

Supporting information

CuCl₂/TBHP Mediated Synthesis of β -Enaminones via a Coupling Reaction of Vinyl Azides with Aldehydes

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1. General Information

Commercially available materials were used as received. Purifications of all the desired products were carried out by chromatography (silica gel 200-300 mesh). NMR spectra were recorded on a 400 MHz spectrometer, data are reported as follows: chemical shift, integration, multiplicity (s=singlet, d=doublet, t=triplet, q=quartet, m=multiplet). Chemical shifts (δ) were reported in ppm and the coupling constants J are given in Hz. For ^1H NMR, DMSO- d_6 ($\delta=2.50$) or CDCl_3 ($\delta=7.26$) was used as internal standard. For ^{13}C NMR, DMSO- d_6 ($\delta=39.50$) or CDCl_3 ($\delta=77.16$) was used as internal standard. HR-MS data was obtained using Waters XEVO G2-XS QTQF/H-CLASS LC/MS. Melting points were measured on a BÜCHI B-540 melting point apparatus and uncorrected. The starting material of vinyl azides **2** were prepared according to the reported methods.^[1-3]

2. General procedures for synthesis of compounds **3aa-3ua**

A mixture of aldehydes **1** (1.5 mmol, 3.0 equiv), vinyl azides **2** (0.5 mmol), TBHP (1.0 mmol, 2.0 equiv) and $\text{CuCl}_2 \cdot 2\text{H}_2\text{O}$ (0.05 mmol) in DMSO (3 mL) was stirred at 80 °C for 8h. Upon completion of the reaction, the resulting mixture was diluted with saturated NaCl solution (5 mL) and extracted with EtOAc (3×10 mL). The combined organic phase was dried with anhydrous Na_2SO_4 , concentrated and purified by chromatography (petroleum ether/ethylacetate = 15:1) on silica gel to afford the desired products β -enaminones (**3aa-3ua**).

3. Typical procedures for control experiments

(a) Typical procedure for radical trapping experiment

A mixture of benzaldehyde **1a** (1.5 mmol, 3.0 equiv), α -phenylvinyl azide **2a** (0.5 mmol), TBHP (1.0 mmol, 2.0 equiv), $\text{CuCl}_2 \cdot 2\text{H}_2\text{O}$ (0.05 mmol) and TEMPO (1.0 mmol, 2.0 equiv) in DMSO (3 mL) was stirred at 80 °C for 8h. Upon completion of the reaction, the resulting mixture was diluted with saturated NaCl solution (5 mL) and extracted with EtOAc (3×10 mL). Then the resulting mixture was detected by LC-MS, no desired product (**3aa**) was detected.

(b) Typical procedure for radical trapping experiment in the absence of α -phenylvinyl azide

A mixture of benzaldehyde **1a** (1.5 mmol, 3.0 equiv), TBHP (1.0 mmol, 2.0 equiv), $\text{CuCl}_2 \cdot 2\text{H}_2\text{O}$ (0.05 mmol) and TEMPO (1.0 mmol, 2.0 equiv) in DMSO (3 mL) was stirred at 80 °C for 8h. Upon completion of the reaction, the resulting mixture was diluted with saturated NaCl solution (5 mL) and extracted with EtOAc (3×10 mL). The combined organic phase was dried with anhydrous Na_2SO_4 , concentrated and purified by chromatography on silica gel, the coupling product (**8**) was obtained in 76% yield (petroleum ether/ethylacetate = 15:1).

(c) Typical procedure for the reaction of 3-phenyl-2H-azirine (**9**) instead of **2a** to with **1a**

A mixture of benzaldehyde **1a** (1.5 mmol, 3.0 equiv), 3-phenyl-2H-azirine **9** (0.5 mmol), TBHP (1.0 mmol, 2.0 equiv) and $\text{CuCl}_2 \cdot 2\text{H}_2\text{O}$ (0.05 mmol) in DMSO (3 mL) was stirred at 80 °C for 8h. The resulting mixture was detected by LC-MS, no desired product (**3aa**) was detected.

(d) Typical procedure for studying the role of enaminones **4 with benzaldehyde**

A mixture of benzaldehyde **1a** (1.5 mmol, 3.0 equiv.), enaminones **4** (0.5 mmol), TBHP (1.0 mmol, 2.0 equiv., 70% aqueous solution) and CuCl₂·2H₂O (0.05 mmol) in DMSO (3 mL) was stirred at 80 °C for 8h. Upon completion of the reaction, the resulting mixture was diluted with saturated NaCl solution (5 mL) and extracted with EtOAc (3×10 mL). The combined organic phase was dried with anhydrous Na₂SO₄, concentrated and purified by chromatography (petroleum ether/ethylacetate = 15:1) on silica gel to afford the desired products 73% **3aa**.

(e) Typical procedure for radical trapping experiment for the reaction of benzaldehyde with enaminones **4**

A mixture of benzaldehyde **1a** (1.5 mmol, 3.0 equiv.), enaminones **4** (0.5 mmol), TBHP (1.0 mmol, 2.0 equiv., 70% aqueous solution), CuCl₂·2H₂O (0.05 mmol) and TEMPO (1.0 mmol, 2.0 equiv.) in DMSO (3 mL) was stirred at 80 °C for 8h. Upon completion of the reaction, the resulting mixture was diluted with saturated NaCl solution (5 mL) and extracted with EtOAc (3×10 mL). Then the resulting mixture was detected by LC-MS, no desired product (**3aa**) was detected.

4. Typical procedures for synthetic applications of **3aa**

(a) Typical synthesis of N-unsubstituted β-enaminone **4**

To a solution of compound **3aa** (0.1 mmol, 1.0 equiv) in MeOH (1.0 mL) was added NH₄HCO₃ (1.6 mmol, 16.0 equiv). The reaction mixture was stirred at 65 °C in oil bath for 24 h. Upon completion, the mixture was then concentrated under vacuum and the residue was purified by chromatography on silica gel (PE/EA) to afford **4** as a yellow oil in 92% yield.

(b) Typical synthesis of 1,3-diketone **5**

Compound **3aa** (0.3 mmol) was added into a 5 mL reaction tube. THF (1.0 mL) and concentrated hydrochloric acid (1.0 mL) were then added at 0 °C sequentially by syringe. The resulting mixture was stirred at 50 °C for 24 hours. Upon completion as monitored by TLC, the solvent was removed under vacuum. The residue was purified directly by column chromatography, eluting with petroleum ether/ethyl acetate to afford **5** in 95% yield as colorless oil.

(c) Typical synthesis of 2,3,5-triphenyl-1H-pyrrole **6**

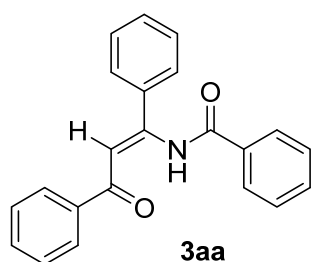
Under anhydrous conditions, titanium tetrachloride (2 mmol) was added dropwise using a syringe to a stirred suspension of samarium powder (2 mmol) in THF (15 mL) at room temperature under a nitrogen atmosphere. After the completion of addition, the mixture was refluxed for 2 h. The suspension of the low-valent titanium reagent formed was cooled to room temperature and a solution of substrates **3aa** (1 mmol) in anhydrous THF (2 mL) was added via a syringe. The mixture was refluxed for 1 h, and the deep dark color of the solution changed into a brownish red gradually. After completion monitored by TLC, the reaction was quenched with dilute HCl and extracted with ether (3 x 20 mL). The combined extract was washed with saturated brine (15 mL) and dried over anhydrous Na₂SO₄. After evaporating the solvent under reduced

pressure, the resulting crude product was purified silica gel column chromatography to afford **6** in 80% yield.

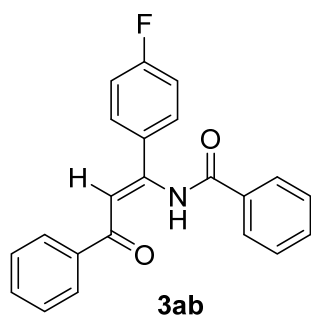
(d) Typical synthesis of 2,4,6-triphenyl-4H-1,3-oxazine **7**

To a solution of BINAPO (10 mol%) and **3aa** (0.25 mmol) in dry dichloromethane (1 mL) was added dropwise trichlorosilane (ca. 3 M CH₂Cl₂ solution, 3 equiv.) at 0 °C. The reaction was stirred at rt for 24 h and quenched with water (3 mL) and dichloromethane (5 mL). The mixture was stirred for 1 h, filtered through a Celite pad with dichloromethane and extracted with dichloromethane for three times. The combined organic layers were dried over anhydrous Na₂SO₄, filtered, evaporated, and purified by silica gel column chromatography to afford **7** in 70% yield.

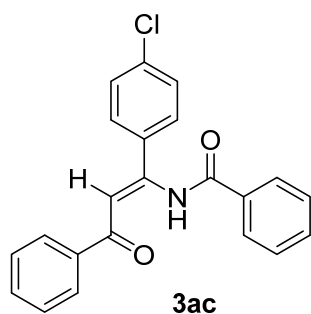
5. Characterization of Synthesized Compounds 3aa-3sa



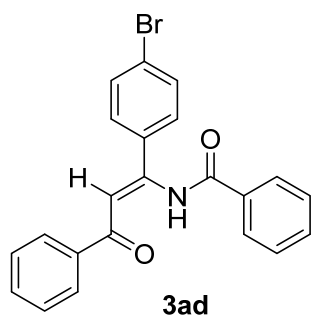
(Z)-N-(3-oxo-1,3-diphenylprop-1-en-1-yl)benzamide (3aa): Yellow oil, yield 88%, ¹H NMR (400 MHz, CDCl₃) δ 13.40 (s, 1H), 8.16 – 8.14 (m, 2H), 8.04 – 8.02 (m, 2H), 7.64 – 7.45 (m, 11H), 6.48 (s, 1H). ¹³C NMR (100 MHz, CDCl₃) δ 192.11, 165.34, 157.17, 138.64, 136.46, 133.44, 132.89, 132.86, 130.49, 129.90, 128.98, 128.76, 128.22, 127.96, 127.47, 105.45. HRMS (ESI): m/z calcd for C₂₂H₁₈NO₂[M+H]⁺: 328.1338, found: 328.1336.



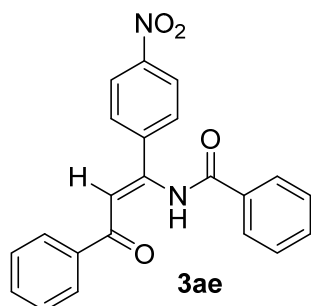
(Z)-N-(1-(4-fluorophenyl)-3-oxo-3-phenylprop-1-en-1-yl)benzamide (3ab): Yellow solid, m.p. 125.6 – 126.1°C, yield 83%, ¹H NMR (400 MHz, CDCl₃) δ 13.36 (s, 1H), 8.12-8.10 (m, 2H), 8.01 – 7.99 (m, 2H), 7.64 – 7.48 (m, 8H), 7.17 – 7.11 (m, 2H), 6.42 (s, 1H). ¹³C NMR (100 MHz, CDCl₃) δ 192.18, 165.54, 163.81 (d, J = 249 Hz), 156.08, 138.62, 133.36, 133.06, 132.50, 132.47, 129.55 (d, J = 8 Hz), 129.10, 128.88, 128.27, 128.03, 115.48 (d, J = 22 Hz), 105.50. HRMS (ESI): m/z calcd for C₂₂H₁₆FNO₂[M+H]⁺: 346.1243, found: 346.1245.



(Z)-N-(1-(4-chlorophenyl)-3-oxo-3-phenylprop-1-en-1-yl)benzamide (3ac): Yellow solid, m.p. 144.8 – 145.2°C, yield 84%, ^1H NMR (400 MHz, DMSO- d_6) δ 12.77 (s, 1H), 8.13 (d, $J = 7.2$, Hz, 2H), 8.01 (d, $J = 7.2$ Hz, 2H), 7.73 – 7.61 (m, 6H), 7.57 – 7.51 (m, 4H), 6.77 (s, 1H). ^{13}C NMR (100 MHz, DMSO- d_6) δ 191.30, 164.76, 153.78, 137.87, 134.78, 134.57, 133.28, 133.12, 133.06, 129.62, 129.15, 128.84, 128.24, 128.13, 127.79, 106.65. HRMS (ESI): m/z calcd for $\text{C}_{22}\text{H}_{17}\text{ClNO}_2[\text{M}+\text{H}]^+$: 362.0948, found: 362.0947.

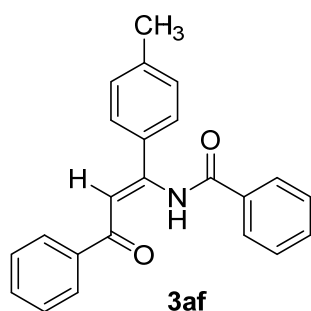


(Z)-N-(1-(4-bromophenyl)-3-oxo-3-phenylprop-1-en-1-yl)benzamide (3ad): Yellow solid, m.p. 181.4 – 181.8°C, yield 87%, ^1H NMR (400 MHz, DMSO- d_6) δ 12.79 (s, 1H), 8.12 (d, $J = 7.6$ Hz, 2H), 8.01 (d, $J = 7.2$ Hz, 2H), 7.72 – 7.52 (m, 10H), 6.75 (s, 1H). ^{13}C NMR (100 MHz, DMSO- d_6) δ 191.31, 164.74, 153.92, 137.86, 135.15, 133.29, 133.09, 131.05, 129.84, 129.16, 128.85, 128.25, 127.80, 123.37, 106.56. HRMS (ESI): m/z calcd for $\text{C}_{22}\text{H}_{17}\text{BrNO}_2[\text{M}+\text{H}]^+$: 406.0443, found: 406.0445.

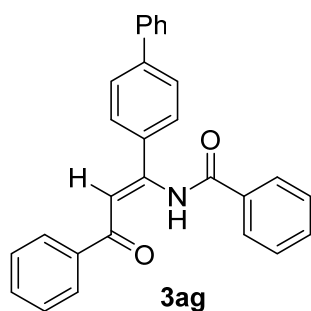


(Z)-N-(1-(4-nitrophenyl)-3-oxo-3-phenylprop-1-en-1-yl)benzamide (3ae): Yellow solid, m.p. 195.6 – 196.1°C, yield 82%, ^1H NMR (400 MHz, CDCl_3) δ 13.37 (s, 1H), 8.31 (d, $J = 8.8$ Hz, 2H), 8.08 (d, $J = 7.6$ Hz, 2H), 8.01 (d, $J = 7.6$ Hz, 2H), 7.69 (d, $J = 8.4$ Hz, 2H), 7.64 – 7.59 (m, 2H), 7.57 – 7.46 (m, 4H), 6.45 (s, 1H). ^{13}C NMR (100 MHz, CDCl_3) δ 192.22, 165.46, 154.29, 148.41,

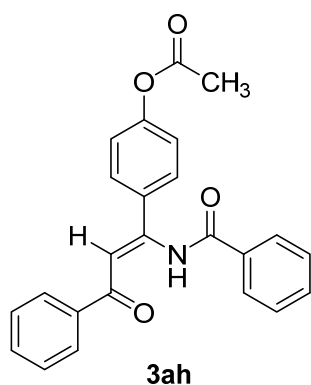
143.16, 138.25, 133.47, 133.34, 132.79, 129.20, 129.00, 128.62, 128.44, 128.27, 123.62, 106.35. HRMS (ESI): m/z calcd for $C_{22}H_{16}N_2O_4[M+H]^+$: 373.1188, found: 372.1190.



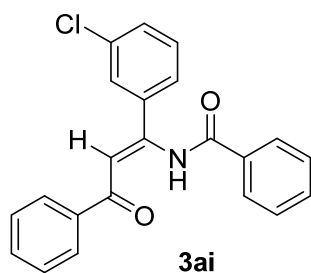
(Z)-N-(3-oxo-3-phenyl-1-(p-tolyl)prop-1-en-1-yl)benzamide(3af): White solid, m.p. 96.4 – 96.7, yield 89%, 1H NMR (400 MHz, DMSO- d_6) δ 12.82 (s, 1H), 8.11 (d, $J = 7.2$ Hz, 2H), 8.02 (d, $J = 7.2$ Hz, 2H), 7.71– 7.68 (m, 1H), 7.63 (q, $J = 6.8$ Hz, 3H), 7.55– 7.52 (m, 4H), 7.25 (d, $J = 8.0$ Hz, 2H), 6.70 (s, 1H), 2.37 (s, 3H). ^{13}C NMR (100 MHz, DMSO- d_6) δ 191.13, 164.66, 155.46, 139.78, 138.03, 133.29, 132.97, 132.91, 132.85, 129.02, 128.71, 128.60, 128.02, 127.69, 127.65, 105.69, 20.91. HRMS (ESI): m/z calcd for $C_{23}H_{20}NO_2[M+H]^+$: 342.1494, found: 342.1491.



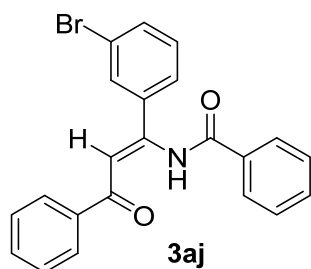
(Z)-N-(1-([1,1'-biphenyl]-4-yl)-3-oxo-3-phenylprop-1-en-1-yl)benzamide(3ag): White solid, m.p. 188.5 – 188.7, yield 89%, 1H NMR (400 MHz, DMSO- d_6) δ 12.83 (s, 1H), 8.15 (d, $J = 7.2$ Hz, 2H), 8.04 (d, $J = 7.2$ Hz, 2H), 7.75– 7.40 (m, 15H), 6.82 (s, 1H). ^{13}C NMR (100 MHz, DMSO- d_6) δ 191.24, 164.82, 154.83, 141.64, 139.40, 138.02, 134.93, 133.23, 133.18, 129.15, 129.10, 128.84, 128.44, 128.20, 127.95, 127.81, 126.79, 126.34, 106.36. HRMS (ESI): m/z calcd for $C_{28}H_{22}NO_2[M+H]^+$: 404.1651, found: 404.1654.



(Z)-4-(1-benzamido-3-oxo-3-phenylprop-1-en-1-yl)phenyl acetate(3ah): White solid, m.p. 92.8 – 93.4, yield 87%. ¹H NMR (400 MHz, DMSO-d₆) δ 12.81 (s, 1H), 8.14 (d, *J* = 7.6 Hz, 2H), 8.03 (d, *J* = 7.2 Hz, 2H), 7.71– 7.69 (m, 3H), 7.66– 7.61 (m, 3H), 7.54 (t, *J* = 7.6 Hz, 2H), 7.22 (d, *J* = 8.4 Hz, 2H), 6.77 (s, 1H), 2.31 (s, 3H). ¹³C NMR(100 MHz, DMSO-d₆) δ 191.23, 169.10, 164.75, 154.29, 151.77, 137.95, 133.30, 133.21,133.19,133.00,129.12, 129.08, 128.81, 128.21, 127.80, 121.56, 106.47, 20.93.HRMS (ESI): m/z calcd for C₂₄H₂₀NO₄[M+H]⁺: 386.1392, found: 386.1391.

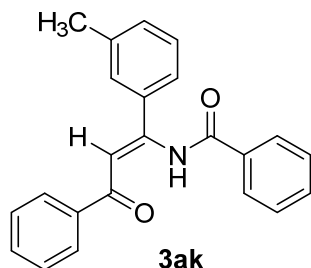


(Z)-N-(1-(3-chlorophenyl)-3-oxo-3-phenylprop-1-en-1-yl)benzamide(3ai): Yellow solid, m.p. 104.2 – 104.5°C, yield 82%. ¹H NMR (400 MHz, DMSO-d₆) δ 12.80 (s, 1H), 8.14 (d, *J* = 7.6 Hz, 2H), 8.01 (d, *J* = 7.2 Hz, 2H), 7.73– 7.67 (m, 2H), 7.64 – 7.60 (m, 3H), 7.58– 7.53 (m, 4H), 7.48 – 7.44 (m, 1H), 6.77 (s, 1H). ¹³C NMR (100 MHz, DMSO-d₆) δ 191.37, 164.66, 153.33, 138.08, 137.78, 133.28, 133.06, 133.03, 132.84, 129.88, 129.54, 129.11, 128.79, 128.28, 127.78, 127.30 , 126.47, 106.91.HRMS (ESI): m/z calcd for C₂₂H₁₇ClNO₂[M+H]⁺: 362.0948, found: 362.0945.

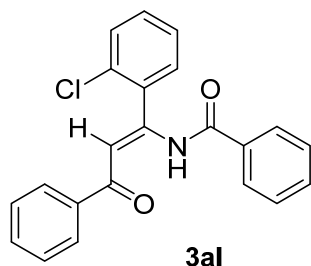


(Z)-N-(1-(3-bromophenyl)-3-oxo-3-phenylprop-1-en-1-yl)benzamide(3aj): Yellow solid, m.p. 96.3 – 96.5°C, yield 82%. ¹H NMR (400 MHz, DMSO-d₆) δ 12.82 (s, 1H), 8.14 (d, *J* = 7.6 Hz, 2H), 8.01 (d, *J* = 7.6Hz, 2H), 7.84 (s, 1H), 7.69 – 7.60(m, 6H), 7.53 (t, *J* = 7.6 Hz, 2H), 7.39 (t, *J* =

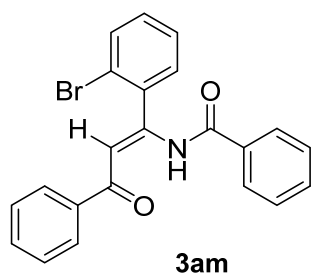
7.6 Hz, 1H), 6.74 (s, 1H). ^{13}C NMR(100 MHz, DMSO- d_6) δ 191.30, 164.57, 153.25, 138.25, 137.75, 133.19, 133.01, 132.94, 132.36, 130.04, 129.98, 129.03, 128.71, 128.21, 127.72, 126.78, 121.28, 106.80. HRMS (ESI): m/z calcd for $\text{C}_{22}\text{H}_{17}\text{BrNO}_2[\text{M}+\text{H}]^+$: 406.0443, found: 406.0446.



(Z)-N-(3-oxo-3-phenyl-1-(m-tolyl)prop-1-en-1-yl)benzamide(3ak): Yellow solid, m.p.113.7 – 114.1 °C, yield 85%. ^1H NMR (400 MHz, CDCl_3) δ 13.36 (s, 1H), 8.14 – 8.12 (m, 2H), 8.03 – 8.01 (m, 2H), 7.64– 7.48 (m, 6H), 7.37– 7.29 (m, 4H), 6.46 (s, 1H), 2.44 (s, 3H). ^{13}C NMR (100 MHz, CDCl_3) δ 192.18, 165.41, 157.50, 138.76, 138.02, 136.52, 133.55, 132.89, 130.80, 129.02, 128.80, 128.29, 128.16, 128.00, 127.93, 124.72, 105.41, 21.63. HRMS (ESI): m/z calcd for $\text{C}_{23}\text{H}_{20}\text{NO}_2[\text{M}+\text{H}]^+$: 342.1494, found: 342.1496.

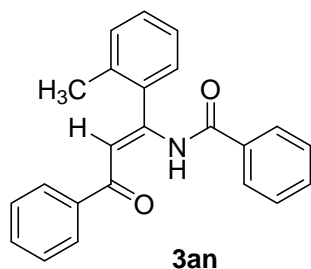


(Z)-N-(1-(2-chlorophenyl)-3-oxo-3-phenylprop-1-en-1-yl)benzamide(3al): Yellow solid, m.p. 142.3 – 142.6°C, yield 81%. ^1H NMR (400 MHz, DMSO- d_6) δ 13.54 (s, 1H), 8.11 (d, $J = 7.6$ Hz, 2H), 7.97 (d, $J = 7.2$ Hz, 2H), 7.71 (t, $J = 7.2$ Hz, 1H), 7.67– 7.62 (m, 3H), 7.59 – 7.44 (m, 6H), 6.53 (s, 1H). ^{13}C NMR (100 MHz, DMSO- d_6) δ 191.90, 163.59, 153.02, 137.58, 135.42, 133.39, 133.38, 133.17, 132.67, 131.25, 130.43, 129.83, 129.30, 128.92, 128.89, 128.19, 127.57, 127.13, 104.71. HRMS (ESI): m/z calcd for $\text{C}_{22}\text{H}_{17}\text{ClNO}_2[\text{M}+\text{H}]^+$: 362.0948, found: 362.0949.

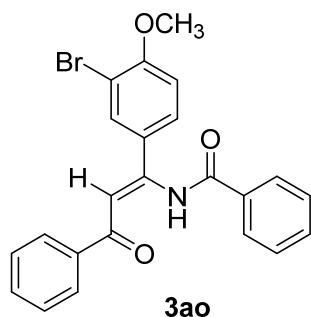


(Z)-N-(1-(2-bromophenyl)-3-oxo-3-phenylprop-1-en-1-yl)benzamide(3am): Yellow solid, m.p. 106.3 – 106.5°C, yield 82%. ^1H NMR (400 MHz, DMSO- d_6) δ 13.55 (s, 1H), 8.12 (d, $J = 7.2$ Hz,

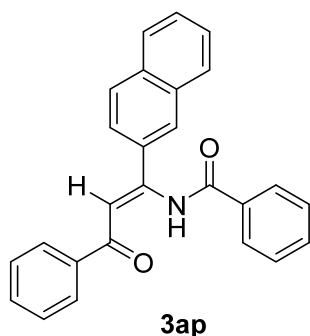
2H), 7.97 (d, $J = 7.2$ Hz, 2H), 7.74 – 7.63 (m, 5H), 7.56 – 7.45 (m, 4H), 7.40 (td, $J = 7.6, 1.6$ Hz, 1H), 6.52 (s, 1H). ^{13}C NMR (100 MHz, DMSO- d_6) δ 191.93, 163.45, 154.31, 137.55, 137.39, 133.41, 133.18, 132.69, 132.04, 130.46, 129.84, 129.32, 128.90, 128.19, 127.56, 120.99, 104.48. HRMS (ESI): m/z calcd for $\text{C}_{22}\text{H}_{17}\text{BrNO}_2[\text{M}+\text{H}]^+$: 406.0443, found: 406.0447.



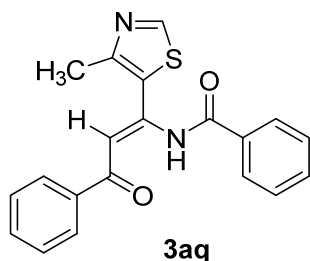
(Z)-N-(3-oxo-3-phenyl-1-(o-tolyl)prop-1-en-1-yl)benzamide(3an): White solid, m.p. 89.2 – 89.3°C, yield 84%. ^1H NMR (400 MHz, DMSO- d_6) δ 13.60 (s, 1H), 8.09 (d, $J = 7.2$ Hz, 2H), 8.00 (d, $J = 6.8$ Hz, 2H), 7.70 (t, $J = 7.2$ Hz, 1H), 7.65– 7.61 (m, 3H), 7.52 (t, $J = 7.6$ Hz, 2H), 7.35 (t, $J = 7.6$ Hz, 2H), 7.29– 7.24 (m, 2H), 6.43 (s, 1H), 2.27 (s, 3H). ^{13}C NMR (100 MHz, DMSO- d_6) δ 191.62, 163.72, 156.18, 137.80, 136.34, 134.96, 133.16, 133.08, 132.92, 129.61, 129.23, 128.83, 128.70, 128.09, 127.72, 127.61, 125.58, 104.42, 19.30. HRMS (ESI): m/z calcd for $\text{C}_{23}\text{H}_{20}\text{NO}_2[\text{M}+\text{H}]^+$: 342.1494, found: 342.1493.



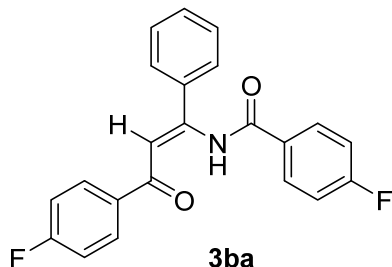
(Z)-N-(1-(3-bromo-4-methoxyphenyl)-3-oxo-3-phenylprop-1-en-1-yl)benzamide(3ao): White solid, m.p. 135.8 – 136.2°C, yield 88%. ^1H NMR (400 MHz, CDCl_3) δ 13.31 (s, 1H), 8.11 (d, $J = 7.2$ Hz, 2H), 8.00 (d, $J = 7.2$ Hz, 2H), 7.76 (d, $J = 1.2$ Hz, 1H), 7.62– 7.47 (m, 7H), 6.95 (d, $J = 8.8$ Hz, 1H), 6.42 (s, 1H), 3.95 (s, 3H). ^{13}C NMR (100 MHz, CDCl_3) δ 192.11, 165.60, 157.34, 155.38, 138.70, 133.47, 133.01, 132.34, 129.93, 129.08, 128.86, 128.41, 128.29, 128.04, 111.59, 111.31, 105.30, 56.48. HRMS (ESI): m/z calcd for $\text{C}_{23}\text{H}_{19}\text{BrNO}_3[\text{M}+\text{H}]^+$: 436.0548, found: 436.0541.



(Z)-N-(1-(naphthalen-2-yl)-3-oxo-3-phenylprop-1-en-1-yl)benzamide(3ap): White solid, m.p. 167.6 – 167.9 °C, yield 89%. ¹H NMR (400 MHz, DMSO-d₆) δ 12.96 (s, 1H), 8.29 (s, 1H), 8.17 (d, *J* = 7.6 Hz, 2H), 8.04 (d, *J* = 7.2 Hz, 3H), 7.99 – 7.93 (m, 2H), 7.74 – 7.55 (m, 9H), 6.89 (s, 1H). ¹³C NMR (100 MHz, DMSO-d₆) δ 191.30, 164.77, 155.31, 138.03, 133.67, 133.58, 133.14, 133.22, 133.06, 132.52, 129.18, 128.86, 128.61, 128.23, 127.83, 127.57, 127.24, 127.05, 126.55, 125.49, 106.53. HRMS (ESI): *m/z* calcd for C₂₆H₂₀NO₂[M+H]⁺: 378.1494, found: 378.1497.

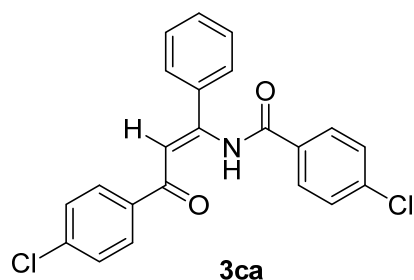


(Z)-N-(1-(4-methylthiazol-5-yl)-3-oxo-3-phenylprop-1-en-1-yl)benzamide(3aq): Yellow solid, m.p. 121.3 – 121.8 °C, yield 86%. ¹H NMR (400 MHz, DMSO-d₆) δ 12.87 (s, 1H), 9.14 (s, 1H), 8.08 (d, *J* = 7.6 Hz, 2H), 8.00 (d, *J* = 7.2 Hz, 2H), 7.72 – 7.67 (m, 1H), 7.65 – 7.60 (m, 3H), 7.54 (t, *J* = 7.6 Hz, 2H), 6.76 (s, 1H), 2.49 (s, 3H). ¹³C NMR (100 MHz, DMSO-d₆) δ 190.84, 164.42, 153.82, 152.02, 145.61, 137.65, 133.35, 133.11, 132.93, 129.18, 128.89, 128.19, 127.73, 126.58, 107.85, 16.24. HRMS (ESI): *m/z* calcd for C₂₀H₁₇N₂O₂S[M+H]⁺: 349.1011, found: 349.1015.

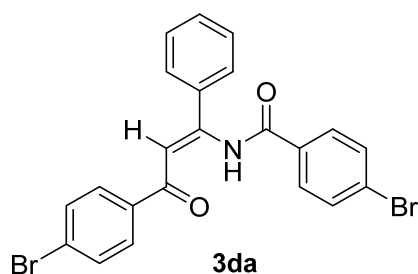


(Z)-4-fluoro-N-(3-(4-fluorophenyl)-3-oxo-1-phenylprop-1-en-1-yl)benzamide(3ba): White solid, m.p. 144.2 – 144.7 °C, yield 77%. ¹H NMR (400 MHz, DMSO-d₆) δ 12.68 (s, 1H), 8.20 (dd, *J* = 8.8, 5.6 Hz, 2H), 8.07 (dd, *J* = 8.8, 5.6 Hz, 2H), 7.63 (d, *J* = 6.8 Hz, 2H), 7.45 – 7.42 (m, 5H),

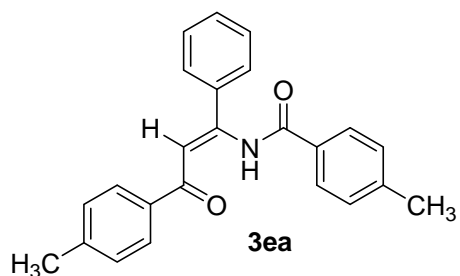
7.34 (t, $J = 8.8$ Hz, 2H), 6.73 (s, 1H). ^{13}C NMR (100 MHz, DMSO- d_6) δ 189.74, 165.05 (d, $J = 250$ Hz), 164.85 (d, $J = 249$ Hz), 163.68, 155.10, 135.81, 134.59 (d, $J = 3$ Hz), 131.20 (d, $J = 10$ Hz), 130.65 (d, $J = 10$ Hz), 129.97, 129.84 (d, $J = 3$ Hz), 128.09, 127.73, 116.13 (d, $J = 22$ Hz), 115.79 (d, $J = 21$ Hz), 106.41. HRMS (ESI): m/z calcd for $\text{C}_{22}\text{H}_{16}\text{F}_2\text{NO}_2[\text{M}+\text{H}]^+$: 364.1149, found: 364.1147.



(Z)-4-chloro-N-(3-(4-chlorophenyl)-3-oxo-1-phenylprop-1-en-1-yl)benzamide(3ca): Yellow solid, m.p. 119.1 – 119.6°C, yield 74%. ^1H NMR (400 MHz, CDCl_3) δ 13.36 (s, 1H), 8.04 (d, $J = 8.4$ Hz, 2H), 7.94 (d, $J = 8.8$ Hz, 2H), 7.54 – 7.44 (m, 9H), 6.39 (s, 1H). ^{13}C NMR (100 MHz, CDCl_3) δ 190.83, 164.32, 157.68, 139.49, 139.44, 136.90, 136.14, 131.85, 130.19, 129.67, 129.44, 129.35, 129.15, 128.35, 127.50, 105.13. HRMS (ESI): m/z calcd for $\text{C}_{22}\text{H}_{16}\text{Cl}_2\text{NO}_2[\text{M}+\text{H}]^+$: 396.0558, found: 396.0555.

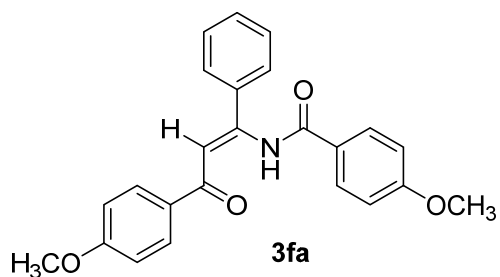


(Z)-4-bromo-N-(3-(4-bromophenyl)-3-oxo-1-phenylprop-1-en-1-yl)benzamide(3da): Yellow solid, m.p. 128.3 – 128.7°C, yield 74%. ^1H NMR (400 MHz, CDCl_3) δ 13.35 (s, 1H), 7.96 (d, $J = 4.8$ Hz, 2H), 7.86 (d, $J = 4.8$ Hz, 2H), 7.68 (d, $J = 4.8$ Hz, 2H), 7.63 (d, $J = 5.2$ Hz, 2H), 7.53 – 7.45 (m, 5H), 6.39 (s, 1H). ^{13}C NMR (100 MHz, CDCl_3) δ 191.06, 164.51, 157.76, 137.37, 136.15, 132.39, 132.34, 132.18, 130.24, 129.82, 129.58, 128.39, 128.24, 128.11, 127.53, 105.14. HRMS (ESI): m/z calcd for $\text{C}_{22}\text{H}_{16}\text{Br}_2\text{NO}_2[\text{M}+\text{H}]^+$: 483.9548, found: 483.9551.

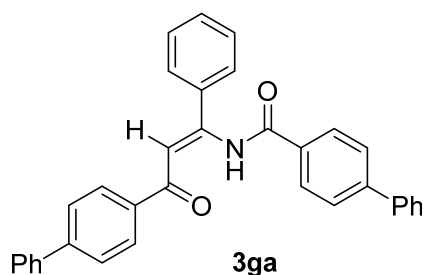


(Z)-4-methyl-N-(3-oxo-1-phenyl-3-(p-tolyl)prop-1-en-1-yl)benzamide(3ea): Yellow oil, yield 70%. ^1H NMR (400 MHz, CDCl_3) δ 13.38 (s, 1H), 8.02 (d, $J = 8.0$ Hz, 2H), 7.93 (d, $J = 8.0$ Hz, 2H), 7.57 – 7.54 (m, 2H), 7.48 – 7.43 (m, 3H), 7.32 (dd, $J = 16.8, 8.0$ Hz, 4H), 6.43 (s, 1H), 2.45 (s, 3H), 2.43 (s, 3H). ^{13}C NMR (100 MHz, CDCl_3) δ 191.77, 165.34, 156.98, 143.73, 143.54, 136.75, 136.18, 130.79, 129.78, 129.67, 129.49, 128.32, 128.21, 128.12, 127.48, 105.31, 21.75, 21.72.

HRMS (ESI): m/z calcd for $\text{C}_{24}\text{H}_{22}\text{NO}_2[\text{M}+\text{H}]^+$: 356.1651, found: 356.1655.

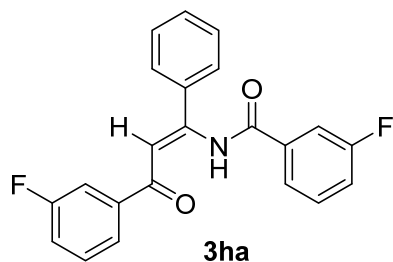


(Z)-4-methoxy-N-(3-(4-methoxyphenyl)-3-oxo-1-phenylprop-1-en-1-yl)benzamide(3fa): Light yellow oil, yield 69%. ^1H NMR (400 MHz, CDCl_3) δ 13.38 (s, 1H), 8.07 (d, $J = 8.8$ Hz, 2H), 8.00 (d, $J = 7.2$ Hz, 2H), 7.54 – 7.52 (m, 2H), 7.46 – 7.43 (m, 3H), 6.99 (dd, $J = 17.0, 9.0$ Hz, 4H), 6.38 (s, 1H), 3.89 (s, 3H), 3.88 (s, 3H). ^{13}C NMR (100 MHz, CDCl_3) δ 190.78, 164.93, 163.53, 163.35, 156.84, 136.96, 131.64, 130.36, 130.30, 129.72, 128.23, 127.49, 126.02, 114.24, 114.04, 105.02, 55.64. HRMS (ESI): m/z calcd for $\text{C}_{24}\text{H}_{22}\text{NO}_4[\text{M}+\text{H}]^+$: 388.1549, found: 388.1551.

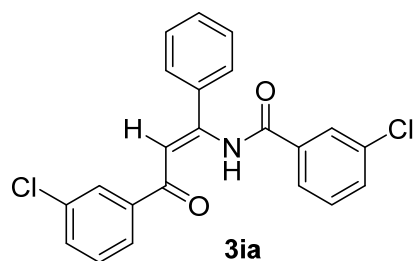


(Z)-N-(3-([1,1'-biphenyl]-4-yl)-3-oxo-1-phenylprop-1-en-1-yl)-[1,1'-biphenyl]-4-carboxamide (3ga): White solid, m.p. 148.4 – 148.8°C, yield 73%. ^1H NMR (400 MHz, CDCl_3) δ 13.50 (s, 1H), 8.21 (d, $J = 8.4$ Hz, 2H), 8.11 (d, $J = 8.4$ Hz, 2H), 7.78 (d, $J = 8.4$ Hz, 2H), 7.73 (d, $J = 8.4$ Hz, 2H), 7.68 – 7.65 (m, 4H), 7.61 – 7.58 (m, 2H), 7.52 – 7.46 (m, 7H), 7.44 – 7.40 (m, 2H), 6.52 (s, 1H). ^{13}C NMR (100 MHz, CDCl_3) δ 191.67, 183.53, 165.17, 157.31, 145.68, 145.66, 140.01, 139.97, 137.47, 136.62, 132.23, 129.99, 129.11, 128.88, 128.68, 128.38, 128.33, 127.70, 127.58, 127.48,

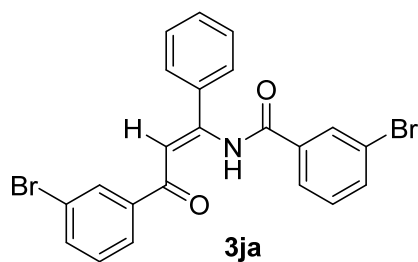
127.43, 127.41, 105.49. HRMS (ESI): m/z calcd for $C_{34}H_{26}NO_2[M+H]^+$: 480.1964, found: 480.1966.



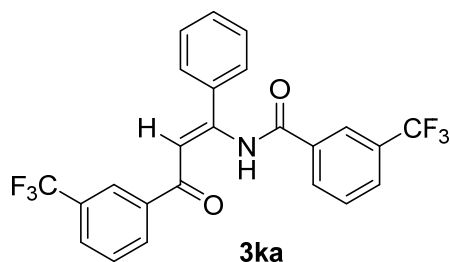
(Z)-3-Fluoro-N-(3-(3-fluorophenyl)-3-oxo-1-phenylprop-1-en-1-yl)benzamide(3ha): White solid, m.p. 90.3 – 90.6°C, yield 74%. 1H NMR (400 MHz, DMSO- d_6) δ 12.61 (s, 1H), 7.95 (d, J = 7.6 Hz, 1H), 7.91-7.85 (m, 2H), 7.75 (d, J = 9.6 Hz, 1H), 7.68 – 7.64 (m, 3H), 7.58 – 7.51 (m, 2H), 7.49-7.43 (m, 4H), 6.75 (s, 1H). ^{13}C NMR (100 MHz, DMSO) δ 189.69, 162.30 (d, J = 244Hz), 162.21 (d, J = 244Hz), 155.08, 140.16 (d, J = 7 Hz), 135.63 (d, J = 7 Hz), 135.56, 131.27 (d, J = 8 Hz), 130.83 (d, J = 8 Hz), 130.06, 128.07, 127.81, 124.33, 124.31, 123.79, 123.76, 119.99 (d, J = 9 Hz), 119.78 (d, J = 9 Hz), 119.88 (dd, J = 21, 9 Hz), 114.68 (dd, J = 23, 3 Hz), 106.78. HRMS (ESI): m/z calcd for $C_{22}H_{16}F_2NO_2[M+H]^+$: 364.1149, found: 364.1152.



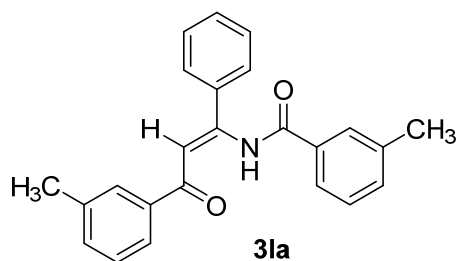
(Z)-3-Chloro-N-(3-(3-chlorophenyl)-3-oxo-1-phenylprop-1-en-1-yl)benzamide(3ia): Yellow oil, yield 72%. 1H NMR (400 MHz, DMSO- d_6) δ 12.36 (s, 1H), 8.13 (s, 1H), 8.07 (d, J = 8.0 Hz, 1H), 7.99 (s, 1H), 7.95 (d, J = 8.0 Hz, 1H), 7.77 (d, J = 8.0 Hz, 1H), 7.72 – 7.63 (m, 4H), 7.57 (t, J = 8.0 Hz, 1H), 7.52– 7.44 (m, 3H), 6.82 (s, 1H). ^{13}C NMR (100 MHz, DMSO- d_6) δ 189.57, 163.55, 154.32, 139.82, 135.57, 135.36, 133.73, 132.71, 132.57, 130.96, 130.67, 130.10, 128.28, 128.10, 127.86, 127.77, 127.59, 126.82, 126.37, 107.51. HRMS (ESI): m/z calcd for $C_{22}H_{16}Cl_2NO_2[M+H]^+$: 396.0558, found: 396.0555.



(Z)-3-Bromo-N-(3-(3-bromophenyl)-3-oxo-1-phenylprop-1-en-1-yl)benzamide(3ja): Yellow oil, yield 73%. ^1H NMR (400 MHz, CDCl_3) δ 13.27 (s, 1H), 8.21 (t, $J = 1.6$ Hz, 1H), 8.13 (t, $J = 1.6$ Hz, 1H), 8.03 (d, $J = 8.0$ Hz, 1H), 7.92 (d, $J = 8.0$ Hz, 1H), 7.75–7.69 (m, 2H), 7.54–7.35 (m, 7H), 6.39 (s, 1H). ^{13}C NMR (100 MHz, CDCl_3) δ 190.63, 164.05, 157.83, 140.39, 135.98, 135.86, 135.39, 131.73, 131.14, 131.05, 130.59, 130.42, 130.32, 128.42, 127.53, 126.57, 126.49, 123.36, 123.22, 105.31. HRMS (ESI): m/z calcd for $\text{C}_{22}\text{H}_{16}\text{Br}_2\text{NO}_2[\text{M}+\text{H}]^+$: 483.9548, found: 483.9550.

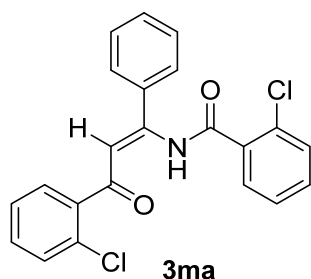


(Z)-N-(3-oxo-1-phenyl-3-(3-(trifluoromethyl)phenyl)prop-1-en-1-yl)-3-(trifluoromethyl)benzamide(3ka): Yellow oil, yield 74%. ^1H NMR (400 MHz, CDCl_3) δ 13.43 (s, 1H), 8.37 (s, 1H), 8.31 (d, $J = 7.6$ Hz, 1H), 8.27 (s, 1H), 8.19 (d, $J = 8.0$ Hz, 1H), 7.88 (d, $J = 7.6$ Hz, 1H), 7.84 (d, $J = 8.0$ Hz, 1H), 7.72 (t, $J = 7.6$ Hz, 1H), 7.65 (t, $J = 7.6$ Hz, 1H), 7.57–7.55 (m, 2H), 7.53–7.46 (m, 3H), 6.48 (s, 1H). ^{13}C NMR (100 MHz, CDCl_3) δ 190.70, 164.08, 158.21, 139.12, 135.86, 134.28, 131.99, 131.68, 131.19, 131.05, 130.99, 130.46, 129.78, 129.59, 129.54, 129.47, 128.48, 127.57, 125.75, 124.97, 122.42, 105.21. HRMS (ESI): m/z calcd for $\text{C}_{24}\text{H}_{16}\text{F}_6\text{NO}_2[\text{M}+\text{H}]^+$: 464.1085, found: 464.1089.

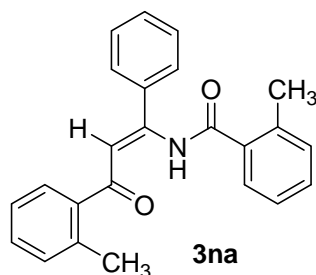


(Z)-3-Methyl-N-(3-oxo-1-phenyl-3-(m-tolyl)prop-1-en-1-yl)benzamide(3la): Yellow oil, yield 68%. ^1H NMR (400 MHz, $\text{DMSO}-d_6$) δ 12.84 (s, 1H), 7.94 (s, 1H), 7.90 (d, $J = 7.2$ Hz, 1H), 7.82 (s, 2H), 7.62 (d, $J = 6.8$ Hz, 2H), 7.50 (d, $J = 5.2$ Hz, 2H), 7.51–7.39 (m, 5H), 6.69 (s, 1H), 2.41

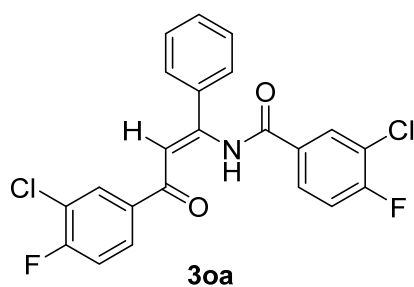
(s, 3H), 2.38 (s, 3H). ¹³C NMR (100 MHz, DMSO-d₆) δ 191.33, 164.73, 155.26, 138.49, 138.18, 138.00, 135.94, 133.70, 133.51, 133.27, 129.79, 128.93, 128.62, 128.54, 128.26, 128.02, 127.64, 125.31, 124.81, 106.18, 20.93, 20.84. HRMS (ESI): m/z calcd for C₂₄H₂₂NO₂[M+H]⁺: 356.1651, found: 356.1655.



(Z)-2-Chloro-N-(3-(2-chlorophenyl)-3-oxo-1-phenylprop-1-en-1-yl)benzamide(3ma): Yellow oil, yield 71%. ¹H NMR (400 MHz, CDCl₃) δ 12.27 (s, 1H), 7.73 (dd, *J* = 7.6, 1.6 Hz, 1H), 7.59 (dd, *J* = 7.6, 1.6 Hz, 2H), 7.56 (dd, *J* = 7.6, 1.6 Hz, 1H), 7.50 – 7.41 (m, 6H), 7.40 – 7.32 (m, 3H), 6.25 (s, 1H). ¹³C NMR (100 MHz, CDCl₃) δ 193.35, 165.51, 155.15, 139.69, 135.66, 134.60, 132.34, 132.00, 131.38, 130.91, 130.70, 130.30, 130.26, 129.82, 128.41, 127.67, 127.31, 127.13, 110.15. HRMS (ESI): m/z calcd for C₂₂H₁₆Cl₂NO₂[M+H]⁺: 396.0558, found: 396.0562.

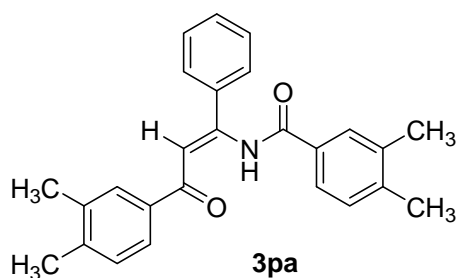


(Z)-2-Methyl-N-(3-oxo-1-phenyl-3-(o-tolyl)prop-1-en-1-yl)benzamide(3na): Yellow solid, m.p. 121.2 – 121.5°C, yield 68%. ¹H NMR (400 MHz, DMSO-d₆) δ 11.94 (s, 1H), 7.74 (t, *J* = 6.8 Hz, 2H), 7.66– 7.64 (m, 2H), 7.48– 7.44(m, 4H), 7.42– 7.28 (m, 5H), 6.32 (s, 1H), 2.45 (s, 3H), 2.41 (s, 3H). ¹³C NMR (100 MHz, DMSO-d₆) δ 195.19, 167.11, 152.85, 139.18, 137.01, 136.88, 135.90, 134.62, 131.42, 131.36, 131.07, 129.88, 128.58, 128.16, 127.61, 127.54, 126.13, 125.85, 110.60, 20.39, 19.83. HRMS (ESI): m/z calcd for C₂₄H₂₂NO₂[M+H]⁺: 356.1651, found: 356.1653.



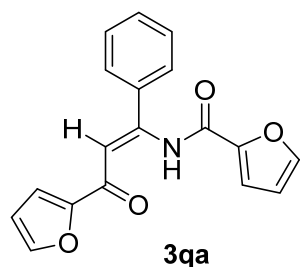
(Z)-3-chloro-N-(3-(3-chloro-4-fluorophenyl)-3-oxo-1-phenylprop-1-en-1-yl)-4-fluorobenzamide(30a):

White solid, m.p.153.8 – 154.1°C, yield 76%. ¹H NMR (400 MHz, CDCl₃) δ 13.29 (s, 1H), 8.15 (dd, *J* = 6.8, 2.0 Hz, 1H), 8.09 (dd, *J* = 6.8, 2.0 Hz, 1H), 8.02–7.98 (m, 1H), 7.93 – 7.89 (m, 1H), 7.52 – 7.44 (m, 5H), 7.32 (d, *J* = 8.5 Hz, 1H), 7.29–7.24 (m, 1H), 6.37 (s, 1H).¹³C NMR (100 MHz, CDCl₃) δ 189.47, 163.24, 161.13(d, *J* = 255 Hz), 161.09 (d, *J* = 249 Hz), 158.07, 135.86, 135.65 (d, *J* = 3 Hz), 131.53, 131.03, 130.68 (d, *J* = 2 Hz), 130.44, 128.46, 128.31 (d, *J* = 9 Hz), 127.52, 122.42 (d, *J* =19 Hz), 122.19 (d, *J* =18 Hz), 117.31 (d, *J* =19 Hz), 117.18, 117.09 (d, *J* =18 Hz), 104.92.HRMS (ESI): m/z calcd for C₂₂H₁₄Cl₂F₂NO₂[M+H]⁺: 432.0370, found:432.0371.

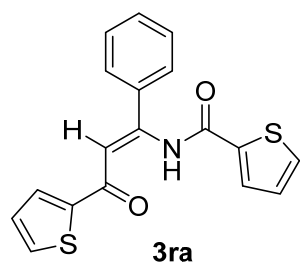


(Z)-N-(3-(3,4-dimethylphenyl)-3-oxo-1-phenylprop-1-en-1-yl)-3,4-dimethylbenzamide(3pa):

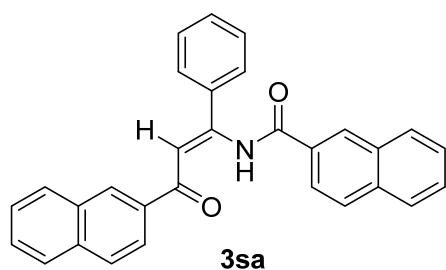
Light yellow oil, yield 64%. ¹H NMR (400 MHz, CDCl₃) δ 13.31 (s, 1H), 7.86 (d, *J* = 6.4 Hz, 2H), 7.79 (s, 1H), 7.74 (d, *J* = 8.0 Hz, 1H), 7.55 – 7.53 (m, 2H), 7.47 – 7.42 (m, 3H), 7.28 (d, *J* = 8.4 Hz, 1H), 7.24 (d, *J* = 8.0 Hz, 1H), 6.42 (s, 1H), 2.36 – 2.34 (m, 12H).¹³C NMR (100 MHz, CDCl₃) δ 192.03, 165.64, 156.85, 142.49, 142.25, 137.37, 137.20, 136.95, 136.68, 131.20, 131.16, 130.21, 130.04, 129.71, 129.64, 129.20, 128.23, 127.51, 125.71, 105.44, 20.03, 19.99, 19.97, 19.93.HRMS (ESI): m/z calcd for C₂₆H₂₆NO₂[M+H]⁺: 384.1964, found: 384.1965.



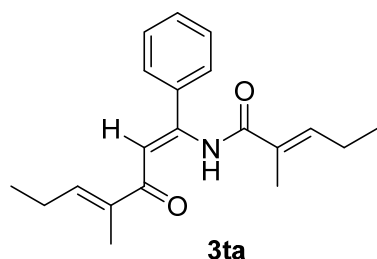
(Z)-N-(3-(furan-2-yl)-3-oxo-1-phenylprop-1-en-1-yl)furan-2-carboxamide(3qa): White solid, m.p.137.1 – 137.4°C, yield 73%. ¹H NMR (400 MHz, DMSO-d₆) δ 12.72 (s, 1H), 8.06 (d, *J* = 12.0 Hz, 2H), 7.69 (d, *J* = 3.2 Hz, 1H), 7.55 (d, *J* = 7.2 Hz, 2H), 7.49– 7.41 (m, 3H), 7.33 (d, *J* = 3.2 Hz, 1H), 6.82 – 6.70 (m, 2H), 6.45 (s, 1H).¹³C NMR (100 MHz, DMSO-d₆) δ 178.90, 155.04, 154.22, 152.71, 148.32, 147.06, 146.75, 135.42, 129.85, 127.98, 127.64, 118.64, 117.00, 113.01, 105.65.HRMS (ESI): *m/z* calcd for C₁₈H₁₄NO₄[M+H]⁺: 308.0923, found: 308.0925.



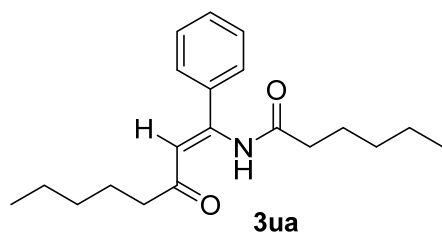
(Z)-N-(3-oxo-1-phenyl-3-(thiophen-2-yl)prop-1-en-1-yl)thiophene-2-carboxamide(3ra):White solid, m.p.160.1 – 160.4°C, yield 74%. ¹H NMR (400 MHz, CDCl₃) δ 13.17 (s, 1H), 7.94 (dd, *J* = 3.6, 0.8 Hz, 1H), 7.78 (dd, *J* = 3.6, 0.8 Hz, 1H), 7.68 (dd, *J* = 4.8, 0.8 Hz, 1H), 7.61 (dd, *J* = 4.8, 0.8 Hz, 1H), 7.54 – 7.52 (m, 2H), 7.48 – 7.42 (m, 3H), 7.19 – 7.15(m, 2H), 6.26 (s, 1H). ¹³C NMR(100 MHz, CDCl₃) δ 184.47, 159.88, 156.63, 145.78, 139.12, 135.97, 134.06, 132.82, 131.23, 130.61, 130.05, 128.56, 128.32, 128.27, 127.61, 105.05.HRMS (ESI): *m/z* calcd for C₁₈H₁₄NO₂S₂[M+H]⁺: 340.0466, found: 340.0470.



(Z)-N-(3-(naphthalen-2-yl)-3-oxo-1-phenylprop-1-en-1-yl)-2-naphthamide (3sa): White solid, m.p. 194.1 – 194.5 °C, yield 75%. ¹H NMR (400 MHz, DMSO-d₆) δ 13.01 (s, 1H), 8.90 (s, 1H), 8.72 (s, 1H), 8.18 – 8.12 (m, 4H), 8.06 – 8.02 (m, 3H), 7.99 (d, *J* = 8.0 Hz, 1H), 7.73 – 7.60 (m, 6H), 7.50 (d, *J* = 7.2 Hz, 3H), 6.97 (s, 1H). ¹³C NMR (100 MHz, DMSO-d₆) δ 191.47, 165.35, 155.63, 136.52, 135.75, 135.46, 135.29, 132.78, 132.66, 131.13, 130.37, 130.16, 129.78, 129.31, 129.27, 129.14, 129.03, 128.88, 128.60, 128.22, 128.10, 127.68, 127.36, 124.27, 106.96. HRMS (ESI): *m/z* calcd for C₃₀H₂₂NO₂[M+H]⁺: 428.1651, found: 428.1654.



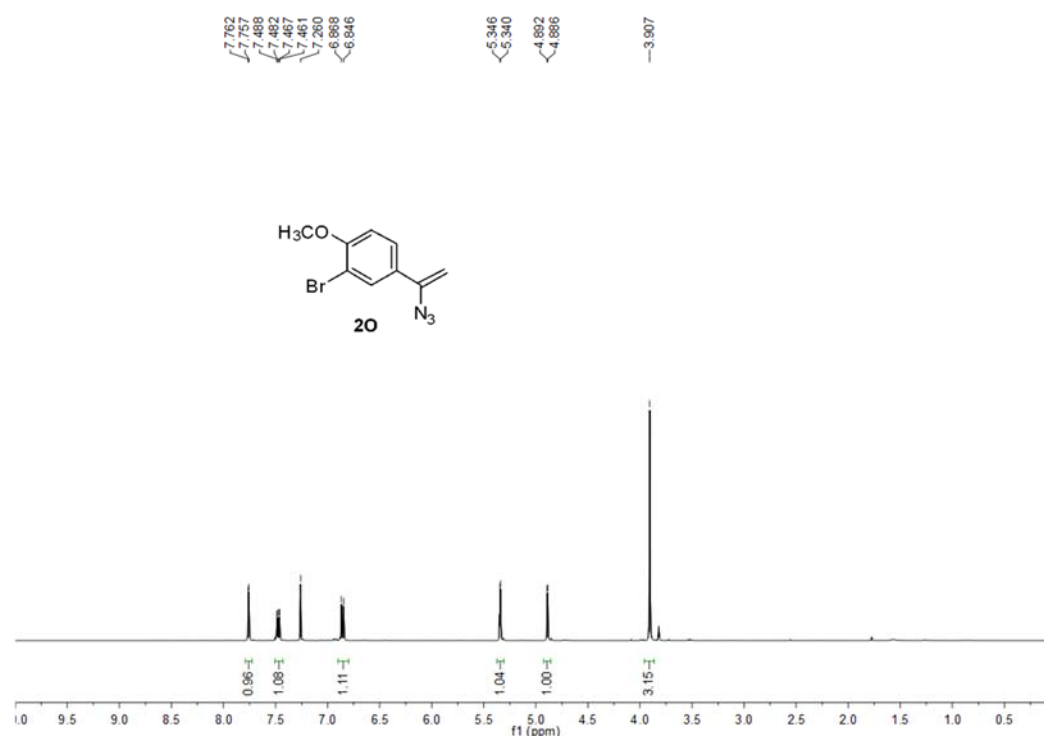
(Z)-2-Methyl-N-((1Z,4E)-4-methyl-3-oxo-1-phenylhepta-1,4-dien-1-yl)pent-2-enamide(3ta): Light yellow oil, yield 63%. ¹H NMR (400 MHz, CDCl₃) δ 12.47 (s, 1H), 7.42 – 7.37 (m, 5H), 6.70 (td, *J* = 7.2, 1.2 Hz, 1H), 6.62 (td, *J* = 7.2, 1.2 Hz, 1H), 6.06 (s, 1H), 2.30 – 2.21 (m, 4H), 1.93 (s, 3H), 1.88 (s, 3H), 1.11 – 1.06 (m, 6H). ¹³C NMR (100 MHz, CDCl₃) δ 194.26, 167.71, 155.20, 142.78, 141.69, 137.68, 137.35, 131.01, 129.35, 128.13, 127.20, 104.92, 22.50, 22.27, 13.23, 13.05, 12.46, 11.79. HRMS (ESI): *m/z* calcd for C₂₀H₂₆NO₂[M+H]⁺: 312.1964, found: 312.1967.



(Z)-N-(3-oxo-1-phenyloct-1-en-1-yl)hexanamide(3ua): Light yellow oil, yield 61%. ¹H NMR (400 MHz, CDCl₃) δ 11.86 (s, 1H), 7.41 – 7.35 (m, 5H), 5.59 (s, 1H), 2.48 (t, *J* = 7.6 Hz, 2H), 2.41 (d, *J* = 7.6 Hz, 2H), 1.68 – 1.61 (m, 4H), 1.34 – 1.31 (m, 8H), 0.92 – 0.87 (m, 6H). ¹³C NMR (100 MHz, CDCl₃) δ 203.05, 172.11, 154.28, 136.04, 129.63, 128.04, 127.31, 108.01, 43.92, 38.00, 31.51, 31.33, 24.75, 24.50, 22.55, 22.41, 13.99, 13.96. HRMS (ESI): *m/z* calcd for C₂₀H₃₀NO₂[M+H]⁺: 316.2277, found: 316.2276.

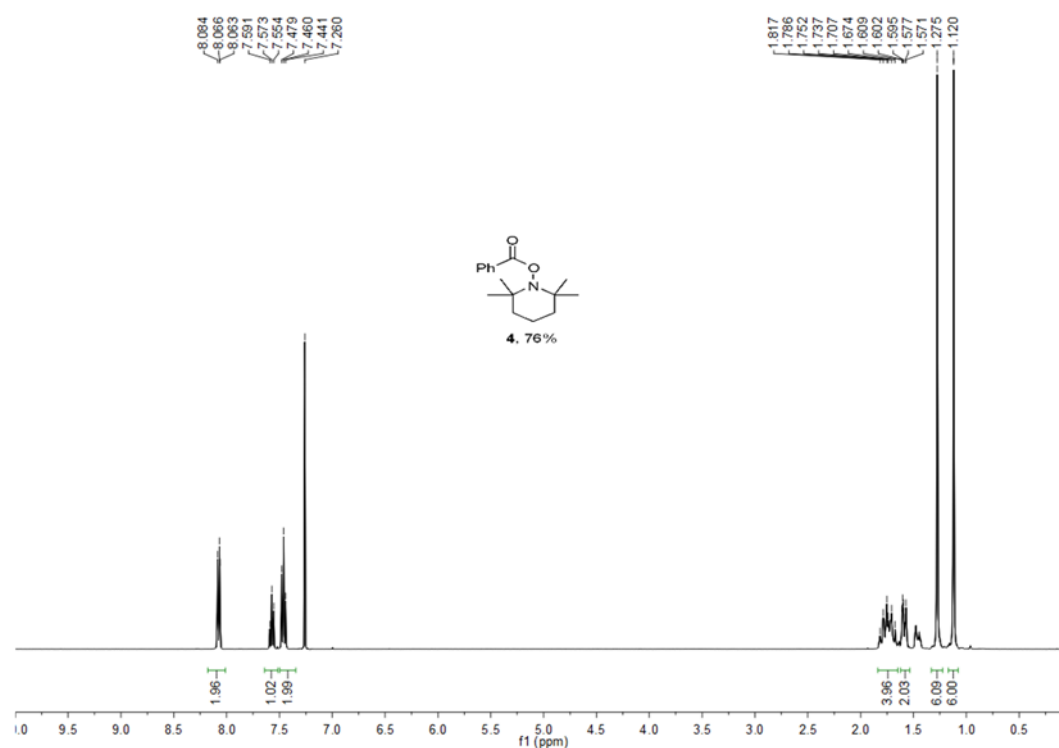
6. Characterization and NMR spectra of starting materials (2o)

^1H NMR (400 MHz, CDCl_3) δ 7.76 (d, $J = 2.0$ Hz, 1H), 7.48 (dd, $J = 8.8, 2.0$ Hz, 2H), 6.86 (d, $J = 8.8$ Hz, 1H), 5.34 (d, $J = 2.4$ Hz, 1H), 4.89 (d, $J = 2.4$ Hz, 1H), 3.91 (s, 3H).

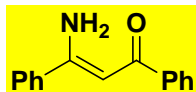


7. Characterization and NMR spectra of product 4 for control experiments

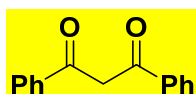
^1H NMR (400 MHz, CDCl_3) δ 8.08 – 8.06 (m, 2H), 7.57 (t, $J = 7.6$ Hz, 1H), 7.46 (t, $J = 7.6$ Hz, 2H), 1.82 – 1.67 (m, 4H), 1.61 – 1.57 (m, 2H), 1.28 (s, 6H), 1.12 (s, 6H).



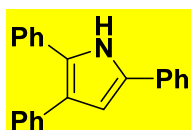
8. Characterization and NMR spectra of products for synthetic applications of 3aa



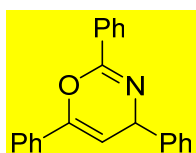
(Z)-3-Amino-1,3-diphenylprop-2-en-1-one (**4**): Yellow oil, yield 92%. ^1H NMR (400 MHz, CDCl_3) δ 10.50 (s, 1H), 8.01 (d, $J = 8.5$ Hz, 2H), 7.67 (d, $J = 8.5$ Hz, 2H), 7.57 – 7.45 (m, 6H), 6.21 (s, 1H), 5.53 (s, 1H). ^{13}C NMR (100 MHz, CDCl_3) δ 190.33, 163.04, 140.53, 137.54, 131.14, 130.68, 129.00, 128.41, 127.21, 126.49, 91.99. HRMS (ESI): m/z calculated for $\text{C}_{15}\text{H}_{14}\text{NO}$ $[\text{M} + \text{H}]^+$: 224.1070, found: 224.1075.



1,3-Diphenylpropane-1,3-dione (**5**): colorless oil, yield 95%. ^1H NMR (400 MHz, CDCl_3) δ 8.03 - 7.8.01 (m, 4H), 7.60 - 7.55 (m, 2H), 7.54 - 7.45 (m, 4H), 6.86 (s, 1H). ^{13}C NMR (100 MHz, CDCl_3) δ 185.03, 135.81, 132.86, 128.98, 127.52, 93.54. HRMS m/z : calcd for $\text{C}_{15}\text{H}_{13}\text{O}_2^+$ $[\text{M} + \text{H}]^+$ 225.0910, found: 225.0906.

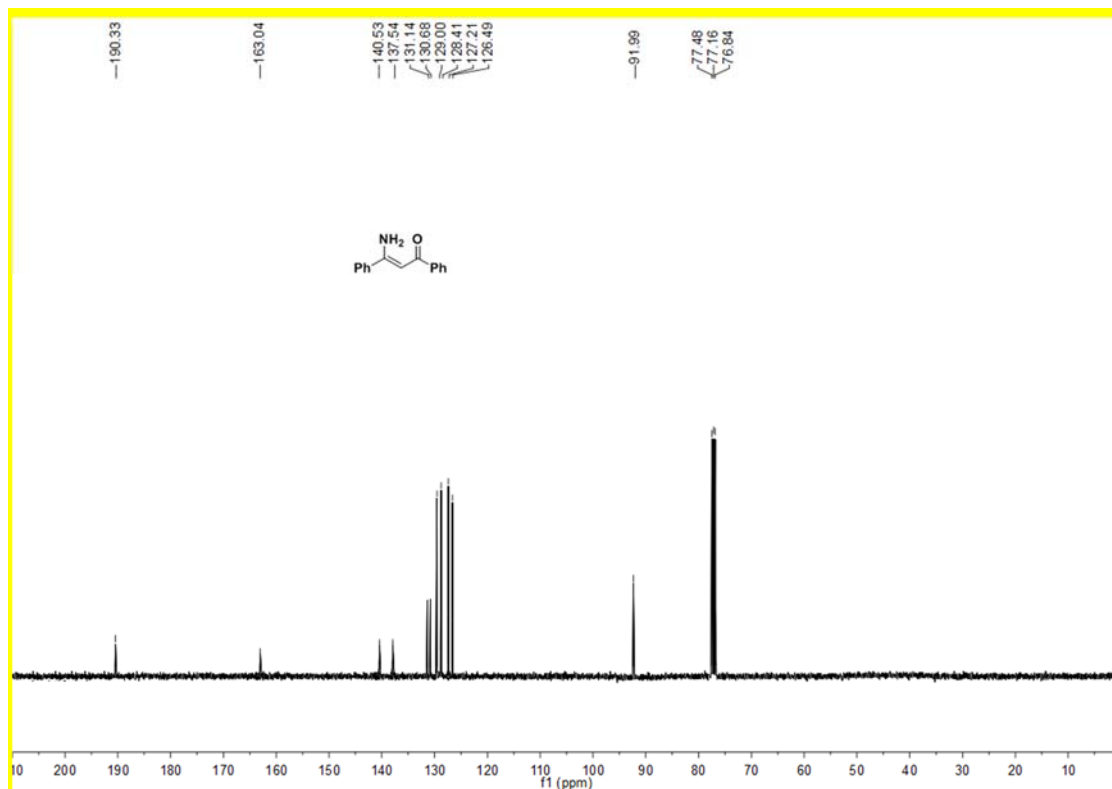
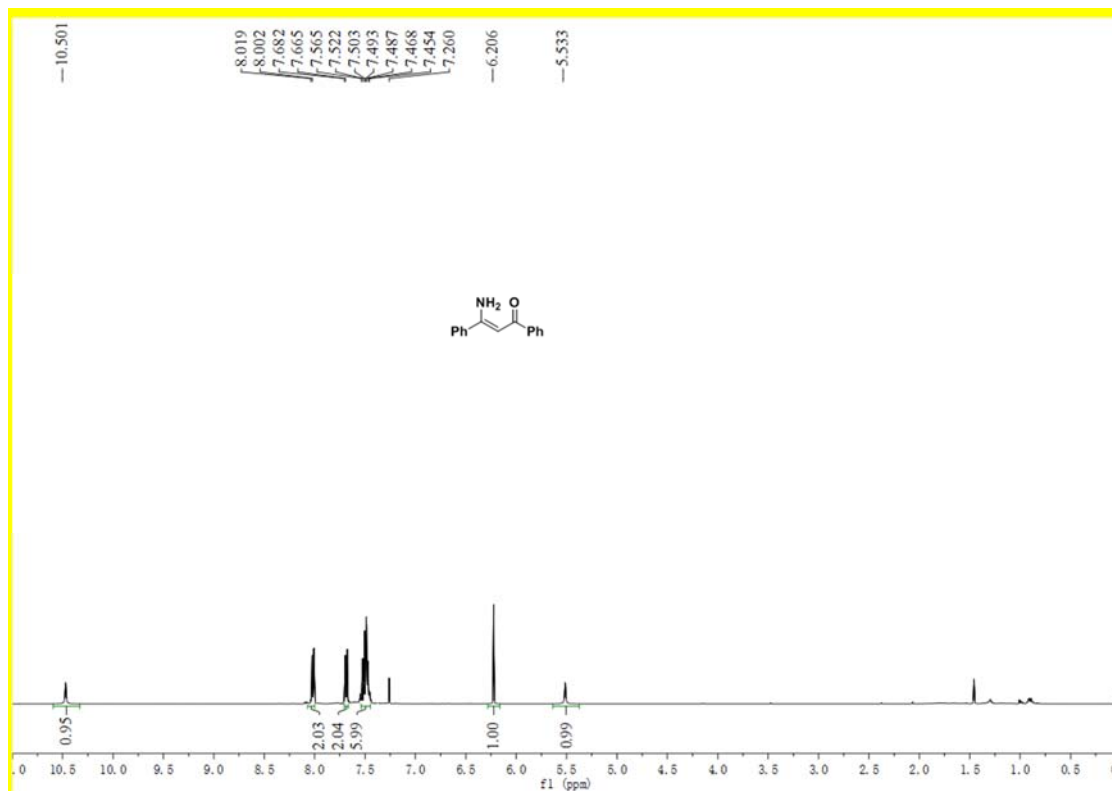


2,3,5-Triphenyl-1H-pyrrole (**6**): Light yellow solid, yield 80%, mp 135-138 °C. ^1H NMR (400 MHz, CDCl_3): δ 8.44 (s, 1H), 7.57 (d, $J = 7.6$ Hz, 2H), 7.48 - 7.21 (m, 13H), 6.74 (d, $J = 2.8$ Hz, 1H). ^{13}C NMR (100 MHz, CDCl_3) δ 136.42, 133.15, 132.38, 132.19, 129.76, 129.56, 129.00, 128.81, 128.36, 127.60, 127.09, 126.69, 126.05, 123.99, 123.86, 108.71. HRMS m/z : calcd for $\text{C}_{22}\text{H}_{17}\text{N}^+$ $[\text{M} + \text{H}]^+$ 295.1361, found: 295.1365.

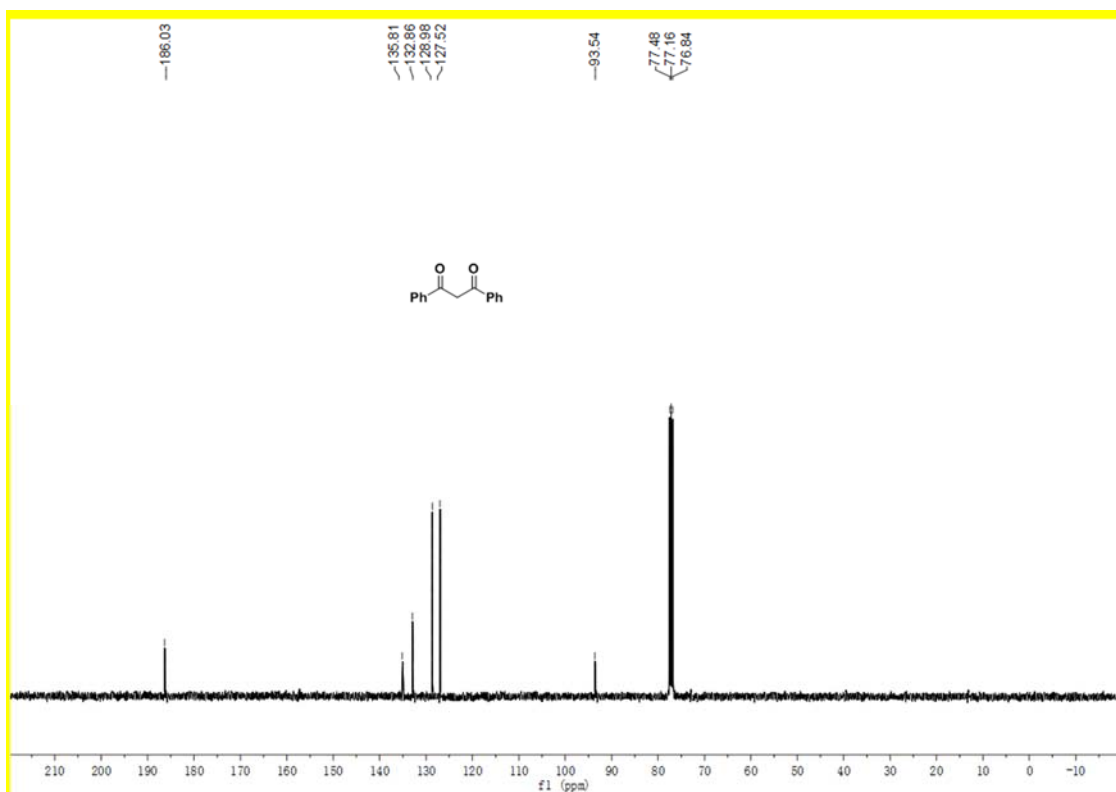
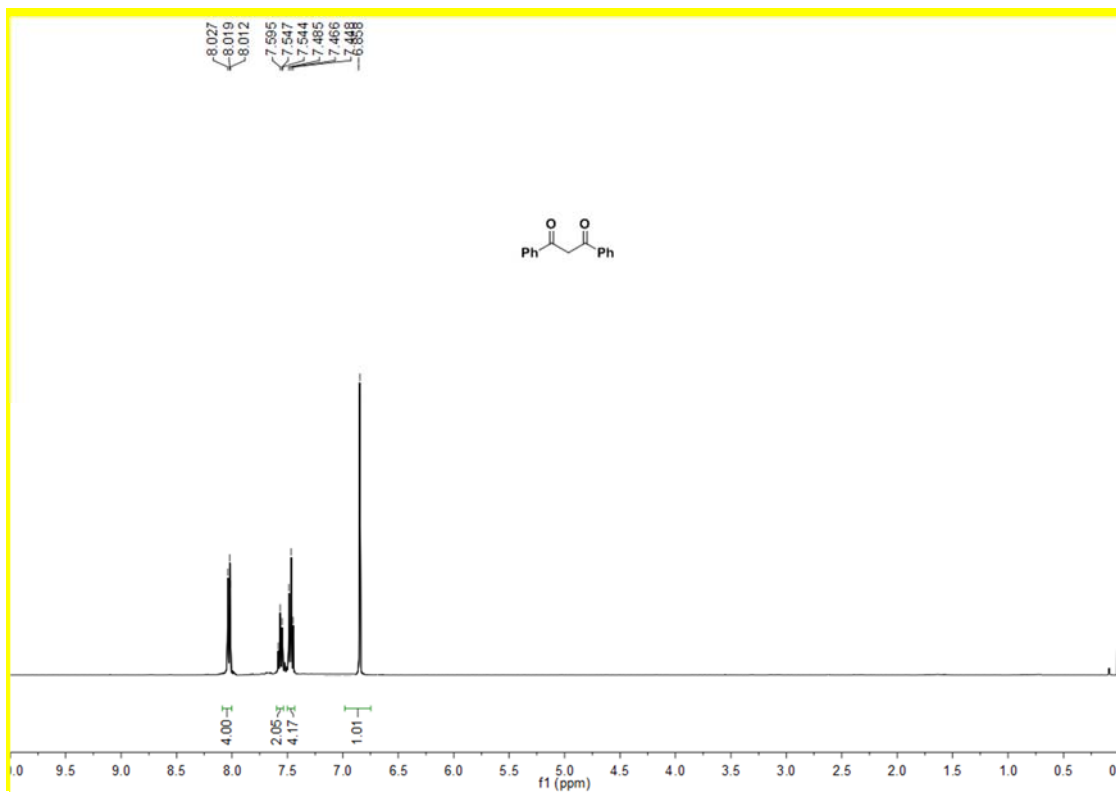


2,4,6-Triphenyl-4H-1,3-oxazine (**7**): Colorless solid, yield 70%, mp 97 - 99 °C, ^1H NMR (400 MHz, CDCl_3) δ 8.12 (d, $J = 7.2$ HZ, 2H), 7.78 (d, $J = 7.6$ HZ, 2H), 7.54 - 7.49 (m, 2H), 7.39 - 7.35 (m, 8H), 7.32-7.23 (m, 1H), 5.66 (d, $J = 4.0$ Hz, 1H), 5.46 (d, $J = 4.0$ Hz, 1H). ^{13}C NMR (100 MHz, CDCl_3) δ 152.31, 146.30, 144.52, 132.93, 132.50, 131.14, 129.00, 128.81, 128.61, 128.36, 127.60, 127.42, 127.27, 124.30, 100.86, 56.64. HRMS (ESI): m/z calcd. for $\text{C}_{22}\text{H}_{18}\text{NO}$ $(\text{M} + \text{H}^+)$ 312.1383, found 312.1386.

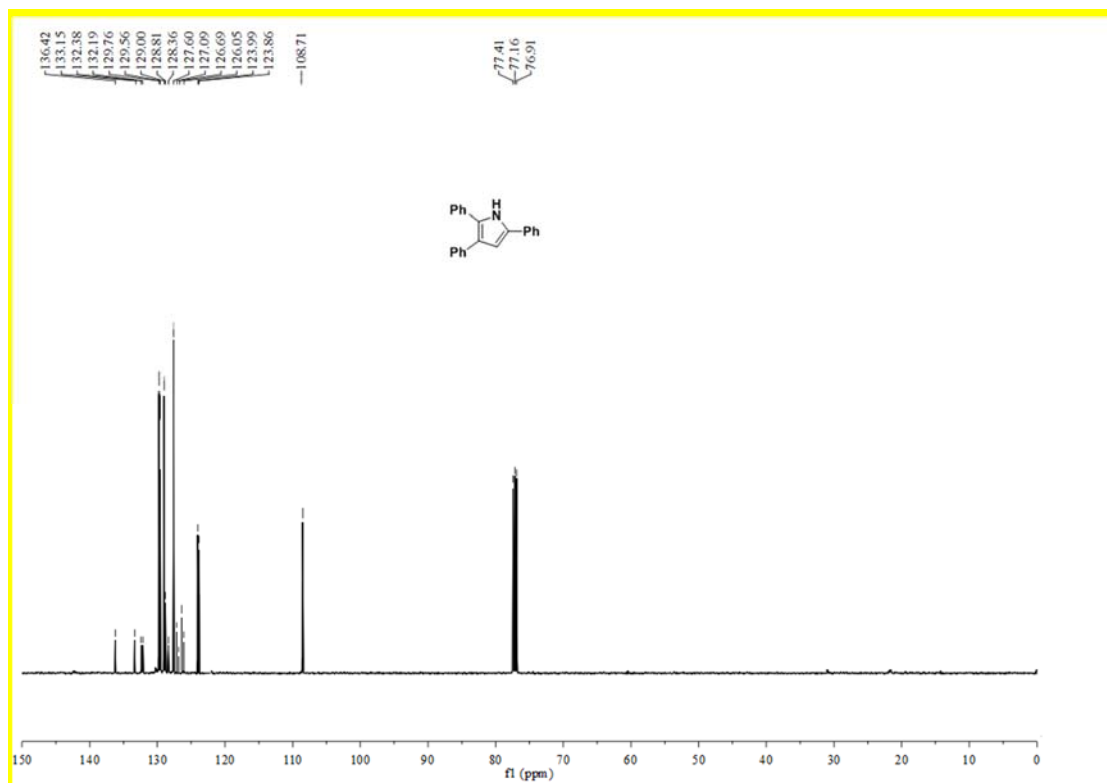
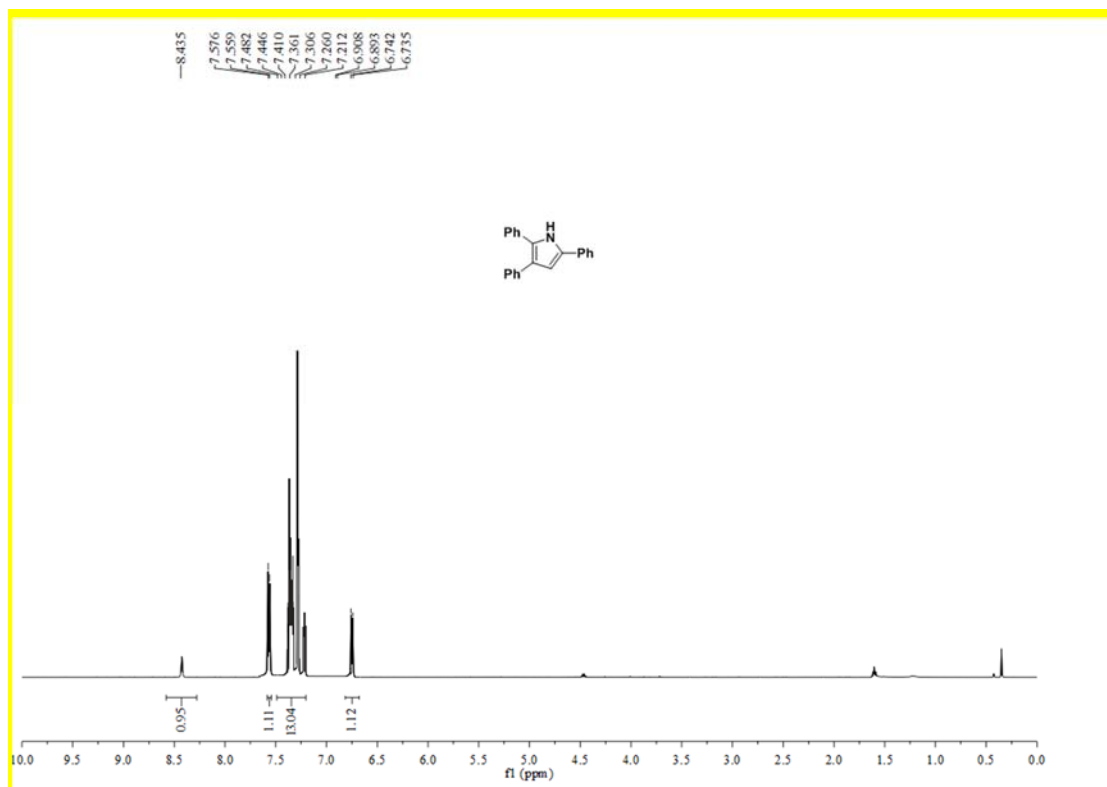
NMR spectra of 4



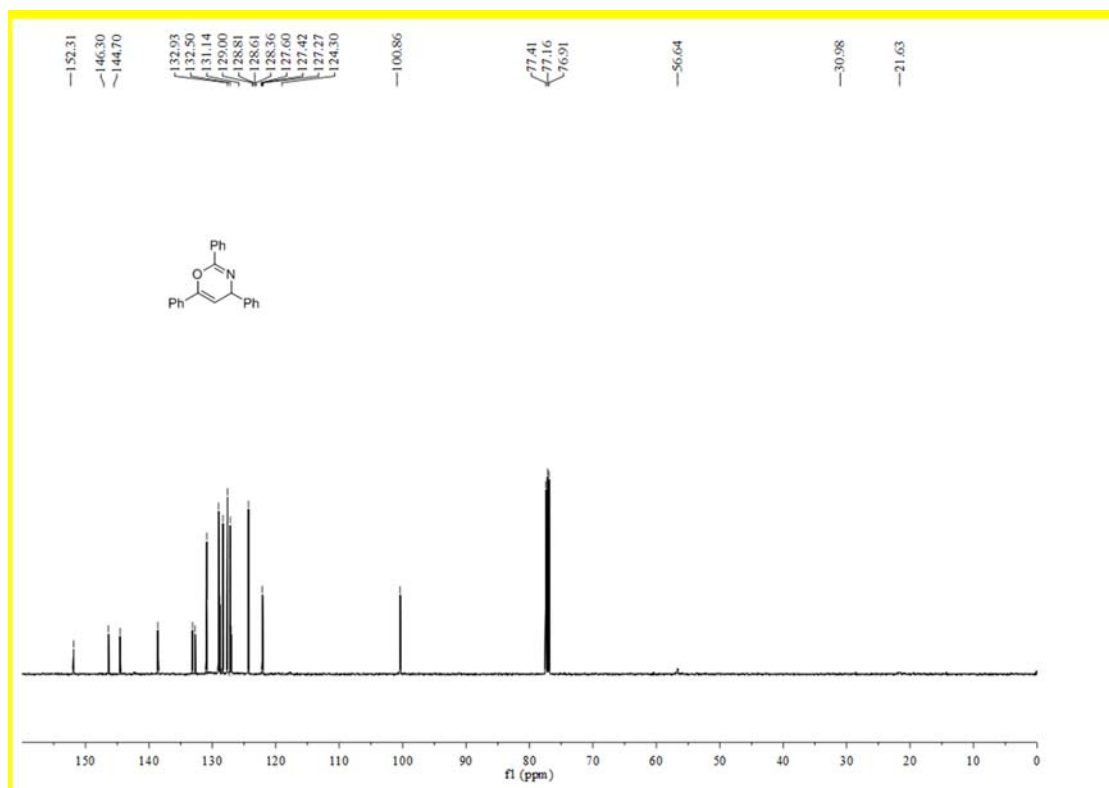
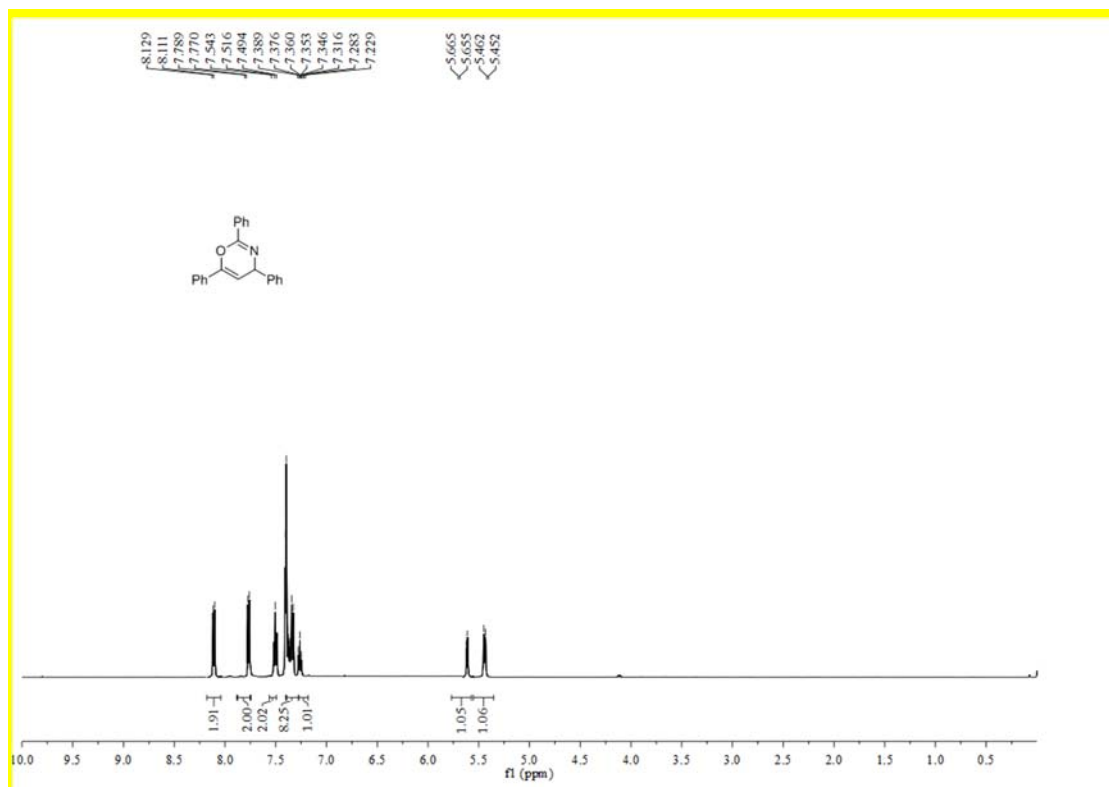
NMR spectra of 5



NMR spectra of 6



NMR spectra of 7



9. Crystallography of 3na

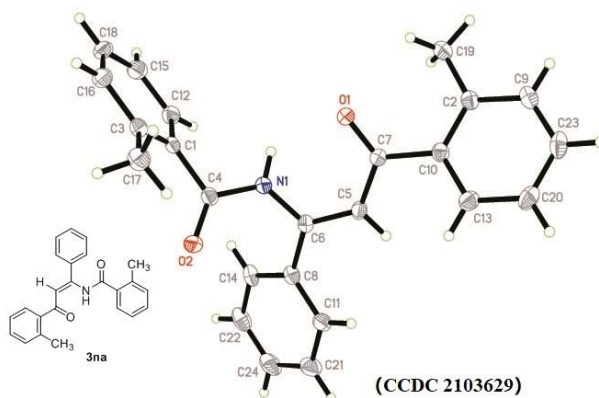
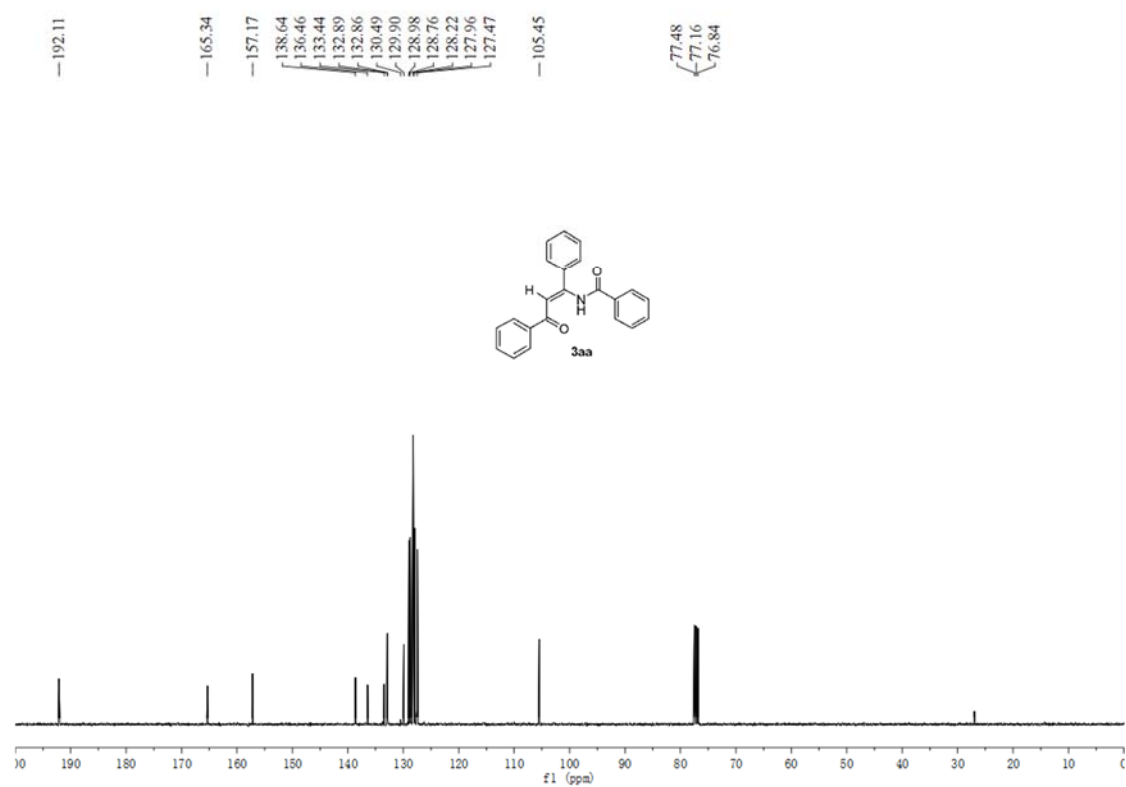
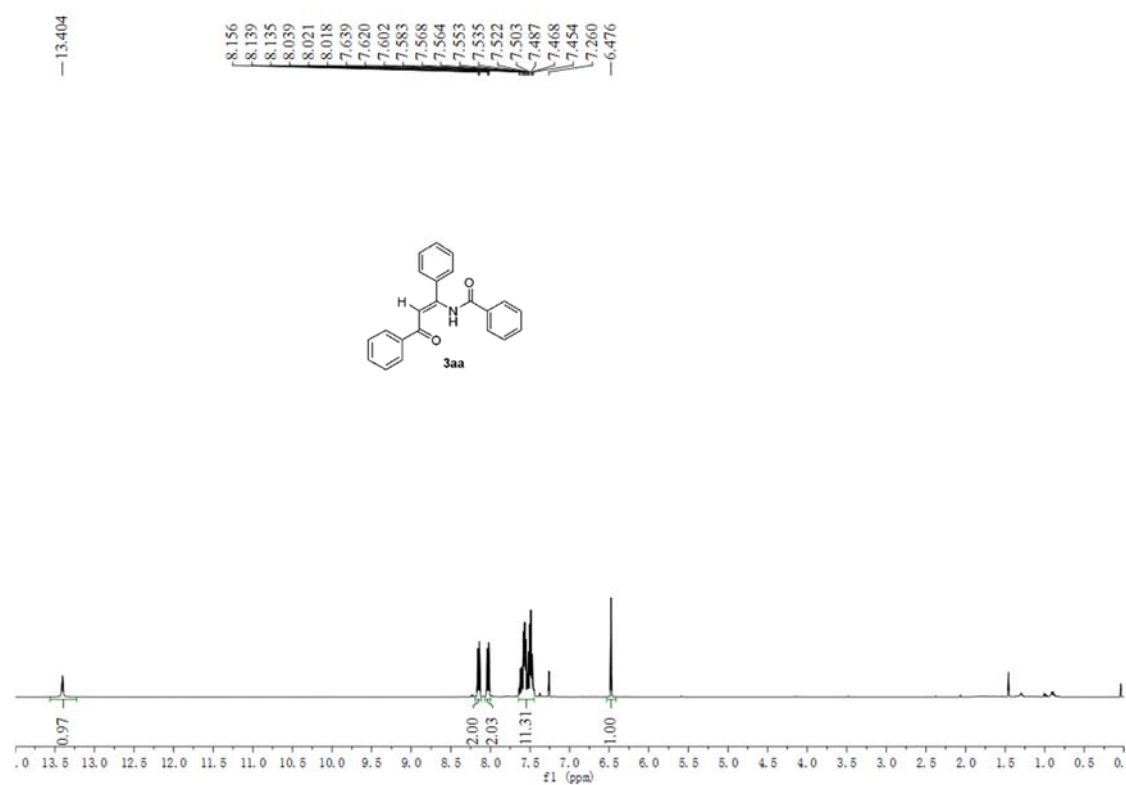
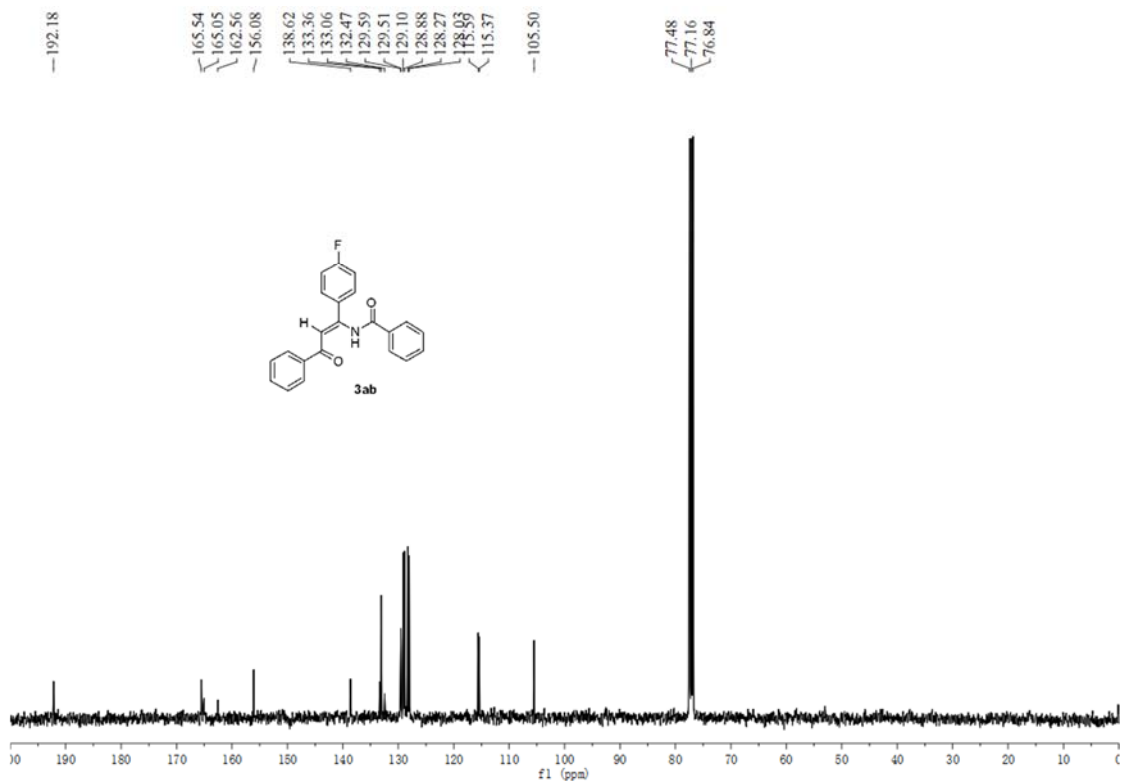
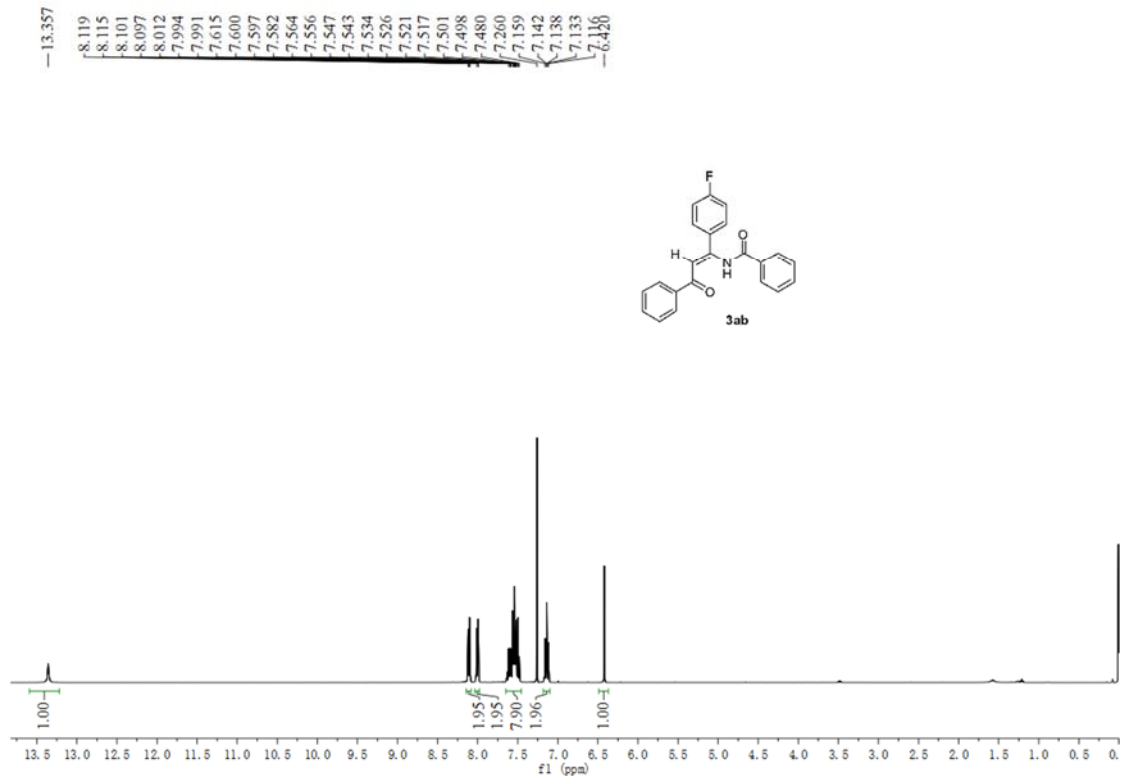


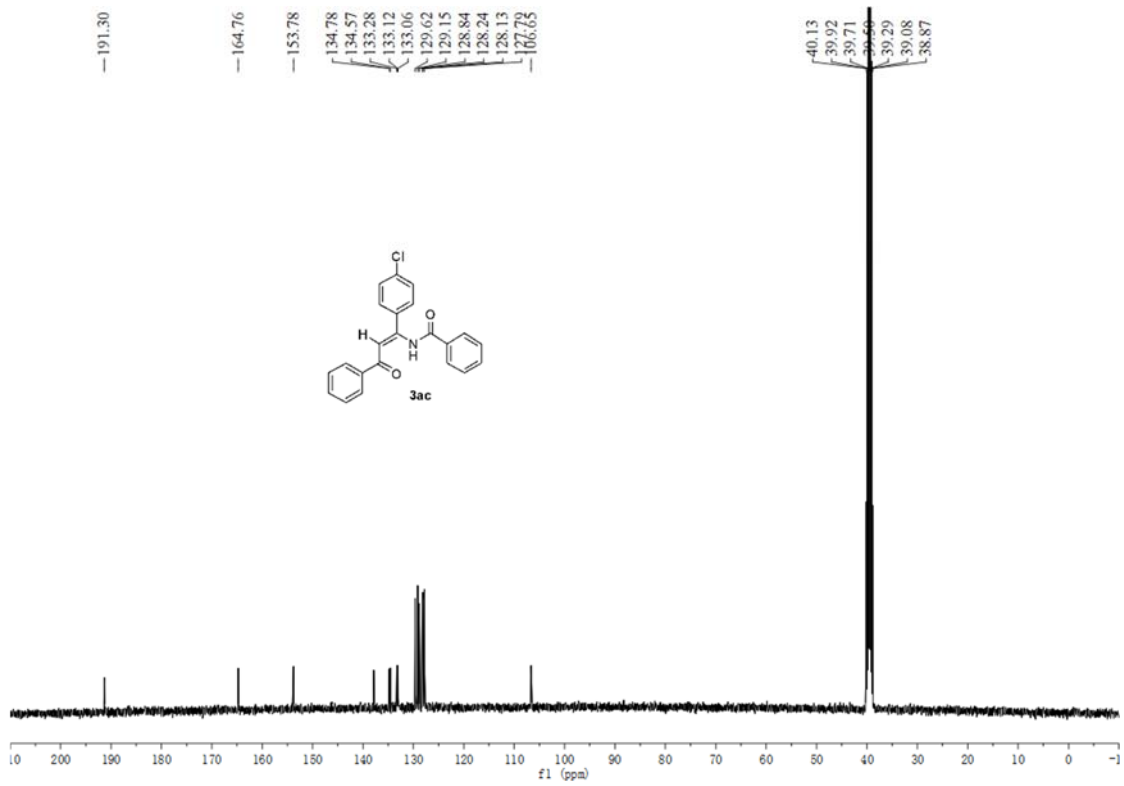
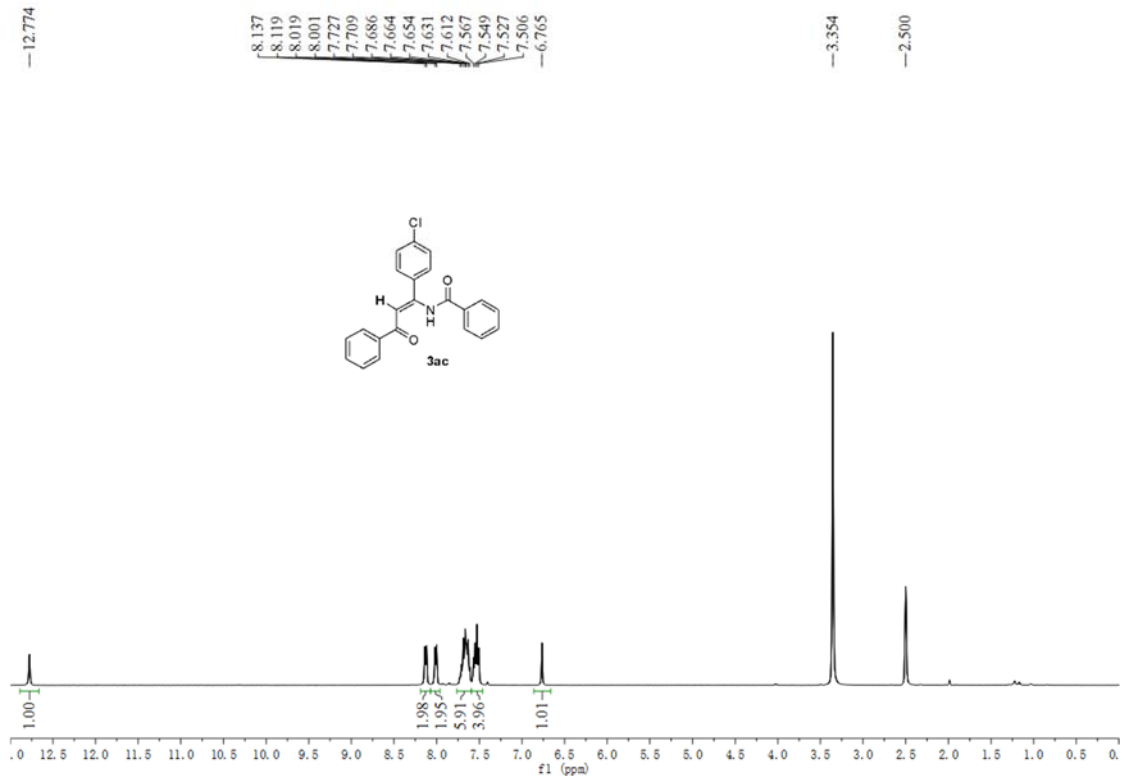
Table 1 Datablock of 3na

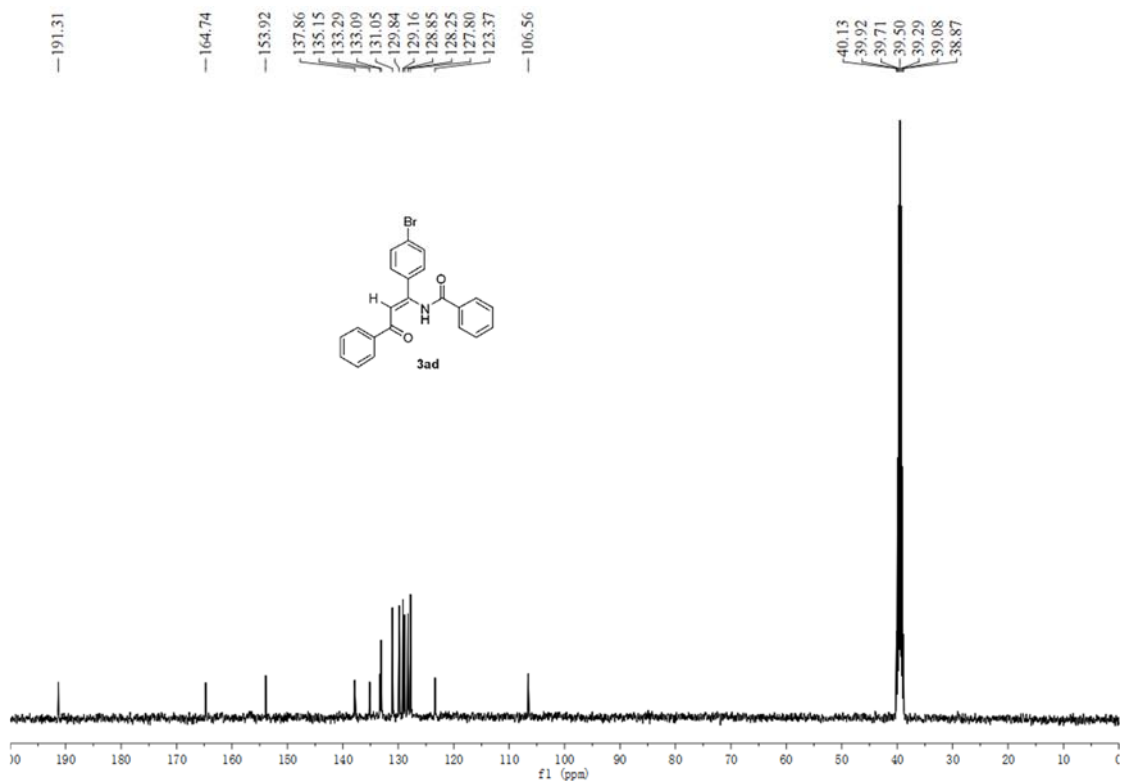
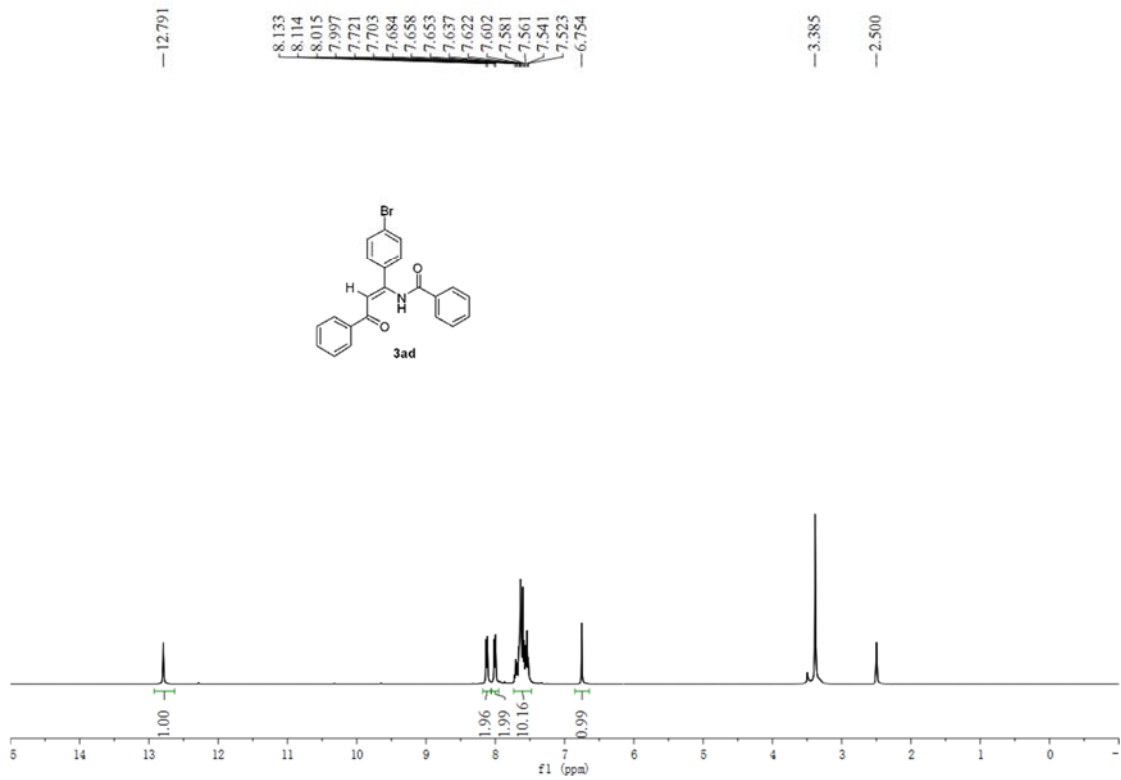
Empirical formula	C ₂₄ H ₂₁ NO ₂	
Moiety formula	C ₂₄ H ₂₁ NO ₂	
Sum formula	C ₂₄ H ₂₁ NO ₂	
Bond precision	C-C = 0.0030 Å, Wavelength=1.54178	
Unit cell dimensions	a=9.8259(3) alpha=97.864(2), b=9.8256(2) beta=108.797(2), c=10.8672(3) gamma=103.162(2)	
Temperature	153 K	
	Calculated	Reported
Volume	941.65(5)	941.65(4)
Space group	P -1	P -1
Hall group	-P 1	
Mr	355.42	355.42
D _x , g cm ⁻³	1.253	1.254
Z	2	2
Mu (mm ⁻¹)	0.627	0.627
F ₀₀₀	376.0	376.0
F ₀₀₀ '	377.07	
h,k,l _{max}	11,11,12	11,11,12
N _{ref}	3332	3333
T _{min} ,T _{max}	0.882,0.939	0.378,1.000
T _{min} '	0.882	
Correction method= # Reported T Limits:	T _{min} =0.378, T _{max} =1.000,AbsCorr = MULTI-SCAN	
Data completeness	1.000	
Theta(max)	66.590	
R(reflections)	0.0597(2887)	
wR2(reflections)	0.2913(3333)	
S	1.383	
N _{par}	244	

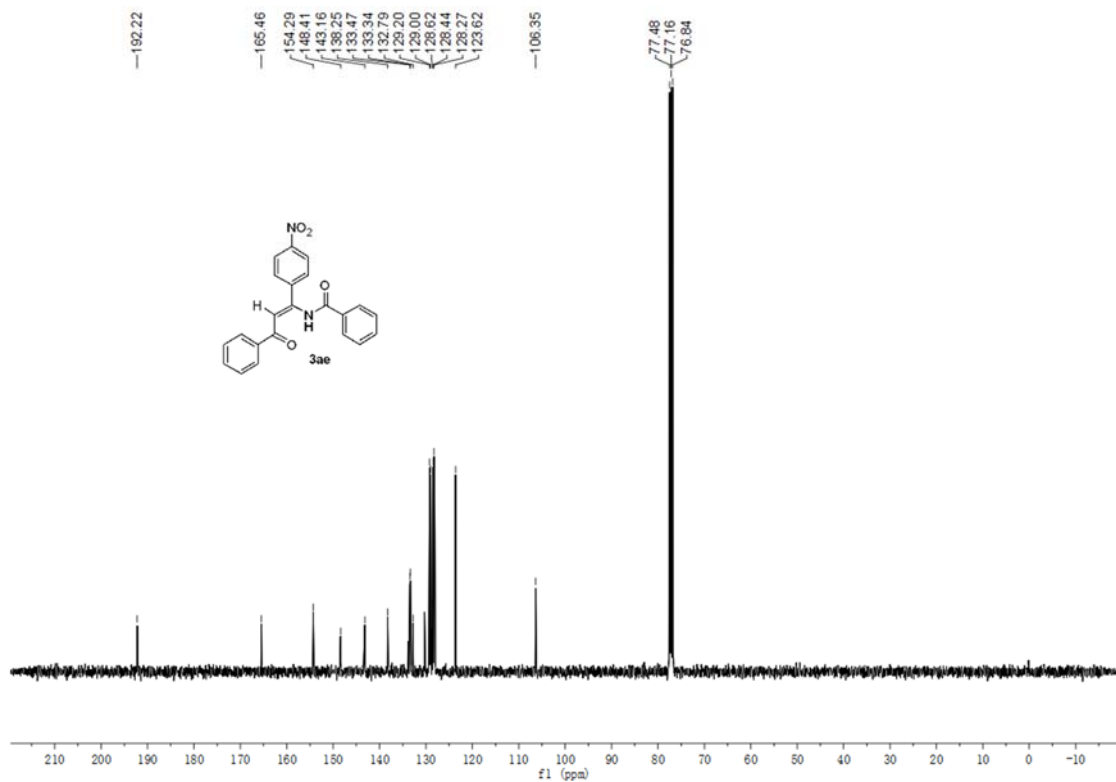
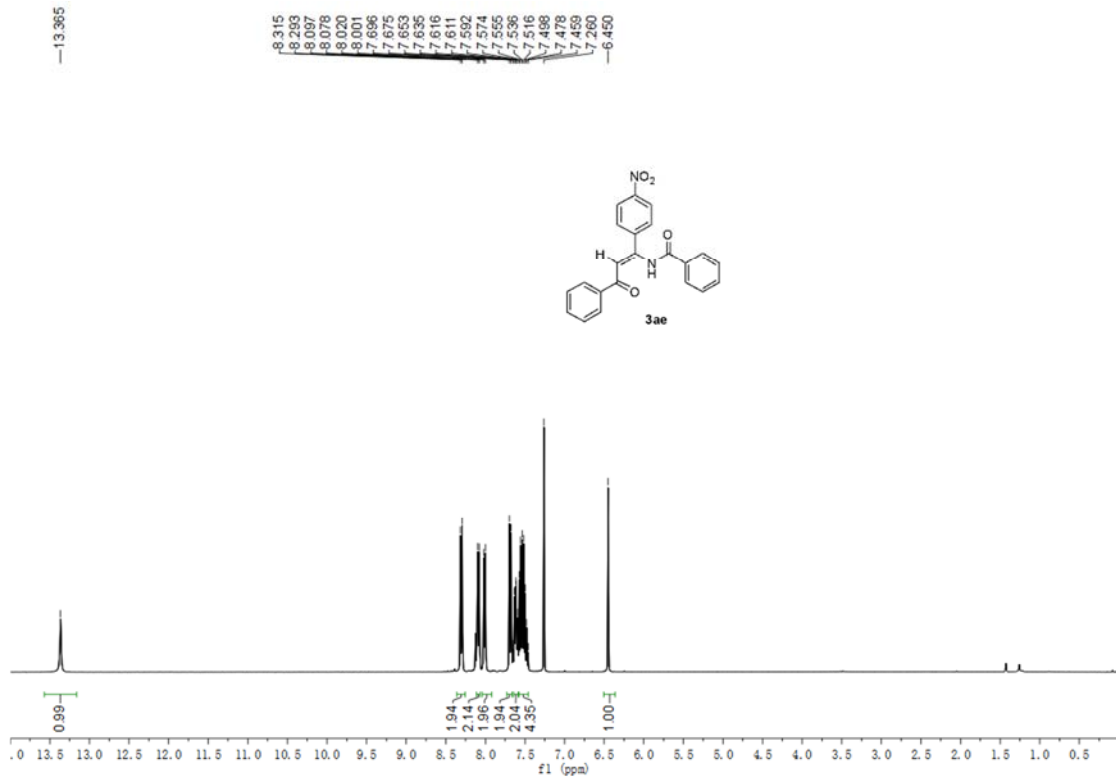
10. ^1H and ^{13}C NMR spectra of compounds 3aa-3ua

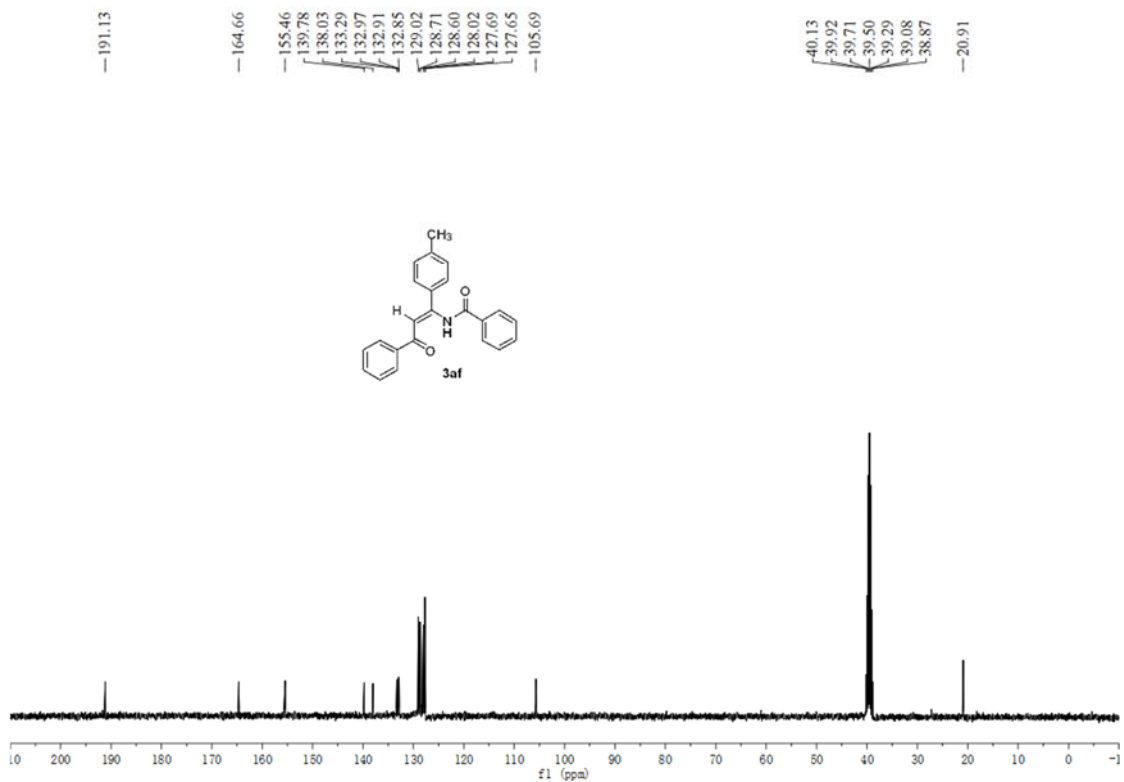
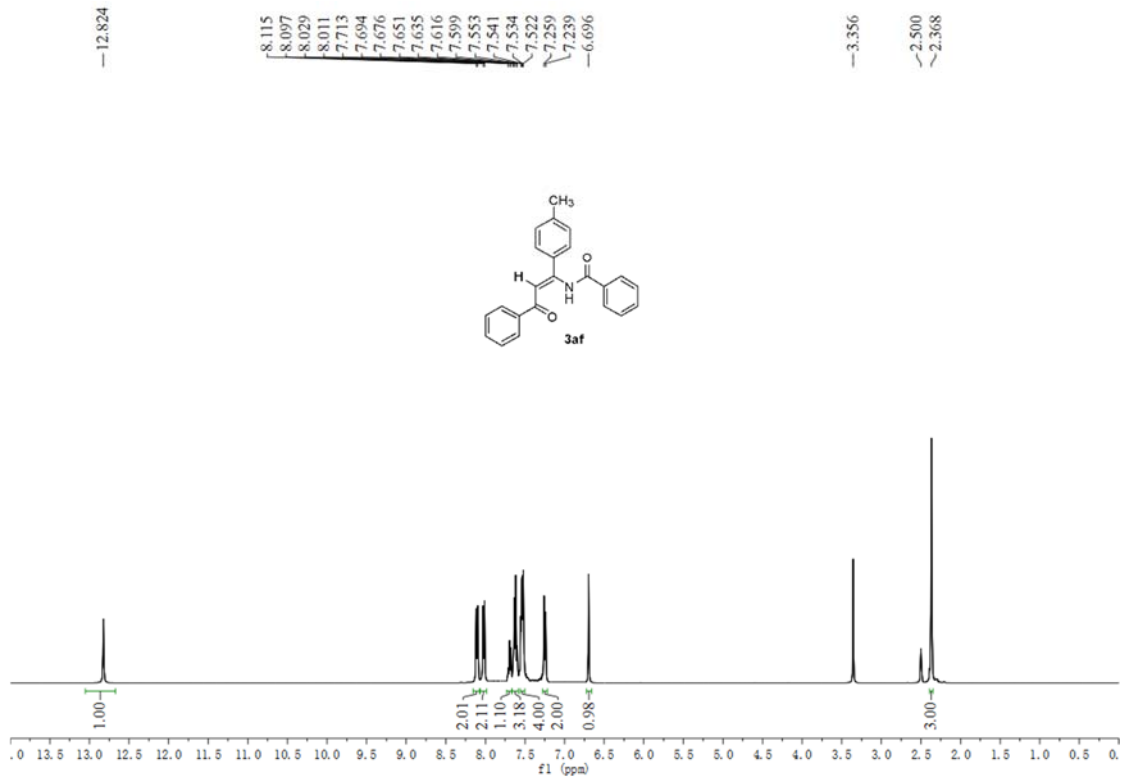


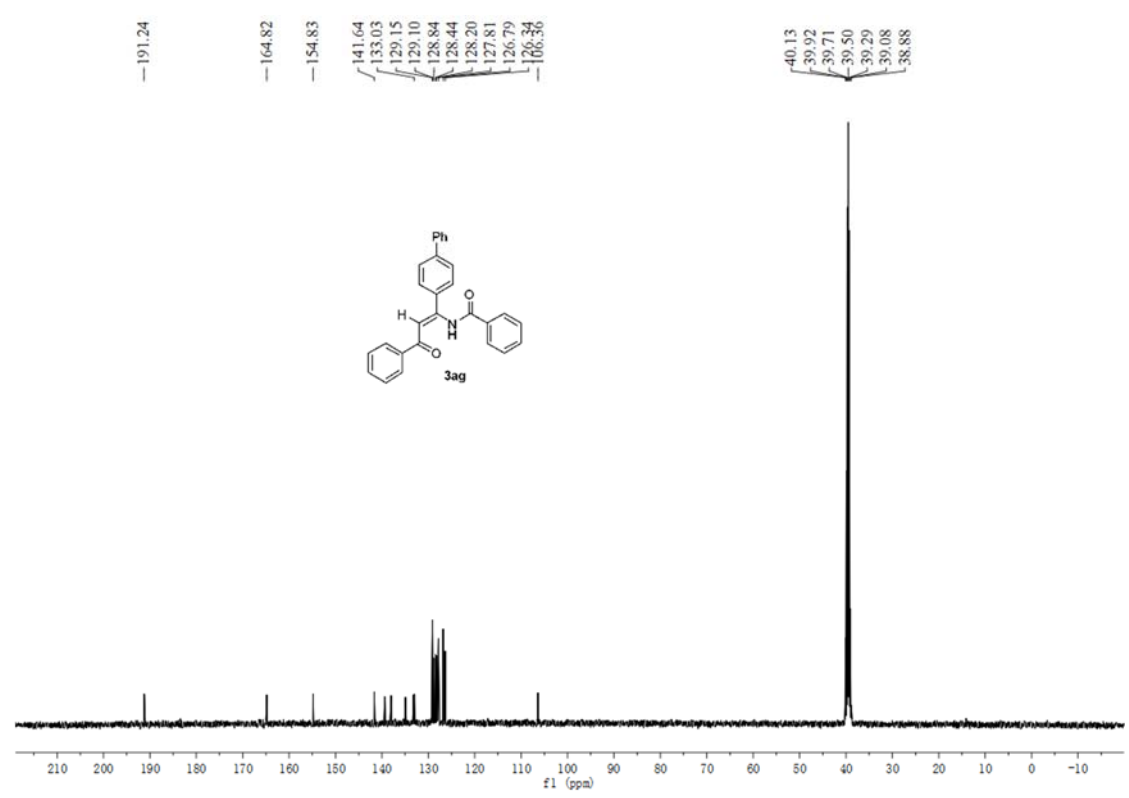
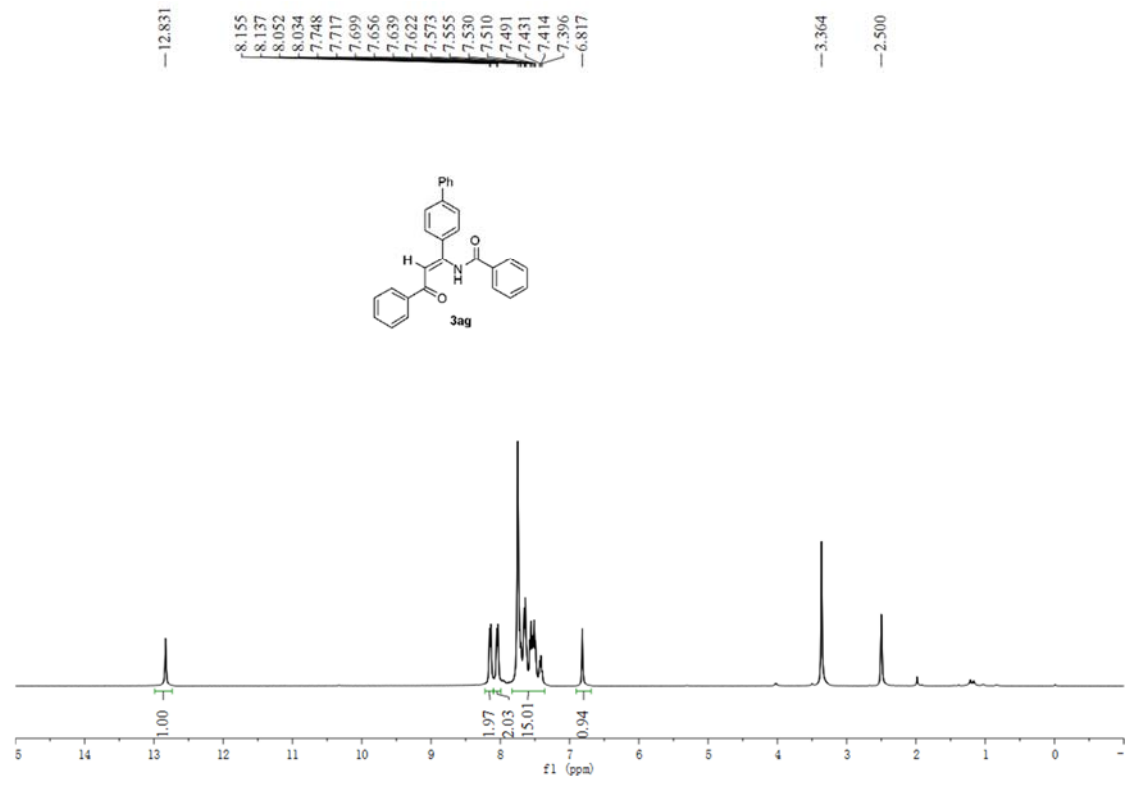


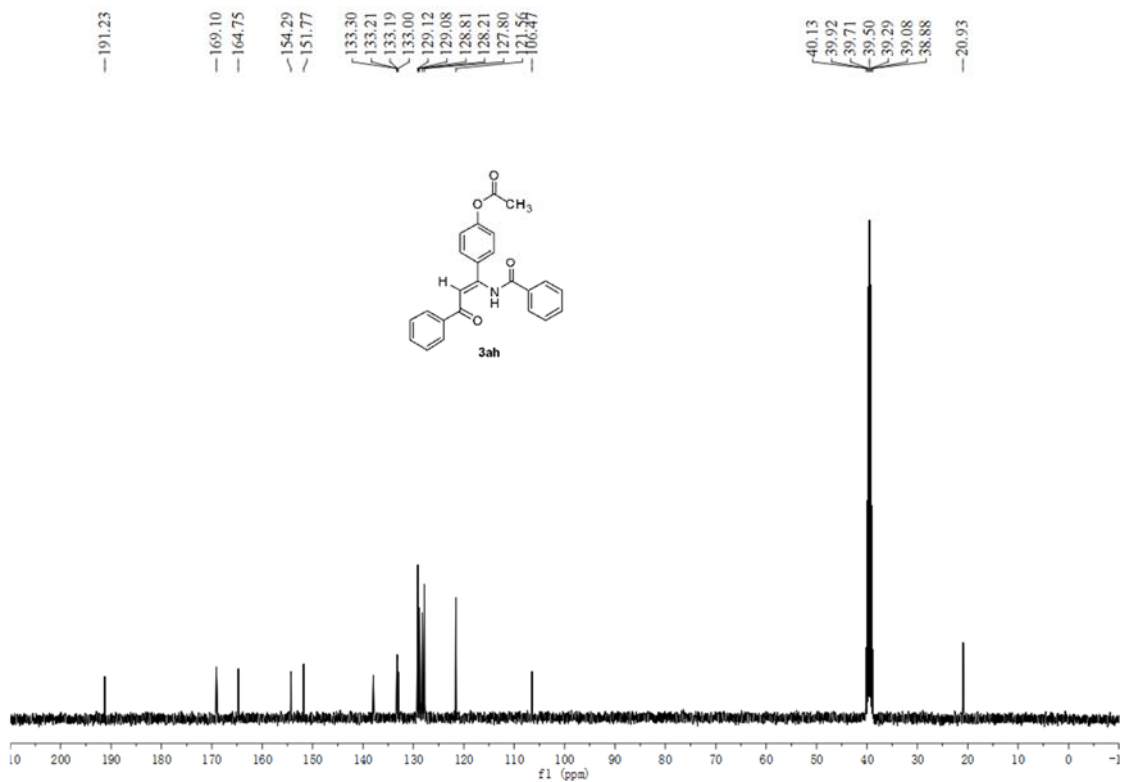
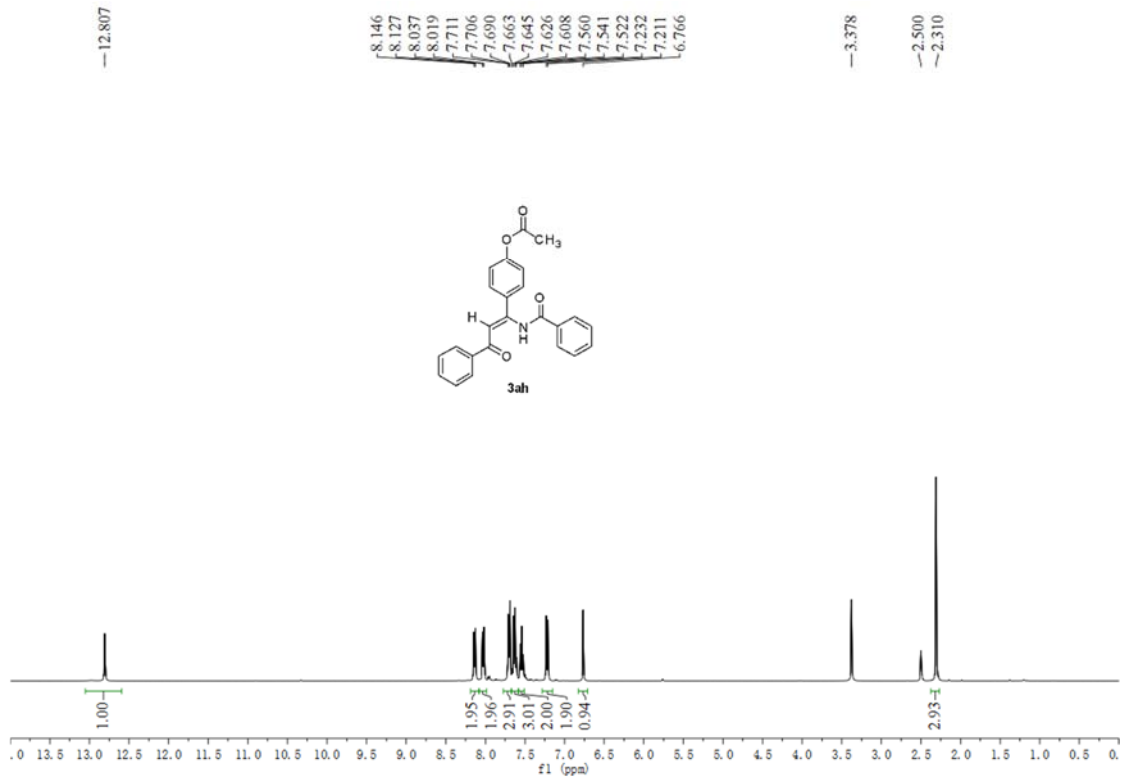


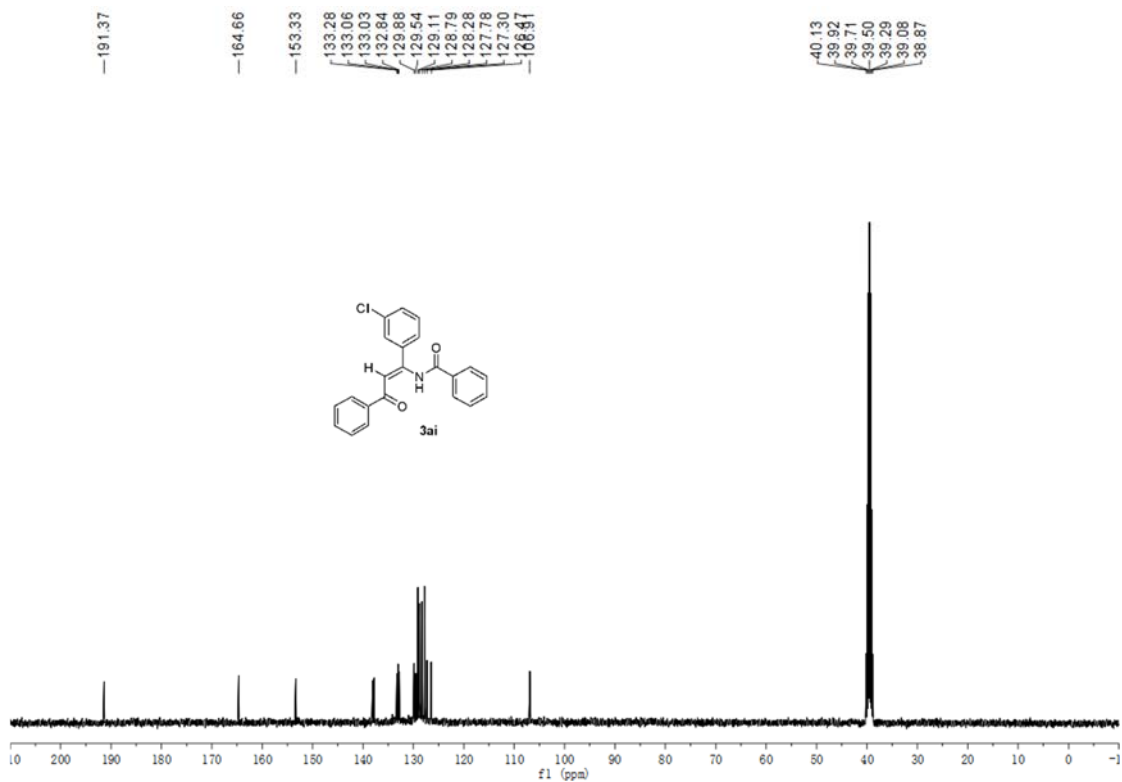
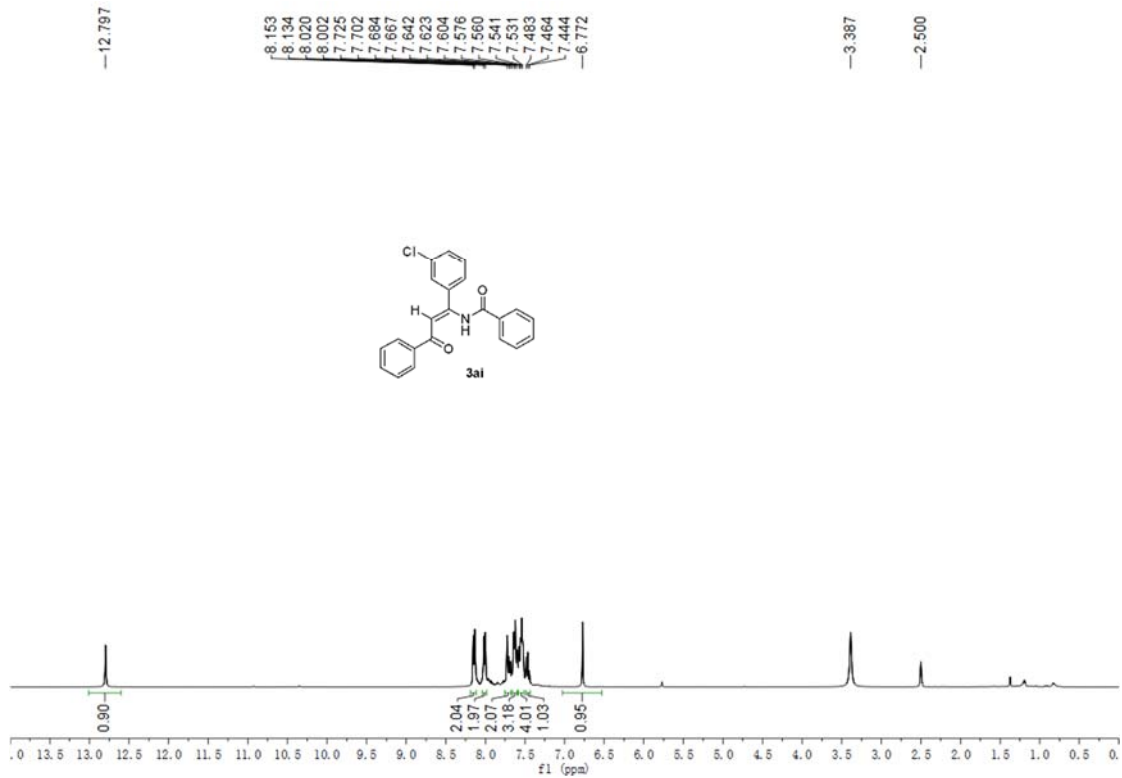


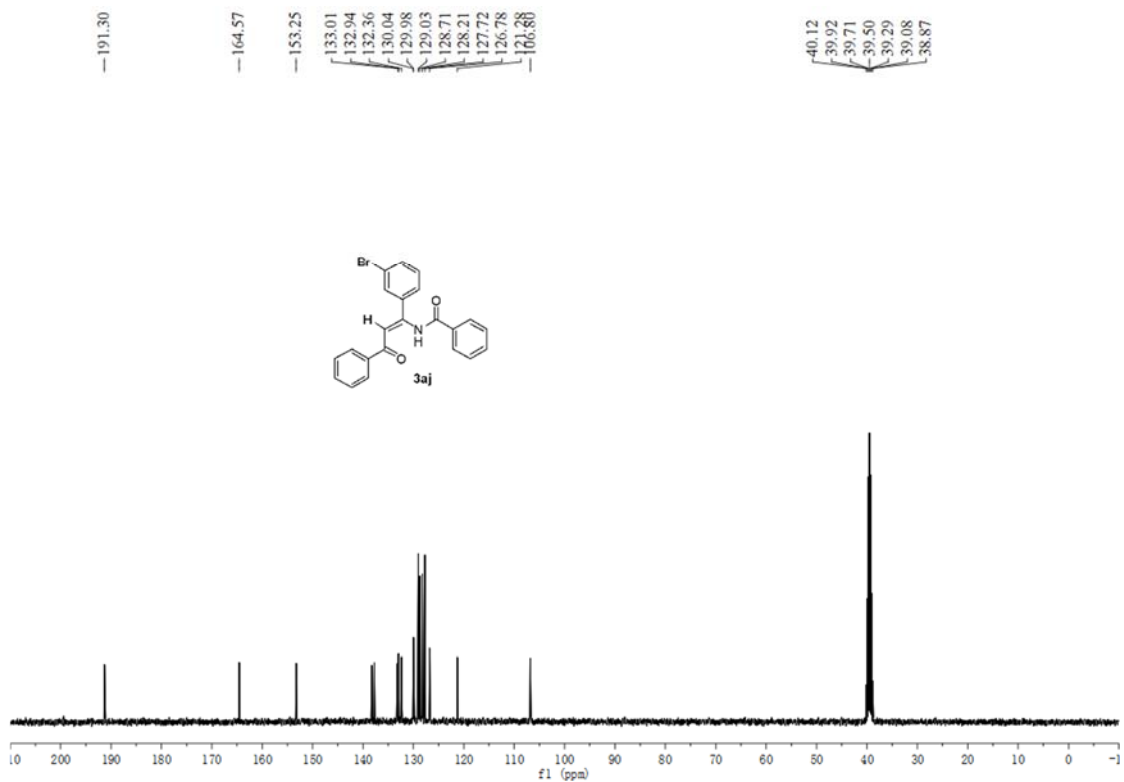
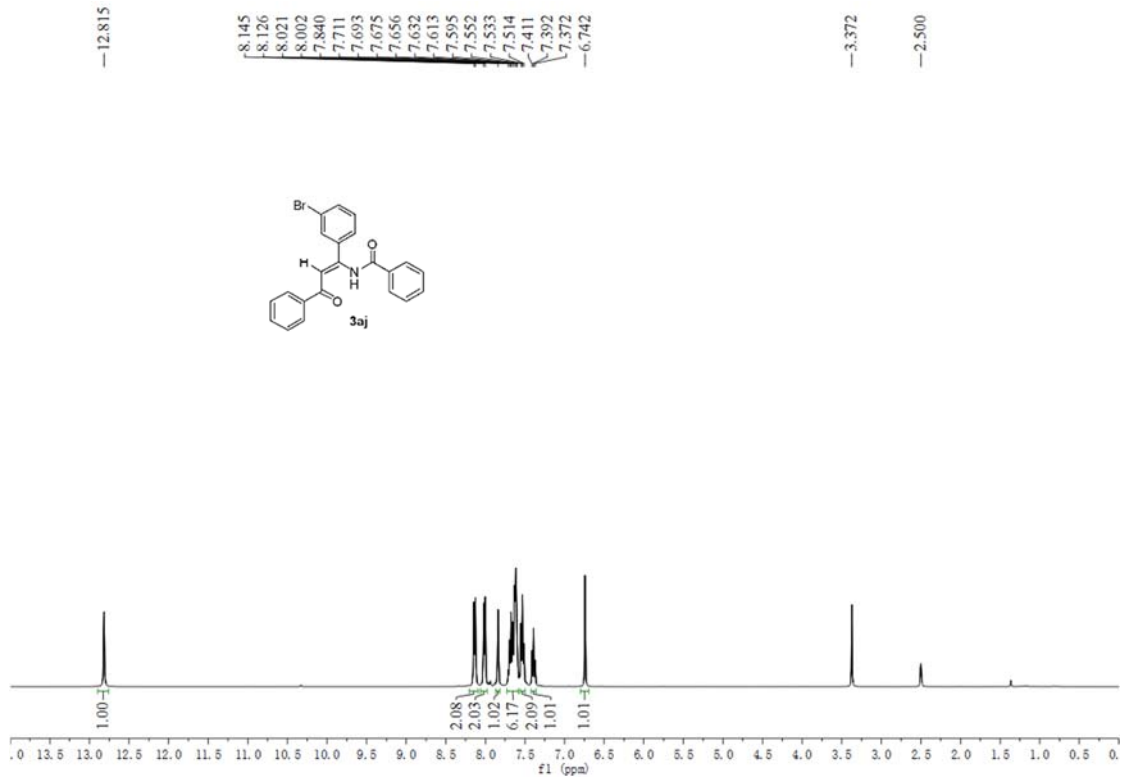


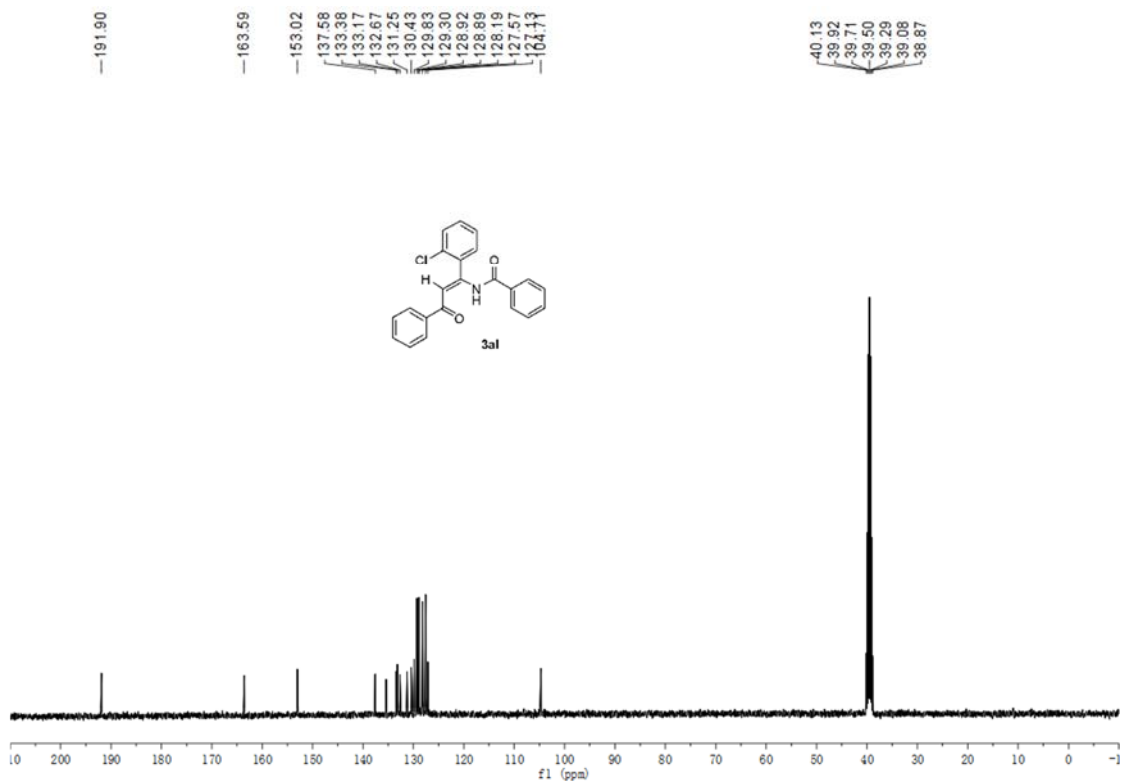
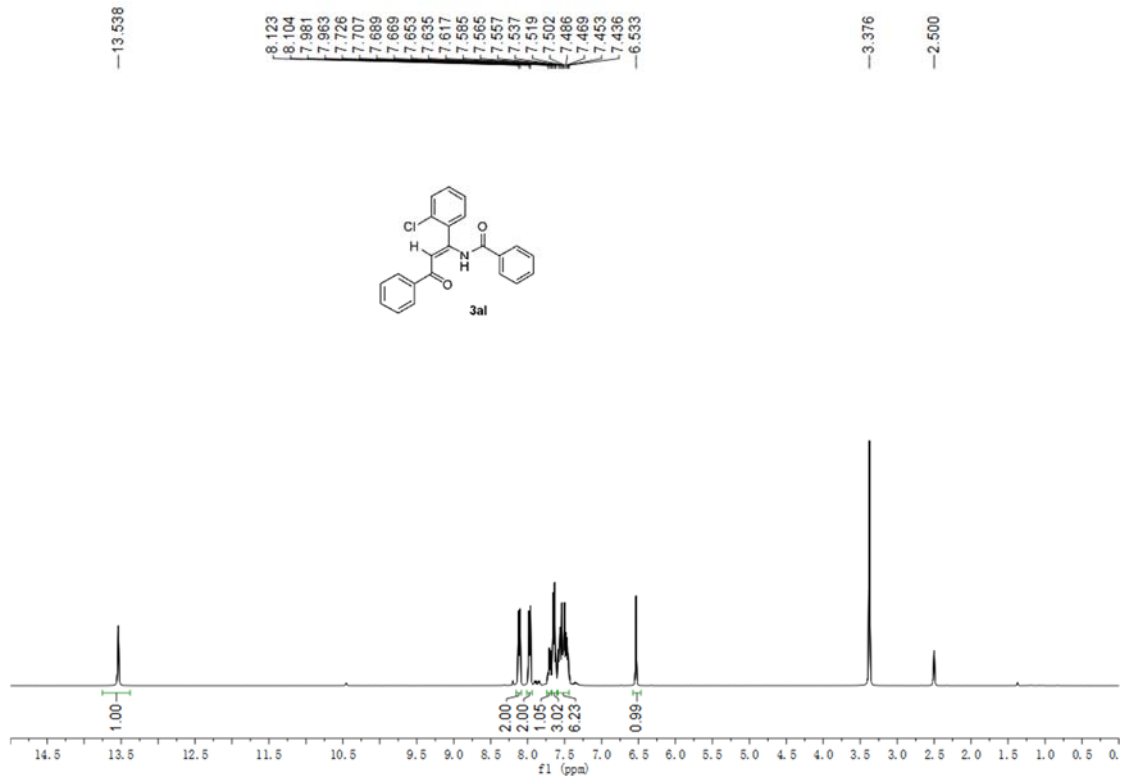


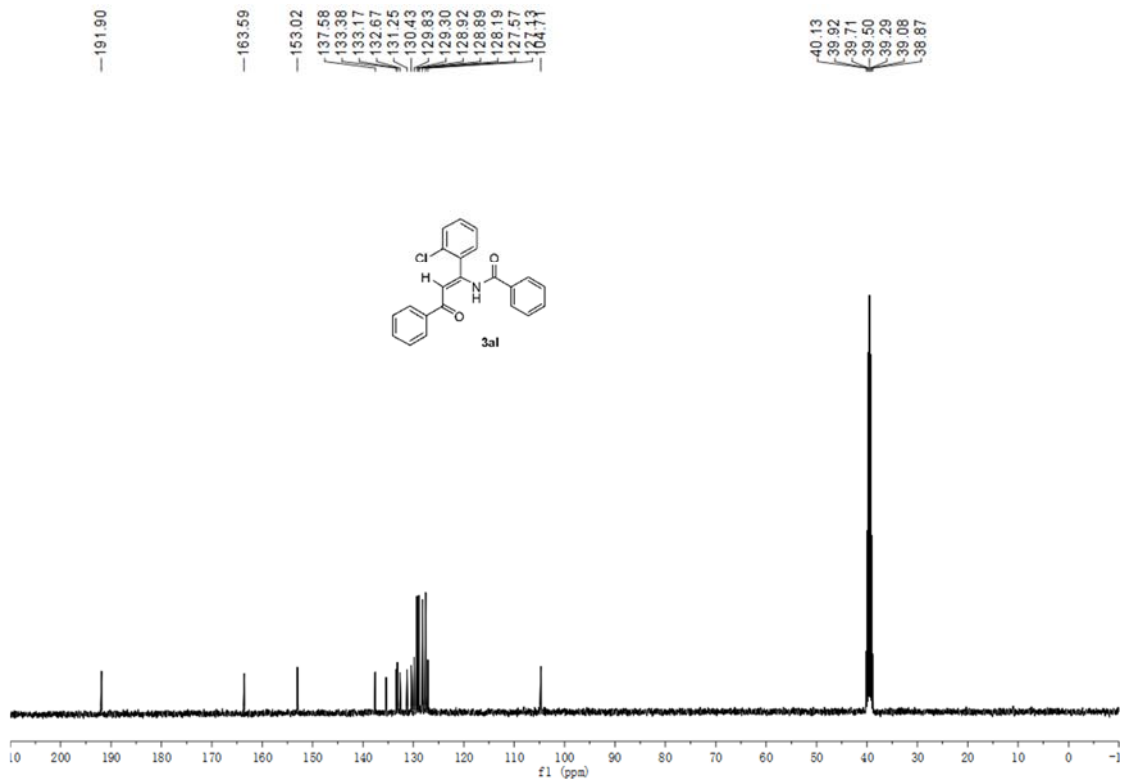
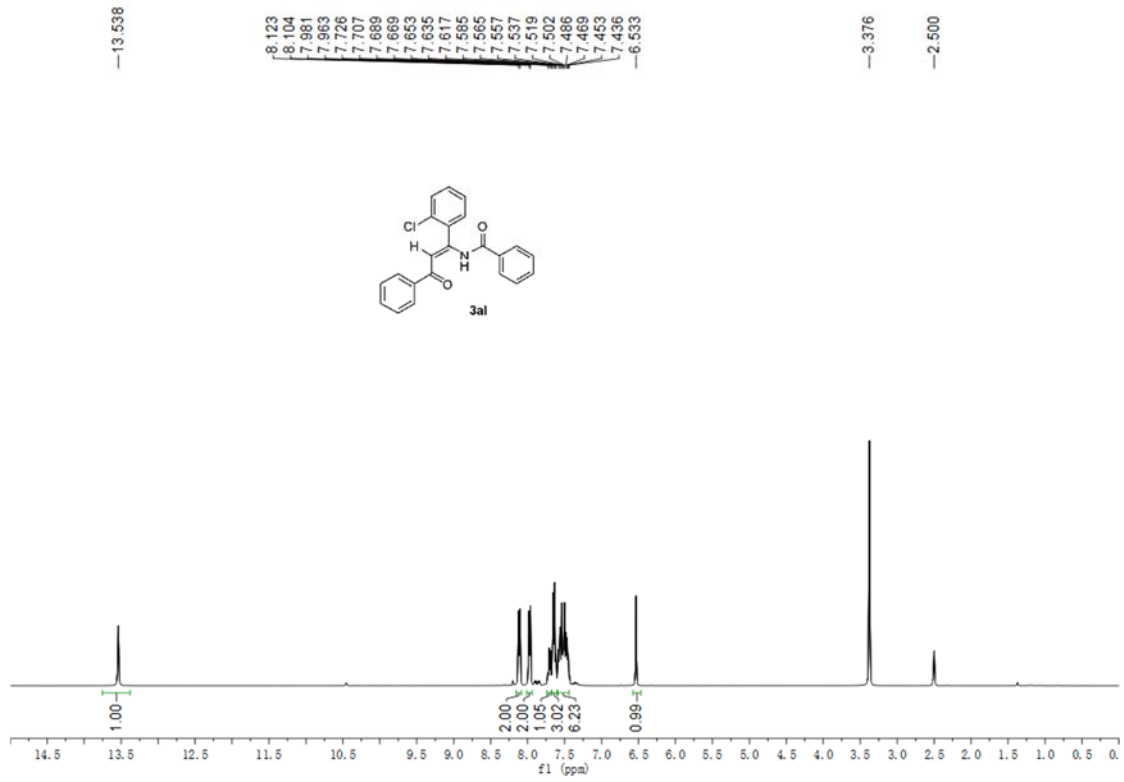


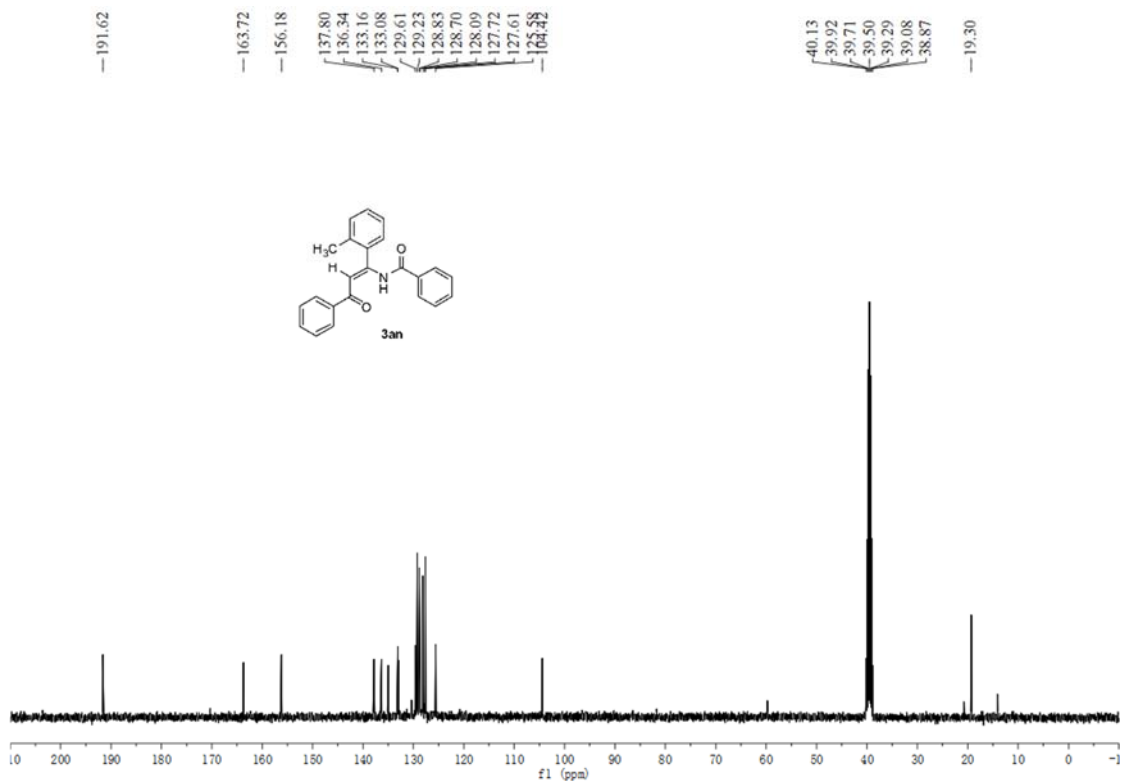
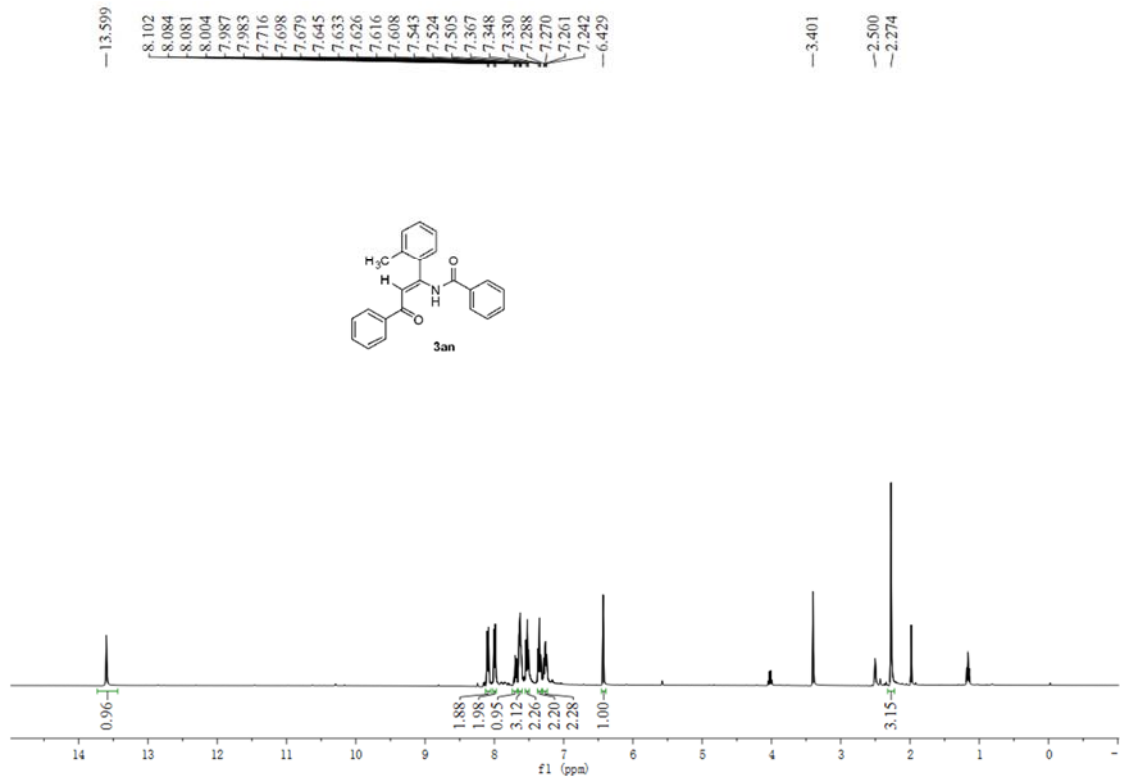


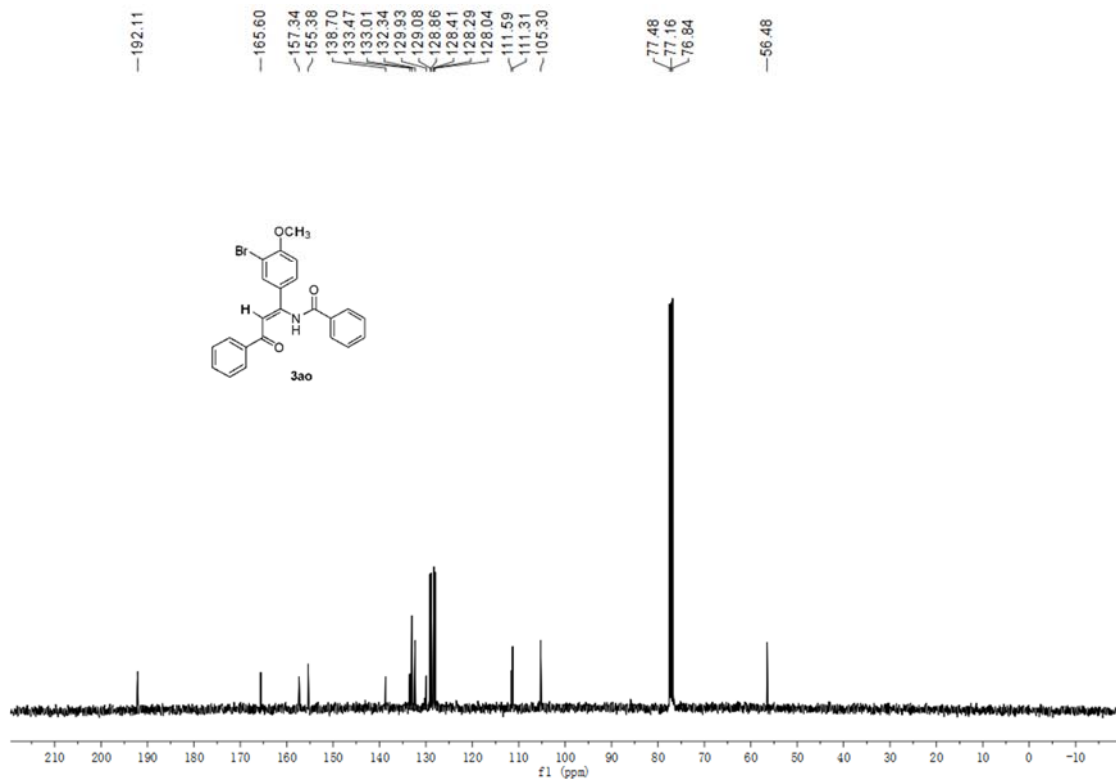
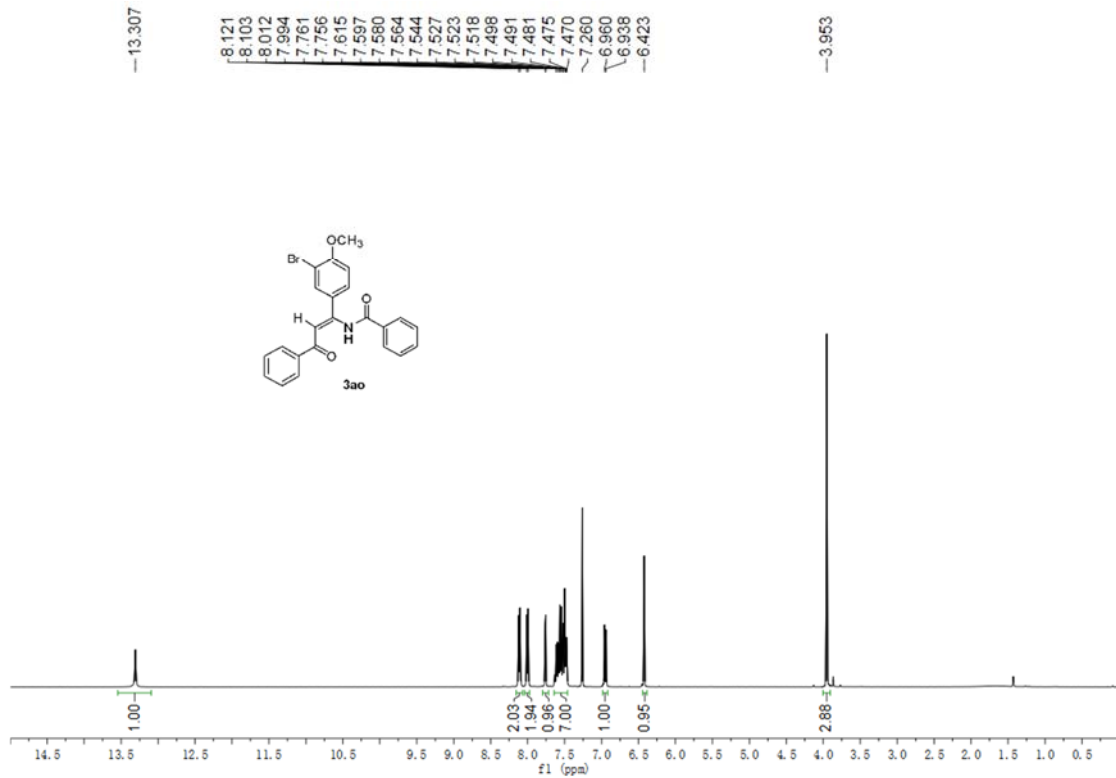


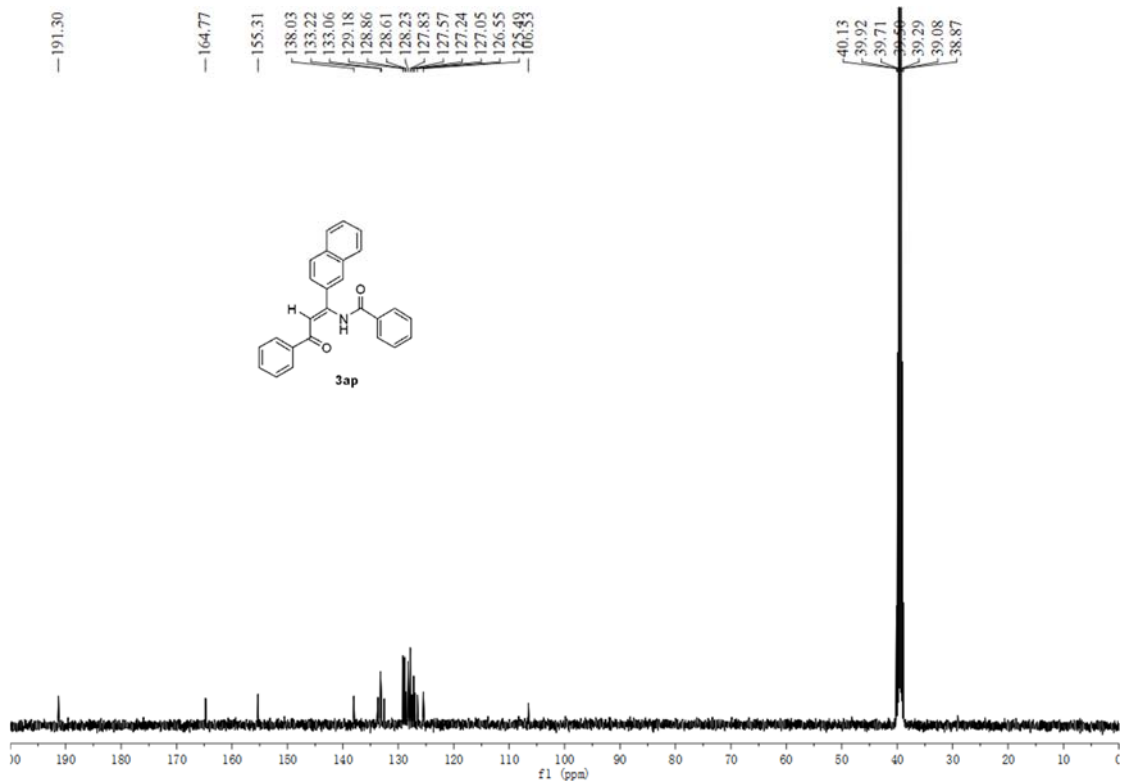
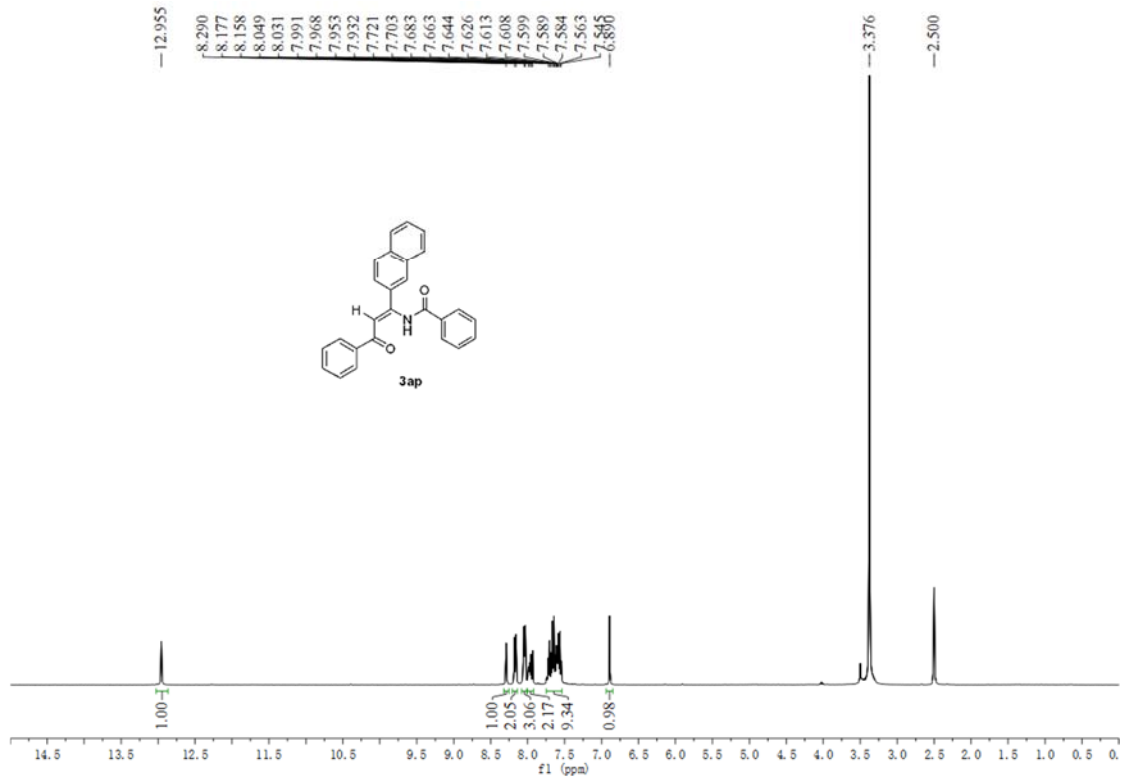


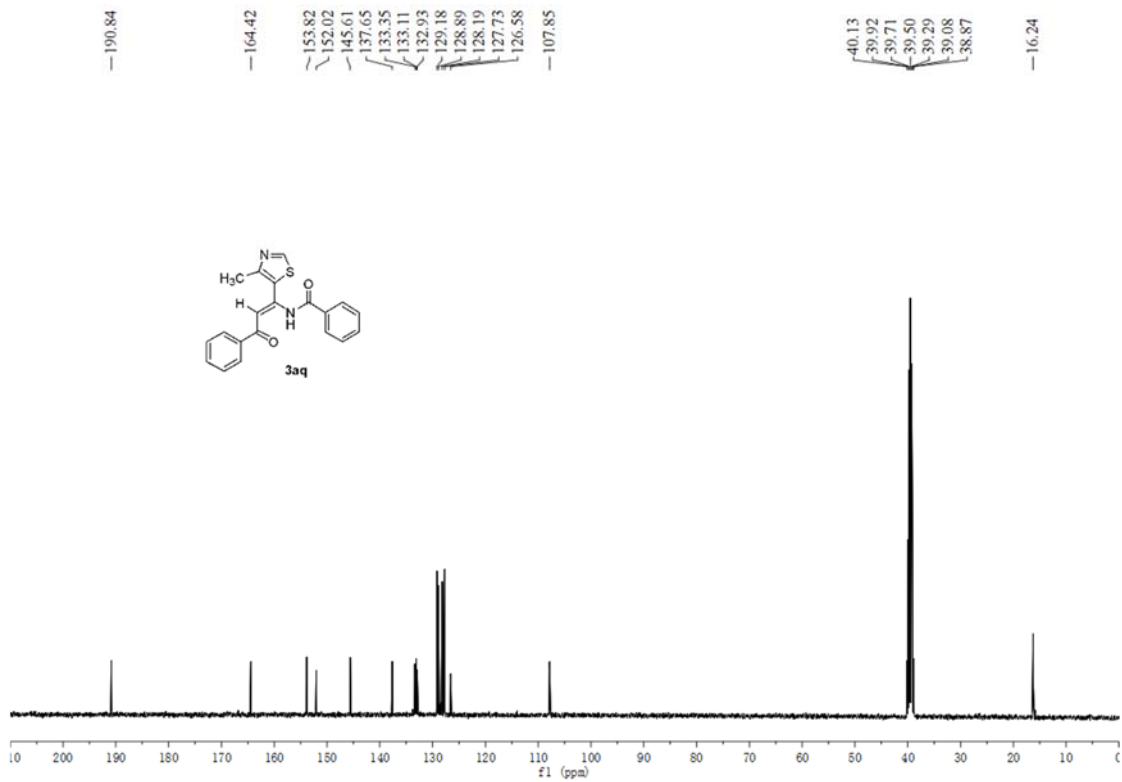
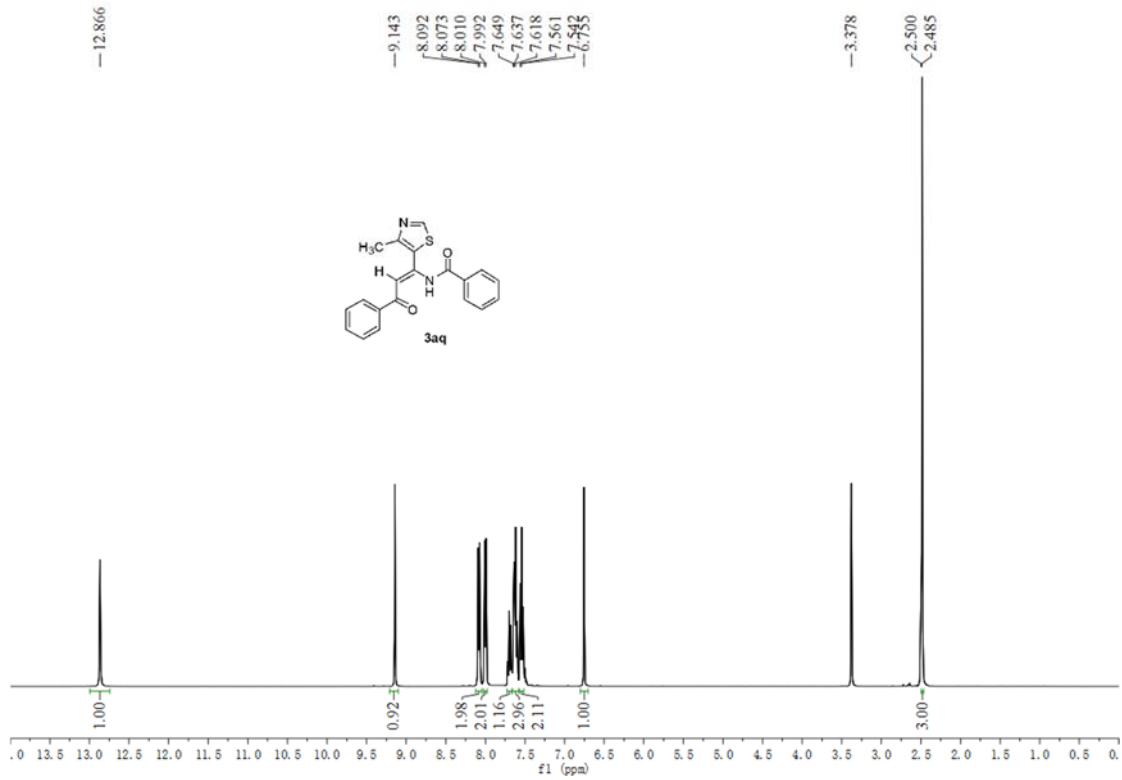


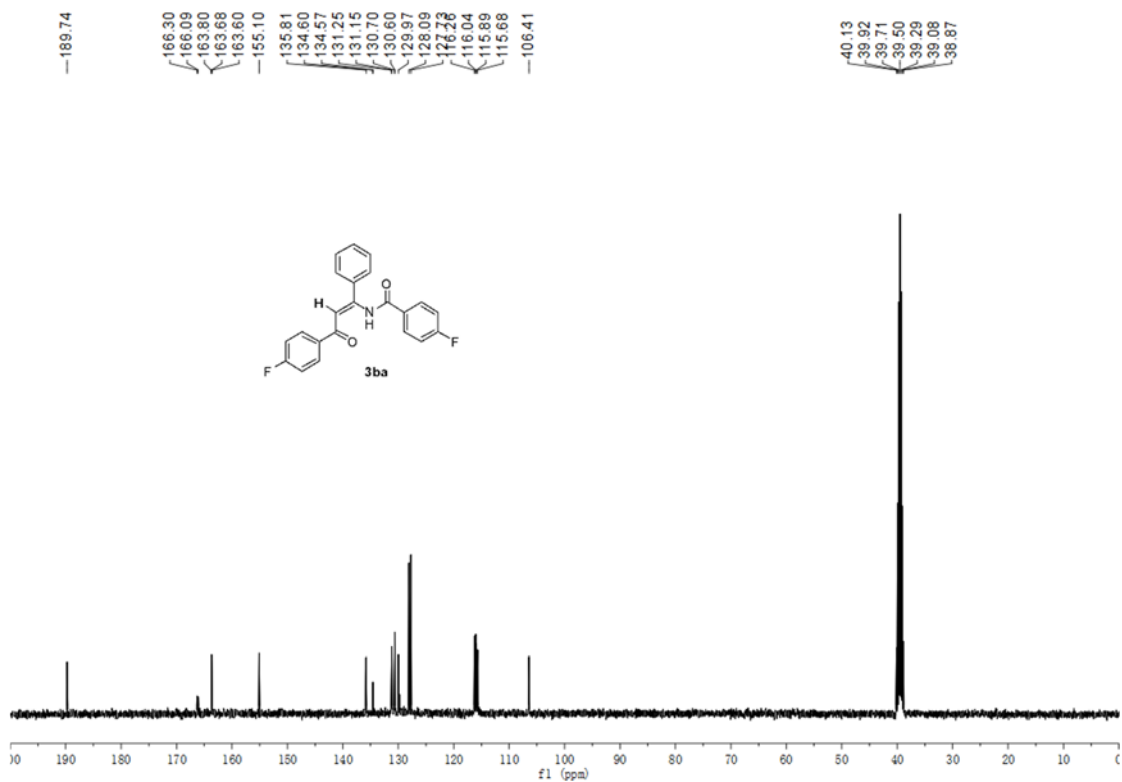
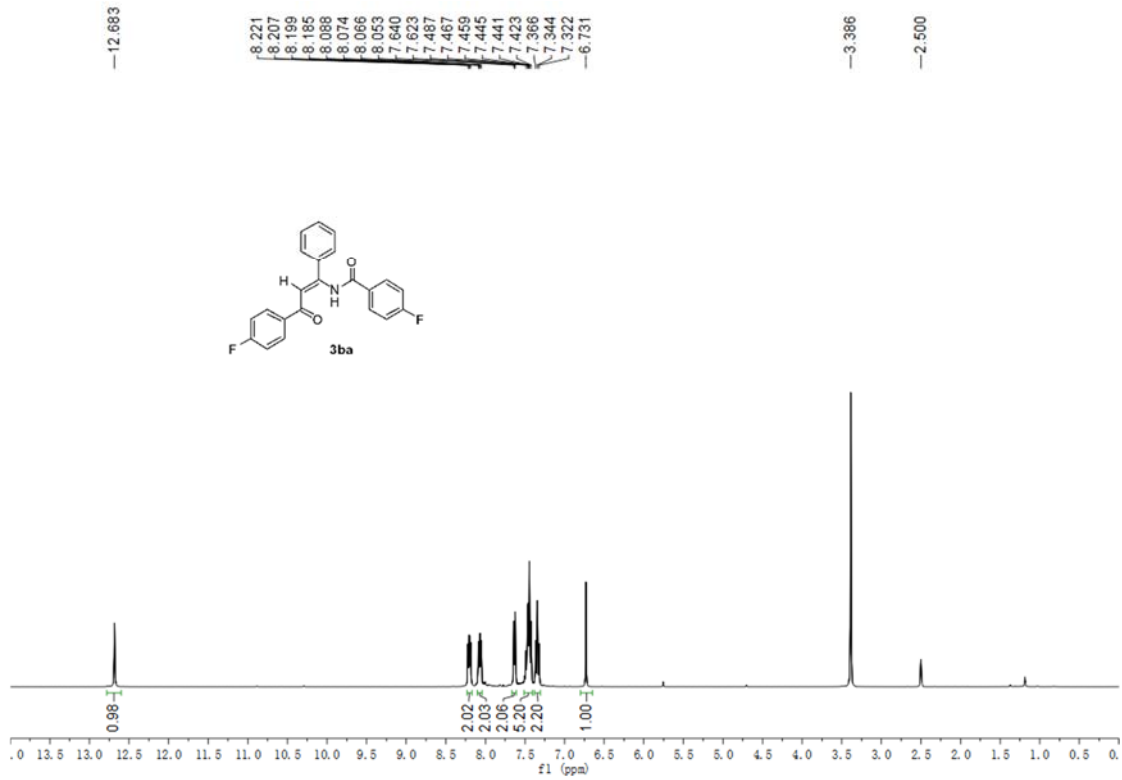


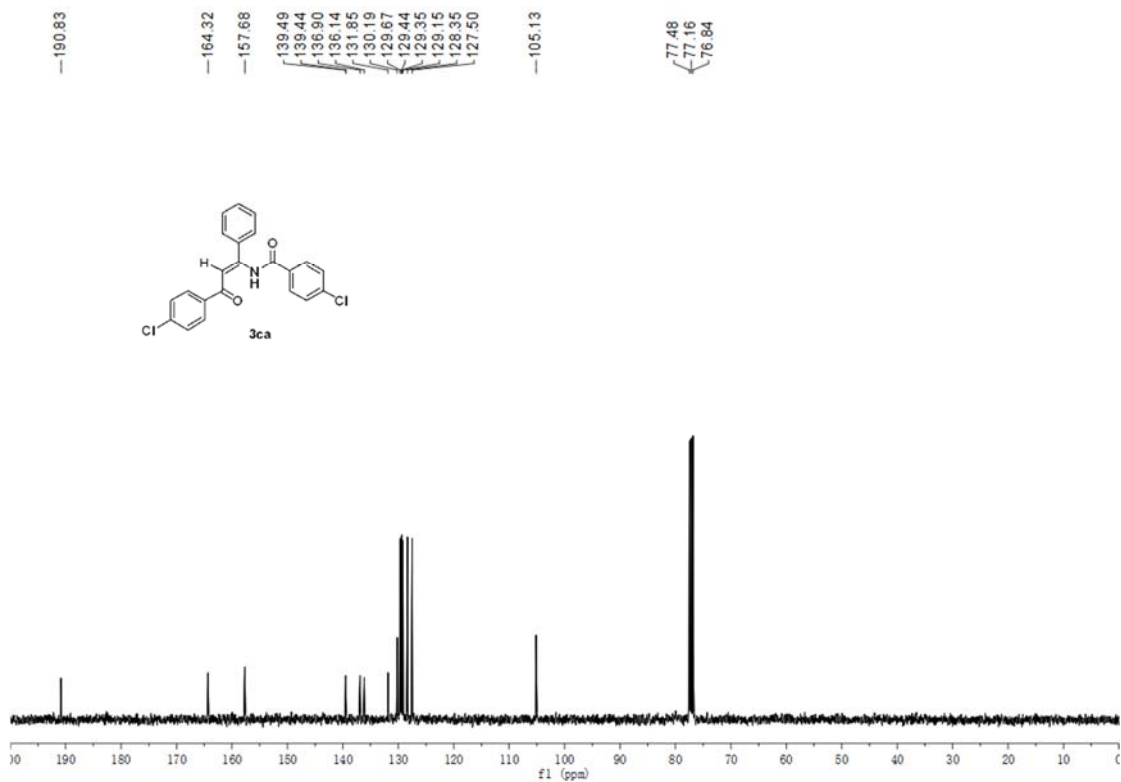
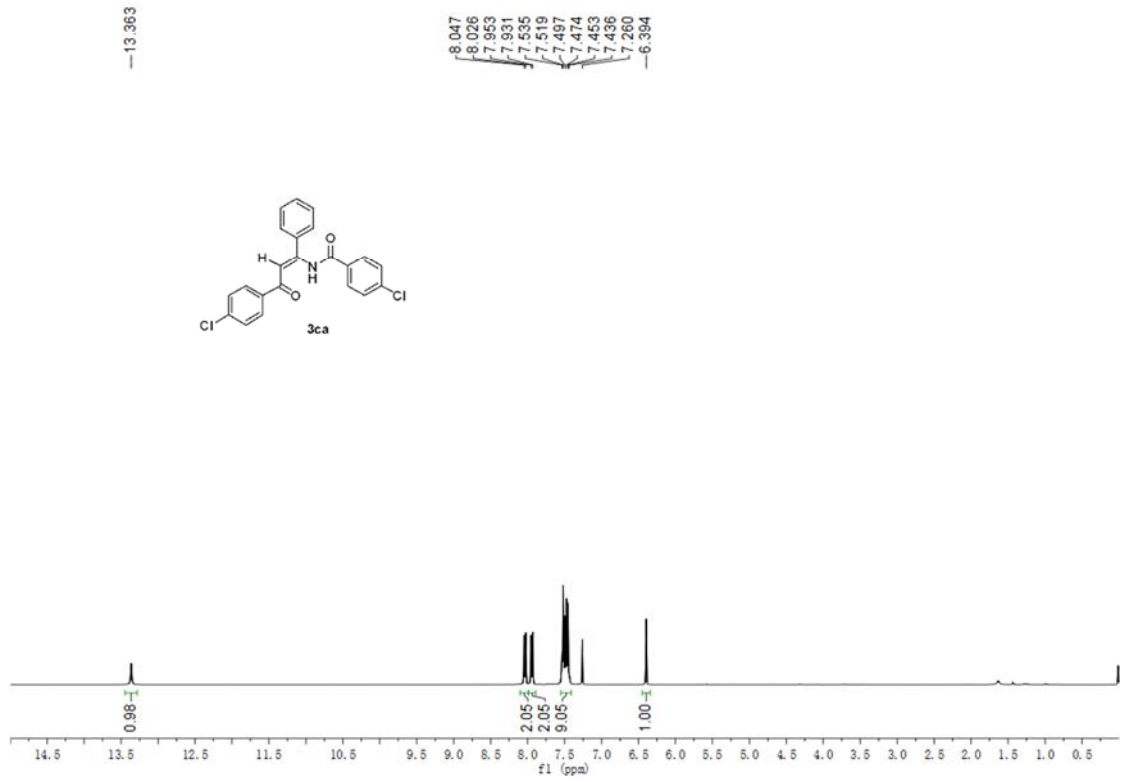


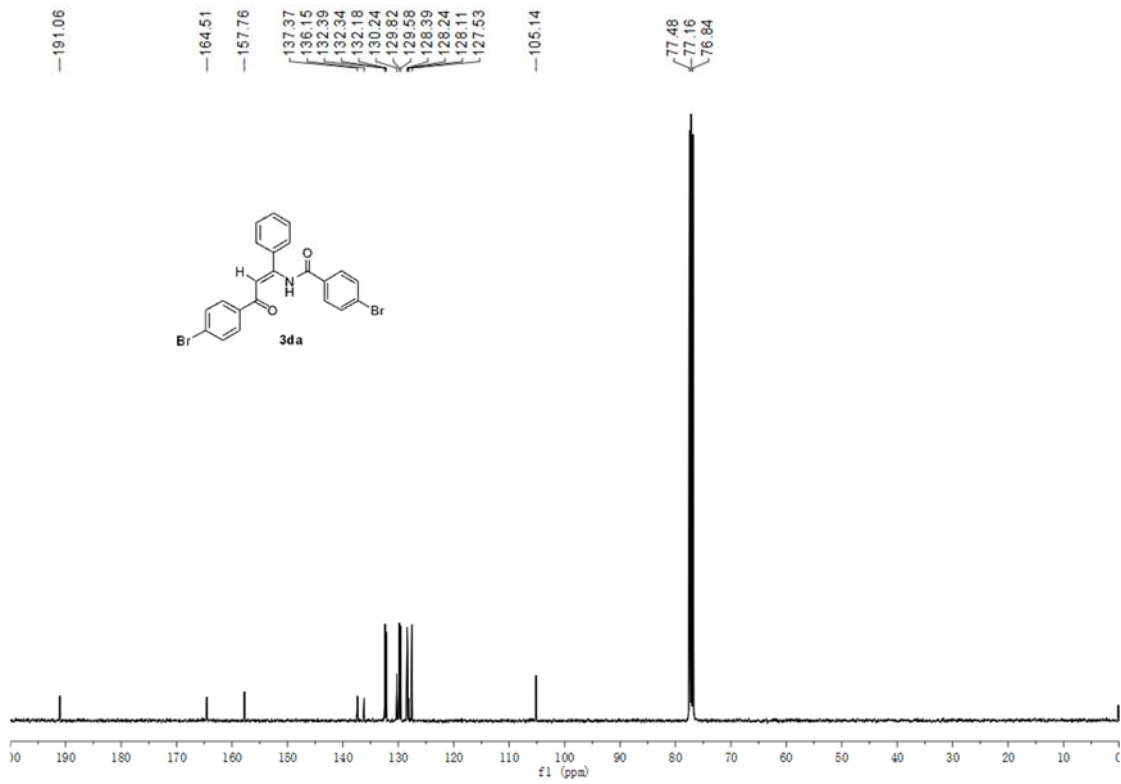
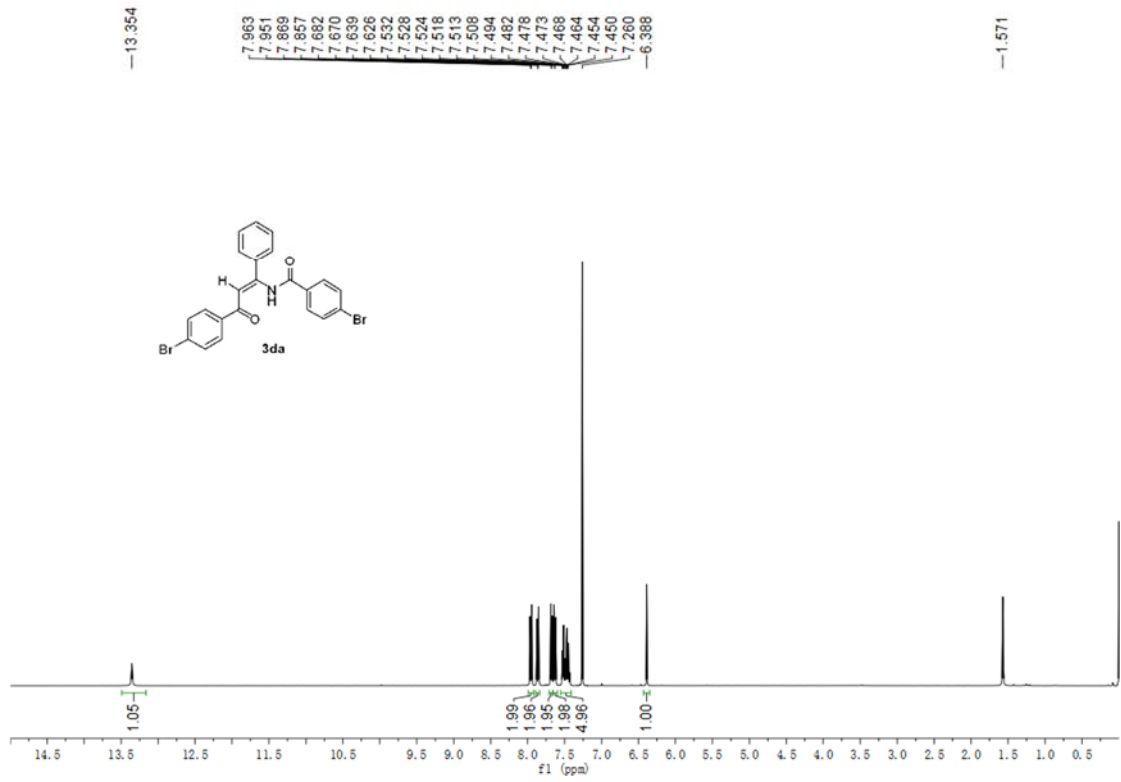


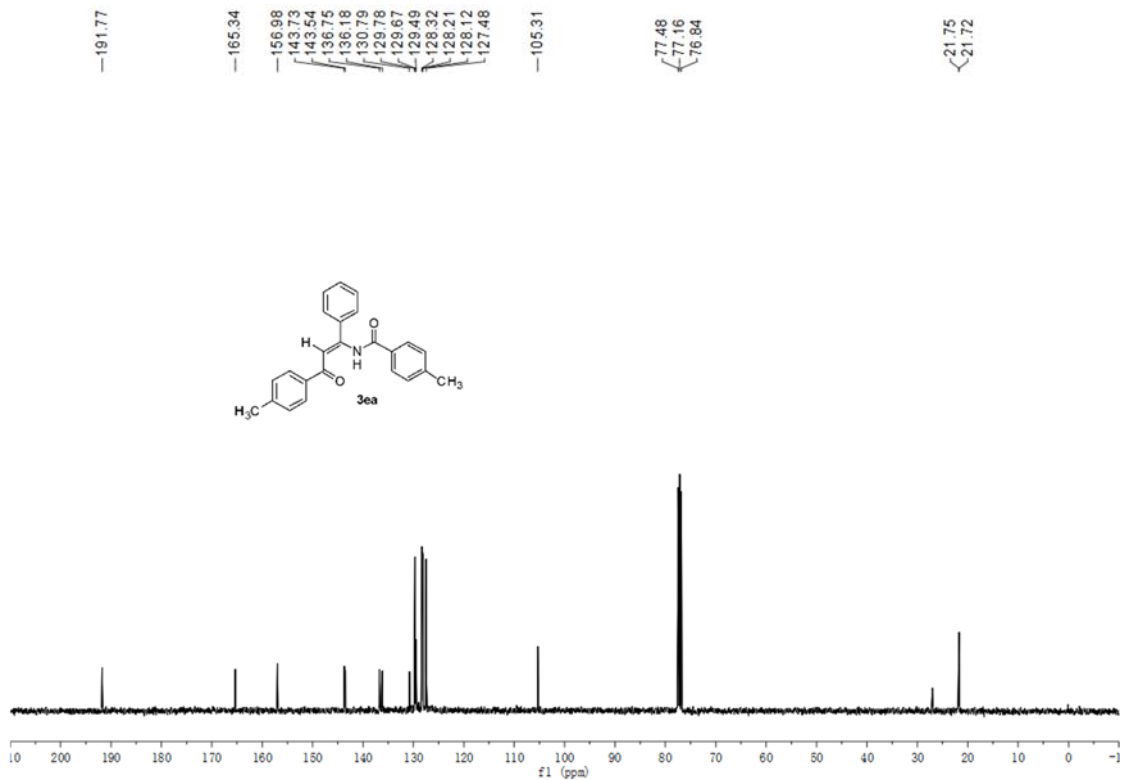
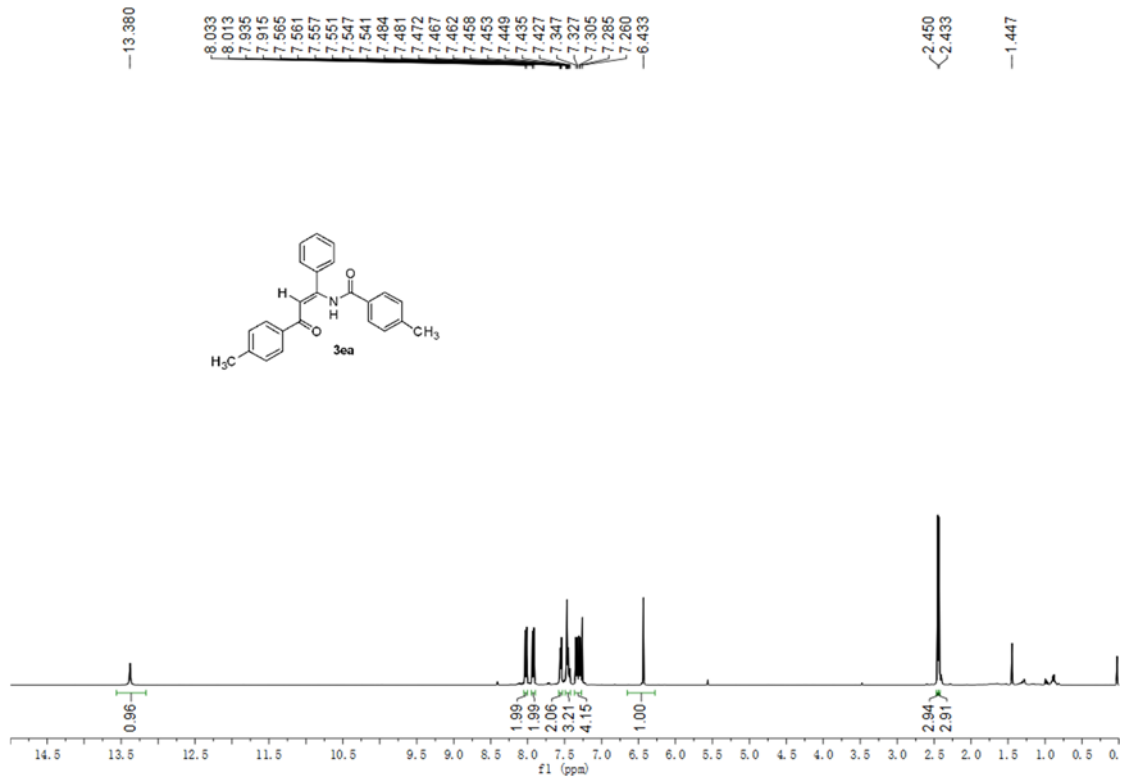


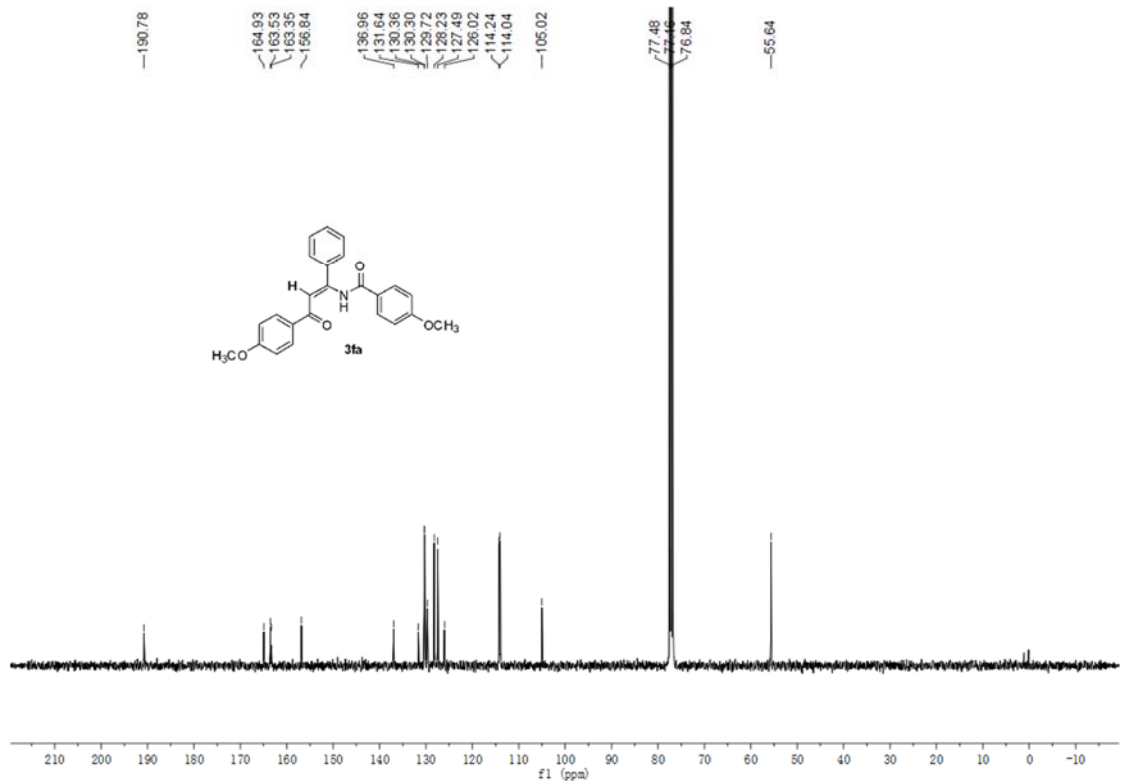
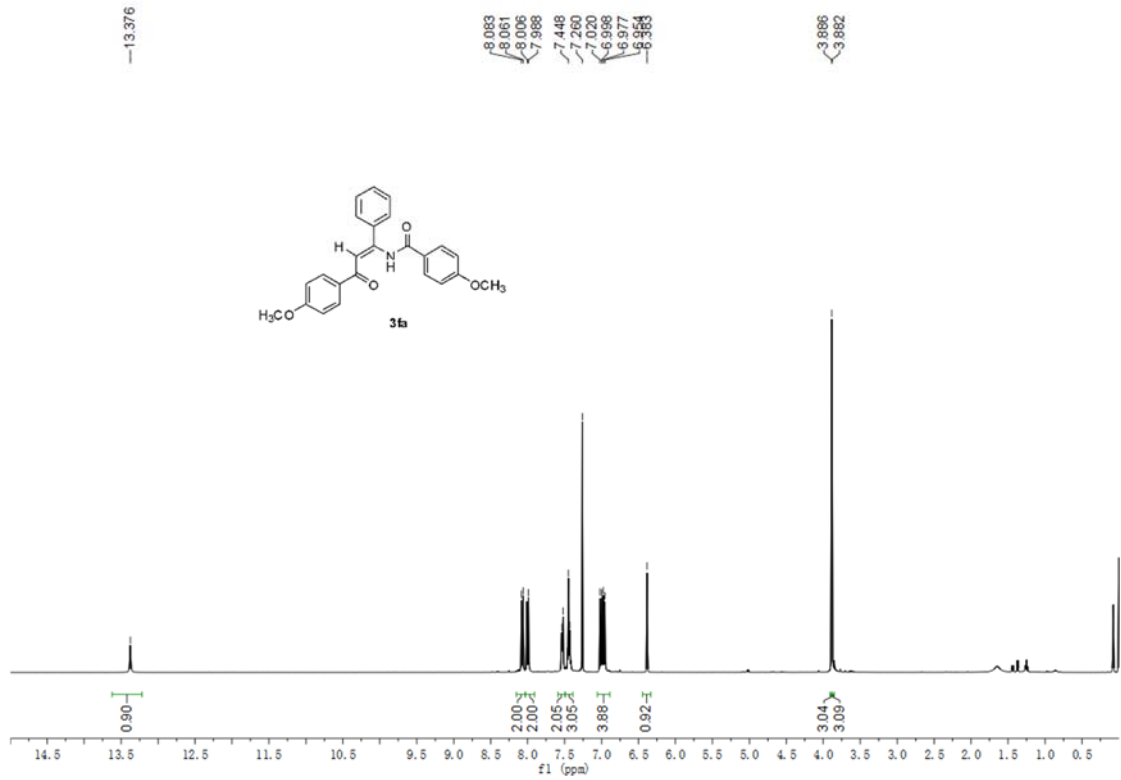




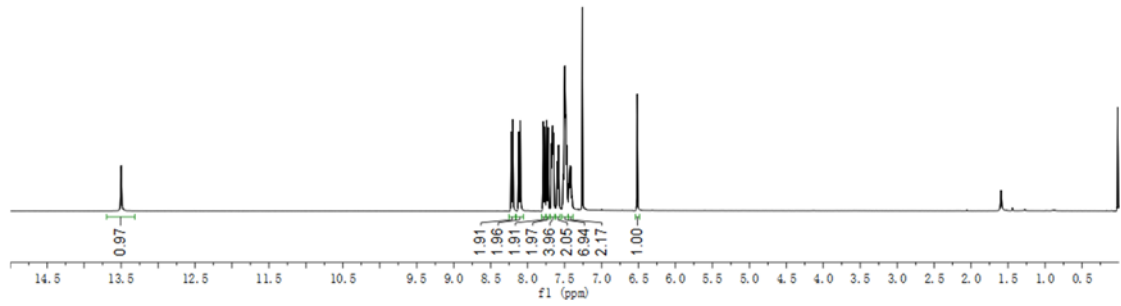
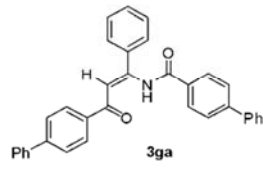




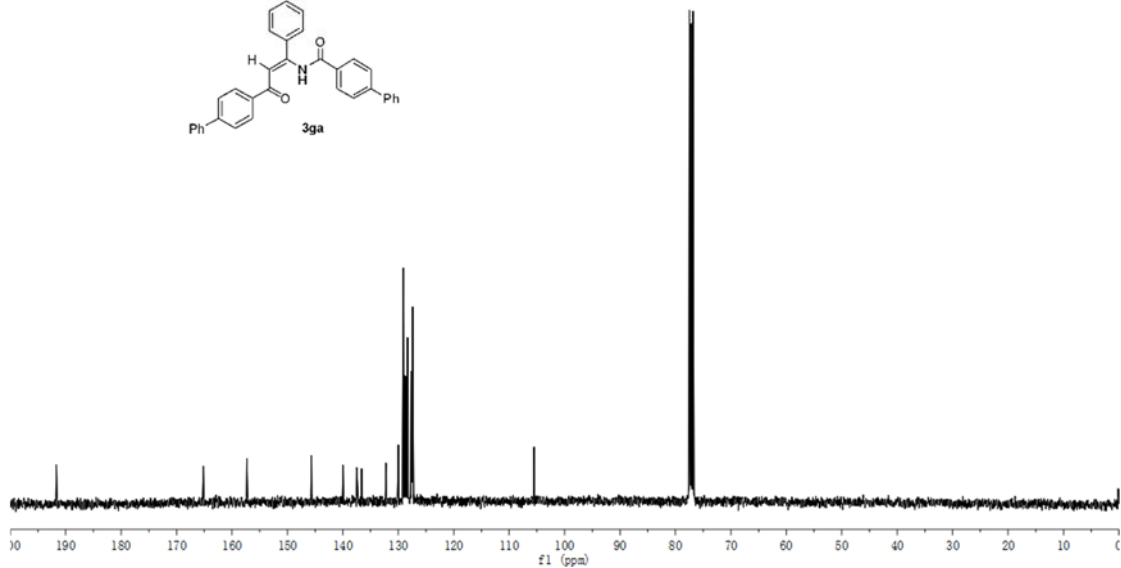
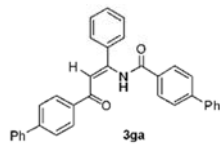


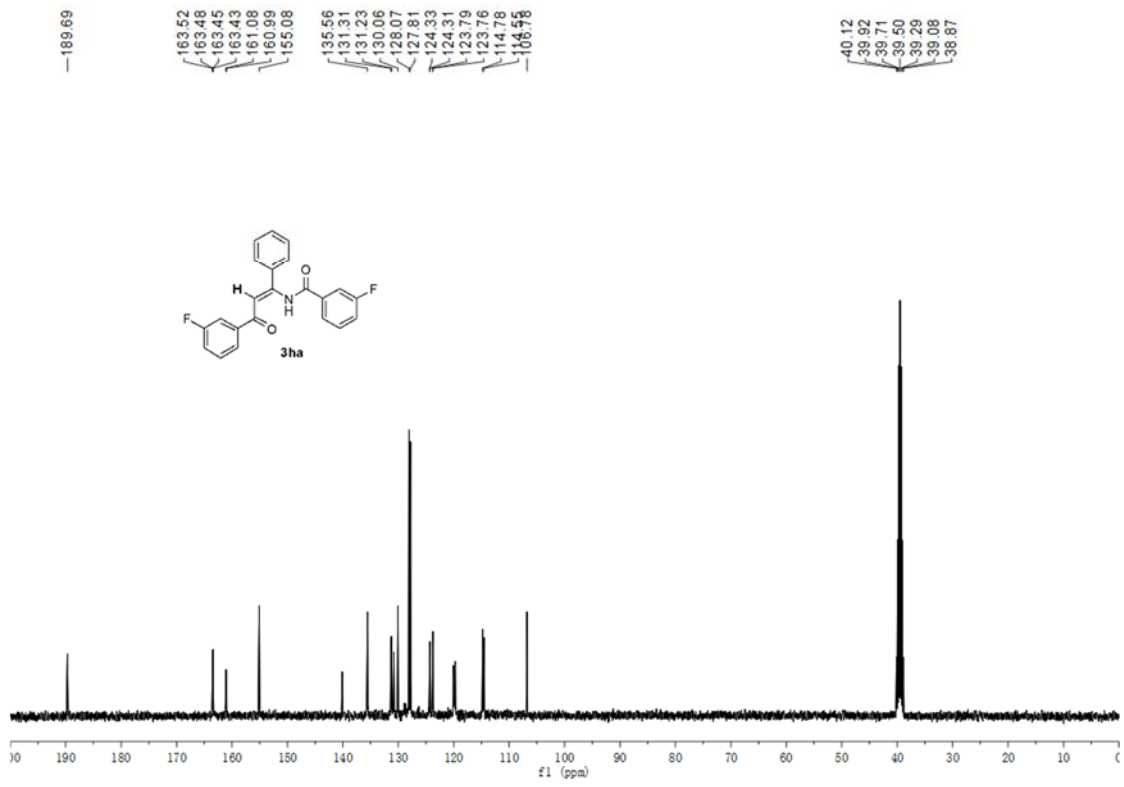
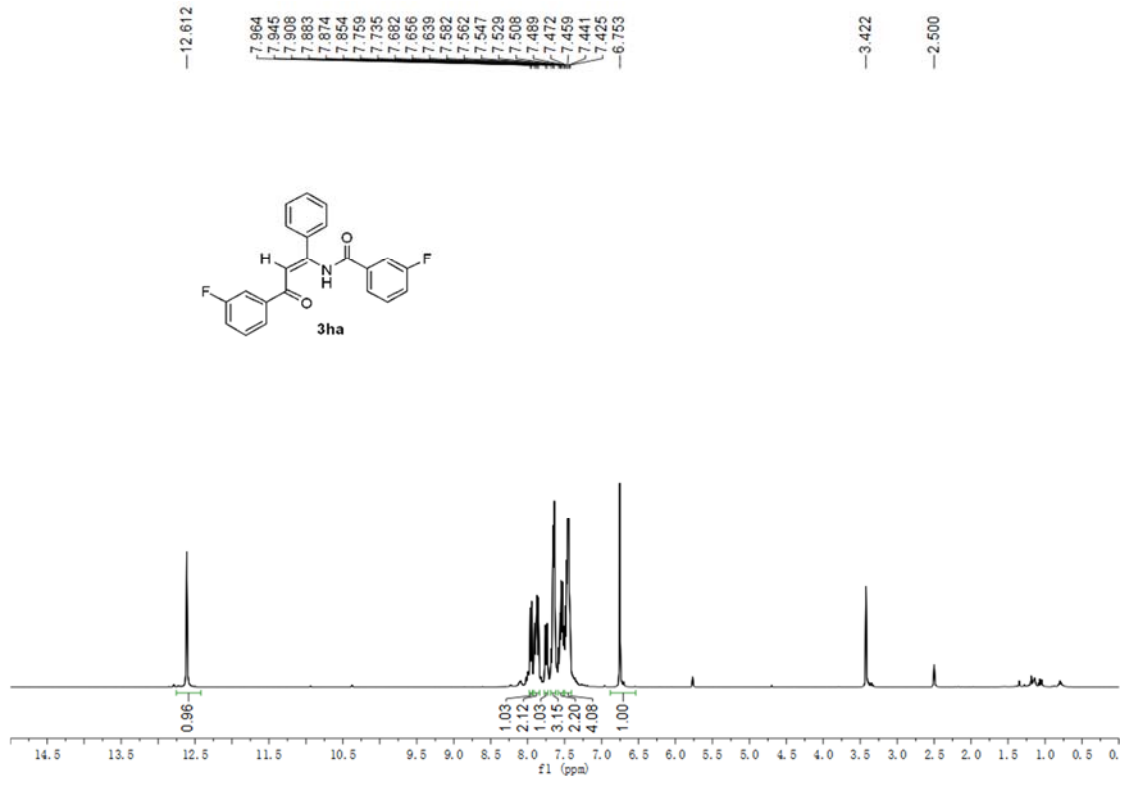


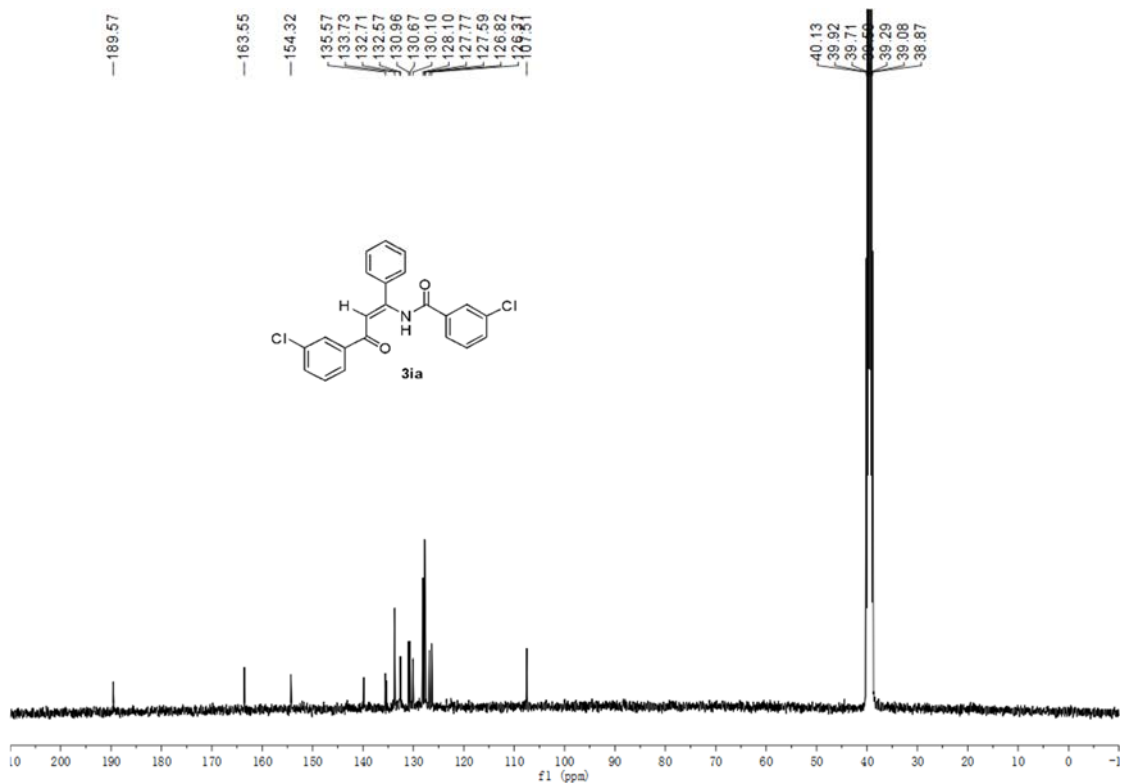
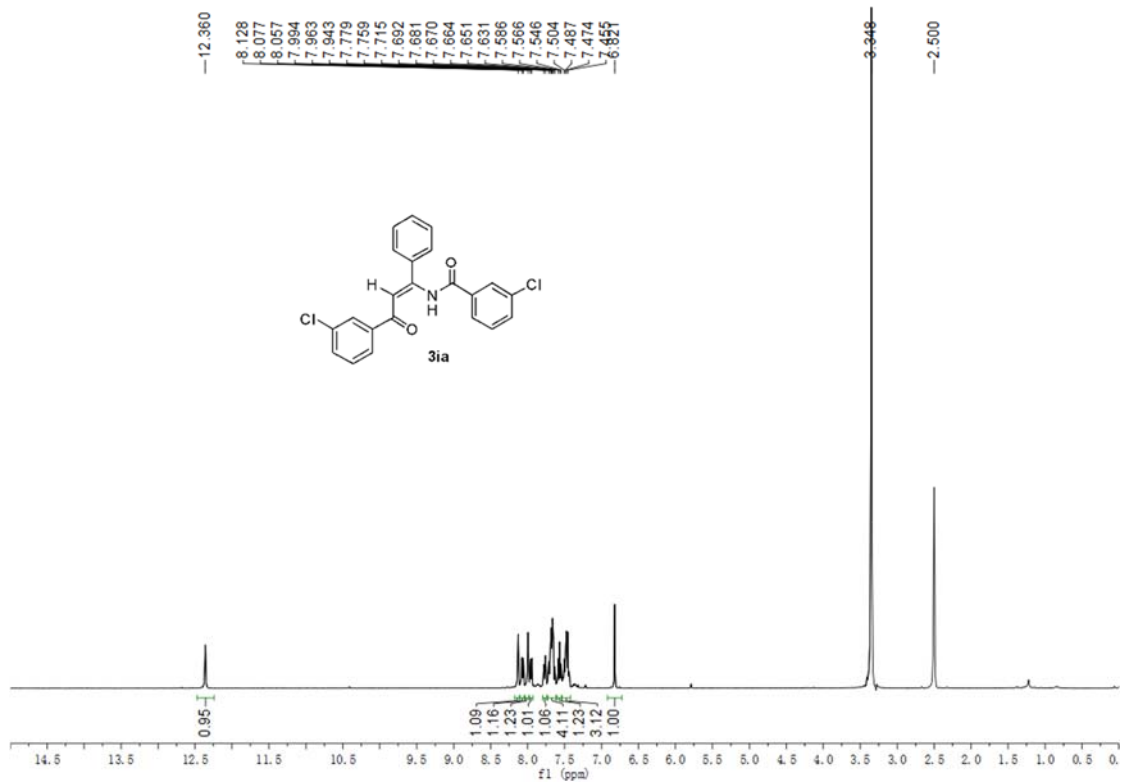
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 — 7.674
 — 7.670
 — 7.661
 — 7.652
 — 7.605
 — 7.601
 — 7.587
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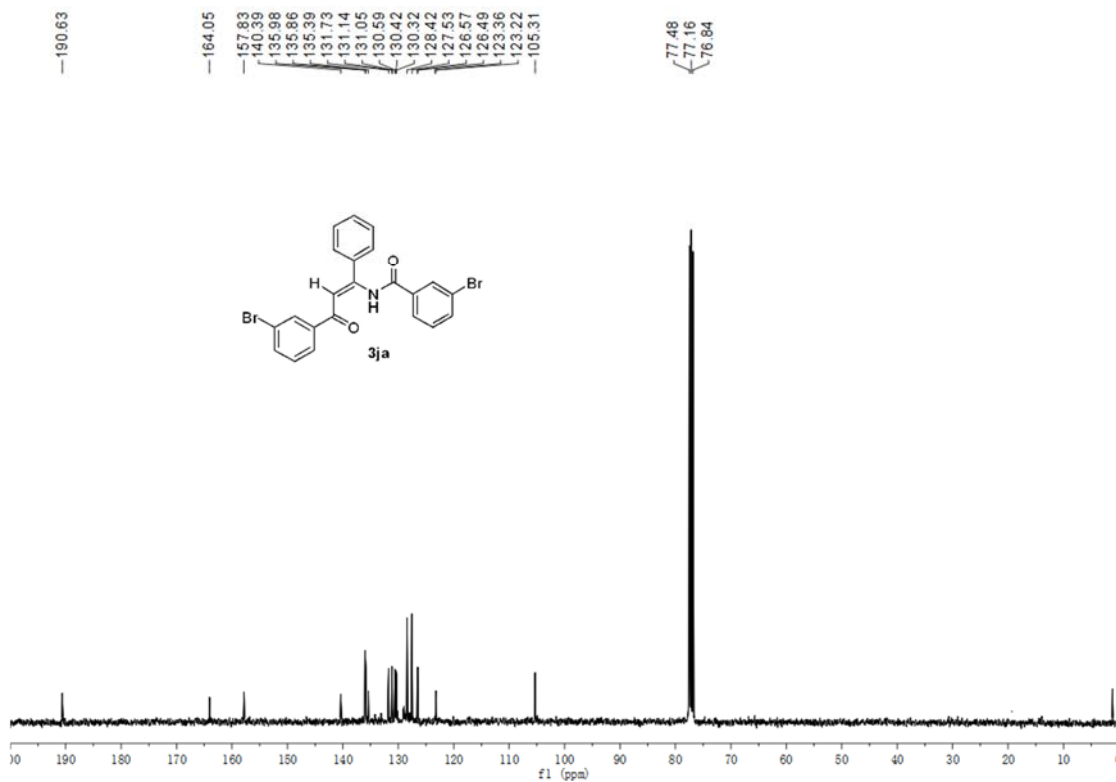
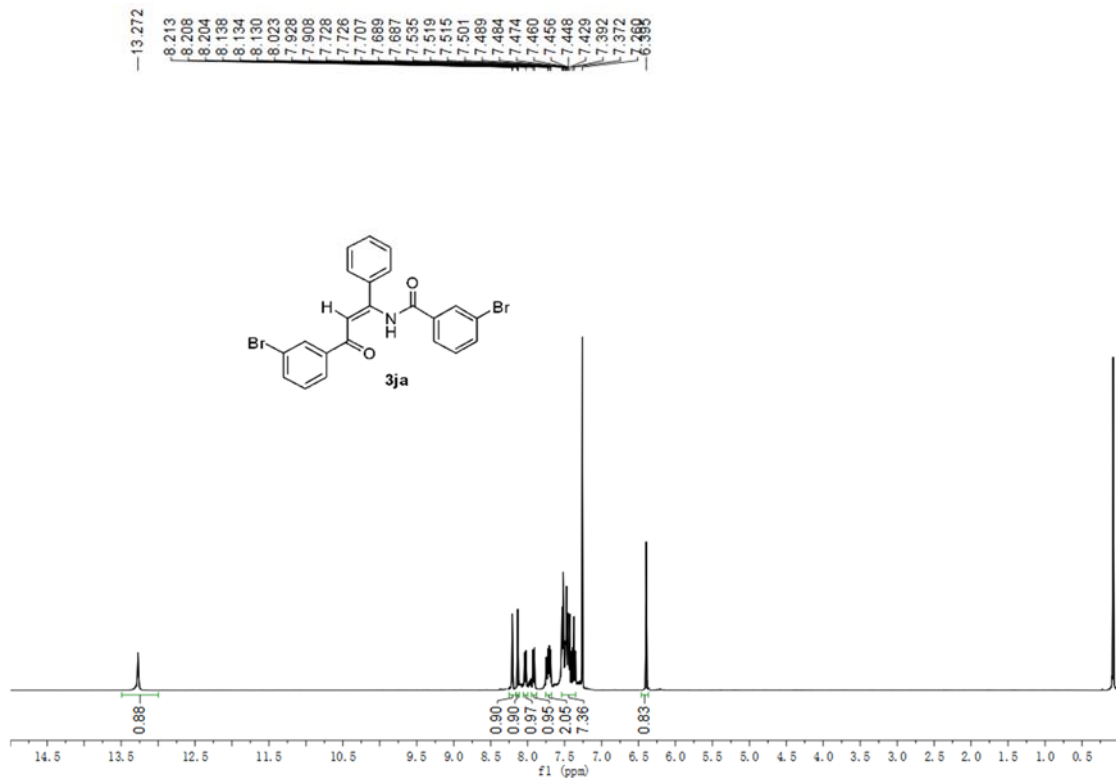


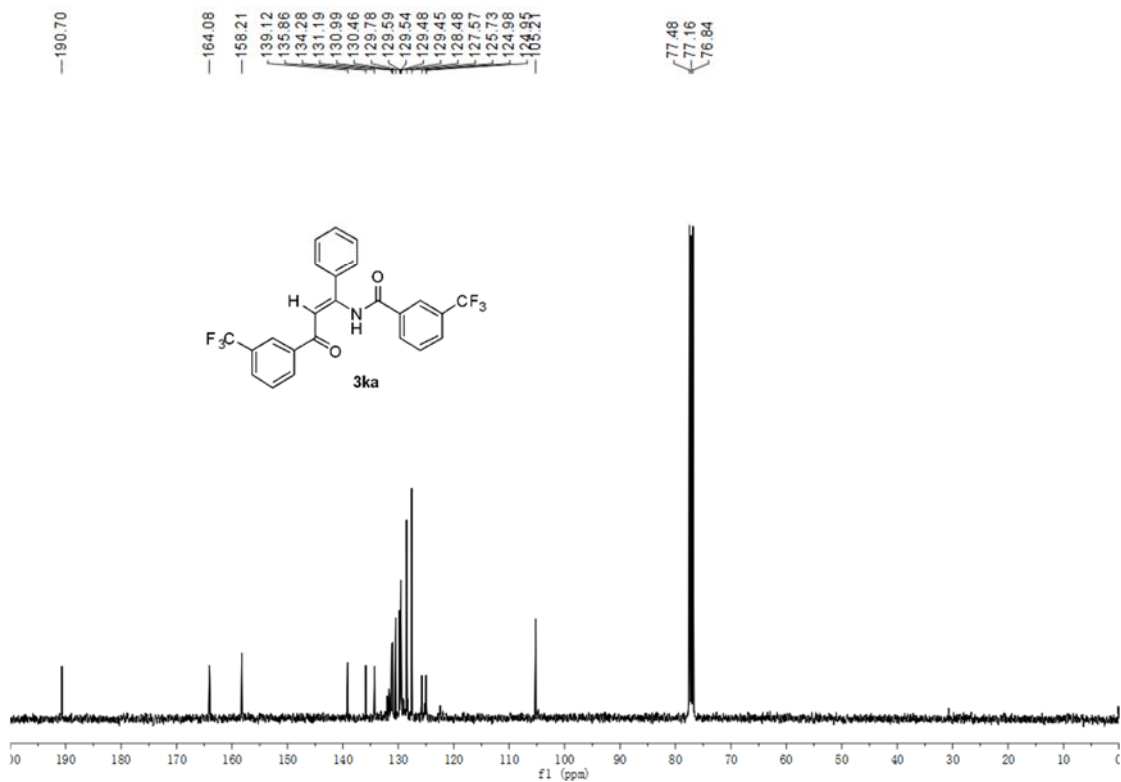
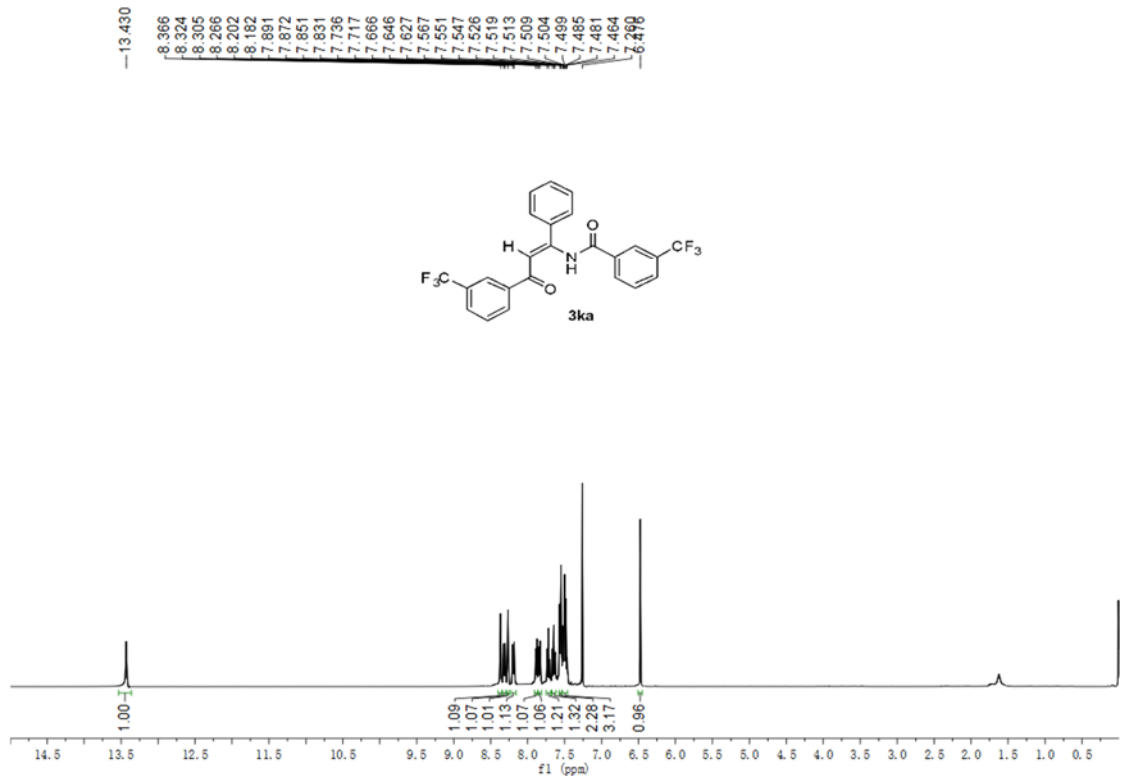
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 — 139.97
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 — 132.23
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 — 129.11
 — 128.88
 — 128.68
 — 128.38
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 — 127.48
 — 127.43
 — 127.41
 — 77.48
 — 77.16
 — 76.84

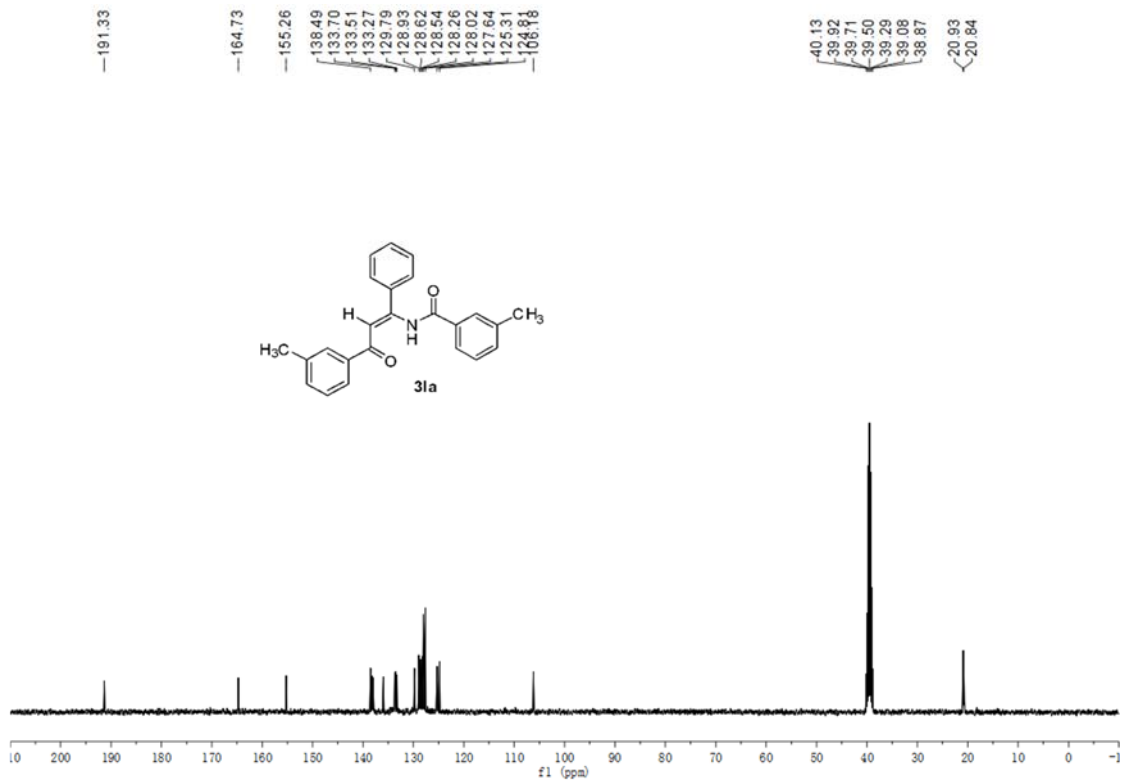
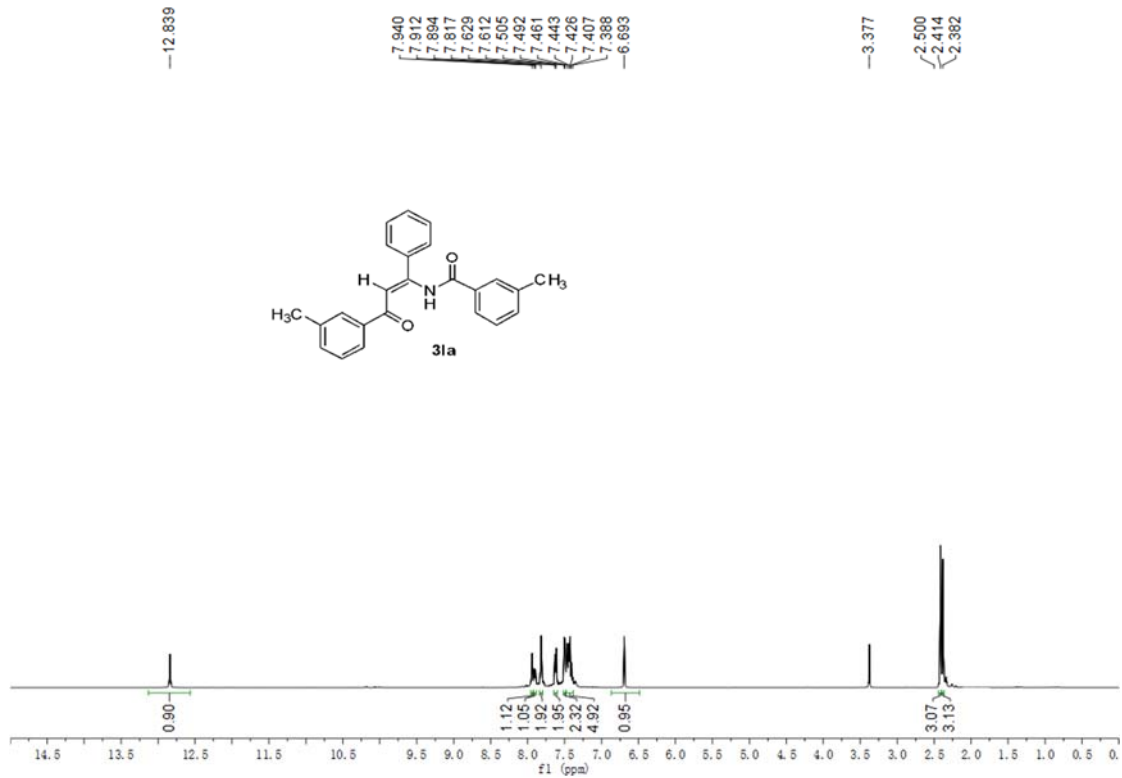


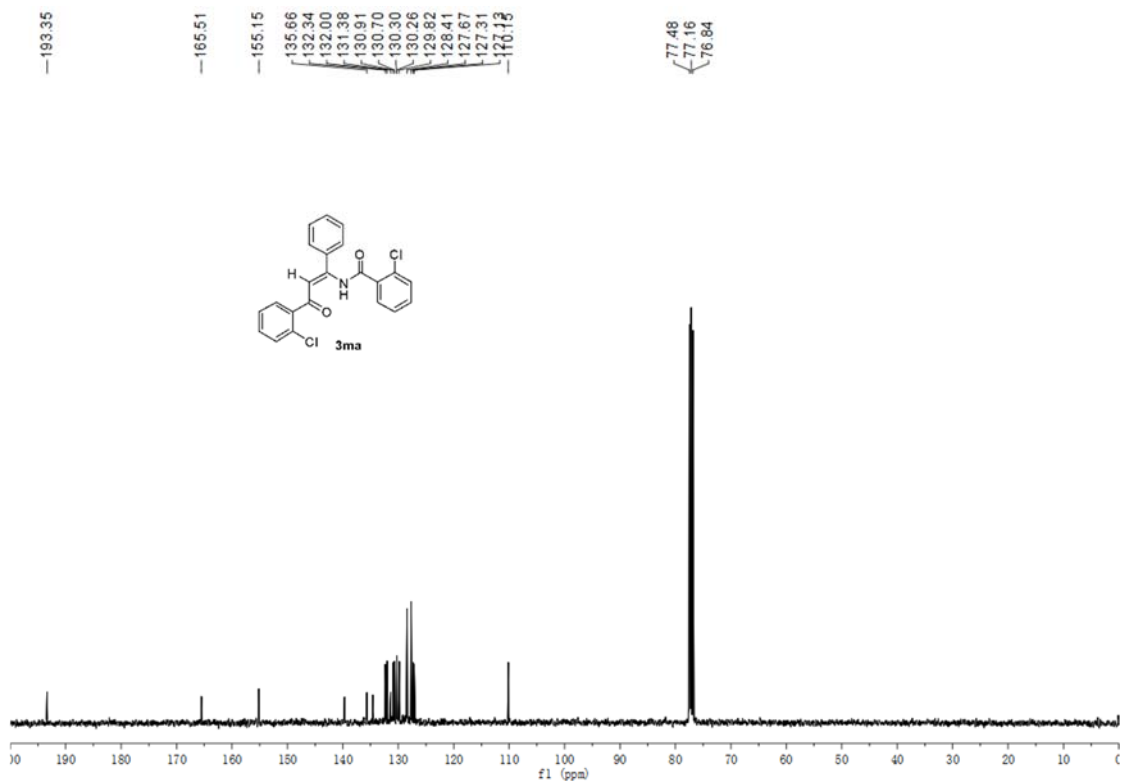
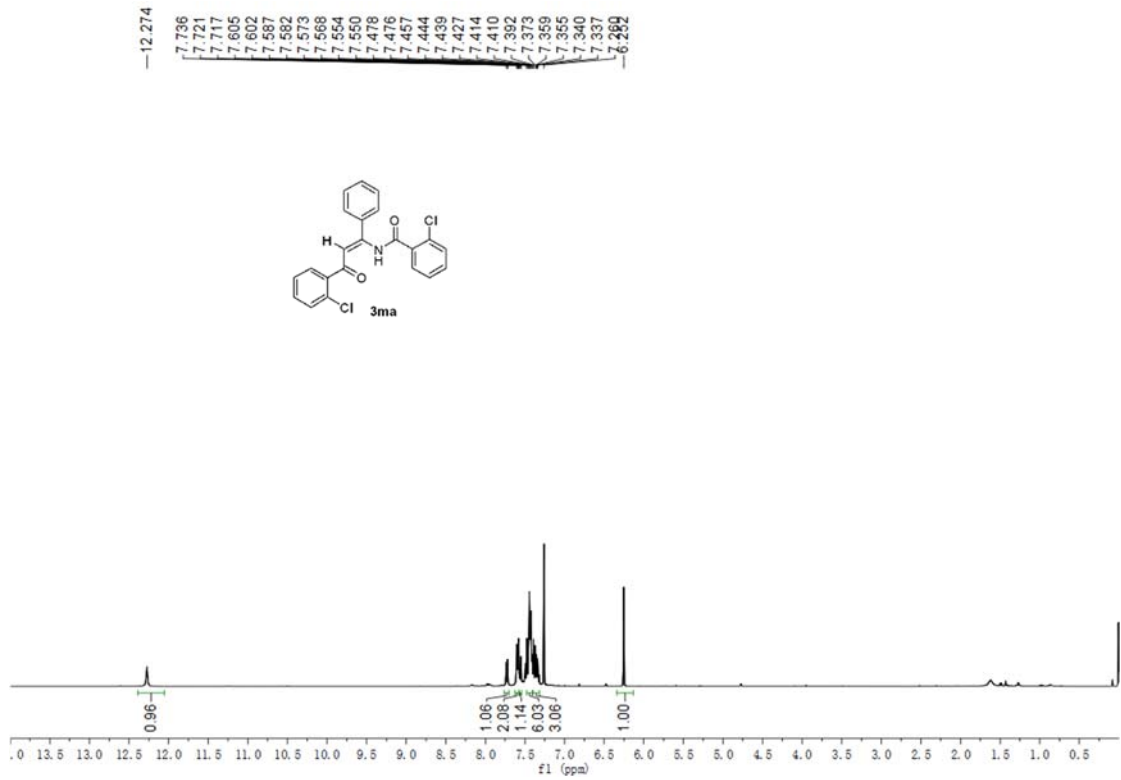


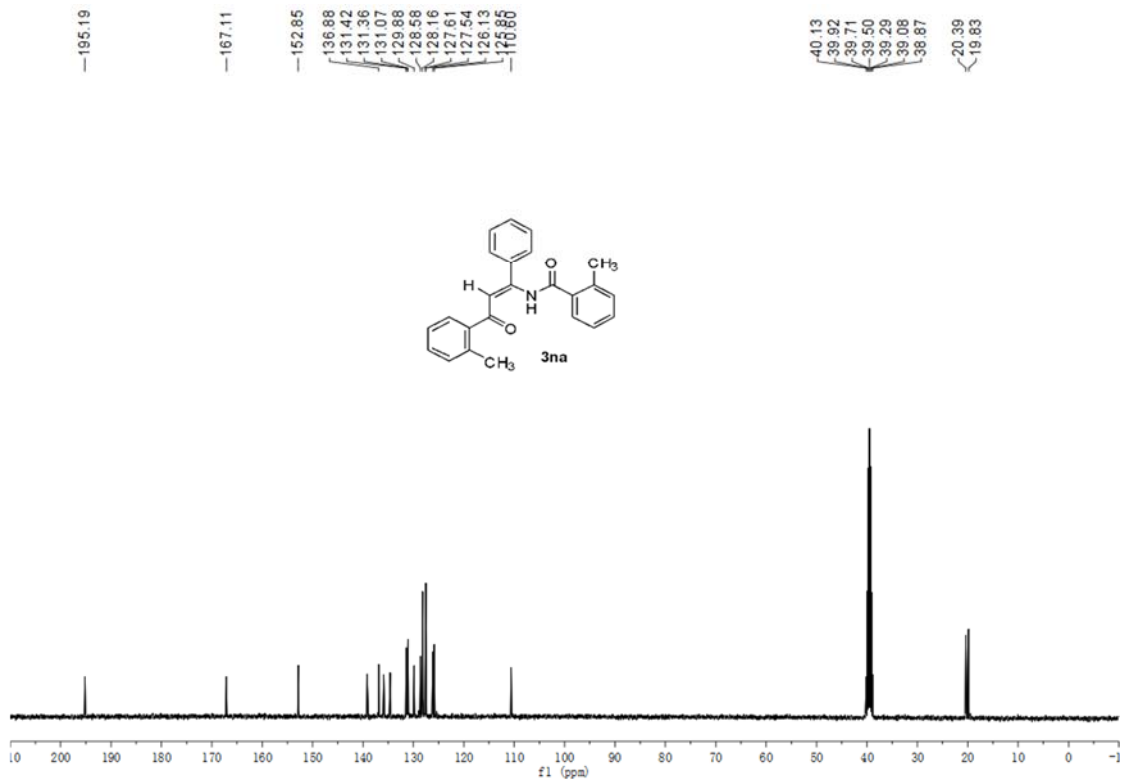
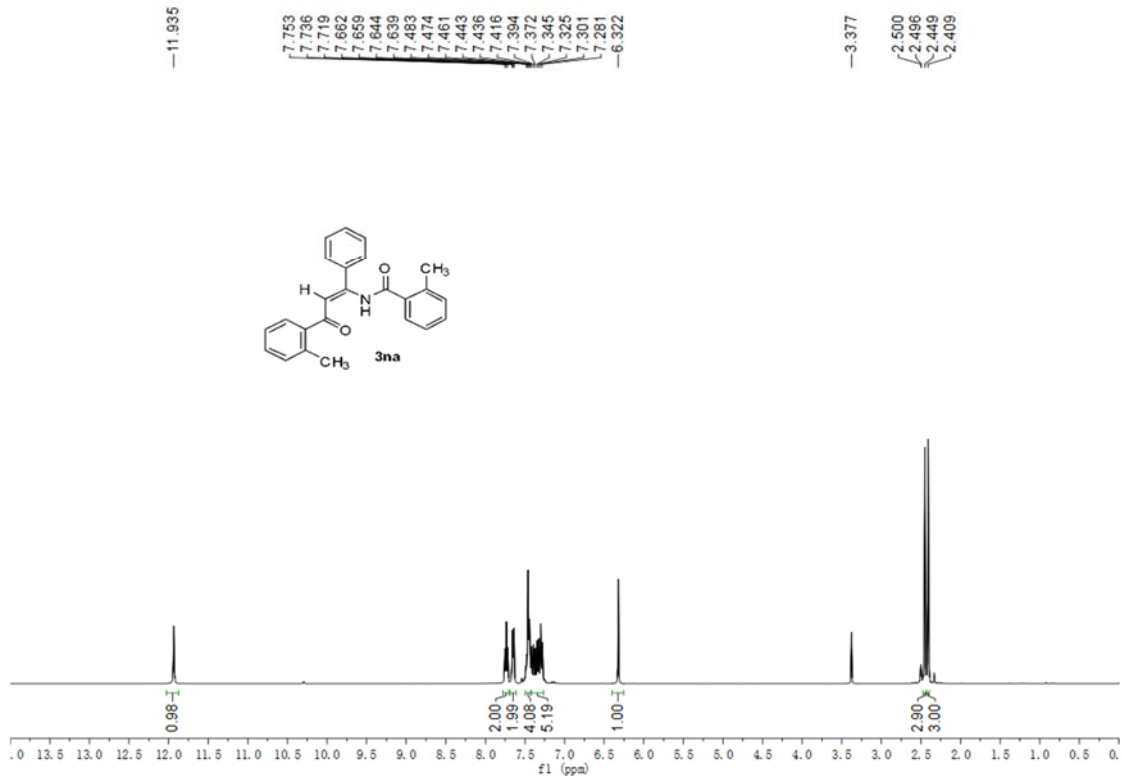


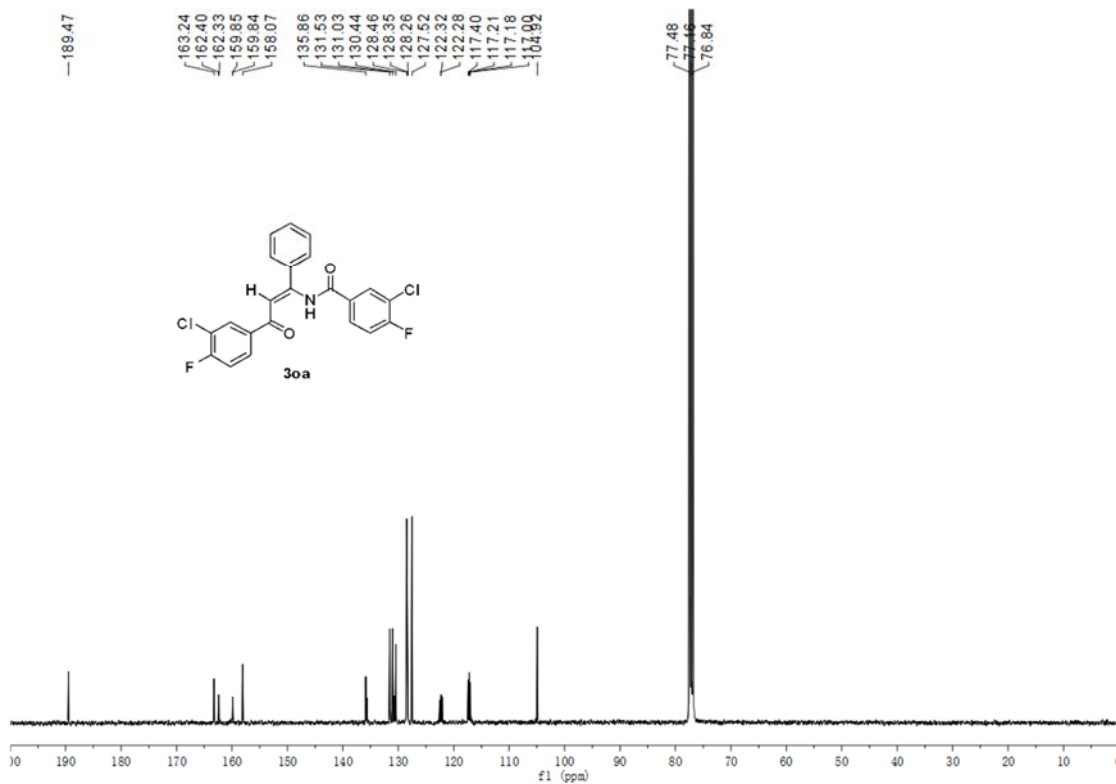
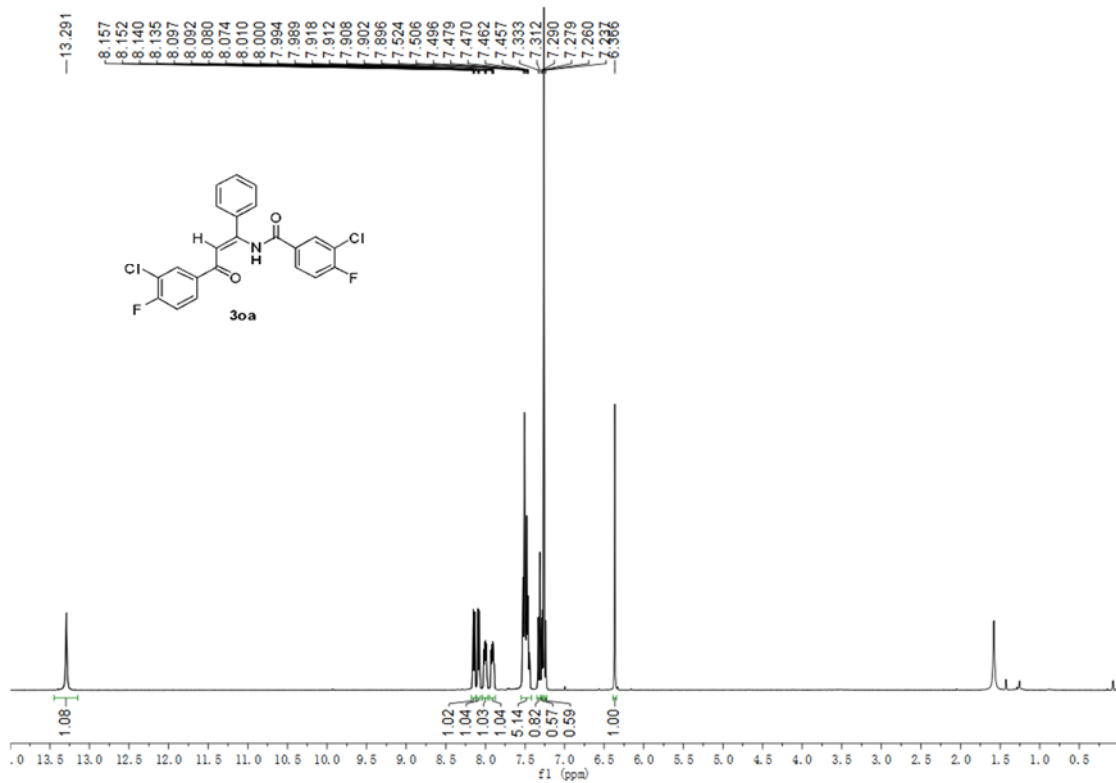


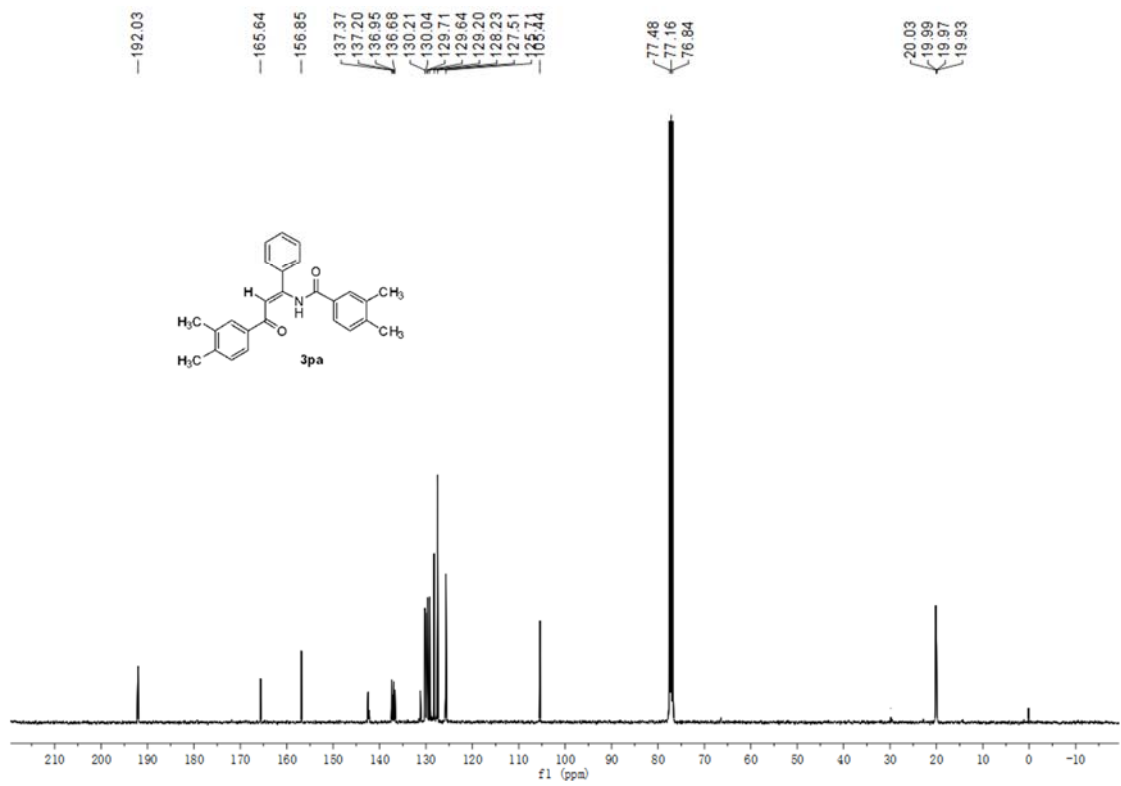
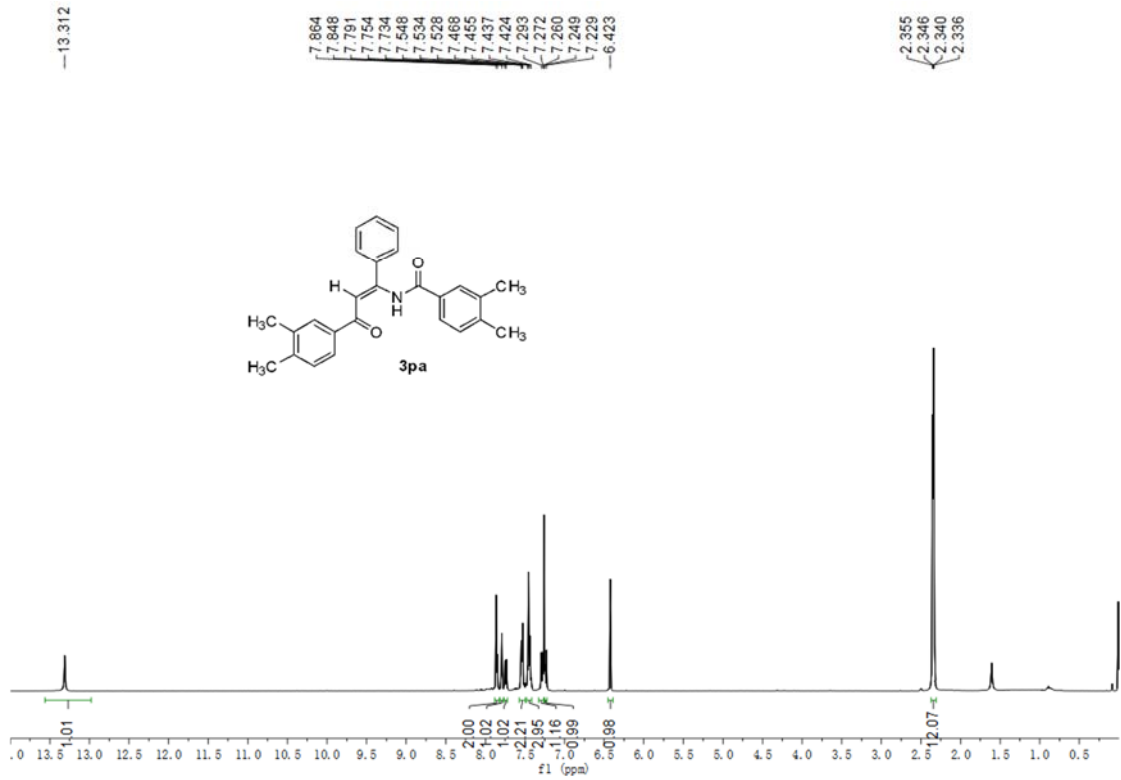


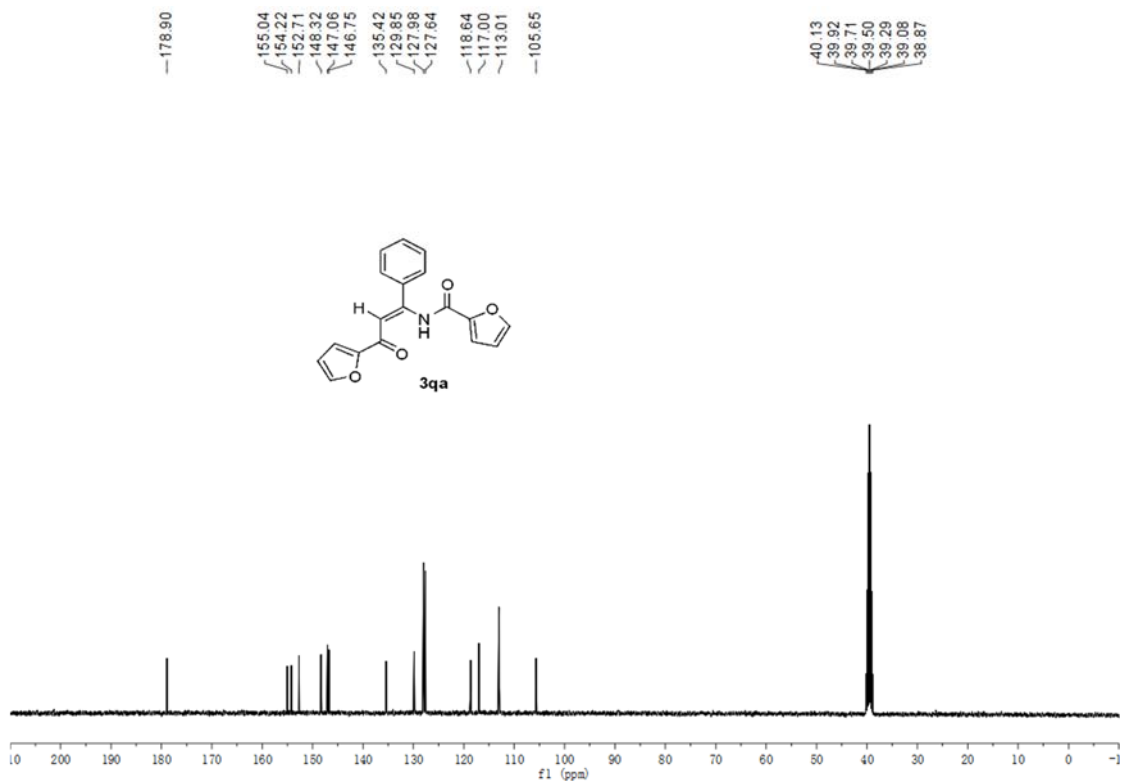
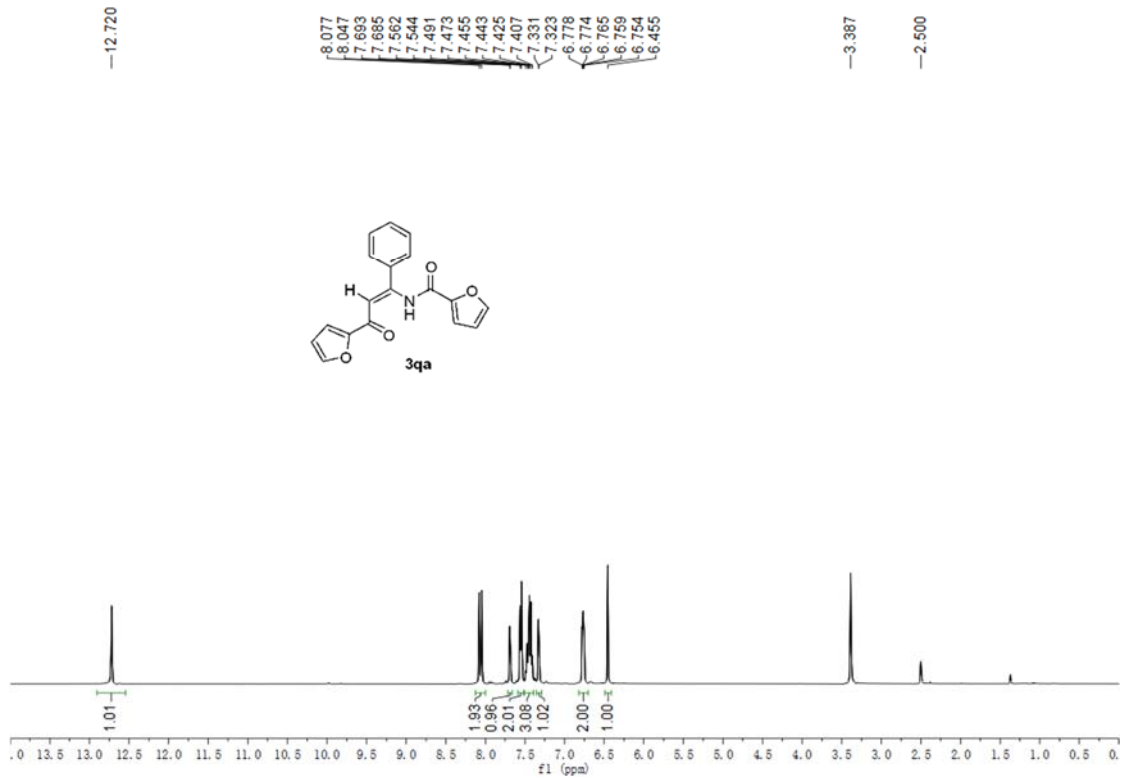


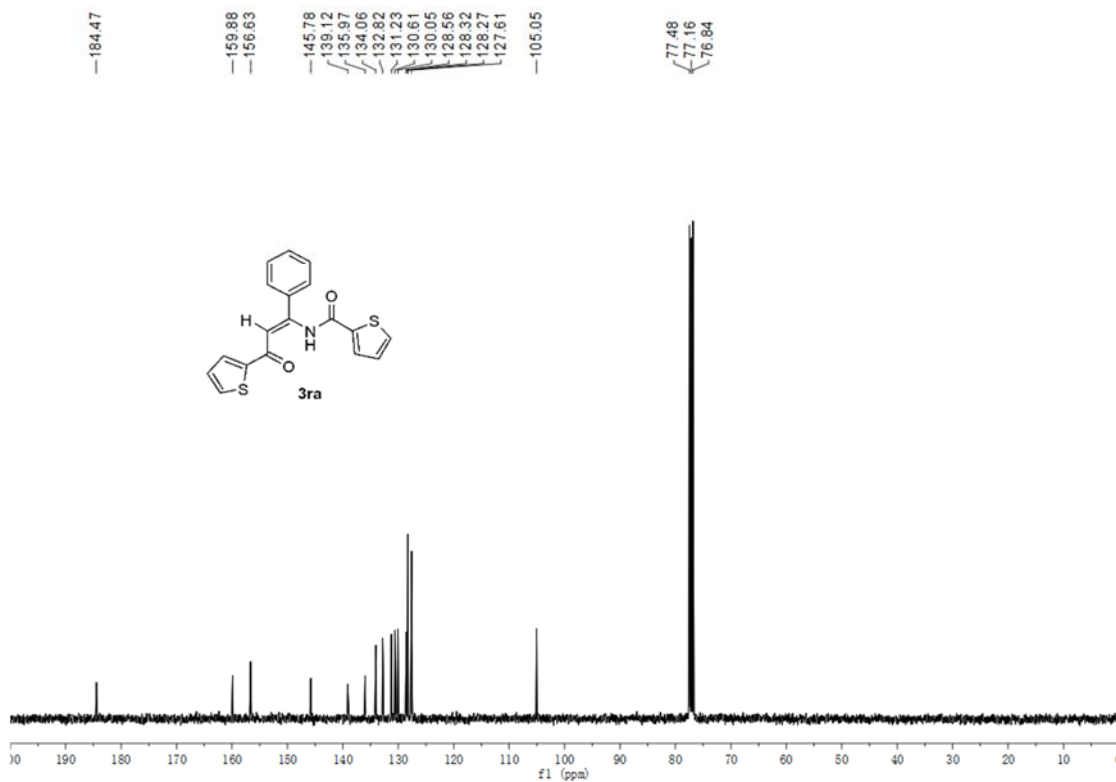
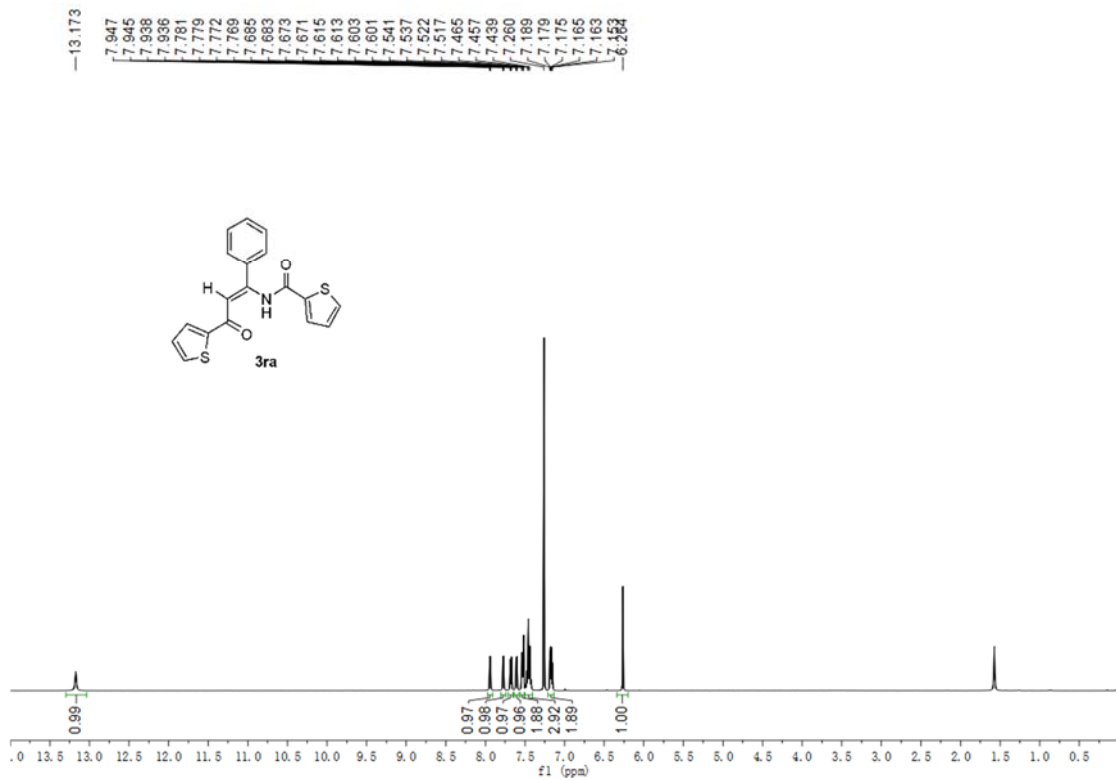


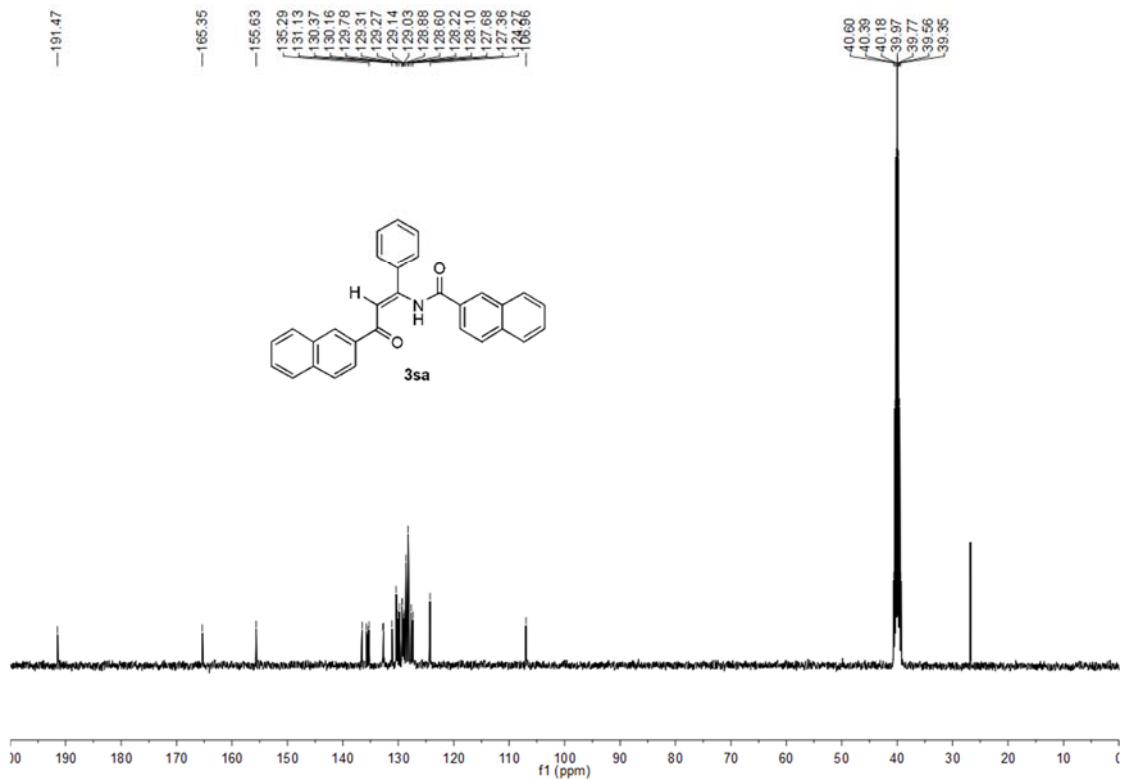
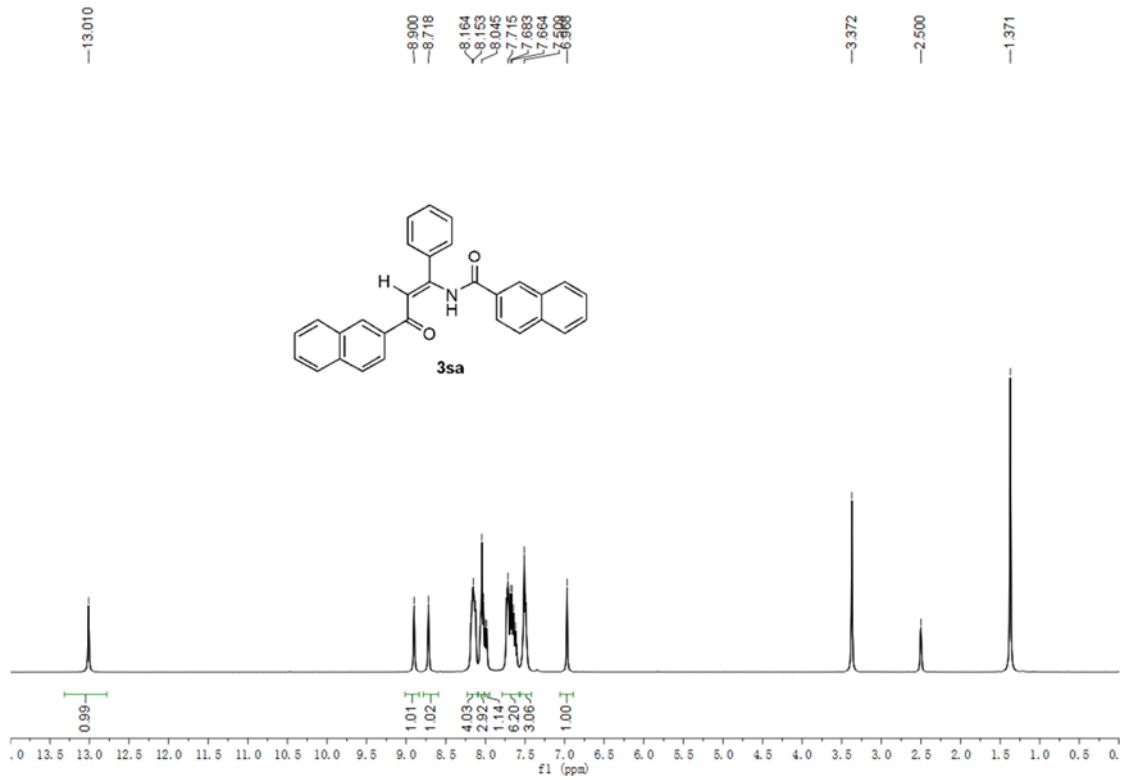


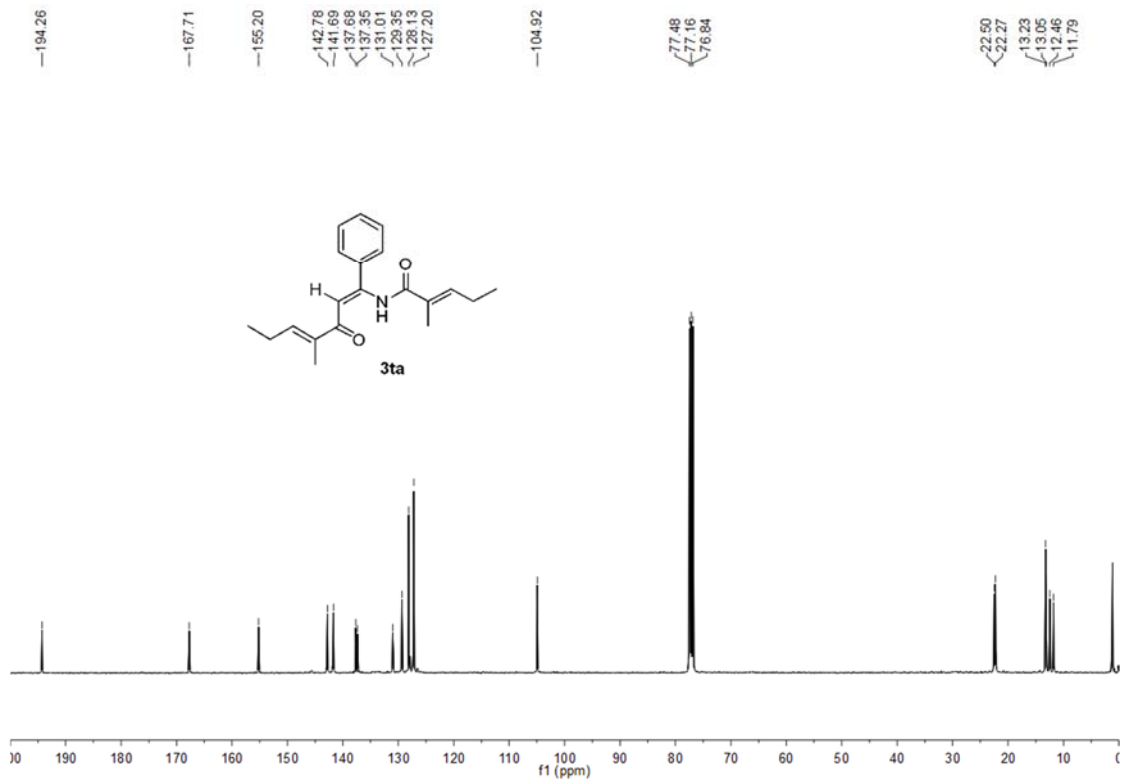
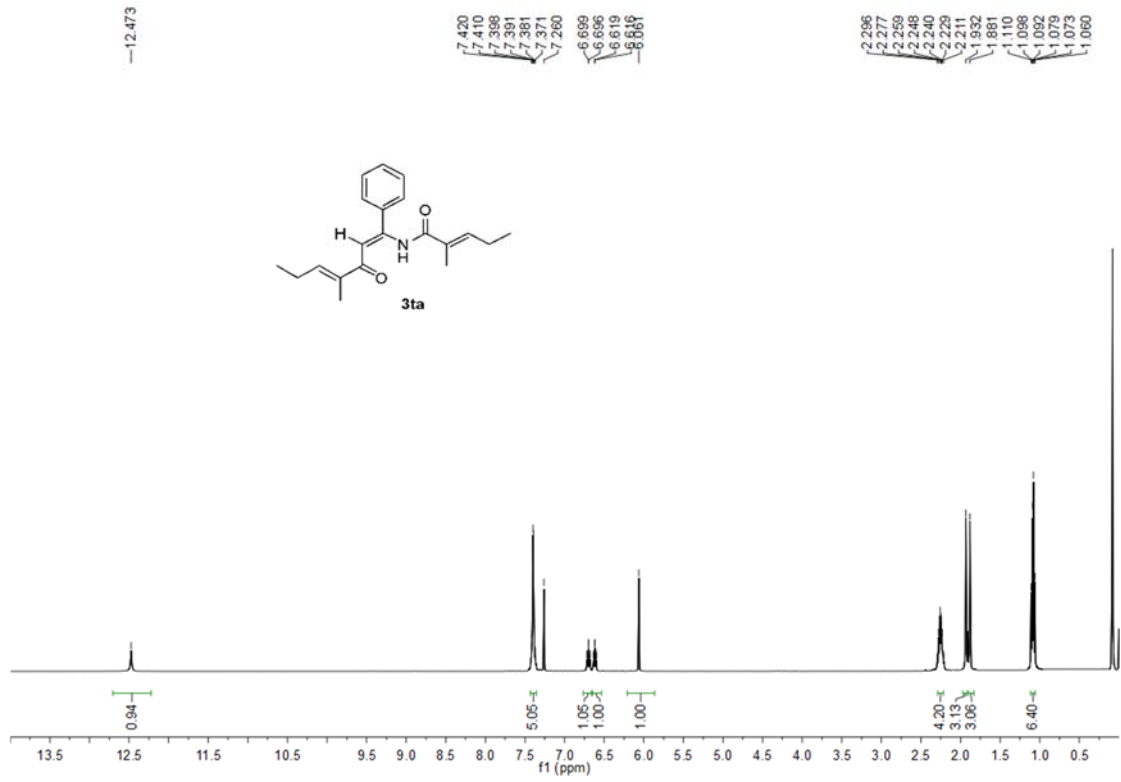


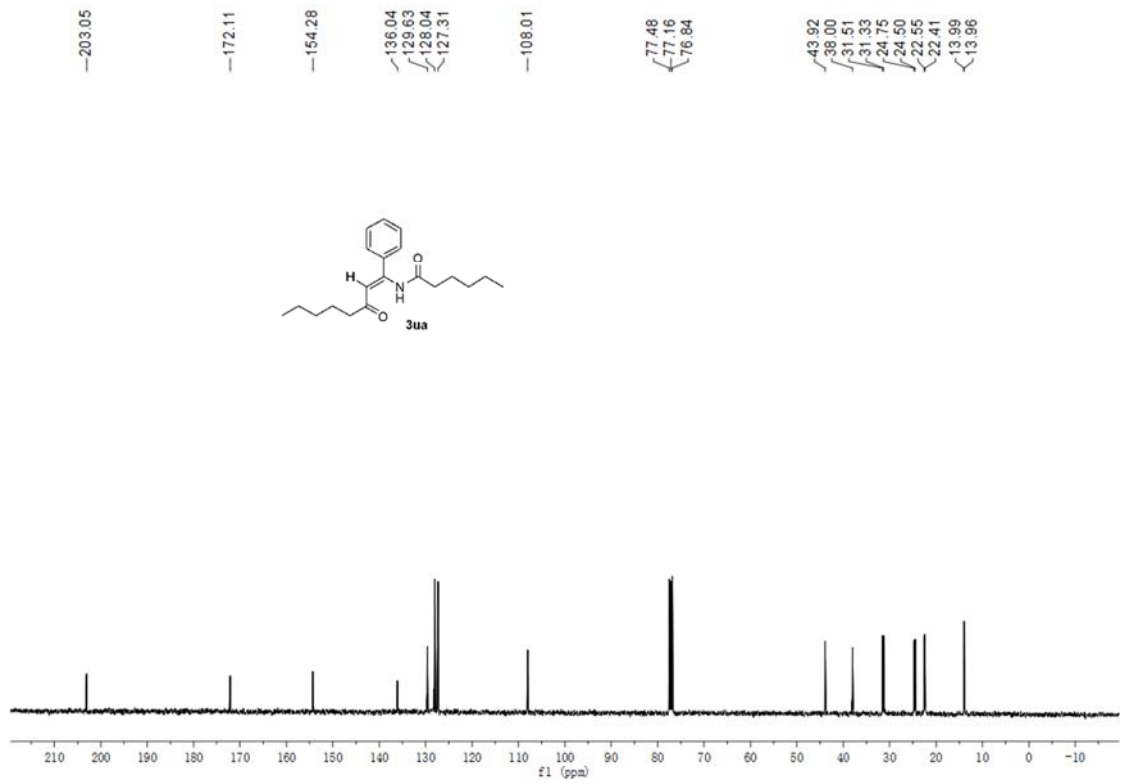
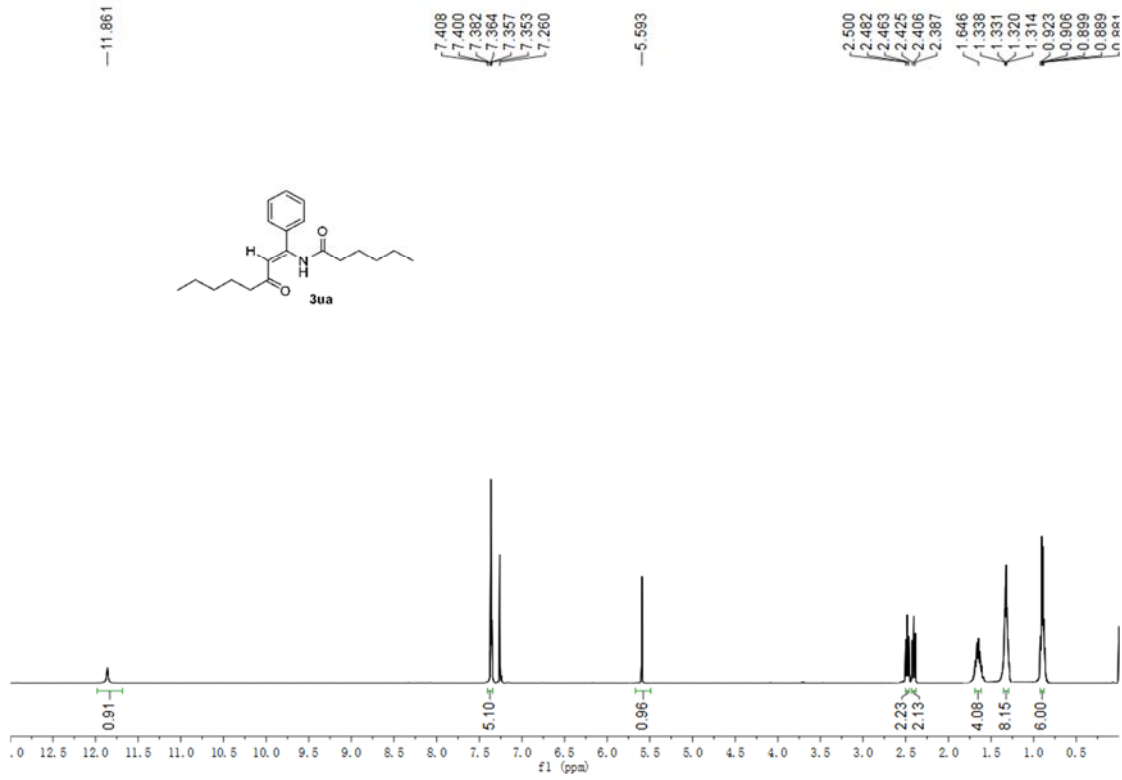












11. References

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