Electronic Supplementary Information

Sunlight-induced Three-Component Synthesis of α-Aminoketones: A Green and Sustainable Pathway Through EDA Complex

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1. General information

1.1 General information

Unless otherwise noted, all materials were purchased from commercial suppliers. All reactions were set up on the bench top and conducted under air atmosphere while subject to sunlight or blue-LED light irradiation.

Sunlight-induced reactions were carried out directly on the outdoor at 10:00 am – 16:00 pm (temperature: 17 – 25 °C; humidity: 10 – 30%) under ambient condition without any requirement of inert gas protection. Blue-LED reactions were performed in a photoreaction set-up (KDE1205PHV3; page S3).

The reactions were monitored by thin-layer chromatography on silica gel 60-F254 coated 0.2 mm plates. Visualization was accomplished by UV light (254 nm). Column chromatography was performed on silica gel (normal phase, 200–300 mesh) from Anhui Liangchen Silicon Material Co., Ltd, with petroleum ether (PE, bp. 60 - 90 °C) and ethyl acetate (EtOAc) as eluent.

^{1}H NMR spectra were recorded on a 400 MHz spectrometer at ambient temperature. Data were reported as follows: (1) chemical shift in parts per million (δ, ppm) from $CDCl_3$ (7.26 ppm); (2) multiplicity (s = singlet, br = broad, d = doublet, t = triplet, q = quartet, and m = multiplet); (3) coupling constants (Hz). ^{13}C NMR spectra were recorded on a 100 MHz spectrometer at ambient temperature. Chemical shifts were reported in ppm from $CDCl_3$ (77.00 ppm).

Melting points were obtained on a melting point apparatus and the data were uncorrected.

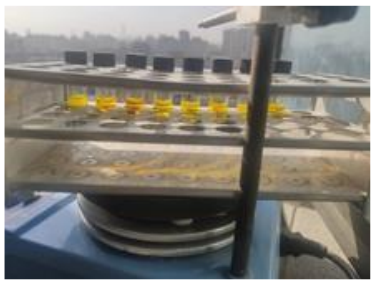
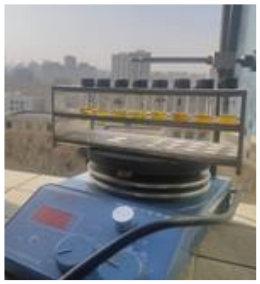
HR-MS analyses were carried out using a time-of-flight (TOF)-MS instrument with an electrospray ionization (ESI) source.

All commercial materials were used as received unless otherwise noted.

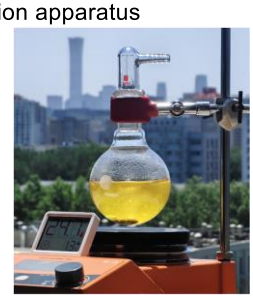
1.2 Photoreaction set-up and scale-up experimental reaction devices

1. Sunlight-induced reaction apparatus

a) 0.2 mmol scale reaction apparatus

b) 20 mmol and 50 mmol scale reaction apparatus

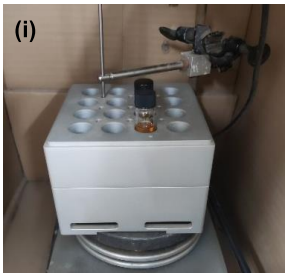
Sunlight-induced reactions were performed outside direct at 10:00 – 16:00 on an ambient condition (temperature: 17 – 25 °C; humidity: 10 – 30%).

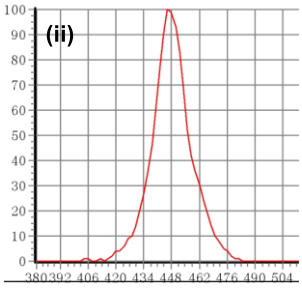
a) 0.2 mmol scale reactions were performed on a 3 mL screw-top glass vial.

b) 20 and 50 mmol scale reactions were performed on a 250 mL round-bottom flask.

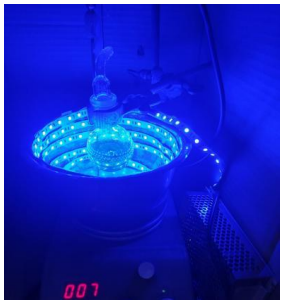
2. Blue-LED light-induced reaction apparatus

c) 0.2 mmol scale reaction apparatus





d) 10 mmol scale reaction apparatus



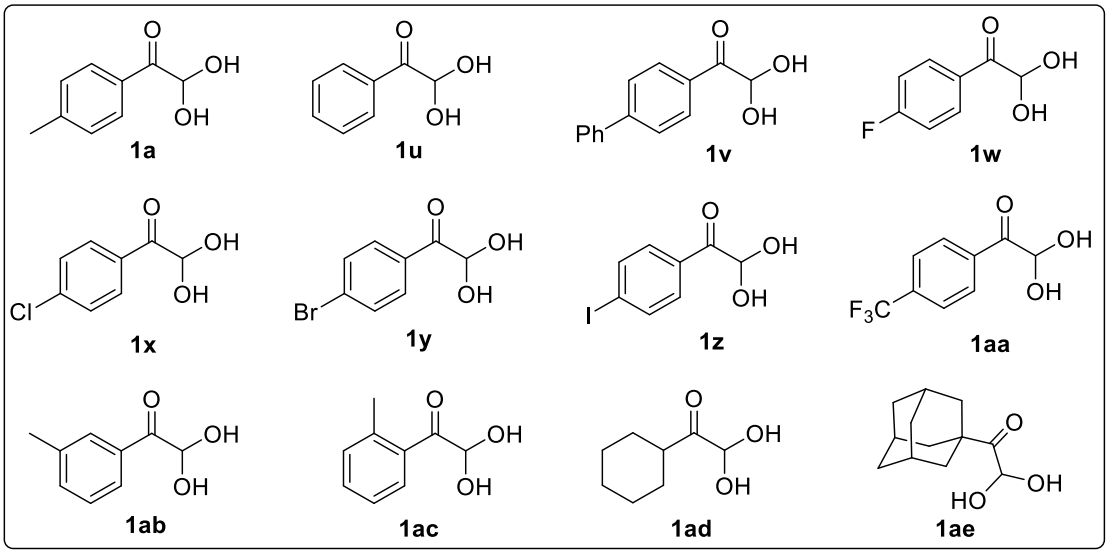

Blue-LED induced reaction were performed under commerical LED light:

c) commercial KDE1205PHV3 with irradiation by blue LEDs (1 W, λ_{max} = 447 nm)

d) Scale-up reaction device with blue-LED stripe (25 W, λ_{max} = 455 nm).

2 Starting materials information

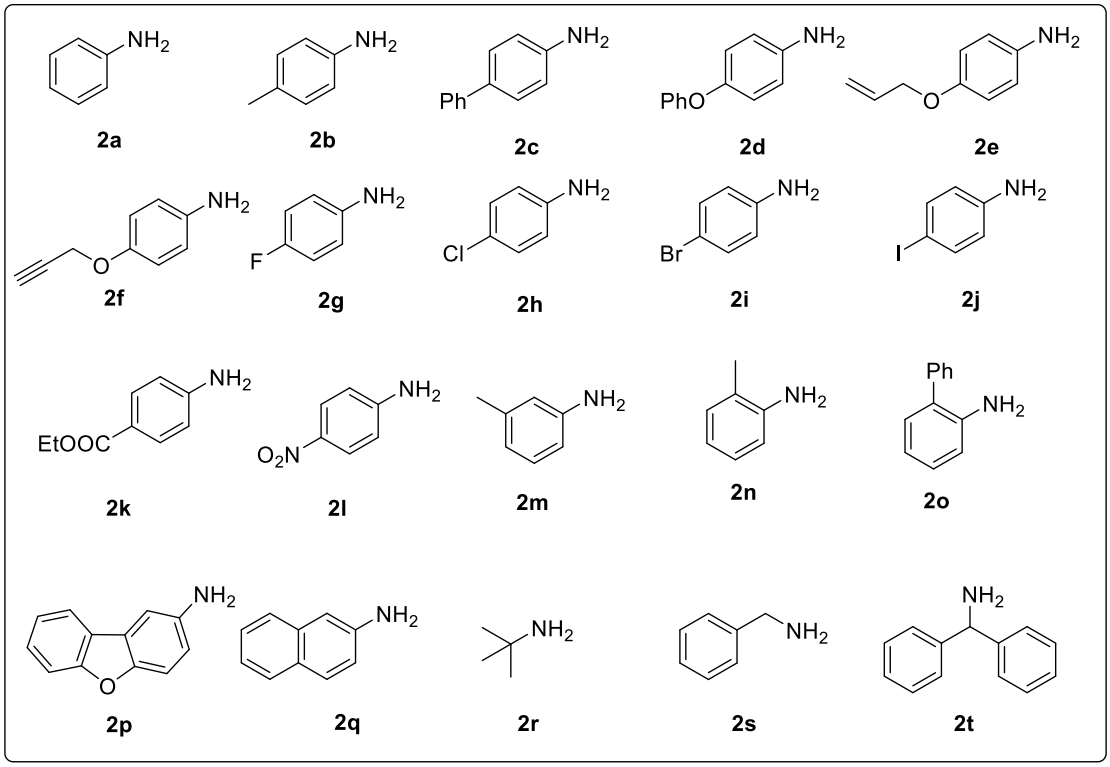
2.1 Starting materials of aryl/alkyl glyoxal hydrates **1**



According to the modified literature procedure,[1] the acetophenones (30 mmol, 1.0 equiv.), I_2 (15 mmol, 0.5 equiv.), and 30 mL of dimethyl sulfoxide (DMSO) were added in a 100 mL round-bottom flask. The mixture was stirred at 120 °C for 2 h. After acetophenones entirely consumed, the mixture was cooled to room temperature and saturated NaS_2O_3 solution was added to consume I_2. The reaction mixture was extracted with EtOAc (30 mL × 3), washed with saturated brine (20 mL) and H_2O (20 mL). The organic phases were dried over anhydrous Na_2SO_4. After filtration, the organic solvent was evaporated under reduced pressure. The obtained crude product was recrystallized with PE and EtOAc to give colorless solids. All of Compounds **1** were synthesized from above procedure.

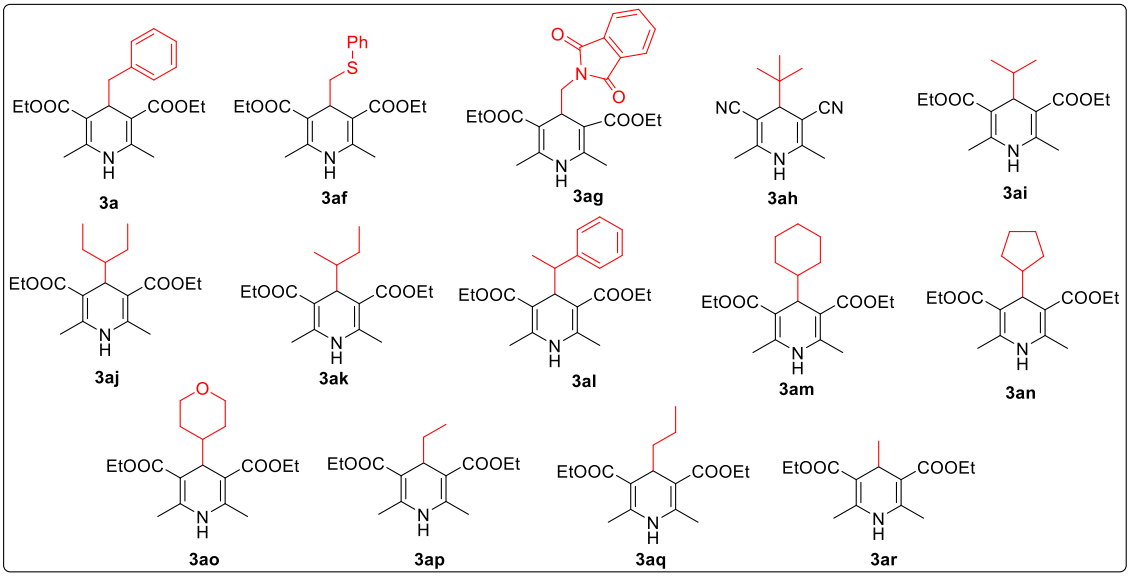
[1] (a) H.-Y. Wang and D.-Q. Shi, Efficient Synthesis of Functionalized Dihydro-1H-indol-4(5H)-ones via One-Pot Three-Component Reaction under Catalyst-Free Conditions. *ACS Comb. Sci.*, 2013, **15**, 261–266. (b) P. Wang, W.-J. Tao and X.-L. Sun, A Highly Efficient and Enantioselective Intramolecular Cannizzaro Reaction under TOX/Cu(II) Catalysis. *J. Am. Chem. Soc.*, 2013, **135**, 16849–16852. (c) X. Chang, X. Zhang and Z. Chen, *Org. Biomol. Chem.*, 2018, **16**, 4279-4287. (d) S. Aryal, C. A. Hone, M. I. J. Polson and D. J. Foley, Enantioselective synthesis of hydantoins by chiral acid-catalysed condensation of glyoxals and ureas. *Chem. Sci.*, 2023, **14**, 7905–7912. (e) P. Jiang, L. Liu, J. Tan and H. Du, Visible-light-promoted photocatalyst-free alkylation and acylation of benzothiazoles. *Org. Biomol. Chem.*, 2021, **19**, 4487–4491.

2.2 Anilines and aliphatic amines **2**



All anilines and aliphatic amines are commercially available.

2.3 4-alkyl DHPs **3**



3a, **3ag**–**3ar** were synthesized from our previous work.[2]

3af is a new compound, and the synthetic procedure is listed below:

2-(Phenylthio)acetaldehyde (0.97 g, 10 mmol), ethyl acetoacetate (1.2 mL, 10 mmol) and ethyl 3-amino-2-butenoate (1.2 mL, 10 mmol) was dissolved in ethylene glycol (5 mL). The reaction system was stirred at 80 °C for 3 h. After the 2-(phenylthio)acetaldehyde ($PhSCH_2CHO$) entirely consumed, the mixture was cooled to room temperature. After cooling the reaction system to 0 °C, the crude **3af** was filtered and then was recrystallized from PE:EtOAc (10:1, *v/v*) to give a pure **3af** as colorless crystals, 2.57 g, 66%.

Characterization data of **3af**:

Diethyl-2,6-dimethyl-4-((phenylthio)methyl)-1,4-dihydropyridine-3,5-dicarboxylate (**3af**)

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[2] (a) L. Liu, P. Jiang, Y. Liu, H. Du and J. Tan, Direct radical alkylation and acylation of 2H-indazoles using substituted Hantzsch esters as radical reservoirs. *Org. Chem. Front.*, 2020, **7**, 2278–2283. (b) Z. Yao, J. Yang, Z. Luo, H. Wang, X. Zhang, J. Ye, L. Xu and Q. Shi, Photo-driven metal-free multicomponent reaction between aldehydes, anilines and 4-substituted-DHPs for the synthesis of secondary amines. *Green Chem.*, 2022, **24**, 7968–7973. (c) Z. Liang, K. Lv, S. Zhou, C. Zhu and X. Bao, Visible-light photocatalytic preparation of alkenyl thioethers from 1,2,3-thiadiazoles and Hantzsch esters: synthetic and mechanistic investigations. *Org. Chem. Front.*, 2021, **8**, 6499–6507. (d) T. Rogova, P. Gabriel, S. Zavitsanou, J. A. Leitch, F. Duarte and D. J. Dixon, Reverse Polarity Reductive Functionalization of Tertiary Amides via a Dual Iridium-Catalyzed Hydrosilylation and Single Electron Transfer Strategy. *ACS Catal.*, 2020, **10**, 11438–11447.

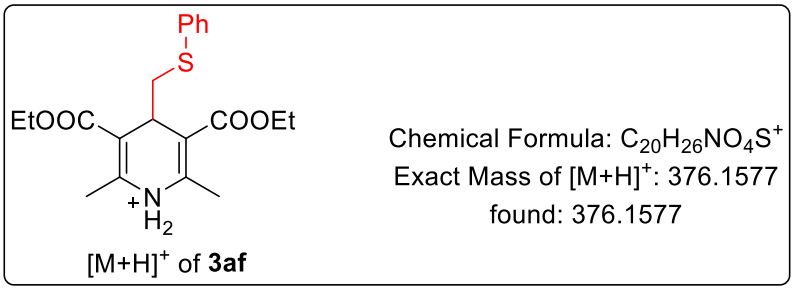
R_f = 0.20 (PE: EtOAc = 5: 1).

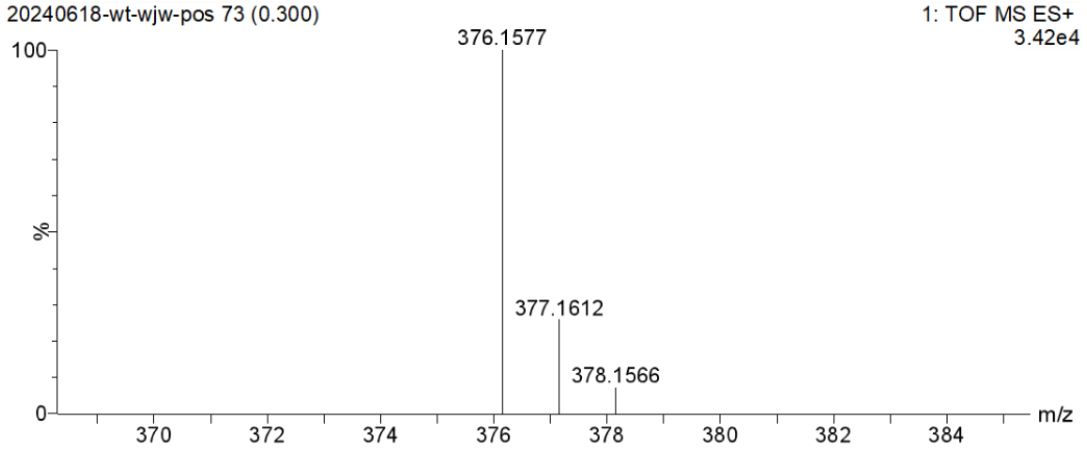
M.p. 122 – 124 °C.

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.32 (d, J = 8.0 Hz, 2H, ArH) , 7.22 (t, J = 8.0 Hz, 2H, ArH) , 7.08 (t, J = 8.0 Hz, 1H, ArH) , 5.94 (s, 1H, NH) , 4.36 (t, J = 6.0 Hz, 1H, CH) , 4.17 – 4.04 (m, 4H, **CH_2**CH_3) , 2.98 (d, J = 6.0 Hz, 2H, CH**CH_2**) , 2.26 (s, 6H, CH_3) , 1.18 (t, J = 7.1 Hz, 6H, CH_2**CH_3**) .

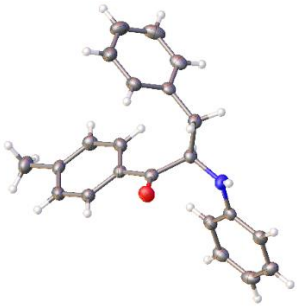
^{13}C NMR (101 MHz, $CDCl_3$) δ 167.7, 145.8, 138.3, 128.6, 127.2, 124.8, 101.9, 59.9, 38.9, 33.15, 19.4, 14.3.

HRMS (ESI): Calcd for $C_{20}H_{26}NO_4S^+$ $[M+H]^+$ 376.1577, found 376.1577.





3. X-Ray crystallographic analysis of **4a** [CCDC:2364621]



The X-ray crystallographic structure of **4a** could be accessed from the Cambridge Crystallographic Data Centre (CCDC: 2364621). https://www.ccdc.cam.ac.uk/structures/.

Table 1: Crystal data and structure refinement for **4a** [CCDC: 2364621]

Identification code	**4a**
Empirical formula	$C_{22}H_{21}NO$
Formula weight	315.40
Temperature / K	114.55(10)
Crystal system	triclinic
Space group	P-1
a / Å, b / Å, c / Å	9.1511(11), 9.4553(12), 10.6950(12)
α/°, β/°, γ/°	104.602(10), 96.752(10), 99.319(10)
Volume / $Å^3$	871.45(18)
Z	2
ρ_{calc} / mg mm^{-3}	1.202
μ / mm^{-1}	0.073
F (000)	336
Crystal size / mm^3	0.40 × 0.39 × 0.37
2Θ range for data collection	6.72 to 51.98°
Index ranges	$-10 \le h \le 11$, $-11 \le k \le 10$, $-13 \le l \le 13$
Reflections collected	5969
Independent reflections	3341[R(int) = 0.0364 (inf-0.9Å)]
Data/restraints/parameters	3341/0/218
Goodness-of-fit on F^2	1.031
Final R indexes [I>2σ (I) i.e. F_o>4σ (F_o)]	R_1 = 0.0512, wR_2 = 0.1049
Final R indexes [all data]	R_1 = 0.0715, wR_2 = 0.1203
Largest diff. peak/hole / e $Å^{-3}$	0.190/-0.226
Flack Parameters	N
Completeness	0.9971

4. General procedure for the synthesis of α-aminoketones **4** and their characterization data (for scheme 2).

4.1 General procedure for the synthesis of α-aminoketones **4**

4.1.1 General procedure A for the sunlight-induced process with various anilines

In a 3 mL screw-top glass vial, aryl/alkyl glyoxal hydrates **1** (1.0 equiv., 0.2 mmol), anilines **2** (1.0 equiv., 0.2 mmol), 4-alkyl DHPs **3** (1.5 equiv., 0.3 mmol) were dissolved in dichloromethane (1 mL). The reaction system was stirred for 10 – 28 h at outdoor with sunlight irradiation (sunshine time: from 10:00 am to 4:00 pm; the temperature was around from 17 °C to 25 °C and humility was from 10% to 30%). The solvent was evaporated in vacuo, and the residue was purified by column chromatography on silica gel with PE/EtOAc as eluent to afford the desired products **4**.

4.1.2 General procedure B for the blue-light-induced process with various anilines

In a 3 mL screw-top glass vial, aryl/alkyl glyoxal hydrates **1** (1.0 equiv., 0.2 mmol), anilines **2** (1.0 equiv., 0.2 mmol), 4-alkyl DHPs **3** (1.5 equiv., 0.3 mmol) were dissolved in dichloromethane (1 mL). The reaction system was stirred for 8 h with irradiation of 1W blue light (λ = 447 nm). The solvent was evaporated in vacuo, and the residue was purified by column chromatography on silica gel with PE/EtOAc as eluent to afford the desired products **4**.

4.1.3 General procedure C for the sunlight-induced process with electron-deficient anilines

In a 3 mL screw-top glass vial, aryl/alkyl glyoxal hydrates **1** (1.0 equiv., 0.2 mmol), electron-deficient anilines **2** (1.0 equiv., 0.2 mmol) and $BF_3{\cdot}OEt_2$ (0.02 mmol; 2.5 μL) were dissolved in dichloromethane (1 mL). The reaction system was stirred for 1 h and then 4-alkyl DHPs **3** (1.5 equiv., 0.3 mmol) was added. The whole system was stirred for 10 h at outdoor with sunlight irradiation (sunshine time: from 10:00 am to 4:00 pm; the temperature was around from 17 °C to 25 °C and humility was from 10% to 30%). The solvent was evaporated in vacuo, and the residue was purified by column chromatography on silica gel with PE/EtOAc as eluent to afford the desired products **4**.

4.1.4 General procedure D for the blue-light-induced process with electron-deficient anilines

In a 3 mL screw-top glass vial, aryl/alkyl glyoxal hydrates **1** (1.0 equiv., 0.2 mmol), electron-deficient anilines **2** (1.0 equiv., 0.2 mmol) and $BF_3{\cdot}OEt_2$ (0.02 mmol; 2.5 μL) were dissolved in dichloromethane (1 mL). The reaction system was stirred for 1 h and then 4-alkyl DHPs **3** (1.5 equiv., 0.3 mmol) was added. The whole system was stirred for 8 h with blue-light irradiation. The solvent was evaporated in vacuo, and the residue was purified by column chromatography on silica gel with PE/EtOAc as eluent to afford the desired products **4**.

4.1.5 General procedure E for the aliphatic amine with photosensitizer with sunlight-irradiation

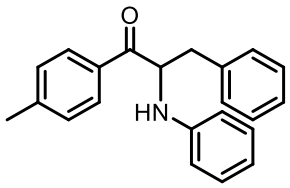
In a 3 mL screw-top glass vial, aryl/alkyl glyoxal hydrates **1** (1.0 equiv., 0.2 mmol), electron-deficient anilines **2** (1.0 equiv., 0.2 mmol), 4-alkyl DHPs **3** (1.5 equiv., 0.3 mmol), and 2,4,5,6-tetra(9H-carbazol-9-yl)isophthalonitrile (4CzIPN; 0.01 mmol, 7.9 mg) were dissolved in dichloromethane (1 mL). The reaction system was stirred for 10 h at outdoor with sunlight irradiation (sunshine time: from 10:00 am to 16:00 pm; the temperature was around from 17 °C to 25 °C and humility was from 10% to 30%). The solvent was evaporated in vacuo, and the residue was purified by column chromatography on silica gel with PE/EtOAc as eluent to afford the desired products **4**.

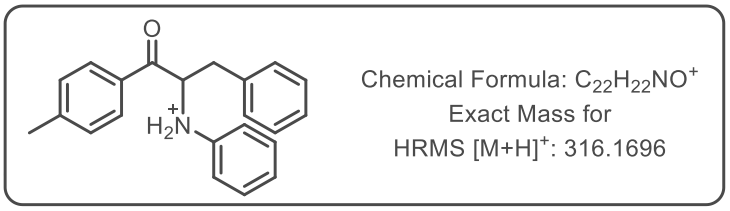
4.1.6 General procedure F for the aliphatic amine with photosensitizer with blue-light-irradiation

In a 3 mL screw-top glass vial, aryl/alkyl glyoxal hydrates **1** (1.0 equiv., 0.2 mmol), electron-deficient anilines **2** (1.0 equiv., 0.2 mmol), 4-alkyl DHPs **3** (1.5 equiv., 0.3 mmol), and 2,4,5,6-tetra(9H-carbazol-9-yl)isophthalonitrile (4CzIPN; 0.01 mmol, 7.9 mg) were dissolved in dichloromethane (1 mL). The reaction system was stirred for 8 h with irradiation of 1W blue light (λ = 447 nm). The solvent was evaporated in vacuo, and the residue was purified by column chromatography on silica gel with PE/EtOAc as eluent to afford the desired products **4**.

4.2 All characterization data of **4** and their HRMS spectra (for new compounds).

3-phenyl-2-(phenylamino)-1-(*p*-tolyl)propan-1-one (**4a**)





Following the general procedure A and B, the product **4a** was obtained by silica gel flash chromatography (PE: EtOAc = 60: 1 as the eluent) to give a colorless crystal. 37.8 mg, 60% for sunlight (10 h), 51.0 mg, 81% for sunlight (20 h; procedure A); 55.5 mg, 88% yield for blue-light (procedure B).

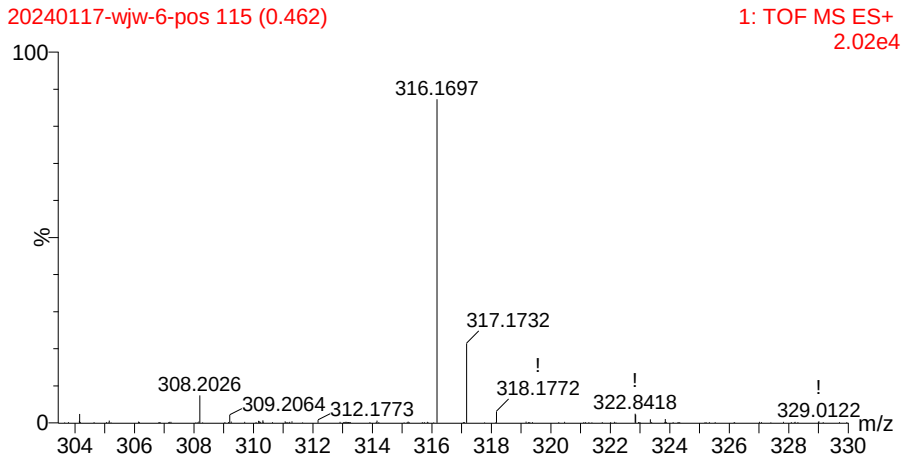
R_f = 0.62 (PE: EtOAc = 5: 1).

M. p. 112 – 113 °C.

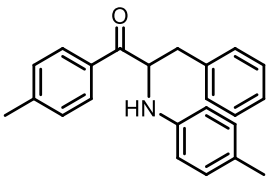
^{1}H NMR (400 MHz, $CDCl_3$) δ 7.85 (d, J = 8.4 Hz, 2H, ArH), 7.26 (d, J = 8.4 Hz, 2H, ArH), 7.22 – 7.11(m, 5H, ArH), 7.03 (dd, J = 7.8, 2.0 Hz, 2H, ArH), 6.70 (t, J = 7.8 Hz, 1H, ArH), 6.63 (d, J = 7.8 Hz, 2H, ArH), 5.28 (dt, J = 7.8, 5.6 Hz, 1H, CH), 4.61 (d, J = 7.8 Hz, 1H, NH), 3.28 (dd, J = 13.8, 5.6 Hz, 1H, 1H in CH_2), 3.01 (dd, J = 13.8, 5.6 Hz, 1H, 1H in CH_2), 2.42 (s, 3H, CH_3).

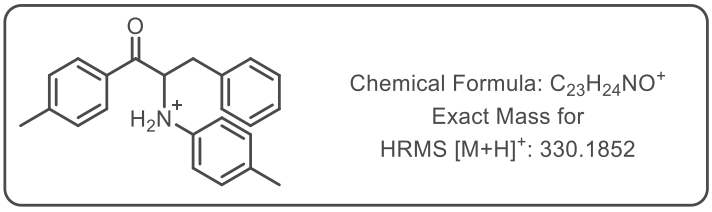
^{13}C NMR (101 MHz, $CDCl_3$) δ 198.9, 146.5, 144.5, 136.5, 132.8, 129.5, 129.5, 129.3, 128.5, 128.3, 126.7, 117.9, 113.6, 58.8, 38.7, 21.7.

HRMS (ESI): Calcd. for $C_{22}H_{22}NO^+$ $[M+H]^+$ 316.1696, found 316.1697.



3-phenyl-1-(*p*-tolyl)-2-(*p*-tolylamino)propan-1-one (**4b**)





Following the general procedure A and B, the product **4b** was purified by silica gel flash chromatography (PE: EtOAc = 60: 1 as the eluent) to give a colorless crystal, 51.9 mg, 79% for sunlight (10 h, procedure A); 56.6 mg, 86% yield for blue-light (procedure B).

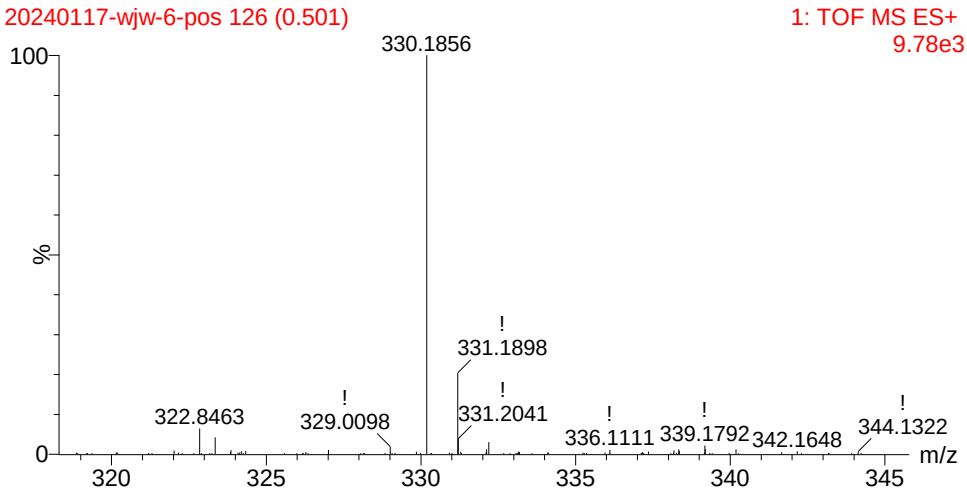
R_f = 0.55 (PE: EtOAc = 5: 1).

M. p. 114 – 115 °C.

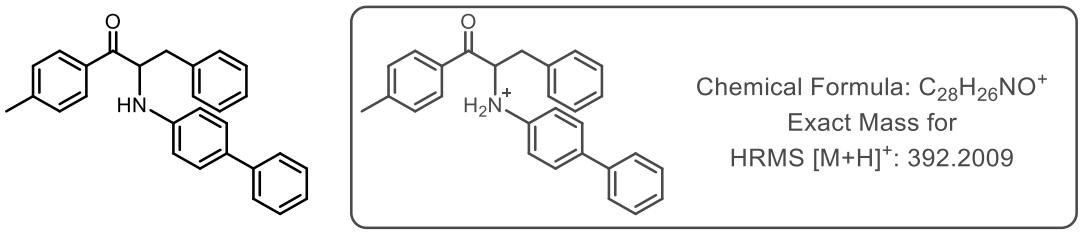
^{1}H NMR (400 MHz, $CDCl_3$) δ 7.84 (d, J = 7.7 Hz, 2H, ArH), 7.24 (d, J = 8.0 Hz, 2H, ArH), 7.22 – 7.13(m, 3H, ArH), 7.04 (d, J = 7.7 Hz, 2H, ArH), 6.95 (d, J = 8.0 Hz, 2H, ArH), 6.55(d, J = 8.0 Hz, 2H, ArH), 5.25 (t, J = 5.6 Hz, 1H, CH), 4.48 (s, 1H, NH), 3.25 (dd, J = 13.7, 5.6 Hz, 1H, 1H in CH_2), 2.99(dd, J = 13.8, 5.6 Hz, 1H, 1H in CH_2), 2.97, 2.39 (s, 3H, CH_3), 2.21 (s, 3H, CH_3).

^{13}C NMR (101 MHz, $CDCl_3$) δ 199.2, 144.4, 144.3, 136.6, 132.8, 129.8, 129.4 (2C), 128.5, 128.23, 127.1, 126.6, 113.9, 59.2, 38.7, 21.6, 20.3.

HRMS (ESI): Calcd for $C_{23}H_{24}NO^+$ $[M+H]^+$ 330.1852, found 330.1856.



2-([1,1'-biphenyl]-4-ylamino)-3-phenyl-1-(*p*-tolyl)propan-1-one (**4c**)



Following the general procedure A and B, the product **4c** was purified by silica gel flash chromatography (PE: EtOAc = 60: 1 as the eluent) to give a colorless crystal, 64.1 mg, 82% for sunlight (10 h, procedure A); 61.0 mg, 78% yield for blue-light (procedure B).

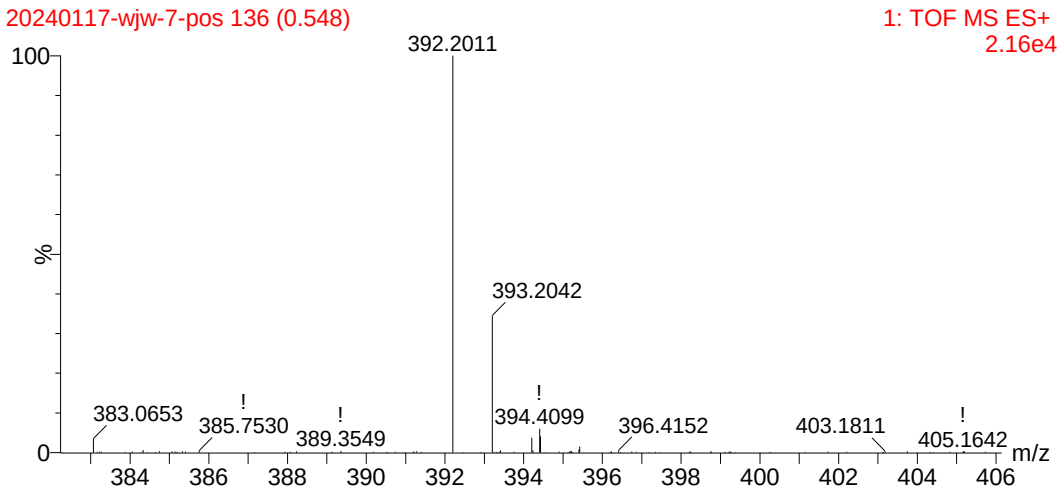
R_f = 0.52 (PE: EtOAc = 5: 1).

M. p. 111 – 113 °C.

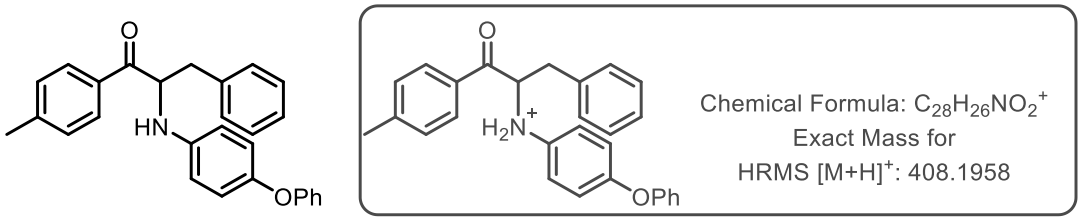
^{1}H NMR (400 MHz, $CDCl_3$) δ 7.88 (d, J = 8.2 Hz, 2H, ArH), 7.51 (d, J = 8.2 Hz, 2H, ArH), 7.41 (d, J = 8.5 Hz, 2H, ArH), 7.37 (t, J = 7.6 Hz, 2H, ArH), 7.45 – 7.34 (m, 4H, ArH), 7.28 (d, J = 7.6 Hz, 2H, ArH), 7.24 – 7.16 (m, 4H, ArH), 7.06 (d, J = 7.6 Hz, 2H, ArH), 6.70 (d, J = 8.5 Hz, 2H, ArH), 5.34 (t, J = 5.6 Hz, 1H, CH), 4.74 (s, 1H, NH), 3.32 (dd, J = 13.8, 5.6 Hz, 1H, 1H in CH_2), 3.04 (dd, J = 13.8, 5.6 Hz, 1H, 1H in CH_2), 2.42 (s, 3H, CH_3).

^{13}C NMR (101 MHz, $CDCl_3$) δ 198.8, 146.0, 144.6, 141.0, 136.4, 132.7, 130.8, 129.6, 129.5, 128.6, 128.6, 128.3, 128.0, 126.8, 126.2, 126.1, 113.9, 58.8, 38.8, 21.7.

HRMS (ESI): Calcd for $C_{28}H_{26}NO^+$ $[M+H]^+$ 392.2009, found 392.2011.



2-((4-phenoxyphenyl)amino)-3-phenyl-1-(*p*-tolyl)propan-1-one (**4d**)



Following the general procedure A and B, the product **4d** was purified by silica gel flash chromatography (PE: EtOAc = 55: 1 as the eluent) to give a colorless crystal, 61.0 mg, 75% for sunlight (10 h), 67.6 mg, 83% for sunlight (20 h, procedure A); 74.1 mg, 91% yield for blue-light (procedure B).

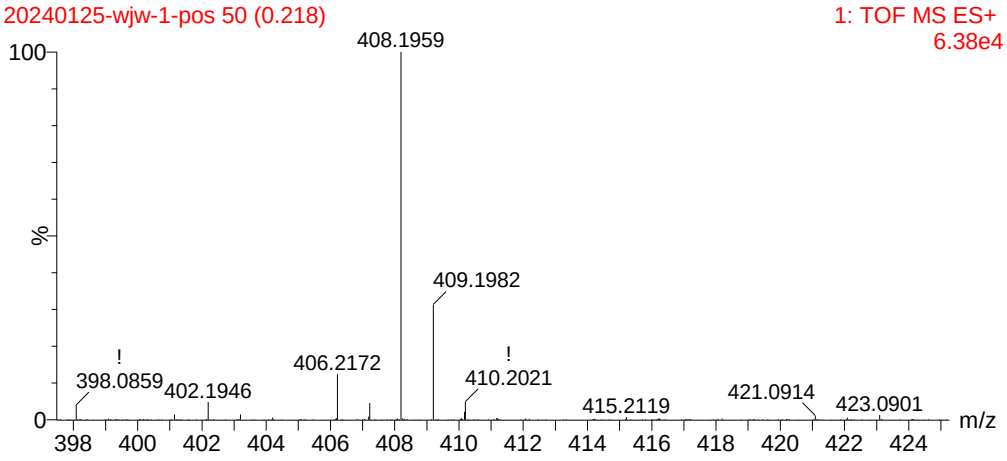
R_f = 0.55 (PE: EtOAc = 5: 1).

M. p. 115 – 117 °C.

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.87 (d, J = 8.2 Hz, 2H, ArH), 7.31 – 7.27 (m, 2H, ArH), 7.27 – 7.16 (m, 5H, ArH), 7.08 (d, J = 7.8 Hz, 2H, ArH), 6.99 (t, J = 7.8 Hz, 1H, ArH), 6.91 (d, J = 7.8 Hz, 2H, ArH), 6.86 (d, J = 8.8 Hz, 2H, ArH), 6.60 (d, J = 8.8 Hz, 2H, ArH), 5.24 (s, 1H, CH), 4.55 (s, 1H, NH), 3.27 (dd, J = 13.8, 5.3 Hz, 1H, 1H in CH_2), 3.01 (dd, J = 13.8, 5.3 Hz, 1H, 1H in CH_2), 2.43 (s, 3H, CH_3).

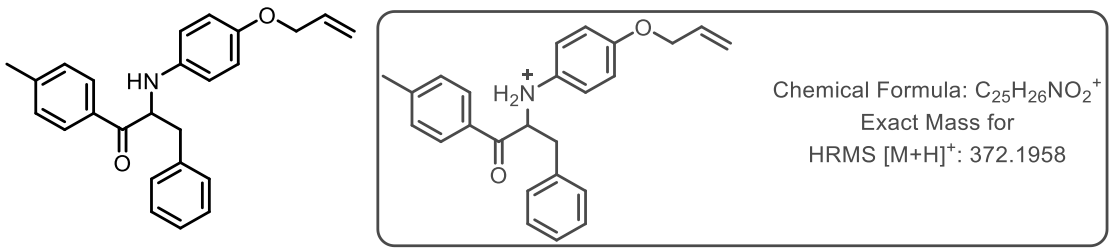
^{13}C NMR (101 MHz, $CDCl_3$) δ 199.2, 158.8, 148.2, 144.6, 143.2, 136.6, 132.8, 129.6, 129.5 (2C), 128.6, 128.4, 126.8, 122.0, 121.2, 117.2, 114.9, 59.6, 39.0, 21.7.

HRMS (ESI): Calcd for $C_{28}H_{26}NO_2^+$ $[M+H]^+$ 408.1958, found 408.1959.



2-((4-(allyloxy)phenyl)amino)-3-phenyl-1-(*p*-tolyl)propan-1-one (**4e**)

Following the general procedure A and B, the product **4e** was obtained by silica gel flash chromatography (PE: EtOAc = 40: 1 and then PE: CH_2Cl_2 = 1: 1 as the eluent) to give a colorless oil. 40 mg, 54% for sunlight (20 h; procedure A); 49 mg, 67% yield for blue-light (procedure B).

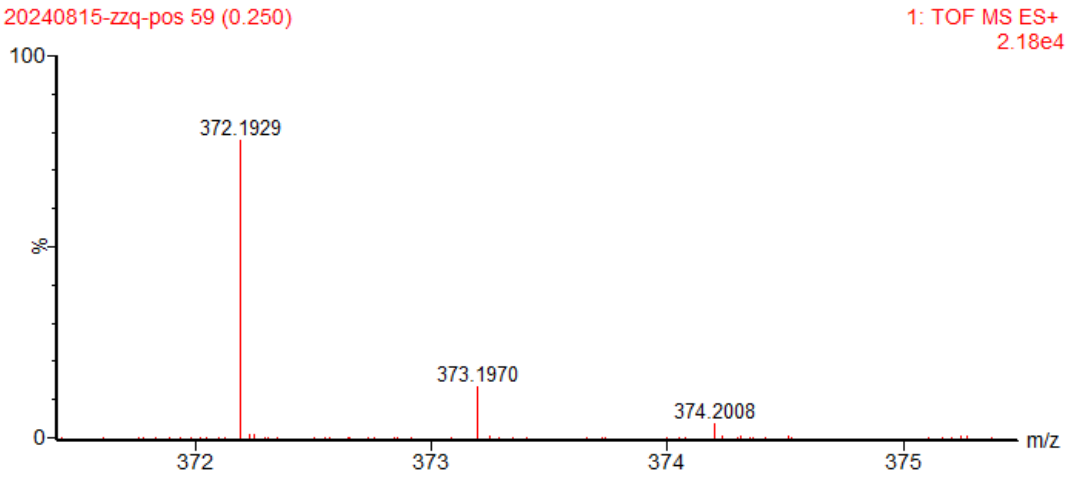


R_f = 0.22 (PE: EtOAc = 15: 1).

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.85 (d, J = 8.3 Hz, 2H, ArH), 7.26 (d, J = 7.4 Hz, 2H, ArH), 7.26 – 7.14 (m, 3H, ArH), 7.08 (dd, J = 5.4, 1.8 Hz, 2H, ArH), 6.79 (app. d, J = 8.9 Hz, 2H, ArH), 6.57 (app. d, J = 8.9 Hz, 2H, ArH), 6.61 (ddt, J = 17.2, 10.5, 5.6 Hz, 1H, CH in $CH{=}CH_2$), 5.36 (dq, J = 17.2, 1.6 Hz, 1H, CH_{trans} in $CH{=}CH_2$), 5.24 (dq, J = 10.5, 1.6 Hz, 1H, CH_{cis} in $CH{=}CH_2$), 5.19 (t, J = 5.6 Hz, 1H, CHN), 4.43 (dt, J = 5.4, 1.6 Hz, 2H, CH_2O), 4.34 (br s, 1H, NH), 3.24 (dd, J = 13.8, 5.5 Hz, 1H in CH_2Ar), 2.99 (dd, J = 13.8, 6.2 Hz, 1H in CH_2Ar), 2.42 (s, 3H, CH_3).

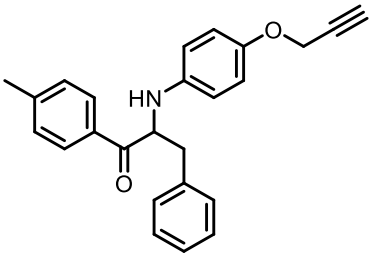
^{13}C NMR (101 MHz, $CDCl_3$) δ 199.6, 151.5, 144.5, 141.0, 136.8, 133.8, 132.9, 129.52, 129.46, 128.5, 128.3, 126.7, 117.3, 116.0, 115.3, 69.6, 60.1, 39.0, 21.7.

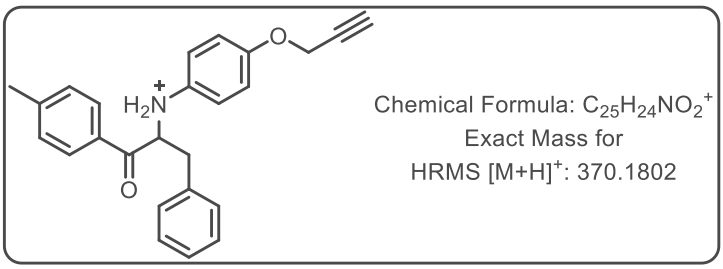
HRMS (ESI): calcd for $C_{25}H_{26}NO_2^+$ $[M+H]^+$ 372.1958, found 372.1929.



3-phenyl-2-((4-(prop-2-yn-1-yloxy)phenyl)amino)-1-(*p*-tolyl)propan-1-one (**4f**)

Following the general procedure A and B, the product **4f** was obtained by silica gel flash chromatography (PE: EtOAc = 40: 1 and then PE: CH_2Cl_2 = 1: 1as the eluent) to give a colorless oil. 49 mg, 67% for sunlight (20 h; procedure A); 59 mg, 80% yield for blue-light (procedure B).



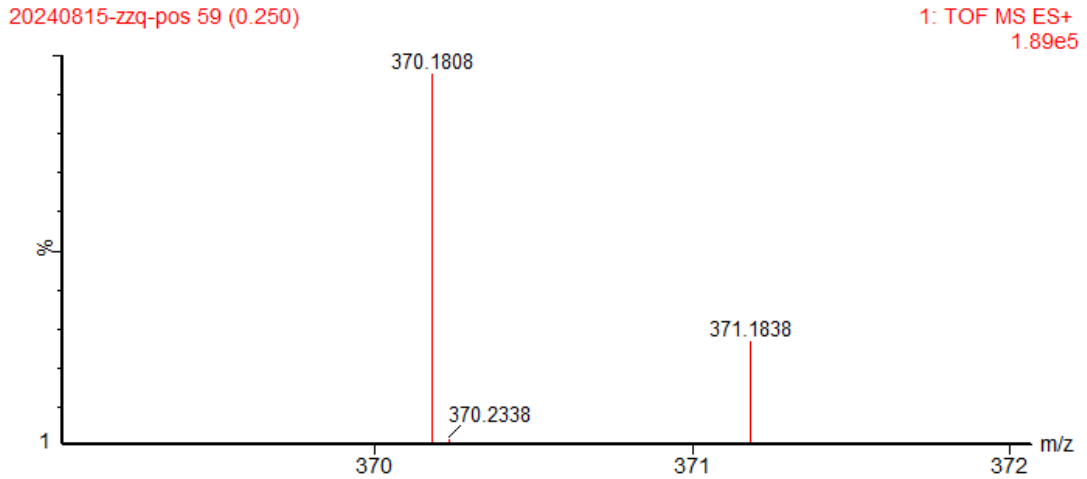


R_f = 0.13 (PE : EtOAc = 15 : 1)

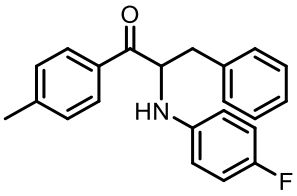
^{1}H NMR (400 MHz, CDCl3) δ 7.85 (d, J = 8.3 Hz, 2H, ArH), 7.27 (d, J = 7.8 Hz, 2H, Ar H), 7.26 – 7.14 (m, 3H, Ar H), 7.11 – 6.98 (m, 2H, ArH), 6.82 (app d, J = 8.9 Hz, 2H, ArH), 6.58 (app d, J = 8.9 Hz, 2H, ArH), 5.20 (t, J = 5.8 Hz, 1H in CHN), 4.58 (d, J = 2.4 Hz, 2H in $CH_2C{\equiv}C$), 4.39 (br s, 1H, NH), 3.24 (dd, J = 13.8, 5.8 Hz, 1H in CH_2Ph), 2.99 (dd, J = 13.8, 5.8 Hz, 1H in CH_2Ph), 2.47 (t, J = 2.4 Hz, 1H, C≡CH), 2.43 (s, 3H, CH_3).

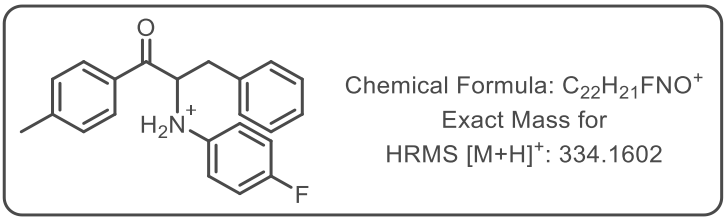
^{13}C NMR (101 MHz, $CDCl_3$) δ 199.5, 150.4, 144.5, 141.7, 136.8, 132.8, 129.5, 129.5, 128.5, 128.4, 126.8, 116.5, 115.0, 76.8, 75.1, 60.0, 56.7, 39.0, 21.7.

HRMS (ESI): Calcd for $C_{25}H_{24}NO_2^+$ $[M+H]^+$ 370.1802, found 370.1809.



2-((4-fluorophenyl)amino)-3-phenyl-1-(*p*-tolyl)propan-1-one (**4g**)





Following the general procedure A and B, the product **4g** was purified by silica gel flash chromatography (PE: EtOAc = 60: 1 as the eluent) to give a colorless crystal, 47.3 mg, 71% for sunlight (10 h), 57.9 mg, 87% for sunlight (15 h, procedure A); 56.6 mg, 85% yield for blue-light (procedure B).

R_f = 0.52 (PE: EtOAc = 5: 1).

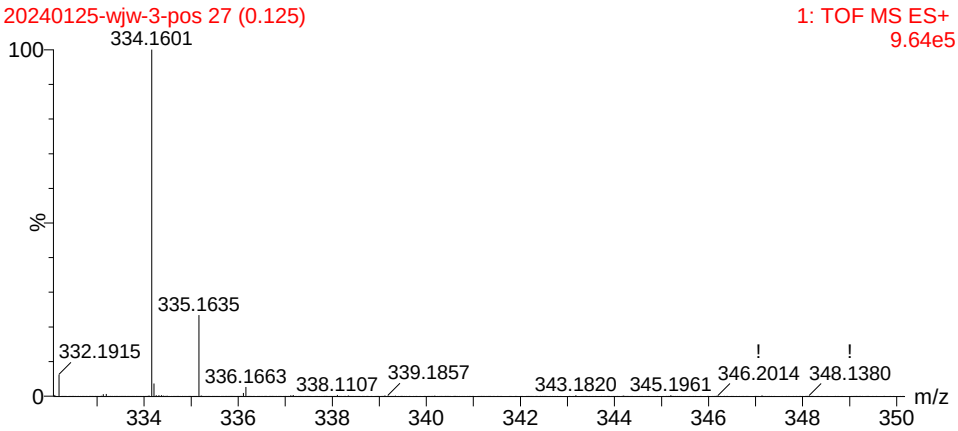
M. p. 102 – 103 °C.

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.85 (d, J = 8.2 Hz, 2H, ArH), 7.27 (d, J = 8.2 Hz, 2H, ArH), 7.25 – 7.14 (m, 3H, ArH), 7.09 – 7.02 (m, 2H, ArH), 6.84 (t, J = 8.9 Hz, 2H, ArH), 6.54 (dd, J = 8.9, 4.4 Hz, 2H, ArH), 5.19 (ddd, J = 7.0, 6.2, 5.3 Hz 1H, CH), 4.50 (d, J = 7.0 Hz, 1H, NH), 3.25 (dd, J = 13.8, 5.3 Hz, 1H, 1H in CH_2), 2.98 (dd, J = 13.8, 6.2 Hz, 1H, 1H in CH_2), 2.42 (s, 3H, CH_3).

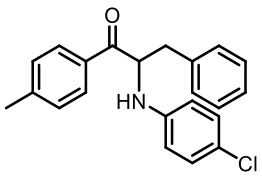
^{13}C NMR (101 MHz, $CDCl_3$) δ 199.1, 156.0 (d, $^1J_{F\text{-}C}$ = 235.9 Hz), 144.6, 143.0, 136.5, 132.7, 129.6, 129.4, 128.5, 128.4, 126.8, 115.7 (d, $^3J_{F\text{-}C}$ = 22.4 Hz), 114.7 (d, $^2J_{F\text{-}C}$ = 7.4 Hz). 59.8, 38.9, 21.7.

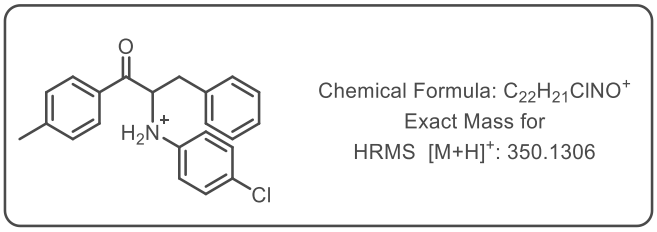
^{19}F NMR (376 MHz, $CDCl_3$) δ -127.16.

HRMS (ESI): Calcd for $C_{22}H_{21}FNO^+$ $[M+H]^+$ 334.1602, found 334.1601.



2-((4-chlorophenyl)amino)-3-phenyl-1-(*p*-tolyl)propan-1-one (**4h**)





Following the general procedure A and B, the product **4h** was purified by silica gel flash chromatography (PE: EtOAc = 60: 1 as the eluent) to give a colorless crystal, 55.8 mg, 80% for sunlight (10 h), 62.9 mg, 90% for sunlight (20 h, procedure A); 62.8 mg, 90% yield for blue-light (procedure B).

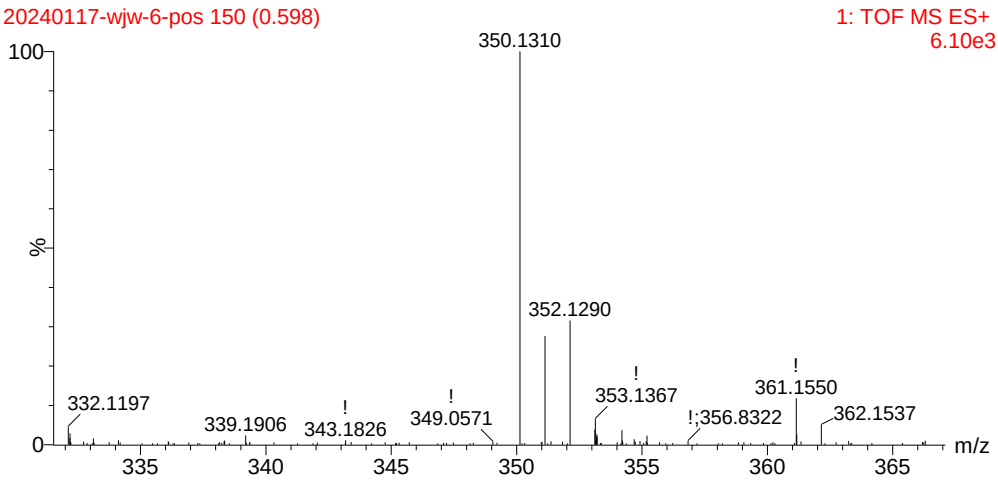
R_f = 0.51 (PE: EtOAc = 5: 1).

M. p. 119 – 120 °C.

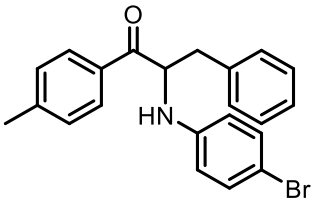
^{1}H NMR (400 MHz, $CDCl_3$) δ 7.85 (d, J = 8.2 Hz, 2H, ArH), 7.28 (d, J = 8.2 Hz, 2H, ArH), 7.23-7.15 (m, 3H, ArH), 7.08 (d, J = 8.8 Hz, 2H, ArH), 7.01 (dd, J = 7.3, 2.0 Hz, 2H, ArH), 6.52 (d, J = 8.8 Hz, 2H, ArH), 5.23 (ddd, J =6.0, 5.7, 5.4 Hz, 1H, CH), 4.65 (d, J = 5.7 Hz, 1H, NH), 3.27 (dd, J = 13.8, 5.4 Hz, 1H, 1H in CH_2), 2.99 (dd, J = 13.8, 6.0 Hz, 1H, 1H in CH_2), 2.42 (s, 3H, CH_3).

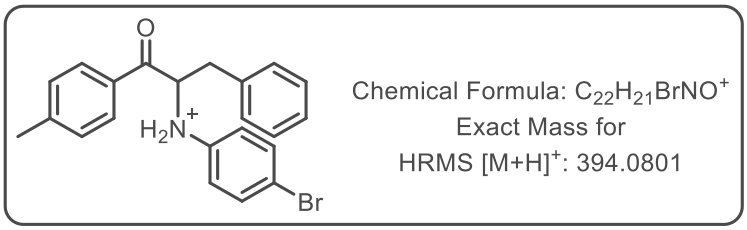
^{13}C NMR (101 MHz, $CDCl_3$) δ 198.6, 145.2, 144.7, 136.2, 132.5, 129.6, 129.4, 129.1, 128.5, 128.3, 126.9, 122.4, 114.7, 58.9, 38.7, 21.7.

HRMS (ESI): Calcd for $C_{22}H_{21}ClNO^+$ $[M+H]^+$ 350.1306, found 350.1310.



2-((4-bromophenyl)amino)-3-phenyl-1-(*p*-tolyl)propan-1-one (**4i**)





Following the general procedure A and B, the product **4i** was purified by silica gel flash chromatography (PE: EtOAc = 60: 1 as the eluent) to give a colorless crystal, 47.9 mg, 61% for sunlight (10 h), 57.4 mg, 73% for sunlight (18 h, procedure A); 53.4 mg, 68% yield for blue-light (procedure B).

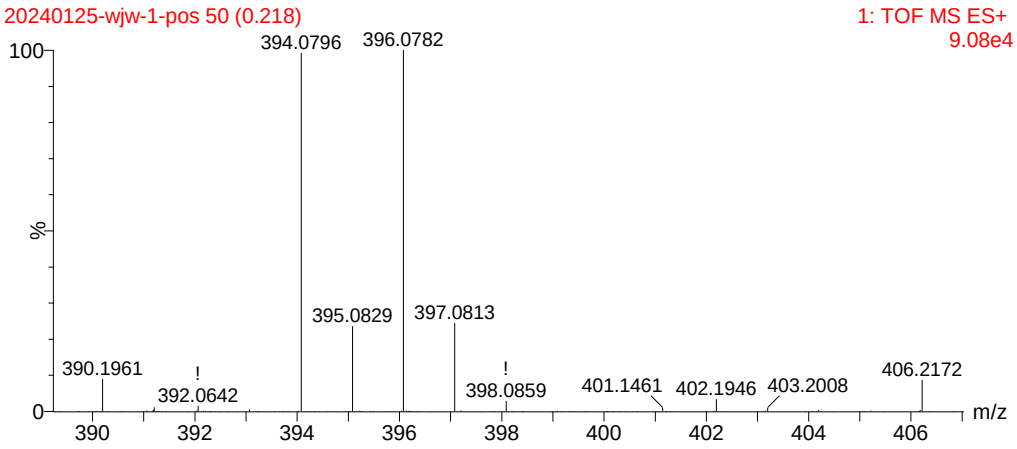
R_f = 0.51 (PE: EtOAc = 5: 1).

M. p. 116 – 117 °C.

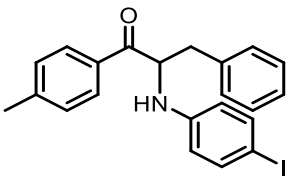
^{1}H NMR (400 MHz, $CDCl_3$) δ 7.85 (d, J = 8.2 Hz, 2H, ArH), 7.29 (d, J = 8.2 Hz, 2H, ArH), 7.24 – 7.13 (m, 5H, ArH), 7.00 (dd, J = 7.2, 2.1 Hz, 2H, ArH), 6.48 (d, J = 8.9 Hz, 2H, ArH), 5.23 (ddd, J = 6.8, 5.9, 5.3 Hz, 1H, CH), 4.67 (d, J = 6.8 Hz, 1H, NH), 3.27 (dd, J = 13.8, 5.3 Hz, 1H, 1H in CH_2), 2.99 (dd, J = 13.8, 5.9 Hz, 1H, 1H in CH_2), 2.43 (s, 3H, CH_3).

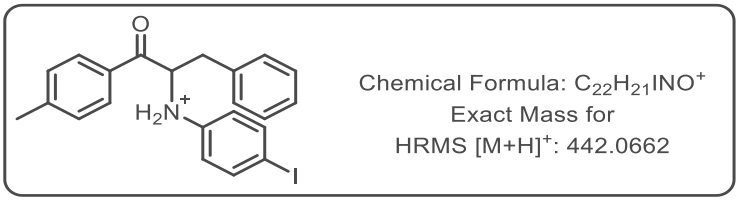
^{13}C NMR (101 MHz, $CDCl_3$) δ 198.5, 145.6, 144.7, 136.2, 132.5, 132.0, 129.6, 129.4, 128.5, 128.4, 126.9, 115.2, 109.5, 58.8, 38.6, 21.7.

HRMS (ESI): Calcd for $C_{22}H_{21}BrNO^+$ $[M+H]^+$ 394.0801, found 394.0796.



2-((4-iodophenyl)amino)-3-phenyl-1-(*p*-tolyl)propan-1-one (**4j**)





Following the general procedure A and B, the product **4j** was purified by silica gel flash chromatography (PE: EtOAc = 60: 1 as the eluent) to give a colorless crystal, 52.9 mg, 60% for sunlight (10 h), 61.7 mg, 70% for sunlight (20 h, procedure A); 58.2 mg, 66% yield for blue-light (procedure B).

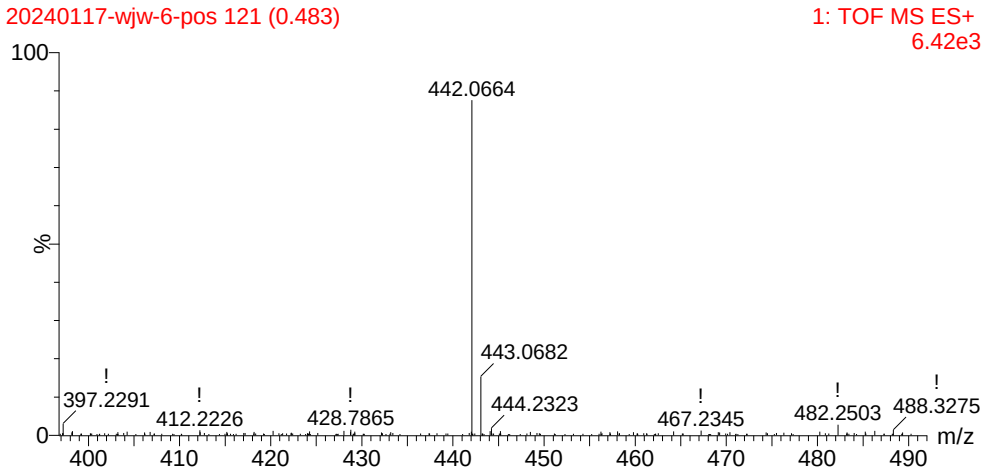
R_f = 0.60 (PE: EtOAc = 5: 1).

M. p. 119 – 120 °C.

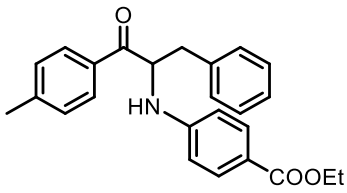
^{1}H NMR (400 MHz, $CDCl_3$) δ 7.85 (d, J = 8.2 Hz, 2H, ArH), 7.39 (d, J = 8.8 Hz, 2H, ArH), 7.29 (d, J = 8.2 Hz, 2H, ArH), 7.24 – 7.15 (m, 3H, ArH), 7.00 (dd, J = 7.1, 2.1 Hz, 2H, ArH), 6.40 (d, J = 8.8 Hz, 2H, ArH), 5.23 (dt, J = 8.2, 5.7 Hz, 1H, CHN), 4.69 (d, J = 8.2 Hz, 1H, NH), 3.27 (dd, J = 13.8, 5.7 Hz, 1H, 1H in CH_2), 2.99 (dd, J = 13.8, 5.7 Hz, 1H, 1H in CH_2), 2.43 (s, 3H, CH_3).

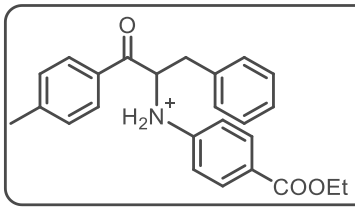
^{13}C NMR (101 MHz, $CDCl_3$) δ 198.4, 146.1, 144.7, 137.9, 136.1, 132.5, 129.6, 129.4, 128.6, 128.4, 126.9, 115.8, 78.6, 58.6, 38.6, 21.7.

HRMS (ESI): Calcd for $C_{22}H_{21}INO^+$ $[M+H]^+$ 442.0662, found 442.0664.



ethyl 4-((1-oxo-3-phenyl-1-(*p*-tolyl)propan-2-yl)amino)benzoate (**4k**)





Chemical Formula: $C_{25}H_{26}NO_3^+$
Exact Mass for
HRMS $[M+H]^+$: 388.1907

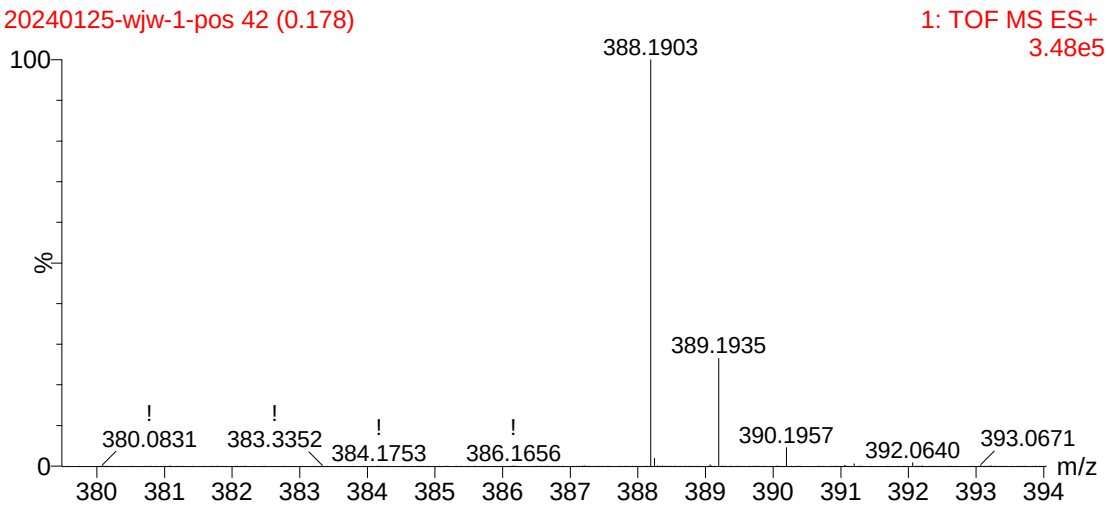
Following the general procedure A, C and D, the product **4k** was purified by silica gel flash chromatography (PE: EtOAc = 80: 1 as the eluent) to give a colorless oil, 42.2 mg, 52% yield for sunlight (10 h, procedure A), 58.2 mg, 67% for sunlight (procedure C); 34.1 mg, 44% for blue-light (procedure D).

R_f = 0.35 (PE: EA = 5: 1).

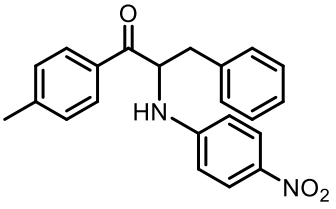
^{1}H NMR (400 MHz, $CDCl_3$) δ 7.91 – 7.81 (m, 4H, ArH), 7.27 (d, J = 8.0 Hz, 2H, ArH), **7.16** (m, 3H, ArH), 6.94 (dd, J = 7.3, 3.6 Hz, 2H, ArH), 6.58 (d, J = 8.7 Hz, 2H, ArH), 5.34 (dt, J = 5.4, 7.5 Hz, 1H, CH), 5.20 (d, J = 6.7 Hz, 1H, NH), 4.30 (q, J = 7.1 Hz, 2H, OCH_2), 3.33 (dd, J = 13.8, 5.4 Hz, 1H, 1H in **CH_2**Ph), 3.02 (dd, J = 13.8, 5.4 Hz, 1H, 1H in **CH_2**Ph), 2.40 (s, 3H, CH_3), 1.33 (t, J = 7.1 Hz, 3H, CH_3 in Et).

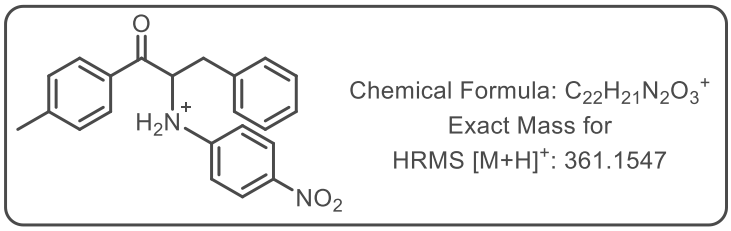
^{13}C NMR (101 MHz, $CDCl_3$) δ 197.6, 166.6, 150.0, 144.7, 135.7, 132.2, 131.4, 129.5, 129.4, 128.5, 128.2, 126.8, 119.1, 112.1, 60.0, 57.8, 38.3, 21.6, 14.3.

HRMS (ESI): Calcd for $C_{25}H_{26}NO_3^+$ $[M+H]^+$ 388.1907, found 388.1903.



2-((4-nitrophenyl)amino)-3-phenyl-1-(*p*-tolyl)propan-1-one (**4l**)





Following the general procedure A, C and D, the product **4l** was purified by silica gel flash chromatography (PE: EtOAc = 60: 1 as the eluent) to give a colorless crystal, 15.1 mg, 21% yield for sunlight (10 h, procedure A); 45.4 mg, 63% for sunlight (procedure C); 40.0 mg, 56% for blue-light (procedure D).

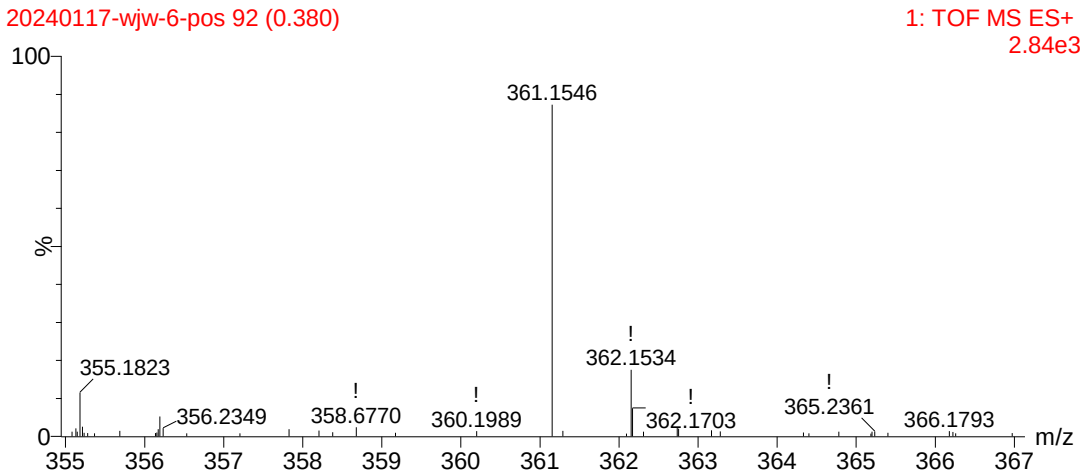
R_f = 0.28 (PE: EtOAc = 5: 1).

M. p. 152 – 154 °C.

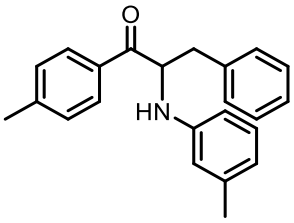
^{1}H NMR (400 MHz, $CDCl_3$) δ 8.05 (d, J = 9.2 Hz, 2H, ArH), 7.90 (d, J = 8.2 Hz, 2H, ArH), 7.34 (d, J = 8.2 Hz, 2H, ArH), 7.23 – 7.17 (m, 3H, ArH), 6.94 (dd, J = 6.3, 3.1 Hz, 2H, ArH), 6.54 (d, J = 9.2 Hz, 2H, ArH), 5.57 (d, J = 7.7 Hz, 1H, NH), 5.38 (dt, J = 7.7, 5.5 Hz, 1H, CH), 3.35 (dd, J = 13.9, 5.5 Hz, 1H, 1H in CH_2), 3.05 (dd, J = 13.9, 5.5 Hz, 1H, 1H in CH_2), 2.46 (s, 3H, CH_3).

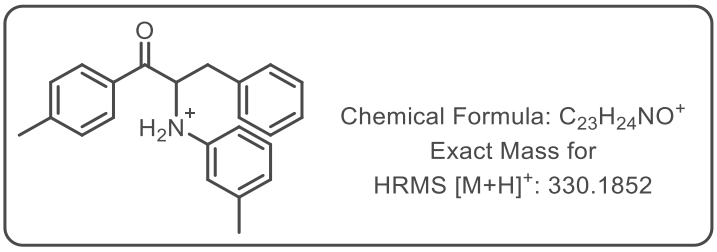
^{13}C NMR (101 MHz, $CDCl_3$) δ 196.8, 151.6, 145.3, 138.3, 135.2, 131.8, 129.8, 129.4, 128.6, 128.5, 127.2, 126.4, 111.7, 57.9, 38.7, 21.8.

HRMS (ESI): Calcd for $C_{22}H_{21}N_2O_3^+$ $[M+H]^+$ 361.1547, found 361.1546.



3-phenyl-1-(*p*-tolyl)-2-(*m*-tolylamino)propan-1-one (**4m**)





Following the general procedure A and B, the product **4m** was purified by silica gel flash chromatography (PE: EtOAc = 60: 1 as the eluent) to give a colorless crystal, 44.1 mg, 67% for sunlight (10 h), 52.6 mg, 80% for sunlight (20 h, procedure A); 51.3 mg, 78% yield for blue-light (procedure B).

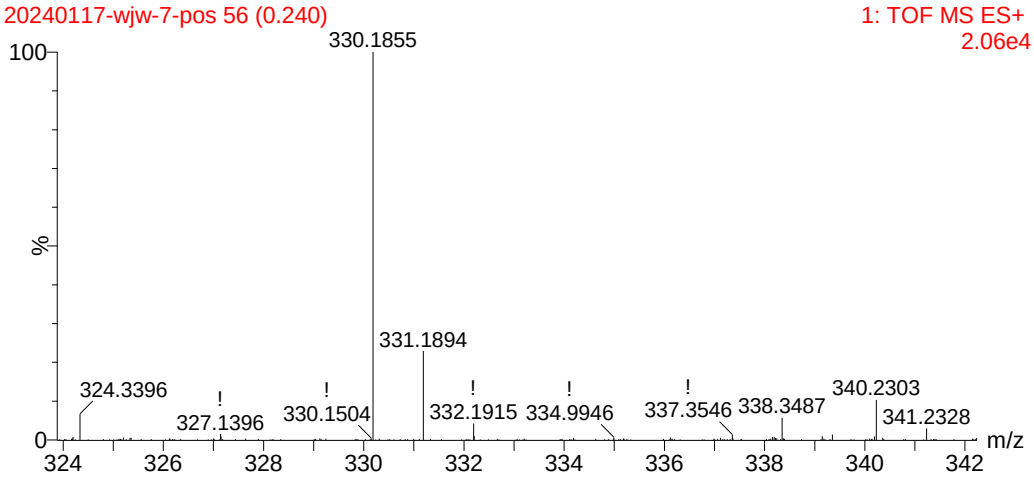
R_f = 0.60 (PE: EtOAc = 5: 1).

M. p. 100 – 102 °C.

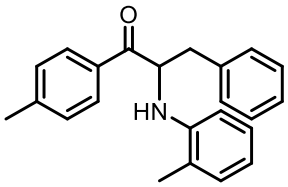
^{1}H NMR (400 MHz, $CDCl_3$) δ 7.85 (d, J = 8.1 Hz, 2H, ArH), 7.26 (d, J = 8.1 Hz, 2H, ArH), 7.22 – 7.14 (m, 3H, ArH), 7.01 (dd, J = 7.3, 1.9 Hz, 2H, ArH), 6.66 (t, J = 7.3 Hz, 1H, ArH), 6.57 (d, J = 8.2 Hz, 2H, ArH), 5.34 (t, J = 5.6 Hz, 1H, CH), 4.52 (s, 1H, NH), 3.33 (dd, J = 13.7, 5.6 Hz, 1H, 1H in CH_2), 3.05 (dd, J = 13.7, 5.6 Hz, 1H, 1H in CH_2), 2.43 (s, 3H, CH_3), 2.15 (s, 3H, CH_3).

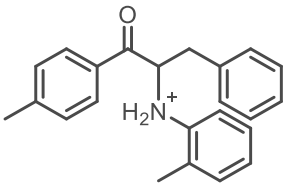
^{13}C NMR (101 MHz, $CDCl_3$) δ 199.0, 146.6, 144.4, 139.1, 136.6, 132.8, 129.5 (2C), 129.2, 128.5, 128.2, 126.7, 118.9, 114.5, 110.6, 58.9, 38.8, 21.66, 21.56.

HRMS (ESI): Calcd for $C_{23}H_{24}NO^+$ $[M+H]^+$ 330.1852, found 330.1855.



3-phenyl-1-(*p*-tolyl)-2-(*o*-tolylamino)propan-1-one (**4n**)





Chemical Formula: $C_{23}H_{24}NO^+$
Exact Mass for
HRMS $[M+H]^+$: 330.1852

Following the general procedure A and B, the product **4n** was purified by silica gel flash chromatography (PE: EtOAc = 60: 1 as the eluent) to give a colorless crystal, 33.6 mg, 51% for sunlight (10 h), 50.0 mg, 76% for sunlight (28 h, procedure A); 39.5 mg, 60% yield for blue-light (procedure B).

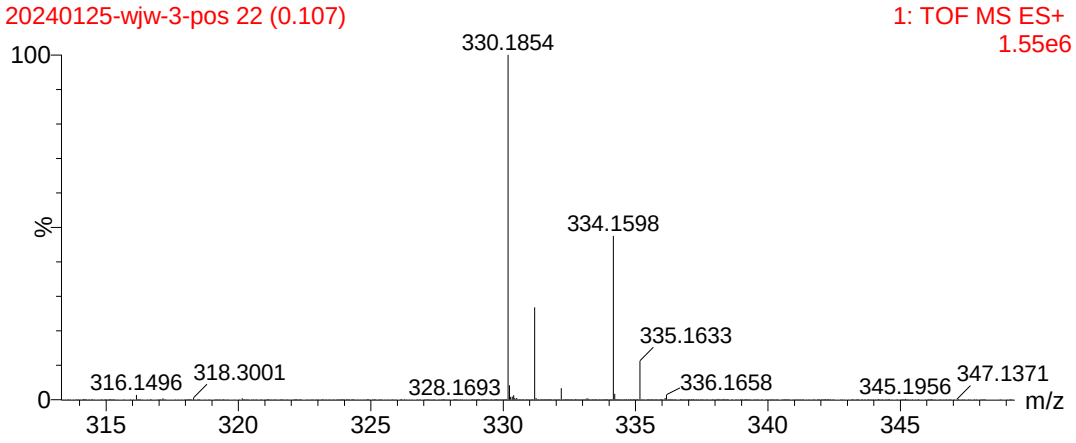
R_f = 0.59 (PE: EtOAc = 5: 1).

M. p. 99 – 100 °C.

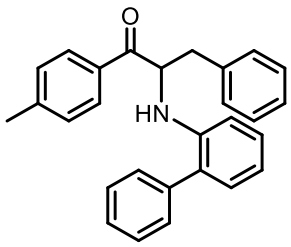
^{1}H NMR (400 MHz, $CDCl_3$) δ 7.88 (d, J = 8.2 Hz, 2H, ArH), 7.28 (d, J = 8.2 Hz, 2H, ArH), 7.23 – 7.13 (m, 3H, ArH), 7.09 – 7.03 (m, 2H, ArH), 7.00 (dd, J = 7.4, 2.0 Hz, 2H, ArH), 6.65 (t, J = 7.4 Hz, 1H, ArH), 6.57 (d, J = 8.2 Hz, 1H, ArH), 5.34 (t, J = 5.3 Hz, 1H, CH), 4.52 (s, 1H, NH), 3.32 (dd, J = 13.7, 5.3 Hz, 1H, 1H in CH_2), 3.04 (dd, J = 13.7, 5.3 Hz, 1H, 1H in CH_2), 2.42 (s, 3H, CH_3), 2.15 (s, 3H, CH_3).

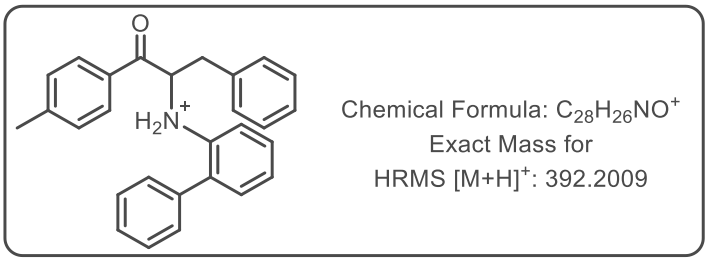
^{13}C NMR (101 MHz, $CDCl_3$) δ 199.0, 144.5, 136.4, 132.7, 130.4, 129.53, 129.47 (2C) , 128.5, 128.2, 127.0, 126.8, 123.0, 117.4, 110.4, 58.7, 38.5, 21.7, 17.5.

HRMS (ESI): Calcd for $C_{23}H_{24}NO^+$ $[M+H]^+$ 330.1852, found 330.1854.



2-([1,1'-biphenyl]-2-ylamino)-3-phenyl-1-(*p*-tolyl)propan-1-one (**4o**)





Following the general procedure A and B, the product **4o** was purified by silica gel flash chromatography (PE: EtOAc = 60: 1 as the eluent) to give a colorless crystal, 60.0 mg, 77% for sunlight (10 h, procedure A); 52.4 mg, 67% yield for blue-light (procedure B).

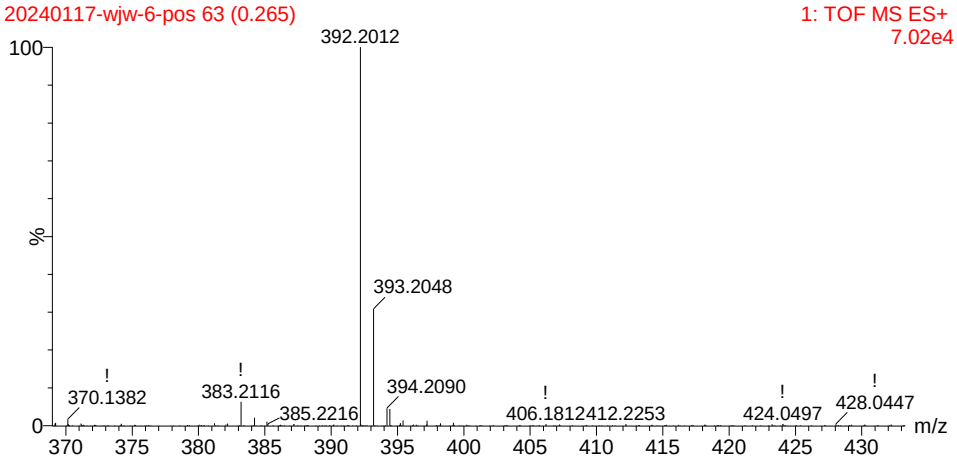
R_f = 0.57 (PE: EtOAc =5: 1).

M.p. 106 – 107 °C.

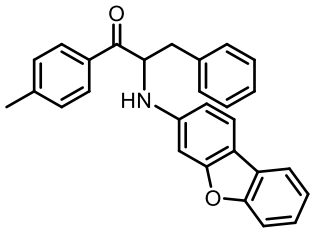
^{1}H NMR (400 MHz, $CDCl_3$) δ 7.85 (d, J = 7.8 Hz, 2H, ArH), 7.42 – 7.29 (m, 5H, ArH), 7.25 (d, J = 7.8 Hz, 2H, ArH), 7.18 – 7.05 (m, 5H, ArH), 6.99 – 6.90 (m, 2H, ArH), 6.74 (t, J = 7.4 Hz, 1H, ArH), 6.59 (d, J = 7.4 Hz, 1H, ArH), 5.27 (dd, J = 6.3, 4.5 Hz, 1H, CH), 4.80 (d, J = 4.5 Hz, 1H, NH), 3.22 (dd, J = 13.7, 4.5 Hz, 1H, 1H in CH_2), 2.91 (dd, J = 13.7, 6.3 Hz, 1H, 1H in CH_2), 2.39 (s, 3H, CH_3).

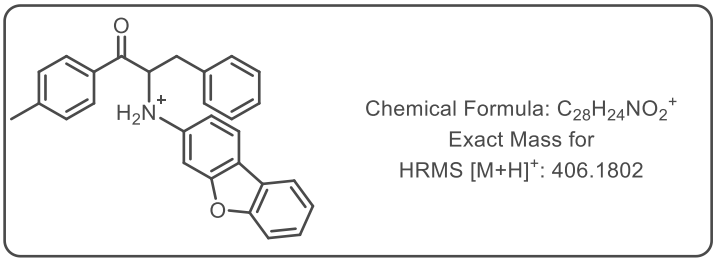
^{13}C NMR (101 MHz, $CDCl_3$) δ 199.0, 144.4, 143.4, 139.1, 136.4, 132.8, 130.5, 129.5, 129.3, 129.2, 128.8, 128.53, 128.49, 128.43, 128.3, 127.2, 126.7, 117.6, 110.8, 58.9, 38.56, 21.6.

HRMS (ESI): Calcd for $C_{28}H_{26}NO^+$ $[M+H]^+$ 392.2009, found 392.2012.



2-(dibenzo[*b*, *d*]furan-3-ylamino)-3-phenyl-1-(*p*-tolyl)propan-1-one (**4p**)





Following the general procedure A and B, the product **4p** was purified by silica gel flash chromatography (PE: EtOAc = 50: 1 as the eluent) to give a colorless crystal, 62.4 mg, 77% for sunlight (10 h), 67.2 mg, 83% for sunlight (20 h, procedure A); 68.9 mg, 85% yield for blue-light (procedure B).

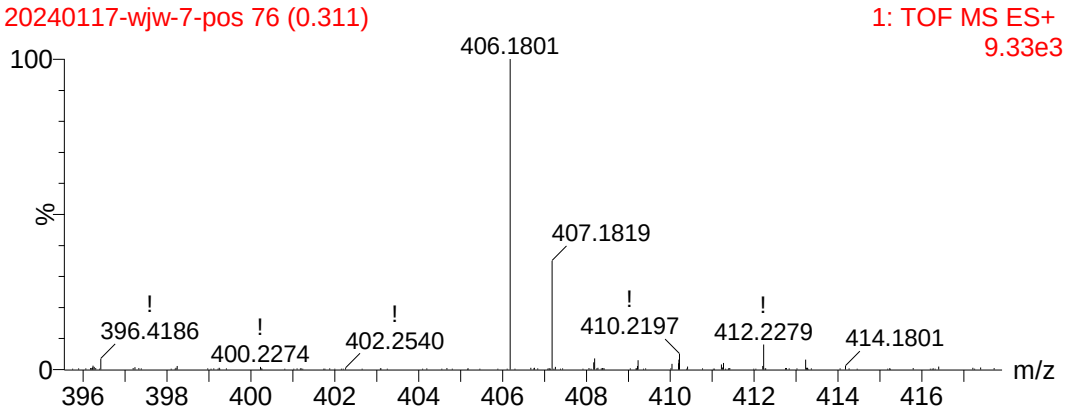
R_f = 0.50 (PE: EtOAc = 5: 1).

M. p. 101 – 102 °C.

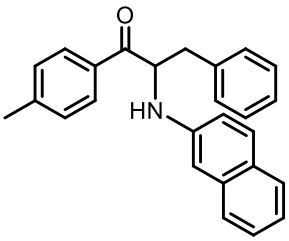
^{1}H NMR (400 MHz, $CDCl_3$) δ 7.89 (d, J = 8.1 Hz, 2H, ArH), 7.76 (d, J = 7.0 Hz, 1H, ArH), 7.67 (d, J = 8.3 Hz, 1H, ArH), 7.45 (d, J = 7.5 Hz, 1H, ArH), 7.31 – 7.18 (m, 7H, ArH), 7.04 (d, J = 7.5 Hz, 2H, ArH), 6.77 (d, J = 1.7 Hz, 1H, ArH), 6.66 (dd, J = 8.3, 1.7 Hz, 1H, ArH), 5.38 (dt, J = 8.0, 5.5 Hz, 1H, CH), 4.94 (d, J = 8.0 Hz, 1H, NH), 3.37 (dd, J = 13.8, 5.5 Hz, 1H, 1H in CH_2), 3.07 (dd, J = 13.8, 5.5 Hz, 1H, 1H in CH_2), 2.43 (s, 3H, CH_3).

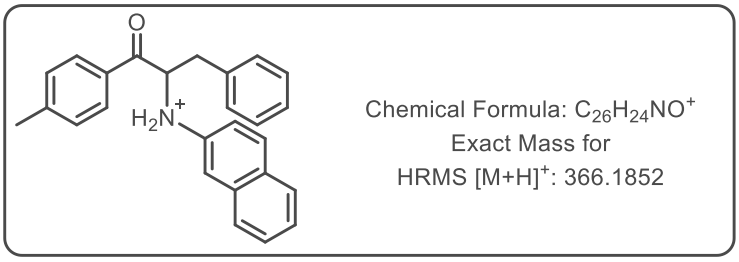
^{13}C NMR (101 MHz, $CDCl_3$) δ 198.5, 158.2, 155.8, 146.9, 144.7, 136.2, 132.6, 129.6, 129.5, 128.6, 128.4, 126.9, 124.9 (2C), 122.5, 121.3, 119.2, 114.9, 111.0, 110.8, 95.2, 59.0, 38.6, 21.7.

HRMS (ESI): Calcd for $C_{28}H_{24}NO_2^+$ $[M+H]^+$ 406.1802, found 406.1801.



2-(naphthalen-2-ylamino)-3-phenyl-1-(*p*-tolyl)propan-1-one (**4q**)





Following the general procedure A, C and D, the product **4q** was purified by silica gel flash chromatography (PE: EtOAc = 80: 1 as the eluent) to give colorless crystals, 9.5 mg, 13% yield for sunlight (10 h, procedure A). 43.8 mg, 60% for sunlight (procedure C); 40.9 mg, 56% for blue-light (procedure D).

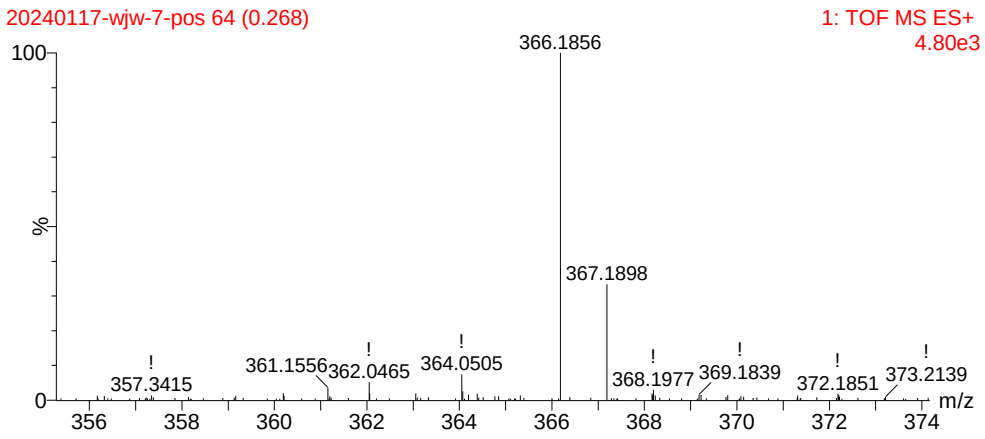
R_f = 0.52 (PE: EtOAc = 5: 1).

M. p. 170 – 172 °C.

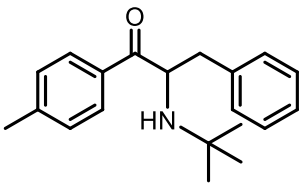
^{1}H NMR (400 MHz, $CDCl_3$) δ 7.91 (d, J = 8.2 Hz, 2H, ArH), 7.90 – 7.85 (m, 1H, ArH), 7.82 – 7.72 (m, 1H, ArH), 7.49 – 7.37 (m, 2H, ArH), 7.33 – 7.22 (m, 4H, ArH), 7.21 – 7.15 (m, 3H, ArH), 7.03 (dd, J = 6.6, 2.9 Hz, 2H, ArH), 6.60 (d, J = 8.1 Hz, 1H, ArH), 5.58 – 5.33 (m, 2H, CH and NH), 3.43 (dd, J = 13.8, 5.0 Hz, 1H, 1H in CH_2), 3.15 (dd, J = 13.8, 5.0 Hz, 1H, 1H in CH_2), 2.44 (s, 3H, CH_3).

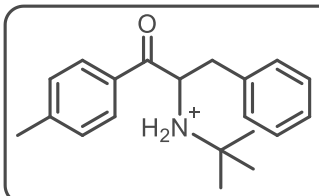
^{13}C NMR (101 MHz, $CDCl_3$) δ 198.9, 144.6, 141.7, 136.4, 134.5, 132.7, 129.6 (2C), 128.6, 128.5, 128.3, 126.8, 126.3, 125.9, 124.9, 123.8, 120.3, 117.9, 105.0, 58.8, 38.4, 21.7.

HRMS (ESI): Calcd for $C_{26}H_{24}NO^+$ $[M+H]^+$ 366.1852, found 366.1856.



2-(*tert*-butylamino)-3-phenyl-1-(*p*-tolyl)propan-1-one (**4r**)





Chemical Formula: $C_{20}H_{26}NO^+$
Exact Mass for
HRMS $[M+H]^+$: 296.2009

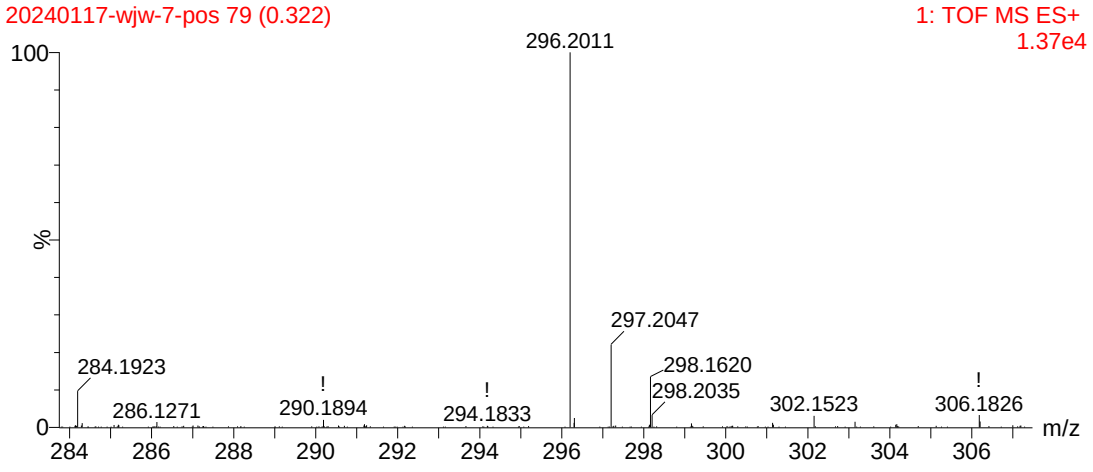
Following the general procedure E and F, the product **4r** was purified by silica gel flash chromatography (PE: EtOAc = 80: 1 as the eluent) to give a colorless oil, 52.5 mg, 89% for sunlight (procedure E); 44.2 mg, 75% yield for blue-light (procedure F).

R_f = 0.30 (PE: EtOAc = 5: 1).

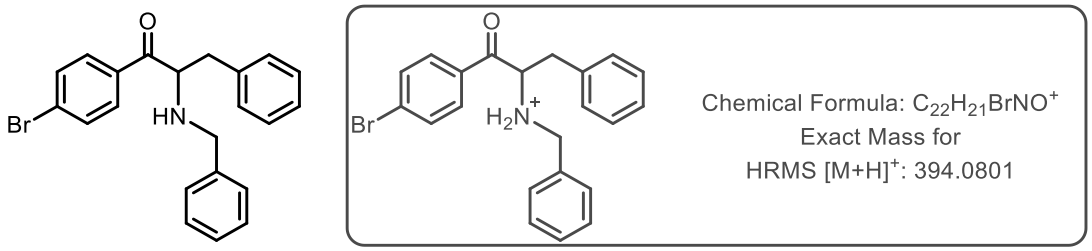
^{1}H NMR (400 MHz, $CDCl_3$) δ 8.01 (d, J = 8.2 Hz, 2H, ArH), 7.76 (dd, J = 5.5, 3.0 Hz, 2H, ArH), 7.66 (dd, J = 5.5, 3.0 Hz, 2H, ArH), 7.24 (d, J = 8.2 Hz, 2H, ArH), 7.06 (dd, J = 8.5, 7.4 Hz, 2H, ArH), 6.67 (d, J = 8.5 Hz, 2H, ArH), 6.61 (t, J = 7.4 Hz, 1H, ArH), 5.56 (t, J = 7.0 Hz, 1H, CH), 4.63 (s, 1H, NH), 4.02 (d, J = 7.0 Hz, 2H, CH_2), 2.35 (s, 3H, CH_3).

^{13}C NMR (101 MHz, $CDCl_3$) δ 203.9, 144.0, 138.6, 133.0, 129.6, 129.4, 128.4, 128.0, 126.3, 58.3, 50.6, 42.0, 29.6, 21.6.

HRMS (ESI): Calcd for $C_{20}H_{26}NO^+$ $[M+H]^+$ 296.2009, found 296.2011.



2-(benzylamino)-3-phenyl-1-(*p*-tolyl)propan-1-one (**4s**)



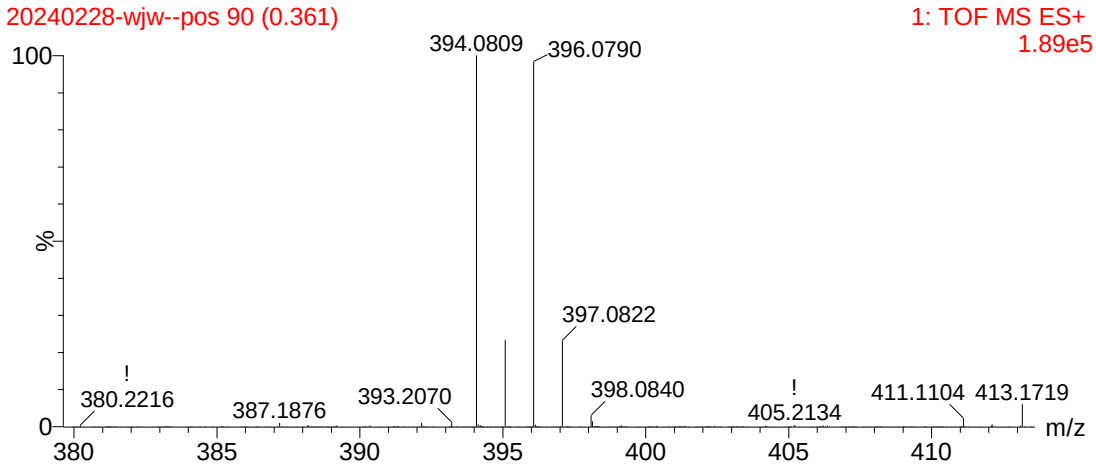
Following the general procedure E and F, the product **4s** was purified by silica gel flash chromatography (PE: EtOAc = 50: 1 as the eluent) to give a colorless oil, 51.1 mg, 65% for sunlight (procedure E); 47.1 mg, 60% yield for blue-light (procedure F).

R_f = 0.42 (PE: EtOAc = 5: 1).

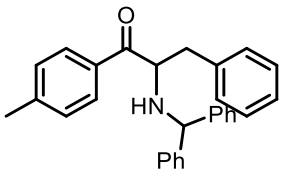
^{1}H NMR (400 MHz, $CDCl_3$) δ 7.69 (d, J = 8.6 Hz, 2H, ArH), 7.53 (d, J = 8.6 Hz, 2H, ArH), 7.25 – 7.16 (m, 8H, ArH), 7.13 (d, J = 6.8 Hz, 2H, ArH), 4.37 (dd, J = 7.0, 5.8 Hz, 1H, CH), 3.79 (d, J = 13.2 Hz, 1H, 1H in NH**C**$\mathbf{H_2}$), 3.58 (d, J = 13.2 Hz, 1H, 1H in NH**C**$\mathbf{H_2}$), 3.00 (dd, J = 13.7, 5.8 Hz, 1H, 1H in CH**C**$\mathbf{H_2}$), 2.89 (dd, J = 13.7, 7.0 Hz, 1H, 1H in CH**C**$\mathbf{H_2}$), 2.25 (s, 1H, NH).

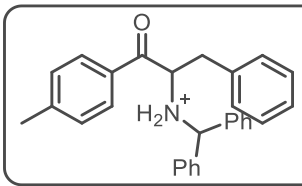
^{13}C NMR (101 MHz, $CDCl_3$) δ 201.9, 139.7, 137.4, 135.0, 131.9, 129.7, 129.3, 128.4, 128.3, 128.3, 128.1, 127.0, 126.6, 77.00, 62.91, 51.75, 39.72.

HRMS (ESI): Calcd for $C_{22}H_{21}BrNO^+$**[M+H]$^+$** 394.0801, found 394.0809



2-(benzhydrylamino)-3-phenyl-1-(*p*-tolyl)propan-1-one (**4t**)





Chemical Formula: $C_{29}H_{28}NO^+$
Exact Mass for
HRMS $[M+H]^+$: 406.2165

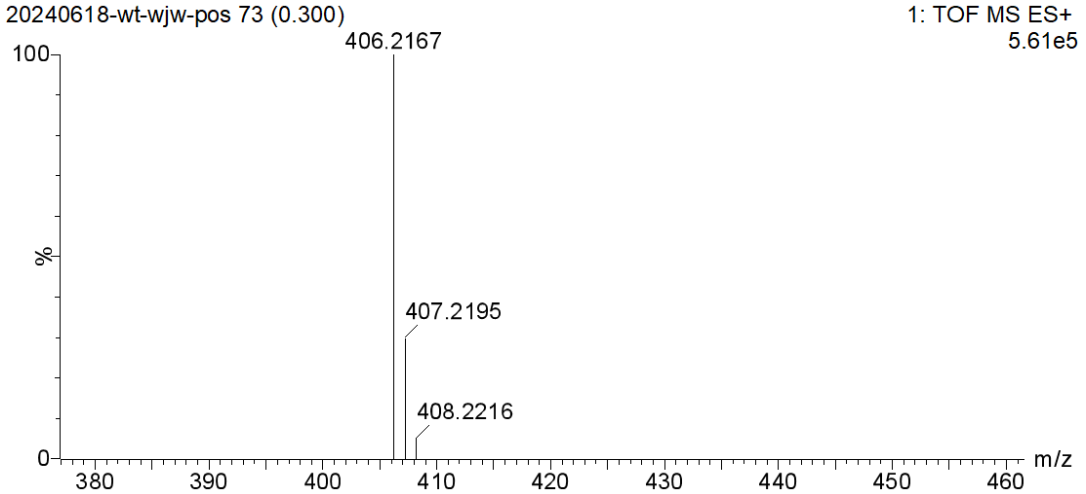
Following the general procedure E and F, the product **4t** was purified by silica gel flash chromatography (PE: EtOAc = 70: 1 as the eluent) to give a colorless oil, 67.2 mg, 83% for sunlight (procedure E); 62.4 mg, 77% yield for blue-light (procedure F).

R_f = 0.57 (PE: EtOAc = 5: 1).

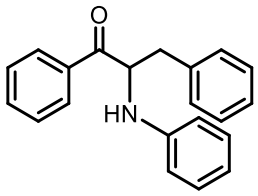
^{1}H NMR (400 MHz, $CDCl_3$) δ 7.67 (d, J = 7.8 Hz, 2H, ArH), 7.31 (d, J = 7.8 Hz, 2H, ArH), 7.25 – 7.12 (m, 15H, ArH), 4.68 (s, 1H, CH), 4.35 (dd, J = 8.3, 4.2 Hz, 1H, **CH**CH_2), 2.99 (dd, J = 13.6, 4.2 Hz, 1H,1H in CH_2), 2.75 (dd, J = 13.6, 8.3 Hz, 1H,1H in CH_2), 2.57 (s, 1H, NH), 2.37 (s, 3H, CH_3).

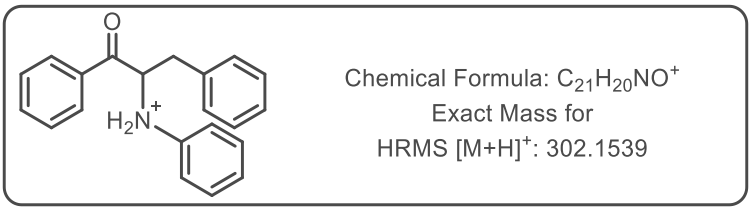
^{13}C NMR (101 MHz, $CDCl_3$) δ 203.0, 144.5, 144.2, 142.9, 138.0, 133.7, 129.6, 129.4, 128.4, 128.3, 128.3, 128.1, 127.6, 127.2, 127.0, 126.9, 126.4, 65.3, 61.5, 40.3, 21.6.

HRMS (ESI): Calcd for $C_{29}H_{28}NO^+$ $[M+H]^+$ 406.2165, found 406.2167.



1,3-diphenyl-2-(phenylamino)propan-1-one (**4u**)





Following the general procedure A and B, the product **4u** was purified by silica gel flash chromatography (PE: EtOAc = 50: 1 as the eluent) to give a colorless crystal, 51.2 mg, 85% for sunlight (10 h, procedure A); 51.8 mg, 86% yield for blue-light (procedure B).

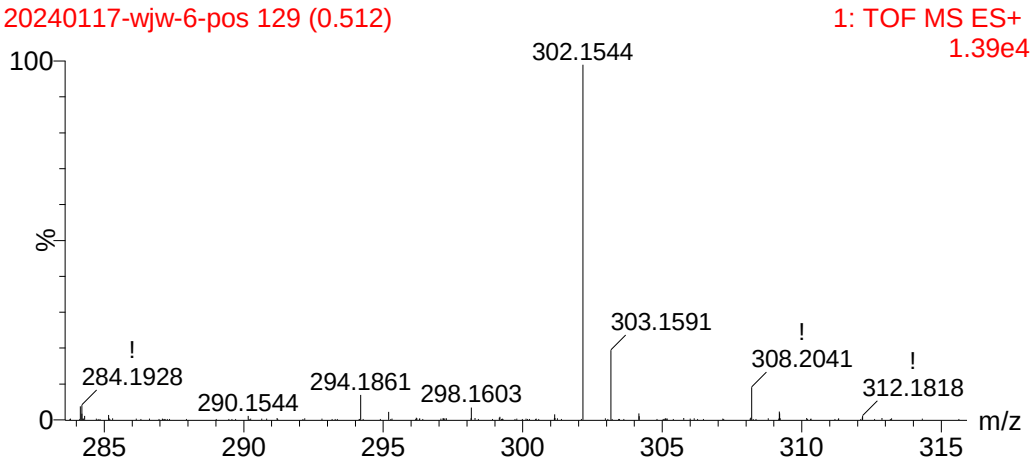
R_f = 0.55 (PE: EtOAc = 5: 1).

M. p. 97 – 98 °C.

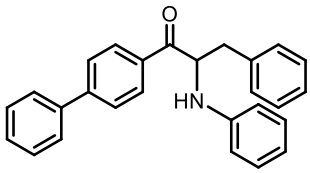
^{1}H NMR (400 MHz, $CDCl_3$) δ 7.95 (dd, J = 7.2, 1.1 Hz, 2H, ArH), 7.59 (dt, J = 7.8, 1.1Hz, 1H, ArH), 7.47 (td, J = 7.2, 1.1Hz, 2H, ArH), 7.25 – 7.11 (m, 5H, ArH), 7.04 (d, J = 7.2 Hz, 2H, ArH), 6.72 (d, J = 7.2 Hz, 1H, ArH), 6.65 (d, J = 7.8 Hz, 2H, ArH), 5.32 (dt, J = 7.6, 5.7 Hz, 1H, CH), 4.61 (d, J = 7.6 Hz, 1H, NH), 3.29 (dd, J = 13.8, 5.7 Hz, 1H, 1H in CH_2), 3.03 (dd, J = 13.8, 5.7 Hz, 1H, 1H in CH_2).

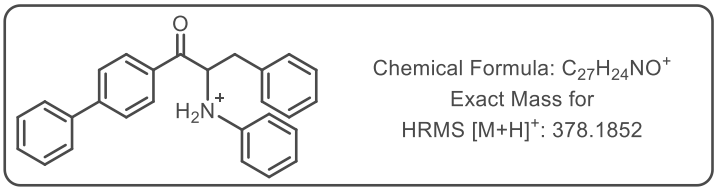
^{13}C NMR (101 MHz, $CDCl_3$) δ 199.4, 146.5, 136.4, 135.3, 133.5, 129.5, 129.4, 128.8, 128.4, 128.3, 126.8, 118.0, 113.7, 59.0, 38.6.

HRMS (ESI): Calcd for $C_{21}H_{20}NO^+$ $[M+H]^+$ 302.1539, found 302.1544.



1-([1,1'-biphenyl]-4-yl)-3-phenyl-2-(phenylamino)propan-1-one (**4v**)





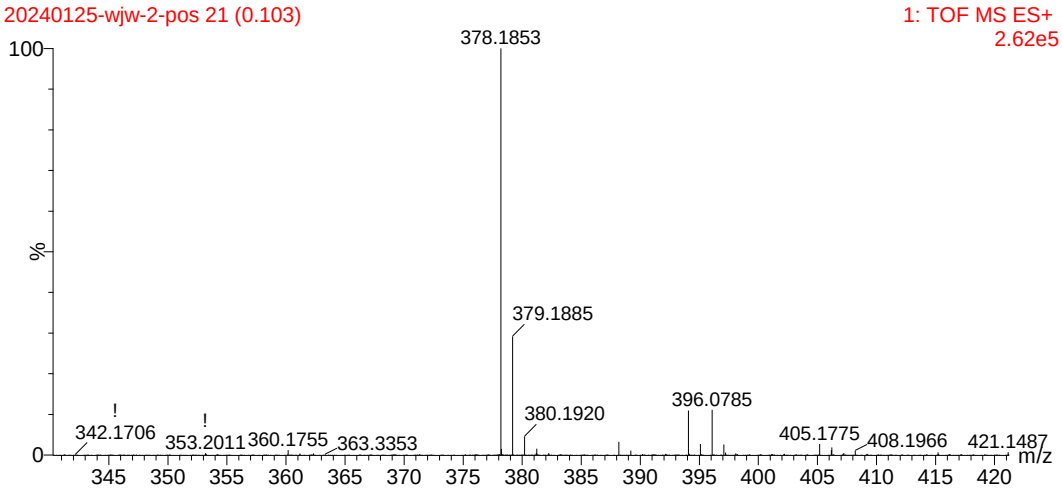
Following the general procedure A and B, the product **4v** was purified by silica gel flash chromatography (PE: EtOAc = 60: 1 as the eluent) to give a colorless oil, 61.1 mg, 81% for sunlight (10 h, procedure A); 55.8 mg, 74% yield for blue-light (procedure B).

R_f = 0.50 (PE: EtOAc = 5: 1).

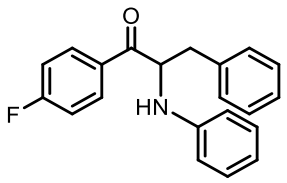
^{1}H NMR (400 MHz, $CDCl_3$) δ 7.99 (d, J = 8.2 Hz, 2H, ArH), 7.65 (d, J = 8.2 Hz, 2H, ArH), 7.60 (d, J = 7.9 Hz, 2H, ArH), 7.44 (t, J = 7.5 Hz, 2H, ArH), 7.37 (t, J = 6.8 Hz, 1H, ArH), 7.20 – 7.11 (m, 5H, ArH), 7.06 (d, J = 7.3 Hz, 2H, ArH), 6.71 (t, J = 7.3 Hz, 1H, ArH), 6.66 (d, J = 8.0 Hz, 2H, ArH), 5.33 (dt, J = 7.6, 5.6 Hz, 1H, CH), 4.68 – 4.60 (d, J = 7.6 Hz, 1H, NH), 3.30 (dd, J = 13.8, 5.6 Hz, 1H, 1H in CH_2), 3.05 (dd, J = 13.8, 5.6 Hz, 1H, 1H in CH_2).

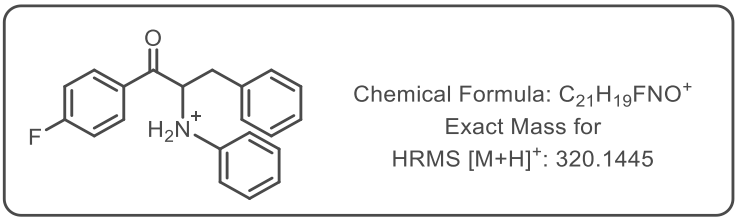
^{13}C NMR (101 MHz, $CDCl_3$) δ 198.9, 146.4, 146.1, 139.5, 136.4, 133.9, 129.4, 129.3, 128.96 (2C), 128.91, 128.3, 127.3, 127.2, 126.7, 118.0, 113.6, 58.9, 38.6.

HRMS (ESI): Calcd for $C_{27}H_{24}NO^+$ $[M+H]^+$ 378.1852, found 378.1853.



1-(4-fluorophenyl)-3-phenyl-2-(phenylamino)propan-1-one (**4w**)





Following the general procedure A and B, the product **4w** was purified by silica gel flash chromatography (PE: EtOAc = 70: 1 as the eluent) to give a colorless crystal, 42.7 mg, 67% for sunlight (10 h, procedure A), 47.9 mg, 75% for sunlight (18 h, procedure A); 42.1 mg, 66% yield for blue-light (procedure B).

R_f = 0.52 (PE: EtOAc = 5: 1).

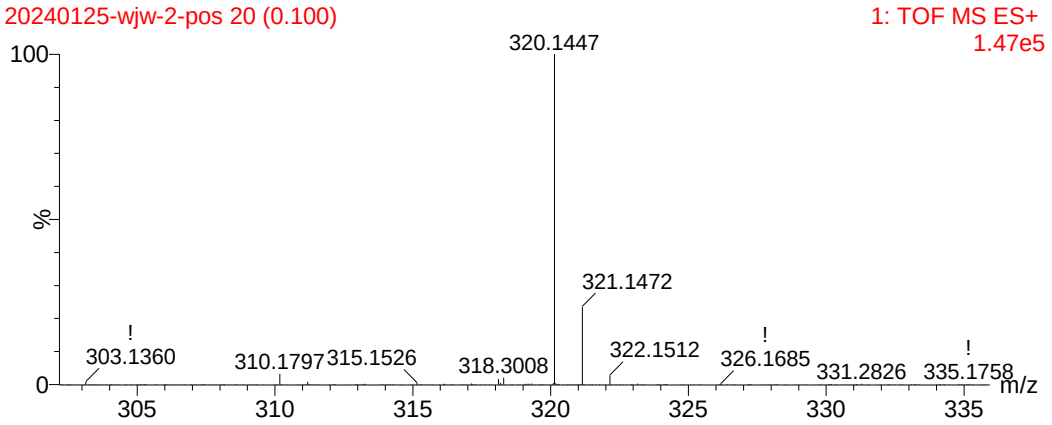
M. p. 118 – 119 °C.

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.93 (dd, J = 7.6, 5.6 Hz, 2H, ArH), 7.24 – 7.13 (m, 5H, ArH), 7.10 (t, J = 8.6 Hz, 2H, ArH), 7.03 (dd, J = 7.6, 1.9 Hz, 2H, ArH), 6.72 (t, J = 7.4, Hz, 1H, ArH), 6.63 (d, J = 8.6, Hz, 2H, ArH), 5.25 (t, J = 5.6 Hz, 1H, CH), 4.58 (s, 1H, NH), 3.23 (dd, J = 13.7, 5.6 Hz, 1H, 1H in CH_2), 3.04 (dd, J = 13.7, 5.6 Hz, 1H, 1H in CH_2).

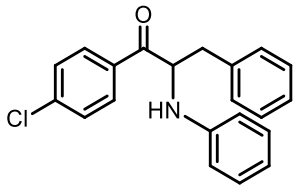
^{13}C NMR (101 MHz, $CDCl_3$) δ 198.0, 165.8 (d, $^1J_{F\text{-}C}$ = 256.0 Hz), 146.3, 136.3, 131.8, 131.77, 131.0 (d, $^2J_{F\text{-}C}$ = 9.3 Hz), 129.4 (2C) , 128.4, 126.8, 118.2, 115.9 (d, $^3J_{F\text{-}C}$ = 21.9 Hz), 113.6, 58.9, 38.7.

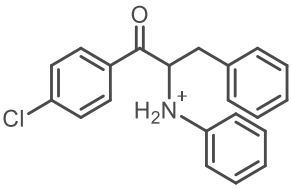
^{19}F NMR (376 MHz, $CDCl_3$) δ -103.95.

HRMS (ESI): Calcd for $C_{21}H_{19}FNO^+$ $[M+H]^+$ 320.1445, found 320.1447.



1-(4-chlorophenyl)-3-phenyl-2-(phenylamino)propan-1-one (**4x**)





Chemical Formula: $C_{21}H_{19}ClNO^+$
Exact Mass for
HRMS $[M+H]^+$: 336.1150

Following the general procedure A and B, the crude product **4x** was purified by silica gel flash chromatography (PE: EtOAc = 70: 1 as the eluent) to give a colorless crystal, 46.9 mg, 70% for sunlight (10 h, procedure A); 44.9 mg, 67% yield for blue-light (procedure B).

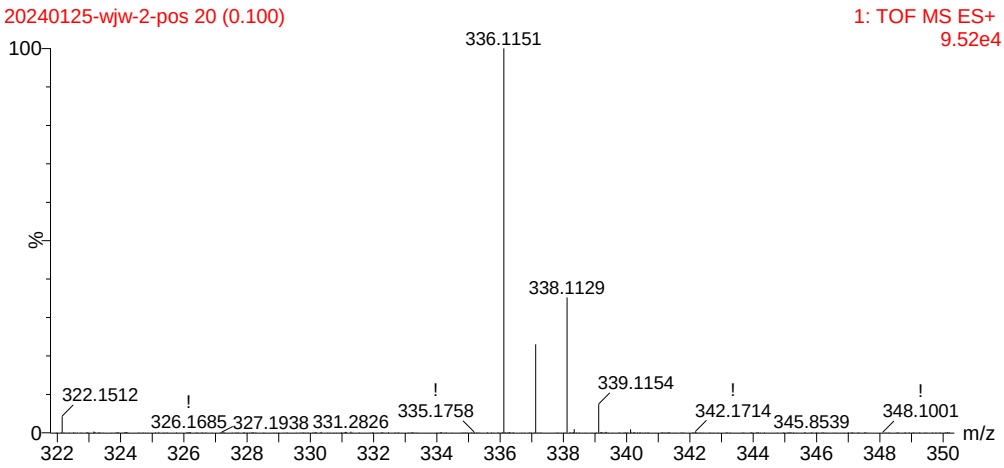
R_f = 0.63 (PE: EtOAc = 5: 1).

M. p. 119 – 120 °C.

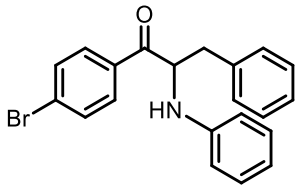
^{1}H NMR (400 MHz, $CDCl_3$) δ 7.85 (d, J = 8.6 Hz, 2H, ArH), 7.41 (d, J = 8.6 Hz, 2H, ArH), 7.25 – 7.11 (m, 5H, ArH), 7.03 (dd, J = 7.4, 1.9 Hz, 2H, ArH), 6.73 (t, J = 7.4 Hz, 1H, ArH), 6.63 (d, J = 7.4 Hz, 2H, ArH), 5.24 (t, J = 5.8 Hz, 1H, CH), 4.56 (s, 1H, NH), 3.24 (dd, J = 13.8, 5.8 Hz, 1H, 1H in CH_2), 3.04 (dd, J = 13.8, 5.8 Hz, 1H, 1H in CH_2).

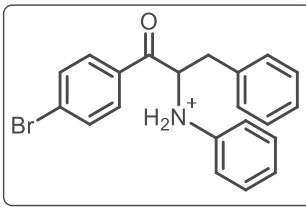
^{13}C NMR (101 MHz, $CDCl_3$) δ 198.5, 146.2, 140.0, 136.2, 133.7, 129.8, 129.4 (2C), 129.1, 128.4, 126.9, 118.2, 113.7, 59.0, 38.7.

HRMS (ESI): Calcd for $C_{21}H_{19}ClNO^+$ $[M+H]^+$ 336.1150, found 336.1151.



1-(4-bromophenyl)-3-phenyl-2-(phenylamino)propan-1-one (**4y**)





Chemical Formula: $C_{21}H_{19}BrNO^+$
Exact Mass for
HRMS $[M+H]^+$: 380.0645

Following the general procedure A and B, the product **4y** was purified by silica gel flash chromatography (PE: EtOAc = 60: 1 as the eluent) to give a colorless crystal, 56.8 mg, 75% for sunlight (10 h, procedure A); 53.8mg, 71% yield for blue-light (procedure B).

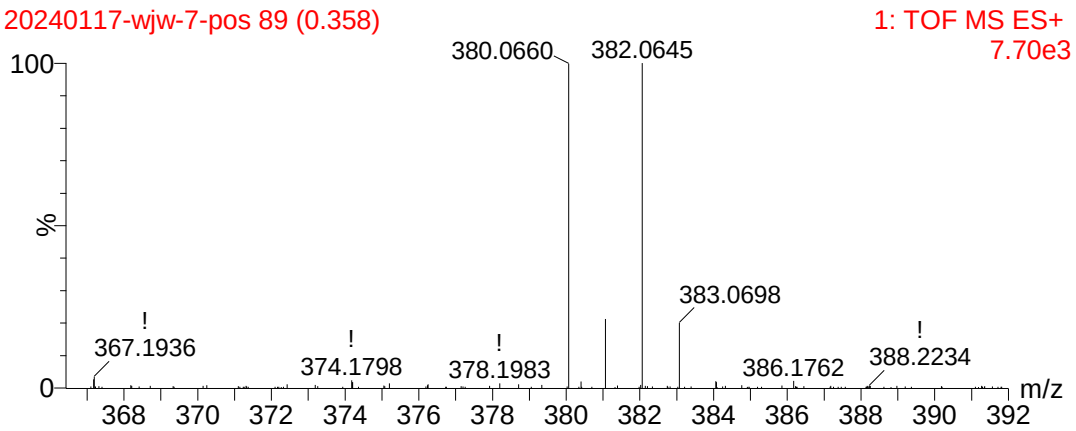
R_f = 0.57 (PE: EtOAc = 5: 1).

M. p. 121 – 123 °C.

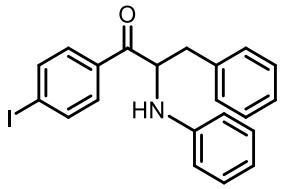
^{1}H NMR (400 MHz, $CDCl_3$) δ 7.76 (d, J = 8.6 Hz, 2H, ArH), 7.59 (d, J = 8.6 Hz, 2H, ArH), 7.24 – 7.12 (m, 5H, ArH), 7.02 (dd, J = 7.3, 1.8 Hz, 2H, ArH), 6.73 (tt, J = 7.3, 1.8 Hz, 1H, ArH), 6.63 (d, J = 7.8 Hz, 2H, ArH), 5.27 (t, J = 5.9 Hz, 1H, CH), 4.56 (s, 1H, NH), 3.24 (dd, J = 13.8, 5.9 Hz, 1H, 1H in CH_2), 3.03 (dd, J = 13.8, 5.9 Hz, 1H, 1H in CH_2).

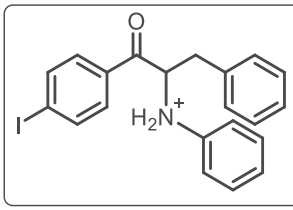
^{13}C NMR (101 MHz, $CDCl_3$) δ 198.6, 146.2, 136.1, 134.1, 132.1, 129.8, 129.4 (2C), 128.7, 128.4, 126.9, 118.2, 113.6, 59.0, 38.6.

HRMS (ESI): Calcd for $C_{21}H_{19}BrNO^+$ $[M+H]^+$ 380.0645, found 380.0660.



1-(4-iodophenyl)-3-phenyl-2-(phenylamino)propan-1-one (**4z**)





Chemical Formula: $C_{21}H_{19}INO^+$
Exact Mass for
HRMS $[M+H]^+$: 428.0506

Following the general procedure A and B, the product **4z** was purified by silica gel flash chromatography (PE: EtOAc = 60: 1 as the eluent) to give a colorless crystal, 63.2 mg, 74% for sunlight (10 h, procedure A); 58.1 mg, 68% yield for blue-light (procedure B).

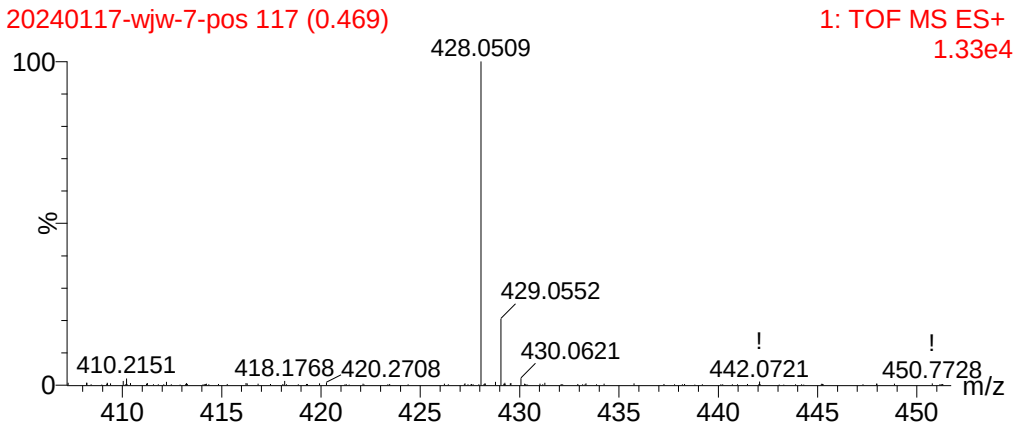
R_f = 0.60 (PE: EtOAc = 5: 1).

M.p. 102 – 104 °C.

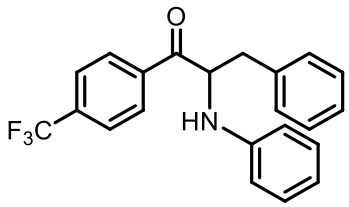
^{1}H NMR (400 MHz, $CDCl_3$) δ 7.76 (d, J = 8.4 Hz, 2H, ArH), 7.58 (d, J = 8.4 Hz, 2H, ArH), 7.21 – 7.10 (m, 5H, ArH), 7.00 (d, J = 7.5 Hz, 2H, ArH), 6.71 (t, J = 7.5 Hz, 1H, ArH), 6.61 (d, J = 8.4 Hz, 2H, ArH), 5.20 (d, J = 5.7 Hz, 1H, CH), 4.56 (s, 1H, NH), 3.22 (dd, J = 13.7, 5.7 Hz, 1H, 1H in CH_2), 3.00 (dd, J = 13.8, 5.7 Hz, 1H, 1H in CH_2).

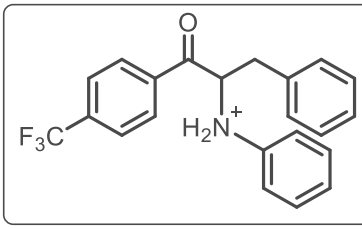
^{13}C NMR (101 MHz, $CDCl_3$) δ 198.8, 146.1, 138.0, 136.1, 134.5, 129.6, 129.3 (2C) , 128.3, 126.8, 118.1, 113.6, 101.6, 58.8, 38.4.

HRMS (ESI): Calcd for $C_{21}H_{19}INO^+$ $[M+H]^+$ 428.0506, found 428.0509.



3-phenyl-2-(phenylamino)-1-(4-(trifluoromethyl)phenyl)propan-1-one (**4aa**)





Chemical Formula: $C_{22}H_{19}F_3NO^+$
Exact Mass for
HRMS $[M+H]^+$: 370.1413

Following the general procedure A and B, the product **4aa** was purified by silica gel flash chromatography (PE: EtOAc = 40:1 as the eluent) to give a colorless crystal, 33.9 mg, 46% for sunlight (10 h, procedure A), 50.2 mg, 68% for sunlight (20 h, procedure A); 27.3 mg, 37% yield for blue-light (procedure B).

R_f = 0.62 (PE: EtOAc = 5: 1).

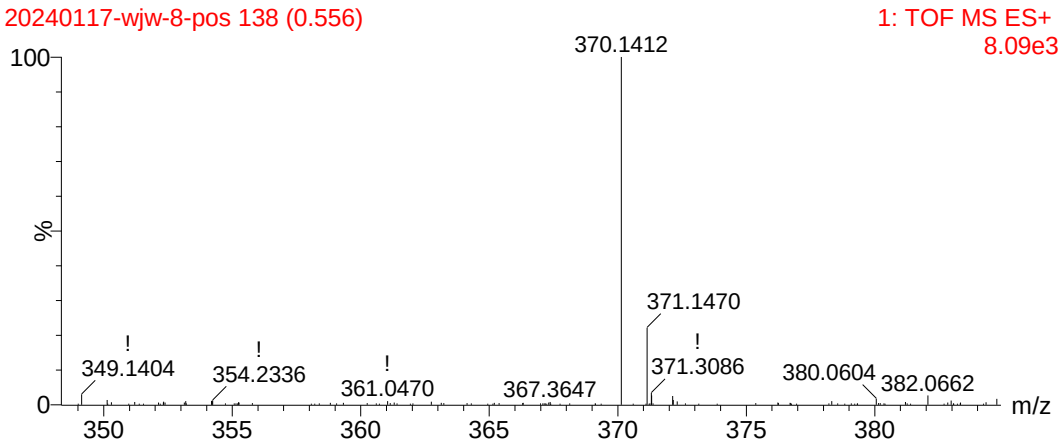
M. p. 98 – 99 °C.

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.99 (d, J = 8.2 Hz, 2H, ArH), 7.69 (d, J = 8.2 Hz, 2H, ArH), 7.36 – 7.08 (m, 5H, ArH), 7.03 (dt, J = 7.4, 1.5 Hz, 2H, ArH), 6.74 (t, J = 7.4 Hz, 1H, ArH), 6.65 (d, J = 8.4 Hz, 2H, ArH), 5.29 (t, J = 5.9 Hz, 1H, CH), 4.41 (s, 1H, NH), 3.25 (dd, J = 13.8, 5.9 Hz, 1H, 1H in CH_2), 3.06 (dd, J = 13.8, 5.9 Hz, 1H, 1H in CH_2).

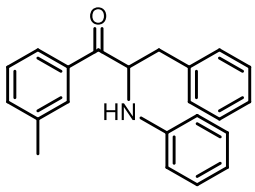
^{13}C NMR (101 MHz, $CDCl_3$) δ 199.0, 146.1, 138.2, 136.7 (q, J = 32.8 Hz), 134.5, 134.2, 129.5, 129.4, 128.7, 127.5, 127.0, 125.8 (q, J = 3.5 Hz), 123.6 (q, J = 272.4 Hz), 118.4, 113.7, 59.5, 38.5.

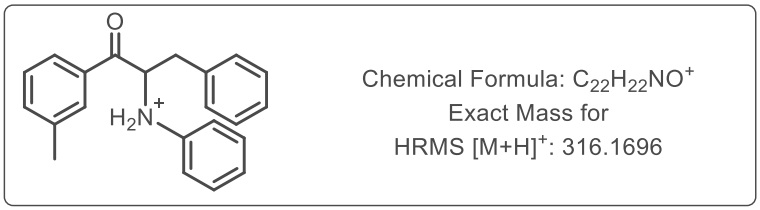
^{19}F NMR (376 MHz, $CDCl_3$) δ -63.17.

HRMS (ESI): Calcd for $C_{22}H_{19}F_3NO^+$ $[M+H]^+$ 370.1413, found 370.1412.



3-phenyl-2-(phenylamino)-1-(*m*-tolyl)propan-1-one (**4ab**)





Following the general procedure A and B, the product **4ab** was purified by silica gel flash chromatography (PE: EtOAc = 60: 1 as the eluent) to give a colorless crystal, 47.2 mg, 75% for sunlight (10 h, procedure A); 44.1 mg, 70% yield for blue-light (procedure B).

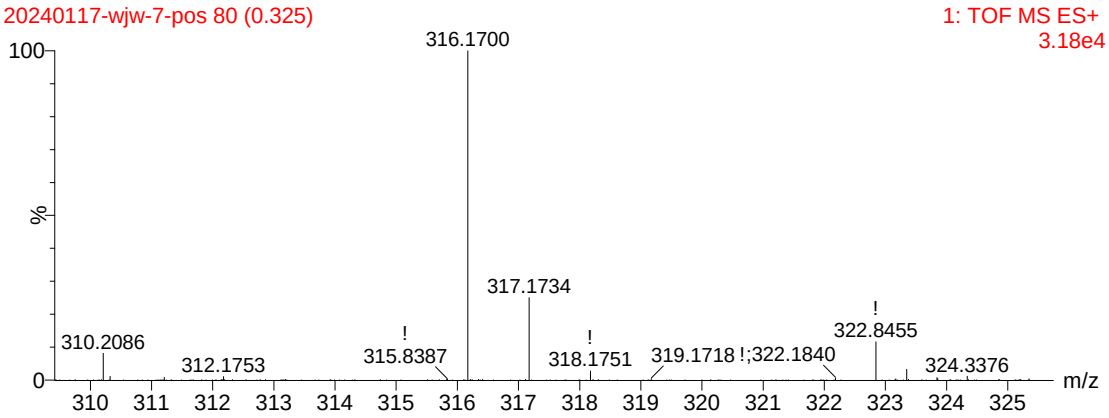
R_f = 0.50 (PE: EtOAc = 5: 1).

M. p. 80 – 82 °C.

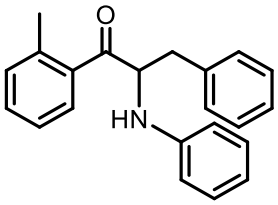
^{1}H NMR (400 MHz, $CDCl_3$) δ 7.74 (d, J = 7.4 Hz, 1H, ArH), 7.72 (s, 1H, ArH), 7.39 (d, J = 7.4 Hz, 1H, ArH), 7.34 (t, J = 7.4 Hz, 1H, ArH), 7.24 – 7.11 (m, 5H, ArH), 7.04 (d, J = 7.8 Hz, 2H, ArH), 6.71 (t, J = 7.8 Hz, 1H, ArH), 6.64 (d, J = 7.8 Hz, 2H, ArH), 5.30 (t, J = 5.7 Hz, 1H, CH), 4.62 (s, 1H, NH), 3.27 (dd, J = 13.8, 5.7 Hz, 1H, 1H in CH_2), 3.03 (dd, J = 13.8, 5.7 Hz, 1H, 1H in CH_2), 2.39 (s, 3H, CH_3).

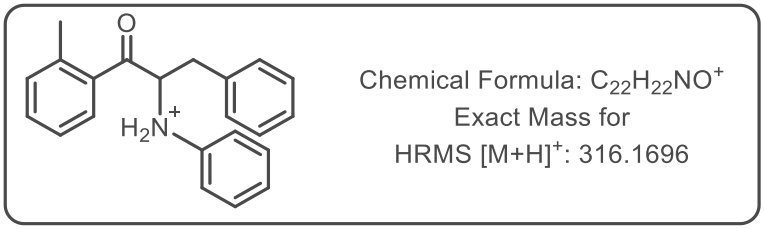
^{13}C NMR (101 MHz, $CDCl_3$) δ 199.6, 146.5, 138.6, 136.5, 135.3, 134.3, 129.5, 129.3, 129.0, 128.6, 128.3, 126.7, 125.6, 118.0, 113.7, 58.9, 38.7, 21.3.

HRMS (ESI): Calcd for $C_{22}H_{22}NO^+$ $[M+H]^+$ 316.1696, found 316.1700.



3-phenyl-2-(phenylamino)-1-(*o*-tolyl)propan-1-one (**4ac**)





Following the general procedure A and B, the product **4ac** was purified by silica gel flash chromatography (PE: EtOAc = 60: 1 as the eluent) to give a colorless crystal, 32.8 mg, 52% for sunlight (10 h, procedure A), 46.6 mg, 74% for sunlight (28 h, procedure A); 29.0 mg, 46% yield for blue-light (procedure B).

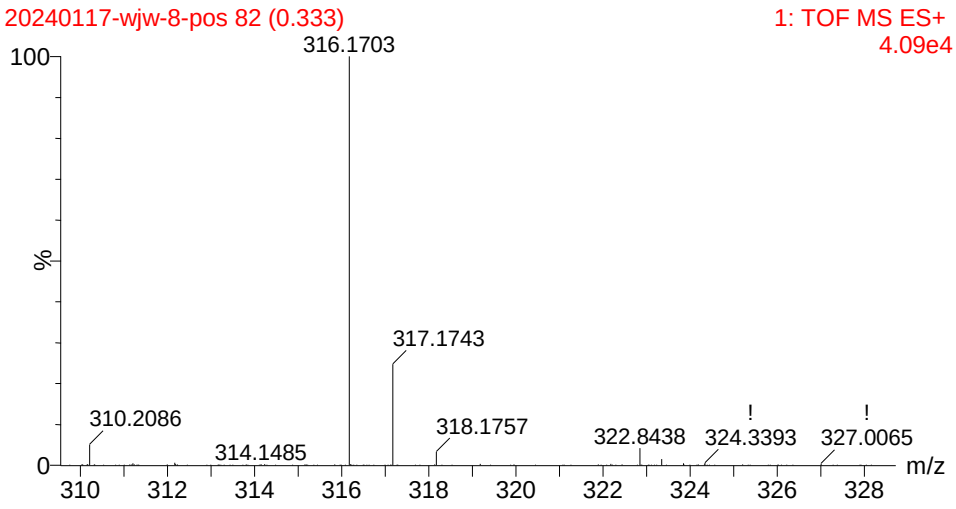
R_f = 0.63 (PE: EtOAc = 5: 1).

M. p. 69 – 71 °C.

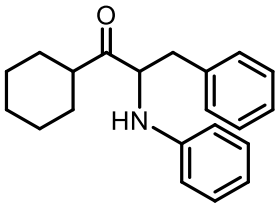
^{1}H NMR (400 MHz, $CDCl_3$) δ 7.61 (d, J = 7.7 Hz, 1H, ArH), 7.35 (t, J = 7.7 Hz, 1H, ArH), 7.22 (d, J = 7.7 Hz, 2H, ArH), 7.19 – 7.12 (m, 5H, ArH), 6.99 (d, J = 7.5 Hz, 2H, ArH), 6.71 (t, J = 7.5 Hz, 1H, ArH), 6.65 (d, J = 8.2 Hz, 2H, ArH), 5.22 (dd, J = 5.8, 5.4 Hz, 1H, CH), 4.74 (s, 1H, NH), 3.21 (dd, J = 13.8, 5.4 Hz, 1H, 1H in CH_2), 2.94 (dd, J = 13.8, 5.8 Hz, 1H, 1H in CH_2), 2.31 (s, 3H, CH_3).

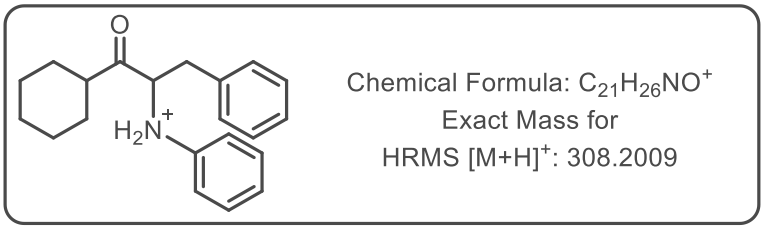
^{13}C NMR (101 MHz, $CDCl_3$) δ 202.2, 146.4, 139.3, 136.4, 135.6, 132.1, 131.7, 129.3 (2C), 128.2, 128.2, 126.6, 125.6, 117.9, 113.5, 60.6, 37.9, 21.0.

HRMS (ESI): Calcd for $C_{22}H_{22}NO^+$ $[M+H]^+$ 316.1696, found 316.1703.



1-cyclohexyl-3-phenyl-2-(phenylamino)propan-1-one (**4ad**)





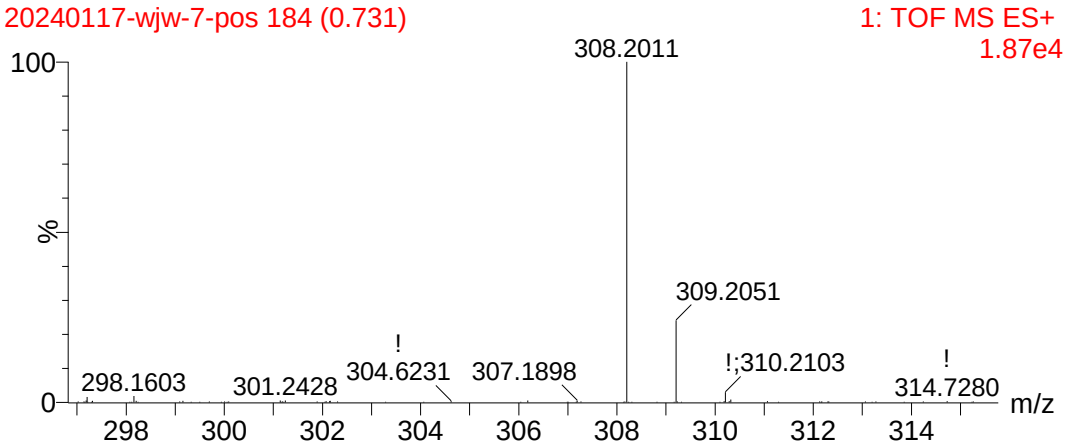
Following the general procedure A and B, the product **4ad** was purified by silica gel flash chromatography (PE: EtOAc = 60: 1 as the eluent) to give a yellow oil, 32.5 mg, 53% for sunlight (10 h, procedure A), 44.8 mg, 73% for sunlight (22 h, procedure A); 42.4 mg, 69% yield for blue-light (procedure B).

R_f = 0.62 (PE: EtOAc = 5: 1).

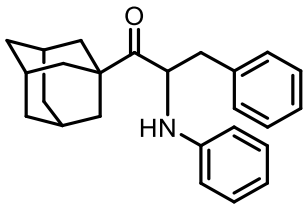
^{1}H NMR (400 MHz, Chloroform-d) δ 7.34 – 7.07 (m, 7H, ArH), 6.71 (t, J = 7.3 Hz, 1H, ArH), 6.57 (d, J = 8.4 Hz, 2H, ArH), 4.43 (t, J = 6.4 Hz, 1H, CH), 4.29 (s, 1H, NH), 3.07 (dd, J = 13.8, 6.4 Hz, 1H, 1H in CH_2), 2.99 (dd, J = 13.8, 6.4 Hz, 1H, 1H in CH_2), 2.41 (tt, J = 11.2, 3.2 Hz, 1H, CH), 1.82 – 1.55 (m, 5H, He in cyclohexyl), 1.37 – 1.09 (m, 5H, Ha in cyclohexyl).

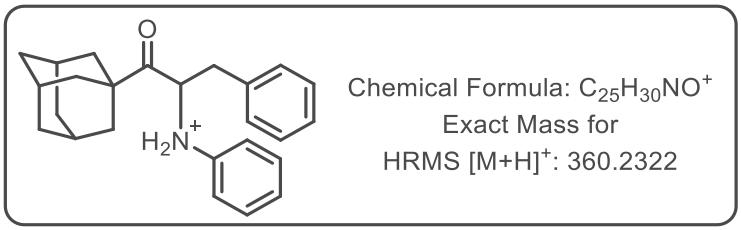
^{13}C NMR (101 MHz, $CDCl_3$) δ 213.5, 146.5, 136.8, 129.3, 129.2, 128.5, 126.8, 118.0, 113.5, 62.0, 48.4, 37.8, 29.2, 27.4, 25.8, 25.6, 25.2.

HRMS (ESI): Calcd for $C_{21}H_{26}NO^+$ $[M+H]^+$ 308.2009, found 308.2011.



N-(1-((3*r*,5*r*,7*r*)-adamantan-1-yl)-1-*oxo*-3-phenylpropan-2-yl)benzenaminium (**4ae**)





Following the general procedure A and B, the product **4ae** was purified by silica gel flash chromatography (PE: EtOAc = 80: 1 as the eluent) to give a colorless crystal, 56.0 mg, 78% for sunlight (10 h, procedure A), 58.9 mg, 82% for sunlight (16 h, procedure A); 52.4 mg, 73% yield for blue-light (procedure B).

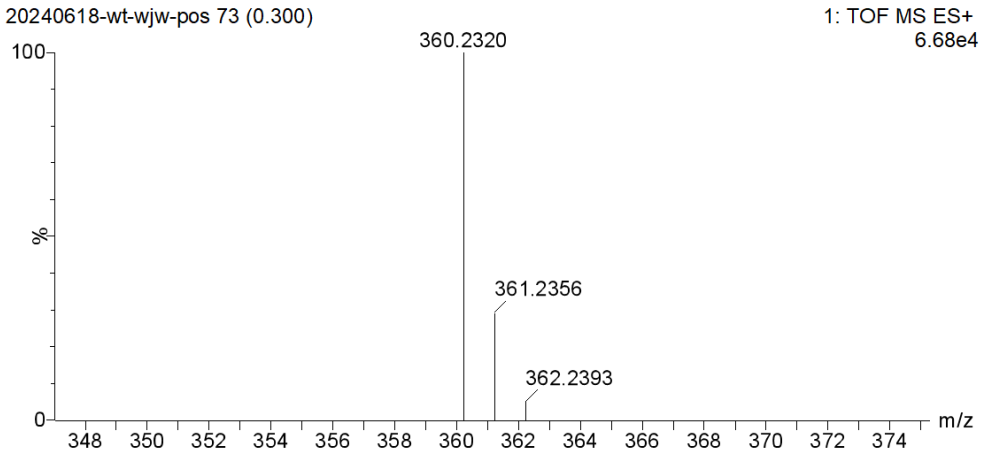
R_f = 0.50 (PE: EtOAc = 5: 1).

M. p. 100 – 102 °C.

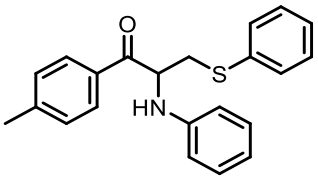
^{1}H NMR (400 MHz, $CDCl_3$) δ 7.25 (d, J = 8.3 Hz, 2H, ArH), 7.22 – 7.11 (m, 5H, ArH), 6.72 (t, J = 7.0 Hz, 1H, ArH), 6.60 (d, J = 8.3 Hz, 2H, ArH), 4.74 (s, 1H, CH), 4.00 (s, 1H, NH), 3.03 (dd, J = 13.3, 7.5 Hz, 1H, 1H in CH**C**$\mathbf{H_2}$), 2.86 (dd, J = 13.3, 5.7 Hz, 1H, 1H in CH**C**$\mathbf{H_2}$), 1.95 (s, 3H, three CH in Adamantane), 1.72 – 1.56 (m, 12H, six CH_2 in Adamantane).

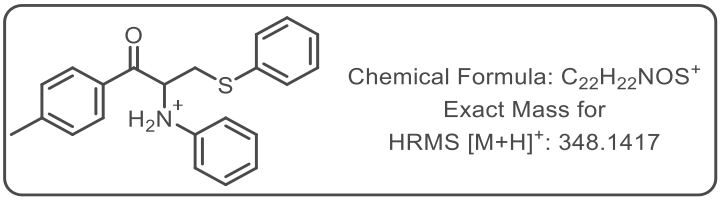
^{13}C NMR (101 MHz, $CDCl_3$) δ 214.3, 146.4, 137.4, 129.5, 129.3, 128.4, 126.6, 118.2, 113.8, 57.1, 45.9, 38.2, 37.6, 36.3, 27.6.

HRMS (ESI): Calcd for $C_{25}H_{30}NO^+$ $[M+H]^+$ 360.2322, found 360.2320.



2-(phenylamino)-3-(phenylthio)-1-(*p*-tolyl)propan-1-one (**4af**)





Following the general procedure A and B, the product **4af** was purified by silica gel flash chromatography (PE: EtOAc = 50:1 as the eluent) to give a colorless crystal, 34.7 mg, 50% for sunlight (10 h, procedure A), 54.1 mg, 78% for sunlight (20 h, procedure A); 51.4 mg, 74% yield for blue-light (procedure B).

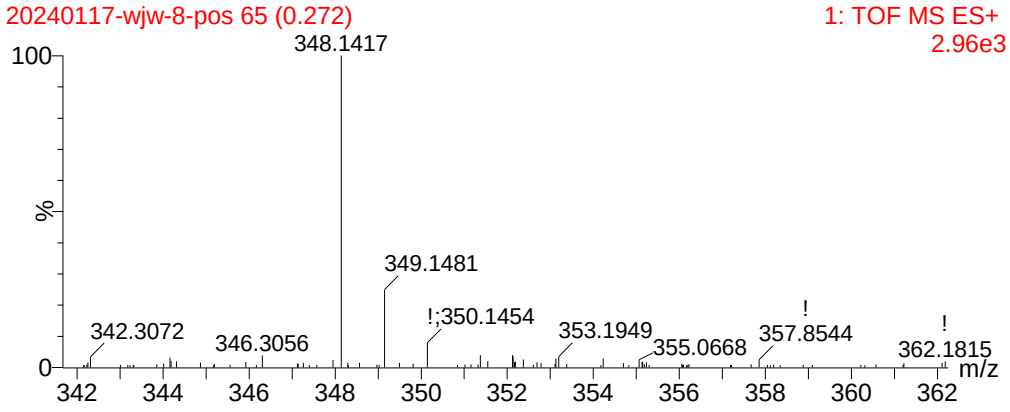
R_f = 0.54 (PE: EtOAc = 5: 1).

M. p. 113 – 114 °C.

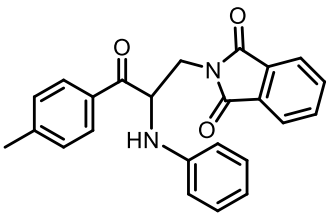
^{1}H NMR (400 MHz, $CDCl_3$) δ 7.76 (d, J = 8.2 Hz, 2H, ArH), 7.31 (d, J = 8.2 Hz, 2H, ArH), 7.28 – 7.17 (m, 5H, ArH), 7.13 (t, J = 7.8 Hz, 2H, ArH), 6.72 (t, J = 7.8 Hz, 1H, ArH), 6.60 (d, J = 7.8 Hz, 2H, ArH), 5.17 (t, J = 5.9 Hz, 1H, CH), 4.63 (s, 1H, NH), 3.45 (dd, J = 13.5, 5.9 Hz, 1H, 1H in CH_2), 3.24 (dd, J = 13.5, 5.9 Hz, 1H, 1H in CH_2), 2.40 (s, 3H, CH_3).

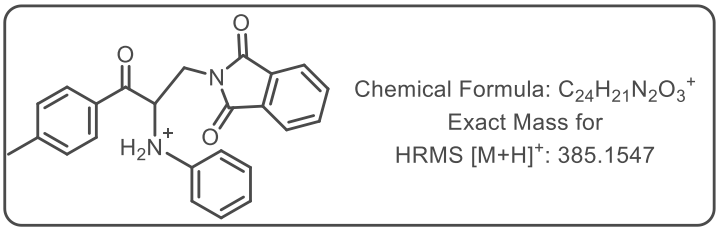
^{13}C NMR (101 MHz, $CDCl_3$) δ 198.00, 146.2, 144.8, 135.1, 132.6, 130.8, 129.4, 129.3, 129.0, 128.6, 126.9, 118.5, 113.8, 56.8, 37.1, 21.7.

HRMS (ESI): Calcd for $C_{22}H_{22}NOS^+$ $[M+H]^+$ 348.1417, found 348.1417.



2-(3-oxo-2-(phenylamino)-3-(*p*-tolyl)propyl)isoindoline-1,3-dione (**4ag**)





Following the general procedure A and B, the product **4ag** was purified by silica gel flash chromatography (PE: EtOAc = 40: 1 as the eluent) to give a colorless crystal, 40.7 mg, 53% for sunlight (10 h, procedure A), 72.2 mg, 81% for sunlight (20 h, procedure A); 59.1 mg, 77% yield for blue-light (procedure B).

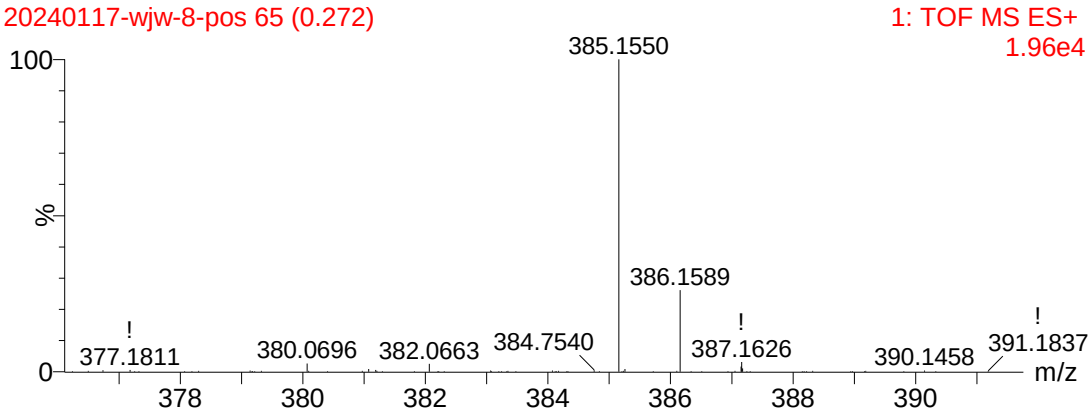
R_f = 0.25 (PE: EtOAc = 5: 1).

M. p. 162 – 163 °C.

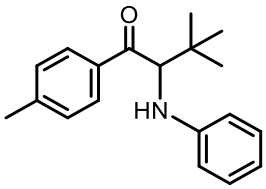
^{1}H NMR (400 MHz, $CDCl_3$) δ 8.01 (d, J = 8.2 Hz, 2H, ArH), 7.76 (dd, J = 5.5, 3.0 Hz, 2H, ArH), 7.66 (dd, J = 5.5, 3.0 Hz, 2H, ArH), 7.24 (d, J = 8.2 Hz, 2H, ArH), 7.05 (tt, J = 7.3, 1.2 Hz, 2H, ArH), 6.67 (d, J = 7.7 Hz, 2H, ArH), 6.61 (t, J = 7.3 Hz, 1H, ArH), 5.56 (t, J = 7.0 Hz, 1H, CH), 4.63 (s, 1H, NH), 4.02 (d, J = 7.0 Hz, 2H, CH_2), 2.35 (s, 3H, CH_3).

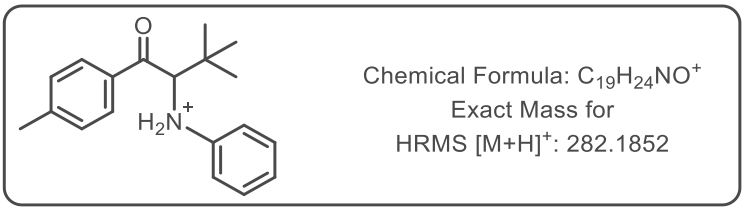
^{13}C NMR (101 MHz, $CDCl_3$) δ 197.9, 168.2, 146.4, 145.0, 134.0, 132.6, 131.7, 129.6, 129.2, 128.7, 123.2, 118.3, 113.6, 56.3, 40.3, 21.6.

HRMS (ESI): Calcd for $C_{24}H_{21}N_2O_3^+$ $[M+H]^+$ 385.1547, found 385.1550.



3,3-dimethyl-2-(phenylamino)-1-(*p*-tolyl)butan-1-one (**4ah**)





Following the general procedure A and B, the product **4ah** was purified by silica gel flash chromatography (PE: EtOAc = 60: 1 as the eluent) to give a colorless crystal, 20.8 mg, 37% for sunlight (10 h, procedure A), 33.7 mg, 68% for sunlight (20 h, procedure A); 25.8 mg, 46% yield for blue-light (procedure B).

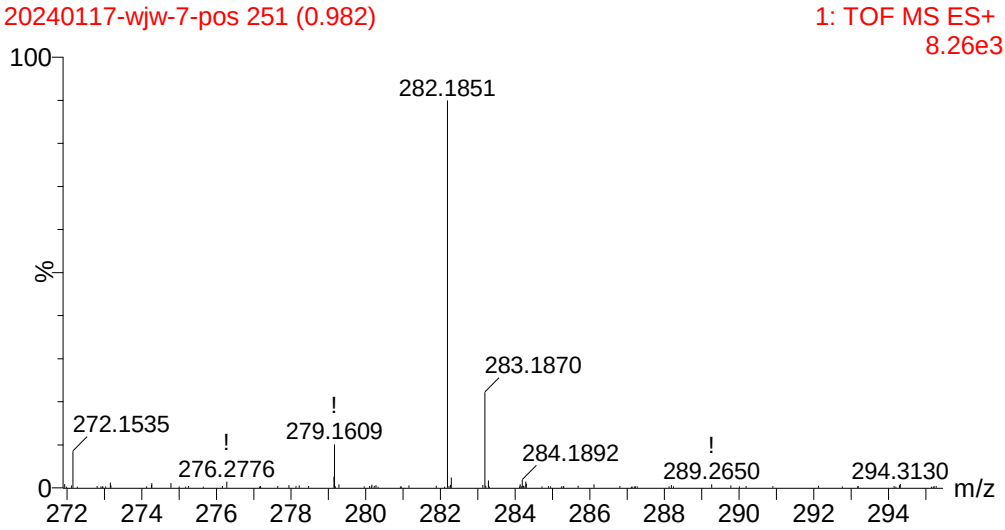
R_f = 0.65 (PE: EtOAc = 5: 1).

M. p. 124 – 126 °C.

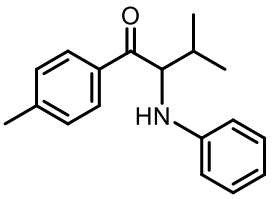
^{1}H NMR (400 MHz, $CDCl_3$) δ 7.86 (d, J = 8.2 Hz, 2H, ArH), 7.25 (d, J = 8.2 Hz, 2H, ArH), 7.12 (t, J = 7.7 Hz, 2H, ArH), 6.72 (d, J = 8.5 Hz, 2H, ArH), 6.67 (t, J = 7.7 Hz, 1H, ArH), 4.84 (d, J = 9.7 Hz, 1H, CH), 4.61 (d, J = 9.7 Hz, 1H, NH), 2.39 (s, 3H, CH_3), 1.01 (s, 9H, C $(CH_3)_3$).

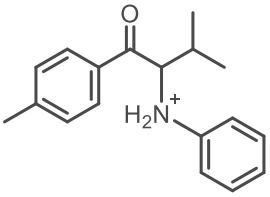
^{13}C NMR (101 MHz, $CDCl_3$) δ 202.6, 148.2, 144.2, 135.7, 129.4, 129.2, 128.4, 118.0, 114.0, 64.2, 35.8, 27.3, 21.6.

HRMS (ESI): Calcd for $C_{19}H_{24}NO^+$ $[M+H]^+$ 282.1852, found 282.1851.



3-methyl-2-(phenylamino)-1-(*p*-tolyl)butan-1-one (**4ai**)





Chemical Formula: $C_{18}H_{22}NO^+$
Exact Mass for
HRMS $[M+H]^+$: 268.1696

Following the general procedure A and B, the product **4ai** was purified by silica gel flash chromatography (PE: EtOAc = 60: 1 as the eluent) to give a colorless crystal, 36.3 mg, 68% for sunlight (10 h, procedure A), 43.8 mg, 82% for sunlight (20 h, procedure A); 40.0 mg, 75% yield for blue-light (procedure B).

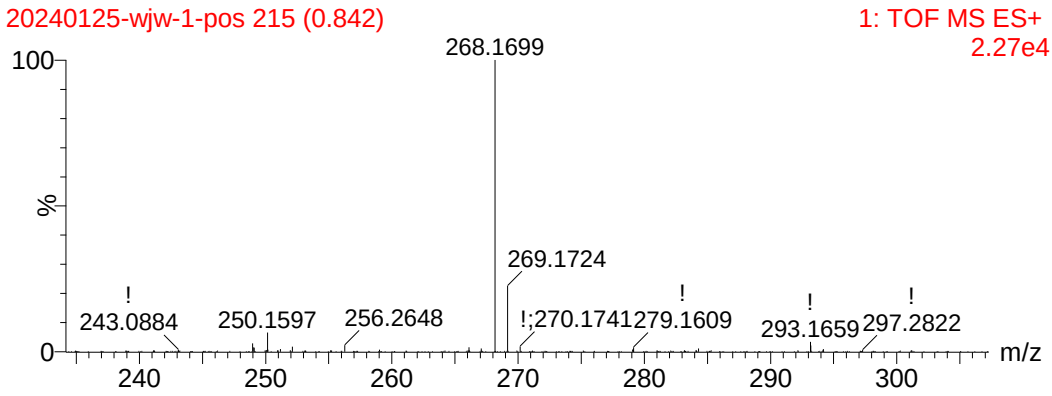
R_f = 0.67 (PE: EtOAc = 5: 1).

M. p. 114 – 115 °C.

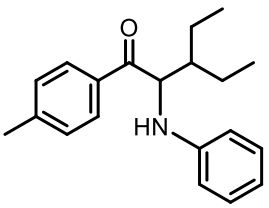
^{1}H NMR (400 MHz, $CDCl_3$) δ 7.87 (d, J = 8.0 Hz, 2H, ArH), 7.26 (d, J = 8.0 Hz, 2H, ArH), 7.14 (t, J = 7.9 Hz, 2H, ArH), 6.74 – 6.65 (m, 3H, ArH), 4.88 (d, J = 4.1 Hz, 1H, NH–**CH**), 4.64 (s, 1H, NH), 2.39 (s, 3H, Ar–**CH_3**), 2.22 (hept d, J = 6.8, 4.1 Hz, 1H, CH in **CH**$(CH_3)_2$), 1.09 (d, J = 6.8 Hz, 3H, CH_3 in CH(**CH_3**)$_2$), 0.87 (d, J = 6.8 Hz, 3H, CH_3 in CH(**CH_3**)$_2$).

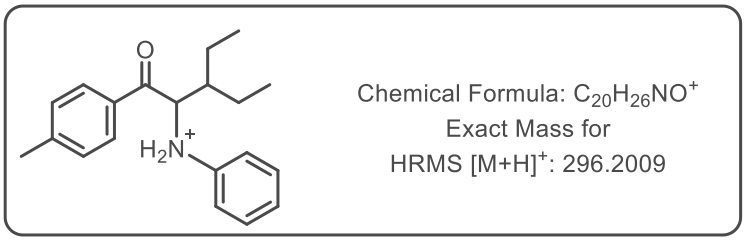
^{13}C NMR (101 MHz, $CDCl_3$) δ 200.6, 148.2, 144.3, 133.4, 129.4, 129.2, 128.4, 117.8, 113.9, 63.0, 31.9, 21.6, 20.3, 17.1.

HRMS (ESI): Calcd for $C_{18}H_{22}NO^+$ $[M+H]^+$ 268.1696, found 268.1699.



3-ethyl-2-(phenylamino)-1-(*p*-tolyl)pentan-1-one (**4aj**)





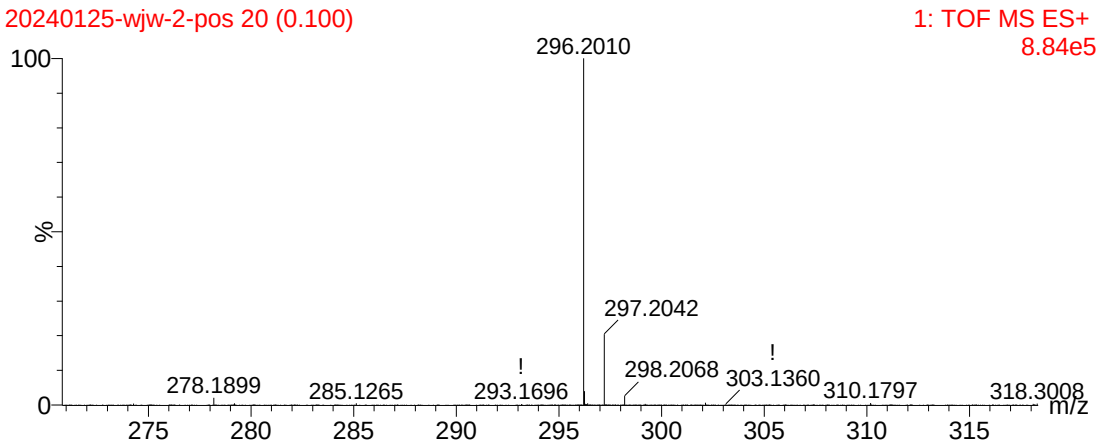
Following the general procedure A and B, the product **4aj** was purified by silica gel flash chromatography (PE: EtOAc = 60: 1 as the eluent) to give a yellow oil, 36.6 mg, 62% for sunlight (10 h, procedure A), 50.1 mg, 85% for sunlight (20 h, procedure A); 50.1 mg, 85% yield for blue-light (procedure B).

R_f = 0.68 (PE:EtOAc = 5: 1).

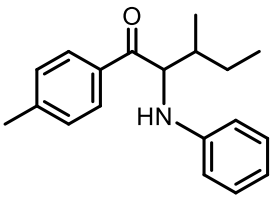
^{1}H NMR (400 MHz, $CDCl_3$) δ 7.79 (d, J = 8.2 Hz, 2H, ArH), 7.19 (d, J = 8.2 Hz, 2H, ArH), 7.09 – 7.00 (m, 2H, ArH), 6.61 (d, J = 6.8 Hz, 3H, ArH), 5.02 (d, J = 3.7 Hz, 1H, CH), 4.40 (s, 1H, NH), 2.33 (s, 3H, CH_3), 1.67 – 1.58 (m, 1H, CH), 1.45 (quint, J = 7.4 Hz, 2H, CH_2), 1.47 – 1.27 (m, 1H, 1H in CH_2), 1.24 – 1.11 (m, 1H, 1H in CH_2), 1.00 (t, J = 7.4 Hz, 3H, $CH_2\mathbf{CH_3}$), 0.75 (t, J = 7.4 Hz, 3H, $CH_2\mathbf{CH_3}$).

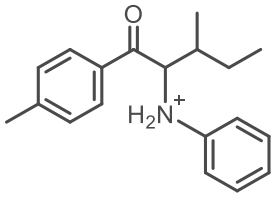
^{13}C NMR (101 MHz, $CDCl_3$) δ 201.2, 148.2, 144.2, 133.5, 129.5, 129.2, 128.3, 118.0, 114.0, 59.7, 45.0, 23.3, 21.6, 21.4, 12.3, 11.9.

HRMS (ESI): Calcd for $C_{20}H_{26}NO^+$ $[M+H]^+$ 296.2009, found 296.2010.



3-methyl-2-(phenylamino)-1-(*p*-tolyl)pentan-1-one (**4ak**)





Chemical Formula: $C_{19}H_{24}NO^+$
Exact Mass
for HRMS $[M+H]^+$: 282.1852

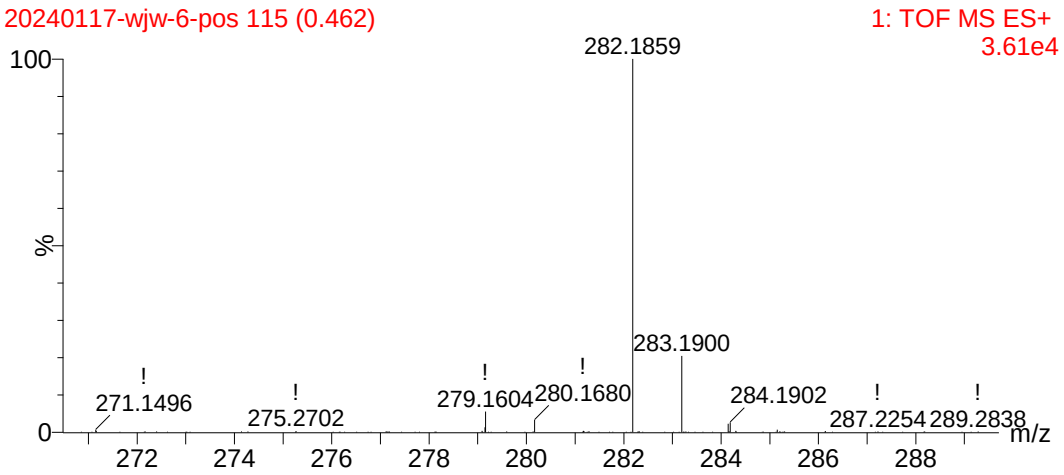
Following the general procedure A and B, the product **4ak** was purified by silica gel flash chromatography (PE: EtOAc = 100: 1 as the eluent) to give as a yellow oil, 28.1 mg, 50% for sunlight (10 h, procedure A), 43.3 mg, 77% for sunlight (20 h, procedure A); 44.9 mg, 80% yield for blue-light (procedure B); dr = 1:1.

R_f = 0.67 (PE:EtOAc = 5: 1).

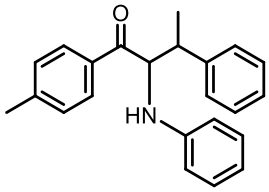
^{1}H NMR (400 MHz, $CDCl_3$) δ 7.79 (dd, J = 7.0, 3.5 Hz, 2H, ArH) , 7.19 (dd, J = 8.1, 2.8 Hz, 2H, ArH) , 7.06 (t, J = 7.5 Hz, 2H, ArH) , 6.65 – 6.59 (m, 3H, ArH) , 4.97 – 4.93 (m, 0.5 H, CH), 4.82 (d, J = 4.5 Hz, 0.5H, CH), 4.50 (s, 1H, NH), 2.33 (s, 3H, CH_3), 1.93 – 1.81 (m, 1H), 1.60 (dddd, J = 13.7, 7.6, 6.3, 1.5 Hz, 1H), 1.47 – 1.38 (m, 1H), 1.37 – 1.25 (m, 1H), 1.07 (ddtd, J = 14.7, 9.8, 7.2, 1.5 Hz, 1H), 0.99 – 0.90 (m, 3H, CH_3), 0.79 – 0.74 (m, 3H, CH_3), with diastereoisomer ratio = 1:1.

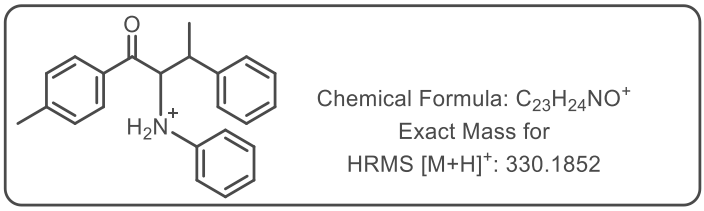
^{13}C NMR (101 MHz, $CDCl_3$) δ 201.0, 200.6, 148.3, 148.0, 144.3, 144.3, 133.85, 133.2, 129.5, 129.4, 129.2, 128.4, 118.0, 117.85, 114.1, 113.81, 38.7, 38.3, 27.3, 24.4, 21.6, 16.5, 13.8, 12.2, 11.75.

HRMS (ESI): Calcd for $C_{19}H_{24}NO^+$ $[M+H]^+$ 282.1852, found 282.1859.



3-phenyl-2-(phenylamino)-1-(*p*-tolyl)butan-1-one (**4al**)





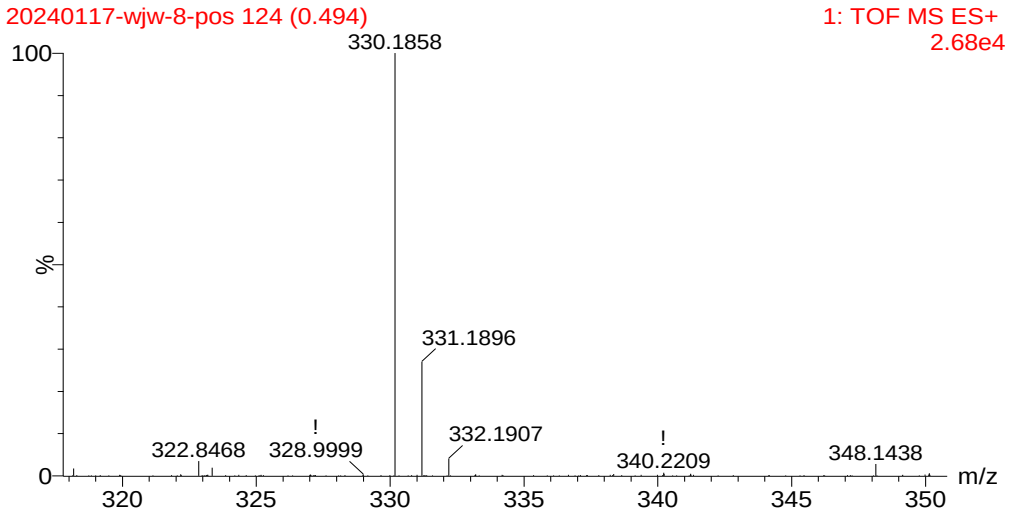
Following the general procedure A and B, the product **4al** was purified by silica gel flash chromatography (PE: EtOAc = 40: 1 as the eluent) to give a colorless oil, 34.9 mg, 53% for sunlight (10 h, procedure A), 48.7 mg, 74% for sunlight (18 h, procedure A); 46.1 mg, 70% yield for blue-light (procedure B); dr = 1:1.

R_f = 0.52 (PE: EtOAc = 5: 1).

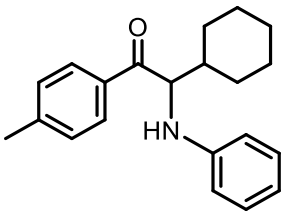
^{1}H NMR (400 MHz, $CDCl_3$) δ 7.92 (dd, J = 7.7, 5.5 Hz, 2H, ArH), 7.42 (d, J = 7.7 Hz, 1H, ArH), 7.44 – 7.06 (m, 5H, ArH), 7.24 – 7.15 (m, 2H, ArH), 7.12 (t, J = 7.7 Hz, 1H, ArH), 6.79 – 6.70 (m, 2H, ArH), 6.50 (d, J = 8.2 Hz, 1H, ArH), 5.27 –5.14 (m, 1H, CH), 4.88 (s, 0.5H, NH), 4.51 (s, 0.5H, NH), 3.59 – 3.46 (m, 0.5H, CH), 3.46 – 3.35 (m, 0.5H, CH), 2.48 (d, J = 3.1 Hz, 3H, CH_3), 1.53 (d, J = 7.1 Hz, 1.5H, CH_3), 1.37 (d, J = 7.1 Hz, 1.5H, CH_3), diastereoisomer ratio = 1:1.

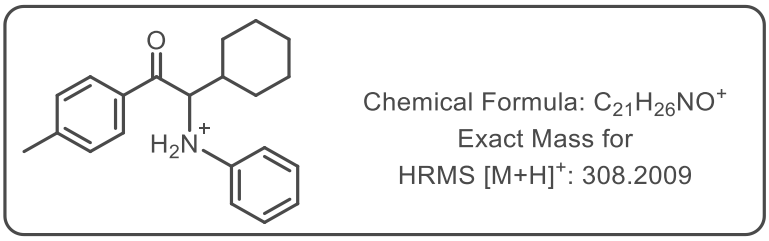
^{13}C NMR (101 MHz, $CDCl_3$) δ 200.0, 199.8, 148.1, 147.7, 144.5, 144.4, 143.6, 141.3, 133.7, 133.1, 129.6, 129.5, 129.3, 129.2, 128.6, 128.3, 128.15, 128.0, 127.1, 126.9, 118.2, 118.2, 114.35, 114.1, 64.5, 63.7, 43.1, 42.7, 21.8, 18.3, 15.1.

HRMS (ESI): Calcd for $C_{23}H_{24}NO^+$ $[M+H]^+$ 330.1852, found 330.1858.



2-cyclohexyl-2-(phenylamino)-1-(*p*-tolyl)ethan-1-one (**4am**)





Following the general procedure A and B, the product **4am** was purified by silica gel flash chromatography (PE: EtOAc = 60: 1 as the eluent) to give a colorless crystal, 45.4 mg, 74% for sunlight (10 h, procedure A); 38.1 mg, 62% yield for blue-light (procedure B).

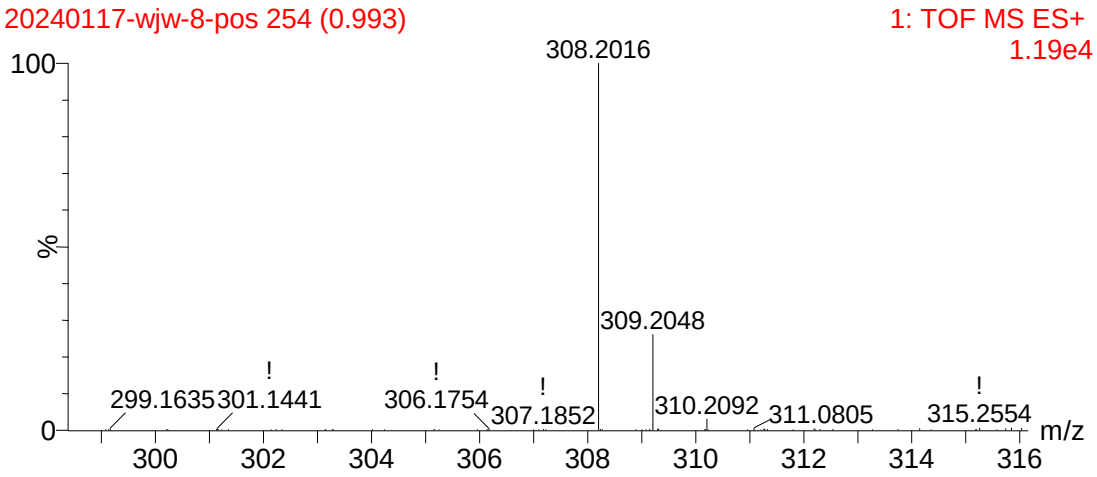
R_f = 0.68 (PE: EtOAc = 5: 1).

M. p. 99 – 100 °C.

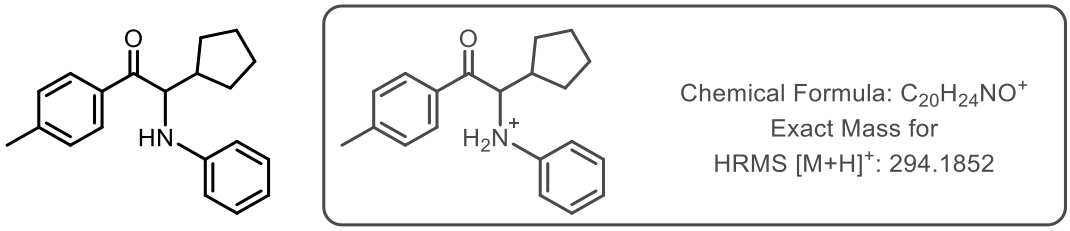
^{1}H NMR (400 MHz, $CDCl_3$) δ 7.87 (d, J = 8.1 Hz, 2H, ArH), 7.26 (d, J = 8.1 Hz, 2H, ArH), 7.12 (t, J = 7.8 Hz, 2H, ArH), 7.73 – 7.63 (m, ArH), 4.87 (s, 1H, NH), 4.67 (d, J = 4.9 Hz, 1H, CH), 2.39 (s, 3H, CH_3), 1.93 – 1.53 (m, 6H, equatorial Hs in cyclohexyl), 1.47 – 0.98 (m, 5H, axial Hs in cyclohexyl).

^{13}C NMR (101 MHz, $CDCl_3$) δ 200.6, 148.2, 144.3, 133.5, 129.4, 129.1, 128.4, 117.7, 113.7, 62.7, 42.0, 30.7, 27.7, 26.3, 26.1, 25.9, 21.6.

HRMS (ESI): Calcd for $C_{21}H_{26}NO^+$ $[M+H]^+$ 308.2009, found 308.2016.



2-cyclopentyl-2-(phenylamino)-1-(*p*-tolyl)ethan-1-one (**4an**)



Following the general procedure A and B, the product **4an** was purified by silica gel flash chromatography (PE: EtOAc = 60: 1 as the eluent) to give a colorless crystal, 35.1 mg, 60% for sunlight (10 h, procedure A), 46.9 mg, 80% for sunlight (20 h, procedure A); 42.2 mg, 72% yield for blue-light (procedure B).

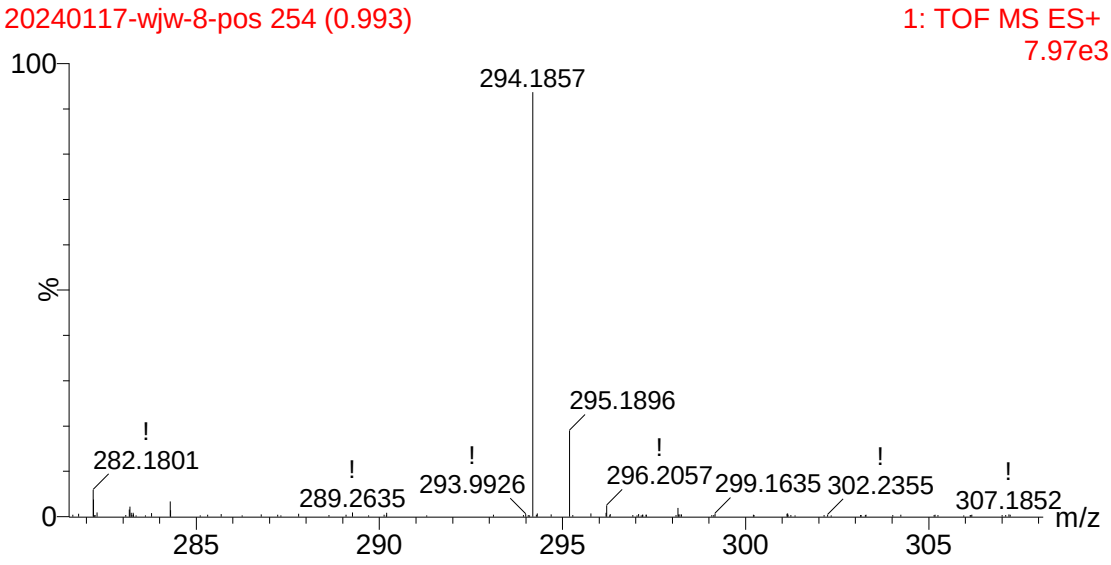
R_f = 0.61 (PE: EtOAc = 5: 1).

M. p. 114 – 116 °C.

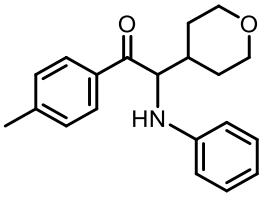
^{1}H NMR (400 MHz, $CDCl_3$) δ 7.90 (d, J = 8.2 Hz, 2H, ArH), 7.27 (d, J = 8.2 Hz, 2H, ArH), 7.13 (t, J = 8.2, 1.0 Hz, ArH), 7.75 – 7.63 (m, 3H, ArH), 4.98 (d, J = 5.4 Hz, 1H, CH), 4.69 (s, 1H, NH), 2.41 (s, 3H, CH_3), 2.36 – 2.24 (m, 1H, CH in cyclopentyl), 1.80 – 1.68 (m, 1H, CH in cyclopentyl), 1.67 – 1.35 (m, 7H, CH_2 in cyclopentyl).

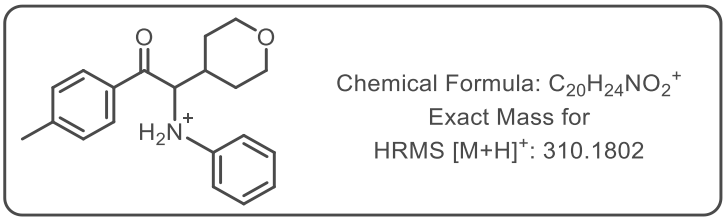
^{13}C NMR (101 MHz, $CDCl_3$) δ 200.90, 148.22, 144.30, 133.40, 129.44, 129.21, 128.45, 117.86, 113.75, 60.68, 43.96, 29.77, 27.48, 25.28, 24.73, 21.65.

HRMS (ESI): Calcd for $C_{20}H_{24}NO^+$ $[M+H]^+$ 294.1852, found 294.1857.



2-(phenylamino)-2-(tetrahydro-2*H*-pyran-4-yl)-1-(*p*-tolyl)ethan-1-one (**4ao**)





Following the general procedure A and B, the product **4ao** was purified by silica gel flash chromatography (PE: EtOAc = 60: 1 as the eluent) to give a colorless crystal, 26.0 mg, 42% for sunlight (10 h, procedure A), 43.3 mg, 70% for sunlight (24 h, procedure A); 32.8 mg, 53% yield for blue-light (procedure B).

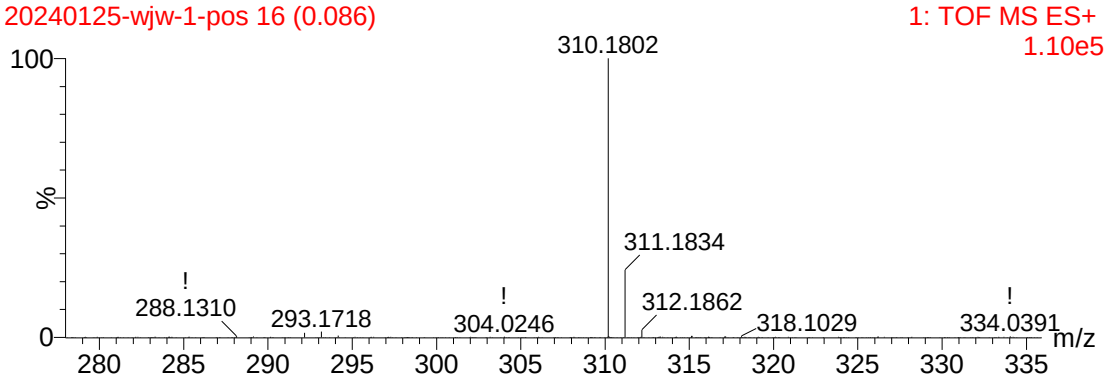
R_f = 0.68 (PE: EtOAc = 5: 1).

M. p. 227 – 229 °C.

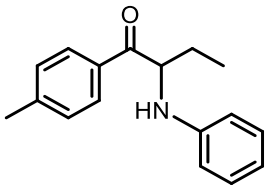
^{1}H NMR (400 MHz, $CDCl_3$) δ 7.87 (d, J = 8.2 Hz, 2H, ArH), 7.28 (d, J = 8.2 Hz, 2H, ArH), 7.14 (t, J = 7.7 Hz, 2H, ArH), 6.75 – 6.65 (m, 3H, ArH), 4.91 (s, 1H, NH), 4.64 (d, J = 6.5 Hz, 1H, CH), 4.00 – 3.87 (m, 2H, O–He in CH_2), 3.29 (m, 2H, O–Ha in CH_2), 2.41 (s, 3H, CH_3), 2.13 – 2.00 (m, 1H, CH), 1.75 – 1.60 (m, 1H, CH), 1.60 – 1.44 (m, 3H, CH).

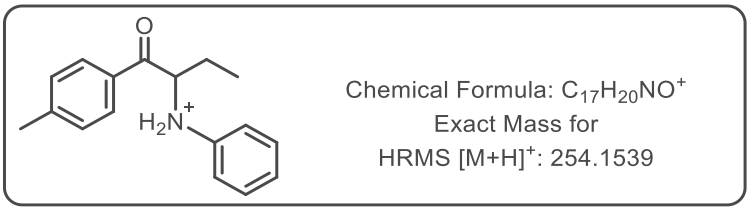
^{13}C NMR (101 MHz, $CDCl_3$) δ 200.2, 147.8, 144.7, 133.4, 129.6, 129.2, 128.4, 118.0, 113.8, 67.8, 67.6, 61.6, 39.4, 30.2, 28.2, 21.6.

HRMS (ESI): Calcd for $C_{20}H_{24}NO_2^+$ $[M+H]^+$ 310.1802, found 310.1802.



2-(phenylamino)-1-(*p*-tolyl)butan-1-one (**4ap**)





Following the general procedure A and B, the product **4ap** was purified by silica gel flash chromatography (PE: EtOAc = 60: 1 as the eluent) to give a colorless crystal, 10.1 mg, 20% for sunlight (10 h, procedure A), 26.3 mg, 52% for sunlight (20 h, procedure A); 18.7 mg, 37% yield for blue-light (procedure B).

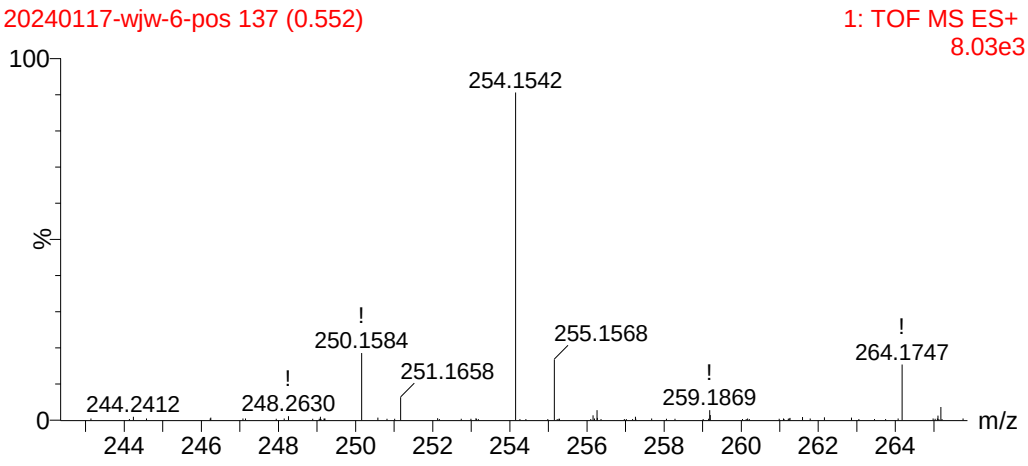
R_f = 0.60 (PE: EtOAc = 5: 1).

M. p. 63 – 65 °C.

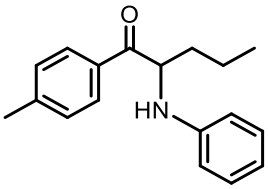
^{1}H NMR (400 MHz, $CDCl_3$) δ 7.89 (d, J = 8.2 Hz, 2H, ArH), 7.28 (d, J = 8.1 Hz, 2H, ArH), 7.16 (t, J = 8.1 Hz, 2H, ArH), 6.73 – 6.65 (m, 3H, ArH), 5.04 (t, J = 5.3 Hz, 1H, CH), 4.74 (s, 1H, NH), 2.41 (s, 3H, CH_3), 2.06 (dqd, J = 14.8, 7.4, 5.3 Hz, 1H, 1H in **CH_2**CH_3), 1.73 (dqd, J = 14.8, 7.4, 5.3 Hz, 1H, 1H in **CH_2**CH_3), 0.88 (t, J = 7.4 Hz, 3H, CH_2**CH_3**).

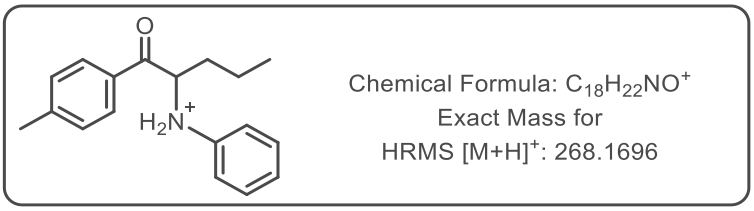
^{13}C NMR (101 MHz, $CDCl_3$) δ 199.9, 147.0, 144.4, 132.6, 129.5, 129.3, 128.4, 117.6, 113.5, 58.4, 25.9, 21.6, 9.1.

HRMS (ESI): Calcd for $C_{17}H_{20}NO^+$ $[M+H]^+$ 254.1539, found 254.1542.



2-(phenylamino)-1-(*p*-tolyl)pentan-1-one (**4aq**)





Following the general procedure A and B, the product **4aq** was purified by silica gel flash chromatography (PE: EtOAc = 60: 1 as the eluent) to give a colorless crystal, 14.4 mg, 27% for sunlight (10 h, procedure A), 33.6 mg, 63% for sunlight (20 h, procedure A); 23.0 mg, 43% yield for blue-light (procedure B).

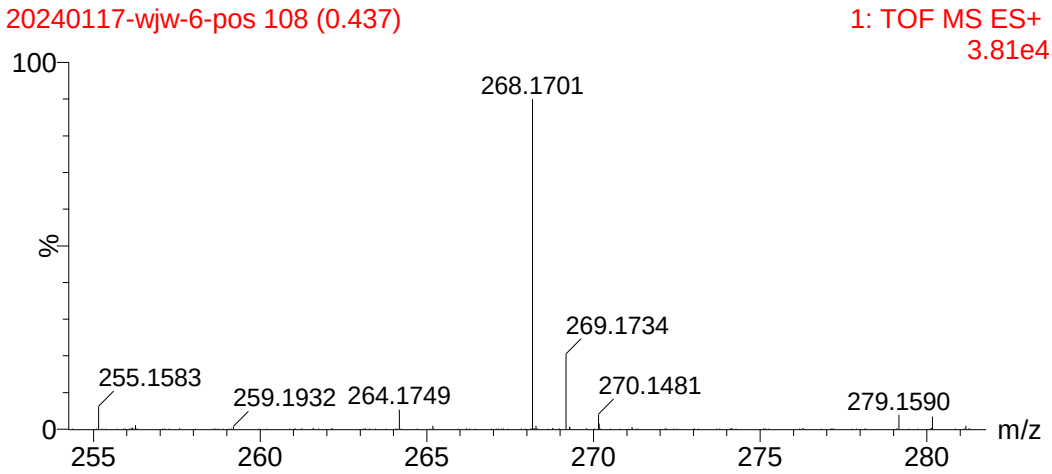
R_f = 0.61 (PE: EtOAc = 5: 1).

M. p. 65 – 67 °C.

^{1}H NMR (400 MHz, $CDCl_3$)) δ 7.90 (d, J = 8.1 Hz, 2H, ArH), 7.28 (d, J = 8.1 Hz, 2H, ArH), 7.15 (t, J = 7.9 Hz, 2H, ArH), 6.75 – 6.62 (m, 3H, ArH), 5.05 (dd, J = 6.6, 4.8 Hz, 1H, CH), 4.66 (s, 1H, NH), 2.41 (s, 3H, Ar**CH_3**), 2.01 – 1.86 (m, 1H, 1H in **CH_2**CH_2), 1.71 – 1.60 (m, 1H, 1H in **CH_2**CH_2), 1.53 – 1.29 (m, 2H, **CH_2**CH_3), 0.87 (t, J = 7.3 Hz, 3H, CH_2**CH_3**).

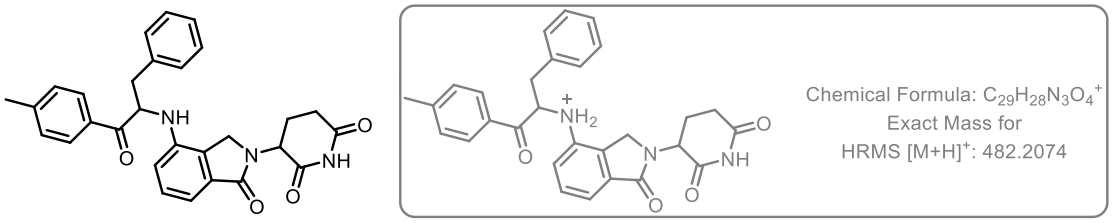
^{13}C NMR (101 MHz, $CDCl_3$) δ 200.3, 147.2, 144.4, 132.7, 129.5, 129.3, 128.4, 117.7, 113.5, 57.6, 35.5, 21.6, 18.50, 14.0.

HRMS (ESI): Calcd for $C_{18}H_{22}NO^+$ $[M+H]^+$ 268.1696, found 168.1701.



3-(1-oxo-4-((1-oxo-3-phenyl-1-(p-tolyl)propan-2-yl)amino)isoindolin-2-yl)piperidine-2,6-dione (**4as**)

Following the general procedure C and D, the product **4as** was obtained by silica gel flash chromatography (PE: EtOAc = 2: 1 to 1: 1 as the eluent) to give a colorless crystal. 48 mg, 50% for sunlight (20 h; procedure C); 50 mg, 52% yield for blue-light (procedure D).

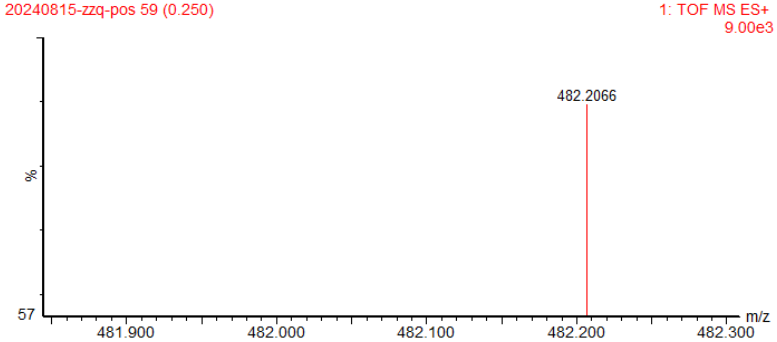


M. p = 208 – 210 °C. R_f = 0.16 (PE : EtOAc = 1:1)

^{1}H NMR (400 MHz, $CDCl_3$) δ 8.60 (s, 0.6H in CONHCO), 8.58 (s, 0.4H in CONHCO), 7.91 (dd, J = 8.4, 2.3 Hz, 2H, Ar H), 7.31 (d, J = 8.0 Hz, 2H, Ar H), 7.25 – 7.15 (m, 5H, Ar H), 7.07 (dd, J = 7.4, 2.0 Hz, 1H, Ar H), 7.02 (dd, J = 7.4, 2.0 Hz, 1H, Ar H), 6.71 (dd, J = 6.0, 2.8 Hz, 0.6H in Ar H), 6.66 (dd, J = 5.6, 3.4 Hz, 0.4H in Ar H), 5.39 (hep, J = 6.0 Hz, 1H, $NHCHCH_2$), 5.23 (dd, J = 13.2, 5.2 Hz, 0.6H in $NHCHCH_2$), 5.17 (dd, J = 13.2, 5.2 Hz, 0.4H in $NHCHCH_2$), 4.88 (d, J = 8.4 Hz, 0.4H, NH), 4.68 (d, J = 8.4 Hz, 0.6H, NH), 4.27 (d, J = 6.4 Hz, 0.4H in $NCHCH_2CH_2$), 4.23 (d, J = 6.4 Hz, 0.6H in $NCHCH_2CH_2$), 4.15 (d, J = 15.8 Hz, 0.6H in $NHCHCH_2$), 4.06 (d, J = 15.8 Hz, 0.4H in $NHCHCH_2$), 3.30 (dd, J = 14.0, 5.0 Hz, 1H in CH_2N), 3.04 (ddd, J = 14.0, 8.2, 6.6 Hz, 1H in CH_2N), 2.83 – 2.64 (m, 2H, $NCHCH_2CH_2$), 2.44 (s, 3H, CH_3), 2.26 – 2.13 (m, 1H in $NCHCH_2CH_2$), 2.06 (ddt, J = 10.0, 5.0, 2.7 Hz, 1H in $NCHCH_2CH_2$).

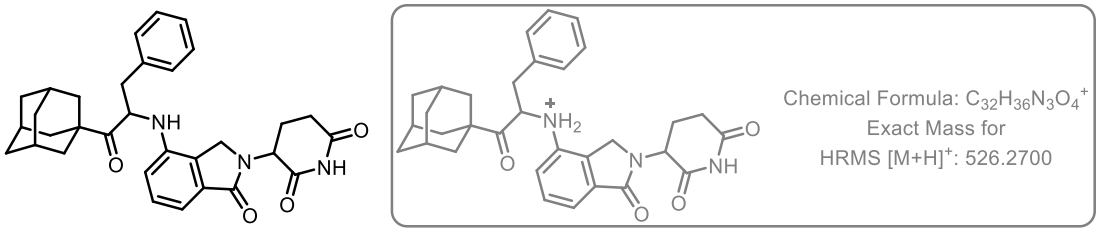
^{13}C NMR (101 MHz, $CDCl_3$) δ 198.8, 171.6, 169.9, 169.8, 145.0, 141.6, 136.4, 136.1, 132.2, 129.7, 129.6, 129.45, 129.40, 128.6, 128.4, 128.3, 127.6, 127.4, 127.0, 126.9, 114.1, 113.8, 113.6, 113.3, 58.8, 51.61, 45.0, 44.9, 38.7, 31.4, 23.3, 21.7. Numbers underlines are peaks from diastereoisomers.

HRMS (ESI$^+$): Calcd for $C_{29}H_{24}N_3O_4^+$ $[M+H]^+$ 482.2074, found 482.2066.



3-(4-((1-(adamantan-1-yl)-1-oxo-3-phenylpropan-2-yl)amino)-1-oxoisoindolin-2-yl)piperidine-2,6-dione (**4at**)

Following the general procedure C and D, the product **4at** was obtained by silica gel flash chromatography (PE: EtOAc = 2: 1 to 1: 1 as the eluent) to give a colorless oil. 48 mg, 50% for sunlight (20 h; procedure C); 50 mg, 52% yield for blue-light (procedure D).

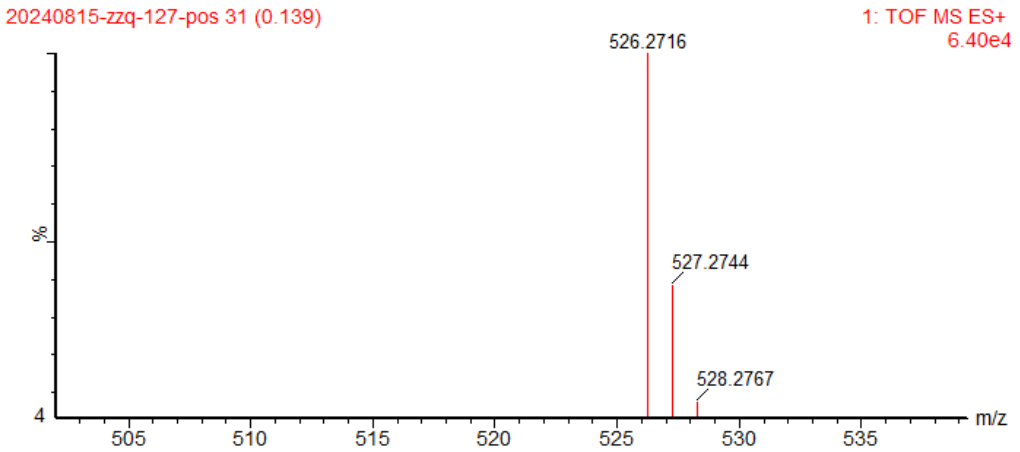


R_f = 0.13 (PE : EtOAc = 1 : 1).

^{1}H NMR (400 MHz, $CDCl_3$) δ 8.00 (s, 0.6H in CONHCO), 7.99 (s, 0.4H in CONHCO), 7.35 – 7.26 (m, 3H, ArH), 7.26 – 7.18 (m, 2H, ArH), 7.15 (dt, *J* = 6.7, 2.7 Hz, 2H, ArH), 6.75 – 6.69 (m, 1H, ArH), 5.20 (td, *J* = 13.1, 5.1 Hz, 1H, $NHCHCH_2$), 4.86 – 4.78 (m, 1H, NH), 4.21 (dd, *J* = 15.5, 8.2 Hz, 1H, $CHCH_2CH_2$), 4.06 (d, *J* = 15.5 Hz, 0.4H in $NHCHCH_2$), 4.00 (d, *J* = 15.5 Hz, 0.6H in $NHCHCH_2$), 3.95 (dd, *J* = 9.7, 3.9 Hz, 1H in $NHCHCH_2$), 3.08 (dd, *J* = 13.6, 5.8 Hz, 1H, in NCH_2), 2.97 – 2.89 (m, 1H, in NCH_2), 2.95 – 2.89 (m, 1H in $NCHCH_2CH_2$), 2.88 – 2.76 (m, 1H in $NCHCH_2CH_2$), 2.41 – 2.25 (m, 1H in $NCHCH_2CH_2$), 2.18 (tdd, *J* = 8.3, 6.5, 3.9 Hz, 1H in $NCHCH_2CH_2$), 2.01 (s, 3H, three CH in Adamantane), 1.79 – 1.61 (m, 12H, six CH_2 in Adamantane).

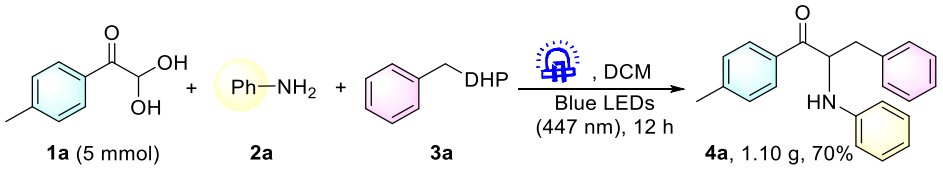
^{13}C NMR (101 MHz, $CDCl_3$) δ 214.5, 171.0, 169.7, 169.5, 141.5, 136.7, 132.2, 129.65, 129.56, 128.6, 128.5, 127.5, 127.0, 114.7, 114.1, 113.8, 57.2, 56.9, 51.7, 46.0, 44.8, 38.5, 37.83, 37.76, 36.3, 31.5, 27.6, 23.5. Numbers underlines are peaks from diastereoisomers.

HRMS (ESI$^+$): Calcd for $C_{32}H_{36}N3O_4^+$ $[M+H]^+$ 526.2700, found 526.2720.

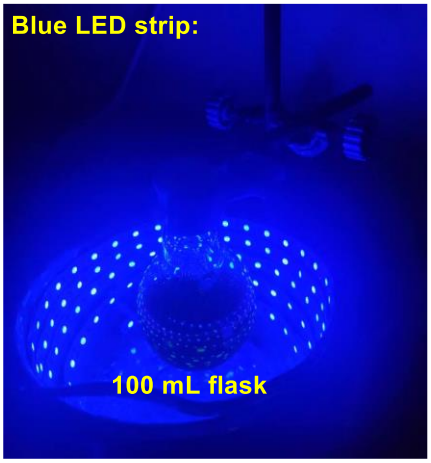


5. Gram-Scale synthesis of **4a** and **4ai** (for scheme 3)

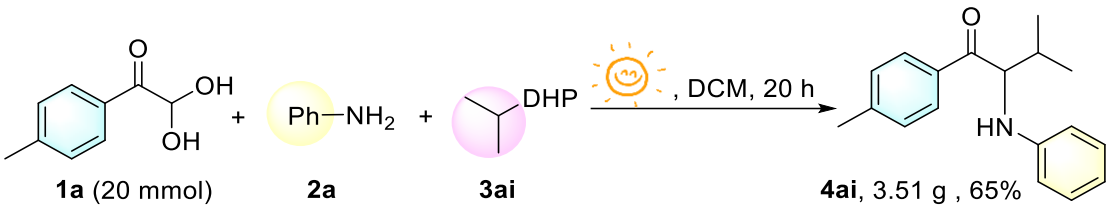
5.1 5 mmol scale synthesis of **4a** with blue-LEDs



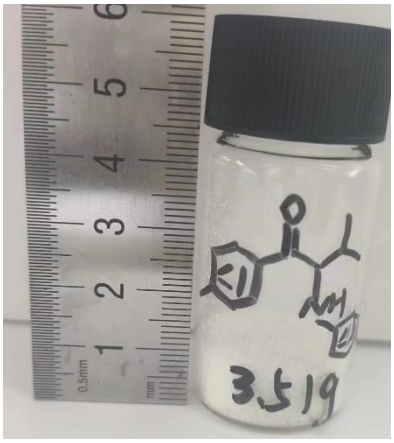
In a 100 mL round-bottom flask, 2,2-dihydroxy-1-(*p*-tolyl)ethan-1-one (**1a** 1.0 equiv, 5 mmol, 830.1 mg), aniline (**2a** 1.0 equiv, 5 mmol, 465 μL), 4-benzyl DHP (**3a**, 1.5 eq, 0.75 mmol, 3.43 g) were dissolved in DCM (25 mL), and then the vial was stirred for 12 h with irradiation of 1W blue light (λ = 447 nm). After the reaction, the solvent was evaporated in vacuo, and the residue was purified by column chromatography on silica gel to afford the desired products **4a** (1.10 g, 70%).



5.2 20 mmol scale synthesis of **4ai** with sunlight

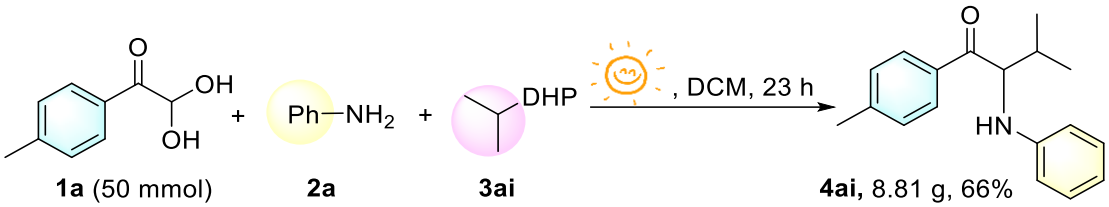


In a 250 mL round-bottom flask, 2,2-dihydroxy-1-(*p*-tolyl)ethan-1-one (**1a** 1.0 equiv, 20 mmol, 3.32 g), aniline (**2a** 1.0 equiv, 20 mmol, 1.86 mL), 4-isopropyl DHP (**3ai**, 1.5 eq, 30 mmol, 8.85 g) were dissolved in DCM (125 mL), and then the vial was stirred for 20 h with sunlight (about 4 days from 10: 00 am to 16: 00 pm; the temperature was around from 17 °C to 25 °C and humility was from 10% to 30%). After the reaction, the solvent was evaporated in vacuo, and the residue was purified by column chromatography on silica gel to afford the desired products **4ai** (3.51 g, 65%).

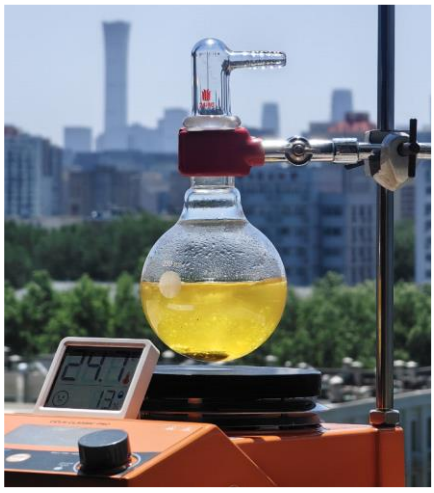


Open-air sunlight induced reactions were performed outside direct at 10:00 am – 16:00 pm (temperature: 17 – 25 °C; humidity: 10 – 30%).

5.3 50 mmol scale synthesis of **4ai** with sunlight



In a 250 mL round-bottom flask, 2,2-dihydroxy-1-(*p*-tolyl)ethan-1-one (**1a** 1.0 equiv, 50 mmol, 8.30 g), aniline (**2a** 1.0 equiv, 50 mmol, 4.65 mL), 4-isopropyl DHP (**3ai**, 1.5 eq, 75 mmol, 22.13 g) were dissolved in DCM (100 mL), and then the vial was stirred for 23 h with sunlight (about 4 days from 10: 00 am to 16: 00 pm; the temperature was around from 17 °C to 25 °C and humility was from 10% to 30%). After the reaction, the solvent was evaporated in vacuo, and the residue was purified by column chromatography on silica gel to afford the desired products **4ai** (8.81 g, 66%).



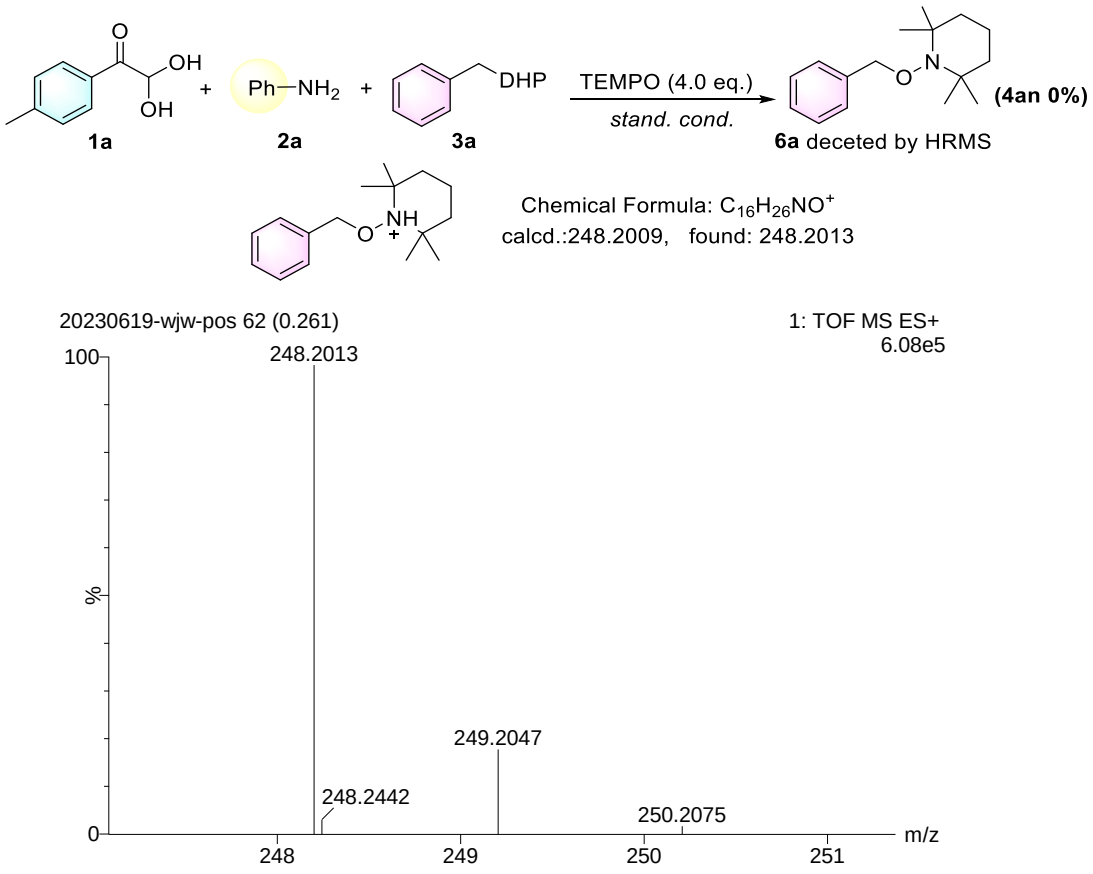
Open-air sunlight induced reactions were performed outside direct at 10:00 am – 16:00 pm (temperature: 17 – 25 ºC; humidity: 10 – 30%).

6. Mechanistic studies

6.1 TEMPO trapping experiment (for scheme 4a)

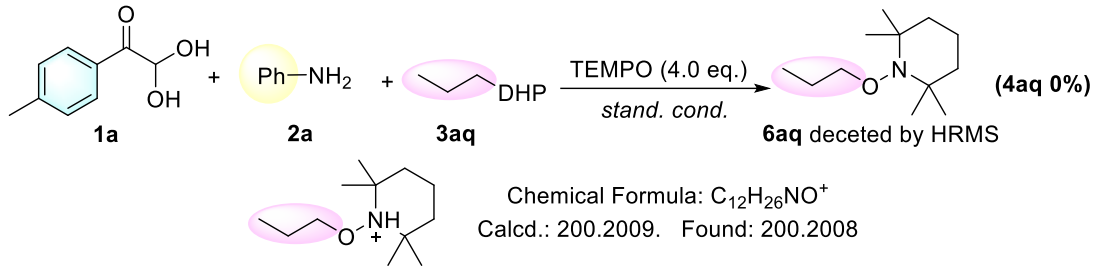
6.1.1 Trapping benzyl radical

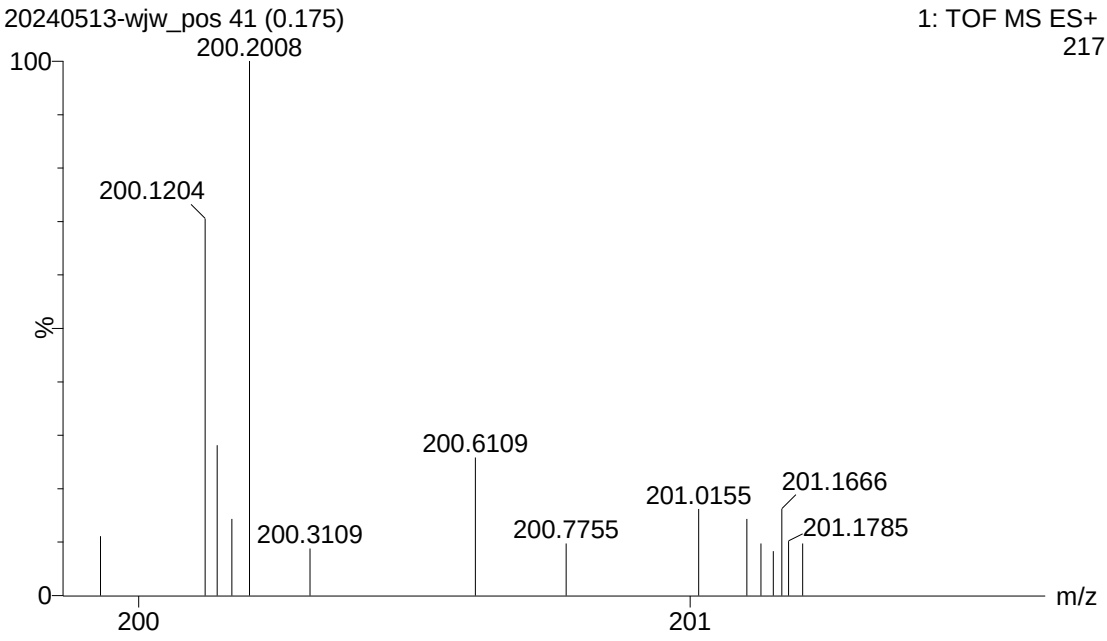
In a 3 mL screw-top glass bottle, **1a** (1.0 equiv, 0.2 mmol), **2a** (1.0 equiv, 0.2 mmol), **3a** (1.5 equiv, 0.3 mmol) were dissolved in DCM (1 mL). Afterward, 2,2,6,6-Tetramethylpiperidinooxy (TEMPO, 4.0 equiv) was added in the mixture. then the vial was stirred for 8 h with irradiation of 1W blue light (λ = 447 nm). **4a** was not observed by TLC. To understand the reaction mechanism more deeply, we employed high-resolution mass spectrometry (HRMS) to analyze the reaction solution of the model reaction. The result of HRMS showed that the coupling product, 1-(benzyloxy)-2,2,6,6-tetramethylpiperidine from the benzyl radical and TEMPO, was generated in current condition.



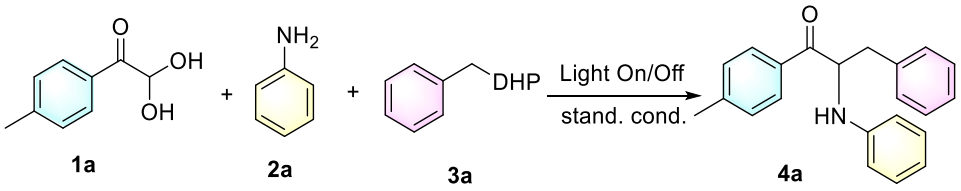
6.1.2 Trapping primary carbon radical

In a 3 mL screw-top glass bottle, **1a** (1.0 equiv, 0.2 mmol), **2a** (1.0 equiv, 0.2 mmol), **3aq** (1.5 equiv, 0.3 mmol) were dissolved in DCM (1 mL). Afterward, 2,2,6,6-Tetramethylpiperidinooxy (TEMPO, 4.0 equiv) was added in the mixture. then the vial was stirred for 8 h with irradiation of 1W blue light (λ = 447 nm). **4aq** was not observed by TLC. To understand the reaction mechanism more deeply, we employed high-resolution mass spectrometry (HRMS) to analyze the reaction solution of the model reaction. The result of HRMS showed that the coupling product, 2,2,6,6-tetramethyl-1-propoxypiperidine from the propyl radical and TEMPO, was generated in current condition.

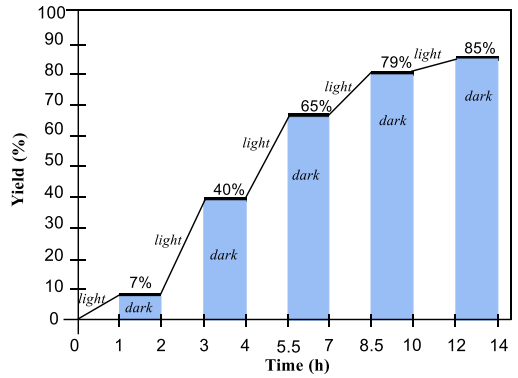




6.2 Light on/off experiment (for scheme 4b)



In a 3 mL screw-top glass vial, **1a** (1.0 equiv, 0.1 mmol, 33.2 mg), **2a** (1.0 equiv, 0.1 mmol, 18 μL), **3a** (1.5 equiv, 0.15 mmol, 103.2 mg) and 1,3,5- trimethoxybenzene (0.1 mmol, 16.8 mg) were dissolved in DCM (1 mL). The vial was stirred in dark condition for 1 h. Subsequently, the yield of **4a** was obtained by ^{1}H NMR and the LEDs were turned on. After 1 hour, the LEDs were turned off, and the yield of **4a** was assessed once more by ^{1}H NMR. The steps above were repeated for one time. The vial was stirred in dark condition for 1.5 h. The yield of **4a** was obtained by ^{1}H NMR and the LEDs were turned on. After 1.5 hour, the LEDs were turned off, and the yield of **4a** was assessed once more by ^{1}H NMR. The steps above were repeated for one time. At last, the vial was stirred in dark condition for 2 h. The yield of **4a** was obtained by ^{1}H NMR and the LEDs were turned on. After 2 h, the LEDs were turned off, and the yield of **4a** was assessed once more by ^{1}H NMR.

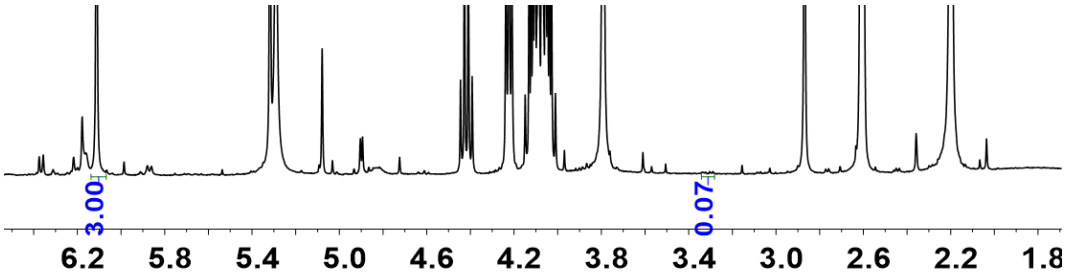


The NMR yields are as follows：

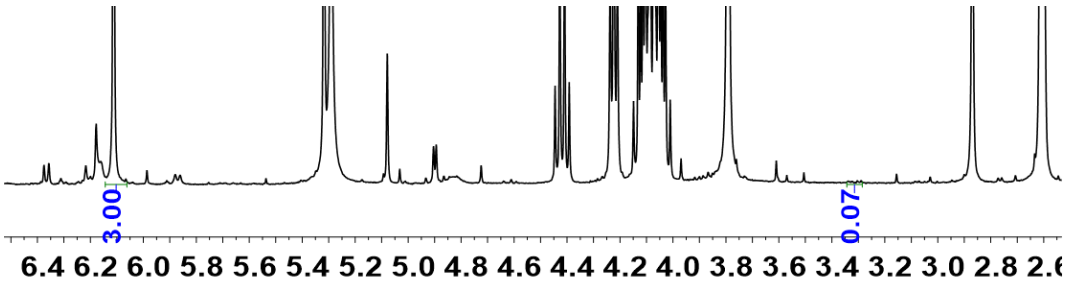
Time	Integration	NMR yield
1 h	0.07	7%
2 h	0.07	7%
3 h	0.40	40%
4 h	0.40	40%
5.5 h	0.65	65%
7 h	0.65	65%
8.5 h	0.79	79%
10 h	0.79	79%
12 h	0.85	85%
14 h	0.85	85%

Integrations of at each time were listed as follows:

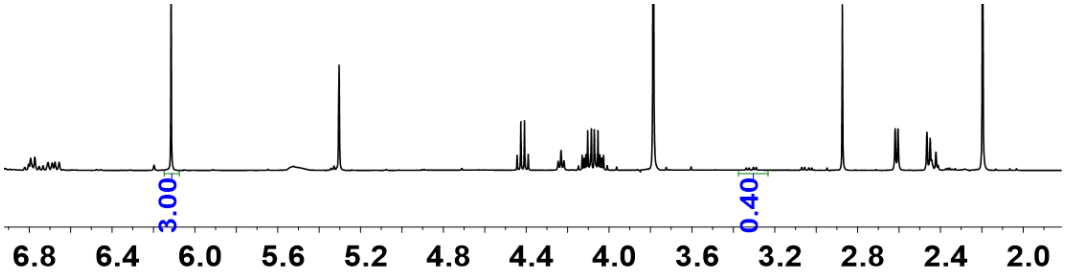
1 h



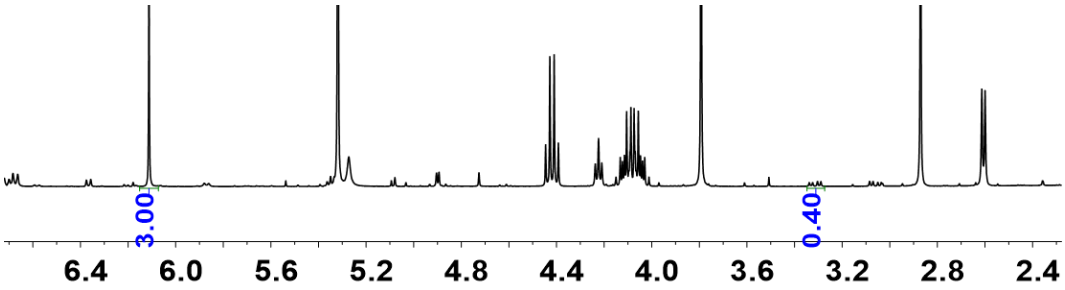
2 h



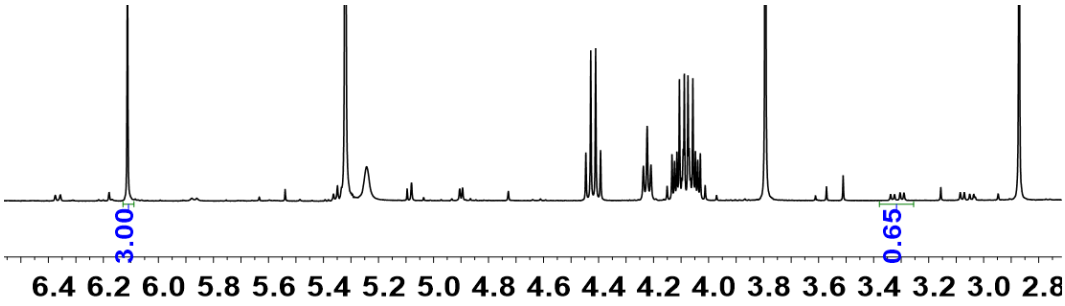
3 h



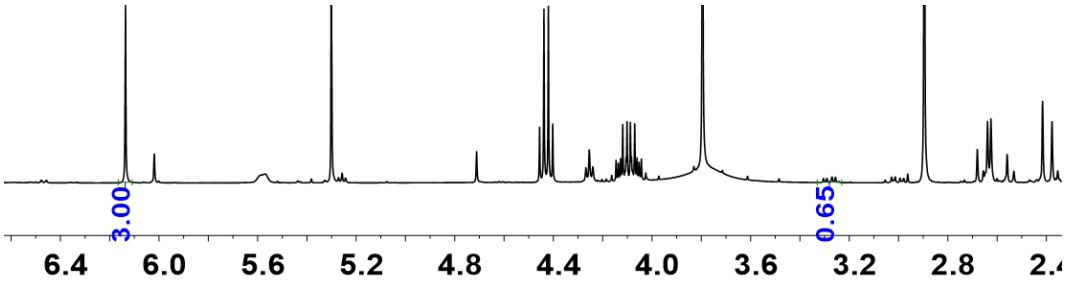
4 h



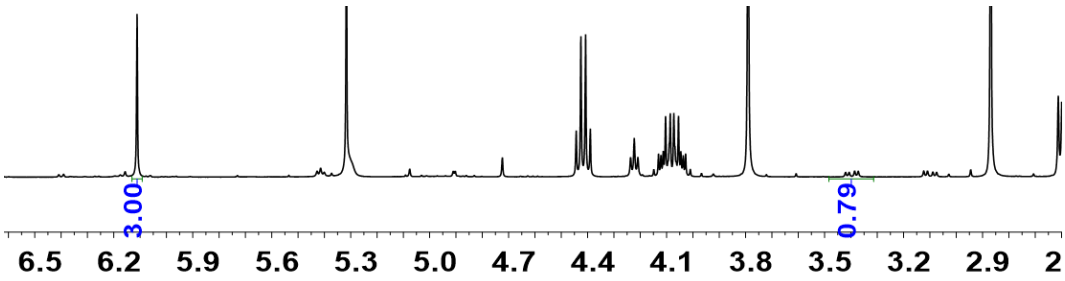
5.5 h



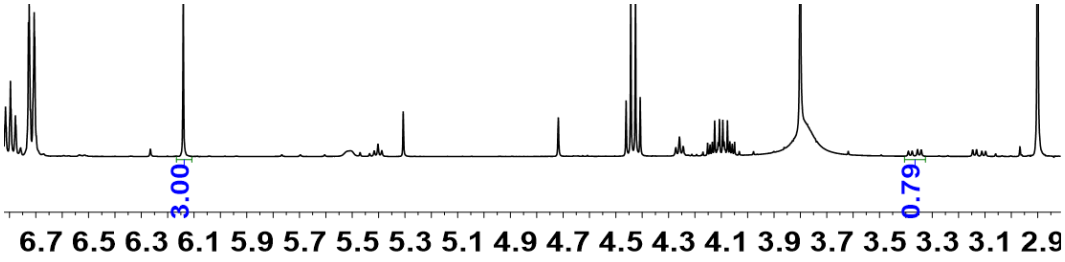
7 h



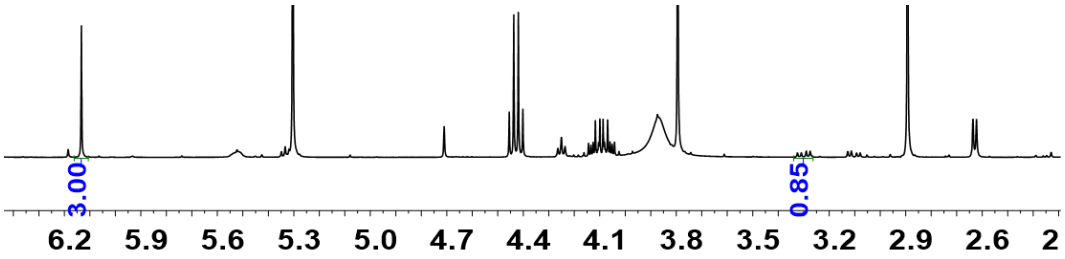
8.5 h



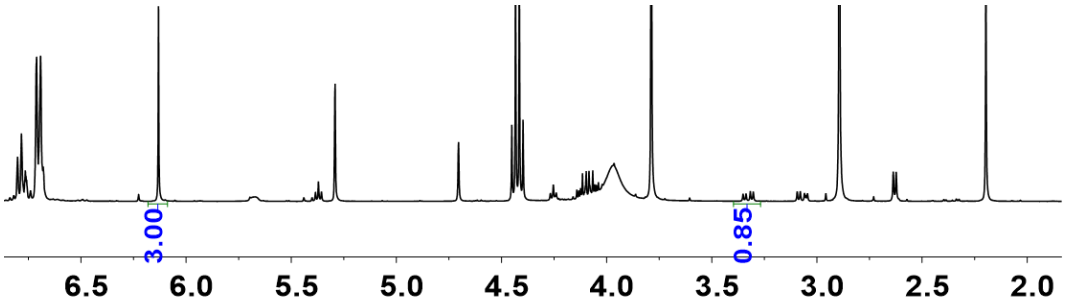
10 h



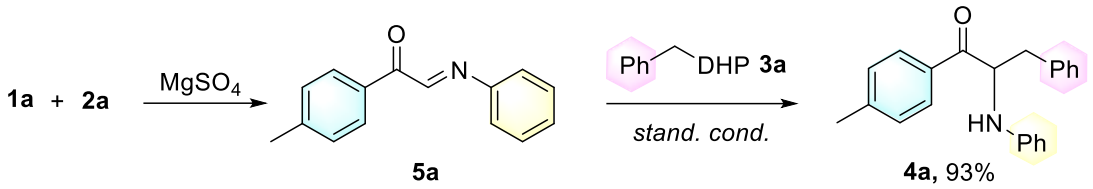
12 h


3.00
0.85
6.2
5.9
5.6
5.3
5.0
4.7
4.4
4.1
3.8
3.5
3.2
2.9
2.6
2

14 h


3.00
0.85
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0

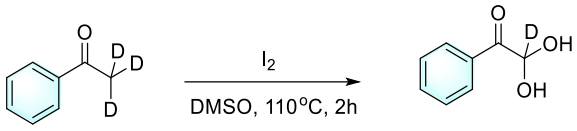
6.3 Intermediate probing (for scheme 4c)



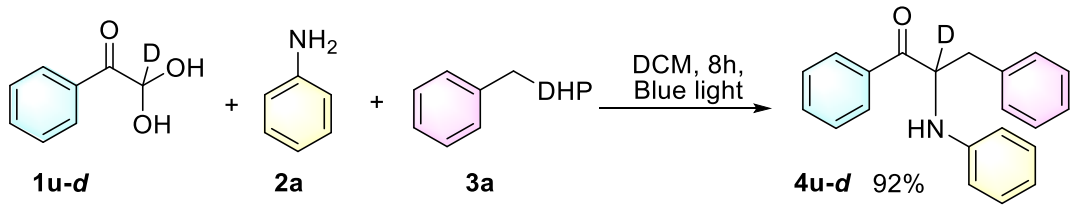
1a (332 mg, 2 mmol) , **2a** (180 μL, 2 mmol) and anhydrous $MgSO_4$ (0.24 g, 2 mmol) was added to dichloromethane (DCM) (5 mL). The reaction system was stirred at room temperature for 2 h. After filtration, the organic solvent was evaporated in vacuo. The residue was recrystallized from anhydrous ethanol to give the pure **5a**.

5a (44.6 mg, 0.2 mmol) and **3a** (103.5 mg, 0.3 mmol) was dissolved in dichloromethane (DCM) (1 mL). The vial was stirred for 8 h with irradiation of 1W blue light (λ = 447 nm). The solvent was evaporated in vacuo, and the residue was purified by column chromatography on silica gel with PE/EtOAc as eluent to afford the desired products **4a** (58.6 mg, 93%).

6.4 Isotope tracing experiments (for scheme 4d)



Acetophenone-d_3 (1.0 equiv, 1.17 mL, 10 mmol) and I_2 (0.5 equiv, 1 g, 5 mmol) was dissolved in dimethyl sulfoxide (10 mL). The reaction system was stirred at 120 °C for 2 h. After the acetophenone-d_3 entirely consumed, the mixture was cooled to room temperature. 10 mL saturated $Na_2S_2O_3$ solution was added to the reaction. The reaction mixture was extracted with EtOAc (2 mL × 3), washed the organic phase with saturated brine (2 mL) and H_2O (2 mL). The organic phase was dried over anhydrous Na_2SO_4. The organic solvent was evaporated under reduced pressure. The crude product was recrystallized with PE and EtOAc to give a colorless solid **1u-*d*** (1.62 g, 51 %). M. p. 64 – 65 ℃, CAS Registry Number: 81027-63-6.[3]



In a 3 mL screw-top glass vial, **1u-*d*** (1.0 equiv, 0.2 mmol, 30.4 mg), **2a** (1.0 equiv, 0.2 mmol, 18 μL), **3a** (1.5 equiv.0.3 mmol, 103.5 mg) were dissolved in DCM (1 mL). The vial was stirred for 8 h with irradiation of 1W blue light (λ = 447 nm). The solvent was evaporated in vacuo, and the residue was purified by column chromatography on silica gel with PE: EtOAc = 80:1 as eluent to afford the desired products **4u-*d*** (58.1 mg, 92 %) as a colorless crystal. R_f = 0.35 (PE:EA = 5: 1), M. p. 90 – 92 ℃.

1,3-diphenyl-2- (phenylamino) propan-1-one-2-*d* **(4u-*d*)**

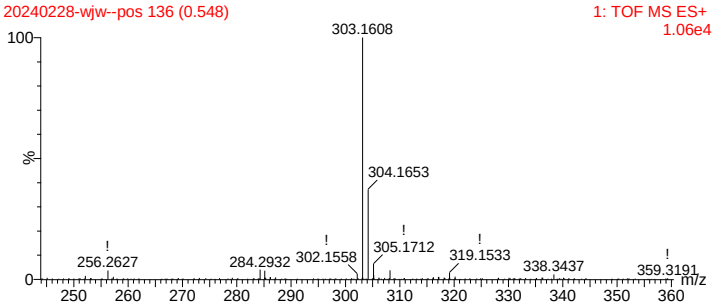
^{1}H NMR (400 MHz, $CDCl_3$) δ 7.94 (d, J = 7.4 Hz, 2H, ArH) , 7.57 (t, J = 7.4 Hz, 1H, ArH) , 7.46 (t, J = 7.4 Hz, 2H, ArH) , 7.22 – 7.13 (m, 5H, ArH) , 7.04 (dd, J = 7.5, 1.6 Hz, 2H, ArH) , 6.71 (t, J = 7.5 Hz, 1H, ArH) , 6.64 (d, J = 8.4 Hz, 2H, ArH) , 4.60 (s, 1H, NH) , 3.27 (d, J = 13.8 Hz, 1H, 1H in CH_2) , 3.02 (d, J = 13.8 Hz, 1H, 1H in CH_2) .

^{13}C NMR (101 MHz, $CDCl_3$) δ 199.6, 146.55, 136.5, 135.4, 133.6, 129.5, 129.45, 128.9,

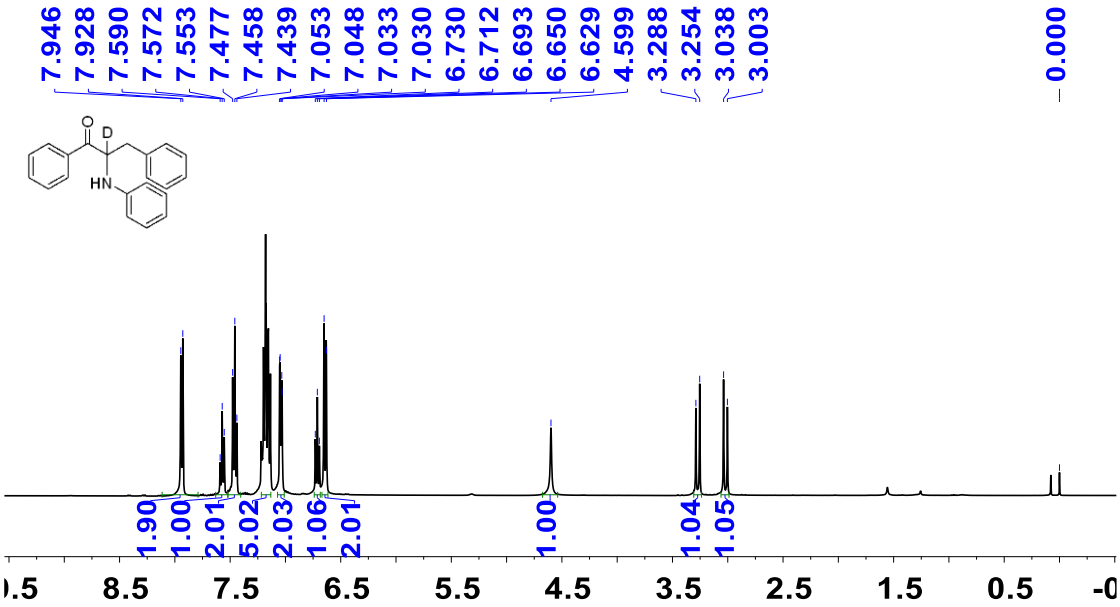
[3] P. Wang, W.-J. Tao, X.-L. Sun, S. Liao and Y. Tang, *J. Am. Chem. Soc.*, 2013, **135**, 16849-16852.

128.5, 128.4, 126.9, 118.1, 113.8, 58.7 (t (1:1:1), $^{1}J_{D\text{-}C}$ = 20.78 Hz), 38.65.

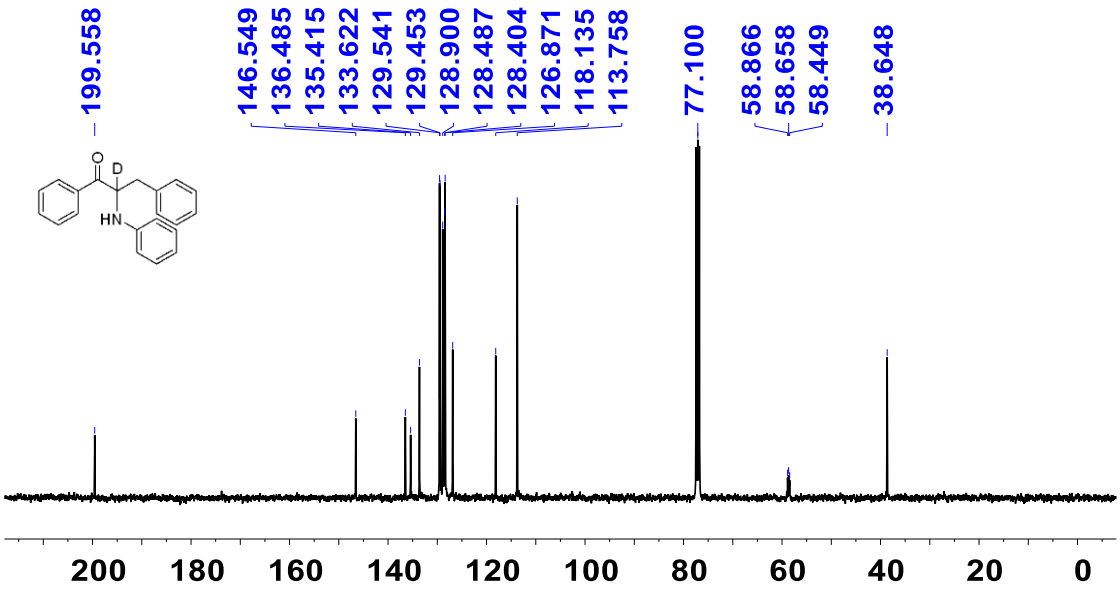
HRMS (ESI) : Calcd for $C_{21}H_{19}DNO^{+}$ [M+H] $^{+}$ m/z: 303.1602, found 303.1608.



^{1}H NMR (400 MHz, $CDCl_3$) of **4u-*d***



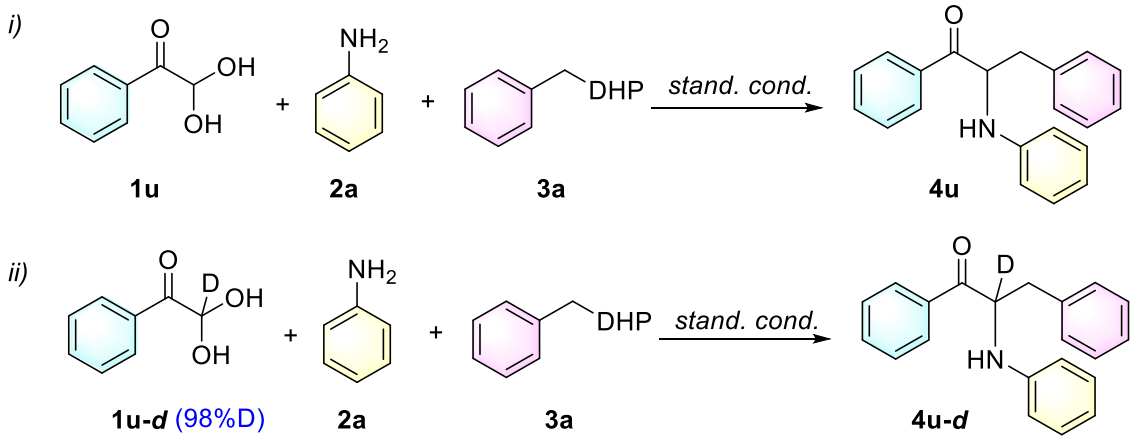
^{13}C NMR (101 MHz, $CDCl_3$) of **4u-*d***



6.5 Kinetic isotope effect studies (for scheme 4d)

6.5.1 The competition ratio of reactions between **1s** and **1u-*d***. (for scheme 4d-i)

The kinetic isotope effect was studied by performing two parallel reactions to test the competition ratio between reactions with **1u** and **1u-*d***.



For **1u**: To a 3 mL screw-top glass vial was added **1u** (1.0 equiv, 0.2 mmol, 30.2 mg), **2a** (1.0 equiv, 0.2 mmol, 18 μL), **3a** (1.5 equiv, 0.3 mmol, 103.2 mg), 1,3,5-trimethoxybenzene (0.1 mmol, 16.8 mg) and DCM (1 mL). The vial was stirred with irradiation of 1W blue light (λ = 447 nm). 50 μL of the reaction system was pipetted from the vial every 30 min to test the system ^{1}H NMR. The organic solvent, CH_2Cl_2, was evaporated in vacuo and then the residue was dissolved in 0.5 mL $CDCl_3$. ^{1}H NMR yield was determined using 1,3,5-trimethoxybenzene as internal standard.

For **1u-*d***: To a 3 mL screw-top glass vial was added **1u-*d*** (1.0 equiv, 0.2 mmol, 30.4 mg), **2a** (1.0 equiv, 0.2 mmol, 18 μL), **3a** (1.5 equiv, 0.3 mmol, 103.2 mg), 1,3,5-trimethoxybenzene (0.1 mmol, 16.8 mg) and DCM (1 mL). The vial was stirred with irradiation of 1W blue light (λ = 447 nm). 50 μL of the reaction system was pipetted from the vial every 30 min to test the system ^{1}H NMR. The organic solvent, CH_2Cl_2, was evaporated in vacuo and then the residue was dissolved in 0.5 mL $CDCl_3$. ^{1}H NMR yield was determined using 1,3,5-trimethoxybenzene as internal standard.

Table S1. Kinetic isotope effeft studies of triple component reaction of **4u** and **4u-*d***

Entry	Time (h)	**4u** yield (%)	**4u-*d*** yield (%)
1	0.5 h	4	6
2	1.0 h	10	11.5
3	1.5 h	17	23
4	2.0 h	22	31
5	2.5 h	26	36

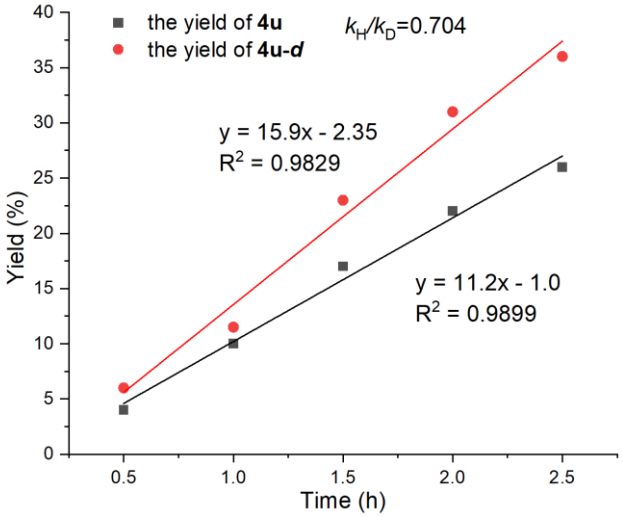


Figure S1. Kinetic isotope effect studies of triple component reaction of **4u** and **4u-*d***

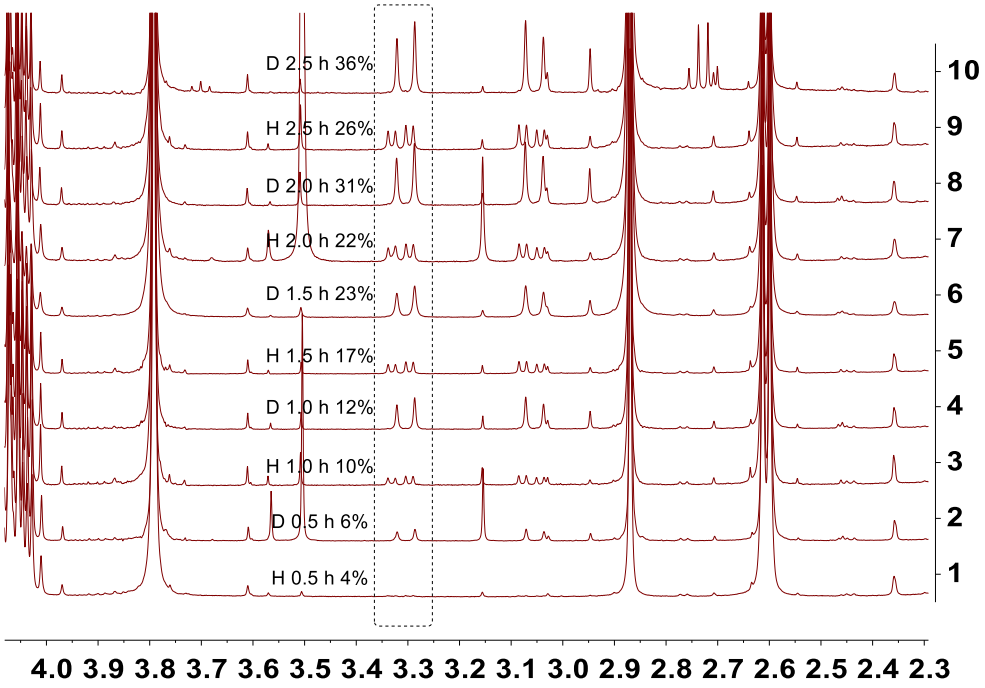
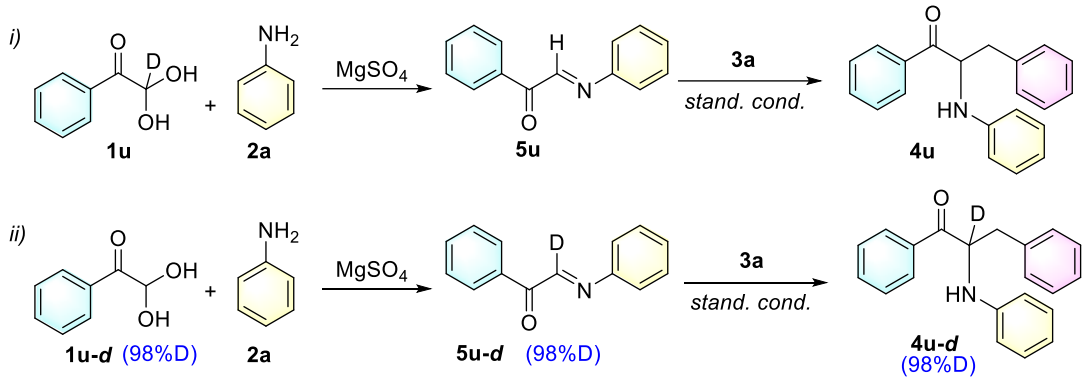


Figure S2. Yield of **4u**/**4u-*d*** for three-component reactions

6.5.2 Kinetic isotope effect studies with the competition ratio between reactions with **5u** and **5u-*d***. (for scheme 4d-ii)

The kinetic isotope effect was studied by conducting two parallel reactions to test the competition ratio between reactions with **5u** and **5u-*d***.



For **5u**: To a 3 mL screw-top glass vial was added **1u** (1.0 equiv, 0.2 mmol, 30.2 mg), **2a** (1.0 equiv, 0.2 mmol, 18 μL) and anhydrous $MgSO_4$ (20% mmol, 4.8 mg) and DCM (1 mL). The system was stirred for 1 h. Then, **3a** (1.5 equiv, 0.3 mmol, 103.2 mg) and 1,3,5- trimethoxybenzene (0.1 mmol, 16.8 mg) were added in the vial. The vial was stirred with irradiation of 1W blue light (λ = 447 nm). 50 μL of the reaction system was pipetted from the vial every 30 min. The organic solvent was evaporated in vacuo and then the residue was dissolved in 0.5 mL $CDCl_3$. ^{1}H NMR yield was determined using 1,3,5-trimethoxybenzene as internal standard.

For **5u-*d***: To a 3 mL screw-top glass vial was added **1u-*d*** (1.0 equiv, 0.2 mmol, 30.4 mg), **2a** (1.0 equiv, 0.2 mmol, 18 μL), anhydrous $MgSO_4$ (20% mmol, 4.8 mg) and DCM (1 mL). The system was stirred for 1 h. Then, **3a** (1.5 equiv, 0.3 mmol, 103.2 mg) and 1,3,5- trimethoxybenzene (0.1 mmol, 16.8 mg) were added in the vial. The vial was stirred with irradiation of 1W blue light (λ = 447 nm). 50 μL of the reaction system was pipetted from the vial every 30 min. The organic solvent was evaporated in vacuo and then the residue was dissolved in 0.5 mL $CDCl_3$. ^{1}H NMR yield was determined using 1,3,5-trimethoxybenzene as internal standard.

Table S2. Kinetic isotope effect studies of two - component reaction of **4u** and **4u-*d***

Entry	Time (h)	**4u** yield (%)	**4u-*d*** yield (%)
1	0.5 h	7	9
2	1.0 h	15	17
3	1.5 h	19	22
4	2.0 h	24	29
5	2.5 h	30	37

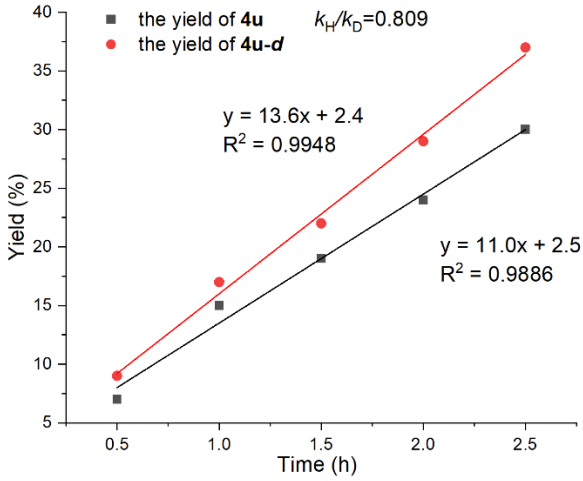


Figure S3. Kinetic isotope effect studies of two - component reaction of **4u** and **4u-*d***

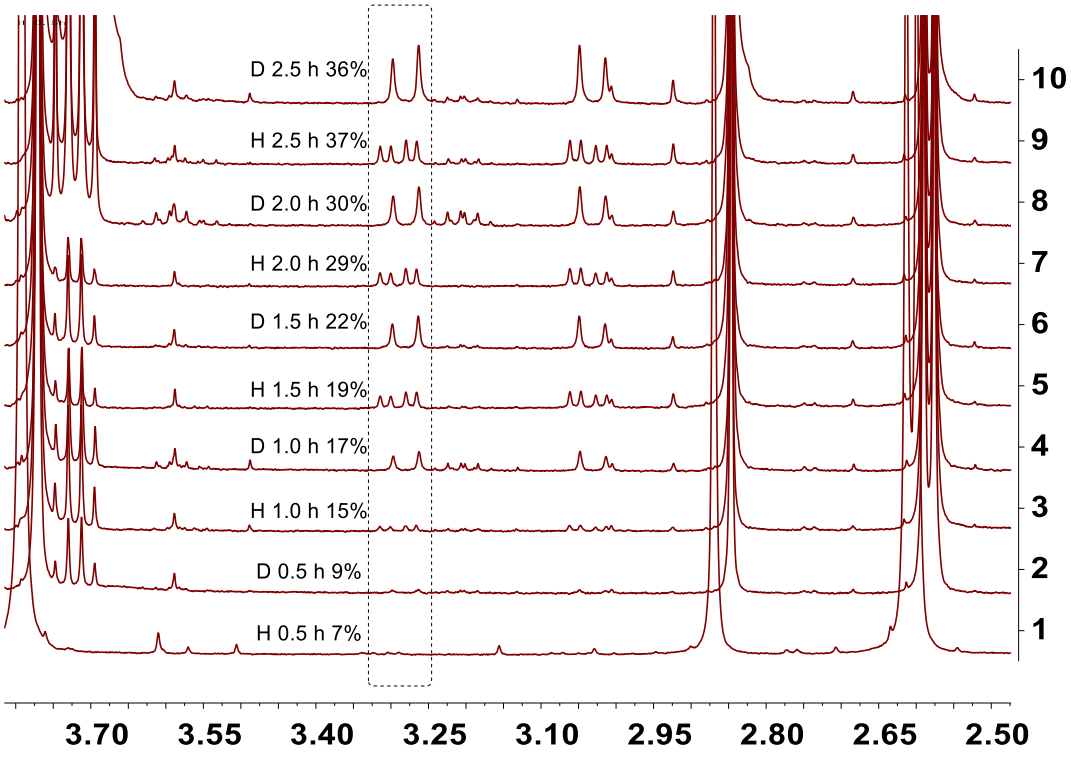
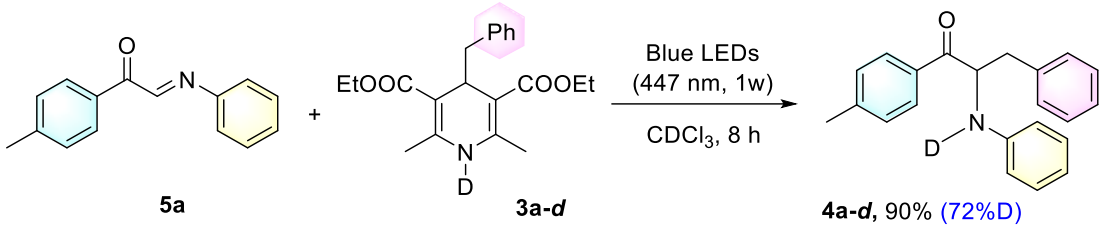


Figure S4. Yield of **4u**/**4u-*d*** for two-component reactions

6.6 Isotope labelling experiment with **3a-*d*** (for scheme 4e)

3a-*d* were synthesized from previous work.[4]



In a 3 mL screw-top glass vial, **5a** (44.6 mg, 0.2 mmol) and **3a-*d*** (103.2 mg, 0.3 mmol) was dissolved in $CDCl_3$ (1 mL). The vial was stirred for 8 h with irradiation of 1W blue light (λ = 447 nm). The solvent was then removed in vacuo. The **4a-*d*** was obtained in yield of 90% with 72% deuterium-labelled from the ^1H NMR yield.

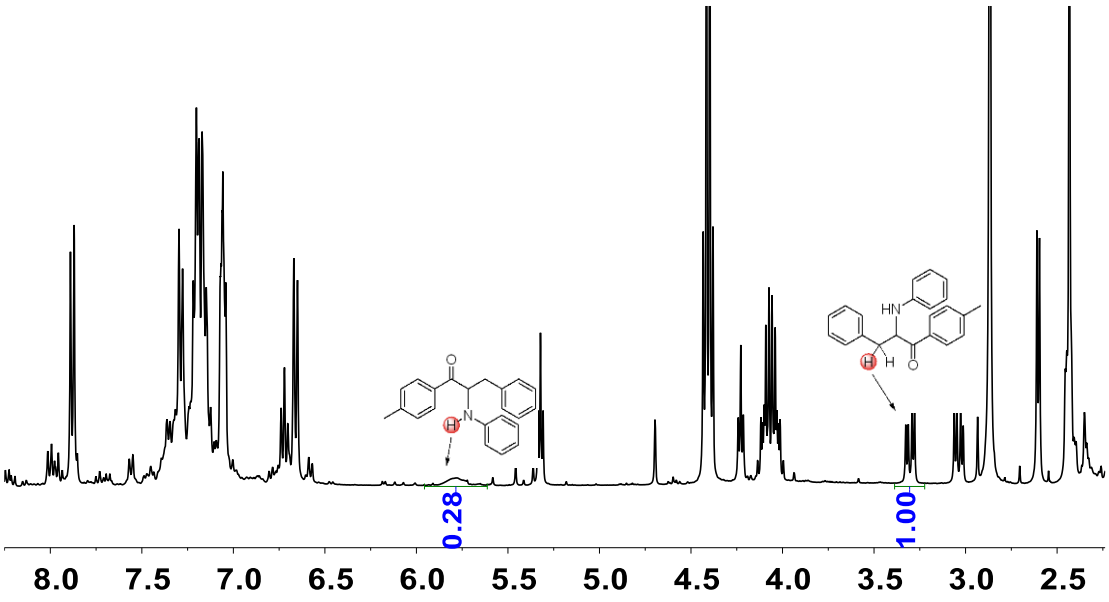


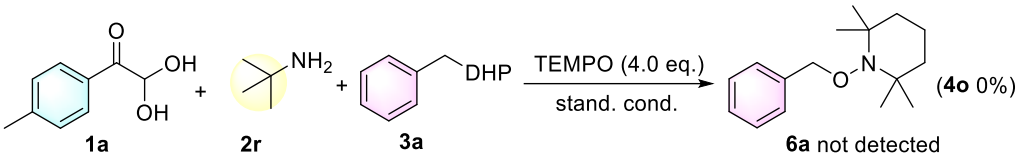
Fig. S5 ^1H NMR spectrum of 3a-*d* (400 MHz, $CDCl_3$)

[4] Z. Liang, K. Lv, S. Zhou, C. Zhu and X. Bao, *Org. Chem. Front*. 2021, **8**, 6499-6507.

6.7 TEMPO trapping experiments with aliphatic amine (for scheme 4f)

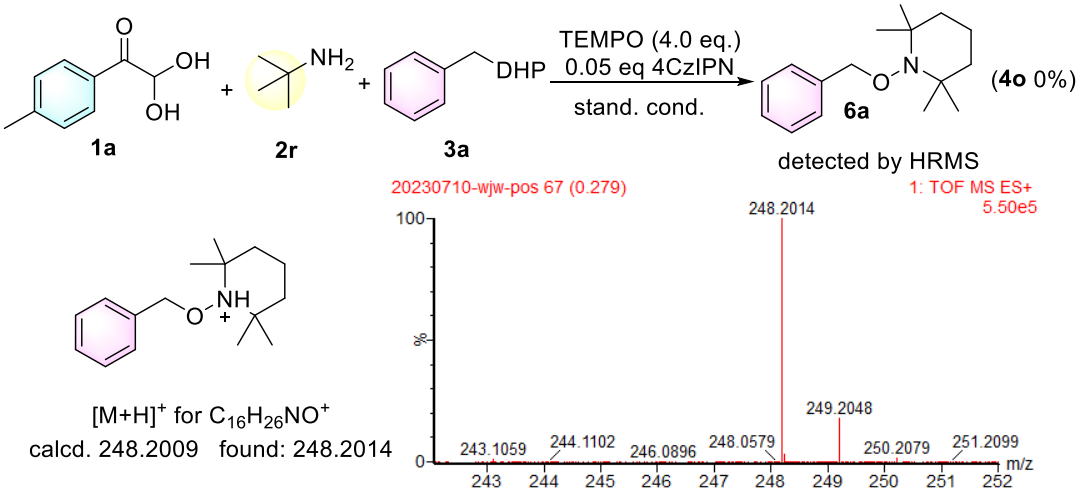
6.7.1 TEMPO trapping experiment of *tert*-butyl amine **2r** without the use of photosensitizer.

In a 3 mL screw-top glass bottle, **1a** (1.0 equiv, 0.2 mmol, 33.2 mg), **2r** (1.0 equiv, 0.2 mmol, 21 μL), **3a** (1.5 equiv, 0.3 mmol, 103.2 mg) were dissolved in DCM (1 mL). 2,2,6,6-Tetramethylpiperidinooxy (TEMPO, 4.0 equiv) was then added into the mixture. The reaction system was stirred for 8 h with irradiation of 1W blue light (λ = 447 nm). **4a** was not observed by TLC. High-resolution mass spectrometry (HRMS) was tested. 1-(Benzyloxy)-2,2,6,6-tetramethylpiperidine (**6a**), the coupling product from the benzyl radical and TEMPO, wasn't detected in HRMS.



6.7.2 TEMPO trapping experiment of *tert*-butyl amine **2r** by using photosensitizer.

In a 3 mL screw-top glass bottle, **1a** (1.0 equiv, 0.2 mmol, 33.2 mg), **2r** (1.0 equiv, 0.2 mmol, 21 μL), **3a** (1.5 equiv, 0.3 mmol, 103.2 mg), 2,4,5,6-tetra(9*H*-carbazol-9-yl)isophthalonitrile (4CzIPN) (0.5% mol, 4 mg) were dissolved in DCM (1 mL).2,2,6,6-Tetramethylpiperidinooxy (TEMPO, 4.0 equiv.) was then added into the mixture. The vial was stirred for 8 h with irradiation of 1W blue light (λ = 447 nm). **4a** was not observed by TLC. High-resolution mass spectrometry (HRMS) indicates that the coupling product, 1-(benzyloxy)-2,2,6,6-tetramethylpiperidine from the benzyl radical and TEMPO, was generated in current condition.



6.8 UV-vis absorption spectra for EDA complex (for Scheme 4g)

UV-vis absorption spectra were measured in a 1 cm path quartz cuvette. The results of each experimental UV-vis absorption spectra are as follows:

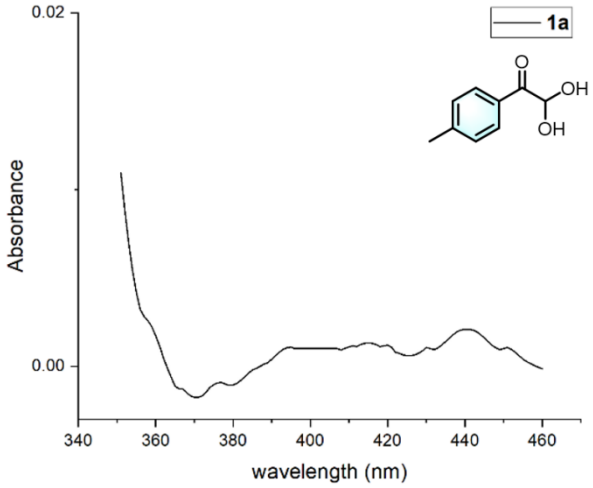


Figure S6. UV-vis absorption spectra of **1a**.

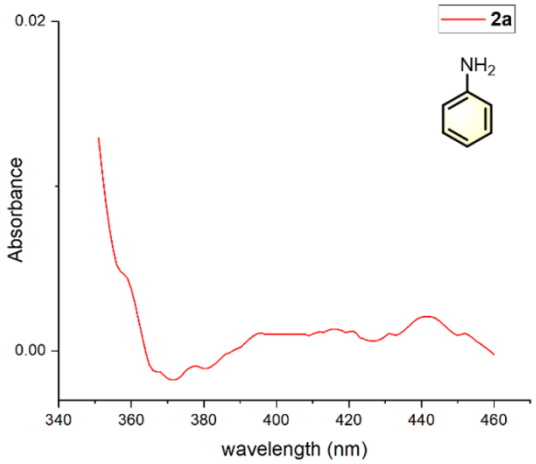


Figure S7. UV-vis absorption spectra of **2a**.

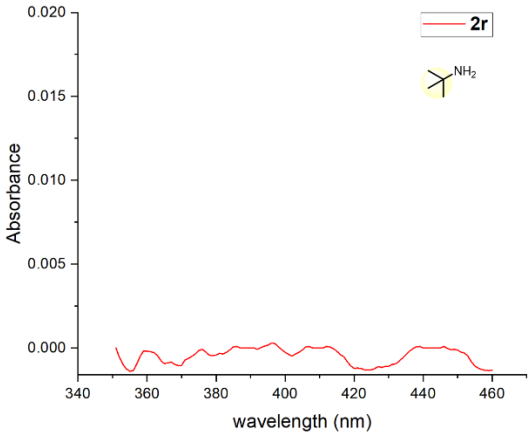


Figure S8. UV-vis absorption spectra of **2r**.

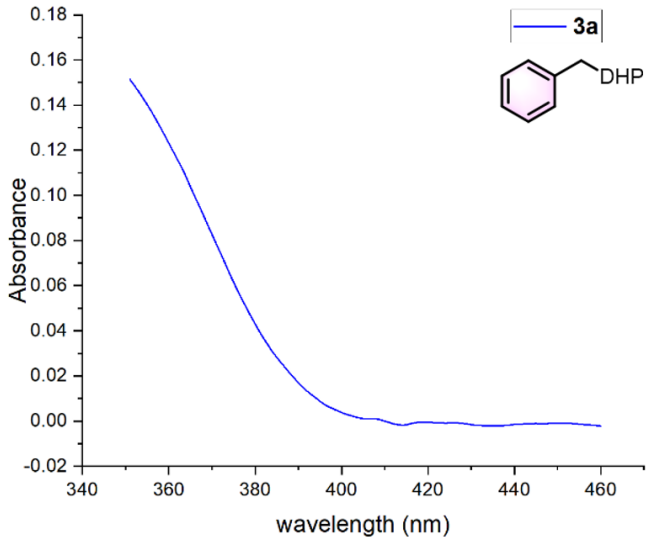


Figure S9. UV-vis absorption spectra of **3a**.

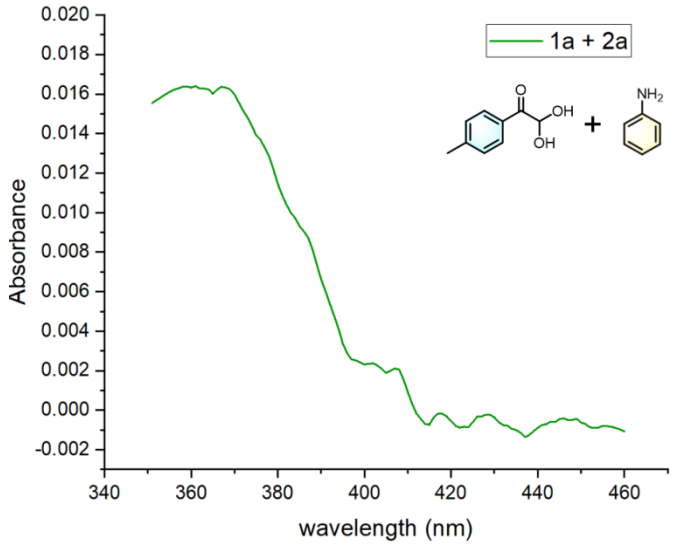


Figure S10. UV-vis absorption spectra of **1a** and **2a**.

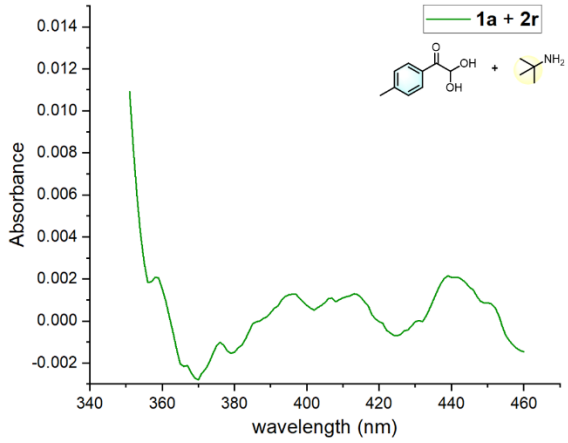


Figure S11. UV-vis absorption spectra of **1a** and **2r** after 1h.

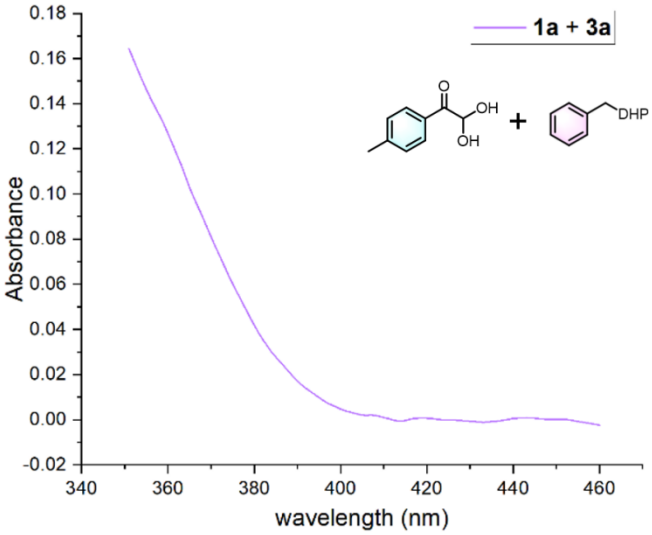


Figure S12. UV-vis absorption spectra of **1a** and **3a**.

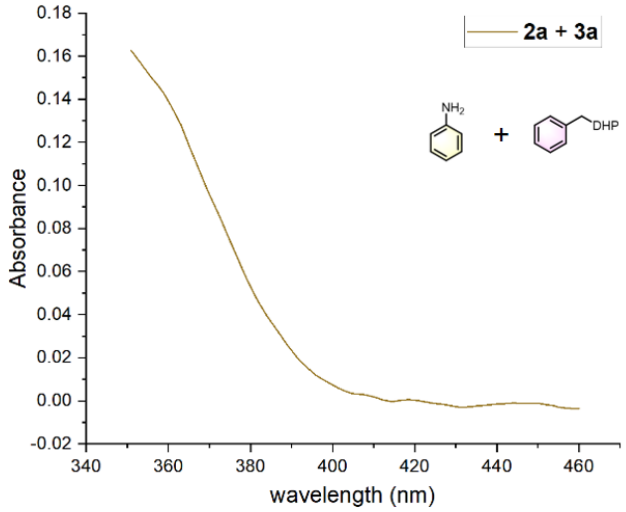


Figure S13. UV-vis absorption spectra of **2a** and **3a**.

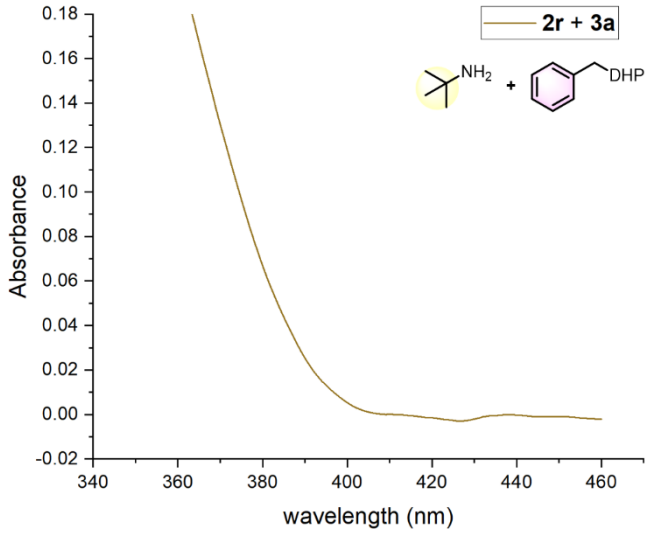


Figure S14. UV-vis absorption spectra of **2r** and **3a**.

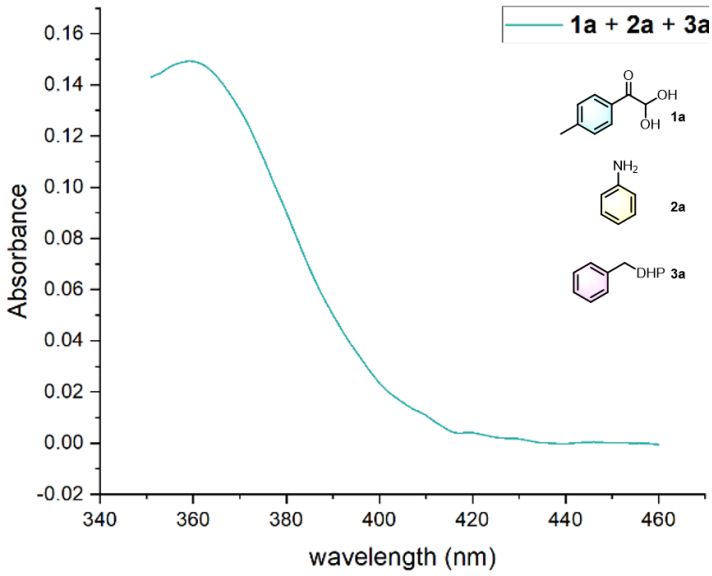


Figure S15. UV-vis absorption spectra of **1a, 2a** and **3a**.

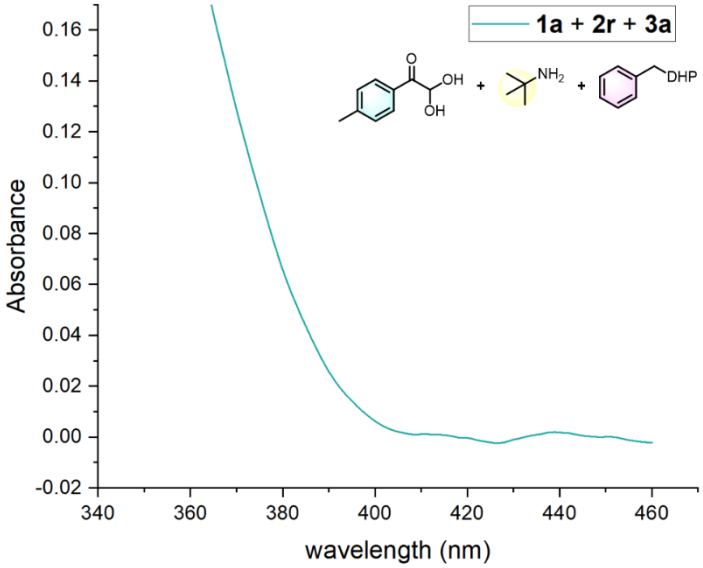


Figure S16. UV absorption spectra of **1a, 2r** and **3a**.

The combined UV-vis spectra are listed as follows:

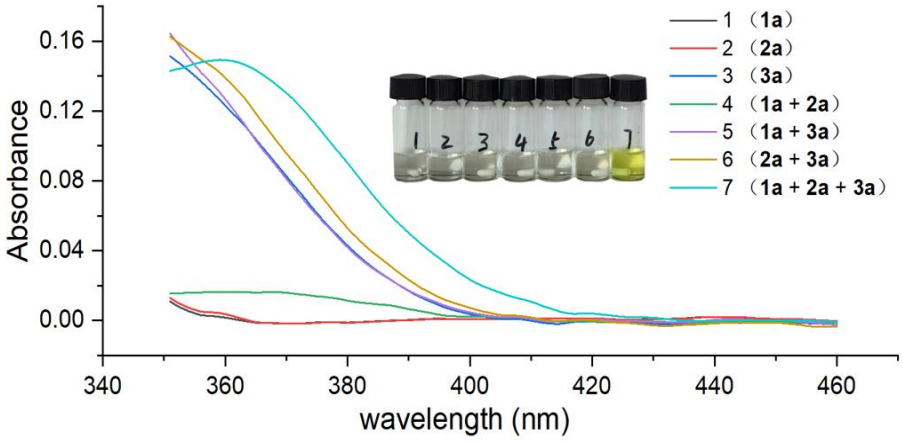


Figure S17. The combined UV-vis spectra of the aniline series.

A bathochromic shift was observed for a mixture of **1a**, **2a** and 4-alkyl-1,4-DHPs **3a** in DCM, which was visibly yellow in color (see Figure S17), whereby direct photoexcitation of 4- alkyl-1,4-DHP derivatives is a plausible pathway.

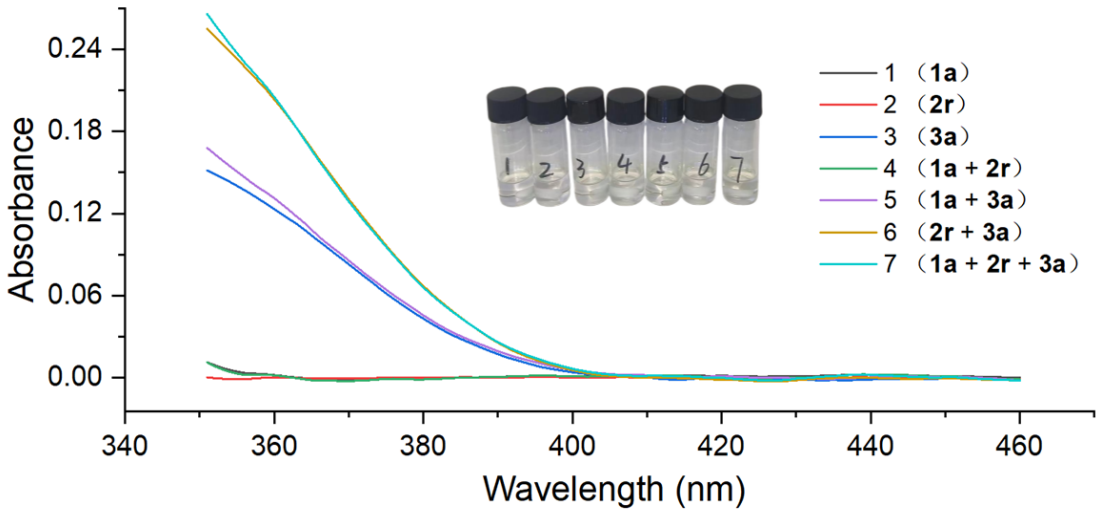


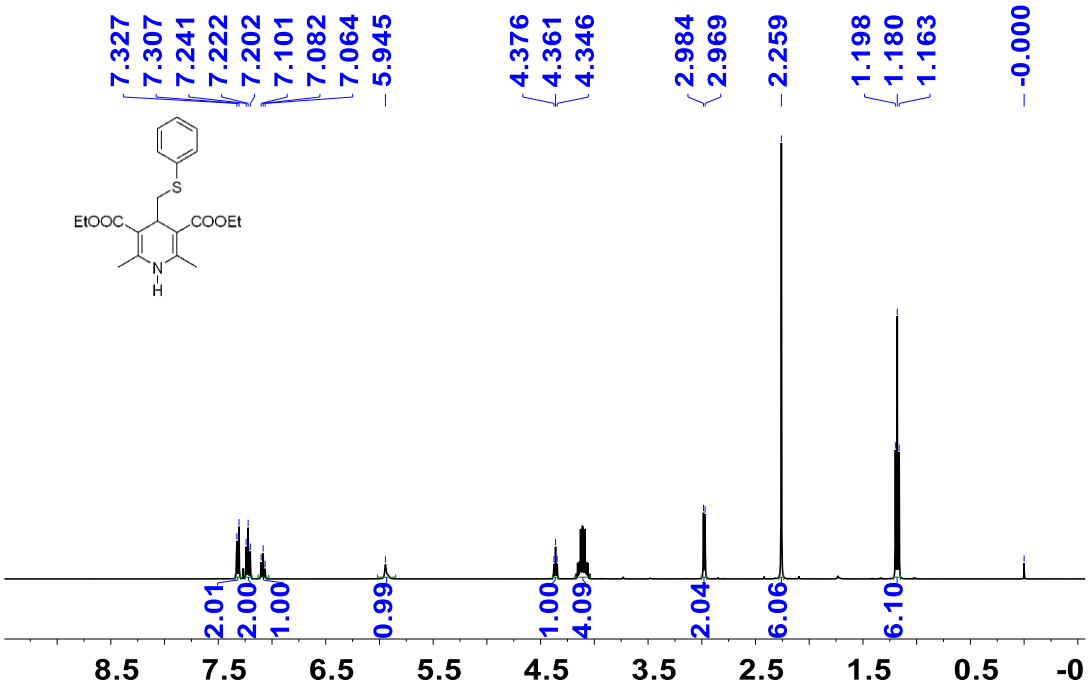
Figure S18. The combined UV-vis spectra of the *tert*-butyl amine series.

No obvious wavelength peak shift was observed, indicating that no electron-donor-acceptor (EDA) complex were generated in the reaction of *tert*-butylamine.

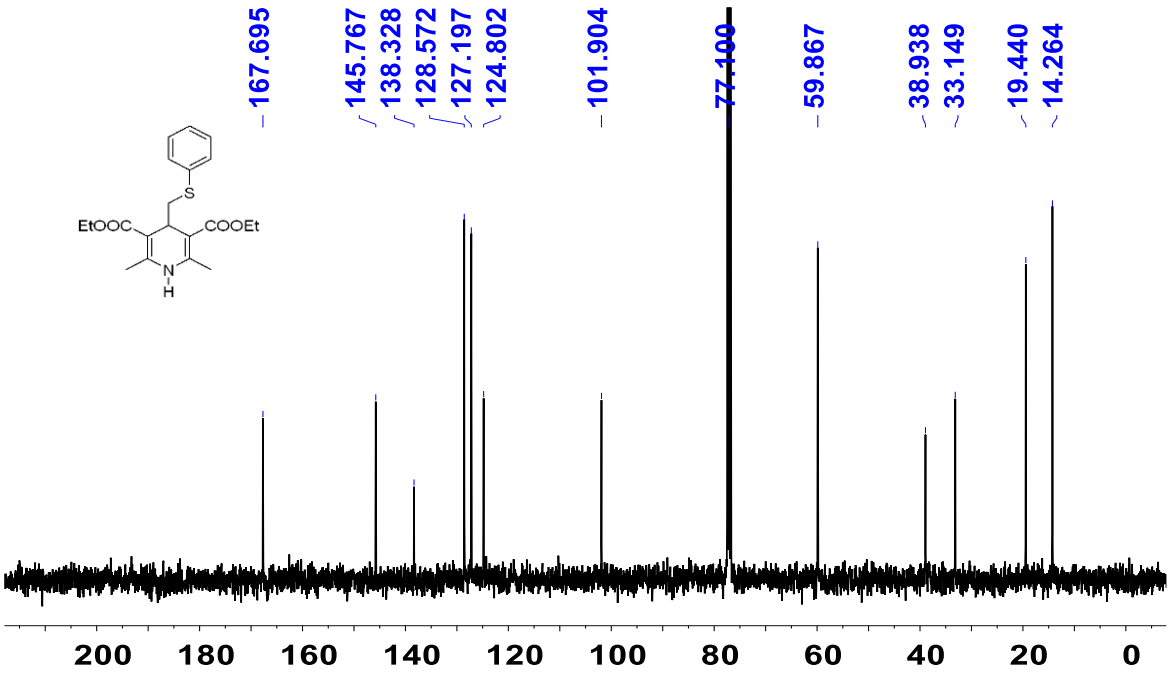
7. All NMR Spectra of 3af and 4

Diethyl 2,6-dimethyl-4-((phenylthio)methyl)-1,4-dihydropyridine-3,5-dicarboxylate (**3af**)

^{1}H NMR (400 MHz, $CDCl_3$) of **3af**

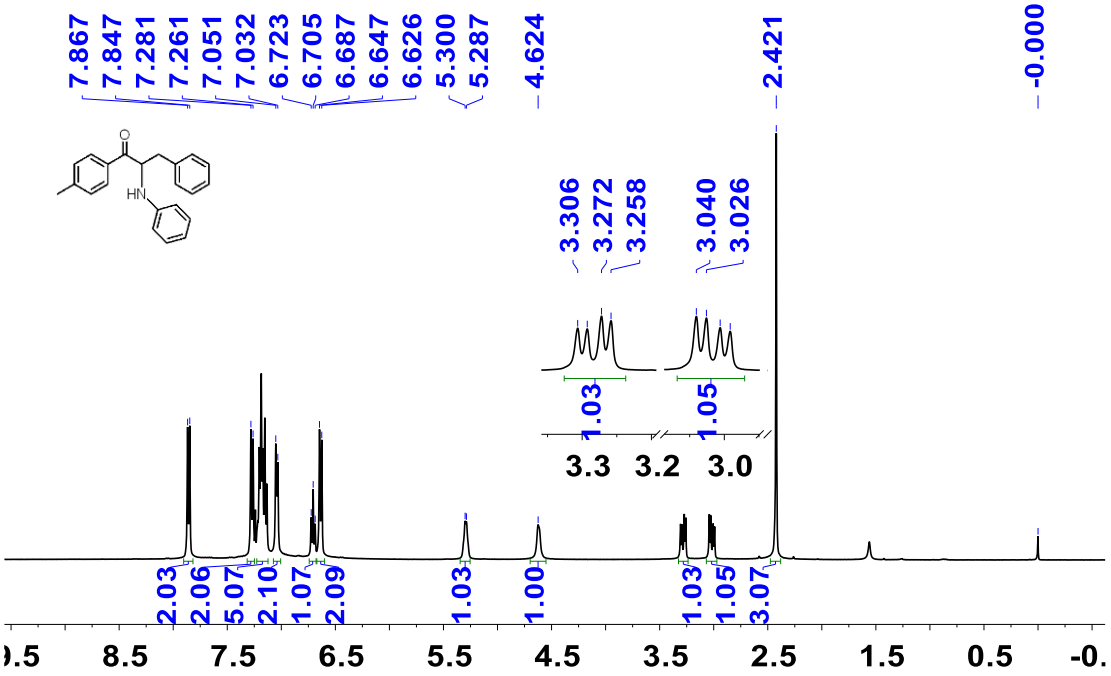


^{13}C NMR (101 MHz, $CDCl_3$) of **3af**

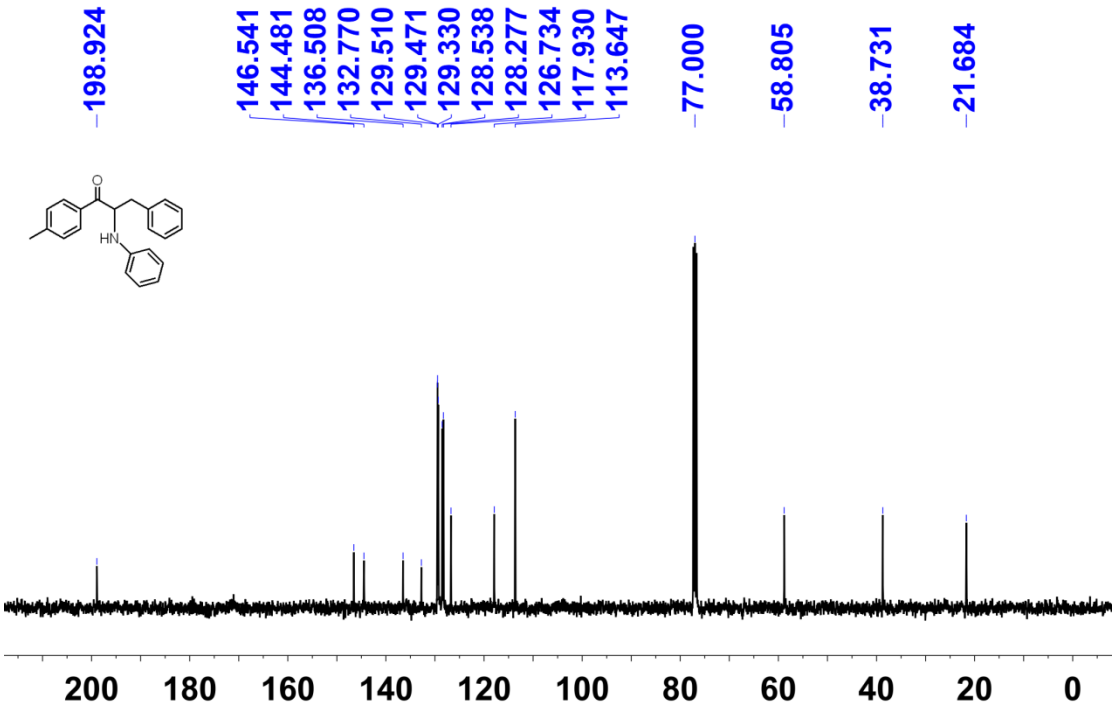


3-phenyl-2-(phenylamino)-1-(*p*-tolyl)propan-1-one (**4a**)

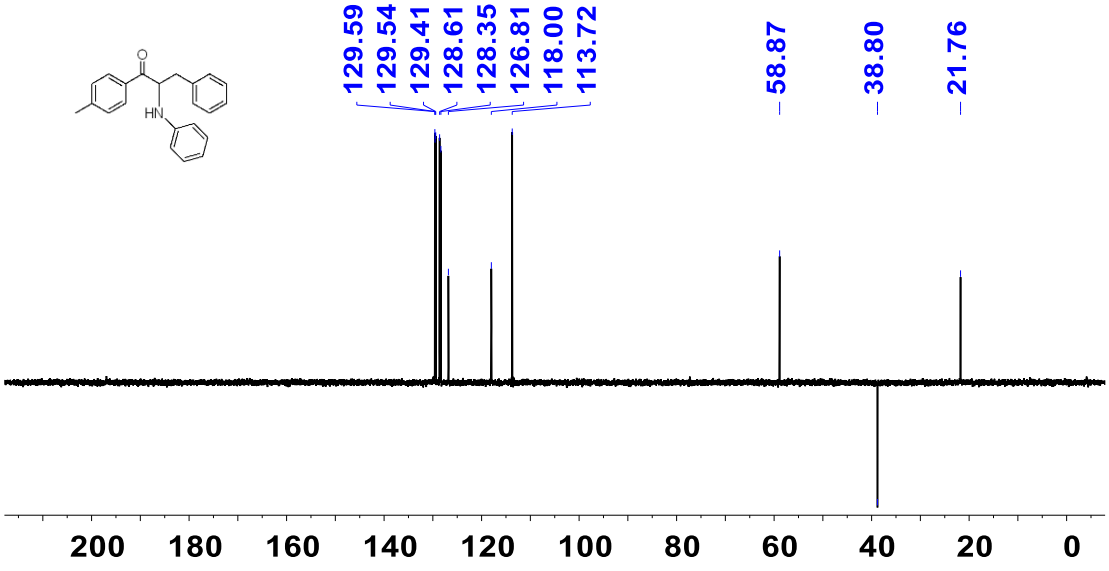
^{1}H NMR (400 MHz, $CDCl_3$) of **4a**



^{13}C NMR (101 MHz, $CDCl_3$) of **4a**

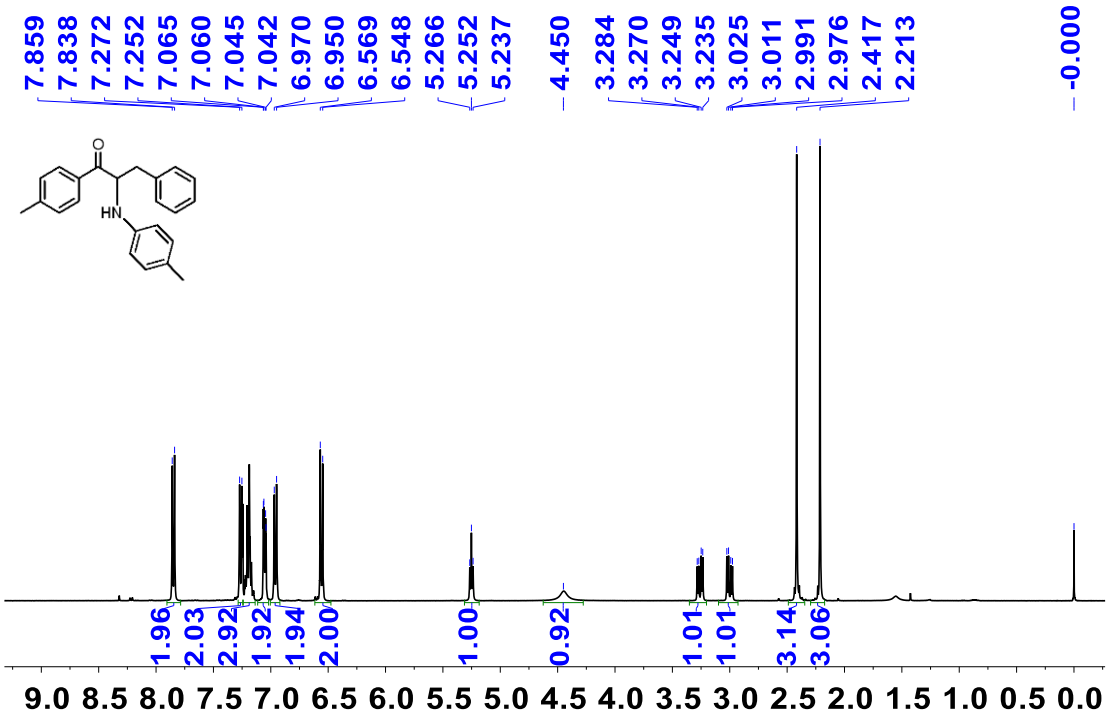


DEPT135 spectrum of **4a**

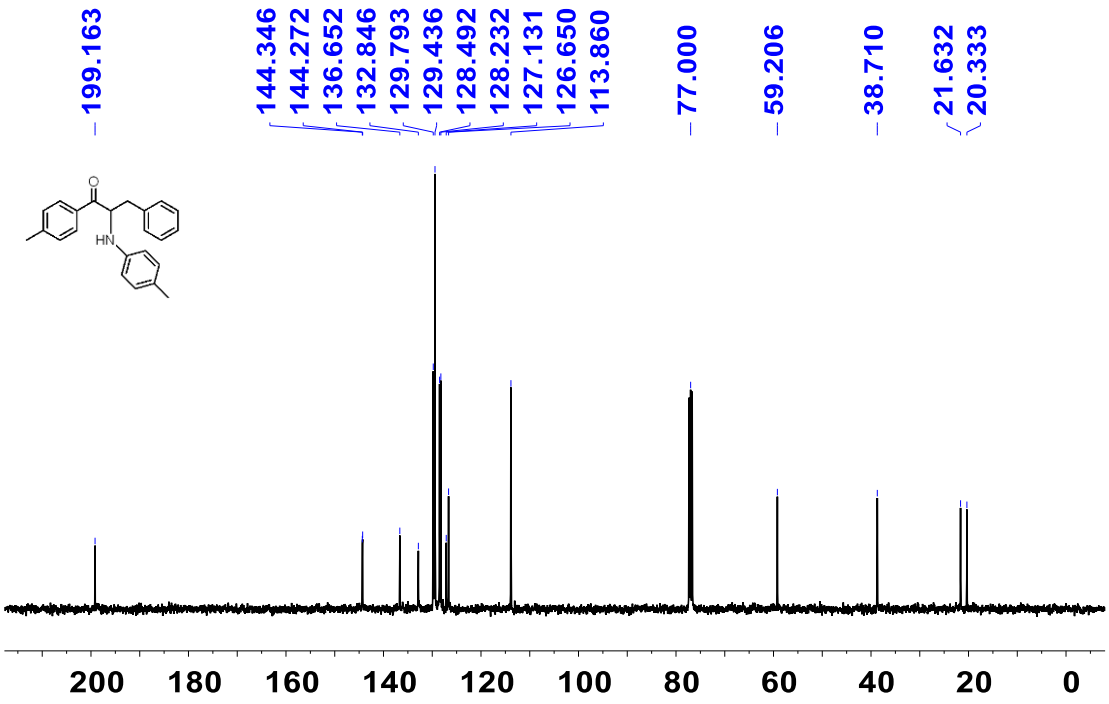


3-phenyl-1-(*p*-tolyl)-2-(*p*-tolylamino)propan-1-one (**4b**)

^{1}H NMR (400 MHz, $CDCl_3$) of **4b**

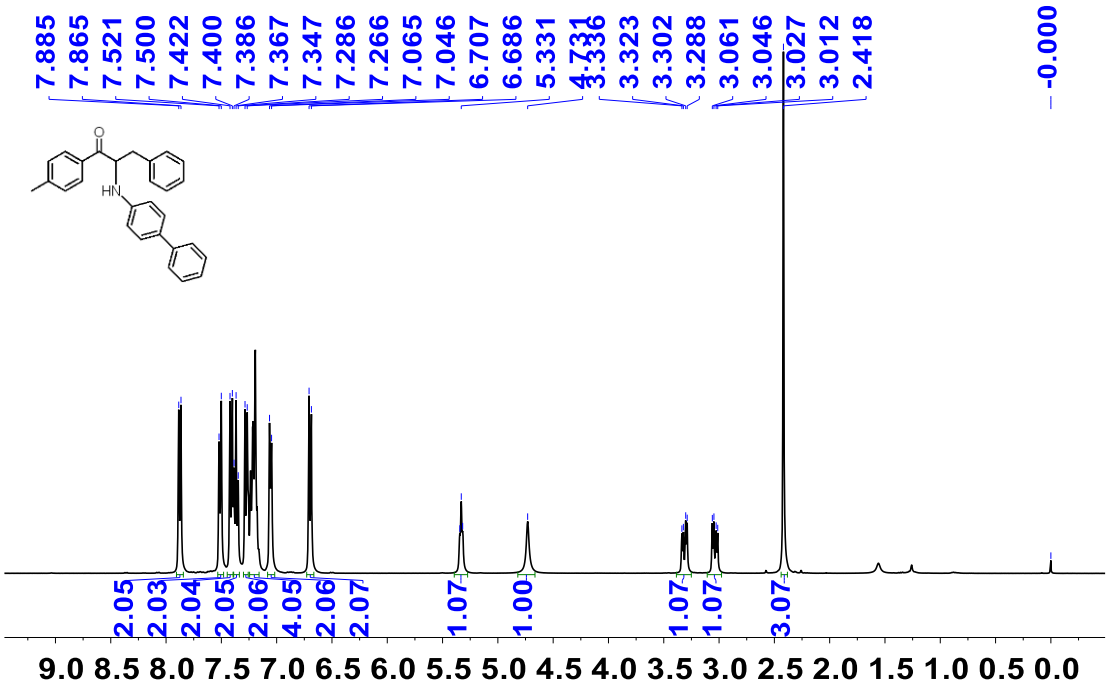


^{13}C NMR (101 MHz, $CDCl_3$) of **4b**

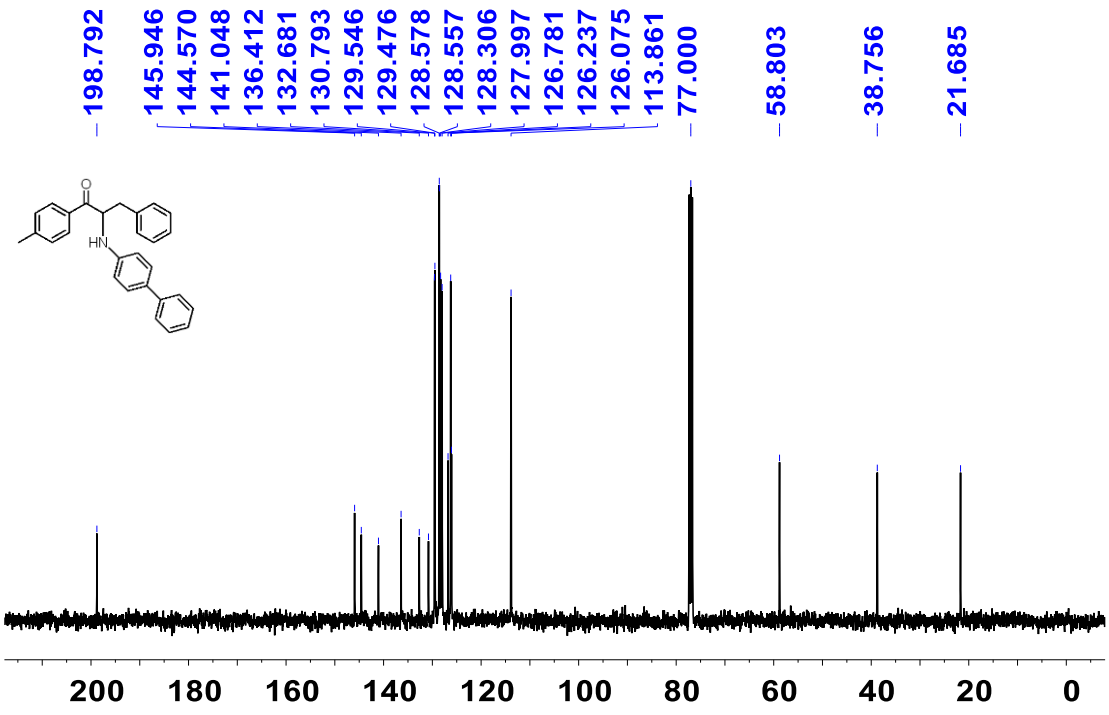


2-([1,1'-biphenyl]-4-ylamino)-3-phenyl-1-(*p*-tolyl)propan-1-one (**4c**)

^{1}H NMR (400 MHz, $CDCl_3$) of **4c**

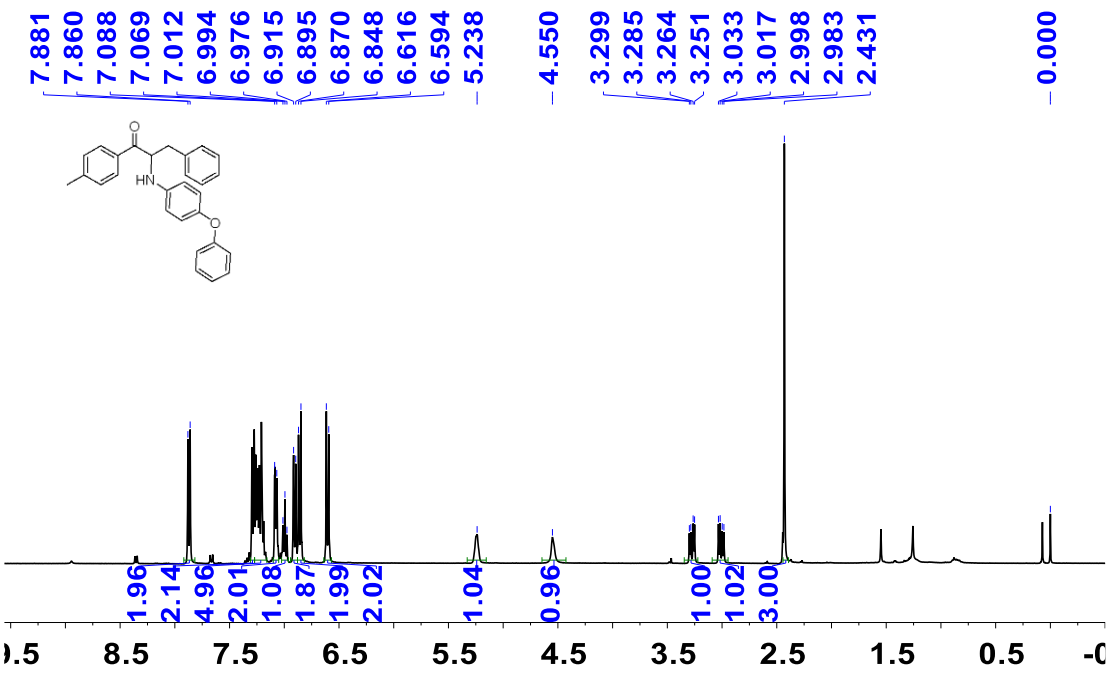


^{13}C NMR (101 MHz, $CDCl_3$) of **4c**

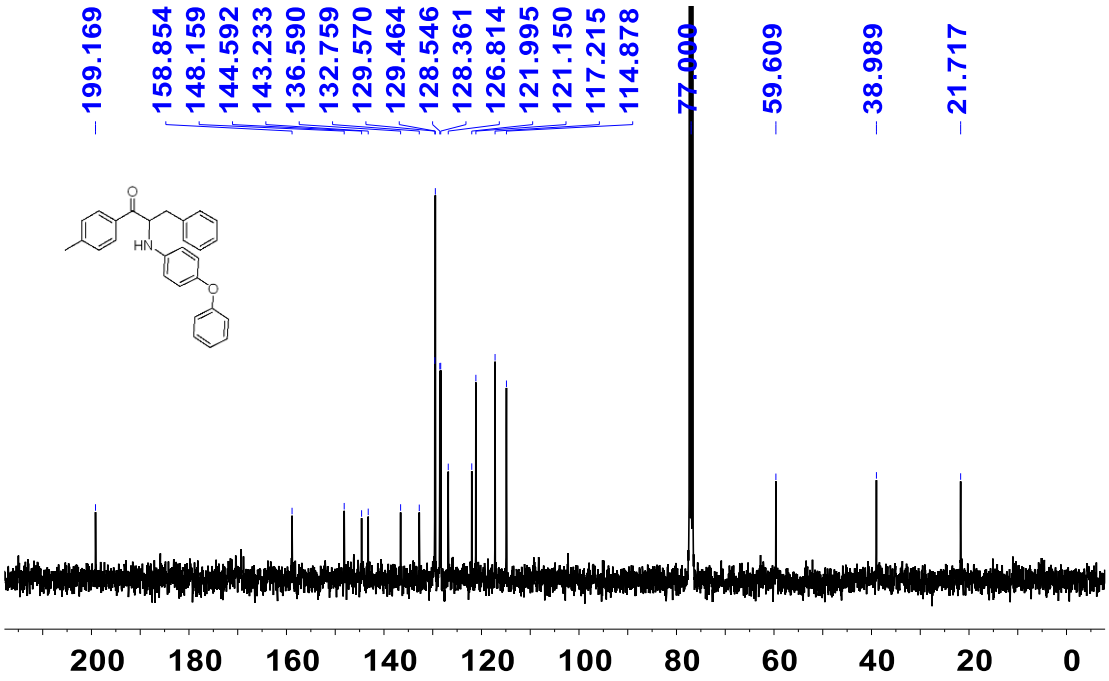


2-((4-phenoxyphenyl)amino)-3-phenyl-1-(p-tolyl)propan-1-one (**4d**)

^{1}H NMR (400 MHz, $CDCl_3$) of **4d**

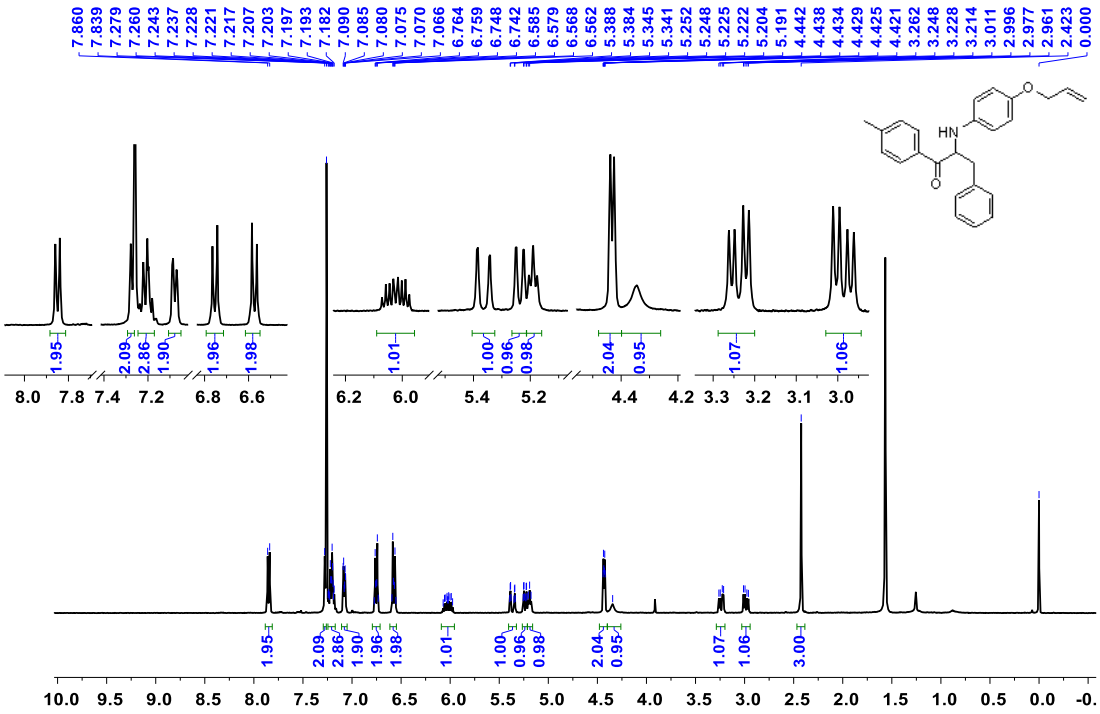


^{13}C NMR (101 MHz, $CDCl_3$) of **4d**

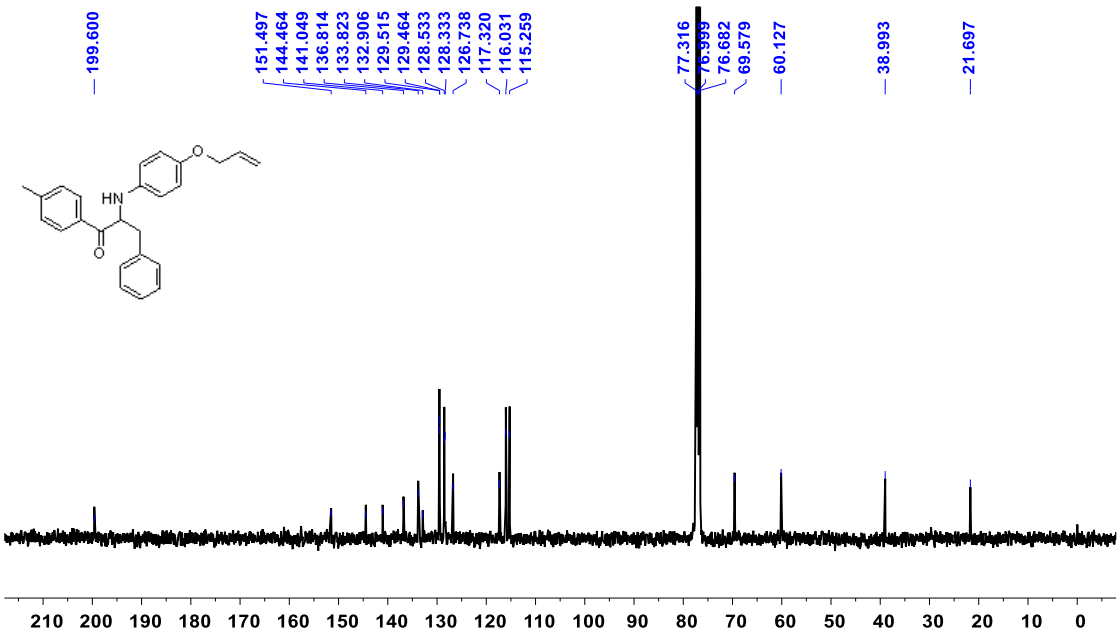


2-((4-(allyloxy)phenyl)amino)-3-phenyl-1-(*p*-tolyl)propan-1-one (**4e**)

^{1}H NMR (400 MHz, $CDCl_3$) of **4e**

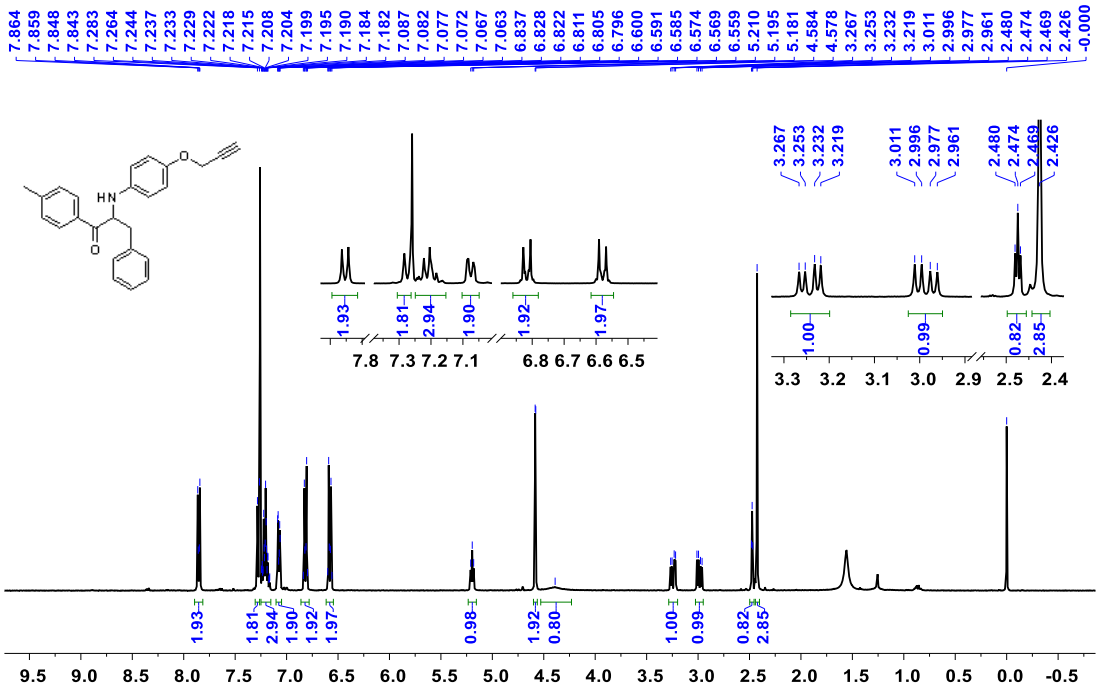


^{13}C NMR (101 MHz, $CDCl_3$) of **4e**

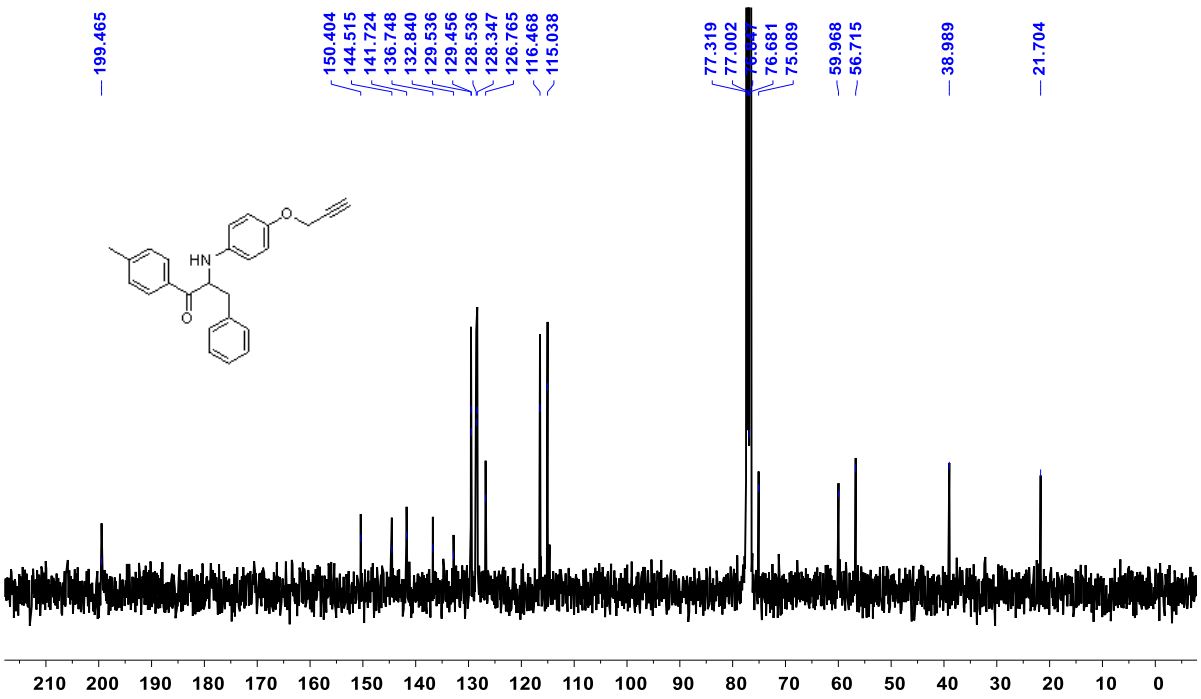


3-phenyl-2-((4-(prop-2-yn-1-yloxy)phenyl)amino)-1-(*p*-tolyl)propan-1-one (**4f**)

^{1}H NMR (400 MHz, $CDCl_3$) of **4f**

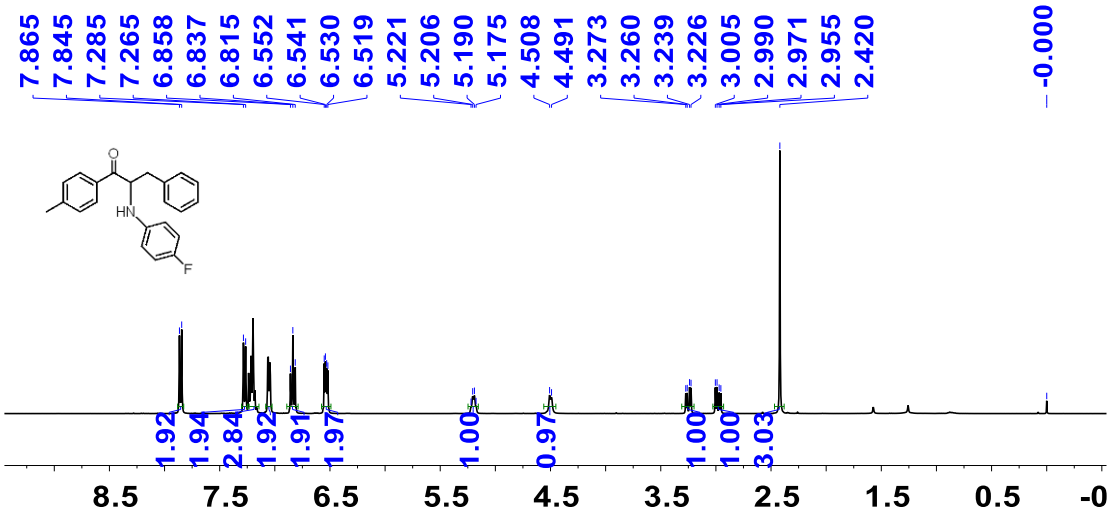


^{13}C NMR (101 MHz, $CDCl_3$) of **4f**

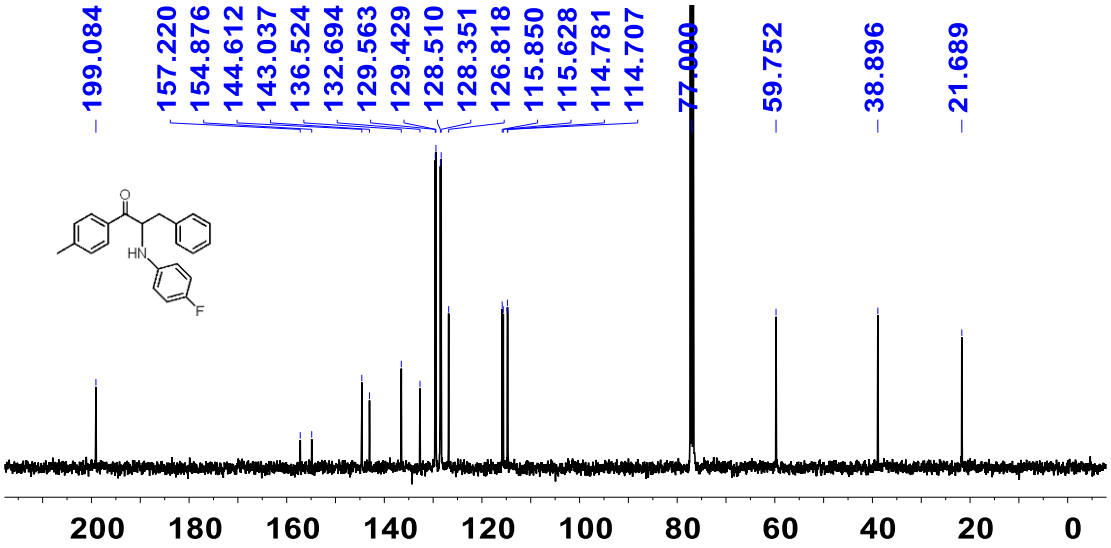


2-((4-fluorophenyl)amino)-3-phenyl-1-(*p*-tolyl)propan-1-one (**4g**)

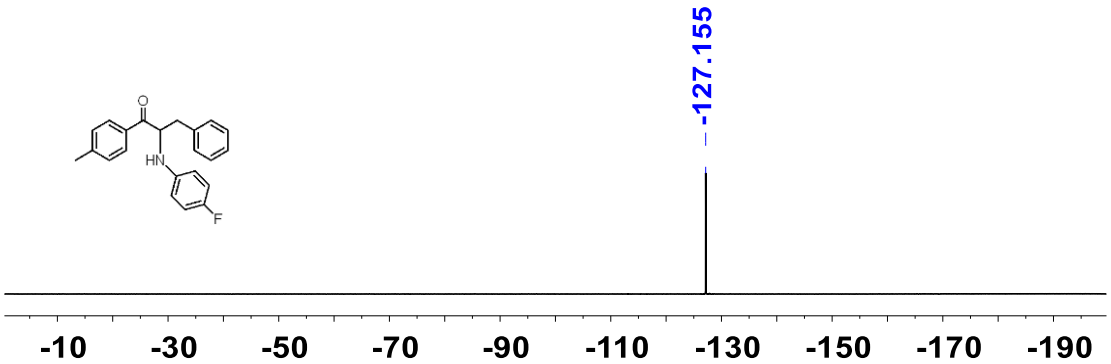
^{1}H NMR (400 MHz, $CDCl_3$) of **4g**



^{13}C NMR (101 MHz, $CDCl_3$) of **4g**

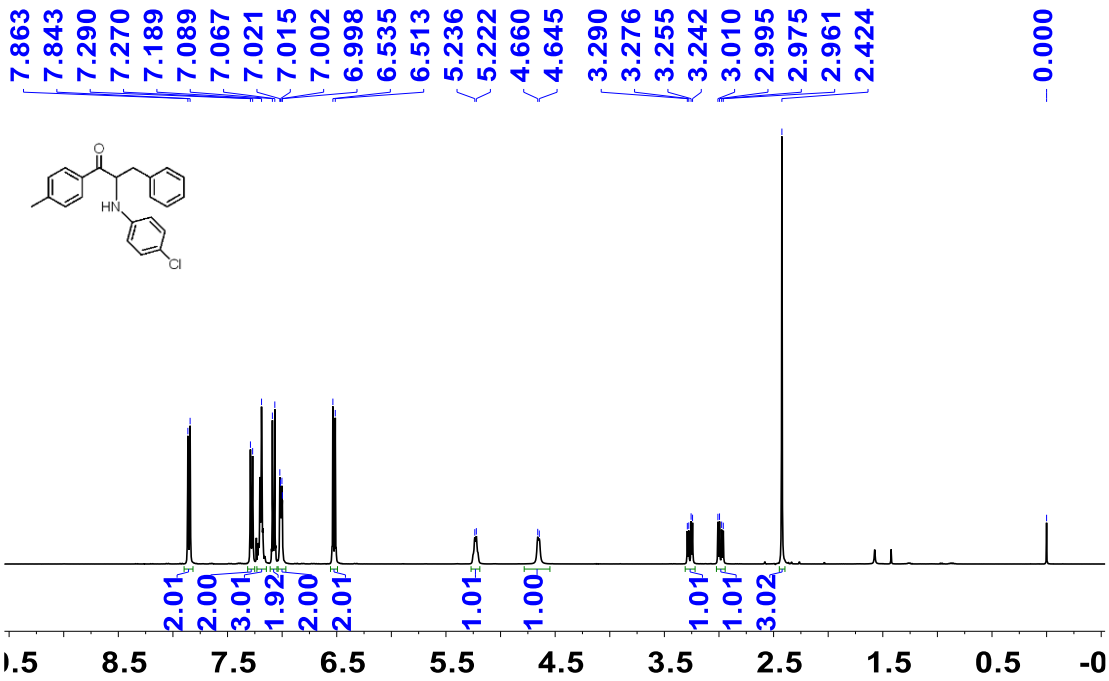


^{19}F NMR (376.5 MHz, $CDCl_3$) of **4g**

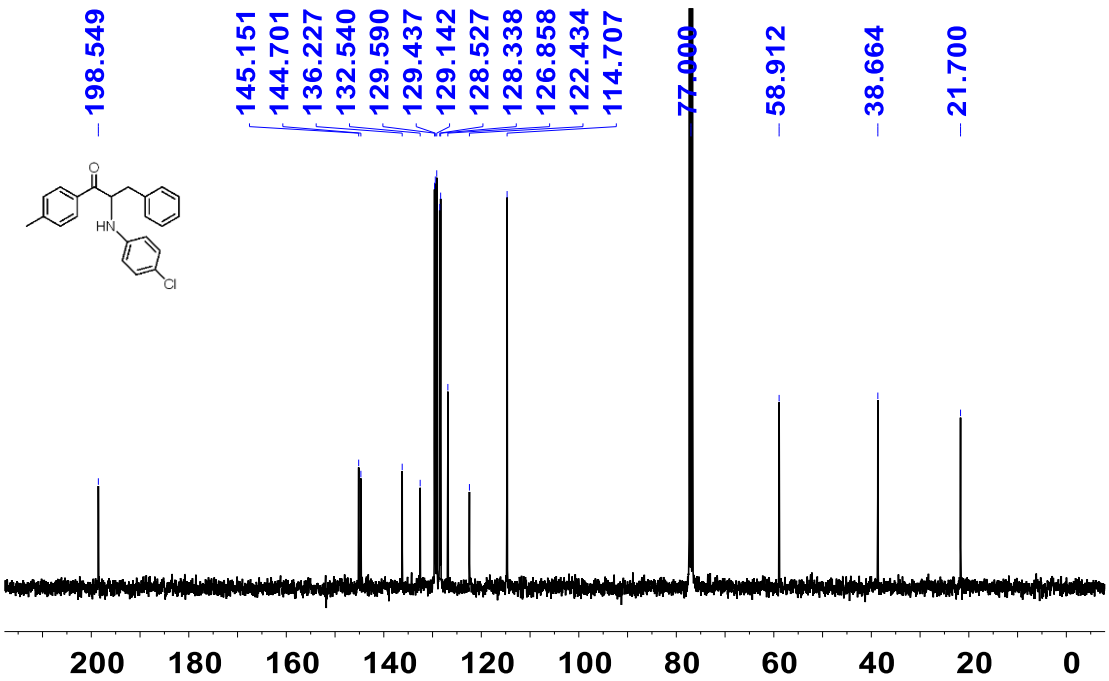


2-((4-chlorophenyl)amino)-3-phenyl-1-(*p*-tolyl)propan-1-one (**4h**)

^{1}H NMR (400 MHz, $CDCl_3$) of **4h**

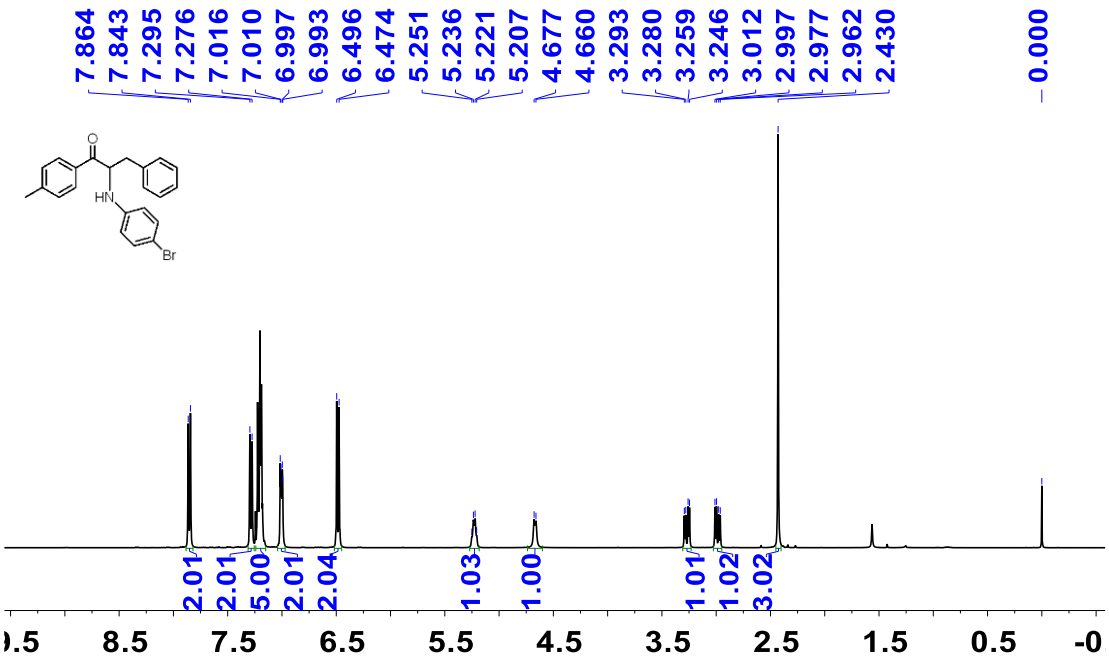


^{13}C NMR (101 MHz, $CDCl_3$) of **4h**

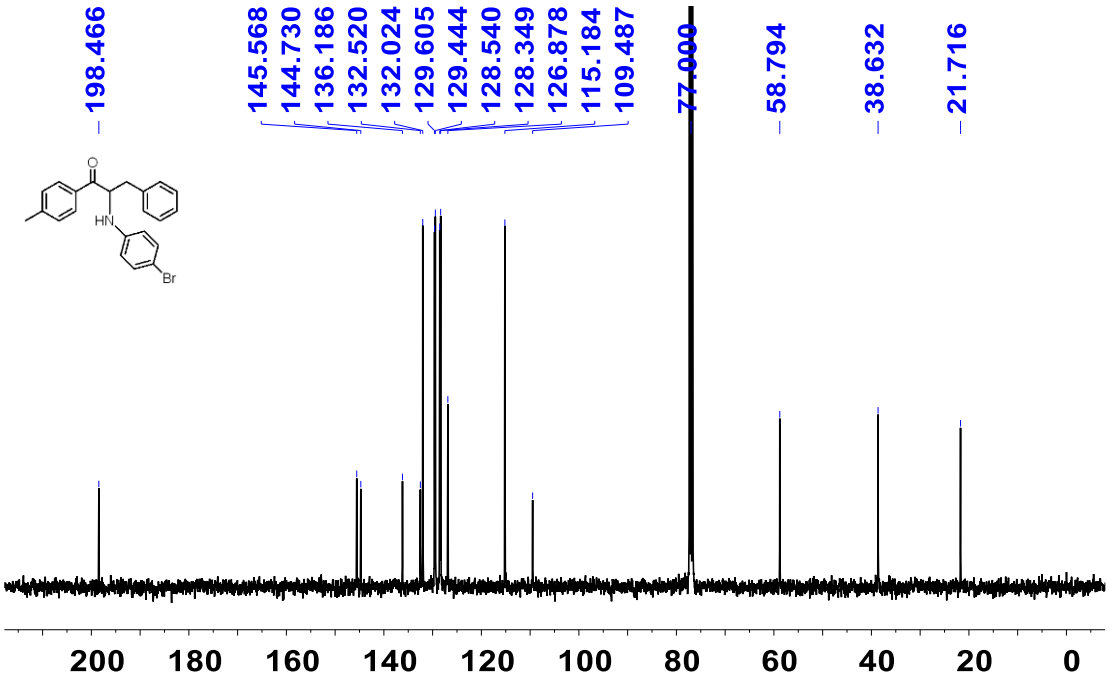


2-((4-bromophenyl)amino)-3-phenyl-1-(*p*-tolyl)propan-1-one (**4i**)

^{1}H NMR (400 MHz, $CDCl_3$) of **4i**

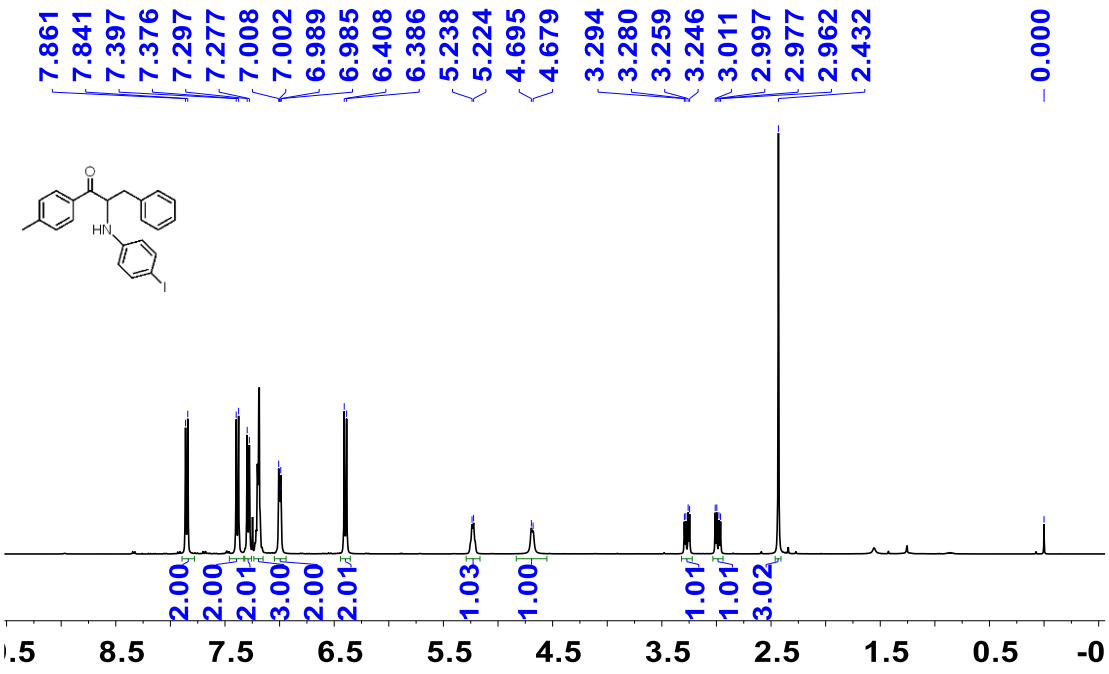


^{13}C NMR (101 MHz, $CDCl_3$) of **4i**

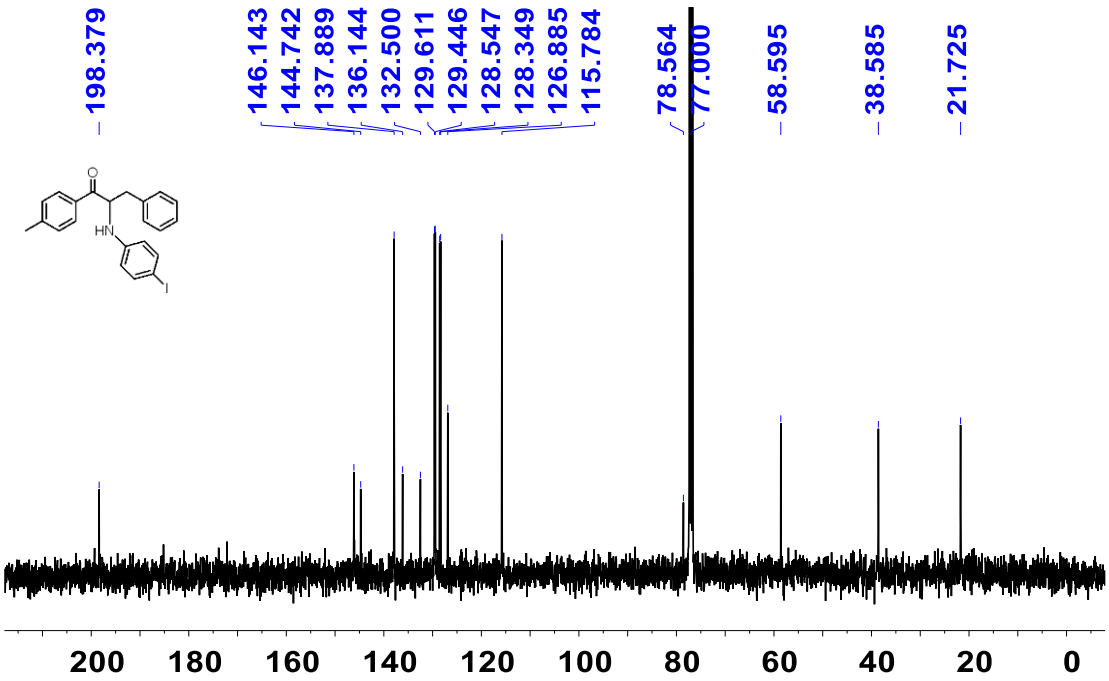


2-((4-iodophenyl)amino)-3-phenyl-1-(p-tolyl)propan-1-one (**4j**)

^{1}H NMR (400 MHz, $CDCl_3$) of **4j**

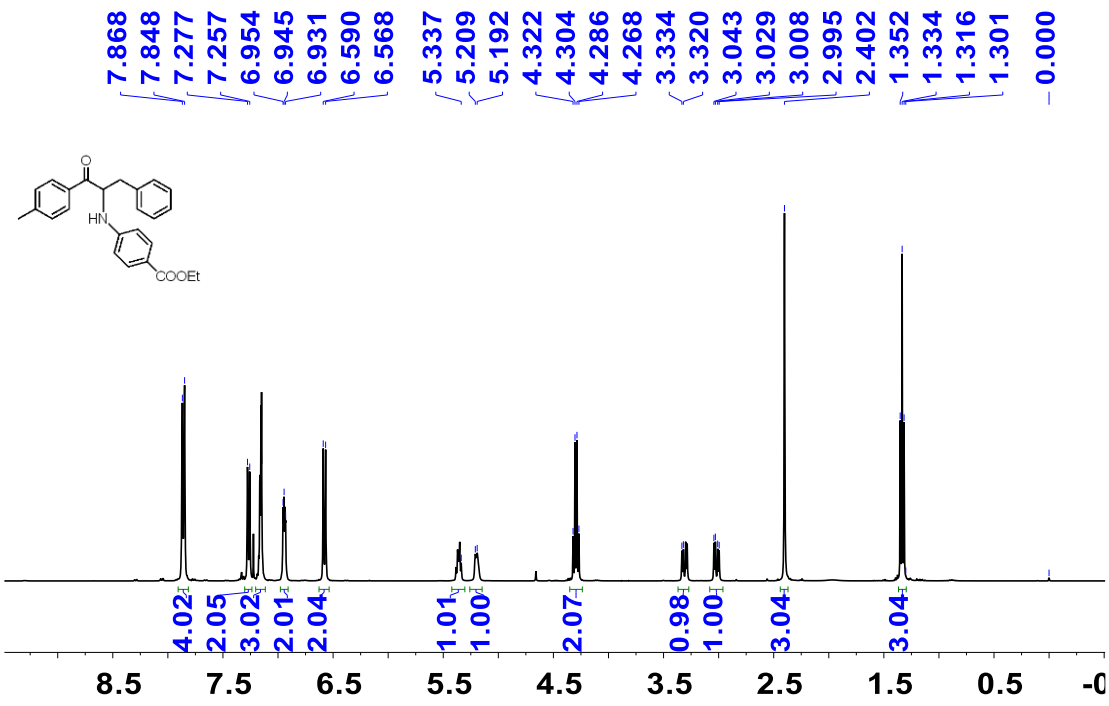


^{13}C NMR (101 MHz, $CDCl_3$) of **4j**

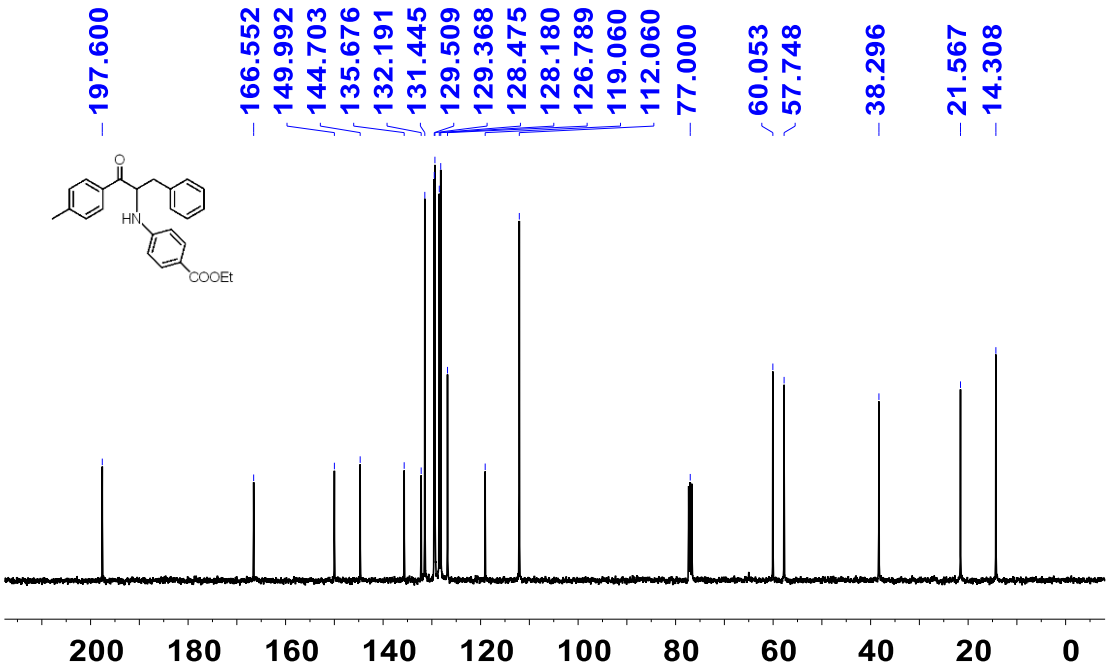


ethyl 4-((1-oxo-3-phenyl-1-(*p*-tolyl)propan-2-yl)amino)benzoate (**4k**)

^{1}H NMR (400 MHz, $CDCl_3$) of **4k**

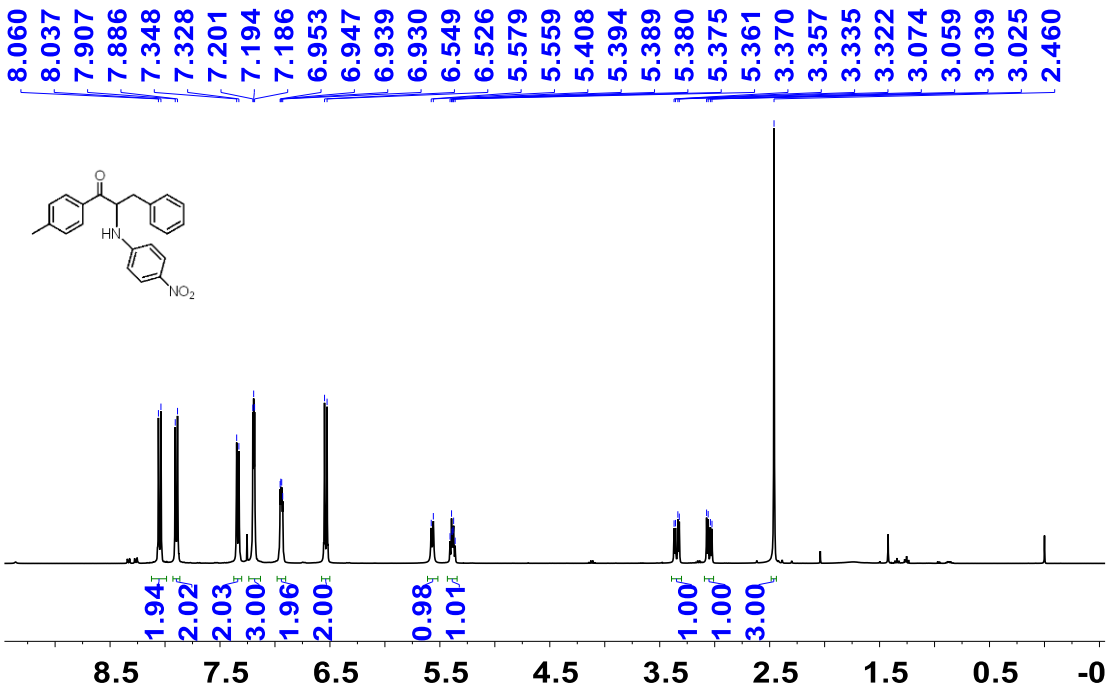


^{13}C NMR (101 MHz, $CDCl_3$) of **4k**

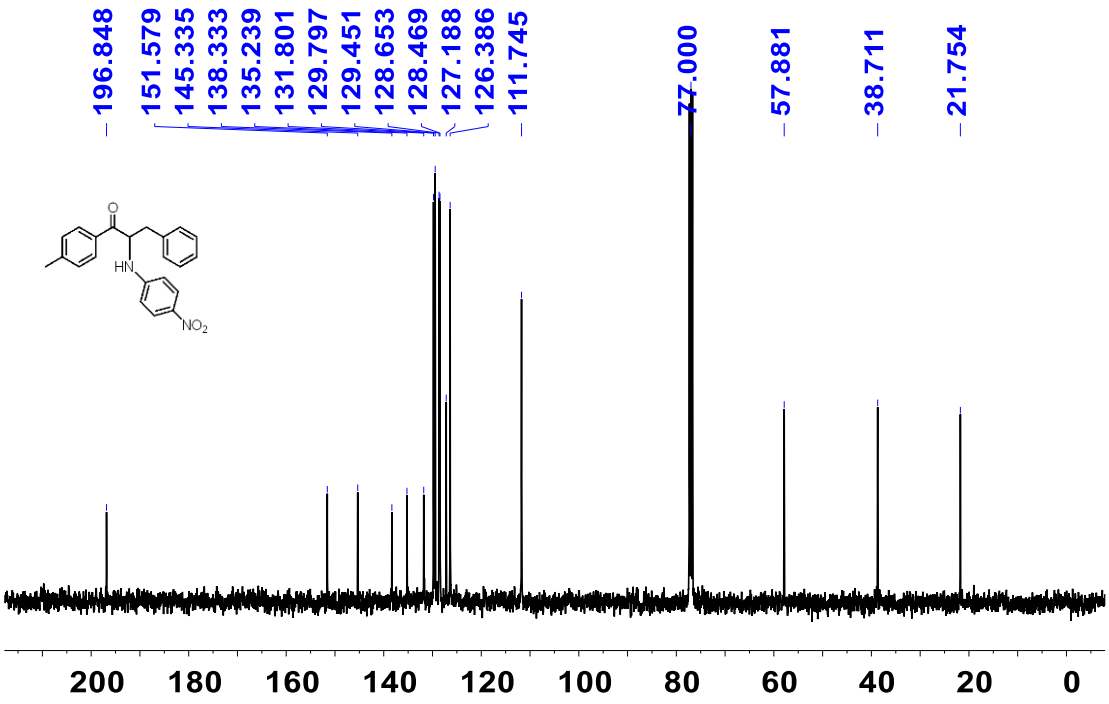


2-((4-nitrophenyl)amino)-3-phenyl-1-(*p*-tolyl)propan-1-one (**4l**)

^{1}H NMR (400 MHz, $CDCl_3$) of **4l**

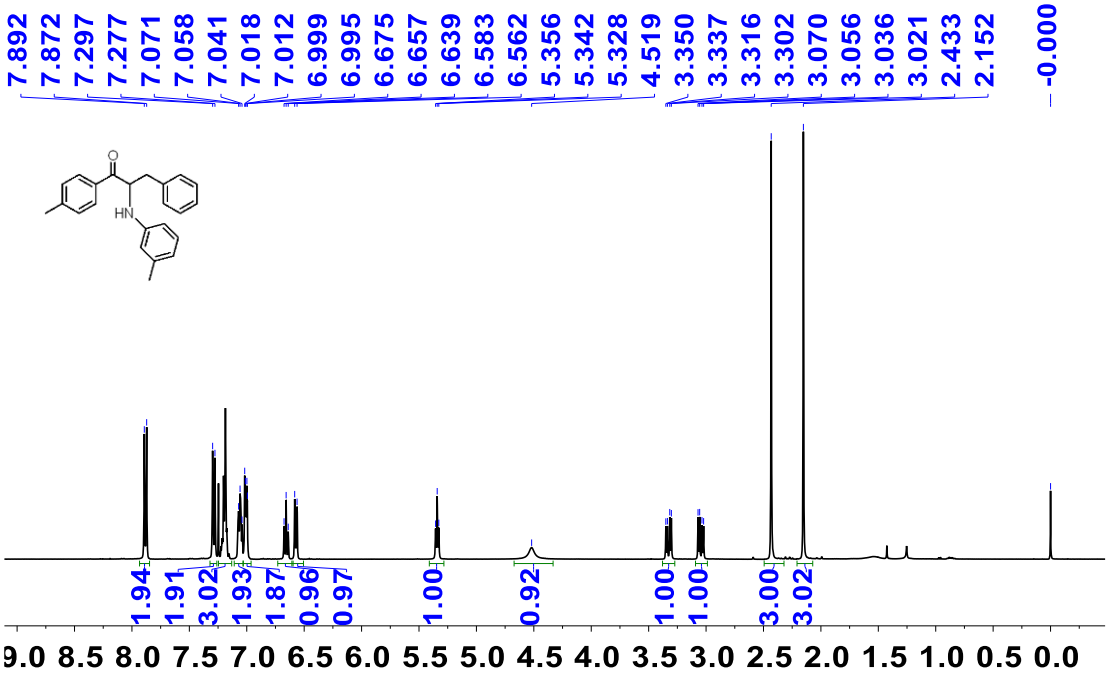


^{13}C NMR (101 MHz, $CDCl_3$) of **4l**

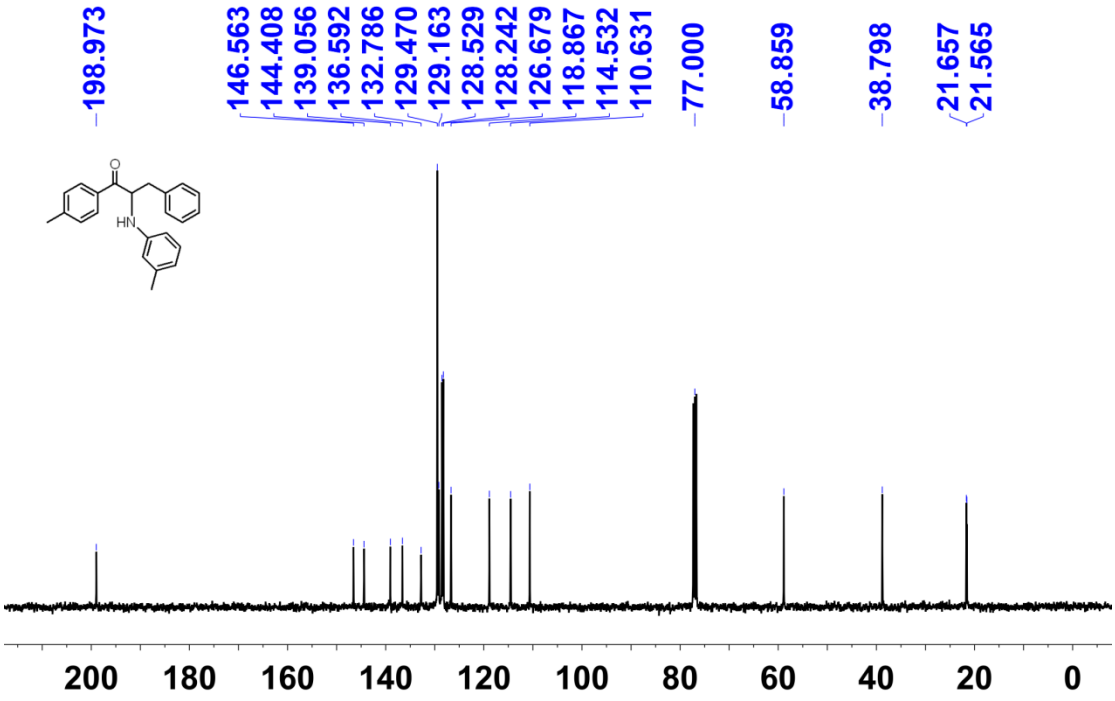


3-phenyl-1-(*p*-tolyl)-2-(*m*-tolylamino)propan-1-one (**4m**)

^{1}H NMR (400 MHz, $CDCl_3$) of **4m**

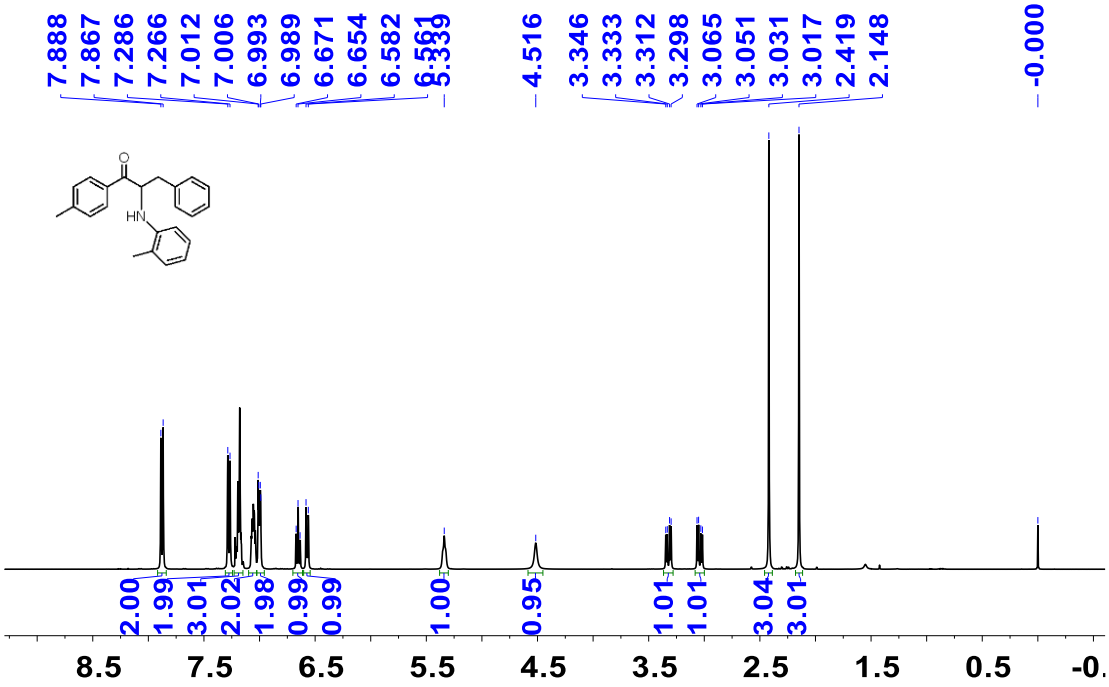


^{13}C NMR (101 MHz, $CDCl_3$) of **4m**

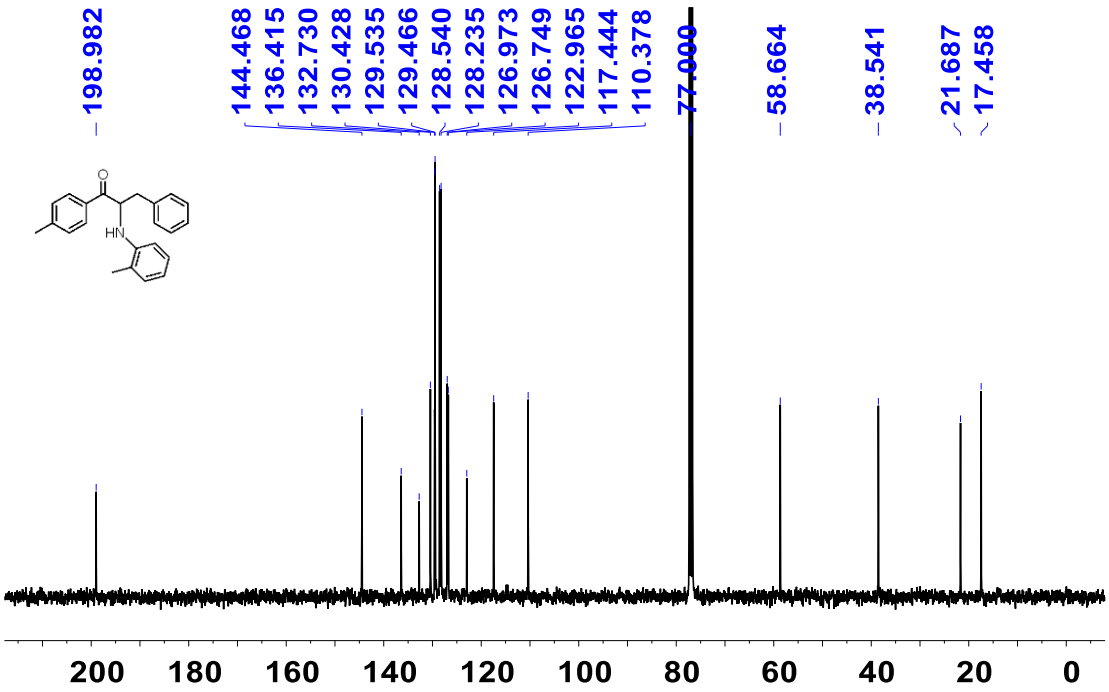


3-phenyl-1-(*p*-tolyl)-2-(*o*-tolylamino)propan-1-one (**4n**)

^{1}H NMR (400 MHz, $CDCl_3$) of **4n**

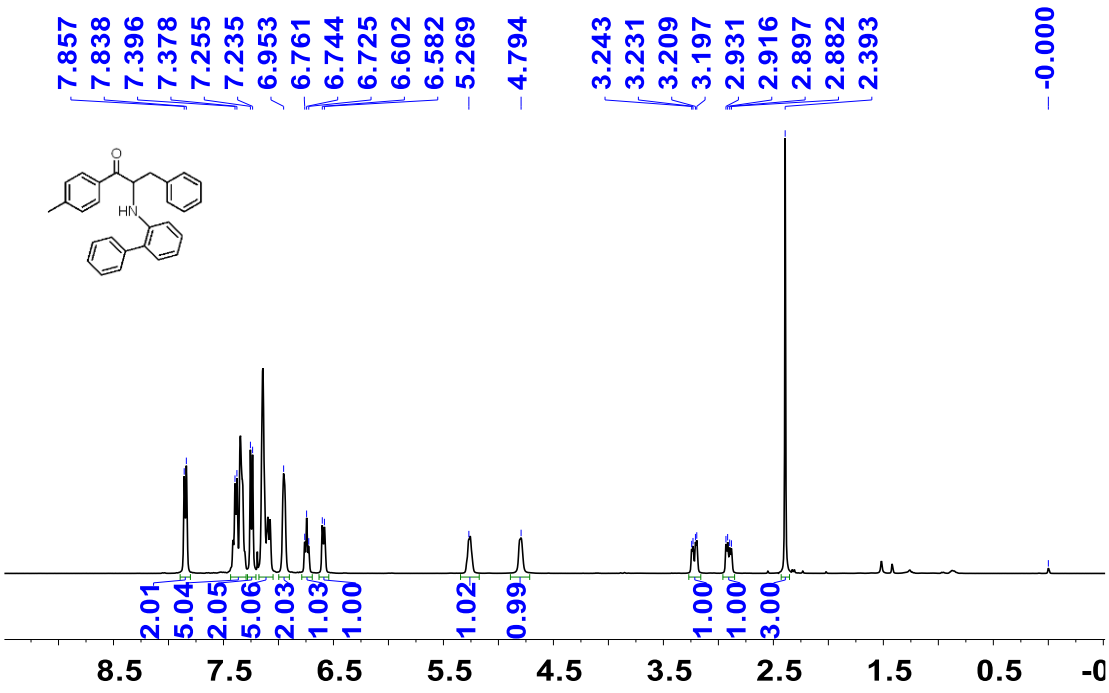


^{13}C NMR (101 MHz, $CDCl_3$) of **4n**

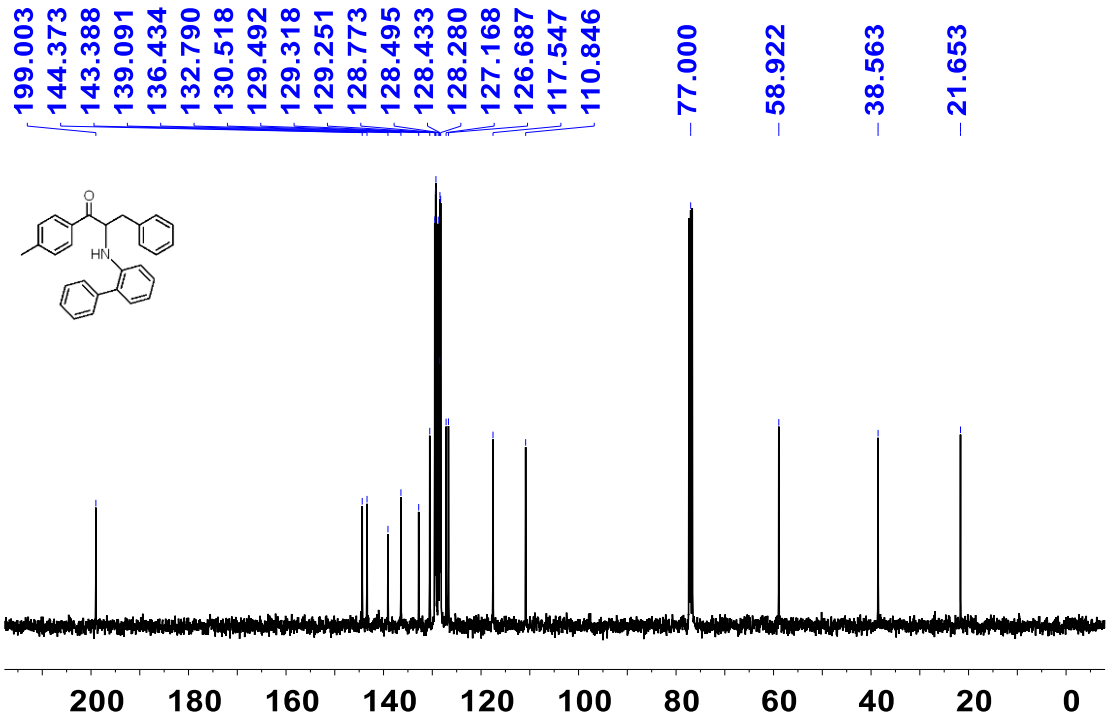


2-([1,1'-biphenyl]-2-ylamino)-3-phenyl-1-(*p*-tolyl)propan-1-one (**4o**)

^{1}H NMR (400 MHz, $CDCl_3$) of **4o**

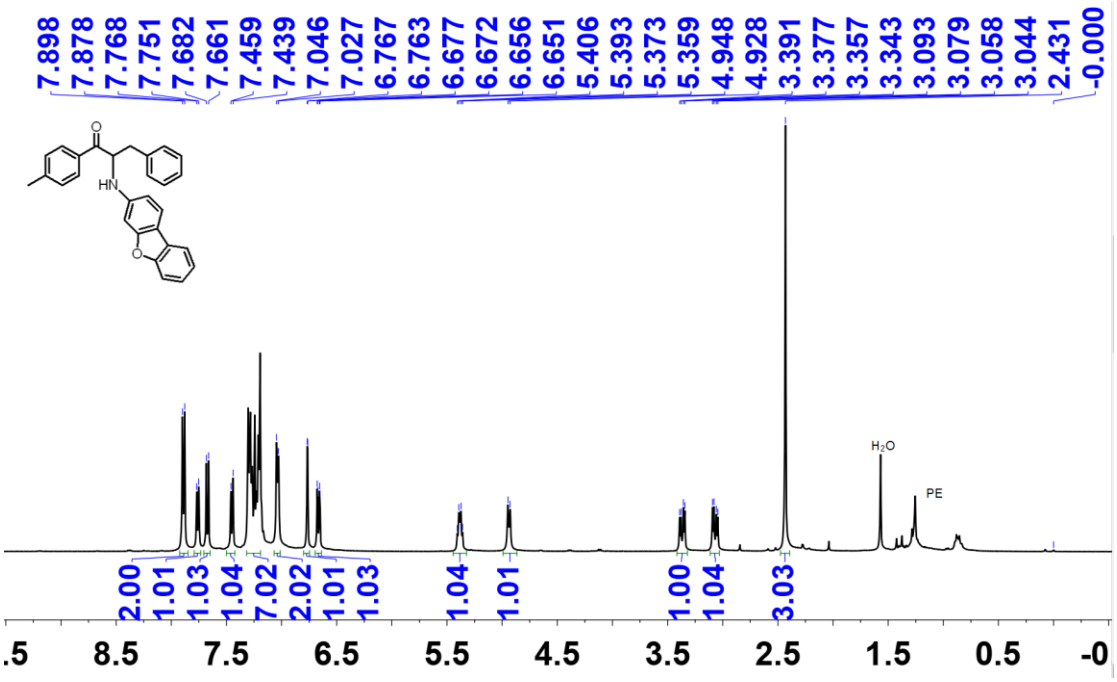


^{13}C NMR (101 MHz, $CDCl_3$) of **4o**

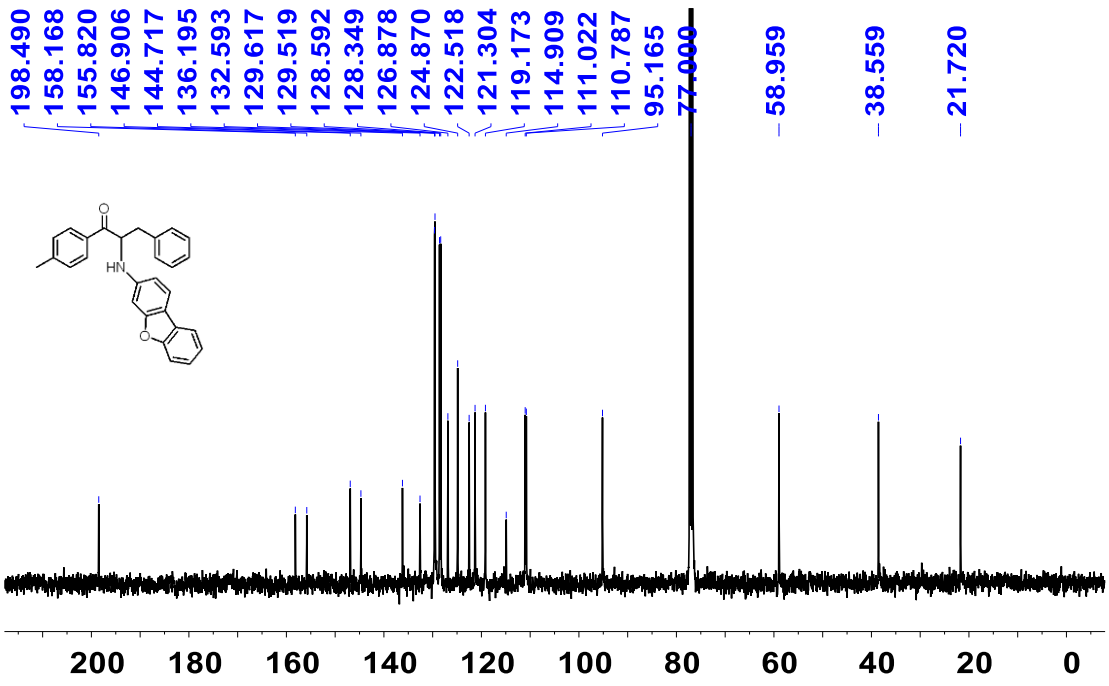


2-(dibenzo[*b*, *d*]furan-3-ylamino)-3-phenyl-1-(*p*-tolyl)propan-1-one (**4p**)

^{1}H NMR (400 MHz, $CDCl_3$) of **4p**

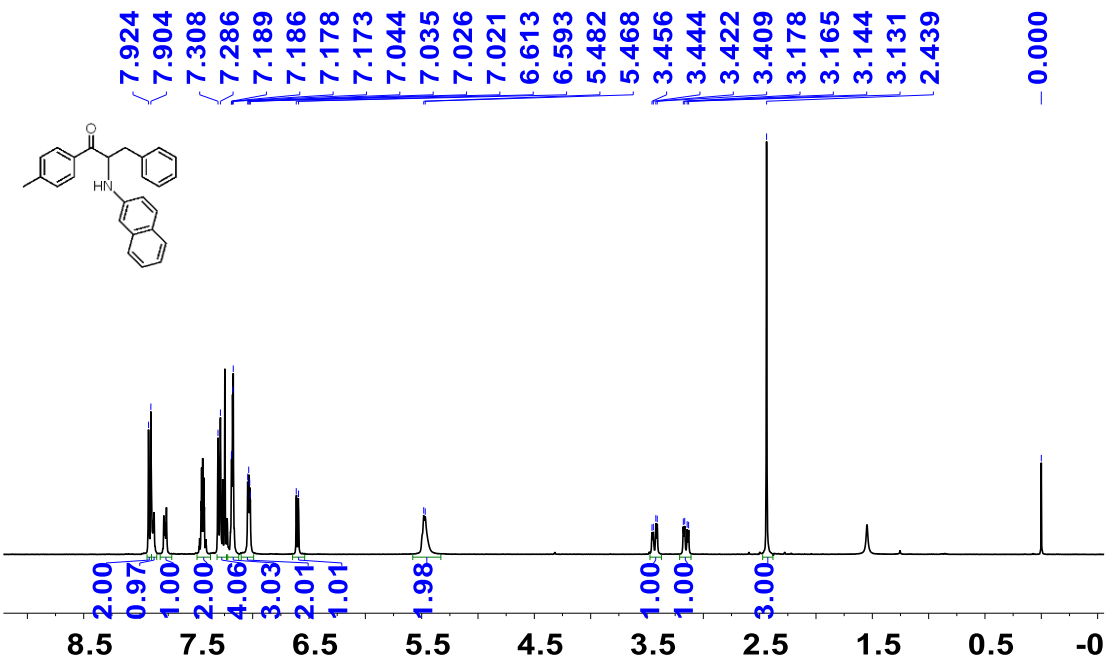


^{13}C NMR (101 MHz, $CDCl_3$) of **4p**

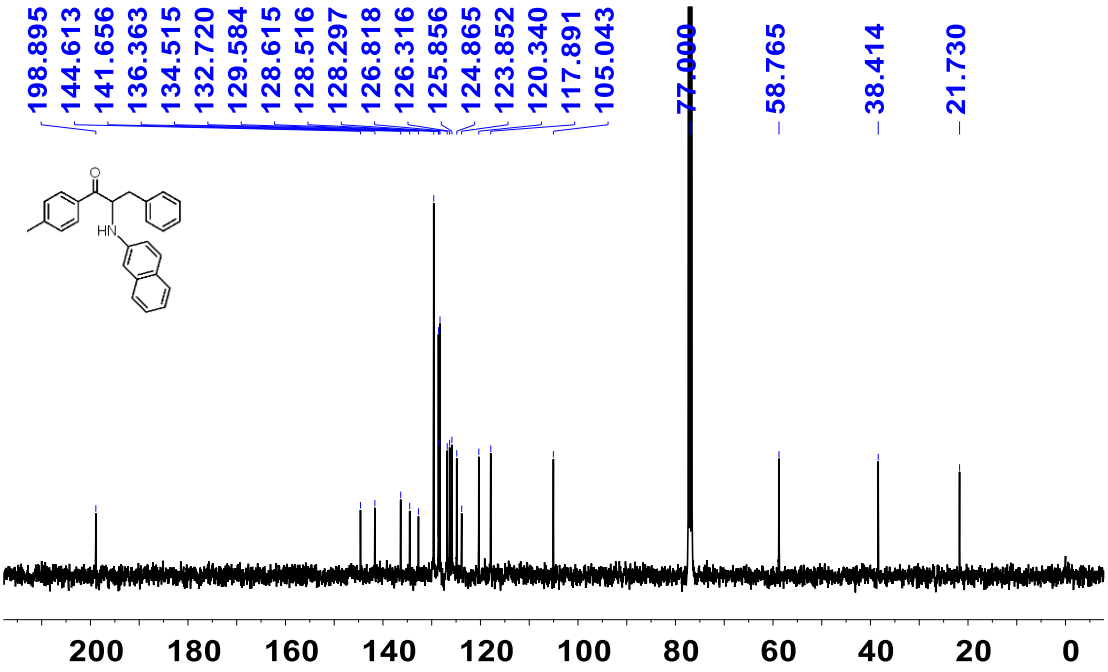


2-(naphthalen-2-ylamino)-3-phenyl-1-(*p*-tolyl)propan-1-one (**4q**)

^{1}H NMR (400 MHz, $CDCl_3$) of **4q**

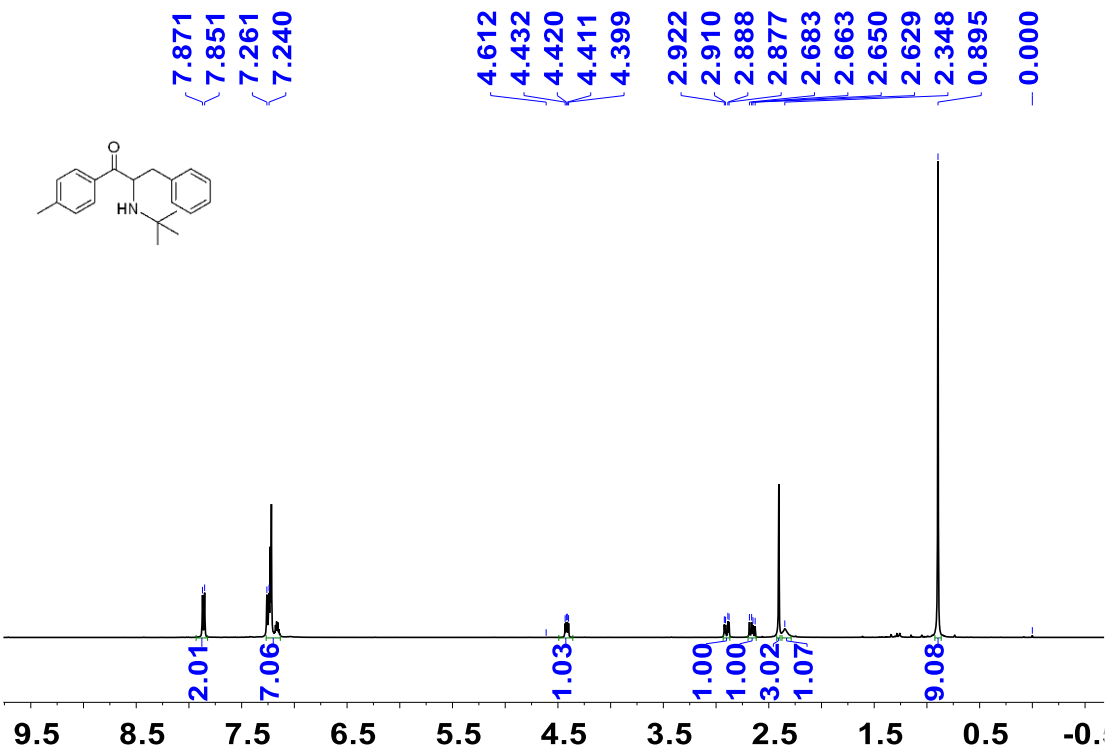


^{13}C NMR (101 MHz, $CDCl_3$) of **4q**

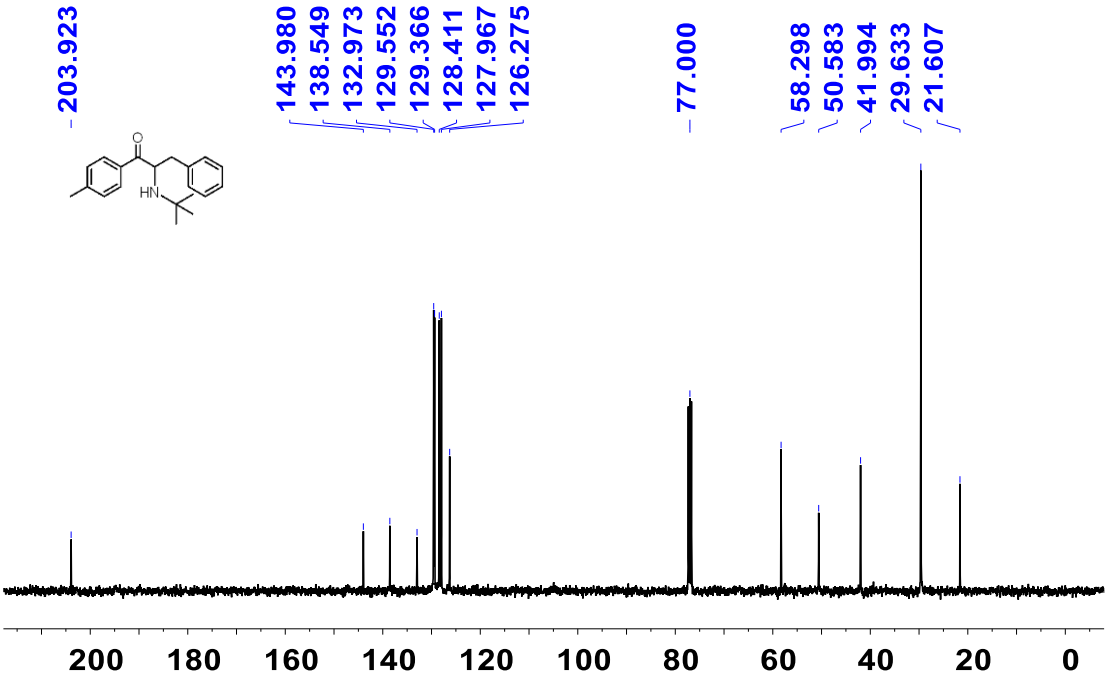


2-(tert-butylamino)-3-phenyl-1-(p-tolyl)propan-1-one (**4r**)

^{1}H NMR (400 MHz, $CDCl_3$) of **4r**

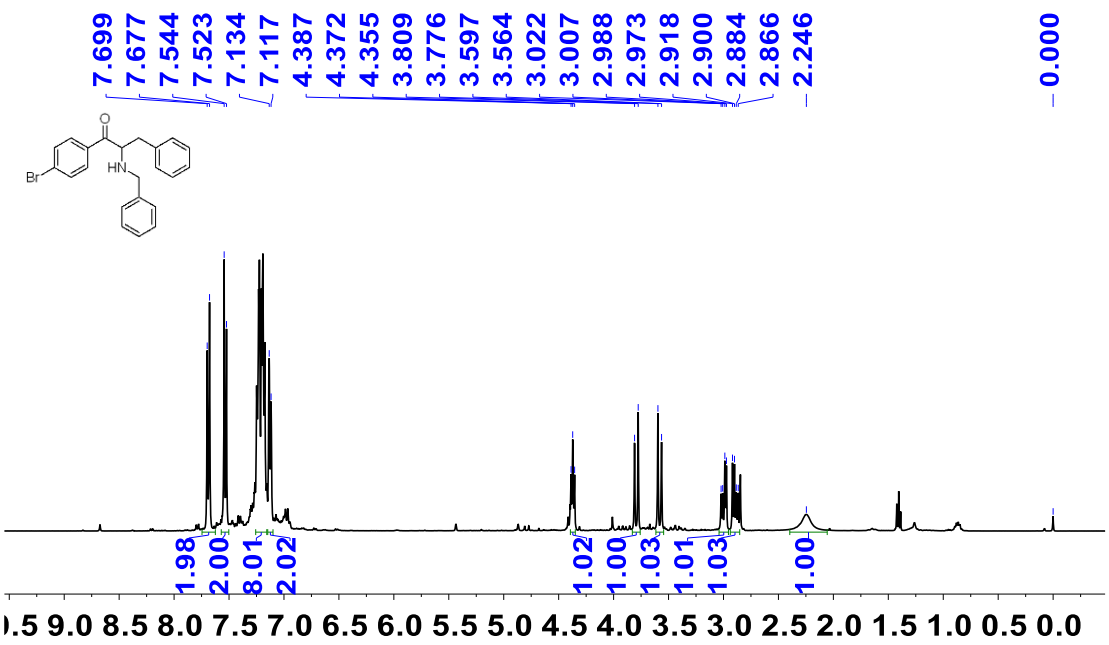


^{13}C NMR (101 MHz, $CDCl_3$) of **4r**

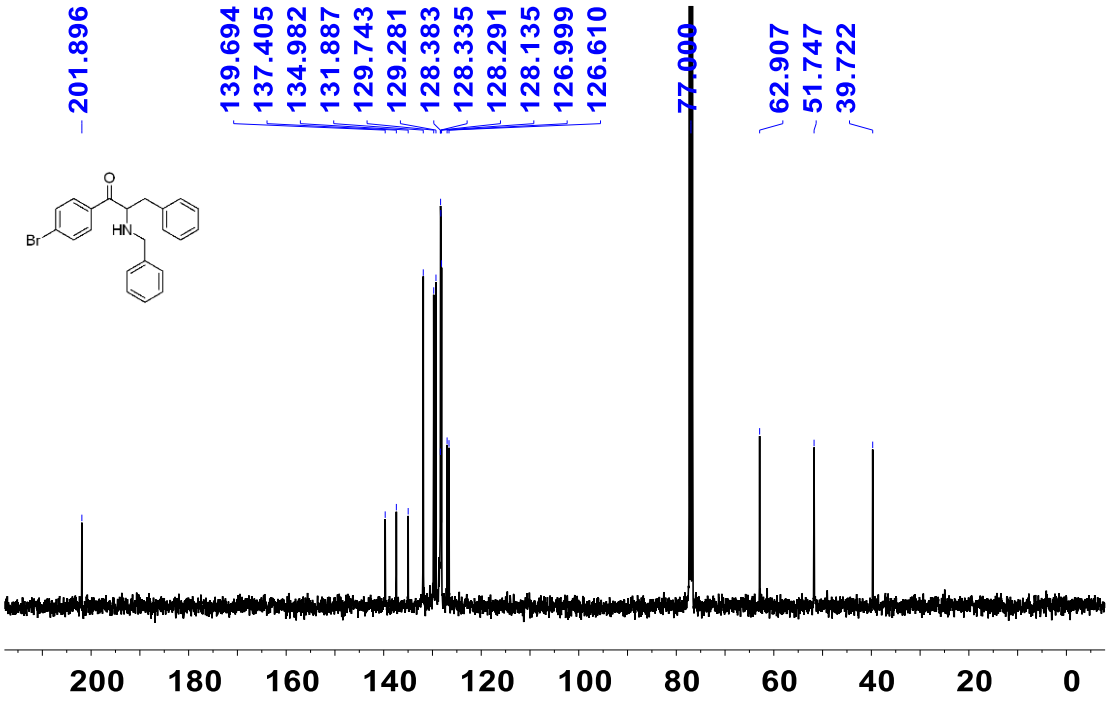


2-(benzylamino)-3-phenyl-1-(p-tolyl)propan-1-one (**4s**)

^{1}H NMR (400 MHz, $CDCl_3$) of **4s**

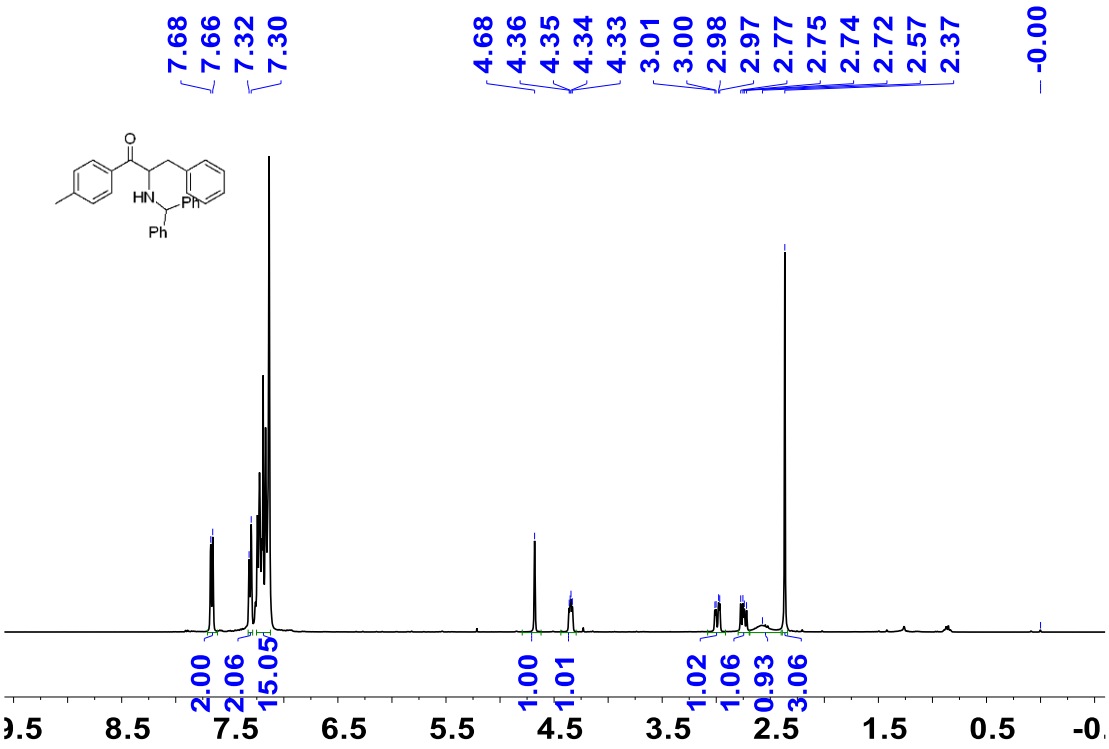


^{13}C NMR (101 MHz, $CDCl_3$) of **4s**

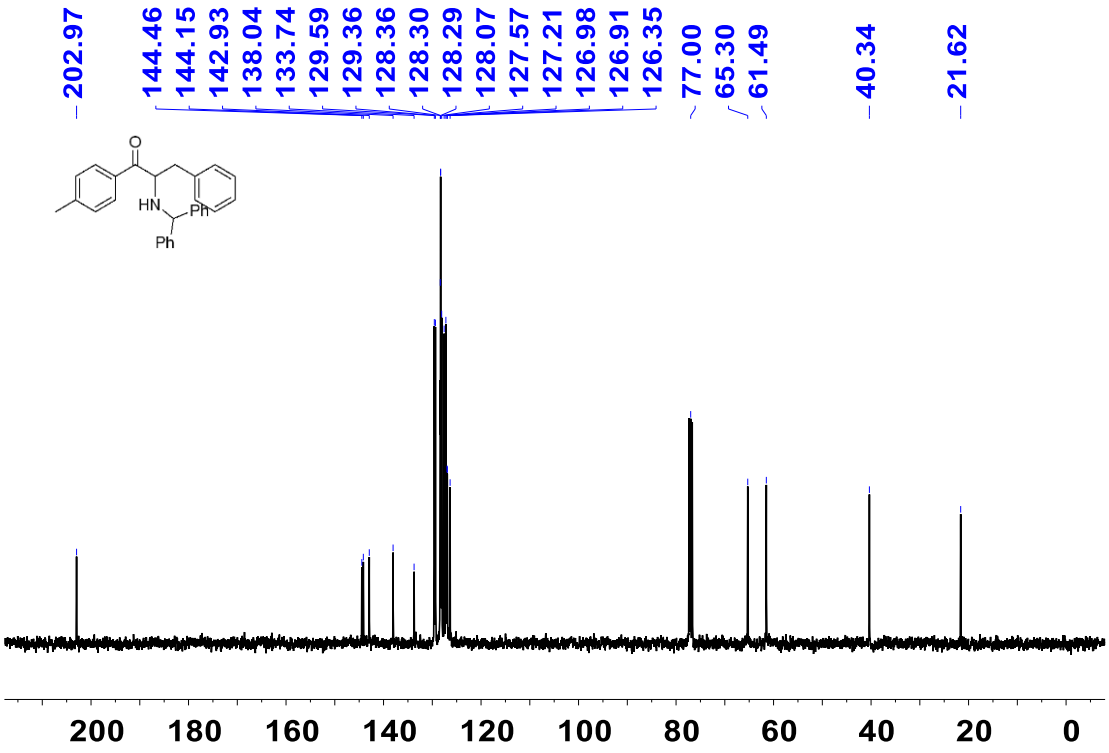


2-(benzhydrylamino)-3-phenyl-1-(p-tolyl)propan-1-one (**4t**)

^{1}H NMR (400 MHz, $CDCl_3$) of **4t**

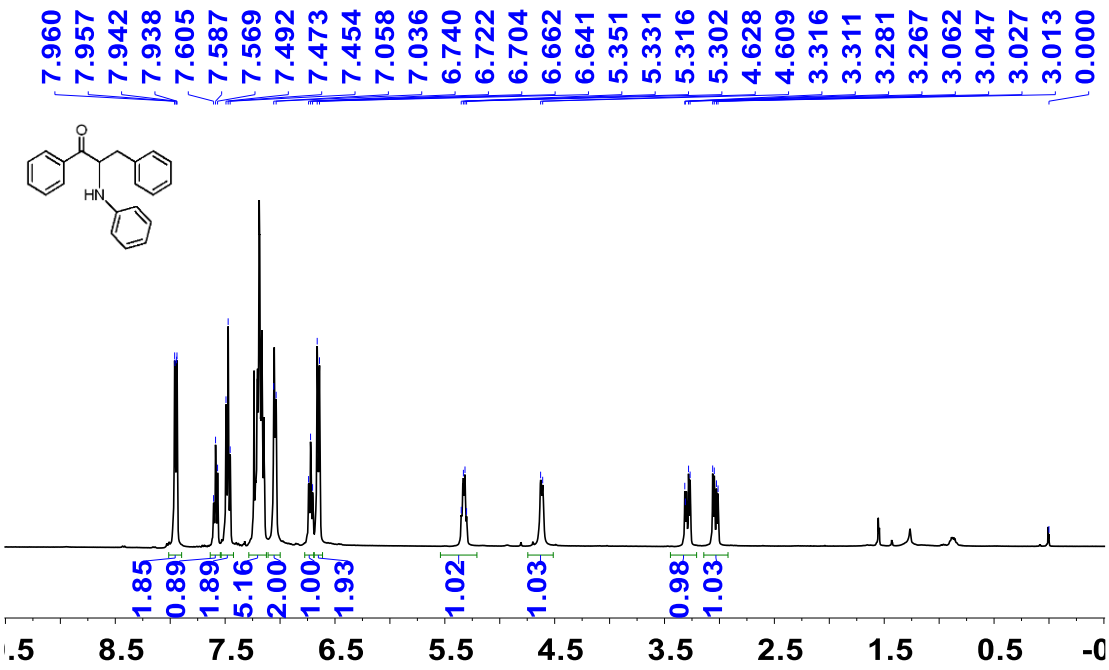


^{13}C NMR (101 MHz, $CDCl_3$) of **4t**

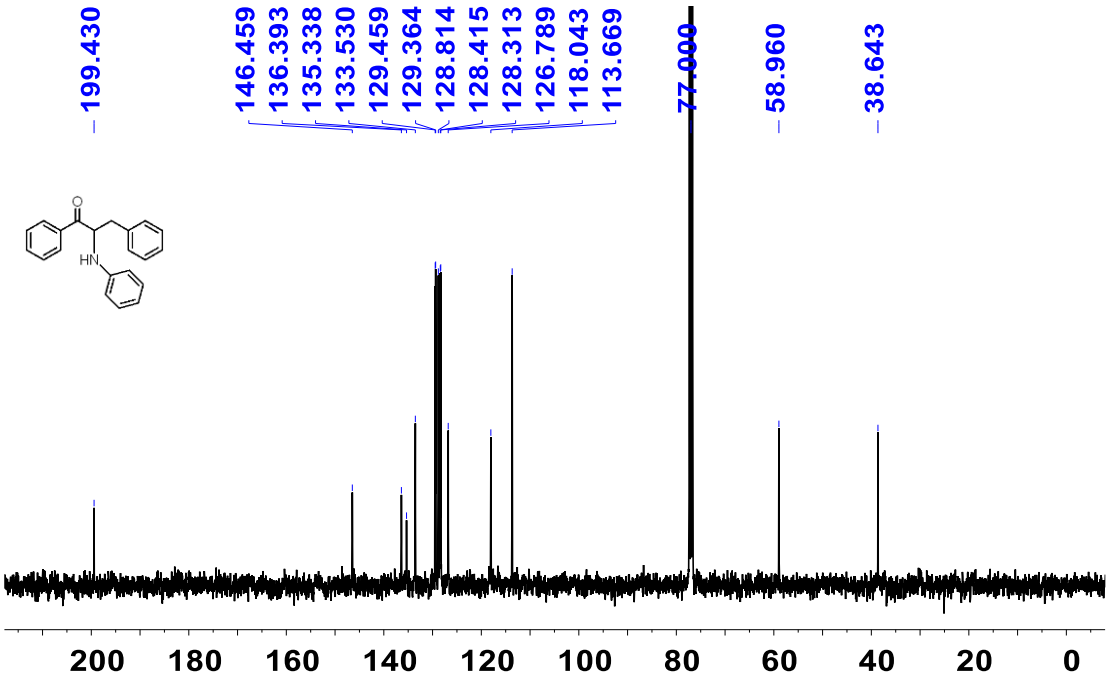


1,3-diphenyl-2-(phenylamino)propan-1-one (**4u**)

^{1}H NMR (400 MHz, $CDCl_3$) of **4u**

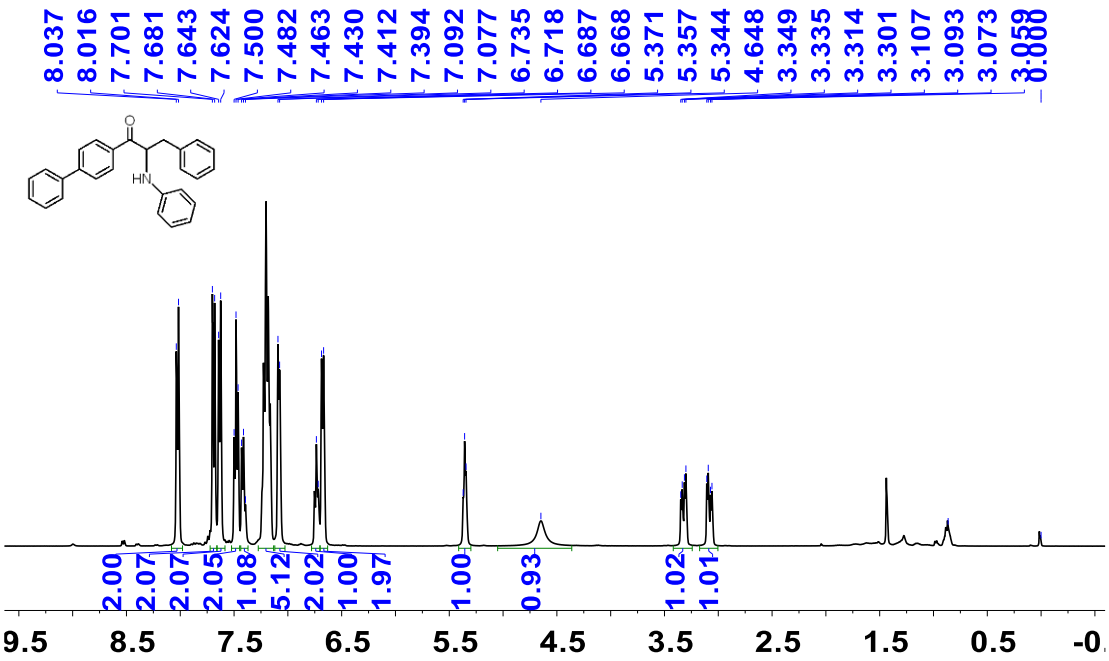


^{13}C NMR (101 MHz, $CDCl_3$) of **4u**

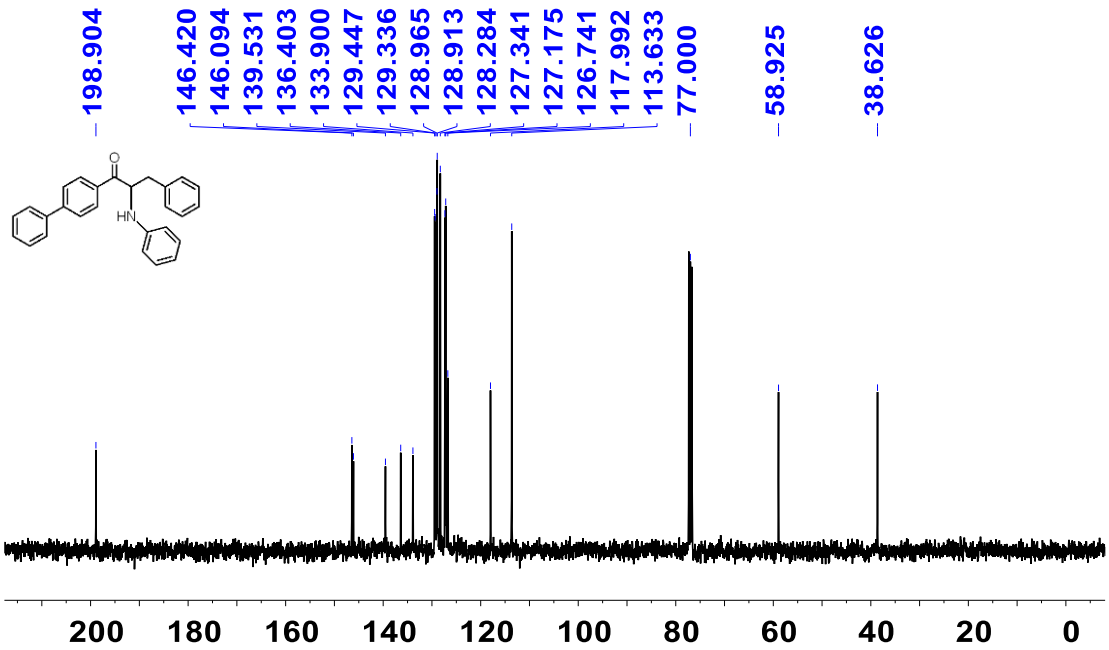


1-([1,1'-biphenyl]-4-yl)-3-phenyl-2-(phenylamino)propan-1-one (**4v**)

^{1}H NMR (400 MHz, $CDCl_3$) of **4v**

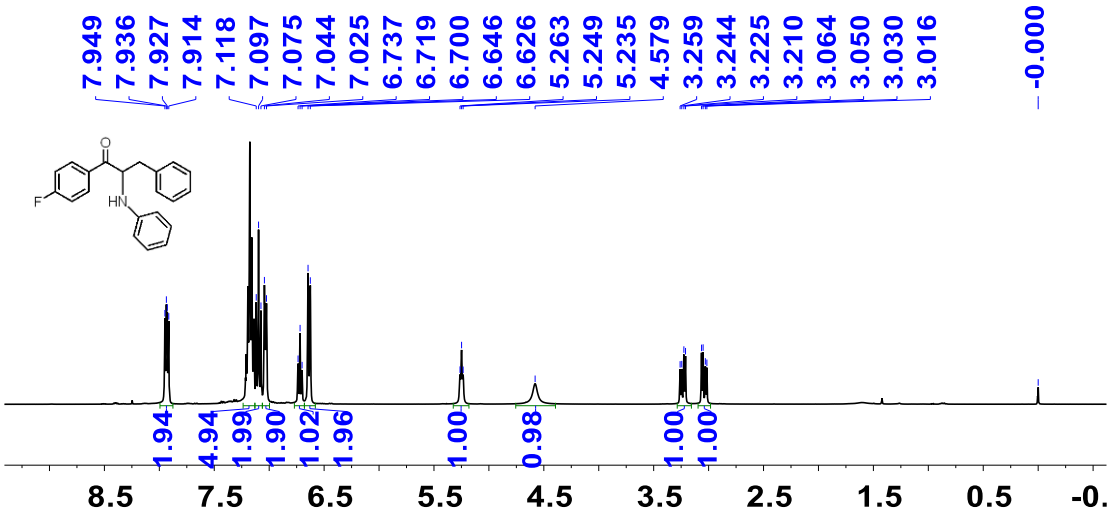


^{13}C NMR (101 MHz, $CDCl_3$) of **4v**

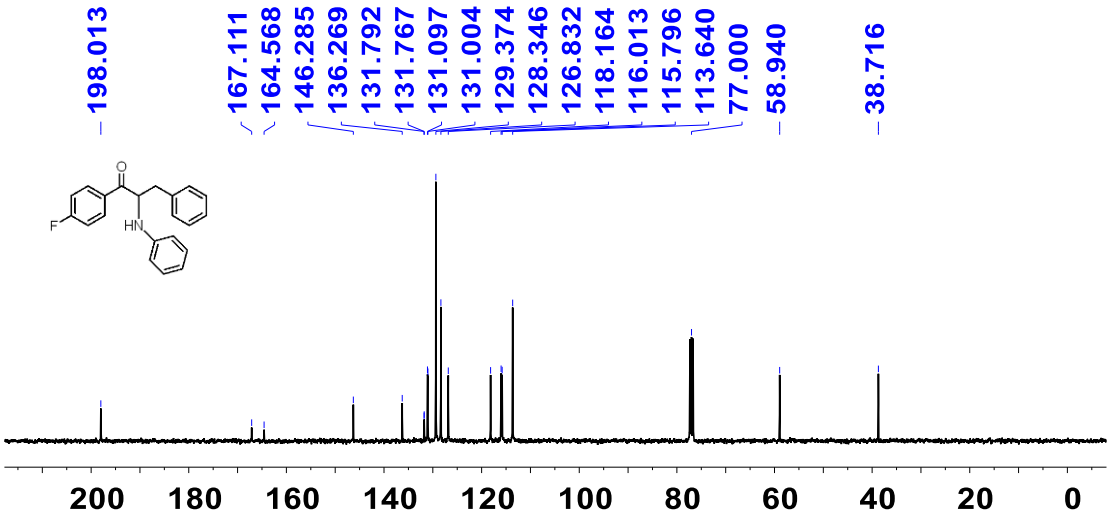


1-(4-fluorophenyl)-3-phenyl-2-(phenylamino)propan-1-one (**4w**)

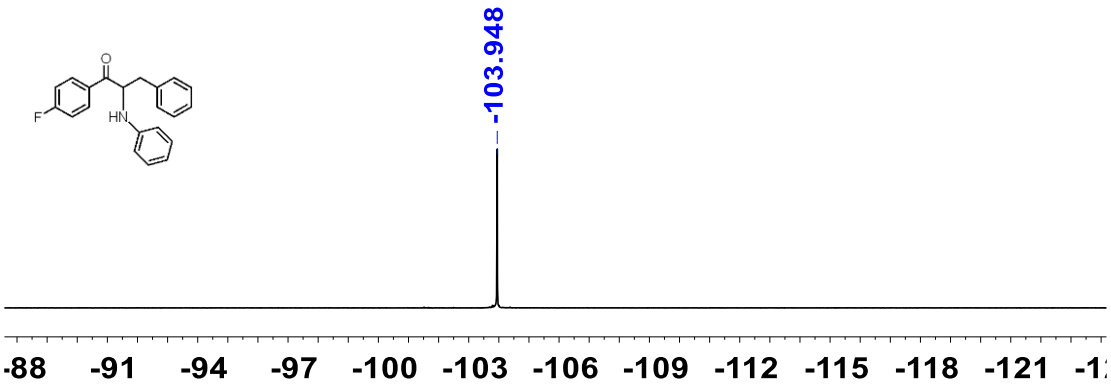
^{1}H NMR (400 MHz, $CDCl_3$) of **4w**



^{13}C NMR (101 MHz, $CDCl_3$) of **4w**

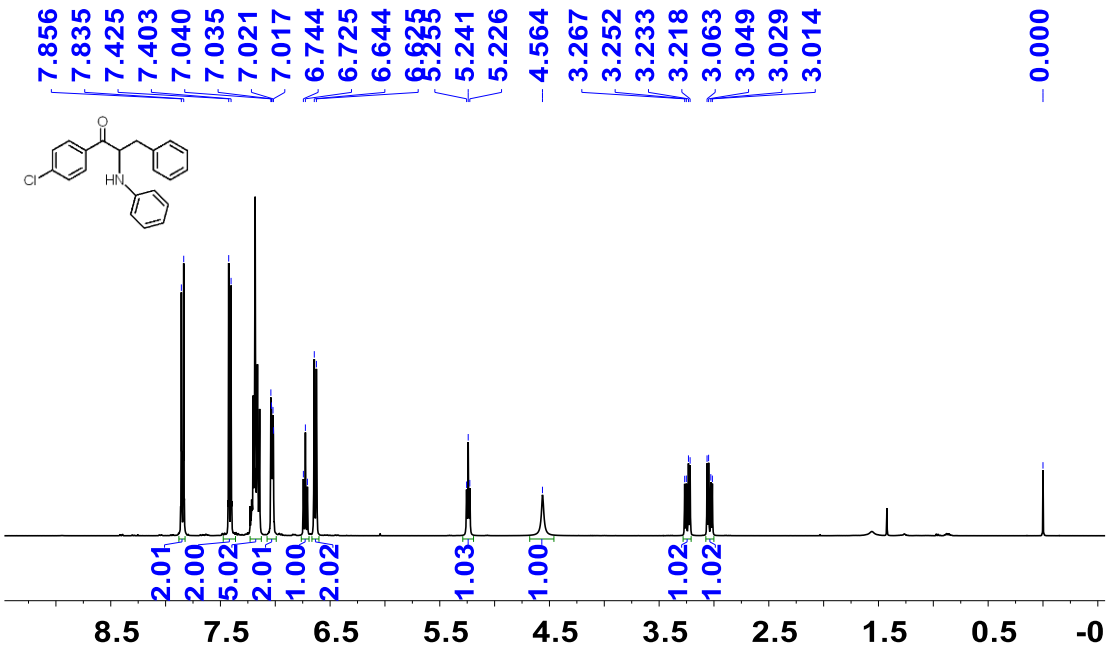


^{19}F NMR (376.5 MHz, $CDCl_3$) of **4w**

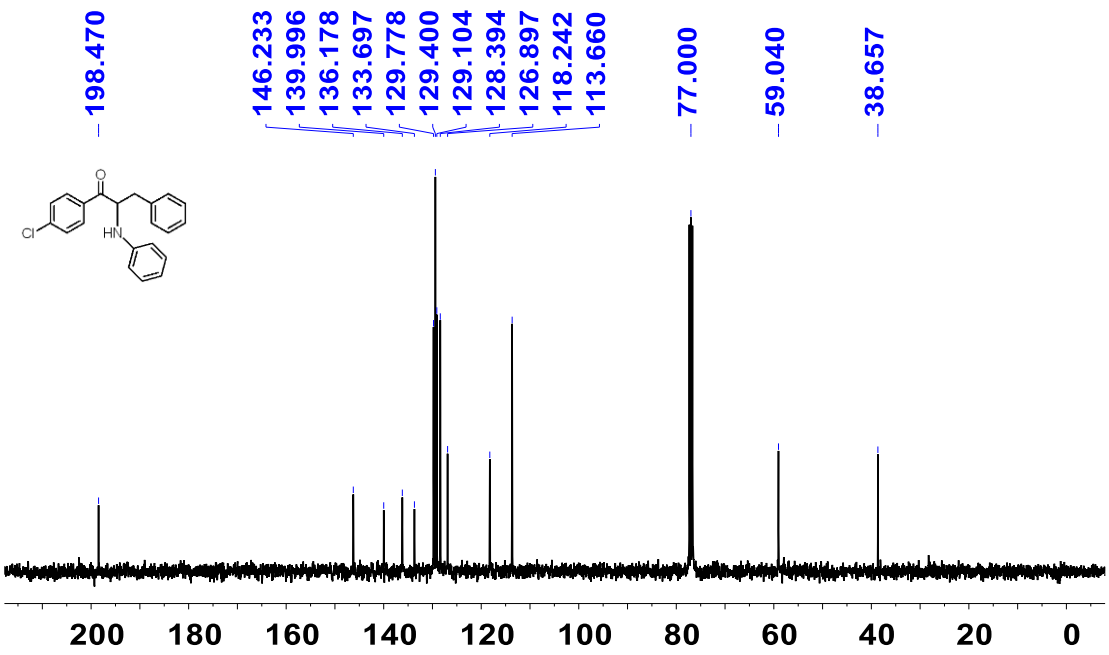


1-(4-chlorophenyl)-3-phenyl-2-(phenylamino)propan-1-one (**4x**)

^{1}H NMR (400 MHz, $CDCl_3$) of **4x**

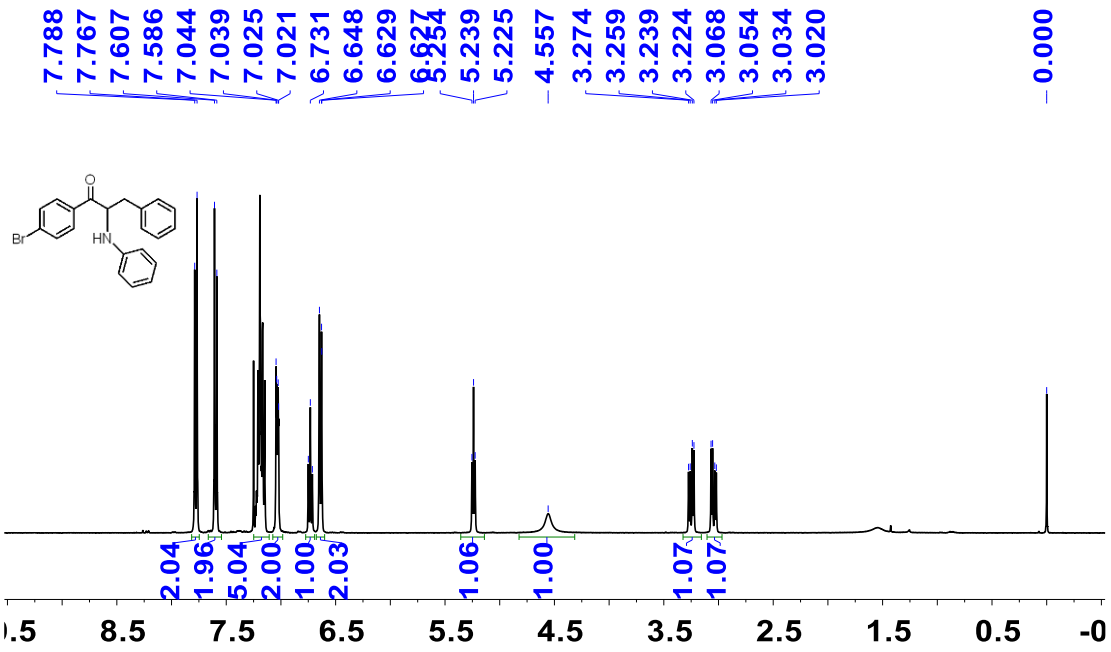


^{13}C NMR (101 MHz, $CDCl_3$) of **4x**

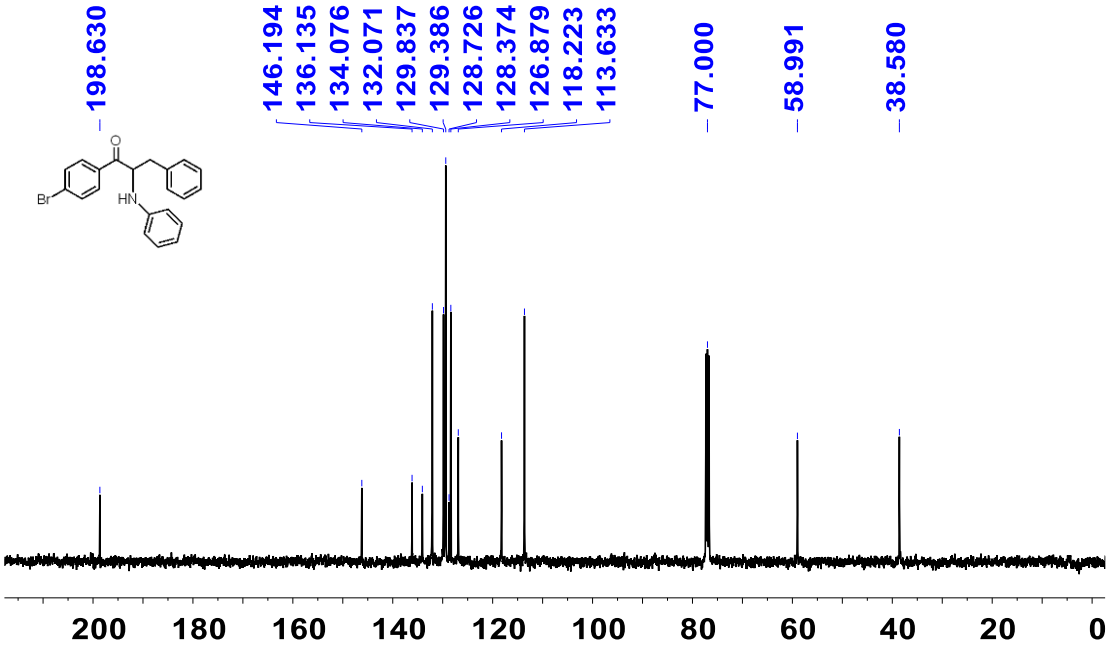


1-(4-bromophenyl)-3-phenyl-2-(phenylamino)propan-1-one (**4y**)

^{1}H NMR (400 MHz, $CDCl_3$) of **4y**

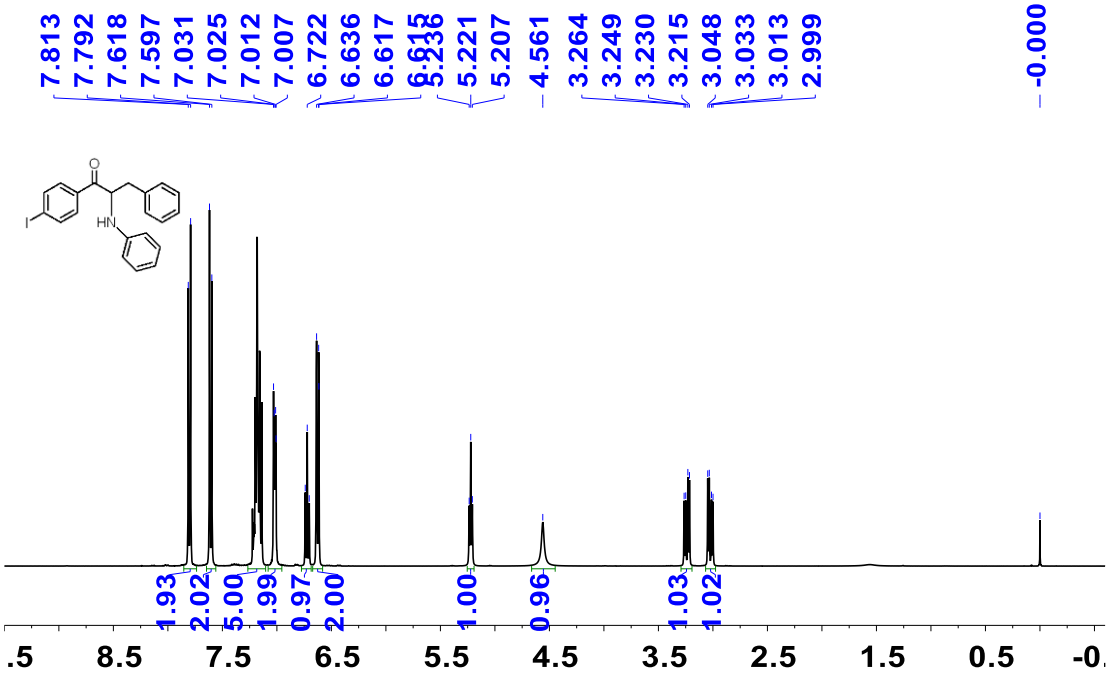


^{13}C NMR (101 MHz, $CDCl_3$) of **4y**

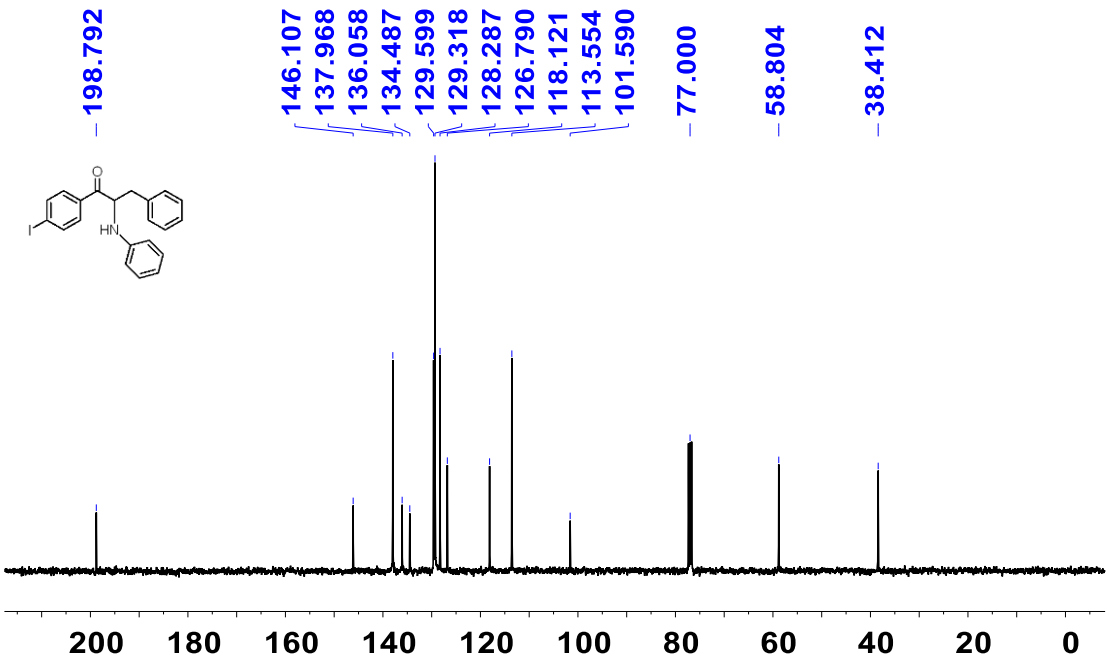


1-(4-iodophenyl)-3-phenyl-2-(phenylamino)propan-1-one (**4z**)

^{1}H NMR (400 MHz, $CDCl_3$) of **4z**

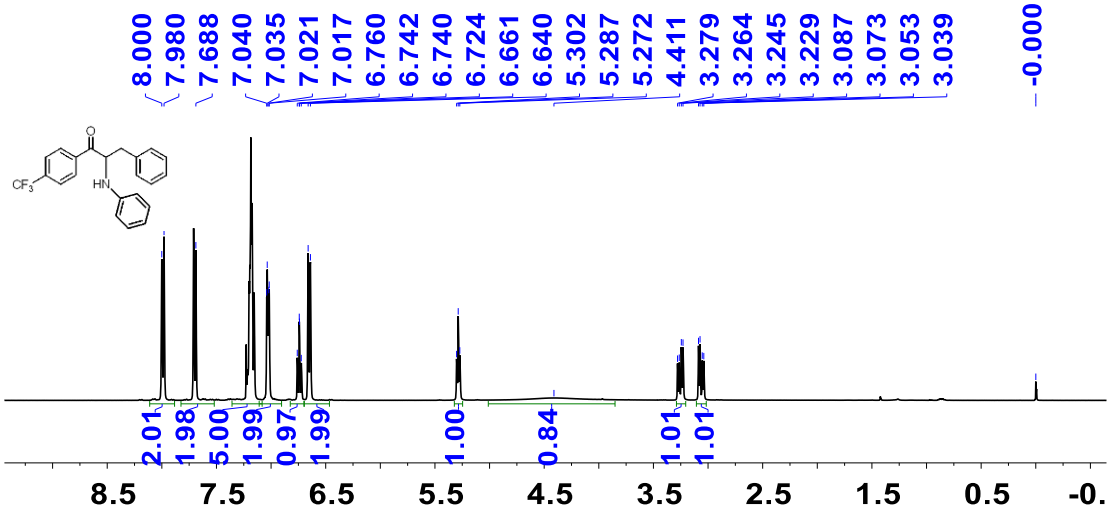


^{13}C NMR (101 MHz, $CDCl_3$) of **4z**

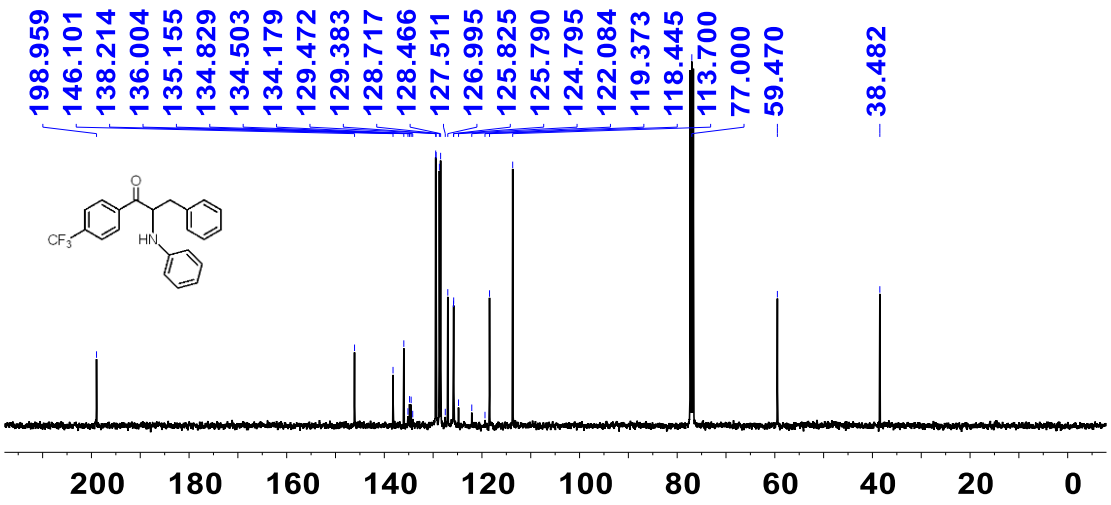


3-phenyl-2-(phenylamino)-1-(4-(trifluoromethyl)phenyl)propan-1-one (**4aa**)

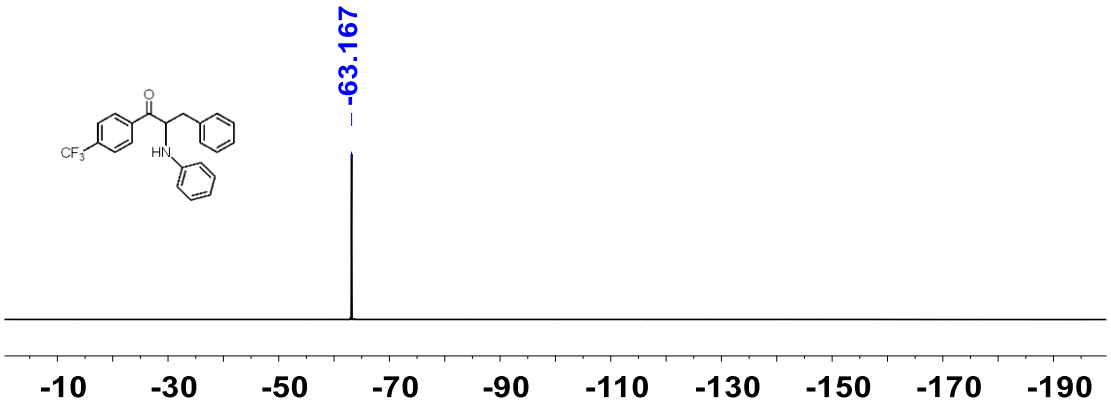
^{1}H NMR (400 MHz, $CDCl_3$) of **4aa**



^{13}C NMR (101 MHz, $CDCl_3$) of **4aa**

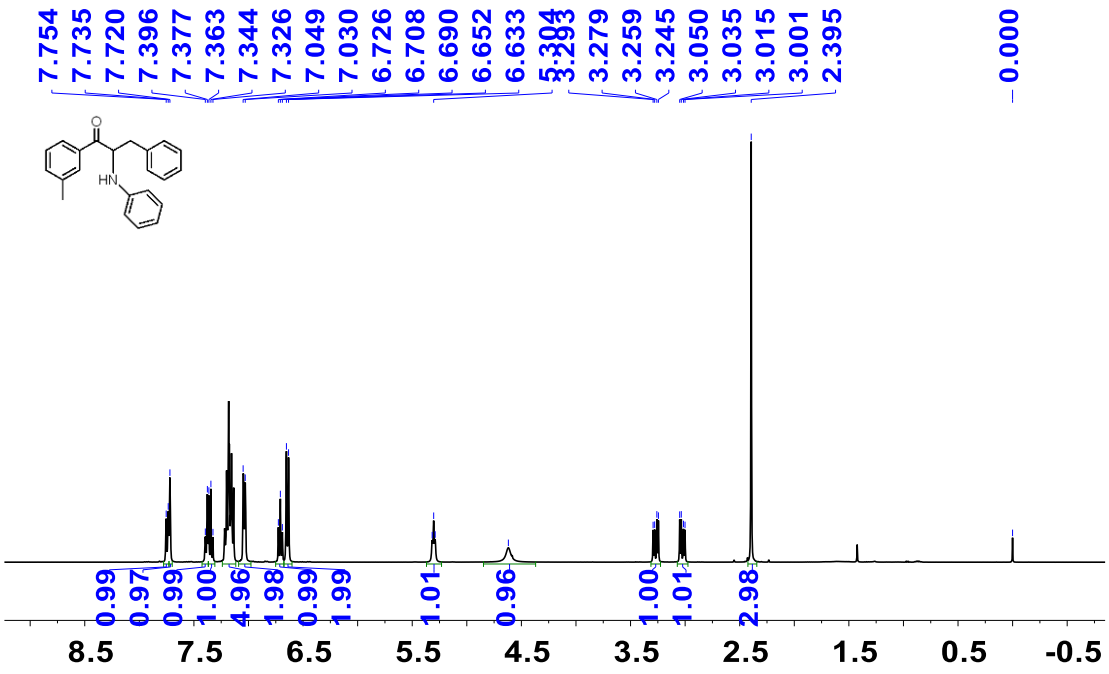


^{19}F NMR (376.5 MHz, $CDCl_3$) of **4aa**

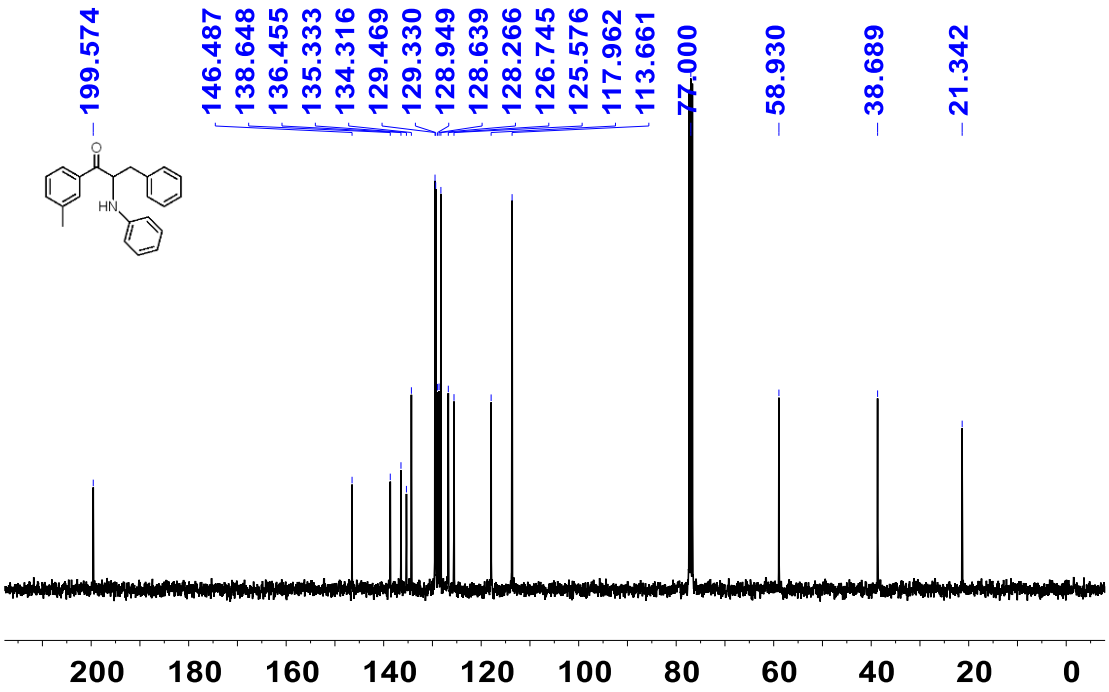


3-phenyl-2-(phenylamino)-1-(*m*-tolyl)propan-1-one (**4ab**)

^{1}H NMR (400 MHz, $CDCl_3$) of **4ab**

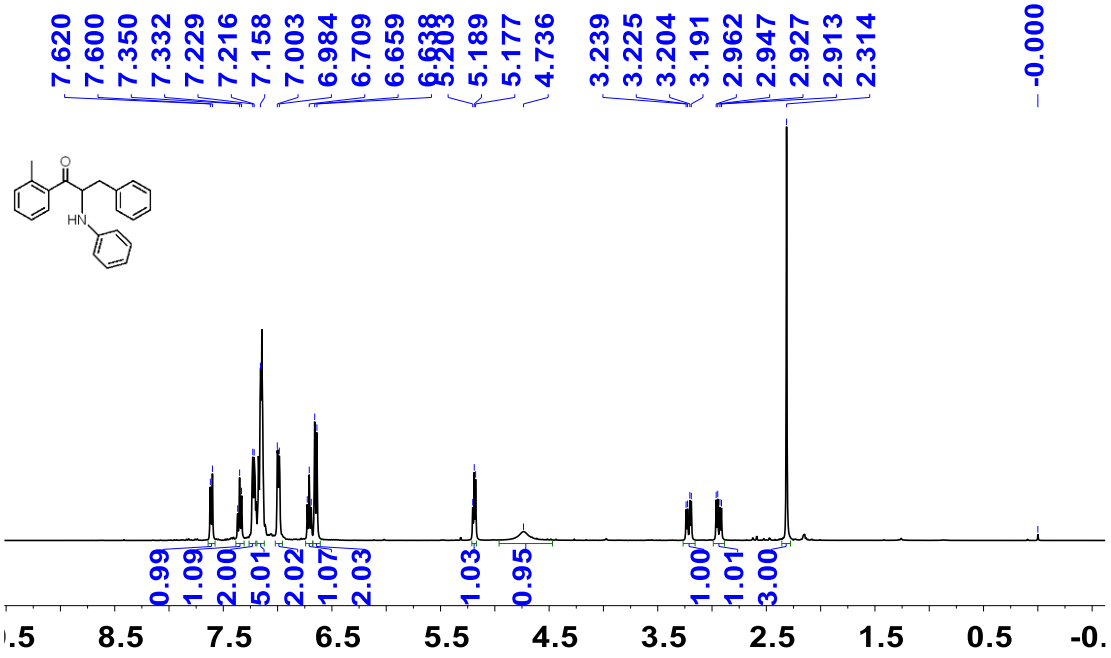


^{13}C NMR (101 MHz, $CDCl_3$) of **4ab**

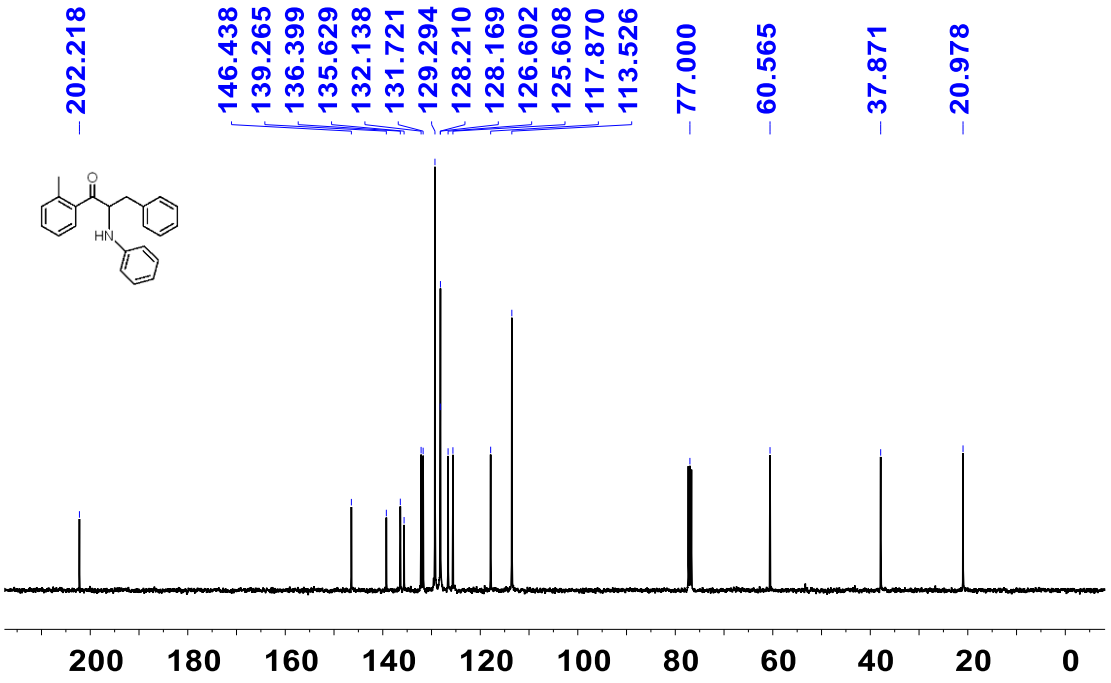


3-phenyl-2-(phenylamino)-1-(*o*-tolyl)propan-1-one (**4ac**)

^{1}H NMR (400 MHz, $CDCl_3$) of **4ac**

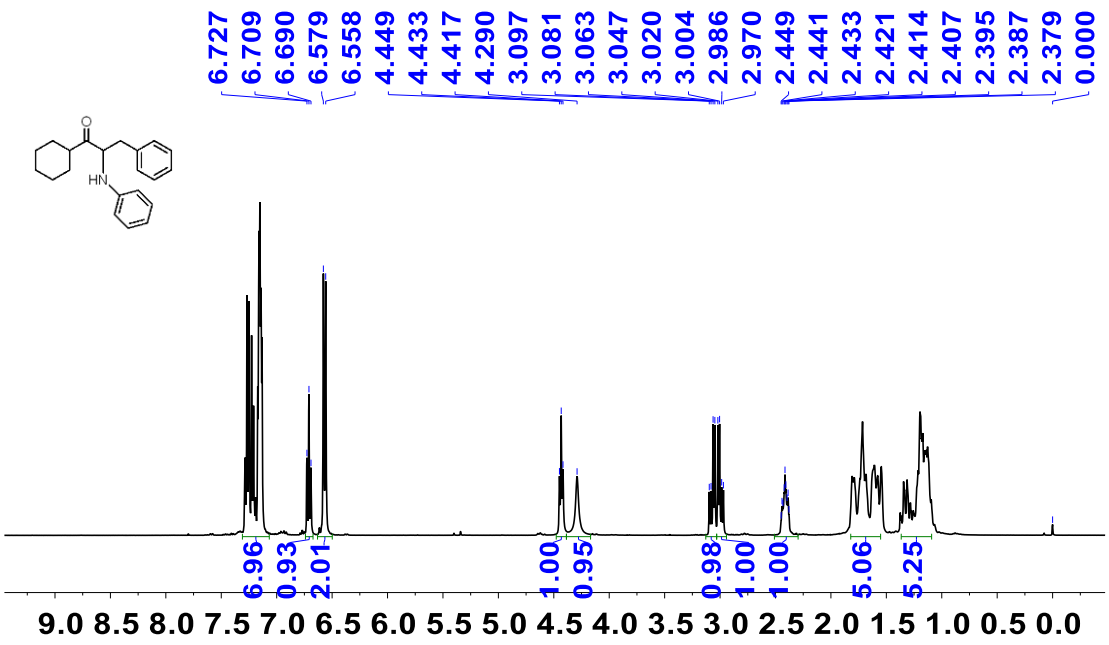


^{13}C NMR (101 MHz, $CDCl_3$) of **4ac**

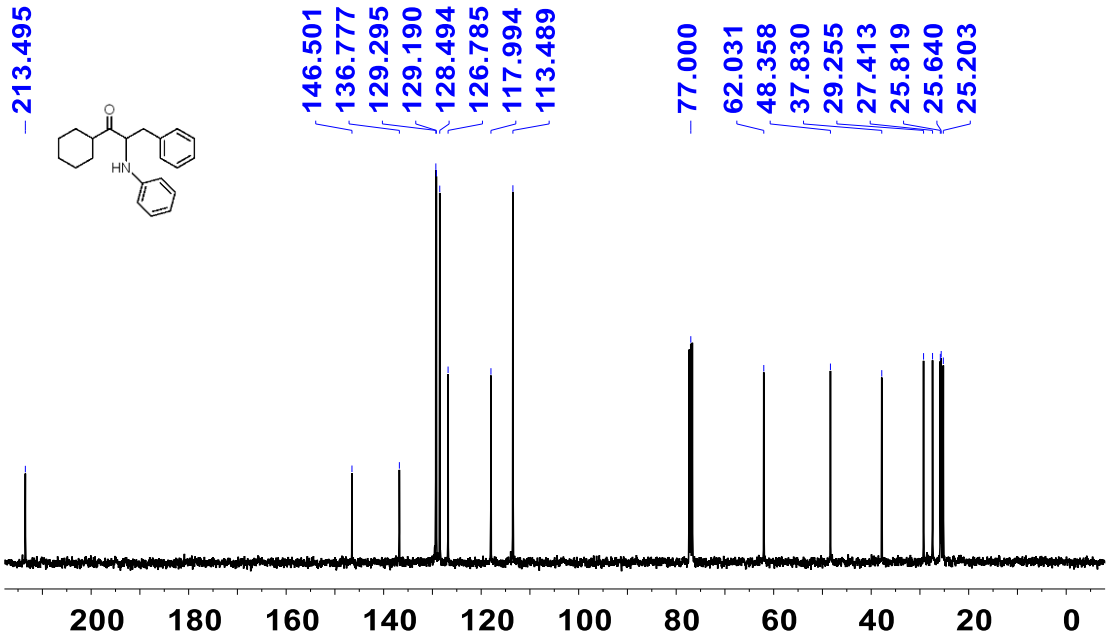


1-cyclohexyl-3-phenyl-2-(phenylamino)propan-1-one (**4ad**)

^{1}H NMR (400 MHz, $CDCl_3$) of **4ad**

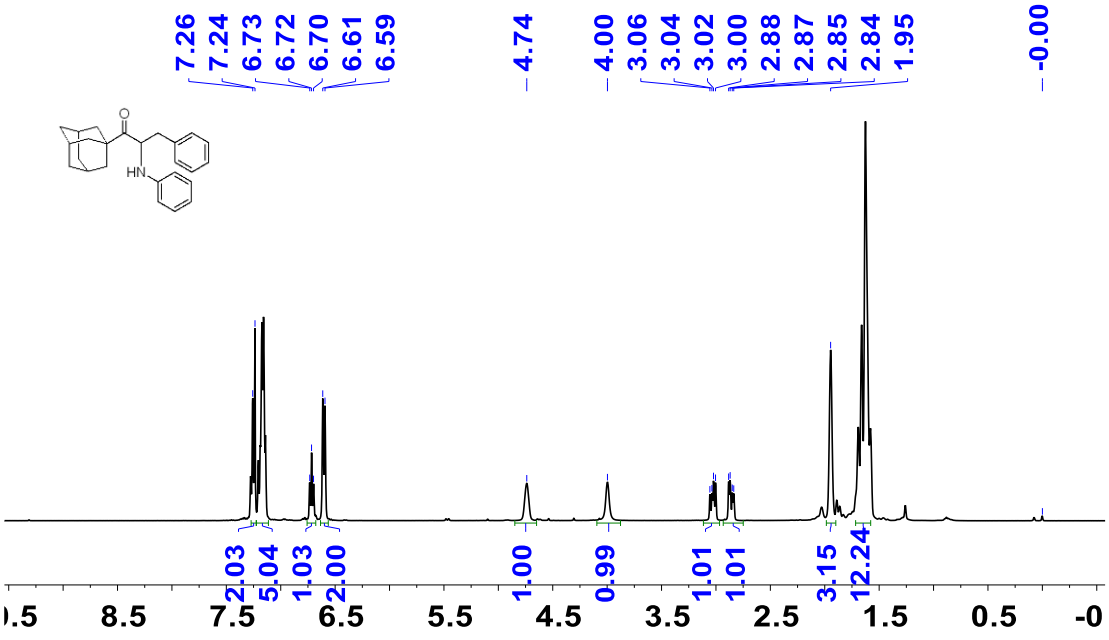


^{13}C NMR (101 MHz, $CDCl_3$) of **4ad**

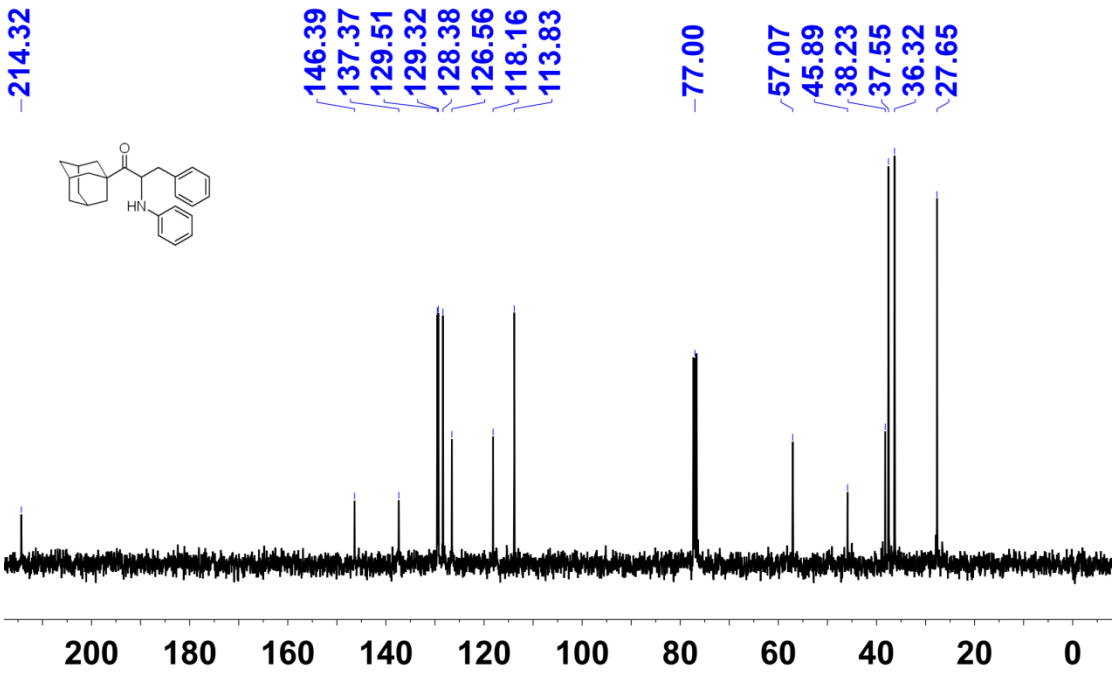


N-(1-((3*r*,5*r*,7*r*)-adamantan-1-yl)-1-oxo-3-phenylpropan-2-yl)benzenaminium (**4ae**)

^{1}H NMR (400 MHz, $CDCl_3$) of **4ae**

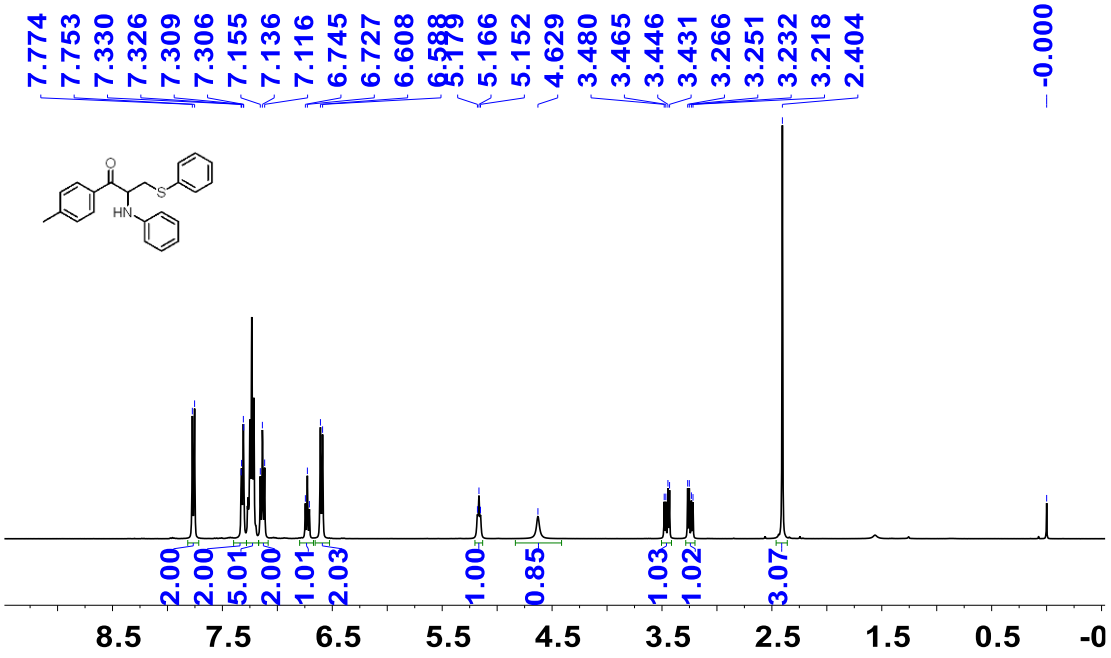


^{13}C NMR (101 MHz, $CDCl_3$) of **4ae**

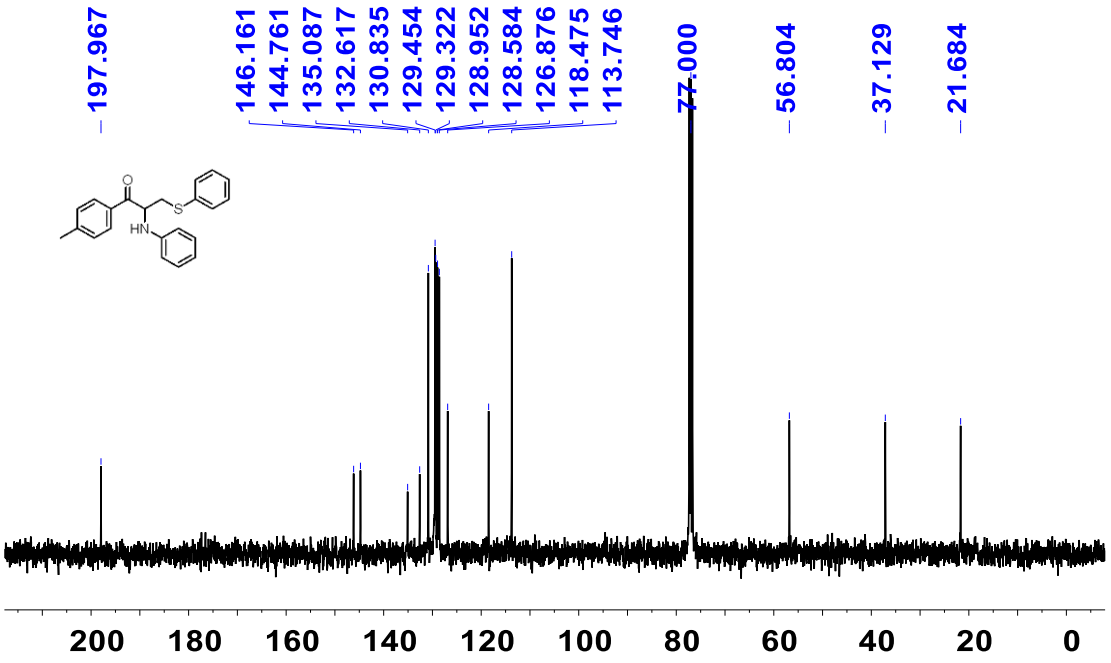


2-(phenylamino)-3-(phenylthio)-1-(p-tolyl)propan-1-one (**4af**)

^{1}H NMR (400 MHz, $CDCl_3$) of **4af**

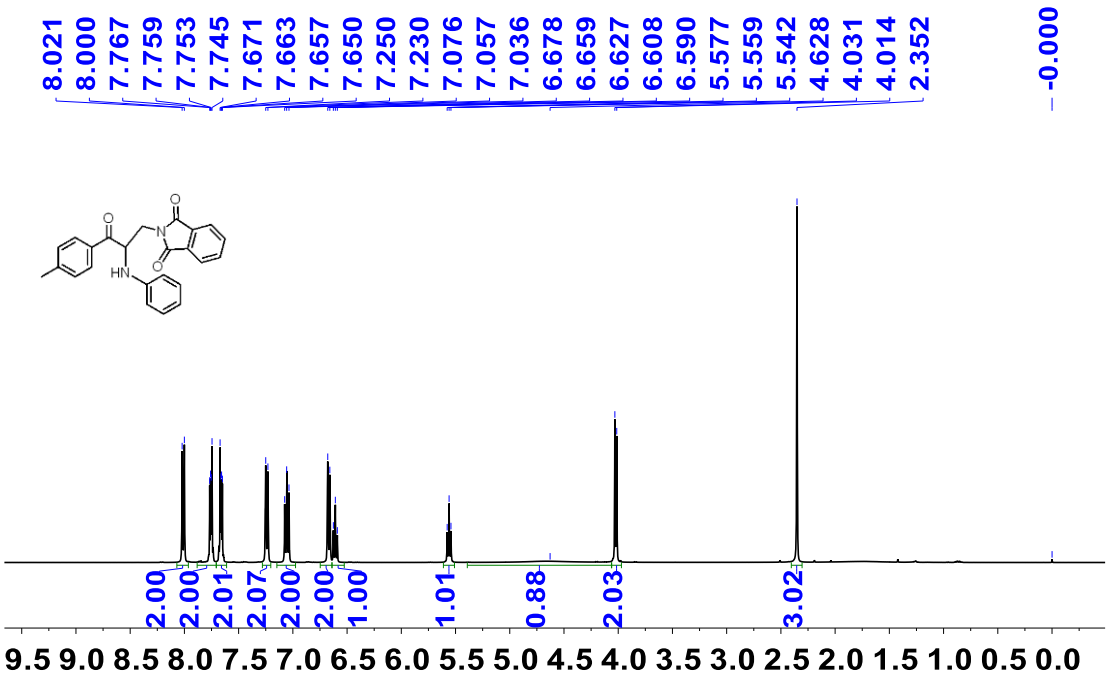


^{13}C NMR (101 MHz, $CDCl_3$) of **4af**

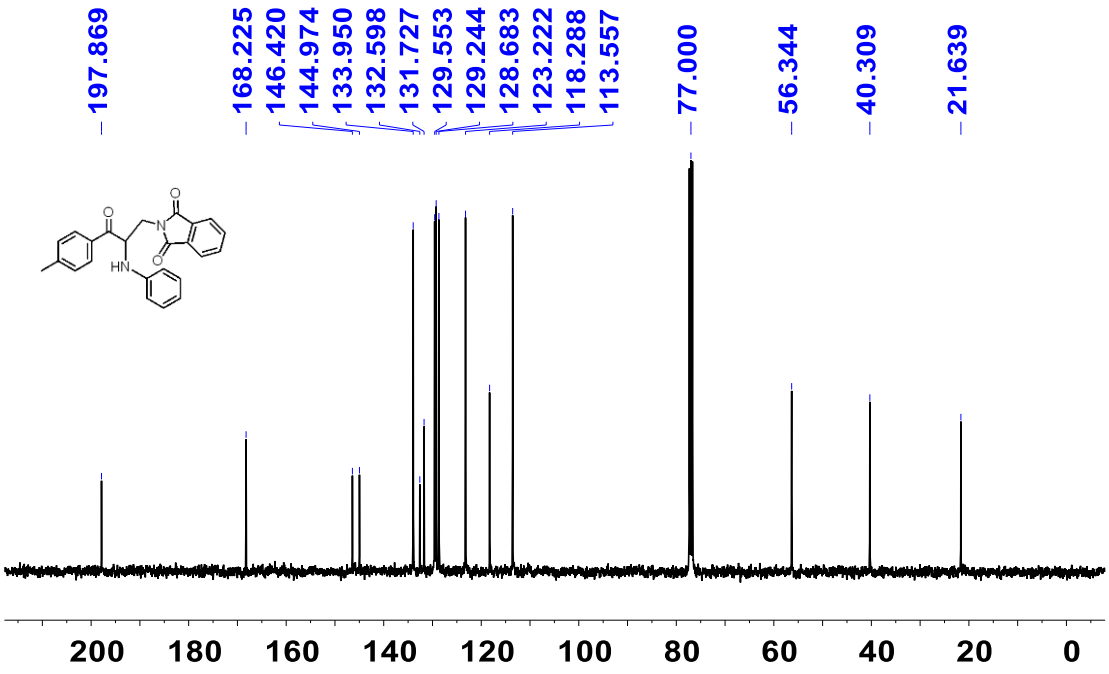


2-(3-oxo-2-(phenylamino)-3-(p-tolyl)propyl)isoindoline-1,3-dione (**4ag**)

^{1}H NMR (400 MHz, $CDCl_3$) of **4ag**

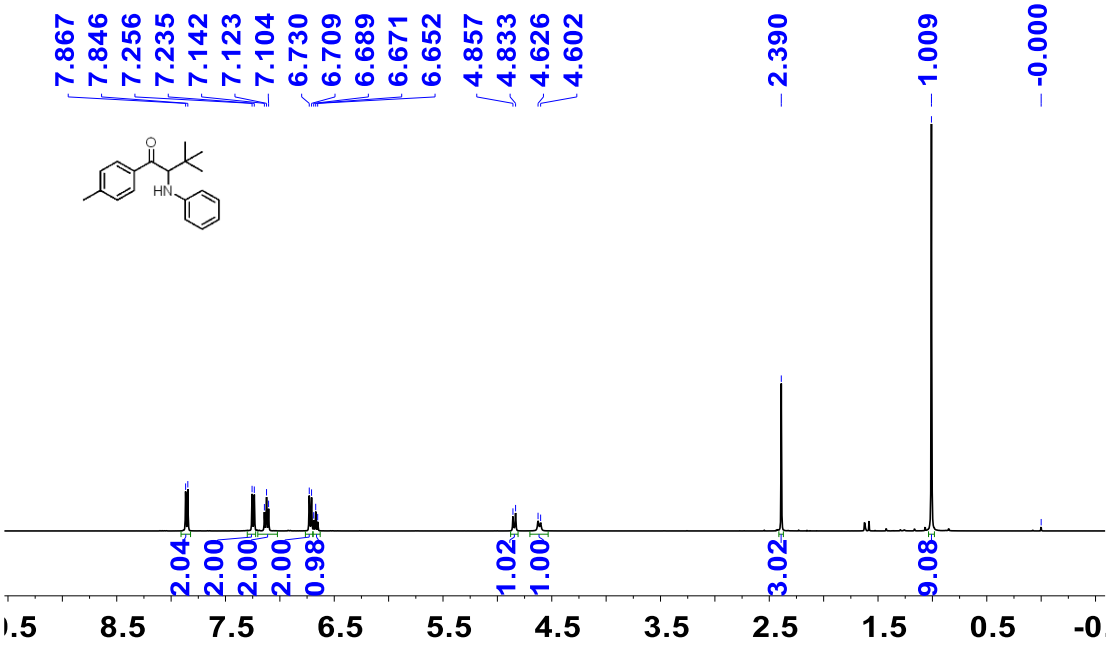


^{13}C NMR (101 MHz, $CDCl_3$) of **4ag**

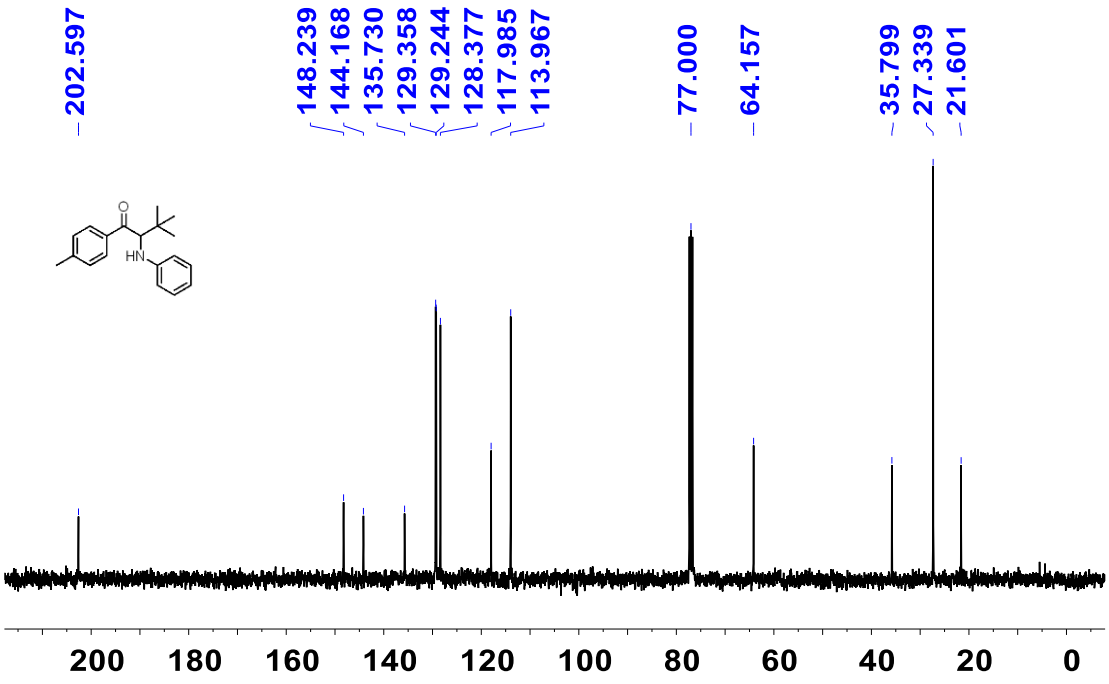


3,3-dimethyl-2-(phenylamino)-1-(*p*-tolyl)butan-1-one (**4ah**)

^{1}H NMR (400 MHz, $CDCl_3$) of **4ah**

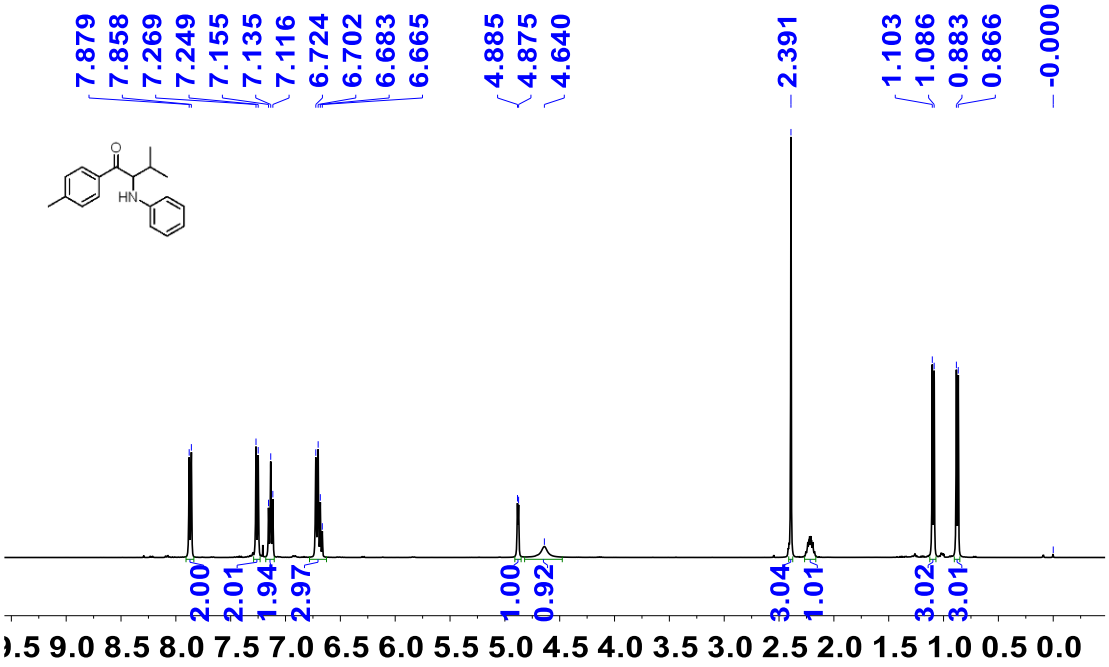


^{13}C NMR (101 MHz, $CDCl_3$) of **4ah**

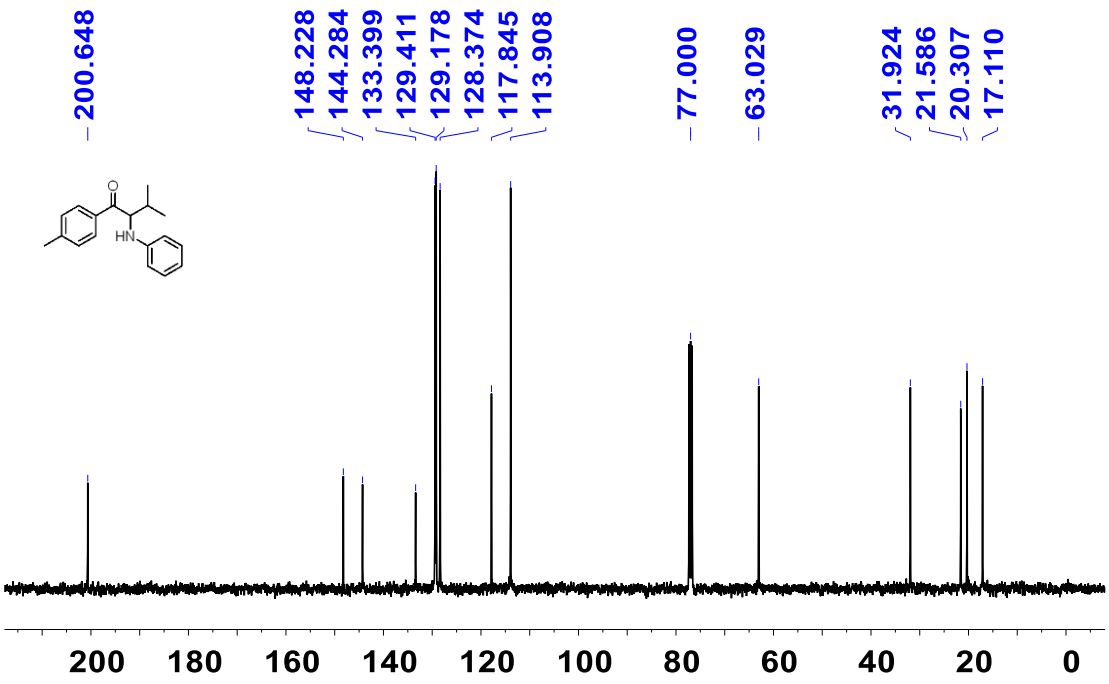


3-methyl-2-(phenylamino)-1-(*p*-tolyl)butan-1-one (**4ai**)

^{1}H NMR (400 MHz, $CDCl_3$) of **4ai**

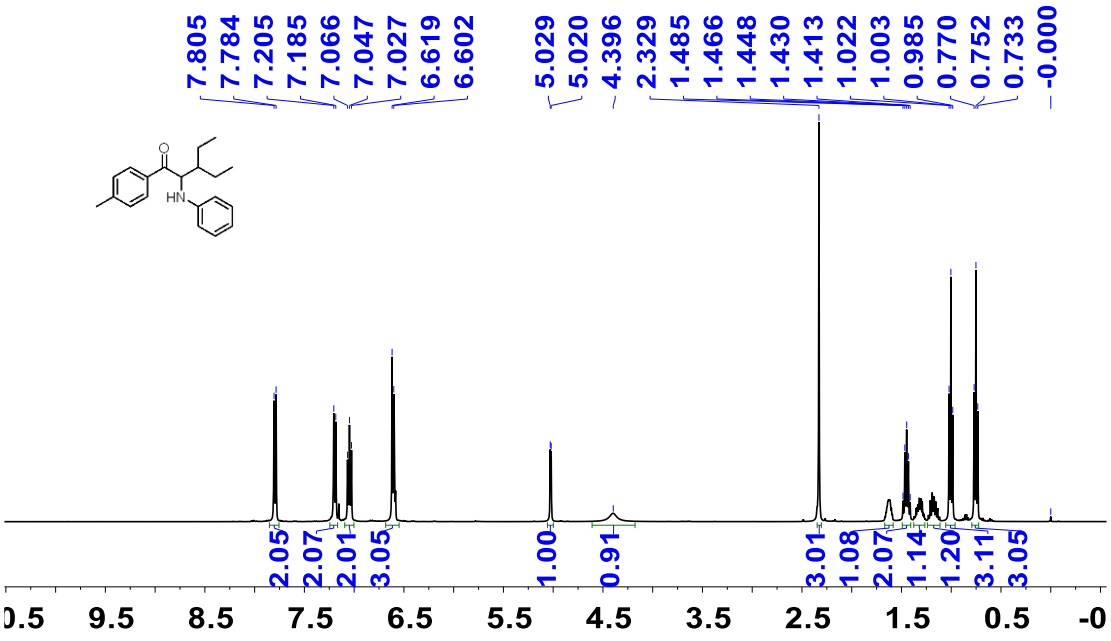


^{13}C NMR (101 MHz, $CDCl_3$) of **4ai**

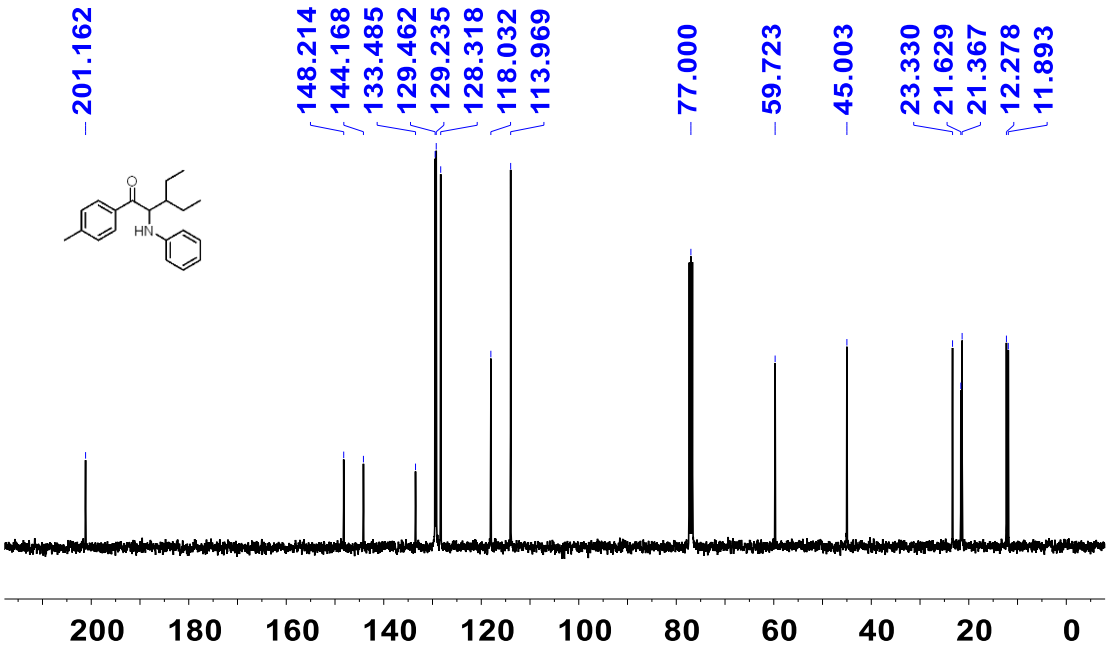


3-ethyl-2-(phenylamino)-1-(p-tolyl)pentan-1-one (**4aj**)

^{1}H NMR (400 MHz, $CDCl_3$) of **4aj**

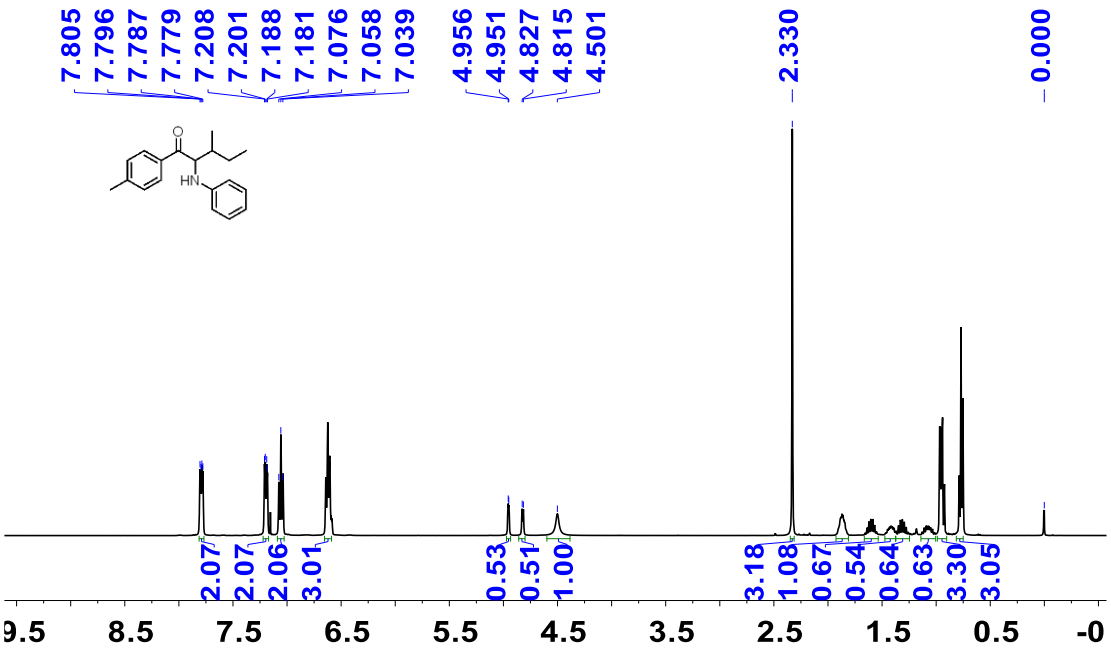


^{13}C NMR (101 MHz, $CDCl_3$) of **4aj**

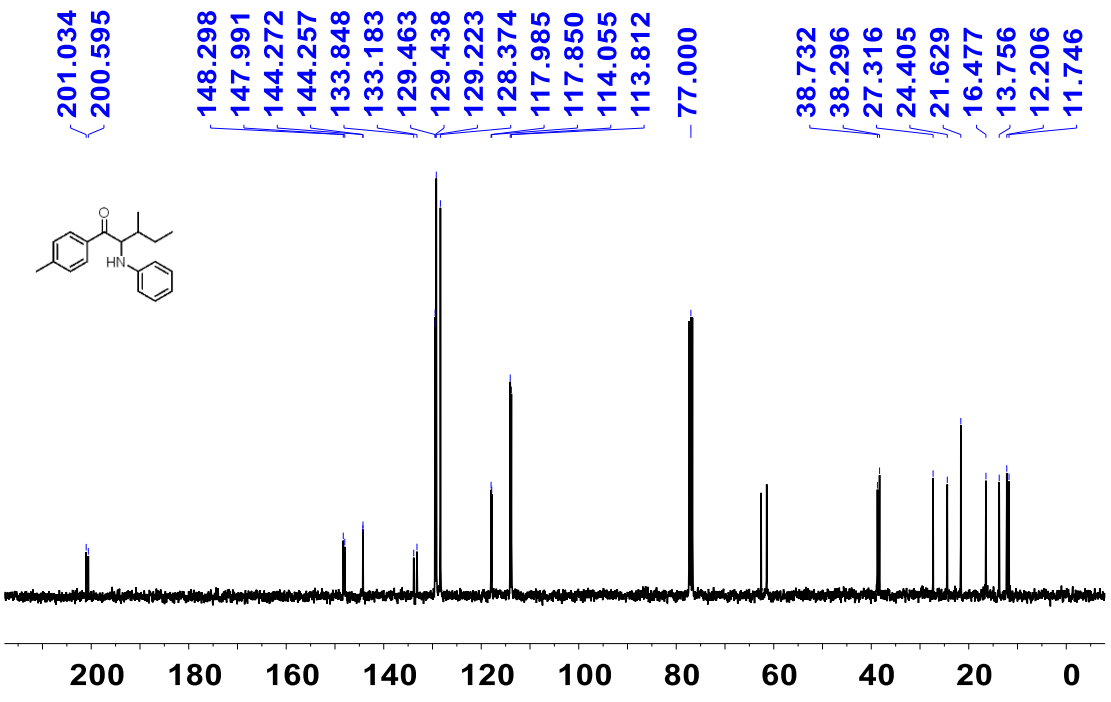


3-methyl-2-(phenylamino)-1-(p-tolyl)pentan-1-one (**4ak**)

^{1}H NMR (400 MHz, $CDCl_3$) of **4ak**

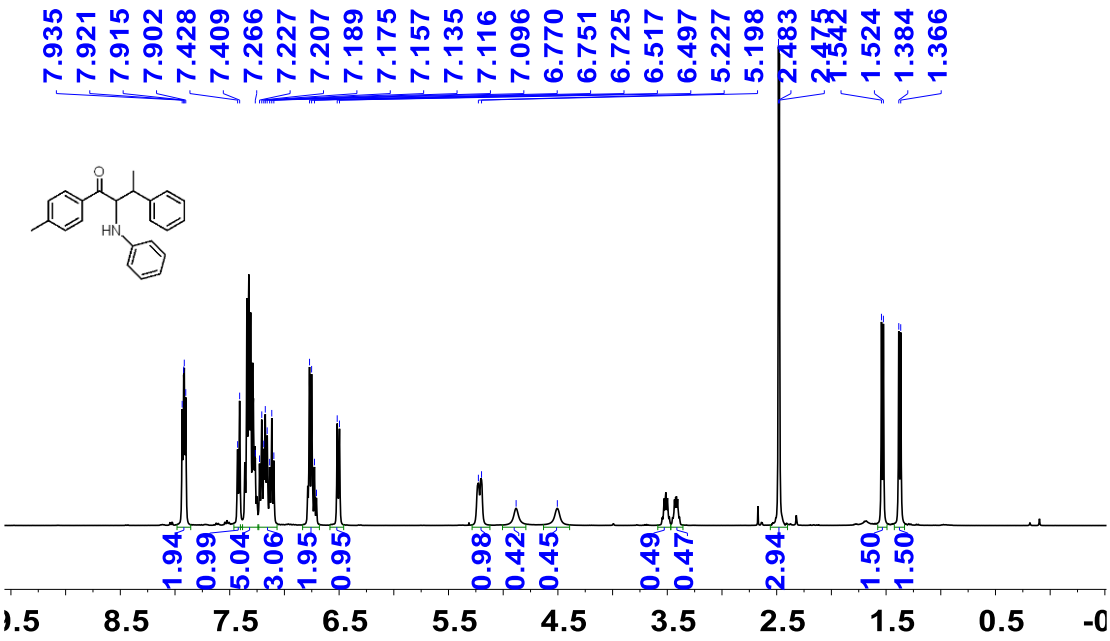


^{13}C NMR (101 MHz, $CDCl_3$) of **4ak**

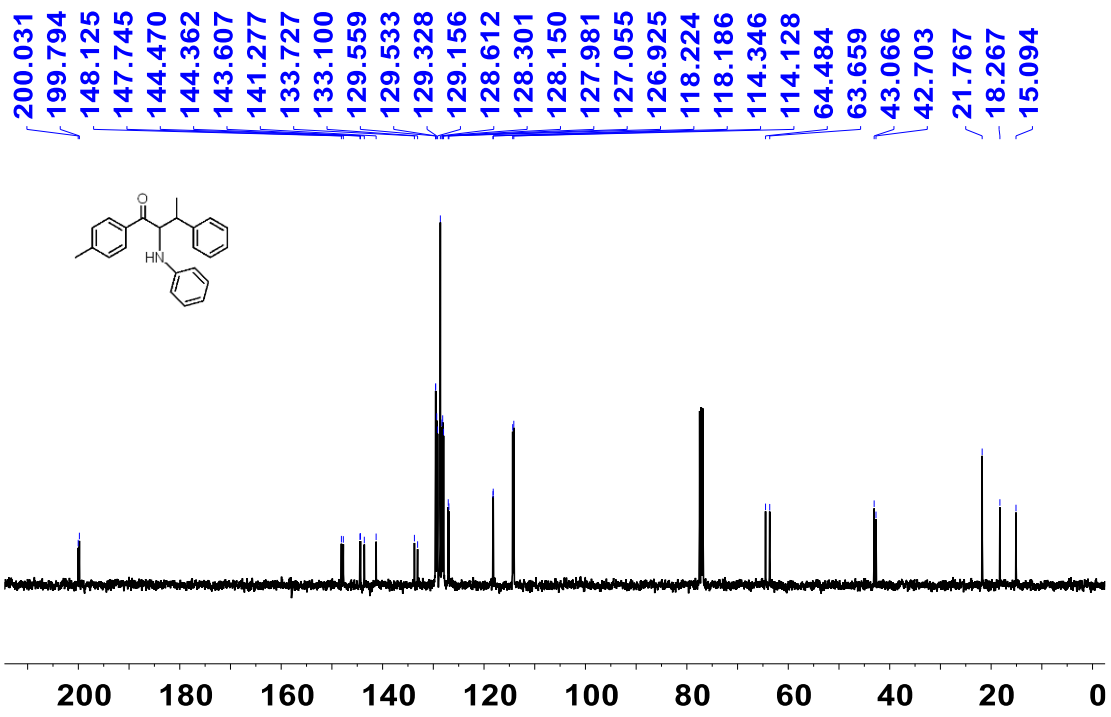


3-phenyl-2-(phenylamino)-1-(p-tolyl)butan-1-one (**4al**)

^{1}H NMR (400 MHz, $CDCl_3$) of **4al**

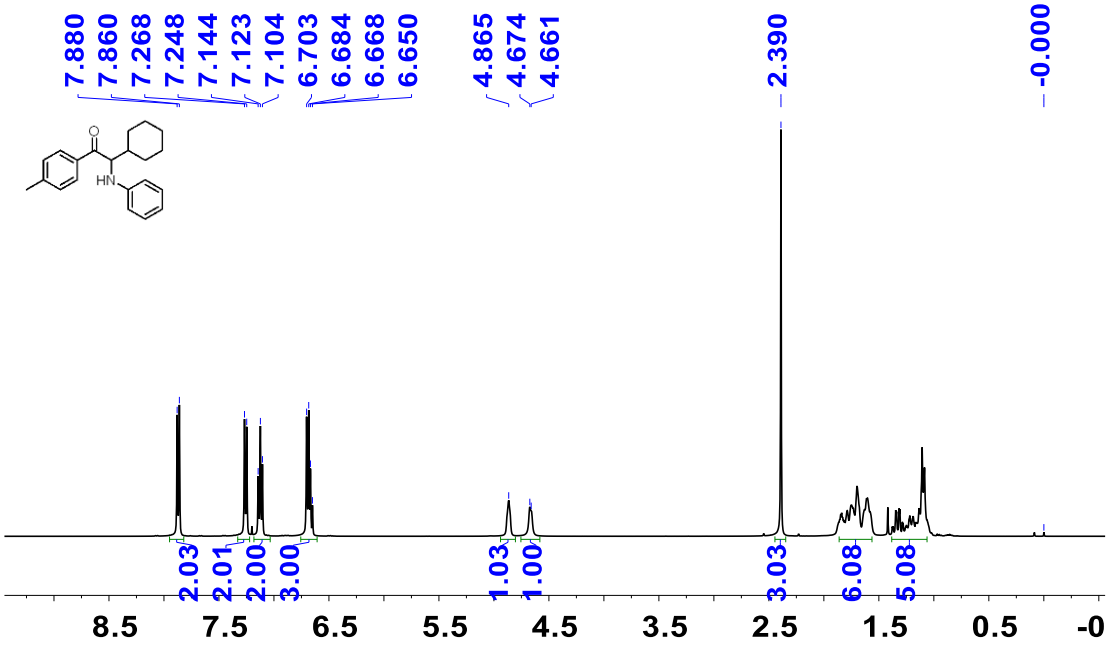


^{13}C NMR (101 MHz, $CDCl_3$) of **4al**

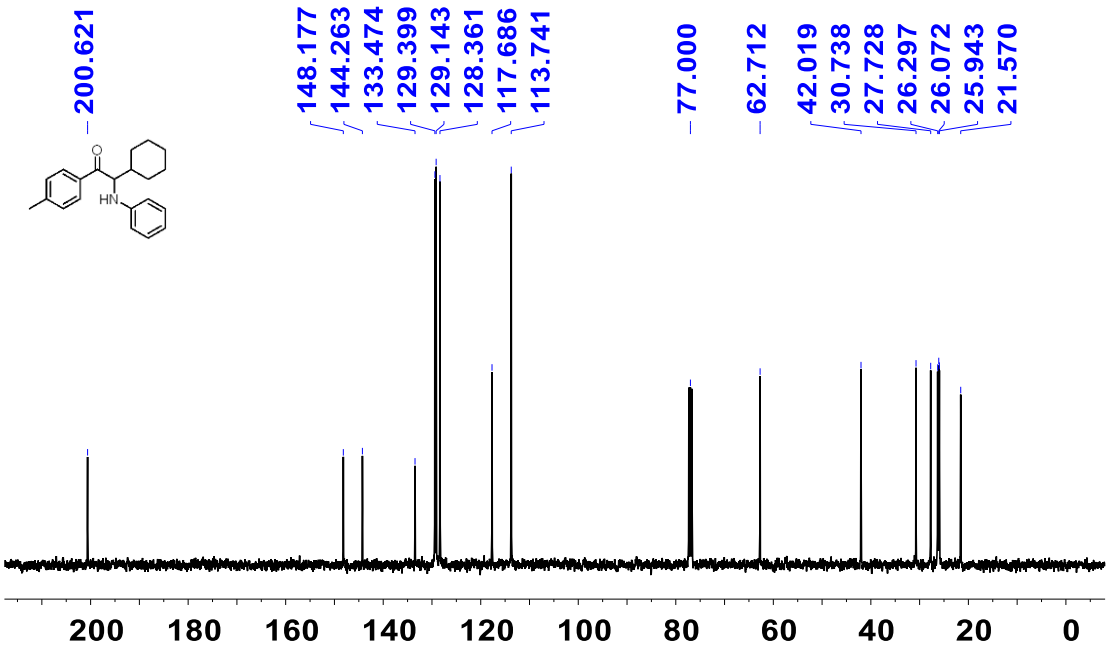


2-cyclohexyl-2-(phenylamino)-1-(*p*-tolyl)ethan-1-one (**4am**)

^{1}H NMR (400 MHz, $CDCl_3$) of **4am**

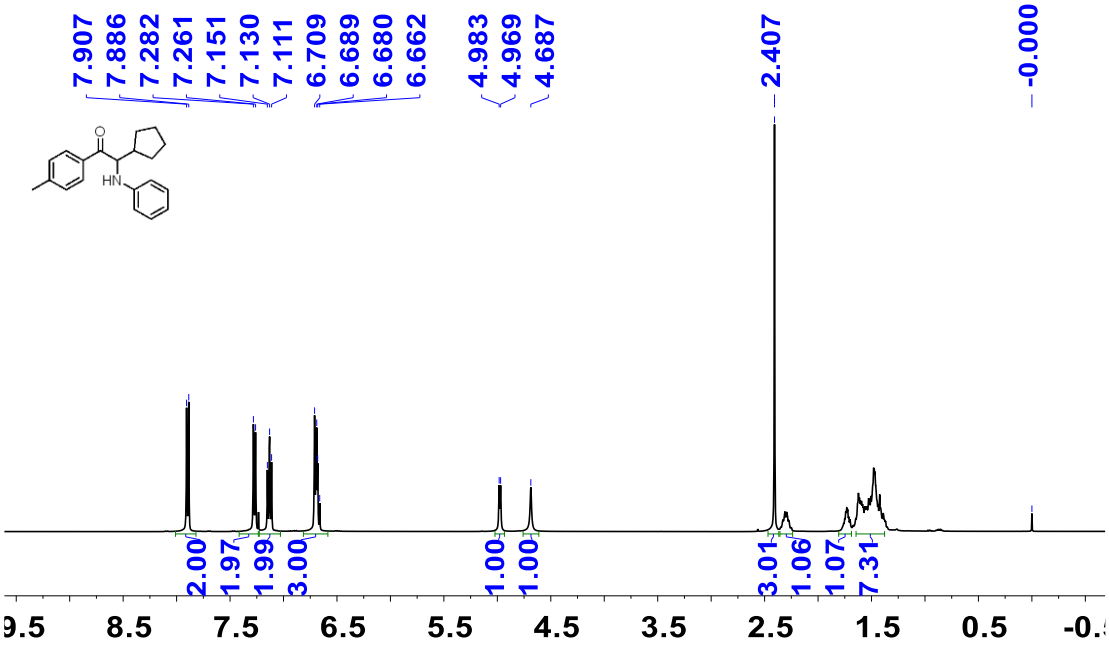


^{13}C NMR (101 MHz, $CDCl_3$) of **4am**

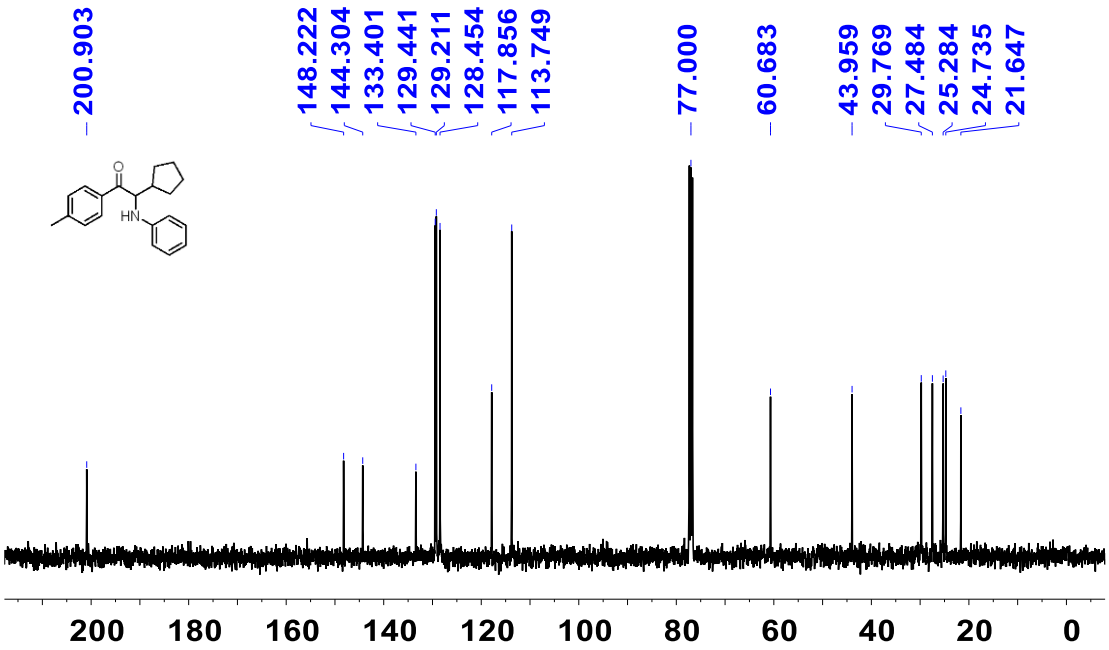


2-cyclopentyl-2-(phenylamino)-1-(*p*-tolyl)ethan-1-one (**4an**)

^{1}H NMR (400 MHz, $CDCl_3$) of **4an**

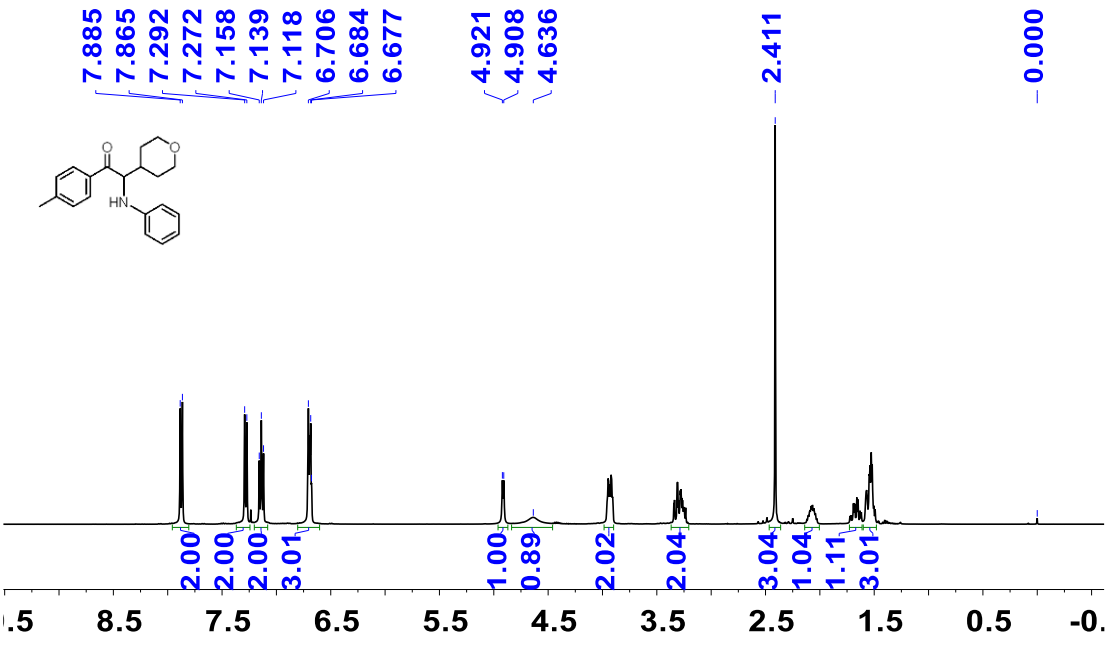


^{13}C NMR (101 MHz, $CDCl_3$) of **4an**

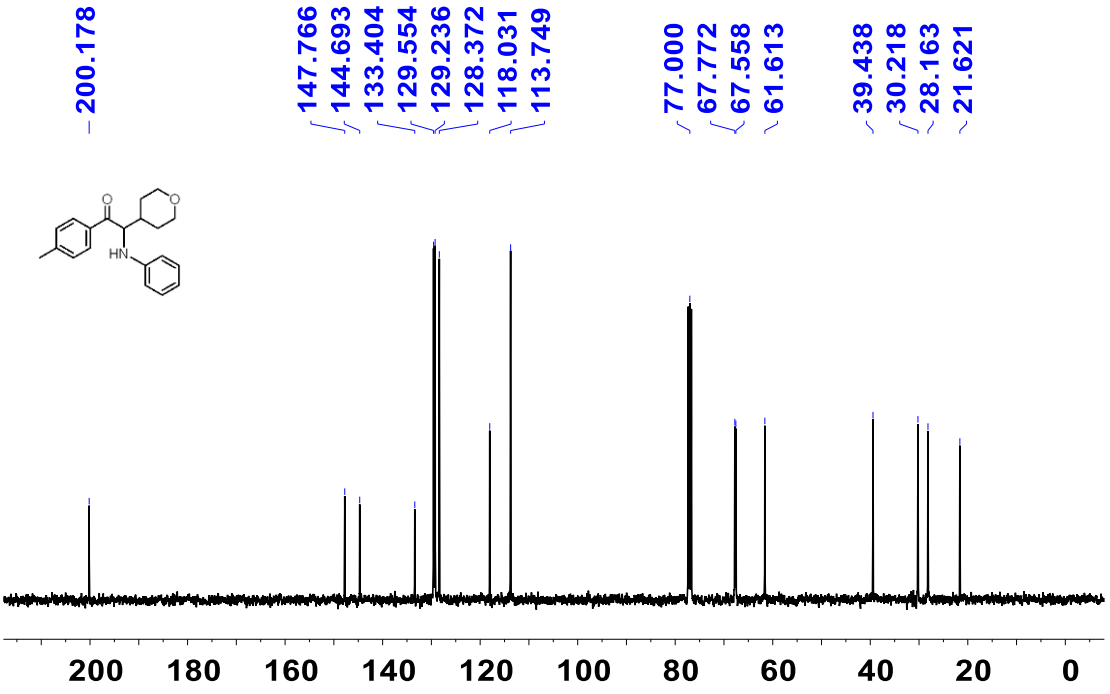


2-(phenylamino)-2-(tetrahydro-2*H*-pyran-4-yl)-1-(*p*-tolyl)ethan-1-one (**4ao**)

^{1}H NMR (400 MHz, $CDCl_3$) of **4ao**

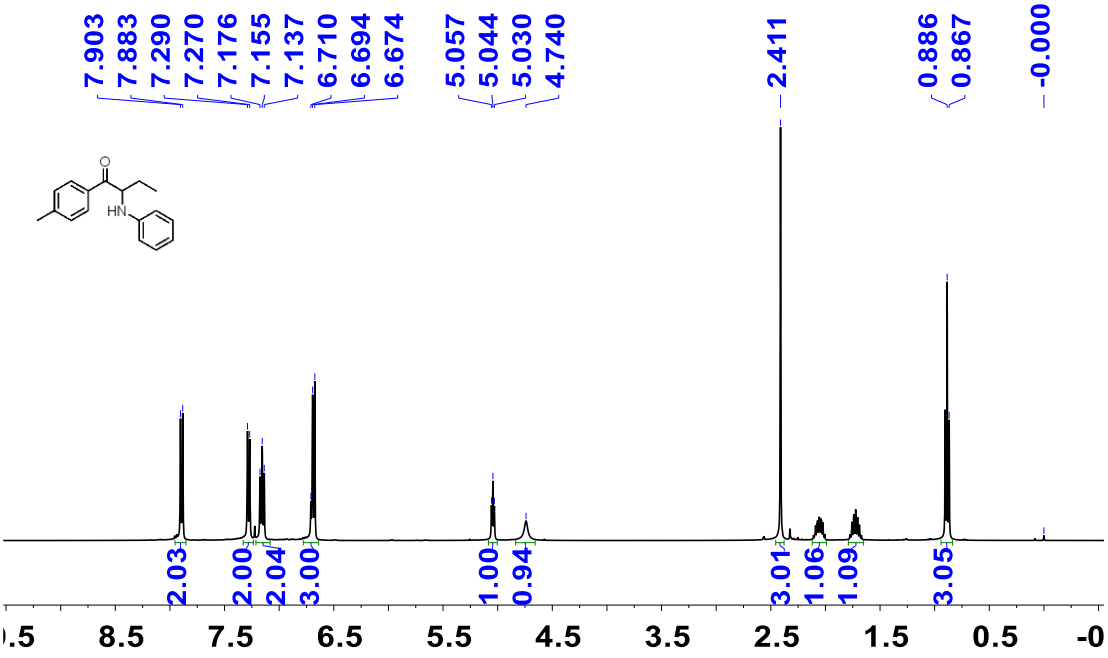


^{13}C NMR (101 MHz, $CDCl_3$) of **4ao**

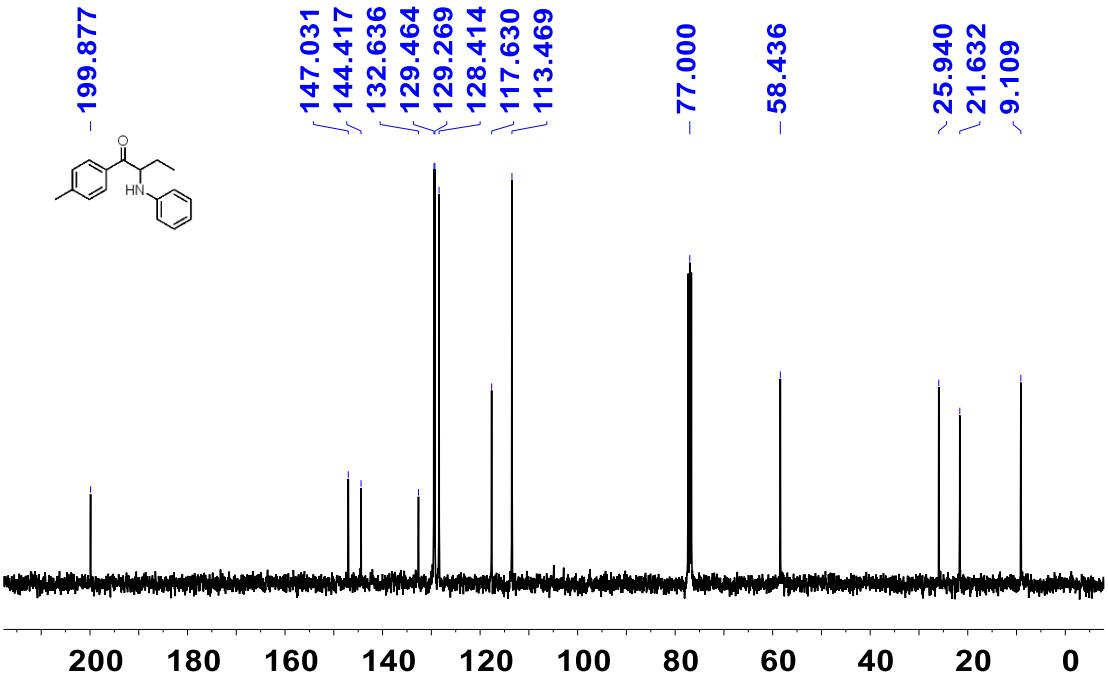


2-(phenylamino)-1-(p-tolyl)butan-1-one (**4ap**)

^{1}H NMR (400 MHz, $CDCl_3$) of **4ap**

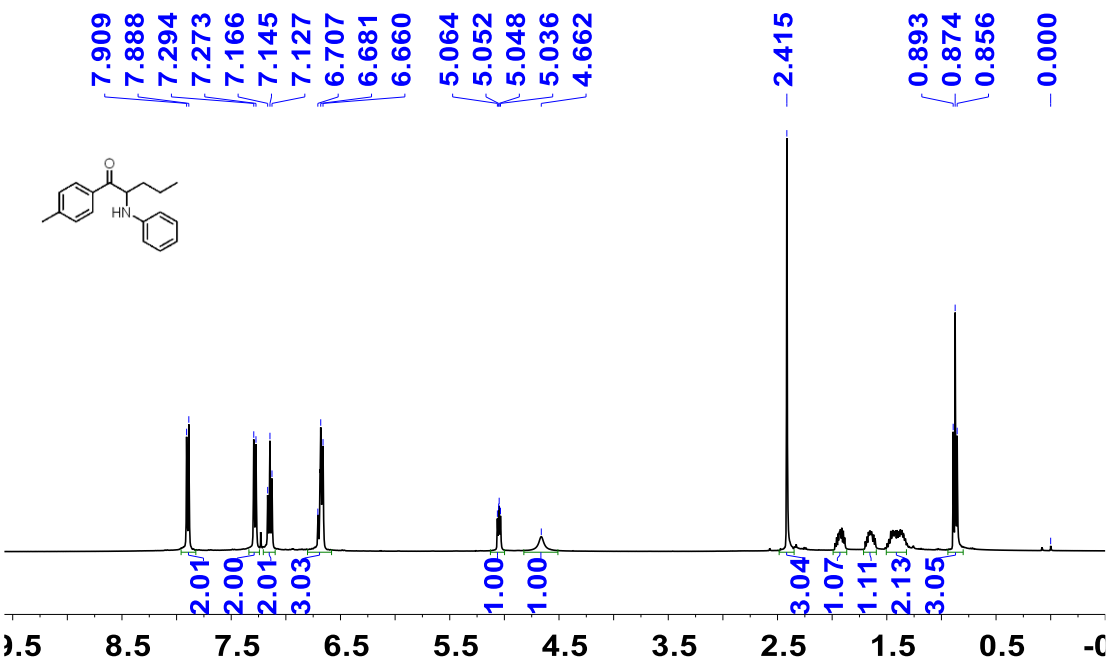


^{13}C NMR (101 MHz, $CDCl_3$) of **4ap**

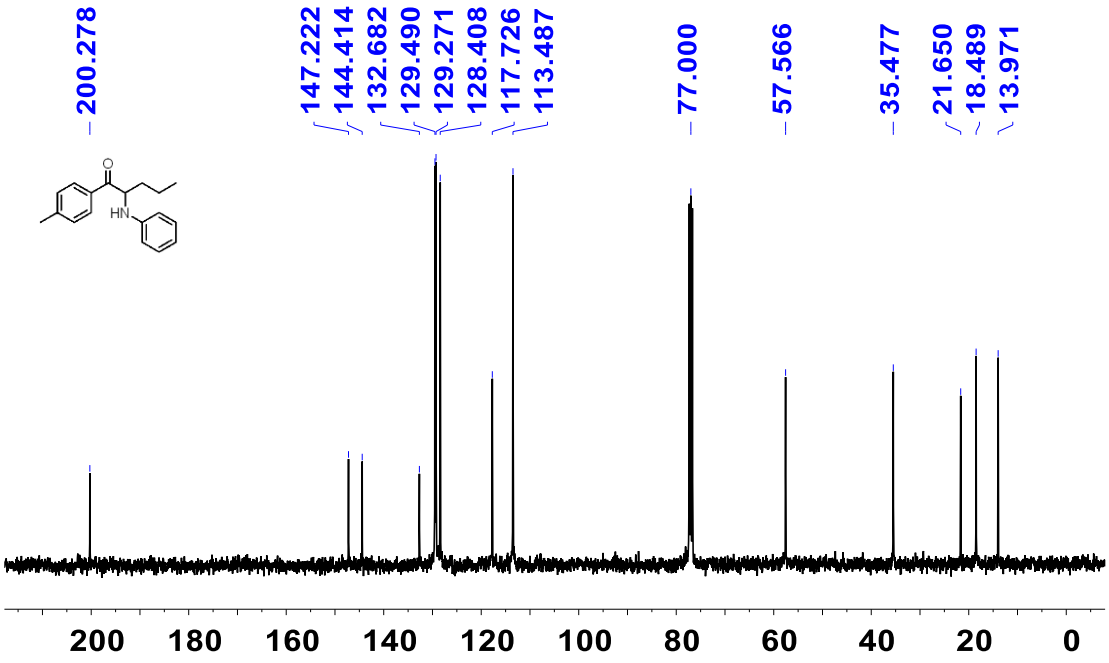


2-(phenylamino)-1-(*p*-tolyl)pentan-1-one (**4aq**)

^{1}H NMR (400 MHz, $CDCl_3$) of **4aq**

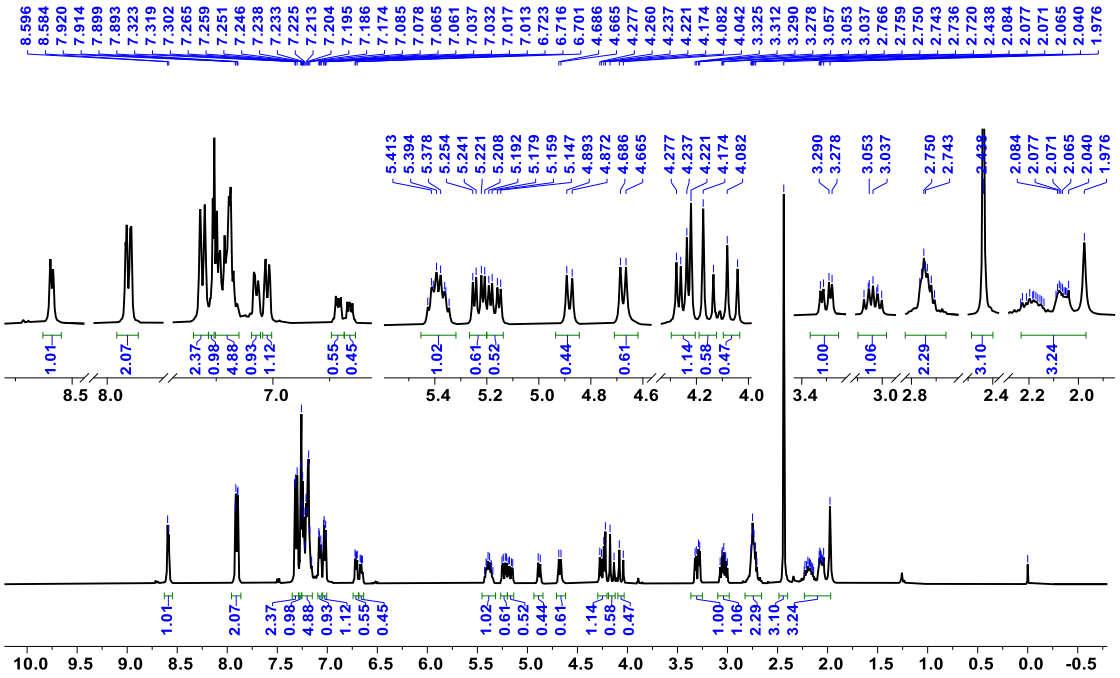


^{13}C NMR (101 MHz, $CDCl_3$) of **4aq**

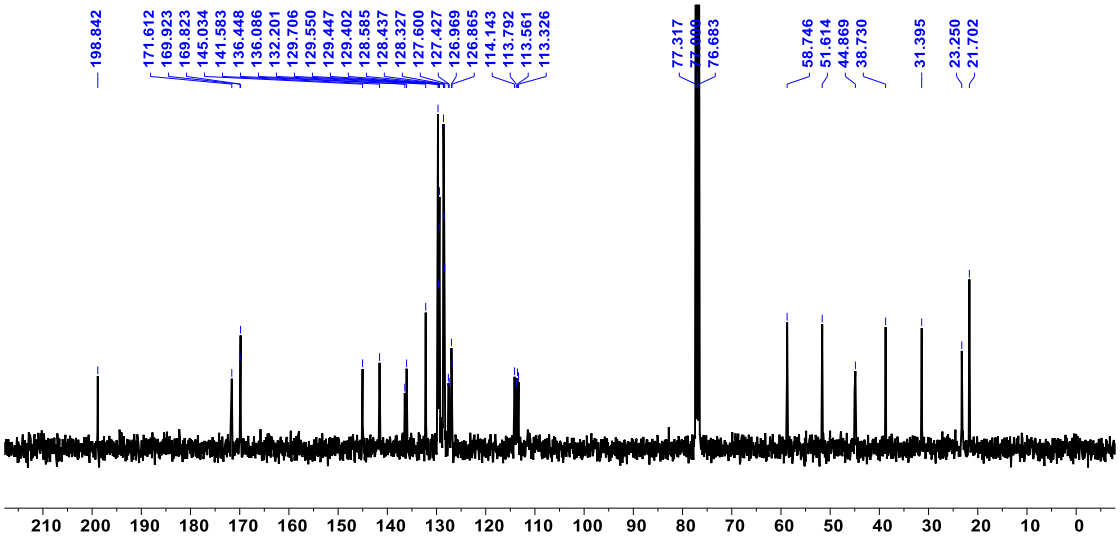


3-(1-oxo-4-((1-oxo-3-phenyl-1-(p-tolyl)propan-2-yl)amino)isoindolin-2-yl)piperidine-2,6-dione (**4as**)

^{1}H NMR (400 MHz, $CDCl_3$) of **4as**

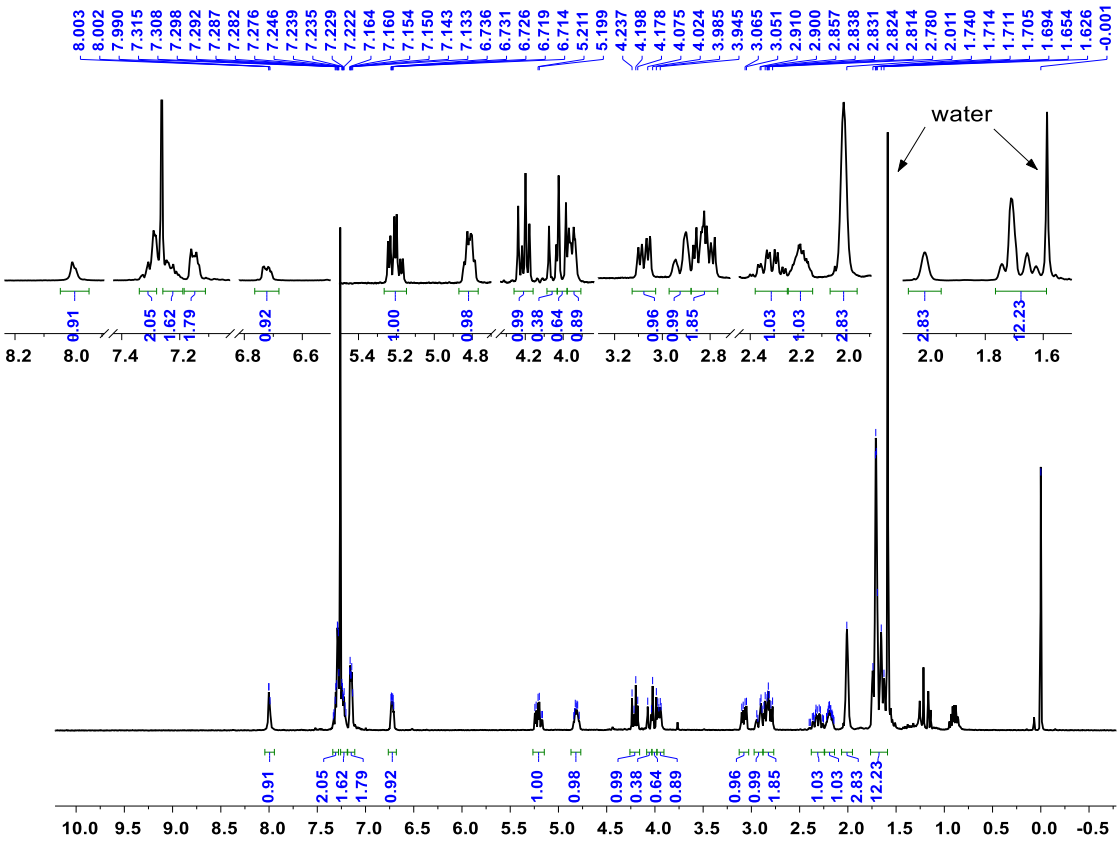


^{13}C NMR (101 MHz, $CDCl_3$) of **4as**



3-(4-((1-(adamantan-1-yl)-1-oxo-3-phenylpropan-2-yl)amino)-1-oxoisoindolin-2-yl)piperidine-2,6-dione (**4at**)

^{1}H NMR (400 MHz, $CDCl_3$) of **4at**



^{13}C NMR (101 MHz, $CDCl_3$) of **4at**