Electronic Supplementary Material (ESI) for Organic Chemistry Frontiers.
This journal is © the Partner Organisations 2024

Supporting Information

Photoredox-Catalyzed Hydrogenation of Alkenes Assisted by *in situ* Generated $PPh_3(OH)$ Radical and Acetic Acid

Zhen-Zhen Xie,[a] Yu Zheng,[a,b] Zi-Hao Liao,[a] Chu-Ping Yuan,[a] Ming-Zhi Li,[a] Ke-Yi Deng,[a] Hao-Yue Xiang,[a] Kai Chen,[a,*] Hua Yang[a,*]

[a]College of Chemistry and Chemical Engineering, Central South University, Changsha 410083, P. R. China. E-mail: hyangchem@csu.edu.cn; kaichen@csu.edu.cn

[b]School of Physical Science and Technology, ShanghaiTech University, Shanghai 201210, P. R. China

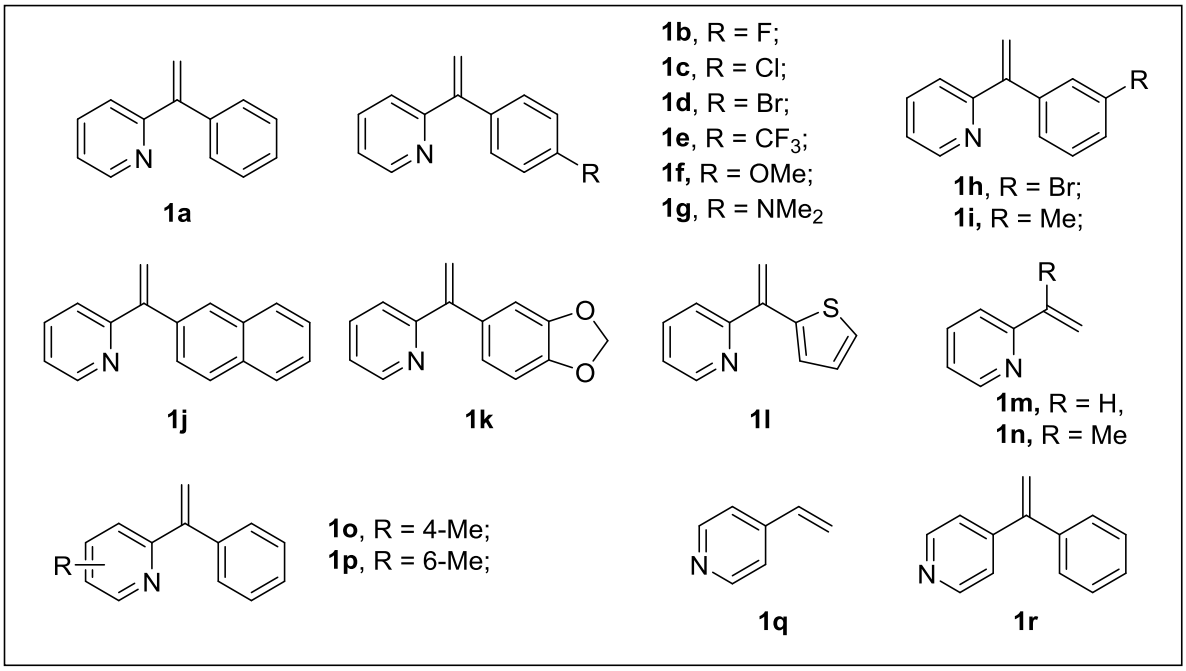
Table of Contents

1. General Information

Unless otherwise noted, all solvents and reagents were purchased from commercial suppliers and used without further purification. The light source for the photocatalytic reaction is manufactured by XINNENGYUAN with power of 30 W (450 nm), and the reaction is carried out in a borosilicate glass vessel without use of filters. A clip fan was placed over the reaction vials to cool down the reaction system during the whole process. ^{1}H NMR spectra were recorded at 400 MHz. The chemical shifts were recorded in *ppm* relative to teramethylsilane and with the solvent resonance as the internal standard. Data were reported as follows: chemical shift, multiplicity (s = singlet; d = doublet; dd = doublet of doublet; t = triplet; q = quartet; m = multiplet), coupling constants (Hz), integration. ^{13}C NMR data were collected at 100 MHz with complete proton decoupling. ^{19}F NMR data were collected at 376 MHz with complete proton decoupling. Infrared spectra (IR) were measured by FT-IR apparatus. High resolution mass spectroscopy (HRMS) was recorded on TOF MS ES^{+} mass spectrometer, and acetonitrile was used to dissolve the sample. Column chromatography was carried out on silica gel (200 - 300 mesh).

2. General Procedures for the Synthesis of Alkene

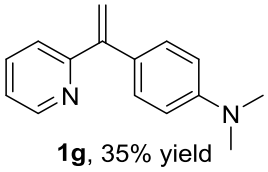
2.1 General procedures for the preparation of vinylpyridine (Scheme S1)



Vinylpyridines **1m** and **1q** were purchased from commercial suppliers (https://www.energy-chemical.com/front/index.htm) and used without further purification. And vinylpyridines **1a**, **1n,** and **1r** were prepared by Wittig reaction from the corresponding ketones according to reported literature procedures.[1] Other vinylpyridines **1b-1l** and **1o-1p** were prepared according to the reported procedures.[2]

Vinylpyridines **1a-1f**, **1i-1j**, **1l-1r** shown in Scheme S1 are known compounds.

Characterization data for vinylpyridines 1g-1h** and **1k.



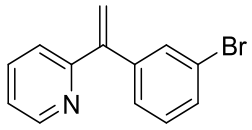
1g: yellow oil, 35% yield (393 mg), purified by flash chromatography (PE/EA = 10%);

IR (neat) *v* 2920, 1519, 1467, 1225, 1061, 946, 750, 578 cm^{-1};

^{1}H NMR (400 MHz, Chloroform-*d*) δ 8.54 (d, *J* = 4.3 Hz, 1H), 7.51 (td, *J* = 7.7, 1.8 Hz, 1H), 7.22 (d, *J* = 7.9 Hz, 1H), 7.17 – 7.13 (m, 2H), 7.09 (dd, *J* = 7.4, 4.9 Hz, 1H), 6.61 (d, *J* = 8.8 Hz, 2H), 5.67 (d, *J* = 1.5 Hz, 1H), 5.43 (d, *J* = 1.5 Hz, 1H), 2.86 (s, 6H);

^{13}C NMR (100 MHz, Chloroform-*d*) δ 158.4, 149.2, 148.2, 147.9, 135.1, 128.1, 127.2, 122.0, 121.2, 113.9, 111.0, 39.5;

HRMS (ESI): $C_{15}H_{17}N_2^+$, $[M+H]^+$, Calcd 225.1386, Found 225.1365.



1h, 45% yield

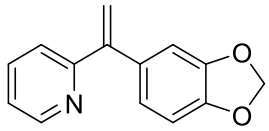
1h: yellow oil, 45% yield (585 mg), purified by flash chromatography (PE/EA = 4%);

IR (neat) *v* 2927, 1582, 1467, 1281, 1068, 917, 746, 582 cm^{-1};

^{1}H NMR (400 MHz, Chloroform-*d*) δ 8.63 (d, *J* = 4.2 Hz, 1H), 7.64 (td, *J* = 7.8, 1.7 Hz, 1H), 7.51 (s, 1H), 7.45 (d, *J* = 7.8 Hz, 1H), 7.27 (d, *J* = 8.2 Hz, 2H), 7.23 – 7.19 (m, 2H), 5.99 (s, 1H), 5.60 (s, 1H);

^{13}C NMR (100 MHz, Chloroform-*d*) δ 157.9, 149.5, 148.0, 142.5, 136.5, 131.4, 130.8, 129.8, 127.1, 122.7, 122.5, 118.7;

HRMS (ESI): $C_{13}H_{11}BrN^+$, $[M+H]^+$, Calcd 226.0069, Found 226.0057.



1k, 49% yield

1k: yellow oil, 49% yield (552 mg), purified by flash chromatography (PE/EA = 4%);

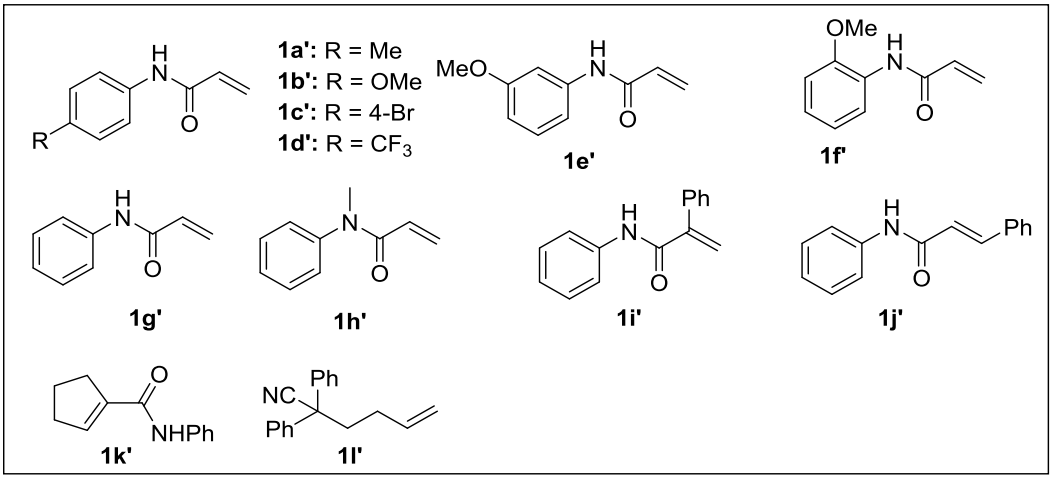
IR (neat) *v* 2892, 1583, 1487, 1231, 1035, 935, 748, 558 cm^{-1};

^{1}H NMR (400 MHz, Chloroform-*d*) δ 8.54 (d, *J* = 4.4 Hz, 1H), 7.57 – 7.53 (m, 1H), 7.22 (d, *J* = 7.9 Hz, 1H), 7.13 – 7.10 (m, 1H), 6.76 – 6.70 (m, 3H), 5.87 (s, 2H), 5.76 (s, 1H), 5.46 (s, 1H);

^{13}C NMR (100 MHz, Chloroform-*d*) δ 158.8, 149.3, 148.8, 147.5, 147.4, 136.3, 134.5, 122.9, 122.5, 122.1, 116.8, 108.9, 108.2, 101.1;

HRMS (ESI): $C_{14}H_{12}NO_2^+$, $[M+H]^+$ Calcd 226.0863, Found 226.0843.

2.2 General procedure for the preparation of acrylamide (Scheme S2)



Acrylamide **1a'-1h'**[3], **1i'**[4], **1j'**[5] and **1k'**[6], **1l'**[7] were synthesized according to reported literature procedures. And all substrates shown above are known compounds.

3. Experimental Details for the Preparation of Compounds 2-31

3.1 Photoreaction set-up (Figure S1)

The light source used for illuminating the reaction vessel (commercial supplier Synthware) consists of blue LEDs (λ_{max} = 450 nm) purchased from Taobao (https://gpiled.taobao.com). And a clip fan was placed over the reaction vials to cool down the reaction system during the whole process of the reaction.

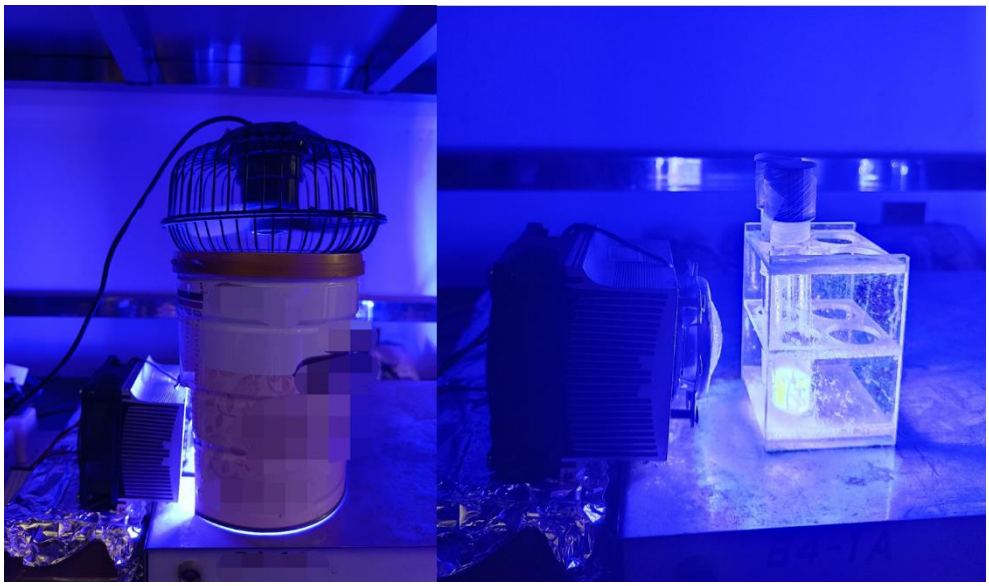


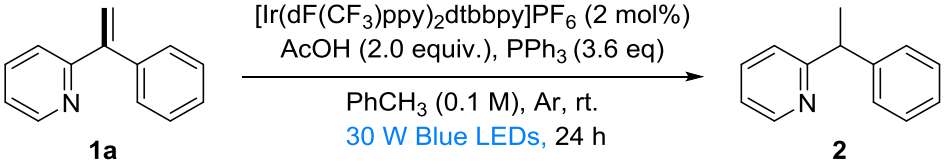
Figure S1. The set-up for the reaction (photographed by Zhen-Zhen Xie)

※ **Notes:**

In the optimized reaction conditions, the reaction is not significantly affected by the reaction temperature. The fan was used to maintain the reaction temperature in a range of 25 ~ 40 °C.

3.2 Detailed optimization of hydrogenation reaction conditions

Table S1. Control experiments[a]



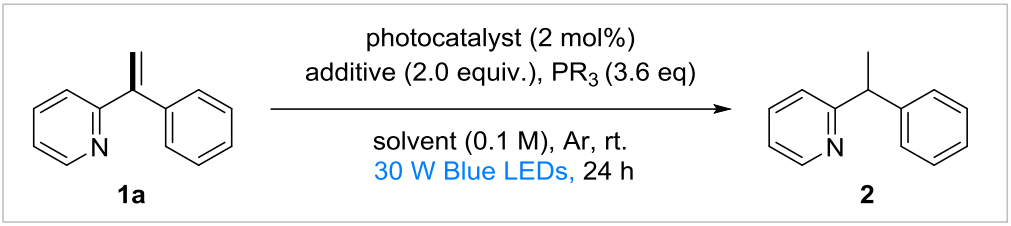
1a 2

Entry	Solvent	Photocatalyst	LEDs	AcOH	Yield (%)
1	**$PhCH_3$**	**$[Ir(dF(CF_3)ppy)_2dtbbpy]PF_6$**	**Blue**	**AcOH**	**97**
2	$PhCH_3$	$[Ir(dF(CF_3)ppy)_2dtbbpy]PF_6$	Blue	--	trace

3[b]	$PhCH_3$	$[Ir(dF(CF_3)ppy)_2dtbbpy]PF_6$	Blue	AcOH	32
4[c]	$PhCH_3$	$[Ir(dF(CF_3)ppy)_2dtbbpy]PF_6$	Blue	AcOH	n.r.
5	$PhCH_3$	--	Blue	AcOH	n.r.
6	$PhCH_3$	$[Ir(dF(CF_3)ppy)_2dtbbpy]PF_6$	--	AcOH	n.r.

[a]Reaction conditions: **1a** (0.15 mmol, 1.0 equiv.), $[Ir(dF(CF_3)ppy)_2dtbbpy]PF_6$ (2 mol%), AcOH (0.3 mmol, 2.0 equiv.), PPh_3 (0.54 mmol, 3.6 equiv.), $PhCH_3$ (0.1 M, 1.5 mL), 30 W blue LEDs, ambient temperature, argon atmosphere, 24 hours, isolated yield. [b]in air; [c]no PPh_3.

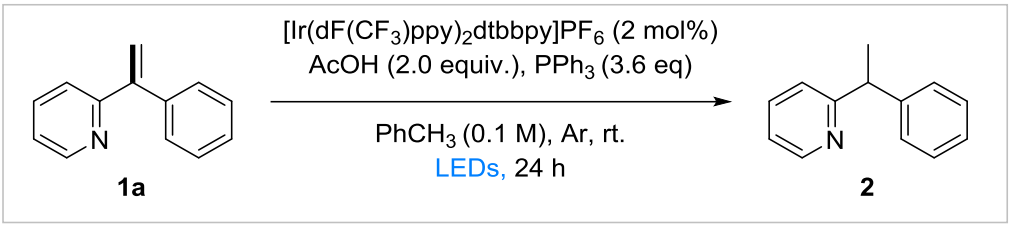
Table S2. Reaction condition screening[a]



Entry	Solvent	Photocatalyst	PR_3	Additive	Yield (%)
1	$PhCH_3$	$[Ir(dF(CF_3)ppy)_2dtbbpy]PF_6$	PPh_3	HCOOH	72
2	$PhCH_3$	$[Ir(dF(CF_3)ppy)_2dtbbpy]PF_6$	PPh_3	TFA	n.d.
3	$PhCH_3$	$Ir(ppy)_2(dtbpy)PF_6$	PPh_3	AcOH	32
4	$PhCH_3$	$Ir(dF(CF_3)ppy)_2(4,4'dCF_3bpy]PF_6$	PPh_3	AcOH	39
5	CH_3CN	$[Ir(dF(CF_3)ppy)_2dtbbpy]PF_6$	PPh_3	AcOH	91
6	Acetone	$[Ir(dF(CF_3)ppy)_2dtbbpy]PF_6$	PPh_3	AcOH	89
7	MeOH	$[Ir(dF(CF_3)ppy)_2dtbbpy]PF_6$	PPh_3	AcOH	81
8	DMF	$[Ir(dF(CF_3)ppy)_2dtbbpy]PF_6$	PPh_3	AcOH	95
9	DCE	$[Ir(dF(CF_3)ppy)_2dtbbpy]PF_6$	PPh_3	AcOH	87
10	THF	$[Ir(dF(CF_3)ppy)_2dtbbpy]PF_6$	PPh_3	AcOH	46
11	$PhCH_3$	$[Ir(dF(CF_3)ppy)_2dtbbpy]PF_6$	*n*-PBu_3	AcOH	n.d.
12	$PhCH_3$	$[Ir(dF(CF_3)ppy)_2dtbbpy]PF_6$	$MePh_2P$	AcOH	94
13	$PhCH_3$	$[Ir(dF(CF_3)ppy)_2dtbbpy]PF_6$	(*p*-OMePh)$_3$P	AcOH	82
14	$PhCH_3$	$[Ir(dF(CF_3)ppy)_2dtbbpy]PF_6$	(*p*-FPh)$_3$P	AcOH	n.r.
15[b]	$PhCH_3$	$[Ir(dF(CF_3)ppy)_2dtbbpy]PF_6$	PPh_3	AcOH	89
16[c]	$PhCH_3$	$[Ir(dF(CF_3)ppy)_2dtbbpy]PF_6$	PPh_3	AcOH	trace
17[d]	$PhCH_3$	$[Ir(dF(CF_3)ppy)_2dtbbpy]PF_6$	PPh_3	AcOH	51
18[e]	$PhCH_3$	$[Ir(dF(CF_3)ppy)_2dtbbpy]PF_6$	PPh_3	AcOH	61

[a]Reaction conditions: **1a** (0.15 mmol, 1.0 equiv.), photocatalyst (2 mol%), additive (0.3 mmol, 2.0 equiv.), PR_3 (0.54 mmol, 3.6 equiv.), solvent (0.1 M, 1.5 mL), 30 W blue LEDs, ambient temperature, argon atmosphere, 24 hours, isolated yield. [b]3.0 equiv. of PPh_3.. [c]0.5 equiv. AcOH was used. [d]1.0 equiv. AcOH was used. [e]1.5 equiv. AcOH was used. TFA = Triflic acid

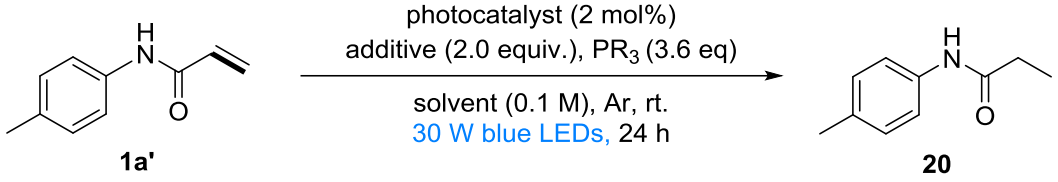
Table S3. Investigation of light source and water amount in the system[a]



Entry	Solvent	Photocatalyst	LEDs	Yield (%)
1	$PhCH_3$	$[Ir(dF(CF_3)ppy)_2dtbbpy]PF_6$	White LEDs	89
2	$PhCH_3$	$[Ir(dF(CF_3)ppy)_2dtbbpy]PF_6$	Purple LEDs	86
3	$PhCH_3$	$[Ir(dF(CF_3)ppy)_2dtbbpy]PF_6$	Green LEDs	n.r
4[b]	$PhCH_3$	$[Ir(dF(CF_3)ppy)_2dtbbpy]PF_6$	Blue LEDs	76
5[c]	$PhCH_3$	$[Ir(dF(CF_3)ppy)_2dtbbpy]PF_6$	Blue LEDs	97
6[d]	$PhCH_3$	$[Ir(dF(CF_3)ppy)_2dtbbpy]PF_6$	Blue LEDs	95
7[e]	$PhCH_3$	$[Ir(dF(CF_3)ppy)_2dtbbpy]PF_6$	Blue LEDs	74

[a]Standard conditions: **1a** (0.15 mmol, 1.0 equiv.), $[Ir(dF(CF_3)ppy)_2dtbbpy]PF_6$ (2 mol%), AcOH (0.3 mmol, 2.0 equiv.), PPh_3 (0.54 mmol, 3.6 equiv.), $PhCH_3$ (0.1 M, 1.5 mL), LEDs, ambient temperature, argon atmosphere, 24 hours, isolated yield. [b]dry $PhCH_3$ was used, 4 Å Ms (40 mg); [c]dry $PhCH_3$ was used. [d]20 equiv H_2O was added. [e]V($PhCH_3$):V(H_2O) = 9:1.

Table S4. Optimization of reaction conditions for hydrogenation of substrate **1a'**[a]

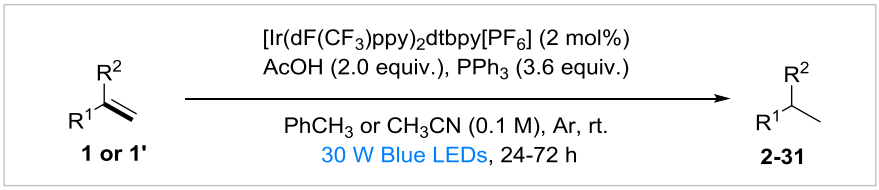


Entry	Solvent	Photocatalyst	PR_3	Additive	Yield (%)
1	$PhCH_3$	$[Ir(dF(CF_3)ppy)_2dtbbpy]PF_6$	PPh_3	AcOH	13
2	Acetone	$[Ir(dF(CF_3)ppy)_2dtbbpy]PF_6$	PPh_3	AcOH	25
3	MeOH	$[Ir(dF(CF_3)ppy)_2dtbbpy]PF_6$	PPh_3	AcOH	trace
4	DMF	$[Ir(dF(CF_3)ppy)_2dtbbpy]PF_6$	PPh_3	AcOH	n.r.
5	DMSO	$[Ir(dF(CF_3)ppy)_2dtbbpy]PF_6$	PPh_3	AcOH	n.d.
6	THF	$[Ir(dF(CF_3)ppy)_2dtbbpy]PF_6$	PPh_3	AcOH	n.r.
7	DCE	$[Ir(dF(CF_3)ppy)_2dtbbpy]PF_6$	PPh_3	AcOH	trace
8	**CH_3CN**	**$[Ir(dF(CF_3)ppy)_2dtbbpy]PF_6$**	**PPh_3**	**AcOH**	**49**
9	CH_3CN	$[Ir(dF(CF_3)ppy)_2dtbbpy]PF_6$	PPh_3	PhCOOH	n.d.
10	CH_3CN	$[Ir(dF(CF_3)ppy)_2dtbbpy]PF_6$	PPh_3	$(PhO)_2PO_2H$	33
11	CH_3CN	$[Ir(dF(CF_3)ppy)_2dtbbpy]PF_6$	PPh_3	HCOOH	37

12	CH_3CN	[Ir(dF(CF_3)ppy)$_2$dtbbpy]PF_6	PPh_3	CF_3SO_3H	trace
13	CH_3CN	[Ir(dF(CF_3)ppy)$_2$dtbbpy]PF_6	PPh_3	CF_3COOH	trace
14	CH_3CN	[Ir(dF(CF_3)ppy)$_2$dtbbpy]PF_6	PPh_3	NH_4Cl	n.r.
15	CH_3CN	[Ir(dF(CF_3)ppy)$_2$dtbbpy]PF_6	PPh_3	K_2CO_3	n.r.
16	CH_3CN	*fac*-Ir(ppy)$_3$	PPh_3	AcOH	trace
17	CH_3CN	4-CZIPN	PPh_3	AcOH	n.d.
18	CH_3CN	$MesAcr^+ClO_4^-$	PPh_3	AcOH	n.r.
19	CH_3CN	Ru(bpy)$_3PF_6$	PPh_3	AcOH	n.r.
20	CH_3CN	Rhodamin B	PPh_3	AcOH	n.r.
21	CH_3CN	Ir(ppy)$_2$(dtbpy)PF_6	PPh_3	AcOH	25
22	CH_3CN	Ir(dF(CF_3)ppy)$_2$(4,4'dCF_3bpy]PF_6	PPh_3	AcOH	trace
23	CH_3CN	[Ir(dF(CF_3)ppy)$_2$dtbbpy]PF_6	*n*-Bu_3	AcOH	trace
24	CH_3CN	[Ir(dF(CF_3)ppy)$_2$dtbbpy]PF_6	$MePh_2P$	AcOH	37
25	CH_3CN	[Ir(dF(CF_3)ppy)$_2$dtbbpy]PF_6	(*p*-OMePh)$_3$P	AcOH	33
26	CH_3CN	[Ir(dF(CF_3)ppy)$_2$dtbbpy]PF_6	(*p*-FPh)$_3$P	AcOH	41
27[b]	CH_3CN	[Ir(dF(CF_3)ppy)$_2$dtbbpy]PF_6	PPh_3	AcOH	25
28	CH_3CN	--	PPh_3	AcOH	n.r.
29	CH_3CN	[Ir(dF(CF_3)ppy)$_2$dtbbpy]PF_6	--	AcOH	n.r.
30	CH_3CN	[Ir(dF(CF_3)ppy)$_2$dtbbpy]PF_6	PPh_3	--	trace
31[c]	CH_3CN	[Ir(dF(CF_3)ppy)$_2$dtbbpy]PF_6	PPh_3	AcOH	n.r.

[a]Reaction conditions: **1a'** (0.15 mmol, 1.0 equiv.), photocatalyst (2 mol%), Additive (0.3 mmol, 2.0 equiv.), PR_3 (0.54 mmol, 3.6 equiv.), solvent (0.1 M, 1.5 mL), 30 W blue LEDs, ambient temperature, argon atmosphere, 24 hours, isolated yield. [b]in air; [c]in dark.

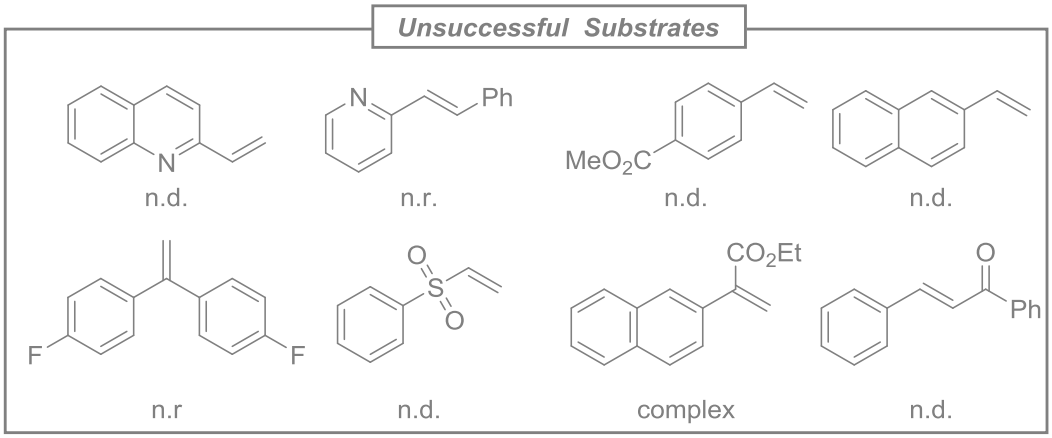
3.3 General procedure for the hydrogenation reactions of alkenes



***Standard conditions*:** alkene **1** or **1'** (0.15 mmol, 1.0 equiv.), [Ir(dF(CF_3)ppy)$_2$dtbpy][PF_6] (**PC1**, 2 mol%), PPh_3 (0.54 mmol, 3.6 equiv.), AcOH (0.30 mmol, 2.0 equiv.), $PhCH_3$ or CH_3CN (0.1 M, 1.5 mL), 30 W blue LEDs, ambient temperature, argon atmosphere, 24-72 h, isolated yield.

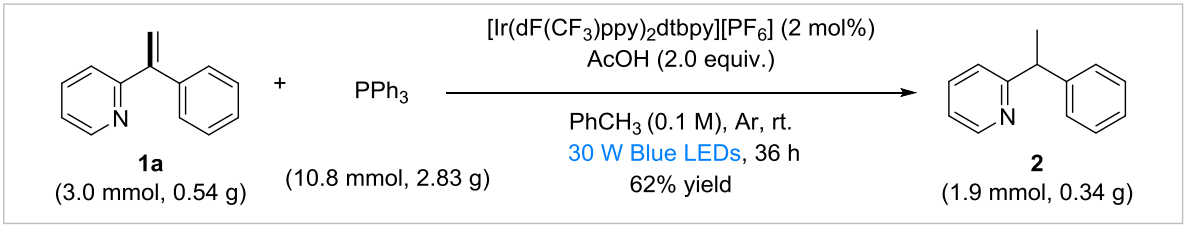
To an oven-dried 20 mL quartz flask equipped with a magnetic stirring bar was added alkene **1** or **1'** (0.15 mmol, 1.0 equiv.), AcOH (0.3 mmol, 2.0 equiv.), PPh_3 (0.54 mmol, 3.6 equiv.), $PhCH_3$ or CH_3CN (1.5 mL, 0.1 M) and [Ir(dFCF_3ppy)$_2$dtbbpy]PF_6 (**PC1**, 2 mol%). The reaction tube was

evacuated and backfilled with Ar three times before light irradiation. After consumption of alkene (monitored by TLC), the reaction mixture was stirred at ambient temperature (*note: the reaction temperature ranges from 25 ℃ to 40 ℃*) under irradiation of 30 W blue LEDs (distance app. 3 cm) for specific time. After completion (monitored by TLC), the solvent was removed under reduced pressure, and then the resulting residue was purified by flash chromatography on silica gel with a mixture of ethyl acetate and petroleum ether (1:9 to 1:4) as the eluent to afford the desired products **2-31**.



3.4 Scale-up reaction (Figure S2)

Scale-up reaction for the preparation of hydrogenated product 2 (Figure S2)



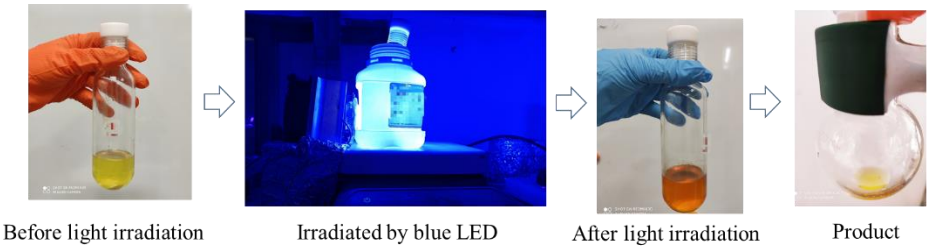


Figure S2. Process of scale-up reaction for the synthesis of **2** (Photographed by Zhen-Zhen Xie)

To an oven-dried 120 mL schlenk flask equipped with a magnetic stirring bar was charged with 2-(1-phenylvinyl)pyridine **1a** (3.0 mmol, 1.0 equiv.), AcOH (6.0 mmol, 2.0 equiv.) and $PhCH_3$ (30

mL, 0.1 M). Then, PPh_3 (10.8 mmol, 3.6 equiv.) and $[Ir(dFCF_3ppy)_2dtbbpy]PF_6$ (**PC1**, 2 mol%) were added. The vessel was evacuated and backfilled with Ar three times before light irradiation. After that, the tube was stirred at ambient temperature (*note: the reaction temperature ranges from 25 ℃ to 40 ℃*) under irradiation of 30 W blue LEDs for 36 h. The solvent was removed under reduced pressure, and then the resulting residue was purified by flash chromatography on silica gel with a mixture of ethyl acetate and petroleum ether (PE/EA=9:1) as the eluent to afford the desired product **2** in 62% yield.

4. Mechanistic Studies

Emission Quenching Experiments (Stern-Volmer Studies) (Figure S3)

All fluorescence measurements were recorded using a Hitachi FL-7000 Fluorometer. Quenching studies were conducted in $PhCH_3$. All $[Ir(dF(CF_3)ppy)_2dtbpy][PF_6]$ solutions (concentration of 5 μM) were excited at 312 nm and the emission intensity was collected at 478 nm (Figure S3). Measurements using corresponding quenchers were taken in triplicate at different concentrations.

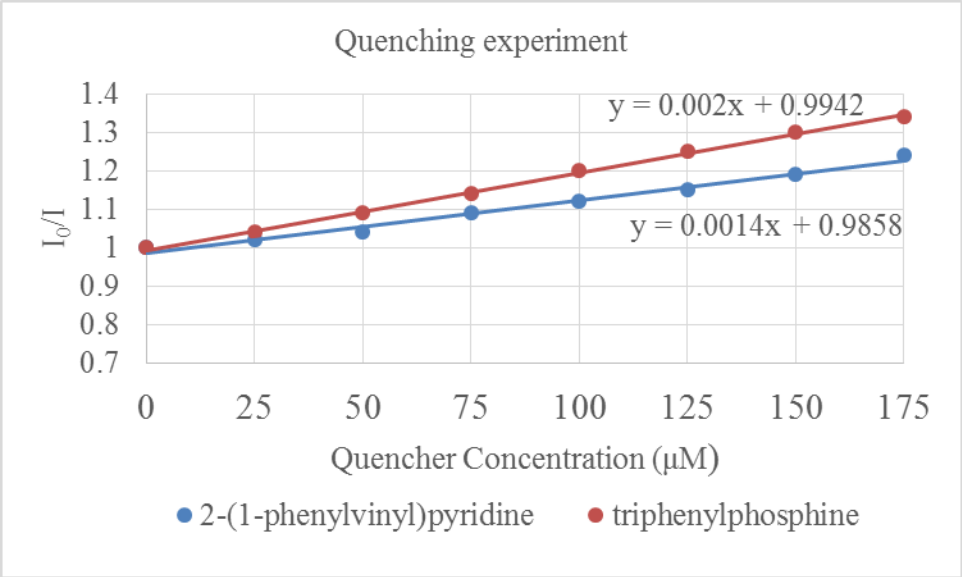
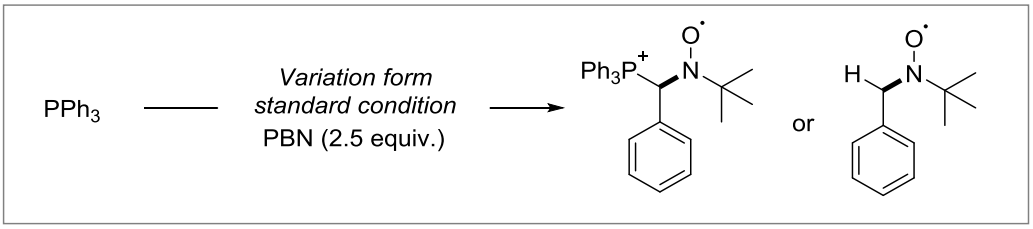


Figure S3. Stern-Volmer experiments of PPh_3 and vinylpyridine **1a** in $PhCH_3$

Trapping Experiments

a) Trapping experiment with PBN for hydrogenation reaction of alkene (Figure S4 – S5)



Trapping experiment was designed according to the following conditions: To an oven-dried 20 mL quartz flask equipped with a magnetic stirring bar, AcOH (0.30 mmol, 2.0 equiv.), $PhCH_3$ (1.5 mL, 0.1 M), PPh_3 (0.54 mmol, 3.6 equiv.), $[Ir(dF(CF_3)ppy)_2dtbbpy]PF_6$ (**PC1**, 2 mol%) and *N*-*tert*-butyl-*α*-phenylnitrone (PBN, 0.375 mmol, 2.5 equiv.) were added in sequence. The reaction tube was evacuated and backfilled with Ar three times before light irradiation. The reaction mixture was stirred at ambient temperature under irradiation of 30 W blue LEDs (distance app. 3 cm) for

24 h. After that, the reaction mixture was analyzed by HRMS (Figure S4). The corresponding PBN-trapping products were supported by HRMS. HRMS (EI): $C_{29}H_{30}NOP^{+}$ $[M]^{+}$ calcd: 439.2060, found: 439.2076; $C_{11}H_{16}NO$ $[M]^{+}$ calcd: 178.1232, found: 178.1251.

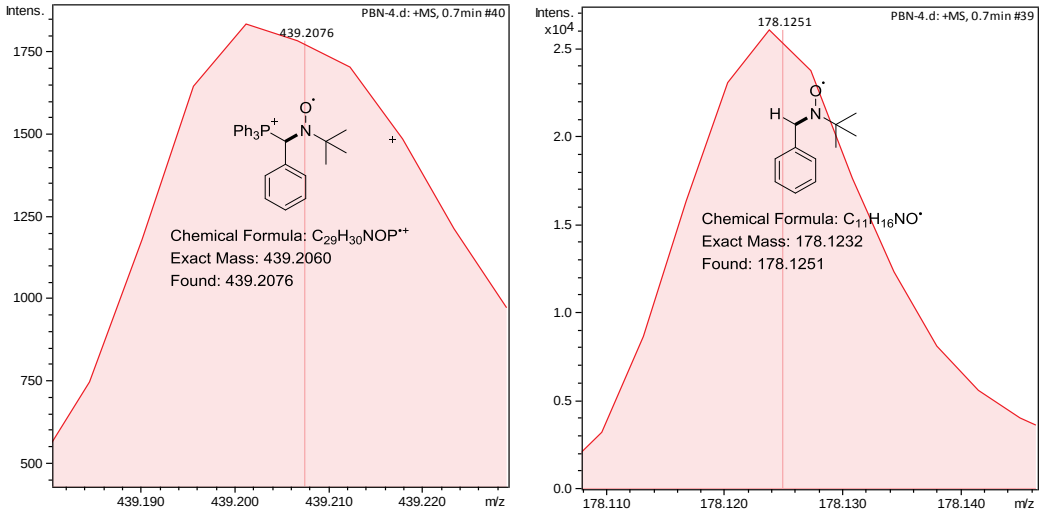
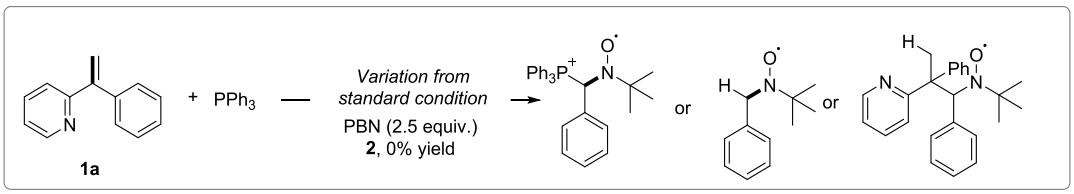


Figure S4. Crude ESI-MS of the PBN-trapping adducts for hydrogenation reaction



Another Trapping experiment was also designed according to the following conditions: To an oven-dried 20 mL quartz flask equipped with a magnetic stirring bar, **1a** (0.15 mmol, 1.0 equiv.), AcOH (0.30 mmol, 2.0 equiv.), $PhCH_3$ (1.5 mL, 0.1 M), PPh_3 (0.54 mmol, 3.6 equiv.), $[Ir(dF(CF_3)ppy)_2dtbbpy]PF_6$ (**PC1**, 2 mol%) and PBN (0.375 mmol, 2.5 equiv.) were added in sequence. The reaction tube was evacuated and backfilled with Ar three times before light irradiation. The reaction mixture was stirred at ambient temperature under irradiation of 30 W blue LEDs (distance app. 3 cm) for 24 h. And no product **2** was detected when PBN was employed as radical scavenger, indicating that the reaction was completely inhibited. After, the reaction mixture was analyzed by HRMS (Figure S5). The corresponding PBN-trapping products were supported by HRMS. HRMS (EI): $C_{29}H_{30}NOP^{+}$ $[M]^{+}$ calcd: 439.2060, found: 439.2077; $C_{11}H_{16}NO^{\cdot}$ $[M]^{+}$ calcd: 178.1232, found: 178.1253; $C_{24}H_{27}N_2NaO^{+}$ $[M+Na]^{+}$ calcd: 382.2016, found: 382.2025.

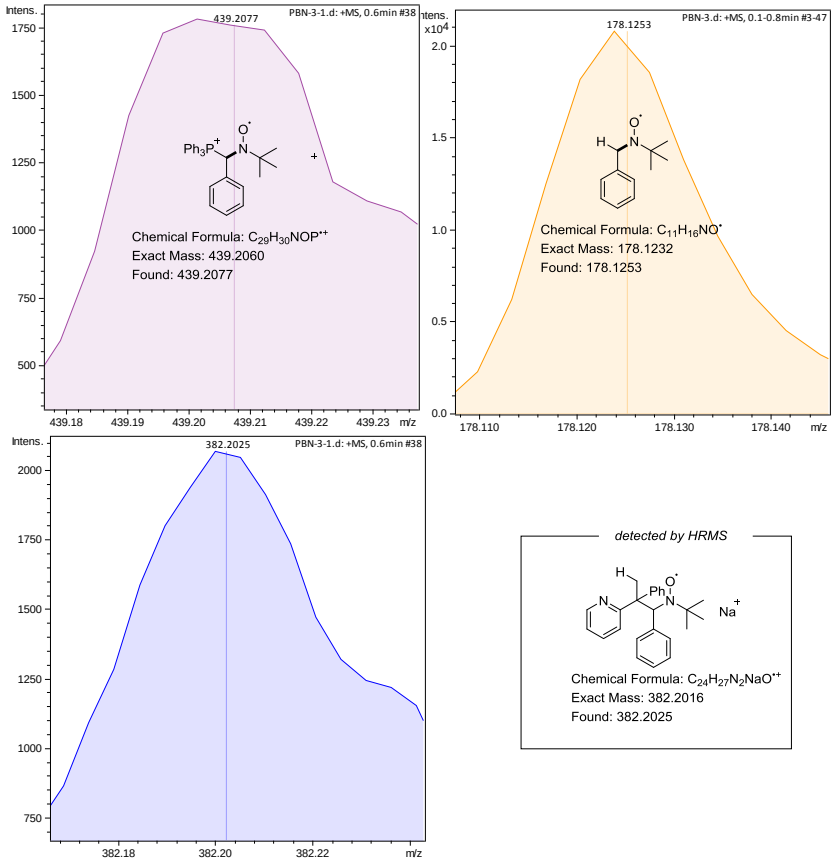
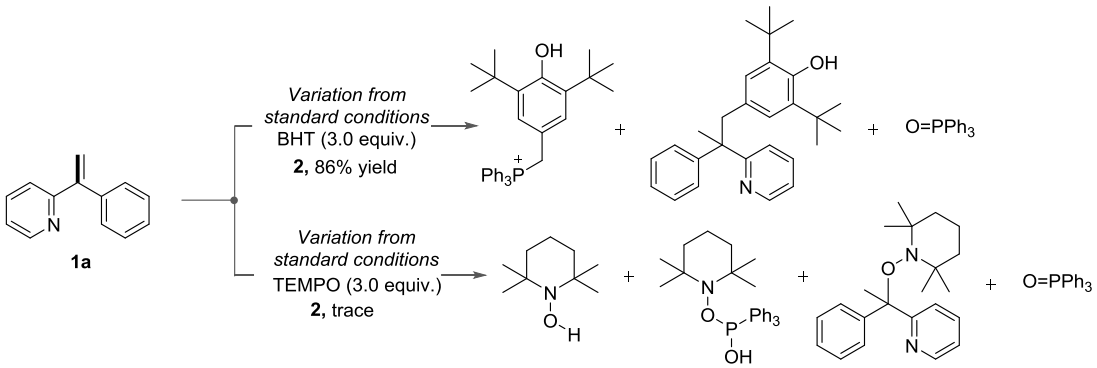


Figure S5. Crude ESI-MS of the PBN-trapping adducts for hydrogenation reaction

b) Trapping experiment with TEMPO and BHT for hydrogenation reactions of alkene (Figure S6 – S7)



Radical trapping experiments for the olefin reduction reaction were conducted under standard conditions with two trapping agents (BHT and TEMPO) to catch the putative radical. The desired product **2** was obtained in 86% yield when BHT was added, and trace product **2** was detected when TEMPO was employed as radical scavenger, indicating that the reaction was completely inhibited. ESI-MS analysis of the crude reaction mixture was performed, and the corresponding radical

trapped product was successfully detected by HRMS in the presence of BHT (Figure S6). HRMS (EI): $C_{33}H_{38}OP^+$, $[M]^+$ calcd: 481.2656, found: 481.2654; $C_{28}H_{35}NNaO^+$ $[M+Na]^+$ calcd: 424.2611, found: 424.2599; $C_{18}H_{16}OP^+$ $[M+H]^+$ calcd: 279.0933, found: 279.0952 (BHT-adduct). Notably, the corresponding coupled product between TEMPO radical and the expected radical was successfully detected by HRMS (Figure S7). HRMS (EI): $C_9H_{20}NO^+$, $[M+H]^+$ calcd: 158.1539, found: 158.1550; $C_{22}H_{31}N_2O^+$ $[M+H]^+$ calcd: 339.2431, found: 339.2450; $C_{27}H_{35}NO_2P+$ $[M+H]^+$ calcd: 436.2400, found: 436.2421; $C_{18}H_{16}OP^+$ $[M+H]^+$ calcd: 279.0933, found: 279.0949 (TEMPO-adduct).

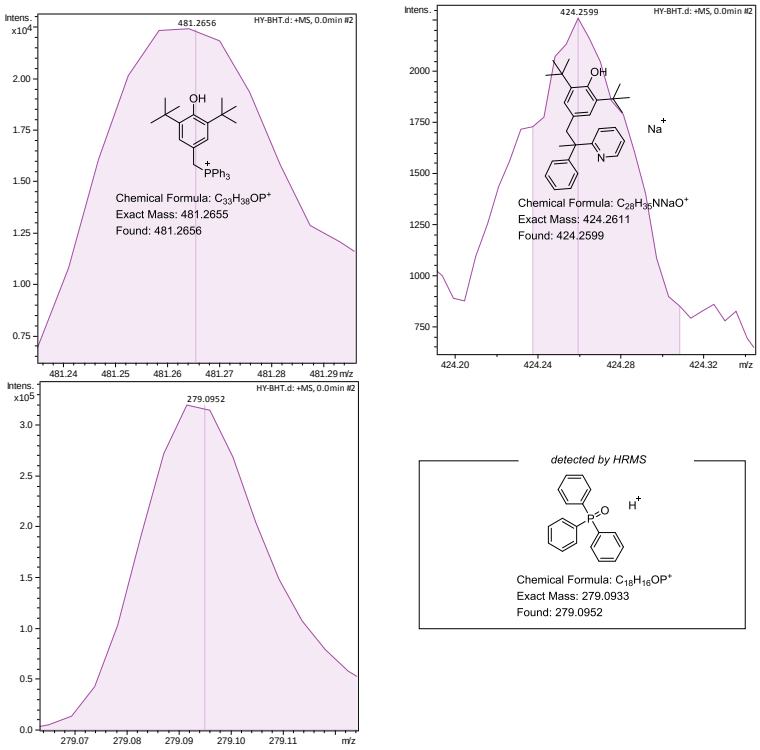


Figure S6 Crude ESI-MS of the BHT-trapping adducts for hydrogenation reaction

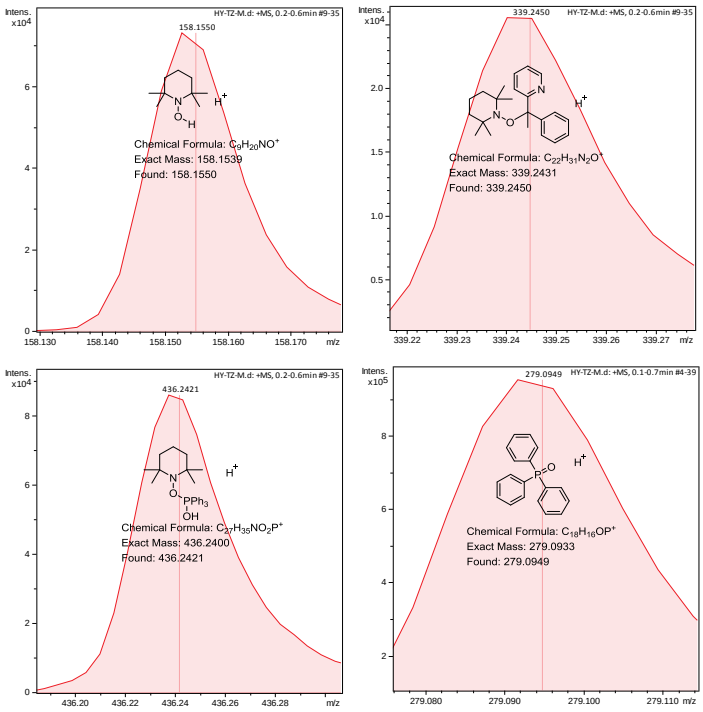


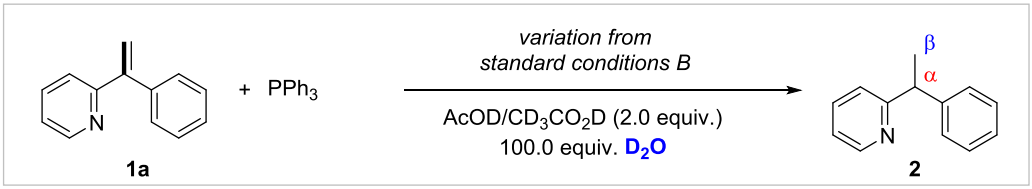
Figure S7 Crude ESI-MS of the TEMPO-trapping adducts for hydrogenation reaction

Labelling Experiments

a) Deuterium Labelling Experiments for hydrogenation reaction (Figure S8-Figure-S17*)*

A series of labelling experiments for olefin reduction transformation reaction were performed under standard condition by using D_2O or AcOH/CD_3CO_2D as deuterium reagent. The resulting mixture was purified by flash chromatography to afford the corresponding pure product. Further, the deuterated ratio of the desired products were analyzed by ^1H NMR, and these results were depicted in Table S5. As detected by ^1H NMR and HRMS, deuterated product **2** was observed (Figure S8-Figure-S17)

Table S5 Labelling Experiments for the hydrogenation reaction[a]



Entry	Acid	D_2O	Yield (%)	*d*-ratio (*α*, %)[b]	*β*-ratio (*β*, %)[b]
1	AcOH	100 equiv.	98	82	220
2	AcOD	100 equiv.	95	82	212
3	AcOD	--	89	19	52
4	CD_3CO_2D	100 equiv.	89	83	221
5	CD_3CO_2D	--	80	15	38

[a]Reaction conditions: **1a** (0.15 mmol, 1.0 equiv.), PPh_3 (0.54 mmol, 3.6 equiv.), $[Ir(dF(CF_3)ppy)_2dtbbpy]PF_6$ (2 mmol%), $AcOH/ACOD/CD_3CO_2D$ (0.30 mmol, 2.0 equiv.), $PhCH_3$ (0.1 M, 1.5 mL), 30 W blue LEDs, ambient temperature (25 ~ 40 °C), argon atmosphere, 24 hours, isolated yield. [b]The deuterated ratio was determined by ^1H NMR analysis.

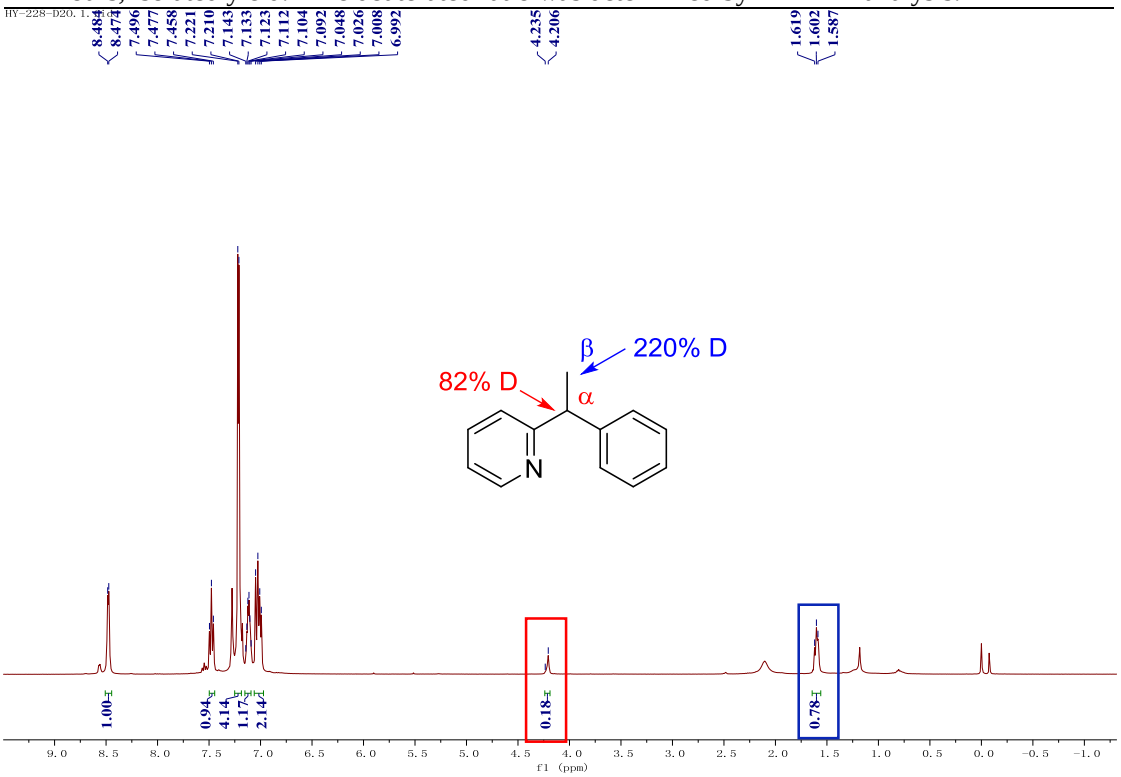


Figure S8. ^1H NMR of deuterated product **2** (2.0 equiv. AcOH and 100 equiv. D_2O)

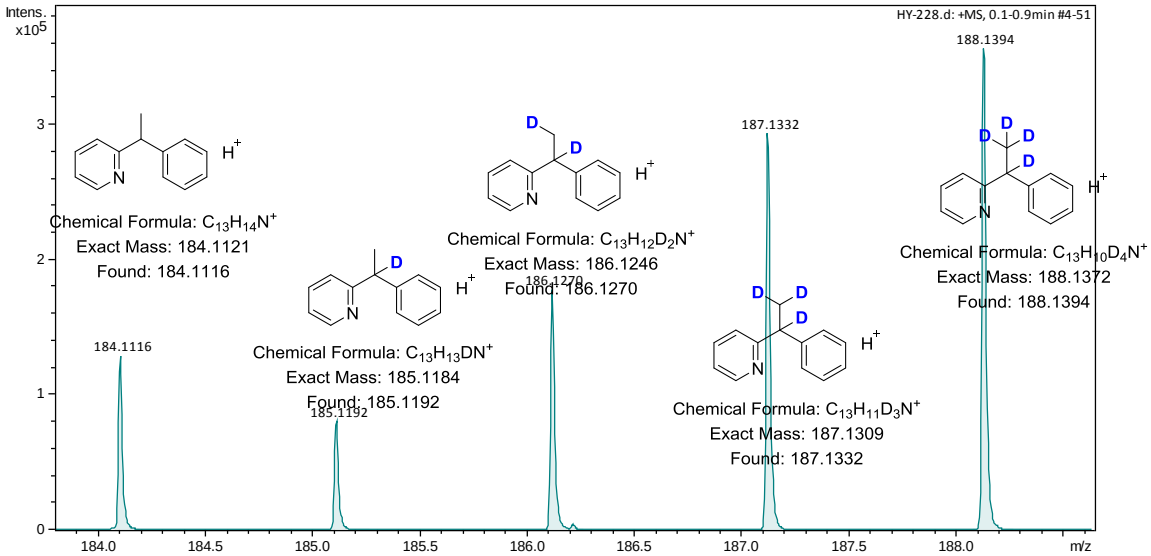


Figure 9. HRMS of deuterated product **2** (2.0 equiv. AcOH and 100 equiv. D_2O)

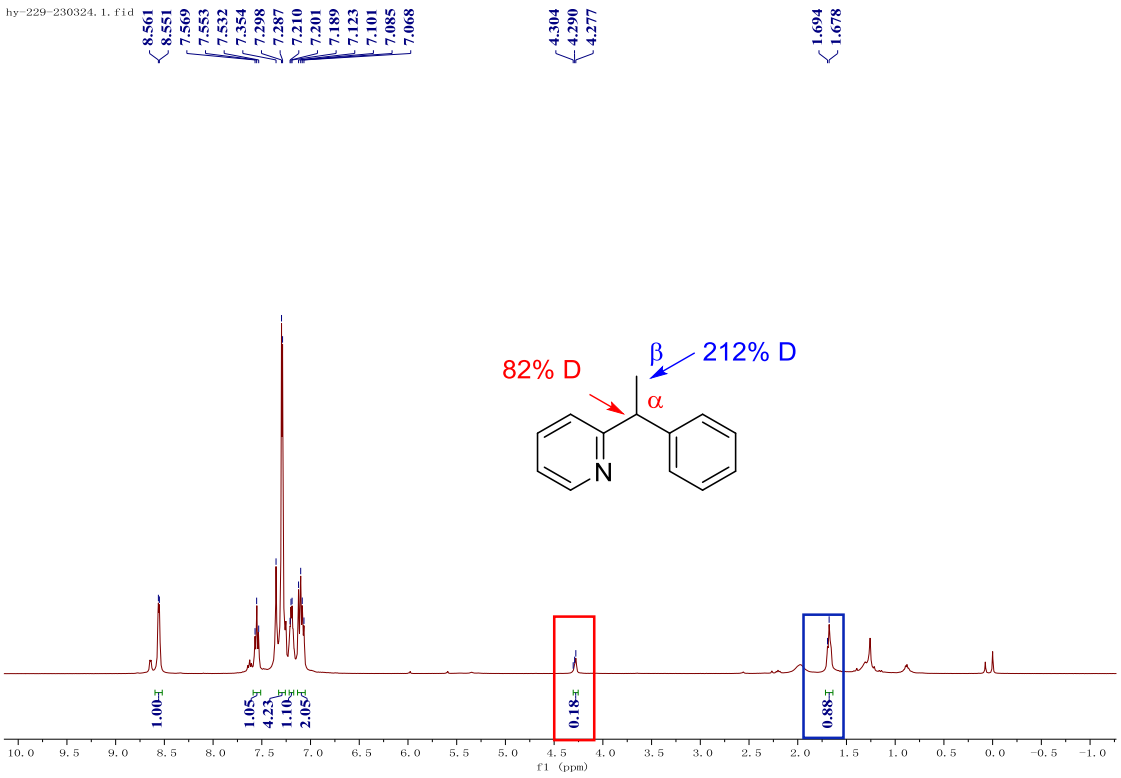


Figure S10. ^{1}H NMR of deuterated product **2** (2.0 equiv. AcOD and 100 equiv. D_2O)

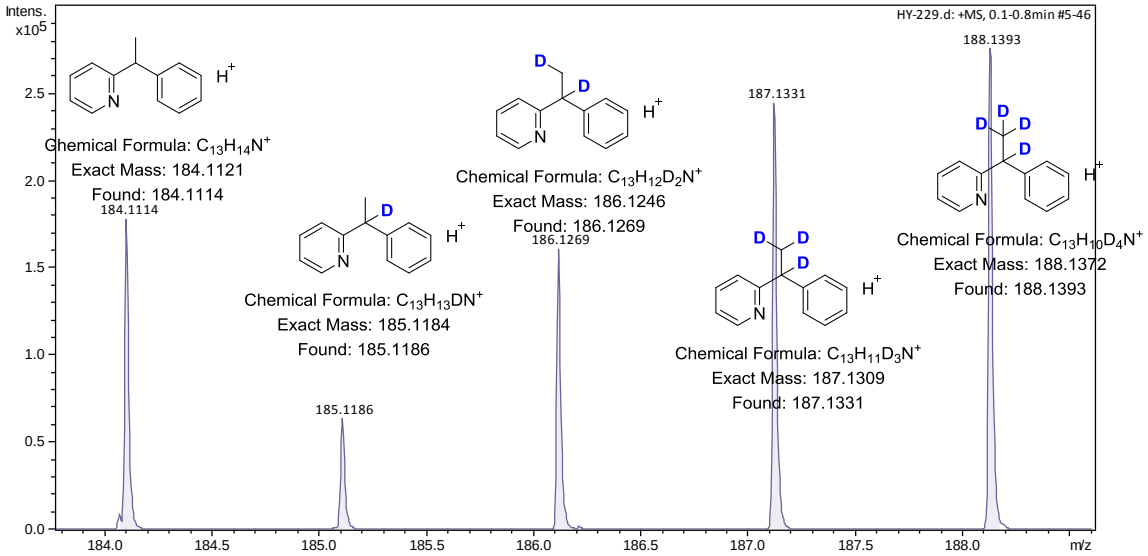


Figure 11. HRMS of deuterated product **2** (2.0 equiv. AcOD and 100 equiv. D_2O)

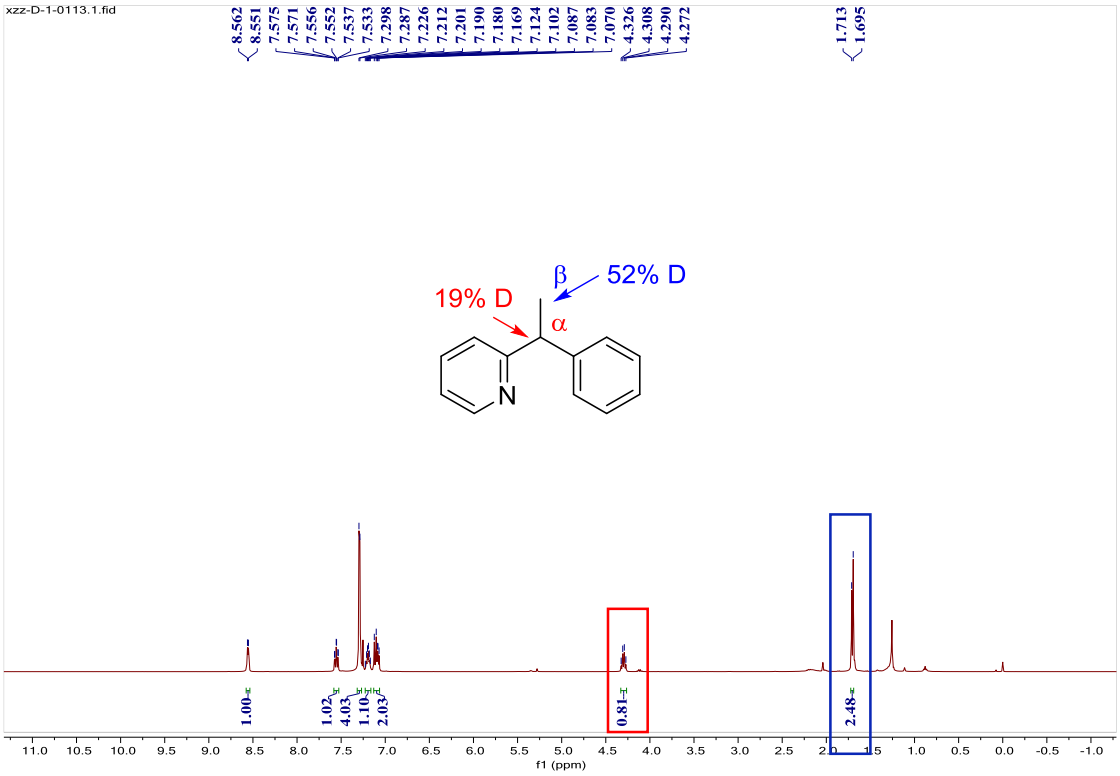
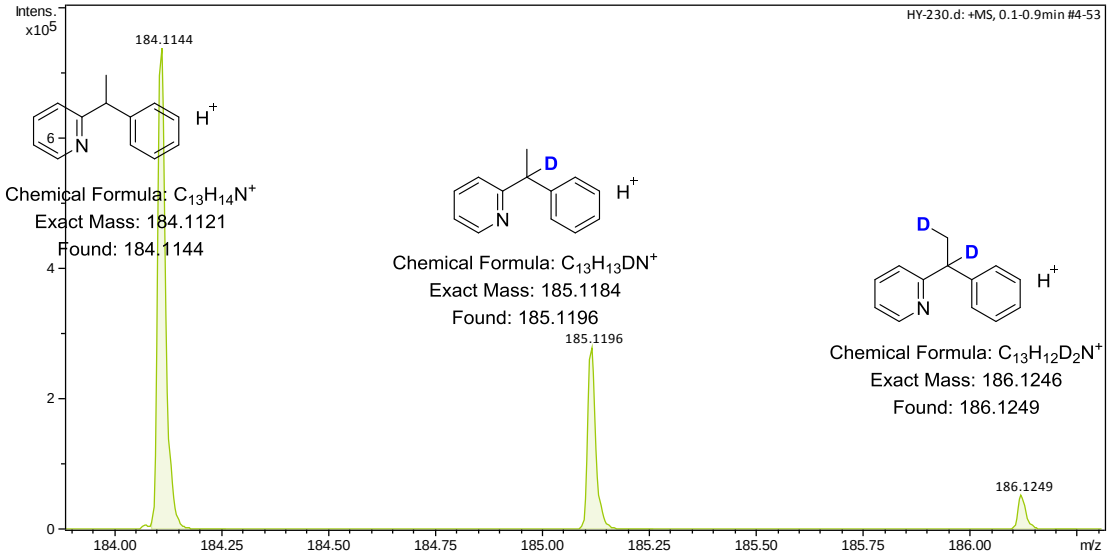


Figure S12. ^{1}H NMR of deuterated product **2** (2.0 equiv. AcOD)



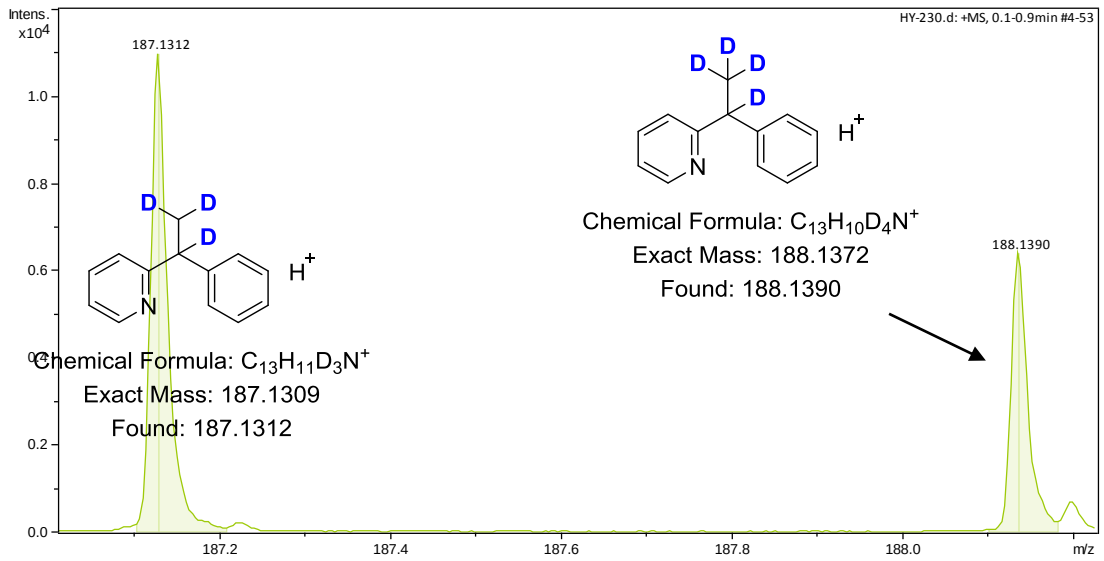


Figure 13. HRMS of deuterated product **2** (2.0 equiv. AcOD)

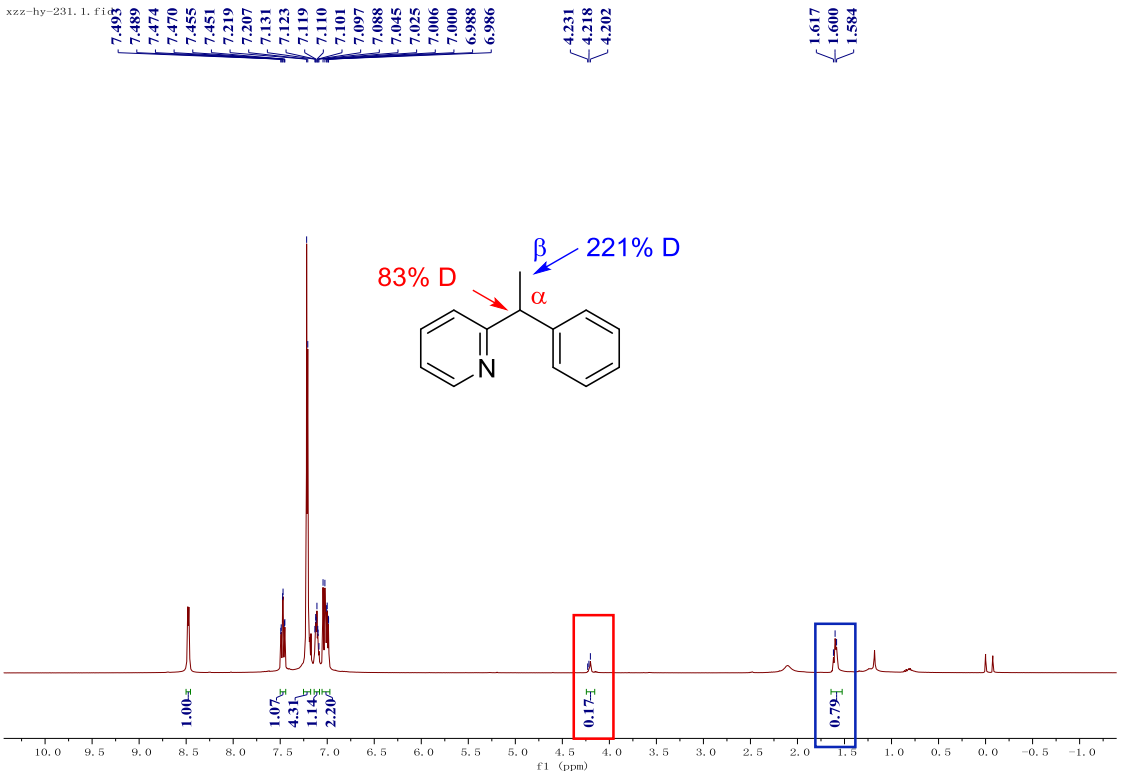


Figure S14. ^{1}H NMR of deuterated product **2** (2.0 equiv. CD_3COOD and 100 equiv. D_2O)

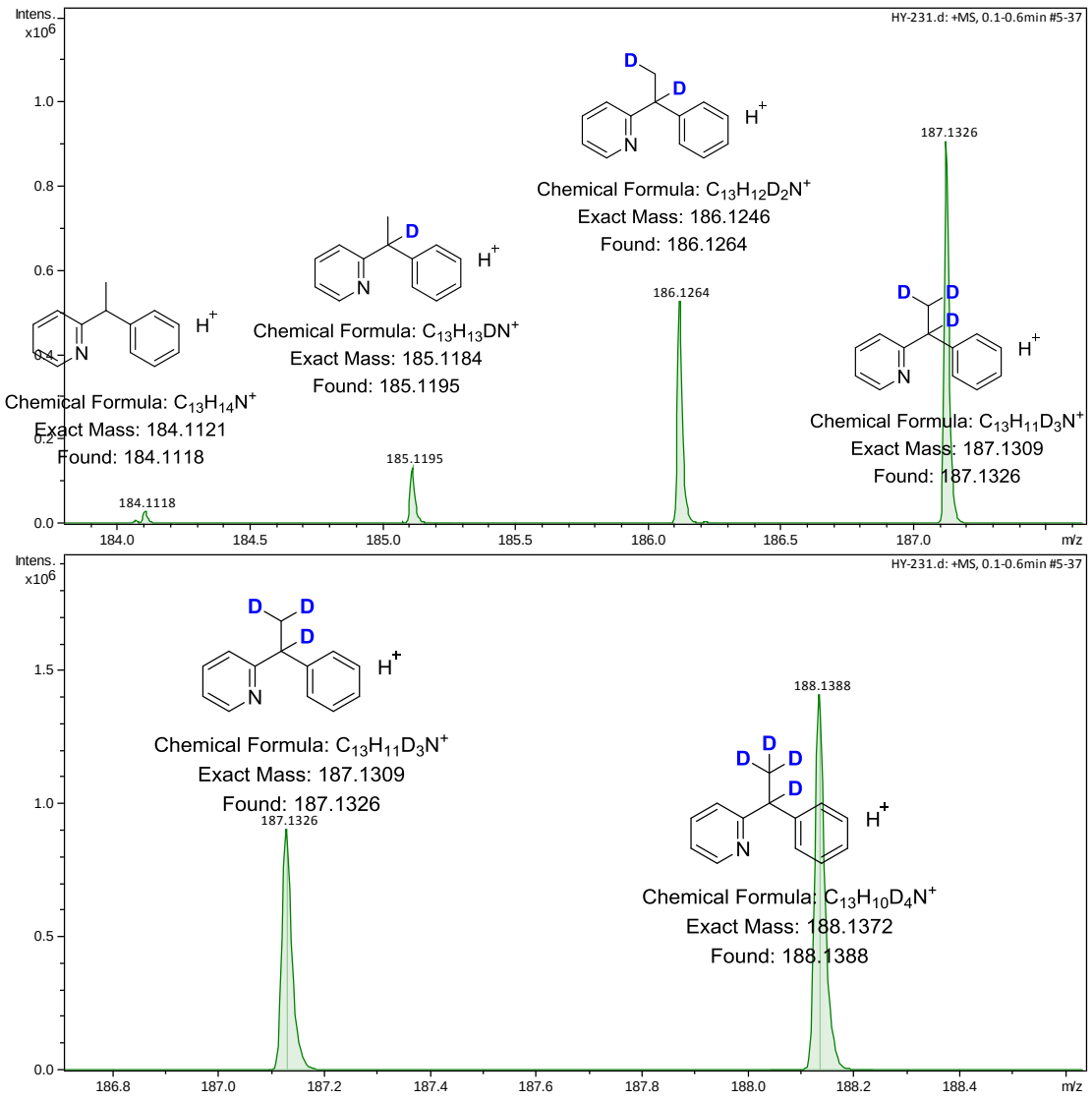


Figure 15. HRMS of deuterated product **2** (2.0 equiv. CD_3COOD and 100 equiv. D_2O)

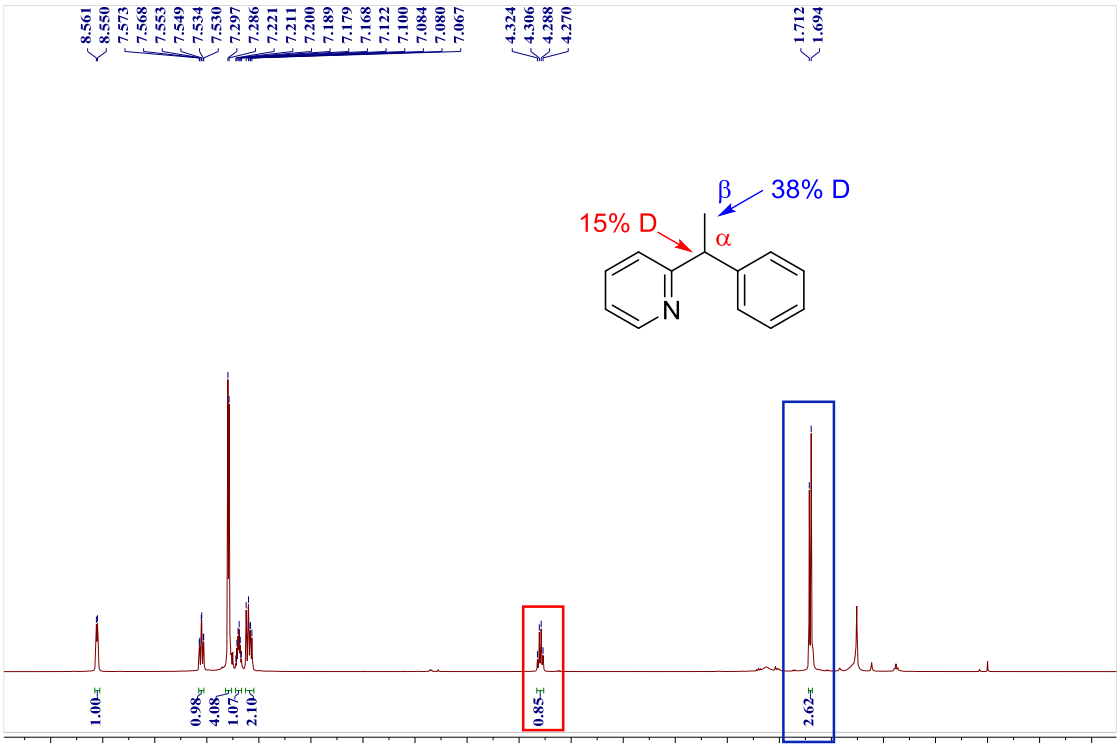
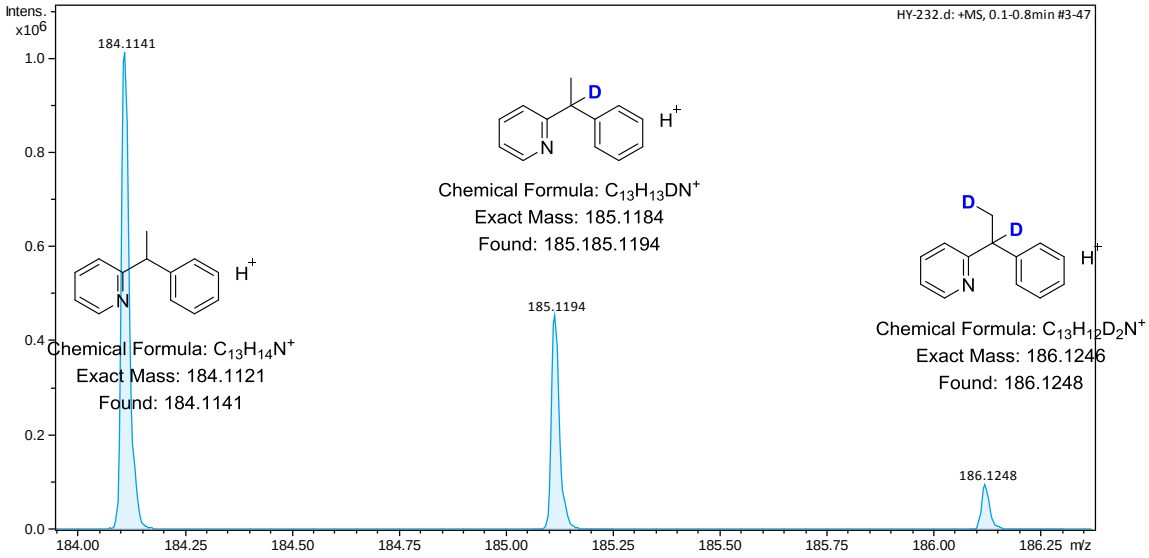


Figure S16. ^{1}H NMR of deuterated product **2** (2.0 equiv. CD_3COOD)



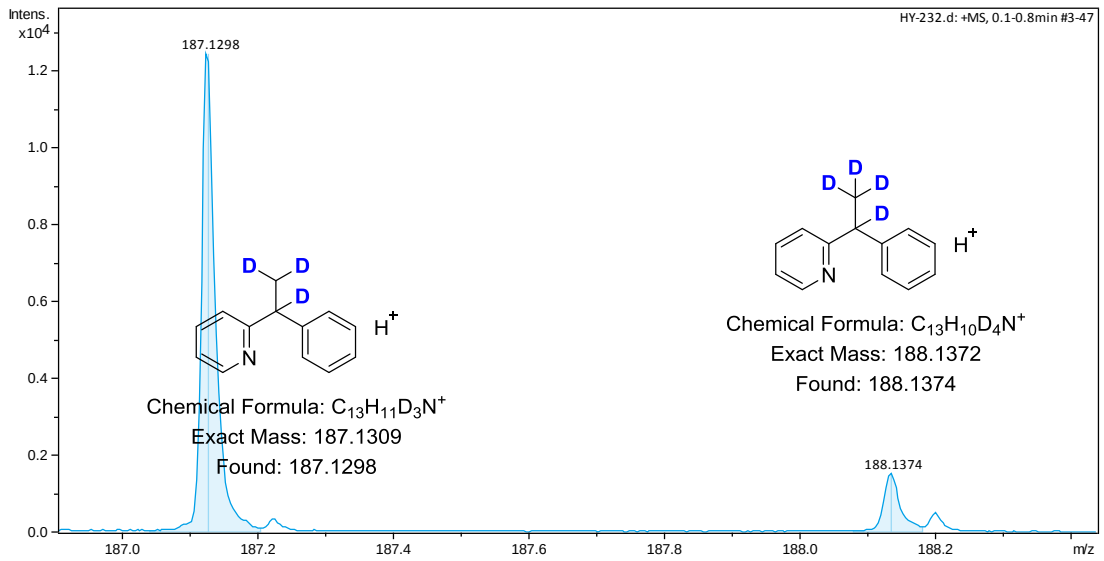
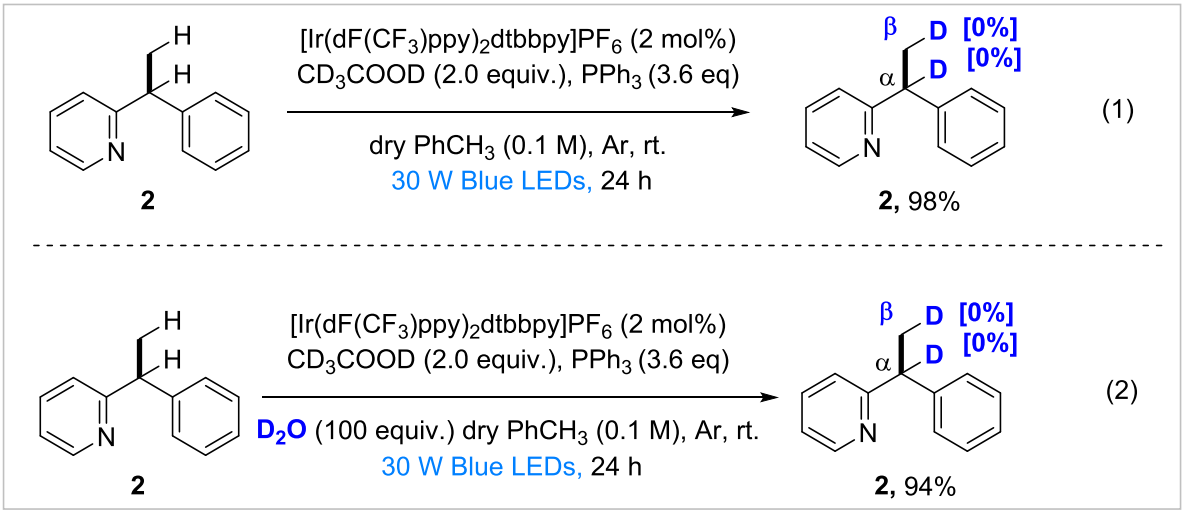
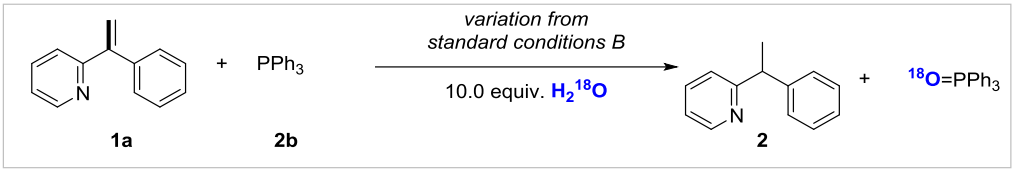


Figure17. HRMS of deuterated product **2** (2.0 equiv. CD_3COOD)

Another labelling experiments with D_2O were performed as follows: To an oven-dried 20 mL quartz flask equipped with a magnetic stirring bar, **2**, CD_3COOD (0.30 mmol, 2.0 equiv.), D_2O (100.0 equiv.), dry $PhCH_3$ (1.5 mL, 0.1 M), PPh_3 (0.54 mmol, 3.6 equiv.) and $[Ir(dF(CF_3)ppy)_2dtbbpy]PF_6$ (**PC1**, 2 mol%) were added in sequence. The reaction tube was evacuated and backfilled with Ar three times before light irradiation. The reaction mixture was stirred at ambient temperature under irradiation of 30 W blue LEDs (distance app. 3 cm) for 24 h. After that, the resulting mixture was purified by flash chromatography to afford the corresponding pure product, and the product was analysed by ^1H NMR. It revealed product **2** was not deuterated at all, demonstrating that deuterium was introduced into the product during the reaction.



b) Labelling Experiments by adding H_2O^{18} for hydrogenation reaction (Figure S18)



Another designated labelling experiment was set up under the standard conditions with 10.0 equivalent of H_2O^{18}. And ESI-MS of the crude reaction mixture was performed (Figure S18). The desired labelled ^{18}O product triphenylphosphine oxide-^{18}O was observed by HRMS. HRMS (EI): **[^{18}O]-** ^{18}O=PPh_3 $C_{18}H_{15}Na^{18}OP^+$, $[M+Na]^+$ calcd: 303.0795, Found: 303.0789. Additionaly, none ^{18}O-labled triphenylphosphine oxide (^{18}O=PPh_3) and product **2** were also observed by HRMS. HRMS (EI): O=PPh_3 $C_{18}H_{15}NaOP^+$, $[M+Na]^+$ calcd: 301.0753, Found: 301.0746; **2** $C_{13}H_{13}NNa^+$, $[M+Na]^+$ calcd: 206.0940, Found: 206.0940.

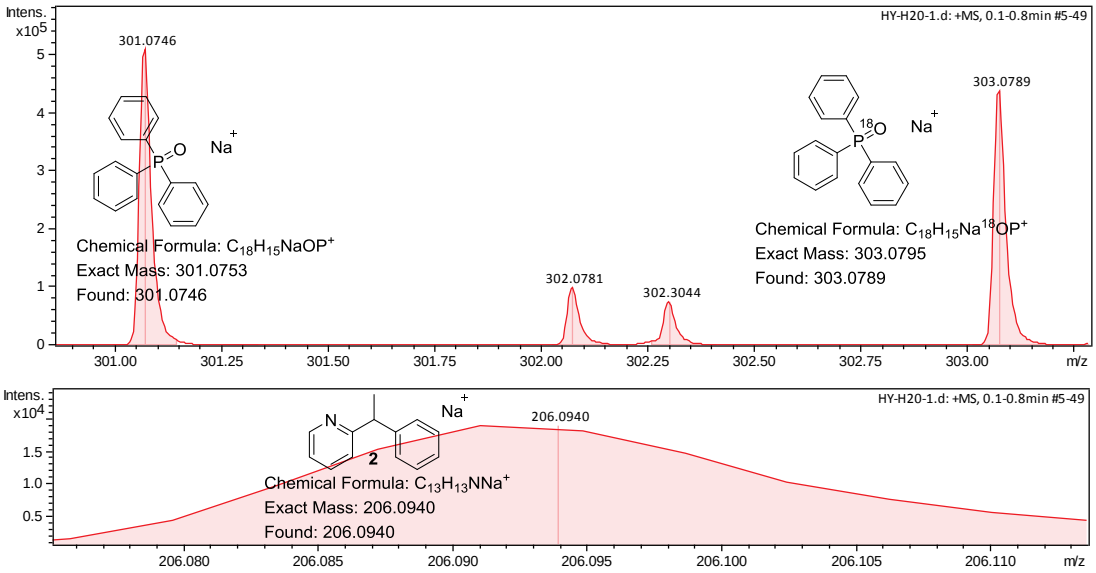
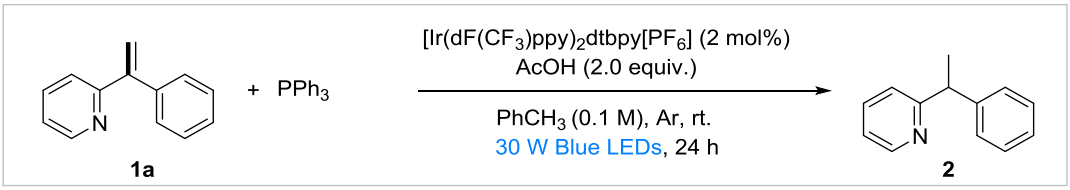


Figure 18 ESI-MS analysis of ^{18}O labeling experiment for hydrogenation reaction

In situ ^{31}P NMR

In situ ^{31}P NMR for olefin hydrogenation reaction (Figure S19)



In situ ^{31}P NMR monitoring experiments were set up according to the standard reaction conditions:

1a (0.45 mmol, 1.0 equiv.), AcOH (0.90 mmol, 2.0 equiv.), PPh_3 (1.62 mmol, 3.6 equiv.) and $[Ir(dF(CF_3)ppy)_2dtbbpy]PF_6$ (**PC1**, 2 mol%) were added in $PhCH_3$ (4.5 mL, 0.1 M). The reaction tube was evacuated and backfilled with Ar three times before light irradiation. The reaction was stopped over time interval of 5 min, 30 min, 1 h, 2 h, 6 h, 12 h, 24h, and the reaction solution was analyzed by ^{31}P NMR in $CDCl_3$. As detected by ^{31}P NMR (Figure S19), the amount of the triphenylphosphine oxide ($O=PPh_3$) gradually increases over time.

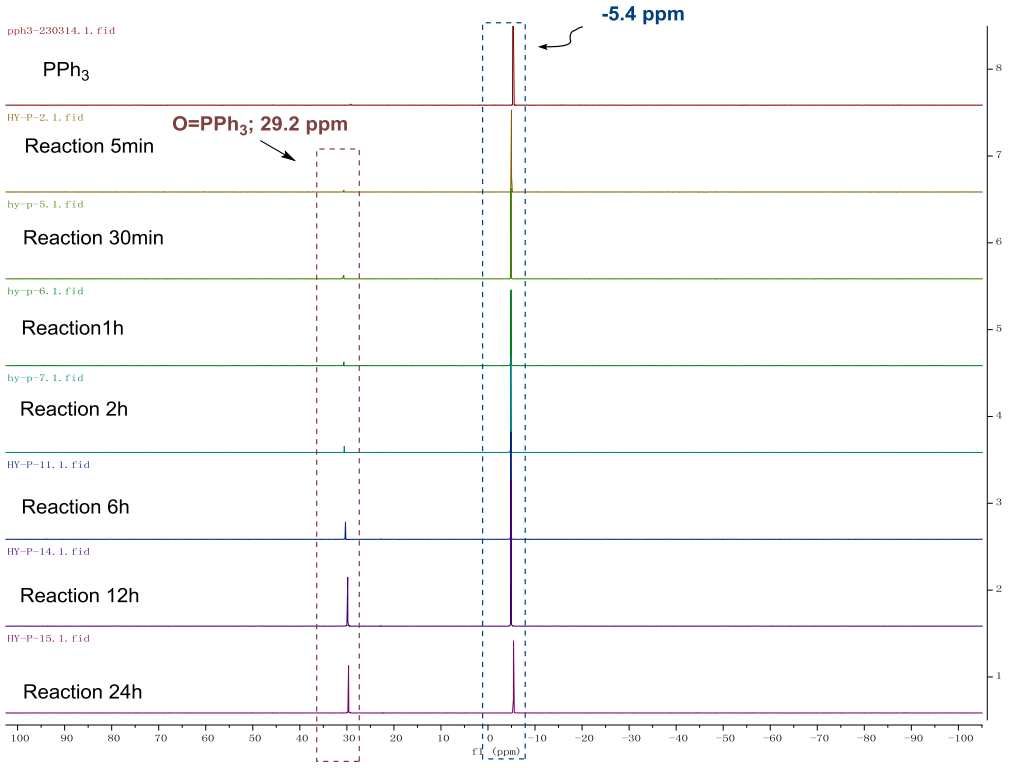
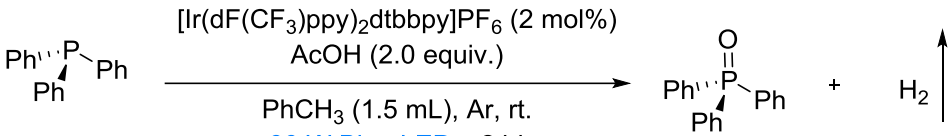


Figure S19. *In* situ ^{31}P NMR studies for olefin hydrogenation reaction

Detection of hydrogen gas H_2



To an oven-dried 15 mL quartz flask equipped with a magnetic stirring bar, triphenyl phosphine PPh_3 (0.54 mmol, 3.6 equiv.) and $[Ir(dFCF_3ppy)_2dtbbpy]PF_6$ (**PC1**, 2 mol%) were added. The reaction tube was evacuated and backfilled with argon three times. Then, $PhCH_3$ (1.5 mL) and AcOH (0.3 mmol, 2.0 equiv.) were added under argon atmosphere *via* syringe. The tube was placed in the photoreactor and stirred at ambient temperature (*note: the reaction temperature ranges from*

25 ℃ to 40 ℃) under irradiation of 30 W blue LEDs (distance app. 3 cm). After 24 hours, the irradiation was stopped, and the upper atmosphere was analyzed by GC. The sample was subjected to GC-TCD analysis. Moreover, 10 mL of $CDCl_3$ was added and the reaction mixture was continued to be analyzed by ^{31}P NMR.

GC spectrum

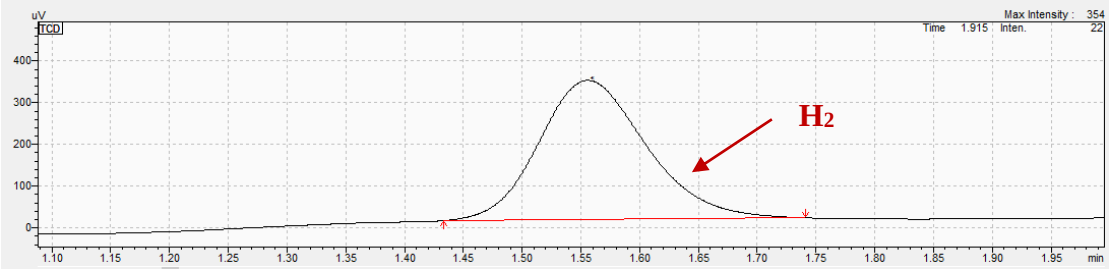


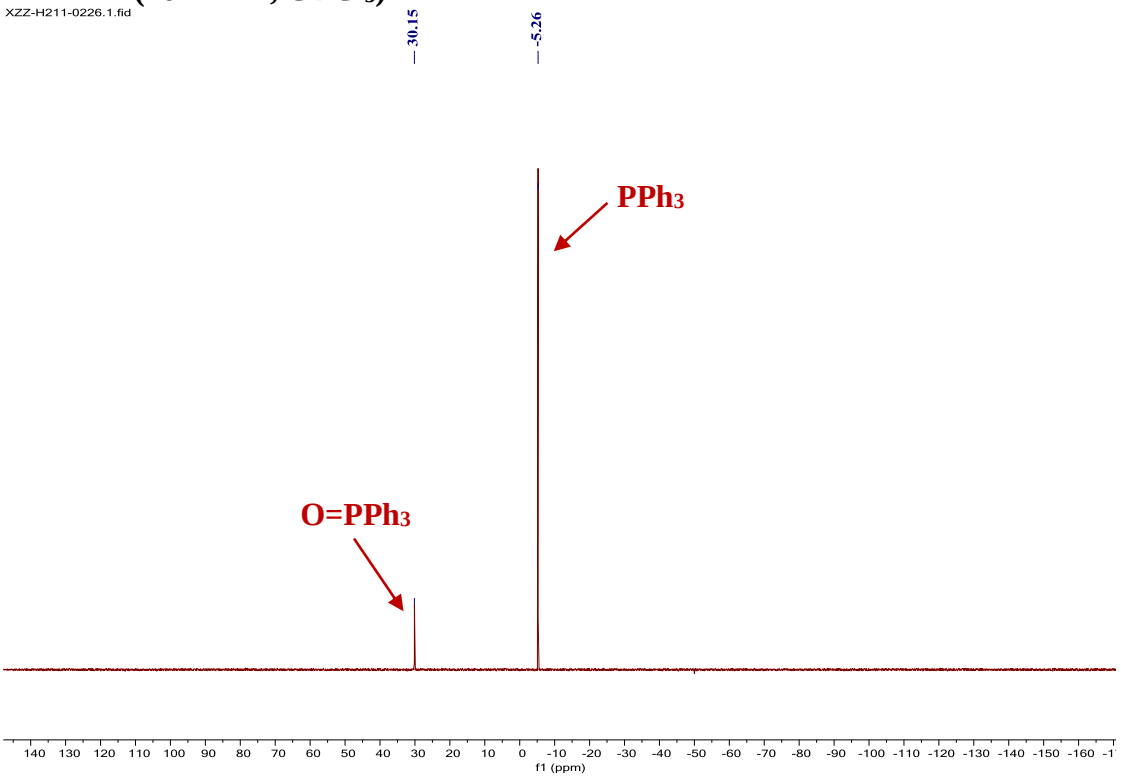
Figure S20. The GC spectrum for detection of hydrogen gas H_2

※ **Notes:**

No hydrogen gas was detected without PPh_3

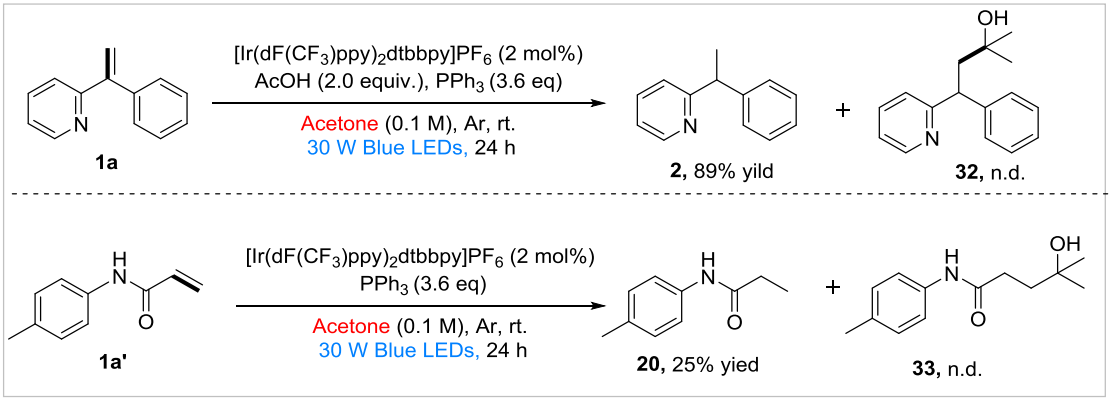
1) Detected by NMR

^{31}P NMR (162 MHz, $CDCl_3$)



Verification of radical anion intermediate

To investigate whether reductive activation π bonds of alkene to a nucleophilic radical anion, a reaction between 2-(1-phenylvinyl)pyridine **(1a)** or acrylamide (**1a'**) with acetone was conducted under standard conditions. Notably, acetone not only used as reaction solvent, but also utilized as the electrophilic partner. Only hydrogenated product **2** or **20** was observed, without the formation of the tertiary alcohol product **32** or **33** which generated from a direct addition of nucleophilic radical anion to ketones. These results confirm that the direct reductive activation of **1a** or **1a'** to a radical anion intermediate did not occur under the reaction conditions, which was differ from the previous work of Polyzos[8].



ON-OFF study

Time profile for the hydrogenation reaction with the light ON-OFF over time (Figure S21)

ON-OFF experiments were set up parallel on a 0.30 mmol scale according to the standard condition, and extra 1.0 equiv. of benzotrifluoride was added as internal standard. The reaction started with successive irradiation and black periods to study the influence of continuous irradiation of the visible-light for the progress. After being irradiated with 30 W blue LEDs for 2 h, an aliquot (0.25 mL) from the reaction mixture was transferred into a nuclear magnetic tube charged with 0.35 mL $CDCl_3$-d_1. The yield of the product **2** was determined by ^{19}F NMR. Then, the reaction mixture was stirred with light-off for 2 h. All of the following yields were analyzed in the identical way after a 2-hour light-on or light-off. These results revealed that light is a necessary component of the reaction (Figure S21).

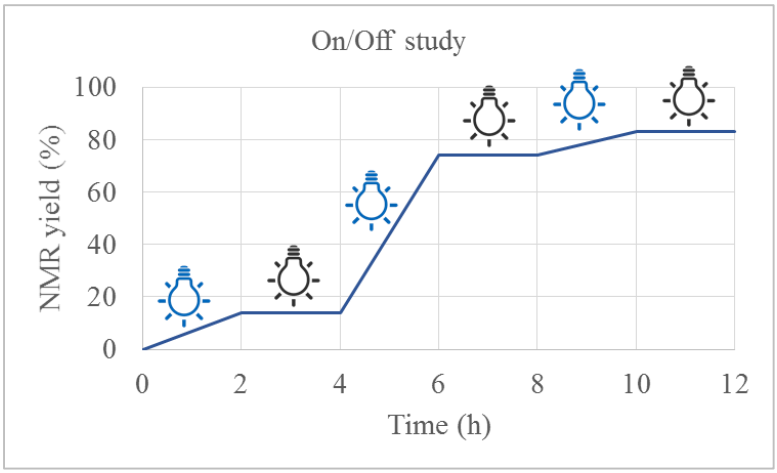
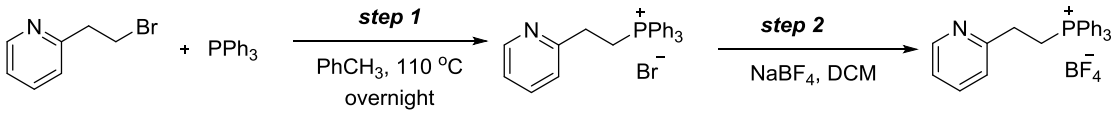


Figure S21. Time profile for hydrogenation reaction with the light On/Off over time

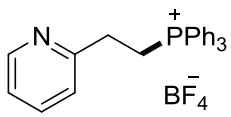
Verification of intermediate

General Procedures for the synthesis of phosphonium tetrafluoroborate 2a



Step 1: 2-(2-bromoethyl)pyridine (5.0 mmol, 1.0 equiv.), $PhCH_3$ (2.0 mL) and PPh_3 (6.0 mmol, 1.20 equiv.) were added sequentially to a 15 mL Schlenk flask. The vial was evacuated and backfilled with Ar three times. Then reaction mixture was placed in an oil bath at 110 ℃ (pre-heated) for 12 h. After cooling to rt., diethyl ether was added. The mixture was filtered, and the obtained precipitate was washed by diethyl ether. Then, the precipitate was dried in vacuum to give the corresponding phosphonium bromide.

Step 2: The corresponding phosphonium bromide was dissolved in DCM (25 mL). Then, the solution was repeatedly treated with 5% aqueous $NaBF_4$ solution (3 × 15 mL) and washed with H_2O (2 × 10 mL). The organic layer was removed in *vacuo* and dried under high vacuum to afford the corresponding phosphonium tetrafluoroborate **2a**.



2a, 57%

2a: white solid, 57% yield (1.30 g);

m.p. 114.4 – 116.4 ℃;

IR (neat) *v* 1596, 1438, 1285, 1191, 1032, 935, 752, 527 cm^{-1};

^{1}H NMR (400 MHz, Chloroform-*d*) δ 8.35 (d, *J* = 4.3 Hz, 1H), 7.80 – 7.68 (m, 15H), 7.55 (t, *J* = 7.8 Hz, 1H), 7.28 (d, *J* = 7.7 Hz, 1H), 7.10 – 7.07 (m, 1H), 3.77 (dt, *J* = 12.5, 7.7 Hz, 2H), 3.25 (dt, *J* = 14.4, 7.6 Hz, 2H).

^{19}F NMR (376 MHz, Chloroform-*d*) δ -152.69;

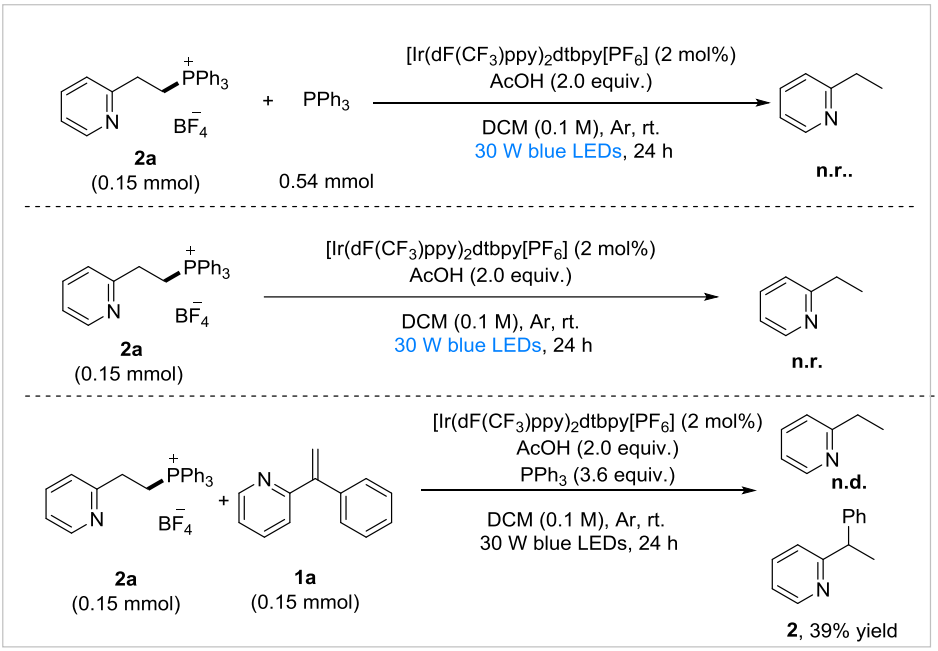
^{11}B NMR (128 MHz, Chloroform-*d*) δ -0.88;

^{31}P NMR (162 MHz, Chloroform-*d*) δ 23.76;

^{13}C NMR (100 MHz, Chloroform-*d*) δ 156.7, 156.6, 148.9, 137.2, 135.2 (d, $^{4}J_{C\text{-}P}$ = 3.0 Hz), 133.4 (d, $^{3}J_{C\text{-}P}$ = 10.1 Hz), 130.5 (d, $^{2}J_{C\text{-}P}$ = 12.7 Hz), 123.7, 122.3, 117.9 (d, $^{1}J_{C\text{-}P}$ = 86.7 Hz), 29.9 (d, $^{2}J_{C\text{-}P}$ = 3.4 Hz, Py<u>C</u>H$_2$CH$_2$P), 21.4 (d, $^{1}J_{C\text{-}P}$ = 53.0 Hz, PyCH$_2$<u>C</u>H$_2$P);

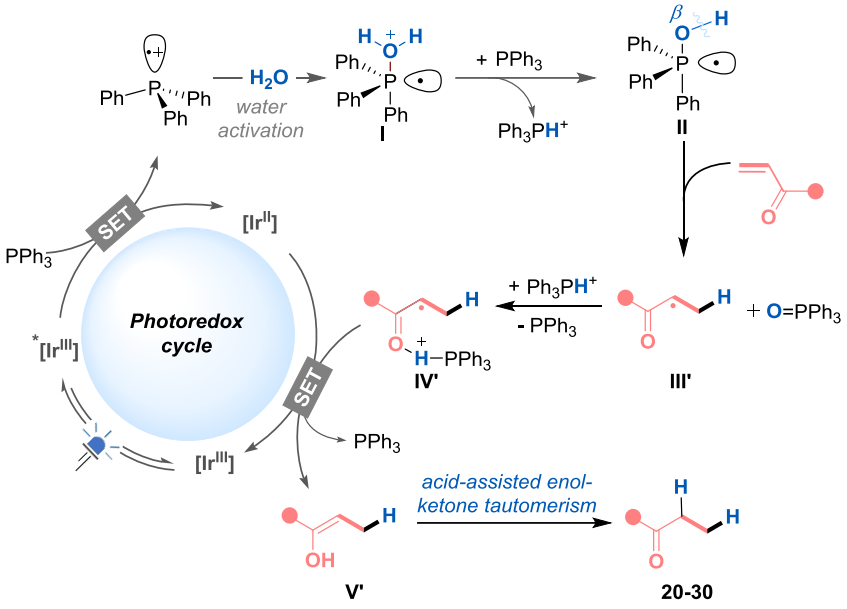
HRMS (ESI): $C_{25}H_{23}NP^{+}$, $[M]^{+}$ Calcd 368.1563, Found 368.1547.

Verification of intermediate for hydrogenation reaction (Scheme S3)

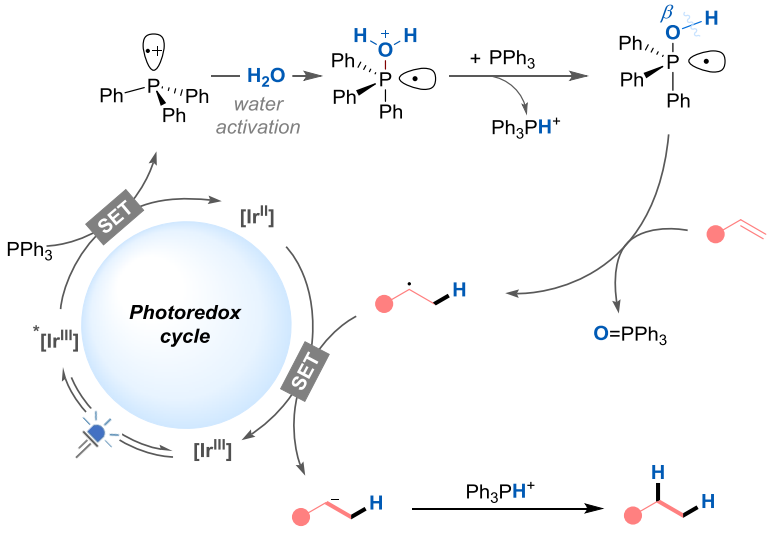


A series of control experiments were set up by subjected phosphonium tetrafluoroborate **2a** to the variation standard conditions to determine whether phosphonium salt was involved in reduction transformation process. Unfortunately, no desired product was obtained, which indicated that phosphonium salt **2a** not intermediate in the reduction reaction.

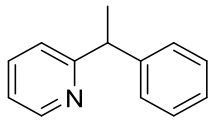
Proposed mechanism for product 20-30



Proposed mechanism for product 31



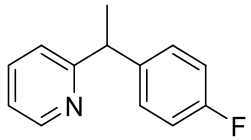
5. Characterization Data of Compounds 2-31



2, 24h
97% yield

2: colorless oil (27 mg, 97% yield) from **1a** (0.15 mmol, 27 mg) under standard conditions (PE/EA = 3%);

^{1}H NMR (400 MHz, Chloroform-*d*) δ 8.55 (d, *J* = 4.7 Hz, 1H), 7.55 (t, *J* = 7.7 Hz, 1H), 7.30 – 7.28 (m, 4H), 7.19 (dq, *J* = 8.6, 4.2 Hz, 1H), 7.12 – 7.06 (m, 2H), 4.29 (q, *J* = 7.2 Hz, 1H), 1.70 (d, *J* = 7.2 Hz, 3H).

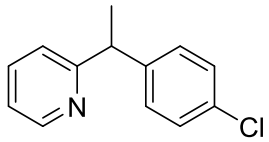


3, 24h
60% yield

3: colorless oil (18 mg, 60% yield) from **1b** (0.15 mmol, 30 mg) under standard conditions (PE/EA = 3%);

^{1}H NMR (400 MHz, Chloroform-*d*) δ 8.56 (dd, *J* = 5.7, 1.5 Hz, 1H), 7.57 (td, *J* = 7.7, 1.8 Hz, 1H), 7.27 – 7.23 (m, 2H), 7.11 – 7.08 (m, 2H), 7.00 – 6.95 (m, 2H), 4.27 (q, *J* = 7.2 Hz, 1H), 1.68 (d, *J* = 7.2 Hz, 3H);

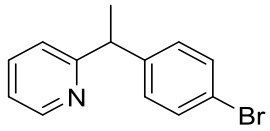
^{19}F NMR (376 MHz, Chloroform-*d*) δ -117.08.



4, 24h
77% yield

4: colorless oil (25 mg, 77% yield) from **1c** (0.15 mmol, 32 mg) under standard conditions (PE/EA = 4%);

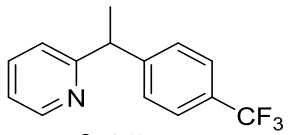
^{1}H NMR (400 MHz, Chloroform-*d*) δ 8.55 (dd, *J* = 5.0, 1.6 Hz, 1H), 7.57 (td, *J* = 7.7, 1.7 Hz, 1H), 7.26 – 7.21 (m, 4H), 7.11 – 7.09 (m, 2H), 4.26 (q, *J* = 7.2 Hz, 1H), 1.68 (d, *J* = 7.2 Hz, 3H).



5, 24h
84% yield

5: yellow oil **(**33 mg, 84% yield) from **1d** (0.15 mmol, 39 mg) under standard conditions (PE/EA = 3%);

^{1}H NMR (400 MHz, Chloroform-*d*) δ 8.55 (d, *J* = 3.6 Hz, 1H), 7.59 – 7.55 (m, 1H), 7.40 (d, *J* = 8.3 Hz, 2H), 7.17 (d, *J* = 8.3 Hz, 2H), 7.10 (d, *J* = 7.7 Hz, 2H), 4.24 (q, *J* = 7.2 Hz, 1H), 1.68 (d, *J* = 7.2 Hz, 3H);

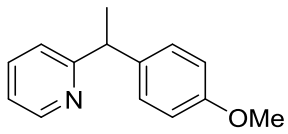


6, 24h
74% yield

6: colorless oil (28 mg, 74% yield) from **1e** (0.15 mmol, 37 mg) under standard conditions(PE/EA = 4%);

^{1}H NMR (400 MHz, Chloroform-*d*) δ 8.49 (d, *J* = 4.6 Hz, 1H), 7.54 (td, *J* = 7.7, 1.8 Hz, 1H), 7.46 (d, *J* = 8.1 Hz, 2H), 7.33 (d, *J* = 8.1 Hz, 2H), 7.04 (t, *J* = 7.1 Hz, 2H), 4.26 (q, *J* = 7.2 Hz, 1H), 1.64 (d, *J* = 7.2 Hz, 3H);

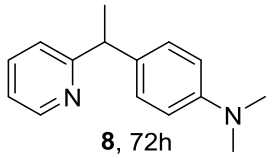
^{19}F NMR (376 MHz, Chloroform-*d*) δ -62.39;



7, 24h
75% yield

7: yellow oil (24 mg, 75% yield) from **1f** (0.15 mmol, 32 mg) under standard conditions (PE/EA = 5%);

^{1}H NMR (400 MHz, Chloroform-*d*) δ 8.47 (d, *J* = 4.3 Hz, 1H), 7.47 (td, *J* = 7.7, 1.5 Hz, 1H), 7.14 (d, *J* = 8.6 Hz, 2H), 7.03 – 6.98 (m, 2H), 6.76 (d, *J* = 8.6 Hz, 2H), 4.17 (q, *J* = 7.2 Hz, 1H), 3.69 (s, 3H), 1.60 (d, *J* = 7.2 Hz, 3H).



8, 72h
30% yield

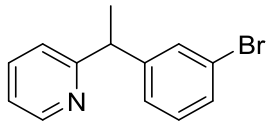
8: colorless oil **(**10 mg, 30% yield) from **1g** (0.15 mmol, 34 mg) under standard conditions (PE/EA = 12%);

IR (neat) *v* 2798, 1519, 1431, 1224, 1059, 946, 748, 550 cm^{-1};

^{1}H NMR (400 MHz, Chloroform-*d*) δ 8.54 (d, *J* = 4.1 Hz, 1H), 7.54 (td, *J* = 7.7, 1.8 Hz, 1H), 7.17 (d, *J* = 8.7 Hz, 2H), 7.12 – 7.05 (m, 2H), 6.70 (d, *J* = 8.7 Hz, 2H), 4.21 (q, *J* = 7.2 Hz, 1H), 2.90 (s, 6H), 1.67 (d, *J* = 7.2 Hz, 3H);

^{13}C NMR (100 MHz, Chloroform-*d*) δ 165.9, 149.2, 148.9, 136.4, 133.1, 128.3, 122.0, 121.0, 112.9, 46.4, 40.8, 20.8;

HRMS (ESI): $C_{15}H_{18}N_2Na^+$, $[M+Na]^+$ Calcd 249.1362, Found 249.1343.



9, 24h
66% yield

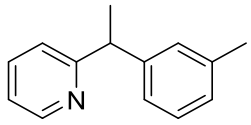
9: colorless oil (26 mg, 66% yield) from **1h** (0.15 mmol, 39 mg) under standard conditions (PE/EA = 4%);

IR (neat) *v* 2928, 1567, 1431, 1283, 1073, 996, 746, 591 cm^{-1};

^{1}H NMR (400 MHz, Chloroform-*d*) δ 8.49 (d, *J* = 4.0 Hz, 1H), 7.51 (td, *J* = 7.7, 1.6 Hz, 1H), 7.37 (s, 1H), 7.25 (d, *J* = 7.8 Hz, 1H), 7.15 (d, *J* = 7.6 Hz, 1H), 7.09 (d, *J* = 8.0 Hz, 1H), 7.05 – 7.02 (m, 2H), 4.17 (q, *J* = 7.1 Hz, 1H), 1.61 (d, *J* = 7.2 Hz, 3H);

^{13}C NMR (100 MHz, Chloroform-*d*) δ 164.1, 149.3, 147.5, 136.6, 130.8, 130.0, 129.4, 126.4, 122.6, 122.1, 121.5, 47.1, 20.7;

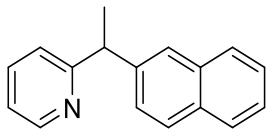
HRMS (ESI): $C_{13}H_{13}BrN^+$, $[M+H]^+$ Calcd 262.0226, Found 262.0249.



10, 24h
74% yield

10: colorless oil (22.0 mg, 74% yield) from **1i** (0.15 mmol, 29 mg) under standard conditions (PE/EA = 4%);

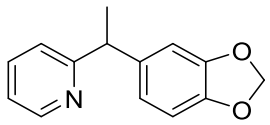
^{1}H NMR (400 MHz, Chloroform-*d*) δ 8.56 (d, *J* = 4.4 Hz, 1H), 7.55 (td, *J* = 7.7, 1.7 Hz, 1H), 7.18 (t, *J* = 7.6 Hz, 1H), 7.13 – 7.06 (m, 4H), 7.00 (d, *J* = 7.4 Hz, 1H), 4.26 (q, *J* = 7.2 Hz, 1H), 2.31 (s, 3H), 1.69 (d, *J* = 7.2 Hz, 3H).



11, 24h
57% yield

11: colorless oil (20 mg, 57% yield) from **1j** (0.15 mmol, 35 mg) under standard conditions (PE/EA = 4%);

^{1}H NMR (400 MHz, Chloroform-*d*) δ 8.58 (d, *J* = 4.5 Hz, 1H), 7.77 (q, *J* = 8.8, 8.0 Hz, 4H), 7.54 (td, *J* = 7.7, 1.6 Hz, 1H), 7.46 – 7.38 (m, 3H), 7.15 – 7.07 (m, 2H), 4.46 (q, *J* = 7.2 Hz, 1H), 1.80 (d, *J* = 7.2 Hz, 3H);



12, 24h
65% yield

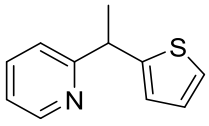
12: colorless oil (22 mg, 65% yield) from **1k** (0.15 mmol, 34 mg) under standard conditions (PE/EA = 5%);

IR (neat) *v* 2928, 1588, 1432, 1233, 1036, 935, 748, 547 cm^{-1};

^{1}H NMR (400 MHz, Chloroform-*d*) δ 8.55 (d, *J* = 4.1 Hz, 1H), 7.57 (td, *J* = 7.7, 1.8 Hz, 1H), 7.13 – 7.08 (m, 2H), 6.78 – 6.72 (m, 3H), 5.90 (s, 2H), 4.21 (q, *J* = 7.2 Hz, 1H), 1.66 (d, *J* = 7.2 Hz, 3H);

^{13}C NMR (100 MHz, Chloroform-*d*) δ 165.0, 149.1, 147.7, 145.9, 139.1, 136.5, 122.0, 121.3 120.6, 108.21, 108.15, 100.9, 47.0, 21.0.

HRMS (ESI): $C_{14}H_{13}NNaO_2^+$, $[M+Na]^+$ Calcd 250.0838, Found 250.0842.



13, 24h
39% yield

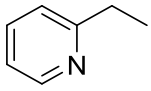
13: yellow oil (11mg, 39% yield) from **1l** (0.15 mmol, 28 mg) under standard conditions (PE/EA = 4%);

IR (neat) *v* 2928, 1589, 1432, 1233, 1044, 993, 748, 540 cm^{-1};

^{1}H NMR (400 MHz, Chloroform-*d*) δ 8.57 (d, *J* = 4.6 Hz, 1H), 7.62 – 7.58 (m, 1H), 7.19 – 7.11 (m, 3H), 6.95 – 6.92 (m, 1H), 6.89 – 6.88 (m, 1H), 4.53 (q, *J* = 7.1 Hz, 1H), 1.76 (d, *J* = 7.2 Hz, 3H);

^{13}C NMR (100 MHz, Chloroform-*d*) δ 164.5, 149.1, 148.7, 136.7, 126.6, 123.9, 123.8, 121.6, 43.2, 22.1;

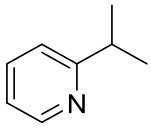
HRMS (ESI): $C_{11}H_{12}NS^+$, $[M+Na]^+$ Calcd 190.0685, Found 190.0708.



14, 24h
80% yield

14: colorless oil (80% yield), yield of the product was determined by ^{1}H NMR using dibromomethane as internal standard from **1m** (0.15 mmol, 16 mg);

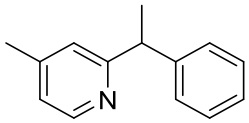
^{1}H NMR (400 MHz, Chloroform-*d*) δ 8.36 (d, *J* = 4.8 Hz, 1H), 7.38 (td, *J* = 7.7, 1.6 Hz, 1H), 6.96 (d, *J* = 7.8 Hz, 1H), 6.90 – 6.87 (m, 1H), 2.66 (q, *J* = 7.6 Hz, 2H), 1.15 (t, *J* = 8.0 Hz, 3H).



15, 24h
61% yield

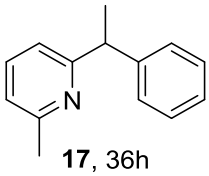
15: colorless oil (11 mg, 61% yield) from **1n** (0.15 mmol, 18 mg) under standard conditions (PE/EA = 3%);

^{1}H NMR (400 MHz, Chloroform-*d*) δ 8.54 (d, *J* = 4.5 Hz, 1H), 7.61 (td, *J* = 7.7, 1.6 Hz, 1H), 7.18 (d, *J* = 7.9 Hz, 1H), 7.12 – 7.08 (m, 1H), 3.06 (dq, *J* = 13.7, 6.9 Hz, 1H), 1.31 (t, *J* = 6.9 Hz, 6H).



16, 24h
51% yield

16: colorless oil (15 mg, 51% yield) from **1o** (0.15 mmol, 29 mg) under standard conditions (PE/EA = 4%);**^{1}H NMR** (400 MHz, Chloroform-*d*) δ 8.41 (d, *J* = 5.0 Hz, 1H), 7.30 -7.29 (m, 4H), 7.21 – 7.17 (m, 1H), 6.93 – 6.91 (m, 2H), 4.25 (q, *J* = 7.2 Hz, 1H), 2.27 (s, 3H), 1.69 (d, *J* = 7.2 Hz, 3H).



17, 36h
81% yield

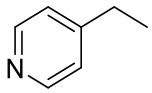
17: colorless oil (24 mg, 81% yield) from **1p** (0.15 mmol, 29 mg) under standard conditions (PE/EA = 3%);

IR (neat) *v* 2928, 1589, 1451, 1155, 1029, 991, 744, 544 cm^{-1};

^{1}H NMR (400 MHz, Chloroform-*d*) δ 7.43 (t, *J* = 7.7 Hz, 1H), 7.32 -7.27 (m, 4H), 7.20 – 7.17 (m, 1H), 6.93 (d, *J* = 7.6 Hz, 1H), 6.86 (d, *J* = 7.6 Hz, 1H), 4.28 (q, *J* = 7.2 Hz, 1H), 2.54 (s, 3H), 1.68 (d, *J* = 7.2 Hz, 3H);

^{13}C NMR (100 MHz, Chloroform-*d*) δ 164.7, 157.6, 145.1, 136.6, 128.4, 127.8, 126.2, 120.7, 118.7, 47.5, 24.6, 21.0;

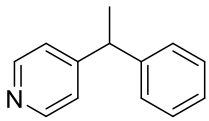
HRMS (ESI): $C_{14}H_{15}NNa^+$, $[M+Na]^+$ Calcd 220.1097, Found 220.1101.



18, 24h
56% yield

18: colorless oil (56% yield), yield of the product was determined by ^{1}H NMR using dibromomethane as internal standard from **1q** (0.15 mmol, 16 mg);

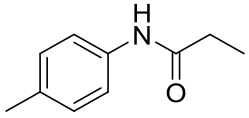
^{1}H NMR (400 MHz, Chloroform-*d*) δ 8.49 (d, *J* = 3.6 Hz, 2H), 7.13 (d, *J* = 5.4 Hz, 2H), 2.65 (q, *J* = 7.6 Hz, 2H), 1.26 (t, *J* = 7.6 Hz, 3H).



19, 24h
69% yield

19: yellow oil (19 mg, 69% yield) from **1r** (0.15 mmol, 27 mg) under standard conditions (PE/EA = 10%);

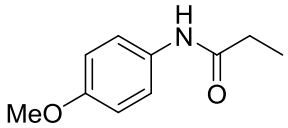
^{1}H NMR (400 MHz, Chloroform-*d*) δ 8.49 (d, *J* = 3.6 Hz, 2H), 7.31 (t, *J* = 7.2 Hz, 2H), 7.24 – 7.18 (m, 3H), 7.13 (d, *J* = 5.6 Hz, 2H), 4.11 (q, *J* = 7.2 Hz, 1H), 1.64 (d, *J* = 7.2 Hz, 3H),



20, 24h
49% yield

20: a white solid (12 mg, 49% yield) from **1a'** (0.15 mmol, 25 mg) under standard conditions (PE/EA = 15%);

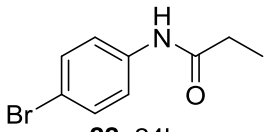
^{1}H NMR (400 MHz, Chloroform-*d*) δ 7.39 (d, *J* = 8.3 Hz, 2H), 7.23 (*br* s, 1H), 7.11 (d, *J* = 8.1 Hz, 2H), 2.37 (q, *J* = 7.5 Hz, 2H), 2.31 (s, 3H), 1.24 (t, *J* = 7.5 Hz, 3H);



21, 24h
56% yield

21: a white solid (15 mg, 56% yield) from **1b'** (0.15 mmol, 27 mg) under standard conditions (PE/EA = 15%);

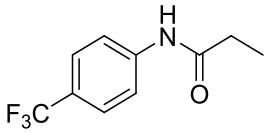
^{1}H NMR (400 MHz, Chloroform-*d*) δ 7.41 (d, *J* = 8.9 Hz, 2H), 7.17 (*br* s, 1H), 6.85 (d, *J* = 8.9 Hz, 2H), 3.79 (s, 3H), 2.37 (q, *J* = 7.6 Hz, 2H), 1.24 (t, *J* = 7.5 Hz, 3H).



22, 24h
21% yield

22: a white solid (7 mg, 21% yield) from **1c'** (0.15 mmol, 34 mg) under standard conditions (PE/EA = 15%);

^{1}H NMR (400 MHz, Chloroform-*d*) δ 7.42 (s, 4H), 7.22 (*br* s, 1H), 2.39 (q, *J* = 7.5 Hz, 2H), 1.24 (t, *J* = 7.5 Hz, 3H).



23, 24h
61% yield

23: a white solid (20.0 mg, 61% yield) from **1d'** (0.15 mmol, 32 mg) under standard conditions (PE/EA = 15%);

m.p. 131.0 – 133.0 ℃;

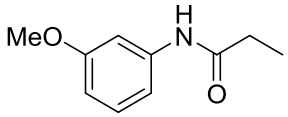
IR (neat) *v* 2917, 1541, 1410, 1150, 1016, 928, 731, 507 cm^{-1};

^{1}H NMR (400 MHz, Chloroform-*d*) δ 7.65 (d, *J* = 8.3 Hz, 2H), 7.59 (s, 1H), 7.56 (d, *J* = 8.5 Hz, 2H), 2.43 (q, *J* = 7.5 Hz, 2H), 1.25 (t, *J* = 7.5 Hz, 3H);

^{19}F NMR (376 MHz, Chloroform-*d*) δ -62.11;

^{13}C NMR (100 MHz, Chloroform-*d*) δ 172.5, 141.0, 126.2 (q, $^3J_{C\text{-}F}$ = 3.7 Hz, $\underline{C}HCCF_3$), 124.1 (q, $^1J_{C\text{-}F}$ = 271.5 Hz, $\underline{C}F_3$), 119.3, 30.8, 9.5;

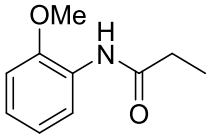
HRMS (ESI): $C_{10}H_{10}F_3NNaO^+$, $[M+Na]^+$ Calcd 240.0607, Found 240.0631.



24, 24h
48% yield

24: a white solid (13 mg, 48% yield) from **1e'** (0.15 mmol, 27 mg) under standard conditions (PE/EA = 20%);

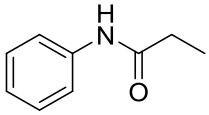
^{1}H NMR (400 MHz, Chloroform-*d*) δ 7.33 (s, 1H), 7.23 – 7.17 (m, 2H), 6.95 (d, *J* = 7.6 Hz, 1H), 6.65 (d, *J* = 7.2 Hz, 1H), 3.80 (s, 3H), 2.38 (q, *J* = 7.5 Hz, 2H), 1.24 (t, *J* = 7.5 Hz, 3H).



25, 24h
45% yield

25: colorless oil (12 mg, 45% yield) from **1f'** (0.15 mmol, 27 mg) under standard conditions (PE/EA = 15%);

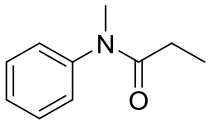
^{1}H NMR (400 MHz, Chloroform-*d*) δ 8.39 (d, *J* = 7.7 Hz, 1H),, 7.77 (*br* s, 1H), 7.05 -7.01 (m, 1H), 6.98 – 6.94 (m, 1H), 6.88 – 6.86 (m, 1H), 3.88 (s, 3H). 2.43 (q, *J* = 7.6 Hz, 2H), 1.26 (t, *J* = 7.5 Hz, 3H).



26, 24h
40% yield

26: a white solid (9 mg, 40% yield) from **1g'** (0.15 mmol, 22 mg) under standard conditions (PE/EA = 17%);

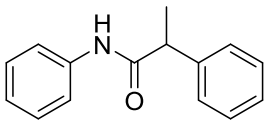
^{1}H NMR (400 MHz, Chloroform-*d*) δ 7.52 (d, *J* = 7.8 Hz, 2H), 7.30 (t, *J* = 7.8 Hz, 2H), 7.09 (t, *J* = 7.4 Hz, 1H), 2.38 (q, *J* = 7.5 Hz, 2H), 1.23 (t, *J* = 7.6 Hz, 3H).



27, 24h
29% yield

27: a white solid (7 mg, 29% yield) from **1h'** (0.15 mmol, 24 mg) under standard conditions (PE/EA = 15%);

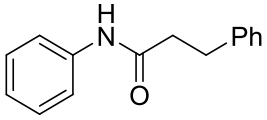
^{1}H NMR (400 MHz, Chloroform-*d*) δ 7.42 (t, *J* = 7.5 Hz, 2H), 7.34 (t, *J* = 7.2 Hz, 1H), 7.18 (d, *J* = 7.5 Hz, 2H), 3.27 (s, 3H), 2.08 (q, *J* = 6.9 Hz, 2H), 1.05 (t, *J* = 7.4 Hz, 3H).



28, 24h
50% yield

28: a white solid (17 mg, 50% yield) from **1i'** (0.15 mmol, 34 mg) under standard conditions (PE/EA = 7%);

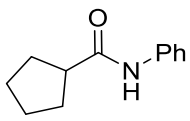
^{1}H NMR (400 MHz, Chloroform-*d*) δ 7.42 – 7.37 (m, 5H), 7.33 – 7.28 (m, 2H), 7.26 – 7.25 (m, 1H), 7.08 – 7.05 (m, 2H), 3.72 (q, *J* = 7.1 Hz, 1H), 1.65 (*br* s, 1H), 1.60 (d, *J* = 7.1 Hz, 3H).



29, 24h
50% yield

29: a white solid (17 mg, 50% yield) from **1j'** (0.15 mmol, 34 mg) under standard conditions (PE/EA = 8%);

^{1}H NMR (400 MHz, Chloroform-*d*) δ 7.42 (d, *J* = 7.7 Hz, 2H), 7.31 – 7.28 (m, 4H), 7.25 – 7.20 (m, 3H), 7.11 – 7.07 (m, 2H), 3.05 (t, *J* = 7.4 Hz, 2H), 2.65 (t, *J* = 7.5 Hz, 2H).



30, 72h
32% yield

30: a white solid (9 mg, 32% yield) from **1k'** (0.15 mmol, 28 mg) under standard conditions (PE/EA = 8%);

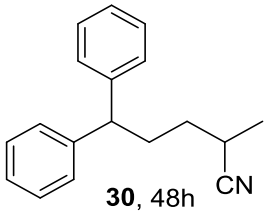
m.p. 154.9 – 155.5 ℃;

IR (neat) *v* 2922, 1654, 1439, 1244, 1080, 908, 753, 542 cm^{-1};

^{1}H NMR (400 MHz, Chloroform-*d*) δ 7.53 (d, *J* = 7.9 Hz, 2H), 7.31 (t, *J* = 7.8 Hz, 3H), 7.09 (t, *J* = 7.3 Hz, 1H), 2.68 (p, *J* = 8.0 Hz, 1H), 1.95 – 1.87 (m, 4H), 1.82 – 1.75 (m, 2H), 1.65 – 1.59 (m, 2H);

^{13}C NMR (100 MHz, Chloroform-*d*) δ 173.7, 137.1, 127.9, 123.0, 118.6, 45.8, 29.5, 25.0;

HRMS (ESI): $C_{12}H_{15}NNaO^+$, $[M+Na]^+$ Calcd 212.1046, Found 212.1059.



30, 48h
16% yield

31: colorless oil (6 mg, 16% yield) from **1l'** (0.15 mmol, 27 mg) under standard conditions (PE/EA = 2%);

IR (neat) *v* 2927, 2238, 1646, 1599, 1451, 1074, 748, 550 cm^{-1};

^{1}H NMR (400 MHz, Chloroform-*d*) δ 7.24 – 7.19 (m, 4H), 7.17 – 7.10 (m, 6H), 3.82 (t, *J* = 7.8 Hz, 1H) 2.52 (dq, *J* = 14.0, 7.0 Hz, 1H), 2.23 (dtd, *J* = 16.0, 8.1, 5.1 Hz, 1H) 2.13 – 2.04 (m, 1H) 1.55 – 1.39 (m, 2H), 1.20 (d, *J* = 7.1 Hz, 3H);

^{13}C NMR (100 MHz, Chloroform-*d*) δ 144.3, 144.0, 128.64, 128.62, 127.73, 127.70, 126.5, 126.4, 122.8, 51.0, 33.0, 32.6, 25.6, 18.0;

HRMS (ESI): $C_{18}H_{19}NNa^+$, $[M+Na]^+$ Calcd 272.1410, Found 272.1417.

Reference of knowncompound:

Entry	Compounds	Reference
8	**2-7**, **10-11**	1
9	**14**	9
10	**15**	10
11	**16**	11

12	**18**	12
13	**19**	13
14	**20-21**	14
15	**22**	15
16	**24**	16
17	**25**	17
18	**26**	18
19	**27**	19
20	**28**	20
21	**29**	21

6. Computational Details

All calculations were carried out using DFT as implemented in Gaussian16 software package.[22] The PBE hybrid functional[23] in conjugation with def2-TZVP basis set for iridium and def2-SVP basis sets for other atoms was applied for the optimization of all stationary points.[24], [25] Frequency calculations were performed at the same level to verify the stationary points are minima (0 imaginary frequency) or saddle points (only 1 imaginary frequency). Enthalpy and Gibbs free energy corrections were obtained from frequency calculations at 298 K. Single point energy calculations were carried out with the same hybrid functional using def2-TZVPP basis set for all atoms, and solvation effects of toluene were considered using Truhlar's SMD solvent model during the single point energy calculations.[26] Time-dependent DFT (TD-DFT) calculations were performed for the excited state structures. Broken symmetry functional was chosen for open shell systems. Possible conformers for all intermediates and transition states were searched and only the most stable ones were discussed in this paper. Computed structures were illustrated by CYLView[27] and GaussView 6.0.[28]

6.1 Table of energies and other thermodynamic parameters.

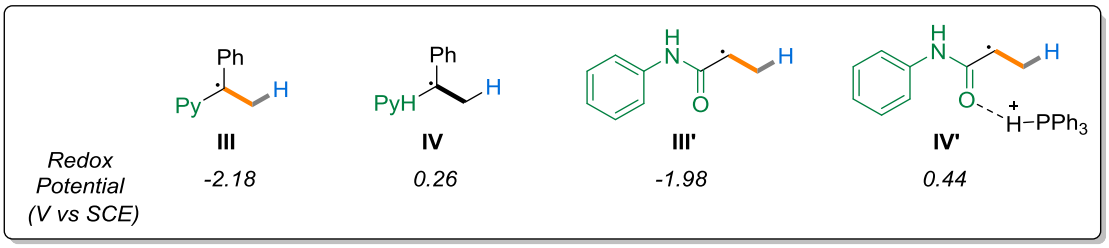
Table S6. Table of energies and other thermodynamic parameters for PPh_3-mediated reactions.[a]

Structure	E_{ele}	E_{ele}(SP)	E(SP)	H(SP)	G(SP)
PPh_3	-1034.76890	-1035.63170	-1035.34010	-1035.33916	-1035.40167
$PPh_3^{\bullet+}$	-1034.51475	-1035.41724	-1035.12500	-1035.12406	-1035.18670
Ir(III)	-2937.70014	-2940.89760	-2940.15702	-2940.15607	-2940.29997
Ir(III)-S1		-2940.78560			
Ir(III)-T1	-2937.60043	-2940.79698	-2940.06000	-2940.05906	-2940.20456
Ir(II)	-2937.85541	-2941.01777	-2940.28046	-2940.27951	-2940.42464
H_2O	-76.27633	-76.38476	-76.36034	-76.35940	-76.38083
HOAc	-228.66765	-228.94121	-228.87435	-228.87340	-228.90592
1a	-555.69621	-556.29592	-556.08061	-556.07967	-556.12925
I	-1110.81113	-1111.80945	-1111.48962	-1111.48868	-1111.56026
TS1	-2145.59924	-2147.44549	-2146.83632	-2146.83537	-2146.94422
II	-1110.41992	-1111.38917	-1111.08302	-1111.08207	-1111.14751
$HPPh_3^+$	-1035.15163	-1036.05817	-1035.75560	-1035.75465	-1035.81864
TS2	-1666.13637	-1667.69610	-1667.17544	-1667.17449	-1667.26607
III	-556.28749	-556.88726	-556.66148	-556.66053	-556.71164
$OPPh_3$	-1109.88617	-1110.86039	-1110.56302	-1110.56208	-1110.62595
TS3	-1591.47268	-1592.96078	-1592.43274	-1592.43179	-1592.52684
IV	-556.67903	-557.32309	-557.08311	-557.08216	-557.13356
V	-556.89556	-557.49798	-557.25910	-557.25816	-557.30914
TS4	-785.58126	-786.44506	-786.14189	-786.14095	-786.20398
2	-556.92330	-557.52409	-557.28481	-557.28387	-557.33528

[a]E_{ele} were the electronic energies at PBE1PBE-D3/def2TZVP(Ir)-def2SVP theoretical level. E_{ele}(SP) were electronic energies from single point energy calculations at PBE1PBE/def2TZVPP-SMD(toluene) theoretical level. E(SP), H(SP), and G(SP) were sum of electronic and thermal energies, sum of electronic and thermal enthalpies, and sum of electronic and thermal free energies, respectively, which were obtained by adding the corresponding corrections from frequency calculations at PBE1PBE-D3/def2TZVP(Ir)-def2SVP level to E_{ele}(SP).

6.2 Redox potential calculations.

The protonation of pyridine ring in intermediate **III** could decrease the redox potential from -2.18 V to 0.26 V (vs SCE), which facilitate the SET process significantly. Similar phenomenon was also observed in acrylamides, which could help us understand why both vinylpyridines and acrylamides were well-accommodated in this transformation.



Calculations were performed at PBE1PBE/def2TZVPP-SMD(toluene)/PBE1PBE-D3/def2SVP theoretical level.

6.3 Coordinates of all stationary points.

Ir(III)
0 imaginary frequency

C	-2.1197	-0.1226	-0.7300
C	-3.2795	-0.2658	-1.4849
C	-3.2241	-0.5017	-2.8652
C	-1.9458	-0.5728	-3.4285
C	-0.8226	-0.4231	-2.6252
N	-0.8999	-0.2109	-1.3086
H	-4.2483	-0.1986	-0.9913
H	-1.8015	-0.7495	-4.4936
H	0.1862	-0.4828	-3.0415
C	-2.1198	0.1205	0.7299
C	-3.2797	0.2624	1.4848
C	-0.8230	0.4226	2.6249
C	-3.2245	0.4984	2.8651
H	-4.2484	0.1941	0.9912
C	-1.9463	0.5710	3.4283
H	0.1858	0.4834	3.0412
H	-1.8021	0.7479	4.4934
N	-0.9001	0.2101	1.3084
C	-4.5088	-0.6743	-3.6678
C	-5.2732	-1.8872	-3.1109
C	-5.3625	0.5957	-3.5192
C	-4.2250	-0.9080	-5.1524
H	-4.6735	-2.8068	-3.1895
H	-5.5541	-1.7532	-2.0553
H	-6.2017	-2.0372	-3.6823
H	-4.8296	1.4812	-3.8979
H	-6.2938	0.4880	-4.0953
H	-5.6445	0.7892	-2.4732
H	-5.1744	-1.0248	-5.6946
H	-3.6906	-0.0602	-5.6080
H	-3.6385	-1.8241	-5.3208
C	-4.5094	0.6696	3.6677
C	-5.2752	1.8816	3.1109
C	-5.3616	-0.6014	3.5192
C	-4.2257	0.9035	5.1524
H	-4.6765	2.8019	3.1894
H	-5.5560	1.7472	2.0553
H	-6.2038	2.0306	3.6823
H	-4.8277	-1.4863	3.8979
H	-6.2930	-0.4948	4.0954
H	-5.6434	-0.7953	2.4732
H	-5.1753	1.0193	5.6945
H	-3.6904	0.0564	5.6080
H	-3.6403	1.8204	5.3207
Ir	0.7836	0.0005	-0.0001
C	2.5434	1.1363	-1.9968
C	2.2213	-0.1116	-1.3900
C	2.8845	-1.2632	-1.8191
C	3.8443	-1.1746	-2.8223
C	4.1805	0.0305	-3.4329
C	3.5215	1.1689	-3.0053
H	2.6860	-2.2441	-1.3846
H	4.9360	0.0818	-4.2165
C	1.8037	2.2834	-1.4977
C	1.9479	3.6221	-1.9031
C	1.1658	4.6097	-1.3319
H	2.6824	3.8707	-2.6648
C	0.1341	2.9298	0.0181
C	0.2330	4.2587	-0.3514
H	1.2803	5.6515	-1.6398
H	-0.5692	2.6185	0.7900
N	0.8904	1.9723	-0.5325
C	-0.6619	5.2954	0.2716
F	-1.3276	4.7981	1.3187
F	-1.5633	5.7365	-0.6073
F	0.0402	6.3460	0.6876

F	3.8415	2.3206	-3.5922
F	4.4643	-2.2747	-3.2166
C	2.5447	-1.1334	1.9965
C	2.2212	0.1141	1.3897
C	2.8833	1.2664	1.8187
C	3.8432	1.1788	2.8219
C	4.1807	-0.0259	3.4325
C	3.5228	-1.1650	3.0049
H	2.6838	2.2471	1.3842
H	4.9363	-0.0764	4.2161
C	1.8061	-2.2812	1.4973
C	1.9517	-3.6198	1.9028
C	1.1707	-4.6082	1.3316
H	2.6865	-3.8677	2.6644
C	0.1371	-2.9294	-0.0184
C	0.2375	-4.2582	0.3511
H	1.2862	-5.6500	1.6395
H	-0.5664	-2.6189	-0.7902
N	0.8925	-1.9711	0.5322
F	3.8441	-2.3164	3.5918
F	4.4620	2.2796	3.2161
C	-0.6564	-5.2958	-0.2718
F	0.0466	-6.3460	-0.6874
F	-1.5576	-5.7375	0.6070
F	-1.3224	-4.7994	-1.3192

Ir(III)-T1

0 imaginary frequency

C	-2.1177	-0.0416	-0.7408
C	-3.2553	-0.4016	-1.4554
C	-3.1926	-0.6779	-2.8278
C	-1.9428	-0.5144	-3.4352
C	-0.8397	-0.1612	-2.6690
N	-0.9132	0.0427	-1.3510
H	-4.2034	-0.5055	-0.9290
H	-1.8004	-0.6868	-4.5012
H	0.1544	-0.0715	-3.1137
C	-2.1214	0.2272	0.7135
C	-3.2846	0.3471	1.4676
C	-0.8318	0.6047	2.5988
C	-3.2337	0.6019	2.8445
H	-4.2510	0.2530	0.9734
C	-1.9570	0.7241	3.4039
H	0.1762	0.7071	3.0098
H	-1.8168	0.9168	4.4667
N	-0.9053	0.3683	1.2868
C	-4.4300	-1.1694	-3.5687
C	-4.8603	-2.5040	-2.9335
C	-5.5544	-0.1318	-3.4253
C	-4.1506	-1.3954	-5.0553
H	-4.0490	-3.2470	-2.9733
H	-5.1555	-2.3844	-1.8800
H	-5.7270	-2.9126	-3.4747
H	-5.2637	0.8351	-3.8635
H	-6.4553	-0.4845	-3.9495
H	-5.8336	0.0397	-2.3747
H	-5.0670	-1.7442	-5.5527
H	-3.8358	-0.4694	-5.5608
H	-3.3797	-2.1642	-5.2170
C	-4.5214	0.7387	3.6492
C	-5.3310	1.9168	3.0821
C	-5.3289	-0.5631	3.5168
C	-4.2419	0.9982	5.1304
H	-4.7661	2.8589	3.1511
H	-5.6086	1.7625	2.0283
H	-6.2635	2.0375	3.6538
H	-4.7628	-1.4249	3.9018
H	-6.2613	-0.4835	4.0957
H	-5.6075	-0.7769	2.4739
H	-5.1934	1.0870	5.6741
H	-3.6766	0.1748	5.5933
H	-3.6879	1.9364	5.2872
Ir	0.7852	0.1635	-0.0380
C	2.6224	1.2948	-1.9623
C	2.2169	0.0379	-1.4286
C	2.8020	-1.1328	-1.9148
C	3.7746	-1.0534	-2.9061
C	4.1958	0.1596	-3.4452
C	3.6115	1.3161	-2.9600
H	2.5292	-2.1174	-1.5323
H	4.9603	0.2030	-4.2207
C	1.9504	2.4603	-1.4094
C	2.1758	3.8051	-1.7518
C	1.4424	4.8078	-1.1431
H	2.9299	4.0464	-2.4965
C	0.2969	3.1294	0.1141
C	0.4781	4.4664	-0.1900
H	1.6136	5.8539	-1.4073
H	-0.4414	2.8204	0.8540
N	1.0085	2.1585	-0.4704
C	-0.3297	5.5291	0.5053
F	-1.2954	4.9914	1.2568

F	-0.9010	6.3451	-0.3785
F	0.4397	6.2712	1.2996
F	4.0154	2.4731	-3.4792
F	4.3239	-2.1673	-3.3587
C	2.3900	-1.2115	1.9332
C	2.1726	0.1368	1.3723
C	2.9170	1.2081	1.8575
C	3.8440	1.0096	2.8737
C	4.0743	-0.2680	3.4454
C	3.3657	-1.3378	2.9817
H	2.8021	2.2159	1.4554
H	4.8091	-0.3941	4.2417
C	1.6273	-2.2508	1.3810
C	1.6573	-3.6436	1.7193
C	0.8369	-4.5414	1.0977
H	2.3541	-3.9753	2.4860
C	-0.0503	-2.7099	-0.2320
C	-0.0574	-4.0617	0.0899
H	0.8643	-5.6008	1.3562
H	-0.7126	-2.3452	-1.0165
N	0.7363	-1.8207	0.3592
F	3.5873	-2.5341	3.5218
F	4.5441	2.0278	3.3423
C	-0.9964	-4.9970	-0.6051
F	-0.3409	-5.9871	-1.2109
F	-1.8473	-5.5579	0.2585
F	-1.7283	-4.3637	-1.5359

Ir(II)
0 imaginary frequency

C	2.0745	0.0866	0.7321
C	3.2567	-0.1803	1.4726
C	3.2205	-0.6034	2.7850
C	1.9371	-0.7293	3.3882
C	0.8107	-0.4820	2.6281
N	0.8474	-0.1117	1.3419
H	4.2155	-0.0794	0.9630
H	1.8115	-1.0336	4.4252
H	-0.1888	-0.6050	3.0544
C	2.0497	0.5076	-0.6285
C	3.1993	0.8539	-1.3870
C	0.7234	0.9649	-2.5106
C	3.1159	1.2551	-2.7046
H	4.1711	0.8157	-0.8935
C	1.8173	1.3011	-3.2845
H	-0.2872	0.9981	-2.9275
H	1.6546	1.5967	-4.3189
N	0.8057	0.5901	-1.2283
C	4.5146	-0.9693	3.5153
C	5.1404	-2.1853	2.8121
C	5.4926	0.2137	3.4717
C	4.2612	-1.3319	4.9804
H	4.4382	-3.0333	2.7932
H	5.4092	-1.9549	1.7703
H	6.0562	-2.5058	3.3350
H	5.0616	1.0991	3.9641
H	6.4299	-0.0450	3.9899
H	5.7511	0.4962	2.4404
H	5.2149	-1.5712	5.4753
H	3.7986	-0.4991	5.5322
H	3.6096	-2.2136	5.0765
C	4.3791	1.6490	-3.4744
C	5.0175	2.8701	-2.7936
C	5.3712	0.4763	-3.4660
C	4.0724	2.0108	-4.9295
H	4.3175	3.7197	-2.7747
H	5.3058	2.6515	-1.7546
H	5.9240	3.1837	-3.3362
H	4.9315	-0.4143	-3.9409
H	6.2860	0.7437	-4.0189
H	5.6688	0.1983	-2.4440
H	5.0041	2.2777	-5.4514
H	3.6166	1.1682	-5.4719
H	3.3940	2.8745	-5.0017
Ir	-0.8085	0.0377	0.0313
C	-2.7128	0.7739	2.0866
C	-2.2304	-0.3710	1.3860
C	-2.7614	-1.6260	1.7071
C	-3.7335	-1.7363	2.6909
C	-4.2202	-0.6349	3.3923
C	-3.6978	0.6051	3.0724
H	-2.4332	-2.5343	1.1984
H	-4.9837	-0.7399	4.1622
C	-2.1124	2.0389	1.6946
C	-2.4078	3.3105	2.2169
C	-1.7445	4.4268	1.7422
H	-3.1596	3.4021	2.9963
C	-0.5241	3.0002	0.2590
C	-0.7791	4.2716	0.7427
H	-1.9688	5.4164	2.1465
H	0.2223	2.8258	-0.5164
N	-1.1710	1.9203	0.7138

C	-0.0474	5.4640	0.1983
F	0.9205	5.1119	-0.6483
F	0.5081	6.1779	1.1826
F	-0.8785	6.2839	-0.4542
F	-4.1683	1.6587	3.7483
F	-4.2277	-2.9344	2.9864
C	-2.3113	-1.1800	-2.1241
C	-2.2215	0.0421	-1.3933
C	-3.0778	1.0943	-1.7394
C	-3.9854	0.9375	-2.7772
C	-4.0909	-0.2431	-3.5096
C	-3.2478	-1.2840	-3.1645
H	-3.0567	2.0484	-1.2094
H	-4.8089	-0.3493	-4.3219
C	-1.3957	-2.2276	-1.7003
C	-1.2777	-3.5183	-2.2468
C	-0.3515	-4.4080	-1.7341
H	-1.9188	-3.8034	-3.0766
C	0.3051	-2.7283	-0.1633
C	0.4603	-4.0072	-0.6687
H	-0.2521	-5.4087	-2.1603
H	0.9181	-2.3706	0.6635
N	-0.5916	-1.8673	-0.6587
F	-3.3543	-2.4147	-3.8705
F	-4.7906	1.9461	-3.0960
C	1.4677	-4.9475	-0.0727
F	0.8696	-5.9478	0.5833
F	2.2260	-5.5045	-1.0221
F	2.2781	-4.3292	0.7885

H_2O

0 imaginary frequency

O	0.0000	0.0000	0.1199
H	0.0000	0.7542	-0.4788
H	0.0000	-0.7542	-0.4788

HOAc

0 imaginary frequency

C	-0.9812	0.3065	0.0600
H	-0.1936	-0.3476	-0.3420
H	-1.3261	1.0028	-0.7117
H	-1.8075	-0.3433	0.3835
C	-0.4518	1.0762	1.2329
O	-0.4059	2.2735	1.3268
O	-0.0171	0.2586	2.2057
H	0.3053	0.8304	2.9193

1a

0 imaginary frequency

C	-0.5964	1.2004	-0.4137
C	-0.1658	2.2005	0.4732
C	-1.0999	3.0874	1.0000
C	-2.4352	2.9580	0.6312
C	-2.7657	1.9394	-0.2655
N	-1.8830	1.0901	-0.7698
H	-0.7836	3.8747	1.6892
H	0.8902	2.2844	0.7345
H	-3.2050	3.6270	1.0215
H	-3.8059	1.8071	-0.5874
C	0.3646	0.2478	-1.0343
C	0.0198	-0.4236	-2.1461
H	0.7047	-1.1403	-2.6050
H	-0.9664	-0.2732	-2.5902
C	1.7022	0.0573	-0.4165
C	2.8655	0.1305	-1.1949
C	1.8308	-0.2411	0.9491
C	4.1195	-0.0935	-0.6292
H	2.7779	0.3800	-2.2553
C	3.0830	-0.4673	1.5144
H	0.9331	-0.3087	1.5692
C	4.2327	-0.3934	0.7273
H	5.0149	-0.0267	-1.2523
H	3.1618	-0.7085	2.5776
H	5.2155	-0.5672	1.1723

PPh_3

0 imaginary frequency

P	-1.0161	0.2546	-0.0130
C	-0.1359	1.1081	-1.3875
C	-0.6760	0.9660	-2.6743
C	1.0183	1.8840	-1.2214
C	-0.0646	1.5660	-3.7725
H	-1.5868	0.3758	-2.8147
C	1.6221	2.4958	-2.3201
H	1.4495	2.0098	-0.2251
C	1.0862	2.3355	-3.5970
H	-0.4944	1.4408	-4.7696
H	2.5214	3.1001	-2.1755
H	1.5621	2.8146	-4.4563
C	-0.1668	0.9598	1.4614
C	0.9225	0.3584	2.1045
C	-0.6610	2.1739	1.9607

C	1.5081	0.9635	3.2165
H	1.3169	-0.5904	1.7322
C	-0.0670	2.7841	3.0629
H	-1.5218	2.6454	1.4767
C	1.0190	2.1780	3.6956
H	2.3565	0.4820	3.7098
H	-0.4603	3.7330	3.4364
H	1.4804	2.6507	4.5662
C	-0.2744	-1.4295	-0.0925
C	-0.8767	-2.4277	0.6877
C	0.8343	-1.7647	-0.8799
C	-0.3695	-3.7249	0.6981
H	-1.7534	-2.1821	1.2948
C	1.3332	-3.0675	-0.8791
H	1.3125	-1.0006	-1.4977
C	0.7367	-4.0486	-0.0884
H	-0.8465	-4.4900	1.3159
H	2.1980	-3.3155	-1.4999
H	1.1303	-5.0681	-0.0885

$PPh_3^{\bullet+}$

0 imaginary frequency

P	-0.3302	0.2222	-0.0118
C	0.1704	1.1208	-1.4615
C	-0.3527	0.7239	-2.7089
C	1.0376	2.2261	-1.3736
C	0.0143	1.4146	-3.8565
H	-1.0464	-0.1185	-2.7772
C	1.3916	2.9086	-2.5316
H	1.4468	2.5343	-0.4089
C	0.8833	2.5056	-3.7686
H	-0.3867	1.1087	-4.8251
H	2.0755	3.7578	-2.4703
H	1.1644	3.0491	-4.6736
C	0.1225	0.9977	1.5223
C	0.8817	0.3148	2.4911
C	-0.3297	2.3100	1.7675
C	1.2010	0.9553	3.6828
H	1.2361	-0.7011	2.3028
C	0.0015	2.9366	2.9619
H	-0.9409	2.8339	1.0275
C	0.7637	2.2607	3.9186
H	1.8021	0.4348	4.4314
H	-0.3447	3.9543	3.1546
H	1.0168	2.7559	4.8589
C	0.0074	-1.5217	-0.0779
C	-0.5690	-2.3522	0.9044
C	0.7980	-2.0756	-1.1023
C	-0.3298	-3.7199	0.8713
H	-1.2043	-1.9281	1.6868
C	1.0242	-3.4470	-1.1228
H	1.2484	-1.4344	-1.8632
C	0.4636	-4.2669	-0.1408
H	-0.7724	-4.3664	1.6320
H	1.6488	-3.8796	-1.9072
H	0.6442	-5.3441	-0.1657

I

0 imaginary frequency

O	-5.9540	-0.1551	2.0349
H	-6.1497	0.4535	1.3126
P	-6.4314	-2.9430	1.5406
H	-5.9936	0.3854	2.8327
C	-4.7616	-3.4282	1.9319
C	-4.4368	-4.7803	2.1503
C	-3.7694	-2.4324	2.0187
C	-3.1205	-5.1285	2.4321
H	-5.2038	-5.5547	2.0796
C	-2.4584	-2.8005	2.2976
H	-4.0469	-1.3838	1.8860
C	-2.1336	-4.1433	2.5045
H	-2.8614	-6.1777	2.5896
H	-1.6841	-2.0332	2.3650
H	-1.1019	-4.4247	2.7282
C	-7.6191	-4.2321	1.8536
C	-8.5091	-4.6752	0.8576
C	-7.6848	-4.7748	3.1530
C	-9.4347	-5.6680	1.1591
H	-8.4610	-4.2609	-0.1518
C	-8.6122	-5.7687	3.4375
H	-7.0103	-4.4182	3.9363
C	-9.4876	-6.2140	2.4433
H	-10.1161	-6.0244	0.3836
H	-8.6607	-6.1938	4.4423
H	-10.2191	-6.9922	2.6729
C	-6.6037	-2.2145	-0.0780
C	-5.5443	-2.2416	-0.9991
C	-7.8095	-1.5650	-0.3999
C	-5.7055	-1.6410	-2.2446
H	-4.6053	-2.7396	-0.7471
C	-7.9569	-0.9717	-1.6483
H	-8.6261	-1.5214	0.3260

C	-6.9066	-1.0094	-2.5696
H	-4.8881	-1.6709	-2.9683
H	-8.8935	-0.4716	-1.9045
H	-7.0262	-0.5395	-3.5486

TS1

1 imaginary frequency, -580.0i

O	-1.1483	4.2213	-6.6100
H	-0.3153	5.1013	-5.9281
H	-1.0505	4.4002	-7.5591
P	-0.6927	2.2475	-6.3299
P	0.5377	6.0420	-4.9933
C	-2.0113	1.6018	-7.3874
C	-3.1383	2.3867	-7.6906
C	-1.9205	0.3001	-7.9066
C	-4.1514	1.8717	-8.4941
H	-3.2156	3.3994	-7.2920
C	-2.9363	-0.2017	-8.7162
H	-1.0561	-0.3258	-7.6765
C	-4.0525	0.5798	-9.0112
H	-5.0249	2.4875	-8.7208
H	-2.8542	-1.2149	-9.1161
H	-4.8475	0.1815	-9.6458
C	0.6301	0.9734	-6.3493
C	1.5277	1.0114	-7.4286
C	0.8123	0.0196	-5.3362
C	2.5798	0.1024	-7.5032
H	1.3995	1.7583	-8.2183
C	1.8724	-0.8822	-5.4124
H	0.1199	-0.0279	-4.4930
C	2.7561	-0.8429	-6.4913
H	3.2674	0.1340	-8.3516
H	2.0038	-1.6276	-4.6243
H	3.5847	-1.5528	-6.5448
C	-1.2355	2.3232	-4.6039
C	-0.2809	2.5317	-3.5961
C	-2.5866	2.1959	-4.2575
C	-0.6732	2.5973	-2.2625
H	0.7785	2.6286	-3.8468
C	-2.9722	2.2639	-2.9202
H	-3.3386	2.0237	-5.0307
C	-2.0187	2.4622	-1.9224
H	0.0770	2.7600	-1.4858
H	-4.0265	2.1506	-2.6570
H	-2.3246	2.5114	-0.8749
C	-0.2572	5.9845	-3.3717
C	-1.6504	5.8307	-3.3544
C	0.4527	6.1245	-2.1739
C	-2.3305	5.8420	-2.1395
H	-2.1993	5.6846	-4.2891
C	-0.2352	6.1240	-0.9627
H	1.5406	6.2255	-2.1832
C	-1.6244	5.9912	-0.9461
H	-3.4158	5.7213	-2.1252
H	0.3162	6.2323	-0.0260
H	-2.1597	5.9971	0.0064
C	0.6079	7.7757	-5.5149
C	1.3473	8.0996	-6.6622
C	-0.0873	8.7744	-4.8237
C	1.3899	9.4165	-7.1093
H	1.9025	7.3259	-7.2005
C	-0.0397	10.0911	-5.2802
H	-0.6608	8.5278	-3.9269
C	0.6957	10.4123	-6.4195
H	1.9697	9.6684	-8.0001
H	-0.5791	10.8705	-4.7374
H	0.7318	11.4455	-6.7724
C	2.2401	5.4421	-4.8984
C	2.5282	4.1617	-5.3898
C	3.2647	6.2267	-4.3498
C	3.8231	3.6550	-5.3047
H	1.7441	3.5581	-5.8539
C	4.5570	5.7145	-4.2675
H	3.0557	7.2423	-4.0024
C	4.8348	4.4293	-4.7378
H	4.0362	2.6548	-5.6898
H	5.3554	6.3245	-3.8389
H	5.8514	4.0346	-4.6713

II

0 imaginary frequency

O	0.1021	2.7863	-6.3899
H	0.5933	2.6409	-7.2103
P	-0.9136	1.4825	-6.1155
C	-1.6435	2.0932	-4.5807
C	-1.5405	3.4365	-4.1875
C	-2.4628	1.2209	-3.8453
C	-2.2433	3.8908	-3.0725
H	-0.9007	4.1147	-4.7533
C	-3.1431	1.6767	-2.7223
H	-2.5602	0.1786	-4.1618
C	-3.0398	3.0162	-2.3357

H	-2.1592	4.9385	-2.7725
H	-3.7669	0.9865	-2.1494
H	-3.5848	3.3766	-1.4598
C	-0.2152	-0.1008	-5.8711
C	0.2903	-0.4716	-4.5885
C	0.0453	-0.9831	-6.9630
C	0.9315	-1.6855	-4.4072
H	0.1653	0.2048	-3.7400
C	0.6853	-2.1918	-6.7563
H	-0.2589	-0.7034	-7.9742
C	1.1292	-2.5678	-5.4785
H	1.2931	-1.9508	-3.4100
H	0.8563	-2.8547	-7.6088
H	1.6408	-3.5202	-5.3267
C	-2.0081	1.5088	-7.5263
C	-2.2784	2.7422	-8.1597
C	-2.7587	0.3749	-7.9075
C	-3.2415	2.8231	-9.1606
H	-1.7231	3.6337	-7.8606
C	-3.6998	0.4647	-8.9225
H	-2.6030	-0.5764	-7.3937
C	-3.9497	1.6886	-9.5574
H	-3.4364	3.7854	-9.6413
H	-4.2607	-0.4268	-9.2142
H	-4.7001	1.7552	-10.3484

$HPPh_3^+$

0 imaginary frequency

H	0.7170	5.1783	-5.8477
P	1.0393	6.2493	-4.9820
C	0.4419	7.7551	-5.7480
C	-0.8554	7.7792	-6.2826
C	1.2469	8.9014	-5.7642
C	-1.3413	8.9586	-6.8364
H	-1.4859	6.8854	-6.2689
C	0.7461	10.0767	-6.3199
H	2.2590	8.8758	-5.3522
C	-0.5420	10.1040	-6.8535
H	-2.3475	8.9846	-7.2600
H	1.3677	10.9743	-6.3387
H	-0.9283	11.0273	-7.2917
C	2.8215	6.2693	-4.7965
C	3.6269	6.1519	-5.9397
C	3.3932	6.4491	-3.5304
C	5.0098	6.2131	-5.8069
H	3.1819	6.0134	-6.9293
C	4.7801	6.5113	-3.4127
H	2.7618	6.5336	-2.6422
C	5.5837	6.3935	-4.5462
H	5.6443	6.1168	-6.6905
H	5.2341	6.6491	-2.4292
H	6.6708	6.4389	-4.4477
C	0.2200	5.9384	-3.4189
C	0.2946	4.6562	-2.8536
C	-0.4409	6.9793	-2.7541
C	-0.2995	4.4217	-1.6183
H	0.8120	3.8429	-3.3706
C	-1.0291	6.7306	-1.5159
H	-0.5018	7.9746	-3.2016
C	-0.9585	5.4574	-0.9516
H	-0.2513	3.4253	-1.1737
H	-1.5483	7.5358	-0.9918
H	-1.4250	5.2668	0.0177

TS2

1 imaginary frequency, -483.6i

C	-0.3377	0.8896	-1.9311
C	-0.3789	2.1773	-2.5183
C	-1.5983	2.7571	-2.8284
C	-2.7777	2.0586	-2.5465
C	-2.6446	0.7923	-1.9760
N	-1.4890	0.2197	-1.6868
H	-1.6314	3.7482	-3.2885
H	0.5448	2.7148	-2.7319
H	-3.7628	2.4779	-2.7586
H	-3.5430	0.2022	-1.7518
C	0.9058	0.1905	-1.5889
C	0.8613	-1.1454	-1.2317
H	1.7366	-1.6268	-0.7882
H	-0.1133	-1.6274	-1.1325
C	2.2099	0.8890	-1.5856
C	3.3741	0.2262	-2.0201
C	2.3595	2.1954	-1.0848
C	4.6184	0.8443	-1.9799
H	3.2925	-0.7853	-2.4227
C	3.6057	2.8166	-1.0481
H	1.4888	2.7184	-0.6843
C	4.7432	2.1488	-1.5012
H	5.4979	0.3052	-2.3405
H	3.6898	3.8289	-0.6439
H	5.7203	2.6373	-1.4724

O	1.4204	-2.1257	-3.7769
H	1.1865	-1.6827	-2.8784
P	1.2464	-1.2046	-5.0664
C	2.4532	0.1110	-5.2110
C	3.7750	-0.2239	-5.5554
C	2.1474	1.4289	-4.8385
C	4.7625	0.7571	-5.5514
H	4.0261	-1.2520	-5.8287
C	3.1372	2.4031	-4.8465
H	1.1337	1.6803	-4.5245
C	4.4470	2.0697	-5.2015
H	5.7884	0.4925	-5.8186
H	2.8920	3.4245	-4.5480
H	5.2266	2.8349	-5.1907
C	1.6153	-2.3903	-6.3882
C	1.6830	-3.7641	-6.1256
C	1.7060	-1.9246	-7.7078
C	1.8517	-4.6613	-7.1791
H	1.6106	-4.1184	-5.0956
C	1.8783	-2.8256	-8.7529
H	1.6484	-0.8519	-7.9155
C	1.9501	-4.1960	-8.4898
H	1.9101	-5.7328	-6.9727
H	1.9571	-2.4592	-9.7792
H	2.0822	-4.9031	-9.3124
C	-0.4062	-0.5906	-5.1433
C	-1.4220	-1.3369	-4.5002
C	-0.7702	0.5081	-5.9588
C	-2.7504	-0.9711	-4.6517
H	-1.1583	-2.1916	-3.8748
C	-2.1020	0.8708	-6.0787
H	-0.0074	1.0724	-6.4999
C	-3.1023	0.1405	-5.4234
H	-3.5234	-1.5465	-4.1372
H	-2.3694	1.7335	-6.6938
H	-4.1504	0.4285	-5.5277

III

0 imaginary frequency

C	-0.9709	2.4451	-1.3088
C	-1.4192	1.8628	-0.0961
C	-2.3695	2.5219	0.6692
C	-2.8622	3.7517	0.2318
C	-2.3409	4.2705	-0.9575
N	-1.4326	3.6561	-1.6952
H	-2.7139	2.0856	1.6105
H	-0.9902	0.9218	0.2502
H	-3.6128	4.3048	0.7998
H	-2.6846	5.2454	-1.3254
C	0.0400	1.8275	-2.1459
C	0.8278	2.7099	-3.0585
H	1.0709	2.2053	-4.0053
H	1.7846	3.0129	-2.5927
C	0.3398	0.4069	-2.1021
C	1.6363	-0.0597	-2.4214
C	-0.6442	-0.5691	-1.8162
C	1.9397	-1.4157	-2.4126
H	2.4225	0.6605	-2.6563
C	-0.3391	-1.9246	-1.8196
H	-1.6730	-0.2535	-1.6318
C	0.9564	-2.3588	-2.1080
H	2.9563	-1.7421	-2.6462
H	-1.1258	-2.6536	-1.6089
H	1.1948	-3.4250	-2.1072
H	0.2604	3.6276	-3.2597

$OPPh_3$

0 imaginary frequency

P	-0.7783	0.2417	-0.0107
C	-0.0245	1.0952	-1.4304
C	-0.8296	1.2234	-2.5679
C	1.2743	1.6163	-1.4327
C	-0.3281	1.8469	-3.7083
H	-1.8534	0.8413	-2.5337
C	1.7724	2.2377	-2.5769
H	1.8938	1.5564	-0.5336
C	0.9736	2.3491	-3.7151
H	-0.9587	1.9475	-4.5952
H	2.7859	2.6464	-2.5763
H	1.3649	2.8402	-4.6096
C	-0.0527	0.9958	1.4783
C	1.1997	0.6529	1.9999
C	-0.8311	1.9688	2.1154
C	1.6808	1.3004	3.1368
H	1.7946	-0.1359	1.5311
C	-0.3470	2.6118	3.2525
H	-1.8218	2.1966	1.7129
C	0.9100	2.2820	3.7601
H	2.6579	1.0298	3.5445
H	-0.9568	3.3702	3.7497
H	1.2875	2.7855	4.6537

C	-0.1626	-1.4701	-0.0631
C	-1.0351	-2.4515	0.4210
C	1.0952	-1.8363	-0.5551
C	-0.6401	-3.7874	0.4354
H	-2.0269	-2.1491	0.7676
C	1.4868	-3.1741	-0.5369
H	1.7650	-1.0798	-0.9732
C	0.6217	-4.1483	-0.0382
H	-1.3233	-4.5526	0.8122
H	2.4683	-3.4589	-0.9239
H	0.9293	-5.1970	-0.0286
O	-2.2786	0.3160	-0.0225

TS3

1 imaginary frequency, -606.3i

C	-3.9940	-1.1116	0.7218
C	-2.8483	-1.9284	0.6231
C	-2.6792	-2.9889	1.5012
C	-3.6519	-3.2439	2.4721
C	-4.7642	-2.4137	2.5054
N	-4.9222	-1.3899	1.6684
H	-1.7821	-3.6098	1.4413
H	-2.0836	-1.6881	-0.1168
H	-3.5515	-4.0647	3.1837
H	-5.5711	-2.5760	3.2283
C	-4.1891	0.0737	-0.0991
C	-4.7226	1.3063	0.5600
H	-5.0333	1.1041	1.5929
H	-5.5692	1.7408	0.0049
C	-3.8334	0.0990	-1.4963
C	-3.7053	1.3297	-2.1858
C	-3.7006	-1.0895	-2.2595
C	-3.4363	1.3673	-3.5469
H	-3.8065	2.2702	-1.6426
C	-3.4391	-1.0452	-3.6217
H	-3.8439	-2.0607	-1.7808
C	-3.3000	0.1828	-4.2754
H	-3.3288	2.3318	-4.0486
H	-3.3510	-1.9772	-4.1850
H	-3.0899	0.2156	-5.3467
H	-6.2954	-0.9323	1.4757
P	-7.8240	-0.6442	1.0728
H	-3.9401	2.0842	0.6131
C	-7.8591	0.2223	-0.5148
C	-7.1462	-0.3348	-1.5867
C	-8.5132	1.4500	-0.6688
C	-7.0836	0.3376	-2.8029
H	-6.6260	-1.2897	-1.4727
C	-8.4481	2.1159	-1.8922
H	-9.0671	1.8878	0.1654
C	-7.7325	1.5641	-2.9544
H	-6.5089	-0.0901	-3.6277
H	-8.9587	3.0738	-2.0136
H	-7.6769	2.0944	-3.9079
C	-8.6964	0.3576	2.2982
C	-7.9872	1.3377	3.0065
C	-10.0691	0.1852	2.5209
C	-8.6515	2.1448	3.9266
H	-6.9155	1.4747	2.8412
C	-10.7252	0.9951	3.4447
H	-10.6223	-0.5849	1.9771
C	-10.0188	1.9734	4.1451
H	-8.0984	2.9073	4.4793
H	-11.7948	0.8602	3.6199
H	-10.5371	2.6048	4.8704
C	-8.7267	-2.2030	0.8873
C	-8.6543	-3.1375	1.9309
C	-9.5005	-2.4794	-0.2460
C	-9.3514	-4.3380	1.8388
H	-8.0638	-2.9230	2.8265
C	-10.1927	-3.6866	-0.3326
H	-9.5634	-1.7538	-1.0606
C	-10.1188	-4.6137	0.7056
H	-9.2964	-5.0629	2.6540
H	-10.7963	-3.9010	-1.2174
H	-10.6632	-5.5581	0.6334

IV

0 imaginary frequency

C	-0.9282	2.4620	-1.3340
C	-0.9252	3.8186	-0.9288
C	-2.0532	4.3908	-0.3721
C	-3.2289	3.6363	-0.2084
C	-3.2203	2.3216	-0.6230
N	-2.1101	1.7879	-1.1569
H	-2.0290	5.4360	-0.0551
H	-0.0137	4.4037	-1.0452
H	-4.1321	4.0651	0.2264
H	-4.0892	1.6646	-0.5499
C	0.1816	1.8018	-1.9381
C	1.3430	2.6234	-2.3917
H	1.8975	3.0134	-1.5190

H	1.0389	3.4901	-2.9993
C	0.1874	0.3540	-2.1228
C	0.6759	-0.2083	-3.3215
C	-0.2618	-0.5240	-1.1075
C	0.6775	-1.5844	-3.5107
H	1.0262	0.4442	-4.1243
C	-0.2386	-1.9011	-1.2968
H	-0.5624	-0.1259	-0.1339
C	0.2205	-2.4354	-2.5021
H	1.0403	-1.9994	-4.4536
H	-0.5607	-2.5641	-0.4908
H	0.2347	-3.5175	-2.6507
H	2.0570	2.0230	-2.9670
H	-2.1329	0.8176	-1.4762

V

0 imaginary frequency

C	-0.9298	2.4438	-1.3643
C	-1.8070	1.8342	-0.3840
C	-2.7000	2.5640	0.3351
C	-2.8149	3.9845	0.1542
C	-1.9701	4.5686	-0.7336
N	-1.0688	3.8365	-1.4438
H	-3.3280	2.0641	1.0769
H	-1.7070	0.7625	-0.2148
H	-3.5313	4.5825	0.7160
H	-1.9597	5.6437	-0.9257
C	0.0172	1.8110	-2.1330
C	0.9440	2.6471	-2.9759
H	1.6372	2.0192	-3.5506
H	1.5588	3.3506	-2.3810
C	0.1714	0.3471	-2.1565
C	1.4491	-0.2430	-2.0960
C	-0.9303	-0.5206	-2.2872
C	1.6148	-1.6243	-2.1389
H	2.3286	0.3982	-1.9924
C	-0.7664	-1.9031	-2.3208
H	-1.9307	-0.0941	-2.3947
C	0.5073	-2.4661	-2.2449
H	2.6206	-2.0490	-2.0798
H	-1.6436	-2.5471	-2.4277
H	0.6368	-3.5505	-2.2772
H	0.3927	3.2523	-3.7231
H	-0.4644	4.3225	-2.0914

TS4

1 imaginary frequency, -1142.9i

C	-0.9879	2.5256	-1.7846
C	-2.1197	1.8811	-1.2138
C	-2.9225	2.5394	-0.3104
C	-2.6587	3.8796	0.0487
C	-1.5839	4.4901	-0.5477
N	-0.7959	3.8259	-1.4113
H	-3.7647	2.0118	0.1450
H	-2.3110	0.8421	-1.4808
H	-3.2819	4.4209	0.7602
H	-1.3148	5.5341	-0.3714
C	-0.0587	1.9496	-2.7197
C	1.4199	2.1651	-2.4162
H	2.0267	1.8889	-3.2916
H	1.7663	1.5578	-1.5608
C	-0.4259	0.6282	-3.2972
C	0.4168	-0.4925	-3.2225
C	-1.6364	0.4808	-4.0016
C	0.0563	-1.7083	-3.8033
H	1.3702	-0.4194	-2.6954
C	-2.0023	-0.7333	-4.5732
H	-2.2896	1.3511	-4.1150
C	-1.1564	-1.8396	-4.4762
H	0.7329	-2.5636	-3.7248
H	-2.9480	-0.8125	-5.1159
H	-1.4366	-2.7924	-4.9319
H	1.6483	3.2165	-2.1946
H	-0.1193	4.3922	-2.0166
C	0.6688	5.7437	-5.4982
H	1.5152	5.3142	-6.0551
H	0.9317	6.7453	-5.1386
H	-0.1815	5.7908	-6.1931
C	0.3344	4.8344	-4.3442
O	0.5232	5.2194	-3.1792
O	-0.1270	3.6876	-4.6788
H	-0.1812	2.8883	-3.7875

2

0 imaginary frequency

C	-1.1961	2.4078	-1.5355
C	-2.5283	2.2984	-1.1157
C	-2.9291	2.9537	0.0434
C	-1.9889	3.6987	0.7522
C	-0.6873	3.7464	0.2567
N	-0.3005	3.1231	-0.8526
H	-3.9637	2.8850	0.3897

H	-3.2356	1.7016	-1.6964
H	-2.2550	4.2323	1.6670
H	0.0831	4.3207	0.7850
C	-0.7137	1.6795	-2.7757
C	0.2662	2.5226	-3.5910
H	0.5873	1.9747	-4.4890
H	1.1534	2.7675	-2.9911
C	-0.1163	0.3326	-2.4031
C	0.9576	0.2479	-1.5072
C	-0.6147	-0.8475	-2.9634
C	1.5172	-0.9860	-1.1855
H	1.3418	1.1649	-1.0526
C	-0.0553	-2.0847	-2.6432
H	-1.4537	-0.7968	-3.6641
C	1.0138	-2.1577	-1.7528
H	2.3533	-1.0346	-0.4831
H	-0.4586	-2.9959	-3.0926
H	1.4537	-3.1254	-1.4991
H	-0.1987	3.4703	-3.9032
H	-1.6013	1.4769	-3.3967

Reference:

1. H. Yang, E. Wang, P. Yang, H. Lv and X. Zhang, Pyridine-Directed Asymmetric Hydrogenation of 1,1-Diarylalkenes, *Org. Lett.*, 2017, **19**, 5062-5065.
2. M. Chaitanya and P. Anbarasan, Rhodium-Catalyzed Cyanation of C(sp^2)-H Bond of Alkenes, *Org. Lett*., 2015, **17**, 3766-3769.
3. Z. Z. Xie, Y. Zheng, C. P. Yuan, J. P. Guan, Z. P. Ye, J. A. Xiao, H. Y. Xiang, K. Chen, X. Q. Chen and H. Yang, Photoredox-Catalyzed Deoxygenation of Hexafluoroacetone Hydrate Enables Hydroxypolyfluoroalkylation of Alkenes, *Angew. Chem. Int. Ed*., 2022, **61**, *DOI: 10.1002/anie.202211035.*
4. Y. Cao, H. Zhao, D. Zhang-Negrerie, Y. Du and K. Zhao, Metal-Free Synthesis of 3-Arylquinolin-2-Ones from N,2-Diaryl- Acrylamides *via* Phenyliodine(III) Bis(2,2-Dimethylpropanoate)- Mediated Direct Oxidative C−C Bond Formation, *Adv. Synth. Catal*., 2016, **358**, 3610-3615.
5. D. N. Zakusilo, D. S. Ryabukhin, I. A. Boyarskaya, O. S. Yuzikhin and A. V. Vasilyev, Tandem Superelectrophilic Hydroarylation of C=C Bond and Carbonyl Reduction in Cinnamides: Synthetic Rout to 3,3-Diarylpropylamines, Valuable Pharmaceuticals, *Tetrahedron*., 2015, **71**, 102-108.
6. Y.-W. Huo, L. Yao, X. Qi and X.-F. Wu, Nickel-Catalyzed Reductive Aminocarbonylation of Vinyl Triflates with Nitro Compounds for the Synthesis of *α,β*-Unsaturated Amides, *Org. Chem. Front*., 2021, **8**, 6974-6978.
7. C. Chang, H. Zhang, X. Wu and C. Zhu, Radical Trifunctionalization of Hexenenitrile via Remote Cyano Migration, *Chem. Commun*., 2022, **58**, 1005-1008.
8. M. L. Czyz, M. S. Taylor, T. H. Horngren and A. Polyzos, Reductive Activation and Hydrofunctionalization of Olefins by Multiphoton Tandem Photoredox Catalysis, *ACS Catal.*, 2021, **11**, 5472-5480.
9. C. A. Blakemore, S. P. France, L. Samp, D. M. Nason, E. Yang, R. M. Howard, K. J. Coffman, Q. Yang, A. C. Smith, E. Evrard, W. Li, L. Dai, L. Yang, Z. Chen, Q. Zhang, F. He and J. Zhang, Scalable, Telescoped Hydeogenolysis-Enzymatic Decarboxylation Process for the Asymmetric Synthrsis of (R)-α-Heteroaryl Propionic Acids, *Org. Process. Res. Dev.*, 2021, **25**, 421-426.
10. A. M. Bergmann, A. M. Oldham, W. You and M. K. Brown, Copper-Catalyzed Cross-Coupling of Aryl-, Primary Alkyl-, and Secondary Alkylboranes with Heteroaryl Bromides, *Chem. Commun*., 2018, **54**, 5381-5384.
11. J. Llaveria, D. Leonori, and V. K. Aggarwal, Stereospecific Coupling of Boronic Esters with N-Heteroaromatic Compounds, *J. Am. Chem. Soc*., 2005, **13**7, 10958-10961.
12. T. Liu, Y. Zeng, H. Zhang, T. Wei, X. Wu and N. Li, Facile Pd-Catalyzed Chemoselective Transfer Hydrogenation of Olefins Using Formic Acid in Water, *Tetrahedron Letters*., 2016, **57**, 4845-4849.
13. Y. Nakao, Y. Yamada, N. Kashihara and T. Hiyama, Selective C-4 Alkylation of Pyridine by Nickel/Lewis Acid Catalysis, *J. Am. Chem. Soc*., 2010, **132**, 13666-13668.
14. X. Sun, M. Wang, P. Li, X. Zhang and L. Wang, H_2O_2-Mediated Oxidative

Formation of Amides from Aromatic Amines and 1,3-Diketones as Acylation Agents *via* C-C Bond Cleavage at Room Temperature in Water under Metal-Free Conditions, *Green. Chem*., 2013, **15**, 3289-3294.

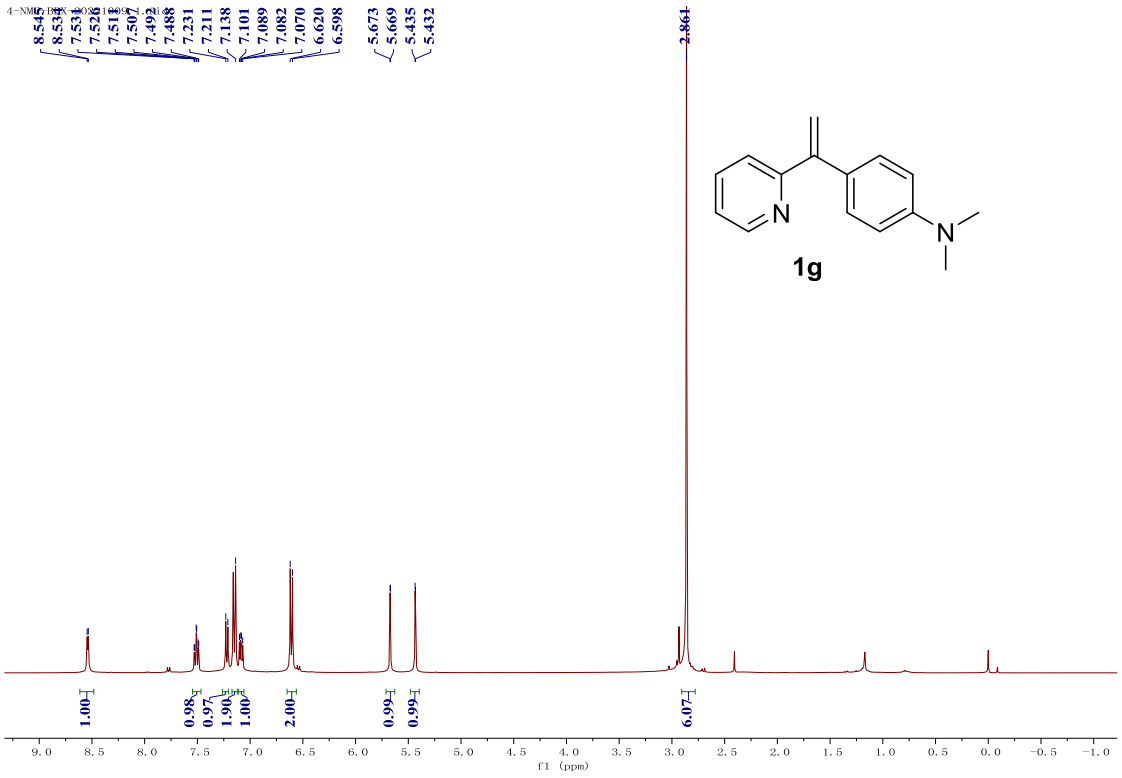
15. R. Guo, C. Zhu, Z. Sheng, Y. Li, W. Yin and C. Chu, Silica Sulfuric Acid Mediated Acylation of Amines with 1,3-Diketones *via* C-C Bond Cleavage under Solvent-Free Conditions, *Tetrahedron Letters*., 2015, **56**, 6223-6226.
16. L. Cicco, J. A. Hernandez-Fernandez, A. Salomone, P. Vitale, M. Ramos-Martin, J. Gonzalez-Sabin, A. Presa Soto, F. M. Perna, V. Capriati and J. Garcia-Alvarez, Copper-Catalyzed Goldberg-Type C-N Coupling in Deep Eutectic Solvents (DESs) and Water under Aerobic Conditions, *Org. Biomol. Chem*., 2021, **19**, 1773-1779.
17. A. Correa, S. Elmore and C. Bolm, Iron-Catalyzedn-Arylations of Amides, *Chem. Eur. J*., 2008, **14**, 3527-3529.
18. Y. Gao, J. Liu, Z. Li, T. Guo, S. Xu, H. Zhu, F. Wei, S. Chen, H. Gebru and K. Guo, Dichloroimidazolidinedione-Activated Beckmann Rearrangement of Ketoximes for Accessing Amides and Lactams, *J. Org. Chem*., 2018, **83**, 2040-2049.
19. F. Dobah, C. M. Mazodze and W. F. Petersen, Cross-Dehydrogenative Cyclization-Dimerization Cascade Sequence for the Synthesis of Symmetrical 3,3′-Bisoxindoles, *Org. Lett*., 2021, **23**, 5466-5470.
20. J. Zhu, B. Gao and H. Huang, Palladium-Catalyzed Highly Regioselective Hydroaminocarbonylation of Aromatic Alkenes to Branched Amides, *Org. Biomol. Chem*., 2017, **15**, 2910-2913.
21. P. Yang, X. Wang, Y. Ma, Y. Sun, L. Zhang, J. Yue, K. Fu, J. S. Zhou and B. Tang, Nickel-Catalyzed C-Alkylation of Thioamide, Amides and Esters by Primary Alcohols through a Hydrogen Autotransfer Strategy, *Chem. Commun*., 2020, **56**, 14083-14086.
22. Gaussian 16 Rev. A.03, M. J. Frisch, G. W. Trucks, H. B. Schlegel, G. E. Scuseria, M. A. Robb, J. R. Cheeseman, G. Scalmani, V. Barone, G. A. Petersson, H. Nakatsuji, X. Li, M. Caricato, A. V. Marenich, J. Bloino, B. G. Janesko, R. Gomperts, B. Mennucci, H. P. Hratchian, J. V. Ortiz, A. F. Izmaylov, J. L. Sonnenberg, Williams; F. Ding, F. Lipparini, F. Egidi, J. Goings, B. Peng, A. Petrone, T. Henderson, D. Ranasinghe, V. G. Zakrzewski, J. Gao, N. Rega, G. Zheng, W. Liang, M. Hada, M. Ehara, K. Toyota, R. Fukuda, J. Hasegawa, M. Ishida, T. Nakajima, Y. Honda, O. Kitao, O. Nakai, T. Vreven, K. Throssell, J. A. Montgomery Jr, J. E. Peralta, F. Ogliaro, M. J. Bearpark, J. J. Heyd, E. N. Brothers, K. N. Kudin, V. N. Staroverov, T. A. Keith, R. Kobayashi, J. Normand, K. Raghavachari, A. P. Rendell, J. C. Burant, S. S. Iyengar, J. Tomasi, M. Cossi, J. M.

Millam, M. Klene, C. Adamo, R. Cammi, J. W. Ochterski, R. L. Martin, K. Morokuma, O. Farkas, J. B. Foresman and D. J. Fox, Gaussian Inc. Wallingford CT, 2016.

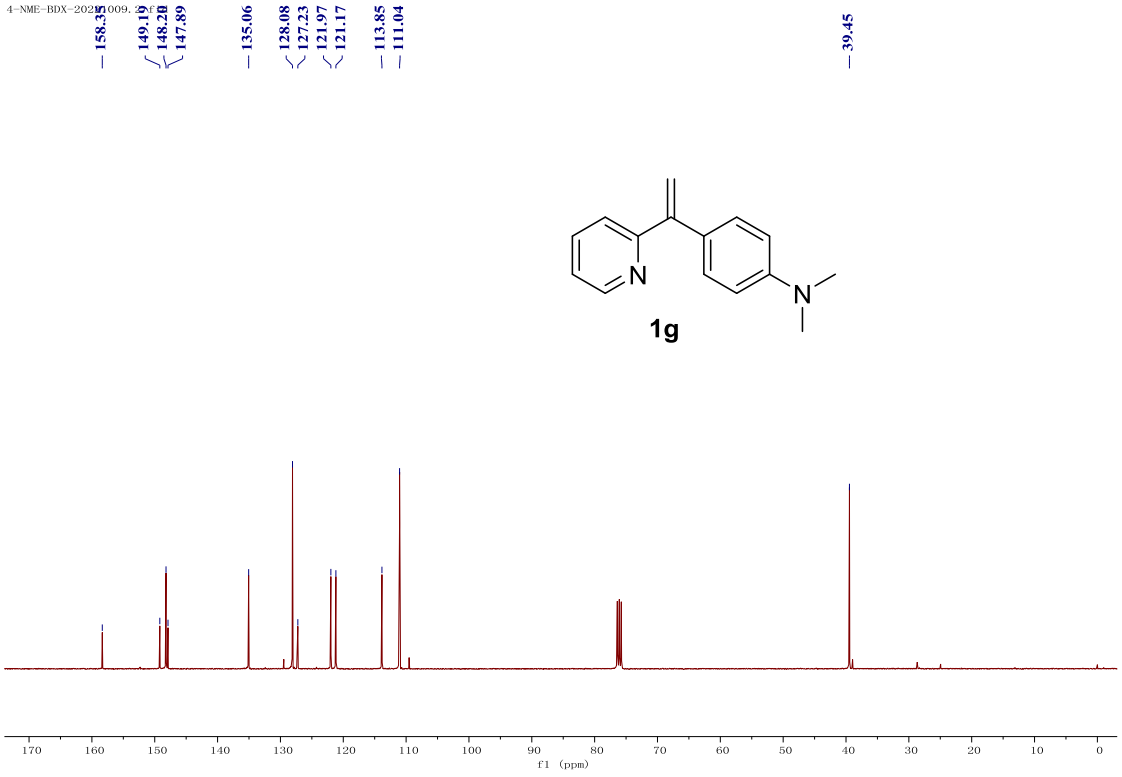
23. M. Ernzerhof and G. E. Scuseria, Assessment of The Perdew-Burke-Wrnzerhof Exchange-Correlation Functional, *J. Chem. Phys.*, 1999, **110**, 5029-5036.
24. F. Weigend and R. Ahlrichs, Balanced Basic Sets of Split Valence, Triple Zeta Valence and Quadruple Zeta Valence Quality for H to Rn: Design and Asseddment of accuracy, *Phys. Chem. Chem. Phys.*, 2005, **7**, 3297-3305.
25. F. Weigend, Accurate Coulomb-Fitting Basis Sets for H to Rn, *Phys. Chem. Chem. Phys.*, 2006, **8**, 1057-1065.
26. A. V. Marenich, C. J. Cramer and D. G. Truhlar, Universal Solvation Model Based On Solute Electron Density and On A Continuum Model of The Solvent Defined by The Bulk Dielectric Constant and Atomic Surface Tensions, *J. Phys. Chem. B*, 2009, **113**, 6378-6396.
27. CYLview, 1.0b, C. Y. Legault, Université de Sherbrooke, 2009.
28. GaussView, Version 6, R. Dennington, T. A. Keith and J. M. Millam, Semichem Inc., Shawnee Mission, KS, 2016.

7. NMR Spectra of Compounds 1g-1h, 1k, 2a and 2-31

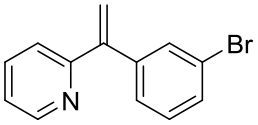
^{1}H NMR (400MHz, $CDCl_3$) spectrum of product 1g



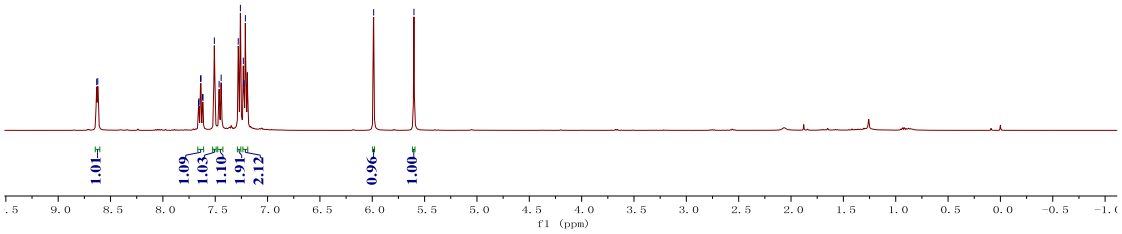
^{13}C NMR (100MHz, $CDCl_3$) spectrum of product 1g



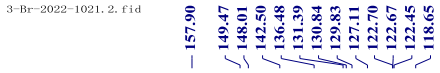
^{1}H NMR (400MHz, $CDCl_3$) spectrum of product 1h

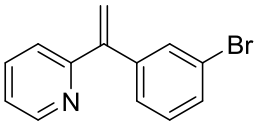


1h

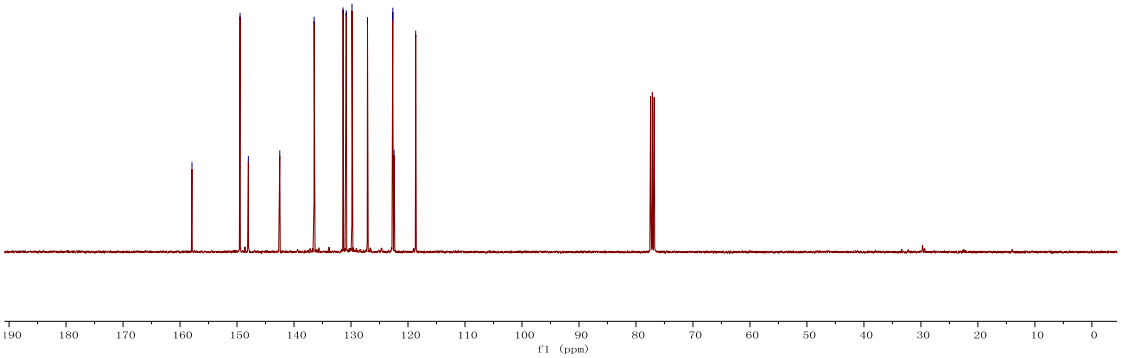


^{13}C NMR (100MHz, $CDCl_3$) spectrum of product 1h

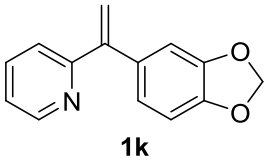




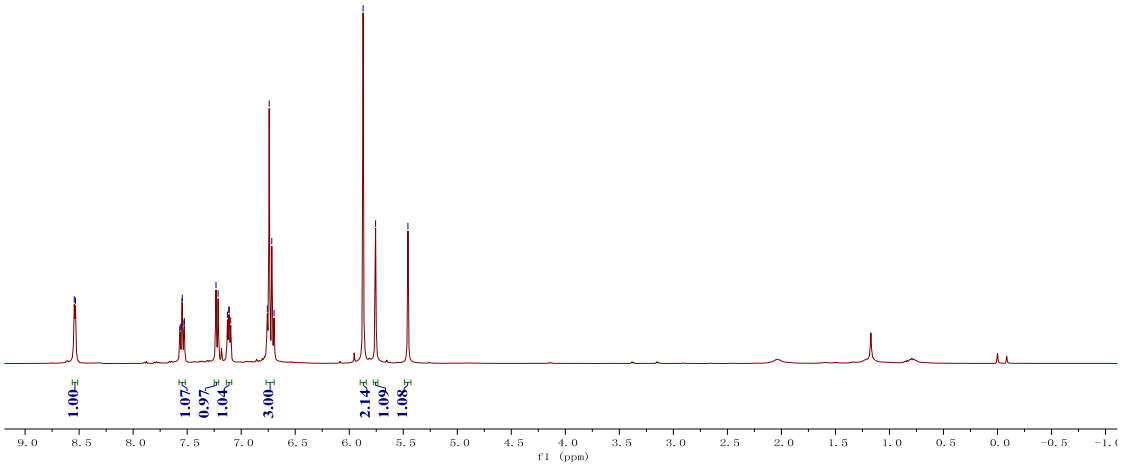
1h



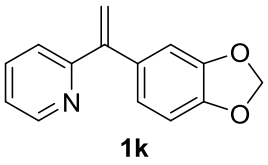
^{1}H NMR (400MHz, $CDCl_3$) spectrum of product 1k



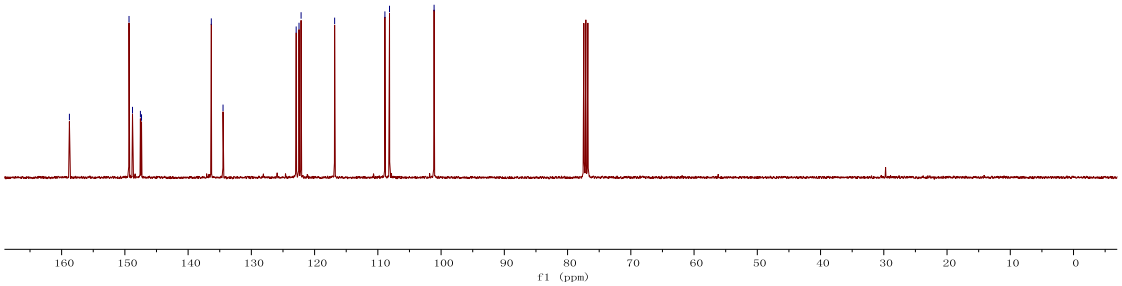
1k



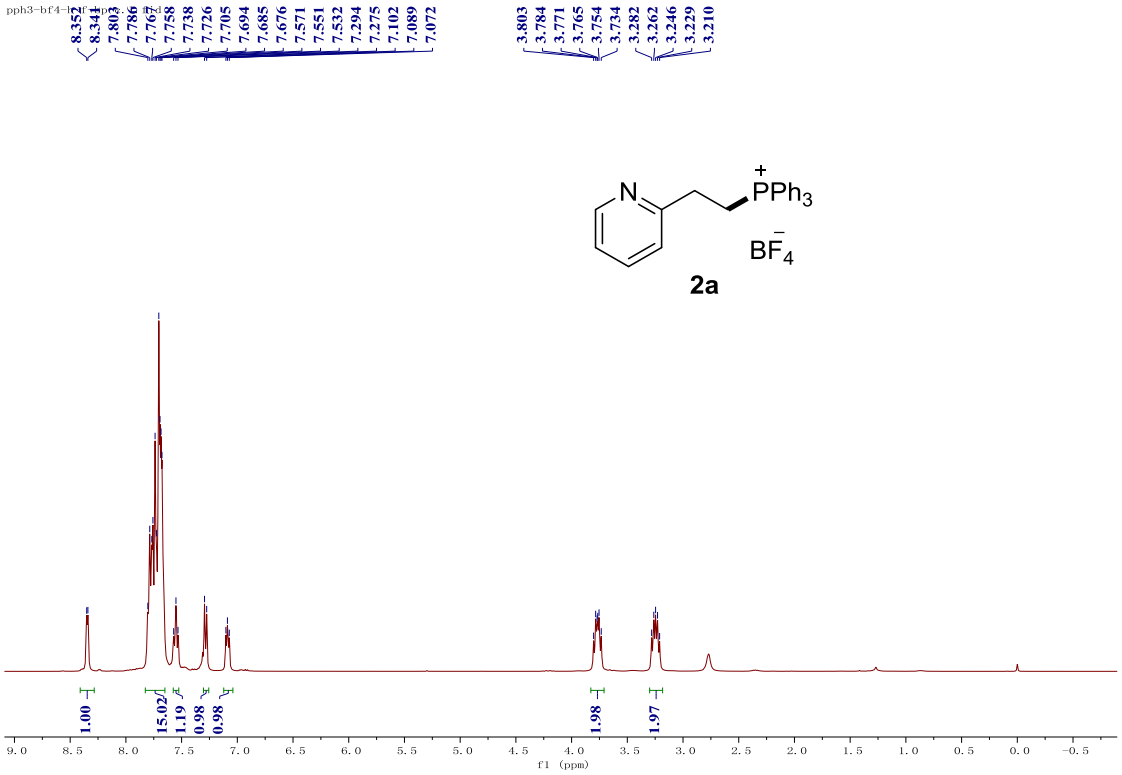
^{13}C NMR (100MHz, $CDCl_3$) spectrum of product 1k



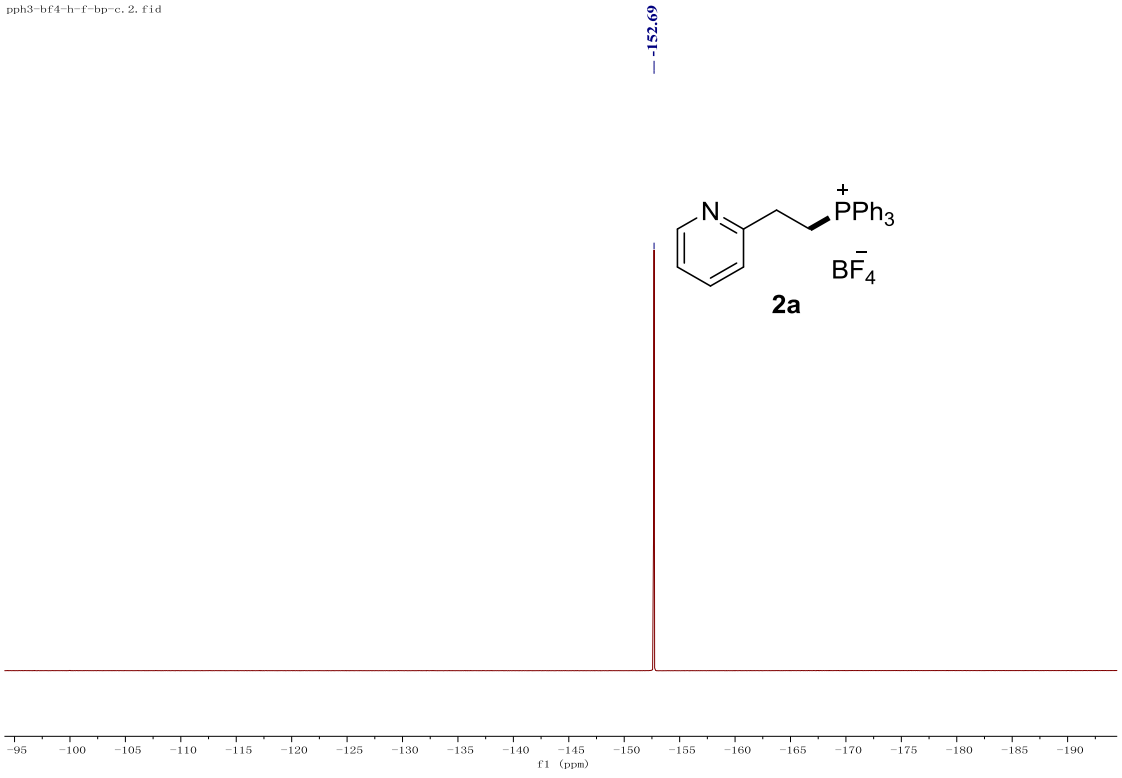
1k



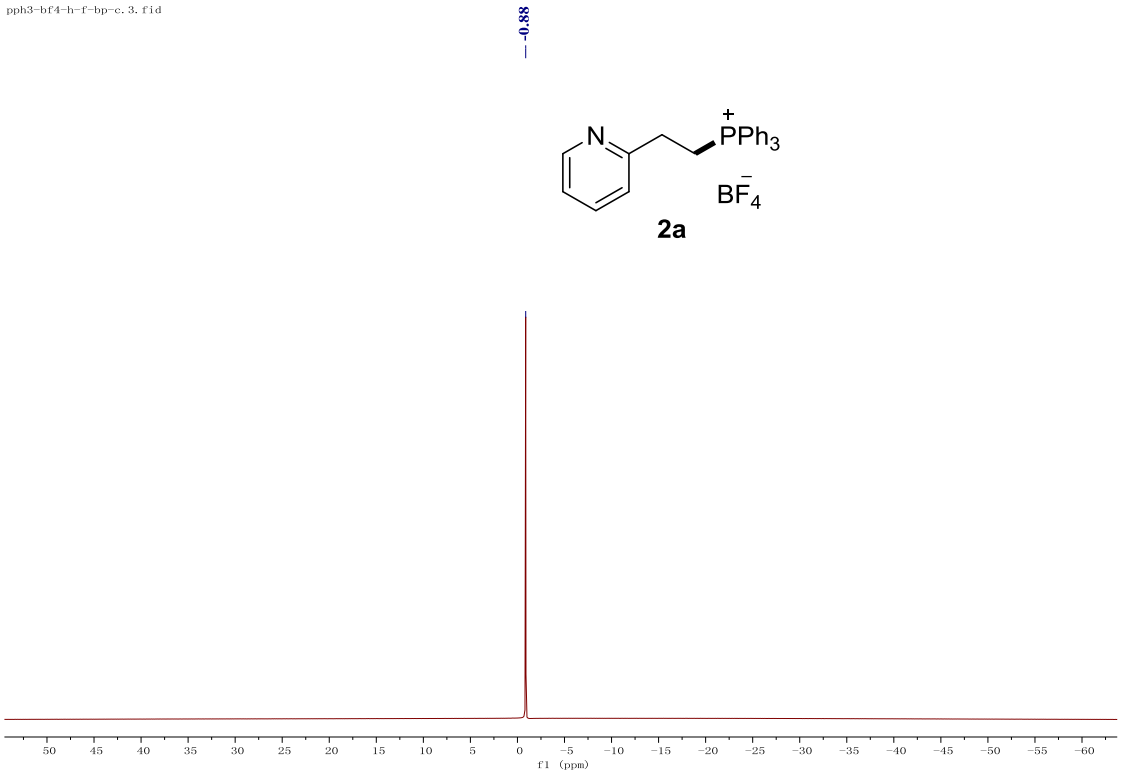
^{1}H NMR (400MHz, CDCl$_3$) spectrum of product 2a



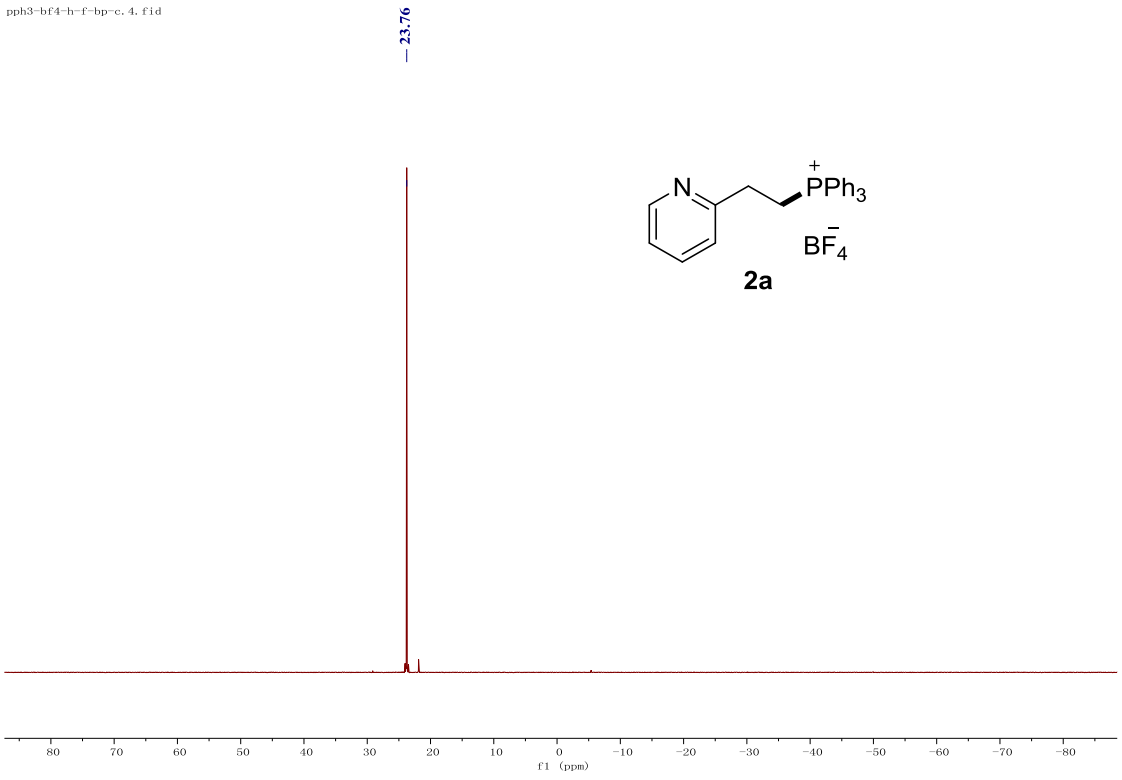
^{19}F NMR (376 MHz, CDCl3) spectrum of product 2a



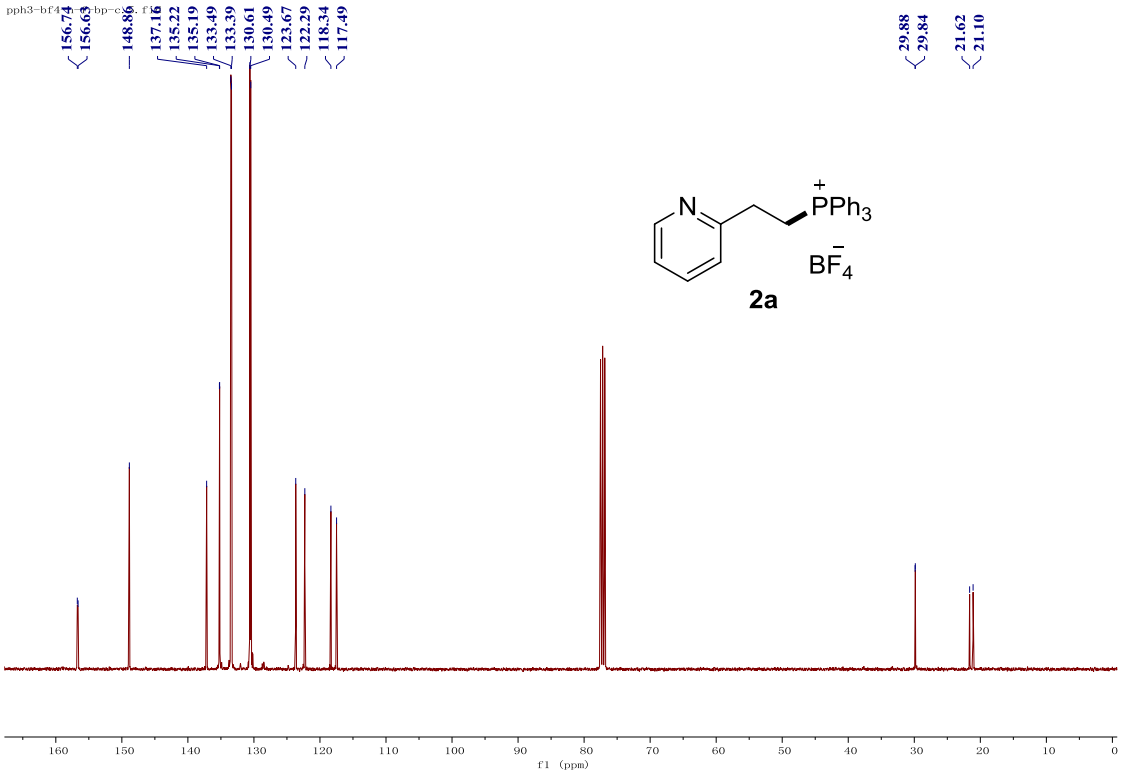
^{11}B NMR (128 MHz, $CDCl_3$) spectrum of product 2a



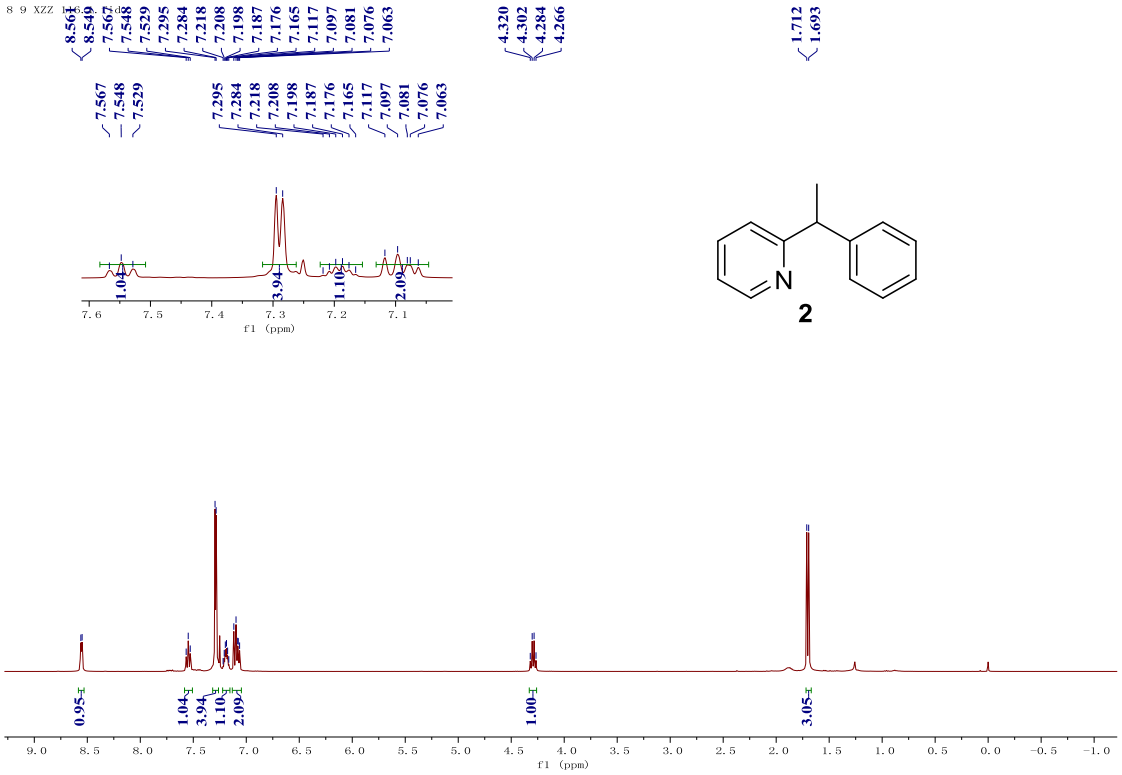
^{31}P NMR (162 MHz, $CDCl_3$) spectrum of product 2a



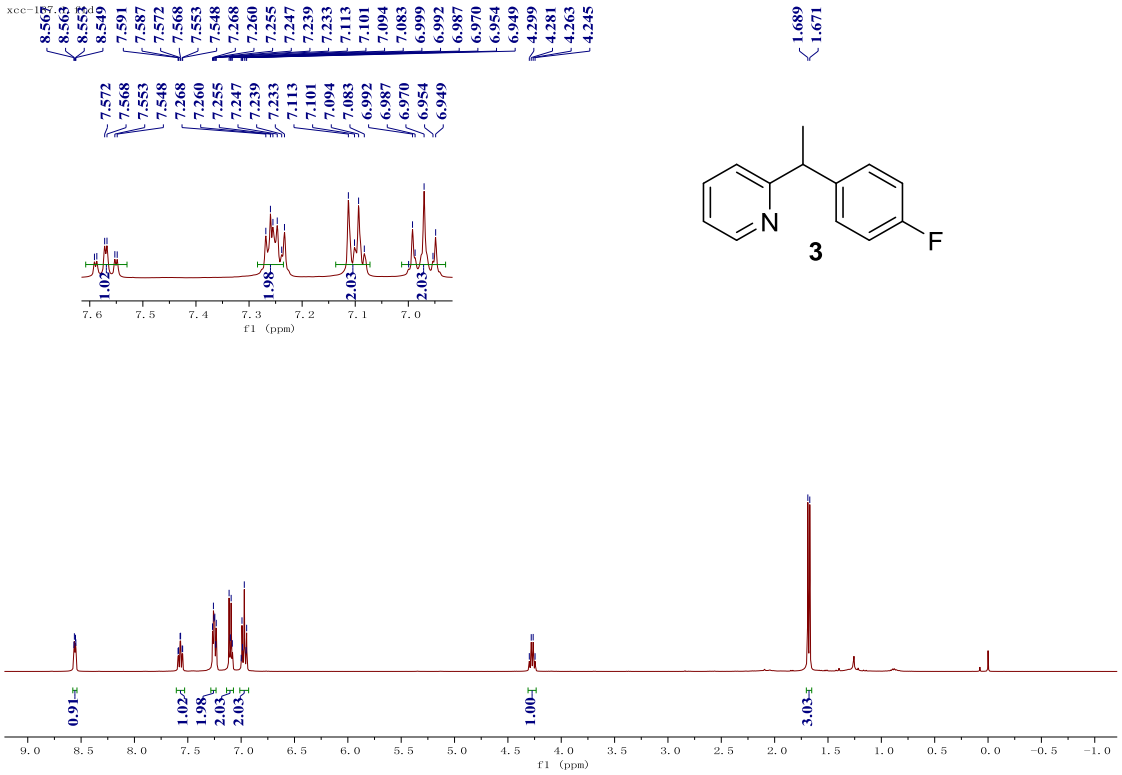
^{13}C NMR (100MHz, $CDCl_3$) spectrum of product 2a



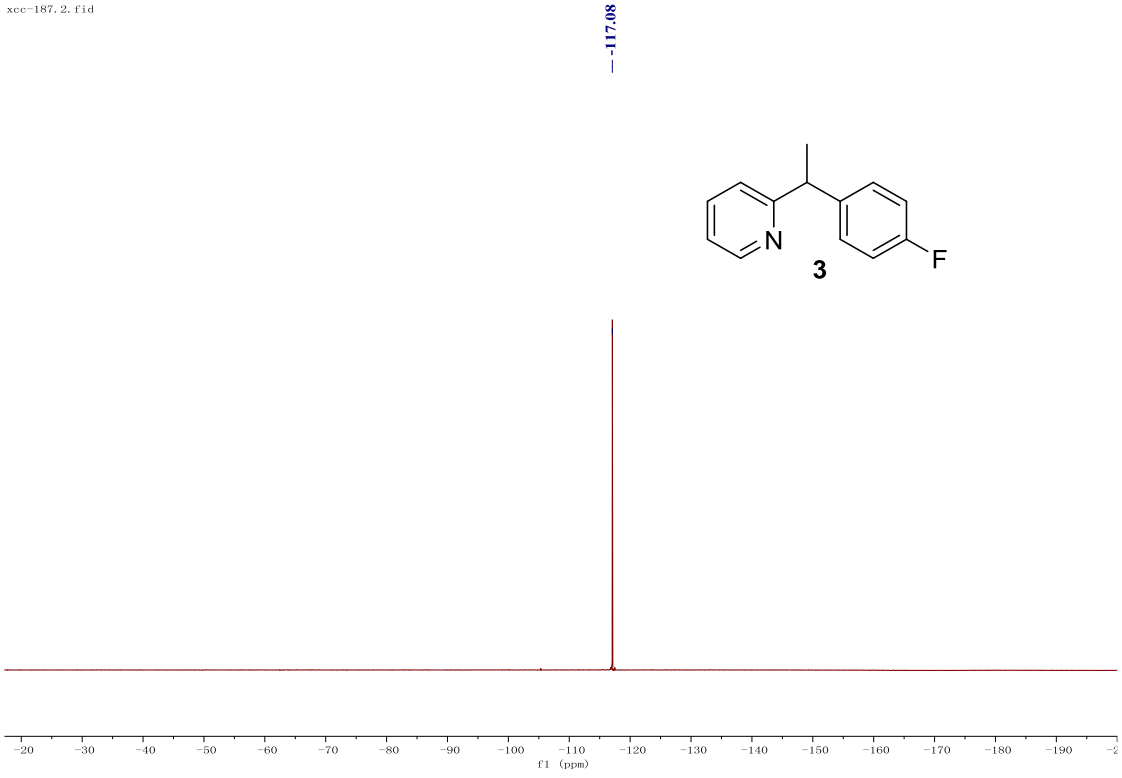
^{1}H NMR (400MHz, $CDCl_3$) spectrum of product 2



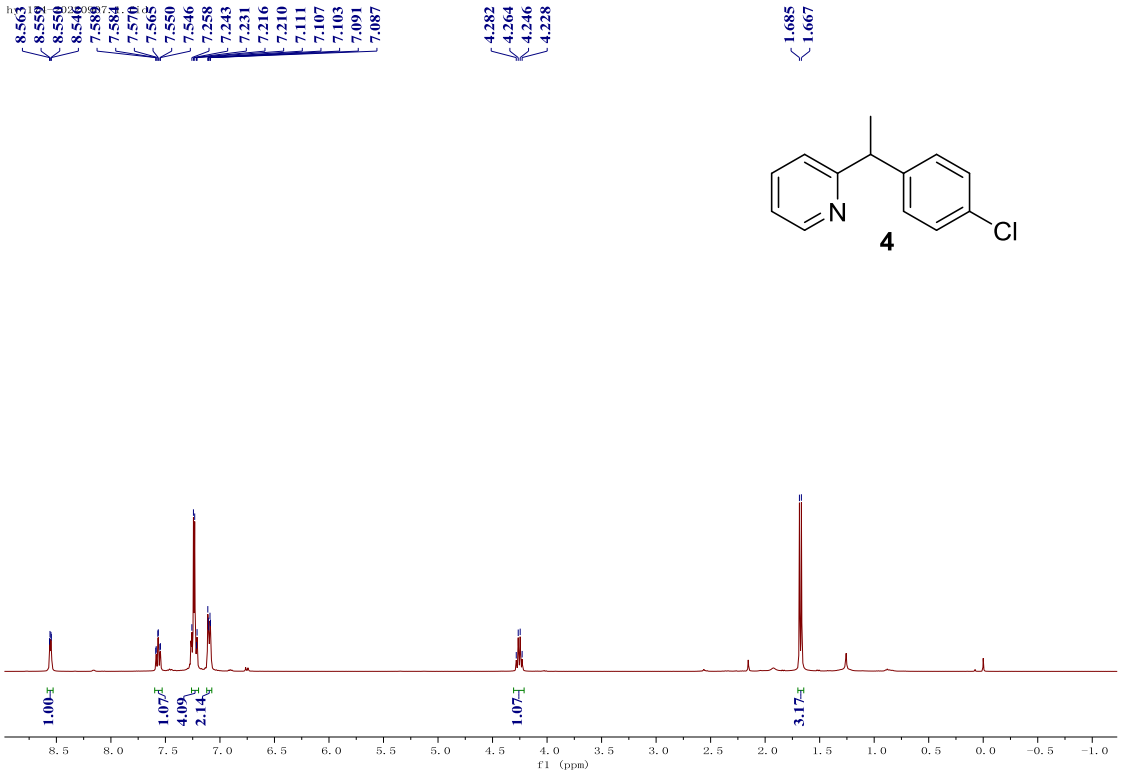
^{1}H NMR (400MHz, $CDCl_3$) spectrum of product 3



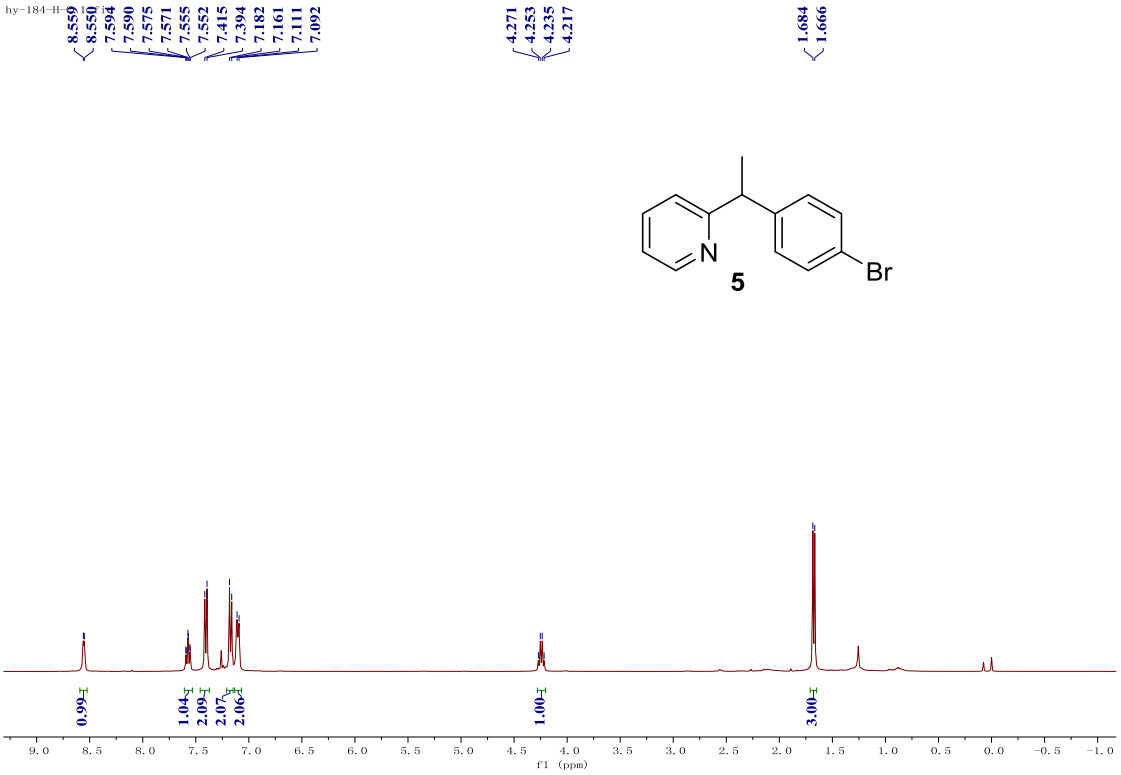
^{19}F NMR (376 MHz, $CDCl_3$) spectrum of product 3



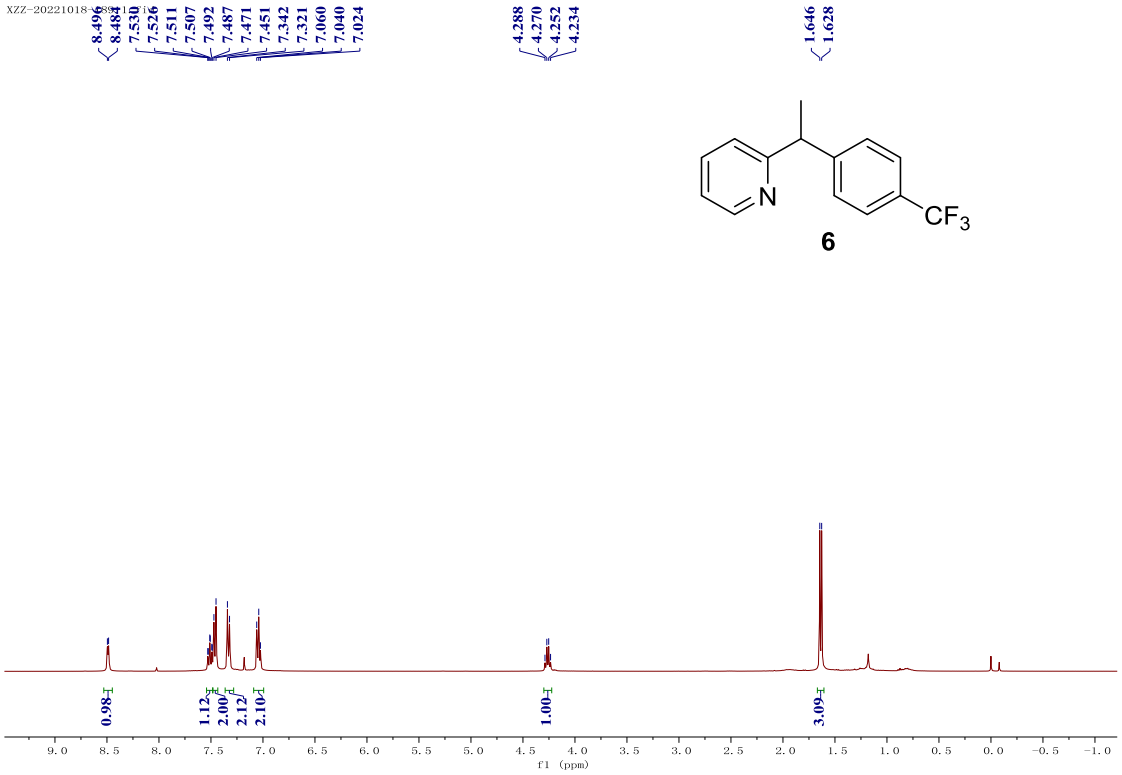
^{1}H NMR (400MHz, $CDCl_3$) spectrum of product 4



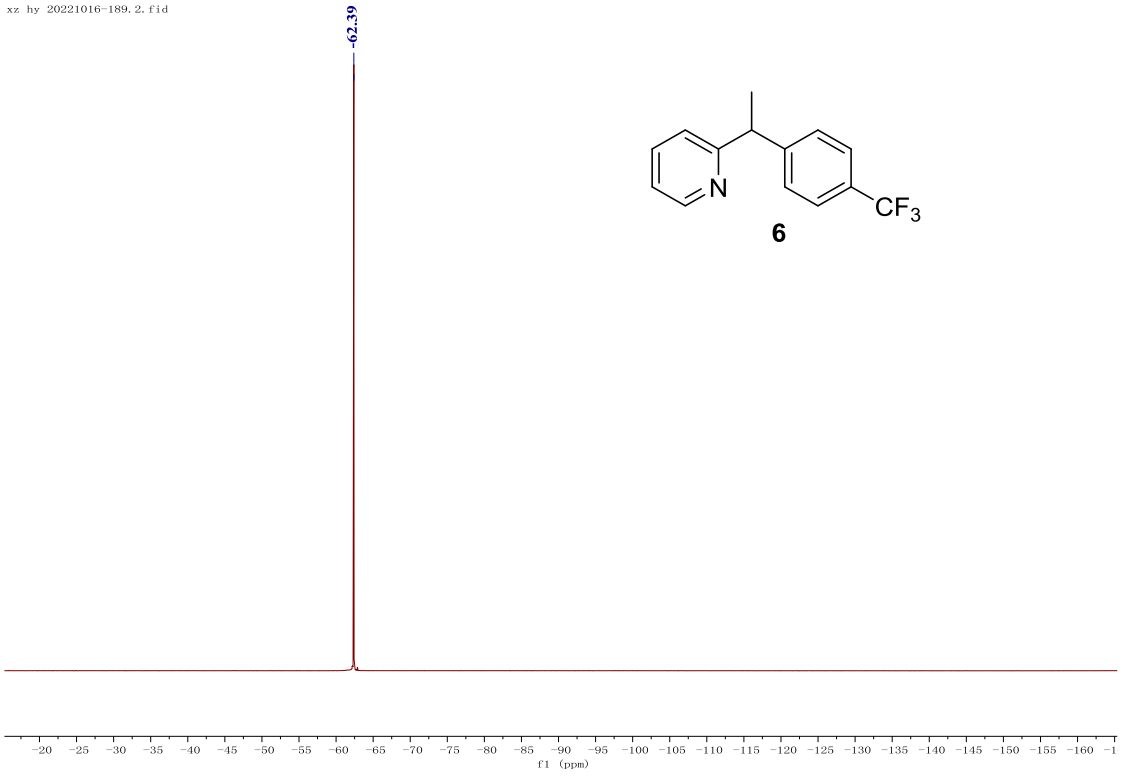
^{1}H NMR (400MHz, $CDCl_3$) spectrum of product 5



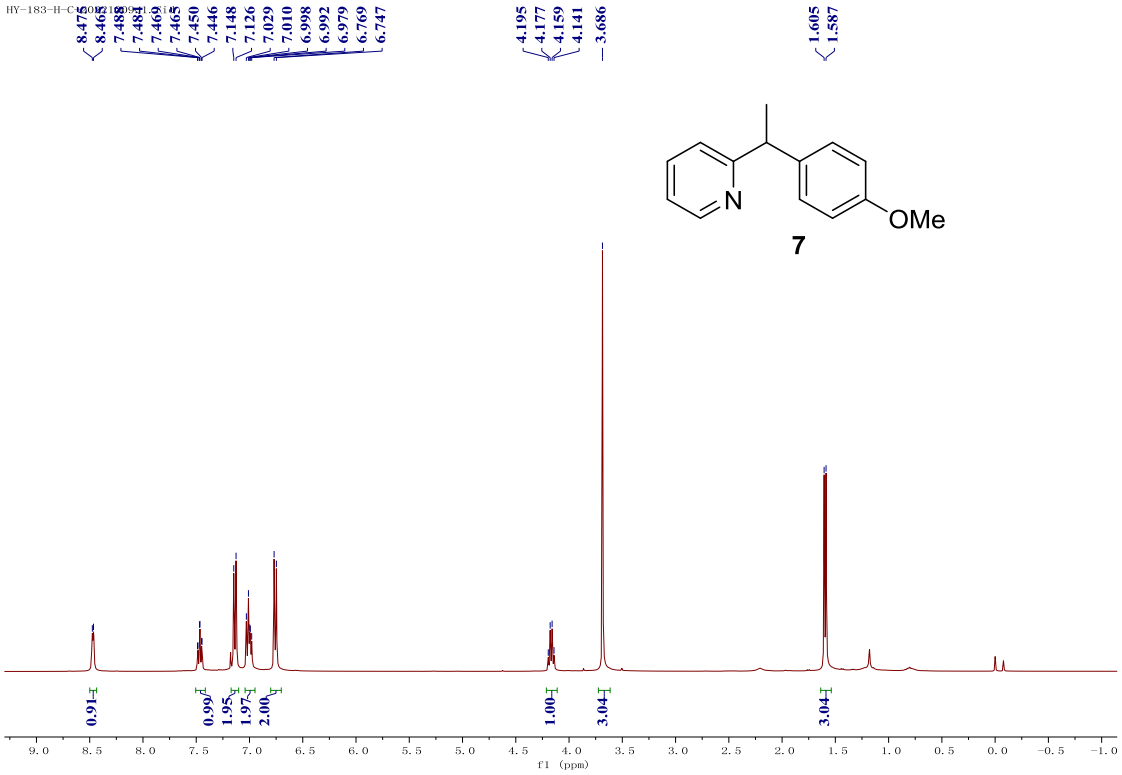
^{1}H NMR (400MHz, $CDCl_3$) spectrum of product 6



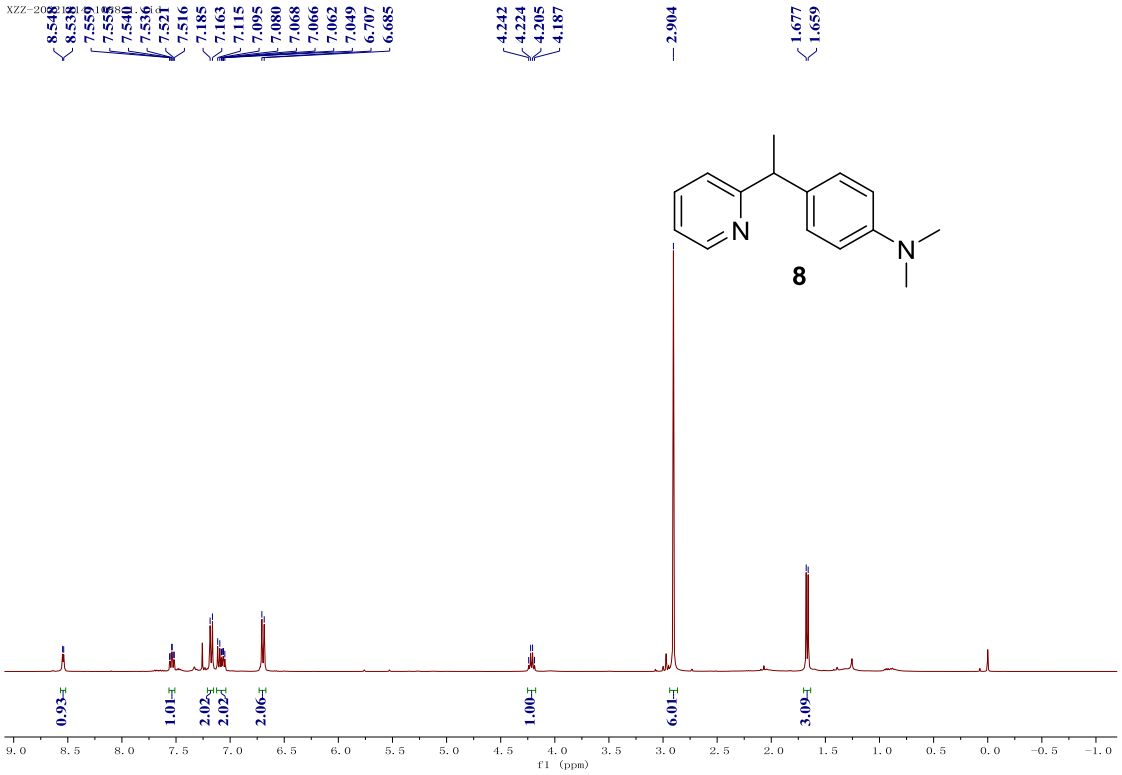
^{19}F NMR (376 MHz, $CDCl_3$) spectrum of product 6



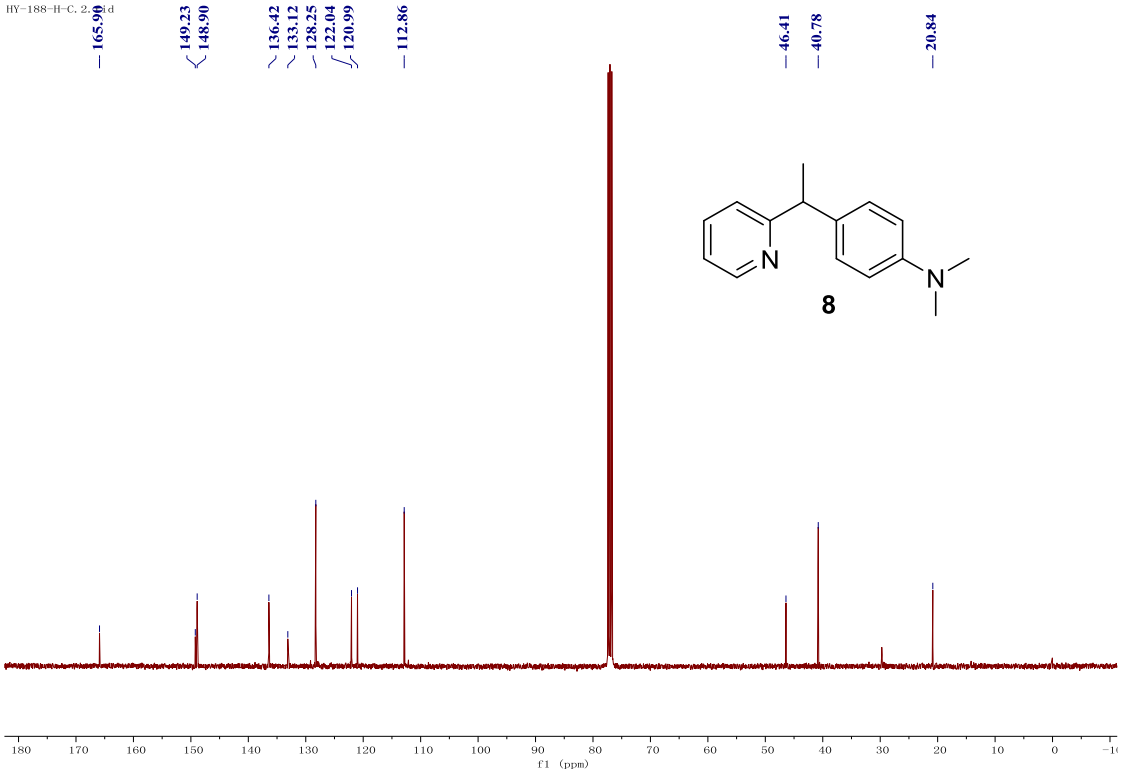
^{1}H NMR (400MHz, $CDCl_3$) spectrum of product 7



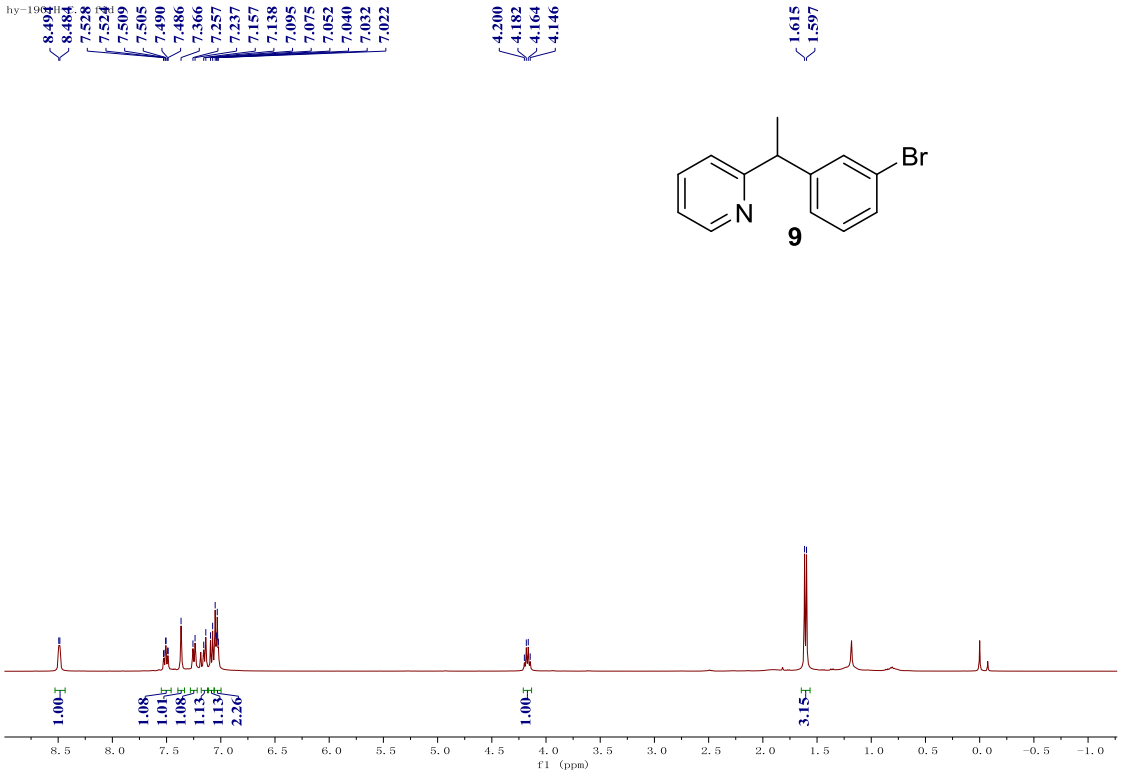
^{1}H NMR (400MHz, $CDCl_3$) spectrum of product 8



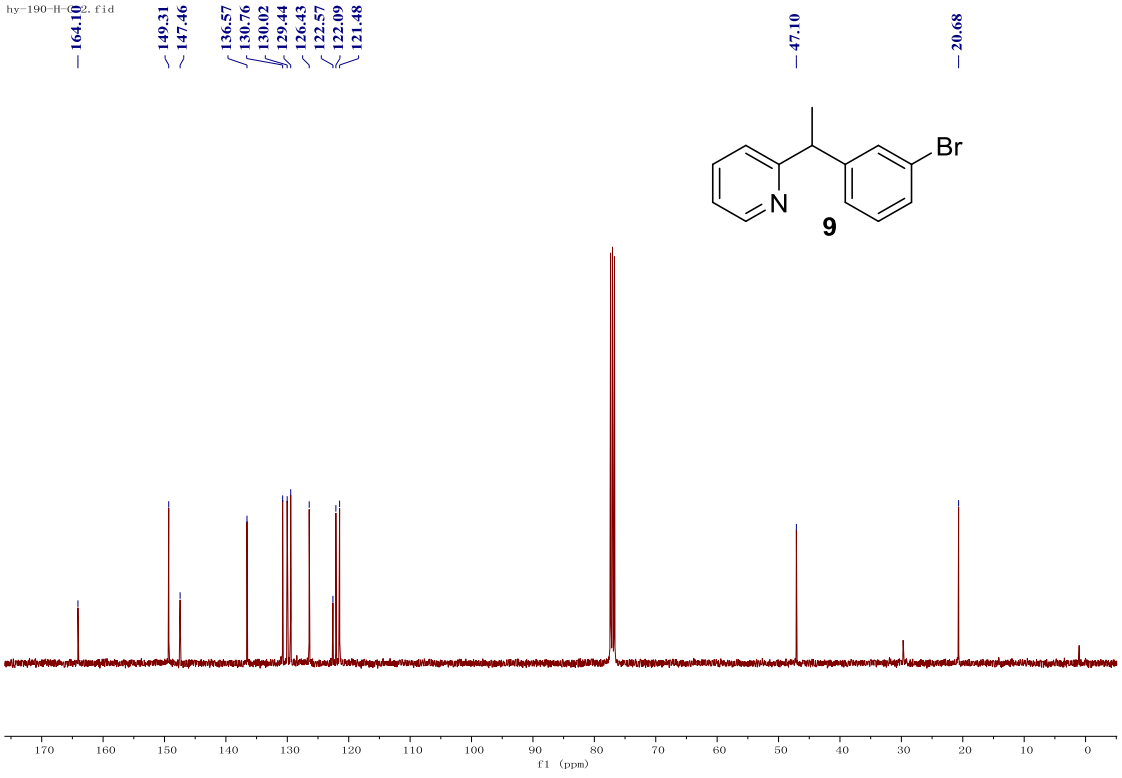
^{13}C NMR (100MHz, $CDCl_3$) spectrum of product 8



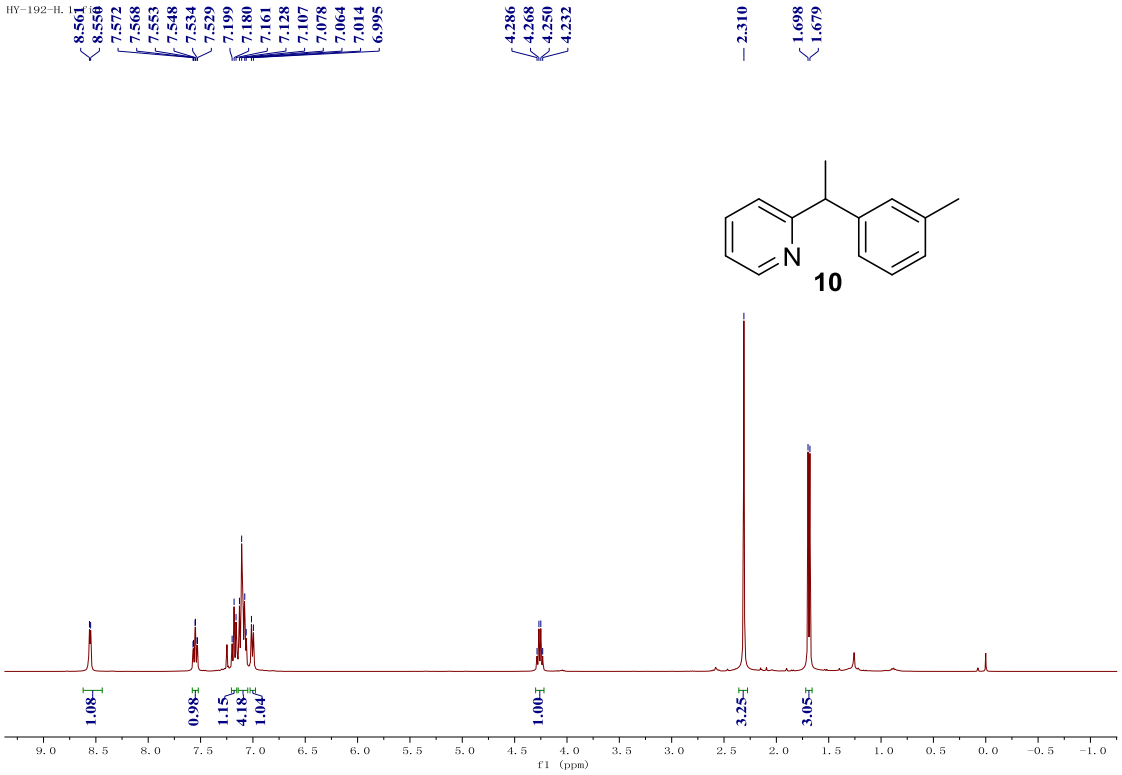
^{1}H NMR (400MHz, $CDCl_3$) spectrum of product 9



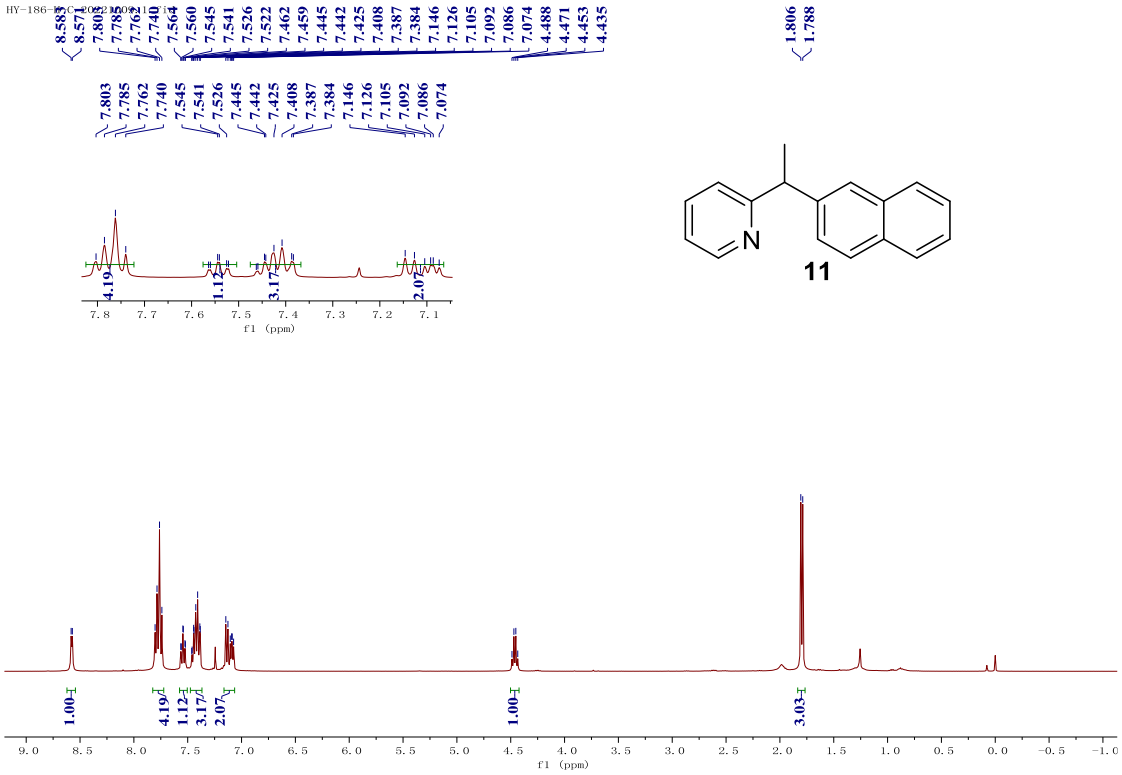
^{13}C NMR (100MHz, $CDCl_3$) spectrum of product 9



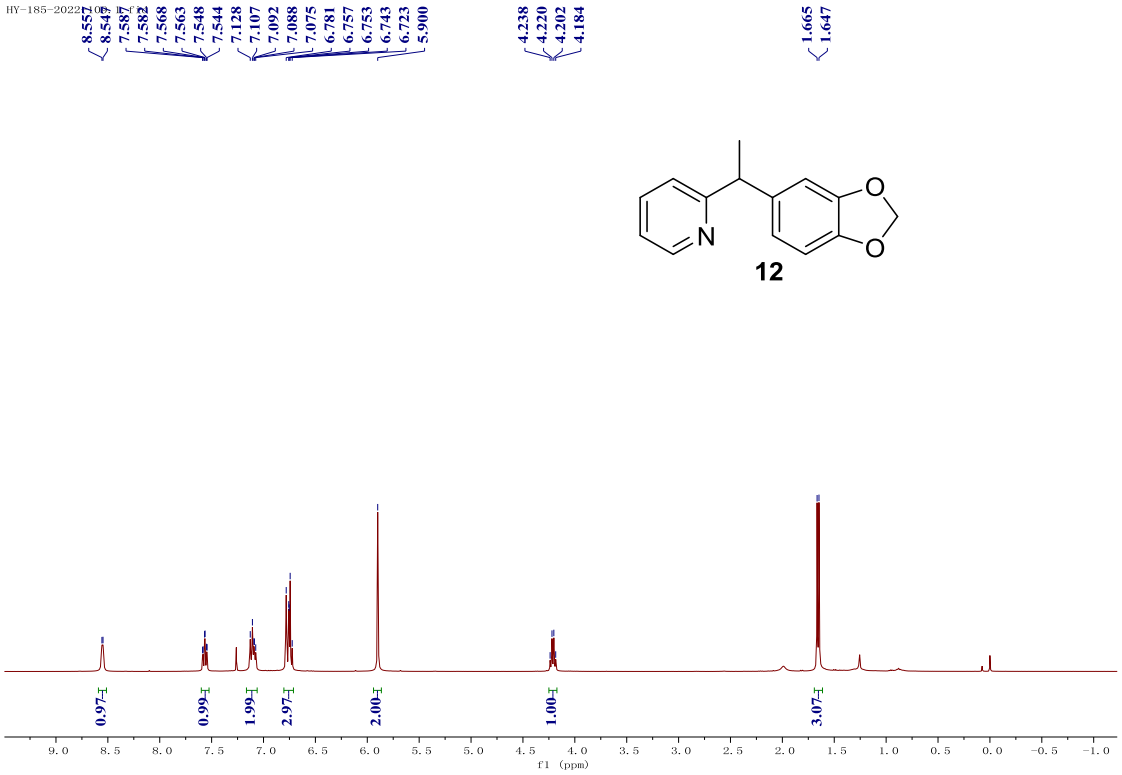
^{1}H NMR (400MHz, $CDCl_3$) spectrum of product 10



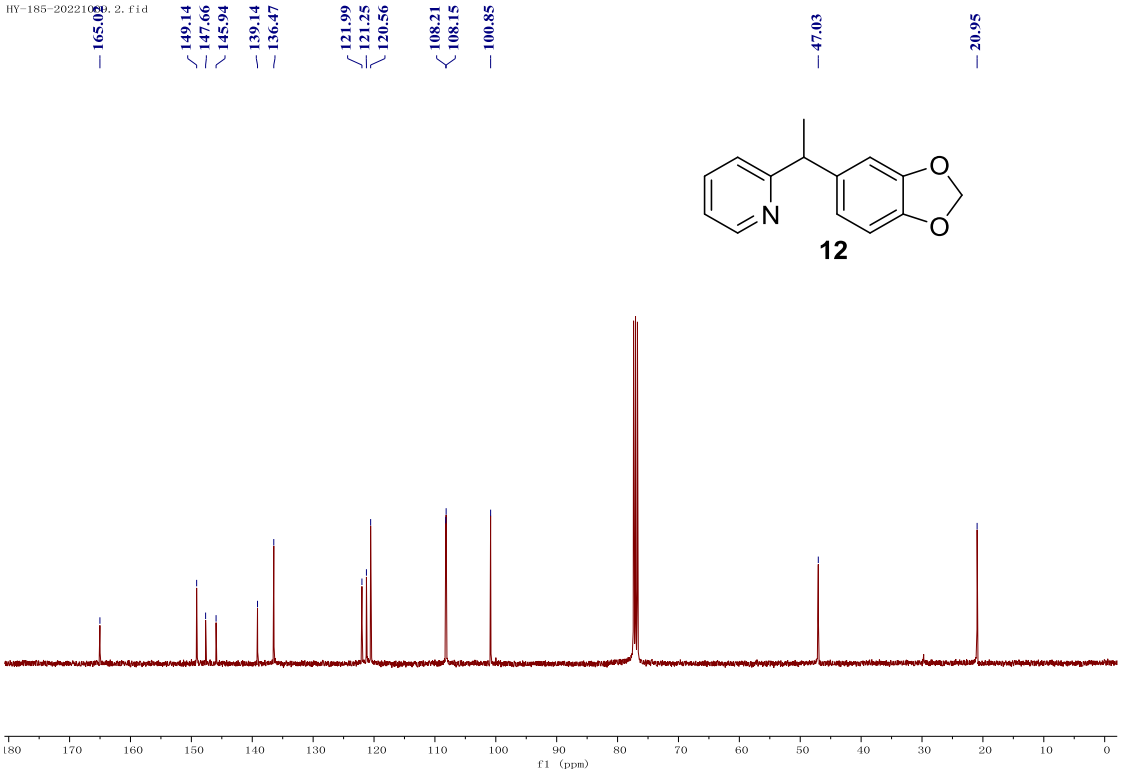
^{1}H NMR (400MHz, $CDCl_3$) spectrum of product 11



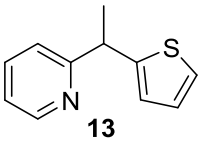
^{1}H NMR (400MHz, $CDCl_3$) spectrum of product 12

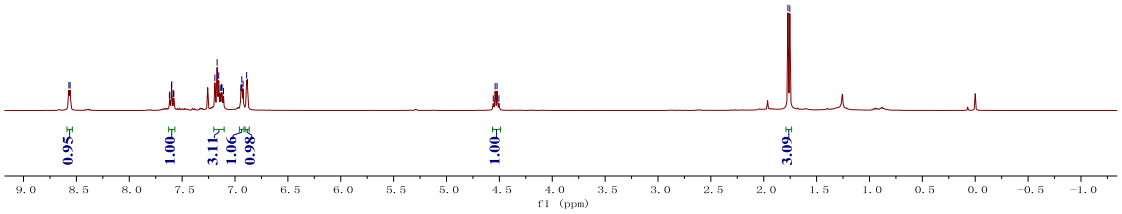


^{13}C NMR (100MHz, $CDCl_3$) spectrum of product 12

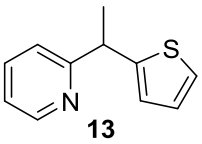


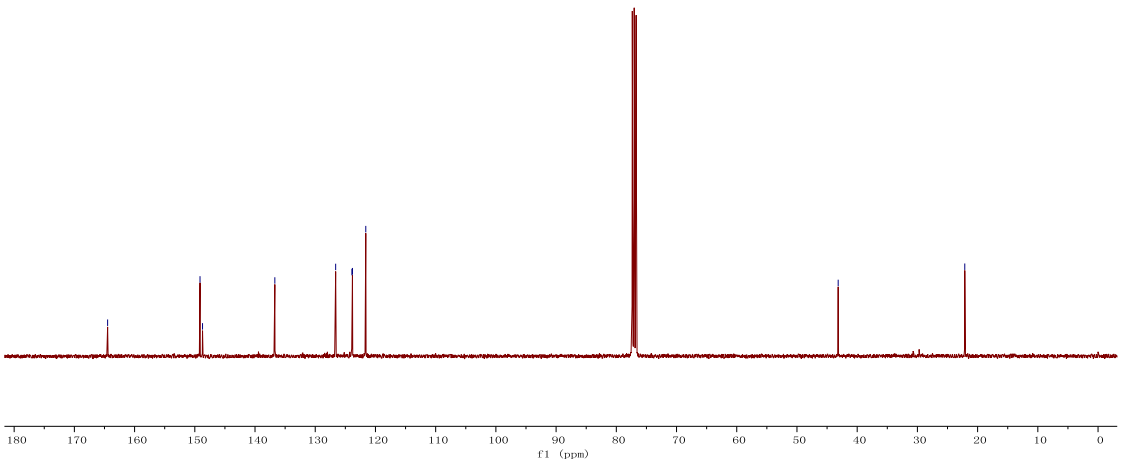
^{1}H NMR (400MHz, $CDCl_3$) spectrum of product 13



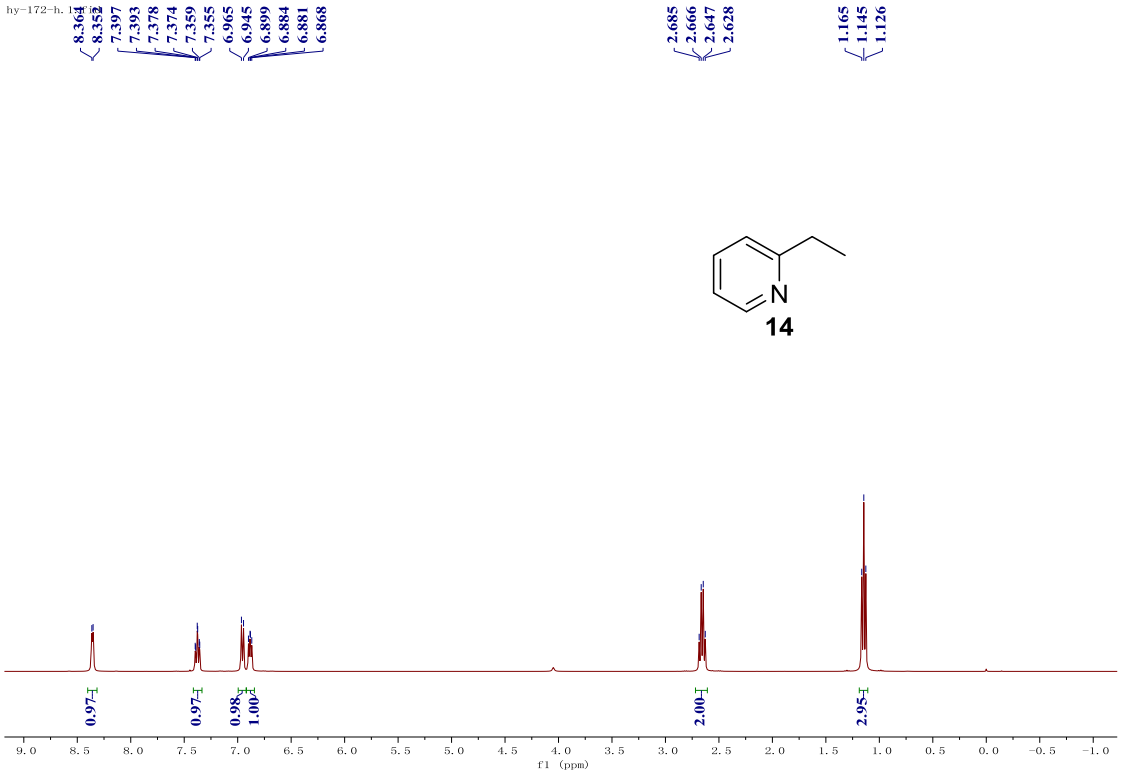


^{13}C NMR (100MHz, $CDCl_3$) spectrum of product 13

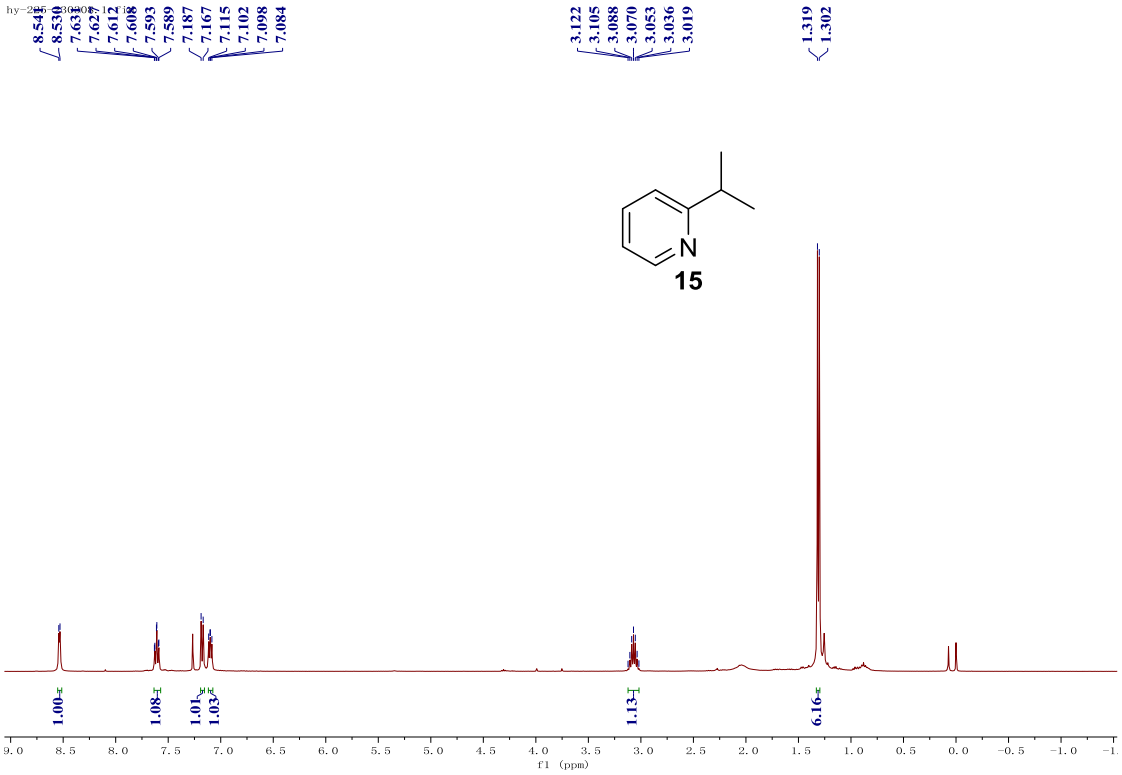




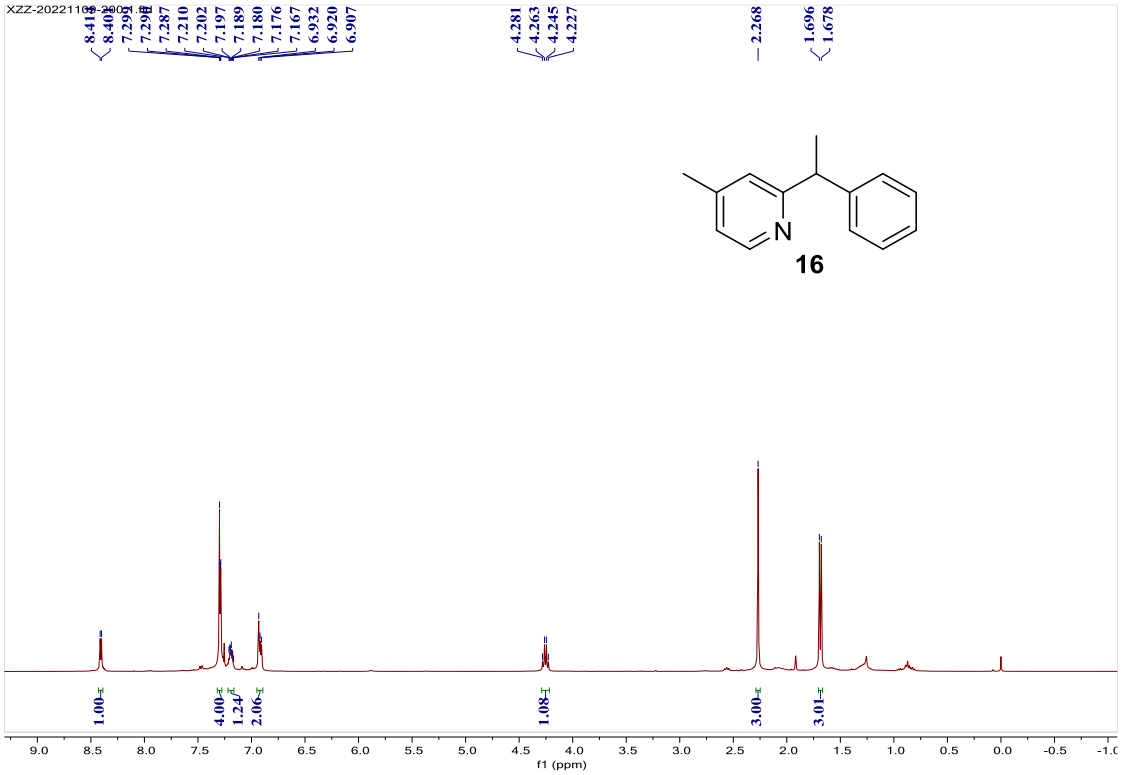
^{1}H NMR (400MHz, $CDCl_3$) spectrum of product 14



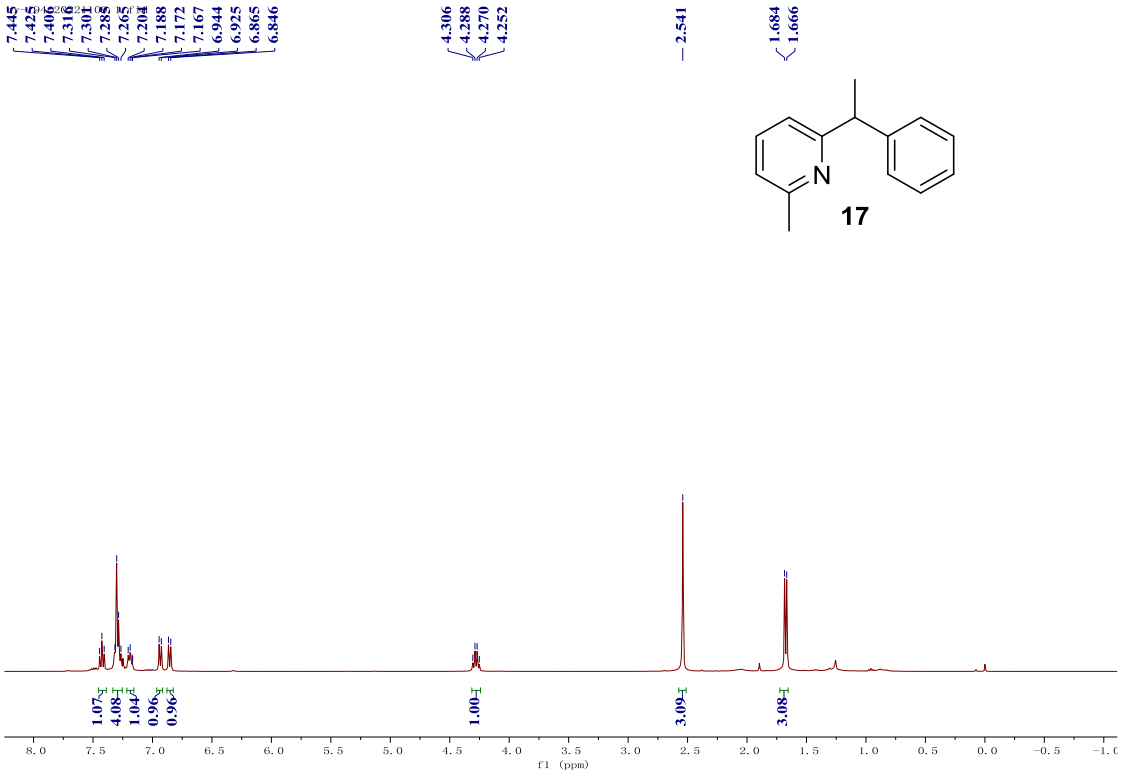
^{1}H NMR (400MHz, $CDCl_3$) spectrum of product 15



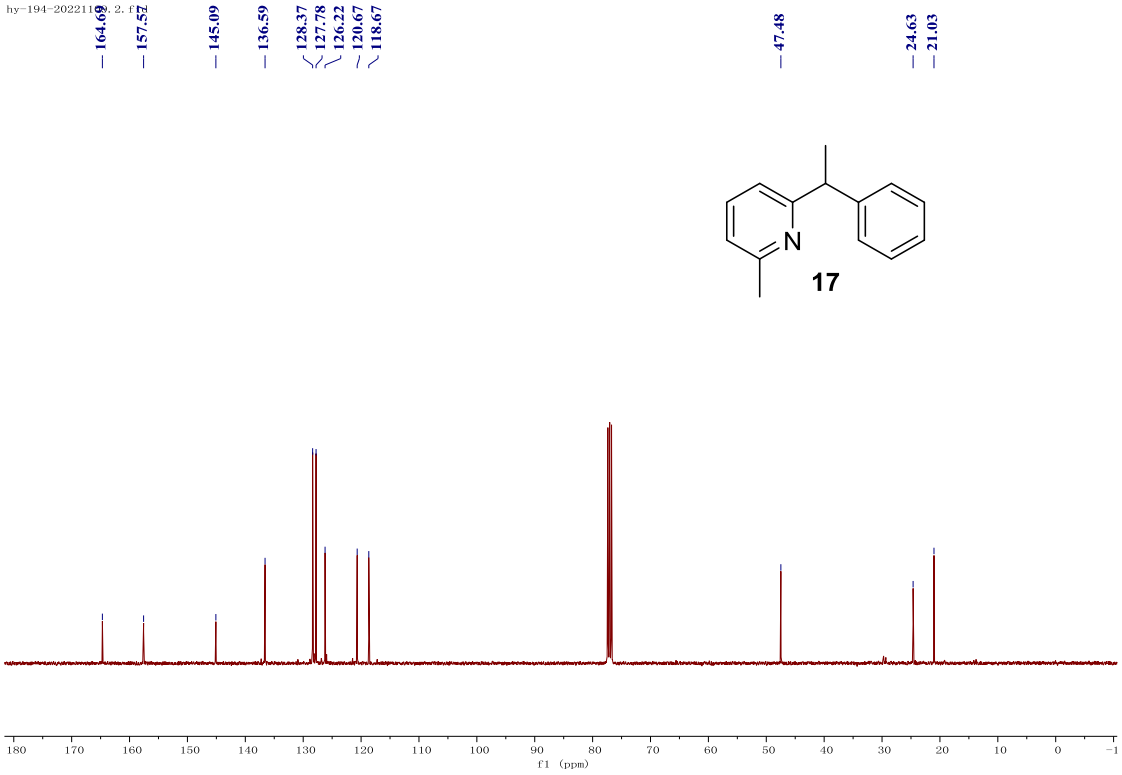
^{1}H NMR (400MHz, $CDCl_3$) spectrum of product 16



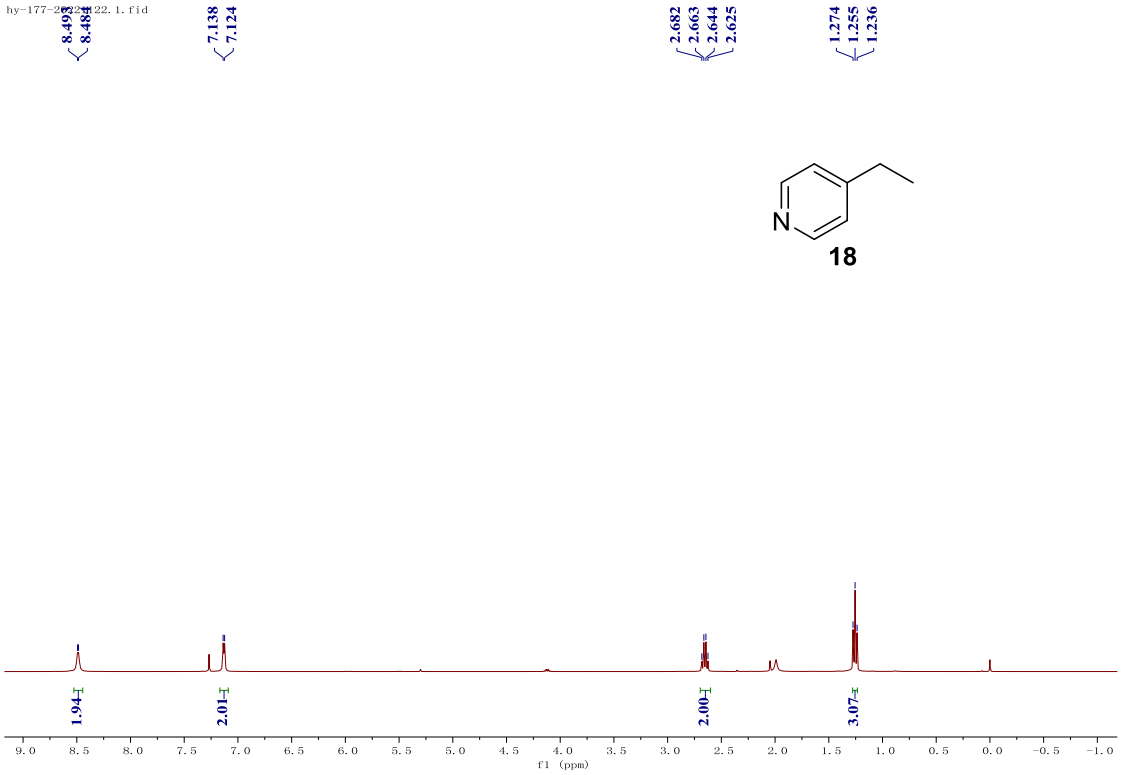
^{1}H NMR (400MHz, $CDCl_3$) spectrum of product 17



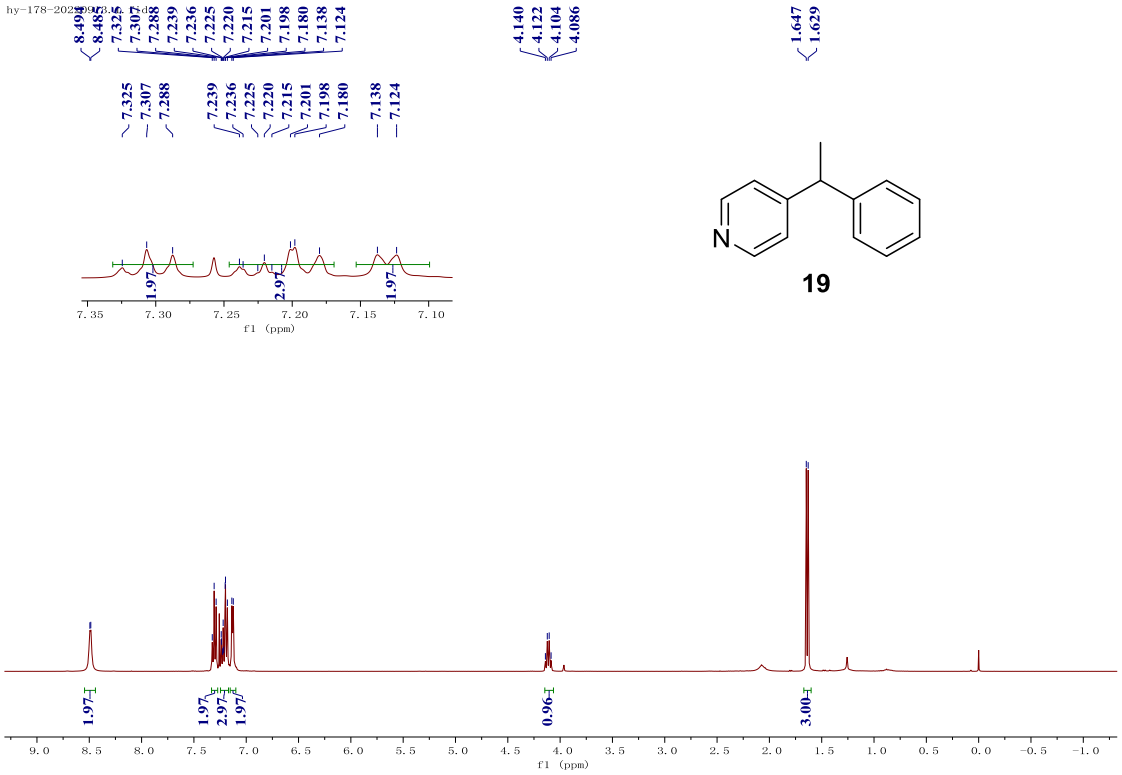
^{13}C NMR (100MHz, $CDCl_3$) spectrum of product 17



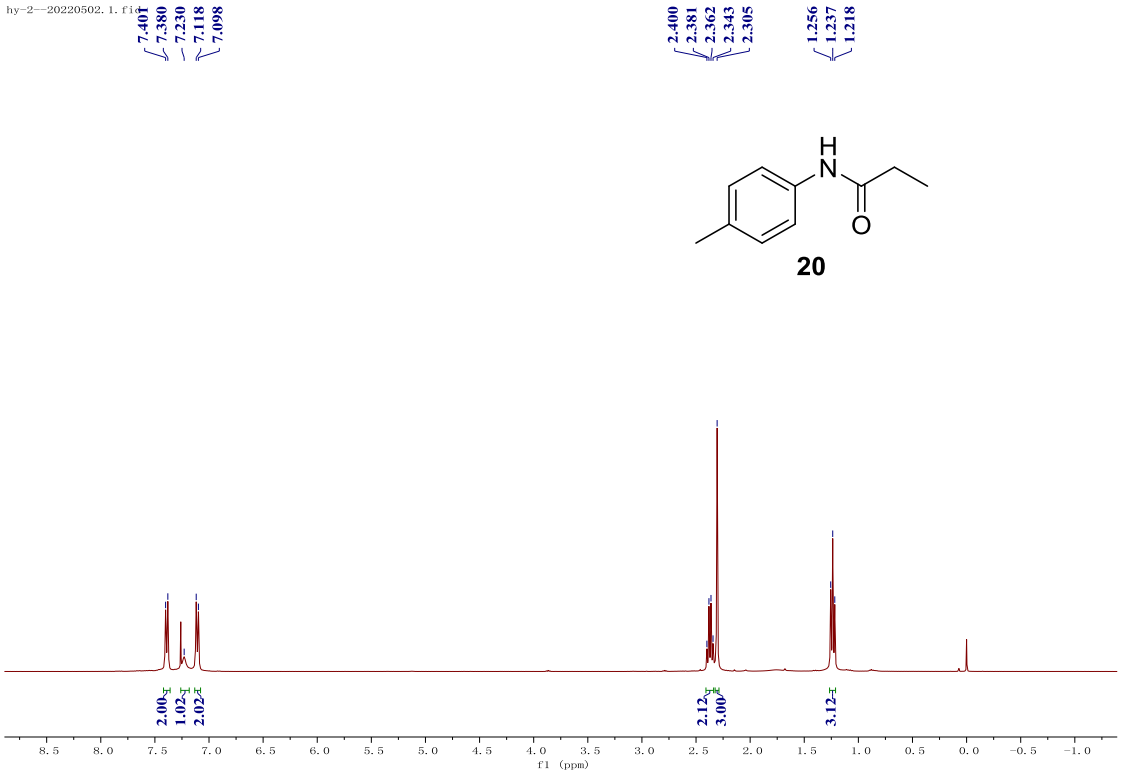
^{1}H NMR (400MHz, $CDCl_3$) spectrum of product 18



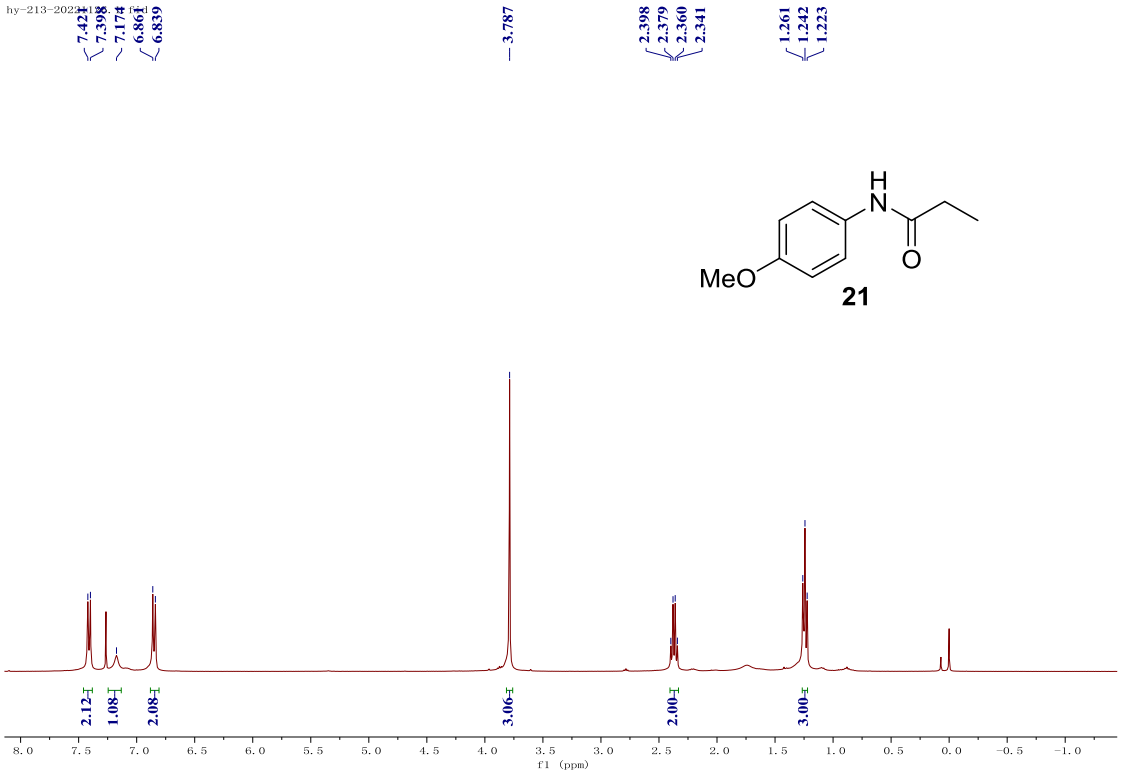
^{1}H NMR (400MHz, $CDCl_3$) spectrum of product 19



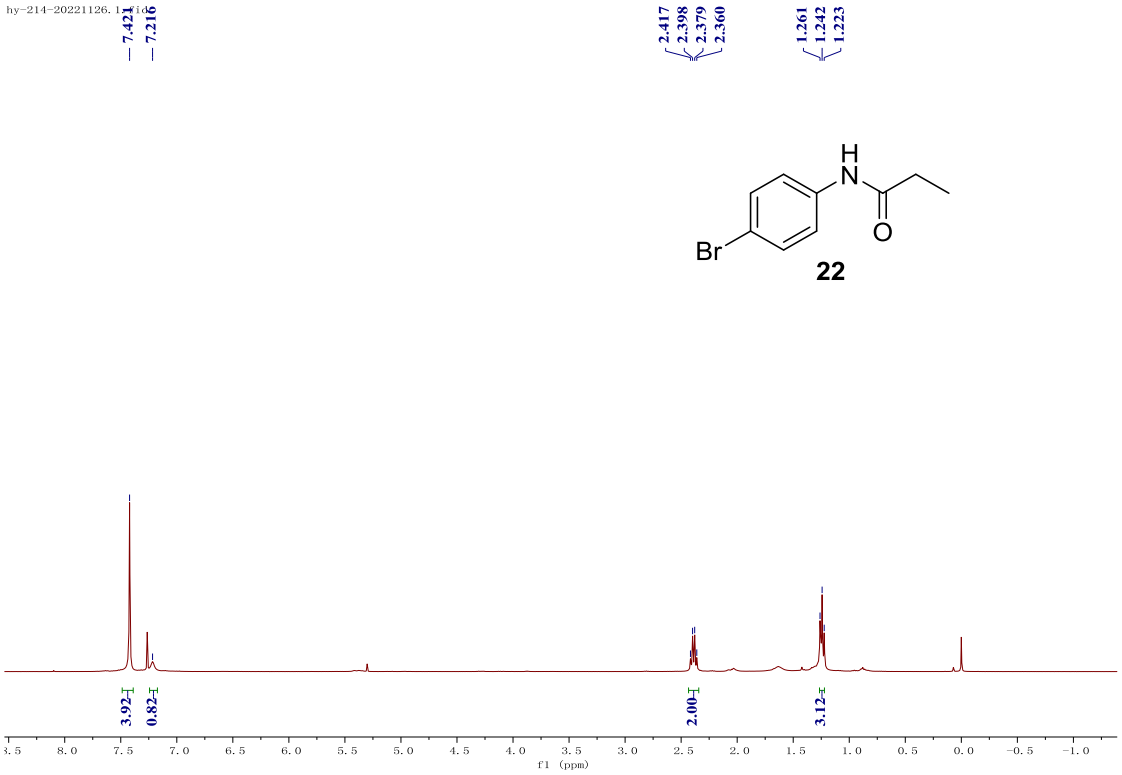
^{1}H NMR (400MHz, $CDCl_3$) spectrum of product 20



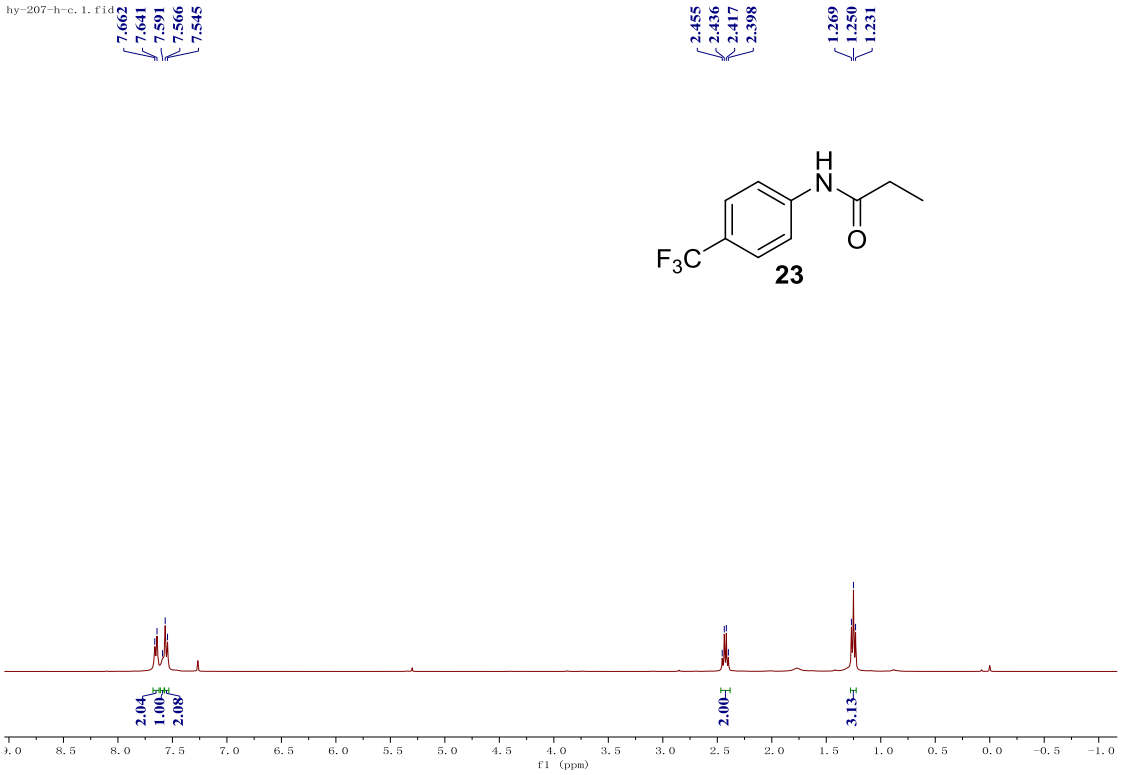
^{1}H NMR (400MHz, $CDCl_3$) spectrum of product 21



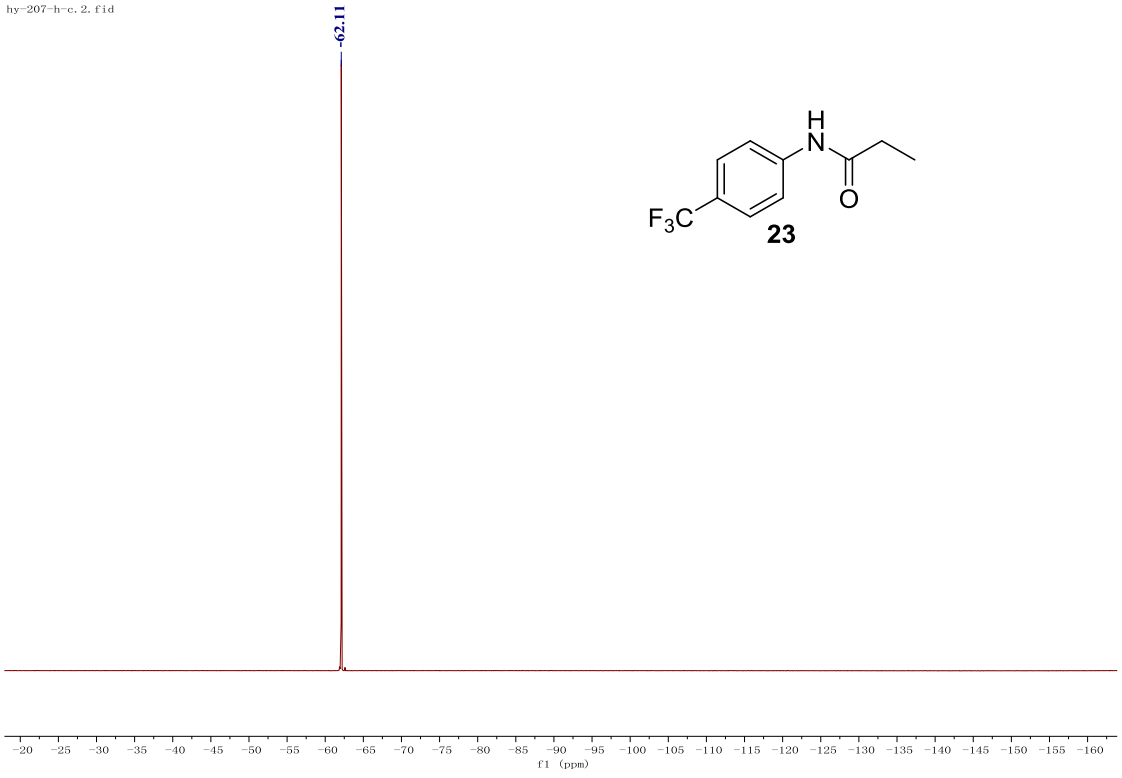
^{1}H NMR (400MHz, $CDCl_3$) spectrum of product 22



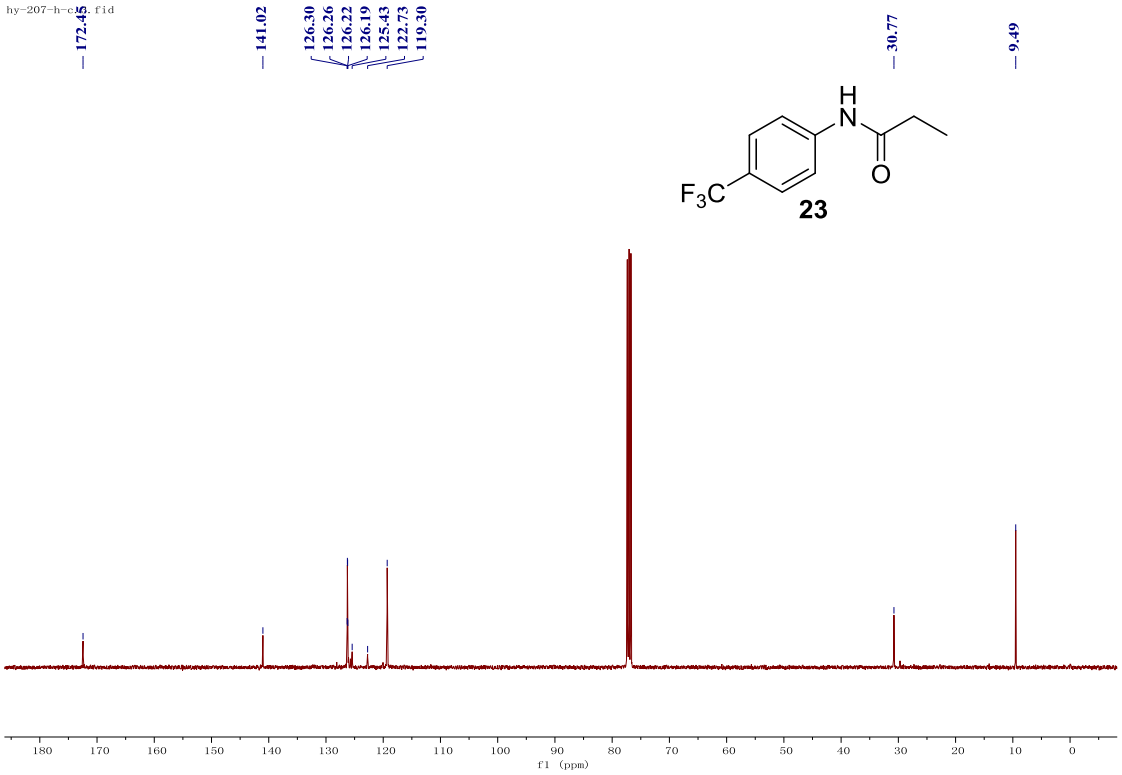
^{1}H NMR (400MHz, $CDCl_3$) spectrum of product 23



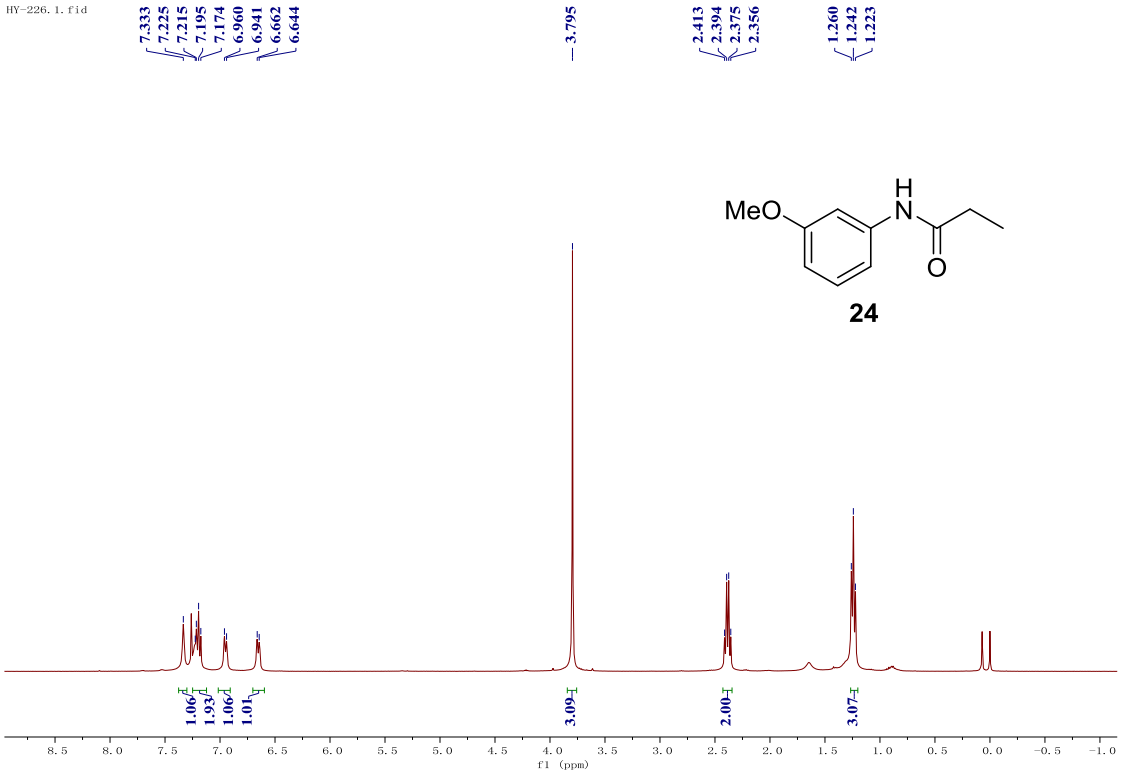
^{19}F NMR (376 MHz, $CDCl_3$) spectrum of product 23



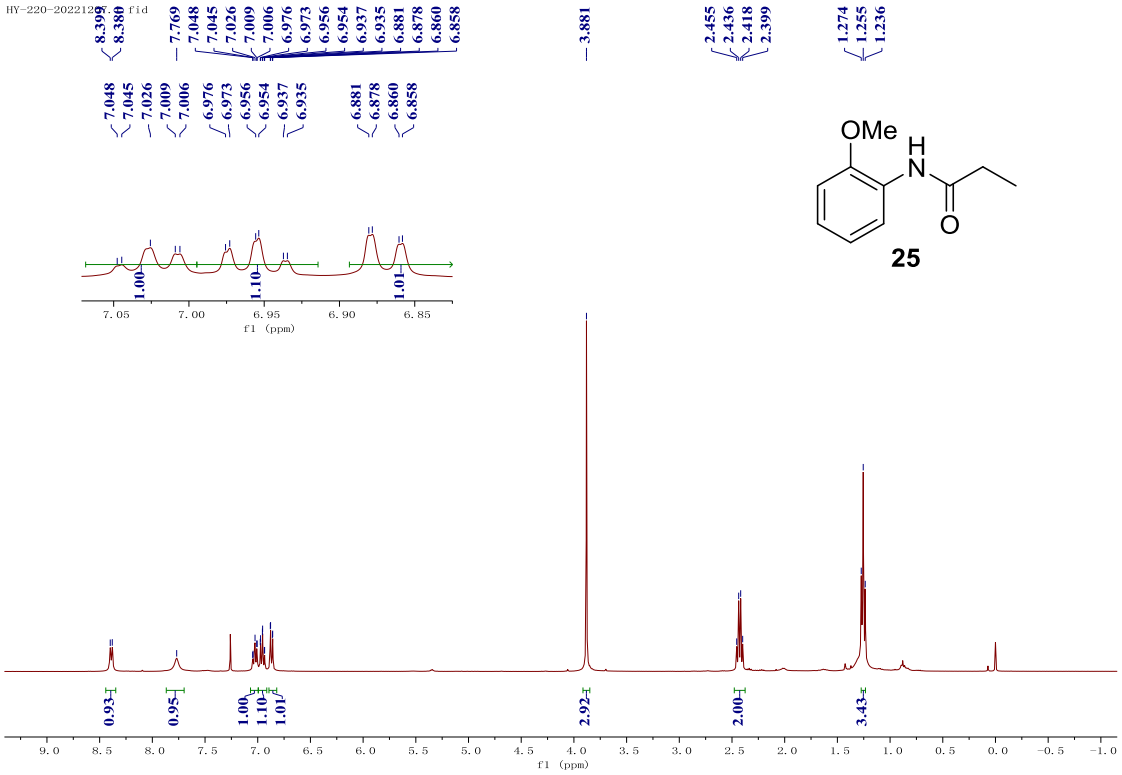
^{13}C NMR (100MHz, $CDCl_3$) spectrum of product 23



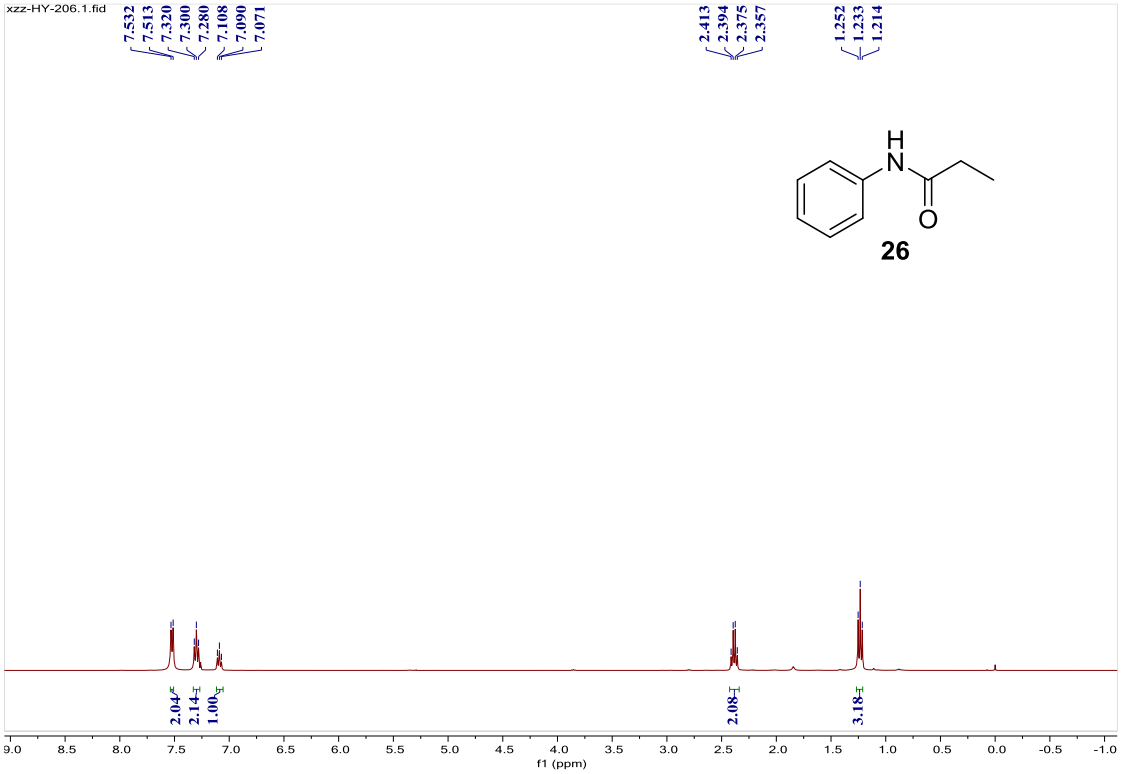
^{1}H NMR (400MHz, $CDCl_3$) spectrum of product 24



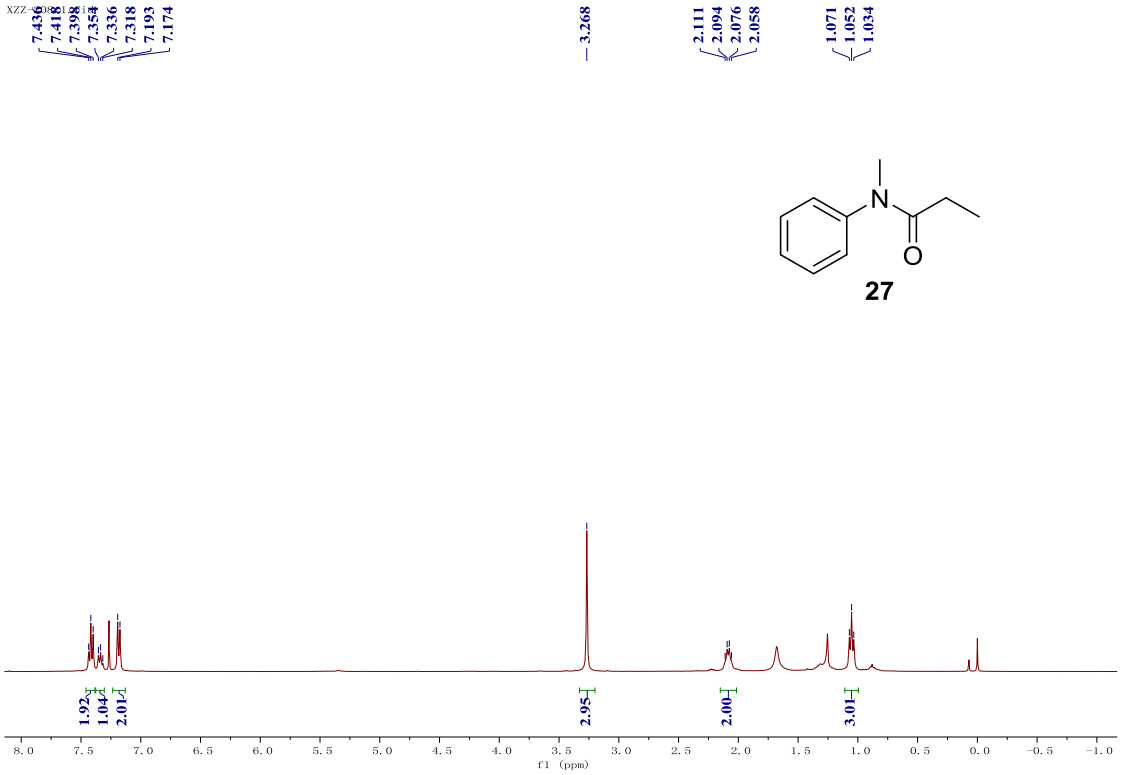
^{1}H NMR (400MHz, $CDCl_3$) spectrum of product 25



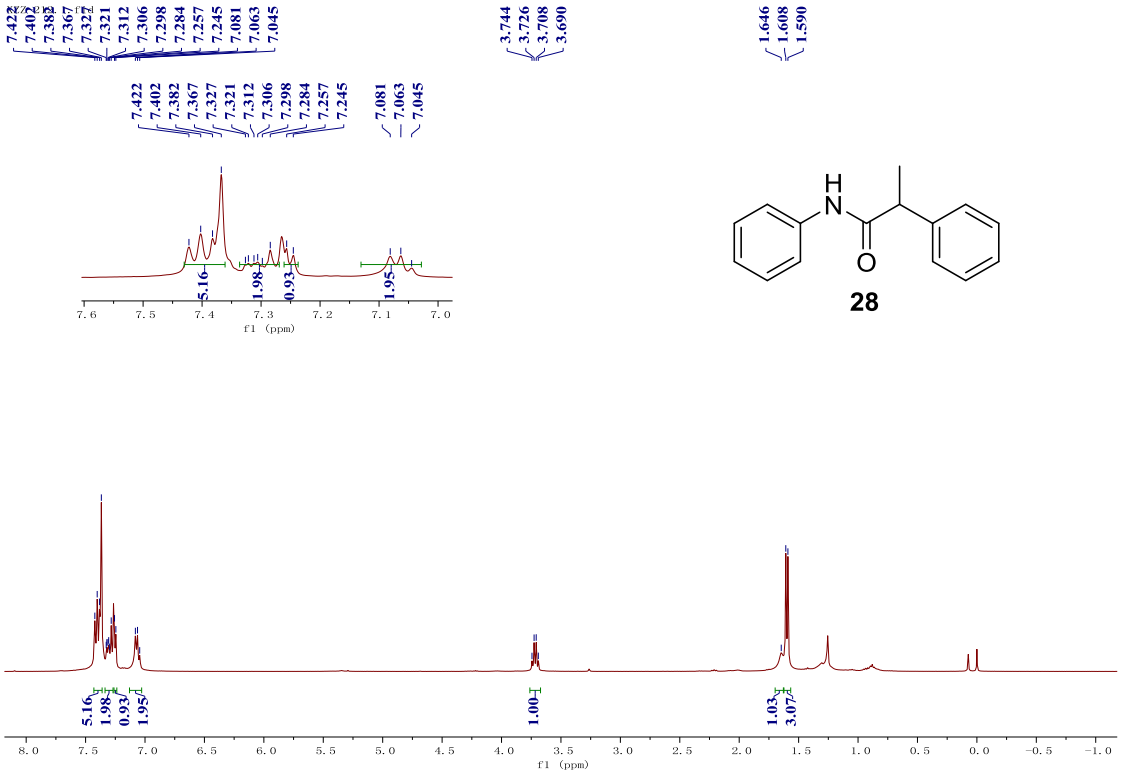
^{1}H NMR (400MHz, $CDCl_3$) spectrum of product 26



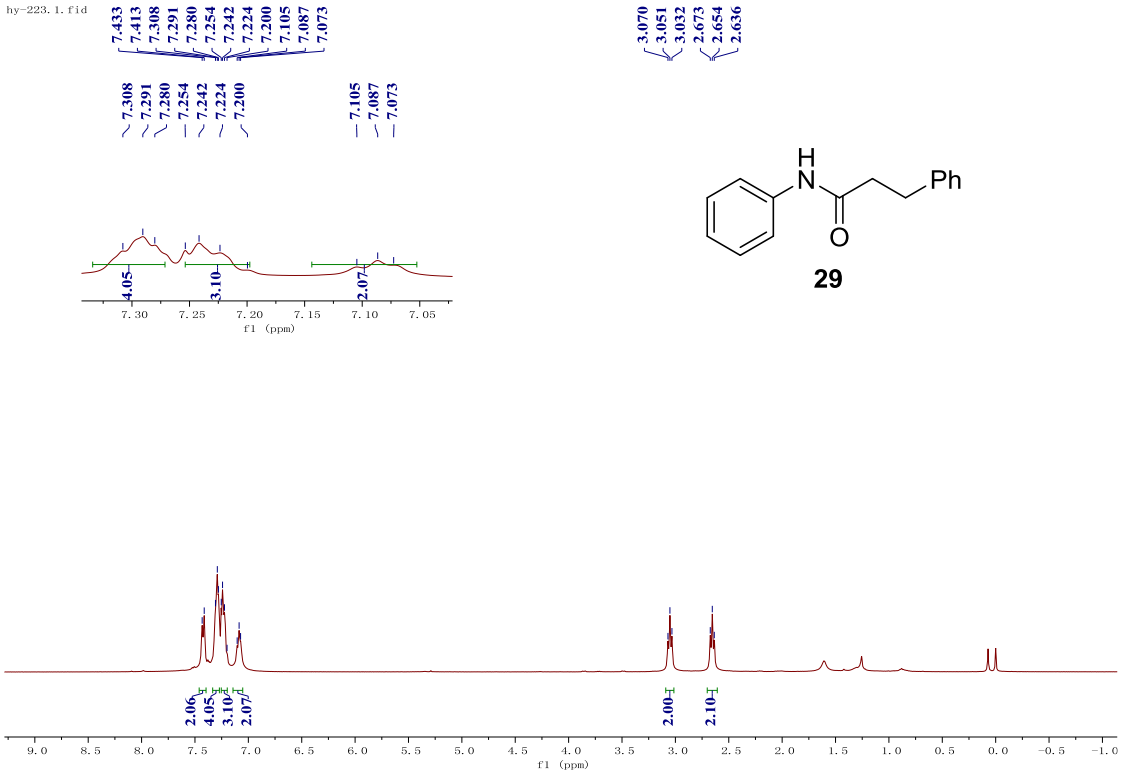
^{1}H NMR (400MHz, $CDCl_3$) spectrum of product 27



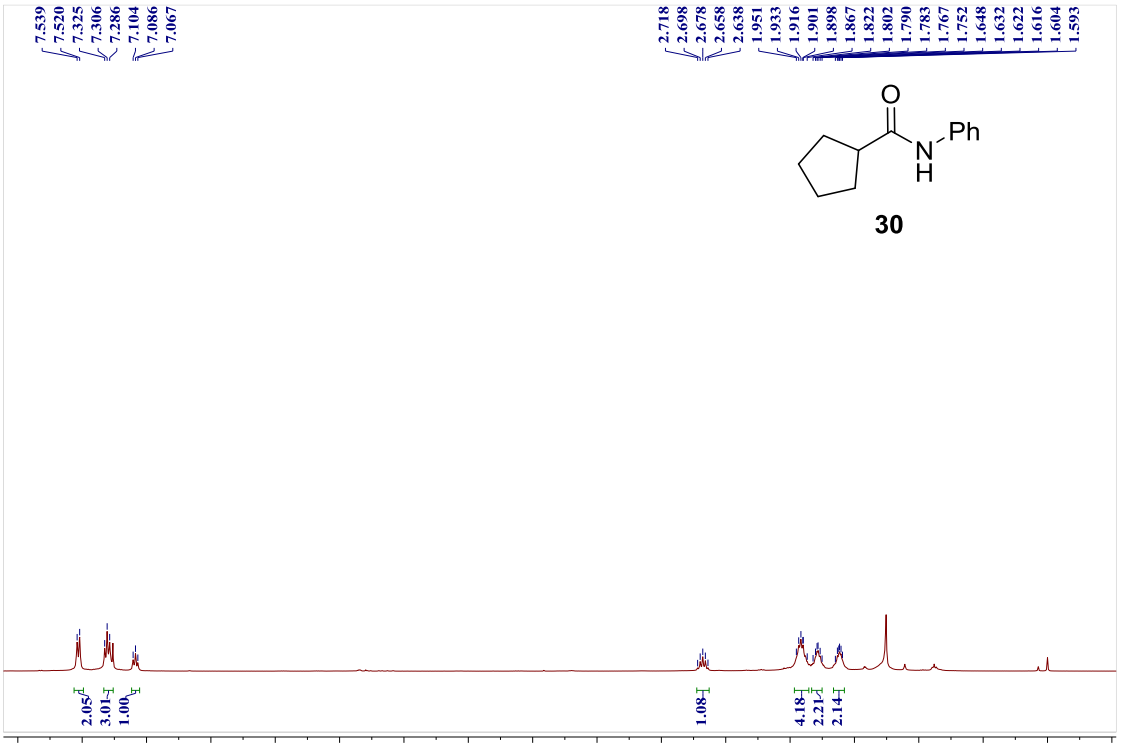
^{1}H NMR (400MHz, $CDCl_3$) spectrum of product 28



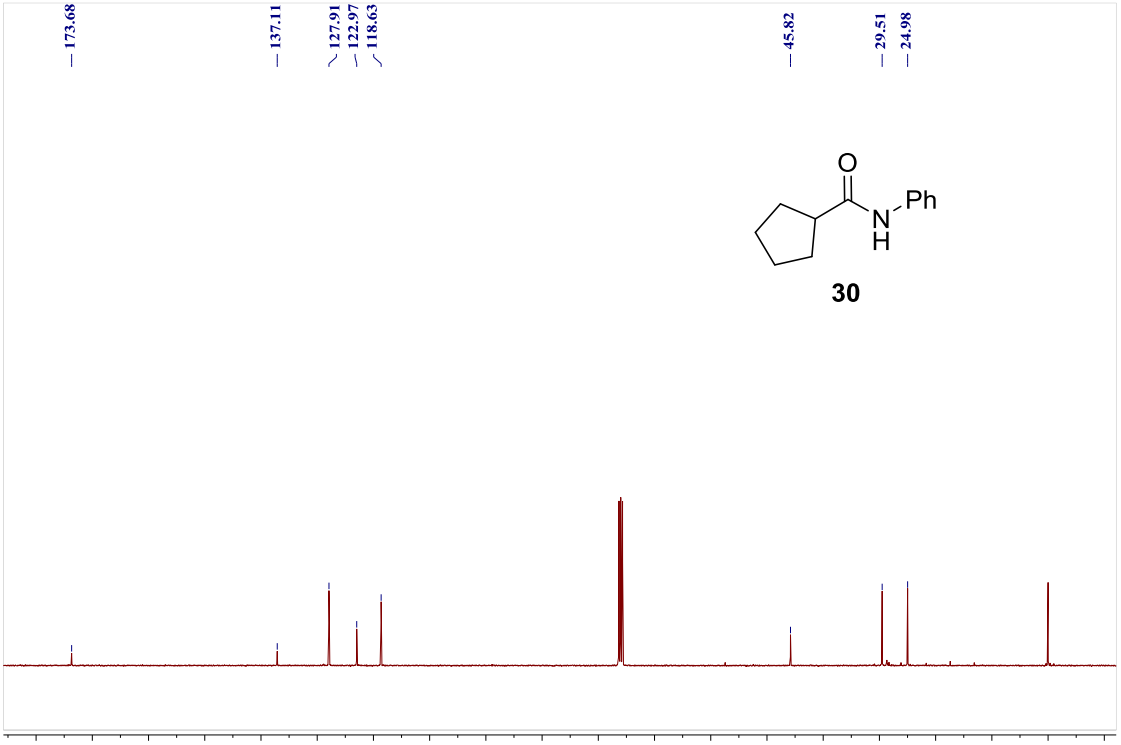
^{1}H NMR (400MHz, $CDCl_3$) spectrum of product 29



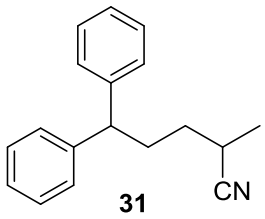
^{1}H NMR (400MHz, $CDCl_3$) spectrum of product 30



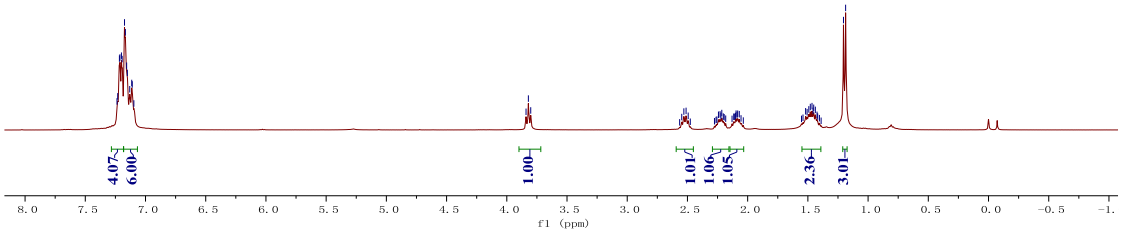
^{13}C NMR (100MHz, $CDCl_3$) spectrum of product 30



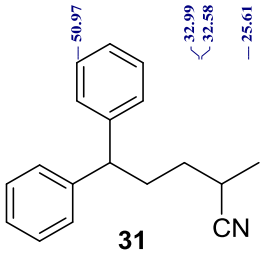
^{1}H NMR (400MHz, $CDCl_3$) spectrum of product 31



31



^{13}C NMR (100MHz, $CDCl_3$) spectrum of product 31



31