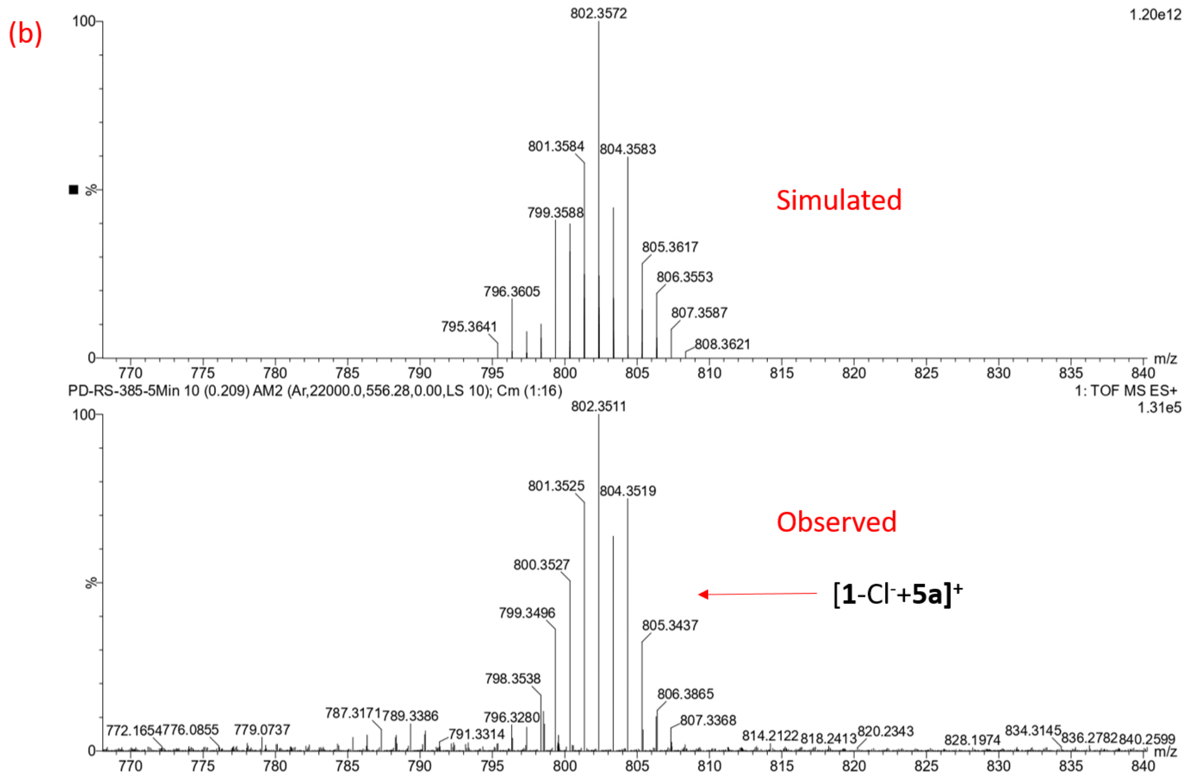
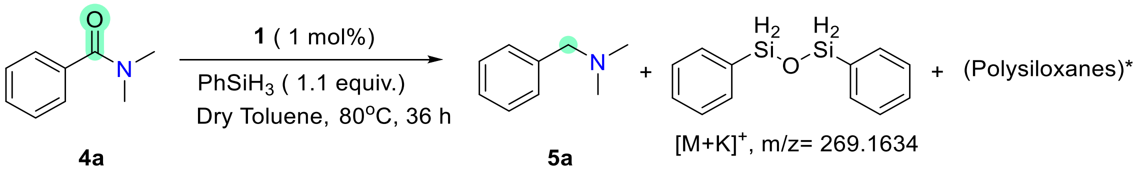


Figure S18. ESI-HRMS analysis spectrum of a 1:1:1 mixture of complex 1, $PhSiH_3$ and 4a

16.6. Identification of siloxane by-product



Inside a glove box, a 25 mL pressure tube equipped with a magnetic stirring bar was charged with **1** (3.53 mg, 1 mol%) and **4a** (0.503 mmol). 1 mL of dry toluene was added followed by the addition of phenylsilane (0.553 mmol) and the closed vessel was heated at 80 ºC for 36 hours. The solution was cooled to room temperature and a little aliquot was analyzed using ESI-HRMS in acetonitrile solvent which showed the formation of phenyl disiloxane with a peak signal, m/z = 269.1634 assigned as $[M+K]^+$. (M= $C_{12}H_{14}OSi_2$) along with the polysiloxanes.[25]

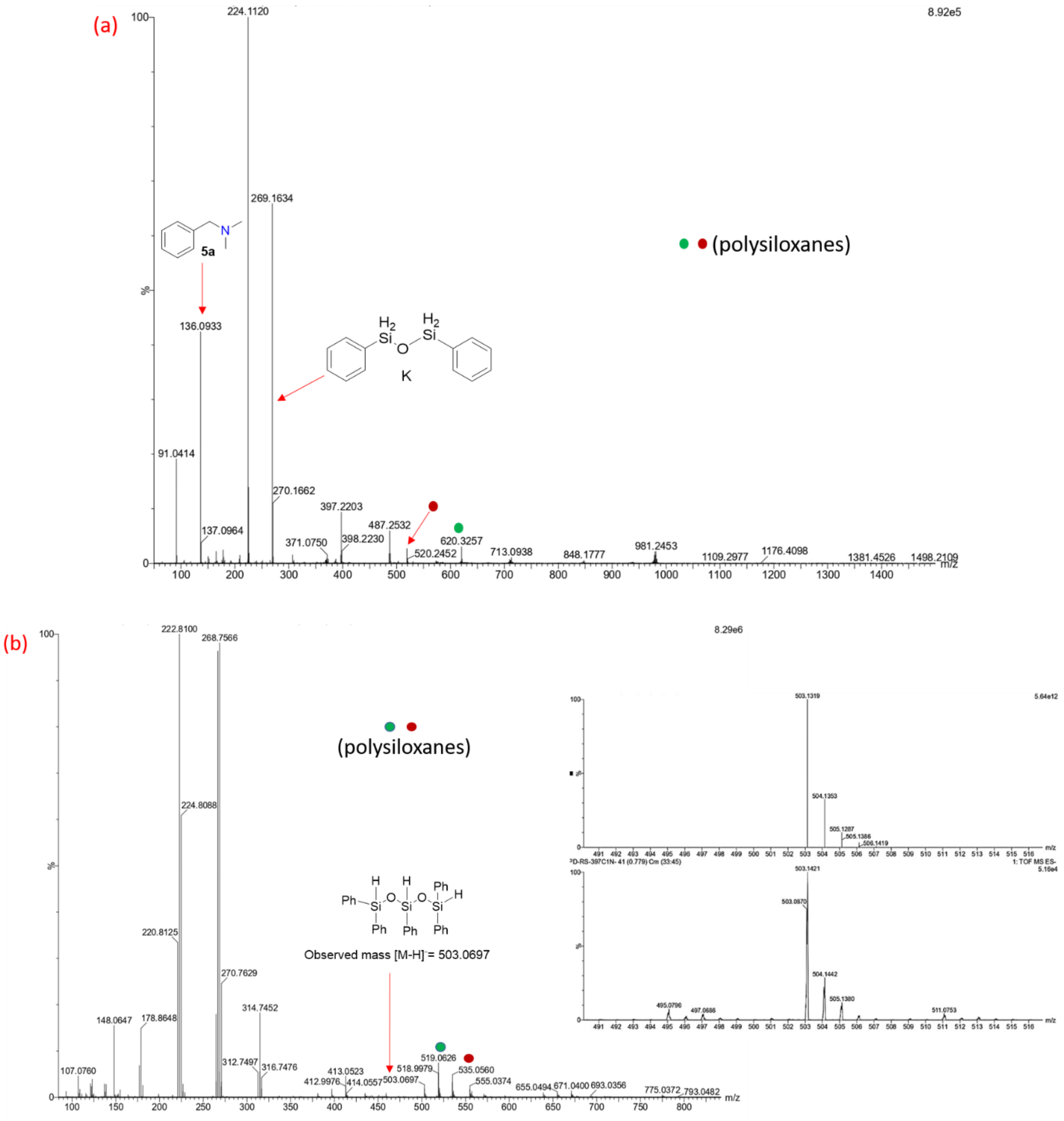
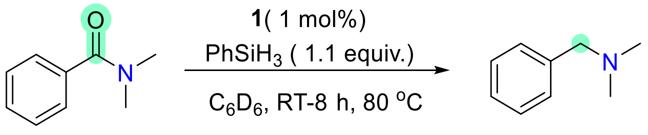


Figure S19. ESI-HRMS spectrum analysis of the siloxane and polysiloxane byproduct measured in acetonitrile (a) +ve region (b) –ve region

17. ^{1}H NMR monitoring of 5a formation with progress of time



4a **5a**

Inside the glove box, in a pre-dried NMR tube, **4a** (1 equiv., 0.503 mmol), catalyst **1** (1 mol %), 0.6 mL of C_6D_6 and followed by $PhSiH_3$ (1.1 equiv., 0.553 mmol) were added and the tube was brought out of the glove box and ^{1}H NMR was measured in different intervals of time from RT- 8 hours after heating at 80 ^{o}C in an oil bath. It was observed that with the progress of time, the formation of **5a** gradually increased with the decrease in the concentration of amide **4a** and phenylsilane.

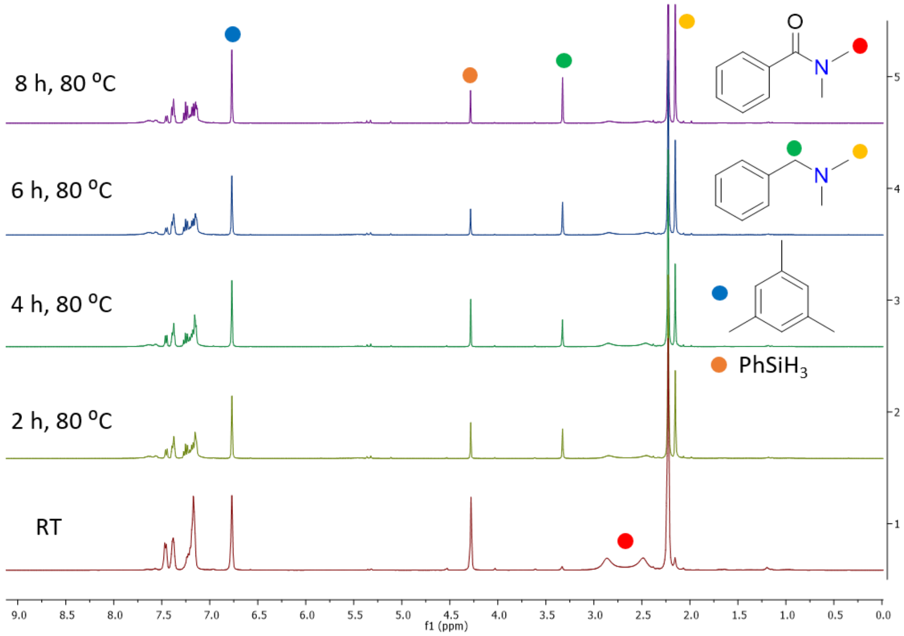


Figure S20. ^{1}H NMR spectrum of NMR tube experiment for the progress of **5a** formation measured in intervals of RT-8 hours in C_6D_6

18. Spectroscopic data

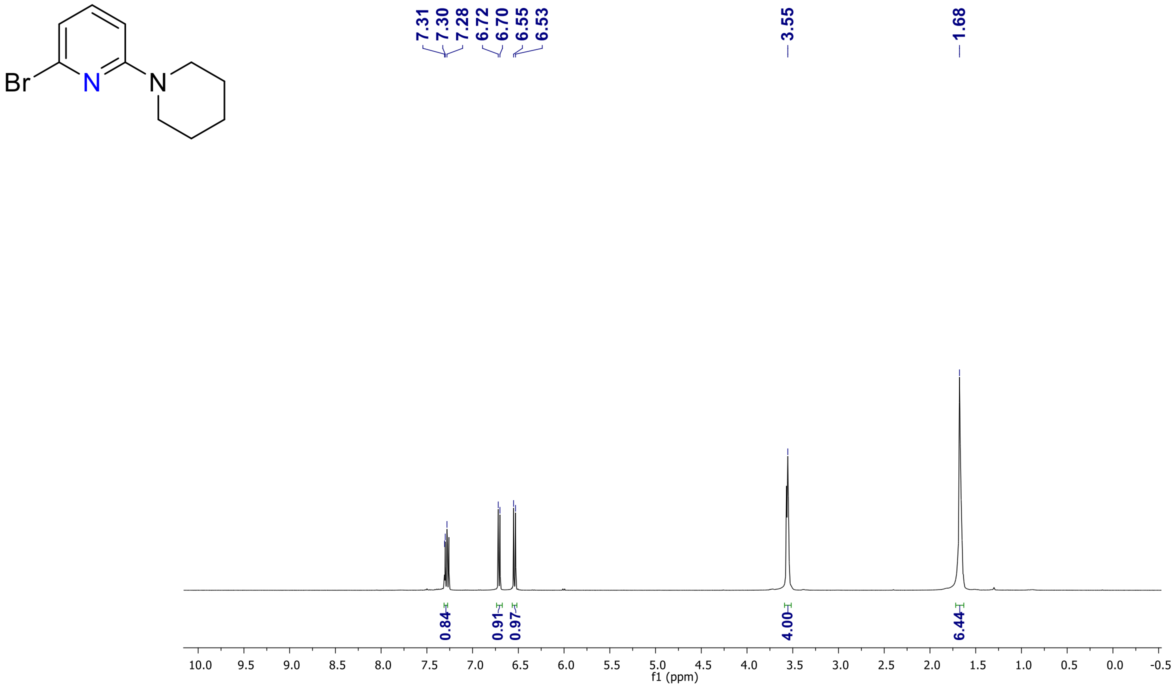


Figure S21. ^{1}H NMR spectrum of 2-bromo-6-(piperidine-1-yl)pyridine in $CDCl_3$

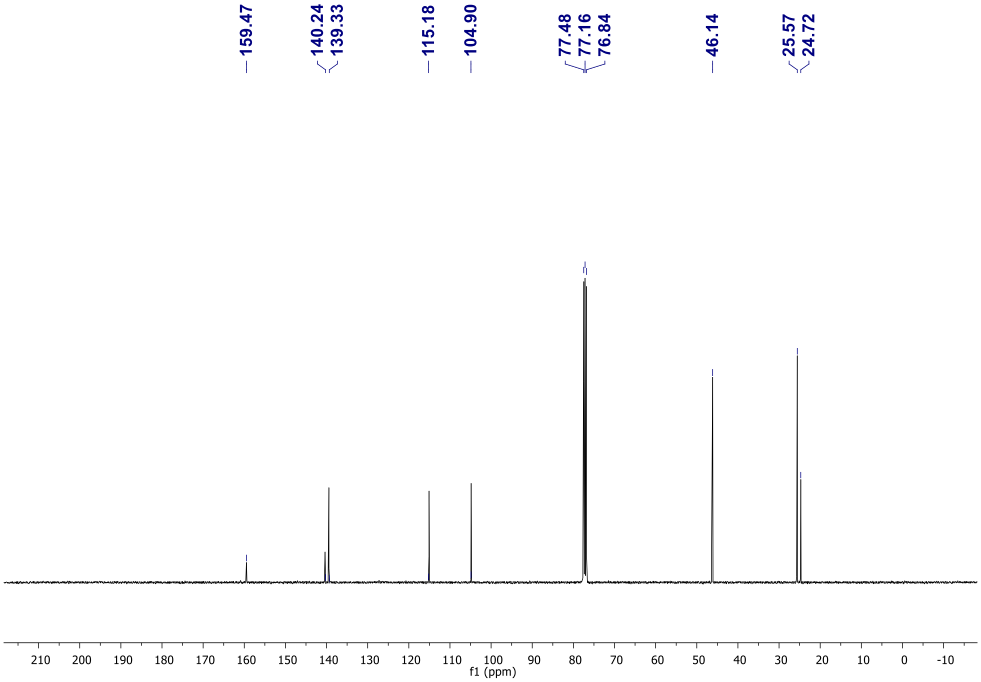


Figure S22. ^{13}C NMR spectrum of 2-bromo-6-(piperidine-1-yl)pyridine in $CDCl_3$

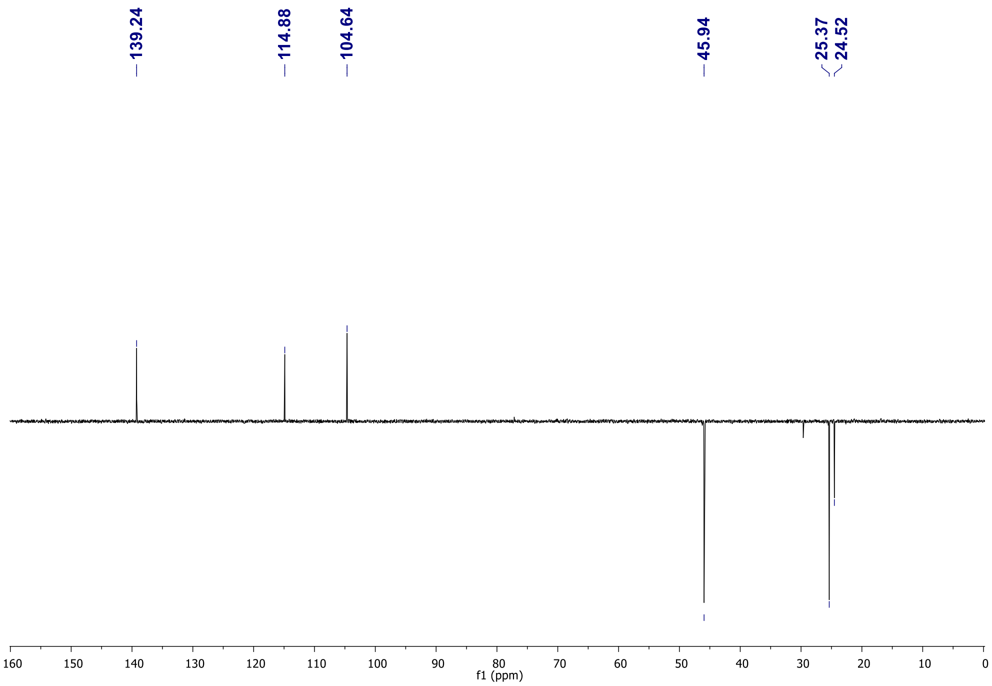


Figure S23. 135-DEPT NMR spectrum of 2-bromo-6-(piperidine-1-yl)pyridine in $CDCl_3$

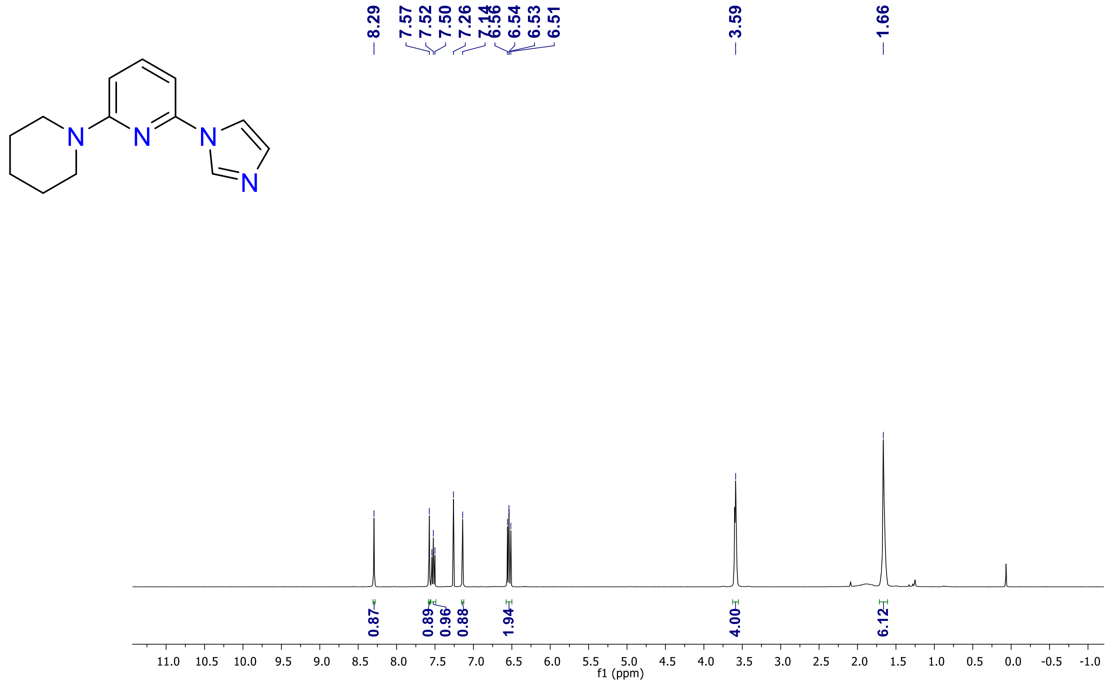


Figure S24. ^{1}H NMR spectrum of 2-(1H-imidazol-1-yl)-6-(piperidin-1-yl)pyridine in $CDCl_3$

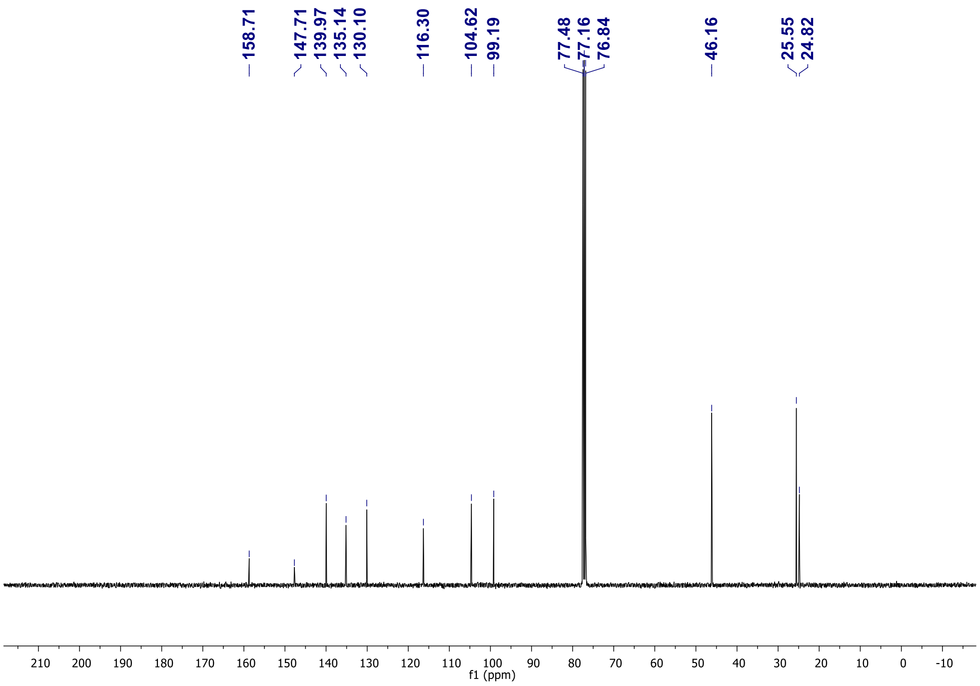


Figure S25. ^{13}C NMR spectrum of 2-(1H-imidazol-1-yl)-6-(piperidin-1-yl)pyridine in $CDCl_3$

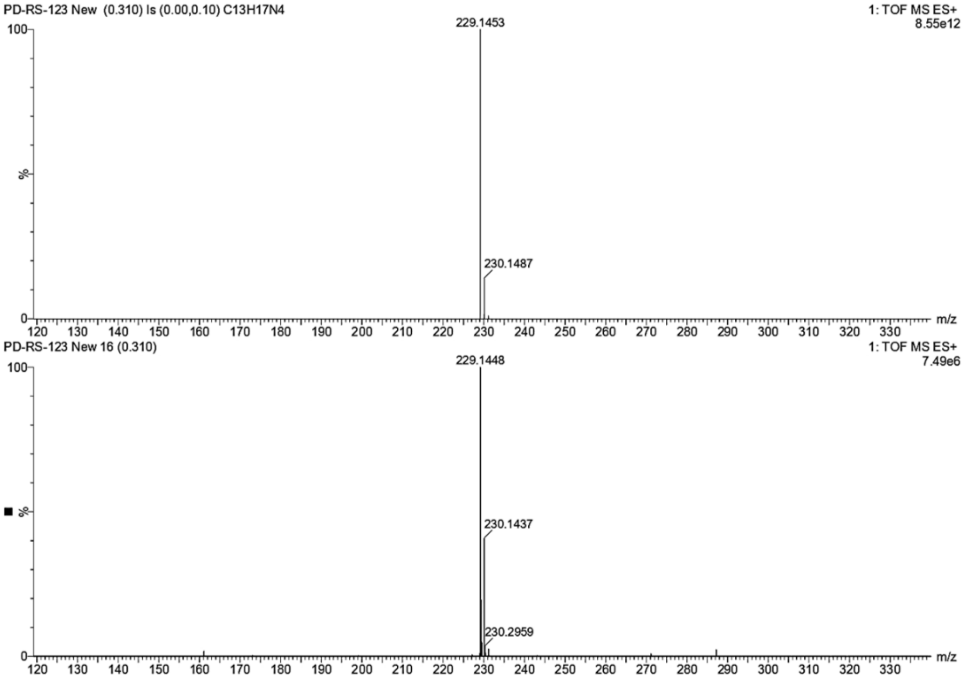


Figure S26. ESI-HRMS of 2-(1H-imidazol-1-yl)-6-(piperidin-1-yl)pyridine in methanol

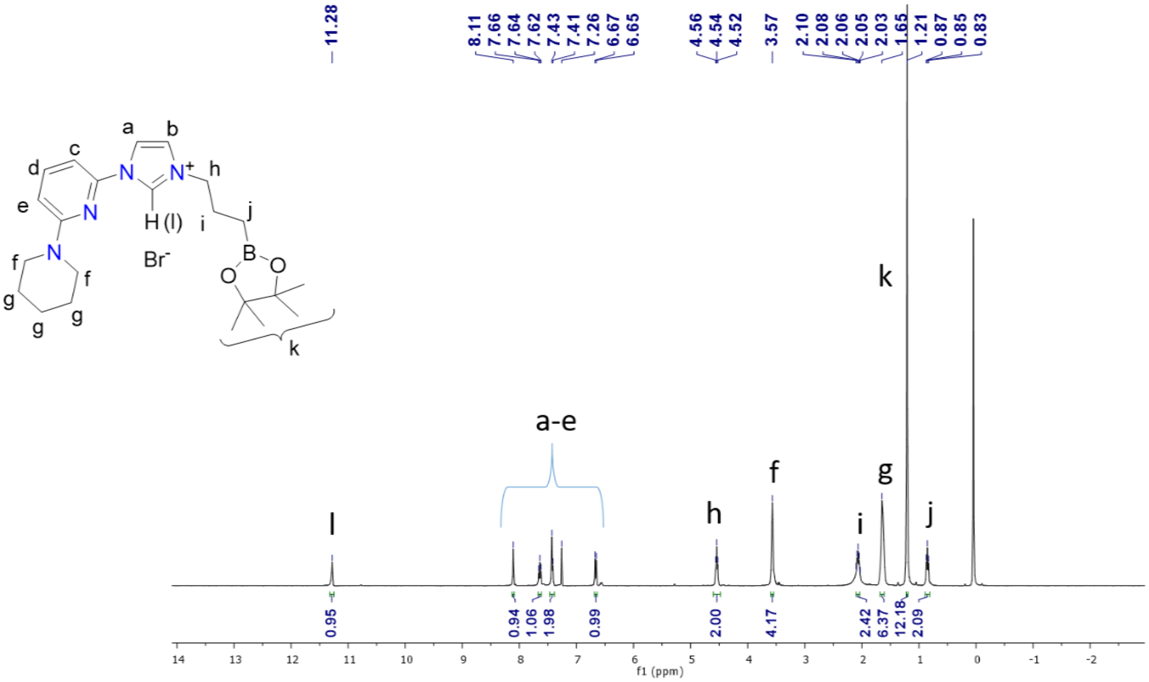


Figure S27. ^{1}H NMR spectrum of **L1** in $CDCl_3$

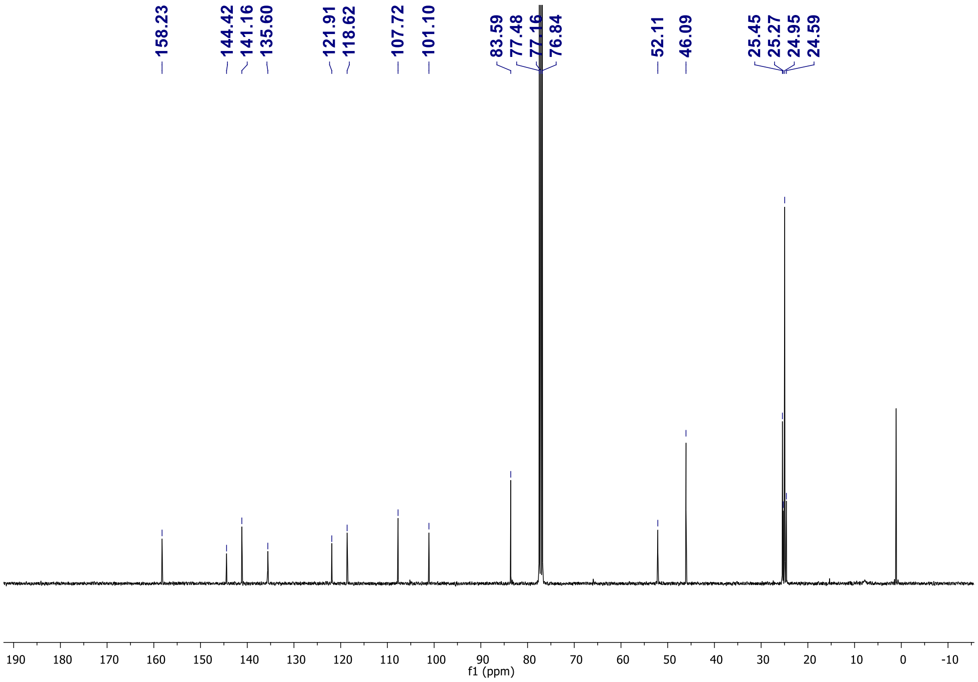


Figure S28. ^{13}C NMR spectrum of **L1** in $CDCl_3$

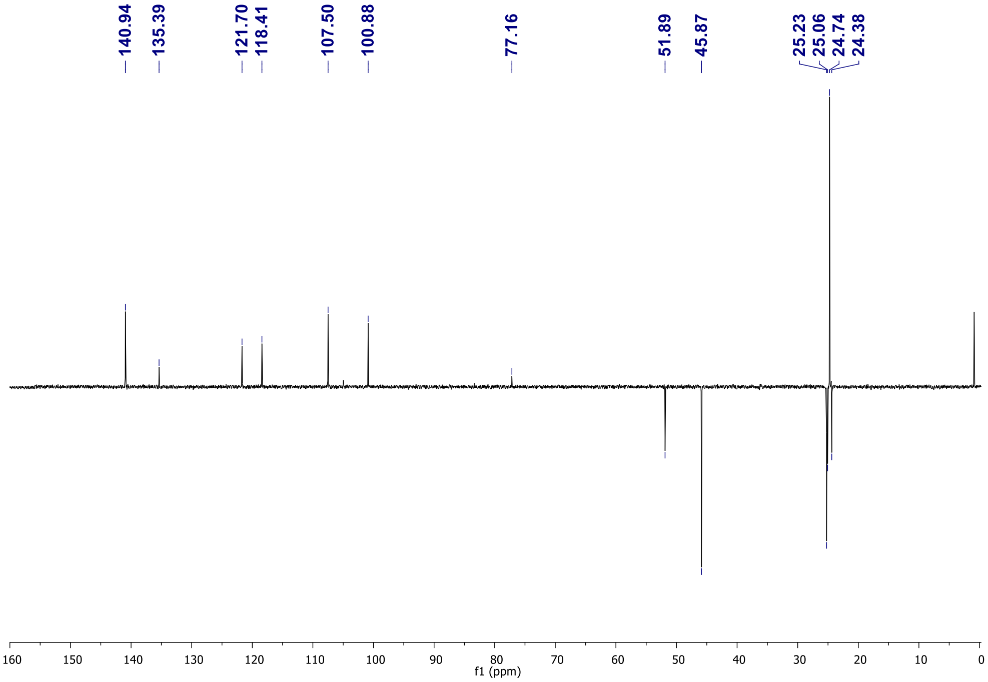


Figure S29. 135-DEPT NMR spectrum of **L1** in $CDCl_3$

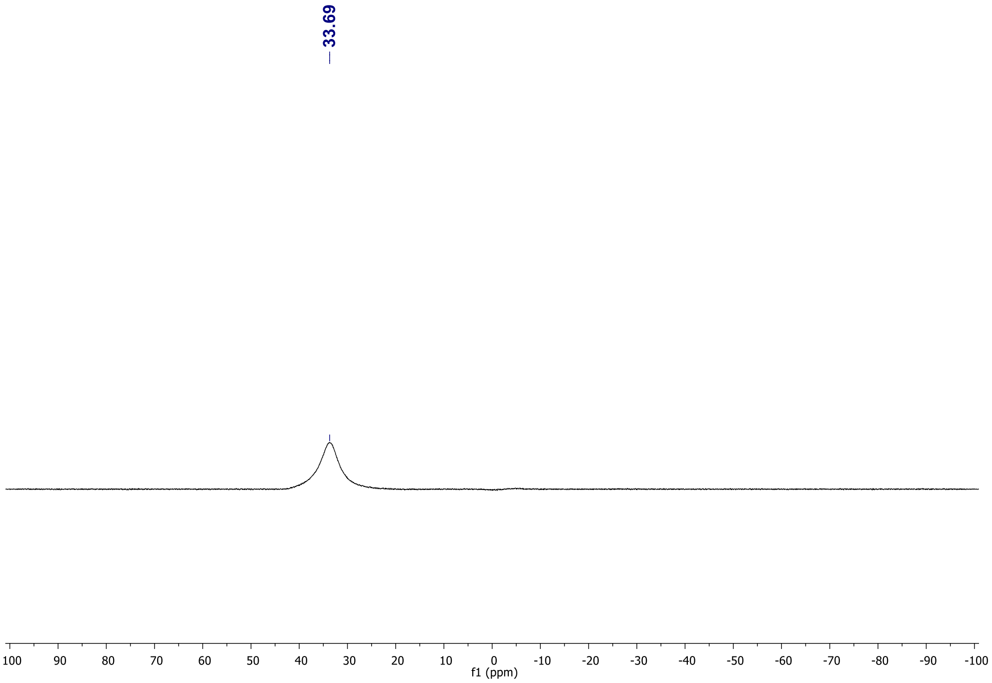


Figure S30. ^{11}B NMR spectrum of **L1** in $CDCl_3$

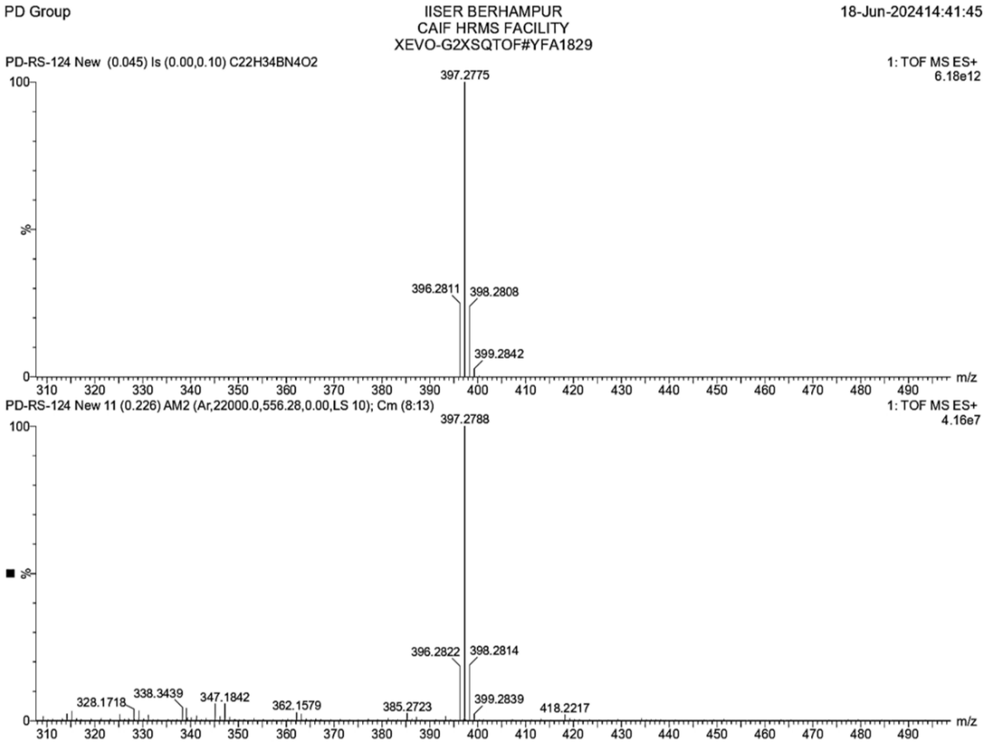


Figure S31. ESI-HRMS of **L1** in acetonitrile

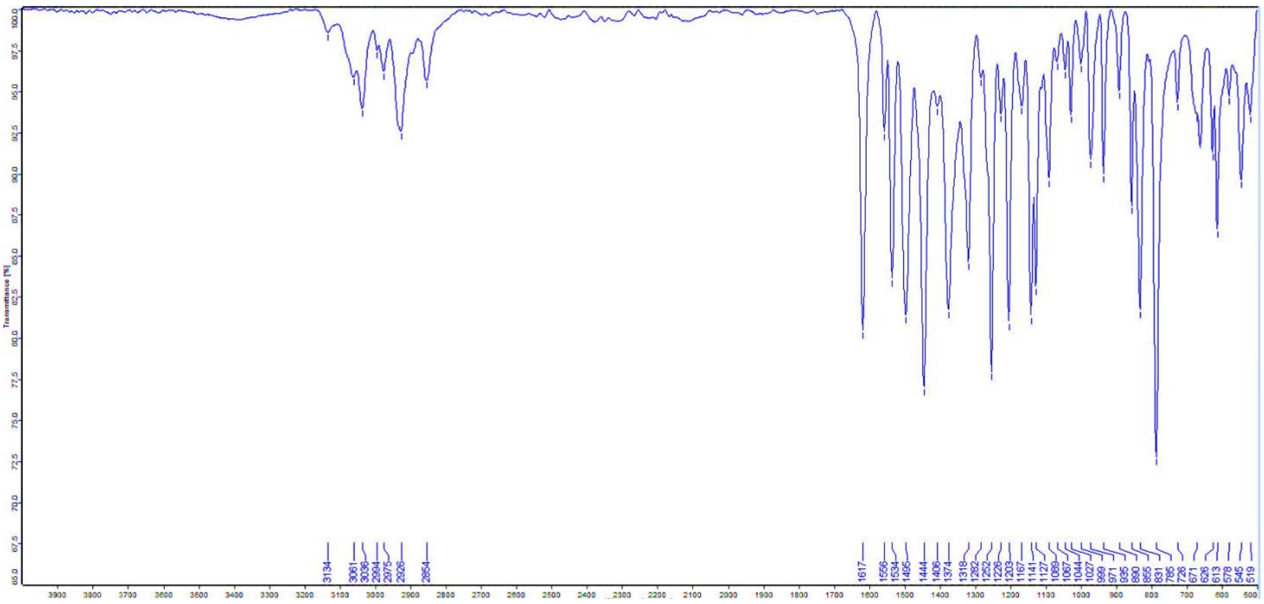


Figure S32. IR Spectrum of **L1**

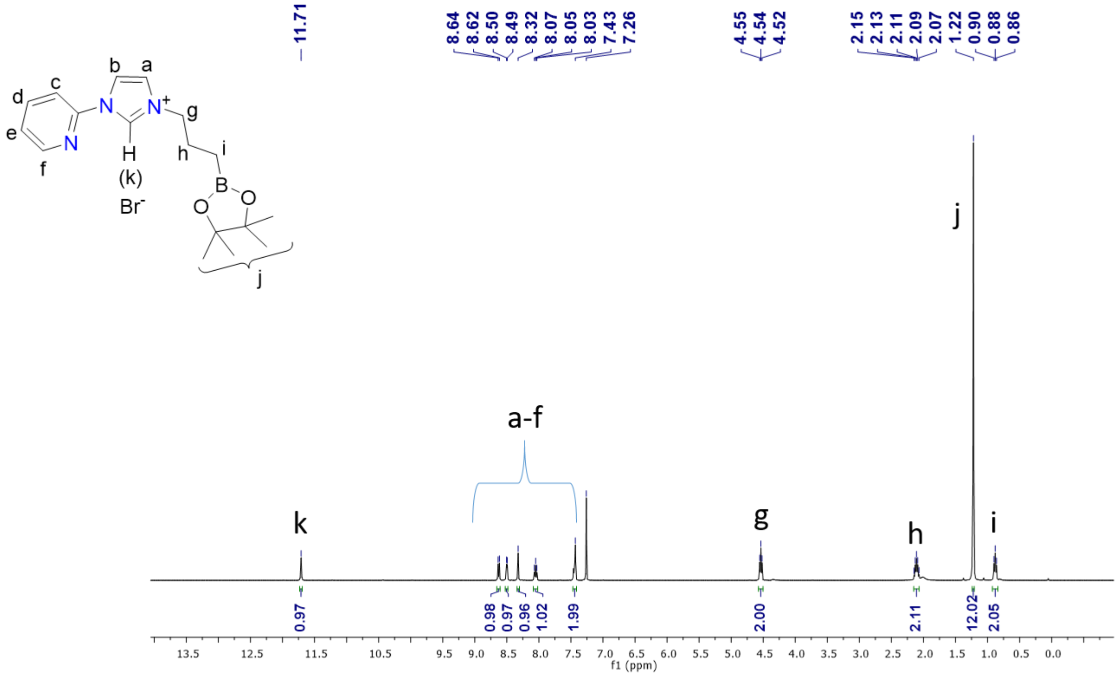


Figure S33. ^{1}H NMR spectrum of **L2** in $CDCl_3$

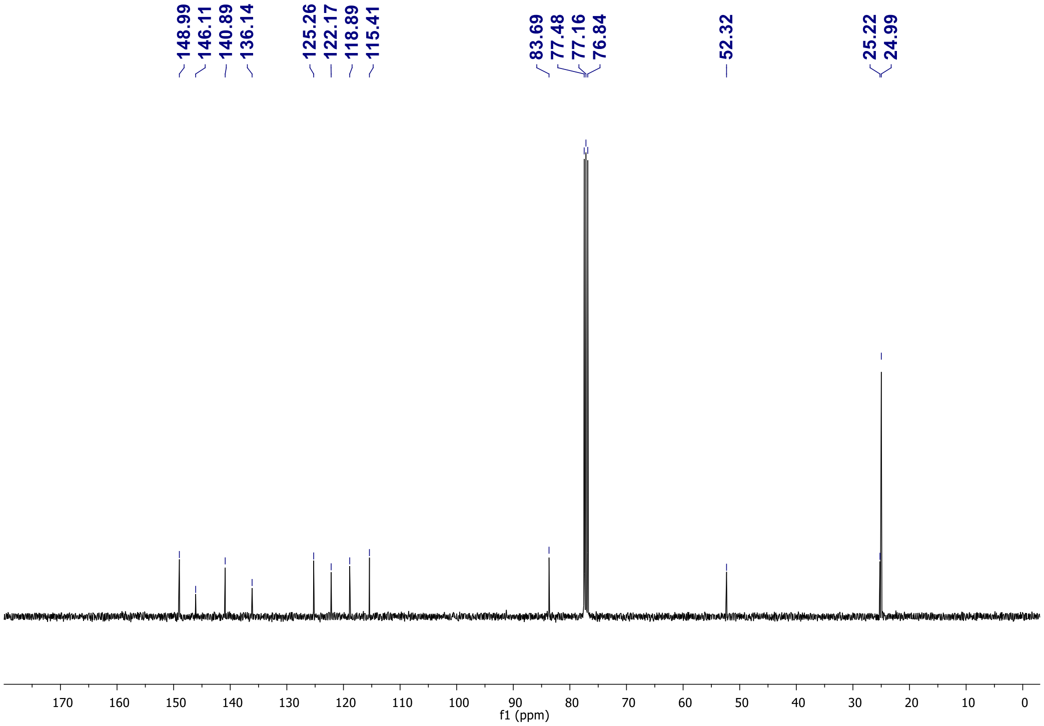


Figure S34. ^{13}C NMR spectrum of **L2** in $CDCl_3$

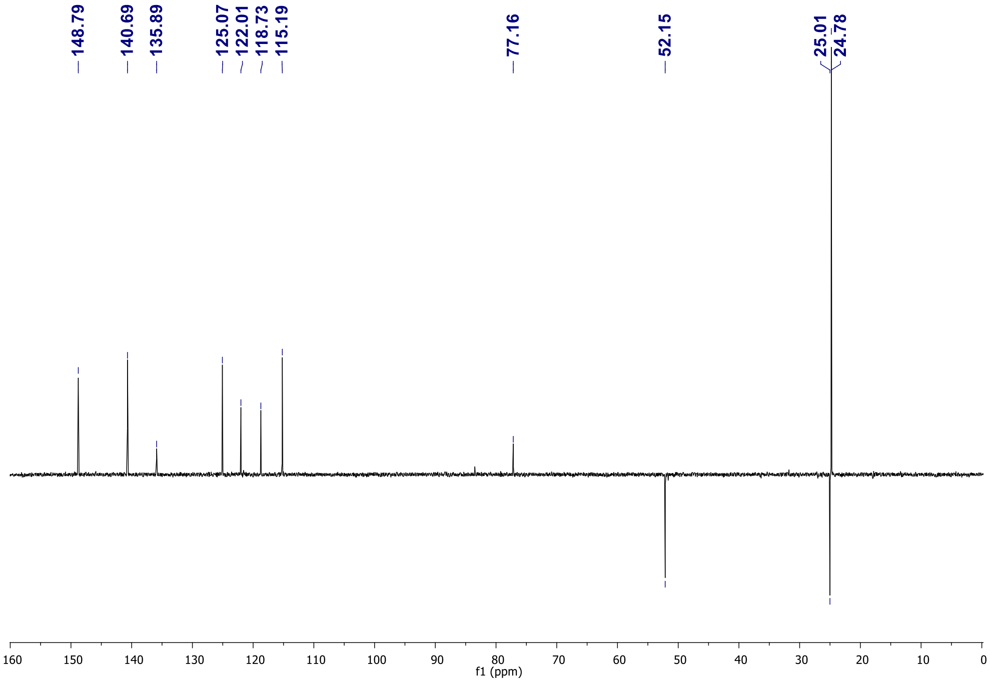


Figure S35. 135-DEPT NMR spectrum of **L2** in $CDCl_3$

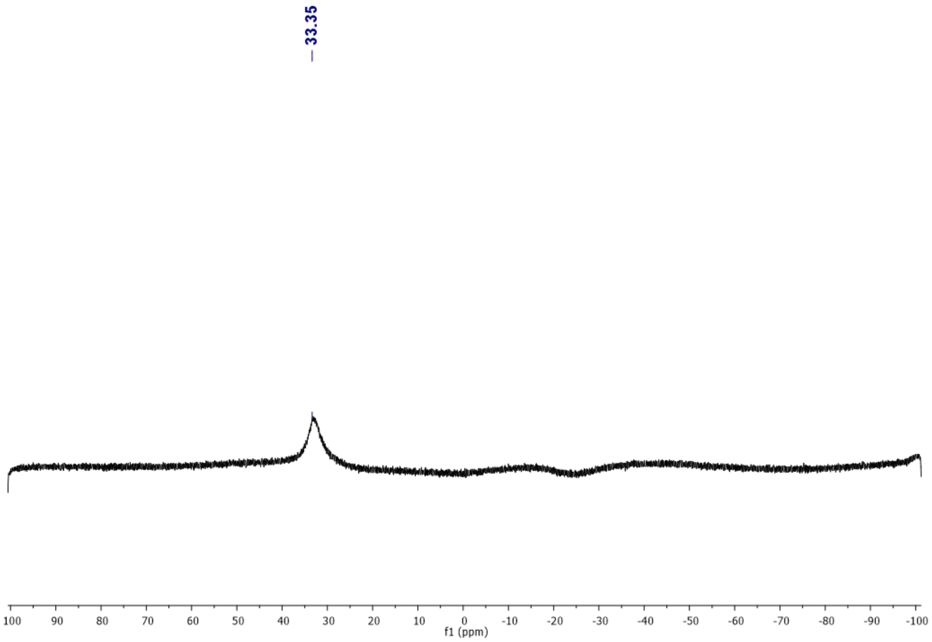


Figure S36. ^{11}B NMR spectrum of **L2** in $CDCl_3$

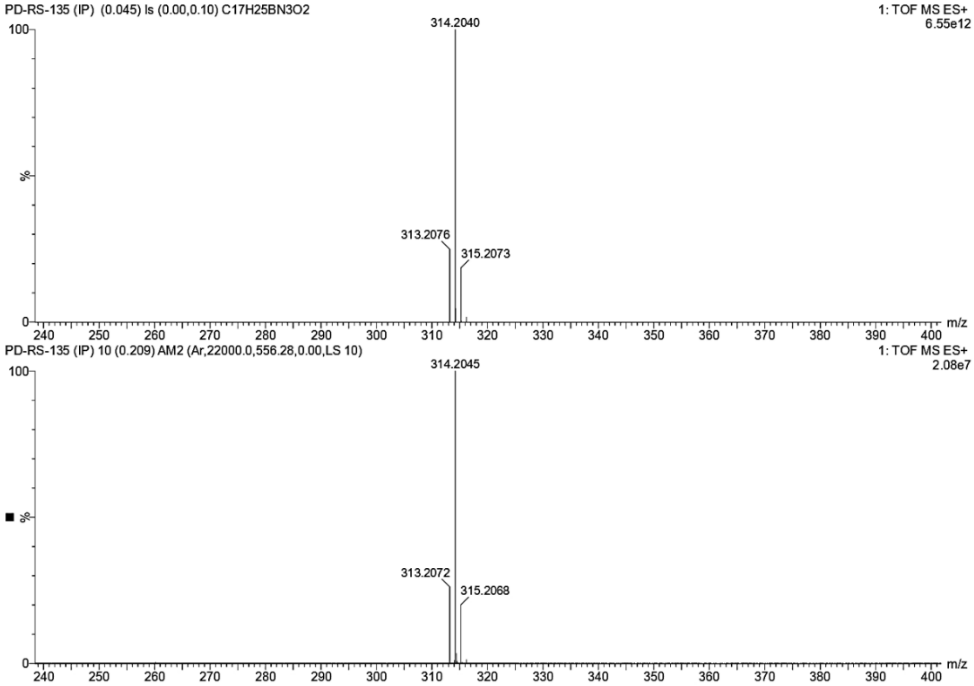


Figure S37. ESI-HRMS of **L2** in acetonitrile

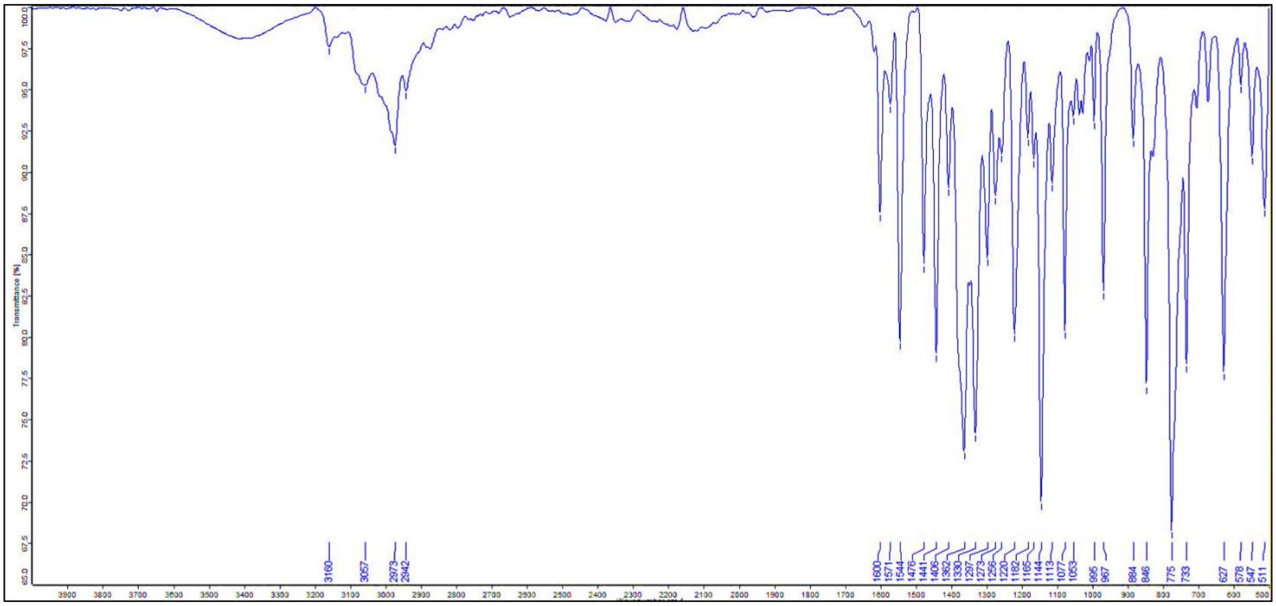
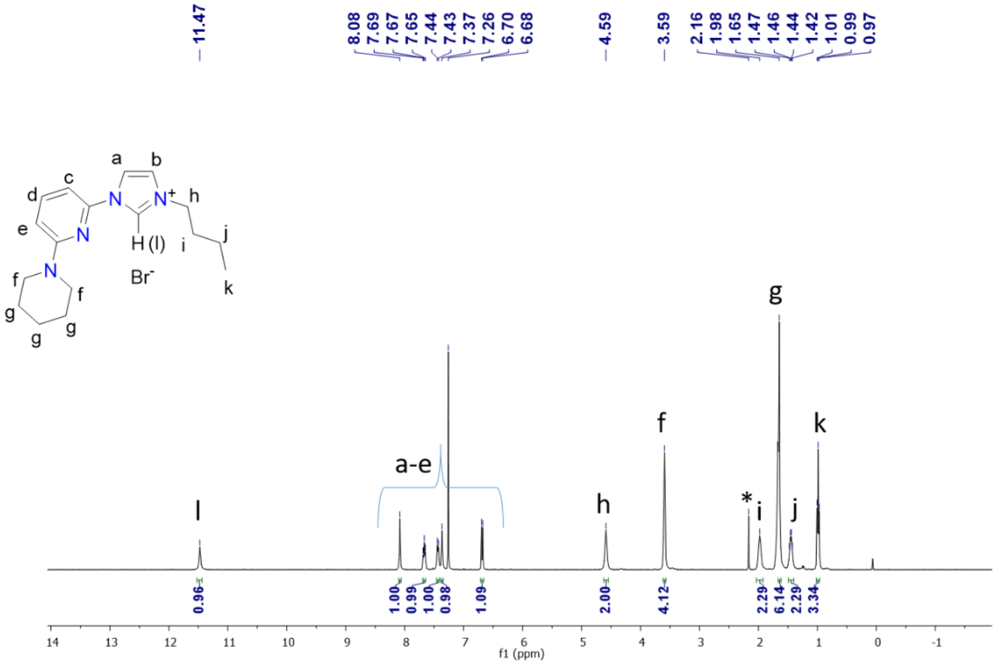


Figure S38. IR Spectrum of **L2**



* = Acetone impurity

Figure S39. ^{1}H NMR spectrum of **L3** in $CDCl_3$

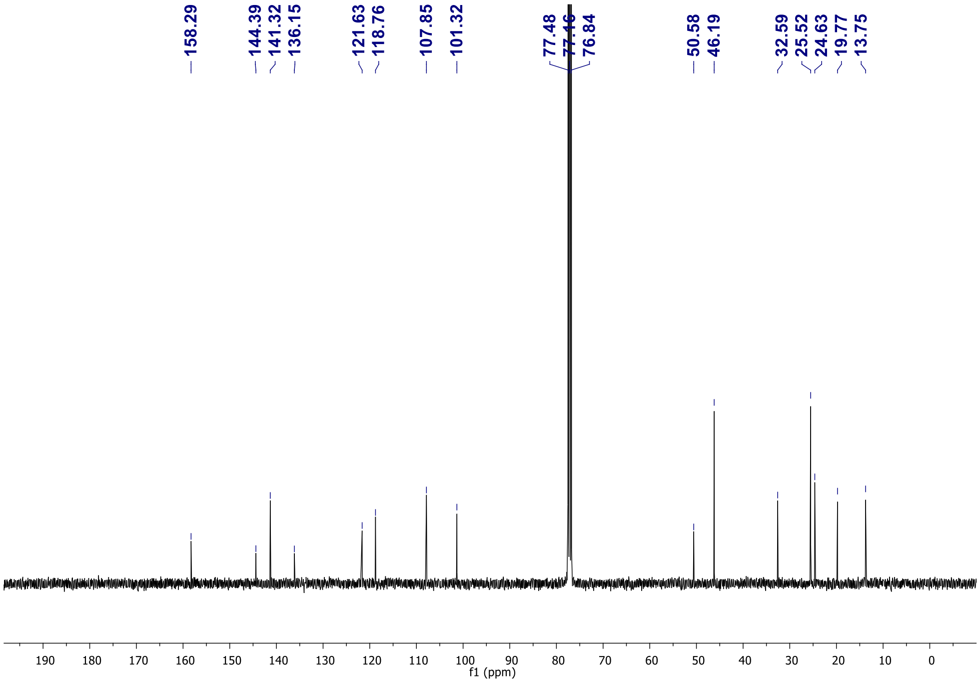


Figure S40. ^{13}C NMR spectrum of **L3** in $CDCl_3$

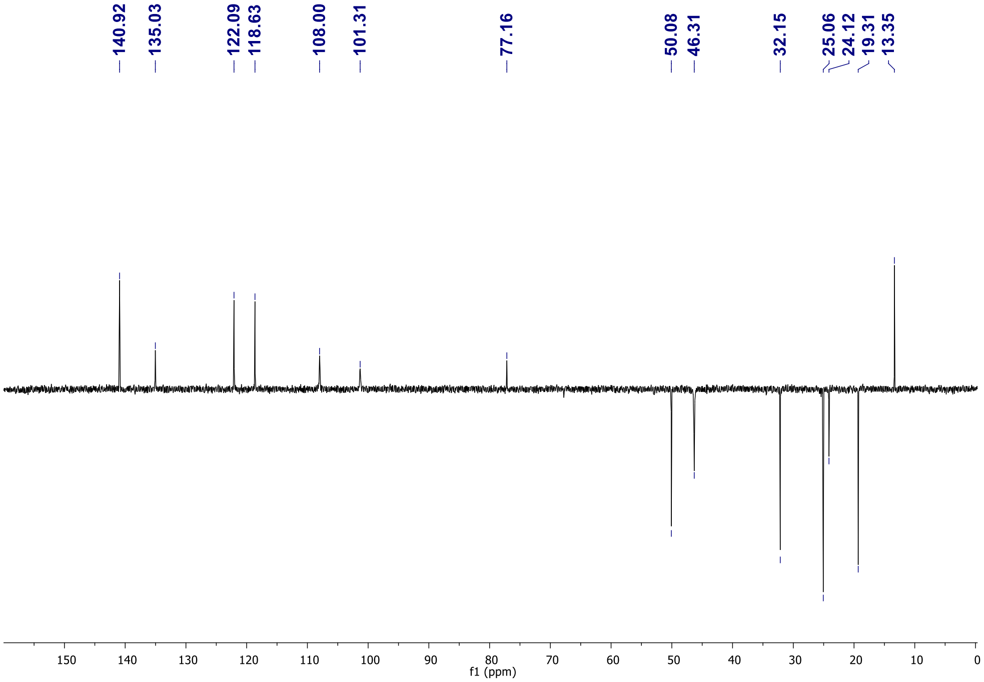


Figure S41. 135-DEPT NMR spectrum of **L3** in $CDCl_3$

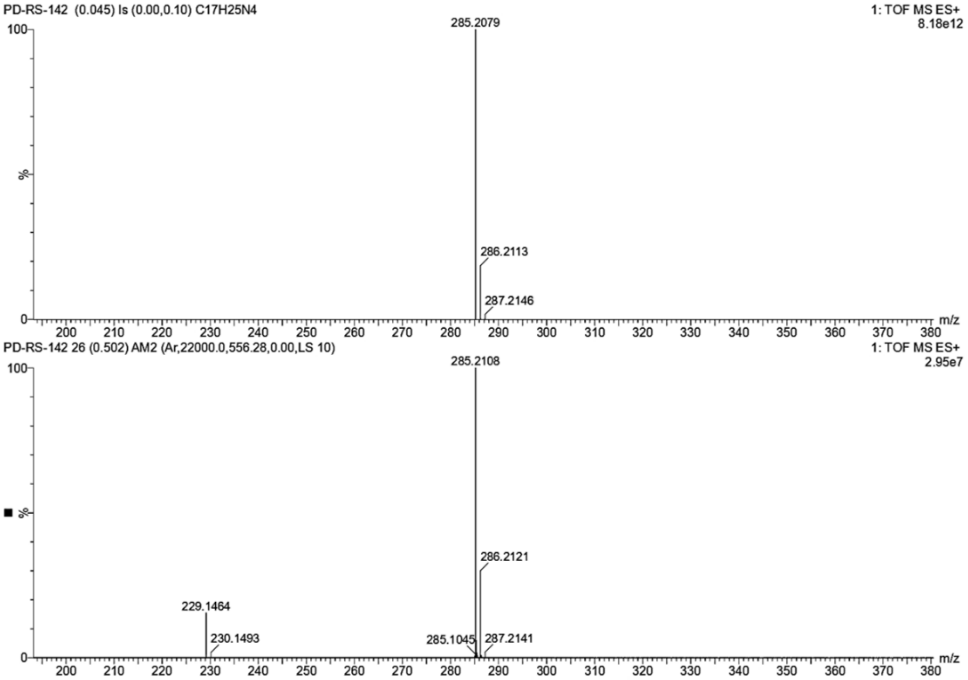


Figure S42. ESI-HRMS of **L3** in acetonitrile

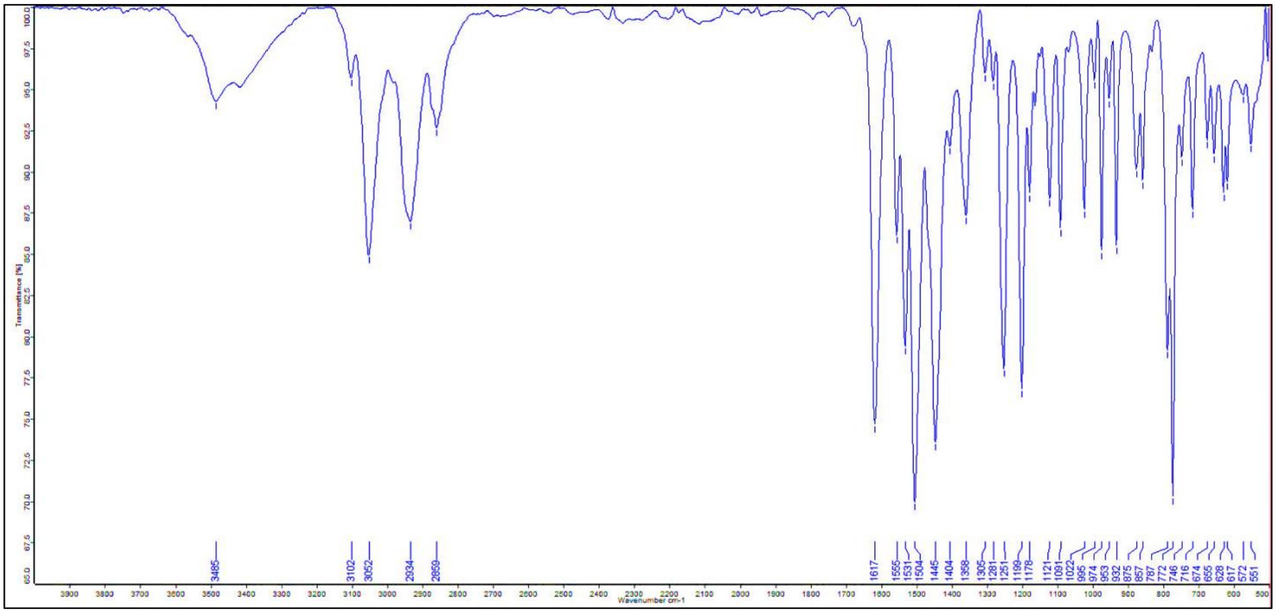


Figure S43. IR Spectrum of **L3**

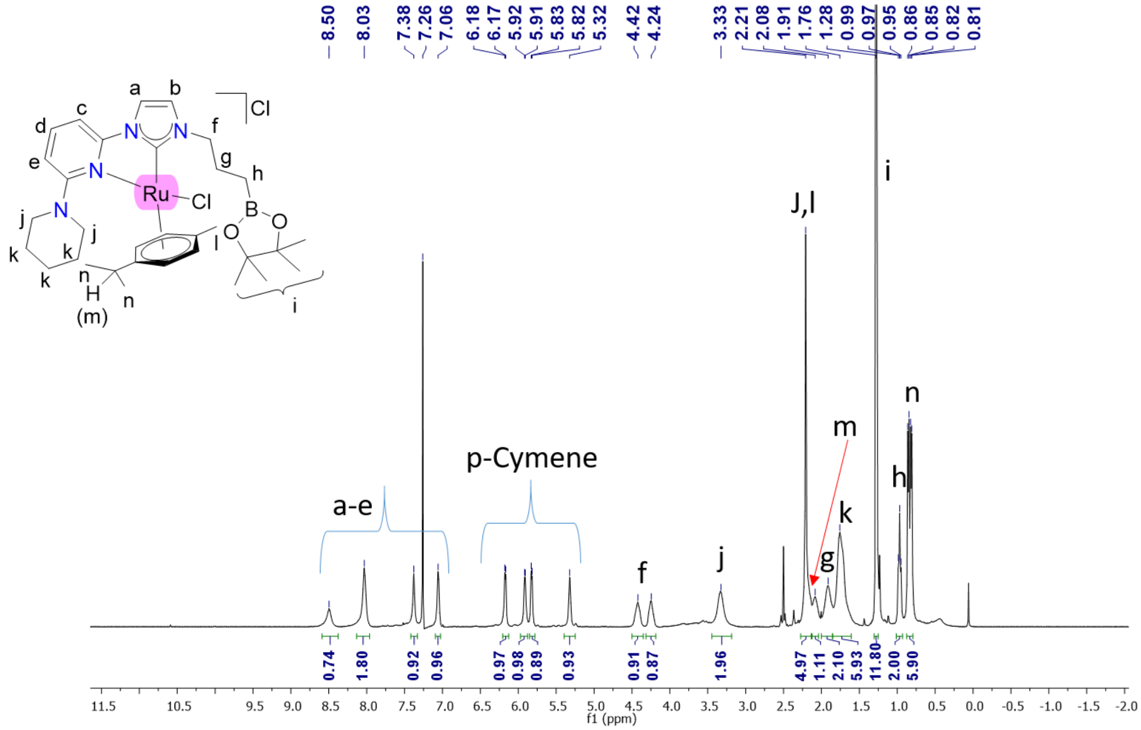


Figure S44. ^{1}H NMR spectrum of complex **1** in $CDCl_3$

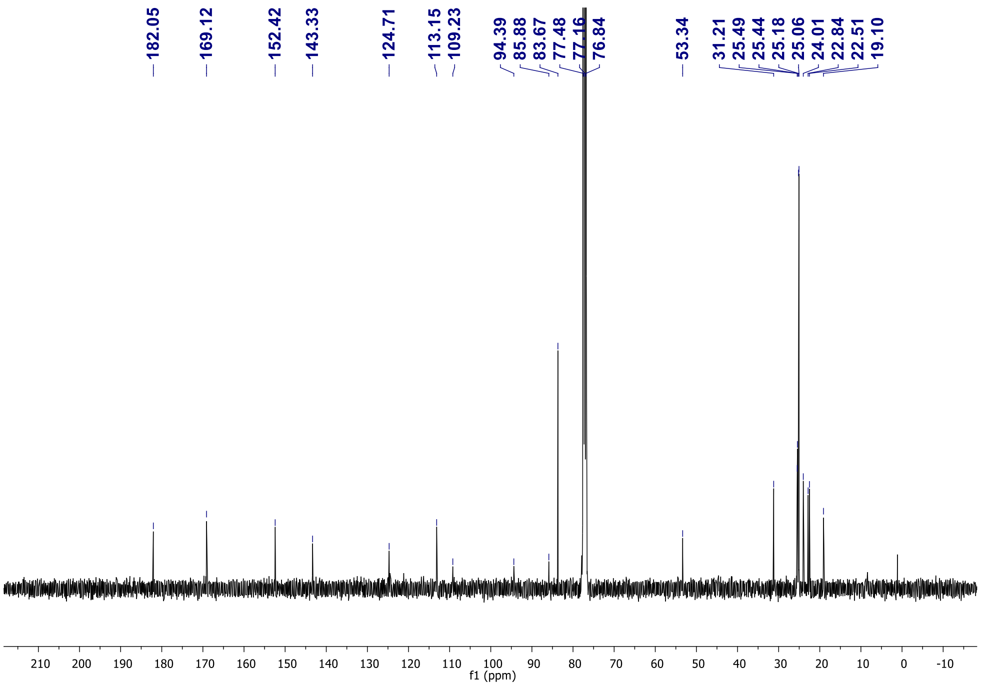


Figure S45. ^{13}C NMR spectrum of complex **1** in $CDCl_3$

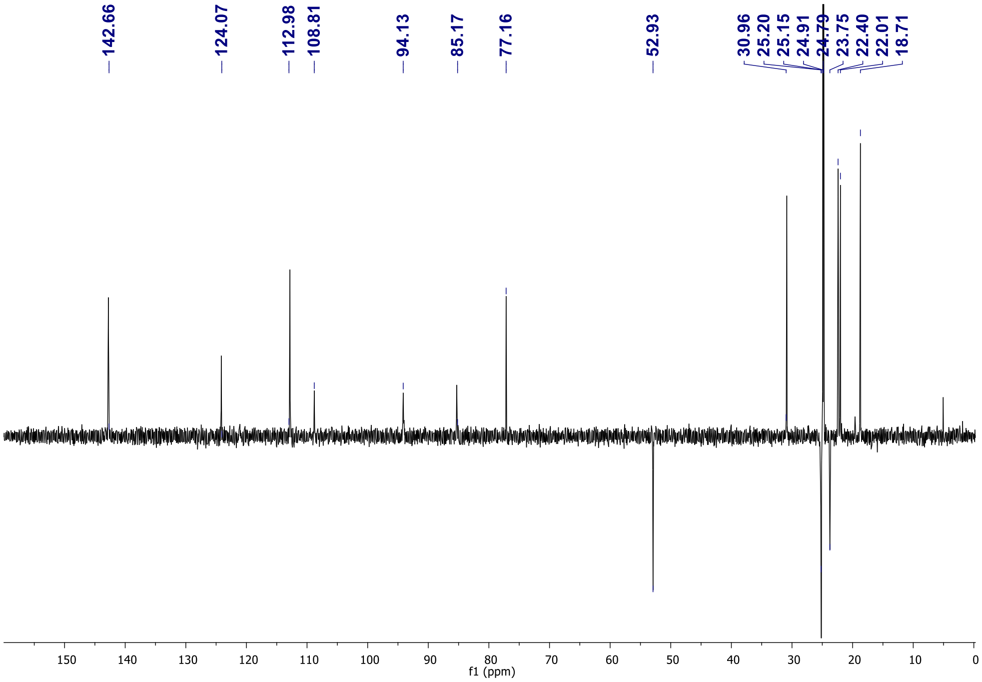


Figure S46. 135-DEPT NMR spectrum of complex **1** in $CDCl_3$

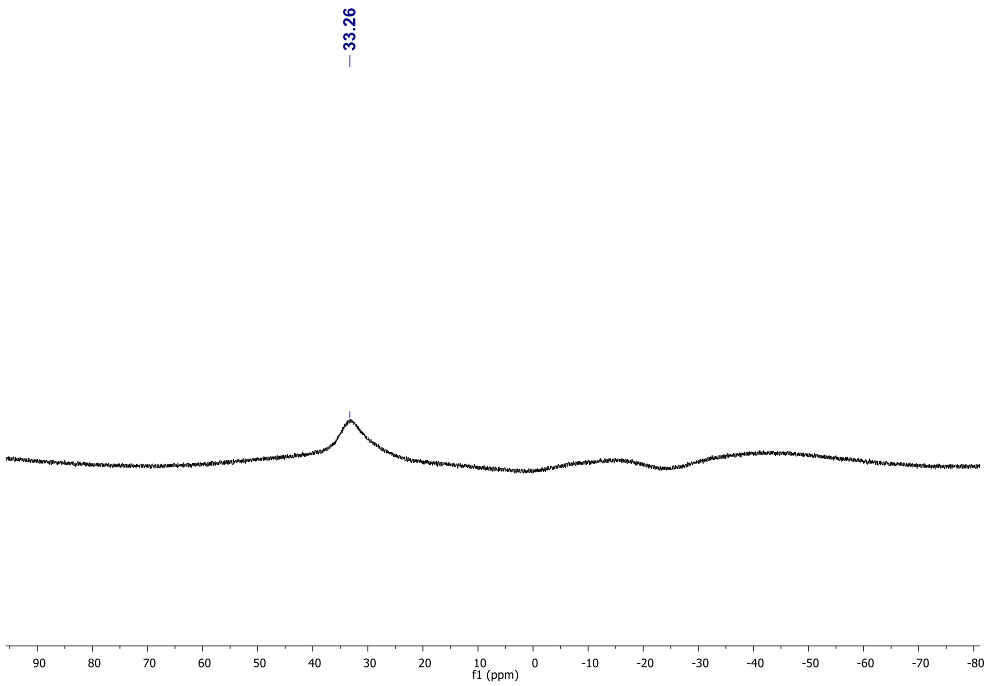


Figure S47. ^{11}B NMR spectrum of complex **1** in $CDCl_3$

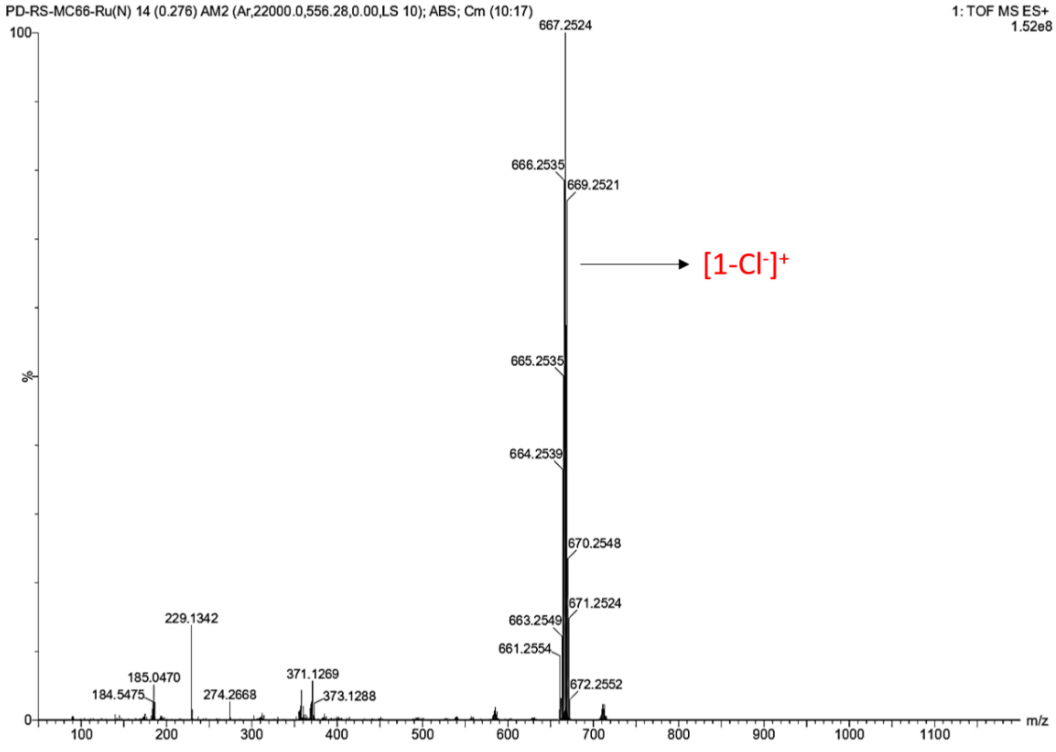


Figure S48. ESI-HRMS of complex **1** in acetonitrile

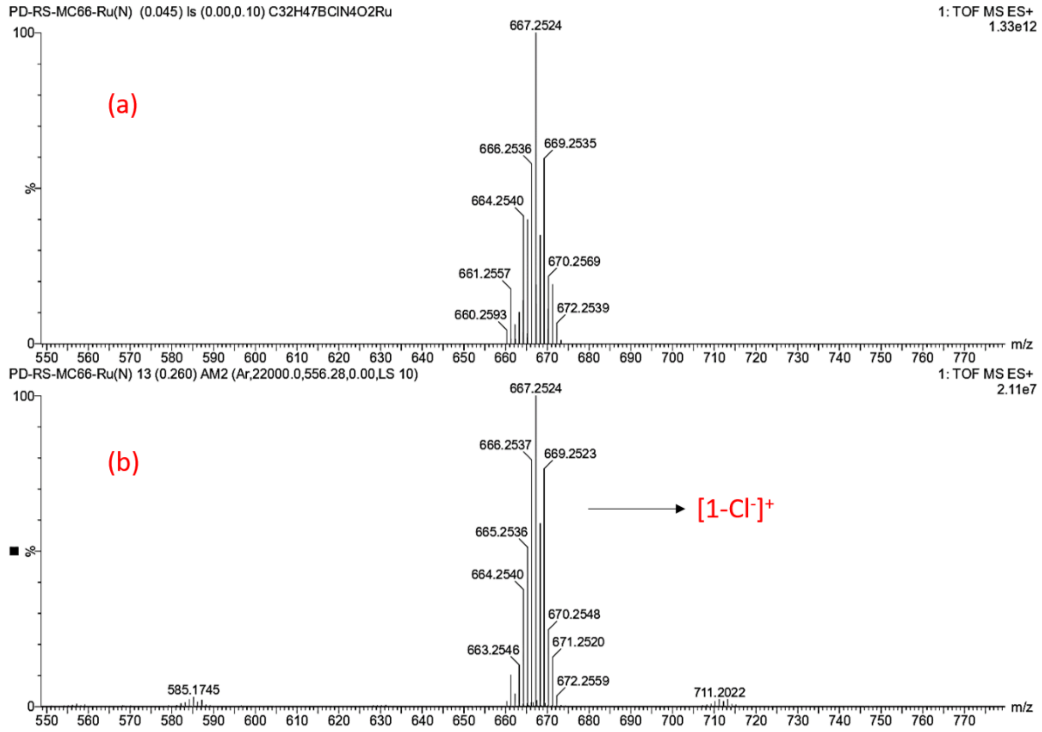


Figure S49. Isotopic mass distribution analysis of complex **1**. Simulated (a) and Experimental (b)

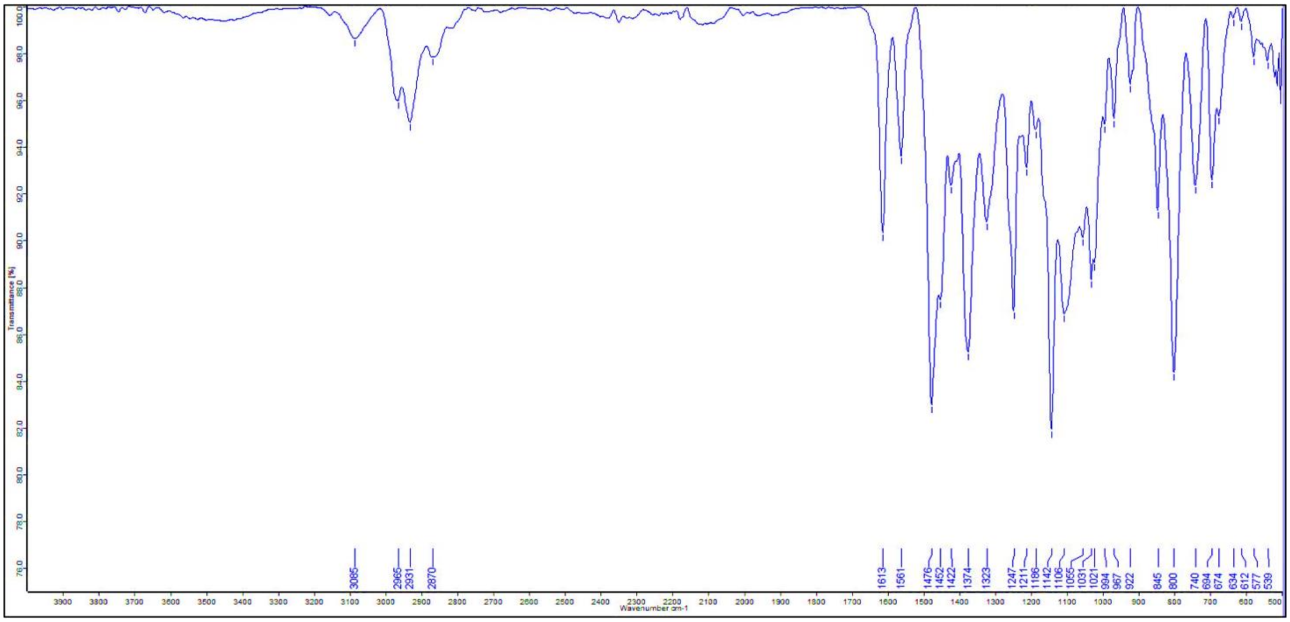


Figure S50. IR spectrum of complex **1**

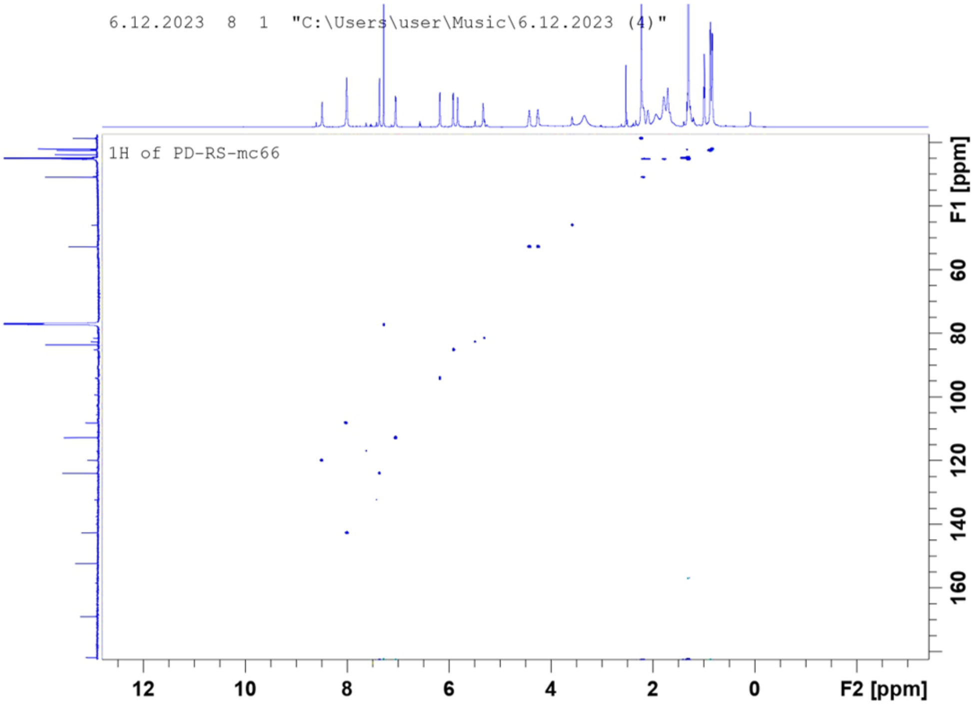
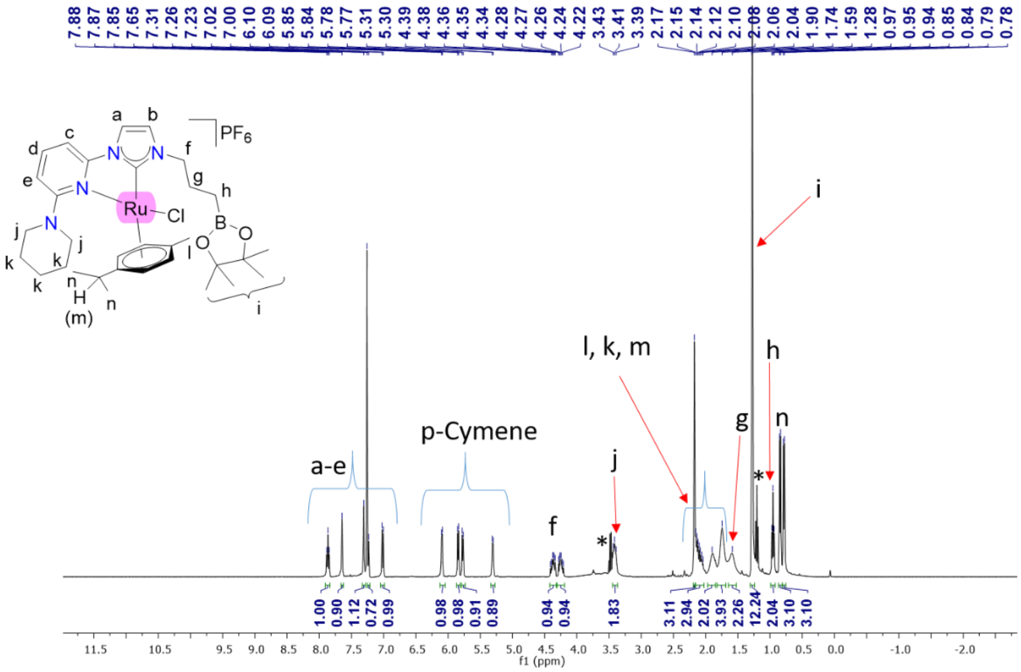


Figure S51. HSQC spectrum of complex **1** in $CDCl_3$



* = Diethylether

Figure S52. ^{1}H NMR spectrum of complex **1-PF$_6$** in $CDCl_3$

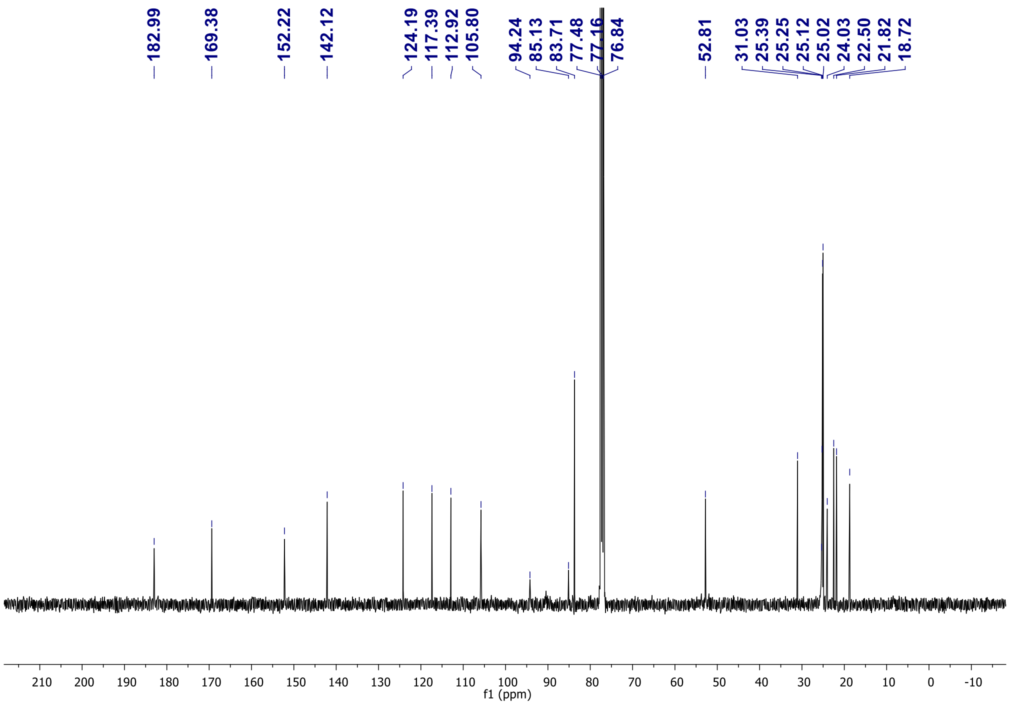


Figure S53. ^{13}C NMR spectrum of complex **1-PF$_6$** in CDCl$_3$

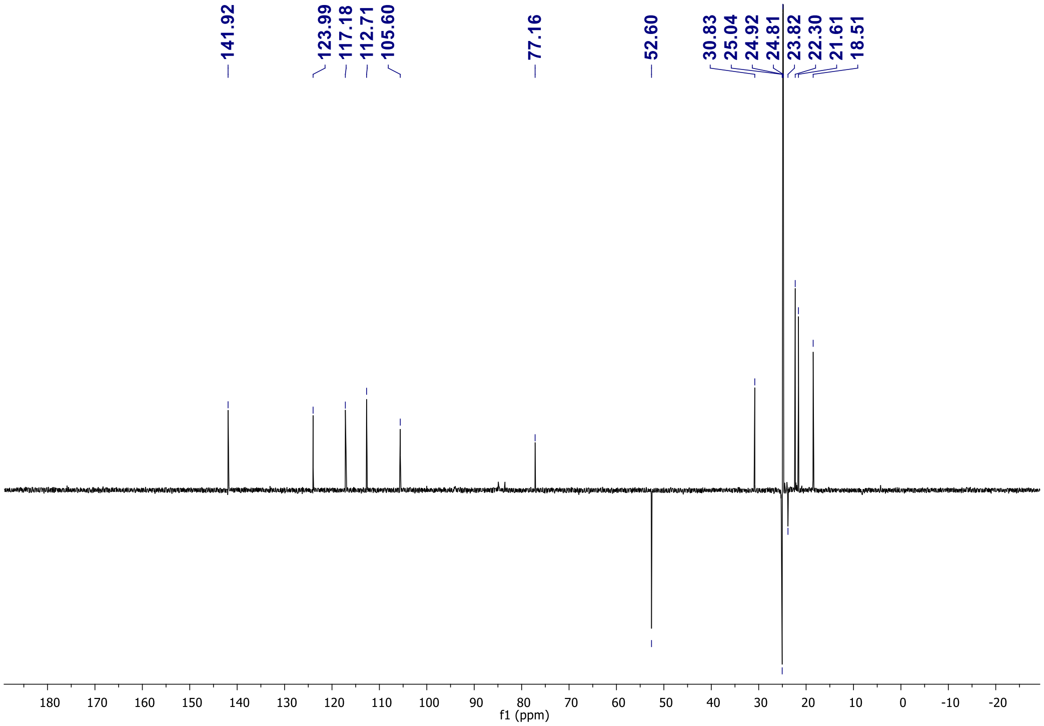


Figure S54. 135-DEPT NMR spectrum of complex **1-PF$_6$** in CDCl$_3$

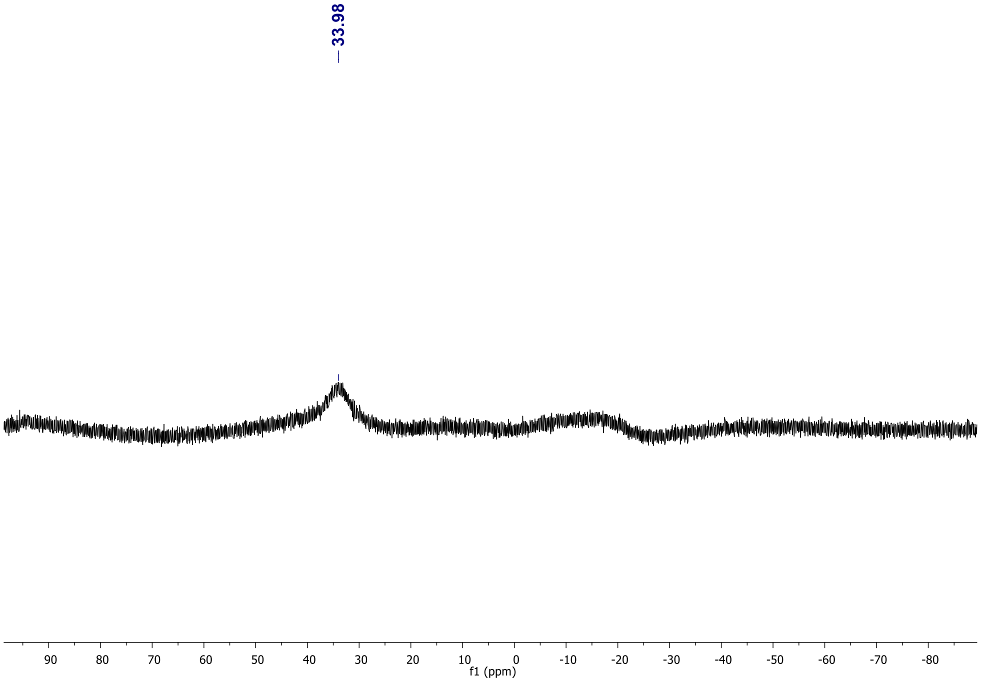


Figure S55. ^{11}B NMR spectrum of complex **1-PF$_6$** in CDCl$_3$

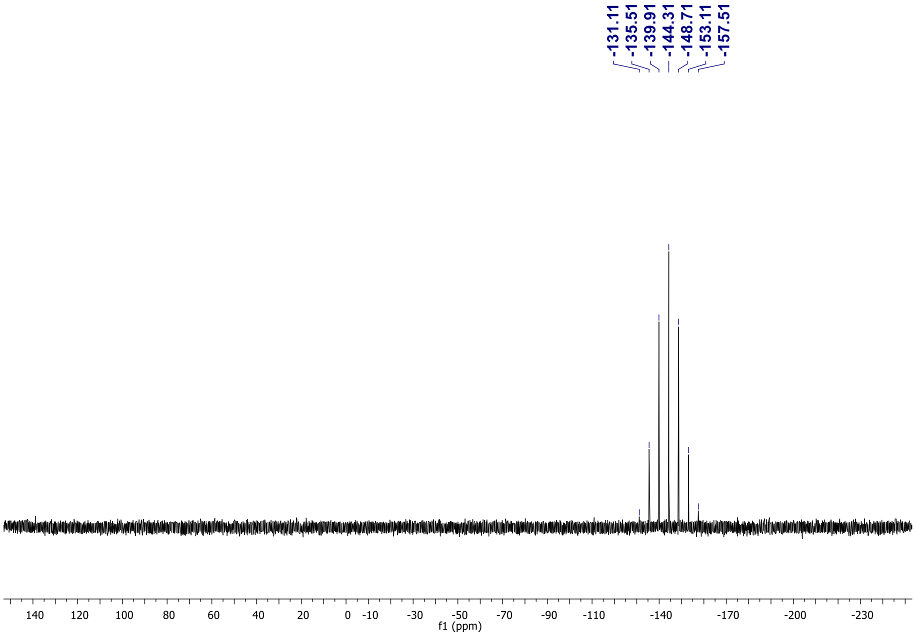


Figure S56. ^{31}P NMR spectrum of complex **1-PF$_6$** in CDCl$_3$

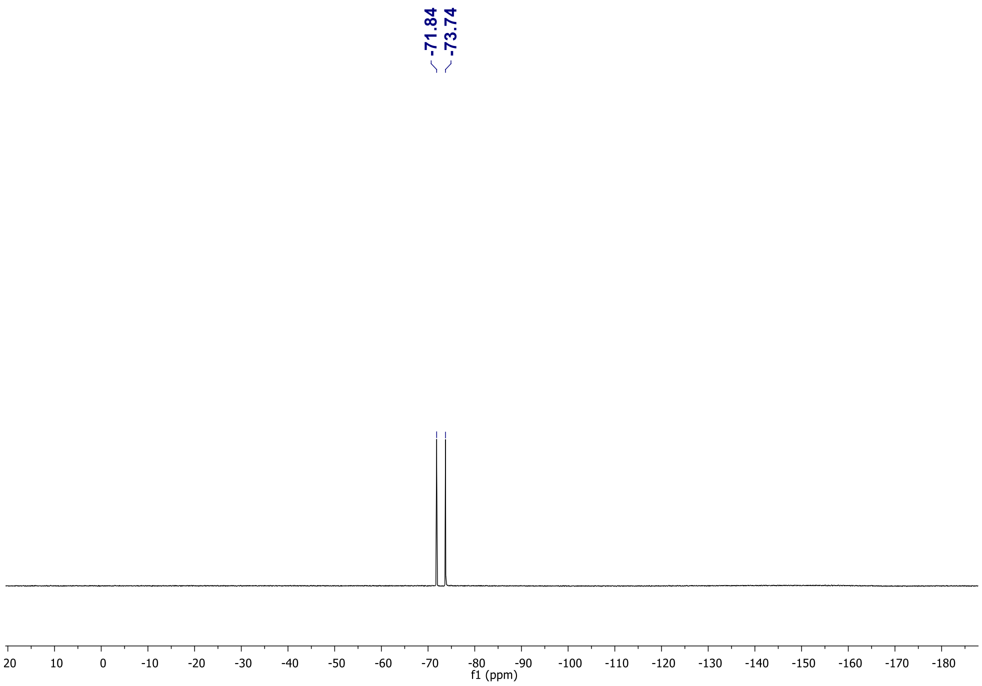


Figure S57. ^{19}F NMR spectrum of complex **1-PF_6** in $CDCl_3$

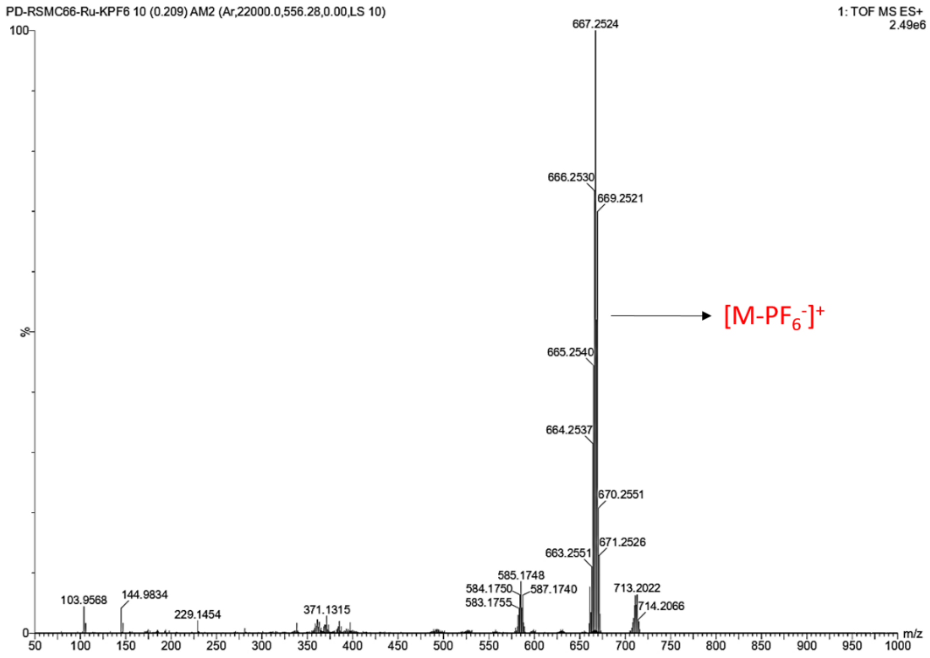


Figure S58. ESI-HRMS of complex **1-PF_6** in acetonitrile (**M**= $C_{32}H_{47}BClF_6N_4O_2PRu$)

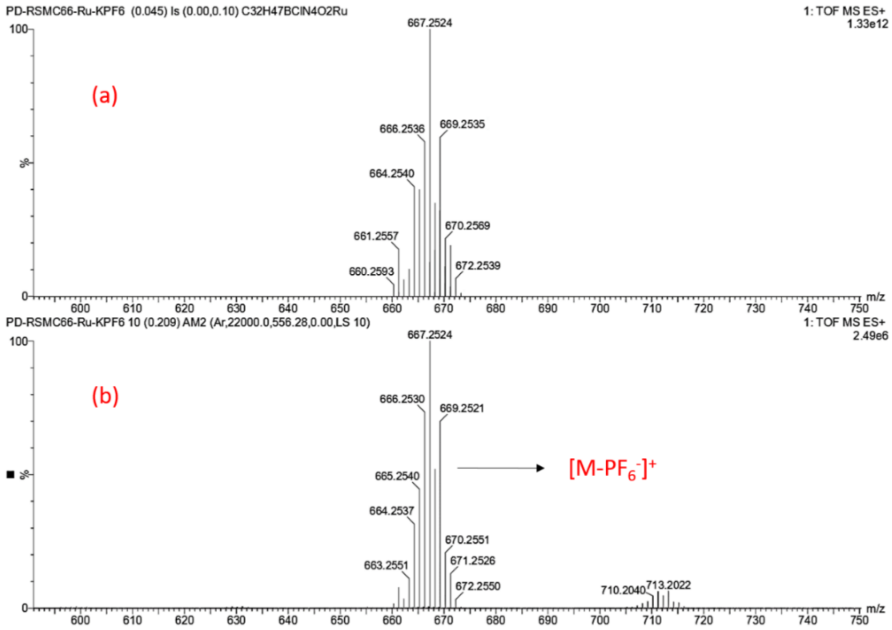


Figure S59. Isotopic mass distribution analysis of complex **1-PF$_6$**. Simulated (a) and Experimental (b) (**M**= $C_{32}H_{47}BClF_6N_4O_2PRu$)

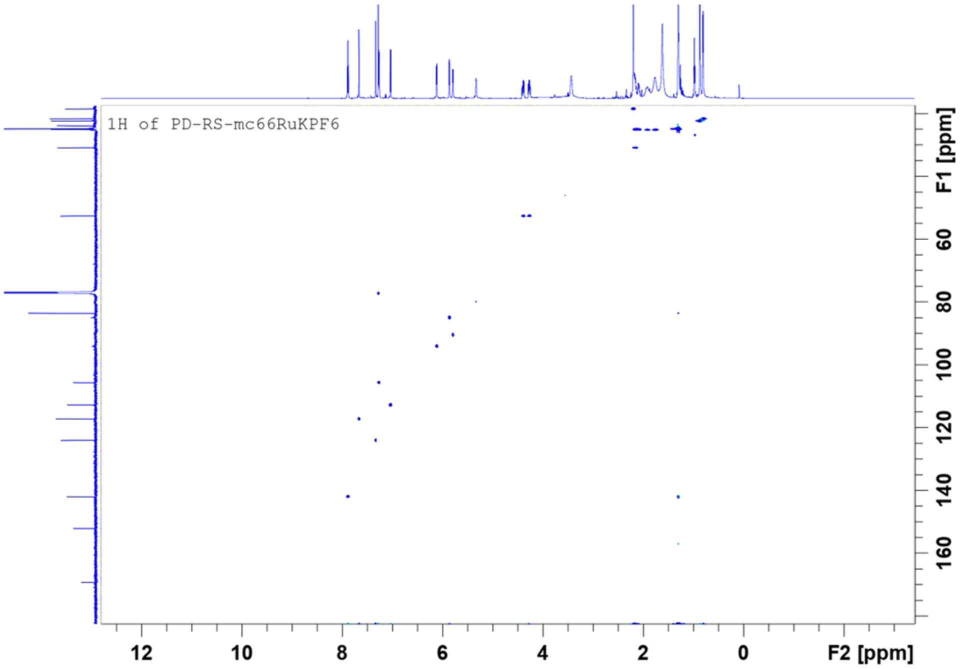


Figure S60. HSQC spectrum of complex **1-PF$_6$** in $CDCl_3$

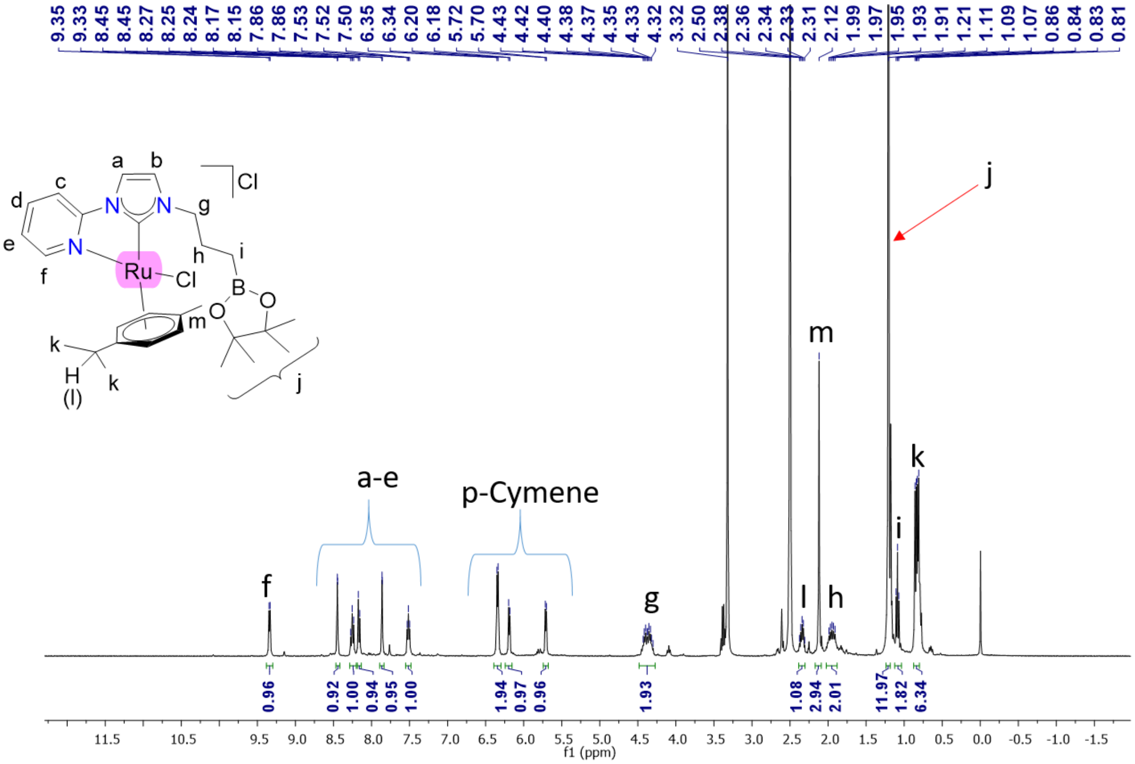


Figure S61. ^{1}H NMR spectrum of complex **2** in DMSO-d$_6$

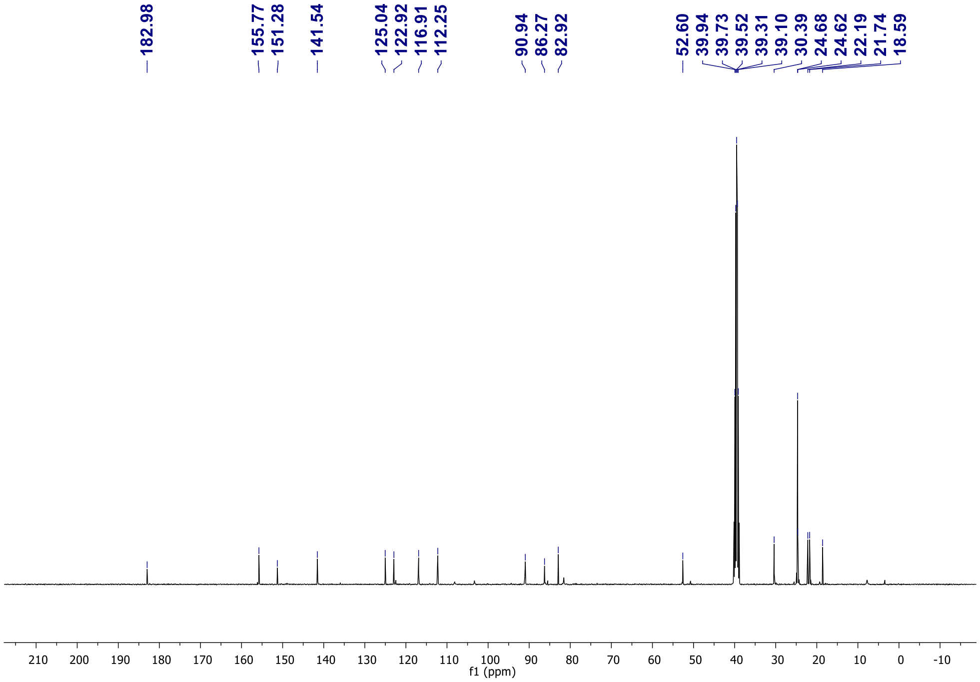


Figure S62. ^{13}C NMR spectrum of complex **2** in DMSO-d$_6$

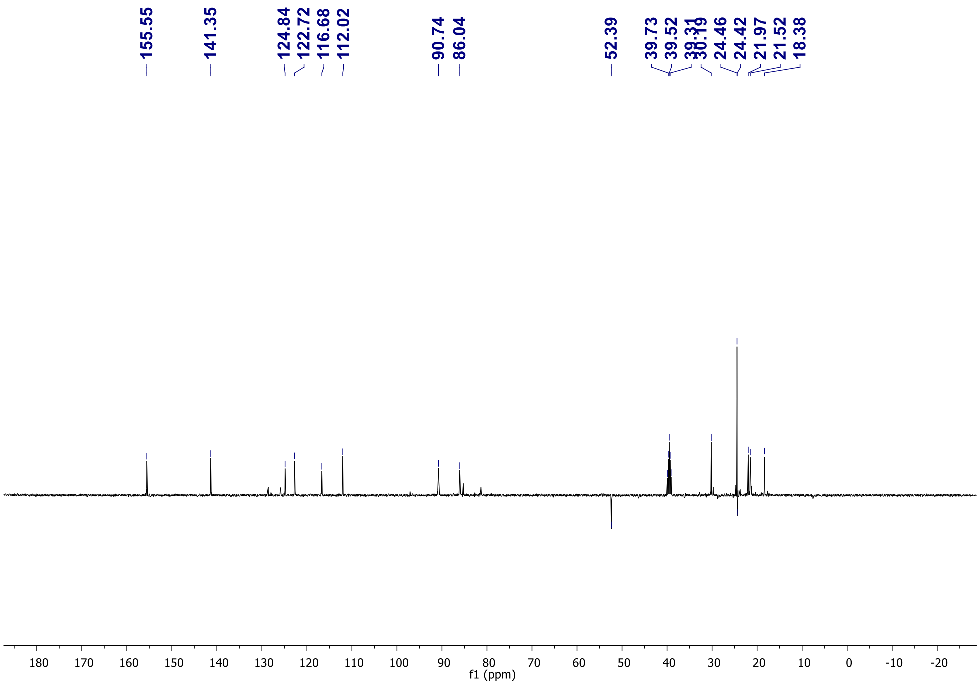


Figure S63. 135-DEPT NMR spectrum of complex **2** in DMSO-d6

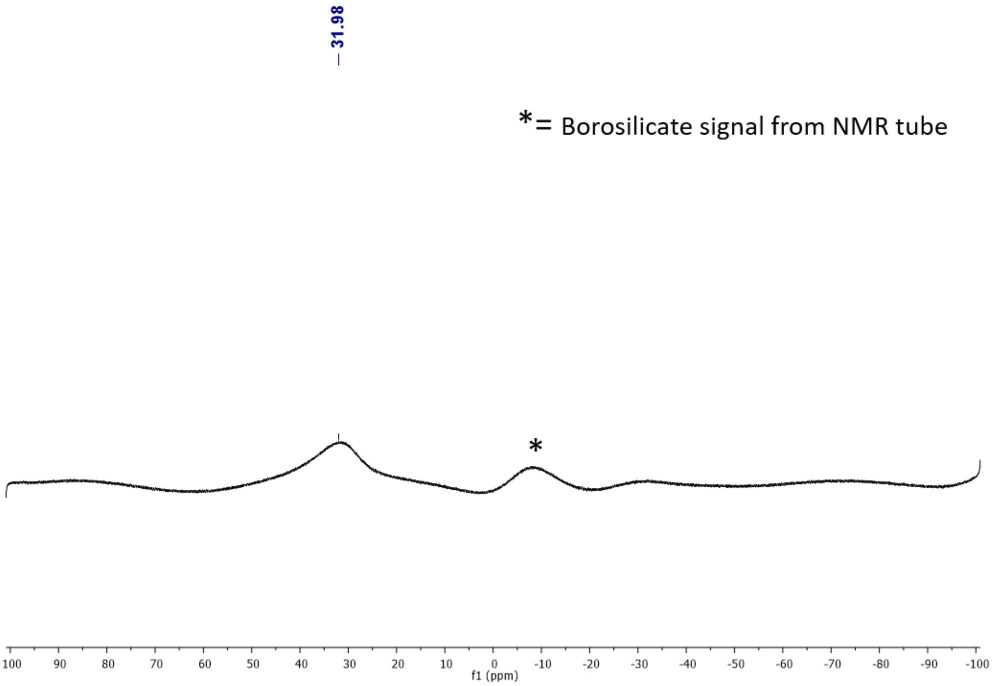

*= Borosilicate signal from NMR tube

Figure S64. ^{11}B NMR spectrum of complex **2** in DMSO-d_6

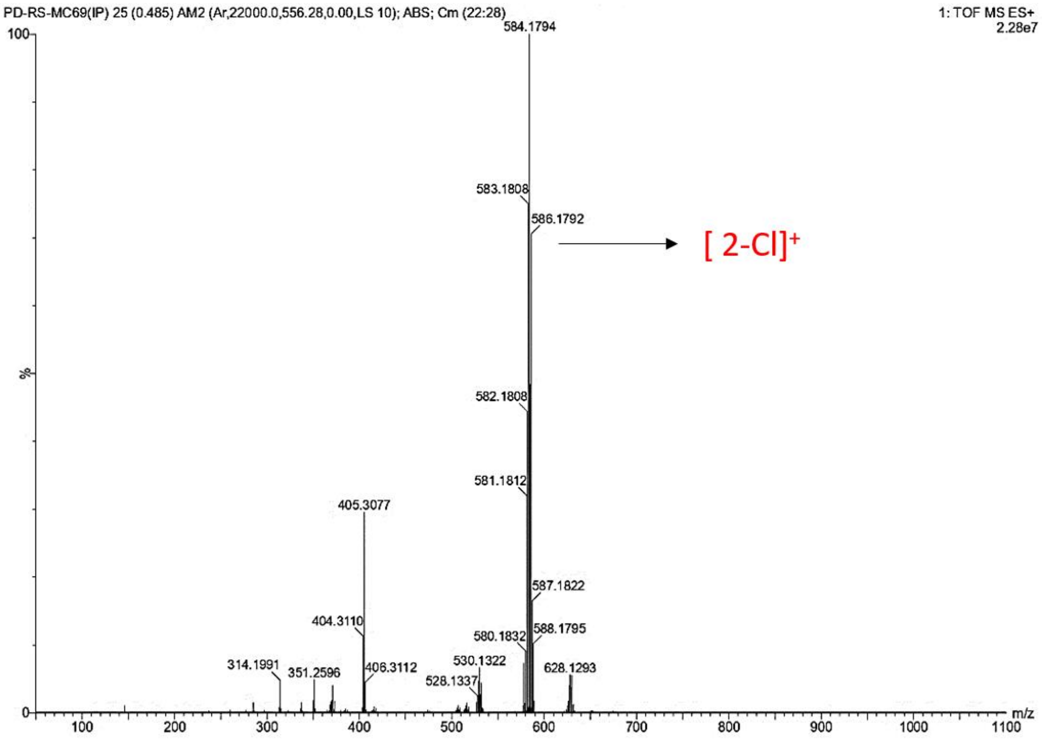


Figure S65. ESI-HRMS of complex **2** in acetonitrile

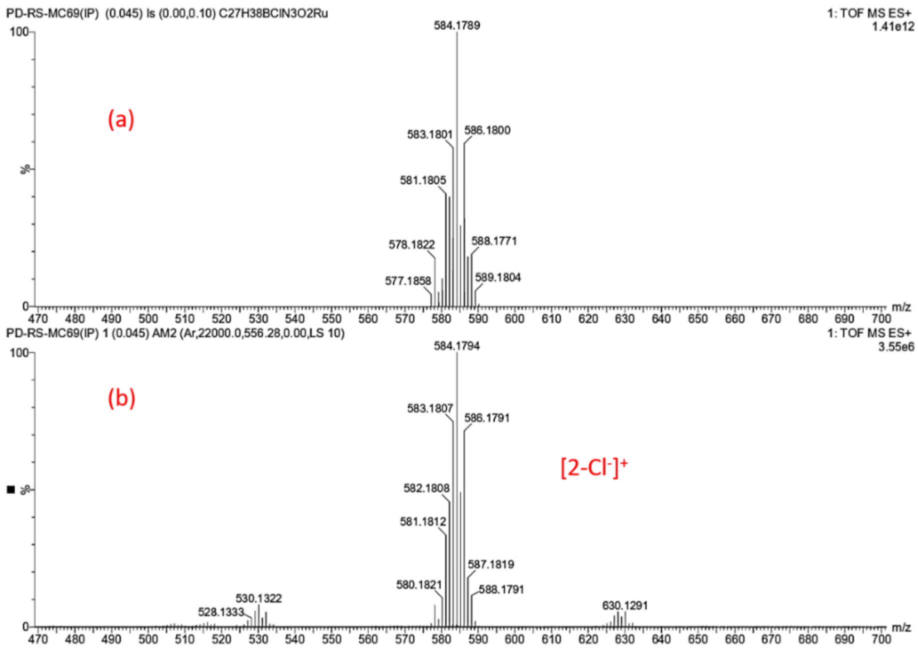


Figure S66. Isotopic mass distribution analysis of complex **2**. Simulated (a) and Experimental (b)

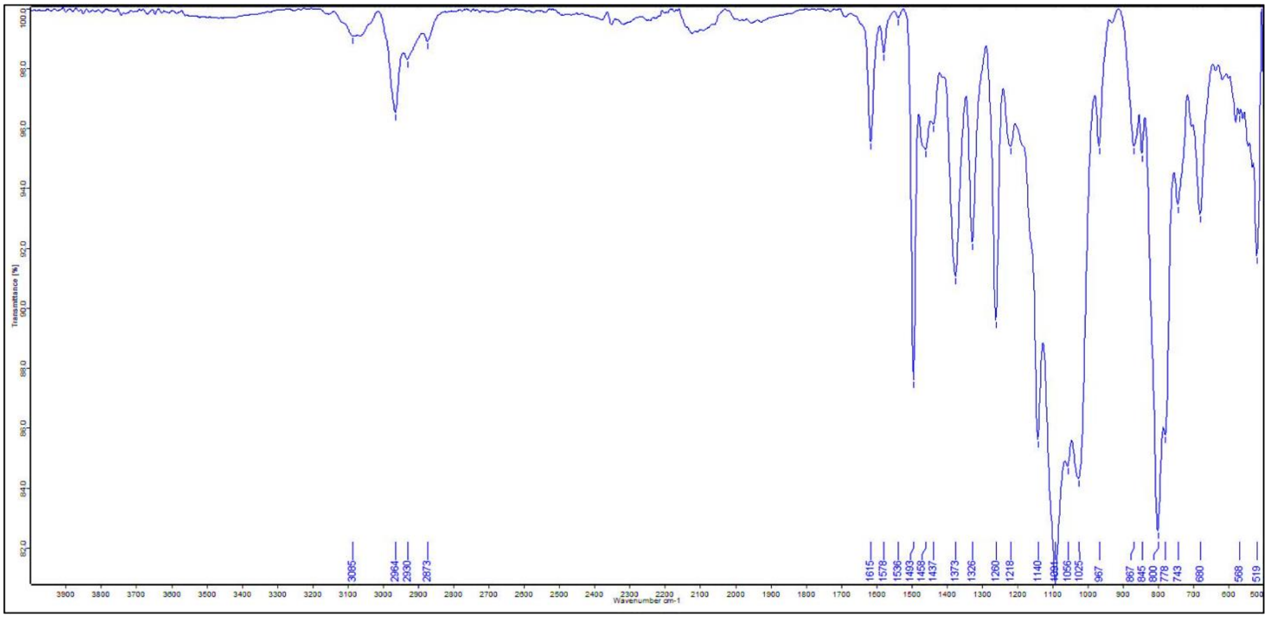


Figure S67. IR spectrum of complex **2**

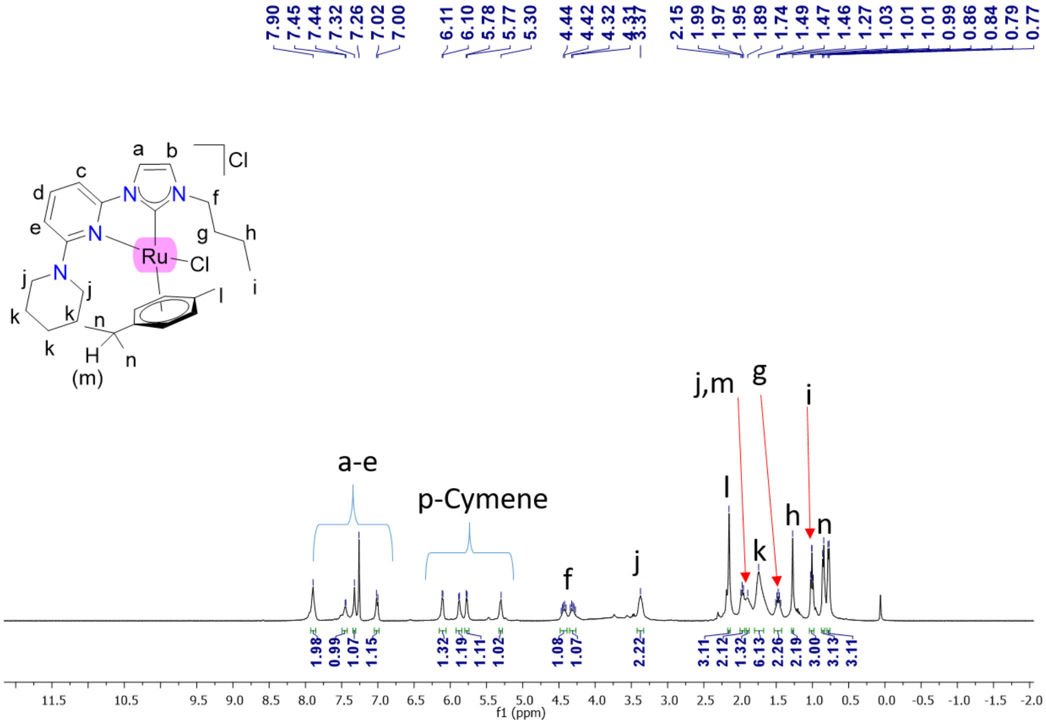


Figure S68. ^{1}H NMR spectrum of complex **3** measured in $CDCl_3$

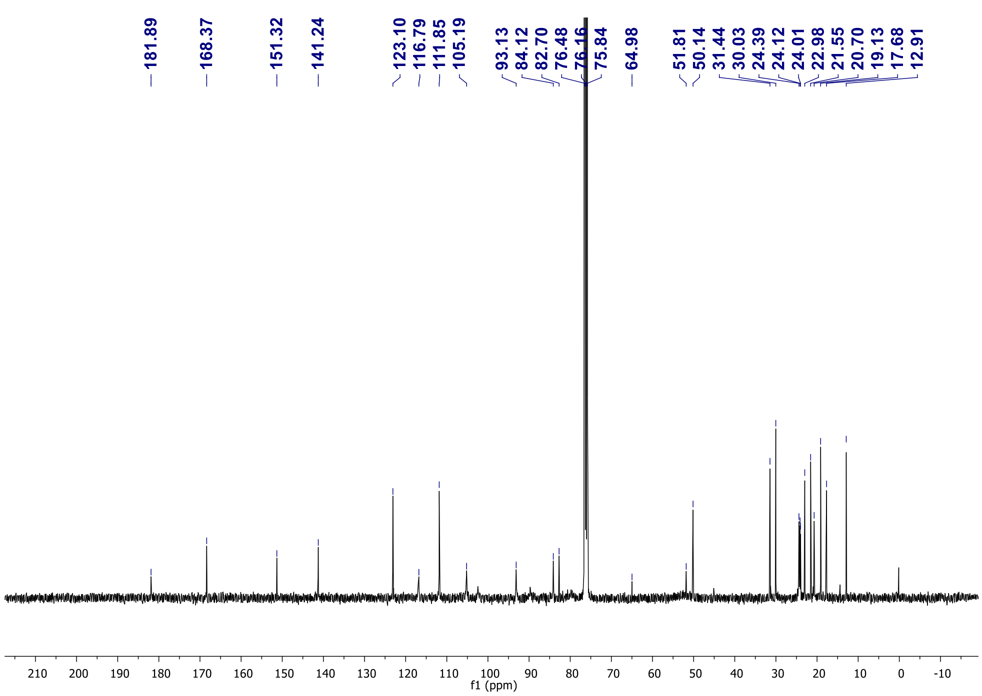


Figure S69. ^{13}C NMR spectrum of complex **3** measured in $CDCl_3$

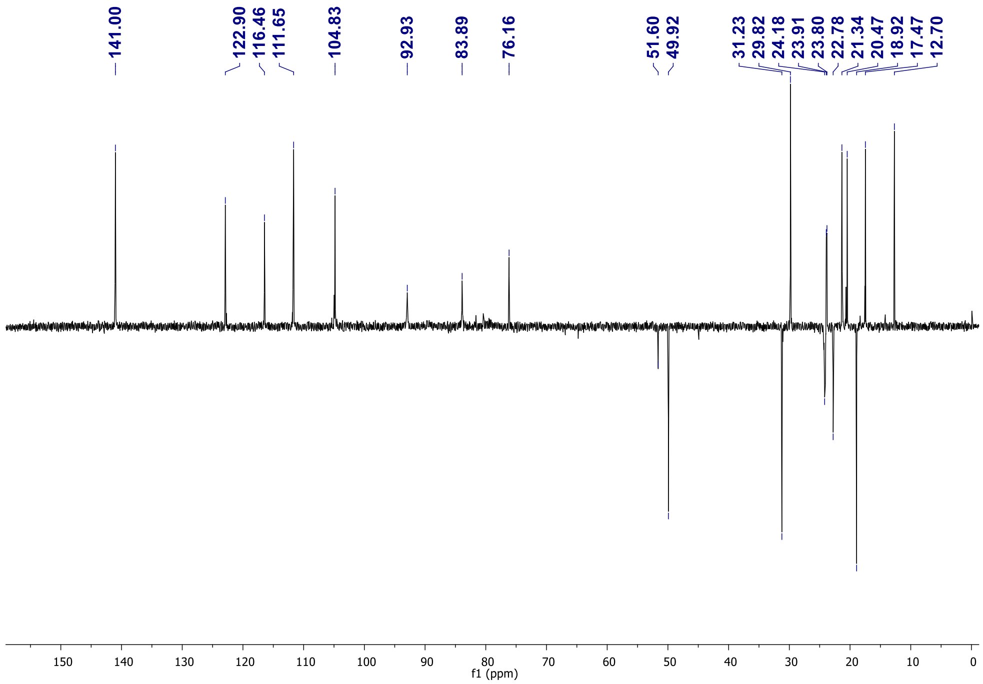


Figure S70. 135 DEPT NMR spectrum of complex **3** measured in $CDCl_3$

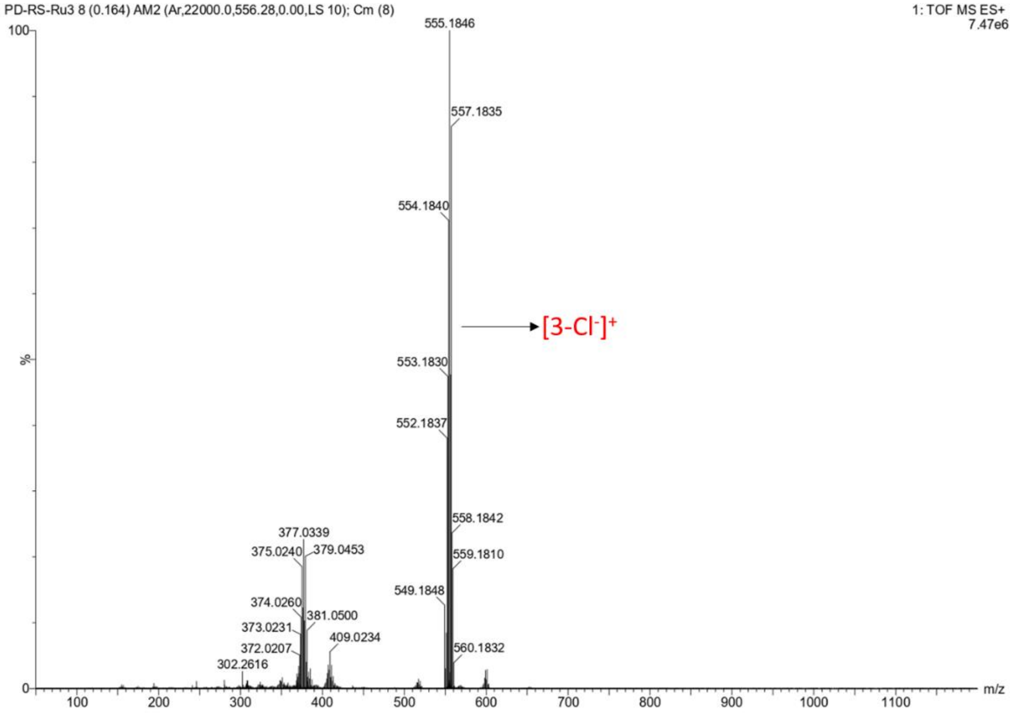


Figure S71. ESI-HRMS of complex **3** in acetonitrile

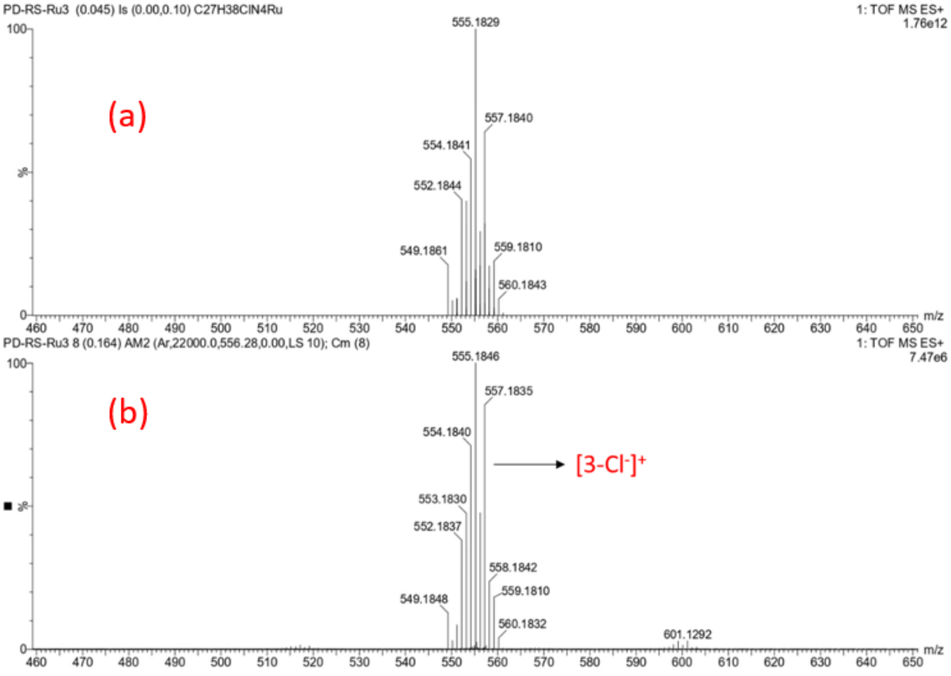


Figure S72. Isotopic mass distribution analysis of complex **3**. Simulated (a) and Experimental (b)

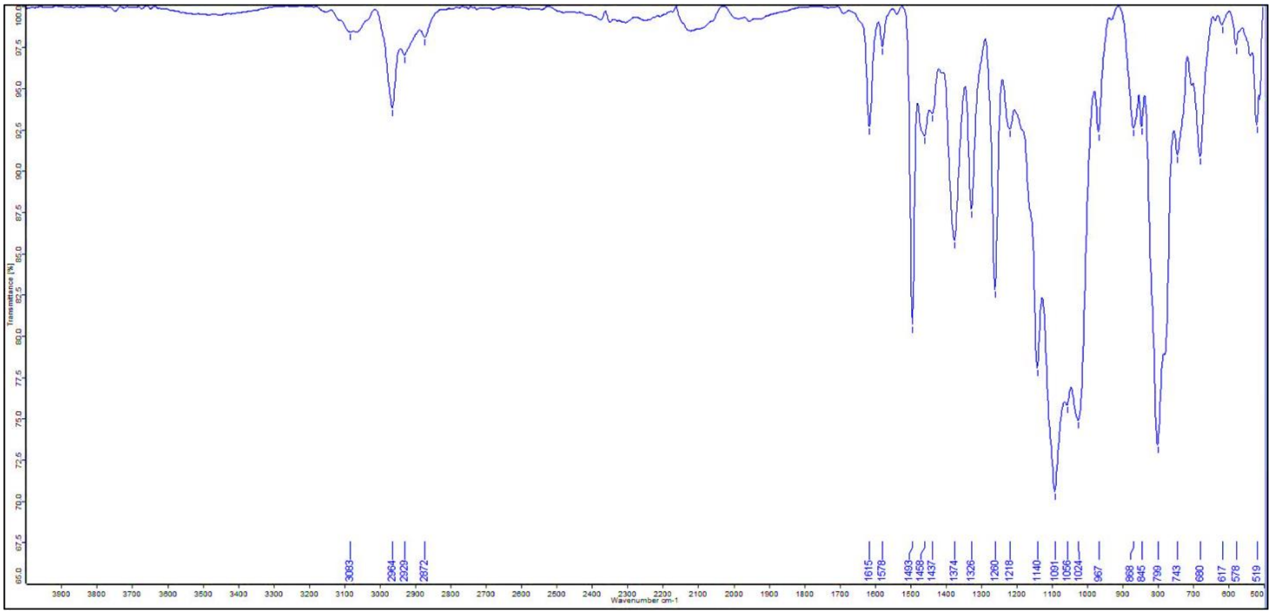


Figure S73. IR spectrum of complex **3**

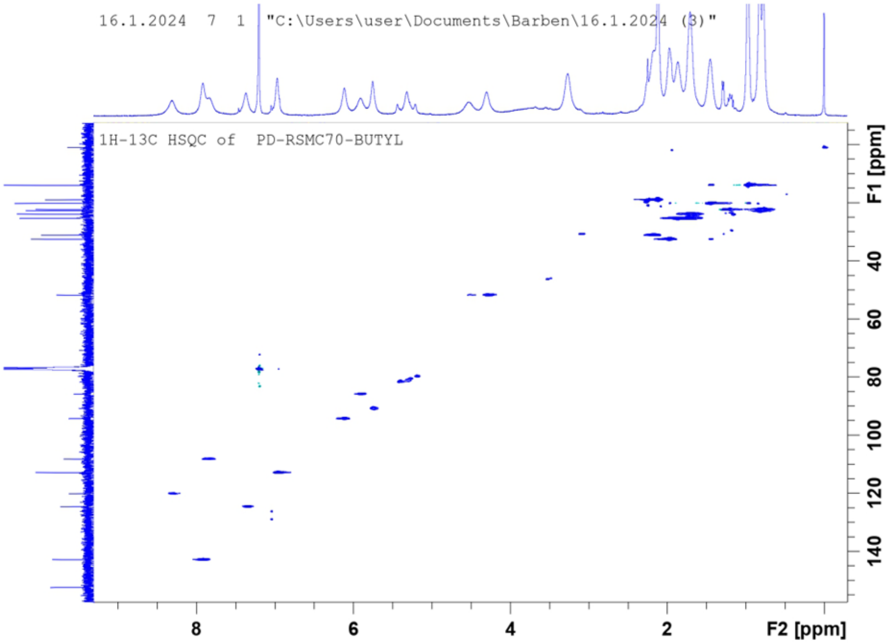


Figure S74. HSQC spectrum of complex **3** in $CDCl_3$

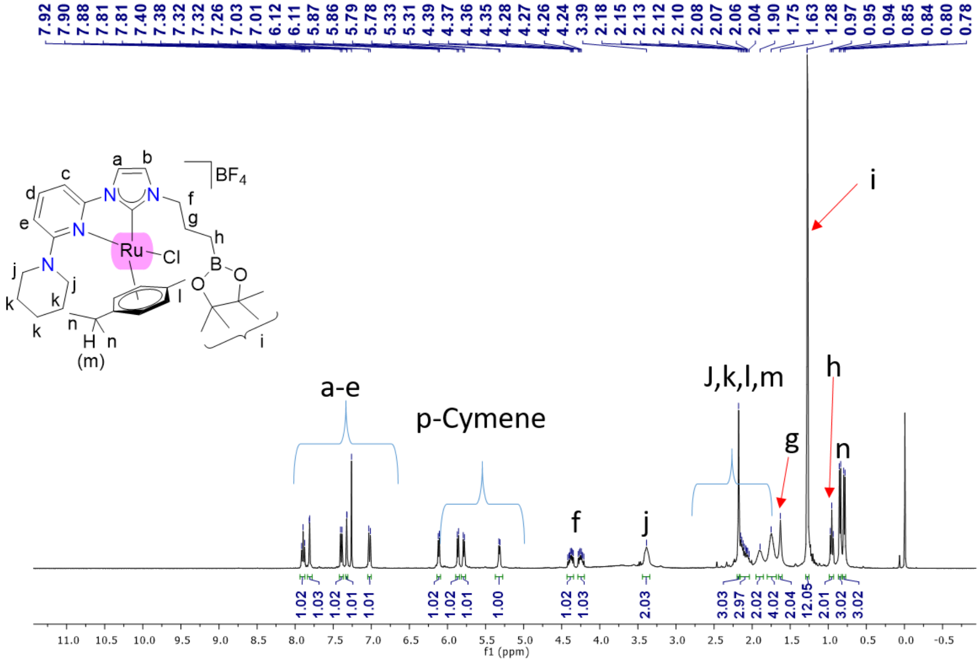


Figure S75. ^{1}H NMR spectrum of complex **1–BF$_4$** measured in CDCl$_3$

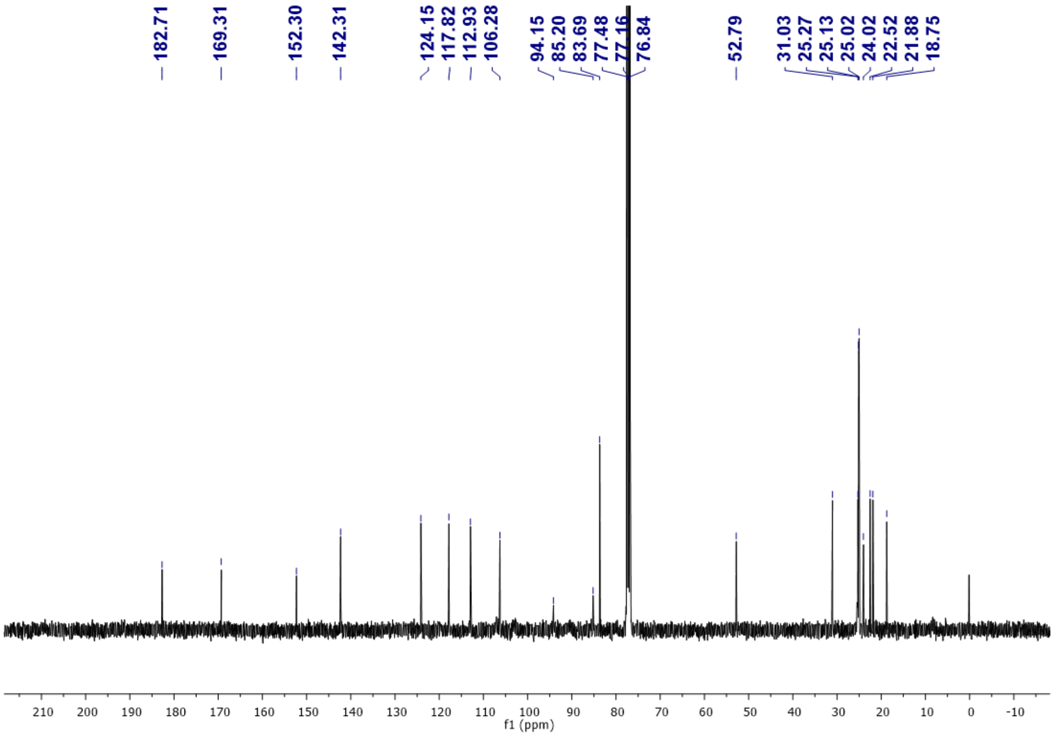


Figure S76. ^{13}C NMR spectrum of complex **1-BF$_4$** measured in CDCl$_3$

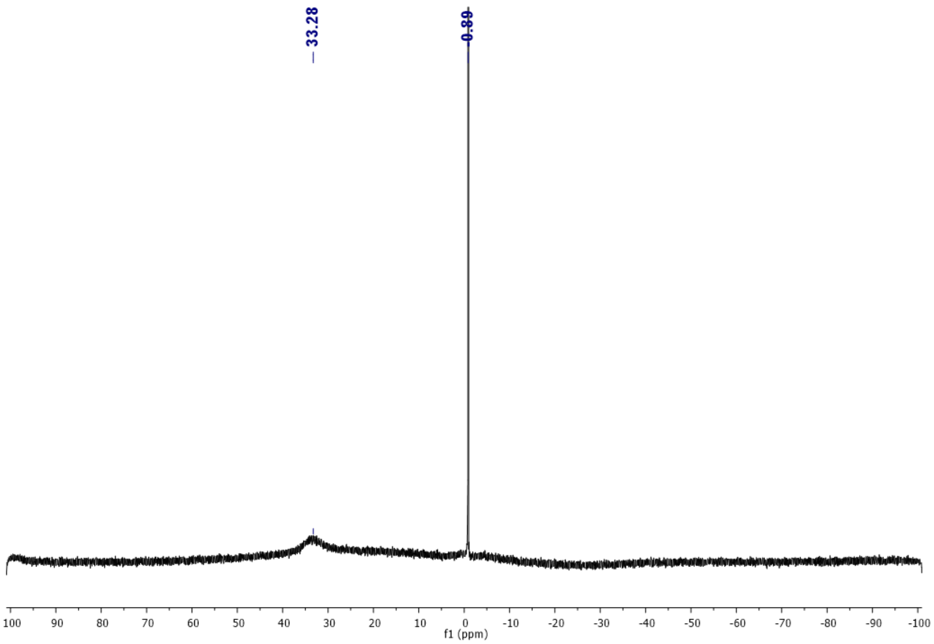


Figure S77. ^{11}B NMR spectrum of complex **1-BF$_4$** measured in CDCl$_3$

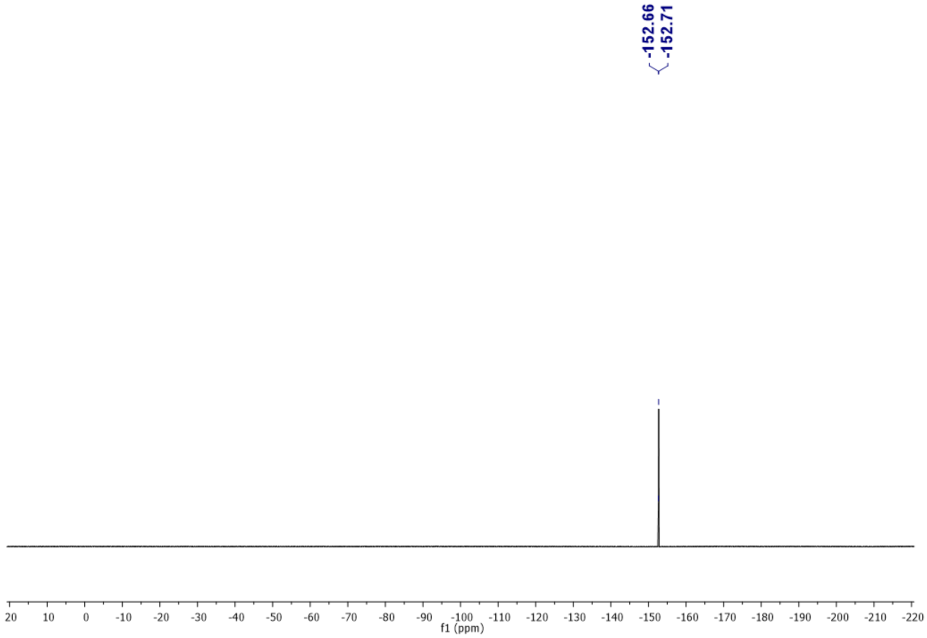


Figure S78. ^{19}F NMR spectrum of complex **1-BF$_4$** in CDCl$_3$

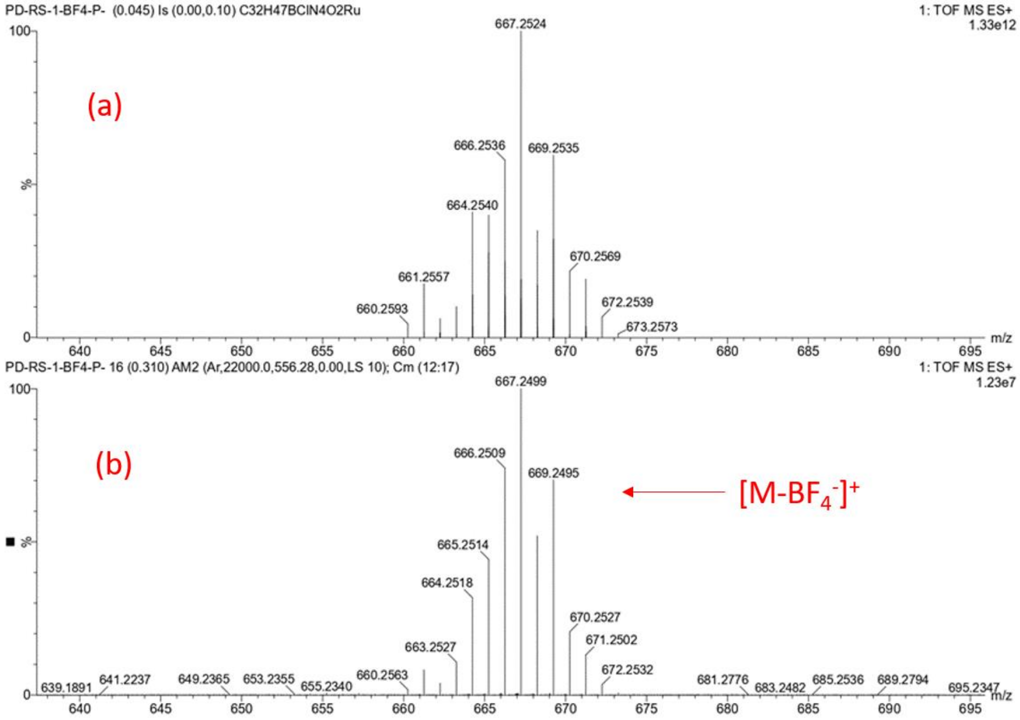


Figure S79. Isotopic mass distribution analysis of complex **1-BF$_4$**. Simulated (a) and Experimental (b) measured in acetonitrile

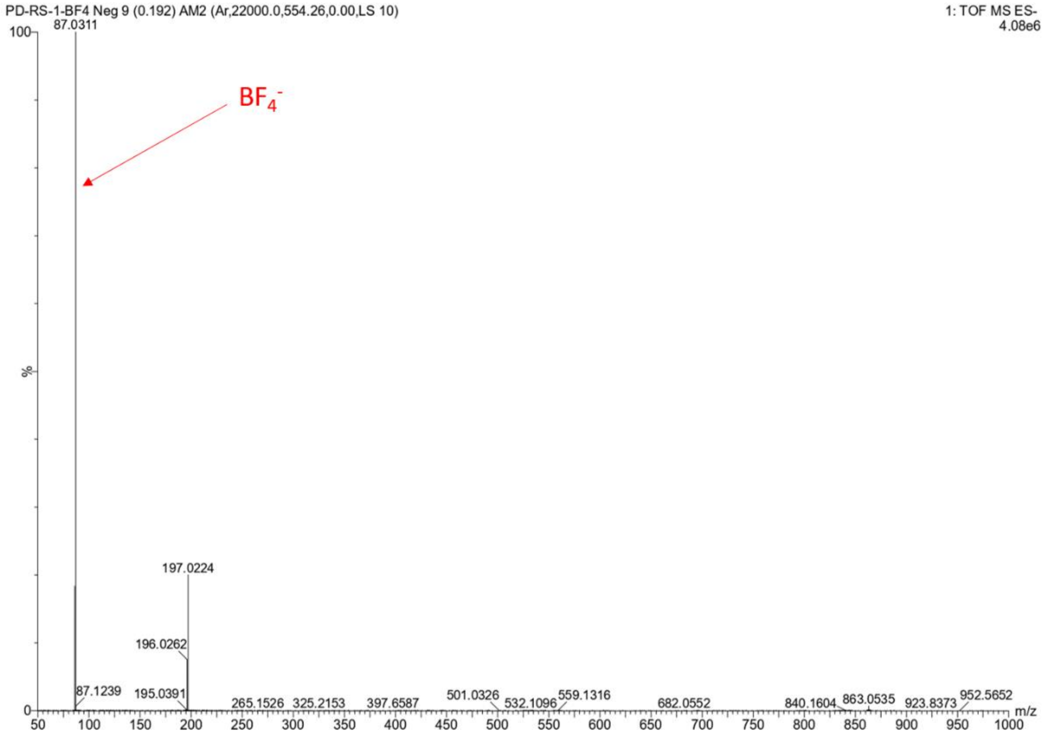
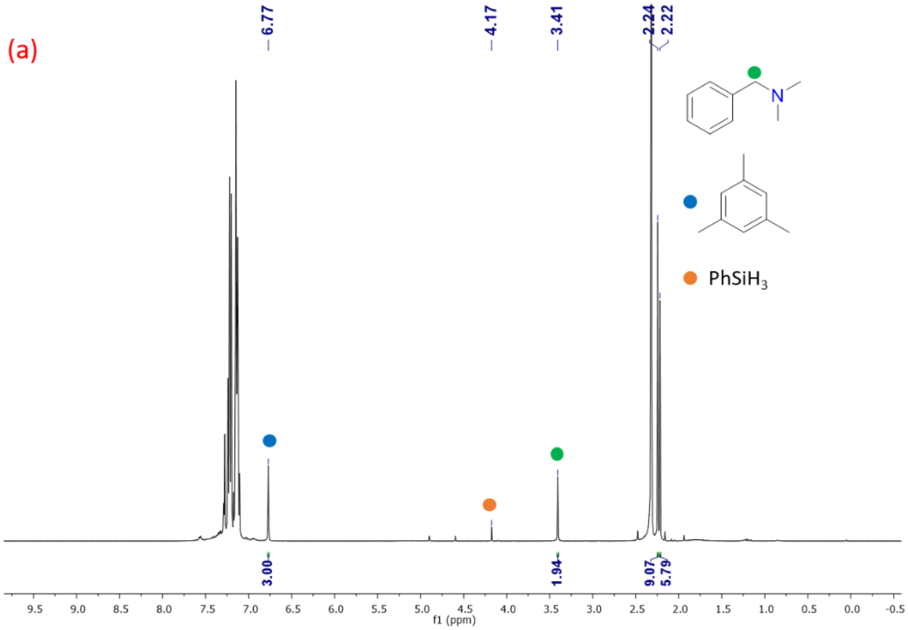
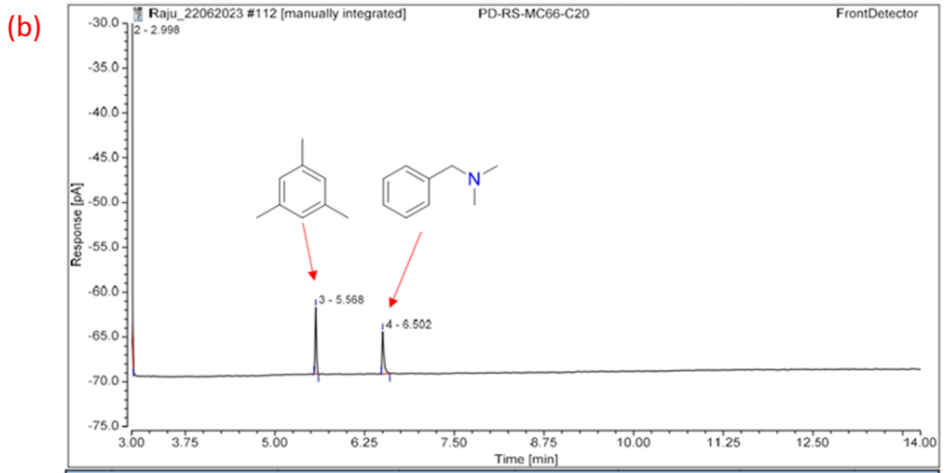


Figure S80. ESI-HRMS mass spectrum for **BF$_4^-$** counter anion measured in acetonitrile



% Conversion of **4a** = 100%, % Yield of **5a** = 97%



Integration Results

No.	Peak Name	Retention Time min	Area pA*min	Height pA	Relative Area %	Relative Height %	Amount n.a.
1		2.047	434.626	18608.233	89.77	98.84	n.a.
2		2.998	49.261	206.526	10.17	1.10	n.a.
3		5.568	0.154	7.432	0.03	0.04	n.a.
4		6.502	0.130	4.713	0.03	0.03	n.a.
Total:			**484.172**	**18826.904**	**100.00**	**100.00**	

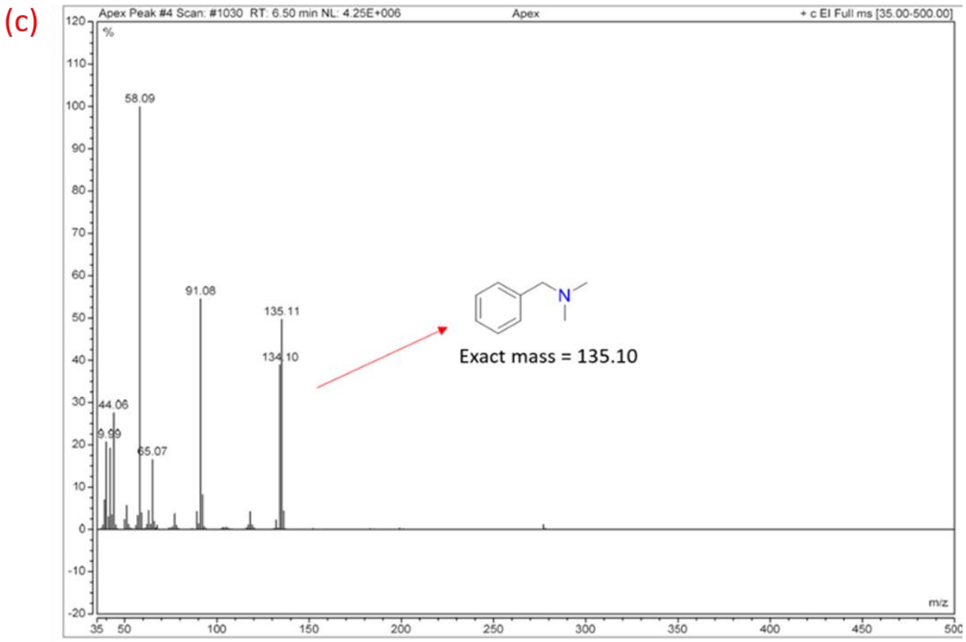
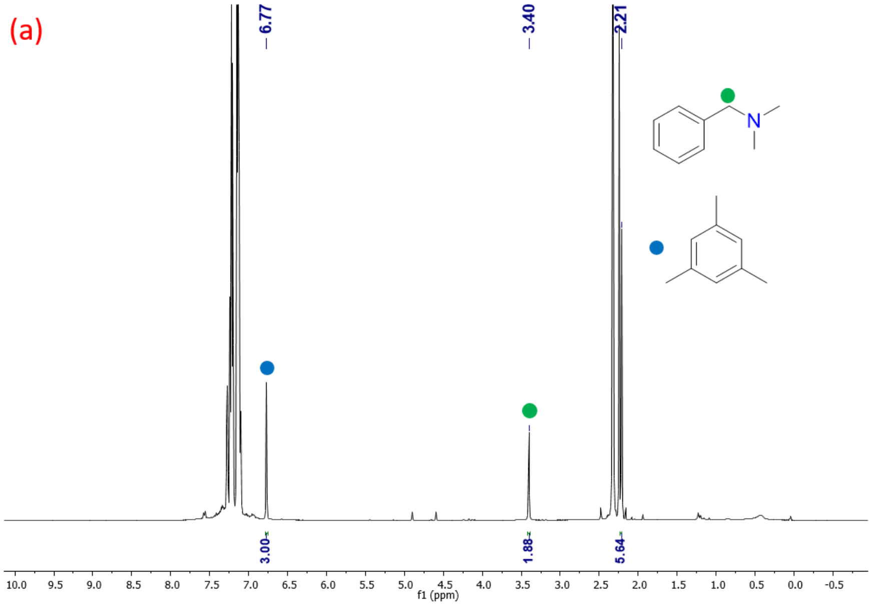
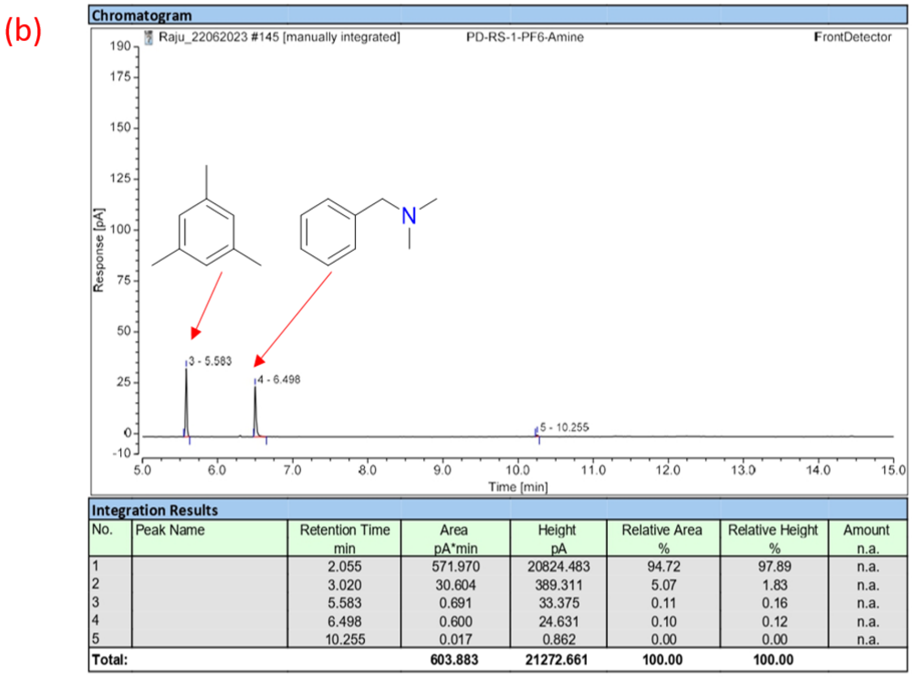


Figure S81. Spectral data for deoxygenative hydrogenation of **4a** to **5a** by **1** (a) ^{1}H NMR in $CDCl_3$ (b) GC-MS spectrum (c) Mass pattern for **5a** (Table S1, entry 9)



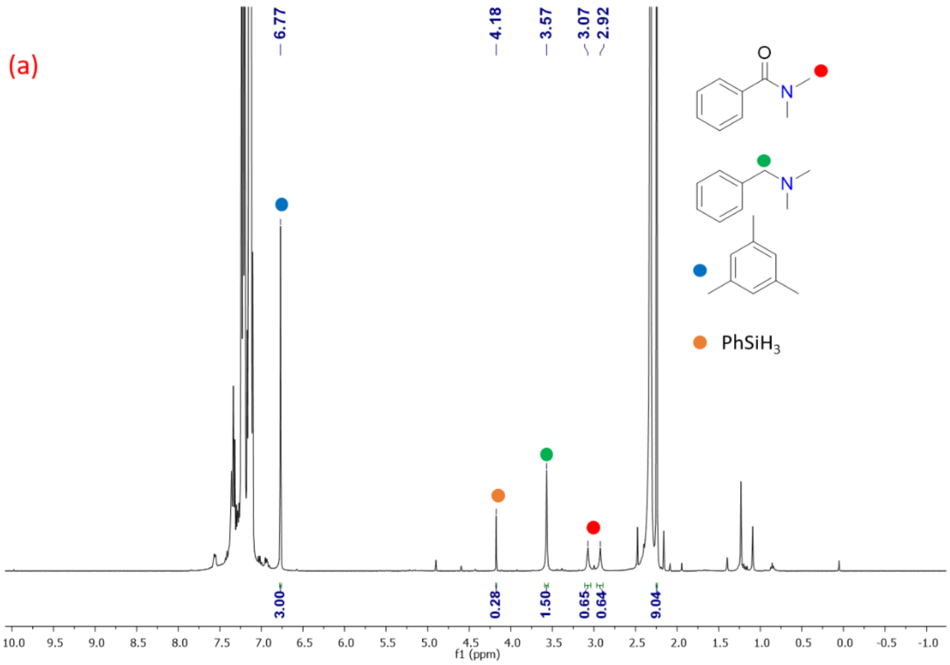
% Conversion of **4a** = 100%, % Yield of **5a** = 94%



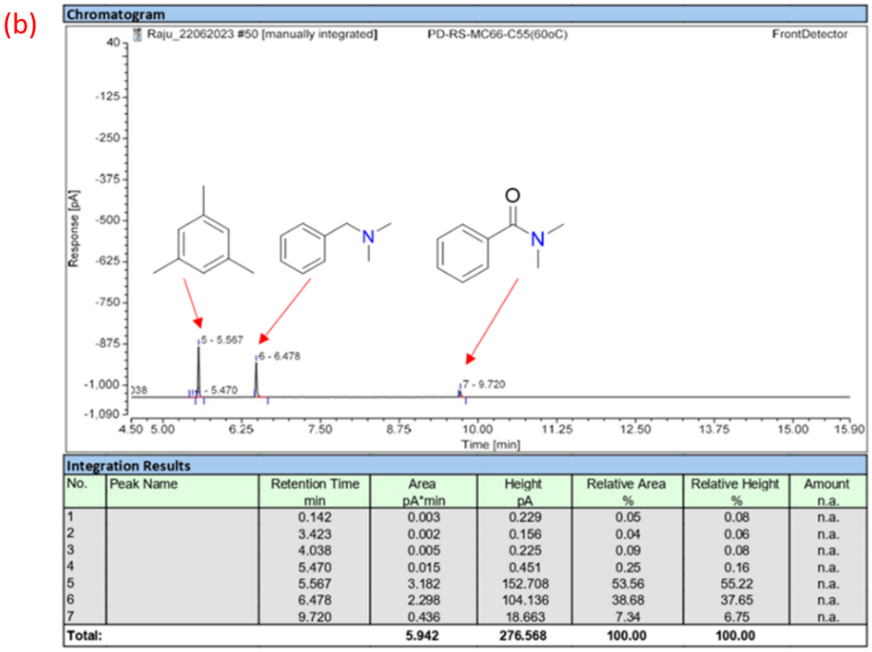
Integration Results

No.	Peak Name	Retention Time min	Area pA*min	Height pA	Relative Area %	Relative Height %	Amount n.a.
1		2.055	571.970	20824.483	94.72	97.89	n.a.
2		3.020	30.604	389.311	5.07	1.83	n.a.
3		5.583	0.691	33.375	0.11	0.16	n.a.
4		6.498	0.600	24.631	0.10	0.12	n.a.
5		10.255	0.017	0.862	0.00	0.00	n.a.
Total:			**603.883**	**21272.661**	**100.00**	**100.00**	

Figure S82. Spectral data for deoxygenative hydrogenation of **4a** to **5a** by **1-PF$_6$** (a) ^{1}H NMR in CDCl$_3$ (b) GC-MS spectrum (Table S1, entry 23)



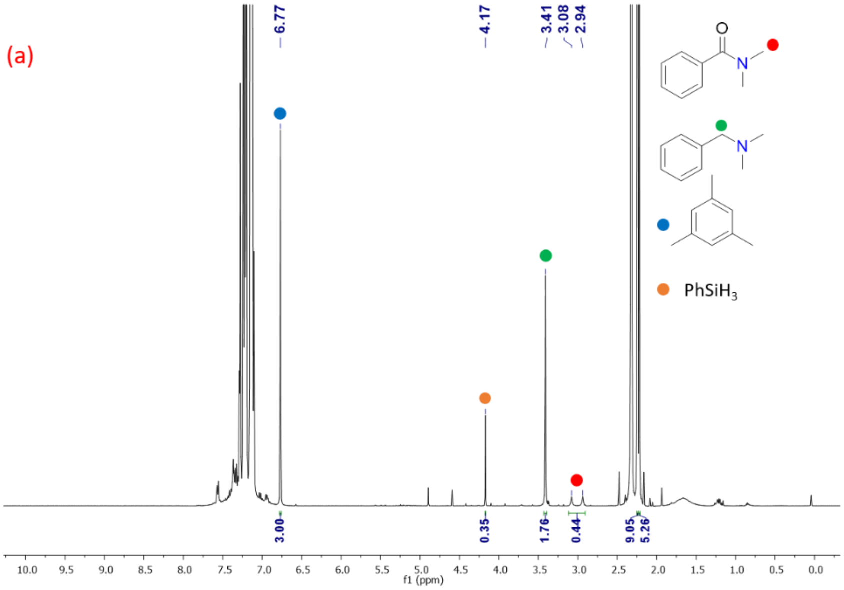
% conversion of **4a** = 78.5 %, % yield of **5a** = 75%



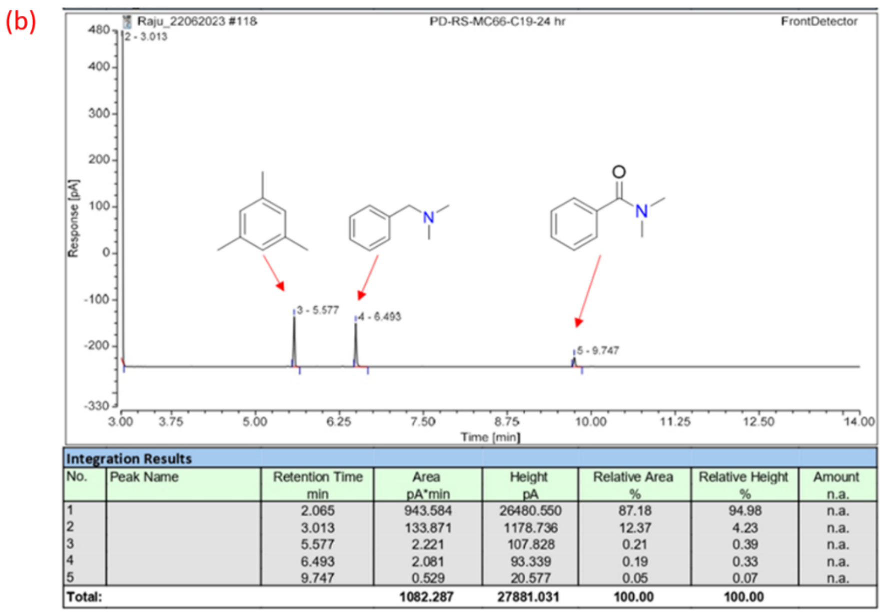
Integration Results

No.	Peak Name	Retention Time min	Area pA*min	Height pA	Relative Area %	Relative Height %	Amount n.a.
1		0.142	0.003	0.229	0.05	0.08	n.a.
2		3.423	0.002	0.156	0.04	0.06	n.a.
3		4.038	0.005	0.225	0.09	0.08	n.a.
4		5.470	0.015	0.451	0.25	0.16	n.a.
5		5.567	3.182	152.708	53.56	55.22	n.a.
6		6.478	2.298	104.136	38.68	37.65	n.a.
7		9.720	0.436	18.663	7.34	6.75	n.a.
Total:			**5.942**	**276.568**	**100.00**	**100.00**	

Figure S83. Spectral data for deoxygenative hydrogenation of **4a** to **5a** by 1 at 60 ºC (a) ^{1}H NMR in CDCl$_3$ (b) GC-MS spectrum (Table S1, entry 11)



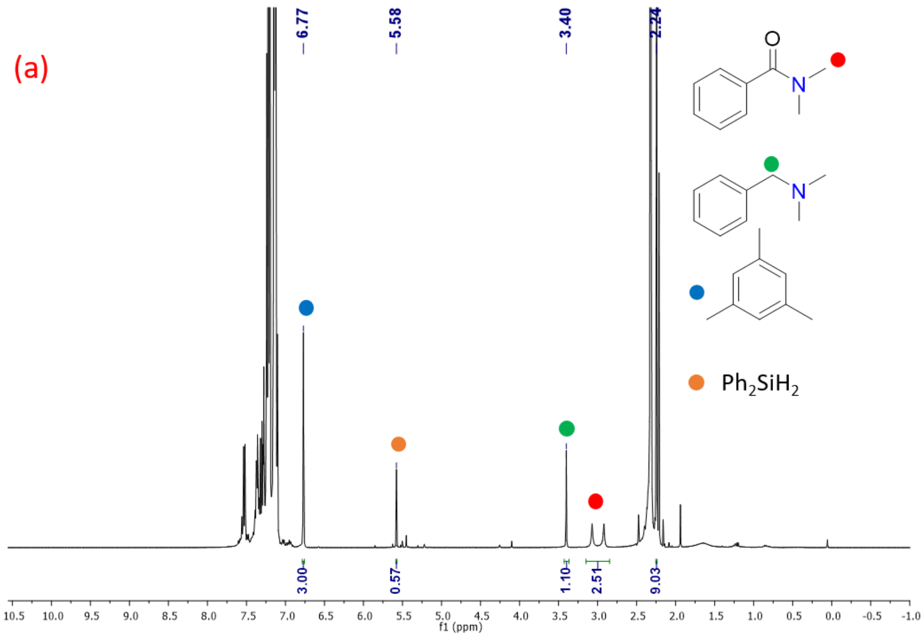
% Conversion of **4a** = 92.6 %, % yield of **5a** = 88%



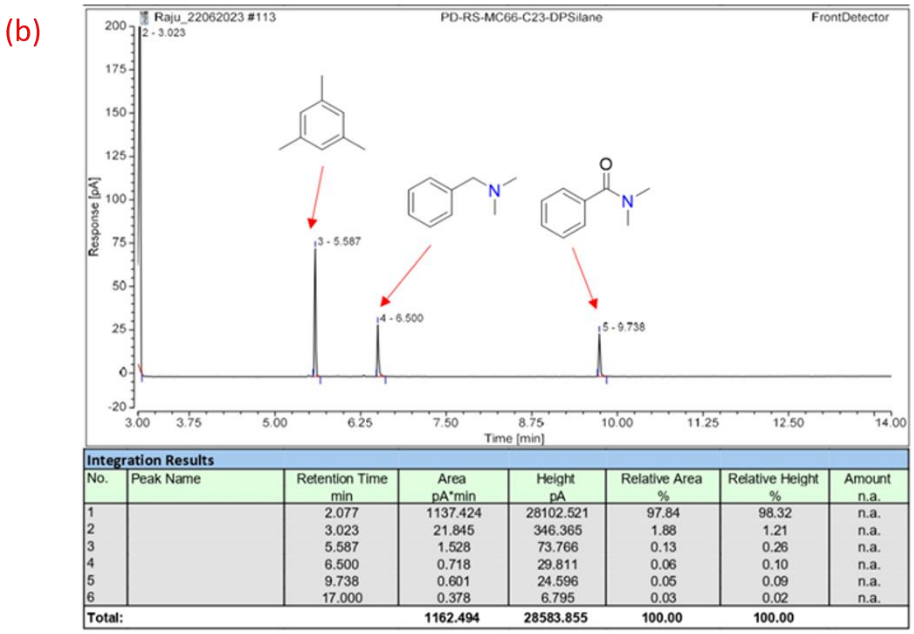
Integration Results

No.	Peak Name	Retention Time min	Area pA*min	Height pA	Relative Area %	Relative Height %	Amount n.a.
1		2.065	943.584	26480.550	87.18	94.98	n.a.
2		3.013	133.871	1178.736	12.37	4.23	n.a.
3		5.577	2.221	107.828	0.21	0.39	n.a.
4		6.493	2.081	93.339	0.19	0.33	n.a.
5		9.747	0.529	20.577	0.05	0.07	n.a.
Total:			**1082.287**	**27881.031**	**100.00**	**100.00**	

Figure S84. Spectral data for deoxygenative hydrogenation of **4a** to **5a** by **1** for 24 hours (a) ^{1}H NMR in $CDCl_3$ (b) GC-MS spectrum (Table S1, entry 10)



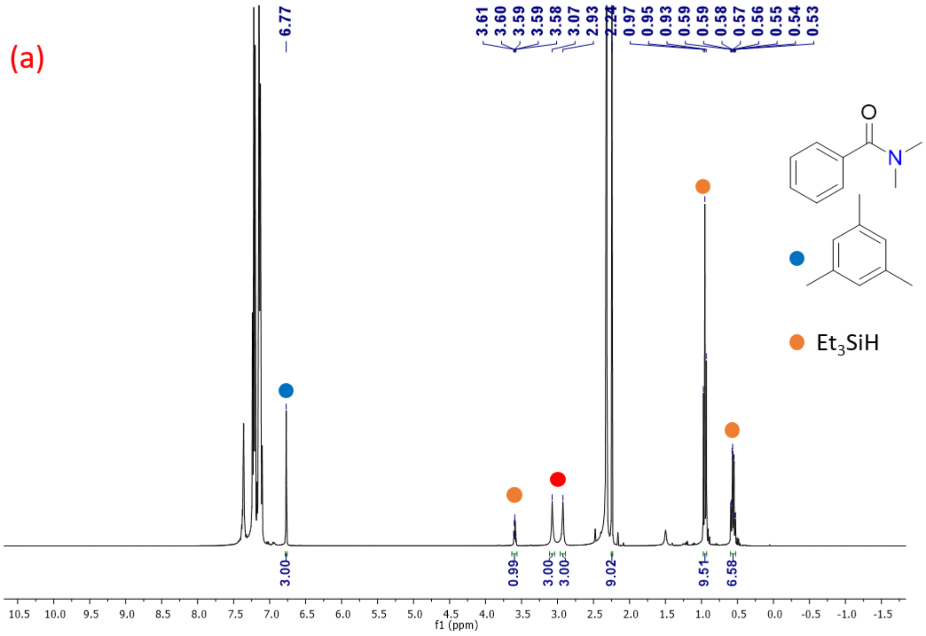
% Conversion of **4a** = 58%, % yield of **5a** = 55%



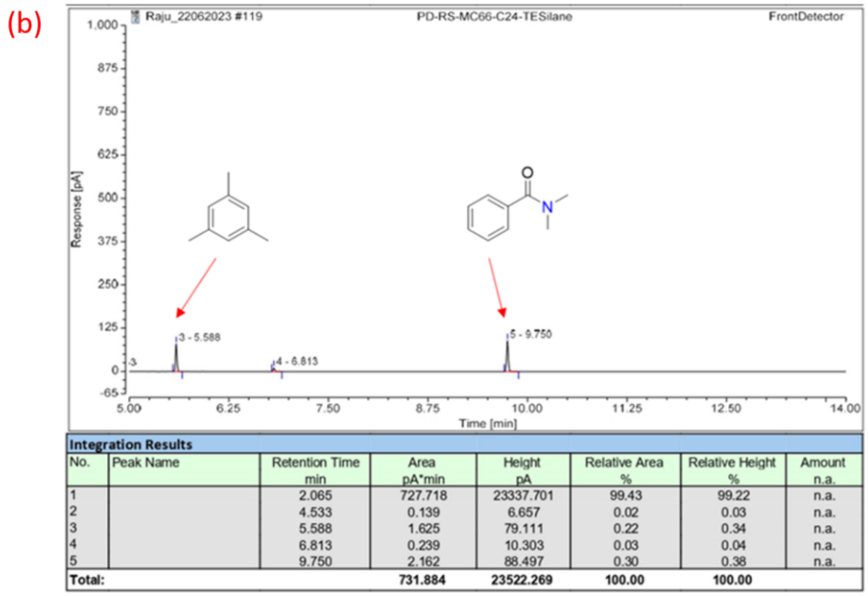
Integration Results

No.	Peak Name	Retention Time min	Area pA*min	Height pA	Relative Area %	Relative Height %	Amount n.a.
1		2.077	1137.424	28102.521	97.84	98.32	n.a.
2		3.023	21.845	346.365	1.88	1.21	n.a.
3		5.587	1.528	73.766	0.13	0.26	n.a.
4		6.500	0.718	29.811	0.06	0.10	n.a.
5		9.738	0.601	24.596	0.05	0.09	n.a.
6		17.000	0.378	6.795	0.03	0.02	n.a.
Total:			**1162.494**	**28583.855**	**100.00**	**100.00**	

Figure S85. Spectral data for deoxygenative hydrogenation of **4a** to **5a** by **1** using diphenylsilane (a) ^{1}H NMR in $CDCl_3$ (b) GC-MS spectrum (Table S1, entry 12)



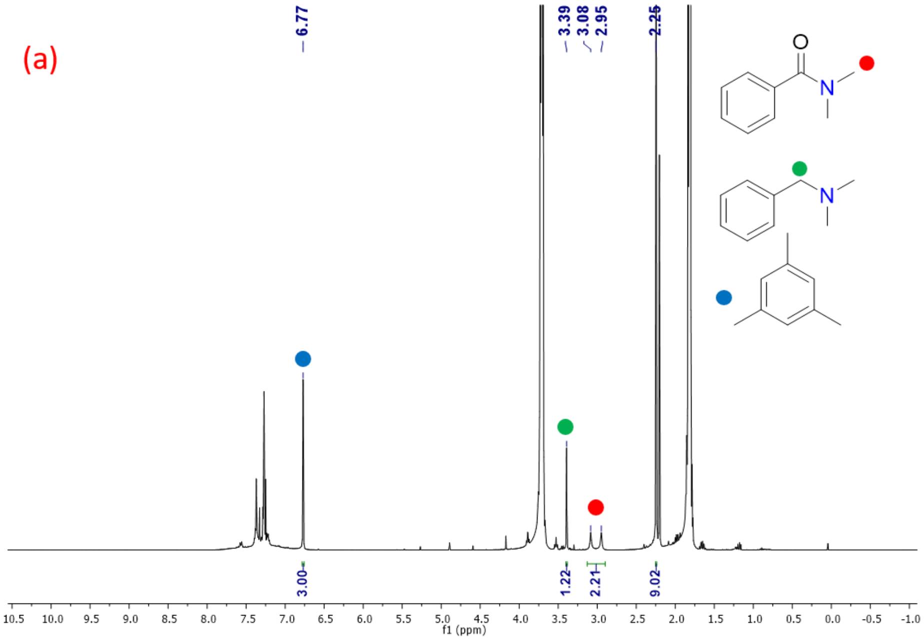
% Conversion of **4a** = 0%



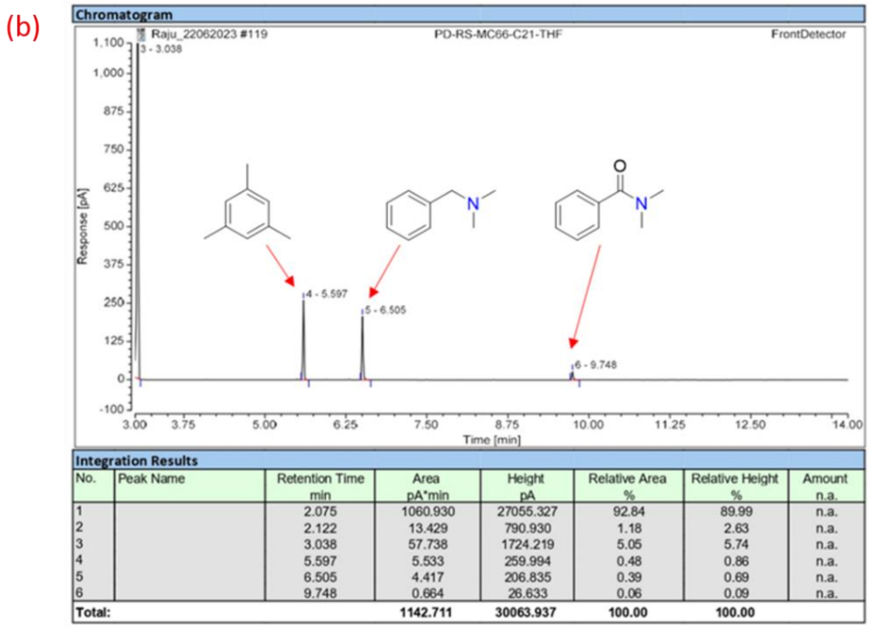
Integration Results

No.	Peak Name	Retention Time min	Area pA*min	Height pA	Relative Area %	Relative Height %	Amount n.a.
1		2.065	727.718	23337.701	99.43	99.22	n.a.
2		4.533	0.139	6.657	0.02	0.03	n.a.
3		5.588	1.625	79.111	0.22	0.34	n.a.
4		6.813	0.239	10.303	0.03	0.04	n.a.
5		9.750	2.162	88.497	0.30	0.38	n.a.
Total:			731.884	23522.269	100.00	100.00	

Figure S86. Spectral data for deoxygenative hydrogenation of **4a** to **5a** by **1** using triethylsilane (a) ^{1}H NMR in CDCl$_3$ (b) GC-MS spectrum (Table S1, entry 13)



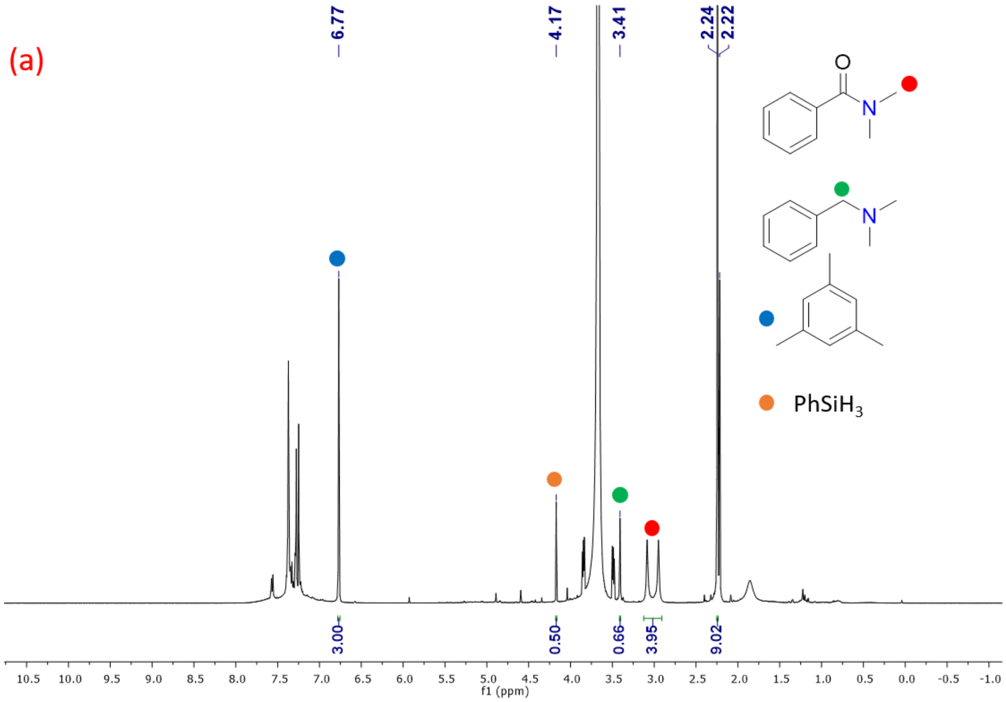
% Conversion of **4a** = 63%, % yield of **5a** = 61%



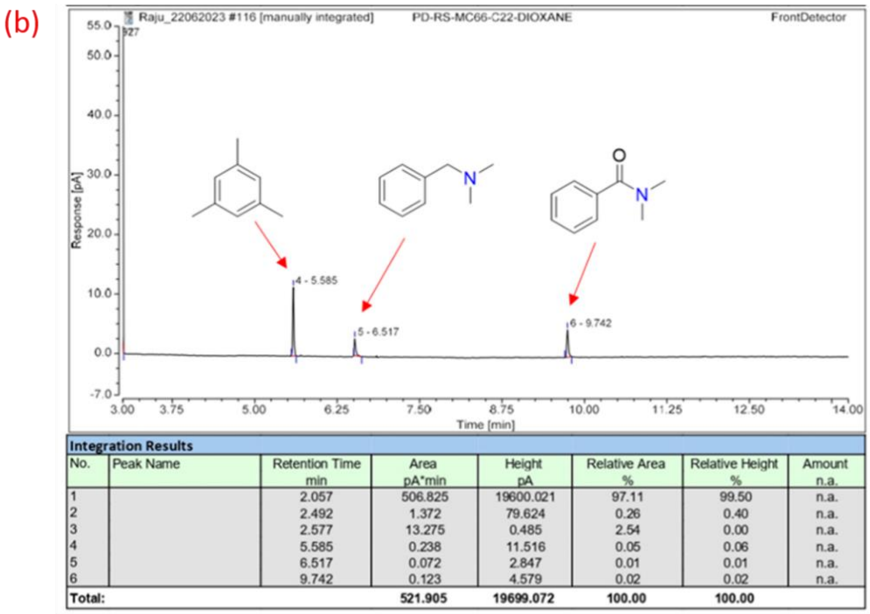
Integration Results

No.	Peak Name	Retention Time min	Area pA*min	Height pA	Relative Area %	Relative Height %	Amount n.a.
1		2.075	1060.930	27055.327	92.84	89.99	n.a.
2		2.122	13.429	790.930	1.18	2.63	n.a.
3		3.038	57.738	1724.219	5.05	5.74	n.a.
4		5.597	5.533	259.994	0.48	0.86	n.a.
5		6.505	4.417	206.835	0.39	0.69	n.a.
6		9.748	0.664	26.633	0.06	0.09	n.a.
Total:			**1142.711**	**30063.937**	**100.00**	**100.00**	

Figure S87. Spectral data for deoxygenative hydrogenation of **4a** to **5a** by **1** using THF as the solvent (a) ^{1}H NMR in CDCl$_3$ (b) GC-MS spectrum (Table S1, entry 15)

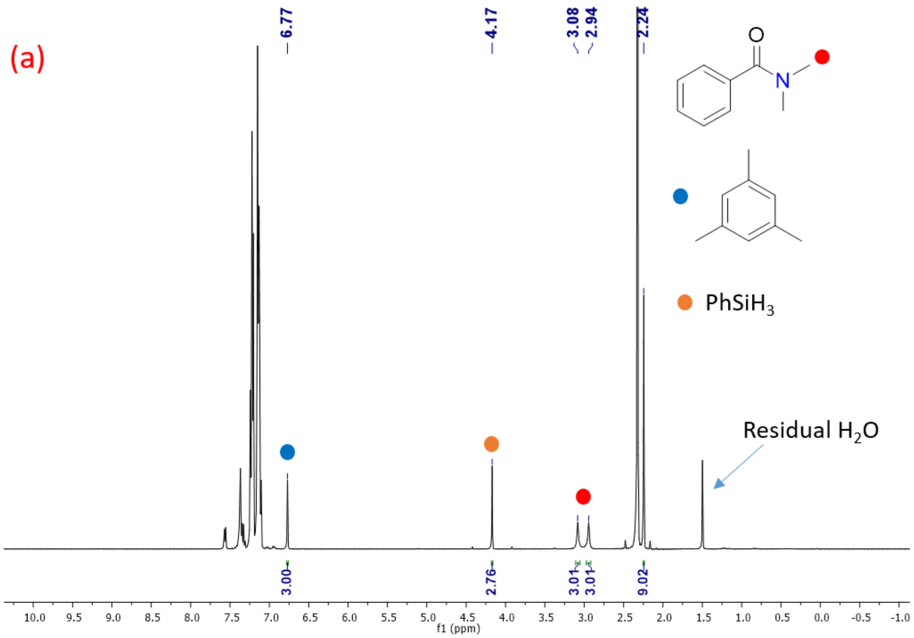


% Conversion of **4a** = 39.9%, % yield of **5a** = 33%

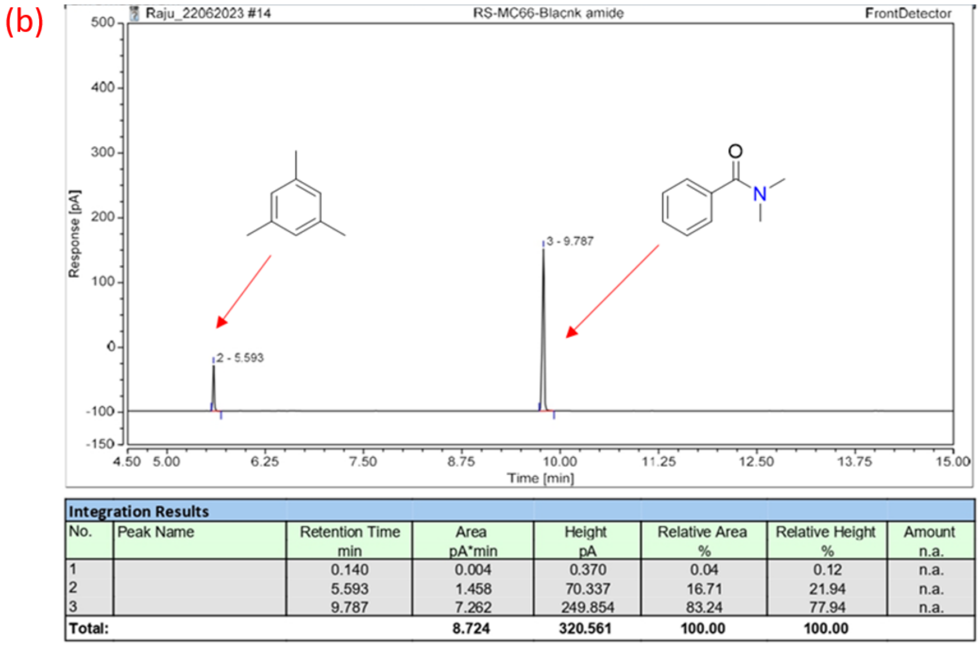


Integration Results							
No.	Peak Name	Retention Time min	Area pA*min	Height pA	Relative Area %	Relative Height %	Amount n.a.
1		2.057	506.825	19600.021	97.11	99.50	n.a.
2		2.492	1.372	79.624	0.26	0.40	n.a.
3		2.577	13.275	0.485	2.54	0.00	n.a.
4		5.585	0.238	11.516	0.05	0.06	n.a.
5		6.517	0.072	2.847	0.01	0.01	n.a.
6		9.742	0.123	4.579	0.02	0.02	n.a.
Total:			**521.905**	**19699.072**	**100.00**	**100.00**	

Figure S88. Spectral data for deoxygenative hydrogenation of **4a** to **5a** by **1** using 1,4-dioxane as the solvent (a) ^{1}H NMR in $CDCl_3$ (b) GC-MS spectrum (Table S1, entry 16)



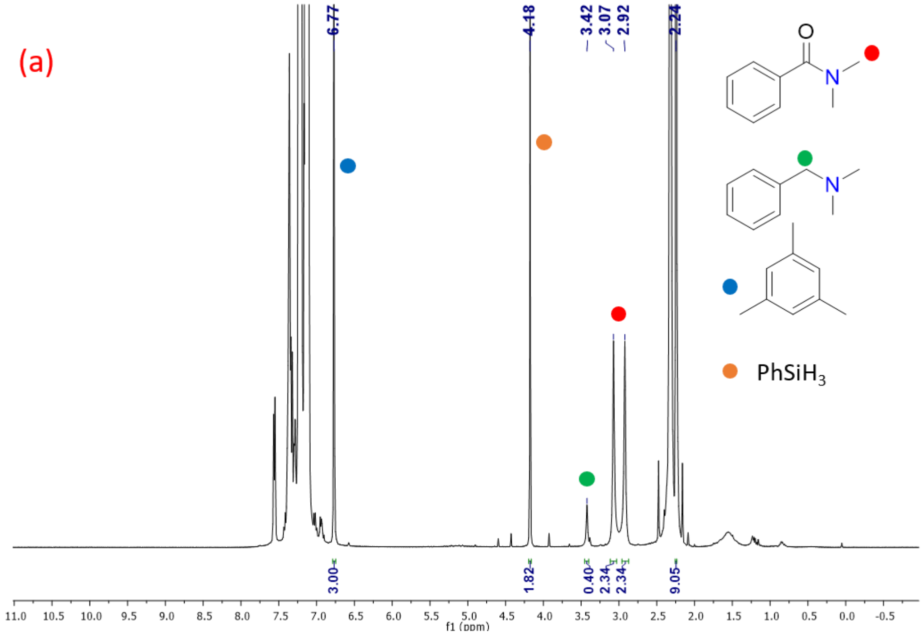
% yield of **5a** = 0

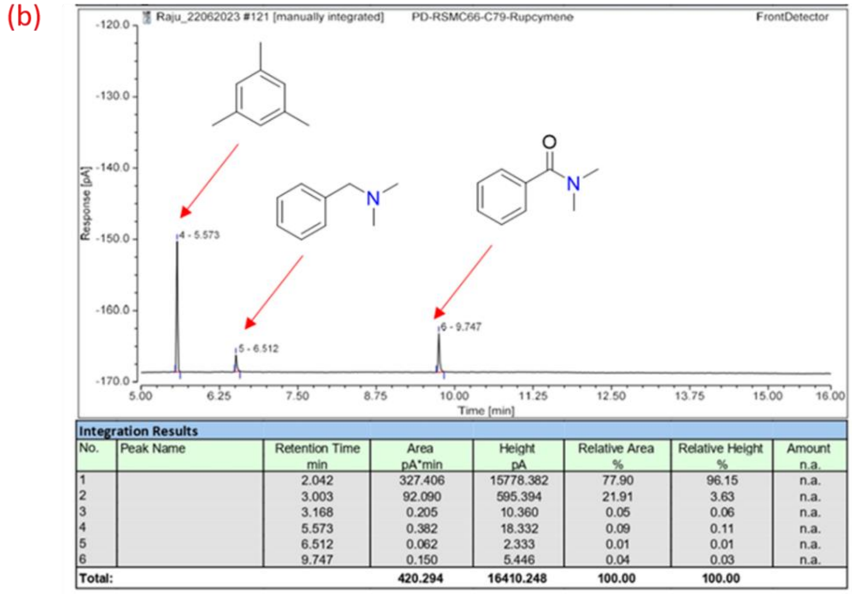


Integration Results

No.	Peak Name	Retention Time min	Area pA*min	Height pA	Relative Area %	Relative Height %	Amount n.a.
1		0.140	0.004	0.370	0.04	0.12	n.a.
2		5.593	1.458	70.337	16.71	21.94	n.a.
3		9.787	7.262	249.854	83.24	77.94	n.a.
Total:			8.724	320.561	100.00	100.00	

Figure S89. Spectral data for deoxygenative hydrogenation of **4a** to **5a** in absence of catalyst (a) ^{1}H NMR in CDCl$_3$ (b) GC-MS spectrum (Table S1, entry 18)

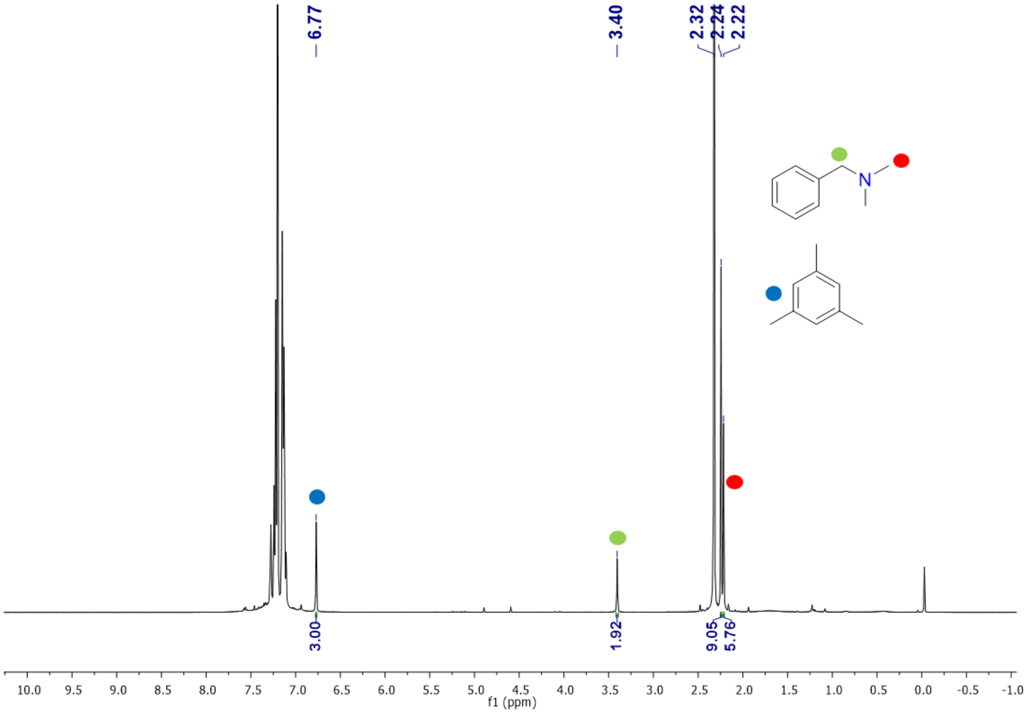




Integration Results

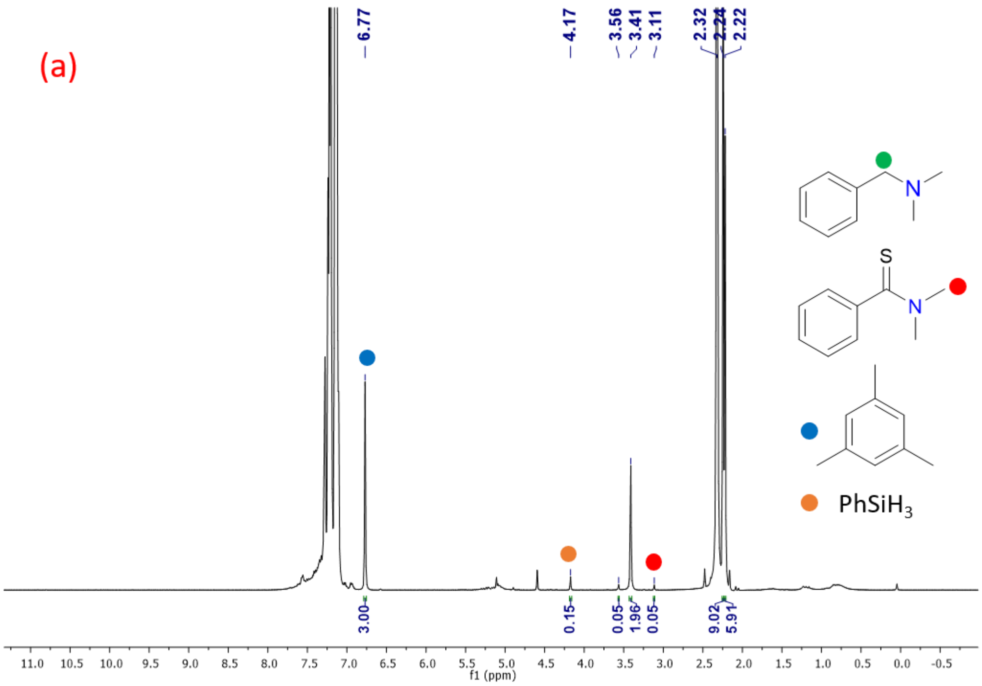
No.	Peak Name	Retention Time min	Area pA*min	Height pA	Relative Area %	Relative Height %	Amount n.a.
1		2.042	327.406	15778.382	77.90	96.15	n.a.
2		3.003	92.090	595.394	21.91	3.63	n.a.
3		3.168	0.205	10.360	0.05	0.06	n.a.
4		5.573	0.382	18.332	0.09	0.11	n.a.
5		6.512	0.062	2.333	0.01	0.01	n.a.
6		9.747	0.150	5.446	0.04	0.03	n.a.
Total:			**420.294**	**16410.248**	**100.00**	**100.00**	

Figure S90. Spectral data for deoxygenative hydrogenation of **4a** to **5a** (a) ^{1}H NMR in CDCl$_3$ (b) GC-MS spectrum (Table S1, entry 19)

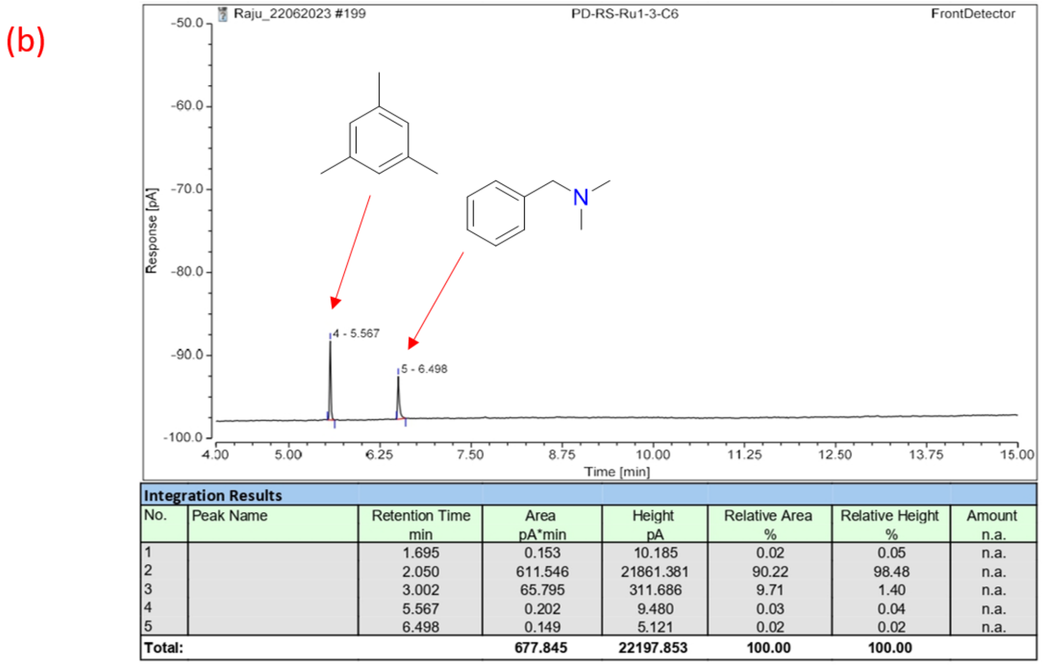


% amine **5a** formation = 96%

Figure S91. ^{1}H NMR Spectral data for deoxygenative hydrogenation of **4a** to **5a** using complex **1-BF$_4$** in CDCl$_3$ (Table S1, entry 24)



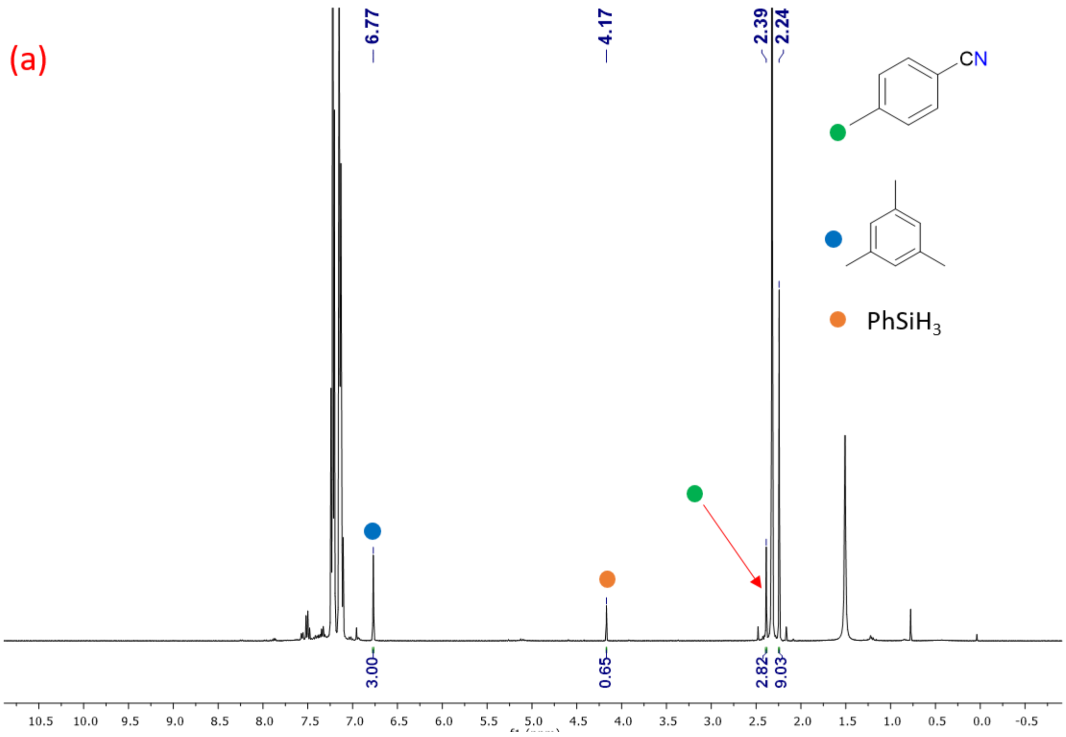
% Conversion of **6a** = 98.33%, % yield of **5a** = 98%



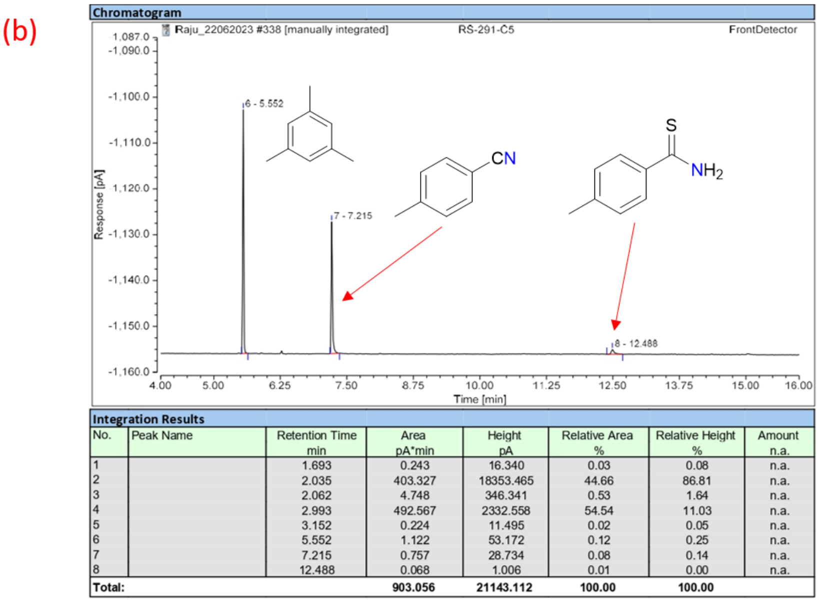
Integration Results

No.	Peak Name	Retention Time min	Area pA*min	Height pA	Relative Area %	Relative Height %	Amount n.a.
1		1.695	0.153	10.185	0.02	0.05	n.a.
2		2.050	611.546	21861.381	90.22	98.48	n.a.
3		3.002	65.795	311.686	9.71	1.40	n.a.
4		5.567	0.202	9.480	0.03	0.04	n.a.
5		6.498	0.149	5.121	0.02	0.02	n.a.
Total:			**677.845**	**22197.853**	**100.00**	**100.00**	

Figure S92. Spectral data for deoxygenative hydrogenation of **6a** to **5a** (a) ^{1}H NMR in CDCl$_3$ (b) GC-MS spectrum (Table S2, entry 5)

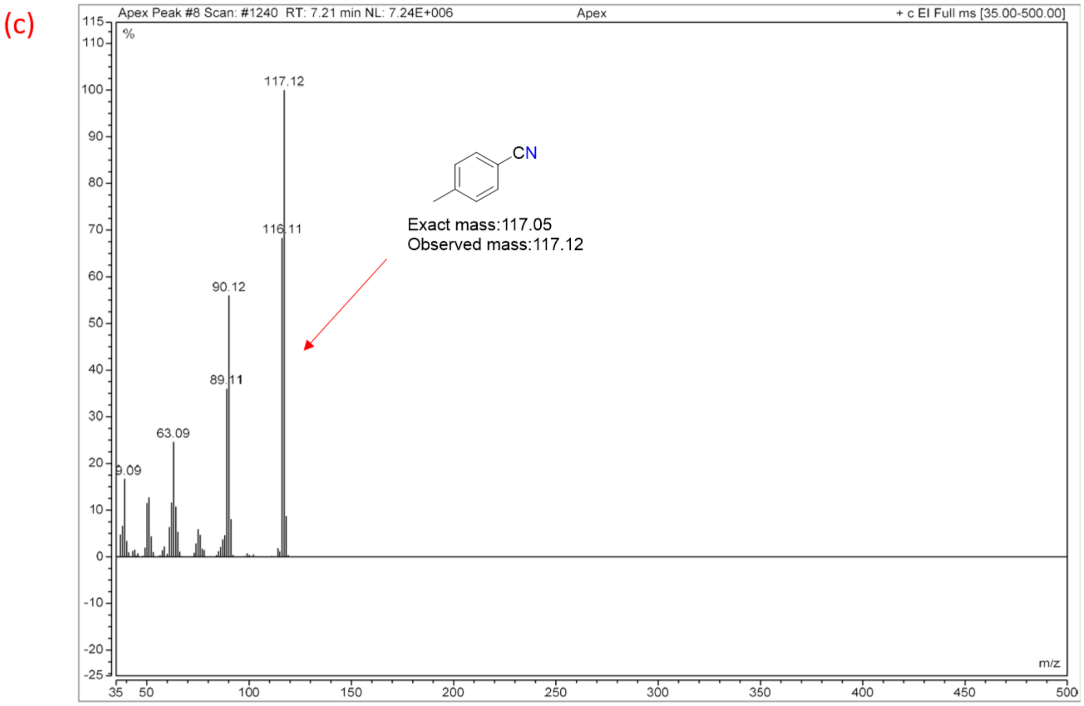


% yield of **9a** = 94%



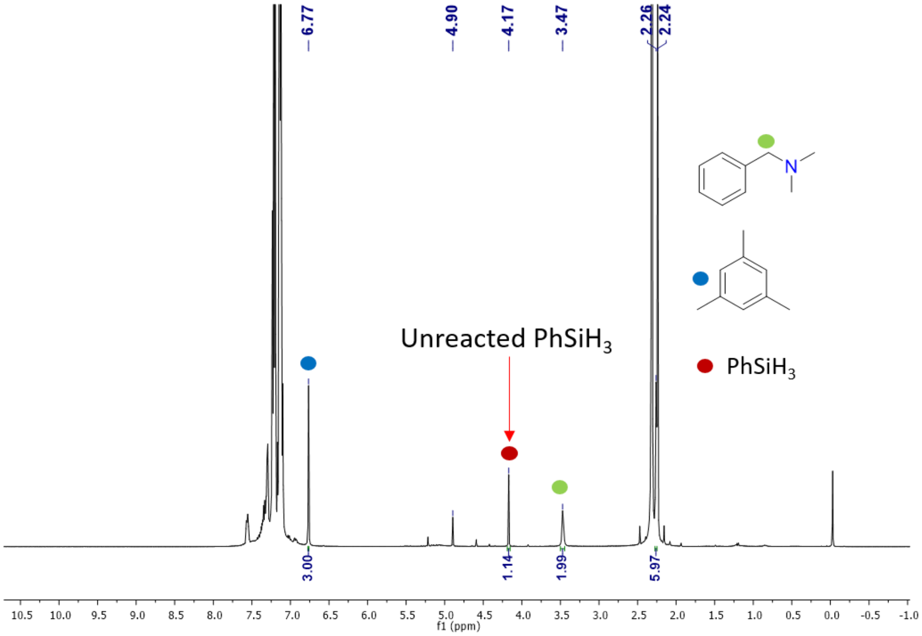
Integration Results

No.	Peak Name	Retention Time min	Area pA*min	Height pA	Relative Area %	Relative Height %	Amount n.a.
1		1.693	0.243	16.340	0.03	0.08	n.a.
2		2.035	403.327	18353.465	44.66	86.81	n.a.
3		2.062	4.748	346.341	0.53	1.64	n.a.
4		2.993	492.567	2332.558	54.54	11.03	n.a.
5		3.152	0.224	11.495	0.02	0.05	n.a.
6		5.552	1.122	53.172	0.12	0.25	n.a.
7		7.215	0.757	28.734	0.08	0.14	n.a.
8		12.488	0.068	1.006	0.01	0.00	n.a.
Total:			**903.056**	**21143.112**	**100.00**	**100.00**	



Exact mass:117.05
Observed mass:117.12

Figure S93. Spectral data for dehydrosulfurization of **8a** to **9a** by **1** (a) ^{1}H NMR in CDCl$_3$ (b) GC-MS spectrum (c) Mass pattern for **9a** (Table S3, entry 2)



Unreacted PhSiH$_3$

● PhSiH$_3$

Figure S94. ^{1}H NMR data measured in CDCl$_3$ for deoxygenative hydrogenation of **4a** to **5a** with 2 equiv. of PhSiH$_3$ at 80 ºC for 6 h catalyzed by complex **1**

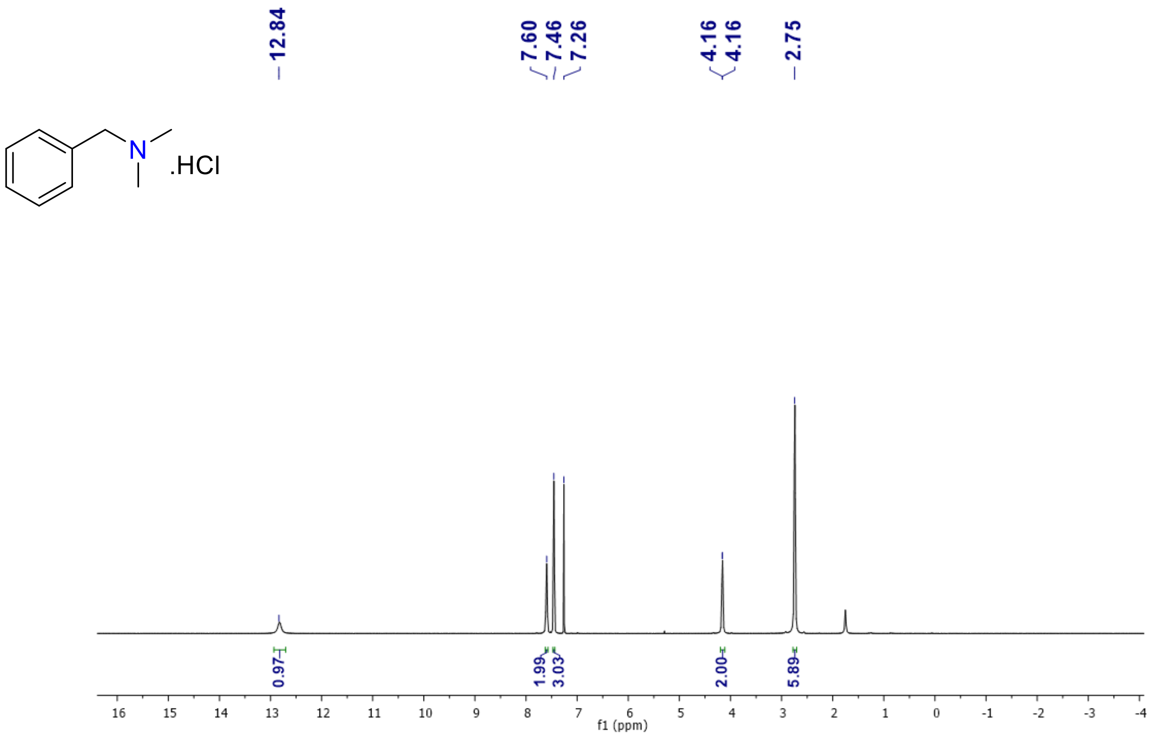


Figure S95. ^{1}H NMR spectrum of **5a** measured in $CDCl_3$

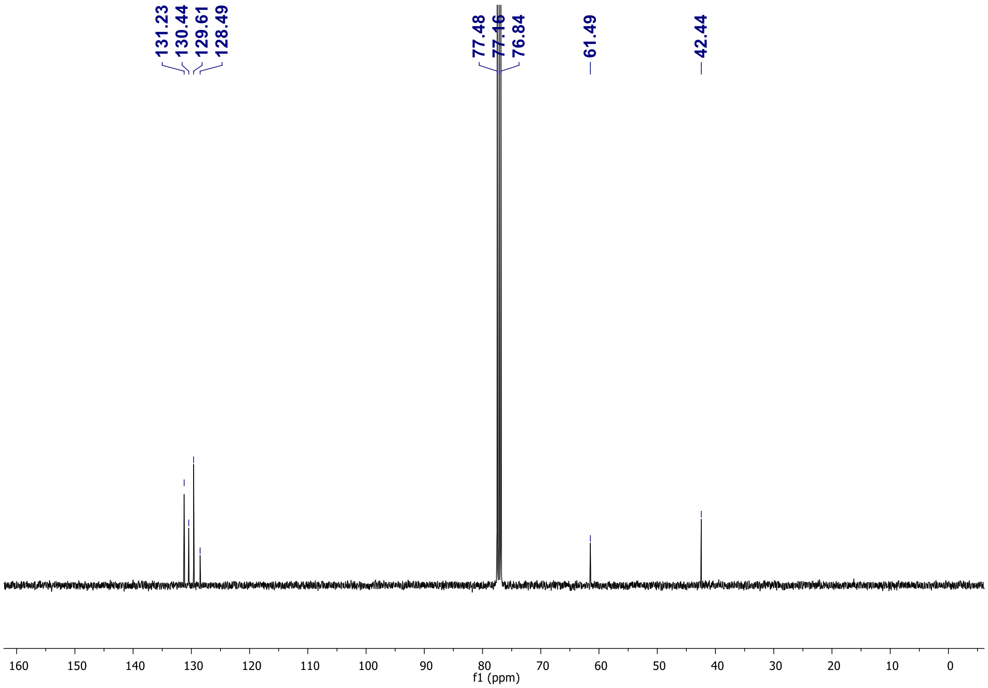


Figure S96. ^{13}C NMR spectrum of **5a′** measured in $CDCl_3$

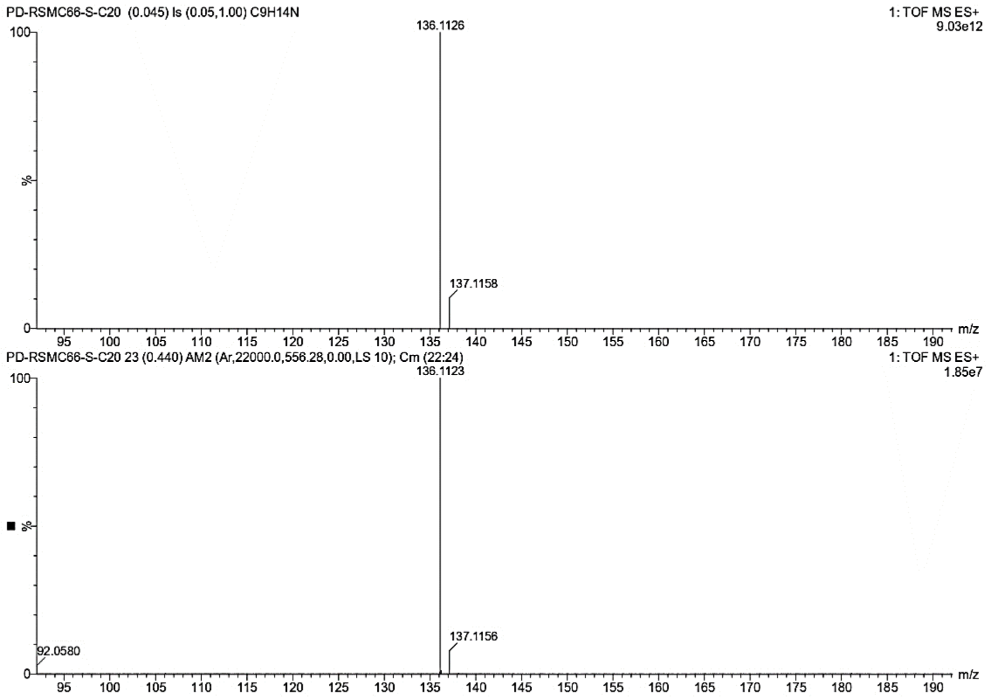


Figure S97. ESI-HRMS spectrum of **5a′** measured in methanol; (*top*, simulated; *bottom*, experimental)

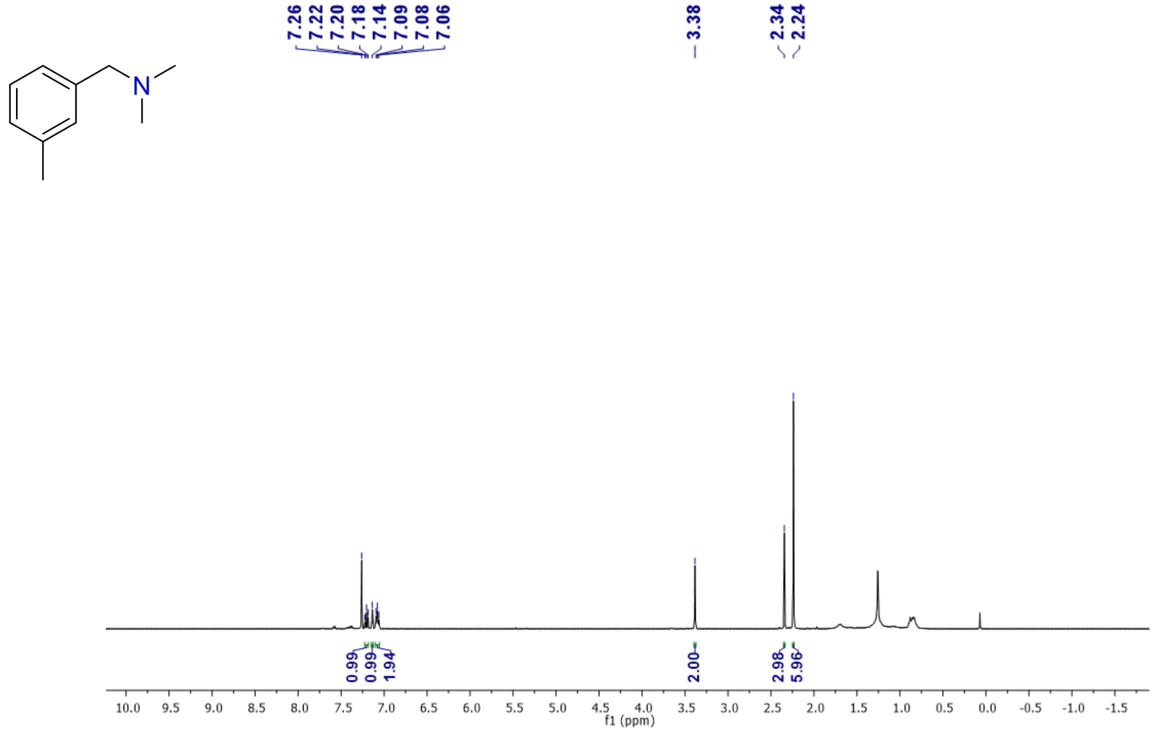


Figure S98. ^{1}H NMR spectrum of **5b** measured in $CDCl_3$

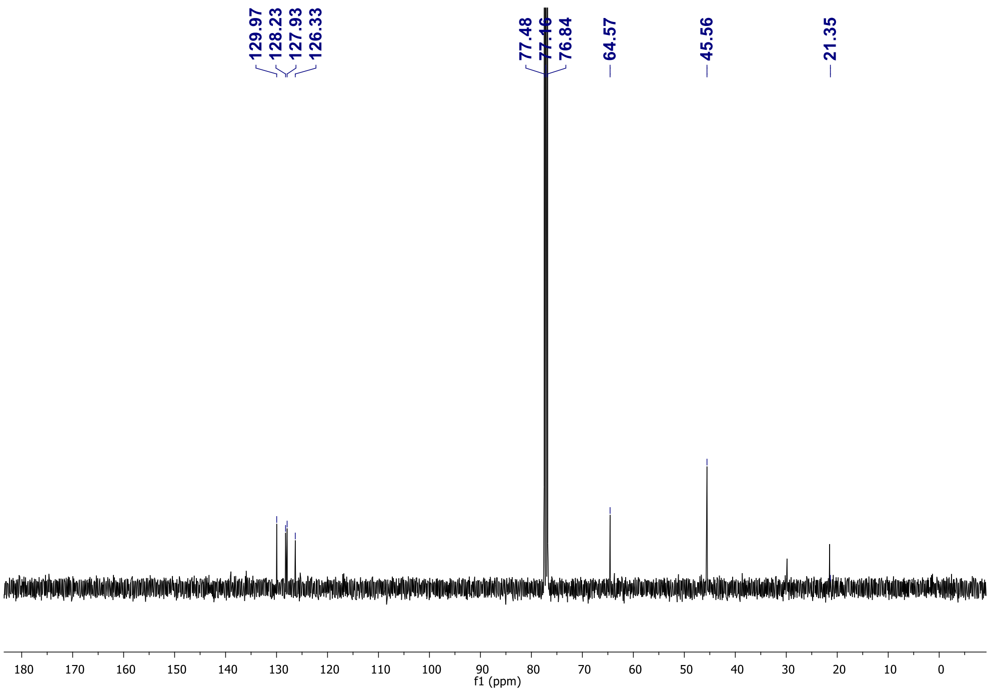


Figure S99. ^{13}C NMR spectrum of **5b** measured in CDCl$_3$

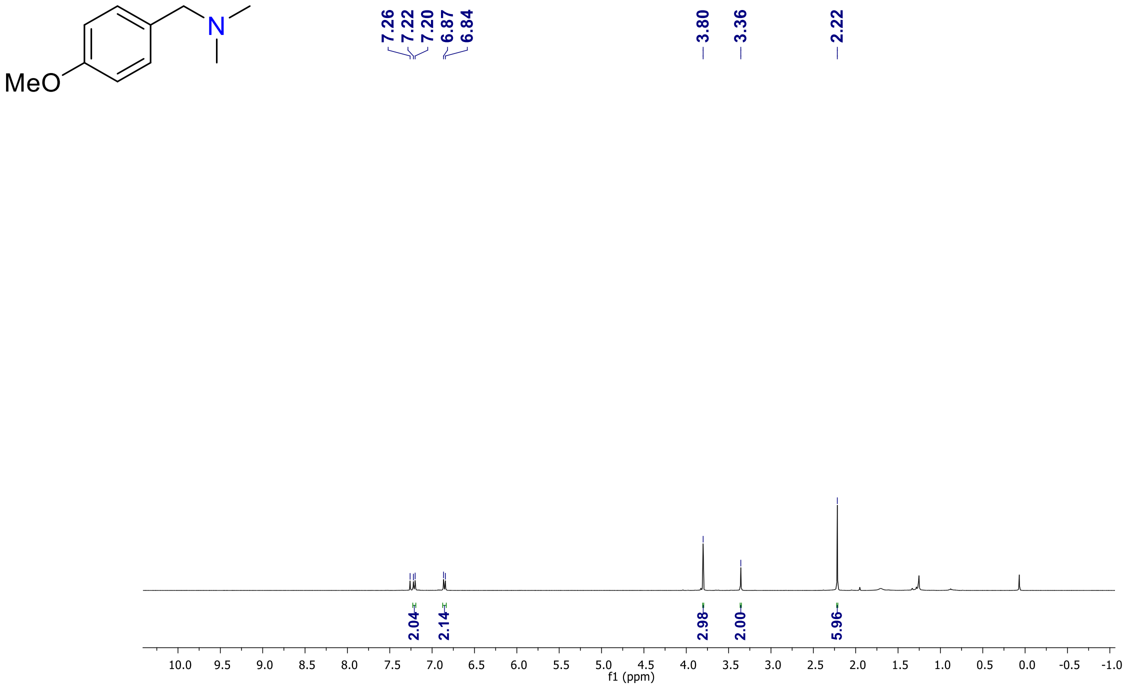


Figure S100. ^{1}H NMR spectrum of **5c** measured in CDCl$_3$

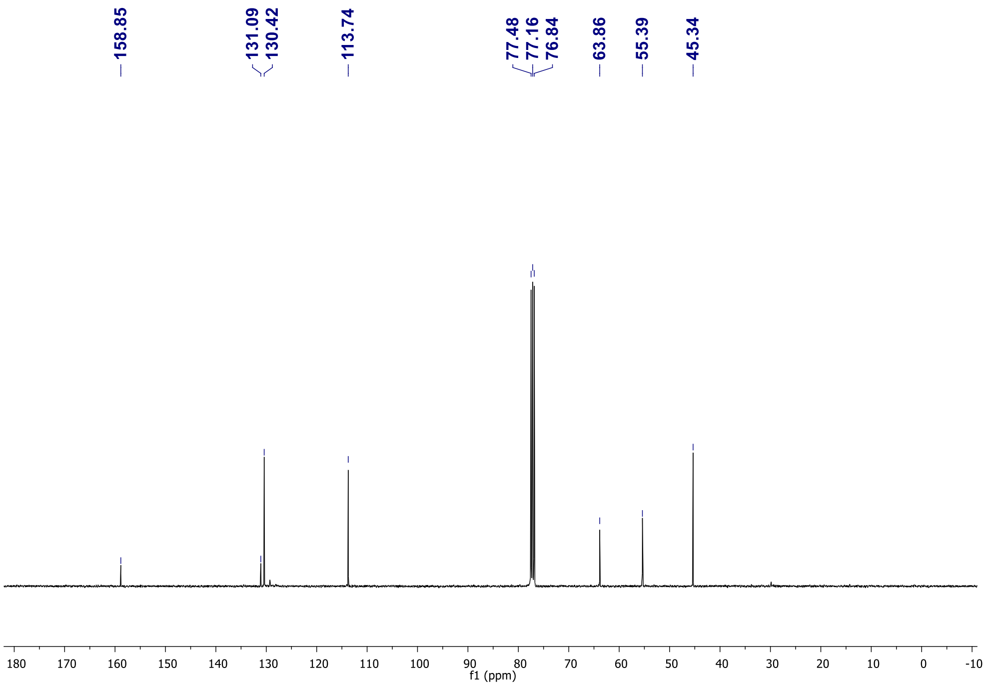


Figure S101. ^{13}C NMR spectrum of **5c** measured in $CDCl_3$

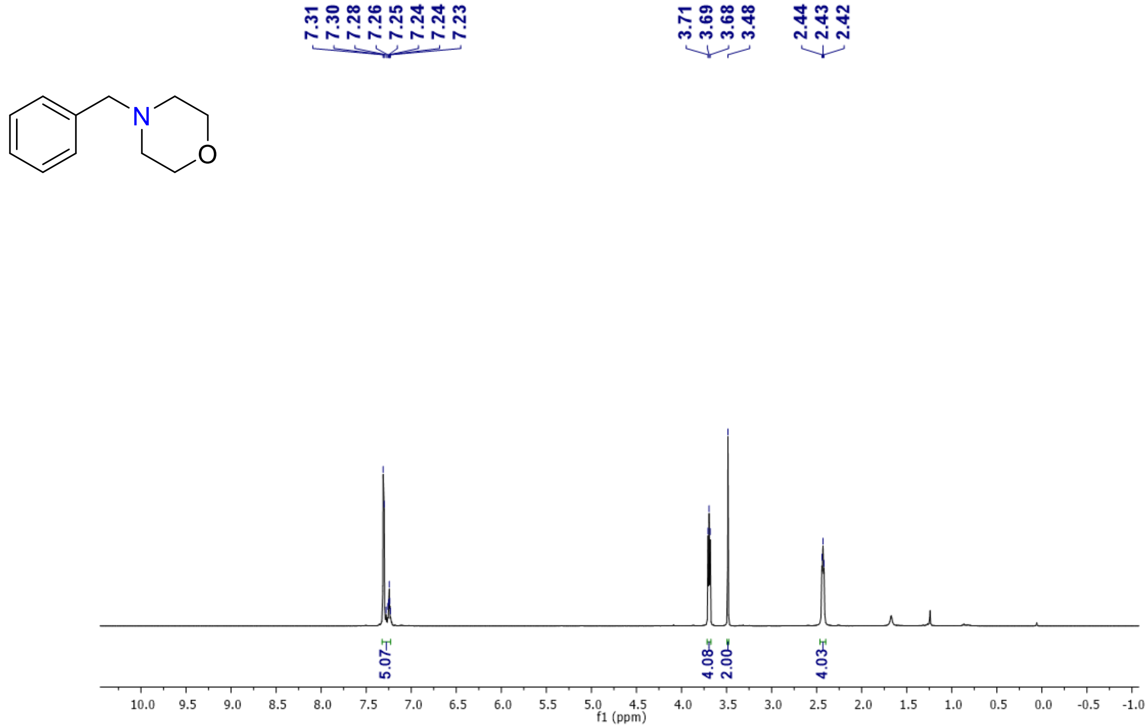


Figure S102. ^{1}H NMR spectrum of **5d** measured in $CDCl_3$

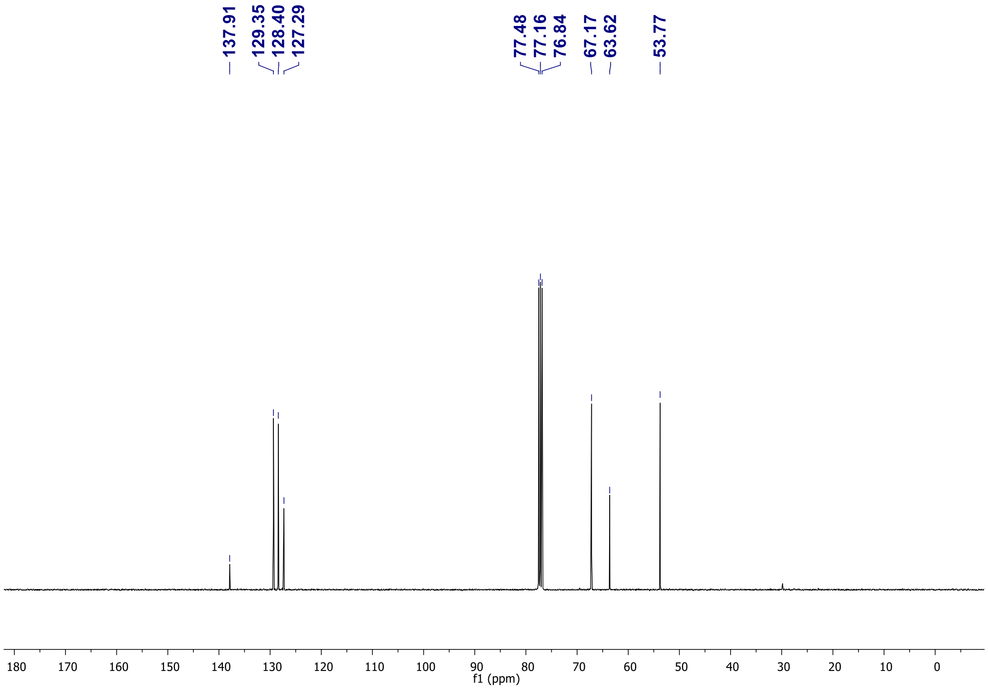


Figure S103. ^{13}C NMR spectrum of **5d** measured in $CDCl_3$

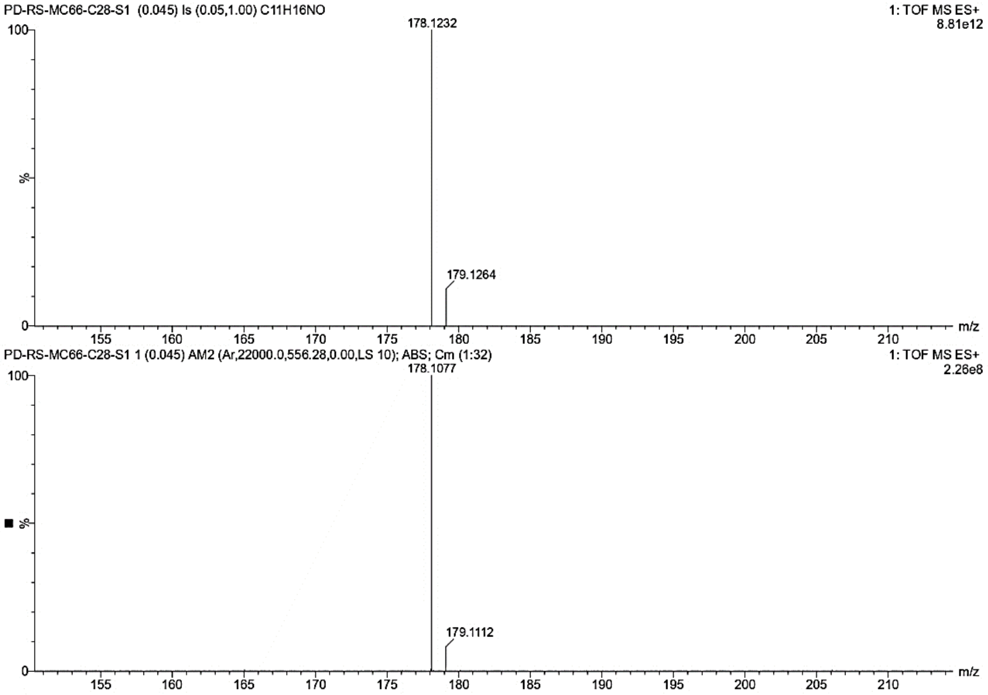


Figure S104. ESI-HRMS spectrum of **5d** measured in methanol; (*top*, simulated; *bottom*, experimental)

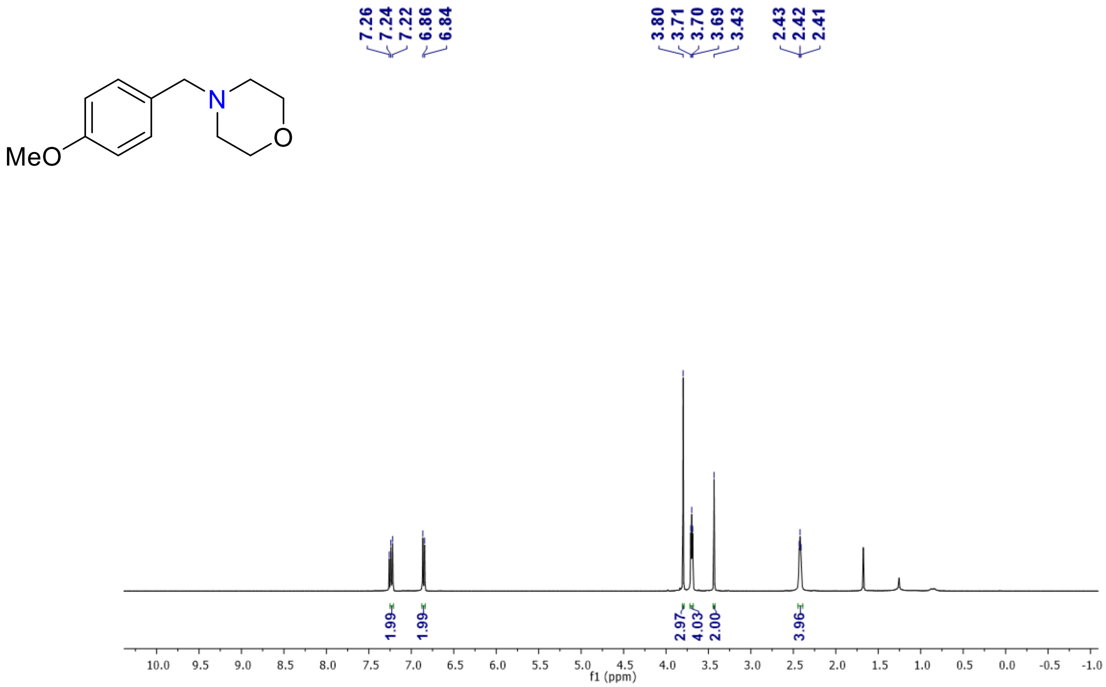


Figure S105. ^{1}H NMR spectrum of **5e** measured in $CDCl_3$

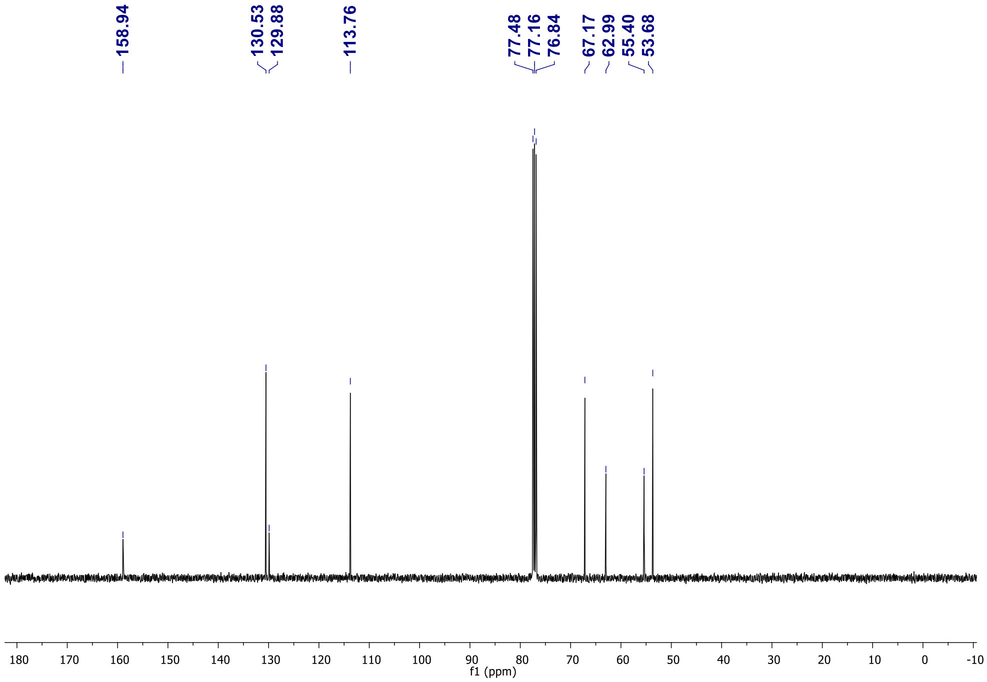


Figure S106. ^{13}C NMR spectrum of **5e** measured in $CDCl_3$

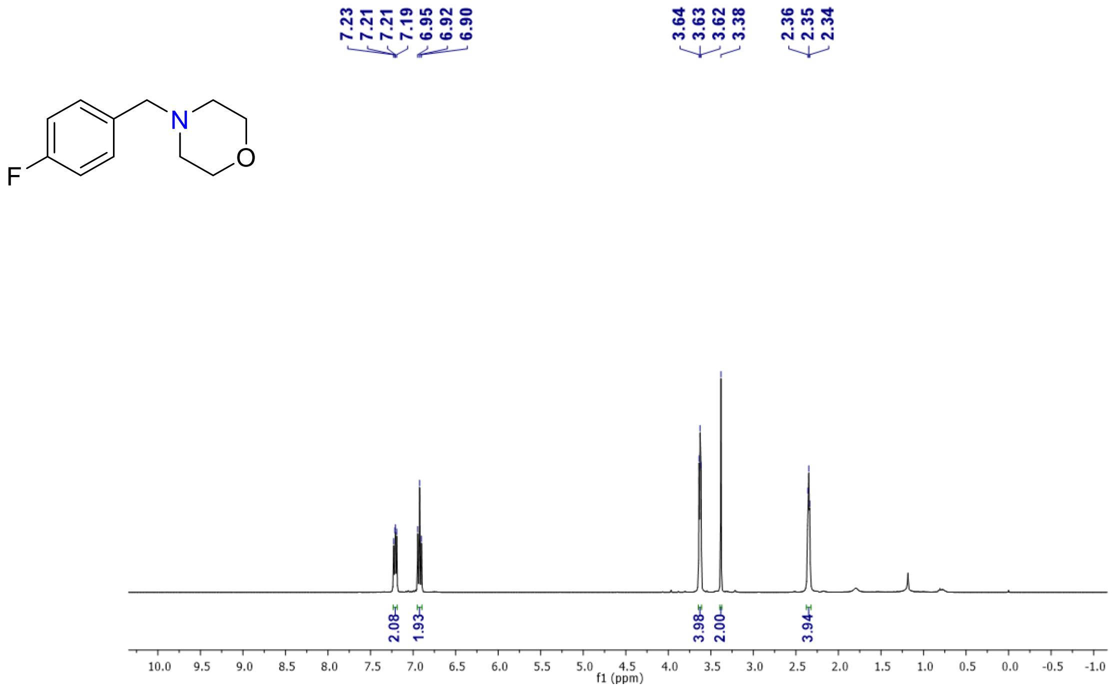


Figure S107. ^{1}H NMR spectrum of **5f** measured in $CDCl_3$

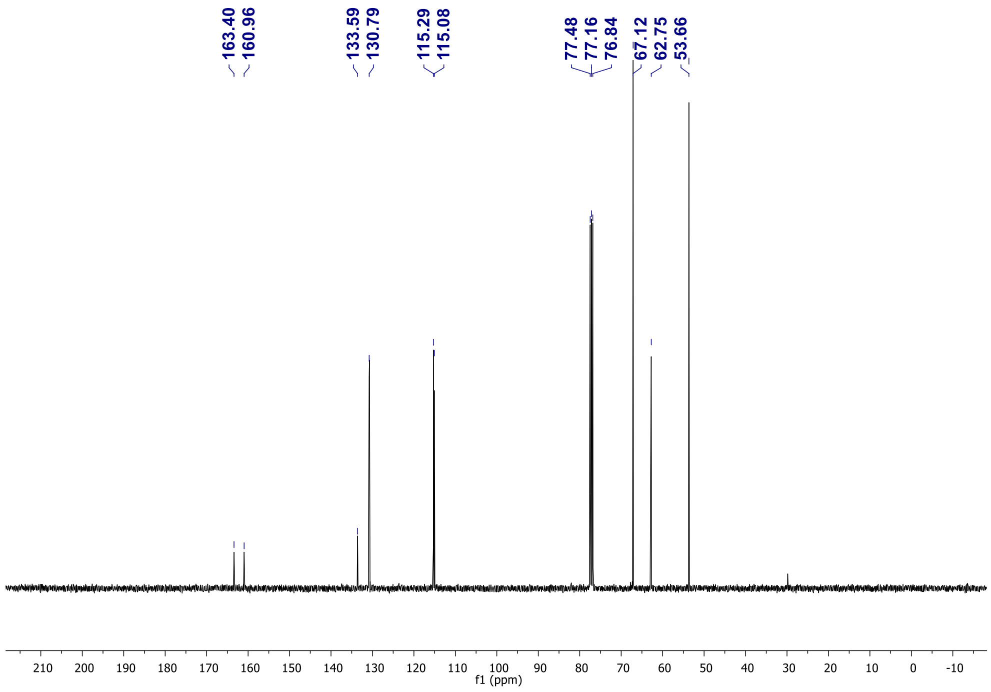


Figure S108. ^{13}C NMR spectrum of **5f** measured in $CDCl_3$

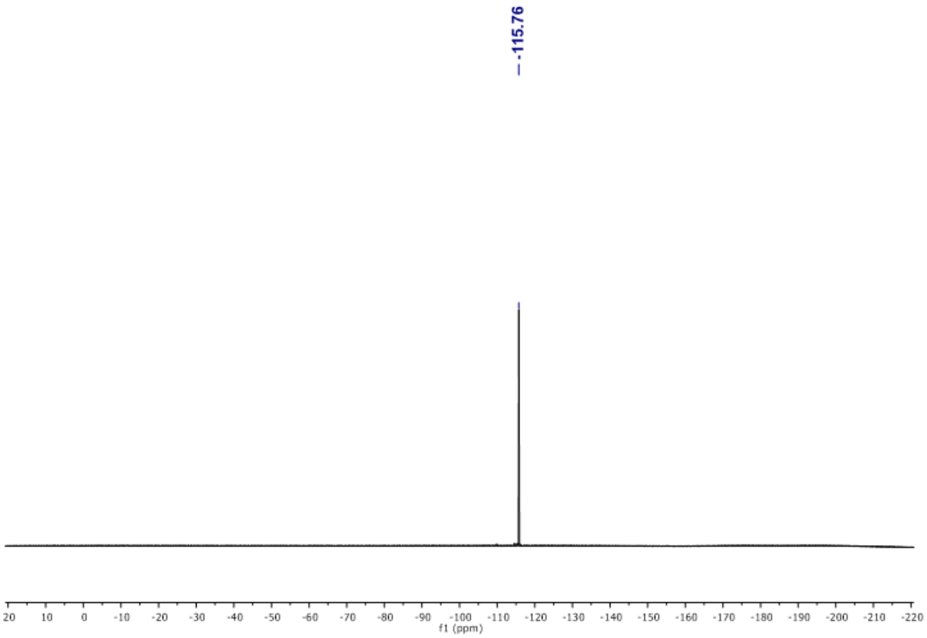


Figure S109. ^{19}F NMR spectrum of **5f** measured in $CDCl_3$

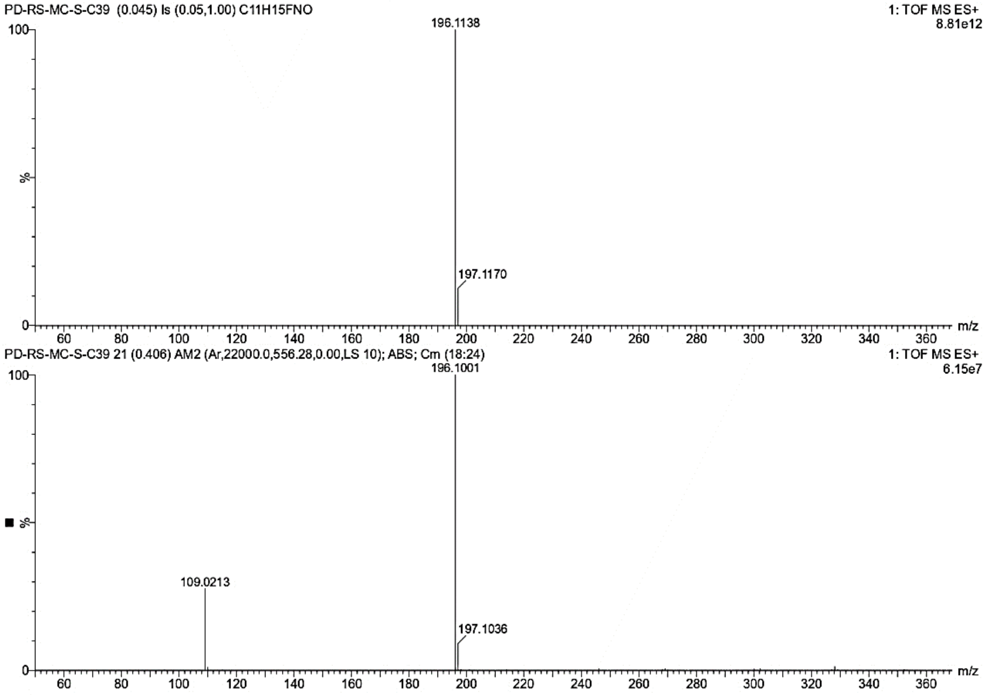


Figure S110. ESI-HRMS spectrum of **5f** measured in methanol; (*top*, simulated; *bottom*, experimental)

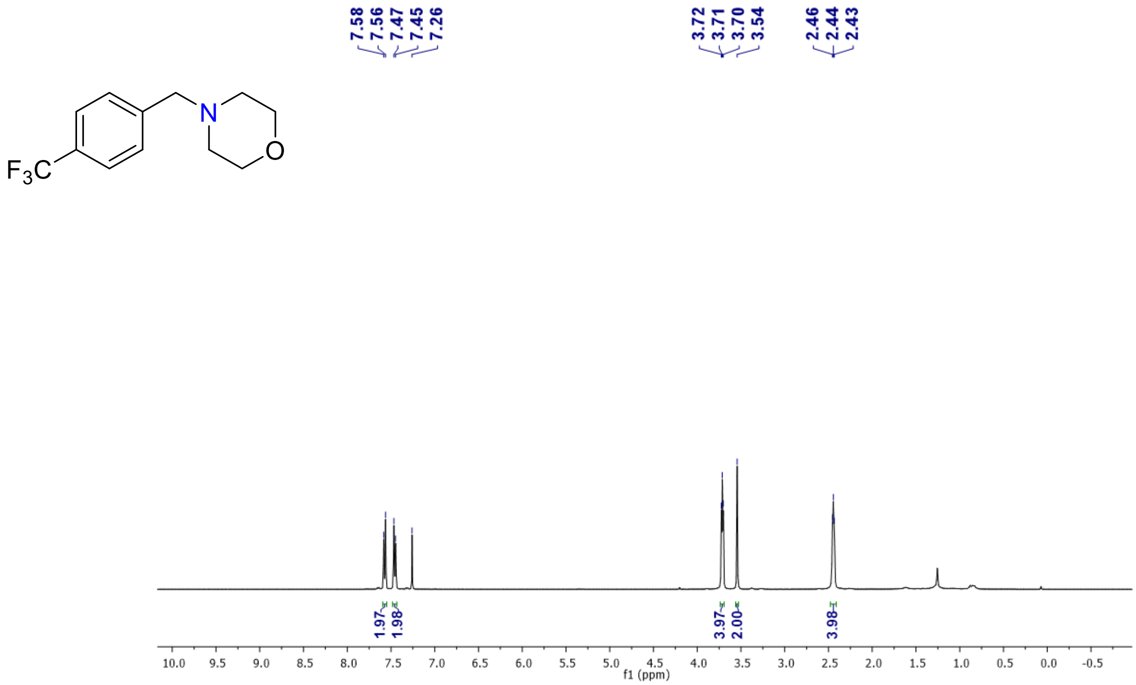


Figure S111. ^{1}H NMR spectrum of **5g** measured in $CDCl_3$

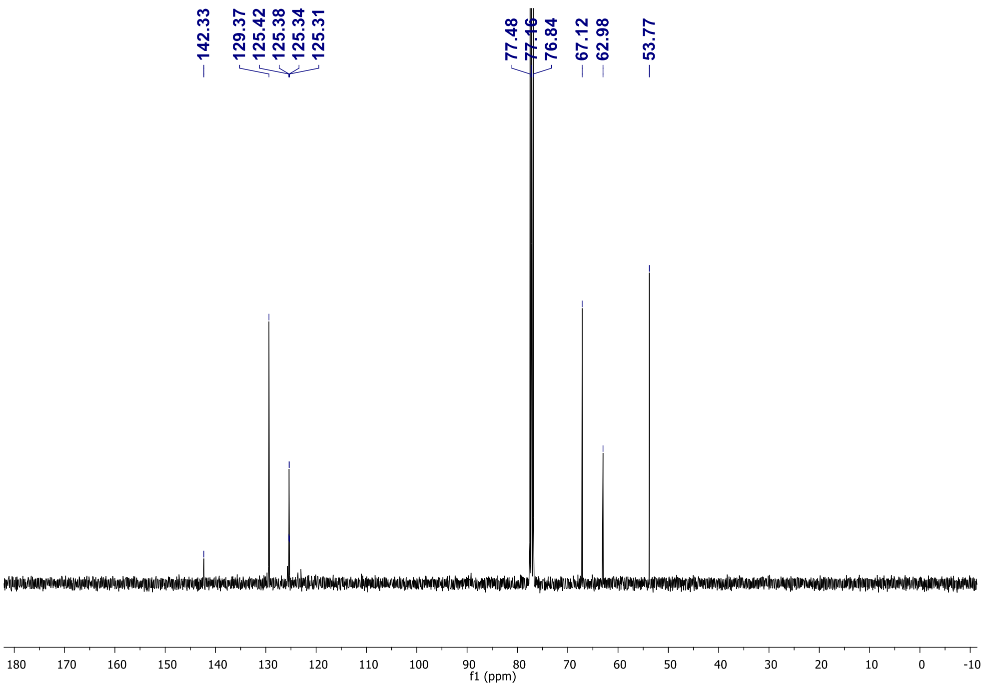


Figure S112. ^{13}C NMR spectrum of **5g** measured in $CDCl_3$

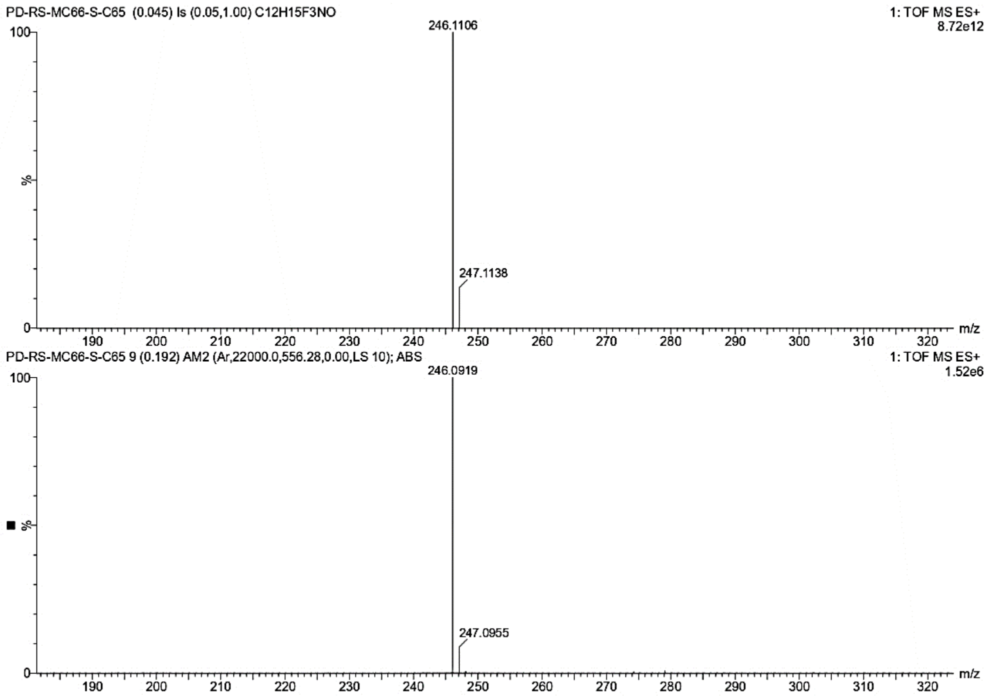


Figure S113. ESI-HRMS spectrum of **5g** measured in methanol; (*top*, simulated; *bottom*, experimental)

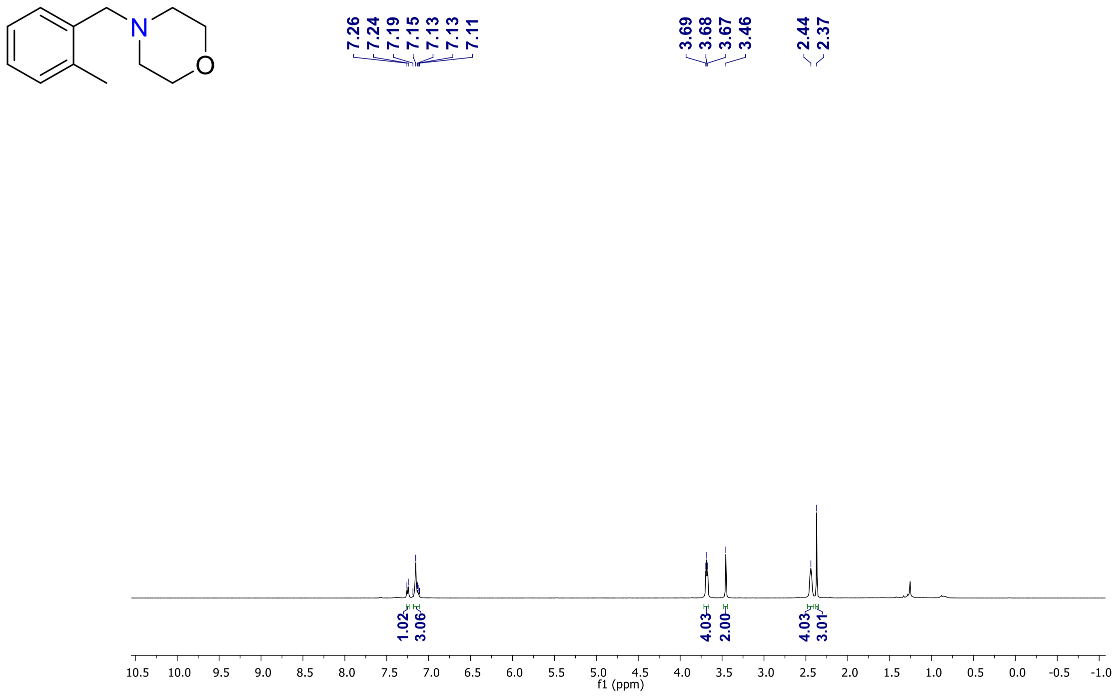


Figure S114. ^{1}H NMR spectrum of **5h** measured in CDCl$_3$

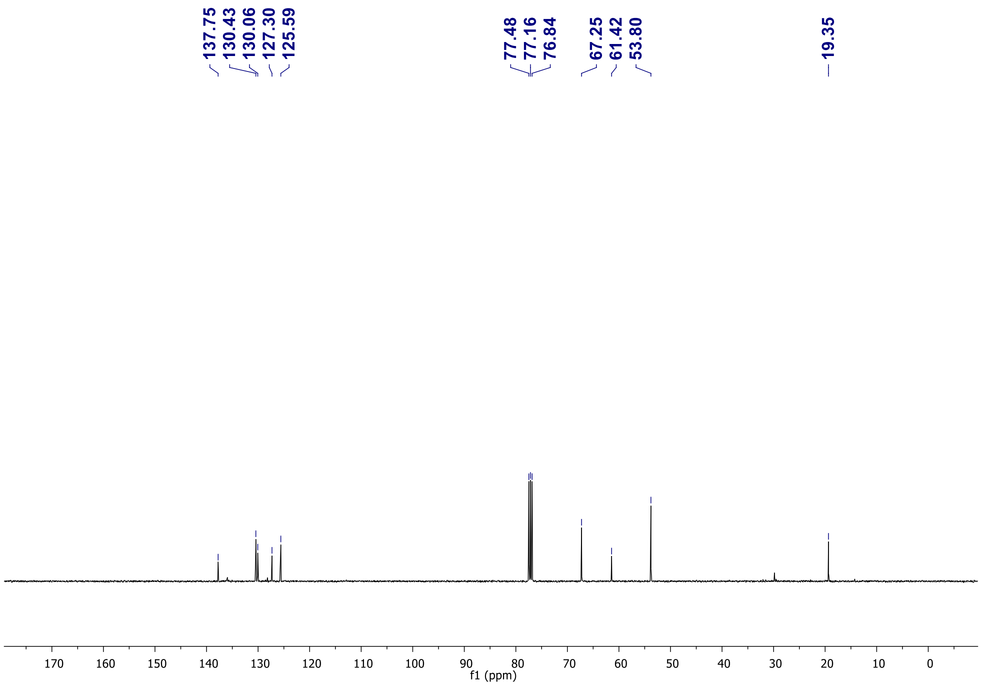


Figure S115. ^{13}C NMR spectrum of **5h** measured in CDCl$_3$

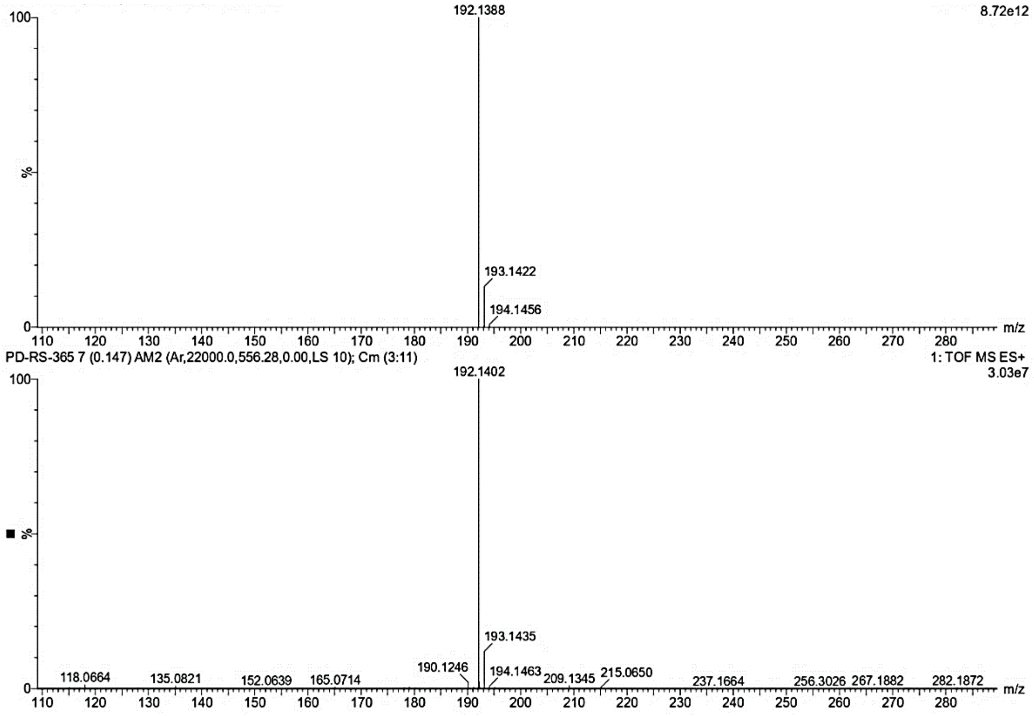


Figure S116. ESI-HRMS spectrum of **5h** measured in methanol; (*top*, simulated; *bottom*, experimental)

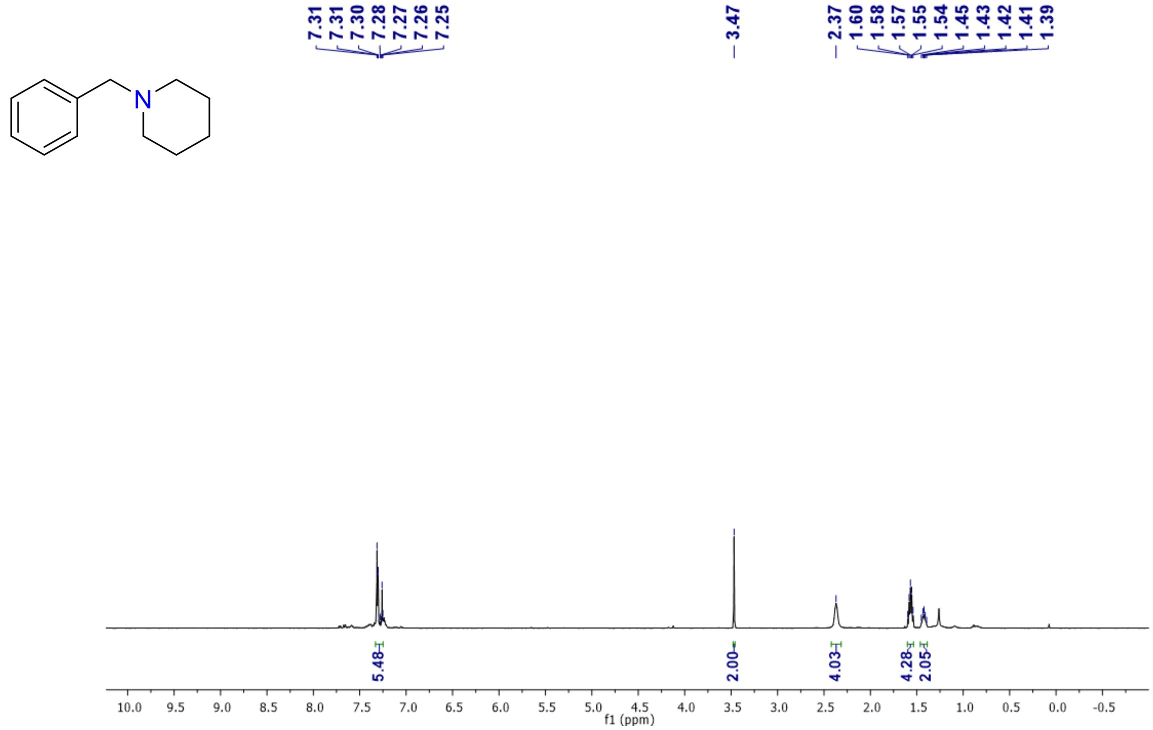


Figure S117. ^{1}H NMR spectrum of **5i** measured in $CDCl_3$

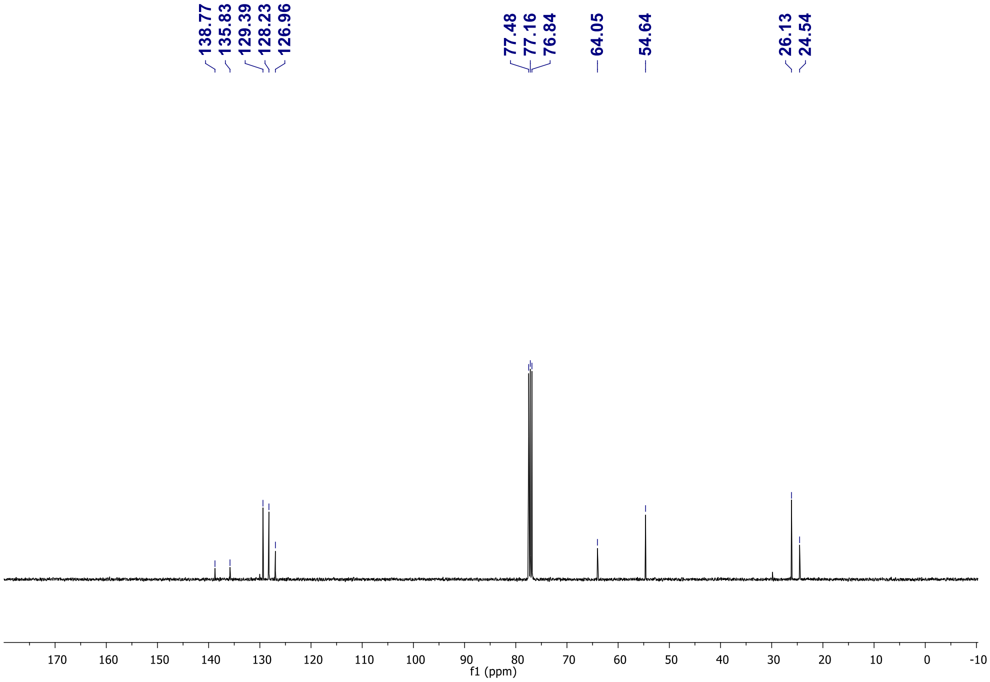


Figure S118. ^{13}C NMR spectrum of **5i** measured in $CDCl_3$

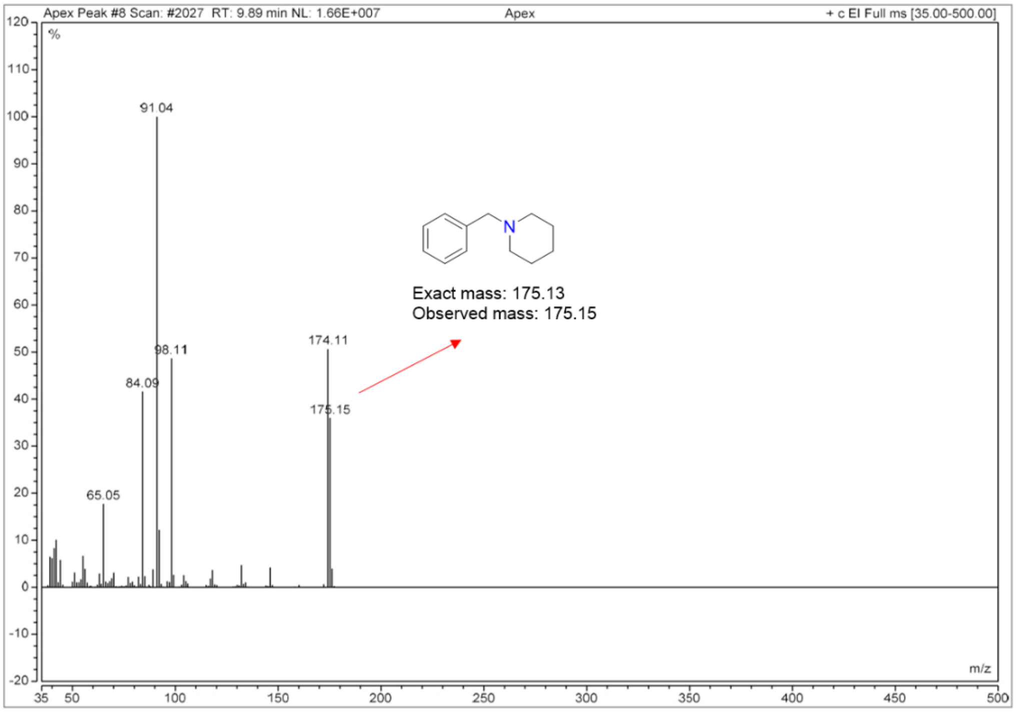


Figure S119. Mass pattern of GC-MS spectrum of compound **5i**

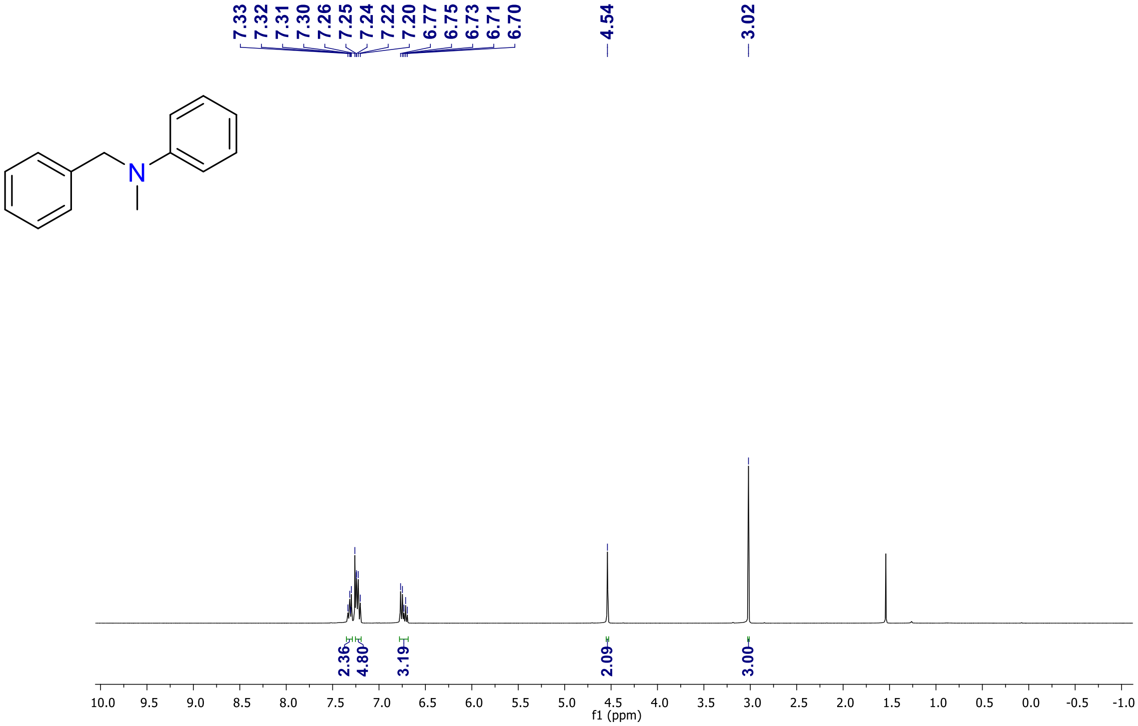


Figure S120. ^{1}H NMR spectrum of **5j** measured in $CDCl_3$

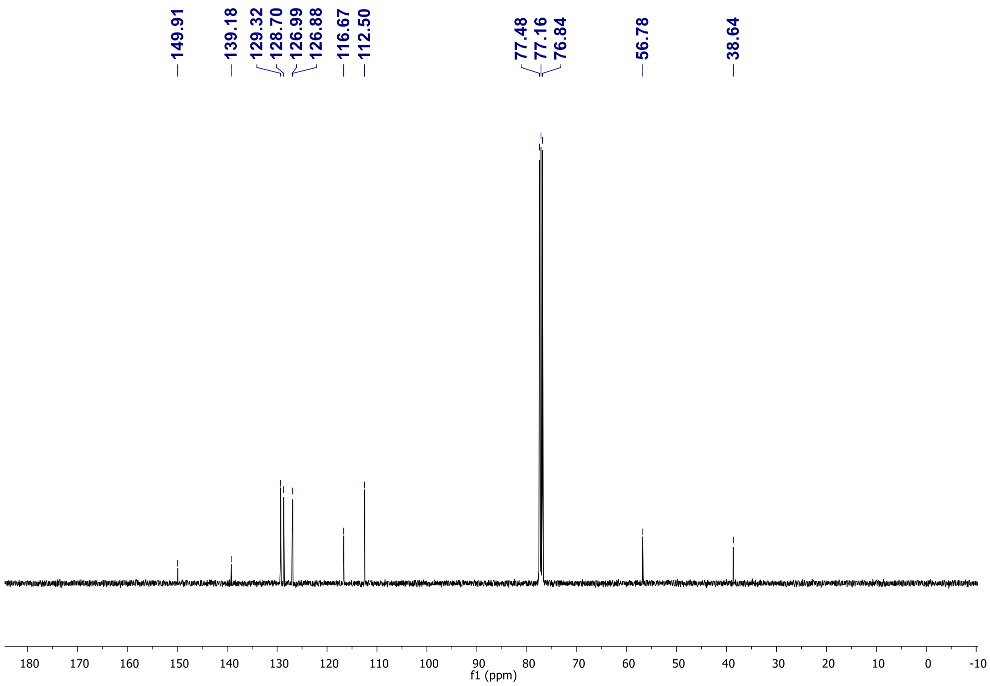


Figure S121. ^{13}C NMR spectrum of **5j** measured in $CDCl_3$

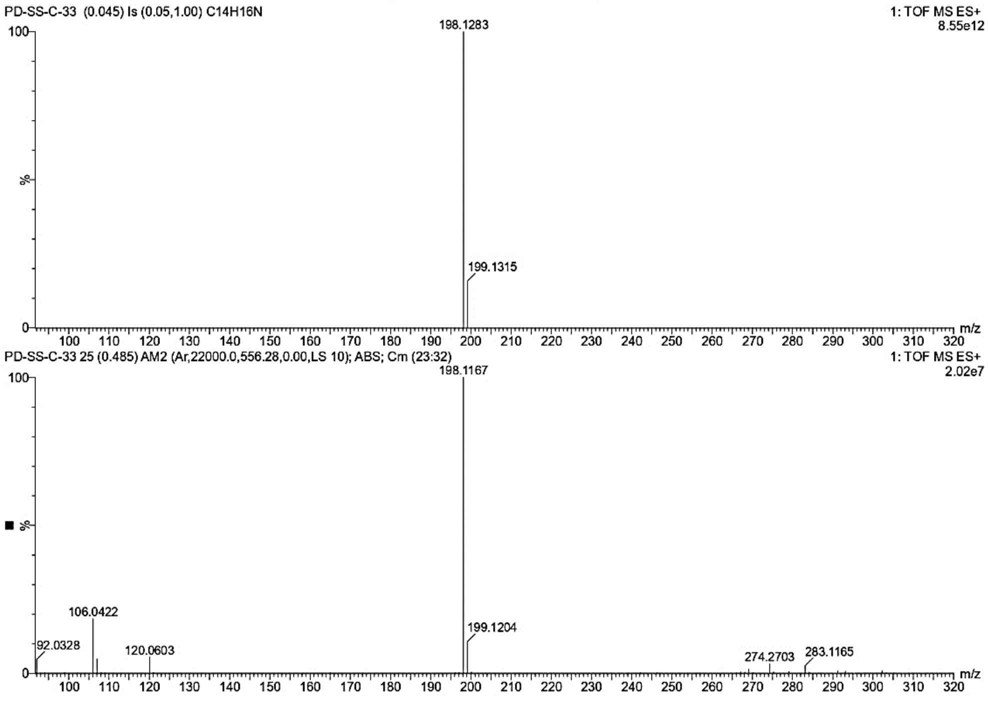


Figure S122. ESI-HRMS spectrum of **5j** measured in methanol; (*top*, simulated; *bottom*, experimental)

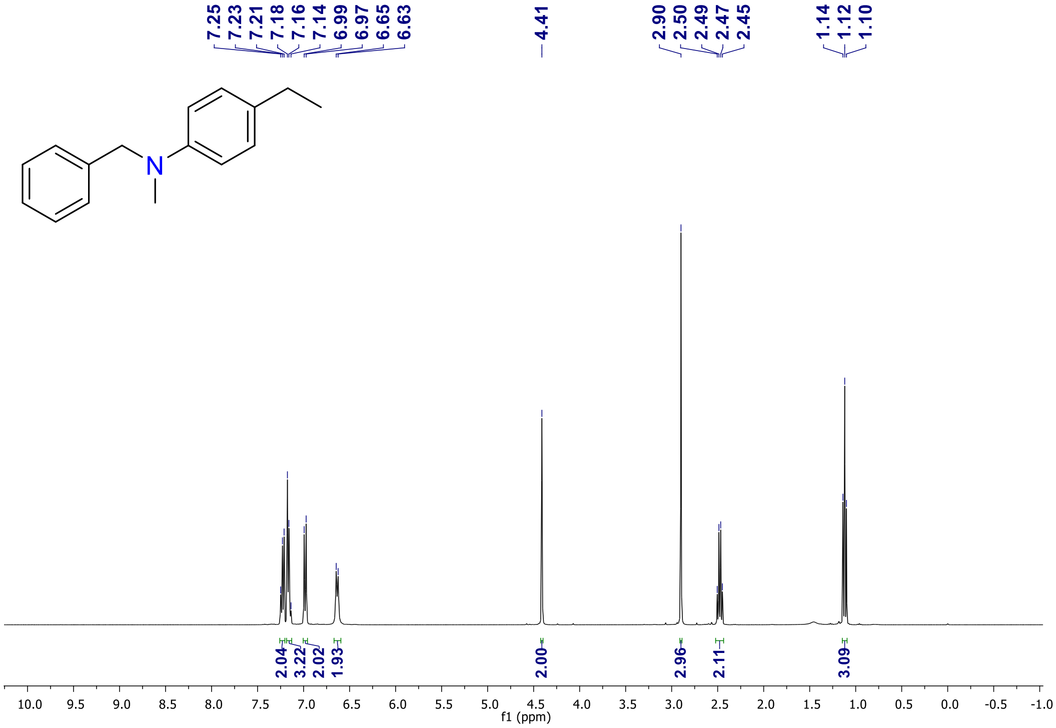


Figure S123. ^{1}H NMR spectrum of **5k** measured in $CDCl_3$

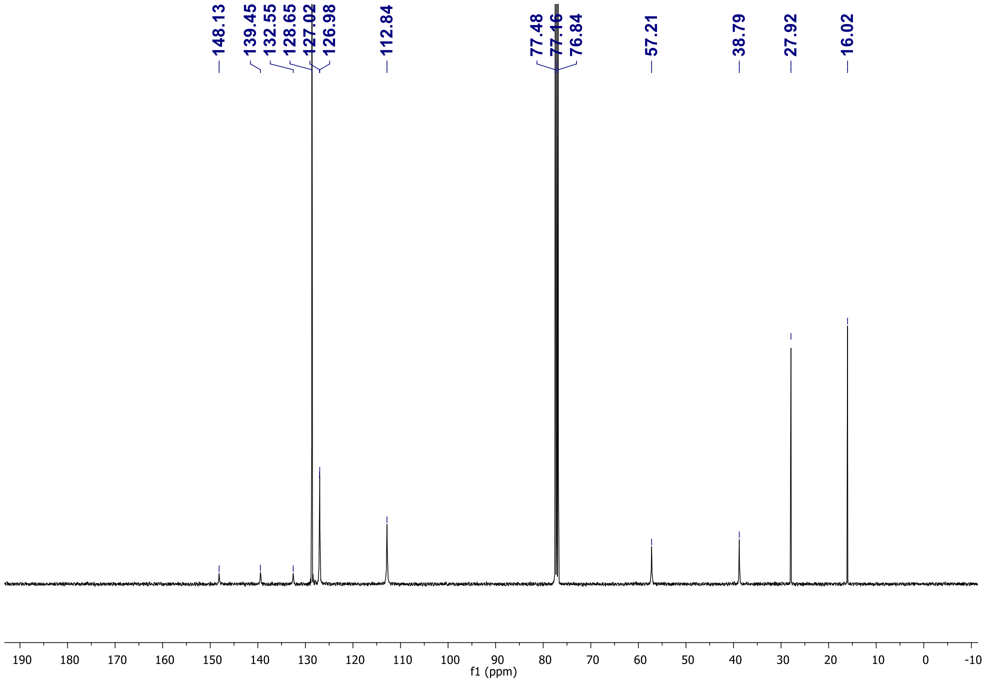


Figure S124. ^{13}C NMR spectrum of **5k** measured in $CDCl_3$

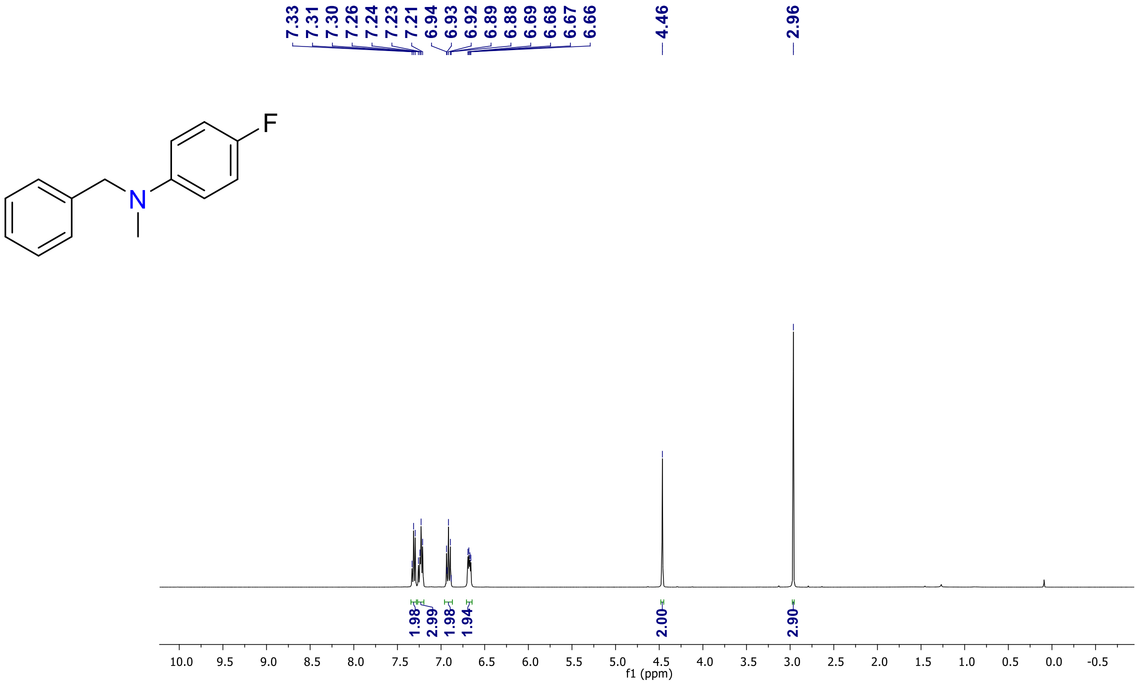


Figure S125. ^{1}H NMR spectrum of **5l** measured in $CDCl_3$

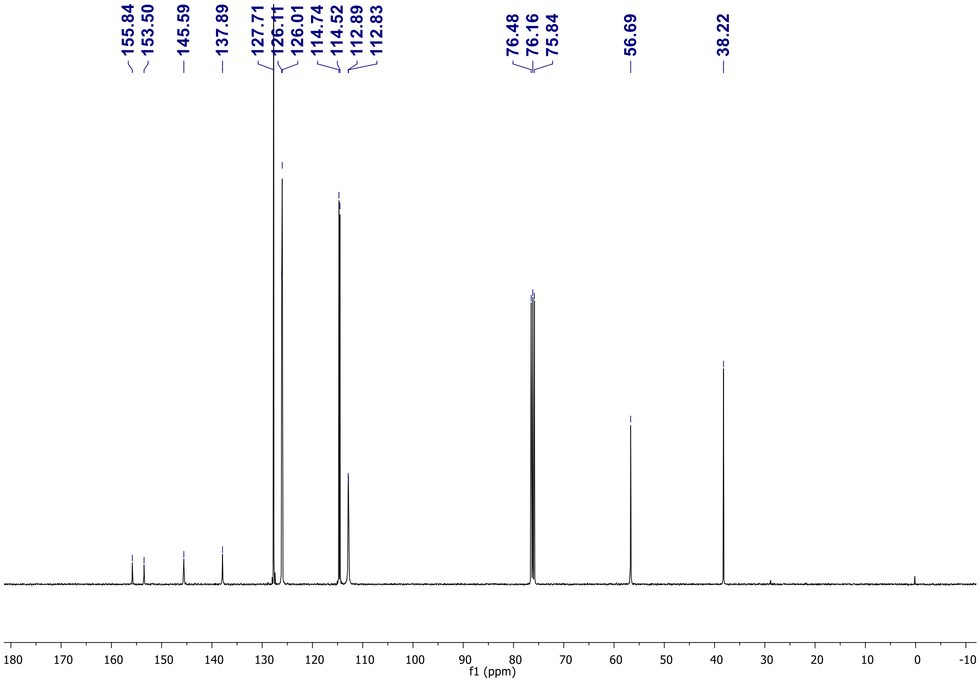


Figure S126. ^{13}C NMR spectrum of **5l** measured in $CDCl_3$

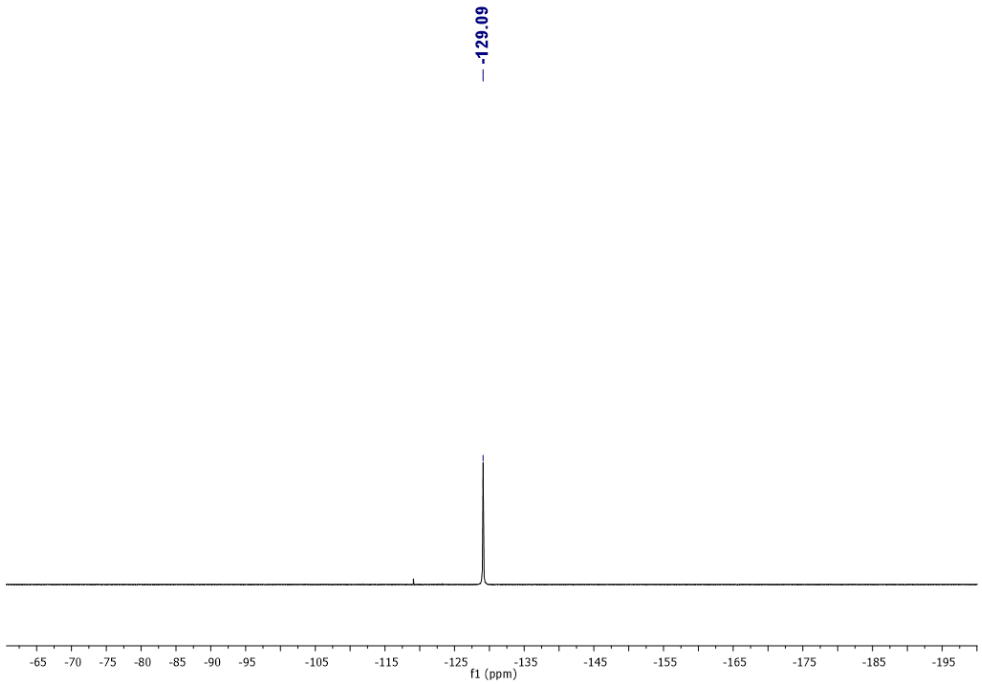


Figure S127. ^{19}F NMR spectrum of **5l** measured in CDCl$_3$

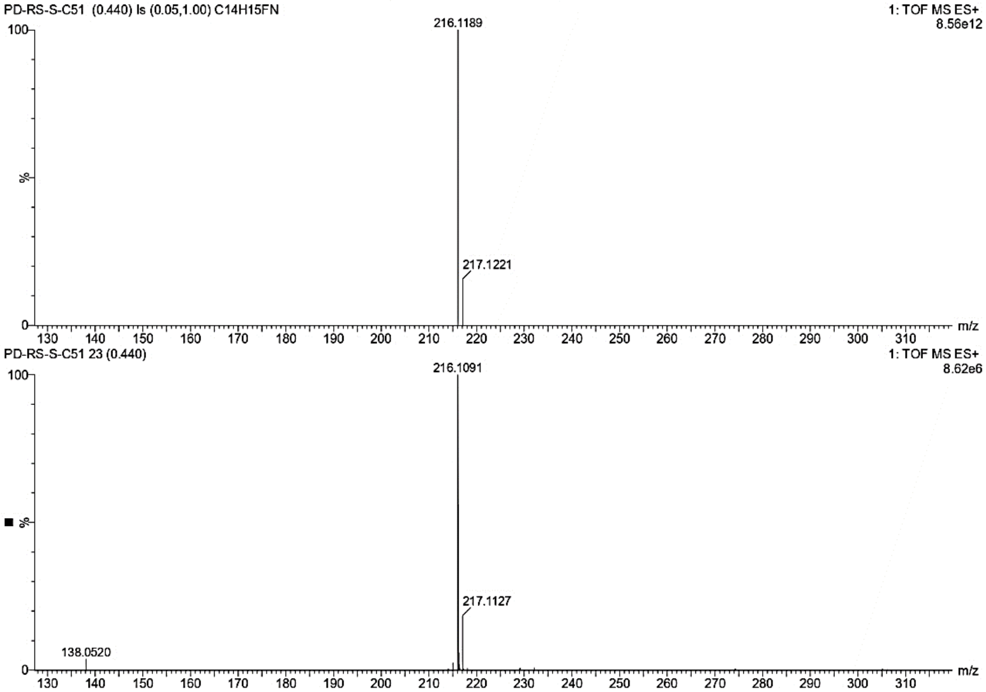


Figure S128. ESI-HRMS spectrum of **5l** measured in methanol; (*top,* simulated; *bottom*, experimental)

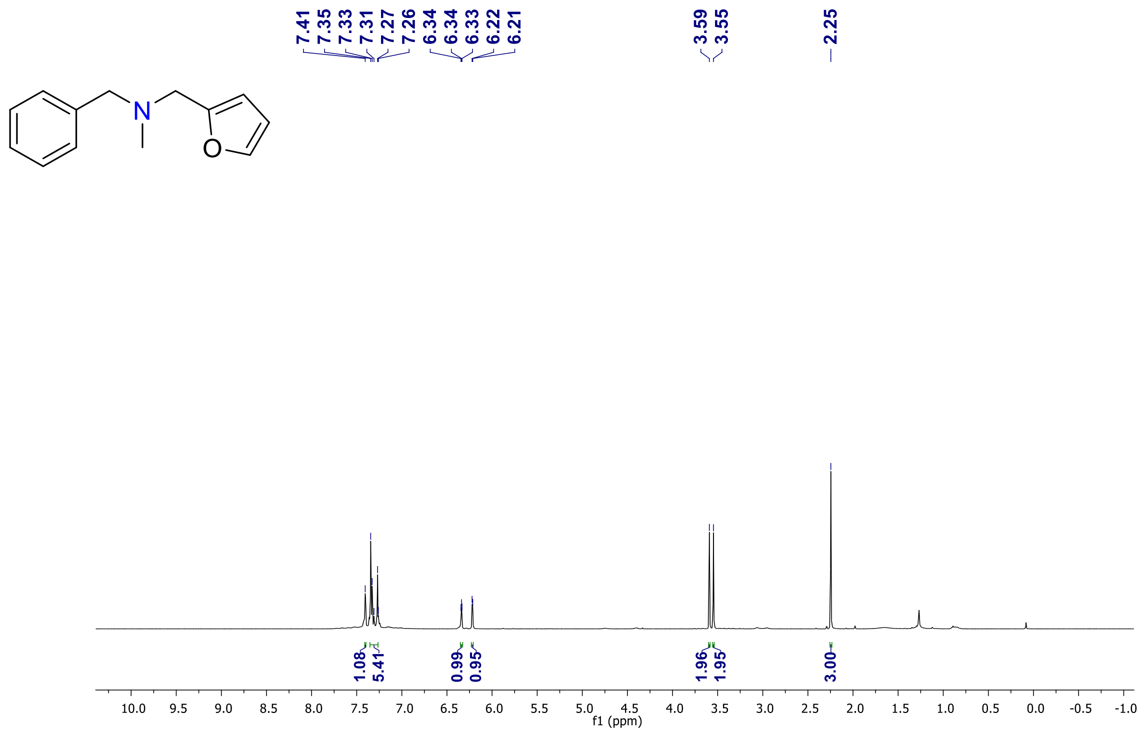


Figure S129. ^{1}H NMR spectrum of **5m** measured in $CDCl_3$

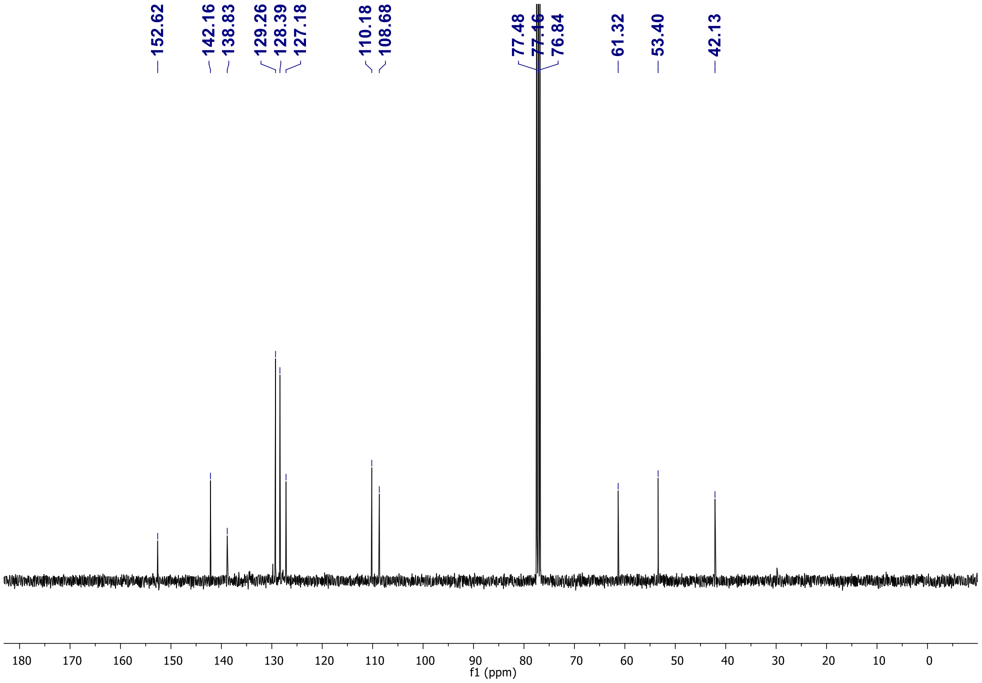


Figure S130. ^{13}C NMR spectrum of **5m** measured in $CDCl_3$

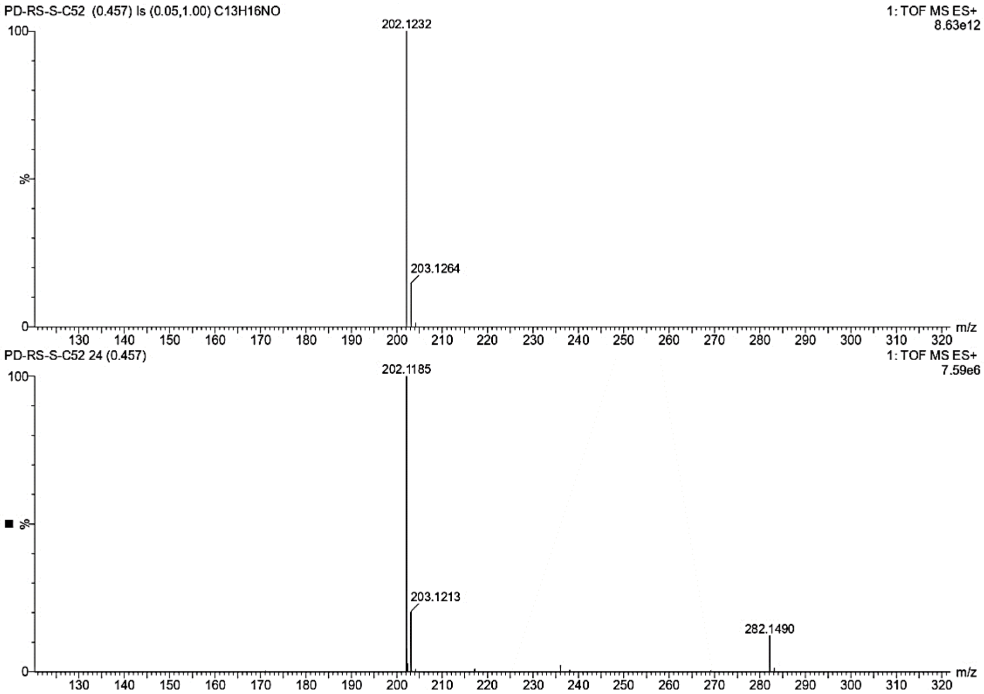


Figure S131. ESI-HRMS spectrum of **5m** measured in methanol; (*top*, simulated; *bottom*, experimental)

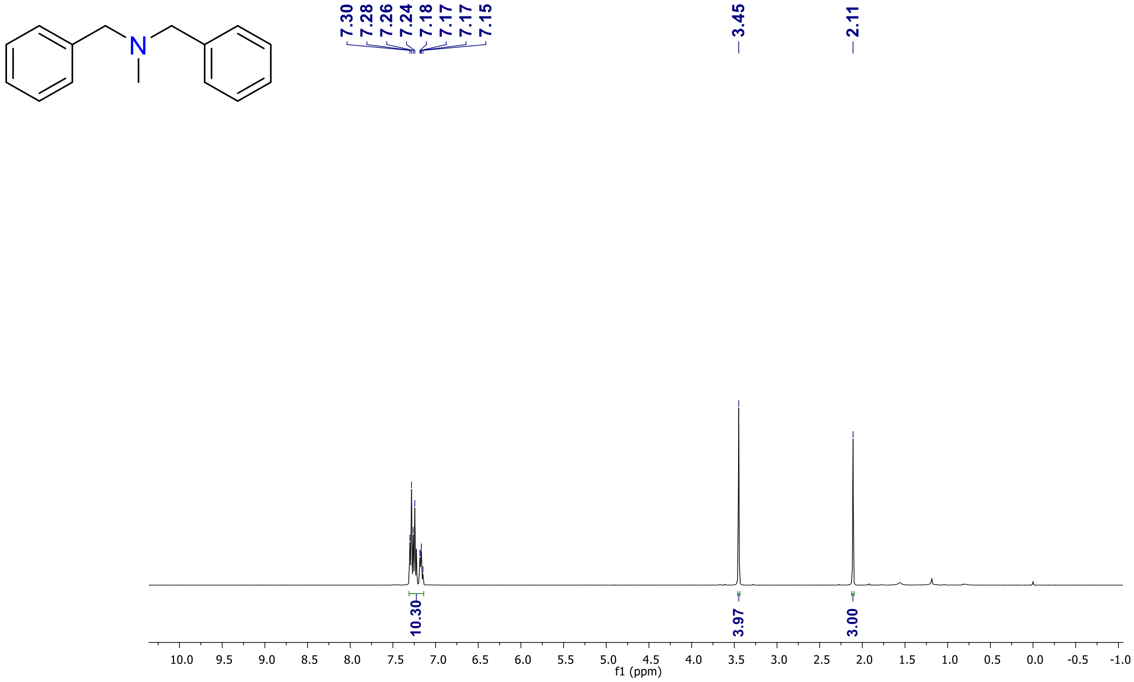


Figure S132. ^{1}H NMR spectrum of **5n** measured in $CDCl_3$

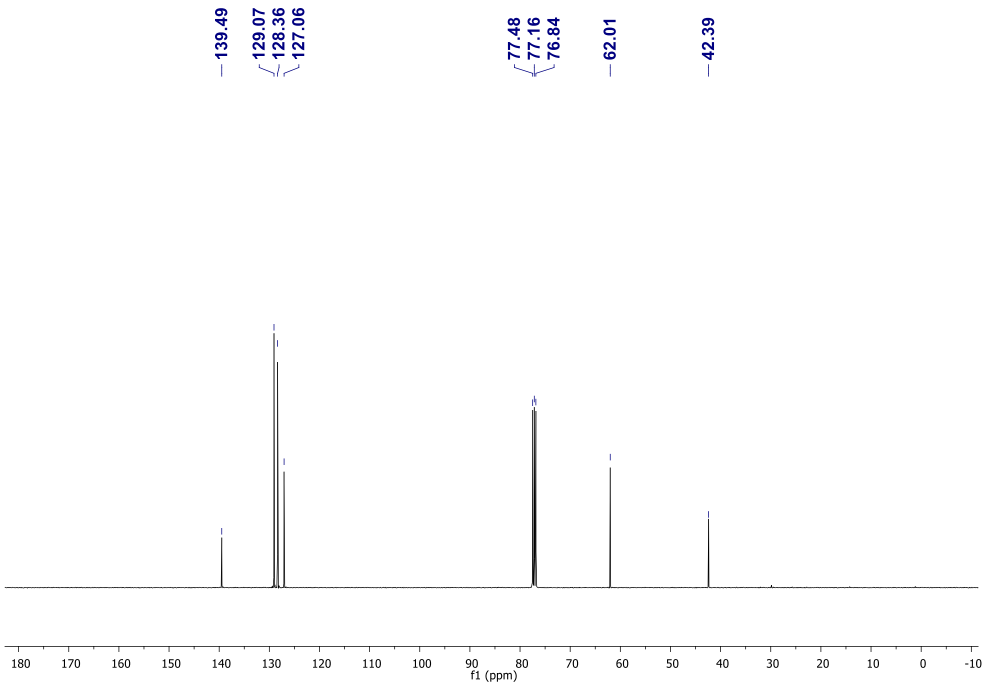


Figure S133. ^{13}C NMR spectrum of **5n** measured in CDCl$_3$

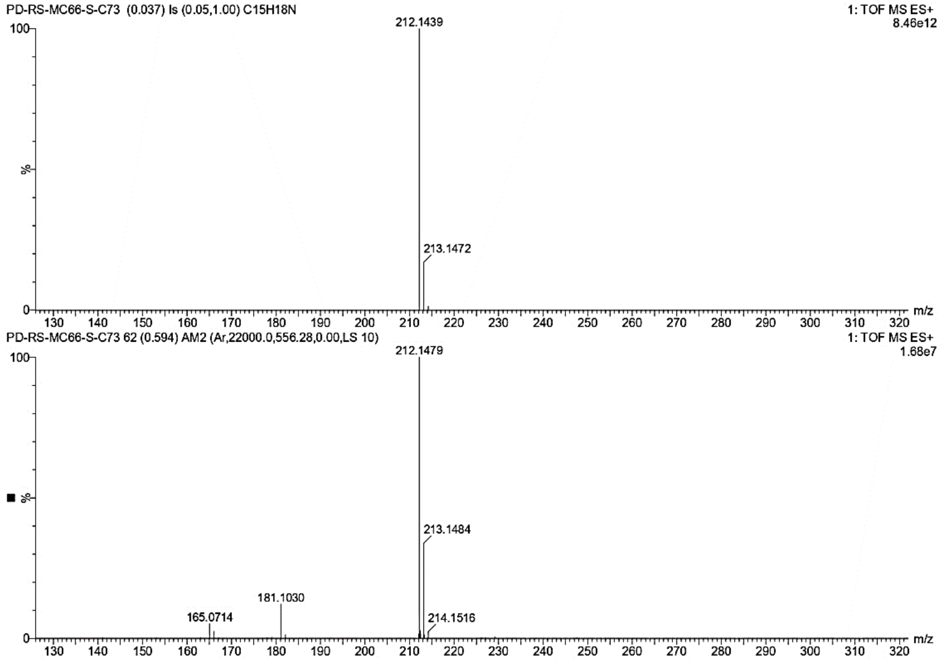


Figure S134. ESI-HRMS spectrum of **5n** measured in methanol; (*top*, simulated; *bottom*, experimental)

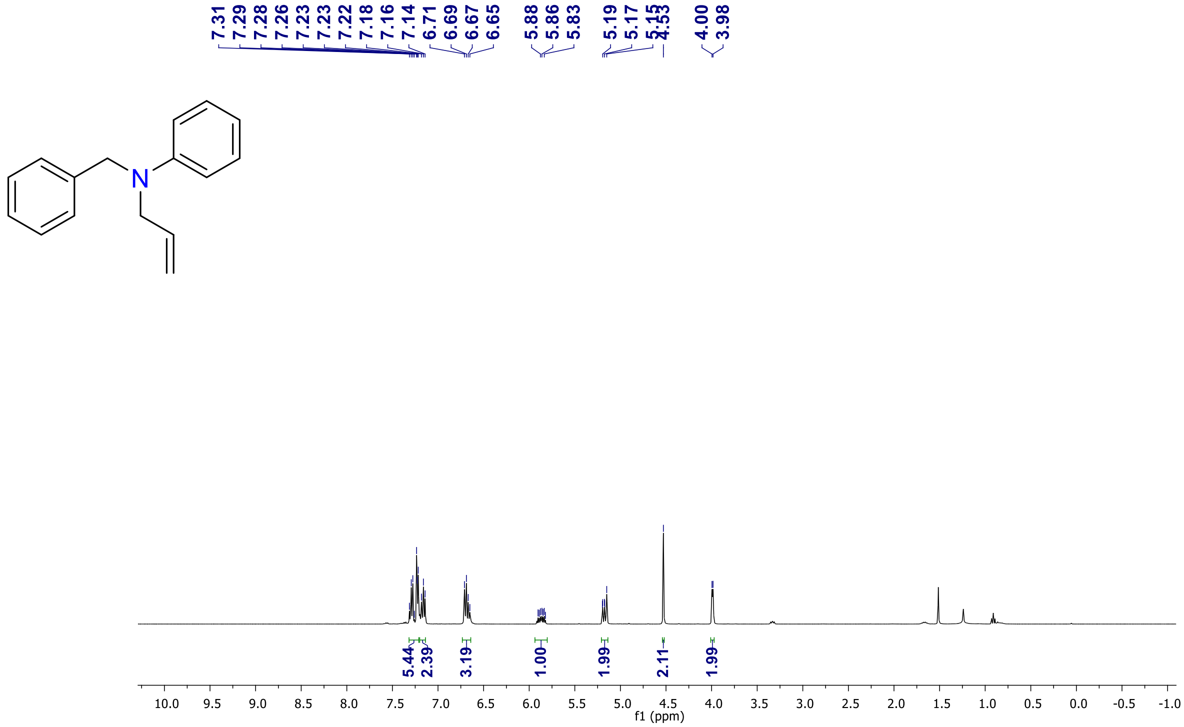


Figure S135. ^{1}H NMR spectrum of **5o** measured in $CDCl_3$

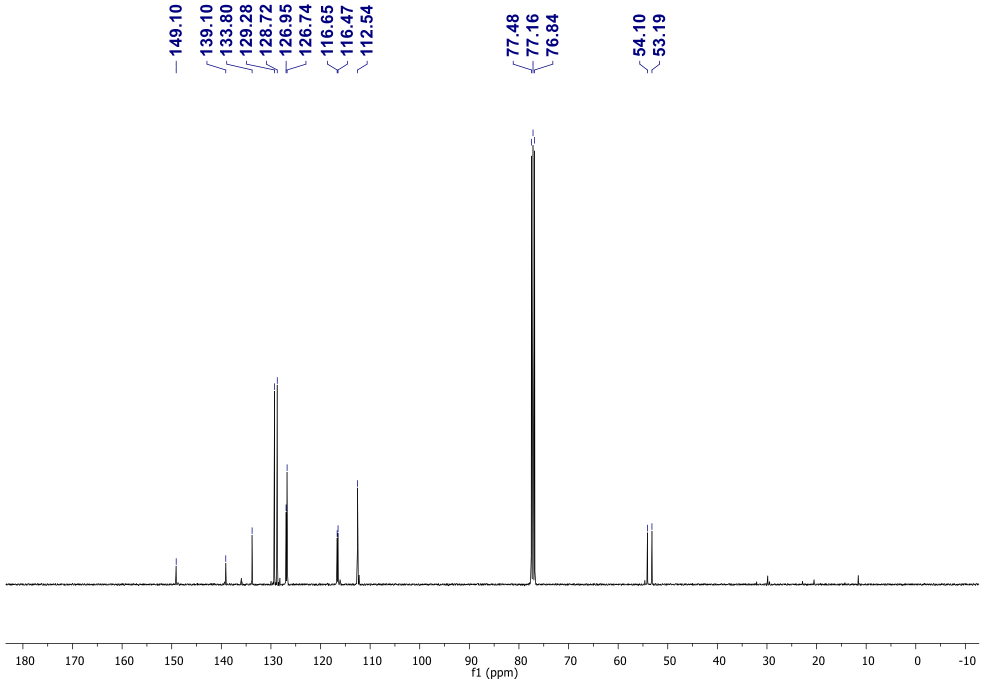


Figure S136. ^{13}C NMR spectrum of **5o** measured in $CDCl_3$

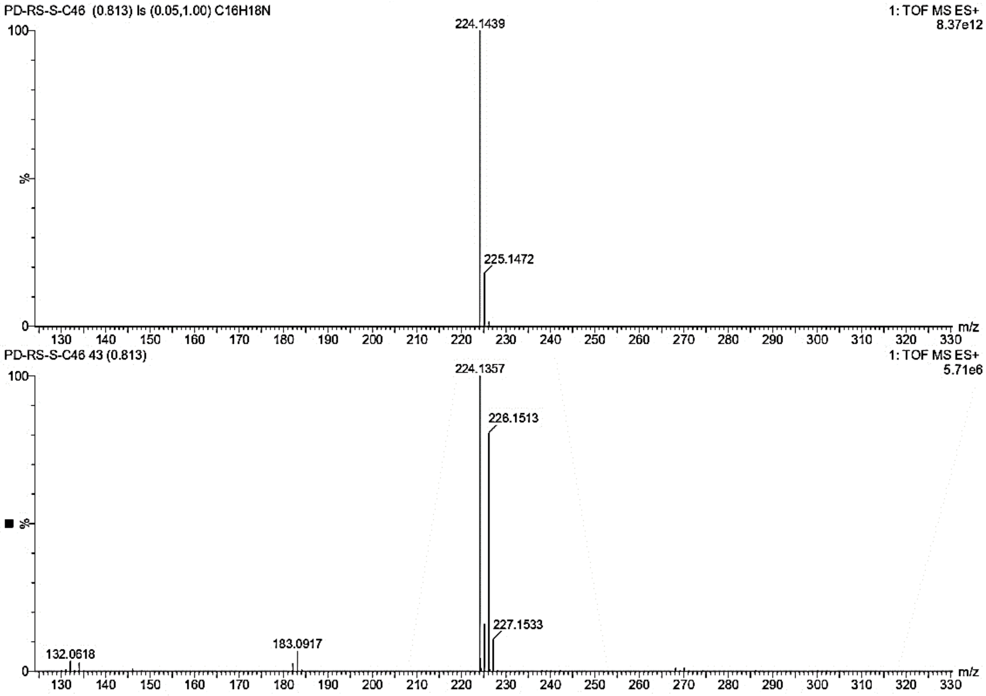


Figure S137. ESI-HRMS spectrum of **5o** measured in methanol; (*top*, simulated; *bottom*, experimental)

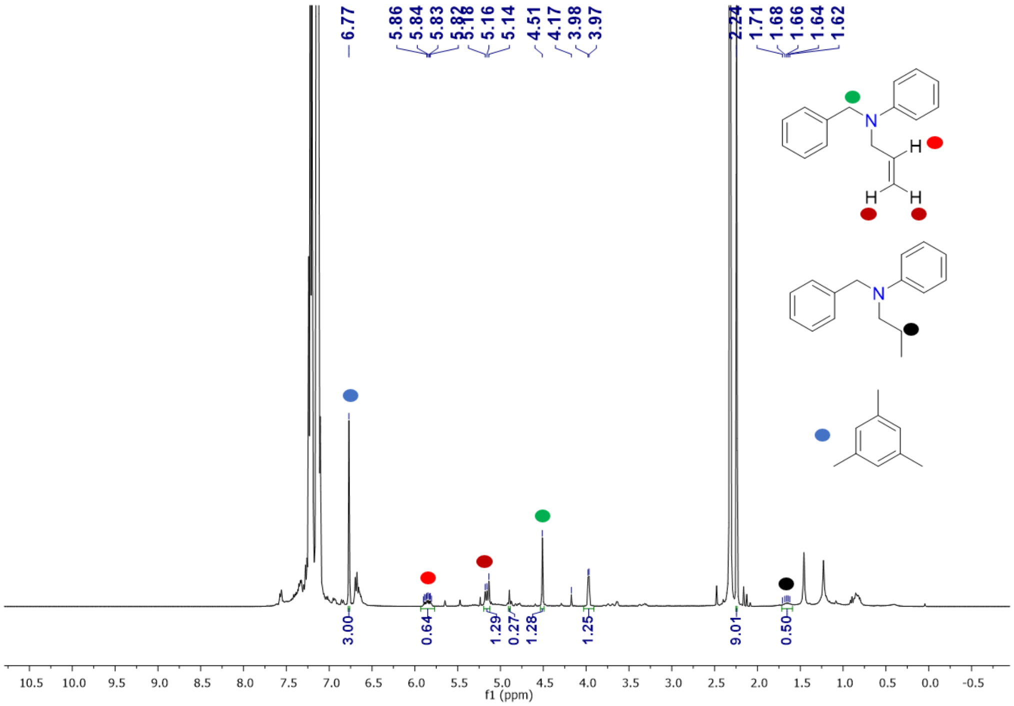


Figure S138. ^{1}H NMR spectrum of crude reaction mixture of hydrogenated product **5o’** measured in $CDCl_3$

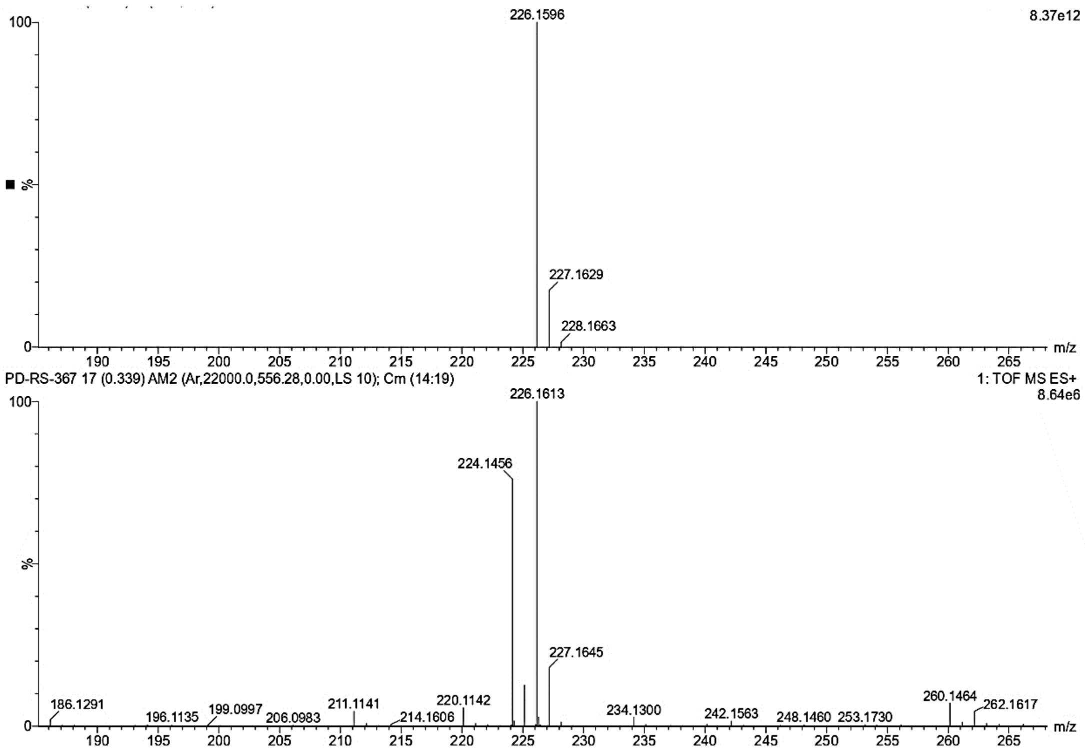


Figure S139. ESI-HRMS spectrum of **5o’** measured in methanol; (*top*, simulated; *bottom*, experimental)

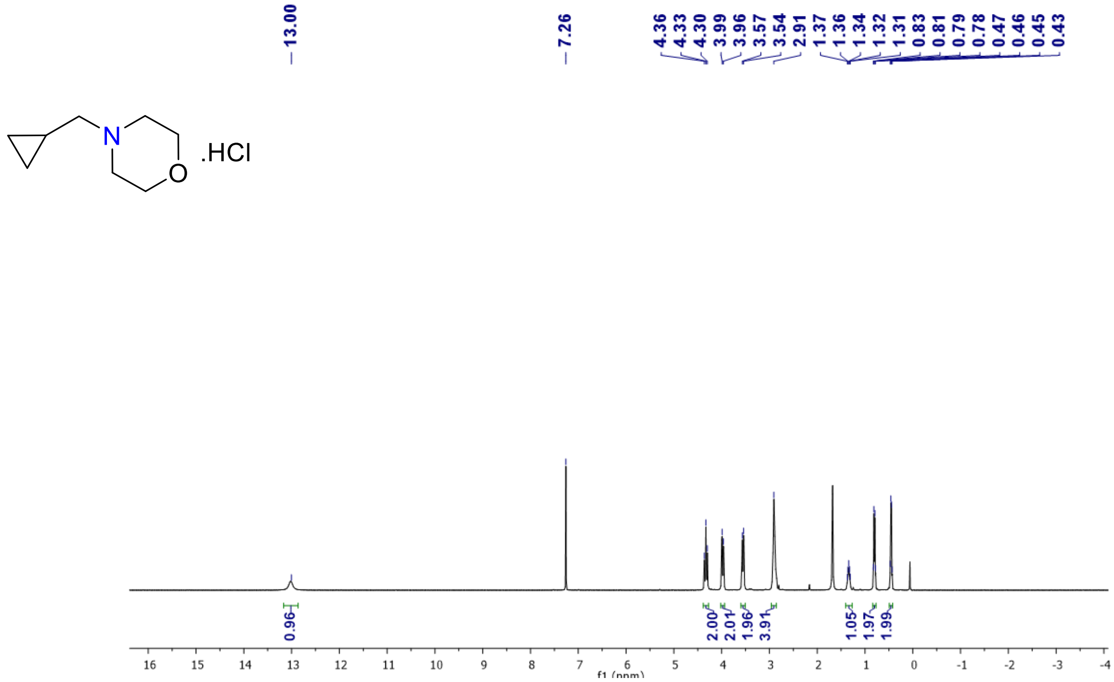


Figure S140. ^{1}H NMR spectrum of **5p** measured in $CDCl_3$

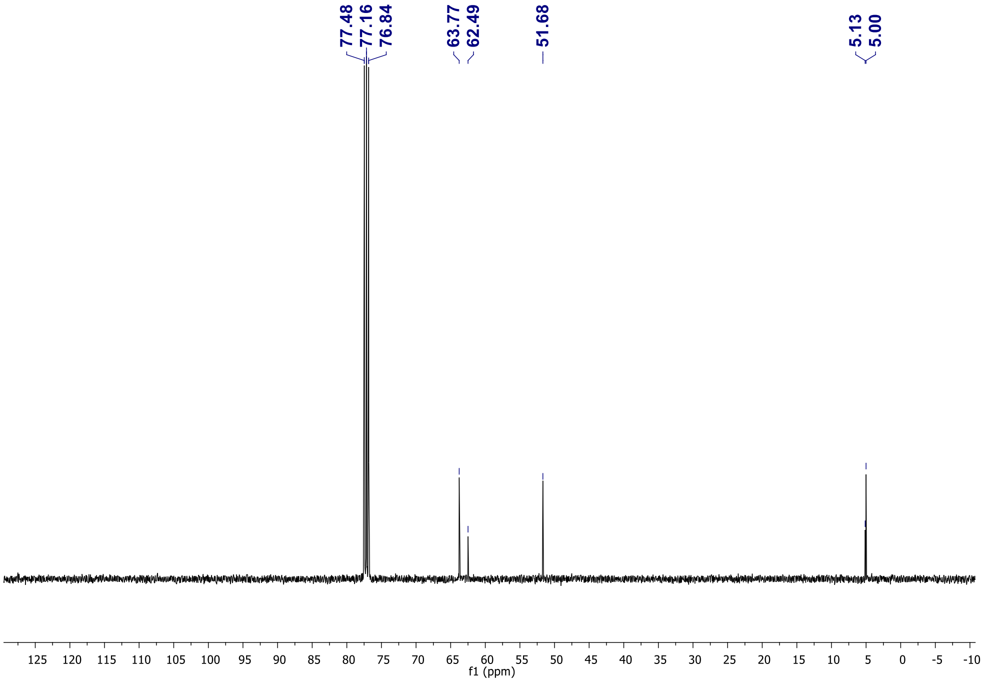


Figure S141. ^{13}C NMR spectrum of **5p** measured in $CDCl_3$

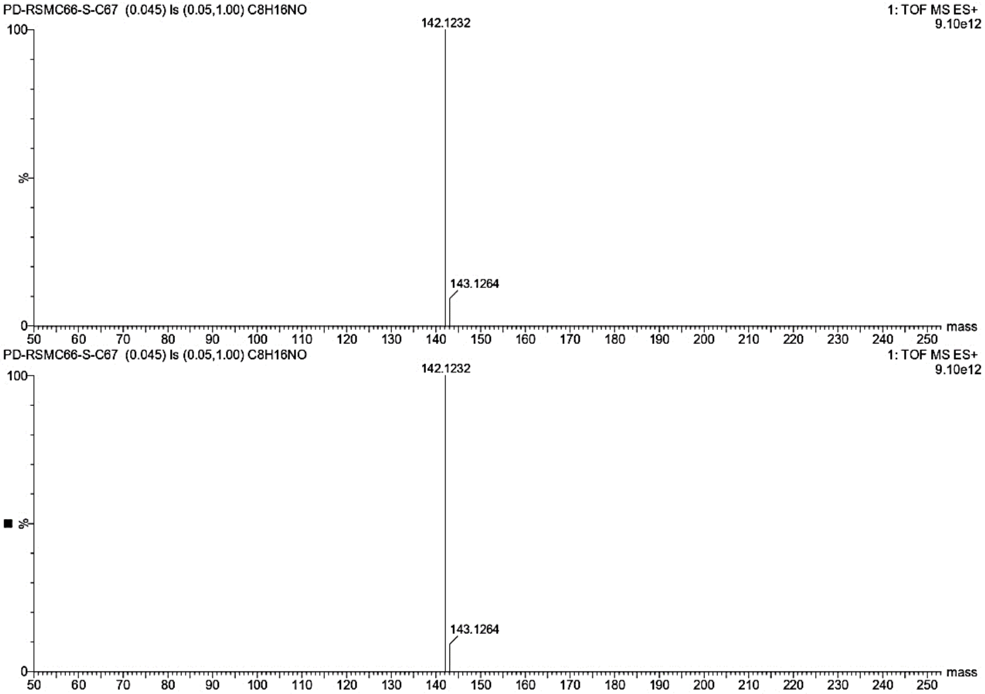


Figure S142. ESI-HRMS spectrum of **5p** measured in methanol; (*top*, simulated; *bottom*, experimental)

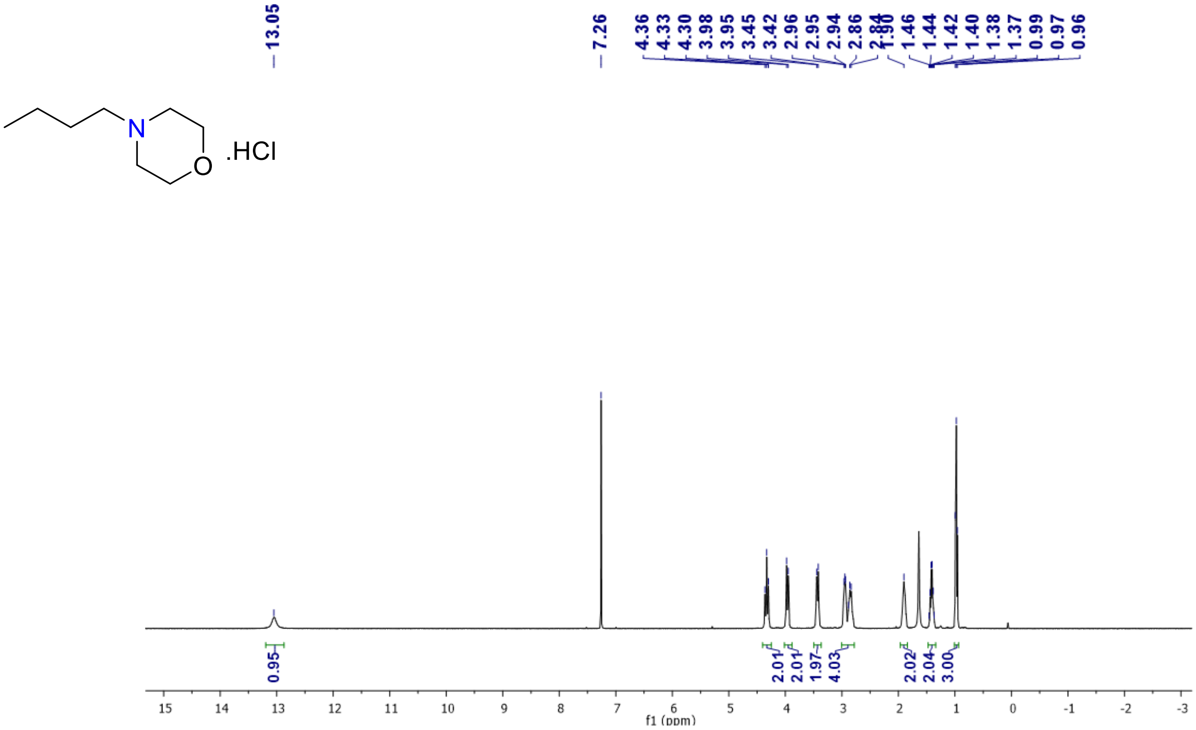


Figure S143. ^{1}H NMR spectrum of **5q** measured in $CDCl_3$

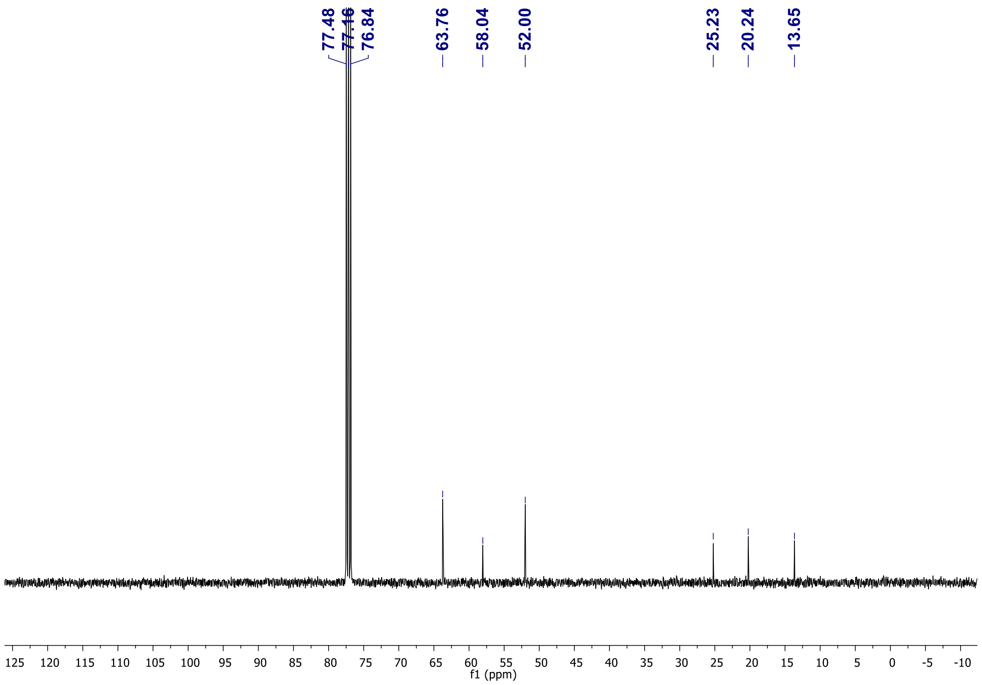


Figure S144. ^{13}C NMR spectrum of **5q** measured in CDCl$_3$

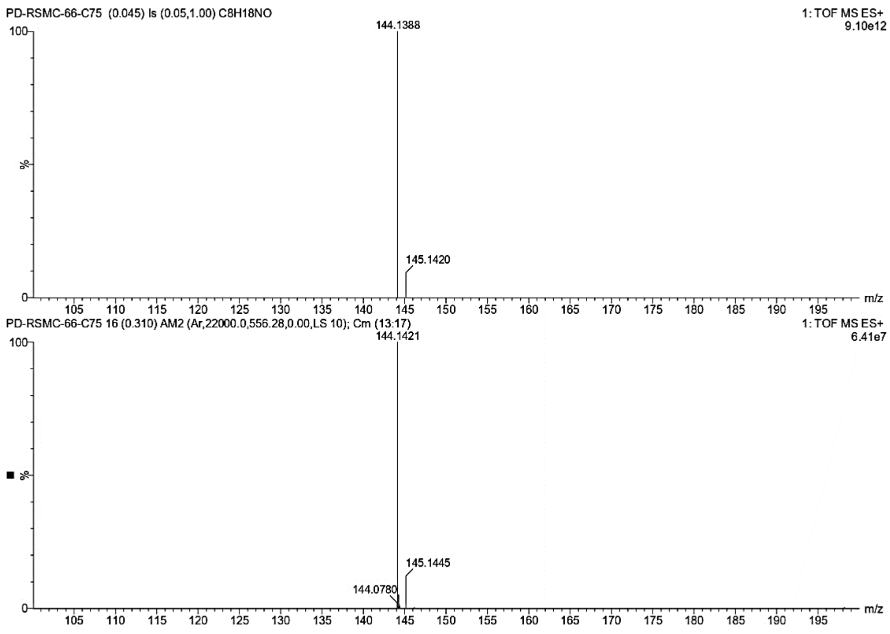


Figure S145. ESI-HRMS spectrum of **5q** measured in methanol; (*top*, simulated; *bottom*, experimental)

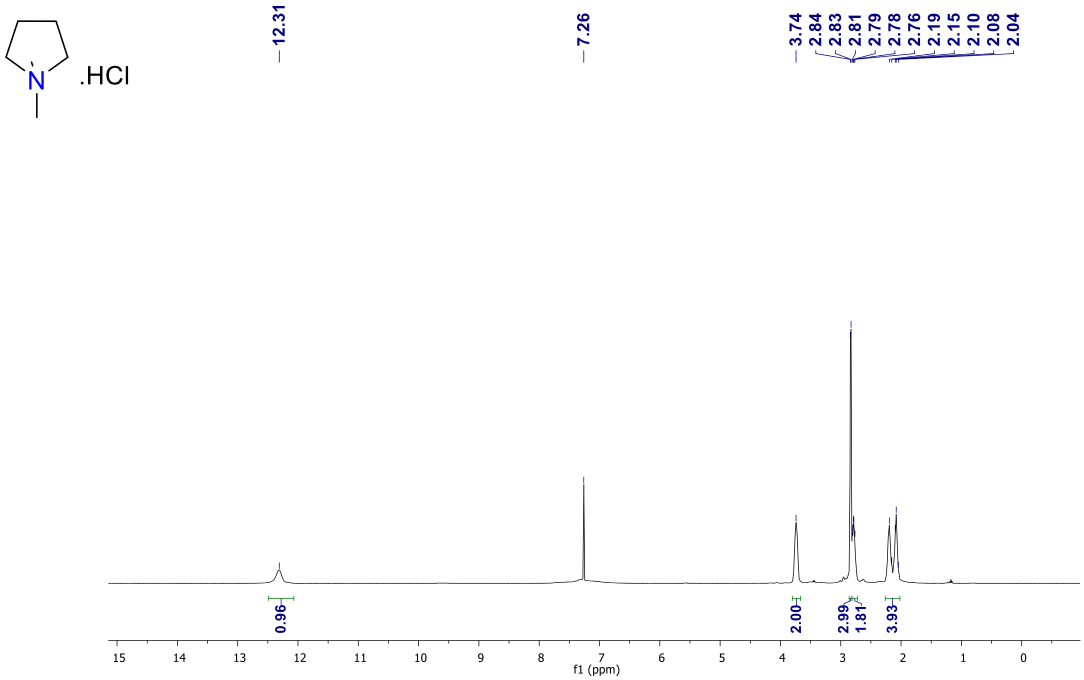


Figure S146. ^{1}H NMR spectrum of **5r** measured in CDCl$_3$

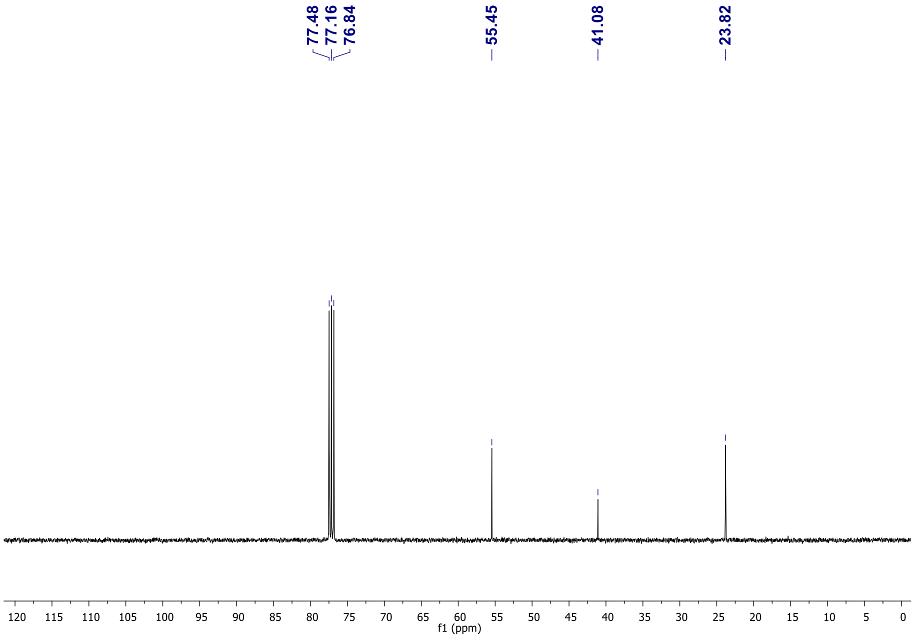


Figure S147. ^{13}C NMR spectrum of **5r** measured in CDCl$_3$

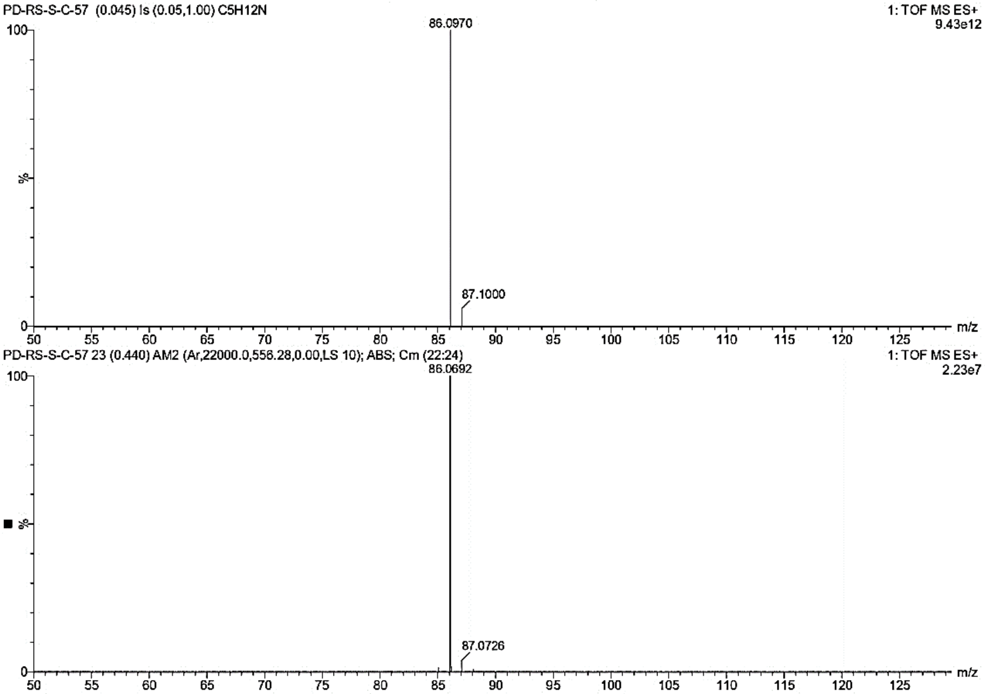


Figure S148. ESI-HRMS spectrum of **5r** measured in methanol; (*top*, simulated; *bottom*, experimental)

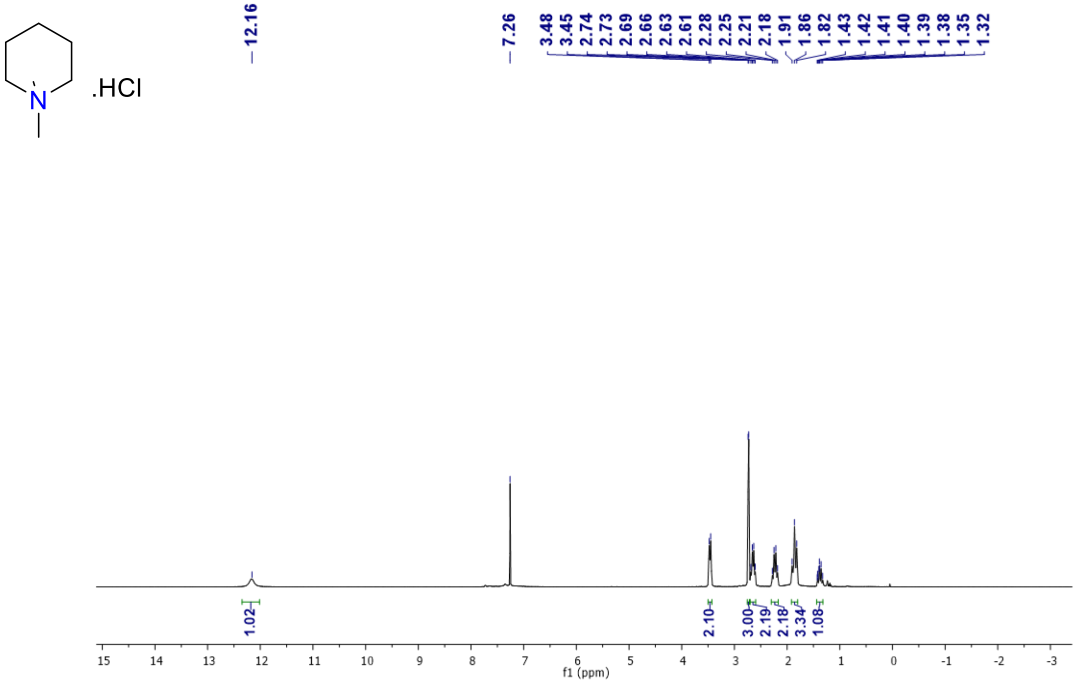


Figure S149. ^{1}H NMR spectrum of **5s** measured in $CDCl_3$

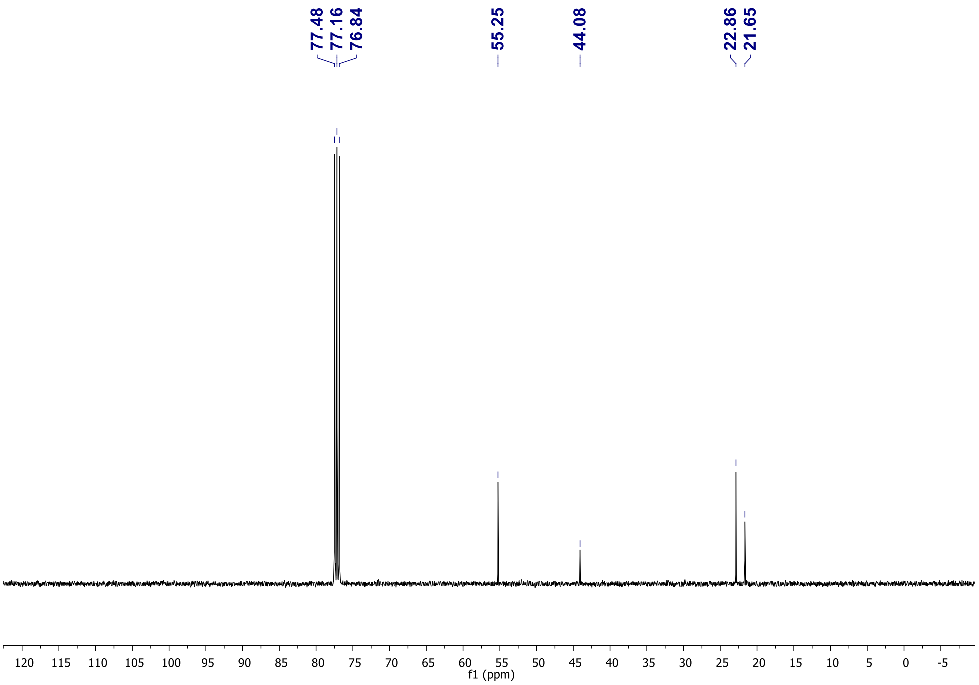


Figure S150. ^{13}C NMR spectrum of **5s** measured in CDCl$_3$

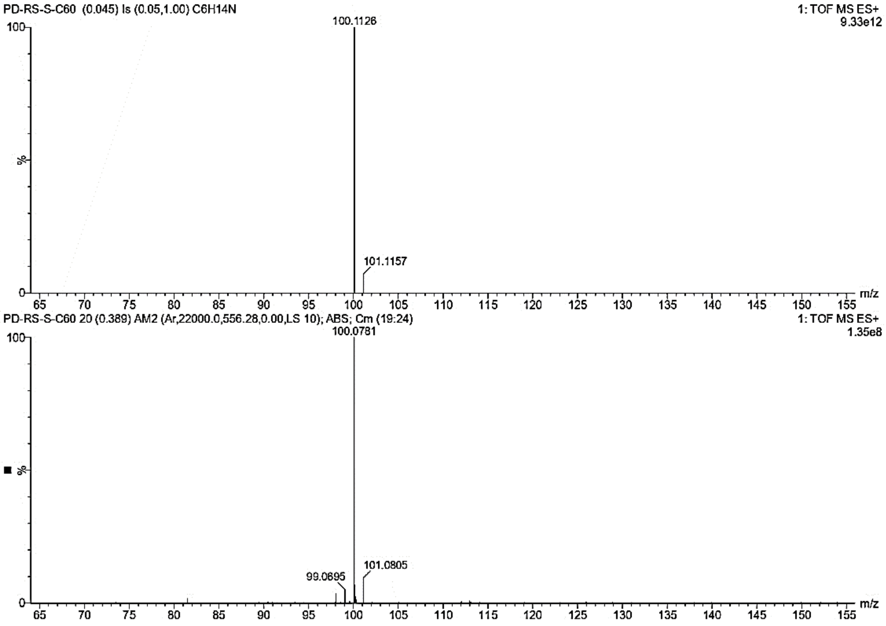
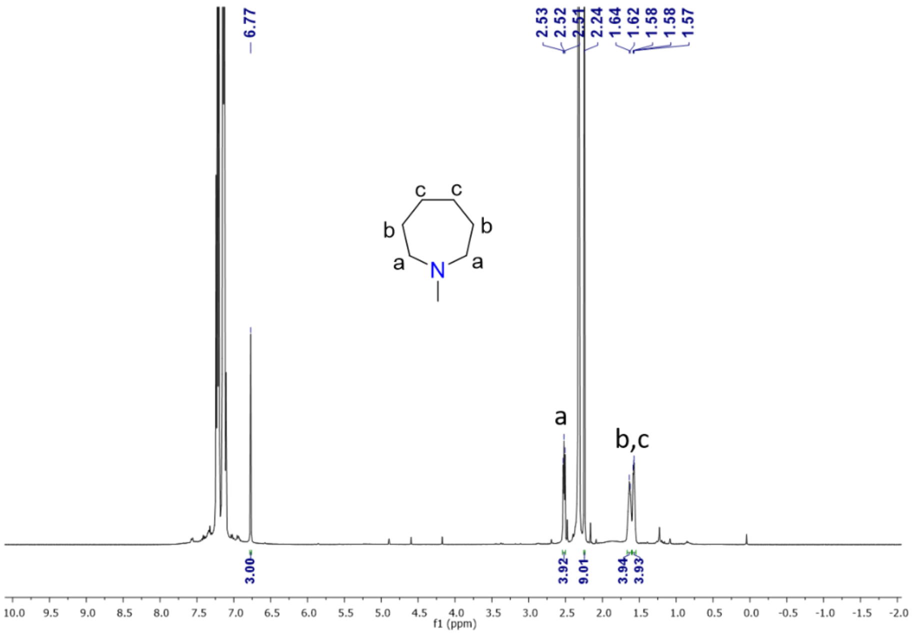


Figure S151. ESI-HRMS spectrum of **5s** measured in methanol; (*top*, simulated; *bottom*, experimental)



% NMR yield= 98%

Figure S152. ^{1}H NMR spectrum of crude reaction mixture of **5t** measured in $CDCl_3$

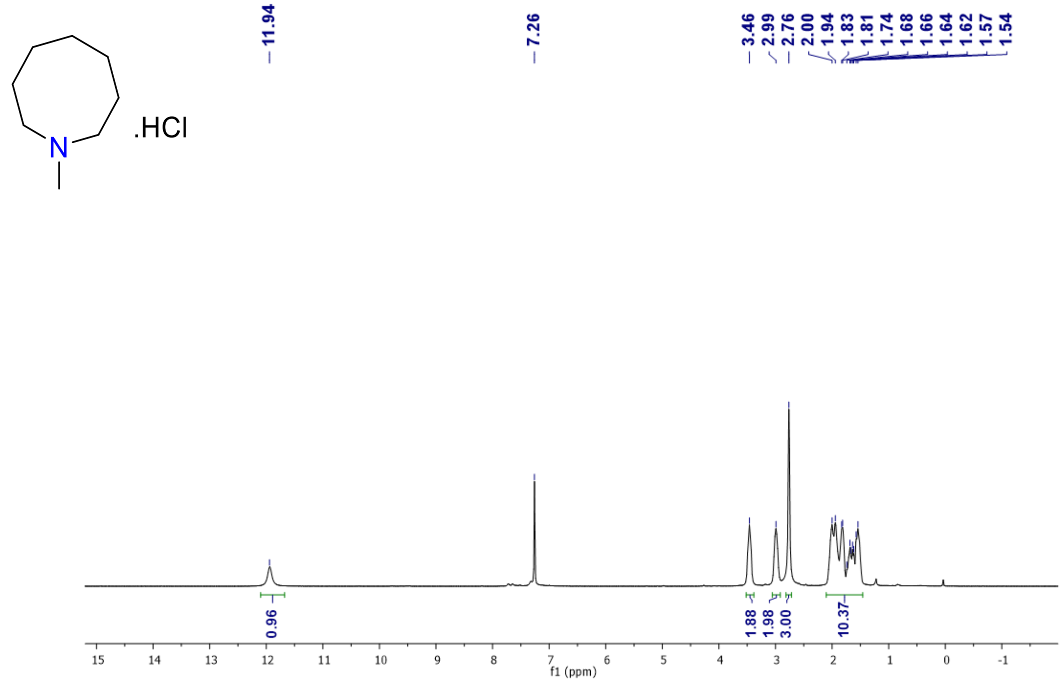


Figure S153. ^{1}H NMR spectrum of **5u** measured in $CDCl_3$

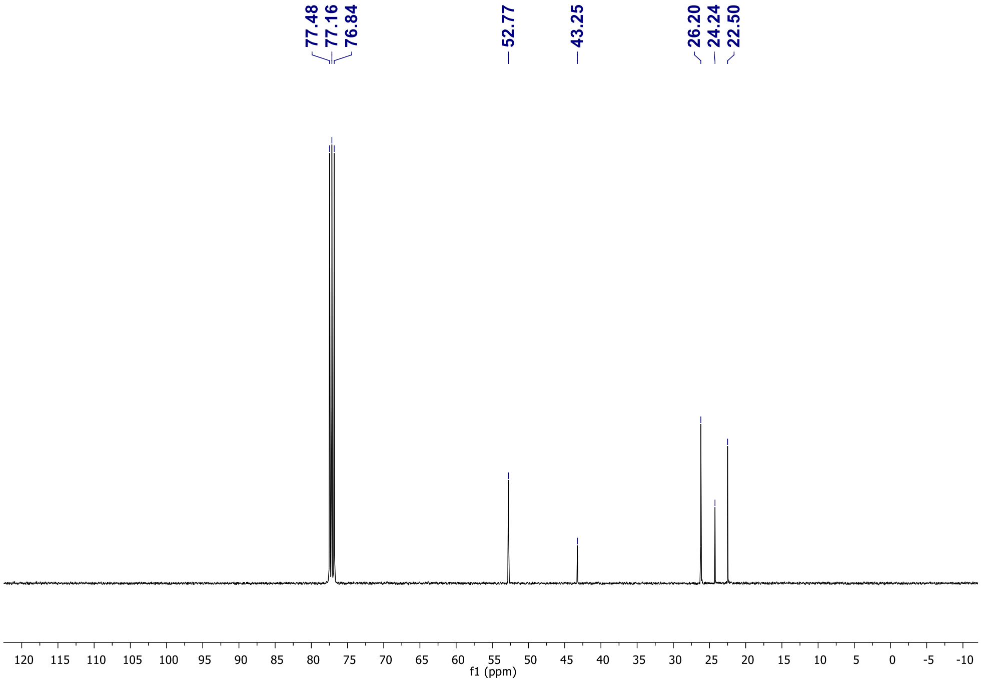


Figure S154. ^{13}C NMR spectrum of **5u** measured in $CDCl_3$

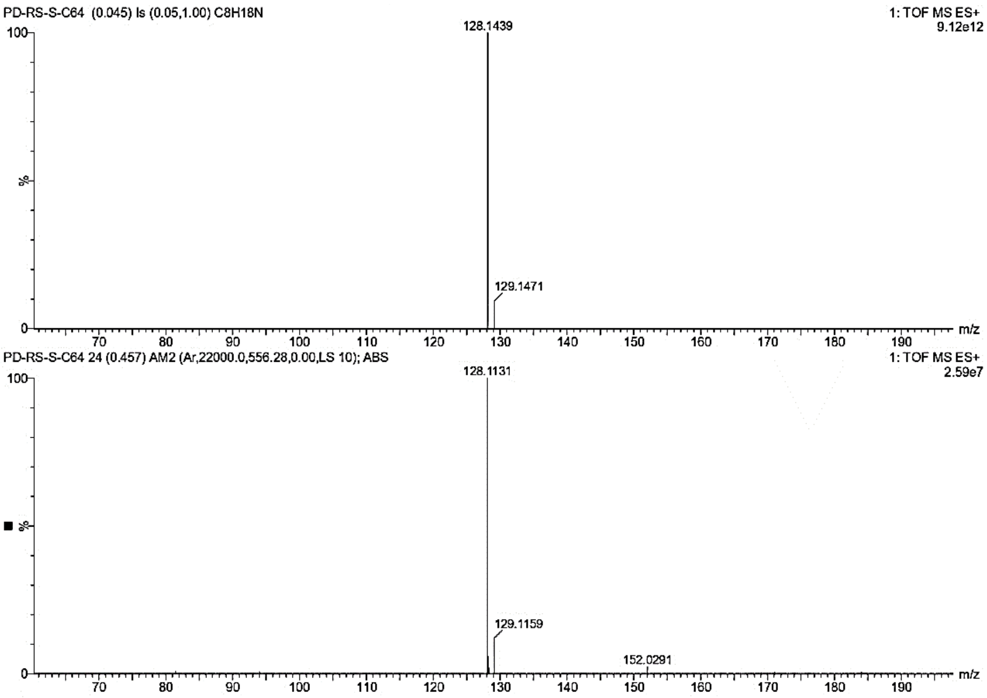
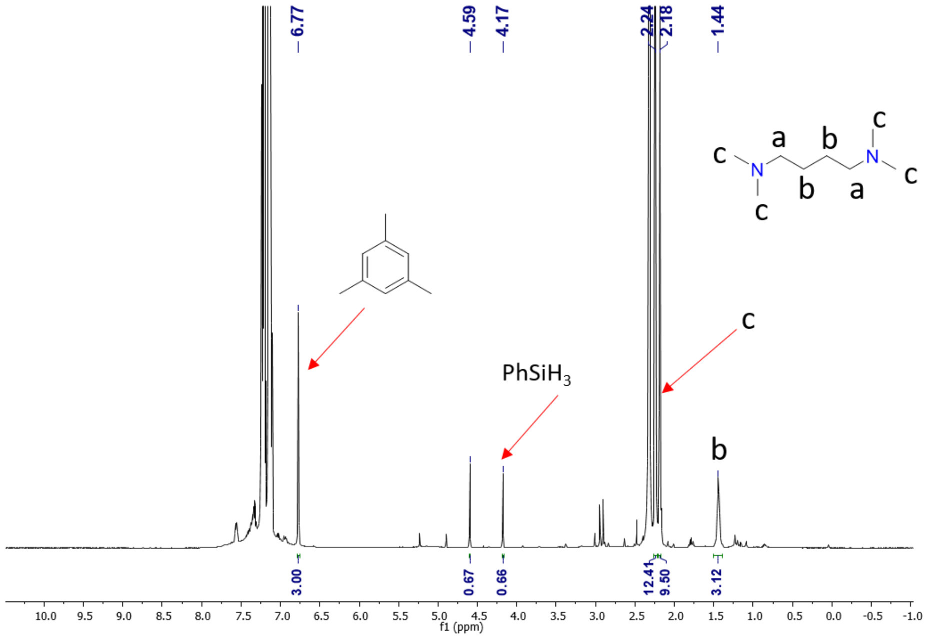


Figure S155. ESI-HRMS spectrum of **5u** measured in methanol; (*top*, simulated; *bottom*, experimental)



% NMR Yield= 78%

Figure S156. ^{1}H NMR spectrum of crude reaction mixture of **5v** measured in $CDCl_3$

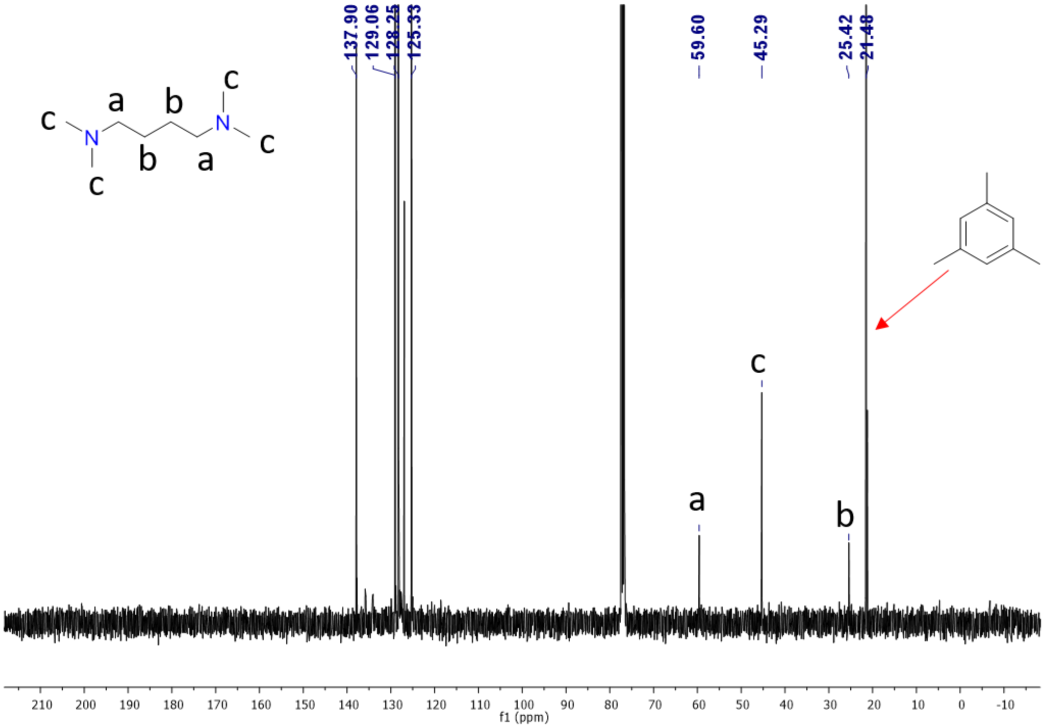
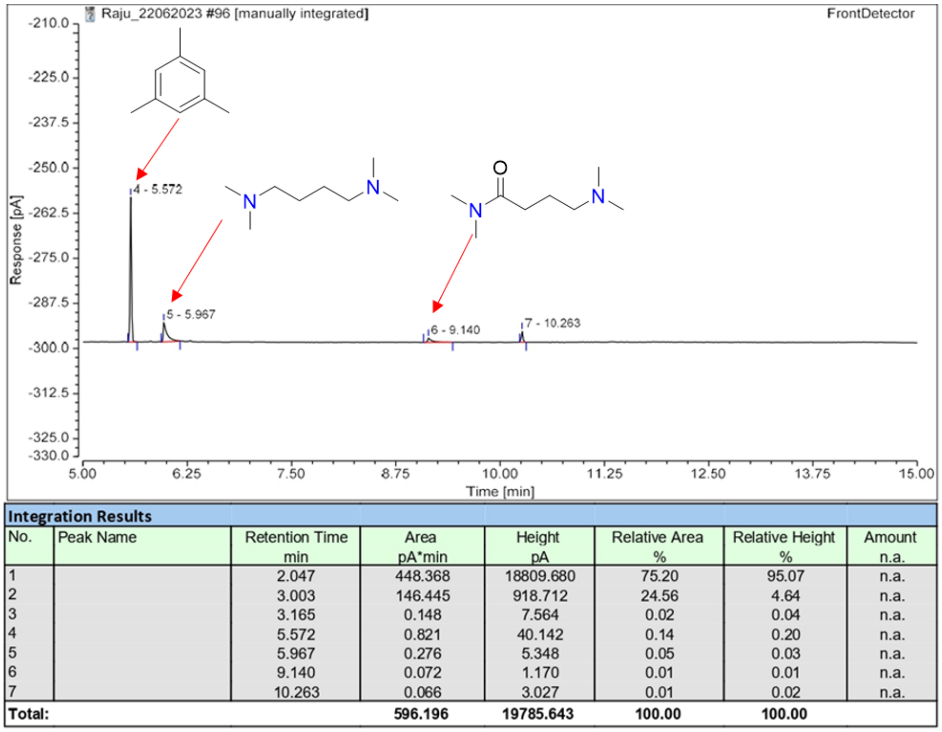


Figure S157. ^{13}C NMR spectrum of crude reaction mixture of **5v** measured in $CDCl_3$



Integration Results

No.	Peak Name	Retention Time min	Area pA*min	Height pA	Relative Area %	Relative Height %	Amount n.a.
1		2.047	448.368	18809.680	75.20	95.07	n.a.
2		3.003	146.445	918.712	24.56	4.64	n.a.
3		3.165	0.148	7.564	0.02	0.04	n.a.
4		5.572	0.821	40.142	0.14	0.20	n.a.
5		5.967	0.276	5.348	0.05	0.03	n.a.
6		9.140	0.072	1.170	0.01	0.01	n.a.
7		10.263	0.066	3.027	0.01	0.02	n.a.
Total:			**596.196**	**19785.643**	**100.00**	**100.00**	

Figure S158. GC-MS spectrum of crude reaction mixture of **5v**

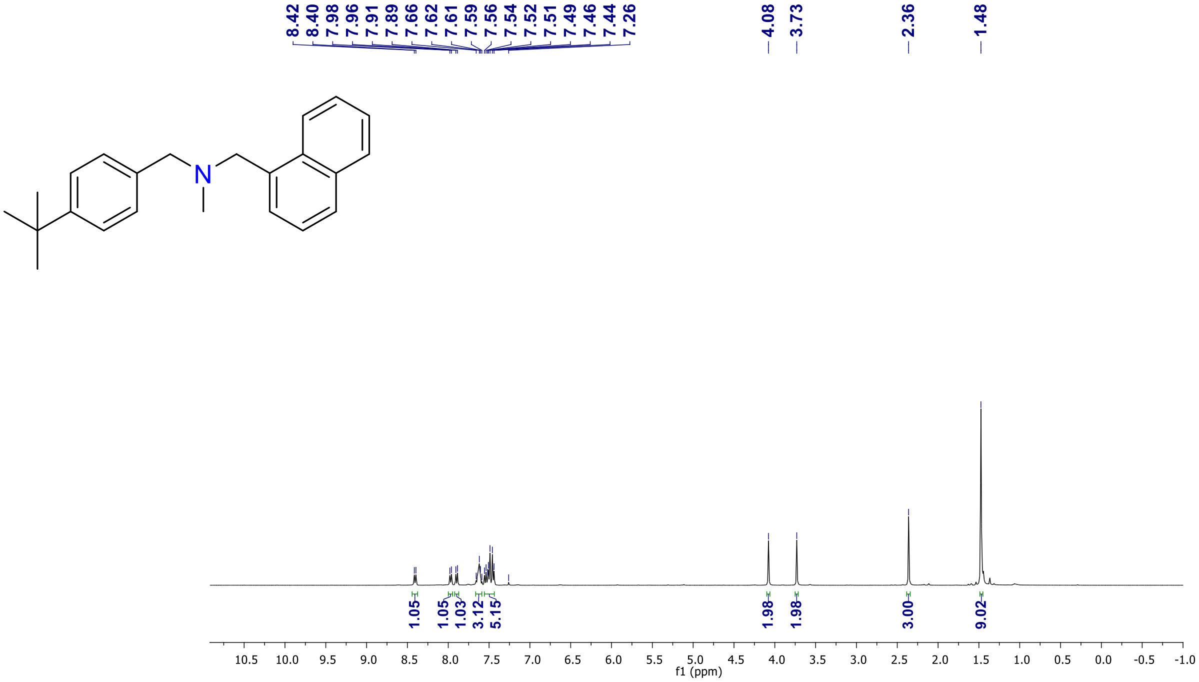


Figure S159. ^{1}H NMR spectrum of butenafine (**5x)** measured in CDCl$_3$

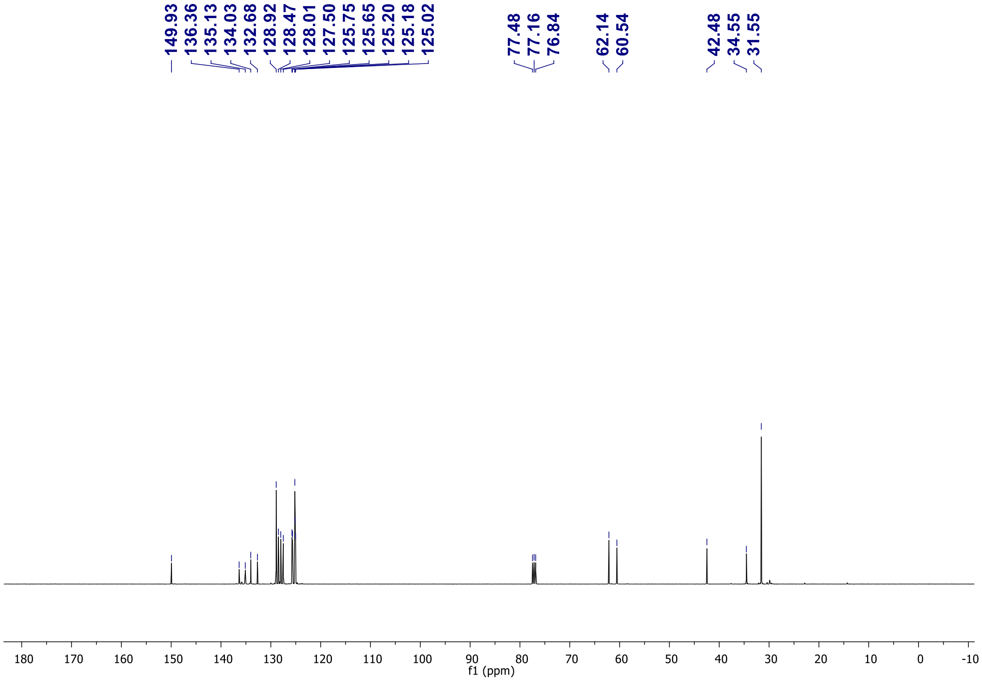


Figure S160. ^{13}C NMR spectrum of butenafine (**5x**) measured in C DCl$_3$

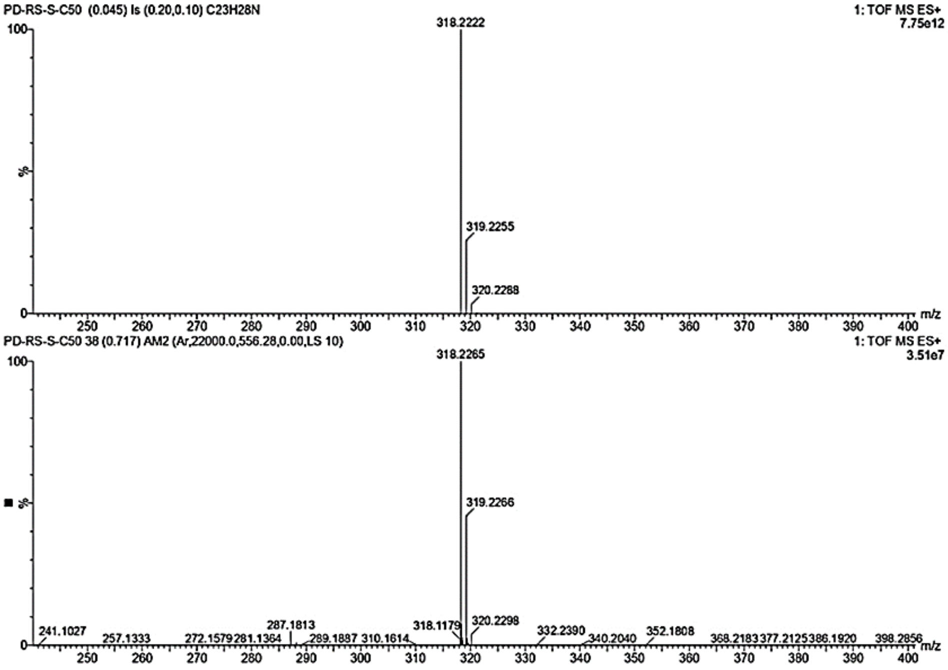


Figure S161. ESI-HRMS spectrum of **5x** measured in methanol; (*top*, simulated; *bottom*, experimental)

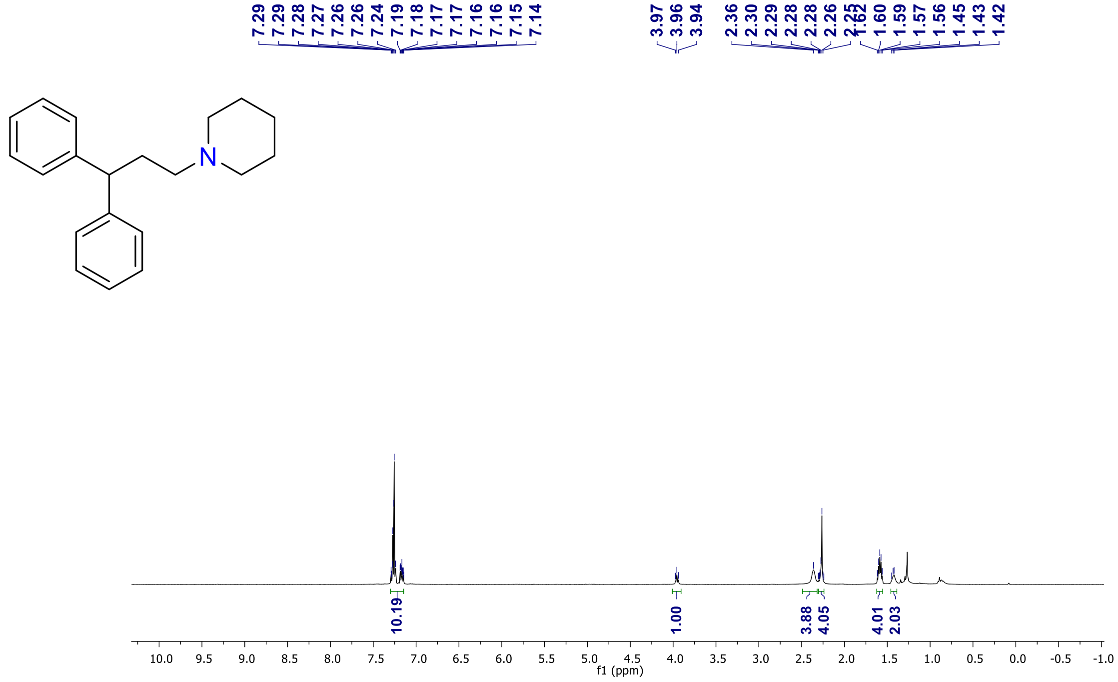


Figure S162. ^{1}H NMR spectrum of fenpiprane (**5y**) measured in $CDCl_3$

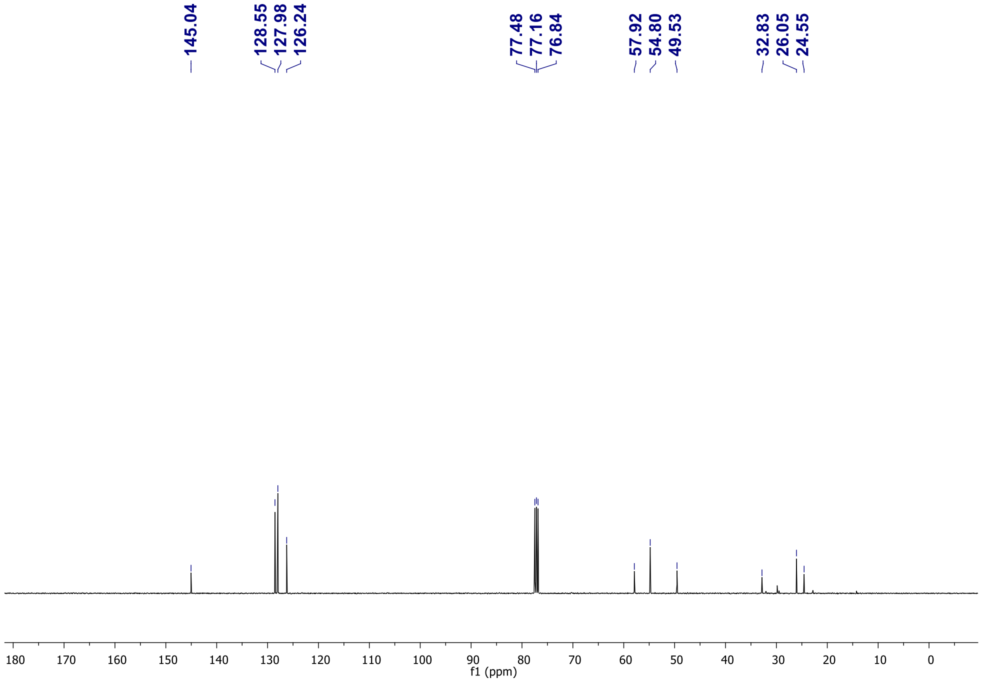


Figure S163. ^{13}C NMR spectrum of fenpiprane (**5y**) measured in $CDCl_3$

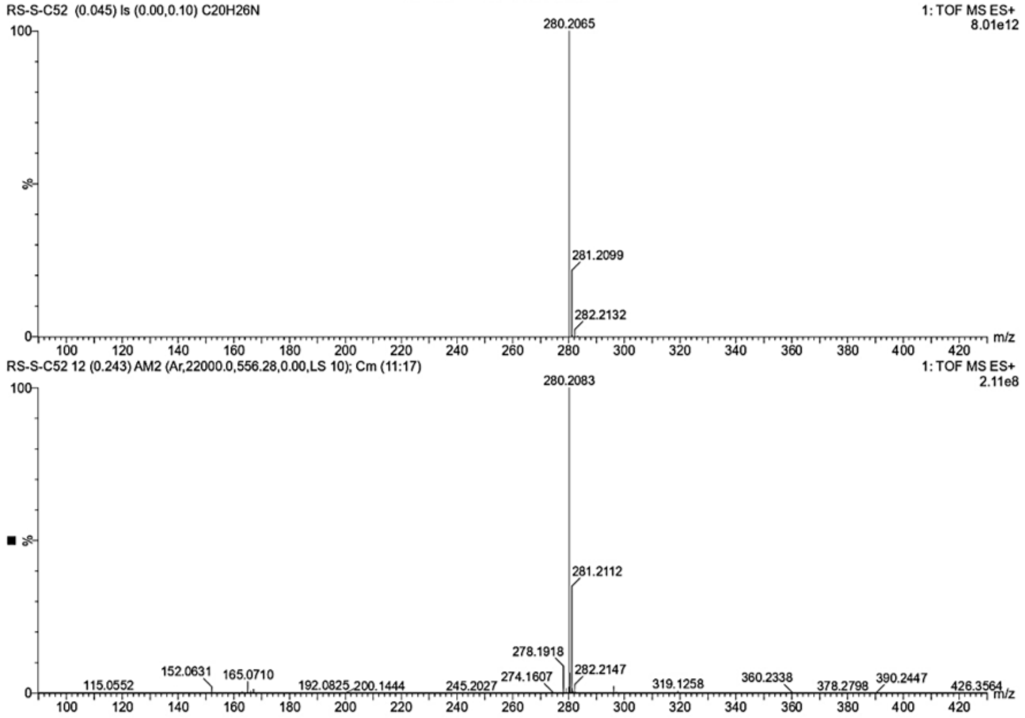


Figure S164. ESI-HRMS spectrum of **5y** measured in methanol; (*top*, simulated; *bottom*, experimental)

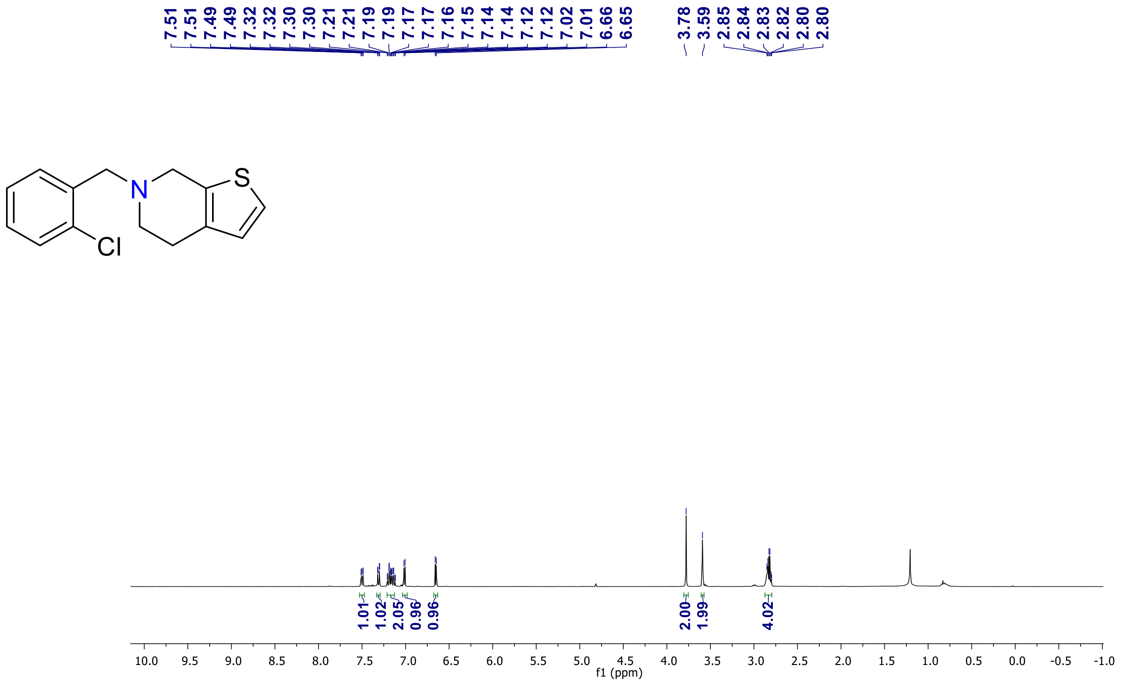


Figure S165. ^{1}H NMR spectrum of ticlopidine (**5z)** measured in $CDCl_3$

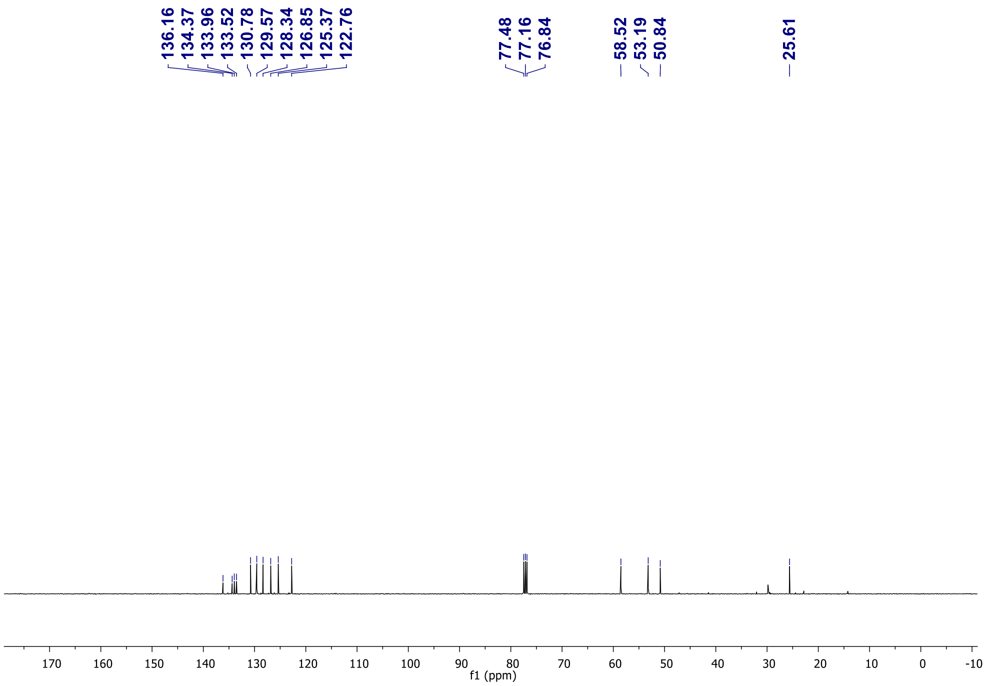


Figure S166. ^{13}C NMR spectrum of ticlopidine (**5z**) measured in $CDCl_3$

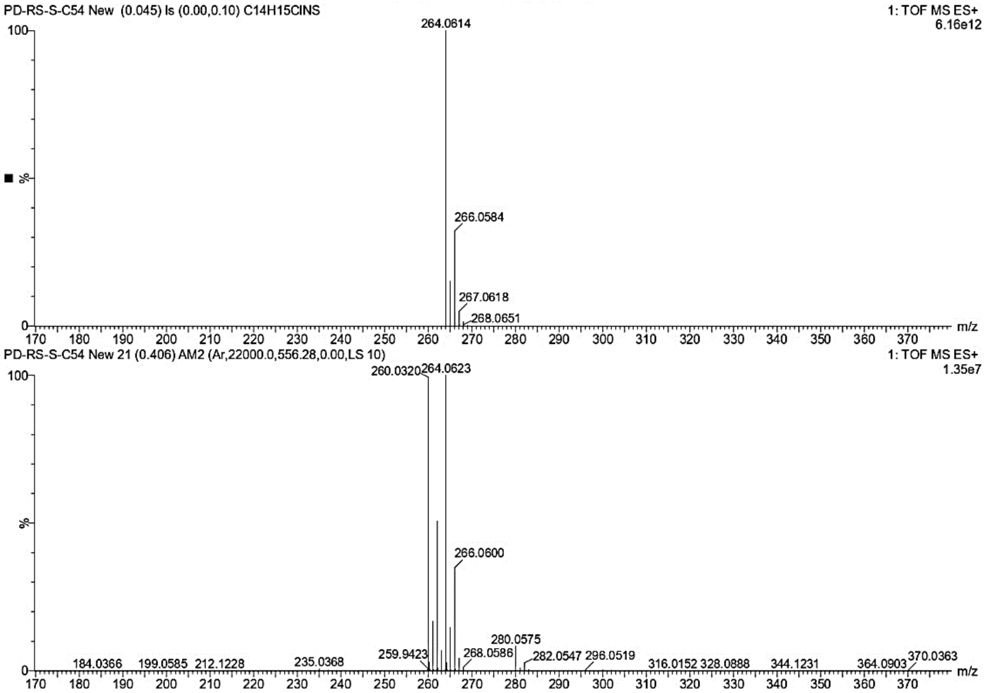


Figure S167. ESI-HRMS spectrum of **5z** measured in methanol; (*top*, simulated; *bottom*, experimental)

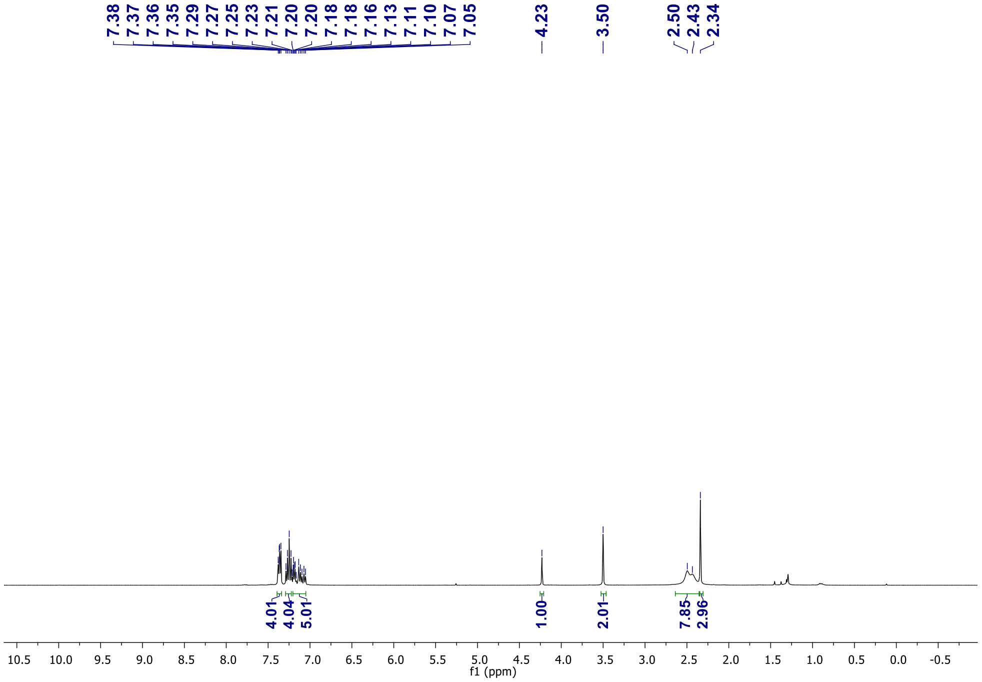


Figure S168. ^{1}H NMR spectrum of meclizine (**5z'**) measured in CDCl$_3$

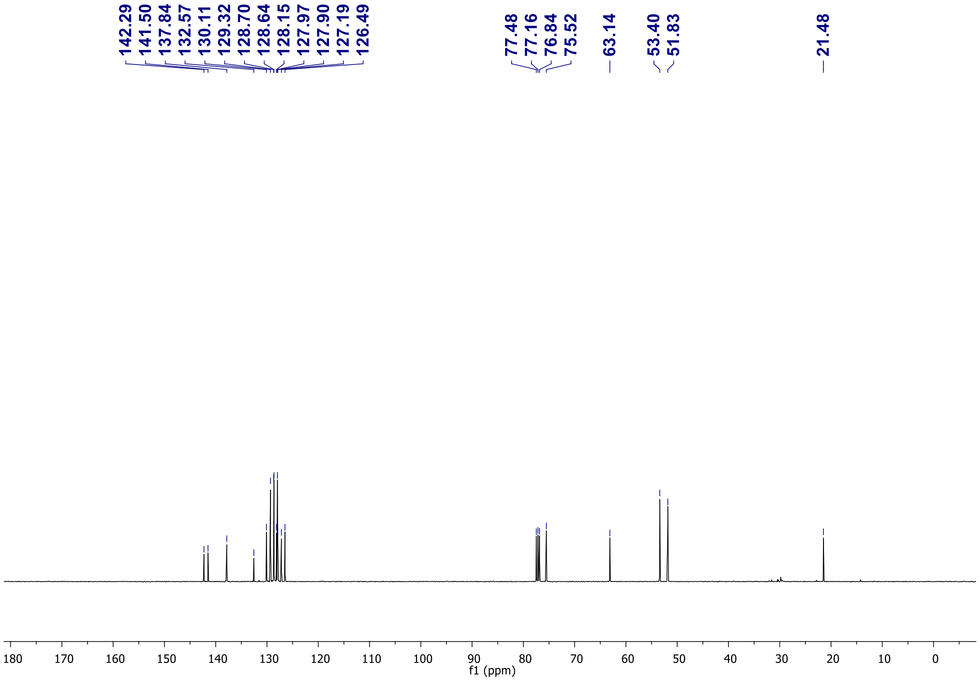


Figure S169. ^{13}C NMR spectrum of meclizine (**5z'**) measured in CDCl$_3$

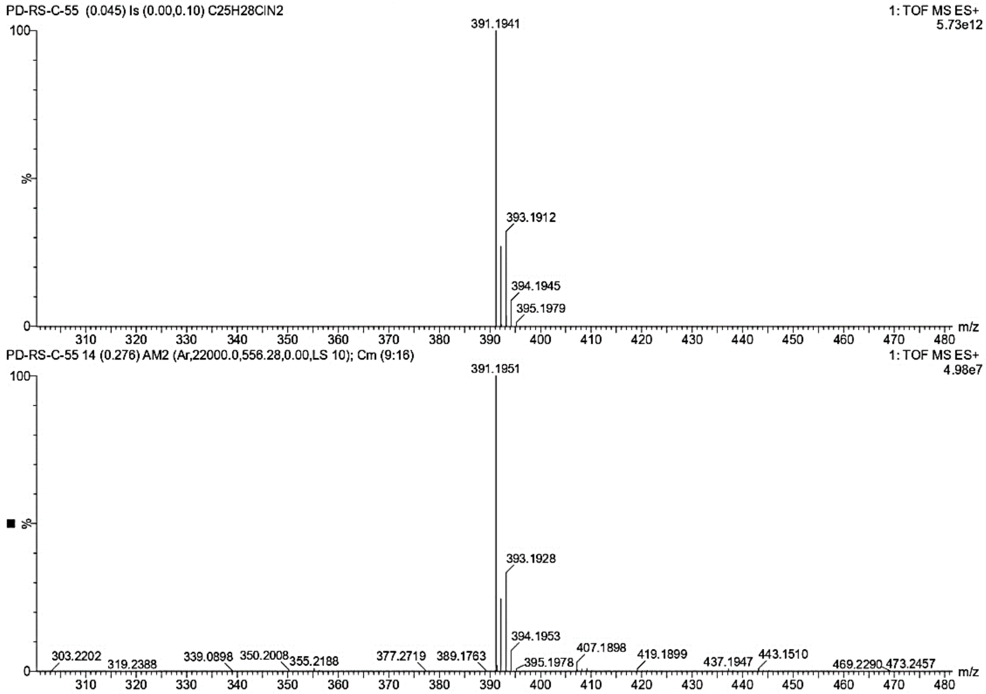
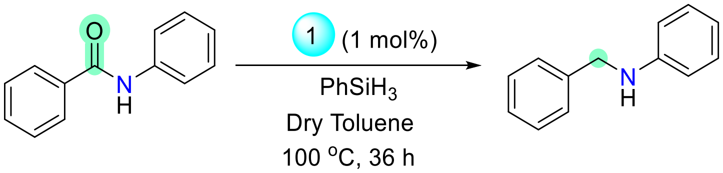
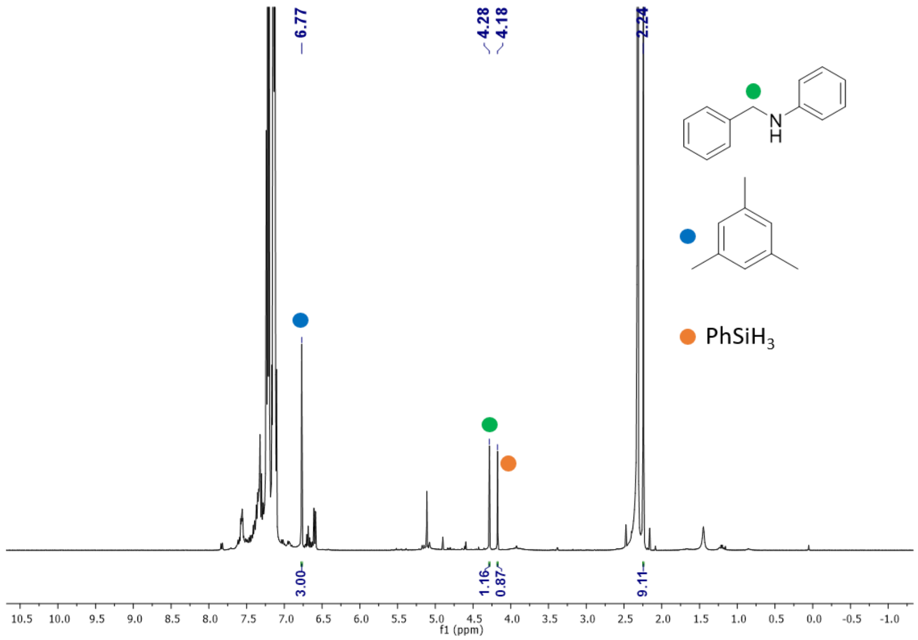


Figure S170. ESI-HRMS spectrum of **5z'** measured in methanol; (*top*, simulated; *bottom*, experimental)

19. Deoxygenative hydrogenation of secondary amide

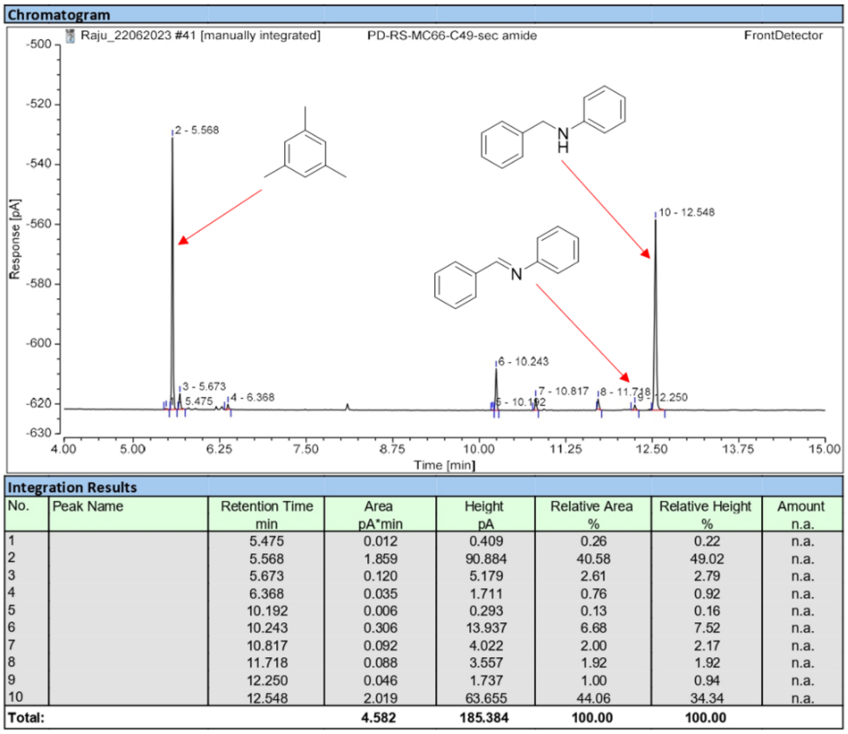


Inside a glove box, a 25 mL pressure tube equipped with a magnetic stirring bar was charged with **1** (3.53 mg , 1 mol%) and N-Phenylbenzamide (99.2 mg, 0.503 mmol). 1 mL of dry toluene was added followed by the addition of 124 μL of phenylsilane (108.9 mg, 1.006 mmol) and the closed vessel was heated at 100 ºC for 36 hours. The solution was cooled to room temperature and 70 μL of mesitylene (60.5 mg, 0.503 mmol) was added as internal standard and yield was analyzed using ^{1}H NMR in $CDCl_3$ which yielded 0.291 mmol (58 %) of desired deoxygenated amine product.



NMR Yield of N-Benzylaniline = 58%

Figure S171. ^{1}H NMR spectrum of deoxygenative hydrogenation of N-phenylbenzamide catalyzed by complex **1** in CDCl$_3$



Integration Results

No.	Peak Name	Retention Time min	Area pA*min	Height pA	Relative Area %	Relative Height %	Amount n.a.
1		5.475	0.012	0.409	0.26	0.22	n.a.
2		5.568	1.859	90.884	40.58	49.02	n.a.
3		5.673	0.120	5.179	2.61	2.79	n.a.
4		6.368	0.035	1.711	0.76	0.92	n.a.
5		10.192	0.006	0.293	0.13	0.16	n.a.
6		10.243	0.306	13.937	6.68	7.52	n.a.
7		10.817	0.092	4.022	2.00	2.17	n.a.
8		11.718	0.088	3.557	1.92	1.92	n.a.
9		12.250	0.046	1.737	1.00	0.94	n.a.
10		12.548	2.019	63.655	44.06	34.34	n.a.
Total:			**4.582**	**185.384**	**100.00**	**100.00**	

Figure S172. GC-MS spectrum of reaction mixture of N-phenylbenzamide hydrogenation

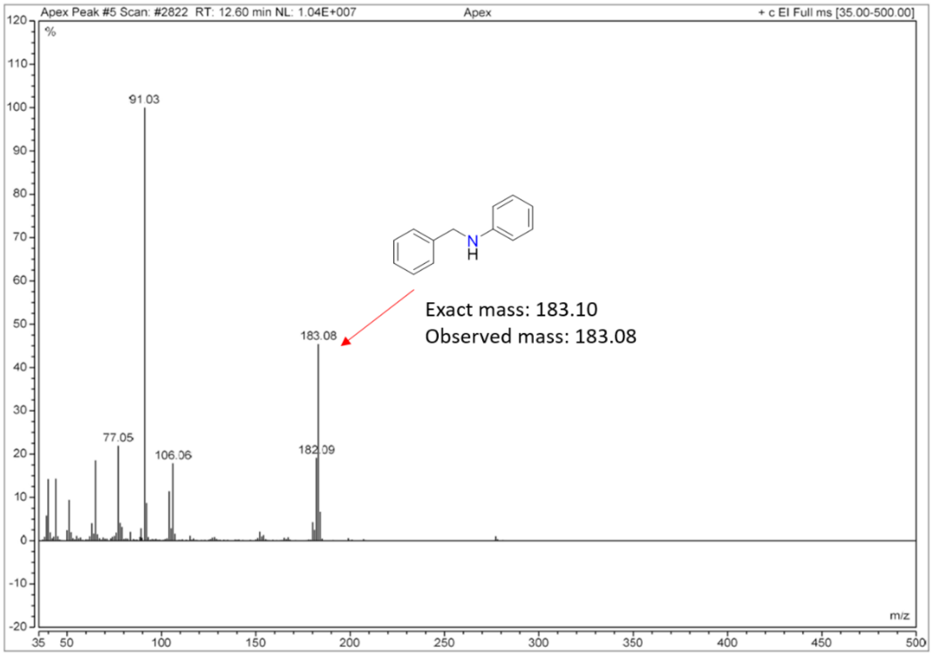


Figure S173. Mass pattern of GC-MS spectrum for N-benzylaniline

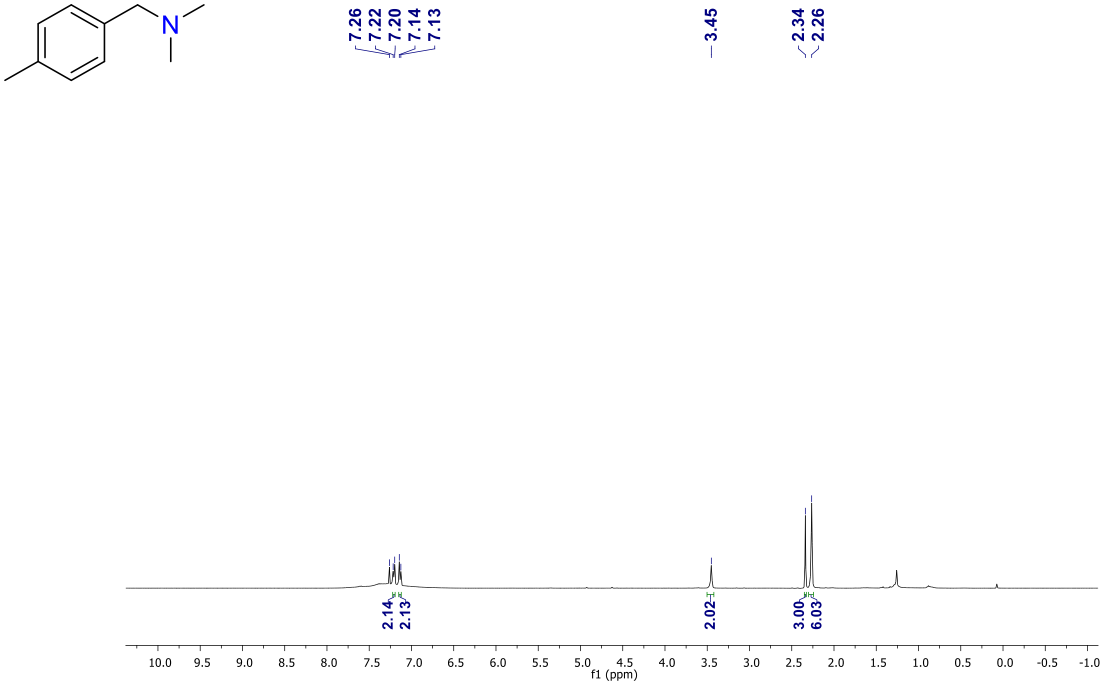


Figure S174. ^{1}H NMR spectrum of **7b** measured in $CDCl_3$

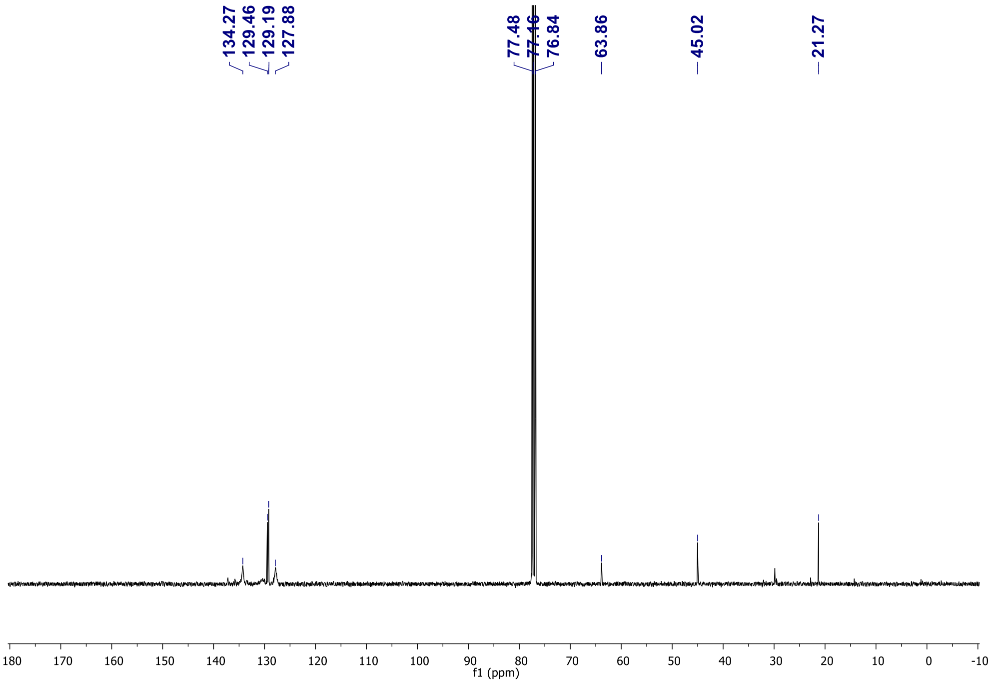


Figure S175. ^{13}C NMR spectrum **7b** measured in $CDCl_3$

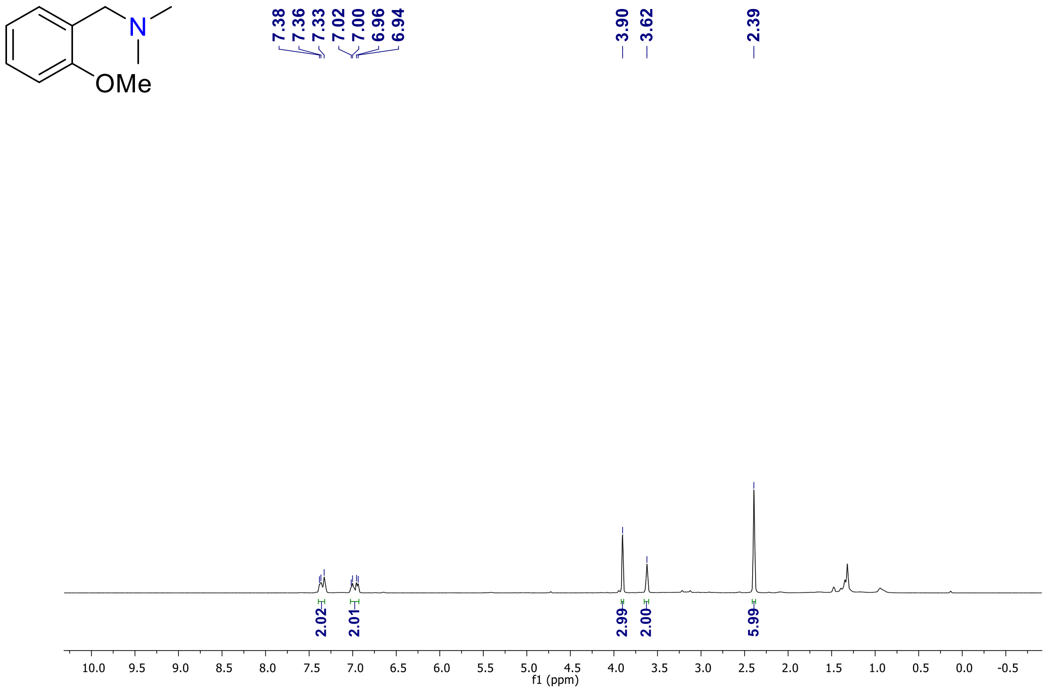


Figure S176. ^{1}H NMR spectrum of **7c** measured in $CDCl_3$

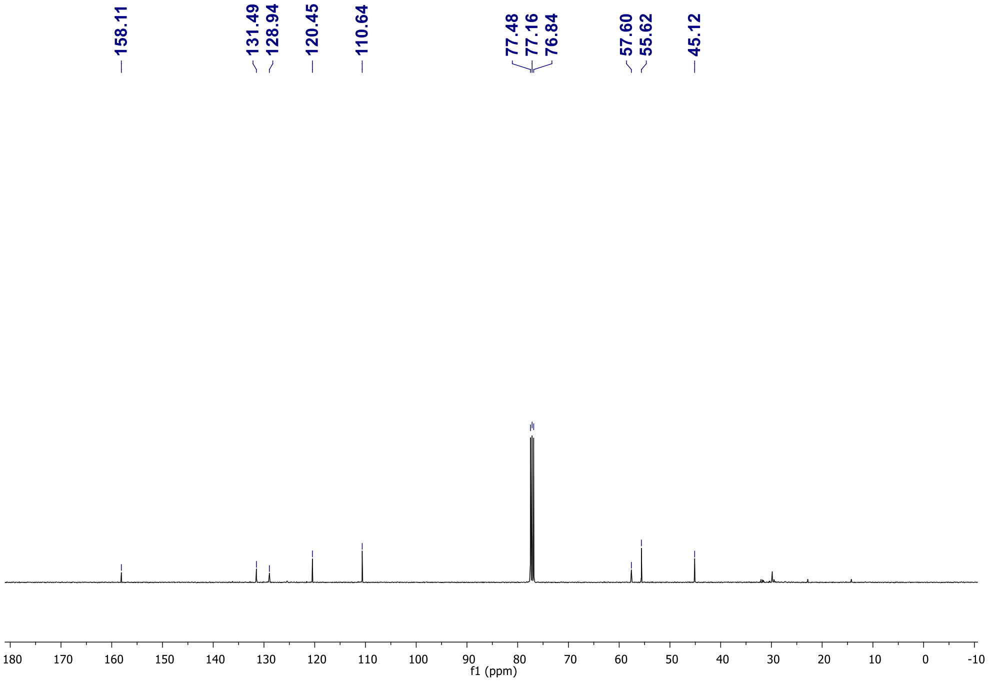


Figure S177. ^{13}C NMR spectrum **7c** measured in $CDCl_3$

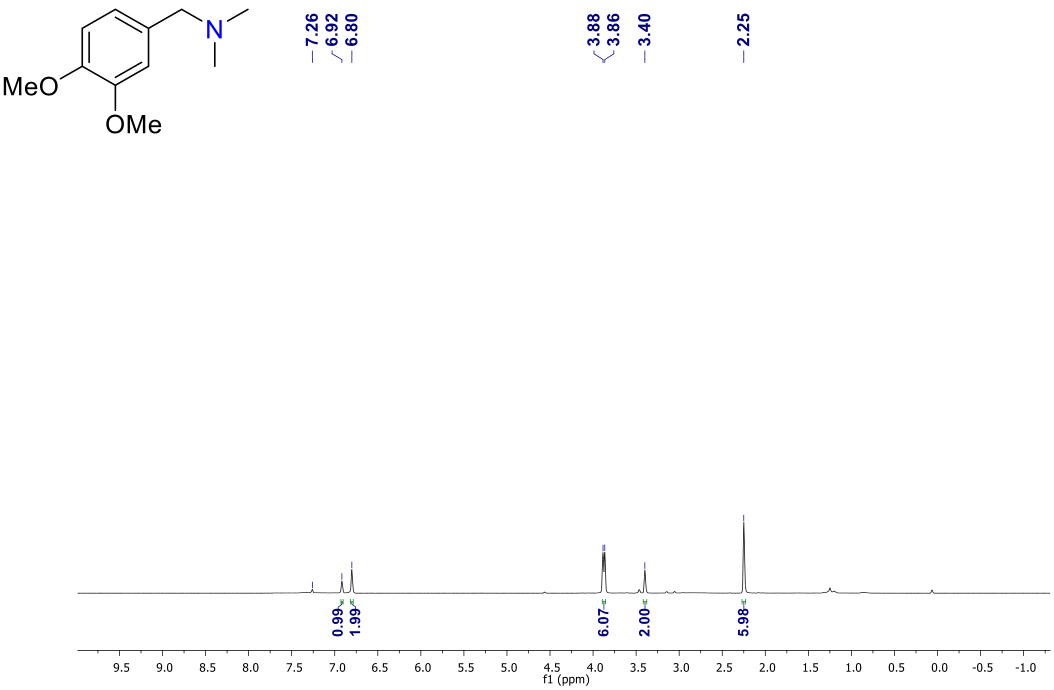


Figure S178. ^{1}H NMR spectrum of **7d** measured in $CDCl_3$

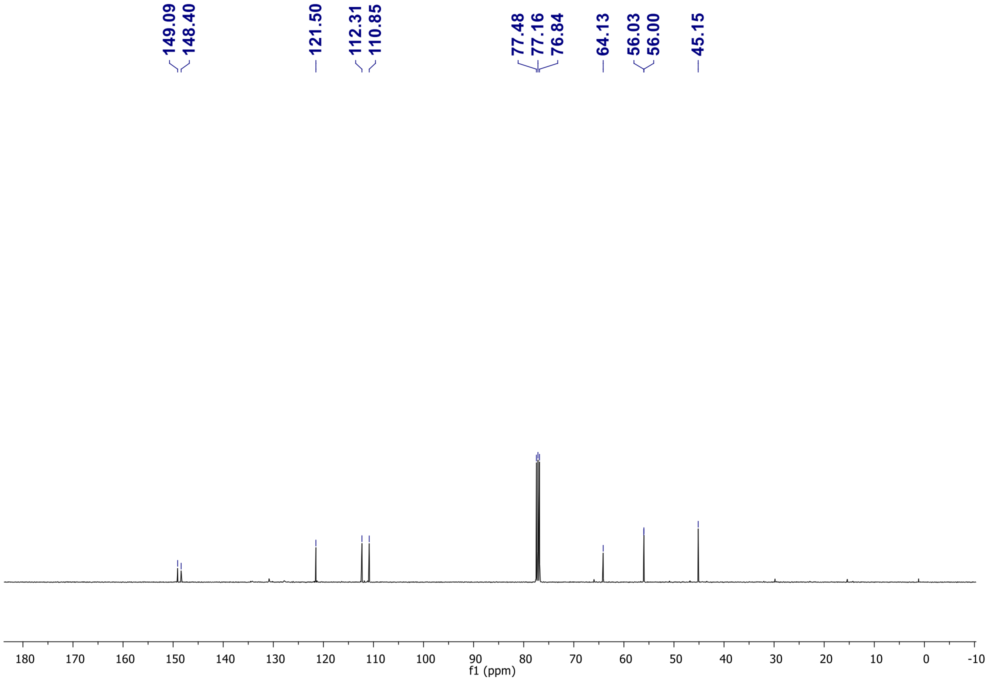


Figure S179. ^{13}C NMR spectrum **7d** measured in $CDCl_3$

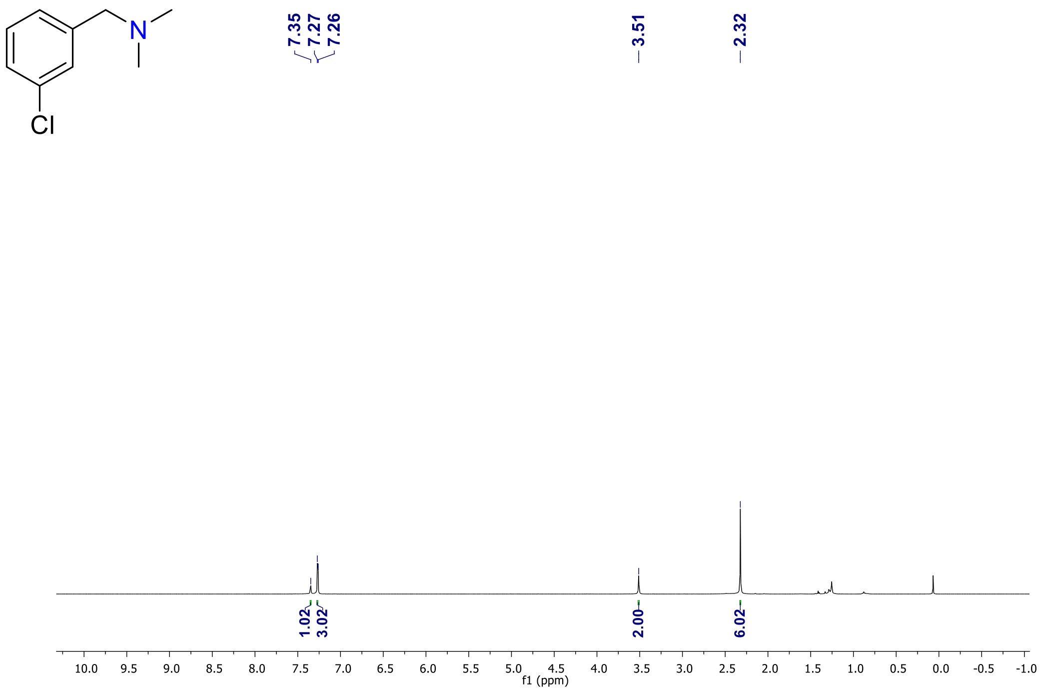


Figure S180. ^{1}H NMR spectrum of **7e** measured in CDCl$_3$

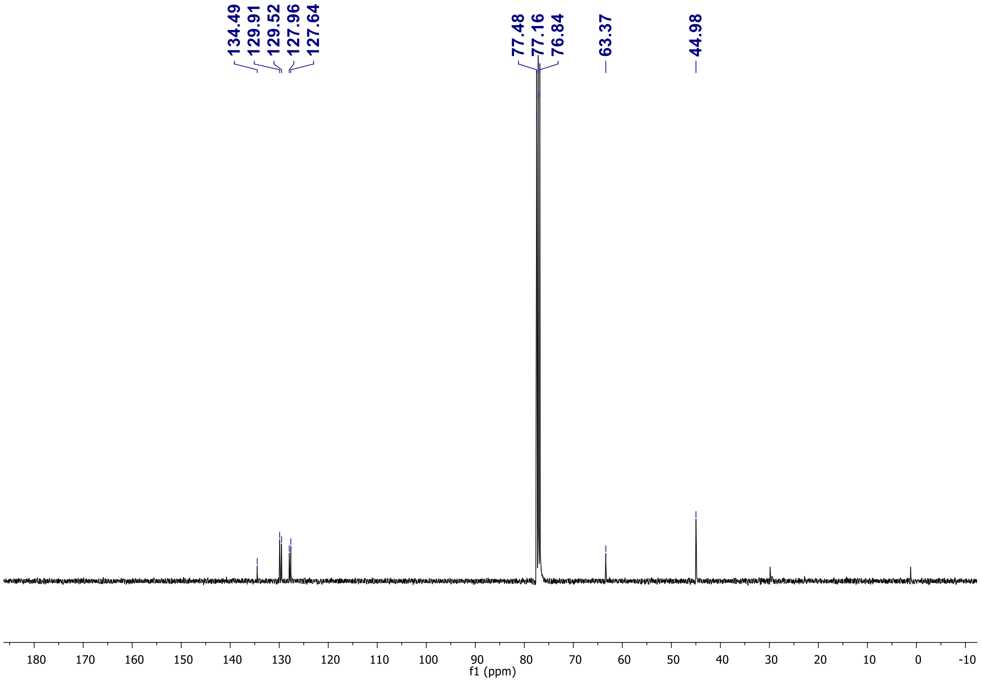


Figure S181. ^{13}C NMR spectrum **7e** measured in CDCl$_3$

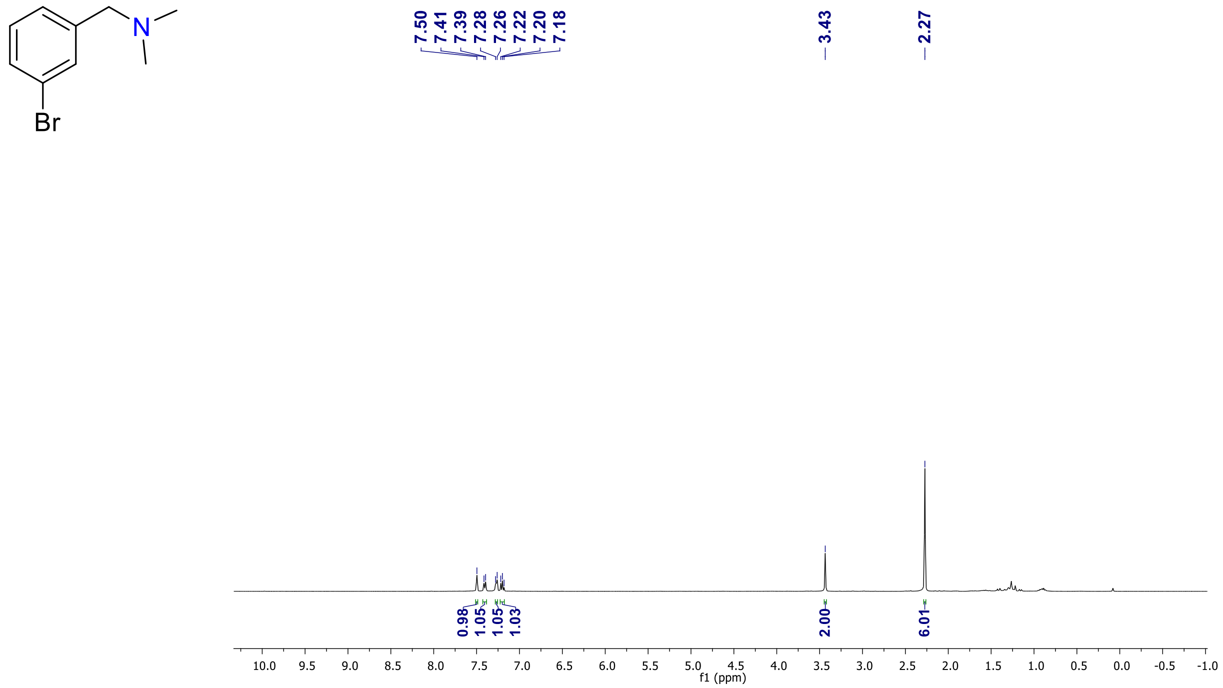


Figure S182. ^{1}H NMR spectrum of **7f** measured in CDCl$_3$

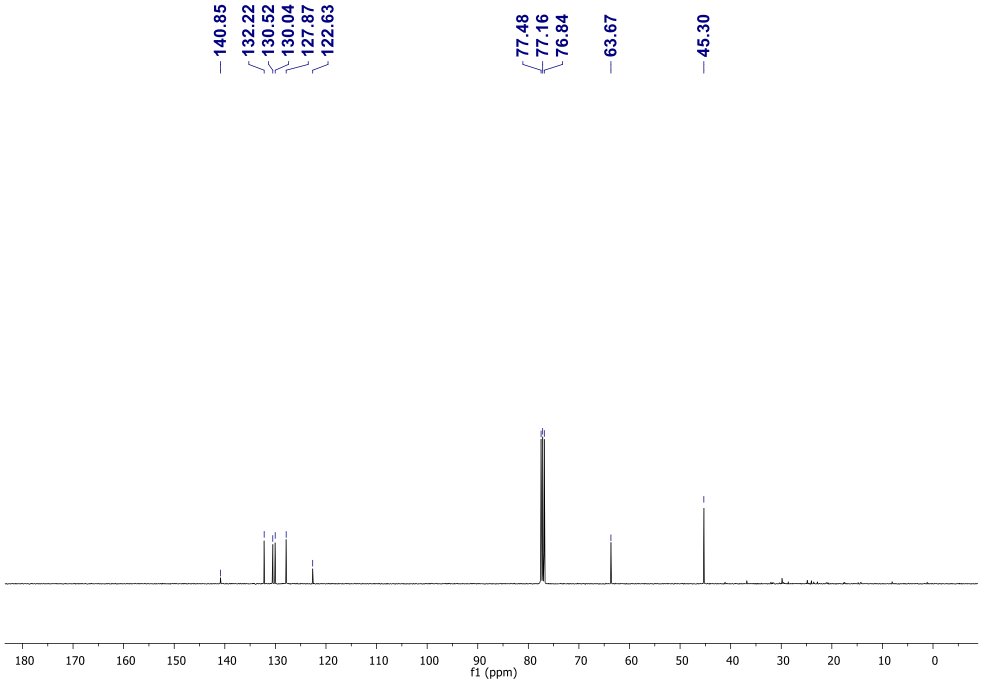


Figure S183. ^{13}C NMR spectrum **7f** measured in CDCl$_3$

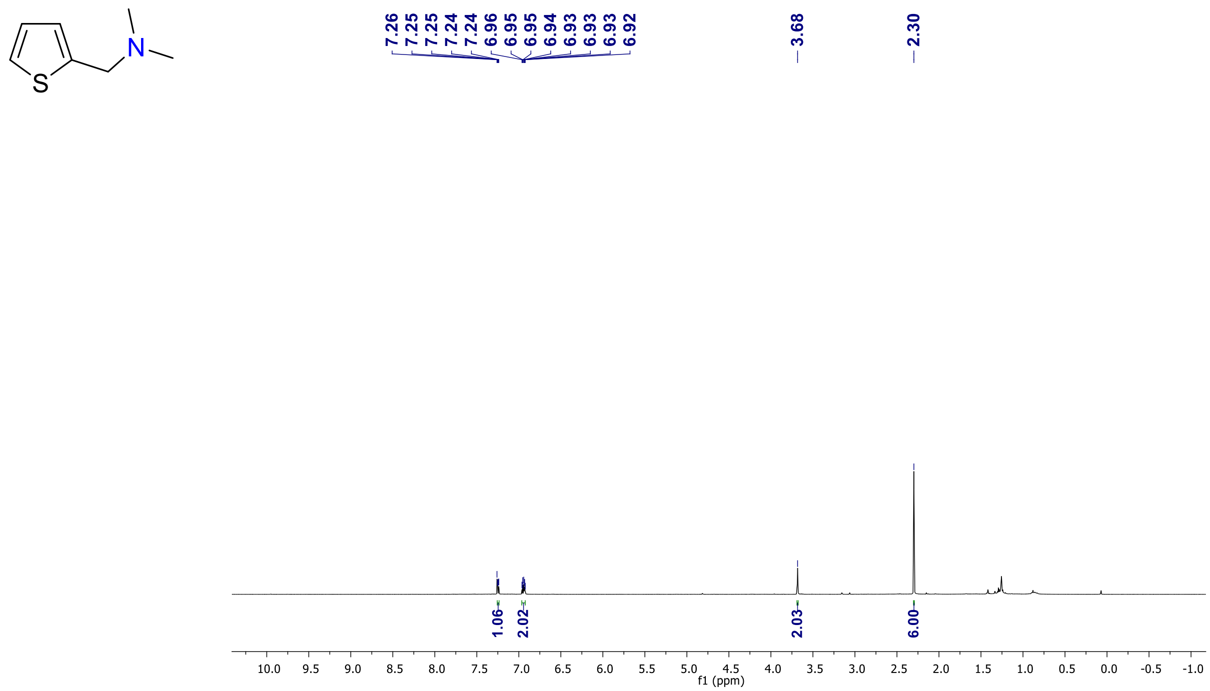


Figure S184. ^{1}H NMR spectrum of **7g** measured in $CDCl_3$

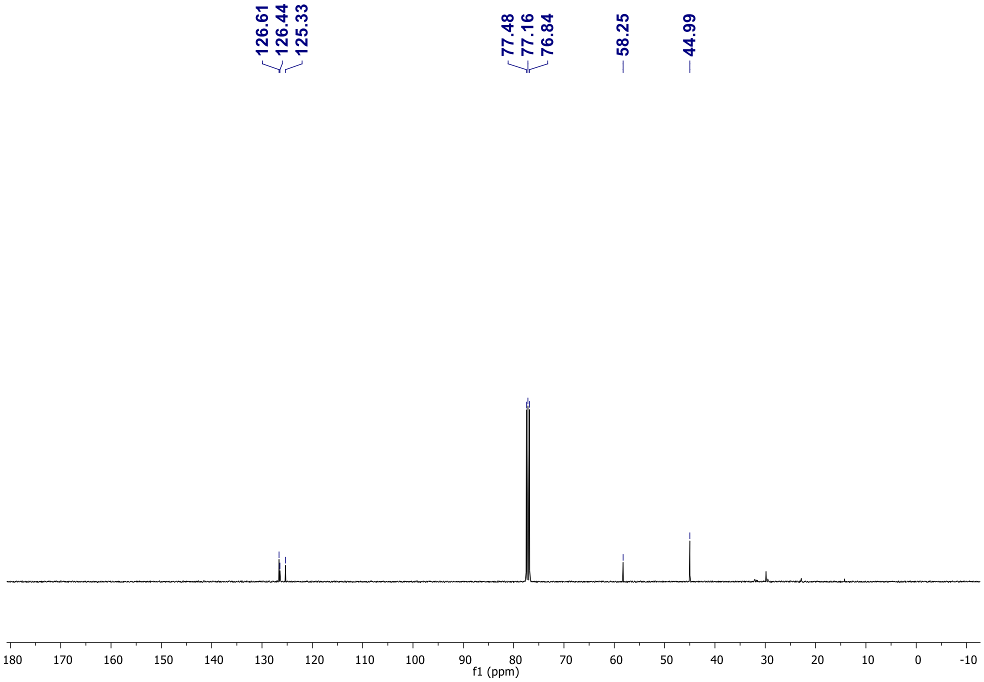


Figure S185. ^{13}C NMR spectrum **7g** measured in $CDCl_3$

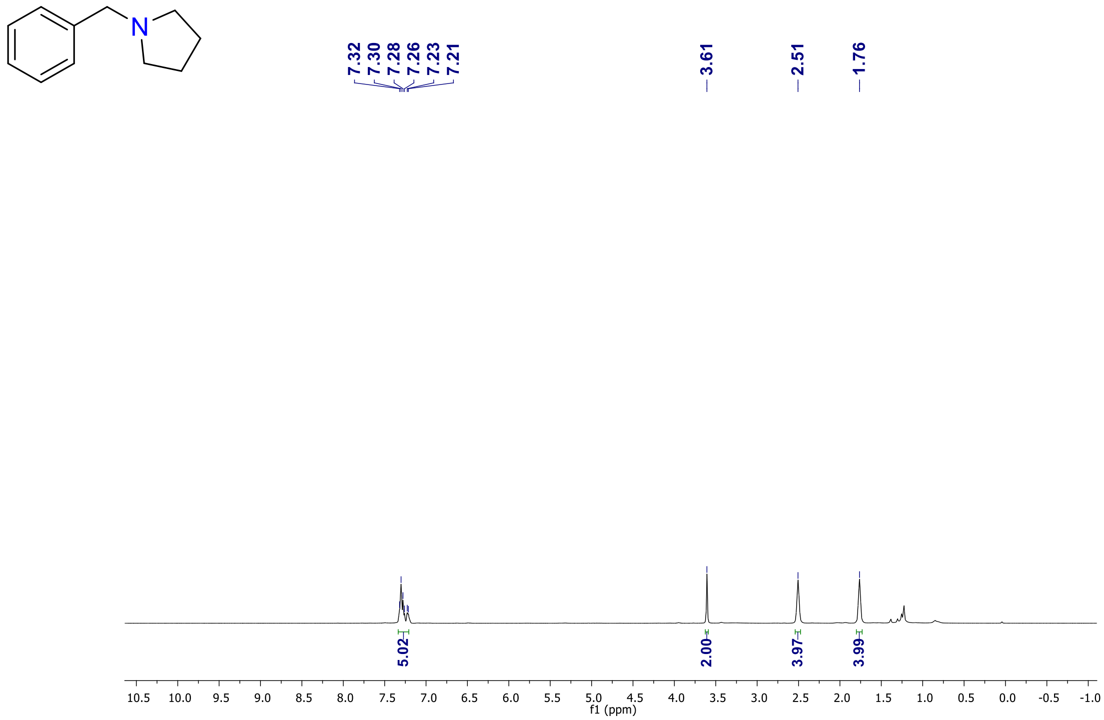


Figure S186. ^{1}H NMR spectrum of **7h** measured in CDCl$_3$

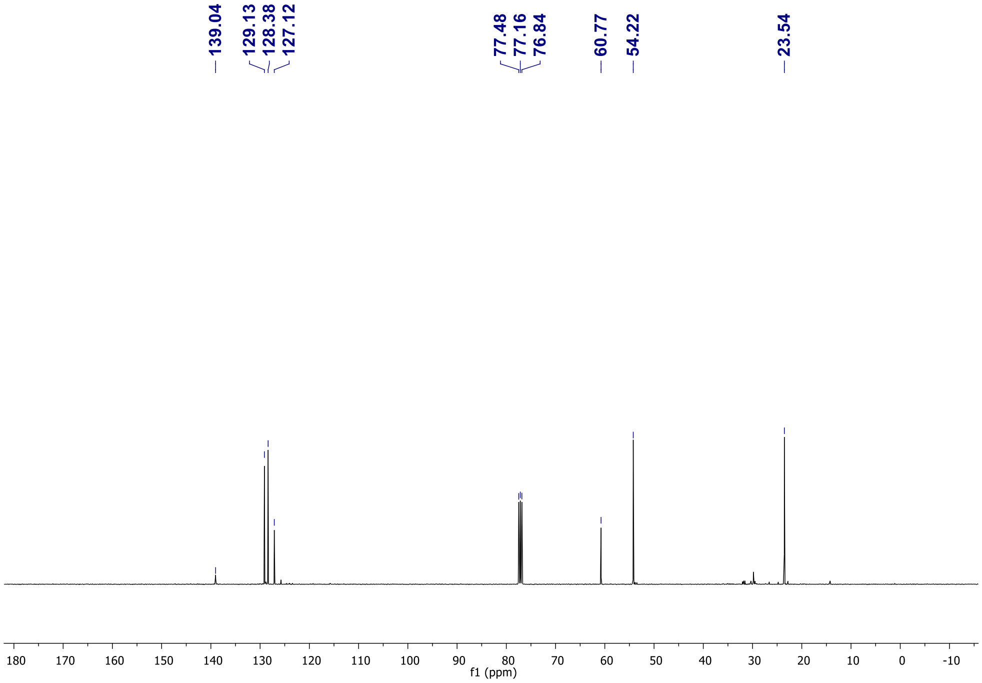


Figure S187. ^{13}C NMR spectrum **7h** measured in CDCl$_3$

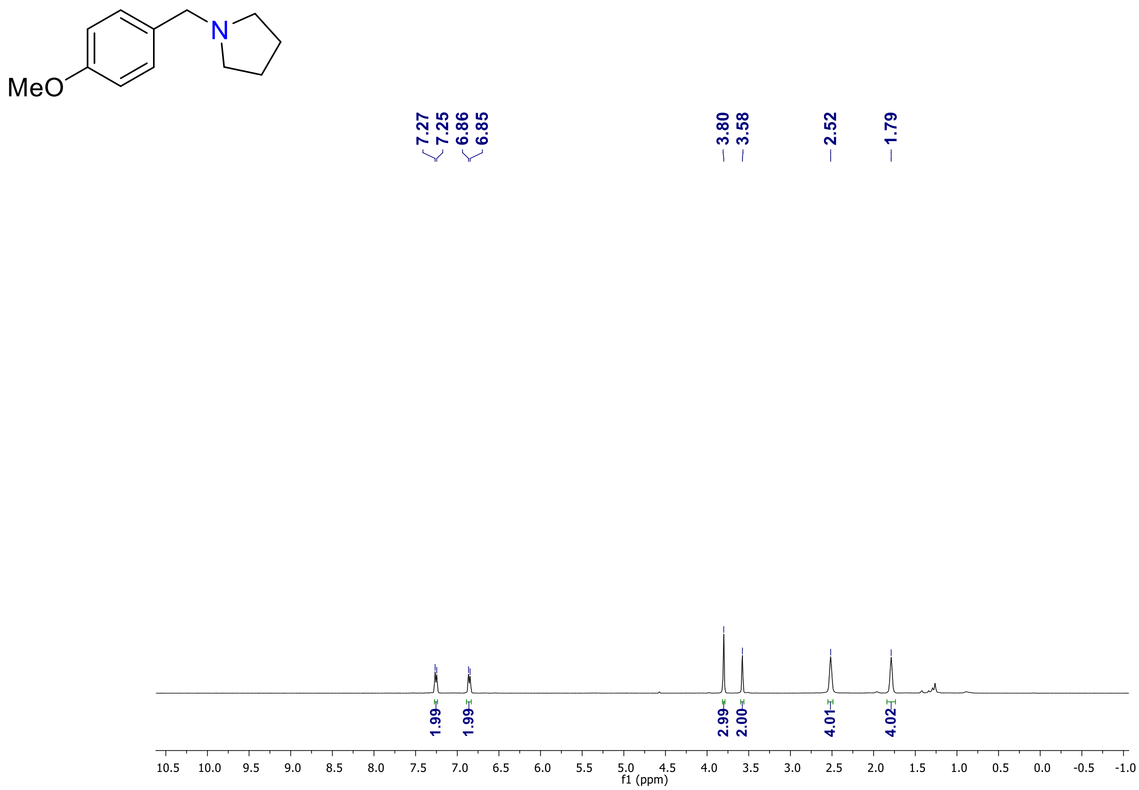


Figure S188. ^{1}H NMR spectrum of **7i** measured in CDCl$_3$

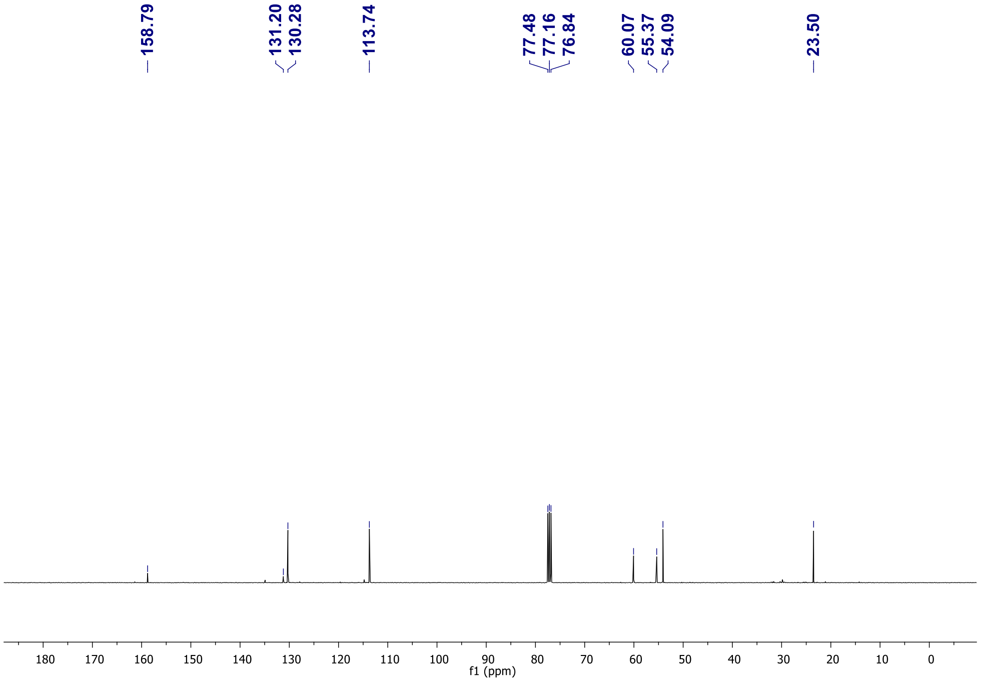


Figure S189. ^{13}C NMR spectrum **7i** measured in CDCl$_3$

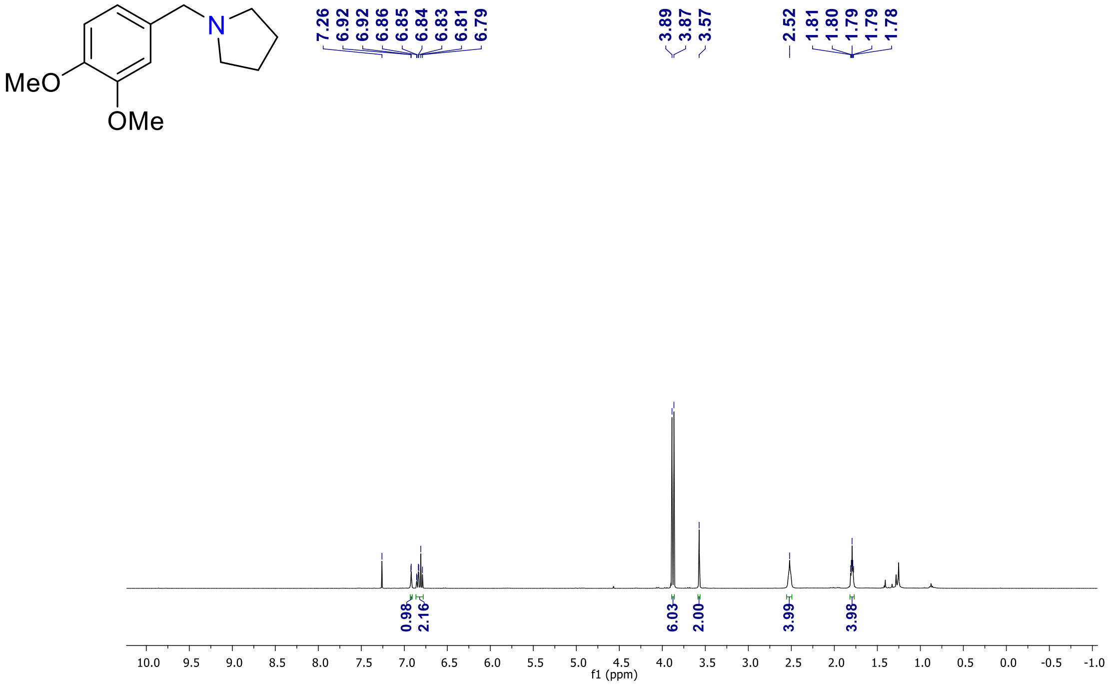


Figure S190. ^{1}H NMR spectrum of **7j** measured in $CDCl_3$

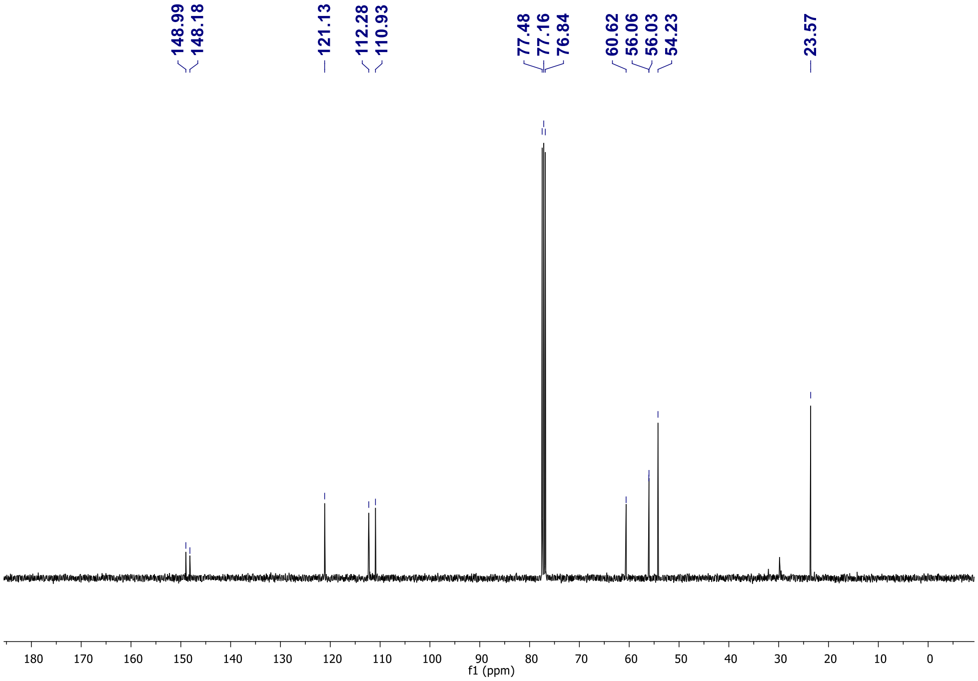
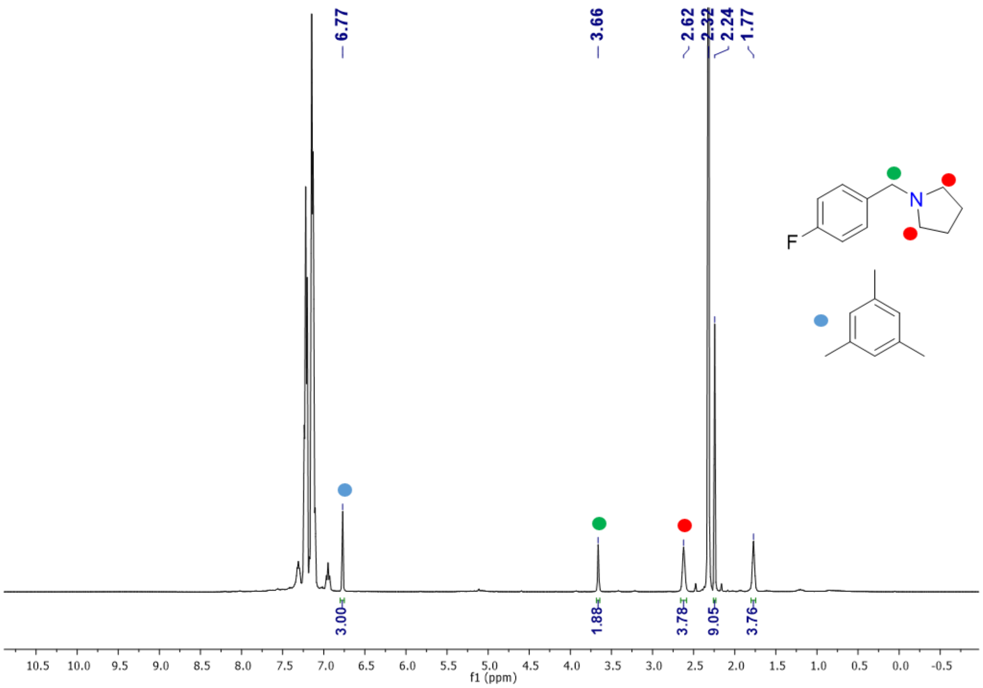
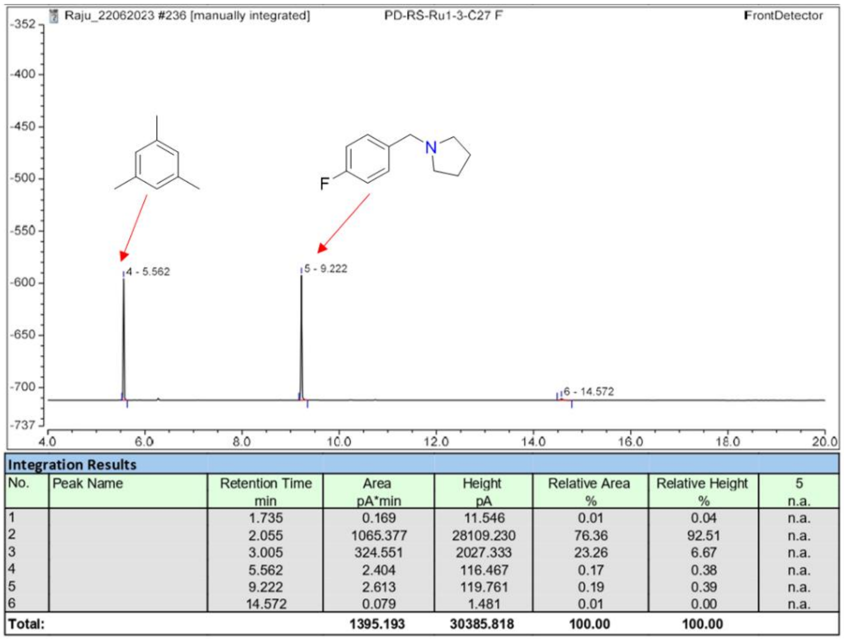


Figure S191. ^{13}C NMR spectrum **7j** measured in $CDCl_3$



% NMR Yield= 94%

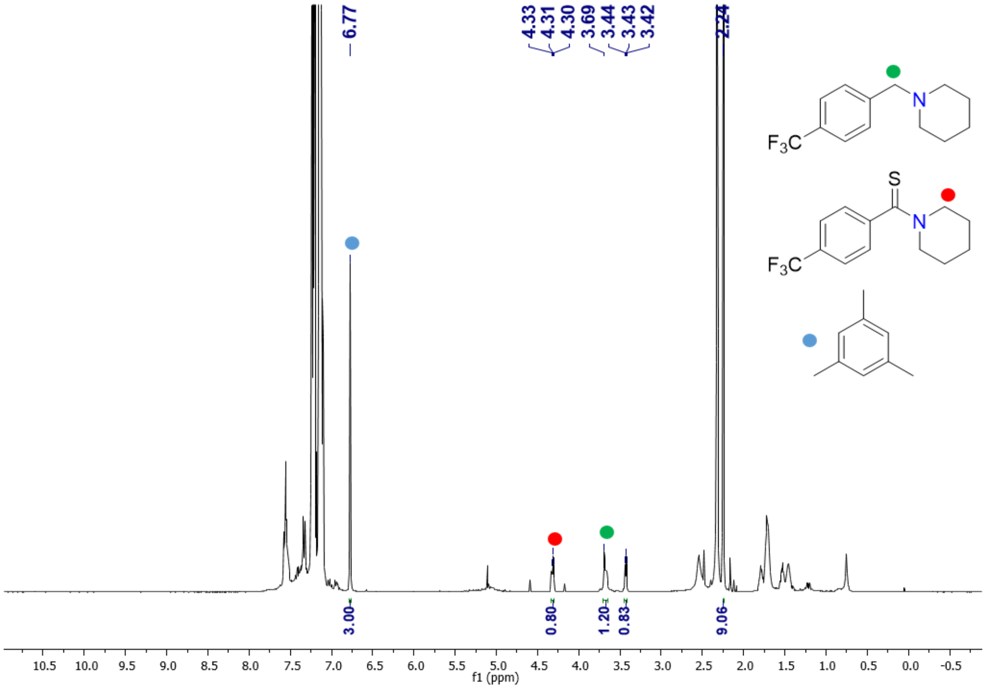
Figure S192. ^{1}H NMR spectrum of crude reaction mixture of **7k** measured in $CDCl_3$



Integration Results

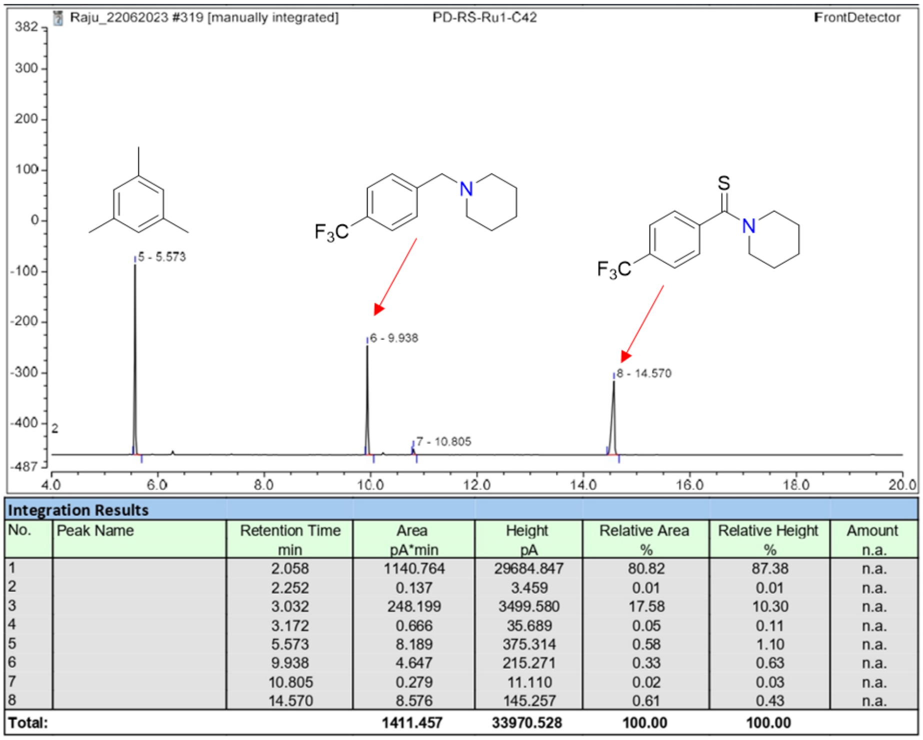
No.	Peak Name	Retention Time min	Area pA*min	Height pA	Relative Area %	Relative Height %	5 n.a.
1		1.735	0.169	11.546	0.01	0.04	n.a.
2		2.055	1065.377	28109.230	76.36	92.51	n.a.
3		3.005	324.551	2027.333	23.26	6.67	n.a.
4		5.562	2.404	116.467	0.17	0.38	n.a.
5		9.222	2.613	119.761	0.19	0.39	n.a.
6		14.572	0.079	1.481	0.01	0.00	n.a.
Total:			**1395.193**	**30385.818**	**100.00**	**100.00**	

Figure S193. GC-MS spectrum of crude reaction mixture of **7k**



% NMR Yield= 60%

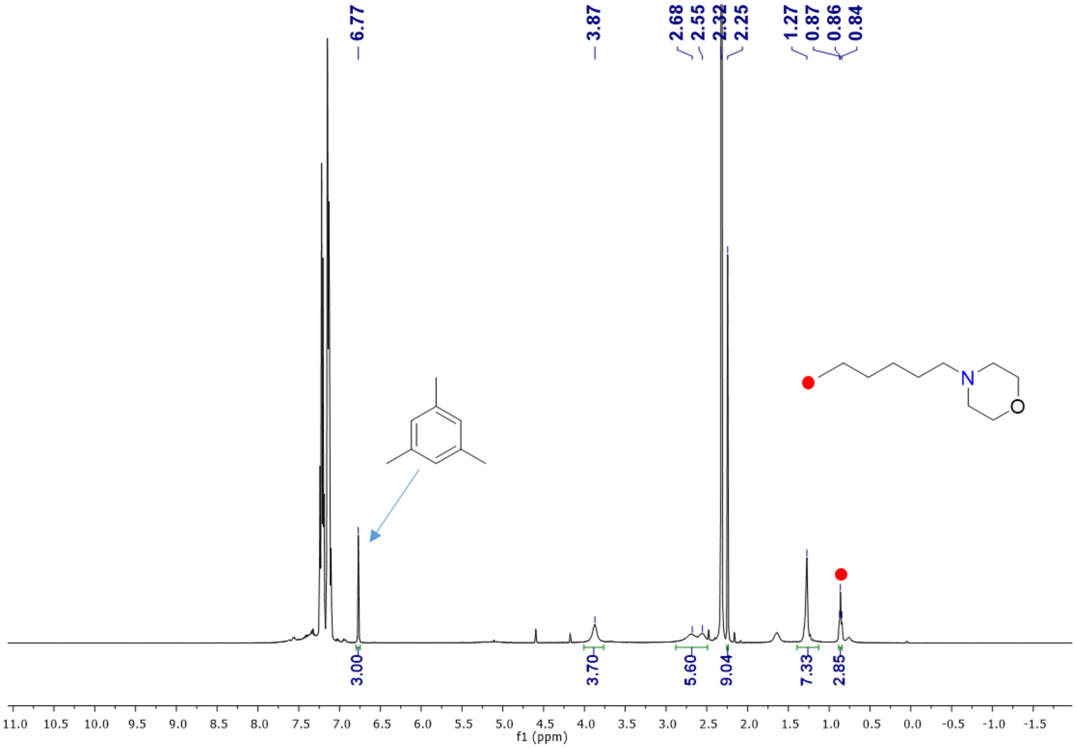
Figure S194. ^{1}H NMR spectrum of crude reaction mixture of **7l** measured in CDCl$_3$



Integration Results

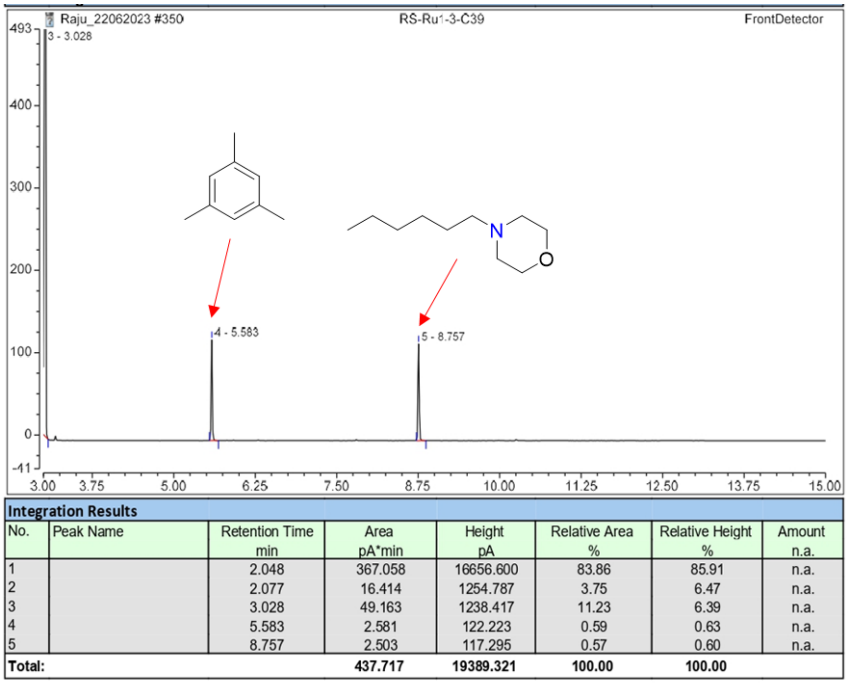
No.	Peak Name	Retention Time min	Area pA*min	Height pA	Relative Area %	Relative Height %	Amount n.a.
1		2.058	1140.764	29684.847	80.82	87.38	n.a.
2		2.252	0.137	3.459	0.01	0.01	n.a.
3		3.032	248.199	3499.580	17.58	10.30	n.a.
4		3.172	0.666	35.689	0.05	0.11	n.a.
5		5.573	8.189	375.314	0.58	1.10	n.a.
6		9.938	4.647	215.271	0.33	0.63	n.a.
7		10.805	0.279	11.110	0.02	0.03	n.a.
8		14.570	8.576	145.257	0.61	0.43	n.a.
Total:			**1411.457**	**33970.528**	**100.00**	**100.00**	

Figure S195. GC-MS spectrum of crude reaction mixture of **7l**



% NMR Yield= 95%

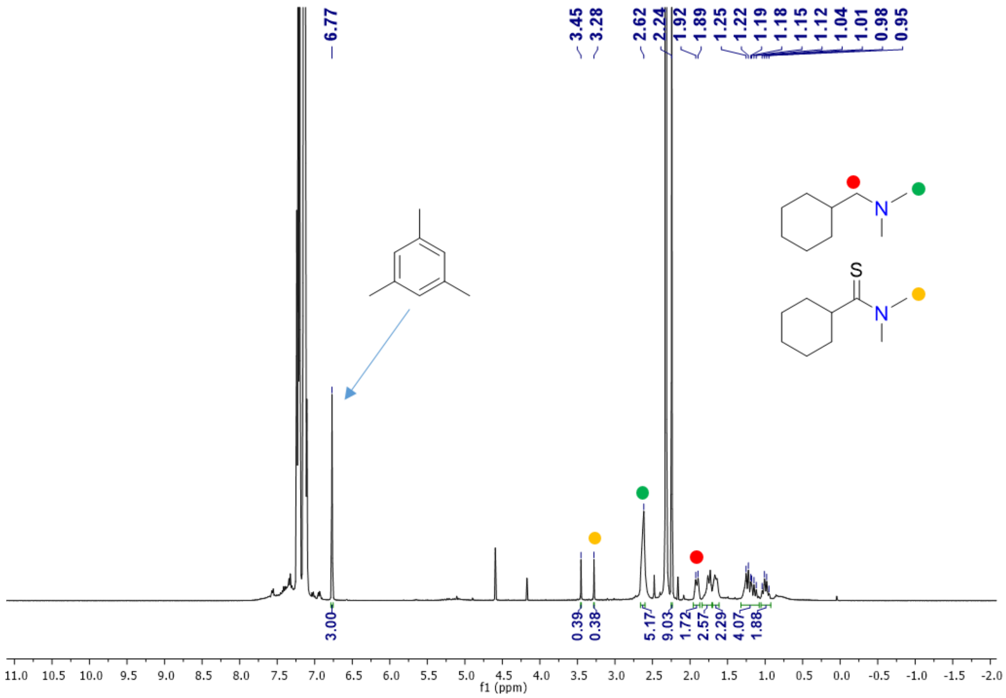
Figure S196. ^{1}H NMR spectrum of crude reaction mixture of **7m** measured in $CDCl_3$



Integration Results

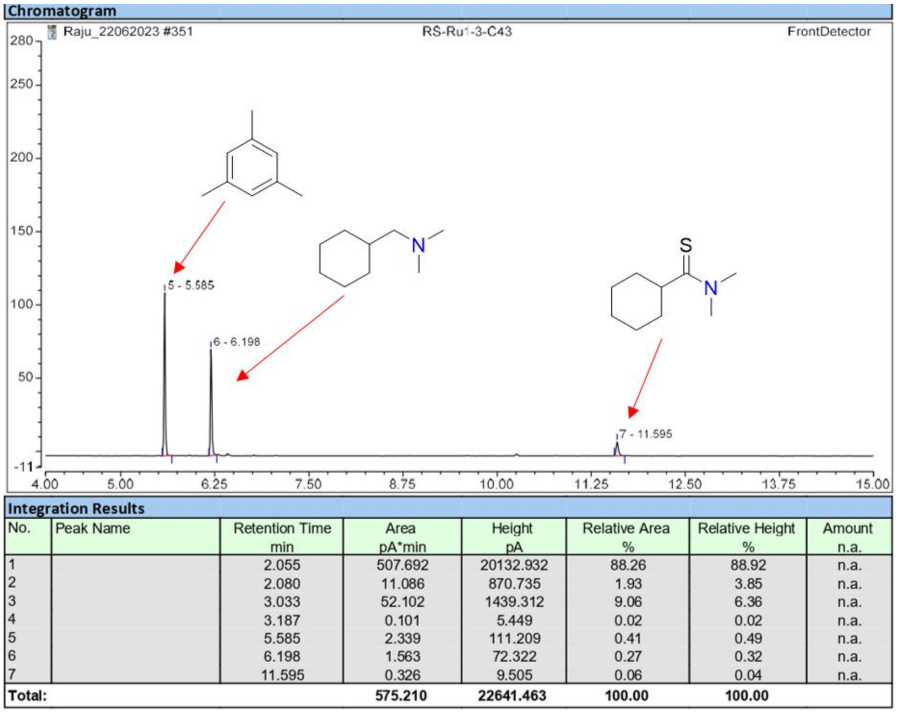
No.	Peak Name	Retention Time min	Area pA*min	Height pA	Relative Area %	Relative Height %	Amount n.a.
1		2.048	367.058	16656.600	83.86	85.91	n.a.
2		2.077	16.414	1254.787	3.75	6.47	n.a.
3		3.028	49.163	1238.417	11.23	6.39	n.a.
4		5.583	2.581	122.223	0.59	0.63	n.a.
5		8.757	2.503	117.295	0.57	0.60	n.a.
Total:			**437.717**	**19389.321**	**100.00**	**100.00**	

Figure S197. GC-MS spectrum of crude reaction mixture of **7m**



% NMR Yield= 86%

Figure S198. ^{1}H NMR spectrum of crude reaction mixture of **7n** measured in $CDCl_3$



Integration Results

No.	Peak Name	Retention Time min	Area pA*min	Height pA	Relative Area %	Relative Height %	Amount n.a.
1		2.055	507.692	20132.932	88.26	88.92	n.a.
2		2.080	11.086	870.735	1.93	3.85	n.a.
3		3.033	52.102	1439.312	9.06	6.36	n.a.
4		3.187	0.101	5.449	0.02	0.02	n.a.
5		5.585	2.339	111.209	0.41	0.49	n.a.
6		6.198	1.563	72.322	0.27	0.32	n.a.
7		11.595	0.326	9.505	0.06	0.04	n.a.
Total:			575.210	22641.463	100.00	100.00	

Figure S199. GC-MS spectrum of crude reaction mixture of **7n**

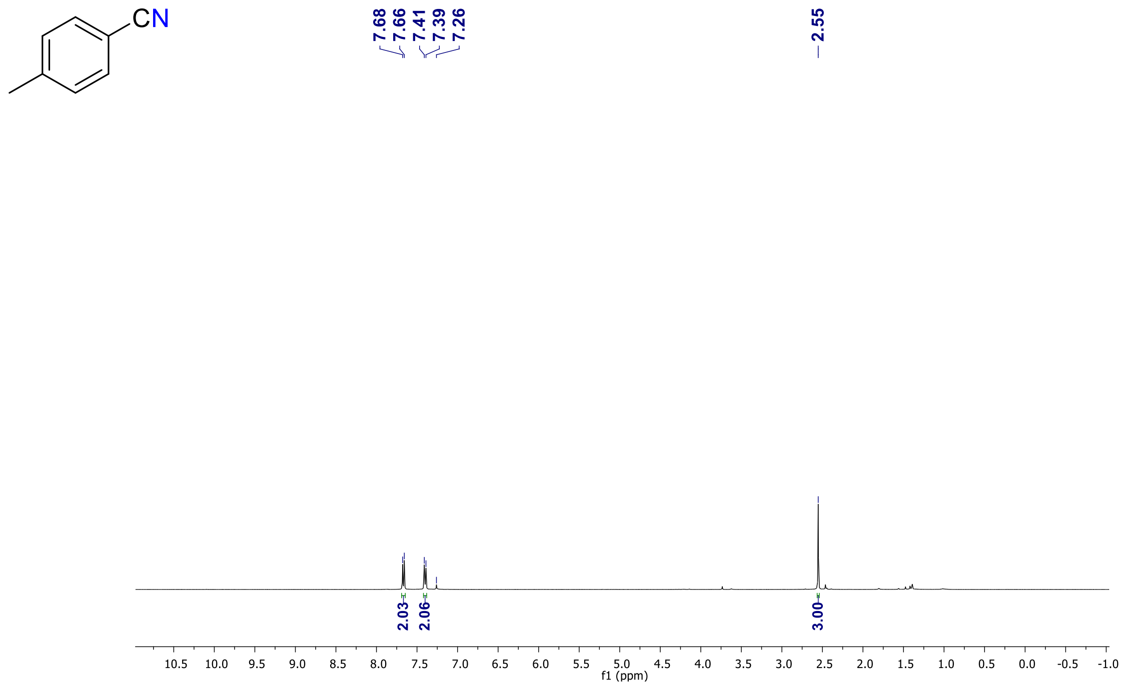


Figure S200. ^{1}H NMR spectrum of **9a** measured in $CDCl_3$

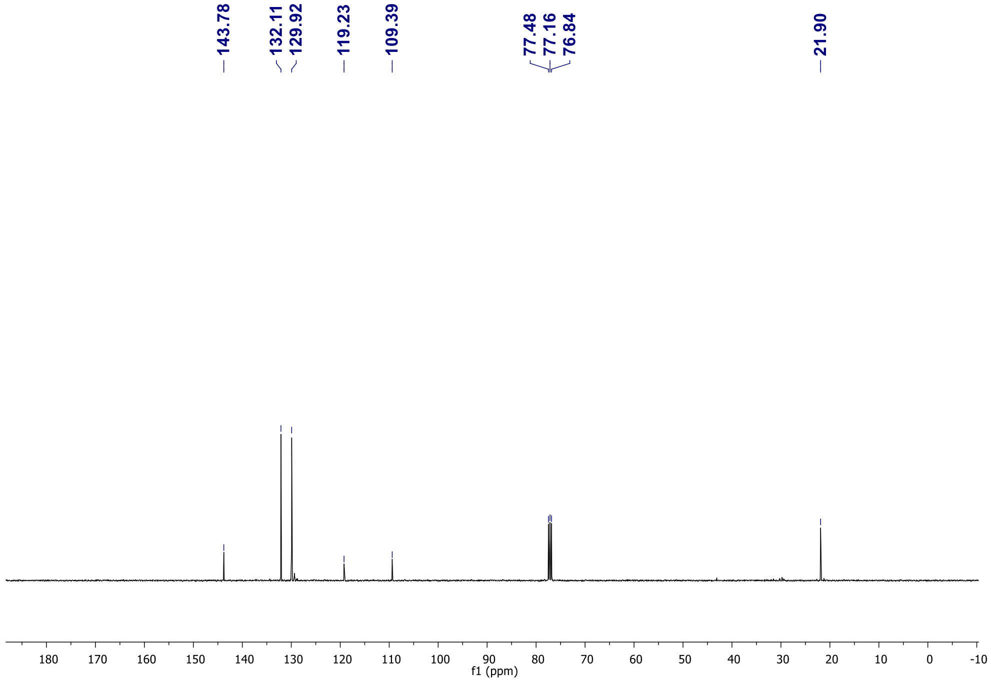


Figure S201. ^{13}C NMR spectrum **9a** measured in $CDCl_3$

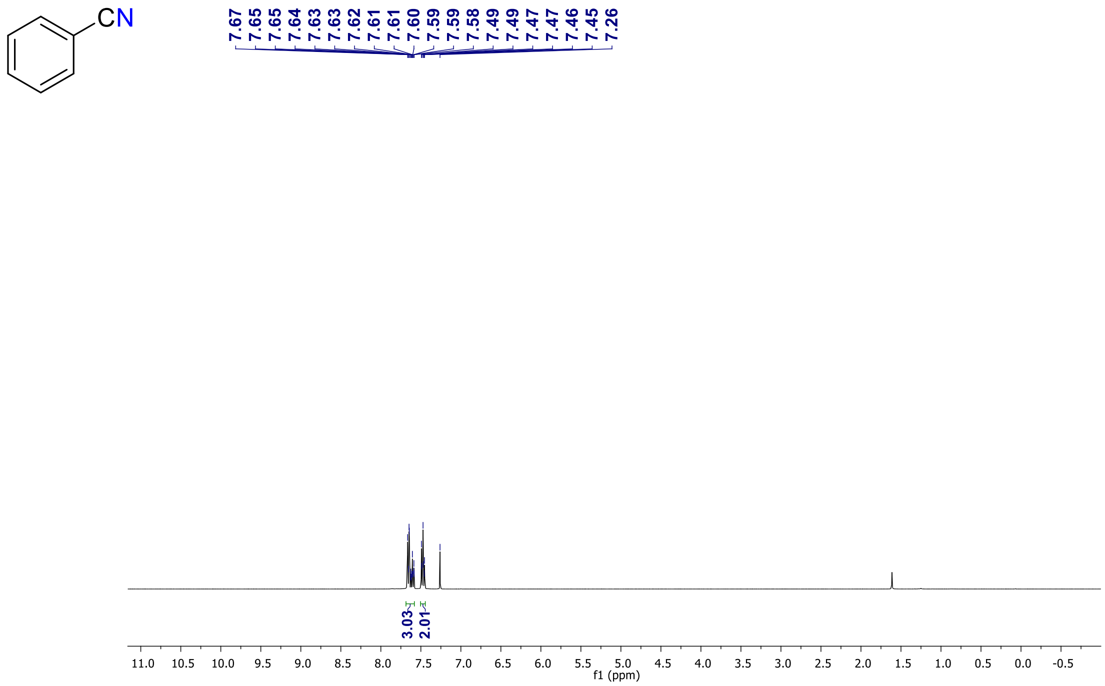


Figure S202. ^{1}H NMR spectrum of **9b** measured in $CDCl_3$

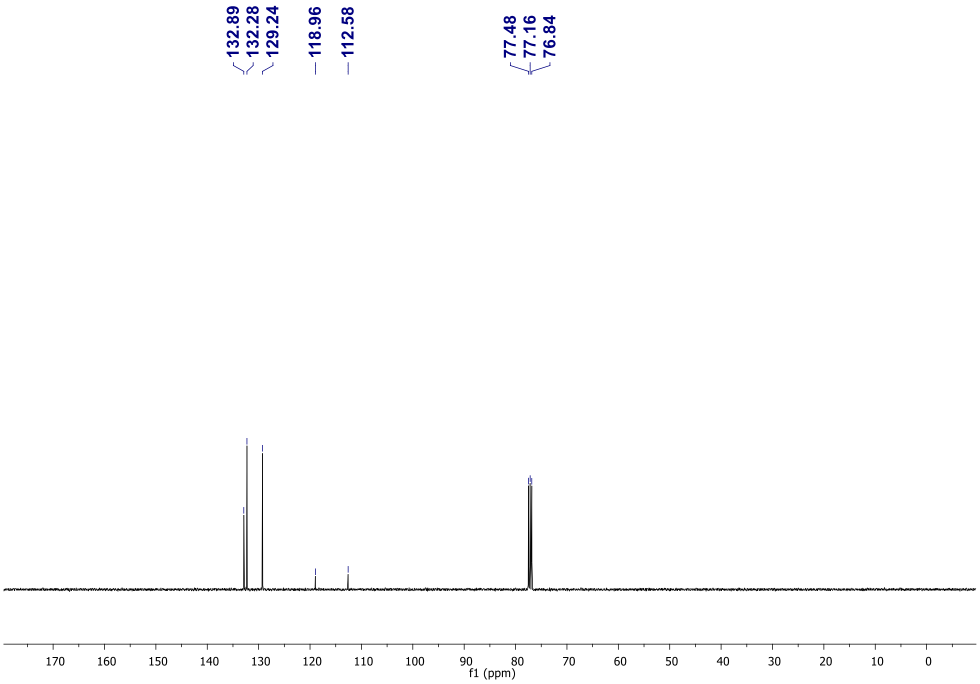


Figure S203. ^{13}C NMR spectrum **9b** measured in $CDCl_3$

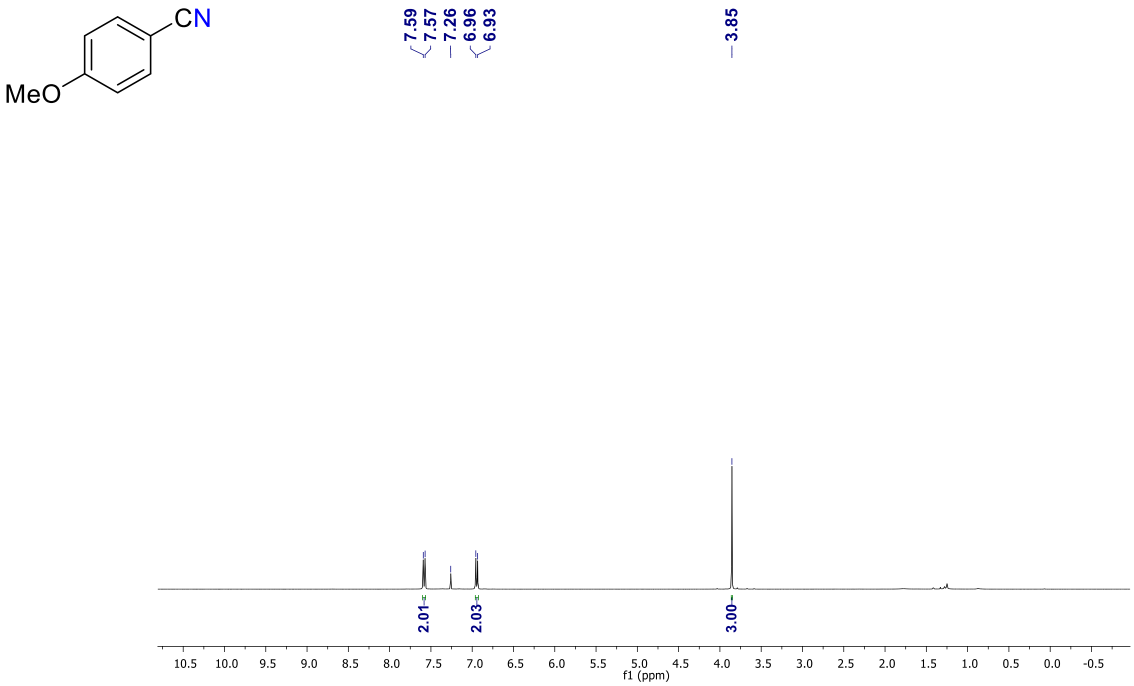


Figure S204. ^{1}H NMR spectrum of **9d** measured in $CDCl_3$

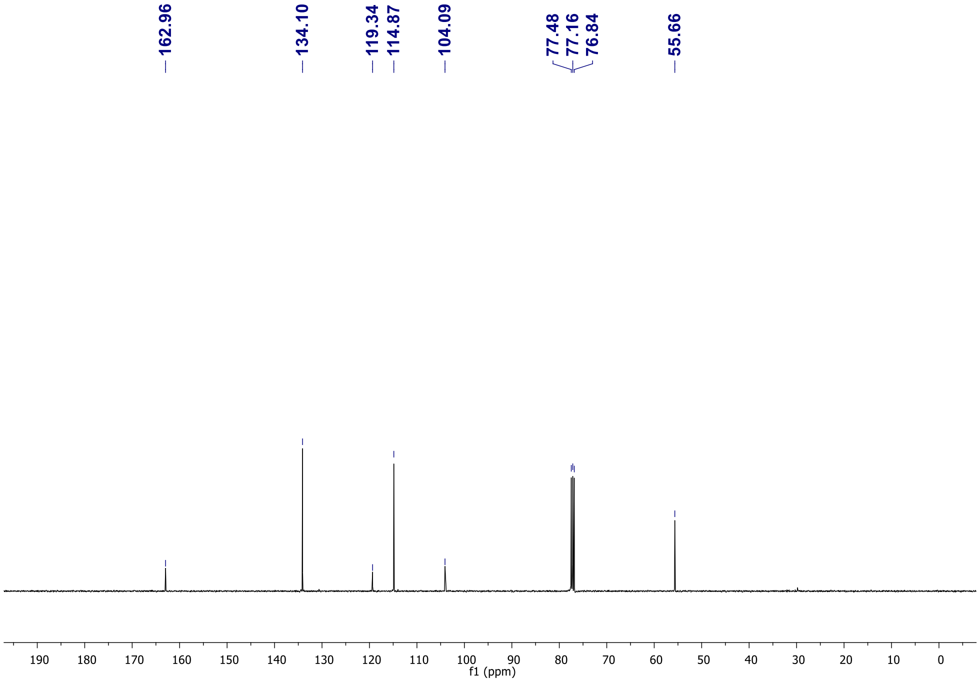


Figure S205. ^{13}C NMR spectrum **9d** measured in $CDCl_3$

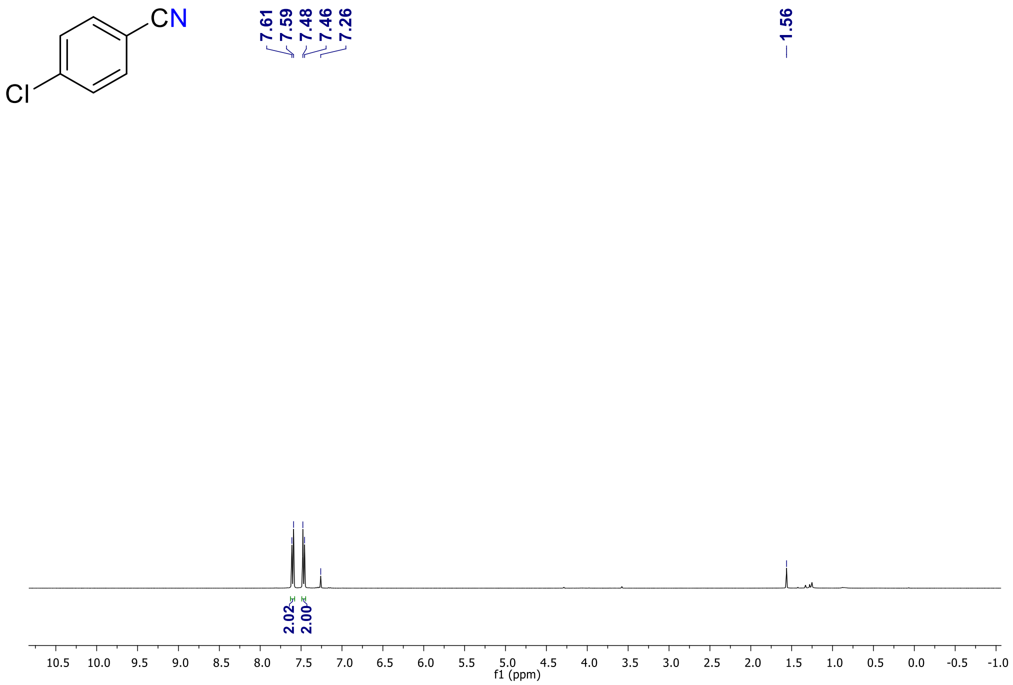


Figure S206. ^{1}H NMR spectrum of **9e** measured in CDCl$_3$

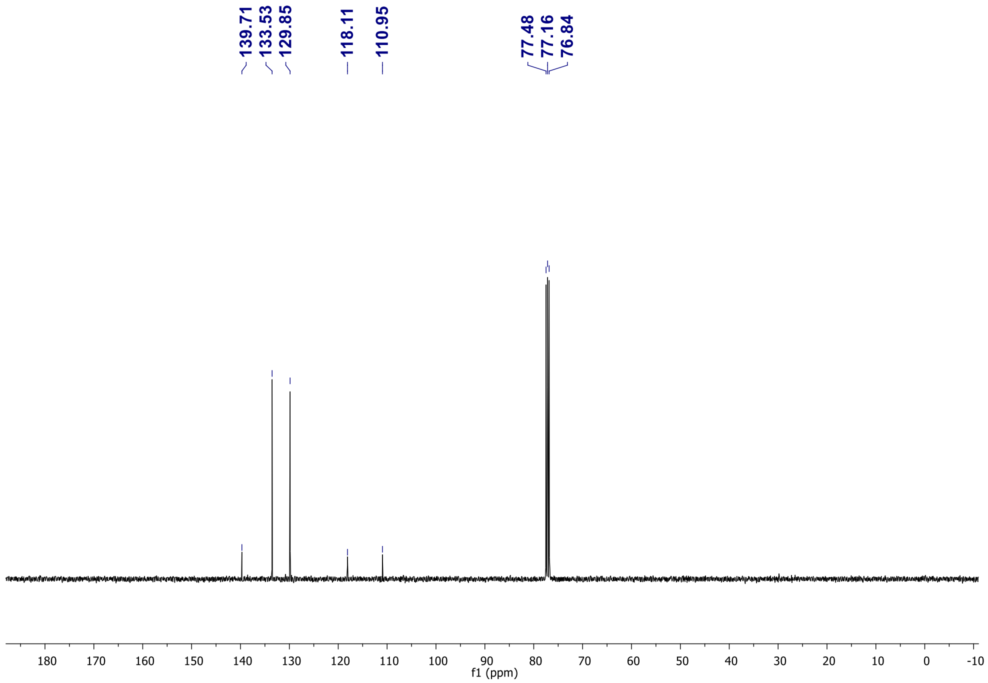


Figure S207. ^{13}C NMR spectrum **9e** measured in CDCl$_3$

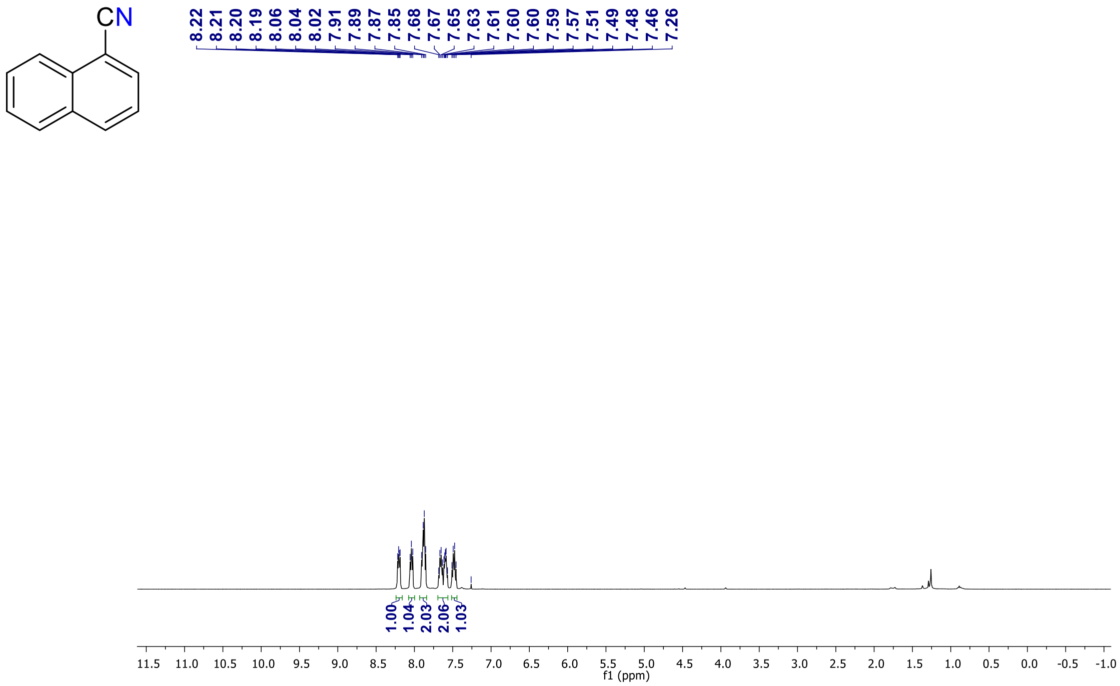


Figure S208. ^{1}H NMR spectrum of **9f** measured in $CDCl_3$

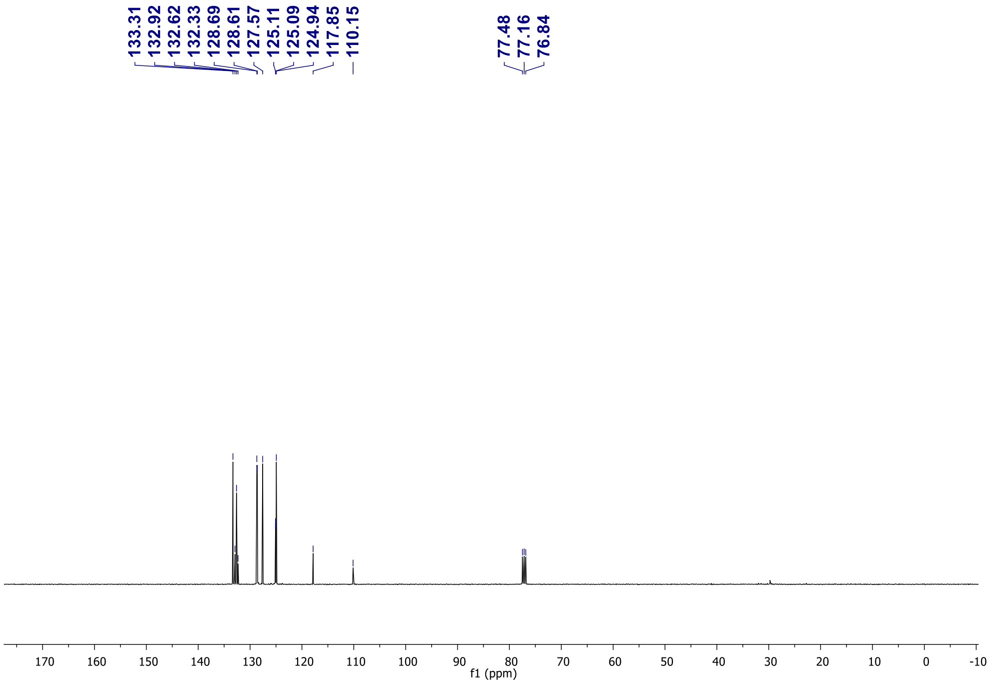
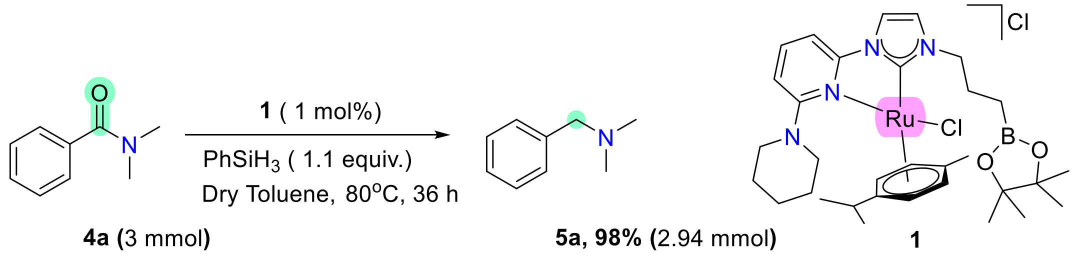
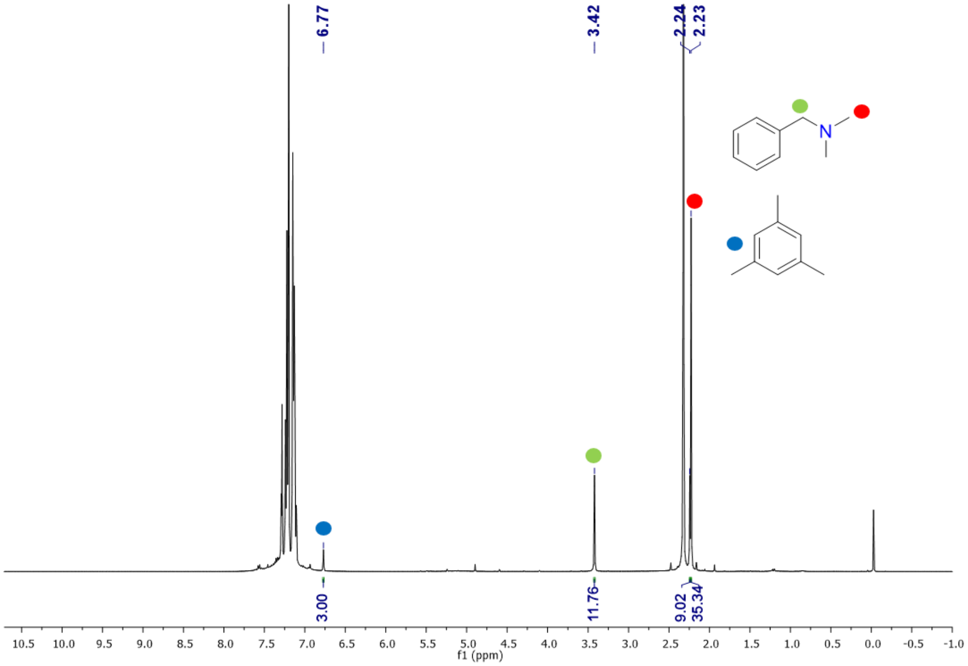


Figure S209. ^{13}C NMR spectrum **9f** measured in $CDCl_3$

20. Scale-up reaction of deoxygenative hydrogenation of 4a to 5a using complex 1



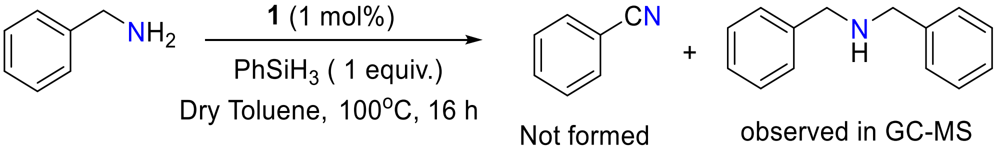
Inside a N$_2$ filled glove box, a 25 mL pressure tube equipped with a magnetic stirring bar was charged with **1** (21.07 mg, 1 mol%), **4a** (447.57 mg, 3 mmol). 3 mL of dry toluene was added followed by the addition of phenylsilane (357.12 mg, 3.3 mmol) and the closed vessel was heated at 80 ºC for 36 hours. After completion of reaction, the solution was cooled down to room temperature and mesitylene (0.5 mmol w.r.t. to **4a**) was added as internal standard and NMR yield was analyzed using ^{1}H NMR in CDCl$_3$ as the solvent, which yielded 2.94 mmol of desired amine **5a** (98%).



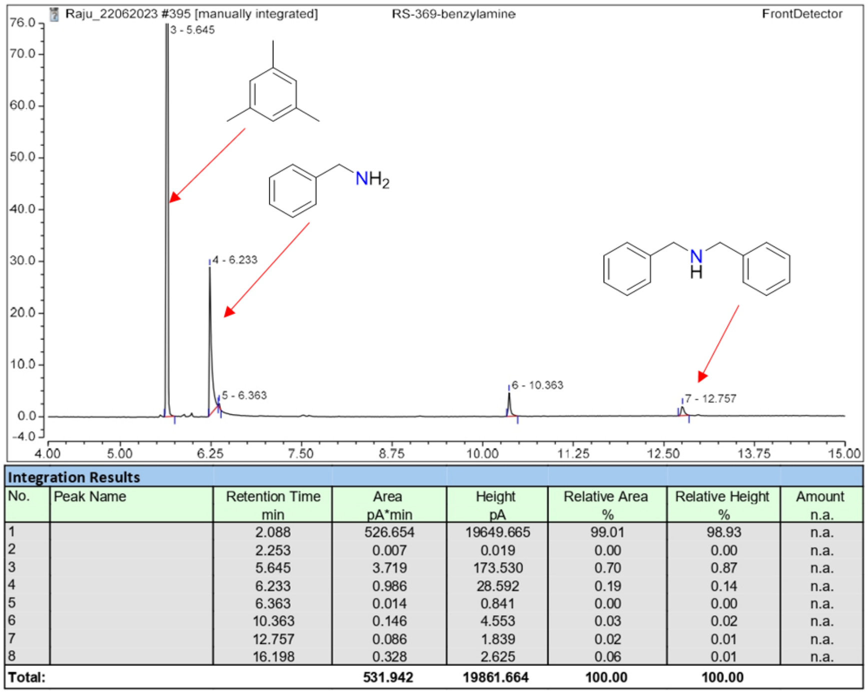
% amine **5a** formation = 98%

Figure S210. ^{1}H NMR spectrum of crude reaction measured in CDCl$_3$ for deoxygenative hydrogenation of **4a** to **5a** with 3 mmol scale reaction catalyzed by complex **1**

21. Dehydrogenation of benzylamine using complex 1



Inside a N_2 filled glove box, a 25 mL pressure tube equipped with a magnetic stirring bar was charged with **1** (3.53 mg, 1 mol%), benzylamine (53.9 mg, 0.503 mmol). 1 mL of dry toluene was added followed by the addition of phenylsilane (54.43 mg, 0.503 mmol) and the closed vessel was heated at 100 ºC for 16 hours. After completion of the reaction, solution was cooled down to room temperature. 0.5 mL of ethylacetate and mesitylene (0.503 mmol) was added as internal standard and GC-MS analysis was performed, where a major amount of unreacted benzylamine was observed along with the formation of a small amount of dibenzylamine at a retention time of 12.757 min with m/z=197.11 and no benzonitrile formation was detected.

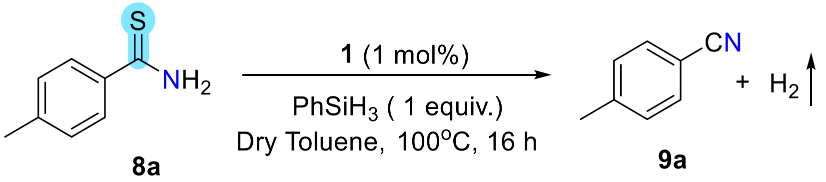


Integration Results

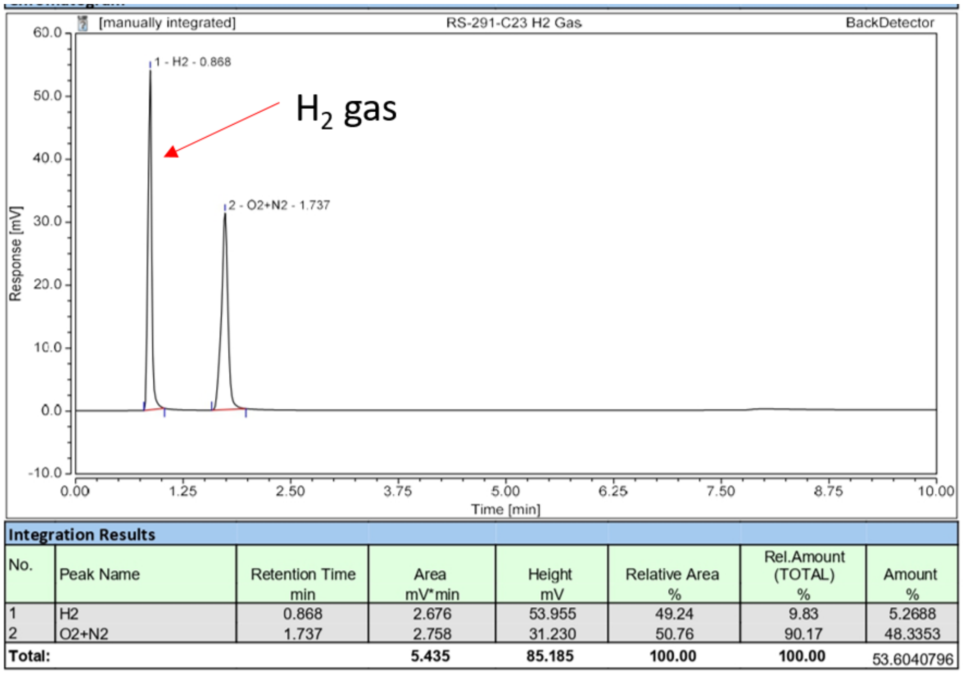
No.	Peak Name	Retention Time min	Area pA*min	Height pA	Relative Area %	Relative Height %	Amount n.a.
1		2.088	526.654	19649.665	99.01	98.93	n.a.
2		2.253	0.007	0.019	0.00	0.00	n.a.
3		5.645	3.719	173.530	0.70	0.87	n.a.
4		6.233	0.986	28.592	0.19	0.14	n.a.
5		6.363	0.014	0.841	0.00	0.00	n.a.
6		10.363	0.146	4.553	0.03	0.02	n.a.
7		12.757	0.086	1.839	0.02	0.01	n.a.
8		16.198	0.328	2.625	0.06	0.01	n.a.
Total:			**531.942**	**19861.664**	**100.00**	**100.00**	

Figure S211. GC-MS spectrum of crude reaction for dehydrogenation of benzylamine catalyzed by complex **1**

22. GC-TCD analysis of H_2 gas release during desulfurization of thioamide 8a to nitrile 9a using complex 1



Inside a N_2 filled glove box, a 25 mL pressure tube equipped with a magnetic stirring bar was charged with **1** (3.53 mg, 1 mol%), **8a** (76 mg, 0.503 mmol). 1.5 mL of dry toluene was added followed by the addition of phenylsilane (54.43 mg, 0.503 mmol) and the closed vessel was heated at 100 ºC for 16 hours. After completion of the reaction, solution was cooled down to room temperature, and 300 µL of evolved gas in the solution was injected into the GC-TCD, which showed the formation of H_2 gas at a retention time of 0.868 min.



Integration Results

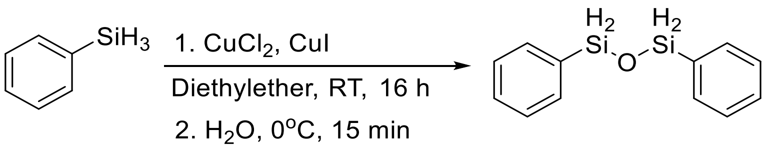
No.	Peak Name	Retention Time min	Area mV*min	Height mV	Relative Area %	Rel.Amount (TOTAL) %	Amount %
1	H2	0.868	2.676	53.955	49.24	9.83	5.2688
2	O2+N2	1.737	2.758	31.230	50.76	90.17	48.3353
Total:			**5.435**	**85.185**	**100.00**	**100.00**	53.6040796

Figure S212. GC-TCD spectrum for the detection of H_2 gas

23. Synthetic procedure and characterization data for 1,3-Diphenyldisiloxane

The titled compound was synthesized according to the known literature procedure.[26]

The characterization data of 1,3-Diphenyldisiloxane are in accordance with the data observed in the literature.[26,27]



^{1}H NMR (400 MHz, CDCl$_3$) δ (ppm) = 7.64 – 7.55 (m, 4H), 7.49-7.39 (m, 6H), 5.17 (s, 4H)

^{13}C NMR (101 MHz, CDCl$_3$) δ (ppm) = 134.22, 130.67, 128.25

^{29}Si NMR (80 MHz, C$_6$D$_6$) δ (ppm) = -25.43.

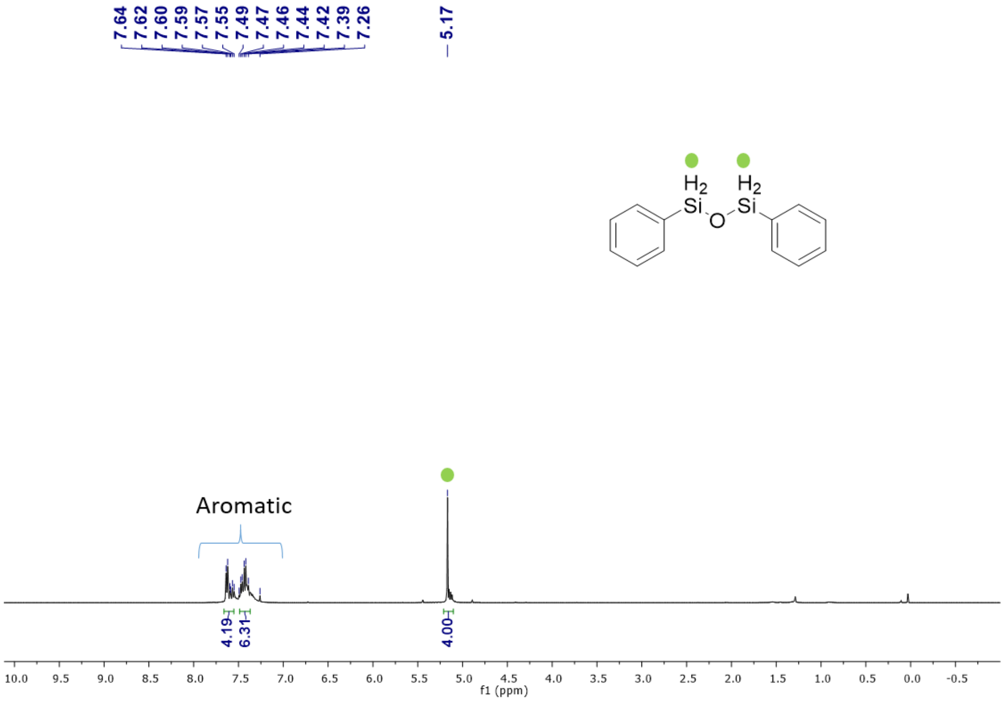


Figure S213. ^{1}H NMR spectrum of 1,3-diphenyldisiloxane in CDCl$_3$

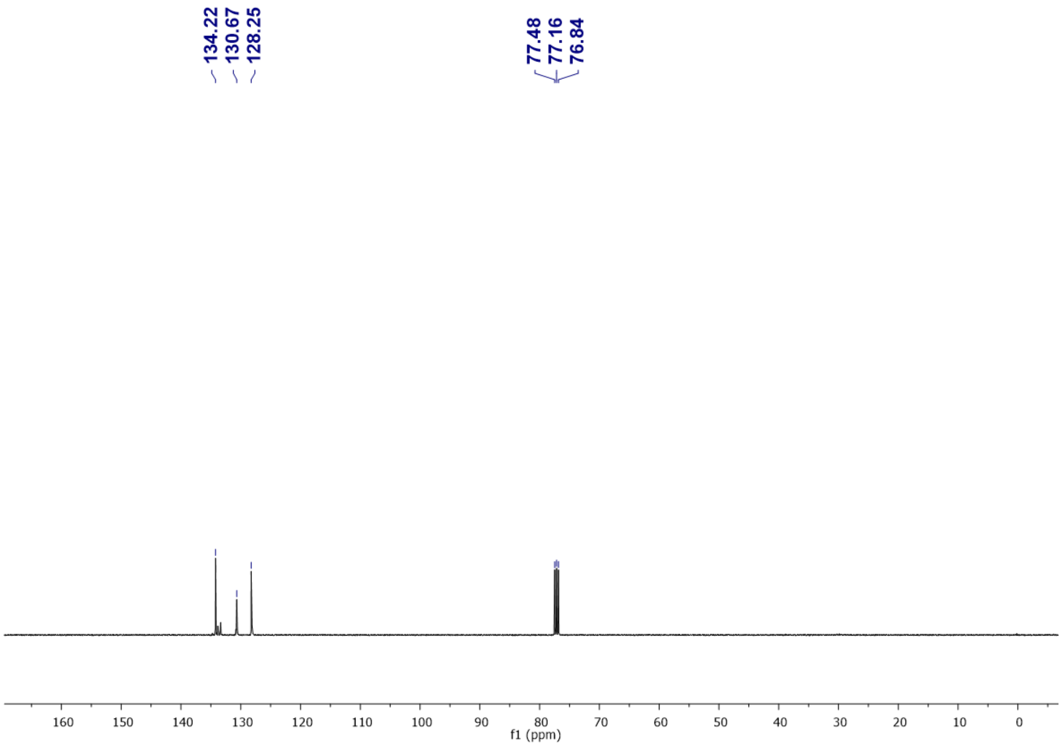


Figure S214. ^{13}C NMR spectrum of 1,3-diphenyldisiloxane in $CDCl_3$

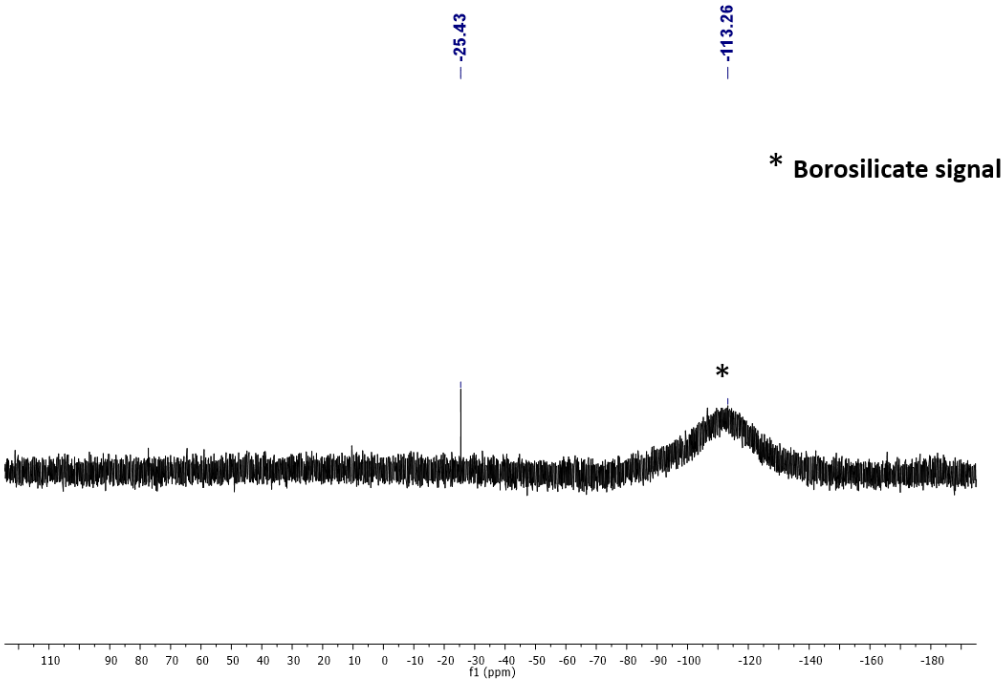
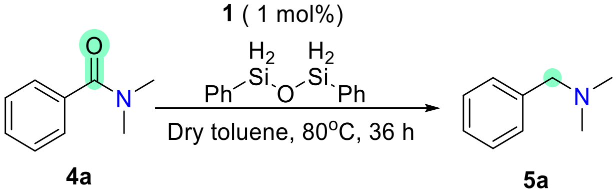


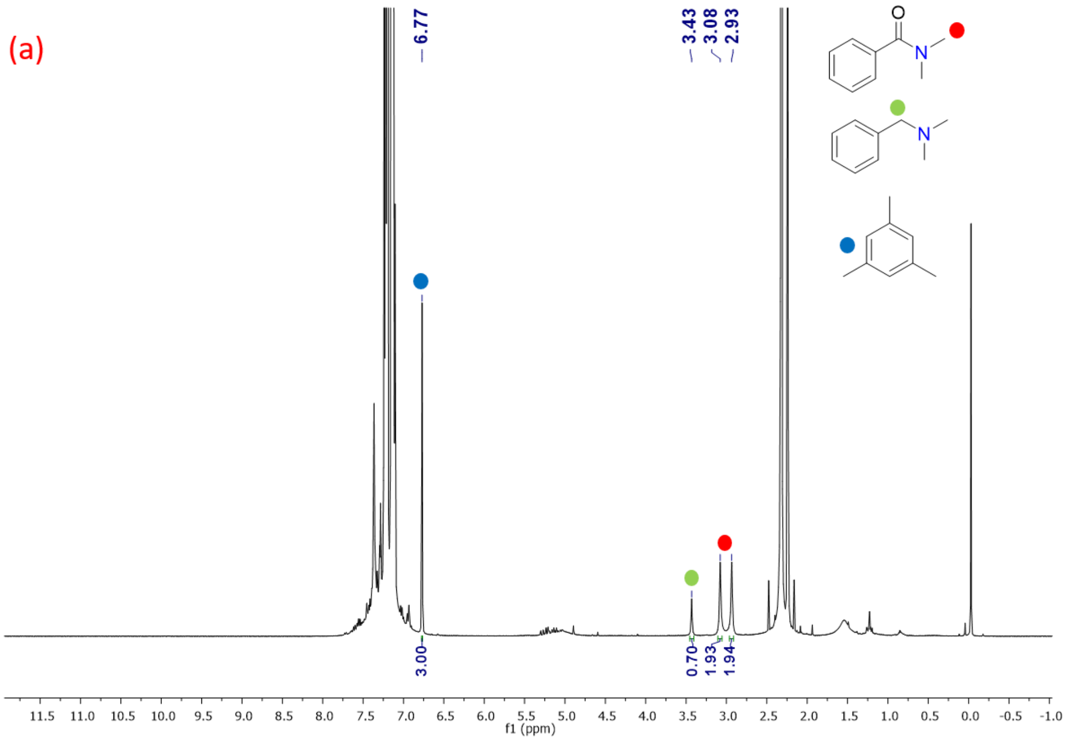
Figure S215. ^{29}Si NMR spectrum of 1,3-Diphenyldisiloxane in $CDCl_3$

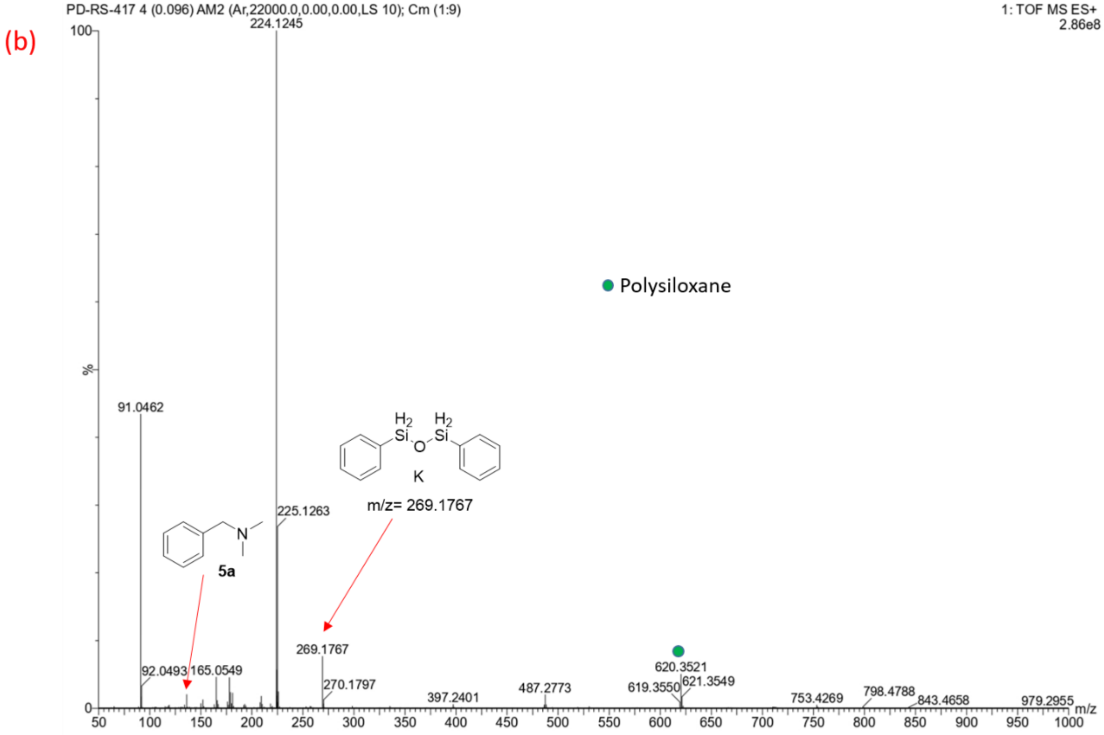
24. Deoxygenative hydrogenation of 4a to 5a using 1,3-diphenyldisiloxane (DPDS) as the hydride source



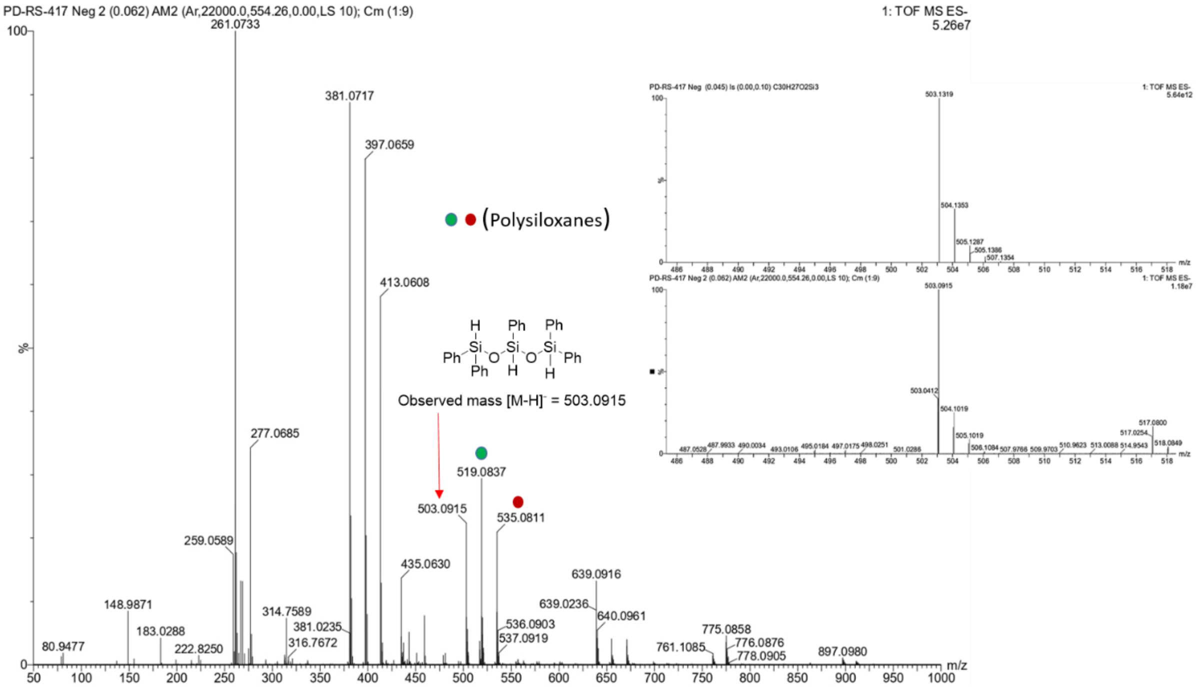
Inside a N_2 filled glove box, a 25 mL pressure tube equipped with a magnetic stirring bar was charged with **1** (1.76 mg, 1 mol%), **4a** (37.5 mg, 0.25 mmol). 0.5 mL of dry toluene was added, followed by the addition of 1,3-diphenyldisiloxane (63.36 mg, 0.275 mmol), and the closed vessel was heated at 80 ºC for 36 hours. After completion of the reaction, solution was cooled down to room temperature, and mesitylene (35 µL, 0.25 mmol w.r.t. to **4a**) was added as internal standard and NMR yield was analyzed using ^{1}H NMR in $CDCl_3$ as the solvent, which yielded 0.0875 mmol of desired amine **5a** (35%), whereas using 2 equiv. of 1,3-diphenyldisiloxane under the optimized reaction conditions yielded 61% of amine **5a** formation. However, in the absence of a catalyst, using 1.1 equiv. of 1,3-diphenyldisiloxane, no **5a** formation was detected.

Entry	Catalyst (1 mol %)	$(PhSiH_2)_2O$ (equiv.)	NMR yield of **5a** (%)
1	**1**	2	61
2	**1**	1.1	35
3	-	1.1	Not detected

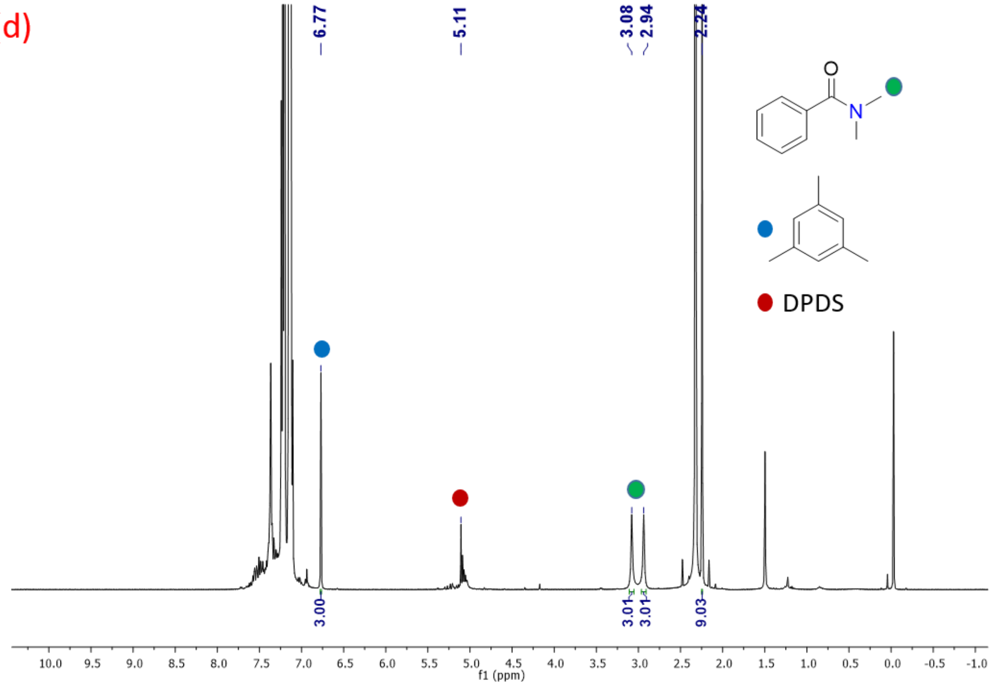

(a)
6.77
3.43
3.08
2.93
3.00
0.70
1.93
1.94
11.5 11.0 10.5 10.0 9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0 -0.5 -1.0
f1 (ppm)
O
N
N


(b)
PD-RS-417 4 (0.096) AM2 (Ar,22000.0,0.00,0.00,LS 10); Cm (1:9)
1: TOF MS ES+
2.86e8
100
%
0
224.1245
91.0462
225.1263
92.0493
165.0549
269.1767
270.1797
397.2401
487.2773
620.3521
619.3550
621.3549
753.4269
798.4788
843.4658
979.2955
m/z
50 100 150 200 250 300 350 400 450 500 550 600 650 700 750 800 850 900 950 1000
● Polysiloxane
H2 H2
Si O Si
K
m/z= 269.1767
N
5a

(c)


PD-RS-417 Neg 2 (0.062) AM2 (Ar,22000.0,554.26,0.00,LS 10); Cm (1:9)
1: TOF MS ES-
5.26e7
100
%
0
261.0733
381.0717
397.0659
413.0608
277.0685
259.0589
435.0630
519.0837
503.0915
535.0811
639.0916
639.0236
640.0961
148.9871
183.0288
80.9477
222.8250
314.7589
381.0235
316.7672
536.0903
537.0919
775.0858
776.0876
778.0905
761.1085
897.0980
● ● (Polysiloxanes)
H Ph Ph
Ph Si O Si O Si Ph
Ph H H
Observed mass [M-H]⁻ = 503.0915
m/z
50 100 150 200 250 300 350 400 450 500 550 600 650 700 750 800 850 900 950 1000
PD-RS-417 Neg (0.045) Is (0.00,0.10) C30H27O2Si3
1: TOF MS ES-
5.64e12
503.1319
504.1353
505.1287
505.1386
507.1354
PD-RS-417 Neg 2 (0.062) AM2 (Ar,22000.0,554.26,0.00,LS 10); Cm (1:9)
1: TOF MS ES-
1.18e7
503.0915
503.0412
504.1019
505.1019
517.0800
517.0254
518.0949
486 488 490 492 494 496 498 500 502 504 506 508 510 512 514 516 518

(d)


6.77
5.11
3.08
2.94
2.24
3.00
3.01
3.01
9.03
N
O
DPDS
10.0 9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0 -0.5 -1.0
f1 (ppm)

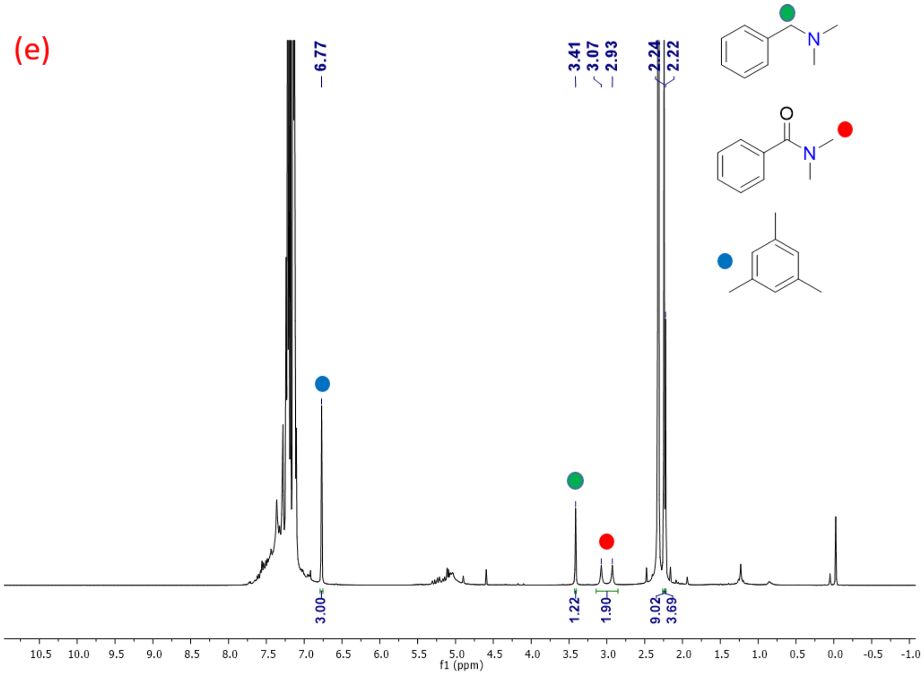
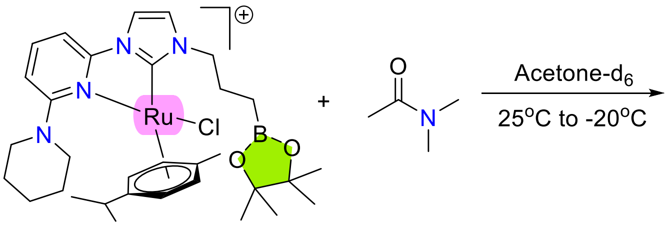


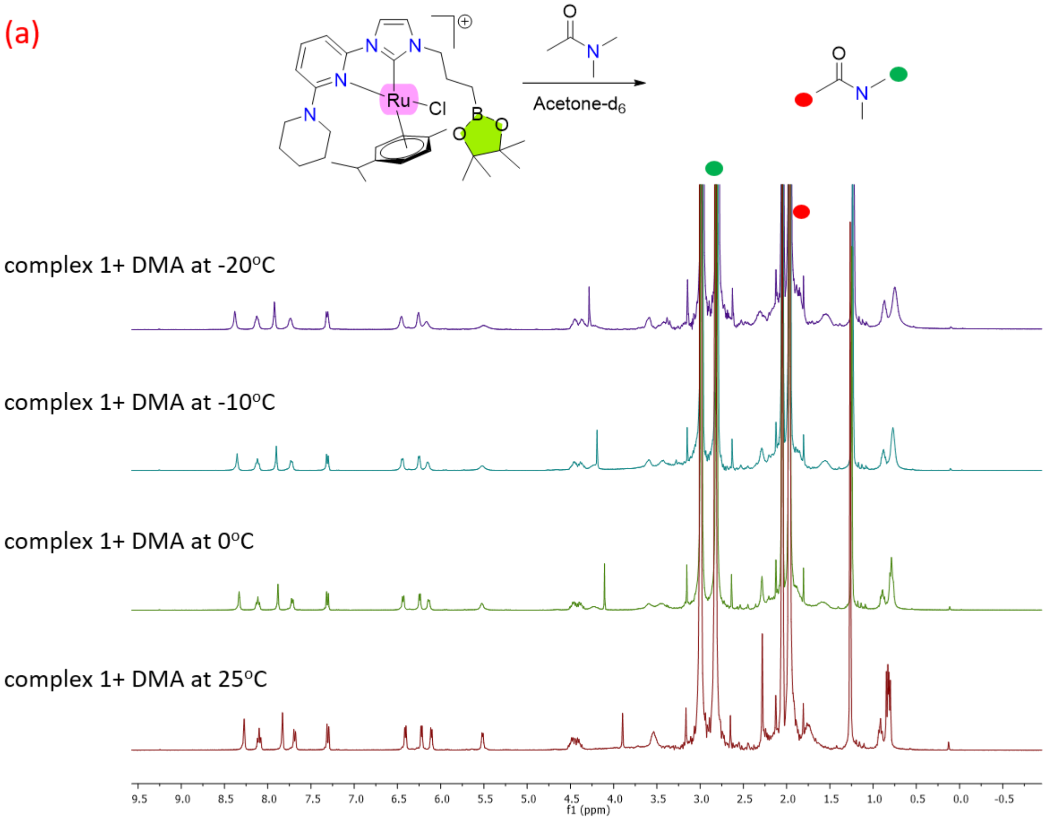
Figure S216. Deoxygenative hydrogenation of **4a** to **5a** using 1,3- diphenyldisiloxane and complex **1** **(a)** ^{1}H NMR of the crude reaction mixture in CDCl$_3$ using 1.1 equiv. of 1,3-diphenyldisiloxane **(b,c)** +ve and –ve region ESI-HRMS spectrum analysis of the polysiloxane by-products measured in acetonitrile **(d)** ^{1}H NMR of the crude reaction mixture in CDCl$_3$ using without complex **1** and 1.1 equiv. of 1,3-diphenyldisiloxane **(e)** ^{1}H NMR of the crude reaction mixture in CDCl$_3$ using 2 equiv. of 1,3-diphenyldisiloxane.

25. Variable Temperature (VT) NMR study for the interaction of appended boron in complex 1 with N,N-Dimethylacetamide (DMA)

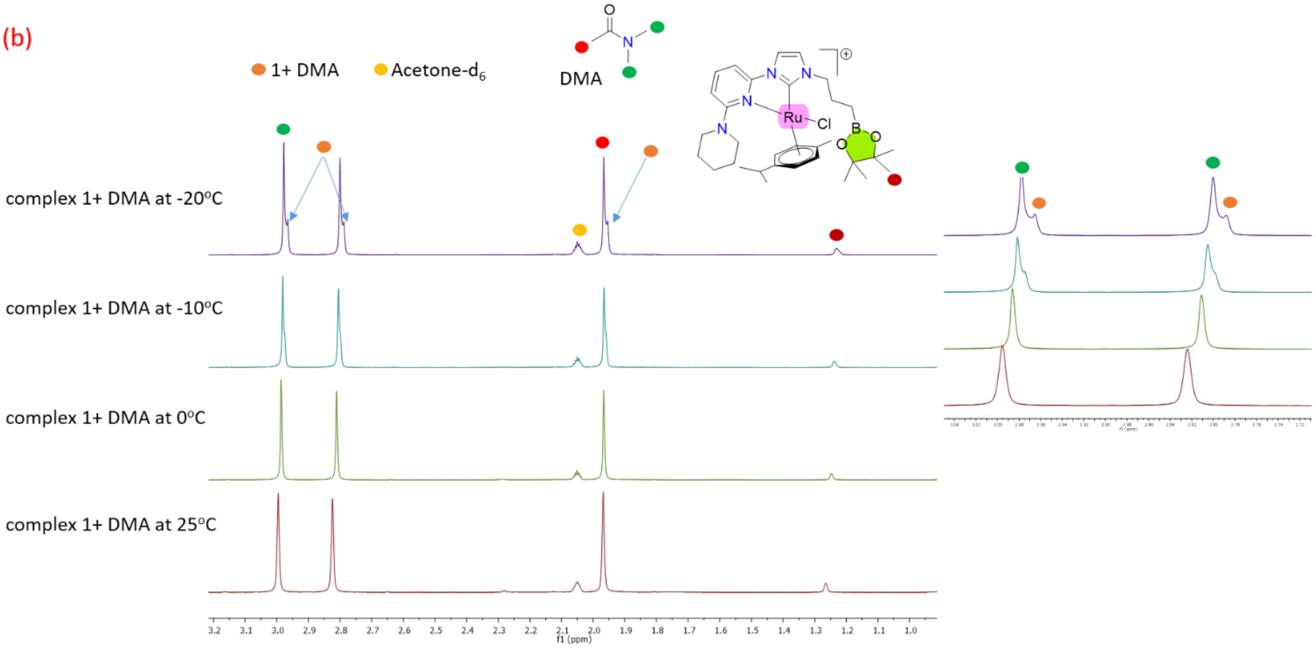


In a pre-dried NMR tube, a 1:20 mixture of complex **1** (0.0142 mmol)**,** N,N-dimethylacetamide (DMA) (0.284 mmol), and 0.6 mL acetone-d$_6$ was added and variable temperature NMR study was performed from 25 °C to -20 °C. The ^{1}H NMR analysis showed a slight shifting of the –Methyl protons attached to the N-atom of DMA with the generation of small new peaks at 2.97 and 2.79 ppm upon lowering the temperature to -20 °C, whereas ^{11}B NMR showed a very minor broad peak around 22.48 ppm.

(a)


N
N
N
N
Ru
Cl
B
O
O
⊕
O
N
Acetone-d6
O
N
complex 1+ DMA at -20°C
complex 1+ DMA at -10°C
complex 1+ DMA at 0°C
complex 1+ DMA at 25°C
9.5
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
-0.5
f1 (ppm)

(b)


● 1+ DMA
● Acetone-d6
O
N
DMA
N
N
N
N
Ru
Cl
B
O
O
⊕
complex 1+ DMA at -20°C
complex 1+ DMA at -10°C
complex 1+ DMA at 0°C
complex 1+ DMA at 25°C
3.2
3.1
3.0
2.9
2.8
2.7
2.6
2.5
2.4
2.3
2.2
2.1
2.0
1.9
1.8
1.7
1.6
1.5
1.4
1.3
1.2
1.1
1.0
f1 (ppm)

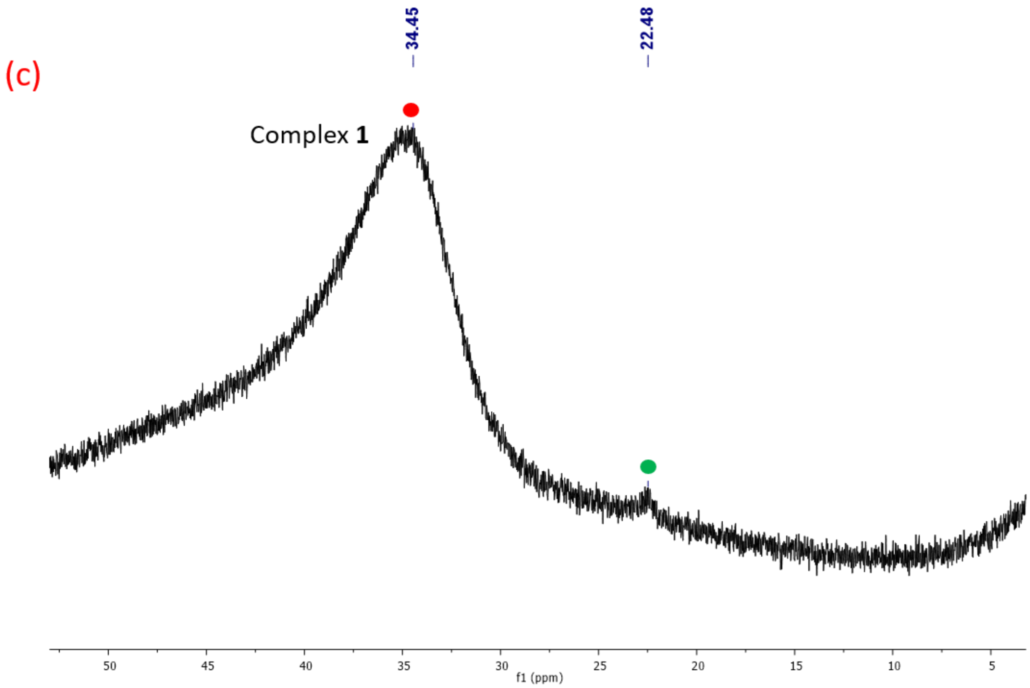
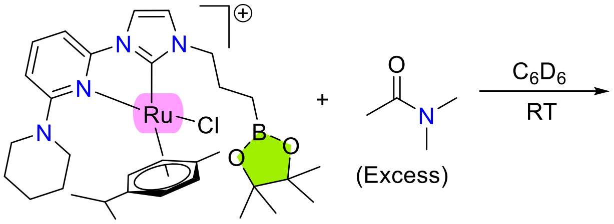


Figure S217: Variable temperature (VT) NMR spectrum for the interaction of DMA with complex **1** (a) Full region ^{1}H NMR spectrum from 25 ºC to -20 ºC (b) Zoom region ^{1}H NMR spectrum from 25 ºC to -20 ºC showing the generation of new peaks at 2.97 and 2.79 ppm (c) Zoom region ^{11}B NMR at -20 ºC.



In a pre-dried NMR tube, NMR scale reaction was performed using an excess amount of N,N-dimethylacetamide (3.22 mmol, 300 µL) and complex **1** (0.0142 mmol, 10 mg) in benzene-d$_6$ (300 µL) at room temperature. ^{11}B NMR analysis showed the formation of a new broad peak signal at 22.29 ppm.[28,29]

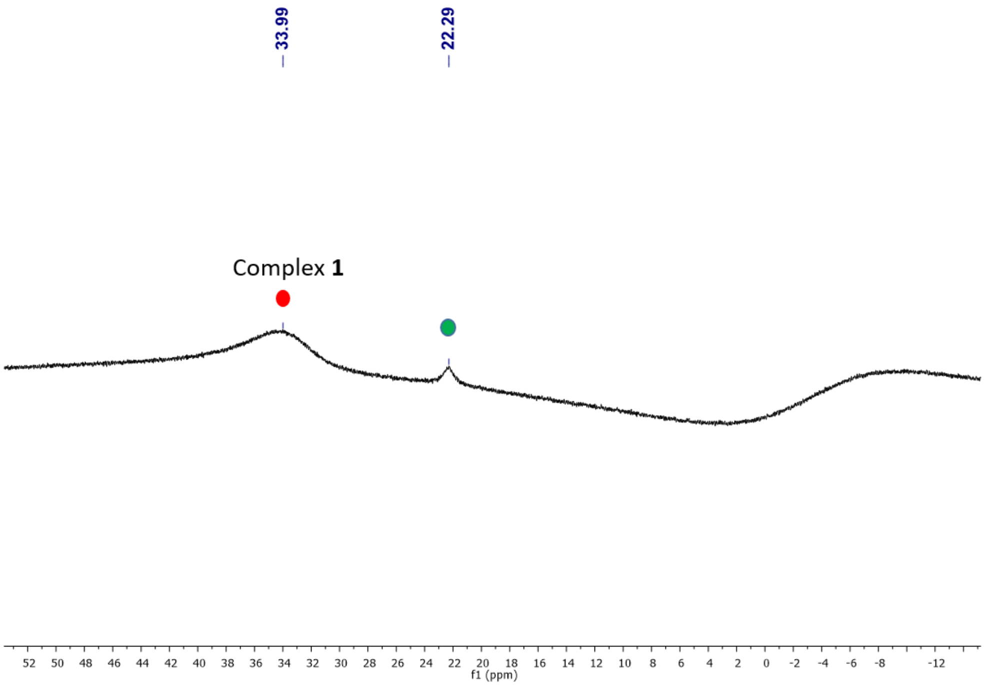
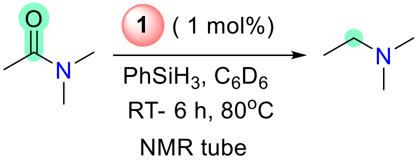


Figure S218: ^{11}B NMR spectrum using excess DMA and complex **1** at room temperature

26. ^{1}H NMR monitoring of N,N-Dimethylethanamine formation with the progress of time



Inside the glove box, in a pre-dried NMR tube, N,N-dimethylacetamide (1 equiv., 0.25 mmol), catalyst **1** (1 mol %), 0.6 mL of C_6D_6 and followed by $PhSiH_3$ (1.1 equiv., 0.275 mmol) were added and the tube was brought out of the glove box and ^{1}H NMR was measured in different intervals of time from RT- 6 hours after heating at 80 ºC in an oil bath, where the generation of a new peak signal at 1.95 ppm (q) and 0.75 ppm (t) was observed within 2 hours, which are corresponds to hydrogenated amine product N, N-dimethylethanamine. Further, heating the reaction for 6 hours resulted in an increased concentration of amine formation with a decrease in N,N-dimethylacetamide and $PHSiH_3$ concentration.

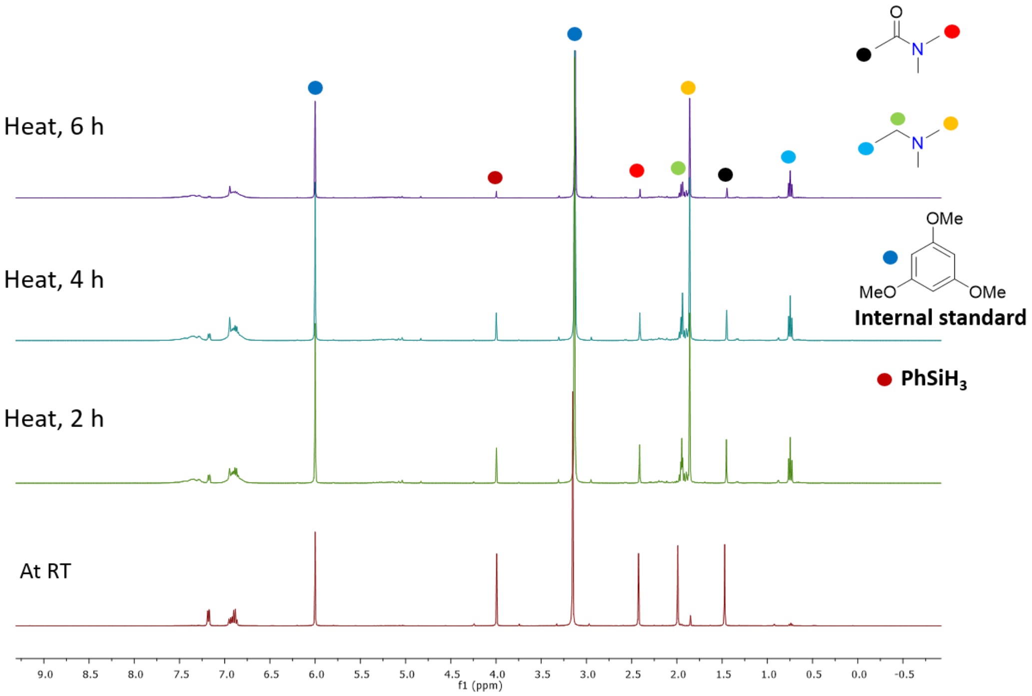
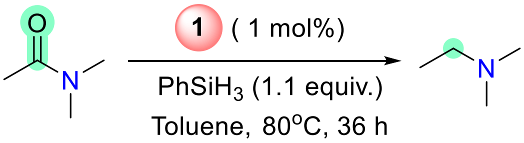
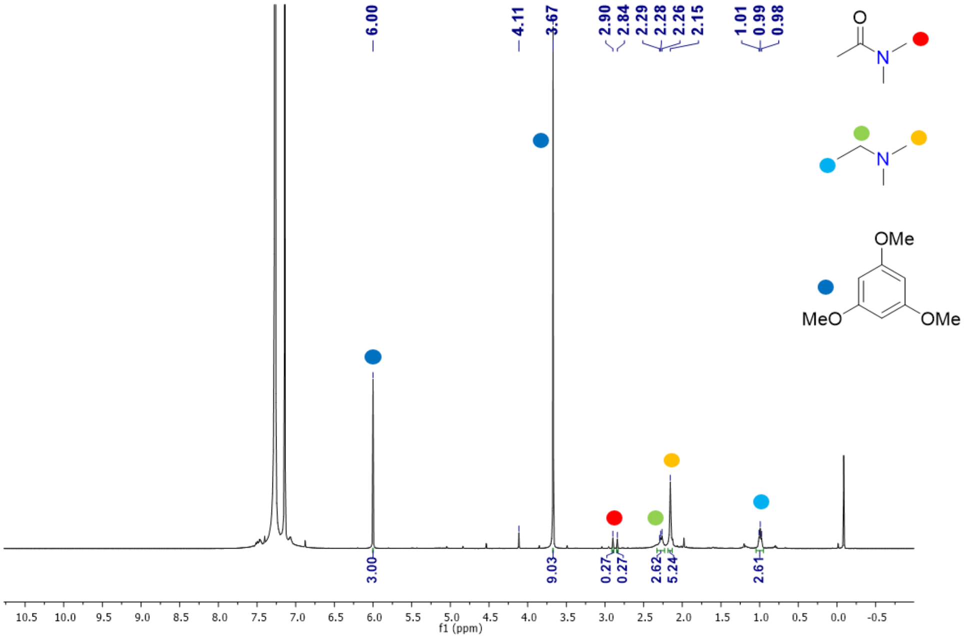


Figure S219. ^{1}H NMR spectrum of NMR tube experiment for the progress of N, N-dimethylethanamine formation measured in intervals of RT-6 hours in C_6D_6

27. Catalytic deoxygenative hydrogenation of N,N-dimethylacetamide using complex 1



Inside a N_2 filled glove box, a 25 mL pressure tube equipped with a magnetic stirring bar was charged with **1** (3.53 mg, 1 mol%), N,N-dimethylacetamide (43.9 mg, 0.503 mmol). 1 mL of dry toluene was added, followed by the addition of phenylsilane (59.9 mg, 0.553 mmol), and the closed vessel was heated at 80 ºC for 36 hours. After completion of the reaction, the solution was cooled down to room temperature, and 1,3,5-trimethoxybenzene (0.503 mmol) was added as an internal standard, and NMR yield was analyzed using ^{1}H NMR in $CDCl_3$ as the solvent, where 87% NMR yield (0.4376 mmol) of hydrogenated product N,N-dimethylethanamine was observed.



% DMA conversion = 91%, % N,N-dimethylethanamine formation = 87%

Figure S220: Deoxygenative hydrogenation of N,N-dimethylacetamide to N,N-dimethylethanamine using complex **1** in $CDCl_3$

28. Plausible Reaction Mechanism

Initially, complex **1**, reacts with $PhSiH_3$ to generate the active [**Ru-H**] intermediate (**A**) and the appended boron arm in SCS cooperatively participate for the activation of incoming amide substrate to generate the intermediate **(B)**. The subsequent hydride insertion and coordination of silylium cation ($PhSiH_2^+$)[30–32] generates intermediate **(C)**. Further, intermediate **(C)**, might undergoes σ-bond metathesis[25] with $PhSiH_3$ to generate the active hydride intermediate **(A)** with the release of diphenyldisiloxane and imine[31] molecule. The generated disiloxane further acts as a secondary hydride source and generate the desired amine product with the formation of dehydrogenated polymerize product polysiloxanes.

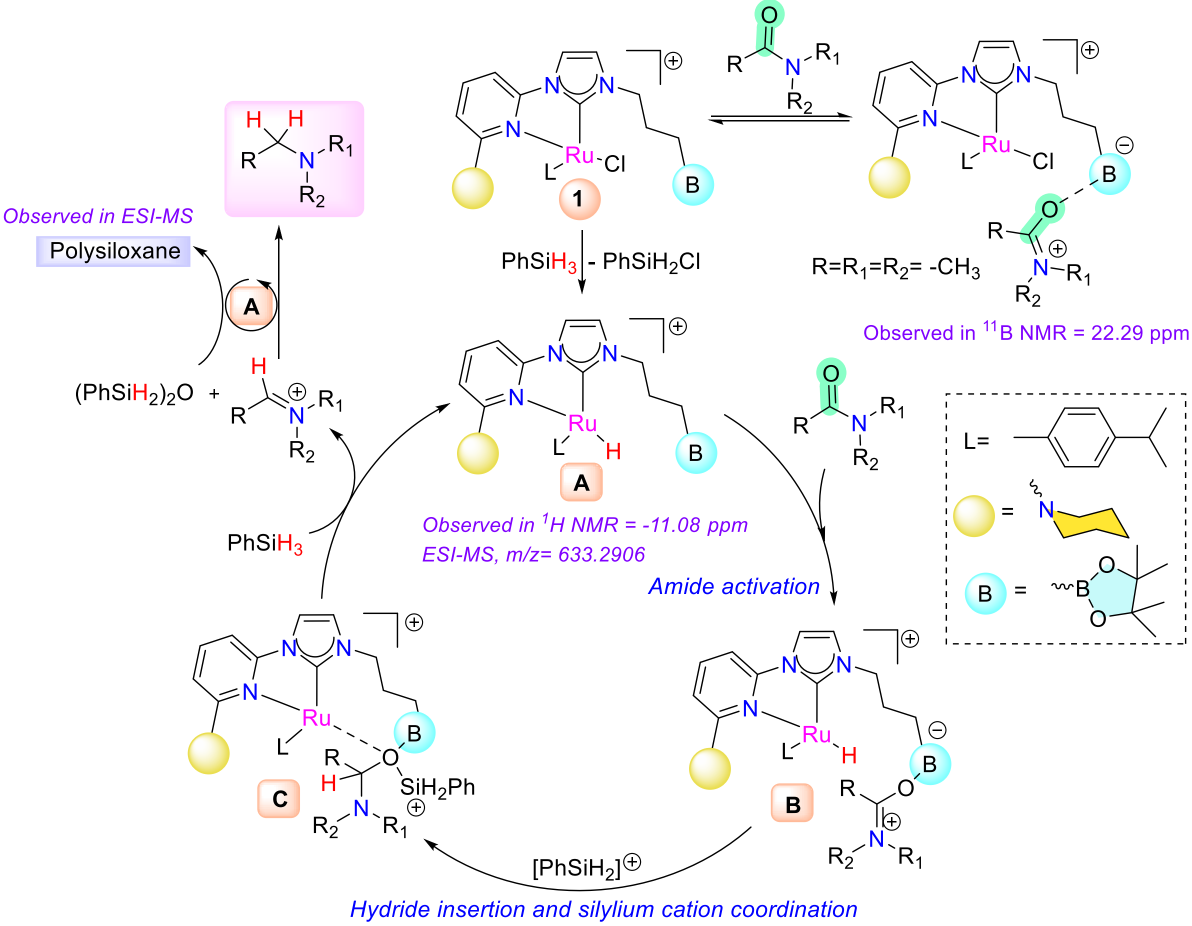


Figure S221: Plausible reaction mechanism

29. X-Ray Crystallographic data

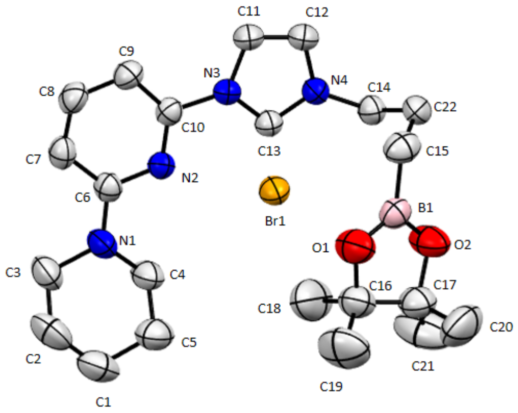


Figure S222. Molecular structure of Ligand **L1**

Table S4. Crystal data and structure refinement for Ligand **L1**

Name	**L1**
CCDC Number	**2346559**
Empirical formula	$C_{22}H_{34}BBrN_4O_2$
Formula weight	477.25
Temperature/K	298(2)
Crystal system	triclinic
Space group	P-1
a/Å	8.5419(6)
b/Å	12.0415(9)
c/Å	13.3740(11)
α/°	68.584(2)
β/°	76.132(2)
γ/°	76.223(2)
Volume/Å^3	1225.92(16)
Z	2
ρ_{calc}g/cm^3	1.293
μ/mm^{-1}	1.701
F(000)	500.0
Crystal size/mm^3	0.24 × 0.22 × 0.2
Radiation	MoKα (λ = 0.71073)
2Θ range for data collection/°	5.452 to 52.794
Index ranges	$-10 \leq h \leq 10$, $-15 \leq k \leq 15$, $-16 \leq l \leq 16$
Reflections collected	21580
Independent reflections	4960 [R_{int} = 0.0442, R_{sigma} = 0.0392]
Data/restraints/parameters	4960/0/275
Goodness-of-fit on F^2	0.861
Final R indexes [I>=2σ (I)]	R_1 = 0.0395, wR_2 = 0.1153
Final R indexes [all data]	R_1 = 0.0571, wR_2 = 0.1325
Largest diff. peak/hole / e Å^{-3}	0.47/-0.33

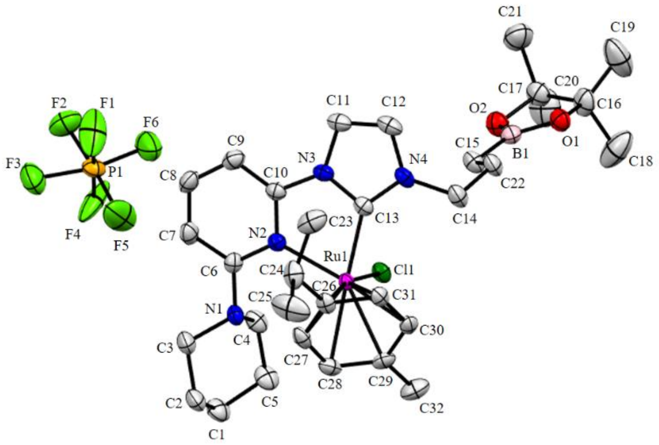


Figure S223. Molecular structure of Complex **1-PF$_6$**

Table S5. Crystal data and structure refinement for complex **1-PF$_6$**

Name	**1-PF$_6$**
CCDC Number	**2349798**
Empirical formula	$C_{32}H_{47}BClF_6N_4O_2PRu$
Formula weight	812.03
Temperature/K	273.15
Crystal system	monoclinic
Space group	$P2_1/c$
a/Å	18.2664(10)
b/Å	13.8510(7)
c/Å	14.4079(8)
α/°	90
β/°	90.422(2)
γ/°	90
Volume/Å^3	3645.2(3)
Z	4
ρ_{calc}g/cm^3	1.480
μ/mm-1	0.613
F(000)	1672.0
Crystal size/mm^3	0.24 × 0.18 × 0.12
Radiation	MoKα (λ = 0.71073)
2Θ range for data collection/°	6.03 to 52.898
Index ranges	$-22 \leq h \leq 22$, $-17 \leq k \leq 17$, $-18 \leq l \leq 18$
Reflections collected	66172
Independent reflections	7465 [Rint = 0.0443, Rsigma = 0.0228]
Data/restraints/parameters	7465/141/504
Goodness-of-fit on F^2	1.073
Final R indexes [I>=2σ (I)]	R1 = 0.0424, wR2 = 0.1025
Final R indexes [all data]	R1 = 0.0486, wR2 = 0.1072
Largest diff. peak/hole / e Å^{-3}	1.77/-0.93

30. References

1 M. A. Bennett, T. N. Huang, T. W. Matheson and A. K. Smith, *Inorg. Synth.*, 1982, **21**, 74–78.

2 M. Toure, O. Chuzel and J. L. Parrain, *Dalt. Trans.*, 2015, **44**, 7139–7143.

3 S. Kisan, V. Krishnakumar and C. Gunanathan, *ACS Catal.*, 2017, **7**, 5950–5954.

4 J. L. Bolliger, M. Oberholzer and C. M. Frech, *Adv. Synth. Catal.*, 2011, **353**, 945–954.

5 M. Toure, O. Chuzel and J. L. Parrain, *Dalt. Trans.*, 2015, **44**, 7139–7143.

6 N. Schröder, J. Wencel-Delord and F. Glorius, *J. Am. Chem. Soc.*, 2012, **134**, 8298–8301.

7 N. A. Sitte, M. Bursch, S. Grimme and J. Paradies, *J. Am. Chem. Soc.*, 2019, **141**, 159–162.

8 J. W. Ciszek, Z. K. Keane, L. Cheng, M. P. Stewart, L. H. Yu, D. Natelson and J. M. Tour, *J. Am. Chem. Soc.*, 2006, **128**, 3179–3189.

9 G. Zhen, G. Zeng, F. Wang, X. Cao and B. Yin, *Adv. Synth. Catal.*, 2023, **365**, 43–52.

10 A. Gupta, J. K. Vankar, J. P. Jadav and G. N. Gururaja, *J. Org. Chem.*, 2022, **87**, 2410–2420.

11 L. Wang, F. Y. Dai, J. Zhu, K. K. Dong, Y. L. Wang and T. Chen, *J. Chem. Res.*, 2011, **35**, 313–316.

12 X. Tian, Z. Jiang, S. Hou, H. Hu, J. Li and B. Zhao, *Angew. Chem. Int. Ed.*, 2023, **62**, e202301764.

13 S. Zhou, K. Junge, D. Addis, S. Das and M. Beller, *Angew. Chem. Int. Ed.*, 2009, **48**, 9507–9510.

14 X. Cui, X. Dai, Y. Deng and F. Shi, *Chem. Eur. J.*, 2013, **19**, 3665–3675.

15 A. Tillack, I. Rudloff and M. Beller, *Eur. J. Org. Chem.*, 2001, 523–528.

16 E. L. Stoll, T. Tongue, K. G. Andrews, D. Valette, D. J. Hirst and R. M. Denton, *Chem. Sci.*, 2020, **11**, 9494–9500.

17 F. Xiong, Q. Cheng, Y. Dang and K. Gao, *Org. Chem. Front.*, 2022, **9**, 4882–4889.

18 S. Peishan, T. T. Dang, A. M. Seayad and B. Ramalingam, *ChemCatChem*, 2014, **6**, 808–814.

19 I. Šolić, D. Reich, J. Lim and R. W. Bates, *Asian J. Org. Chem.*, 2017, **6**, 658–661.

20 M. C. Fu, R. Shang, W. M. Cheng and Y. Fu, *Angew. Chem. Int. Ed.*, 2015, **54**, 9042–9046.

21 V. G. Chandrashekhar, W. Baumann, M. Beller and R. V. Jagadeesh, *Science*, 2022, **376**, 1433–1441.

22 Y. Wang, H. Zhang, S. Xie, H. Sun, X. Li, O. Fuhr and D. Fenske, *Organometallics*, 2020, **39**, 824–833.

23 E. Gopi, V. Geertsen, E. Gravel and E. Doris, *ChemCatChem*, 2019, **11**, 5758–5761.

24 F. Lima, M. A. Kabeshov, D. N. Tran, C. Battilocchio, J. Sedelmeier, G. Sedelmeier, B. Schenkel and S. V. Ley, *Angew. Chem. Int. Ed.*, 2016, **55**, 14085–14089.

25 P. Pandey and J. K. Bera, *Chem. Commun.*, 2021, **57**, 9204–9207.

26 J. A. Buonomo, C. G. Eiden and C. C. Aldrich, *Synth.*, 2018, **50**, 278–281.

27 N. W. Mitzel, A. Schier, H. Beruda and H. Schmidbaur, *Chem. Ber.*, 1992, **125**, 1053–1059.

28 A. Di Wu, Y. Wang, S. Tao, T. Wang, F. Chen, H. Du, C. Bo, M. Li, B. Dai and D. Wei, *Adv, synth. catal.* 2025, DOI:10.1002/adsc.202401441.

29 J. Li, H. Wang, Z. Qiu, C. Y. Huang and C. J. Li, *J. Am. Chem. Soc.*, 2020, **142**, 13011–13020.

30 M. Yasuda, Y. Onishi, M. Ueba, T. Miyai and A. Baba, *J. Org. Chem.*, 2001, **66**, 7741–7744.

31 D. Mukherjee, S. Shirase, K. Mashima and J. Okuda, *Angew. Chem. Int. Ed.*, 2016, **55**, 13326–13329.

32 E. Blondiaux and T. Cantat, *Chem. Commun.*, 2014, **50**, 9349–9352.