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

Supporting information

Aza-Claisen rearrangement as a key step in synthesis of specialized anilines used in production of efficient ethenolysis catalysts

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1 Materials and methods

1.1 General remarks

All reactions requiring the exclusion of oxygen and moisture were carried out in dry glassware (kept overnight in an oven at 120 °C) with dry anhydrous solvents (purified using mBraun's SPS) under a dry and oxygen-free argon atmosphere using the Schlenk technique. The addition of dry solvents or reagents was carried out using argon flushed stainless steel cannulas and plastic syringes.

For spectroscopic and analytic characterizations, the following devices were used:

Analytical thin layer chromatography (TLC) was performed on Merck Silica gel 60 F254 precoated aluminum sheets. Components were visualized by observation under UV light (254 or 365 nm) or dyed by aqueous $KMnO_4$ or anisaldehyde reagent.

Flash column chromatography was performed using silica gel 60 (230–400 mesh), purchased from Merck.

GC chromatograms were recorded using a PerkinElmer Clarus 580 model. As capillary column, an IntertCap 5MS-Sil column was employed with helium as carrier gas. GC conversions were determined based on the ratio of an internal standard (methyl stearate) present in the starting material (methyl oleate).

^{1}H NMR spectra were recorded in $CDCl_3$ or CD_2Cl_2 at room temperature on Agilent Mercury spectrometers (400 MHz). The data were interpreted in first-order spectra. Chemical shifts δ are reported in parts per million (ppm) downfield from trimethylsilane as a reference to the residual solvent signal: chloroform (δ_H = 7.26 ppm), dichloromethane (δ_H = 5.32 ppm). The following abbreviations are used to indicate the signal multiplicity: s (singlet), d (doublet), t (triplet), q (quartet), hept (heptet), dd (doublet of doublet), dt (doublet of triplet), ddd (doublet of doublet of doublet), etc., bs (broad signal), m (multiplet). Coupling constants (J) are given in Hz and refer to H,H-couplings.

^{13}C NMR spectra were recorded in $CDCl_3$ or CD_2Cl_2 at room temperature on Agilent Mercury spectrometers (400 MHz). Chemical shifts are reported in δ units relative to the solvent signal: chloroform (δ_C = 77.16 ppm, central line of the triplet), dichloromethane (δ_C = 53.84 ppm, central line of the quintet). If no coupling constants are given, the multiplicity refers to ^{1}H-decoupled spectra; otherwise, the coupling constants belong to heteroatoms.

High Resolution Mass Spectra (HRMS) were provided by analytical laboratory at the Institute of Organic Chemistry, PAS or at the Institute of Biochemistry and Biophysics, PAS.

Elemental Analyses (EA) were provided by the EA analytical laboratory at the Institute of Organic Chemistry, Polish Academy of Sciences (PAS).

IR spectra were recorded on a Perkin-Elmer Spectrum One FTIR spectrometer. Substances were applied as films, solids, or in solution. The obtained data were processed with the software Omni32. The wavenumbers are given in cm^{-1}.

X-ray diffraction data was collected on the Agilent Technologies SuperNova Dual Source diffractometer with MoKα (λ = 0.71073 Å) radiation using CrysAlis RED software in Biological and Chemical Research Centre, University of Warsaw.

1.2 Reagents and solvents

All reagents were purchased from Sigma-Aldrich, Apeiron Synthesis, TCI, Fluorochem, Alfa Aesar, and POCH and used without further purification unless otherwise stated.

Ru8 was synthetized according to previously reported procedure.[1]

Aniline, 2-methylaniline, 2,4-dimethylaniline, crotonaldehyde, and allyl bromide were used after distillation under standard or reduced pressure.

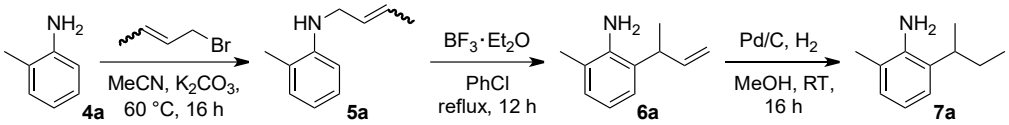
THF, which was used in "Synthesis of ruthenium complexes"—and PhMe—which was used for the addition of catalyst in "Ethenolysis of methyl oleate"—were distilled over sodium under argon atmosphere.

SnatchCat (1,4-bis(2-isocyanopropyl)piperazine) was used as a solution in dichloromethane (c = 10 mg/mL) in order to quench the ethenolysis reactions.

Ethylene gas was purchased and used as received from Air Liquide (3.5, 99.95% purity).

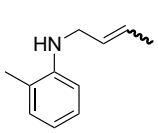
2 Synthesis of anilines

2.1 Synthesis of 2-(*sec-butyl*)-6-methylaniline (**7a**)



2.1.1 *N*-(but-2-en-1-yl)-2-methylaniline (**5a**)

Crotyl bromide (6.20 mL, 50.0 mmol, 1.00 equiv.) was added to a 250 mL round bottom flask equipped with magnetic stirring bar containing mixture of 2-methylaniline (18.6 mL, 175 mmol, 3.50 equiv.) and K_2CO_3 (14.0 g, 100 mmol, 2.00 equiv.) in CH_3CN (50 mL). The resulting mixture was stirred at 60 ℃ for 16 h. After completion of the reaction (monitored by TLC), water (50 mL) and CH_3CN (50 mL) were added to the mixture, stirred for 5 min and the layers were separated. The combined organic layers were washed with water (2×30 mL), dried over anh. Na_2SO_4, filtered, and the solvent was evaporated under reduced pressure to provide the crude product. It was purified by column chromatography using *n*-hexane as eluent to obtain the desired product **5a** as a pale yellow viscous liquid (3.60 g, 22.3 mmol, 44%).

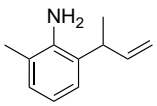


^{1}H NMR (400 MHz, $CDCl_3$): δ 7.24 – 7.18 (m, 1H), 7.16 – 7.11 (m, 1H), 6.80 – 6.68 (m, 2H), 5.89 – 5.67 (m, 2H), 3.92 – 3.77 (m, 2H), 3.59 (bs, 1H), 2.23 (s, 3H), 1.85 – 1.78 (m, 3H); **^{13}C NMR (101 MHz, $CDCl_3$):** δ 146.2, 130.1, 128.2, 128.0, 127.2, 122.0, 117.0, 110.0, 46.1, 17.9, 17.6; **HRMS-ESI (*m*/*z*)**: calculated for $C_{11}H_{16}N^+$([M+H$^+$]$^+$): 162.1277, found:, 162.1276; **IR**: 3428, 3015, 2964, 2933, 2916, 2854, 1605, 1586, 1509, 1474, 1445, 1377, 1314, 1254, 1131, 1051, 964, 919, 743, 714, 441.

^{1}H NMR spectrum is in agreement with the previously reported.[2,3]

2.1.2 2-(but-3-en-2-yl)-6-methylaniline (**6a**)

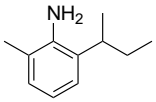
Boron trifluoride etherate (2.70 mL, 21.6 mmol, 1.50 equiv.) was slowly added to a solution of **5a** (2.33 g, 14.4 mmol, 1.00 equiv.) in chlorobenzene (20 mL) and the mixture was refluxed for 12 h. Next, the reaction mixture was cooled to room temperature (RT), quenched with a saturated aqueous solution of $NaHCO_3$ (20 mL), and the aqueous layer was extracted with EtOAc (2×25 mL). The combined organic phases were washed successively with water (25 mL), brine (25 mL), and then dried over anh. Na_2SO_4. Next filtered, concentrated under reduced pressure, and the residue was purified by column chromatography using *n*-hexane as eluent to obtain the desired product **6a** as a pale yellow viscous liquid (980 mg, 6.08 mmol, 42%).



^{1}H NMR (400 MHz, $CDCl_3$): δ 7.04 – 6.95 (m, 2H), 6.73 (t, J = 7.5 Hz, 1H), 6.02 – 5.91 (m, 1H), 5.13 (dt, J = 5.1, 1.5 Hz, 1H), 5.11 – 5.09 (m, 1H), 3.69 (bs, 2H), 3.55 – 3.46 (m, 1H), 2.19 (s, 3H), 1.42 (d, J = 7.0 Hz, 3H); **^{13}C NMR (101 MHz, $CDCl_3$):** δ 142.6, 142.5, 128.6, 128.3, 125.0, 122.6, 118.3, 113.9, 38.5, 19.0, 17.9; **HRMS-ESI (*m*/*z*)**: calculated for $C_{11}H_{16}N^+$([M+H$^+$]$^+$): 162.1277, found: 162.1276; **IR**: 3389, 3076, 2966, 2928, 2855, 1623, 1470, 1377, 1331, 1273, 1161, 1091, 912, 813, 746, 712.

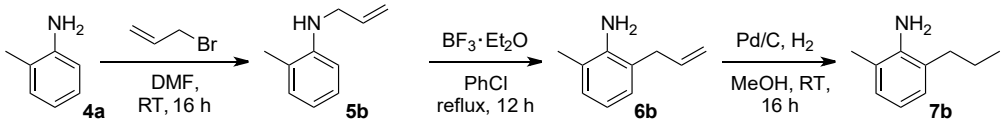
2.1.3 2-(*sec*-butyl)-6-methylaniline (**7a**)

In 250 mL round bottom flask equipped with magnetic stirring bar to a solution of **6a** (800 mg, 4.96 mmol, 1.00 equiv.) in MeOH (50 mL), palladium on carbon (10% wt., 50.0 μmol, 50.0 mg, 0.01 equiv.) was added. The reaction flask was purged with hydrogen and the reaction mixture was magnetically stirred for 16 h under H_2 (1 atm.). After that time, the reaction mixture was filtrated through neutral celite, the filtrate was concentrated under reduced pressure to afford the crude product which was purified by column chromatography with *n*-hexane as eluent to obtain **7a** as a reddish-brown oil (640 mg, 3.92 mmol, 79%).



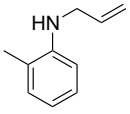
^{1}H NMR (400 MHz, $CDCl_3$): δ 7.02 – 6.98 (m, 1H), 6.96 – 6.91 (m, 1H), 6.73 (t, J = 7.5 Hz, 1H), 3.65 (bs, 2H), 2.66 (h, J = 6.9 Hz, 1H), 2.20 (d, J = 0.7 Hz, 3H), 1.78 – 1.52 (m, 2H), 1.24 (d, J = 6.9 Hz, 3H), 0.92 (t, J = 7.4 Hz, 3H); **^{13}C NMR (101 MHz, $CDCl_3$):** δ 141.9, 131.2, 127.9, 124.0, 122.4, 118.4, 34.9, 29.6, 20.3, 18.2, 12.4; **HRMS-ESI (*m*/*z*)**: calculated for $C_{11}H_{18}N^+$([M+H$^+$]$^+$): 164.1433, found: 164.1432; **Elemental analysis**: calculated for $C_{11}H_{17}N$: C, 80.92; H, 10.50; N, 8.58; found: C, 81.02; H, 10.58; N, 8.55; **IR**: 3481, 3397, 3047, 2961, 2930, 2872, 1618, 1465, 1377, 1272, 1059, 1019, 999, 769, 742, 703, 521.

2.2 Synthesis of 2-methyl-6-propylaniline (**7b**)



2.2.1 *N*-allyl-2-methylaniline (**5b**)

Allyl bromide (6.20 mL, 70.0 mmol, 1.00 equiv.) was added dropwise to a 250 mL round bottom flask equipped with magnetic stirring bar containing a solution of 2-methylaniline (14.9 mL, 140 mmol, 1.50 equiv.) in DMF (20 mL) at 0 ℃. The resulting mixture was magnetically stirred at RT for 16 h. After the completion of reaction (monitored by TLC), water (50 mL) and EtOAc (50 mL) were added, the mixture was stirred for 5 min, and the layers were separated. The aqueous layer was extracted with EtOAc (2×25 mL). The combined organic layers were washed with water (2×30 mL) to remove traces of DMF, dried over anh. Na_2SO_4, filtered, and the solvent was evaporated under reduced pressure. The crude product was purified by column chromatography using *n*-hexane:EtOAc (*v*:*v* = 99:1) as eluent to obtain the desired product **5b** as a pale yellow viscous liquid (6.10 g, 41.4 mmol, 59%).

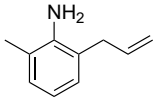


^{1}H NMR (400 MHz, $CDCl_3$): δ 7.21 – 7.15 (m, 1H), 7.14 – 7.08 (m, 1H), 6.73 (td, J = 7.4, 1.2 Hz, 1H), 6.67 (dd, J = 8.1, 1.2 Hz, 1H), 6.06 (ddt, J = 17.2, 10.5, 5.4 Hz, 1H), 5.35 (dq, J = 17.2, 1.7 Hz, 1H), 5.24 (dq, J = 10.2, 1.5 Hz, 1H), 3.88 (dt, J = 5.4, 1.6 Hz, 2H), 3.68 (bs, 1H), 2.21 (s, 3H); **^{13}C NMR (101 MHz, $CDCl_3$):** δ 146.0, 135.7, 130.2, 127.2, 122.1, 117.2, 116.3, 110.1, 46.6, 17.6; **HRMS-ESI (*m*/*z*)**: calculated for $C_{10}H_{14}N^+$([M+H$^+$]$^+$): 148.1121, found: 148.1120; **IR**: 3433, 3074, 3053, 3013, 2973, 2915, 2851, 1605, 1586, 1510, 1475, 1446, 1313, 1303, 1256, 1138, 1051, 993, 917, 744, 715, 441.

^{1}H and ^{13}C NMR spectra are in agreement with those previously reported.[4]

2.2.2 2-allyl-6-methylaniline (**6b**)

Boron trifluoride etherate (5.20 mL, 42.0 mmol, 1.50 equiv.) was slowly added to a solution of **5b** (4.12 g, 28.0 mmol, 1.00 equiv.) in chlorobenzene (25 mL) and the mixture was refluxed for 12 h. Then, reaction mixture was cooled to RT, quenched with saturated aqueous solution of $NaHCO_3$ (20 mL), and the aqueous layer was extracted with EtOAc (2×25 mL). The combined organic phases were washed successively with water (25 mL), brine (25 mL), and then dried over anh. Na_2SO_4. Next filtered, concentrated under reduced pressure, and the residue was purified by column chromatography using *n*-hexane as eluent to obtain the desired product **6b** as a pale yellow viscous liquid (2.30 g, 15.6 mmol, 55%).

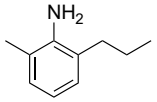


^{1}H NMR (400 MHz, $CDCl_3$): δ 7.04 – 7.01 (m, 1H), 7.00 – 6.96 (m, 1H), 6.72 (t, J = 7.5 Hz, 1H), 6.05 – 5.94 (m, 1H), 5.18 (t, J = 1.7 Hz, 1H), 5.15 (dq, J = 8.0, 1.7 Hz, 1H), 3.68 (bs, 2H), 3.36 (dt, J = 6.2, 1.7 Hz, 2H), 2.22 (s, 3H); **^{13}C NMR (101 MHz, $CDCl_3$):** δ 143.1, 136.2, 128.9, 128.1, 123.4, 122.4, 118.3, 116.2, 36.9, 17.7; **HRMS-ESI (*m*/*z*)**: calculated for $C_{10}H_{14}N^+$([M+H$^+$]$^+$): 148.1121, found: 148.1120; **IR**: 3481, 3398, 3038, 2956, 2929, 2869, 1619, 1598, 1465, 1455, 1377, 1266, 1110, 744.

^{1}H and ^{13}C NMR spectra are in agreement with those previously reported.[5]

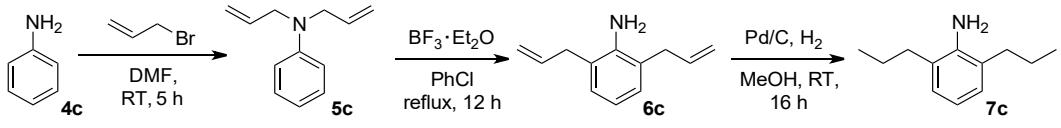
2.2.3 2-methyl-6-propylaniline (**7b**)

In 250 mL round bottom flask equipped with magnetic stirring bar to a solution of **6b** (1.91 g, 13.1 mmol, 1.00 equiv.) in MeOH (50 mL), palladium on carbon (10% wt., 130 μmol, 140 mg, 0.01 equiv.) was added. The reaction flask was purged with hydrogen and the reaction mixture was magnetically stirred for 16 h under H_2 (1 atm.). Next, the reaction mixture was filtrated through neutral celite, the filtrate was concentrated under reduced pressure to afford the crude product which was purified by short-path distillation under reduced pressure to obtain **7b** as a reddish-brown oil (1.71 g, 11.6 mmol, 88%).



^{1}H NMR (400 MHz, $CDCl_3$): δ 7.03 – 6.86 (m, 2H), 6.68 (t, J = 7.5 Hz, 1H), 3.71 (bs, 2H), 2.55 – 2.45 (m, 2H), 2.20 (s, 3H), 1.74 – 1.59 (m, 2H), 1.02 (t, J = 7.3 Hz, 3H); **^{13}C NMR (101 MHz, $CDCl_3$):** δ 142.2, 128.3, 127.5, 126.3, 122.3, 118.2, 33.8, 22.0, 17.9, 14.4; **HRMS-ESI (*m*/*z*)**: calculated for $C_{10}H_{16}N^+$([M+H$^+$]$^+$): 150.1277, found: 150.1275; **Elemental analysis**: calculated for $C_{10}H_{15}N$: C, 80.48; H, 10.13; N, 9.39; found: C, 80.61; H, 10.18; N, 9.34 **IR**: 3480, 3392, 3042, 3020, 2957, 2929, 2870, 1619, 1467, 1435, 1377, 1268, 1103, 761, 742, 634, 537.

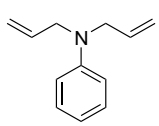
2.3 Synthesis of 2,6-dipropylaniline (**7c**)



2.3.1 *N*,*N*-diallylaniline (**5c**)

Allyl bromide (4.50 mL, 50.0 mmol, 1.00 equiv.) was added dropwise to a 250 mL round bottom flask equipped with magnetic stirring bar containing a solution of aniline **4c** (6.80 mL, 75.0 mmol, 1.50 equiv.) in DMF (20 mL) at 0 ℃. The resulting mixture was magnetically stirred at RT for 5 h. After the completion of reaction (monitored by TLC), water (50 mL) and EtOAc

(50 mL) were added to the mixture, stirred for 5 min, and the layers were separated. The aqueous layer was extracted with EtOAc (2×25 mL). The combined organic layers were washed with water (2×30 mL) to remove traces of DMF, dried over anh. Na_2SO_4, filtered, and the solvent was evaporated under reduced pressure. The residue was purified by column chromatography using *n*-hexane:EtOAc (*v*:*v* = 99:1) as eluent to obtain the desired product **5c** as a pale yellow viscous liquid (3.16 g, 18.2 mmol, 72%).

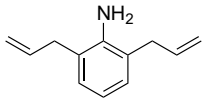


^{1}H NMR (400 MHz, $CDCl_3$): δ 7.25 – 7.19 (m, 2H), 6.76 – 6.66 (m, 3H), 5.94 – 5.83 (m, 2H), 5.24 – 5.15 (m, 4H), 3.97 – 3.92 (m, 4H); **^{13}C NMR (101 MHz, $CDCl_3$):** δ 148.8, 134.1, 129.2, 116.4, 116.1, 112.4, 52.8; **HRMS-ESI (*m*/*z*)**: calculated for $C_{12}H_{16}N^+$([M+H$^+$]$^+$): 174.1277, found: 174.1276; **IR**: 3084, 3061, 3040, 3025, 3007, 2979, 2911, 2858, 1642, 1597, 1574, 1504, 1387, 1356, 1345, 1231, 1180, 1038, 988, 916, 745, 690, 554, 512.

^{1}H and ^{13}C NMR spectra are in agreement with those previously reported.[6]

2.3.2 2,6-diallylaniline (**6c**)

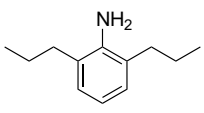
Boron trifluoride etherate (3.30 mL, 27.0 mmol, 1.50 equiv.) was slowly added to a solution of **5c** (3.12 g, 18.0 mmol, 1.00 equiv.) in chlorobenzene (20 mL) and the mixture was refluxed for 12 h. Then, reaction mixture was cooled to RT, quenched with saturated aqueous solution of $NaHCO_3$ (20 mL), and the aqueous layer was extracted with EtOAc (2×25 mL). The combined organic phases were washed successively with water (25 mL), brine (25 mL), and then dried over anh. Na_2SO_4. Next filtered, concentrated under reduced pressure, and the residue was purified by column chromatography using *n*-hexane as eluent to obtain the desired product **6c** as a pale yellow viscous liquid (1.20 g, 6.93 mmol, 38%).



^{1}H NMR (400 MHz, $CDCl_3$): δ 7.01 (d, J = 7.5 Hz, 2H), 6.83 – 6.71 (m, 1H), 5.99 (ddt, J = 17.1, 10.2, 6.2 Hz, 2H), 5.18 – 5.10 (m, 4H), 3.75 (bs, 2H), 3.35 (dt, J = 6.2, 1.7 Hz, 4H); **^{13}C NMR (101 MHz, $CDCl_3$):** δ 143.4, 136.1, 128.7, 124.1, 118.5, 116.3, 36.8; **HRMS-ESI (*m*/*z*)**: calculated for $C_{12}H_{16}N^+$([M+H$^+$]$^+$): 174.1277, found: 174.1276; **IR**: 3457, 3383, 3076, 3003, 2975, 2911, 2893, 2836, 1635, 1621, 1462, 1433, 1276, 1078, 996, 911, 748, 641, 530.

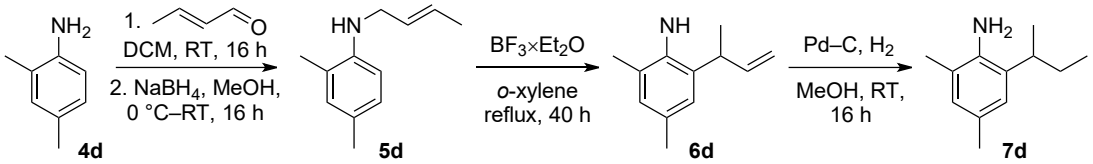
2.3.3 2,6-dipropylaniline (**7c**)

In 250 mL round bottom flask equipped with magnetic stirring bar to a solution of **6c** (1.11 g, 6.40 mmol, 1.00 equiv.) in MeOH (50 mL), palladium on carbon (10% wt., 80.0 μmol, 90.0 mg, 0.01 equiv.) was added. The reaction flask was purged with hydrogen and the reaction mixture was magnetically stirred for 16 h under H_2 (1 atm.). After that time, reaction mixture was filtrated through neutral celite, the filtrate was concentrated under reduced pressure to afford the crude product which was purified by short-path distillation under reduced pressure to obtain **7c** as a reddish-brown oil (840 mg, 4.74 mmol, 74%).



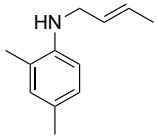
^{1}H NMR (400 MHz, $CDCl_3$): δ 6.97 (d, J = 7.5 Hz, 2H), 6.73 (t, J = 7.5 Hz, 1H), 3.64 (bs, 2H), 2.55 – 2.48 (m, 4H), 1.76 – 1.65 (m, 4H), 1.05 (t, J = 7.4 Hz, 6H); **^{13}C NMR (101 MHz, $CDCl_3$):** δ 141.9, 127.3, 126.6, 118.1, 33.9, 22.0, 14.4; **HRMS-ESI (*m*/*z*)**: calculated for $C_{12}H_{20}N^+$([M+H$^+$]$^+$): 178.1590, found: 178.1588; **IR**: 3467, 3385, 3075, 3045, 3022, 3005, 2975, 2915, 2898, 2854, 1621, 1468, 1433, 1267, 1084, 997, 913, 745, 703, 623, 539, 526.

2.4 Synthesis of 2-(*sec-butyl*)-4,6-dimethylaniline (**7d**)



2.4.1 *N*-(but-2-en-1-yl)-2,4-dimethylaniline (**5d)**

In a Schlenk flask equipped with magnetic stirring bar and dried under reduced pressure, magnesium sulphate (49.2 g, 408 mmol, 1.25 equiv.) and anh. DCM were placed (C = 1.0 M) followed by addition of 2,4-dimethylaniline (40.4 mL, 39.6 g, 327 mmol, 1.00 equiv.) and crotonaldehyde (40.3 mL, 34.4 g, 490 mmol, 1.50 equiv.). The resulting mixture was stirred at RT for 16 h. After the completion of reaction (monitored by TLC), the reaction mixture was filtered through neutral Celite, and the solvent was evaporated under reduced pressure to afford imine. Then, MeOH (500 mL) was added to the residue and the flask was placed in an ice-cooled bath. Sodium borohydride (13.6 g, 359 mmol, 1.10 equiv.) was added portion-wise, the mixture was stirred for 3 h at 0 ℃, and then for 16 h at RT. The solvent was evaporated, the crude mixture was washed with saturated $NaHCO_3$ (aq), and the aqueous phase was extracted with *n*-hexane (3×200 mL). The combined organic layers were washed with brine (200 mL), dried over $MgSO_4$, and evaporated. The product **5d** was obtained as an orange liquid (45.1 g, 258 mmol, 78%) and used in the next step without further purification.

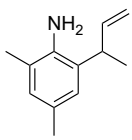


^{1}H NMR (400 MHz, $CDCl_3$): δ 6.98 – 6.94 (m, 1H), 6.93 – 6.91 (m, 1H), 6.57 (d, J = 8.1 Hz, 1H), 5.81 – 5.62 (m, 2H), 3.73 (dt, J = 1.3, 5.6 Hz, 2H), 3.42 (bs, 1H), 2.26 (s, 3H), 2.15 (s, 3H), 1.75 (dq, J = 1.3, 6.2 Hz, 3H); **^{13}C NMR (101 MHz, $CDCl_3$):** δ 144.0, 131.0, 128.5, 127.9, 127.4, 126.2, 122.3, 110.3, 46.4, 20.5, 17.9, 17.6.

^{1}H and ^{13}C NMR spectra are in agreement with those previously reported.[6]

2.4.2 2-(but-3-en-2-yl)-4,6-dimethylaniline (**6d**)

Boron trifluoride etherate (15.0 mL, 122 mmol, 1.30 equiv.) was slowly added to a solution of **5d** (16.4 g, 93.7 mmol, 1.00 equiv.) in dry *o*-xylene (170 mL) at 0 ℃ and the mixture was refluxed for 40 h. The reaction mixture was cooled to RT, quenched with saturated aqueous solution of $NaHCO_3$ (100 mL), and the aqueous layer was extracted with Et_2O (3×50 mL). The combined organic phases were washed with brine (30 mL), dried over anh. Na_2SO_4, and filtered. The solution was concentrated under reduced pressure to provide the product **6d** as an orange liquid (16.3 g, 93.6 mmol, >99%) which was used in the next step without further purification.

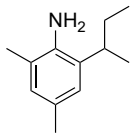


^{1}H NMR (400 MHz, $CDCl_3$): δ 6.82 (d, J = 0.7 Hz, 2H), 6.02 – 5.92 (m, 1H), 5.13 (dt, J = 6.5, 1.6 Hz, 1H), 5.11 – 5.09 (m, 1H), 3.58 (bs, 2H), 3.54 – 3.43 (m, 1H), 2.25 (s, 3H), 2.18 (s, 3H), 1.41 (d, J = 7.0 Hz, 3H); **^{13}C NMR (101 MHz, $CDCl_3$):** δ 142.6, 140.0, 129.3, 128.5, 127.4, 125.6, 122.8, 113.8, 38.5, 20.7, 19.0, 17.9.

2.4.3 2-(*sec*-butyl)-4,6-dimethylaniline (**7d**)

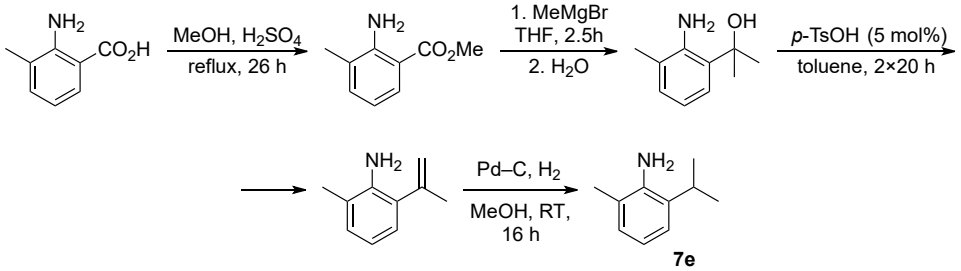
In a 500 mL round bottom flask equipped with magnetic stirring bar, **6d** (16.3 g, 93.6 mmol, 1.00 equiv.) was dissolved in MeOH (275 mL) and the mixture was barbotage with argon.

Then, palladium on carbon (10 wt.%, 996 mg, 936 mmol, 0.01 equiv.) was added. The reaction flask was purged with hydrogen and the reaction mixture was magnetically stirred for 16 h under H_2 (1 atm.), until full consumption of substrate (monitored by ^{1}H NMR measurement). After that, the reaction mixture was filtrated through neutral celite, the filtrate was concentrated under reduced pressure, and *n*-hexane (100 mL) was added followed by second filtration through neutral celite, and the solvent evaporation under reduced pressure. The crude mixture was purified by distillation under reduced pressure and the desired product **7d** was obtained as a colorless liquid (14.7 g, 83.1 mmol, 88%).



^{1}H NMR (400 MHz, $CDCl_3$): δ 6.84 – 6.79 (m, 1H), 6.81 – 6.75 (m, 1H), 3.51 (bs, 2H), 2.74 – 2.59 (m, 1H), 2.25 (s, 3H), 2.18 (s, 3H), 1.77 – 1.65 (m, 1H), 1.64 – 1.51 (m, 1H), 1.25 (d, J = 6.8 Hz, 3H), 0.93 (t, J = 7.4 Hz, 3H); **^{13}C NMR (101 MHz, $CDCl_3$):** δ 139.3, 131.4, 128.6, 127.4, 124.5, 122.6, 34.9, 29.8, 20.8, 20.3, 18.2, 12.5; **HRMS-ESI (*m*/*z*):** calculated for $C_{12}H_{20}N^+$ ([M+H]$^+$): 178.1590, found: 178.1587; **Elemental analysis**: calculated for $C_{12}H_{19}N$: C, 81.30; H, 10.80; N, 7.90; found: C, 81.36; H, 10.72; N, 7.71; **IR:** 3471, 3389, 3007, 2959, 2916, 2874, 2728, 1623, 1602, 1483, 1444, 1377, 1359, 1298, 1259, 1231, 1153, 1077, 1029, 1010, 965, 856, 827, 800, 765, 750, 581, 554, 460.

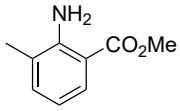
2.5 Synthesis of 2-isopropyl-6-methylaniline (**7e**)



2.5.1 Methyl 2-amino-3-methylbenzoate

2-Amino-3-methylbenzoic acid (51.95 g, 337 mmol, 1.0 equiv.) was placed in a 1 L round two-neck round bottom flask equipped with a large stirring bar and a reflux condenser with a bubbler (Ar inlet) mounted on top. The reaction setup was flushed with argon for a few minutes and solid was suspended in methanol (500 mL). Dropping funnel was mounted in the side neck and was charged with concentrated sulfuric acid, which was then was added dropwise (34 mL, 647 mmol, 36.6 equiv.) over 10 min; the substrate dissolved and the mixture warmed up spontaneously. Dropping funnel was removed and replaced with a stopper. The reaction flask was placed in an oil bath and the mixture was refluxed for 27 h at vigorous reflux (bath temp. = 110 °C). Heating bath was removed, the mixture was transferred to 1 L round bottom flask and the solvent was removed under reduced pressure. Obtained residue (wet, soapy solid) was suspended in water (200 mL) and DCM (250 mL). The flask was placed in cold water bath and 10% NaOH solution (ca. 260 mL) was slowly added until pH reached 7 and all the solid was dissolved. The mixture was transferred to a 1 L separatory funnel and the phases were separated. Water phase was extracted with DCM (2 × 100 mL). Combined organic phase was extracted with brine (100 mL), dried with Na_2SO_4, and filtered through cotton plug into 1 L round bottom flask. Solvents were removed under reduced pressure to give thick oil with some precipitated solid (35.2 g). The residue was diluted with hexane (30 mL) and the crystalline solid was filtered off on a sintered funnel. The solid was washed with hexane (2 × 15 mL). Combined filtrate was transferred to a 100 mL round bottom flask and concentrated under

reduced pressure. Small stirring bar was placed in the flask and the oil was further dried under vacuum (rotary vane pump). Product was obtained as brown oil (26.2 g, 159 mmol, 47%) and used further without purification.

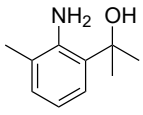


^{1}H NMR (400 MHz, $CDCl_3$): δ = 7.78 (ddq, J = 8.1, 1.7, 0.6 Hz, 1H), 7.19 (ddq, J = 7.2, 1.6, 0.8 Hz, 1H), 6.59 (ddd, J = 8.1, 7.2, 0.4 Hz, 1H), 5.85 (s, 2H), 3.87 (s, 3H), 2.17 (s, 3H); **^{13}C NMR (101 MHz, $CDCl_3$)**: δ 169.2, 149.1, 135.0, 129.3, 123.1, 115.7, 110.3, 51.6, 17.6.

^{1}H and ^{13}C NMR spectra are in agreement with those previously reported.[7]

2.5.2 2-(2-amino-3-methylphenyl)propan-2-ol

A 2 L 3-neck round-bottom flask equipped with a vacuum adapter and all joints stoppered was evacuated and heated with heat gun on high setting for ca. 3 min. After the flask cooled down, it was refilled with argon and the procedure was repeated two more times without heating, with 5 minutes of evacuation each time. The flask was then equipped with mechanical stirrer, a thermometer, and a septum. The flask was charged with methyl 2-amino-3-methylbenzoate (27.3 g, 165 mmol, 1 equiv.) and anhydrous THF (400 mL) *via* cannula. Septum was replaced with a 250 mL dropping funnel (previously flushed with argon). Reaction flask was placed in a cooling bath (dry ice/water/ethanol) to reach temperature below 0 °C. Methylmagnesium bromide (165 mL, 3 M solution in Et_2O, 495 mmol, 3 equiv.) was transferred to the dropping funnel *via* cannula and then was added dropwise over 40 min, not exceeding 5 °C. Mixture initially became yellow and with the progress of the addition the color changed to deep orange/brown. Cooling bath was removed and the mixture was warmed up to 20 °C over 30 min using a water bath. Thick, bright yellow precipitate formed. The mixture was left stirring at RT for another 2 h. The mixture was placed in a cooling bath (dry ice/water/ethanol) and cooled to 0 °C. The reaction mixture was quenched by very slow addition of sat. NH_4Cl solution (50 mL). [Caution: quenching is strongly exothermic; the mixture warmed up to ca. 15 °C] The cooling bath was removed and the mixture was diluted with water (50 mL) and 3M HCl_{aq} (ca. 165 mL) was added to reach pH = 7 and dissolve inorganic salts. The mixture was transferred to 2 L separatory funnel and phases were separated. Aqueous layer was extracted with Et_2O (250 mL). [Note: if an emulsion forms few more drops of HCl_{aq} can be added]. Combined organic phases were washed with brine (100 mL), dried with Na_2SO_4, and filtered through cotton plug to 1 L round bottom flask. Solvents were removed under reduced pressure to obtain pale oil, which solidified shortly after cooling down. Solid was roughly ground with a spatula and then was dissolved in hot hexane (100 mL). After cooling down to RT crystalline precipitate formed, which was filtered off on a sintered funnel. Solid was washed with cold hexane (50 mL), initially dried on the funnel and transferred to 250 mL round bottom flask and dried under vacuum to give product as beige crystalline solid (25.73 g, 156 mmol, 94%)

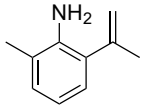


^{1}H NMR (400 MHz, $CDCl_3$): δ = 7.04 (dd, J = 7.9, 1.1 Hz, 1H), 7.01 (ddt, J = 7.4, 1.6, 0.8 Hz, 1H), 6.63 (t, J = 7.6 Hz, 1H), 3.89 (broad s, 2H), 2.18 (s, 3H), 1.68 (s, 6H); **^{13}C NMR (101 MHz, $CDCl_3$)**: δ 144.0, 129.9, 129.7, 129.7, 123.8, 123.6, 117.0, 74.5, 29.5, 18.0.

^{1}H NMR spectrum is in agreement with the previously reported.[8]

2.5.3 2-methyl-6-(prop-1-en-2-yl)aniline

A 1 L 2-neck round bottom equipped with a large stirring bar, Dean-Stark apparatus and a reflux condenser with a bubbler mounted on top was charged with 2-(2-amino-3-methylphenyl)-propan-2-ol (28.4 g, 172 mmol, 1.00 equiv.) and was flushed with argon. The solid was dissolved in toluene (650 mL) and *p*-toluenesulfonic acid (1.64 g, 8.60 mmol, 0.05 equiv.) was added. White precipitate was formed. The reaction mixture was placed in an oil bath preheated to 140 °C and the Dean-Stark apparatus was insulated. After ca. 30 min of reflux the mixture clarified. The mixture was refluxed overnight. Heating bath was removed and the mixture was transferred to 1 L round bottom flask and ca. 2/3 of the solvent was removed under reduced pressure. Saturated solution of $NaHCO_3$ (150 mL) was added, the mixture was transferred to a separatory funnel, shaken, and the phases were separated. Water phase was extracted with ethyl acetate (100 mL) and the combined organic phases were extracted with brine (100 mL). Organic phase was dried with anh. Na_2SO_4, filtered through cotton plug into 0.5 L round bottom flask and solvents were removed under reduced pressure. Stirring bar was placed in the flask and the oil was further dried under vacuum (rotary vane pump). Product was obtained as brown oil with ca. 93%$_w$ purity by NMR (24.9 g, 157 mmol, 91%) and used further without purification.

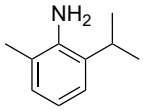


^{1}H NMR (101 MHz, $CDCl_3$): δ = 6.98 (ddd, J = 7.3, 1.7, 0.8 Hz, 1H), 6.93 (dd, J = 7.6, 1.6 Hz, 1H), 6.69 (t, J = 7.5 Hz, 1H), 5.32 – 5.30 (m, 1H), 5.06 (dq, J = 2.0, 1.0 Hz, 1H), 3.81 (s, 2H), 2.19 (s, 3H), 2.08 (dd, J = 1.6, 1.0 Hz, 3H); **^{13}C NMR (101 MHz, $CDCl_3$)**: δ 144.0, 141.0, 129.22, 129.20, 126.1, 122.5, 117.8, 115.5, 24.2, 18.1.

^{1}H NMR spectrum is in agreement with the previously reported.[8]

2.5.4 2-isopropyl-6-methylaniline (**7e**)

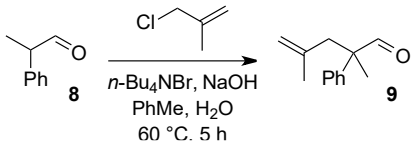
A 1 L 2-neck flask equipped with a magnetic stirring bar, a rotaflo valve/bubbler adapter and a silicone septum was charged with palladium on carbon (10 wt.%, 1.67 g). Flask was evacuated and placed under argon atmosphere (repeated 3 times). Solid was suspended in degassed methanol (400 mL, degassed by bubbling argon for 30 min) and 2-methyl-6-(prop-1-en-2-yl)aniline (22.7 g, 157 mmol, 1 equiv.) dissolved in degassed methanol (100 mL) was added. A rubber balloon with H_2 (ca. 4 L) was attached through a needle submerged in the suspension and the mixture was purged with the gas within ca. 30 min. The balloon was refilled and the flow of gas was reduced to ca. 1–2 bubbles per second (regulated by the rotaflo adapter). When all the hydrogen was consumed (ca. 8 h) the balloon was refilled once again and the reaction was stirred overnight. The mixture was filtered through celite pad to a 1 L round bottom flask and the pad was washed with methanol (50 mL). Solvent was removed under reduced pressure and the crude oil was transferred to 50 mL round bottom flask equipped with a stirring bar. Small amount of hexane was used to transfer all the remaining crude oil to the 50 mL flask. Solvent was removed under reduced pressure and obtained oil was purified by distillation under reduced pressure (without Vigreux) using diaphragm pump. After discarding small forerun, product was collected as fraction boiling in 86–90 °C range at 5 mbar (heating bath temp = 105–115 °C). Product was obtained as clear, slightly yellowish oil (22.40 g, 150 mmol, 96%) and was stored under argon in a fridge (4 °C).



^{1}H NMR (400 MHz, $CDCl_3$): δ = 7.08 – 7.02 (m, 1H), 6.95 (d, J = 7.0 Hz, 1H), 6.73 (t, J = 7.5 Hz, 1H), 3.66 (s, 2H), 2.93 (hept, J = 6.8 Hz, 1H), 2.20 (s, 3H), 1.28 (d, J = 6.8 Hz, 6H); **^{13}C NMR (101 MHz, $CDCl_3$)**: δ = 141.6, 132.1, 128.1, 123.2, 122.4, 118.4, 27.9, 22.5, 18.1.

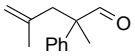
3 Synthesis of aldehyde 9

Synthesis of 2,4 dimethyl-2-phenylpent-4-enal (**9**)



Aldehyde was synthesized according to procedure based on patent.[9]

In a 1 L three-necked round bottom flask equipped with a reflux condenser, dropping funnel, and magnetic stirring bar, sodium hydroxide (17.9 g, 447 mmol, 1.50 equiv.), (n-Bu)$_4$NBr (9.61 g, 29.8 mmol, 0.100 equiv.), distilled water (60 mL), and toluene (400 mL) were placed. The mixture was warmed up to 60 °C and a mixture of 2-phenylpropanal (39.9 mL, 40.0 g, 298 mmol, 1.00 equiv.) and 3-chloro-2-methylpropene (38.8 mL, 384 mmol, 1.33 equiv.) was added. The resulting solution was stirred at 60 °C for 5 h, until full conversion of aldehyde (monitored by TLC). After cooling to RT, distilled water (400 mL) was added, layers were separated and aqueous layer was extracted with toluene (3×100 mL). The organic layers were combined, dried over $MgSO_4$, filtered through neutral celite, and the solvent was evaporated. The residue was purified by distillation to afford the desired product **9** as a colorless liquid (48.0 g, 209 mmol, 70%).



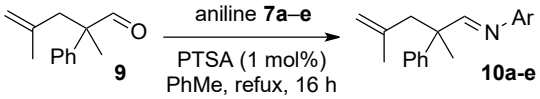
^{1}H NMR (400 MHz, $CDCl_3$): δ 9.55 (s, 1H), 7.41 – 7.35 (m, 2H), 7.31 – 7.28 (m, 3H), 4.81 (dq, J = 2.2, 1.5 Hz, 1H), 4.63 (dq, J = 1.8, 0.9 Hz, 1H), 2.76 – 2.63 (m, 2H), 1.47 (s, 3H), 1.40 (dd, J = 1.3, 0.9 Hz, 3H); **^{13}C NMR (101 MHz, $CDCl_3$):** δ 202.1, 141.6, 139.9, 128.9, 127.5, 127.4, 115.6, 53.6, 44.3, 24.3, 18.7.

^{1}H and ^{13}C NMR spectra are in agreement with those previously reported.[10]

4 Synthesis of imines

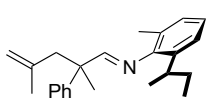
4.1 General procedure for synthesis of imines

In a round bottom flask equipped with Dean-Stark apparatus and magnetic stirring bar **9** (1.00 equiv.), aniline (**7a**–**7e**, 1.00 equiv.), and *p*-toluenesulfonic acid (PTSA, 1 mol%) were dissolved in PhMe (c = 0.3 M). The reaction mixture was refluxed until the full consumption of the substrates (monitored by ^{1}H NMR measurements). The solvent was evaporated under reduced pressure, the crude reaction mixture was filtrated on short pad of neutral aluminum oxide (Al_2O_3, neutral, Broockman Grade I), and dried *in vacuo* to afford imines **10a**–**10e** which were used in the next step without further purification.



4.1.1 *N*-(2-(*sec*-butyl)-6-methylphenyl)-2,4-dimethyl-2-phenylpent-4-en-1-imine (**10a**)

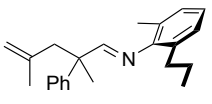
Imine was synthesized according to "General procedure for synthesis of imines". **9** (1.33 g, 7.03 mmol), **7a** (1.15 g, 7.03 mmol), and PTSA (12.1 mg, 70.4 μmol) were used to afford product **10a** as a yellow oily liquid (1.35 g, 4.06 mmol, 57%).



^{1}H NMR (400 MHz, $CDCl_3$): δ 7.68 – 7.66 (m, 1H), 7.46 – 7.40 (m, 2H), 7.39 – 7.32 (m, 2H), 7.28 – 7.22 (m, 1H), 7.08 – 6.93 (m, 3H), 4.83 – 4.78 (m, 1H), 4.65 – 4.61 (m, 1H), 2.94 (d, J = 14.0 Hz, 1H), 2.88 – 2.81 (m, 1H), 2.77 – 2.63 (m, 1H), 2.11 – 2.02 (m, 3H), 1.65 (bs, 3H), 1.61 – 1.40 (m, 2H), 1.37 – 1.33 (m, 3H), 1.14 – 1.06 (m, 3H), 0.84 – 0.75 (m, 3H); **^{13}C NMR (101 MHz, $CDCl_3$):** δ 172.2, 150.0, 150.0, 143.4, 142.5, 142.5, 137.1, 137.1, 128.5, 128.5, 127.8, 127.8, 127.4, 127.4, 126.8, 126.7, 126.7, 123.7, 123.7, 115.1, 115.1, 47.7, 47.1, 47.1, 34.4, 30.5, 30.3, 24.6, 21.9, 21.8, 21.1, 19.1, 12.4, 12.3.

4.1.2 *N*-(2,6-dipropylphenyl)-2,4-dimethyl-2-phenylpent-4-en-1-imine (**10b**)

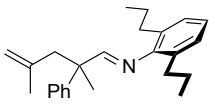
Imine was synthesized according to "General procedure for synthesis of imines". **9** (1.26 g, 6.70 mmol), **7b** (1.00 g, 6.70 mmol), and PTSA (11.5 mg, 67.0 μmol) were used to afford product **10** as a yellow oily liquid (1.40 g, 4.38 mmol, 65%).



^{1}H NMR (400 MHz, $CDCl_3$): δ 7.72 – 7.67 (m, 1H), 7.46 – 7.41 (m, 2H), 7.40 – 7.33 (m, 2H), 7.33 – 7.21 (m, 1H), 7.03 – 6.97 (m, 2H), 6.94 – 6.88 (m, 1H), 4.83 – 4.78 (m, 1H), 4.66 – 4.60 (m, 1H), 2.98 – 2.79 (m, 2H), 2.43 – 2.32 (m, 2H), 2.11 – 2.06 (m, 3H), 1.68 – 1.61 (m, 3H), 1.54 – 1.43 (m, 2H), 1.37 – 1.33 (m, 3H), 0.89 (td, J = 7.3, 1.4 Hz, 3H); **^{13}C NMR (101 MHz, $CDCl_3$):** δ 172.0, 150.3, 143.4, 142.5, 131.8, 128.5, 128.1, 127.4, 127.3, 126.9, 126.8, 123.5, 115.1, 47.7, 47.1, 33.9, 24.6, 23.6, 21.8, 18.8, 14.3.

4.1.3 *N*-(2,6-dipropylphenyl)-2,4-dimethyl-2-phenylpent-4-en-1-imine (**10c**)

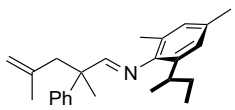
Imine was synthesized according to "General procedure for synthesis of imines". **9** (744 mg, 3.96 mmol), **7c** (700 mg, 3.95 mmol), and PTSA (6.80 mg, 39.5 μmol) were used to afford product **10c** as a yellow oily liquid (1.25 g, 3.60 mmol, 91%).



^{1}H NMR (400 MHz, $CDCl_3$): δ 7.67 (s, 1H), 7.46 – 7.41 (m, 2H), 7.39 – 7.33 (m, 2H), 7.33 – 7.23 (m, 1H), 7.02 – 6.90 (m, 3H), 4.83 – 4.77 (m, 1H), 4.65 – 4.60 (m, 1H), 2.96 (d, J = 14.0 Hz, 1H), 2.80 (dd, J = 14.0, 0.8 Hz, 1H), 2.42 – 2.32 (m, 4H), 1.68 – 1.61 (m, 3H), 1.58 – 1.39 (m, 4H), 1.34 (t, J = 1.1 Hz, 3H), 0.89 (t, J = 7.3 Hz, 6H); **^{13}C NMR (101 MHz, $CDCl_3$):** δ 171.5, 150.0, 143.3, 142.5, 131.7, 128.5, 127.4, 127.2, 126.8, 123.4, 115.1, 47.6, 47.1, 34.0, 24.6, 23.7, 21.7, 14.3.

4.1.4 *N*-(2-(*sec*-butyl)-4,6-dimethylphenyl)-2,4-dimethyl-2-phenylpent-4-en-1-imine (**10d**)

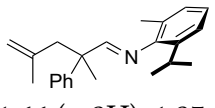
Imine was synthesized according to "General procedure for synthesis of imines". **9** (1.77 g, 9.41 mmol), **7d** (1.67 g, 9.41 mmol), and PTSA (17.9 mg, 94.1 μmol) were used to afford product **10d** as a yellow oily liquid (2.86 g, 8.24 mmol, 87%).



^{1}H NMR (400 MHz, $CDCl_3$): δ 7.73 – 7.68 (m, 1H), 7.49 – 7.44 (m, 2H), 7.41 – 7.33 (m, 2H), 7.32 – 7.25 (m, 1H), 6.90 – 6.87 (m, 1H), 6.87 – 6.82 (m, 1H), 4.86 – 4.82 (m, 1H), 4.69 – 4.65 (m, 1H), 2.97 (d, J = 14.0 Hz, 1H), 2.88 (ddd, J = 13.9, 2.9, 0.9 Hz, 1H), 2.80 – 2.64 (m, 1H), 2.30 (s, 3H), 2.08 (s, 0.5×3H), 2.07 (s, 0.5×3H), 1.68 (s, 3H), 1.65 – 1.41 (m, 2H), 1.40 – 1.38 (m, 3H), 1.14 (d, J = 5.8 Hz, 0.5×3H), 1.12 (d, J = 5.9 Hz, 0.5×3H), 0.84 (t, J = 7.4 Hz, 0.5×3H), 0.83 (t, J = 7.4 Hz, 0.5×3H); **^{13}C NMR (101 MHz, $CDCl_3$):** δ 172.4, 147.6, 147.6, 143.5, 142.6, 142.5, 137.1, 137.0, 132.8, 128.6, 128.6, 128.5, 128.5, 128.4, 127.4, 127.4, 126.7, 126.5, 126.5, 124.3, 124.2, 115.1, 115.1, 47.7, 47.1, 47.1, 34.4, 30.5, 30.3, 24.6, 24.6, 22.0, 21.9, 21.1, 21.1, 18.9, 18.9, 12.4, 12.4.

4.1.5 *N*-(2-isopropyl-6-methylphenyl)-2,4-dimethyl-2-phenylpent-4-en-1-imine (**10e**)

Imine was synthesized according to "General procedure for synthesis of imines". **9** (4.83 g, 25.6 mmol), 2-isopropyl-6-methylaniline (2.83 g, 25.6 mmol), and PTSA (49.2 mg, 256 μmol) were used to afford product **10e** as a yellow oily liquid (5.93 g, 16.6 mmol, 72%).

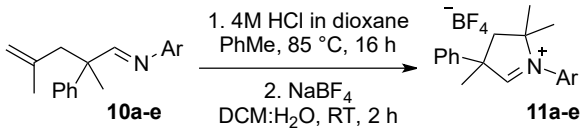


^{1}H NMR (400 MHz, $CDCl_3$): δ 7.70 (s, 1H), 7.47 – 7.41 (m, 3H), 7.40 – 7.34 (m, 3H), 7.32 – 7.23 (m, 1H), 7.11 (dd, J = 6.7, 2.4 Hz, 1H), 7.02 – 6.94 (m, 2H), 4.84 – 4.80 (m, 1H), 4.66 – 4.63 (m, 1H), 3.03 – 2.83 (m, 3H), 2.08 (s, 3H), 1.66 (s, 3H), 1.37 (s, 3H), 1.15 (dd, J = 6.7 Hz, 6H); **^{13}C NMR (101 MHz, $CDCl_3$):** δ 172.2, 149.6, 143.4, 142.5, 138.0, 128.5, 127.9, 127.4, 126.8, 126.6, 123.8, 123.2, 115.1, 47.8, 47.1, 27.6, 24.6, 23.5, 23.4, 21.9, 19.0.

5 Synthesis of tetrafluoroborate CAACs precursors

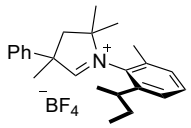
5.1 General procedure for salts synthesis

Under protective argon atmosphere in a round bottom flask equipped with magnetic stirring bar imine (**10a**–**10e**, 1.00 equiv.) was dissolved in anh. PhMe (c = 0.5M), followed by addition of hydrogen chloride (c = 4.0 M in dioxane, 2.50 equiv.) at 0 °C. The reaction mixture was stirred at 85 °C for 16 hours, cooled to RT, and the solvent was evaporated under reduced pressure. The crude product was dissolved in a small amount of DCM, $NaBF_4$ (2.00 equiv.) dissolved in H_2O was added, and the mixture stirred at RT for 2 hours. The reaction mixture was transferred to separation funnel and extracted with DCM three times, organic layers were combined, dried over anh. $MgSO_4$, and filtrated on Schott funnel through neutral celite. The solvent was evaporated under reduced pressure and the crude product was dissolved in small amount of MeOH followed by addition of Et_2O. Precipitate was formed, filtered, and dried *in vacuo* to afford the final products **11a-e**.



5.1.1 1-(sec-butyl)-6-methylphenyl)-2,2,4-trimethyl-4-phenyl-3,4-dihydro-2*H*-pyrrol-1-ium tetrafluoroborate (**11a**)

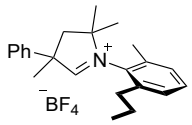
Salt **11a** was synthesized according to "General procedure for salts synthesis". **10a** (1.35 g, 4.10 mmol), hydrogen chloride (2.56 mL, 4.0 M in dioxane, 10.25 mmol), and sodium tetrafluoroborate (890 mg, 8.11 mmol) were used to afford product as a colorless solid (912 g, 2.16 mmol, 53%).



^{1}H NMR (400 MHz, $CDCl_3$): δ 9.58 (s, 0.19×1H), 9.49 (s, 0.51×1H), 9.45 (s, 0.30×1H), 7.57 – 7.51 (m, 1H), 7.50 – 7.38 (m, 4H), 7.38 – 7.30 (m, 1H), 7.31 – 7.14 (m, 2H), 3.28 – 3.11 (m, 1H), 2.78 – 2.61 (m, 1H), 2.45 – 2.30 (m, 2H), 2.15 – 1.86 (m, 5H), 1.84 – 1.64 (m, 1H), 1.64 – 1.40 (m, 5H), 1.37 - 1.13 (m, 4H+0.6×1H), 1.02 (t, J = 7.4 Hz, 0.6×1H), 0.94 (d, J = 6.7 Hz, 0.79×1H), 0.81 (t, J = 7.4 Hz, 0.79×1H), 0.68 (t, J = 7.4 Hz, 0.8×1H), 0.55 (t, J = 7.4 Hz, 0.83×1H); **^{13}C NMR (101 MHz, $CDCl_3$):** δ 190.0, 189.9, 144.7, 144.5, 144.0, 143.6, 140.5, 140.3, 140.3, 134.3, 134.1, 133.4, 133.3, 131.7, 131.6, 131.5, 131.4, 131.3, 131.3, 131.0, 130.8, 130.3, 130.2, 130.1, 130.1, 130.1, 130.1, 130.0, 128.8, 128.7, 128.6, 125.9, 125.9, 125.9, 125.6, 125.6, 125.5, 125.5, 84.5, 84.2, 83.8, 83.7, 55.7, 55.6, 55.6, 55.5, 48.8, 48.6, 48.3, 47.9, 37.0, 36.9, 36.3, 36.0, 33.3, 33.2, 29.5, 29.4, 29.1, 29.0, 28.9, 28.8, 28.0, 27.9, 27.7, 27.6, 27.3, 26.8, 26.8, 26.0, 22.6, 22.5, 19.8, 19.8, 19.7, 19.6, 19.4, 19.3, 12.5, 12.5, 12.1, 12.0; **HRMS-ESI (*m*/*z*)**: calculated for $C_{24}H_{32}N^+$ ($[M]^+$): 334.2535, found: 334.2537; **Elemental analysis**: calculated for $C_{24}H_{32}BF_4N$: C, 68.42; H, 7.66; N, 3.32; found: C, 68.70; H, 7.87; N, 3.42; **IR:** 3061, 2978, 2882, 1646, 1490, 1446, 1370, 1266, 1053, 1037, 766, 731, 700, 566, 520.

5.1.2 1-(2-methyl-6-propylphenyl)-2,2,4-trimethyl-4-phenyl-3,4-dihydro-2*H*-pyrrol-1-ium tetrafluoroborate (**11b**)

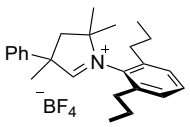
Salt **11b** was synthesized according to "General procedure for salts synthesis". **10b** (1.40 g, 4.38 mmol), hydrogen chloride (2.74 mL, 4.0 M in dioxane, 11.0 mmol), and sodium tetrafluoroborate (962 mg, 8.76 mmol) were used to afford product **11b** as a colorless solid (1.49 g, 3.66 mmol, 84%).



^{1}H NMR (400 MHz, $CDCl_3$): δ 9.50 (s, 0.49×1H), 9.45 (s, 0.51×1H), 7.54 – 7.46 (m, 2H), 7.45 – 7.40 (m, 2H), 7.40 – 7.27 (m, 2H+0.49×1H), 7.24 – 7.15 (m, 1H+0.51×1H), 3.17 (dd, J = 14.1, 3.8 Hz, 1H), 2.68 (dd, J = 14.1, 3.5 Hz, 1H), 2.55 (ddd, J = 14.4, 10.1, 5.8 Hz, 0.51×1H), 2.45 – 2.27 (m, 1H+0.51×3H), 2.10 (s, 0.49×3H), 2.05 – 1.93 (m, 2H), 1.90 (s, 0.49×3H), 1.70 – 1.60 (m, 1H), 1.58 (s, 0.51×3H), 1.54 (s, 0.49×3H), 1.49 – 1.40 (m, 1H), 1.38 (s, 0.51×3H), 1.35 (s, 0.49×3H), 0.95 (t, J = 7.3 Hz, 0.49×3H), 0.67 (t, J = 7.3 Hz, 0.51×3H); **^{13}C NMR (101 MHz, $CDCl_3$):** δ 189.8, 189.6, 140.6, 140.4, 138.7, 138.2, 134.2, 133.2, 132.0, 131.8, 131.1, 131.1, 130.1, 130.1, 130.1, 130.1, 128.7, 128.6, 128.3, 128.3, 125.8, 125.8, 84.4, 84.0, 55.6, 55.5, 48.7, 48.2, 34.3, 34.1, 29.3, 28.9, 27.8, 27.6, 26.9, 26.8, 25.1, 24.3, 19.4, 19.2, 14.3, 14.0; **HRMS-ESI (*m*/*z*)**: calculated for $C_{23}H_{30}N^+$ ([M]$^+$): 320.2378, found: 320.2386; **Elemental analysis**: calculated for $C_{23}H_{30}BF_4N$: C, 64.82; H, 7.42; F, 18.66; N, 3.44; found: C, 67.86; H, 7.38; F, 18.57; N, 3.47; **IR:** 3061, 2979, 2971, 2936, 2876, 1649, 1497, 1463, 1445, 1386, 1353, 1286, 1181, 1163, 1058, 1023, 998, 950, 886, 803, 773, 705, 645, 607, 571, 560, 519.

5.1.3 1-(2,6-dipropylphenyl)-2,2,4-trimethyl-4-phenyl-3,4-dihydro-2*H*-pyrrol-1-ium tetrafluoroborate (**11c**)

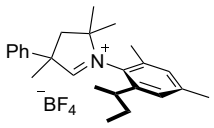
Salt **11c** was synthesized according to "General procedure for salts synthesis". **10c** (1.25 g, 3.60 mmol), hydrogen chloride (2.27 mL, 4.0 M in dioxane, 9.06 mmol), and sodium tetrafluoroborate (800 mg, 7.25 mmol) were used to afford product **11c** as a colorless solid (1.19 g, 2.73 mmol, 75%).



^{1}H NMR (400 MHz, $CDCl_3$): δ 9.50 (s, 1H), 7.54 – 7.49 (m, 2H), 7.47 – 7.38 (m, 3H), 7.37 – 7.31 (m, 1H), 7.30 – 7.26 (m, 1H), 7.24 – 7.20 (m, 1H), 3.22 (d, J = 14.1 Hz, 1H), 2.67 (d, J = 14.1 Hz, 1H), 2.59 – 2.38 (m, 2H), 2.36 – 2.23 (m, 1H), 2.11 – 1.99 (m, 1H), 1.92 (s, 3H), 1.80 – 1.41 (m, 7H), 1.33 (s, 3H), 0.97 (t, J = 7.3 Hz, 3H), 0.71 (t, J = 7.3 Hz, 3H); **^{13}C NMR (101 MHz, $CDCl_3$):** δ 189.6, 140.4, 138.6, 138.0, 131.2, 131.0, 130.1, 128.6, 128.4, 128.2, 125.9, 84.0, 55.6, 48.3, 34.3, 34.1, 29.2, 27.1, 26.9, 25.0, 24.1, 14.4, 14.1; **HRMS-ESI (*m*/*z*)**: calculated for $C_{25}H_{34}N^+$ ([M]$^+$): 348.2691, found: 348.2694; **Elemental analysis**: calculated for $C_{25}H_{34}BF_4N$: C, 68.97; H, 7.87; F, 17.46; N, 3.22; found: C, 68.93; H, 7.80; F, 17.41; N, 3.17; **IR:** 3050, 2970, 2934, 2874, 1647, 1500, 1465, 1446, 1377, 1347, 1286, 1234, 1178, 1105, 1059, 1041, 1023, 812, 768, 703, 654, 607, 568, 558, 520.

5.1.4 1-(2-(*sec*-butyl)-4,6-dimethylphenyl)-2,2,4-trimethyl-4-phenyl-3,4-dihydro-2*H*-pyrrol-1-ium tetrafluoroborate (**11d**)

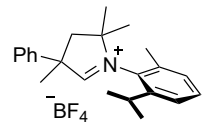
Salt **11d** was synthesized according to "General procedure for salts synthesis". **10d** (2.86 g, 8.24 mmol), hydrogen chloride (5.15 mL, 4.0 M in dioxane, 20.6 mmol), and sodium tetrafluoroborate (1.81 g, 16.5 mmol) were used to afford product **11d** as a colorless solid (2.08 g, 4.77 mmol, 57%).



^{1}H NMR (400 MHz, $CDCl_3$): δ 9.51 (s, 0.22×1H), 9.43 (s, 0.28×1H), 9.42 (s, 0.24×1H), 9.39 (s, 0.26×1H)z, 7.57 – 7.51 (m, 1H), 7.50 – 7.39 (m, 3H), 7.38 – 7.29 (m, 1H), 7.07 – 6.90 (m, 2H), 3.21 (d, J = 14.1 Hz, 0.46×1H), 3.20 (d, J = 14.4 Hz, 0.28×1H), 3.13 (d, J = 14.1 Hz, 0.26×1H), 2.71 (d, J = 14.0 Hz, 0.28×1H), 2.68 (d, J = 14.1 Hz, 0.24×1H), 2.64 (d, J = 14.1 Hz, 0.22×1H), 2.63 (d, J = 14.2 Hz, 0.26×1H), 2.42 – 1.21 (m, 18H + 0.24×3H), 1.17 (d, J = 6.7 Hz, 0.28×3H), 1.12 (d, J = 6.7 Hz, 0.22×3H), 1.01 (t, J = 7.4 Hz, 0.22×3H), 0.92 (d, J = 6.7 Hz, 0.26×3H), 0.80 (t, J = 7.3 Hz, 0.24×3H), 0.67 (t, J = 7.4 Hz, 0.26×3H), 0.54 (t, J = 7.4 Hz, 0.28×3H); **^{13}C NMR (101 MHz, $CDCl_3$):** δ 189.9, 189.9, 189.7, 189.7, 144.3, 144.1, 143.7, 143.3, 141.8, 141.7, 141.6, 141.5, 140.5, 140.5, 140.4, 140.3, 133.8, 133.6, 132.9, 132.8, 130.9, 130.9, 130.9, 130.8, 130.1, 130.1, 130.0, 129.9, 128.9, 128.9, 128.7, 128.6, 128.5, 128.5, 128.4, 126.2, 126.0, 126.0, 125.9, 125.9, 84.3, 84.0, 83.5, 83.4, 55.5, 55.4, 55.4, 55.3, 48.7, 48.5, 48.3, 47.9, 36.8, 36.8, 36.1, 35.9, 33.3, 29.4, 29.4, 29.0, 29.0, 28.9, 28.7, 27.9, 27.9, 27.6, 27.5, 27.2, 26.7, 26.7, 26.0, 22.6, 22.5, 21.3, 21.3, 21.3, 19.9, 19.7, 19.6, 19.4, 19.2, 19.1, 12.6, 12.5, 12.1, 12.0; **HRMS-ESI (*m*/*z*)**: calculated for $C_{25}H_{34}N^+$ ([M]$^+$): 348.2686, found: 348.2687; **Elemental analysis**: calculated for $C_{25}H_{34}BF_4N$: C, 68.97; H, 7.87; F, 17.46; N, 3.22; found: C, 68.89; H, 7.97; F, 17.28; N, 3.18; **IR:** 3059, 2967, 2934, 2876, 1638, 1601, 1585, 1498, 1463, 1448, 1396, 1376, 1350, 1277, 1262, 1234, 1202, 1164, 1049, 1035, 947, 877, 861, 765, 752, 702, 660, 620, 571, 559, 520.

5.1.5 1-(2-isopropyl-6-methylphenyl)-2,2,4-trimethyl-4-phenyl-3,4-dihydro-2H-pyrrol-1-ium tetrafluoroborate (**11e**)

Salt **11e** was synthesized according to "General procedure for salts synthesis". **10e** (5.75 g, 18.0 mmol), hydrogen chloride (11.2 mL, 4.0 M in dioxane, 45.0 mmol), and sodium tetrafluoroborate (3.95 g, 36.0 mmol) were used to afford product **11e** as a colorless solid (5.69 g, 11.0 mmol, 78%).

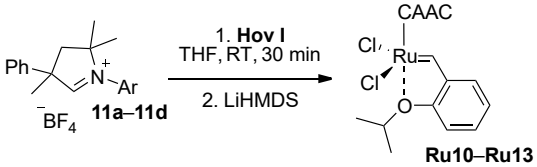


^{1}H NMR (400 MHz, CD_2Cl_2): δ 9.38 (s, 1H), 7.54 – 7.47 (m, 4H), 7.45 – 7.35 (m, 3H), 7.32 – 7.25 (m, 1H), 3.18 – 3.06 (m, 1H), 2.76 – 2.63 (m, 1H+0.43×1H), 2.46 (hept, J = 6.7 Hz, 0.57×1H), 2.36 (s, 0.57×3H), 2.16 (s, 0.43×3H), 1.98 (s, 0.57×3H), 1.92 (s, 0.43×3H), 1.63 (s, 0.57×3H), 1.57 (s, 0.43×3H), 1.43 – 1.39 (m, (3H+0.43×3H)), 1.25 (d, J = 6.7 Hz, 2H), 1.18 (d, J = 6.8 Hz, 1H), 1.05 (d, J = 6.8 Hz, 2H); **^{13}C NMR (101 MHz, CD_2Cl_2):** δ 189.7, 189.5, 145.1, 144.7, 141.1, 140.8, 134.2, 133.6, 132.0, 131.9, 130.5, 130.4, 130.4, 130.3, 129.1, 129.0, 126.0, 125.9, 125.7, 125.6, 84.8, 84.3, 55.8, 55.7, 49.3, 49.2, 30.2, 29.8, 29.1, 28.5, 28.1, 28.0, 27.2, 27.2, 26.1, 25.9, 22.1, 22.0, 19.7, 19.5; **HRMS-ESI (*m*/*z*)**: calculated for $C_{23}H_{30}N^+$ ([M]$^+$): 320.2378, found: 320.2379; **Elemental analysis**: calculated for $C_{23}H_{30}BF_4N$: C, 67.82; H, 7.42; F, 18.66; N, 3.44; found: C, 68.03; H, 7.27; F, 18.56; N, 3.48; **IR:** 3068, 2979, 2961, 2869, 1646, 1601, 1497, 1461, 1447, 1388, 1344, 1286, 1163, 1051, 1030, 997, 954, 884, 801, 773, 704, 650, 557, 521.

6 Synthesis of ruthenium complexes

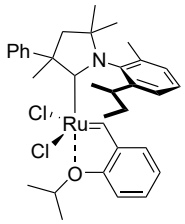
6.1 General procedure for ruthenium complexes synthesis

In a dry Schlenk flask equipped with magnetic stirring bar, salt (**11a**–**11e**, 2.20 equiv.) and Hoveyda-Grubbs 1st generation complex (1.00 equiv.) were suspended in THF (c_{CAAC} = 0.10 M), and the mixture was stirred for 1 minute. Next LiHMDS was added (2.20 equiv.) and the resulting mixture was stirred till full consumption of substrates. Then, the crude mixture was filtered through short pad of neutral aluminum oxide (Al_2O_3, neutral, Broockman Grade I) with Et_2O or DCM as an eluent. Green fraction was collected and evaporated under reduced pressure. Next small amount of *n*-pentane was added to the residue and the mixture was placed in a sonic bath. The product was filtered and washed with cold *n*-pentane, **Ru11** was additionally washed with diethyl ether.



6.1.1 **Ru10**

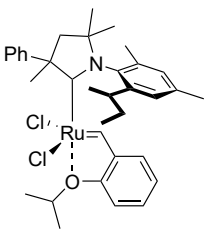
Complex **Ru10** was synthesized according to "General procedure for ruthenium complexes synthesis". Hoveyda-Grubbs catalyst (100 mg, 167 μmol), **11a** (155 mg, 367 μmol), and LiHMDS (61.4 mg, 367 μmol) were used to afford product as a green powder (64 mg, 97.9 μmol, 58%).



^{1}H NMR (400 MHz, $CDCl_3$): 16.31 (bs, 0.70×1H), 16.27 (s, 0.15×1H), 16.22 (s, 0.0.15×1H), 8.27 – 8.04 (m, 2H), 7.59 – 7.40 (m, 5H), 7.39 – 7.25 (m, 2H), 6.96 – 6.76 (m, 3H) , 5.10 –4.86 (m, 1H), 3.24 – 2.94 (m, 1H), 2.93 – 2.65 (m, 1H), 2.55 – 2.14 (m, 7H), 1.64 – 1.43 (m, 10H), 1.41 – 1.22 (m, 6H), 1.02 (t, J = 7.4 Hz, 0.5×1H), 0.93 – 0.90 (m, 0.5×1H), 0.83 – 0.75 (m, 1H), 0.69 – 0.58 (m, 2H); **HRMS-ESI (*m*/*z*)**: calculated for $C_{34}H_{43}NOCl_2Ru^+$ ($[M]^+$): 653.1760, found: 653.1759; **Elemental analysis**: calculated for $C_{34}H_{43}NOCl_2Ru$: C, 62.47; H, 6.63; N, 2.14; found: C, 62.23; H, 6.67; N, 2.19; **IR:** 3064, 2995, 2965, 2929, 2871, 1588, 1578, 1561, 1475, 1454, 1437, 1403, 1374, 1325, 1299, 1265, 1224, 1202, 1160, 1138, 1127, 1114, 1101, 1064, 1040, 997, 956, 938, 883, 865, 846, 822, 805, 752, 724, 697, 614, 577, 556.

6.1.2 **Ru11**

Complex **Ru11** was synthesized according to "General procedure for ruthenium complexes synthesis". Hoveyda-Grubbs catalyst (294 mg, 480 μmol), **11d** (374 mg, 1.08 mmol), and LiHMDS (180 mg, 1.08 mmol) were used to afford product as a green powder (180 mg, 270 μmol, 55%).

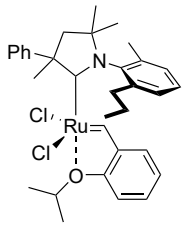


^{1}H NMR (400 MHz, $CDCl_3$): δ 16.51 – 16.28 (m, 1H), 8.16 (dd, J = 7.8, 52.6 Hz, 2H), 7.59 – 7.44 (m, 3H), 7.32 (t, J = 7.4 Hz, 1H), 7.19 (d, J = 2.2 Hz, 1H), 7.10 (d, J = 2.1 Hz, 1H), 6.93 – 6.66 (m, 3H), 4.99 (h, J = 6.1 Hz, 1H), 3.22 – 0.50 (m, 31H); **^{13}C NMR (101 MHz, $CDCl_3$):** δ 300.1, 265.5, 264.0, 152.6, 149.1, 148.9, 144.3, 144.1, 144.0, 142.0, 138.9, 138.6, 138.1, 138.1, 137.8, 136.0, 135.9, 131.1, 131.0, 130.9, 130.6, 130.6, 129.8, 129.7, 129.2, 129.1, 129.0, 128.9,

127.6, 127.3, 127.0, 126.5, 124.0, 123.8, 121.9, 121.9, 113.4, 63.6, 63.5, 49.5, 49.3, 35.2, 31.3, 30.3, 28.5, 27.8, 27.7, 27.5, 27.2, 22.5, 22.5, 22.4, 22.3, 22.1, 21.6, 21.4, 21.4, 21.3, 12.7, 12.7, 12.4; **HRMS-ESI (*m*/*z*)**: calculated for $C_{35}H_{45}NOCl_2Ru^+$ ([M]$^+$): 667.1916, found: 667.1917; **Elemental analysis**: calculated for $C_{35}H_{45}NOCl_2Ru$: C, 62.96; H, 6.79; Cl, 10.62; N, 2.10; found: C, 62.71; H, 6.97; Cl, 10.47; N, 10.47; **IR:** 2975, 2955, 2922, 2862, 1607, 1586, 1576, 1492, 1474, 1452, 1443, 1393, 1381, 1372, 1312, 1297, 1275, 1241, 1227, 1169, 1157, 1144, 1112, 1096, 1076, 1038, 1007, 995, 966, 933, 882, 845, 799, 794, 765, 752, 743, 709, 697, 606, 591, 568, 547, 537, 518, 485, 445.

6.1.3 **Ru12**

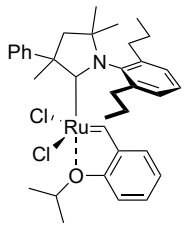
Complex **Ru12** was synthesized according to "General procedure for ruthenium complexes synthesis". Hoveyda-Grubbs catalyst (200 mg, 333 μmol), **11b** (298 mg, 733 μmol), and LiHMDS (122 mg, 733 μmol) were used to afford product as a green powder (95 mg, 149 μmol, 44%). *Note: only diagnostic benzylidene proton signals are reported due to the presence of conformational and rotational isomers resulting in high complexity of spectra, which precluded further assignment.*



^{1}H NMR (400 MHz, CD_2Cl_2): δ 17.60 (s, 0.35×1H), 16.30 (s, 0.65×1H)—alkylidene protons signals; **HRMS-ESI (*m*/*z*)**: calculated for $C_{33}H_{40}NO_2Ru^+$ ([M–HCl_2^-]$^+$): 568.2153, found: 568.2170; **Elemental analysis**: calculated for $C_{33}H_{41}NOCl_2Ru^+$ 0.25×C_5H_{12}: C, 62.55; H, 6.74; Cl, 10.78; N, 2.13; found: C, 62.10; H, 6.43; Cl, 10.27; N, 2.33; **IR**: 3055, 2954, 2928, 2869, 1589, 1576, 1476, 1467, 1454, 1408, 1383, 1374, 1316, 1299, 1225, 1158, 1139, 1115, 1096, 1073, 1037, 1012, 996, 935, 882, 845, 804, 786, 749, 697, 616, 608, 583, 569, 544, 490, 443.

6.1.4 **Ru13**

Complex **Ru13** was synthesized according to "General procedure for ruthenium complexes synthesis". Hoveyda-Grubbs catalyst (200 mg, 333 μmol), **11c** (319 mg, 733 μmol), and LiHMDS (122 mg, 733 μmol) were used to afford product as a green powder (212 mg, 317 μmol, 95%).



^{1}H NMR (400 MHz, CD_2Cl_2): δ 17.64 (bs, 0.18×1H), 16.43 (s, 0.82×1H), 8.24 (s, 2H), 7.70 – 7.30 (m, 7H), 7.09 – 6.65 (m, 3H), 4.97 (hept, J = 6.2 Hz, 1H), 3.29 – 2.19 (m, 9H), 1.67 – 1.28 (m, 16H), 1.08 – 0.73 (m, 6H); **^{13}C NMR (101 MHz, CD_2Cl_2):** δ 299.7, 263.5, 152.6, 144.3, 144.0, 142.7, 142.5, 139.1, 131.1, 129.4, 129.2, 127.9, 127.6, 127.5, 123.9, 122.3, 113.6, 78.6, 75.0, 63.9, 48.7, 35.1, 34.0, 31.3, 28.1, 27.7, 24.2, 23.7, 22.5, 22.3, 14.7; **HRMS-ESI (*m*/*z*)**: calculated for $C_{35}H_{44}NORu^+$ ([M–HCl_2^-]$^+$): 594.2466, found: 594.2476; **Elemental analysis**: calculated for $C_{35}H_{45}Cl_2NORu$: C, 62.96; H, 6.79; N, 2.10; found: C, 62.62; H, 6.84; N, 2.12; **IR**: 3070, 3052, 3002, 2957, 2930, 2870, 1589, 1576, 1499, 1476, 1466, 1454, 1444, 1410, 1384, 1375, 1314, 1300, 1243, 1222, 1196, 1170, 1159, 1138, 1113, 1100, 1080, 1054, 1040, 1034, 997, 934, 912, 881, 864, 844, 810, 801, 787, 779, 761, 747, 702, 683, 625, 616, 607, 597, 569, 545, 445.

7 Ethenolysis of methyl oleate

7.1 Preparation of methyl oleate

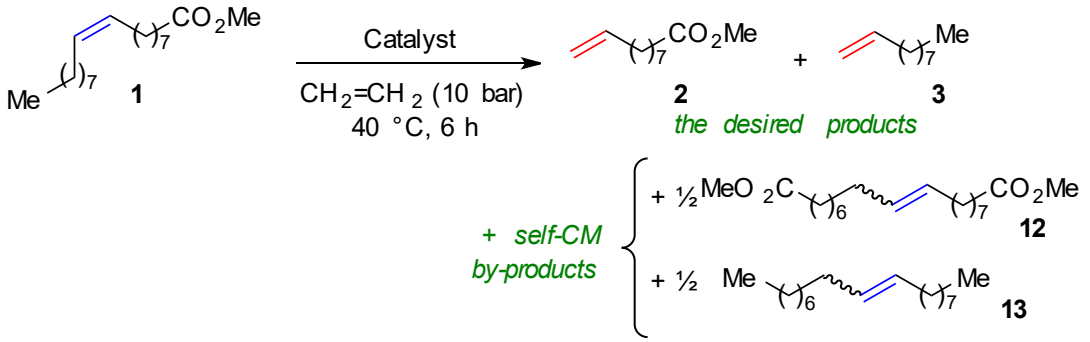
Oleic acid (500 g) was dissolved in acetone (99.9% in ratio 1g of acid in 11 mL of solvent). The mixture was cooled to −40 °C and stirred for 16 hours. Solid was filtered through Buchner funnel, transferred to a round bottom flask and remaining acetone was evaporated on rotary evaporator and under high vacuum. Process was repeated 2–4 times. Remaining oleic acid was dissolved in MeOH and stirred under argon for 16 hours with catalytic amount of PTSA. After cooling to RT, $MgSO_4$ was added and the reaction mixture was stirred for 2 hours, solid was filtered, and MeOH was evaporated under reduced pressure. Freshly prepared methyl oleate was placed in a round bottom flask equipped with magnetic stirring bar. Activated alumina (2.5 wt%) was added and distillation setup was assembled. Flask content was heated under high vacuum at 60 °C for 1 hour before distillation started. 10% of heads and 10% of tails were left. Freshly distilled methyl oleate was treated with 2.5 wt% of activated alumina and 0.1 mol% of BHT, gases were evacuated and content of the flask was stirred at 100 °C for ca. 1 hour under gentle flow of argon. After cooling to RT, methyl oleate was filtered through pad of activated alumina under argon to flask and stored over activated alumina in the dark.

7.2 General procedure for ethenolysis of methyl oleate

Under protective argon atmosphere complex (**Ru8**, **Ru10**–**Ru13**, ca. 5 mg) was placed in Schlenk flask and dissolved in 5 mL of anh. PhMe. Methyl oleate (6.0 mL, 5.2 g, 17.7 mmol) was filtered through pad of alumina to Schlenk flask equipped with magnetic stirring bar and degassed under vacuum ($p \sim 1 \times 10^{-2}$). Stock solution of catalyst containing 3 ppm Ru-complex was added under argon to methyl oleate. The mixture was immediately transferred via canula (under vacuum) to an autoclave containing glass vessel with a magnetic stirring bar. Next, autoclave was filled with ethylene 3.5 (10 bar) and reaction mixture was stirred at 40 °C for 6 h. After that time, pressure was normalized, autoclave was disassembled, solution of Snatch-Cat in DCM was added, a sample was taken, and subjected to GC analysis 4 times.

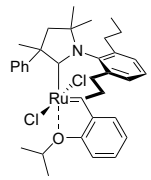
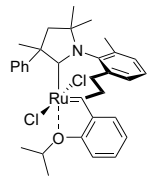
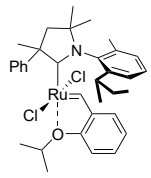
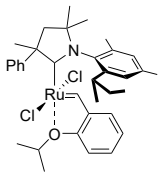
7.3 Procedure for GC analysis of results

Before reactions, sample of methyl oleate and ethenolysis products were used to determine response factors (RF) on GC. To GC vial known masses of substrates and products were added, dissolved in PhMe and analyzed 7 times on GC.



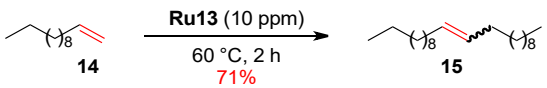
Conversion = 100 × [1 – (A_1 × A^0_{IS})/(A^0_1 × A_{IS})]; Selectivity = 100×(n_2 + n_3)/[(n_2 + n_3) + 2×(n_{12} + n_{13})]; Yield = (Conversion × Selectivity)/100; TON = Yield × [(n^0_{MO} /$n^0_{[Ru]}$)]/100; A_{MO}, A_{IS} = GC area of methyl oleate and internal standard at the end of the reaction; A^0_{MO}, A^0_{IS} = GC area of methyl oleate and internal standard before the reaction; n^0_{MO}, $n^0_{[Ru]}$ = initial moles of methyl oleate and catalyst used; IS = Internal Standard (methyl stearate).

7.4 Results

	Load. [ppm]	Time [h]	Conv. [%]	Sel. [%]	Yield [%]	TON
	10	3	71	88	63	63 000
	3	6	35	92	33	108 000
	10	3	69	84	58	58 000
	3	6	44	89	39	132 000
	10	3	59	93	55	55 000
	3	6	61	95	58	192 000
	10	3	59	92	54	54 000
	3	6	60	93	56	186 000

8 Self-cross metathesis of 1–dodecane (14)

Before reaction 1-dodecene (**14**) was distilled from activated neutral alumina (Al_2O_3) under reduced pressure.



8.1 Procedure for SCM of **14**

Schlenk flask equipped with stirring bar were dried under reduced pressure with hating. To Schlenk flask, 1,3,5-trimethoxybenzene (ca. 5 g) was added. To dried vial **Ru13** (1.78 mg, 2.67 µmol, 0.001 mol%) was added. Freshly distilled and stored with activated aluminum oxide **14** (47.0 g, 267 mmol, 1 equiv., 95.6% pure), was transferred using syringe glass filter (1–2 µm) to previously prepared Schlenk flask and then reaction mixture was degassed *in vacuo*.

Vial with solid catalyst was dipped in reaction mixture and stirred at 60 °C under argon atmosphere for 2 h. Conversion and selectivity were estimated using GC.

9 Calculation of reaction parameters

9.1 EcoScale

The EcoScale allows the evaluation of the effectiveness of a reaction. It gives a score from 0 to 100, not only for yield, but also includes other parameters such as cost, safety, technical set-up, energy and purification aspects.

$$EcoScale = 100 - sum\ of\ penalty\ points$$

Table S1. Calculation of EcoScale score.

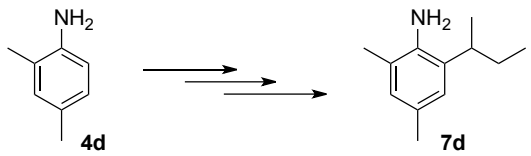
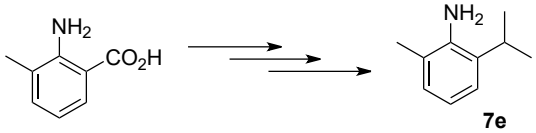
Parameter	7d[a]	7e[b]
1. Yield (%)	16 (68%)	31 (38%)
2. Price of reaction components[c]	0	10
3. Safety		
N (dangerous for environment)	5	-
T (toxic)	5	5
F (highly flammable)	5	5
4. Technical Setup		
Instruments for controlled addition of chemicals		1
Any additional special glassware		1
(Inert) gas atmosphere	1	1
5. Temperature/time		
Room temperature, < 24 h	1	1
Heating, > 1 h	3	3
Cooling to 0°C	4	4
6. Workup and purification		
None		
Cooling to room temperature		
Crystallization and filtration		1
Distillation	3	3
Summary of penalty points	**43**	**66**
EcoScale score	57	34

[a] Starting from 2,4-dimethylaniline (Scheme 2, main article). [b] Starting from 2-amino-3-methylbenzoic acid (Scheme 3, main article). [c] Price calculated for 10 mmol reaction scale, prices obtained from Sigma Aldrich (14.04.2023).

9.2 Environmental (E) factor

The calculation of **E** is defined by the ratio of the mass of waste per mass of product.[7] E = total waste / product by incorporating yield, stoichiometry and solvent usage the E-factor is an excellent metric.

$$E = \frac{\Sigma m(substrates) + \Sigma m(solvents) - \Sigma m(products)}{\Sigma m(products)}$$

 **4d** **7d**	 **7e**
$E = \frac{105.8+1411.9-14.7}{14.7} = 102.2$	$E = \frac{159.5+902.8-12.4}{12.4} = 85.5$[a]

[a] Recalculated for 83.1 mmol to keep the same scale.

10 Copies of NMR spectra

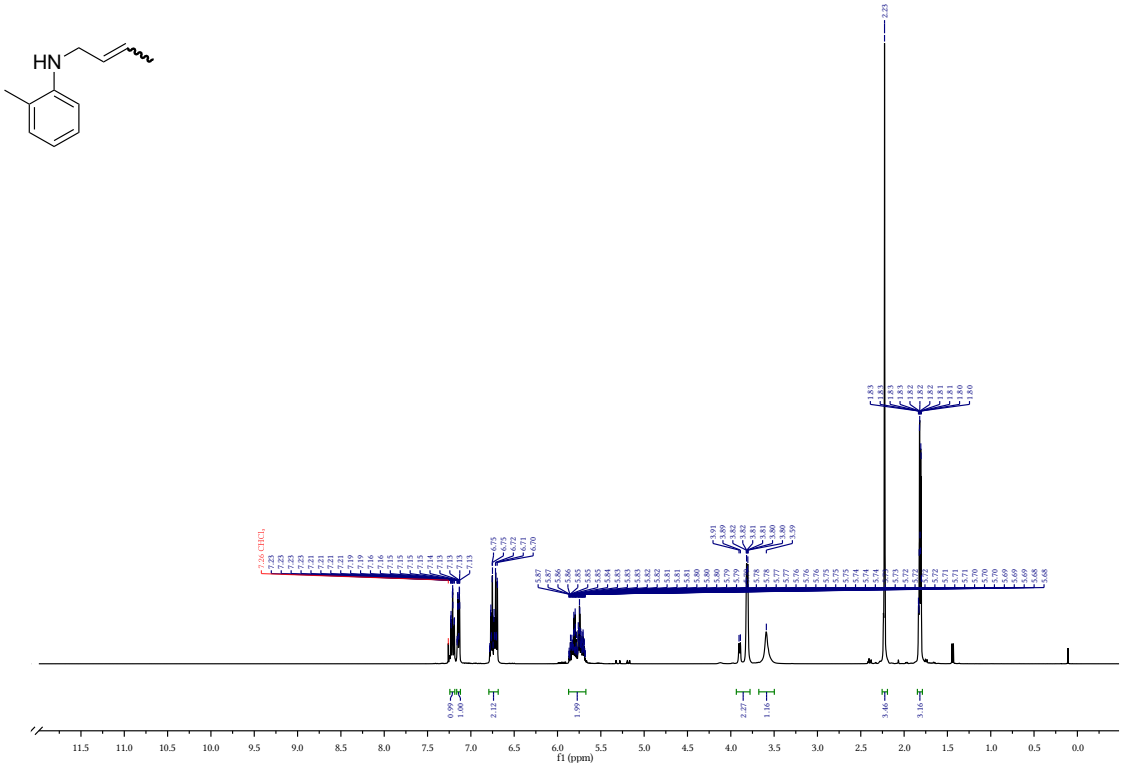


Figure **S1** ^{1}H NMR spectrum of **5a**

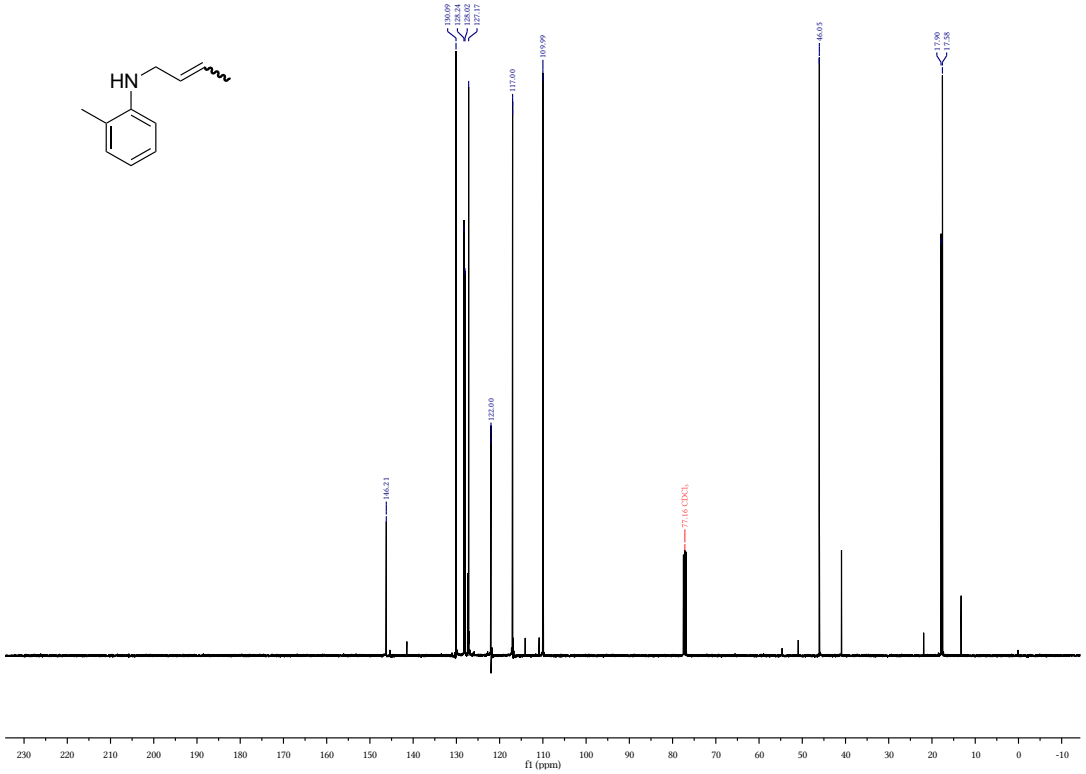


Figure **S2** ^{13}C NMR spectrum of **5a**

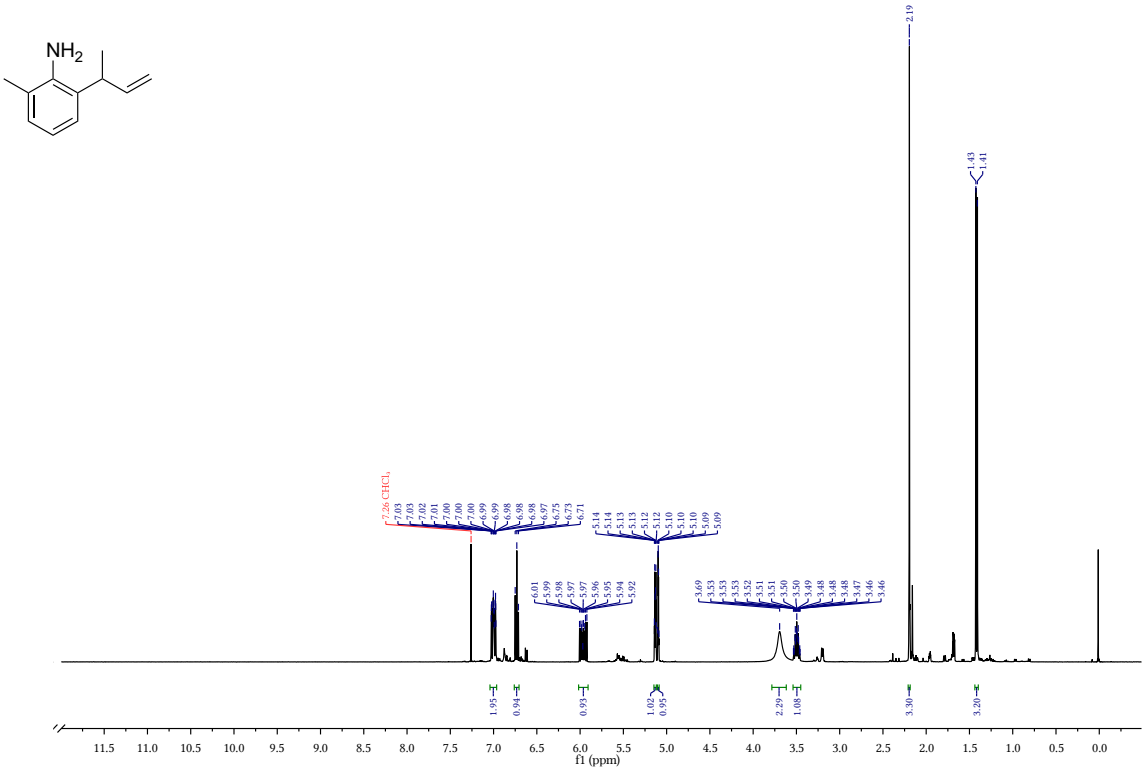


Figure **S3** ^{1}H NMR spectrum of **6a**

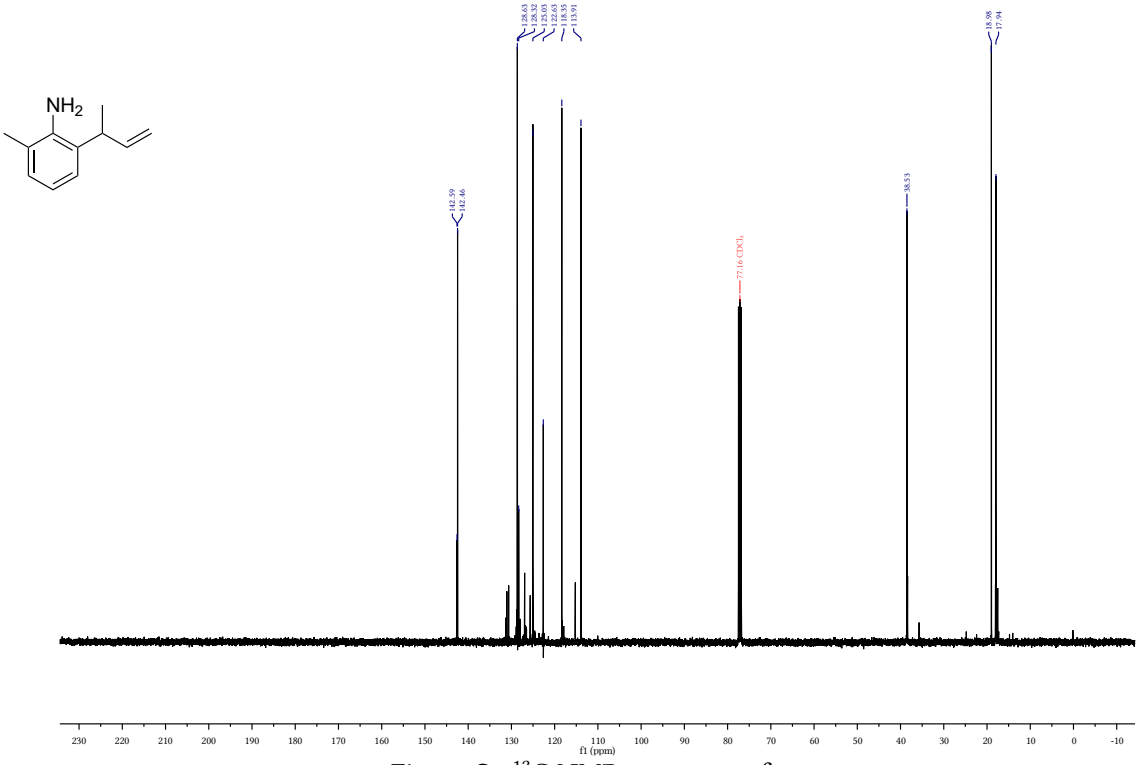


Figure **S4** ^{13}C NMR spectrum of **6a**

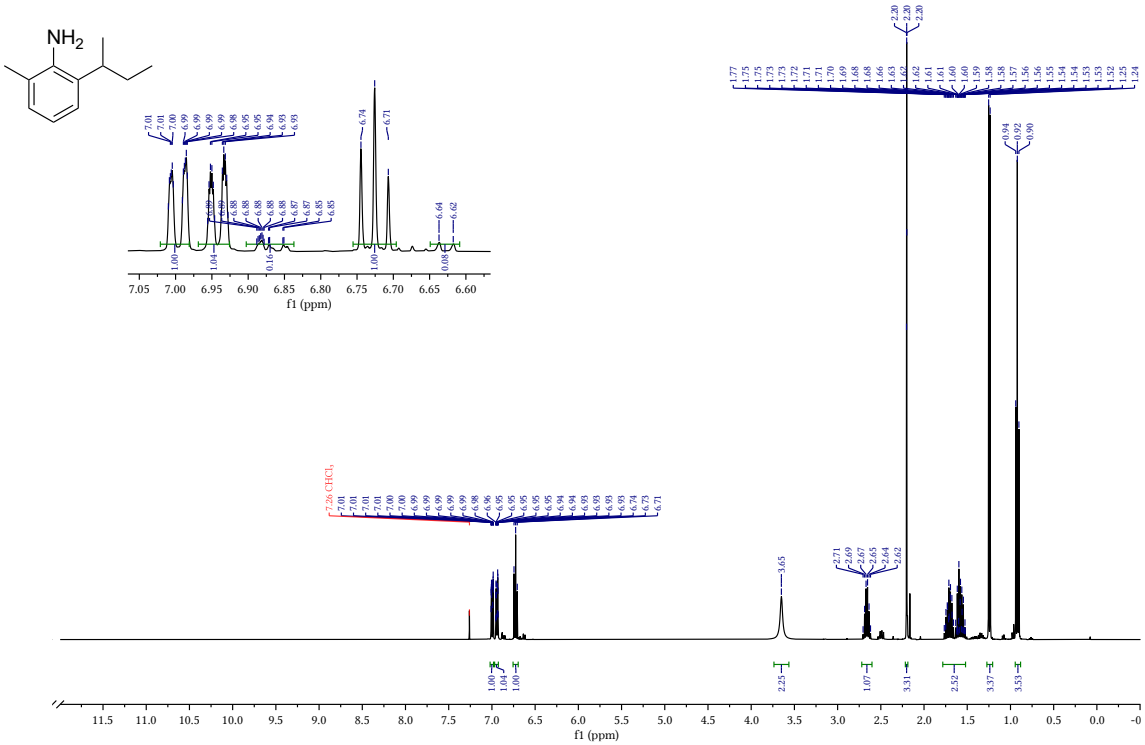


Figure **S5** ^{1}H NMR spectrum of **7a**

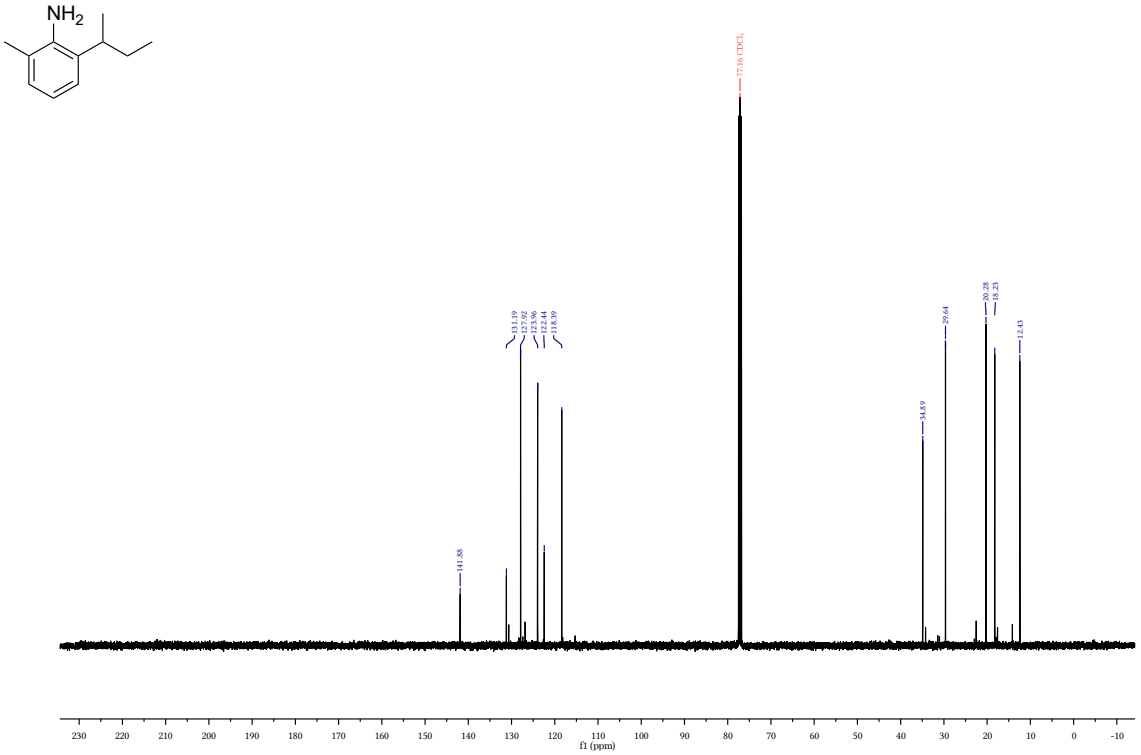


Figure **S6** ^{13}C NMR spectrum of **7a**

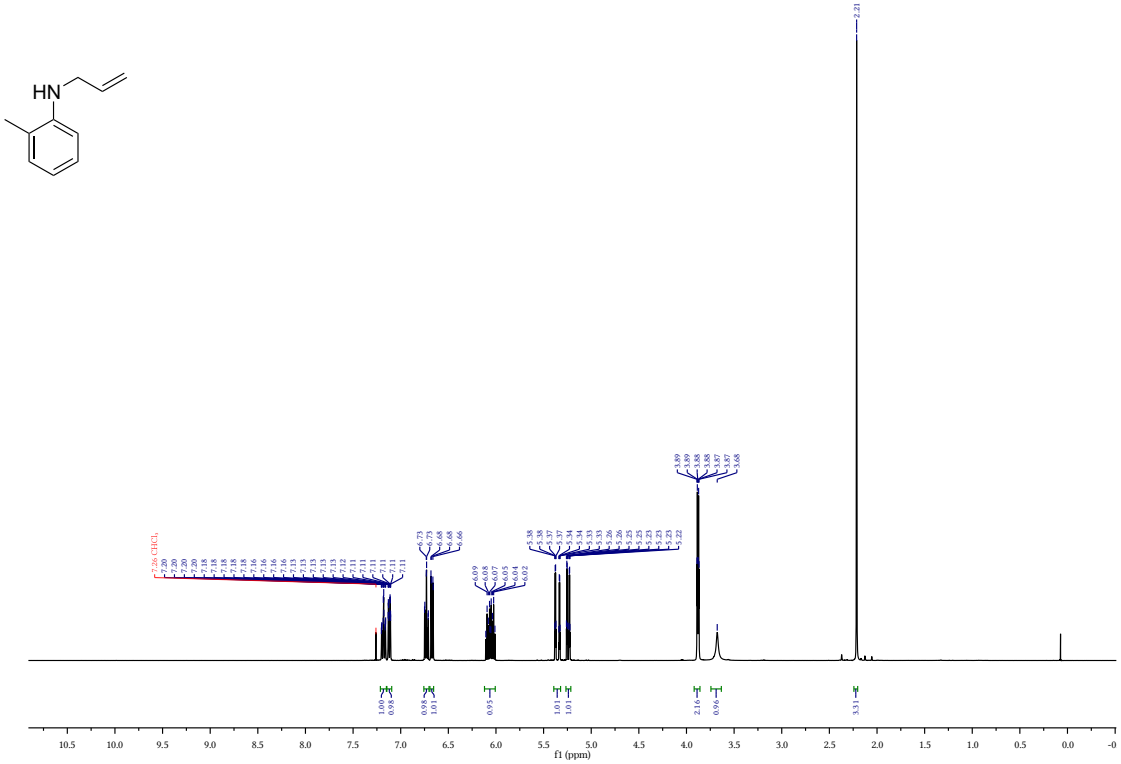


Figure **S7** ^{1}H NMR spectrum of **5b**

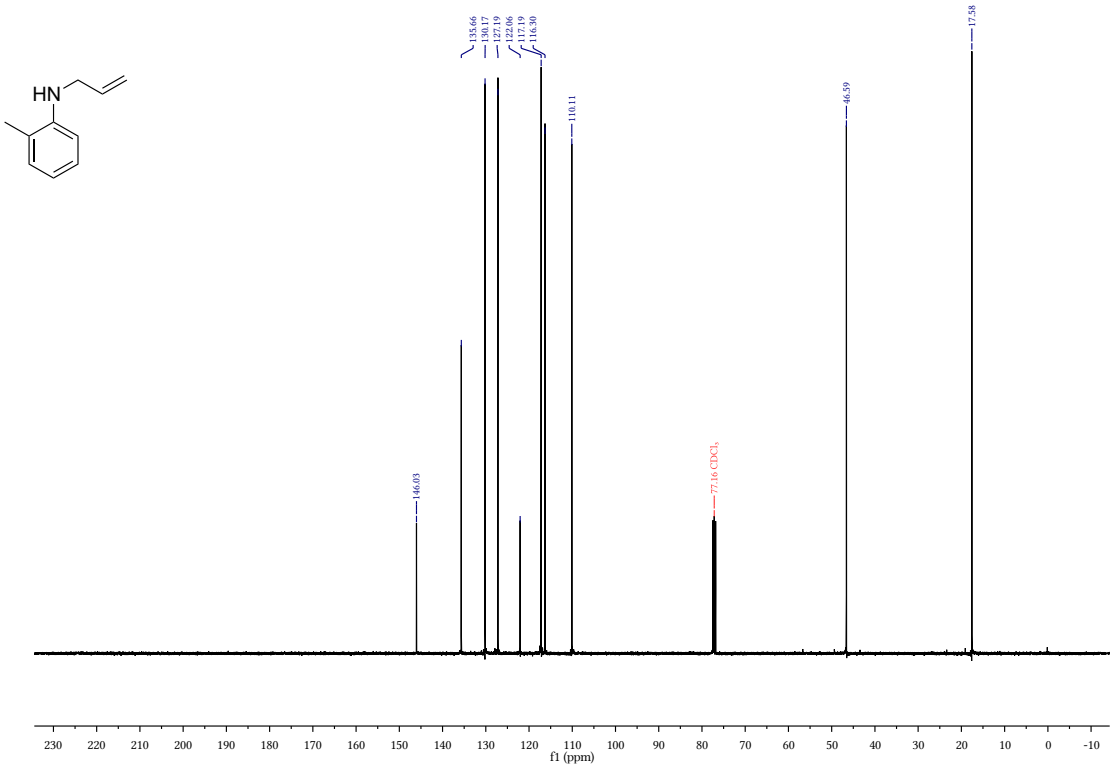


Figure **S8** ^{13}C NMR spectrum of **5b**

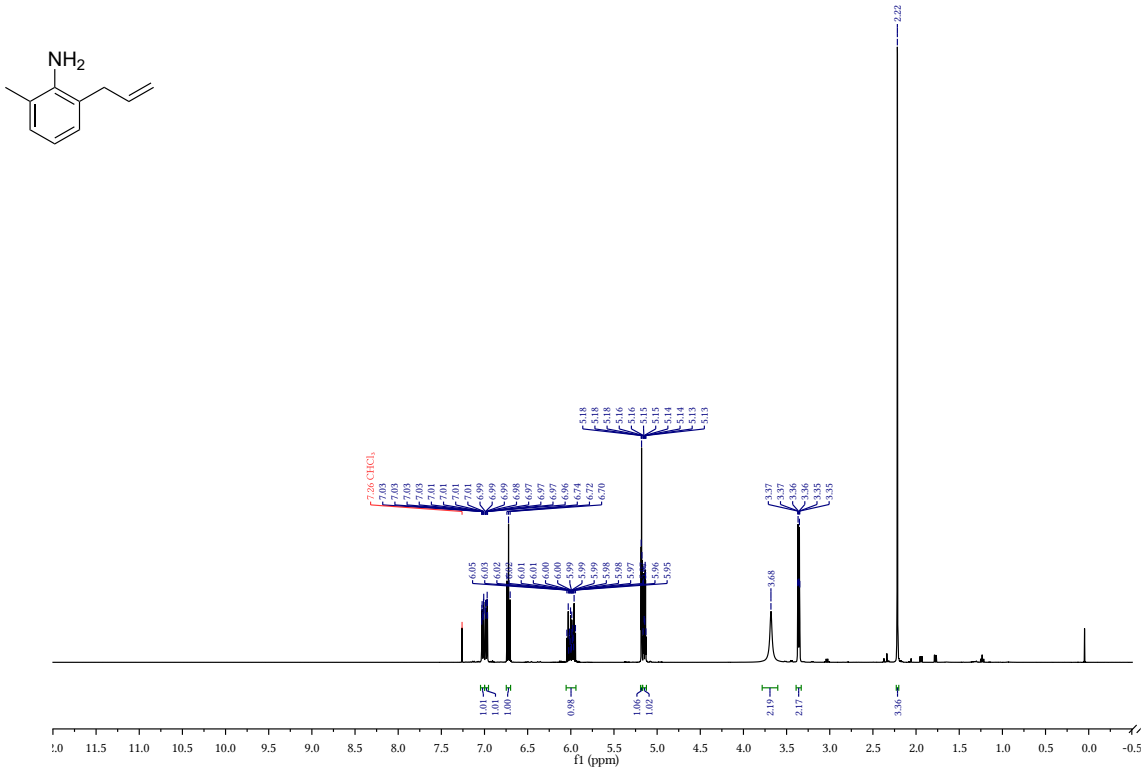


Figure **S9** ^{1}H NMR spectrum of **6b**

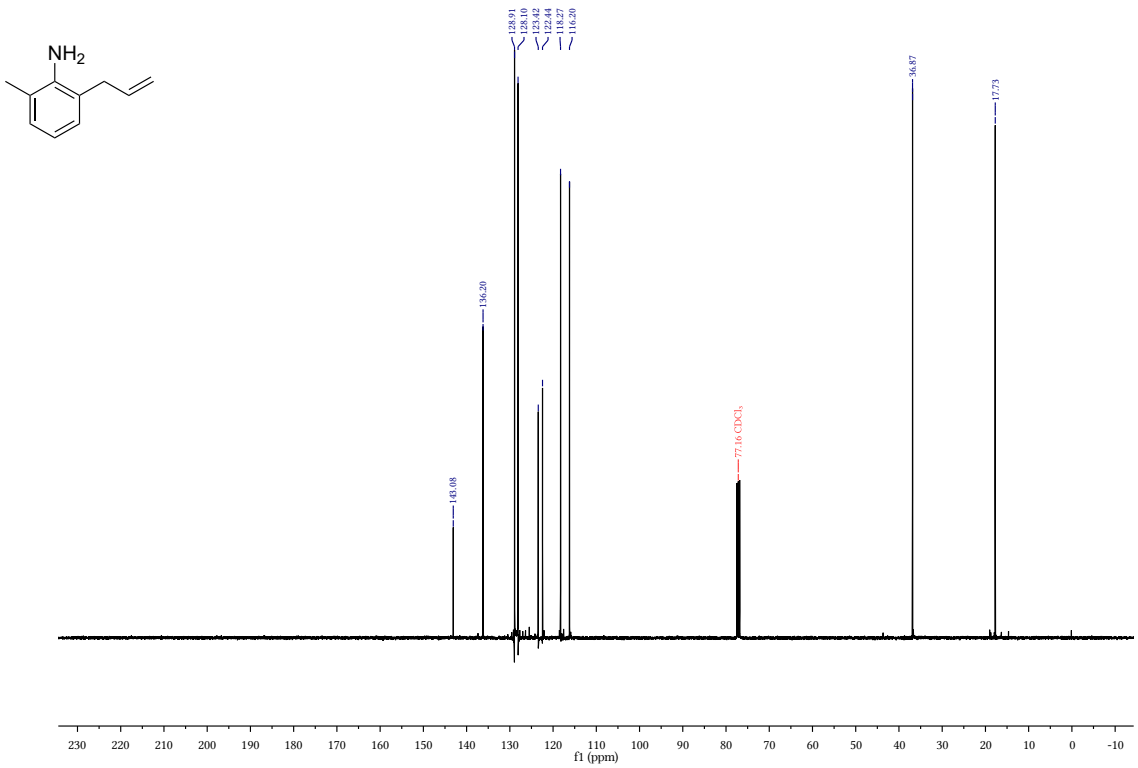


Figure **S10** ^{13}C NMR spectrum of **6b**

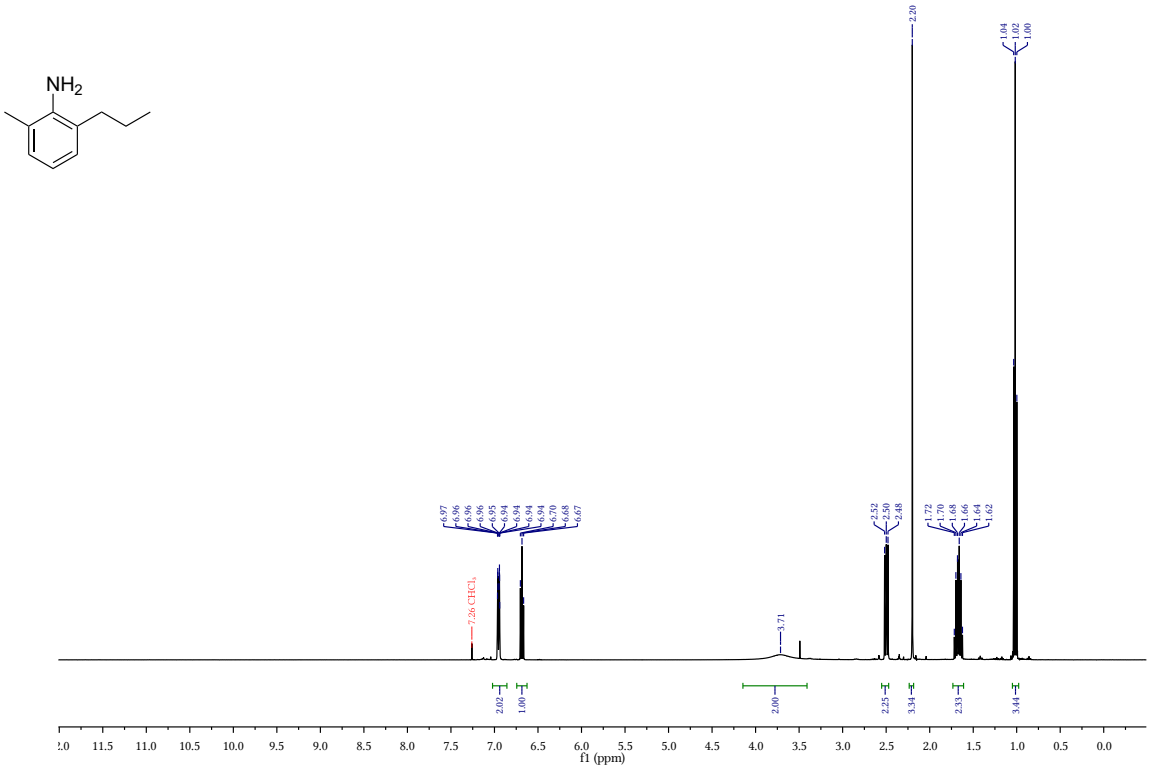


Figure **S11** ^{1}H NMR spectrum of **7b**

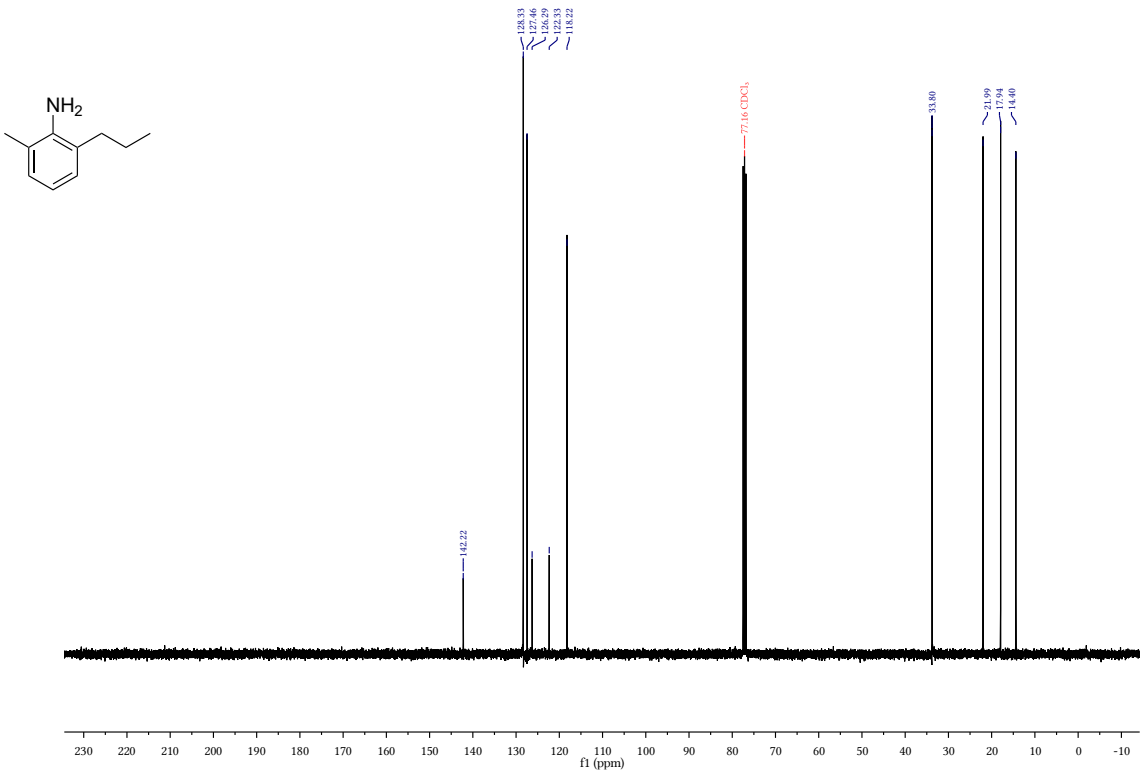


Figure **S12** ^{13}C NMR spectrum of **7b**

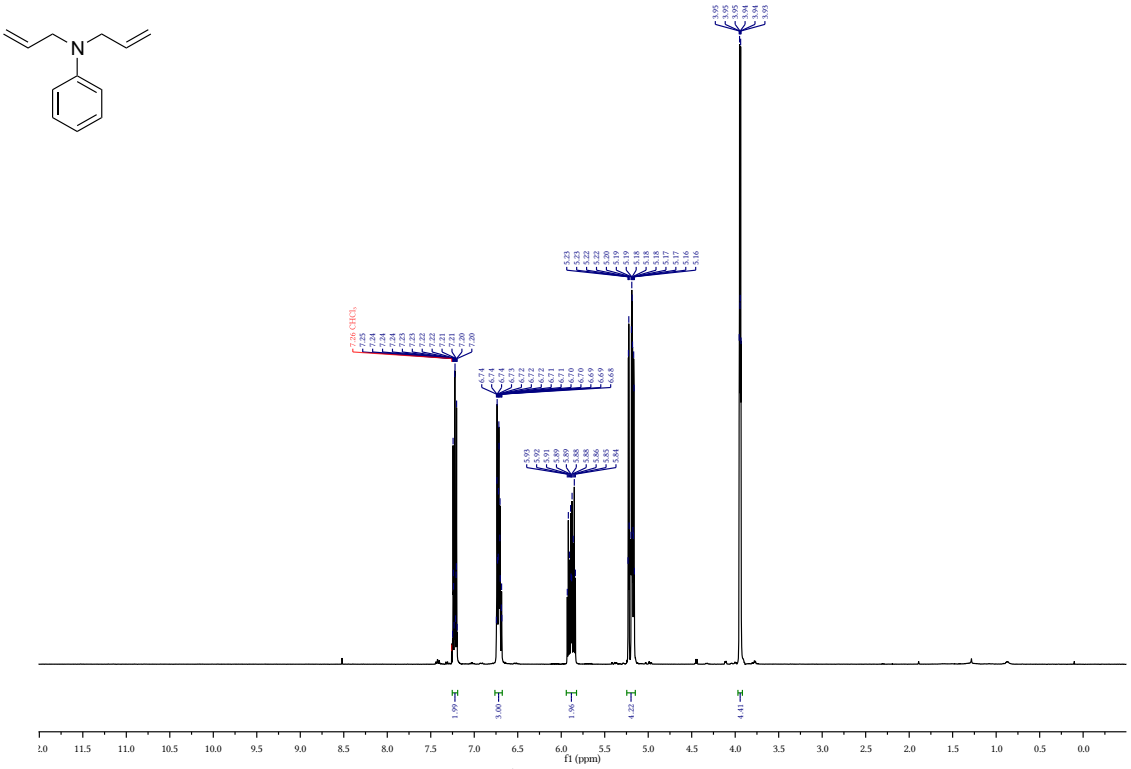


Figure **S13** ^{1}H NMR spectrum of **5c**

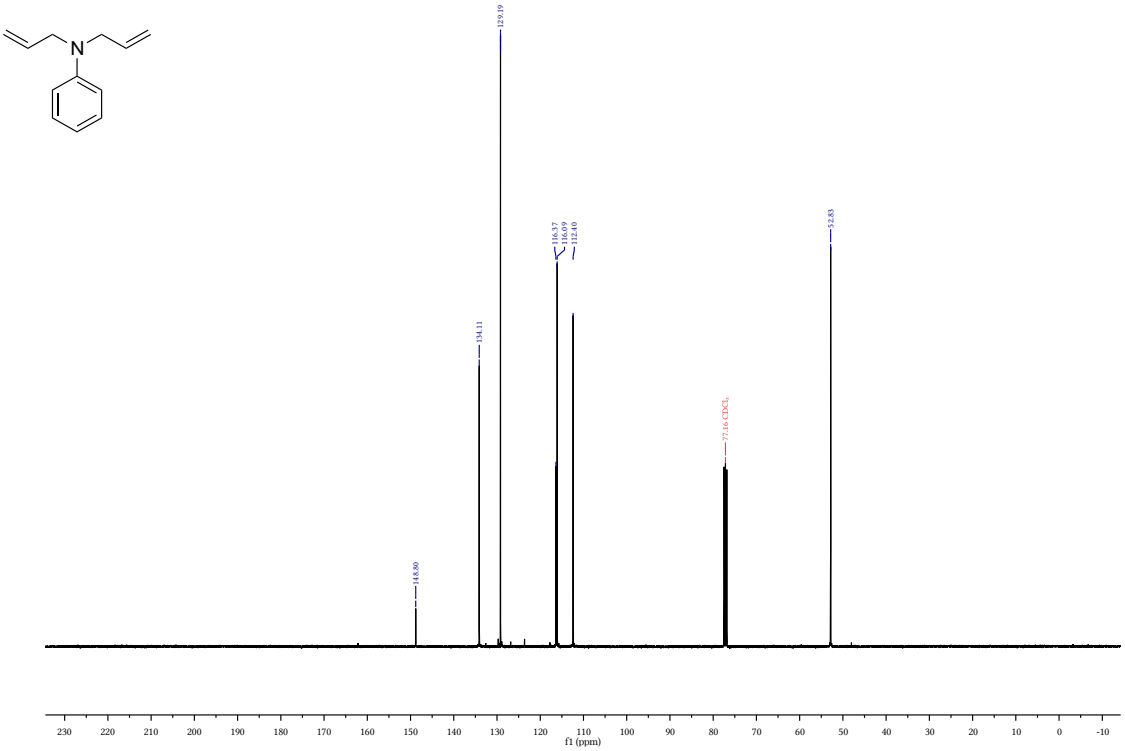


Figure **S14** ^{13}C NMR spectrum of **5c**

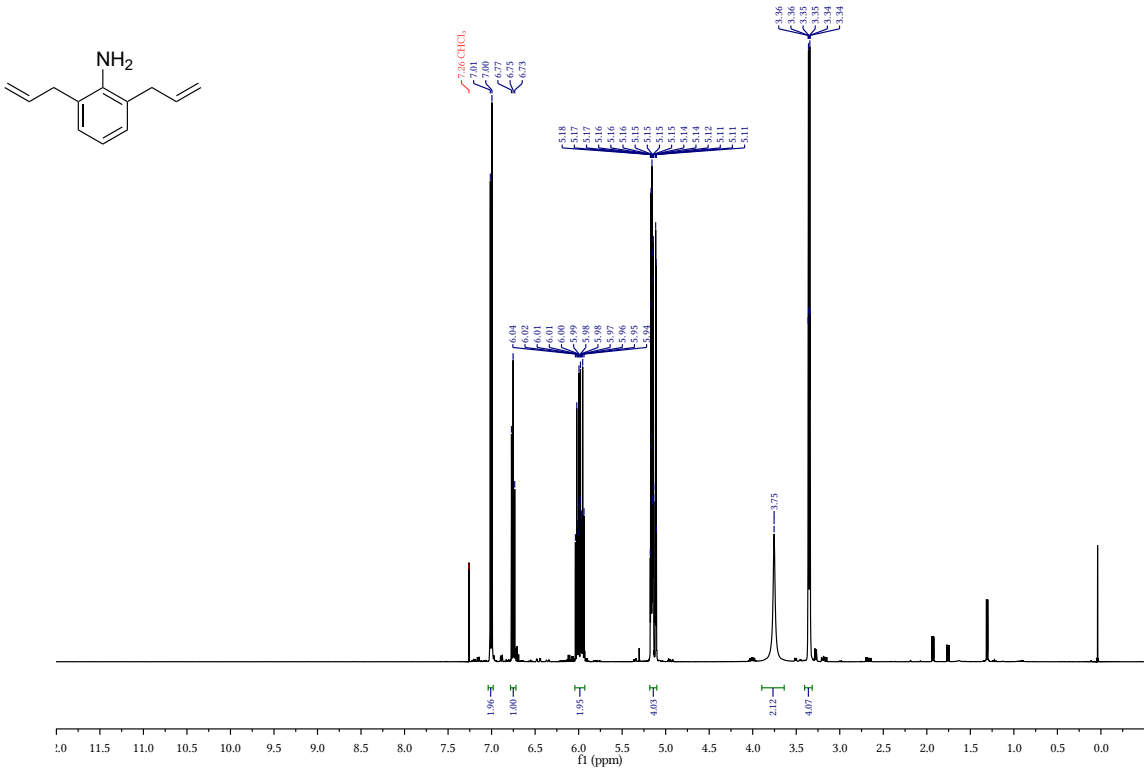


Figure **S15** ^{1}H NMR spectrum of **6c**

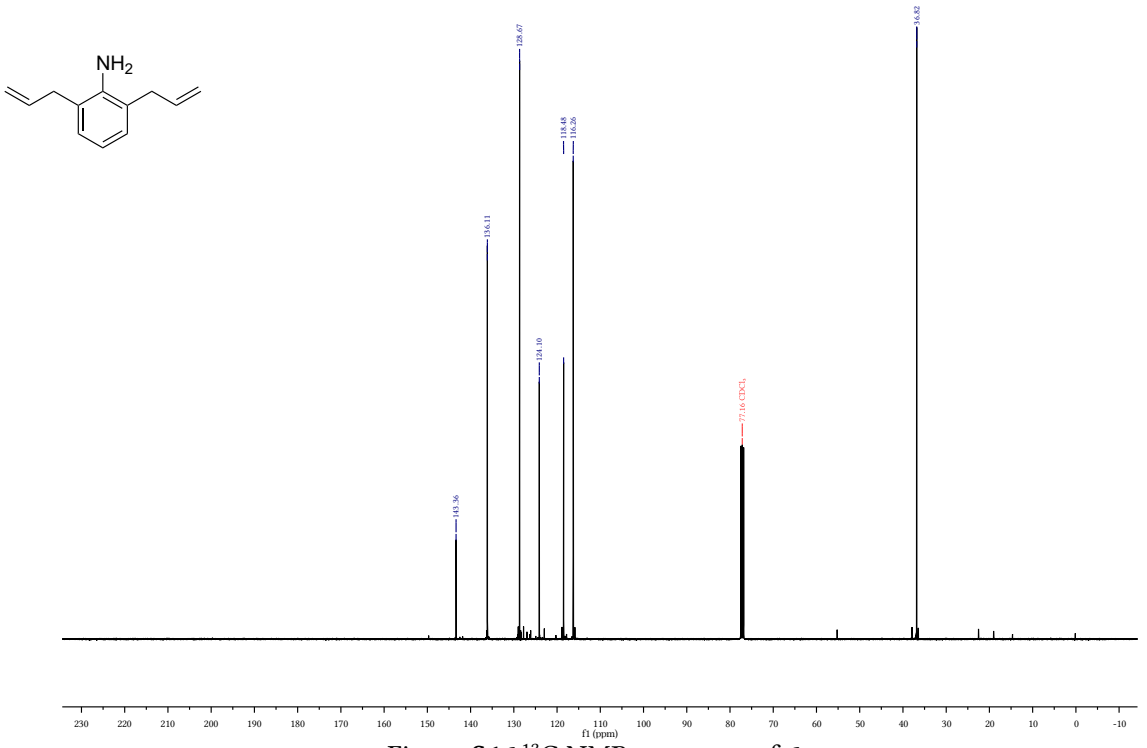


Figure **S16** ^{13}C NMR spectrum of **6c**

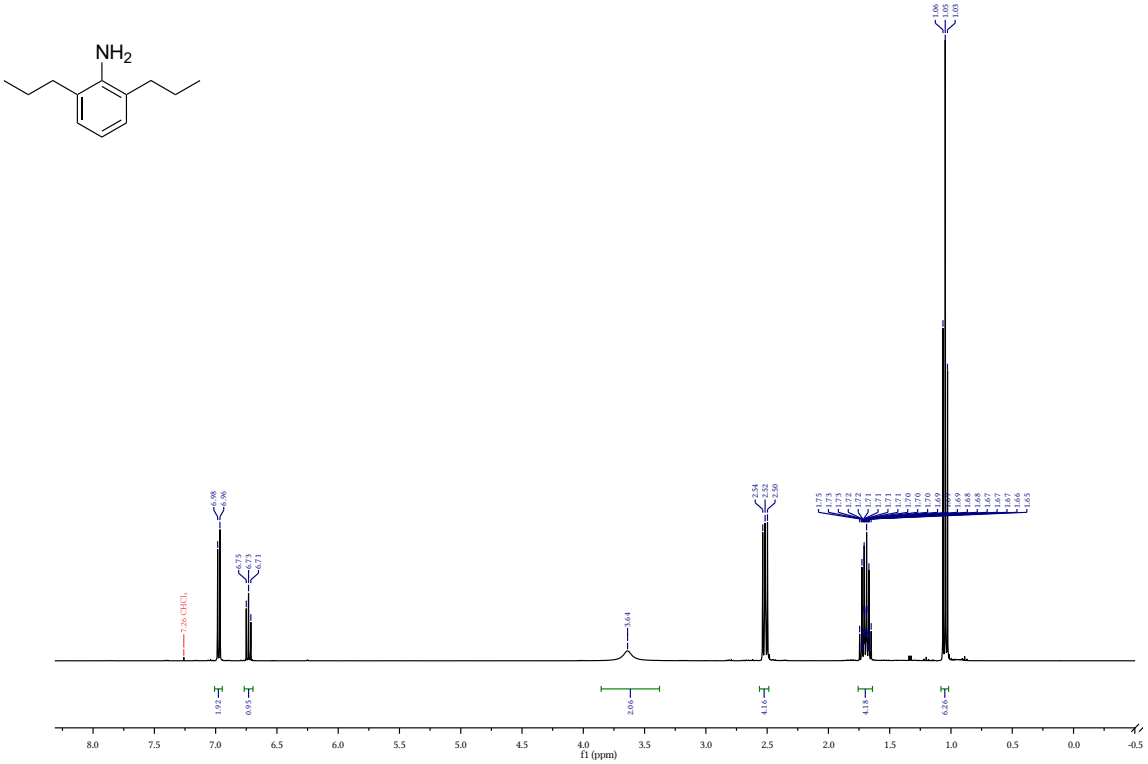


Figure **S17** ^{1}H NMR spectrum of **7c**

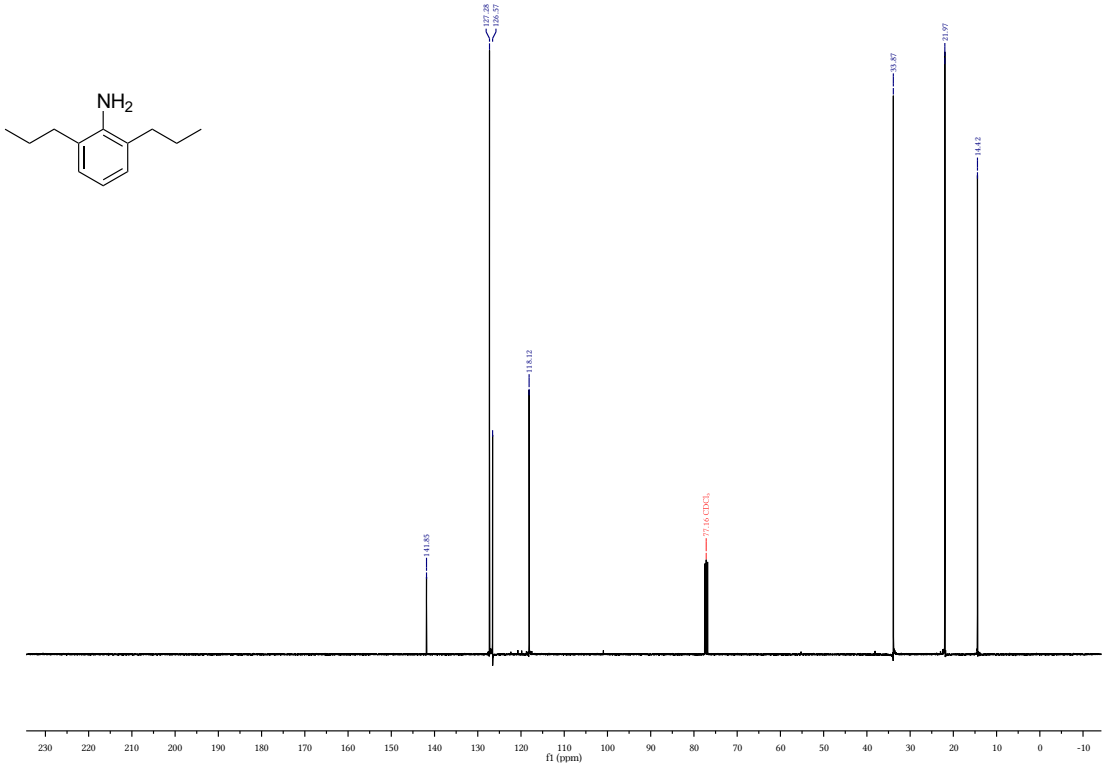


Figure **S18** ^{13}C NMR spectrum of **7c**

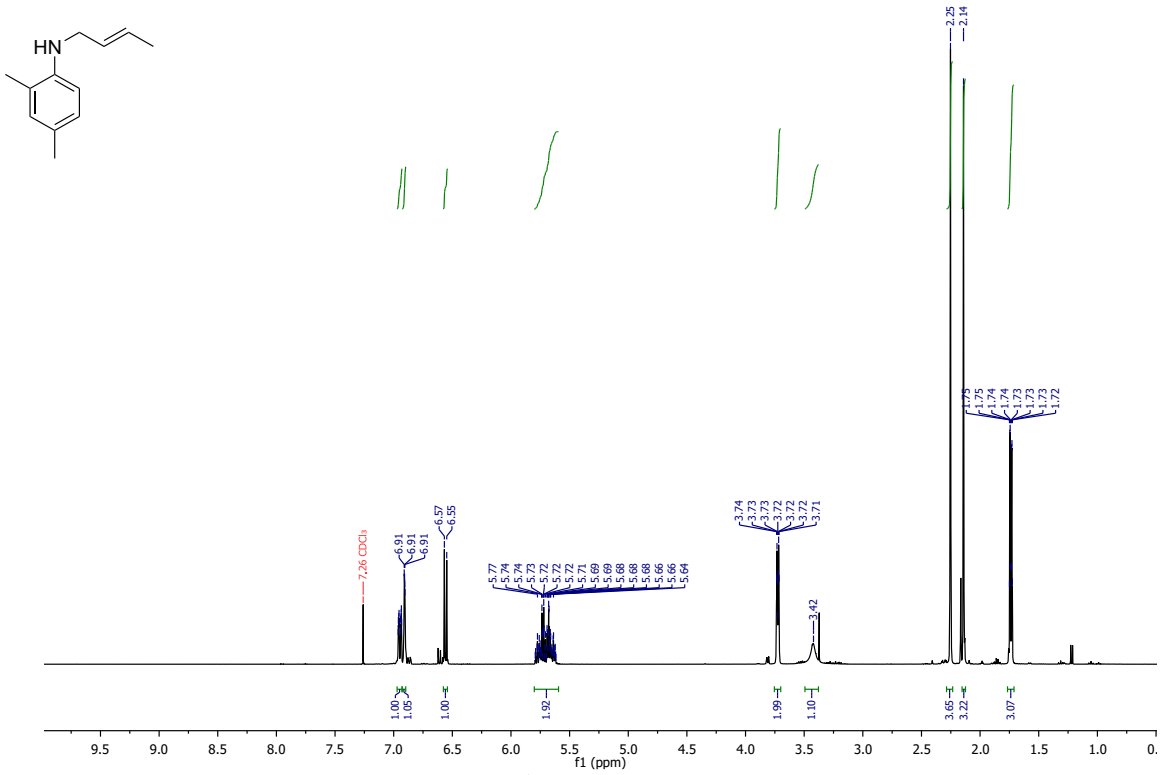


Figure **S19** ^{1}H NMR spectrum of **5d**

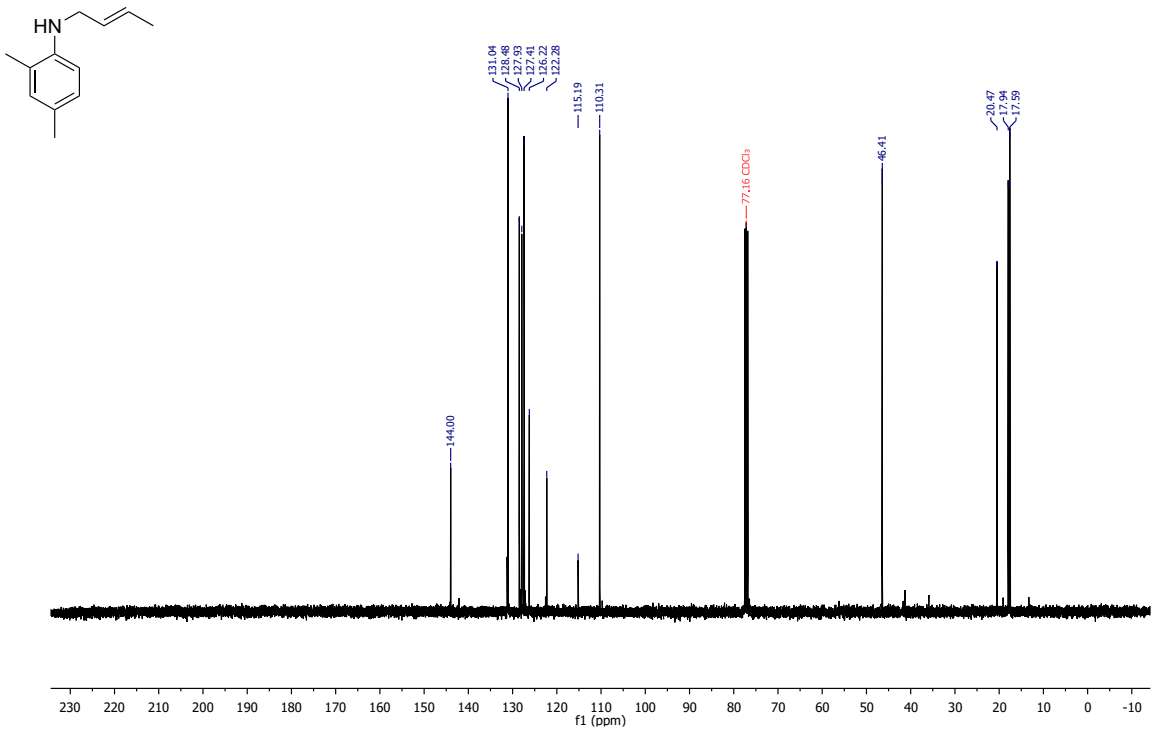


Figure **S20** ^{13}C NMR spectrum of **5d**

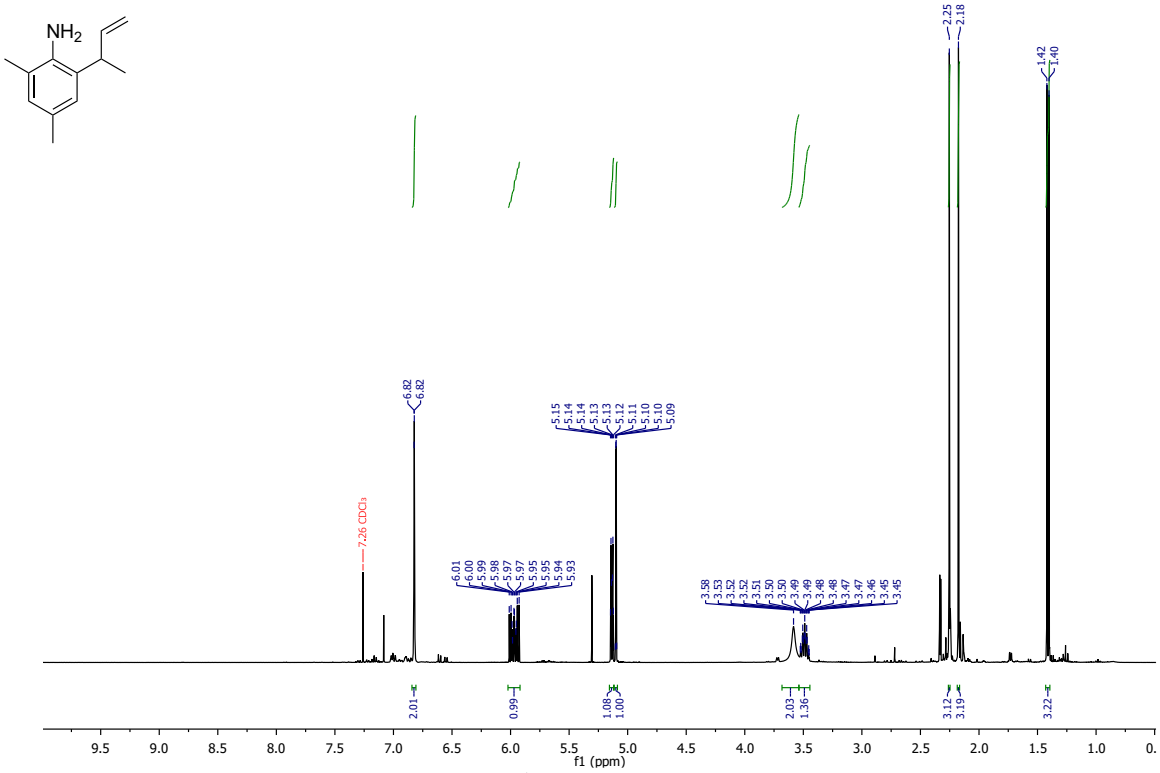


Figure **S21** ^{1}H NMR spectrum of **6d**

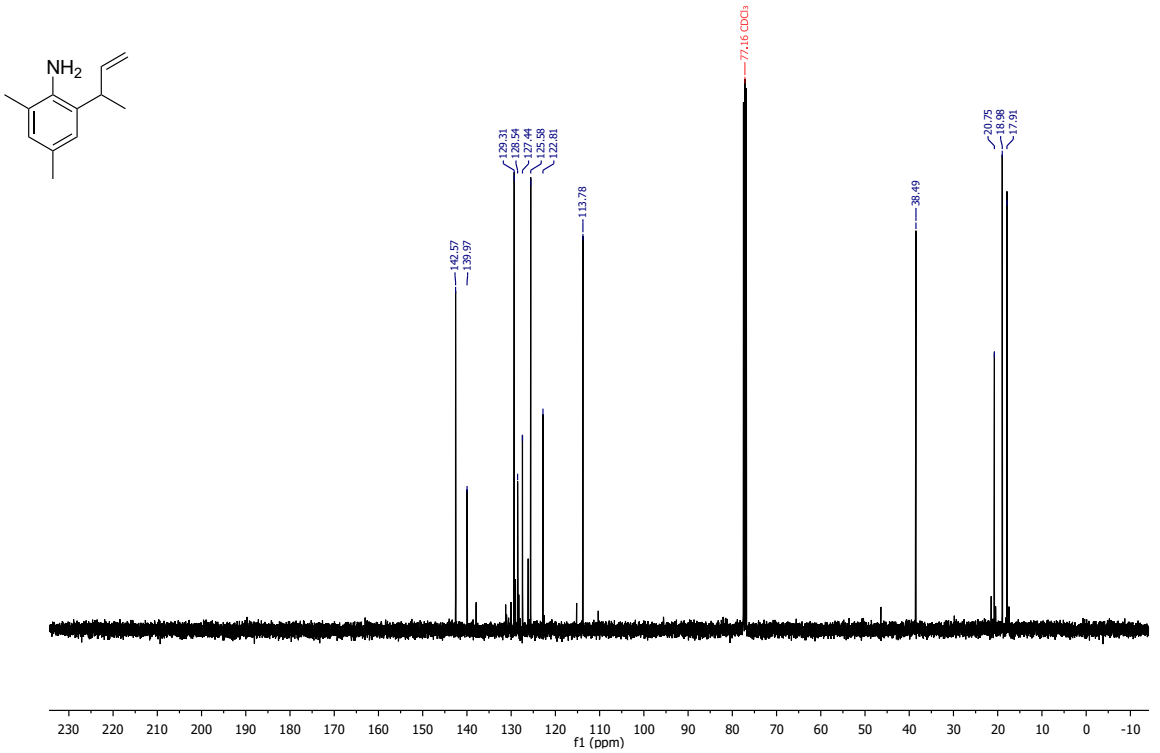


Figure **S22** ^{13}C NMR spectrum of **6d**

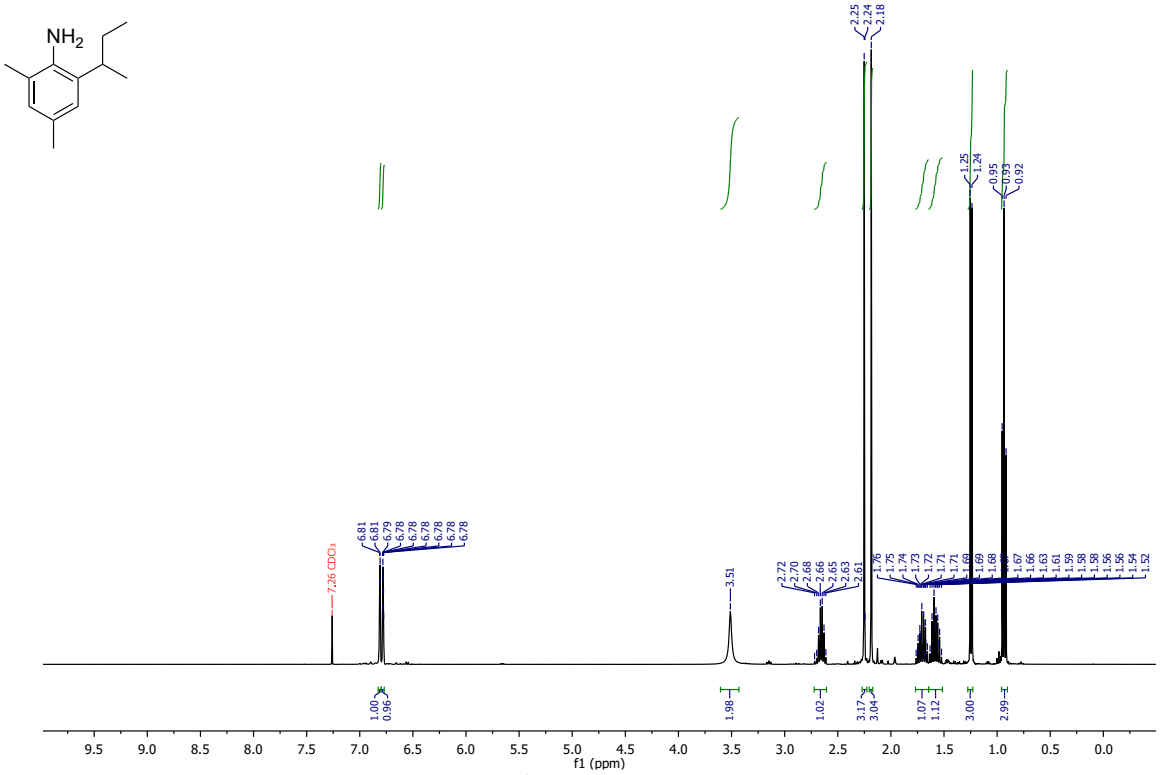


Figure **S23** ^{1}H NMR spectrum of **7d**

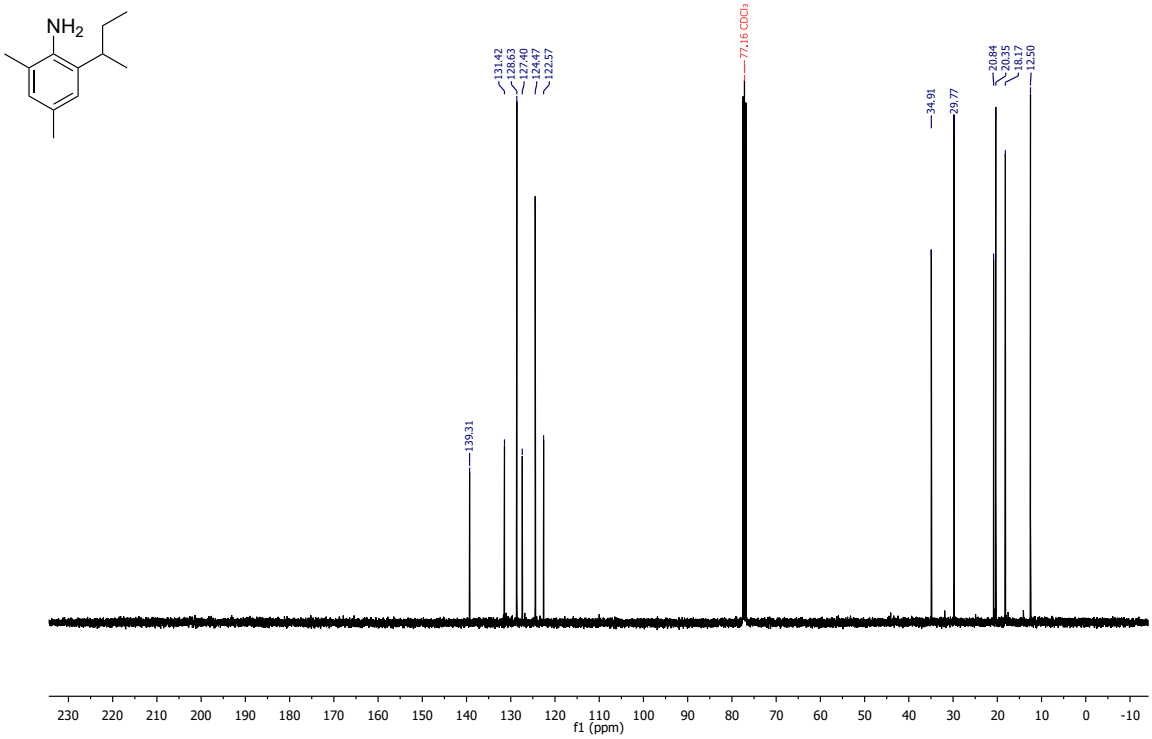


Figure **S24** ^{13}C NMR spectrum of **7d**

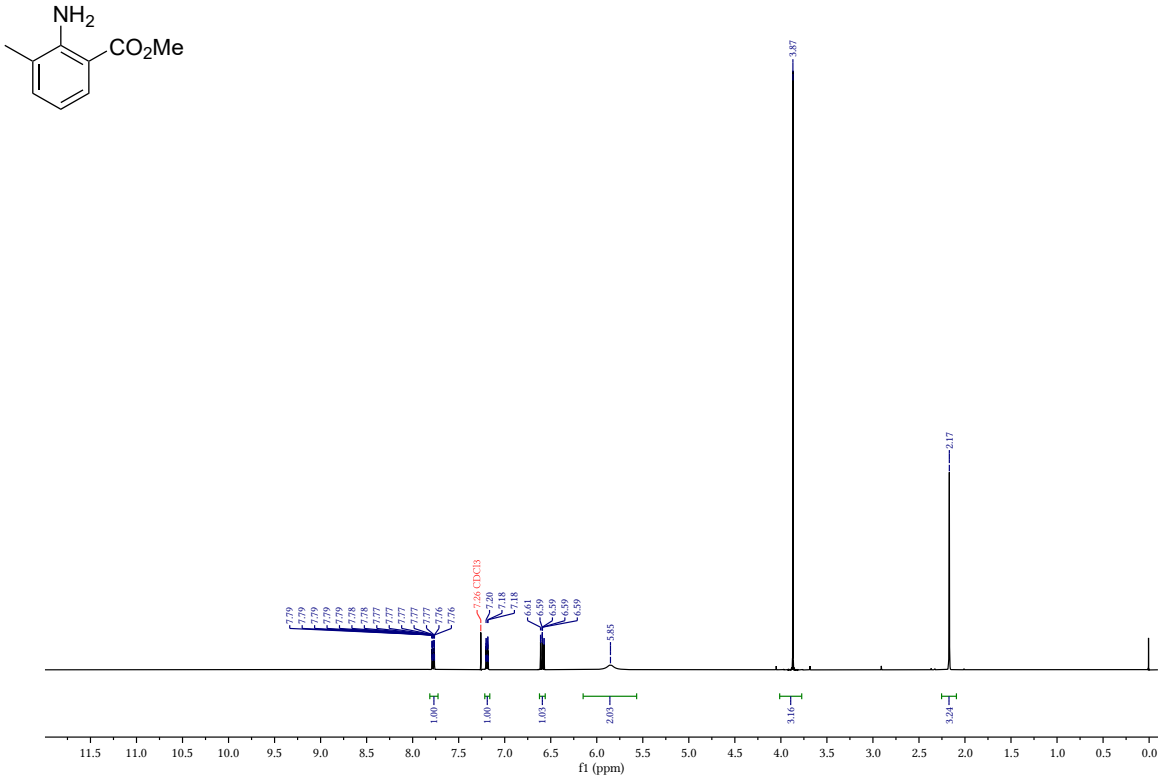


Figure **S25** ^{1}H NMR spectrum of methyl 2-amino-3-methylbenzoate

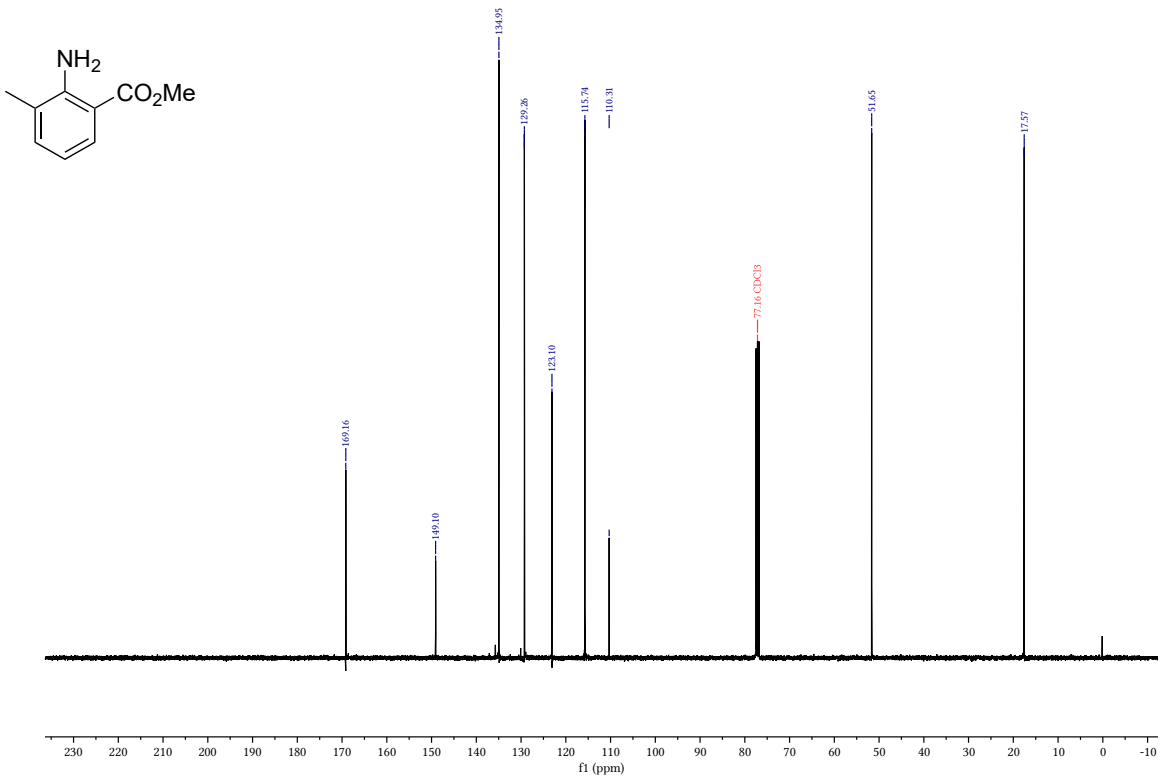


Figure **S26** ^{13}C NMR spectrum of methyl 2-amino-3-methylbenzoate

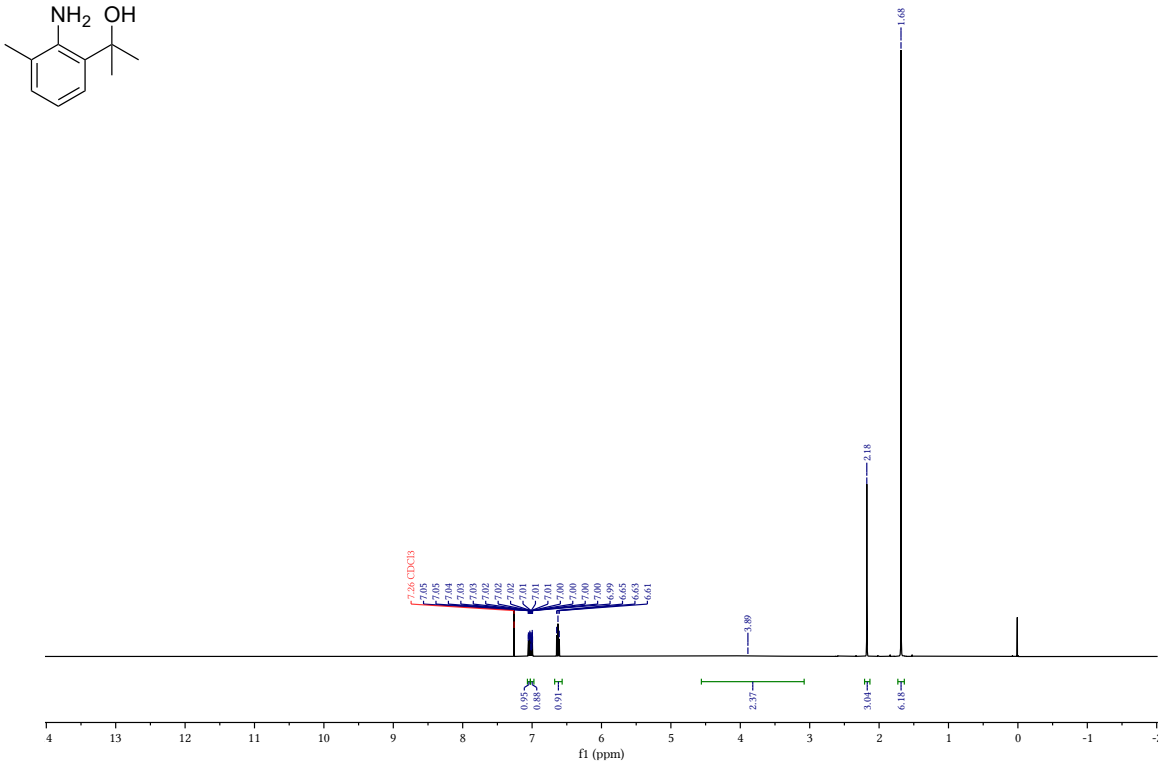


Figure **S27** ^{1}H NMR spectrum of 2-(2-amino-3-methylphenyl)propan-2-ol

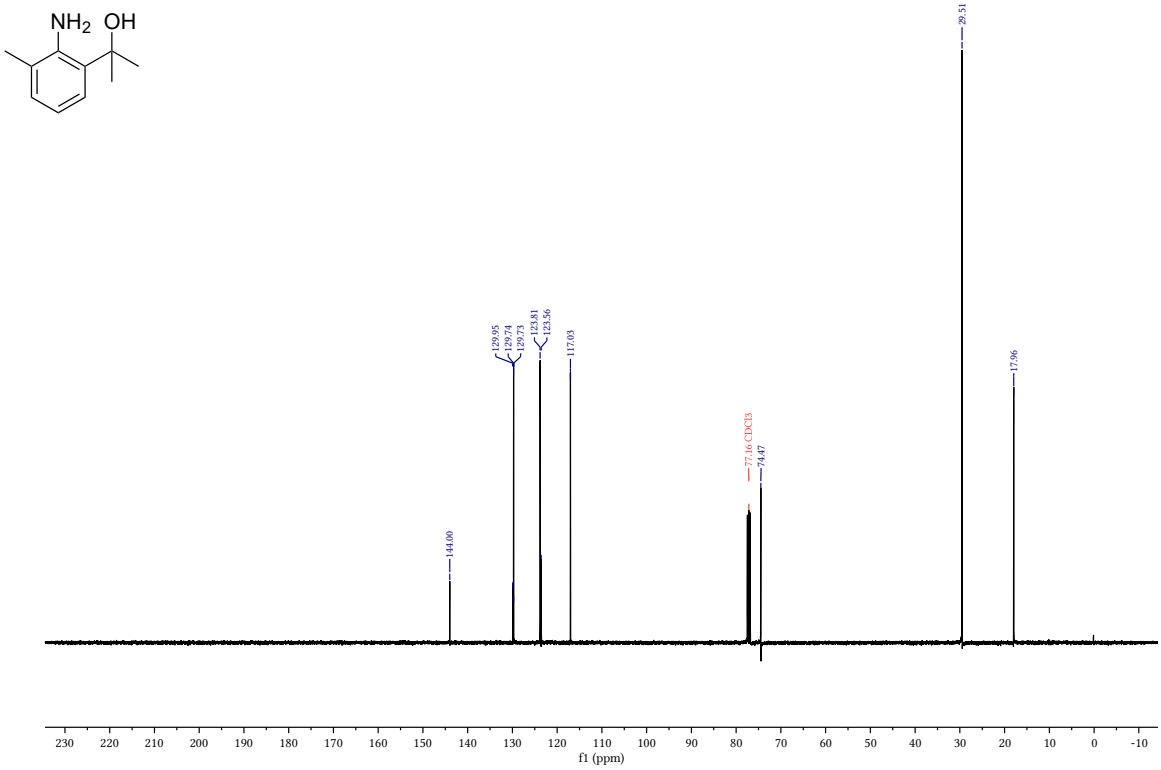


Figure **S28** ^{13}C NMR spectrum of 2-(2-amino-3-methylphenyl)propan-2-ol

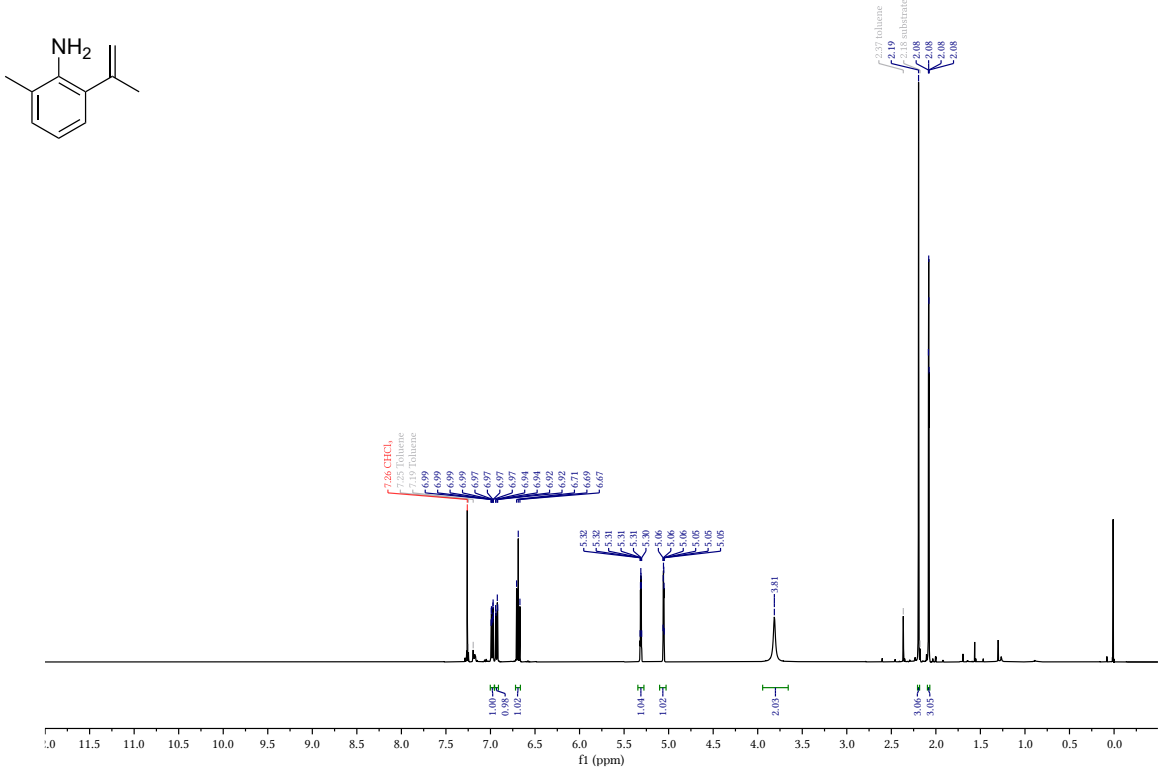


Figure **S29** ^{1}H NMR spectrum of 2-methyl-6-(prop-1-en-2-yl)aniline

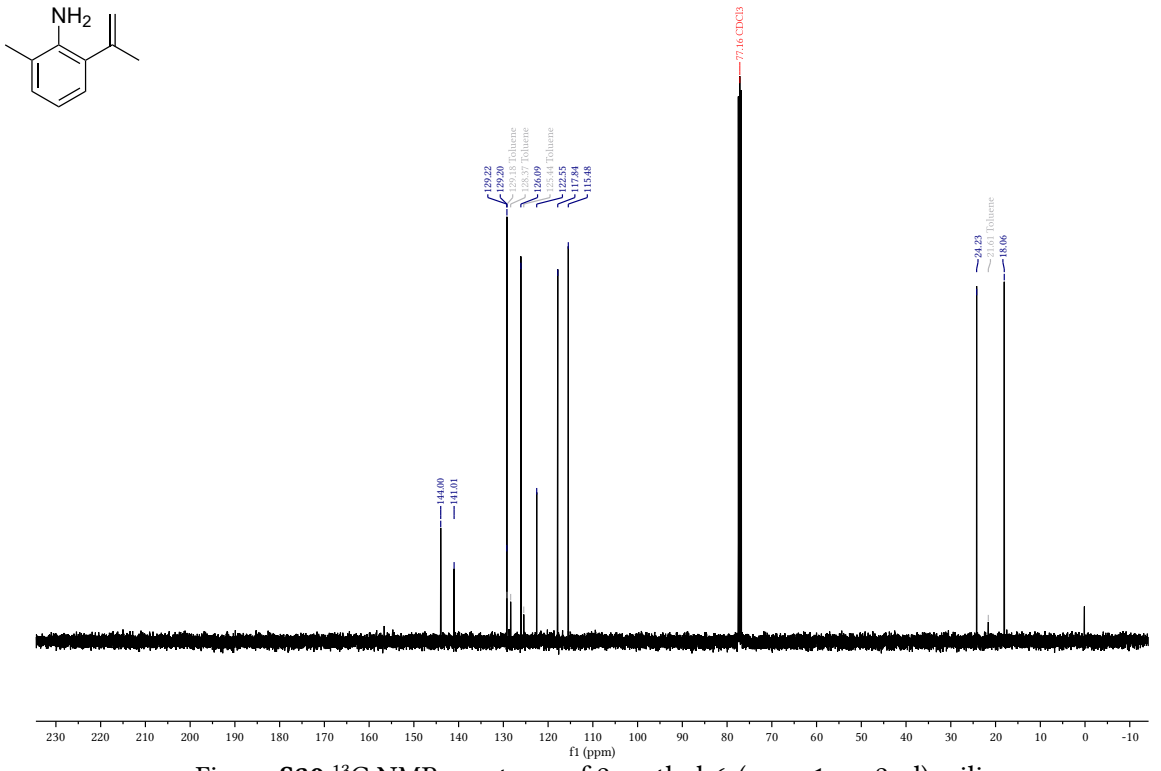


Figure **S30** ^{13}C NMR spectrum of 2-methyl-6-(prop-1-en-2-yl)aniline

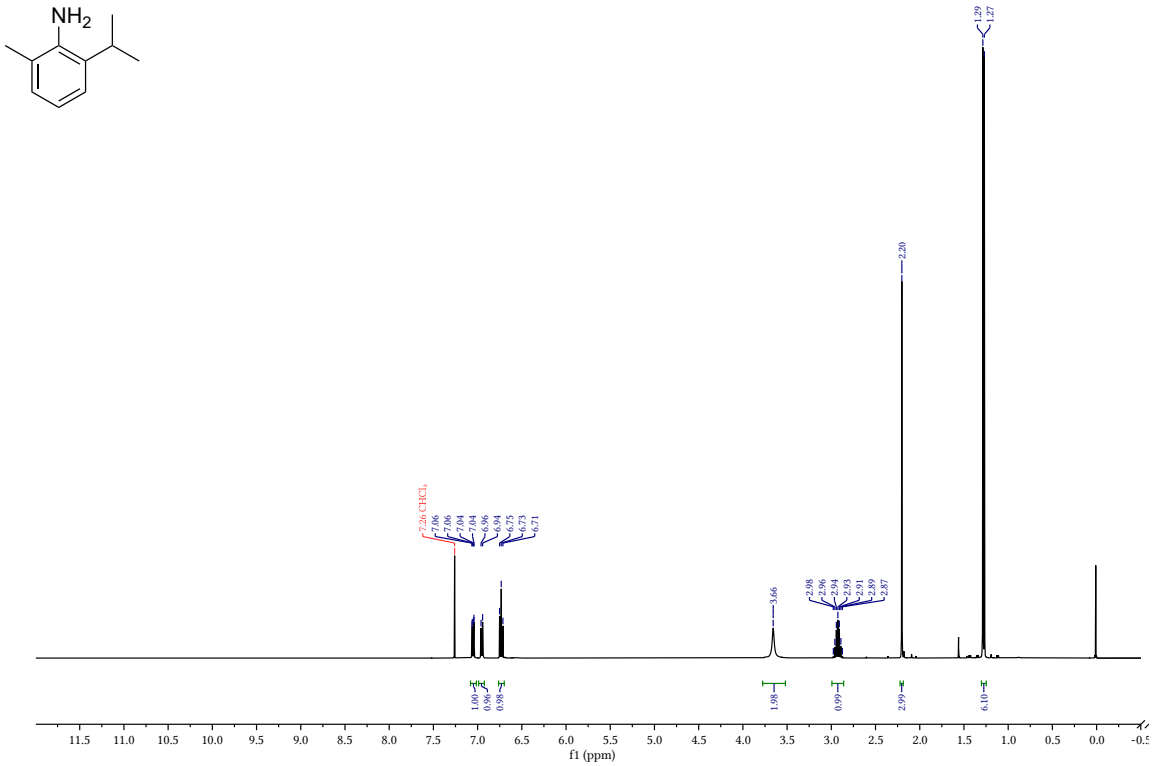


Figure **S31** ^{1}H NMR spectrum of **7e**

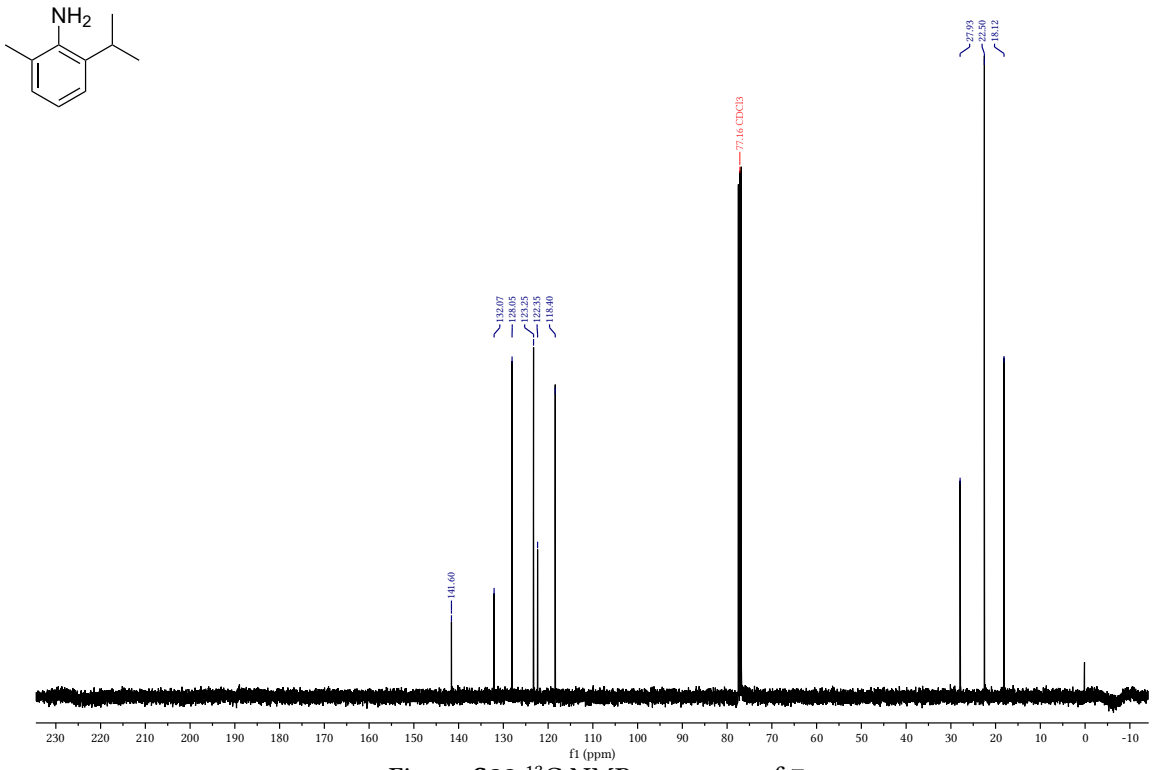


Figure **S32** ^{13}C NMR spectrum of **7e**

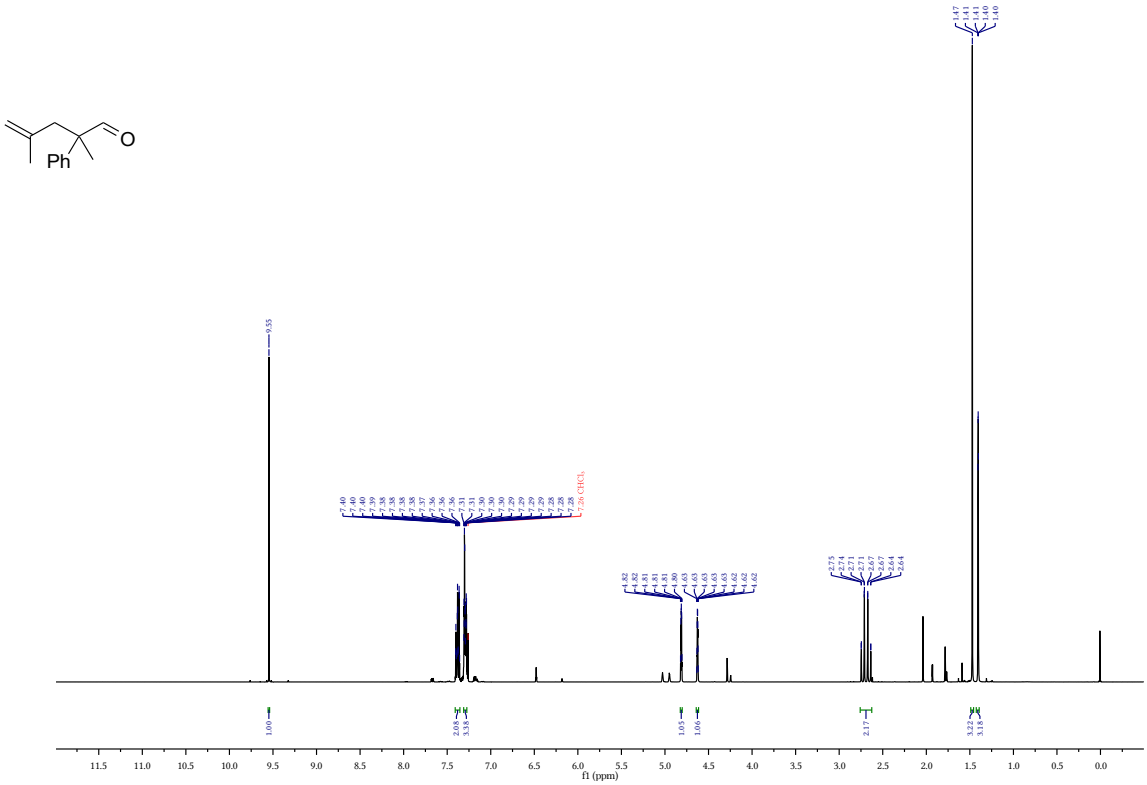


Figure **S33** ^{1}H NMR spectrum of **9**

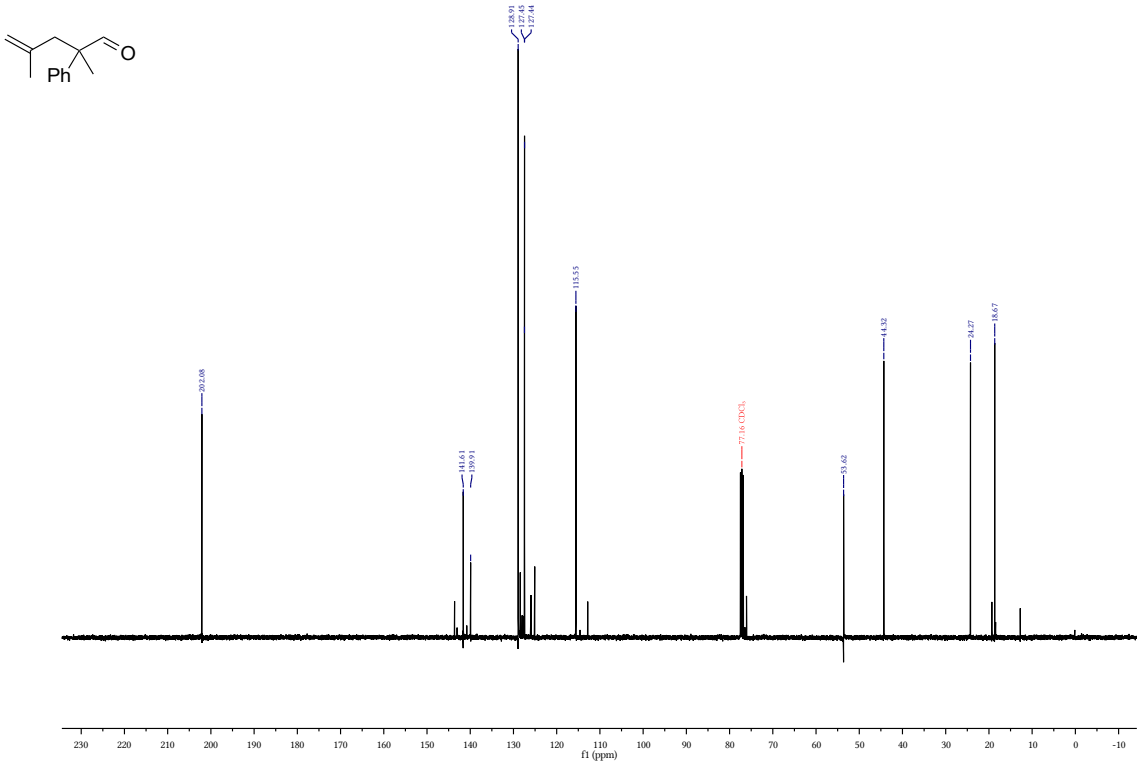


Figure **S34** ^{13}C NMR spectrum of **9**

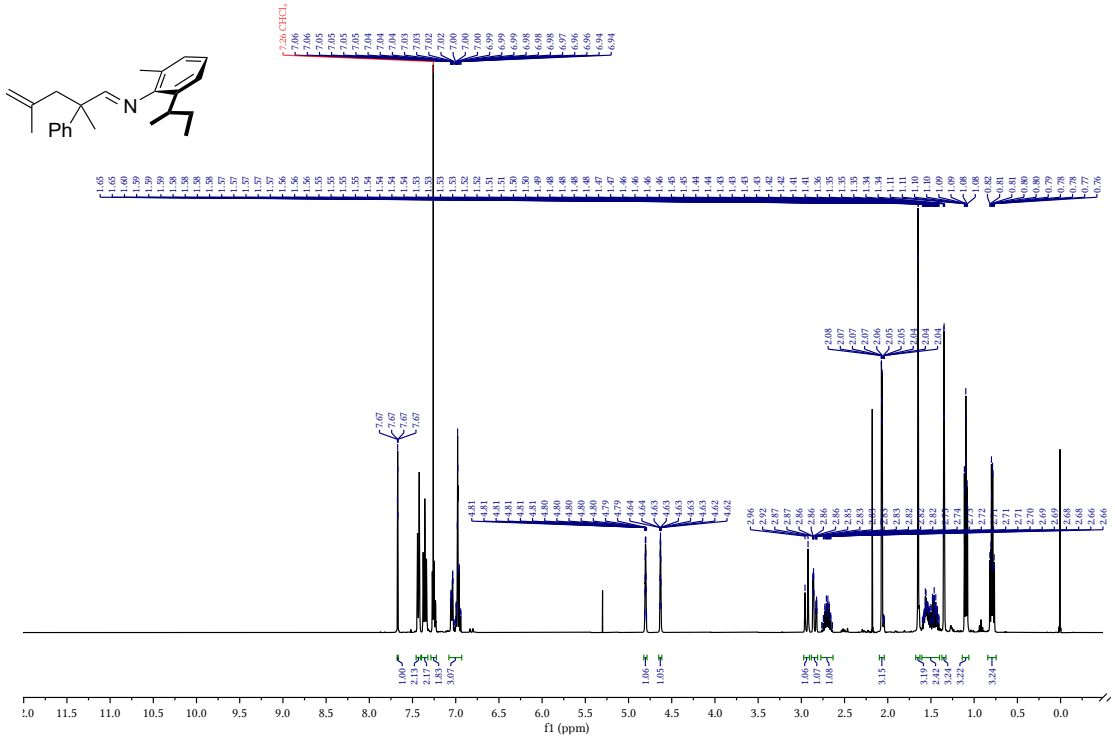


Figure **S35** ^{1}H NMR spectrum of **10a**

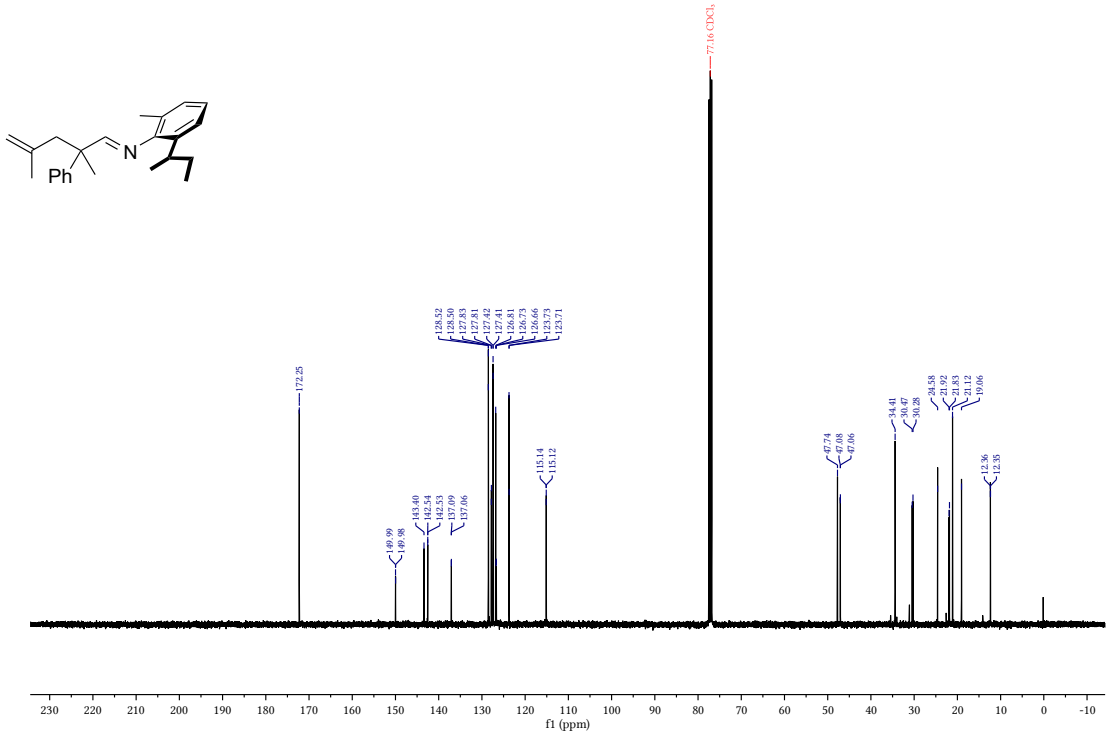


Figure **S36** ^{13}C NMR spectrum of **10a**

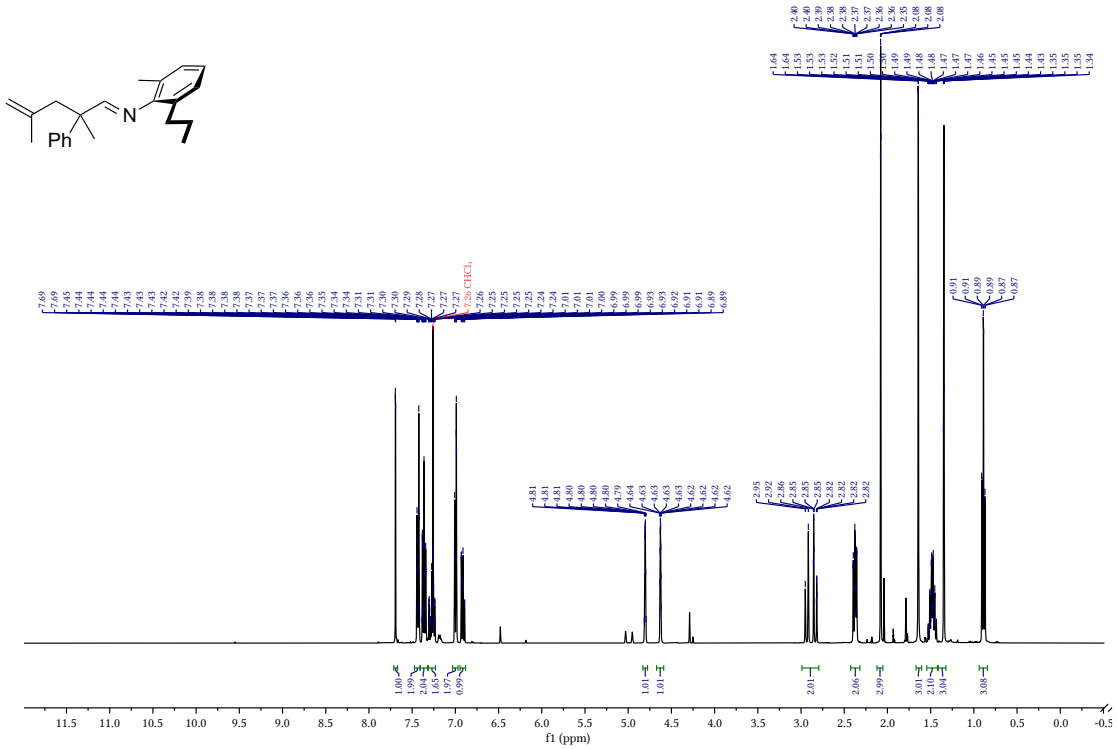


Figure **S37** ^{1}H NMR spectrum of **10b**

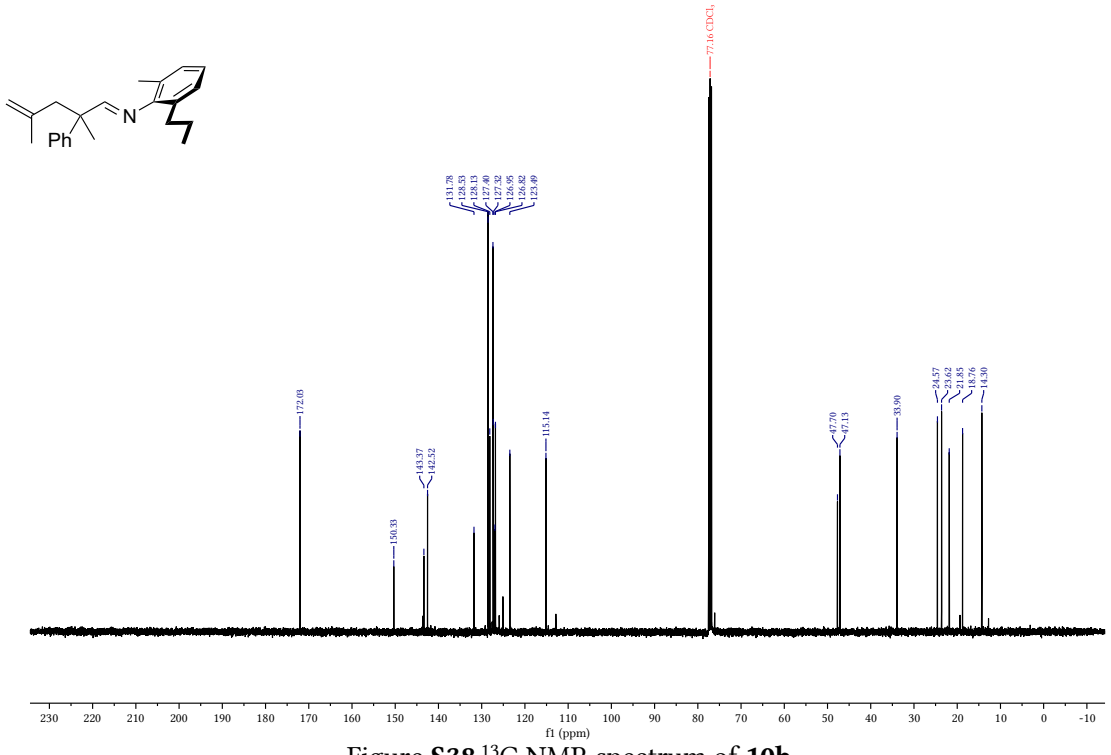


Figure **S38** ^{13}C NMR spectrum of **10b**

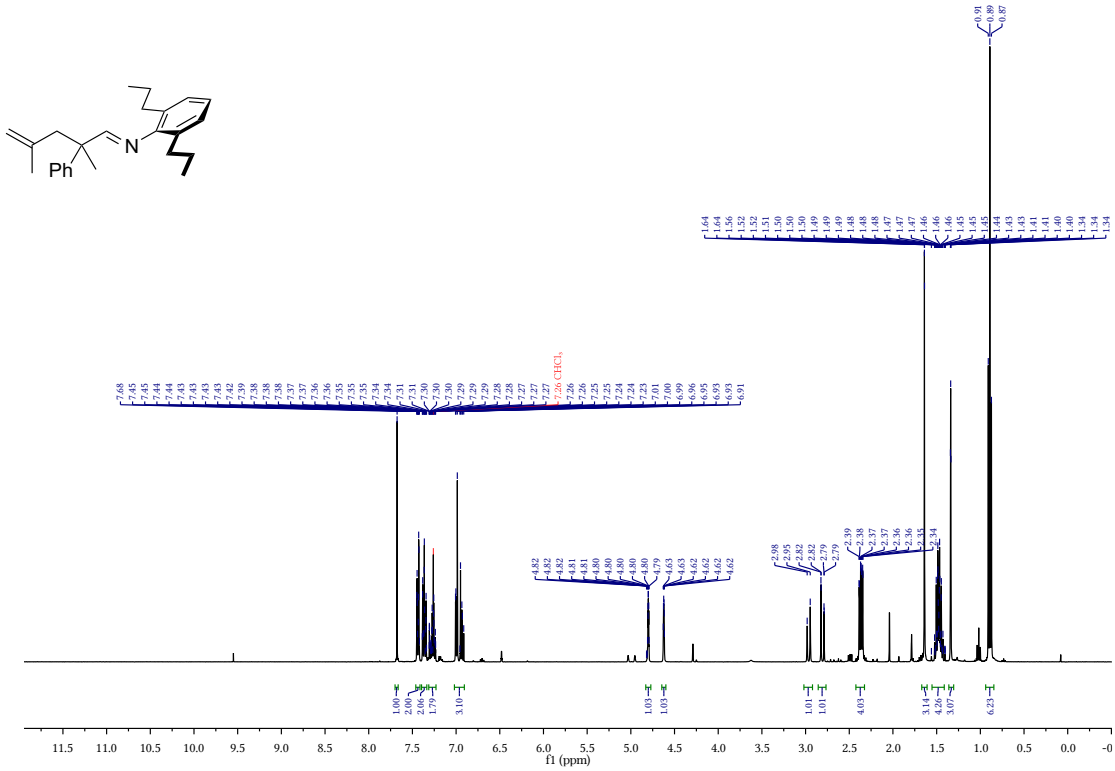


Figure **S39** ^{1}H NMR spectrum of **10c**

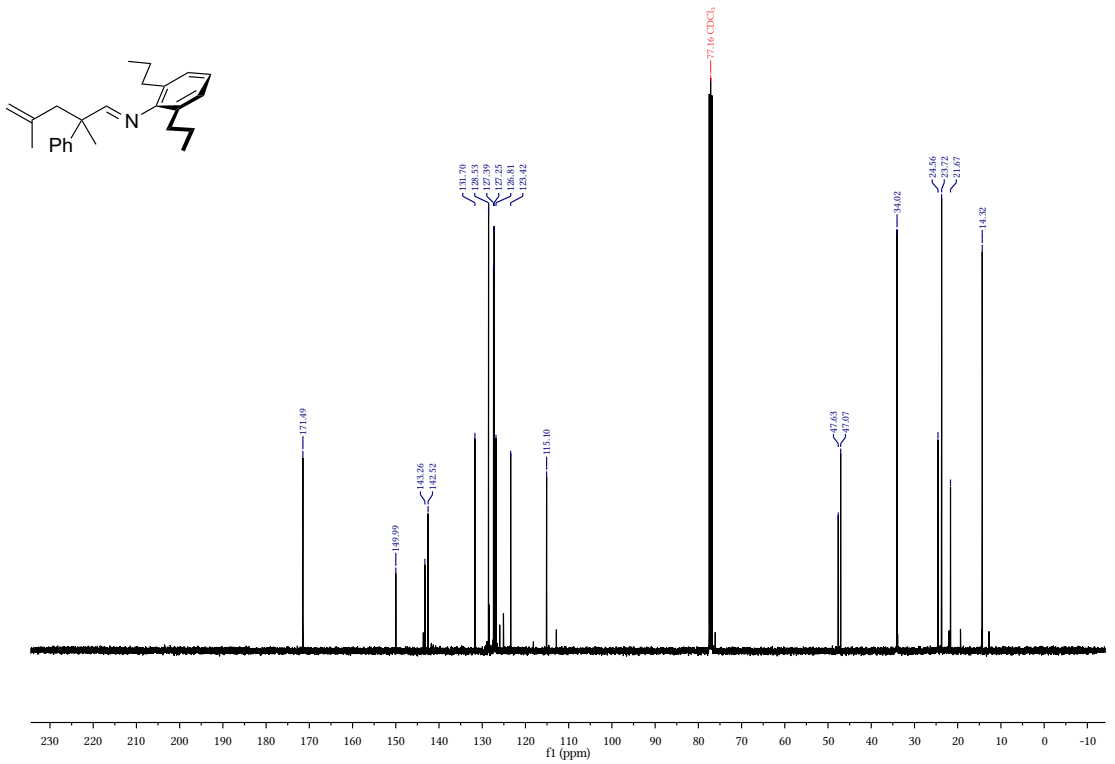


Figure **S40** ^{13}C NMR spectrum of **10c**

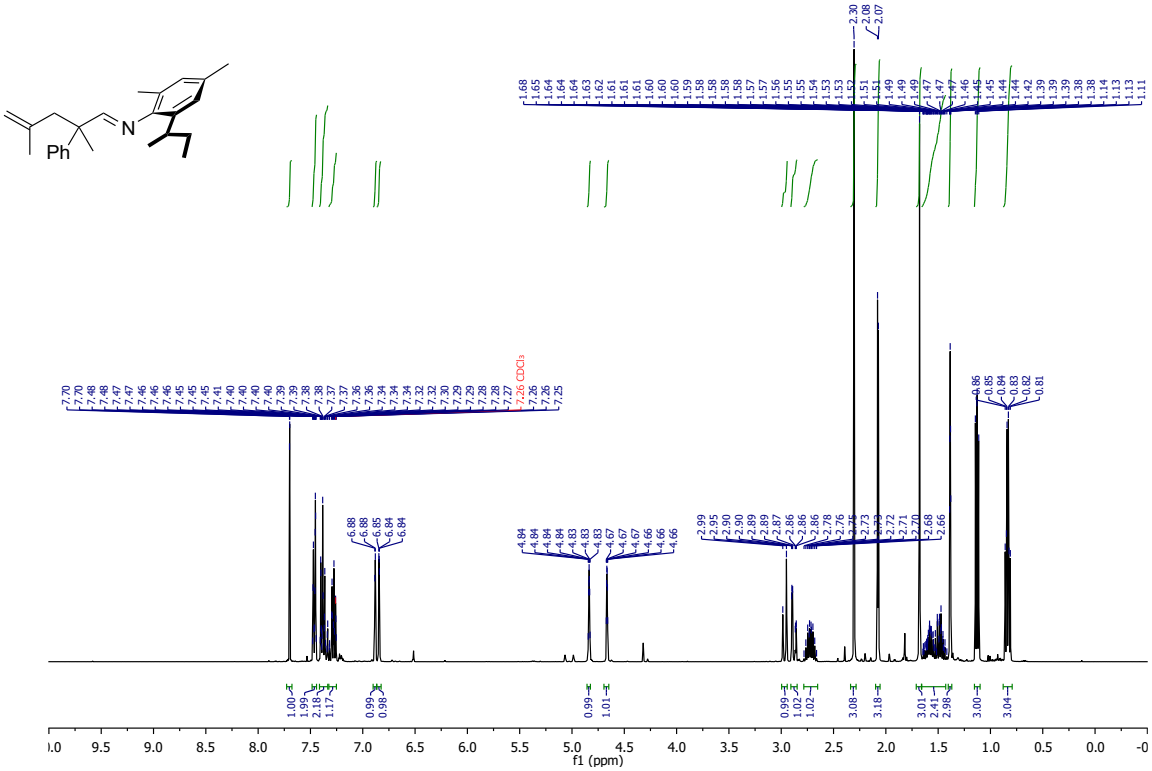


Figure **S41** ^{1}H NMR spectrum of **10d**

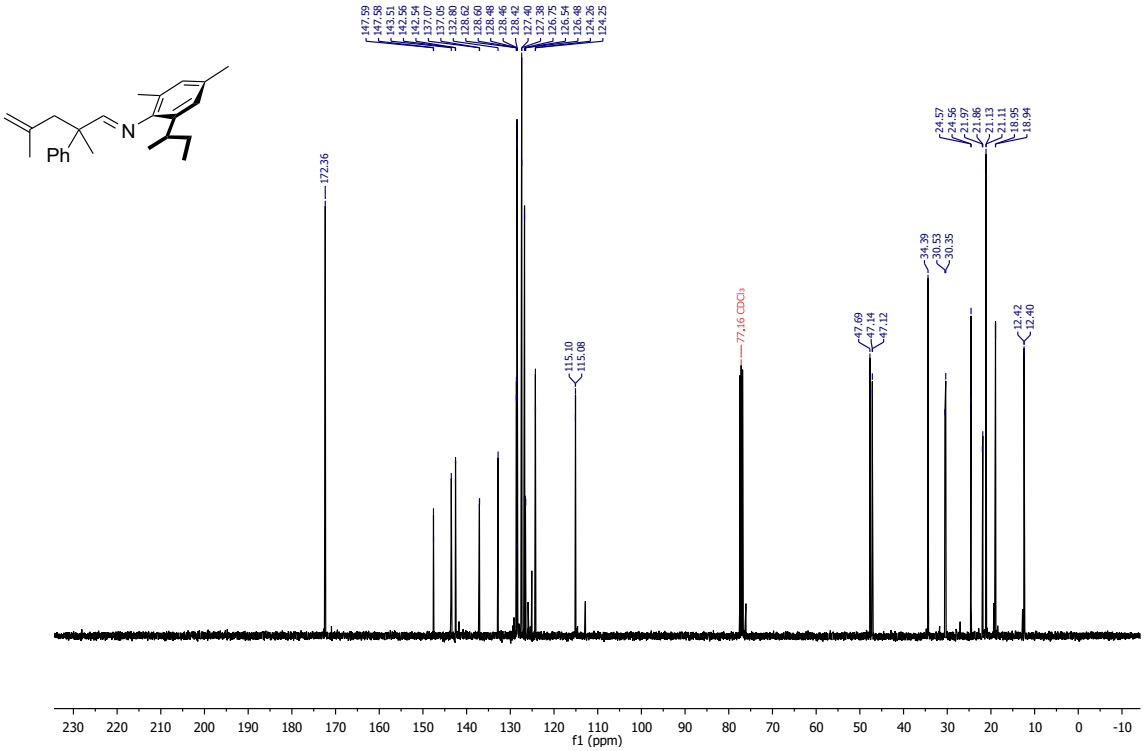


Figure **S42** ^{13}C NMR spectrum of **10d**

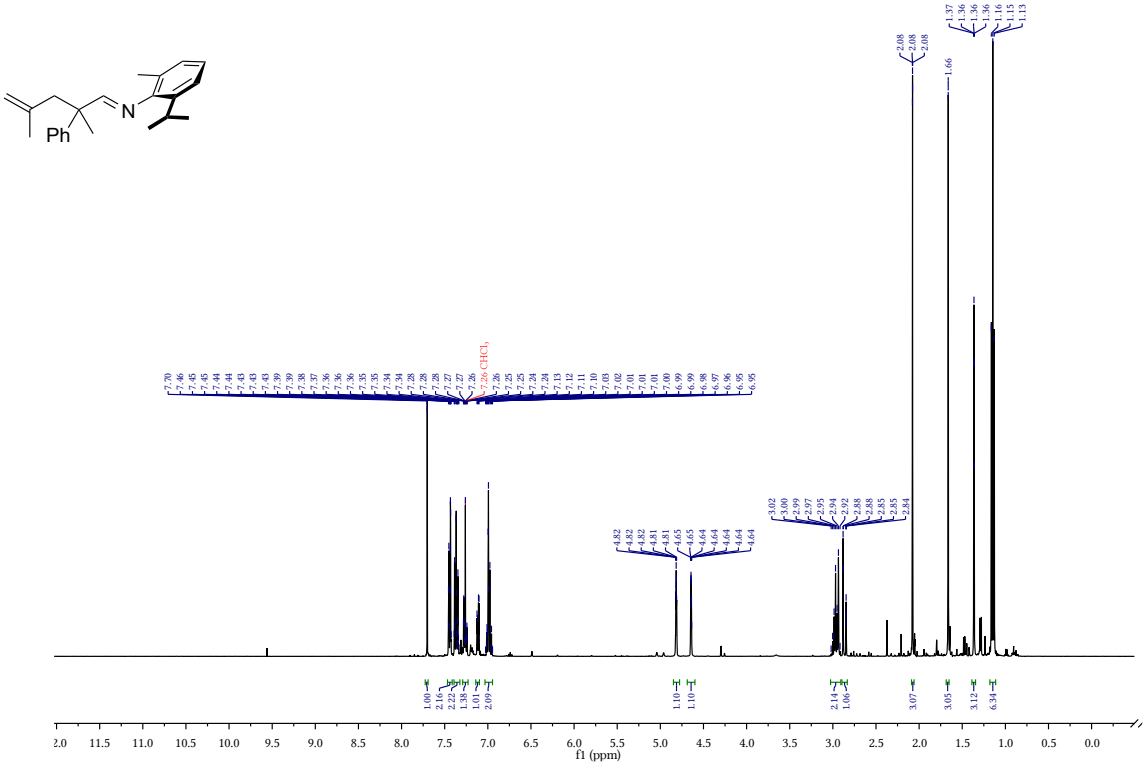


Figure **S43** ^{1}H NMR spectrum of **10e**

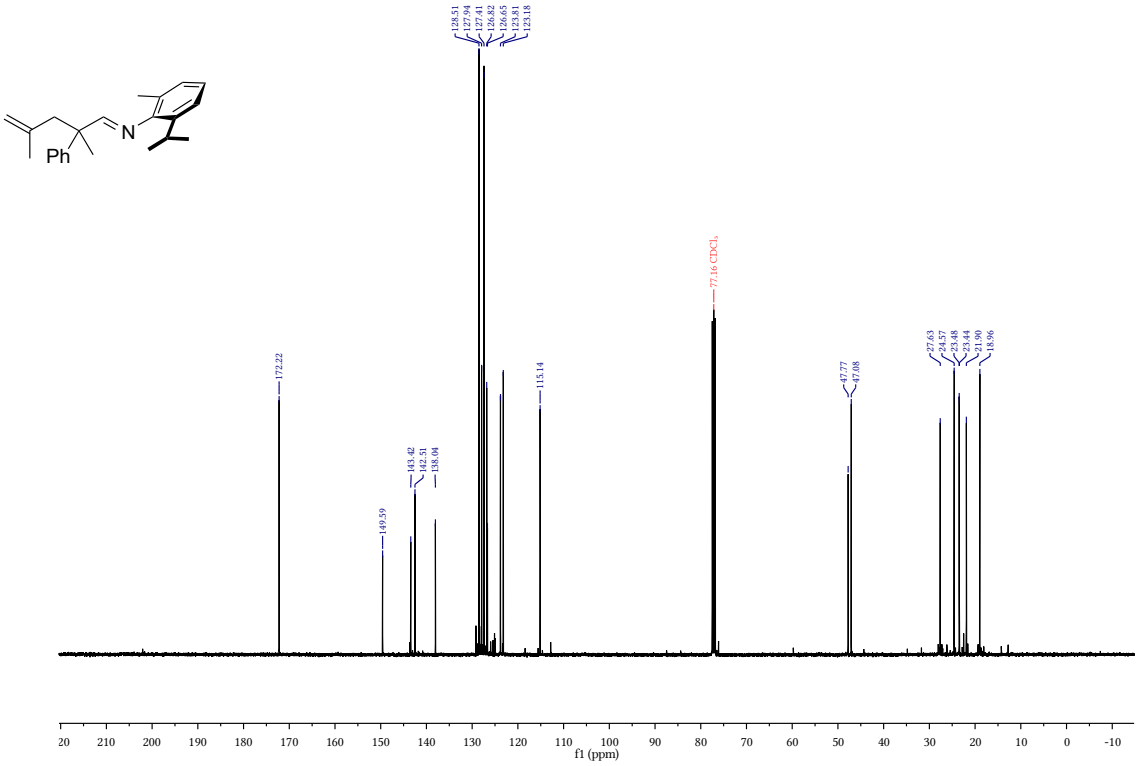


Figure **S44** ^{13}C NMR spectrum of **10e**

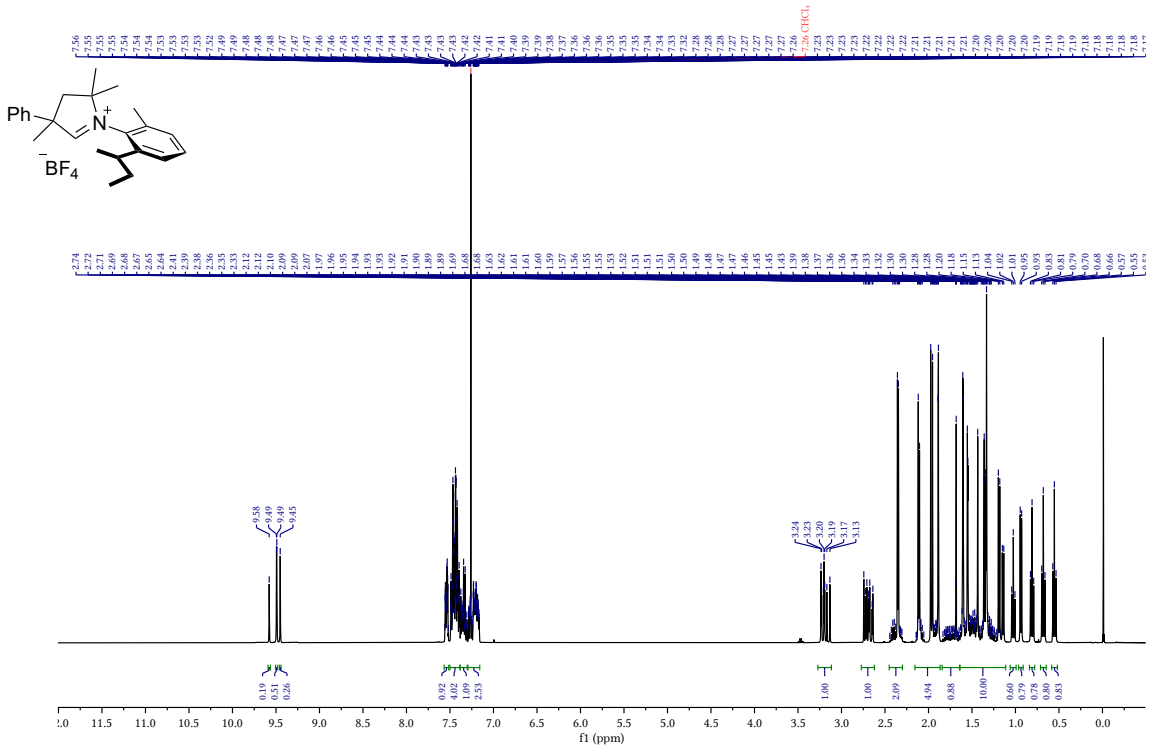


Figure **S45** ^{1}H NMR spectrum of **11a**

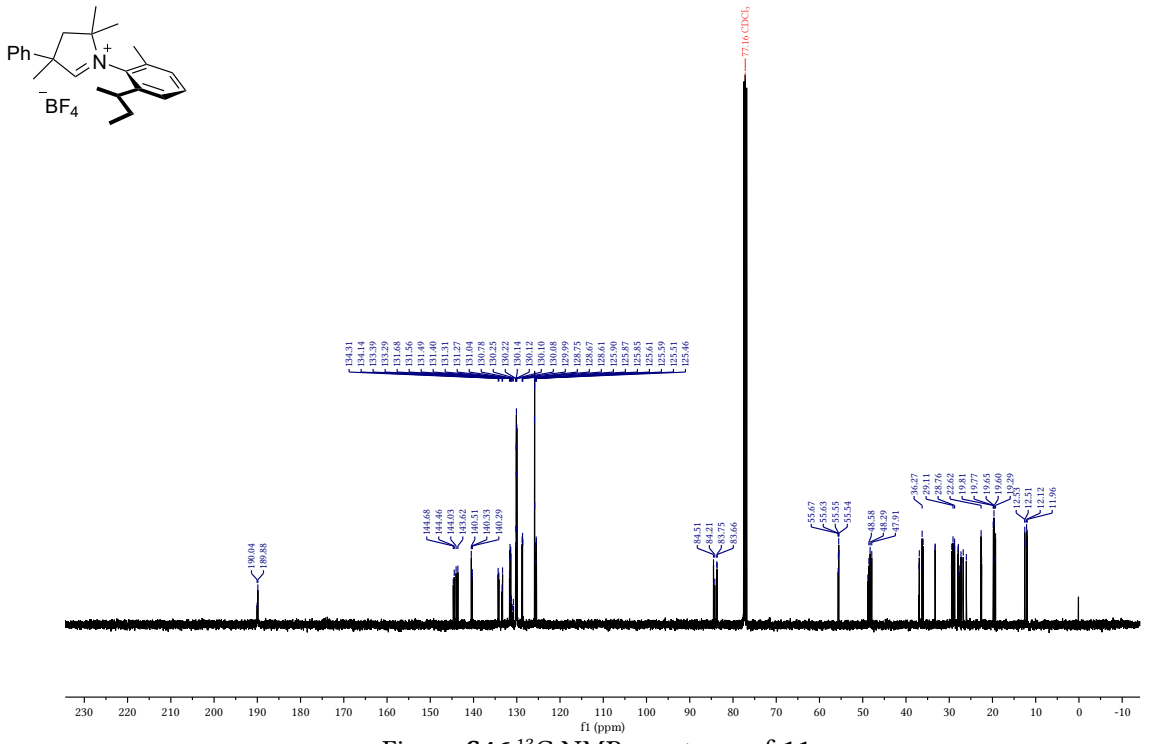


Figure **S46** ^{13}C NMR spectrum of **11a**

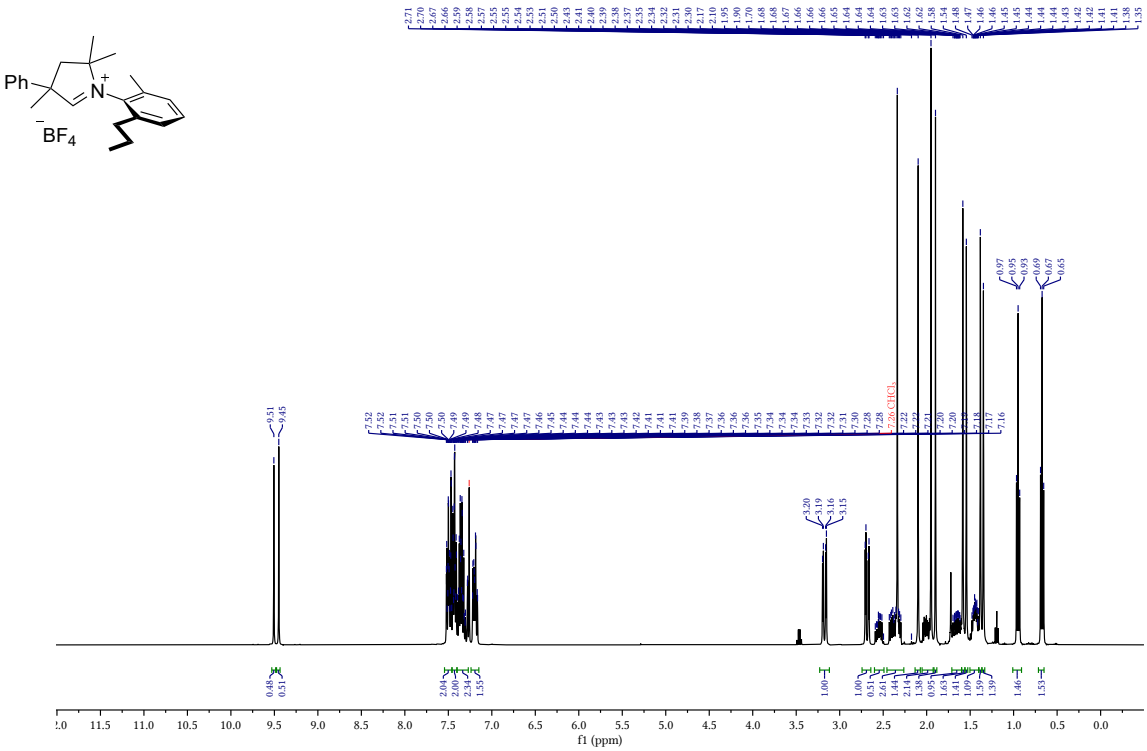


Figure **S47** ^{1}H NMR spectrum of **11b**

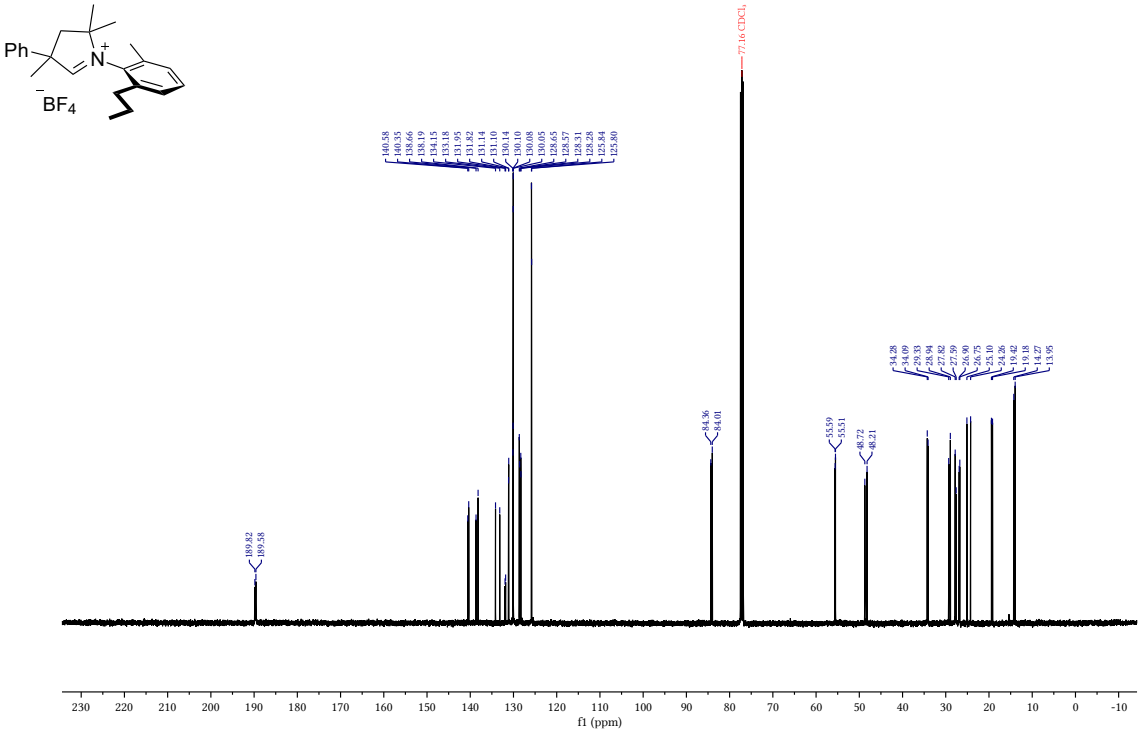


Figure **S48** ^{13}C NMR spectrum of **11b**

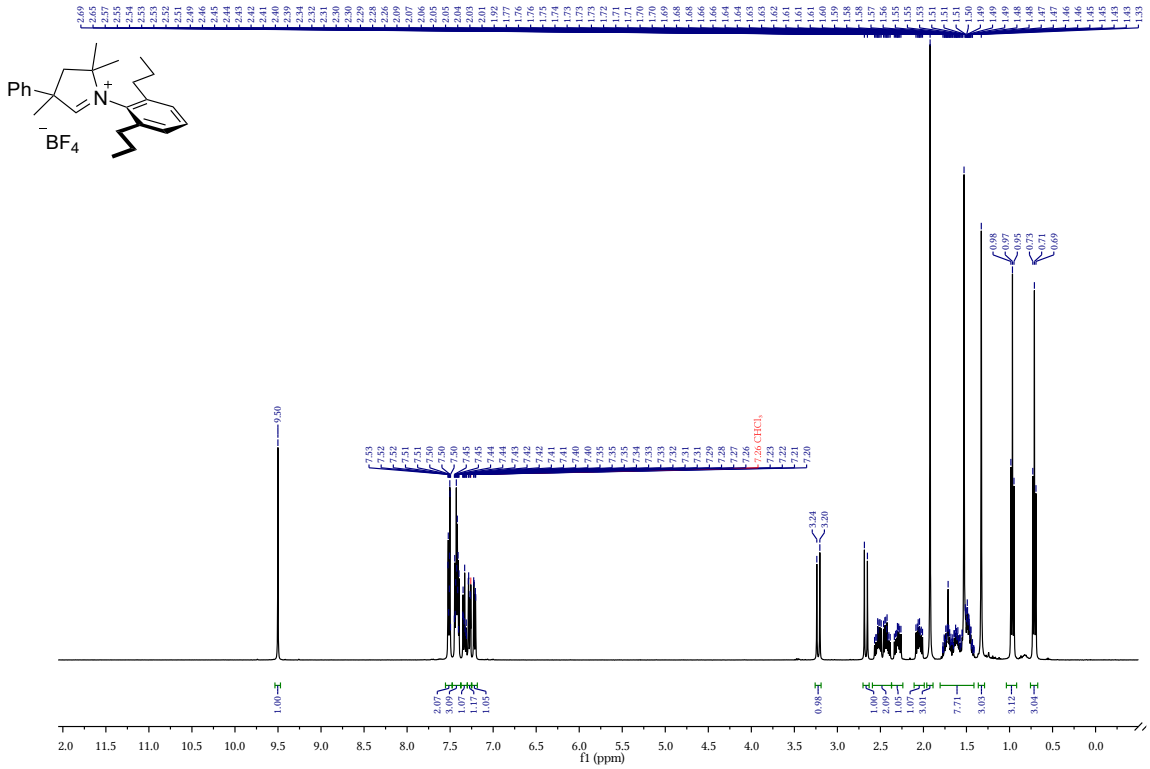


Figure **S49** ^{1}H NMR spectrum of **11c**

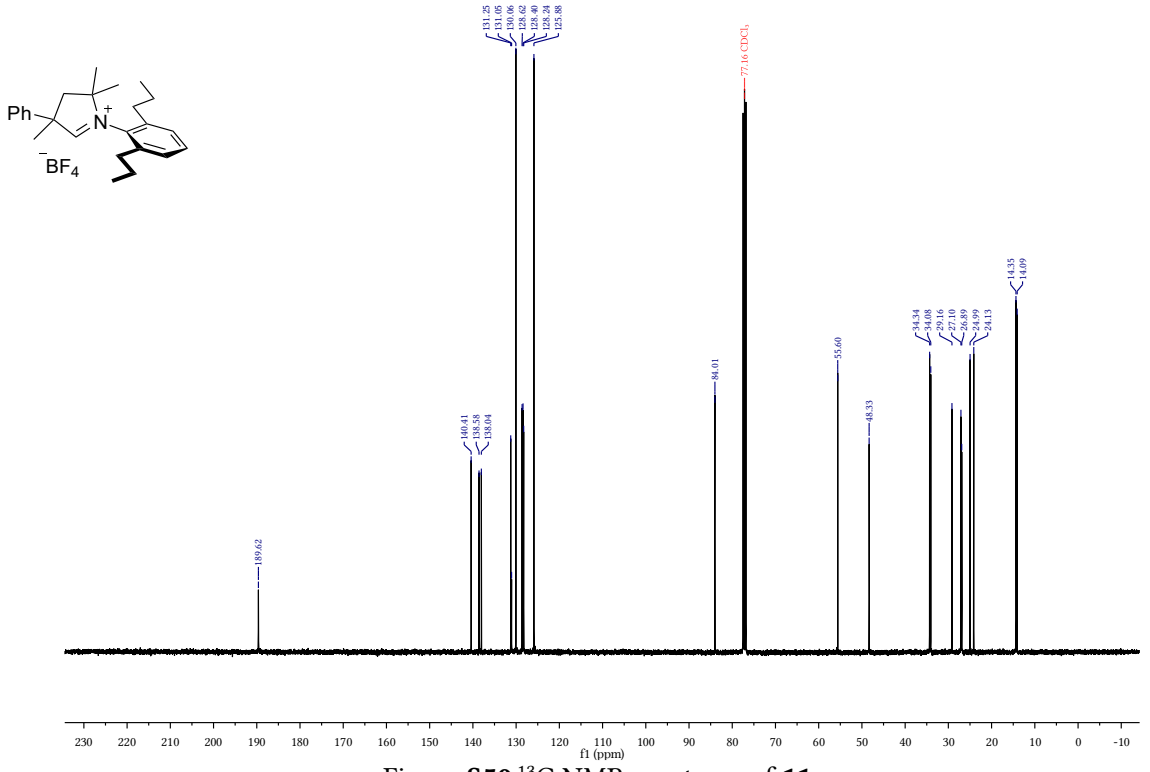


Figure **S50** ^{13}C NMR spectrum of **11c**

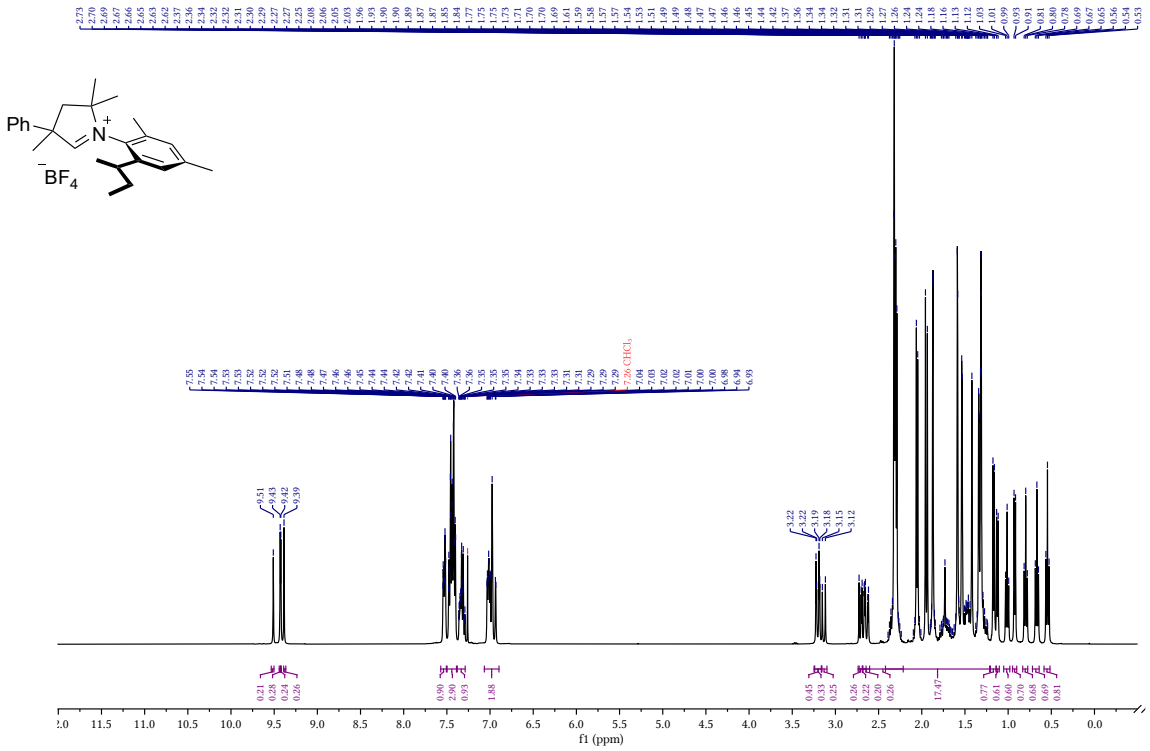


Figure **S51** ^{1}H NMR spectrum of **11d**

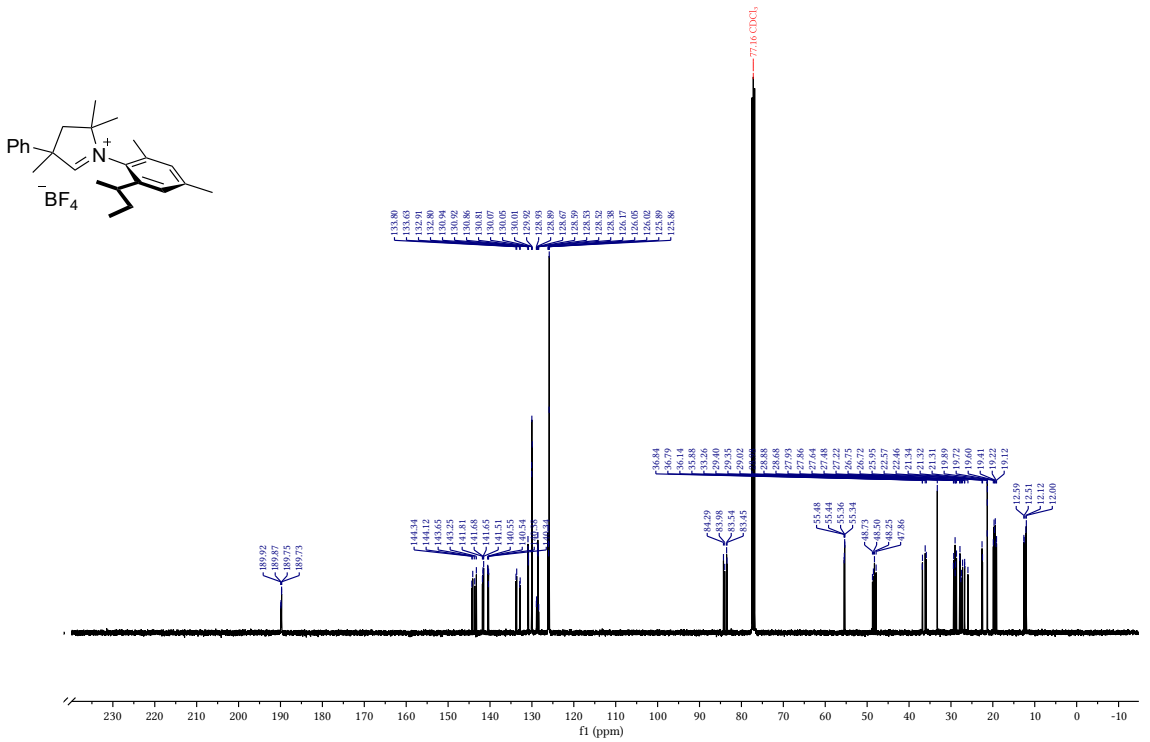


Figure **S52** ^{13}C NMR spectrum of **11d**

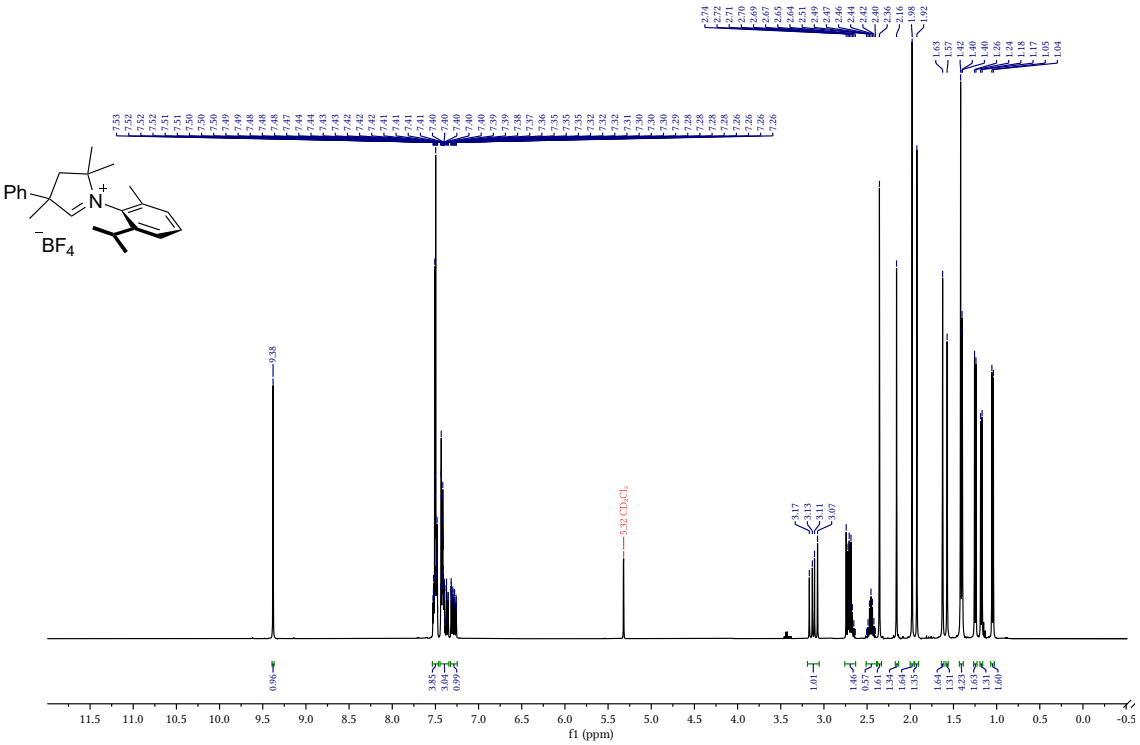


Figure **S53** ^{1}H NMR spectrum of **11e**

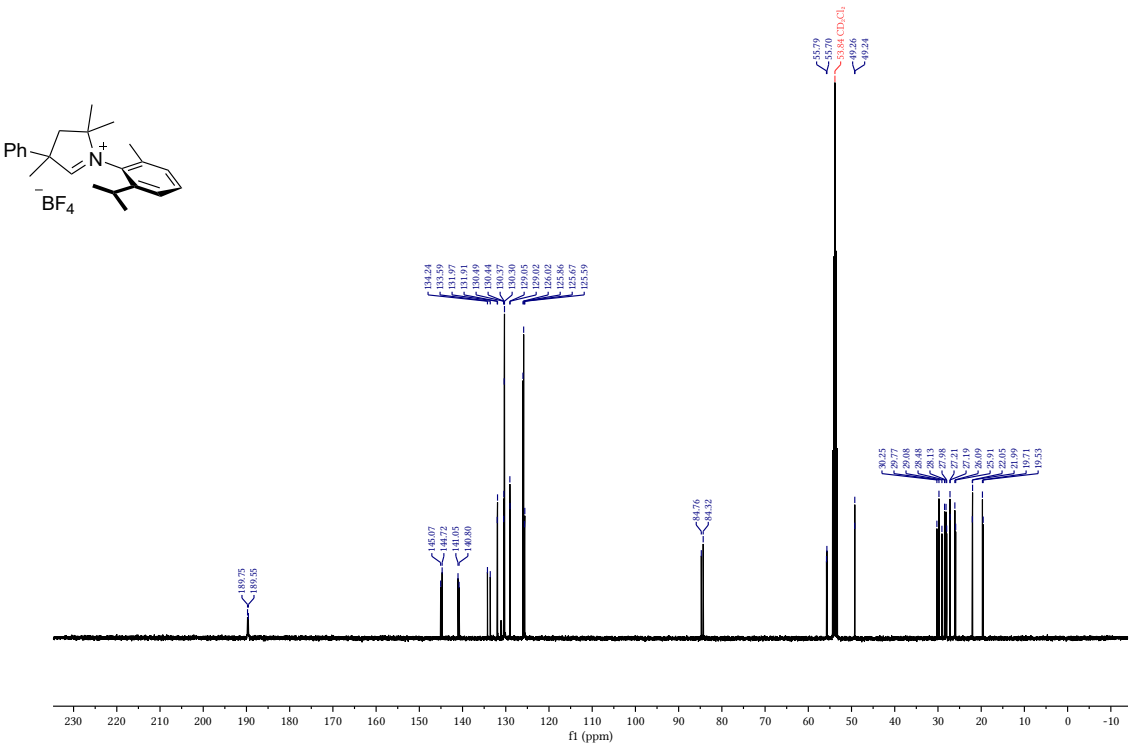


Figure **S54** ^{13}C NMR spectrum of **11e**

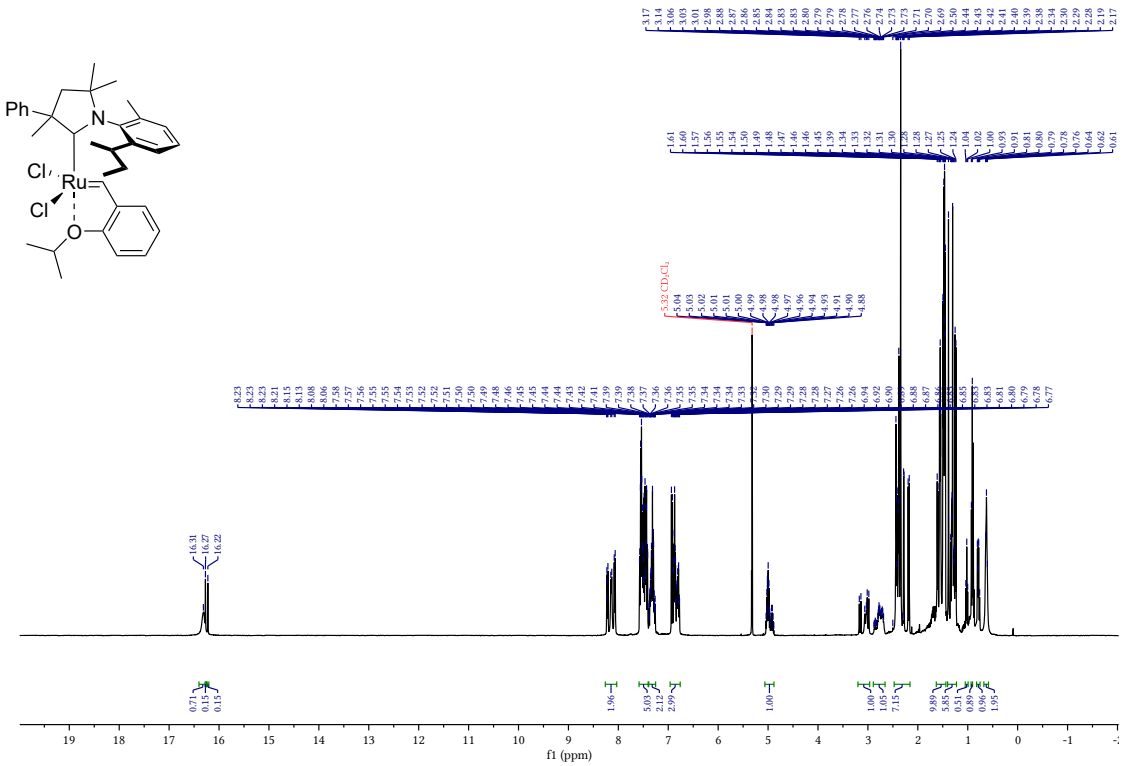


Figure **S55** ^{1}H NMR spectrum of **Ru10**

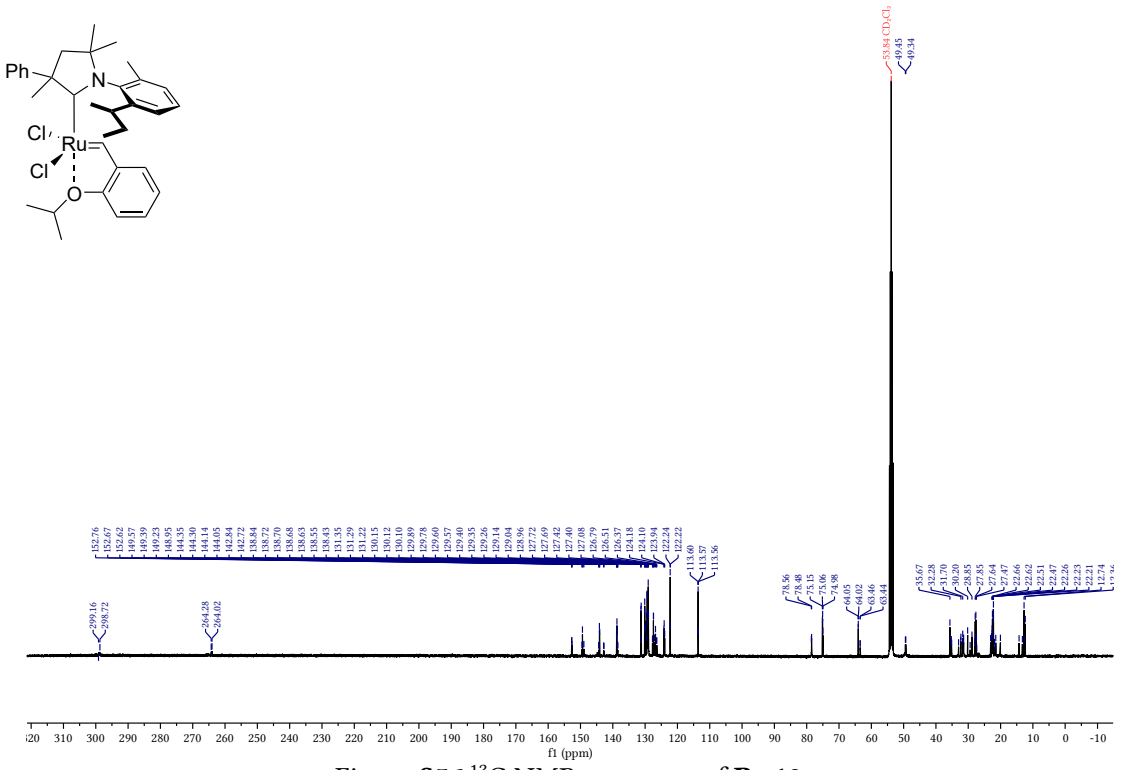


Figure **S56** ^{13}C NMR spectrum of **Ru10**

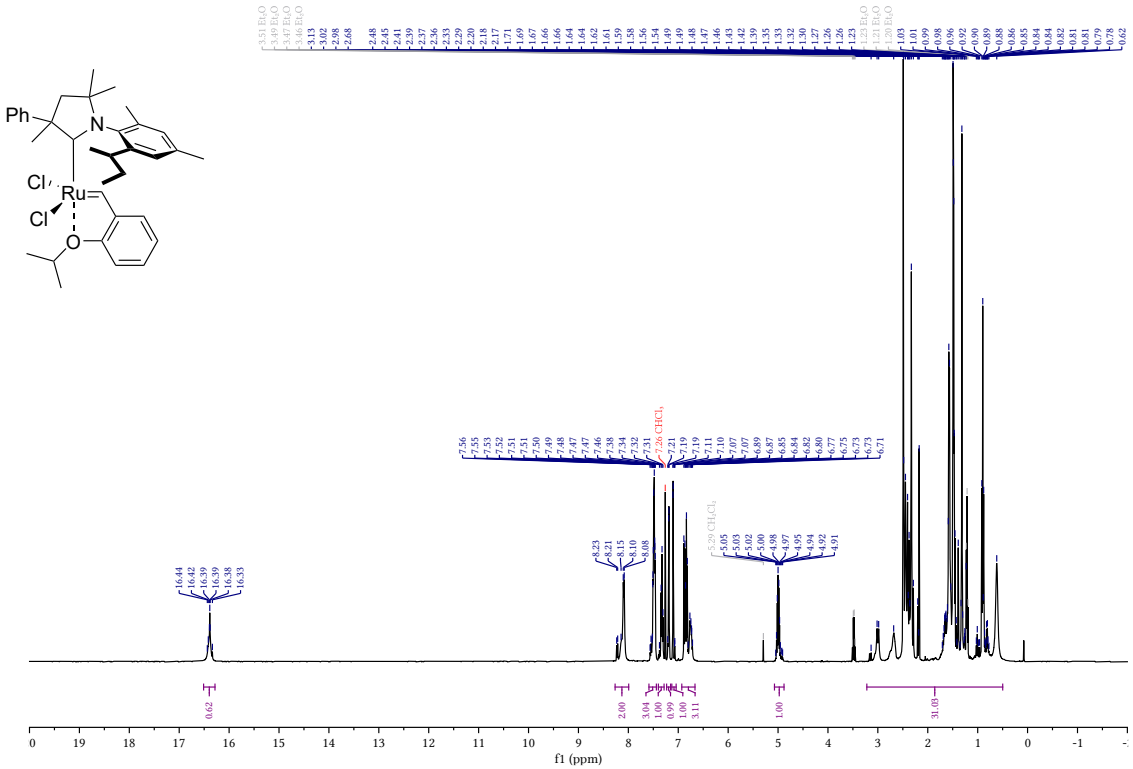


Figure **S57** ^{1}H NMR spectrum of **Ru11**

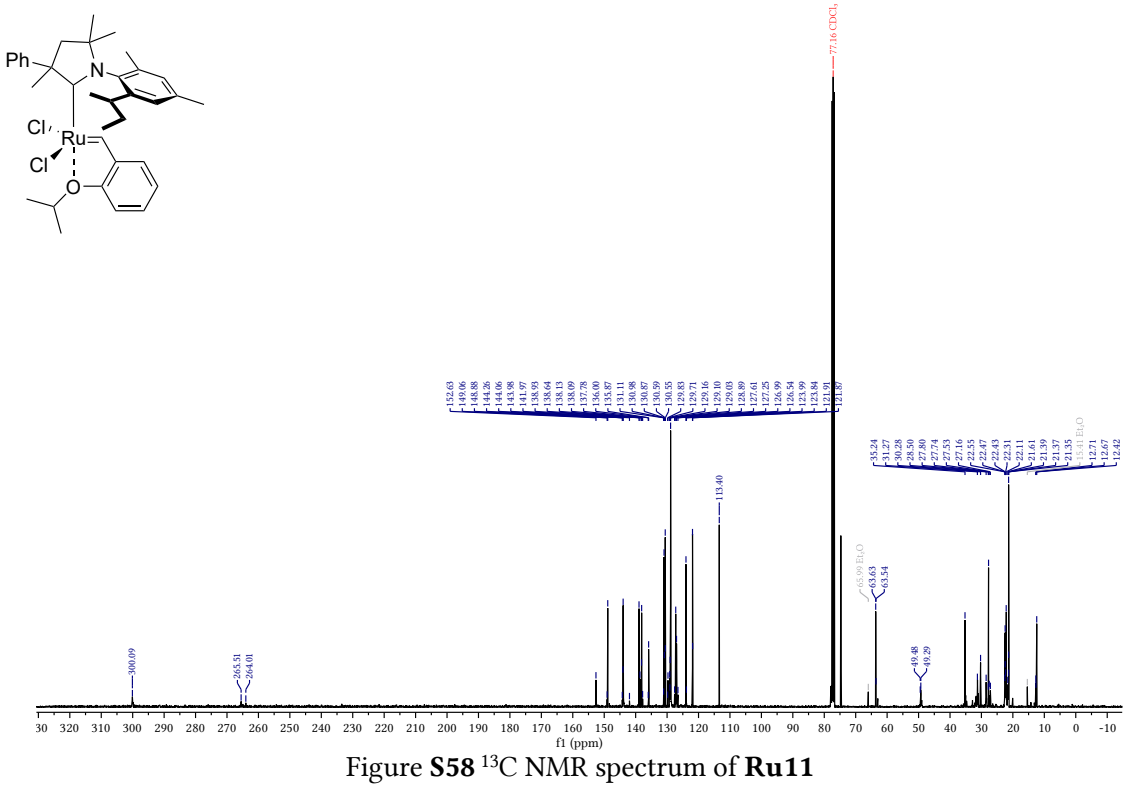


Figure **S58** ^{13}C NMR spectrum of **Ru11**

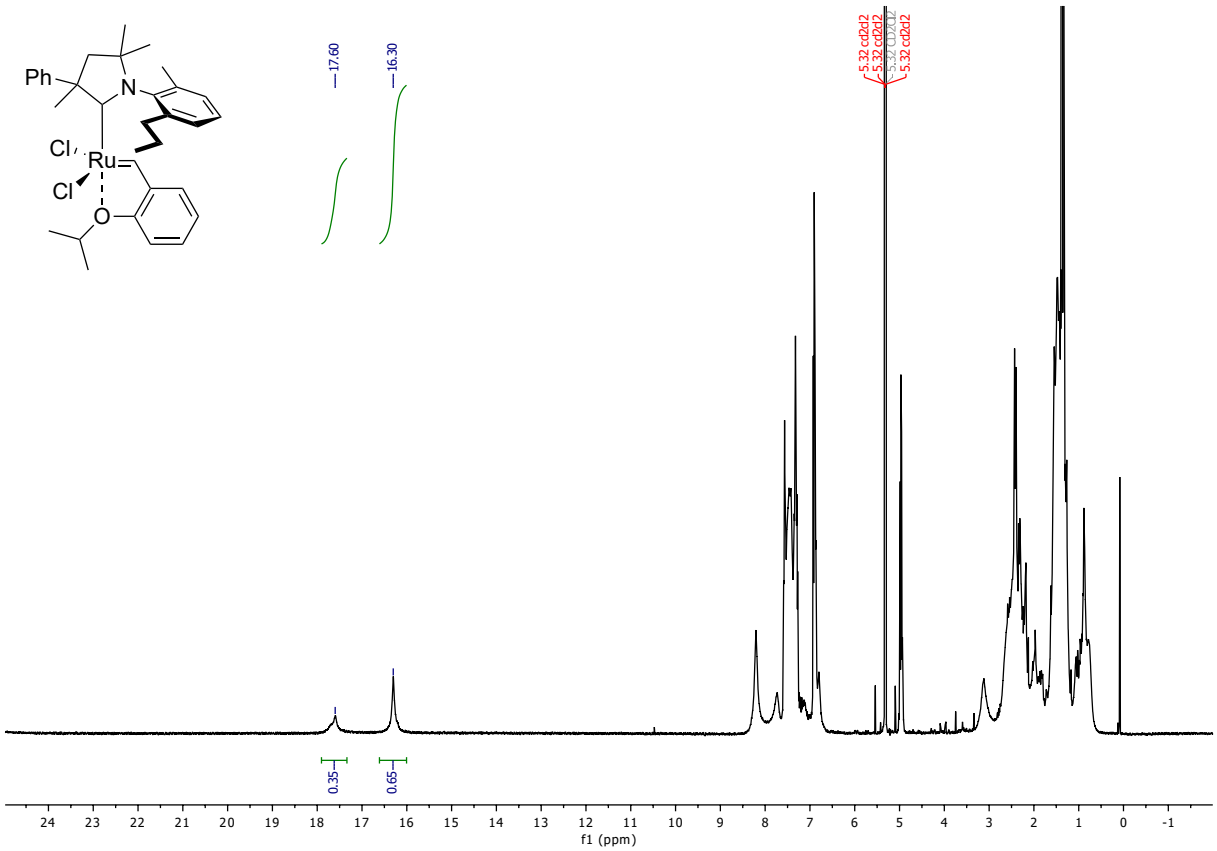


Figure **S59** ^{1}H NMR spectrum of **Ru13**

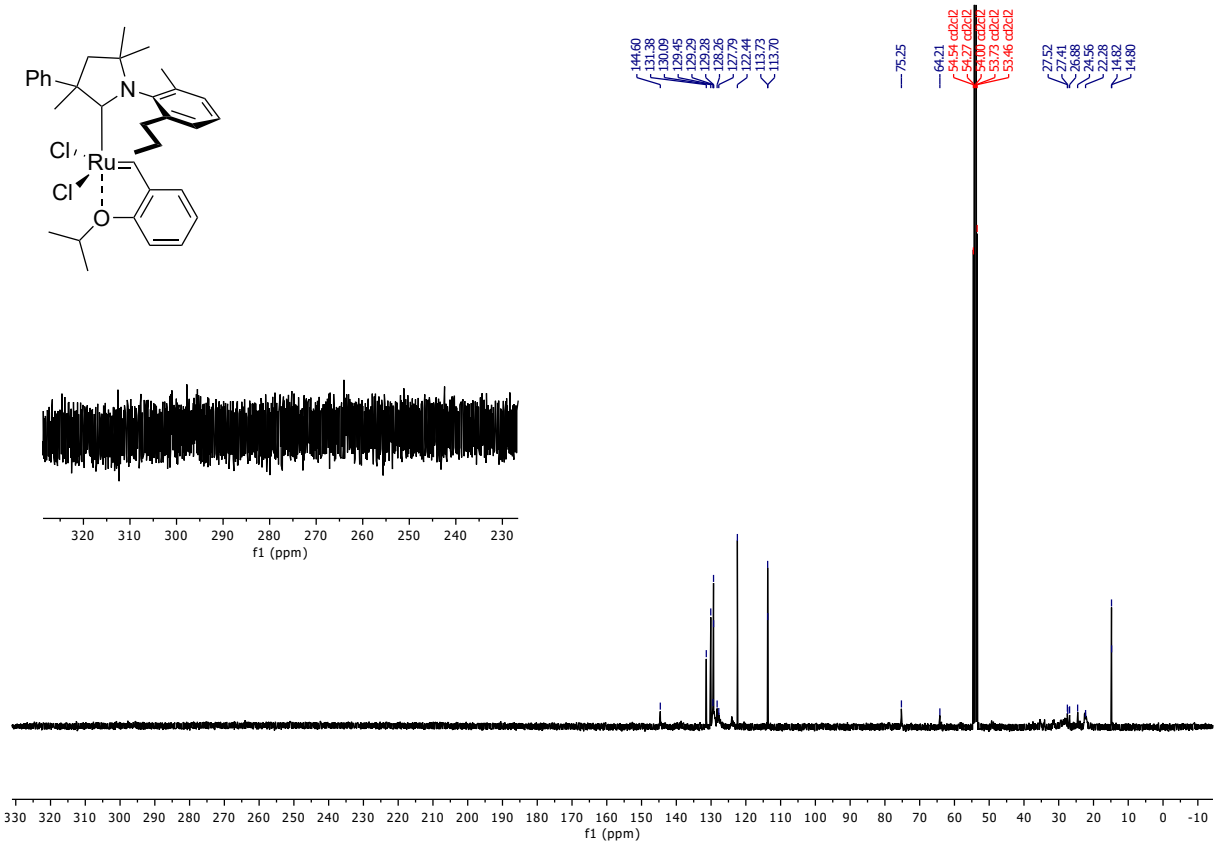


Figure **S60** ^{1}H NMR spectrum of **Ru13**

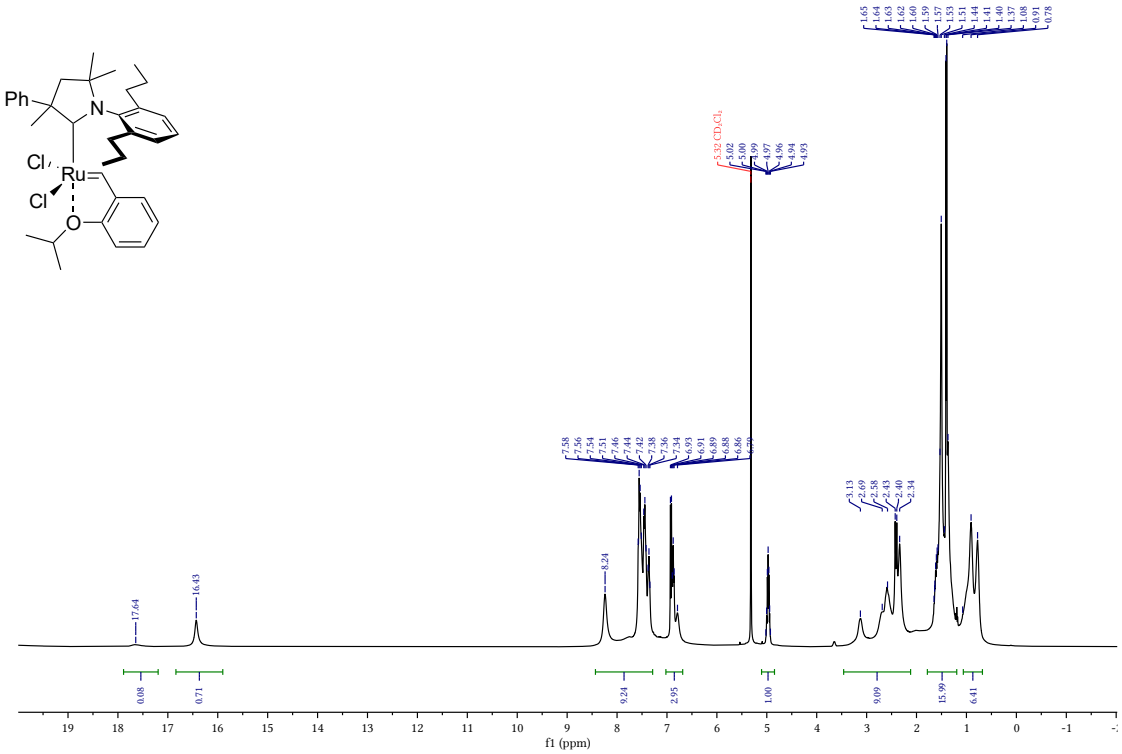


Figure **S61** ^{1}H NMR spectrum of **Ru13**

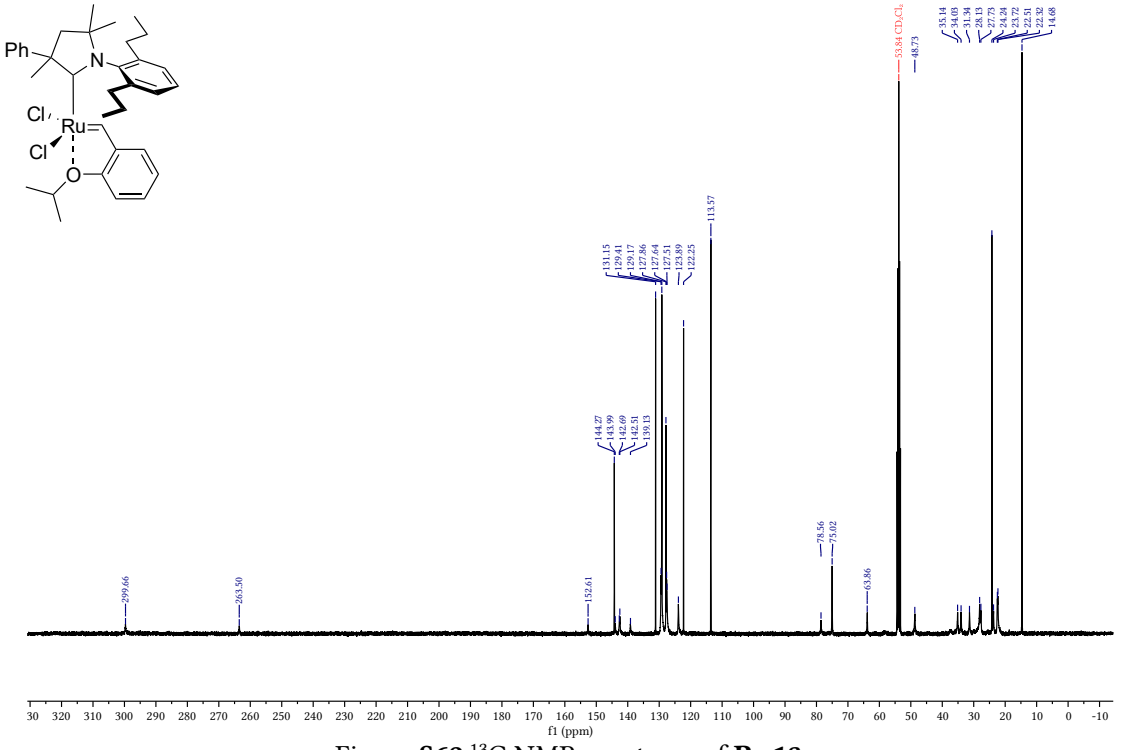


Figure **S62** ^{13}C NMR spectrum of **Ru13**

11 Crystal structure of Ru13

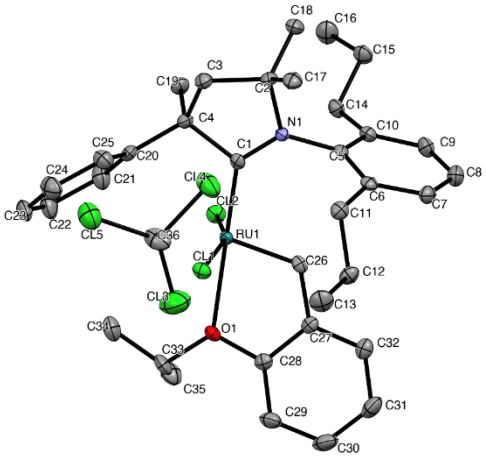


Table S2 X-Ray information for **Ru13**

Compound	**Ru13**
Empirical formula	$C_{35}H_{45}Cl_2NORu \cdot CHCl_3$
Formula weight	787.06
Temperature/K	100(2)
Crystal system	monoclinic
Space group	$P2_1/n$
a/Å	10.7816(3)
b/Å	16.0450(5)
c/Å	21.2485(7)
α/°	90
β/°	100.265(3)
γ/°	90
Volume/Å^3	3616.9(2)
Z	4
ρ_{calc}g/cm^3	1.445
μ/mm^{-1}	0.832
F(000)	1624.0
Crystal size/mm^3	0.45 × 0.25 × 0.13
Radiation	MoKα (λ = 0.71073)
2Θ range for data collection/°	4.602 to 52.74
Index ranges	-13 ≤ h ≤ 13, -20 ≤ k ≤ 20, -26 ≤ l ≤ 26
Reflections collected	60338
Independent reflections	7380 [R_{int} = 0.0465, R_{sigma} = 0.0265]
Data/restraints/parameters	7380/0/404
Goodness-of-fit on F^2	1.058
Final R indexes [I>=2σ (I)]	R_1 = 0.0300, wR_2 = 0.0688
Final R indexes [all data]	R_1 = 0.0370, wR_2 = 0.0736
Largest diff. peak/hole / e Å^{-3}	1.02/−0.69

Table S3 Bonds lengths for **Ru13**

Atom	Atom	Length [Å]	Atom	Atom	Length [Å]
Ru1	Cl1	2.3495(5)	C2	C18	1.533(3)
Ru1	Cl2	2.3487(6)	C14	C10	1.513(3)
Ru1	O1	2.3346(15)	C14	C15	1.531(3)
Ru1	C26	1.832(2)	C10	C9	1.400(3)
Ru1	C1	1.936(2)	C6	C11	1.516(3)
O1	C28	1.371(3)	C6	C7	1.402(3)
O1	C33	1.476(3)	C11	C12	1.533(3)
N1	C1	1.330(3)	C28	C29	1.382(3)
N1	C5	1.452(3)	C33	C34	1.500(4)
N1	C2	1.525(3)	C33	C35	1.513(3)
C27	C26	1.444(3)	C9	C8	1.383(4)
C27	C32	1.404(3)	C7	C8	1.380(4)
C27	C28	1.407(3)	C15	C16	1.520(3)
C1	C4	1.555(3)	C25	C24	1.392(4)
C20	C4	1.535(3)	C21	C22	1.393(4)
C20	C25	1.392(3)	C12	C13	1.527(3)
C20	C21	1.391(3)	C29	C30	1.391(4)
C5	C10	1.408(3)	C31	C30	1.390(4)
C5	C6	1.404(3)	C24	C23	1.374(4)
C4	C3	1.537(3)	C23	C22	1.371(4)
C4	C19	1.559(3)	Cl4	C36	1.766(3)
C32	C31	1.378(4)	Cl5	C36	1.761(3)
C2	C17	1.526(3)	Cl3	C36	1.749(3)
C2	C3	1.535(3)			

Table S4 Bonds angles for **Ru13**

Atom	Atom	Atom	Angle [°]	Atom	Atom	Atom	Angle [°]
Cl2	Ru1	Cl1	159.08(2)	N1	C2	C3	100.22(16)
O1	Ru1	Cl1	83.28(4)	N1	C2	C18	112.01(18)
O1	Ru1	Cl2	88.19(4)	C17	C2	C3	110.66(19)
C26	Ru1	Cl1	99.44(7)	C17	C2	C18	107.79(18)
C26	Ru1	Cl2	97.38(7)	C18	C2	C3	115.12(19)
C26	Ru1	O1	77.95(8)	C10	C14	C15	115.58(19)
C26	Ru1	C1	101.75(9)	C5	C10	C14	123.2(2)
C1	Ru1	Cl1	90.35(6)	C9	C10	C5	117.6(2)
C1	Ru1	Cl2	98.31(6)	C9	C10	C14	118.8(2)
C1	Ru1	O1	173.46(7)	C5	C6	C11	123.9(2)
C28	O1	Ru1	108.74(12)	C7	C6	C5	117.4(2)
C28	O1	C33	118.77(18)	C7	C6	C11	118.5(2)
C33	O1	Ru1	132.33(14)	C6	C11	C12	112.83(19)
C1	N1	C5	124.71(18)	O1	C28	C27	113.09(19)
C1	N1	C2	116.15(18)	O1	C28	C29	125.5(2)
C5	N1	C2	118.83(16)	C29	C28	C27	121.4(2)
C32	C27	C26	122.1(2)	C2	C3	C4	107.02(18)
C32	C27	C28	118.7(2)	O1	C33	C34	106.27(19)
C28	C27	C26	119.2(2)	O1	C33	C35	108.90(19)
C27	C26	Ru1	119.56(16)	C34	C33	C35	112.4(2)
N1	C1	Ru1	133.45(16)	C8	C9	C10	121.3(2)
N1	C1	C4	107.04(18)	C8	C7	C6	121.5(2)
C4	C1	Ru1	119.21(15)	C16	C15	C14	110.7(2)
C25	C20	C4	123.3(2)	C20	C25	C24	121.0(2)
C21	C20	C4	119.6(2)	C20	C21	C22	121.6(2)
C21	C20	C25	117.1(2)	C13	C12	C11	111.7(2)
C10	C5	N1	117.99(19)	C28	C29	C30	118.5(2)
C6	C5	N1	120.04(19)	C32	C31	C30	119.8(2)
C6	C5	C10	122.0(2)	C7	C8	C9	119.9(2)
C1	C4	C19	107.58(18)	C23	C24	C25	120.8(2)
C20	C4	C1	113.05(18)	C31	C30	C29	121.4(2)
C20	C4	C3	115.89(19)	C22	C23	C24	119.2(2)
C20	C4	C19	107.97(18)	C23	C22	C21	120.3(3)
C3	C4	C1	102.61(17)	Cl5	C36	Cl4	109.94(15)
C3	C4	C19	109.40(19)	Cl3	C36	Cl4	111.43(17)
C31	C32	C27	120.3(2)	Cl3	C36	Cl5	109.40(15)
N1	C2	C17	110.96(18)				

Table S5 Torsion angles for **Ru13**

Atom	Atom	Atom	Angle [°]	Atom	Atom	Atom	Angle [°]
Ru1	O1	C28	C27	−8.7(2)	C4	C20	C21
Ru1	O1	C28	C29	170.7(2)	C32	C27	C26
Ru1	O1	C33	C34	−19.6(3)	C32	C27	C28
Ru1	O1	C33	C35	101.7(2)	C32	C27	C28
Ru1	C1	C4	C20	27.6(2)	C32	C31	C30
Ru1	C1	C4	C3	153.15(15)	C2	N1	C1
Ru1	C1	C4	C19	−91.51(19)	C2	N1	C1
Cl1	Ru1	C26	C27	71.02(17)	C2	N1	C5
Cl2	Ru1	C26	C27	−96.51(16)	C2	N1	C5
O1	Ru1	C26	C27	−9.96(16)	C14	C10	C9
O1	C28	C29	C30	−178.9(2)	C10	C5	C6
N1	C1	C4	C20	−146.91(19)	C10	C5	C6
N1	C1	C4	C3	−21.4(2)	C10	C14	C15
N1	C1	C4	C19	94.0(2)	C10	C9	C8
N1	C5	C10	C14	−10.1(3)	C6	C5	C10
N1	C5	C10	C9	176.16(19)	C6	C5	C10
N1	C5	C6	C11	8.9(3)	C6	C11	C12
N1	C5	C6	C7	−175.43(19)	C6	C7	C8
N1	C2	C3	C4	−21.7(2)	C17	C2	C3
C27	C32	C31	C30	−0.1(4)	C11	C6	C7
C27	C28	C29	C30	0.4(4)	C28	O1	C33
C26	C27	C32	C31	177.3(2)	C28	O1	C33
C26	C27	C28	O1	1.8(3)	C28	C27	C26
C26	C27	C28	C29	−177.6(2)	C28	C27	C32
C1	Ru1	C26	C27	163.37(16)	C28	C29	C30
C1	N1	C5	C10	80.3(3)	C19	C4	C3
C1	N1	C5	C6	−98.4(3)	C33	O1	C28
C1	N1	C2	C17	125.4(2)	C33	O1	C28
C1	N1	C2	C3	8.5(2)	C18	C2	C3
C1	N1	C2	C18	−114.1(2)	C7	C6	C11
C1	C4	C3	C2	26.7(2)	C15	C14	C10
C20	C4	C3	C2	150.36(19)	C15	C14	C10
C20	C25	C24	C23	0.4(4)	C25	C20	C4
C20	C21	C22	C23	0.0(4)	C25	C20	C4
C5	N1	C1	Ru1	21.3(3)	C25	C20	C4
C5	N1	C1	C4	−165.28(18)	C25	C20	C21
C5	N1	C2	C17	−60.7(2)	C25	C24	C23
C5	N1	C2	C3	−177.60(18)	C21	C20	C4
C5	N1	C2	C18	59.8(2)	C21	C20	C4
C5	C10	C9	C8	0.6(4)	C21	C20	C4
C5	C6	C11	C12	123.8(2)	C21	C20	C25
C5	C6	C7	C8	−2.2(3)	C24	C23	C22
C4	C20	C25	C24	178.1(2)			

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