Electronic Supplementary Material for

# Acceptorless dehydrogenative synthesis of primary amides from alcohols and ammonia

Jie Luo†, Quan-Quan Zhou†, Michael Montag, Yehoshoa Ben-David, David Milstein*

*Department of Molecular Chemistry and Materials Science, Weizmann Institute of Science, Rehovot, 76100, Israel*

*E-mail: david.milstein@weizmann.ac.il
†These authors contributed equally.

## Table of Contents:

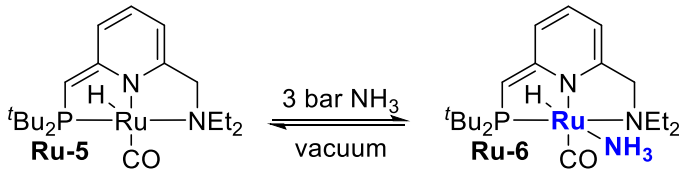
## 1. General considerations

All experiments with metal complexes and phosphine ligands were carried out under an atmosphere of purified nitrogen in a Vacuum Atmosphere glovebox equipped with a MO 40-2 inert gas purifier or using standard Schlenk techniques. All solvents were reagent grade or better. All non-deuterated solvents were purified according to standard procedures under argon atmosphere. Deuterated solvents were degassed with argon and directly used. All solvents were degassed with argon and kept in the glove box over 3Å molecular sieves. All $^{1}H$ NMR, $^{13}C$ NMR or $^{31}P$ NMR spectra were recorded on a Bruker AVANCE III 300 MHz, 400 MHz and AVANCE III HD 500 MHz NMR spectrometer and reported in ppm (δ). Chemical shifts were referenced to the residual solvent peaks ($^{1}H$ NMR, $^{13}C$ NMR) or an external standard of phosphoric acid (85% solution in $D_2O$) at 0.0 ppm ($^{31}P$ NMR). NMR spectroscopy abbreviations: br, broad; s, singlet; d, doublet; t, triplet; q, quartet; m, multiplet. GC analysis was performed on HP 6890 series GC system with Hp-5 column and SUPELCO 1-2382 column, flame ionization detector, and helium as carrier gas (Column: HP-5, 30 m, 320 μm, Inlets: 280 °C; Detector: FID 280 °C; Flow: 1 mL/min; Oven:50 °C, hold 8 min; 15 °C/min to 280 °C, hold 2 min). GC-gas analysis was performed on an HP 6890 chromatograph (TCD detector) with helium as the carrier gas. GC-MS was carried out on HP 6890 / HP 5973 (MS detector) instruments equipped with a 30 m column (Restek 5MS, 0.32 mm internal diameter) with a 5% phenylmethylsilicone coating (0.25 mm) and helium as carrier gas. IR spectra were recorded on Thermo Nicolet 6700 FT-IR.

Analytical TLC was performed on Merck silica gel 60 F254 plates. Complexes **Ru-1**[1], **Ru-2**[2], **Ru-3**[3]were prepared according to literature procedures. All the primary amides are reported thus only $^{1}H$ and $^{13}C$ characteristic data of the products were provided.

## 2. Mechanistic studies

### Note S1 Reaction of Ru-5 with $NH_3$

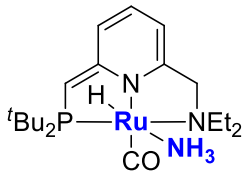



$^{31}$P: 94.2 ppm
$^{1}$H: -26.5 (d) ppm

$^{31}$P: 100.4 ppm
$^{1}$H: -16.0 (d) ppm

To a suspension of complex **Ru-1** (14.7 mg, 0.03 mmol) in THF (3 ml) was added $^{t}$BuOK (3.4 mg, 0.03 mmol) and the mixture was stirred at room temperature for 0.5 h in a $N_2$ glove box to generate **Ru-5**. Then the solvent was removed and 0.6 mL bezene-*d*6 was added. The solution was transferred into a J. Young NMR tube and 3 bar $NH_3$ was pressured. After shaking the tube for seconds, a quick color change from dark purple (**Ru-5**) to brown (**Ru-6**) was observed. Subsequently, the sample was analyzed by NMR, indicating that a new species **Ru-6** was formed. Note: starting from **Ru-1** with 2 equivalents $^{t}$BuOK also afforded **Ru-5** and **Ru-6** (under ammonia) without other changes observed.

After NMR analysis, the J. Young NMR tube was transferred back into the glovebox and ammonia was carefully released in the box. The sample was kept under vacuum to remove the solvent after which 0.6 mL bezene-*d*6 was added again for NMR analysis. Both the signals of $^{1}$H NMR and $^{31}$P NMR indicate the regeneration of dearomatized complex **Ru-5**.




**Ru-6**: $^{1}$H NMR (500 MHz, $C_6D_6$) δ 6.56 (t, *J* = 7.0 Hz, 1H, pyridine-H), 6.37 (d, *J* = 8.7 Hz, 1H, pyridine-H), 5.34 (d, *J* = 5.8 Hz, 1H, pyridine-H), 3.53 (s, 1H, =C*H*P), 3.27 (d, *J* = 13.8 Hz, 1H, -CH*H*N), 3.06 – 2.93 (m, 1H, N(C*H*HCH$_3$)$_2$), 2.85 – 2.75 (m, 1H, N(C*H*HCH$_3$)$_2$), 2.72 (d, *J* = 13.7 Hz, 1H, -CH*H*N), 2.23 – 2.09 (m, 1H, N(C*H*HCH$_3$)$_2$), 1.94 – 1.82 (m, 1H, N(C*H*HCH$_3$)$_2$), 1.49 (d, *J* = 12.9 Hz, 9H, P(C(CH$_3$)$_3$)$_2$), 1.27 (d, *J*

= 12.3 Hz, 9H, P(C(CH$_3$)$_3$)$_2$), 0.81 (t, $J$ = 6.7 Hz, 3H, N(CH$_2$C$H_3$)$_2$), 0.66 (t, $J$ = 6.6 Hz, 3H, N(CH$_2$C$H_3$)$_2$), -16.04 (d, $J$ = 25.0 Hz, 1H, Ru-H). $^{13}$C NMR (126 MHz, C$_6$D$_6$) δ 208.46 (d, $J$ = 14.9 Hz, Ru-CO), 167.84 (d, $J$ = 15.1 Hz, py-C), 155.85 (s, Py-C), 132.14 (s, Py-C), 113.00 (d, $J$ = 16.4 Hz, Py-C), 97.53 (s, Py-C), 63.32 (d, J = 47.3 Hz, =CHP), 55.98 (s, N($C$H$_2$CH$_3$)$_2$), 49.17 (s, N($C$H$_2$CH$_3$)$_2$), 38.84 (d, $J$ = 25.9 Hz, P($C$(CH$_3$)$_3$)$_2$), 36.92 (d, $J$ = 24.7 Hz, P($C$(CH$_3$)$_3$)$_2$), 30.42 (d, $J$ = 3.2 Hz, P(C($C$H$_3$)$_3$)$_2$), 29.60 (d, $J$ = 3.1 Hz, P(C($C$H$_3$)$_3$)$_2$), 10.00 (s, N(CH$_2$$C$H$_3$)$_2$), 9.81 (s, N(CH$_2$$C$H$_3$)$_2$). $^{31}$P NMR (202 MHz, C$_6$D$_6$) δ 100.37.

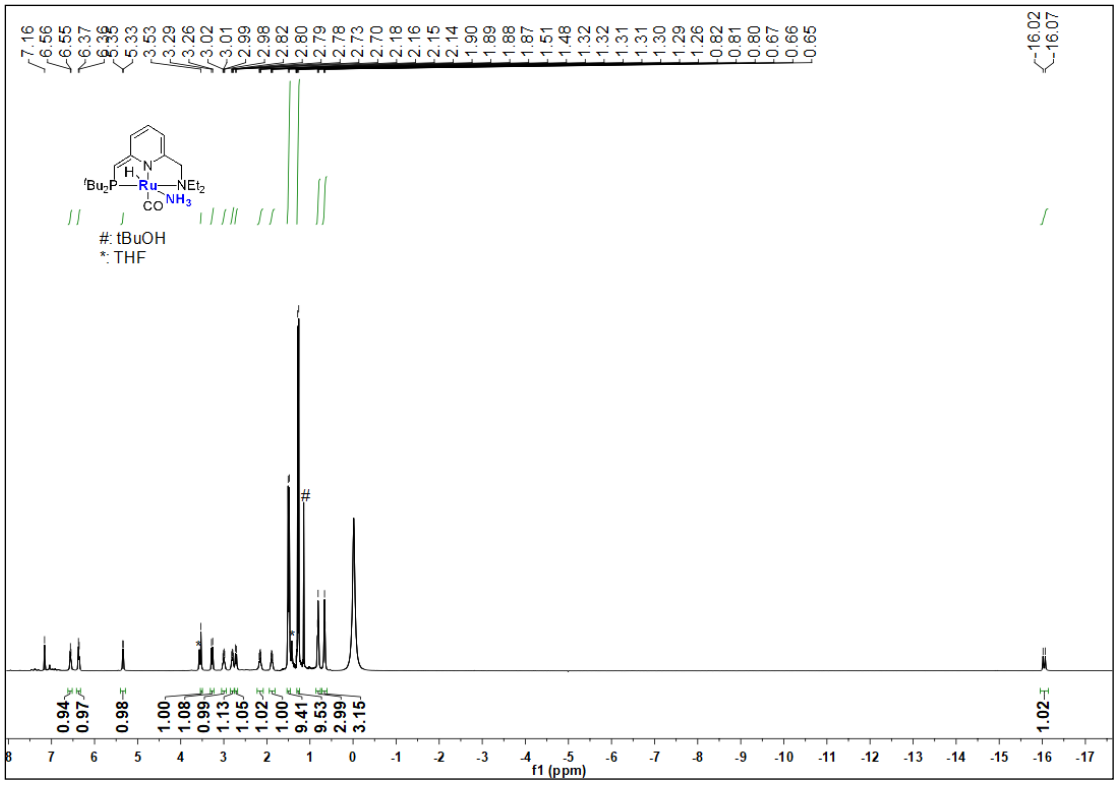



**Fig. S1** $^{1}$H NMR spectrum of **Ru-6** in C$_6$D$_6$.

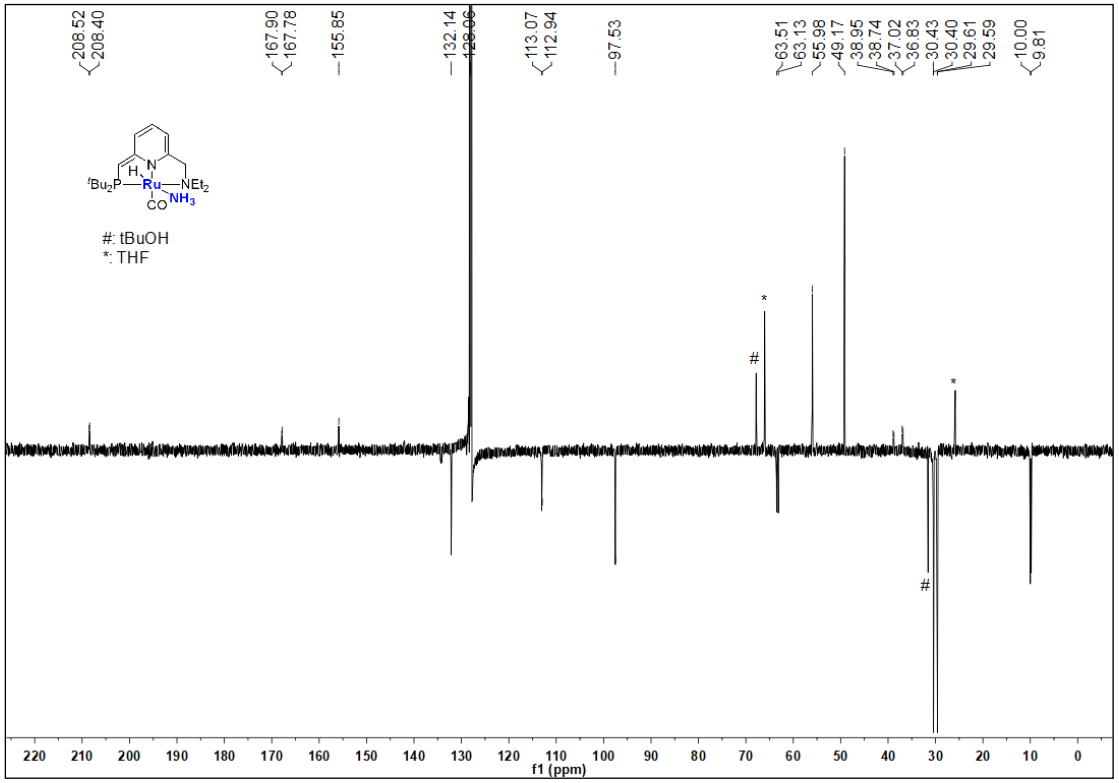



**Fig. S2** $^{13}$C-DEPTQ NMR spectrum of **Ru-6** in $C_6D_6$.

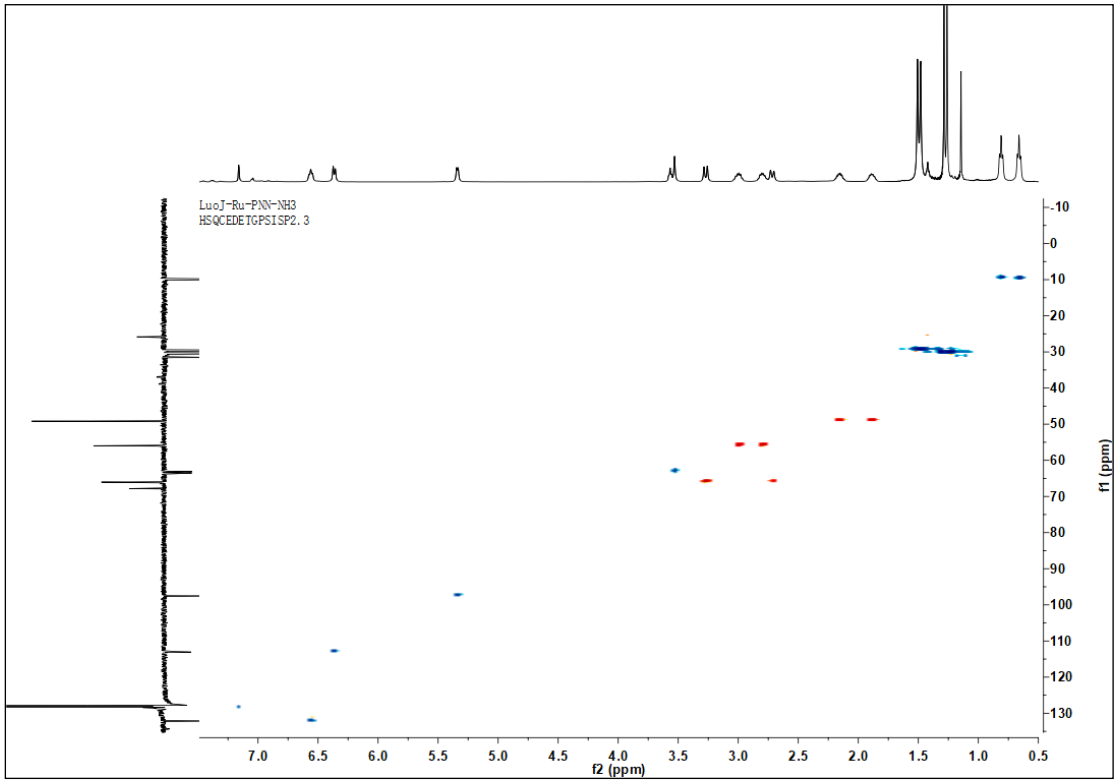



**Fig. S3** HSQC spectrum of **Ru-6** in $C_6D_6$.

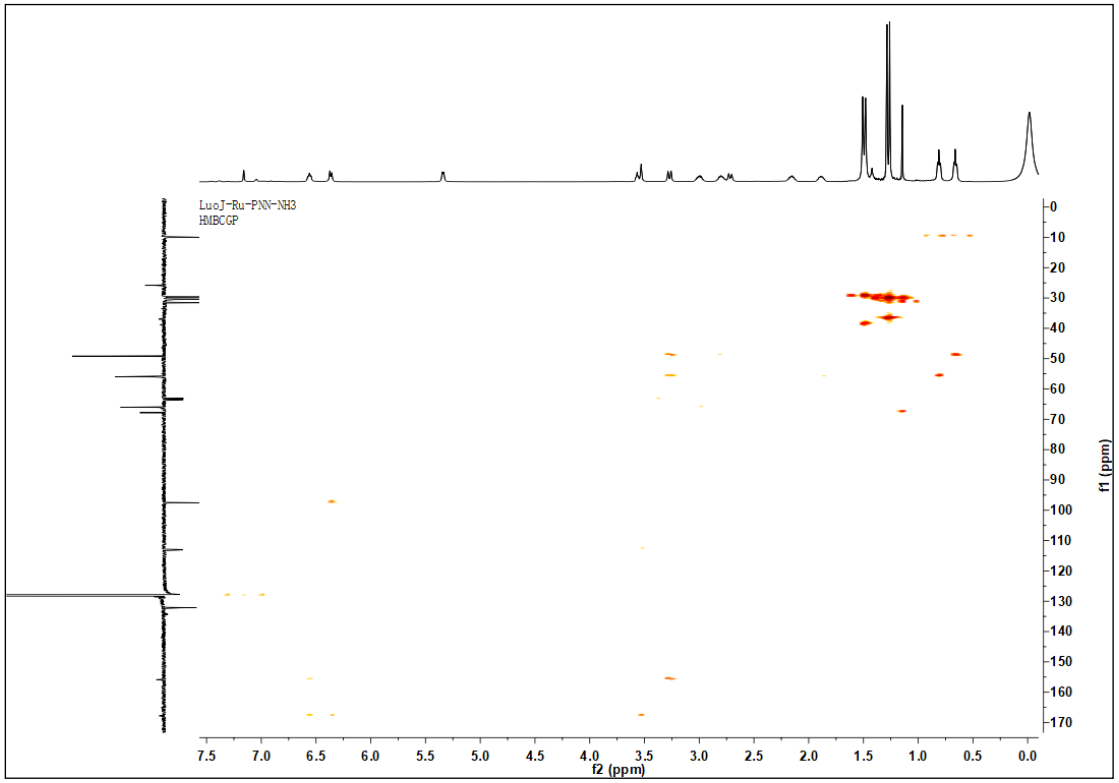



**Fig. S4** HMBC spectrum of **Ru-6** in $C_6D_6$.

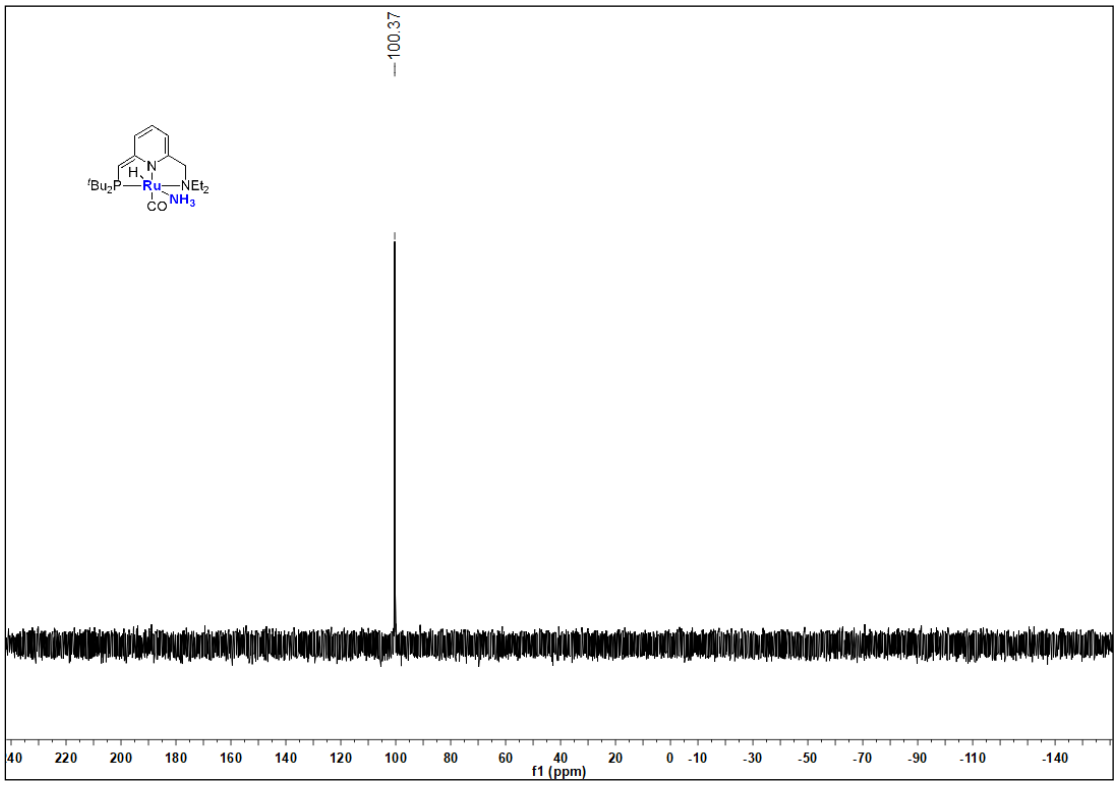



**Fig. S5** $^{31}P$ NMR spectrum of **Ru-6** in $C_6D_6$.

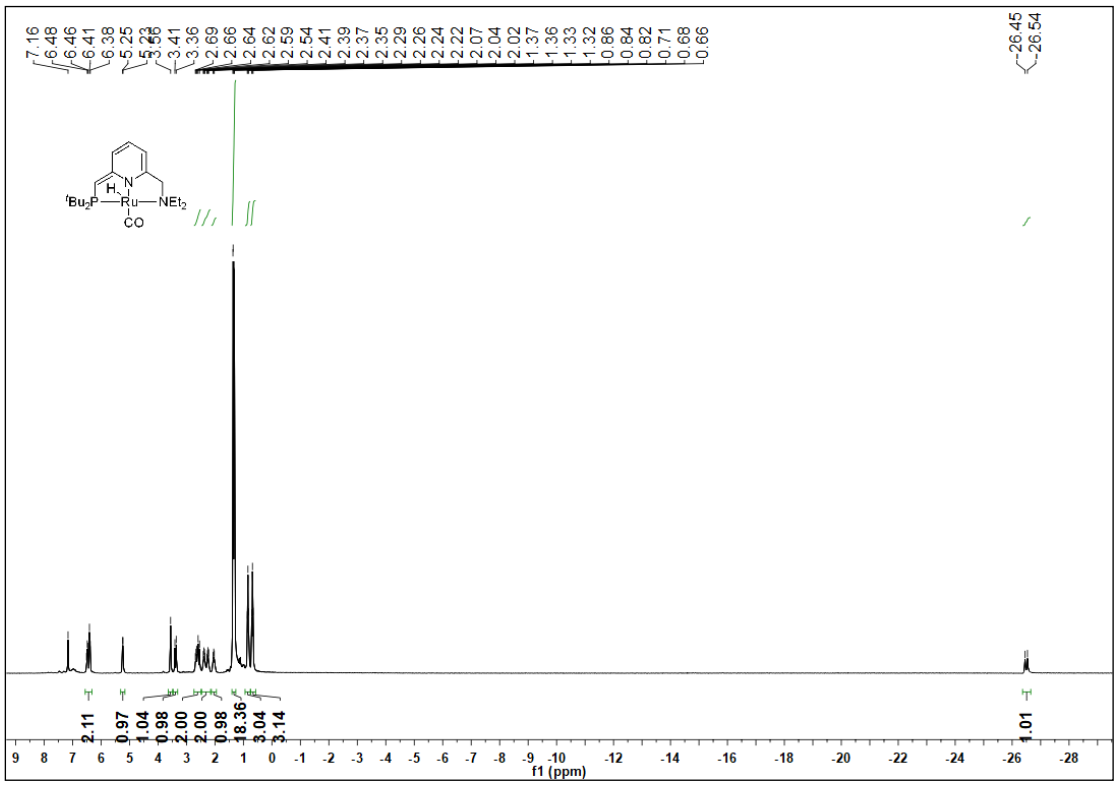


**Fig. S6** $^{1}$H NMR spectrum of the resulting species (**Ru-5**) after vacuum in $C_6D_6$.

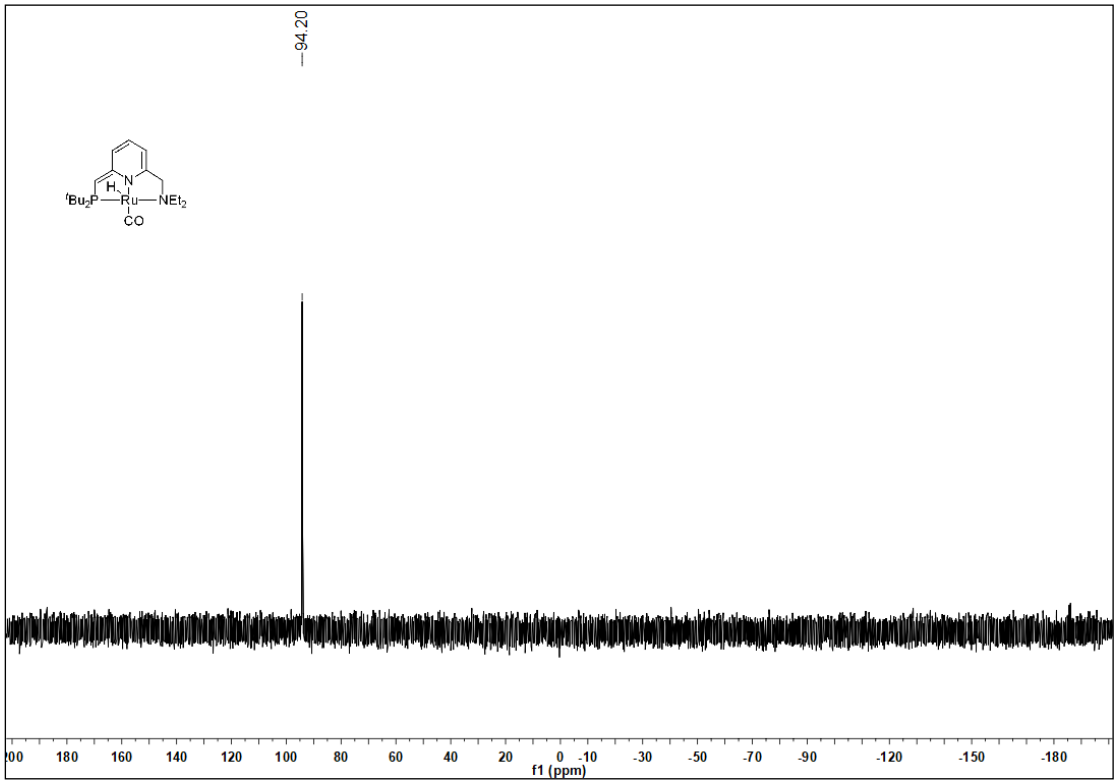
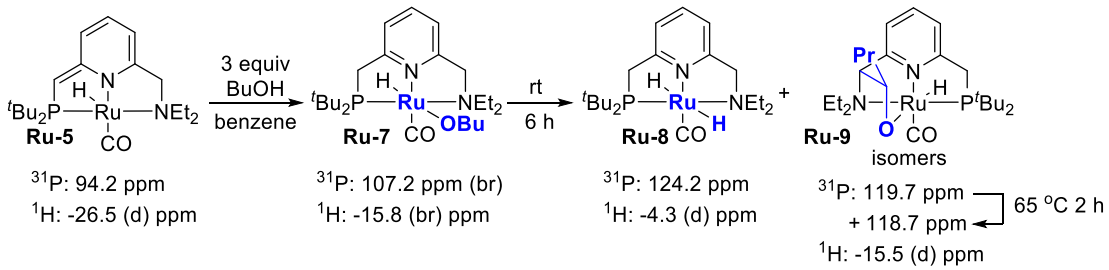


**Fig. S7** $^{31}$P NMR spectrum of the resulting species (**Ru-5**) after vacuum in $C_6D_6$.

**Note S2 Reaction of Ru-5 with n-Butanol**




To a solution of complex **Ru-5** (13.5 mg, 0.03 mmol) in benzene-$d_6$ (0.6 ml) in a J. Young NMR tube was added BuOH (6.7 mg, 0.1 mmol). The NMR tube was taken out of the glovebox for immediate NMR analysis. A broad signal at 107.2 ppm was detected by $^{31}$P NMR and a broad hydride peak around -15.8 ppm was detected by $^{1}$H NMR. These signals were attributed to the alkoxide species **Ru-7** as compared to our previous study on the synthesis of methoxide analogue (see ref. 4).

The NMR tube was allowed to rotate at room temperature for another 6 h. Three new peaks were observed by $^{31}$P NMR, which were supposed to be **Ru-8** (major one, see ref. 4) and isomers of **Ru-9** (aldehyde adduct species, see ref. 5). After further heating at 65 $^{o}$C for 2 h, the signals of proposed isomers in $^{31}$P NMR converged to one major peak at 118.7 ppm and signals in $^{1}$H NMR and $^{13}$C NMR are quite similar with the characterized **Ru-9** with only little chemical shifts observed (possibly effected by the existed alcohol). After the whole process, n-butyl butyrate was generated (detected by NMR, confirmed by GC-MS) along with the evolution of $H_2$ gas (confirmed by GC-gas).

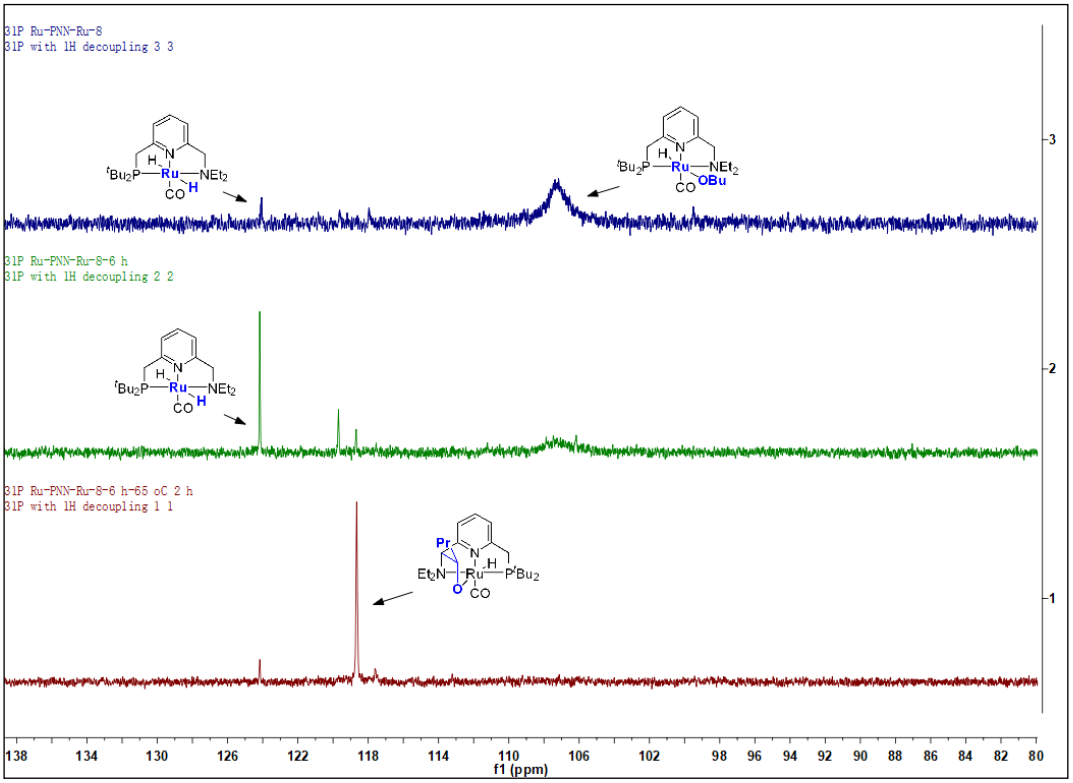
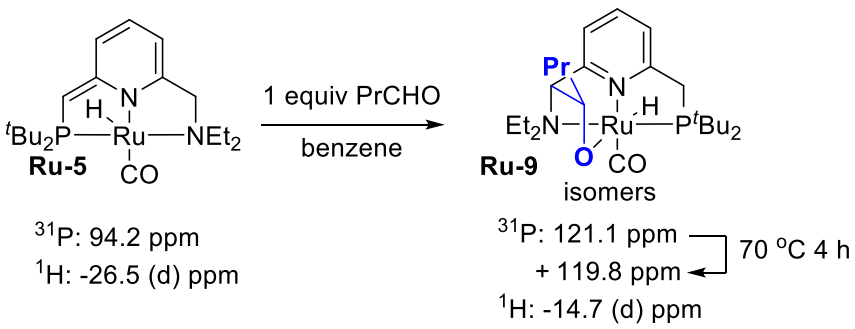



**Fig. S8** $^{31}$P NMR spectrum of the resulting species of the reaction of n-butanol with **Ru-5** upon heating in $C_6D_6$.

## Note S3 Reaction of Ru-5 with n-Butanal




To a solution of complex **Ru-5** (13.5 mg, 0.03 mmol) in benzene-$d_6$ (0.6 mL) in a J. Young NMR tube was added PrCHO (2.7 $\mu$L, 0.03 mmol). The NMR tube was taken out of the glovebox for immediate NMR analysis. Two signals 121.1 and 119.8 ppm were detected by $^{31}$P NMR, which were attributed to isomers of **Ru-9**.[5] The NMR tube was heated at 70 °C for 4 h, the $^{31}$P NMR signals of the isomers converged to the peak at 119.8 ppm with a doublet hydride peak in $^{1}$H NMR at -14.7 ppm.

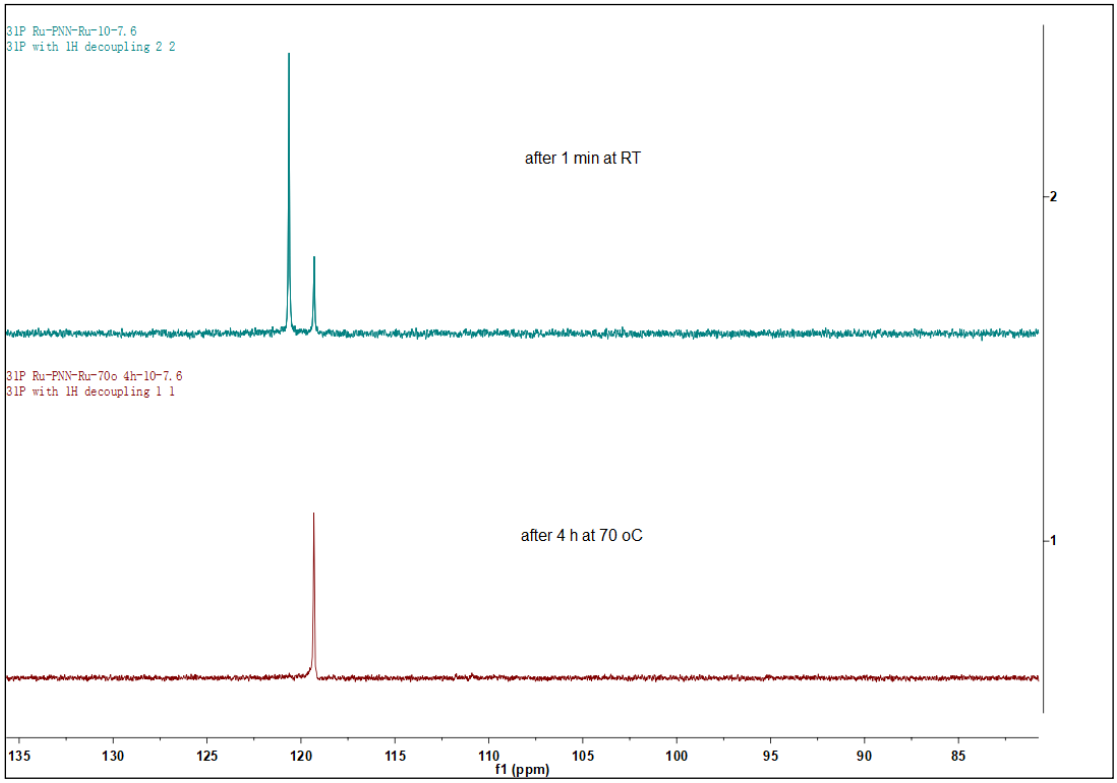
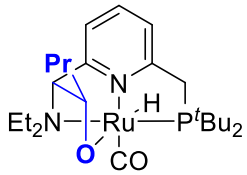



**Fig. S9** $^{31}$P NMR spectrum of the resulting species of **Ru-5** with aldehyde in $C_6D_6$.




**Ru-9:** IR: 2955, 1893, 1600, 1468, 1072 cm$^{-1}$. $^1$H NMR (500 MHz, $C_6D_6$) δ 6.94 (t, *J* = 7.7 Hz, 1H, pyridine-H), 6.58 (dd, *J* = 16.6, 7.7 Hz, 2H, pyridine-H), 4.75 (d, *J* = 9.0 Hz, 1H, -C*H*N-), 3.77 (s, 1H, OCHC*H*$_2$CH$_2$CH$_3$), 3.66 – 3.54 (m, 2H, OCHC*H*$_2$CH$_2$CH$_3$, OC*H*CH$_2$CH$_2$CH$_3$), 2.99 – 2.81 (m, 2H, -C*H*$_2$P), 2.42 (m, 1H, N(*C*H$_2$Me)$_2$), 2.34 – 2.24 (m, 1H, N(*C*H$_2$Me)$_2$), 2.01 (m, 1H, OCHCH$_2$C*H*$_2$CH$_3$), 1.69 – 1.55 (m, 1H, OCHCH$_2$C*H*$_2$CH$_3$), 1.32 – 1.24 (m, 18H, P(C(CH$_3$)$_3$)$_2$), 1.07 – 0.99 (m, 6H, N(CH$_2$C*H*$_3$)$_2$), 0.98 – 0.92 (m, 1H, N(*C*H$_2$Me)$_2$), 0.86 (t, *J* = 7.0 Hz, 3H, OCHCH$_2$CH$_2$C*H*$_3$), 0.46 – 0.32 (m, 1H, N(*C*H$_2$Me)$_2$), -14.67 (d, *J* = 28.0 Hz, 1H, Ru-H). $^{13}$C NMR (126 MHz, $C_6D_6$) δ209.66 (d, *J* = 15.8 Hz, Ru-CO), 161.01 (d, *J* = 1.6 Hz, py-C), 160.62 (d, *J* = 4.5 Hz, py-C), 135.29 (s, Py-C), 120.29 (s, Py-C), 118.58 (s, Py-C), 118.51 (s, Py-C), 78.78 (d, *J* = 1.3 Hz, O*C*HCH$_2$CH$_2$CH$_3$), 73.14 (s, -*C*HN-), 49.84 (s, N(*C*H$_2$Me)$_2$), 46.47 (s, OCHCH$_2$*C*H$_2$CH$_3$), 41.97 (s, N(*C*H$_2$Me)$_2$), 38.23 (d, *J*

= 11.0 Hz, P($C$(CH$_3$)$_3$)$_2$), 37.19 (d, $J$ = 19.5 Hz, -$C$H$_2$P), 34.36 (d, $J$ = 23.0 Hz, P($C$(CH$_3$)$_3$)$_2$), 30.48 (d, $J$ = 3.1 Hz, P(C($C$H$_3$)$_3$)$_2$), 29.65 (d, $J$ = 4.7 Hz, P(C($C$H$_3$)$_3$)$_2$), 20.81 (s,OCHCH$_2$C$H_2$CH$_3$), 15.27 (s, N(CH$_2$$C$H$_3$)$_2$), 12.02 (s, N(CH$_2$$C$H$_3$)$_2$), 7.88 (s, OCHCH$_2$CH$_2$$C$H$_3$). $^{31}$P NMR (202 MHz, C$_6$D$_6$) δ 119.82.

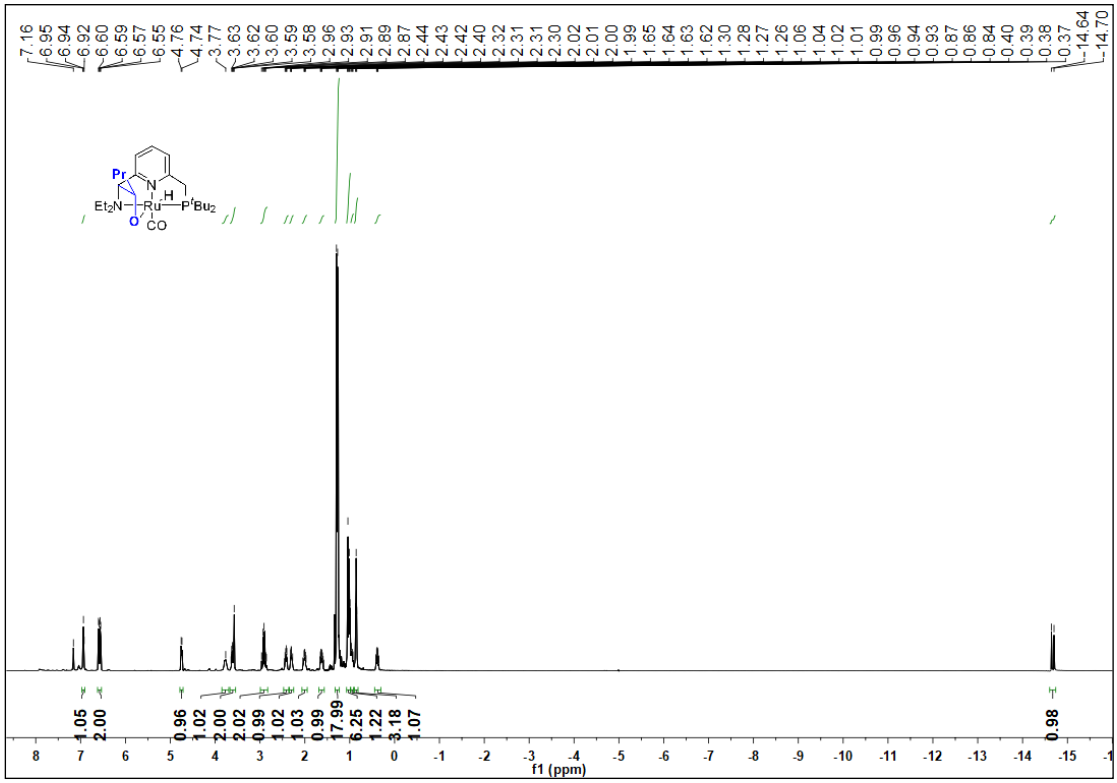



**Fig. S10** $^1$H NMR spectrum of **Ru-9** in C$_6$D$_6$.

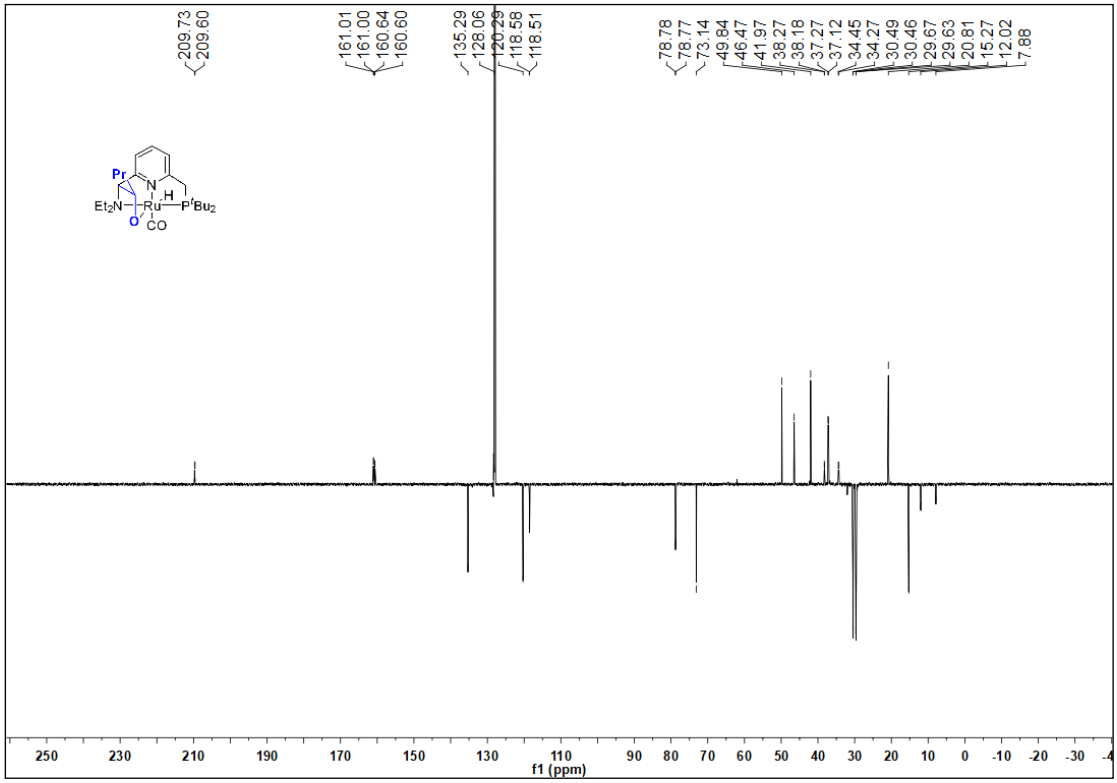



**Fig. S11** $^{13}$C-DEPTQ NMR spectrum of **Ru-9** in $C_6D_6$.

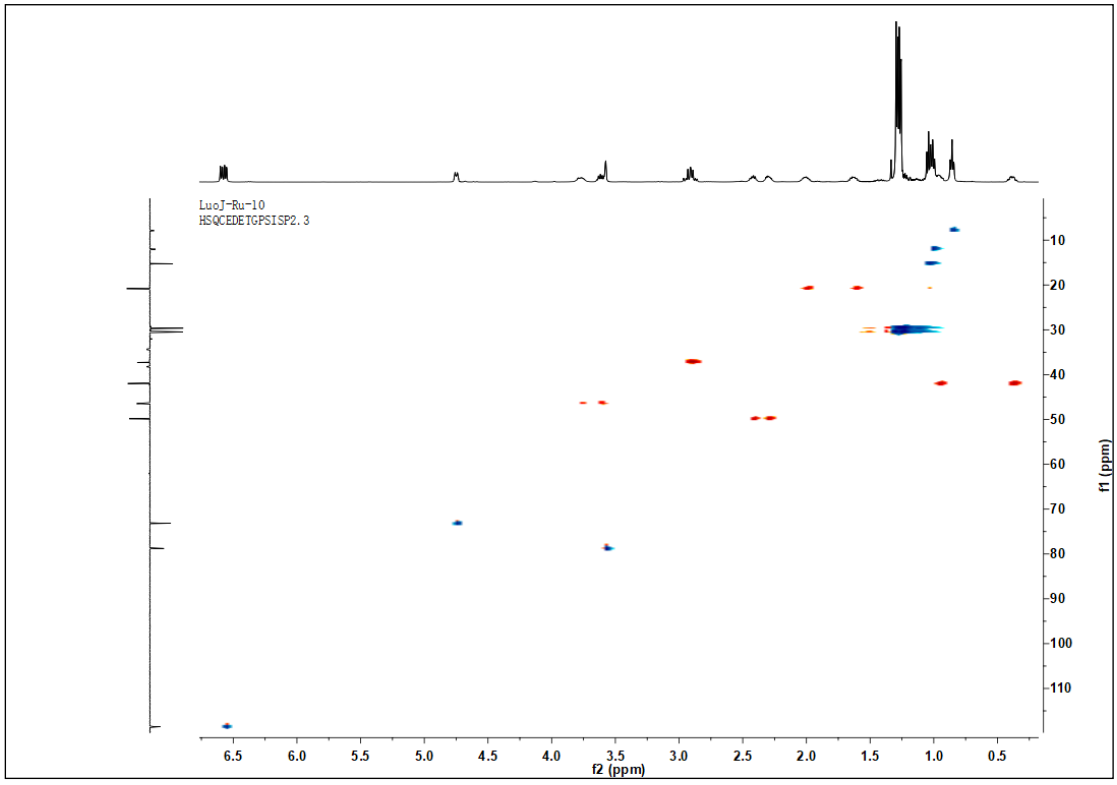



**Fig. S12** HSQC spectrum of **Ru-9** in $C_6D_6$.

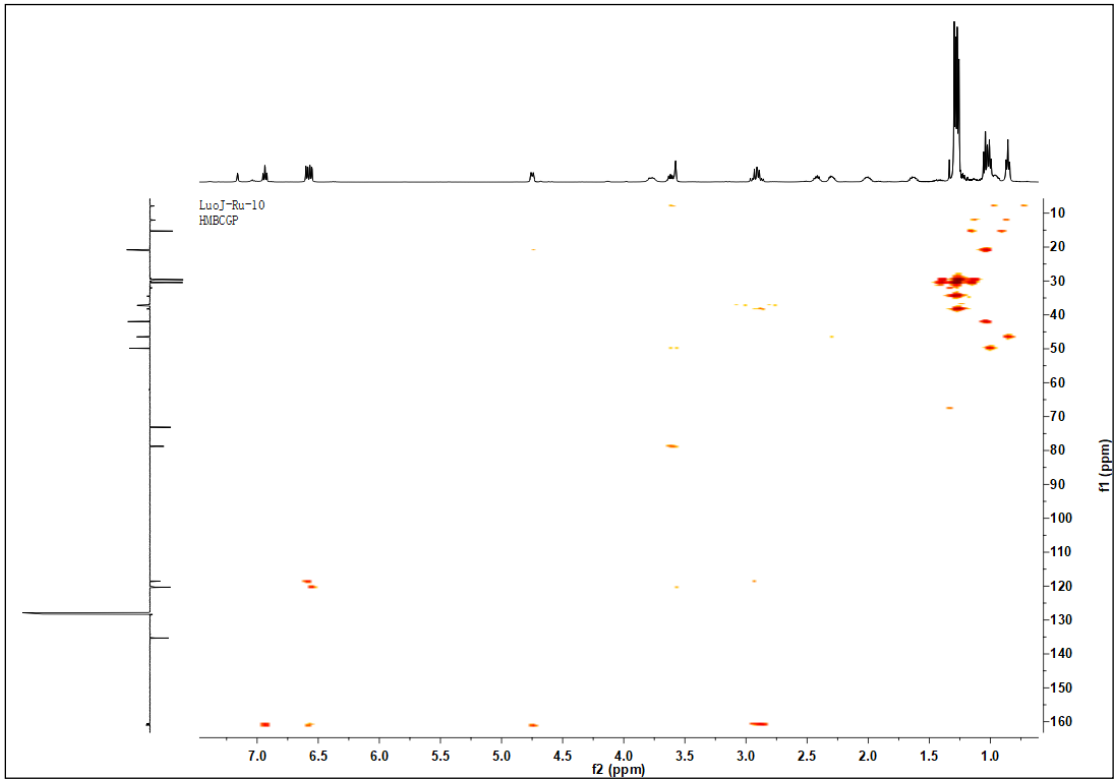



**Fig. S13** HMBC spectrum of **Ru-9** in $C_6D_6$.

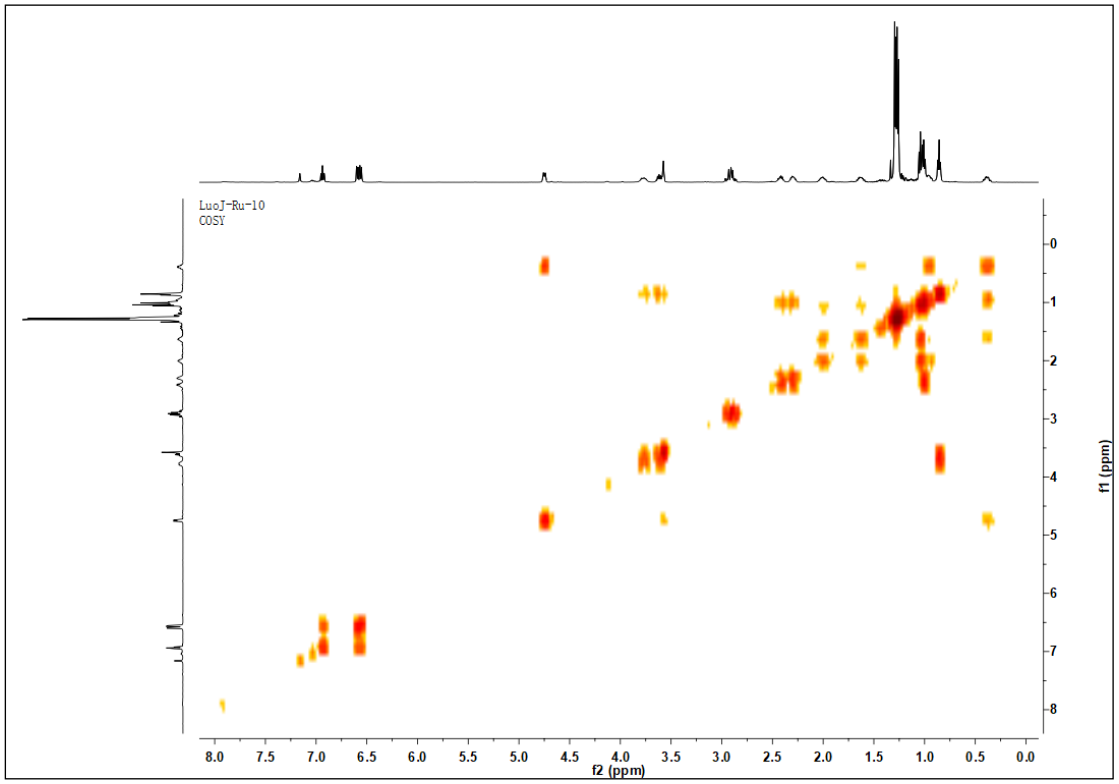



**Fig. S14** COSY spectrum of **Ru-9** in $C_6D_6$.

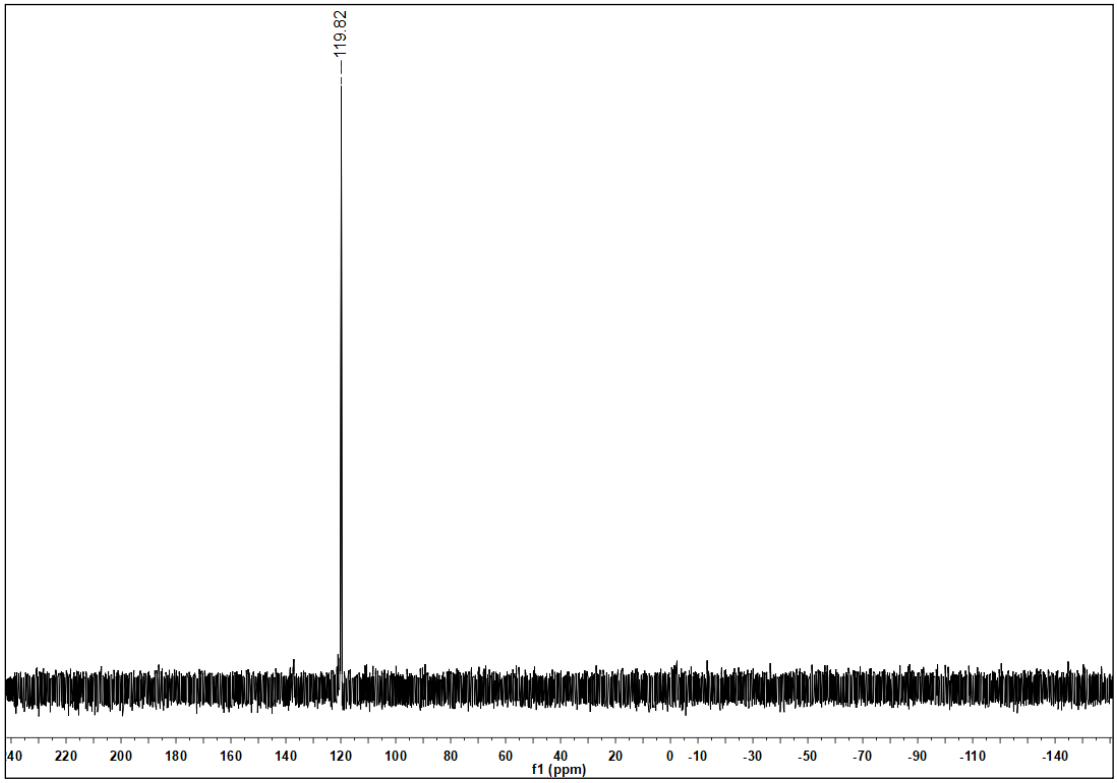
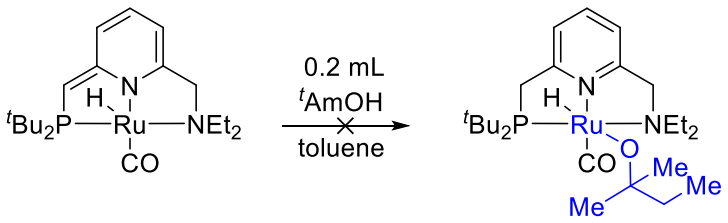



**Fig. S15** $^{31}$P NMR spectrum of **Ru-9** in $C_6D_6$.

**Note S4 No reaction of Ru-5 with $^t$AmOH**




To a solution of complex **Ru-5** (4.5 mg, 0.01 mmol) in toluene (0.4 ml) in a J. Young NMR tube was added $^t$AmOH (0.2 mL). The NMR tube was taken out of the glovebox for immediate NMR analysis, indicating no change of the phosphorus peak and hydride peak of **Ru-5**. The NMR tube was allowed to rotate at room temperature for 1 h and then was measured by NMR again. However, still no change was observed. The result suggests $^t$AmOH is hardly activated by the dearomatized catalyst **Ru-5**, possibly because of the steric hindrance of the alcohol.

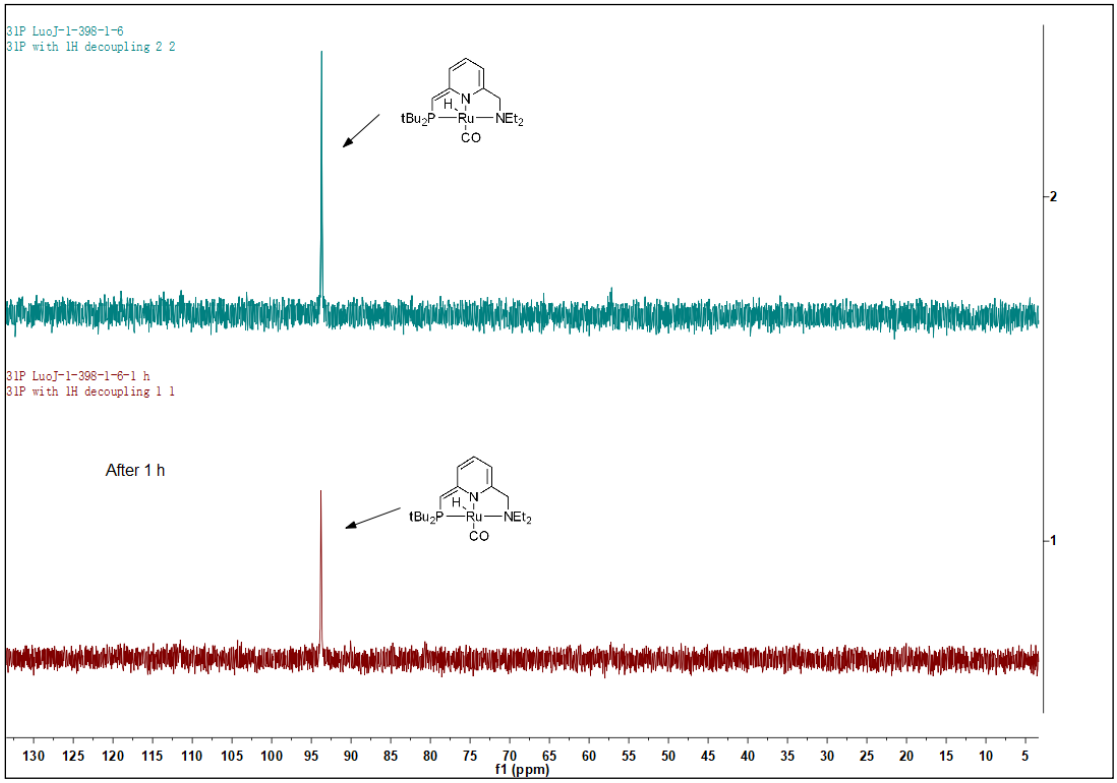
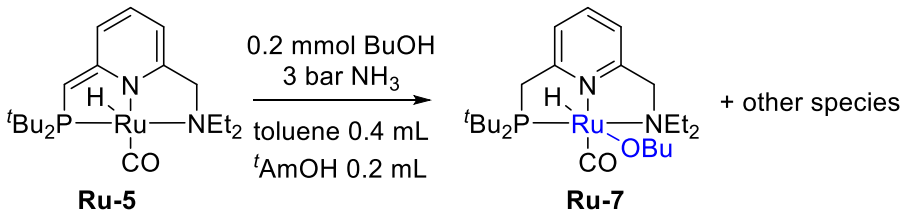



**Fig. S16** $^{31}$P NMR spectrum of the resulting species, indicating no change of **Ru-5** in the presence of $^{t}$AmOH.

**Note S5 Ru-7 as evident species under catalytic conditions**




To a solution of complex **Ru-5** (9.0 mg, 0.02 mmol) in toluene (0.4 ml) and $^{t}$AmOH (0.2 mL) in a J. Young NMR tube was added BuOH (14.8 mg, 0.2 mmol). The NMR tube was taken out of the glovebox and pressured with $NH_3$ (3 bar) afterwards it was analyzed by NMR. The resulting phosphorus peaks indicated the generation of **Ru-7**, along with other two broad peaks with similar chemical shifts, which were possibly the related species of **Ru-7**. The NMR tube was allowed to rotate at room temperature for several hours and was measured by NMR again, indicating the slow generation of **Ru-9** (Fig. S17)

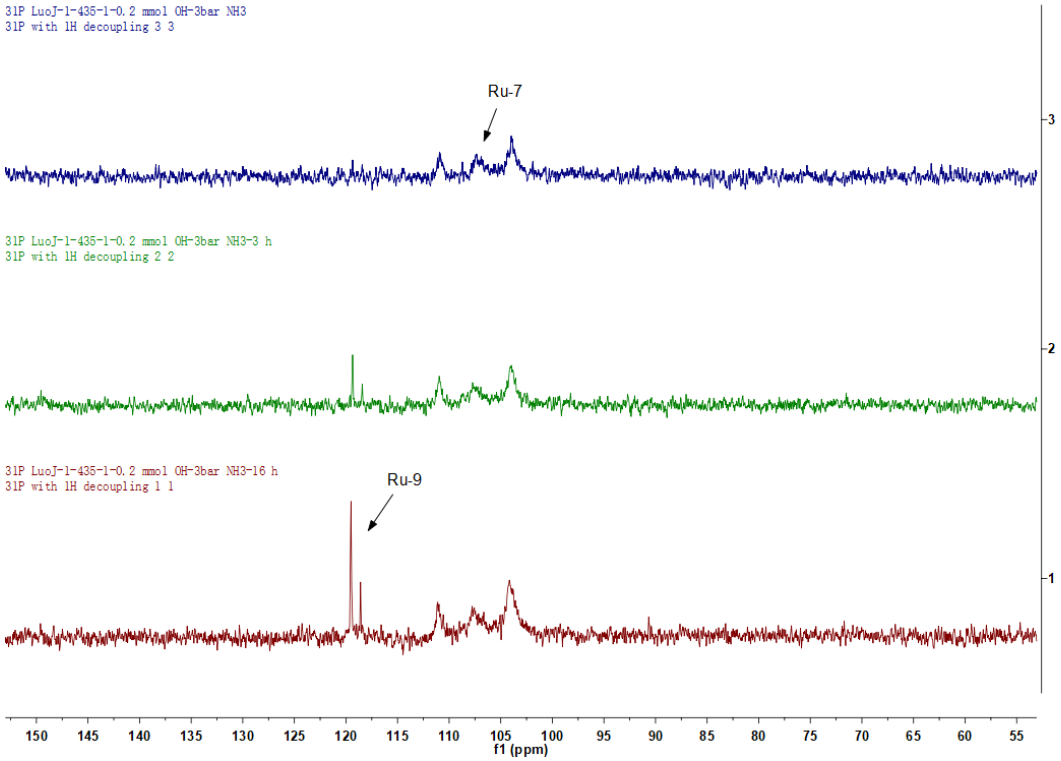
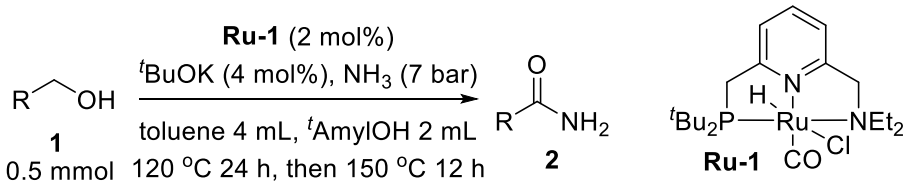



**Fig. S17** $^{31}$P NMR spectrum of catalytic reaction with 0.2 mmol BuOH under 3 bar $NH_3$.

## 3. General experimental procedures

### 3.1 Acceptorless dehydrogenative synthesis of primary amides from alcohols and ammonia




To a 90 mL Fischer-Porter tube added **Ru-1** (4.9 mg, 0.01 mmol), $^t$BuOK (2.2 mg, 0.02 mmol) and toluene (4 mL, dry over 3 Å molecular sieves) in a $N_2$ glovebox. The resulting mixture was stirred at room temperature for 0.5 h, and the color of the solution changed to dark purple. Then alcohol **1** (0.5 mmol) was directly added into the solution, followed by 2 mL $^t$AmylOH (dry over 3 Å molecular sieves). The Fischer-Porter tube was sealed and taken out of the glovebox, and filled with 7 bar $NH_3$ (wait for $NH_3$ to dissolve in the solvent). After heating at 120 °C with stirring for 24 h, the tube was cooled to room temperature, and the gas mixture of $NH_3$ and generated $H_2$ was released carefully. Then the tube was refilled with 7 bar $NH_3$ (without waiting for $NH_3$ to dissolve in solution) and heated at 150 °C for another 12 h. The reaction tube was then cooled to room temperature and the gas mixture was released carefully. Subsequently, the solvent was removed and the primary amide product was obtained after washing with pentane, which was pure enough (in most case). Note: The pressure during heating was approximately 10-11 bar.

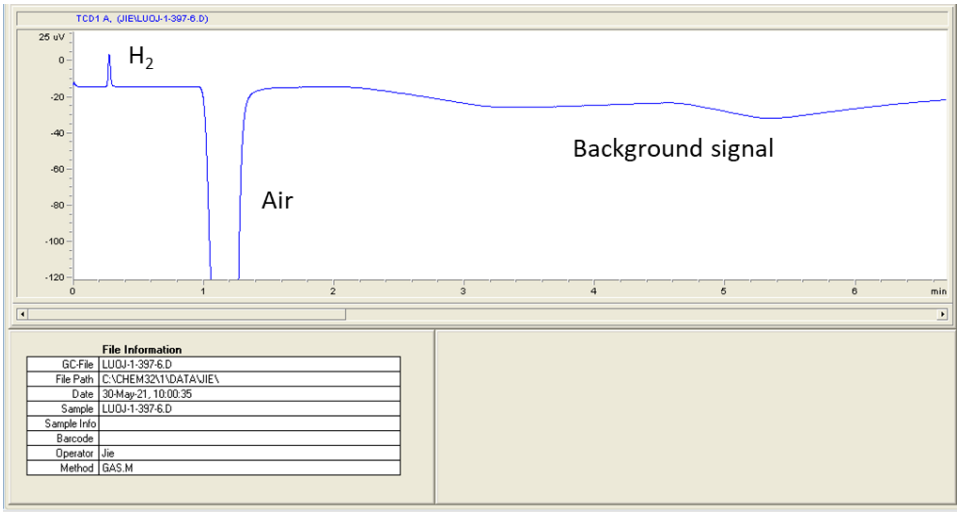
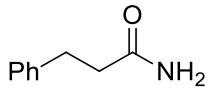
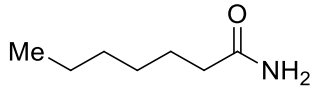


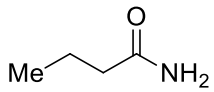
**Fig. S18** GC-gas analysis of collected gas after the first 24 h heating.



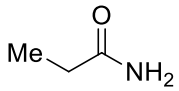

**3-Phenylpropanamide (2a)**: 87% yield.$^{1}$H NMR (300 MHz, $CDCl_3$) δ 7.16 (dd, *J* = 20.0, 5.7 Hz, 5H), 5.76 (br, 2H), 2.87 (t, *J* = 7.6 Hz, 2H), 2.43 (t, *J* = 7.7 Hz, 2H). $^{13}$C NMR (75 MHz, $CDCl_3$) δ 175.10, 140.74, 128.63, 128.37, 126.35, 37.57, 31.45.



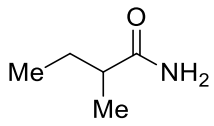

**Heptanamide (2b)**: 82% yield. $^{1}$H NMR (400 MHz, DMSO-d6) δ 7.22 (s, 1H), 6.66 (s, 1H), 2.01 (t, *J* = 7.4 Hz, 2H), 1.46 (t, *J* = 7.2 Hz, 2H), 1.27-1.21 (m, 6H), 0.85 (t, *J* = 6.7 Hz, 3H). $^{13}$C NMR (101 MHz, DMSO-d6) δ 174.48, 35.18, 31.10, 28.43, 25.13, 22.07, 13.99.




**Butyramide (2c)**: 87% yield. $^{1}$H NMR (400 MHz, DMSO-d6) δ 6.95 (br, 2H), 2.00 (t, *J* = 7.3 Hz, 2H), 1.48 (q, *J* = 7.3 Hz, 2H), 0.84 (t, *J* = 7.3 Hz, 3H). $^{13}$C NMR (101 MHz, DMSO-d6) δ 174.34, 37.15, 18.56, 13.73.

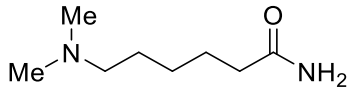



**Propionamide (2d)**: 81% yield. $^{1}$H NMR (400 MHz, DMSO-d6) δ 6.95 (br, 2H), 2.03 (q, J = 7.6 Hz, 2H), 0.96 (t, *J* = 7.5 Hz, 3H). $^{13}$C NMR (101 MHz, DMSO-d6) δ 175.25, 28.27, 9.84.

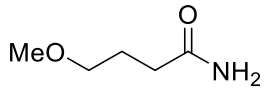



**2-Methylbutanamide (2e)**: 51% yield. $^{1}$H NMR (500 MHz, DMSO-d6) δ 6.94 (br, 2H), 2.12 (p, *J* = 7.0 Hz, 1H), 1.47 (dq, *J* = 15.0, 7.5 Hz, 1H), 1.26 (dq, *J* = 13.9, 7.0 Hz,

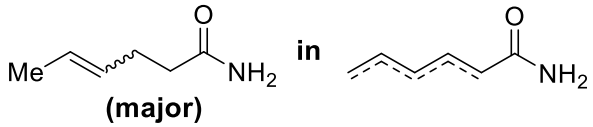
1H), 0.96 (d, *J* = 6.8 Hz, 3H), 0.80 (t, *J* = 7.4 Hz, 3H). $^{13}$C NMR (126 MHz, DMSO-d6) δ 177.79, 41.08, 26.74, 17.52, 11.84.



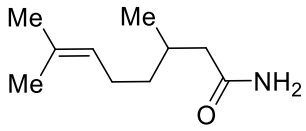

**6-(Dimethylamino)hexanamide (2f)**: 81% yield. $^{1}$H NMR (300 MHz, $CDCl_3$) δ 6.07 (br, 2H), 2.13 – 1.91 (m, 10H), 1.56 – 1.05 (m, 6H). $^{13}$C NMR (75 MHz, $CDCl_3$) δ 176.16, 59.44, 45.37, 35.80, 27.25, 26.94, 25.31.



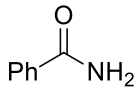

**4-Methoxybutanamide (2g)**: 85% yield. $^{1}$H NMR (300 MHz, $CDCl_3$) δ 6.20 (br, 2H), 3.36 (t, *J* = 5.2 Hz, 2H), 3.26 (s, 3H), 2.24 (t, *J* = 6.8 Hz, 2H), 1.92 – 1.72 (m, 2H). $^{13}$C NMR (75 MHz, $CDCl_3$) δ 175.94, 71.73, 58.48, 32.54, 25.30.



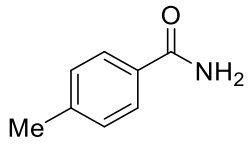

**Hex-4-enamide (2h)**: 61% total yield, contains other isomers with double bond shifts. $^{1}$H NMR (500 MHz, $CDCl_3$) δ 6.35 – 5.71 (m, 2H), 5.59 – 5.29 (m, 2H), 2.40 – 2.22 (m, 4H), 1.62 (m, 3H). $^{13}$C NMR (126 MHz, $CDCl_3$) δ 175.75, 129.43, 128.56, 126.35, 125.57, 35.83, 35.68, 28.41, 22.95, 17.93.



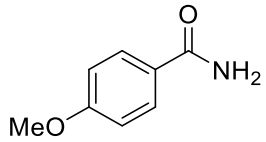

**3,7-Dimethyloct-6-enamide (2i)**: Purified by flash silica gel column chromatography (eluent: hexane/EtOAc = 3:1 v/v), 61% yield. $^{1}$H NMR (500 MHz, $CDCl_3$) δ 5.79 (br, 2H), 5.07 (t, *J* = 6.5 Hz, 1H), 2.21 (dd, *J* = 12.3, 4.0 Hz, 1H), 2.06 – 1.88 (m, 4H), 1.62 (d, *J* = 39.4 Hz, 6H), 1.36 (dt, *J* = 13.7, 5.6 Hz, 1H), 1.20 (dt, *J* = 13.9, 7.6 Hz, 1H), 0.94 (d, *J* = 5.8 Hz, 3H). $^{13}$C NMR (126 MHz, $CDCl_3$) δ 175.54, 131.65, 124.37, 43.80, 36.98, 30.46, 25.80, 25.55, 19.60, 17.75.



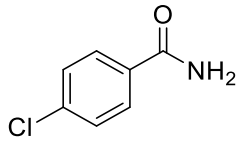
**Benzamide (2j)**: 82% yield. $^{1}$H NMR (500 MHz, DMSO-d6) δ 8.01 (br, 1H), 7.89 (d, *J* = 7.5 Hz, 2H), 7.51 (t, *J* = 7.0 Hz, 1H), 7.44 (t, *J* = 7.2 Hz, 2H), 7.39 (br, 1H). $^{13}$C NMR (126 MHz, DMSO-d6) δ 168.13, 134.30, 131.33, 128.30, 127.55.



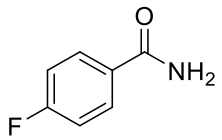

**4-Methylbenzamide (2k)**: 88% yield. $^{1}$H NMR (400 MHz, DMSO-d6) δ 7.88 (s, 1H), 7.80 – 7.73 (m, 2H), 7.24 (d, *J* = 7.8 Hz, 3H), 2.34 (s, 3H). $^{13}$C NMR (100 MHz, DMSO-d6) δ 167.76, 141.03, 131.47, 128.71, 127.48, 20.94.




**4-Methoxybenzamide (2l)**: 91% yield. $^{1}$H NMR (400 MHz, DMSO-d6) δ7.85-7.81 (m, 3H), 7.16 (s, 1H), 6.97 (d, *J* = 8.7 Hz, 2H), 3.79 (s, 3H). $^{13}$C NMR (100 MHz, DMSO-d6) δ 167.55, 161.64, 129.41, 126.51, 113.45, 55.37.

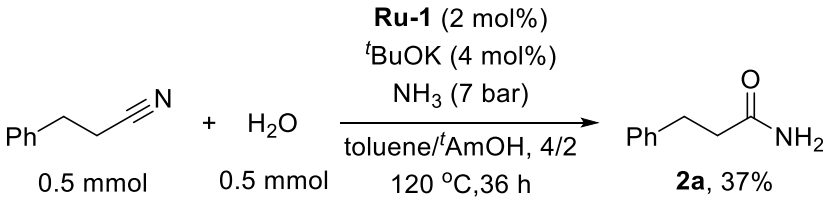



**4-Chlorobenzamide (2m)**: 85% yield. $^{1}$H NMR (400 MHz, DMSO-d6) δ8.04 (s, 1H), 7.88 (d, J = 8.5 Hz, 2H), 7.52 (d, *J* = 8.5 Hz, 2H), 7.45 (s, 1H). $^{13}$C NMR (100 MHz, DMSO-d6) δ 166.93, 136.15, 133.05, 129.45, 128.36



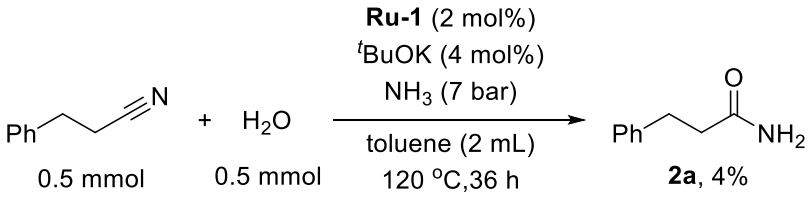

**4-Fluorobenzamide (2n)**: 82% yield. $^{1}$H NMR (500 MHz, DMSO-d6) δ 8.00 (s, 1H), 7.97 – 7.90 (m, 2H), 7.39 (s, 1H), 7.31 – 7.24 (m, 2H). $^{13}$C NMR (126 MHz, DMSO-d6) δ 166.93, 163.98 (d, *J* = 248.3 Hz), 130.77, 130.17 (d, *J* = 9.0 Hz), 115.17 (d, *J* = 21.7 Hz).

### 3.2 Control experiments involving hydration of nitriles

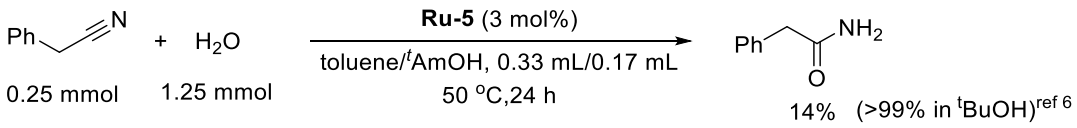



To a 90 mL Fischer-Porter tube were added **Ru-1** (4.9 mg, 0.01 mmol), $^t$BuOK (2.2 mg, 0.02 mmol) and toluene (4 mL, dried over 3 Å molecular sieves) in a $N_2$ glovebox. The resulting mixture was stirred at room temperature for 0.5 h, then $H_2O$ (9.0 mg, 0.5 mmol) was added, followed by 3-phenylpropionitrile (65.5 mg, 0.5 mmol) and 2 mL $^t$AmylOH (dried over 3 Å molecular sieves). The Fischer-Porter tube was sealed and taken out of the glovebox, and filled with 7 bar $NH_3$. After heating at 120 °C with stirring for 36 h, the tube was cooled to room temperature, and the gas was released carefully. The resulting solution was directly analyzed by GC-MS, indicating the generation of **2a**. The solvent was then removed and the resulting mixture was analyzed by NMR with the addition of an internal standard (37% NMR yield of **2a** was obtained, vs 71% yield of **2a** from alcohol and ammonia).

This result indicates that nitrile hydration is slower than the generation of primary amide from alcohol and ammonia under the same reaction conditions. This conclusion was further supported by another control experiment carried out with 3-phenylpropionitrile in toluene, wherein the primary amide was obtained in only 4% yield under the conditions noted in Table 1, entry 8, relative to 40% obtained from the corresponding alcohol under the same conditions. These results, combined with the fact that no nitrile was observed during the catalytic reaction using alcohol as substrate (as noted in the manuscript), clearly demonstrate that nitrile hydration is not the main reaction pathway in the current catalytic process.



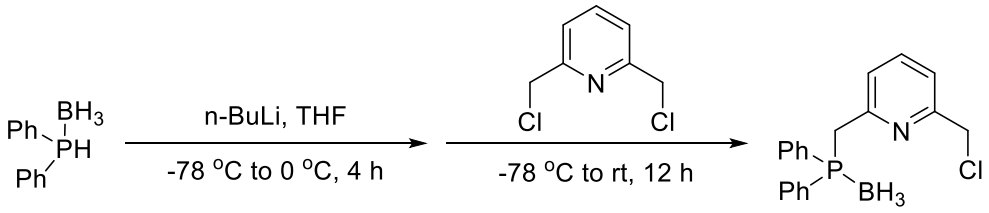
We've also applied the same catalytic conditions reported by Guo et al.,[6] using benzyl cyanide as substrate, but changed the solvent to toluene/$^t$AmOH = 2:1, as was used in our work. The result, shown in eq. 1 below, indicates that our solvent system is not adequate for the hydration of nitriles, since a yield of only 14% was obtained in toluene/$^t$AmOH, whereas >99% was reported in ref 6 for $^t$BuOH. The reason for this difference is presumably the incorporation of toluene as a cosolvent, which significantly increases the hydrophobicity of the resulting solvent mixture relative to $^t$BuOH, and consequently impedes hydration. It is important to note that in the supporting information for Guo's work, the authors report no hydration when using toluene or dioxane as solvents and acetonitrile as substrate. By contrast, in our present work, primary amides could be obtained in 40% or 80% yield in toluene or toluene/dioxane, respectively, as mentioned in our manuscript. These results imply that the current catalytic process does not involve the hydration of nitriles.




It seems that the presence of ammonia does promote nitrile hydration to some extent. Nevertheless, as already noted above, we can exclude nitrile hydration as the main reaction pathway in our catalytic system on the basis of the following arguments: (i) hydration of nitriles is inefficient in our solvent mixture, as indicated by the control experiments, and its rate is significantly slower than the generation of primary amides from alcohols and ammonia under the same reaction conditions; (ii) no nitrile was observed when the catalytic reaction mixture containing alcohol and ammonia was monitored in real time (see Figure 1 in the manuscript); (iii) the dehydration of the hemiaminal intermediate, which eventually leads to the formation of nitriles, was shown by our mechanistic DFT study to be both kinetically and thermodynamically unfavorable, as compared to the direct dehydrogenation of hemiaminal to generate the primary amide.

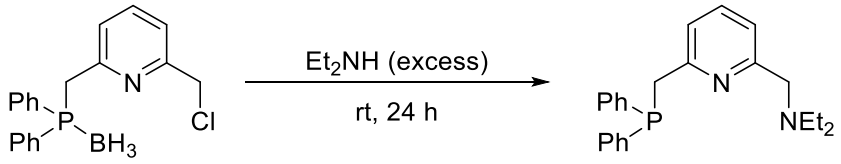
# 4. Synthesis of complex Ru-4

## 4.1 Synthetic Routes



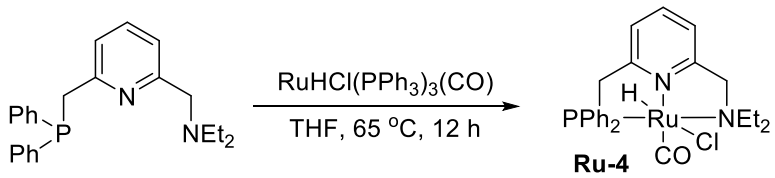

In an oven-dried argon-filled 100 mL Schleck flask was dissolved 2.86 g $HPPh_2(BH_3)$ (14.3 mmol, commercial) in 50 mL dry THF and cooled to -78 °C. 11.9 mL n-BuLi (14.3 mmol, 1.2 M in hexane) were then added by syringe during few minutes. At first the solution turned light yellow and then gradually transformed into a brown-red solution and stirred at 0 ˚C for 4 hours. It was then re-cooled to -20 °C and added dropwise during 2 hours to a solution of 2.6 g 2,6-bis(chloromethyl)pyridine (14.3 mmol) in 50 mL dry THF at -78 °C. The temperature was slowly increased to 0 °C and the resulting solution was stirred at room temperature for 12 hrs. The reaction solution was treated with 100 mL water and extracted with $CH_2Cl_2$ (2×150 mL) and dried with sodium sulfate. The liquid phase was concentrated and the residue was purified by flash chromatography on silica gel to provide the pure product in 40% yield (white solid, 1.93 g).

2-(Chloromethyl)-6-((diphenylphosphanyl)borane-methyl)pyridine: $^{1}H$ NMR (300 MHz, $CDCl_3$) δ 7.77 – 7.70 (m, 4H), 7.58 (t, *J* = 7.8 Hz, 1H), 7.52 – 7.40 (m, 6H), 7.30 – 7.18 (m, 2H), 4.46 (s, 2H), 3.87 (d, J = 12.0 Hz, 2H), 1.813 – 0.57 (m, 3H). $^{13}C$ NMR (75 MHz, $CDCl_3$) δ 155.66, 152.97 (d, *J* = 4.5 Hz), 137.17, 132.70 (d, *J* = 9.3 Hz), 131.25 (d, *J* = 2.6 Hz), 128.42 (d, *J* = 54.0 Hz), 128.58 (d, *J* = 10.1 Hz), 124.44 (d, *J* = 3.4 Hz), 120.85 (d, *J* = 2.5 Hz), 46.34, 36.29 (d, *J* = 31.5 Hz). $^{31}P\{^{1}H\}$ NMR (121 MHz, $CDCl_3$) δ 19.65 (broad peak).




In a glovebox, to an oven-dried argon-filled 100 mL Schleck flask were added 1.93 g 2-(chloromethyl)-6-((diphenylphosphanyl)borane-methyl)pyridine (5.7 mmol) and 40 mL diethylamine. The resulting solution was vigorously stirred at room temperature for 24 hours. The liquid phase was concentrated and the residue was purified by flash chromatography on silica gel to provide the pure product (note: column chromatography should be performed in a glove box) in 68% yield (light yellow liquid, 1.4 g).

*N*-((6-((Diphenylphosphanyl)methyl)pyridin-2-yl)methyl)-*N*-ethylethanamine: $^{1}$H NMR (400 MHz, $CDCl_3$) δ 7.41 – 7.27 (m, 6H), 7.21 – 7.14 (m, 6H), 6.75 (d, *J* = 7.6 Hz, 1H), 3.58 (s, 2H), 3.53 (s, 2H), 2.45 (q, *J* = 7.1 Hz, 4H), 0.94 (t, *J* = 7.1 Hz, 6H). $^{13}$C NMR (100 MHz, $CDCl_3$) δ 160.19, 156.78 (d, J = 7.8 Hz), 138.28 (d, *J* = 15.0 Hz), 136.21, 132.86 (d, *J* = 18.8 Hz), 128.51, 128.20 (d, *J* = 6.5 Hz), 121.41 (d, *J* = 6.6 Hz), 119.94 (d, *J* = 2.3 Hz), 59.41, 47.26, 38.62, 38.45, 11.91, 0.97. $^{31}$P{$^{1}$H} NMR (162 MHz, $CDCl_3$) δ -9.47.




In a glovebox, $RuHCl(PPh_3)_3(CO)$ (286.3 mg, 0.3 mmol) and N-((6-((diphenylphosphanyl)methyl)pyridin-2-yl)methyl)-N-ethylethanamine (130.5 mg, 0.36 mmol) were suspended in THF (10 mL) in an oven-dried 100 mL Schlenk flask equipped with a magnetic stirring bar. The flask was sealed and taken out of the glovebox, and stirred at 65 °C for 12 hours. After cooling the reaction mixture to room temperate, the Schlenk flask was transferred back to the glovebox and the solvent was removed under vacuum. The resulting yellow solid was washed with ether and pentane for several times to give the desired product **Ru-4** in 73% yield (yellow solid, 115.6 mg).

**Ru-4**: $^{1}$H NMR (400 MHz, $CD_2Cl_2$) δ 7.71– 7.60 (m, 5H), 7.42 – 7.37 (m, 7H), 7.23 (d, *J* = 7.8 Hz, 1H), 4.99 (d, *J* = 14.7 Hz, 1H), 4.41 (dd, *J* = 17.7, 11.0 Hz, 1H), 4.09 – 3.86 (m, 2H), 3.74-3.67 (m, 1H), 3.57-3.48 (m,1H), 2.95 (dt, *J* = 8.4, 6.1 Hz, 2H), 1.32 (t, J = 7.0 Hz, 3H), 1.16 (t, J = 7.2 Hz, 3H), -14.36 (d, *J* = 28.9 Hz, 1H). $^{13}$C NMR (75 MHz, $CD_2Cl_2$) δ 207.62 (d, *J* = 16.4 Hz), 160.63 (d, *J* = 2.6 Hz), 159.89 (d, *J* = 5.9 Hz), 138.78 (d, *J* = 54.3 Hz), 137.62, 135.00 (d, *J* = 41.8 Hz), 133.05 (d, *J* = 11.0 Hz), 132.70 (d, *J* = 10.5 Hz), 130.39 (d, *J* = 2.4 Hz), 130.13 (d, *J* = 2.4 Hz), 128.61 (d, *J* = 10.4 Hz), 128.24 (d, *J* = 10.1 Hz), 121.21 (d, *J* = 11.4 Hz). 120.06, 65.68, 55.33, 50.85, 45.85, 45.46, 11.68, 8.86. $^{31}$P{$^{1}$H} NMR (162 MHz, $CD_2Cl_2$) δ 72.01.

## 4.2 Copies of NMR Spectra

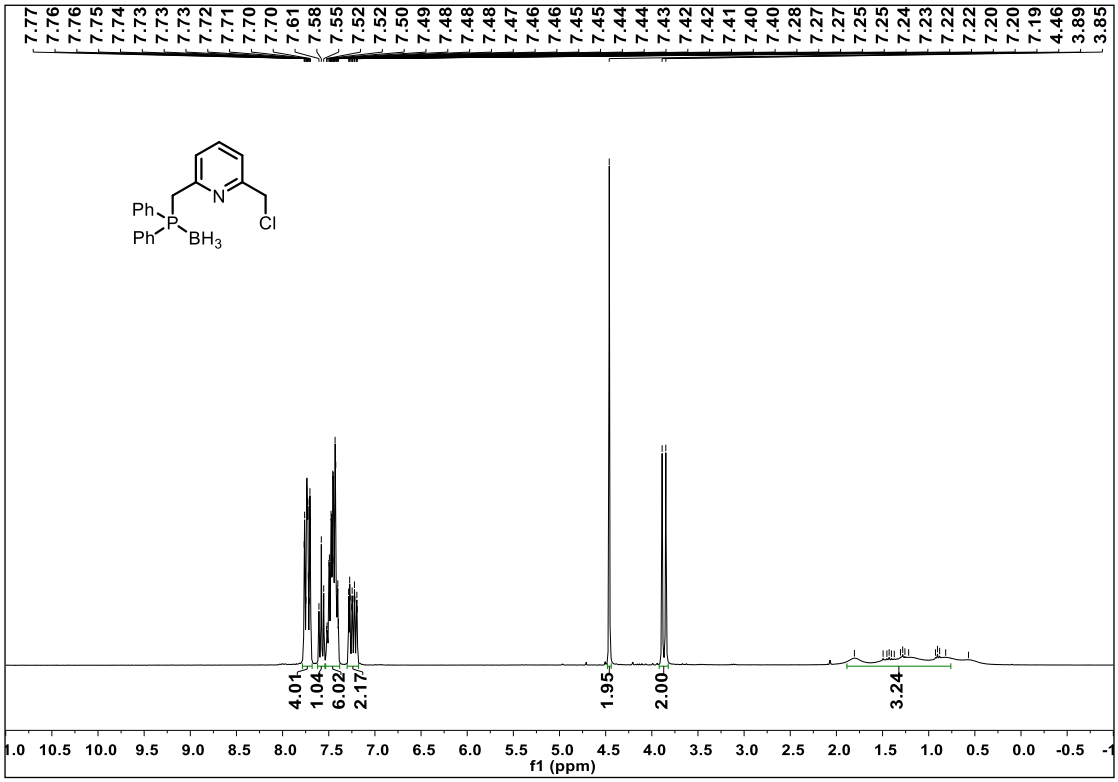



**Fig. S19** $^{1}$H NMR spectrum of 2-(chloromethyl)-6-((diphenylphosphanyl)borane-methyl)pyridine.

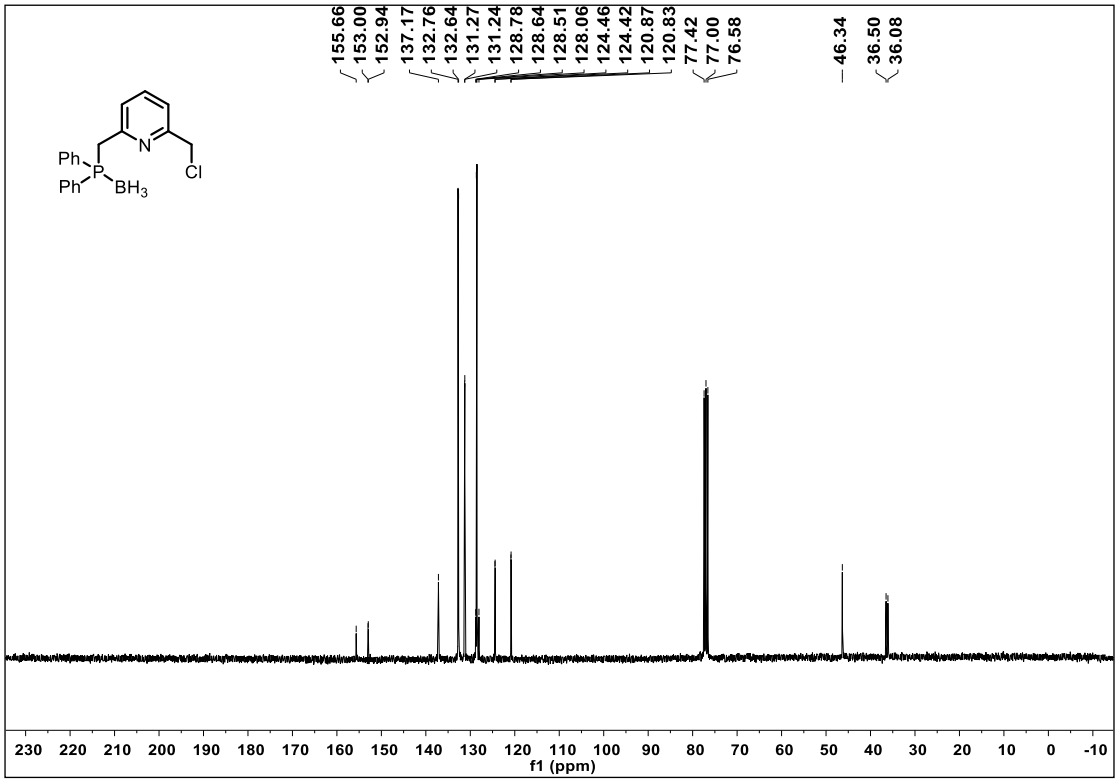



**Fig. S20** $^{13}$C NMR spectrum of 2-(chloromethyl)-6-((diphenylphosphanyl)borane-methyl)pyridine.

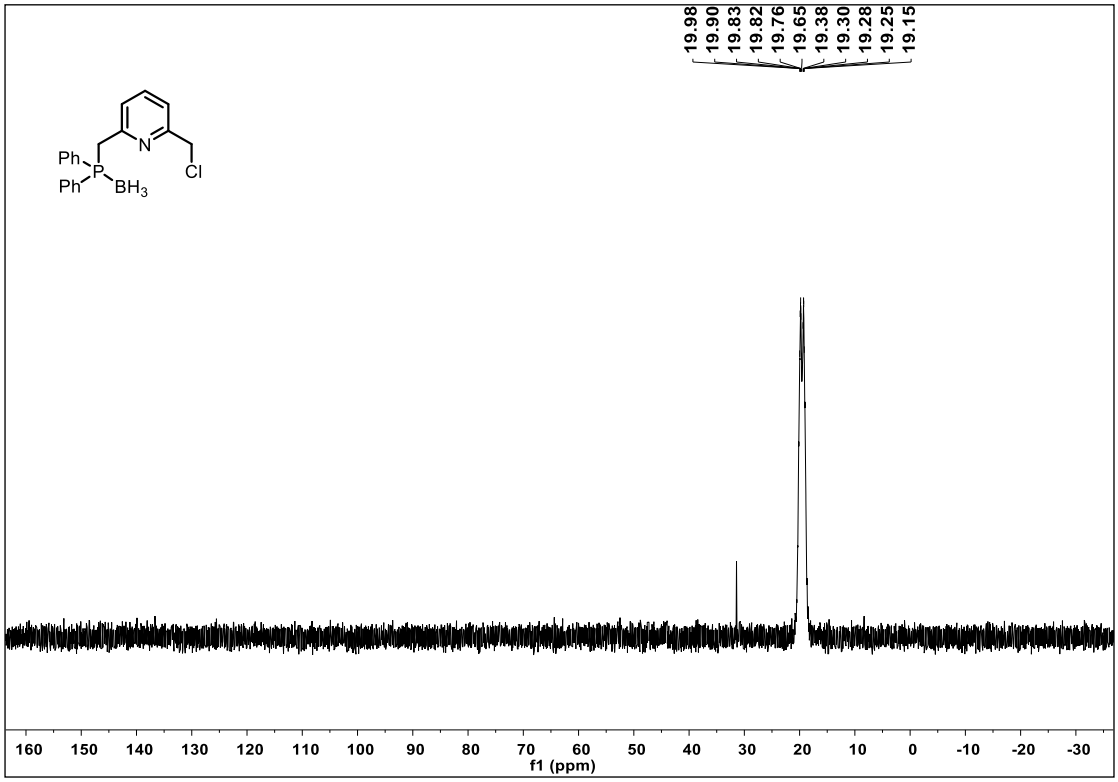



**Fig. S21** $^{31}$P NMR spectrum of 2-(chloromethyl)-6-((diphenylphosphanyl)borane-methyl)pyridine.

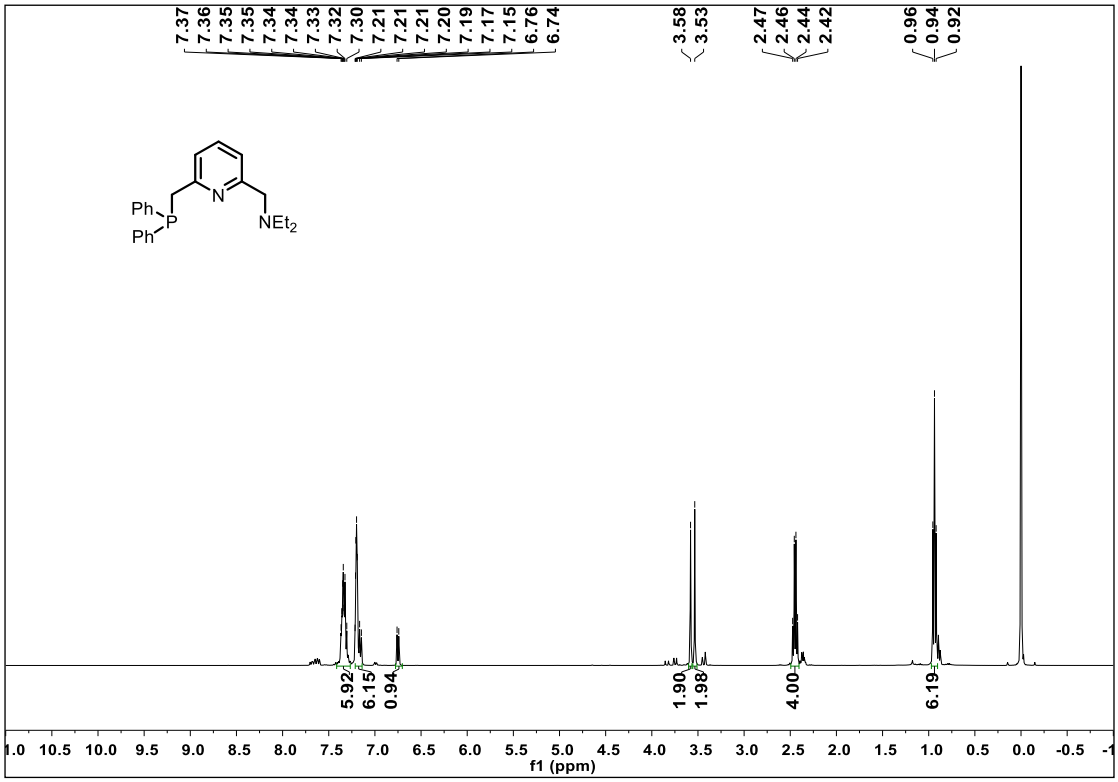



**Fig. S22** $^{1}$H NMR spectrum of *N*-((6-((diphenylphosphanyl)methyl)pyridin-2-yl)methyl)-N-ethylethanamine.

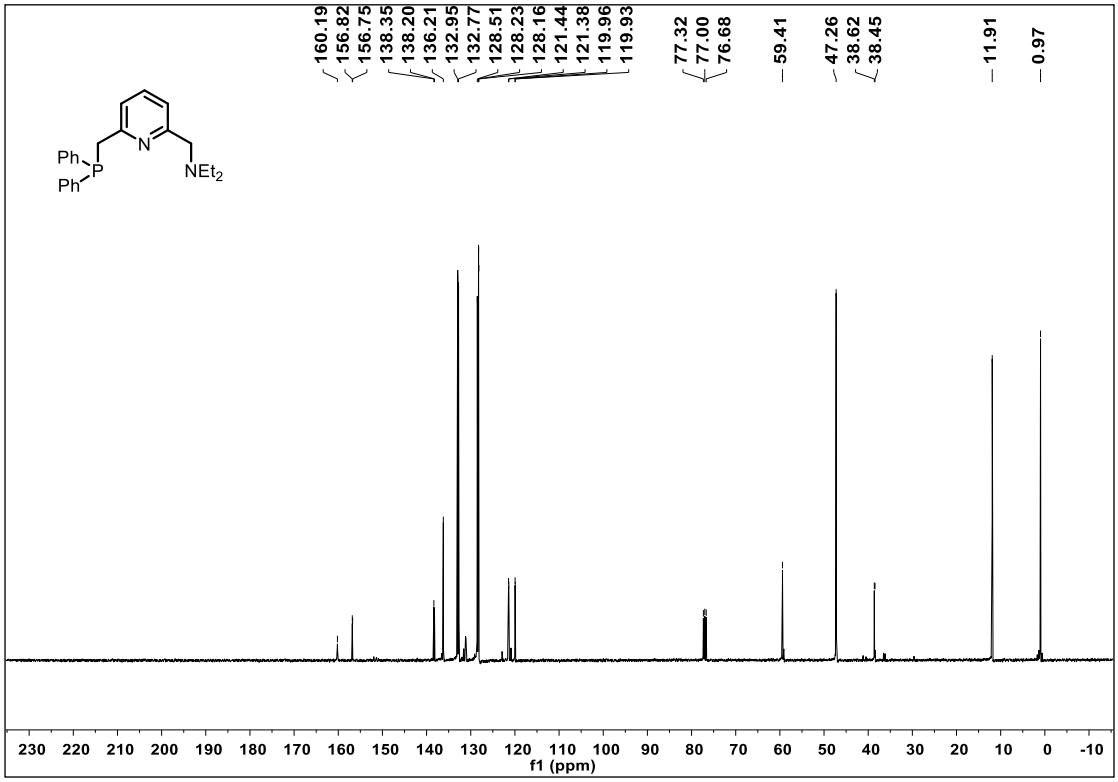



**Fig. S23** $^{13}$C NMR spectrum of *N*-((6-((diphenylphosphanyl)methyl)pyridin-2-yl)methyl)-N-ethylethanamine.

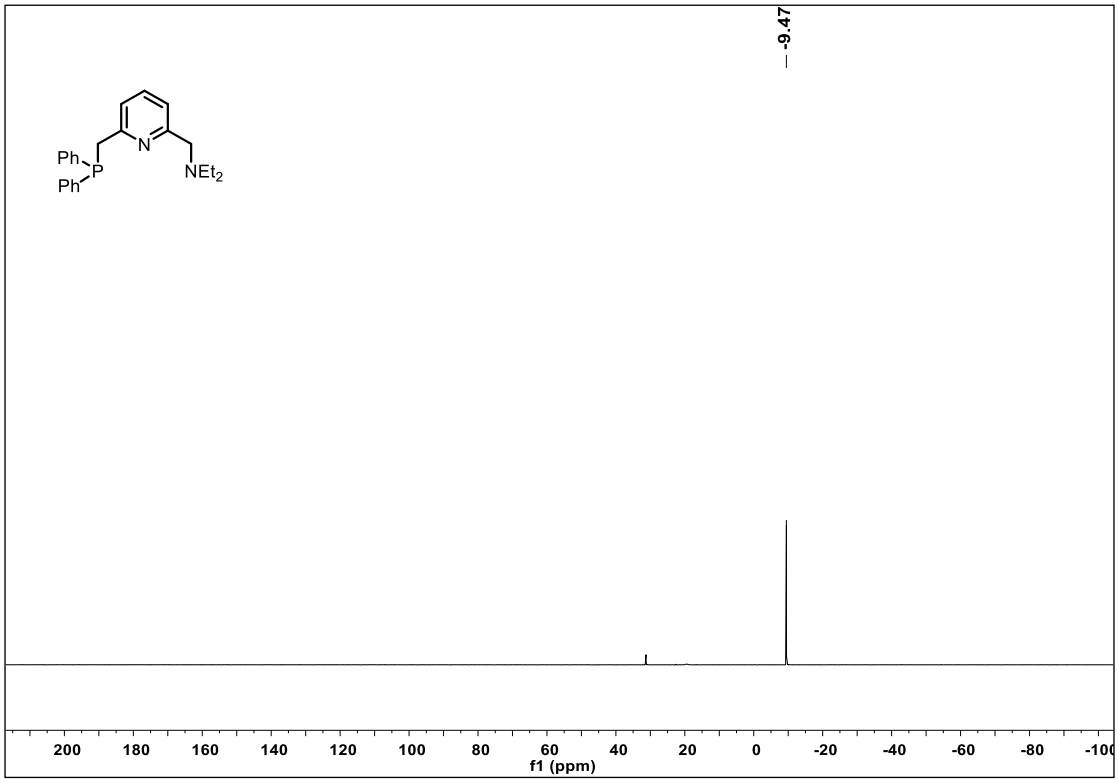



**Fig. S24** $^{31}$P NMR spectrum of *N*-((6-((diphenylphosphanyl)methyl)pyridin-2-yl)methyl)-N-ethylethanamine.

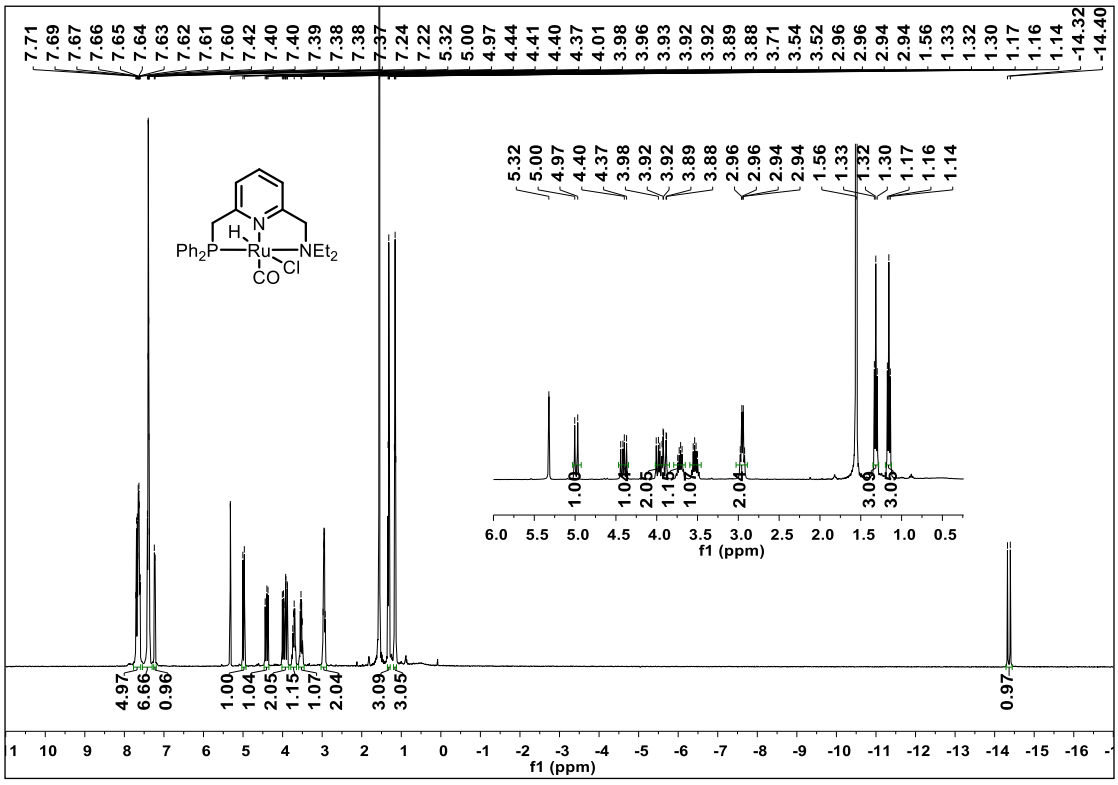



**Fig. S25** $^{1}$H NMR spectrum of **Ru-4**.

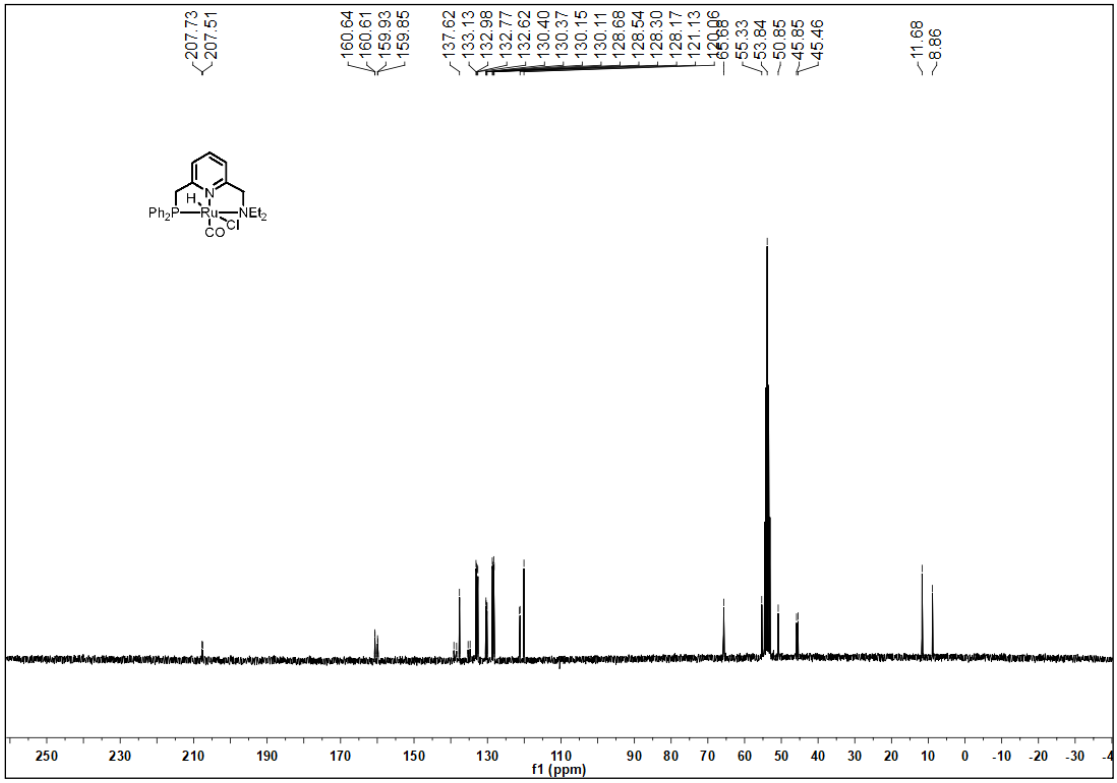



**Fig. S26** $^{13}$C NMR spectrum of **Ru-4**.

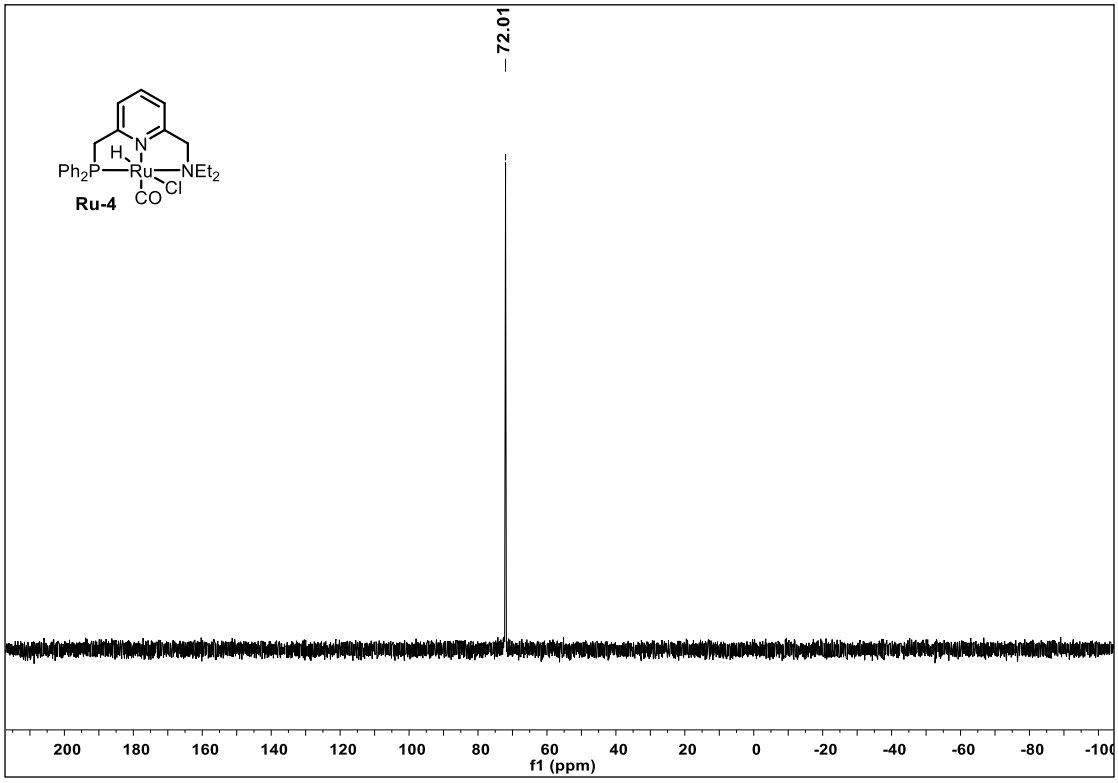



**Fig. S27** $^{31}$P NMR spectrum of **Ru-4**.

## 5. NMR spectra of isolated products

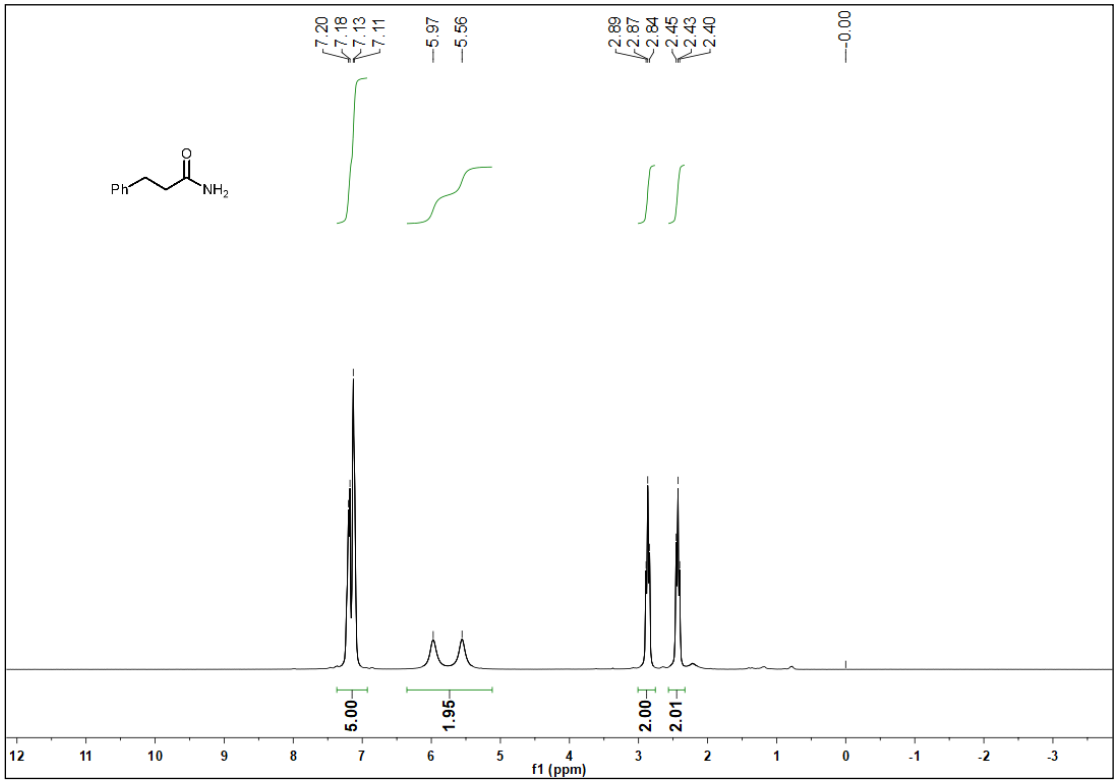



**Fig. S28** $^{1}$H NMR spectrum of **2a** in $CDCl_3$.

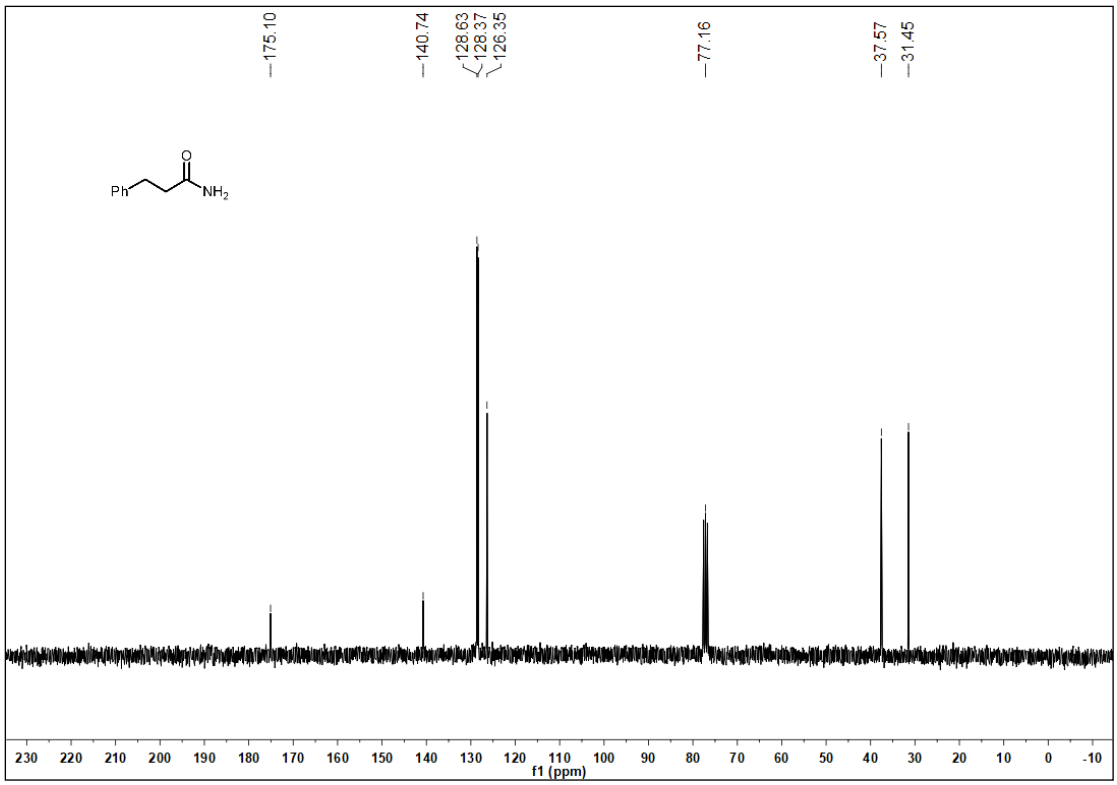



**Fig. S29** $^{13}$C NMR spectrum of **2a** in $CDCl_3$.

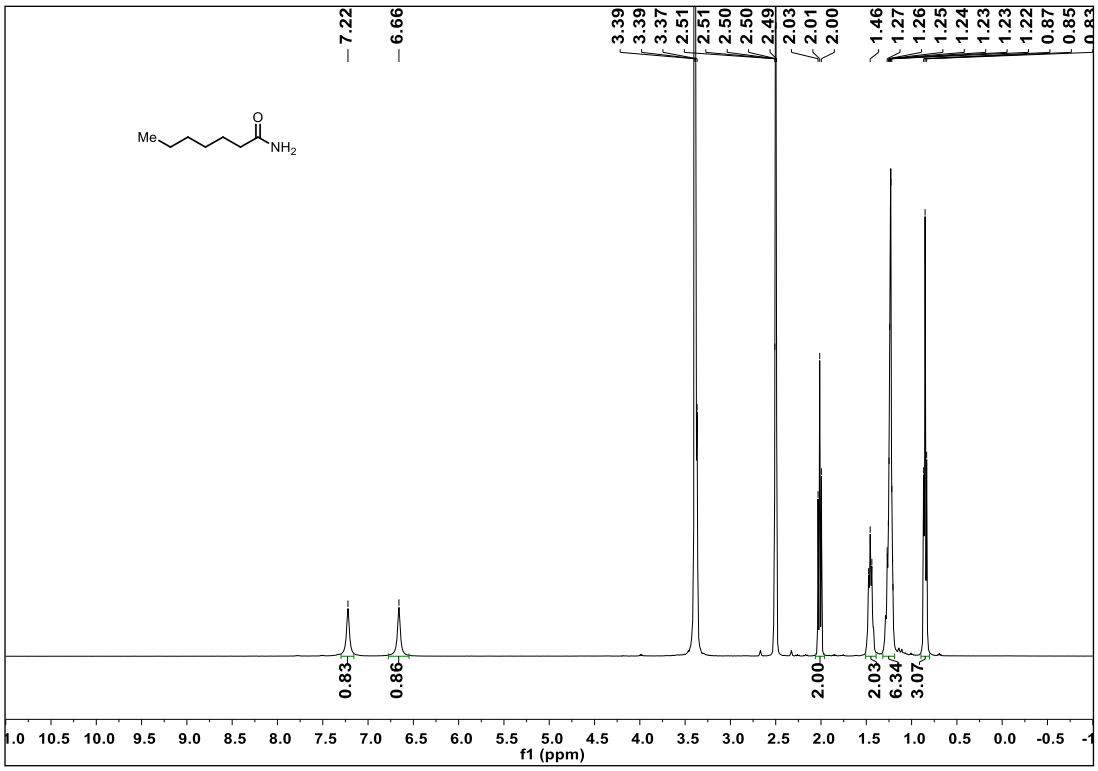



**Fig. S30** $^{1}$H NMR spectrum of **2b** in DMSO-$d_6$.

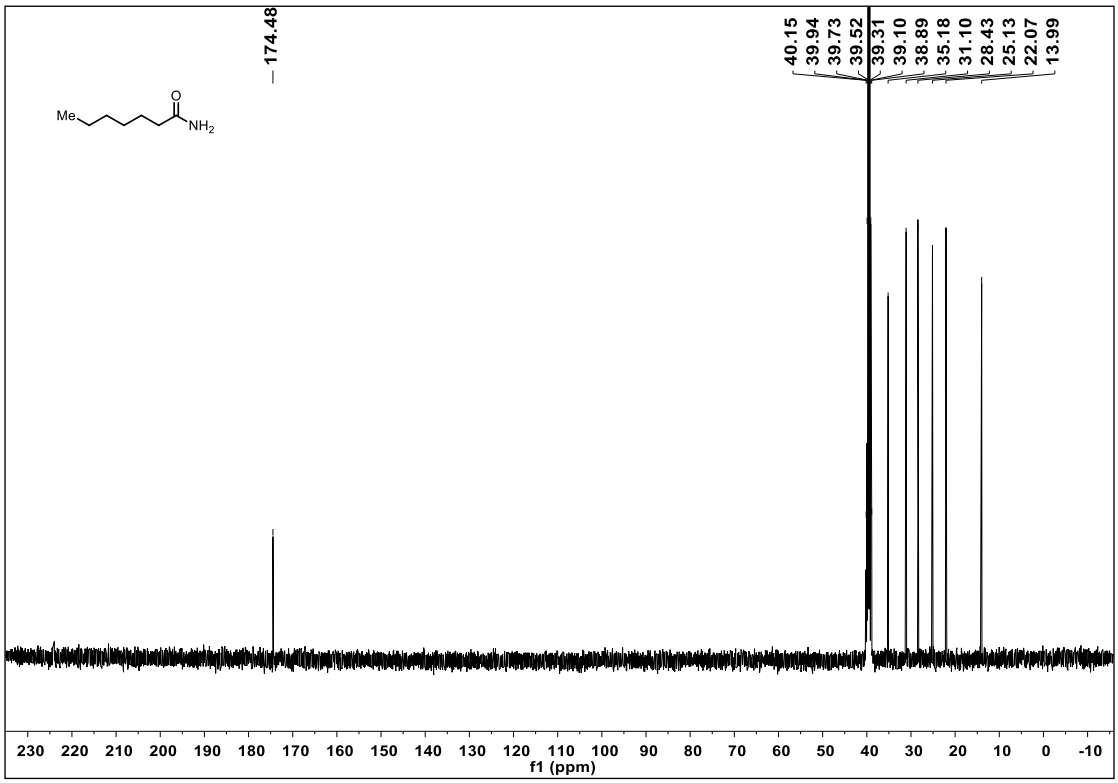



**Fig. S31** $^{13}$C NMR spectrum of **2b** in DMSO-$d_6$.

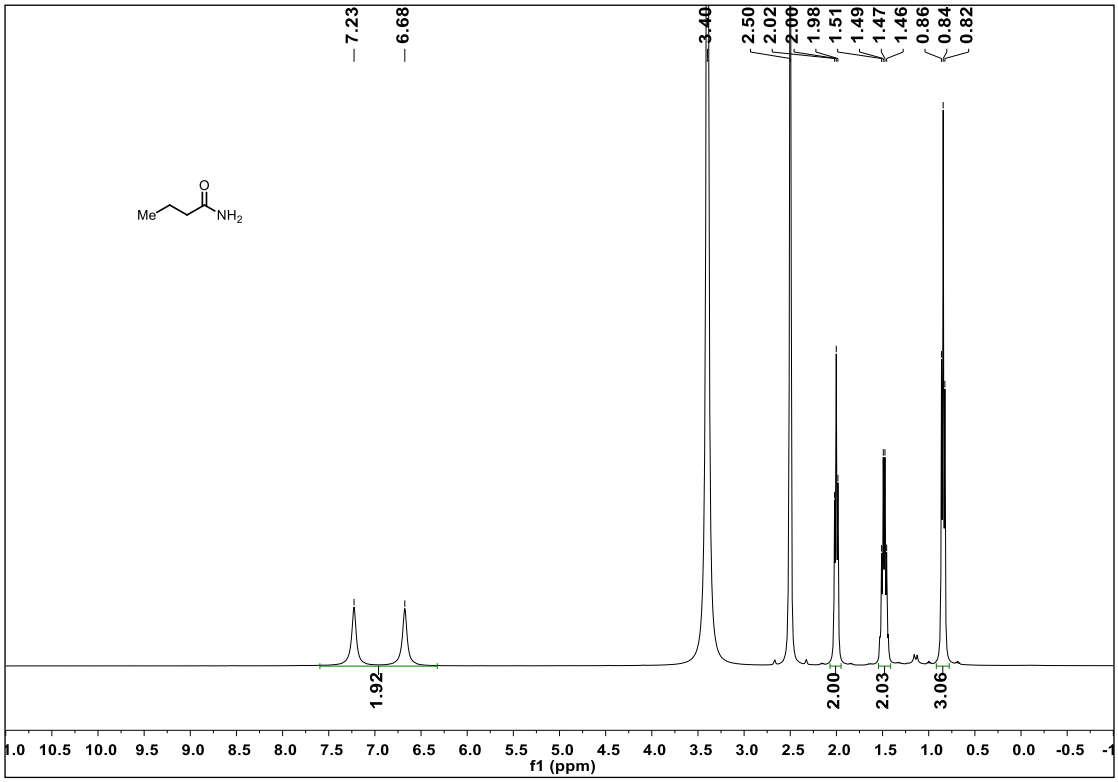



**Fig. S32** [1]H NMR spectrum of **2c** in DMSO-$d_6$.

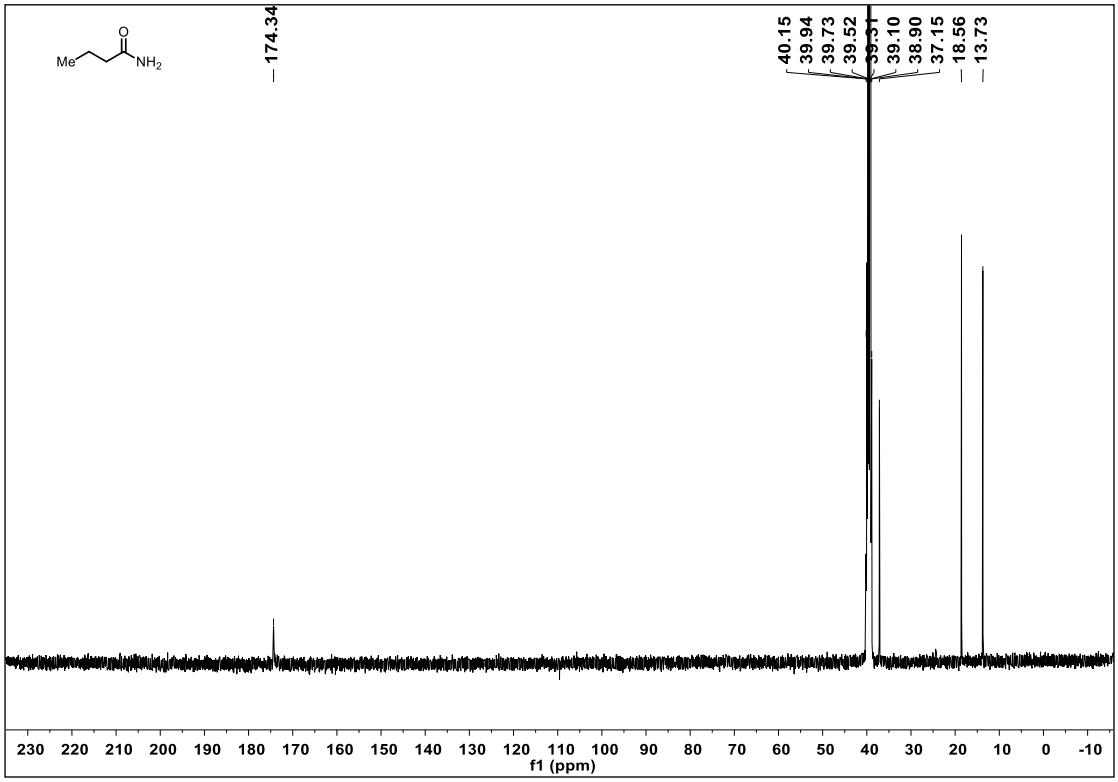



**Fig. S33** [13]C NMR spectrum of **2c** in DMSO-$d_6$.

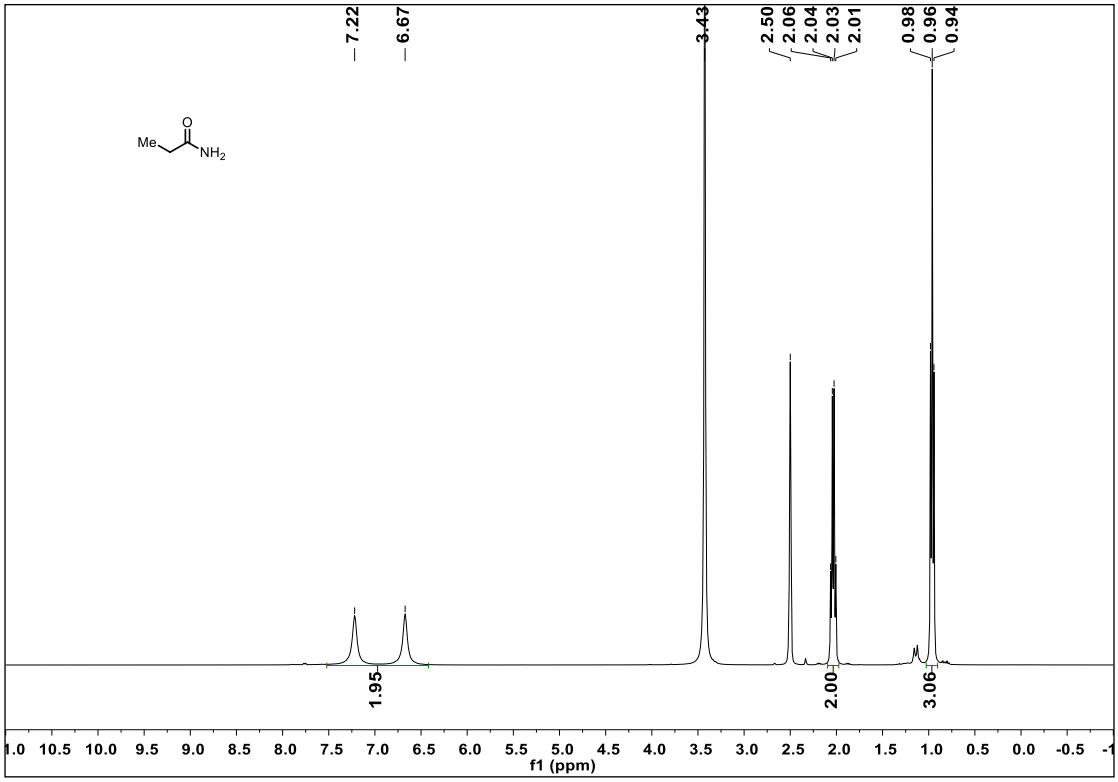



**Fig. S34** $^{1}$H NMR spectrum of **2d** in DMSO-$d_6$.

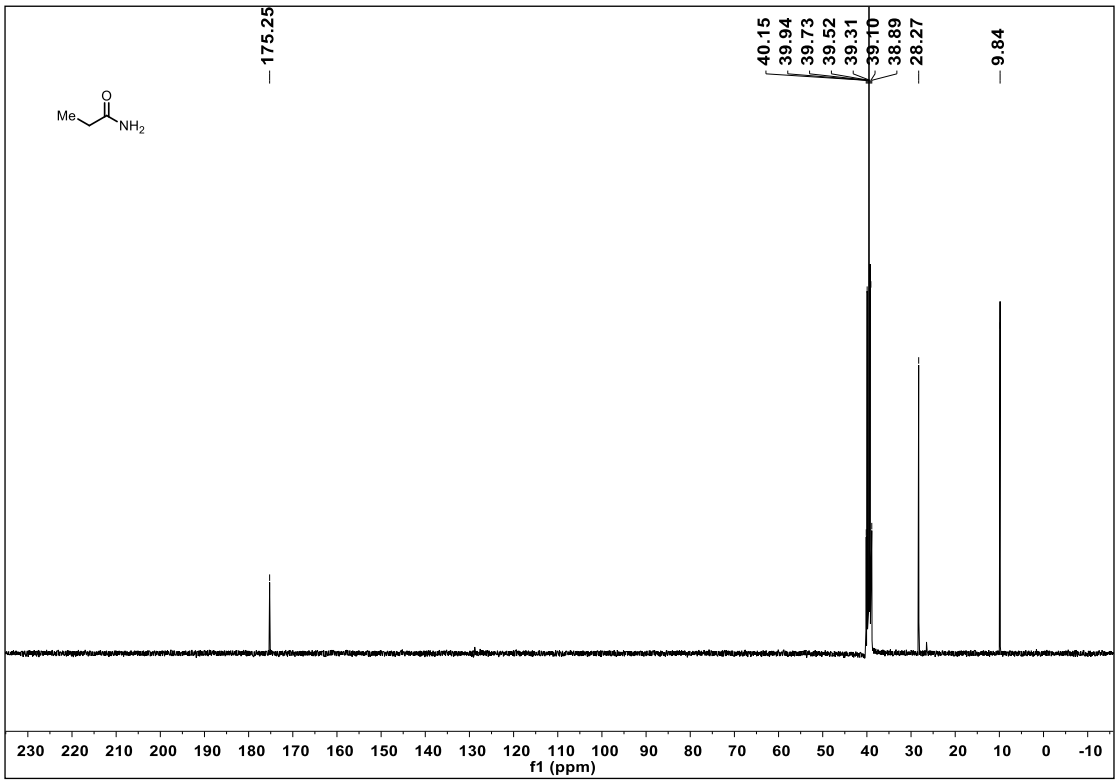



**Fig. S35** $^{13}$C NMR spectrum of **2d** in DMSO-$d_6$.

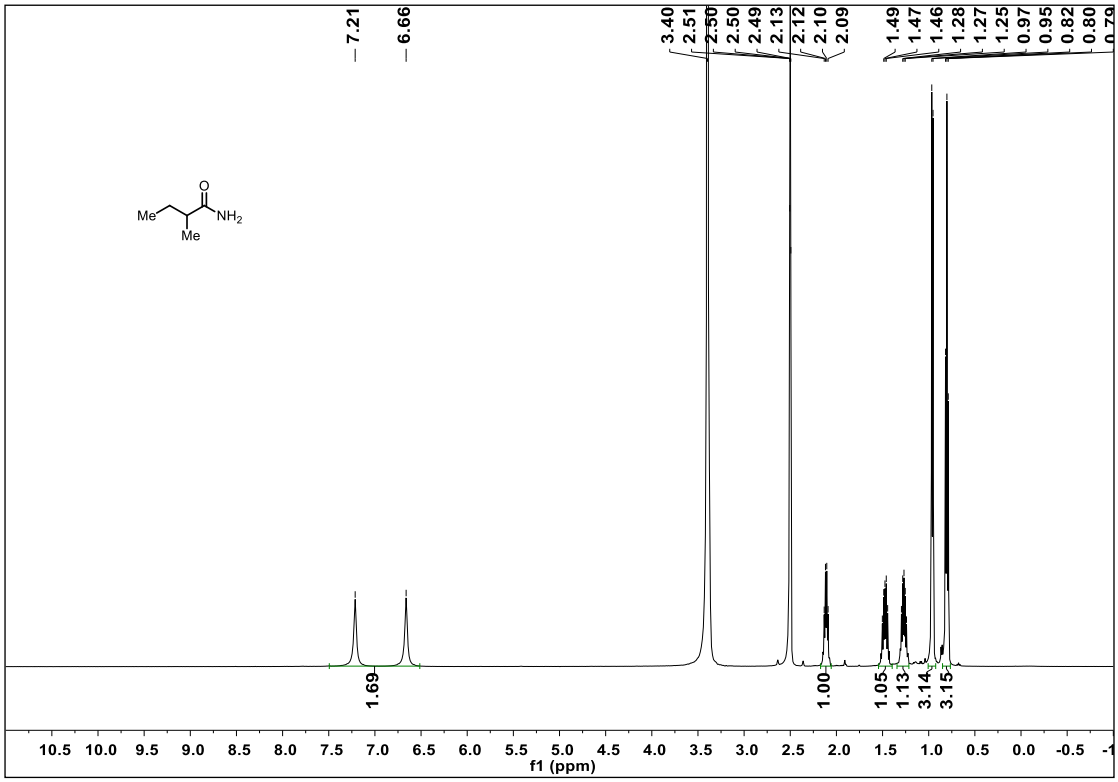



**Fig. S36** [1]H NMR spectrum of **2e** in DMSO-$d_6$.

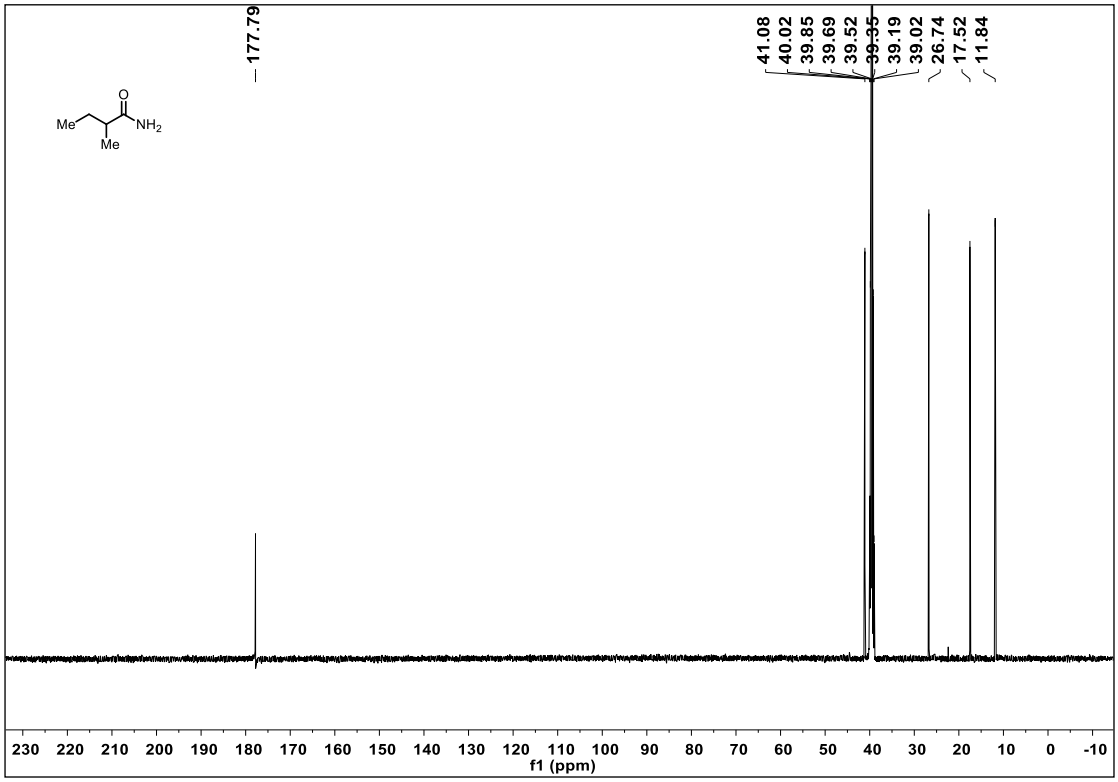



**Fig. S37** [13]C NMR spectrum of **2e** in DMSO-$d_6$.

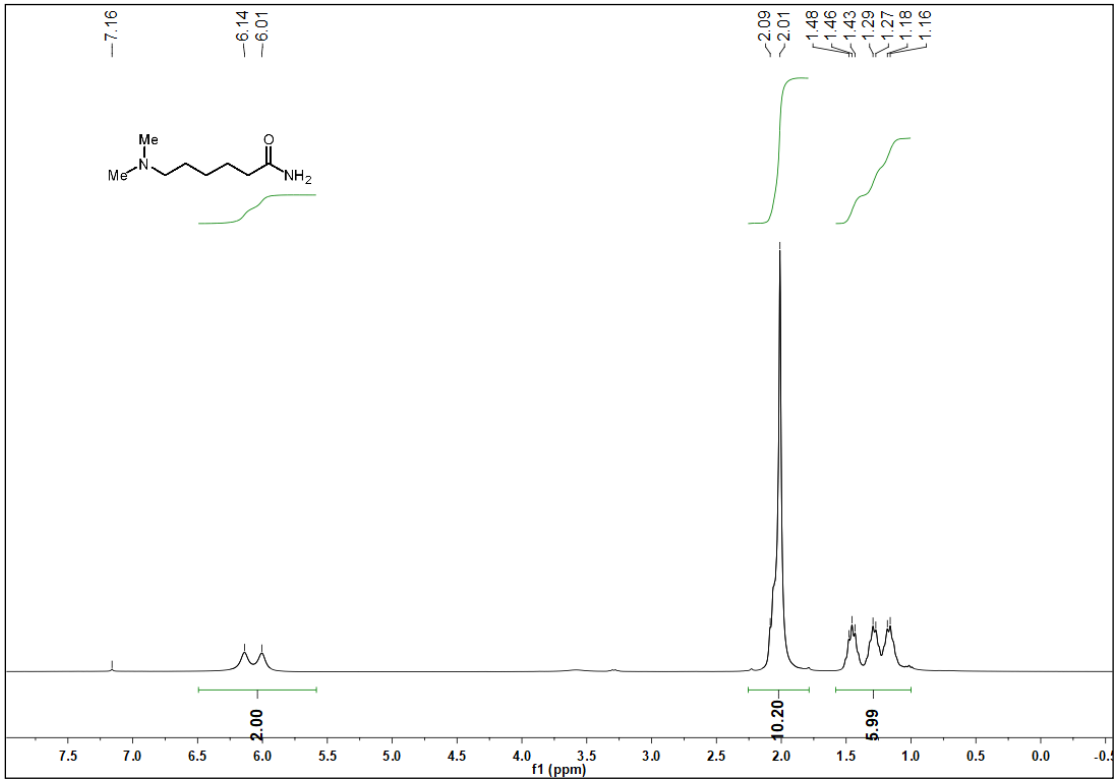



**Fig. S38** $^{1}$H NMR spectrum of **2f** in $CDCl_3$.

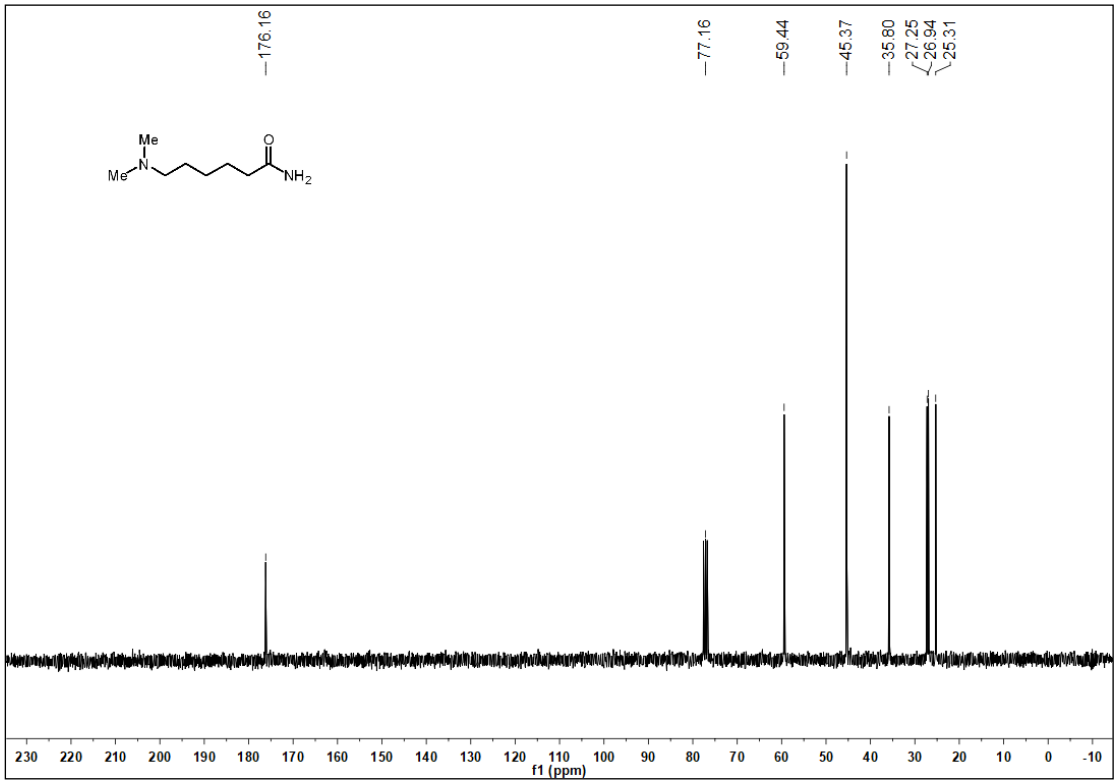



**Fig. S39** $^{13}$C NMR spectrum of **2f** in $CDCl_3$.

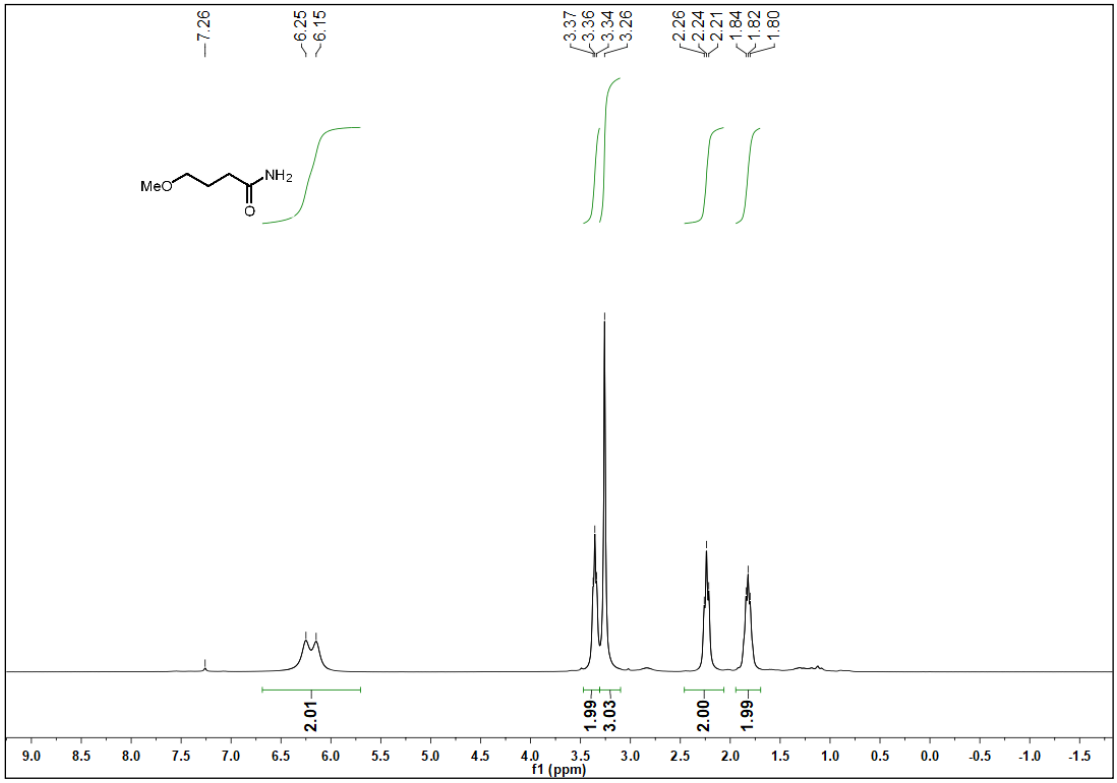



**Fig. S40** $^{1}$H NMR spectrum of **2g** in $CDCl_3$.

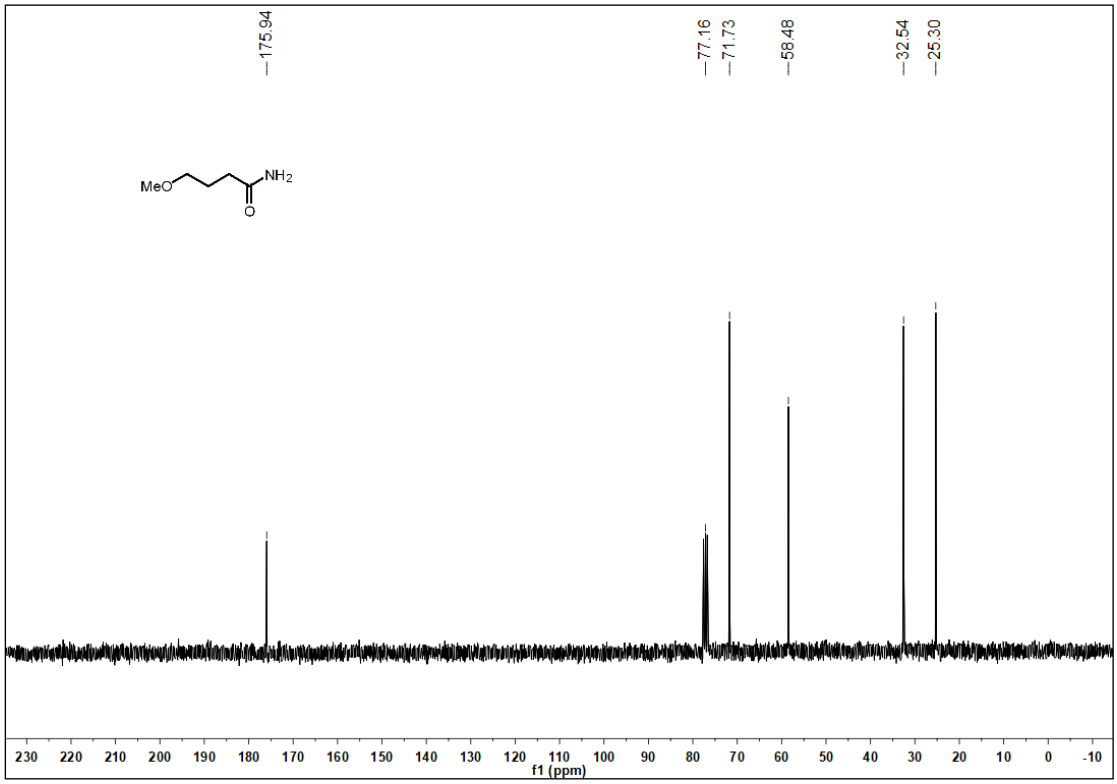



**Fig. S41** $^{13}$C NMR spectrum of **2g** in $CDCl_3$.

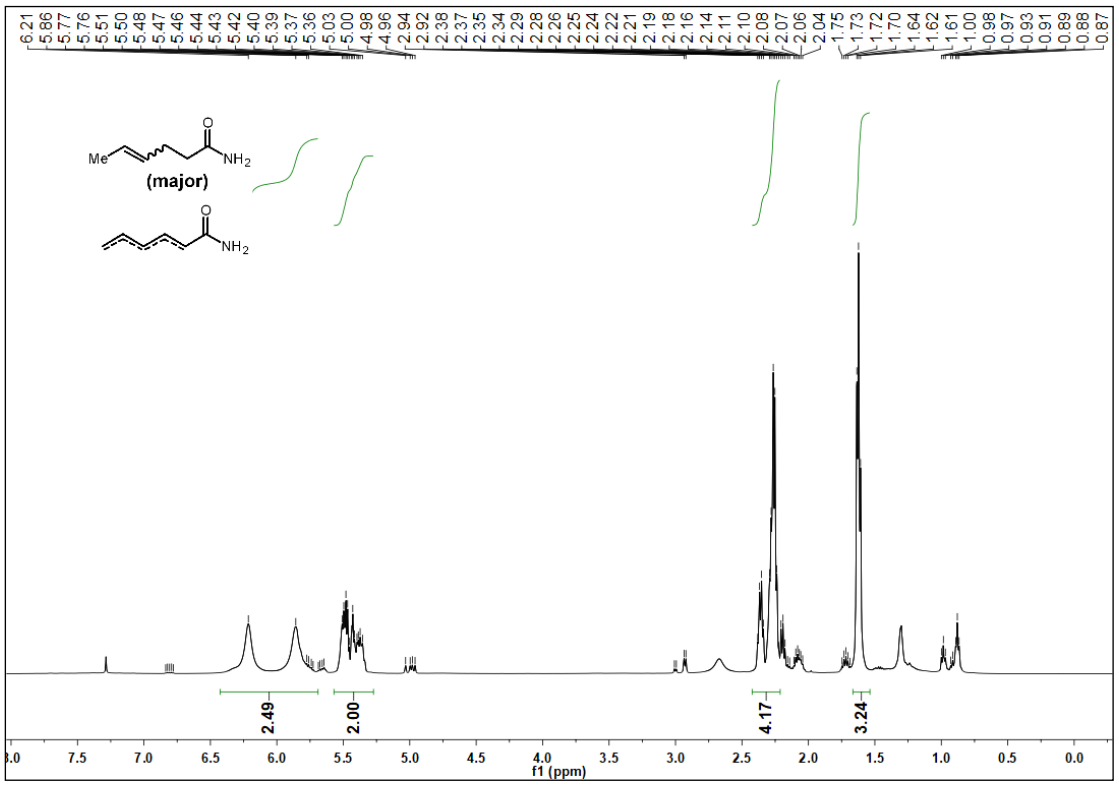



**Fig. S42** $^{1}$H NMR spectrum of **2h** in $CDCl_3$.

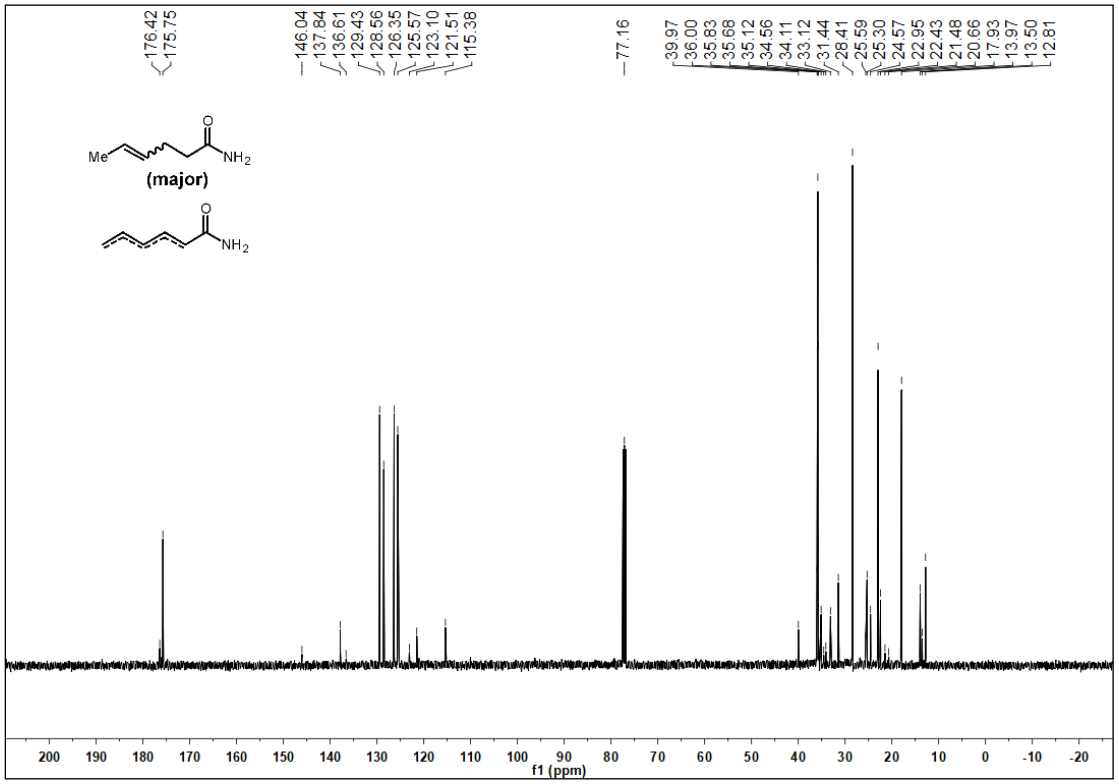



**Fig. S43** $^{13}$C NMR spectrum of **2h** in $CDCl_3$.

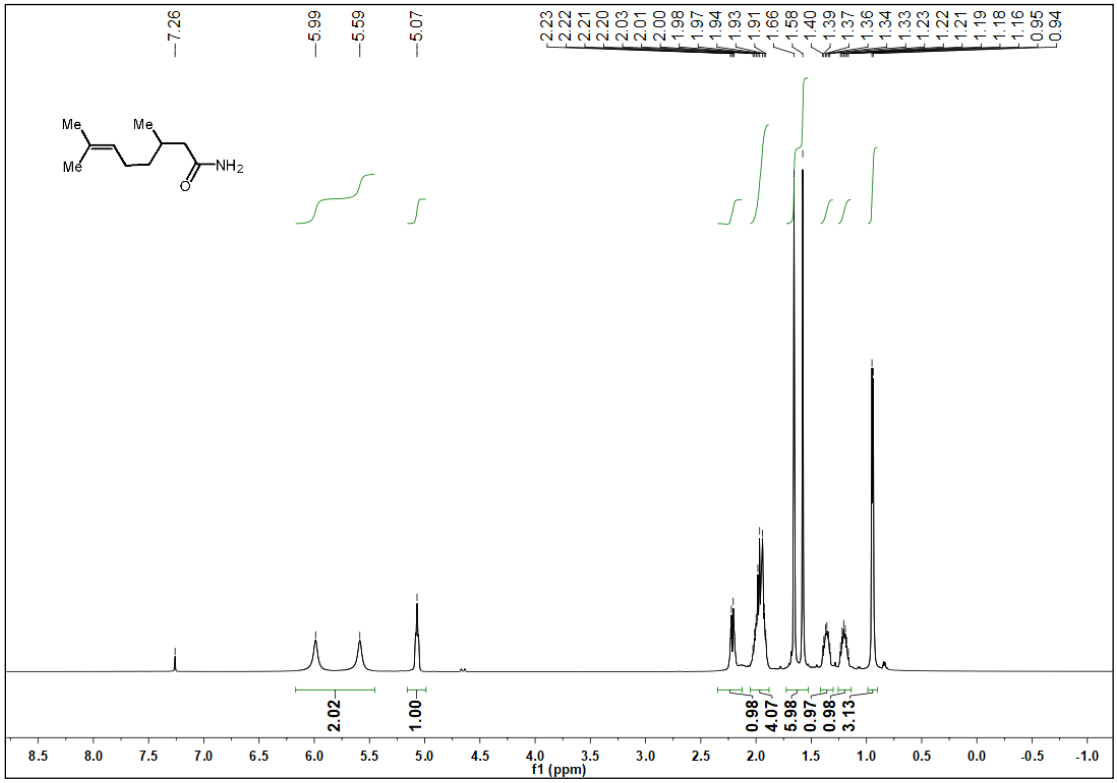



**Fig. S44** $^{1}$H NMR spectrum of **2i** in $CDCl_3$.

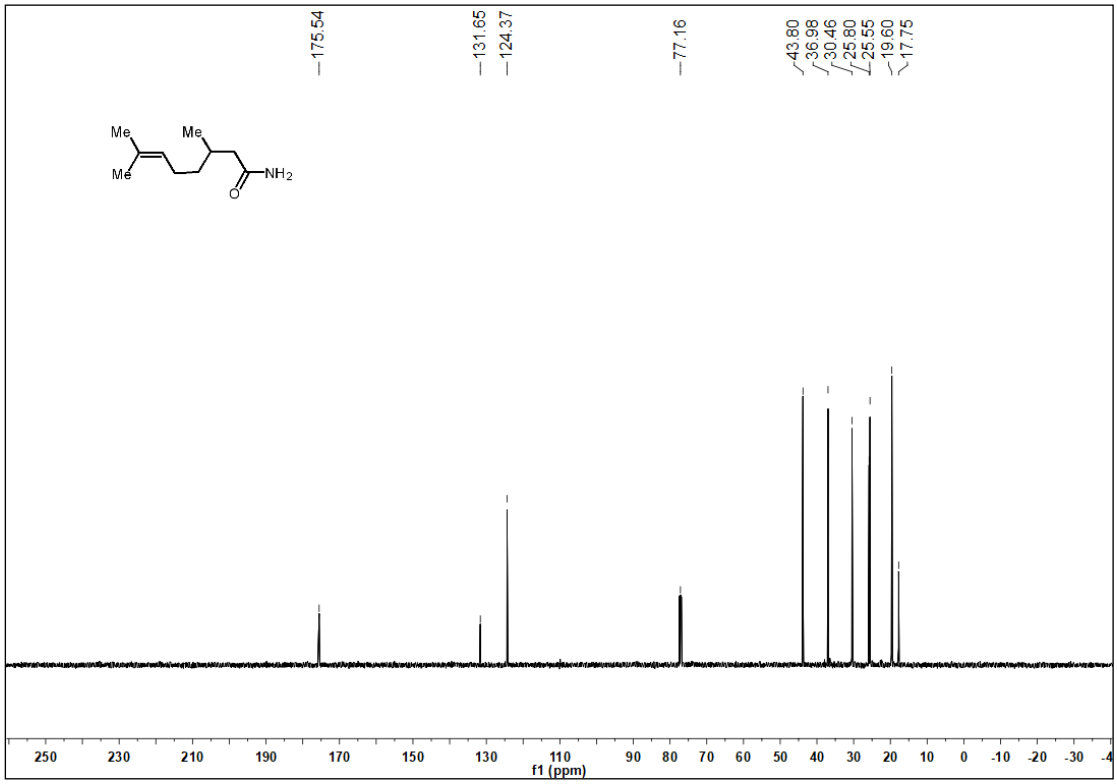



**Fig. S45** $^{13}$C NMR spectrum of **2i** in $CDCl_3$.

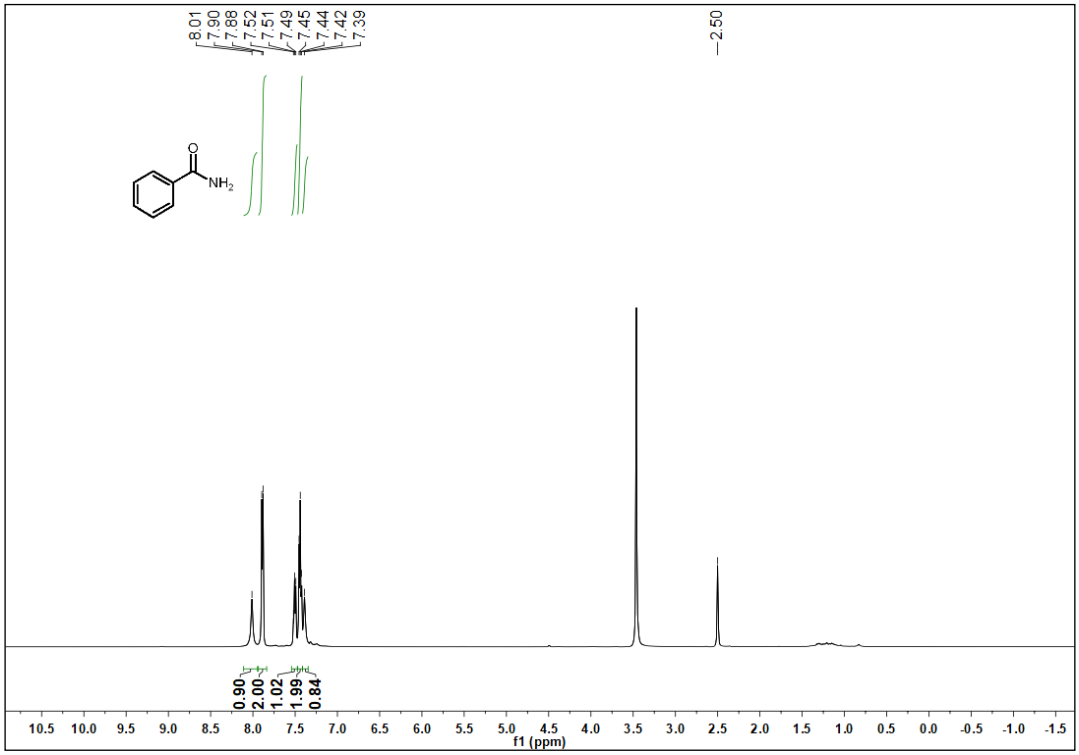



**Fig. S46** $^{1}$H NMR spectrum of **2j** in DMSO-$d_6$.

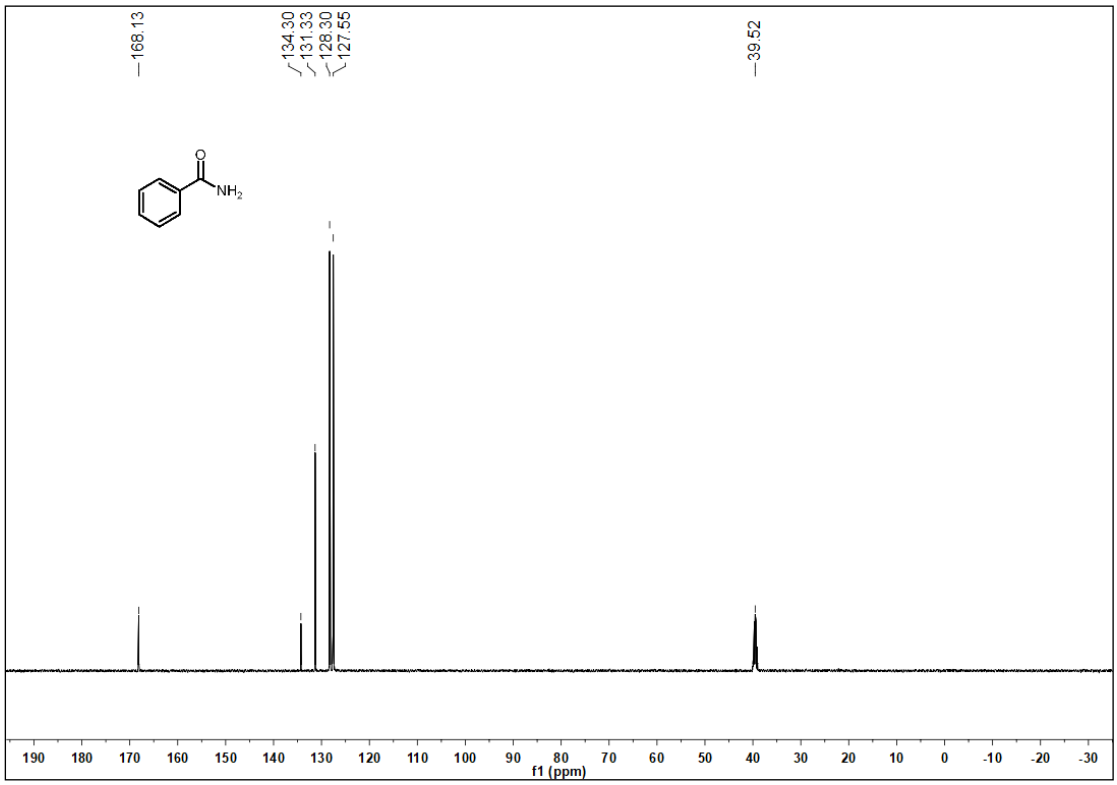



**Fig. S47** $^{13}$C NMR spectrum of **2j** in DMSO-$d_6$.

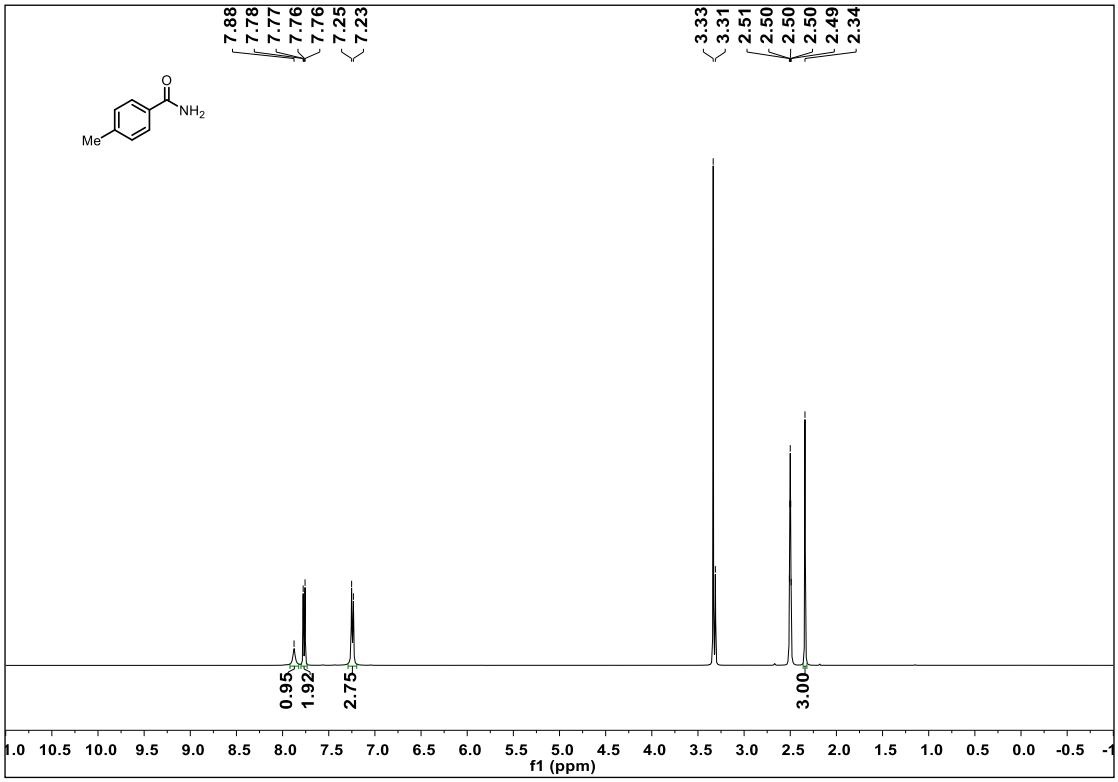



**Fig. S48** [1]H NMR spectrum of **2k** in DMSO-$d_6$.

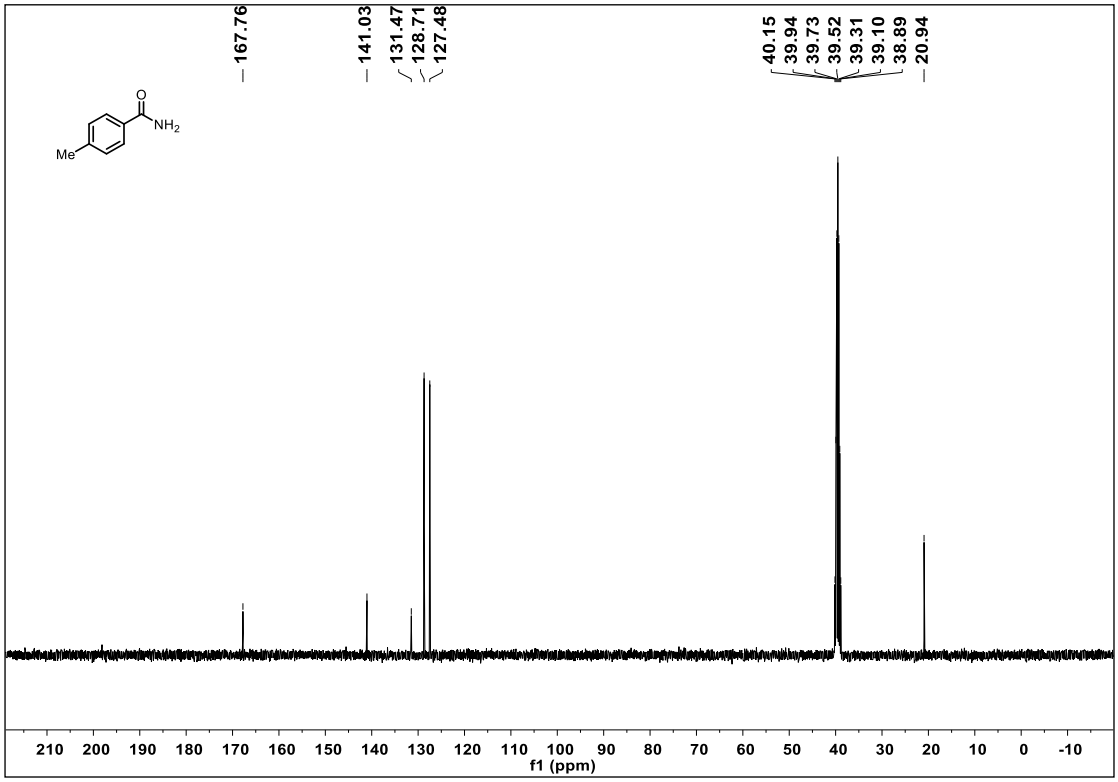



**Fig. S49** [13]C NMR spectrum of **2k** in DMSO-$d_6$.

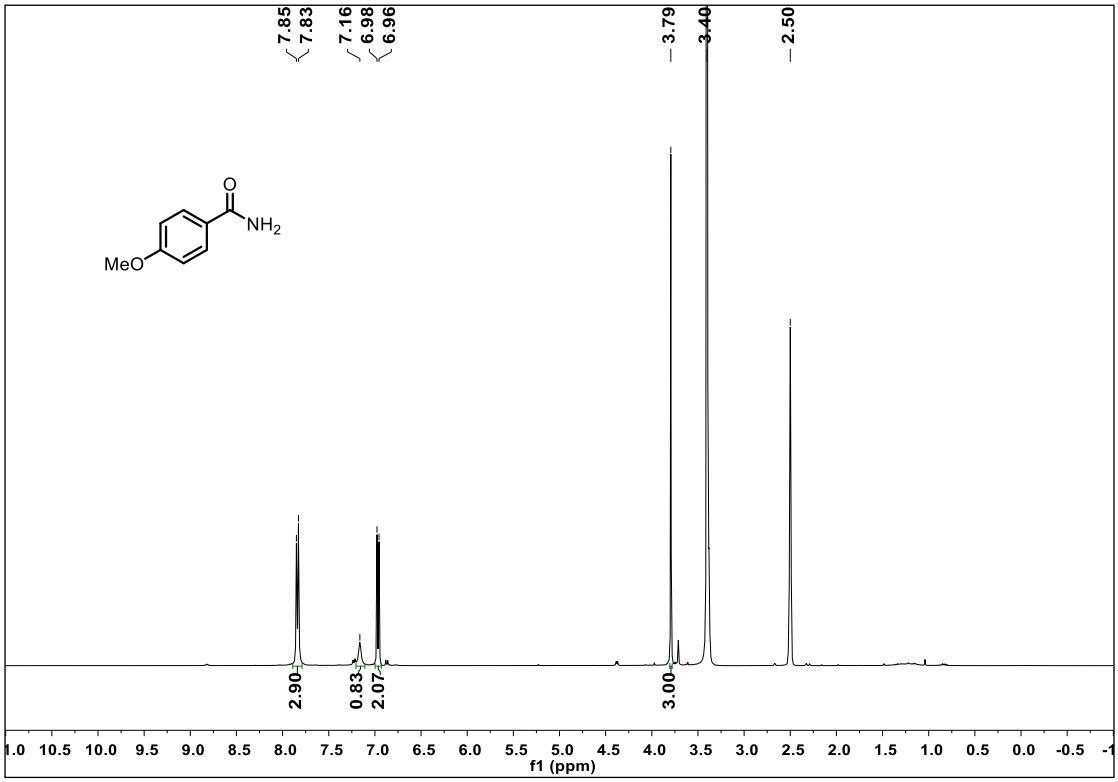
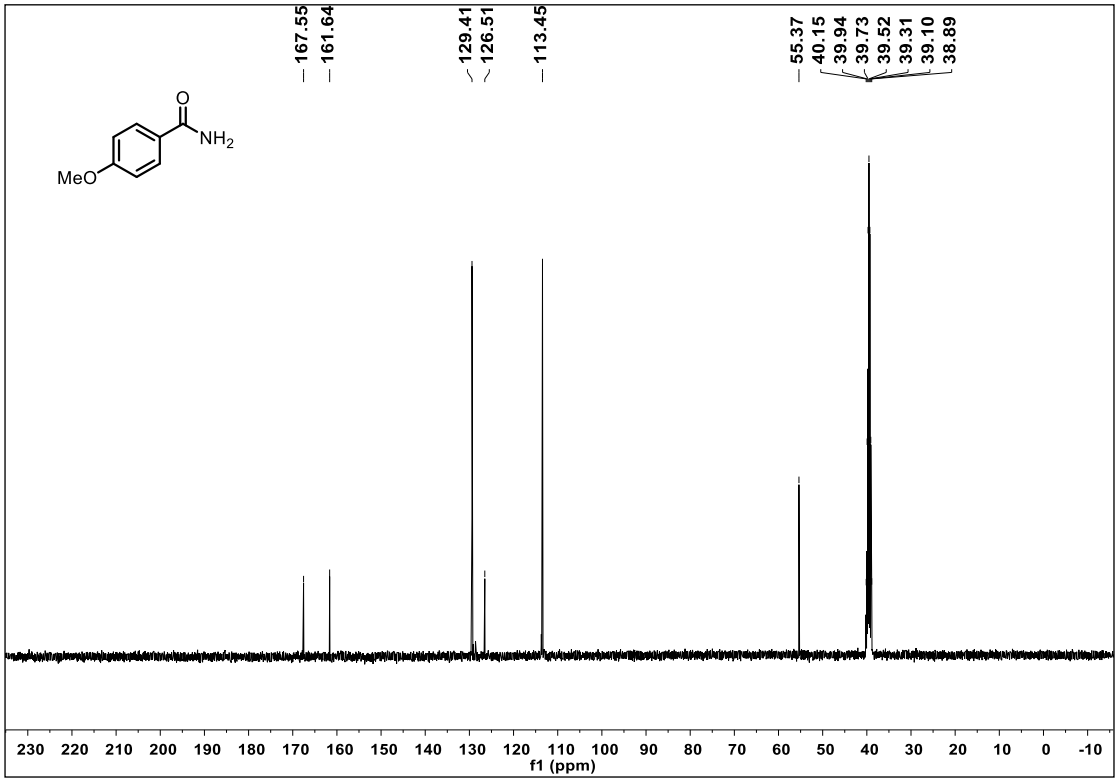



**Fig. S50** $^{1}$H NMR spectrum of **2l** in DMSO-$d_6$.




**Fig, S51** $^{13}$C NMR spectrum of **2l** in DMSO-$d_6$.

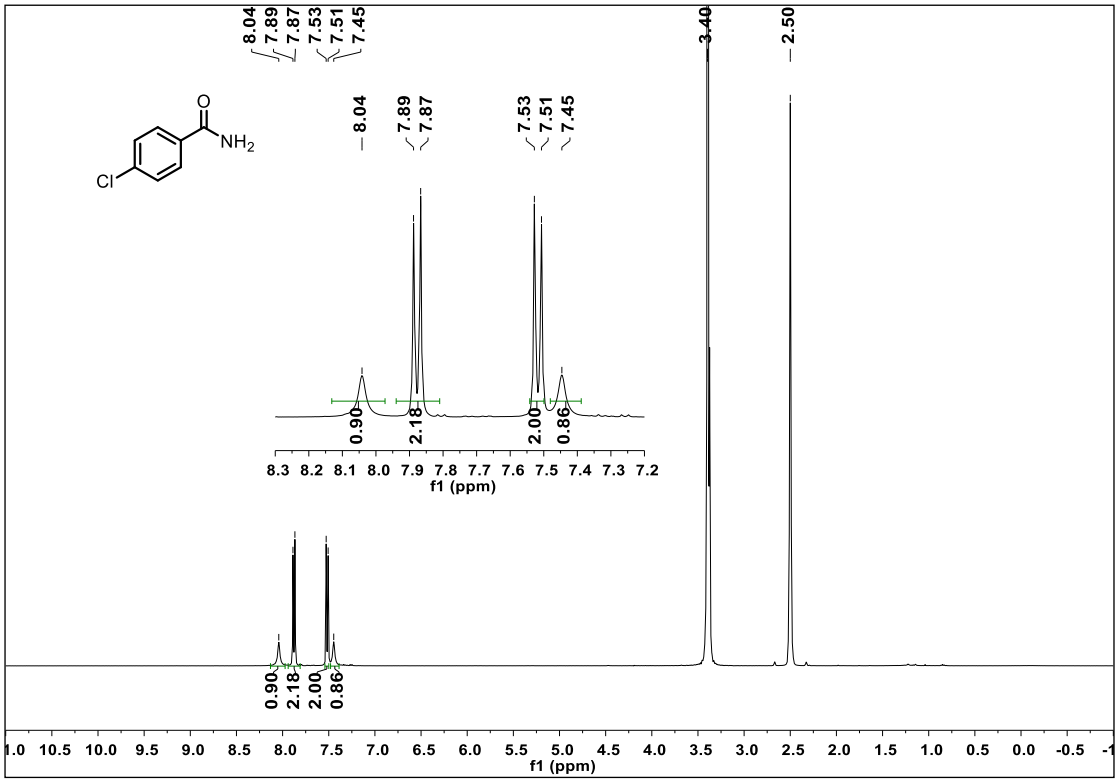



**Fig. S52** $^{1}$H NMR spectrum of **2m** in DMSO-$d_6$.

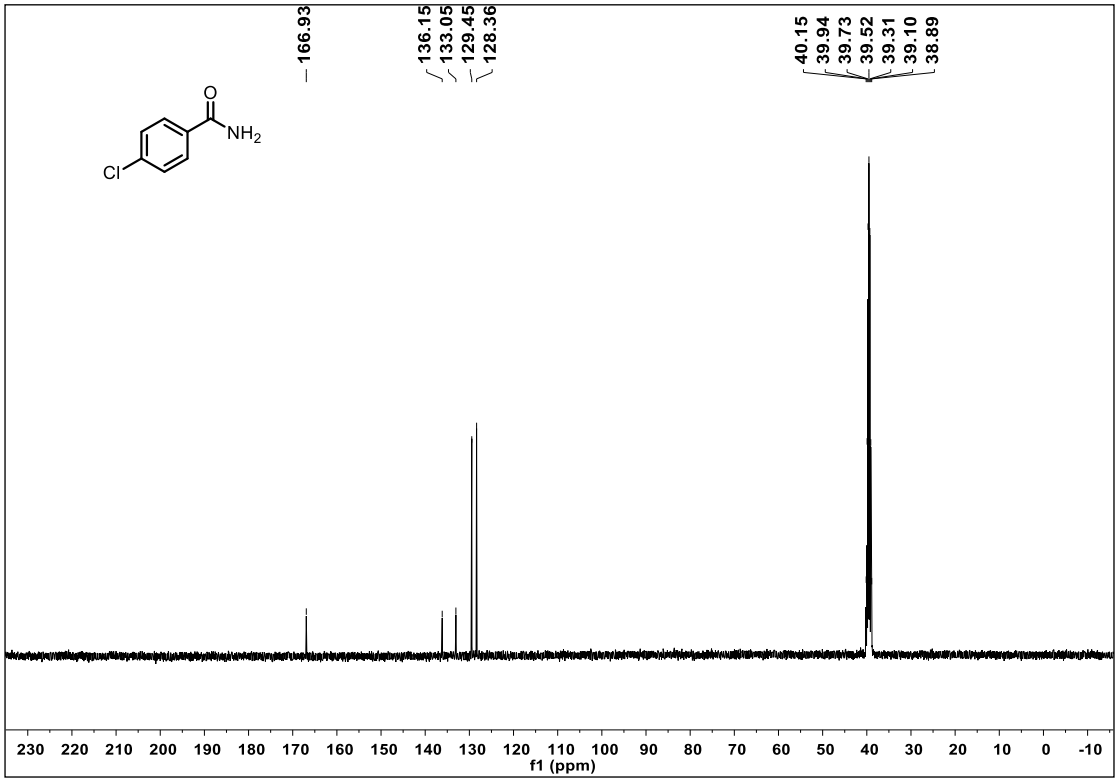



**Fig. S53** $^{13}$C NMR spectrum of **2m** in DMSO-$d_6$.

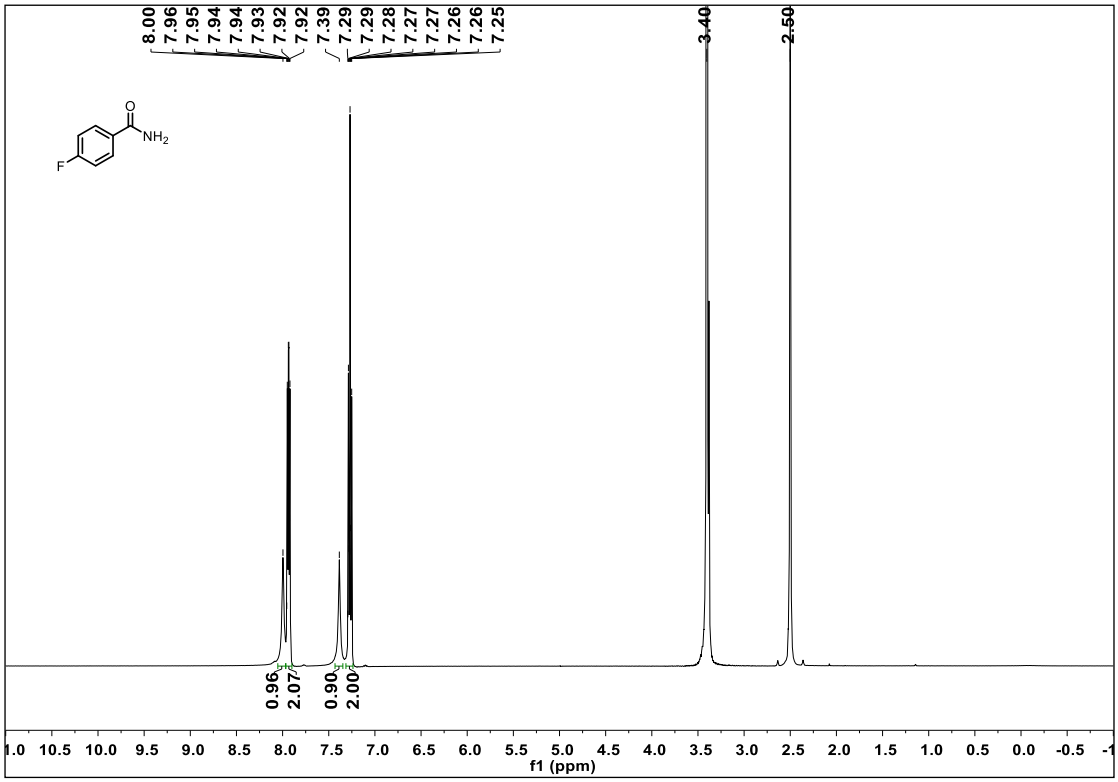



**Fig. S54** [1]H NMR spectrum of **2n** in DMSO-$d_6$.

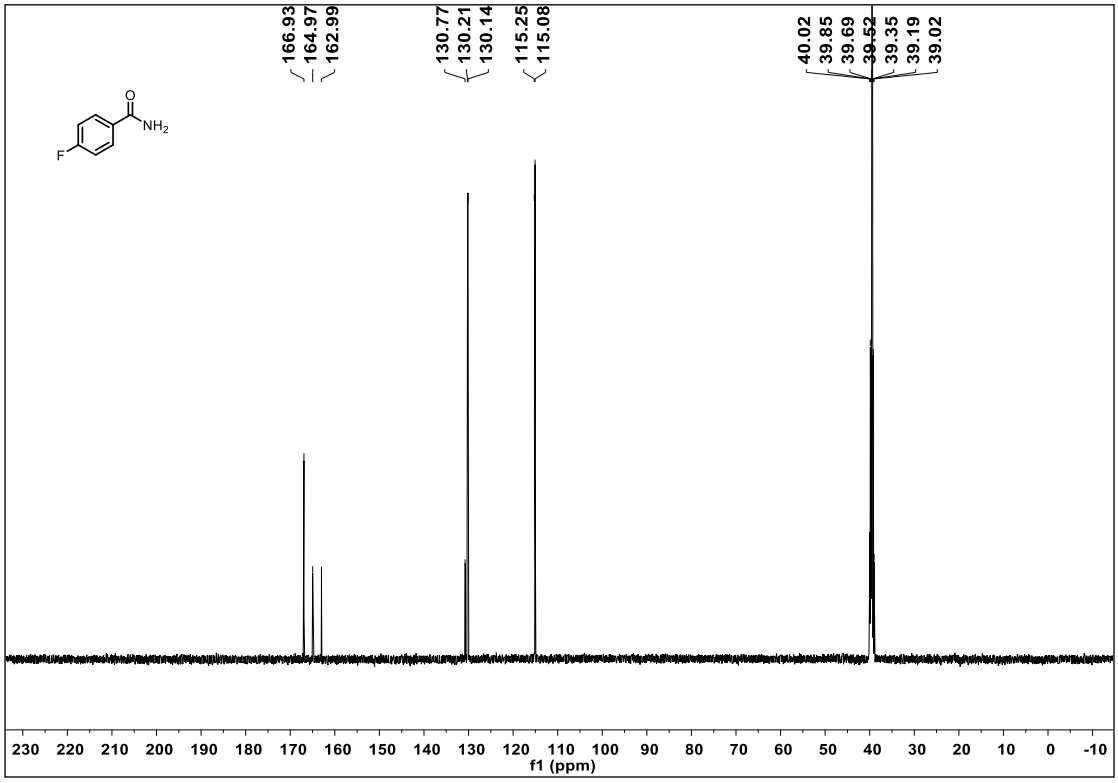



**Fig. S55** [13]C NMR spectrum of **2n** in DMSO-$d_6$.

## 6. Computational details

DFT calculations were performed with Gaussian 16 (C.01 revision)[7] using Truhlar's M06-L functional,[8] the triple-ξ def2-TZVP basis set,[9] W06 density fitting,[10] and Grimme's D3(0) empirical dispersion correction.[11] Frequency calculations at this level of theory were run at 393.15K to confirm stationary points and transition states and to obtain thermodynamic corrections. Single point energies of the M06-L optimized structures were computed with ORCA (4.2.1)[12] using the range-separated meta-GGA hybrid functional ωB97M-V of the Head-Gordon group[13] including dispersion correction,[14,15] together with the triple-ξ def2-TZVPP basis set[9] and the corresponding auxiliary basis sets, def2/J[10] and def2-TZVPP/C[16] for RIJCOSX density fitting. The functional and basis set selections are based on recent benchmark studies.[17] The polarizable continuum model (IEFPCM) was used in all calculations (optimization and single point) with the SMD solvation (Toluene) model of Truhlar and co-workers.[18]

Gibbs free energies were computed by adding the free energy correction term from the frequency calculation to the single point energy in methanol, according to

$$\mathbf{G}^{\mathbf{o}\omega\mathbf{B97M\text{-}V}}{}_{\mathbf{(Toluene,393.15K)}} = \mathbf{E}^{\omega\mathbf{B97M\text{-}V}}{}_{\mathbf{Toluene}} + \mathbf{corr}^{M06\text{-}L}{}_{freq\mathbf{(Toluene,10\ atm,393.15K)}}$$

where $\mathbf{E}^{\omega\mathbf{B97M\text{-}V}}{}_{\mathbf{Toluene}}$ is the single point energy; and

where $\mathbf{corr}^{M06\text{-}L}{}_{freq}$ is the thermal correction to the Gibbs free energy from the frequency calculation (at T = 393.15K and P = 10 atm).

Free energy values ($G^o$) were then corrected to account for changes in standard states ($G^o \rightarrow G$).

Standard state corrections[19] were employed such that all species are treated as 1M (using an ideal gas approximation), with the exception of $H_2$ (maintained as 1 atm).[19-22] Other than these standard state corrections, the transformation of hydrogen from the condensed phase to the gas phase is not additionally corrected in the free energy quantities provided.

ΔG of **Ru-8** from **Ru-5** and $H_2$ was calculated using the current method, the value of which is quite in close to the reported one by Gusev (-4.7 kcal/mol with M06-L

functionals and -5.9 kcal/mol with MN15-L functionals),[22] thus support the feasibility of this calculation method.

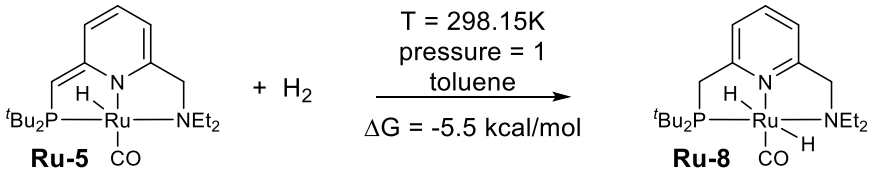



**Fig. S56** Example of a ΔG employing the current method.

Ethanol was studied as minimal model for alcohol in the system. The configurations of hemiaminal in the corresponding intermediates and transitions states have been considered. (*S*) configuration of hemiaminal in the corresponding structures is presented in Fig. 3. Configurations of hemiaminal with lower overall barriers than the other are presented in Fig. S57-61, 64, 65. Directionality of ΔG and $\Delta G_{TS}$ values are indicated by the ordering of X,Y and all energies are reported in kcal/mol. Mass balance is ensured throughout.

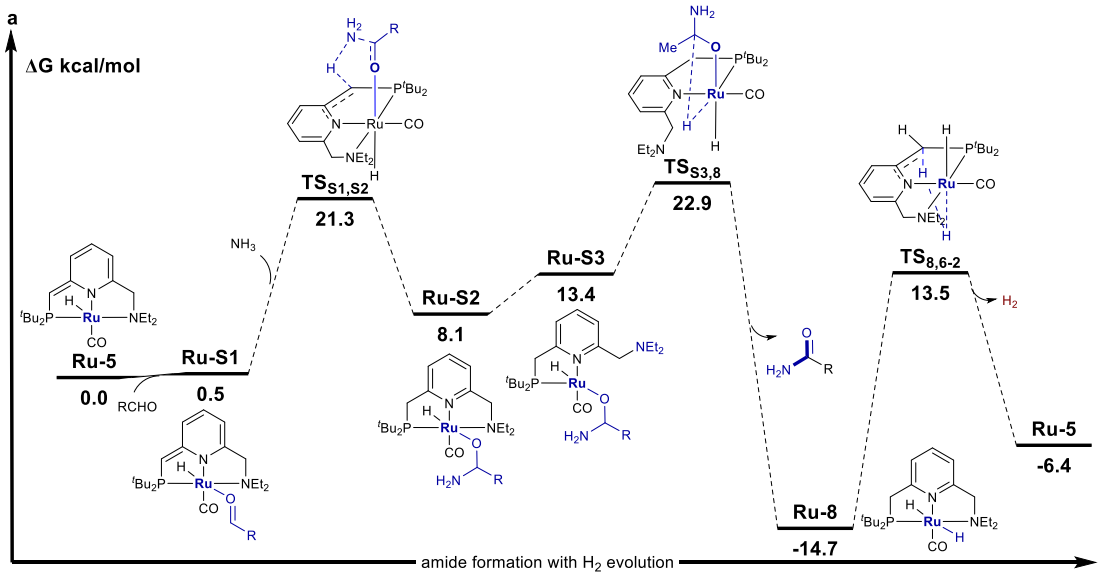



**Fig. S57** Energy profile of a pathway involving MLC and arm-opening mechanism, (*S*) configuration of hemiaminal in the corresponding structures.

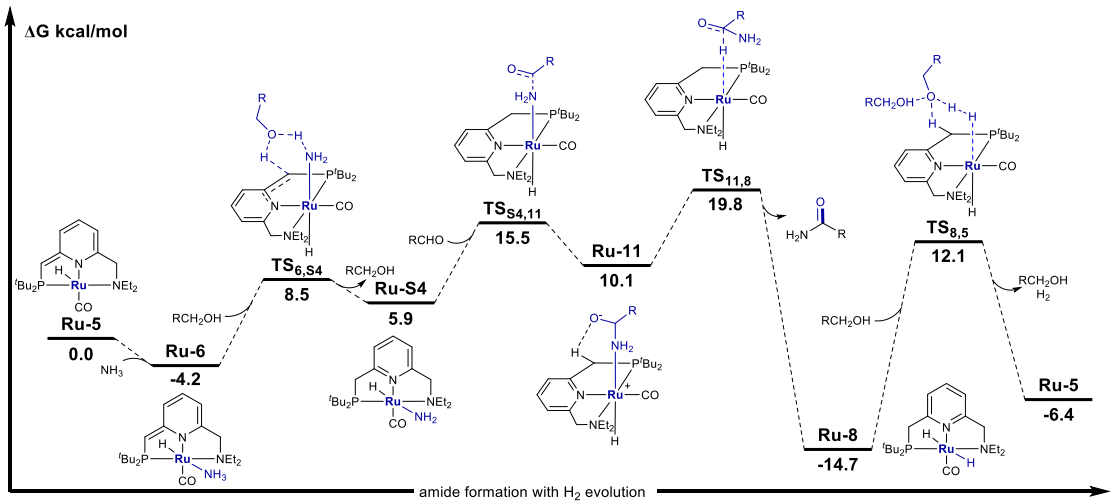



**Fig. S58** Energy profile of a pathway involving ammonia activation, (*R*) configuration of hemiaminal in the corresponding structures.

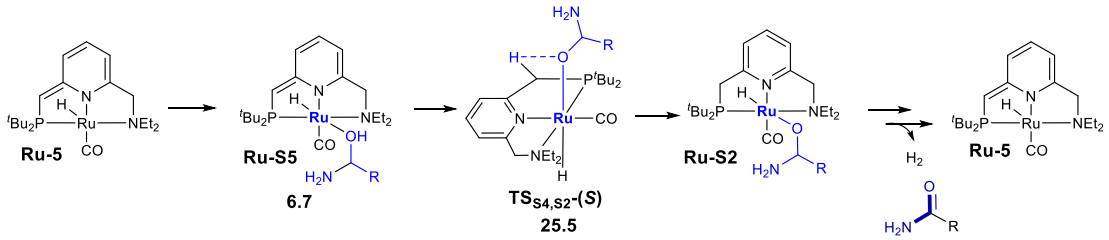



**Fig. S59** Alternative pathway involving activation of hemiaminal on **Ru-5**.

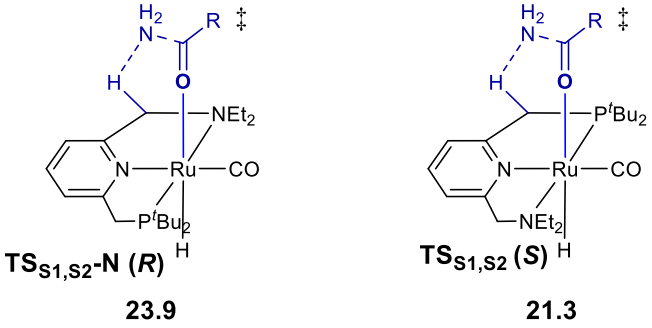



**Fig. S60** Metal ligand cooperation on *N* "arm".

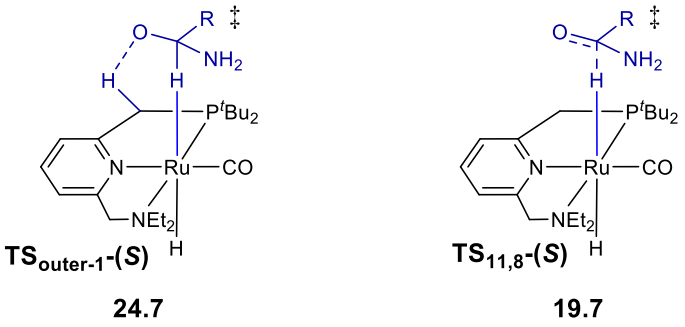



**Fig. S61** Outer-sphere dehydrogenation of hemiaminal on **Ru-5**.

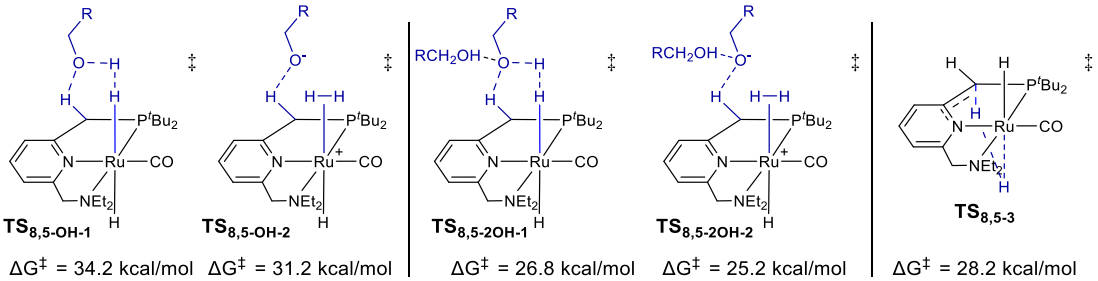



**Fig. S62** Minimizing $H_2$ elimination from **Ru-8**.

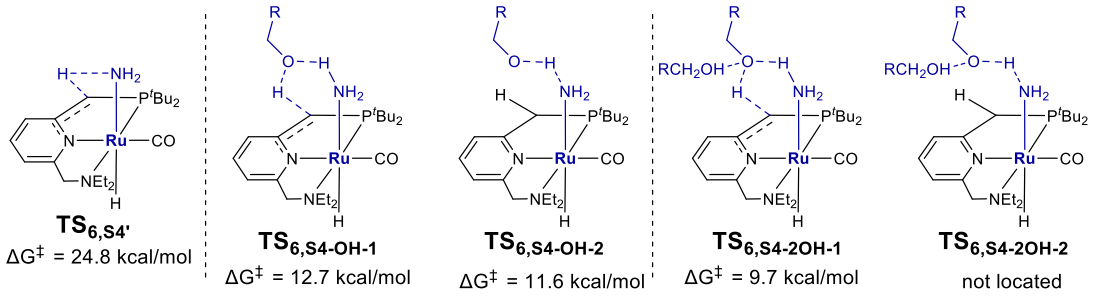



**Fig. S63** Minimizing $NH_3$ N-H activation on **Ru-6**. Although **TS$_{6,S4-2OH-2}$** was not located, which might exhibit a slightly lower kinetic barrier than **TS$_{6,S4-OH-2}$**, it didn't change the major conclusion of the computational results since (i) Such step was not the rate-determining step, (ii) and the expected energy difference $\Delta\Delta G^{‡}$ between **TS$_{6,S4-OH-2}$** and **TS$_{6,S4-2OH-2}$** should be less than 1.6 kcal/mol.

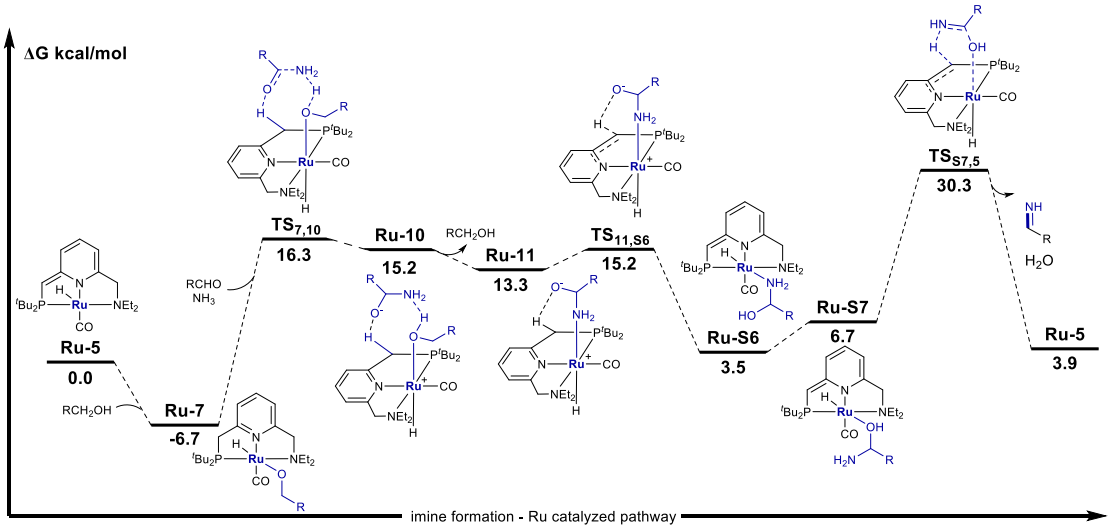



**Fig. S64** Energy profile of Ru-catalyzed imine formation, (*S*) configuration of hemiaminal in the corresponding structures.

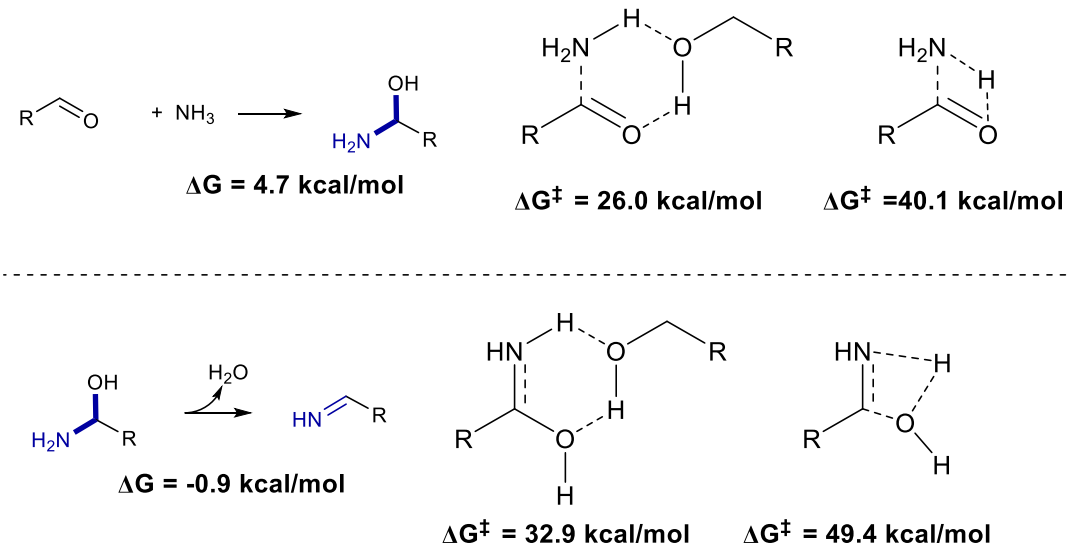



**Fig. S65** Uncatalyzed transition states for hemiaminal formation and its dehydration with or without an alcohol as a proton shuttle, (*R*) configuration of hemiaminal in the corresponding structures.

**Table S1 Energy data**

| Structure | $E^{\omega B97M\text{-}V}_{Toluene}$ | $G^{o\omega B97M\text{-}V}_{Toluene}$ | Imaginary Frequency | G *T = 393.15K* |
|---|---|---|---|---|
| Energy Unit | Hartree | Hartree | $cm^{-1}$ | kcal |
| **Ru-5** | -1404.153348 | -1403.718392 | - | -880830.7918 |
| **Ru-6** | -1460.736474 | -1460.264266 | - | -916313.328 |
| **Ru-7** | -1559.221809 | -1558.710896 | - | -978088.588 |
| **Ru-8** | -1405.354234 | -1404.89625 | - | -881569.8976 |
| **Ru-10** | -1769.619455 | -1769.02147 | - | -1110058.473 |
| **Ru-11** | -1614.571459 | -1614.042636 | - | -1012809.255 |
| **$TS_{7,10}$** | -1769.613819 | -1769.019644 | -968.9705 | -1110057.328 |
| **$TS_{11,8}$** | -1614.553495 | -1614.032554 | -710.4368 | -1012802.929 |
| **$TS_{8,5\text{-}1}$** | -1715.414648 | -1714.817193 | -41.5489 | -1076045.29 |
| **$TS_{8,5\text{-}2}$** | -1715.412009 | -1714.819714 | -1572.0743 | -1076046.871 |
| **EtOH** | -155.0333526 | -154.9857776 | - | -97251.07646 |
| **aldehyde** | -153.834057 | -153.810242 | - | -96513.42782 |
| **amide** | -209.2327504 | -209.1950424 | - | -131267.3901 |
| **hydrogen** | -1.161074769 | -1.164683769 | - | -730.8390651 |
| **ammonia** | -56.55395385 | -56.54322485 | - | -35478.37458 |

## Cartesian Coordinates

### Ru-5

Ru -0.4076850000 -0.5825650000 0.0309790000
H -0.4042540000 -0.6750100000 -1.5230200000
P 1.7480480000 0.1250690000 -0.0965510000
O 0.1843180000 -3.5205430000 -0.0085750000
N -2.7196190000 -0.4492680000 0.1067090000
N -0.7769400000 1.4935660000 -0.0382190000
C 1.5292080000 1.8242580000 -0.5033510000
C 0.2544170000 2.3536790000 -0.3808030000
C -0.0897300000 3.7274900000 -0.5632270000
H 0.6925890000 4.4230390000 -0.8374140000
C -1.3748520000 4.1518900000 -0.3966870000
H -1.6173140000 5.1973730000 -0.5465730000
C -2.3900320000 3.2494840000 -0.0217040000
H -3.4094000000 3.5706260000 0.1368340000
C -2.0309080000 1.9353840000 0.1563060000
C -2.9719770000 0.8942810000 0.6824400000
H -2.8237650000 0.8099190000 1.7641260000
H -4.0117130000 1.2015780000 0.5279440000
C -0.0463990000 -2.3762090000 0.0264140000
C 2.5138890000 0.0522320000 1.6452530000
C 2.5964570000 -1.3706150000 2.1931670000
H 2.8758400000 -1.3349170000 3.2496640000
H 1.6373730000 -1.8856150000 2.1274490000
H 3.3379260000 -1.9857200000 1.6906010000
C 3.8775630000 0.7243520000 1.7273890000
H 4.1899080000 0.8082380000 2.7720190000
H 4.6491950000 0.1542190000 1.2104730000
H 3.8602150000 1.7332230000 1.3121670000
C 1.5265060000 0.8244960000 2.5246220000
H 1.3954070000 1.8539460000 2.1933630000
H 0.5402470000 0.3494130000 2.5415870000
H 1.8883350000 0.8439810000 3.5553040000
C 2.9502430000 -0.5635420000 -1.3726820000
C 3.5941980000 -1.8665810000 -0.9153500000
H 4.3288240000 -1.7101080000 -0.1263080000
H 2.8595110000 -2.5913500000 -0.5634760000
H 4.1226660000 -2.3232140000 -1.7556700000
C 4.0379620000 0.4527330000 -1.7185980000
H 4.7295940000 0.0060620000 -2.4370080000
H 3.6193280000 1.3444390000 -2.1827970000
H 4.6248290000 0.7643050000 -0.8564440000
C 2.1394610000 -0.8366190000 -2.6394570000

H 1.4467840000 -1.6665090000 -2.5053410000
H 1.5637690000 0.0377070000 -2.9468840000
H 2.8191220000 -1.0941820000 -3.4554590000
C -3.2768520000 -0.4832790000 -1.2701900000
H -2.7366780000 0.2791940000 -1.8332220000
H -4.3264330000 -0.1624430000 -1.2386360000
C -3.1615200000 -1.8205710000 -1.9538020000
H -3.8156870000 -2.5727470000 -1.5132760000
H -3.4481760000 -1.7196220000 -2.9994530000
H -2.1387400000 -2.1953240000 -1.9231300000
C -3.2855610000 -1.5061380000 0.9798420000
H -2.9744990000 -2.4651290000 0.5670130000
H -2.7781620000 -1.4103970000 1.9424380000
C -4.7865940000 -1.4755360000 1.1731790000
H -5.0840990000 -2.2810920000 1.8429180000
H -5.1299170000 -0.5422670000 1.6185680000
H -5.3262100000 -1.6205660000 0.2375930000
H 2.3560370000 2.4858050000 -0.7258190000

## Ru-6

Ru 0.0530760000 0.4668350000 -0.7179150000
H 1.3705540000 1.2557120000 -1.0955430000
P 1.5835440000 -1.1046860000 -0.0888170000
O -0.1729310000 -0.4079900000 -3.5718740000
N -1.0436040000 2.5484580000 -0.6337080000
N 0.3825360000 1.1637490000 1.2661940000
C 2.1327010000 -0.4384620000 1.4448380000
C 1.4267060000 0.6195770000 1.9956390000
C 1.6910350000 1.2050410000 3.2715040000
H 2.4880600000 0.7892660000 3.8742200000
C 0.9703720000 2.2768220000 3.7113620000
H 1.1960750000 2.7148610000 4.6766310000
C -0.0554050000 2.8269180000 2.9199330000
H -0.6267620000 3.6862960000 3.2402220000
C -0.3090960000 2.2235710000 1.7086140000
C -1.4127680000 2.6728710000 0.7961320000
H -2.2992200000 2.0513600000 0.9552720000
H -1.7045190000 3.7001450000 1.0412450000
C -0.0945880000 -0.0787370000 -2.4516860000
C 0.8625870000 -2.8342730000 0.3028800000
C -0.0032880000 -3.3187810000 -0.8585910000
H -0.5466480000 -4.2229120000 -0.5700790000
H -0.7322360000 -2.5695650000 -1.1682380000
H 0.5815050000 -3.5657720000 -1.7428800000

C 1.8796760000 -3.9141790000 0.6557360000
H 1.3517130000 -4.8060450000 1.0062700000
H 2.4905340000 -4.2221030000 -0.1909690000
H 2.5423230000 -3.6004280000 1.4629390000
C -0.0122700000 -2.6288080000 1.5432260000
H 0.5940400000 -2.5535950000 2.4446580000
H -0.6041750000 -1.7166640000 1.4960350000
H -0.6929430000 -3.4754660000 1.6660450000
C 3.1317660000 -1.3521050000 -1.1579050000
C 2.8620500000 -2.2867640000 -2.3325330000
H 2.7155000000 -3.3210540000 -2.0262860000
H 1.9919250000 -1.9755850000 -2.9110390000
H 3.7195490000 -2.2756140000 -3.0101070000
C 4.3060480000 -1.8735530000 -0.3283460000
H 5.1766480000 -1.9906920000 -0.9784720000
H 4.5809890000 -1.1674140000 0.4546920000
H 4.1221100000 -2.8383760000 0.1358750000
C 3.5553640000 0.0037690000 -1.7205010000
H 2.8533330000 0.3773370000 -2.4637160000
H 3.6485000000 0.7568240000 -0.9371260000
H 4.5308160000 -0.1024130000 -2.2023690000
C -0.0662180000 3.6213470000 -0.9592640000
H 0.8028950000 3.4419550000 -0.3264230000
H -0.4852800000 4.5890700000 -0.6523460000
C 0.3398980000 3.6668090000 -2.4090680000
H -0.4674190000 4.0044000000 -3.0591060000
H 1.1656450000 4.3657660000 -2.5334440000
H 0.6752740000 2.6890670000 -2.7543040000
C -2.2440810000 2.6192410000 -1.4979250000
H -1.9266050000 2.3717220000 -2.5107090000
H -2.9076610000 1.8143130000 -1.1806600000
C -3.0022380000 3.9308140000 -1.4882610000
H -3.8781050000 3.8490010000 -2.1305290000
H -3.3560220000 4.2004650000 -0.4933460000
H -2.4030140000 4.7579580000 -1.8670300000
H 2.9149750000 -0.9066480000 2.0299100000
H -2.8186440000 -0.1175740000 -0.5411740000
N -2.0209680000 -0.4542620000 -0.0135860000
H -2.0298870000 -1.4622900000 -0.1177920000
H -2.2237400000 -0.2759100000 0.9645110000

## Ru-7

Ru 4.6701790000 1.1223600000 -7.2200640000
N 4.1627590000 3.3289590000 -6.6302160000

P 4.8789520000 -0.6739310000 -8.5369160000
C 2.8173530000 3.5237110000 -7.2158010000
C 4.1032000000 3.4476250000 -5.1527260000
C 5.1045430000 4.2939640000 -7.2462600000
N 3.4367570000 1.8348810000 -8.8126430000
O 2.7197610000 0.8782490000 -6.2473780000
C 5.7853940000 0.5202000000 -5.9112940000
H 5.9450810000 1.6708050000 -8.0515330000
C 3.6595640000 -2.0891610000 -8.2404220000
C 6.5760730000 -1.3896490000 -8.9761400000
C 4.3237740000 0.0439470000 -10.1595230000
C 2.6907800000 2.9238300000 -8.5800200000
H 2.1183810000 2.9930970000 -6.5649000000
H 2.5440010000 4.5841330000 -7.2437890000
C 3.6508770000 4.7885390000 -4.6155870000
H 5.0934850000 3.1986650000 -4.7722070000
H 3.4340600000 2.6519630000 -4.8291460000
C 6.4937990000 4.2618190000 -6.6634670000
H 4.6868160000 5.3069900000 -7.1668930000
H 5.1374020000 4.0530120000 -8.3103610000
C 3.3752060000 1.1839100000 -9.9854500000
C 2.4634670000 0.2367550000 -5.0606920000
O 6.5174520000 0.1438180000 -5.0841950000
C 3.7289890000 -3.2517460000 -9.2225590000
C 2.2730750000 -1.4452880000 -8.3447490000
C 3.8523760000 -2.6092830000 -6.8160210000
C 7.6067140000 -0.2622650000 -8.9649060000
C 6.9880530000 -2.4172330000 -7.9244540000
C 6.6123560000 -2.0314770000 -10.3644080000
H 5.2331850000 0.4367800000 -10.6250220000
H 3.9258820000 -0.7037050000 -10.8482980000
C 1.8165330000 3.4009460000 -9.5438940000
H 3.6506070000 4.7618610000 -3.5265530000
H 4.3065070000 5.6064070000 -4.9165170000
H 2.6368460000 5.0385420000 -4.9285350000
H 7.1620460000 4.8632240000 -7.2783060000
H 6.8854670000 3.2450440000 -6.6387930000
H 6.5303740000 4.6706220000 -5.6541390000
C 2.4952570000 1.6031330000 -10.9726680000
C 1.2411290000 0.8271640000 -4.3765940000
H 3.3159250000 0.2828150000 -4.3507530000
H 2.2726230000 -0.8493170000 -5.1930520000
H 4.6445240000 -3.8338030000 -9.1279980000
H 3.6317240000 -2.9306100000 -10.2608930000

H 2.8979110000 -3.9334610000 -9.0233410000
H 2.1853770000 -0.5626100000 -7.7033500000
H 1.5207640000 -2.1728700000 -8.0303330000
H 2.0301260000 -1.1660990000 -9.3719680000
H 2.9884370000 -3.2124750000 -6.5277160000
H 3.9387040000 -1.7941760000 -6.0986980000
H 4.7324070000 -3.2413600000 -6.7171340000
H 7.7319180000 0.1695980000 -7.9743680000
H 7.3452370000 0.5499100000 -9.6439620000
H 8.5699860000 -0.6659150000 -9.2864880000
H 6.8874860000 -2.0315090000 -6.9095810000
H 6.4167720000 -3.3410400000 -7.9970470000
H 8.0387280000 -2.6781850000 -8.0691640000
H 5.8906080000 -2.8323060000 -10.4959780000
H 6.4556590000 -1.3025090000 -11.1591690000
H 7.6029560000 -2.4628470000 -10.5260430000
C 1.7098880000 2.7208920000 -10.7450050000
H 1.2252920000 4.2843840000 -9.3443260000
H 2.4402940000 1.0628140000 -11.9079380000
H 1.3955800000 1.8819480000 -4.1342630000
H 0.3732410000 0.7689570000 -5.0363820000
H 0.9965630000 0.3034670000 -3.4496620000
H 1.0230780000 3.0664980000 -11.5068380000

## Ru-8

Ru -0.4368030000 -0.6193900000 0.0980540000
H -0.4709590000 -0.7514930000 -1.5942490000
P 1.7076420000 -0.0125320000 -0.0700930000
O 0.0719850000 -3.5327200000 0.5632350000
N -2.7459200000 -0.4094680000 0.1195500000
N -0.7613960000 1.4602190000 -0.2205670000
C 1.5185360000 1.5953140000 -0.9863320000
C 0.2160930000 2.2595490000 -0.6828540000
C -0.0231850000 3.6117330000 -0.8786390000
H 0.7727700000 4.2487860000 -1.2402890000
C -1.2846720000 4.1234840000 -0.6219990000
H -1.4883940000 5.1742590000 -0.7814970000
C -2.2835470000 3.2799260000 -0.1627610000
H -3.2783740000 3.6489890000 0.0472650000
C -1.9842070000 1.9443420000 0.0432280000
C -2.9266840000 0.9586970000 0.6535360000
H -2.7018790000 0.9073480000 1.7240060000
H -3.9610900000 1.3026190000 0.5420140000
C -0.1280770000 -2.3975220000 0.3776450000

C 2.5762570000 0.5056300000 1.5392830000
C 2.4982850000 -0.6482980000 2.5368900000
H 2.8856760000 -0.3183780000 3.5037660000
H 1.4671480000 -0.9714820000 2.6786140000
H 3.0855100000 -1.5123190000 2.2309780000
C 4.0218680000 0.9629540000 1.3848380000
H 4.3764920000 1.3511520000 2.3431610000
H 4.6960690000 0.1560310000 1.1036970000
H 4.1297300000 1.7694220000 0.6577690000
C 1.7739790000 1.6782050000 2.1085030000
H 1.8813830000 2.5843480000 1.5103560000
H 0.7147380000 1.4358050000 2.1977900000
H 2.1458330000 1.9112630000 3.1085790000
C 2.9312610000 -0.9616360000 -1.1606500000
C 3.5376370000 -2.1131830000 -0.3618910000
H 4.2336030000 -1.7748190000 0.4037890000
H 2.7724880000 -2.7240020000 0.1179370000
H 4.0959910000 -2.7655710000 -1.0370120000
C 4.0427900000 -0.0882310000 -1.7436540000
H 4.6891220000 -0.7118310000 -2.3659010000
H 3.6517630000 0.6976260000 -2.3898220000
H 4.6761880000 0.3759880000 -0.9939560000
C 2.1574220000 -1.5603040000 -2.3343350000
H 1.4049550000 -2.2744300000 -2.0078790000
H 1.6435940000 -0.8026460000 -2.9261300000
H 2.8627400000 -2.0758560000 -2.9909900000
C -3.3367730000 -0.4784750000 -1.2409570000
H -2.7704090000 0.2237080000 -1.8545200000
H -4.3711170000 -0.1101480000 -1.2051480000
C -3.2903470000 -1.8542860000 -1.8516930000
H -3.9855790000 -2.5447480000 -1.3745150000
H -3.5622100000 -1.7981560000 -2.9046770000
H -2.2838590000 -2.2687730000 -1.7869010000
C -3.3442570000 -1.4040090000 1.0482770000
H -3.0605980000 -2.3903570000 0.6838210000
H -2.8254390000 -1.2724100000 1.9973490000
C -4.8446040000 -1.3203410000 1.2287200000
H -5.1650780000 -2.0780530000 1.9425110000
H -5.1656960000 -0.3555800000 1.6215890000
H -5.3882970000 -1.5037890000 0.3016750000
H 1.5127780000 1.3145190000 -2.0445300000
H 2.3566550000 2.2821560000 -0.8512510000
H -0.5964480000 -0.3503380000 1.7865880000

## Ru-10

Ru 4.1445220000 2.7400600000 -6.6948860000
N 2.1650930000 3.7954710000 -6.1786040000
P 5.8783220000 2.0165060000 -7.9455540000
C 1.2362980000 3.4355210000 -7.2816240000
C 1.6035770000 3.3026010000 -4.8876930000
C 2.3566580000 5.2696250000 -6.1780240000
N 3.2096860000 2.9926090000 -8.5908680000
O 2.8967100000 0.7723130000 -6.4787450000
C 4.9987250000 2.5975590000 -5.0844540000
H 4.8082810000 4.1577070000 -6.8994110000
C 6.0295700000 0.1539790000 -8.2283880000
C 7.5997470000 2.7664920000 -7.7086110000
C 5.3731840000 2.6641760000 -9.6091250000
C 1.8989030000 3.2919360000 -8.5955760000
H 0.7265320000 2.4685910000 -7.0149790000
H 0.4271620000 4.1704550000 -7.3572000000
C 0.2982830000 3.9372720000 -4.4628910000
H 2.3717560000 3.4411920000 -4.1261100000
H 1.4484900000 2.2354420000 -5.0251300000
C 3.1919110000 5.7932390000 -5.0388420000
H 1.3703670000 5.7505630000 -6.1688200000
H 2.8157220000 5.5216090000 -7.1353880000
C 3.8922510000 2.8155410000 -9.7390770000
C 2.6130620000 -0.0046300000 -5.3174670000
O 5.5536720000 2.5335270000 -4.0629020000
C 7.2047560000 -0.2951010000 -9.0878860000
C 4.7427780000 -0.2796860000 -8.9369120000
C 6.0963400000 -0.5217620000 -6.8601080000
C 7.4421670000 4.2177420000 -7.2547730000
C 8.3451370000 2.0103580000 -6.6110010000
C 8.4327890000 2.7745660000 -8.9914690000
H 5.8099690000 3.6654770000 -9.6801720000
H 5.7951770000 2.0892150000 -10.4352370000
C 1.1995390000 3.3522380000 -9.7973840000
H -0.0392650000 3.4698590000 -3.5388190000
H 0.3832220000 5.0077830000 -4.2718920000
H -0.4857170000 3.7726600000 -5.2007660000
H 3.3753750000 6.8576650000 -5.1803010000
H 4.1578750000 5.2917510000 -4.9871800000
H 2.6953960000 5.6777540000 -4.0760120000
C 3.2342530000 2.8436570000 -10.9566410000
C 2.7351770000 -1.4855900000 -5.5845320000
H 1.5980360000 0.2273420000 -4.9746300000

H 3.3135180000 0.3159840000 -4.5416630000
H 8.1699420000 -0.1338960000 -8.6116450000
H 7.2158000000 0.1918450000 -10.0639250000
H 7.1165570000 -1.3690260000 -9.2706290000
H 3.8478660000 0.0608910000 -8.4206880000
H 4.7045790000 -1.3712020000 -8.9667760000
H 4.7064000000 0.0681720000 -9.9702560000
H 6.0263840000 -1.6050370000 -6.9818130000
H 5.2741220000 -0.1992240000 -6.2229930000
H 7.0282920000 -0.3155050000 -6.3370520000
H 6.9864670000 4.2930900000 -6.2697200000
H 6.8400270000 4.8116840000 -7.9432940000
H 8.4320920000 4.6768750000 -7.2045390000
H 7.7549300000 1.9244880000 -5.6985130000
H 8.6460100000 1.0107010000 -6.9188790000
H 9.2567190000 2.5549530000 -6.3560630000
H 8.6131560000 1.7861660000 -9.4024720000
H 7.9837650000 3.3887620000 -9.7717460000
H 9.4089160000 3.2124740000 -8.7715940000
C 1.8706110000 3.1030410000 -10.9785840000
H 0.1418450000 3.5803700000 -9.7867100000
H 3.7870970000 2.6799420000 -11.8713580000
H 2.0628430000 -1.7890490000 -6.3878410000
H 3.7476210000 -1.7719570000 -5.8664550000
H 2.4593400000 -2.0542720000 -4.6958240000
H 1.3392600000 3.1287170000 -11.9213030000
N 0.9064110000 0.1135060000 -8.1928250000
H 2.1641540000 0.5837040000 -7.1526490000
H 0.6809700000 0.8115450000 -8.8993860000
H 0.9899950000 -0.7646480000 -8.7004210000
O -0.2617400000 1.1072680000 -6.4075910000
C -0.2738380000 0.0565610000 -7.2054730000
H -0.0850840000 -0.9210800000 -6.6847450000
C -1.5720400000 -0.1038340000 -7.9994380000
H -1.7382410000 0.7910500000 -8.6065190000
H -1.5696030000 -0.9754220000 -8.6609160000
H -2.4181250000 -0.1981570000 -7.3177940000

## Ru-11

Ru -0.5364080000 0.2847170000 0.7998960000
H -1.7254170000 0.8218860000 1.7195290000
P -2.1937310000 -0.8975510000 -0.1767270000
O 0.0117170000 -1.7232590000 2.9445360000
N 0.5530900000 2.2384250000 1.5517970000

N -1.0797940000 1.7446310000 -0.6658420000
C -2.3372090000 0.0215380000 -1.7658490000
C -2.0004210000 1.4577630000 -1.6047170000
C -2.5015960000 2.4679720000 -2.4174150000
H -3.2396120000 2.2287710000 -3.1706980000
C -2.0408460000 3.7607890000 -2.2558740000
H -2.4322230000 4.5587670000 -2.8734790000
C -1.0578810000 4.0275390000 -1.3127640000
H -0.6538400000 5.0228150000 -1.1873090000
C -0.5828650000 2.9855250000 -0.5388010000
C 0.6055720000 3.1149700000 0.3635610000
H 1.4807170000 2.8178500000 -0.2213040000
H 0.7552410000 4.1624220000 0.6471760000
C -0.1902700000 -0.9463900000 2.0977980000
C -1.9947870000 -2.7135410000 -0.6753890000
C -2.4238980000 -3.6401940000 0.4599260000
H -2.1354590000 -4.6620690000 0.2035180000
H -1.9220640000 -3.3940080000 1.3963570000
H -3.4965380000 -3.6485430000 0.6402090000
C -2.7482580000 -3.0515600000 -1.9610780000
H -2.6038460000 -4.1108260000 -2.1862460000
H -3.8200420000 -2.8799740000 -1.8999170000
H -2.3597610000 -2.4918590000 -2.8114270000
C -0.5080980000 -2.9593490000 -0.9289970000
H -0.1030110000 -2.2715760000 -1.6779090000
H 0.0658510000 -2.8690440000 -0.0045390000
H -0.3804480000 -3.9832120000 -1.2898840000
C -3.9124040000 -0.6628720000 0.6045680000
C -3.8940700000 -1.0698880000 2.0765390000
H -3.6788250000 -2.1258050000 2.2252610000
H -3.1586650000 -0.4957060000 2.6386500000
H -4.8747240000 -0.8749040000 2.5169540000
C -5.0210200000 -1.4168720000 -0.1277060000
H -5.9837440000 -1.1361840000 0.3064550000
H -5.0650660000 -1.1588700000 -1.1863390000
H -4.9403950000 -2.4977070000 -0.0440980000
C -4.2676910000 0.8243510000 0.5204330000
H -3.4895340000 1.4656030000 0.9336330000
H -4.4700140000 1.1404120000 -0.5030150000
H -5.1795640000 1.0016540000 1.0947500000
C -0.2834250000 2.9133050000 2.5815760000
H -1.2747820000 3.0284780000 2.1411280000
H 0.1081780000 3.9266160000 2.7408280000
C -0.3727270000 2.1859150000 3.8964560000

H 0.5784330000 2.1706240000 4.4281230000
H -1.0908590000 2.6913660000 4.5406920000
H -0.7092920000 1.1590670000 3.7628790000
C 1.9218030000 1.9582740000 2.0524060000
H 1.8303420000 1.1993040000 2.8291920000
H 2.4598540000 1.4908360000 1.2279950000
C 2.7020210000 3.1508390000 2.5631410000
H 3.7036910000 2.8332060000 2.8492120000
H 2.8149890000 3.9270660000 1.8062190000
H 2.2446650000 3.6017880000 3.4431940000
H -1.4875230000 -0.3736300000 -2.3589170000
H 1.3253410000 -1.2701640000 -0.3722940000
N 1.3127390000 -0.2686100000 -0.5302450000
H 2.1893860000 0.0448140000 -0.1145160000
C 1.4614720000 -0.1341830000 -2.1151930000
O 0.3835840000 -0.4968090000 -2.7428280000
H -3.2767230000 -0.1334670000 -2.2970830000
H 2.3523690000 -0.7989350000 -2.2924750000
C 1.9245080000 1.2953470000 -2.3981310000
H 2.7589960000 1.6231370000 -1.7683360000
H 2.2557360000 1.3560750000 -3.4350670000
H 1.0917330000 1.9907070000 -2.2894690000

**$TS_{7,10}$**

Ru 4.1273640000 2.7555670000 -6.6603200000
N 2.1711000000 3.8596960000 -6.1212050000
P 5.8283800000 2.0069060000 -7.9305140000
C 1.2211180000 3.5086270000 -7.2053670000
C 1.6282020000 3.3853700000 -4.8190430000
C 2.3857340000 5.3303760000 -6.1356940000
N 3.1661040000 3.0245010000 -8.5435630000
O 2.8087830000 0.8981980000 -6.4081000000
C 5.0135840000 2.6224730000 -5.0693750000
H 4.8149030000 4.1701690000 -6.8995520000
C 5.9455410000 0.1419800000 -8.2296560000
C 7.5702500000 2.7176300000 -7.7195940000
C 5.3134980000 2.6687370000 -9.5869760000
C 1.8629360000 3.3487300000 -8.5335240000
H 0.6943490000 2.5607130000 -6.9627060000
H 0.4221000000 4.2550430000 -7.2751080000
C 0.3235750000 4.0166290000 -4.3852220000
H 2.4032080000 3.5430200000 -4.0682630000
H 1.5041030000 2.3115390000 -4.9307070000
C 3.2484270000 5.8501620000 -5.0154610000

H 1.4081410000 5.8289610000 -6.1161250000
H 2.8346050000 5.5653220000 -7.1021090000
C 3.8341230000 2.8456120000 -9.7002650000
C 2.8047100000 0.0930620000 -5.2616490000
O 5.5927650000 2.5716690000 -4.0596930000
C 7.0845830000 -0.3275990000 -9.1249940000
C 4.6243320000 -0.2513200000 -8.8948310000
C 6.0277150000 -0.5498400000 -6.8704790000
C 7.4586740000 4.1678640000 -7.2505650000
C 8.3171310000 1.9322940000 -6.6436850000
C 8.3794240000 2.7169200000 -9.0177690000
H 5.7649070000 3.6637100000 -9.6562520000
H 5.7170260000 2.0928970000 -10.4217650000
C 1.1489890000 3.4288420000 -9.7243810000
H 0.0086580000 3.5746050000 -3.4409000000
H 0.4049950000 5.0922380000 -4.2254630000
H -0.4752340000 3.8330650000 -5.1029550000
H 3.4533080000 6.9081730000 -5.1742980000
H 4.2036070000 5.3277900000 -4.9716610000
H 2.7636860000 5.7594060000 -4.0439460000
C 3.1624130000 2.8956880000 -10.9100030000
C 2.6606830000 -1.3832260000 -5.5751920000
H 1.9905450000 0.3803580000 -4.5740540000
H 3.7321510000 0.2530140000 -4.6947320000
H 8.0662750000 -0.1927650000 -8.6744420000
H 7.0811110000 0.1662260000 -10.0976750000
H 6.9667370000 -1.3979560000 -9.3128380000
H 3.7732040000 0.1098200000 -8.3201540000
H 4.5571720000 -1.3410860000 -8.9429990000
H 4.5492880000 0.1179100000 -9.9188650000
H 5.9263380000 -1.6298200000 -7.0006720000
H 5.2284610000 -0.2122060000 -6.2119380000
H 6.9757510000 -0.3742780000 -6.3658610000
H 7.0146560000 4.2470920000 -6.2605870000
H 6.8660530000 4.7843420000 -7.9272190000
H 8.4620510000 4.5979050000 -7.2069320000
H 7.7420080000 1.8511710000 -5.7211080000
H 8.5868120000 0.9289560000 -6.9679430000
H 9.2466820000 2.4513760000 -6.4005840000
H 8.5222210000 1.7291590000 -9.4448970000
H 7.9346450000 3.3546740000 -9.7814380000
H 9.3723400000 3.1224970000 -8.8112930000
C 1.8031650000 3.1782540000 -10.9156540000
H 0.0945030000 3.6683030000 -9.6967410000

H 3.7026540000 2.7316830000 -11.8323660000
H 1.6855500000 -1.6080100000 -6.0099160000
H 3.4271930000 -1.7165830000 -6.2765440000
H 2.7532280000 -1.9809440000 -4.6674030000
H 1.2622400000 3.2200900000 -11.8522930000
N 1.0957740000 0.1026610000 -8.0626930000
H 1.9338230000 0.5182160000 -7.2379650000
H 1.0491430000 0.7208560000 -8.8700240000
H 1.3711380000 -0.8140980000 -8.4087340000
O -0.6863340000 1.2967920000 -7.0420630000
C -0.3672470000 0.0983140000 -7.4087250000
H -0.2047480000 -0.6484650000 -6.5857230000
C -1.2868220000 -0.5412960000 -8.4478660000
H -1.3532300000 0.1020220000 -9.3287780000
H -0.9616690000 -1.5369650000 -8.7624750000
H -2.2901270000 -0.6307910000 -8.0317820000

**$TS_{11,8}$**

Ru -1.1305510000 0.6880960000 -0.4323420000
H -1.9691250000 0.5806490000 -1.8209160000
P -2.3634480000 -1.0534060000 0.2843240000
O -3.0140890000 2.8109940000 0.5142900000
N 0.4029860000 1.8600270000 -1.7373180000
N 0.2040640000 -0.8499710000 -1.0675140000
C -1.0578540000 -2.3593760000 0.3259090000
C -0.0036140000 -2.1291370000 -0.7049230000
C 0.7877540000 -3.1408240000 -1.2295610000
H 0.6094130000 -4.1663060000 -0.9365830000
C 1.8011340000 -2.8158730000 -2.1144360000
H 2.4176220000 -3.5945170000 -2.5448040000
C 2.0396570000 -1.4871940000 -2.4247250000
H 2.8501080000 -1.2009400000 -3.0813330000
C 1.2288680000 -0.5138250000 -1.8631890000
C 1.5485790000 0.9451970000 -1.9571920000
H 2.2608190000 1.1258080000 -1.1472680000
H 2.0544050000 1.1682650000 -2.9018270000
C -2.2778890000 1.9827470000 0.1480130000
C -3.1129330000 -1.1161460000 2.0169860000
C -2.1943030000 -0.2864630000 2.9107580000
H -2.5540620000 -0.3441450000 3.9414240000
H -1.1628930000 -0.6439400000 2.8885490000
H -2.1928110000 0.7618560000 2.6146950000
C -4.4948840000 -0.4683190000 2.0257470000
H -4.8183770000 -0.3392610000 3.0610560000

H -4.4836020000 0.5215700000 1.5682750000
H -5.2547730000 -1.0667980000 1.5262900000
C -3.1836950000 -2.5266390000 2.6003460000
H -3.8081040000 -3.2083780000 2.0292600000
H -2.1953160000 -2.9738740000 2.7035080000
H -3.6079640000 -2.4690180000 3.6055370000
C -3.6203900000 -1.7328960000 -0.9653630000
C -4.6084210000 -0.6377020000 -1.3614010000
H -5.2316910000 -0.3104410000 -0.5316220000
H -4.0934090000 0.2352740000 -1.7607370000
H -5.2761550000 -1.0174550000 -2.1383150000
C -4.3822820000 -2.9580060000 -0.4679330000
H -4.9861490000 -3.3564160000 -1.2869860000
H -3.7155980000 -3.7596140000 -0.1471920000
H -5.0654280000 -2.7344440000 0.3484730000
C -2.8433080000 -2.1589850000 -2.2132770000
H -2.2106060000 -1.3596960000 -2.5987570000
H -2.2233660000 -3.0379110000 -2.0324000000
H -3.5536030000 -2.4267100000 -2.9985620000
C -0.1724780000 2.2058060000 -3.0648240000
H -0.5039740000 1.2649010000 -3.5060230000
H 0.6339660000 2.5866430000 -3.7054400000
C -1.3060920000 3.1951230000 -3.0292910000
H -2.1164130000 2.8499780000 -2.3896970000
H -0.9893560000 4.1793620000 -2.6851670000
H -1.7047040000 3.3209930000 -4.0352630000
C 0.8495240000 3.0651920000 -0.9870360000
H -0.0431960000 3.6394520000 -0.7410310000
H 1.2496340000 2.6886200000 -0.0451810000
C 1.8661700000 3.9379920000 -1.6906170000
H 2.1625580000 4.7542170000 -1.0330320000
H 2.7720580000 3.3888190000 -1.9492410000
H 1.4736280000 4.3873970000 -2.6028670000
H -1.4449390000 -3.3791090000 0.2936720000
C 1.1215300000 0.3264300000 1.9319480000
H 0.0612740000 0.6753310000 1.0194530000
O 0.9633250000 -0.8735520000 2.2781010000
C 0.8521650000 1.4533420000 2.9201270000
H 1.6164370000 1.4238410000 3.7023720000
H -0.1167900000 1.3288740000 3.3933950000
N 2.3053400000 0.6226690000 1.1285560000
H 2.9251910000 1.2498400000 1.6272580000
H 2.7945700000 -0.2553360000 0.9983460000
H 0.8808350000 2.4329740000 2.4417150000

H -0.5615760000 -2.2151680000 1.2949520000

**$TS_{8,5\text{-}1}$**

Ru 0.1811620000 -0.0081210000 1.1376040000
H -0.1803520000 -1.3989100000 1.8499400000
P -1.9377030000 0.1362980000 0.2984420000
O -0.5526590000 1.2027090000 3.7773420000
N 2.3857890000 -0.6943620000 1.2298800000
N 0.4642560000 -1.1366520000 -0.6598100000
C -1.5443880000 -0.1205220000 -1.4805160000
C -0.4240030000 -1.0703900000 -1.6673320000
C -0.2184870000 -1.8244400000 -2.8172560000
H -0.9266280000 -1.7572190000 -3.6317970000
C 0.8967660000 -2.6358590000 -2.9053930000
H 1.0745570000 -3.2165540000 -3.8012600000
C 1.7876370000 -2.7068200000 -1.8429550000
H 2.6616080000 -3.3423850000 -1.8806140000
C 1.5321960000 -1.9453510000 -0.7186180000
C -0.2374140000 0.7696630000 2.7474210000
C -2.8543730000 1.7833600000 0.3267390000
C -1.8005570000 2.8909770000 0.2859160000
H -2.3099860000 3.8528430000 0.1959980000
H -1.1187700000 2.7841880000 -0.5604330000
H -1.2063120000 2.9163390000 1.1990220000
C -3.6583020000 1.9371090000 1.6147990000
H -4.0336180000 2.9608630000 1.6738160000
H -3.0481740000 1.7686320000 2.5023890000
H -4.5227760000 1.2773330000 1.6632390000
C -3.7622440000 1.9599800000 -0.8897750000
H -4.5279120000 1.1939000000 -0.9823070000
H -3.1904830000 1.9870310000 -1.8169420000
H -4.2753550000 2.9204020000 -0.8063510000
C -3.0954050000 -1.2793200000 0.7689290000
C -3.2283690000 -1.3608290000 2.2883380000
H -3.6965890000 -0.4808960000 2.7240190000
H -2.2580980000 -1.4969370000 2.7647010000
H -3.8494360000 -2.2206710000 2.5488760000
C -4.4739590000 -1.1680250000 0.1244800000
H -5.0408580000 -2.0765700000 0.3403640000
H -4.4152020000 -1.0792940000 -0.9609580000
H -5.0564750000 -0.3320680000 0.5053650000
C -2.4573300000 -2.5792220000 0.2742280000
H -1.4410290000 -2.7086440000 0.6458230000
H -2.4410960000 -2.6445480000 -0.8138130000

H -3.0496320000 -3.4216750000 0.6370090000
C 2.9068710000 -0.9138950000 2.6026790000
H 2.1666760000 -1.5329920000 3.1111590000
H 3.8304870000 -1.5040920000 2.5476610000
C 3.1556200000 0.3559890000 3.3732150000
H 2.2955170000 1.0238670000 3.3379800000
H 4.0220740000 0.9033090000 3.0044100000
H 3.3454330000 0.1169650000 4.4182170000
C 3.2154050000 0.2705050000 0.4489780000
H 3.1338460000 1.2323630000 0.9522830000
H 2.7295410000 0.4099080000 -0.5158640000
C 4.6681520000 -0.0967780000 0.2527920000
H 5.1558280000 0.7077780000 -0.2951070000
H 4.8001600000 -1.0049000000 -0.3358110000
H 5.2043050000 -0.2223880000 1.1939750000
H -2.4060870000 -0.3616210000 -2.1042220000
C 3.2455810000 0.8170930000 -3.1254180000
H 4.3373290000 0.7581840000 -3.2089730000
O 2.9446930000 1.9090400000 -2.3078790000
C 2.6263480000 0.9120140000 -4.5021670000
H 1.5392230000 0.9508860000 -4.4208690000
H 2.9551220000 1.8167470000 -5.0149300000
H 2.9289140000 -0.1361410000 -2.6599610000
H -1.1064360000 0.8568260000 -1.8107940000
H 2.8929710000 0.0532760000 -5.1220100000
C 2.3315970000 -2.0039030000 0.5407280000
H 1.8355800000 -2.6978040000 1.2256800000
H 3.3334480000 -2.4017260000 0.3552850000
H 0.9151610000 1.6349100000 0.5906950000
H 0.5423590000 1.5192550000 -0.1175070000
H 1.9375640000 1.9461740000 -2.2135500000
O 0.3358710000 1.9898170000 -2.1455350000
C -0.0413670000 2.9974200000 -2.9969070000
C -1.0192220000 2.5377490000 -4.0714930000
H 0.8305600000 3.4528250000 -3.5132240000
H -0.5144090000 3.8544720000 -2.4652060000
H -1.2765160000 3.3385510000 -4.7697730000
H -0.5973300000 1.7105140000 -4.6476790000
H -1.9513510000 2.1774400000 -3.6280340000

**$TS_{8,5\text{-}2}$**

Ru 0.3082060000 0.0784570000 1.1869270000
H -0.0685300000 -1.2556720000 1.9976460000
P -1.7923560000 0.1601800000 0.2548350000

O -0.5049430000 1.4807390000 3.7079130000
N 2.5142770000 -0.6152650000 1.3914270000
N 0.6298030000 -1.1708750000 -0.5138940000
C -1.3474190000 -0.2169950000 -1.4594470000
C -0.2421860000 -1.1541300000 -1.5492040000
C 0.0146190000 -1.9742260000 -2.6561500000
H -0.6718780000 -1.9607910000 -3.4924390000
C 1.1363730000 -2.7722350000 -2.6711250000
H 1.3426810000 -3.3971090000 -3.5311440000
C 2.0049350000 -2.7812780000 -1.5820300000
H 2.8841450000 -3.4099560000 -1.5631760000
C 1.7044220000 -1.9707420000 -0.5069810000
C -0.1560530000 0.9751430000 2.7217510000
C -2.7244610000 1.8017890000 0.1817610000
C -1.6975750000 2.9338730000 0.1246240000
H -2.2317640000 3.8805380000 0.0138400000
H -1.0158040000 2.8307620000 -0.7208540000
H -1.1103400000 2.9938860000 1.0408290000
C -3.5781000000 2.0159460000 1.4287100000
H -3.9782860000 3.0319980000 1.4090900000
H -2.9955910000 1.9197790000 2.3451520000
H -4.4288510000 1.3406150000 1.4914750000
C -3.5900770000 1.8916800000 -1.0749560000
H -4.3562390000 1.1219810000 -1.1306930000
H -2.9880480000 1.8392070000 -1.9814730000
H -4.1008720000 2.8572850000 -1.0844630000
C -2.9605190000 -1.2178060000 0.8293290000
C -3.1328400000 -1.1823660000 2.3461280000
H -3.6217010000 -0.2787470000 2.7023030000
H -2.1732890000 -1.2684530000 2.8551070000
H -3.7497060000 -2.0282160000 2.6586670000
C -4.3204550000 -1.1696230000 0.1382550000
H -4.8877190000 -2.0647100000 0.4046840000
H -4.2268880000 -1.1636070000 -0.9485700000
H -4.9225620000 -0.3131350000 0.4336750000
C -2.3062240000 -2.5501240000 0.4572390000
H -1.2994430000 -2.6438170000 0.8634570000
H -2.2585740000 -2.6986480000 -0.6212200000
H -2.9055580000 -3.3638480000 0.8710650000
C 2.9786210000 -0.7539180000 2.7939400000
H 2.2138550000 -1.3354890000 3.3101170000
H 3.8986650000 -1.3522010000 2.8133170000
C 3.2059230000 0.5602020000 3.4940280000
H 2.3459530000 1.2217470000 3.3945510000

H 4.0817160000 1.0865460000 3.1162200000
H 3.3674590000 0.3855370000 4.5564290000
C 3.3940000000 0.2800650000 0.5818700000
H 3.2895700000 1.2808520000 0.9996520000
H 2.9707960000 0.3188350000 -0.4237110000
C 4.8553820000 -0.1056850000 0.5150360000
H 5.3843690000 0.6337910000 -0.0845740000
H 5.0142820000 -1.0706400000 0.0338510000
H 5.3351950000 -0.1323250000 1.4938140000
H -2.1845070000 -0.4762940000 -2.1083370000
C 2.7106100000 0.4030850000 -3.8064100000
H 3.5639880000 -0.2806740000 -3.7427050000
O 2.4195410000 0.8238300000 -2.4983230000
C 3.0346740000 1.5515480000 -4.7343350000
H 2.1884980000 2.2353050000 -4.8176780000
H 3.8849760000 2.1237330000 -4.3622720000
H 1.8801990000 -0.1860940000 -4.2239220000
H -0.8067610000 0.8579820000 -1.9735560000
H 3.2770170000 1.1967270000 -5.7376010000
C 2.4616120000 -1.9647200000 0.7805650000
H 1.9323950000 -2.6071080000 1.4904400000
H 3.4630400000 -2.3863660000 0.6546420000
H 1.1063410000 1.6220610000 0.4826120000
H 0.5389400000 1.4802210000 -0.0791940000
H 1.5177440000 1.2465600000 -2.5125640000
O -0.0443740000 1.8296300000 -2.4592580000
C -0.5909760000 2.5240660000 -3.5239760000
C -1.0307590000 1.6242950000 -4.6657090000
H 0.1387730000 3.2551830000 -3.9111200000
H -1.4562270000 3.1380980000 -3.2062090000
H -1.4289250000 2.1968910000 -5.5059100000
H -0.1928770000 1.0275550000 -5.0326100000
H -1.8086980000 0.9291910000 -4.3422950000

## EtOH

C -8.3599870000 0.2276330000 -0.0196400000
C -6.8537510000 0.2746450000 -0.0416610000
H -8.7281410000 -0.7243120000 -0.4027840000
H -8.7887200000 1.0172250000 -0.6397260000
H -8.7403320000 0.3554960000 0.9935760000
H -6.4816760000 0.1133510000 -1.0619730000
H -6.4354650000 -0.5253290000 0.5714650000
O -6.3294030000 1.4775090000 0.4996420000
H -6.6840340000 2.2062630000 -0.0201640000

### aldehyde

C 0.9691880000 0.0527680000 -0.0247670000
C 2.4556660000 0.0222760000 -0.0104800000
O 3.1277780000 -0.8816530000 0.4130890000
H 2.9403620000 0.9319340000 -0.4364480000
H 0.5418020000 -0.8527020000 0.3979450000
H 0.6160830000 0.1864960000 -1.0490660000
H 0.6164640000 0.9238830000 0.5307060000

### amide

C 1.0130380000 0.1021070000 -0.1010890000
C 2.5108160000 0.2088310000 -0.0113930000
O 3.1086630000 0.0804440000 1.0420360000
N 3.1495780000 0.4588390000 -1.1815560000
H 0.7028440000 -0.8714600000 0.2741370000
H 0.6204080000 0.2317180000 -1.1074670000
H 0.5641460000 0.8504770000 0.5496860000
H 2.6599270000 0.5628400000 -2.0506770000
H 4.1514140000 0.5407650000 -1.1860910000

### hydrogen

H -5.8397280000 -0.7819140000 0.0000000000
H -5.0989870000 -0.8555830000 0.0000000000

### ammonia

N 4.6874400000 -2.5327010000 1.9186660000
H 5.6983170000 -2.4893450000 1.8722620000
H 4.3803560000 -2.7607150000 0.9807370000
H 4.3803380000 -1.5815410000 2.0829440000

## 7. References


1. J. Zhang, G. Leitus, Y. Ben-David and D. Milstein, *J. Am. Chem. Soc.* 2005, **127**, 10840-10841.
2. B. Gnanaprakasam, J. Zhang and D. Milstein, *Angew. Chem. Int. Ed.* 2010, **49**, 1468-1471.
3. E. Fogler, J. A. Garg, P. Hu, G. Leitus, L. J. W. Shimon and D. Milstein, *Chem. Eur. J.* 2014, **20**, 15727-15731.
4. E. Balaraman, C. Gunanathan, J. Zhang, L. J. W. Shimon and D. Milstein, *Nat. Chem.* 2011,**3**, 609-614.
5. C. A. Huff, J. W. Kampf, M. S. Sanford, *Chem. Commun.* 2013, **49**, 7147-7149.
6. B. Guo, J. G. de Vries and E. Otten, *Chem. Sci.* 2019, **10**, 10647-10652.
7. Gaussian 16, Revision C.01, M. J. Frisch et al., Gaussian, Inc., Wallingford CT, 2016.
8. Y. Zhao, D. G. Truhlar, *J. Chem. Phys.* 2006, **125**, 194101/1-18.
9. F. Weigend, R. Ahlrichs, *Phys. Chem. Chem. Phys.* 2005, **7**, 3297-3305.
10. F. Weigend, *Phys. Chem. Chem. Phys.* 2006, **8**, 1057-1065.
11. S. Grimme, J. Antony, S. Ehrlich, H. Krieg, *J. Chem. Phys.* 2010, **132**, 154104/1-19.
12. F. Neese, *WIREs Computational Molecular Science* 2018, **8**, e1327-e1332.
13. N. Mardirossian, M. H.-Gordon, 2014, **16**, 9904-9924.
14. O. A. Vydrov, T. van. Voorhis, *J. Chem. Phys.* 2010, **133**, 244103/1-9.
15. W. Hujo, S. Grimme, *J. Chem. Theory and Comp.* 2011, **7**, 3866-3871.
16. A. Hellweg, C. Hättig, S. Höfener, W. Klopper, *Theor. Chem. Acc.* 2007, **117**, 587-597.
17. M. Iron, T. Janes, *J. Phys. Chem. A* 2019, **123**, 3761-3781.
18. A. V. Marenich, C. J. Cramer, D. G. Truhlar, *J. Phys. Chem. B* 2009, **113**, 6378-6396.
19. C. J. Cramer, *Essentials of Computational Chemistry: Theories and Models. 2nd Edition*; John Wiley & Sons Ltd: West Sussex, England, 2004.

20. M. Sparta, C. Riplinger, F. Neese, *J. Chem. Theory and Computation* 2014, **10**, 1099-1108.
21. K. H. Hopmann, *Organometallics* 2016, **35**, 3795-3807.
22. D. G. Gusev, *Organometallics* 2020, **39**, 258-270.