

Supporting Information

Fe-Catalyzed Enaminones Synthesis from Ketones and amines

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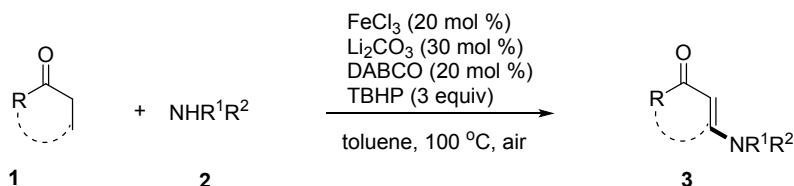
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General Information

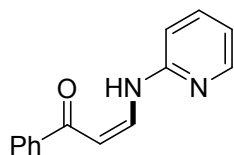
^1H and ^{13}C NMR spectra were recorded on BRUKER DRX-400 spectrometer. The chemical shifts are referenced to signals at 7.26 and 77.0 ppm, respectively, and CDCl_3 is solvent with TMS as the internal standard. HRMS was obtained with a LCMS-IT-TOF mass spectrometer. TLC was performed by using commercially prepared 100-400 mesh silica gel plates, and visualization was effected at 254 nm.

Experimental Procedure for Compounds 3



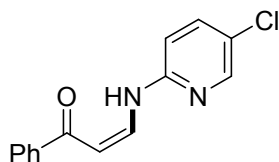
The mixture of ketones **1** (0.5 mmol), amines **2** (1.0 mmol), FeCl₃ (20 mol %), Li₂CO₃ (30 mol %), DABCO (20 mol %), TBHP (1.5 mmol) in toluene (2 mL) was stirred at 100 °C under air for 6 h. At ambient temperature, the reaction mixture was diluted with H₂O (15 mL) and extracted with EtOAc (3 × 15 mL). The organic extracts were dried over MgSO₄. After filtration and evaporation of the solvents under reduced pressure, the crude product was purified by column chromatography on silica gel to afford desired product.

Characterization Data for All Products 3



(Z)-1-Phenyl-3-(pyridin-2-ylamino)prop-2-en-1-one (**3a**)¹

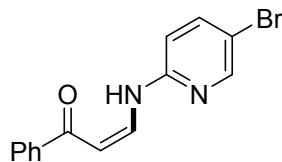
Yellow solid (78.4 mg, 70%); m.p.= 169-170 °C. ^1H NMR (400 MHz, CDCl_3) δ 12.14 (br, 1H), 8.28 (ddd, J = 19.8, 8.2, 4.7 Hz, 2H), 7.99 – 7.92 (m, 2H), 7.62 (ddd, J = 8.1, 7.4, 1.9 Hz, 1H), 7.55 – 7.43 (m, 3H), 6.95 (ddd, J = 7.3, 4.9, 0.8 Hz, 1H), 6.84 (d, J = 8.2 Hz, 1H), 6.15 (d, J = 8.2 Hz, 1H). ^{13}C NMR (100 MHz, CDCl_3) δ 191.9, 151.7, 148.5, 142.9, 139.0, 138.4, 131.8, 128.5, 127.5, 118.5, 111.7, 95.3.



(Z)-3-((5-Chloropyridin-2-yl)amino)-1-phenylprop-2-en-1-one (**3b**)

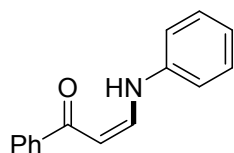
Yellow solid (86.4 mg, 67%); m.p.= 180-181 °C. ^1H NMR (400 MHz, CDCl_3) δ 12.20 (br, 1H), 8.25 (d, J = 2.2 Hz, 1H), 8.16 (dd, J = 11.4, 8.3 Hz, 1H), 7.95 (d, J = 7.5 Hz, 2H), 7.62 – 7.43 (m, 4H), 6.80 (d, J = 8.6

Hz, 1H), 6.17 (d, J = 8.2 Hz, 1H). ^{13}C NMR (100 MHz, CDCl_3) δ 192.0, 150.2, 147.1, 142.6, 139.1, 138.1, 132.0, 128.5, 127.5, 125.6, 112.3, 95.8. HRMS (ESI) m/z : $[\text{M} + \text{H}]^+$ calcd for $\text{C}_{14}\text{H}_{12}\text{ClN}_2\text{O}^+$: 259.0633; found: 259.0637.



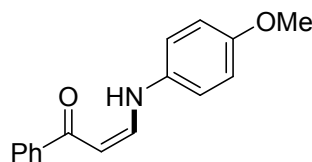
(Z)-3-((5-Bromopyridin-2-yl)amino)-1-phenylprop-2-en-1-one (3c)¹

Yellow solid (89.4 mg, 59%); m.p.= 182-183 °C. ^1H NMR (400 MHz, CDCl_3) δ 12.15 (br, 1H), 8.48-8.34 (m, 1H), 8.16 (dd, J = 11.4, 8.3 Hz, 1H), 7.95 (d, J = 7.4 Hz, 2H), 7.87-7.69 (m, 1H), 7.55-7.45 (m, 3H), 6.76-6.67 (m, 1H), 6.17 (d, J = 8.3 Hz, 1H). ^{13}C NMR (100 MHz, CDCl_3) δ 192.5, 154.4, 149.4, 146.2, 142.2, 140.8, 138.8, 132.0, 128.5, 127.5, 112.8, 95.9.



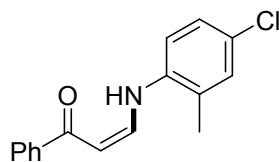
(Z)-1-Phenyl-3-(phenylamino)prop-2-en-1-one (3d)¹

Yellow solid (82.5 mg, 74%); m.p.= 135-136 °C. ^1H NMR (400 MHz, CDCl_3) δ 12.15 (s, brH), 7.94 (d, J = 7.0 Hz, 2H), 7.59 – 7.43 (m, 4H), 7.35 (t, J = 7.2 Hz, 2H), 7.10 (dd, J = 15.8, 7.8 Hz, 3H), 6.04 (dd, J = 7.9, 1.3 Hz, 1H). ^{13}C NMR (100 MHz, CDCl_3) δ 191.5, 144.9, 140.0, 139.2, 131.6, 129.8, 128.4, 127.3, 123.7, 116.4, 93.7.



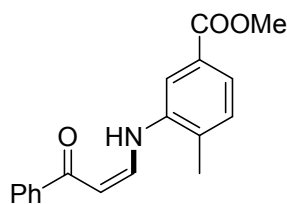
(Z)-3-((4-Methoxyphenyl)amino)-1-phenylprop-2-en-1-one (3e)²

Yellow solid (97.4 mg, 77%); m.p.= 140-141 °C. ^1H NMR (400 MHz, CDCl_3) δ 8.86 (br, 1H), 8.42 (d, J = 7.4 Hz, 2H), 7.68 – 7.43 (m, 7H), 6.93 (d, J = 9.0 Hz, 2H), 3.82 (s, 3H). ^{13}C NMR (101 MHz, CDCl_3) δ 187.7, 158.9, 157.1, 134.6, 133.2, 131.5, 129.9, 128.5, 121.5, 114.4, 92.6, 55.5.



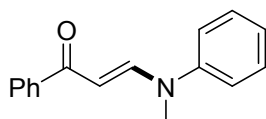
(Z)-3-((4-Chloro-2-methylphenyl)amino)-1-phenylprop-2-en-1-one (3f)

Yellow solid (84.0 mg, 62%); m.p.= 158-159 °C. ^1H NMR (400 MHz, CDCl_3) δ 12.30 (br, 1H), 7.95 (d, J = 7.0 Hz, 2H), 7.58 – 7.42 (m, 4H), 7.20 (d, J = 8.0 Hz, 2H), 7.10 (d, J = 8.3 Hz, 1H), 6.09 (d, J = 7.8 Hz, 1H), 2.42 (s, 3H). ^{13}C NMR (100 MHz, CDCl_3) δ 191.3, 144.8, 139.1, 137.5, 131.7, 130.9, 128.5, 128.3, 128.1, 127.3, 127.1, 114.9, 94.5, 17.6. HRMS (ESI) m/z : $[\text{M} + \text{H}]^+$ calcd for $\text{C}_{16}\text{H}_{15}\text{ClN}_2\text{O}^+$: 272.0837; found: 272.0840.



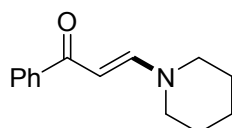
Methyl (Z)-4-methyl-3-((3-oxo-3-phenylprop-1-en-1-yl)amino)benzoate (3g)

Yellow solid (84.1 mg, 57%); m.p.= 153-154 °C. ¹H NMR (400 MHz, CDCl₃) δ 12.35 (br, 1H), 7.98 – 7.94 (m, 2H), 7.87 (s, 1H), 7.71 – 7.63 (m, 2H), 7.52 – 7.45 (m, 3H), 7.29 (d, *J* = 7.8 Hz, 1H), 6.14 (d, *J* = 7.8 Hz, 1H), 3.93 (s, 3H), 2.50 (s, 3H). ¹³C NMR (100 MHz, CDCl₃) δ 191.5, 166.8, 144.7, 139.1, 139.0, 131.7, 131.5, 131.2, 129.3, 128.5, 127.4, 124.3, 114.5, 94.8, 52.2, 18.0. HRMS (ESI) *m/z*: [M + H]⁺ calcd for C₁₈H₁₈NO₃⁺: 296.1281; found: 296.1284.



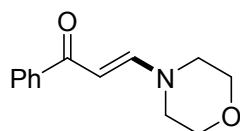
(E)-3-(Methyl(phenyl)amino)-1-phenylprop-2-en-1-one (3h)

Yellow solid (41.5 mg, 35%) m.p.= 110-112 °C. ¹H NMR (400 MHz, CDCl₃) δ 8.23 (d, *J* = 12.7 Hz, 1H), 7.96–7.93 (m, 2H), 7.51–7.42 (m, 3H), 7.40 – 7.36 (m, 2H), 7.22–7.15 (m, 3H), 6.10 (d, *J* = 12.7 Hz, 1H), 3.39 (s, 3H); ¹³C NMR (100 MHz, CDCl₃) δ 189.4, 149.9, 146.4, 140.0, 131.3, 129.5, 128.2, 127.6, 124.9, 120.4, 96.8, 37.2; HRMS (ESI) *m/z*: [M+H]⁺ calcd for C₁₆H₁₆NO⁺: 238.1232. Found: 238.1234.



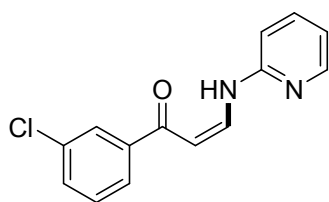
(E)-1-Phenyl-3-(piperidin-1-yl)prop-2-en-1-one (3i)¹

Yellow liquid (61.3 mg, 57%). ¹H NMR (400 MHz, CDCl₃) δ 7.87 (d, *J* = 6.7 Hz, 2H), 7.77 (d, *J* = 12.5 Hz, 1H), 7.41 (tt, *J* = 14.0, 6.9 Hz, 3H), 5.81 (d, *J* = 12.5 Hz, 1H), 3.35 (s, 4H), 1.65 (s, 6H). ¹³C NMR (101 MHz, CDCl₃) δ 189.0, 153.1, 140.7, 130.7, 128.0, 127.4, 91.2, 54.8, 24.0.



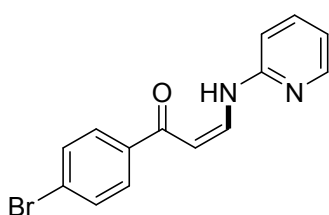
(E)-3-Morpholino-1-phenylprop-2-en-1-one (3j)¹

Yellow solid (69.4 mg, 64%); m.p.= 93-94 °C. ¹H NMR (400 MHz, CDCl₃) δ 7.91 – 7.87 (m, 2H), 7.70 (d, *J* = 12.6 Hz, 1H), 7.48 – 7.35 (m, 3H), 5.87 (d, *J* = 12.6 Hz, 1H), 3.73 – 3.65 (m, 4H), 3.37 – 3.27 (m, 4H). ¹³C NMR (100 MHz, CDCl₃) δ 188.6, 152.5, 139.9, 130.8, 127.9, 127.2, 92.0, 65.9.



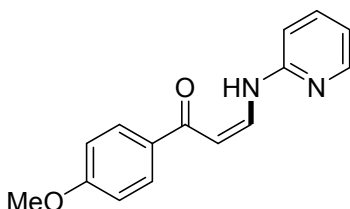
(Z)-1-(3-Chlorophenyl)-3-(pyridin-2-ylamino)prop-2-en-1-one (3k)

Yellow solid (78.7 mg, 61%); m.p.= 183-184 °C. ¹H NMR (400 MHz, CDCl₃) δ 12.15 (br, 1H), 8.33 – 8.24 (m, 2H), 7.89 (d, *J* = 8.5 Hz, 2H), 7.66 – 7.59 (m, 1H), 7.43 (d, *J* = 8.5 Hz, 2H), 6.97 (dd, *J* = 7.2, 5.0 Hz, 1H), 6.84 (d, *J* = 8.2 Hz, 1H), 6.09 (d, *J* = 8.2 Hz, 1H). ¹³C NMR (100 MHz, CDCl₃) δ 190.4, 151.6, 148.6, 143.4, 138.4, 138.1, 137.4, 128.9, 128.7, 118.7, 111.7, 94.9. HRMS (ESI) *m/z*: [M + H]⁺ calcd for C₁₄H₁₂ClN₂O⁺: 259.0633; found: 259.0637.



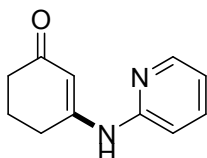
(Z)-1-(4-Bromophenyl)-3-(pyridin-2-ylamino)prop-2-en-1-one (3l)³

Yellow solid (89.4 mg, 59%); m.p.= 189-190 °C. ¹H NMR (400 MHz, CDCl₃) δ 12.15 (br, H), 8.35 – 8.24 (m, 2H), 7.82 (d, *J* = 8.6 Hz, 2H), 7.68 – 7.58 (m, 3H), 6.97 (dd, *J* = 6.1, 4.5 Hz, 1H), 6.85 (d, *J* = 8.2 Hz, 1H), 6.08 (d, *J* = 8.2 Hz, 1H). ¹³C NMR (101 MHz, CDCl₃) δ 190.8, 158.2, 155.4, 151.7, 148.6, 143.4, 138.4, 131.7, 129.1, 118.7, 111.8, 94.8.



(Z)-1-(4-Methoxyphenyl)-3-(pyridin-2-ylamino)prop-2-en-1-one (3m)³

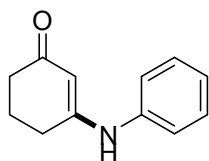
Yellow solid (92.7 mg, 73%); m.p.= 153-154 °C. ¹H NMR (400 MHz, CDCl₃) δ 12.13 (br, 1H), 8.29 (s, 1H), 8.20 (ddd, *J* = 12.2, 8.3, 4.2 Hz, 1H), 7.94 (dd, *J* = 8.6, 2.3 Hz, 2H), 7.63 – 7.56 (m, 1H), 6.99 – 6.90 (m, 3H), 6.81 (dd, *J* = 8.0, 3.7 Hz, 1H), 6.10 (dd, *J* = 8.3, 3.6 Hz, 1H), 3.87 (s, 3H). ¹³C NMR (100 MHz, CDCl₃) δ 190.8, 162.7, 151.9, 148.4, 142.2, 138.3, 131.8, 129.5, 118.2, 113.7, 111.5, 95.0, 55.4.



3-(Pyridin-2-ylamino)cyclohex-2-en-1-one (3n)⁴

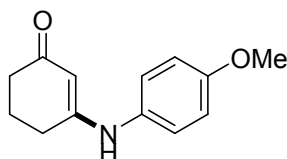
Yellow solid (67.7 mg, 72%); m.p.= 176-177 °C. ¹H NMR (400 MHz, CDCl₃) δ 8.67 (br, 1H), 8.17 (d, *J* = 3.4 Hz, 1H), 7.49 (dd, *J* = 10.9, 4.6 Hz, 1H), 7.28 (d, *J* = 11.9 Hz, 1H), 7.00 (d, *J* = 8.3 Hz, 1H), 6.86 –

6.82 (m, 1H), 6.65 (d, $J = 4.5$ Hz, 1H), 2.55 (t, $J = 6.0$ Hz, 2H), 2.31 (t, $J = 6.3$ Hz, 2H), 1.99 – 1.92 (m, 2H). ^{13}C NMR (100 MHz, CDCl_3) δ 199.7, 159.8, 153.2, 147.7, 137.5, 118.0, 114.2, 103.9, 36.4, 29.4, 21.6.



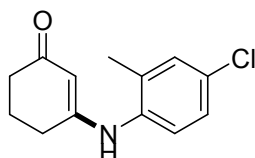
3-(Phenylamino)cyclohex-2-en-1-one (3o)⁵

Yellow solid (64.5 mg, 69%); m.p. = 161–162 °C. ^1H NMR (400 MHz, CDCl_3) δ 7.34 (t, $J = 7.8$ Hz, 2H), 7.17 (t, $J = 8.5$ Hz, 3H), 6.02 (s, 1H), 5.59 (s, 1H), 2.50 (t, $J = 6.2$ Hz, 2H), 2.37 (t, $J = 6.5$ Hz, 2H), 2.11 – 2.02 (m, 2H). ^{13}C NMR (100 MHz, CDCl_3) δ 198.3, 162.0, 129.4, 125.6, 123.9, 100.1, 36.5, 29.8, 21.8.



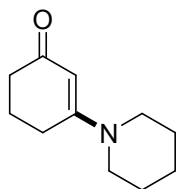
3-((4-Methoxyphenyl)amino)cyclohex-2-en-1-one (3p)⁵

Yellow solid (79.2 mg, 73%); m.p. = 173–174 °C. ^1H NMR (400 MHz, CDCl_3) δ 7.78 (br, 1H), 6.99 (d, $J = 8.8$ Hz, 2H), 6.76 (d, $J = 8.8$ Hz, 2H), 5.30 (s, 1H), 3.73 (s, 3H), 2.44 (t, $J = 6.1$ Hz, 2H), 2.24 (t, $J = 6.3$ Hz, 2H), 1.91 (dd, $J = 12.0, 6.0$ Hz, 2H). ^{13}C NMR (100 MHz, CDCl_3) δ 197.9, 164.8, 157.4, 130.8, 126.0, 114.2, 98.0, 55.3, 36.2, 29.1, 21.7.



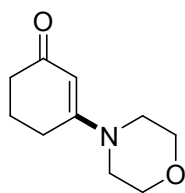
3-((4-Chloro-2-methylphenyl)amino)cyclohex-2-en-1-one (3q)

Yellow solid (68.2 mg, 58%); m.p. = 170–171 °C. ^1H NMR (400 MHz, CDCl_3) δ 7.12 (s, 3H), 6.63 (s, 1H), 4.99 (d, $J = 1.9$ Hz, 1H), 2.49 (t, $J = 5.4$ Hz, 2H), 2.30 (dd, $J = 9.1, 3.7$ Hz, 2H), 2.14 (s, 3H), 2.05 – 1.97 (m, 2H). ^{13}C NMR (100 MHz, CDCl_3) δ 198.0, 163.2, 137.3, 132.7, 132.0, 127.1, 126.7, 99.6, 36.4, 29.1, 21.9, 17.2. HRMS (ESI) m/z : $[\text{M} + \text{H}]^+$ calcd for $\text{C}_{13}\text{H}_{15}\text{ClNO}^+$: 236.0837; found: 236.0834.



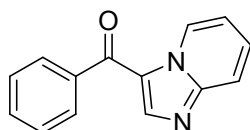
3-(Piperidin-1-yl)cyclohex-2-en-1-one (3r)⁶

Yellow liquid (48.3 mg, 54%). ^1H NMR (400 MHz, CDCl_3) δ 5.29 (s, 1H), 3.42 – 3.30 (m, 4H), 2.40 (t, $J = 6.3$ Hz, 2H), 2.30 – 2.25 (m, 2H), 2.01 – 1.94 (m, 2H), 1.69 – 1.63 (m, 2H), 1.58 (dt, $J = 11.0, 5.4$ Hz, 4H). ^{13}C NMR (100 MHz, CDCl_3) δ 197.3, 164.7, 99.2, 47.5, 35.4, 27.0, 25.5, 24.3, 22.2.



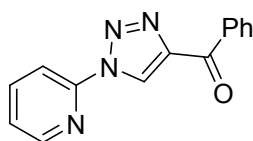
3-Morpholinocyclohex-2-en-1-one (3s)⁷

Yellow liquid (44.3 mg, 49%). ¹H NMR (400 MHz, CDCl₃) δ 5.26 (s, 1H), 3.76 – 3.68 (m, 4H), 3.33 – 3.27 (m, 4H), 2.40 (t, *J* = 6.2 Hz, 2H), 2.31 – 2.26 (m, 2H), 2.06 – 1.95 (m, 2H). ¹³C NMR (100 MHz, CDCl₃) δ 197.6, 165.0, 100.5, 66.2, 46.2, 35.6, 26.7, 22.0.



Imidazo[1,2-a]pyridin-3-yl(phenyl)methanone (4a)³

Yellow solid (51.3 mg, 77%); m.p.= 120-121 °C. ¹H NMR (400 MHz, CDCl₃) δ 9.71 (d, *J* = 6.9 Hz, 1H), 8.18 (s, 1H), 7.85 (dd, *J* = 15.4, 8.4 Hz, 2H), 7.77 (d, *J* = 9.0 Hz, 1H), 7.60 – 7.55 (m, 1H), 7.54 – 7.47 (m, 3H), 7.15 – 7.08 (m, 1H). ¹³C NMR (100 MHz, CDCl₃) δ 184.7, 145.6, 139.2, 131.9, 129.3, 128.8, 128.7, 128.5, 117.6, 115.0.



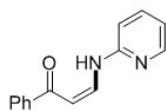
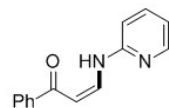
Phenyl(1-(pyridin-2-yl)-1H-1,2,3-triazol-4-yl)methanone (5a)⁸

White solid (60.0 mg, 80%); m.p.= 129-130 °C. ¹H NMR (400 MHz, CDCl₃) δ 9.20 (s, 1H), 8.51 (ddd, *J* = 4.8, 1.6, 0.7 Hz, 1H), 8.41 (dt, *J* = 8.5, 1.7 Hz, 2H), 8.22 (d, *J* = 8.2 Hz, 1H), 7.96 – 7.90 (m, 1H), 7.63 – 7.59 (m, 1H), 7.55 – 7.48 (m, 2H), 7.38 (ddd, *J* = 7.5, 4.9, 0.9 Hz, 1H). ¹³C NMR (100 MHz, CDCl₃) δ 185.4, 148.8, 148.4, 147.8, 139.2, 136.5, 133.3, 130.4, 128.4, 125.6, 124.2, 114.0.

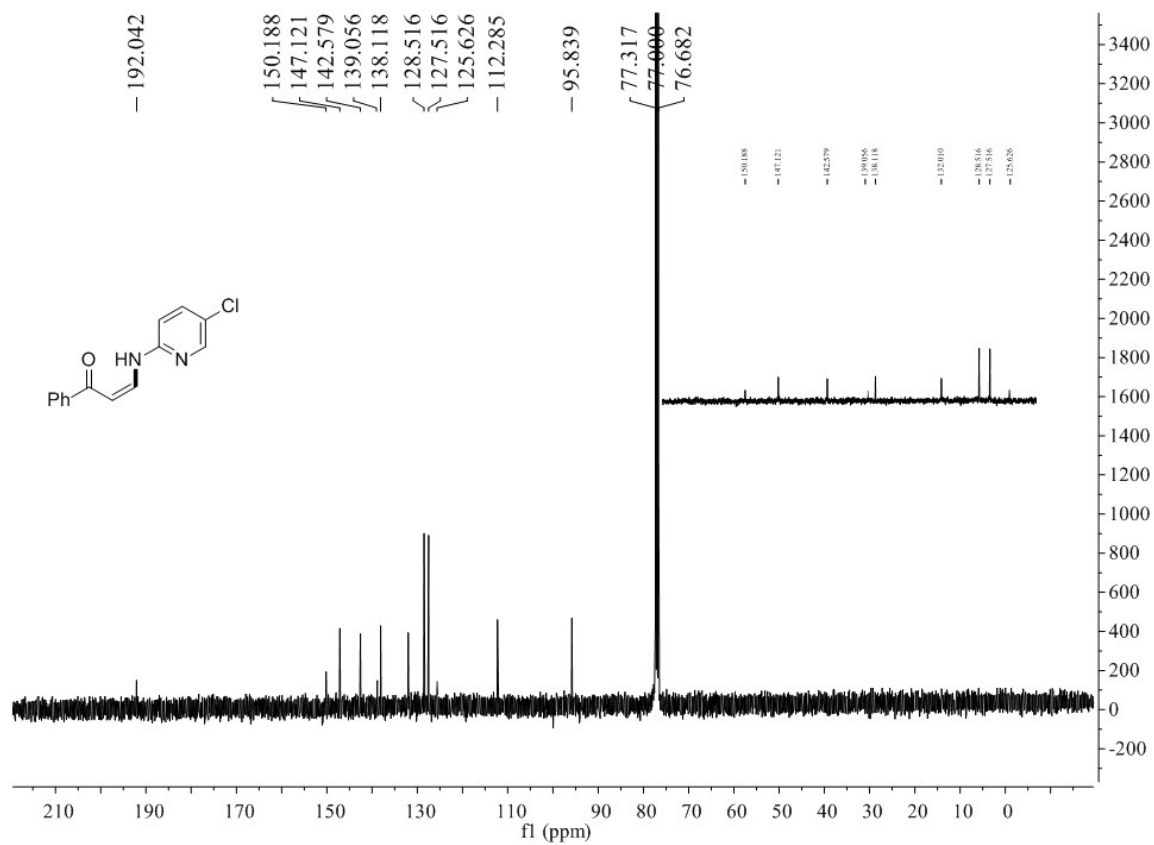
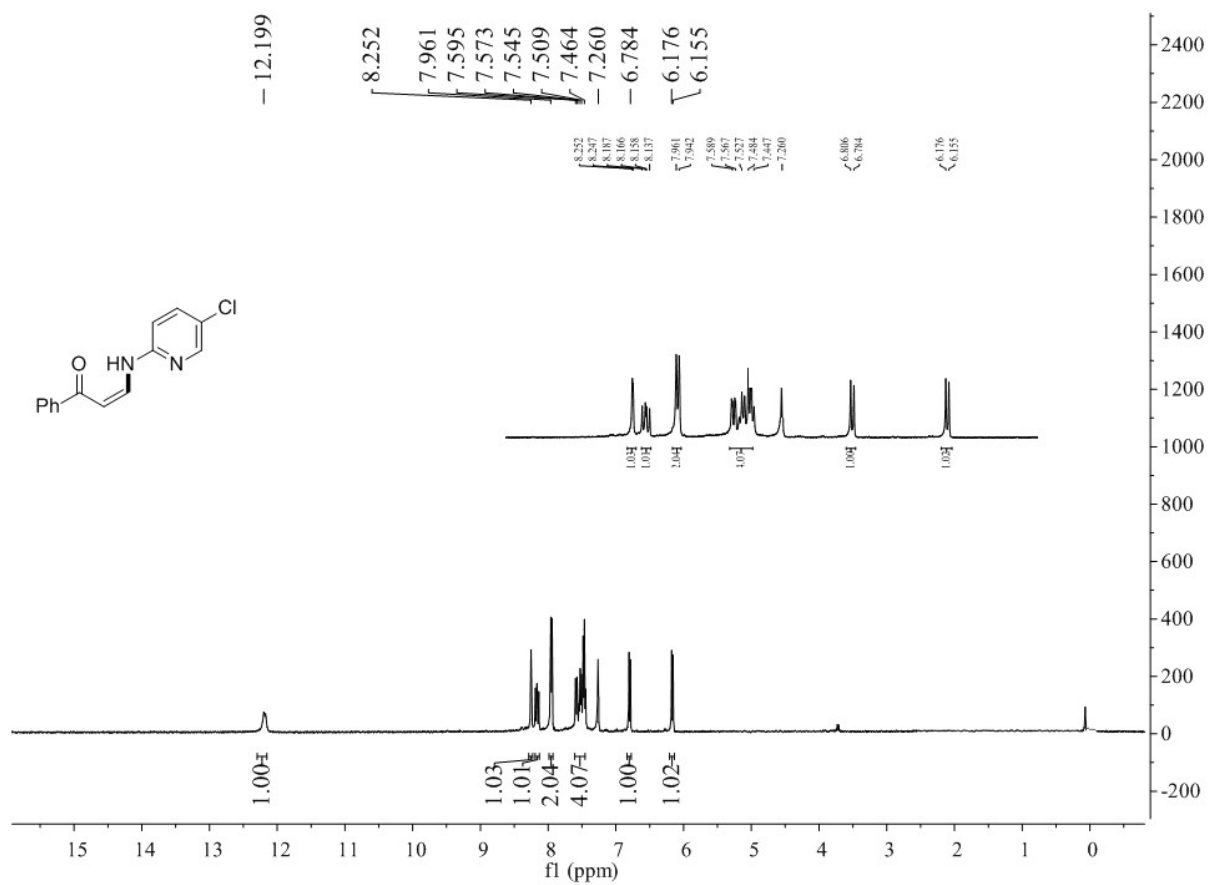
References

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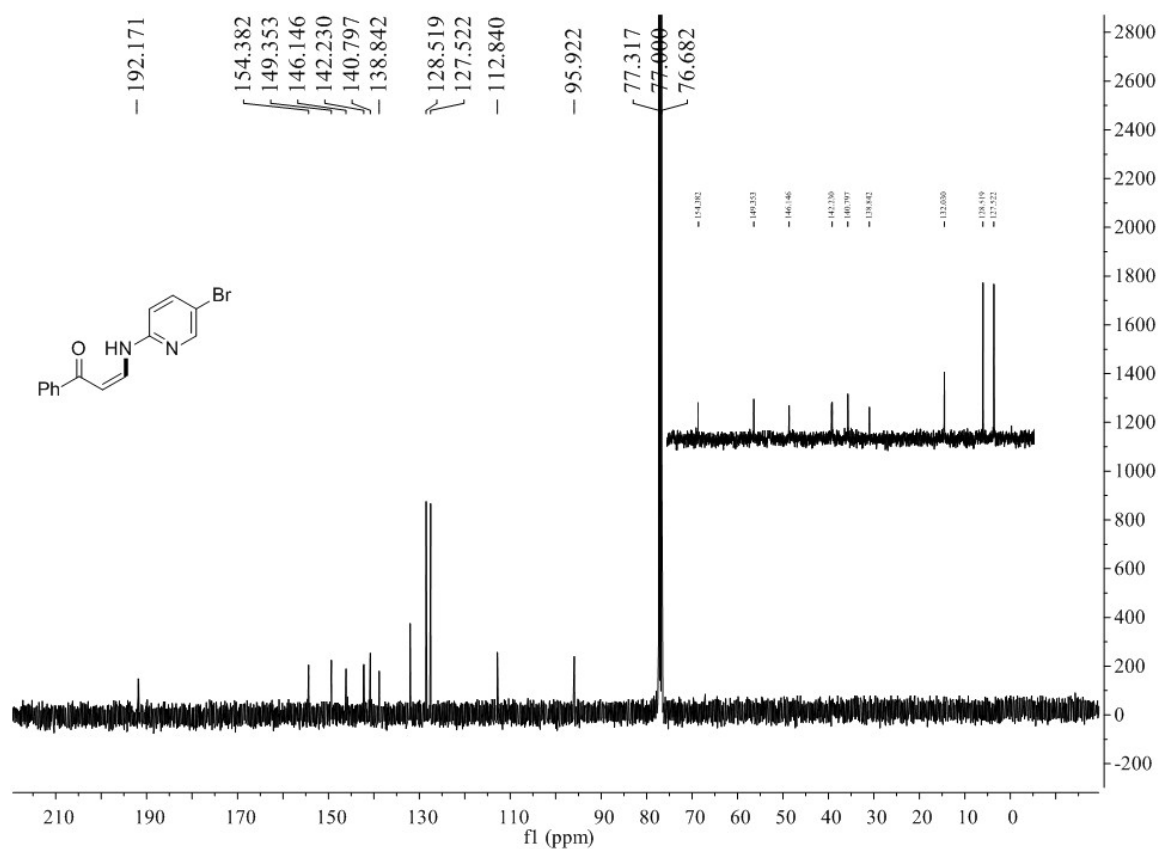
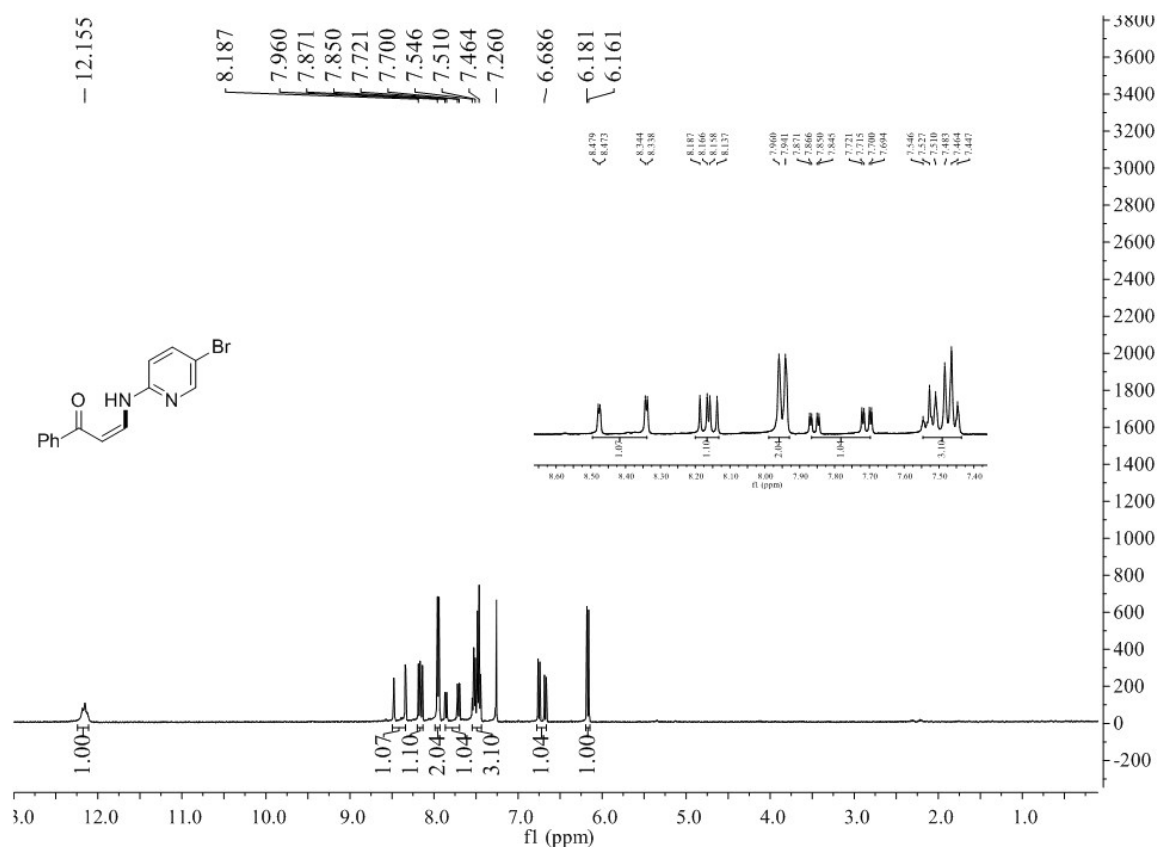
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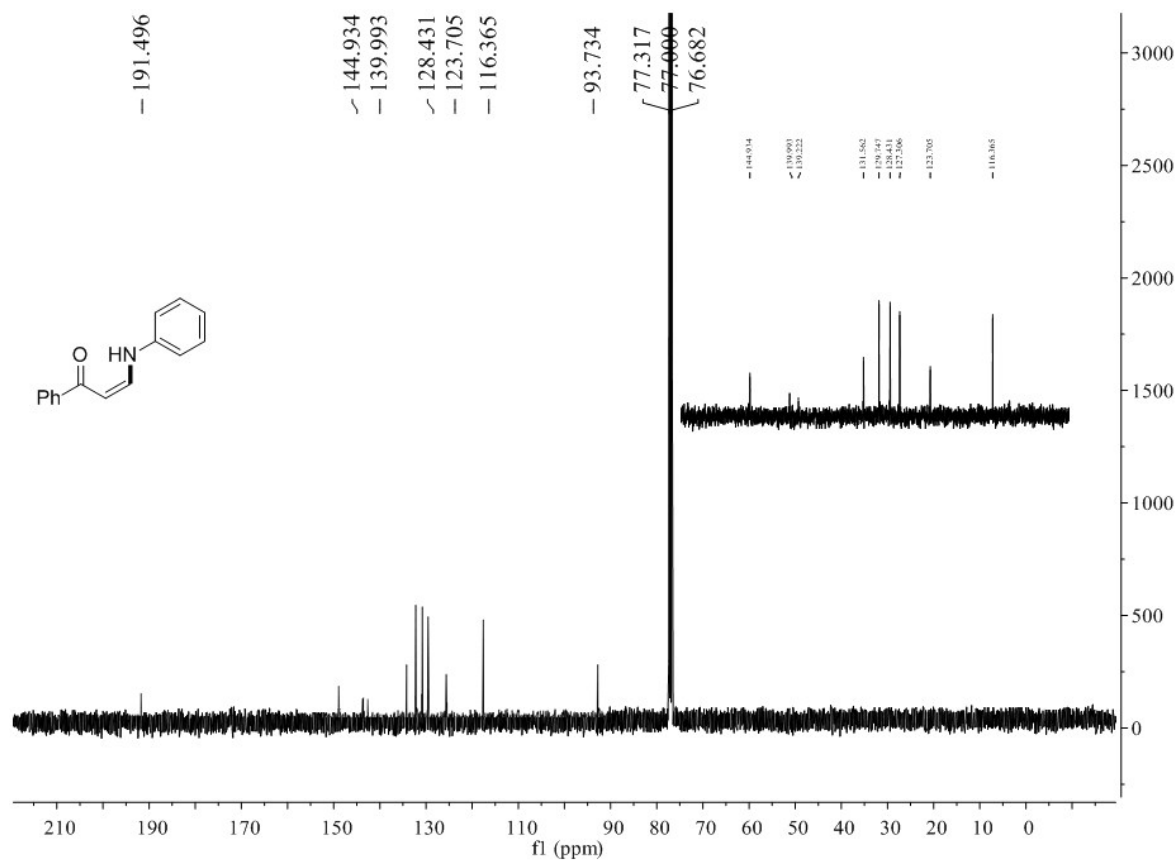
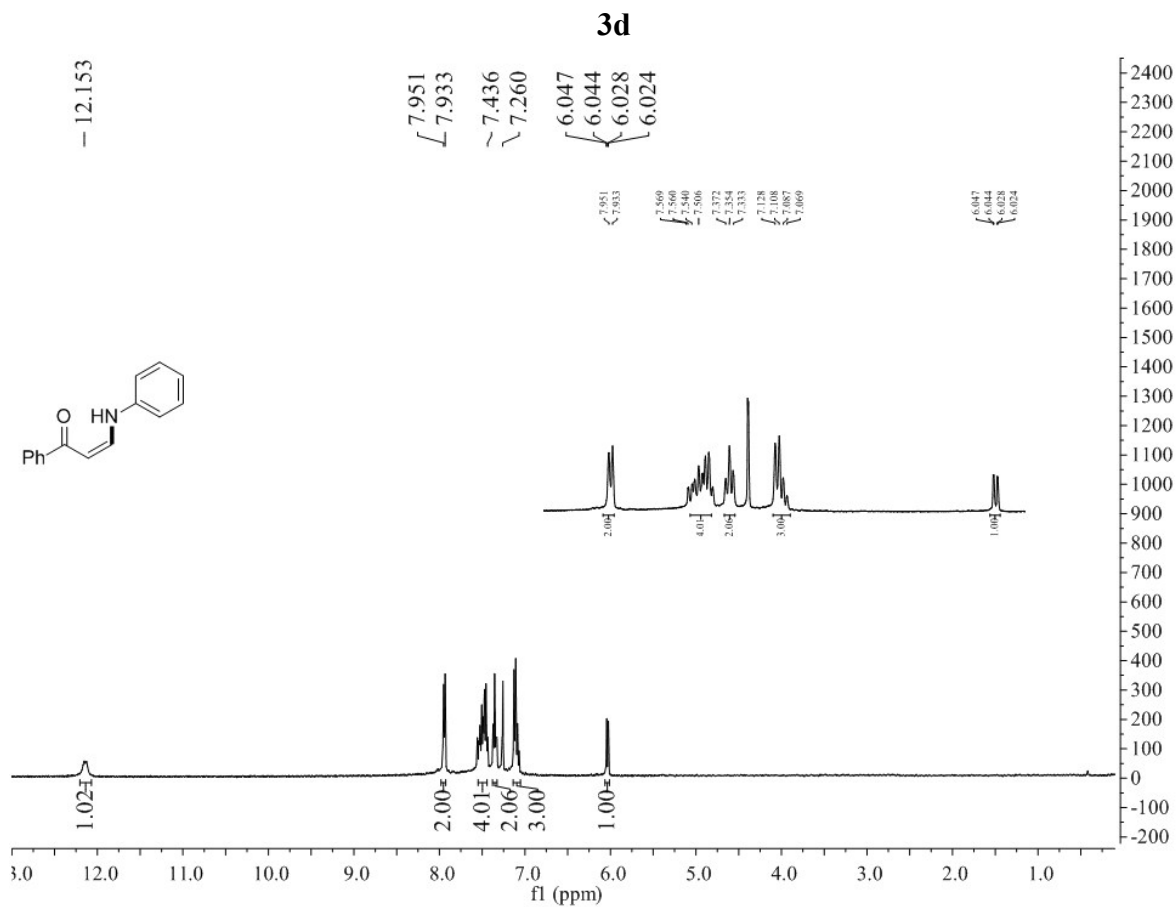


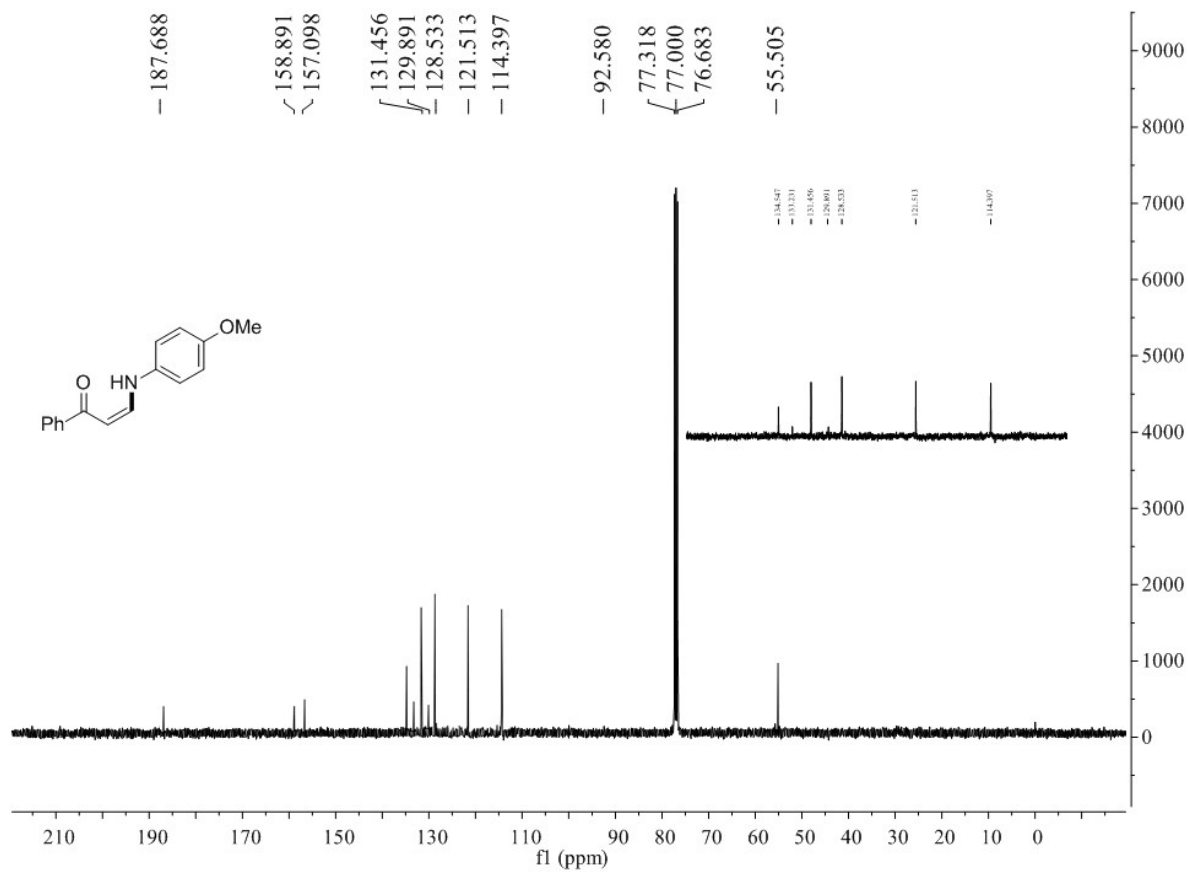
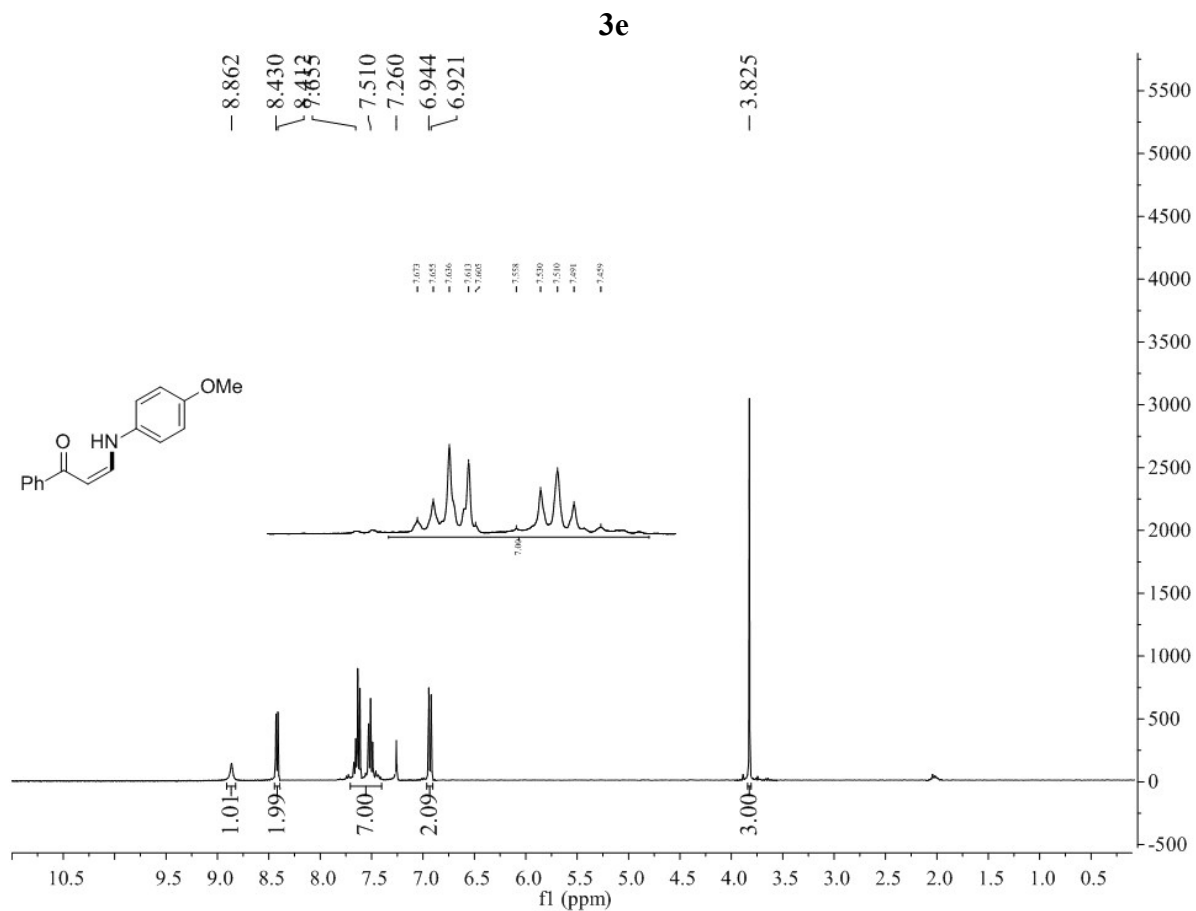
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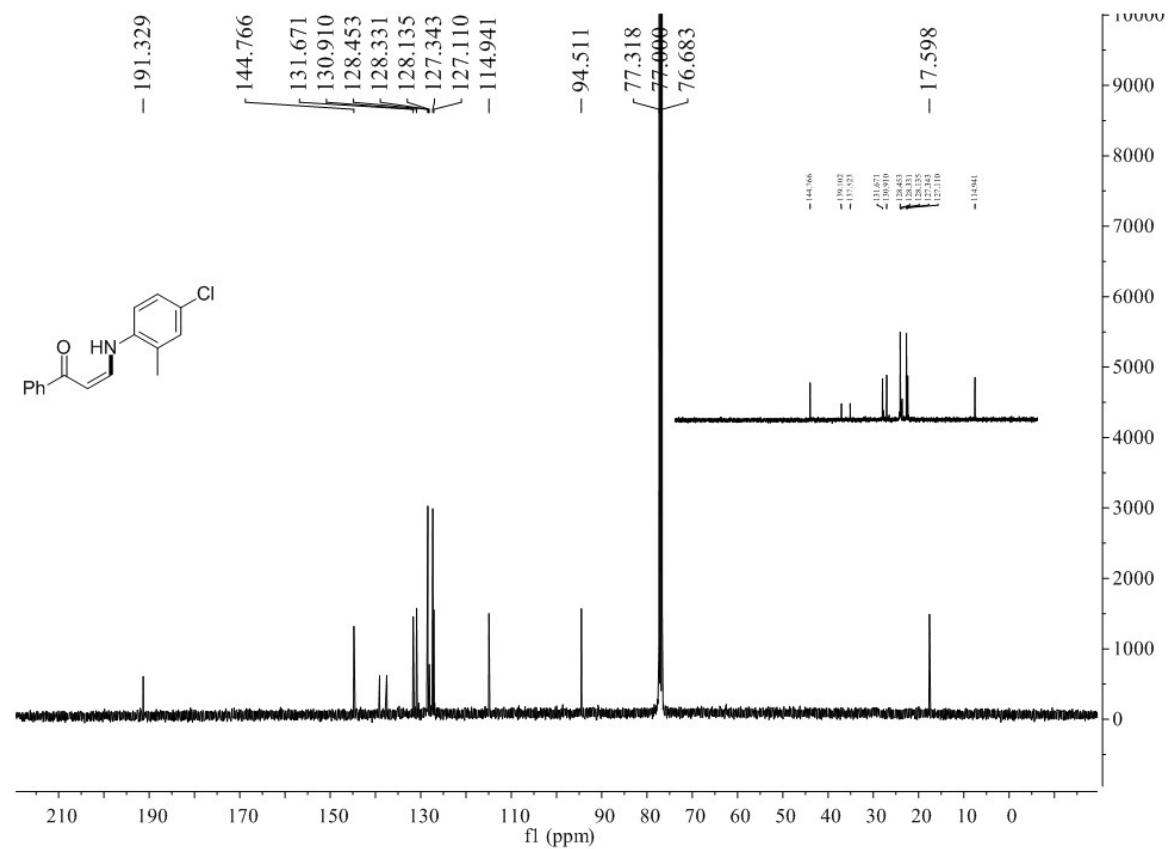
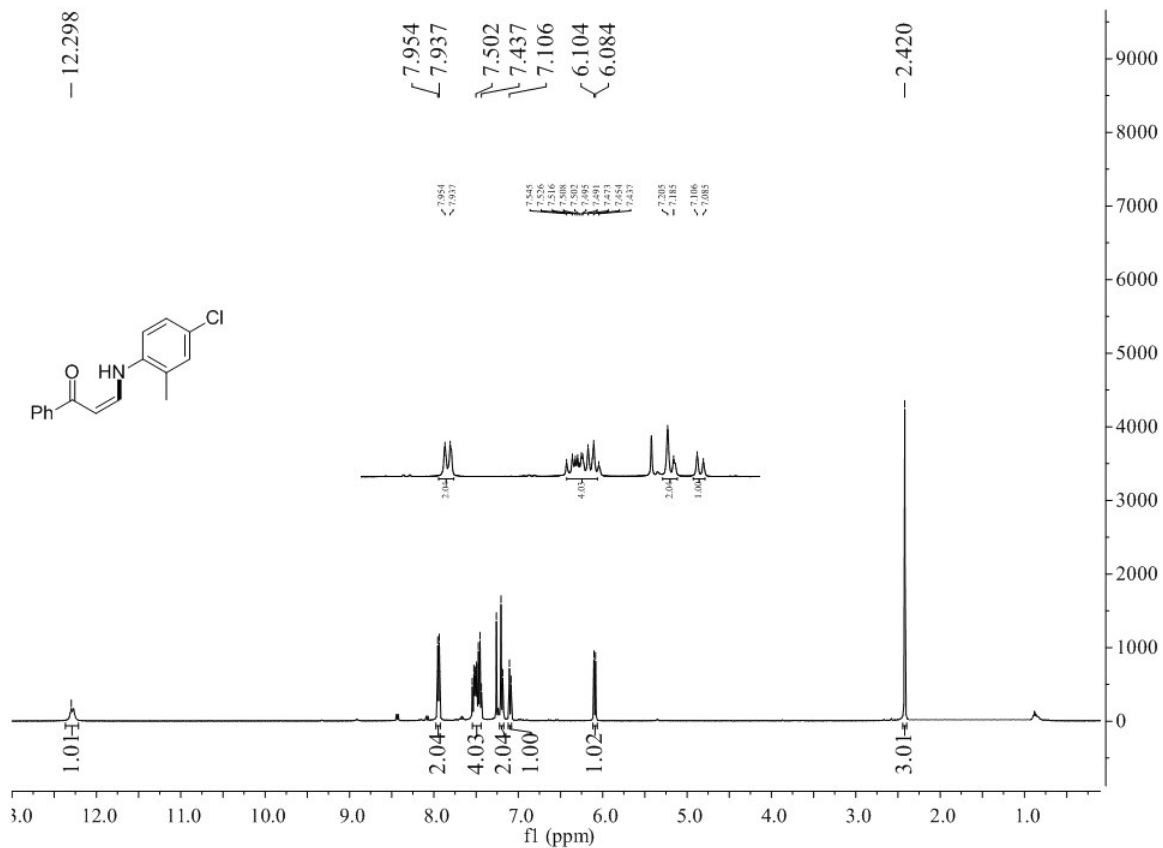
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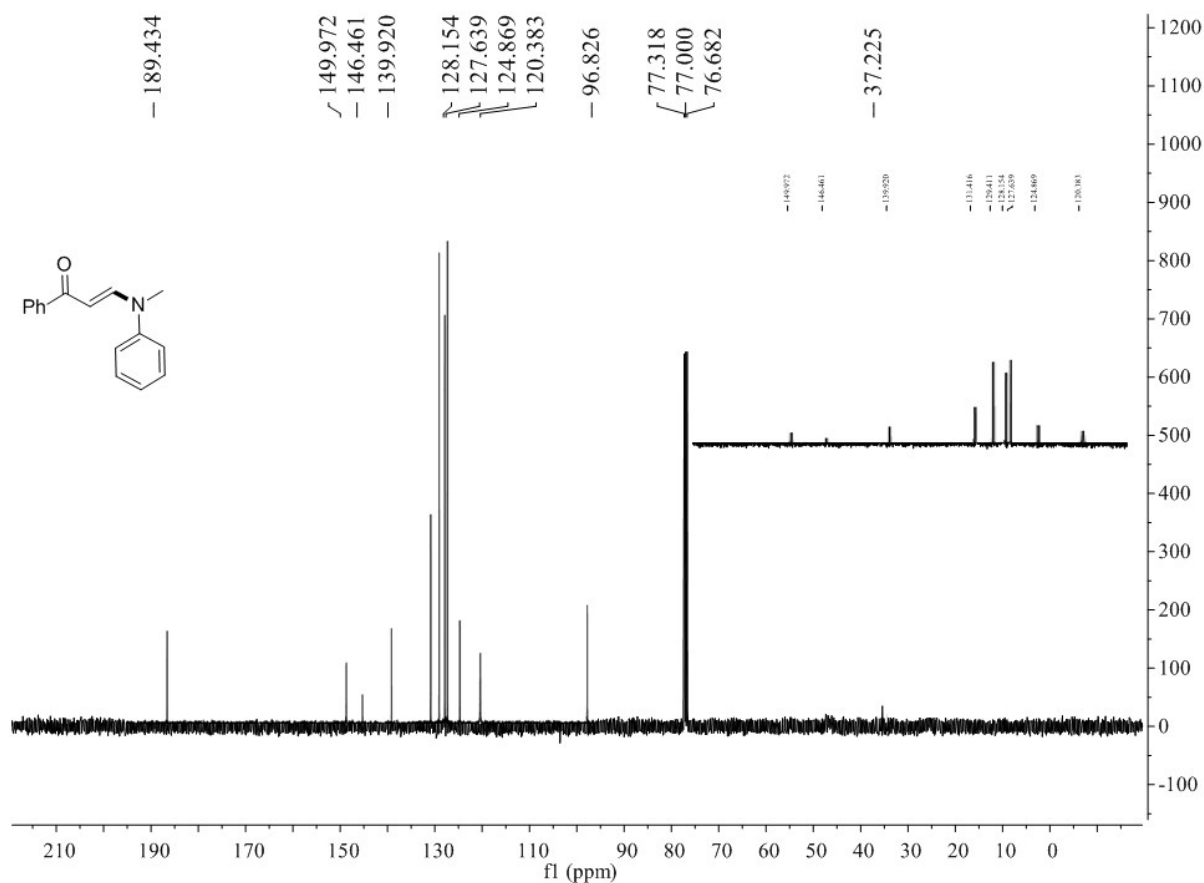
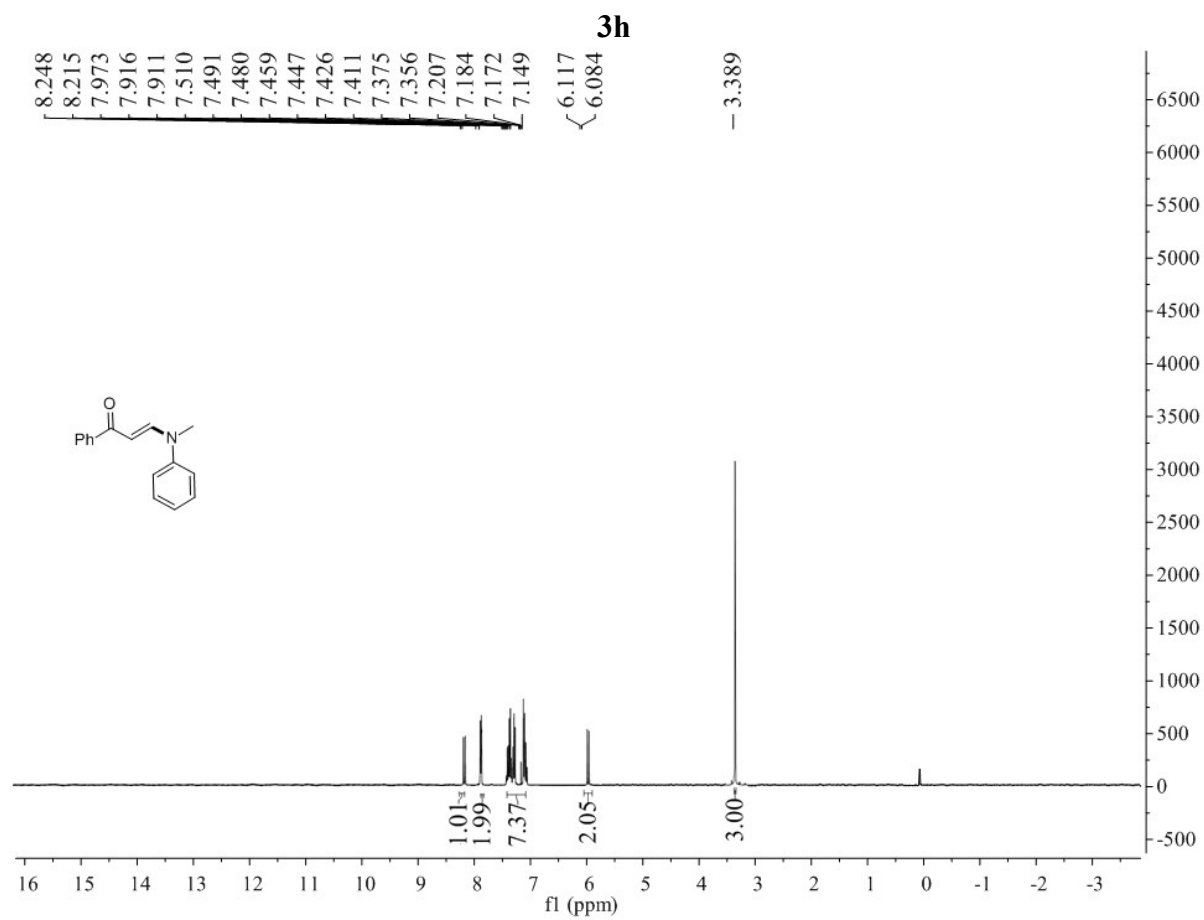




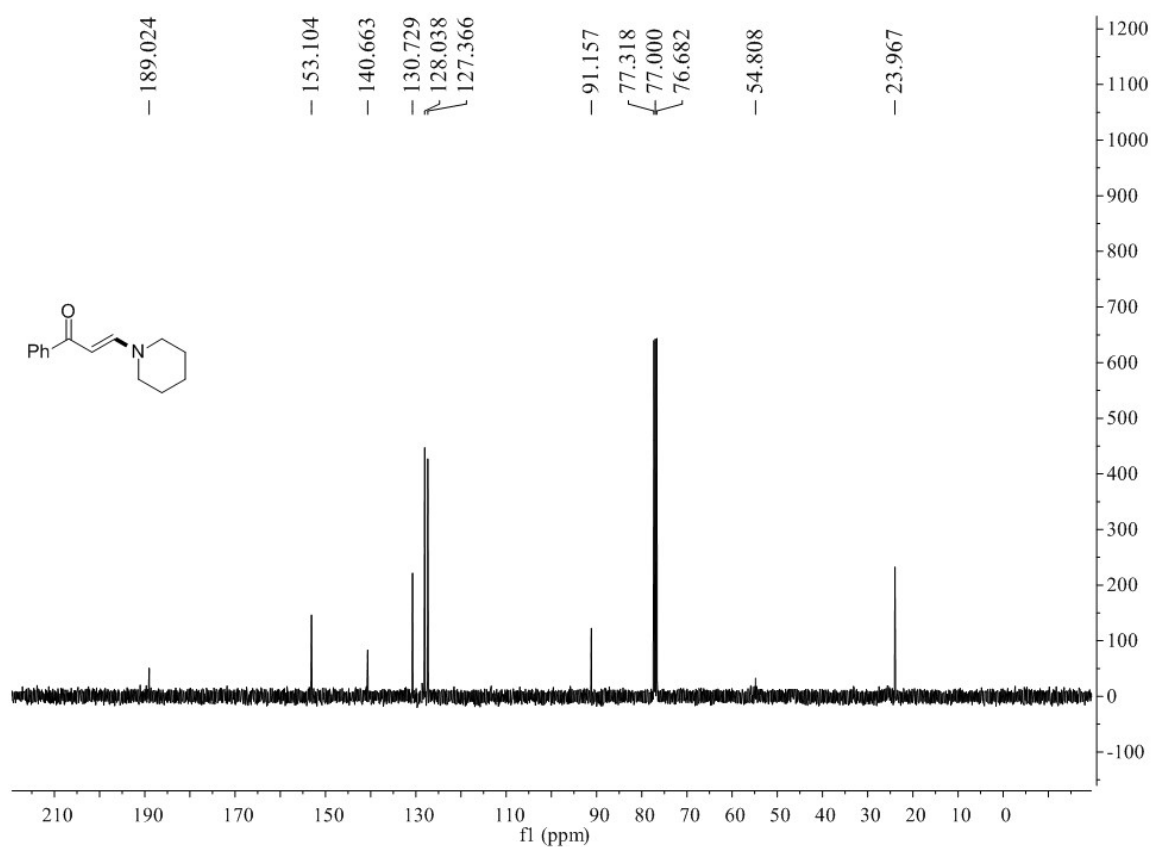
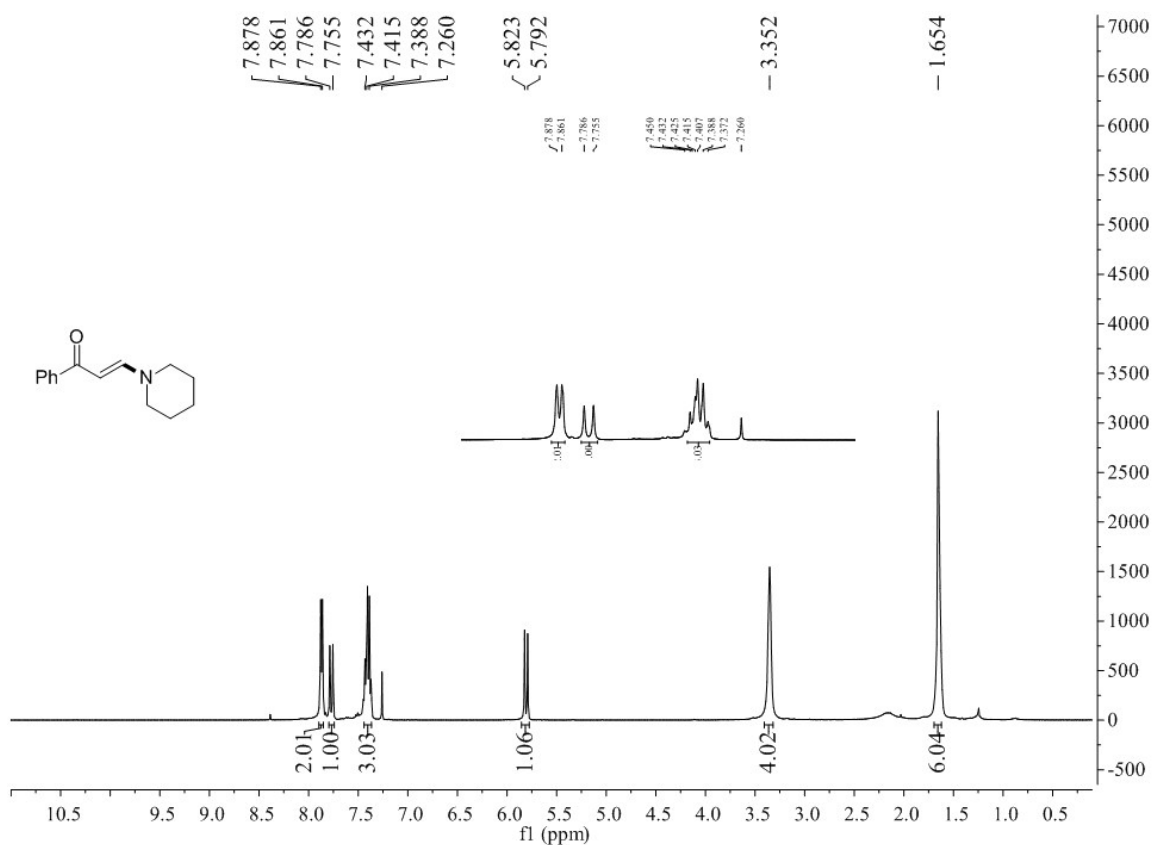


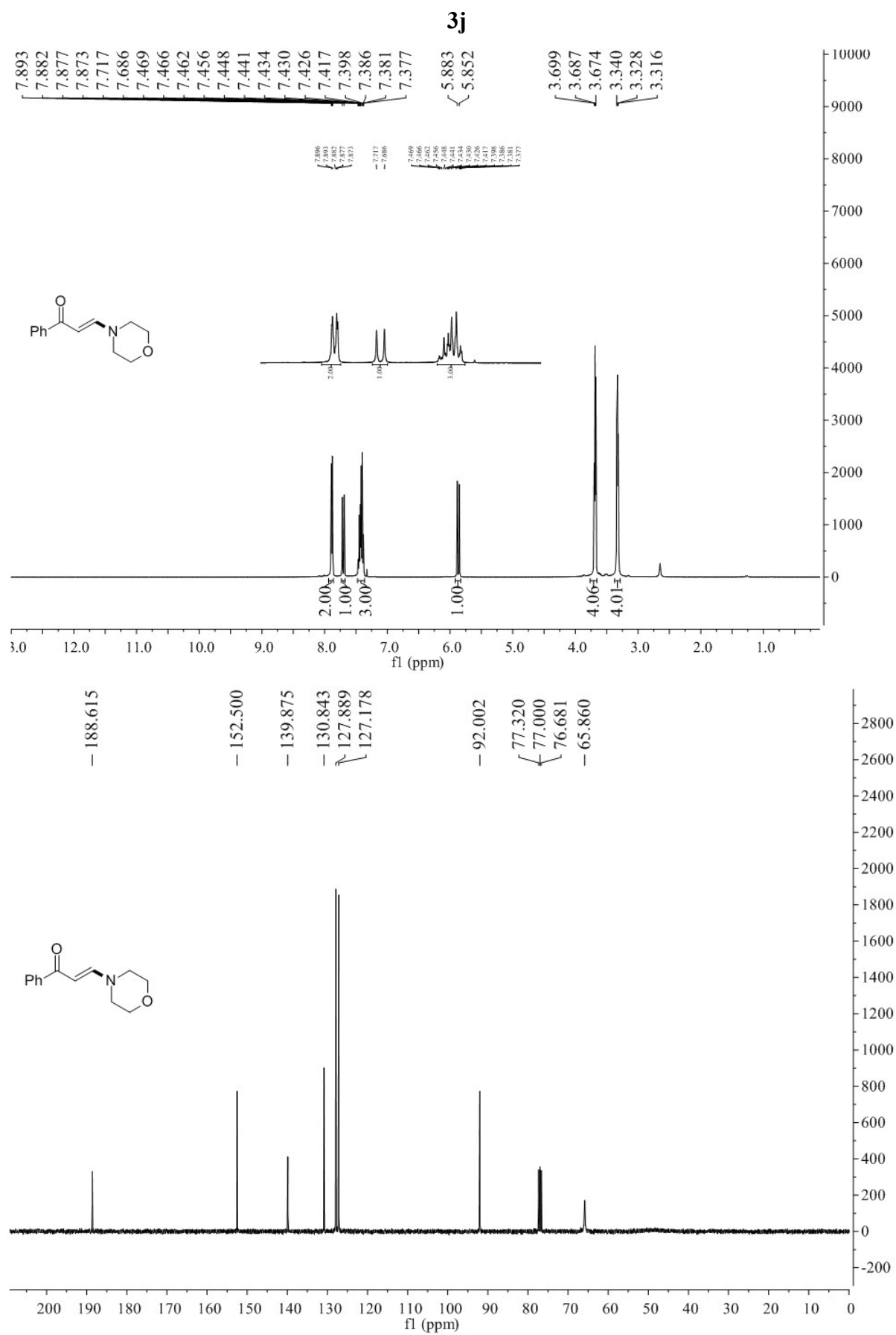
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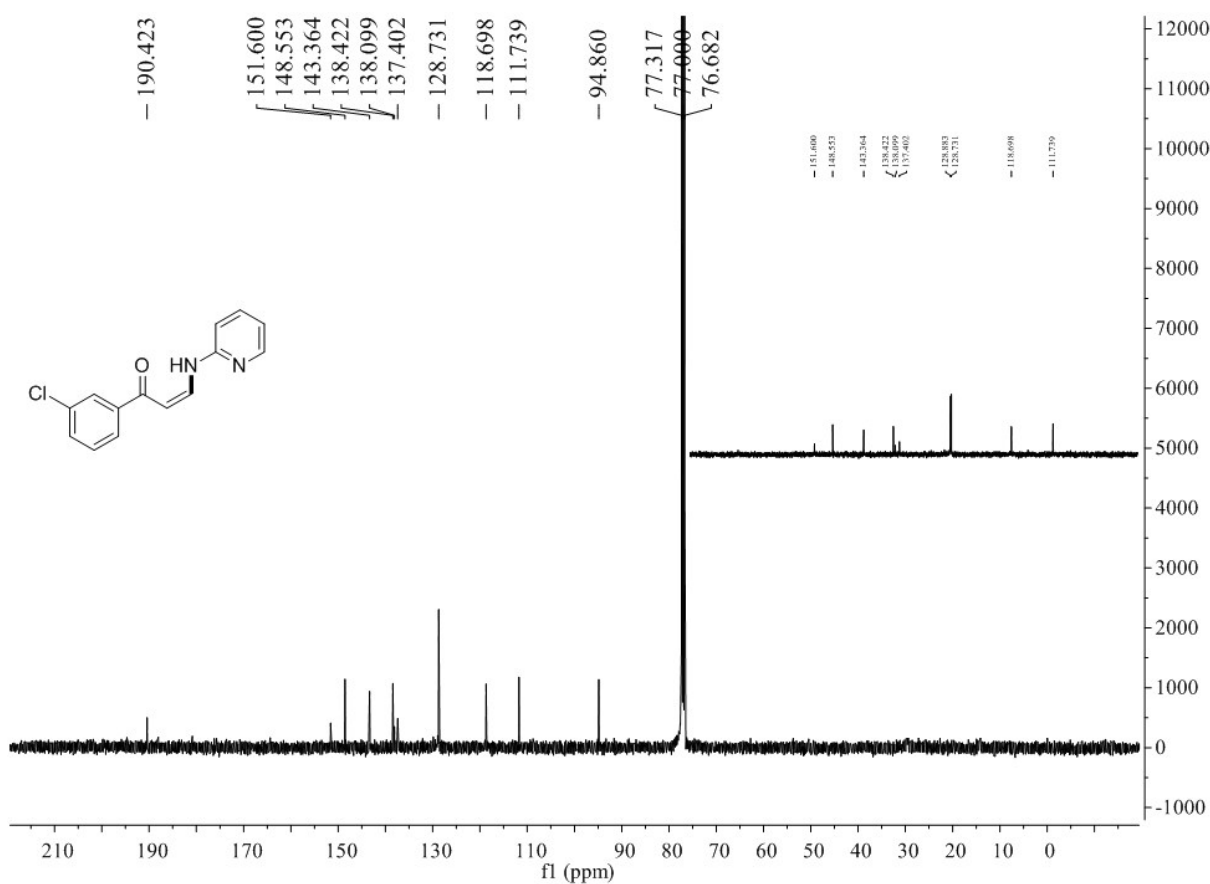
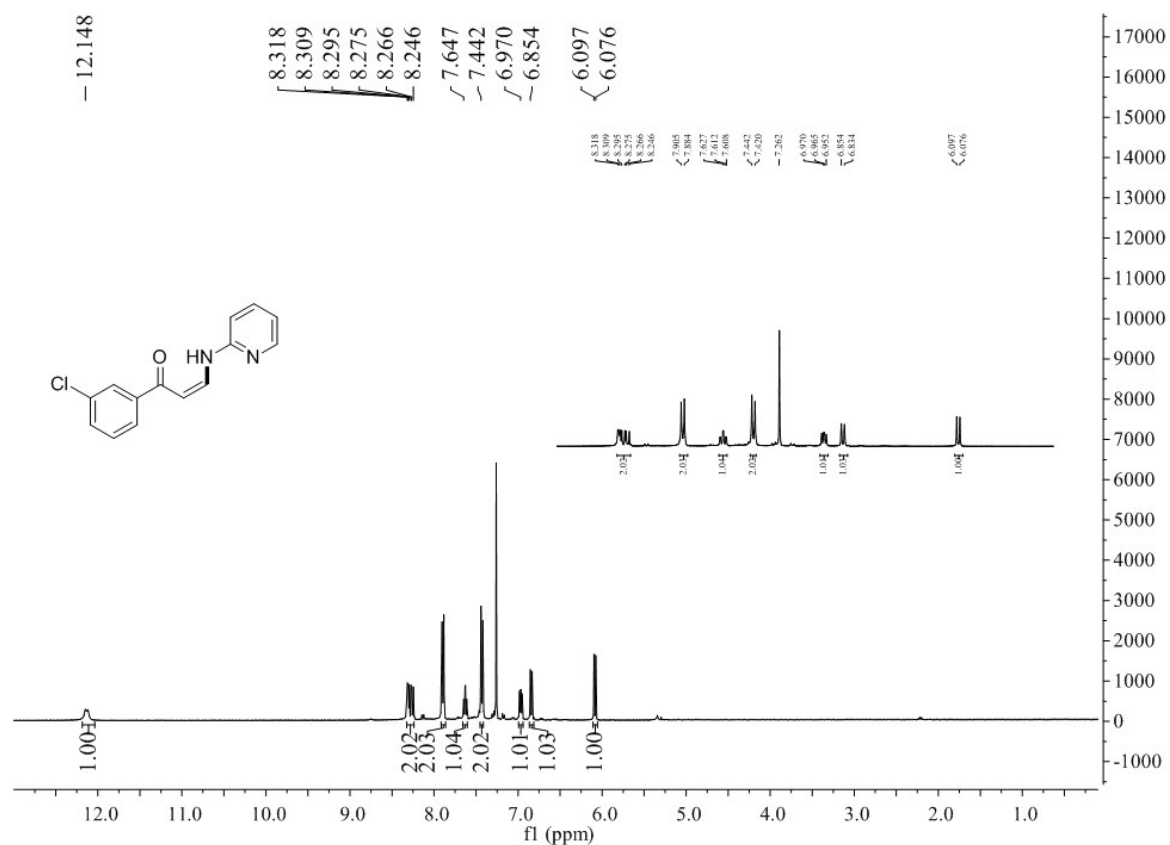


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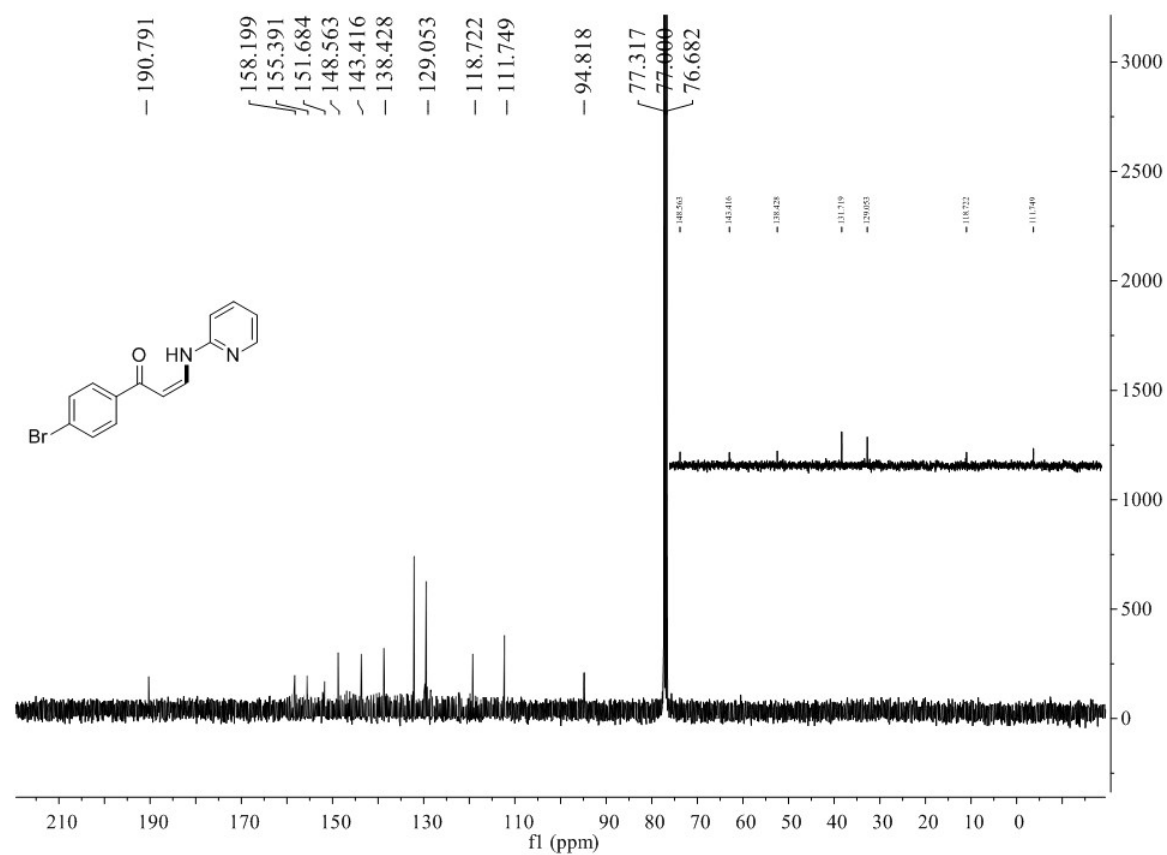
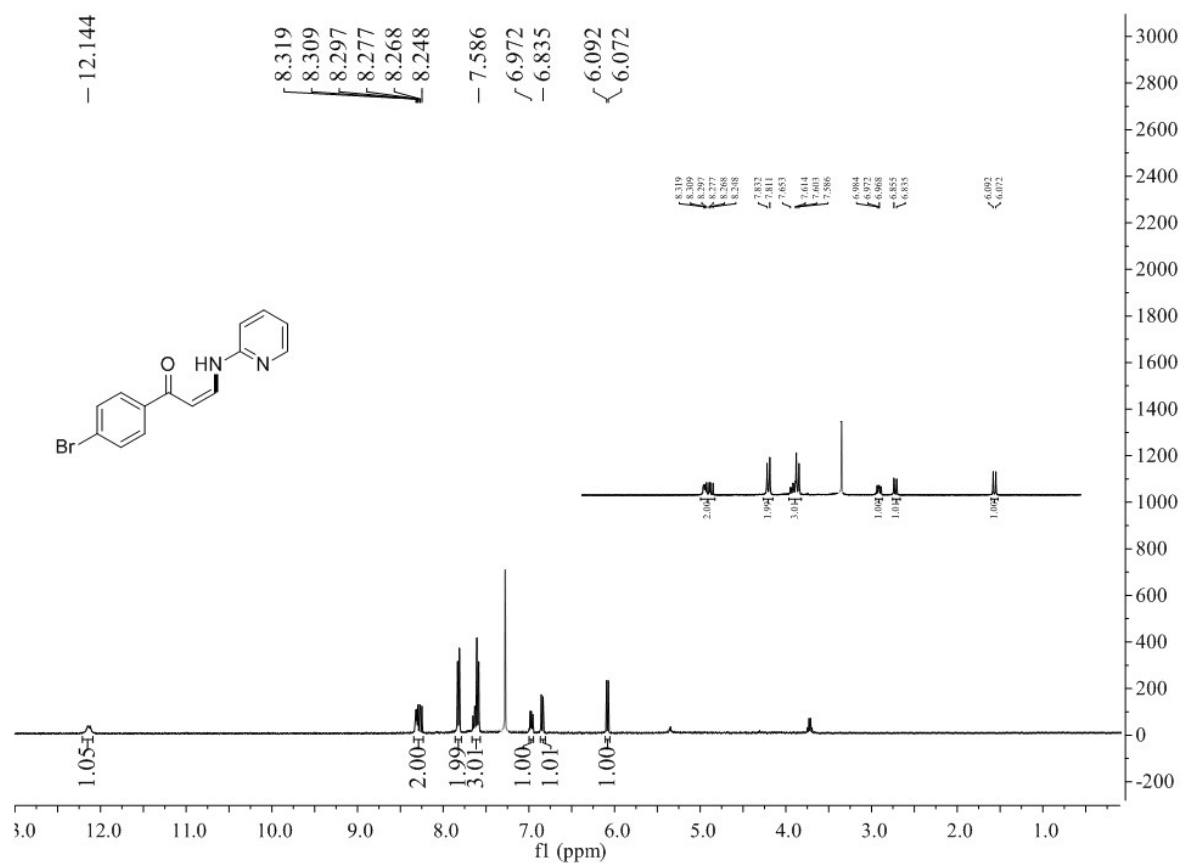


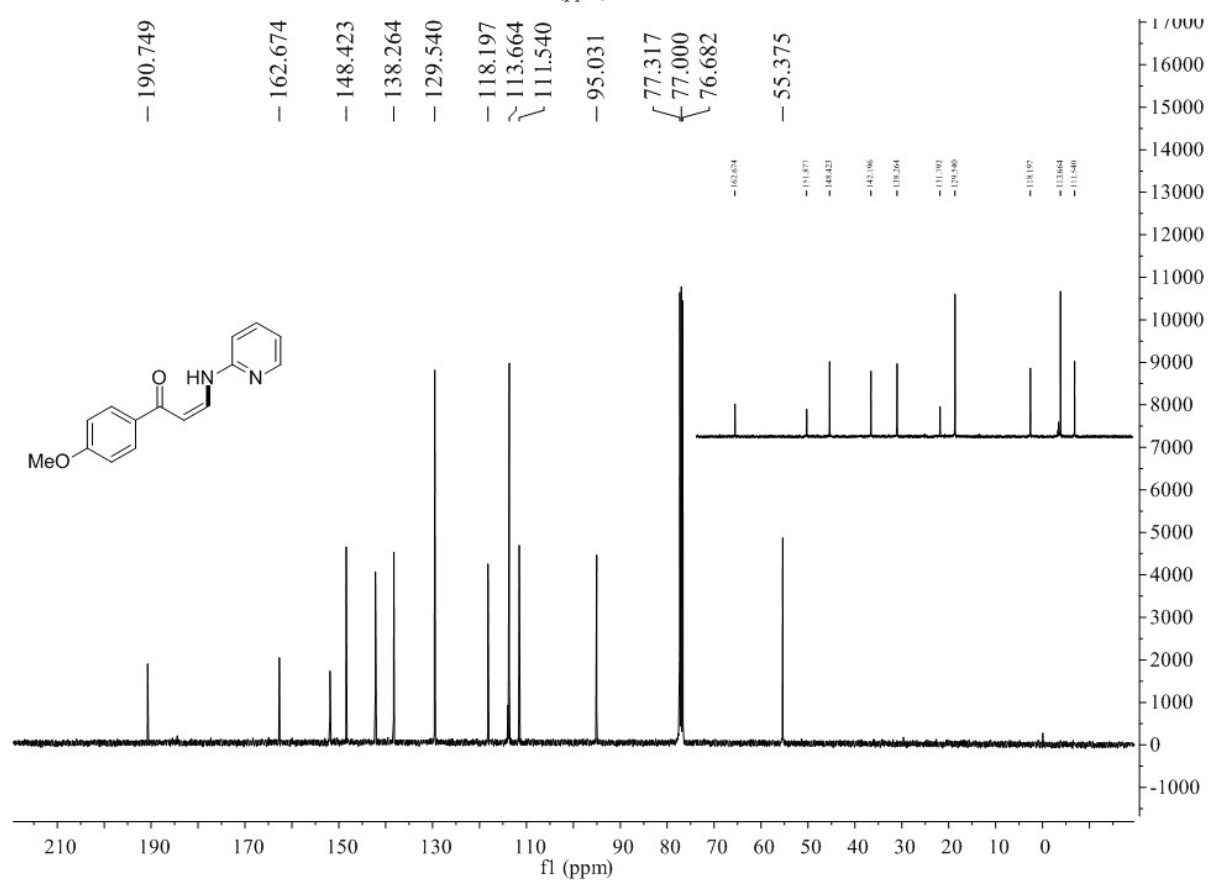
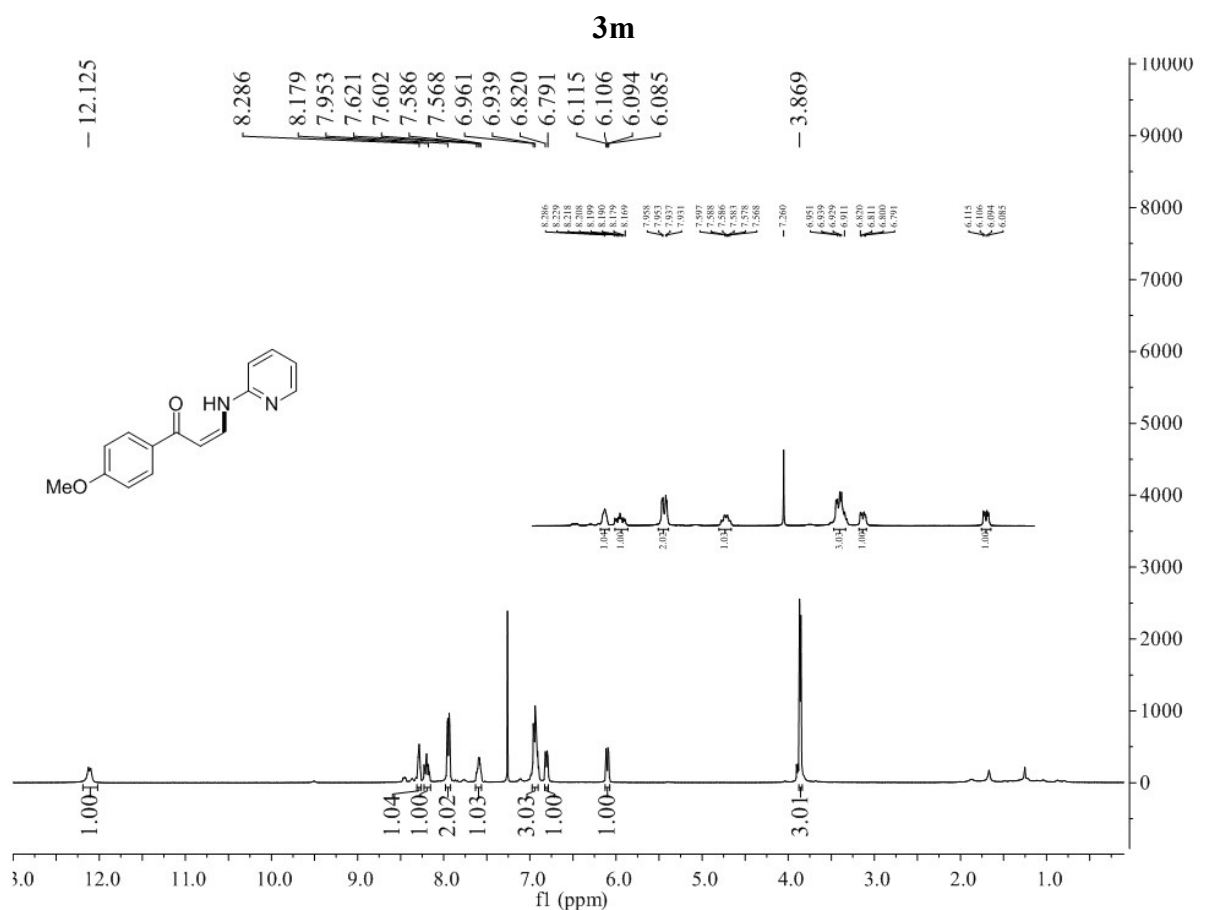


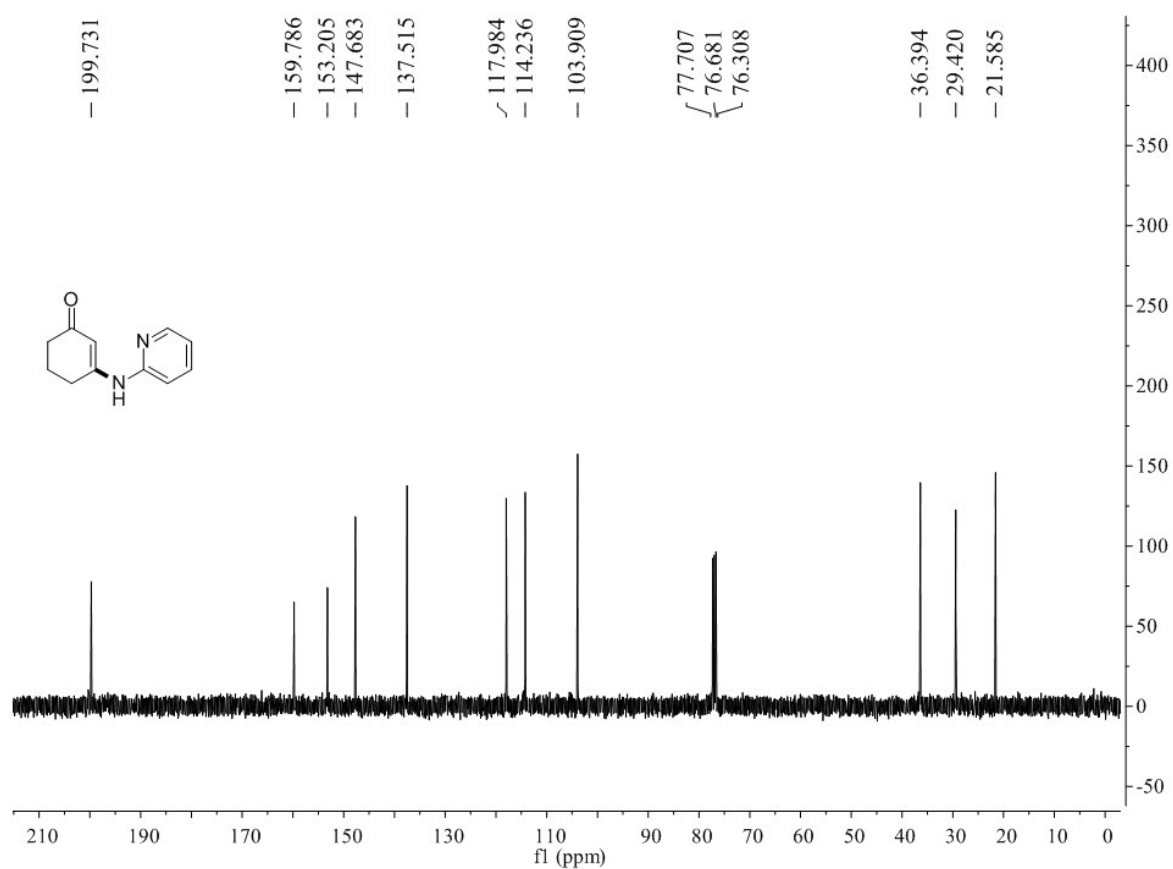
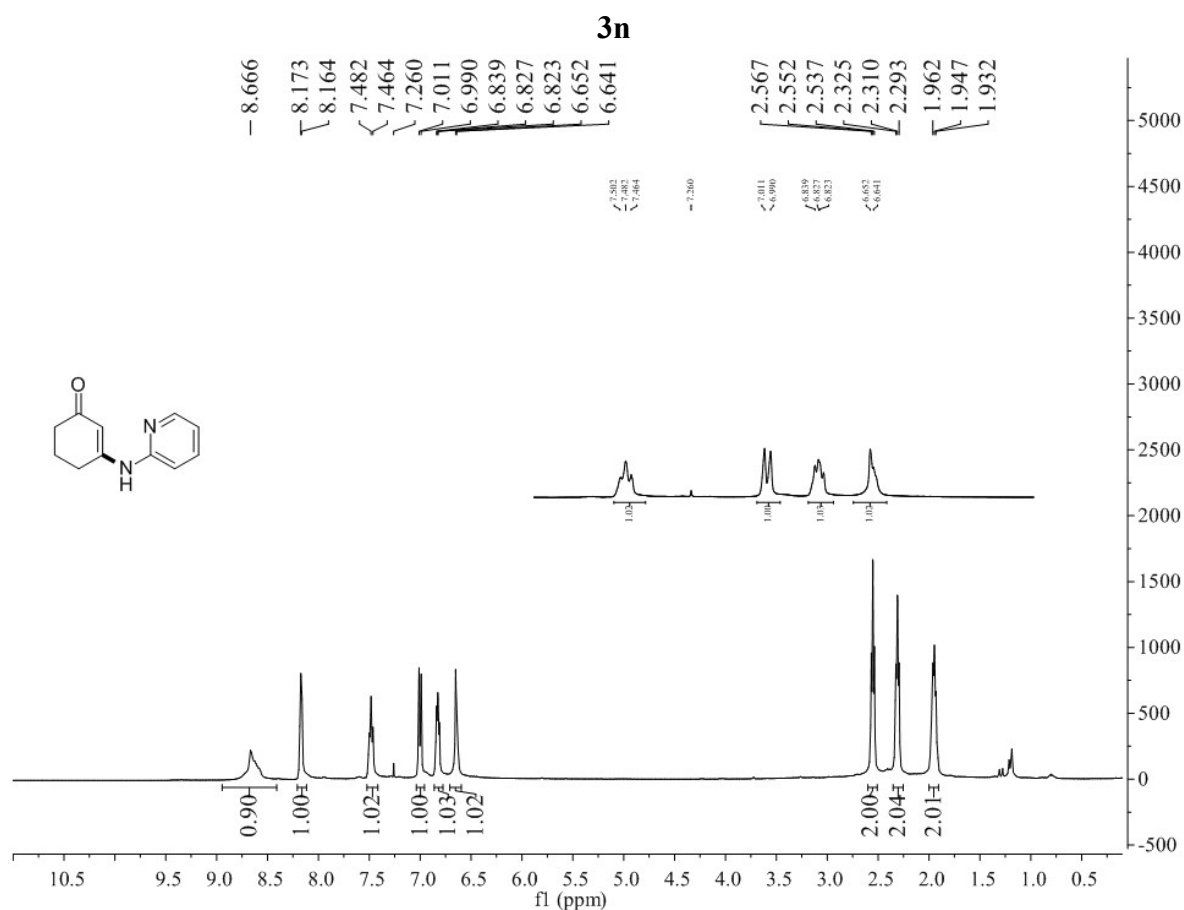
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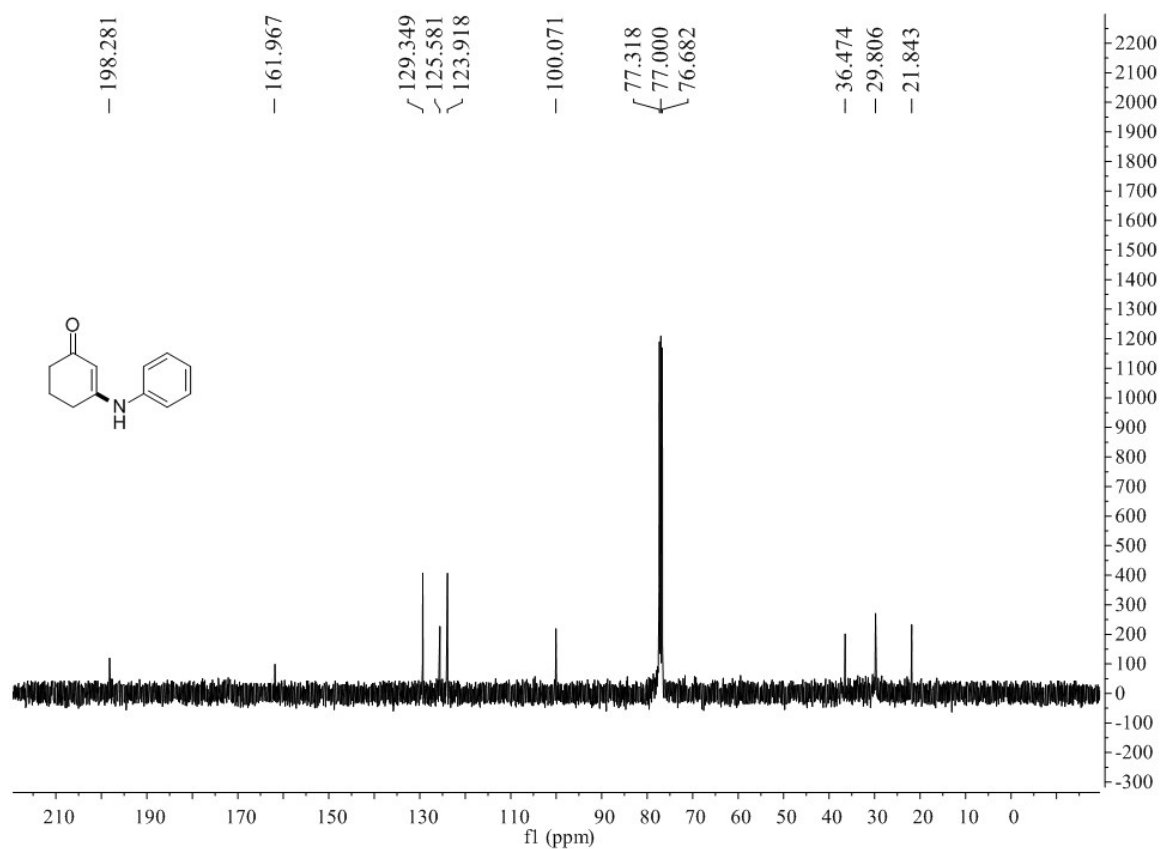
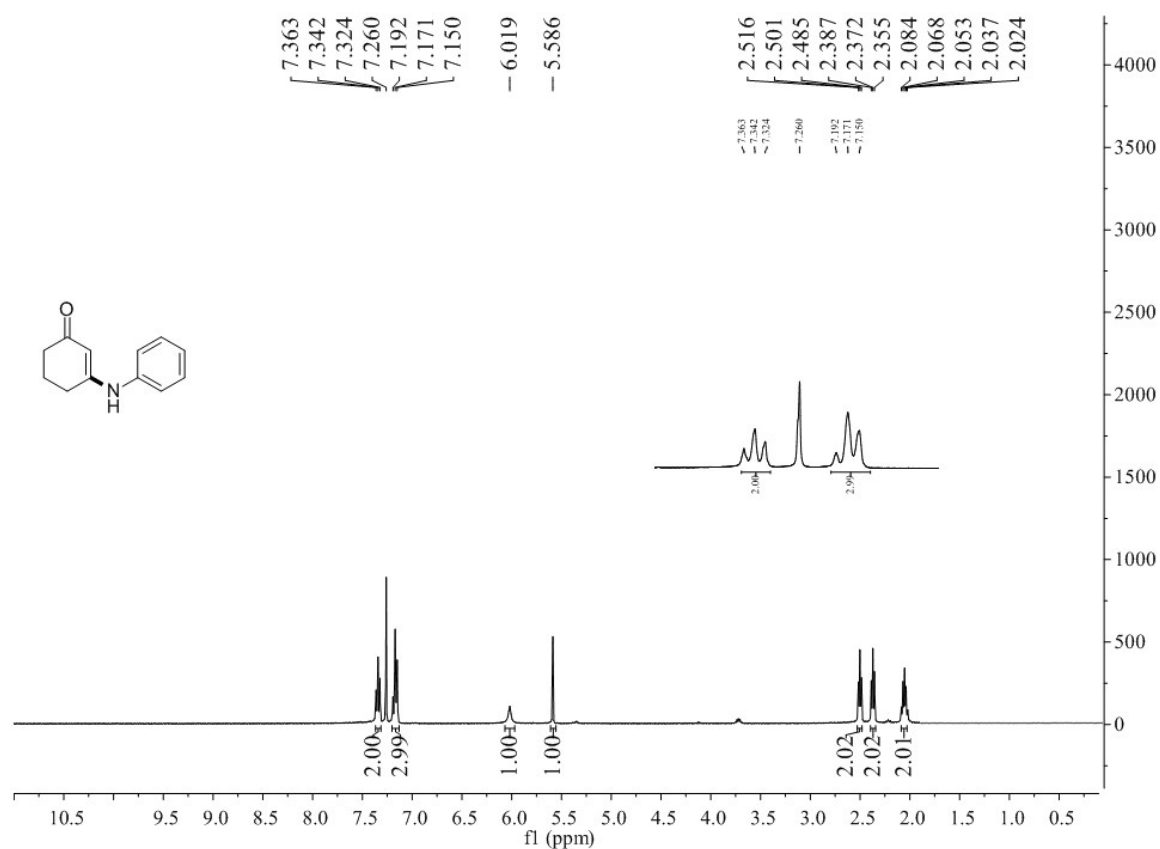
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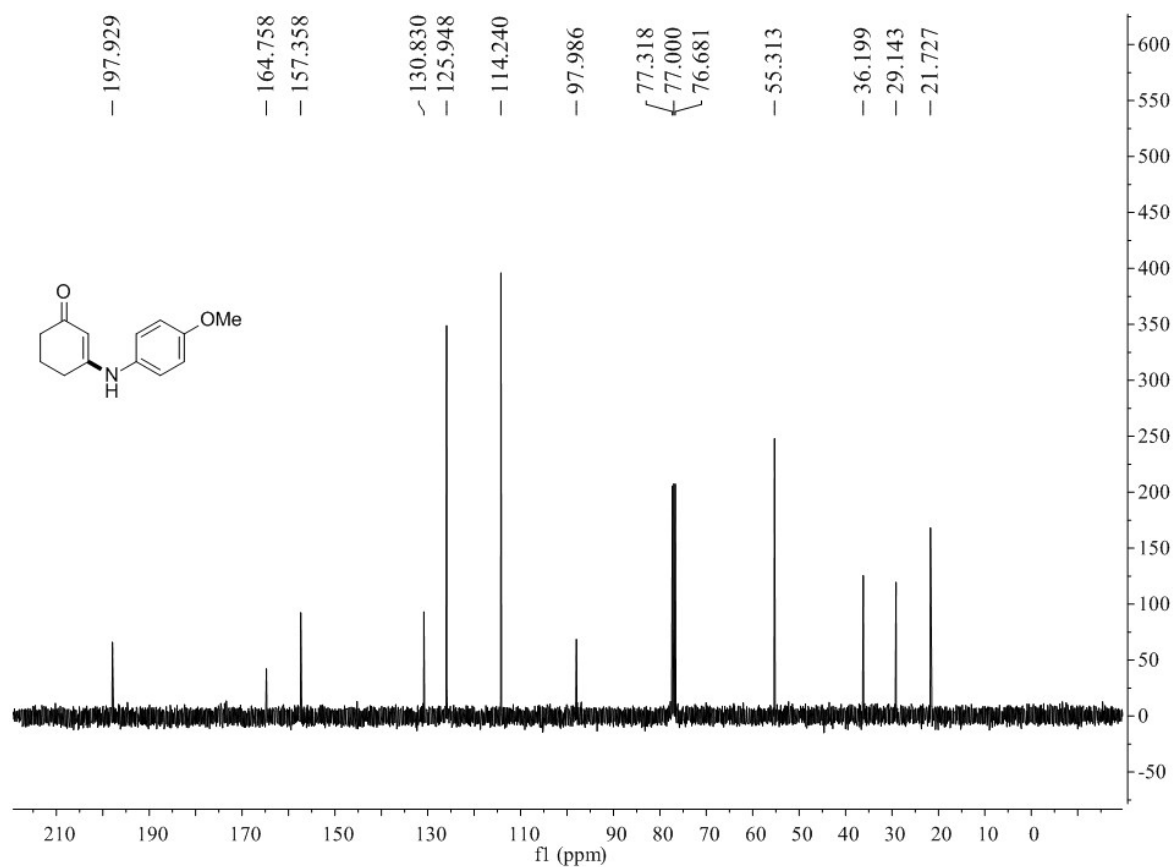
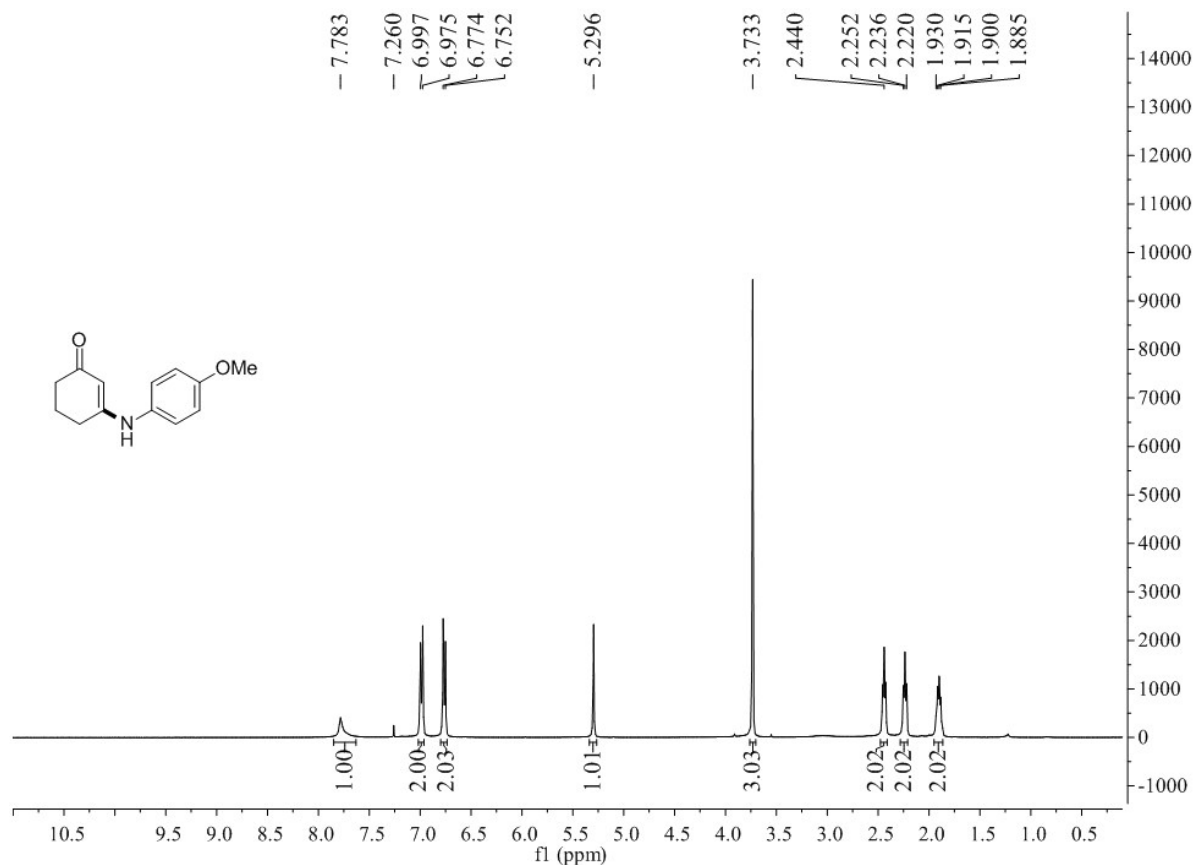


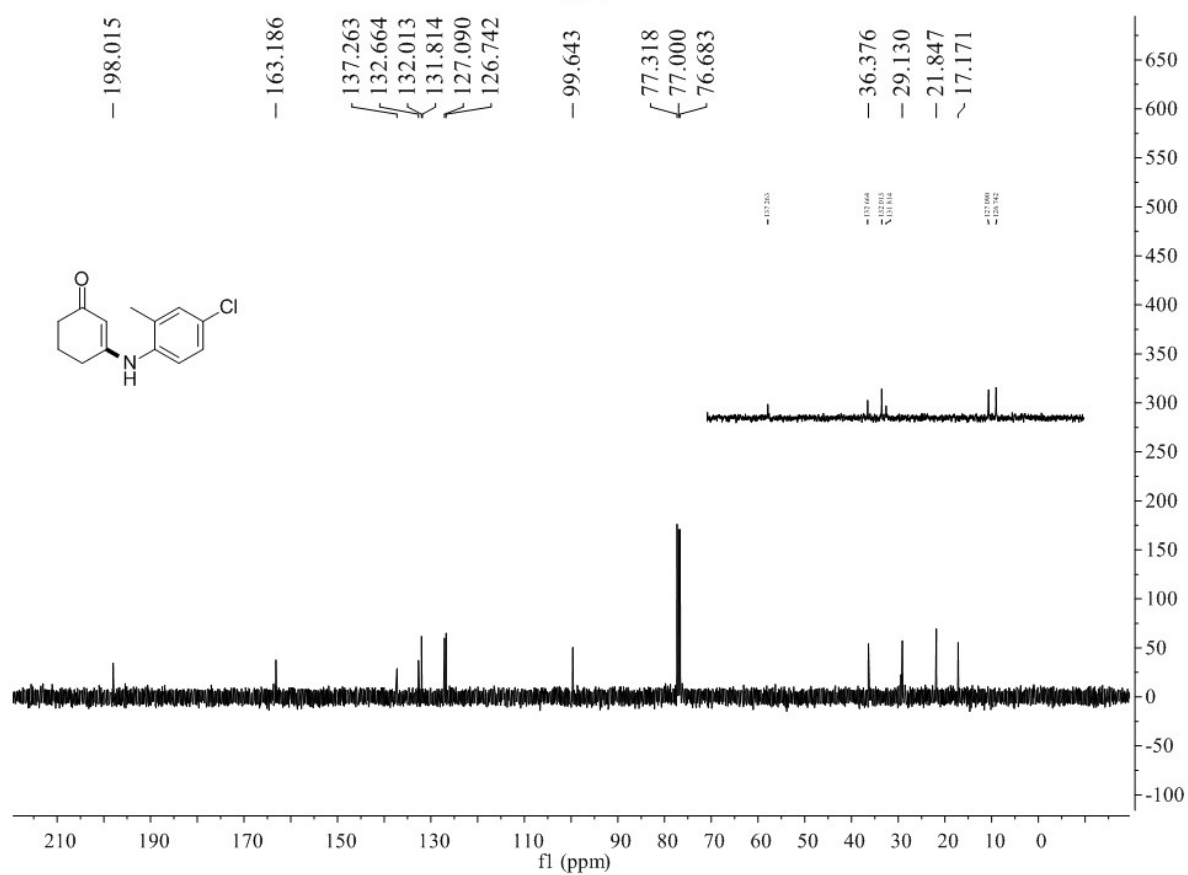
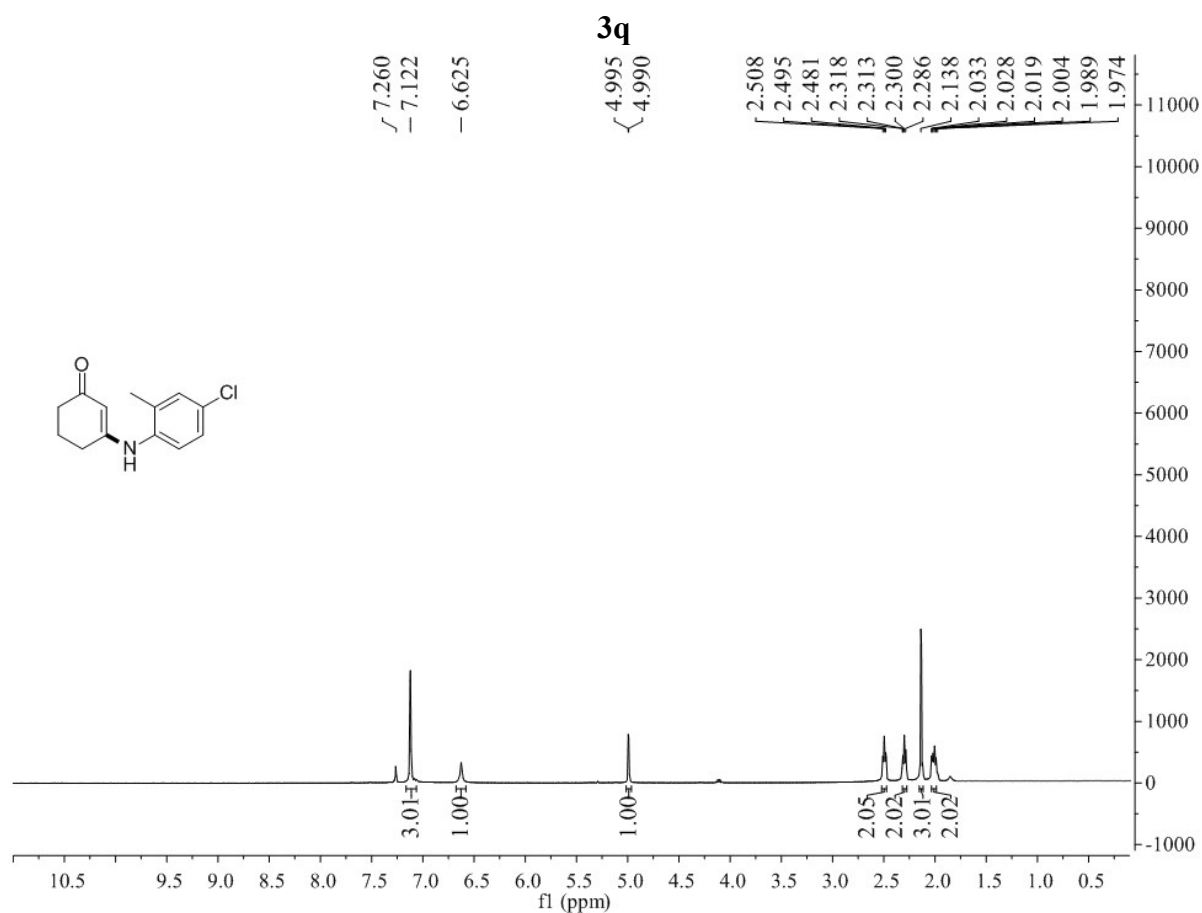


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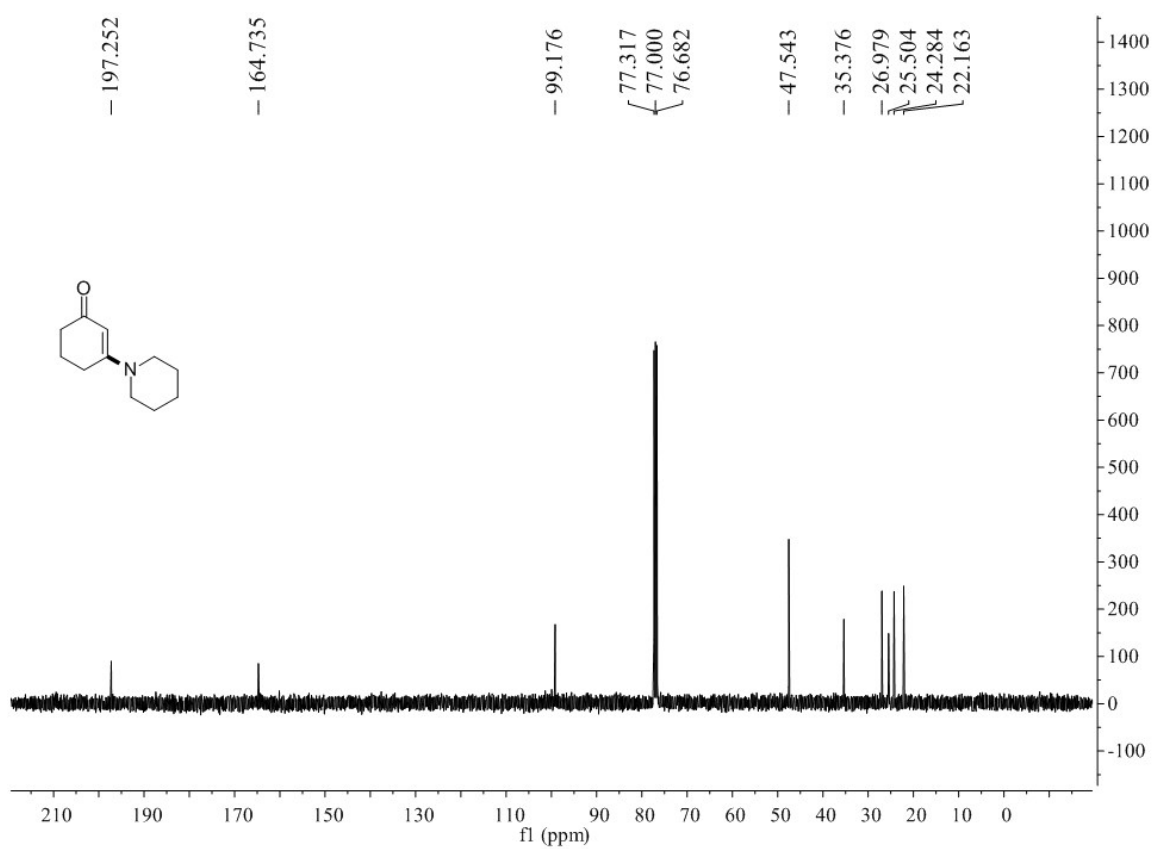
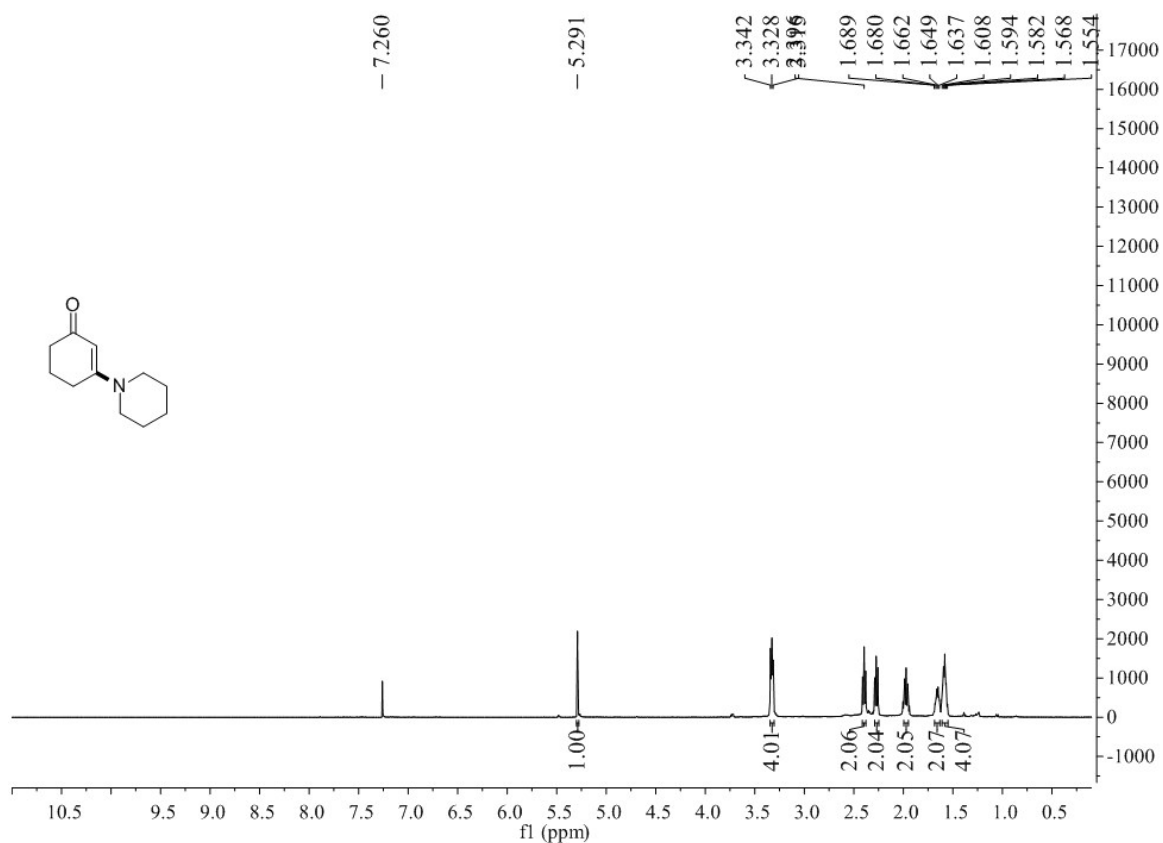


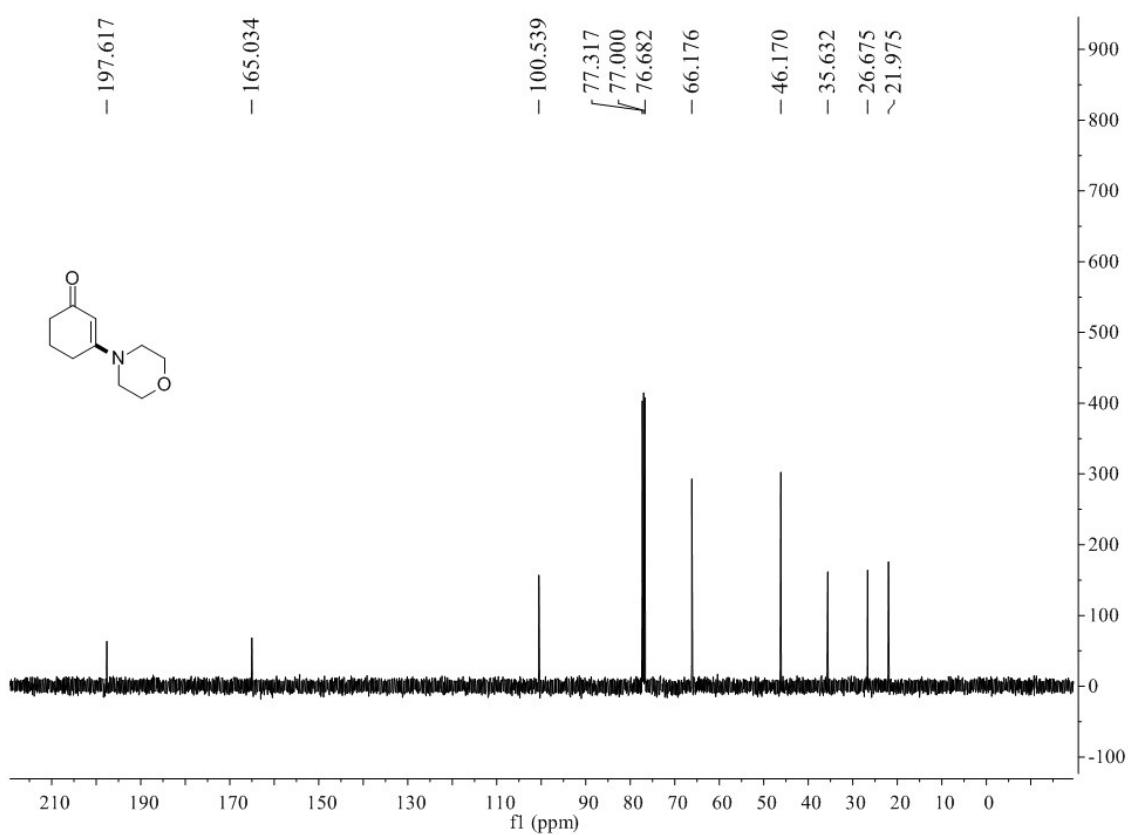
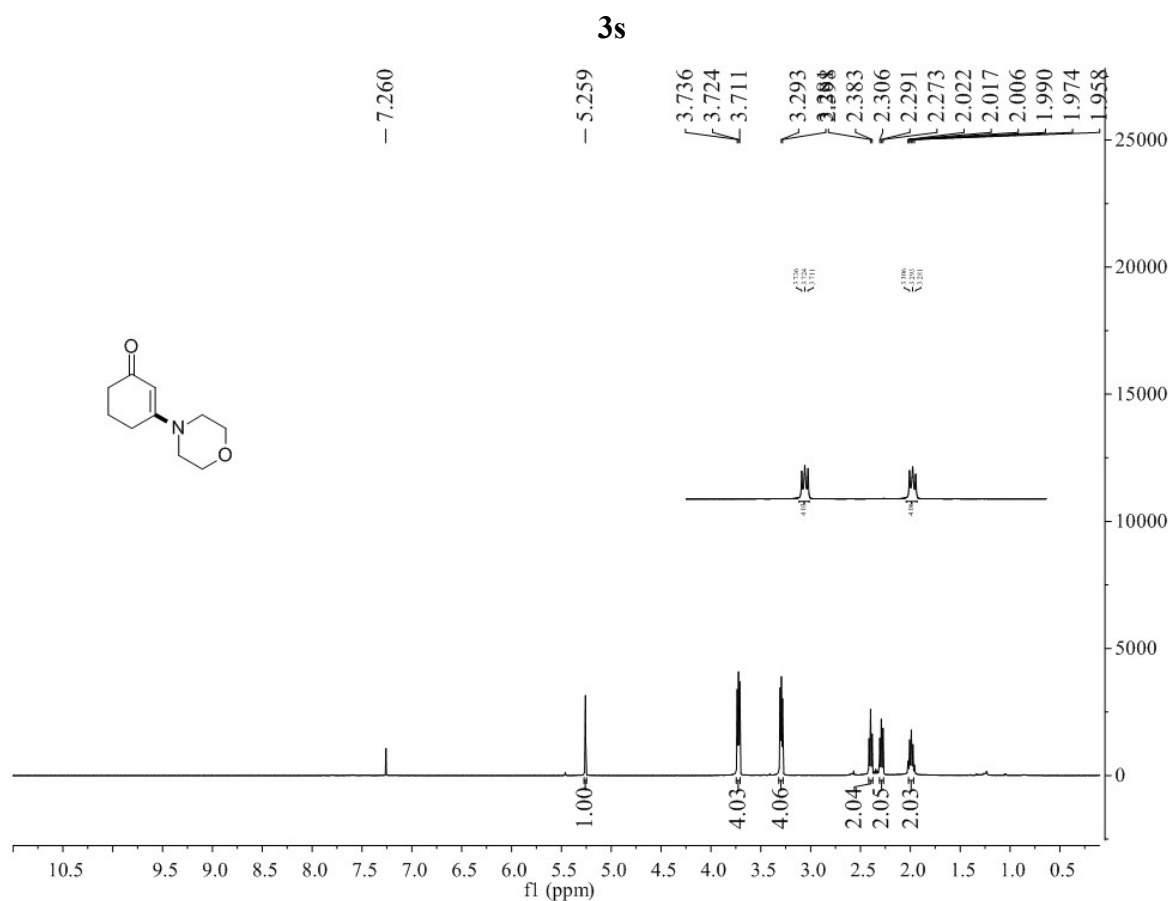
3p





3r





Chemical structure: O=C1C=CC2=CC=CC=C2N1C3=CC=CC=C3

¹H NMR spectrum (CDCl₃) showing peaks in the aromatic region (7.0-8.2 ppm) and a reference peak at 0 ppm. Integration values are provided below the peaks.

Peak list (ppm): 8.183, 7.854, 7.837, 7.833, 7.781, 7.759, 7.588, 7.585, 7.576, 7.570, 7.564, 7.555, 7.551, 7.529, 7.526, 7.515, 7.512, 7.508, 7.503, 7.499, 7.495, 7.486, 7.482, 7.478, 7.260, 7.126, 7.110, 7.109, 7.093, 7.091.

Integration values: 1.00, 1.00, 2.00, 3.00, 1.03.

