Electronic Supplementary Material (ESI)

Ruthenium-Catalysed Chemoselective Alkylation of Nitroarenes with Alkanols

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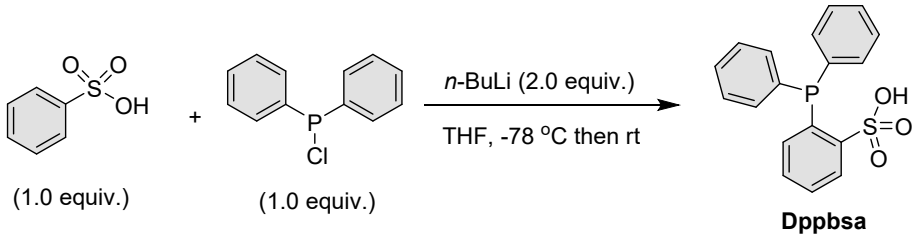
1. General information

All commercial reagents were purchased from Beijing Innochem Science & Technology co., LTD without further purification, and were used without further purification unless otherwise stated. Iso-Propyl-d_7 Alcohol ($(CD_3)_2CDOH$) (99% (isotopic)) was purchased from CDN isotopes. 2-Propanol-d_8 (99%(Isotopic)) was purchased from Alfa Aesar. Toluene was dried and distilled under argon prior to use. All reaction vials were purchased from Beijing Synthware Glass. All catalytic reactions were carried out in 25 mL autoclaves (Tokyo Rikakikai Co., LTD (PPM-5512)). The autoclaves were made from stainless steel and an insert (Teflon) was also used to avoid cross-contaminations with metals from previous runs in the autoclave. ESI-MS analysis was performed on a Bruker time of flight mass spectrometer micro TOF-Q II using an electrospray ionization (ESI) source. NMR spectra were recorded on a Bruker ASCEND spectrometer (^{1}H, 600 MHz; ^{13}C{^{1}H}, 151 MHz; ^{31}P, 243 MHz). ^{1}H NMR, ^{13}C NMR and ^{31}P NMR, chemical shift δ is given relative to TMS and referenced to the solvent signal. Chemical shifts were reported in ppm with the internal TMS signal at 0.0 ppm as a standard. The spectra are interpreted as: s = singlet, d = doublet, t = triplet, m = multiplet, dd = doublet of doublets, dt = doublet of triplets, ddd = doublet of doublet of doublets, coupling constants (*J*) are reported in Hz and relative integrations are reported. Column chromatography was performed using silica gel. Analytical TLC was done using pre-coated silica gel 60 F254 plates. GC analysis was performed using Aglient GC-7890B equipped with a capillary column (DB-FFAP, 30 m × 0.32 mm) using a flame ionization detector. GC-MS was performed using GCMS-QP2020 with Rtx-5MS (30 m × 0.25 mm) column.

2 Synthesis of ligand and catalysts

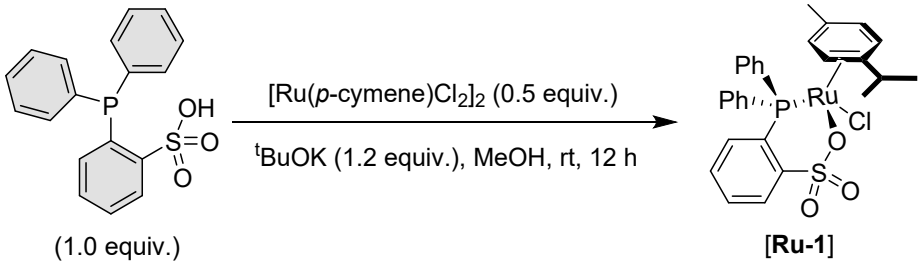
2.1 Synthesis of 2-(diphenylphosphaneyl)benzenesulfonic acid (**Dppbsa**).[1-7]



Scheme S1. Synthesis of ligand (**Dppbsa**)

Under protection of argon, dry benzenesulfonic acid (1.580 g, 10 mmol) and THF (30 mL) were added in a 100 mL Schlenk tube equipped with a Teflon stopcock and a magnetic stirring bar. *n*-BuLi (*2.5 M solution in hexane, 8.0 mL, 20 mmol*) was added dropwise to the mixture at -78 °C over 10 min. The mixture was stirring at 25 °C for 45 minutes and then cooled at -78 °C. a solution of bis(phenyl)chlorophosphane (2.200 g, 10 mmol) in THF (10 mL) was added at -78 °C over 30 min. After stirring for 12 h at room temperature, the solvent was removed in vacuo to leave a white solid. The solid was dissolved in dichloromethane (40 mL) and extracted with acidic water (2 mL of concentrated HCl in 30 mL of water), and then twice with degassed water (30 mL). The organic layers were dried over $MgSO_4$ evaporated under vacuum to yield a pale white solid. The solid was recrystallized from dichloromethane/n-hexane followed by concentration under vacuum to afford a white powder in 65% yield. **^{1}H NMR** (600 MHz, 298K, $CDCl_3$): δ = 8.39 (m, 1H), 7.80 (m, 1H), 7.73 (m, 2H), 7.66 (m, 2H), 7.64 (m, 2H), 7.59 (m, 4H), 7.49 (m, 1H), 7.25 (m, 1H), N.O. (-SO_3H). **^{13}C{^{1}H} NMR** (151 MHz, 298K, $CDCl_3$): δ = 152.9 (J_{PC} = 8.9 Hz, *i*-Ph-SO_3H), 135.5 (J_{PC} = 3.2 Hz, *i*-Ph), 134.6 (J_{PC} = 3.0 Hz, 2×*i*-Ph), 134.5, 134.4, 134.0, 133.9, 130.2, 130.1(4), 130.1(1), 130.0(5), 129.4(2), 129.3(6), 119.1, 118.5, 113.7, 113.1 (Ph). **^{31}P{^{1}H} NMR** (243 MHz, 298K, $CDCl_3$): δ = 3.8. **HRMS** (ESI) m/z calcd for $C_{18}H_{15}O_3NaPS^+$ $(M+Na)^+$, 365.03717; Found: 365.0368.

2.2 Synthesis of Complexes Ru(dppbsa) ([**Ru-1**]).[1-7]



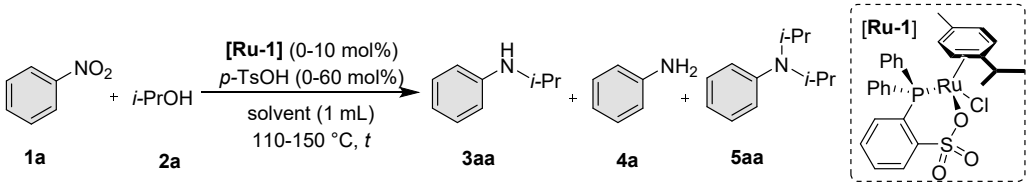
Scheme S2. Synthesis of Ru(dppbsa) ([**Ru-1**]).

Under protection of argon, 2-(diphenylphosphaneyl)benzenesulfonic acid (Dppbsa) (342 mg, 1.0 mmol, 1.0 equiv.) and t-BuOK (146.5 mg, 1.2 mmol, 1.2 equiv.) were added to a 25 mL Schlenk tube equipped with a magnetic stirring bar. Degassed MeOH (10 mL) was added and the solution was stirred for one hour at room temperature which generated white unclear solution. To this solution [Ru(*p*-cymene)Cl_2]$_2$ (307 mg, 0.5 mmol, 0.5 equiv.) was added. The red colored solution becomes slurry after 30min. After stirring for 12 h, MeOH was evaporated, and then the crude was dissolved in 30 ml of dichloromethane. The solution was filtered by diatomite to remove the inorganic salt. Then, the solvent was reduced to a minimum amount, and covering with hexane led to red crystals. Yield: 92%. **^{1}H NMR** (600 MHz, 298 K, $CDCl_3$): δ = 8.08 (m, 1H), 7.92 (m, 2H), 7.64 (m, 1H), 7.62 (m, 1H), 7.54 (m, 1H), 7.50 (m, 1H), 7.46 (m, 4H), 7.44 (m, 1H), 7.25 (m, 1H), 6.96 (m, 1H), 5.83 (d, $^3J_{HH}$ = 6.5 Hz, 1H), 5.78 (d, $^3J_{HH}$ = 6.5 Hz, 1H), 5.54 (d, $^3J_{HH}$ = 5.5 Hz, 1H), 5.44 (d, $^3J_{HH}$ = 5.5 Hz, 1H), 2.62 (sept, $^3J_{HH}$ = 6.8 Hz, $^3J_{HH}$ = 6.8 Hz, 1H), 1.89 (s, 3H, CH_3), 1.15 (d, $^3J_{HH}$ = 6.8 Hz, 3H), 0.94 (d, $^3J_{HH}$ = 6.8 Hz, 3H). **^{13}C{^{1}H} NMR** (151 MHz, 298K, $CDCl_3$): δ = 147.2 (J_{PC} = 12.8 Hz, *i*-Ph-SO_3Ru), 136.1 (J_{PC} = 9.8 Hz), 134.1 (J_{PC} = 9.8 Hz), 133.3, 133.0(0), 132.9(6), 131.8 (J_{PC} = 2.5 Hz), 131.5, 131.3 (J_{PC} = 2.0 Hz), 131.2, 131.0 (J_{PC} = 2.5 Hz), 129.9 (J_{PC} = 6.8 Hz), 128.7 (J_{PC} = 8.3 Hz), 128.5 (J_{PC} = 9.7 Hz), 128.4 (J_{PC} = 10.3 Hz), 128.2, 128.1, 108.0, 94.4, 92.9 (J_{PC} = 5.3 Hz), 87.3 (J_{PC} = 7.7 Hz), 85.6 (J_{PC} = 2.2 Hz), 83.9 (J_{PC} = 2.2 Hz), 30.2, 22.9, 20.5, 17.8. **^{31}P{^{1}H} NMR** (243 MHz, 298K, $CDCl_3$): δ = 22.9. **HRMS** (ESI) m/z calcd for $C_{28}H_{28}O_3PRuS^+$ $(M\text{-}Cl)^+$, 577.05403; Found: 577.0535.

3 Reaction condition optimization.

3.1 Ru(dppbsa) catalyzed alkylation of nitroarenes with secondary alkanols.

Table S1. Screening of the reaction conditions[a]



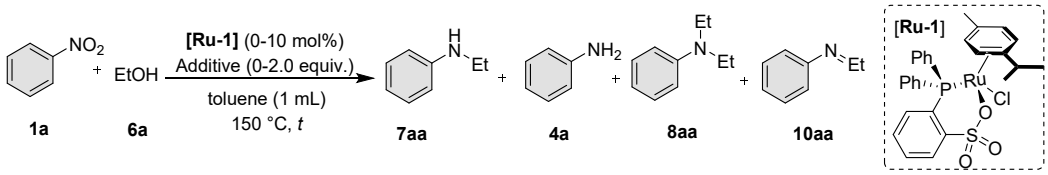
1a 2a 3aa 4a 5aa

Entry[a]	[Ru-1] (mol%)	*p*-TsOH (mol%)	Time (h)	Solvent	Temp. (°C)	Conv. (%)	Yield[b] (%)		
							3aa	**4aa**	**5aa**
1	3	(20)	20	toluene	150	33	30	3	0
2	3	(40)	20	toluene	150	75	48	27	0
3	3	(60)	20	toluene	150	95	48	47	0
4	5	(20)	20	toluene	150	100	92	0	6
5	10	(20)	20	toluene	150	100	97	0	2
6	5	(20)	20	anisole	150	85	78	2	trace
7	5	(20)	20	PhCl	150	89	58	21	7
8	5	(20)	20	DMF	150	95	80	6	8
9	-	(20)	20	toluene	150	0	0	0	0
10	5	-	20	toluene	150	100	90	5	2
11	5	-	16	toluene	150	100	89	4	2
12	**5**	**-**	**12**	**toluene**	**150**	**100**	**88/85**[c]	**3**	**2**
13	5	-	8	toluene	150	98	85	2	2
14	5	-	6	toluene	150	92	81	5	1
15	5	-	4	toluene	150	83	72	6	1
16	5	-	3	toluene	150	72	55	10	0
17	5	-	2	toluene	150	65	46	5	0
18	5	-	1	toluene	150	28	15	6	0
19	5	-	12	toluene	130	52	39	13	0
20	5	-	12	toluene	110	25	7	18	0
21[d]	5	-	12	toluene	150	100	14	76	0
22[e]	5	-	12	toluene	150	98	81	10	2
23[f]	5	-	12	toluene	150	100	6	70	trace
24[g]	5	-	12	toluene	150	100	7	72	trace
25[h]	5	-	12	toluene	150	100	85	5	trace

[a] Reaction condition: **1a** (0.2 mmol), **2a** (1 mL), **[Ru-1]** (0~10 mol%), *p*-TsOH (0~60 mol%), solvent (1 mL), at T °C for t h. [b] Conversions and yield were determined by GC analysis using biphenyl as the internal standard. [c] Isolated yield. [d] Na_2CO_3 (1 equiv.) was added in reaction. [e] Mercury (4 equiv.) was added in reaction. [f] Tempo. (0.2 equiv.) was added in reaction. [g] Tempo. (2 equiv.) was added in reaction. DMF = *N*,*N*-Dimethyl-formamide, PhCl = Chlorobenzene. [h] t-BuOH (1 mL) was added in reaction.

3.2 **Ru(dppbsa)** catalyzed Alkylation of nitroarenes with primary alkanols

Table S2. Screening of the reaction conditions[a]



Entry[a]	[Ru] (mol%)	Additive (equiv.)	EtOH (mL)	Time (h)	Conv. (%)	Yield[b] (%)			
						7aa	**10aa**	**4a**	**8aa**
1[d]	5	-	1.0	12	100	0	0	0	80
2[e]	5	*p*-TsOH (0.2)	1.0	12	99	0	0	0	66
3	5	-	0.5	12	98	0	0	0	90
4	5	-	0.25	12	45	0	0	0	34
5	5	Na_2CO_3 (0.2)	1.0	12	100	72	0	0	20
6	5	Na_2CO_3 (0.5)	1.0	12	100	82	0	0	14
7	5	Na_2CO_3 (1.0)	1.0	12	100	83	0	0	4
8	5	Na_2CO_3 (2.0)	1.0	12	100	85	0	0	4
9	5	Na_2CO_3 (1.0)	1.0	1	43	7	31	4	0
10	5	Na_2CO_3 (1.0)	1.0	2	65	30	32	3	0
11	5	Na_2CO_3 (1.0)	1.0	3	89	38	46	5	0
12	5	Na_2CO_3 (1.0)	1.0	4	100	60	31	5	0
13	5	Na_2CO_3 (1.0)	1.0	8	100	81	0	5	2
14	5	Na_2CO_3 (1.0)	1.0	16	100	85	0	0	4
15	5	Na_2CO_3 (1.0)	1.0	20	100	88	0	0	6
16	**5**	**Na_2CO_3 (1.0)**	**1.0**	**24**	**100**	**93 (85[c])**	**0**	**0**	**6**
17	5	K_2CO_3 (1.0)	1.0	24	99	68	13	0	5
18	5	Cs_2CO_3 (1.0)	1.0	24	99	17	20	34	10
19	5	DBU (1.0)	1.0	24	96	37	0	12	42
20	5	KO^{t}Bu (1.0)	1.0	24	97	48	15	5	24
21	5	NaOH (1.0)	1.0	24	99	71	0	10	3
22	5	KOH (1.0)	1.0	24	99	63	0	5	16
23	-	Na_2CO_3 (1.0)	1.0	24	12	0	0	0	0

[a] Reaction condition: **1a** (0.2 mmol), **6a** (1 mL), **[Ru-1]** (0~10 mol%), Aditive (0~2.0 equiv.), toluene (1 mL), at 150 °C for t h. [b] Conversions and yield were determined by GC analysis using biphenyl as the internal standard. [c] Isolated yield. [d] 15% GC yield of the **8aa** of the phenyl group replaced by the ethyl group. [e] 30% GC yield of the **8aa** of the phenyl group replaced by the ethyl group. DBU = 1,8-Diazabicyclo[5.4.0]-undec-7-ene.

4 General procedure for alkylation of nitroarenes with alkanols

Under protection of argon, Nitroarenes **1** or secondary amine **7** (0.2 mmol, 1.0 equiv.), alcohol **2** or **6** (1 mL) and Ru(dppbsa) ([**Ru-1**]) (5 mol%) were charged in a 25 mL autoclave with magnetic bar. Then 1 mL of toluene was added into the mixture. The mixture was stirred at the desired temperature (150 °C) for a certain time. After the desired reaction time, the reaction mixture was allowed to cool to room temperature. The distribution of the product was determined by GC and GC-MS analysis using biphenyl as an internal standard. The solvent was removed under vacuum and then the product was purified by column chromatography and the product was analyzed by NMR spectroscopy.

Figure S1. 25-mL autoclaves (Tokyo Rikakikai Co., LTD (PPM-5512))

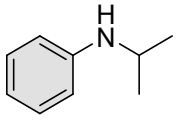
5 General procedure for monoalkylation of nitroarenes with alkanols

Under protection of argon, Nitroarenes **1** (0.2 mmol, 1.0 equiv.), primary alcohol **6** (1 mL), Na_2CO_3 (1.0 equiv.) and Ru(dppbsa) ([**Ru-1**]) (5 mol%) were charged in a 25 mL autoclave with magnetic bar. Then 1 mL of toluene was added into the mixture. The mixture was stirred at the desired temperature (150 °C) for a certain time. After the desired reaction time, the reaction mixture was allowed to cool to room temperature.

The distribution of the product was determined by GC and GC-MS analysis using biphenyl as an internal standard. The solvent was removed under vacuum and then the product was purified by column chromatography and the product was analyzed by NMR spectroscopy.

6 The characterization data of products

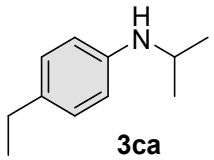
N-isopropylaniline **(3aa)**



3aa

Isolated yield: 85%, (petroleum ether/ethyl acetate = 50:1); Yellow oil; ^{1}H NMR (600 MHz, $CDCl_3$, 298 K): δ = 7.21 (m, 2H), 6.72 (t, $^{3}J_{HH}$ = 7.2 Hz, 1H), 6.63 (d, $^{3}J_{HH}$ = 8.4 Hz, 2H), 3.67 (m, 1H), 3.46 (br. s, 1H), 1.25 (d, $^{3}J_{HH}$ = 6.6 Hz, 6H). ^{13}C{^{1}H} NMR (151 MHz, $CDCl_3$, 298 K): δ = 147.6, 129.4 (2C), 117.1, 113.3 (2C), 44.3, 23.1 (2C). HRMS (ESI) m/z calcd for $C_9H_{14}N^+$ $(M+H)^+$: 136.1121; found: 136.1118.

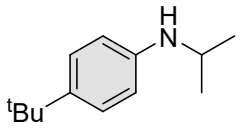
4-ethyl-N-isopropylaniline **(3ca)**



3ca

Isolated yield: 90%, (petroleum ether/ethyl acetate = 50:1); Yellow oil; ^{1}H NMR (600 MHz, $CDCl_3$, 298 K): δ = 7.08 (d, 3JHH = 8.4 Hz, 2H), 6.61 (m, 2H), 3.67 (m, 1H), 3.29 (br. s, 1H), 2.62 (m, 2H), 1.27 (m, 9H). ^{13}C{^{1}H} NMR (151 MHz, $CDCl_3$, 298 K): δ = 145.5, 132.9, 128.6 (2C), 113.5 (2C), 44.5, 28.0, 23.1 (2C), 16.0. HRMS (ESI) m/z calcd for $C_{11}H_{18}N^+$ $(M+H)^+$: 164.1434; found: 164.1404.

4-(tert-butyl)-N-isopropylaniline (**3da**)

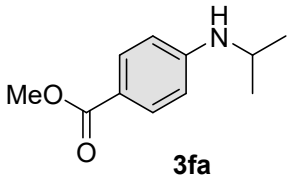


3da

Isolated yield: 90%, (petroleum ether/ethyl acetate = 100:1); Yellow oil; ^{1}H NMR (600 MHz, $CDCl_3$, 298 K): δ = 7.21 (d, $^{3}J_{HH}$ = 8.4 Hz, 2H), 6.56 (d, $^{3}J_{HH}$ = 9.0 Hz, 2H), 3.62 (m, 1H), 3.37 (br. s, 1H), 1.30 (s, 9H), 1.22 (d, $^{3}J_{HH}$ = 6.0 Hz, 6H). ^{13}C{^{1}H} NMR (151 MHz, $CDCl_3$, 298 K): δ = 145.3, 139.8, 126.1 (2C), 113.0 (2C), 44.50, 33.93, 31.70

(3C), 23.32 (2C). HRMS (ESI) m/z calcd for $C_{13}H_{22}N^+$ $(M+H)^+$: 192.1747; found: 192.1739.

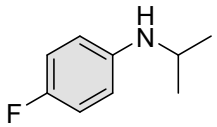
methyl 4-(isopropylamino)benzoate (**3fa**)



3fa

Isolated yield: 87%, (petroleum ether/ethyl acetate = 30:1); Yellow solid; ^{1}H NMR (600 MHz, $CDCl_3$, 298 K): δ = 7.85 (m, 2H), 6.52 (d, $^3J_{HH}$ = 9.0 Hz, 2H), 4.09 (br. s, 1H), 3.84 (s, 3H), 3.69 (m, 1H), 1.23 (d, $^3J_{HH}$ = 6.6 Hz, 6H). ^{13}C{^{1}H} NMR (151 MHz, $CDCl_3$, 298 K): δ = 167.5, 151.2, 131.7 (2C), 117.9, 111.8 (2C), 51.6, 44.1, 22.8 (2C). HRMS (ESI) m/z calcd for $C_{11}H_{16}NO_2^+$ $(M+H)^+$: 194.1176; found: 194.1174.

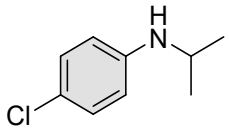
4-fluoro-N-isopropylaniline (**3ha**)



3ha

Isolated yield: 75%, (petroleum ether/ethyl acetate = 50:1); Yellow oil; ^{1}H NMR (600 MHz, $CDCl_3$, 298 K): δ = 6.88 (m, 2H), 6.52 (d, $^3J_{HH}$ = 9.0 Hz, 2H), 3.56 (s, 1H), 3.29 (br. s, 1H), 1.20 (d, $^3J_{HH}$ = 6.6 Hz, 6H). ^{13}C{^{1}H} NMR (151 MHz, $CDCl_3$, 298 K): δ = 155.70, 144.0, 115.7 (2C), 114.3 (2C), 45.1, 23.1(2C). HRMS (ESI) m/z calcd for $C_9H_{13}FN^+$ $(M+H)^+$: 154.1027; found: 154.1024.

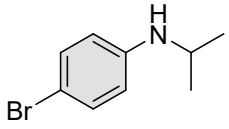
4-chloro-N-isopropylaniline (**3ia**)



3ia

Isolated yield: 70%, (petroleum ether/ethyl acetate = 50:1); Yellow oil; ^{1}H NMR (600 MHz, $CDCl_3$, 298 K): δ = 7.11 (m, 2H), 6.51 (m, 2H), 3.58 (s, 1H), 3.50 (br. s, 1H), 1.20 (d, $^3J_{HH}$ = 6.6 Hz, 6H). ^{13}C{^{1}H} NMR (151 MHz, $CDCl_3$, 298 K): δ = 146.1, 129.2 (2C), 121.6, 114.4 (2C), 44.6, 22.9 (2C). HRMS (ESI) m/z calcd for $C_9H_{13}ClN^+$ $(M+H)^+$: 170.0731; found: 170.0730.

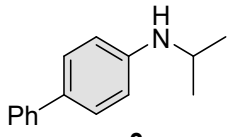
4-bromo-N-isopropylaniline (**3ja**)



3ja

Isolated yield: 78%, (petroleum ether/ethyl acetate = 50:1); Yellow oil; ^{1}H NMR (600 MHz, $CDCl_3$, 298 K): δ = 7.24 (m, 2H), 6.46 (m, 2H), 3.58 (s, 1H), 3.52 (br. s, 1H), 1.20 (d, $^{3}J_{HH}$ = 6.6 Hz, 6H). ^{13}C{^{1}H} NMR (151 MHz, $CDCl_3$, 298 K): δ = 146.5, 132.0 (2C), 114.9 (2C), 108.5, 44.5, 22.9 (2C). HRMS (ESI) m/z calcd for $C_9H_{13}BrN^+$ $(M+H)^+$: 214.0226; found: 214.0224.

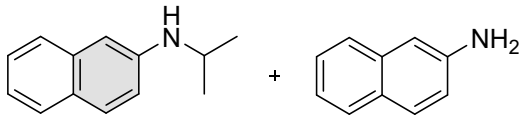
N-isopropyl-[1,1'-biphenyl]-4-amine (**3qa**)



3qa

Isolated yield: 87%, (petroleum ether/ethyl acetate = 20:1); Yellow solid; ^{1}H NMR (600 MHz, $CDCl_3$, 298 K): δ = 7.53 (m, 2H), 7.43 (m, 2H), 7.38 (m, 2H), 7.25 (m, 1H), 6.66 (m, 2H), 3.67 (s, 1H), 3.64 (br. s, 1H), 1.24 (d, $^{3}J_{HH}$ = 6.0 Hz, 6H). ^{13}C{^{1}H} NMR (151 MHz, $CDCl_3$, 298 K): δ = 146.9, 141.4, 130.0, 128.7 (2C), 128.1 (2C), 126.4 (2C), 126.1, 113.5 (2C), 44.5, 23.25 (2C). HRMS (ESI) m/z calcd for $C_{15}H_{18}N^+$ $(M+H)^+$: 212.1434; found: 212.1428.

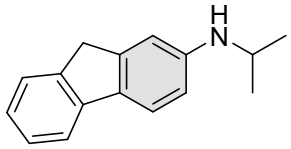
N-isopropylnaphthalen-2-amine (**3ra**)



3ra

Isolated yield: 75%, (petroleum ether/ethyl acetate = 50:1); Yellow solid; ^{1}H NMR (600 MHz, $CDCl_3$, 298 K): δ = 7.84 (m, 1H), 7.57 (d, $^{3}J_{HH}$ = 8.4 Hz, 1H), 7.52 (m, 2H), 7.26 (t, $^{3}J_{HH}$ = 8.4 Hz, 1H), 7.09 (t, $^{3}J_{HH}$ = 8.4 Hz, 1H), 6.73 (s, 1H), 3.67 (m, 1H), 3.64 (br. s, 1H), 1.19 (d, $^{3}J_{HH}$ = 6.0 Hz, 6H). ^{13}C{^{1}H} NMR (151 MHz, $CDCl_3$, 298 K): δ = 145.6, 145.0, 135.9, 135.3, 132.0, 130.1, 129.8, 129.6, 129.0, 128.1, 128.0, 127.7, 127.4, 126.3, 125.9, 124.7, 121.9, 119.4, 118.4, 105.2, 44.5, 22.9 (2C). HRMS (ESI) m/z calcd for $C_{13}H_{16}N^+$ $(M+H)^+$: 186.1277; found: 186.1268.

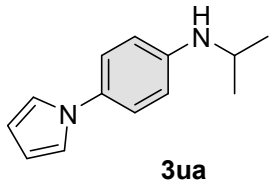
N-isopropyl-9H-fluoren-2-amine (**3sa**)



3sa

Isolated yield: 93%, (petroleum ether/ethyl acetate = 30:1); White solid; ^{1}H NMR (600 MHz, $CDCl_3$, 298 K): δ = 7.64 (d, $^{3}J_{HH}$ = 7.2 Hz, 1H), 7.59 (d, $^{3}J_{HH}$ = 7.8 Hz, 1H), 7.48 (d, $^{3}J_{HH}$ = 7.2 Hz, 1H), 7.33 (t, $^{3}J_{HH}$ = 7.2 Hz, 1H), 7.19 (t, $^{3}J_{HH}$ = 7.2 Hz, 1H), 6.80 (s, 1H), 6.64 (dd, $^{3}J_{HH}$ = 8.4, 1.8 Hz, 1H), 3.83 (s, 2H), 3.72 (m, 1H), 3.57 (br. s, 1H), 1.27 (d, $^{3}J_{HH}$ = 6.6 Hz, 6H). ^{13}C{^{1}H} NMR (151 MHz, $CDCl_3$, 298 K): δ = 147.1, 145.3, 142.5, 142.3, 131.8, 126.7, 124.8, 124.8, 120.8, 118.5, 112.7, 109.8, 44.7, 37.1, 23.2 (2C). HRMS (ESI) m/z calcd for $C_{16}H_{18}N^+$ $(M+H)^+$: 224.1434; found: 224.1410.

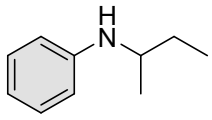
N-isopropyl-4-(1H-pyrrol-1-yl)aniline (**3ua**)



3ua

Isolated yield: 85%, (petroleum ether/ethyl acetate = 30:1); White solid; ^{1}H NMR (600 MHz, $CDCl_3$, 298 K): δ = 7.21 (m, 2H), 6.98 (d, $^{3}J_{HH}$ = 2.4 Hz, 2H), 6.63 (m, 2H), 6.31 (d, $^{3}J_{HH}$ = 1.8 Hz, 2H), 3.65 (m, 1H), 3.62 (br. s, 1H), 1.25 (d, $^{3}J_{HH}$ = 6.0 Hz, 6H). ^{13}C{^{1}H} NMR (151 MHz, $CDCl_3$, 298 K): δ = 145.8, 131.7, 122.6 (2C), 119.9 (2C), 113.8, 109.3, 44.7, 23.0 (2C). HRMS (ESI) m/z calcd for $C_{13}H_{17}N_2^+$ $(M+H)^+$: 201.1386; found: 201.1378.

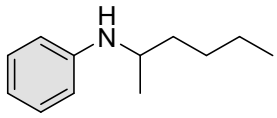
N-(sec-butyl)aniline (**3ab**)



3ab

Isolated yield: 87%, (petroleum ether/ethyl acetate = 100:1); Yellow oil; ^{1}H NMR (600 MHz, $CDCl_3$, 298 K): δ = 7.29 (m, 1H), 7.18 (m, 2H), 6.71 (m, 1H), 6.61 (m, 1H), 1.95 (m, 1H), 3.62 (br. s, 1H), 1.56 (s, 2H), 1.26 (s, 6H). ^{13}C{^{1}H} NMR (151 MHz, $CDCl_3$, 298 K): δ = 141.7, 129.4, 128.5, 126.1, 43.8, 33.4, 31.1, 29.8. HRMS (ESI) m/z calcd for $C_{10}H_{16}N^+$ $(M+H)^+$: 150.1277; found: 150.1254.

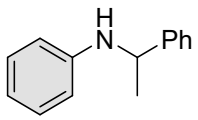
N-(hexan-2-yl)aniline (**3ac**)



3ac

Isolated yield: 89%, (petroleum ether/ethyl acetate = 50:1); Yellow oil; ^{1}H NMR (600 MHz, $CDCl_3$, 298 K): δ = 7.08 (m, 2H), 6.59 (t, $^{3}J_{HH}$ = 7.2 Hz, 1H), 6.51 (d, $^{3}J_{HH}$ = 7.8 Hz, 2H), 3.51 (br. s, 1H), 3.37 (m, 1H), 1.50 (m, 1H), 1.35 (m, 2H), 1.27 (m, 4H), 1.10 (d, $^{3}J_{HH}$ = 6.6 Hz, 3H), 0.83 (t, $^{3}J_{HH}$ = 7.2 Hz, 3H). ^{13}C{^{1}H} NMR (151 MHz, $CDCl_3$, 298 K): δ = 147.7, 129.4 (2C), 117.0, 113.3 (2C), 48.7, 37.0, 28.5, 22.9, 20.9, 14.2. HRMS (ESI) m/z calcd for $C_{12}H_{20}N^+$ $(M+H)^+$: 178.1590; found: 178.1560.

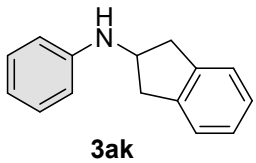
N-(1-phenylethyl)aniline (**3ag**)



3ag

Isolated yield: 85%, (petroleum ether/ethyl acetate = 50:1); Yellow solid; ^{1}H NMR (600 MHz, $CDCl_3$, 298 K): δ = 7.29 (m, 2H), 7.24 (t, $^{3}J_{HH}$ = 7.2 Hz, 2H), 7.15 (m, 1H), 7.01 (m, 2H), 4.42 (m, 1H), 4.10 (br. s, 1H), 1.44 (d, $^{3}J_{HH}$ = 6.6 Hz, 3H), 0.83 (t, $^{3}J_{HH}$ = 7.2 Hz, 3H). ^{13}C{^{1}H} NMR (151 MHz, $CDCl_3$, 298 K): δ = 147.2, 145.2, 129.2, 128.7, 127.0, 126.0, 117.5, 113.6, 53.7, 25.0. HRMS (ESI) m/z calcd for $C_{14}H_{16}N^{+}$ $(M+H)^{+}$: 198.1277; found: 198.1258.

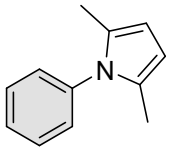
N-phenyl-2,3-dihydro-1*H*-inden-2-amine (**3ak**)



3ak

Isolated yield: 90%, (petroleum ether/ethyl acetate = 50:1); Yellow solid; ^{1}H NMR (600 MHz, $CDCl_3$, 298 K): δ = 7.15 (m, 2H), 7.10 (m, 4H), 6.65 (t, $^{3}J_{HH}$ = 7.2 Hz, 1H), 6.57 (d, $^{3}J_{HH}$ = 7.8 Hz, 2H), 4.27 (m, 1H), 3.94 (br. s, 1H), 3.28 (dd, $^{3}J_{HH}$ = 16.0, 7.8 Hz, 2H), 2.81 (dd, $^{3}J_{HH}$ = 16.0, 4.2 Hz, 2H). ^{13}C{^{1}H} NMR (151 MHz, $CDCl_3$, 298 K): δ = 147.3, 141.5, 129.4, 126.7, 125.0, 117.7, 113.6, 54.2, 40.3 (2C). HRMS (ESI) m/z calcd for $C_{15}H_{16}N^{+}$ $(M+H)^{+}$: 210.1277; found: 210.1260.

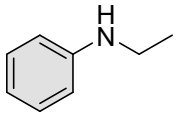
2,5-dimethyl-1-phenyl-1H-pyrrole (**3an**)



3an

Isolated yield: 80%, (petroleum ether/ethyl acetate = 20:1); Yellow oil; ^{1}H NMR (600 MHz, $CDCl_3$, 298 K): δ = 7.46 (t, $^{3}J_{HH}$ = 7.8 Hz, 2H), 7.40 (m, 1H), 7.22 (d, $^{3}J_{HH}$ = 7.2 Hz, 2H), 5.90 (s, 2H), 2.04 (s, 6H). ^{13}C{^{1}H} NMR (151 MHz, $CDCl_3$, 298 K): δ = 139.1, 129.1 (2C), 128.9 (2C), 128.3 (2C), 127.7, 105.7 (2C), 13.2 (2C). HRMS (ESI) m/z calcd for $C_{12}H_{14}N^{+}$ $(M+H)^{+}$: 172.1121; found: 172.1106.

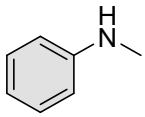
N-ethylaniline (**7aa**)



7aa

Isolated yield: 85%, (petroleum ether/ethyl acetate = 100:1); Yellow oil; ^{1}H NMR (600 MHz, $CDCl_3$, 298 K): δ = 7.22 (m, 2H), 6.75 (t, $^{3}J_{HH}$ = 7.2 Hz, 1H), 6.65 (m, 2H), 3.56 (br. s, 1H), 3.19 (q, $^{3}J_{HH}$ = 15.2, 7.2 Hz, 2H), 1.29 (t, $^{3}J_{HH}$ = 7.2 Hz, 3H). ^{13}C{^{1}H} NMR (151 MHz, $CDCl_3$, 298 K): δ = 148.5, 129.3 (2C), 117.3, 112.8 (2C), 38.6, 14.9. HRMS (ESI) m/z calcd for $C_{8}H_{12}N^{+}$ $(M+H)^{+}$: 122.0964; found: 122.0948.

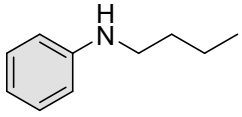
N-methylaniline (**7ab**)



7ab

Isolated yield: 80%, (petroleum ether/ethyl acetate = 50:1); Yellow oil; ^{1}H NMR (600 MHz, $CDCl_3$, 298 K): δ = 7.18 (m, 2H), 6.67 (t, $^{3}J_{HH}$ = 7.2 Hz, 1H), 6.66 (m, 2H), 3.60 (br. s, 1H), 2.80 (s, 3H). $^{13}C\{^{1}H\}$ NMR (151 MHz, $CDCl_3$, 298 K): δ = 149.4, 129.2 (2C), 117.3, 112.5 (2C), 30.85. HRMS (ESI) m/z calcd for $C_7H_{10}N^+$ $(M+H)^+$: 108.0808; found: 108.0724.

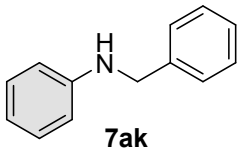
N-butylaniline (**7ac**)



7ac

Isolated yield: 90%, (petroleum ether/ethyl acetate = 30:1); Yellow oil; ^{1}H NMR (600 MHz, $CDCl_3$, 298 K): δ = 7.19 (dd, $^{3}J_{HH}$ = 7.2 Hz, 2H), 6.71 (t, $^{3}J_{HH}$ = 7.8 Hz, 1H), 6.63 (d, $^{3}J_{HH}$ = 7.8 Hz, 2H), 3.63 (br. s, 1H), 3.13 (t, $^{3}J_{HH}$ = 7.2 Hz, 2H), 1.62 (m, 2H), 1.45 (m, 2H), 0.98 (t, $^{3}J_{HH}$ = 7.2 Hz, 3H). $^{13}C\{^{1}H\}$ NMR (151 MHz, $CDCl_3$, 298 K): δ = 148.6, 129.3 (2C), 117.2, 112.8 (2C), 43.8, 31.8, 20.4, 14.0. HRMS (ESI) m/z calcd for $C_{10}H_{16}N^+$ $(M+H)^+$: 150.1277; found: 150.1268.

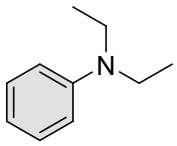
N-benzylaniline (**7ak**)



7ak

Isolated yield: 80%, (petroleum ether/ethyl acetate = 20:1); Yellow solid; ^{1}H NMR (600 MHz, $CDCl_3$, 298 K): δ = 7.37 (m, 4H), 7.29 (t, $^{3}J_{HH}$ = 7.1 Hz, 1H), 7.19 (m, 2H), 6.73 (t, $^{3}J_{HH}$ = 7.2 Hz, 1H), 6.66 (m, 2H), 4.34 (s, 2H), 4.12 (br. s, 1H). $^{13}C\{^{1}H\}$ NMR (151 MHz, $CDCl_3$, 298 K): δ = 148.2, 139.5, 129.4 (2C), 128.8 (2C), 127.7 (2C), 127.3, 117.7, 113.0 (2C), 48.5. HRMS (ESI) m/z calcd for $C_{13}H_{14}N^+$ $(M+H)^+$: 184.1121; found: 184.1118.

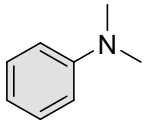
N,N-diethylaniline (**8aa**)



8aa

Isolated yield: 92%, (petroleum ether/ethyl acetate = 100:1); Yellow oil; ^{1}H NMR (600 MHz, $CDCl_3$, 298 K): δ = 7.30 (m, 2H), 6.78 (t, $^{3}J_{HH}$ = 8.4 Hz, 2H), 6.73 (t, $^{3}J_{HH}$ = 7.2 Hz, 1H), 3.43 (q, $^{3}J_{HH}$ = 7.2 Hz, 4H), 1.24 (t, $^{3}J_{HH}$ = 7.2 Hz, 6H). $^{13}C\{^{1}H\}$ NMR (151 MHz, $CDCl_3$, 298 K): δ = 147.9, 129.3 (2C), 115.4, 111.9 (2C), 44.4 (2C), 12.6 (2C). HRMS (ESI) m/z calcd for $C_{10}H_{16}N^+$ $(M+H)^+$: 150.1277; found: 150.1268.

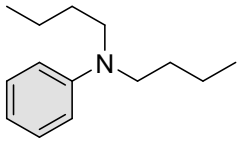
N,N-dimethylaniline (**8ab**)



8ab

Isolated yield: 85%, (petroleum ether/ethyl acetate = 50:1); Yellow oil; ^{1}H NMR (600 MHz, $CDCl_3$, 298 K): δ = 7.29 (m, 2H), 6.78 (m, 3H), 2.99 (s, 6H). $^{13}C\{^{1}H\}$ NMR (151 MHz, $CDCl_3$, 298 K): δ = 150.7, 129.1 (2C), 116.7, 112.7 (2C), 40.7 (2C). HRMS (ESI) m/z calcd for $C_8H_{12}N^+$ $(M+H)^+$: 122.0964; found: 122.0948.

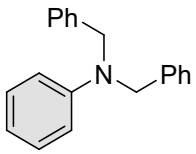
N,N-dibutylaniline (**8ac**)



8ac

Isolated yield: 90%, (petroleum ether/ethyl acetate = 100:1); Yellow oil; ^{1}H NMR (600 MHz, $CDCl_3$, 298 K): δ = 7.21 (m, 2H), 6.66 (d, $^{3}J_{HH}$ = 8.4 Hz, 2H), 6.63 (t, $^{3}J_{HH}$ = 7.2 Hz, 1H), 3.72 (t, $^{3}J_{HH}$ = 7.8 Hz, 4H), 1.58 (m, 4H), 1.37 (m, 4H), 0.97 (t, $^{3}J_{HH}$ = 7.2 Hz, 6H). $^{13}C\{^{1}H\}$ NMR (151 MHz, $CDCl_3$, 298 K): δ = 148.3, 129.3 (2C), 115.2, 111.8 (2C), 50.9 (2C), 29.6 (2C), 20.5 (2C), 14.1 (2C). HRMS (ESI) m/z calcd for $C_{14}H_{24}N^+$ $(M+H)^+$: 206.1903; found: 206.1895.

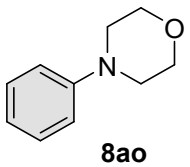
N,N-dibenzylaniline (**8ak**)



8ak

Isolated yield: 82%, (petroleum ether/ethyl acetate = 20:1); Yellow solid; ^{1}H NMR (600 MHz, $CDCl_3$, 298 K): δ = 7.31 (m, 4H), 7.24 (m, 6H), 7.16 (m, 2H), 6.74 (d, $^{3}J_{HH}$ = 8.4 Hz, 2H), 6.70 (t, $^{3}J_{HH}$ = 7.03 Hz, 1H), 4.65 (s, 4H). $^{13}C\{^{1}H\}$ NMR (151 MHz, $CDCl_3$, 298 K): δ = 149.3, 138.7, 129.3 (4C), 128.7 (4C), 127.0 (2C), 126.8 (2C), 116.8, 112.6, 54.3 (2C). HRMS (ESI) m/z calcd for $C_{20}H_{20}N^+$ $(M+H)^+$: 274.1590; found: 274.1582.

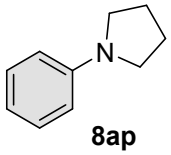
4-phenylmorpholine (**8ao**)



8ao

Isolated yield: 85%, (petroleum ether/ethyl acetate = 30:1); Yellow solid; ^{1}H NMR (600 MHz, $CDCl_3$, 298 K): δ = 7.29 (t, $^{3}J_{HH}$ = 7.8 Hz, 2H), 6.94 (m, 2H), 6.90 (m, 1H), 3.88(m, 4H), 3.17 (m, 4H). $^{13}C\{^{1}H\}$ NMR (151 MHz, $CDCl_3$, 298 K): δ = 151.4, 129.3 (2C), 120.2, 115.9 (2C), 67.0 (2C), 49.5 (2C). HRMS (ESI) m/z calcd for $C_{10}H_{14}NO^+$ $(M+H)^+$: 164.1070; found: 164.1046.

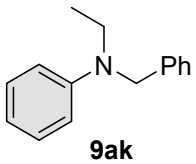
1-phenylpyrrolidine (**8ap**)



8ap

Isolated yield: 89%, (petroleum ether/ethyl acetate = 50:1); Yellow oil; ^{1}H NMR (600 MHz, $CDCl_3$, 298 K): δ = 7.29 (t, $^{3}J_{HH}$ = 7.8 Hz, 2H), 6.72 (t, $^{3}J_{HH}$ = 7.2 Hz, 1H), 6.63 (d, $^{3}J_{HH}$ = 8.4 Hz, 2H), 3.34(m, 4H), 2.05 (m, 4H). $^{13}C\{^{1}H\}$ NMR (151 MHz, $CDCl_3$, 298 K): δ = 148.0, 129.2 (2C), 115.4, 111.7 (2C), 47.6 (2C), 25.5 (2C). HRMS (ESI) m/z calcd for $C_{10}H_{14}N^{+}$ $(M+H)^{+}$: 148.1121; found: 148.1108.

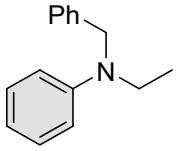
N-benzyl-N-ethylaniline (**9ak**)



9ak

Isolated yield: 84%, (petroleum ether/ethyl acetate = 50:1); Yellow solid; ^{1}H NMR (600 MHz, $CDCl_3$, 298 K): δ = 7.36 (t, $^{3}J_{HH}$ = 7.8 Hz, 2H), 7.29 (m, 3H), 7.24 (t, $^{3}J_{HH}$ = 8.4 Hz, 2H), 6.76 (d, $^{3}J_{HH}$ = 8.4 Hz, 2H), 6.72 (t, $^{3}J_{HH}$ = 7.2 Hz, 1H), 4.58 (s, 2H), 3.53 (m, 2H). 1.26 (t, $^{3}J_{HH}$ = 7.2 Hz, 3H). $^{13}C\{^{1}H\}$ NMR (151 MHz, $CDCl_3$, 298 K): δ = 148.6, 139.4, 129.3 (2C), 128.6 (2C), 126.8, 126.6 (2C), 116.1, 112.2 (2C), 54.0, 45.2, 12.2. HRMS (ESI) m/z calcd for $C_{15}H_{18}N^{+}$ $(M+H)^{+}$: 212.3414; found: 212.3406.

N-benzyl-N-ethylaniline (**9ka**)

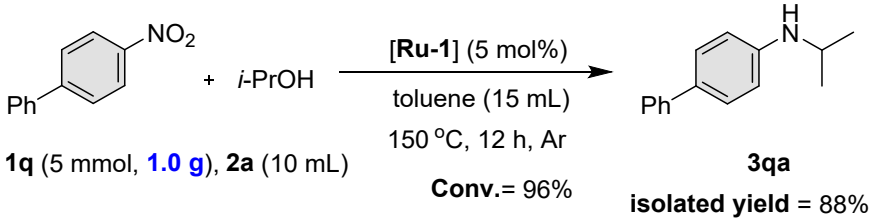


9ka

Isolated yield: 87%, (petroleum ether/ethyl acetate = 50:1); Yellow solid; ^{1}H NMR (600 MHz, $CDCl_3$, 298 K): δ = 7.28 (t, $^{3}J_{HH}$ = 7.8 Hz, 2H), 7.21 (m, 3H), 7.17 (m, 2H), 6.68 (d, $^{3}J_{HH}$ = 8.4 Hz, 2H), 6.65 (t, $^{3}J_{HH}$ = 7.2 Hz, 1H), 4.50 (s, 2H), 3.45 (t, $^{3}J_{HH}$ = 7.2 Hz, 2H). 1.19 (t, $^{3}J_{HH}$ = 7.8 Hz, 3H). $^{13}C\{^{1}H\}$ NMR (151 MHz, $CDCl_3$, 298 K): δ = 148.6, 139.4, 129.3 (2C), 128.7 (2C), 126.8, 126.7 (2C), 116.1, 112.3 (2C), 54.0, 45.2, 12.3. HRMS (ESI) m/z calcd for $C_{15}H_{18}N^{+}$ $(M+H)^{+}$: 212.3414; found: 212.3406.

7 The scale-up alkylation of 4-nitro-1,1'-biphenyl (1q)

Under protection of argon, a 250 mL autoclave equipped with a stirring bar was charged with 4-nitro-1,1'-biphenyl **1q** (5 mmol, 1.0 g), isopropyl alcohol **2a** (10 mL) and Ru(dppbsa) ([**Ru-1**]) (5 mol%). Then, 15 mL toluene was added to dissolve the mixture in the autoclave. The reaction was heated to 150 °C for 12 h. After cooling down to room temperature. The distribution of the product was determined by GC analysis using biphenyl as an internal standard. The solvent was removed under vacuum and then the product was purified by column chromatography and the product was analyzed by NMR spectroscopy. Isolatd yield: 88%.



Scheme S3. Gram-scale N-alkylation of 4-nitro-1,1'-biphenyl (**3q**)

8 Mechanistic studies for the alkylation of nitroarenes

8.1 Compounds distribution of the Ru-catalyzed N-alkylation of nitroarene.

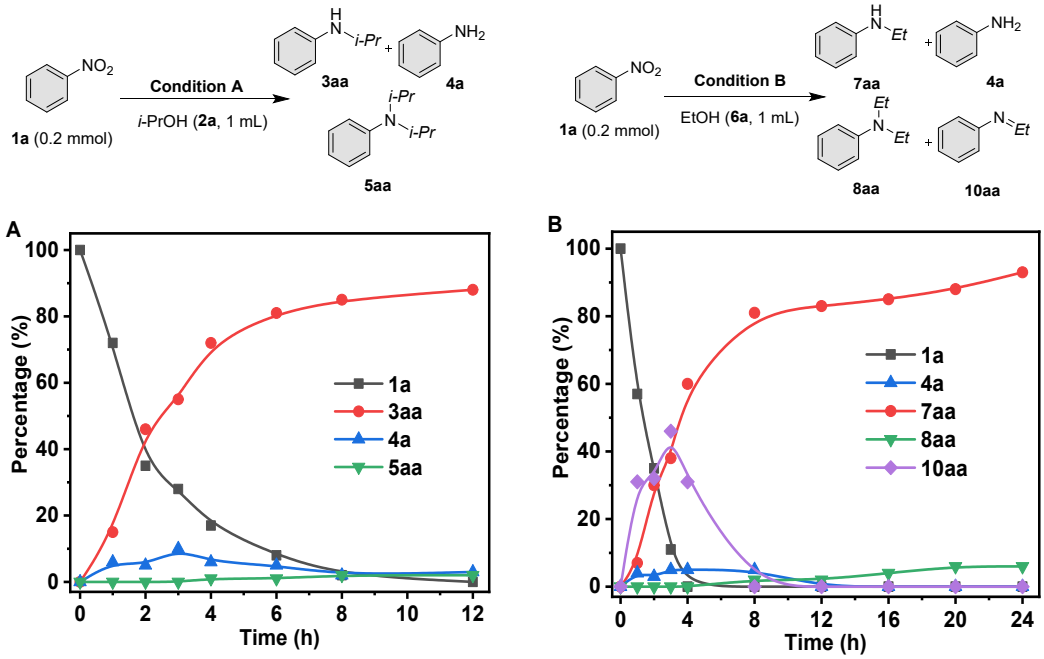


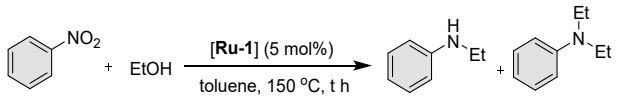
Figure S2. Time-course plot of N-alkylation of **1a** with *i*-PrOH (**2a**) (**A**) and with EtOH (**6a**) (**B**). [a] **Condition A**: **1a** (0.2 mmol), **2a** (1 mL), **[Ru-1]** (5 mol%), toluene (1 mL), 150 °C. [b] **Condition B**: **1a** (0.2 mmol), **6a** (1 mL), **[Ru-1]** (5 mol%), Na_2CO_3 (1.0 equiv.), toluene (1 mL), 150 °C. [c] yield was determined by GC analysis using biphenyl as the internal standard.

Experimental Procedure (**A**): Seven 25 mL autoclaves were charged with the same components, i. e. in every autoclaves, **1a** (0.2 mmol), Ru(dppbsa) (5 mol%), **2a** (1.0

mL), 0.1 mmol standard (biphenyl) and toluene (1.0 mL) were added. The reactions were performed under the standard condition (**A**). Every 30 min, one reaction autoclave was cooled to room temperature. The reaction solution was diluted to 30 mL and then 0.5 mL solution was sampled. After dilution, the sample was tested via GC. Time-course plot of N-alkylation of **1a** with i-PrOH (**2a**) (**A**) is shown in **Fig. S2**. Experimental Procedure (**B**): Nine 25 mL autoclaves were charged with the same components, i. e. in every autoclaves, **1a** (0.2 mmol), Ru(dppbsa) (5 mol%), **6a** (1.0 mL), Na_2CO_3 (1.0 equiv.), 0.1 mmol standard (biphenyl) and toluene (1.0 mL) were added. The reactions were performed under the standard condition (**B**). Every 2 hours, one reaction autoclave was cooled to room temperature. The reaction solution was diluted to 30 mL and then 0.5 mL solution was sampled. After dilution, the sample was tested via GC and GC-MS. Time-course plot of N-alkylation of **1a** with EtOH (**6a**) (**B**) is shown in **Fig. S2**.

8.2 Control experiments of nitrobenzene (**1a**) and N-ethylaniline (**7aa**) with ethanol or isopropanol under neutral and alkaline conditions.

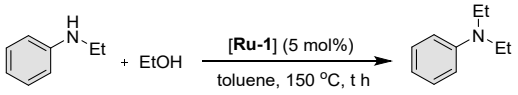
Table S3. Control experiments.[a]



1a **6a** **7aa** **8aa**

Entry	Time (h)	Conv. (%)	7aa	8aa
1	1	28	4	20
2	2	40	1	31
3	3	70	0	63
4	4	97	0	89

[a] Reaction conditions: **1a** (0.2 mmol), **6a** (1 mL), **[Ru-1]** (5 mol %), toluene (1 mL), 150 °C, t h.

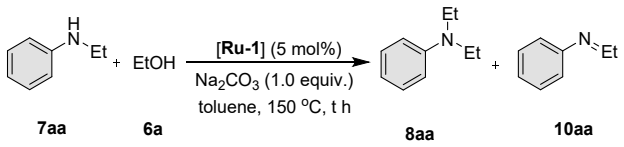


7aa **6a** **8aa**

Entry	Time (h)	Conv. (%)	8aa
1	1	36	35
2	2	59	58
3	3	84	79
4	4	98	95

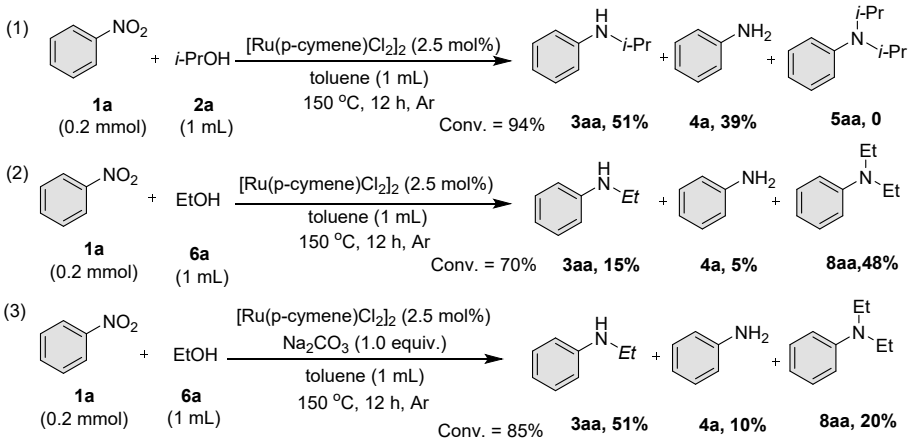
[a] Reaction conditions: **7aa** (0.2 mmol), **6a** (1 mL), **[Ru-1]** (5 mol

%), toluene (1 mL), 150 °C, t h.



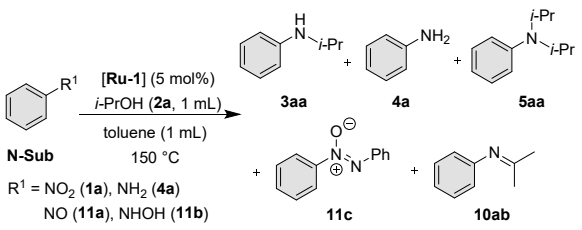
Entry	Time (h)	Conv. (%)	8aa	10aa
1	6	0	0	0
2	12	0	0	0
3	24	3	2	0
4	30	4	3	0
5	36	6	5	0
6	42	8	7	0
7	48	15	12	0
8	54	24	20	0
9	84	47	45	0

[a] Reaction conditions: **7aa** (0.2 mmol), **6a** (1 mL), **[Ru-1]** (5 mol %), Na_2CO_3 (1.0 equiv.), toluene (1 mL), 150 °C, t h.



8.3 Compounds distribution of nitrogen-based species for N-alkylation.

Table S4. Probing nitrogen-based species for N-alkylation.[a]



Entry	N-Sub	Time (h)	Conv. (%)	Yield (%)[a] 3aa	10ab	4a	5aa	11c
1	**1a**	1	28	15	-	6	0	-
2	**1a**	2	65	46	-	5	0	-
3	**1a**	3	72	55	-	10	0	-
4	**1a**	4	83	72	-	6	1	-

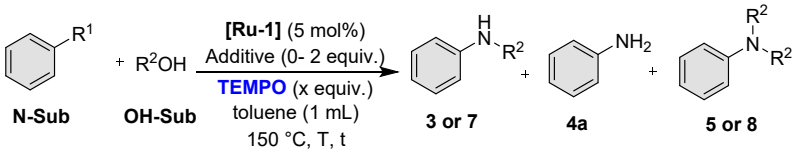
5	**4a**	1	10	2	4	-	-	-
6	**4a**	2	16	5	7	-	-	-
7	**4a**	3	24	6	15	-	-	-
8	**4a**	4	45	10	26	-	-	-
9	**11a**	1	100	0	1	12	-	44
10	**11a**	2	100	2	3	19	-	38
11	**11a**	3	100	4	4	23	-	35
12	**11a**	4	100	5	4	25	-	33
13	**11b**	1	100	2	2	26	-	35
14	**11b**	2	100	4	2	31	-	32
15	**11b**	3	100	5	4	35	-	28
16	**11b**	4	100	10	5	34	-	26

[a] **N-sub** (0.2 mmol), *i*-PrOH (1 mL), [**Ru-1**] (5 mol%), toluene (1 mL), at 150 °C for t h, yield was determined by GC analysis using biphenyl as the internal standard.

8.4 Radical trapping experiments and control experiments for N-alkylation.

The poisoning studies using TEMPO (2,2,6,6-tetramethylpiperidine-1-oxyl) as an inhibitor were performed, as it's a good hydride abstractor for Ru-H. Evidently, while the reaction with 1a was significantly suppressed in the presence of two equivalents of TEMPO (entry 1), the reaction with 1a was relatively retained, where the reduced product (**3a**) was obtained with satisfactory 64% yield (Scheme 4C). We, therefore, suspected the latter hydrogen transfer with **2d** proceeds mainly through a concerted fashion.

Table S5. Screening the reaction performance with TEMPO.



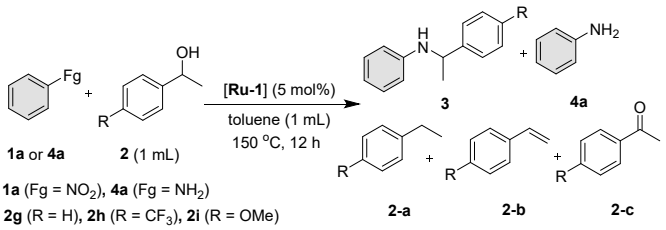
R^1= NO_2 (**1a**), NH_2 (**4a**)

Entry [c]	N-Sub	OH-Sub	TEMPO (x equiv)	Conv. %	3aa (%)	4a (%)	5aa (%)	7aa (%)	8aa (%)
1[a]	**1a**	*i*-PrOH	0	100	88	2	6	-	-
2[a]	**1a**	*i*-PrOH	0.2	100	6	70	0	-	-
3[a]	**1a**	*i*-PrOH	2.0	100	8	72	0	-	-
4[a]	**4a**	*i*-PrOH	0	83	72	-	0	-	-
5[a]	**4a**	*i*-PrOH	2.0	28	22	-	0	-	-
7[b]	**1a**	EtOH	0	100	-	0	-	93	5
8[b]	**1a**	EtOH	0.2	100	-	0	-	90	6
9[b]	**1a**	EtOH	2.0	100	-	0	-	91	6
10[b]	**4a**	EtOH	0	92	-	-	-	82	5
11[b]	**4a**	EtOH	2.0	100	-	-	-	85	8

[a] **N-sub** (0.2 mmol), **OH-Sub** (1 mL), [**Ru-1**] (5 mol%), toluene (1 mL), at 150 °C for 12 h. [b] **N-sub** (0.2 mmol), **OH-Sub** (1 mL), [**Ru-1**] (5 mol%), Na_2CO_3 (1.0 equiv), toluene (1 mL), at 150 °C for 12 h. [c] **Conv.** and yield was determined by GC analysis using biphenyl as the internal standard.

8.5 Control experiments for N-alkylation nitrobenzene **1a** with secondary alcohols.

Table S6. Control experiments



Entry	1a or 4a	2	Conv. % (1a or 4a)	Yield (%)[a] 3 (%)	Yield (%)[a] 4a (%)	Conv. % (2)	Yield (%)[a] 2-a	Yield (%)[a] 2-b	Yield (%)[a] 2-c
1	**1a**	**2g** (R = H)	99	**3ag** (91)	8	58	8	3	21
2	**1a**	**2h** (R = CF_3)	99	**3ah** (8)	76	20	trace	trace	16
3	**1a**	**2i** (R = OMe)	10	**3ai** (9)	0	97	10	50	30
4	**4a**	**2h** (R = CF_3)	21	**3ah** (13)	-	-	trace	trace	-
5	**4a**	**2i** (R = OMe)	89	**3ai** (88)	-	-	-	-	-

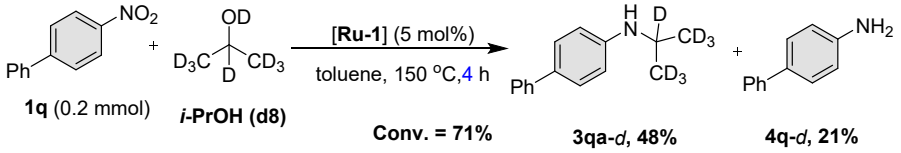
[a] **1a** or **4a** (0.2 mmol), **2** (1 mL), [**Ru-1**] (5 mol%), toluene (1 mL), at 150 °C for 12 h, yields were determined by GC analysis using biphenyl as the internal standard.

Neither the electron-withdrawing (trifluoromethyl in **2h**) nor the electron-donating (methoxy in **2i**) group at the *para*-position of the secondary alcohols with **1a** could afford a comparable reactivity as that of unsubstituted **2g**. Specifically, the reaction mainly provides aniline (**4a**, 76%) with **2h** functioning as the hydrogen surrogate. In contrast, the presence of **2i** significantly inhibits the conversion of **1a** but signifies the dehydrogenation and dehydration of **2i**, delivering the corresponding ketone and ethylene as the major products. In controlled experiment, the reaction results of **4a** with the corresponding secondary alcohols (**2**) further demonstrate this phenomenon. In this test, a relatively electron-rich secondary alcohol promotes the coupled reaction and causes the inhibition of hydrogenation reduction reaction. However, an electron-withdrawing secondary alcohol has exactly the opposite effect.

8.6 Deuterium-labeling experiments of the N-alkylation of nitroarene with deuterated isopropyl alcohol.

General procedure: Under protection of argon, a 25 mL autoclave equipped with a stirring bar was charged with 4-nitro-1,1'-biphenyl **1q** (0.2 mmol), Ru(dppbsa) (5 mol%), the internal standard biphenyl (0.1 mmol) and toluene (1 mL). Then, 1.0 mL $(CD_3)_2CDOH$ (*i*-PrOH-d_7) and $(CD_3)_2CDOD$ (*i*-PrOH-d_8) was added to dissolve the

mixture in the autoclave. The reaction was heated to 150 °C for 12 h. After cooling down to room temperature. The reaction solution was diluted to 30 mL and then 0.5 mL solution was sampled. After dilution, the sample was tested via GC and GC-MS. The pure product of 3qa-*d*, 3qa-*d* or 4q-*d* was obtained by column chromatography on silica gel. In the presence of *i*-PrOH-d_7, the conversion (96%) and the deuterated product 4q-*d* was not detected, while the deuterated product (3qa-*d*) was obtained in 91% GC yield. In contrast, with *i*-PrOH-d_8, the yield of product 3qa-*d* (51%) was decreased and the deuterated product 4q-*d* was obtained in 43% GC yield. In the meantime, with *i*-PrOH-d_8 for 4 h, the conversion (71%) and the yield of product 3qa-*d* (48%) was decreased and the deuterated product 4q-*d* was obtained in 21% GC yield.



Scheme S4. Deuterium-labeling experiments

The ^{1}H NMR and ^{2}D NMR ($CDCl_3$) spectra of the products Deuterium-labeling experiments.

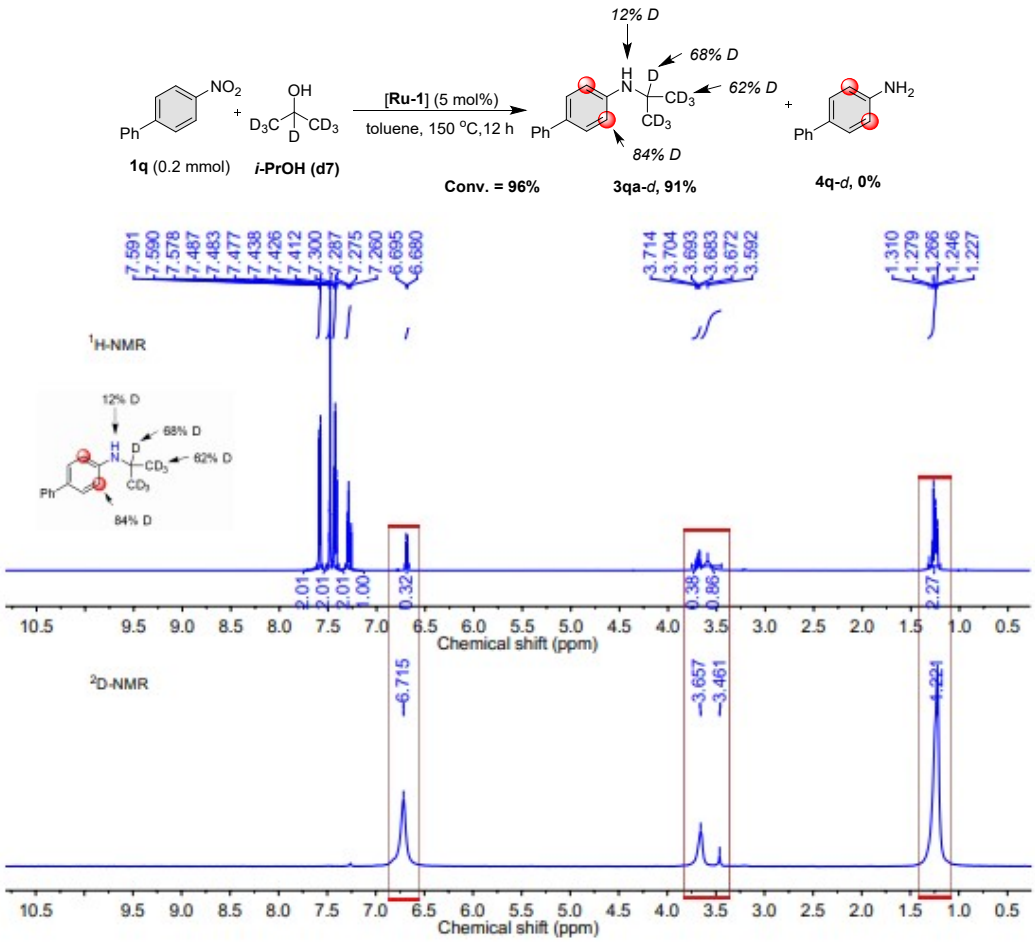


Figure S3. The ^{1}H NMR and ^{2}D NMR ($CDCl_3$) of the product **3qa**-*d*

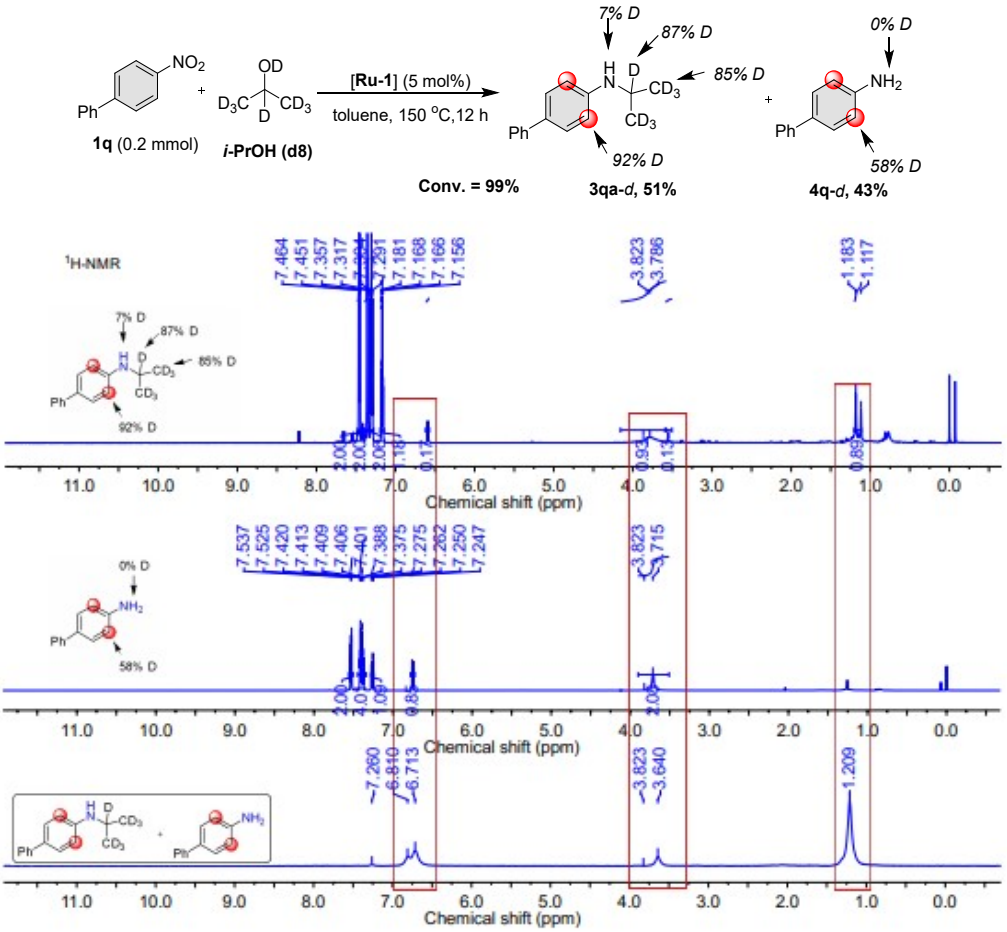
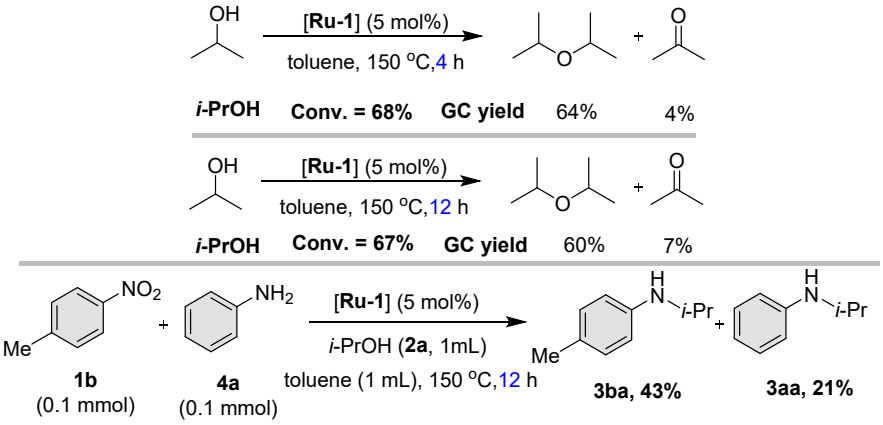


Figure S4. The ^{1}H NMR and ^{2}D NMR ($CDCl_3$) of the product **3qa**-*d* and **4q**-*d*

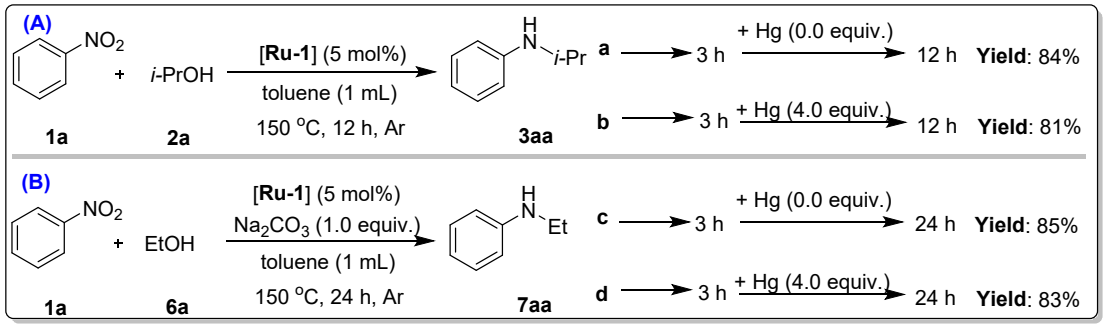
8.7 Cross-over experiment.



Scheme S5. Cross-over experiment

General procedure: Under protection of argon, a 25 mL autoclave equipped with a stirring bar was charged with *i*-PrOH (1 mL), Ru(dppbsa) (5 mol%), the internal standard biphenyl (0.1 mmol) and toluene (1 mL). The reaction was heated to 150 °C for 4 h and 12 h. After cooling down to room temperature. The reaction solution was diluted to 30 mL and then 0.5 mL solution was sampled. After dilution, the sample was tested via GC and GC-MS.

8.8 Amalgamation experiment of N-alkylation of nitroarene.



Scheme S6. Amalgamation reaction.

Experimental Procedure (**A**): Two 25 mL autoclaves were charged with the same components, i. e. in every autoclaves, **1a** (0.2 mmol), Ru(dppbsa) (5 mol%), **2a** (1.0 mL), 0.1 mmol standard (biphenyl) and toluene (1.0 mL) were added. The autoclave moved out of the glove box were heated to 150 °C for 3 h. One of them was opened and the other one was again put into the glove box to add mercury (4.0 mmol). Then the latter was sealed and moved out to continue reacting for 9 h at 150 °C. It turned out that the yield of former was 84%, while the latter was 81% (detected by GC with biphenyl as the internal standard) indicating that the catalyst was homogeneous. (**B**): Two 25 mL autoclaves were charged with the same components, i. e. in every autoclaves, **1a** (0.2 mmol), Ru(dppbsa) (5 mol%), **6a** (1.0 mL), Na_2CO_3 (1.0 equiv.), 0.1 mmol standard (biphenyl) and toluene (1.0 mL) were added. The autoclave moved out of the glove box were heated to 150 °C for 3 h. One of them was opened and the other one was again put into the glove box to add mercury (4.0 mmol). Then the latter was sealed and moved out to continue reacting for 21 h at 150 °C. It turned out that the yield of former was 85%, while the latter was 83% (detected by GC with biphenyl as the internal standard) indicating that the catalyst was homogeneous.

8.9 The GC-MS analysis of the [**Ru-1**]-catalysed alkylation of nitroarenes (**1a**) with secondary alkanols (**2a**) or primary alcohol (**6a**)

Reaction (a): Under protection of argon, Nitroarenes **1a** (0.2 mmol, 1.0 equiv.), alcohol **2**a (1 mL) and Ru(dppbsa) ([**Ru-1**]) (5 mol%) were charged in a 25 mL autoclave with magnetic bar. Then 1 mL of toluene was added into the mixture. The mixture was stirred at the desired temperature (150 °C) for 12 h. After the desired reaction time, the reaction mixture was allowed to cool to room temperature. The distribution of the product was determined by GC and GC-MS analysis using biphenyl as an internal standard.

Reaction (b): Under protection of argon, Nitroarenes **1a** (0.2 mmol, 1.0 equiv.), alcohol **6a** (1 mL) and Ru(dppbsa) ([**Ru-1**]) (5 mol%) were charged in a 25 mL autoclave with magnetic bar. Then 1 mL of toluene was added into the mixture. The mixture was stirred

at the desired temperature (150 °C) for 24 h. After the desired reaction time, the reaction mixture was allowed to cool to room temperature. The distribution of the product was determined by GC and GC-MS analysis using biphenyl as an internal standard.

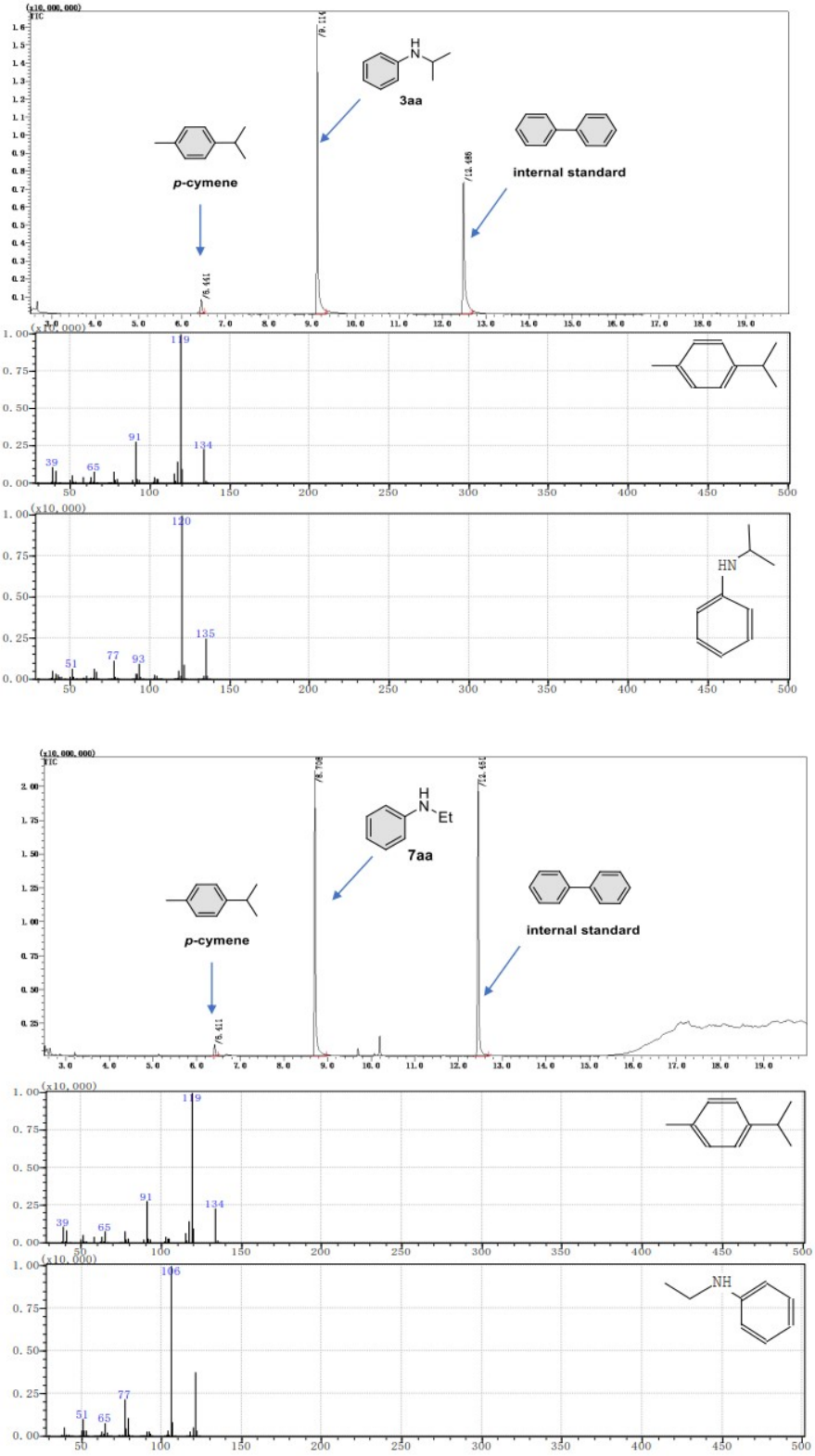
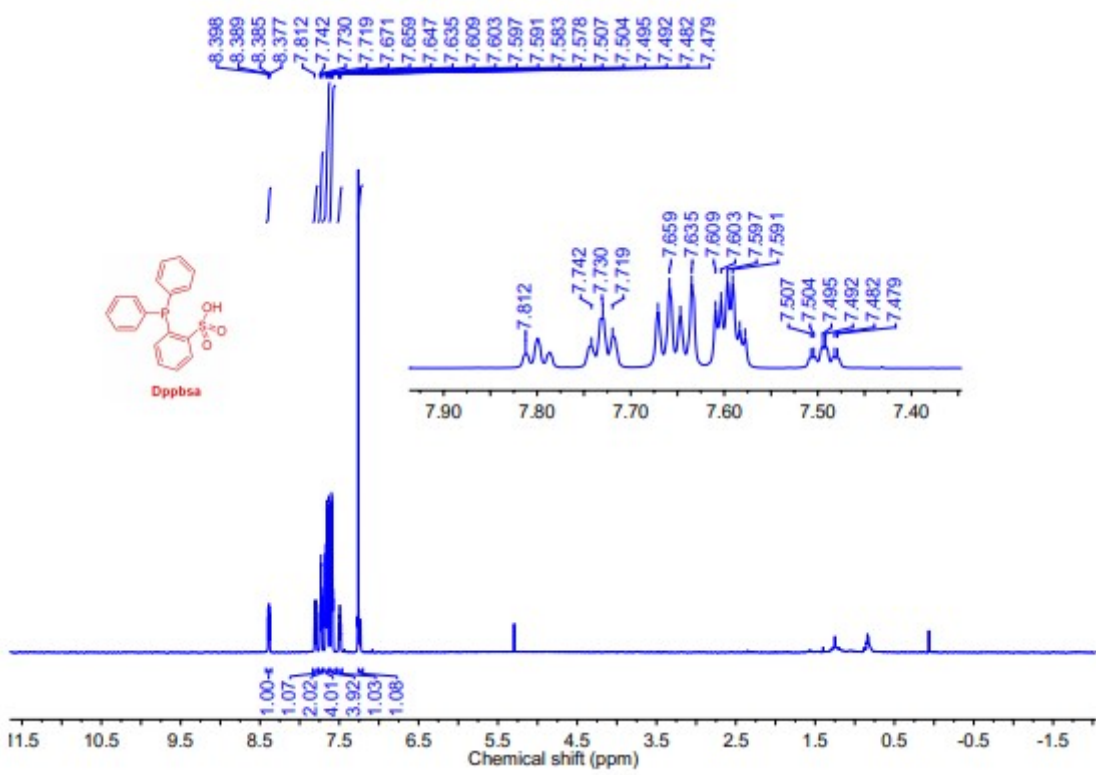
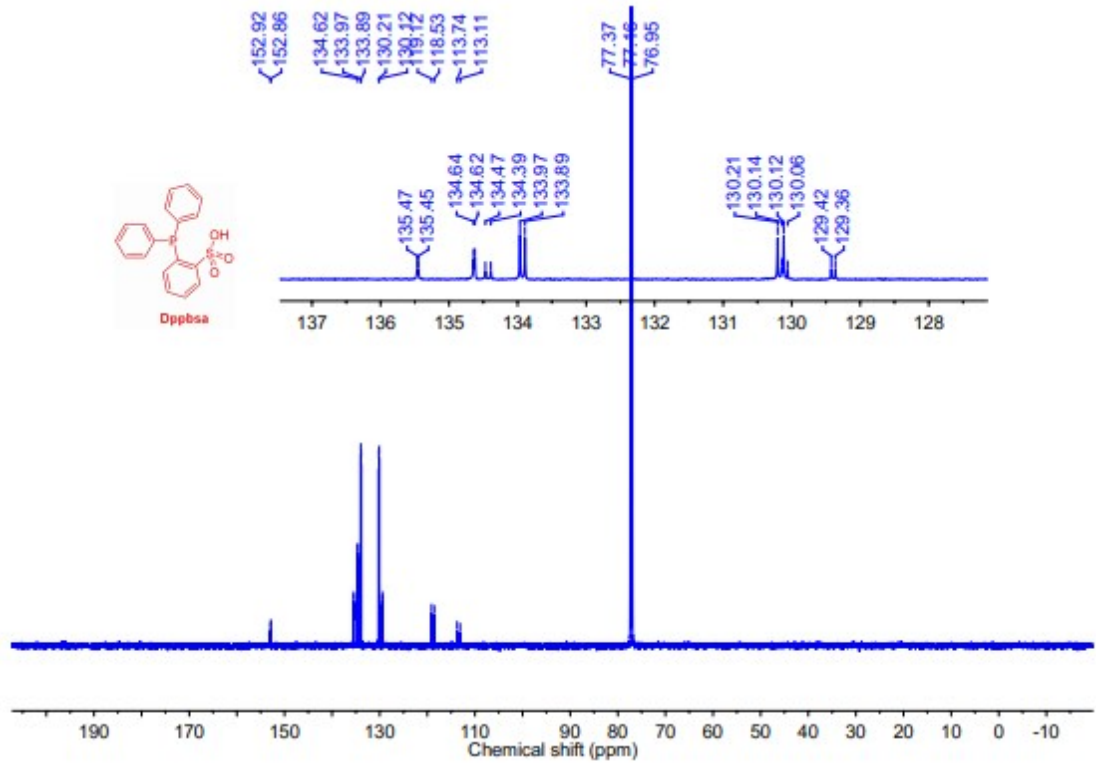


Figure S5. The compounds distribution of the reaction mixture was measured via GC-MS.

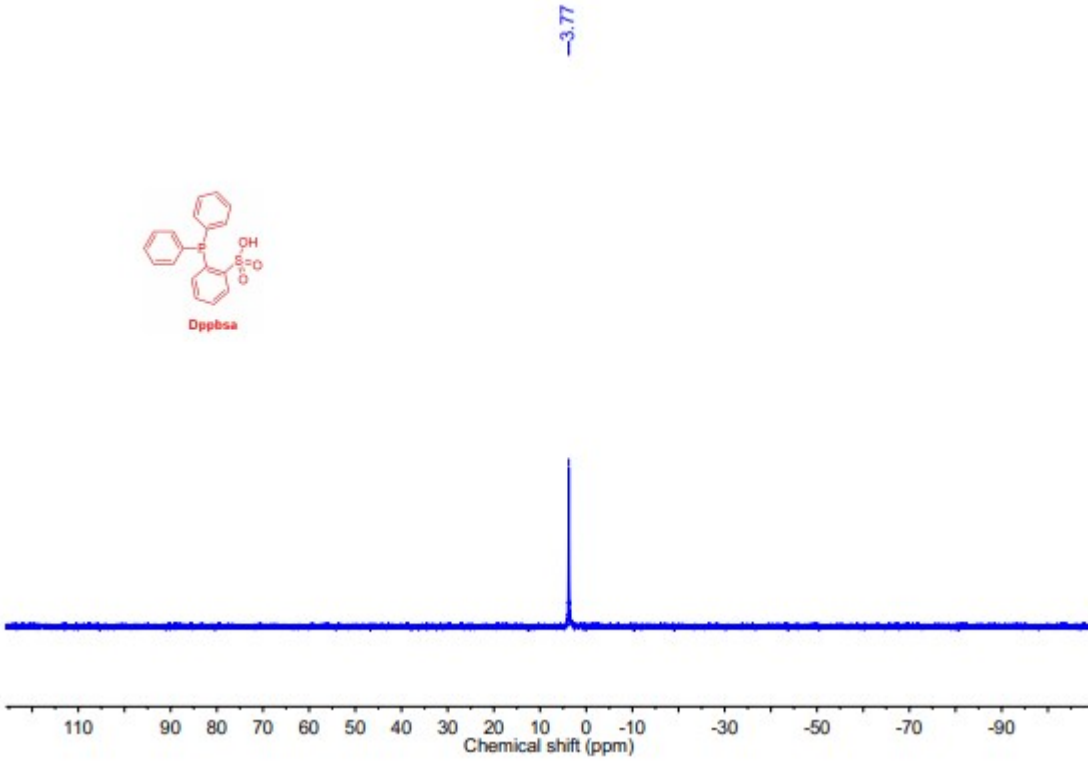
9 ^{1}H, ^{13}C and ^{31}P NMR spectra



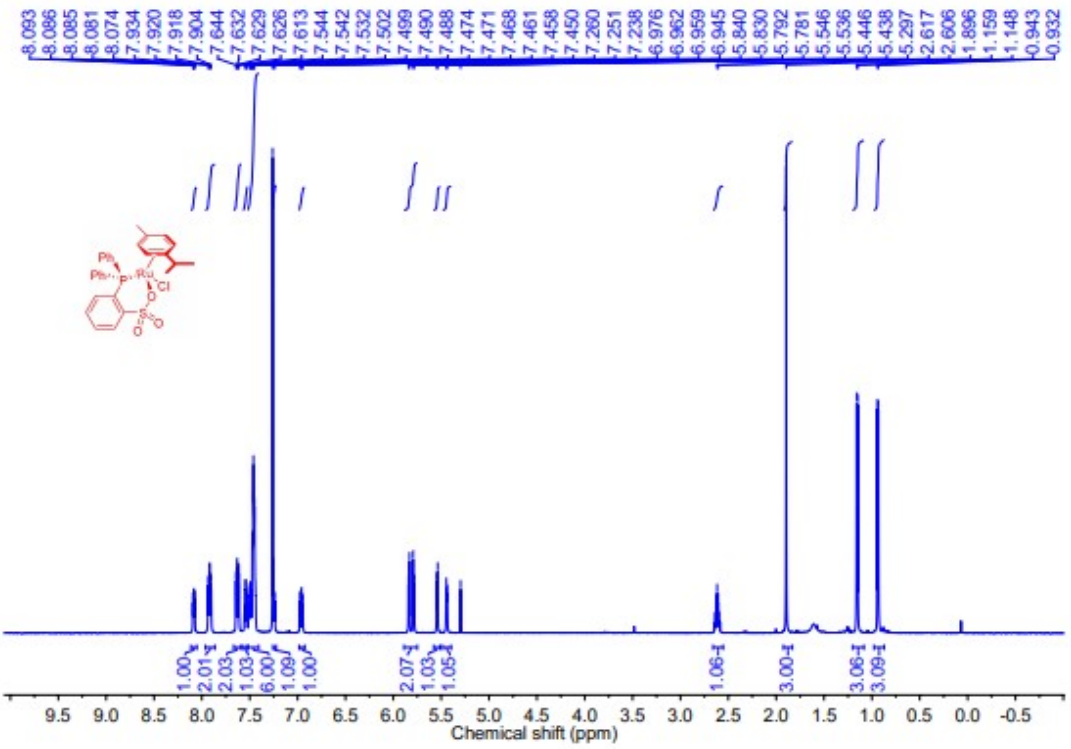
^{1}H NMR (600 MHz, $CDCl_3$, 298 K) of **Dppbsa**



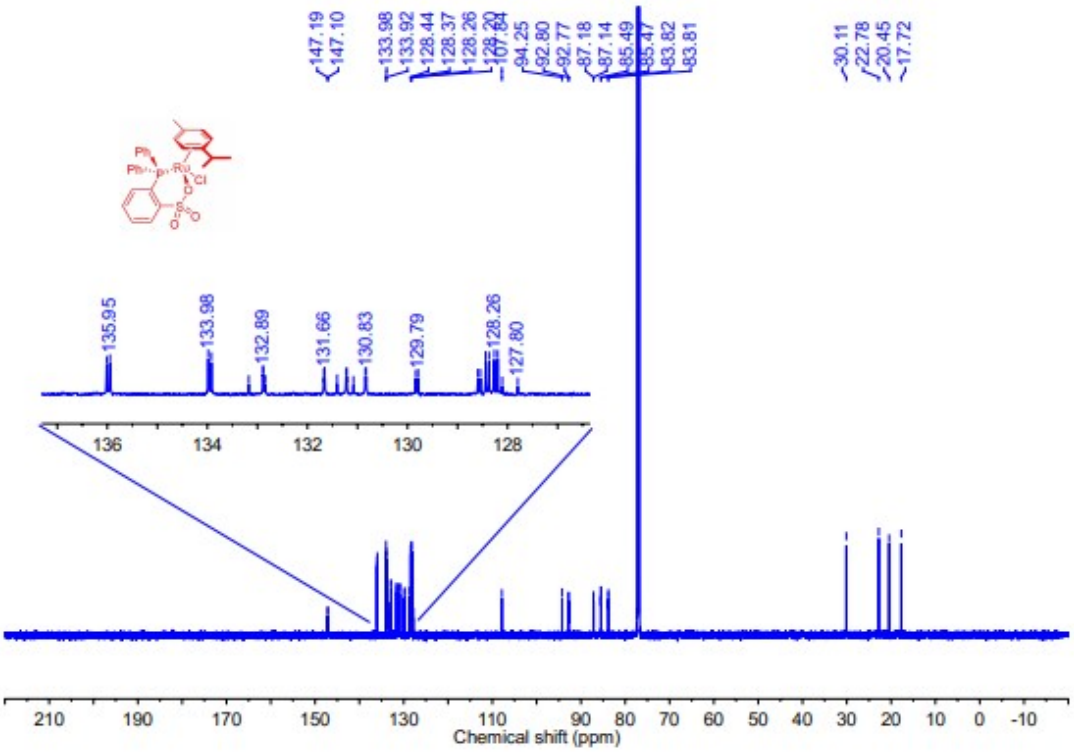
^{13}C{^{1}H} NMR (151 MHz, $CDCl_3$, 298 K) of **Dppbsa**



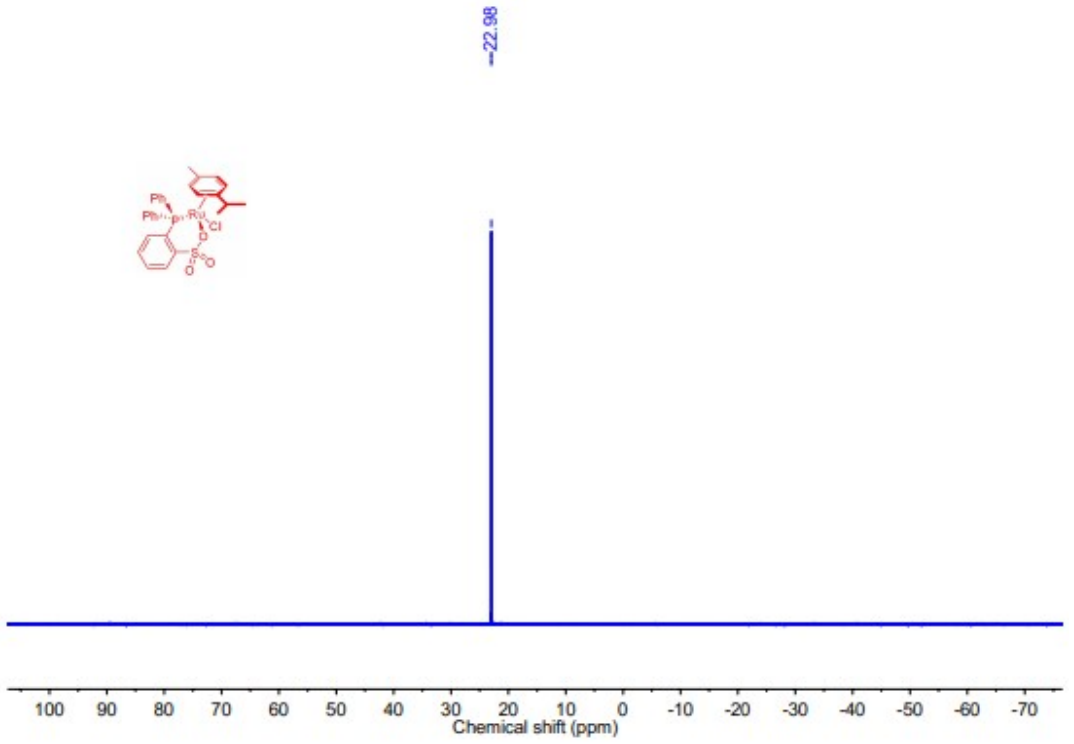
^{31}P NMR (243 MHz, $CDCl_3$, 298 K) of **Dppbsa**



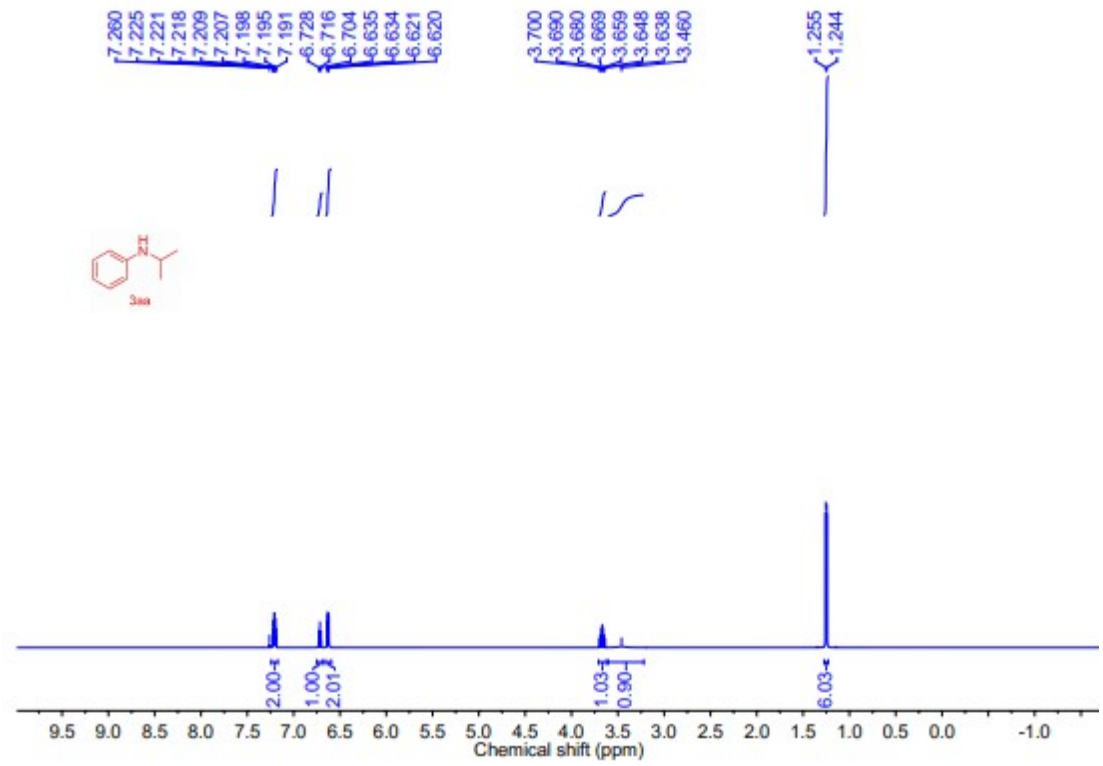
^{1}H NMR (600 MHz, $CDCl_3$, 298 K) of **Ru(dppbsa)**



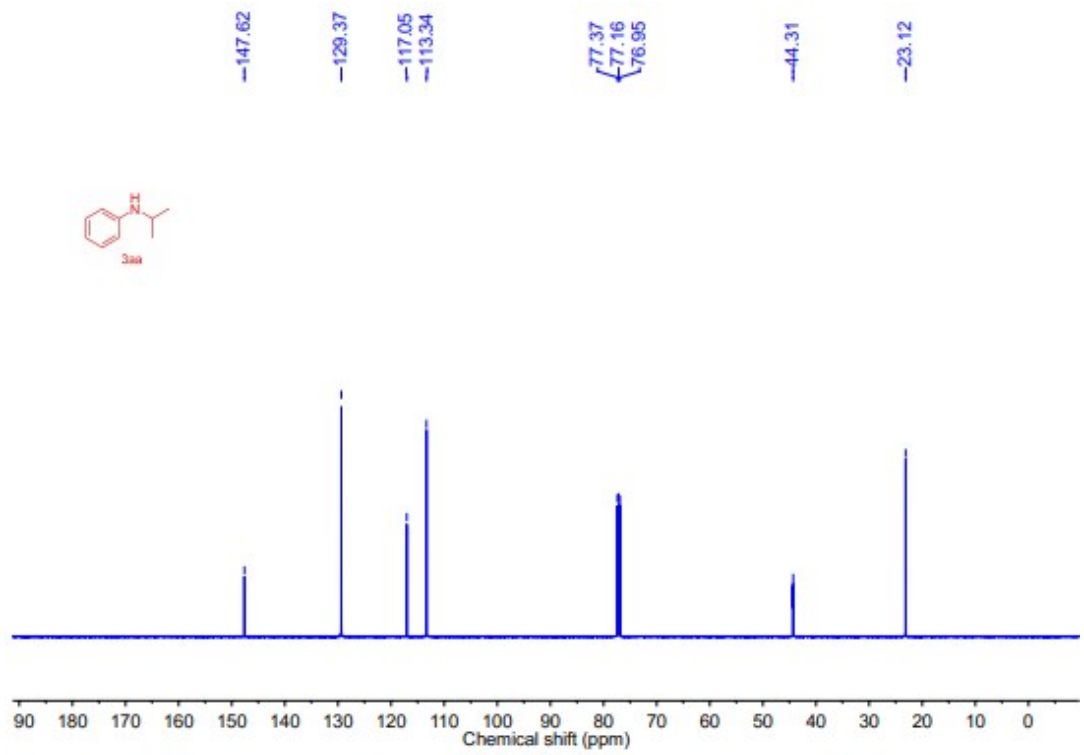
$^{13}C\{^{1}H\}$ NMR (151 MHz, $CDCl_3$, 298 K) of **Ru(dppbsa)**



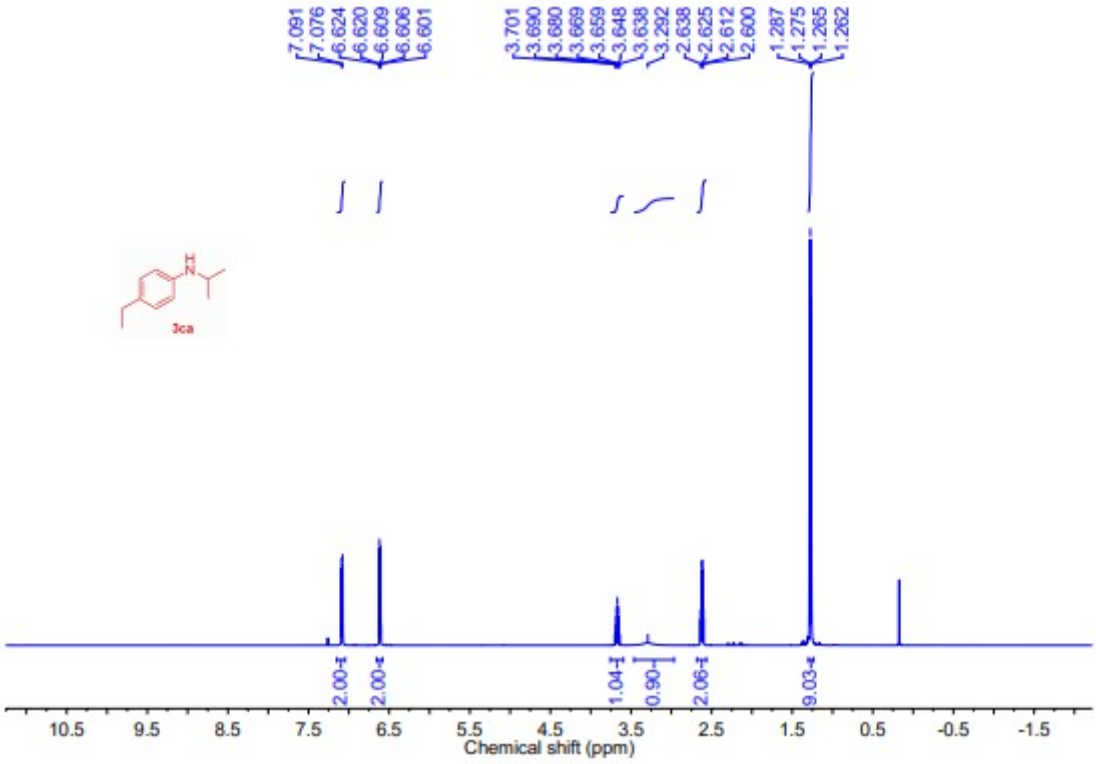
^{31}P NMR (243 MHz, $CDCl_3$, 298 K) of **Ru(dppbsa)**



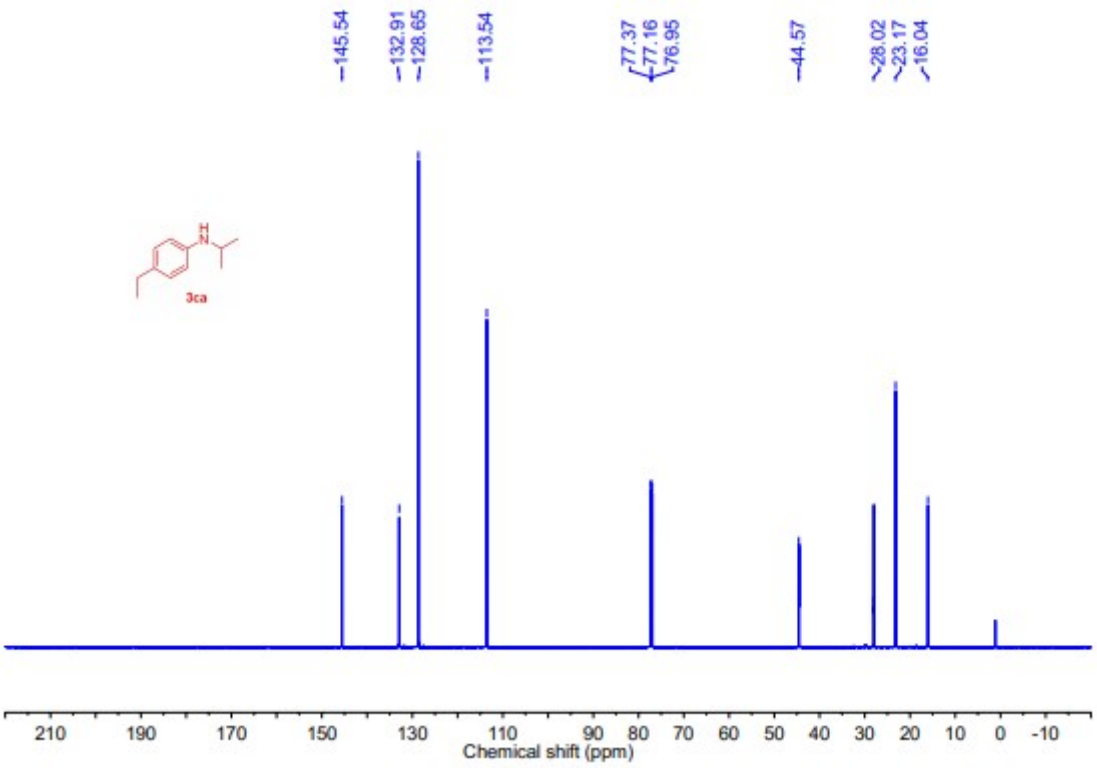
^{1}H NMR (600 MHz, $CDCl_3$, 298 K) of **3aa**



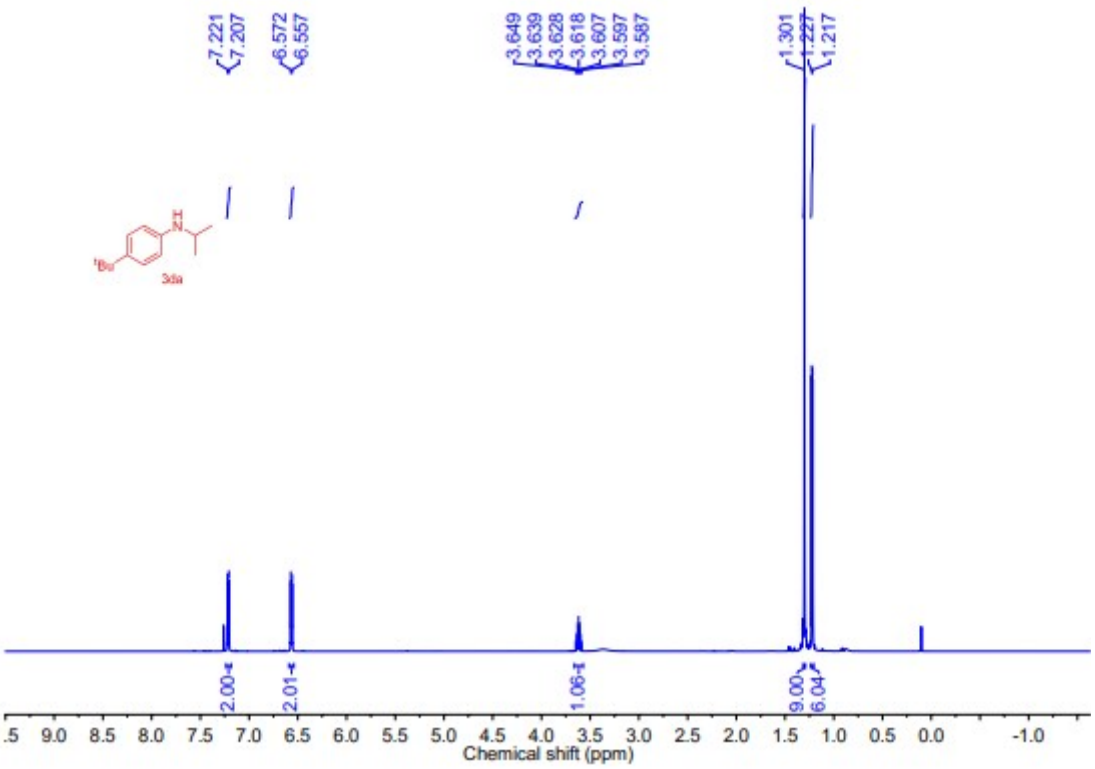
^{13}C{^{1}H} NMR (151 MHz, $CDCl_3$, 298 K) of **3aa**



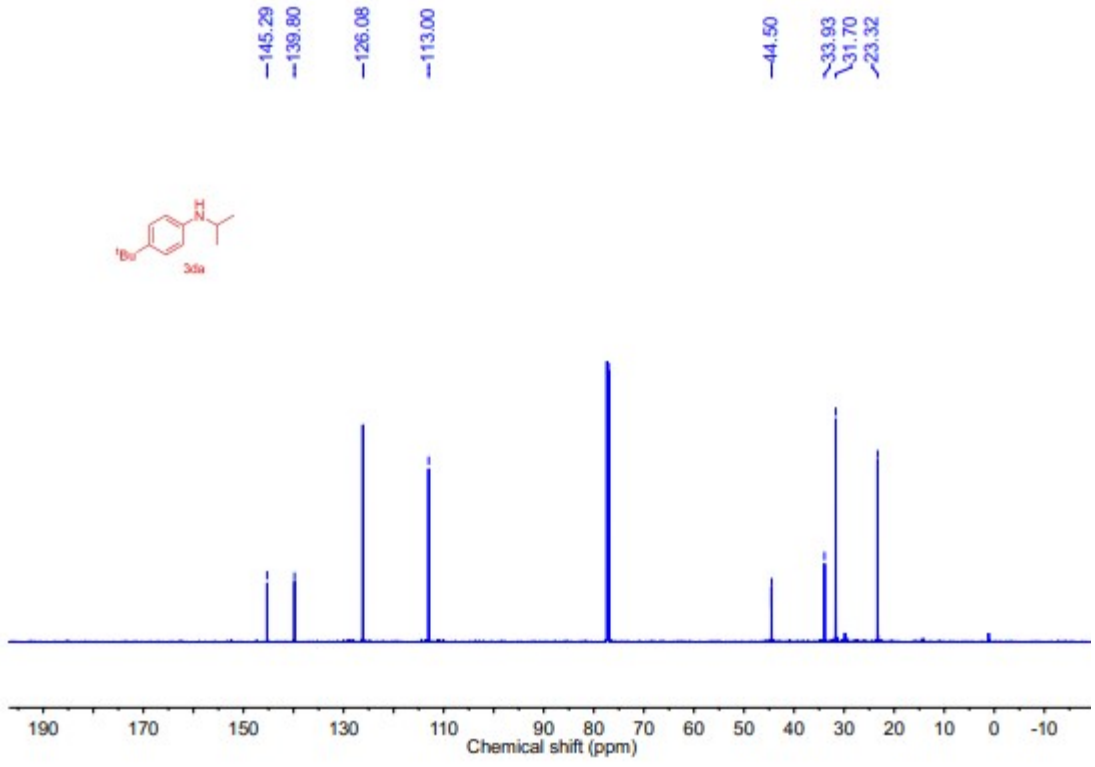
^{1}H NMR (600 MHz, $CDCl_3$, 298 K) of **3ca**



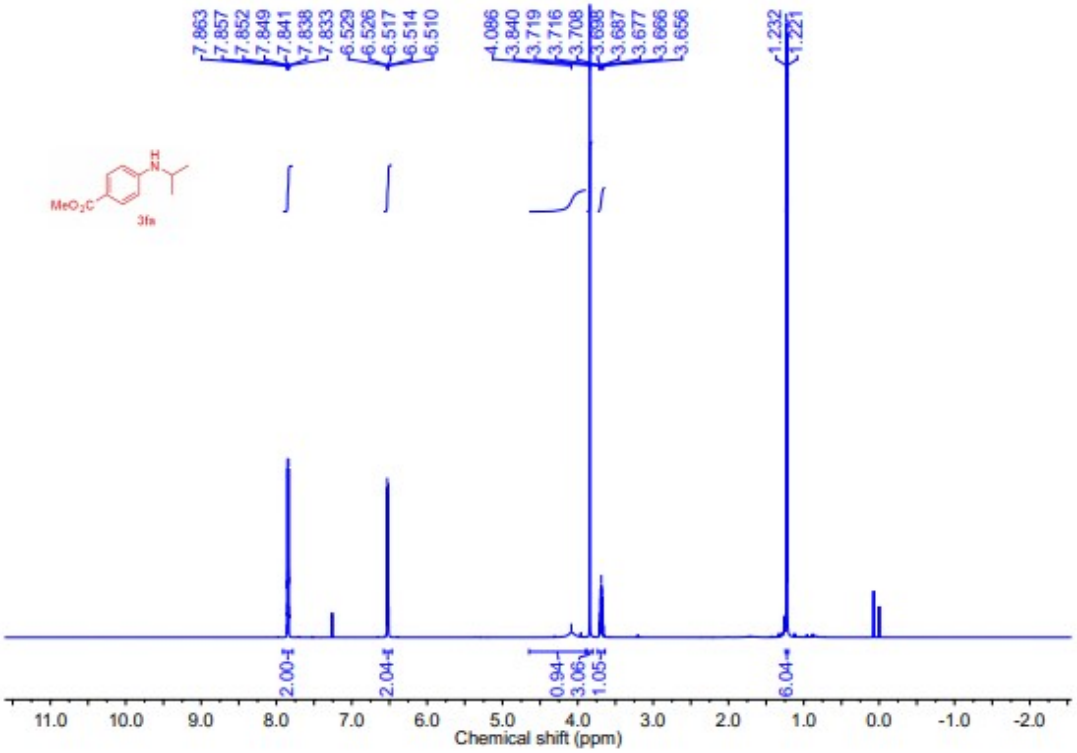
^{13}C{^{1}H} NMR (151 MHz, $CDCl_3$, 298 K) of **3ca**



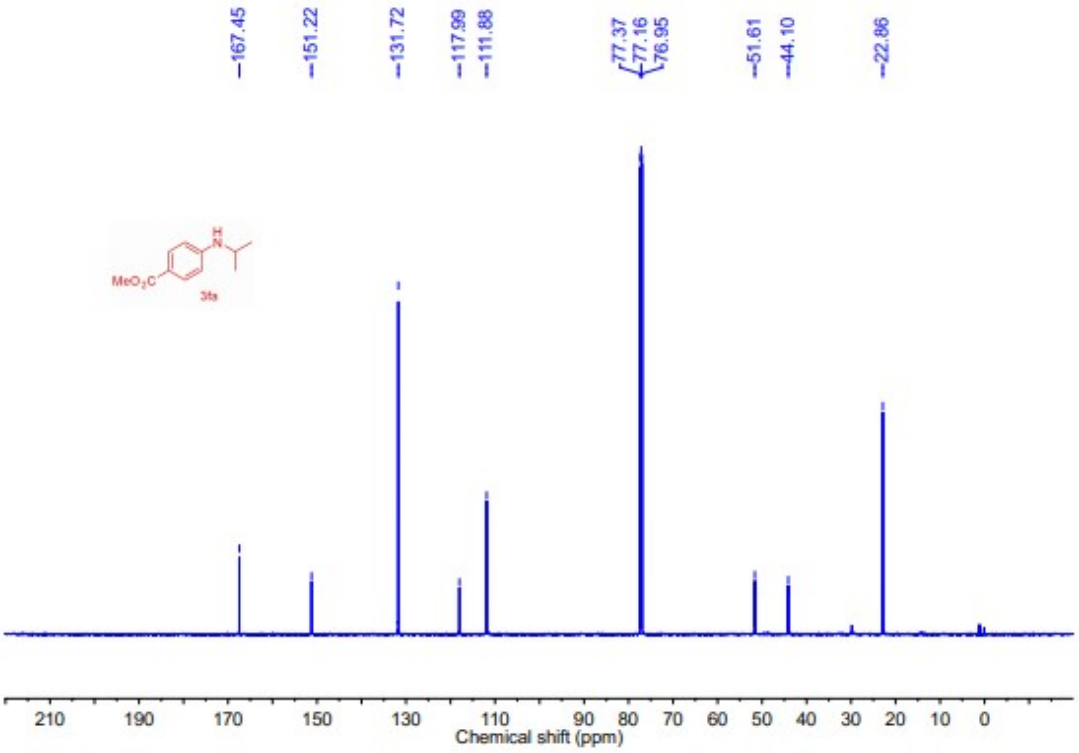
^{1}H NMR (600 MHz, $CDCl_3$, 298 K) of **3da**



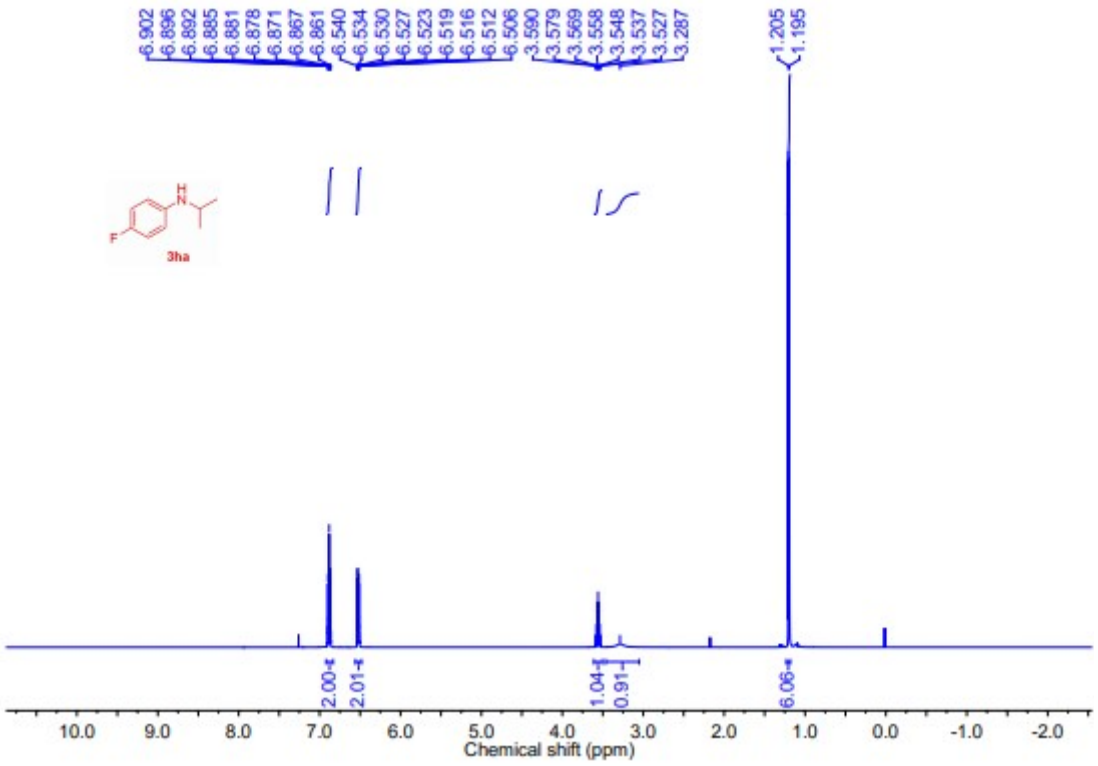
^{13}C{^{1}H} NMR (151 MHz, $CDCl_3$, 298 K) of **3da**



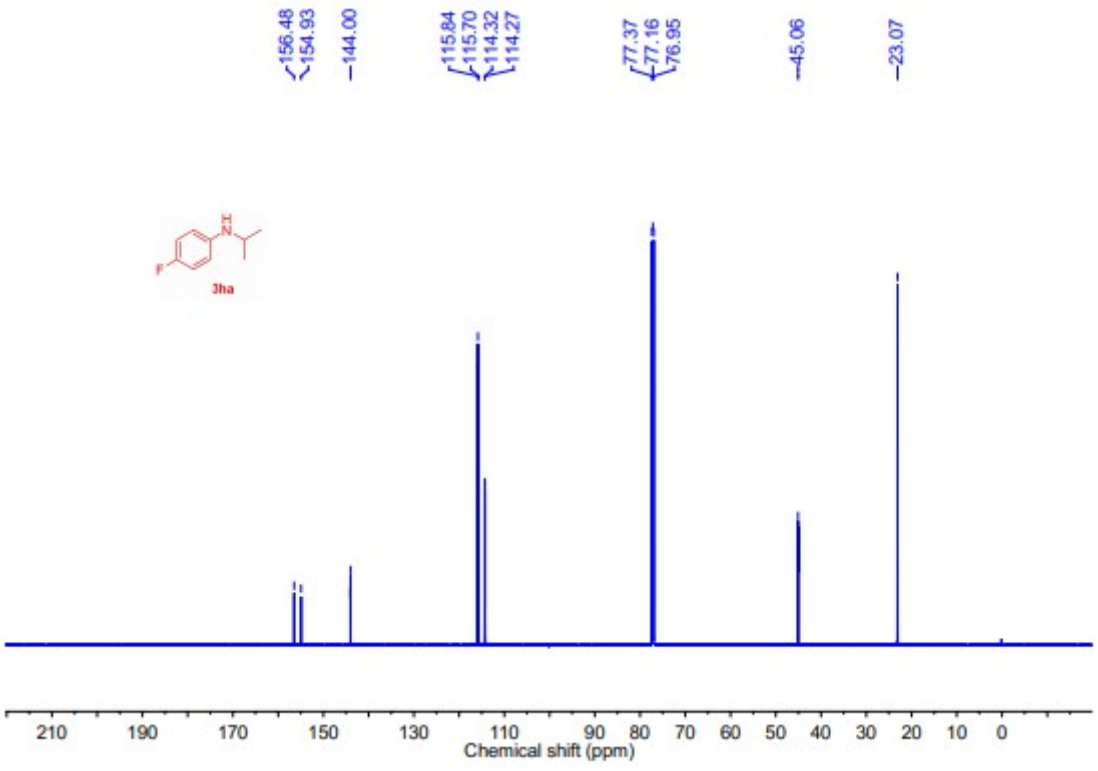
^{1}H NMR (600 MHz, $CDCl_3$, 298 K) of **3fa**



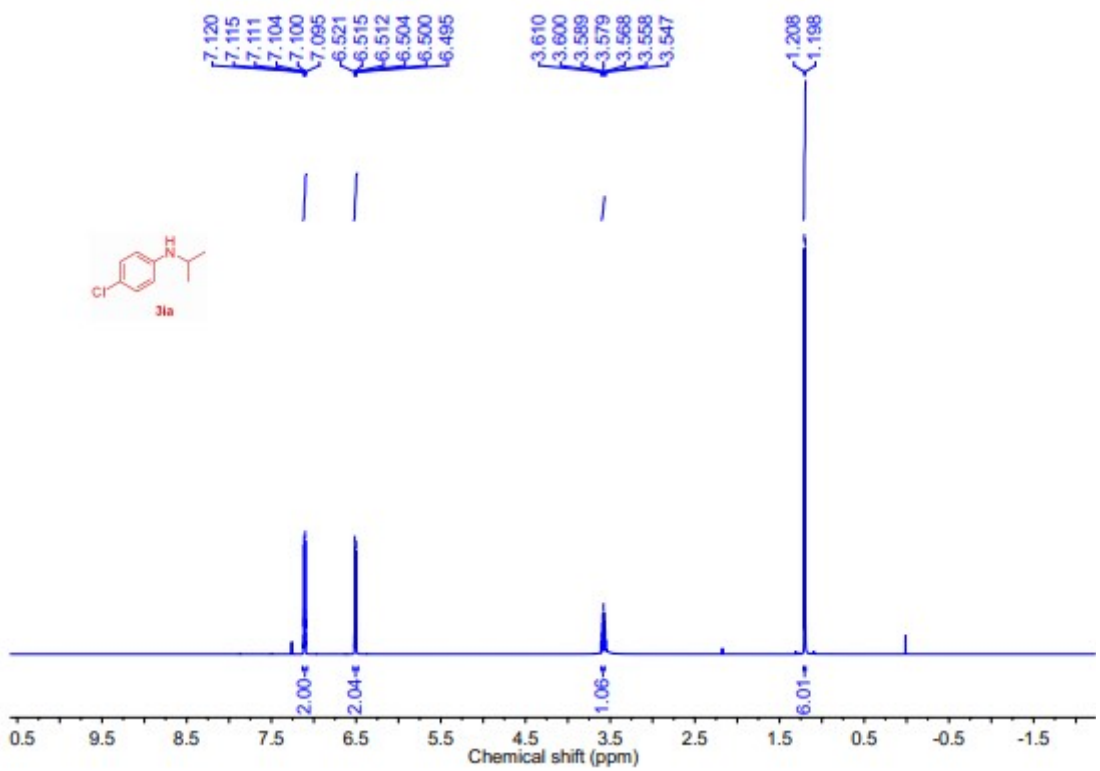
^{13}C{^{1}H} NMR (151 MHz, $CDCl_3$, 298 K) of **3fa**



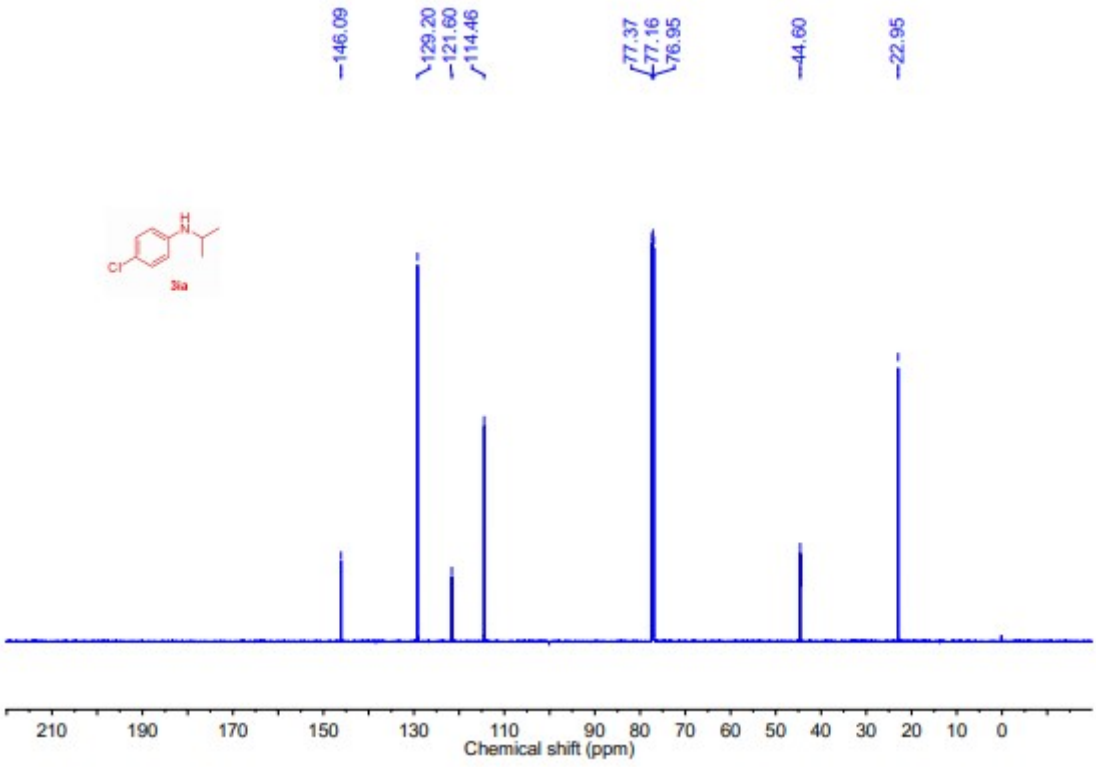
^{1}H NMR (600 MHz, $CDCl_3$, 298 K) of **3ha**



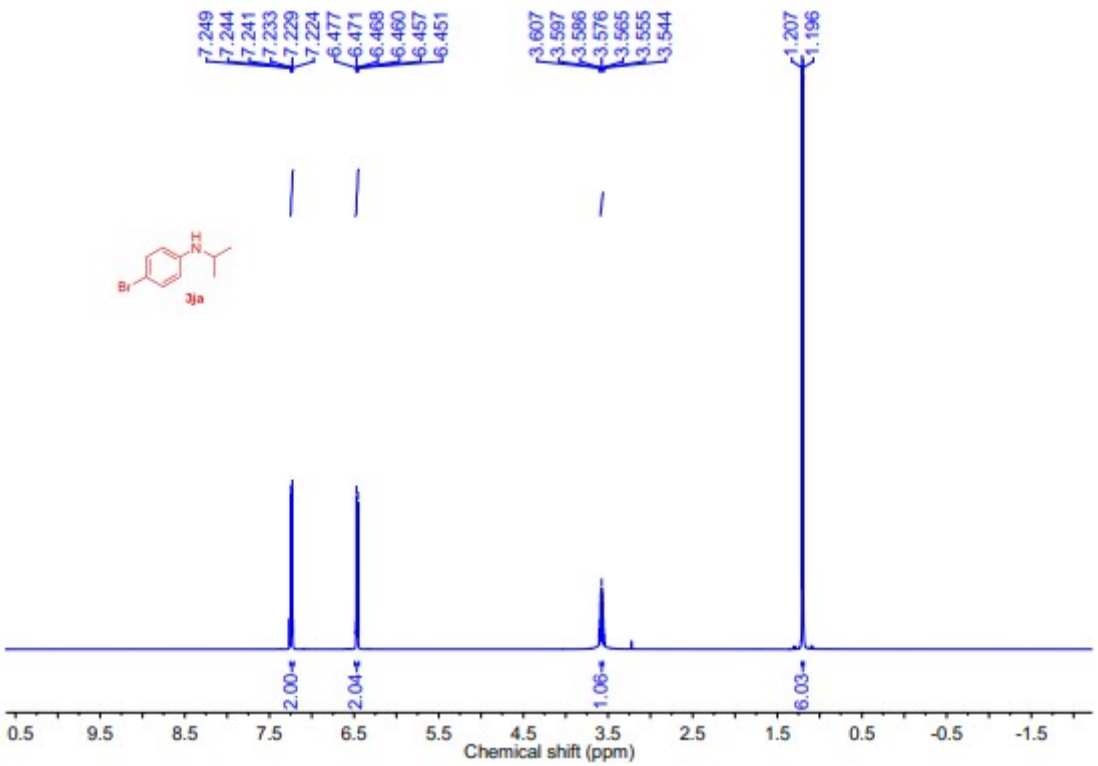
^{13}C{^{1}H} NMR (151 MHz, $CDCl_3$, 298 K) of **3ha**



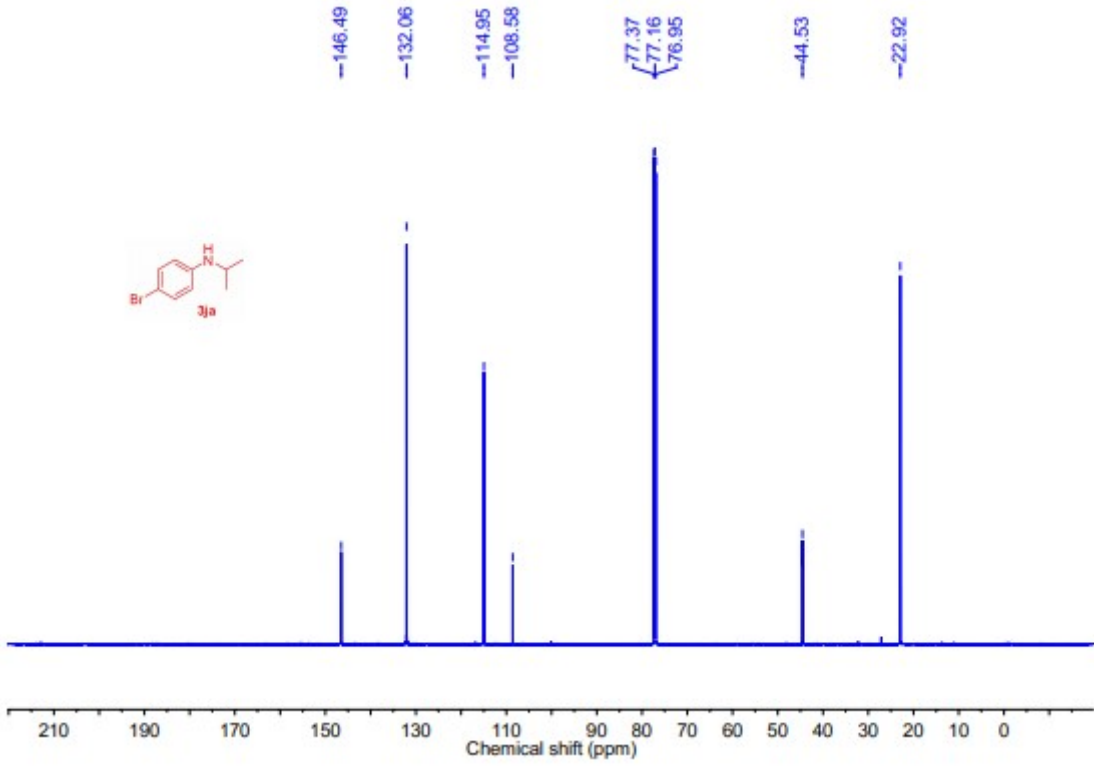
^{1}H NMR (600 MHz, $CDCl_3$, 298 K) of **3ia**



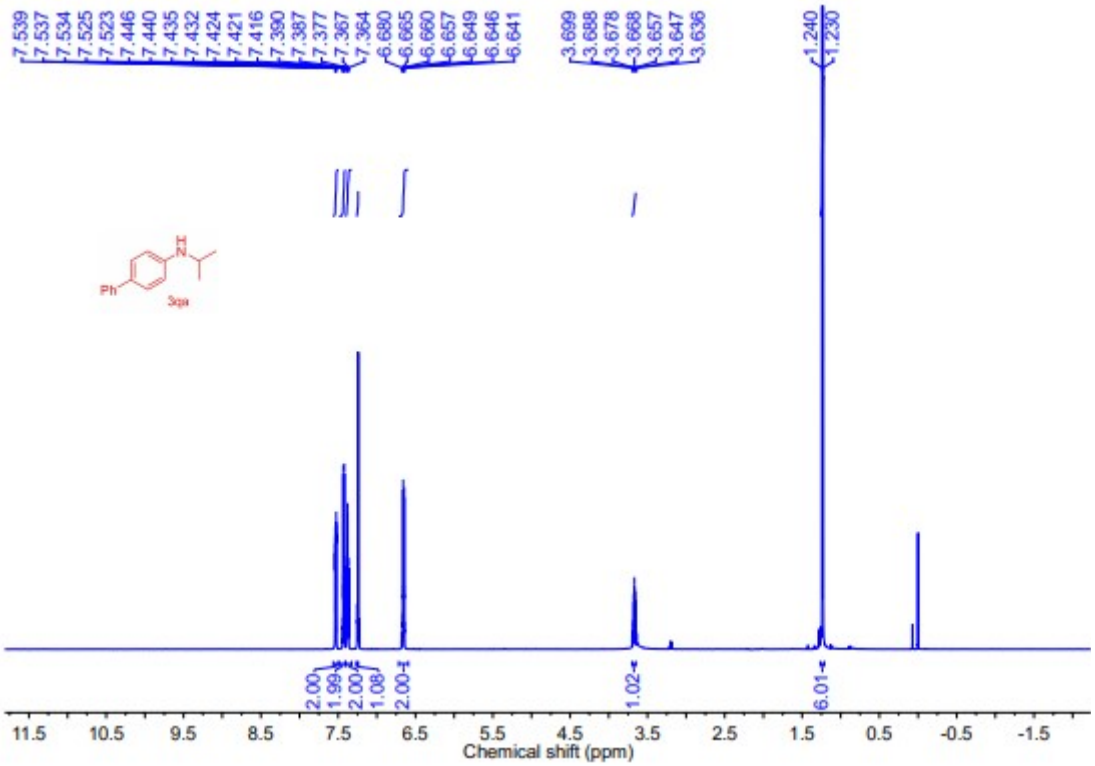
^{13}C{^{1}H} NMR (151 MHz, $CDCl_3$, 298 K) of **3ia**



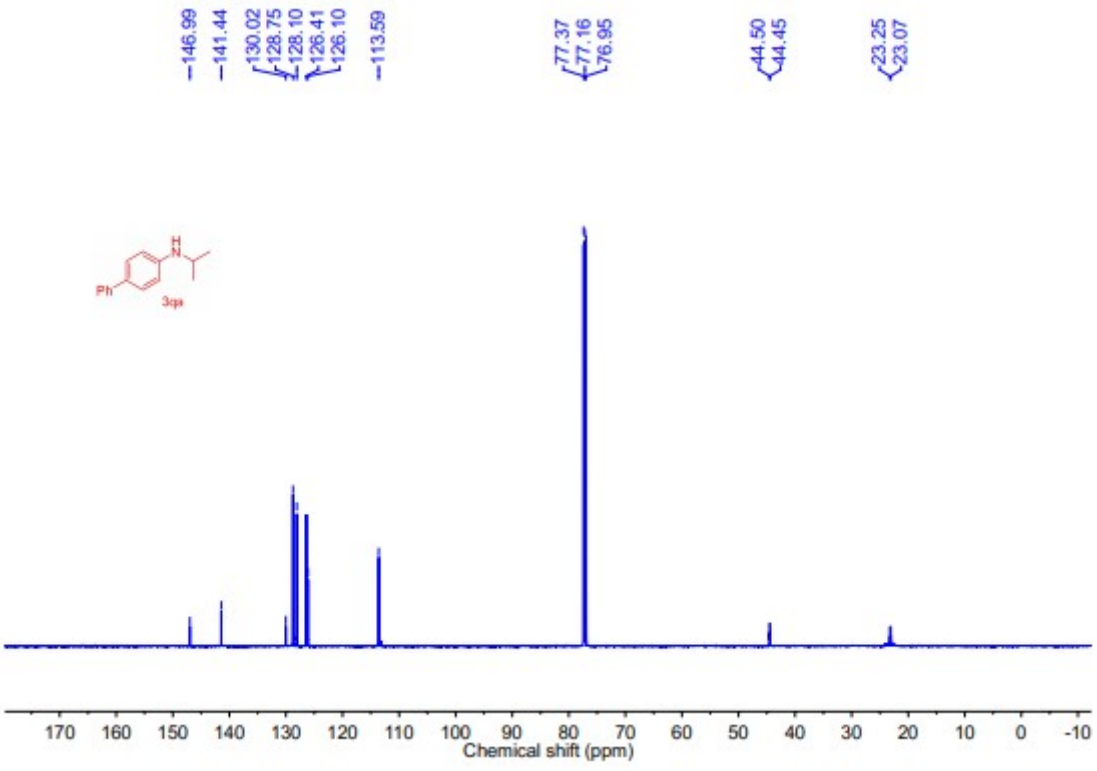
^{1}H NMR (600 MHz, $CDCl_3$, 298 K) of **3ja**



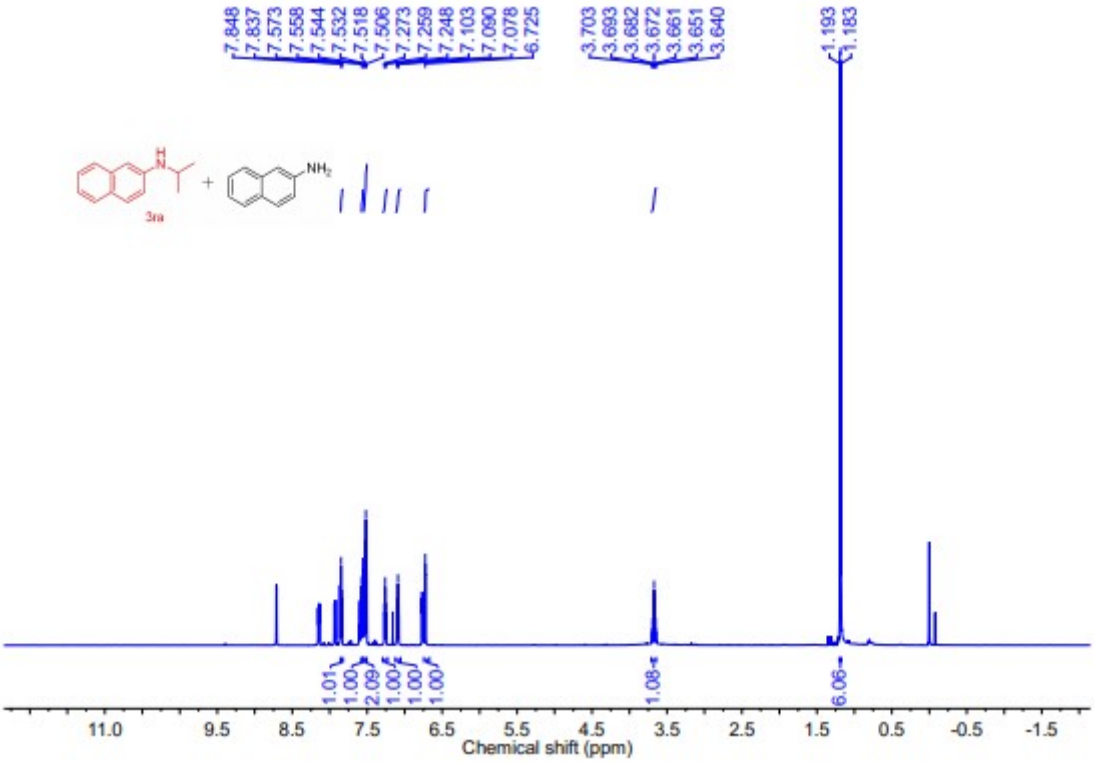
^{13}C{^{1}H} NMR (151 MHz, $CDCl_3$, 298 K) of **3ja**



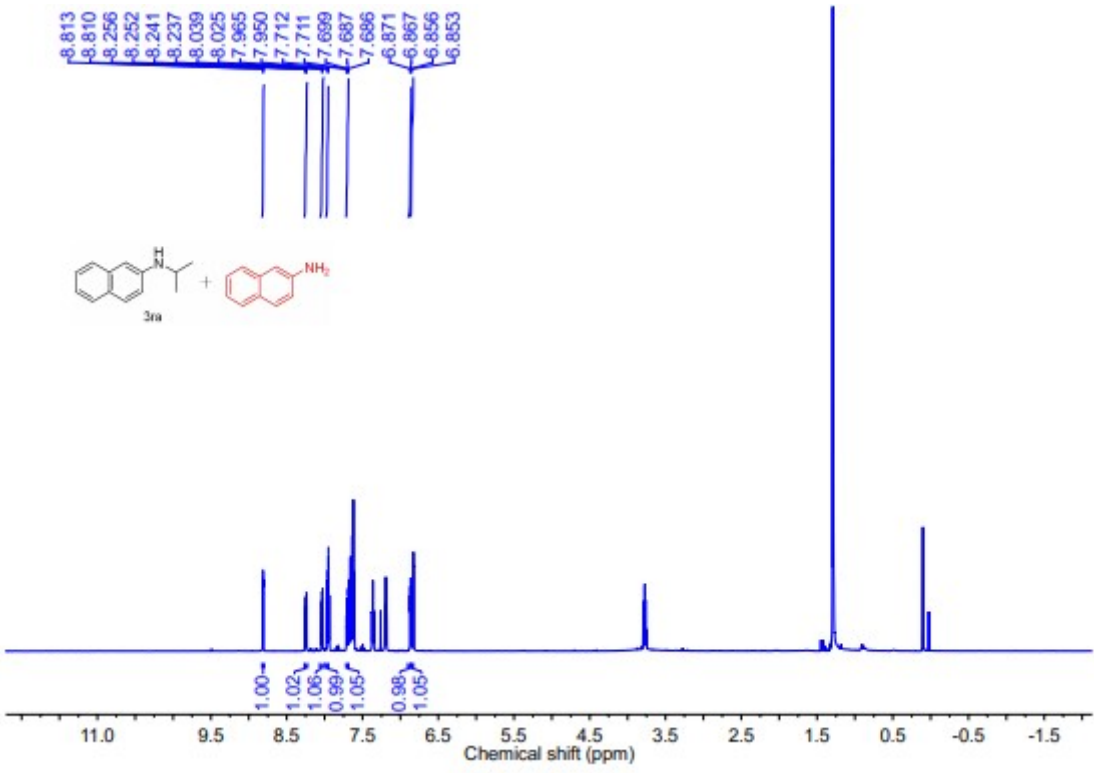
^{1}H NMR (600 MHz, $CDCl_3$, 298 K) of **3qa**



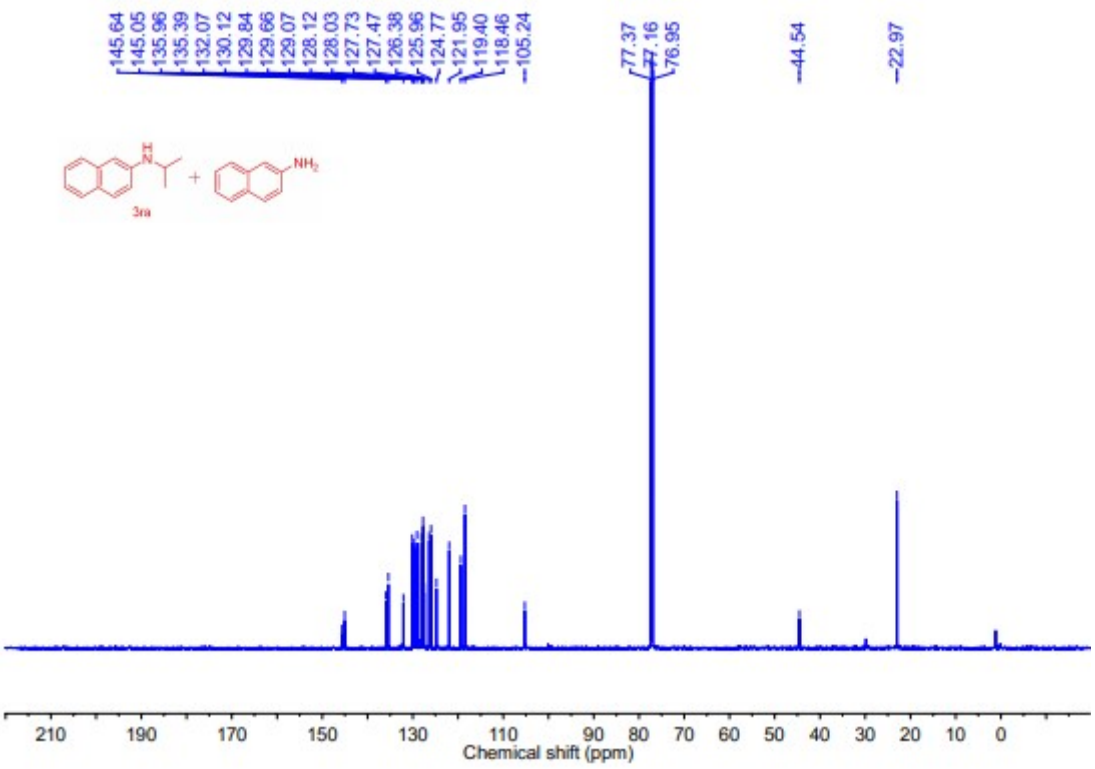
^{13}C{^{1}H} NMR (151 MHz, $CDCl_3$, 298 K) of **3qa**



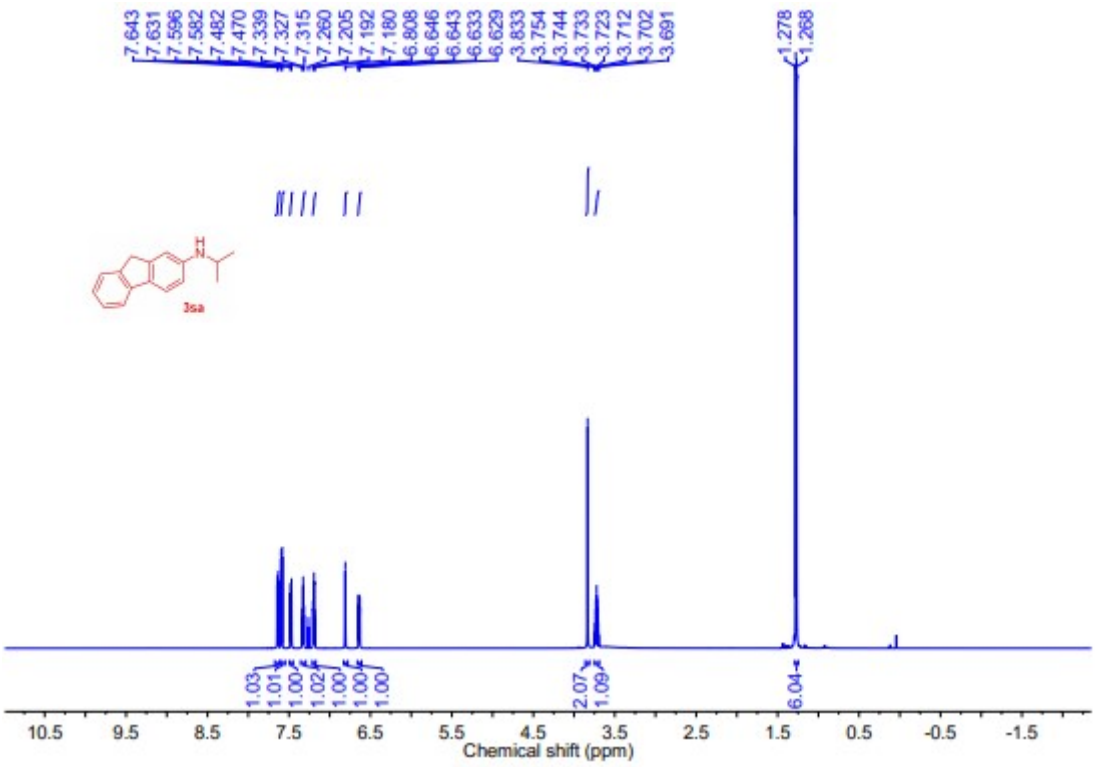
^{1}H NMR (600 MHz, $CDCl_3$, 298 K) of **3ra**



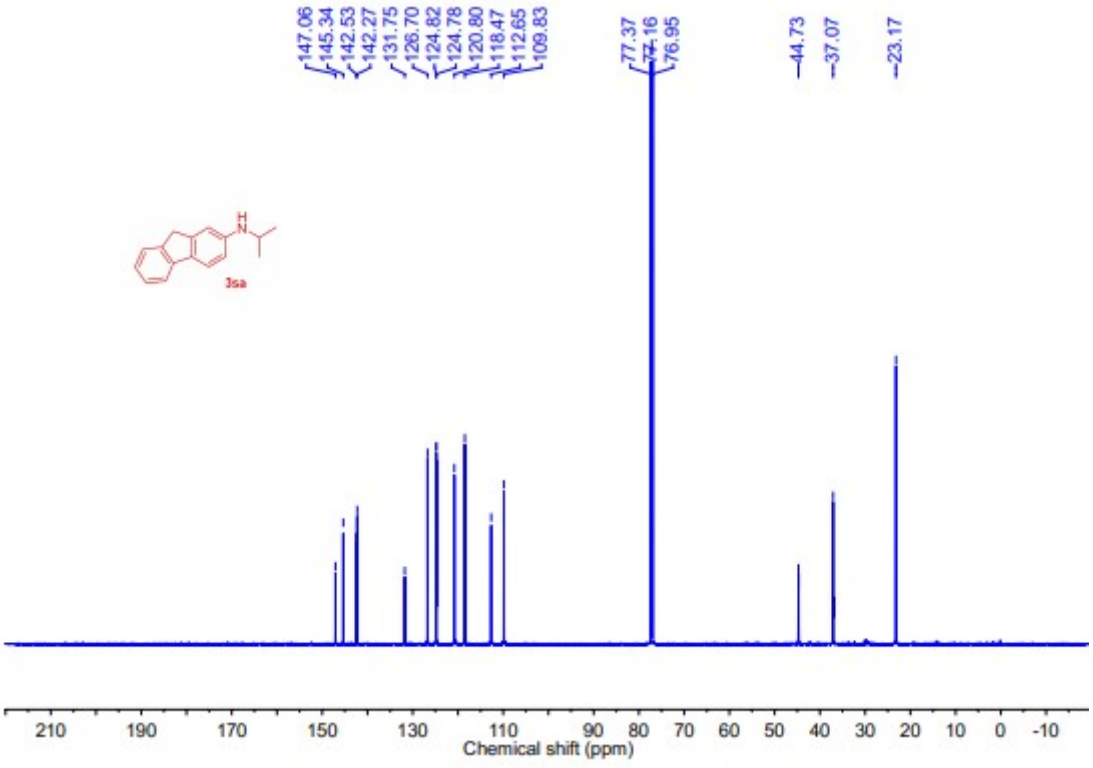
^{1}H NMR (600 MHz, $CDCl_3$, 298 K) of 4**r**



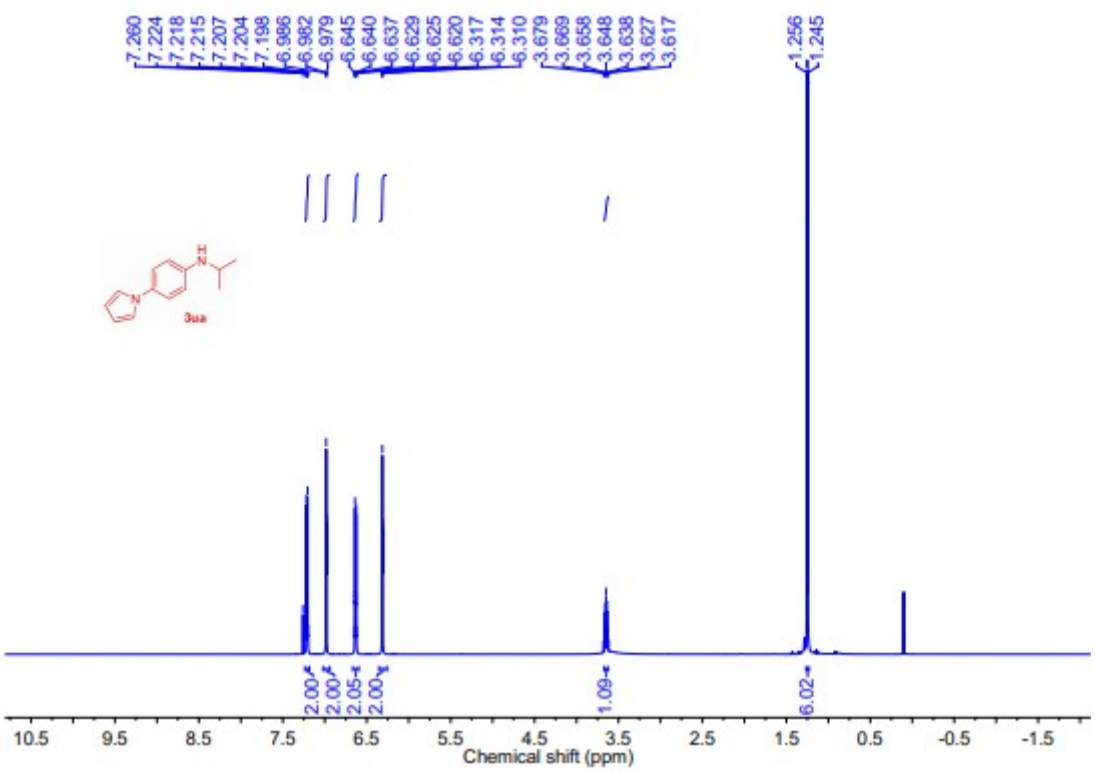
$^{13}C\{^{1}H\}$ NMR (151 MHz, $CDCl_3$, 298 K) of **3ra**



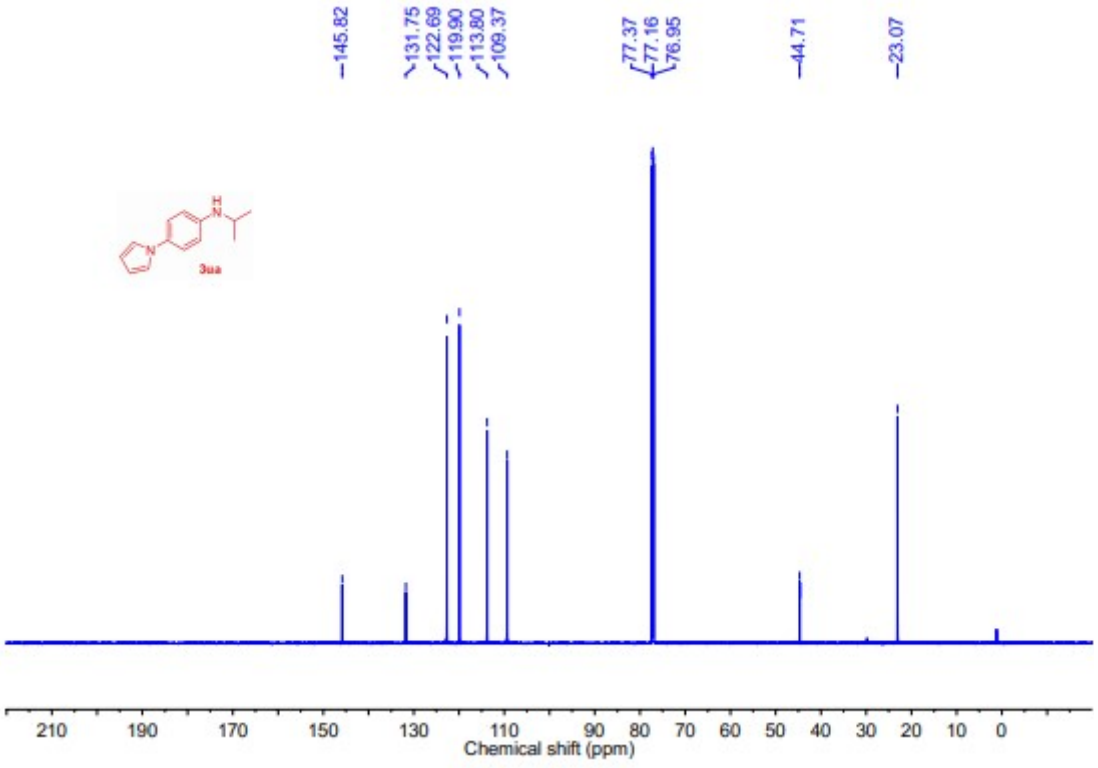
^{1}H NMR (600 MHz, $CDCl_3$, 298 K) of **3sa**



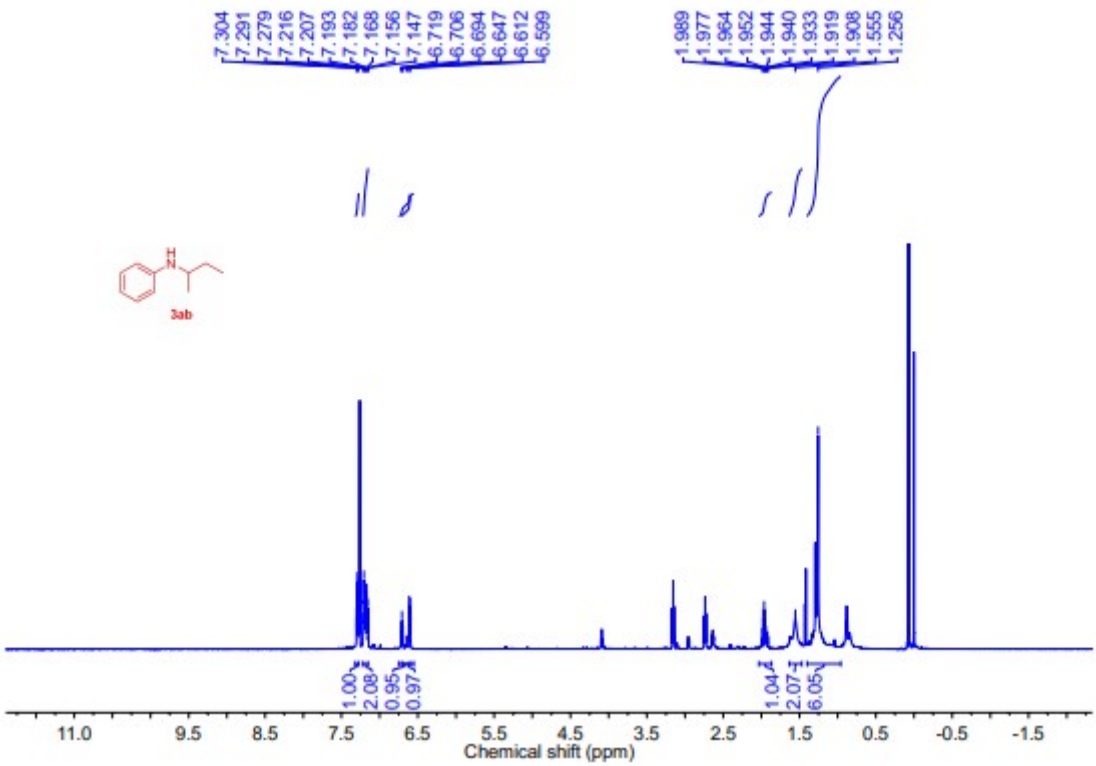
^{13}C{^{1}H} NMR (151 MHz, $CDCl_3$, 298 K) of **3sa**



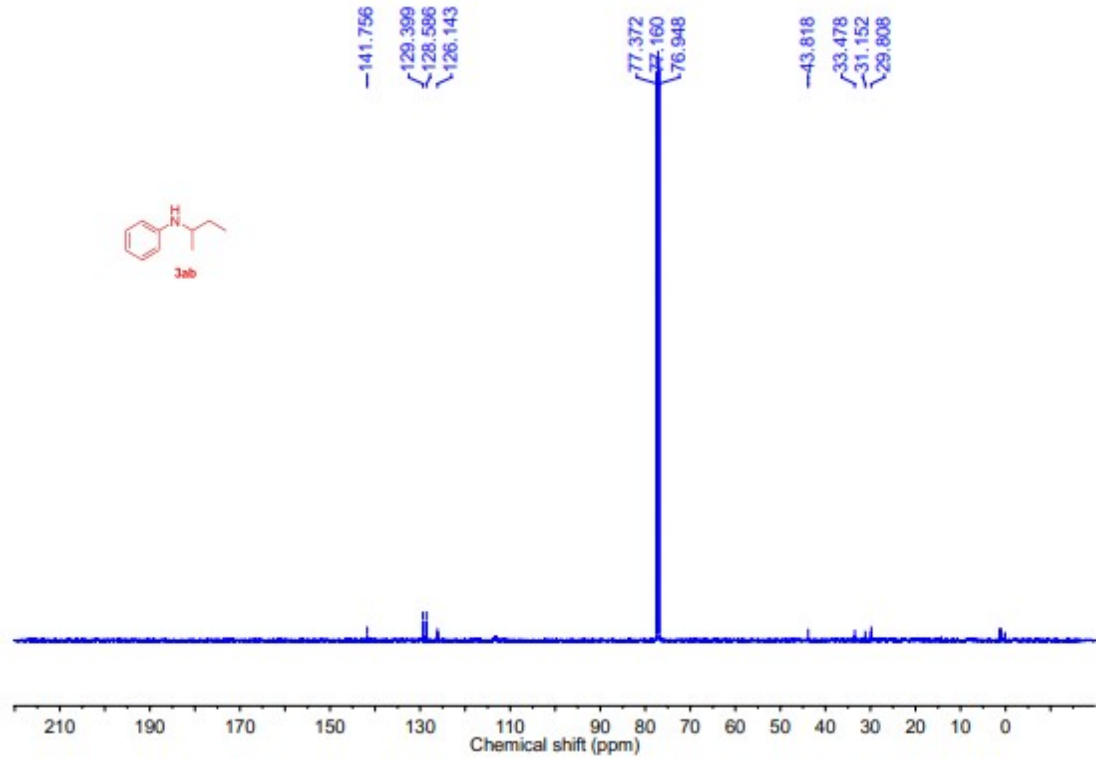
^{1}H NMR (600 MHz, $CDCl_3$, 298 K) of **3ua**



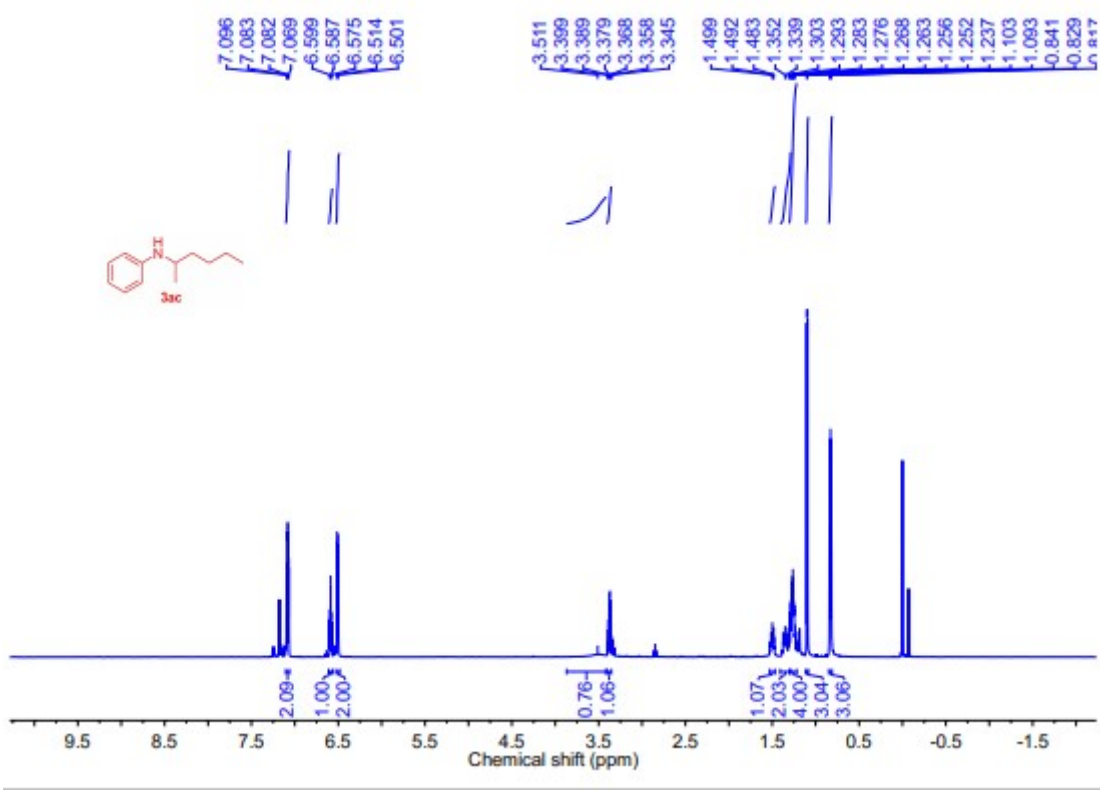
^{13}C{^{1}H} NMR (151 MHz, $CDCl_3$, 298 K) of **3sa**



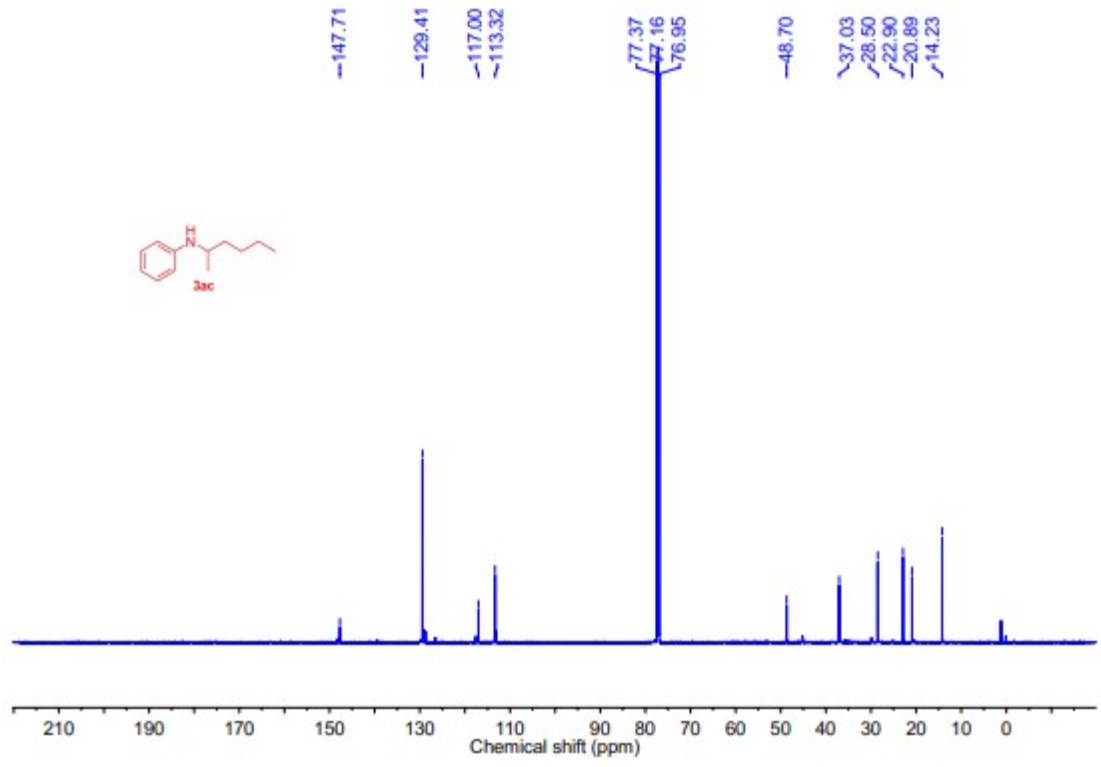
^{1}H NMR (600 MHz, $CDCl_3$, 298 K) of **3ab**



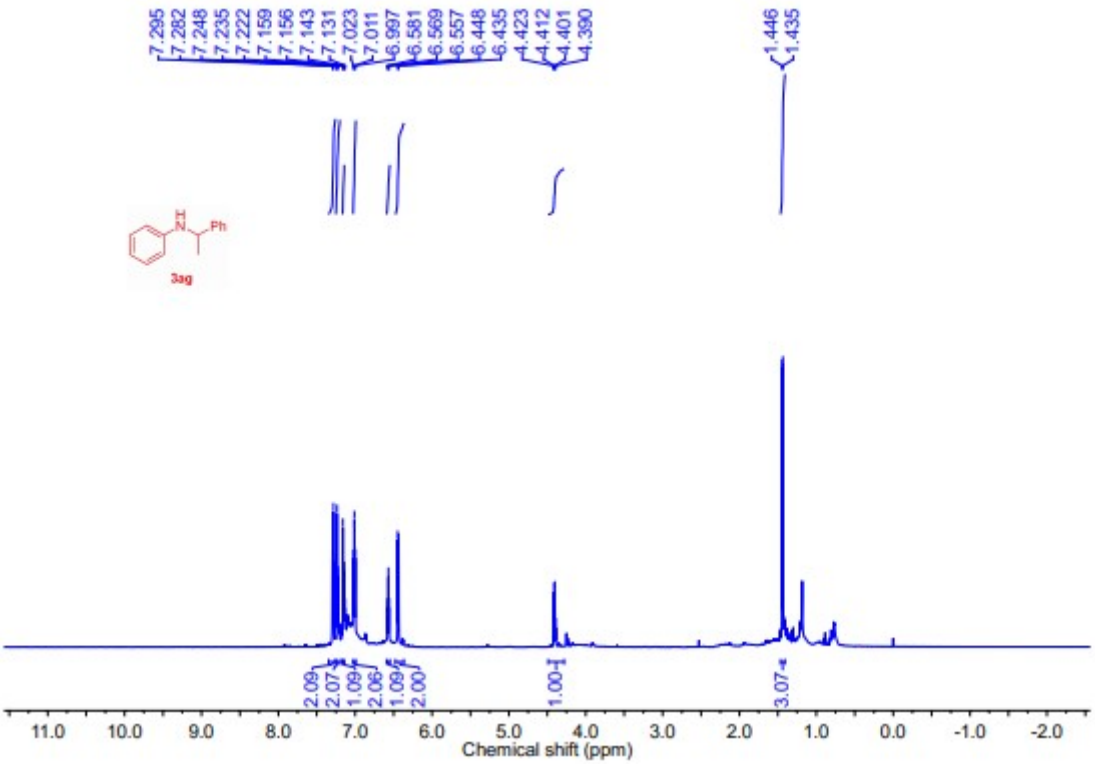
^{13}C{^{1}H} NMR (151 MHz, $CDCl_3$, 298 K) of **3ab**



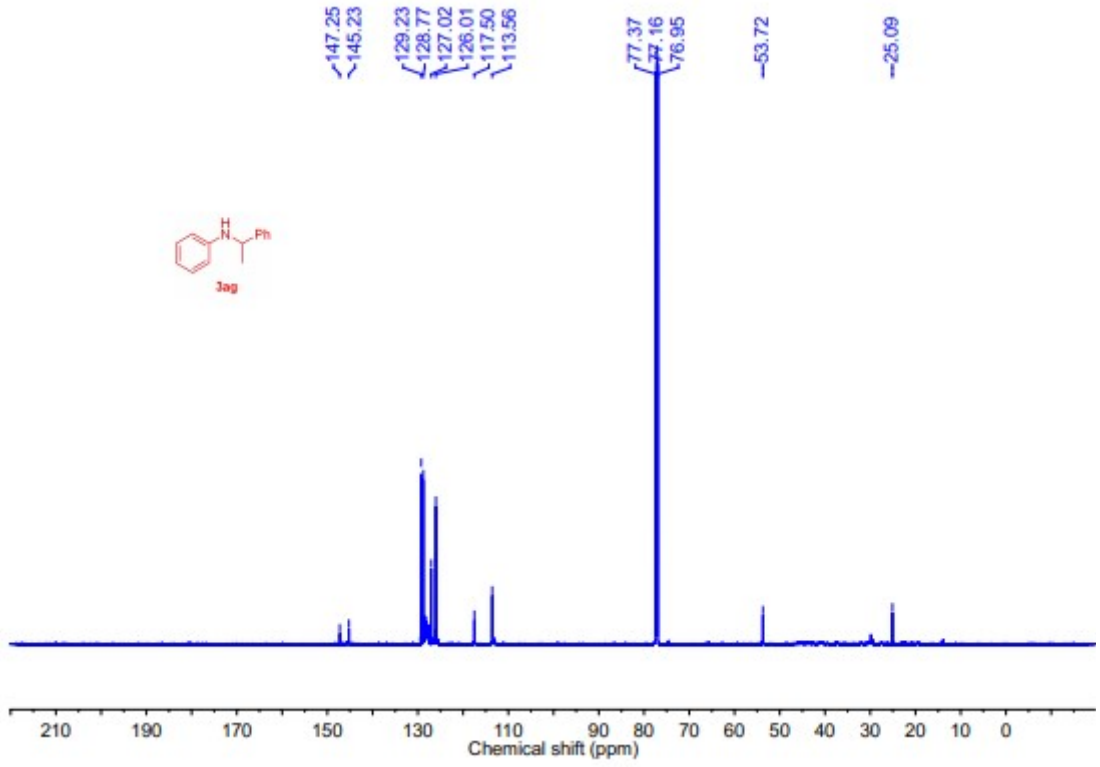
^{1}H NMR (600 MHz, $CDCl_3$, 298 K) of **3ac**



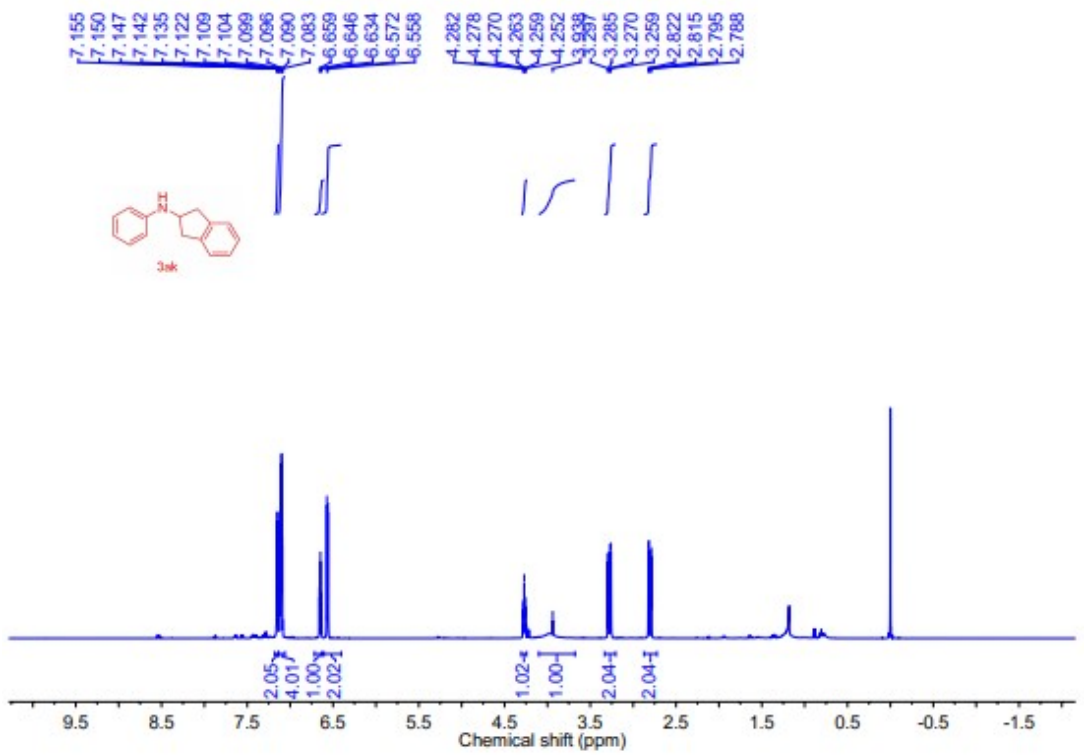
^{13}C{^{1}H} NMR (151 MHz, $CDCl_3$, 298 K) of **3ac**



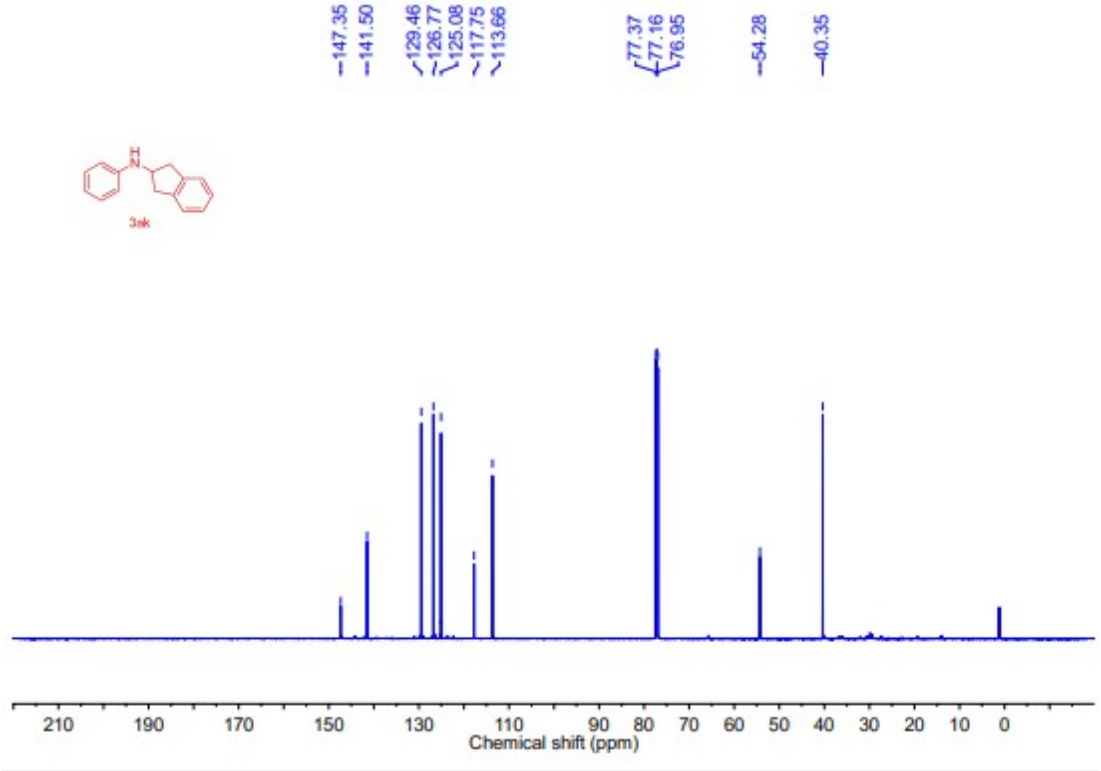
^{1}H NMR (600 MHz, $CDCl_3$, 298 K) of **3ag**



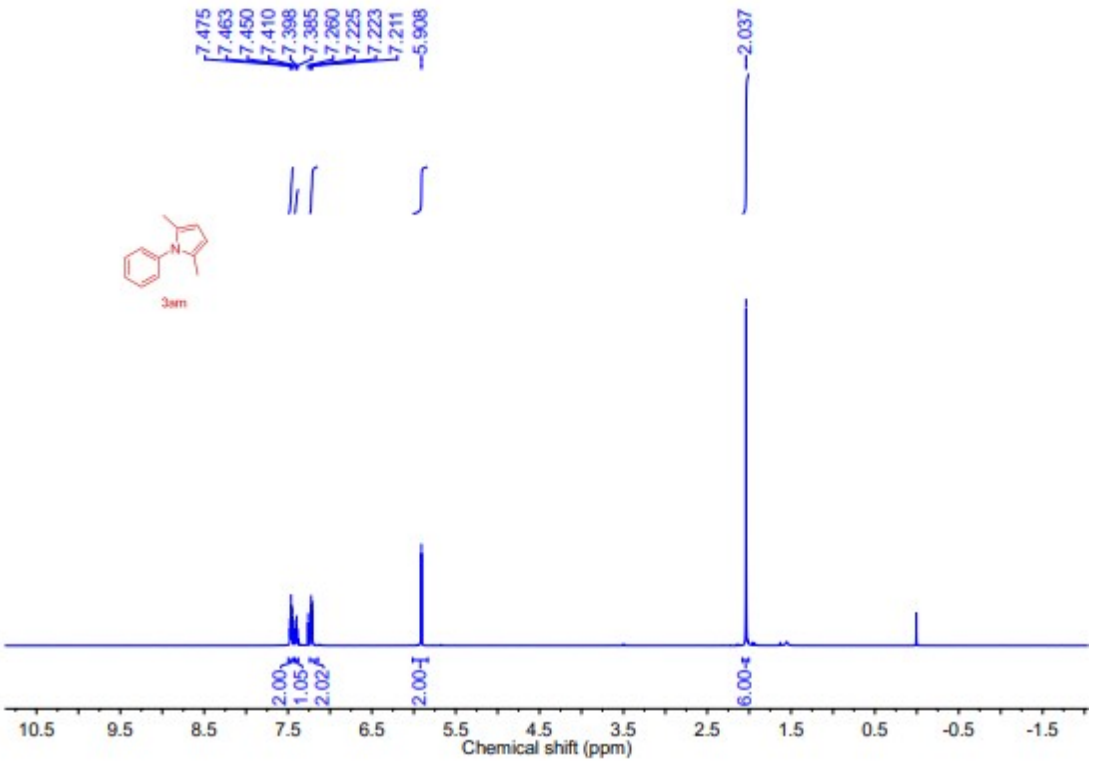
^{13}C{^{1}H} NMR (151 MHz, $CDCl_3$, 298 K) of **3ag**



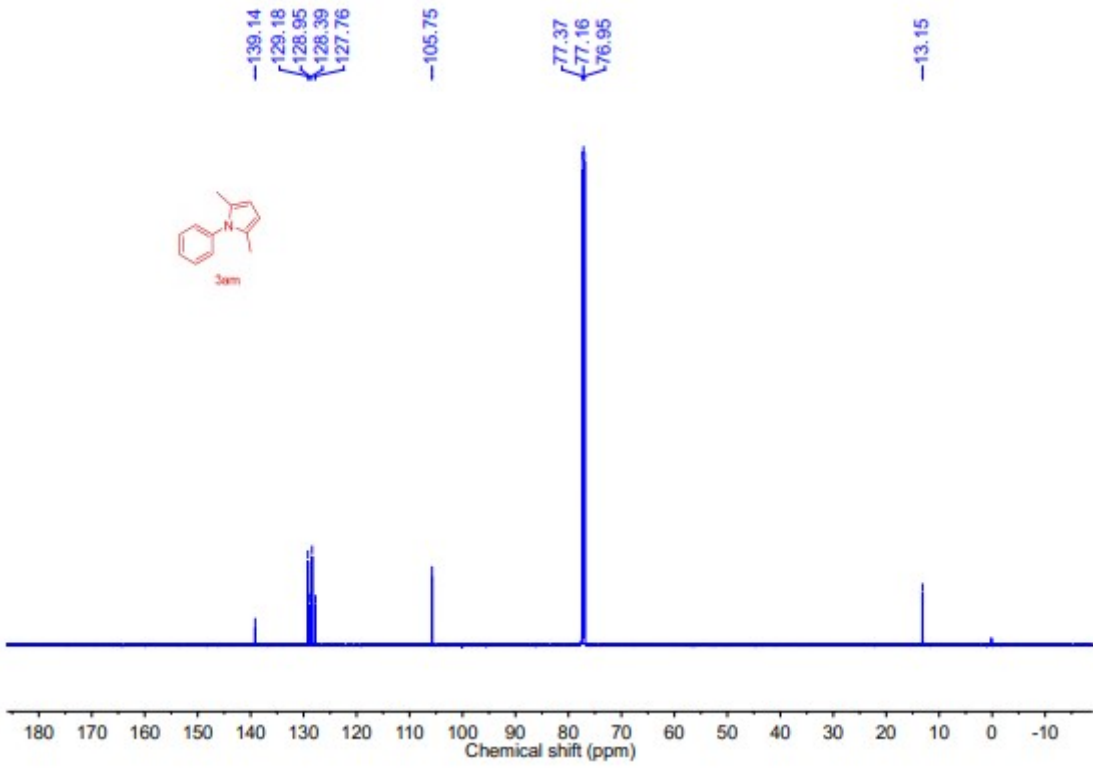
^{1}H NMR (600 MHz, $CDCl_3$, 298 K) of **3ak**



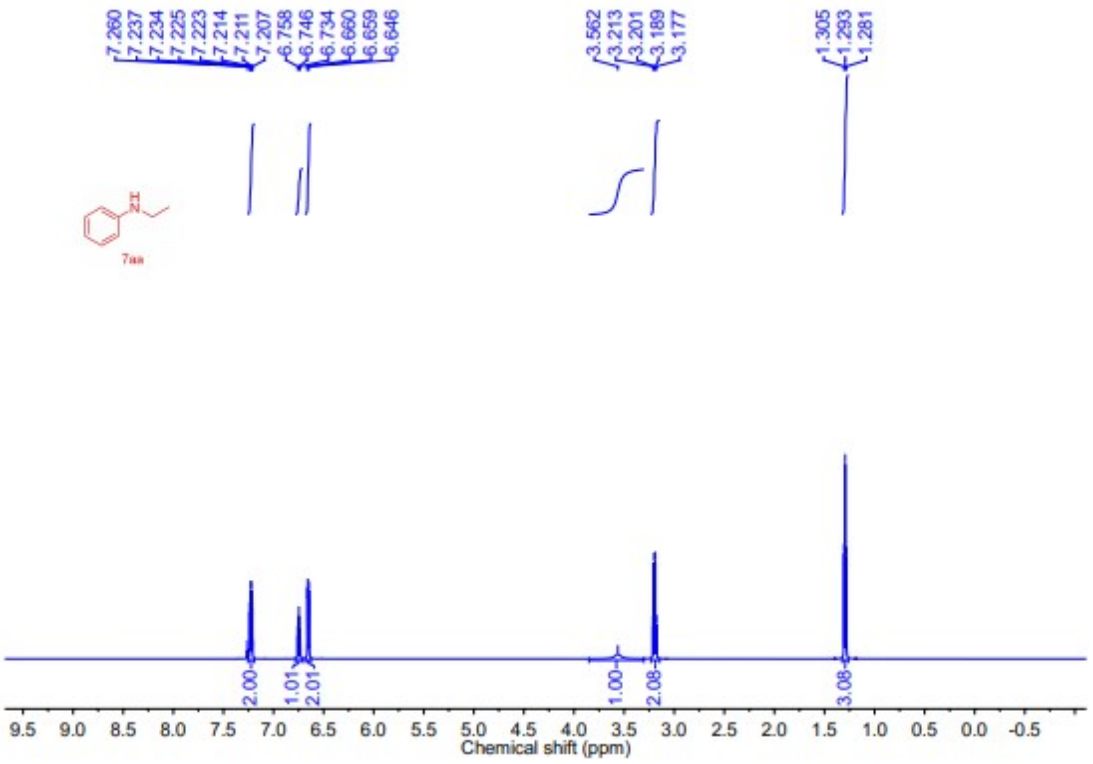
^{13}C{^{1}H} NMR (151 MHz, $CDCl_3$, 298 K) of **3ak**



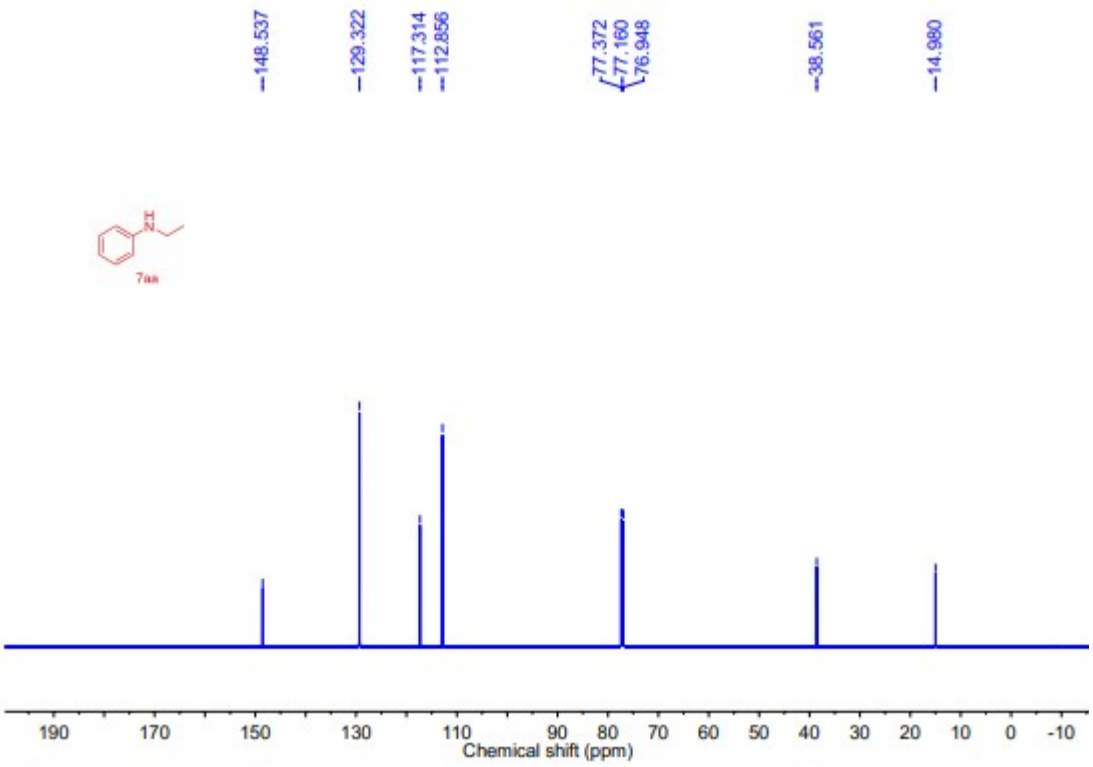
^{1}H NMR (600 MHz, $CDCl_3$, 298 K) of **3an**



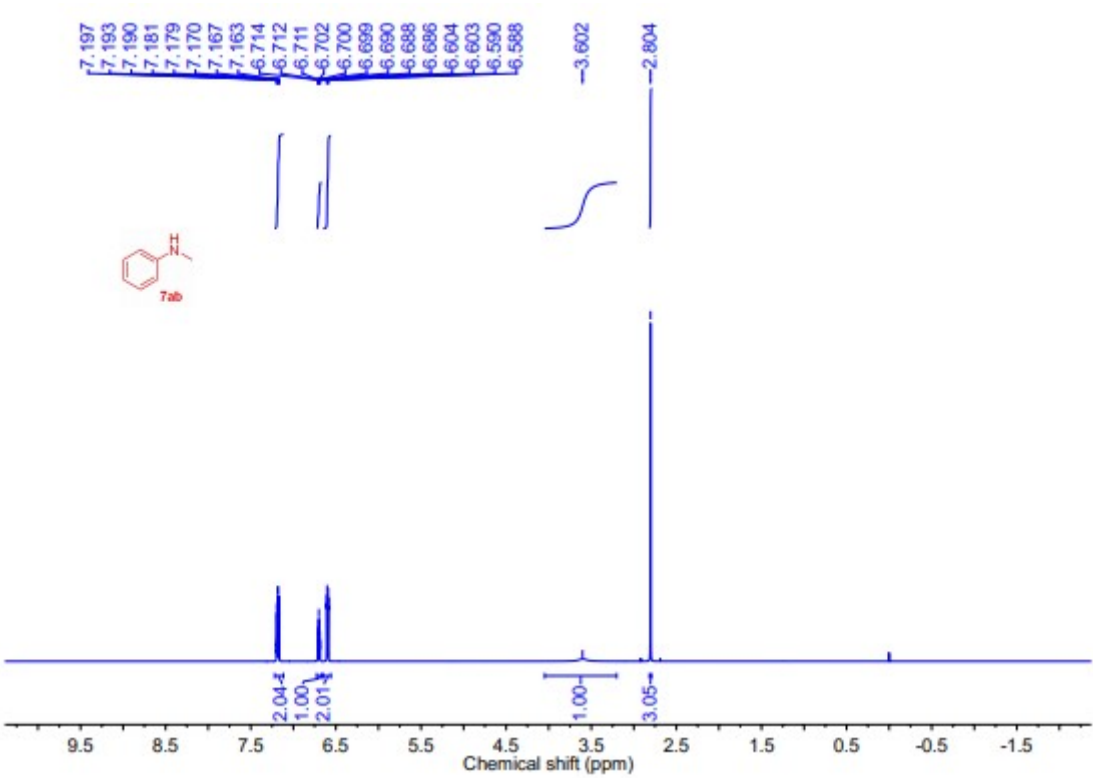
^{13}C{^{1}H} NMR (151 MHz, $CDCl_3$, 298 K) of **3an**



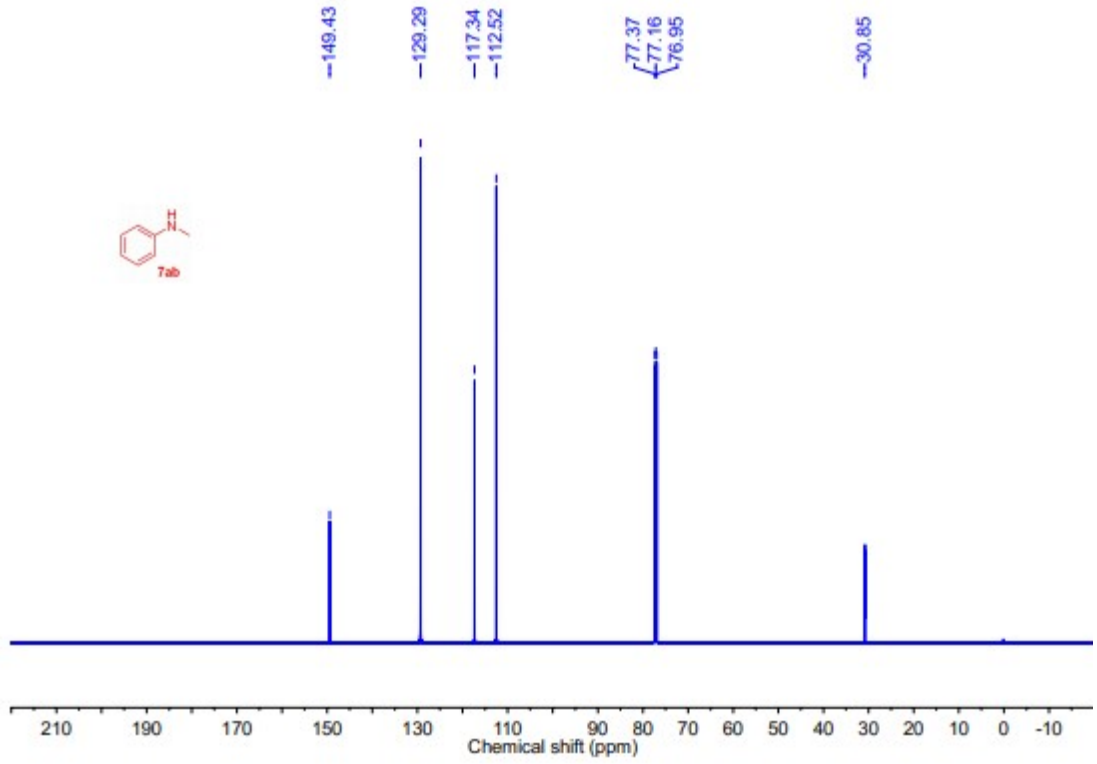
^{1}H NMR (600 MHz, $CDCl_3$, 298 K) of **7aa**



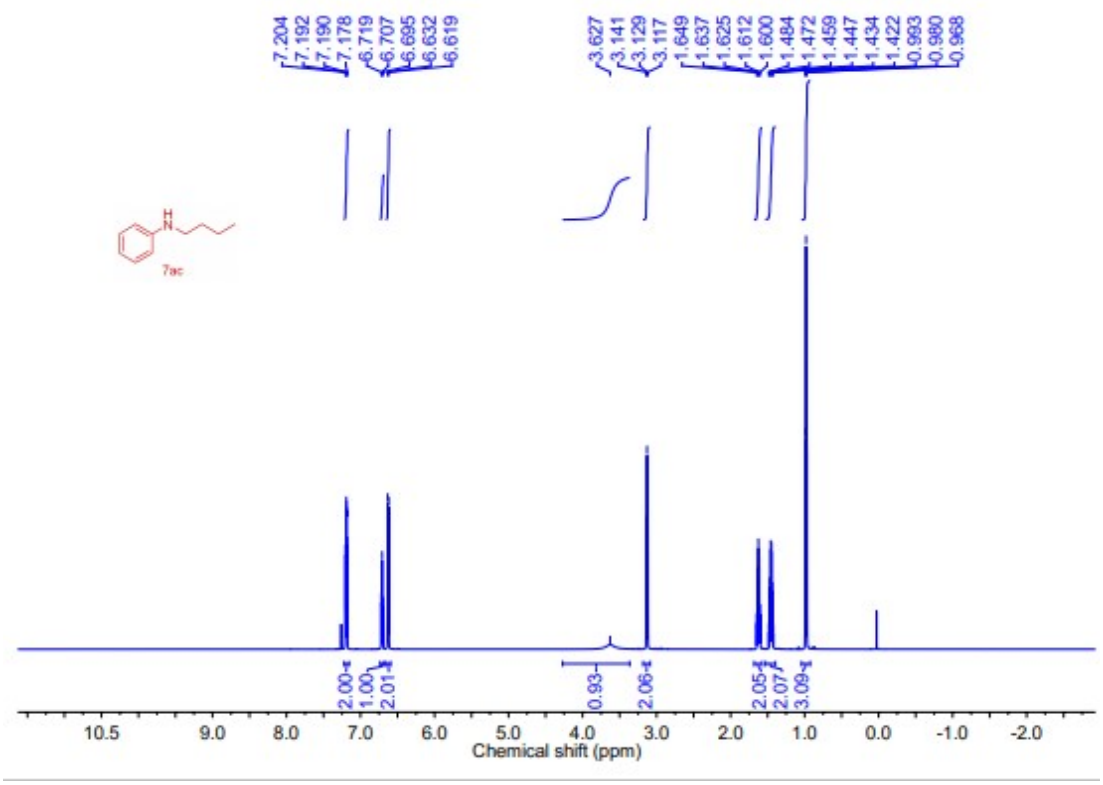
^{13}C{^{1}H} NMR (151 MHz, $CDCl_3$, 298 K) of **7aa**



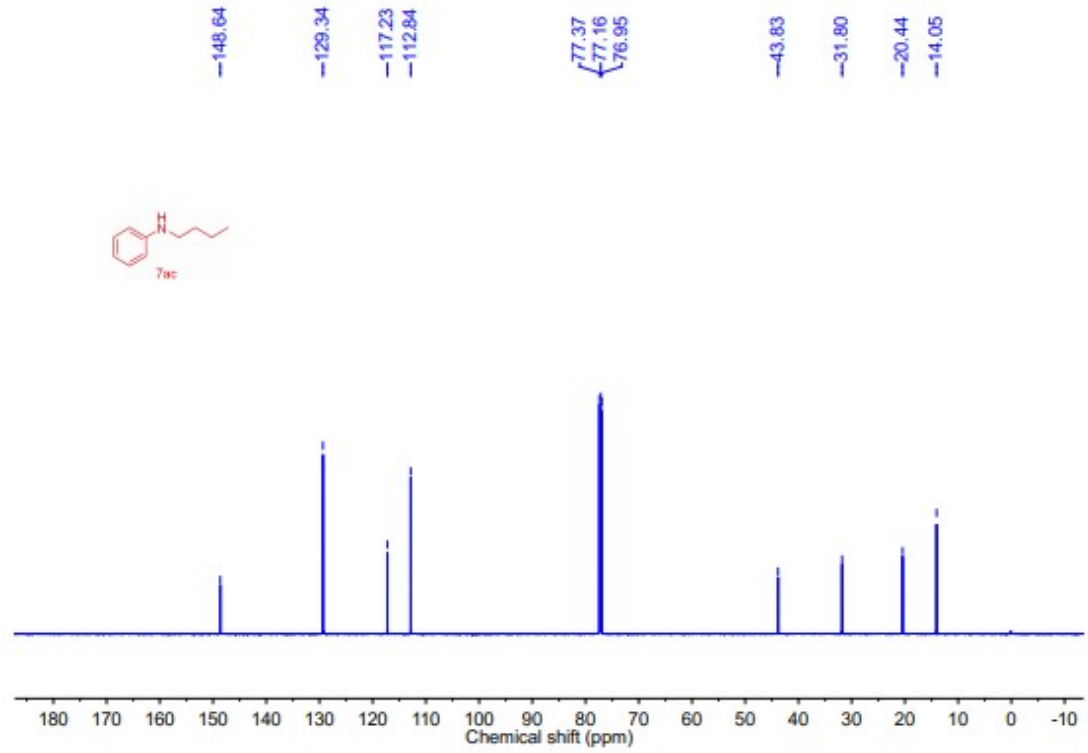
^{1}H NMR (600 MHz, $CDCl_3$, 298 K) of **7ab**



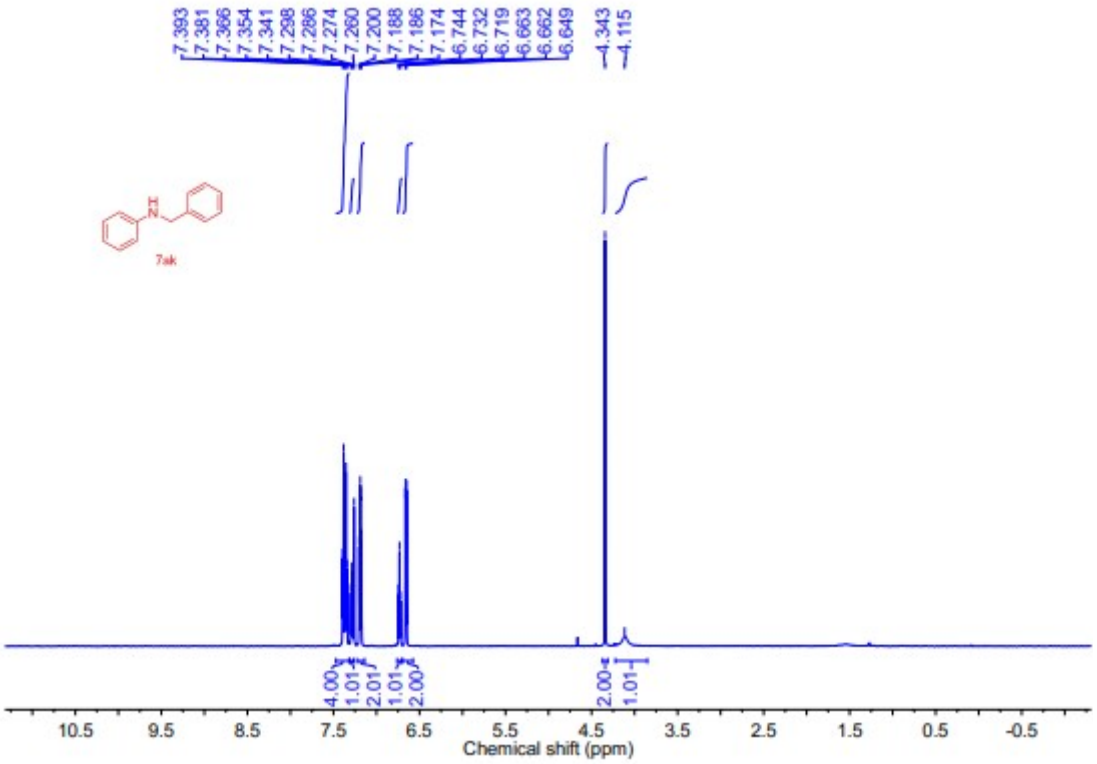
^{13}C{^{1}H} NMR (151 MHz, $CDCl_3$, 298 K) of **7ab**



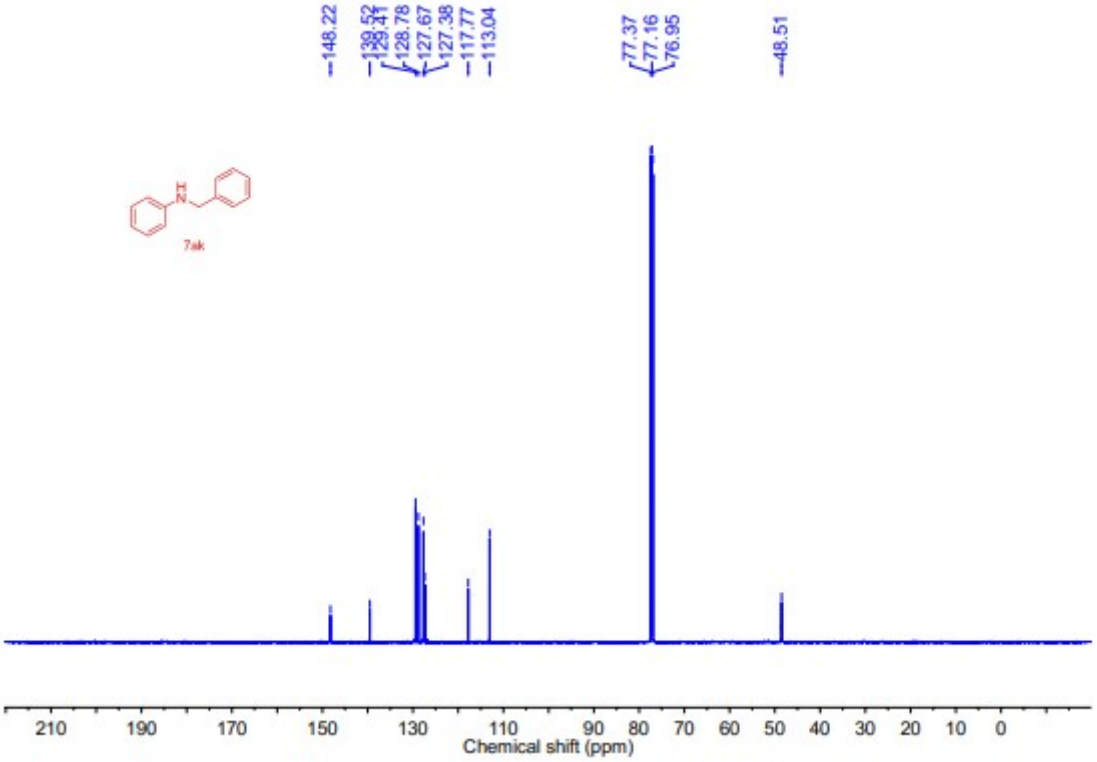
^{1}H NMR (600 MHz, $CDCl_3$, 298 K) of **7ac**



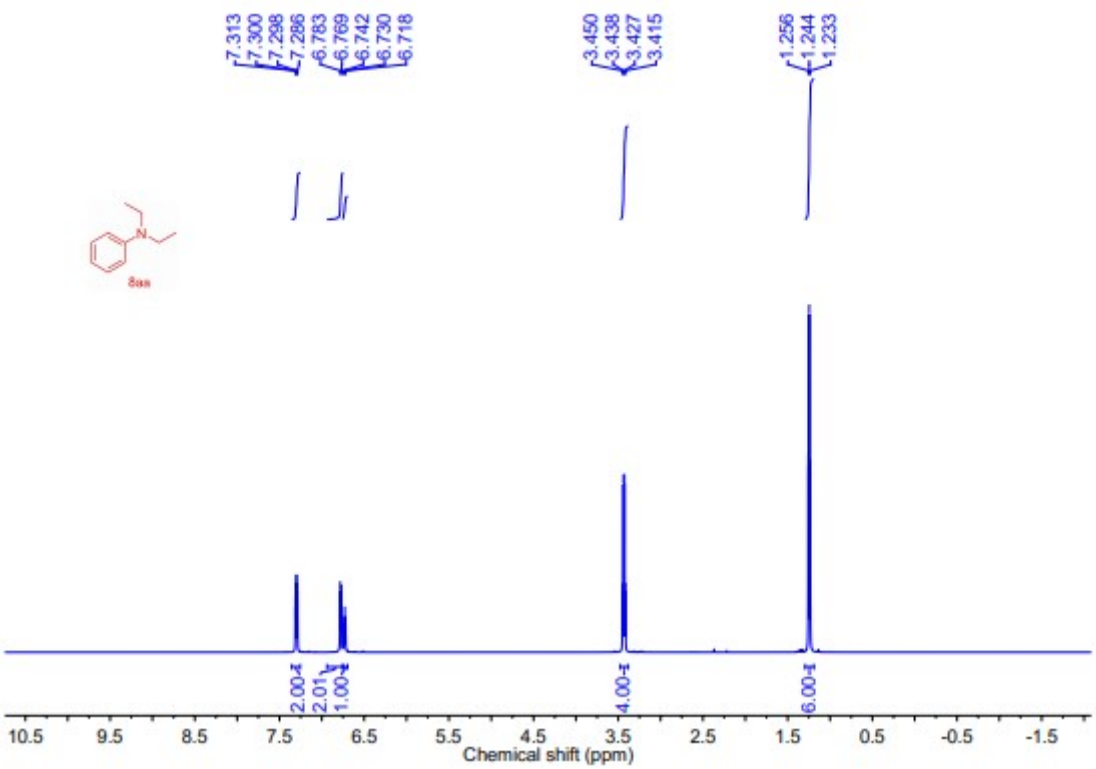
^{13}C{^{1}H} NMR (151 MHz, $CDCl_3$, 298 K) of **7ac**



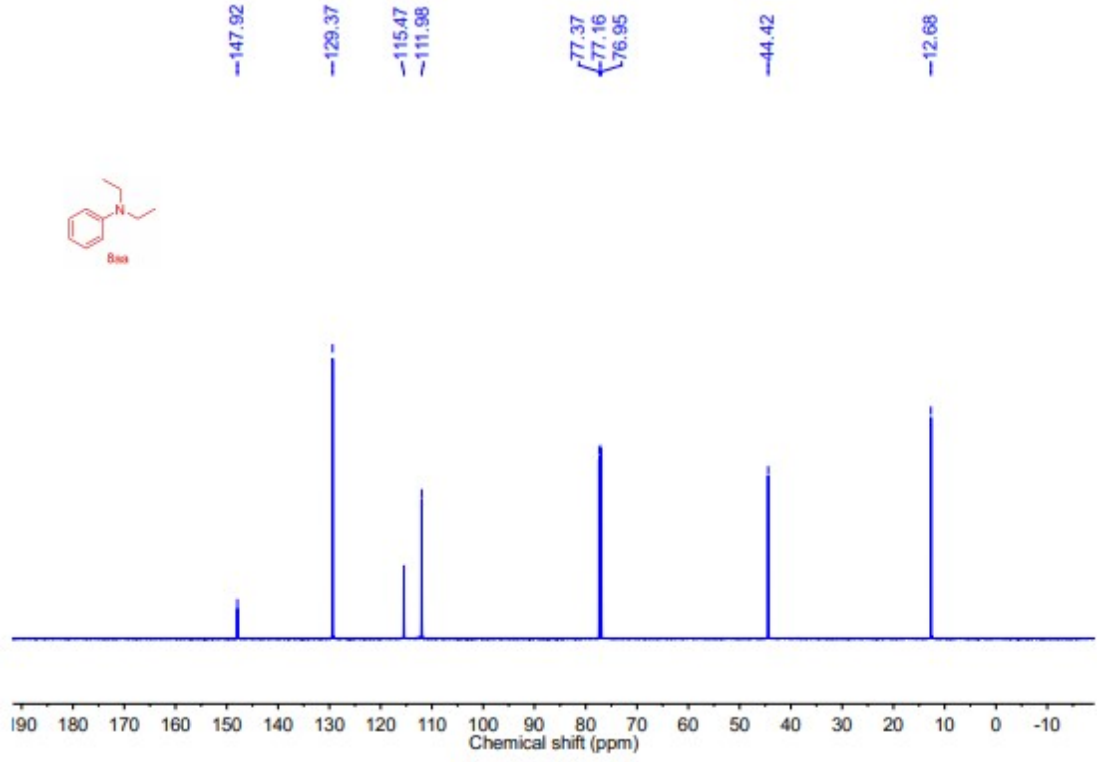
^{1}H NMR (600 MHz, $CDCl_3$, 298 K) of **7ak**



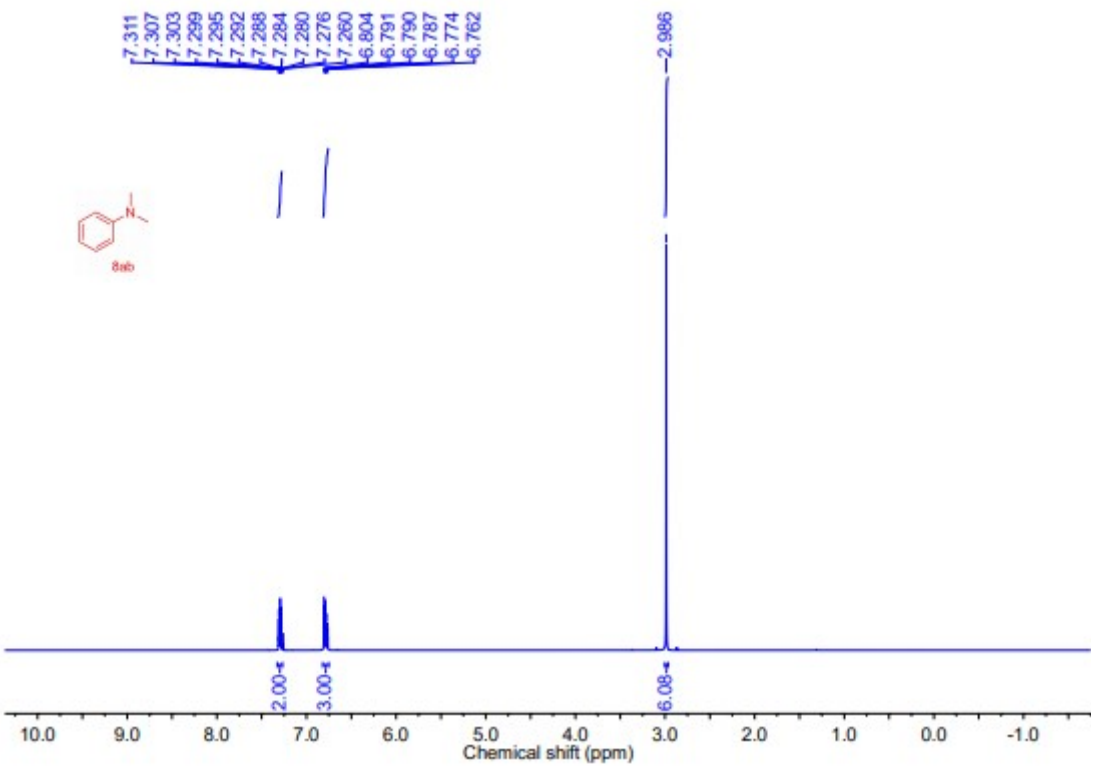
^{13}C{^{1}H} NMR (151 MHz, $CDCl_3$, 298 K) of **7ak**



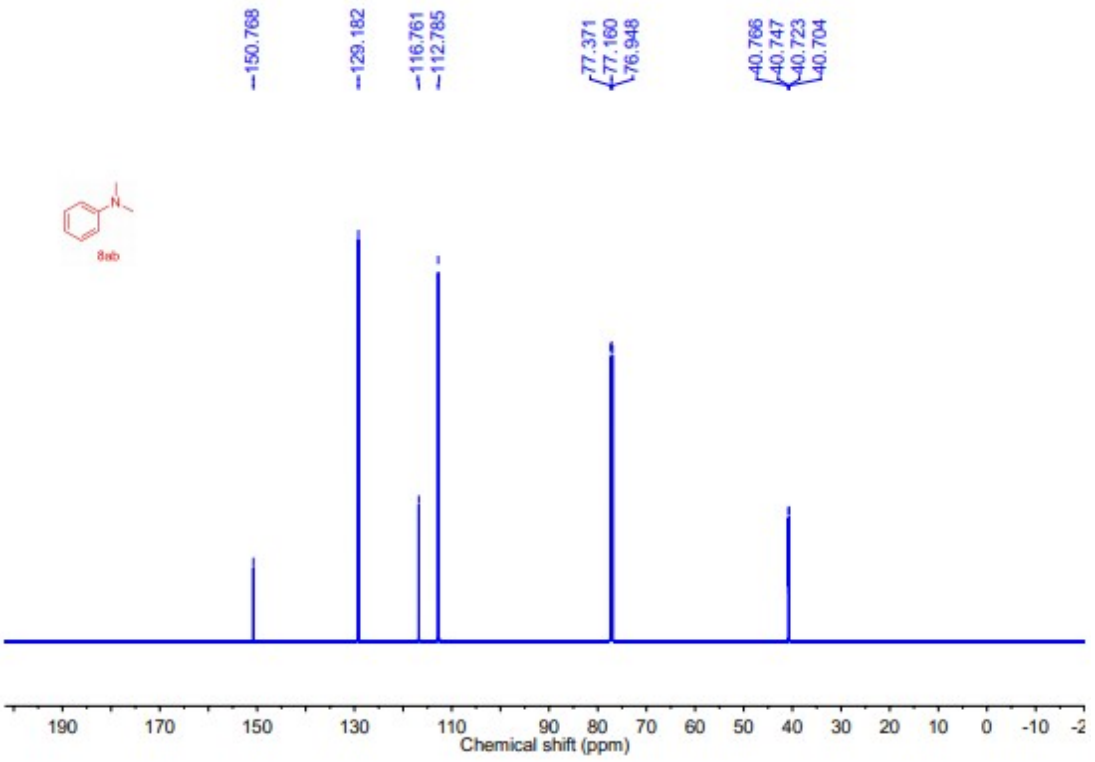
^{1}H NMR (600 MHz, $CDCl_3$, 298 K) of **8aa**



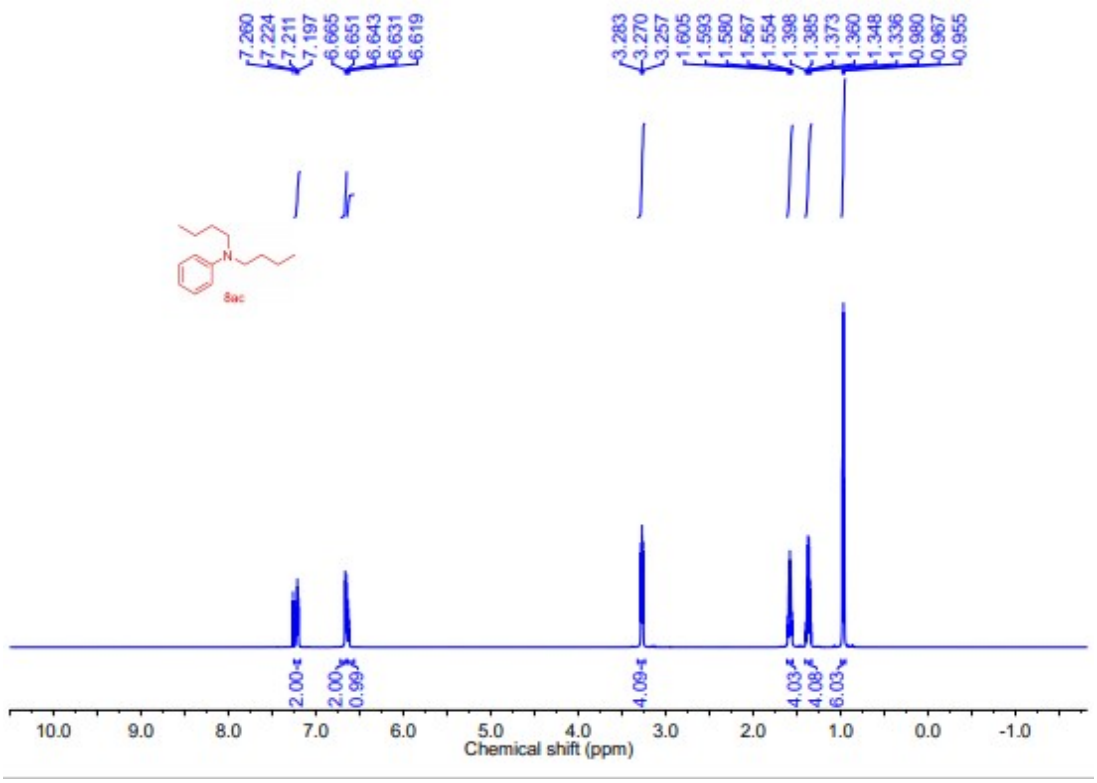
^{13}C{^{1}H} NMR (151 MHz, $CDCl_3$, 298 K) of **8aa**



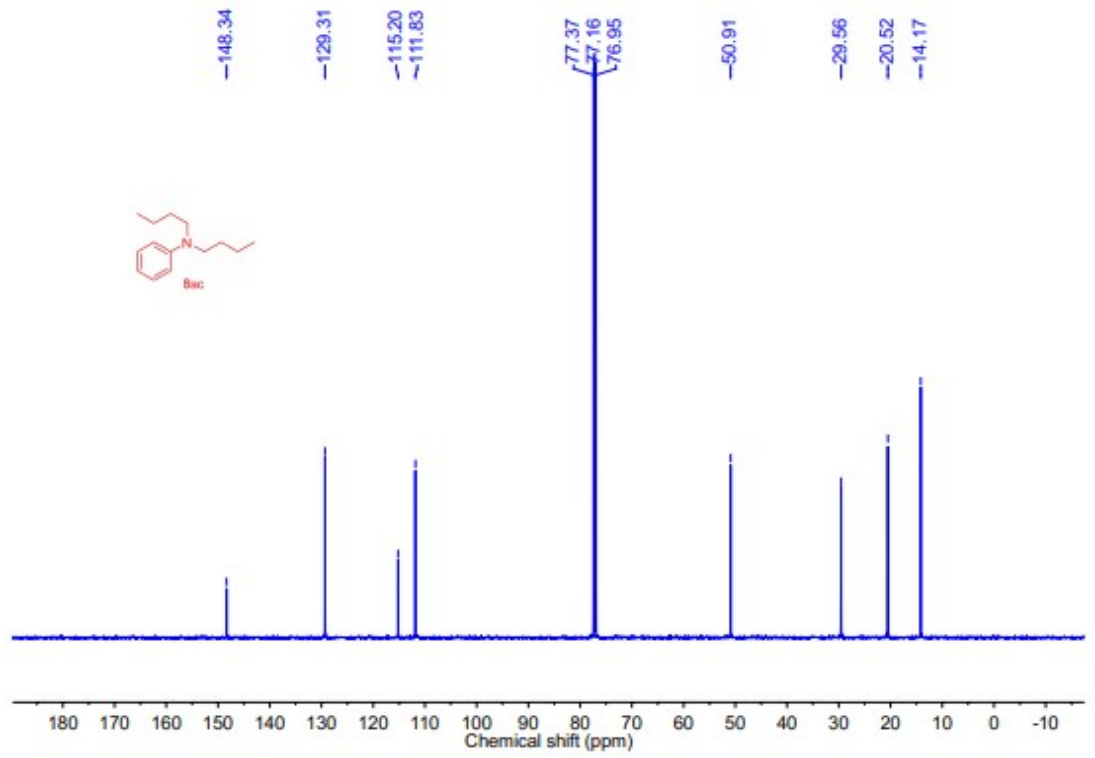
^{1}H NMR (600 MHz, $CDCl_3$, 298 K) of **8ab**



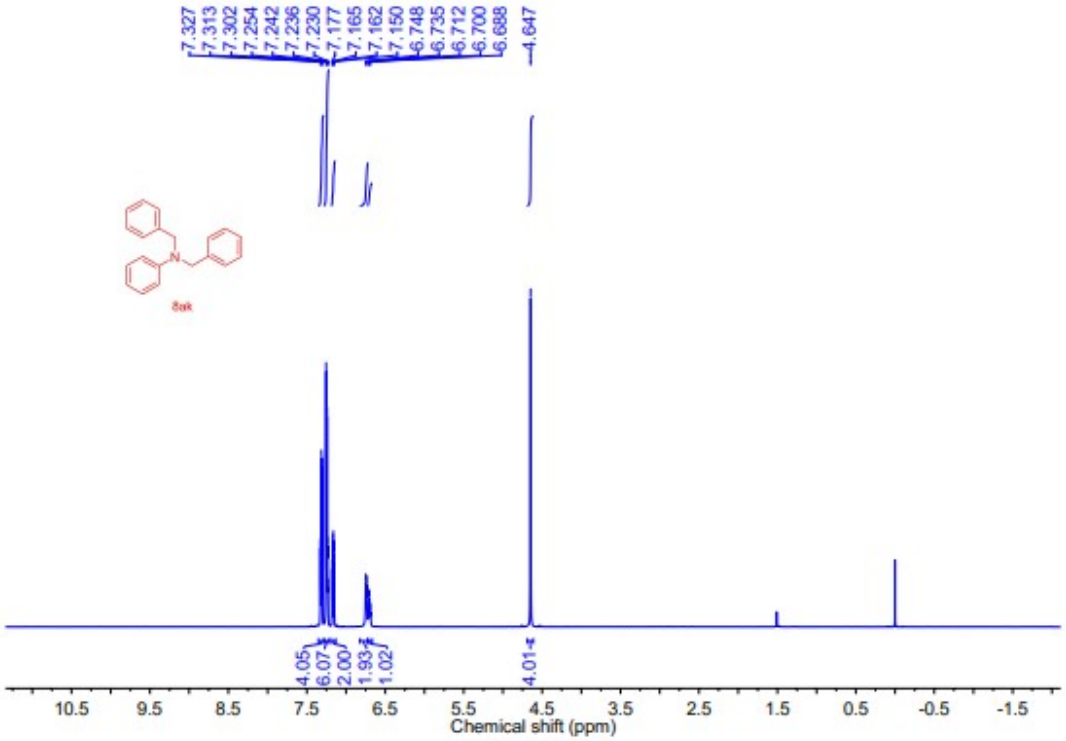
^{13}C{^{1}H} NMR (151 MHz, $CDCl_3$, 298 K) of **8ab**



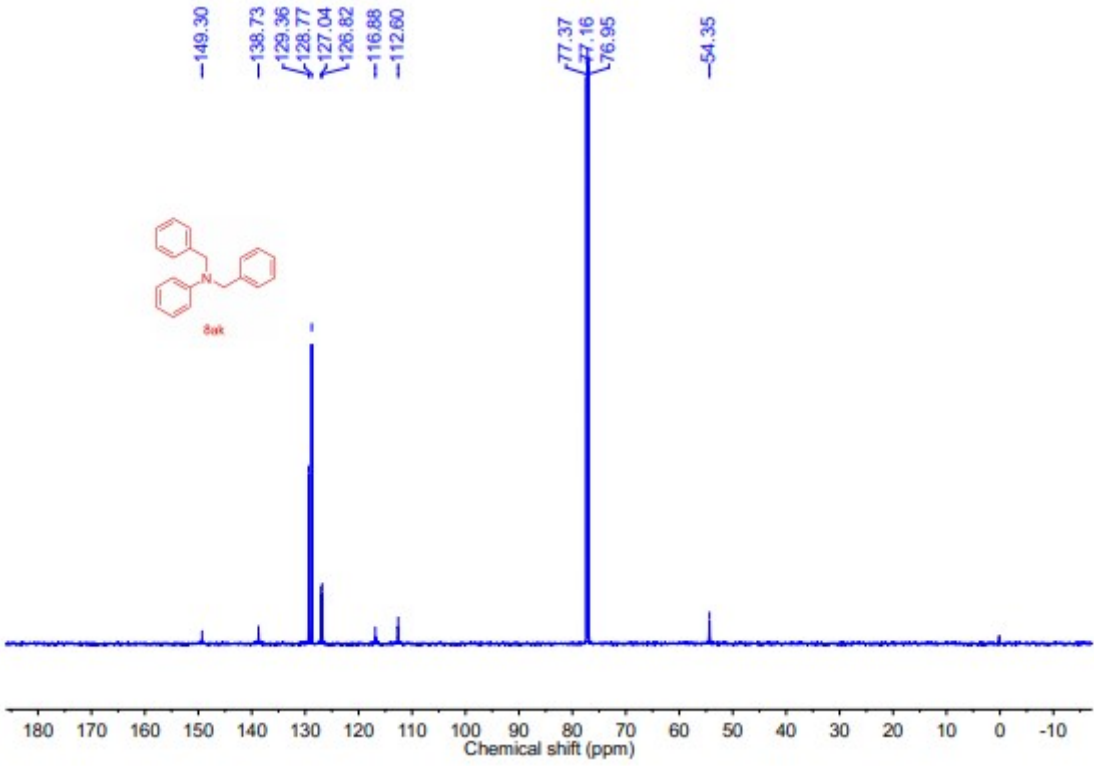
^{1}H NMR (600 MHz, $CDCl_3$, 298 K) of **8ac**



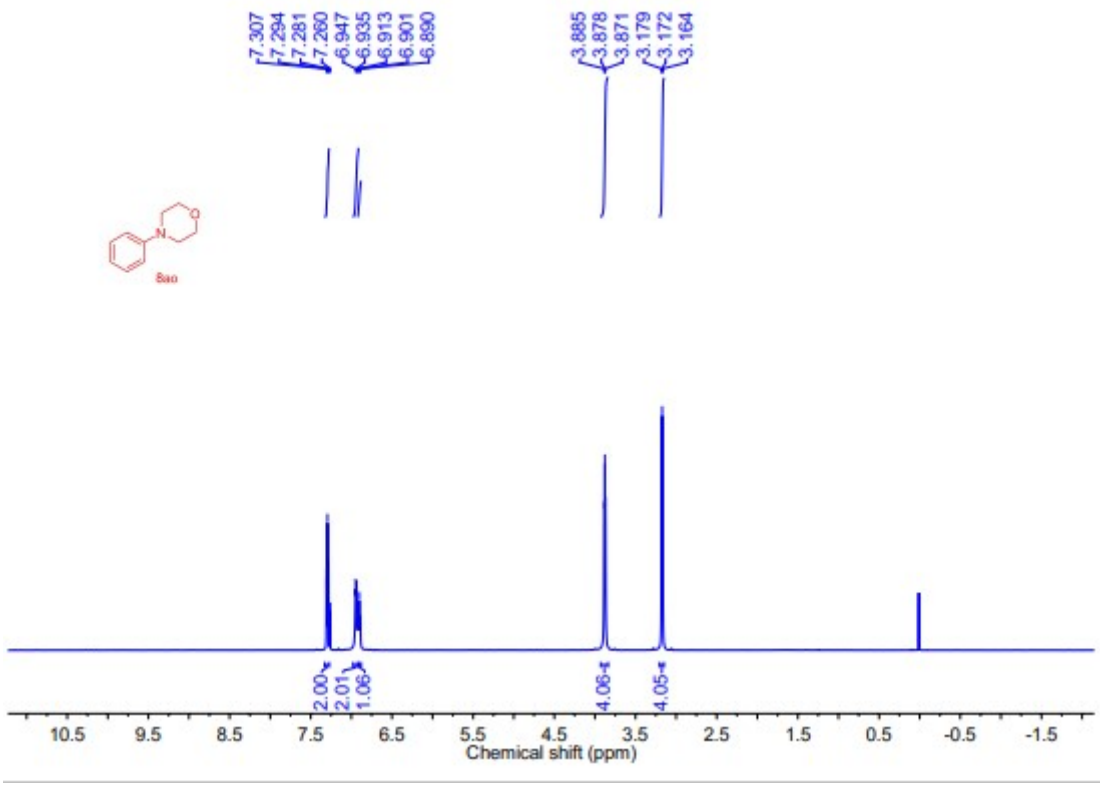
^{13}C{^{1}H} NMR (151 MHz, $CDCl_3$, 298 K) of **8ac**



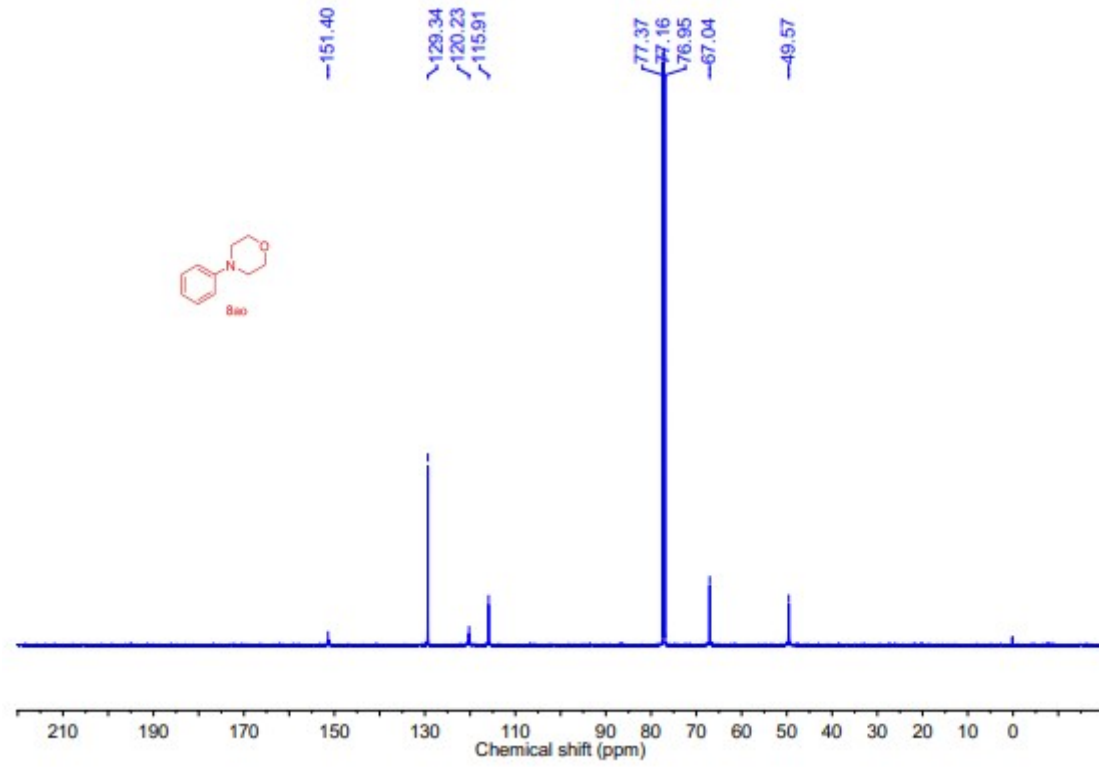
^{1}H NMR (600 MHz, $CDCl_3$, 298 K) of **8ak**



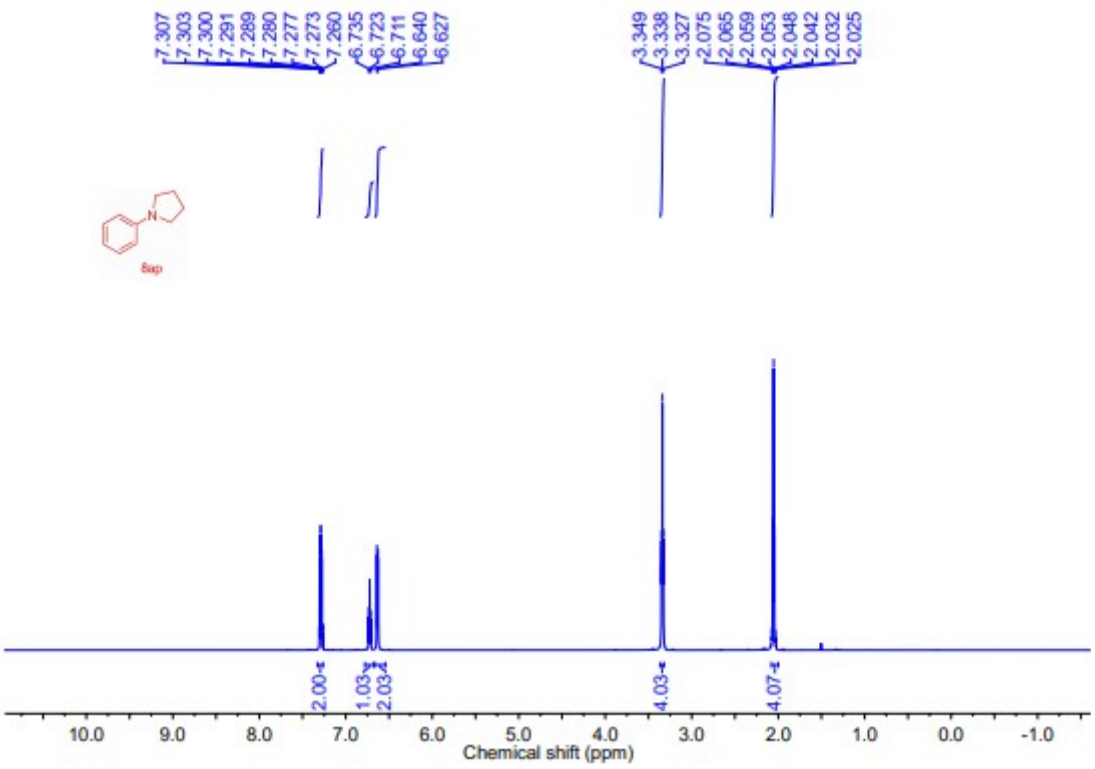
^{13}C{^{1}H} NMR (151 MHz, $CDCl_3$, 298 K) of **8ak**



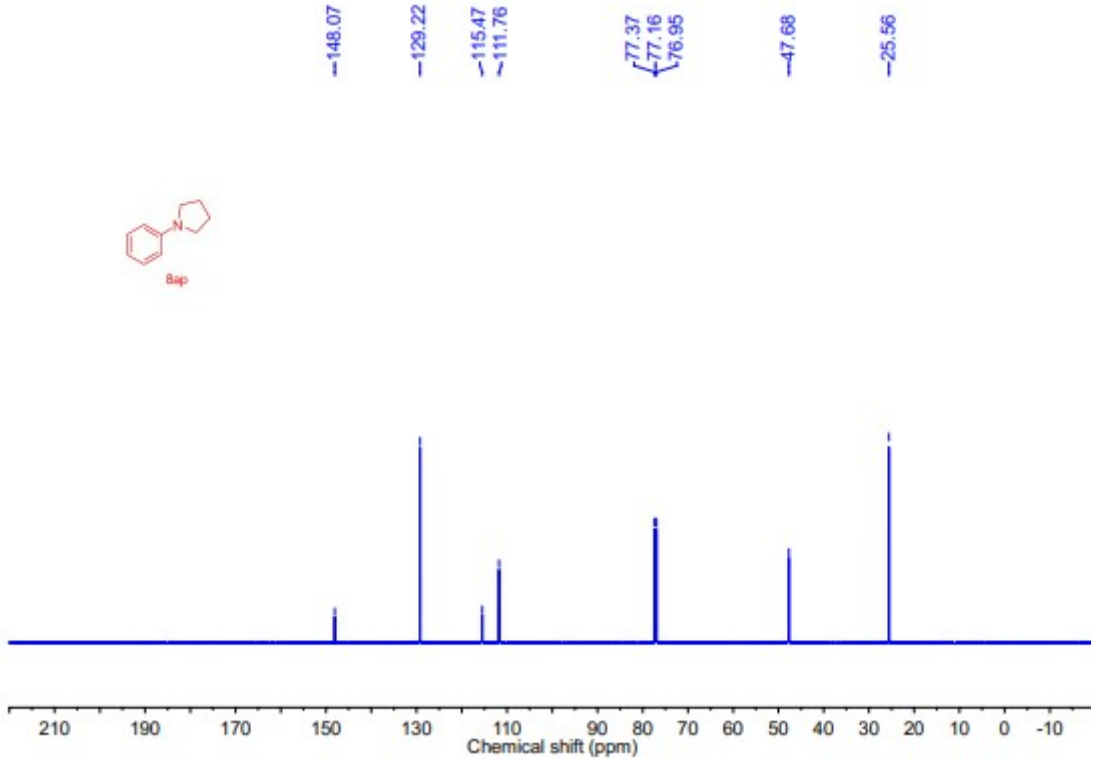
^{1}H NMR (600 MHz, $CDCl_3$, 298 K) of **8ao**



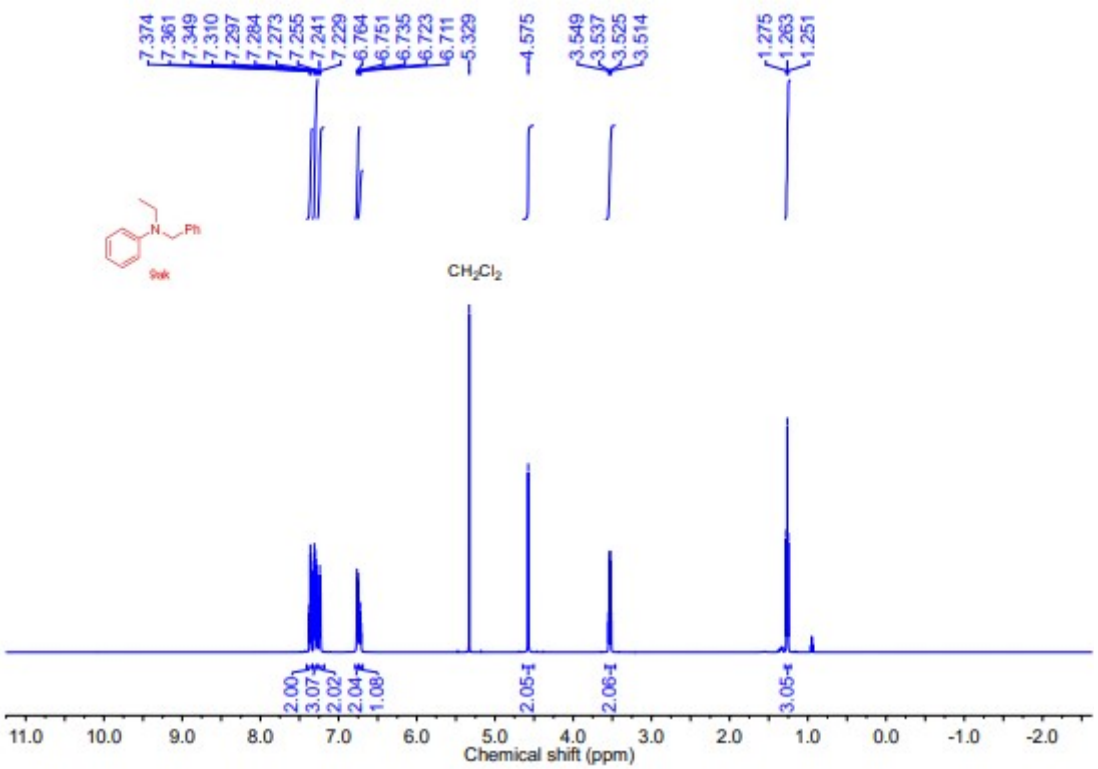
^{13}C{^{1}H} NMR (151 MHz, $CDCl_3$, 298 K) of **8ao**



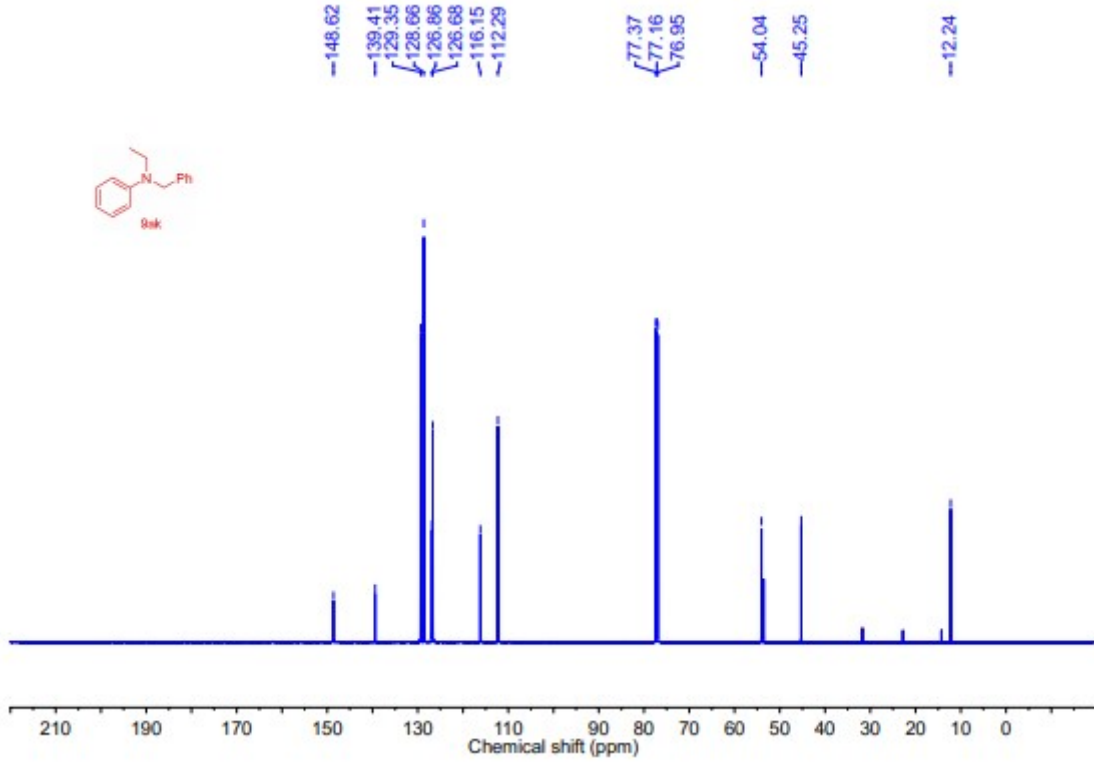
^{1}H NMR (600 MHz, $CDCl_3$, 298 K) of **8ap**



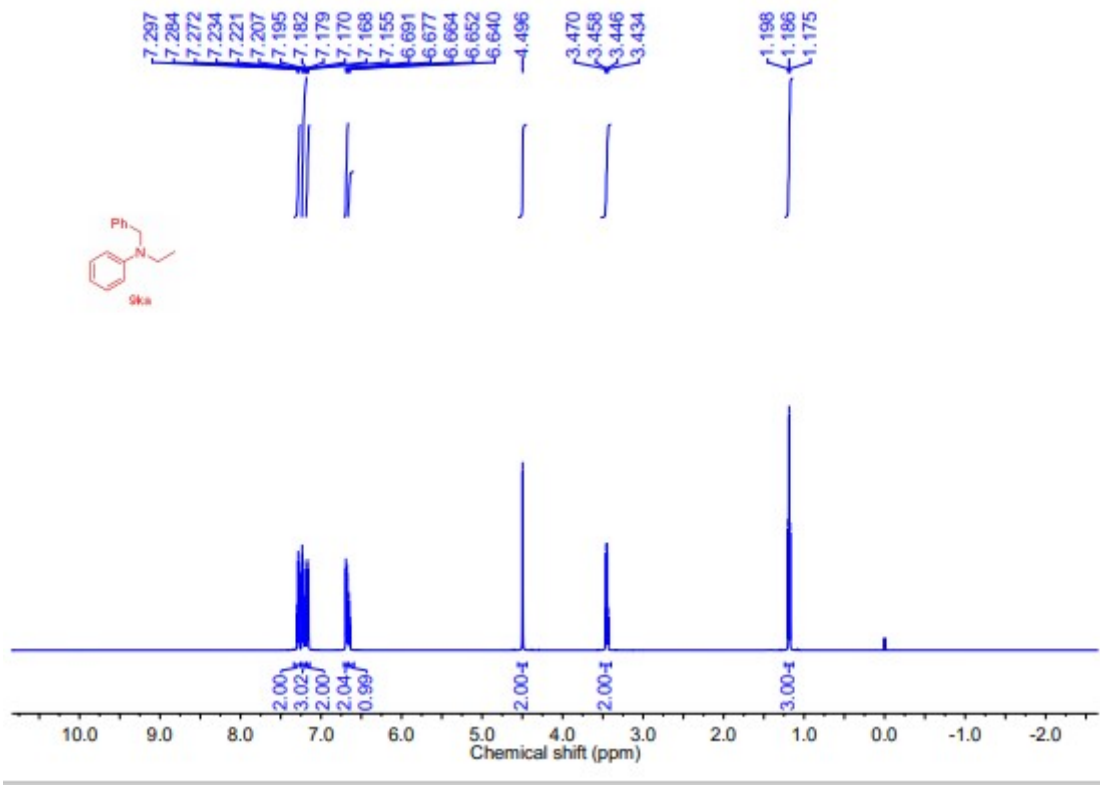
^{13}C{^{1}H} NMR (151 MHz, $CDCl_3$, 298 K) of **8ap**



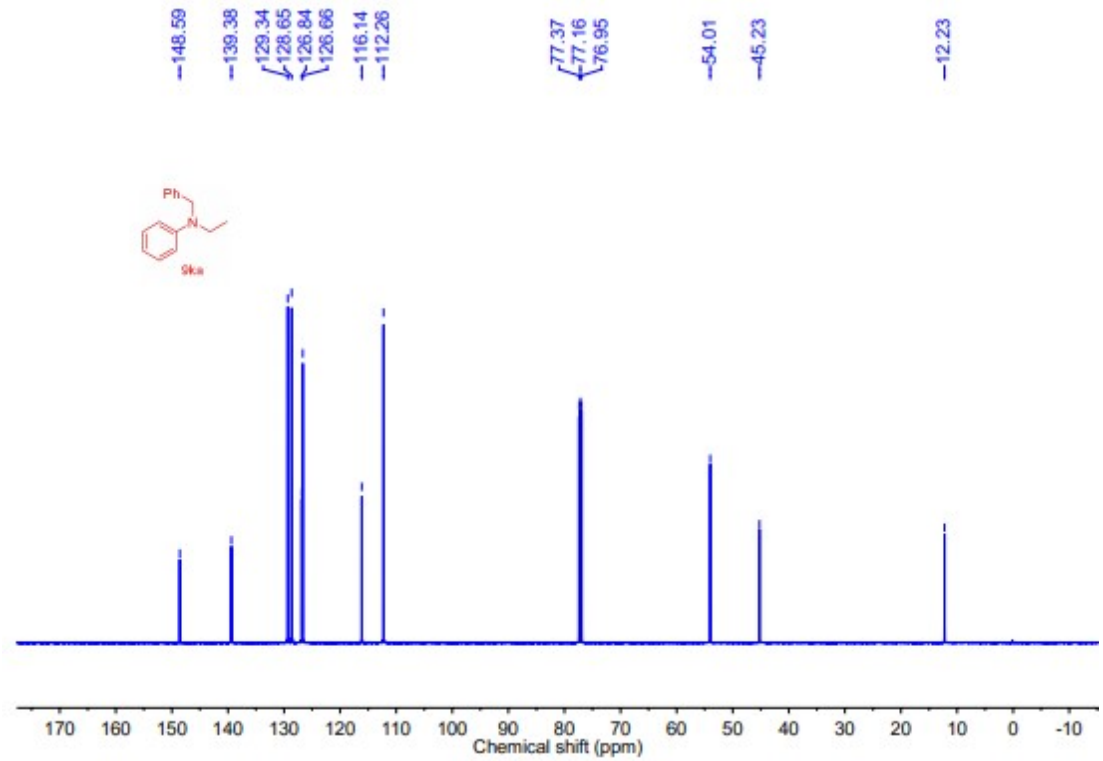
^{1}H NMR (600 MHz, $CDCl_3$, 298 K) of **9ak**



^{13}C{^{1}H} NMR (151 MHz, $CDCl_3$, 298 K) of **9ak**



^{1}H NMR (600 MHz, $CDCl_3$, 298 K) of **9ka**



^{13}C{^{1}H} NMR (151 MHz, $CDCl_3$, 298 K) of **9ka**

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