Electronic Supplementary Information (ESI)

NHC-Amine Ru complex catalyzed selective mono *N*-methylation of amines with methanol: understanding the effect of amine ligands

Xiuju Cai,[+a] Xiaoyu Zhou[+b] and Ming Huang*[a]

[a] *School of pharmacy, School of clinical pharmacy, Guangdong Pharmaceutical University, Guangzhou 510006, P. R. China. Email: 1529236883@qq.com*

[b] School of Materials Science & Engineering, PCFM Lab, School of Chemistry, Sun Yat-sen University, Guangzhou 510275, P. R.

+ These authors contributed equally to this work.

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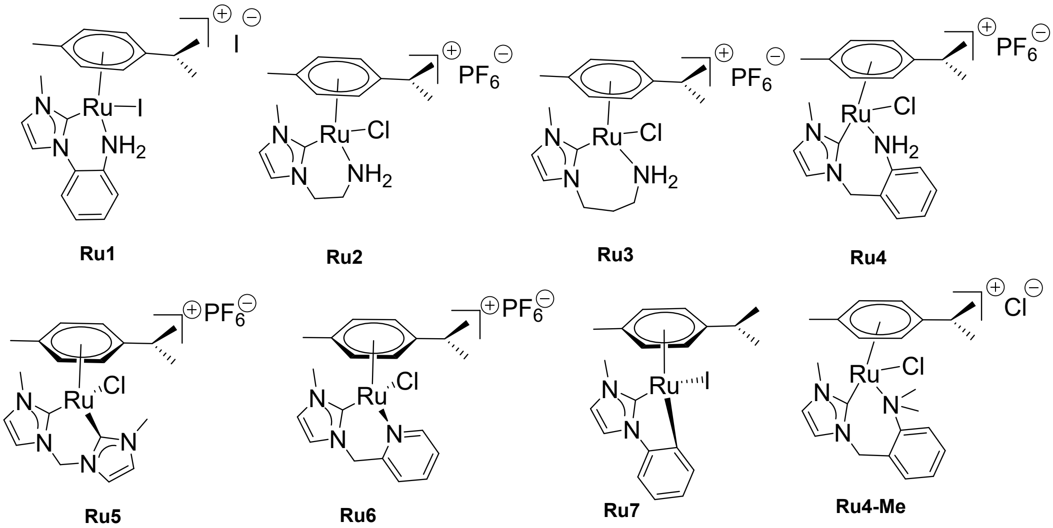
I. General Information

Unless otherwise stated, all manipulations were carried out under dry nitrogen using conventional Schlenk or glove box techniques. Reagents were purchased from Energy-Chemical and Aladdin. These reagents were used without further purification. Analytical thin-layer chromatography (TLC) was conducted with TLC plates (Silica gel GF254, Qingdao Haiyang). Column chromatography was performed on silica gel 300-400 mesh.

NMR spectra were recorded using a Bruker 400 MHz spectrometer, and chemical shifts are reported relative to TMS for ^{1}H and ^{13}C. GC analyses were recorded in a Shimadzu GC-2014C device equipped with a Wondacap 1 column. ESI-MS spectra were taken on a Shimadzu LCMS-2010 instrument. High resolution mass spectrometric (HRMS) data were obtained using an LTQ Orbitrap Elite instrument, using a sample concentration of approximately 1 ppm.

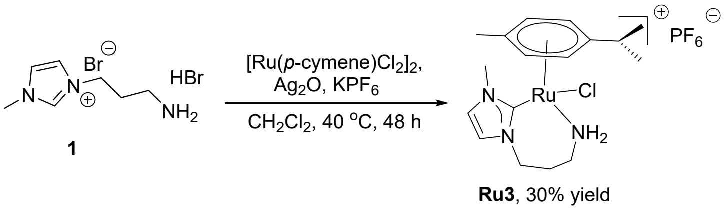
II. Preparation of the Ligands and the NHC-Ru Complexes



Scheme S1. NHC-Ru complexes **Ru1**-**Ru7**, and **Ru4-Me** used in this study.

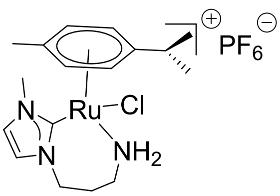
The NHC-Ru Complexes **Ru1**[1], **Ru2**[2], **Ru5**[3], **Ru6**[4], and **Ru7**[5] were synthesized according to the references.

The synthesis of **Ru3** is illustrated in Scheme S2.



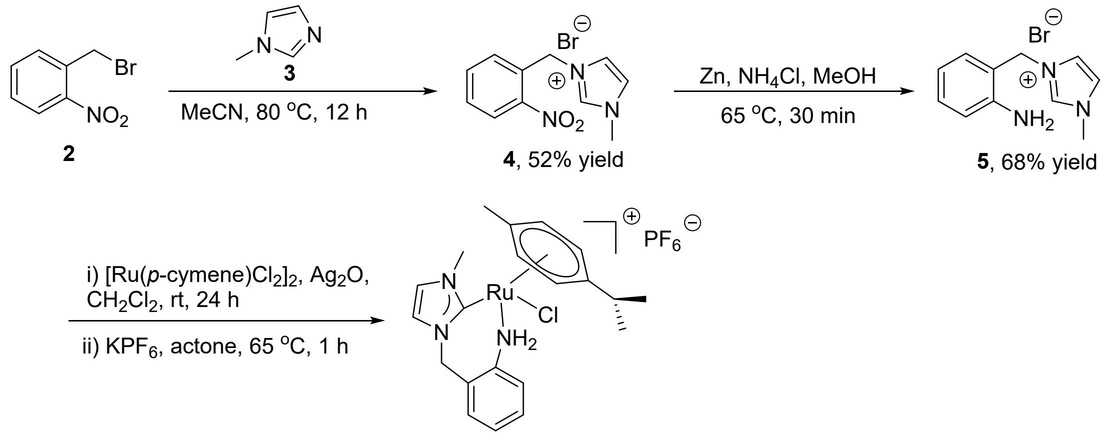
Scheme S2. The synthesis of **Ru3**.

Complex Ru3



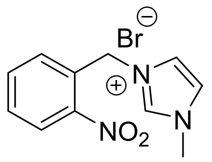
A 50 mL three-necked flask was charged **1**[6] (0.300 g, 1.0 mmol), [(*p*-cymene)$RuCl_2$)]$_2$ (0.258 g, 0.42 mmol), Ag_2O (0.277 g, 1.2 mmol), KPF_6 (0.184 g, 1.0 mmol) and CH_2Cl_2 (100 mL). The reaction mixture was stirred at 40 °C for 48 h in the dark under N_2 atmosphere. After cooling to rt, the mixture was filtered, and the filtrate was evaporated under reduced pressure. Then the crude mixture was purified by re-crystallization from CH_2Cl_2/ethyl ether. After that, the mixture was purified further by column chromatography (SiO_2, CH_2Cl_2: MeOH = 20: 1), giving the product as yellow solid (0.167g, 30% yield). ^1H NMR (400 MHz, Methylene Chloride-d_2) δ 7.15 (d, J = 1.9

Hz, 1H), 7.08 (d, J = 1.9 Hz, 1H), 5.74 (d, J = 5.9 Hz, 1H), 5.47 (d, J = 5.9 Hz, 1H), 5.42 (d, J = 5.9 Hz, 1H), 5.28 (d, J = 6.0 Hz, 1H), 4.45 – 4.31 (m, 2H), 4.12 – 4.06 (m, 1H), 3.91 (s, 3H), 3.27 (d, J = 11.9 Hz, 1H), 2.90 – 2.77 (m, 2H), 2.21 – 2.10 (m, 1H), 1.96 (s, 3H), 1.86 – 1.75 (m, 2H), 1.26 (d, J = 7.0 Hz, 3H), 1.14 (d, J = 6.8 Hz, 3H); ^{13}C NMR (101 MHz, Methylene Chloride-d_2) δ 175.08, 124.86, 122.68, 112.43, 100.69, 85.85, 84.86, 84.13, 81.92, 45.81, 40.55, 38.95, 31.25, 28.49, 24.24, 20.39, 18.52; ^{31}P NMR (162 MHz, Methylene Chloride-d_2) δ -130.98, -135.38, -139.77, -144.17, -148.57, -152.96, -157.36; HRMS (ESI, m/z): calcd for $C_{17}H_{27}ClN_3Ru$ [M – PF_6]$^+$ 410.0931, found 410.0925.
The synthesis of **Ru4** is illustrated in Scheme S3.



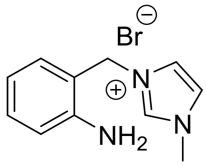
Scheme S3. The synthesis of **Ru4**.

1-methyl-3-(2-nitrobenzyl)-1H-imidazol-3-ium bromide (**4**)[7]



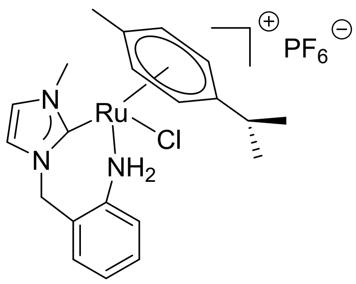
A 250 mL three-necked flask was charged 2-nitrobenzyl bromide **2** (10.36 g, 48 mmol), 1-methylimidazole **3** (4.0 mL, 50 mmol) and MeCN (20 mL). The reaction mixture was stirred at 80 °C for 12 h under N_2 atmosphere. After cooling to room temperature, the precipitate was filtered, and washed with MeCN, and then with diethyl ether. Drying the precipitate under vacuum gave complex **4** as a white solid with good purity and yields. Yield: 52%. ^{1}H NMR (400 MHz, DMSO-d_6) δ 9.25 (s, 1H), 8.21 (dd, J = 8.2, 1.1 Hz, 1H), 7.84 – 7.79 (m, 3H), 7.73 – 7.69 (m, 1H), 7.37 (d, J = 7.6 Hz, 1H), 5.81 (s, 2H), 3.91 (s, 3H); ^{13}C NMR (101 MHz, DMSO-d_6) δ 147.50, 137.41, 134.69, 130.38, 130.15, 129.75, 125.33, 124.01, 122.79, 49.29, 36.00; MS (ESI) [M – Br]$^+$ = 218.11.

3-(2-aminobenzyl)-1-methyl-1H-imidazol-3-ium bromide (**5**)



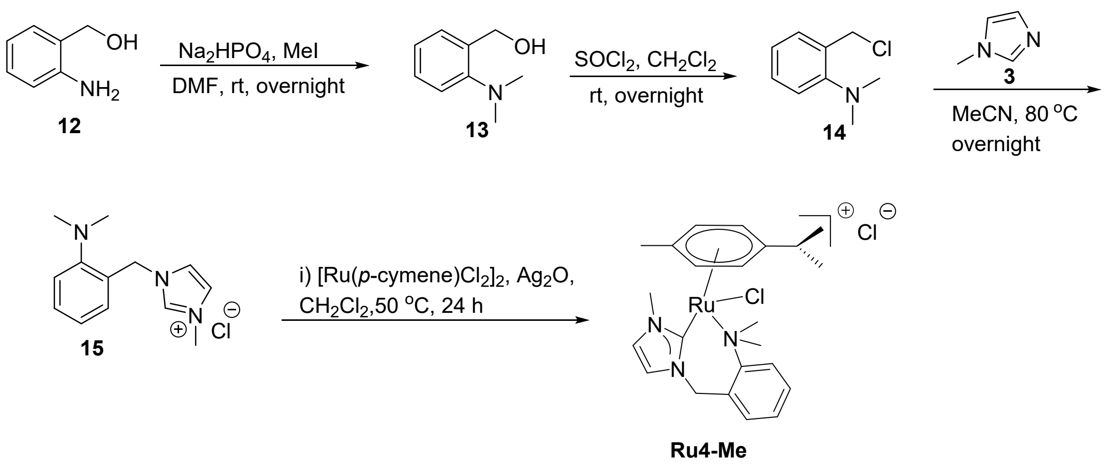
A 150 mL three-necked flask was charged **4** (0.83 g, 2.8 mmol), Zn power (3.64g, 55.7 mmol), NH_4Cl (0.74g, 13.9 mmol), and MeOH (30 mL). The reaction mixture was stirred at 65 °C for 30 min under N_2 atmosphere. After cooling to room temperature, the precipitate was filtered, and the filtrate was evaporated under reduced pressure. The resultant yellowish oil was dissolved with a small amount of methanol, and the methanol solution was kept at 0-8 °C overnight. After that, the methanol solution was filtered, and the filtrate was evaporated under reduced pressure to give the final product as a yellowish oil. The product would turn into yellowish solid when placed at room temperature for a period of time. Yield: 68%. ^{1}H NMR (400 MHz, DMSO-d_6) δ 9.08 (s, 1H), 7.67 (dd, J = 4.2, 2.2 Hz, 2H), 7.14 – 7.07 (m, 2H), 6.72 (d, J = 8.0 Hz, 1H), 6.58 (t, J = 7.4 Hz, 1H), 5.39 (s, 2H), 5.32 (s, 2H), 3.85 (s, 3H); ^{13}C NMR (101 MHz, DMSO-d_6) δ 147.02, 136.22, 130.69, 130.02, 123.57, 122.41, 117.05, 116.41, 115.67, 48.99, 35.82; HRMS (ESI, m/z): calcd for $C_{11}H_{14}N_3$ $[M - Br]^+$ 188.1182, found 188.1179.

Complex Ru4



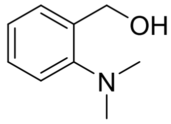
A 250 mL three-necked flask was charged **5** (0.4 g, 1.5 mmol), [(*p*-cymene)$RuCl_2$)]$_2$ (0.485g, 0.8 mmol), Ag_2O (0.185g, 0.85 mmol), and CH_2Cl_2 (100 mL). The reaction mixture was stirred at room temperature overnight in the dark under N_2 atmosphere. The mixture was filtered, and the filtrate was evaporated under reduced pressure. Then the crude mixture was dissolved in acetone (150 mL). KPF_6 (2.93 g, 16 mmol) was added to the solution, which was then heated at reflux for 1 h. The solvent was evaporated under reduced pressure and the crude solid redissolved in CH_2Cl_2 (50 mL). After that, the solution was filtered, and the filtrate was evaporated under reduced pressure. The resulting solid was recrystallized from CH_2Cl_2/ether, giving the product as yellow green solid. Yield: 65%. ^{1}H NMR (400 MHz, Methylene Chloride-d_2) δ 7.66 (d, J = 12.0 Hz, 1H), 7.20 (d, J = 1.6 Hz, 1H), 7.14 – 7.12 (m, 1H), 7.06 – 7.04 (m, 2H), 6.98 (d, J = 1.6 Hz, 1H), 6.91 – 6.89 (m, 1H), 5.83 (d, J = 5.9 Hz, 1H), 5.68 (d, J = 5.9 Hz, 1H), 5.63 (d, J = 5.9 Hz, 1H), 5.57 (s, 1H), 5.54 (d, J = 8.2 Hz, 1H), 5.35 (s, 1H), 4.64 (d, J = 14.3 Hz, 1H), 3.75 (s, 3H), 2.83 (p, J = 6.9 Hz, 1H), 2.06 (s, 3H), 1.28 (d, J = 7.0 Hz, 3H), 1.17 (d, J = 6.8 Hz, 3H); ^{13}C NMR (101 MHz,) δ 173.51, 139.17, 131.45, 129.76, 129.51, 127.03, 126.31, 124.90, 122.85, 112.71, 101.96, 87.53, 85.63, 83.38, 82.73, 51.05, 39.03, 31.56, 24.29, 20.96, 18.59; ^{31}P NMR (162 MHz, Methylene Chloride-d_2) δ -131.06, -135.46, -139.85, -144.25, -148.64, -153.04, -157.43; HRMS (ESI, m/z): calcd for $C_{21}H_{27}ClN_3Ru$ [M – PF_6]$^+$ 458.0931, found 458.0934.

The synthesis of **Ru4-Me** is illustrated in Scheme S4.



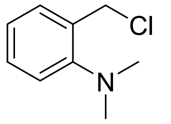
Scheme S4. The synthesis of **Ru4-Me**.

(2-(dimethylamino)phenyl)methanol (**13**)[8]



A 250 mL three-necked flask was charged (2-aminophenyl)methanol **12** (5.0 g, 40.6 mmol), Na_2HPO_4 (20.8 g, 146 mmol), and dry DMF (150 mL). Methyl iodide (6 mL, 97 mmol) was added, and the reaction mixture was stirred at rt overnight under N_2 atmosphere. Then, the reaction mixture was diluted with water (1 L) and extracted with diethyl ether (3 × 300 mL). The organic layers were combined, washed with brine (2 × 150 mL) and H_2O (1 × 200 mL), and dried over anhydrous Na_2SO_4. After filtration, the solvent was removed on a rotary evaporator to furnish 5.6 g (91%) of the product **13** in the form of a colorless oil.

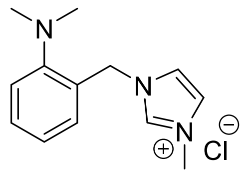
2-(chloromethyl)-N,N-dimethylaniline (**14**)[8]



A 250 mL three-necked flask was charged (2-(dimethylamino)phenyl)methanol **13** (5.5 g, 36.4 mmol), and dry CH_2Cl_2 (130 mL). The mixture was cooled to 0 °C, and $SOCl_2$ was added (4.8 mL, 66 mmol). The mixture was stirred at 0 °C for 20 min and then overnight at rt under N_2 atmosphere. The reaction mixture was diluted with CH_2Cl_2

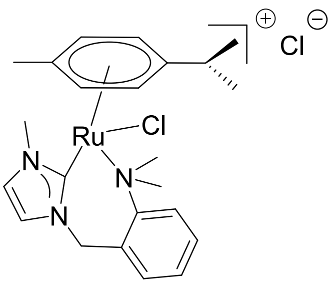
(400 mL) and washed with 10% aqueous sodium bicarbonate to neutralize $SOCl_2$ and acid. The organic layer was dried over anhydrous Na_2SO_4 and filtered, and the solvent was removed on a rotary evaporator to afford **14** as a yellowish oil (5.2g, 85%) which was used without further purification.

1-(2-(dimethylamino)benzyl)-3-methyl-1H-imidazol-3-ium chloride (**15**)



A 250 mL three-necked flask was charged 2-(chloromethyl)-N,N-dimethylaniline **14** (1.69 g, 10 mmol), 1-methylimidazole **3** (0.88 mL, 11 mmol) and MeCN (40 mL). The reaction mixture was stirred at 80 °C overnight under N_2 atmosphere. After cooling to room temperature, the solvent was removed on a rotary evaporator. The resulting solid was recrystallized from CH_2Cl_2/ether, giving the product as a white solid (84% yield). ^{1}H NMR (400 MHz, DMSO-d_6) δ 9.41 (s, 1H), 7.79 (t, J = 1.8 Hz, 1H), 7.75 (t, J = 1.8 Hz, 1H), 7.36 (td, J = 7.6, 1.7 Hz, 1H), 7.27 (dd, J = 8.1, 1.3 Hz, 1H), 7.16 (dd, J = 7.6, 1.7 Hz, 1H), 7.09 (td, J = 7.4, 1.3 Hz, 1H), 5.50 (s, 2H), 3.89 (s, 3H), 2.62 (s, 6H); ^{13}C NMR (101 MHz, DMSO-d_6) δ 152.70, 137.09, 129.73, 129.64, 129.08, 124.00, 123.67, 122.68, 120.65, 48.56, 44.84, 35.79; HRMS (ESI, m/z): calcd for $C_{13}H_{18}N_3$ $[M – Cl]^+$ 216.1495, found 216.1492.

Complex Ru4-Me



A 150 mL three-necked flask was charged **15** (0.25 g, 1.0 mmol), [(*p*-cymene)$RuCl_2$)]$_2$ (0.306g, 0.5 mmol), Ag_2O (0.185g, 0.85 mmol), and CH_2Cl_2 (30 mL). The reaction mixture was stirred at 50 °C overnight in the dark under N_2 atmosphere. The mixture was filtered, and the filtrate was evaporated under reduced pressure. Then the crude mixture was purified by re-crystallization from CH_2Cl_2/ethyl ether. After that, the mixture was purified further by column chromatography (SiO_2, petroleum CH_2Cl_2: MeOH = 20: 1), giving the product as a yellow solid (0.21g, 40% yield). ^{1}H NMR (400 MHz, Chloroform-*d*) δ 7.28 – 7.25 (m, 1H), 7.15 (d, J = 8.0 Hz, 1H), 7.04 – 6.94 (m, 3H), 6.82 (t, J = 1.5 Hz, 1H), 5.74 (d, J = 113.9 Hz, 2H), 5.32 – 5.30 (m, 2H), 5.02 (d, J = 5.7 Hz, 2H), 4.04 (s, 3H), 2.95 - 2.88 (m, 1H), 2.74 (s, 6H), 2.06 (s, 3H), 1.24 (d, J = 6.9 Hz, 6H); ^{13}C NMR (101 MHz, Chloroform-*d*) δ 174.52, 152.23, 132.29, 128.45, 128.30, 123.75, 123.53, 123.40, 119.26, 108.33, 99.03, 85.16, 82.53, 50.95, 45.09, 39.83, 30.83, 18.80; ^{13}C NMR (101 MHz, Chloroform-*d*) δ 174.52, 152.23, 132.29, 128.45, 128.30, 123.75, 123.53, 123.40, 119.26, 108.33, 99.03, 85.16, 85.53, 50.95, 45.09, 39.83, 30.83, 22.33, 18.80; HRMS (ESI, m/z): calcd for $C_{23}H_{31}ClN_3Ru$ $[M - Cl]^+$ 486.1244, found 486.1249.

III. Single crystal X-Ray diffraction of Ru4

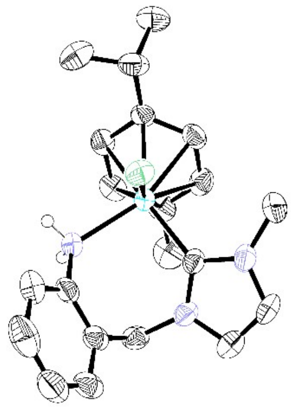


Figure S1. Molecular structure of complex **Ru4** with thermal ellipsoids shown at 50% probability level. Hydrogen atoms and PF_6 group were omitted for clarity.

Table S1. Crystal data and structure refinement for **Ru4**.

Identification code	CCDC 2281550
Empirical formula	$C_{21}H_{27}ClN_3RuPF_6$
Formula weight	603.75
Temperature/K	296.15
Crystal system	trigonal
Space group	R-3c
a/Å	16.2982(12)
b/Å	16.2982(12)
c/Å	96.084(11)
α/°	90
β/°	90
γ/°	120
Volume/Å^3	22103(4)
Z	12
ρ_{calc}g/cm^3	1.588
μ/mm^{-1}	1.139
F(000)	10632.0
Crystal size/mm^3	0.23 × 0.16 × 0.06
Radiation	MoKα (λ = 0.71073)
2Θ range for data collection/°	4.454 to 54.978
Index ranges	$-21 \leq h \leq 21$, $-21 \leq k \leq 19$, $-123 \leq l \leq 124$
Reflections collected	59192
Independent reflections	5641 [R_{int} = 0.0987, R_{sigma} = 0.0409]

Data/restraints/parameters	5641/0/275
Goodness-of-fit on F^2	1.051
Final R indexes [I>=2σ (I)]	R_1 = 0.0627, wR_2 = 0.1821
Final R indexes [all data]	R_1 = 0.0809, wR_2 = 0.1976
Largest diff. peak/hole / e $Å^{-3}$	1.21/-3.71

IV. The *N*-methylation of Amines with Methanol

1, GC analysis method for the condition optimization.

GC analysis method:

Injector: Mode: Split; temp.: 330 °C; Gas: N_2 Pressure: 1.34 bar; Split ratio: 39:1; Split flow: 67.6 mL/min.

Column: Wondacap 1 column Capillary column (30 m x 0.25 mm); Nominal film thickness: 0.250 μm; Temperature program: Initial temperature 100 °C, hold for 0 min, heat to 120 °C with 5 °C/min, hold for 0 min, then heat to 200 °C with 50 °C/min, hold for 5 min.

Initial Flow: 1.62 mL/min; Average velocity: 39.4 cm/sec, Pressure: 1.34 bar. Detector (FID): Temp.: 330 °C; Hydrogen flow: 40.0 mL/min; Air flow: 400.0 mL/min.

Preparation of GC sample:

Firstly, 1 equiv. of internal standard (mesitylene) was added to the reaction mixture. Then, the reaction mixture was diluted with 10 mL of CH_2Cl_2, filtered through syringe filter and collected in GC vials for analysis.

Retention times: cyclohexylamine (**6a**): 2.28 min; *N*-methylcyclohexylamine (**8a**): 2.603 min; mesitylene: 2.871 min; N, N-dimethylcyclohexylamine (**8aa**): 2.97 min.

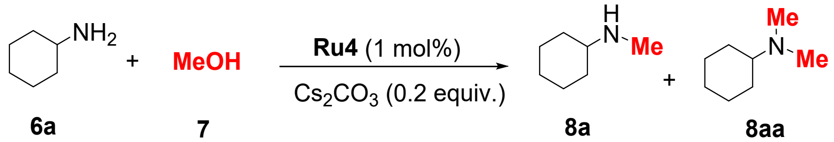
2. The condition optimization.

2.1 General method for the condition optimization.

To a 15 mL seal tube in a glovebox, was added **Ru** (x mol%), base (y mol%), cyclohexylamine (**6a**, 0.5 mmol), and methanol (0.5 mL) in sequence. Then the tube was closed with a screw-top cap and removed from the glovebox. The reaction mixture was stirred at 110 °C for 9 h. After cooled to rt, 1 equiv. of internal standard (mesitylene) was added to the reaction mixture. Then, the reaction mixture was diluted with 10 mL of CH_2Cl_2, filtered through syringe filter and collected in GC vials for analysis.

We have performed the reaction at lower reaction temperatures. However, the yield of product **8a** was descended along with the reaction temperature decreasing (Table S2, entries 1-2). In addition, the influence of the amount of the MeOH on the reaction was investigated (Table S2, entries 3-7). When the amount of methanol is low, the yields of **8a** were sharply decreased (Table S2, entries 3-5). Inferior selectivity was observed when the amount of methanol increases to 1mL (Table S2, entry 7). These results indicated that the amount of methanol plays an important role in the activity and selectivity of the reaction.

Table S2. Further Optimization of the Reaction.[a, b]



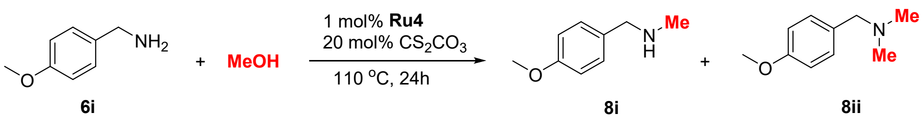
entry	Temperature (°C)	Methnoal (mL)	Yield of **8a** (%)	Ratio (**8a**:**8aa**)
1[c]	100	0.5	47	96:4
2[c]	90	0.5	19	98:2
3	110	0.1	0	-
4	110	0.2	22	99:1
5	110	0.3	52	98:2
6	110	0.5	85	90:10
7	110	1	60	74:25

[a]Reaction conditions: 0.5 mmol **6a**, x mL MeOH, 1.0 mol% **Ru4**, Cs_2CO_3, y °C, 9h. [b]GC yields with mesitylene as an internal standard.[c]24 h

To a 15 mL seal tube in a glovebox, was added **Ru4** (1 mol%), Cs_2CO_3 (20 mol%), 4-methoxybenzylamine (**6i**, 0.5 mmol), and methanol (0.5 mL) in sequence. Then the tube was closed with a screw-top cap and removed from the glovebox. The reaction mixture was stirred at 110 °C for 24 h. After cooled to rt, 1 equiv. of internal standard (1,3,5-trimethoxybenzene) was added to the reaction mixture. Then, the reaction mixture was diluted with 10 mL of CH_2Cl_2, filtered through syringe filter and collected in vials for analysis.

In this reaction, the *N*-mono-methylation product **8i** and dimethylation product **8ii** were obtained in 70% and 5% yields, respectively (Table S3 and Figure S2). In addition, a few byproducts (several signals ranging from 2.5 to 3.6 ppm were observed, Figure S2) besides the dimethylation product were observed. These results indicated that there are other side-products besides the dimethylation product were produced in the *N*-methylation reaction of aliphatic amines with methanol.

Table S3. Yields of **8i** and **8ii** were calculated by ^1H NMR Integration Ratio.



	Internal standard (1,3,5-trimethoxybenzene)	**8i**	**8ii**
Signal δ	6.11 (3H)	2.46 (3H)	2.22 (6H)
Integral Value	3.0	2.1	0.27
Calculated ratio		70%	5%

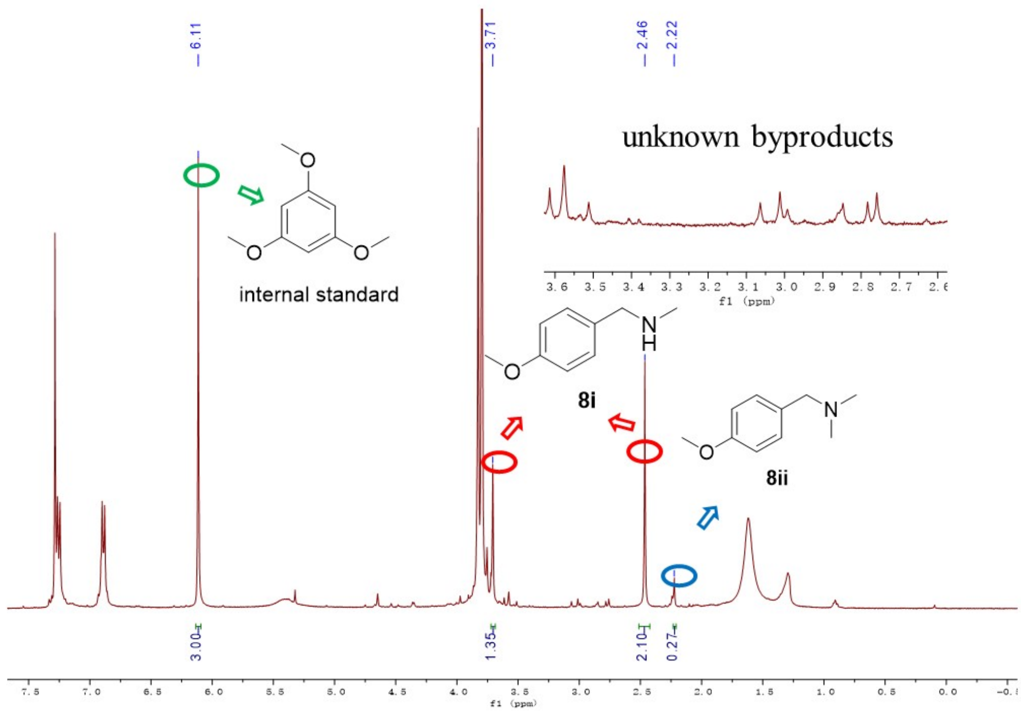


Figure S2. ^{1}H NMR (400 MHz, $CDCl_3$) spectrum of the *N*-methylation reaction of 4-methoxybenzylamine (**6i**) with methanol.

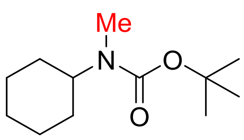
3. Substrate screening.

3.1. Scope of the aliphatic amines.

General method for the substrate screening.

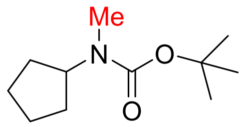
To a 15 mL seal tube in a glovebox, was added **Ru4** (1 mol%), Cs_2CO_3 (20 mol%), aliphatic amines (0.5 mmol), and methanol (0.5 mL) in sequence. Then the tube was closed with a a screw-top cap and removed from the glovebox. The reaction mixture was stirred at 110 ^oC for 24 h. After cooled to rt, *di-tert*-butyl dicarbonate (3.0 mmol), triethylamine (5.0 mmol), and dichloromethane (2 mL) were sequentially added, and the reaction mixture was stirred at room temperature overnight. The product was purified by column chromatography (SiO_2, petroleum ether: ethyl acetate = 80: 1).

tert-butyl cyclohexyl(methyl)carbamate (**9a**)[9]



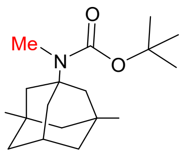
Colorless oil. 58% yield (62 mg).^{1}H NMR (400 MHz, Chloroform-*d*) δ 3.84 (brs, 1H), 2.70 (s, 3H), 1.78 – 1.73 (m, 2H), 1.68 – 1.59 (m, 3H), 1.45 (s, 9H), 1.37 – 1.24 (m, 4H), 1.09 – 1.02 (m, 1H); ^{13}C NMR (101 MHz, Chloroform-*d*) δ 155.83, 79.18, 54.24, 30.48, 28.65, 28.35, 25.99, 25.76; MS $[M+Na]^+$ = 236.25.

tert-butyl cyclopentyl(methyl)carbamate (**9b**)[10]



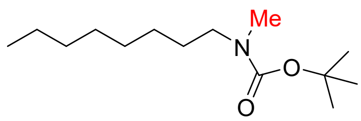
Colorless oil. 54% yield (54 mg). ^{1}H NMR (400 MHz, Chloroform-*d*) δ 4.41 (s, 1H), 2.69 (s, 3H), 1.79 – 1.69 (m, 2H), 1.70 – 1.58 (m, 2H), 1.55 – 1.43 (m, 4H), 1.43 (s, 9H); ^{13}C NMR (101 MHz, Chloroform-*d*) δ 156.03, 79.18, 56.54, 28.61, 28.57, 28.55, 24.20; MS [M+Na]$^+$ = 222.25.

tert-butyl-3,5-dimethyladamantan-1-yl)(methyl)carbamate (**9c**)[11]



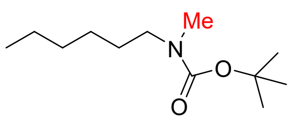
Colorless oil. 55% yield (81 mg). ^{1}H NMR (400 MHz, Chloroform-*d*) δ 2.84 (s, 3H), 2.13 (hept, *J* = 3.4 Hz, 1H), 1.91 (d, *J* = 3.0 Hz, 2H), 1.71 (d, *J* = 5.2 Hz, 4H), 1.45 (s, 9H), 1.37 – 1.30 (m, 2H), 1.27 – 1.23 (m, 2H), 1.12 – 1.10 (m, 2H), 0.83 (s, 6H); ^{13}C NMR (101 MHz, Chloroform-*d*) δ 155.97, 79.22, 57.87, 50.70, 46.39, 42.81, 38.81, 32.84, 30.74, 30.64, 30.37, 28.76; MS [M+Na]$^+$ = 316.47

tert-butyl methyl(octyl)carbamate (**9d**)[11]



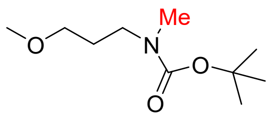
Colorless oil. 63% yield (77 mg). ^{1}H NMR (400 MHz, Chloroform-*d*) δ 3.17 (t, *J* = 7.3 Hz, 2H), 2.81 (s, 3H), 1.55 – 1.48 (m, 2H), 1.44 (s, 9H), 1.26 (s, 10H), 0.87 (t, *J* = 6.3 Hz, 3H); ^{13}C NMR (101 MHz, Chloroform-*d*) δ 156.00, 79.16, 48.94, 34.15, 31.94, 29.47, 29.40, 28.60, 27.92, 26.84, 22.77, 14.20; MS [M+Na]$^+$ = 266.34.

tert-butyl hexyl(methyl)carbamate (**9e**)



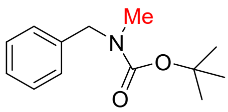
Colorless oil. 56% yield (60 mg). ^{1}H NMR (400 MHz, Chloroform-*d*) δ 3.17 (t, *J* = 7.2 Hz, 2H), 2.82 (s, 3H), 1.51 – 1.47 (m, 2H), 1.44 (s, 9H), 1.27 (s, 6H), 0.87 (t, *J* = 6.1 Hz, 3H); ^{13}C NMR (101 MHz, Chloroform-*d*) δ 155.93, 79.18, 48.93, 34.16, 31.76, 28.60, 27.90, 26.50, 22.76, 14.15; MS [M+Na]$^+$ = 238.58.

tert-butyl (3-methoxypropyl)(methyl)carbamate (**9f**)[12]



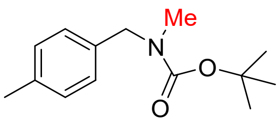
Colorless oil. 60% yield (61 mg). ^{1}H NMR (400 MHz, Chloroform-*d*) δ 3.35 (t, *J* = 6.3 Hz, 2H), 3.30 (s, 3H), 3.25 (t, *J* = 7.1 Hz, 2H), 2.82 (s, 3H), 1.75 (p, J = 6.6 Hz, 2H), 1.43 (s, 9H); ^{13}C NMR (101 MHz, Chloroform-*d*) δ 155.91, 79.31, 70.27, 58.67, 46.13, 34.54, 28.55, 28.35, MS [M+Na]$^+$ = 226.22.

tert-butyl benzyl(methyl)carbamate (**9g**)[13]



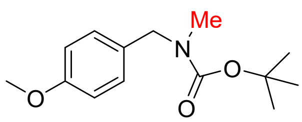
Colorless oil. 57% yield (63 mg). ^{1}H NMR (400 MHz, Chloroform-*d*) δ 7.35 – 7.31 (m, 2H), 7.28 – 7.22 (m, 3H), 4.42 (s, 2H), 2.82 (s, 3H), 1.48 (s, 9H); ^{13}C NMR (101 MHz, Chloroform-*d*) δ 156.21, 138.33, 128.71, 127.58, 127.38, 79.85, 52.69, 34.12, 28.67; MS [M+Na]$^+$ = 244.32.

tert-butyl methyl(4-methylbenzyl)carbamate (**9h**)[11]



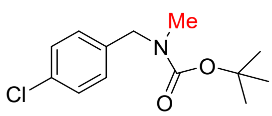
Colorless oil. 64% yield (75 mg). ^{1}H NMR (400 MHz, Chloroform-*d*) δ 7.13 (s, 4H), 4.38 (s, 2H), 2.81 (s, 3H), 2.34 (s, 3H), 1.48 (s, 9H); ^{13}C NMR (101 MHz, Chloroform-*d*) δ (156.26 and 155.94), 136.88, 135.12, 129.32, (127.85 and 127.37), 79.66, (52.44 and 51.77), 33.85, 28.57, 21.17; MS [M+Na]$^+$ = 258.21.

tert-butyl (4-methoxybenzyl)(methyl)carbamate (**9i**)[14]



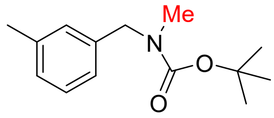
Colorless oil. 52% yield (65 mg). ^{1}H NMR (400 MHz, Chloroform-*d*) δ 7.15 (d, *J* = 7.7 Hz, 2H), 6.86 (d, *J* = 8.5 Hz, 2H), 4.35 (s, 2H), 3.79 (s, 3H), 2.78 (s, 3H), 1.48 (s, 9H); ^{13}C NMR (101 MHz, Chloroform-*d*) δ 158.95, 130.28, (129.12 and 128.74), 114.00, 79.61, 55.36, (52.17 and 51.46), 33.75, 28.59; MS [M+Na]$^+$ = 274.30.

tert-butyl (4-chlorobenzyl)(methyl)carbamate (**9j**)[15]



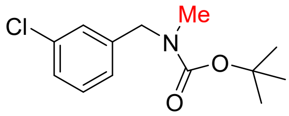
Colorless oil. 51% yield (65 mg). ^{1}H NMR (400 MHz, Chloroform-*d*) δ 7.29 (d, *J* = 8.2 Hz, 2H), 7.15 (d, *J* = 7.3 Hz, 2H), 4.37 (s, 2H), 2.81 (s, 3H), 1.47 (s, 9H); ^{13}C NMR (101 MHz, Chloroform-*d*) δ (156.10 and 155.68), 136.65, 132.96, 129.05, 128.67, 79.87, (52.03 and 51.39), 33.98, 28.44; MS $[M+Na]^+$ = 278.19.

tert-butyl methyl(3-methylbenzyl)carbamate (**9k**)[16]



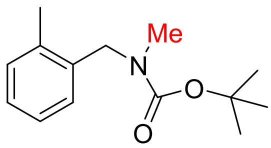
Colorless oil. 64% yield (75 mg). ^{1}H NMR (400 MHz, Chloroform-*d*) δ 7.22 (t, *J* = 7.5 Hz, 1H), 7.08 – 7.00 (m, 3H), 4.39 (s, 2H), 2.82 (s, 3H), 2.34 (s, 3H), 1.48 (s, 9H); ^{13}C NMR (101 MHz, Chloroform-*d*) δ 156.24, 138.26, 138.16, 128.53, 128.04, 124.89 124.51, 79.74, (52.69 and 52.10), 34.02, 28.61, 21.54; MS $[M+Na]^+$ = 258.21.

tert-butyl (3-chlorobenzyl)(methyl)carbamate (**9l**)[16]



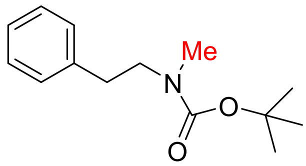
Colorless oil. 70% yield (89 mg). ^{1}H NMR (400 MHz, Chloroform-*d*) δ 7.27 – 7.21 (m, 3H), 7.09 (d, *J* = 6.5 Hz, 1H), 4.38 (s, 2H), 2.83 (s, 3H), 1.47 (s, 9H); ^{13}C NMR (101 MHz, Chloroform-*d*) δ 155.80, 140.42, 134.57, 129.94, 127.73, 127.51, 125.49, 80.08, (52.34 and 51.68) 34.24, 28.53; MS $[M+Na]^+$ = 278.57.

tert-butyl methyl(2-methylbenzyl)carbamate (**9m**)[9]



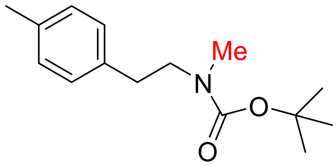
Colorless oil. 53% yield (62 mg). ^{1}H NMR (400 MHz, Chloroform-*d*) δ 7.19 – 7.15 (m, 3H), 7.12 – 7.09 (m, 1H), 4.44 (s, 2H), 2.79 (s, 3H), 2.28 (s, 3H), 1.47 (s, 9H); ^{13}C NMR (101 MHz, Chloroform-*d*) δ 155.77, 136.27, 135.83, 129.26, 128.84, 79.35, 51.10, 34.24, 28.52, 21.12; MS $[M+Na]^+$ = 258.21.

tert-butyl methyl(phenethyl)carbamate (**9n**)[15]



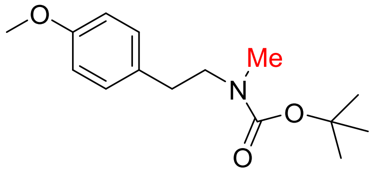
Colorless oil. 52% yield (61 mg). ^{1}H NMR (400 MHz, Chloroform-*d*) δ 7.29 (t, *J* = 7.3 Hz, 2H), 7.22 – 7.19 (m, 3H), 3.42 (t, *J* = 7.2 Hz, 2H), 2.83 – 2.78 (m, 5H), 1.40 (s, 9H); ^{13}C NMR (101 MHz, Chloroform-*d*) δ 155.73, 139.41, 128.98, 128.57, 126.34, 79.36, 50.99, 34.65, 34.36, 28.52; MS $[M+Na]^+$ = 258.29.

tert-butyl methyl(4-methylphenethyl)carbamate (**9o**)[17]

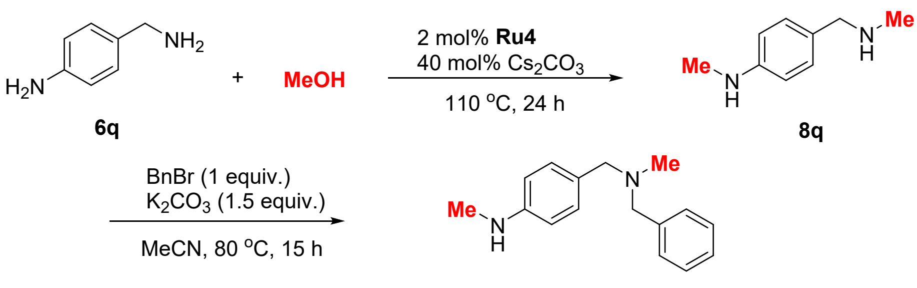


Colorless oil. 58% yield (72 mg). ^{1}H NMR (400 MHz, Chloroform-*d*) δ 7.09 (s, 4H), 3.39 (t, *J* = 7.3 Hz, 2H), 2.82 (s, 3H), 2.75 (t, *J* = 6.9 Hz, 2H), 2.31 (s, 3H), 1.42 (s, 9H); ^{13}C NMR (101 MHz, Chloroform-*d*) δ 155.70, 136.21, 135.76, 129.21, 128.80, 79.27, (51.05 and 50.71), 34.21, 28.46, 21.08; MS $[M+Na]^+$ = 272.32.

tert-butyl (4-methoxyphenethyl)(methyl)carbamate (**9p**)

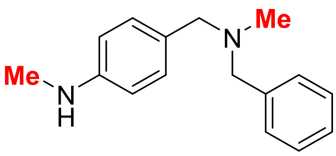


Colorless oil. 67% yield (89 mg). ^{1}H NMR (400 MHz, Chloroform-*d*) δ 7.09 (s, 2H), 6.83 (d, *J* = 7.9 Hz, 2H), 3.78 (s, 3H), 3.38 (t, *J* = 7.4 Hz, 2H), 2.81 (s, 3H), 2.74 (t, *J* = 8.1 Hz, 2H), 1.41 (s, 9H); ^{13}C NMR (101 MHz, Chloroform-*d*) δ 158.25, 155.76, 131.45, 129.89, 114.03, 79.33, 55.39, (51.22 and 50.71), 34.53, 33.82, 28.53; MS $[M+Na]^+$ = 288.32.



Scheme S5 *N*-methylation of 4-aminobenzylamine (**6q**) with methanol

4-((benzyl(methyl)amino)methyl)-*N*-methylaniline (**9q**)[18]



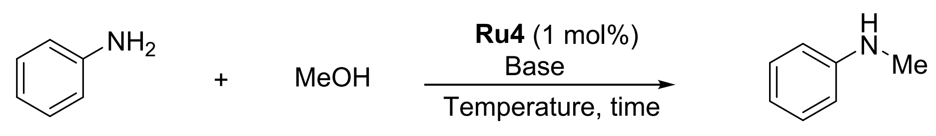
Following the general method for the *N*-mono-methylation of aliphatic with methanol, the crude reaction mixture **8q** was obtained. After cooled to rt, the crude reaction mixture was diluted with 10 mL of EtOAc. The reaction mixture was filtered and dried under vacuum. BnBr (0.5 mmol), K_2CO_3 (0.70 mmol), and MeCN (5 mL) were sequentially added, and the reaction mixture was stirred at 80 °C for 15 h. After cooled to rt, the reaction mixture was filtered and dried under vacuum. The product was purified by column chromatography (SiO_2, 300-400 mesh, *n*-hexane:ethyl acetate =

10:1). Colorless oil. 35% yield (42 mg). ^{1}H NMR (400 MHz, Chloroform-*d*) δ 7.37 – 7.30 (m, 4H), 7.26 – 7.22 (m, 1H), 7.19 – 7.16 (m, 2H), 6.61 – 6.57 (m, 2H), 3.50 (s, 2H), 3.44 (s, 2H), 2.84 (s, 3H), 2.17 (s, 3H); ^{13}C NMR (101 MHz, Chloroform-*d*) δ 148.55, 139.55, 130.23, 129.16, 128.29, 127.73, 126.96, 112.38, 61.64, 61.59, 42.12, 31.03; MS $[M+H]^+$ = 241.14.

3.2. Scope of the aromatic amines.

3.2.1 Condition optimization

Table S4. Optimization of the *N*-methylation of aromatic amines with methanol.[a]



Entry	Base (mol%)	Temperature (°C)	Time (h)	GC Yield (%)
1	CS_2CO_3 (20 mol%)	110	12	89
2	K_2CO_3 (20 mol%)	110	12	84
3	K_2CO_3 (20 mol%)	120	12	96
4	K_2CO_3 (10 mol%)	120	12	91
5	K_2CO_3 (5 mol%)	120	24	84
6	K_2CO_3 (10 mol%)	120	24	96

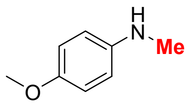
[a] 0.5 mmol aniline, 0.5 mL MeOH, **Ru4** (1 mol%), Base (x mol%), GC yields.

Firstly, the *N*-methylation of aniline (**5a**) with methanol was performed at 110 °C for 12 h with 1 mol% of **Ru4** and 20 mol% of Cs_2CO_3 (entry 2). The desired product **6a** was obtained in 89% yield. When the K_2CO_3 was used as a base, the yield of **6a** was almost kept (entry 2). Additionally, the reaction conditions were optimized further with K_2CO_3 (entries 3-6). To our delight, the yield of **6a** reached up to 96% in the presence of 10 mol% of K_2CO_3 at 120 °C for 24 h (entry 6).

General method for the substrate screening.

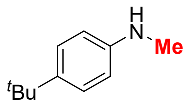
To a 15 mL seal tube in a glovebox, was added **Ru4** (1 mol%), K_2CO_3 (10 mol%), aromatic amines (0.5 mmol), and methanol (0.5 mL) in sequence. Then the tube was closed with a a screw-top cap and removed from the glovebox. The reaction mixture was stirred at 120 °C for 24 h. After cooled to rt, the crude reaction mixture was diluted with 10 mL of EtOAc. The reaction mixture was filtered and dried under vacuum. The product was purified by column chromatography (SiO_2, petroleum ether: ethyl acetate = 80: 1).

4-methoxy-N-methylaniline (**11b**)[19]



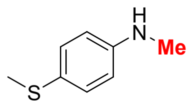
Yellow oil. 88% yield (60 mg). ^{1}H NMR (400 MHz, Chloroform-*d*) δ 6.83 – 6.79 (m, 2H), 6.62 – 6.58 (m, 2H), 3.76 (s, 3H), 3.09 (s, 1H), 2.81 (s, 3H); ^{13}C NMR (101 MHz, Chloroform-*d*) δ 152.29, 143.78, 115.07, 113.83, 55.99, 31.76; MS $[M+H]^+$ = 138.23.

4-(tert-butyl)-N-methylaniline (**11c**)[19]



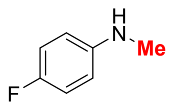
Yellow oil. 82% yield (67 mg). ^{1}H NMR (400 MHz, Chloroform-*d*) δ 7.28 – 7.25 (m, 2H), 6.64 – 6.60 (m, 2H), 2.86 (s, 3H), 1.33 (s, 9H); ^{13}C NMR (101 MHz, Chloroform-*d*) δ 147.10, 140.24, 126.09, 112.39, 33.96, 31.69, 31.12; MS $[M+H]^+$ = 164.17.

N-methyl-4-(methylthio)aniline (**11d**)[20]



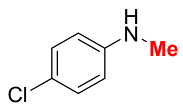
Yellow oil. 84% yield (64 mg). ^{1}H NMR (400 MHz, Chloroform-*d*) δ 7.25 – 7.22 (m, 2H), 6.57 – 6.54 (m, 2H), 3.73 (s, 1H), 2.82 (s, 3H), 2.41 (s, 3H); ^{13}C NMR (101 MHz, Chloroform-*d*) δ 148.37, 131.76; 124.15, 113.12, 30.84, 19.43; MS $[M+H]^+$ = 154.18.

4-fluoro-N-methylaniline (**11e**)[21]



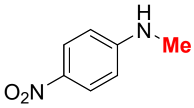
Yellow oil. 86% yield (54 mg). ^{1}H NMR (400 MHz, Chloroform-*d*) δ 6.95 – 6.91 (m, 2H), 6.59 – 6.56 (m, 2H), 3.14 (s, 1H), 2.81 (s, 3H); ^{13}C NMR (101 MHz, Chloroform-*d*) δ 155.99 (d, *J* = 233.1 Hz), 145.77 (d, *J* = 2.0 Hz), 115.73 (d, *J* = 22.2 Hz), 113.33 (d, *J* = 8.0 Hz), 31.49; ^{19}F NMR (377 MHz, Chloroform-*d*) δ -128.41; MS $[M+H]^+$ = 126.09

4-chloro-N-methylaniline (**11f**)[19]



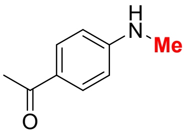
Yellow oil. 86% yield (61 mg). ^{1}H NMR (400 MHz, Chloroform-*d*) δ 7.14 – 7.12 (m, 2H), 6.56 – 6.51 (m, 2H), 2.81 (s, 3H); ^{13}C NMR (101 MHz, Chloroform-*d*) δ 147.96, 129.12, 121.95, 113.59, 30.94; MS $[M+H]^+$ = 142.09.

N-methyl-4-nitroaniline (**11g**)[22]



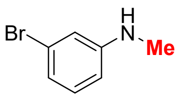
Yellow soild. 55% yield (42 mg). ^{1}H NMR (400 MHz, Chloroform-*d*) δ 8.08 (d, *J* = 9.1 Hz, 2H), 6.52 (d, *J* = 9.1 Hz, 2H), 4.67 (brs, 1H), 2.93 (d, *J* = 5.1 Hz, 3H); ^{13}C NMR (101 MHz, Chloroform-*d*) δ 154.26, 137.91, 126.42, 110.72, 30.15; MS $[M+H]^+$ = 153.26.

1-(4-(methylamino)phenyl)ethan-1-one (**11h**)[22]



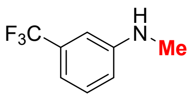
Yellow oil. 46% yield (35 mg). ^{1}H NMR (400 MHz, Chloroform-*d*) δ 7.84 – 7.81 (m, 2H), 6.57 – 6.53 (m, 2H), 4.31 (s, 1H), 2.88 (s, 3H), 2.49 (s, 3H); ^{13}C NMR (101 MHz, Chloroform-*d*) δ 196.52, 153.25, 130.87, 126.69, 111.15, 30.18, 26.06; MS $[M+H]^+$ = 150.14.

3-bromo-N-methylaniline (**11i**)[23]



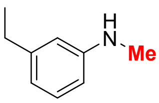
Yellow oil. 84% yield (78 mg). ^{1}H NMR (400 MHz, Chloroform-*d*) δ 7.02 (t, *J* = 8.0 Hz, 1H), 6.82 – 6.80 (m, 1H), 6.73 (t, *J* = 1.8 Hz, 1H), 6.51 (dd, *J* = 8.2, 2.2 Hz, 1H), 3.77 (s, 1H), 2.81 (s, 3H); ^{13}C NMR (101 MHz, Chloroform-*d*) δ 150.69, 130.53, 123.44, 120.05, 114.92, 111.37, 30.64; MS $[M+H]^+$ = 186.24.

N-methyl-3-(trifluoromethyl)aniline (**11j**)[23]



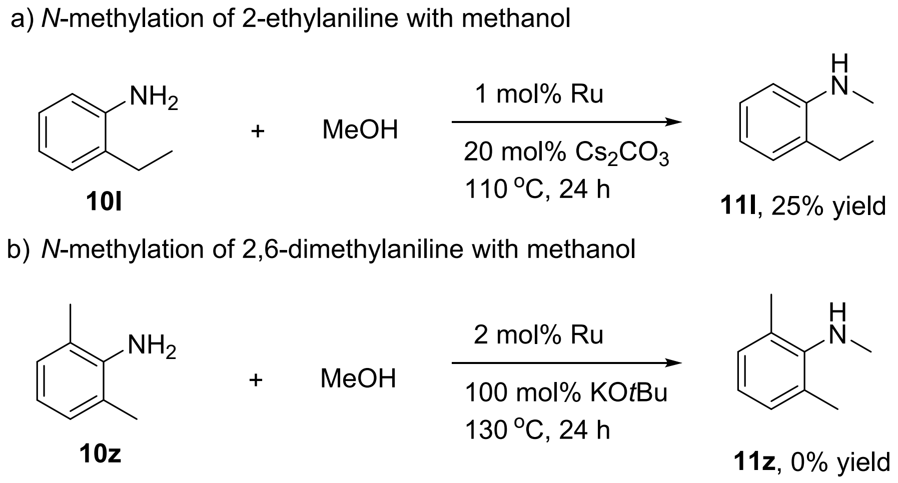
Yellow oil. 83% yield (73 mg). ^{1}H NMR (400 MHz, Chloroform-*d*) δ 7.29 (t, *J* = 7.9 Hz, 1H), 6.96 (d, *J* = 7.6 Hz, 1H), 6.82 (s, 1H), 6.77 (d, *J* = 8.2 Hz, 1H), 3.42 (s, 1H), 2.90 (s, 3H); ^{13}C NMR (101 MHz, Chloroform-*d*) δ 149.55, 131.71 (q, *J* = 32.3 Hz), 129.67, 124.58 (q, *J* = 272.7 Hz), 115.64, 113.69 (q, *J* = 4.0 Hz), 108.53 (q, *J* = 3.0 Hz), 30.59; ^{19}F NMR (377 MHz, Chloroform-*d*) δ -62.87; MS $[M+H]^+$ = 176.20.

3-ethyl-N-methylaniline (**11k**)[24]



Yellow oil. 61% yield (41 mg). ^{1}H NMR (400 MHz, Chloroform-*d*) δ 7.14 (t, *J* = 7.7 Hz, 1H), 6.61 (d, *J* = 7.5 Hz, 1H), 6.50 – 6.47 (m, 2H), 3.31 (s, 1H), 2.86 (s, 3H), 2.62 (q, *J* = 7.6 Hz, 2H), 1.26 (t, *J* = 7.6 Hz, 3H); ^{13}C NMR (101 MHz, Chloroform-*d*) δ

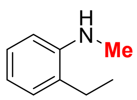
149.55, 145.54, 129.27, 117.19, 112.27, 109.99, 30.94, 29.18, 15.67; MS $[M+H]^+$ = 136.21.



Scheme S6. *N*-methylation of 2-ethylaniline and 2,6-dimethylaniline with methanol.

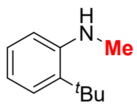
In this catalytic system, the steric hindrance of the substrate has a significant impact on the reaction activity. For example, when 2-ethylaniline (**10l**) was used as the substrate, the product **11l** was obtained in only 25% NMR yield (Scheme S6a). Attempts at the *N*-methylation of 2, 6-dimethylaniline (**10z**) were unsuccessful even at a higher catalyst loading (2 mol%) and a higher temperature of 130 °C (Scheme S6b). These results indicated the methylation reaction between **Ru4** and methanol is relatively difficult.

2-ethyl-N-methylaniline (**11l**)[23]



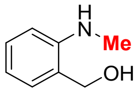
Yellow oil. 73% yield (49 mg). ^{1}H NMR (400 MHz, Chloroform-*d*) δ 7.20 (td, *J* = 7.7, 1.6 Hz, 1H), 7.11 (d, *J* = 7.3 Hz, 1H), 6.75 (td, *J* = 7.4, 1.2 Hz, 1H), 6.67 (d, *J* = 8.0 Hz, 1H), 2.92 (s, 3H), 2.51 (q, *J* = 7.5 Hz, 2H), 1.28 (t, *J* = 7.5 Hz, 3H); ^{13}C NMR (101 MHz, Chloroform-*d*) δ 146.75, 127.80, 127.74, 127.16, 117.22, 109.68, 31.00, 23.85, 12.97; MS $[M+H]^+$ = 136.09.

2-(*tert*-butyl)-N-methylaniline (**11m**)[25]



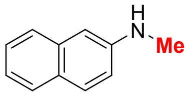
Yellow oil. 37% yield (30 mg). ^{1}H NMR (400 MHz, Chloroform-*d*) δ 7.26 (dd, *J* = 7.7, 1.6 Hz, 1H), 7.20 – 7.15 (m, 1H), 6.74 – 6.68 (m, 2H), 2.93 (s, 3H), 1.43 (s, 9H); ^{13}C NMR (101 MHz, Chloroform-*d*) δ 147.55, 133.38, 127.34, 126.18, 117.04, 111.38, 34.26, 31.38, 30.02; MS $[M+H]^+$ = 164.36.

(2-(methylamino)phenyl)methanol (**11n**)[26]



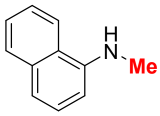
Yellow oil. 51% yield (35 mg). ^{1}H NMR (400 MHz, Chloroform-*d*) δ 7.32 – 7.25 (m, 1H), 7.08 (dd, *J* = 7.7, 1.5 Hz, 1H), 6.73 – 6.69 (m, 2H), 4.65 (s, 2H), 2.90 (s, 3H); ^{13}C NMR (151 MHz, Chloroform-*d*) δ 148.69, 129.82, 129.07, 124.43, 116.47, 110.20, 64.85, 30.42; MS [M+H]$^{+}$ = 138.45.

N-methylnaphthalen-2-amine (**11o**)[19]



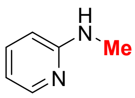
Yellow oil. 82% yield (64 mg). ^{1}H NMR (400 MHz, Chloroform-*d*) δ 7.70 – 7.62 (m, 3H), 7.38 (t, *J* = 7.5 Hz, 1H), 7.21 (t, *J* = 7.5 Hz, 1H), 6.89 (dd, *J* = 8.8, 2.3 Hz, 1H), 6.81 (d, *J* = 2.1 Hz, 1H), 3.88 (brs, 1H), 2.95 (s, 3H); ^{13}C NMR (101 MHz, Chloroform-*d*) δ 147.12, 135.42, 128.94, 127.77, 127.62, 126.43, 126.07, 122.03, 118.01, 103.91, 30.89; MS [M+H]$^{+}$ = 158.06.

N-methylnaphthalen-1-amine (**11p**)[19]



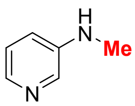
Yellow oil. 78% yield (61 mg). ^{1}H NMR (400 MHz, Chloroform-*d*) δ 7.81 – 7.75 (m, 2H), 7.46 – 7.39 (m, 2H), 7.40 – 7.35 (m, 1H), 7.25 – 7.23 (m, 1H), 6.60 (d, *J* = 7.6 Hz, 1H), 4.42 (brs, 1H), 3.01 (s, 3H); ^{13}C NMR (101 MHz, Chloroform-*d*) δ 144.65, 134.35, 128.79, 126.80, 125.83, 124.82, 123.58, 119.91, 117.45, 103.92, 31.16; MS [M+H]$^{+}$ = 158.11.

N-methylpyridin-2-amine (**11q**)[27]



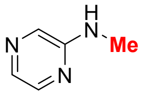
Yellow oil. 56% yield (30 mg). ^{1}H NMR (400 MHz, Chloroform-*d*) δ 8.07 (d, *J* = 4.7 Hz, 1H), 7.44 – 7.40 (m, 1H), 6.57 – 6.54 (m, 1H), 6.38 (d, *J* = 8.4 Hz, 1H), 4.60 (s, 1H), 2.90 (s, 3H); ^{13}C NMR (101 MHz, Chloroform-*d*) δ 159.68, 148.10, 137.62, 112.81, 106.30, 29.19; MS [M+H]$^{+}$ = 109.13.

N-methylpyridin-3-amine (**11r**)[19]



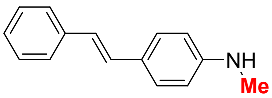
Yellow oil. 71% yield (38 mg). ^{1}H NMR (400 MHz, Chloroform-*d*) δ 8.01 (s, 1H), 7.93 (d, *J* = 4.7 Hz, 1H), 7.08 (dd, *J* = 8.3, 4.6 Hz, 1H), 6.85 (ddd, *J* = 8.4, 3.0, 1.4 Hz, 1H), 2.83 (s, 3H); ^{13}C NMR (101 MHz, Chloroform-*d*) δ 145.36, 138.52, 135.73, 123.84, 118.21, 30.36; MS $[M+H]^+$ = 109.11.

N-methylpyrazin-2-amine (**11s**)[27]



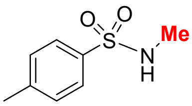
Yellow oil. 58% yield (31 mg). ^{1}H NMR (400 MHz, Chloroform-*d*) δ 7.96 (dd, *J* = 2.7, 1.5 Hz, 1H), 7.87 (s, 1H), 7.76 (d, *J* = 2.8 Hz, 1H), 4.81 (brs, 1H), 2.95 (s, 3H); ^{13}C NMR (101 MHz, Chloroform-*d*) δ 155.52, 142.11, 132.84, 131.99, 28.55; MS $[M+H]^+$ = 110.28.

(E)-N-methyl-4-styrylaniline (**11t**)[19]

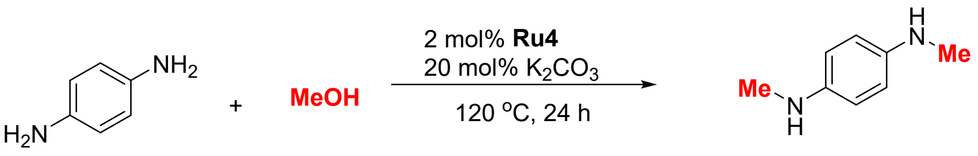


White solid. 90% yield (94 mg). ^{1}H NMR (400 MHz, Chloroform-*d*) δ 7.48 (d, *J* = 7.6 Hz, 2H), 7.39 (d, *J* = 8.5 Hz, 2H), 7.34 (t, *J* = 7.6 Hz, 2H), 7.21 (t, *J* = 7.3 Hz, 1H), 7.05 (d, *J* = 16.3 Hz, 1H), 6.92 (d, *J* = 16.3 Hz, 1H), 6.61 (d, *J* = 8.5 Hz, 2H), 3.81 (brs, 1H), 2.87 (s, 3H); ^{13}C NMR (101 MHz, Chloroform-*d*) δ 149.16, 138.28, 129.03, 128.71, 127.87, 126.84, 126.16, 124.55, 112.59, 30.79; MS $[M+H]^+$ = 210.29.

N, 4-dimethylbenzenesulfonamide (**11x**)[28]

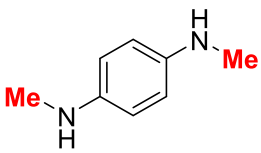


White solid. 70% yield (65 mg). ^{1}H NMR (400 MHz, Chloroform-*d*) δ 7.74 (d, *J* = 8.2 Hz, 2H), 7.32 (d, *J* = 8.0 Hz, 2H), 4.50 – 4.49 (m, 1H), 2.64 (d, *J* = 5.4 Hz, 3H), 2.43 (s, 3H); ^{13}C NMR (101 MHz, Chloroform-*d*) δ 143.66, 135.94, 129.86, 127.41, 29.45, 21.65; MS (ESI) $[M+H]^+$ = 186.23.



Scheme S7. *N*-methylation of *p*-phenylenediamine (**10aa**) with methanol.

N_1,N_4-dimethylbenzene-1,4-diamine (**11aa**) [29]



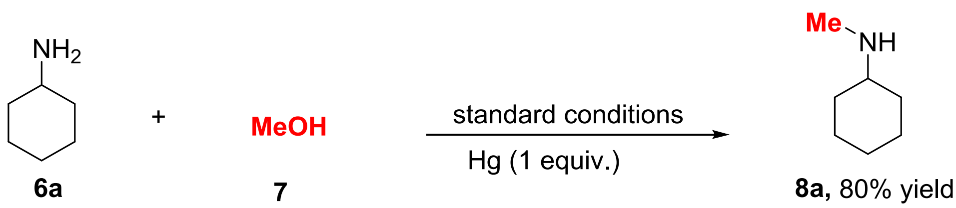
The compound was prepared as described in the general method for the *N*-mono-methylation of anilines with methanol, which was purified by column chromatography over silica-gel (300-400 mesh) with *n*-hexane:ethyl acetate = 4:1. Brown solid. 59%

yield (40 mg). ^{1}H NMR (400 MHz, Methylene Chloride-d_2) δ 6.54 (s, 4H), 2.76 (s, 6H); ^{13}C NMR (101 MHz, Methylene Chloride-d_2) δ 142.55, 114.55, 32.03; MS $[M+H]^+$ = 137.27.

V. Mechanism studies

1. Hg poisoning experiments.

To a 15 mL reaction tube in a glovebox, was added **Ru4** (1 mol%), Cs_2CO_3 (20 mol%), Hg (100 mol%), cyclohexylamine (**6a**, 0.5 mmol), and methanol (0.5 mL) in sequence. Then the tube was closed with a screw-top cap and removed from the glovebox. The reaction mixture was stirred at 110 ^oC for 9 h. After cooled to rt, 1 equiv. of internal standard (mesitylene) was added to the reaction mixture. Then, the reaction mixture was diluted with 10 mL of CH_2Cl_2, filtered through syringe filter and collected in GC vials for analysis.



Scheme S8. The Hg poisoning experiments.

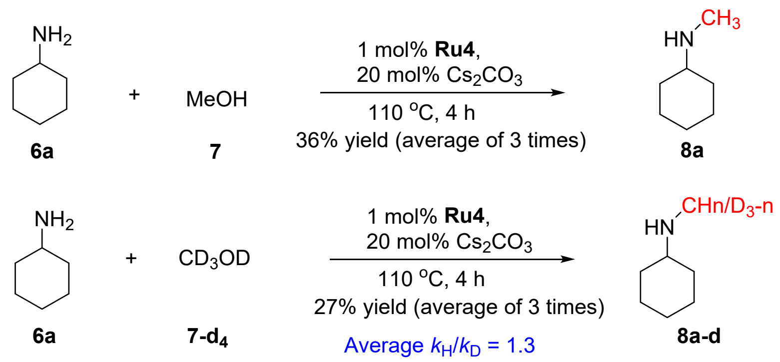
2. Deuteration and kinetic isotopic effect experiments

Parallel reactions

To a 15 mL reaction tube in a glovebox, was added **Ru4** (1 mol%), Cs_2CO_3 (20 mol%), cyclohexylamine (**6a**, 0.5 mmol), and methanol (0.5 mL) or CD_3OD (0.5 mL) in sequence. Then the tube was closed with a screw-top cap and removed from the glovebox. The reaction mixture was stirred at 110 ^oC for 4 h. After cooled to rt, 1 equiv. of internal standard (mesitylene) was added to the reaction mixture. Then, the reaction mixture was diluted with 10 mL of CH_2Cl_2, filtered through syringe filter and collected in GC vials for analysis. When CH_3OH was used as the starting material, the yield of **8a** is 36 ± 2%, and CD_3OD produced the product **8a-d** in 27 ± 4% (Table S5).

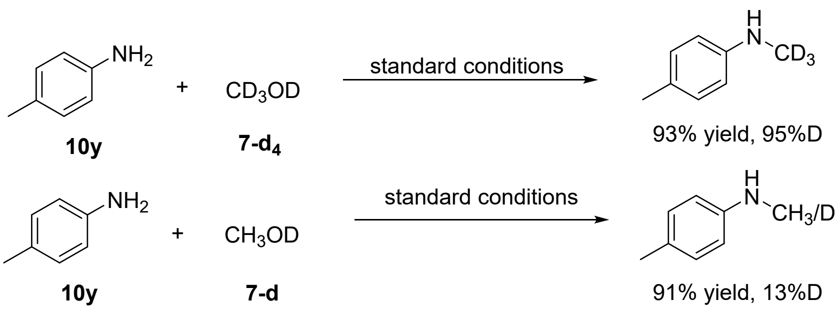
Table S5. The yields of **8a** and **8a-d** in the parallel reactions.

Product \ Entry	1	2	3	Average ± SD
Yield of **8a** (%)	38	34	37	36 ± 2
Yield of **8a-d** (%)	30	23	27	27 ± 4



Scheme S9. The parallel reactions.

The deuterium experiments



Scheme S10. The deuterium experiment using 4-methylaniline and CD_3OD or CH_3OD.

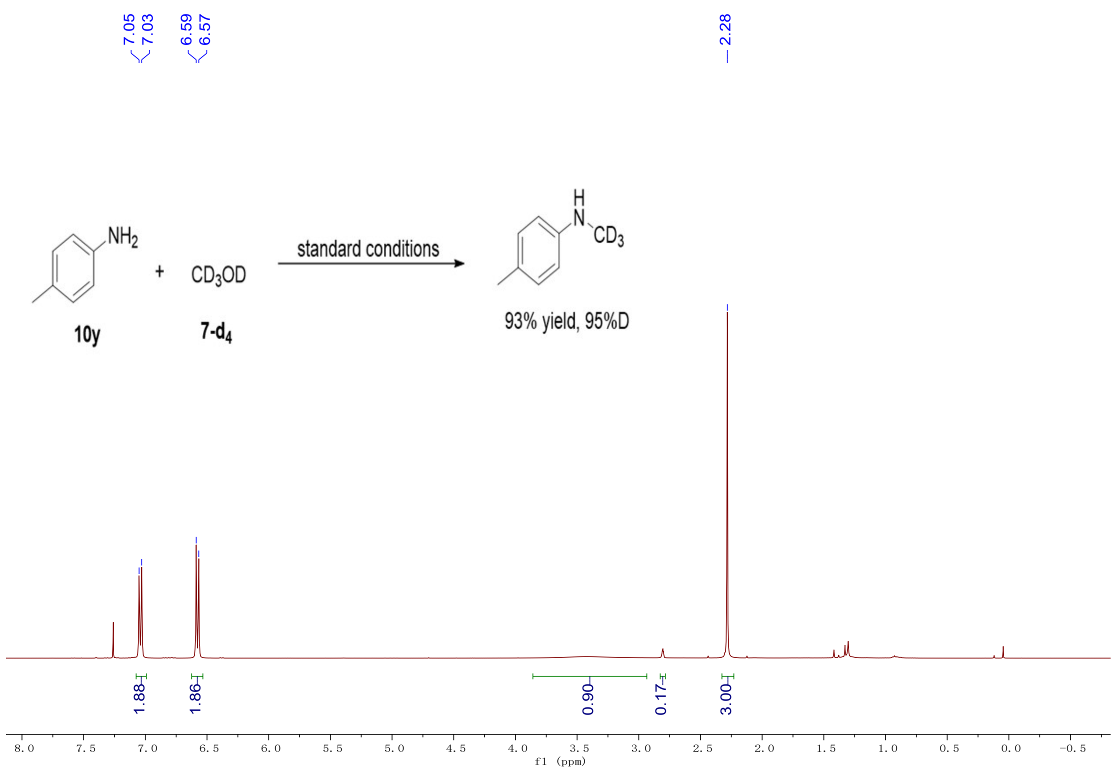


Figure S3. [1] H NMR (400 MHz, $CDCl_3$) spectrum of the product of the reaction of 4-methylaniline with CD_3OD.

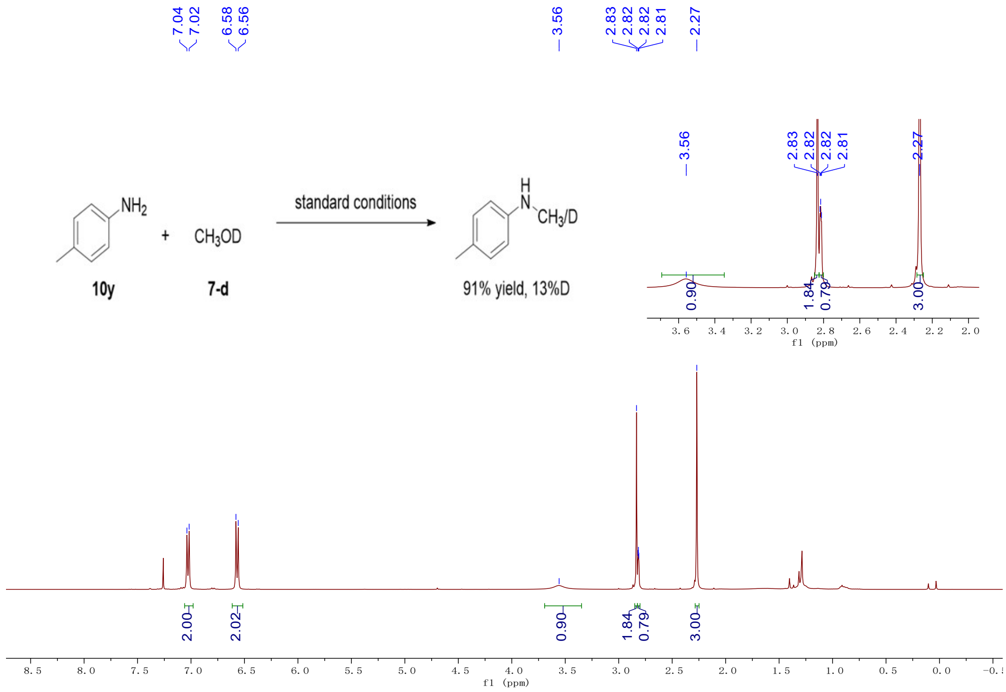


Figure S4. [1] H NMR (400 MHz, $CDCl_3$) spectrum of the product of the reaction of 4-methylaniline with CH_3OD.

3. The studies of the observation of the [RuH] species.

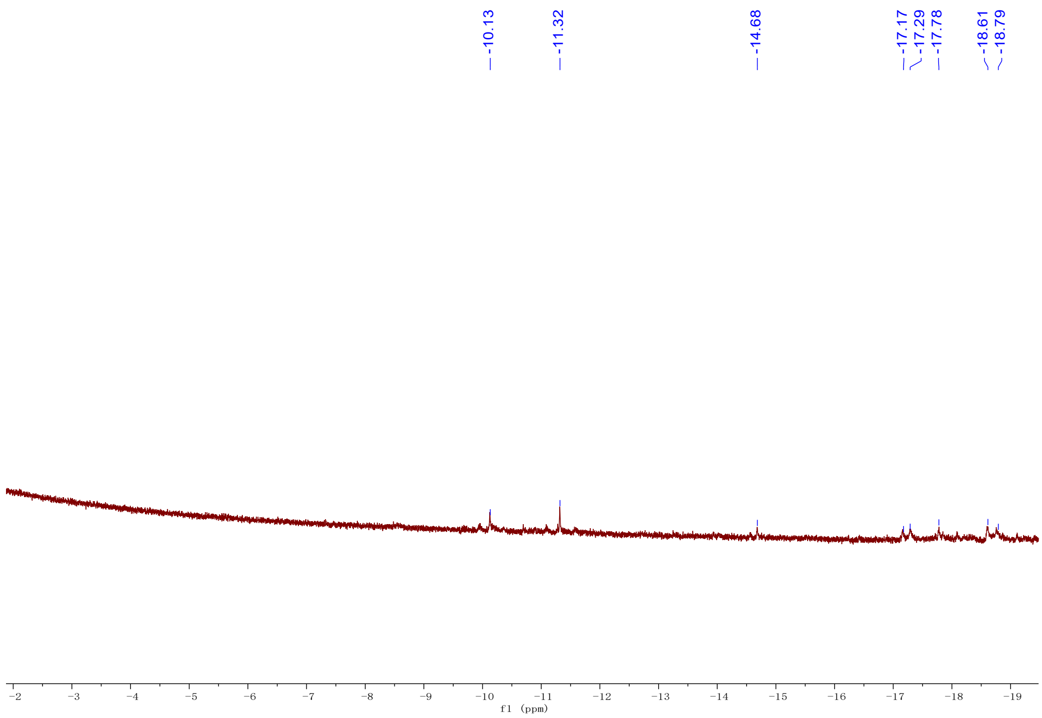


Figure S5. [1]H NMR (400 MHz, CD_2Cl_2) spectrum of reaction mixtures at 2 h of hydride region (-2 - -19ppm)

4. Computational Section

All calculations were performed using the Gaussian 09 package.[30] Full geometry optimization followed by frequency calculations on the stationary points were carried out to ascertain the nature of the stationary points as minima or first order saddle point. Hybrid functional, M06-L was used with the LANL2DZ basis set[31-33] for Ru and 6-31G** basis set[34-36] for non-metal elements. The transition states (TS) were further confirmed by performing intrinsic reaction coordinate (IRC) calculation using same method. The energy results were further refined by calculating the single-point energy at the M06-L/BSII level with a larger basis set (BSII designates SDD for Ru and 6–311++g (d, p) for nonmetal atoms). The solvation effect of MeOH was simulated using the SMD continuum solvent model.[37]

Optimized XYZ coordinates of all species

MeOH			
0 1			
C	0.65463100	-0.01910000	0.00001700
H	1.07675700	0.98823900	0.00003600
H	1.03915300	-0.54028900	-0.89026400
H	1.03911700	-0.54030900	0.89030300
O	-0.74497400	0.12109300	-0.00000900
H	-1.12302100	-0.76178400	-0.00010700
HCHO			
0 1			
C	0.00000000	0.00000000	-0.52616900
H	0.00000000	0.93801500	-1.12847800
H	0.00000000	-0.93801500	-1.12847800
O	0.00000000	0.00000000	0.67674600
Imine			
0 1			
C	2.54894700	0.40057000	0.49681600
H	3.50951500	0.27214400	1.00243800
H	2.18032800	1.43644800	0.42394200
N	1.96031500	-0.62686000	0.04819800
C	0.65790200	-0.52223700	-0.60234300
C	-0.32616900	-1.33386800	0.26521400
C	0.09533600	0.87927900	-0.89105500
C	-1.76477500	-0.93660800	-0.03225200
H	-0.15178300	-2.40369300	0.11977900
C	-0.76372000	1.37909100	0.26325300
H	0.90496000	1.57772800	-1.13033100
C	-2.02751100	0.51549400	0.39670900
H	-1.95048500	-1.05128600	-1.10900000
H	-1.02779500	2.43412000	0.13576500
H	-2.83585800	0.93845000	-0.21140800
H	-0.10387600	-1.13150200	1.32176800
H	-2.46500400	-1.61608400	0.46423000
H	-2.38326200	0.54070000	1.43327900
H	-0.17743400	1.32524000	1.19088300
H	-0.51934100	0.82717600	-1.79854600
H	0.77777800	-1.05174100	-1.55823100
8a			
0 1			
C	2.29272800	0.41585800	0.82343000
H	3.35842600	0.35296400	1.06069100
H	2.05675100	1.47765500	0.62469300
N	1.98719100	-0.50364600	-0.25606600
C	0.58716400	-0.51547600	-0.69270500
C	-0.27295800	-1.29429700	0.30934400
C	-0.04043400	0.87158500	-0.98728200
C	-1.75142100	-1.01481100	0.07345500
H	-0.03824000	-2.36028100	0.23524800
C	-0.89278300	1.37234500	0.17251900
H	0.75221500	1.58980200	-1.23253500
C	-2.09392100	0.44588500	0.40419200
H	-1.98201200	-1.22239100	-0.98111200
H	-1.22723000	2.40094300	-0.00093500
H	-2.94395400	0.77280600	-0.20646700
H	-0.00901200	-0.99963000	1.33472000
H	-2.37984100	-1.69751500	0.65439200
H	-2.42320300	0.52702100	1.44684500
H	-0.27499400	1.40868900	1.07929400
H	-0.66942900	0.80404900	-1.88508700
H	0.58783300	-1.08582600	-1.63175400

H	2.56526100	-0.25899700	-1.05212100
H	1.74684300	0.12969500	1.72887700

IM0

1 1

Ru	-0.66685100	-0.11411200	0.37329300
N	0.73928500	1.28076600	0.51408400
H	0.33687200	2.19605200	0.70745600
N	1.91713000	-1.68064000	-0.11477800
N	0.56602800	-2.16053900	-1.70694700
C	2.10075200	1.43793700	0.33308400
C	-2.65581500	-0.69580600	-0.48272400
H	-2.87043300	-1.04760400	-1.48697000
C	-2.62767700	0.71261600	-0.24274600
C	-2.38046600	1.15292400	1.09221200
H	-2.34083700	2.21545200	1.31346400
C	0.67177900	-1.39777900	-0.57993000
C	3.01706000	0.38098000	0.55907000
C	-2.02292800	0.22614600	2.08994400
H	-1.70687900	0.58785000	3.06483100
C	-1.96723400	-1.18358300	1.83149000
C	2.51920600	-0.95284200	1.00361000
H	3.32649300	-1.56904400	1.40607100
H	1.74081200	-0.85377800	1.77163300
C	1.71995700	-2.88747900	-1.92919700
H	1.82389300	-3.55257900	-2.77170700
C	2.61361000	2.70350900	-0.02327200
H	1.91499900	3.52265300	-0.18217300
C	-2.93214200	1.67852800	-1.35912200
H	-2.74931800	1.13871500	-2.29925900
C	2.57727800	-2.57902400	-0.92442800
H	3.58097600	-2.91485800	-0.71684500
C	-2.34395900	-1.62205800	0.53506300
H	-2.27097300	-2.67932700	0.29647500
C	-2.04132300	2.91385400	-1.34370200
H	-2.22024300	3.53344400	-0.45813000
H	-2.24836100	3.54145100	-2.21346100
H	-0.98130100	2.63995800	-1.36703800
C	4.38116200	0.60675800	0.38713400
H	5.07488200	-0.21005600	0.57642900
C	-0.57835000	-2.19101000	-2.59481400
H	-1.37233500	-2.82828100	-2.19511000
H	-0.26864000	-2.58575000	-3.56221700
H	-0.95799600	-1.17704800	-2.73134000
C	3.97164600	2.90383200	-0.19528200
H	4.33757700	3.88435500	-0.48397500
C	-4.41515900	2.05627700	-1.30646300
H	-5.06353700	1.17705200	-1.35014600
H	-4.67201700	2.70644400	-2.14637800
H	-4.64748000	2.59808800	-0.38357100
C	-1.56175400	-2.14619600	2.89661500
H	-1.09483200	-3.03801600	2.47247300
H	-2.43668100	-2.47228200	3.46984800
H	-0.86096700	-1.69343700	3.60180400
C	4.86717000	1.85196400	0.00581600
H	5.93378100	2.00709700	-0.11773700

IM1

1 1

Ru	0.63300800	-0.23385700	-0.09927500
N	-0.70555300	1.36224800	0.30180600
H	-0.24157500	0.67005500	1.95744200
N	-2.16120900	-1.46079900	-0.21775900
N	-0.96153400	-2.56673200	1.18112800
C	-2.02929800	1.71617100	0.04273800
C	2.77106800	-0.85675600	-0.15088200
H	3.36523600	-1.21270500	0.68899700
C	2.79561600	0.54903200	-0.46552500
C	1.94945000	0.99320800	-1.48961300
H	1.86067900	2.05592300	-1.69512300
C	-0.91945200	-1.52020600	0.31400200
C	-2.98217100	0.86244600	-0.55947400
C	1.08431000	0.08421900	-2.18217300
H	0.38794300	0.46524300	-2.92336100
C	1.14468300	-1.31806800	-1.93598600
C	-2.56930400	-0.43096500	-1.17976000
H	-3.38300700	-0.85185200	-1.77629300
H	-1.70821300	-0.28461000	-1.84107700
C	-2.22302700	-3.13620300	1.19557100
H	-2.46061000	-3.98299400	1.81931700
C	-2.46657800	2.99946200	0.43473700
H	-1.74188300	3.68077900	0.87701200
C	3.71116500	1.46313300	0.30989100
H	3.76346100	1.06235400	1.33280600
C	-2.97982800	-2.43584400	0.31461900
H	-4.01172400	-2.54276300	0.01958000
C	2.02836100	-1.77995600	-0.91024100
H	2.03923400	-2.83448100	-0.65002100
C	3.22381600	2.90241900	0.38331000
H	3.25954500	3.39351900	-0.59465700

H	3.85998200	3.48638900	1.05227800
H	2.19558400	2.97191800	0.75731500
C	-4.31143200	1.27589300	-0.67760400
H	-5.02260200	0.59952800	-1.14922400
C	0.12941100	-3.01619300	2.02531400
H	0.24301600	-4.09861100	1.93791800
H	-0.06167000	-2.75195100	3.06725600
H	1.04629500	-2.52232200	1.70509200
C	-3.78694600	3.39388100	0.30006100
H	-4.08098000	4.38735500	0.62647700
C	5.11932400	1.38625000	-0.28813000
H	5.50017600	0.36126800	-0.30808600
H	5.81595600	1.99160500	0.29717100
H	5.12588300	1.76555700	-1.31498500
C	0.29262300	-2.27975700	-2.69546900
H	-0.08399200	-3.08068100	-2.05305400
H	0.87974400	-2.74537700	-3.49387900
H	-0.55943400	-1.78376500	-3.16571600
C	-4.73171100	2.52577400	-0.24594000
H	-5.76822300	2.82709200	-0.35206400
H	-0.15370900	2.21650300	0.25954200
O	0.43116900	-0.01709900	2.20164700
C	1.45617400	0.57258700	2.99374700
H	1.85215000	1.48823900	2.53618500
H	2.26466600	-0.15615900	3.08960000
H	1.07693900	0.80526300	3.99309900

TS1

1 1

Ru	0.65565900	0.22263900	0.07917600
N	-0.76901000	-1.39193900	-0.32471100
H	-0.40426600	-0.90316000	-1.50821400
N	-2.11324100	1.48003100	0.22080100
N	-0.94390100	2.50063200	-1.26739200
C	-2.12723700	-1.68645000	-0.03497300
C	2.76738000	0.85980200	0.07928700
H	3.32318400	1.20591000	-0.79046100
C	2.83903300	-0.53460900	0.43367000
C	2.02003900	-0.96697000	1.48379600
H	1.96107500	-2.02506700	1.72117700
C	-0.88451700	1.50732800	-0.34534500
C	-2.99954500	-0.80051900	0.62579900
C	1.16747900	-0.05526200	2.18760300
H	0.49852700	-0.43316800	2.95545000
C	1.19034800	1.33628900	1.91145900
C	-2.50670400	0.48178500	1.21762900
H	-3.27396100	0.93473400	1.85108600
H	-1.61926000	0.30648400	1.83481800
C	-2.20289000	3.07524400	-1.28173200
H	-2.45182200	3.88904800	-1.94394900
C	-2.63581600	-2.92397200	-0.45845900
H	-1.96576900	-3.61870900	-0.96088900
C	3.76891000	-1.44309500	-0.32962400
H	3.74941800	-1.10719400	-1.37654300
C	-2.94215000	2.42798600	-0.34673100
H	-3.96671100	2.55613300	-0.03495200
C	2.02093900	1.78680100	0.83413000
H	1.99875800	2.83323300	0.54359900
C	3.36844300	-2.90962600	-0.28648400
H	3.47432000	-3.32931300	0.71940300
H	4.01092600	-3.49889500	-0.94435600
H	2.33259100	-3.06474500	-0.60948800
C	-4.34002200	-1.15516400	0.79971800
H	-4.99791000	-0.45917600	1.31733300
C	0.12885800	2.87748800	-2.16887300
H	0.28048600	3.95840400	-2.13507500
H	-0.10992200	2.57143700	-3.18914600
H	1.03779200	2.36264500	-1.85921500
C	-3.96731500	-3.26462100	-0.26871100
H	-4.32666500	-4.22879700	-0.61550500
C	5.19566600	-1.24610700	0.19245500
H	5.51336500	-0.20121100	0.13357600
H	5.90068600	-1.84359000	-0.39083600
H	5.27387800	-1.56090700	1.23805900
C	0.34878800	2.30273000	2.67662200
H	-0.06970500	3.07565000	2.02568300
H	0.95512600	2.80582500	3.43692300
H	-0.47343700	1.80383000	3.19470100
C	-4.83570000	-2.37340600	0.35655400
H	-5.87893000	-2.62985900	0.50759000
H	-0.24801900	-2.26052000	-0.22361400
O	0.31552400	-0.14877500	-2.05602800
C	1.31332500	-0.79210300	-2.81588100
H	1.67708400	-1.71655400	-2.33955400
H	2.16930300	-0.12085200	-2.96121100
H	0.91586500	-1.04986200	-3.80422500

IM2

1 1

Ru	0.64513000	-0.18908800	-0.06026000
N	-0.94100600	1.19123200	0.80943000
H	-0.91746400	0.64536700	1.68204100
N	-2.09047000	-1.51343100	-0.20105500
N	-0.76209100	-2.75748400	0.94454100
C	-2.27933600	1.59035200	0.43396900
C	2.71789700	-0.73322700	-0.47667700
H	3.35257900	-1.31119800	0.19193000
C	2.78348200	0.70460600	-0.42987100
C	1.85150000	1.40493000	-1.20545100
H	1.78588800	2.48552900	-1.11825000
C	-0.79828400	-1.62270700	0.20646000
C	-3.08726200	0.78752900	-0.38537800
C	0.93837100	0.72697100	-2.07768100
H	0.20994000	1.30447300	-2.64087000
C	0.98299400	-0.67561700	-2.24124100
C	-2.57067300	-0.44319900	-1.07119800
H	-3.35040600	-0.86467000	-1.71164000
H	-1.72548400	-0.18154500	-1.71586800
C	-2.01399900	-3.34320400	1.00475900
H	-2.18885700	-4.26185700	1.54189100
C	-2.77473500	2.79923600	0.92339600
H	-2.14019600	3.41527700	1.55682400
C	3.83017400	1.37647500	0.41972200
H	3.96426700	0.75037000	1.31219900
C	-2.85441300	-2.55927900	0.28509200
H	-3.90673400	-2.65266900	0.06858000
C	1.87150200	-1.40685800	-1.38661700
H	1.85750200	-2.49335400	-1.40967100
C	3.45226200	2.78075100	0.86438700
H	3.42151400	3.47840000	0.02039600
H	4.19065400	3.16872000	1.56943600
H	2.47546200	2.80337000	1.36122700
C	-4.38763100	1.21490100	-0.66403800
H	-5.01379600	0.59546800	-1.30222100
C	0.40915900	-3.27939600	1.62631300
H	0.45058600	-4.36214500	1.49299300
H	0.37256900	-3.02942000	2.68727700
H	1.29619000	-2.81336800	1.19937800
C	-4.06728700	3.21460900	0.62511300
H	-4.43359800	4.15771200	1.01749600
C	5.15708200	1.37923900	-0.34681800
H	5.46232400	0.37056700	-0.63960800
H	5.95258800	1.80349700	0.27112900
H	5.08116900	1.98325000	-1.25688400
C	0.11067200	-1.39445600	-3.21686000
H	-0.37260200	-2.26659300	-2.76558900
H	0.71102200	-1.75829000	-4.05711100
H	-0.66158000	-0.74326400	-3.63241600
C	-4.88341300	2.41435400	-0.16679300
H	-5.89645100	2.72364800	-0.40204000
H	-0.41555300	2.03260500	1.03706100
O	0.63898900	-0.44601700	2.00492900
C	1.79471500	-0.15395400	2.70835300
H	2.14058000	0.89082400	2.59095600
H	2.64901100	-0.80681000	2.43755800
H	1.60956800	-0.31045000	3.78176100

IM3

1 1

Ru	1.25760200	0.15344000	-0.16663200
N	-2.74502800	-1.48821700	-1.47208800
H	-1.78101700	-1.55730400	-1.15394300
N	-1.71894700	0.96547900	0.05574300
N	-0.68905900	2.34309300	-1.23606200
C	-3.71258000	-1.34954300	-0.49092700
C	3.35950000	0.78278100	0.03219900
H	4.00140500	1.08667400	-0.79240000
C	3.35198600	-0.59846300	0.41661300
C	2.41180800	-0.97839500	1.39186400
H	2.27099900	-2.03047200	1.62034000
C	-0.50763600	1.21428400	-0.49814600
C	-3.41877800	-0.68550900	0.72105800
C	1.52212600	-0.02878500	1.98052400
H	0.75947300	-0.36424800	2.67683200
C	1.60519500	1.35739000	1.64827100
C	-2.04625000	-0.15204300	0.96946900
H	-1.97130600	0.21969900	1.99876800
H	-1.25754700	-0.89698300	0.82315000
C	-1.99711300	2.78498000	-1.14177300
H	-2.34446800	3.65833700	-1.67046300
C	-5.02501600	-1.79985500	-0.70068800
H	-5.26343900	-2.31251200	-1.62973000
C	4.25398600	-1.58067500	-0.28891000
H	4.31807100	-1.24450300	-1.33500300
C	-2.64365000	1.91457800	-0.32912200
H	-3.67286100	1.85866000	-0.01073200
C	2.56055200	1.76037000	0.67236200
H	2.60285400	2.79736900	0.35557500

C	3.71471500	-3.00403900	-0.27593200
H	3.76255100	-3.44210000	0.72684400
H	4.31604000	-3.64247800	-0.92650400
H	2.67458700	-3.05286800	-0.61476100
C	-4.42578800	-0.49551600	1.66977000
H	-4.17618900	0.01930900	2.59664800
C	0.32611300	3.00801100	-2.02963200
H	0.51474900	4.01346200	-1.64388800
H	0.00612300	3.08171100	-3.07102800
H	1.24810400	2.42749100	-1.97779500
C	-6.00926900	-1.60294700	0.25682200
H	-7.01422000	-1.96847200	0.06623700
C	5.66082800	-1.50872100	0.31024500
H	6.07656500	-0.49798000	0.26506200
H	6.33880600	-2.17427700	-0.22969100
H	5.65215700	-1.82096700	1.35938100
C	0.67936300	2.35172000	2.26466500
H	0.46436200	3.17870000	1.58301200
H	1.13504200	2.77353700	3.16638700
H	-0.26772400	1.89345900	2.55860900
C	-5.72002000	-0.95101300	1.45494500
H	-6.48876900	-0.80163500	2.20499200
H	-2.96278400	-2.18723800	-2.16622300
O	0.19270600	-1.48463600	-0.88680900
C	0.67420500	-1.10003400	-2.09561500
H	1.47391400	-1.73742800	-2.50454000
H	1.19451600	-0.03509300	-2.05516300
H	-0.10054800	-0.89010100	-2.85518700

TS2

1 1

Ru	1.23875300	0.16623900	-0.21633800
N	-2.79958300	-1.38193600	-1.56429200
H	-1.82875900	-1.47796000	-1.28204600
N	-1.71168500	0.94888700	0.06514100
N	-0.71365500	2.38091500	-1.19485200
C	-3.73405500	-1.30898500	-0.54342100
C	3.33758100	0.80215800	0.10421400
H	3.99524800	1.18101600	-0.67461900
C	3.35006700	-0.59195500	0.39918700
C	2.38940100	-1.04257300	1.33199300
H	2.26688800	-2.10982200	1.49224800
C	-0.50956200	1.22766000	-0.50037400
C	-3.40008200	-0.72497700	0.69914500
C	1.53156100	-0.15001600	2.03793300
H	0.80806700	-0.54517400	2.74372400
C	1.57401100	1.23861000	1.78336400
C	-2.01971900	-0.20563500	0.93736900
H	-1.91641500	0.11765200	1.98016800
H	-1.23807500	-0.94666400	0.74156700
C	-2.02491500	2.80315600	-1.06668600
H	-2.38733500	3.69365100	-1.55504200
C	-5.05305100	-1.74430500	-0.74096900
H	-5.32202100	-2.19304700	-1.69445400
C	4.29666400	-1.51736300	-0.32590100
H	4.38954800	-1.12514500	-1.34960500
C	-2.65100400	1.90133700	-0.27354600
H	-3.67254600	1.82915800	0.06529300
C	2.47534200	1.70856900	0.77945500
H	2.49671800	2.76608500	0.53475700
C	3.79233900	-2.95181400	-0.40505900
H	3.81292200	-3.43858000	0.57586500
H	4.43466400	-3.54208800	-1.06200600
H	2.76816900	-3.01357900	-0.78820400
C	-4.37602600	-0.59910400	1.68992700
H	-4.09661000	-0.14560000	2.63996000
C	0.26040300	3.05278800	-2.03429500
H	0.06357600	4.12537300	-2.02615200
H	0.20401300	2.68962700	-3.06435500
H	1.26257400	2.86601700	-1.64952600
C	-6.00609400	-1.61145900	0.25821300
H	-7.01753900	-1.96288400	0.07578100
C	5.68027900	-1.45147300	0.32576700
H	6.07603000	-0.43211000	0.34806900
H	6.38986600	-2.07471700	-0.22404300
H	5.64246600	-1.81923700	1.35624000
C	0.66971100	2.19173600	2.48906200
H	0.31284000	2.97872900	1.81907500
H	1.21064300	2.67936300	3.30645000
H	-0.19515000	1.68604400	2.92308500
C	-5.67694200	-1.04107100	1.48718900
H	-6.42127600	-0.94087900	2.26945200
H	-3.04132500	-2.03344400	-2.29568900
O	0.19364200	-1.51282100	-1.01164400
C	0.80014700	-1.00680200	-2.04624600
H	1.73618100	-1.47010200	-2.39336600
H	1.36978700	0.51180700	-1.81271100
H	0.18071500	-0.57140400	-2.84780300

IM4

1 1			
Ru	1.22674000	0.20193900	-0.28086400
N	-2.80337900	-1.35034000	-1.60374500
H	-1.82986900	-1.44102200	-1.33088300
N	-1.70771200	0.94716300	0.06229600
N	-0.73541700	2.42629000	-1.16644700
C	-3.72951800	-1.30439200	-0.57483700
C	3.32882200	0.80157300	0.17659800
H	4.00709500	1.23653800	-0.55263100
C	3.34885900	-0.60188500	0.38836800
C	2.36735700	-1.11004700	1.26921500
H	2.25133700	-2.18522100	1.36854000
C	-0.51438500	1.24972500	-0.51553000
C	-3.38811300	-0.74425100	0.67679900
C	1.50437200	-0.26949400	2.02701800
H	0.78964300	-0.71503200	2.71206800
C	1.54079800	1.12887500	1.86734900
C	-2.00725800	-0.22466600	0.91513100
H	-1.90117500	0.08293300	1.96260900
H	-1.22823600	-0.96285400	0.70445100
C	-2.04507500	2.83808400	-0.99966600
H	-2.41861700	3.74375900	-1.44975900
C	-5.04771100	-1.74333900	-0.77019200
H	-5.32235600	-2.17346200	-1.73057600
C	4.33431300	-1.47632100	-0.34849200
H	4.42940600	-1.05267700	-1.35883700
C	-2.65526200	1.90738200	-0.22901200
H	-3.67174600	1.81689900	0.12026000
C	2.42983700	1.65559500	0.88267200
H	2.45158300	2.72681700	0.70638600
C	3.87770400	-2.92336800	-0.47303300
H	3.90714700	-3.43717500	0.49374100
H	4.54342600	-3.47249400	-1.14214500
H	2.85933700	-3.00777200	-0.86682200
C	-4.35612600	-0.64474600	1.67820300
H	-4.07113000	-0.20935900	2.63507000
C	0.23058000	3.15693800	-1.96637500
H	-0.20160200	4.11926100	-2.23937000
H	0.47646600	2.60851600	-2.87858800
H	1.14732300	3.32817800	-1.39934800
C	-5.99254500	-1.63729500	0.23980500
H	-7.00342400	-1.99112200	0.05887700
C	5.70508300	-1.38626400	0.32765800
H	6.07012400	-0.35676500	0.38229900
H	6.44124500	-1.97343100	-0.22674900
H	5.66266700	-1.78242300	1.34740900
C	0.64237800	2.03887200	2.63367200
H	0.22998900	2.82341500	1.99229400
H	1.20425400	2.53474100	3.43172200
H	-0.18376000	1.49818400	3.09887100
C	-5.65608200	-1.09060900	1.47759200
H	-6.39422100	-1.01112900	2.26812900
H	-3.04503000	-1.98525700	-2.34939800
O	0.18012600	-1.51213300	-0.97825900
C	0.83856600	-1.05577800	-1.99724600
H	1.77138800	-1.55140500	-2.30523500
H	1.50787600	0.98272000	-1.63557800
H	0.28928900	-0.53094100	-2.79164500

IM5

1 1			
Ru	-1.00616600	-0.82882700	-0.21506800
N	2.98829200	1.02021400	-1.60447900
H	1.99765900	0.96188000	-1.37299200
N	1.97837800	-1.40918500	-0.07764100
N	1.02000100	-2.85947200	-1.35036200
C	3.90122300	0.97712900	-0.56967200
C	-2.90581700	-1.79687500	0.46730900
H	-3.55122800	-2.36699400	-0.19487600
C	-3.20041900	-0.43078300	0.72751100
C	-2.27458100	0.25937500	1.53220800
H	-2.42233600	1.32320300	1.70720200
C	0.76972900	-1.74352600	-0.60605600
C	3.59107500	0.31826300	0.64271600
C	-1.19015900	-0.38777700	2.18656600
H	-0.53268400	0.18471500	2.83476300
C	-0.96017200	-1.75867600	1.99916200
C	2.24290500	-0.29161900	0.85123700
H	2.16656100	-0.67745000	1.87468600
H	1.42062200	0.41405500	0.69768900
C	2.35871100	-3.20327000	-1.28284000
H	2.75591500	-4.05142900	-1.81716300
C	5.18558000	1.52509000	-0.71848200
H	5.43535200	2.03329400	-1.64710300
C	-4.44590800	0.22556000	0.18674100
H	-4.33828200	1.30545000	0.35737100
C	2.95929300	-2.29167900	-0.48235600
H	3.98689900	-2.16569700	-0.17928100
C	-1.80727400	-2.45383500	1.08523100

H	-1.63062700	-3.50867300	0.89706200
C	-5.66538700	-0.25454500	0.97699700
H	-5.82228600	-1.33014900	0.84089700
H	-6.56887000	0.25580600	0.63385600
H	-5.55827500	-0.06564500	2.04856400
C	4.55870400	0.22525000	1.64550000
H	4.29938800	-0.29039100	2.56929900
C	0.05166900	-3.59190300	-2.14560600
H	0.51504900	-4.51438200	-2.49462600
H	-0.26631200	-3.00745200	-3.01222000
H	-0.82698300	-3.83962500	-1.54773200
C	6.12756400	1.42558700	0.29434500
H	7.11062400	1.86362300	0.14802000
C	-4.62944400	-0.00661300	-1.30876300
H	-3.75027400	0.31848000	-1.87480600
H	-5.49877900	0.54262400	-1.67844700
H	-4.79866700	-1.06491100	-1.53532300
C	0.13708000	-2.48920300	2.69911800
H	0.75591000	-3.05530200	1.99497200
H	-0.28610800	-3.21179600	3.40399400
H	0.78051800	-1.81399600	3.26578600
C	5.82459600	0.77533500	1.48993900
H	6.56137800	0.69703800	2.28185800
H	3.18946300	1.69542600	-2.32506400
C	-0.67555300	0.27831400	-2.09127800
H	-1.57658300	0.66830600	-2.57600700
H	-1.41542200	-1.60748800	-1.52744200
H	-0.07245900	-0.38314100	-2.71541900
N	-0.03211100	0.94986200	-1.12275600
C	-0.47365600	2.31467700	-0.78595300
C	-1.93582300	2.71512800	-0.96218300
C	0.03657300	2.70890800	0.60649700
C	-2.06483700	4.24695100	-0.92397900
H	-2.35734500	2.33812900	-1.89938000
C	-0.69209200	3.93675600	1.16157600
H	-0.08948100	1.85495600	1.28436400
C	-1.05580100	4.89534500	0.03619200
H	-1.93001000	4.65214200	-1.93257300
H	-0.07970300	4.42816500	1.92297200
H	-0.13955200	5.16762500	-0.50420600
H	-1.45566600	5.83258900	0.43268100
H	-3.08732200	4.50764800	-0.63071400
H	-1.61480500	3.62623000	1.67452100
H	1.11744700	2.89192800	0.55271500
H	0.09415700	2.91640000	-1.51853500
H	-2.53416700	2.26907300	-0.15974400

TS3

1 1

Ru	-0.93835100	-0.85285400	-0.19224600
N	2.97185500	1.10817700	-1.57598600
H	1.98493400	1.02974600	-1.32897500
N	2.07942900	-1.34310800	-0.01476500
N	1.16998600	-2.82753600	-1.28225200
C	3.89545700	1.11300300	-0.54874300
C	-2.81834200	-1.94641200	0.28541400
H	-3.39258700	-2.51838200	-0.43580600
C	-3.19709200	-0.59824600	0.57952800
C	-2.34263400	0.09939800	1.45499300
H	-2.53121700	1.14836100	1.66387400
C	0.88553600	-1.71566700	-0.54555200
C	3.62058700	0.45908100	0.67477300
C	-1.24449400	-0.52215000	2.11647200
H	-0.62563400	0.05919500	2.79367100
C	-0.95314400	-1.88154200	1.90211800
C	2.30101000	-0.20489900	0.90071400
H	2.24738600	-0.58155300	1.92915500
H	1.44536800	0.45969700	0.74297000
C	2.51889200	-3.12992500	-1.21259200
H	2.94362900	-3.96856000	-1.74085200
C	5.15679200	1.70686700	-0.71604000
H	5.37961400	2.21053900	-1.65397700
C	-4.42458800	0.04142200	-0.05247000
H	-4.10323400	0.50031400	-1.00008300
C	3.08825700	-2.19683700	-0.41347300
H	4.11019900	-2.04124300	-0.10470300
C	-1.74957000	-2.59109000	0.95351500
H	-1.52003200	-3.62990100	0.73573400
C	-5.01306100	1.14708700	0.82207800
H	-5.29753100	0.76200100	1.80711000
H	-5.91211900	1.55518300	0.35408900
H	-4.32849200	1.98701100	0.97609400
C	4.59774800	0.42029200	1.67187800
H	4.36527600	-0.09029700	2.60549500
C	0.22933900	-3.57347700	-2.09653400
H	0.52550200	-4.62272700	-2.11868000
H	0.20764900	-3.19163100	-3.12139400
H	-0.76903400	-3.48830900	-1.66753900
C	6.10930500	1.65944100	0.29071300

H	7.07372700	2.13266900	0.13015400
C	-5.50047300	-0.99128800	-0.38269800
H	-5.18347300	-1.70879400	-1.14367300
H	-6.38975800	-0.49080200	-0.77236600
H	-5.80204200	-1.55203200	0.50829200
C	0.16214300	-2.57616600	2.60996800
H	0.76582400	-3.17509100	1.92112800
H	-0.24457200	-3.26068100	3.36132800
H	0.81728900	-1.87298200	3.12774100
C	5.83981800	1.01738500	1.49855600
H	6.58409200	0.98132700	2.28663900
H	3.14388400	1.78585600	-2.30220200
C	-0.56305100	0.17184900	-2.13908800
H	-1.42028800	0.55370700	-2.70526000
H	-1.21856100	-1.20829600	-1.75526900
H	0.15175700	-0.38647100	-2.75227600
N	-0.02300100	0.89969100	-1.12170700
C	-0.55514500	2.24602500	-0.85087400
C	-2.03456100	2.53661800	-1.08133200
C	-0.13483200	2.67575400	0.56131300
C	-2.29635700	4.05022900	-1.03616200
H	-2.39026300	2.13333400	-2.03541700
C	-0.97690900	3.84054400	1.09255500
H	-0.22508400	1.80811800	1.22766400
C	-1.37424400	4.77257100	-0.04320200
H	-2.17293300	4.47759700	-2.03693300
H	-0.43369000	4.37450600	1.87728200
H	-0.46387000	5.11471100	-0.55272000
H	-1.85923700	5.67537800	0.33835400
H	-3.34551600	4.21705500	-0.76638900
H	-1.89140200	3.45664600	1.57120900
H	0.93038600	2.93975100	0.55221100
H	0.00130500	2.87800300	-1.56645200
H	-2.61601800	2.03284500	-0.30243200

IM6

1 1

Ru	-0.96964100	-0.85041900	-0.17845500
N	2.96100000	1.07001600	-1.52820100
H	1.97383300	0.97921200	-1.27600100
N	2.07662300	-1.35017700	0.04991800
N	1.17469400	-2.80077900	-1.25899600
C	3.88530200	1.09809400	-0.50215000
C	-2.92092200	-1.87399400	0.15110400
H	-3.53178400	-2.33107200	-0.62146700
C	-3.22217800	-0.53247900	0.57391300
C	-2.32436800	0.04873500	1.48345200
H	-2.45190400	1.08606500	1.77998900
C	0.89021200	-1.70129100	-0.50629800
C	3.61737900	0.45674500	0.72978300
C	-1.20386000	-0.67056100	1.99669500
H	-0.50873800	-0.18277900	2.67377200
C	-1.02971900	-2.05326200	1.69100700
C	2.30191900	-0.21240000	0.96554900
H	2.26067600	-0.58753400	1.99570400
H	1.44377300	0.44997800	0.81412400
C	2.51865100	-3.12135900	-1.17190900
H	2.94448900	-3.95268300	-1.71089700
C	5.14011000	1.70414100	-0.67566400
H	5.35793300	2.19874800	-1.61957900
C	-4.44131800	0.19903600	0.03144900
H	-4.17291900	0.60472600	-0.95651500
C	3.08329100	-2.20721400	-0.34773000
H	4.10292200	-2.06269600	-0.02586600
C	-1.93145400	-2.66174400	0.77579000
H	-1.78424700	-3.69591200	0.48073500
C	-4.86652200	1.36372000	0.92135900
H	-5.11283100	1.01556800	1.93038100
H	-5.75996200	1.83927700	0.51009000
H	-4.10607800	2.14481000	1.01291300
C	4.59393900	0.44128800	1.72802000
H	4.36623300	-0.05910500	2.66832500
C	0.23316600	-3.53347500	-2.08316100
H	0.22036100	-4.58787100	-1.79709700
H	0.50734900	-3.45646200	-3.13818100
H	-0.76252500	-3.11228600	-1.93774900
C	6.09187000	1.68091000	0.33262300
H	7.05070000	2.16383900	0.16723500
C	-5.62289300	-0.75304100	-0.16089400
H	-5.43242900	-1.53201500	-0.90309500
H	-6.49712900	-0.19569700	-0.50495600
H	-5.89354900	-1.24269400	0.78040600
C	0.07847300	-2.84343300	2.30330100
H	0.45133700	-3.61691900	1.62641700
H	-0.28380700	-3.34193100	3.20838200
H	0.91680600	-2.20740800	2.59473100
C	5.82900400	1.05074900	1.54819500
H	6.57263300	1.03400900	2.33757300
H	3.12286500	1.74574800	-2.25875100

C	-0.45713600	0.17488400	-2.24829500
H	-1.09292800	0.77529900	-2.91043400
H	-1.17765700	-0.73629500	-2.04891300
H	0.35204700	-0.30693000	-2.81390500
N	-0.00547600	0.81746000	-1.06359200
C	-0.49085600	2.18732300	-0.84942700
C	-1.96952000	2.49081400	-1.07405300
C	-0.07059900	2.64453500	0.55437800
C	-2.22005100	4.00513400	-1.07348500
H	-2.34255400	2.05156000	-2.00693000
C	-0.90032300	3.83083900	1.05928000
H	-0.18061400	1.79107700	1.23760800
C	-1.29090600	4.74132700	-0.09649100
H	-2.08861100	4.40456500	-2.08491100
H	-0.35077800	4.37763800	1.83071400
H	-0.37821800	5.06448100	-0.61409500
H	-1.76753000	5.65636800	0.26618200
H	-3.26823000	4.19141700	-0.81168400
H	-1.81745100	3.46688700	1.54848400
H	0.99814000	2.89316100	0.54907700
H	0.07114100	2.79579000	-1.58331000
H	-2.53858600	2.01671800	-0.26843700

IM7

1 1

Ru	-0.14547000	-0.78519900	0.18436700
N	1.11510100	0.89149300	1.63504300
H	0.33302600	1.54178100	1.63562700
N	2.84007200	-0.87598600	-0.66738300
N	1.58316500	-0.92489700	-2.40693400
C	2.33818200	1.57612300	1.34785000
C	-2.18915300	-1.74793100	0.28786400
H	-3.10916700	-1.37751300	-0.15960800
C	-1.87720300	-1.37610600	1.60913200
C	-0.61393900	-1.81932500	2.12441200
H	-0.31167600	-1.49977700	3.12045300
C	1.53315300	-0.80157800	-1.05071300
C	3.46038400	0.83036500	0.95926800
C	0.22961100	-2.69178100	1.40235000
H	1.16400600	-3.03265800	1.83796000
C	-0.06871000	-3.00795000	0.05255000
C	3.33041200	-0.64249700	0.69620300
H	4.29633000	-1.14721900	0.78244700
H	2.63083100	-1.13466900	1.37741800
C	2.88568900	-1.05379500	-2.85511600
H	3.12388300	-1.16633700	-3.90080700
C	2.41984900	2.96697200	1.41744000
H	1.54124800	3.53838500	1.70936300
C	-2.81288600	-0.52382700	2.43449100
H	-3.66583200	-0.27374500	1.78593400
C	3.67912700	-1.01289600	-1.75889000
H	4.75116100	-1.07022100	-1.65526100
C	-1.28082700	-2.48986300	-0.51828400
H	-1.53577000	-2.72968700	-1.54674300
C	-2.16307100	0.78628100	2.86957800
H	-1.31090100	0.60681900	3.53772900
H	-2.87304600	1.40986300	3.41980800
H	-1.80818900	1.35504700	2.00166300
C	4.65772800	1.49395900	0.69397200
H	5.53076700	0.91271000	0.40346100
C	0.43274400	-0.93380700	-3.28889900
H	0.30675000	-1.91843600	-3.74896900
H	0.56050000	-0.18858700	-4.07735000
H	-0.45119100	-0.68781200	-2.69969900
C	3.61579900	3.61630100	1.12923000
H	3.66738200	4.69879800	1.19077400
C	-3.34108800	-1.30867100	3.63407900
H	-3.83144100	-2.23657600	3.32849900
H	-4.06518700	-0.71370300	4.19676600
H	-2.52897100	-1.57190700	4.32109200
C	0.86159200	-3.84401600	-0.76262500
H	0.80142800	-3.59508100	-1.82548000
H	0.60756700	-4.90433200	-0.66117600
H	1.90035700	-3.72007800	-0.44390400
C	4.74493000	2.87947100	0.78299500
H	5.68466800	3.38104600	0.57616900
H	1.15450200	0.45561900	2.55359600
N	-0.71933000	1.01942700	-0.55947500
C	0.15278600	1.83519600	-1.37916600
H	1.19950300	1.64701200	-1.12970700
H	0.02833700	1.68927400	-2.46856000
H	-0.02272100	2.90345400	-1.19223700
C	-2.14005800	1.27694400	-0.77962000
C	-2.50824300	2.76022500	-0.65894900
C	-2.71943400	0.70710900	-2.07980900
H	-2.66648600	0.77194200	0.04578400
C	-4.02289400	2.93112800	-0.67009800
H	-2.08132100	3.32297700	-1.50000000
H	-2.06531000	3.17571100	0.25656100

C	-4.23389500	0.89113100	-2.12825900
H	-2.25374700	1.20891100	-2.94151900
H	-2.45685800	-0.35825200	-2.15608100
C	-4.62533100	2.35263200	-1.94502600
H	-4.28571200	3.98879800	-0.56533000
H	-4.45256700	2.41932600	0.20526300
H	-4.63985400	0.49375700	-3.06448500
H	-4.68936100	0.29606300	-1.32028100
H	-5.71493000	2.45661000	-1.93888700
H	-4.26589600	2.93242200	-2.80693100

TS4

1 1

Ru	0.00850600	-0.77700700	0.31512500
N	0.83191500	1.10321800	1.15669100
H	0.02469800	1.44733400	0.33396800
N	2.91478500	-0.80660600	-0.61848200
N	1.65054500	-1.35066600	-2.26782900
C	2.07183000	1.80744700	1.03692700
C	-2.00843100	-1.78107800	0.43726400
H	-2.89654500	-1.51780900	-0.13443500
C	-1.81789500	-1.17878600	1.71012400
C	-0.59263900	-1.46865300	2.36417100
H	-0.35610500	-0.95899100	3.29672700
C	1.60906200	-0.95524000	-0.96393700
C	3.29696300	1.16279700	0.80666100
C	0.35047100	-2.39655100	1.84572600
H	1.26752400	-2.60319900	2.38822500
C	0.12781300	-2.99911600	0.58092000
C	3.36280200	-0.32824800	0.69416400
H	4.38590800	-0.68662800	0.83333800
H	2.72416200	-0.81227400	1.43895400
C	2.95532700	-1.42455700	-2.72311500
H	3.19321800	-1.71802900	-3.73311300
C	2.04701400	3.20480200	1.12397700
H	1.09289400	3.69945900	1.29393400
C	-2.86325000	-0.27914800	2.32878200
H	-3.62970400	-0.10818700	1.55826700
C	3.75183400	-1.07370800	-1.68444100
H	4.82436300	-0.99001000	-1.60732300
C	-1.07505100	-2.68499700	-0.12496300
H	-1.26525600	-3.12934400	-1.09705200
C	-2.30558600	1.07884700	2.74225400
H	-1.55708300	0.98201500	3.53828700
H	-3.10014000	1.71864300	3.13549800
H	-1.84337000	1.60203600	1.89717400
C	4.45815500	1.92688700	0.66499200
H	5.40433000	1.41704800	0.49150900
C	0.50187000	-1.69304900	-3.08305000
H	0.45207300	-2.77391500	-3.24771000
H	0.56924700	-1.19229000	-4.05123500
H	-0.40037700	-1.36185200	-2.56671600
C	3.21102000	3.95117700	0.99315100
H	3.16655400	5.03349400	1.06686700
C	-3.53070100	-0.98568000	3.50888100
H	-3.95767700	-1.94897500	3.21772300
H	-4.33513500	-0.37123300	3.92151200
H	-2.80985200	-1.16962300	4.31312800
C	1.13343500	-3.93701600	-0.00206800
H	1.09171900	-3.94735400	-1.09393300
H	0.93878900	-4.95773900	0.34238700
H	2.15097400	-3.67401100	0.29881700
C	4.42624600	3.31242700	0.76031800
H	5.34012000	3.88825100	0.65613000
H	0.45087000	1.23737100	2.08999500
N	-0.64847300	1.00372500	-0.79802500
C	0.13569800	1.47576800	-1.93100200
H	1.19529200	1.50731900	-1.65703500
H	0.04123100	0.86300100	-2.83851800
H	-0.15460900	2.49829100	-2.20487600
C	-2.09395600	1.16858000	-0.97368900
C	-2.52614300	2.63858700	-1.03011400
C	-2.69048300	0.40518400	-2.15552000
H	-2.55245600	0.75932300	-0.06222400
C	-4.04789800	2.73795700	-0.99649900
H	-2.15526200	3.10629000	-1.95221500
H	-2.07251100	3.18719500	-0.19431800
C	-4.21286100	0.50003900	-2.14413200
H	-2.30085900	0.82016700	-3.09685000
H	-2.36217200	-0.64427700	-2.11862600
C	-4.67644700	1.95342600	-2.14287500
H	-4.36033400	3.78648500	-1.02976700
H	-4.41357700	2.33970500	-0.03686600
H	-4.64079100	-0.04240700	-2.99356100
H	-4.59499300	0.00135900	-1.23833300
H	-5.76849200	2.00502000	-2.09098700
H	-4.39150700	2.42038500	-3.09618500

IM8

1 1

Ru	-0.10606000	-0.84037100	-0.29936300	H	3.11700500	-2.08486200	-3.77494300
N	-0.94677200	0.44560100	-1.80605600	C	-1.43629500	-3.84076300	0.49278500
H	0.41331900	1.70364900	-0.32263100	H	-1.46710900	-3.71449100	1.57770500
N	-3.11028100	-0.51305000	0.48597600	H	-1.30744700	-4.90893700	0.29016900
N	-1.94207100	-0.99873000	2.21849700	H	-2.40532300	-3.54224400	0.08426100
C	-1.71105500	1.56074400	-1.52809700	C	-3.37271200	3.78598400	-0.98892900
C	1.85097600	-1.94027900	0.02164800	H	-4.01225600	4.63716100	-0.78123000
H	2.70376100	-1.62632300	0.62163400	H	-0.11274800	0.75251200	-2.30472800
C	1.82140000	-1.56847200	-1.36041300	N	0.54756100	1.16851400	0.53705200
C	0.66950500	-1.93765000	-2.08566500	C	-0.33339500	1.81987700	1.52603500
H	0.54272100	-1.58508700	-3.10663200	H	-1.35175400	1.84454500	1.13212600
C	-1.82742100	-0.71684200	0.88286400	H	-0.33043300	1.25867200	2.46174300
C	-3.03518300	1.38555500	-1.05570000	H	-0.01688700	2.84821100	1.73188500
C	-0.39838100	-2.66681500	-1.49211700	C	1.99941000	1.27764600	0.86690400
H	-1.29038500	-2.88528500	-2.06951900	C	2.54401000	2.70092600	0.76282700
C	-0.31971300	-3.06794400	-0.12869500	C	2.34372800	0.66557300	2.21524000
C	-3.50856500	-0.01380600	-0.84281400	H	2.50293700	0.68320500	0.09301300
H	-4.59757000	-0.08856300	-0.88571100	C	4.05945100	2.68563600	0.94481200
H	-3.07336100	-0.68094700	-1.59321800	H	2.08997900	3.33787100	1.53403900
C	-3.26213700	-0.96095800	2.62889000	H	2.27122600	3.13703800	-0.20807400
H	-3.55040800	-1.15602400	3.64957100	C	3.85712400	0.64548900	2.40881700
C	-1.26063600	2.88193400	-1.73788400	H	1.87955100	1.25334100	3.01992900
H	-0.25616200	3.03657300	-2.13667600	H	1.92822100	-0.34838300	2.28278200
C	2.97896800	-0.83514000	-2.00000700	C	4.44889600	2.04341100	2.27196700
H	3.65985100	-0.54456100	-1.18531000	H	4.45786600	3.70194200	0.87334500
C	-3.99616600	-0.64707900	1.53468500	H	4.51173400	2.11937300	0.11626800
H	-5.05790600	-0.50660400	1.40657100	H	4.10859500	0.21080100	3.38106800
C	0.84681900	-2.72998000	0.61786400	H	4.30820100	-0.01453800	1.65097800
H	0.92981400	-3.02322800	1.65961100	H	5.53767200	2.00692300	2.37320500
C	2.55190800	0.43416100	-2.72977100	H	4.08433200	2.67020900	3.09768000
H	1.88646300	0.21378200	-3.57255100	**IM9**			
H	3.41996800	0.95826100	-3.13880700	1 1			
H	2.02833700	1.13011300	-2.06159400	Ru	0.62678000	-0.34824800	-0.46158000
C	-3.83856500	2.48794400	-0.78602200	N	-0.65825700	1.12769300	-0.80778500
H	-4.85359800	2.32637800	-0.42528600	H	-0.13250200	1.51981600	1.36507000
C	-0.85728800	-1.28437100	3.13326800	N	-2.10517100	-1.67589700	-0.01974500
H	-0.83515300	-2.34552800	3.40135100	N	-0.85637300	-2.19631400	1.64388800
H	-0.97994400	-0.69713700	4.04657000	C	-2.00942300	1.41634300	-0.69140100
H	0.08405800	-1.01658800	2.65373200	C	2.57709100	-0.56884600	0.57246100
C	-2.08147000	3.97300500	-1.47927600	H	2.76986400	-0.50546900	1.64131200
H	-1.70842400	4.97799300	-1.65693200	C	2.65831100	0.62997100	-0.20957900
C	3.74436300	-1.77485300	-2.93235800	C	2.37386300	0.52455400	-1.58977200
H	4.07569600	-2.67852100	-2.41412000	H	2.34944800	1.41805500	-2.20567500
H	4.62767700	-1.27833800	-3.34273300	C	-0.85879500	-1.46990100	0.48545800

C	-3.00396600	0.42503000	-0.86859400
C	1.96039800	-0.71480000	-2.15241300
H	1.63424600	-0.74600600	-3.18845100
C	1.94059500	-1.92211300	-1.38938000
C	-2.60395200	-0.97258400	-1.20387100
H	-3.44508000	-1.54632100	-1.59950300
H	-1.79393900	-0.98676500	-1.94361200
C	-2.06973300	-2.82546600	1.84255500
H	-2.25894000	-3.44669400	2.70360800
C	-2.41439600	2.74353000	-0.44022000
H	-1.64957400	3.50409300	-0.29751500
C	3.05589000	1.92234200	0.45505100
H	2.71856500	1.85593700	1.49757700
C	-2.86123600	-2.49131000	0.79279300
H	-3.87882000	-2.75903000	0.55623200
C	2.27830800	-1.81945800	-0.01753500
H	2.19300300	-2.70136700	0.60994700
C	2.41263300	3.15803500	-0.15375700
H	2.71017000	3.31366200	-1.19637400
H	2.71966800	4.04780800	0.40030500
H	1.32161400	3.10872600	-0.08839000
C	-4.34749700	0.77853500	-0.76520900
H	-5.10464100	0.01296300	-0.92110200
C	0.24185500	-2.30354000	2.58316600
H	0.77162300	-3.25273900	2.46286100
H	-0.14238700	-2.24318000	3.60287300
H	0.92756400	-1.47342000	2.41899700
C	-3.75437800	3.07106700	-0.33412500
H	-4.04113100	4.09689400	-0.12534000
C	4.58526500	2.02231000	0.43947300
H	5.05953800	1.15403500	0.90591100
H	4.90931000	2.91336100	0.98273600
H	4.96258900	2.09975600	-0.58557300
C	1.52145600	-3.21848900	-1.99657100
H	1.05574200	-3.87317500	-1.25573000
H	2.38729700	-3.74827300	-2.40821800
H	0.81200600	-3.06676900	-2.81351800
C	-4.73184100	2.08733300	-0.49527800
H	-5.78394000	2.34286900	-0.42514000
H	1.21290600	0.64903900	3.14742300
H	-0.17433800	1.97770300	-1.09398700
C	0.37669700	1.36838300	3.22351000
H	0.61811200	2.06572100	4.02778900
H	-0.52464500	0.81073000	3.51890900
O	0.19925800	2.11838000	2.04762500

TS5

1 1

Ru	0.67707100	-0.24848600	-0.08763000
N	-0.58912700	1.43570200	-0.50505200
H	-0.19310000	2.16544100	0.36895200
N	-2.07495900	-1.54080200	-0.13575500
N	-1.10727900	-2.07252300	1.70781100
C	-2.03135500	1.58287400	-0.48151700
C	2.69460500	-1.02361400	0.40096400
H	3.10563500	-1.15865100	1.39885300
C	2.93327100	0.21885600	-0.28309000
C	2.31995500	0.39541700	-1.53438900
H	2.40782400	1.35081600	-2.04339700
C	-0.94613100	-1.32243300	0.58455800
C	-2.91136300	0.58932000	-0.93925200
C	1.48300100	-0.61925700	-2.09832500
H	0.97031100	-0.43101400	-3.03849600
C	1.30909000	-1.87575300	-1.45785200
C	-2.40835500	-0.76383100	-1.33577100
H	-3.16247500	-1.32324200	-1.89454500
H	-1.50097300	-0.70975200	-1.94430000
C	-2.32762800	-2.72741300	1.69212700
H	-2.64228900	-3.36917200	2.49955100
C	-2.55163100	2.78829700	-0.00261200
H	-1.86877300	3.54215900	0.37681200
C	3.79805900	1.27084300	0.36198200
H	3.71329300	1.12170300	1.44829300
C	-2.94098700	-2.38329900	0.53300500
H	-3.90355800	-2.65814800	0.13092900
C	1.94300600	-2.06054700	-0.18679100
H	1.76532900	-2.97954300	0.36504000
C	3.37612100	2.69797100	0.04335200
H	3.51724500	2.93392500	-1.01725700
H	3.99849700	3.40067500	0.60227600
H	2.33231200	2.88809200	0.31796800
C	-4.28571700	0.83337300	-0.92312300
H	-4.96024700	0.05662400	-1.27860200
C	-0.16127200	-2.15631000	2.80466700
H	0.19636000	-3.18147200	2.92784300
H	-0.63280200	-1.82903500	3.73367900
H	0.68234400	-1.50074100	2.58492700
C	-3.92355800	3.01632700	0.00341600
H	-4.30604700	3.96080200	0.37740900

C	5.25571800	1.00802400	-0.03267800
H	5.57802100	-0.00549700	0.22363700
H	5.91768100	1.71085900	0.47900000
H	5.39524200	1.14183300	-1.11045800
C	0.48155200	-2.96035600	-2.06190500
H	-0.03619800	-3.54574200	-1.29721000
H	1.12145400	-3.64932500	-2.62321600
H	-0.26144300	-2.56645400	-2.75933800
C	-4.79758100	2.04167900	-0.46605100
H	-5.86864100	2.21631800	-0.46898000
H	0.56670500	0.64422500	1.56491300
H	-0.25641500	1.85545800	-1.37320800
C	0.59559100	1.68115300	2.18200100
H	1.64648700	1.66781900	2.53363200
H	-0.08699300	1.40536000	3.01218300
O	0.24341200	2.70431500	1.43418700

IM10

1 1

Ru	0.60420200	-0.27022700	-0.07906800
N	-0.71150200	1.34658600	-0.94767500
H	-0.20939000	2.20574900	-0.72006300
N	-2.15999700	-1.58414700	-0.09030800
N	-1.13399200	-2.07389900	1.73197000
C	-2.10641800	1.55523800	-0.63229200
C	2.53056900	-1.04065900	0.58407700
H	2.84037200	-1.15521500	1.61985100
C	2.89403200	0.14960000	-0.13264900
C	2.39542900	0.27378400	-1.43919300
H	2.55964100	1.19855400	-1.98560100
C	-1.00714300	-1.33154100	0.59481700
C	-3.03386200	0.53424000	-0.87138000
C	1.67752100	-0.78994300	-2.08475400
H	1.32553100	-0.65004100	-3.10433400
C	1.42296200	-2.00231600	-1.43249700
C	-2.57237500	-0.83453800	-1.27819700
H	-3.37506600	-1.39704700	-1.76103600
H	-1.72206700	-0.81627200	-1.96850600
C	-2.34082200	-2.75309200	1.75674600
H	-2.61757400	-3.39640600	2.57656200
C	-2.52216400	2.77765900	-0.11061400
H	-1.78546800	3.55687100	0.06656800
C	3.78754200	1.16890600	0.53086200
H	3.42583600	1.27844200	1.56478500
C	-2.99291400	-2.43372000	0.61422700
H	-3.95907100	-2.73386800	0.23997900
C	1.81161800	-2.08362400	-0.05084400
H	1.55570100	-2.97593900	0.51508400
C	3.78135600	2.53476100	-0.13698700
H	4.23139500	2.48975400	-1.13487600
H	4.38112900	3.23865800	0.44520600
H	2.77531200	2.95383400	-0.22997900
C	-4.38100300	0.77288700	-0.60095100
H	-5.10409100	-0.01815600	-0.78965000
C	-0.15617500	-2.14192800	2.79989400
H	0.37255500	-3.09947500	2.78852700
H	-0.65575100	-2.02765700	3.76348300
H	0.55475300	-1.32681300	2.66243300
C	-3.86979300	2.99368100	0.16275400
H	-4.18777000	3.95157800	0.56222300
C	5.20959300	0.60260400	0.59746300
H	5.24710900	-0.36194800	1.11211700
H	5.87001600	1.29200300	1.12956400
H	5.61719700	0.46065900	-0.40873300
C	0.71815000	-3.14122900	-2.09035800
H	-0.00655100	-3.60690700	-1.41555800
H	1.43346400	-3.91913800	-2.37768900
H	0.19507400	-2.82701000	-2.99628600
C	-4.80504900	1.99598400	-0.09186600
H	-5.85794600	2.16680600	0.10720800
H	0.35716800	0.50279800	1.32308500
H	-0.61342600	1.22394300	-1.95332100
C	0.67397600	2.94711600	1.65162000
H	1.65558500	2.66558200	2.08809800
H	-0.21442200	2.71800200	2.27663700
O	0.58426600	3.49445300	0.57325300

IM11

1 1

Ru	-0.44445000	-0.93355800	0.00502800
N	-0.44015200	1.12902500	-0.91207800
H	0.38873800	1.54971000	-0.46242900
N	-3.38888200	-0.22794400	-0.04136800
N	-2.87197800	-0.88325300	1.93898500
C	-1.47951300	2.13510000	-0.90685300
C	1.45481600	-2.18753600	0.15148700
H	2.34128000	-1.97290700	0.74450200
C	1.41283200	-1.77370100	-1.19020800
C	0.21843100	-2.05085000	-1.94246000
H	0.16005500	-1.71898200	-2.97767600

C	-2.32585200	-0.62565300	0.71579200
C	-2.80741900	1.80845200	-1.21313000
C	-0.85349200	-2.75875000	-1.39425500
H	-1.73515700	-2.97520600	-1.99047700
C	-0.83354300	-3.11232800	-0.00463400
C	-3.23469000	0.37765600	-1.36551700
H	-4.19558600	0.30426300	-1.88094100
H	-2.50661100	-0.22845300	-1.91398200
C	-4.23516000	-0.63817900	1.93964400
H	-4.84319500	-0.79530700	2.81630900
C	-1.13320300	3.45751600	-0.63054800
H	-0.09365100	3.69359400	-0.41371300
C	2.62441900	-1.16741100	-1.86009700
H	3.36946200	-0.99757300	-1.07044900
C	-4.55860000	-0.21095300	0.69595100
H	-5.50265300	0.09409600	0.27238000
C	0.33295200	-2.82690600	0.76097500
H	0.37349100	-3.12652900	1.80361100
C	2.34829300	0.17220300	-2.53272100
H	1.55859700	0.09252700	-3.29046700
H	3.24088100	0.53459800	-3.05132200
H	2.06362000	0.94061500	-1.80590500
C	-3.75952300	2.82793600	-1.25156700
H	-4.78993400	2.57445300	-1.49274300
C	-2.14297600	-1.31760900	3.11365900
H	-2.54610000	-2.26289300	3.48637900
H	-2.21906600	-0.56562000	3.90249900
H	-1.09560900	-1.44110200	2.83880000
C	-2.09819900	4.45986700	-0.66041500
H	-1.81443900	5.48562500	-0.44668100
C	3.21530700	-2.16641200	-2.85588700
H	3.43532300	-3.12761700	-2.38402700
H	4.14445000	-1.77882200	-3.28304200
H	2.52407200	-2.35257700	-3.68533000
C	-1.99367900	-3.83134400	0.60360000
H	-1.99697500	-3.73803700	1.69188400
H	-1.94229500	-4.89894700	0.36607200
H	-2.94771200	-3.45528400	0.22272200
C	-3.41505200	4.14811700	-0.98180400
H	-4.17038100	4.92634000	-1.02123300
H	-0.08551100	-0.12151000	1.34445000
H	-0.17807900	0.94151200	-1.87781600
C	1.11359400	2.59012600	1.95958400
H	1.50485700	2.45289600	2.97460600

H	0.16244800	3.12213700	1.87212700
N	1.67573200	2.17627900	0.89945200
C	2.92798600	1.42671900	0.94711400
C	3.97609500	2.10774100	0.06624700
C	3.52078100	1.11688300	2.32305900
C	5.12967300	1.14106400	-0.24579400
H	3.51308800	2.48568100	-0.85136500
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H	2.92070900	0.33549800	2.80902000
H	4.34450700	2.99140700	0.60379400
H	2.66360500	0.47210600	0.45725800

TS6

1 1

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C	-0.99379000	-0.67070400	3.19619600	H	-1.11179000	3.41455400	1.51765600
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H	4.00707800	-3.11705700	-1.64240600	C	4.34465900	0.72218900	1.10235900
C	-1.97471100	-4.18777900	0.91818900	H	4.05109500	1.25991900	-0.98321800
H	-2.23527300	-3.73373300	1.87764600	H	4.04234300	0.61812700	3.25036500
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C	-2.46406900	3.98270800	-1.98117200	H	5.36241600	0.32746500	1.18556900
H	-2.97292200	4.92955100	-2.12803400	H	4.45864400	2.20591700	2.65106400
H	-0.65137100	1.75105900	1.06691300	H	1.76970600	0.79645100	2.58820700
H	0.39200800	0.37702200	-1.96365000	H	3.58053400	3.61547500	0.89255100
C	-0.31721300	2.66643300	1.59318600	H	1.62677600	1.34115600	0.33819100
H	-0.21157800	2.41404700	2.65588200				

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VII. NMR Spectra

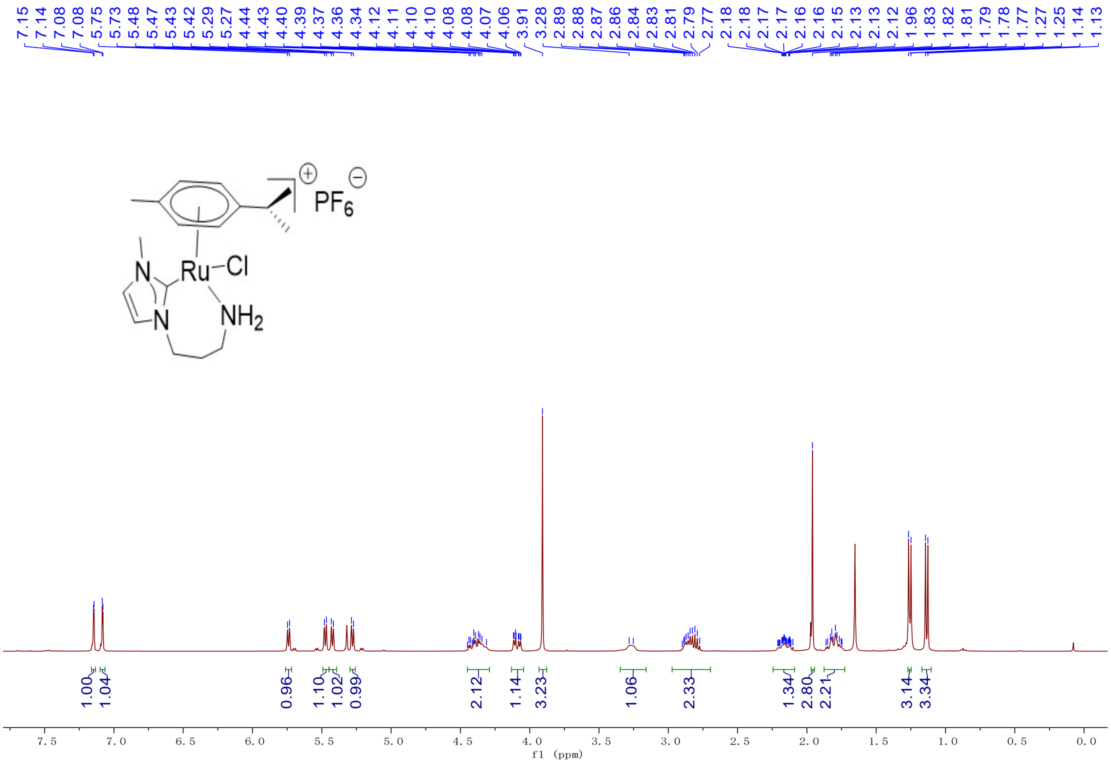


Figure S6: ^{1}H NMR (400 MHz, Methylene Chloride-d_2, 298 K) spectrum for Ru3

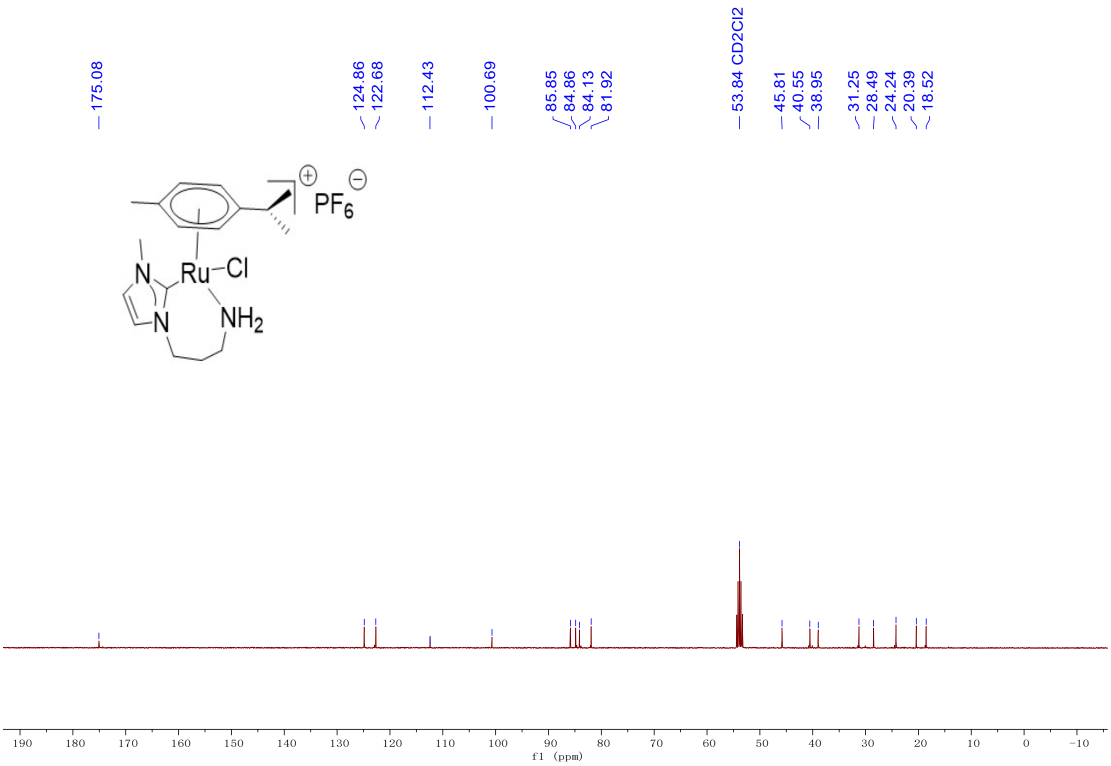


Figure S7: ^{13}C NMR (101 MHz, Methylene Chloride-d_2, 298 K) spectrum for Ru3

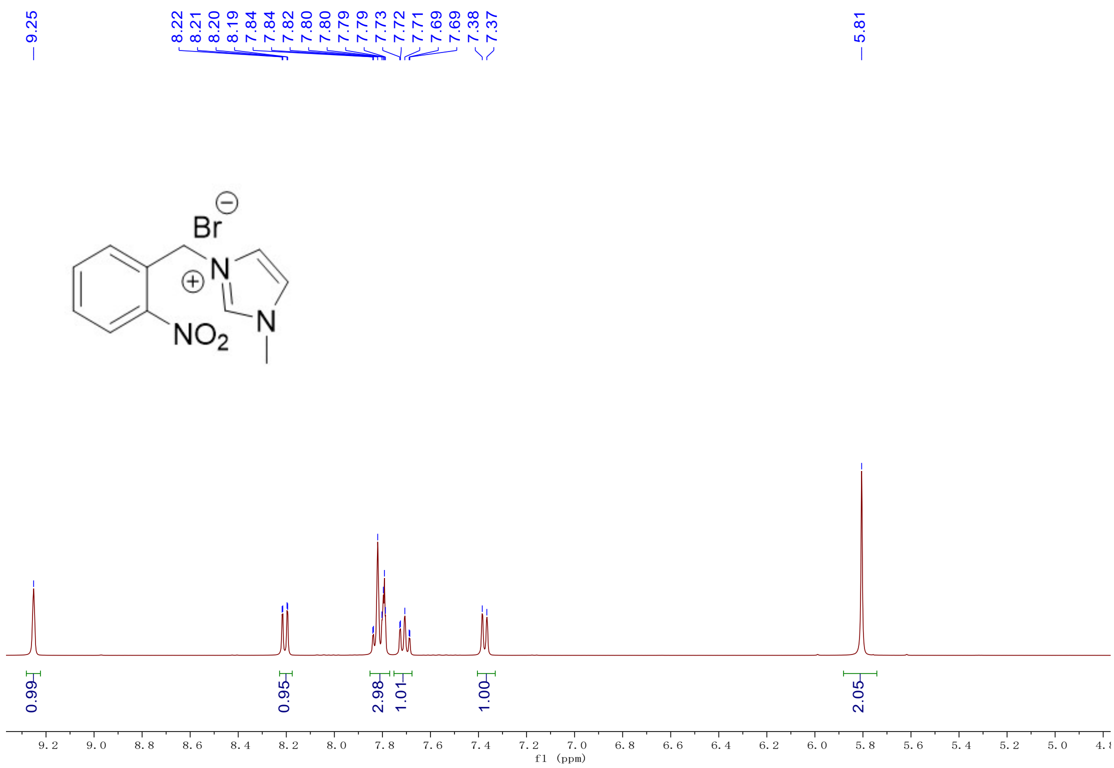


Figure S8: ^{1}H NMR (400 MHz, DMSO-d6, 298 K) spectrum for 4

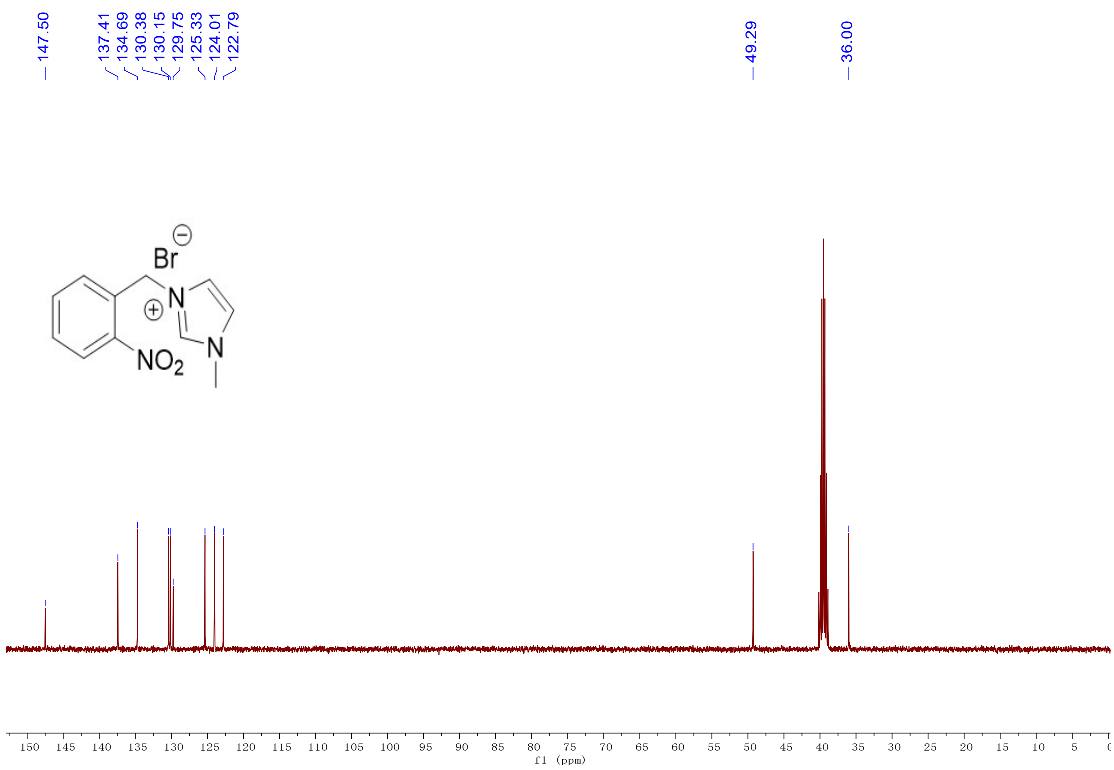


Figure S9: ^{13}C NMR (101 MHz, DMSO-d6, 298 K) spectrum for 4

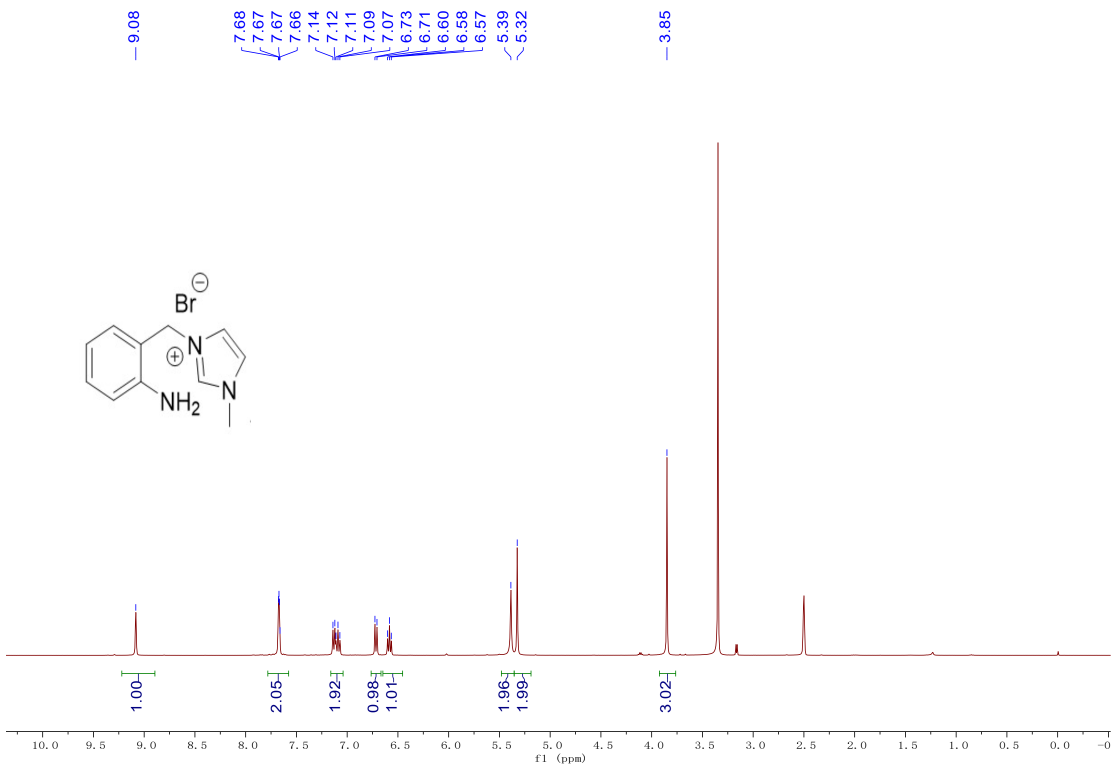
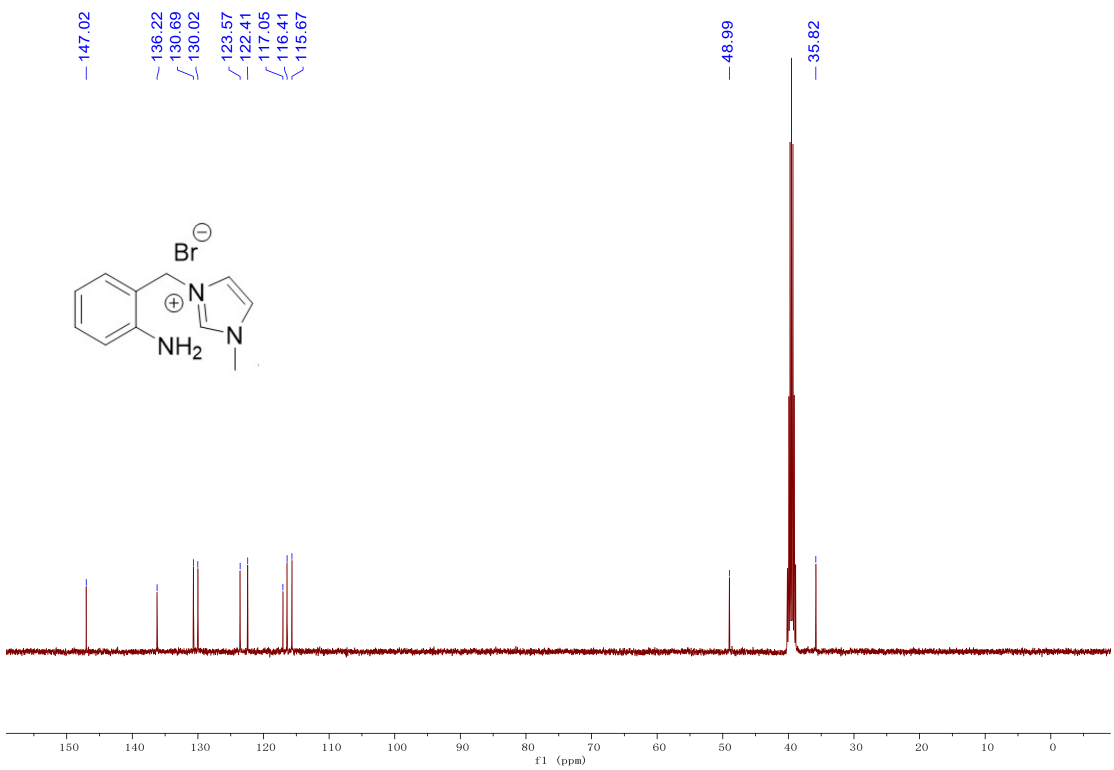


Figure S10: [1]H NMR (400 MHz, DMSO-d6, 298 K) spectrum for 5



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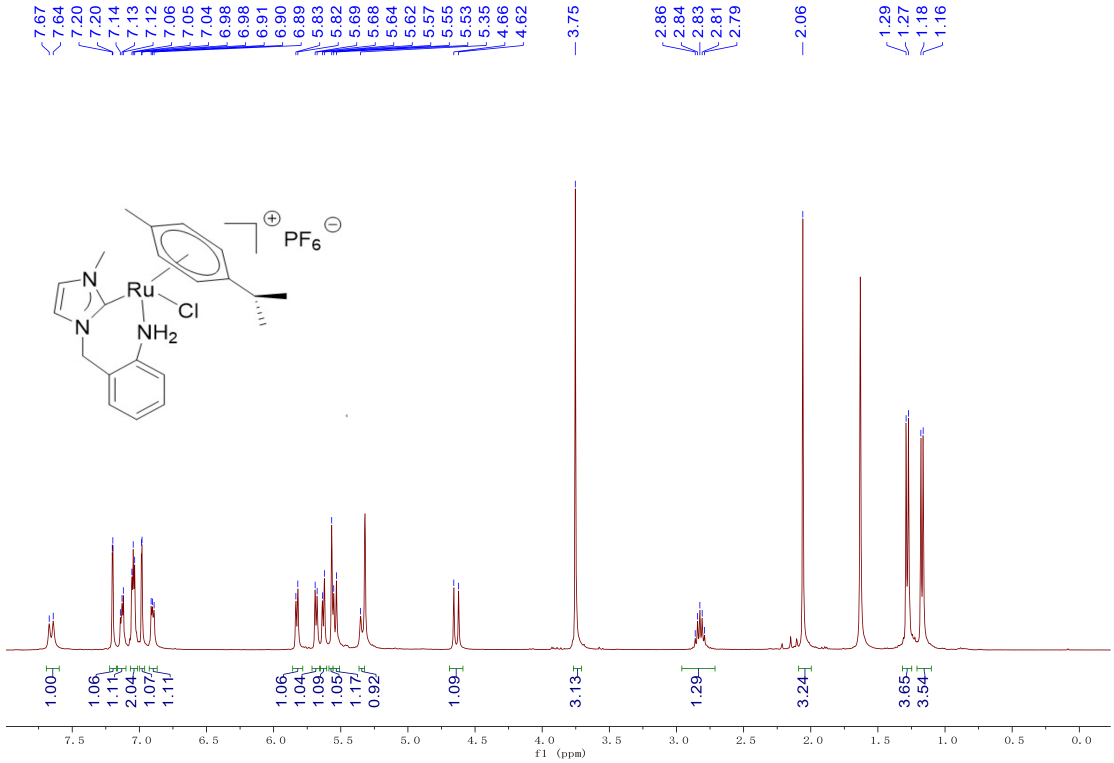

Figure S12: ^{1}H NMR (400 MHz, Methylene Chloride-d_2, 298 K) spectrum for Ru4

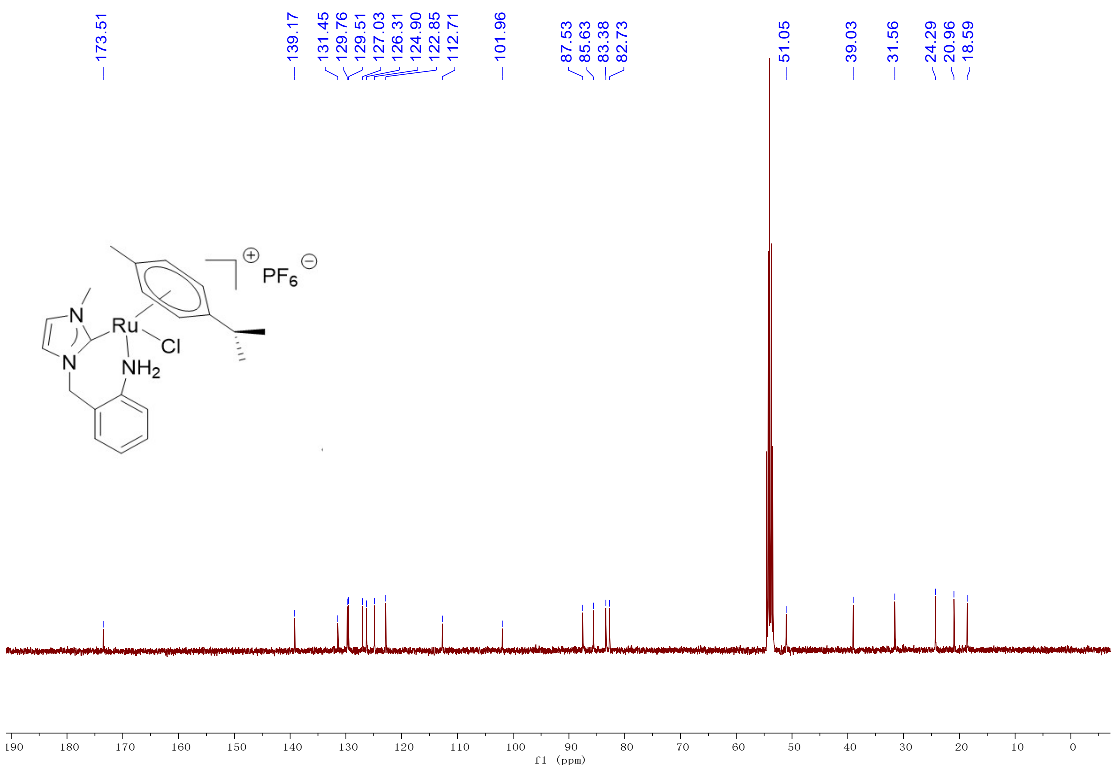

Figure S13: ^{13}C NMR (101 MHz, Methylene Chloride-d_2, 298 K) spectrum for Ru4

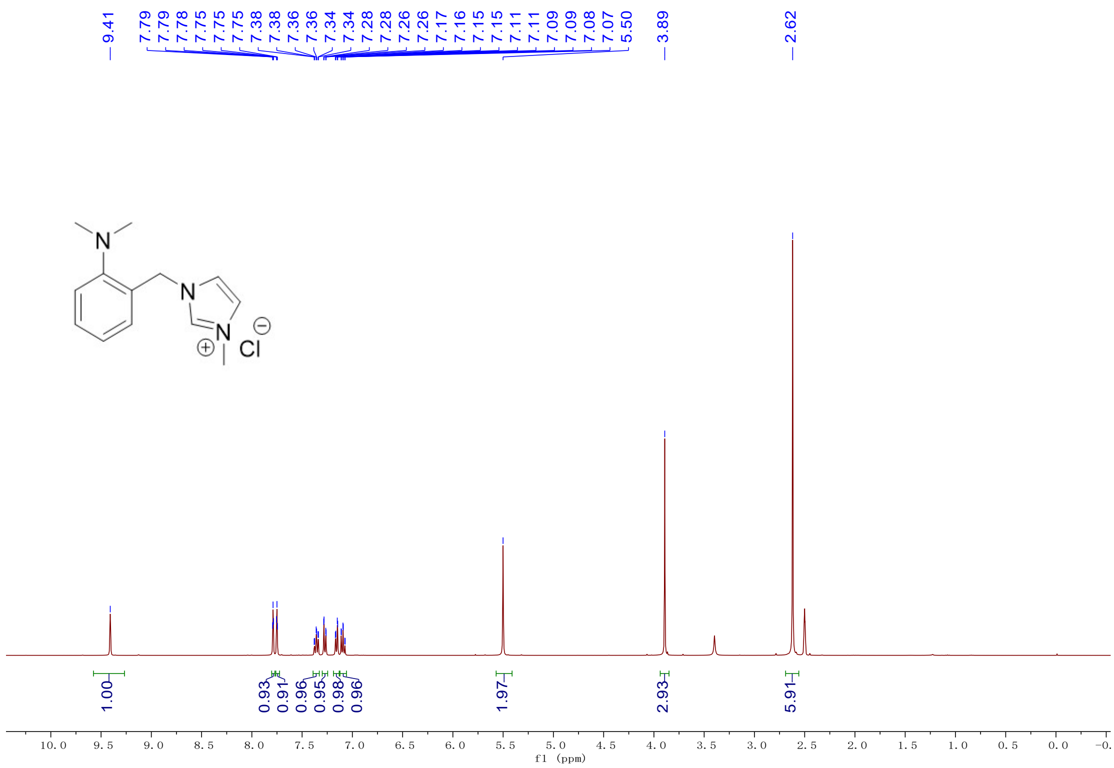

Figure S14: ^{1}H NMR (400 MHz, DMSO-d6, 298 K) spectrum for 15

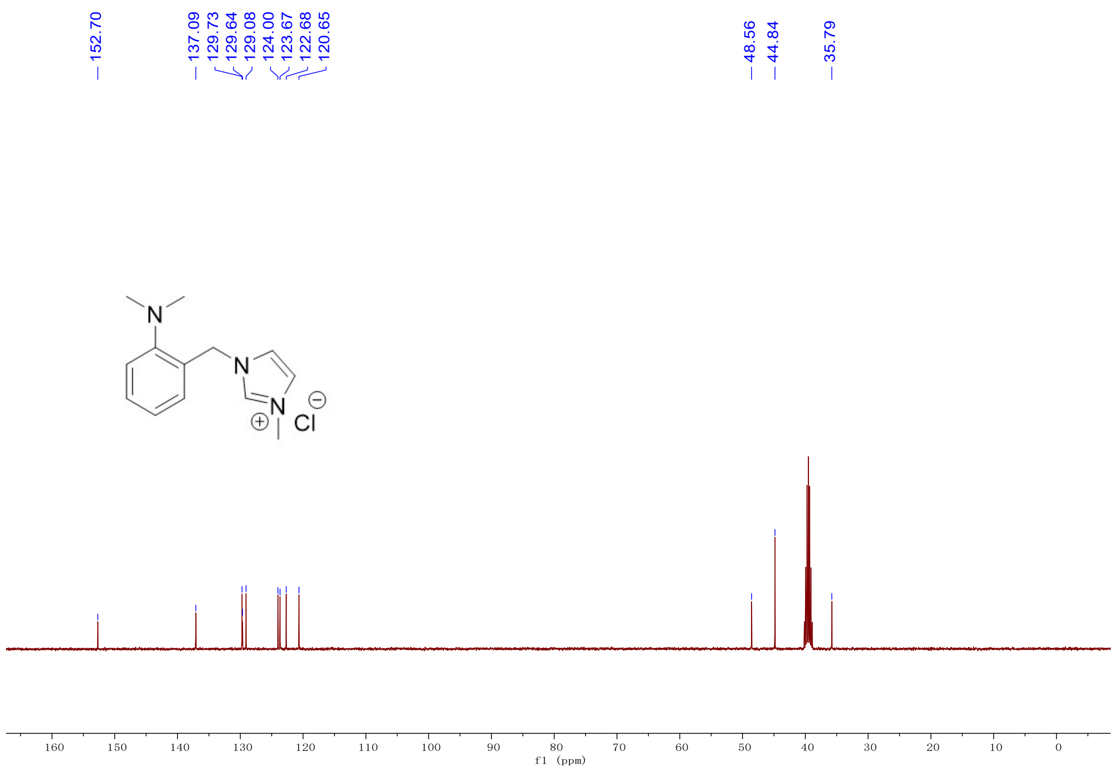

Figure S15: ^{13}C NMR (101 MHz, DMSO-d6, 298 K) spectrum for 15

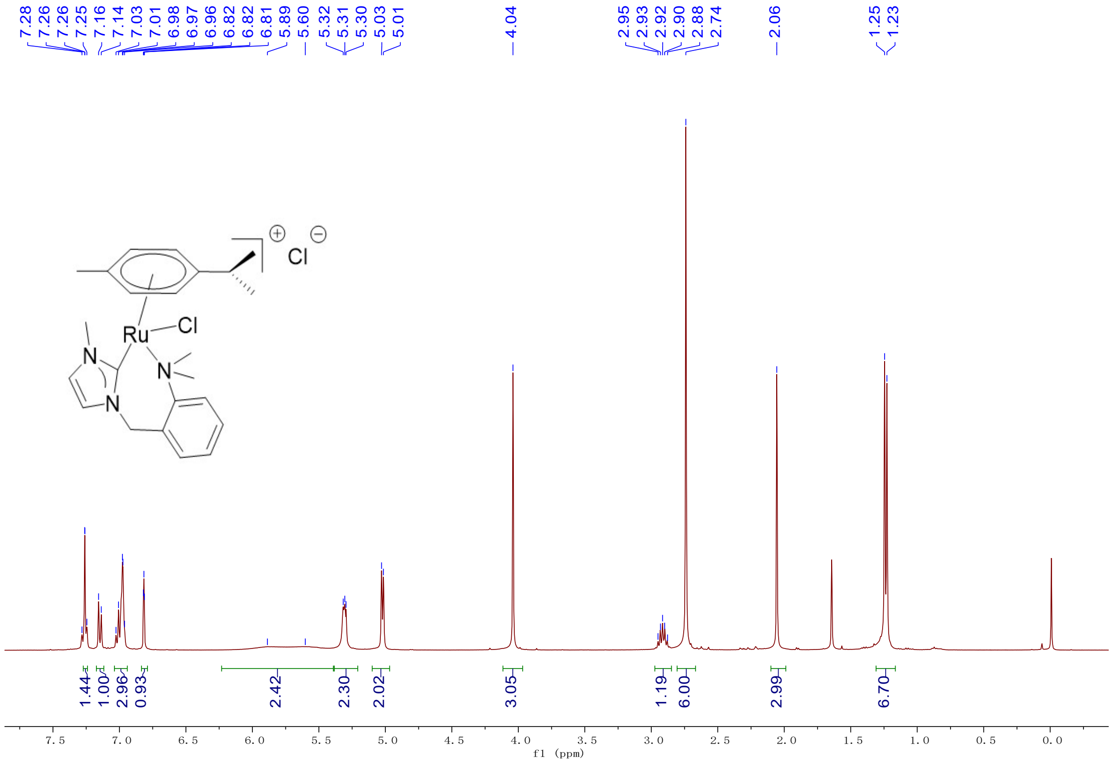

Figure S16: ^{1}H NMR (400 MHz, $CDCl_3$, 298 K) spectrum for Ru4-Me

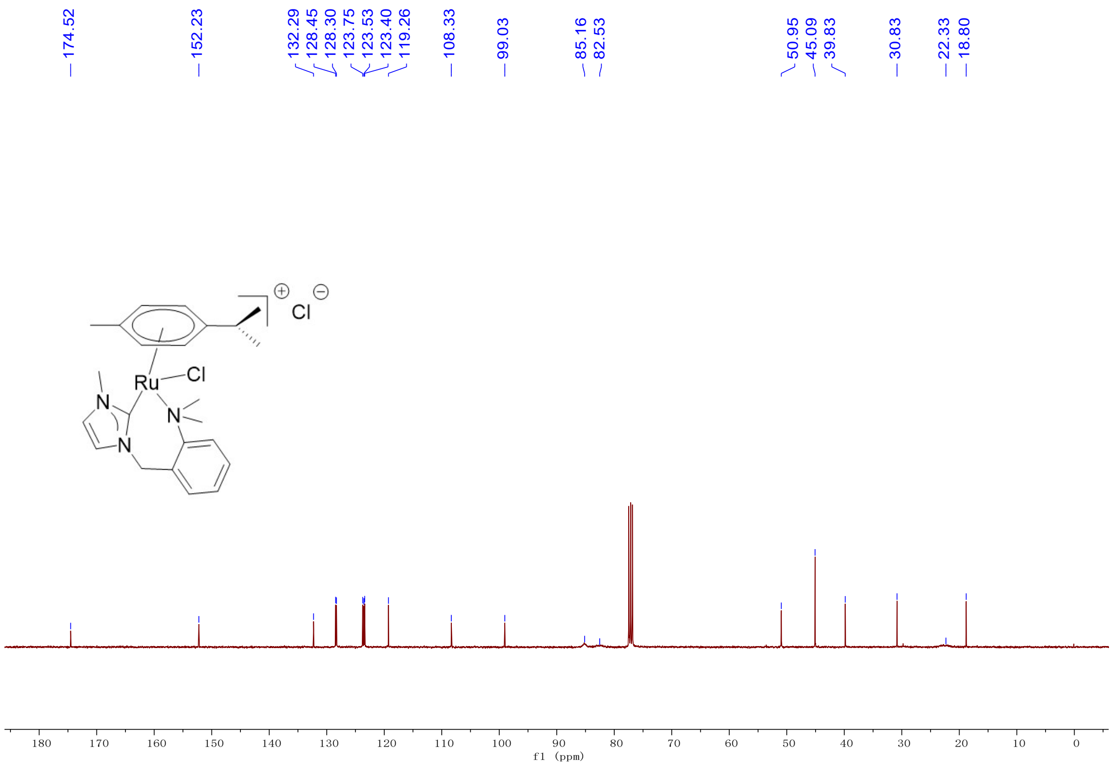

Figure S17: ^{13}C NMR (101 MHz, $CDCl_3$, 298 K) spectrum for Ru4-Me

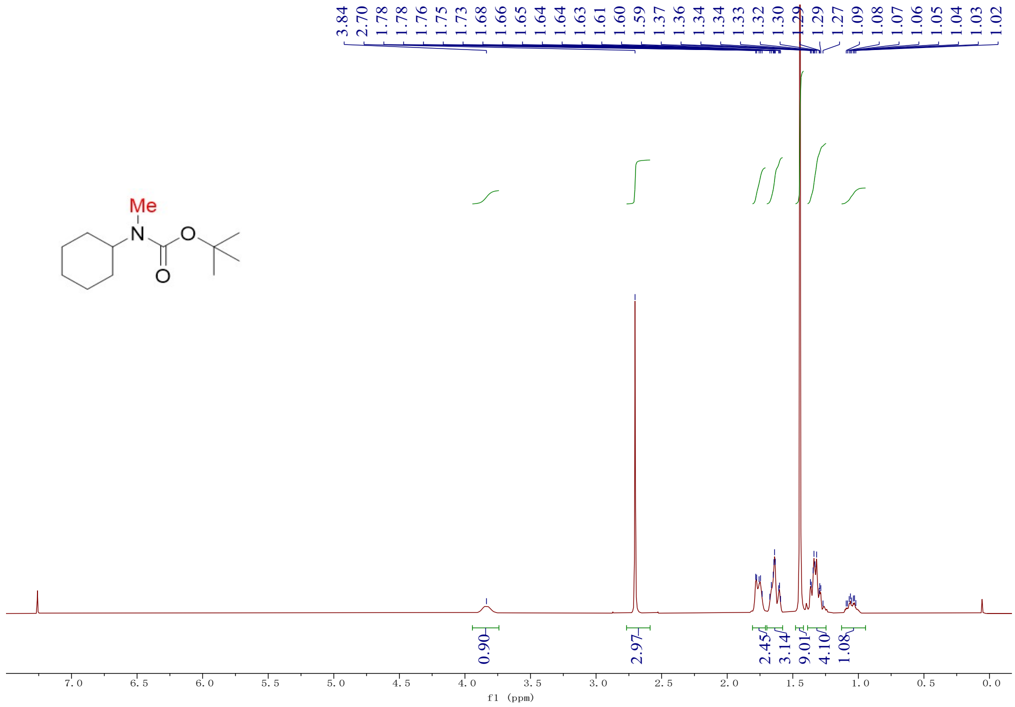

Figure S18: ^{1}H NMR (400 MHz, $CDCl_3$, 298 K) spectrum for 9a

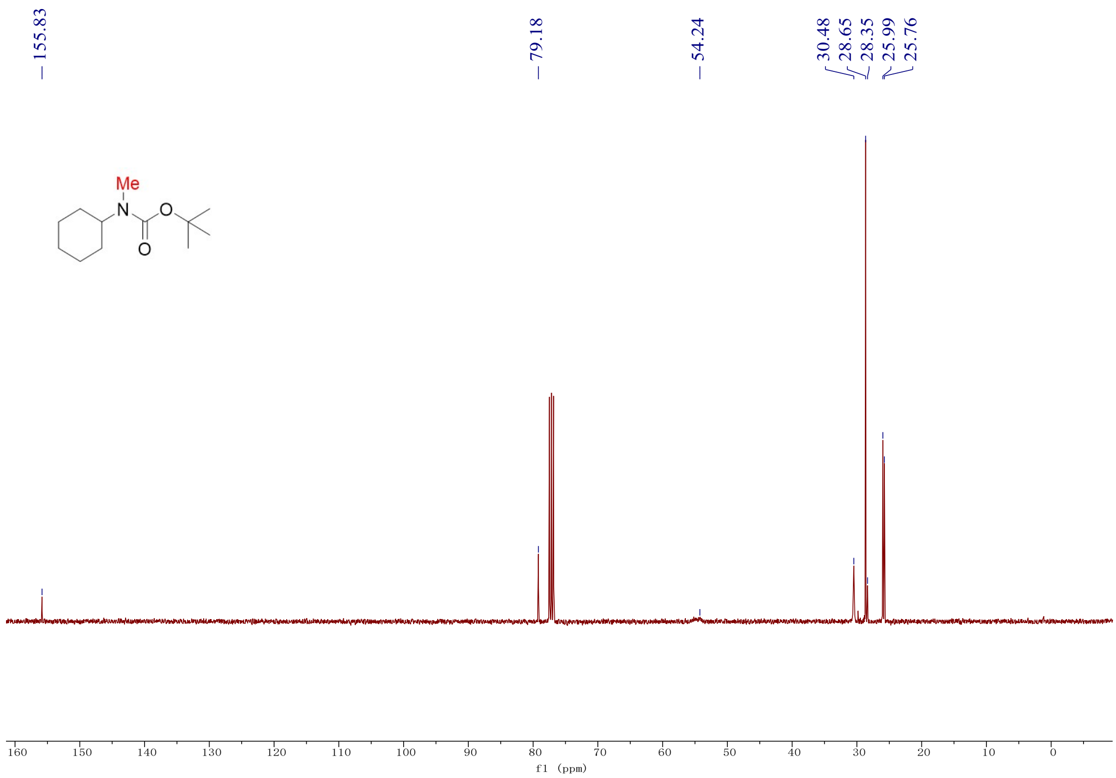

Figure S19: ^{13}C NMR (101 MHz, $CDCl_3$, 298 K) spectrum for 9a

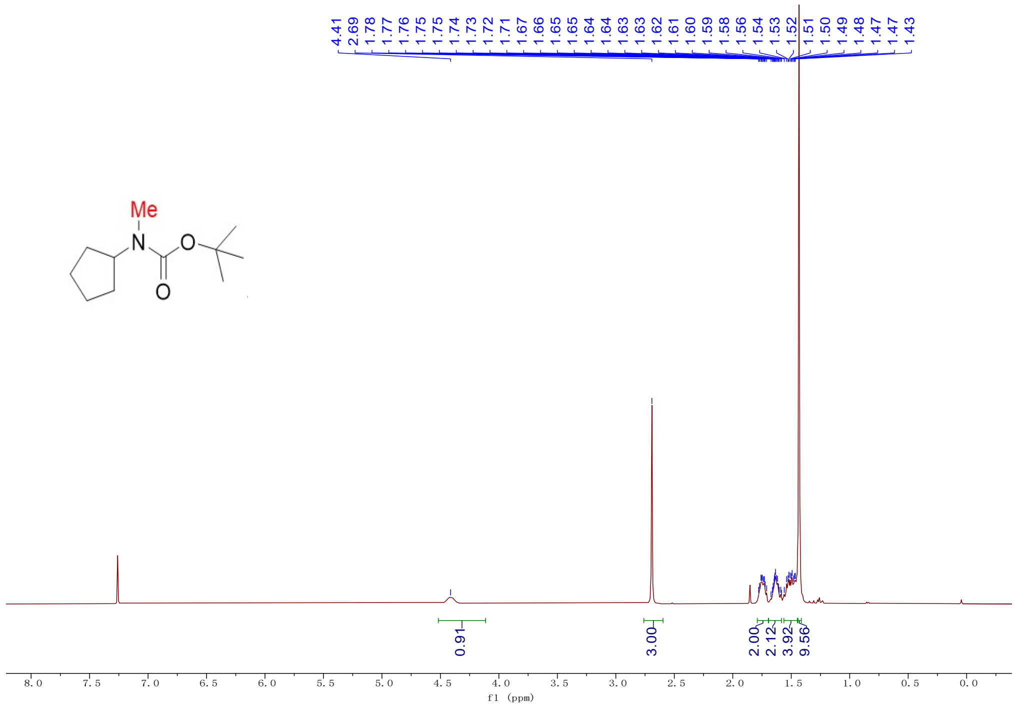

Figure S20: ^{1}H NMR (400 MHz, $CDCl_3$, 298 K) spectrum for 9b

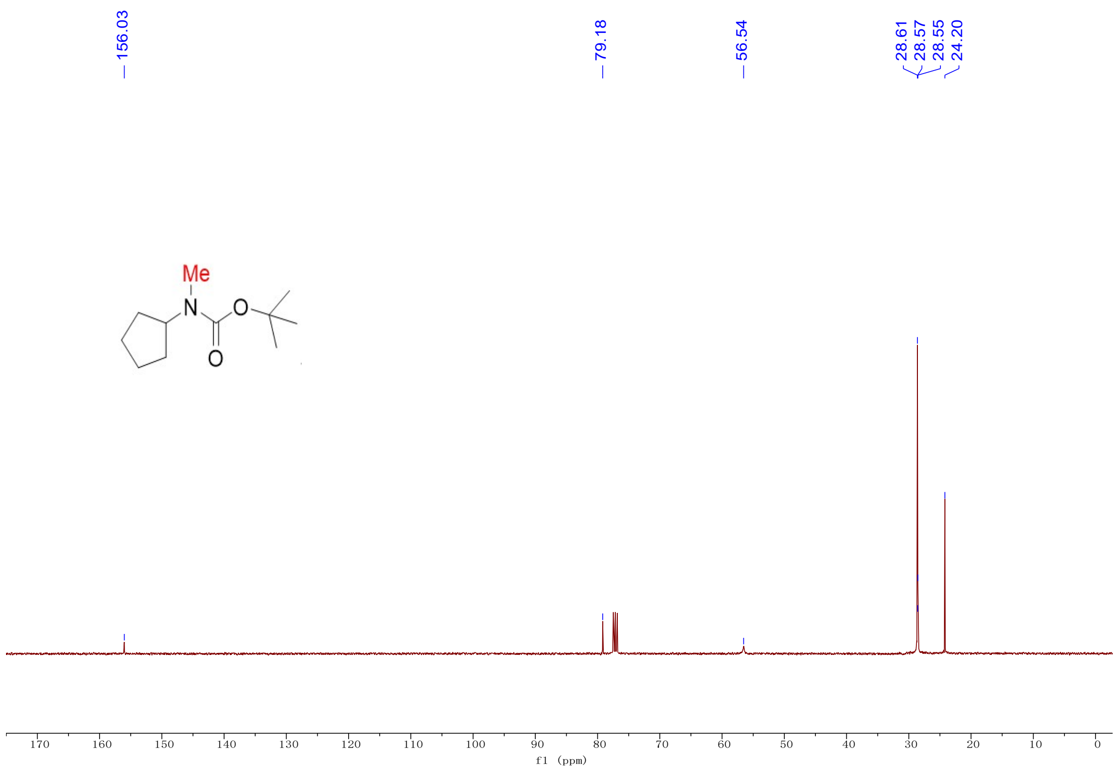

Figure S21: ^{13}C NMR (101 MHz, $CDCl_3$, 298 K) spectrum for 9b

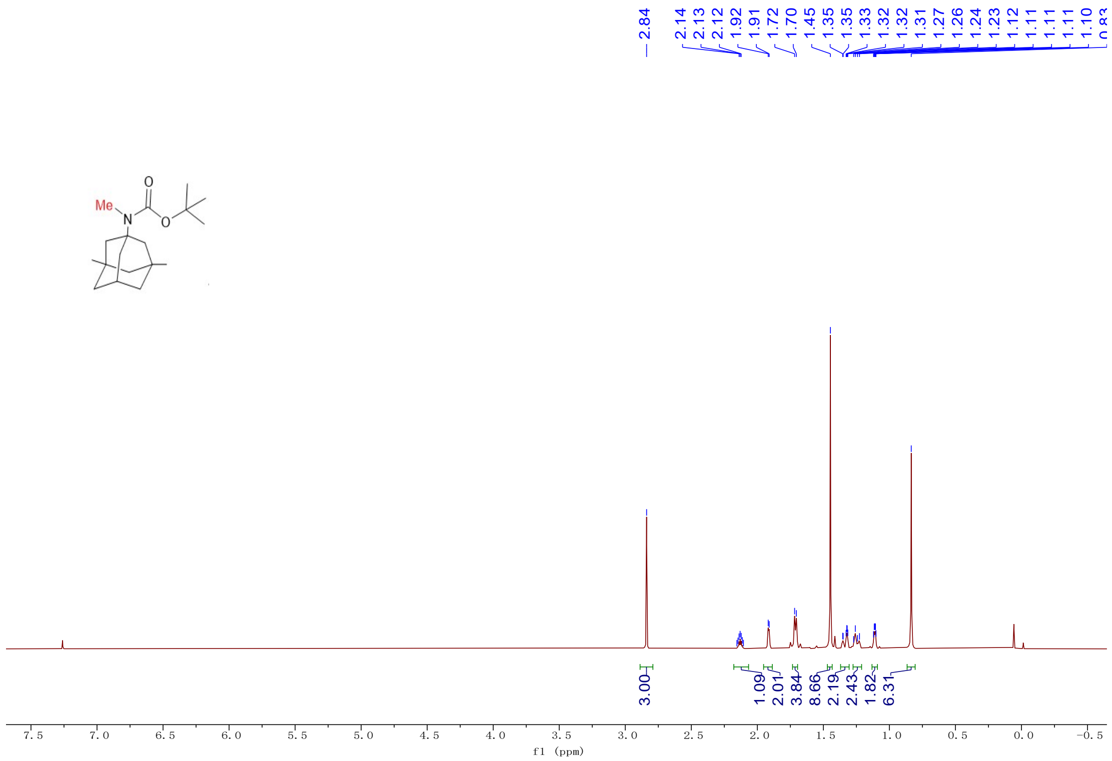

Figure S22: ^{1}H NMR (400 MHz, $CDCl_3$, 298 K) spectrum for 9c

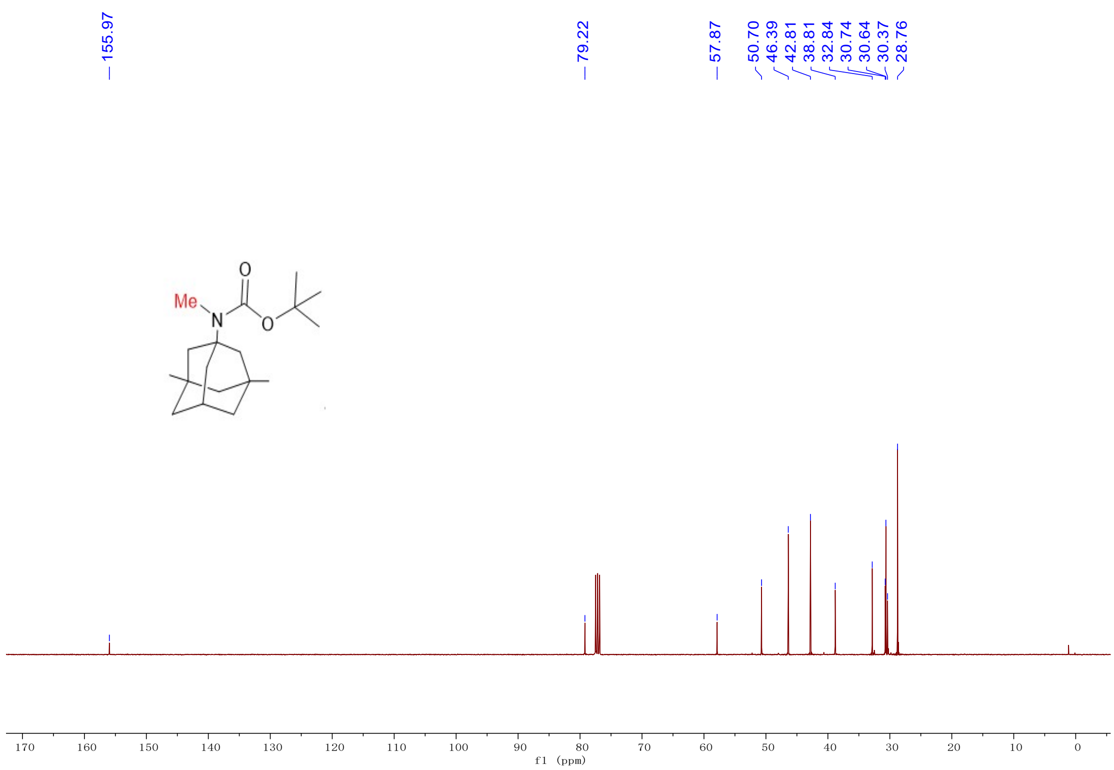

Figure S23: ^{13}C NMR (101 MHz, $CDCl_3$, 298 K) spectrum for 9c

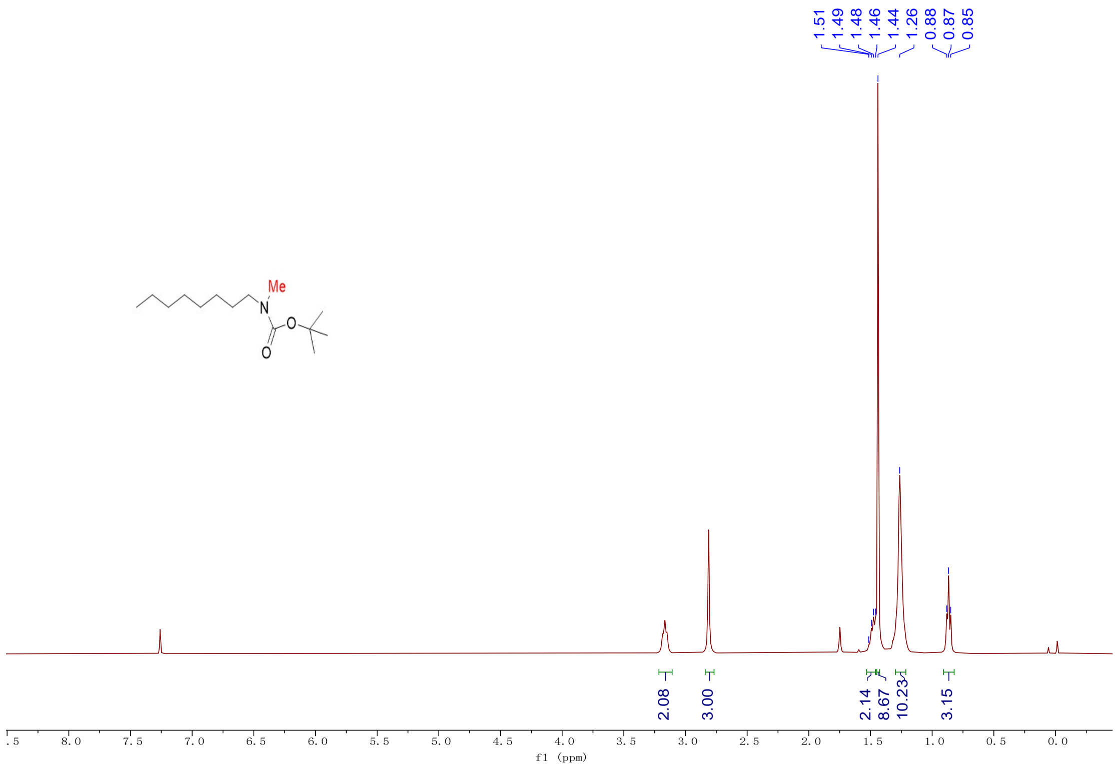

Figure S24: ^{1}H NMR (400 MHz, $CDCl_3$, 298 K) spectrum for 9d

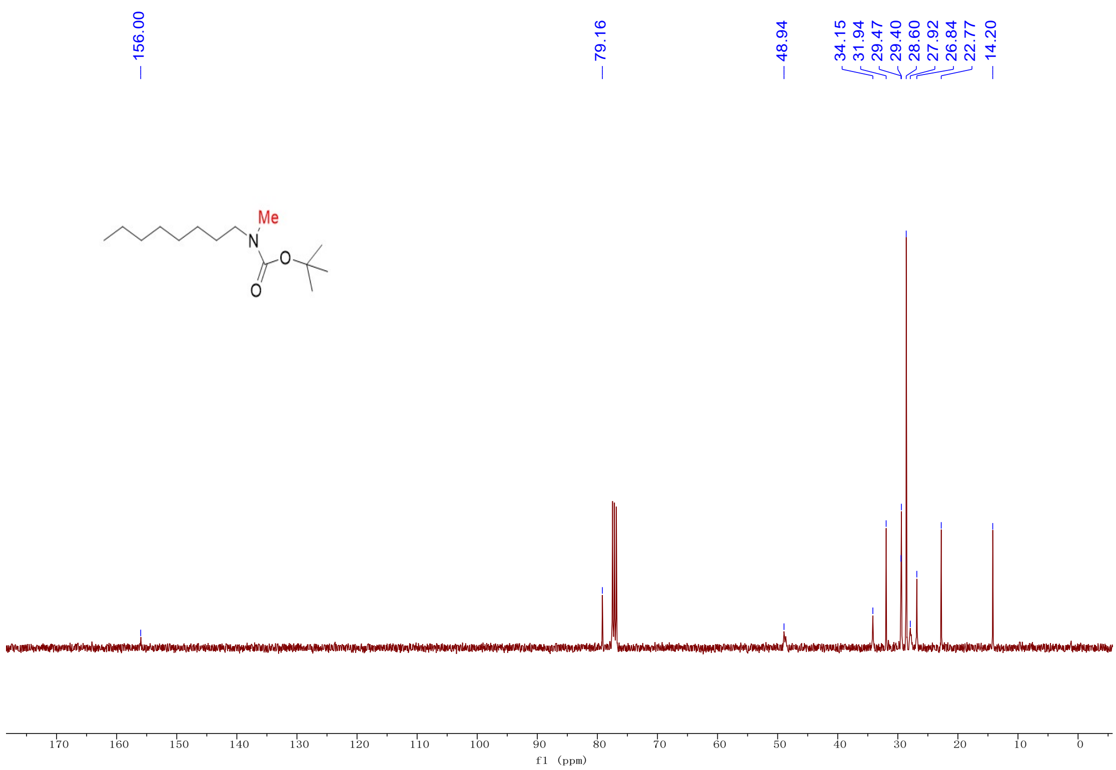

Figure S25: ^{13}C NMR (101 MHz, $CDCl_3$, 298 K) spectrum for 9d

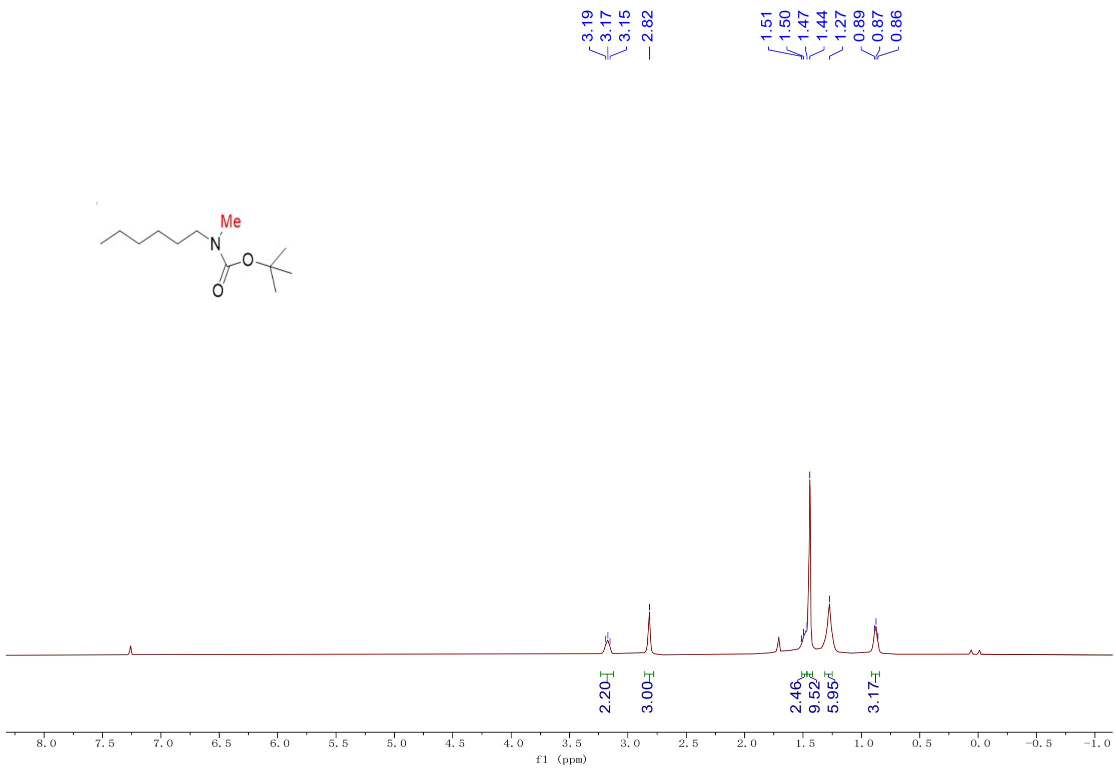

Figure S26: [1]H NMR (400 MHz, $CDCl_3$, 298 K) spectrum for 9e

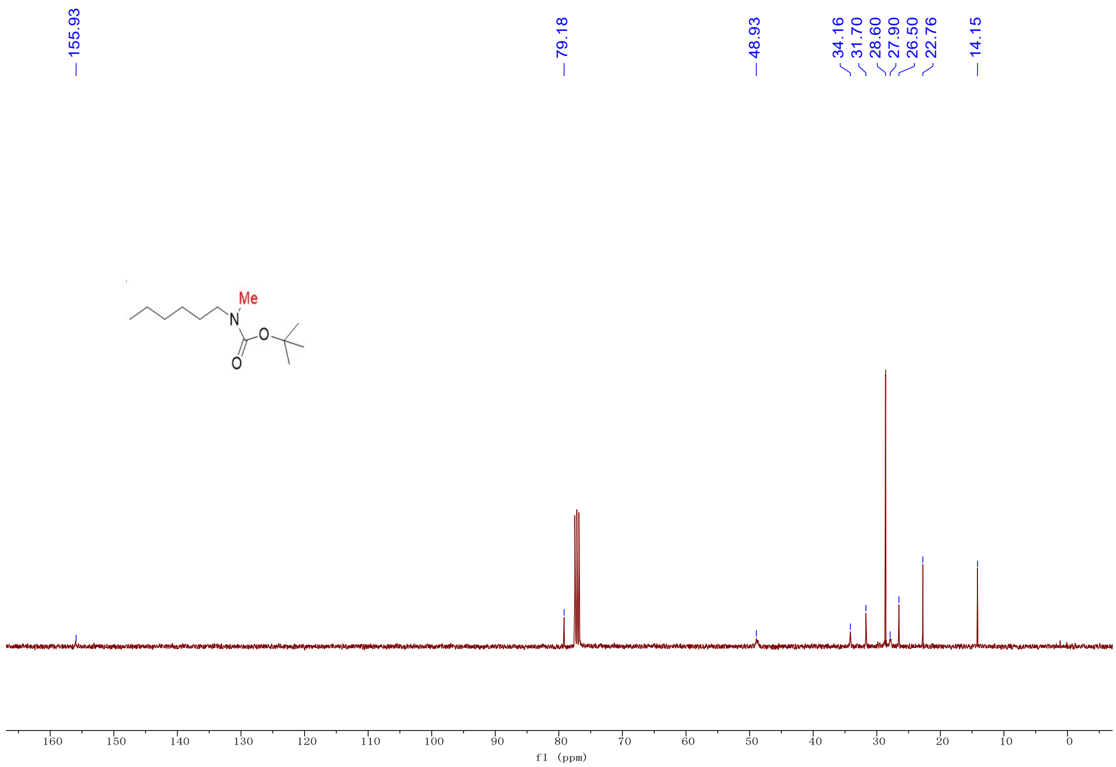

Figure S27: [13]C NMR (101 MHz, $CDCl_3$, 298 K) spectrum for 9e

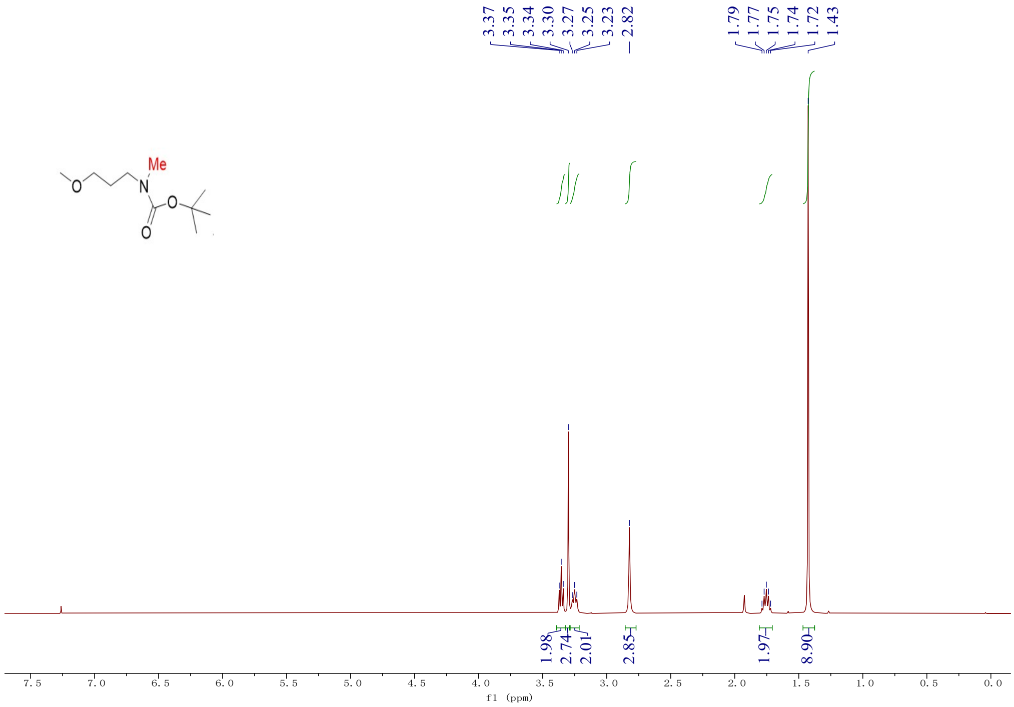

Figure S28: [1]H NMR (400 MHz, $CDCl_3$, 298 K) spectrum for 9f

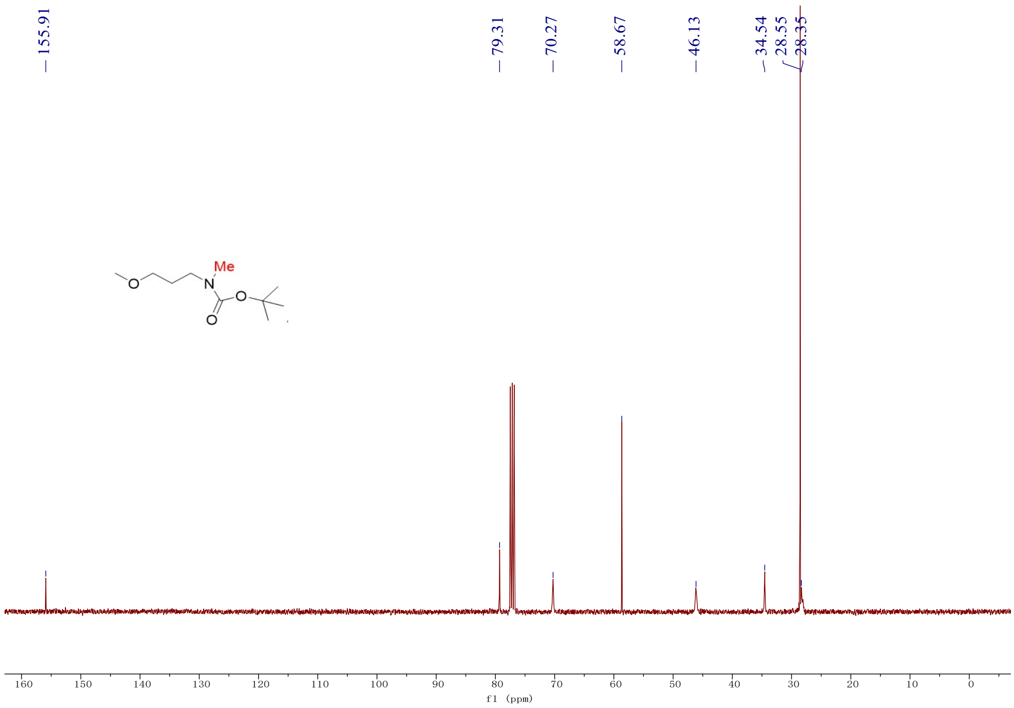

Figure S29: [13]C NMR (101 MHz, $CDCl_3$, 298 K) spectrum for 9f

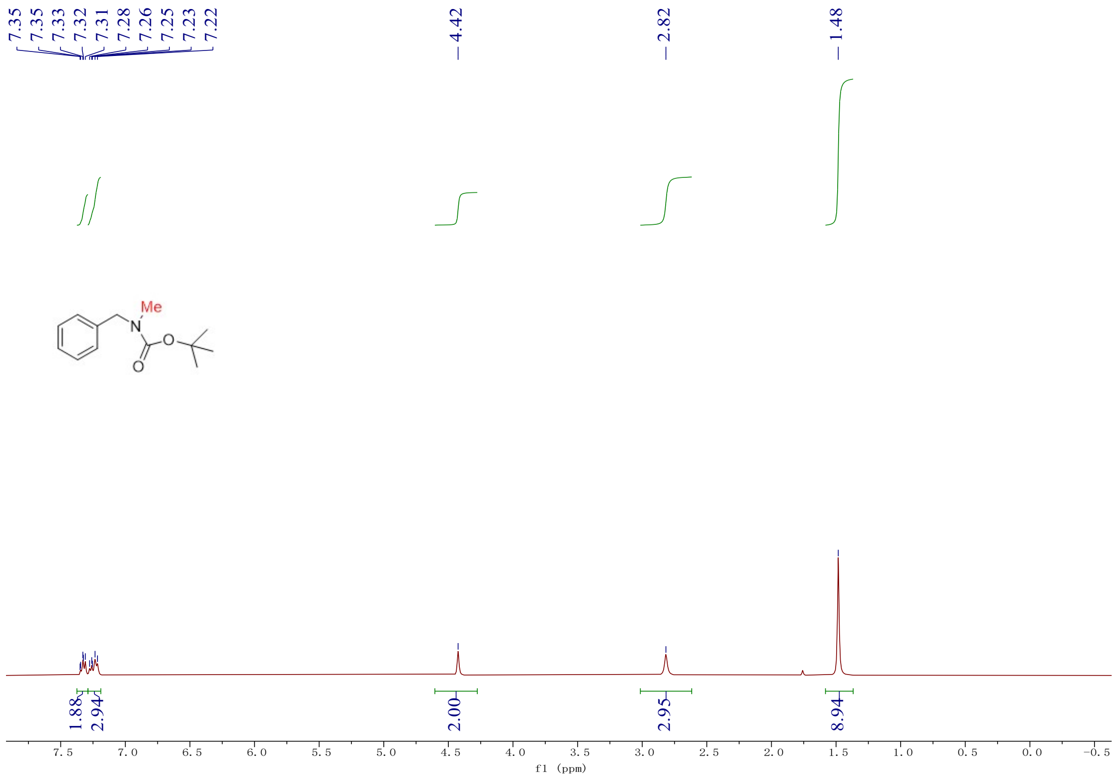

Figure S30: ^{1}H NMR (400 MHz, $CDCl_3$, 298 K) spectrum for 9g

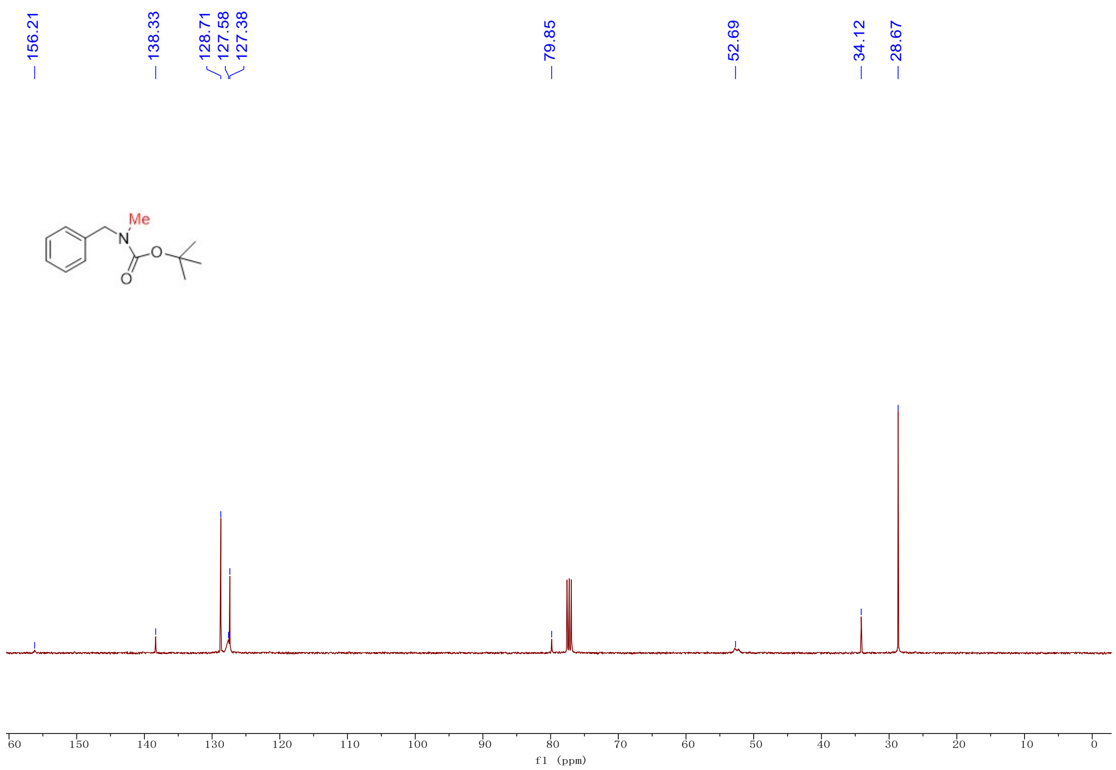

Figure S31: ^{13}C NMR (101 MHz, $CDCl_3$, 298 K) spectrum for 9g

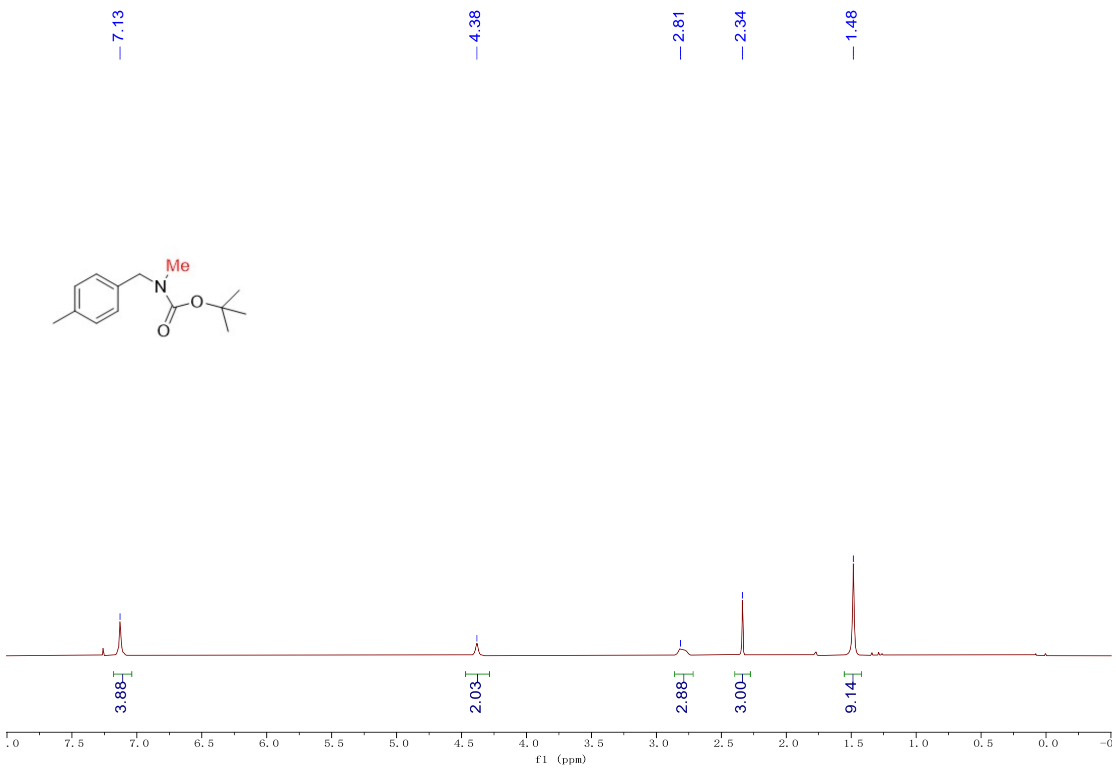

Figure S32: ^{1}H NMR (400 MHz, $CDCl_3$, 298 K) spectrum for 9h

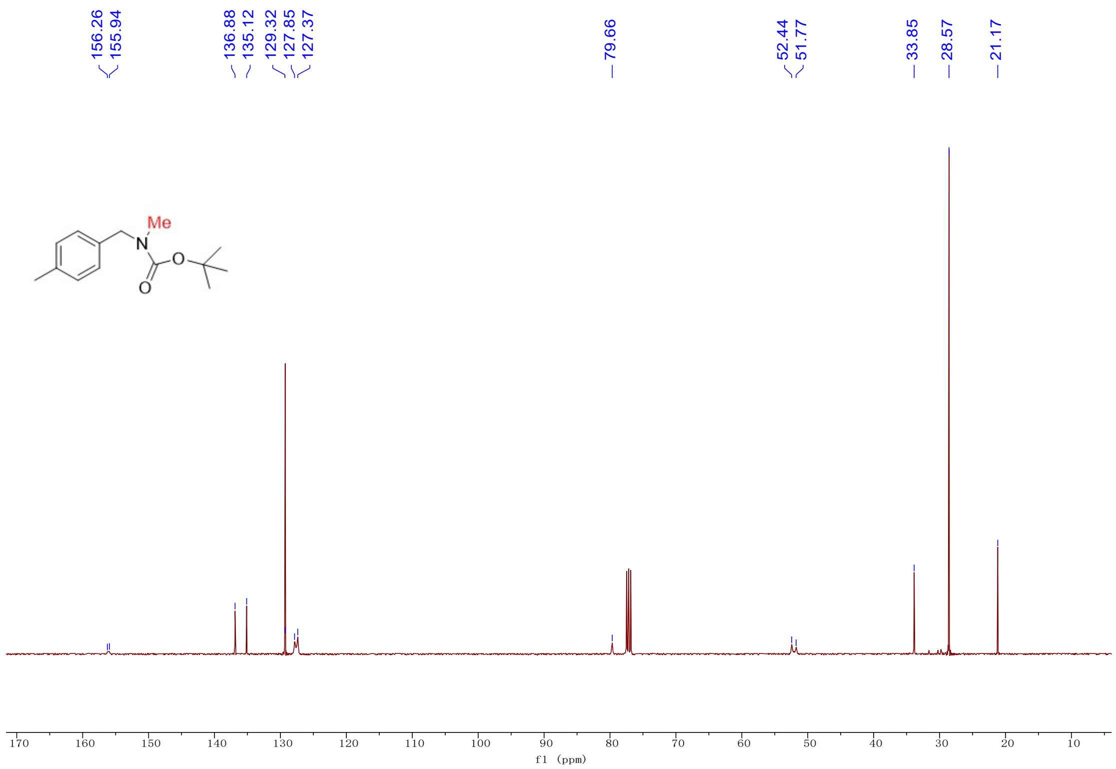

Figure S33: ^{13}C NMR (101 MHz, $CDCl_3$, 298 K) spectrum for 9h

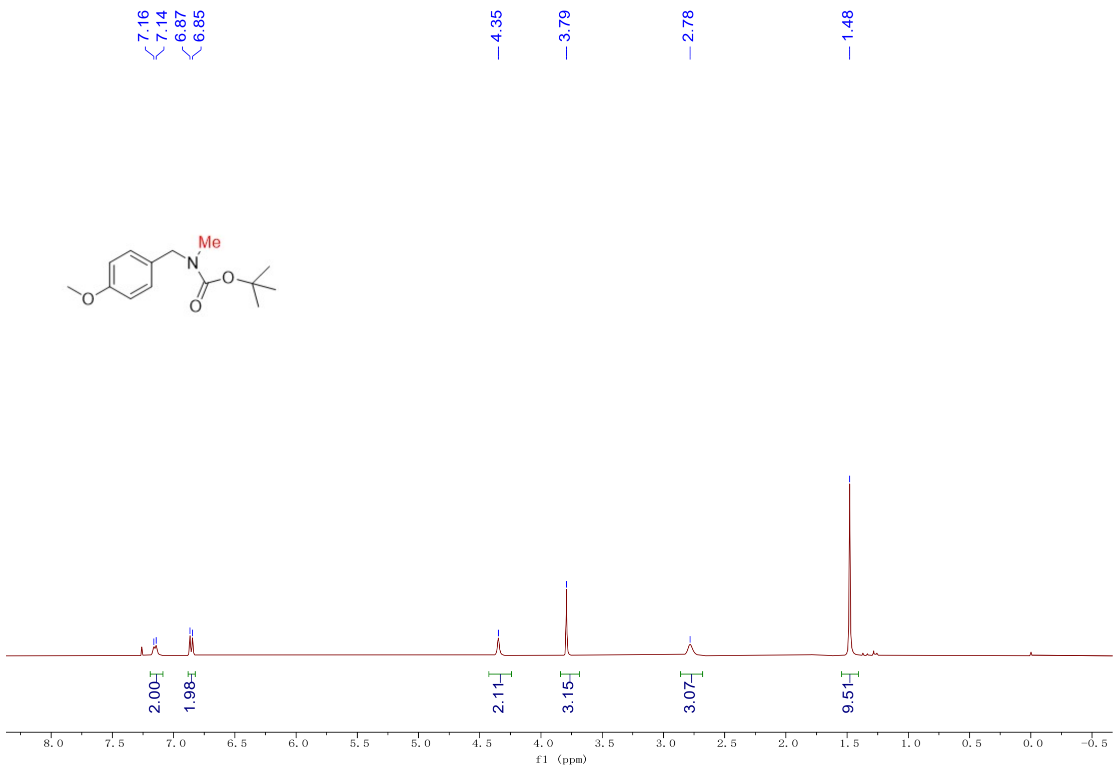

Figure S34: ^{1}H NMR (400 MHz, $CDCl_3$, 298 K) spectrum for 9i

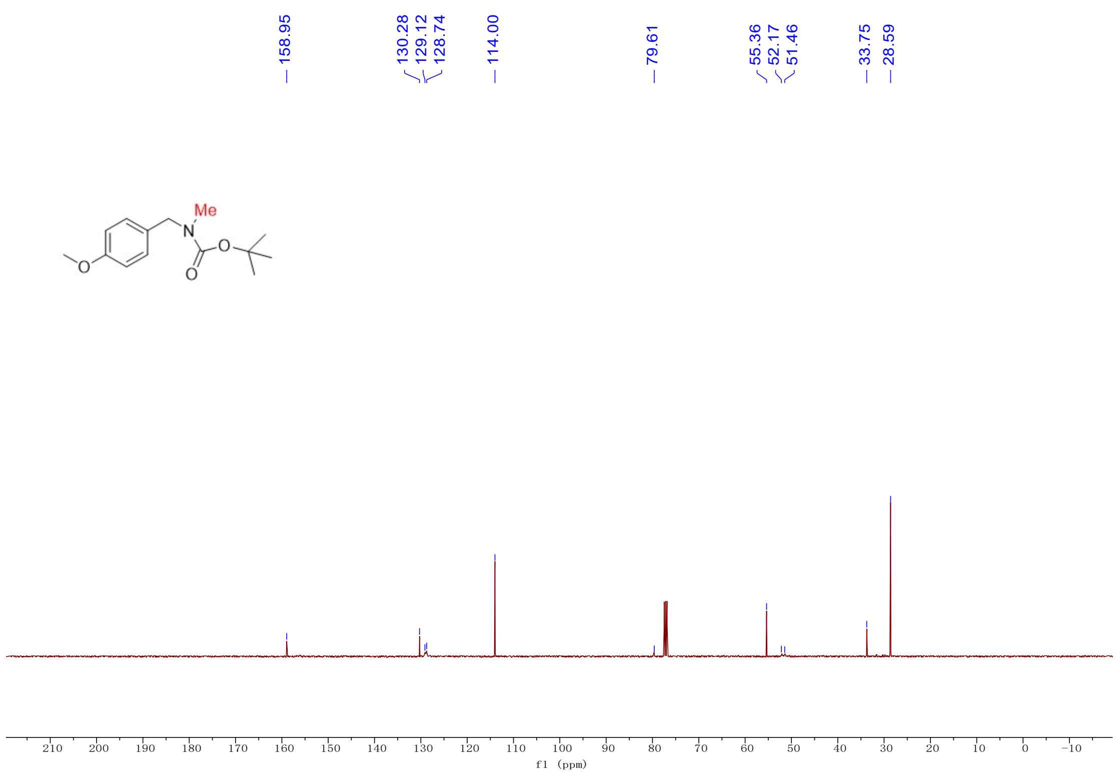

Figure S35: ^{13}C NMR (101 MHz, $CDCl_3$, 298 K) spectrum for 9i

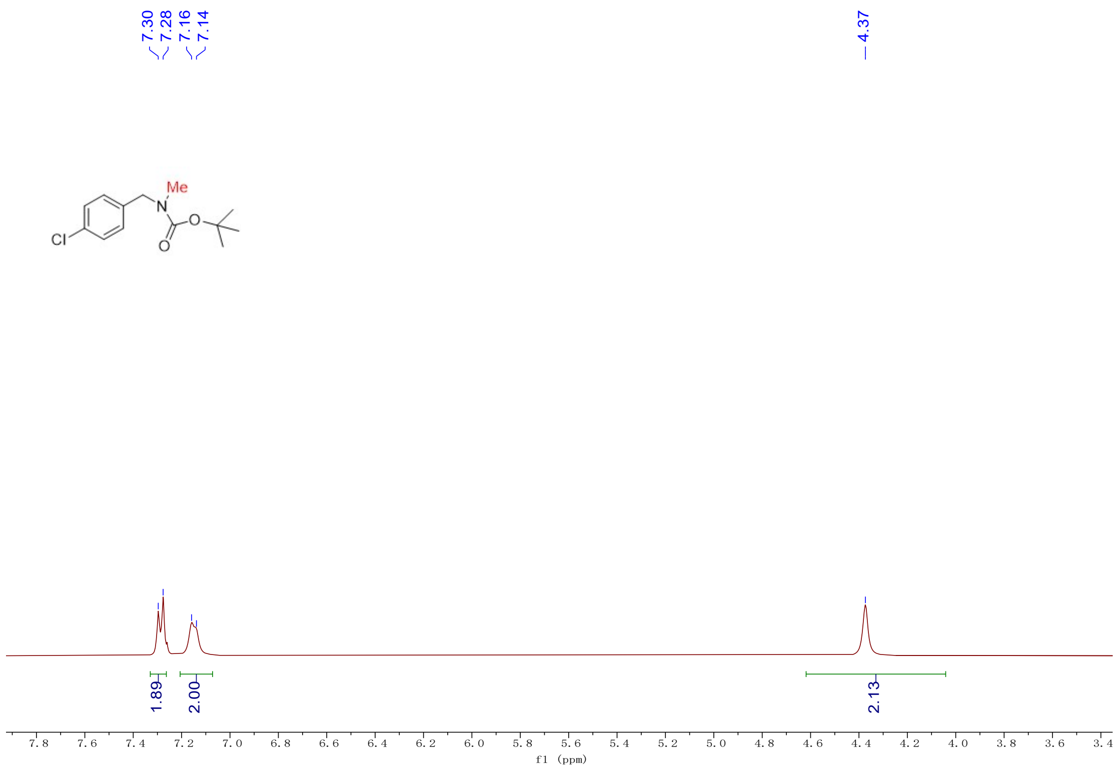

Figure S36: ^{1}H NMR (400 MHz, $CDCl_3$, 298 K) spectrum for 9j

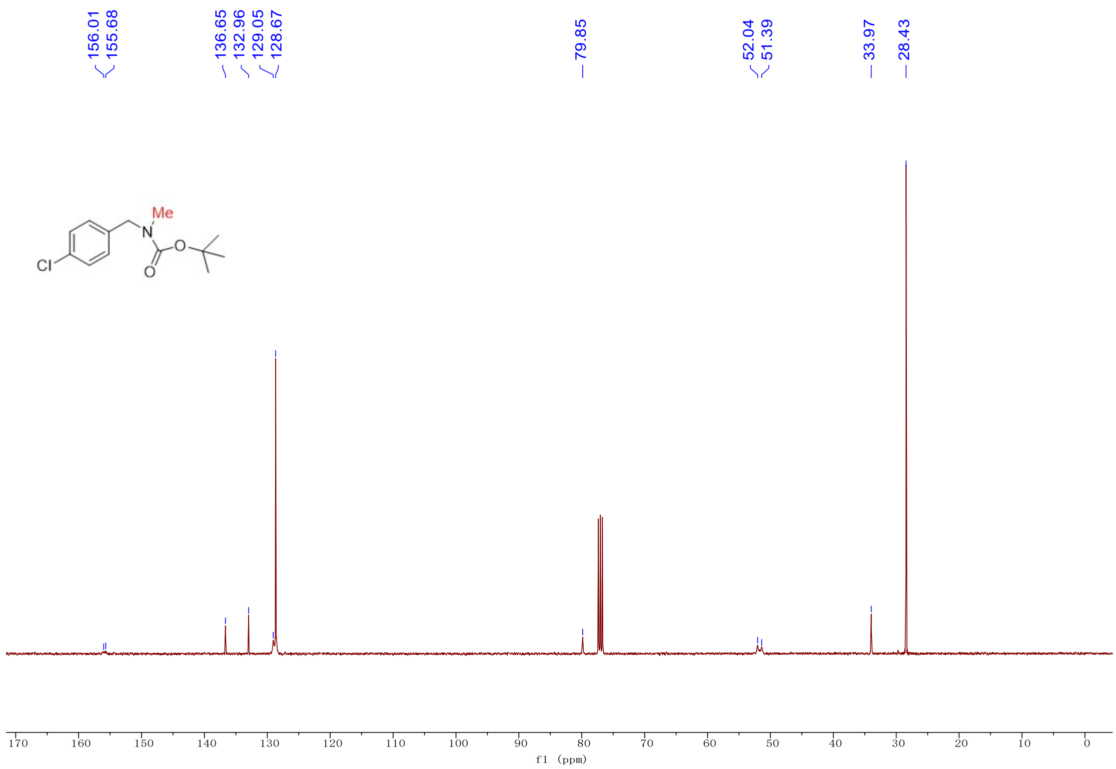

Figure S37: ^{13}C NMR (101 MHz, $CDCl_3$, 298 K) spectrum for 9j

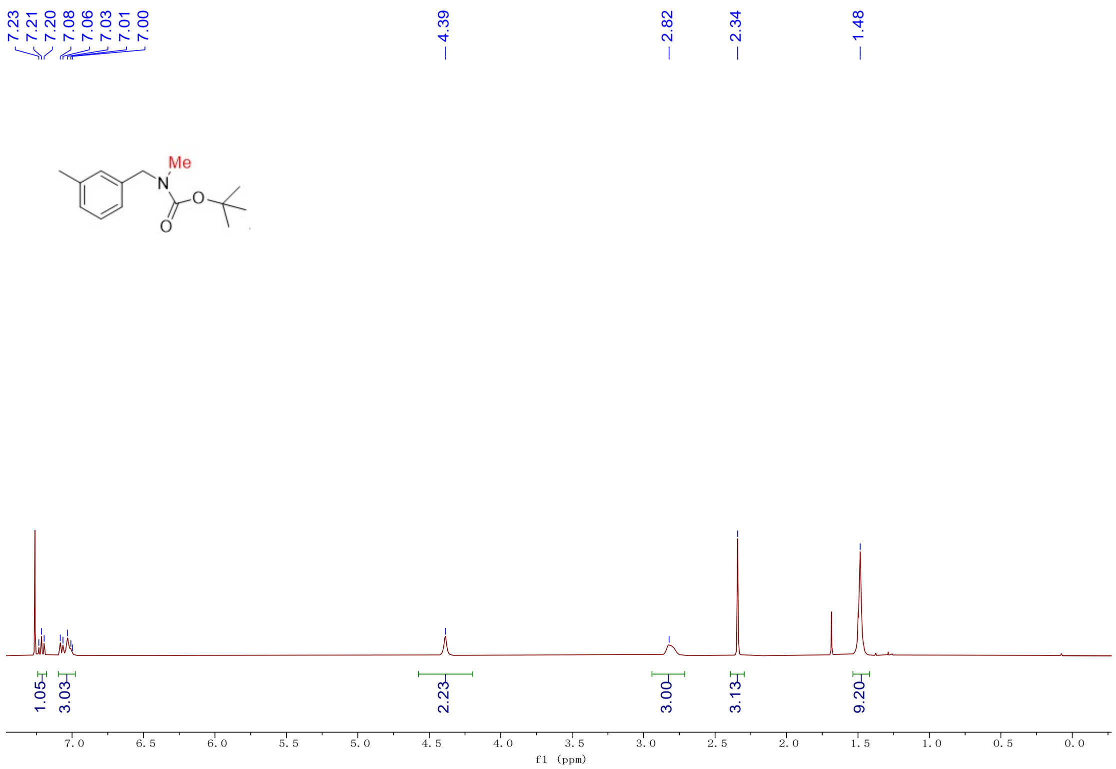

Figure S38: ^{1}H NMR (400 MHz, $CDCl_3$, 298 K) spectrum for 9k

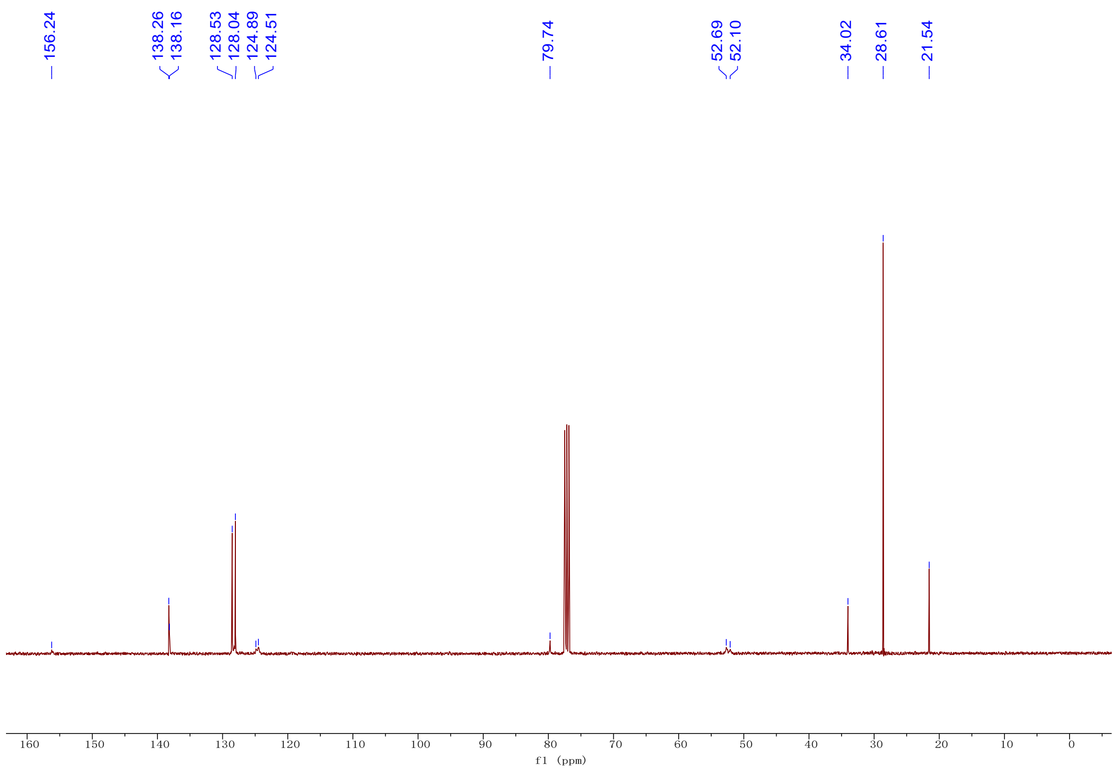

Figure S39: ^{13}C NMR (101 MHz, $CDCl_3$, 298 K) spectrum for 9k

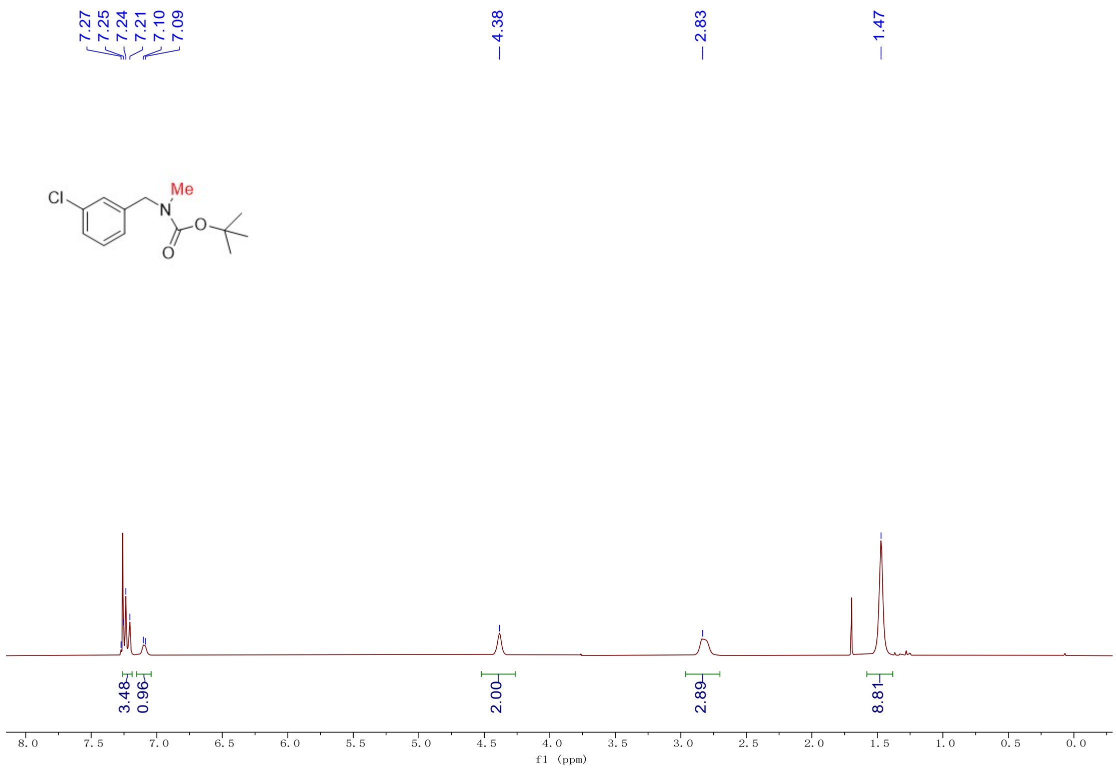

Figure S40: ^{1}H NMR (400 MHz, $CDCl_3$, 298 K) spectrum for 9l

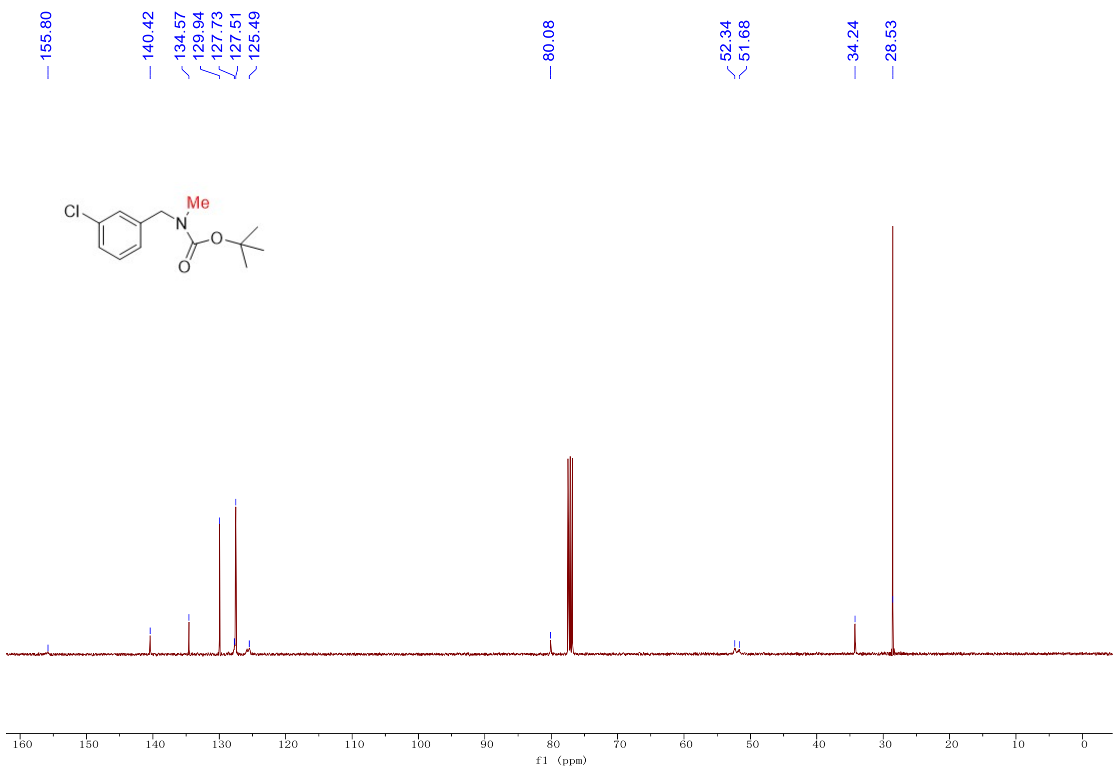

Figure S41: ^{13}C NMR (101 MHz, $CDCl_3$, 298 K) spectrum for 9l

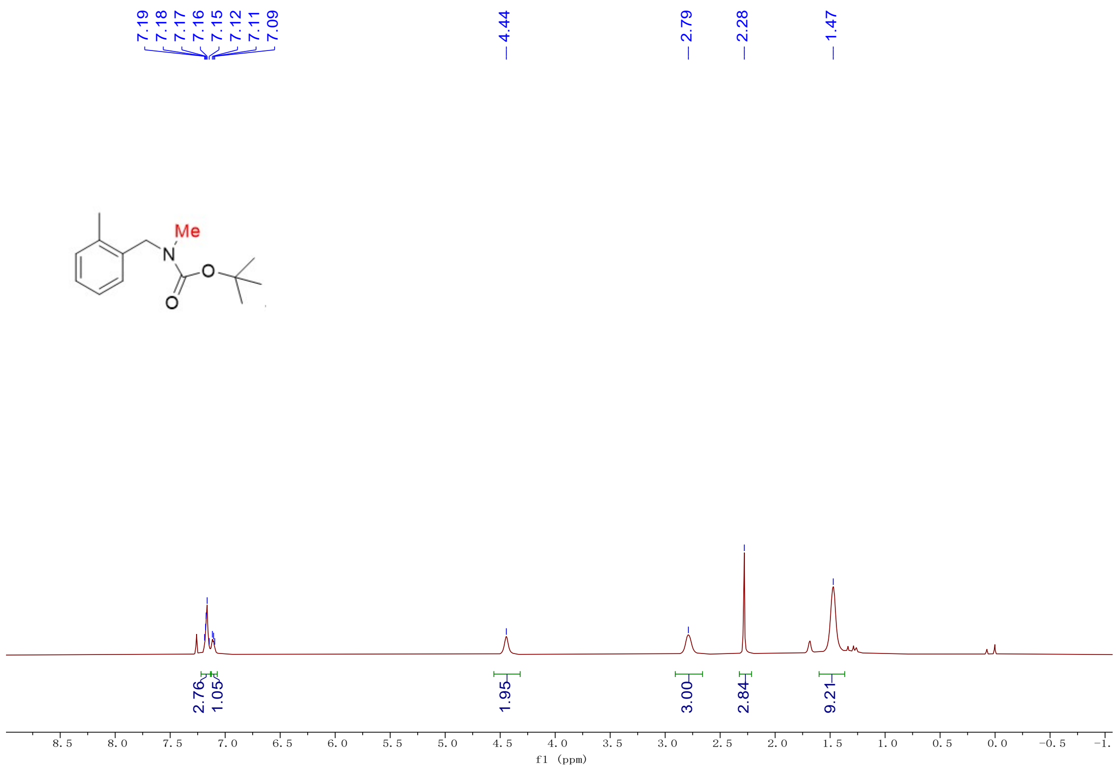

Figure S42: ^{1}H NMR (400 MHz, $CDCl_3$, 298 K) spectrum for 9m

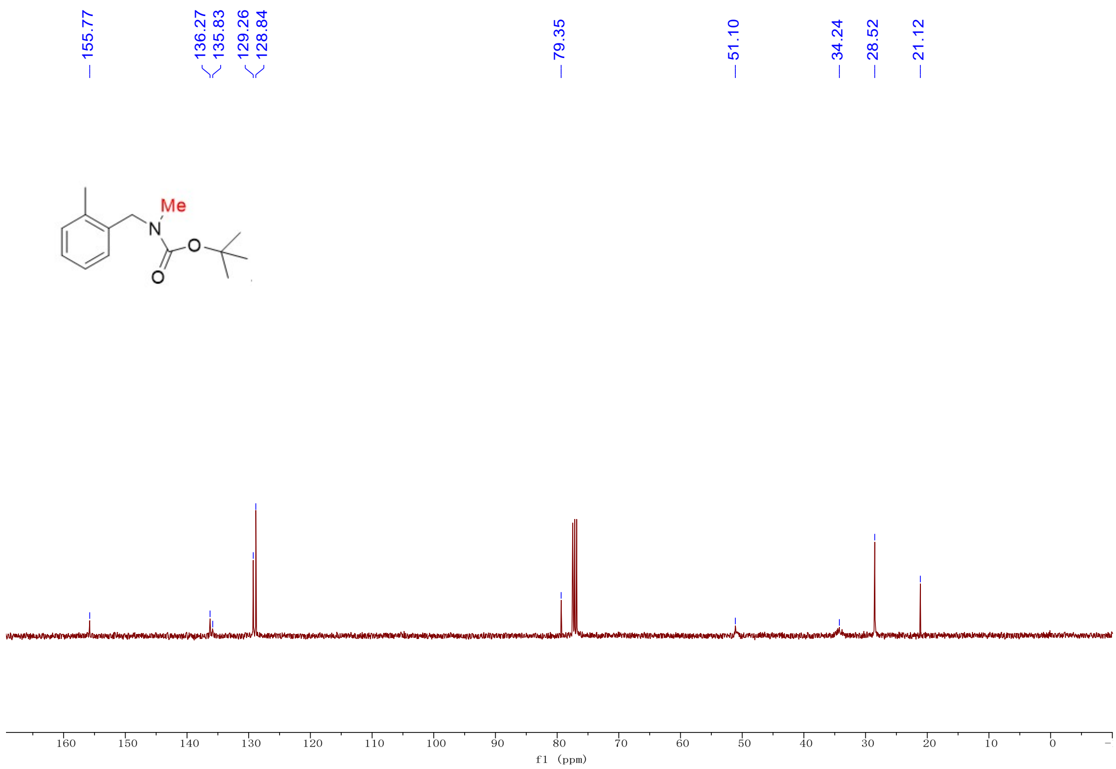

Figure S43: ^{13}C NMR (101 MHz, $CDCl_3$, 298 K) spectrum for 9m

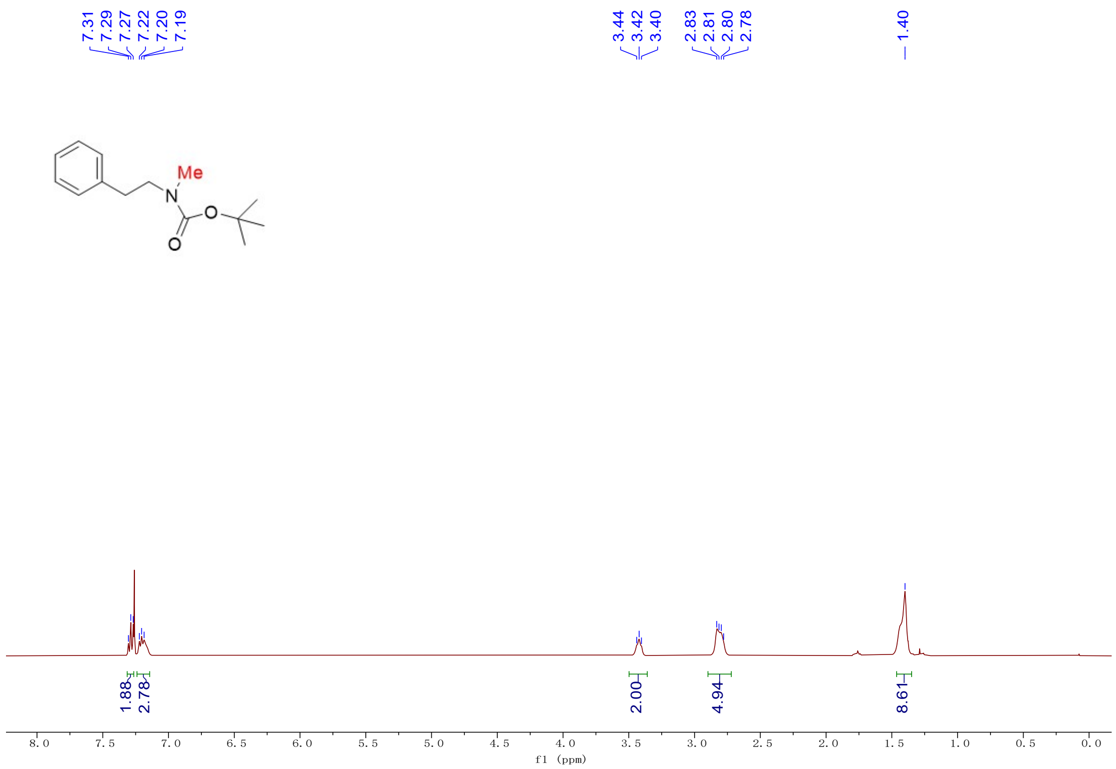

Figure S44: ^{1}H NMR (400 MHz, $CDCl_3$, 298 K) spectrum for 9n

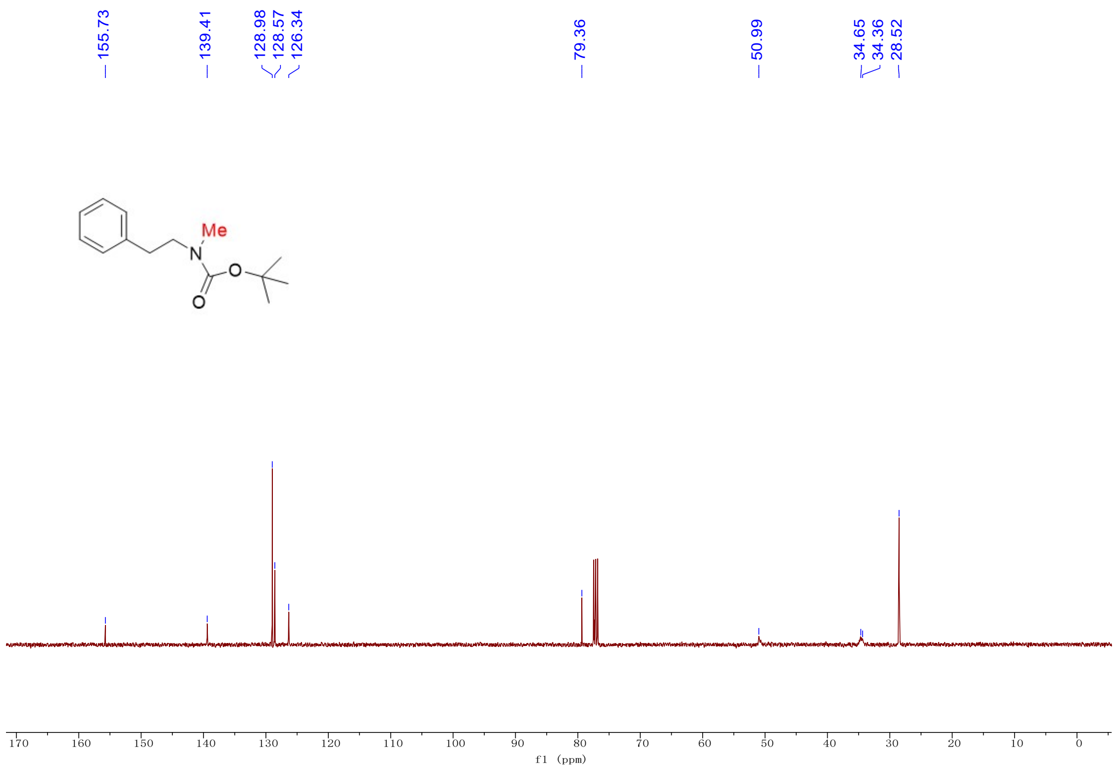

Figure S45: ^{13}C NMR (101 MHz, $CDCl_3$, 298 K) spectrum for 9n

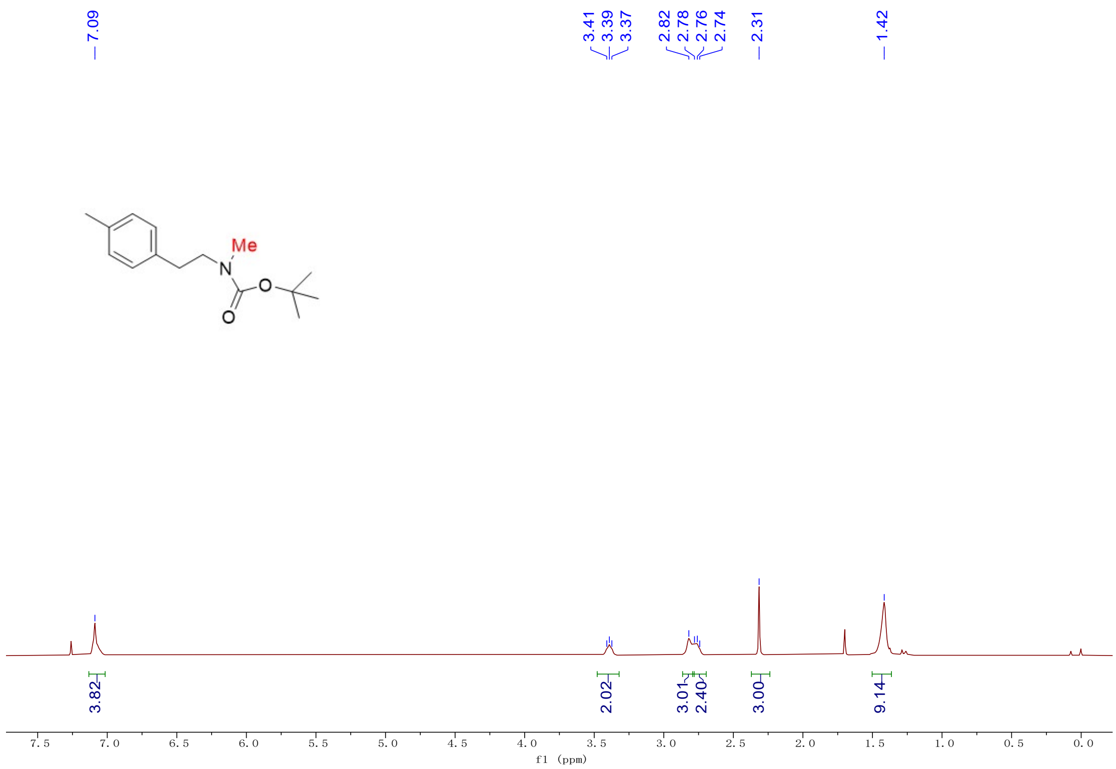

Figure S46: ^{1}H NMR (400 MHz, $CDCl_3$, 298 K) spectrum for 9o

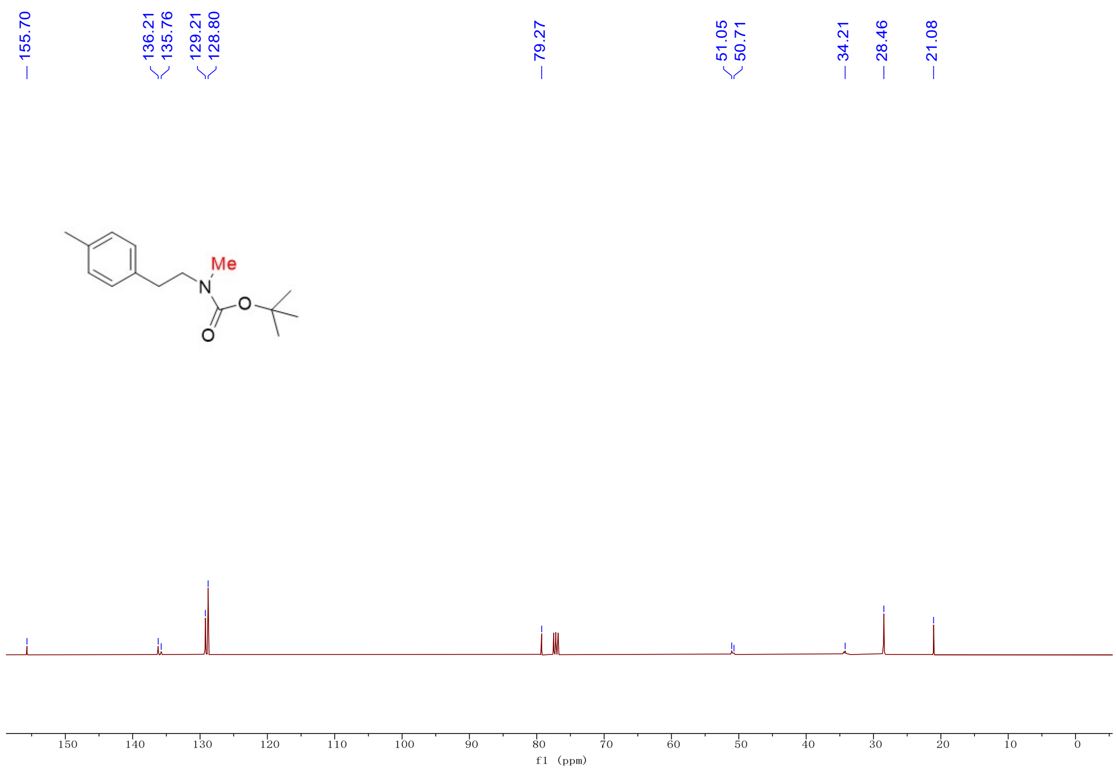

Figure S47: ^{13}C NMR (101 MHz, $CDCl_3$, 298 K) spectrum for 9o

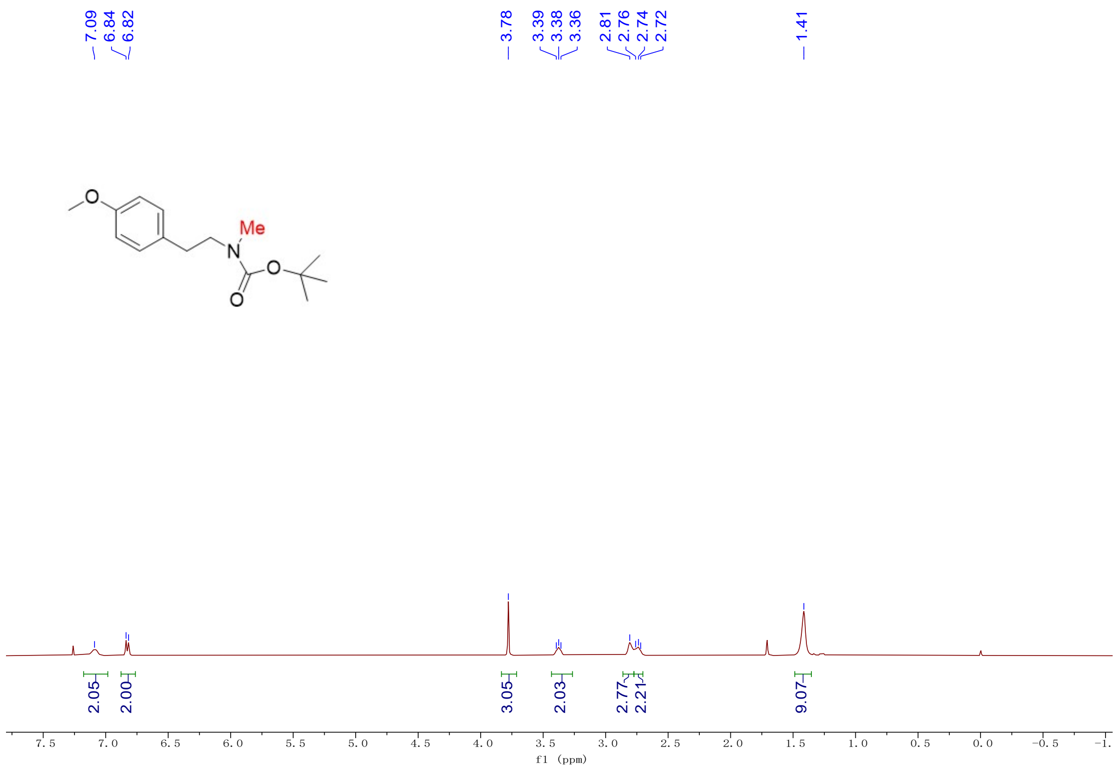

Figure S48: [1]H NMR (400 MHz, $CDCl_3$, 298 K) spectrum for 9p

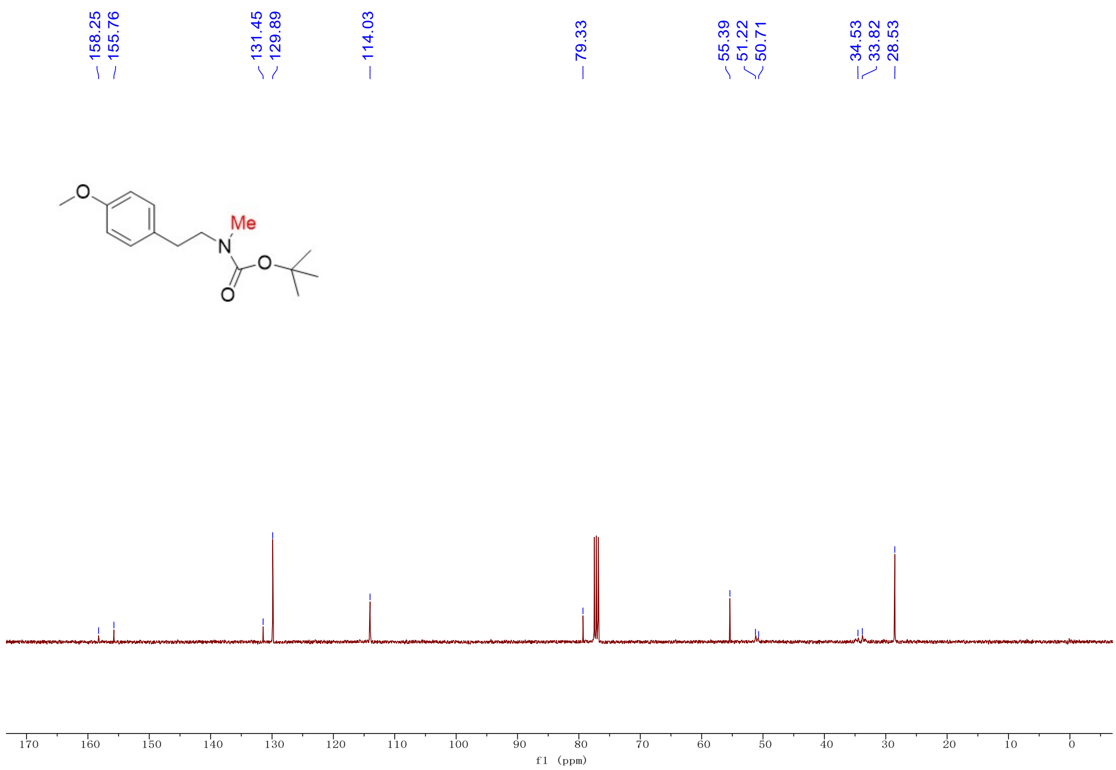

Figure S49: [13]C NMR (101 MHz, $CDCl_3$, 298 K) spectrum for 9p

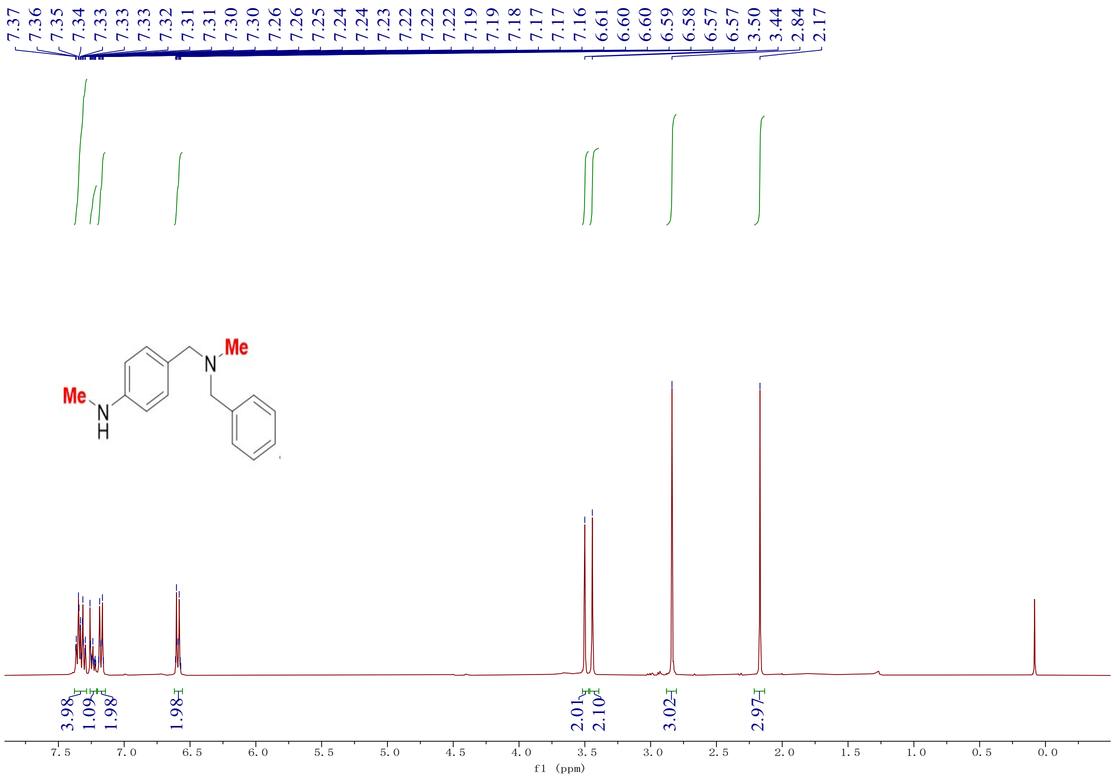

Figure S50: ^{1}H NMR (400 MHz, $CDCl_3$, 298 K) spectrum for 9q

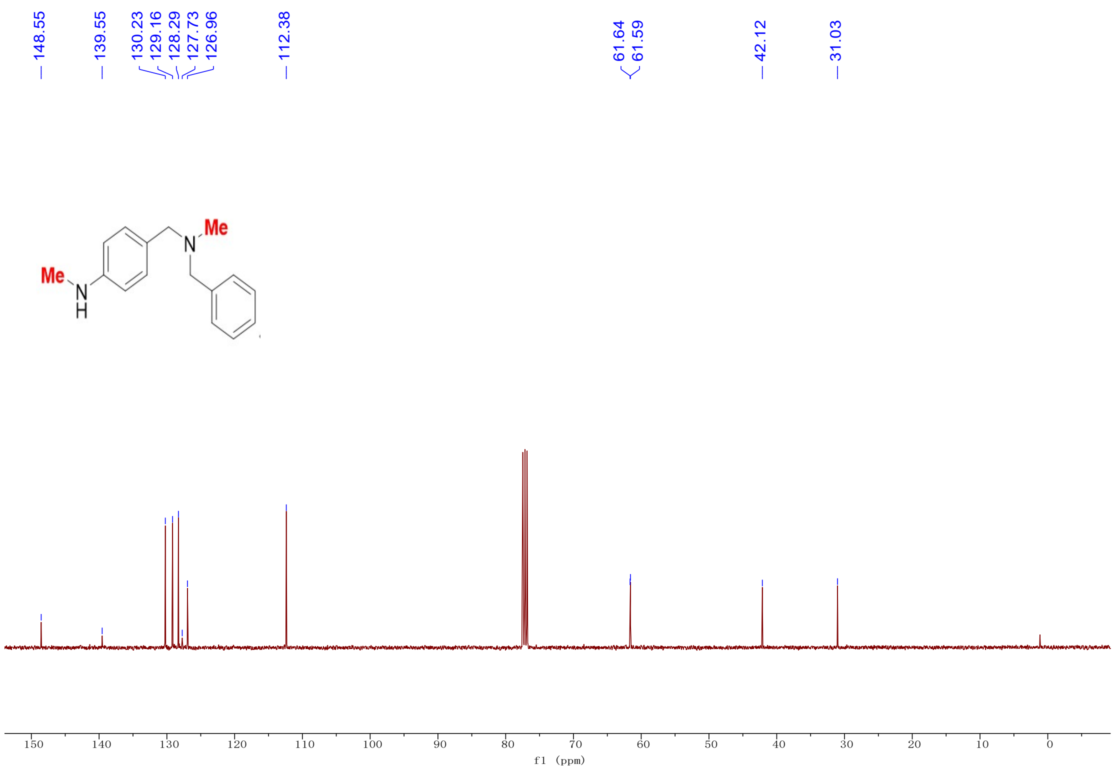

Figure S51: ^{13}C NMR (101 MHz, $CDCl_3$, 298 K) spectrum for 9q

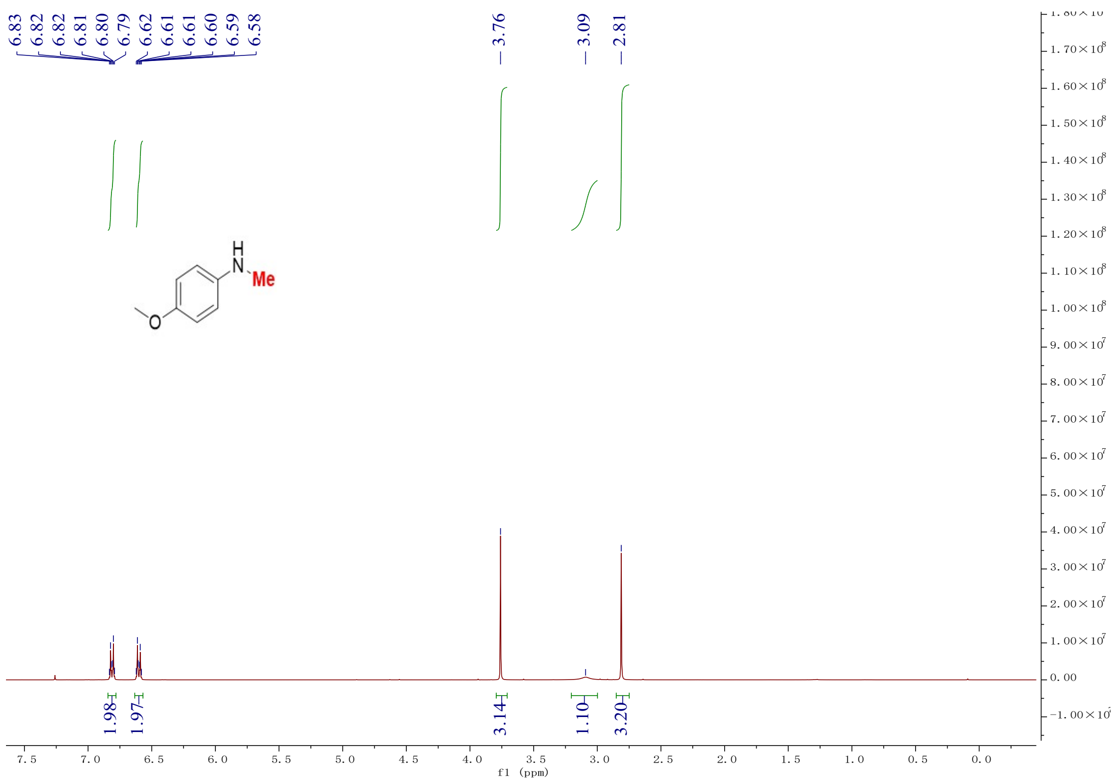

Figure S52: ^{1}H NMR (400 MHz, $CDCl_3$, 298 K) spectrum for 11b

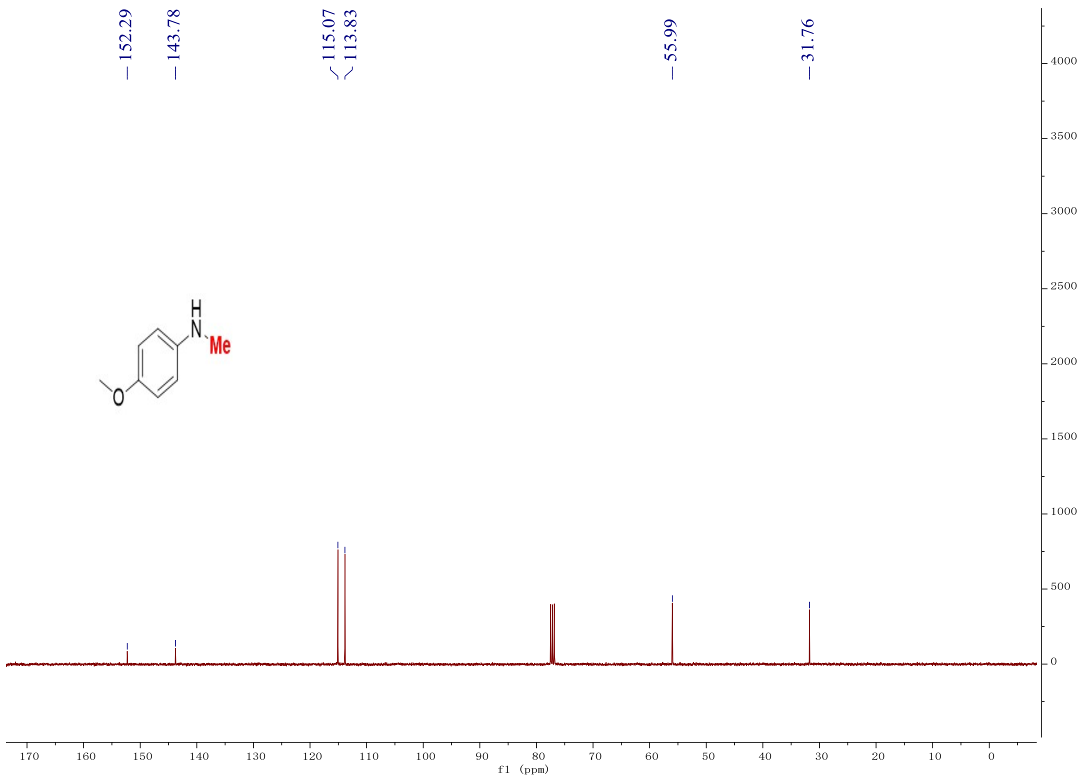

Figure S53: ^{13}C NMR (101 MHz, $CDCl_3$, 298 K) spectrum for 11b

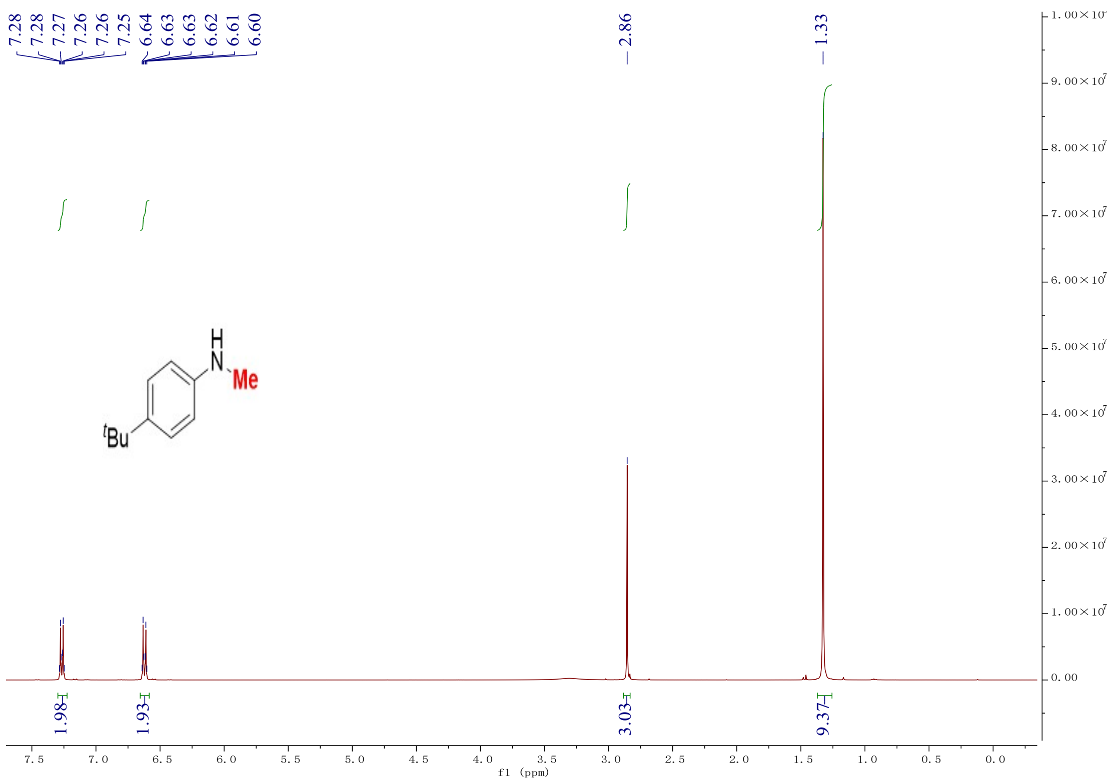

Figure S54: ^{1}H NMR (400 MHz, $CDCl_3$, 298 K) spectrum for 11c

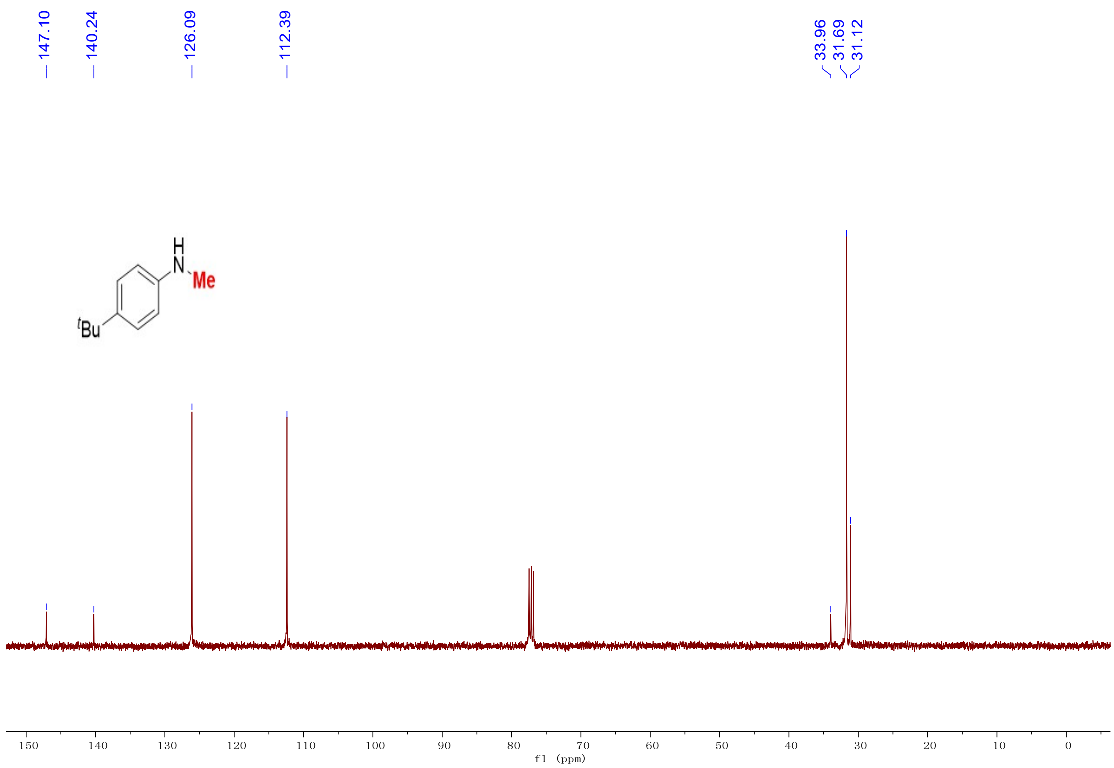

Figure S55: ^{13}C NMR (101 MHz, $CDCl_3$, 298 K) spectrum for 11c

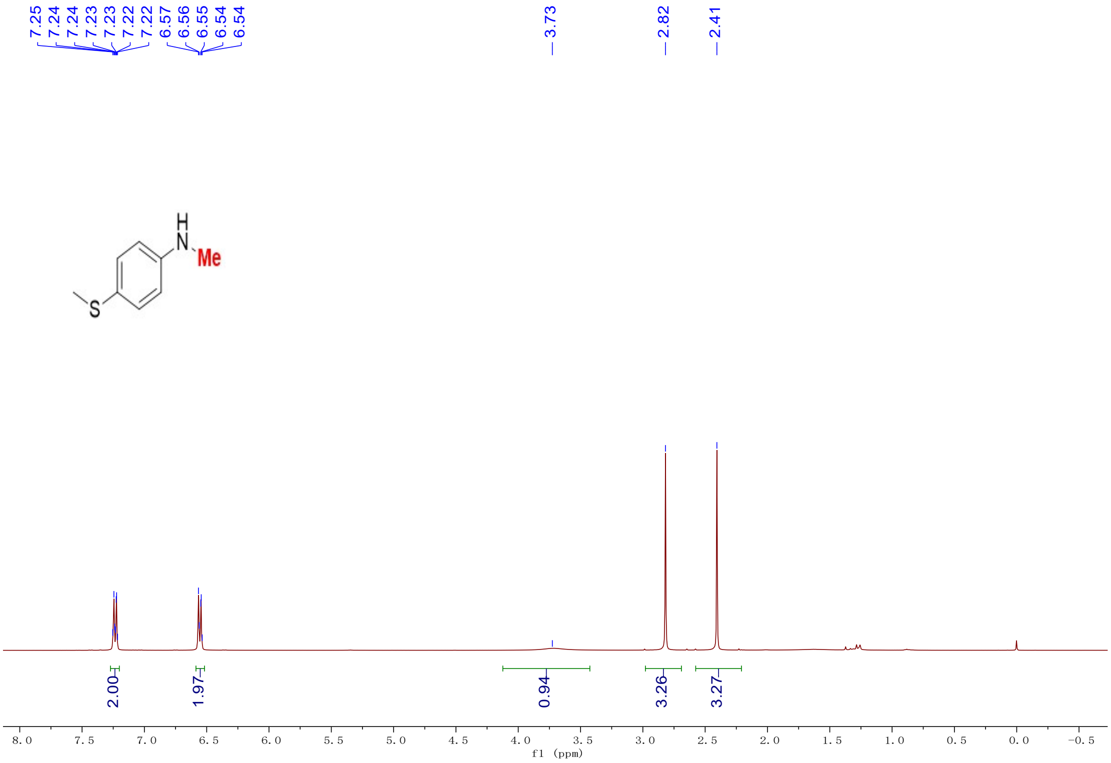

Figure S56: ^{1}H NMR (400 MHz, $CDCl_3$, 298 K) spectrum for 11d

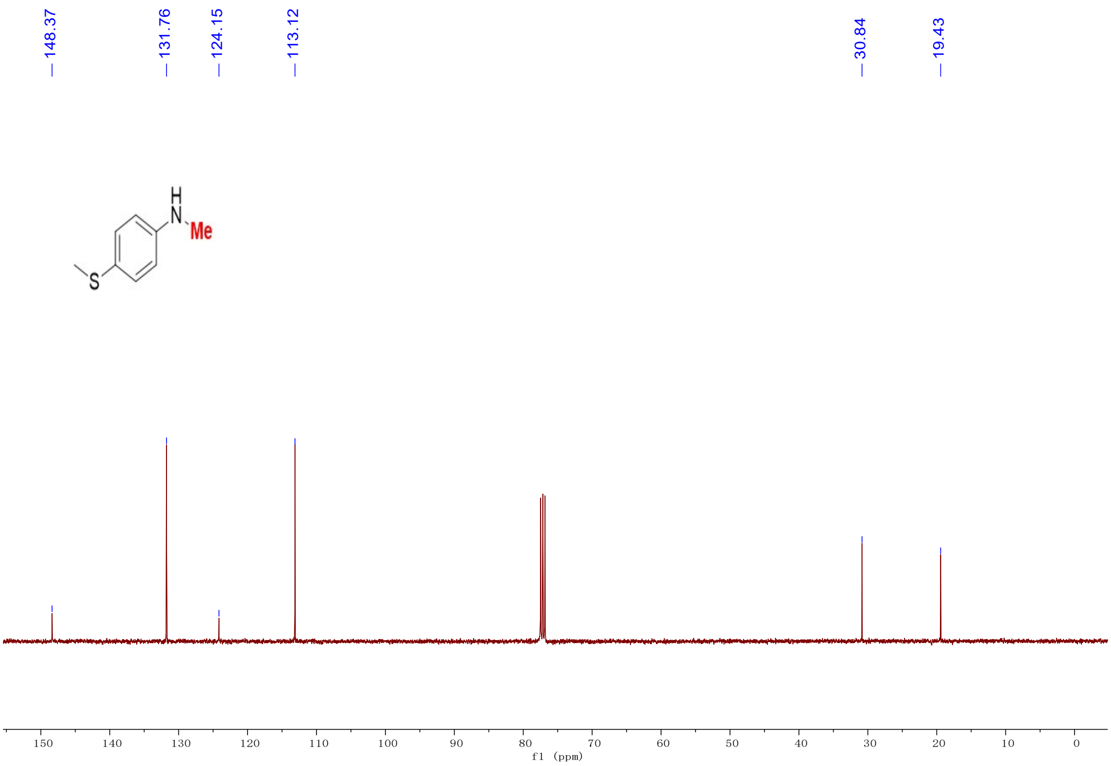

Figure S57: ^{13}C NMR (101 MHz, $CDCl_3$, 298 K) spectrum for 11d

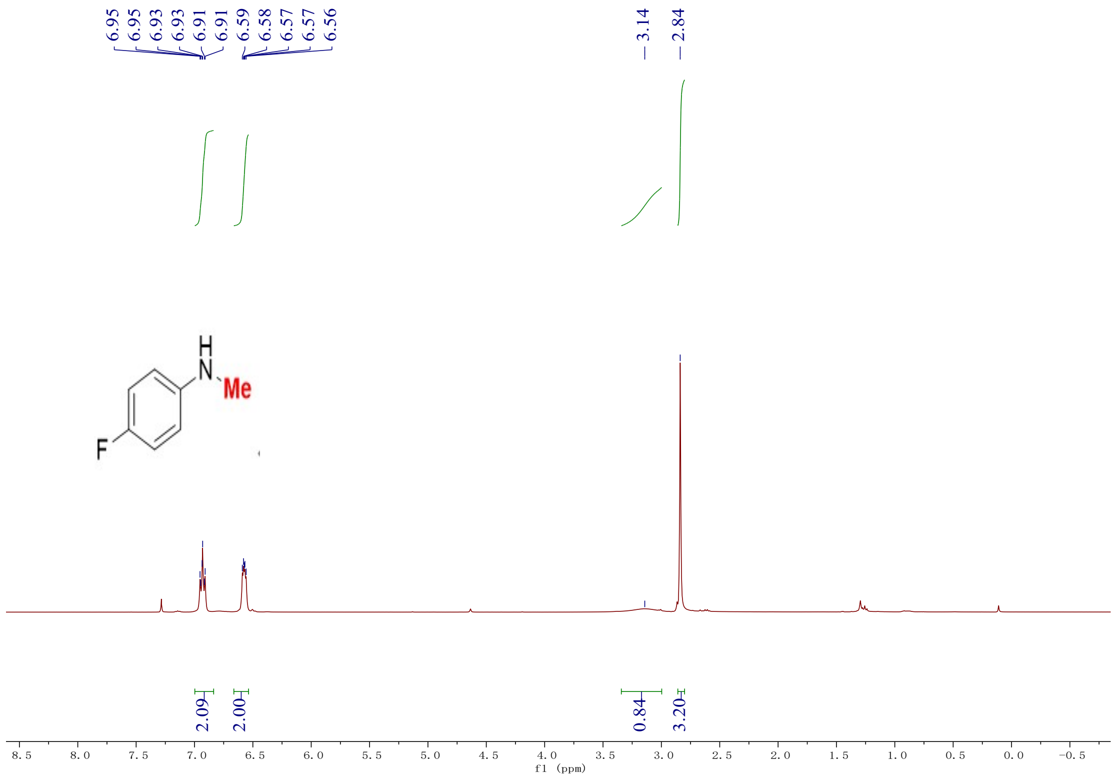

Figure S58: ^{1}H NMR (400 MHz, $CDCl_3$, 298 K) spectrum for 11e

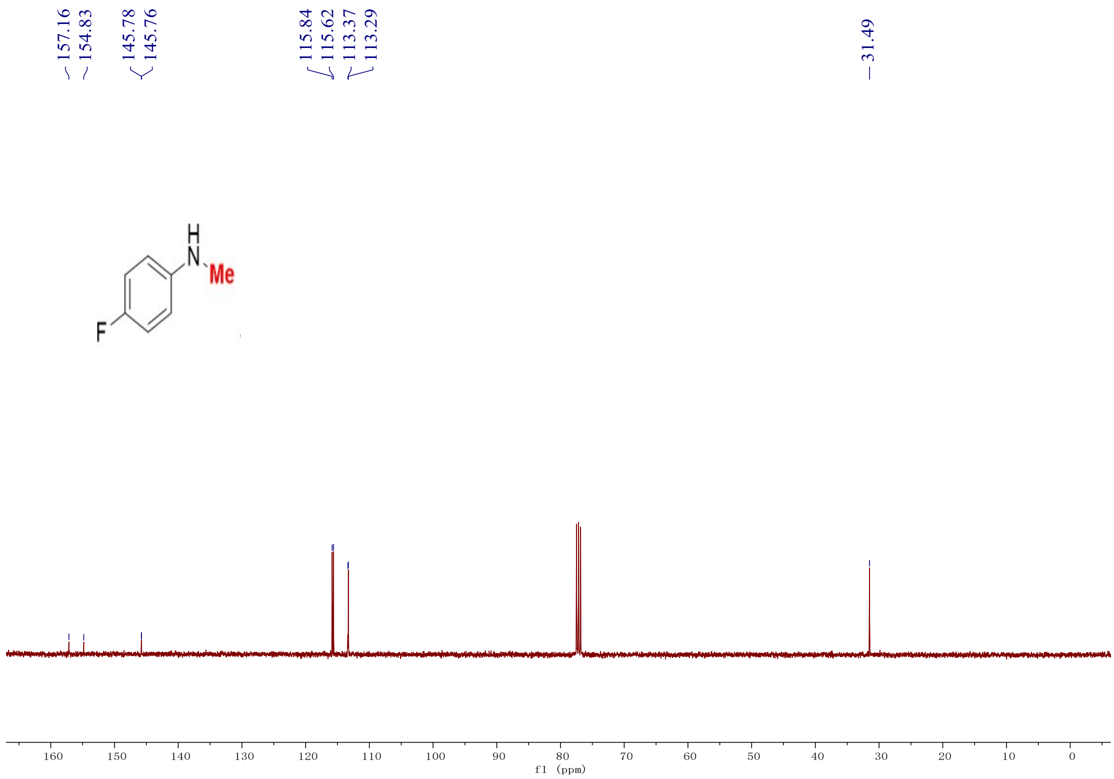

Figure S59: ^{13}C NMR (101 MHz, $CDCl_3$, 298 K) spectrum for 11e

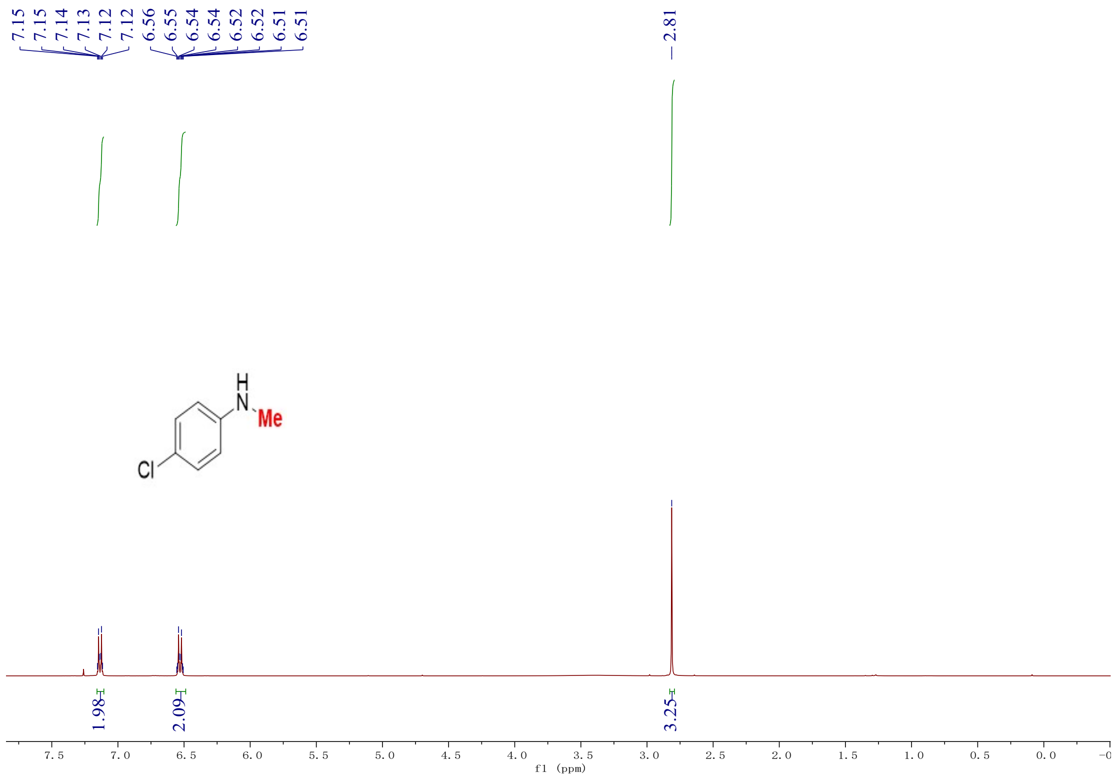

Figure S60: [1]H NMR (400 MHz, $CDCl_3$, 298 K) spectrum for 11f

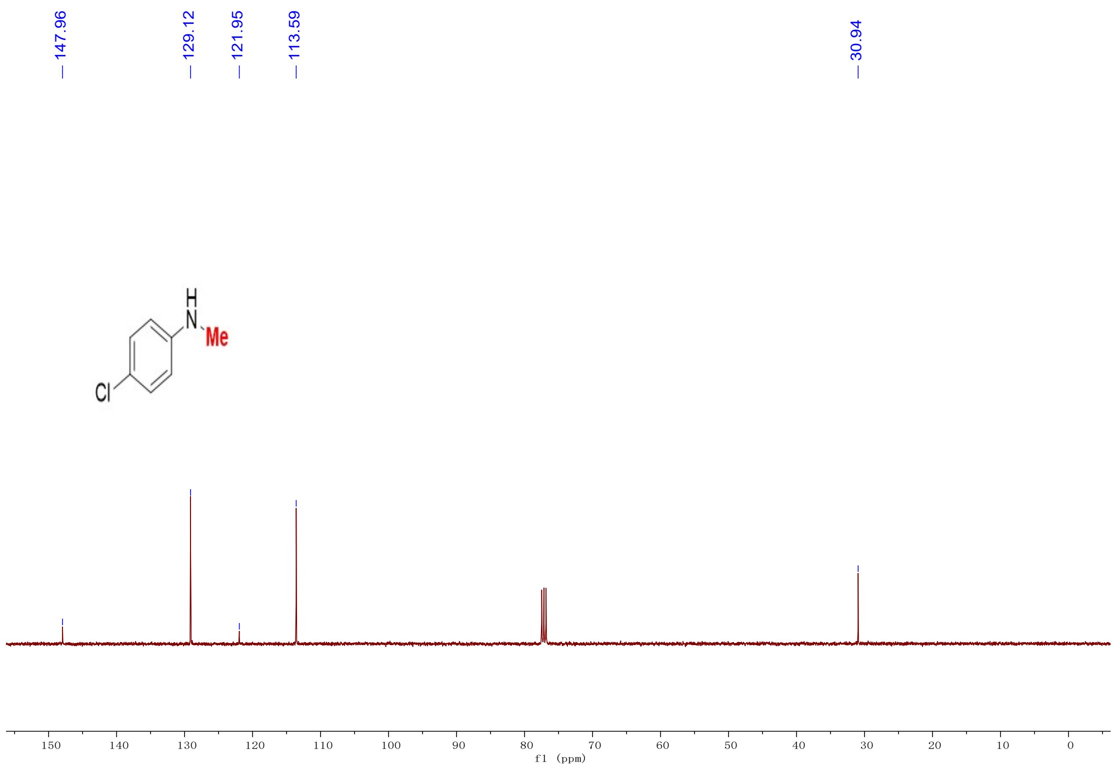

Figure S61: [13]C NMR (101 MHz, $CDCl_3$, 298 K) spectrum for 11f

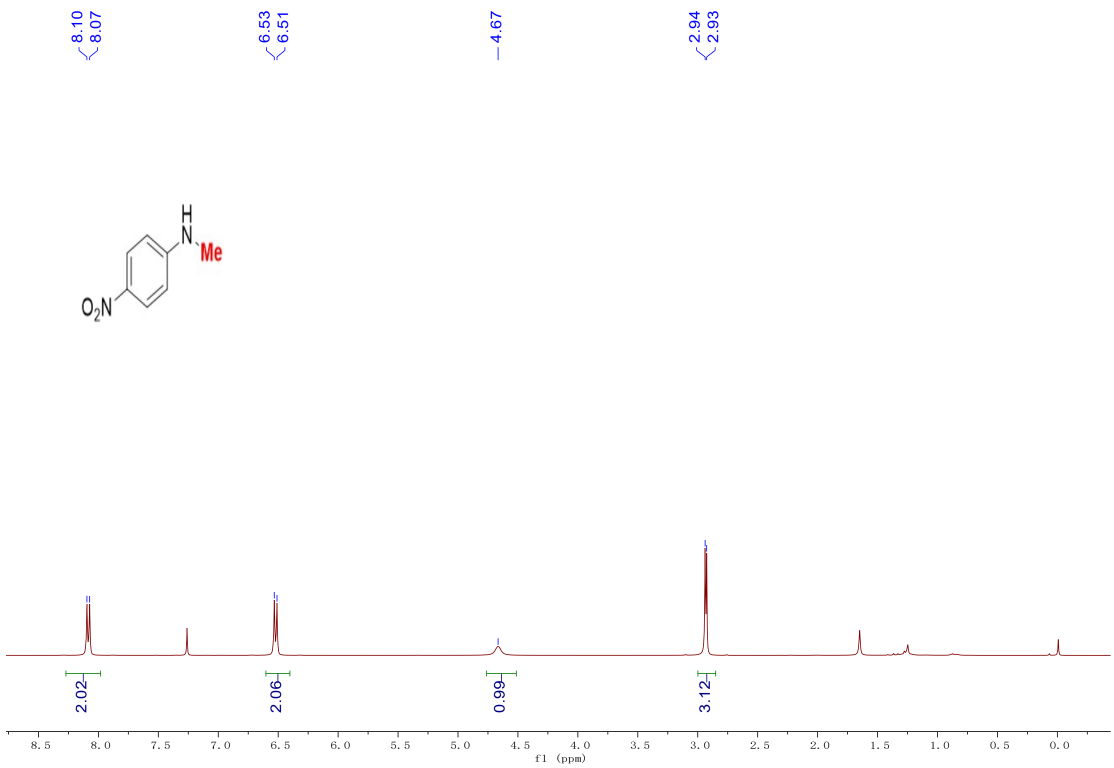

Figure S62: ^{1}H NMR (400 MHz, $CDCl_3$, 298 K) spectrum for 11g

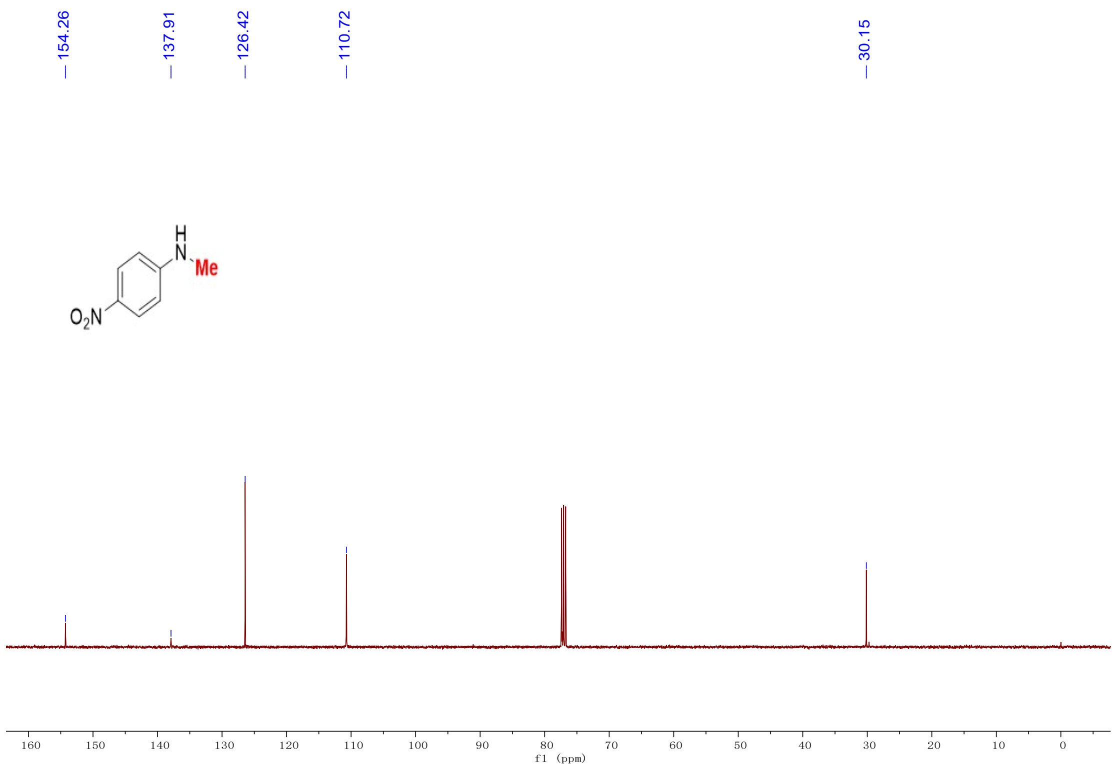

Figure S63: ^{13}C NMR (101 MHz, $CDCl_3$, 298 K) spectrum for 11g

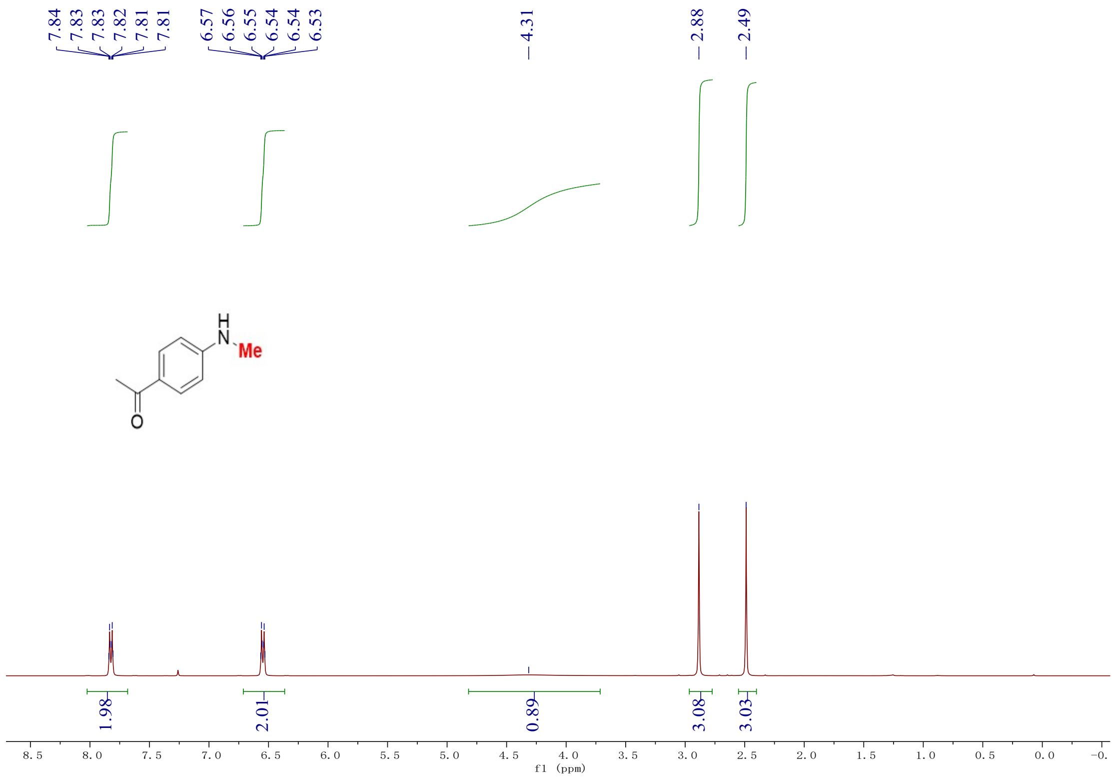

Figure S64: [1]H NMR (400 MHz, $CDCl_3$, 298 K) spectrum for 11h

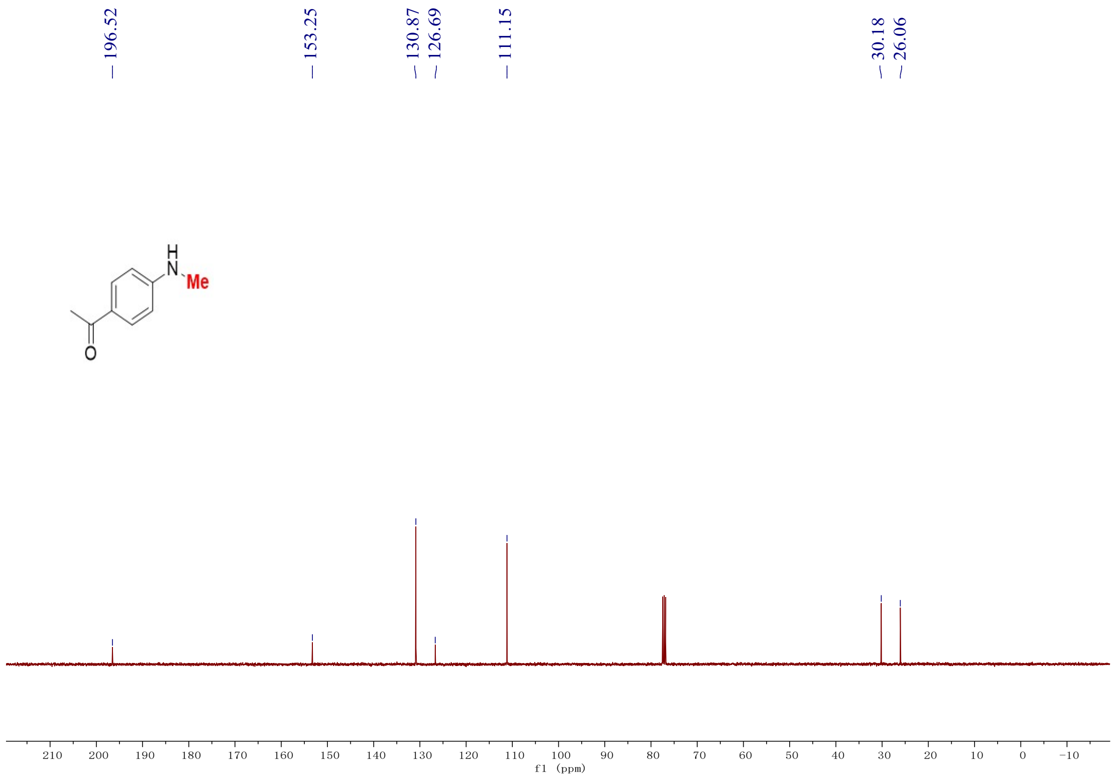

Figure S65: [13]C NMR (101 MHz, $CDCl_3$, 298 K) spectrum for 11h

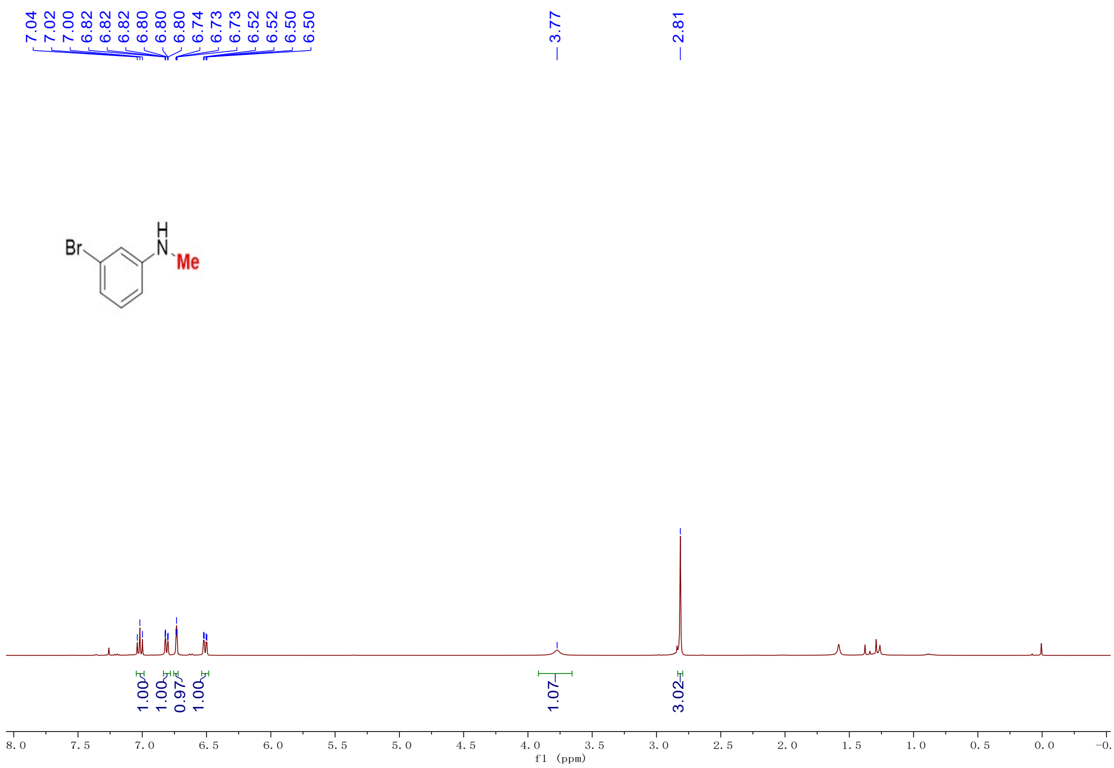

Figure S66: ^{1}H NMR (400 MHz, $CDCl_3$, 298 K) spectrum for 11i

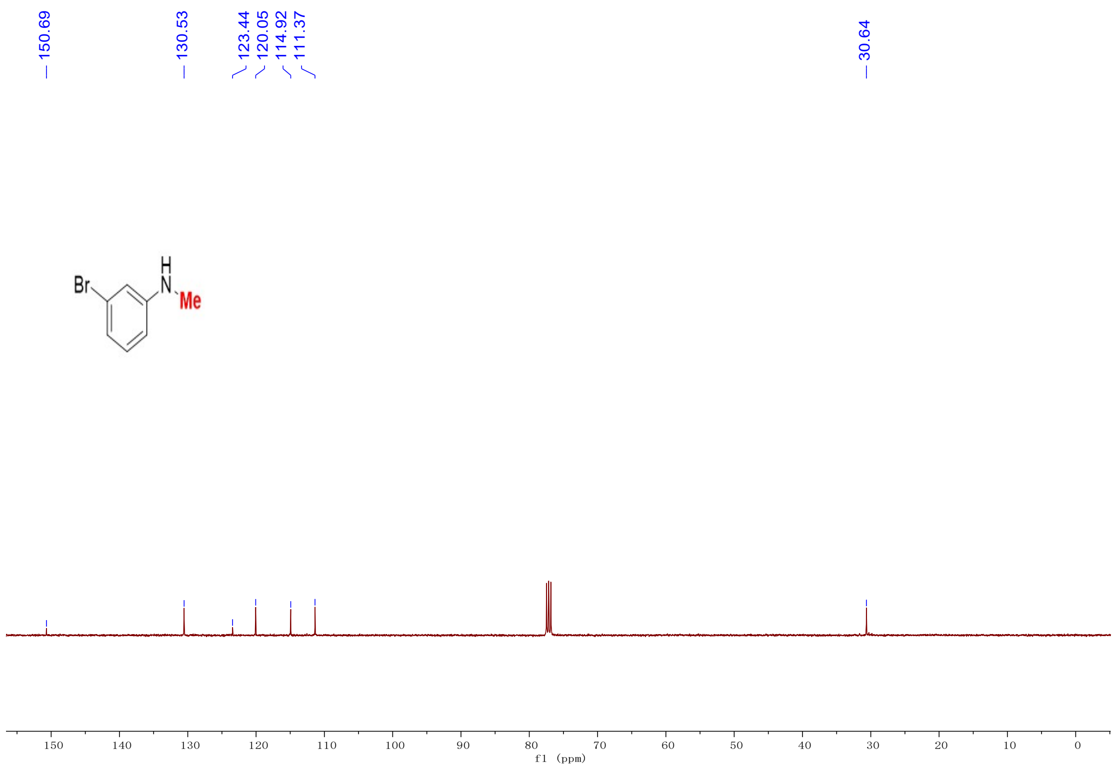

Figure S67: ^{13}C NMR (101 MHz, $CDCl_3$, 298 K) spectrum for 11i

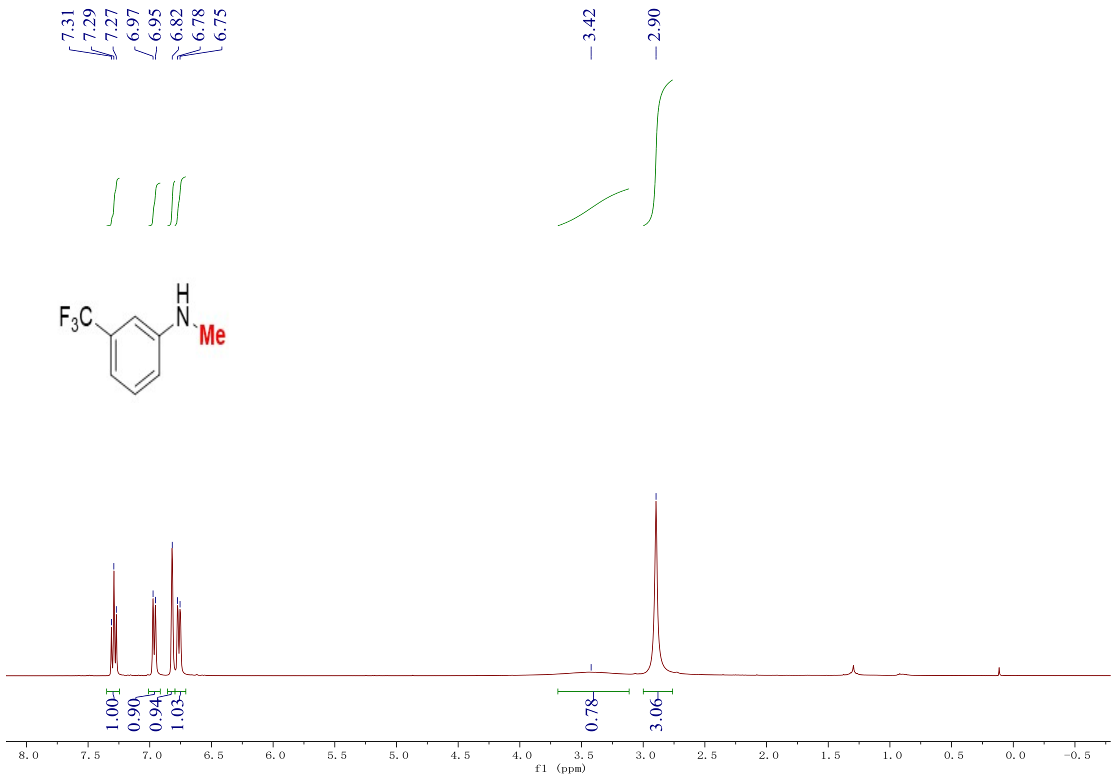

Figure S68: ^{1}H NMR (400 MHz, $CDCl_3$, 298 K) spectrum for 11j

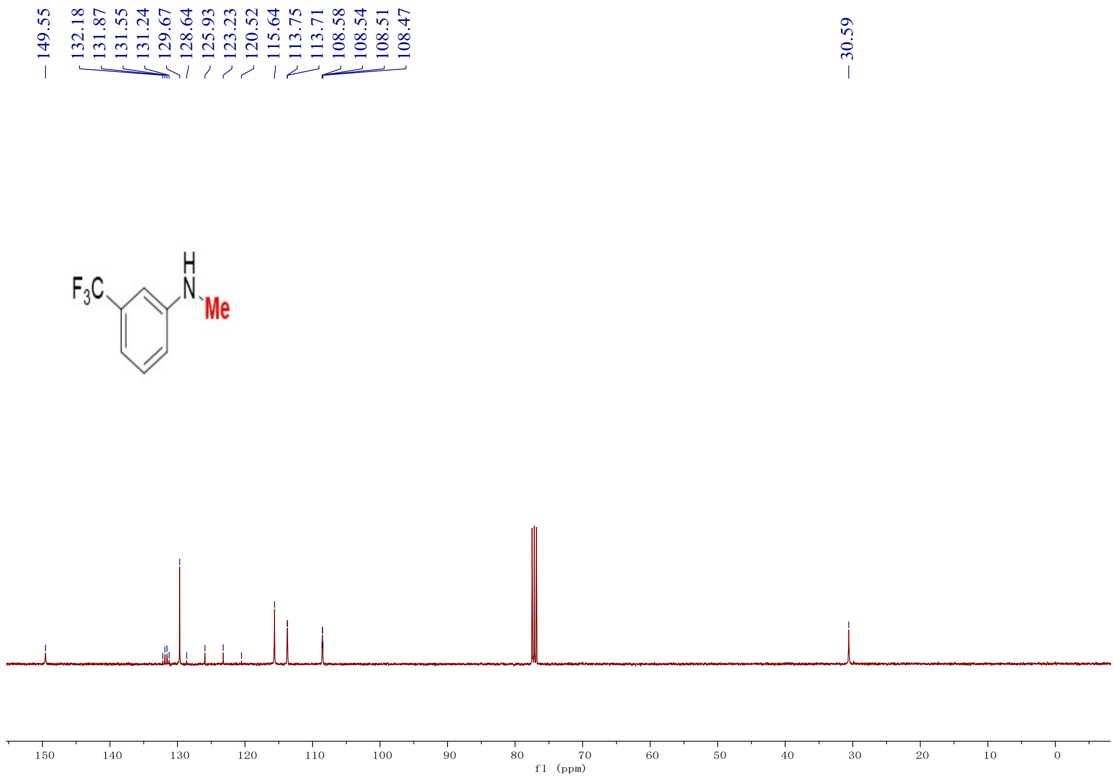

Figure S69: ^{13}C NMR (101 MHz, $CDCl_3$, 298 K) spectrum for 11j

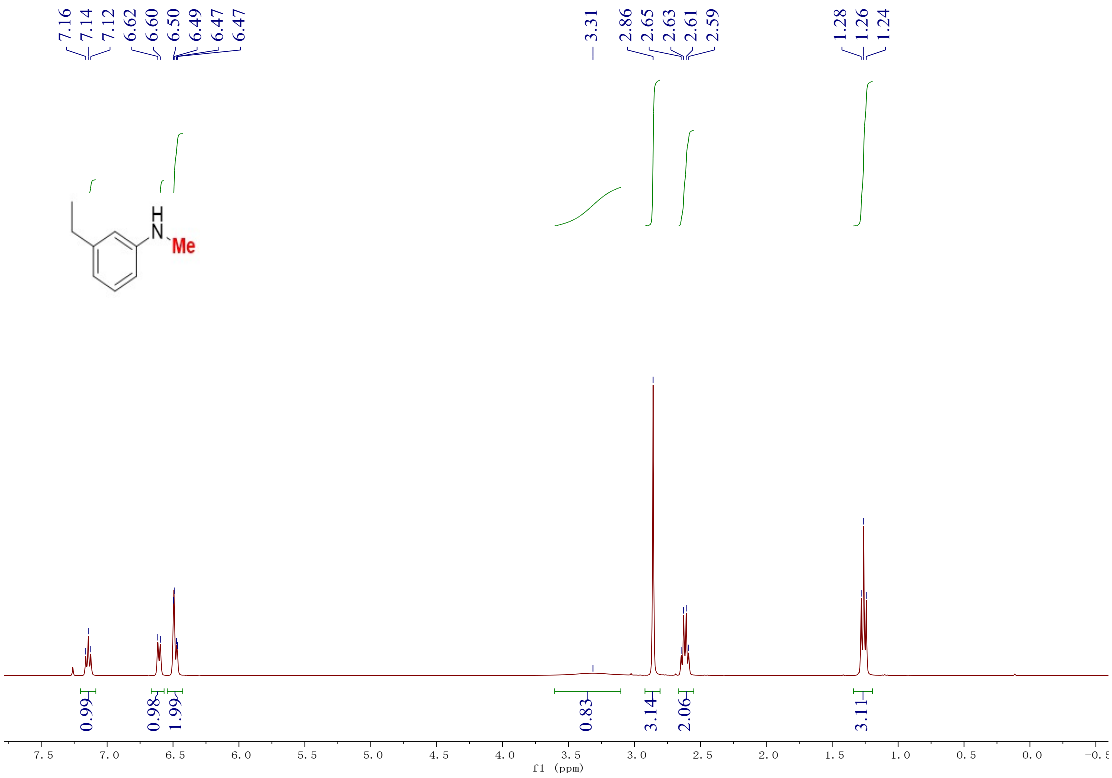

Figure S70: ^{1}H NMR (400 MHz, $CDCl_3$, 298 K) spectrum for 11k

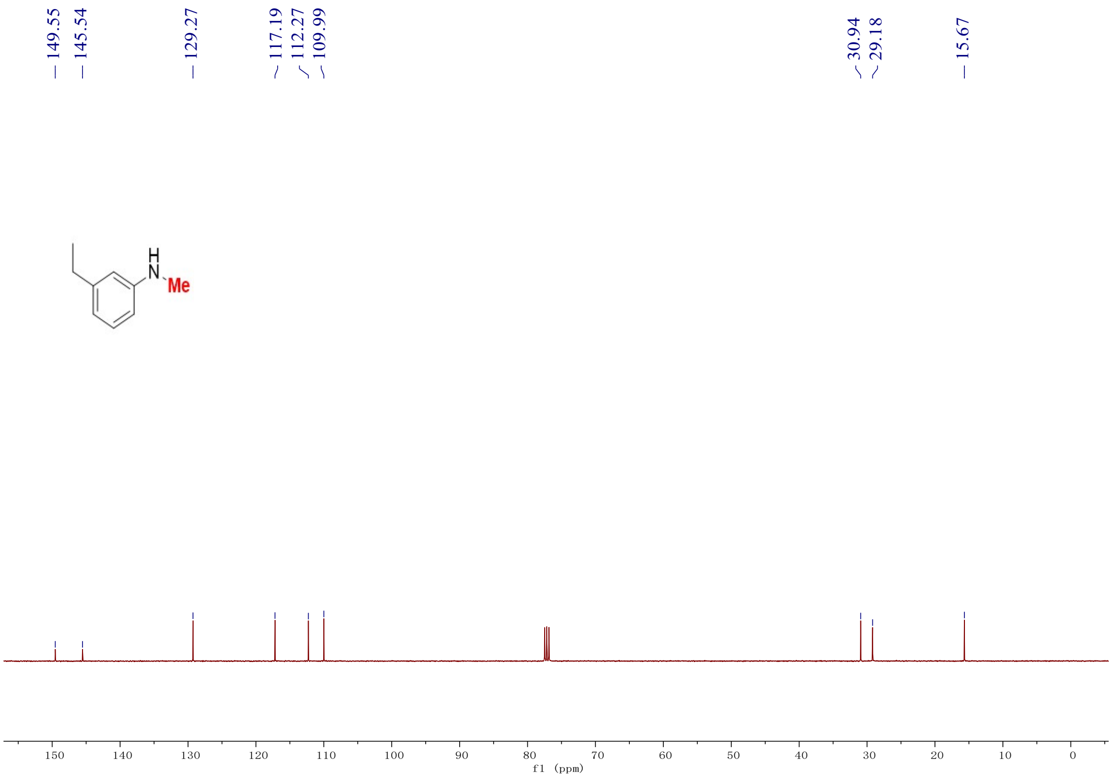

Figure S71: ^{13}C NMR (101 MHz, $CDCl_3$, 298 K) spectrum for 11k

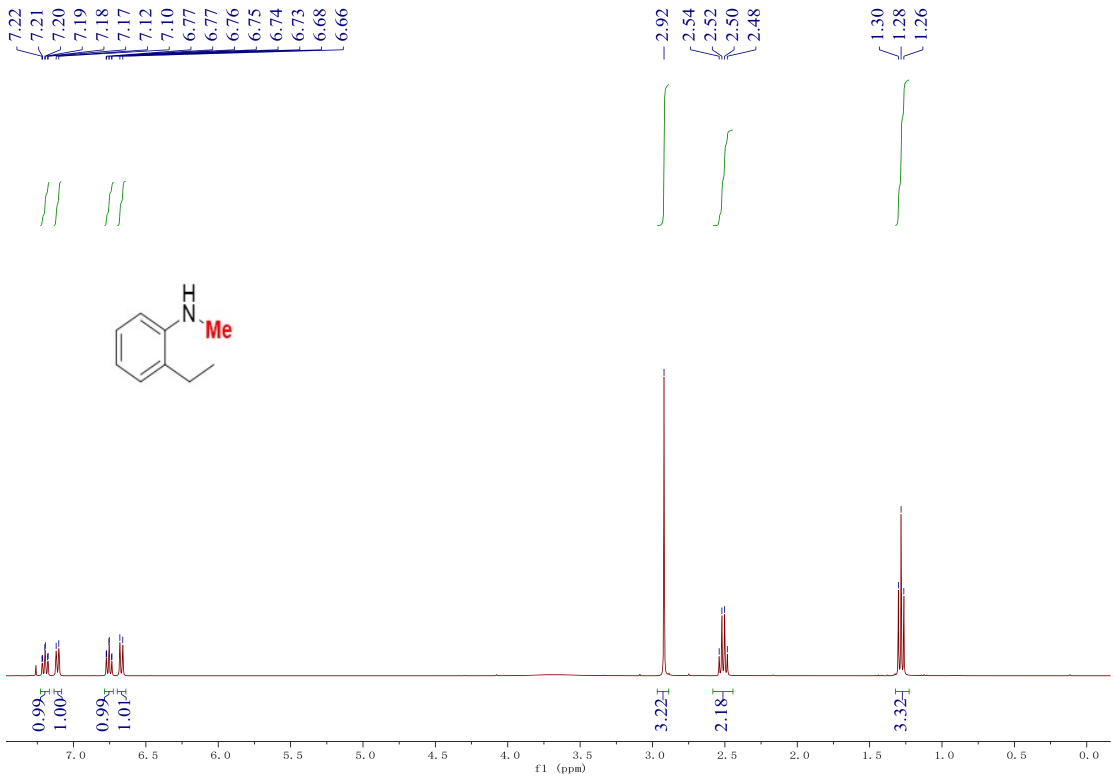

Figure S72: ^{1}H NMR (400 MHz, $CDCl_3$, 298 K) spectrum for 11l

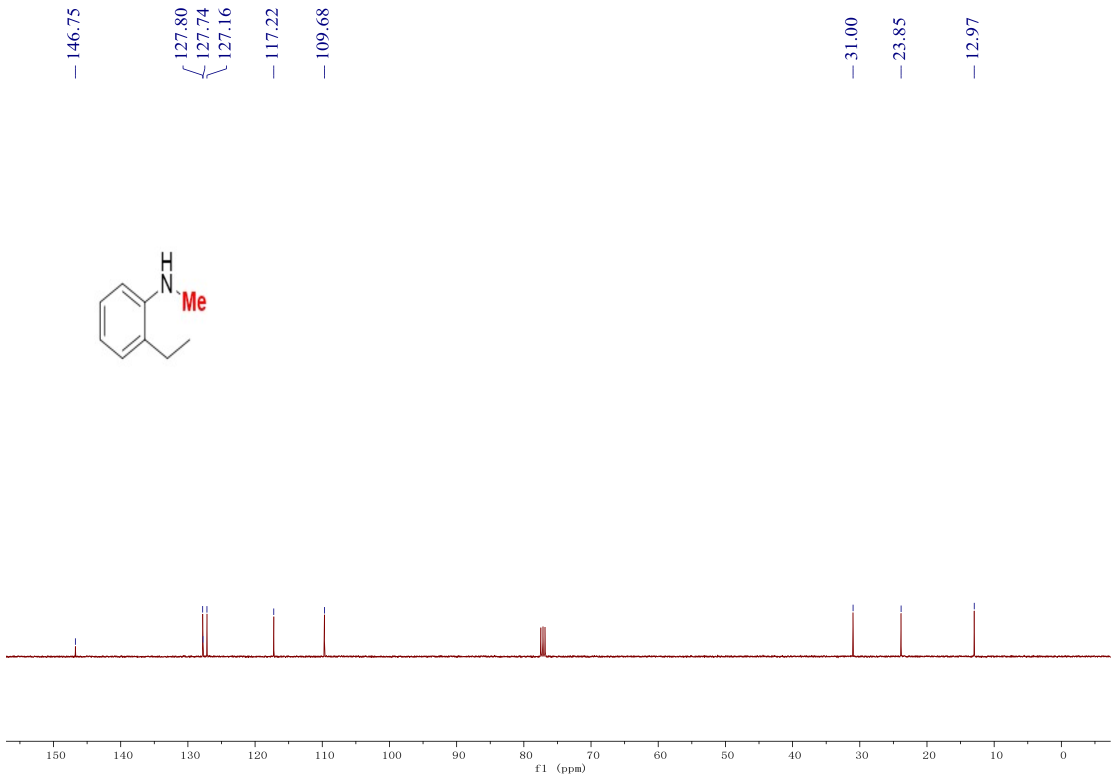

Figure S73: ^{13}C NMR (101 MHz, $CDCl_3$, 298 K) spectrum for 11l

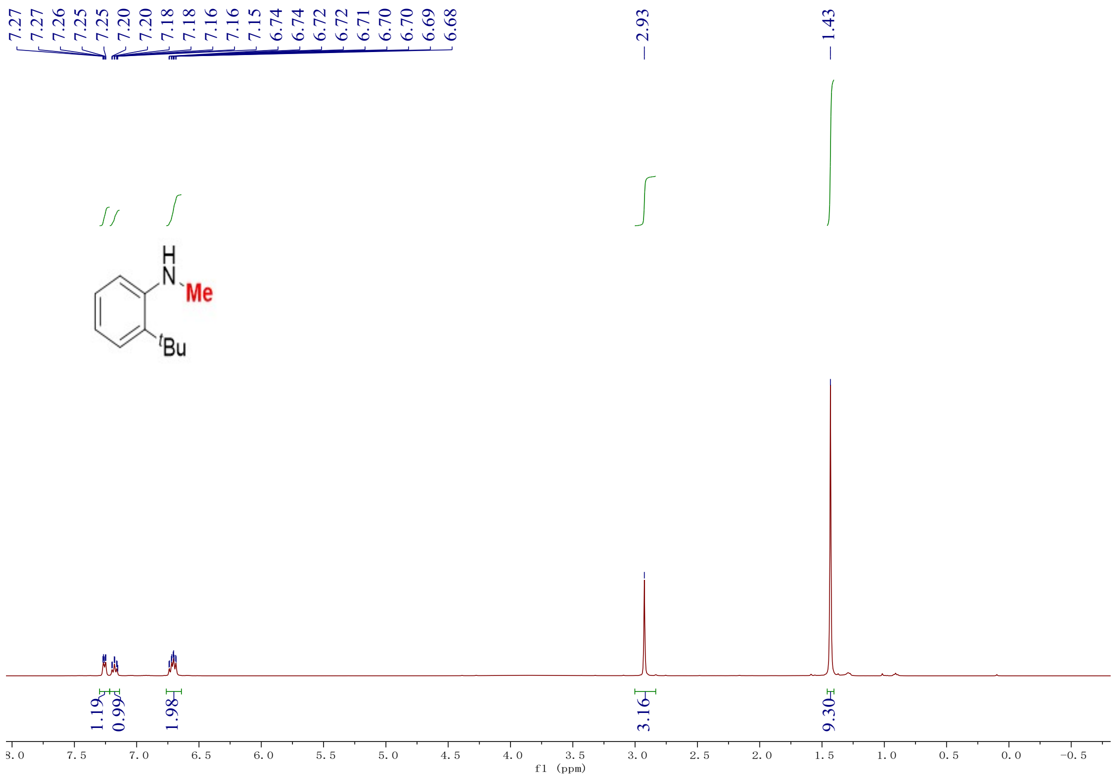

Figure S74: ^{1}H NMR (400 MHz, $CDCl_3$, 298 K) spectrum for 11m

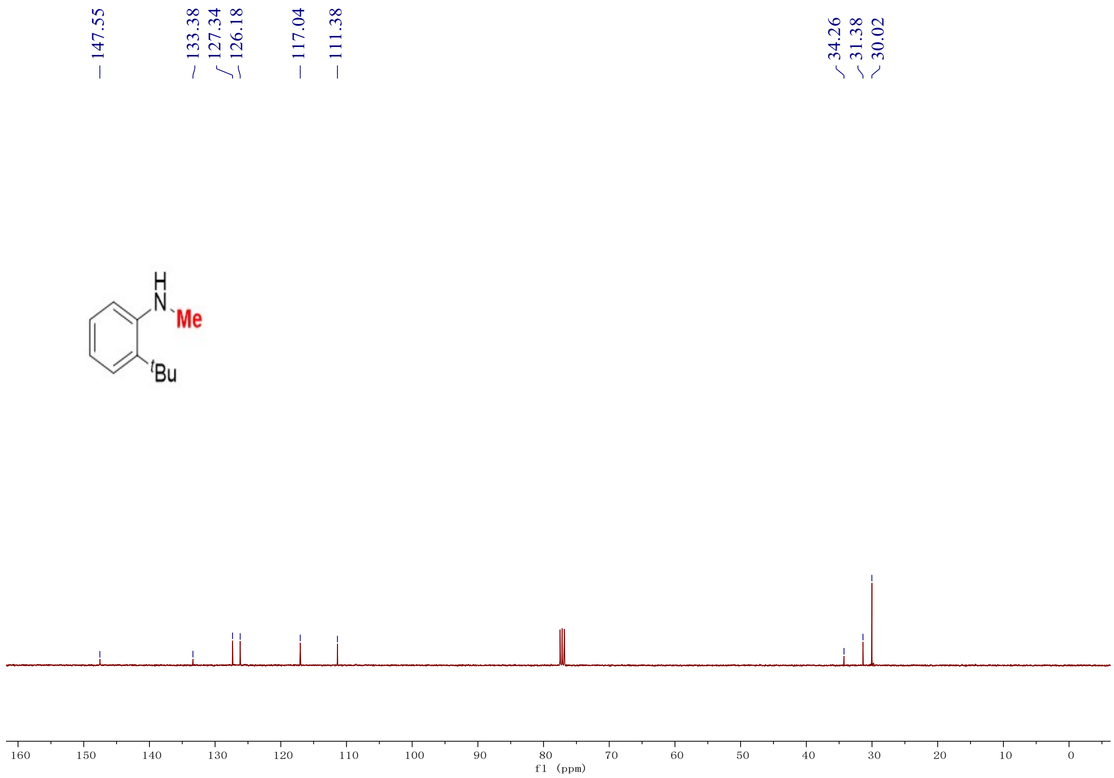

Figure S75: ^{13}C NMR (101 MHz, $CDCl_3$, 298 K) spectrum for 11m

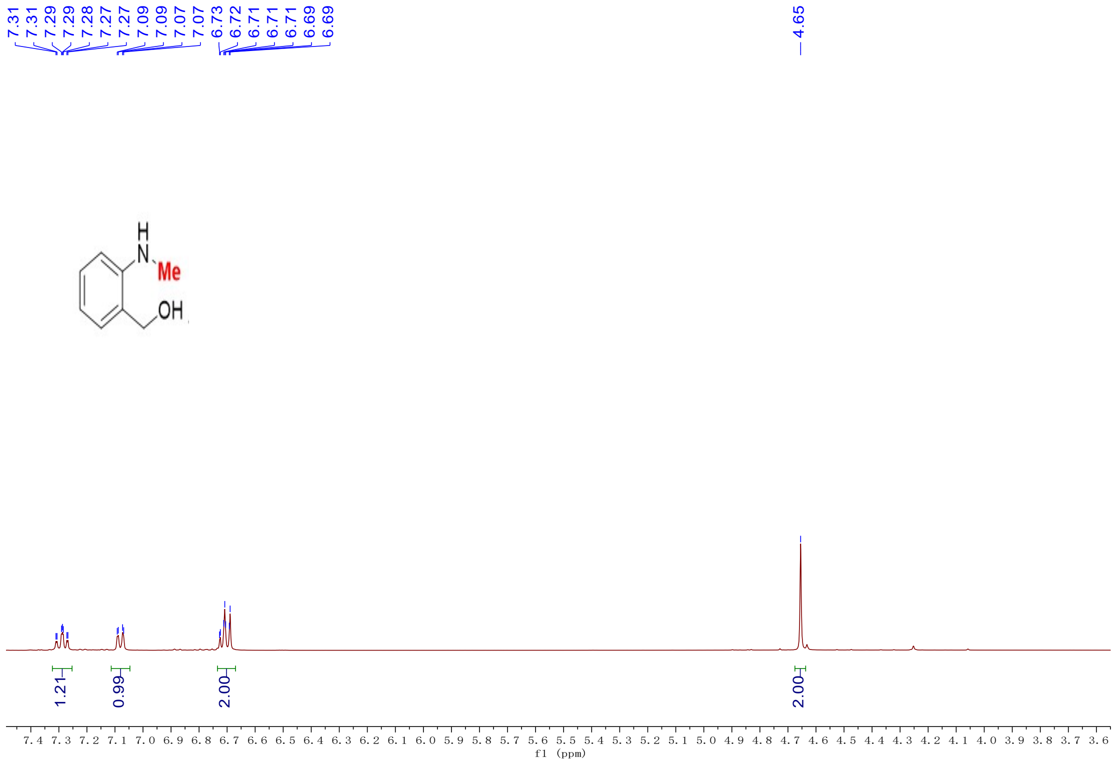

Figure S76: ^{1}H NMR (400 MHz, $CDCl_3$, 298 K) spectrum for 11n

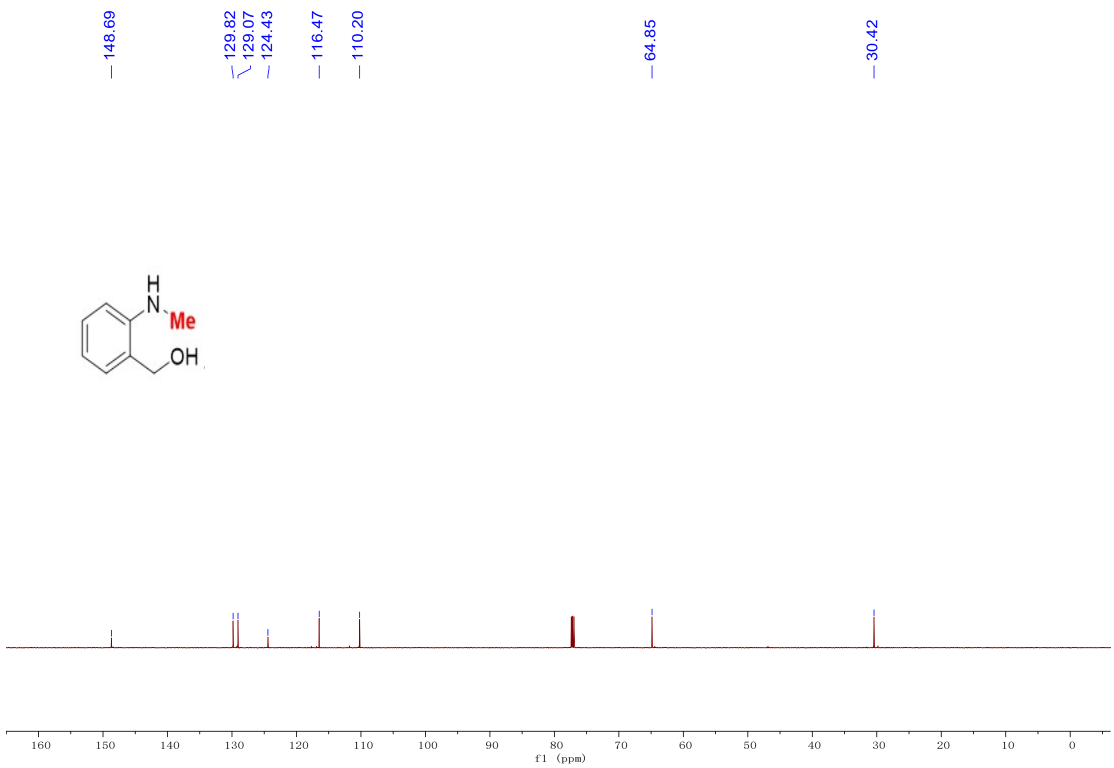

Figure S77: ^{13}C NMR (101 MHz, $CDCl_3$, 298 K) spectrum for 11n

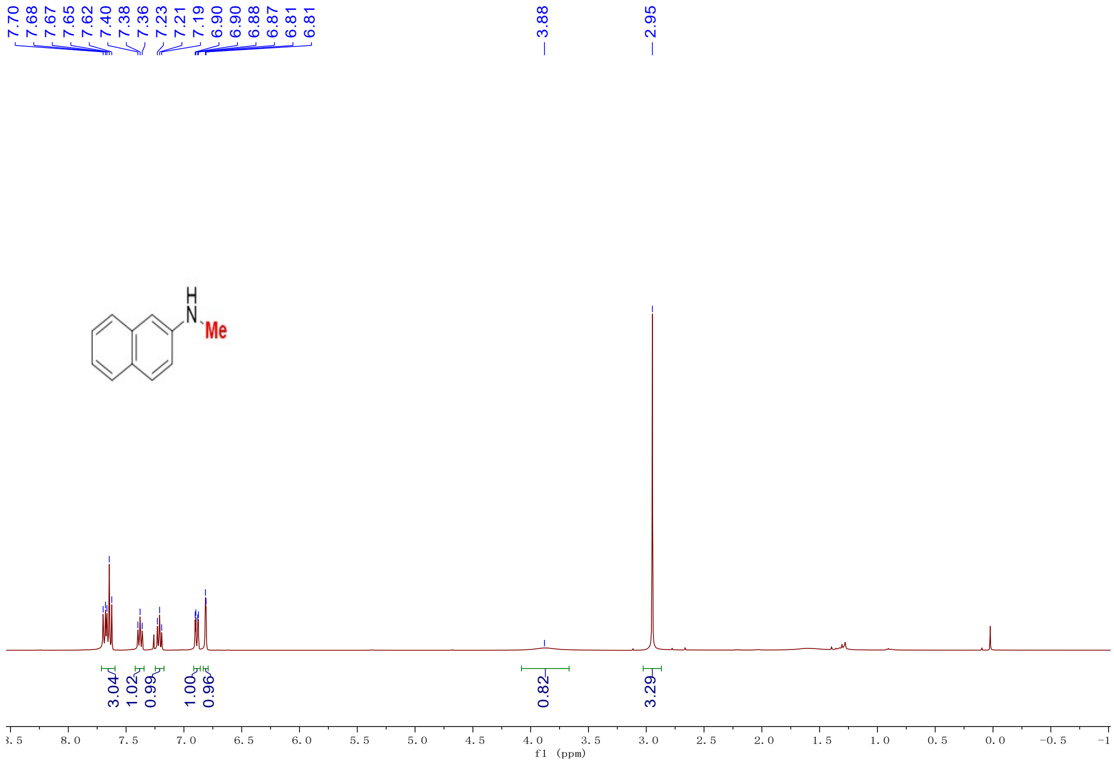

Figure S78: ^{1}H NMR (400 MHz, $CDCl_3$, 298 K) spectrum for 11o

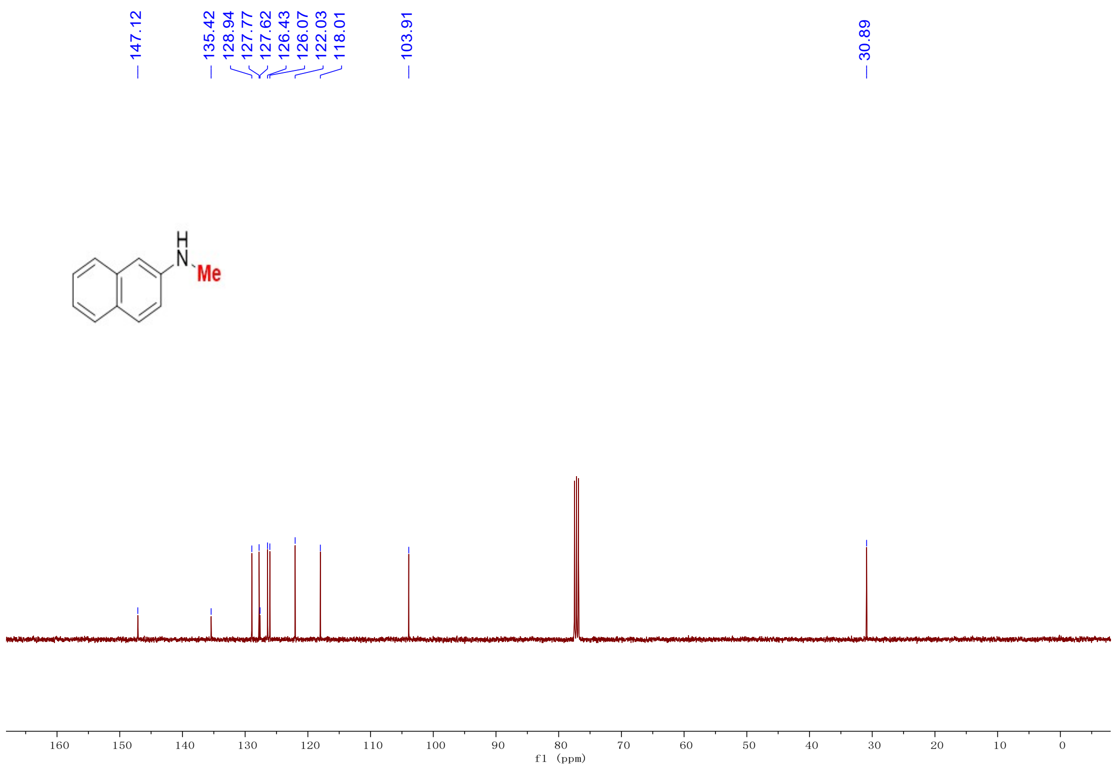

Figure S79: ^{13}C NMR (101 MHz, $CDCl_3$, 298 K) spectrum for 11o

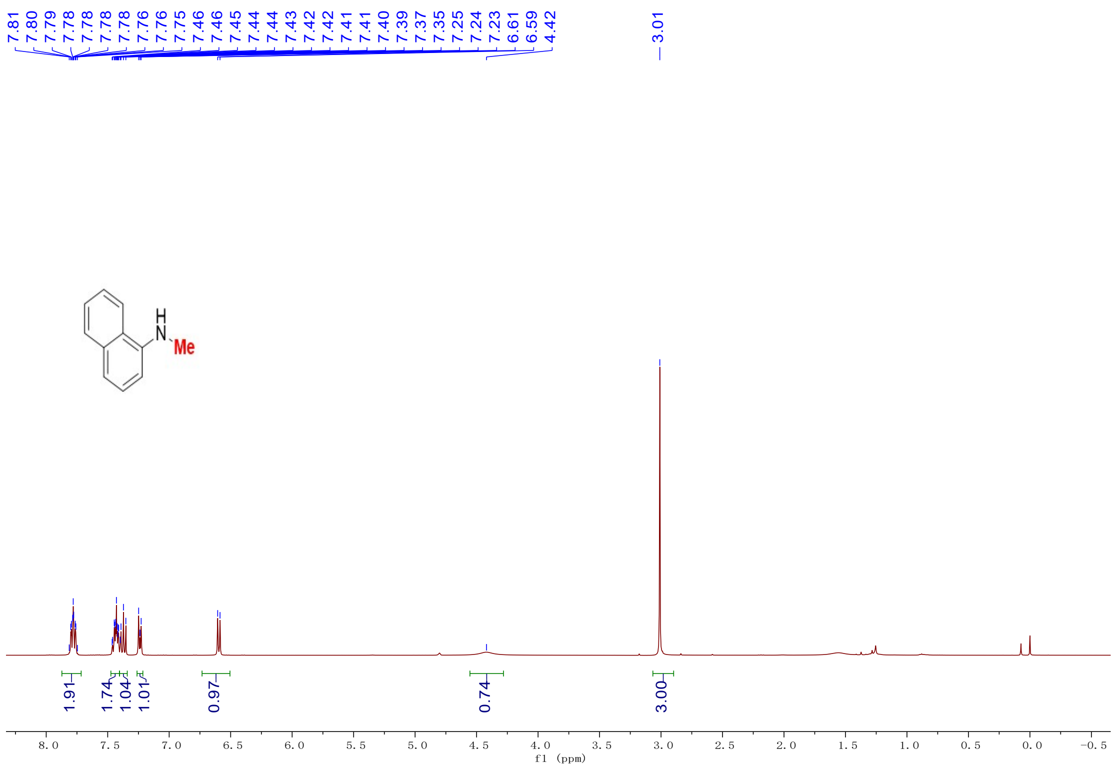

Figure S80: ^{1}H NMR (400 MHz, $CDCl_3$, 298 K) spectrum for 11p

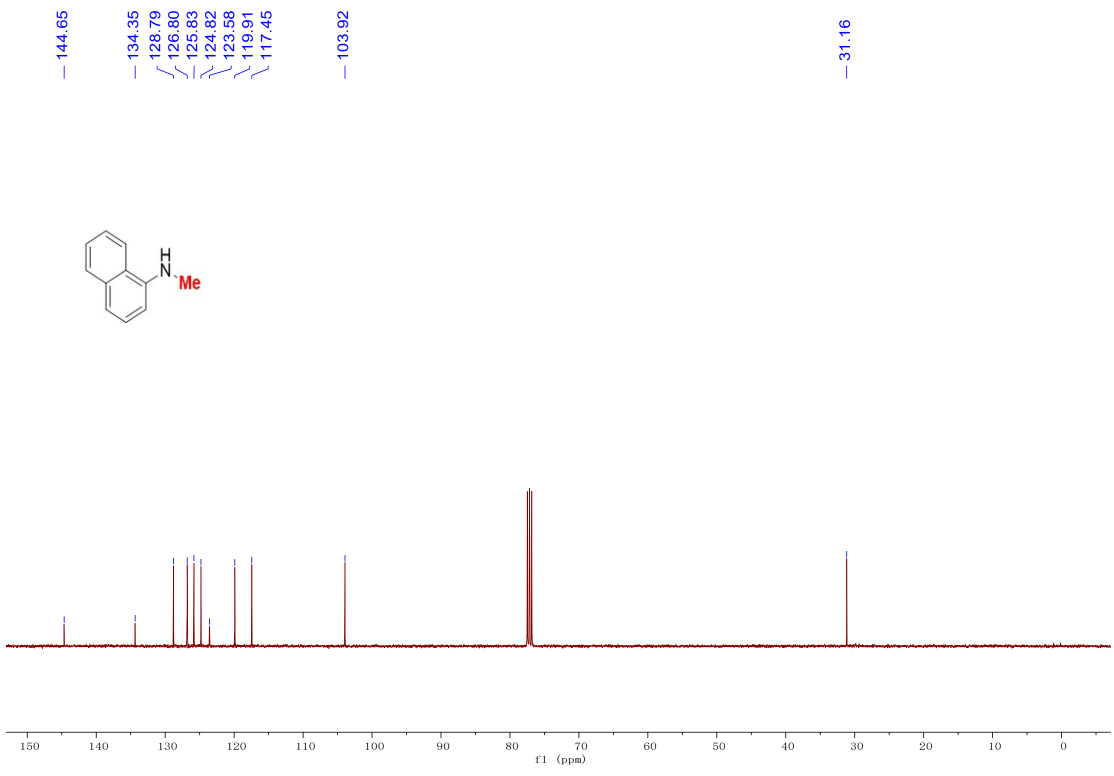

Figure S81: ^{13}C NMR (101 MHz, $CDCl_3$, 298 K) spectrum for 11p

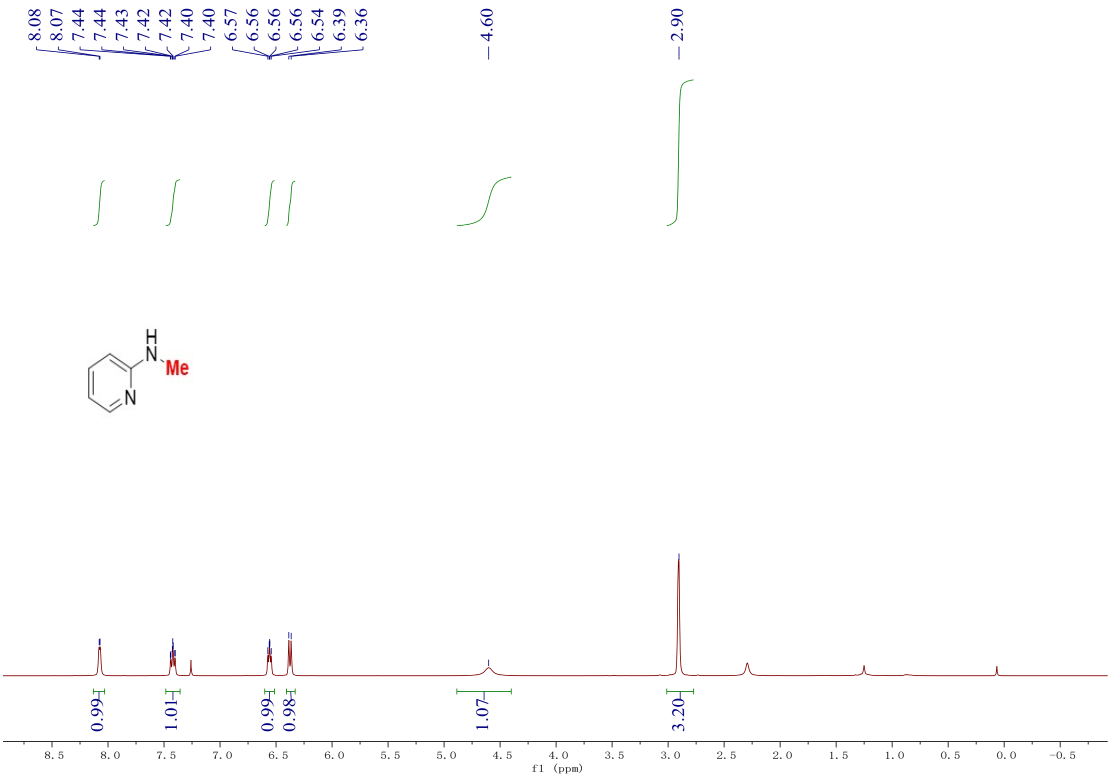

Figure S82: ^{1}H NMR (400 MHz, $CDCl_3$, 298 K) spectrum for 11q

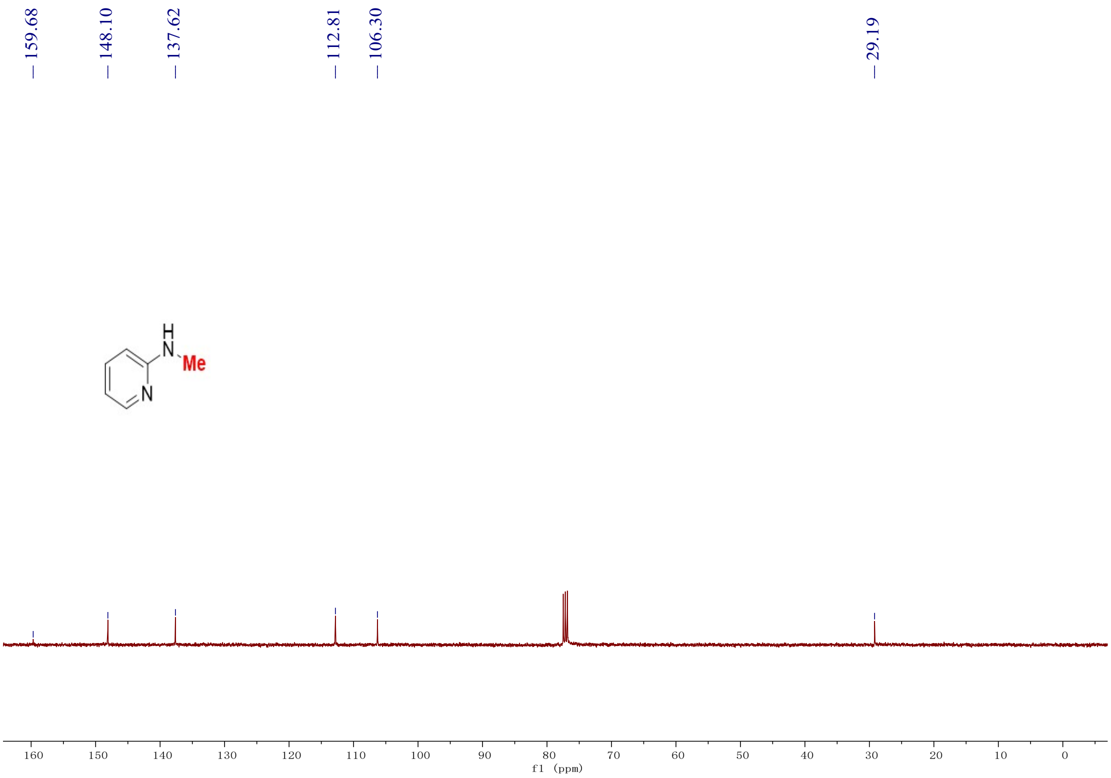

Figure S83: ^{13}C NMR (101 MHz, $CDCl_3$, 298 K) spectrum for 11q

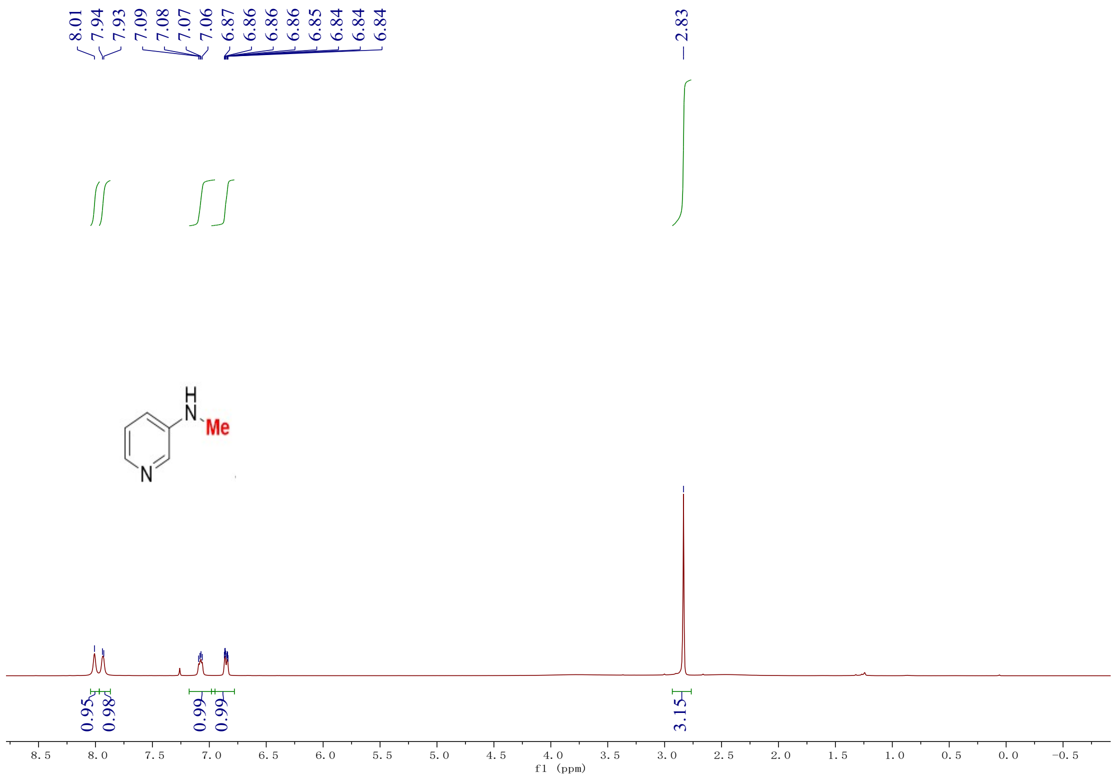

Figure S84: ^{1}H NMR (400 MHz, $CDCl_3$, 298 K) spectrum for 11r

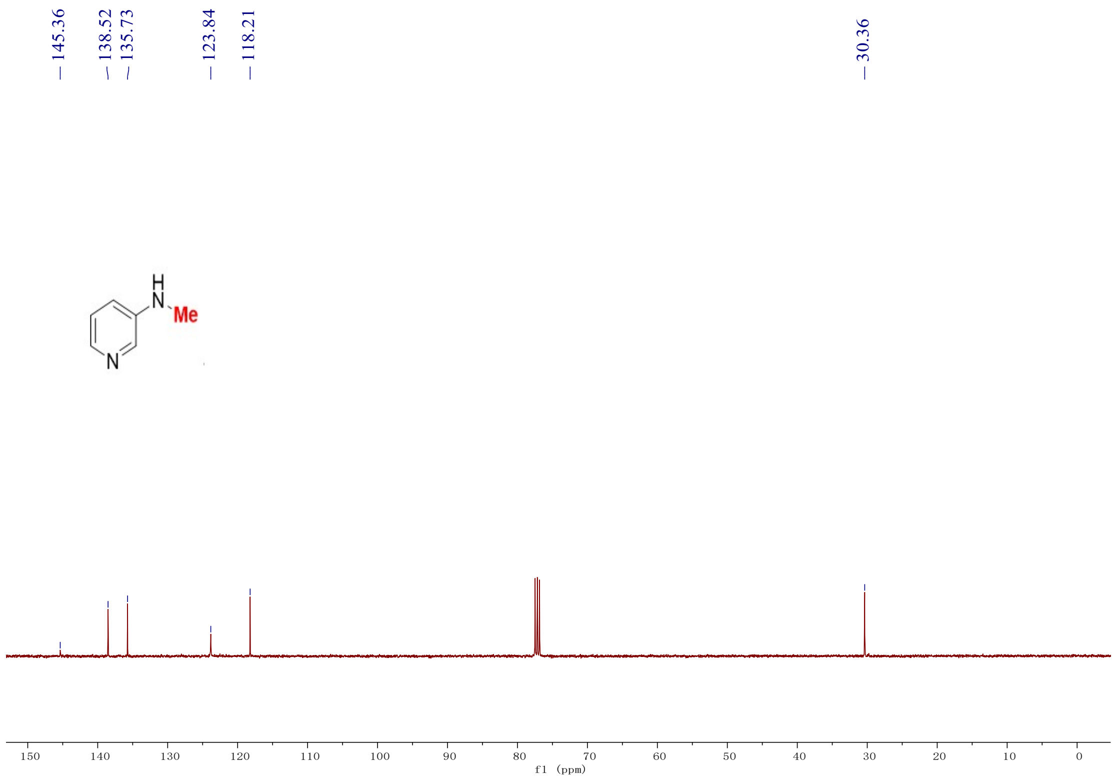

Figure S85: ^{13}C NMR (101 MHz, $CDCl_3$, 298 K) spectrum for 11r

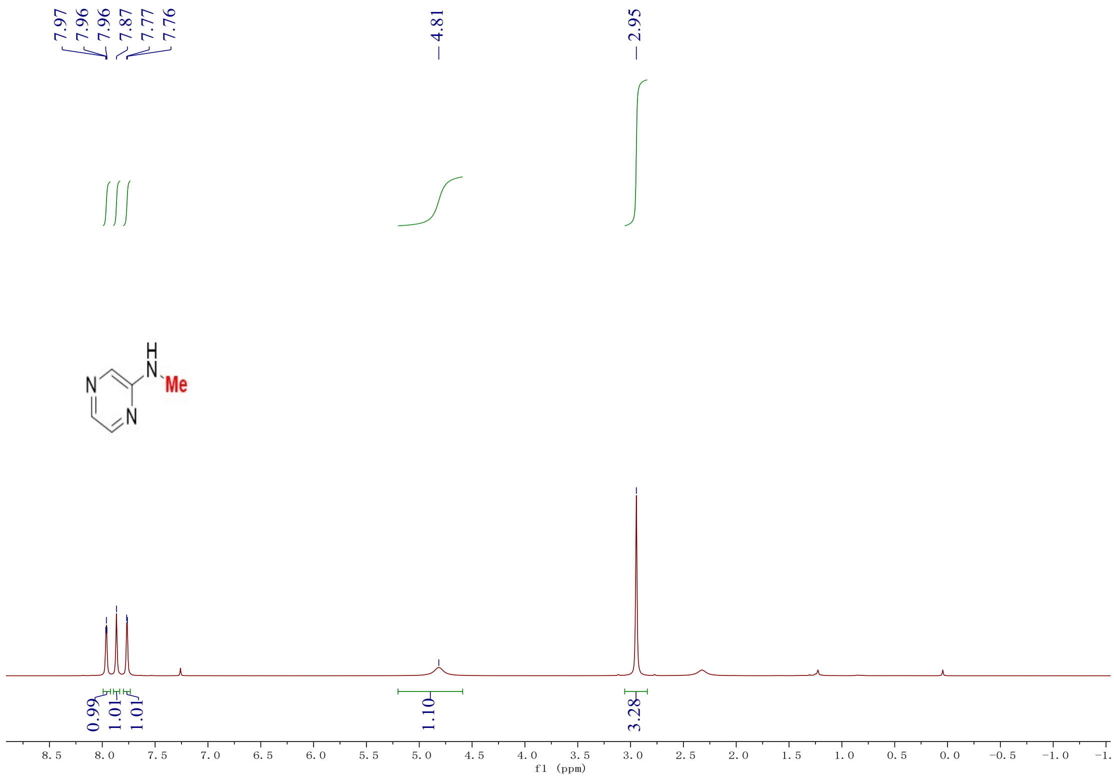

Figure S86: ¹H NMR (400 MHz, $CDCl_3$, 298 K) spectrum for 11s

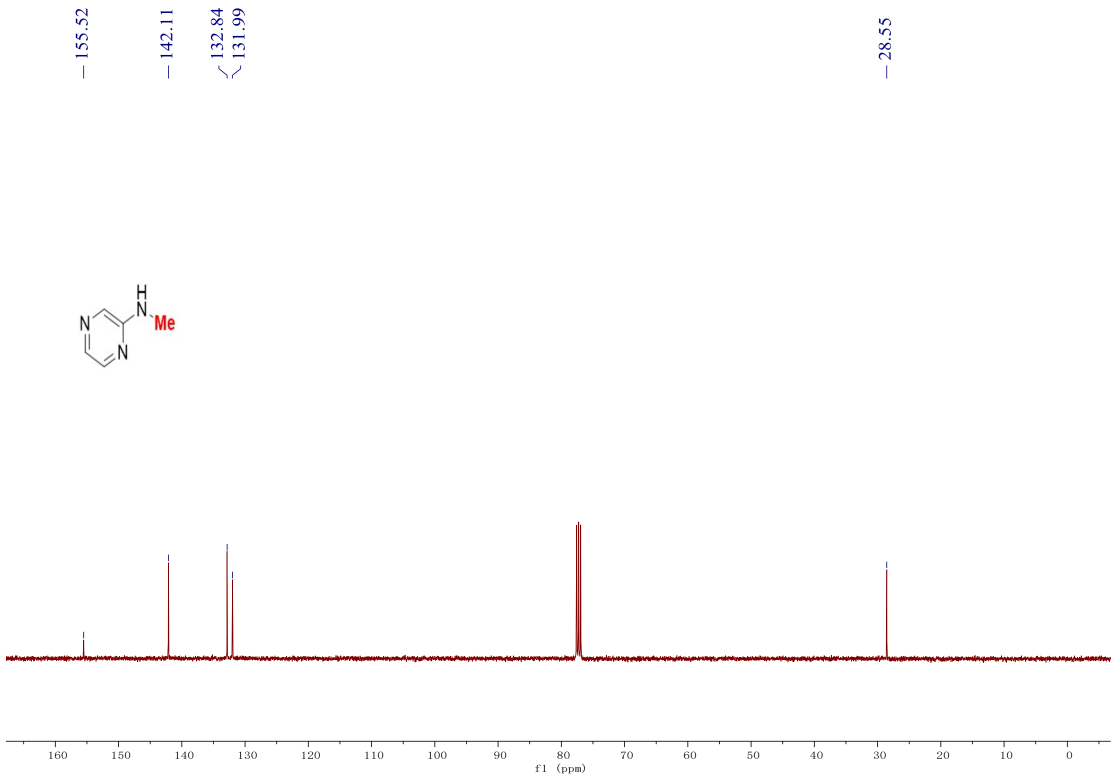

Figure S87: ¹³C NMR (101 MHz, $CDCl_3$, 298 K) spectrum for 11s

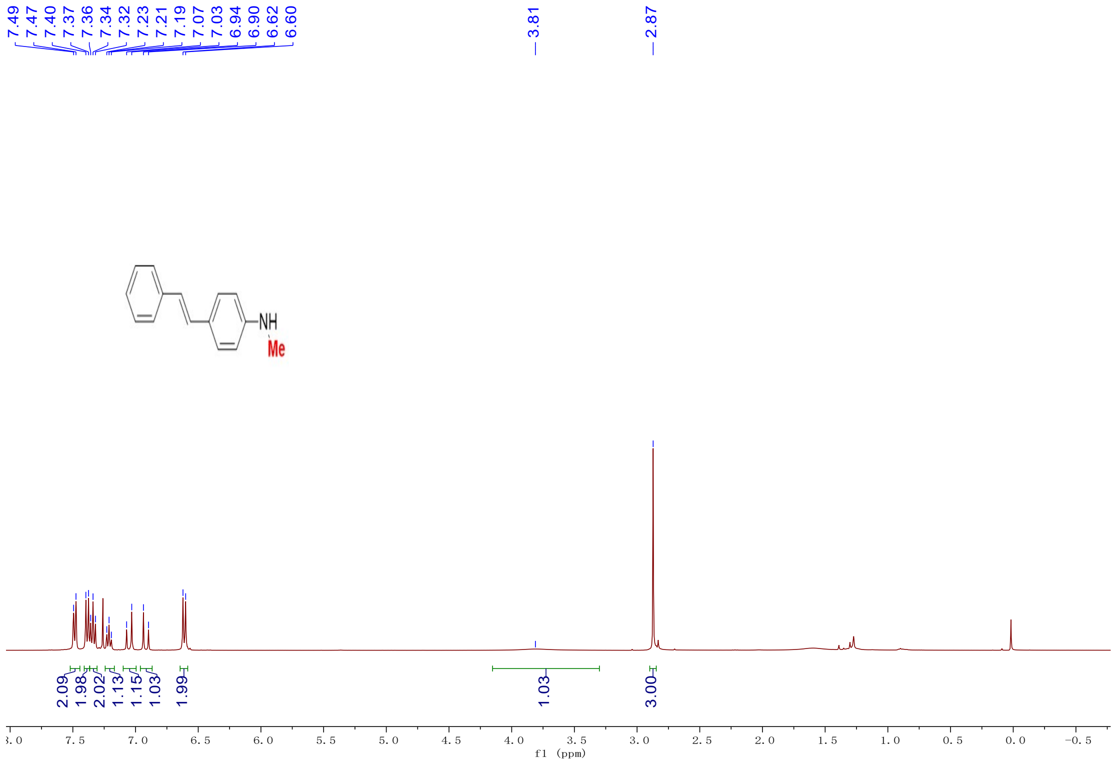

Figure S88: ^{1}H NMR (400 MHz, $CDCl_3$, 298 K) spectrum for 11t

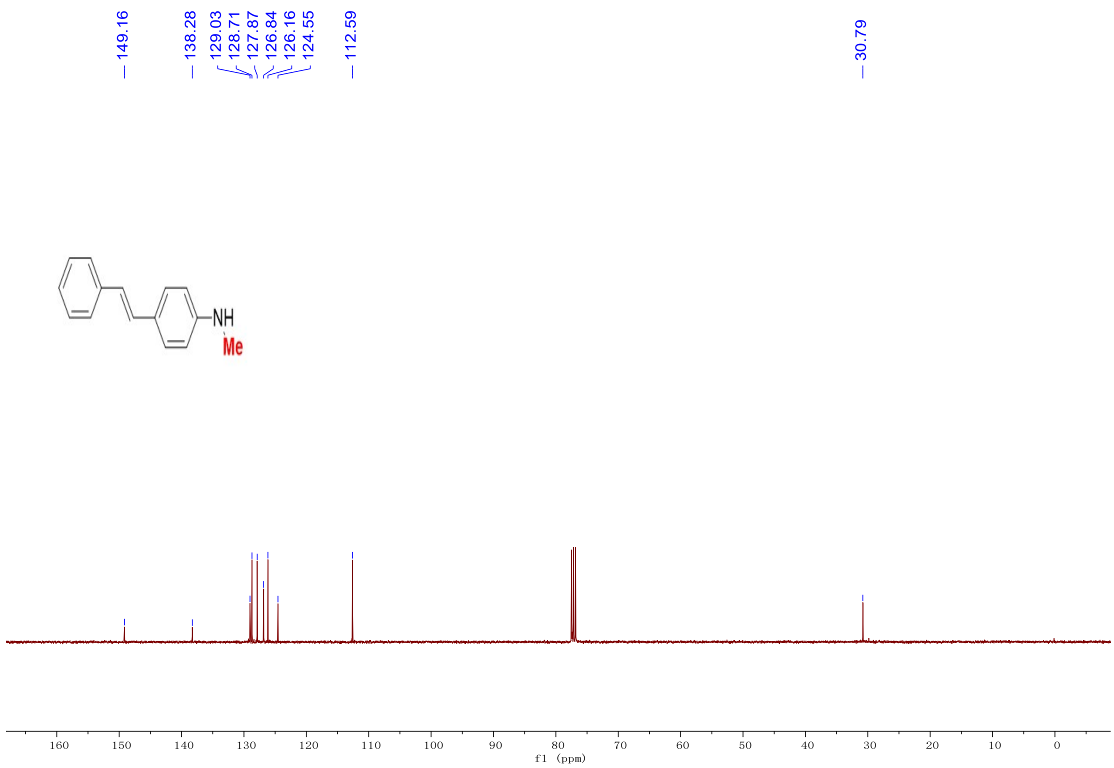

Figure S89: ^{13}C NMR (101 MHz, $CDCl_3$, 298 K) spectrum for 11t

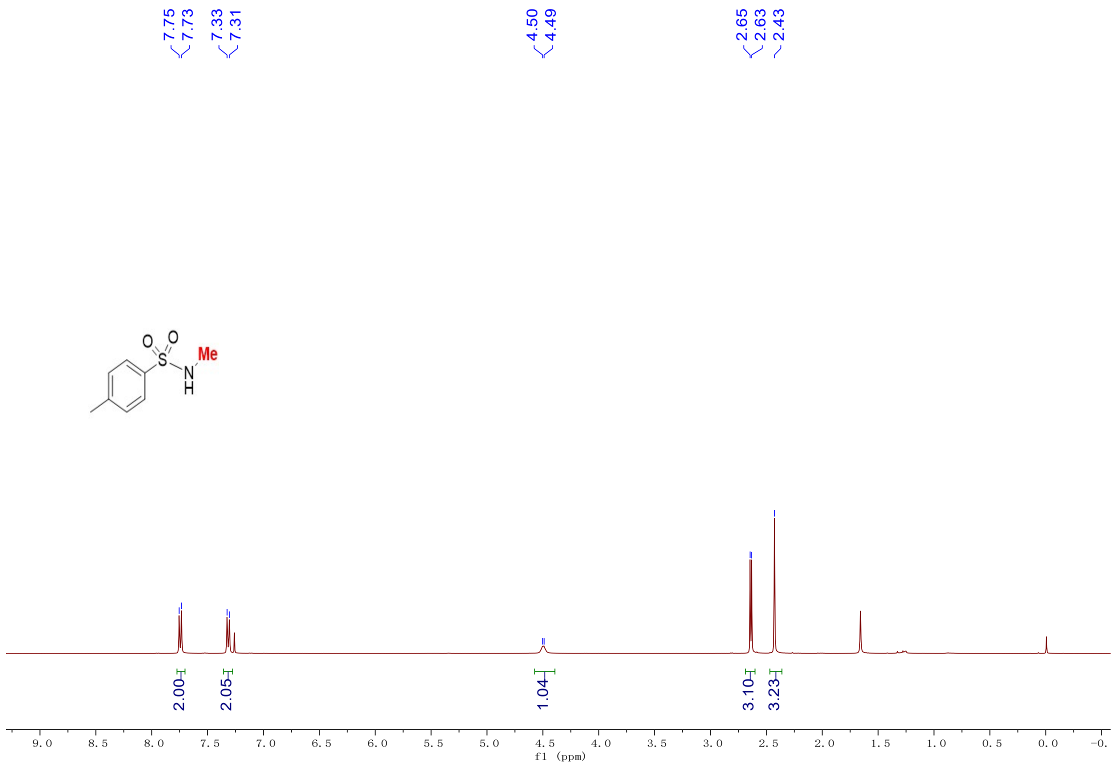

Figure S90: [1]H NMR (400 MHz, $CDCl_3$, 298 K) spectrum for 11x

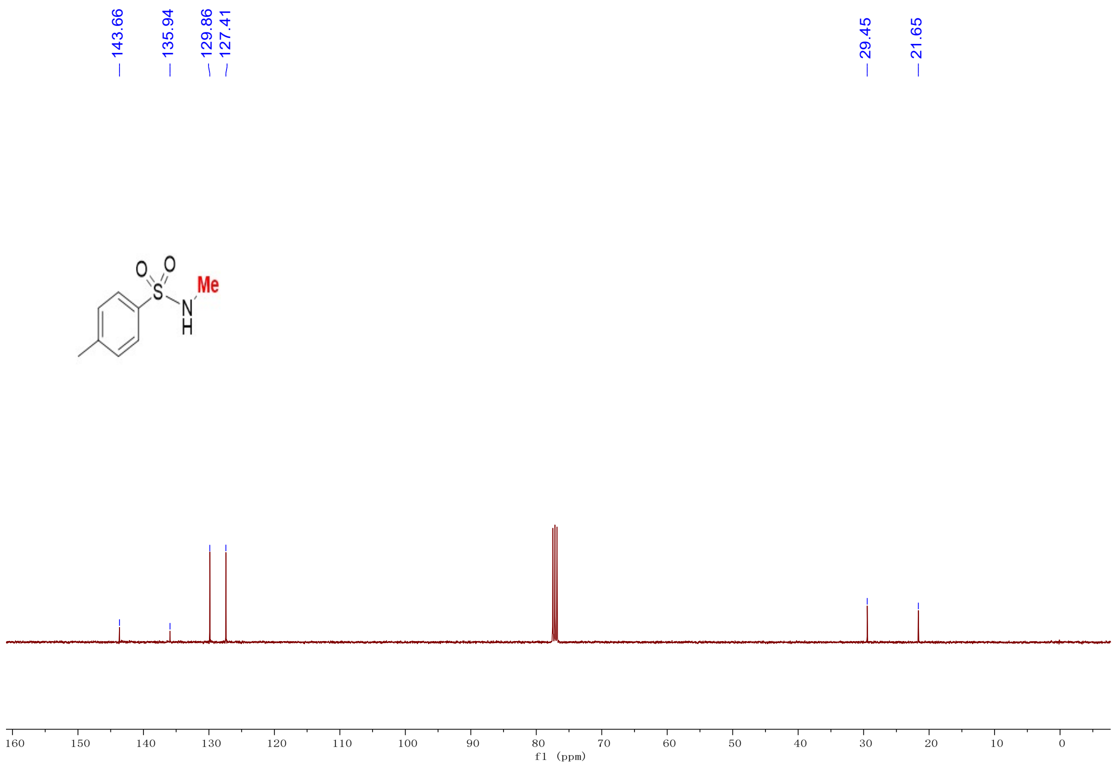

Figure S91: [13]C NMR (101 MHz, $CDCl_3$, 298 K) spectrum for 11x

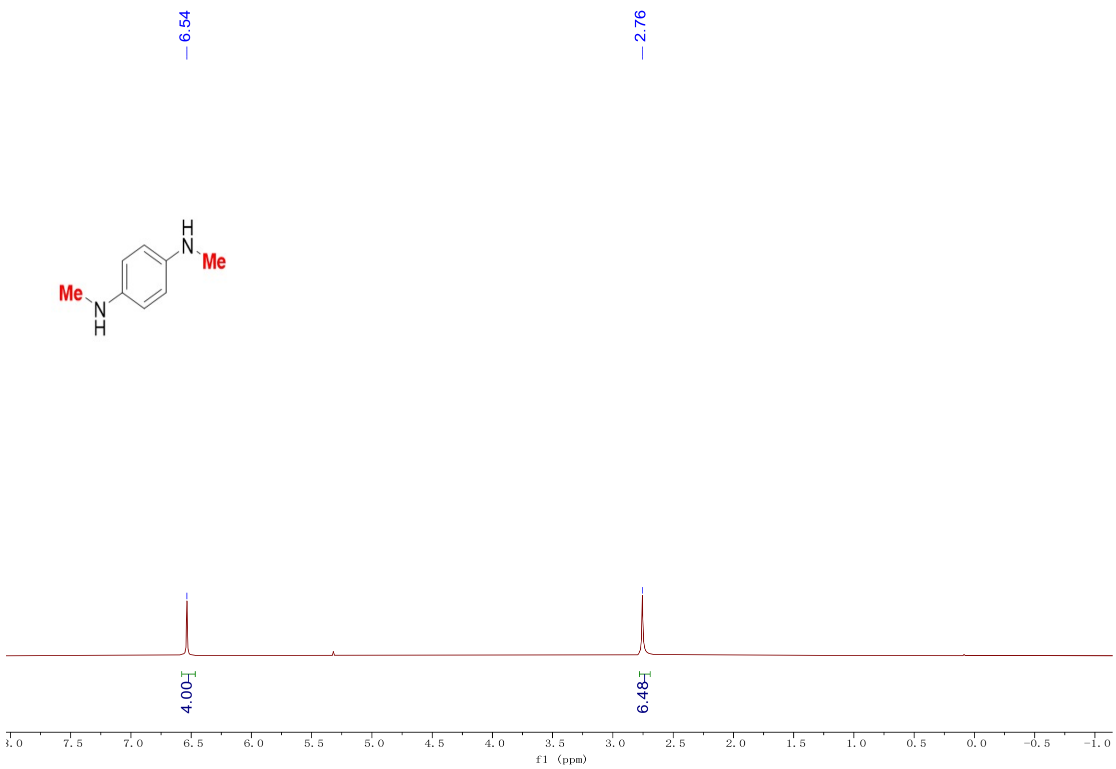

Figure S92: ^{1}H NMR (400 MHz, CD_2Cl_2, 298 K) spectrum for 11aa

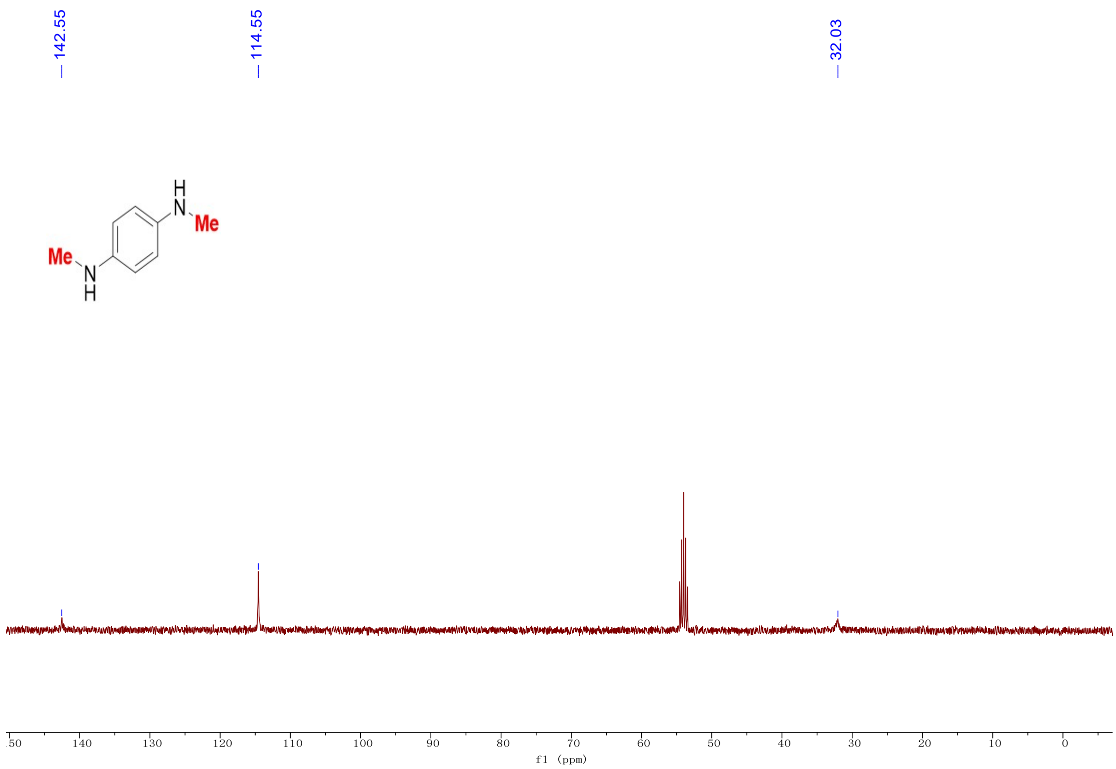

Figure S93: ^{13}C NMR (101 MHz, CD_2Cl_2, 298 K) spectrum for 11aa