Supplementary Information

Iodoarene-directed photoredox β-C(sp^3)-H arylation of 1-(*o*-iodoaryl)alkan-1-ones with cyanoarenes via halogen atom transfer and hydrogen atom transfer

Liang Zeng,[ab†] Chong-Hui Xu,[a†] Xiu-Yuan Zou,[b] Qing Sun,*[b] Ming Hu,*[ab] Xuan-Hui Ouyang,[b] De-Liang He,*[a] and Jin-Heng Li*[acde]

[a.] State Key Laboratory of Chemo/Biosensing and Chemometrics, Hunan University, Changsha 410082, China. E-mail: huming0731@163.com, delianghe@hnu.edu.cn and jhli@hnu.edu.cn

[b.] Key Laboratory of Jiangxi Province for Persistent Pollutants Control and Resources Recycle, Nanchang Hangkong University, Nanchang 330063, China. E-mail: sunqing@nchu.edu.cn

[c.] State Key Laboratory Base of Eco-Chemical Engineering, College of Chemical Engineering, Qingdao University of Science and Technology, Qingdao 266042, China.

[d.] State Key Laboratory of Applied Organic Chemistry, Lanzhou University, Lanzhou 730000, China.

[e.] School of Chemistry and Chemical Engineering, Henan Normal University, Xinxiang, Henan 475004, China.

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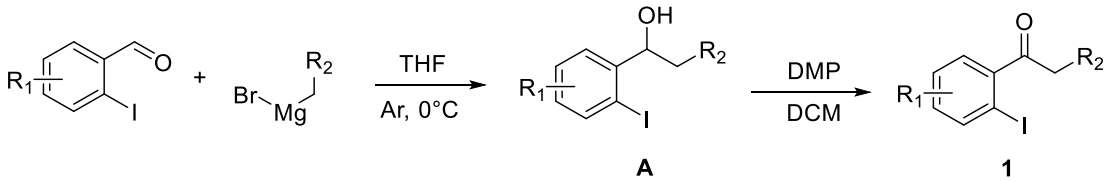
(A) General Experimental Procedures

(a) General Information:

^{1}H NMR, ^{13}C NMR and ^{19}F NMR spectra were recorded on a Bruker 400, 500 MHz advance spectrometer at room temperature in $CDCl_3$ with tetramethylsilane as internal standard. High-resolution mass spectra (HRMS) was recorded on an electrospray ionization (ESI) apparatus using time-of-flight (TOF) mass spectrometry. All products were identified by ^{1}H and ^{13}C NMR, HRMS; High-resolution mass spectra (HRMS) were recorded on an electrospray ionization (ESI) apparatus using time-of-flight (TOF) mass spectrometry; Cyclic voltammograms were obtained on a CHI 605E potentiostat.

Unless otherwise noted, all reactions were carried out using standard Schlenk techniques. Column chromatography was performed on silica gel (300-400 mesh) using petroleum ether/ethyl acetate. The light source were used 36W Blue LEDs (manufacturer: liang yuan lighting, model: LY-PD001, wavelength range: 450-460 nm, λ max = 455 nm), with wrap in foil, less than 5cm from the light source to the irradiation vessel. Unless otherwise noted, all reactions were carried out using standard Schlenk techniques, and the starting materials and solvents were commercially available and were used without further purification.

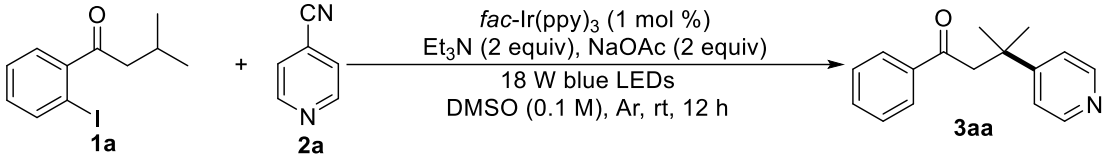
(b) General Procedure for Synthesis of 1-(o-iodoaryl)alkan-1-ones (1)[1-2]:



Following a modified literature procedure[1], to a flame-dried three-neck flask were added 2-Iodobenzaldehyde (50 mmol) and THF (50 mL), cool to 0 ℃ under a nitrogen atmosphere, then corresponding grignard reagent (1.5 equiv) added in dropwise, the resulting mixture was stirred at this temperature for 1.5 – 3 h, and quenched with a saturated aqueous solution of NH_4Cl. After extraction with ethyl acetate, the organic layer was washed with brine (50 mL) and dried over anhydrous Na_2SO_4, purified by column chromatography on silica gel to give desired secondary benzylic alcohol **A**. To

a solution of **A** (1.0 equiv) in DCM (0.1 M) was added DMP (1.5 equiv) under 0 ℃, then the resulted reaction mixture was stirred at room temperature. Upon completion, the reaction mixture was filtered and washed with EtOAc. The resulting mixture was concentrated, and the residue was purified by flash column chromatography on silica gel (eluted with petroleumether/ethyl acetate) to afford 1-(*o*-iodoaryl)alkan-1-ones **1**.

(c) General Procedure for Photoredox Remote C(sp^3)-H Arylation with 1-(o-iodoaryl)alkan-1-ones (1) and 4-Cyanopyridine (2) by Visible Light Photoreductive Catalysis



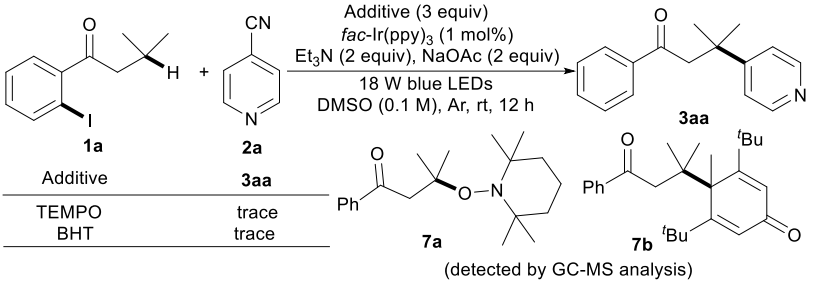
To a Schlenk tube were added **1a** (0.20 mmol), **2a** (0.20 mmol, 1.0 equiv), *fac*-Ir(ppy)$_3$ (1 mol %), Et$_3$N (2 equiv), NaOAc (2 equiv), DMSO (2 mL, 0.1 M), Then the tube was charged with argon three times, and was stirred irradiated with a 18 W blue LED lamp (at approximately 5.0 cm away from the light source) with cooled by a fan at room temperature for 12 h until complete consumption of starting material as monitored by TLC and/or GC-MS analysis. After the reaction was finished, the reaction mixture was concentrated in vacuum, diluted in diethyl ether, and washed with saturated brine. The combined organic extracts were dried over Na_2SO_4 and concentrated in vacuum. The resulting residue was purified by silica gel column chromatography (PE/EA = 10:1: to 4:1) to provide **3aa** in 71% isolated yield.

(d) Typical Experimental Procedure for up to 1mmol of 1-(o-iodoaryl)alkan-1-ones (1):

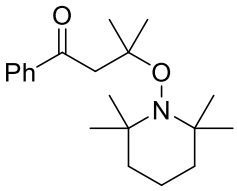
To a Schlenk tube were added **1a** (1 mmol), **2a** (1 mmol, 1 equiv), *fac*-Ir(ppy)$_3$ (1 mol %), Et$_3$N (2 equiv), NaOAc (2 equiv), DMSO (2 mL, 0.1 M), Then the tube was charged with argon three times, and was stirred irradiated with two 18 W blue LED

lamp (at approximately 5.0 cm away from the light source) with cooled by a fan at room temperature for 24 h until complete consumption of starting material as monitored by TLC and/or GC-MS analysis. After the reaction was finished, the reaction mixture was concentrated in vacuum, diluted in diethyl ether, and washed with saturated brine. The combined organic extracts were dried over Na_2SO_4 and concentrated in vacuum. The resulting residue was purified by silica gel column chromatography (PE/EA = 10:1: to 4:1) to provide **3aa** (62% yield; 148.2 mg).

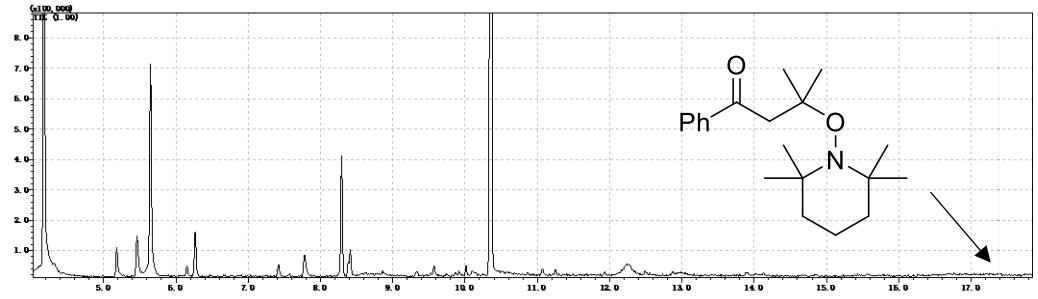
(e) Control Experiments

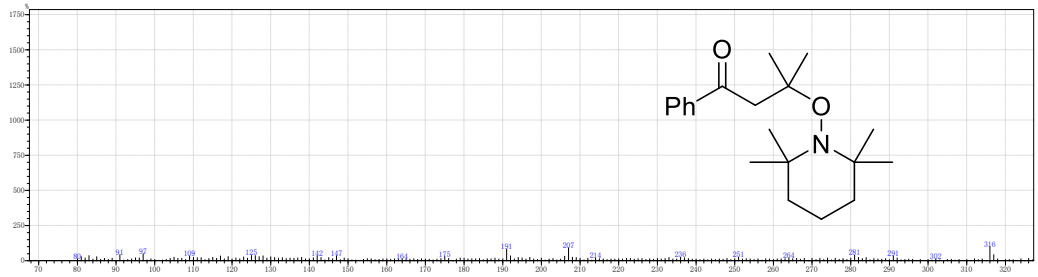


To a Schlenk tube were added **1a** (0.20 mmol), **2a** (0.20 mmol, 1.0 equiv), *fac*-$Ir(ppy)_3$ (1 mol %), Et_3N (2 equiv), NaOAc (2 equiv), additive TEMPO or BHT (3equiv), DMSO (2 mL, 0.1 M), Then the tube was charged with argon three times, and was stirred irradiated with a 18 W blue LED lamp (at approximately 5.0 cm away from the light source) with cooled by a fan at room temperature for 12 h. The reaction mixture was concentrated in vacuum, diluted in diethyl ether, and washed with saturated brine. The combined organic extracts were dried over Na_2SO_4 and concentrated in vacuum. No desired product **3aa** was observed, and the product **7a** (m/z = 317) and **7b** (m/z = 380.3) were detected by GC-MS analysis of the crude mixture.



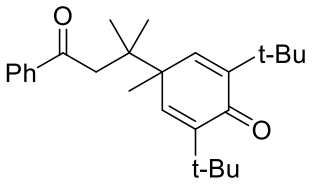
Chemical Formula: $C_{20}H_{31}NO_2$
Molecular Weight: 317



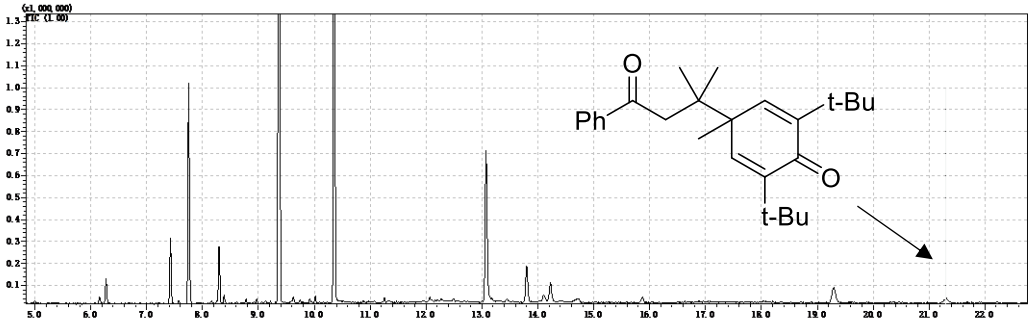


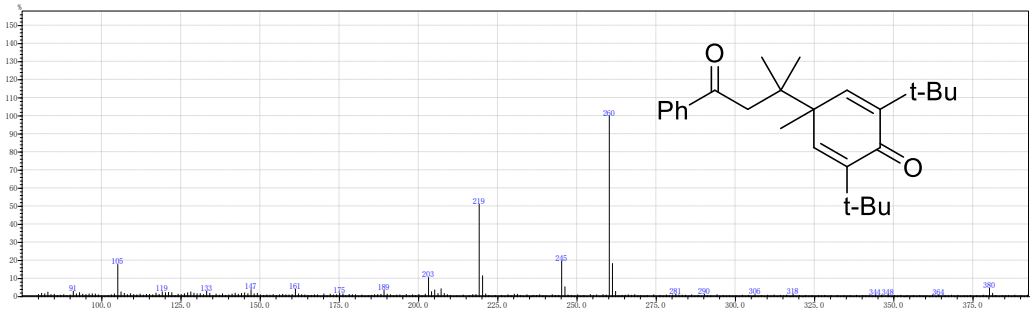
[MS Spectrum]
# of Peaks 448
Raw Spectrum 17.385 (scan : 2678)
Background No Background Spectrum
Base Peak m/z 316.00 (Inten : 348)
Event# 1
m/z Absolute Intensity Relative Intensity

296.00	33	9.48	307.00	16	4.60	318.00	46	13.22
297.00	8	2.30	308.00	29	8.33	320.00	29	8.33
298.00	29	8.33	310.00	29	8.33	321.00	29	8.33
300.00	31	8.91	311.00	6	1.72	322.00	24	6.90
301.00	19	5.46	312.00	47	13.51	324.00	47	13.51
302.00	47	13.51	313.00	26	7.47	325.00	6	1.72
303.00	22	6.32	314.00	44	12.64	326.00	57	16.38
304.00	10	2.87	315.00	5	1.44	327.00	21	6.03
305.00	29	8.33	316.00	348	100.00	328.00	6	1.72
306.00	34	9.77	**317.00**	**148**	**42.53**	329.00	11	



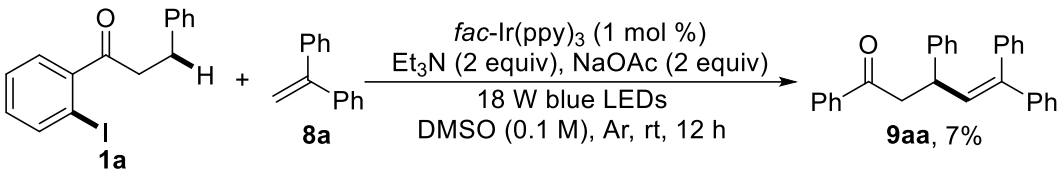
Chemical Formula: $C_{26}H_{36}O_2$
Molecular Weight: 380





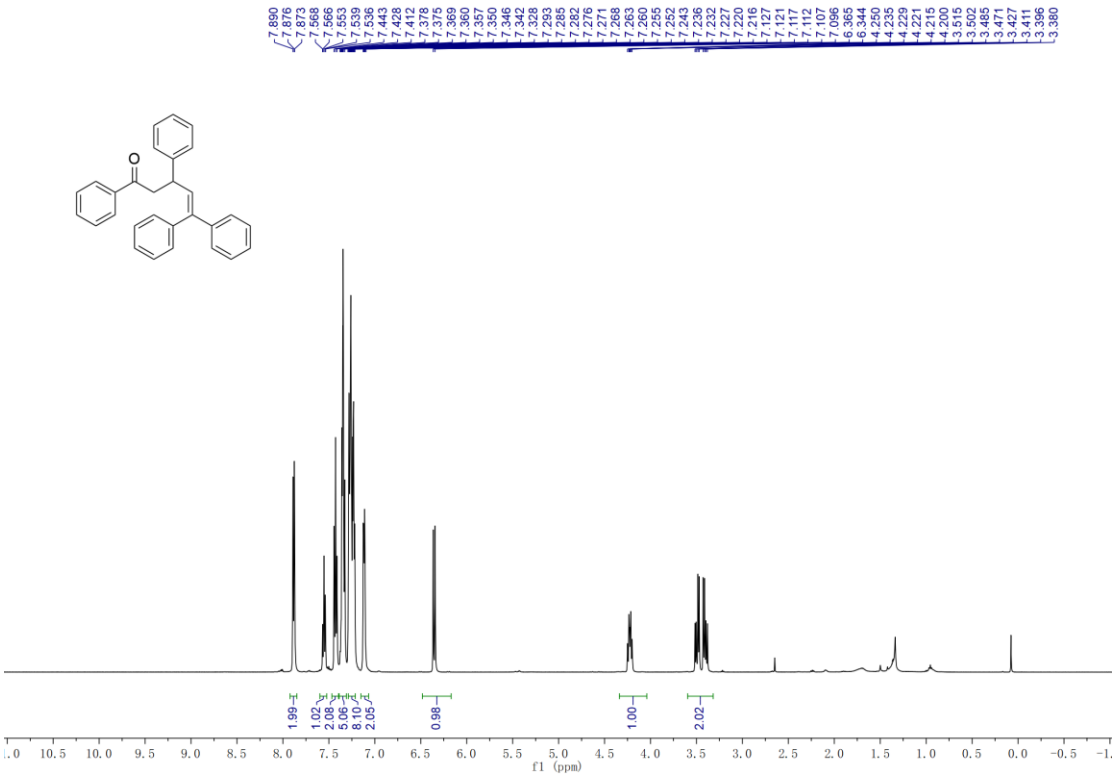
[MS Spectrum]
# of Peaks 511
Raw Spectrum 21.305 (scan : 3462)
Background No Background Spectrum
Base Peak m/z 260.20 (Inten : 6,890)
Event# 1

m/z	Absolute Intensity	Relative Intensity	m/z	Absolute Intensity	Relative Intensity	m/z	Absolute Intensity	Relative Intensity
80.00	82	1.19	88.00	78	1.13	262.20	199	2.89
81.00	121	1.76	90.00	62	0.90	266.20	70	1.02
82.00	111	1.61	256.20	65	0.94	**380.20**	**324**	**4.70**
83.00	170	2.47	258.20	76	1.10	381.20	130	1.89
84.00	81	1.18	259.20	62	0.90	**382.20**	**46**	**0.67**
85.00	89	1.29	260.20	6890	100.00	383.20	16	0.23
87.00	57	0.83	261.20	1263	18.33	384.20	42	0.61

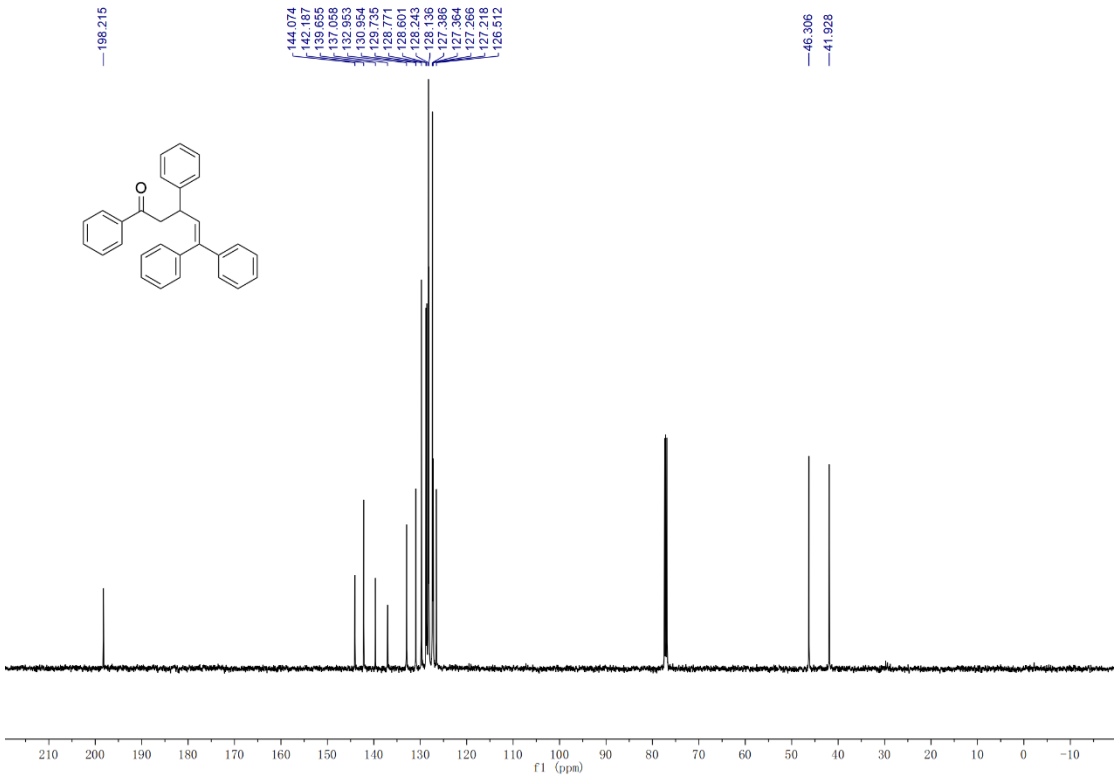


To a Schlenk tube were added **1a** (0.20 mmol), **2a** (0.20 mmol, 1.0 equiv), *fac*-$Ir(ppy)_3$ (1 mol %), Et_3N (2 equiv), NaOAc (2 equiv), and DMSO (2 mL, 0.1 M), Then the tube was charged with argon three times, and was irradiated with a 18 W blue LED lamp (at approximately 5.0 cm away from the light source) with cooled by a fan at room temperature for the indicated time (about 12 h) until complete consumption of starting material as monitored by TLC. The reaction mixture was concentrated in vacuum, diluted in diethyl ether, and washed with saturated brine. The combined organic extracts were dried over Na_2SO_4 and concentrated in vacuum. The resulting residue was purified by silica gel column chromatography (PE/EA = 30:1) to provide **9aa** in 7% isolated yield.

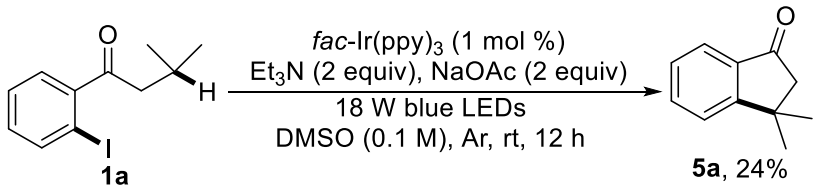
Product **9aa**: yellow oil; ^{1}H NMR (500 MHz, Chloroform-*d*) δ (ppm) 7.89 - 7.87 (m, 2H), 7.55 (t, *J* = 7.5 Hz, 1H), 7.43 (t, *J* = 7.5 Hz, 2H), 7.38 - 7.33 (m, 5H), 7.29 - 7.22 (m, 8H), 7.13 - 7.09 (m, 2H), 6.35 (d, *J* = 10.5 Hz, 1H), 4.25 - 4.20 (m, 1H), 3.52 - 3.38 (m, 2H); ^{13}C NMR (125 MHz, Chloroform-*d*) δ (ppm) 198.22, 144.07, 142.19, 139.66, 137.06, 132.95, 130.95, 129.74, 128.77, 128.60, 128.24, 128.14, 127.39, 127.36, 127.27, 127.22, 126.51, 46.31, 41.93.



^{1}H NMR (500 MHz, $CDCl_3$) of **9aa**

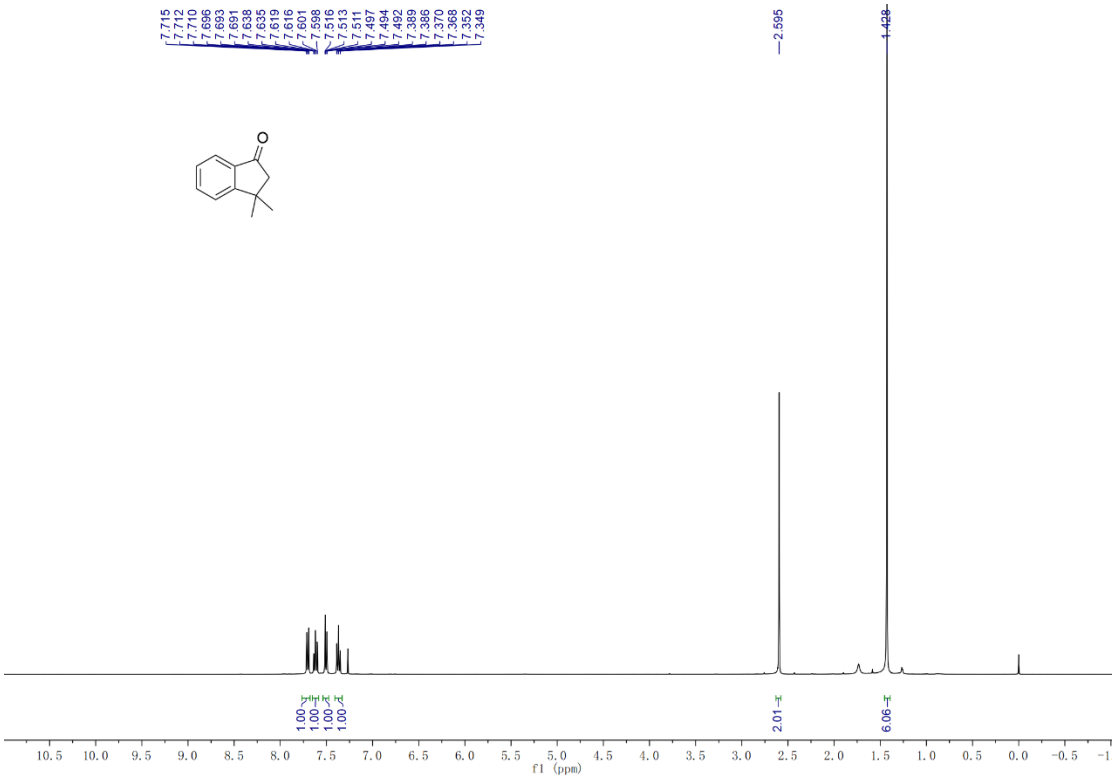


^{13}C NMR (125 MHz, $CDCl_3$) of **9aa**

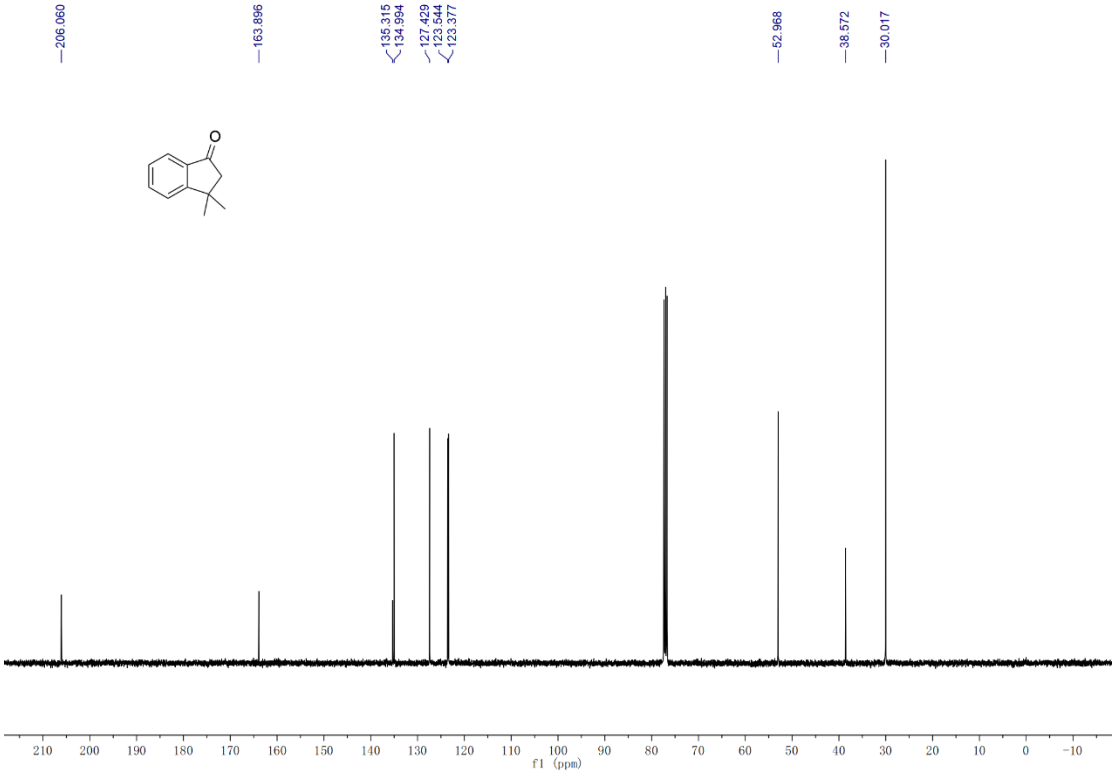


To a Schlenk tube were added **1a** (0.20 mmol), *fac*-Ir(ppy)$_3$ (1 mol %), Et_3N (2 equiv), NaOAc (2 equiv), DMSO (2 mL, 0.1 M), Then the tube was charged with argon three times, and was stirred irradiated with a 18 W blue LED lamp (at approximately 5.0 cm away from the light source) with cooled by a fan at room temperature for 12 h. The reaction mixture was concentrated in vacuum, diluted in diethyl ether, and washed with saturated brine. The combined organic extracts were dried over Na_2SO_4 and concentrated in vacuum. The resulting residue was purified by silica gel column chromatography (PE/EA = 20:1) to provide **5a** in 24% isolated yield.

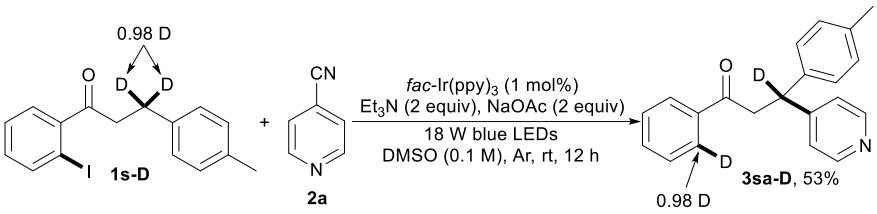
Product **5a**: colorless oil; ^{1}H NMR (400 MHz, Chloroform-*d*) δ (ppm) 7.70 (dt, *J* = 7.6, 1.0 Hz, 1H), 7.62 (td, *J* = 7.4, 1.3 Hz, 1H), 7.50 (dt, *J* = 7.8, 1.0 Hz, 1H), 7.37 (td, *J* = 7.4, 1.0 Hz, 1H), 2.60 (s, 2H), 1.43 (s, 6H); ^{13}C NMR (100 MHz, Chloroform-*d*) δ (ppm) 206.06, 163.90, 135.32, 134.99, 127.43, 123.54, 123.38, 52.97, 38.57, 30.



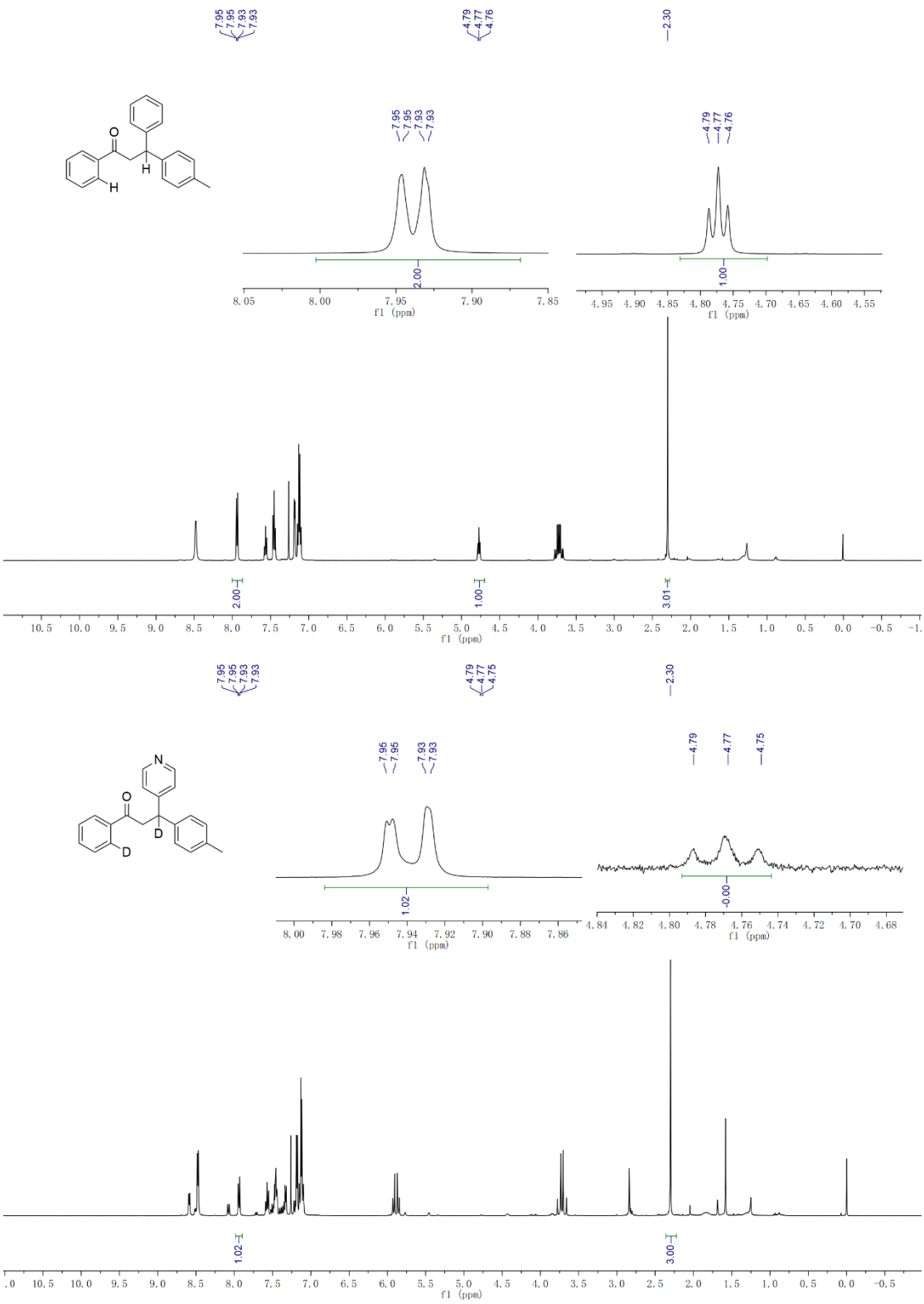
1H NMR (400 MHz, CDCl3) of **5a**



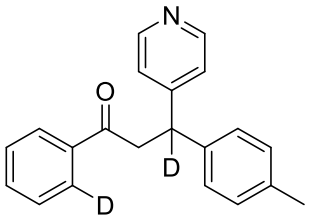
^{13}C NMR (100 MHz, $CDCl_3$) of **5a**



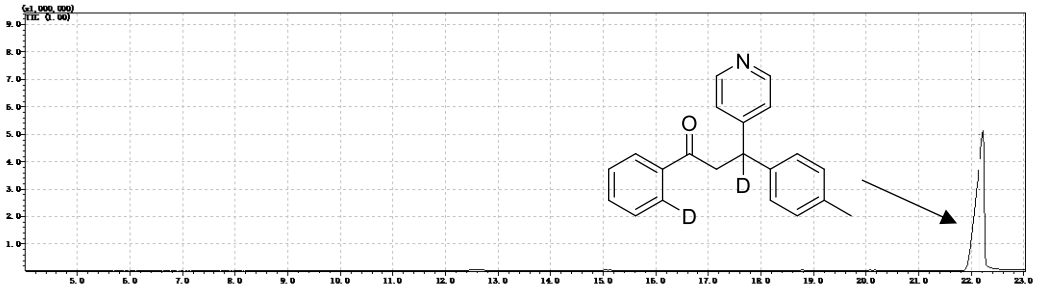
To a Schlenk tube were added **1s-D** (0.05 mmol), **2a** (0.05 mmol, 1.0 equiv), *fac*-$Ir(ppy)_3$ (1 mol %), Et_3N (2 equiv), NaOAc (2 equiv), DMSO (0.5 mL, 0.1 M), Then the tube was charged with argon three times, and was stirred irradiated with a 18 W blue LED lamp (at approximately 5.0 cm away from the light source) with cooled by a fan at room temperature for 12 h until complete consumption of starting material as monitored by TLC and/or GC-MS analysis. After the reaction was finished, the reaction mixture was concentrated in vacuum, diluted in diethyl ether, and washed with saturated brine. The combined organic extracts were dried over Na_2SO_4 and concentrated in vacuum. The resulting residue was purified by silica gel column chromatography to provide product **3sa-D** with 53% yield.

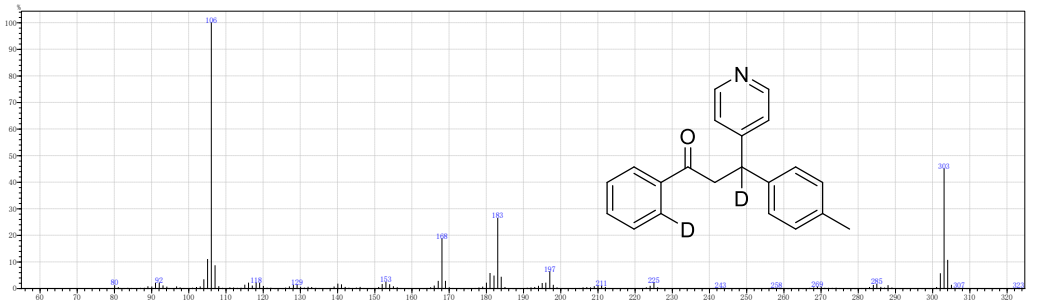


^{1}H-NMR plot of **3sa** vs **3sa**-D



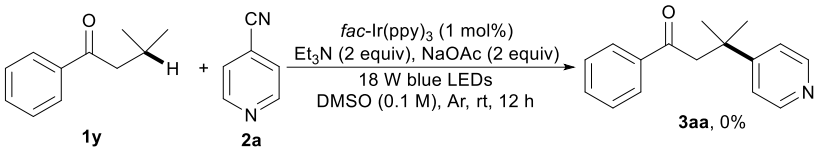
Chemical Formula: $C_{21}H_{17}D_2NO$
Molecular Weight: 303





[MS Spectrum]
# of Peaks 420
Raw Spectrum 22.150 (scan : 3631)
Background No Background Spectrum
Base Peak m/z 106.05 (Inten : 1,196,675)
Event# 1
m/z Absolute Intensity Relative Intensity

293.00	110	0.01	302.05	67146	5.61	312.10	54	0.00
294.00	30	0.00	**303.05**	**539404**	**45.08**	313.10	110	0.01
295.00	148	0.01	304.05	127545	10.66	314.10	108	0.01
296.00	78	0.01	305.05	15337	1.28	315.10	95	0.01
297.00	98	0.01	306.05	1354	0.11	316.10	54	0.00
298.00	84	0.01	307.10	137	0.01	317.10	74	0.01
299.00	415	0.03	309.10	82	0.01	318.10	16	0.00
300.05	677	0.06	310.10	39	0.00	319.10	68	0.01
301.05	5559	0.46	311.10	63	0.01	320.10	10	0.00



To a Schlenk tube were added **1a** (0.20 mmol), **2a** (0.20 mmol, 1.0 equiv), *fac*-$Ir(ppy)_3$ (1 mol %), Et_3N (2 equiv), NaOAc (2 equiv), additive TEMPO or BHT (3 equiv), DMSO (2 mL, 0.1 M), Then the tube was charged with argon three times, and was stirred irradiated with a 18 W blue LED lamp (at approximately 5.0 cm away from the light source) with cooled by a fan at room temperature for 12 h. The reaction mixture was concentrated in vacuum, diluted in diethyl ether, and washed with saturated brine. The combined organic extracts were dried over Na_2SO_4 and concentrated in vacuum. No desired product **3aa** was observed.

(f) Stern-Volmer Fluorescence Quenching Experiments

Fluorescence spectra samples for the quenching experiments were prepared in a glass cuvette with a septum screw cap. $Ir(ppy)_3$ was irradiated at 470 nm and the emission intensity at 515 nm was observed. In a typical experiment, the emission spectrum of a 1.0×10^{-5} M solution of $Ir(ppy)_3$ in DMSO was collected. In Figure S1, a stock solution of Et_3N (10.1 mg, 0.1 mmol) in 1 mL of DMSO was prepared. Then, different amounts of this stock solution were added to a solution of the photocatalyst in DMSO (1.0×10^{-5} M). The obviously sharp decrease of $Ir(ppy)_3$ luminescence was observed, suggesting that the mechanism might operate via a canonical photoredox cycle consisting of a reductive quenching with Et_3N.

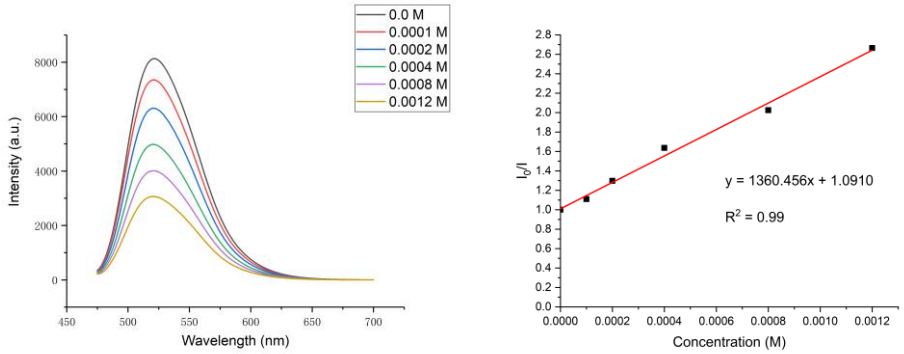


Figure S1. Stern–Volmer fluorescence quenching experiments of $Ir(ppy)_3$ with Et_3N.

In Figure S2, a stock solution of 1-(2-iodophenyl)-3-methylbutan-1-one **1a** (28.8 mg, 0.1 mmol) in 1 mL of DMSO was prepared. Then, different amounts of this stock solution were added to a solution of the photocatalyst in DMSO (1.0×10^{-5} M). The results show that slight decrease of $Ir(ppy)_3$ luminescence was observed.

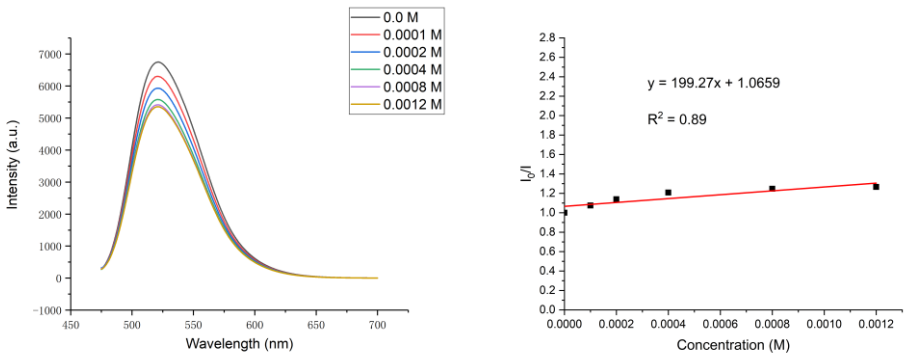


Figure S2. Stern–Volmer fluorescence quenching experiments of $Ir(ppy)_3$ with **1a**.

In Figure S3, a stock solution of cyanopyridine **2a** (10.4 mg, 0.1 mmol) in 1 mL of DMSO was prepared. Then, different amounts of this stock solution were added to a solution of the photocatalyst in DMSO (1.0×10^{-5} M). The results show that slight decrease of $Ir(ppy)_3$ luminescence was observed.

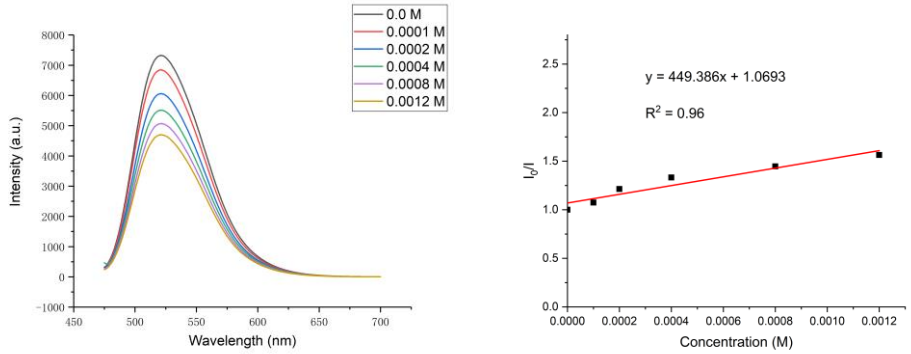


Figure S3. Stern–Volmer fluorescence quenching experiments of $Ir(ppy)_3$ with 4-cyanopyridine **2a**.

(g) Light on-off Experiments

Three parallel reactions were performed between **1a** (0.20 mmol), **2a** (0.20 mmol) according to the General Procedure. The resulting residue was purfied by silica gel column chromatography (PE/EA = 10:1 to 4:1) to afford the **3aa**. The white area indicates the light irradiation, while the grey area indicates time in the dark. The results demonstrate that the visible light is crucial.

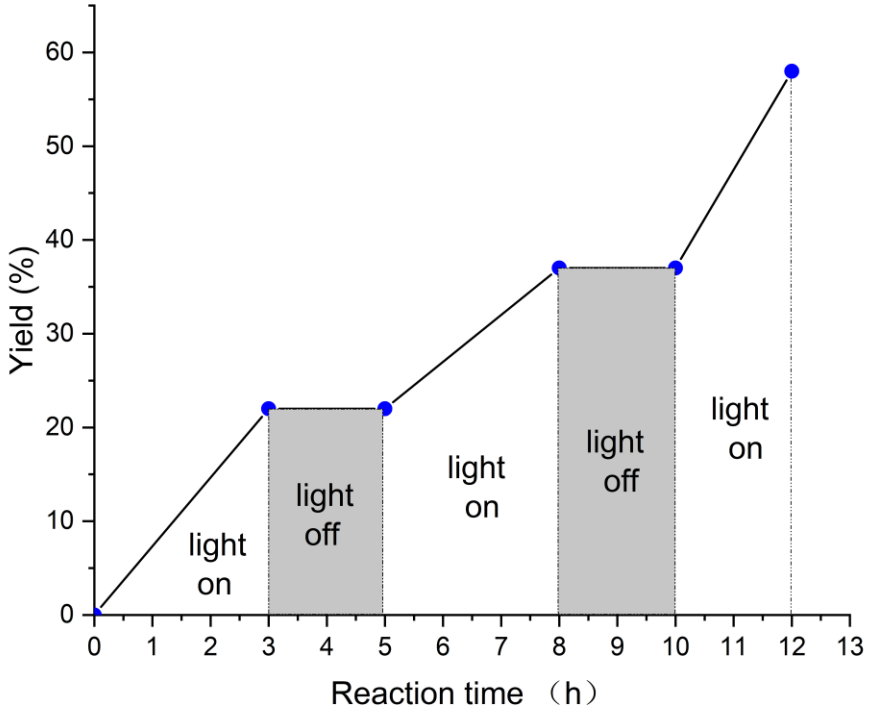
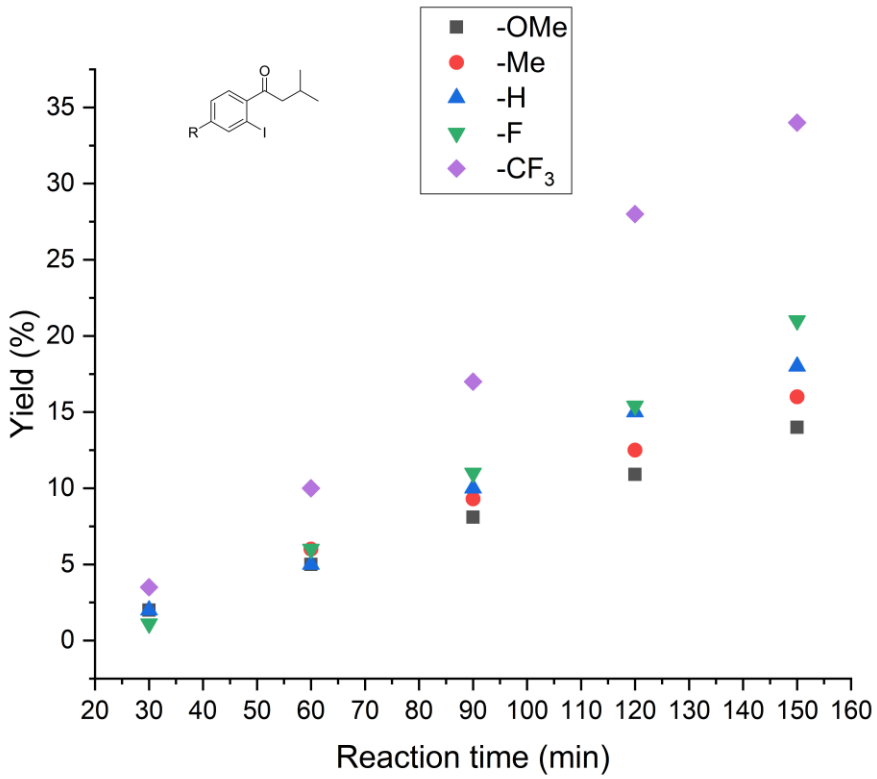


Figure S4: Light on-off experiments plot

(h) Hammett Studies of the Reaction (Substitution Effect of Iodobenzenes)

To a Schlenk tube were added **1** (0.20 mmol), **2a** (0.20 mmol, 1.0 equiv), *fac*-$Ir(ppy)_3$ (1 mol %), Et_3N (2 equiv), NaOAc (2 equiv), DMSO (2 mL, 0.1 M), Then the tube was charged with argon three times, and was stirred irradiated with a 18 W blue LED lamp (at approximately 5.0 cm away from the light source) with cooled by a fan at room temperature, five groups were carried out in parallel and stop the one of reaction every thirty minutes stared from thirty minutes. After that, the reaction system through simple filtration, wash with ethyl acetate (10 mL) and concentrated in vacuum, followed by addition of diphenylacetonitrile as an internal standard determine the yields. As the results shown in **Figure S5**, substituents on iodobenzenes have a significant impact on the reaction rate, and the a positive ρ value (0.53) in Hammett plot was given. These results suggest that there is a buildup of negative charge on the iodobenzene bone in the transition state.



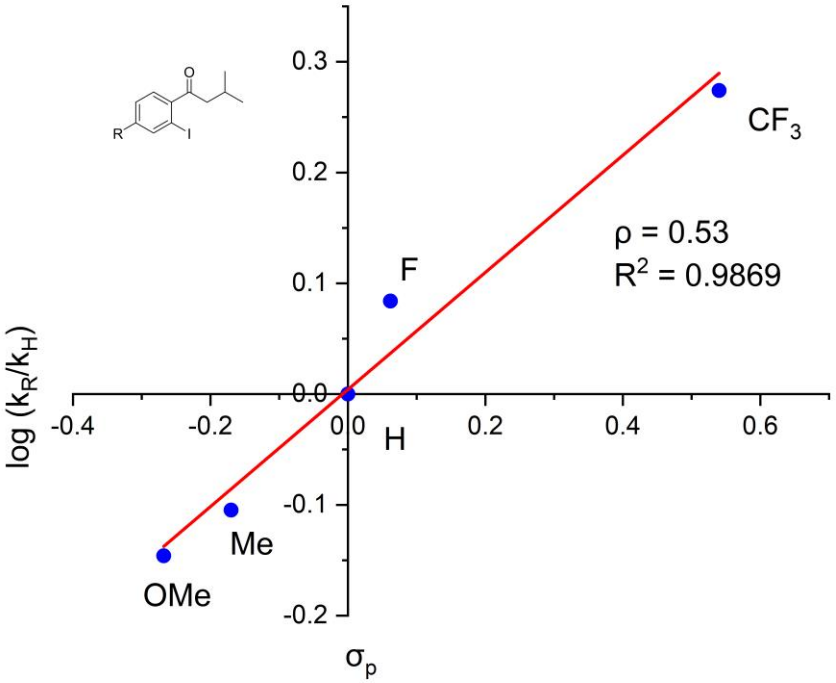


Figure S5. The electronic effect of **1** for the reaction. a) Time course of reaction; b) Hammett plot, $\log(k_R/k_H)$ vs σ.

(i) Cyclic Voltammograms

The cyclic voltammetry was carried out with a Shanghai Chenhua CHI 605E workstation. All CV measurements were conducted in MeCN against saturated calomel electrode (SCE) reference cell and 1 mM nBu_4NBF_4 supporting electrolyte. All samples should be bubbled with argon for 2 min before test. The scan rate was 100 mV/s.

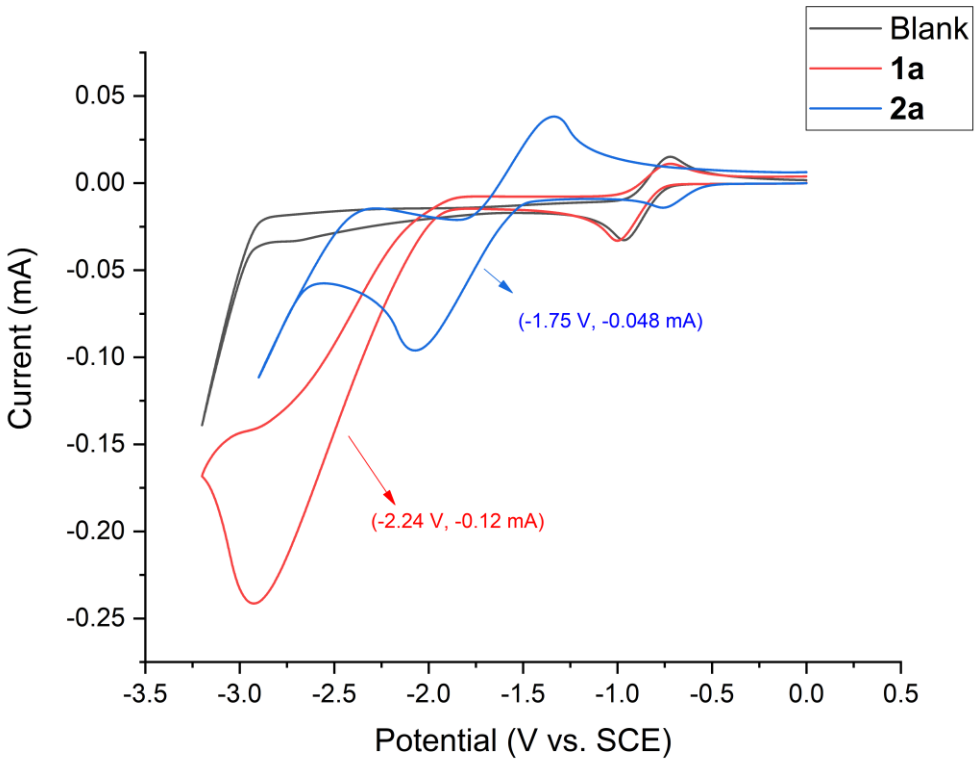


Figure S6. Cyclic Voltammogram Curves. Using GC disk as working electrode, Pt slice, andAg/AgCl as counter and reference electrode at 100 mV/s scan rate. Cyclic Voltammogram of **1a** (2 mM), $Ep_{1/2red}$ = -2.24 V; **2a** (2 mM), $Ep_{1/2red}$ = -1.75 V.

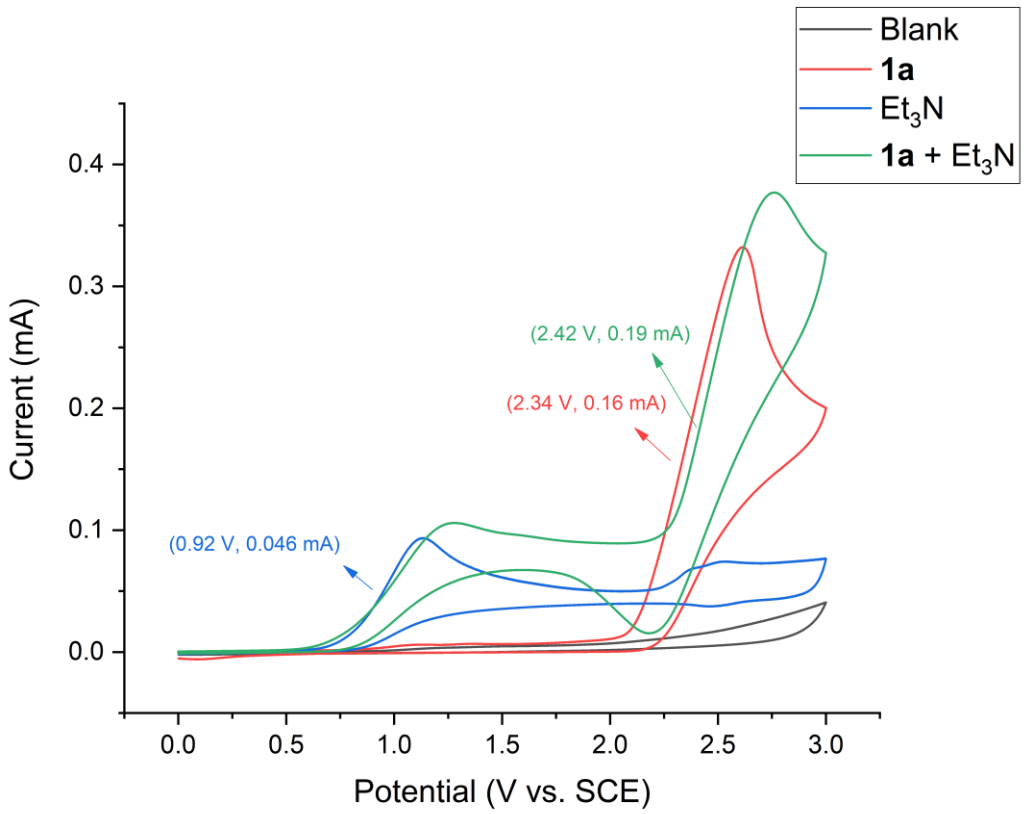
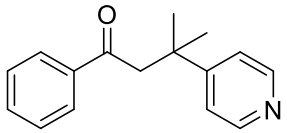


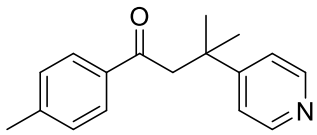
Figure S7. Cyclic Voltammogram Curves. Using GC disk as working electrode, Pt slice, andAg/AgCl as counter and reference electrode at 100 mV/s scan rate.Cyclic Voltammogram of **1a** (2 mM, 1 equiv) $Ep_{1/2ox}$ = 2.34 V; Et_3N (4 mM, 2 equiv) $Ep_{1/2ox}$ = 0.92 V; **1a** (2 mM) + Et_3N (4 Mm, 2 equiv) $Ep_{1/2ox}$ = 2.42V**.**

(B) Analytical data



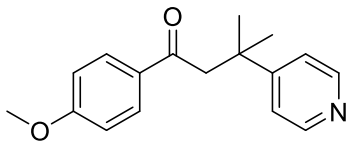
3-methyl-1-phenyl-3-(pyridin-4-yl)butan-1-one (3aa)

33.8 mg, 71% yield; R_f = 0.2 (PE/EA = 5 : 1); Brown oil; ^{1}H NMR (500 MHz, Chloroform-*d*) δ (ppm) 8.48 (d, J = 6.5 Hz, 2H), 7.85 - 7.83 (m, 2H), 7.54 - 7.51 (m, 1H), 7.43 - 7.40 (m, 2H), 7.27 - 7.25 (m, 2H), 3.36 (s, 2H), 1.49 (s, 6H); ^{13}C NMR (125 MHz, Chloroform-*d*) δ (ppm) 197.76, 157.89, 149.72, 137.70, 132.99, 128.54, 127.89, 120.85, 50.02, 37.16, 28.69; HRMS *m/z* (ESI) calcd for $C_{16}H_{18}NO$ ([M+H]$^+$) 240.1383, found 240.1389.



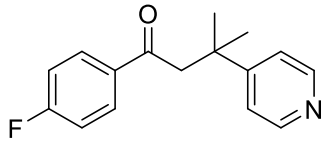
3-methyl-3-(pyridin-4-yl)-1-(p-tolyl)butan-1-one (3ba)

33 mg, 66% yield; R_f = 0.2 (PE/EA = 4 : 1); Yellow oil; ^{1}H NMR (400 MHz, Chloroform-*d*) δ (ppm) 8.42 - 8.41 (m, 2H), 7.69 - 7.67 (m, 2H), 7.20 - 7.18 (m, 2H), 7.13 (d, *J* = 8.0 Hz, 2H), 3.26 (s, 2H), 2.31 (s, 3H), 1.40 (s, 6H). ^{13}C NMR (100 MHz, Chloroform-*d*) δ (ppm) 197.43, 158.07, 149.68, 143.89, 135.12, 129.24, 128.06, 120.90, 49.84, 37.14, 28.76, 21.63. HRMS *m/z* (ESI) calcd for $C_{17}H_{20}NO$ ([M+H]$^+$) 254.1539, found 254.1547.



1-(4-methoxyphenyl)-3-methyl-3-(pyridin-4-yl)butan-1-one (3ca)

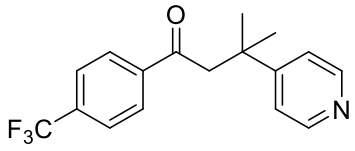
42 mg, 78% yield; R_f = 0.3 (PE/EA = 3 : 1); Brown oil;^{1}H NMR (500 MHz, Chloroform-*d*) δ (ppm) 8.49 (d, *J* = 6.5 Hz, 2H), 7.84 - 7.81 (m, 2H), 7.27 - 7.26 (m, 2H), 6.90 - 6.87 (m, 2H), 3.85 (s, 3H), 3.30 (s, 2H), 1.48 (s, 6H); ^{13}C NMR (125 MHz, Chloroform-*d*) δ (ppm) 196.31, 163.45, 158.14, 149.64, 130.79, 130.22, 120.89, 113.67, 55.45, 49.62, 37.23, 28.72; HRMS *m/z* (ESI) calcd for $C_{17}H_{20}NO_2$ ([M+H]$^+$) 270.1489, found 270.1497.



1-(4-fluorophenyl)-3-methyl-3-(pyridin-4-yl)butan-1-one (3da)

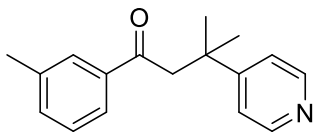
29 mg, 57% yield; R_f = 0.2 (PE/EA = 5 : 1); Brown oil; ^{1}H NMR (400 MHz, Chloroform-*d*) δ (ppm) 8.41 (d, *J* = 6.4 Hz, 2H), 7.57 - 7.53 (m, 1H), 7.43 - 7.37 (m, 1H), 7.19 - 7.17 (m, 2H), 7.10 - 6.98 (m, 2H), 3.34 (d, *J* = 2.4 Hz, 2H), 1.39 (s, 6H); ^{13}C NMR (100 MHz, Chloroform-*d*) δ (ppm) 196.34 (d, *J* = 3.8 Hz), 162.71, 160.19, 157.86, 149.60, 134.44 (d, *J* = 8.9 Hz), 130.36 (d, *J* = 2.6 Hz), 126.53

(d, *J* = 13.1 Hz), 124.52 (d, *J* = 3.4 Hz), 120.89, 116.57 (d, *J* = 23.9 Hz), 55.20 (d, *J* = 7.0 Hz), 37.2(d, *J* = 1.4 Hz), 28.78; ^{19}F NMR (376 MHz, Chloroform-*d*) δ (ppm) -108.89; HRMS *m/z* (ESI) calcd for $C_{16}H_{17}FNO$ ([M+H]$^+$) 258.1289, found 258.1289.



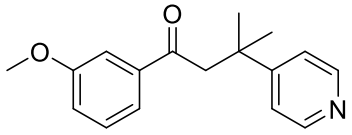
3-methyl-3-(pyridin-4-yl)-1-(4-(trifluoromethyl)phenyl)butan-1-one (3ea)

26.4 mg, 43% yield; R_f = 0.15 (PE/EA = 5 : 1); Light brown oil; ^{1}H NMR (400 MHz, Chloroform-*d*) δ (ppm) 8.43 (d, *J* = 6.4 Hz, 2H), 7.87 (d, *J* = 8.0 Hz, 2H), 7.61 (d, *J* = 8.0 Hz, 2H), 7.20 – 7.18 (m, 2H), 3.32 (s, 2H), 1.43 (s, 6H); ^{13}C NMR (101 MHz, Chloroform-*d*) δ (ppm) 196.76, 157.50, 149.81, 140.11, 134.36 (d, *J* = 32.5 Hz), 128.23, 125.69 - 125.61 (m), 120.81, 50.37, 37.14, 28.69; ^{19}F NMR (376 MHz, Chloroform-*d*) δ (ppm) -63.11; HRMS *m/z* (ESI) calcd for $C_{17}H_{17}F_3NO$ ([M+H]$^+$) 308.1257, found 308.1260.



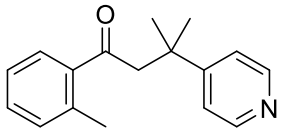
3-methyl-3-(pyridin-4-yl)-1-(m-tolyl)butan-1-one (3fa)

31 mg, 62% yield; R_f = 0.2 (PE/EA = 4 : 1); Colorless oil; ^{1}H NMR (500 MHz, Chloroform-*d*) δ (ppm) 8.48 (d, *J* = 7.0 Hz, 2H), 7.64 - 7.63 (m, 2H), 7.35 – 7.28 (m, 2H), 7.26 – 7.24 (m, 2H), 3.35 (s, 2H), 2.37 (s, 3H), 1.48 (s, 6H); ^{13}C NMR (125 MHz, Chloroform-*d*) δ (ppm) 197.98, 158.03, 149.62, 138.34, 137.72, 133.74, 128.44, 128.40, 125.11, 120.89, 50.09, 37.16, 28.70, 21.29; HRMS *m/z* (ESI) calcd for $C_{17}H_{20}NO$ ([M+H]$^+$) 254.1539, found 254.1549.



1-(3-methoxyphenyl)-3-methyl-3-(pyridin-4-yl)butan-1-one (3ga)

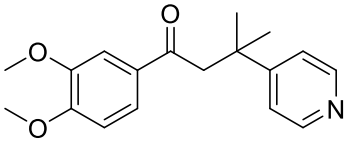
37 mg, 69% yield; R_f = 0.15 (PE/EA = 3 : 1); Yellow oil; ^{1}H NMR (500 MHz, Chloroform-*d*) δ (ppm) 8.49 (d, *J* = 6.0 Hz, 2H), 7.44 - 7.42 (m, 1H), 7.36 – 7.29 (m, 2H), 7.27 – 7.30 (m, 2H), 7.27 - 7.25 (m, 2H), 3.81 (s, 3H), 3.35 (s, 2H), 1.48 (s, 6H); ^{13}C NMR (125 MHz, Chloroform-*d*) δ (ppm) 197.55, 159.82, 158.02, 149.61, 138.98, 129.50, 120.88, 120.54, 119.54, 112.17, 55.40, 50.11, 37.15, 28.73; HRMS *m/z* (ESI) calcd for $C_{17}H_{20}NO_2$ ([M+H]$^+$) 270.1489, found 270.1496.



3-methyl-3-(pyridin-4-yl)-1-(o-tolyl)butan-1-one (3ha)

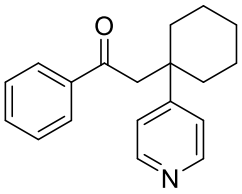
38 mg, 76% yield; R_f = 0.2 (PE/EA = 3 : 1); Brown oil; ^{1}H

NMR (400 MHz, Chloroform-*d*) δ (ppm) 8.41 - 8.40 (m, 2H), 7.39 (d, *J* = 1.6 Hz, 1H), 7.26 - 7.22 (m, 1H), 7.18 - 7.16 (m, 2H), 7.14 - 7.09 (m, 2H), 3.21 (s, 2H), 2.21 (s, 3H), 1.39 (s, 6H); ^{13}C NMR (100 MHz, Chloroform-*d*) δ (ppm) 202.52, 157.71, 149.68, 138.98, 137.44, 131.89, 131.08, 127.94, 125.54, 120.92, 53.27, 37.51, 28.85, 20.86; HRMS *m/z* (ESI) calcd for $C_{17}H_{20}NO$ ($[M+H]^+$) 254.1539, found 254.1538.



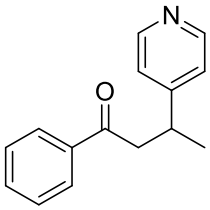
1-(3,4-dimethoxyphenyl)-3-methyl-3-(pyridin-4-yl)butan-1-one (3ja)

47 mg, 78% yield; R_f = 0.1 (PE/EA = 3 : 1); Brown oil; ^{1}H NMR (500 MHz, Chloroform-*d*) δ (ppm) 8.50 (d, *J* = 6.5 Hz, 2H), 7.49 - 7.47 (m, 1H), 7.41 (d, *J* = 2.0 Hz, 1H), 7.28 – 7.26 (m, 2H), 6.83 (d, *J* = 8.5 Hz, 1H), 3.93 (s, 3H), 3.88 (s, 3H), 3.32 (s, 2H), 1.48 (s, 6H); ^{13}C NMR (125 MHz, Chloroform-*d*) δ (ppm) 196.31, 158.15, 153.34, 149.65, 149.09, 130.92, 122.62, 120.88, 110.12, 109.88, 56.06, 55.94, 49.48, 37.23, 28.76; HRMS *m/z* (ESI) calcd for $C_{18}H_{22}NO_3$ ($[M+H]^+$) 300.1594, found 300.1597.



1-phenyl-2-(1-(pyridin-4-yl)cyclohexyl)ethan-1-one (3ka)

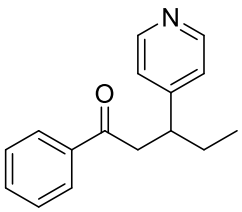
45 mg, 81% yield; R_f = 0.1 (PE/EA = 4 : 1); Colorless oil; ^{1}H NMR (400 MHz, Chloroform-*d*) δ (ppm) 8.42 (d, *J* = 6.4 Hz, 2H), 7.67 - 7.64 (m, 2H), 7.46 - 7.42 (m, 1H), 7.32 - 7.29 (m, 2H), 7.24 - 7.23 (m, 2H), 3.19 (s, 2H), 2.25 - 2.19 (m, 2H), 1.87 - 1.80 (m, 2H), 1.60 - 1.54 (m, 2H), 1.47 - 1.32 (m, 4H); ^{13}C NMR (100 MHz, Chloroform-*d*) δ (ppm) 198.50, 155.27, 149.83, 137.99, 132.95, 128.48, 127.97, 127.96, 122.38, 41.28, 35.90, 35.87, 26.12, 22.30; HRMS *m/z* (ESI) calcd for $C_{19}H_{22}NO$ ($[M+H]^+$) 280.1696, found 280.1700.



1-phenyl-3-(pyridin-4-yl)butan-1-one (3la)

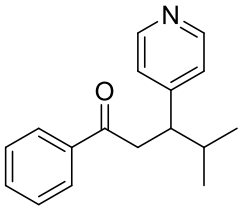
18.5 mg, 41% yield; R_f = 0.2 (PE/EA = 3 : 1); Colorless oil; ^{1}H NMR (400 MHz, Chloroform-*d*) δ (ppm) 8.51 (d, *J* = 6.4 Hz, 2H), 7.93 – 7.91 (m, 2H), 7.59 - 7.54 (m, 1H), 7.44 - 7.44 (m, 2H), 7.21 - 7.19 (m, 2H), 3.56 - 3.48 (m, 1H), 3.34 - 3.18 (m, 2H), 1.35 (d, *J* = 6.8 Hz, 3H); ^{13}C NMR (100 MHz, Chloroform-*d*) δ (ppm) 198.08, 155.49, 149.87, 136.87, 133.29, 128.69, 128.01, 122.43, 45.88, 34.75, 21.31; HRMS *m/z* (ESI) calcd for $C_{15}H_{16}NO$ ($[M+H]^+$)

226.1226, found 226.1230.



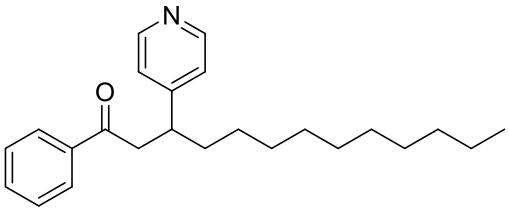
1-phenyl-3-(pyridin-4-yl)pentan-1-one (3ma)

25 mg, 53% yield; R_f = 0.2 (PE/EA = 5 : 1); Brown oil; ^{1}H NMR (500 MHz, Chloroform-*d*) δ (ppm) 8.50 (d, J = 3.5 Hz, 2H), 7.7.90 - 7.88 (m, 2H), 7.57 - 7.53 (m, 1H), 7.46 - 7.42 (m, 2H), 7.16 (d, *J* = 4.5 Hz, 2H), 3.31 - 3.24 (m, 3H), 1.84 - 1.76 (m, 1H), 1.70 - 1.62 (m, 1H), 0.83 (t, *J* = 7.0 Hz, 3H); ^{13}C NMR (125 MHz, Chloroform-*d*) δ (ppm) 198.13, 153.77, 149.84, 136.99, 133.16, 128.62, 127.95, 123.16, 44.44, 42.19, 28.70, 11.85. HRMS *m/z* (ESI) calcd for $C_{16}H_{18}NO$ ($[M+H]^+$) 240.1383, found 240.1386.



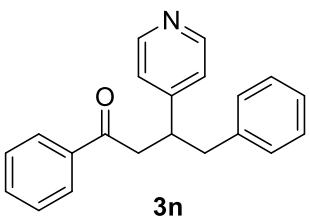
4-methyl-1-phenyl-3-(pyridin-4-yl)pentan-1-one (3na)

14 mg, 27% yield; R_f = 0.3 (PE/EA = 2 : 1); Colorless oil;^{1}H NMR (500 MHz, Chloroform-*d*) δ (ppm) 8.45 (d, *J* = 4.0 Hz, 2H), 7.87 (d, *J* = 8.0 Hz, 2H), 7.55 - 7.52 (m, 1H), 7.45 - 7.41 (m, 2H), 7.11 (d, *J* = 4.5 Hz, 2H), 3.37 (d, *J* = 7.0 Hz, 2H), 3.20 – 3.15 (m, 1H), 1.99 - 1.92 (m, 1H), 0.99 - 0.98 (m, 3H), 0.81 - 0.79 (m, 3H); ^{13}C NMR (125 MHz, Chloroform-*d*) δ (ppm) 198.39, 152.84, 149.51, 137.05, 133.11, 128.61, 127.91, 123.82, 47.11, 41.45, 32.77, 20.61, 20.30; HRMS *m/z* (ESI) calcd for $C_{17}H_{20}NO$ ($[M+H]^+$) 254.1539, found 254.1539.

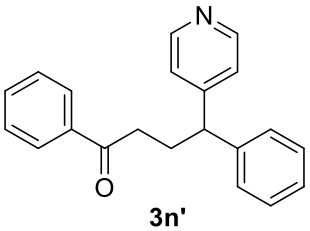


1-phenyl-3-(pyridin-4-yl)tridecan-1-one (3oa)

31 mg, 45% yield; R_f = 0.3 (PE/EA = 3 : 1); Brown oil; ^{1}H NMR (500 MHz, Chloroform-*d*) δ (ppm) 8.49 (d, *J* = 5.0 Hz, 2H), 7.89 (d, *J* = 8.0 Hz, 2H), 7.55 (t, *J* = 7.5 Hz, 1H), 7.44 (t, *J* = 7.5 Hz, 2H), 7.17 (d, *J* = 5.0 Hz, 2H), 3.36 – 3.24 (m, 3H), 1.76 - 1.59 (m, 2H), 1.30 - 1.21 (m, 16H), 0.87 (t, *J* = 7.0 Hz, 3H); ^{13}C NMR (125 MHz, Chloroform-*d*) δ (ppm) 198.17, 154.21, 149.82, 137.00, 133.19, 128.65, 127.98, 123.16, 44.87, 40.56, 35.82, 31.89, 29.71, 29.56, 29.48, 29.42, 29.30, 27.33, 22.67, 14.10; HRMS *m/z* (ESI) calcd for $C_{24}H_{34}NO$ ($[M+H]^+$) 352.2635, found 352.2636.



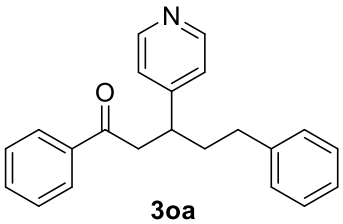
3n



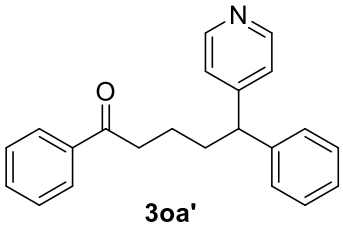
3n'

1,4-diphenyl-3-(pyridin-4-yl)butan-1-one (3pa), 1,4-diphenyl-4-(pyridin-4-yl)butan-1-one (3pa')

3na : **3na'** = 1.5 : 1 (the ratio was determined by ^{1}H NMR), 42 mg, 71% yield; R_f = 0.2 (PE/EA = 3 : 1); White powder, m.p. 135 - 139℃ (uncorrected); ^{1}H NMR (400 MHz, Chloroform-*d*) δ (ppm) 8.50 (d, *J* = 5.2 Hz, 2H), 8.44 (d, *J* = 5.2 Hz, 1.3H), 7.87 - 7.83 (m, 3.4H), 7.55 - 7.51 (m, 1.8H), 7.44 - 7.39 (m, 3.6H), 7.33 - 7.29 (m, 2.3H), 7.25 - 7.15 (m, 7.4H), 7.10 - 7.05 (m, 2.8H), 4.01 (t, *J* = 8.0 Hz, 1H), 3.68 (p, *J* = 7.2 Hz, 0.72H), 3.40 - 3.28 (m, 1.4H), 3.05 - 2.99 (m, 0.8H), 2.93 (t, *J* = 7.2 Hz, 2.8H), 2.53 - 2.47 (m, 2.5H); ^{13}C NMR (101 MHz, Chloroform-*d*) δ (ppm) 199.44, 197.93, 153.46, 153.18, 149.96, 149.76, 142.39, 138.80, 136.82, 136.77, 133.29, 133.17, 129.18, 128.89, 128.67, 128.62, 128.41, 127.98, 127.96, 127.03, 126.49, 123.21, 123.18, 49.81, 43.15, 42.28, 36.41, 28.98; HRMS *m/z* (ESI) calcd for $C_{21}H_{20}NO$ ($[M+H]^+$) 302.1539, found 302.1541.



3oa



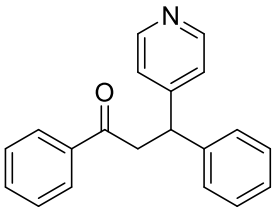
3oa'

1,5-diphenyl-3-(pyridin-4-yl)pentan-1-one (3qa)

1,5-diphenyl-5-(pyridin-4-yl)pentan-1-one(3qa')

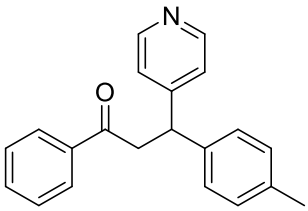
3oa : **3oa'** = 4 : 1 (the ratio was determined by ^{1}H NMR), 30 mg, 48% yield, ; R_f = 0.3 (PE/EA = 3 : 1); colorless oil; ^{1}H NMR (500 MHz, Chloroform-*d*) δ (ppm) 8.53 (d, *J* = 5.0 Hz, 2H), 8.48 (d, *J* = 5.0 Hz, 0.5H), 7.91 - 7.85 (m, 2.7H), 7.56 - 7.52 (m, 1.5H), 7.46 - 7.41 (m, 2.9H), 7.31 - 7.28 (m, 0.8H), 7.26 - 7.14 (m, 5.6H), 7.10 - 7.03 (m, 2.5H), 3.94 - 3.91(m, 0.25 H), 3.44 - 3.37 (m, 1H), 3.34 - 3.26 (m, 2.1H), 3.00 - 2.97 (m, 0.84H), 2.55 - 2.44 (m, 2.4H), 2.22 - 1.93 (m, 4H), 1.76 - 1.71 (m, 0.8H); ^{13}C NMR (126 MHz, Chloroform-*d*) δ 197.84, 153.66, 149.91, 149.78, 141.32, 136.88, 133.22, 128.73, 128.64, 128.59, 128.42, 128.26, 127.94, 127.86, 126.79, 126.00, 123.21, 50.84, 44.89, 40.20, 38.19, 37.24, 34.47, 33.53, 29.68, 22.55; ^{13}C NMR (125 MHz,

Chloroform-*d*) δ (ppm) 197.84, 153.66, 149.91, 149.78, 141.32, 136.88, 133.22, 128.73, 128.64, 128.59, 128.42, 128.26, 127.94, 127.86, 126.79, 126.00, 123.21, 50.84, 44.89, 40.20, 38.19, 37.24, 34.47, 33.53, 29.68, 22.55; HRMS *m/z* (ESI) calcd for $C_{22}H_{22}NO$ ($[M+H]^+$) 316.1696, found 316.1703.



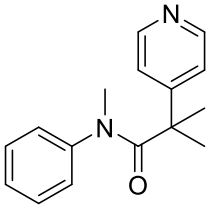
1,3-diphenyl-3-(pyridin-4-yl)propan-1-one (3ra)

44 mg, 76% yield; R_f = 0.2 (PE/EA = 5 : 1); Brown oil; ^{1}H NMR (500 MHz, Chloroform-*d*) δ (ppm) 8.48 (d, *J* = 5.5 Hz, 2H), 7.93 (d, *J* = 8.0 Hz, 2H), 7.55 (t, *J* = 7.5 Hz, 1H), 7.44 (t, *J* = 7.5 Hz, 2H), 7.31 – 7.17 (m, 7H), 4.81 (t, *J* = 7.5 Hz, 1H), 3.79 - 3.68 (m, 2H); ^{13}C NMR (125 MHz, Chloroform-*d*) δ (ppm) 197.16, 152.93, 149.96, 142.51, 136.78, 133.34, 128.84, 128.70, 128.01, 127.88, 126.98, 123.16, 45.30, 43.91; HRMS *m/z* (ESI) calcd for $C_{20}H_{18}NO$ ($[M+H]^+$) 288.1383, found 288.1387.



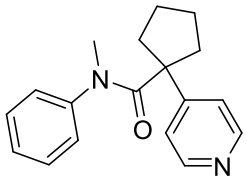
1-phenyl-3-(pyridin-4-yl)-3-(p-tolyl)propan-1-one (3sa)

45 mg, 75% yield; R_f = 0.1 (PE/EA = 5 : 1); Brown oil; ^{1}H NMR (500 MHz, Chloroform-*d*) δ (ppm) 8.48 (d, *J* = 5.0 Hz, 2H), 7.95 - 7.93 (m, 2H), 7.58 - 7.55 (m, 1H), 7.45 (t, *J* = 8.0 Hz, 2H), 7.18 (d, *J* = 6.0 Hz, 2H), 7.15 - 7.10 (m, 4H), 4.77 (t, *J* = 7.0 Hz, 1H), 3.78 - 3.67 (m, 2H), 2.30 (s, 3H); ^{13}C NMR (125 MHz, Chloroform-*d*) δ (ppm) 197.26, 153.27, 149.87, 139.49, 136.80, 136.61, 133.32, 129.52, 128.69, 128.02, 127.71, 123.14, 44.93, 43.96, 20.96; HRMS *m/z* (ESI) calcd for $C_{21}H_{20}NO$ ($[M+H]^+$) 302.1539, found 302.1549.



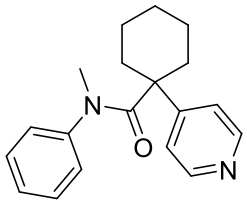
N,2-dimethyl-N-phenyl-2-(pyridin-4-yl)propenamide (3ta)

34 mg, 67% yield; R_f = 0.1 (PE/EA = 3 : 1); White solid, m.p. 133 - 136 ℃ (uncorrected) ; ^{1}H NMR (500 MHz, Chloroform-*d*) δ (ppm) 8.39 (d, *J* = 5.0 Hz, 2H), 7.17 - 6.93 (m, 5H), 6.65 (d, J = 5.0 Hz, 2H), 3.15 (s, 3H), 1.45 (s, 6H); ^{13}C NMR (125 MHz, Chloroform-*d*) δ (ppm) 174.69, 155.14, 149.65, 128.82, 127.50, 120.83, 47.44, 40.72, 28.18; HRMS *m/z* (ESI) calcd for $C_{16}H_{19}N_2O$ ($[M+H]^+$) 255.1492, found 255.1499.



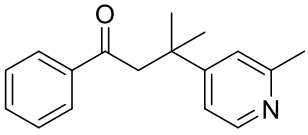
N-methyl-N-phenyl-1-(pyridin-4-yl)cyclopentane-1-carboxamide (3ua)

39 mg, 70% yield; R_f = 0.1 (PE/EA = 2 : 1); White solid, m.p. 140.1 -142.2 ℃ (uncorrected); ^{1}H NMR (400 MHz, Chloroform-*d*) δ (ppm) 8.32 (s, 2H), 7.13 - 6.77 (m, 5H), 6.51 (s, 2H), 3.10 (s, 3H), 2.30 - 2.25 (m, 2H), 1.71 - 1.33 (m, 6H); ^{13}C NMR (100 MHz, Chloroform-*d*) δ (ppm) 174.28, 154.68, 149.35, 128.80, 127.57, 121.25, 59.40, 40.18, 37.98, 23.91; HRMS *m/z* (ESI) calcd for $C_{18}H_{21}N_2O$ ([M+H]$^+$) 281.1648, found 281.1650.



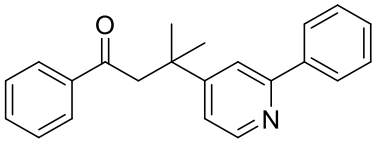
N-methyl-N-phenyl-1-(pyridin-4-yl)cyclohexane-1-carboxamide (3va)

36 mg, 63% yield; R_f = 0.1 (PE/EA = 2 : 1); White solid, m.p. 138.4 -139.7 ℃ (uncorrected); ^{1}H NMR (400 MHz, Chloroform-*d*) δ (ppm) 8.37 (d, *J* = 5.6 Hz, 2H), 7.13 (t, *J* = 7.6 Hz, 1H), 7.04 (t, *J* = 7.6 Hz, 2H), 6.95 (d, *J* = 5.2 Hz, 2H), 6.49 (d, *J* = 7.6 Hz, 2H), 3.10 (s, 3H), 2.07 - 2.03 (m, 2H), 1.63 - 1.45 (m, 5H), 1.40 - 1.33 (m, 2H), 1.18 - 1.11 (m, 1H); ^{13}C NMR (101 MHz, Chloroform-*d*) δ (ppm) 172.91, 154.90, 149.72, 143.66, 129.02, 128.07, 127.67, 121.31, 52.06, 41.08, 36.18, 25.61, 23.34; HRMS *m/z* (ESI) calcd for $C_{19}H_{23}N_2O$ ([M+H]$^+$) 295.1805, found 295.1809.



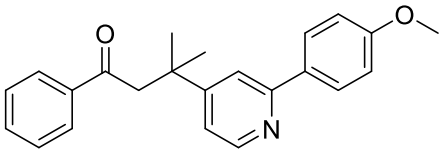
3-methyl-3-(2-methylpyridin-4-yl)-1-phenylbutan-1-one (3ab)

27 mg, 54% yield; R_f = 0.15 (PE/EA = 5 : 1); Yellow oil; ^{1}H NMR (400 MHz, Chloroform-*d*) δ (ppm) 8.31 (d, *J* = 5.6 Hz, 1H), 7.79 (d, *J* = 6.8 Hz, 2H), 7.48 - 7.44 (m, 1H), 7.37 - 7.33 (m, 2H), 7.07 (s, 1H), 7.02 - 6.99 (m, 1H), 3.30 (s, 2H), 2.46 (s, 3H), 1.41 (s, 6H); ^{13}C NMR (100 MHz, Chloroform-*d*) δ (ppm) (ppm) 197.98, 158.26, 158.21, 149.07, 137.69, 133.09, 128.60, 127.98, 120.43, 118.03, 50.08, 37.10, 28.81, 24.72; HRMS *m/z* (ESI) calcd for $C_{17}H_{210}NO$ ([M+H]$^+$) 254.1539, found 254.1547.



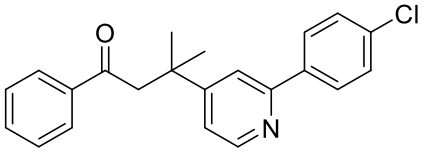
3-methyl-1-phenyl-3-(2-phenylpyridin-4-yl)butan-1-one (3ac)

36 mg, 57% yield; R_f = 0.2 (PE/EA = 10 : 1); Brown oil; ^{1}H NMR (500 MHz, Chloroform-*d*) δ (ppm) 8.57 (d, *J* = 5.0 Hz, 1H), 7.93 - 7.91 (m, 2H), 7.85 - 7.83 (m, 2H), 7.68 (d, *J* = 2.0 Hz, 1H), 7.51 - 7.48 (m, 1H), 7.46 - 7.42 (m, 2H), 7.40 - 7.37 (m, 3H), 7.22 - 7.20 (m, 1H), 3.39 (s, 2H), 1.53 (s, 6H); ^{13}C NMR (125 MHz, Chloroform-*d*) δ (ppm) 197.94, 158.78, 157.61, 149.50, 139.87, 137.77, 133.00, 128.76, 128.64, 128.54, 127.98, 127.93, 127.12, 125.66, 119.43, 118.11, 50.12, 37.48, 28.76; HRMS *m/z* (ESI) calcd for $C_{22}H_{22}NO$ ($[M+H]^+$) 316.1696, found 316.1703.



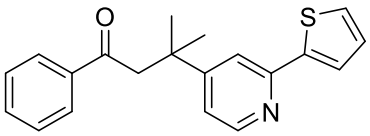
3-(2-(4-methoxyphenyl)pyridin-4-yl)-3-methyl-1-phenylbutan-1-one (3ad)

44 mg, 64% yield; R_f = 0.2 (PE/EA = 10 : 1); Brown oil; ^{1}H NMR (500 MHz, Chloroform-*d*) δ (ppm) 8.52 (d, *J* = 5.0 Hz, 1H), 7.88 - 7.83 (m, 4H), 7.61 (s, 1H), 7.52 - 7.48 (m, 1H), 7.40 - 7.37 (m, 2H), 7.16 – 7.15 (m, 1H), 6.98 - 6.95 (m, 2H), 3.84 (s, 3H), 3.38 (s, 2H), 1.53 (s, 6H); ^{13}C NMR (125 MHz, Chloroform-*d*) δ (ppm) 198.02, 160.33, 158.52, 157.28, 149.45, 137.80, 132.97, 132.58, 128.52, 128.31, 127.93, 118.77, 117.26, 114.03, 55.33, 50.09, 37.45, 28.73; HRMS *m/z* (ESI) calcd for $C_{23}H_{24}NO_2$ ($[M+H]^+$) 346.1802, found 346.1807.



3-(2-(4-chlorophenyl)pyridin-4-yl)-3-methyl-1-phenylbutan-1-one (3ae)

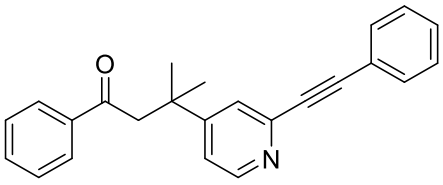
40 mg, 58% yield; R_f = 0.2 (PE/EA = 10 : 1); Brown oil; ^{1}H NMR (400 MHz, Chloroform-*d*) δ (ppm) 8.57 - 8.55 (m, 1H), 7.88 - 7.83 (m, 4H), 7.64 - 7.63 (m, 1H), 7.54 - 7.50 (m, 1H), 7.43 - 7.38 (m, 4H), 7.23 - 7.22 (m, 1H), 3.41 (s, 2H), 1.54 (s, 6H); ^{13}C NMR (100 MHz, Chloroform-*d*) δ (ppm) 197.93, 158.94, 156.45, 149.76, 138.45, 137.65, 134.93, 133.21, 128.93, 128.90, 128.87, 128.68, 128.65, 128.46, 128.43, 128.01, 119.79, 117.91, 50.17, 37.48, 28.95; HRMS *m/z* (ESI) calcd for $C_{22}H_{21}ClNO$ ($[M+H]^+$) 350.1306, found 350.1309.



3-methyl-1-phenyl-3-(2-(thiophen-2-yl)pyridin-4-yl)butan-1-one (3af)

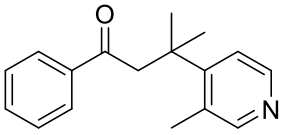
28 mg, 43% yield; R_f = 0.2 (PE/EA = 10 : 1); Yellow oil;^{1}H NMR (400 MHz, Chloroform-*d*) δ (ppm) 8.45 (d, *J* = 5.4 Hz, 1H), 7.86 (d, *J* =

7.2 Hz, 2H), 7.63 (s, 1H), 7.55 - 7.49 (m, 2H), 7.43 - 7.36 (m, 3H), 7.13 - 7.08 (m, 2H), 3.39 (s, 2H), 1.52 (s, 6H); ^{13}C NMR (100 MHz, Chloroform-*d*) δ(ppm) 197.82, 158.71, 152.54, 149.47, 145.21, 137.61, 133.09, 128.59, 127.93, 127.90, 127.34, 124.31, 119.36, 116.07, 50.03, 37.31, 28.71; HRMS *m/z* (ESI) calcd for $C_{20}H_{20}NOS$ ($[M+H]^+$) 322.1260, found 322.1260.



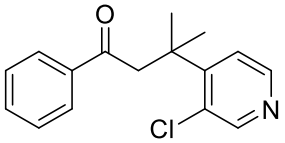
3-methyl-1-phenyl-3-(2-(phenylethynyl)pyridin-4-yl)butan-1-one (3ag)

22 mg, 32% yield; R_f = 0.1 (PE/EA = 4 : 1); Brown oil; ^{1}H NMR (500 MHz, Chloroform-*d*) δ (ppm) 8.49 (d, *J* = 5.0 Hz, 1H), 7.87 - 7.85 (m, 2H), 7.61 - 7.58 (m, 2H), 7.55 - 7.52 (m, 2H), 7.44 - 7.41 (m, 2H), 7.37 - 7.34 (m, 3H), 7.23 - 7.21 (m, 1H), 3.38 (s, 2H), 1.50 (s, 6H); ^{13}C NMR (125 MHz, Chloroform-*d*) δ (ppm) 197.52, 158.38, 149.92, 143.36, 137.61, 133.06, 132.03, 128.81, 128.57, 128.33, 127.90, 124.46, 122.46, 120.19, 89.15, 88.63, 49.99, 37.15, 28.61; HRMS *m/z* (ESI) calcd for $C_{24}H_{22}NO$ ($[M+H]^+$) 340.1696, found 340.1699.



3-methyl-3-(3-methylpyridin-4-yl)-1-phenylbutan-1-one (3ah)

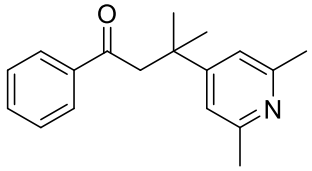
32 mg, 65% yield; R_f = 0.2 (PE/EA = 10 : 1); Brown oil;^{1}H NMR (500 MHz, Chloroform-*d*) δ (ppm) 8.33 (d, *J* = 5.5 Hz, 1H), 8.24 (s, 1H), 7.86 - 7.84 (m, 2H), 7.54 - 7.51 (m, 1H), 7.41 (t, *J* = 8.0 Hz, 2H), 7.22 (d, *J* = 5.0 Hz, 1H), 3.52 (s, 2H), 2.44 (s, 3H), 1.54 (s, 6H); ^{13}C NMR (125 MHz, Chloroform-*d*) δ (ppm) 197.76, 154.92, 152.94, 147.75, 137.48, 133.01, 130.36, 128.58, 127.82, 121.37, 48.92, 38.32, 29.12, 20.25; HRMS *m/z* (ESI) calcd for $C_{17}H_{20}NO$ ($[M+H]^+$) 254.1539, found 254.1546.



3-(3-chloropyridin-4-yl)-3-methyl-1-phenylbutan-1-one (3ai)

27 mg, 50% yield; R_f = 0.2 (PE/EA = 4 : 1); Brown oil; ^{1}H NMR (500 MHz, Chloroform-*d*) δ (ppm) 8.49 (d, *J* = 6.0 Hz, 2H), 7.85 - 7.83 (m, 2H), 7.54 - 7.51 (m, 1H), 7.41 (t, *J* = 7.5 Hz, 2H), 7.26 (d, *J* = 2.0 Hz, 1H), 3.36 (s, 2H), 1.49

(s, 6H); ^{13}C NMR (125 MHz, Chloroform-*d*) δ (ppm) 197.80, 157.98, 149.69, 137.71, 133.03, 128.57, 127.92, 120.90, 50.04, 37.19, 28.72; HRMS *m/z* (ESI) calcd for $C_{16}H_{17}ClNO$ ([M+H]$^+$) 274.0993, found 274.0999.

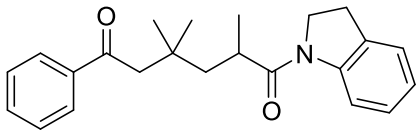


3-(2,6-dimethylpyridin-4-yl)-3-methyl-1-phenylbutan-1-one (3aj)

22 mg, 42% yield; R_f = 0.2 (PE/EA = 3 : 1); Yellow oil; ^{1}H NMR (500 MHz, Chloroform-*d*) δ (ppm) 8.49 (d, *J* = 6.0 Hz, 2H), 7.85 - 7.83 (m, 2H), 7.54 - 7.51 (m, 1H), 7.41 (t, *J* = 7.5 Hz, 2H), 7.26 (d, *J* = 2.0 Hz, 1H), 3.36 (s, 2H), 1.49 (s, 6H); ^{13}C NMR (125 MHz, Chloroform-*d*) δ (ppm) 197.80, 157.98, 149.69, 137.71, 133.03, 128.57, 127.92, 120.90, 50.04, 37.19, 28.72; HRMS *m/z* (ESI) calcd for $C_{18}H_{22}NO$ ([M+H]$^+$) 268.1696, found 268.1700.

3-(benzo[d]thiazol-2-yl)-3-methyl-1-phenylbutan-1-one (3al)

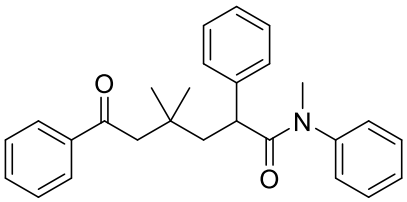
35 mg, 59% yield; R_f = 0.3 (PE/EA = 30 : 1); Brown oil; ^{1}H NMR (400 MHz, Chloroform-*d*) δ (ppm) 7.94 - 7.91 (m, 2H), 7.89 - 7.82 (m, 2H), 7.53 - 7.48 (m, 1H), 7.42 - 7.38 (m, 3H), 7.32 - 7.27 (m, 1H), 3.67 (s, 2H), 1.66 (s, 6H); ^{13}C NMR (100 MHz, Chloroform-*d*) δ (ppm) 197.75, 180.58, 153.34, 137.53, 134.99, 133.07, 128.58, 128.16, 125.79, 124.55, 122.64, 121.64, 50.04, 40.14, 29.16; HRMS *m/z* (ESI) calcd for $C_{18}H_{18}NOS$ ([M+H]$^+$) 296.1104, found 296.1105.



1-(indolin-1-yl)-2,4,4-trimethyl-6-phenylhexane-1,6-dione (3an)

43 mg, 62% yield; R_f = 0.4 (PE/EA = 9 : 1); Brown oil; ^{1}H NMR (400 MHz, Chloroform-*d*) δ (ppm) 8.25 - 8.23 (m, 1H), 7.90 - 7.88 (m, 2H), 7.53 - 7.49 (m, 1H), 7.41 - 7.37 (m, 2H), 7.19 - 7.15 (m, 2H), 7.02 - 6.99 (m, 1H), 4.20 - 4.13 (m, 2H), 3.24 - 3.20 (m, 2H), 2.95 (d, *J* = 14.8 Hz, 1H), 2.78 (d, *J* = 14.8 Hz, 2H), 2.38 - 2.32 (m, 1H), 1.46 - 1.41 (m, 1H), 1.20 (d, *J* = 7.2 Hz, 3H), 1.04 (d, *J* = 14.8 Hz, 6H); ^{13}C NMR (125 MHz, Chloroform-*d*) δ (ppm) 200.15, 175.49, 143.30, 132.76, 131.19, 128.48, 128.13, 127.55, 124.47, 123.57, 117.32, 48.56, 47.99, 46.17, 35.09, 34.30, 28.05, 27.90, 27.85, 20.19; HRMS *m/z* (ESI) calcd for $C_{23}H_{28}NO_2$

([M+H]$^+$) 350.2115, found 350.2106.

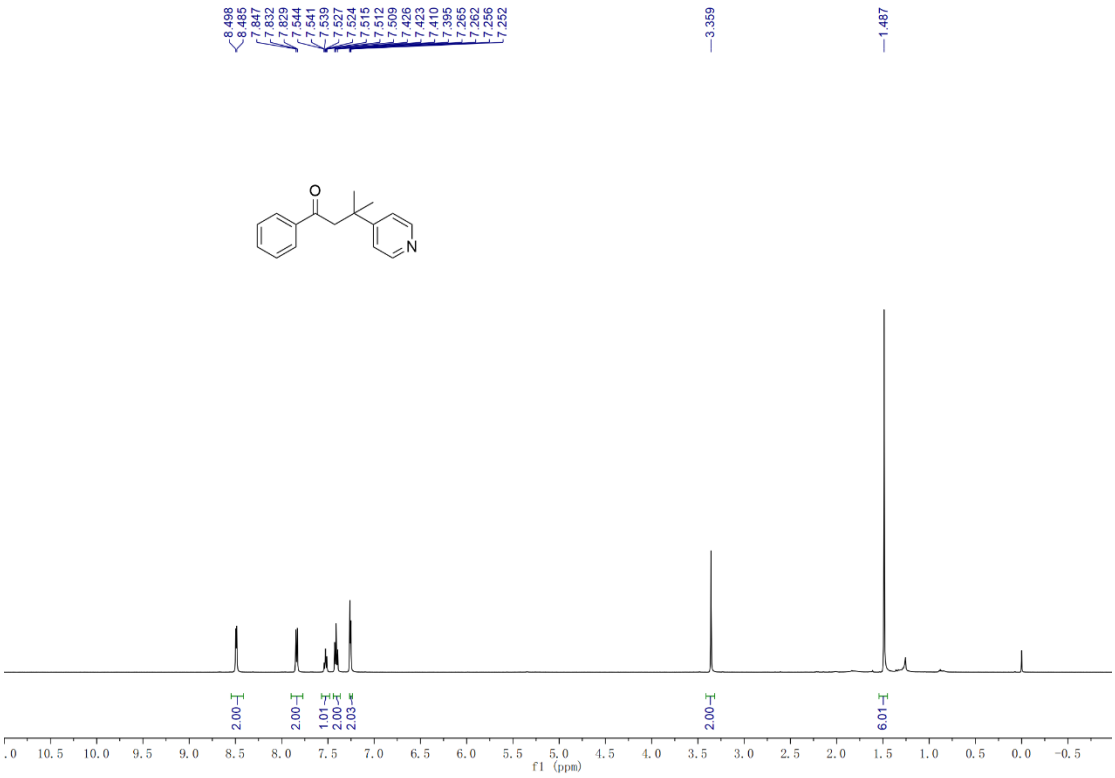


N,4,4-trimethyl-6-oxo-N,2,6-triphenylhexanamide (3ao)

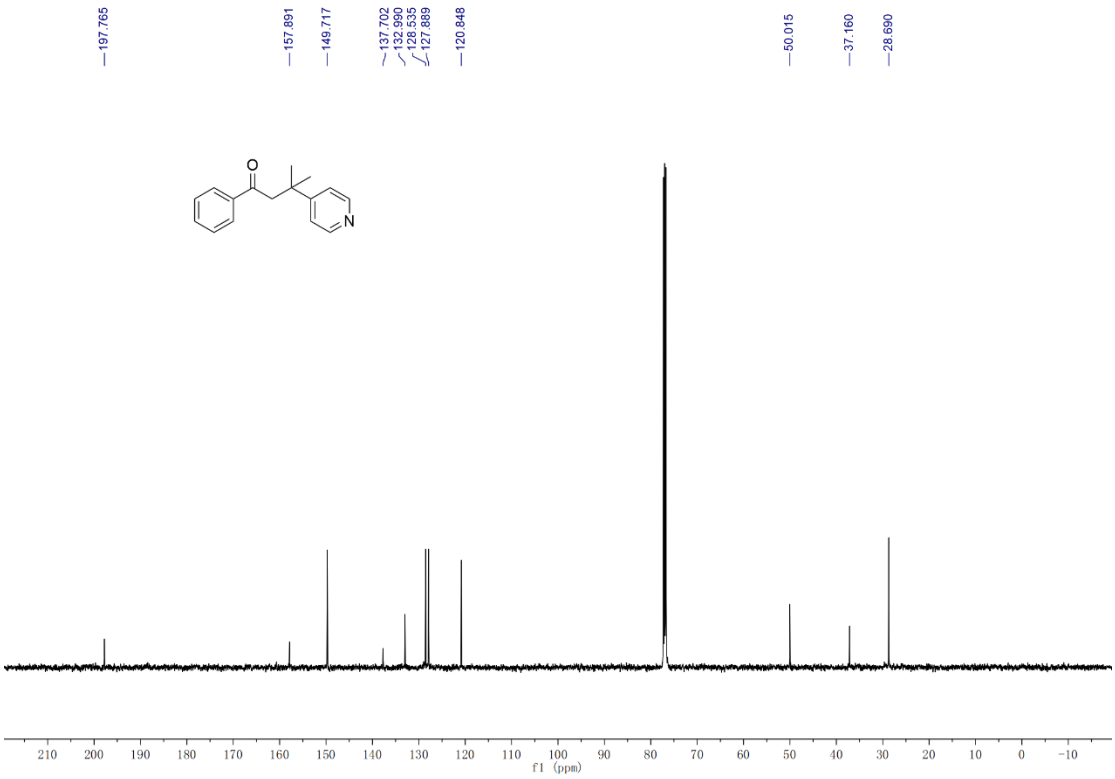
36 mg, 45% yield; R_f = 0.4 (PE/EA = 9 : 1); Yellow oil; ^{1}H NMR (500 MHz, Chloroform-*d*) δ (ppm) 7.81 - 7.79 (m, 2H), 7.53 - 7.50 (m, 1H), 7.42 - 7.35 (m, 5H), 7.22 - 7.16 (m, 3H), 7.05 - 7.03 (m, 4H), 3.62 - 3.40 (m, 1H), 3.22 (s, 3H), 2.76 (d, *J* = 15.5 Hz, 1H), 2.67 (d, *J* = 15.0 Hz, 1H), 2.51 - 2.47 (m, 1H), 1.74 - 1.70 (m, 1H), 0.94 (d, *J* = 11.0 Hz, 6H); ^{13}C NMR (125 MHz, Chloroform-*d*) δ (ppm) 199.82, 173.35, 141.50, 138.46, 132.66, 129.54, 128.42, 128.41, 128.07, 128.06, 128.02, 126.56, 48.03, 47.79, 45.15, 37.78, 34.48, 27.64, 27.44. HRMS *m/z* (ESI) calcd for $C_{27}H_{30}NO_2$ ([M+H]$^+$) 400.2271, found 400.2275.

(C) Spectra

3-methyl-1-phenyl-3-(pyridin-4-yl)butan-1-one (3aa)



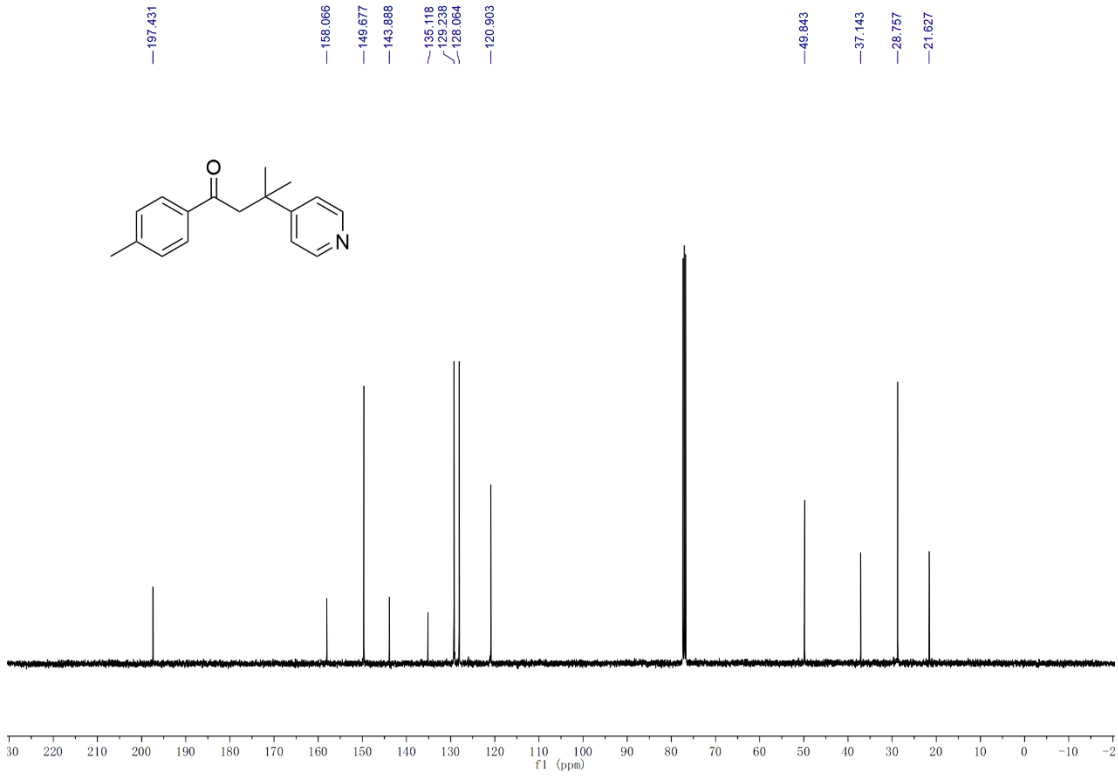
^{1}H NMR (500 MHz, $CDCl_3$)



^{13}C NMR (125 MHz, $CDCl_3$)

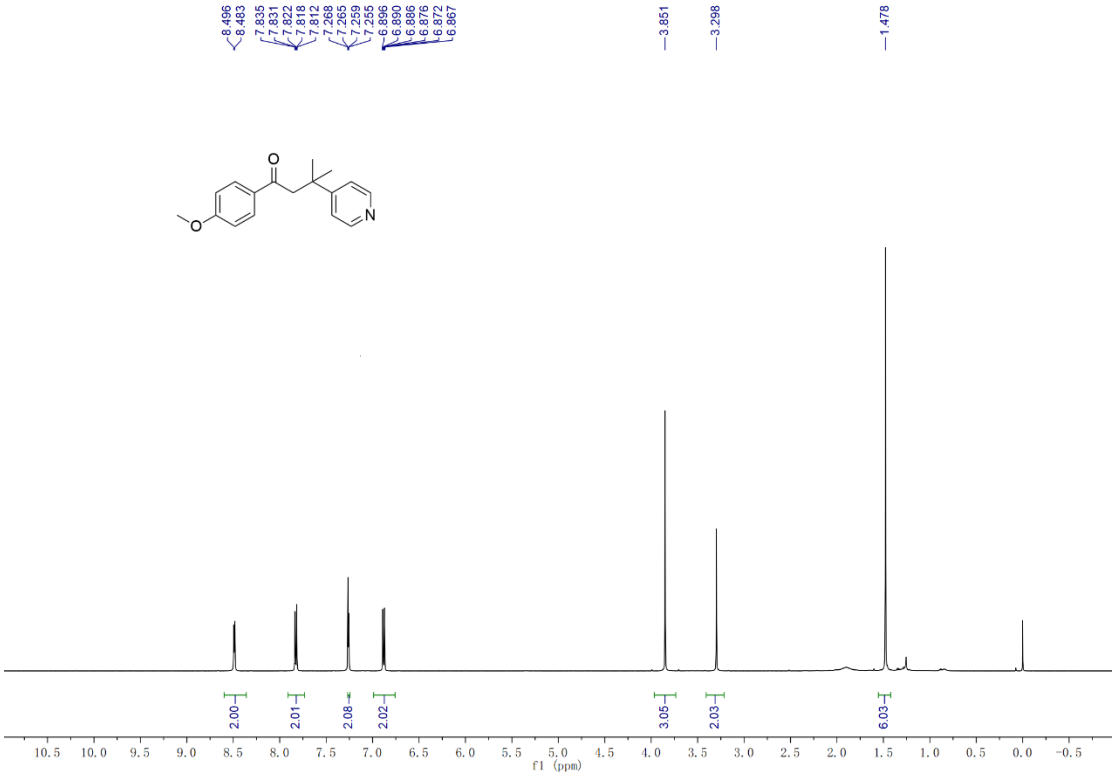
3-methyl-3-(pyridin-4-yl)-1-(p-tolyl)butan-1-one (3ba)

^{1}H NMR (400 MHz, $CDCl_3$)

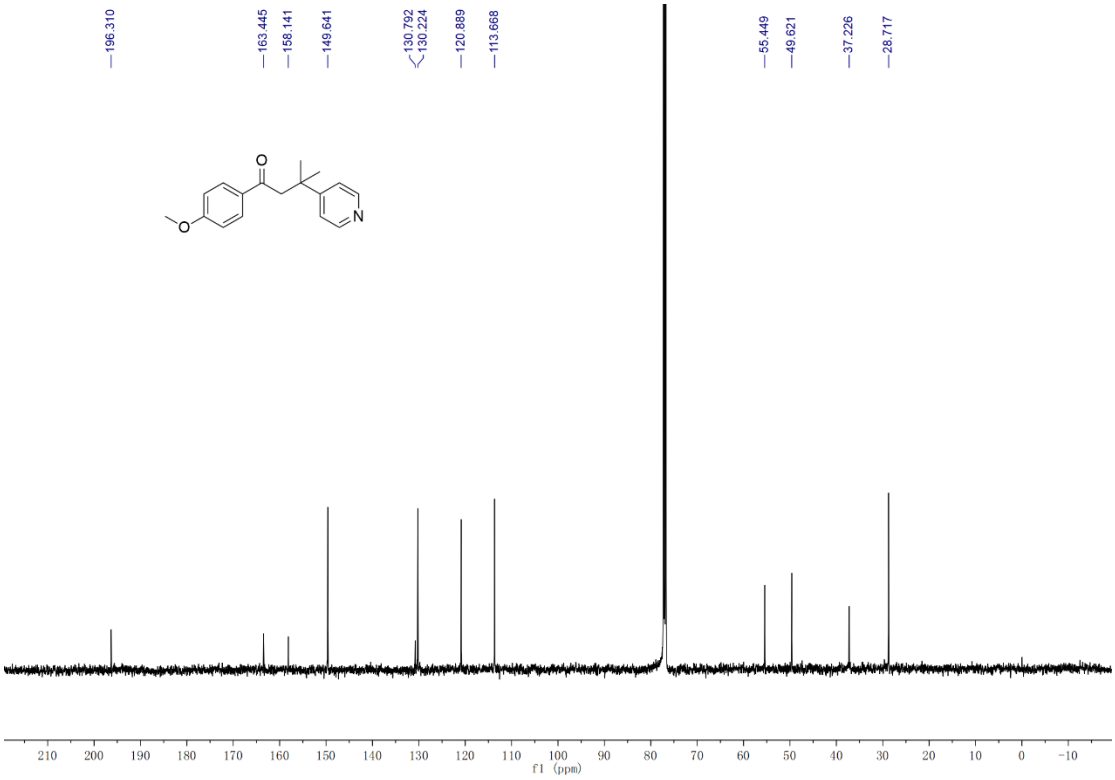


^{13}C NMR (100 MHz, $CDCl_3$)

1-(4-methoxyphenyl)-3-methyl-3-(pyridin-4-yl)butan-1-one (3ca)

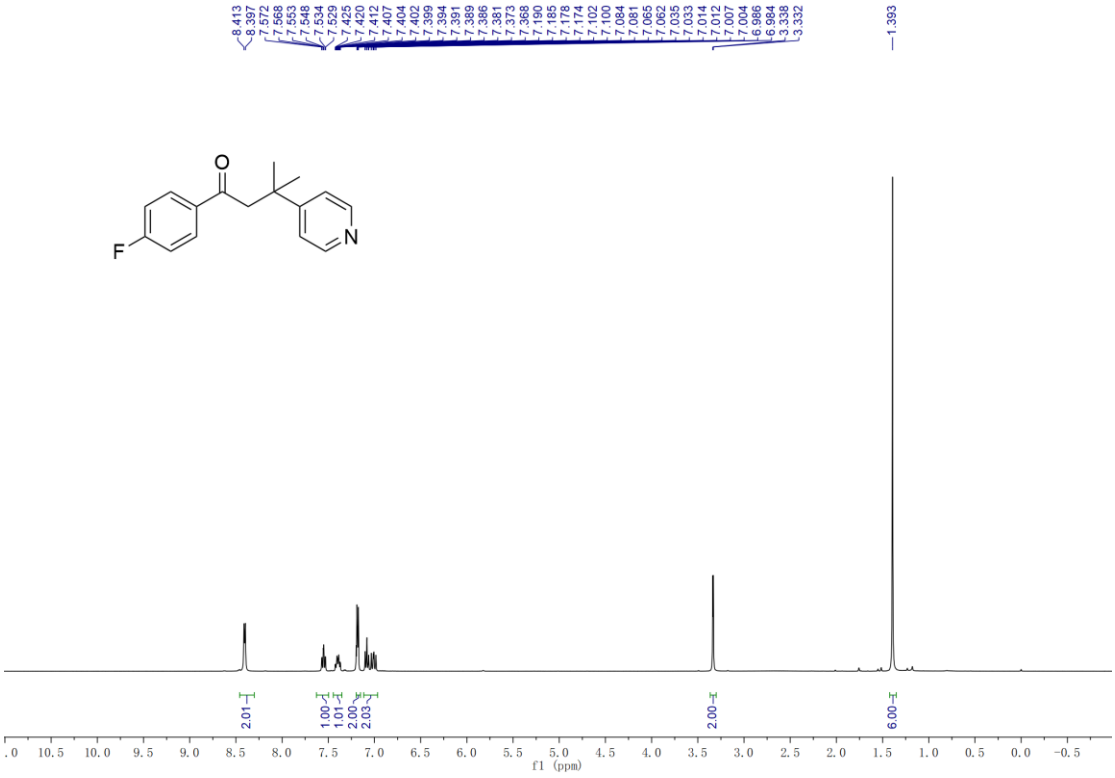


^{1}H NMR (500 MHz, $CDCl_3$)

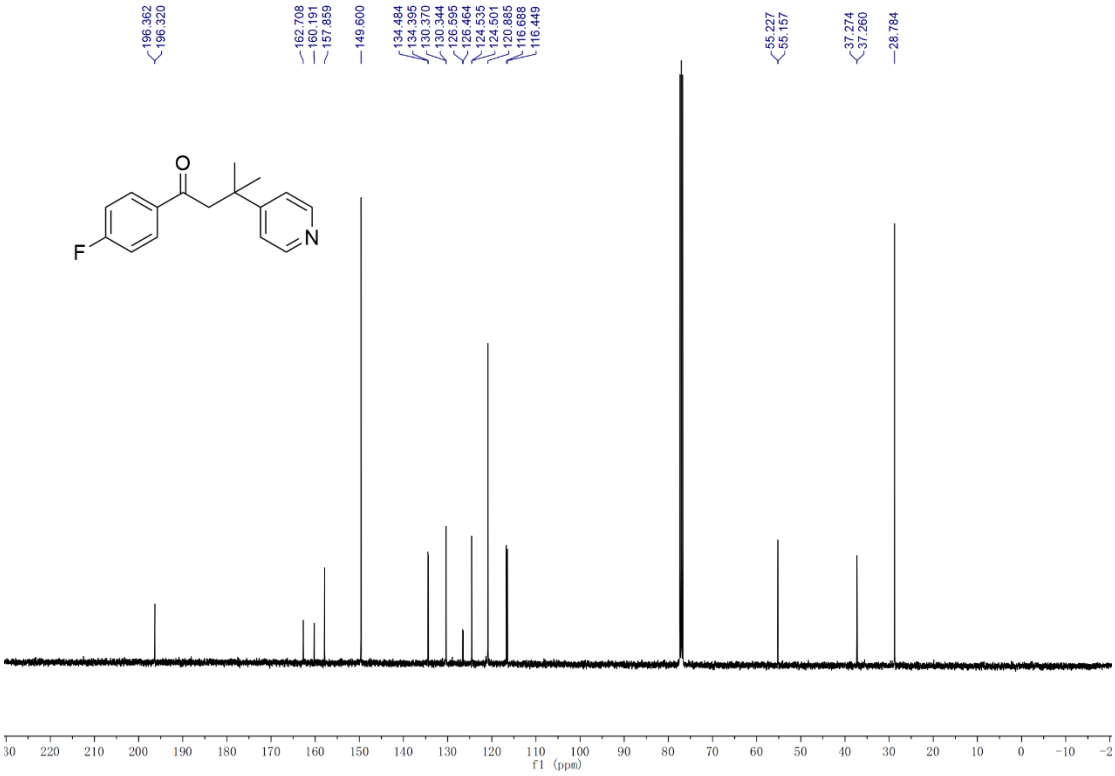


^{13}C NMR (125 MHz, $CDCl_3$)

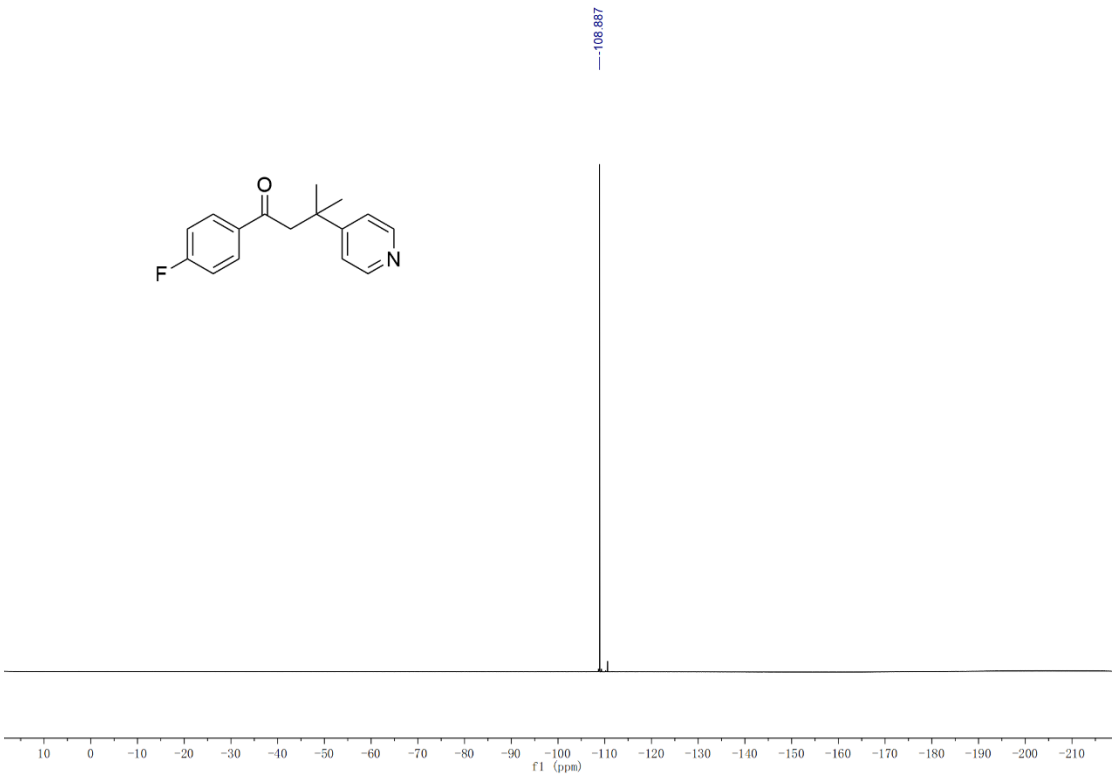
1-(4-fluorophenyl)-3-methyl-3-(pyridin-4-yl)butan-1-one (3da)



^{1}H NMR (400 MHz, $CDCl_3$)

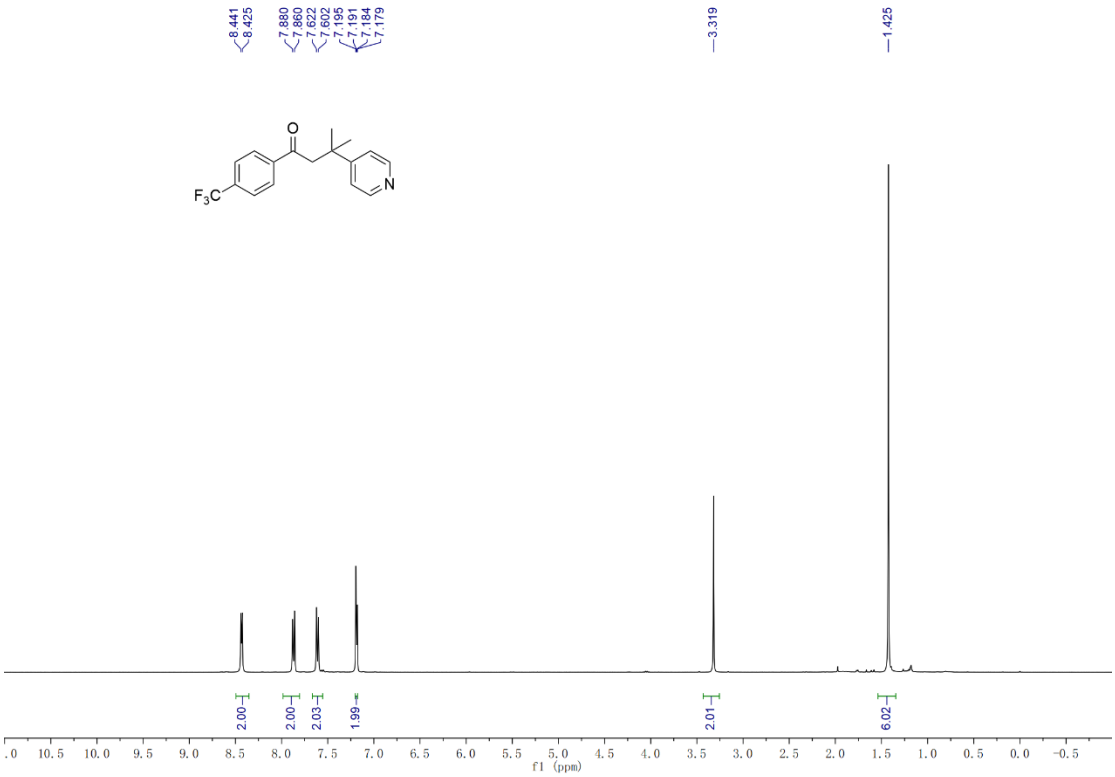


^{13}C NMR (100 MHz, $CDCl_3$)

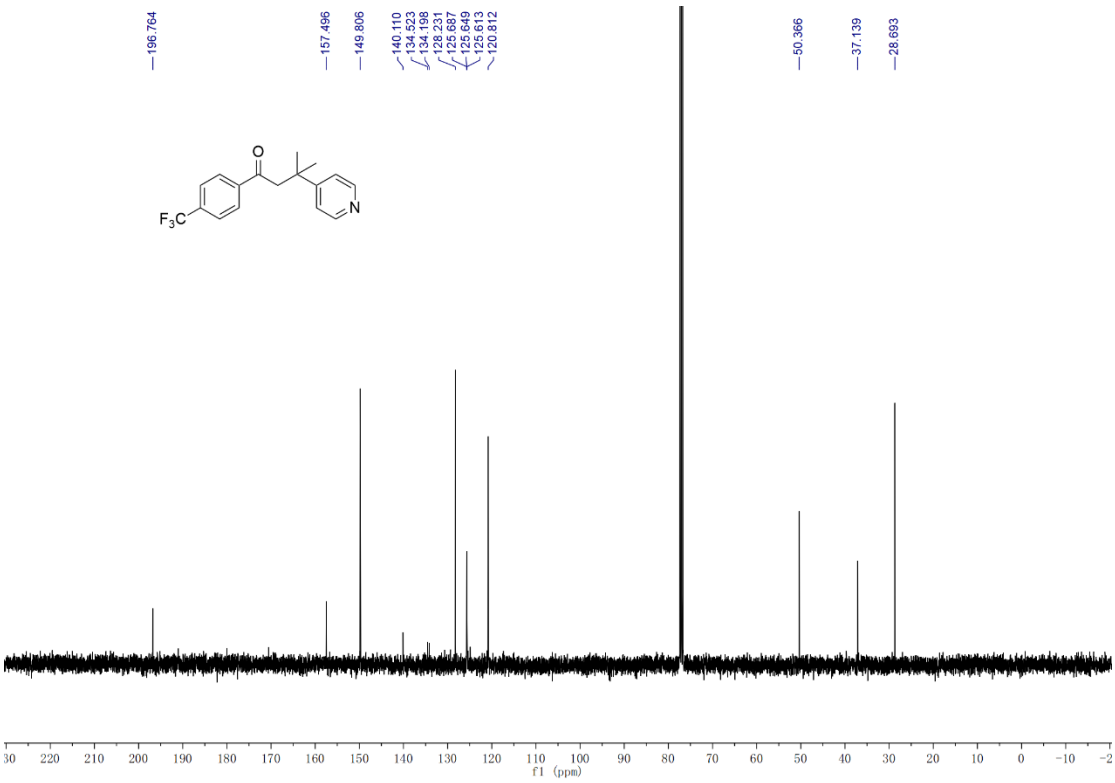


^{19}F NMR (376 MHz, $CDCl_3$)

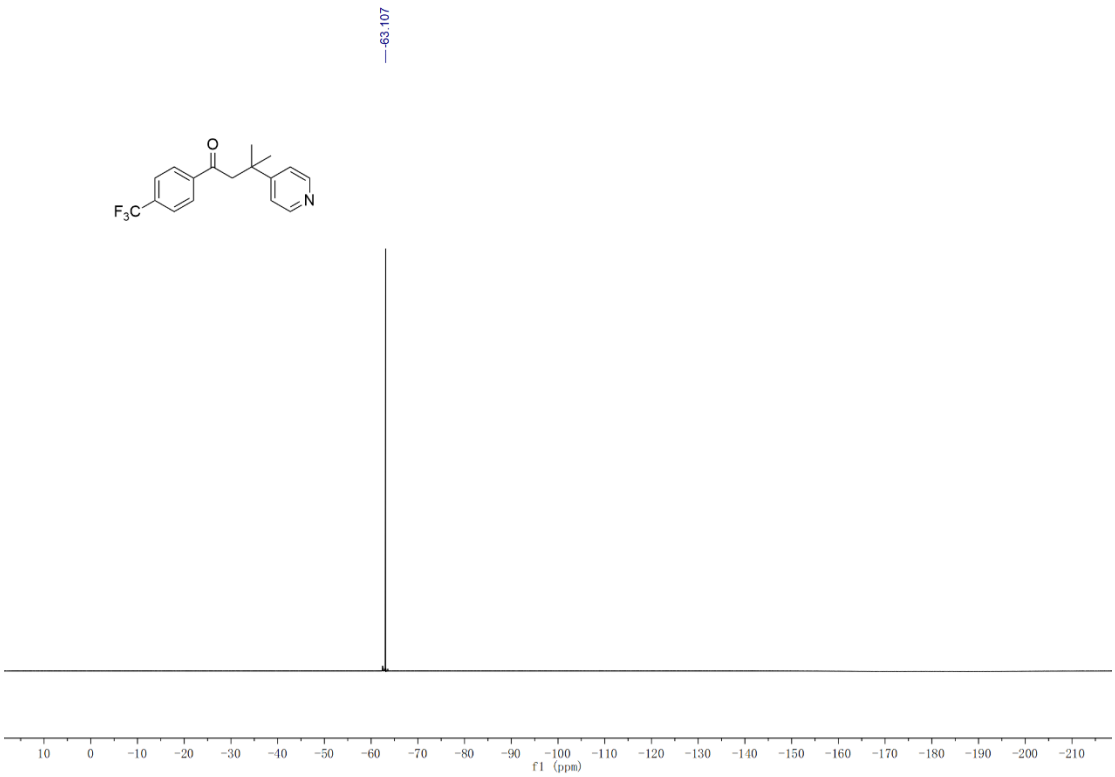
3-methyl-3-(pyridin-4-yl)-1-(4-(trifluoromethyl)phenyl)butan-1-one (3ea)



^{1}H NMR (400 MHz, $CDCl_3$)

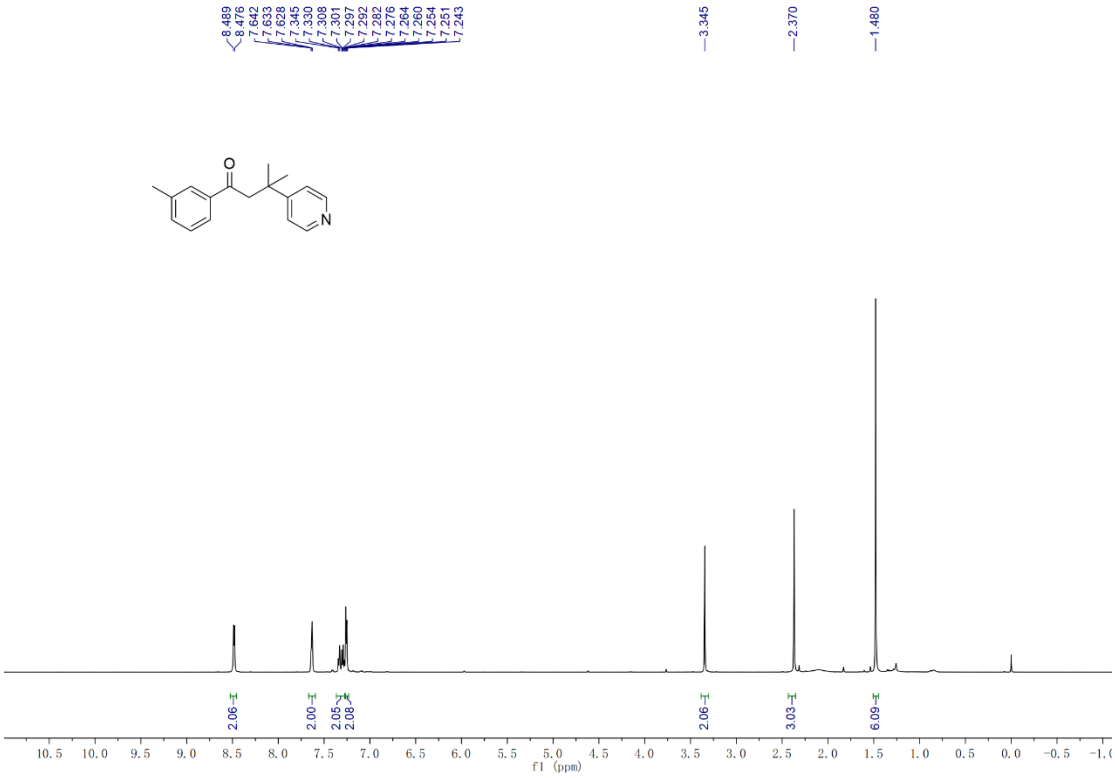


^{13}C NMR (100 MHz, $CDCl_3$)

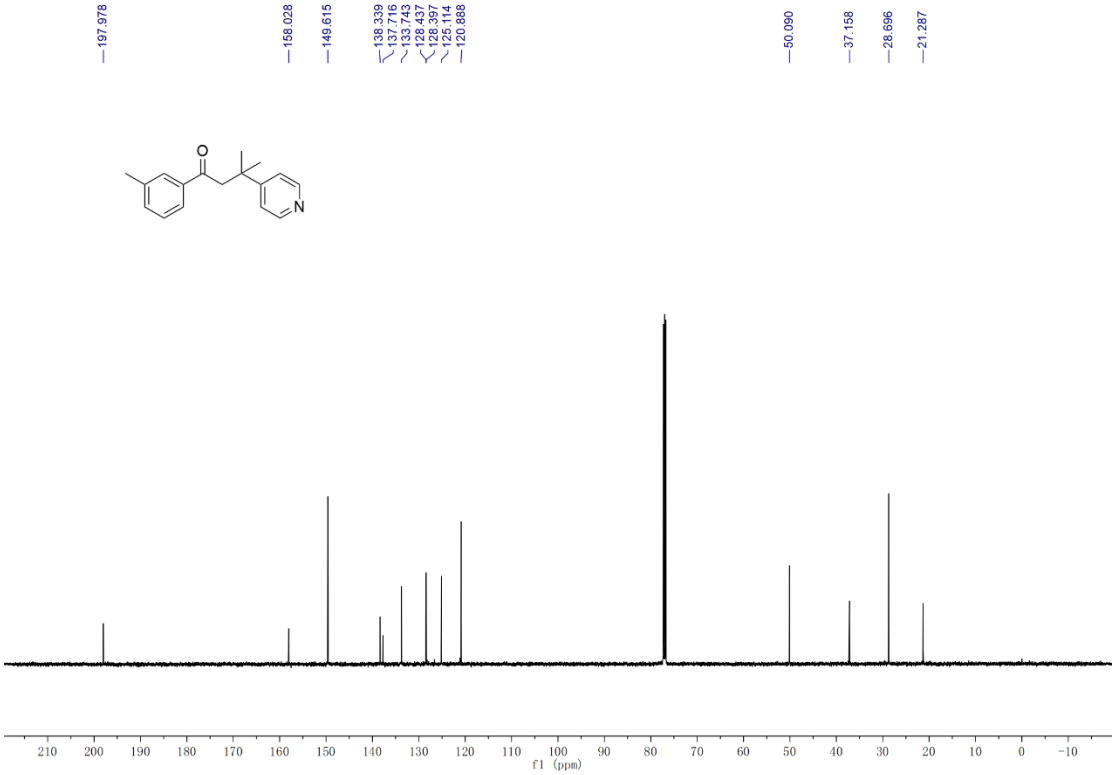


^{19}F NMR (376 MHz, $CDCl_3$)

3-methyl-3-(pyridin-4-yl)-1-(m-tolyl)butan-1-one (3fa)

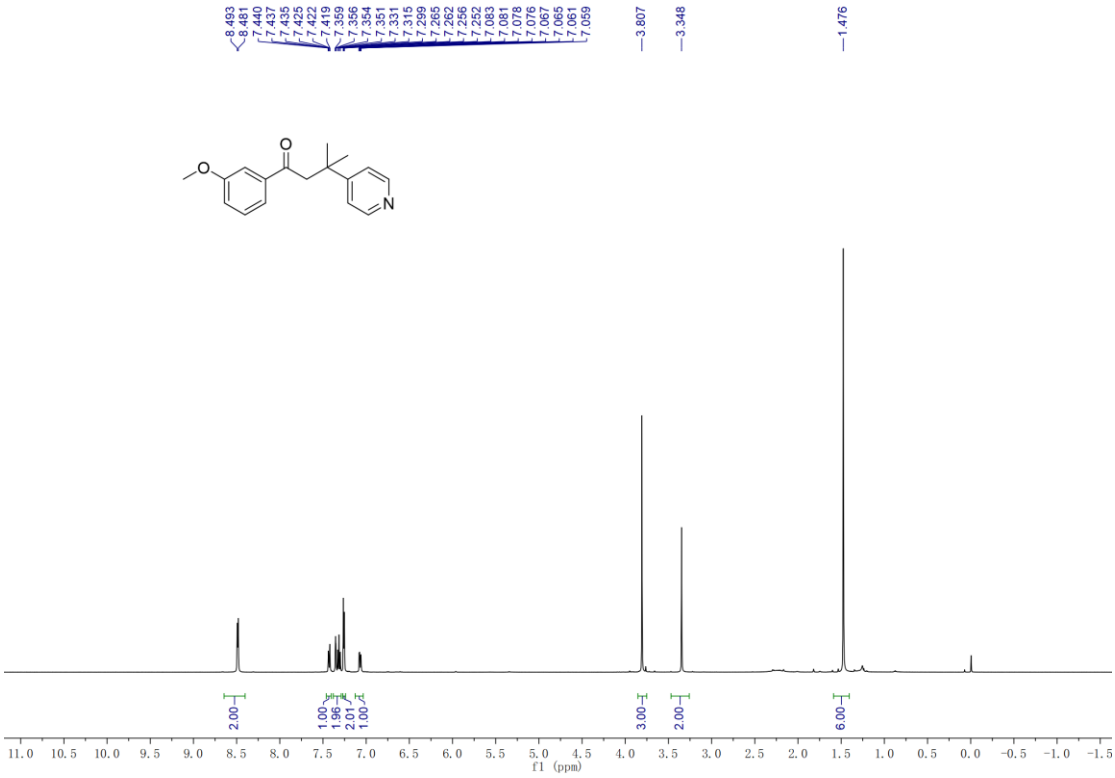


^{1}H NMR (500 MHz, $CDCl_3$)

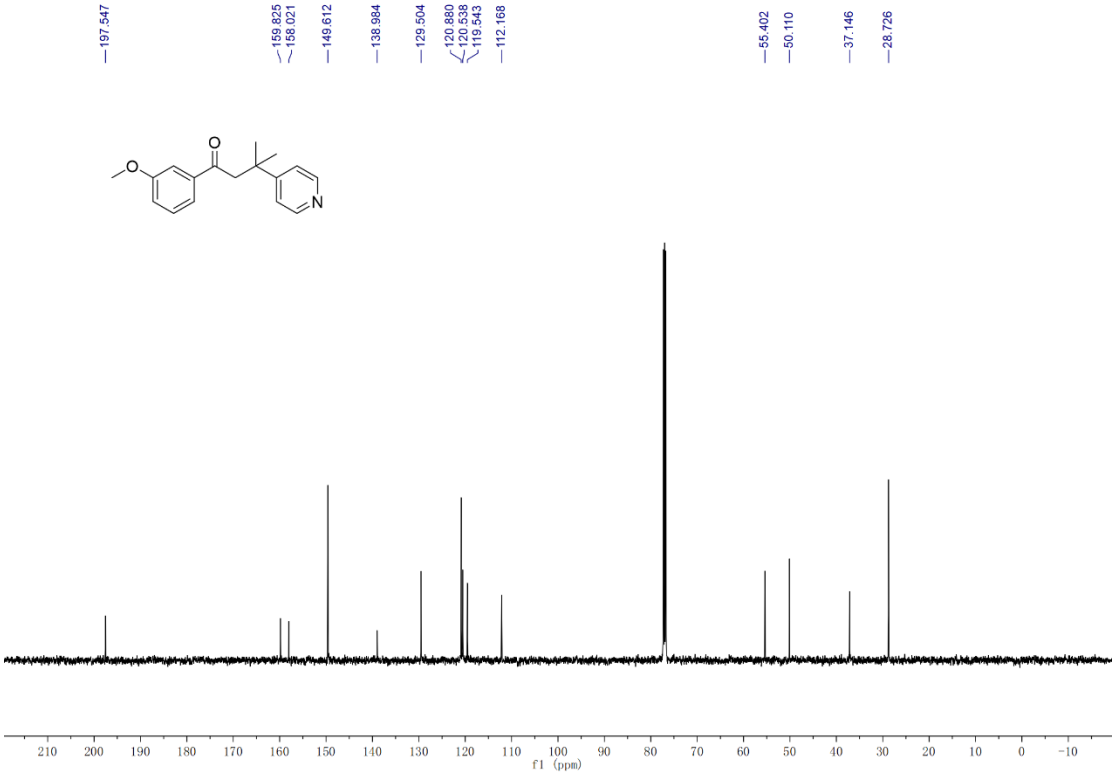


^{13}C NMR (125 MHz, $CDCl_3$)

1-(3-methoxyphenyl)-3-methyl-3-(pyridin-4-yl)butan-1-one (3ga)

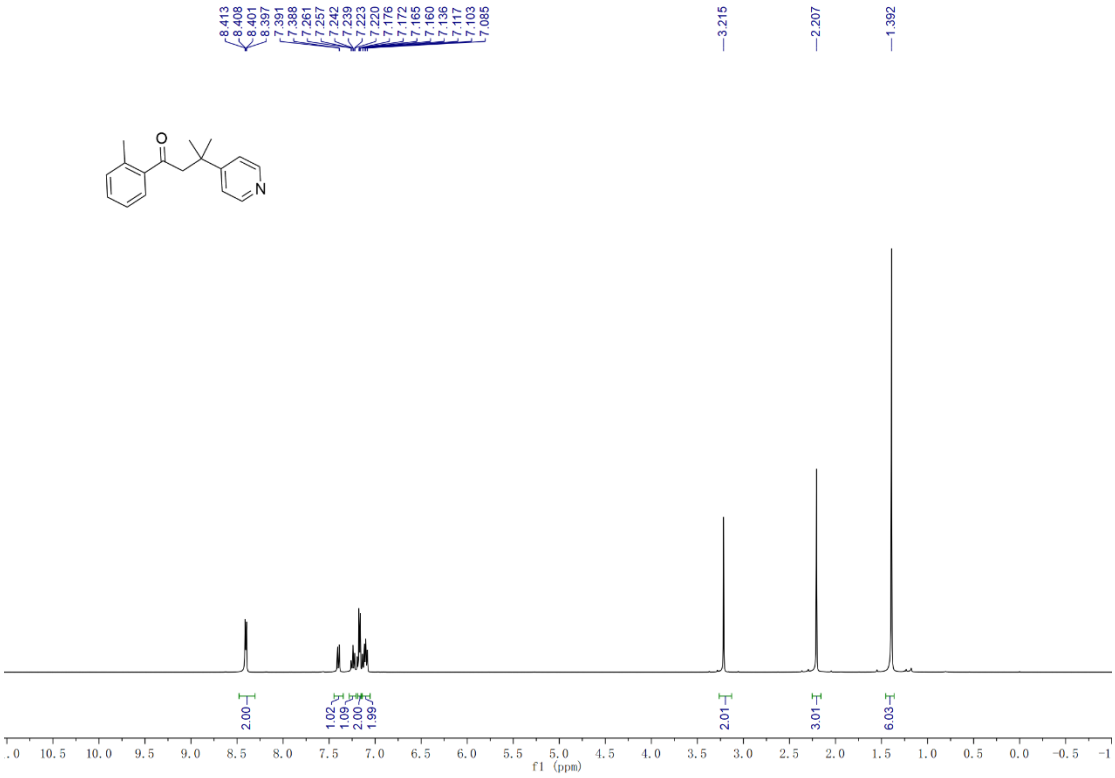


^{1}H NMR (500 MHz, $CDCl_3$)

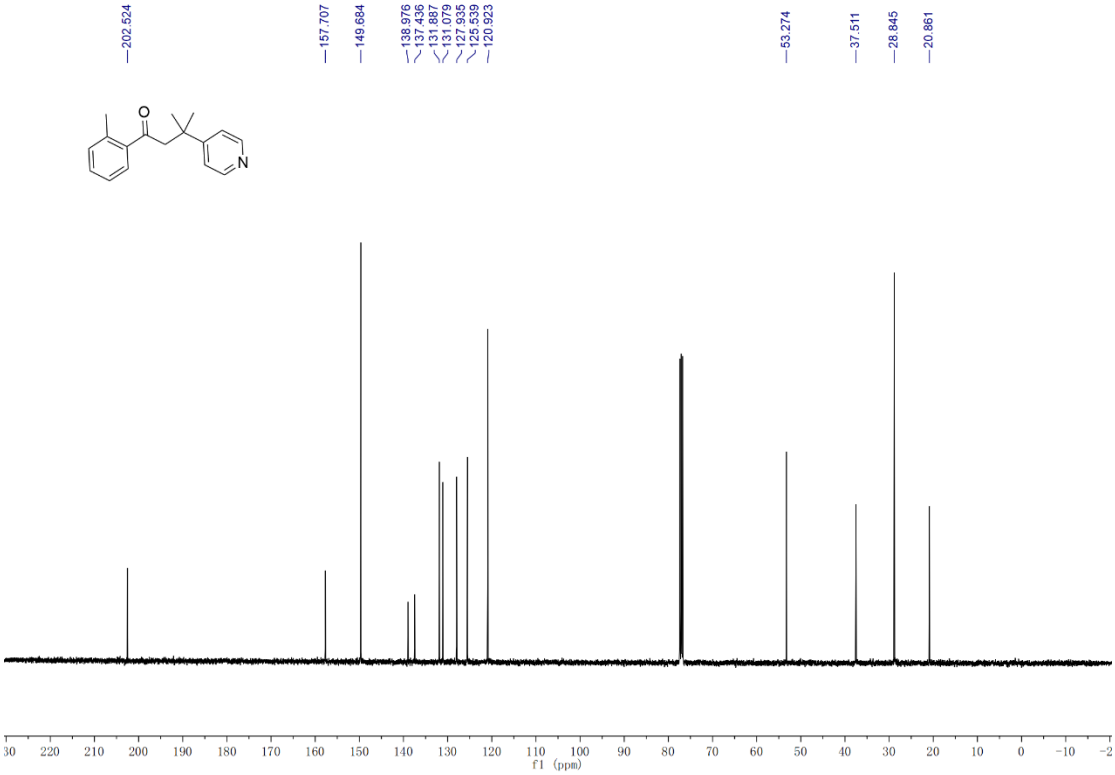


^{13}C NMR (125 MHz, $CDCl_3$)

3-methyl-3-(pyridin-4-yl)-1-(o-tolyl)butan-1-one (3ha)

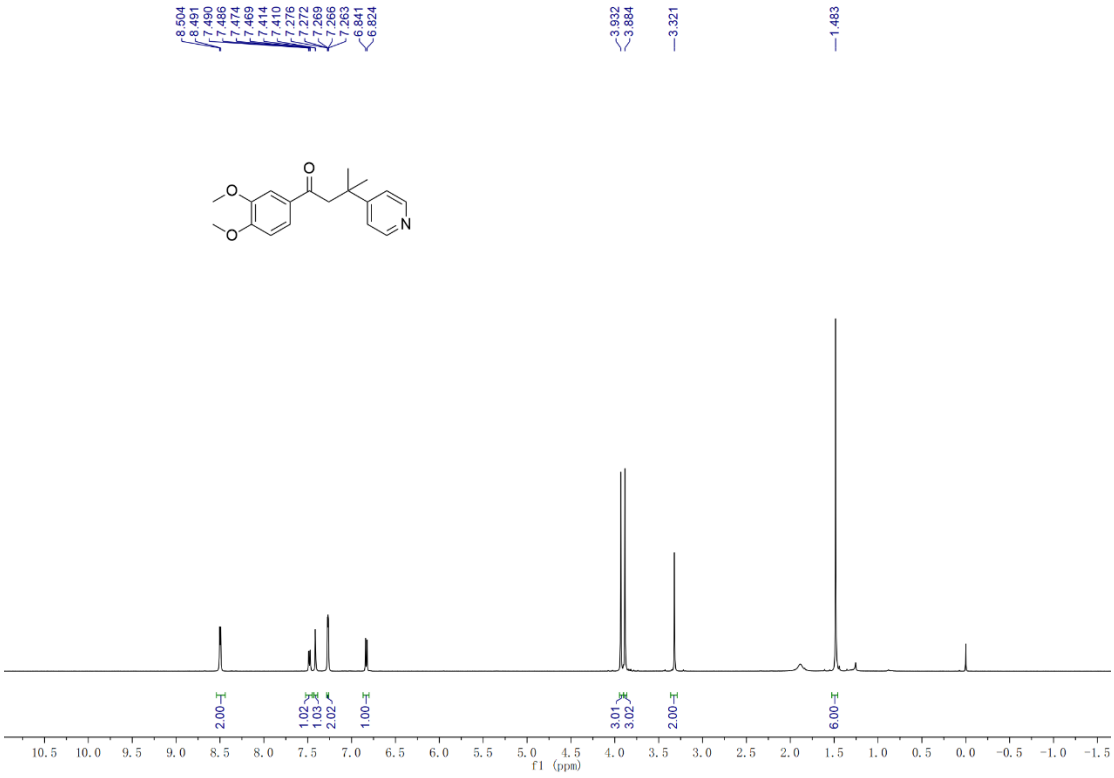


^{1}H NMR (400 MHz, $CDCl_3$)

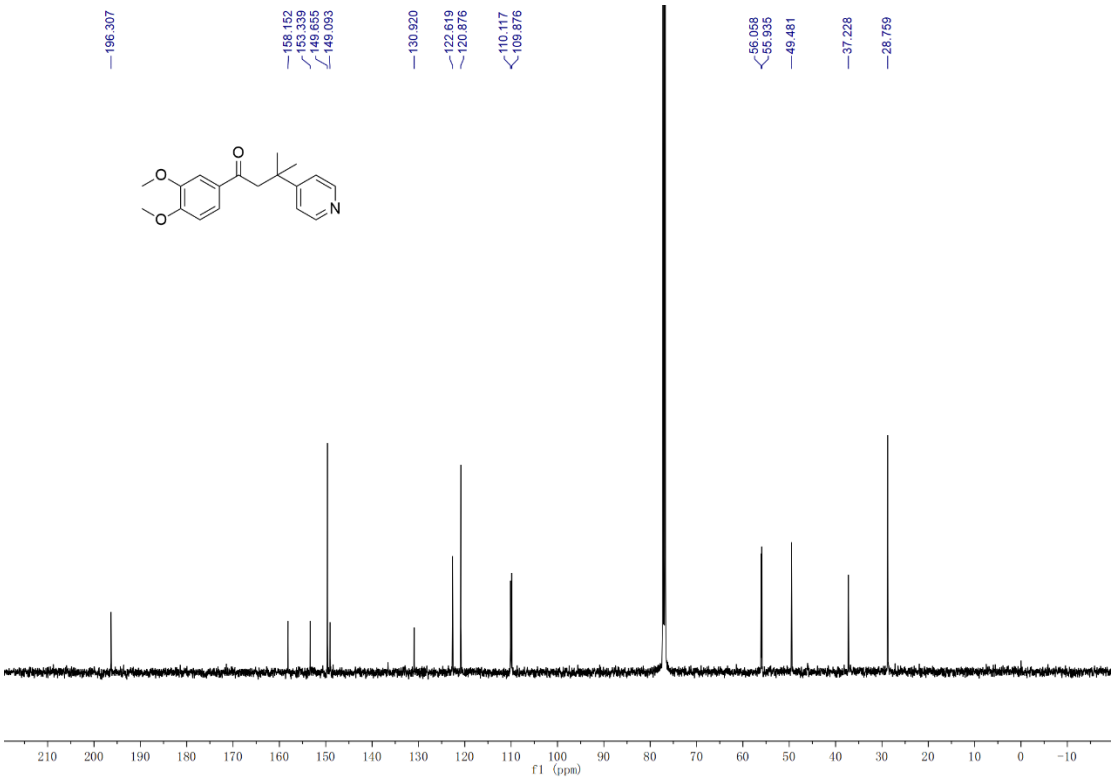


^{13}C NMR (100 MHz, $CDCl_3$)

1-(3,4-dimethoxyphenyl)-3-methyl-3-(pyridin-4-yl)butan-1-one (3ja)

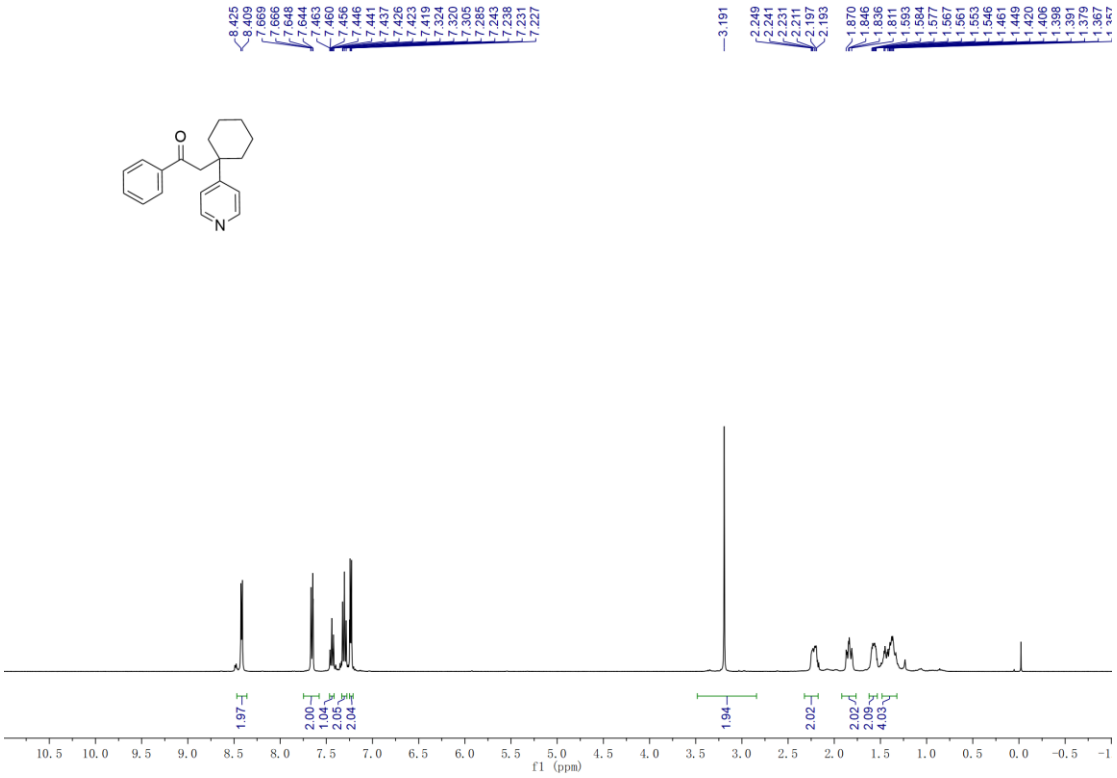


^{1}H NMR (500 MHz, $CDCl_3$)

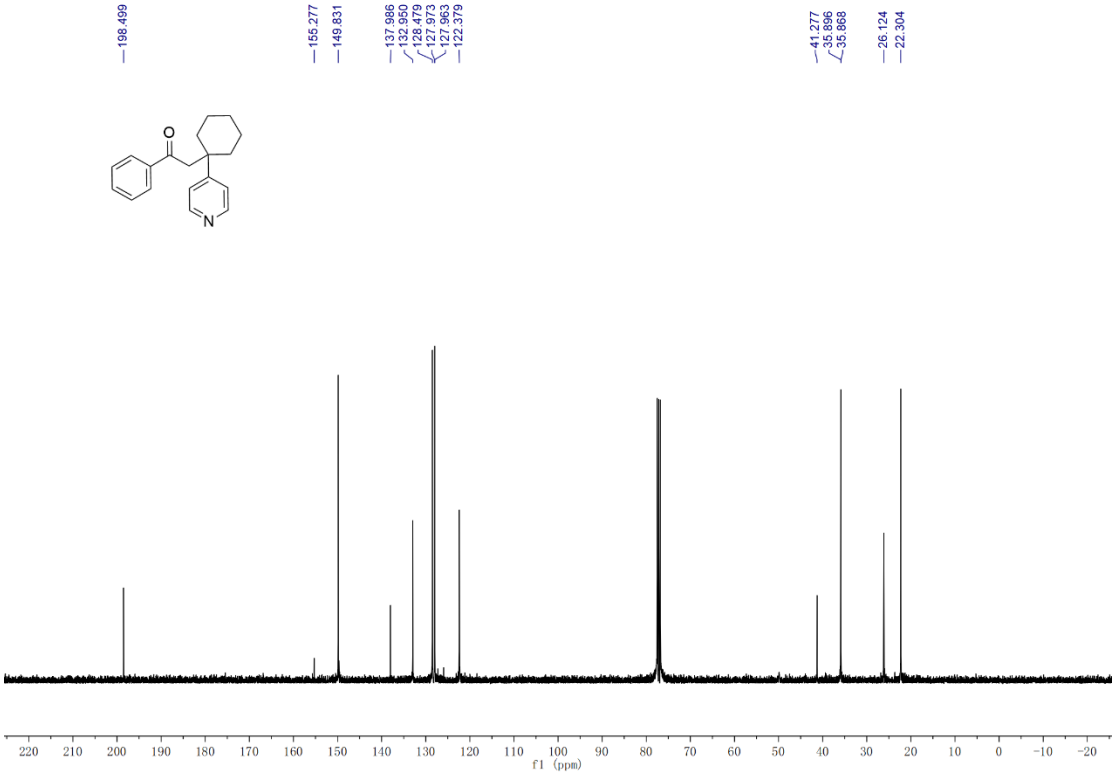


^{13}C NMR (125 MHz, $CDCl_3$)

1-phenyl-2-(1-(pyridin-4-yl)cyclohexyl)ethan-1-one (3ka)

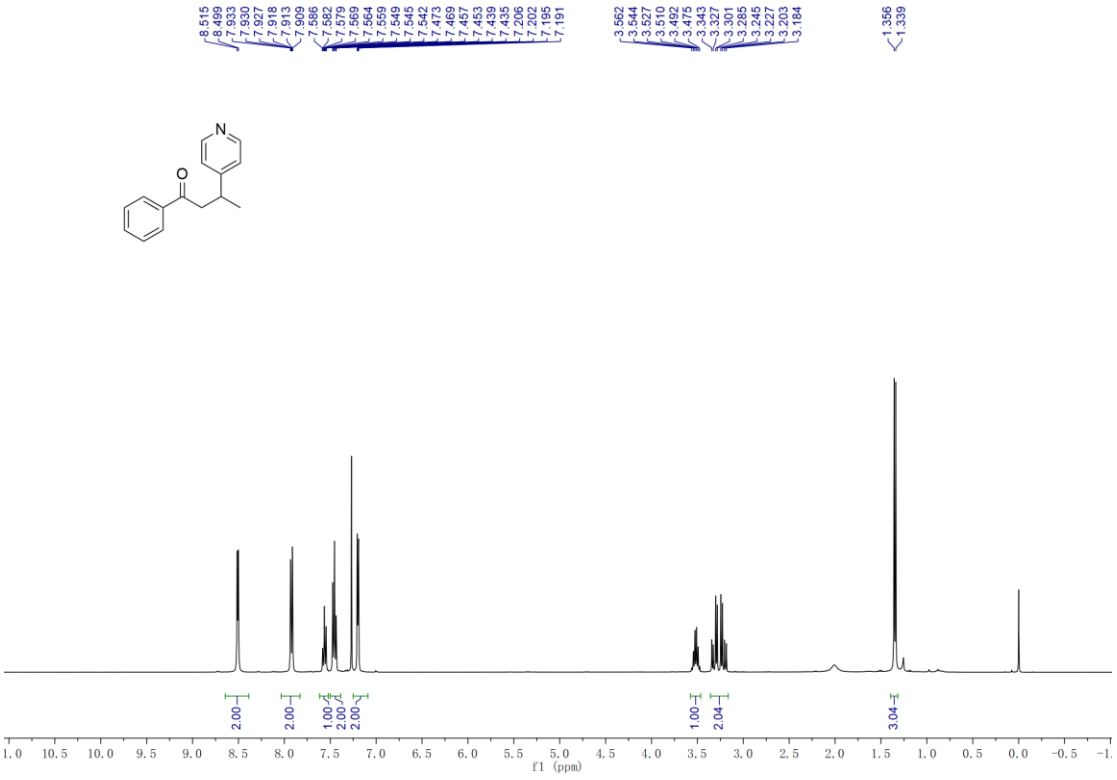


^{1}H NMR (400 MHz, $CDCl_3$)

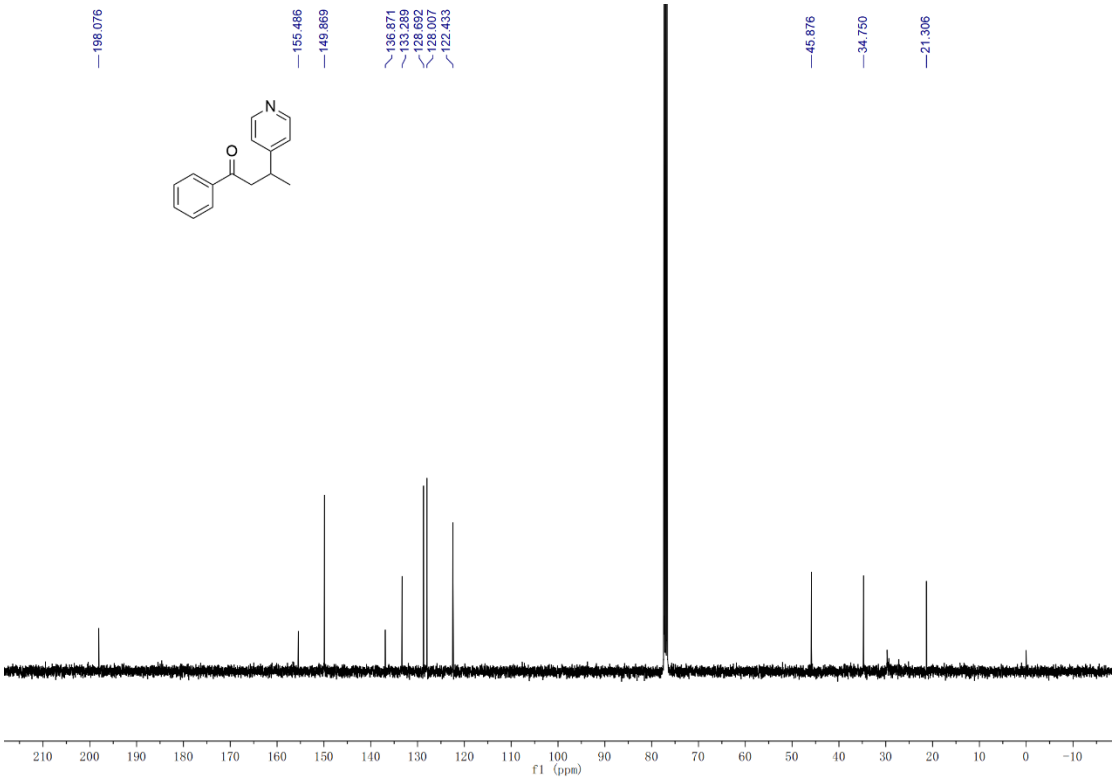


^{13}C NMR (100 MHz, $CDCl_3$)

1-phenyl-3-(pyridin-4-yl)butan-1-one (3la)

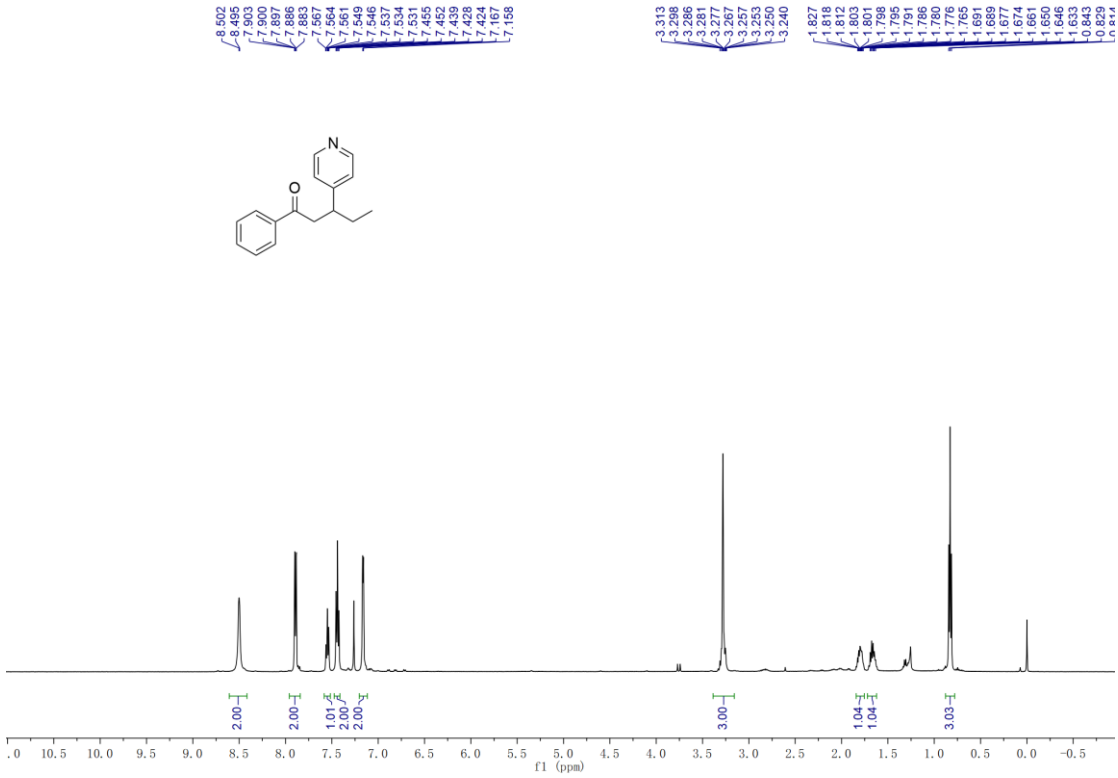


^{1}H NMR (400 MHz, $CDCl_3$)

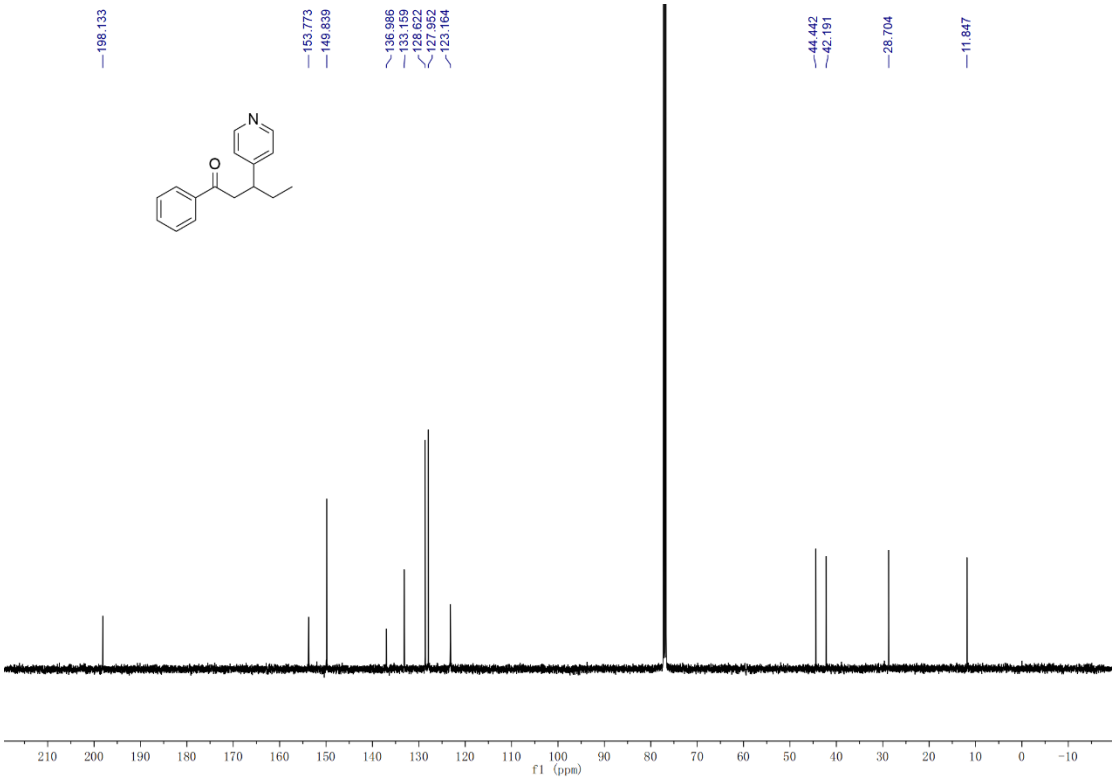


^{13}C NMR (100 MHz, $CDCl_3$)

1-phenyl-3-(pyridin-4-yl)pentan-1-one (3ma)

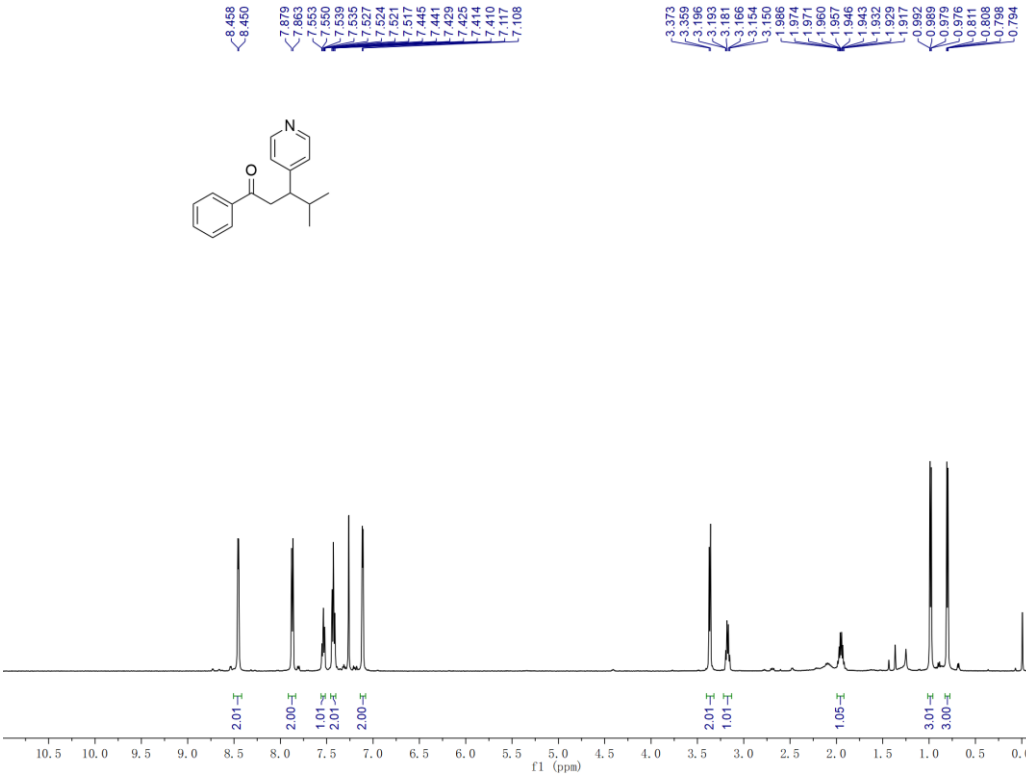


^{1}H NMR (500 MHz, $CDCl_3$)

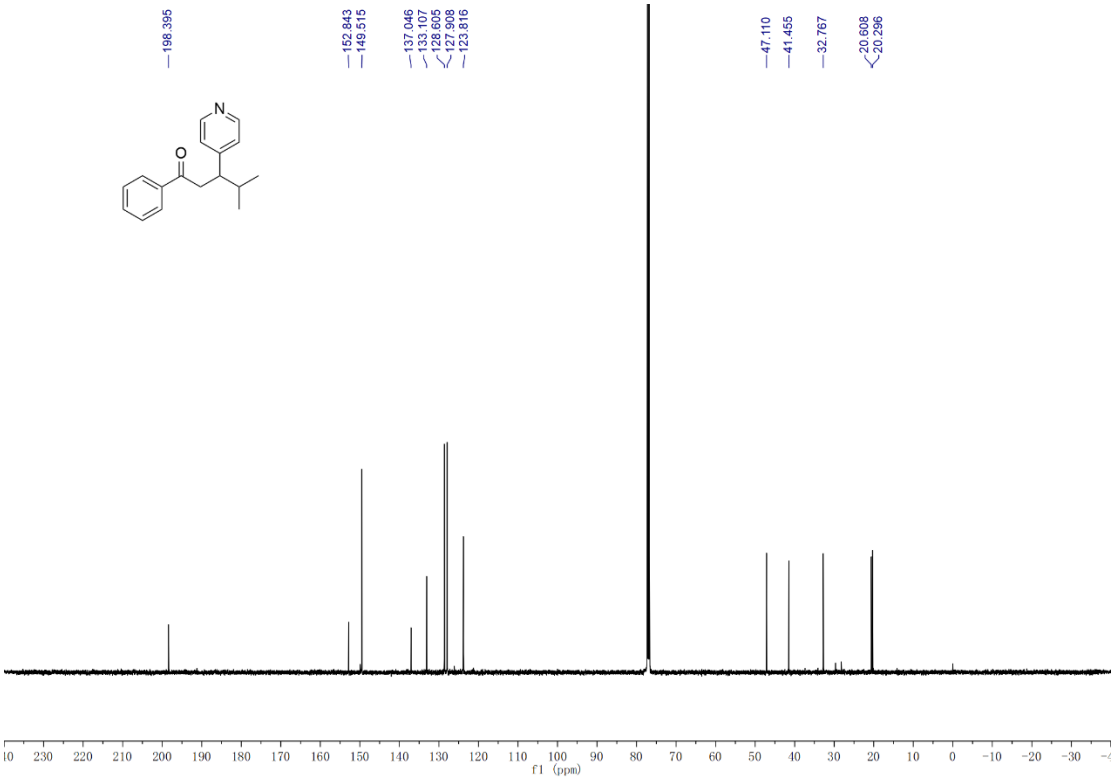


^{13}C NMR (125 MHz, $CDCl_3$)

4-methyl-1-phenyl-3-(pyridin-4-yl)pentan-1-one (3na)

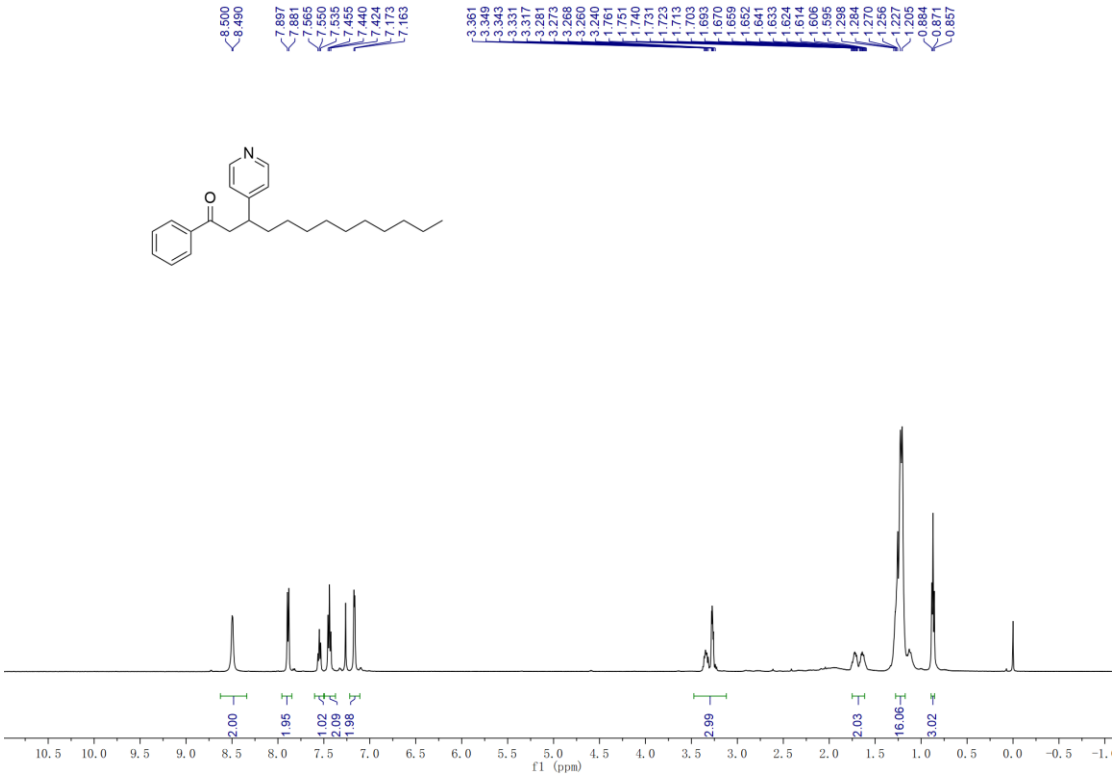


^{1}H NMR (500 MHz, $CDCl_3$)

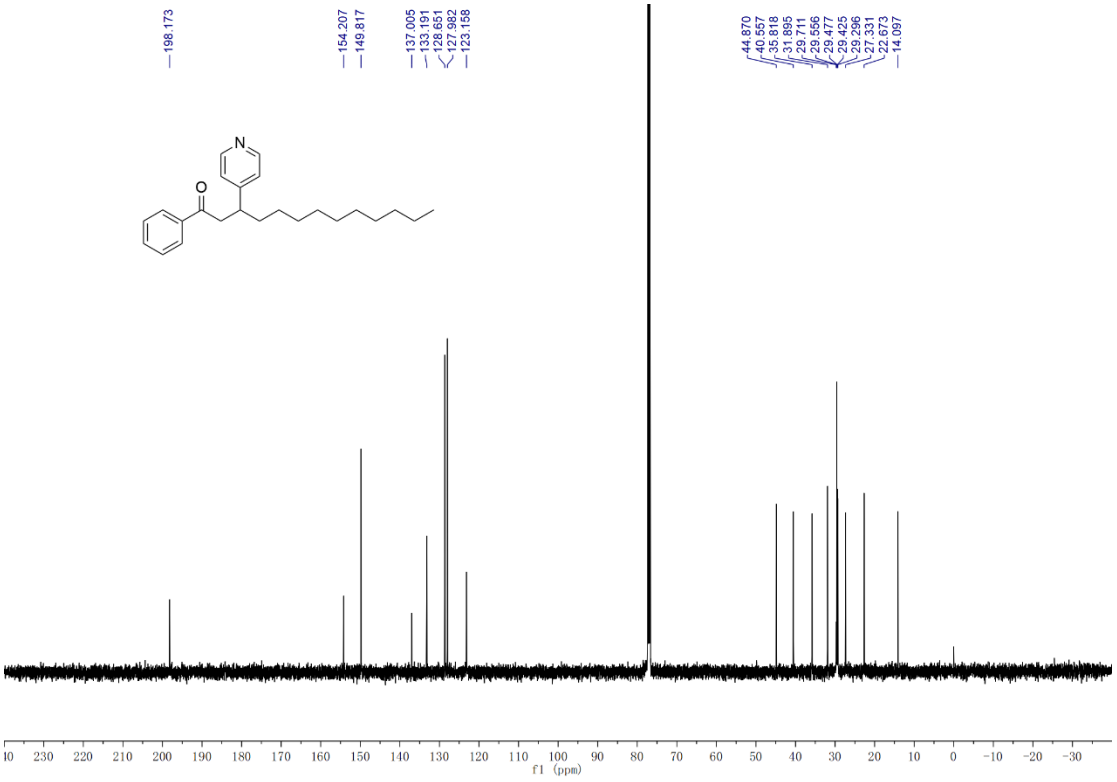


^{13}C NMR (125 MHz, $CDCl_3$)

1-phenyl-3-(pyridin-4-yl)tridecan-1-one (3oa)

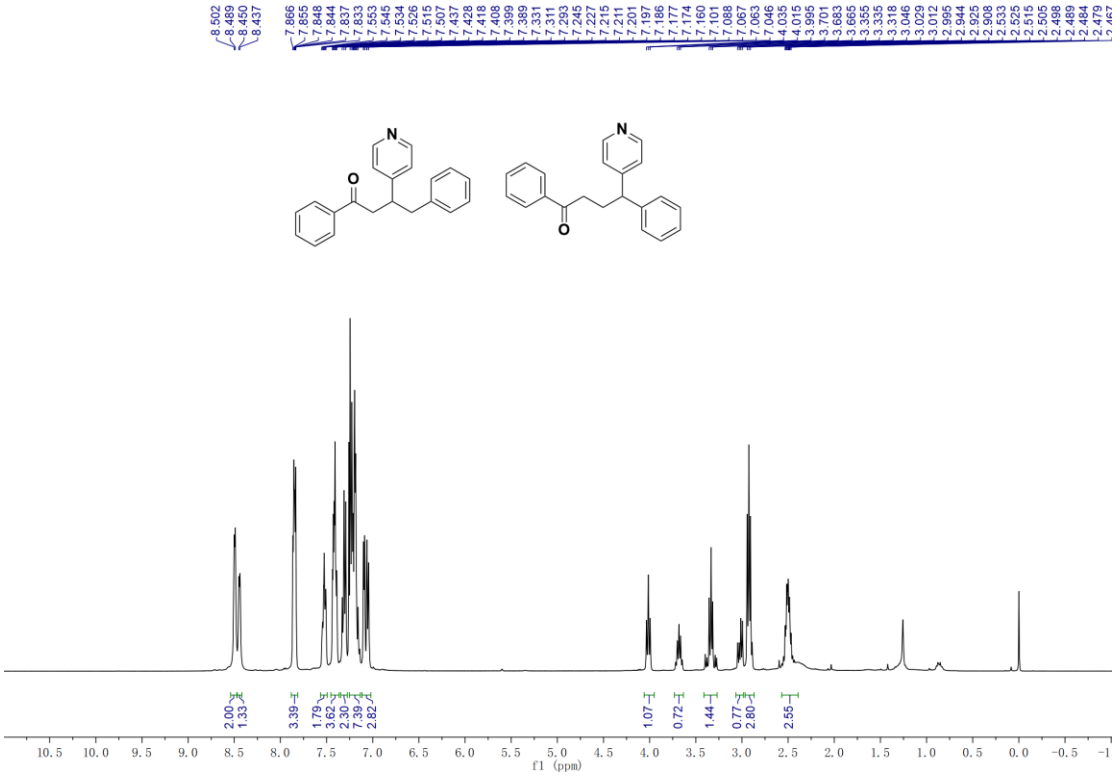


^{1}H NMR (500 MHz, $CDCl_3$)

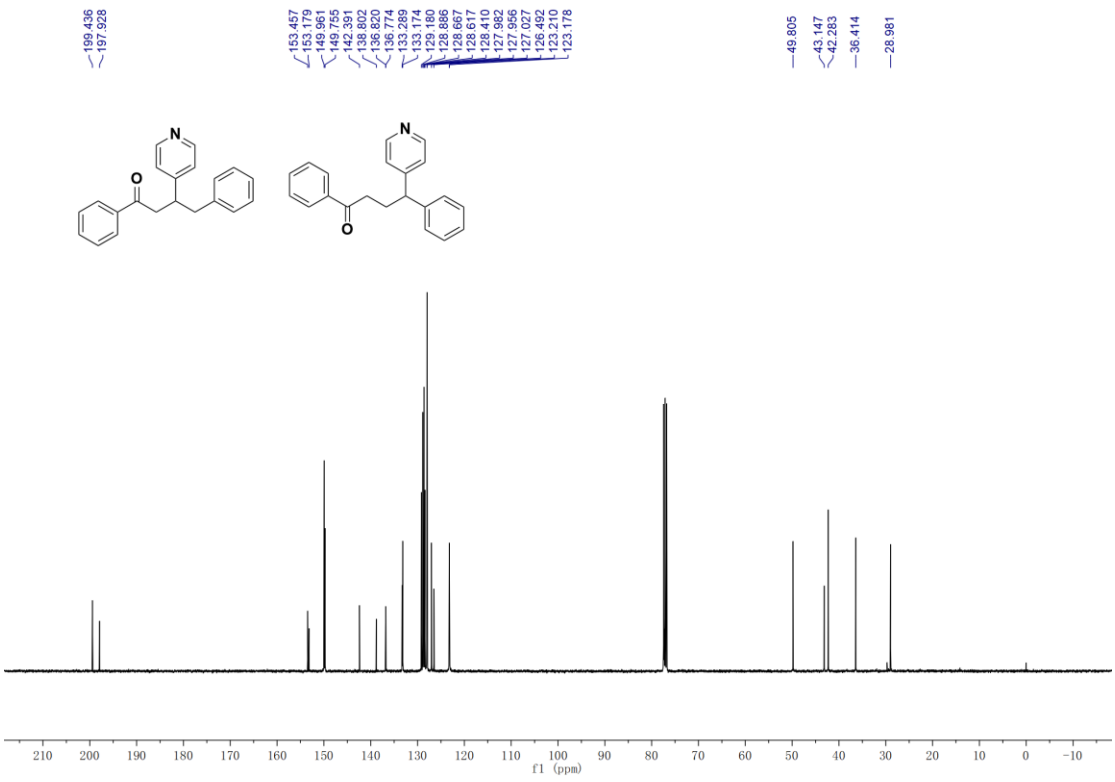


^{13}C NMR (125 MHz, $CDCl_3$)

1,4-diphenyl-3-(pyridin-4-yl)butan-1-one (3pa) + 1,4-diphenyl-4-(pyridin-4-yl)butan-1-one (3pa')

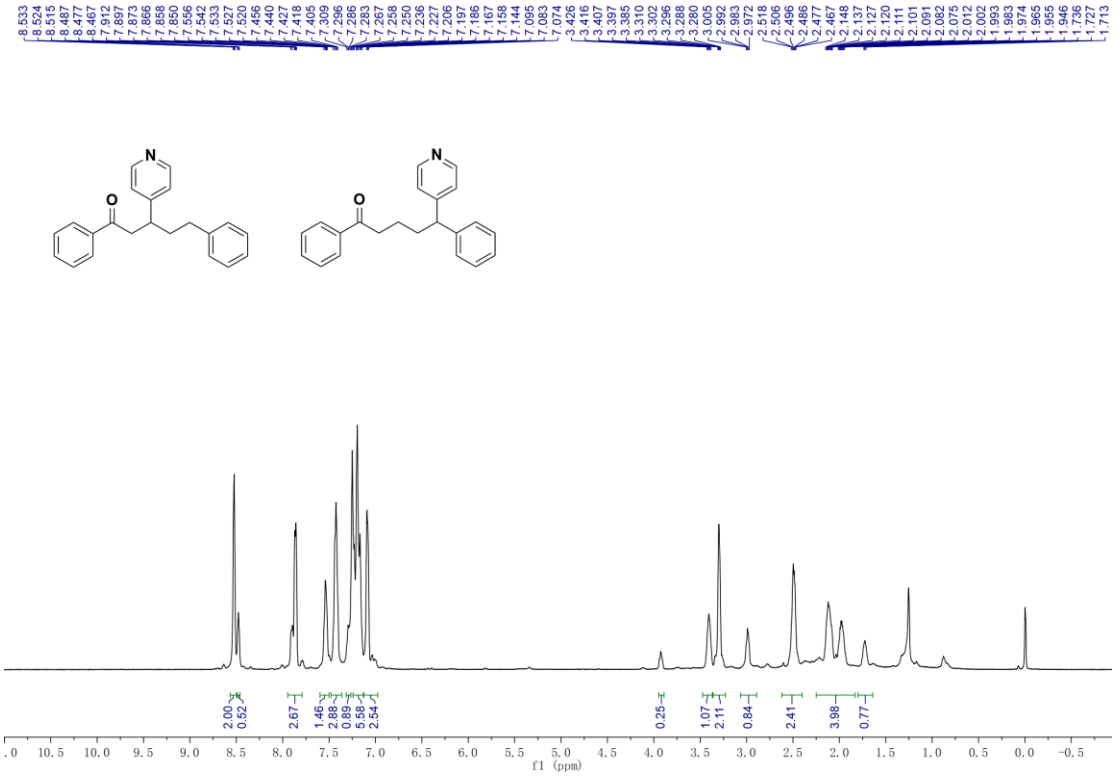


^{1}H NMR (400 MHz, $CDCl_3$)

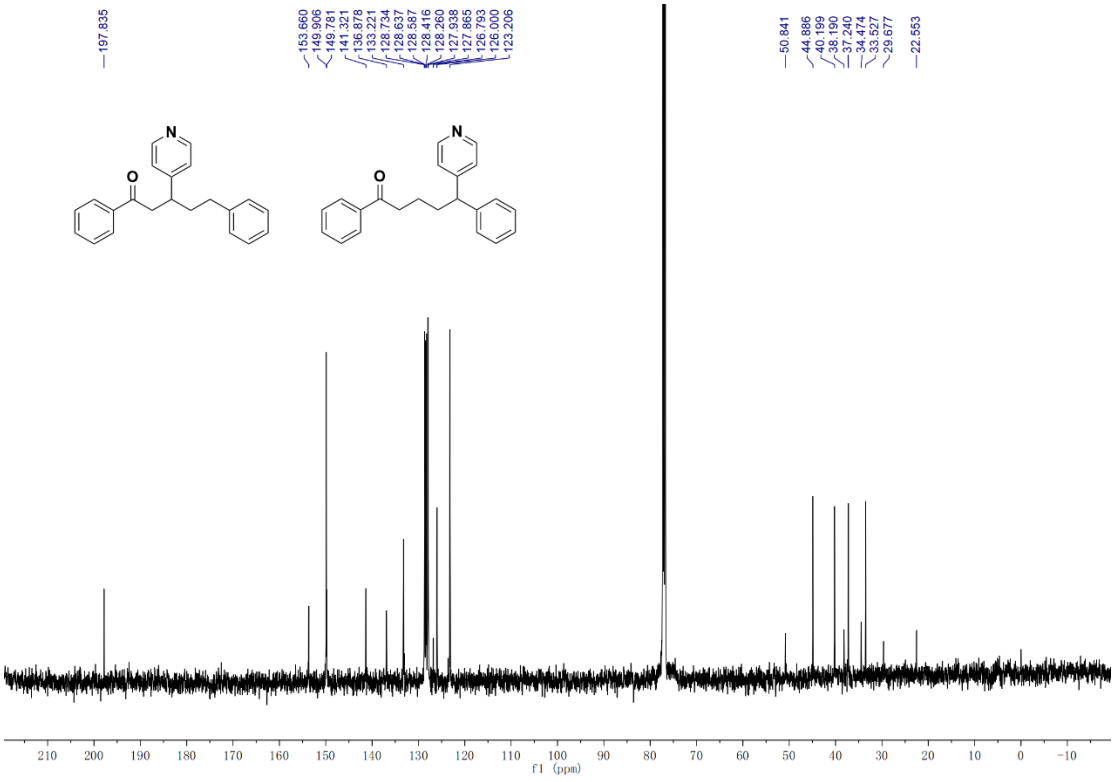


^{13}C NMR (100 MHz, $CDCl_3$)

1,5-diphenyl-3-(pyridin-4-yl)pentan-1-one (3qa) + 1,5-diphenyl-5-(pyridin-4-yl)pentan-1-one(3qa')

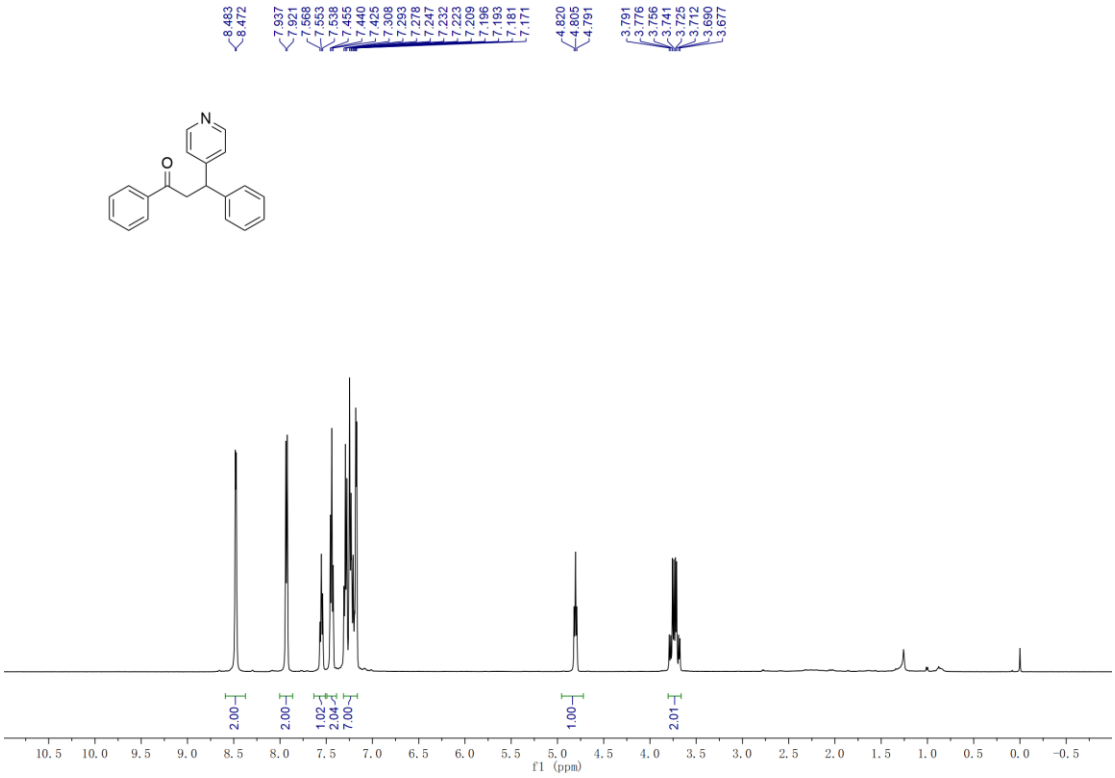


^{1}H NMR (500 MHz, $CDCl_3$)

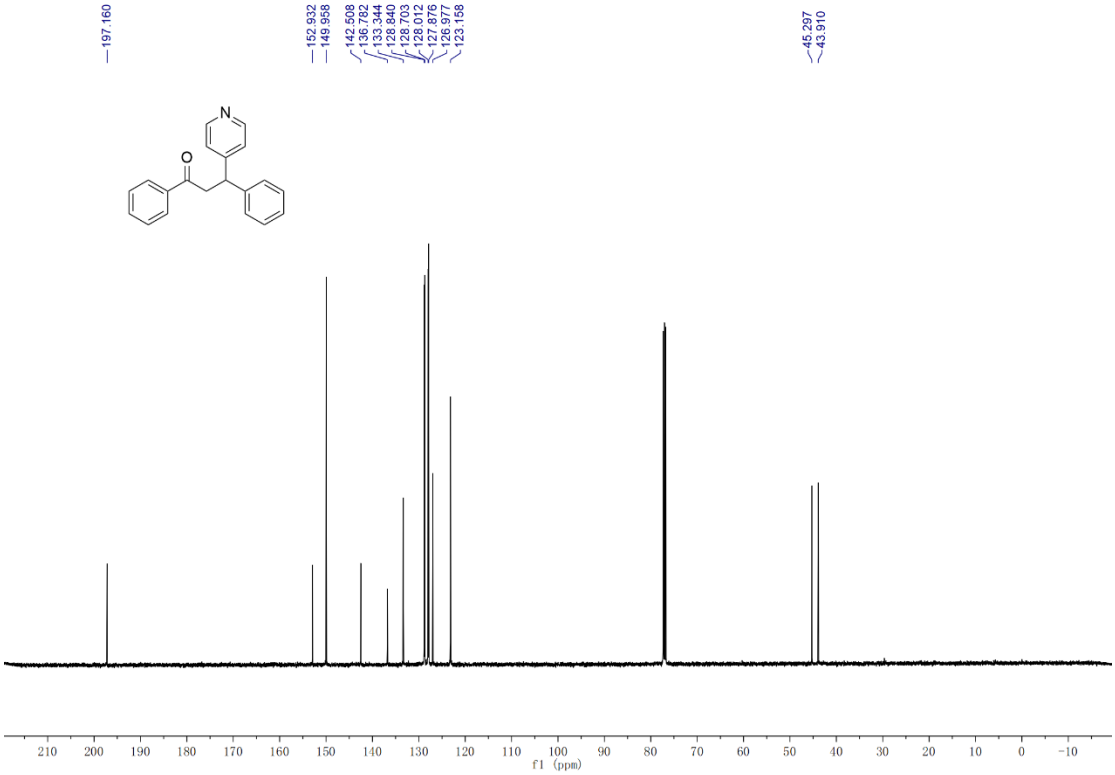


^{13}C NMR (125 MHz, $CDCl_3$)

1,3-diphenyl-3-(pyridin-4-yl)propan-1-one (3ra)

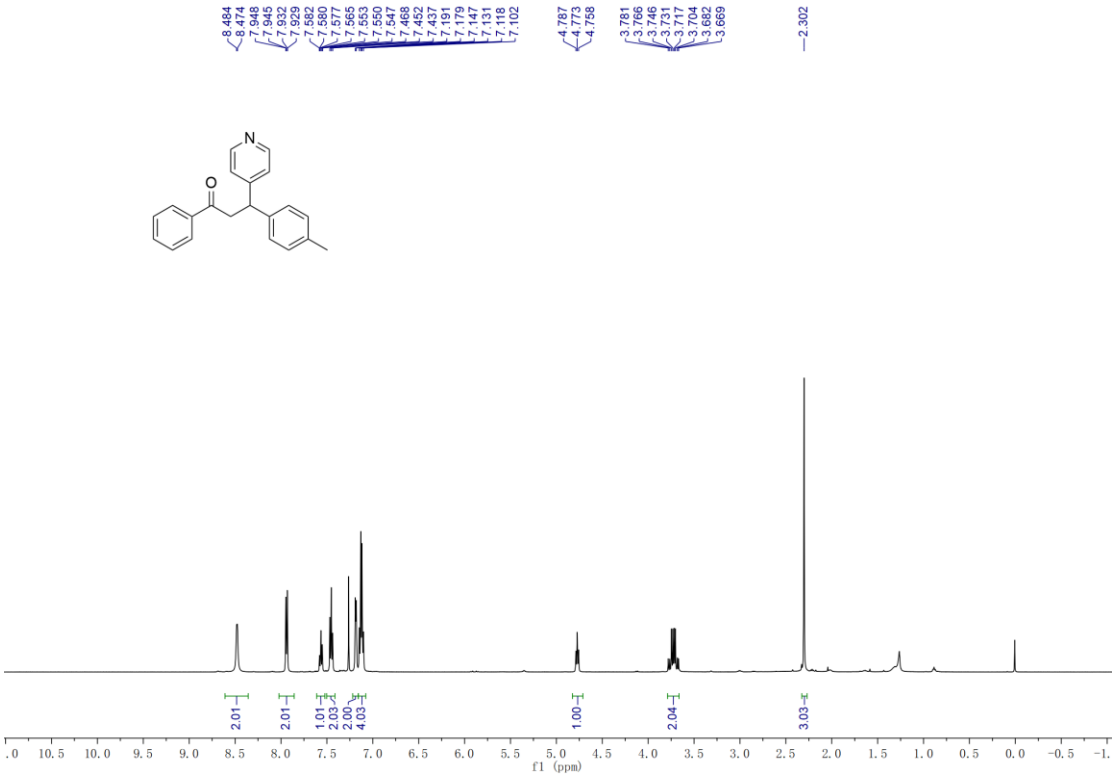


^{1}H NMR (500 MHz, $CDCl_3$)

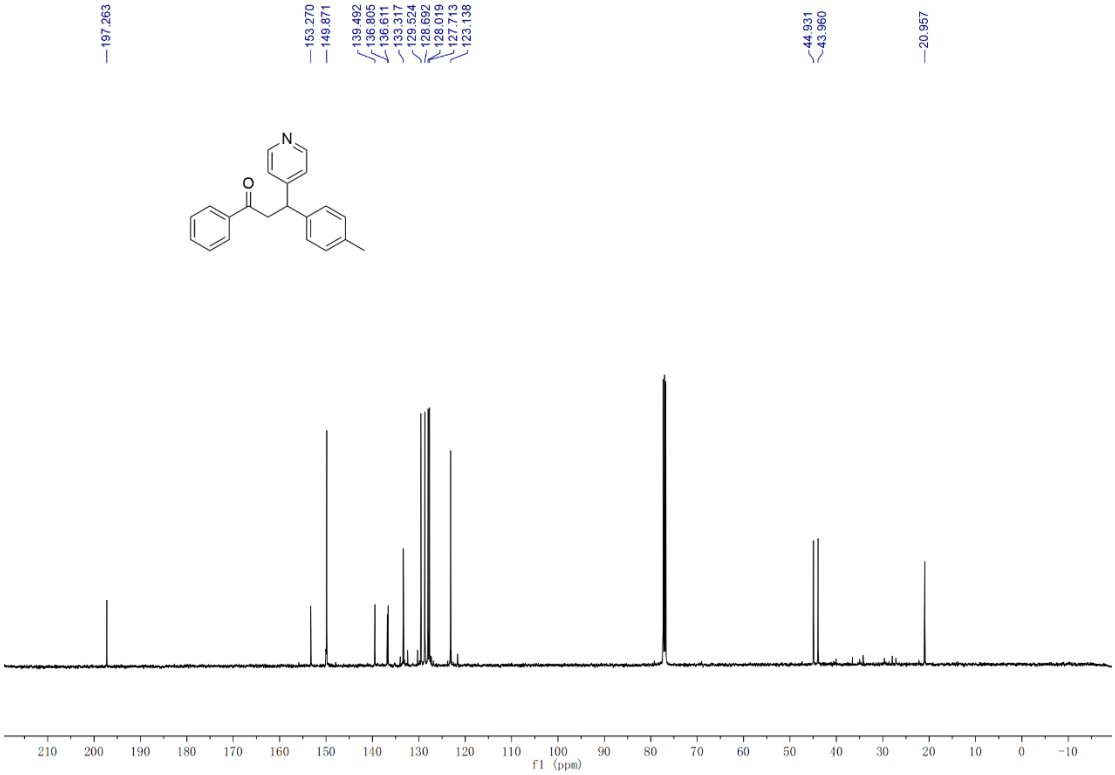


^{13}C NMR (125 MHz, $CDCl_3$)

1-phenyl-3-(pyridin-4-yl)-3-(p-tolyl)propan-1-one (3sa)

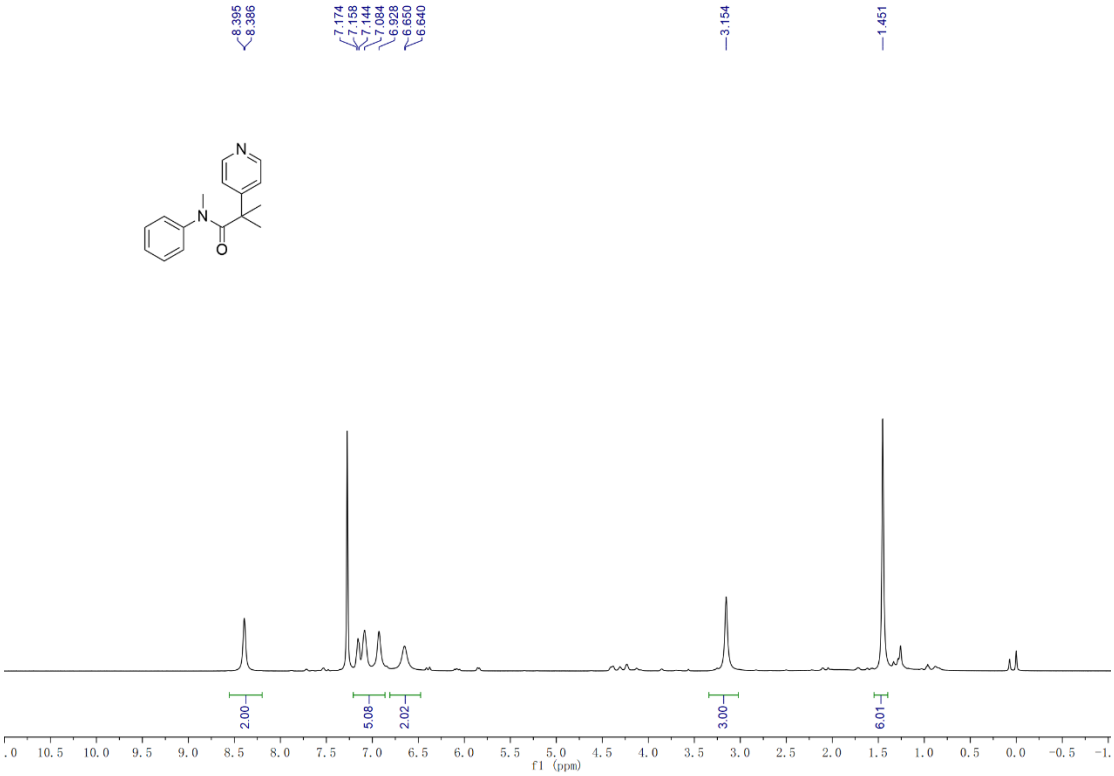


^{1}H NMR (500 MHz, $CDCl_3$)

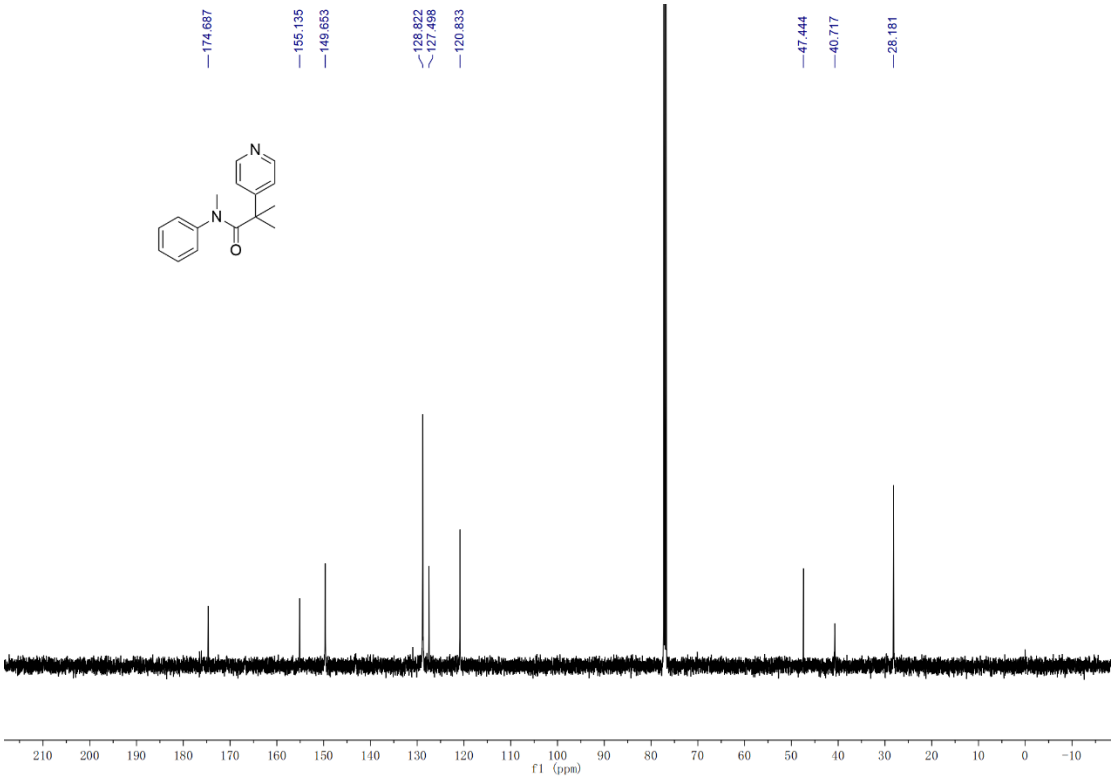


^{13}C NMR (125 MHz, $CDCl_3$)

N,2-dimethyl-N-phenyl-2-(pyridin-4-yl)propenamide (3ta)

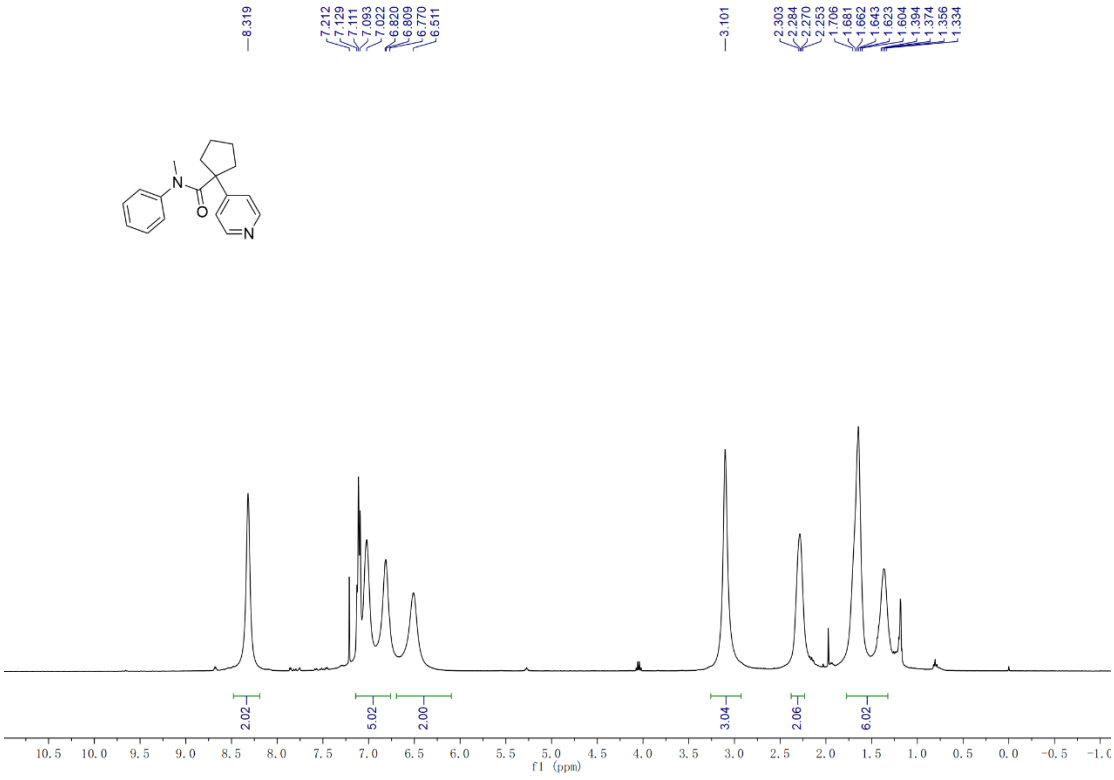


^{1}H NMR (500 MHz, $CDCl_3$)

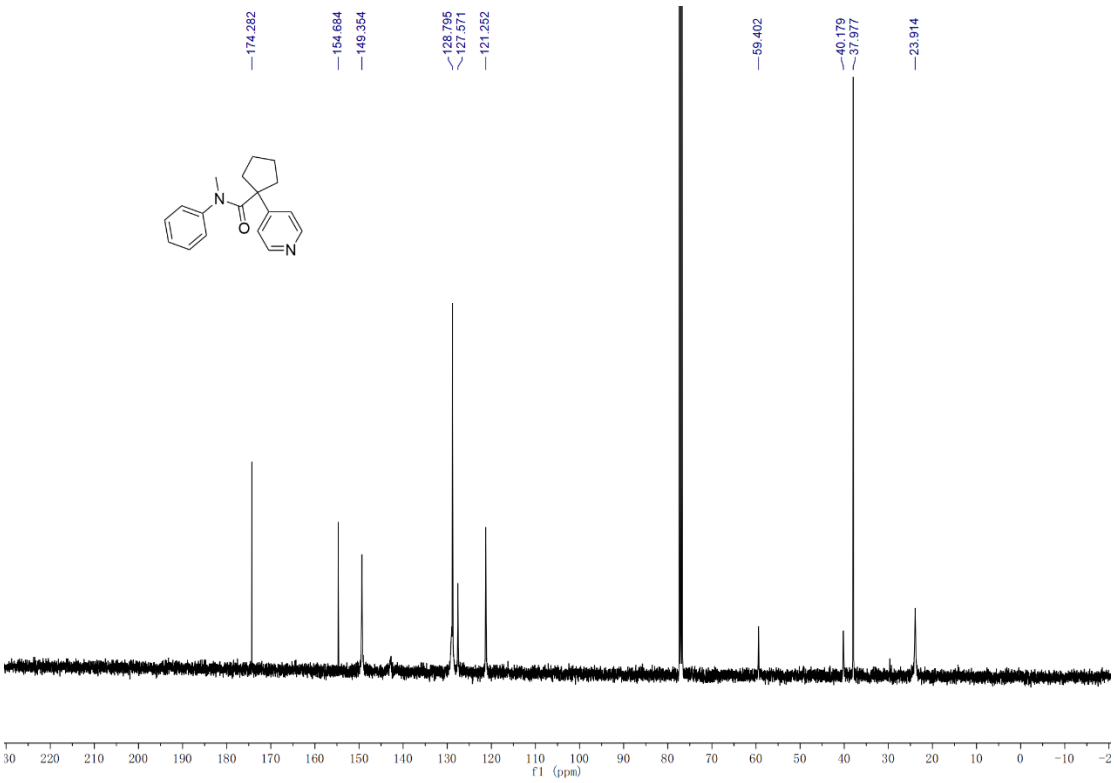


^{13}C NMR (125 MHz, $CDCl_3$)

N-methyl-N-phenyl-1-(pyridin-4-yl)cyclopentane-1-carboxamide (3ua)

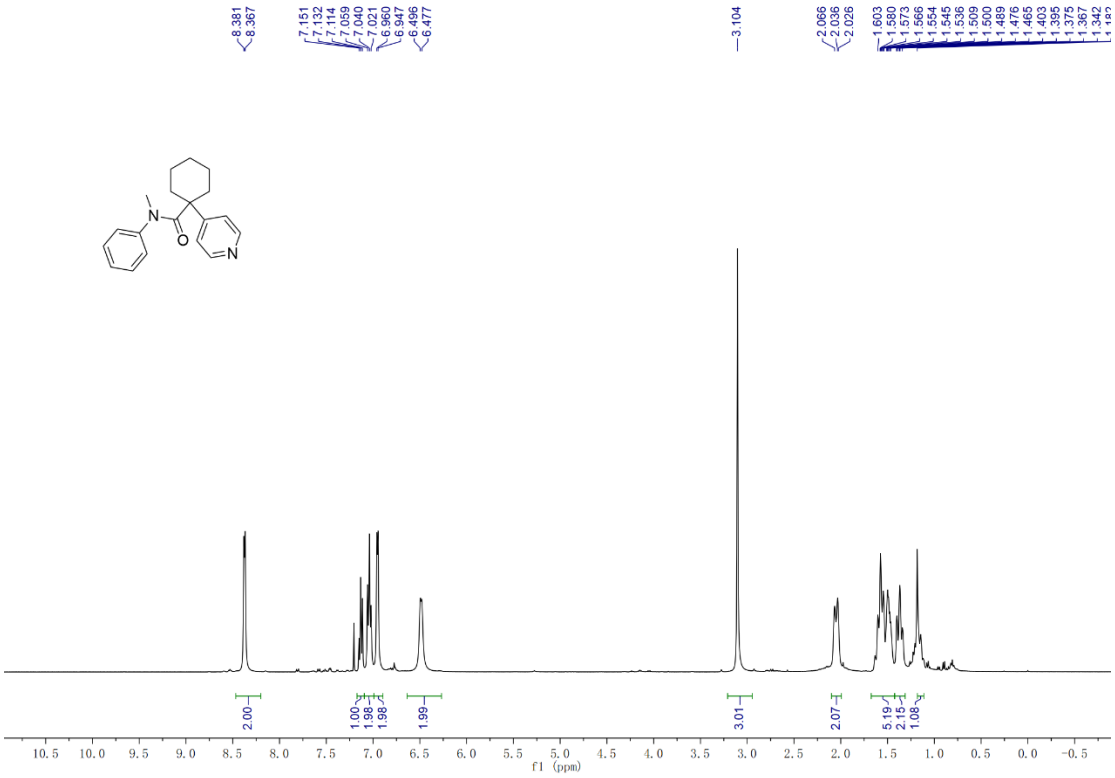


^{1}H NMR (400 MHz, $CDCl_3$)

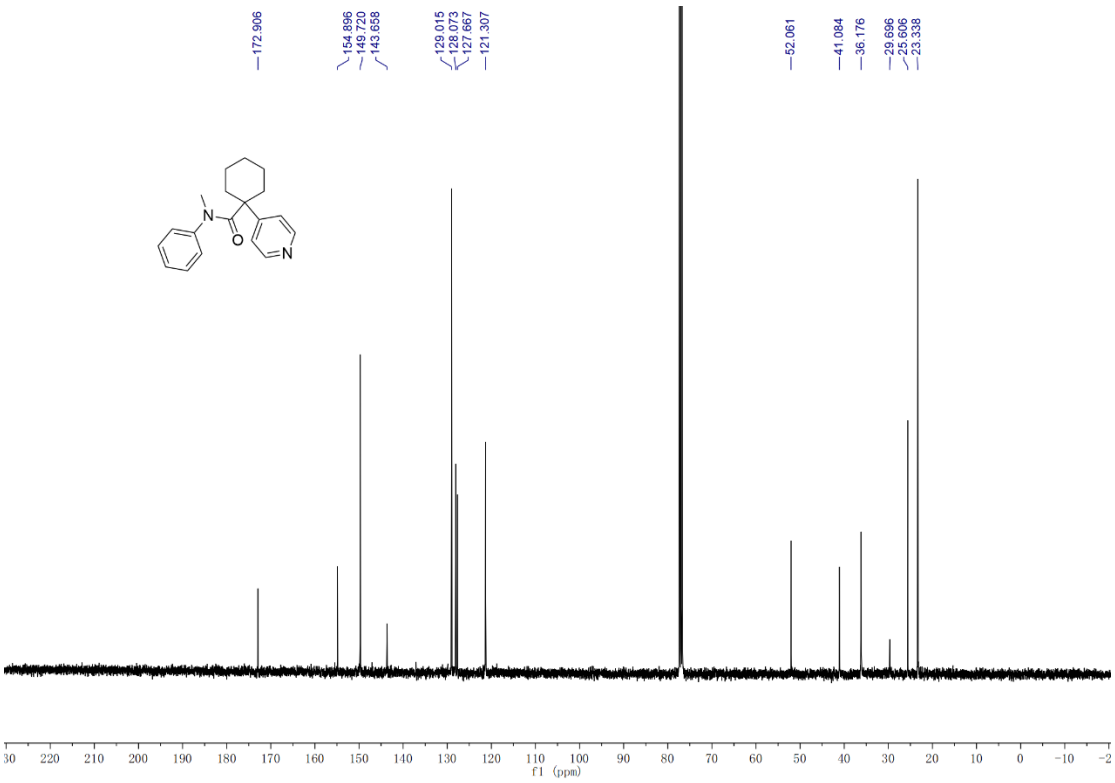


^{13}C NMR (100 MHz, $CDCl_3$)

N-methyl-N-phenyl-1-(pyridin-4-yl)cyclohexane-1-carboxamide (3va)

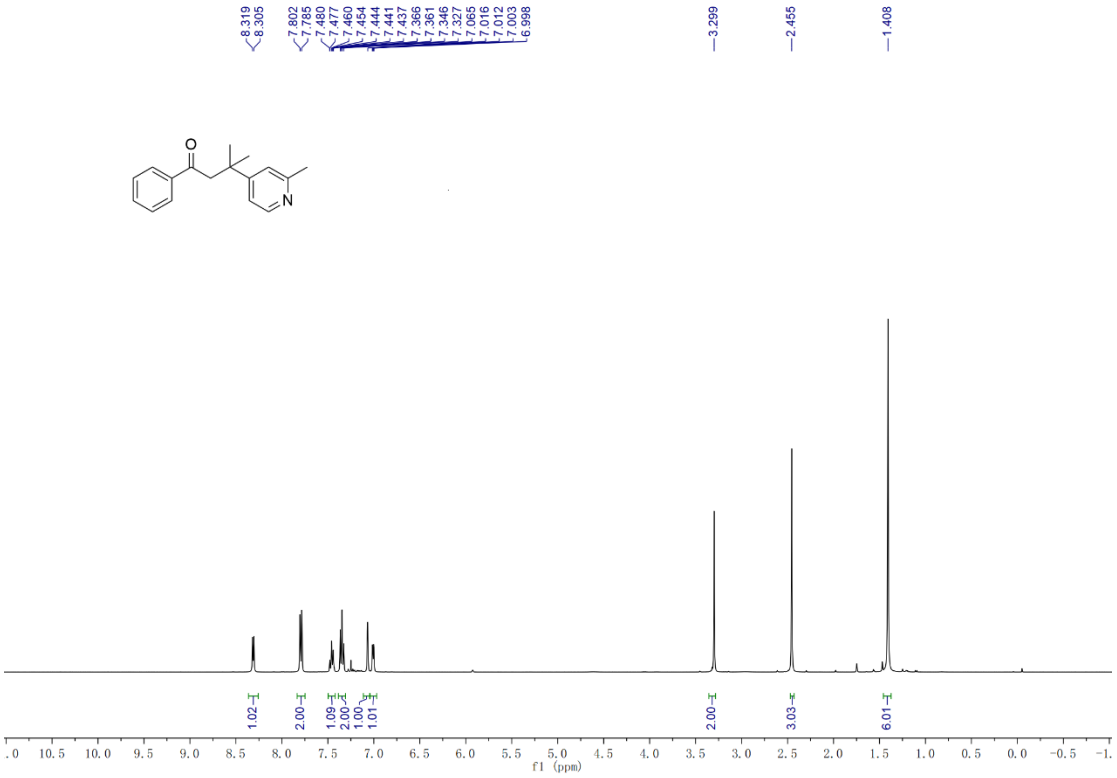


^{1}H NMR (400 MHz, $CDCl_3$)

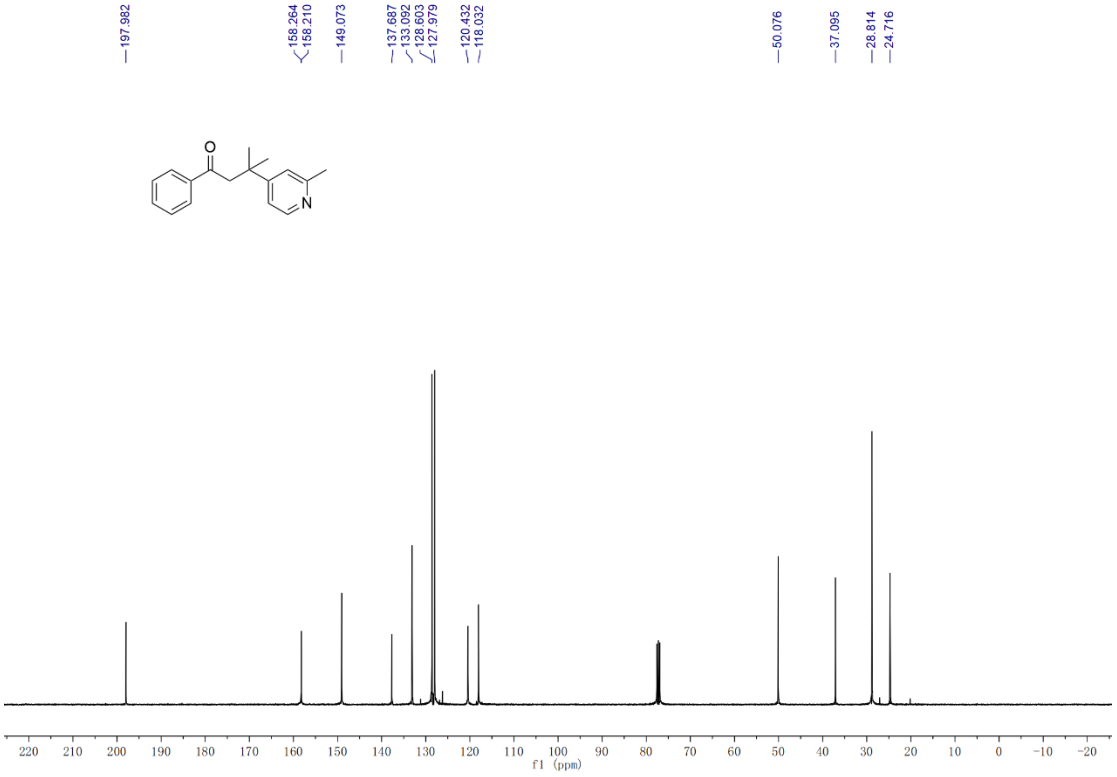


^{13}C NMR (100 MHz, $CDCl_3$)

3-methyl-3-(2-methylpyridin-4-yl)-1-phenylbutan-1-one (3ab)

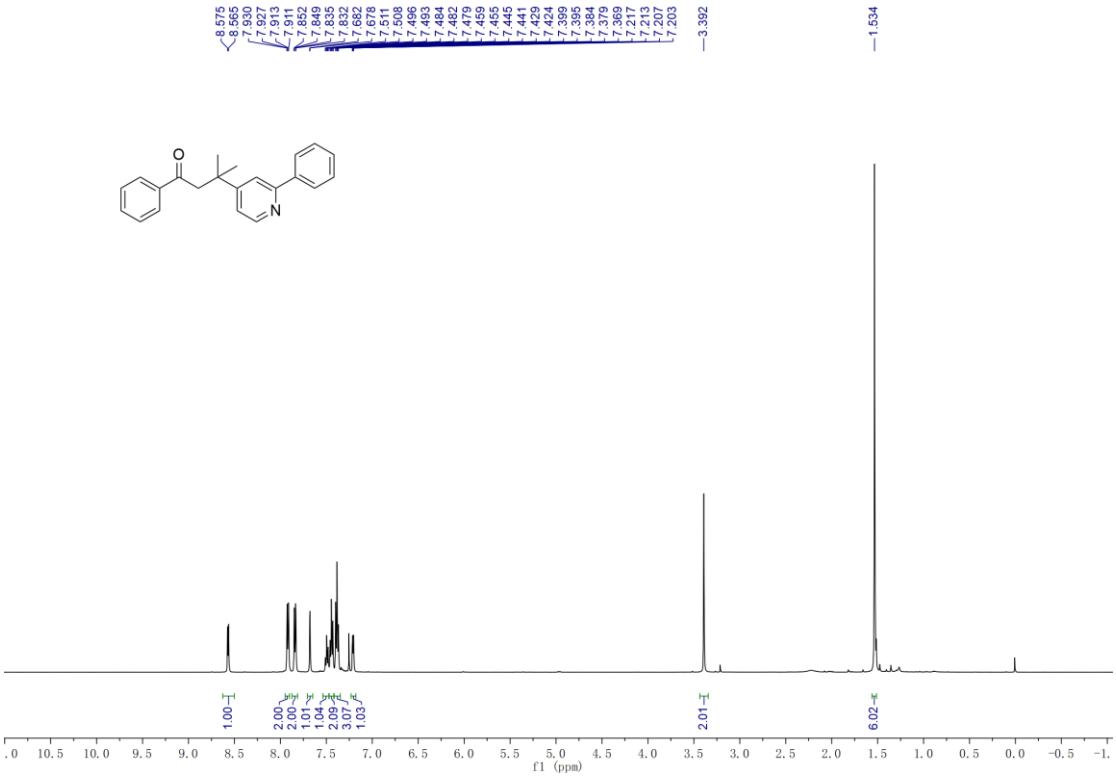


^{1}H NMR (400 MHz, $CDCl_3$)

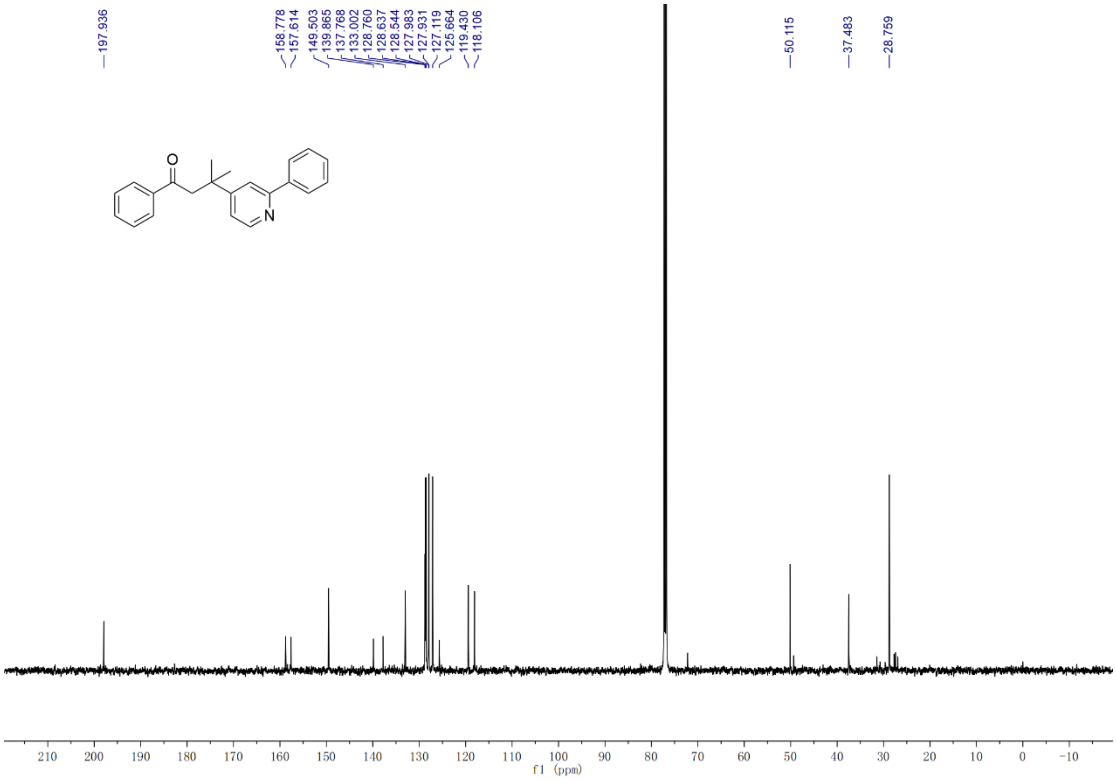


^{13}C NMR (100 MHz, $CDCl_3$)

2-methyl-1-phenyl-3-(2-phenylpyridin-4-yl)butan-1-one (3ac)

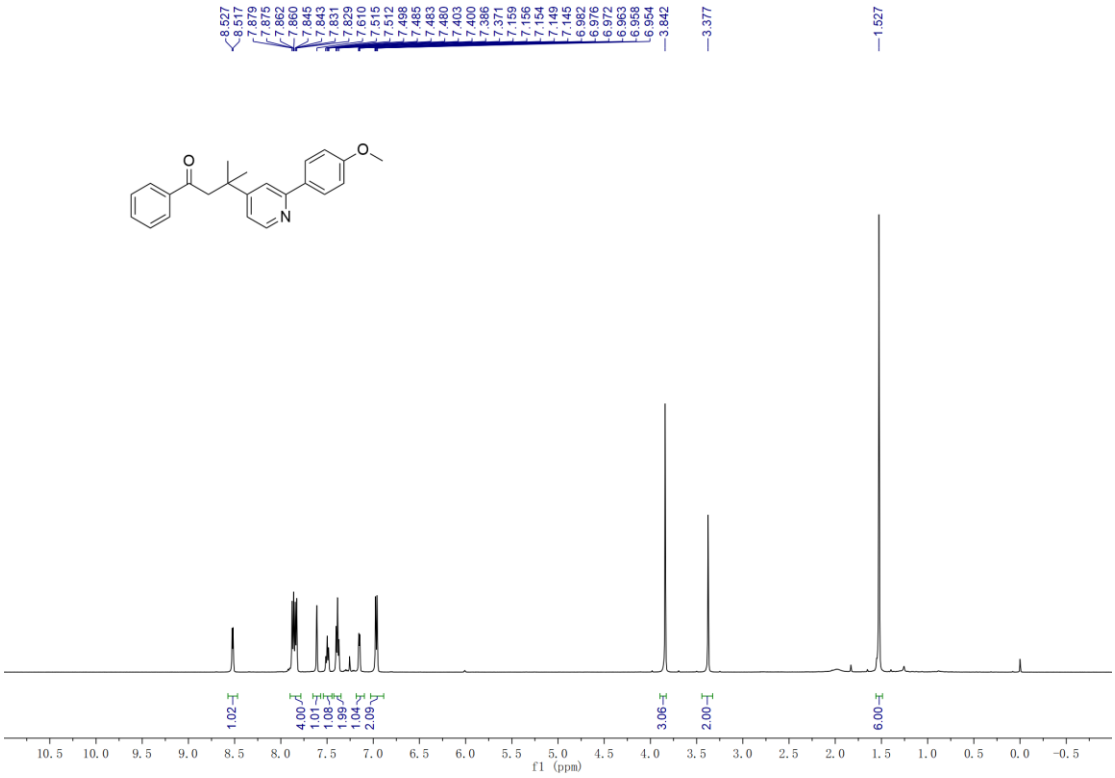


^{1}H NMR (500 MHz, $CDCl_3$)

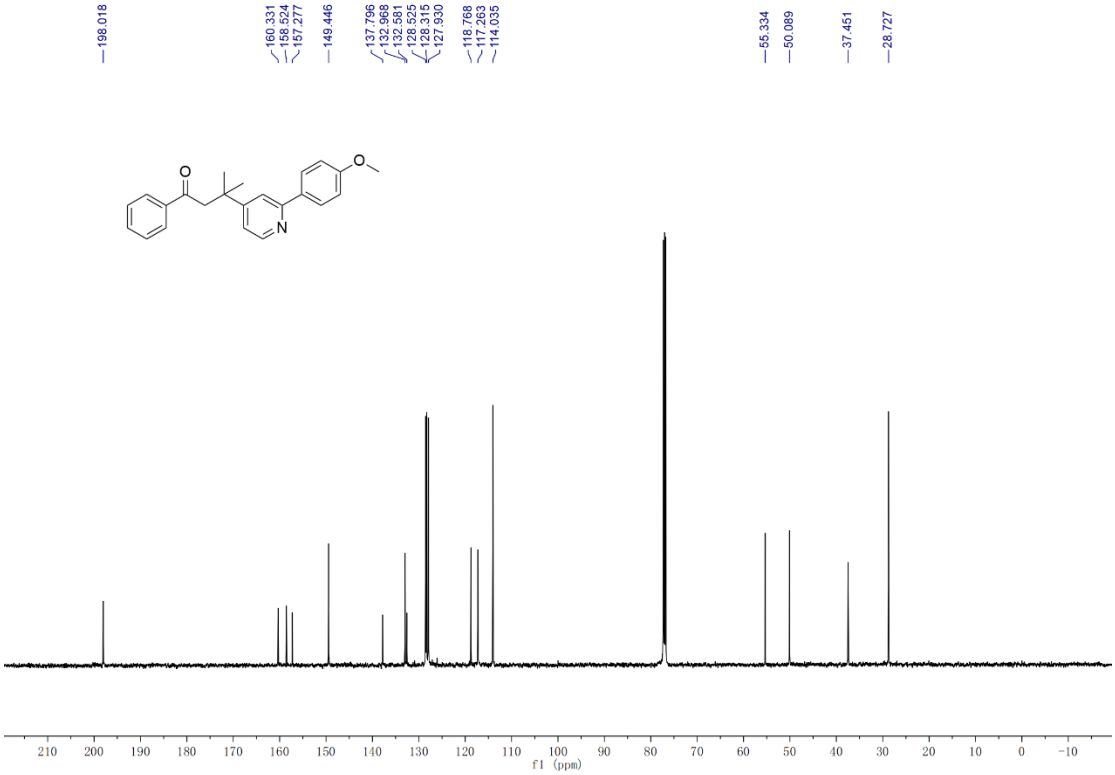


^{13}C NMR (125 MHz, $CDCl_3$)

3-(2-(4-methoxyphenyl)pyridin-4-yl)-3-methyl-1-phenylbutan-1-one (3ad)

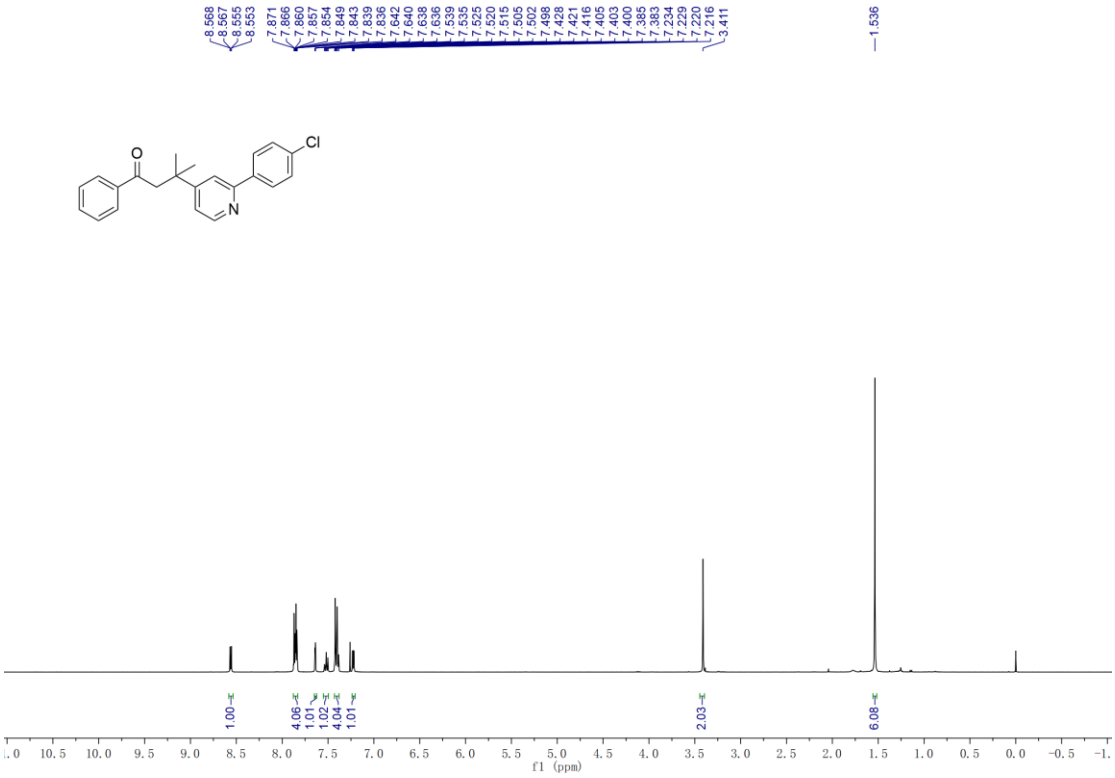


^{1}H NMR (500 MHz, $CDCl_3$)

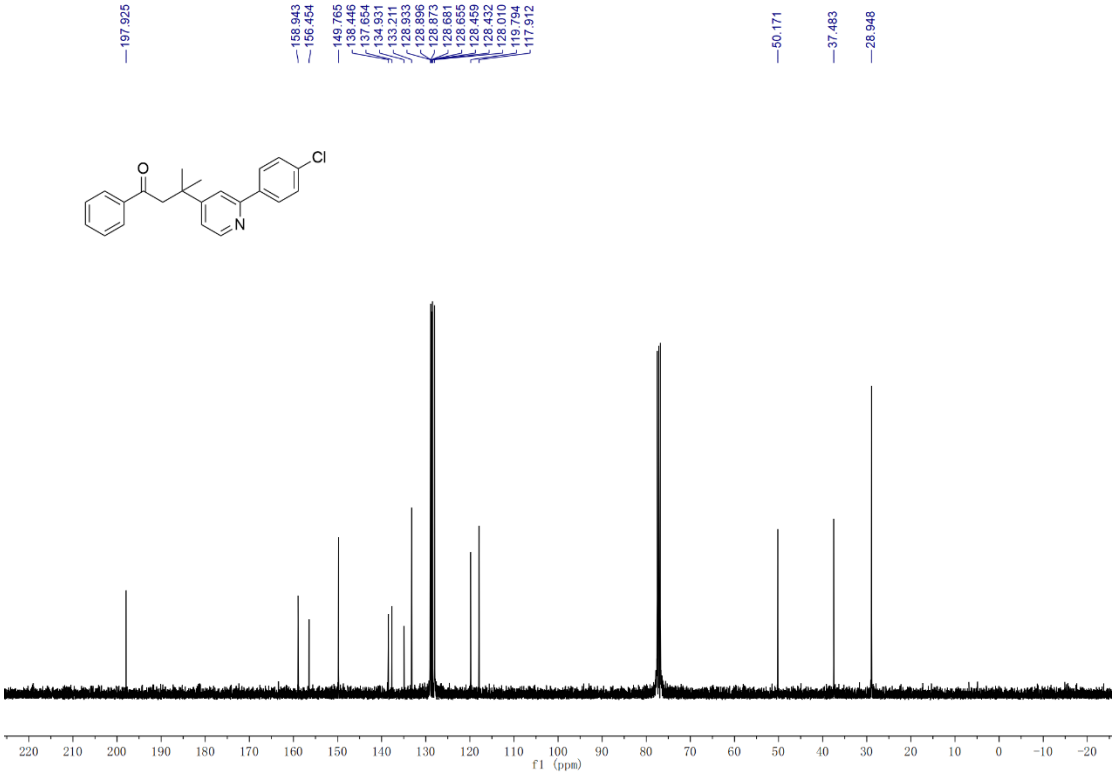


^{13}C NMR (125 MHz, $CDCl_3$)

3-(2-(4-chlorophenyl)pyridin-4-yl)-3-methyl-1-phenylbutan-1-one (3ae)

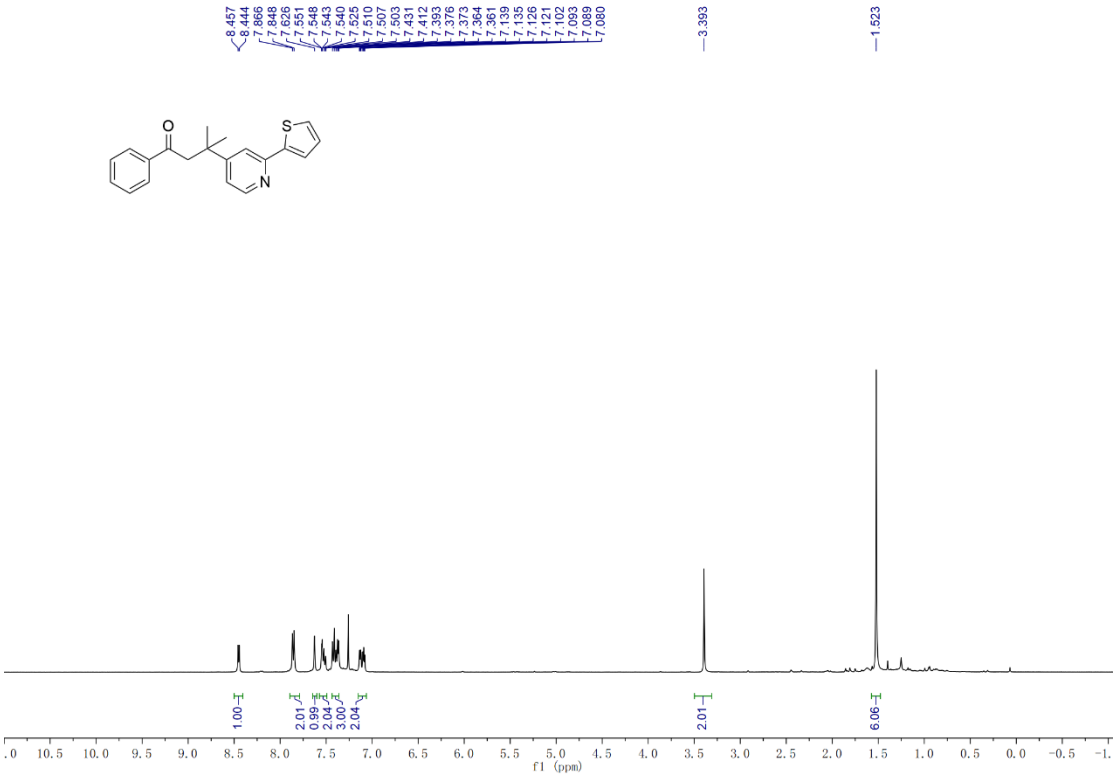


^{1}H NMR (400 MHz, $CDCl_3$)

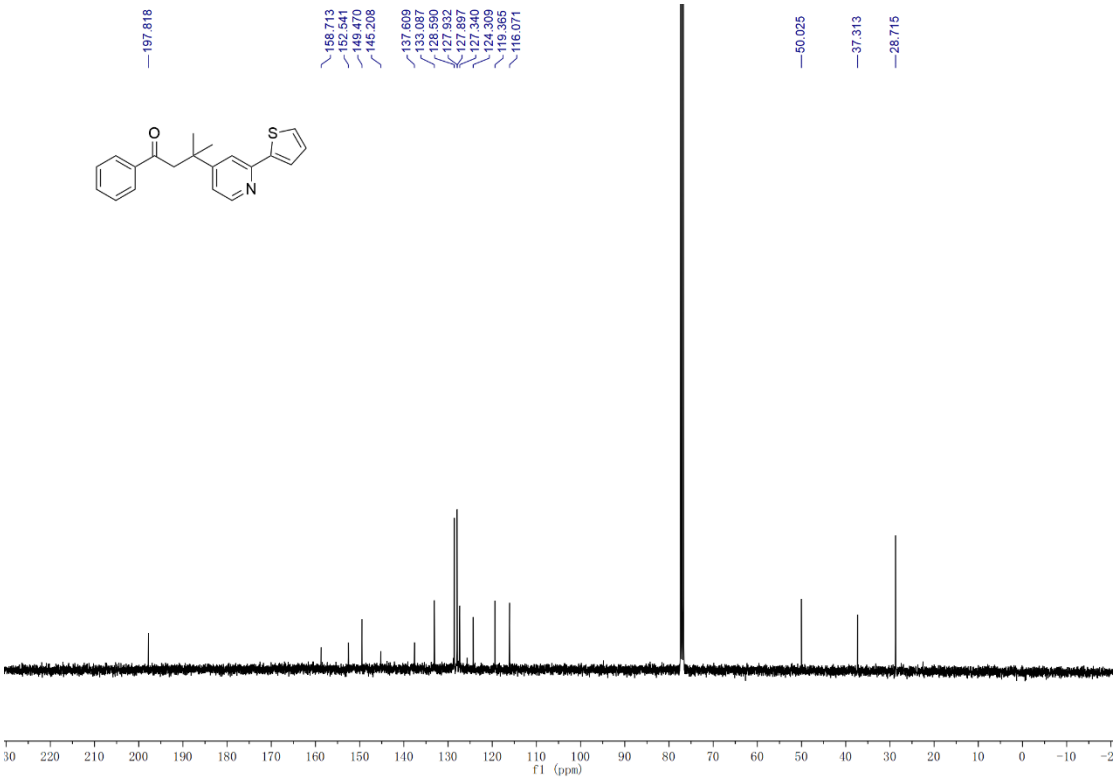


^{13}C NMR (100 MHz, $CDCl_3$)

2-ethyl-1-phenyl-3-(2-(thiophen-2-yl)pyridin-4-yl)butan-1-one (3af)

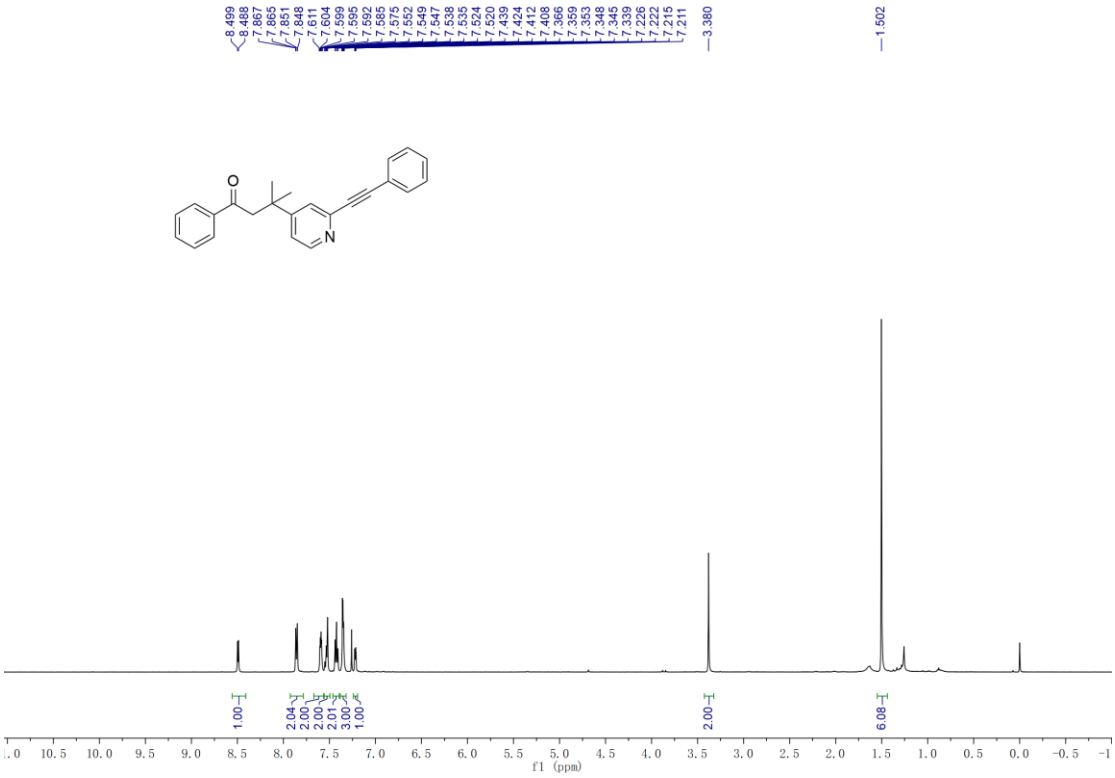


^{1}H NMR (400 MHz, $CDCl_3$)

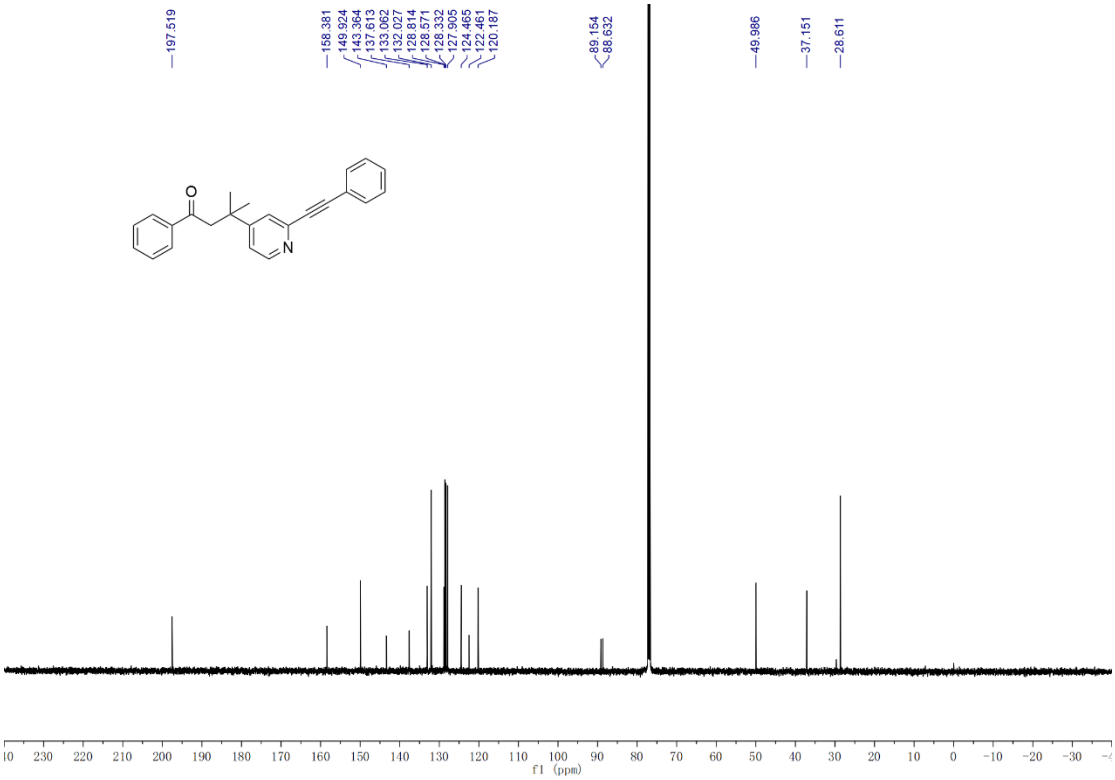


^{13}C NMR (100 MHz, $CDCl_3$)

3-methyl-1-phenyl-3-(2-(phenylethynyl)pyridin-4-yl)butan-1-one (3ag)

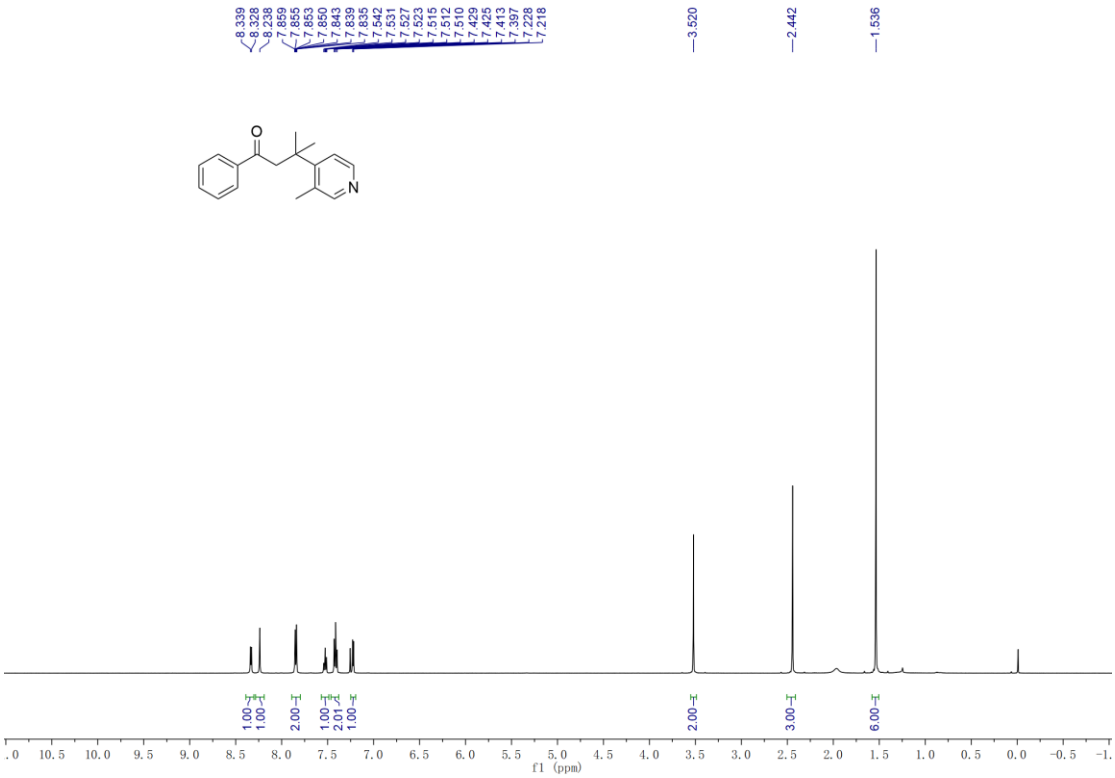


^{1}H NMR (500 MHz, $CDCl_3$)

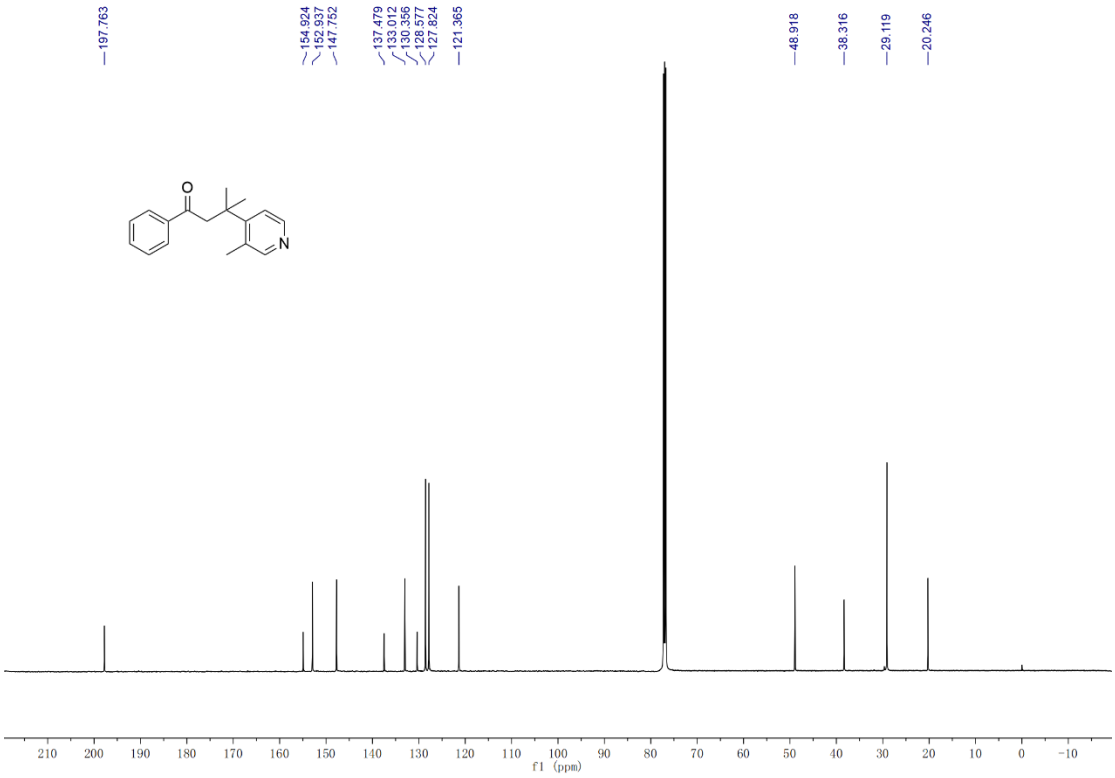


^{13}C NMR (125 MHz, $CDCl_3$)

2-methyl-3-(3-methylpyridin-4-yl)-1-phenylbutan-1-one (3ah)

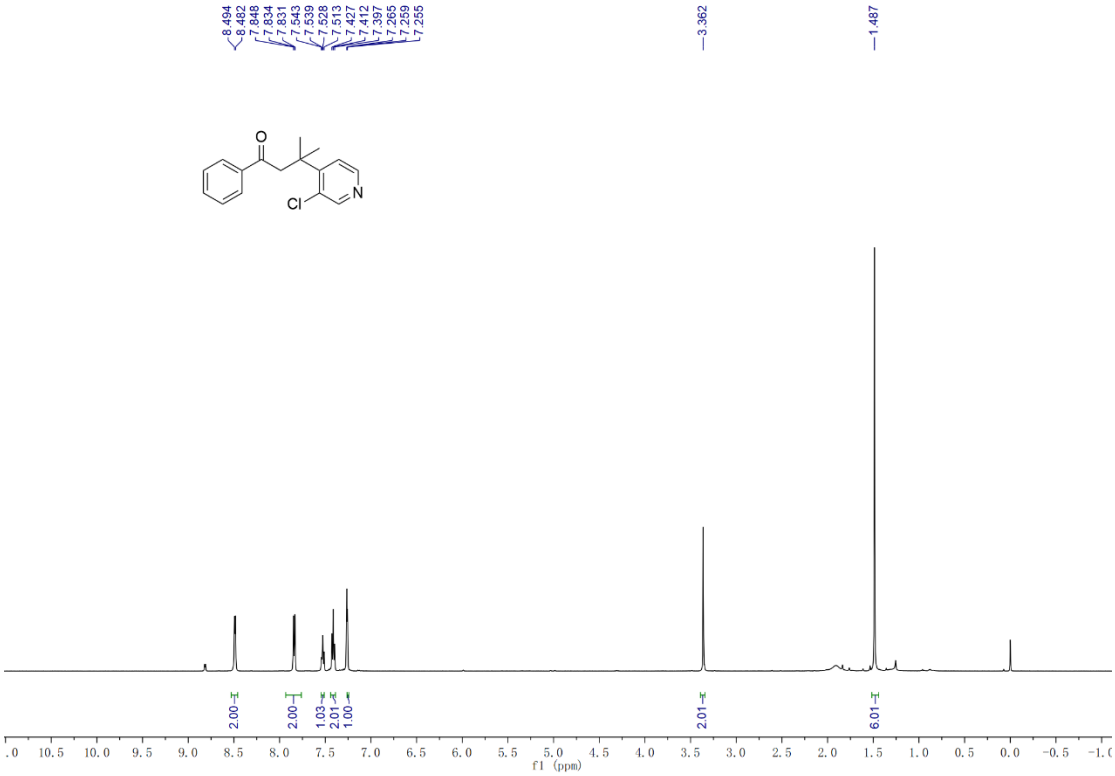


^{1}H NMR (500 MHz, $CDCl_3$)

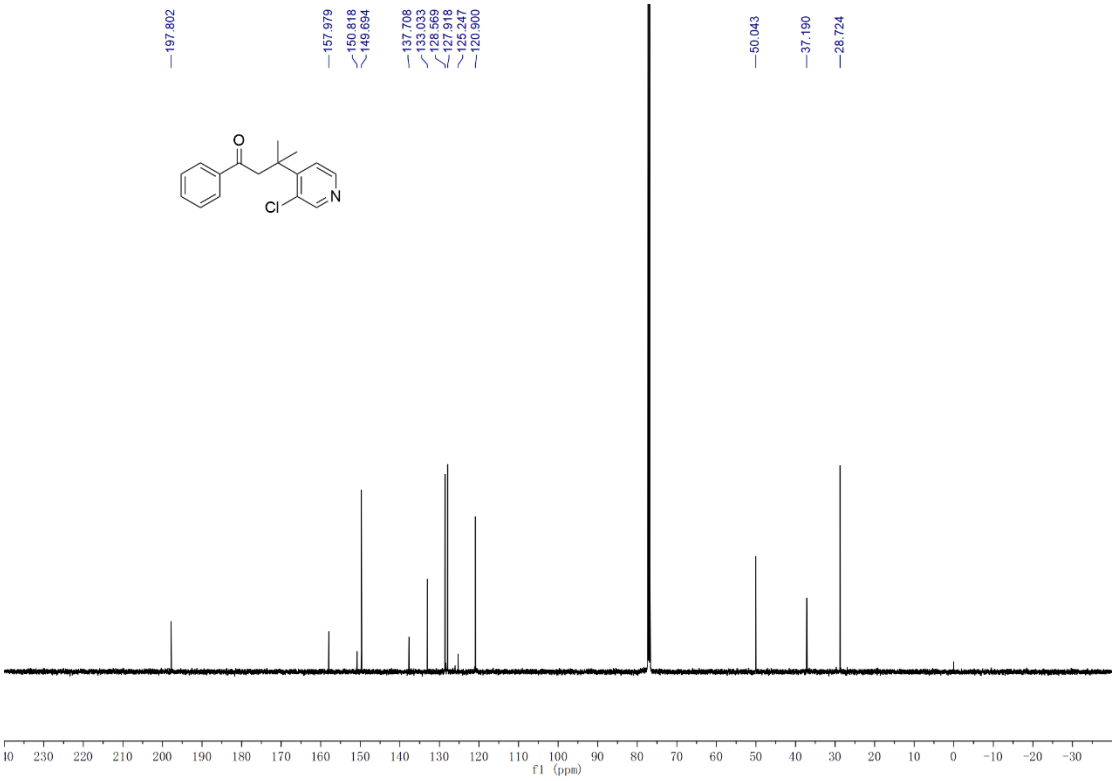


^{13}C NMR (125 MHz, $CDCl_3$)

3-(3-chloropyridin-4-yl)-3-methyl-1-phenylbutan-1-one (3ai)

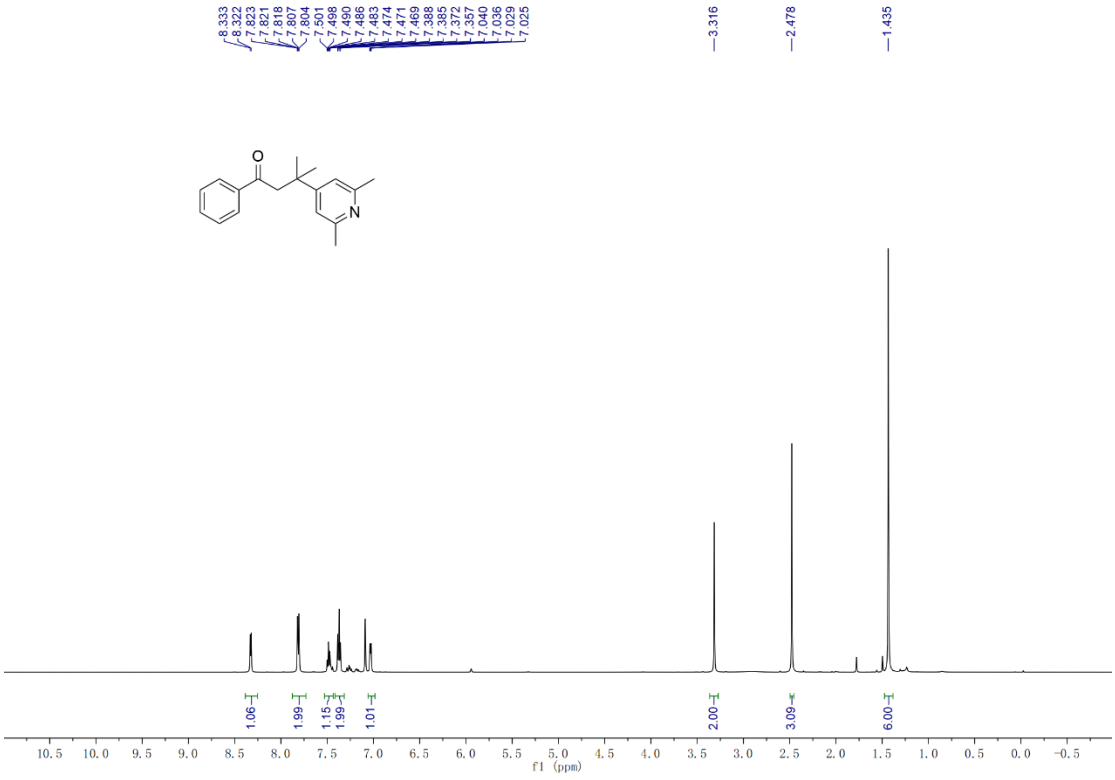


^{1}H NMR (500 MHz, $CDCl_3$)

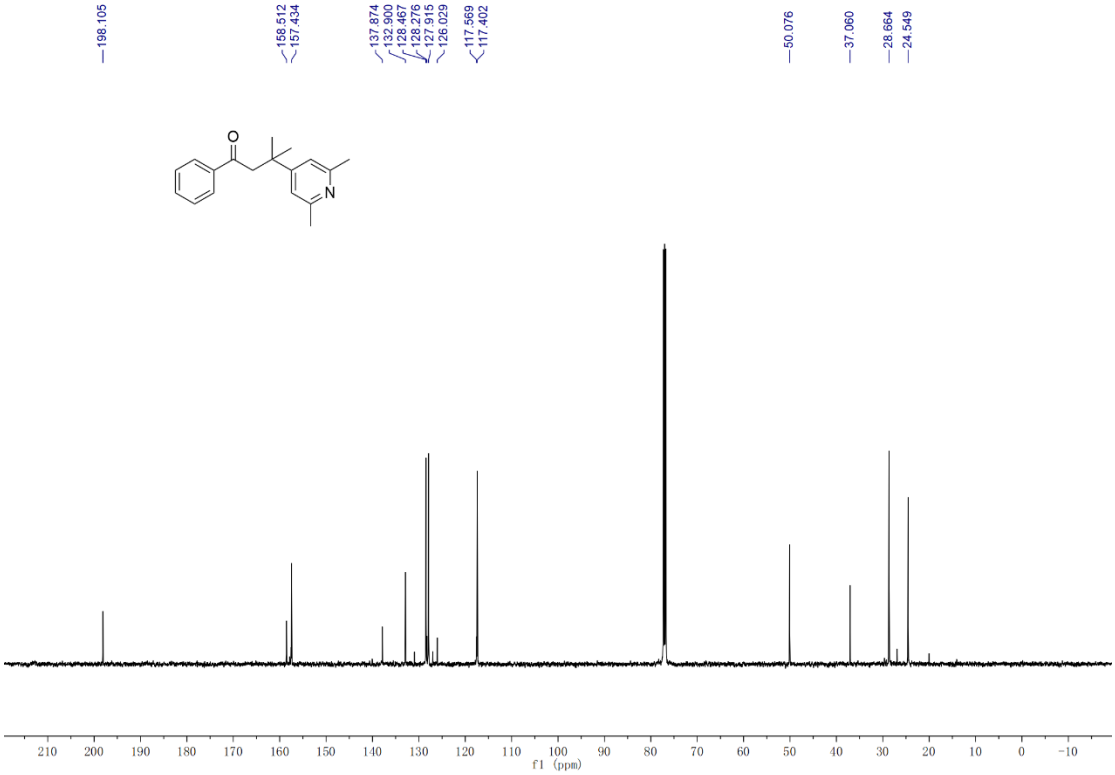


^{13}C NMR (125 MHz, $CDCl_3$)

3-(2,6-dimethylpyridin-4-yl)-3-methyl-1-phenylbutan-1-one (3aj)

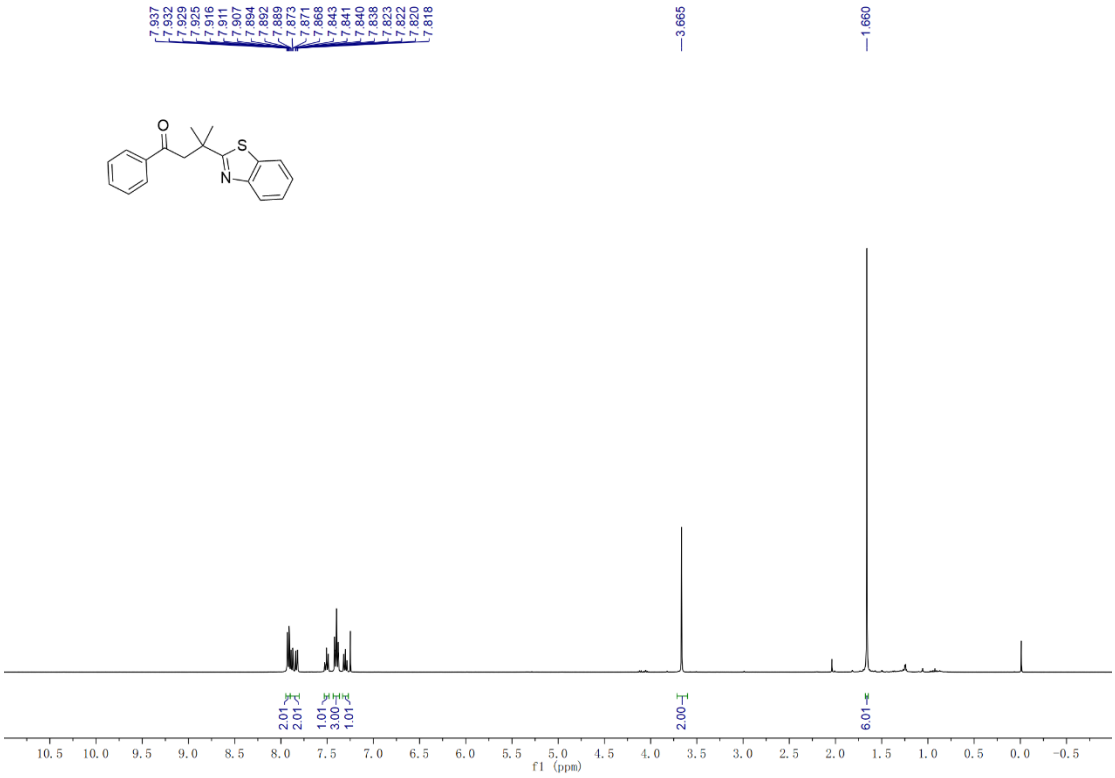


^{1}H NMR (500 MHz, $CDCl_3$)

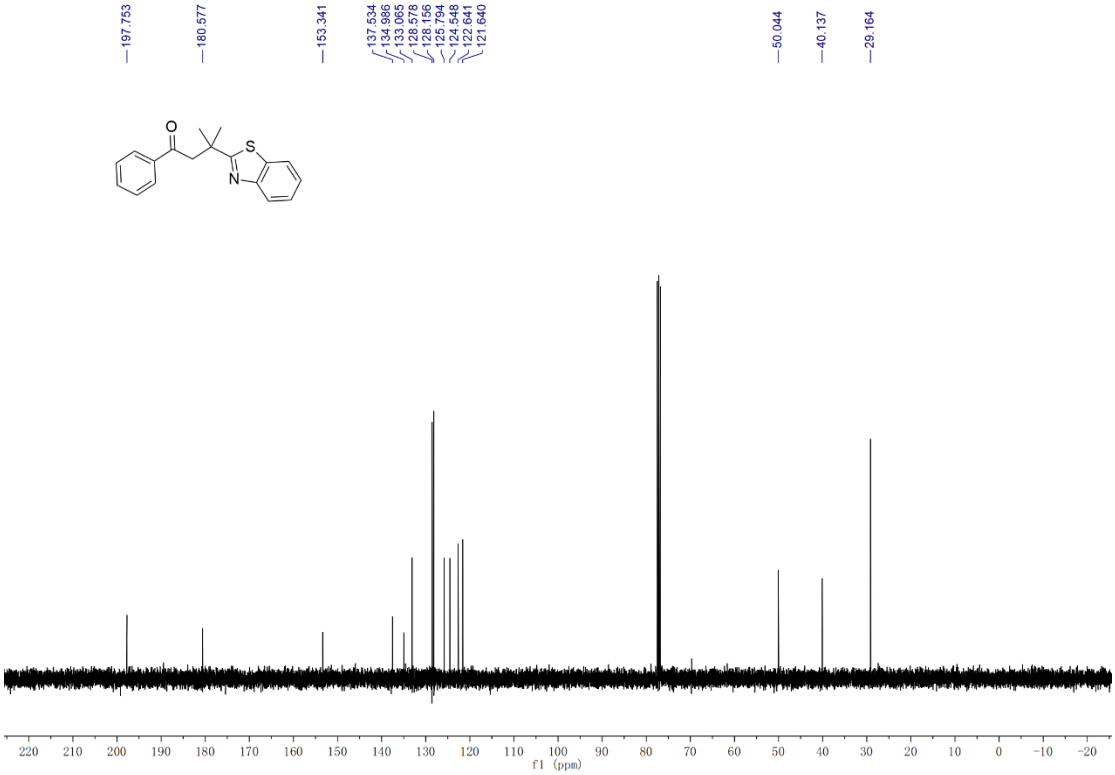


^{13}C NMR (125 MHz, $CDCl_3$)

3-(benzo[d]thiazol-2-yl)-3-methyl-1-phenylbutan-1-one (3al)

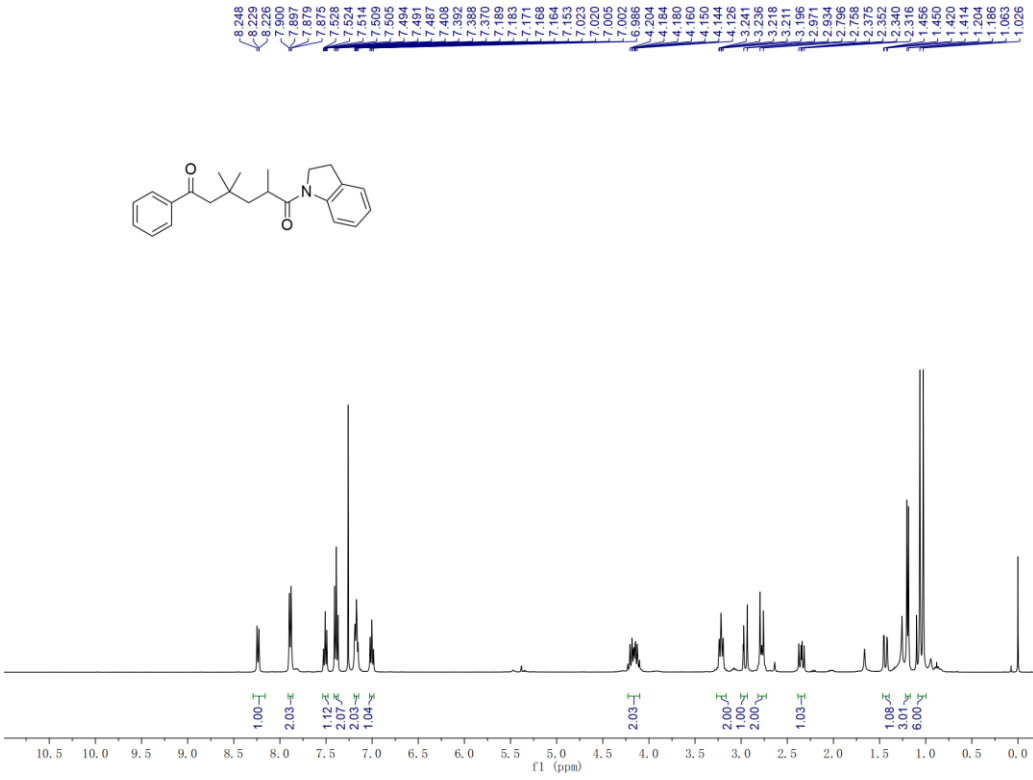


^{1}H NMR (400 MHz, $CDCl_3$)

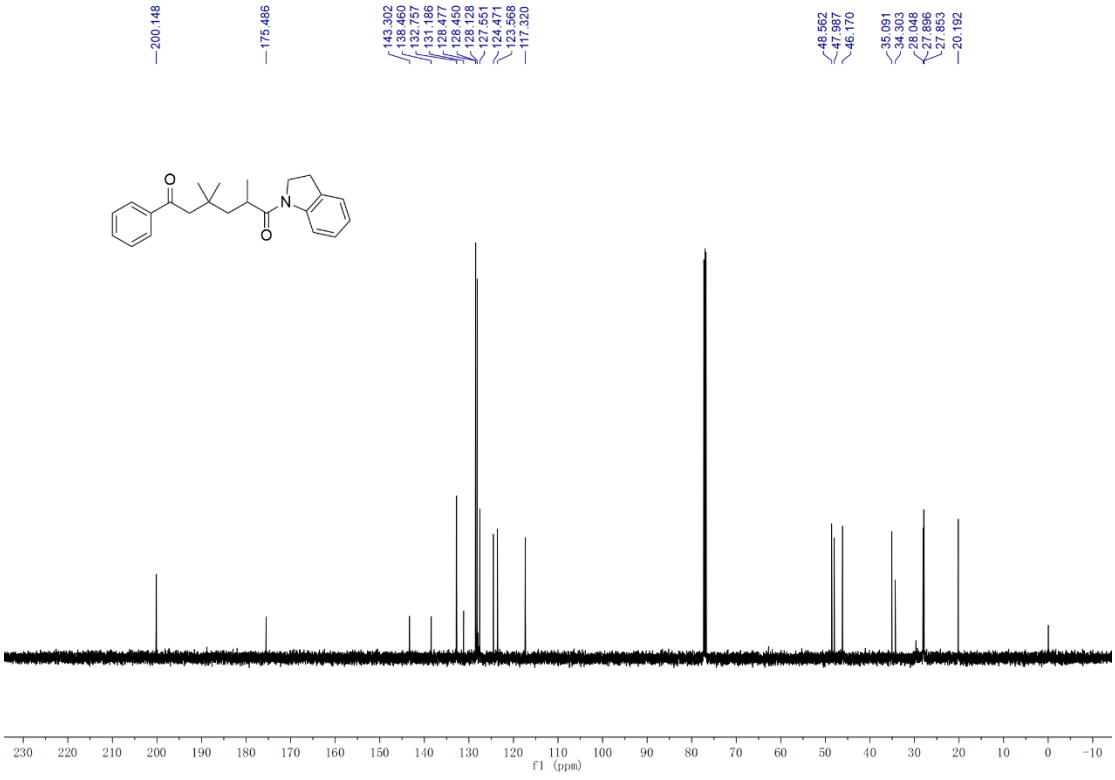


^{13}C NMR (100 MHz, $CDCl_3$)

1-(indolin-1-yl)-2,4,4-trimethyl-6-phenylhexane-1,6-dione (3an)

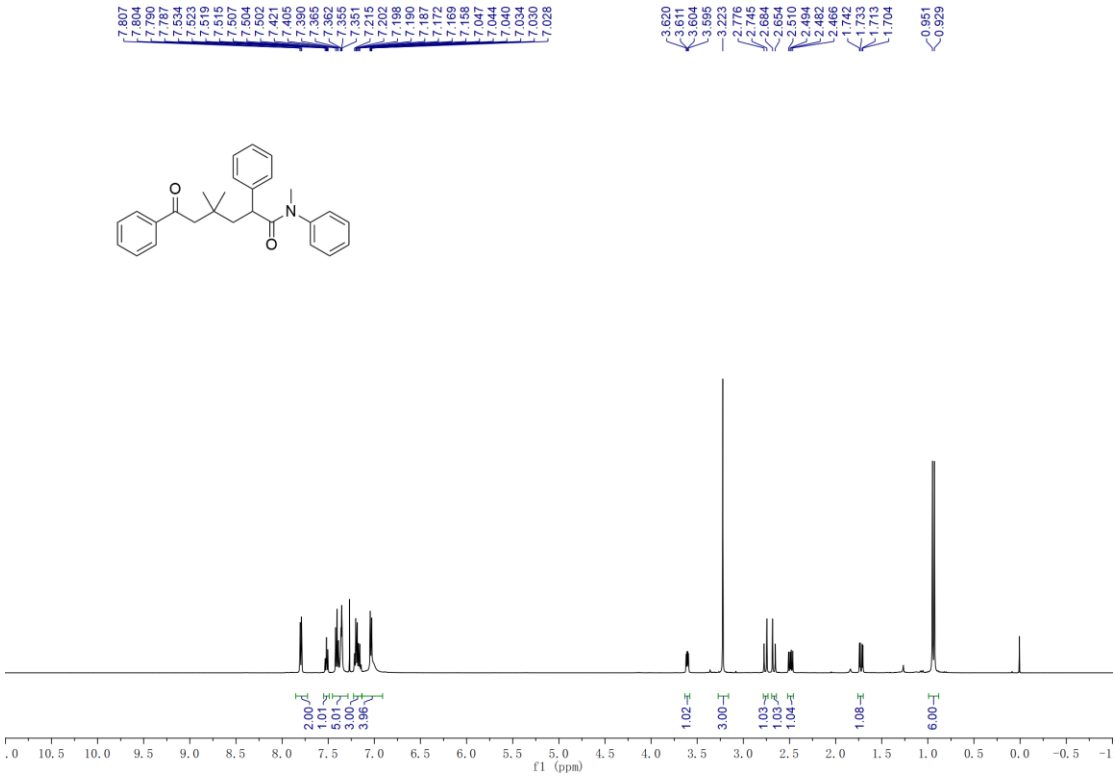


^{1}H NMR (400 MHz, $CDCl_3$)

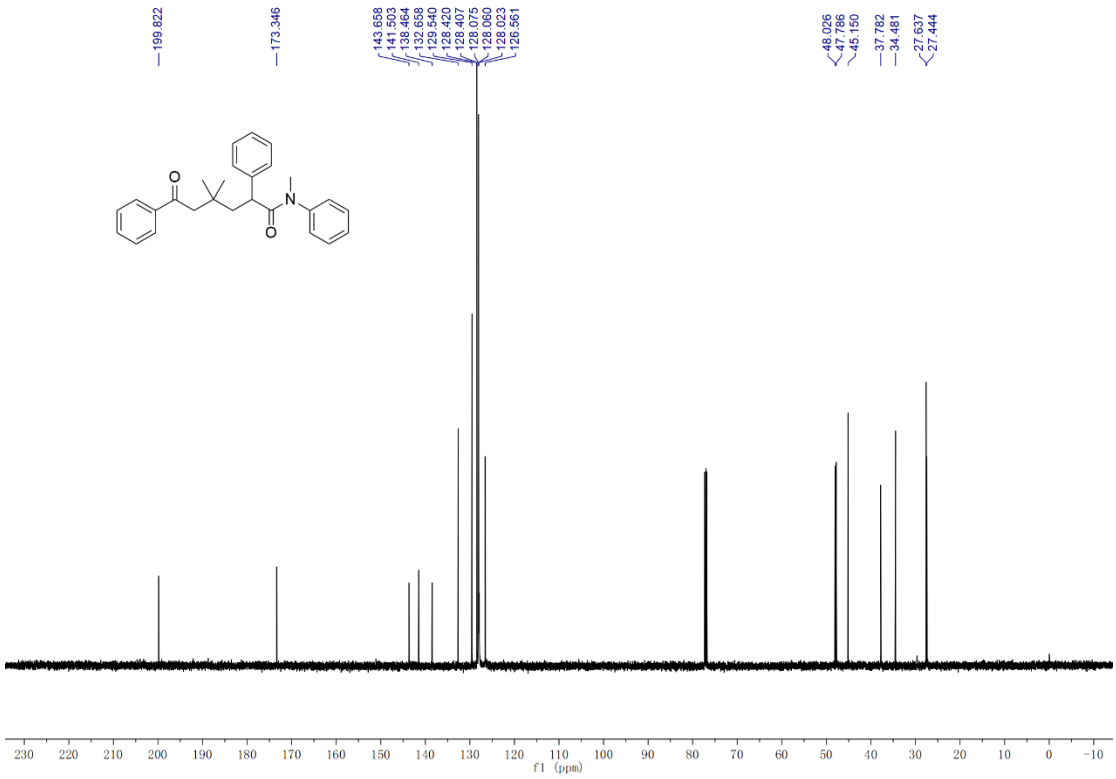


^{13}C NMR (125 MHz, $CDCl_3$)

N,4,4-trimethyl-6-oxo-N,2,6-triphenylhexanamide (3ao)



^{1}H NMR (500 MHz, $CDCl_3$)



^{13}C NMR (125 MHz, $CDCl_3$)

(D) DFT investigations (Calculations):

(a) Computational Details

All calculations were carried out using the Gaussian 16 program[3]. The geometries of all the species were fully optimized using the density functional theory (DFT) method with the M06-2X[4] functional. The 6-31G(d, p)[5] basis set was employed for C, H, N, and O atoms, and the LANL2DZ[6] basis set was used for Ir and I atoms. Frequency calculations at the same level were performed to confirm each stationary point to be either a local minimum or a transition state (TS). The transition states were verified using intrinsic reaction coordinate (IRC)[7] calculations. The intermediates were characterized by all real frequencies. For single-point energy calculations, the M06-2X functional was applied with the mixed basis set of SDD[8] for Ir and I atoms, and 6-311+G(d,p) for other atoms. The solvent effects of dimethylsulfoxide ($\varepsilon = 46.826$) were taken in account by using the SMD-flavor[9] of self-consistent reaction field (SCRF) theory. The Gibbs free energies in dimethylsulfoxide (ΔG) were discussed throughout this paper unless otherwise specified. All 3D structures were generated by the CYLview[10].

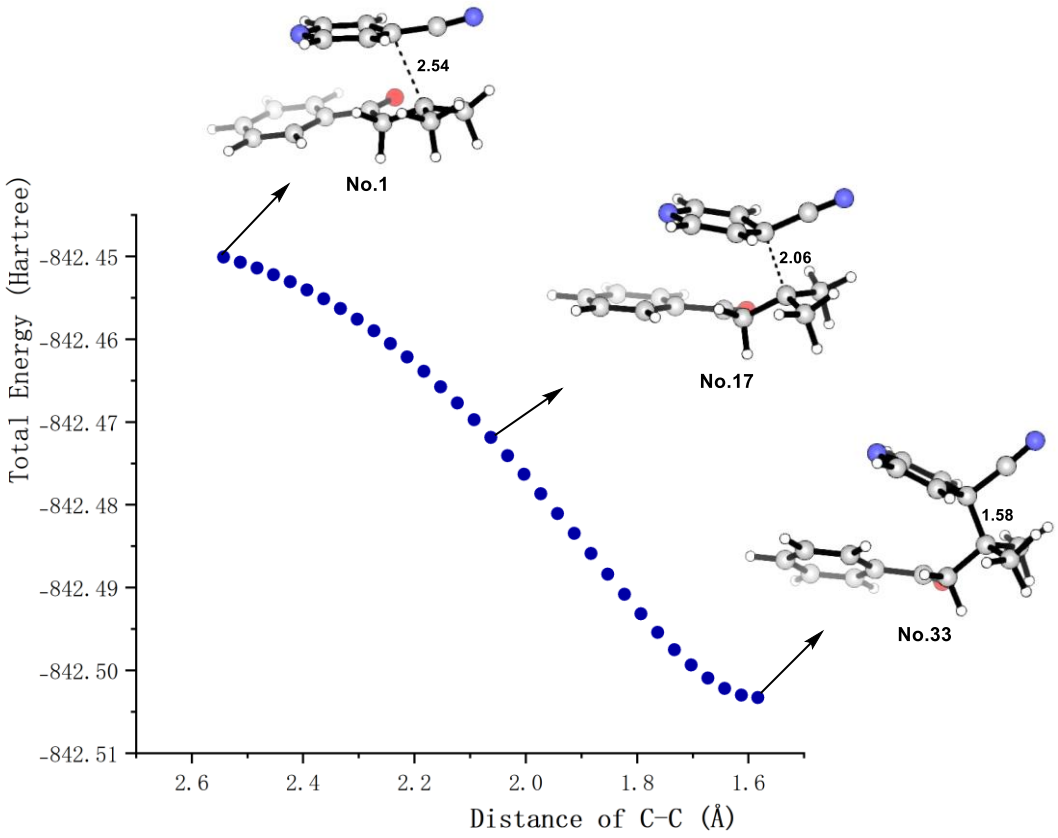


Figure S8. The energy profile (total energy) along the distance of C-C from a relaxed scan (33 points with 0.03 Å per step). Based on our calculations, it can be seen that the radical-radical coupling between intermediate **D** and **2a'** is barrierless.

(b) Cartesian Coordinates and Thermochemical Data (Energies in Hartree)

PC (*fac*-Ir(ppy)$_3$)

Number of imaginary frequencies: 0

Ir	-0.06238300	0.00392600	0.01037800
C	-2.02106900	0.80077400	2.22231300
C	-2.80748500	-0.72591500	0.54050900
C	-3.25609700	0.72074200	2.86147700
H	-1.24733500	1.43407200	2.65181900
C	-4.04977800	-0.80737900	1.18238000
C	-4.27637100	-0.08457300	2.34627300
H	-3.42888200	1.28941800	3.77157600
H	-4.83975000	-1.43534400	0.77945900
C	-0.79855200	-1.87951100	-2.25204100
C	-2.48667800	-1.46170700	-0.68727300
C	-1.62149200	-2.70987300	-2.99419300
H	0.22629300	-1.67992900	-2.54684100
C	-3.36006800	-2.29249600	-1.39572400
C	-2.92760000	-2.91914100	-2.55343100
H	-1.24141700	-3.17832400	-3.89405500
H	-4.37228000	-2.43809800	-1.03692400
N	-1.21726200	-1.27205900	-1.13121200
C	1.64740500	1.20177800	2.23401100
C	0.77595700	2.74413100	0.70761100
C	2.26763400	2.19814300	2.97013400
H	1.71597500	0.15763800	2.51804600
C	1.38006500	3.78902800	1.41310300
C	2.12834800	3.51787800	2.54801700
H	2.84120500	1.93747400	3.85151100
H	1.25717500	4.80987800	1.07223200

H	2.59666300	4.32708600	3.09869700
C	-0.59436000	1.71384900	-1.03230200
C	-1.38184600	1.84483800	-2.18683700
C	-0.04835600	2.90852400	-0.50367300
C	-1.61222100	3.08278200	-2.78733200
H	-1.82748800	0.95678800	-2.63542700
C	-0.27278600	4.15672000	-1.09993200
C	-1.05639500	4.24367500	-2.24494500
H	-2.22638100	3.14740100	-3.68203800
H	0.15898000	5.06295100	-0.68400100
H	-1.23333300	5.20780000	-2.71125600
N	0.92101300	1.46231000	1.13580700
C	0.74526200	-1.64615700	1.01495900
C	2.00018700	-2.10458700	0.53609900
C	0.19777300	-2.36120400	2.09352900
C	2.65295900	-3.20570900	1.10943300
C	0.84198300	-3.45538900	2.67069100
H	-0.76320900	-2.05030300	2.50202300
C	2.07611200	-3.88162500	2.17806700
H	3.61202100	-3.54705500	0.73039700
H	0.38370800	-3.97884700	3.50611200
H	2.58285000	-4.73355400	2.62067300
C	2.29153700	0.39953800	-2.10193100
C	2.59348400	-1.36085600	-0.59887600
C	3.50843600	0.15981900	-2.72208600
H	1.63586900	1.20181000	-2.42795800
C	3.83311900	-1.65153000	-1.18085000
C	4.29063500	-0.88944500	-2.24566800
H	3.82741900	0.77958300	-3.55165300

H	4.43645300	-2.46752600	-0.80226400
H	5.25058900	-1.11225600	-2.70041100
N	1.84765200	-0.33660400	-1.07535100
C	-1.75386700	0.07827700	1.04624300
H	-3.60057800	-3.56382500	-3.10909500
H	-5.23616700	-0.14508200	2.84905000

SMD-M06-2X/6-31G(d,p)/Lanl2DZ

Electronic Energy (0K) = -1540.332939

Electronic Energy (0K) + ZPE = -1539.846964

Enthalpy (298K) = -1539.817457

Free Energy (298K) = -1539.906828

SMD-M06-2X/6-311+G(d,p)/SDD

Electronic Energy (0K) = -1540.351697

PC*-T_1

Number of imaginary frequencies: 0

Ir	0.15578300	0.05969600	-0.09086700
C	1.68101700	1.68168400	-2.13166500
C	2.96315500	0.62016900	-0.37170600
C	2.85914500	2.20194700	-2.66156800
H	0.73226300	1.89937600	-2.61420000
C	4.14074600	1.14633900	-0.90539900
C	4.08647200	1.93577500	-2.05070200
H	2.82397200	2.82006700	-3.55371700
H	5.10036900	0.94783300	-0.43802100
C	1.47508900	-1.42251300	2.22874200
C	2.91960600	-0.22914400	0.82841200
C	2.52458400	-1.84118700	3.03203500
H	0.44658900	-1.70629600	2.42843000

C	4.01551500	-0.61995200	1.59791100
C	3.81493400	-1.42920400	2.70778400
H	2.32699100	-2.47441200	3.88840500
H	5.01281700	-0.29230600	1.32910700
N	1.67175800	-0.63561100	1.16346900
C	-1.67409800	0.45325200	-2.49825400
C	-1.86605700	2.06252800	-0.75373300
C	-2.62295500	1.08274200	-3.26467600
H	-1.17326000	-0.44701100	-2.84495700
C	-2.84888300	2.73805500	-1.52066200
C	-3.23205300	2.27025700	-2.75054000
H	-2.89170400	0.67776200	-4.23261100
H	-3.29794200	3.64001300	-1.11603500
H	-3.98611800	2.79510700	-3.32796100
C	-0.37337200	1.62327800	1.13015100
C	0.14115100	1.92935200	2.38273200
C	-1.36582300	2.46131300	0.52380300
C	-0.28942200	3.06685800	3.08014200
H	0.88667200	1.27888800	2.83720400
C	-1.76714800	3.62595800	1.23223600
C	-1.24453400	3.90433800	2.48469000
H	0.10940000	3.29535900	4.06319800
H	-2.49449400	4.30568600	0.79676800
H	-1.58214000	4.79296900	3.01192200
N	-1.28820900	0.89801000	-1.28293300
C	0.05082900	-1.85472400	-0.89372200
C	-0.99281600	-2.72217900	-0.53133500
C	1.00774000	-2.31047100	-1.81045900
C	-1.08067700	-4.00509300	-1.08887000

C	0.91387200	-3.58572400	-2.36793700
H	1.83227200	-1.66637100	-2.10496600
C	-0.13247000	-4.43468800	-2.00865000
H	-1.88487300	-4.67668000	-0.80481700
H	1.66250500	-3.91703000	-3.08209400
H	-0.20459200	-5.42896200	-2.43744400
C	-2.47542100	-0.46102600	1.88659100
C	-1.95923100	-2.21955500	0.46280200
C	-3.61321300	-1.10309100	2.35678600
H	-2.18893100	0.51640100	2.26026800
C	-3.09158200	-2.92092800	0.88582200
C	-3.92562500	-2.35627700	1.84011600
H	-4.23278400	-0.62463200	3.10601300
H	-3.31928600	-3.89504000	0.47039200
H	-4.80909300	-2.88953400	2.17607400
N	-1.66971900	-0.99981700	0.96454200
C	1.70790200	0.87971700	-0.98054000
H	4.65957100	-1.73763000	3.31480000
H	5.00146700	2.34495800	-2.46657200

SMD-M06-2X/6-31G(d,p)/Lanl2DZ

Electronic Energy (0K) = -1540.236805

Electronic Energy (0K) + ZPE = -1539.753730

Enthalpy (298K) = -1539.723638

Free Energy (298K) = -1539.815481

SMD-M06-2X/6-311+G(d,p)/SDD

Electronic Energy (0K) = -1540.259230

PC$^{\bullet-}$

Number of imaginary frequencies: 0

Ir	-0.03630100	0.03188200	-0.02230000
C	-1.94130300	1.10415800	-2.16583700
C	-1.09720100	2.67100900	-0.53615600
C	-2.63664800	2.13738400	-2.80086100
H	-2.01577600	0.09593200	-2.57052300
C	-1.79748400	3.71107400	-1.17848700
C	-2.56003100	3.44500600	-2.30726100
H	-3.23741500	1.92585200	-3.68161600
H	-1.74185900	4.72856500	-0.80008800
C	1.15344900	1.77767200	2.16595800
C	-0.28095300	2.85771300	0.65005700
C	1.35250300	2.93582600	2.89495600
H	1.63307800	0.84396000	2.44362700
C	-0.12362800	4.06032400	1.36757500
C	0.68451900	4.10430000	2.48366200
H	2.00410500	2.92435700	3.76013600
H	-0.64800200	4.94986100	1.03585900
N	0.36037000	1.72432300	1.08446700
C	-0.13396400	-2.07821200	-2.23328200
C	-1.82117400	-2.23911500	-0.61007000
C	-0.64101100	-3.14276700	-2.95542600
H	0.75233500	-1.54381900	-2.55942700
C	-2.38940800	-3.31381200	-1.31963300
C	-1.80865600	-3.76696600	-2.48649200
H	-0.14173300	-3.46791100	-3.86013600
H	-3.29394100	-3.78012100	-0.94583600
H	-2.25178400	-4.59312300	-3.03331300
C	-1.66141000	-0.53389400	1.12559600
C	-2.14814500	0.02579000	2.31544200

C	-2.34081900	-1.68556100	0.63712600
C	-3.23760700	-0.51620900	3.00422200
H	-1.66058500	0.91161200	2.72499500
C	-3.42850200	-2.24638600	1.33459600
C	-3.87395700	-1.66100800	2.51250500
H	-3.59063000	-0.05350800	3.92243400
H	-3.92434100	-3.14210700	0.96932500
H	-4.71350100	-2.09423600	3.04855400
N	-0.69663800	-1.62522800	-1.10075400
C	1.71183100	0.31781800	-1.13654500
C	2.85508000	-0.40021700	-0.66761100
C	1.89757300	1.09785800	-2.28770100
C	4.08531400	-0.34025400	-1.35722800
C	3.12159200	1.17874100	-2.96060300
H	1.05219900	1.66226900	-2.68272900
C	4.21690900	0.44503500	-2.49412200
H	4.94195800	-0.91532600	-1.01521600
H	3.22188100	1.80360300	-3.84453800
H	5.16868200	0.48641300	-3.01649100
C	1.16108200	-1.96767600	2.15332900
C	2.68481700	-1.19626100	0.54572000
C	2.13338100	-2.67533500	2.83768900
H	0.12751800	-1.95810100	2.49108600
C	3.72259300	-1.87597700	1.21817300
C	3.45389000	-2.61133500	2.35400100
H	1.87327900	-3.24981900	3.71857700
H	4.73826400	-1.81187000	0.84421100
H	4.25568000	-3.13038500	2.86998700
N	1.41210300	-1.24757400	1.05107100

C	-1.14464900	1.33333700	-1.03331300
H	0.80270100	5.03029600	3.03733200
H	-3.09569800	4.24964900	-2.80248700

SMD-M06-2X/6-31G(d,p)/Lanl2DZ

Electronic Energy (0K) = -1540.382352

Electronic Energy (0K) + ZPE = -1539.898838

Enthalpy (298K) = -1539.868993

Free Energy (298K) = -1539.960089

SMD-M06-2X/6-311+G(d,p)/SDD

Electronic Energy (0K) = -1540.413666

AcO^-

Number of imaginary frequencies: 0

C	-1.34528100	0.00193900	-0.00423300
H	-1.74740300	-0.88889800	-0.49489400
H	-1.70015100	-0.00612300	1.03370800
H	-1.74644700	0.90047700	-0.48137400
C	0.20609000	-0.00005200	-0.01280000
O	0.75388800	1.12667900	0.00279600
O	0.74975500	-1.12877600	0.00279900

SMD-M06-2X/6-31G(d,p)

Electronic Energy (0K) = -228.495407

Electronic Energy (0K) + ZPE = -228.446295

Enthalpy (298K) = -228.440926

Free Energy (298K) = -228.474096

SMD-M06-2X/6-311+G(d,p)

Electronic Energy (0K) = -228.594886

AcOH

Number of imaginary frequencies: 0

C	-1.39094800	-0.11130300	-0.00001100
H	-1.67052000	-0.69273600	-0.88211900
H	-1.67071900	-0.69053900	0.88349000
H	-1.91243200	0.84396100	-0.00119300
C	0.09035200	0.12045300	-0.00003300
O	0.64036000	1.19662600	0.00000600
O	0.77653100	-1.03511700	-0.00000200
H	1.72211900	-0.80765800	0.00005400

SMD-M06-2X/6-31G(d,p)

Electronic Energy (0K) = -228.997930

Electronic Energy (0K) + ZPE = -228.935367

Enthalpy (298K) = -228.929920

Free Energy (298K) = -228.962359

SMD-M06-2X/6-311+G(d,p)

Electronic Energy (0K) = -229.074712

Et_3N

Number of imaginary frequencies: 0

N	-0.00001400	-0.00015600	-0.17695000
C	0.23946300	1.36914500	0.28339100
C	-0.77266500	2.38006200	-0.24391700
C	1.06619000	-0.89227400	0.28330700
C	-1.30546000	-0.47725700	0.28387500
C	2.44771000	-0.52065900	-0.24373500
C	-1.67524800	-1.85890400	-0.24403000
H	1.22994200	1.67010200	-0.06687400
H	0.26665800	1.41031300	1.39037900
H	-0.40499700	3.39427500	-0.06555100

H	-1.74867000	2.29651900	0.23980200
H	-0.90960800	2.25134600	-1.32236300
H	0.83210300	-1.90013800	-0.06845200
H	1.08794100	-0.93783200	1.39027100
H	-2.06142400	0.23022900	-0.06586600
H	-1.35443600	-0.47460700	1.39088700
H	3.14187800	-1.34691300	-0.06745000
H	2.86385000	0.36515000	0.24171100
H	2.40425100	-0.33552500	-1.32182500
H	-2.73721200	-2.04811800	-0.06495700
H	-1.11382600	-2.66239700	0.23831100
H	-1.49629800	-1.91198800	-1.32272100

SMD-M06-2X/6-31G(d,p)

Electronic Energy (0K) = -292.271396

Electronic Energy (0K) + ZPE = -292.063693

Enthalpy (298K) = -292.053441

Free Energy (298K) = -292.097723

SMD-M06-2X/6-311+G(d,p)

Electronic Energy (0K) = -292.345065

A

Number of imaginary frequencies: 0

N	0.08948200	-0.12081200	0.22777800
C	1.21144700	-0.94128100	0.23850400
C	2.49621900	-0.46859500	-0.36577900
C	-1.17152200	-0.73516700	0.63167600
C	0.21494800	1.31071700	0.46579000
C	-1.92290700	-1.33303300	-0.55206000
C	-0.73127700	2.11956100	-0.41320200

H	0.96815000	-1.99787400	0.15726600
H	3.19198000	-1.30781200	-0.44412600
H	2.99769300	0.30693000	0.22751100
H	2.36352800	-0.05275700	-1.37835300
H	-1.78927400	0.02412900	1.12153800
H	-0.97204200	-1.51244500	1.38107400
H	1.24443400	1.60535100	0.25268200
H	0.02767400	1.53957700	1.52715500
H	-2.84917000	-1.81359700	-0.22283200
H	-1.30823400	-2.08587200	-1.05515700
H	-2.17400300	-0.55651700	-1.28100800
H	-0.60853700	3.18911600	-0.21934100
H	-1.77766100	1.86353200	-0.21998000
H	-0.52235600	1.93070700	-1.47044400

SMD-M06-2X/6-31G(d,p)

Electronic Energy (0K) = -291.616264

Electronic Energy (0K) + ZPE = -291.422761

Enthalpy (298K) = -291.412145

Free Energy (298K) = -291.458052

SMD-M06-2X/6-311+G(d,p)

Electronic Energy (0K) = -291.692362

2a

Number of imaginary frequencies: 0

C	-1.50069600	1.14475800	0.00000900
C	-1.50080200	-1.14467400	0.00002200
C	-0.11120600	-1.20680500	-0.00000300
C	0.58904700	-0.00006900	-0.00001100
C	-0.11116200	1.20676600	0.00000600

H	-2.08303600	2.06216300	0.00002500
H	-2.08313800	-2.06208600	0.00002700
H	0.40682100	-2.15836900	0.00001400
H	0.40701700	2.15824800	0.00002500
C	2.03024800	-0.00004300	0.00000100
N	3.18651700	0.00002700	-0.00000300
N	-2.18940800	0.00003800	-0.00003100

SMD-M06-2X/6-31G(d,p)

Electronic Energy (0K) = -340.393478

Electronic Energy (0K) + ZPE = -340.304958

Enthalpy (298K) = -340.298063

Free Energy (298K) = -340.335174

SMD-M06-2X/6-311+G(d,p)

Electronic Energy (0K) = -340.393478

2a'

Number of imaginary frequencies: 0

C	-1.49784200	1.14555600	0.00000400
C	-1.49785000	-1.14554700	0.00000300
C	-0.12930000	-1.21609500	0.00000200
C	0.64404700	-0.00000600	0.00000100
C	-0.12929500	1.21609000	0.00000300
H	-2.06940300	2.07416700	0.00000400
H	-2.06941000	-2.07416100	0.00000100
H	0.36789600	-2.18110900	0.00000000
H	0.36791500	2.18109700	0.00000400
C	2.03879800	0.00000600	-0.00000500
N	3.21580300	-0.00000400	-0.00001000
N	-2.23985200	0.00000100	0.00000200

SMD-M06-2X/6-31G(d,p)

Electronic Energy (0K) = -340.472684

Electronic Energy (0K) + ZPE = -340.386865

Enthalpy (298K) = -340.379733

Free Energy (298K) = -340.417966

SMD-M06-2X/6-311+G(d,p)

Electronic Energy (0K) = -340.578644

1a

Number of imaginary frequencies: 0

C	0.16809300	3.45549500	-0.42280700
C	1.32996400	2.96605000	-1.01244000
C	1.68193300	1.62901200	-0.85272400
C	0.85808900	0.77246100	-0.12416100
C	-0.32074000	1.23960500	0.46539600
C	-0.63632800	2.59846800	0.31593600
C	-1.32305600	0.44661600	1.27823000
C	-1.87821000	-0.86454900	0.76043900
C	-2.16784900	-0.89196000	-0.74604700
C	-2.58757200	-2.29916700	-1.16339200
C	-3.24417100	0.13003400	-1.10919900
O	-1.73205200	0.93322900	2.31414900
H	-0.10793200	4.49884300	-0.53301500
H	1.97320200	3.62086900	-1.59140600
H	2.60011800	1.25434600	-1.29113500
H	-1.54081300	2.96694200	0.78990300
H	-1.17520000	-1.66261500	1.02175800
H	-2.79866400	-1.04764200	1.32596100
H	-1.24465800	-0.63630100	-1.28211000

H	-2.80261300	-2.34138600	-2.23558700
H	-1.79989700	-3.02748000	-0.94432100
H	-3.49225500	-2.60675300	-0.62623500
H	-3.44690500	0.11938300	-2.18450000
H	-2.94860000	1.14936100	-0.83598300
H	-4.17985600	-0.09973900	-0.58621300
I	1.57621800	-1.22162400	0.11555300

SMD-M06-2X/6-31G(d,p)/Lanl2DZ

Electronic Energy (0K) = -513.350957

Electronic Energy (0K) + ZPE = -513.136608

Enthalpy (298K) = -513.122410

Free Energy (298K) = -513.178190

SMD-M06-2X/6-311+G(d,p)/SDD

Electronic Energy (0K) = -513.513399

TS_B

Number of imaginary frequencies: 1

C	-4.44967100	-2.10798300	0.76133100
C	-3.32100700	-2.83288500	1.14041600
C	-2.05053400	-2.36021600	0.81453100
C	-1.89356200	-1.15614800	0.13261800
C	-3.01702600	-0.41701700	-0.25175000
C	-4.29295600	-0.91869200	0.06313600
C	-3.02150800	0.89927000	-0.99153600
C	-1.94217400	1.92799500	-0.73943200
C	-1.68375100	2.21485700	0.74679500
C	-0.52762300	3.20181400	0.88472400
C	-2.94729400	2.74362700	1.42355000
O	-3.94566000	1.14693500	-1.74626200

H	-5.44347000	-2.46876500	1.00650000
H	-3.42745500	-3.76676000	1.68523600
H	-1.17629100	-2.94102900	1.09736100
H	-5.16057000	-0.34389900	-0.24714500
H	-1.01675400	1.58906000	-1.21687300
H	-2.26337700	2.84433200	-1.24676800
H	-1.39381500	1.27553000	1.23321200
H	-0.30580500	3.40459400	1.93735800
H	0.38062900	2.80910200	0.41347700
H	-0.77273100	4.15518500	0.40191200
H	-2.76513000	2.95793100	2.48121000
H	-3.76905500	2.02049600	1.36656400
H	-3.28139700	3.67078800	0.94313700
N	3.59734200	0.24155800	0.15256400
C	3.10900700	-0.36877400	-0.93966500
C	3.54598300	-1.75057600	-1.31895100
C	3.25140500	1.63300300	0.45216300
C	4.06667700	-0.53390300	1.30366700
C	3.01991500	2.50729400	-0.76670000
C	5.57014700	-0.77160400	1.25505000
H	2.84529400	0.29416500	-1.75522900
H	4.59728200	-1.73456900	-1.63874000
H	2.94447900	-2.10236400	-2.15838300
H	3.45341000	-2.47155100	-0.50368800
H	4.07243700	2.03697900	1.05205300
H	2.35227000	1.62624600	1.08867400
H	3.51867900	-1.47972500	1.34531700
H	3.80244100	0.02806200	2.20348000
H	2.89722700	3.54091900	-0.43368900

H	2.11458400	2.22505500	-1.31177100
H	3.87282300	2.46682700	-1.45063000
H	5.89257800	-1.30851200	2.15127400
H	6.10723300	0.18027200	1.21155300
H	5.84763100	-1.36467100	0.37983100
I	0.41442600	-0.74472600	-0.39533500

SMD-M06-2X/6-31G(d,p)/Lanl2DZ

Electronic Energy (0K) = -804.979010

Electronic Energy (0K) + ZPE = -804.568900

Enthalpy (298K) = -804.544186

Free Energy (298K) = -804.625658

SMD-M06-2X/6-311+G(d,p)/SDD

Electronic Energy (0K) = -805.215463

B

Number of imaginary frequencies: 0

C	-3.20024800	0.40747600	0.44377200
C	-3.29959500	-0.97413600	0.25734300
C	-2.19540900	-1.71186200	-0.18624400
C	-1.04046500	-1.00434300	-0.42110800
C	-0.88103200	0.35613300	-0.25540100
C	-2.00438100	1.07020000	0.19117600
C	0.40708700	1.06943500	-0.53328300
C	1.59844000	0.22788100	-0.92585200
C	2.16259900	-0.58535300	0.25676900
C	3.38512400	-1.37421800	-0.20601400
C	2.51202300	0.32289800	1.43371700
O	0.47733000	2.27907300	-0.41955000
H	-4.06412900	0.96600300	0.78876700

H	-4.23801500	-1.48291600	0.45747900
H	-2.26004500	-2.78514800	-0.33463100
H	-1.91345700	2.14338600	0.33162800
H	1.30530100	-0.45780800	-1.72977600
H	2.37068200	0.90598300	-1.30281000
H	1.39251000	-1.29796500	0.57988700
H	3.78016800	-1.99182400	0.60648400
H	3.14087900	-2.03178100	-1.04619000
H	4.18061300	-0.69298800	-0.52921500
H	2.95896200	-0.25502000	2.24837600
H	1.62926700	0.83406700	1.83102900
H	3.23377100	1.08875900	1.12612200

SMD-M06-2X/6-31G(d,p)

Electronic Energy (0K) = -501.939997

Electronic Energy (0K) + ZPE = -501.727817

Enthalpy (298K) = -501.715187

Free Energy (298K) = -501.767066

SMD-M06-2X/6-311+G(d,p)

Electronic Energy (0K) = -502.069937

C

Number of imaginary frequencies: 0

N	-1.67305100	0.20214900	-0.01310700
C	-1.31413300	-0.21301400	1.14500400
C	-1.35535500	-1.61139600	1.62476500
C	-1.58448600	1.62203400	-0.42098300
C	-2.16891700	-0.70034500	-1.07480000
C	-1.22370500	2.58797200	0.68489900
C	-3.65382000	-0.97524000	-0.89542800

H	-0.96210000	0.53800000	1.84587000
H	-2.05314100	-1.65015100	2.46896300
H	-0.36561500	-1.85807000	2.02099200
H	-1.65079900	-2.34277200	0.87594300
H	-2.55694700	1.86430500	-0.85906600
H	-0.83816300	1.64559600	-1.22208500
H	-1.57400400	-1.61366100	-1.05584200
H	-1.97363500	-0.19325700	-2.02057800
H	-1.24387700	3.59520400	0.26337200
H	-0.21668500	2.40609800	1.06988000
H	-1.94168400	2.54956300	1.50860700
H	-4.00443600	-1.60277800	-1.71767200
H	-4.22390700	-0.04256400	-0.90450400
H	-3.84624100	-1.49542900	0.04649500
I	2.01820900	-0.14104100	-0.16244100

SMD-M06-2X/6-31G(d,p)/Lanl2DZ

Electronic Energy (0K) = -303.059388

Electronic Energy (0K) + ZPE = -302.860972

Enthalpy (298K) = -302.848597

Free Energy (298K) = -302.901520

SMD-M06-2X/6-311+G(d,p)/SDD

Electronic Energy (0K) = -303.162598

TS_D

Number of imaginary frequencies: 1

C	-3.16745200	0.06493000	0.07666600
C	-2.91971600	-1.30994200	0.01071900
C	-1.61342900	-1.79373600	-0.10667400
C	-0.58428100	-0.86916200	-0.16801300

C	-0.80157100	0.49925100	-0.10006400
C	-2.11533600	0.97164100	0.02630200
C	0.34881000	1.45706000	-0.15800000
C	1.69961900	0.88198700	-0.55490200
C	1.98132300	-0.50177200	0.01474700
C	3.01361900	-1.28607300	-0.76658600
C	2.21932000	-0.48887100	1.51183800
O	0.19130500	2.64496800	0.04891500
H	-4.18758100	0.42338500	0.16981600
H	-3.74976300	-2.00955000	0.05455900
H	-1.42449600	-2.86233500	-0.14875500
H	-2.28992700	2.04230100	0.07952600
H	1.69098000	0.82971200	-1.65258900
H	2.47145300	1.60420900	-0.26421100
H	0.86646800	-1.04859000	-0.14501600
H	3.13896800	-2.29202100	-0.35551400
H	2.73595700	-1.37284400	-1.82135800
H	3.98808200	-0.78140600	-0.71712400
H	2.29604300	-1.50532900	1.90923500
H	1.41124400	0.02614800	2.04282400
H	3.15668900	0.03469000	1.74109400

SMD-M06-2X/6-31G(d,p)

Electronic Energy (0K) = -501.923874

Electronic Energy (0K) + ZPE = -501.717630

Enthalpy (298K) = -501.705436

Free Energy (298K) = -501.755163

SMD-M06-2X/6-311+G(d,p)

Electronic Energy (0K) = -502.053062

D

Number of imaginary frequencies: 0

C	-3.10659400	0.35190100	0.48195100
C	-3.15098000	-1.02438900	0.25693100
C	-2.02325300	-1.69110000	-0.21851400
C	-0.84816400	-0.98643900	-0.46670200
C	-0.79816600	0.39408400	-0.24320500
C	-1.93553200	1.05673600	0.23093500
C	0.43710900	1.20466800	-0.50544300
C	1.70712100	0.47601400	-0.91250900
C	2.21575300	-0.42085900	0.18150300
C	2.94524100	-1.66672100	-0.19729200
C	2.47801400	0.19059300	1.51913000
O	0.42024600	2.41451100	-0.37218400
H	-3.98487400	0.87140300	0.85186500
H	-4.06505000	-1.57679500	0.45199200
H	-2.05810900	-2.76118200	-0.39592700
H	-1.88215900	2.12767200	0.39784200
H	1.51075900	-0.10739900	-1.81980600
H	2.44054900	1.25478000	-1.16812300
H	0.02479500	-1.51661400	-0.83462800
H	2.99142600	-2.37168100	0.63949300
H	2.47349100	-2.16834100	-1.04920600
H	3.98668900	-1.45219700	-0.48980600
H	2.57939900	-0.57514200	2.29461200
H	1.68256800	0.88067200	1.82261600
H	3.41525800	0.77180400	1.51582800

SMD-M06-2X/6-31G(d,p)

Electronic Energy (0K) = -501.963165

Electronic Energy (0K) + ZPE = -501.752814

Enthalpy (298K) = -501.739528

Free Energy (298K) = -501.793853

SMD-M06-2X/6-311+G(d,p)

Electronic Energy (0K) = -502.093786

E

Number of imaginary frequencies: 0

C	4.27451900	0.52551500	-0.56069200
C	4.38300500	-0.64238100	0.19633200
C	3.28183100	-1.11191200	0.90817300
C	2.07551400	-0.41542500	0.87490900
C	1.95833500	0.75385600	0.11687800
C	3.06904100	1.21487300	-0.60159500
C	0.68878000	1.55699900	0.02560200
C	-0.42471500	1.33942500	1.03695700
C	-1.83613300	1.01686400	0.50100800
C	-2.79405100	1.07704700	1.69883400
C	-2.30261300	2.05049400	-0.53075000
O	0.61837800	2.47092600	-0.78121700
H	5.13022100	0.89435800	-1.11782500
H	5.32250200	-1.18582200	0.22667400
H	3.35736300	-2.02667700	1.48796100
H	2.96571700	2.12099100	-1.18943600
H	-0.15216300	0.57968700	1.77155300
H	-0.49660300	2.29476400	1.57321700
H	1.21846400	-0.81073000	1.40976800
H	-3.79878800	0.74195000	1.41746400
H	-2.44585600	0.45775900	2.53056100

H	-2.87654500	2.10692900	2.06100100
H	-3.35389700	1.88097700	-0.78777000
H	-1.70894000	2.02725300	-1.44542700
H	-2.21989500	3.05896300	-0.11345600
C	-0.00119300	-1.65485500	-1.36201200
C	-0.63007800	-2.52945200	0.61595400
C	-1.53645700	-1.54311300	0.86999200
C	-1.83636100	-0.43658800	-0.12548900
C	-0.86011600	-0.59797100	-1.27396700
H	0.64967400	-1.68983700	-2.24033300
H	-0.51183000	-3.30228600	1.38060500
H	-2.12931600	-1.58664200	1.77833200
H	-0.89510100	0.12666000	-2.08109300
C	-3.22474600	-0.66656700	-0.65093100
N	-4.27476700	-0.91563800	-1.07580000
N	0.17342400	-2.66672800	-0.47381100

SMD-M06-2X/6-31G(d,p)

Electronic Energy (0K) = -842.503307

Electronic Energy (0K) + ZPE = -842.200312

Enthalpy (298K) = -842.181598

Free Energy (298K) = -842.245701

SMD-M06-2X/6-311+G(d,p)

Electronic Energy (0K) = -842.736082

TS_{3aa}

Number of imaginary frequencies: 1

C	-4.29930800	-0.31565800	-0.56405600
C	-4.29059800	0.86479100	0.17971400
C	-3.14340600	1.23877700	0.87712000

C	-2.00932600	0.43148200	0.84266800
C	-2.00921100	-0.74973000	0.09418600
C	-3.16217800	-1.11387200	-0.61110000
C	-0.80935400	-1.65008400	-0.01208200
C	0.32093700	-1.55192700	1.00099000
C	1.72346300	-1.15156400	0.46200700
C	2.70029400	-1.31199800	1.63284100
C	2.16516600	-2.09653800	-0.65909100
O	-0.78991100	-2.52016600	-0.86704100
H	-5.19152200	-0.60929000	-1.10829000
H	-5.17559300	1.49297800	0.21215900
H	-3.12837300	2.16268000	1.44695900
H	-3.14872400	-2.02938900	-1.19343300
H	0.05523700	-0.88443500	1.82355200
H	0.41144000	-2.56246300	1.41813500
H	-1.11278400	0.74675200	1.36709100
H	3.68453900	-0.91255400	1.36847400
H	2.35002400	-0.80402800	2.53605500
H	2.81650400	-2.37315100	1.87472000
H	3.20086200	-1.88270600	-0.93854700
H	1.53915100	-2.02299700	-1.54931800
H	2.11180900	-3.13243000	-0.30963900
C	0.18508300	1.82161500	-1.31669600
C	0.80408700	2.51901900	0.73698200
C	1.46903700	1.34650100	1.00832700
C	1.64045400	0.32437900	-0.00961700
C	0.81824400	0.60912000	-1.17012000
H	-0.38153800	2.00084300	-2.23214000
H	0.75501100	3.27904900	1.51868200

H	1.94354300	1.22728800	1.97700500
H	0.75005300	-0.11535100	-1.97531700
C	3.45436400	0.57038200	-0.62222300
N	4.34339900	1.16432000	-1.09410000
N	0.15562300	2.81744500	-0.40860200

SMD-M06-2X/6-31G(d,p)

Electronic Energy (0K) = -842.488982

Electronic Energy (0K) + ZPE = -842.187542

Enthalpy (298K) = -842.168658

Free Energy (298K) = -842.233718

SMD-M06-2X/6-311+G(d,p)

Electronic Energy (0K) = -842.722523

CN^-

Number of imaginary frequencies: 0

C	0.00000000	0.00000000	-0.63228100
N	0.00000000	0.00000000	0.54195500

SMD-M06-2X/6-31G(d,p)

Electronic Energy (0K) = -92.9011119

Electronic Energy (0K) + ZPE = -92.896045

Enthalpy (298K) = -92.892741

Free Energy (298K) = -92.915083

SMD-M06-2X/6-311+G(d,p)

Electronic Energy (0K) = -92.9560978

3aa

Number of imaginary frequencies: 0

C	3.04791300	-1.09777900	0.80816400
C	3.42588800	-0.07406300	-0.06060000

C	2.58929800	0.29389300	-1.11404500
C	1.36262800	-0.34162400	-1.28493600
C	0.97302500	-1.35887100	-0.40788100
C	1.83043300	-1.74521600	0.62755300
C	-0.36315800	-2.03188800	-0.49427000
C	-1.56069100	-1.23976900	-0.97861500
C	-2.09571800	-0.24399600	0.09932100
C	-3.47355900	0.24804100	-0.37222800
C	-2.27821200	-0.97525500	1.43227000
O	-0.49896300	-3.17458800	-0.09363300
H	3.70010600	-1.38607600	1.62645500
H	4.37401400	0.43540000	0.08145800
H	2.88789300	1.08338200	-1.79665000
H	1.51743300	-2.54013600	1.29755100
H	-1.33336300	-0.68935400	-1.89710900
H	-2.35229900	-1.96329000	-1.19318500
H	0.71245000	-0.04188900	-2.10043000
H	-3.86342500	1.00795100	0.31217100
H	-3.43414700	0.67655500	-1.37712500
H	-4.17662300	-0.59017600	-0.39240500
H	-2.71065100	-0.30509900	2.18196200
H	-1.33883700	-1.37018100	1.82951800
H	-2.95908000	-1.82049500	1.29406400
C	0.57753300	2.21689900	1.33115400
C	-0.09506500	2.89817100	-0.72976400
C	-1.01690700	1.86343400	-0.82616400
C	-1.14235500	0.94427700	0.22164300
C	-0.32371300	1.15437100	1.33257100
H	1.22958900	2.36988800	2.18877000

H	0.00775000	3.60948300	-1.54655700
H	-1.61067800	1.76915900	-1.73002500
H	-0.35371200	0.49657000	2.19344600
N	0.70732100	3.08446500	0.32458900

SMD-M06-2X/6-31G(d,p)

Electronic Energy (0K) = -749.623746

Electronic Energy (0K) + ZPE = -749.327870

Enthalpy (298K) = -749.311414

Free Energy (298K) = -749.370756

SMD-M06-2X/6-311+G(d,p)

Electronic Energy (0K) = -749.816291

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