Supporting Information

Formation and Aromatization of Strained Bicyclic Pyrazolidines via Tandem Reaction of Alkyl 2-Aroyl-1-chlorocyclopropanecarboxylates with Acylhydrazones

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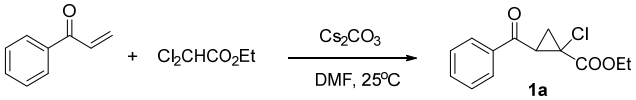
General Methods All reagents and solvents were of commercial grade and purified prior to use when necessary. Reactions were monitored by TLC analysis using silica gel 60 A F-254 thin layer plates. Flash column chromatography was performed on silica gel 60 A, 10-40 μm. All ^{1}H NMR and^{13}C NMR spectra were recorded on a 400 or 600 MHz spectrometer with solvent resonances as the internal standard (^{1}H NMR: $CDCl_3$ at 7.26 ppm; DMSO at 2.51 and 3.34 ppm; ^{13}C NMR: $CDCl_3$ at 77.0 ppm, ^{13}C NMR: DMSO at 40.10 ppm). The following abbreviations are used to describe peak patterns where appropriate: s = singlet, d = doublet, t = triplet, q = quartet, m = multiplet, and br s = broad signal. All coupling constants (*J*) are given in Hz. IR spectra were recorded on an infrared spectrometer. Melting point was recorded on a melting point detector. HRMS was measured on a TOF-Q mass spectrometer equipped with an ESI technique.

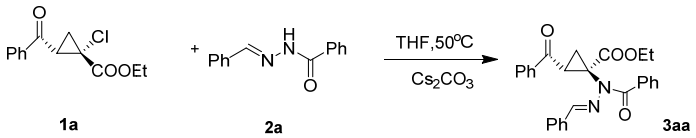
(1) General procedure:

Scheme 1 Typical Procedure for Synthesis of 1a.



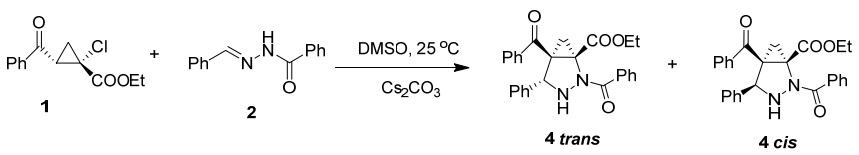
Terminal electron-deficient alkene (10 mmol) was added to a solution of ethyl dichloroacetate (10 mmol) and Cs_2CO_3 (11 mmol) in 20mL DMF, the mixture was stirred at room temperature. The reaction was monitored by TLC until all the substrates terminal electron-deficient alkene disappeared. The mixture was then washed with water and extracted with CH_2Cl_2. Combined extracts were dried over anhydrous Na_2SO_4 and concentrated under reduced pressure. The residue was purified by silica gel column chromatography using petroleum ether and ethyl acetate (20:1) as eluent to afford the corresponding product **1a** in 72% yield. Unless otherwise specified, all other products **1** were synthesized according to this typical procedure.

Scheme 2 Typical Procedure for Synthesis of Compound of 3aa.



Substrates **1a** (50.5mg, 0.2 mmol), **2a** (44mg, 0.2 mmol) and base Cs_2CO_3 (130mg, 0.4mmol) were added into 2.0 mL of THF, and the mixture was stirred at 50 ^{o}C. Followed by thin layer chromatography until all the substrate **1a** disappeared, the reaction was washed by water and extracted by CH_2Cl_2 for two times. Then the organic solvent was dried over anhydrous Na_2SO_4 and concentrated under reduced pressure. The residue was purified by silica gel column chromatography using petroleum ether/ethyl acetate (8:1) as the eluent to afford 66 mg of the corresponding **3aa** in 75% yield. Unless otherwise specified, all other products **4** were synthesized according to this typical procedure.

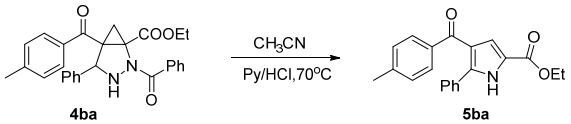
Scheme 3 Typical Procedure for Synthesis of Compound of 4aa.



Substrates **1a** (0.2 mmol), **2a** (0.2 mmol) and base Cs_2CO_3 (0.4mmol) were added into 2.0

mL of DMSO, and the mixture was stirred at room temperature. The reaction was followed by thin layer chromatography until all the substrate **1a** disappeared. The mixture was then washed with water and extracted with CH_2Cl_2 for three times to remove DMSO. Combined extracts were dried over anhydrous Na_2SO_4 and concentrated under reduced pressure. then purified by silica gel column chromatography using petroleum ether/ethyl acetate (8:1 to 2:1) as the eluent to afford **4aa** (trans and cis) successively. Unless otherwise specified, all other products **4** were synthesized according to this typical procedure.

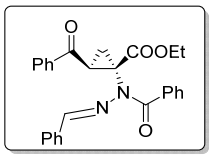
Scheme 4 Typical Procedure for Synthesis of Compound of 5ba.



To a solution of the concentrated crude products of **4ba** in 2.0 ml of CH_3CN was added pyridine (0.4 mmol, 32 μl), concentrated hydrochloric acid (84 μl, 1.0 mmol) which should be enough to keep the pH in 2-3. Then the mixture was stirred at 70 ^oC for 0.5 hour. The mixture was washed with water and extracted by CH_2Cl_2 for two times. Combined extracts were dried over anhydrous Na_2SO_4 and concentrated under reduced pressure. The residue was purified by silica gel column chromatography by using petroleum ether/ethyl acetate (10:1) to afford the corresponding pyrrole derivatives **5ba** in good yield. Unless otherwise specified, all other products **5** were synthesized according to this typical procedure.

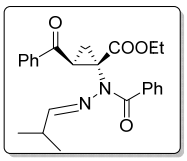
(2) Characterization data of the new compounds.

Ethyl (1S*, 2S*)-2-benzoyl-1-(1-benzoyl-2-((E)-benzylidene) hydrazinyl)cyclopropane-1-carboxylate (3aa)



White solid (66 mg, 75%); mp 167-169 ^oC; ^1H NMR (400 MHz, $CDCl_3$) δ 8.45 (s, 1H), 8.28 (d, *J* = 7.0 Hz, 2H), 7.84 – 7.78 (m, 2H), 7.64 (ddd, *J* = 6.7, 3.9, 1.2 Hz, 1H), 7.57 – 7.50 (m, 6H), 7.48 (dd, *J* = 8.0, 6.4 Hz, 2H), 7.38 – 7.33 (m, 3H), 4.17 (pd, *J* = 7.6, 3.6 Hz, 2H), 3.19 (s, 1H), 2.81 (dd, *J* = 8.8, 5.8 Hz, 1H), 2.07 (s, 1H), 1.15 (t, *J* = 7.1 Hz, 3H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 193.2, 171.0, 167.8, 164.2, 143.1, 136.4, 135.1, 134.4, 133.7, 130.6, 129.9, 129.8, 129.1, 128.7, 128.7, 127.6, 127.5, 127.3, 62.2, 42.5, 41.7, 37.2, 14.0. IR (KBr): 2982, 1734, 1674, 1613 cm^{-1}. HRMS (ESI) m/z calcd.for: $C_{27}H_{24}NaN_2O_4$ $[M + Na]^+$ 463.1634, found 463.1645.

Ethyl (1S*, 2S*)-2-benzoyl-1-(1-benzoyl-2-((E)-2-methylpropylidene) hydrazinyl)cyclopropane-1-carboxylate (3ac)

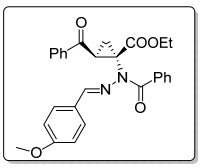


Yellow liquid (68 mg, 80%); ^1H NMR (400 MHz, $CDCl_3$) δ 8.29 (d, *J* = 7.4 Hz, 2H), 7.74 (dd, *J* = 8.1, 1.3 Hz, 2H), 7.66 (d, *J* = 4.3 Hz, 1H), 7.63 – 7.58 (m, 1H), 7.51 (t, *J* = 7.5 Hz, 2H), 7.47 –

7.36 (m, 3H), 4.11 (qd, *J* = 7.1, 3.1 Hz, 2H), 3.14 (t, *J* = 9.3 Hz, 1H), 2.69 (dd, *J* = 8.6, 5.7 Hz, 1H), 2.53 (dtd, *J* = 13.6, 6.8, 4.7 Hz, 1H), 1.89 (dd, *J* = 10.1, 5.6 Hz, 1H), 1.12 (t, *J* = 7.1 Hz, 3H), 1.04 (dd, *J* = 6.8, 1.5 Hz, 6H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 193.1, 170.8, 168.0, 136.4, 135.2, 133.6, 130.4, 129.7, 129.2, 128.7, 127.3, 61.9, 41.9, 37.3, 31.9, 23.9, 19.6, 14.0. IR (KBr): 2966, 1735, 1674, 1594 cm^{-1}. HRMS (ESI) m/z calcd.for: $C_{24}H_{26}NaN_2O_4$ $[M + Na]^+$ 429.1791, found 429.1797.

Ethyl (1S*, 2S*)-2-benzoyl-1-(1-benzoyl-2-((E)-4-chlorobenzylidene)hydrazinyl)

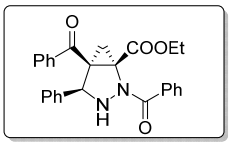
cyclopropane-1-carboxylate (3af)



White solid (81 mg, 85%), mp 159-162 °C. ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.48 (s, 1H), 8.25 (s, 2H), 7.85 – 7.78 (m, 2H), 7.64 (t, *J* = 7.4 Hz, 1H), 7.54 (t, *J* = 7.6 Hz, 3H), 7.48 (dd, *J* = 11.7, 4.8 Hz, 4H), 7.32 (d, *J* = 8.5 Hz, 2H), 4.21 – 4.11 (m, 2H), 3.13 (s, 1H), 2.80 (dd, *J* = 8.8, 5.9 Hz, 1H), 2.08 (d, *J* = 18.6 Hz, 1H), 1.14 (t, *J* = 7.1 Hz, 3H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 193.3, 171.9, 167.8, 136.2, 135.7, 134.8, 133.9, 133.0, 130.8, 129.8, 129.1, 128.9, 128.8, 128.7, 127.5, 62.2, 41.3, 37.1, 22.7, 14.0. IR (KBr): 2929, 1735, 1675, 1603 cm^{-1}. HRMS (ESI) m/z calcd.for: $C_{27}H_{23}NaClN_2O_4$ $[M + Na]^+$ 497.1244, found 497.1239.

The product of **4** was obtained as two separable diastereomers. And the yield was the total mounts of two diastereomers.

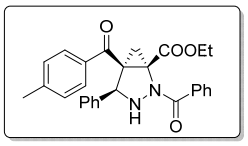
(1R*, 4S*, 5S*)-ethyl 2, 5-dibenzoyl-4-phenyl-2,3-diazabicyclo[3.1.0]hexane-1-carboxylate (4aa)



(78 mg, yield 89%), trans**:** white solid, mp 189-190 °C. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.97 – 7.88 (m, 4H), 7.64 (t, *J* = 7.4 Hz, 1H), 7.53 (t, *J* = 7.9 Hz, 3H), 7.50 – 7.44 (m, 2H), 7.26 – 7.21 (m, 3H), 7.04 (dd, *J* = 6.3, 2.6 Hz, 2H), 5.28 (s, 1H), 4.04 (q, *J* = 7.1 Hz, 2H), 2.77 (d, *J* = 6.3 Hz, 1H), 1.89 (d, *J* = 6.3 Hz, 1H), 1.04 (t, *J* = 7.1 Hz, 3H). **cis:** white solid, mp 222.3-225.7 °C. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.62 (t, *J* = 7.4 Hz, 4H), 7.50 (dd, *J* = 9.1, 6.7 Hz, 1H), 7.43 (t, *J* = 7.5 Hz, 3H), 7.24 – 7.18 (m, 2H), 7.03 (dd, *J* = 6.5, 2.5 Hz, 2H), 6.27 (s, 3H), 5.27 (s, 1H), 4.01 (q, *J* = 7.1 Hz, 1H), 3.24 – 3.17 (m, 2H), 2.75 (d, *J* = 6.3 Hz, 1H), 1.88 (d, *J* = 6.3 Hz, 1H), 1.01 (t, *J* = 7.1 Hz, 3H).^{13}C NMR (101 MHz, $CDCl_3$) δ 194.7, 170.1, 166.3, 137.4, 135.4, 134.3, 133.8, 131.2, 129.1, 129.0, 128.7, 127.9, 126.4, 70.0, 62.0, 59.1, 56.4, 29.2, 13.8. IR (KBr): 3249, 1728, 1686, 1629 cm^{-1}. HRMS (ESI) m/z calcd.for: $C_{27}H_{24}NaN_2O_4$ $[M + Na]^+$463.1634, found 463.1589.

(1R*, 4S*, 5S*)-ethyl

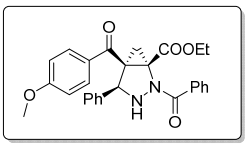
2-benzoyl-5-(4-methylbenzoyl)-4-phenyl-2,3-diazabicyclo[3.1.0]hexane-1-carboxylate (4ba)



(78 mg, yield 86%), trans: white solid; mp 119121 °C, ^{1}H NMR (600 MHz, $CDCl_3$) δ 7.90 (d, *J* = 7.2 Hz, 2H), 7.85 (d, *J* = 8.1 Hz, 2H), 7.51 (t, *J* = 7.3 Hz, 1H), 7.44 (t, *J* = 7.5 Hz, 2H), 7.31 (d, *J* = 7.9 Hz, 2H), 7.27 – 7.16 (m, 3H), 7.03 (d, *J* = 3.5 Hz, 2H), 5.25 (s, 1H), 4.02 (dd, *J* = 14.2, 7.1 Hz, 2H), 2.75 (d, *J* = 6.2 Hz, 1H), 2.44 (s, 3H), 1.87 (d, *J* = 6.3 Hz, 1H), 1.03 (t, *J* = 7.1 Hz, 3H). **cis:** white solid, mp 242-244 °C. ^{1}H NMR (600 MHz, DMSO) δ 7.75 (d, *J* = 7.6 Hz, 2H), 7.66 (d, *J* = 8.1 Hz, 2H), 7.43 (t, *J* = 7.4 Hz, 1H), 7.34 (t, *J* = 7.7 Hz, 2H), 7.32 – 7.28 (m, 2H), 7.26 (d, *J* = 8.0 Hz, 2H), 7.19 – 7.15 (m, 3H), 6.79 (d, *J* = 7.0 Hz, 1H), 4.84 (d, *J* = 7.0 Hz, 1H), 4.32 – 4.02 (m, 2H), 2.44 (d, *J* = 5.9 Hz, 1H), 2.35 (s, 3H), 2.24 (d, *J* = 5.8 Hz, 1H), 1.23 (t, *J* = 7.0 Hz, 3H). ^{13}C NMR (151 MHz, $CDCl_3$) δ 194.22, 170.1, 166.4, 145.0, 137.5, 134.3, 132.8, 131.2, 129.7, 129.2, 129.1, 128.7, 127.8, 127.8, 126.4, 67.1, 62.0, 58.9, 56.5, 29.6, 21.8, 13.9. IR (KBr): 3241, 1731, 1669, 1622 cm^{-1}; HRMS (ESI) m/z calcd. for: $C_{28}H_{26}NaN_2O_4[M + Na]^+$ 477.1791, found 477.1763

(1R*,4S*,5S*)-ethyl

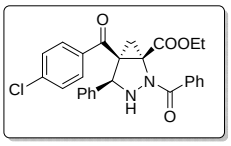
2-benzoyl-5-(4-methoxybenzoyl)-4-phenyl-2,3-diazabicyclo[3.1.0]hexane-1-carboxylate (4ca)



(73 mg, yield 78%), trans**:** white solid; mp 166-170 °C, ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.86 – 7.77 (m, 4H), 7.52 (t, *J* = 7.4 Hz, 1H), 7.45 – 7.38 (m, 3H), 7.34 (t, *J* = 7.3 Hz, 2H), 7.13 – 7.10 (m, 3H), 6.93 (dd, *J* = 6.6, 2.4 Hz, 2H), 5.16 (s, 1H), 3.91 (q, *J* = 7.1 Hz, 2H), 2.65 (d, *J* = 6.3 Hz, 1H), 1.77 (d, *J* = 6.3 Hz, 1H), 0.90 (t, *J* = 7.1 Hz, 3H). **cis:** white solid; mp 245-248 °C, ^{1}H NMR (600 MHz, DMSO) δ 7.76 (d, *J* = 7.4 Hz, 2H), 7.67 (d, *J* = 7.7 Hz, 2H), 7.43 (t, *J* = 7.0 Hz, 1H), 7.34 (t, *J* = 7.5 Hz, 2H), 7.31 (d, *J* = 3.4 Hz, 2H), 7.27 (d, *J* = 7.6 Hz, 2H), 7.17 (s, 1H), 6.79 (s, 3H), 4.84 (s, 1H), 4.29 - 4.13 (m, 2H), 2.45 (d, *J* = 5.3 Hz, 1H), 2.36 (s, 2H), 2.25 (d, *J* = 5.3 Hz, 1H), 1.24 (t, *J* = 6.3 Hz, 3H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 194.7, 170.1, 166.4, 137.4, 135.4, 134.2, 133.9, 131.2, 129.1, 129.0, 128.7, 127.9, 126.4, 67.0, 62.1, 59.1, 56.4, 29.4, 13.8. IR (KBr): 3250, 1729, 1683, 1628 cm^{-1}. HRMS (ESI) m/z calcd.for: $C_{28}H_{26}NaN_2O_5[M + Na]^+$ 477.1791, found 477.1763.

(1R*, 4S*, 5S*)-ethyl

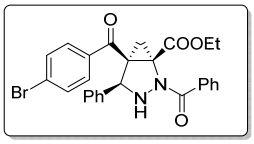
2-ben1zoyl5-(4-chlorobenzoyl)-4-phenyl-2,3-diazabicyclo[3.1.0]hexane-1-carboxylate (4da)



(83 mg, yield 87%), trans: white solid; mp 186-191 °C, ^{1}H NMR (600 MHz, $CDCl_3$) δ 7.88 (dd, *J* = 15.1, 7.9 Hz, 4H), 7.49 (dd, *J* = 19.8, 7.9 Hz, 3H), 7.44 (t, *J* = 7.5 Hz, 2H), 7.25 – 7.19 (m, 3H), 7.02 (d, *J* = 4.0 Hz, 2H), 6.24 (s, 1H), 5.24 (s, 1H), 4.04 (q, *J* = 7.0 Hz, 2H), 2.71 (d, *J* = 6.3 Hz, 1H), 1.92 (d, *J* = 6.3 Hz, 1H), 1.05 (t, *J* = 7.1 Hz, 3H). **cis:** white solid; mp 249-254 °C, ^{1}H NMR (600 MHz, DMSO) δ 7.73 (d, 4H), 7.51 (d, *J* = 7.4 Hz, 2H), 7.43 (t, *J* = 6.9 Hz, 1H), 7.33 (t, *J* = 7.2 Hz, 2H), 7.28 (s, 2H), 7.18 (s, 3H), 6.81 (d, *J* = 6.3 Hz, 1H), 4.83 (d, *J* = 6.5 Hz, 1H),

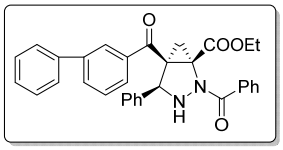
4.30-4.15 (m, 2H), 2.47 (d, *J* = 5.0 Hz, 1H), 2.31 (d, *J* = 5.0 Hz, 1H), 1.24 (d, *J* = 6.5 Hz, 3H). ^{13}C NMR (151 MHz, $CDCl_3$) δ 193.7, 170.0, 166.3, 140.4, 137.2, 134.2, 133.7, 131.3, 130.4, 129.3, 129.1, 128.8, 128.0, 127.9, 126.3, 67.0, 62.1, 58.9, 55.9, 29.0, 13.9. IR (KBr): 3239, 1731, 1685, 1631 cm^{-1}. HRMS (ESI) m/z calcd.for : $C_{27}H_{23}ClNaN_2O_4$ $[M + Na]^+$ 497.1244, found 497.1243.

(1R*,4S*,5S*)-ethyl
2-benzoyl-5-(4-bromobenzoyl)-4-phenyl-2,3-diazabicyclo[3.1.0]hexane-1-carboxylate (4ea)



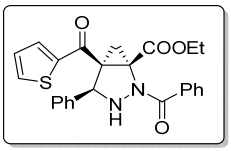
(73 mg, yield 70%), trans: white solid; mp 147 -149 ^{o}C; ^{1}H NMR (600 MHz, $CDCl_3$) δ 7.92 – 7.87 (m, 2H), 7.79 (d, *J* = 8.5 Hz, 2H), 7.66 (d, *J* = 8.2 Hz, 2H), 7.54 – 7.49 (m, 1H), 7.45 (dd, *J* = 10.8, 4.3 Hz, 2H), 7.24 (d, *J* = 5.0 Hz, 3H), 7.05 – 7.00 (m, 2H), 5.24 (s, 1H), 4.05 (dd, *J* = 13.5, 6.4 Hz, 2H), 2.72 (d, *J* = 6.4 Hz, 1H), 1.92 (d, *J* = 6.4 Hz, 1H), 1.06 (td, *J* = 7.1, 1.8 Hz, 3H). **cis:** white solid; mp 265-269 ^{o}C; ^{1}H NMR (600 MHz, DMSO) δ 7.74 (d, *J* = 7.4 Hz, 2H), 7.69 – 7.62 (m, 4H), 7.43 (t, *J* = 7.4 Hz, 1H), 7.33 (t, *J* = 7.7 Hz, 2H), 7.29 (dd, *J* = 6.4, 2.7 Hz, 2H), 7.20 – 7.14 (m, 3H), 6.81 (d, *J* = 7.0 Hz, 1H), 4.83 (d, *J* = 7.0 Hz, 1H), 4.29 – 4.11 (m, 2H), 2.46 (d, *J* = 5.9 Hz, 1H), 2.31 (d, *J* = 5.9 Hz, 1H), 1.24 (t, *J* = 7.0 Hz, 3H).^{13}C NMR (151 MHz, $CDCl_3$) δ 194.0, 170.0, 166.2, 137.1, 134.2, 134.1, 132.3, 131.3, 130.5, 129.2, 129.1, 128.2, 128.8, 128.0, 127.9, 126.3, 67.0, 62.2, 59.0, 55.9, 29.1, 13.9. IR (KBr): 3252, 1727, 1688, 1627 cm^{-1}; HRMS (ESI) m/z calcd.for : $C_{27}H_{23}BrNaN_2O_4$[M + Na]$^+$ 541.0739, found 541.0734.

(1R*, 4S*, 5S*)-ethyl
5-([1,1'-biphenyl]-3-carbonyl)-2-benzoyl-4-phenyl-2,3-diazabicyclo[3.1.0]hexane-1-carboxylate (4fa)



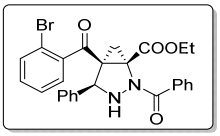
(86 mg, yield 84%), trans: yellow liquid; ^{1}H NMR (600 MHz, $CDCl_3$) δ 8.04 (d, *J* = 8.2 Hz, 2H), 7.92 (t, *J* = 11.4 Hz, 2H), 7.75 (d, *J* = 8.2 Hz, 2H), 7.66 (d, *J* = 7.3 Hz, 2H), 7.52 (dt, *J* = 15.1, 7.6 Hz, 3H), 7.45 (dt, *J* = 13.3, 7.6 Hz, 3H), 7.26 – 7.21 (m, 3H), 7.07 (d, *J* = 3.2 Hz, 2H), 5.31 (s, 1H), 4.06 (q, *J* = 7.0 Hz, 2H), 2.80 (d, *J* = 6.2 Hz, 1H), 1.93 (d, *J* = 6.2 Hz, 1H), 1.06 (t, *J* = 7.1 Hz, 3H). **cis:** white solid; mp 235 -237 ^{o}C. ^{1}H NMR (600 MHz, DMSO) δ 7.85 (d, *J* = 8.2 Hz, 2H), 7.79 – 7.75 (m, 4H), 7.73 (d, *J* = 7.6 Hz, 2H), 7.51 (t, *J* = 7.6 Hz, 2H), 7.44 (dd, *J* = 9.9, 7.4 Hz, 2H), 7.34 (t, *J* = 7.6 Hz, 4H), 7.18 (d, *J* = 4.0 Hz, 3H), 6.85 (d, *J* = 6.8 Hz, 1H), 4.90 (d, *J* = 6.9 Hz, 1H), 4.31 – 4.14 (m, 2H), 2.32 (d, *J* = 5.8 Hz, 1H), 1.25 (t, *J* = 6.9 Hz, 3H). ^{13}C NMR (151 MHz, $CDCl_3$) δ 194.3, 170.1, 166.4, 146.5, 139.5, 137.4, 134.3, 134.0, 131.3, 129.7, 129.1, 129.1, 128.7, 128.6, 127.9, 127.5, 127.3, 126.4, 67.1, 62.1, 60.4, 59.0, 56.4, 29.5, 21.1, 13.9; IR (KBr): 3213, 1733, 1676, 1645, 1602 cm^{-1}. HRMS (ESI) m/z calcd.for: $C_{33}H_{28}NaN_2O_4$ $[M + Na]^+$ 539.1947, found 539,1956.

(1R*, 4S*, 5S*)-ethyl 2-benzoyl-4-phenyl-5-(thiophene-2-carbonyl)-2,3-diazabicyclo [3.1.0]hexane-1-carboxylate (4ga)



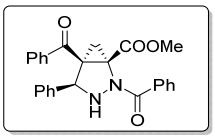
(101 mg, yield 76%), trans: Colourless liquid; ^{1}H NMR (600 MHz, $CDCl_3$) δ 7.88 (d, *J* = 7.3 Hz, 2H), 7.82 (d, *J* = 3.1 Hz, 1H), 7.76 (d, *J* = 4.4 Hz, 1H), 7.50 (t, *J* = 7.4 Hz, 1H), 7.44 (t, *J* = 7.5 Hz, 2H), 7.22 – 7.16 (m, 4H), 7.04 (d, *J* = 4.3 Hz, 2H), 5.28 (s, 1H), 4.08 – 3.96 (m, 2H), 2.82 (d, *J* = 6.2 Hz, 1H), 1.85 (d, *J* = 6.3 Hz, 1H), 1.03 (t, *J* = 7.1 Hz, 3H). **cis:** yellow solid ; mp 190-194 ^{o}C. ^{1}H NMR (600 MHz, DMSO) δ 8.02 (d, *J* = 2.8 Hz, 1H), 7.96 (d, *J* = 4.1 Hz, 1H), 7.75 (d, *J* = 7.2 Hz, 2H), 7.46 – 7.37 (m, 3H), 7.34 (t, *J* = 7.5 Hz, 2H), 7.26 – 7.19 (m, 4H), 6.83 (d, *J* = 6.7 Hz, 1H), 4.93 (d, *J* = 7.0 Hz, 1H), 4.26- 4.13 (m, 2H), 2.41 (d, *J* = 5.6 Hz, 1H), 2.28 (d, *J* = 5.6 Hz, 1H), 1.21 (t, *J* = 6.6 Hz, 3H). ^{13}C NMR (151 MHz, $CDCl_3$) δ 186.8, 170.2, 166.3, 142.1, 137.4, 135.5, 134.3, 133.9, 131.2, 129.1, 128.7, 128.6, 127.8, 127.8, 126.4, 67.6, 62.0, 58.5, 57.4, 30.4, 13.8. IR (KBr): 3240, 1737, 1646, 1632 cm^{-1}; HRMS (ESI) m/z calcd.for: $C_{25}H_{22}NaN_2O_4S$ [M + Na]$^+$ 469.1198, found 469.1190.

Ethyl (1S*,4S*,5R*)-2-benzoyl-5-(4-bromobenzoyl)-4-phenyl-2,3-diazabicyclo[3.1.0]hexane-1-carboxylate (4ha)



(67 mg, yield 56%), trans : yellow liquid; ^{1}H NMR (600 MHz, $CDCl_3$) δ 7.94 (d, *J* = 7.4 Hz, 2H), 7.86 (d, *J* = 7.3 Hz, 2H), 7.64 (t, *J* = 7.4 Hz, 1H), 7.55 – 7.49 (m, 3H), 7.44 (t, *J* = 7.7 Hz, 2H), 7.17 (d, *J* = 8.4 Hz, 2H), 6.95 (d, *J* = 8.4 Hz, 2H), 5.21 (s, 1H), 4.00 (q, *J* = 7.0 Hz, 2H), 2.76 (d, *J* = 6.3 Hz, 1H), 1.80 (d, *J* = 6.3 Hz, 1H), 0.99 (t, *J* = 7.1 Hz, 3H). ^{13}C NMR (151 MHz, $CDCl_3$) δ 194.40, 170.32, 166.31, 136.12, 135.22, 134.16, 133.99, 133.66, 131.30, 129.06, 129.02, 128.87, 128.84, 127.87, 127.80, 66.54, 62.08, 59.43, 56.55, 13.81. **cis:** white solid; mp 128-130 ^{o}C. ^{1}H NMR (400 MHz, DMSO) δ 7.58 (d, *J* = 7.3 Hz, 2H), 7.52 – 7.48 (m, 1H), 7.38 (t, *J* = 7.4 Hz, 1H), 7.28 (dt, *J* = 15.1, 4.7 Hz, 4H), 7.18 (ddd, *J* = 13.8, 9.0, 4.1 Hz, 6H), 6.66 (d, *J* = 5.9 Hz, 1H), 4.48 (d, *J* = 5.9 Hz, 1H), 4.41- 4.18 (m, 2H), 2.61 (d, *J* = 6.0 Hz, 1H), 2.41 (d, *J* = 6.0 Hz, 1H), 1.32 (t, *J* = 7.1 Hz, 3H). ^{13}C NMR (101 MHz, DMSO) δ 197.3, 166. 6, 165.1, 140.5, 139.5, 134.3, 133.8, 132. 8, 131.2, 129.8, 129.5, 128.8, 128.1, 127.9, 127.6, 127.7, 118.8, 63. 6, 61.5, 54.8, 52.5, 25.5, 14.4. IR (KBr): 3245, 1734, 1692, 1619 cm^{-1}; HRMS (ESI) m/z calcd.for: $C_{27}H_{23}NaBrN_2O_4$ [M + Na]$^+$ 541.0739, found 541.0734.

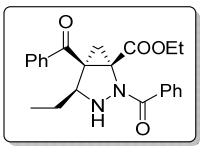
Methyl (1S*,4R*,5R*)-2,5-dibenzoyl-4-phenyl-2,3-diazabicyclo[3.1.0]hexane-1-carboxylate (4ia)



(66 mg, yield 78%), trans: colorless liquid; ^{1}H NMR (600 MHz, $CDCl_3$) δ 7.91 (d, *J* = 7.6 Hz, 4H), 7.61 (t, *J* = 7.2 Hz, 1H), 7.50 (t, *J* = 7.4 Hz, 3H), 7.43 (t, *J* = 7.5 Hz, 2H), 7.21 (s, 3H), 7.03 (d, *J* = 4.1 Hz, 2H), 5.27 (s, 1H), 3.56 (s, 3H), 2.74 (d, *J* = 6.2 Hz, 1H), 1.91 (d, *J* = 6.2 Hz, 1H).

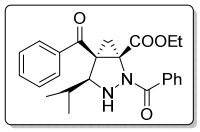
cis: white solid; mp 157-159 °C. ^{1}H NMR (600 MHz, DMSO) δ 7.76 (d, *J* = 7.4 Hz, 2H), 7.73 (d, *J* = 7.3 Hz, 2H), 7.59 (t, *J* = 7.4 Hz, 1H), 7.44 (dd, *J* = 15.8, 7.9 Hz, 3H), 7.34 (t, *J* = 7.7 Hz, 2H), 7.28 – 7.23 (m, 2H), 7.18 – 7.12 (m, 3H), 6.82 (d, *J* = 7.0 Hz, 3H), 4.85 (d, *J* = 7.0 Hz, 1H), 3.76 (s, 3H), 2.49 (d, *J* = 5.9 Hz, 1H), 2.32 (d, *J* = 5.9 Hz, 1H). ^{13}C NMR (151 MHz, DMSO) δ 193.6, 167.5, 167.1, 139.0, 136.2, 134.3, 134.0, 131.4, 129.7, 129.1, 128.8, 128.6, 128.2, 128.1, 128.0, 66.0, 52.8, 52.0, 23.8, 18.8. IR (KBr): 3257, 1730, 1683, 1627 cm^{-1}; HRMS (ESI) m/z calcd.for: $C_{26}H_{22}NaN_2O_4$ $[M + Na]^+$ 449.1478, found 449.1456.

(1R*, 4S*, 5S*)-ethyl 2,5-dibenzoyl-4-ethyl-2,3-diazabicyclo[3.1.0]hexane-1-carboxylate (4ab)



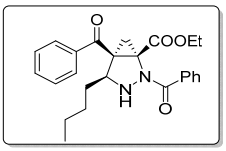
(68 mg, yields 87%), trans: yellow liquid. ^{1}H NMR (600 MHz, $CDCl_3$) δ 8.02 (d, *J* = 7.6 Hz, 2H), 7.86 (d, *J* = 6.9 Hz, 2H), 7.63 (t, *J* = 7.2 Hz, 1H), 7.52 (t, *J* = 7.6 Hz, 2H), 7.46 (t, *J* = 7.2 Hz, 1H), 7.40 (t, *J* = 7.5 Hz, 2H), 4.21-4.11 (m, 2H), 3.44 (s, 1H), 2.70 (d, *J* = 5.5 Hz, 1H), 2.09 (d, *J* = 5.6 Hz, 1H), 1.56 (dd, *J* = 15.5, 7.8 Hz, 2H), 1.18 (t, *J* = 6.5 Hz, 3H), 0.88 (t, *J* = 7.3 Hz, 3H). **cis:** white solid; mp 173-174 °C, ^{1}H NMR (600 MHz, $CDCl_3$) δ 8.01 (d, *J* = 7.9 Hz, 2H), 7.85 (d, *J* = 7.2 Hz, 2H), 7.62 (t, *J* = 7.2 Hz, 1H), 7.51 (t, *J* = 7.6 Hz, 2H), 7.45 (t, *J* = 7.1 Hz, 1H), 7.38 (t, *J* = 7.6 Hz, 2H), 4.20-4.11 (m, 2H), 3.44 (d, *J* = 2.8 Hz, 1H), 2.67 (d, *J* = 5.6 Hz, 1H), 2.09 (d, *J* = 5.7 Hz, 1H), 1.62 – 1.46 (m, 2H), 1.18 (t, *J* = 6.7 Hz, 3H), 0.87 (t, *J* = 7.4 Hz, 3H).^{13}C NMR (151 MHz, $CDCl_3$) δ 192.9, 169.1, 167.1, 135.8, 134.1, 134.0, 131.0, 129.2, 128.9, 127.7, 70.0, 61.9, 56.0, 53.8, 33.4, 23.3, 14.0, 11.6. IR (KBr): 3255, 1730, 1677, 1633 cm^{-1}; HRMS (ESI) m/z calcd.for: $C_{23}H_{24}NaN_2O_4$ $[M + Na]^+$ 415.1634, found 415.1599.

(1R*, 4R*, 5S*)-ethyl 2,5-dibenzoyl-4-isopropyl-2,3-diazabicyclo[3.1.0]hexane-1-carboxylate (4ac)



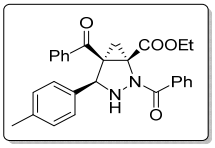
(67 mg, yield 83%), trans: yellow liquid; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.96 – 7.91 (m, 2H), 7.87 – 7.83 (m, 2H), 7.64 – 7.58 (m, 1H), 7.52 (t, *J* = 7.6 Hz, 2H), 7.48 – 7.43 (m, 1H), 7.41 – 7.36 (m, 2H), 3.96 – 3.90 (m, 2H), 3.56 (d, *J* = 10.4 Hz, 1H), 2.89 (d, *J* = 6.2 Hz, 1H), 2.11 – 2.00 (m, 1H), 1.53 (qd, *J* = 19.3, 12.7, 6.4 Hz, 1H), 0.93 (t, *J* = 7.1 Hz, 3H), 0.83 (d, *J* = 6.7 Hz, 3H), 0.80 (d, *J* = 6.5 Hz, 3H). **cis:** white solid; mp 139-140 °C**.**^{1}H NMR (600 MHz, $CDCl_3$) δ 8.02 (d, *J* = 7.6 Hz, 2H), 7.91 (d, *J* = 4.5 Hz, 2H), 7.62 (t, *J* = 7.4 Hz, 1H), 7.51 (t, *J* = 7.8 Hz, 2H), 7.45 (t, *J* = 7.4 Hz, 1H), 7.39 (t, *J* = 7.5 Hz, 2H), 4.18-4.04 (m, 2H), 3.28 (d, *J* = 6.6 Hz, 1H), 2.67 (d, *J* = 5.8 Hz, 1H), 2.07 (d, *J* = 5.9 Hz, 1H), 1.88 (dd, *J* = 13.4, 6.7 Hz, 1H), 1.14 (s, 3H), 1.01 (d, *J* = 6.7 Hz, 3H), 0.86 (d, *J* = 6.6 Hz, 3H).^{13}C NMR (101 MHz, $CDCl_3$) δ 194.3, 169.9, 166.5, 135.4, 134.2, 133.5, 130.9, 129.0, 129.0, 128.5, 127. 7, 70.8, 62.0, 59.5, 55.0, 29.8, 27.1, 21.0, 18.8, 13.8. IR (KBr): 3244, 1730, 1685, 1629 cm^{-1}; HRMS (ESI) m/z calcd.for: $C_{24}H_{26}NaN_2O_4$$[M + Na]^+$ 429.1791, found 429.1786.

(1R*, 4S*, 5S*)-ethyl 2,5-dibenzoyl-4-butyl-2,3-diazabicyclo[3.1.0]hexane-1-carboxylate (4ad)



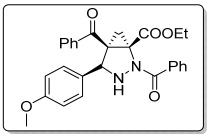
(71 mg, yield 81%), trans: yellow liquid. ^{1}H NMR (600 MHz, $CDCl_3$) δ 7.94 (d, *J* = 7.6 Hz, 2H), 7.86 (d, *J* = 7.4 Hz, 2H), 7.61 (t, *J* = 7.3 Hz, 1H), 7.51 (t, *J* = 7.6 Hz, 2H), 7.45 (t, *J* = 7.3 Hz, 1H), 7.39 (t, *J* = 7.5 Hz, 2H), 4.03-3.93 (m, 3H), 2.74 (d, *J* = 6.3 Hz, 1H), 2.16 (d, *J* = 6.3 Hz, 1H), 1.43 (dd, *J* = 13.7, 8.2 Hz, 2H), 1.22 – 1.09 (m, 4H), 1.01 (t, *J* = 7.1 Hz, 3H), 0.75 (t, *J* = 6.7 Hz, 3H). **cis:** oil. ^{1}H NMR (600 MHz, $CDCl_3$) δ 8.01 (d, *J* = 7.4 Hz, 2H), 7.85 (d, *J* = 7.4 Hz, 2H), 7.63 (t, *J* = 7.4 Hz, 1H), 7.52 (t, *J* = 7.7 Hz, 2H), 7.46 (t, *J* = 7.4 Hz, 1H), 7.40 (t, *J* = 7.6 Hz, 2H), 4.19-4.10 (m, 2H), 3.50 (d, *J* = 3.7 Hz, 1H), 2.71 (d, *J* = 5.6 Hz, 1H), 2.10 (d, *J* = 5.7 Hz, 1H), 1.59 – 1.43 (m, 2H), 1.33 (dt, *J* = 10.6, 5.6 Hz, 1H), 1.17 (dt, *J* = 13.3, 6.6 Hz, 6H), 0.74 (t, *J* = 7.1 Hz, 3H).^{13}C NMR (151 MHz, $CDCl_3$) δ 194.5, 169.7, 166.4, 135.5, 134.2, 133.7, 131.0, 129.1, 128.9, 128.8, 127.7, 63.9, 61. 9, 57.8, 54.8, 30.5, 28.6, 25.5. 22.3, 13.9, 13.7. IR (KBr): 3247, 1736, 1690. 1653 cm^{-1}. HRMS (ESI) m/z calcd.for: $C_{25}H_{28}NaN_2O_4$[M + Na]$^+$443.1947. found 443.1966.

(1R*, 4S*, 5S*)-ethyl 2,5-dibenzoyl-4-(p-tolyl)-2,3-diazabicyclo[3.1.0]hexane-1-carboxylate (4ae)



(73 mg, yield 81%), trans: colorless liquid. ^{1}H NMR (600 MHz, $CDCl_3$) δ 7.94 (d, *J* = 7.4 Hz, 2H), 7.91 (d, *J* = 7.3 Hz, 2H), 7.63 (t, *J* = 7.4 Hz, 1H), 7.54 – 7.48 (m, 3H), 7.45 (t, *J* = 7.5 Hz, 2H), 7.03 (d, *J* = 7.9 Hz, 2H), 6.92 (d, *J* = 7.9 Hz, 2H), 5.24 (s, 1H), 4.03 (q, *J* = 7.0 Hz, 2H), 2.75 (d, *J* = 6.3 Hz, 1H), 2.29 (s, 3H), 1.90 (d, *J* = 6.3 Hz, 1H), 1.03 (t, *J* = 7.1 Hz, 3H).**cis:** white solid; mp 167-170 ^{o}C. ^{1}H NMR (600 MHz, DMSO) δ 7.81 – 7.70 (m, 4H), 7.60 (t, *J* = 7.4 Hz, 1H), 7.48 – 7.40 (m, 3H), 7.34 (t, *J* = 7.7 Hz, 2H), 7.17 (d, *J* = 8.0 Hz, 2H), 6.97 (d, *J* = 7.9 Hz, 2H), 6.75 (d, *J* = 7.0 Hz, 1H), 4.79 (d, *J* = 7.0 Hz, 1H), 4.33 – 4.07 (m, 2H), 2.44 (d, *J* = 5.9 Hz, 1H), 2.26 (d, *J* = 5.9 Hz, 1H), 2.19 (s, 3H), 1.24 (t, *J* = 7.0 Hz, 3H).^{13}C NMR (151 MHz, $CDCl_3$) δ 194.8, 170.0, 166.4, 137.6, 135.4, 134.3, 134.3, 133. 8, 131.2, 129.4, 129.1, 129.0, 128.9, 127.8, 126.3, 66.9, 62.0, 59.0, 56.3, 29.1, 21.0, 13.9. HRMS (ESI) m/z calcd.for: $C_{28}H_{26}NaN_2O_4$[M + Na]$^+$ 477.1791, found: 477.1780. IR (KBr): 3243, 1734, 1690, 1630 cm^{-1}. HRMS (ESI) m/z calcd.for: $C_{28}H_{26}NaN_2O_4$[M + Na]$^+$ 477.1791, found 477.1769.

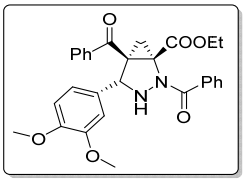
(1R*, 4R*, 5S*)-ethyl
2,5-dibenzoyl-4-(4-methoxyphenyl)-2,3-diazabicyclo[3.1.0]hexane-1-carboxylate (4af)



(85 mg, yield 90%). trans: yellow liquid. ^{1}H NMR (600 MHz, $CDCl_3$) δ 7.91 (dd, *J* = 21.0, 7.5 Hz, 2H), 7.78 (dd, *J* = 19.1, 10.9 Hz, 2H), 7.61 (t, *J* = 7.4 Hz, 1H), 7.54 – 7.47 (m, 3H), 7.43 (t, *J* = 7.6 Hz, 2H), 6.97 (d, *J* = 8.6 Hz, 1H), 6.74 (d, *J* = 8.7 Hz, 2H), 5.22 (s, 1H), 4.03 – 3.95 (m, 2H), 3.74 (s, 3H), 2.74 (d, *J* = 6.3 Hz, 1H), 1.92 (d, *J* = 6.3 Hz, 1H), 1.01 (t, *J* = 7.1 Hz, 3H). **cis:** white solid; mp 228-229 ^{o}C.^{1}H NMR (600 MHz, DMSO) δ 7.75 (d, *J* = 7.5 Hz, 4H), 7.59 (t, *J* = 7.4 Hz, 1H),

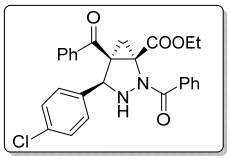
7.48 – 7.41 (m, 3H), 7.34 (t, *J* = 7.7 Hz, 2H), 7.22 (d, *J* = 8.7 Hz, 2H), 6.75 (d, *J* = 7.1 Hz, 1H), 6.72 (d, *J* = 8.7 Hz, 2H), 4.79 (d, *J* = 7.1 Hz, 1H), 4.30 – 4.15 (m, 2H), 3.66 (s, 3H), 2.44 (d, *J* = 5.9 Hz, 1H), 2.27 (d, *J* = 5.9 Hz, 1H), 1.24 (t, *J* = 7.0 Hz, 3H). ^{13}C NMR (151 MHz, DMSO) δ 193.4, 167.5, 166.5, 159.1, 136.2, 134.5, 134.0, 131.3, 131.0, 129.7, 129.4, 129.2, 128.8, 128.0, 113.9, 65. 7, 61.3, 60.2, 55.4, 52.2, 14.4. IR (KBr): 3245, 1733, 1688, 1630 cm^{-1}. HRMS (ESI) m/z calcd.for: $C_{28}H_{26}NaN_2O_5[M + Na]^+$ 493.1730, found 493.1759.

Ethyl (1S*, 4S*, 5R*)-2,5-dibenzoyl-4-(3,4-dimethoxyphenyl)-2,3-diazabicyclo [3.1.0]hexane-1-carboxylate (4ag)



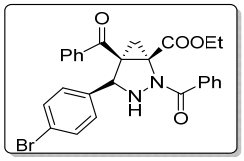
(83 mg, yield 83%), colorless liquid. ^{1}H NMR (600 MHz, $CDCl_3$) δ 7.96 (t, *J* = 6.9 Hz, 4H), 7.63 (dd, *J* = 10.6, 4.2 Hz, 1H), 7.54 – 7.47 (m, 3H), 7.43 (dd, *J* = 10.5, 4.5 Hz, 2H), 6.73 (d, *J* = 8.3 Hz, 1H), 6.59 (d, *J* = 8.2 Hz, 1H), 6.54 (s, 1H), 5.24 (s, 2H), 4.08 – 3.96 (m, 2H), 3.82 (s, 3H), 3.43 (s, 3H), 2.76 (d, *J* = 6.2 Hz, 1H), 1.88 (d, *J* = 6.1 Hz, 1H), 1.04 – 1.00 (m, 3H). **cis:** white solid; mp 234-236 ^{o}C.^{1}H NMR (600 MHz, DMSO) δ 7.76 – 7.73 (m, 4H), 7.60 (t, *J* = 7.4 Hz, 1H), 7.48 – 7.41 (m, 3H), 7.34 (t, *J* = 7.7 Hz, 2H), 7.17 (d, *J* = 8.0 Hz, 2H), 6.97 (d, *J* = 7.9 Hz, 2H), 6.75 (d, *J* = 7.0 Hz, 1H), 4.79 (d, *J* = 7.0 Hz, 2H), 4.30 – 4.11 (m, 1H), 2.44 (d, *J* = 5.9 Hz, 1H), 2.26 (d, *J* = 5.9 Hz, 3H), 1.24 (t, *J* = 7.0 Hz, 3H). ^{13}C NMR (151 MHz, DMSO) δ 193.5, 167.5, 166.6, 148.7, 148.6, 136.3, 134.5, 133.9, 131.4, 131.3, 129.6, 129.1, 128.8, 128.0, 120.5, 111.7, 111.4, 65.8, 61.4, 55.7, 55.7, 52.8, 52.1, 23.8, 14.4. IR (KBr): 3249, 1729, 1683, 1627 cm^{-1}. HRMS (ESI) m/z calcd. for :$C_{29}H_{28}NaN_2O_6[M + Na]^+$ 523.1845. found, 523.1836.

(1R*, 4S*, 5S*)-ethyl 2,5-dibenzoyl-4-(4-chlorophenyl)-2,3-diazabicyclo[3.1.0] hexane-1-carboxylate (4ah)



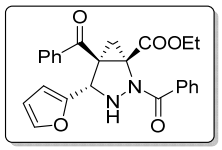
(79 mg, yield 83%), trans: yellow liquid. ^{1}H NMR (600 MHz, $CDCl_3$) δ 7.94 (d, *J* = 7.3 Hz, 2H), 7.85 (d, *J* = 7.3 Hz,2H), 7.63 (t, *J* = 7.2 Hz, 1H), 7.51 (dd, *J* = 16.1, 8.3 Hz, 3H), 7.43 (t, *J* = 7.5 Hz, 2H), 7.17 (d, *J* = 8.4 Hz, 2H), 6.94 (d, *J* = 8.2 Hz, 2H), 5.21 (s, 1H), 4.06 – 3.93 (m, 2H), 2.75 (d, *J* = 6.2 Hz, 1H), 1.80 (d, *J* = 6.2 Hz, 1H), 0.99 (t, *J* = 7.1 Hz, 3H). **cis:** white solid; mp 253-257 ^{o}C.^{1}H NMR (600 MHz, DMSO) δ 7.76 (t, *J* = 7.8 Hz, 4H), 7.62 (t, *J* = 6.9 Hz, 1H), 7.48 (t, *J* = 7.1 Hz, 2H), 7.44 (t, *J* = 6.9 Hz, 1H), 7.35 (t, *J* = 7.2 Hz, 2H), 7.32 (d, *J* = 7.6 Hz, 2H), 7.26 (d, *J* = 7.4 Hz, 2H), 6.84 (d, *J* = 5.7 Hz, 1H), 4.92 (d, *J* = 6.0 Hz, 1H), 4.30- 4.18 (m, 2H), 2.29 (d, *J* = 5.0 Hz, 1H), 1.25 (t, *J* = 6.0 Hz, 3H).^{13}C NMR (151 MHz, $CDCl_3$) δ 194.4, 170.3, 166.3, 136.1, 135.2, 134.2, 134.0, 133.7, 131.3, 129.1, 129.0, 128.9, 128.8, 128.6, 127.9, 127.8, 66.5, 62.1, 59.4, 56.5, 30.1, 13.8. IR (KBr): 3246, 1733, 1685, 1627 cm^{-1}. HRMS (ESI) m/z calcd.for :$C_{27}H_{23}ClNaN_2O_4[M + Na]^+$ 497.1244, found 497.1239.

(1R*, 4S*, 5S*)-ethyl 2,5-dibenzoyl-4-(2-bromophenyl)-2,3-diazabicyclo[3.1.0] hexane-1-carboxylate (4ai)



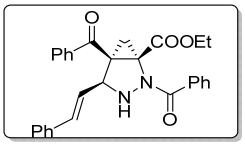
(90 mg, yield 87%), trans: yellow solid; mp 179-180 °C. ^{1}H NMR (600 MHz, $CDCl_3$) δ 7.89 (d, *J* = 7.5 Hz, 2H), 7.79 (d, *J* = 8.4 Hz,2H), 7.65 (d, *J* = 8.4 Hz, 2H), 7.51 (t, *J* = 7.2 Hz, 1H), 7.44 (t, *J* = 7.5 Hz, 2H), 7.25 – 7.21 (m, 3H), 7.02 (d, *J* = 3.8 Hz,2H), 5.24 (s, 1H), 4.04 (dd, *J* = 14.1, 7.0 Hz, 2H), 2.71 (d, *J* = 6.3 Hz, 1H), 1.92 (d, *J* = 6.3 Hz, 1H), 1.05 (t, *J* = 7.1 Hz, 3H)**. cis**:white solid; mp 197-200 °C.^{1}H NMR (600 MHz, DMSO) δ 7.75 (dd, *J* = 12.2, 7.4 Hz, 4H), 7.62 (t, *J* = 7.4 Hz, 1H), 7.47 (t, *J* = 7.8 Hz, 2H), 7.43 (t, *J* = 7.4 Hz, 1H), 7.35 (t, *J* = 7.7 Hz, 2H), 7.31 (d, *J* = 8.5 Hz,2H), 7.25 (d, *J* = 8.5 Hz, 2H), 6.82 (d, *J* = 6.7 Hz, 1H), 4.91 (d, *J* = 6.7 Hz, 1H), 4.34 – 4.05 (m, 2H), 2.49 (d, *J* = 6.2 Hz, 1H), 2.29 (d, *J* = 6.0 Hz, 1H), 1.24 (t, *J* = 7.0 Hz, 3H).^{13}C NMR (151 MHz, $CDCl_3$) δ 194.0, 170.0, 166.3, 137.1, 134.1, 132.3, 131.3, 130.5, 129.2, 129.1, 128.8, 128.0, 127.9, 126.3, 67.0, 62.2, 59.0, 55.9, 29.0, 13.9. IR (KBr): 3260, 1734, 1689, 1632 cm^{-1}. HRMS (ESI) m/z calcd.for:$C_{27}H_{23}BrNaN_2O_4$ $[M + Na]^+$ 541.0739, found 541.0735.

Ethyl-(1S*, 4R*, 5R*)-2,5-dibenzoyl-4-(furan-2-yl)-2,3-diazabicyclo[3.1.0] hexane-1-carboxylate (4aj)



(73 mg, yield 85%), trans: Colorless liquid. ^{1}H NMR (600 MHz, $CDCl_3$) δ 7.99 (d, *J* = 7.4 Hz, 2H), 7.86 (d, *J* = 7.3 Hz, 2H), 7.61 (t, *J* = 7.4 Hz, 1H), 7.51 – 7.46 (m, 3H), 7.41 (dd, *J* = 13.6, 6.1 Hz, 3H), 6.20 (dd, *J* = 3.1, 1.8 Hz, 1H), 5.83 (d, *J* = 2.8 Hz, 1H), 5.12 (d, *J* = 7.2 Hz, 1H), 4.18 – 4.04 (m, 2H), 2.75 (d, *J* = 6.4 Hz, 1H), 2.04 (d, *J* = 6.7 Hz, 1H), 1.10 (t, *J* = 7.1 Hz, 3H). **cis:** white solid; mp 217-220 °C.^{1}H NMR (600 MHz, DMSO) δ 7.84 (d, *J* = 7.4 Hz, 2H), 7.68 (d, *J* = 7.4 Hz, 2H), 7.60 (t, *J* = 7.4 Hz, 1H), 7.47 (t, *J* = 7.7 Hz, 2H), 7.44 (t, *J* = 7.4 Hz, 1H), 7.40 (d, *J* = 0.9 Hz, 1H), 7.35 (t, *J* = 7.7 Hz, 2H), 6.76 (d, *J* = 7.2 Hz, 1H), 6.42 (d, *J* = 3.2 Hz, 1H), 6.35 – 6.26 (m, 1H), 5.01 (d, *J* = 7.4 Hz, 1H), 4.30 – 4.13 (m, 2H), 2.47 (d, *J* = 6.1 Hz, 1H), 2.31 (d, *J* = 6.0 Hz, 1H), 1.22 (t, *J* = 7.1 Hz, 3H).^{13}C NMR (151 MHz, DMSO) δ 193.6, 167.9, 166.3, 150.9, 142.9, 136.2, 134.6, 133.9, 131.2, 129.6, 129.1, 128.8, 127.9, 111.1, 109.2, 61.4, 60.2, 55.3, 52.6, 51.4, 14.3. IR (KBr): 3252, 1741, 1716, 1650 cm^{-1}. HRMS (ESI) m/z calcd.for: $C_{25}H_{22}NaN_2O_5$ $[M + Na]^+$ 453.1427, found, 453.1437.

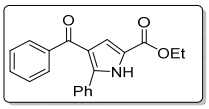
(1R*, 4S*, 5S*)-ethyl 2,5-dibenzoyl-4-((E)-styryl)-2,3-diazabicyclo[3.1.0] hexane-1-carboxylate (4ak)



(70 mg, yield 74%), trans: yellow liquid.^{1}H NMR (600 MHz, $CDCl_3$) δ 7.99 (d, *J* = 7.9 Hz,2H), 7.88 (d, *J* = 7.7 Hz, 2H), 7.64 (dd, *J* = 10.6, 4.0 Hz, 1H), 7.56 – 7.49 (m, 4H), 7.44 (t, *J* = 7.6 Hz, 2H), 7.28 (dd, *J* = 8.7, 5.5 Hz, 2H), 7.24 (d, *J* = 7.0 Hz, 1H), 7.13 (d, *J* = 7.8 Hz, 2H), 6.26 (d, *J* = 15.8 Hz, 1H), 5.97 (dd, *J* = 15.8, 4.5 Hz, 1H), 4.71 (d, *J* = 3.9 Hz, 1H), 4.08 (q, *J* = 7.0 Hz, 2H), 2.78 (d, *J* = 6.1 Hz, 1H), 2.29 (d, *J* = 6.1 Hz, 1H), 1.08 (t, *J* = 7.1 Hz,3H). **cis:** white solid, mp

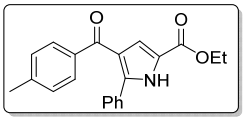
182-185 °C. ^{1}H NMR (600 MHz, DMSO) δ 7.97 (d, *J* = 7.7 Hz, 2H), 7.84 (d, *J* = 7.8 Hz, 2H), 7.65 (t, *J* = 7.4 Hz, 1H), 7.53 (t, *J* = 7.7 Hz, 2H), 7.48 (t, *J* = 7.3 Hz, 1H), 7.42 (t, *J* = 7.6 Hz, 2H), 7.24 (t, *J* = 7.4 Hz, 2H), 7.20 (t, *J* = 7.2 Hz, 1H), 7.08 (d, *J* = 7.8 Hz, 2H), 7.05 (d, *J* = 8.4 Hz, 1H), 6.46 (d, *J* = 15.9 Hz, 1H), 6.08 – 5.98 (m, 1H), 4.43 (t, *J* = 8.9 Hz, 1H), 4.15 – 4.09 (m, 2H), 2.43 (d, *J* = 5.4 Hz, 1H), 2.30 (d, *J* = 5.2 Hz, 1H), 1.13 (t, *J* = 7.1 Hz, 3H). ^{13}C NMR (151 MHz, DMSO) δ 192.9, 168.8, 167.2, 136.2, 136.0, 134.8, 134.6, 134.4, 131.3, 129.6, 129.4, 129.1, 128.6, 128.1, 128.0, 126.7, 126.6, 124.2, 67.5, 61.4, 60.2, 54.4, 54.4, 21.2, 14.3. IR (KBr): 3240, 1720, 1676, 1630 cm^{-1}. HRMS (ESI) m/z calcd.for: $C_{29}H_{26}NaN_2O_4$ [M + Na]$^+$ 489.1791, found, 489.1779.

Ethyl 4-benzoyl-5-phenyl-1H-pyrrole-2-carboxylate (5aa)



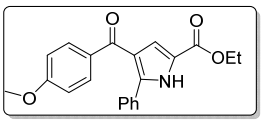
White solid (53 mg, yield 82%), mp 182-186 °C. ^{1}H NMR (400 MHz, $CDCl_3$) δ 9.89 (s, 1H), 7.83 – 7.75 (m, 2H), 7.52 (dt, *J* = 5.5, 3.3 Hz, 2H), 7.47 (d, *J* = 7.4 Hz, 1H), 7.37 (dd, *J* = 10.4, 4.7 Hz, 2H), 7.34 – 7.31 (m, 3H), 7.22 (d, *J* = 2.6 Hz, 1H), 4.27 (q, *J* = 7.1 Hz, 2H), 1.32 (t, *J* = 7.1 Hz, 3H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 191.7, 161.1, 140.6, 138.9, 132.1, 130.8, 129.6, 129.0, 128.7, 128.5, 128.1, 122.3, 121.9, 119.3, 61.0, 14.4. IR (KBr) 3279, 1682, 1657 cm^{-1}. HRMS (ESI) m/z calcd.for: $C_{20}H_{17}NaNO_3$ [M + Na]$^+$ 342.1106, found, 342.1118.

Ethyl 4-(4-methylbenzoyl)-5-phenyl-1H-pyrrole-2-carboxylate (5ba)



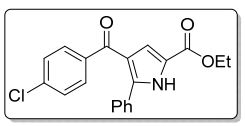
White solid (58 mg, yield 80%); mp 142-145 °C. ^{1}H NMR (400 MHz, $CDCl_3$) δ 10.36 (s, 1H), 7.72 (d, *J* = 8.1 Hz, 2H), 7.61 – 7.42 (m, 2H), 7.36 – 7.25 (m, 3H), 7.19 (d, *J* = 2.7 Hz, 2H), 7.16 (s, 1H), 4.19 (q, *J* = 7.1 Hz, 2H), 2.37 (s, 3H), 1.27 (t, *J* = 7.1 Hz, 3H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 191.5, 161.4, 142.8, 140.6, 136.3, 130.9, 129.9, 128.8, 128.7, 128.3, 122.1, 122.1, 119.4, 61.0, 21.6, 14.4. IR (KBr) 3308, 1688, 1642 cm^{-1}. HRMS (ESI) m/z calcd.for: $C_{21}H_{19}NaNO_3$ [M + Na]$^+$ 356.1263, found, 356.1270

Ethyl 4-(4-methoxybenzoyl)-5-phenyl-1H-pyrrole-2-carboxylate (5ca)



White solid (60 mg, yield 86%); mp 161-163 °C. ^{1}H NMR (400 MHz, $CDCl_3$) δ 10.25 (s, 1H), 7.84 – 7.76 (m, 2H), 7.55 – 7.48 (m, 2H), 7.33 – 7.28 (m, 3H), 7.20 (d, *J* = 2.6 Hz, 1H), 6.86 (d, *J* = 8.8 Hz, 2H), 4.24 (q, *J* = 7.1 Hz, 2H), 3.83 (s, 3H), 1.30 (t, *J* = 7.1 Hz, 3H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 190.6, 163.0, 161.4, 140.1, 132.1, 131.5, 130.9, 130.1, 128.7, 128.7, 128.4, 122.2, 122.1, 119.2, 113.4, 61.0, 55.4, 14.4. IR (KBr) 3297, 1688, 1631 cm^{-1}. HRMS (ESI) m/z calcd.for: $C_{21}H_{19}NaNO_4$ [M + Na]$^+$ 372.1212, found, 372.1120.

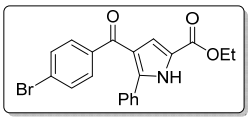
Ethyl 4-(4-chlorobenzoyl)-5-phenyl-1H-pyrrole-2-carboxylate (5da)



White solid (50 mg, yield 71%); mp 142-145 °C. ^{1}H NMR (400 MHz, $CDCl_3$) δ 10.28 (s, 1H), 7.72 (d, *J* = 8.5 Hz, 2H), 7.50 (dd, *J* = 6.5, 3.1 Hz, 2H), 7.36 – 7.30 (m, 5H), 7.18 (d, *J* = 2.6 Hz,

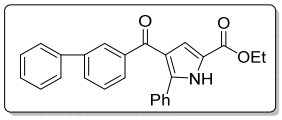
1H), 4.21 (q, *J* = 7.1 Hz, 2H), 1.29 (t, *J* = 7.1 Hz, 3H). ^{13}C NMR(101 MHz, $CDCl_3$) δ 190.4, 161.2, 140.8, 138.4, 137.2, 131.0, 130.6, 129.0, 128.9, 128.4, 128.4, 122.5, 121.6, 119.1, 61.1, 14.3. IR (KBr) 3267, 1687, 1648 cm^{-1}. HRMS (ESI) m/z calcd.for: $C_{20}H_{16}NaClNO_3$ $[M + Na]^+$ 376.0717, found, 376.0730.

Ethyl 4-(4-bromobenzoyl)-5-phenyl-1H-pyrrole-2-carboxylate (5ea)



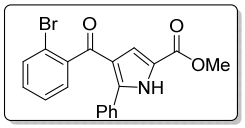
White solid (50 mg, yield 63%); mp 129-130 °C. ^{1}H NMR (400 MHz, $CDCl_3$) δ 10.15 (s, 1H), 7.75 – 7.67 (m, 2H), 7.50 (dd, *J* = 6.5, 3.1 Hz, 2H), 7.33 (dd, *J* = 5.3, 3.1 Hz, 5H), 7.19 (d, *J* = 2.6 Hz, 1H), 4.24 (q, *J* = 7.1 Hz, 2H), 1.31 (t, *J* = 7.1 Hz, 3H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 190.4, 161.2, 140.8, 138.4, 137.2, 131.0, 130.6, 129.1, 128.8, 128.5, 128.4, 122.4, 121.6, 119.1, 61.1, 14.4. IR (KBr) 3274, 1687, 1652 cm^{-1}. HRMS (ESI) m/z calcd.for: $C_{20}H_{16}NaBrNO_3$ $[M + Na]^+$ 420.0212, found,420.0216..

Ethyl 4-([1, 1'-biphenyl]-3-carbonyl)-5-phenyl-1H-pyrrole-2-carboxylate (5fa)



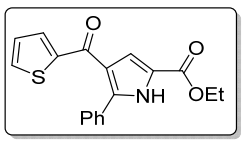
White solid (66 mg, yield 83%); mp 126-128 °C. ^{1}H NMR (400 MHz, $CDCl_3$) δ 10.37 (s, 1H), 7.88 (d, *J* = 8.2 Hz, 2H), 7.62 – 7.57 (m, 4H), 7.55 (dd, *J* = 6.5, 2.7 Hz, 2H), 7.45 (t, *J* = 7.5 Hz, 2H), 7.38 (d, *J* = 7.3 Hz, 1H), 7.33 (dd, *J* = 11.1, 7.1 Hz, 3H), 7.27 (d, *J* = 1.7 Hz, 1H), 4.30 – 4.21 (m, 2H), 1.31 (td, *J* = 7.1, 1.8 Hz, 3H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 191.3, 161.5 144.9, 140.9, 140.1, 137.6, 133.6, 130.8, 130.3, 130.2, 128.9, 128.9, 128.5, 128.4, 128.1, 127.3, 126.8, 122.3, 122.0, 119.5, 61.1, 14.4. IR (KBr) 3261, 1681, 1639 cm^{-1}. HRMS (ESI) m/z calcd.for: $C_{26}H_{21}NaNO_3$ $[M + Na]^+$ 418.1410, found, 418.1425.

Ethyl 4-(2-bromobenzoyl)-5-phenyl-1H-pyrrole-2-carboxylate (5ga)



White solid (56 mg, yield 71%); mp 122 -125 °C. ^{1}H NMR (400 MHz, $CDCl_3$) δ 10.39 (s, 1H), 7.54 (dd, *J* = 6.5, 3.1 Hz, 2H), 7.47 (dd, *J* = 7.9, 0.7 Hz, 1H), 7.31 – 7.27 (m, 3H), 7.22 (td, *J* = 7.4, 1.1 Hz, 1H), 7.17 (td, *J* = 7.6, 1.9 Hz, 1H), 7.07 (d, *J* = 2.6 Hz, 1H), 4.11 (q, *J* = 7.1 Hz, 2H), 1.23 (t, *J* = 7.1 Hz, 3H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 190.7, 161.2, 141.8, 133.1, 130.8, 130.5, 129.2, 129.1, 128.1, 126.9, 122.7, 122.0, 119.6, 119.4, 61.1, 14.3. IR (KBr): 3240, 1683, 1652 cm^{-1}. HRMS (ESI) m/z calcd.for: $C_{20}H_{16}NaBrNO_3$ $[M + Na]^+$ 420.0212, found, 420.0198.

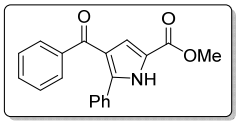
Ethyl 5-phenyl-4-(thiophene-2-carbonyl)-1H-pyrrole-2-carboxylate (5ha)



White solid (41 mg. yields 62%); mp 155-158 °C. ^{1}H NMR (400 MHz, $CDCl_3$) δ 10.27 (s, 1H), 7.61 (ddd, *J* = 13.9, 6.7, 2.3 Hz, 4H), 7.35 (dd, *J* = 4.7, 2.1 Hz, 4H), 7.06 (dd, *J* = 4.8, 3.9 Hz, 1H), 4.24 (q, *J* = 7.1 Hz, 2H), 1.31 (t, *J* = 7.1 Hz, 4H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 183.1, 161.3,

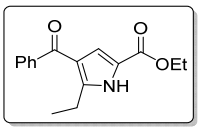
145.2, 140.2, 133.8, 133.4, 130.7, 130.2, 128.9, 128.8, 128.5, 127.8, 122.3, 121.8, 118.6, 61.1, 14.4. IR (KBr): 3272, 1683, 1622 cm^{-1} .HRMS (ESI) m/z calcd.for: $C_{18}H_{15}NaSNO_3$ $[M + Na]^+$ 348.0671, found, 348.0660.

Methyl 4-benzoyl-5-phenyl-1H-pyrrole-2-carboxylate (5ia)



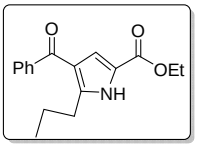
White solid (50 mg, yield 82%); mp 133-136 ^oC.^1H NMR (400 MHz, $CDCl_3$) δ 10.23 (s, 1H), 7.81 – 7.75 (m, 2H), 7.54 – 7.50 (m, 2H), 7.47 (t, *J* = 7.4 Hz, 1H), 7.36 (t, *J* = 7.6 Hz, 2H), 7.32 – 7.30 (m, 3H), 7.21 (d, *J* = 2.6 Hz, 1H), 3.77 (s, 3H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 191.7, 161.7, 140.9, 138.9, 132.2, 130.7, 129.6, 19.0, 128.8, 128.4, 128.1, 121.9, 121.9, 119.7, 77.4, 77.1, 76.8, 52.0. IR (KBr): 3269, 1684, 1627 cm^{-1}. HRMS (ESI) m/z calcd.for: $C_{19}H_{15}NaNO_3$ $[M + Na]^+$ 328.0950, found, 328.0960.

Ethyl 4-benzoyl-5-ethyl-1H-pyrrole-2-carboxylate (5ab)



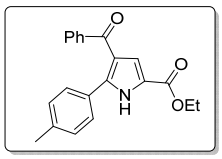
White solid (36 mg, yield 63%); mp 151 -154 ^oC.^1H NMR (400 MHz, $CDCl_3$) δ 10.40 (s, 1H), 7.86 – 7.69 (m, 1H), 7.54 (d, *J* = 7.3 Hz, 1H), 7.47 (t, *J* = 7.3 Hz, 2H), 7.10 (d, *J* = 2.4 Hz, 1H), 4.34 (q, *J* = 7.1 Hz, 2H), 3.10 (q, *J* = 7.5 Hz, 2H), 1.35 (dd, *J* = 13.8, 7.3 Hz, 6H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 191.9, 161.7, 147.0, 139.9, 131.6, 129.1, 128.2, 120.6, 120.3, 119.3, 60.9, 21.1 , 13.3. IR (KBr): 3279, 1687, 1657 cm^{-1}. HRMS (ESI) m/z calcd.for: $C_{16}H_{17}NaNO_3$ $[M + Na]^+$ 294.1106, found, 294.1110.

Ethyl 4-benzoyl-5-propyl-1H-pyrrole-2-carboxylate (5ac)



White solid (36 mg, yield 65%); mp 145-147 ^oC; ^1H NMR (400 MHz, $CDCl_3$) δ 10.64 (s, 1H), 7.86 – 7.77 (m, 2H), 7.57 (ddd, *J* = 11.1, 9.7, 6.3 Hz, 1H), 7.47 (t, *J* = 7.3 Hz, 3H), 7.11 (d, *J* = 2.4 Hz, 1H), 4.35 (q, *J* = 7.1 Hz, 2H), 3.10 – 2.95 (m, 2H), 1.83 – 1.69 (m, 2H), 1.41 – 1.32 (m, 3H), 0.98 (t, *J* = 7.4 Hz, 3H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 192.0, 161.8, 145.9, 139.9, 133.6, 131.6, 130.2, 129.1, 128.5, 128.2, 121.0, 120.3, 119.3, 60.9, 29.5, 22.6, 14.4, 13.9. IR (KBr): 3271, 1693, 1652 cm^{-1} HRMS (ESI) m/z calcd.for: $C_{17}H_{19}NaNO_3$ $[M + Na]^+$ 308.1263, found, 308.1260

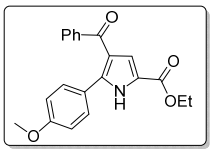
Ethyl 4-benzoyl-5-(p-tolyl)-1H-pyrrole-2-carboxylate (5ae)



White solid (50 mg, 75%); mp 154-158 ^oC; ^1H NMR (400 MHz, $CDCl_3$) δ 10.26 (d, *J* = 67.0 Hz, 1H), 7.73 – 7.68 (m, 2H), 7.39 (t, *J* = 7.4 Hz, 1H), 7.33 (d, *J* = 8.1 Hz, 2H), 7.28 (t, *J* = 7.6 Hz, 2H), 7.09 (t, *J* = 5.3 Hz, 1H), 7.02 (d, *J* = 7.9 Hz, 2H), 4.12 (q, *J* = 7.1 Hz, 2H), 2.23 (s, 3H), 1.19 (t, *J* = 7.1 Hz, 3H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 191.7, 161.4, 141.1, 139.1, 138.9, 132.0, 129.7,

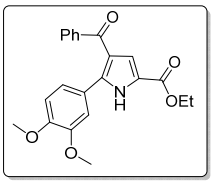
129.0, 128.7, 128.1, 127.9, 122.0, 121.6, 119.5, 61.0, 21.3, 14.4. IR (KBr): 3276, 1711, 1670, 1648 cm^{-1}. HRMS (ESI) m/z calcd.for: $C_{21}H_{19}NaNO_3[M + Na]^+$ 356.1263, found, 356.1252.

Ethyl 4-benzoyl-5-(4-methoxyphenyl)-1H-pyrrole-2-carboxylate (5af)



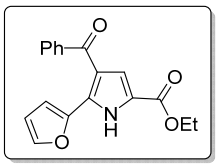
White solid (53 mg, yield 76%); mp 121-122 ^oC; ^1H NMR (400 MHz, $CDCl_3$) δ 10.44 (s, 1H), 7.81 (d, *J* = 8.6 Hz, 2H), 7.51 (d, *J* = 3.6 Hz, 2H), 7.29 (d, *J* = 3.3 Hz, 3H), 7.19 (d, *J* = 2.0 Hz, 1H), 6.85 (d, *J* = 8.6 Hz, 2H), 4.19 (q, *J* = 7.1 Hz, 2H), 3.82 (s, 3H), 1.27 (t, *J* = 7.1 Hz, 3H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 190.6, 163.0, 161.4, 140.2, 132.1, 131.5, 130.9, 128.8, 128.7, 128.3, 122.2, 122.2, 119.1, 113.4, 77.5, 77.1, 76.8, 61.0, 55.4, 14.4. IR (KBr): 3140, 1704, 1626, 1566 cm^{-1}. HRMS (ESI) m/z calcd.for: $C_{21}H_{19}NaNO_4$ $[M + Na]^+$ 372.1212, found, 372.1202.

Ethyl 4-benzoyl-5-(3,4-dimethoxyphenyl)-1H-pyrrole-2-carboxylate (5ag)



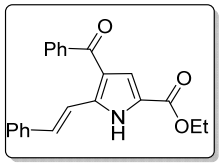
Yellow liquid (48 mg, yield 63%); ^1H NMR (400 MHz, $CDCl_3$) δ 10.12 (s, 1H), 7.80 – 7.70 (m, 1H), 7.49 – 7.44 (m, 1H), 7.36 (t, *J* = 7.6 Hz, 1H), 7.20 (t, *J* = 8.0 Hz, 1H), 7.15 – 7.02 (m, 1H), 6.81 (d, *J* = 8.3 Hz, 1H), 4.24 (q, *J* = 7.1 Hz, 1H), 3.86 (s, 2H), 3.79 (s, 1H), 1.30 (t, *J* = 7.1 Hz, 1H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 191.8, 161.3, 149.7, 148.6, 140.7, 139.1, 132.1, 129.6, 128.1, 123.5, 121.9, 121.5, 121.3, 119.6, 112.5, 110.9, 61.0, 55.9, 55.9, 14.4. IR (KBr): 3269, 1673, 1621 cm^{-1}. HRMS (ESI) m/z calcd.for: $C_{22}H_{22}NO_5$ $[M + H]^+$ 380.1500, found, 380.1520.

Ethyl 4-benzoyl-5-(furan-2-yl)-1H-pyrrole-2-carboxylate (5aj)



White solid (40 mg, yield 65%); mp 154-157 ^oC. ^1H NMR (400 MHz, $CDCl_3$) δ 9.79 (s, 1H), 7.77 – 7.71 (m, 2H), 7.60 (d, *J* = 3.2 Hz, 1H), 7.55 – 7.44 (m, 1H), 7.40 (dd, *J* = 12.8, 4.5 Hz, 3H), 7.05 (d, *J* = 2.7 Hz, 1H), 6.45 (dd, *J* = 3.5, 1.8 Hz, 1H), 4.28 (q, *J* = 7.1 Hz, 2H), 1.29 (t, *J* = 7.1 Hz, 3H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 190.9, 160.7, 145.2, 143.0, 139.6, 131.9, 130.8, 130.2, 129.3, 128.3, 121.6, 120.2, 119.8, 113.1, 112.5, 61.0, 14.4. IR (KBr): 3289, 1690, 1637 cm^{-1}. HRMS (ESI) m/z calcd.for: $C_{18}H_{15}NaNO_4$ $[M + Na]^+$ 332.0899, found, 332.0890.

Ethyl (E)-4-benzoyl-5-styryl-1H-pyrrole-2-carboxylate (5ak)

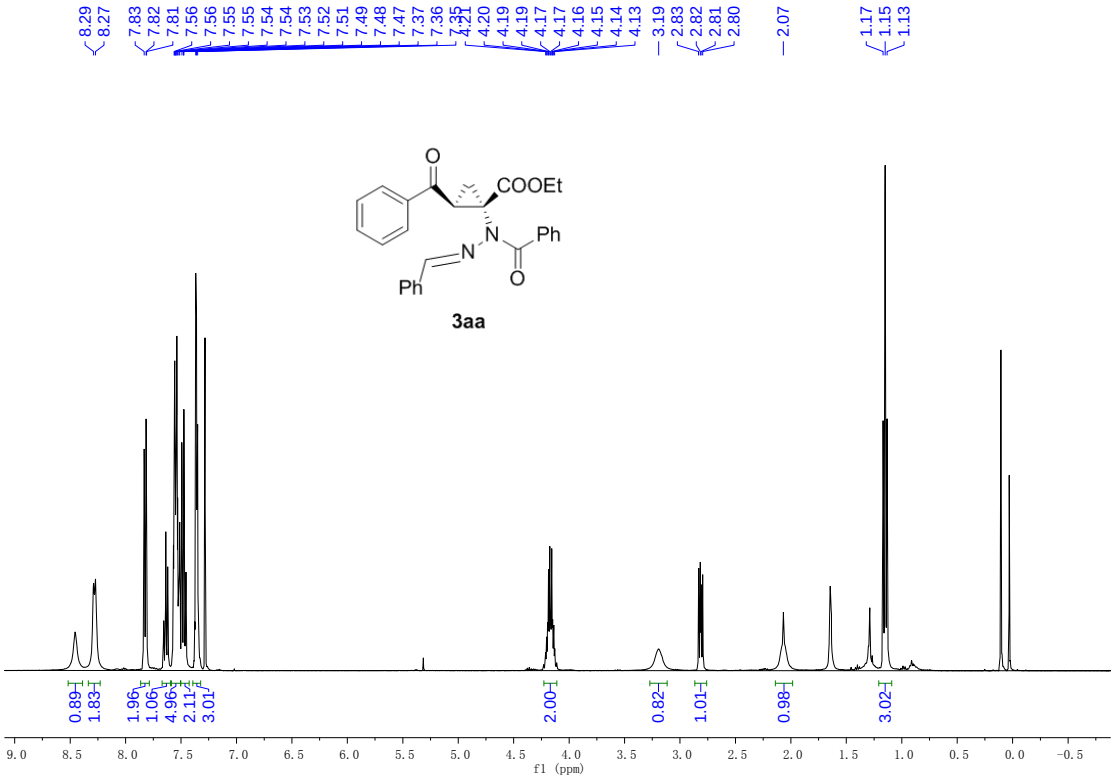


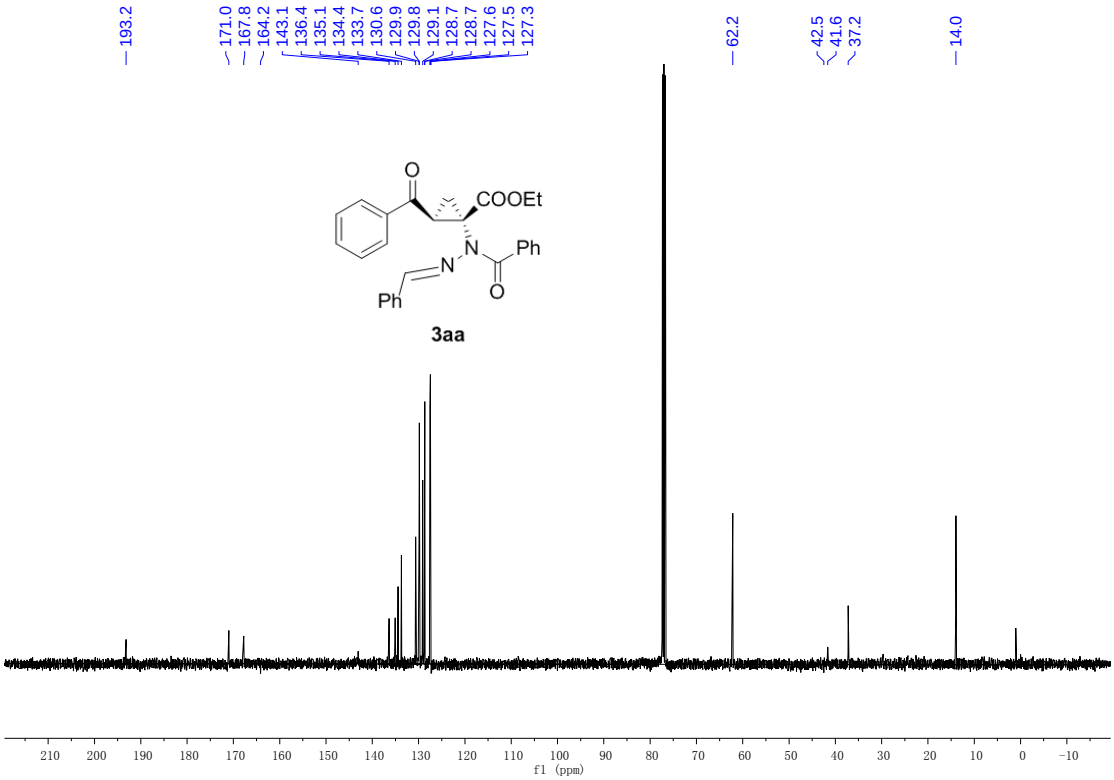
Yellow liquid (34 mg, yield 49%); ^1H NMR (400 MHz, $CDCl_3$) δ 10.38 (s, 1H), 7.84 (d, *J* = 7.3 Hz, 1H), 7.78 (d, *J* = 16.9 Hz, 1H), 7.52 (dt, *J* = 17.0, 7.3 Hz, 3H), 7.35 (t, *J* = 7.3 Hz, 1H), 7.31 – 7.23 (m, 1H), 7.14 (d, *J* = 2.3 Hz, 1H), 4.40 – 4.30 (m, 1H), 1.33 (t, *J* = 7.1 Hz, 2H). ^{13}C NMR

(101 MHz, $CDCl_3$) δ 191.96, 161.4, 139.7, 139.3, 136.3, 132.0, 130.2, 129.3, 128.8, 128.3, 127.0, 122.5, 122.2, 119.6, 117.2, 61.3, 14.4. IR (KBr): 3278, 1687, 1635 cm^{-1}. HRMS (ESI) m/z calcd.for: $C_{22}H_{19}NaNO_3$ $[M + Na]^+$ 368.1263, found, 368.1244.

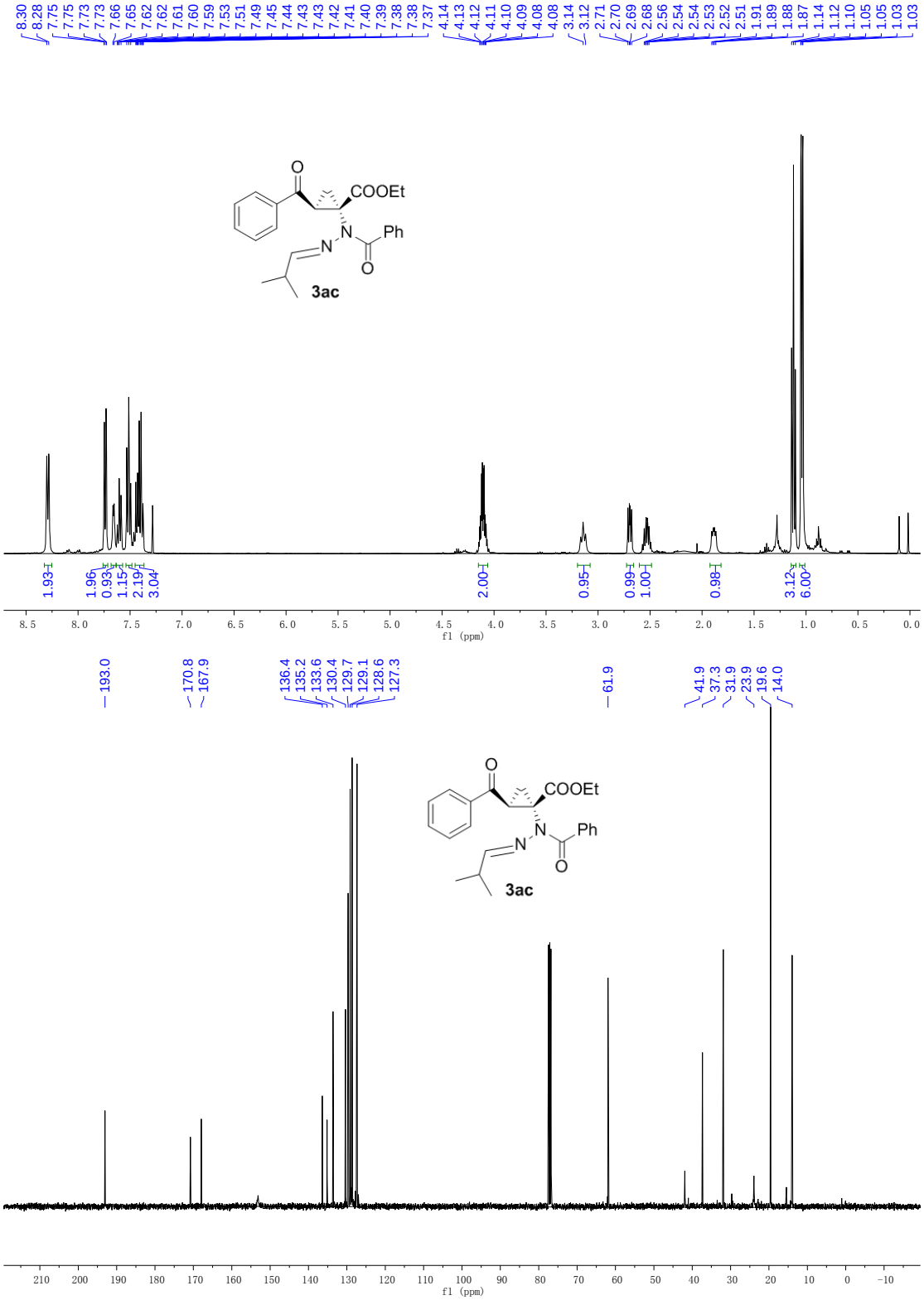
(3) Copies of ^1H and ^{13}C NMR spectra of products

1. 3aa

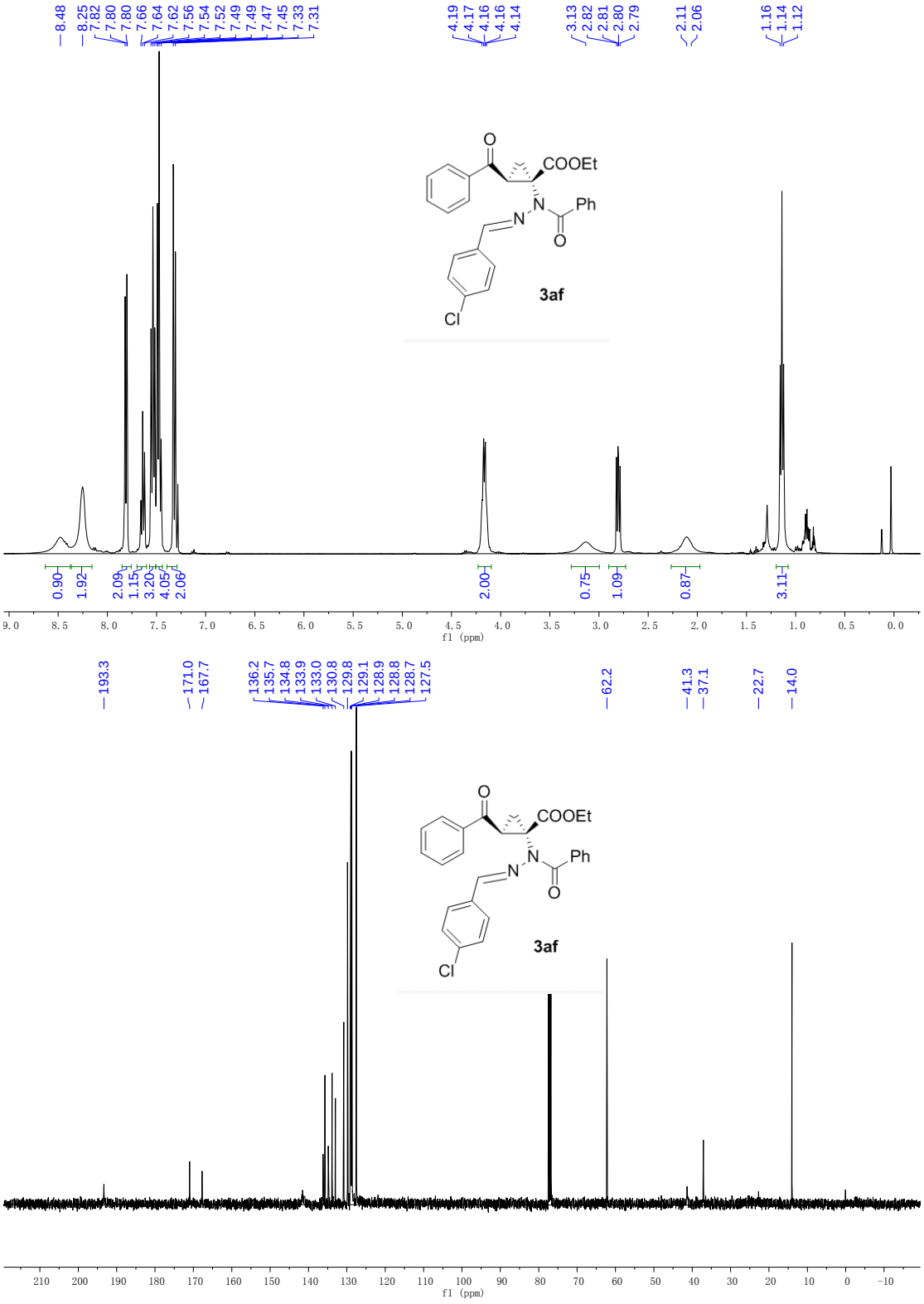




2. 3ac

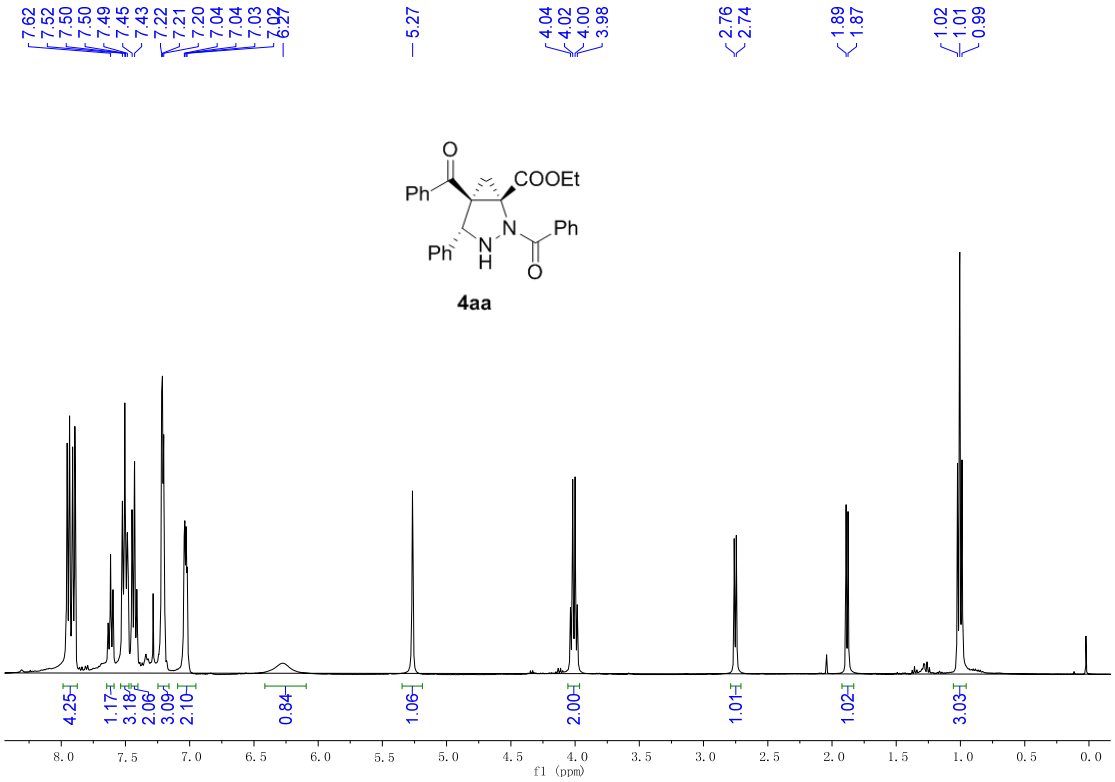

8.30 8.28 7.75 7.75 7.73 7.73 7.66 7.65 7.62 7.62 7.61 7.60 7.59 7.53 7.51 7.49 7.45 7.44 7.43 7.43 7.42 7.41 7.40 7.39 7.38 7.38 7.37 4.14 4.13 4.12 4.11 4.10 4.09 4.08 4.08 3.14 3.12 2.71 2.70 2.69 2.68 2.56 2.54 2.54 2.53 2.52 2.51 1.91 1.89 1.88 1.87 1.14 1.12 1.10 1.05 1.05 1.03 1.03
COOEt
Ph
3ac
1.93 1.96 0.93 1.15 2.19 3.04 2.00 0.95 0.99 1.00 0.98 3.12 6.00
f1 (ppm)
193.0 170.8 167.9 136.4 135.2 133.6 130.4 129.7 129.1 128.6 127.3 61.9 41.9 37.3 31.9 23.9 19.6 14.0
f1 (ppm)

3. 3af



^{1}H NMR and ^{13}C NMR of compound **4**(trans) and **5** were detected by its $CDCl_3$ solution, while the cis isomers were detected by its DMSO solution.

4. 4aa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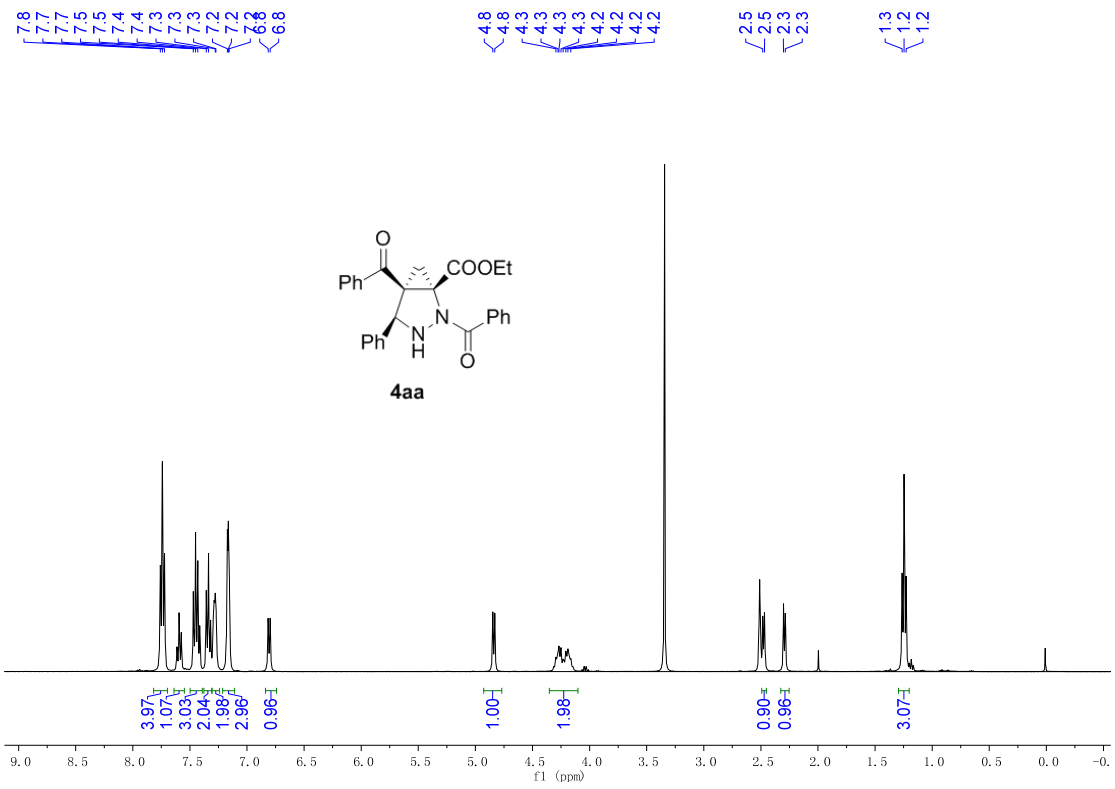
7.49
7.45
7.43
7.22
7.21
7.20
7.04
7.04
7.03
7.02
6.27
5.27
4.04
4.02
4.00
3.98
2.76
2.74
1.89
1.87
1.02
1.01
0.99
O
Ph
COOEt
N
Ph
Ph
N
H
O
4aa
4.25
1.17
3.18
2.06
3.09
2.10
0.84
1.06
2.00
1.01
1.02
3.03
f1 (ppm)


7.8
7.7
7.7
7.5
7.5
7.4
7.4
7.3
7.3
7.3
7.2
7.2
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4.8
4.8
4.3
4.3
4.3
4.2
4.2
4.2
4.2
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2.3
1.3
1.2
1.2
O
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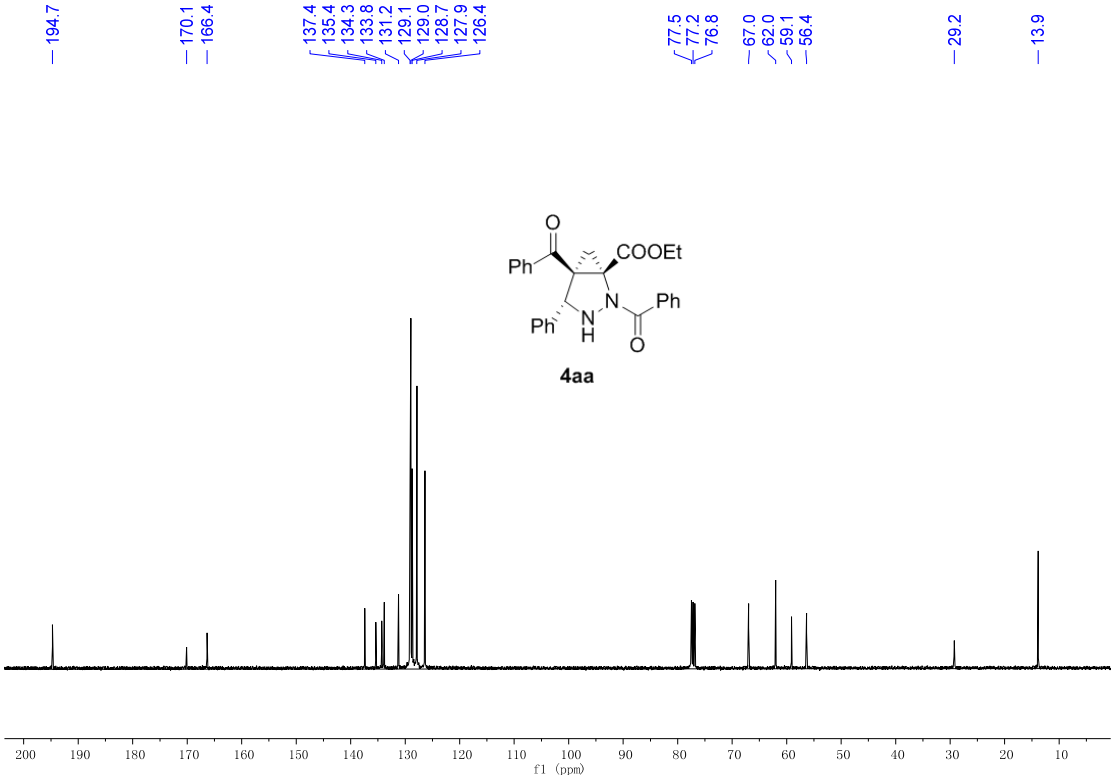
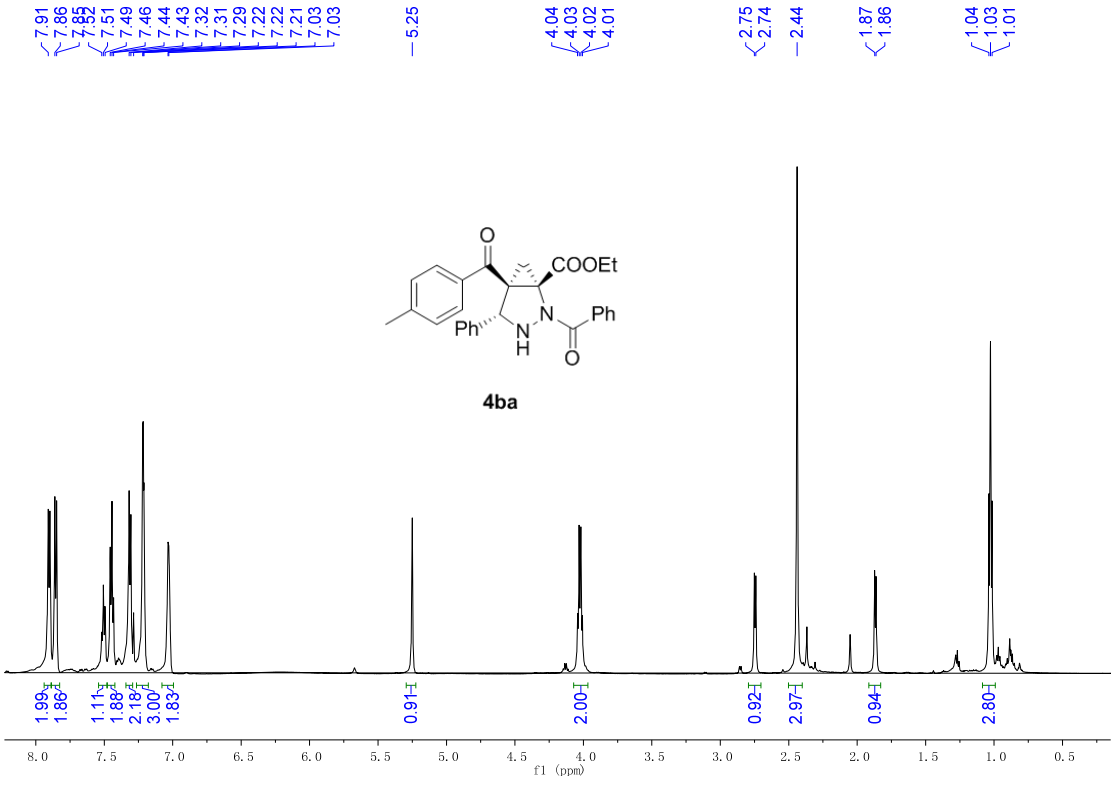
N
Ph
Ph
N
H
O
4aa
3.97
1.07
3.03
2.04
1.98
2.96
0.96
1.00
1.98
0.90
0.96
3.07
f1 (ppm)


194.7
170.1
166.4
137.4
135.4
134.3
133.8
131.2
129.1
129.0
128.7
127.9
126.4
77.5
77.2
76.8
67.0
62.0
59.1
56.4
29.2
13.9
O
Ph
COOEt
N
Ph
Ph
N
H
O
4aa
200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10
f1 (ppm)

5. 4ba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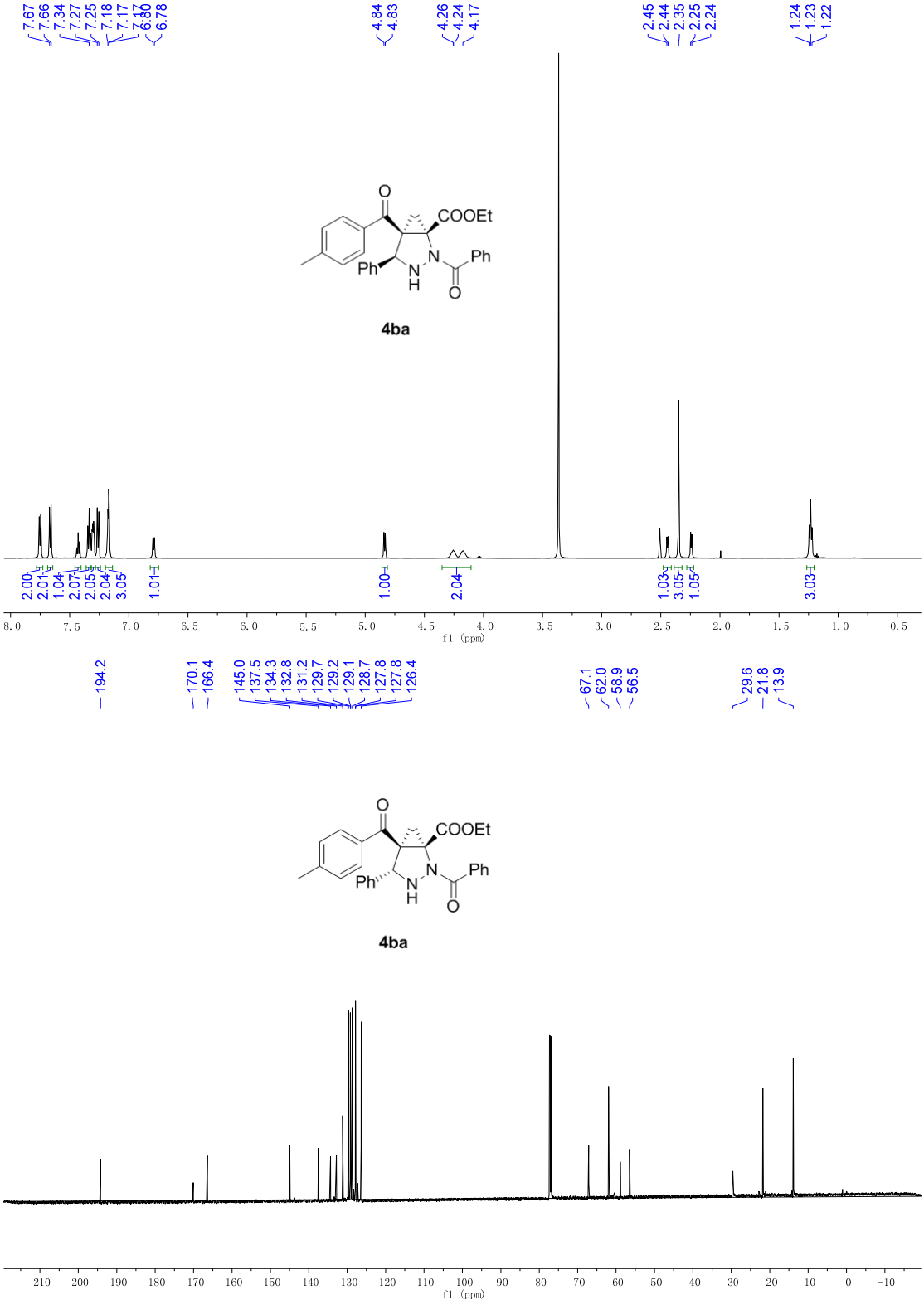
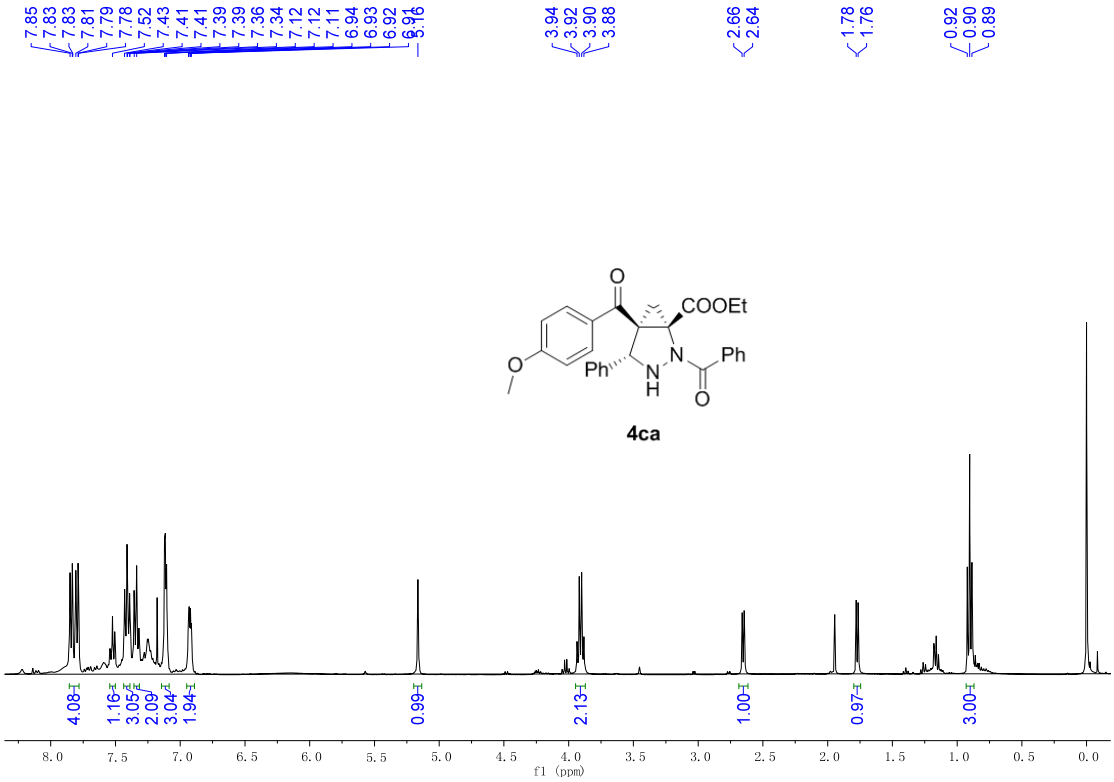
7.51
7.49
7.46
7.44
7.43
7.32
7.31
7.29
7.22
7.22
7.21
7.03
7.03
5.25
4.04
4.03
4.02
4.01
2.75
2.74
2.44
1.87
1.86
1.04
1.03
1.01
O
COOEt
Ph
N
Ph
N
H
O
4ba
1.99
1.86
1.11
1.88
2.18
3.00
1.83
0.91
2.00
0.92
2.97
0.94
2.80
8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5
f1 (ppm)


7.67
7.66
7.34
7.27
7.25
7.18
7.17
7.12
6.80
6.78
4.84
4.83
4.26
4.24
4.17
2.45
2.44
2.35
2.25
2.24
1.24
1.23
1.22
COOEt
Ph
N
H
N
Ph
O
O
4ba
2.00
2.01
1.04
2.07
2.05
2.04
3.05
1.01
1.00
2.04
1.03
3.05
1.05
3.03
f1 (ppm)
194.2
170.1
166.4
145.0
137.5
134.3
132.8
131.2
129.7
129.2
129.1
128.7
127.8
127.8
126.4
67.1
62.0
58.9
56.5
29.6
21.8
13.9
f1 (ppm)

6. 4ca


7.85
7.83
7.83
7.81
7.79
7.78
7.52
7.43
7.41
7.41
7.39
7.39
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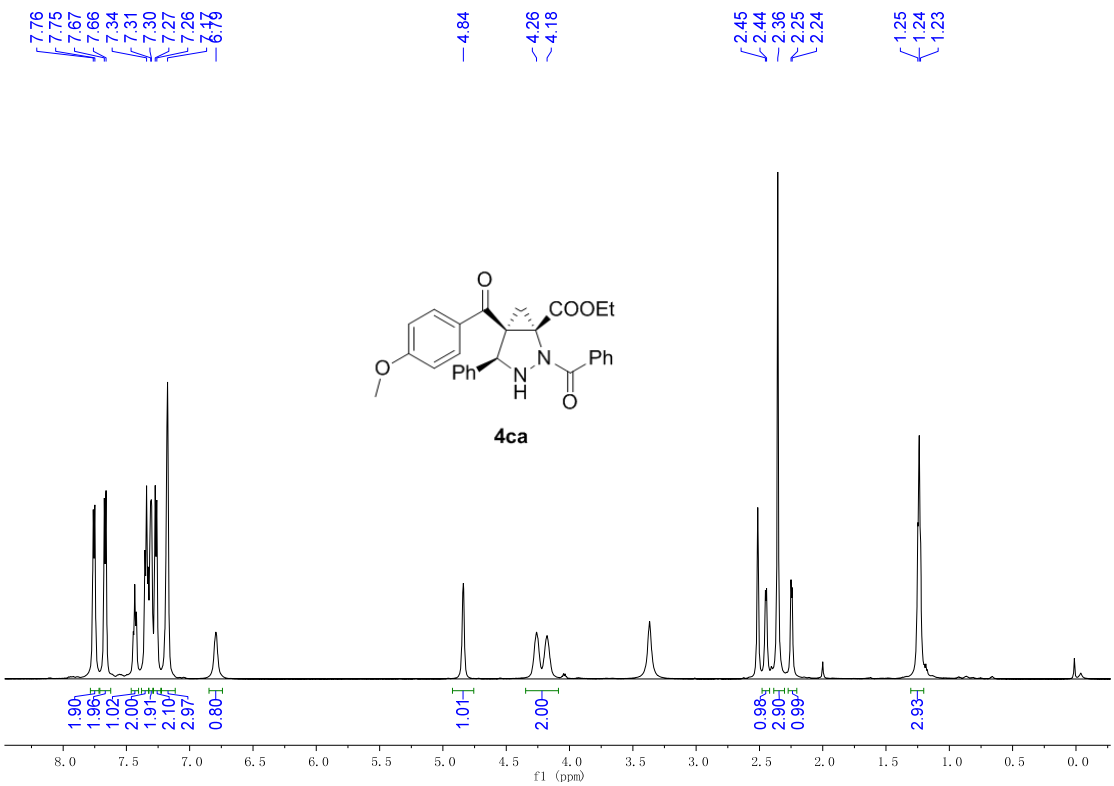
7.34
7.12
7.12
7.11
6.94
6.93
6.92
3.94
3.92
3.90
3.88
2.66
2.64
1.78
1.76
0.92
0.90
0.89
O
COOEt
O
Ph
N
N
H
Ph
O
4ca
4.08
1.16
3.05
2.09
3.04
1.94
0.99
2.13
1.00
0.97
3.00
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
f1 (ppm)


7.76
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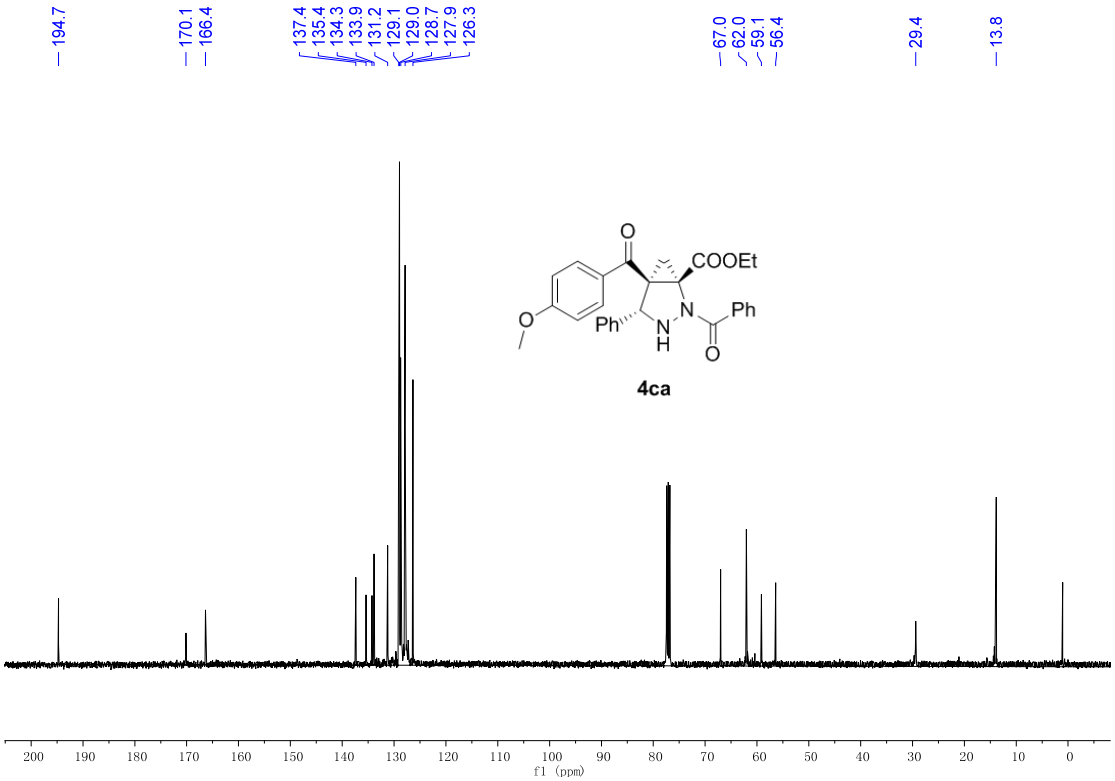
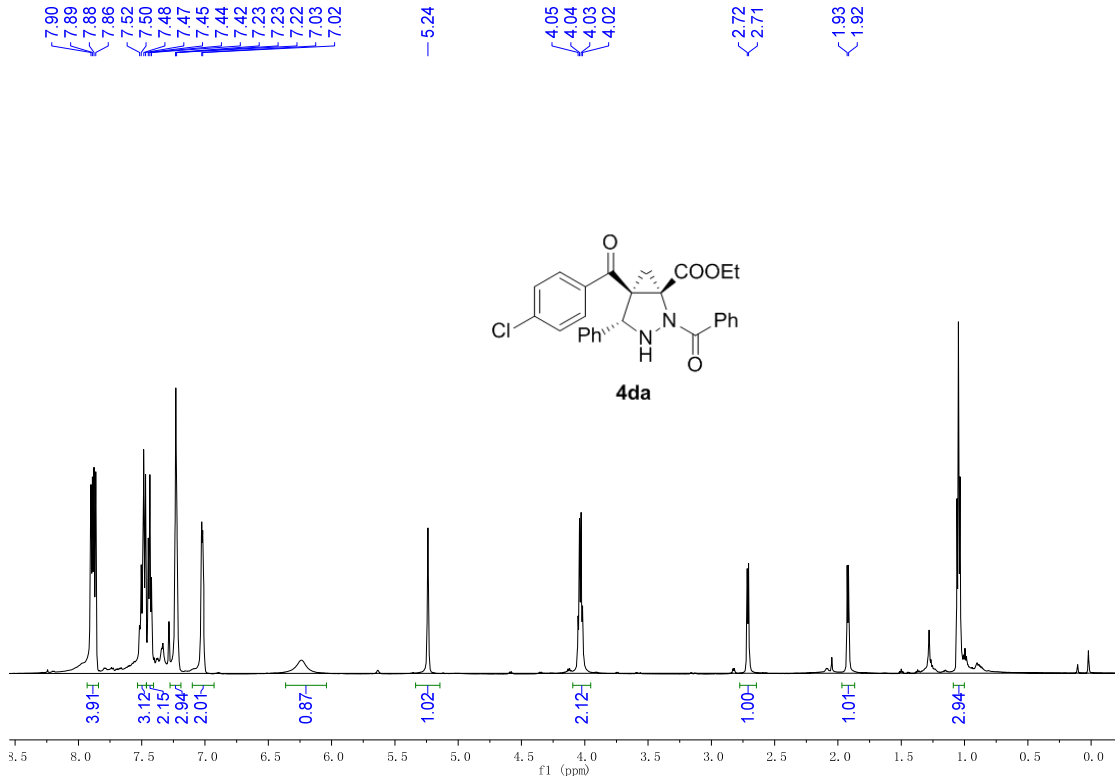
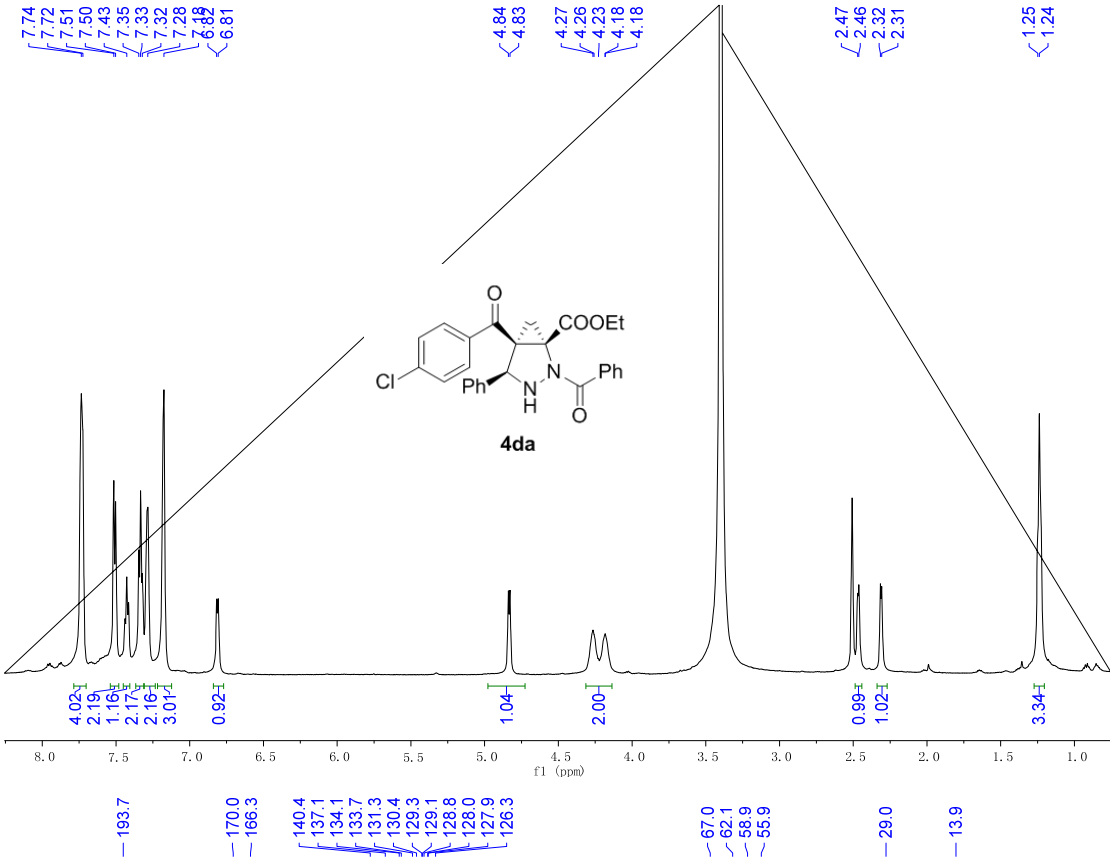
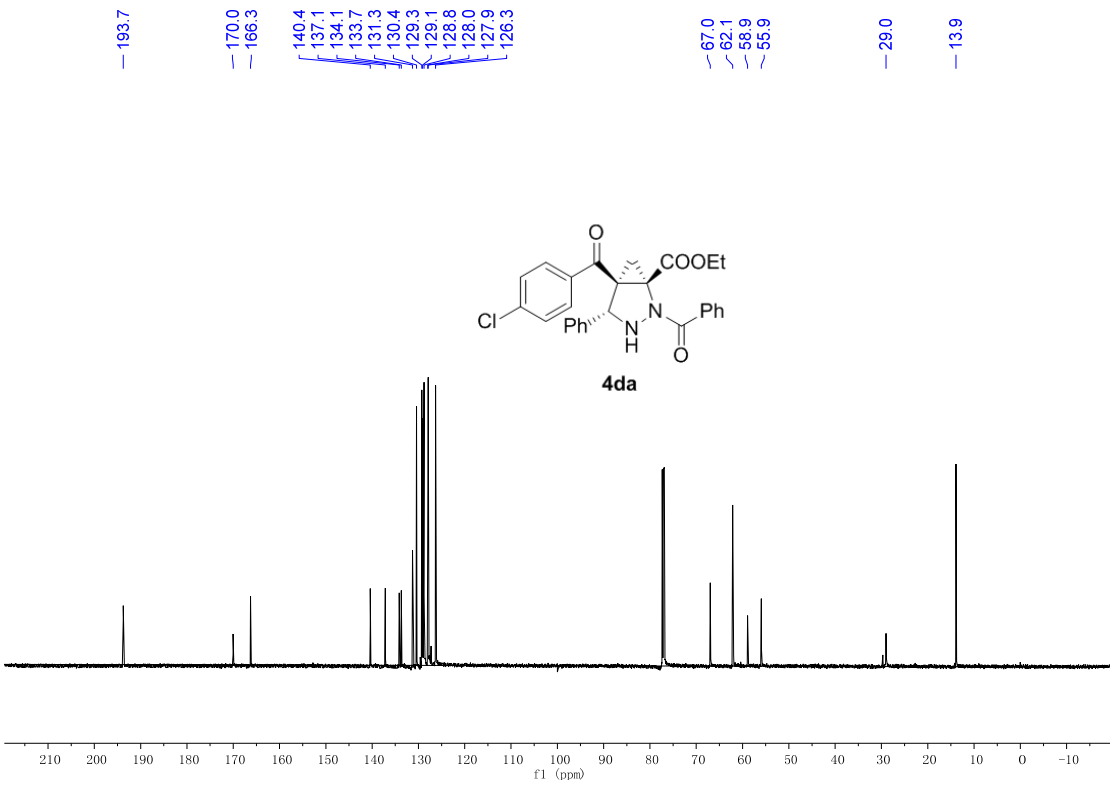
7.66
7.34
7.31
7.30
7.27
7.26
4.84
4.26
4.18
2.45
2.44
2.36
2.25
2.24
1.25
1.24
1.23
O
COOEt
O
Ph
N
N
H
Ph
O
4ca
1.90
1.96
1.02
2.00
1.91
2.10
2.97
0.80
1.01
2.00
0.98
2.90
0.99
2.93
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
f1 (ppm)


194.7
170.1
166.4
137.4
135.4
134.3
133.9
131.2
129.1
129.0
128.7
127.9
126.3
67.0
62.0
59.1
56.4
29.4
13.8
O
COOEt
O
Ph
N
N
H
Ph
O
4ca
200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0
f1 (ppm)

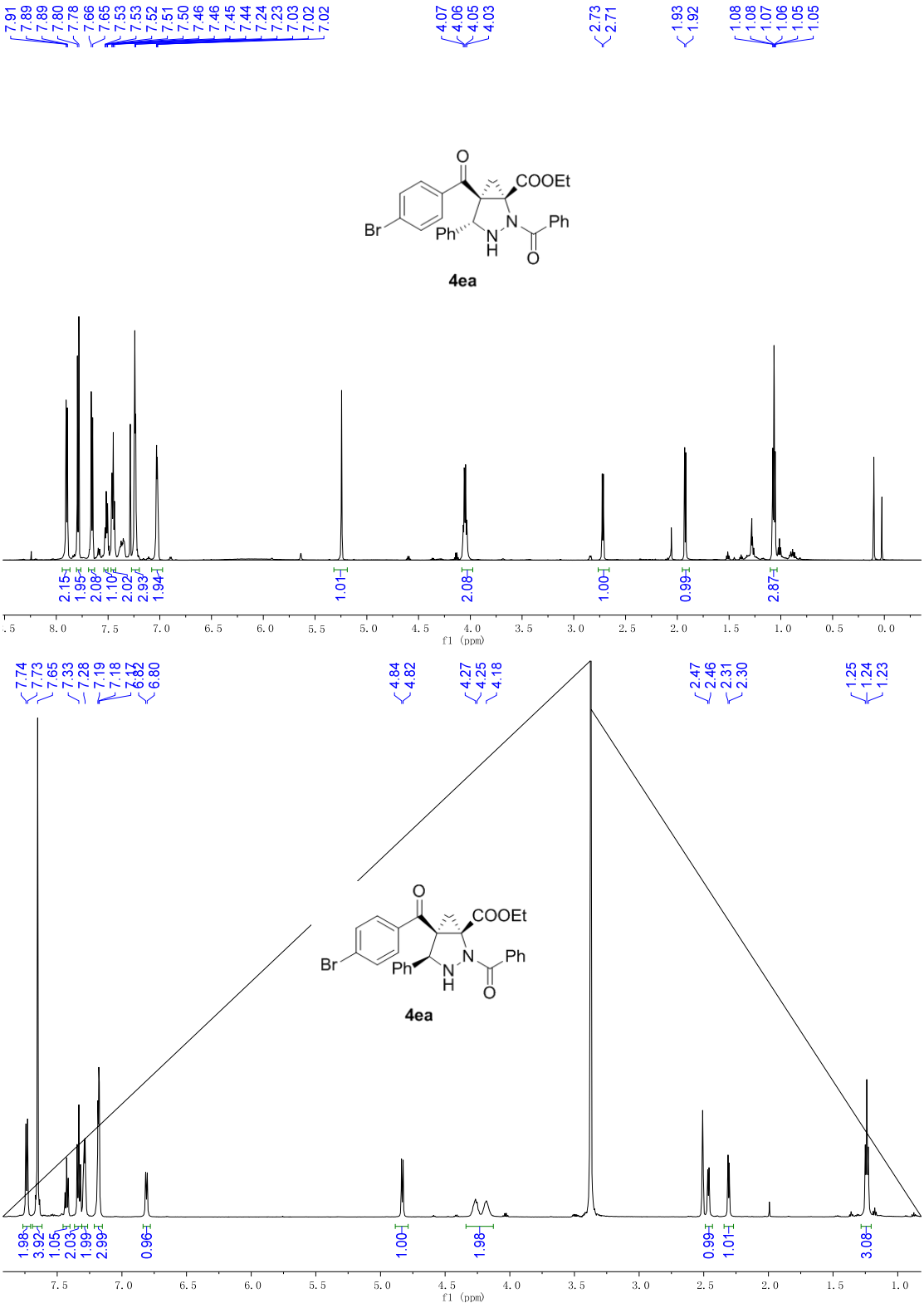
7. **4da**

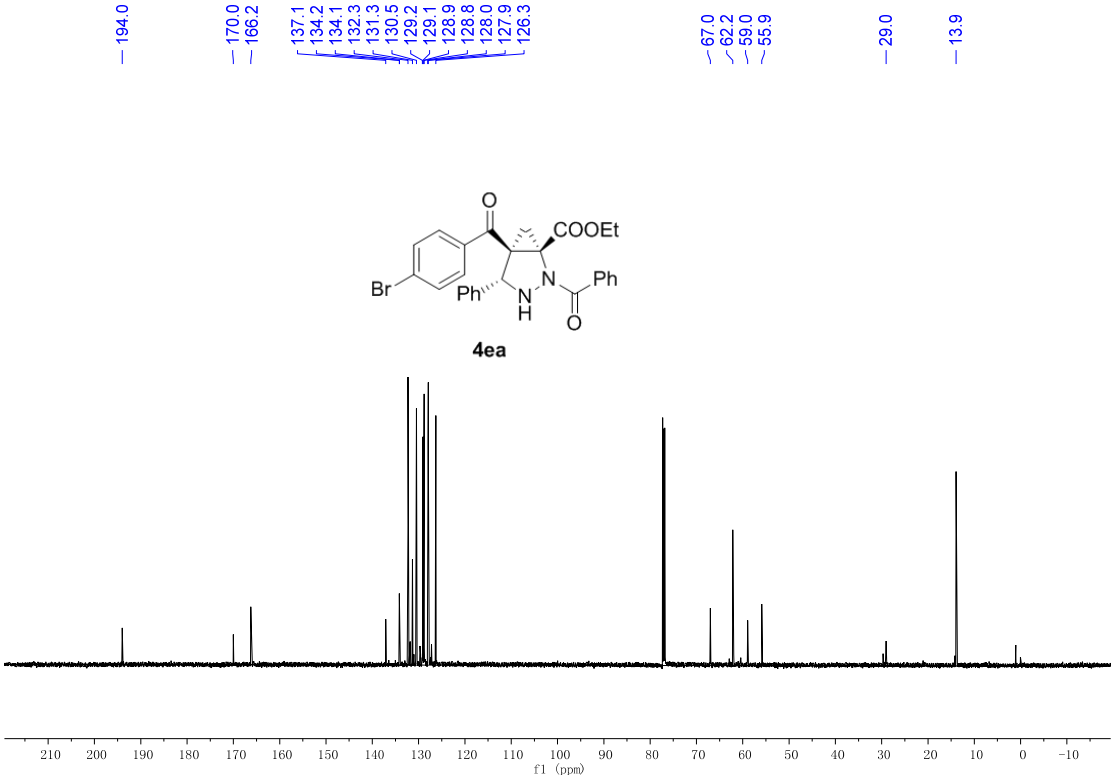

7.90
7.89
7.88
7.86
7.52
7.50
7.48
7.47
7.45
7.44
7.42
7.23
7.23
7.22
7.03
7.02
5.24
4.05
4.04
4.03
4.02
2.72
2.71
1.93
1.92
O
COOEt
Cl
Ph
N
N
H
Ph
O
4da
3.91
3.12
2.15
2.94
2.01
0.87
1.02
2.12
1.00
1.01
2.94
8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0
f1 (ppm)


7.74
7.72
7.51
7.50
7.43
7.35
7.33
7.32
7.28
7.18
6.82
6.81
4.84
4.83
4.27
4.26
4.23
4.18
4.18
2.47
2.46
2.32
2.31
1.25
1.24
O
COOEt
Cl
Ph
N
N
H
Ph
O
4da
4.02
2.19
1.16
2.17
2.16
3.01
0.92
1.04
2.00
0.99
1.02
3.34
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
f1 (ppm)

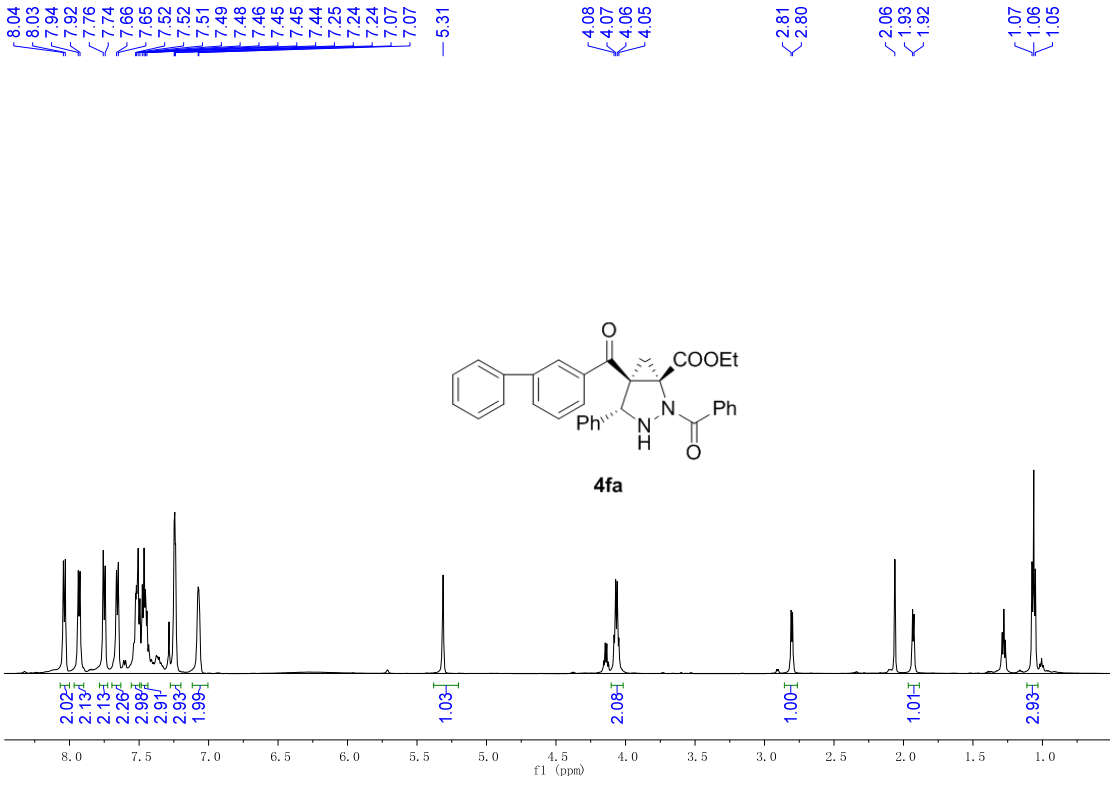

193.7
170.0
166.3
140.4
137.1
134.1
133.7
131.3
130.4
129.3
129.1
128.8
128.0
127.9
126.3
67.0
62.1
58.9
55.9
29.0
13.9
O
COOEt
Cl
Ph
N
N
H
Ph
O
4da
210
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
-10
f1 (ppm)

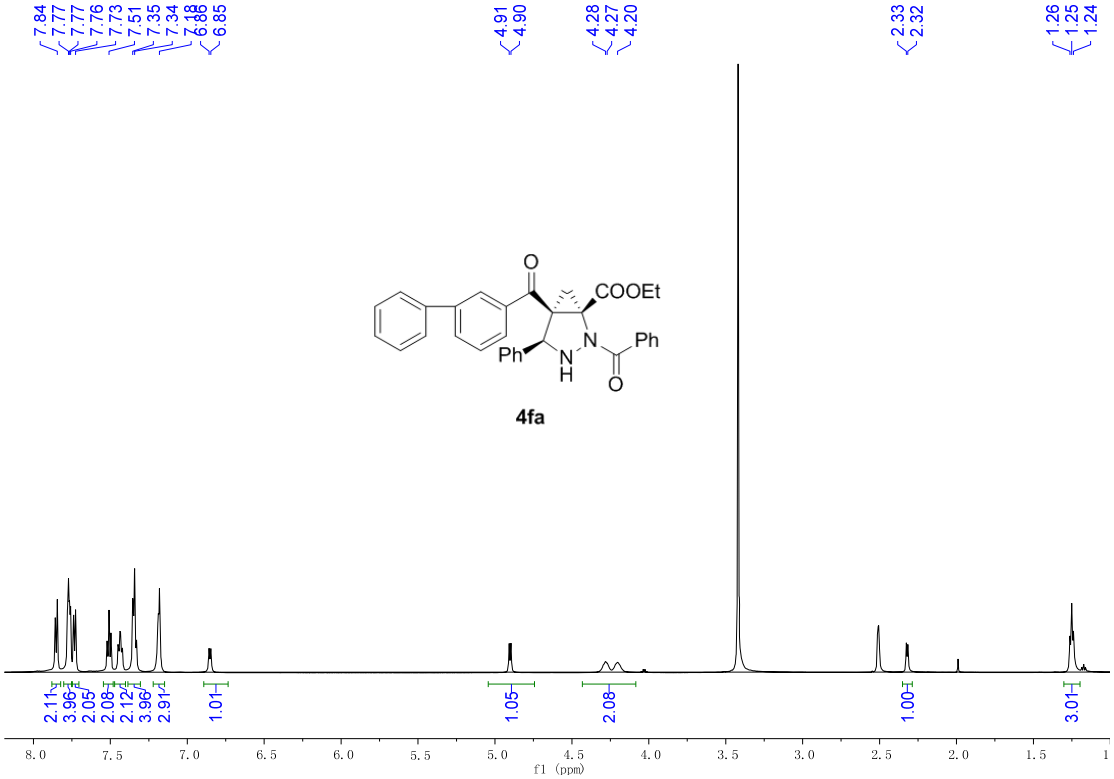
8. 4ea

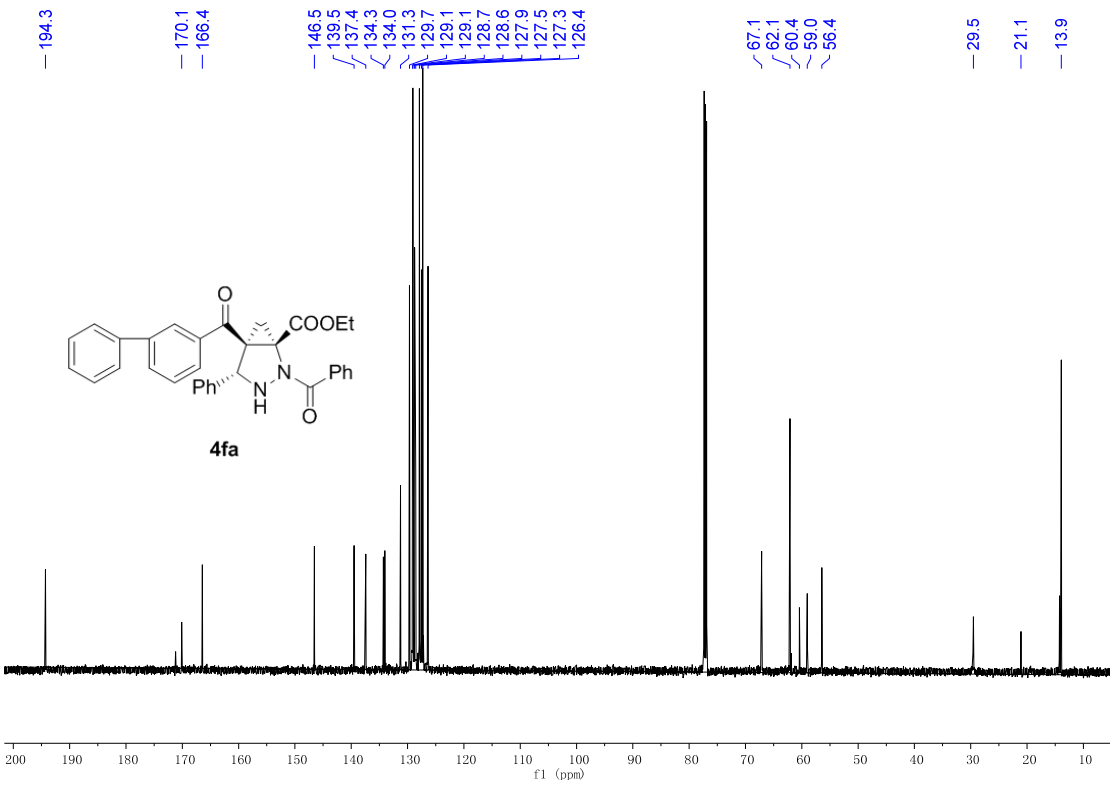

7.91
7.89
7.89
7.80
7.78
7.66
7.65
7.53
7.53
7.52
7.51
7.50
7.46
7.46
7.45
7.44
7.24
7.23
7.03
7.02
7.02
4.07
4.06
4.05
4.03
2.73
2.71
1.93
1.92
1.08
1.08
1.07
1.06
1.05
1.05
O
COOEt
Br
Ph
N
H
N
Ph
O
4ea
2.15
1.95
2.08
1.10
2.02
2.93
1.94
1.01
2.08
1.00
0.99
2.87
f1 (ppm)
7.74
7.73
7.65
7.33
7.28
7.19
7.18
6.82
6.80
4.84
4.82
4.27
4.25
4.18
2.47
2.46
2.31
2.30
1.25
1.24
1.23
O
COOEt
Br
Ph
N
H
N
Ph
O
4ea
1.98
3.92
1.05
2.03
1.99
2.99
0.96
1.00
1.98
0.99
1.01
3.08
f1 (ppm)


194.0
170.0
166.2
137.1
134.2
134.1
132.3
131.3
130.5
129.2
129.1
128.9
128.8
128.0
127.9
126.3
67.0
62.2
59.0
55.9
29.0
13.9
O
COOEt
Br
Ph
N
N
H
Ph
O
4ea
f1 (ppm)

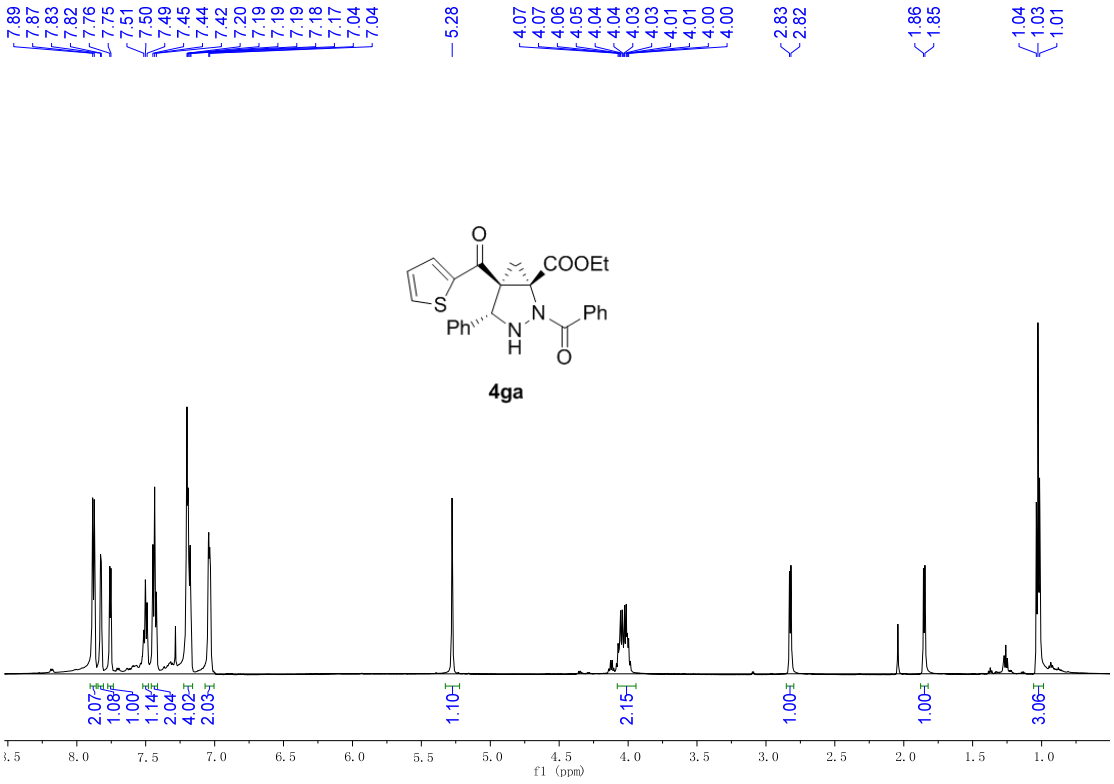
9. **4fa**

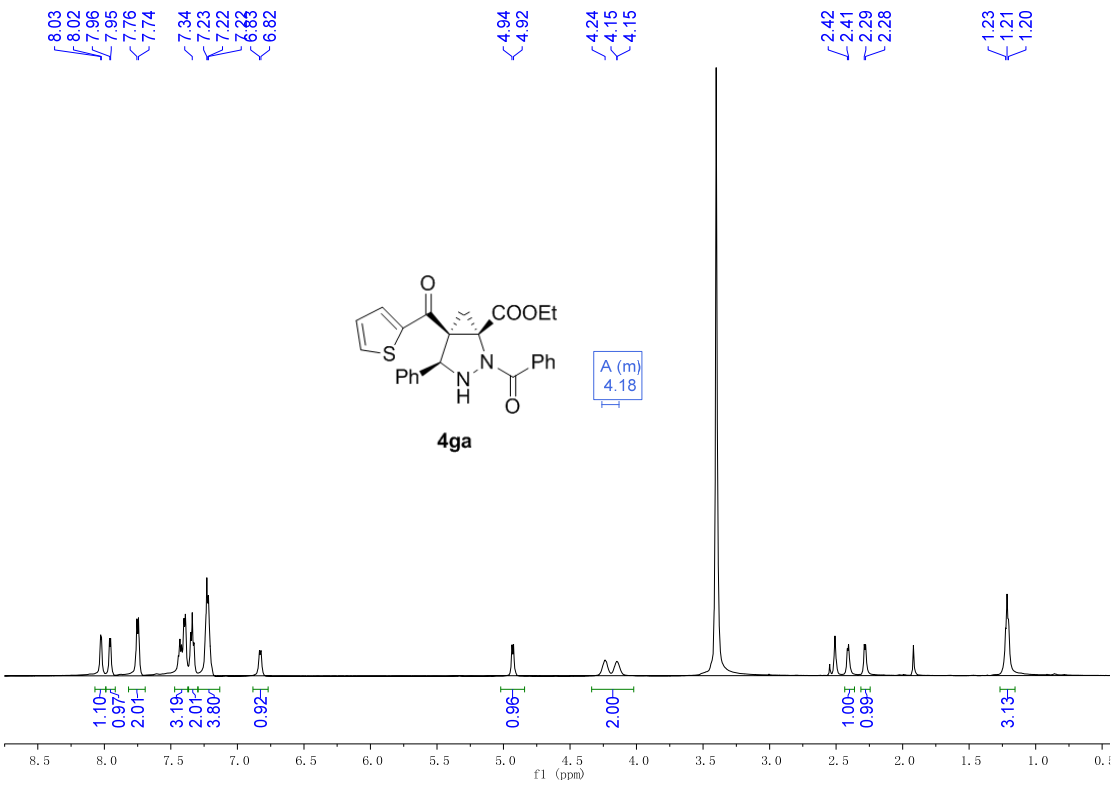

8.04
8.03
7.94
7.92
7.76
7.74
7.66
7.65
7.52
7.52
7.51
7.49
7.48
7.46
7.45
7.45
7.44
7.25
7.24
7.24
7.07
7.07
5.31
4.08
4.07
4.06
4.05
2.81
2.80
2.06
1.93
1.92
1.07
1.06
1.05
O
COOEt
Ph
N
N
H
Ph
O
4fa
2.02
2.13
2.13
2.26
2.98
2.91
2.93
1.99
1.03
2.08
1.00
1.01
2.93
f1 (ppm)

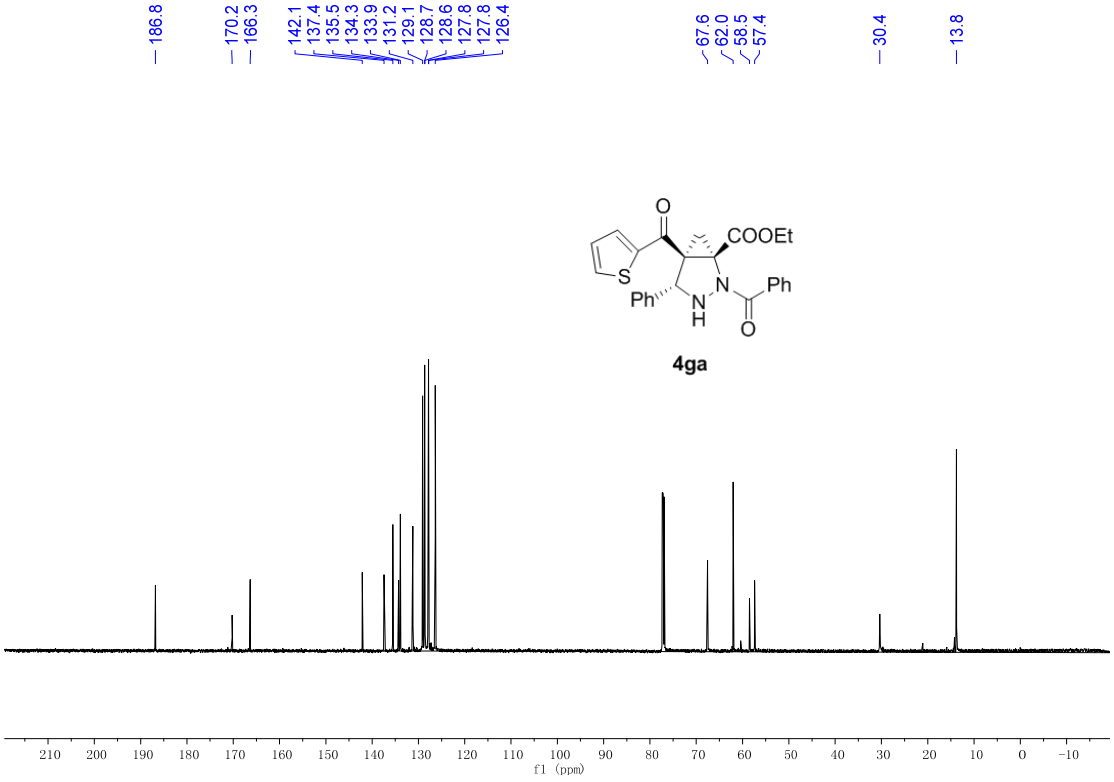

7.84
7.77
7.77
7.76
7.73
7.51
7.35
7.34
6.88
6.85
4.91
4.90
4.28
4.27
4.20
2.33
2.32
1.26
1.25
1.24
O
COOEt
Ph
N
H
N
Ph
O
4fa
2.11
3.96
2.05
2.08
2.12
3.96
2.91
1.01
1.05
2.08
1.00
3.01
f1 (ppm)


194.3
170.1
166.4
146.5
139.5
137.4
134.3
134.0
131.3
129.7
129.1
129.1
128.7
128.6
127.9
127.5
127.3
126.4
67.1
62.1
60.4
59.0
56.4
29.5
21.1
13.9
O
COOEt
Ph
N
H
N
Ph
O
4fa
f1 (ppm)

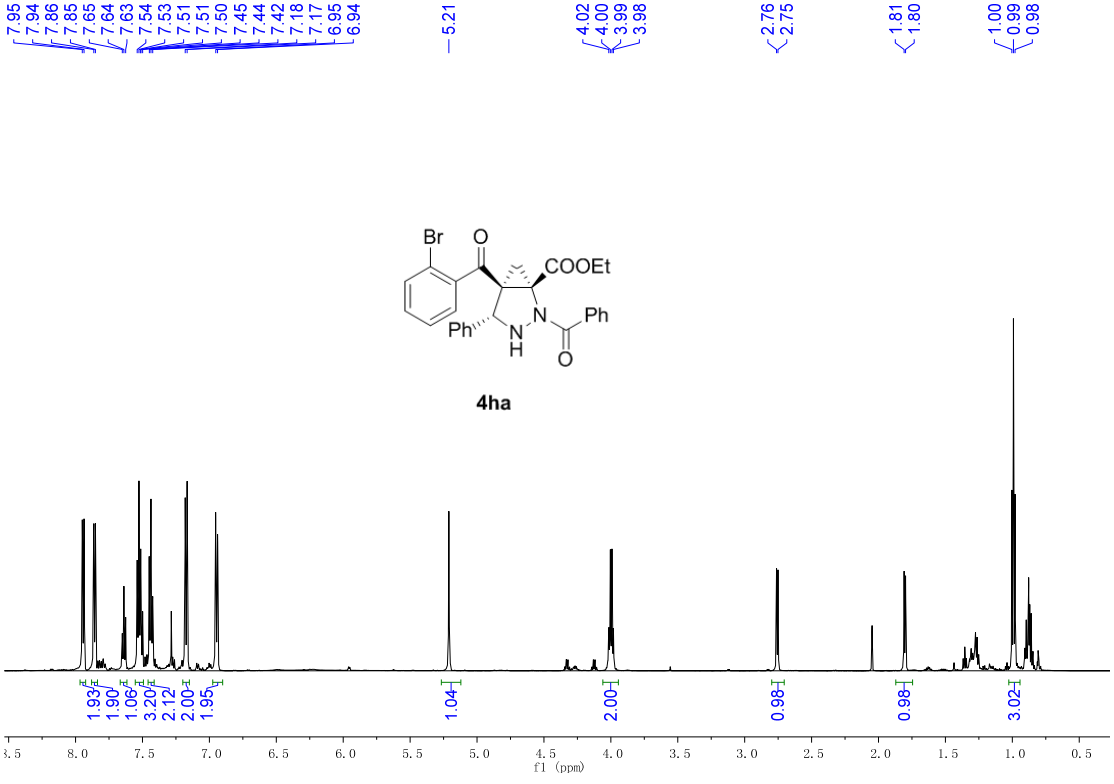
10.4ga

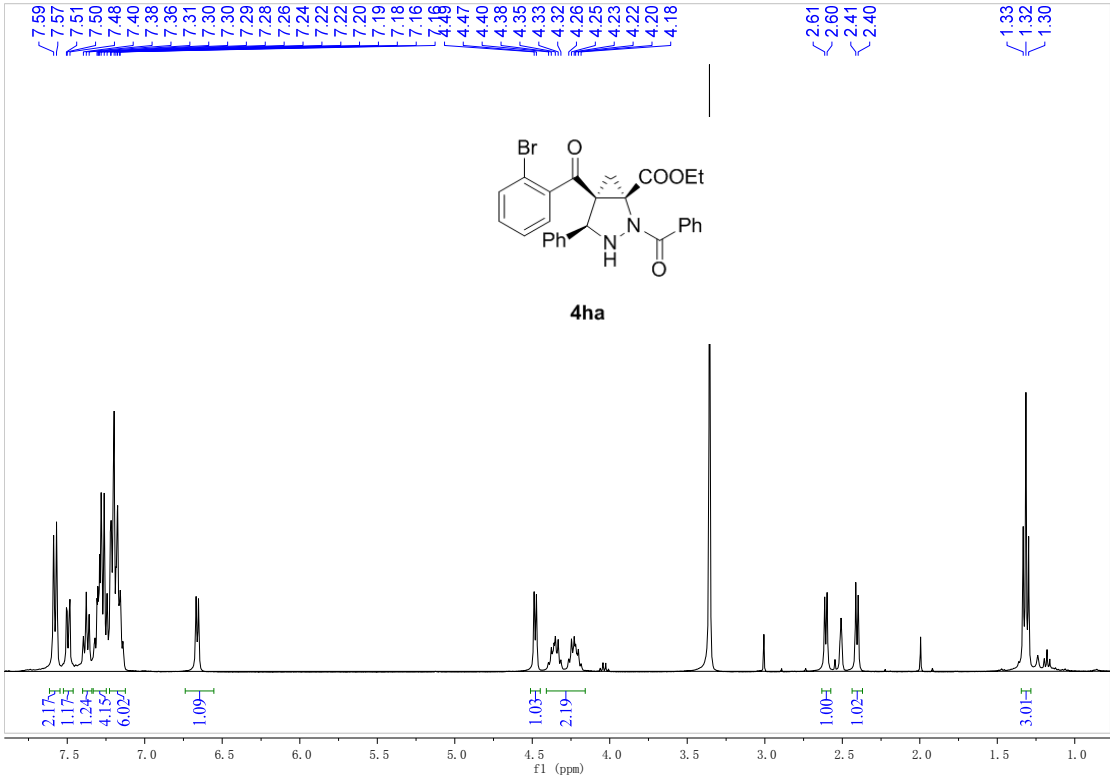

7.89
7.87
7.83
7.82
7.76
7.75
7.51
7.50
7.49
7.45
7.44
7.42
7.20
7.19
7.19
7.19
7.18
7.17
7.04
7.04
5.28
4.07
4.07
4.06
4.05
4.04
4.04
4.03
4.03
4.01
4.01
4.00
4.00
2.83
2.82
1.86
1.85
1.04
1.03
1.01
COOEt
Ph
Ph
N
H
N
O
O
S
4ga
2.07
1.08
1.00
1.14
2.04
4.02
2.03
1.10
2.15
1.00
1.00
3.06
f1 (ppm)

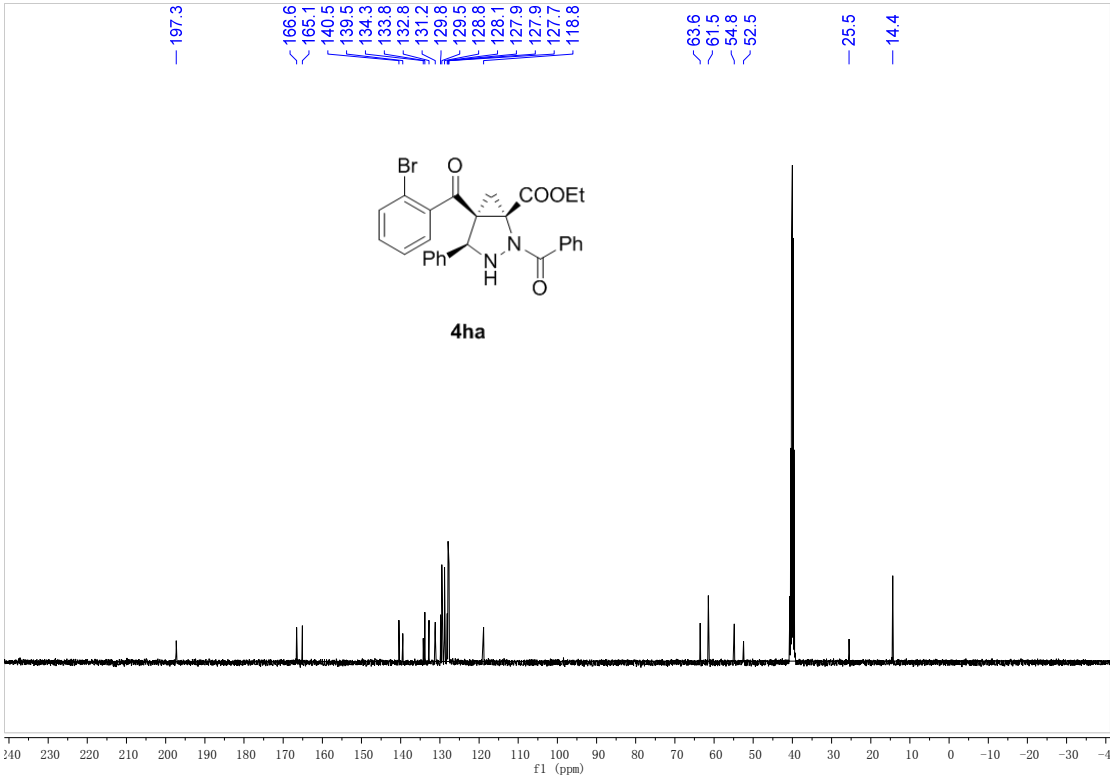

8.03
8.02
7.96
7.95
7.76
7.74
7.34
7.23
7.22
6.83
6.82
4.94
4.92
4.24
4.15
4.15
2.42
2.41
2.29
2.28
1.23
1.21
1.20
COOEt
Ph
Ph
N
H
N
O
O
S
A (m)
4.18
4ga
1.10
0.97
2.01
3.19
2.01
3.80
0.92
0.96
2.00
1.00
0.99
3.13
f1 (ppm)


186.8
170.2
166.3
142.1
137.4
135.5
134.3
133.9
131.2
129.1
128.7
128.6
127.8
127.8
126.4
67.6
62.0
58.5
57.4
30.4
13.8
O
COOEt
S
Ph
N
H
N
Ph
O
4ga
f1 (ppm)

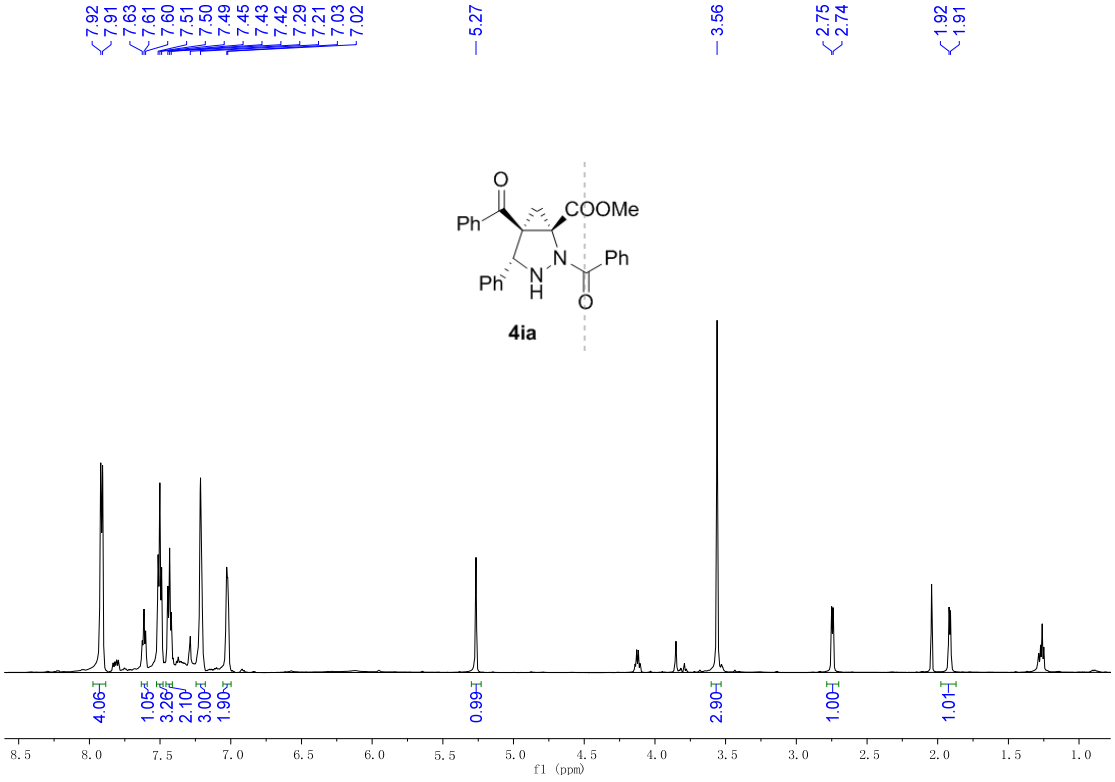
11. 4ha

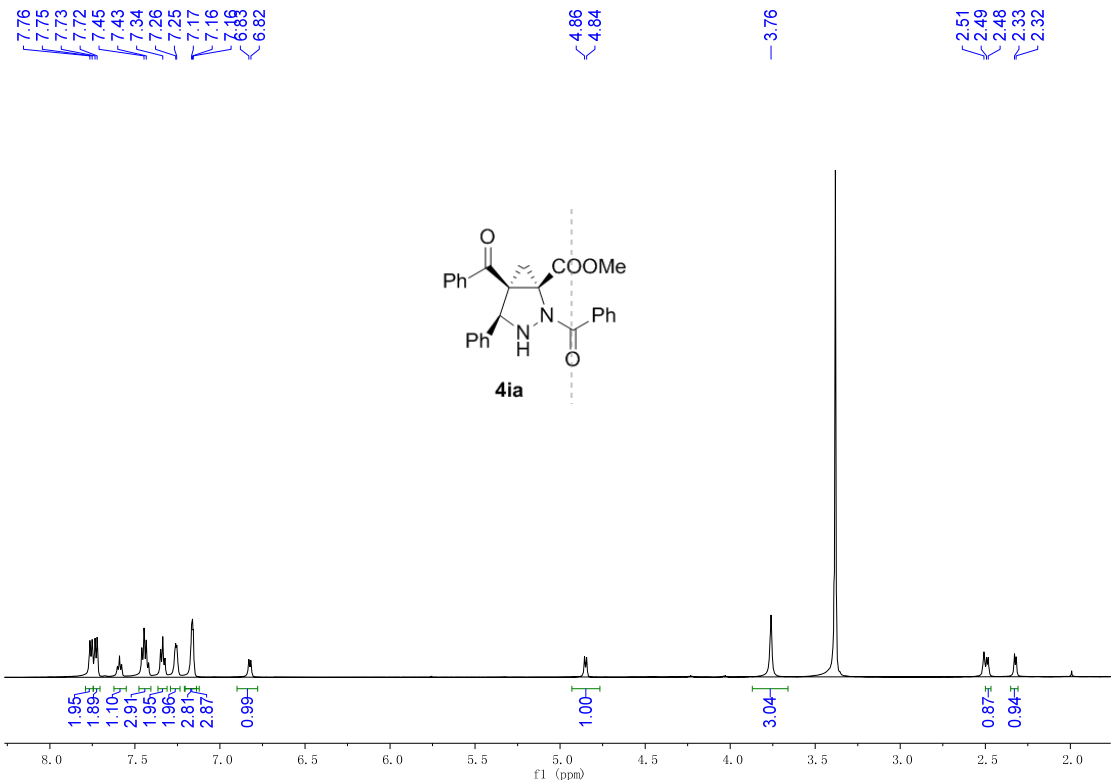

7.95
7.94
7.86
7.85
7.65
7.64
7.63
7.54
7.53
7.51
7.51
7.50
7.45
7.44
7.42
7.18
7.17
6.95
6.94
5.21
4.02
4.00
3.99
3.98
2.76
2.75
1.81
1.80
1.00
0.99
0.98
Br
O
COOEt
Ph
N
H
N
Ph
O
4ha
1.93
1.90
1.06
3.20
2.12
2.00
1.95
1.04
2.00
0.98
0.98
3.02
f1 (ppm)

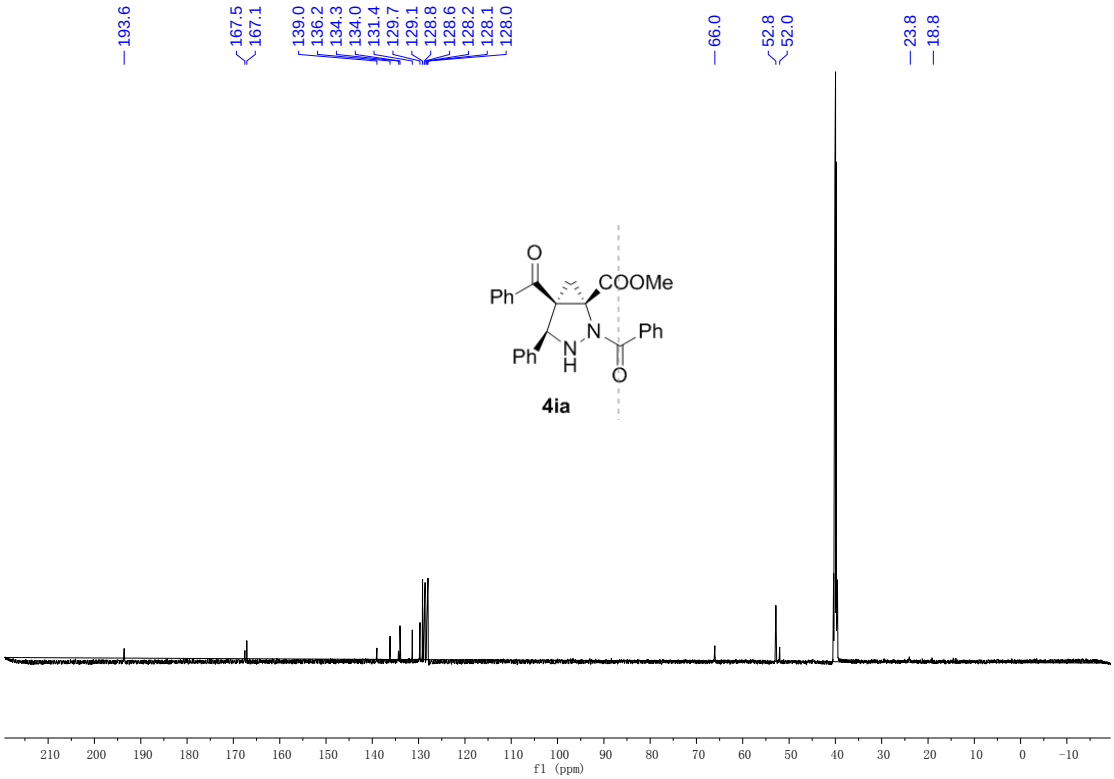

7.59
7.57
7.51
7.50
7.48
7.40
7.38
7.36
7.31
7.30
7.30
7.29
7.28
7.26
7.24
7.22
7.22
7.20
7.19
7.18
7.16
7.16
4.49
4.47
4.40
4.38
4.35
4.33
4.32
4.26
4.25
4.23
4.22
4.20
4.18
2.61
2.60
2.41
2.40
1.33
1.32
1.30
Br
O
COOEt
Ph
N
N
H
Ph
O
4ha
2.17
1.17
1.24
4.15
6.02
1.09
1.03
2.19
1.00
1.02
3.01
f1 (ppm)


197.3
166.6
165.1
140.5
139.5
134.3
133.8
132.8
131.2
129.8
129.5
128.8
128.1
127.9
127.9
127.7
118.8
63.6
61.5
54.8
52.5
25.5
14.4
Br
O
COOEt
Ph
N
N
H
Ph
O
4ha
f1 (ppm)

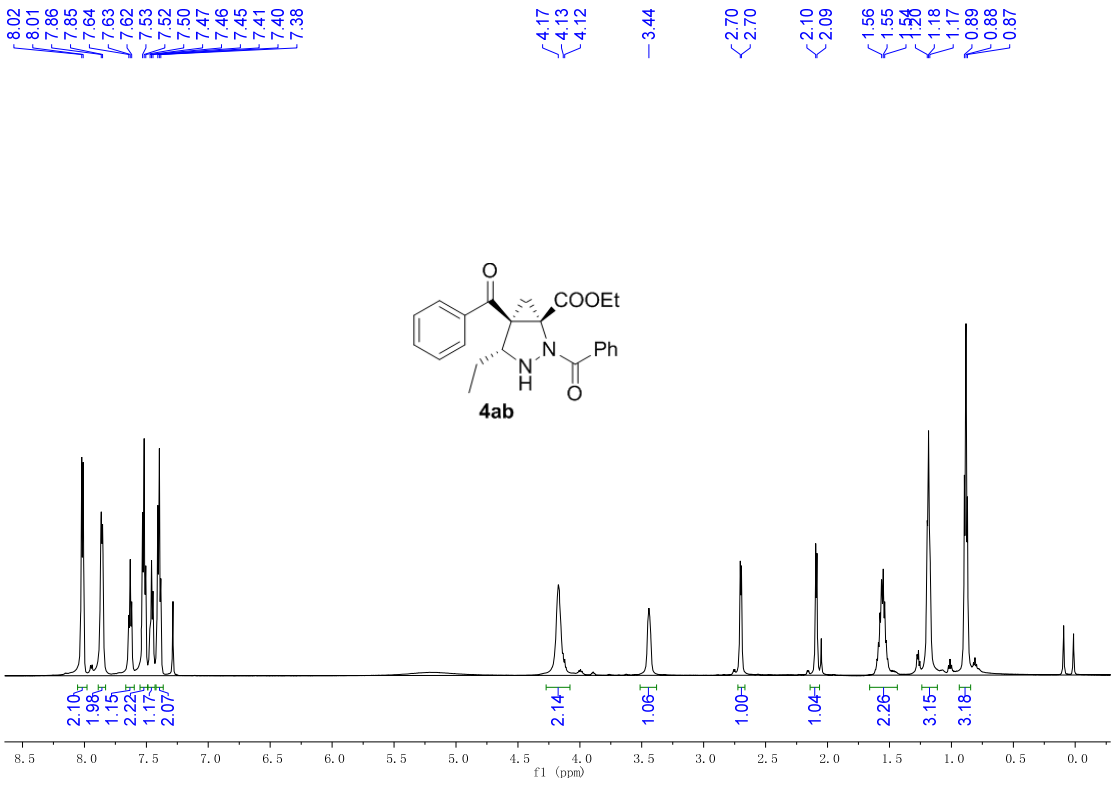
12. 4ia

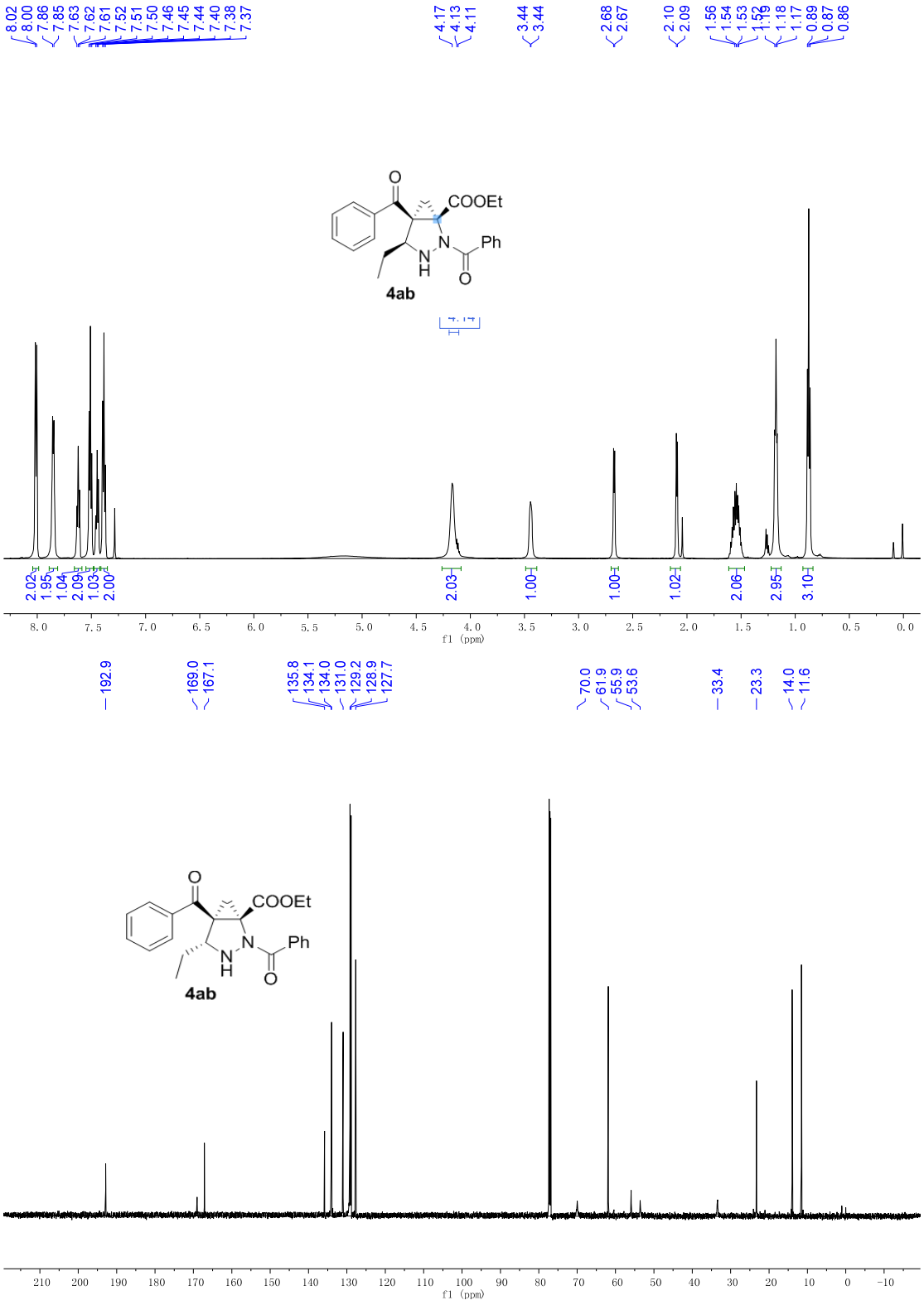

7.92
7.91
7.63
7.61
7.60
7.51
7.50
7.49
7.45
7.43
7.42
7.29
7.21
7.03
7.02
5.27
3.56
2.75
2.74
1.92
1.91
Ph
O
COOMe
N
H
Ph
Ph
O
4ia
4.06
1.05
3.26
2.10
3.00
1.90
0.99
2.90
1.00
1.01
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
f1 (ppm)


7.76
7.75
7.73
7.72
7.45
7.43
7.34
7.26
7.25
7.17
7.16
6.83
6.82
4.86
4.84
3.76
2.51
2.49
2.48
2.33
2.32
Ph
O
COOMe
N
H
Ph
Ph
O
4ia
1.95
1.89
1.10
2.91
1.95
1.96
2.81
2.87
0.99
1.00
3.04
0.87
0.94
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
f1 (ppm)

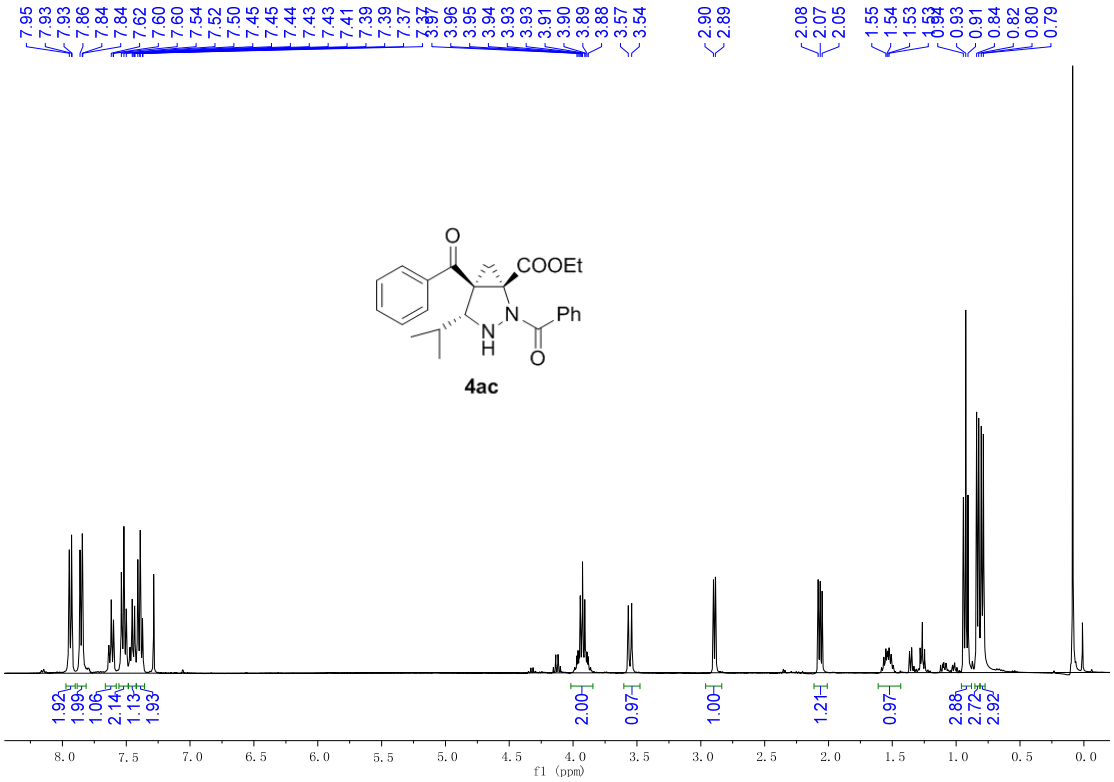

193.6
167.5
167.1
139.0
136.2
134.3
134.0
131.4
129.7
129.1
128.8
128.6
128.2
128.1
128.0
66.0
52.8
52.0
23.8
18.8
O
COOMe
Ph
N
Ph
Ph
N
H
O
4ia
210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 −10
f1 (ppm)

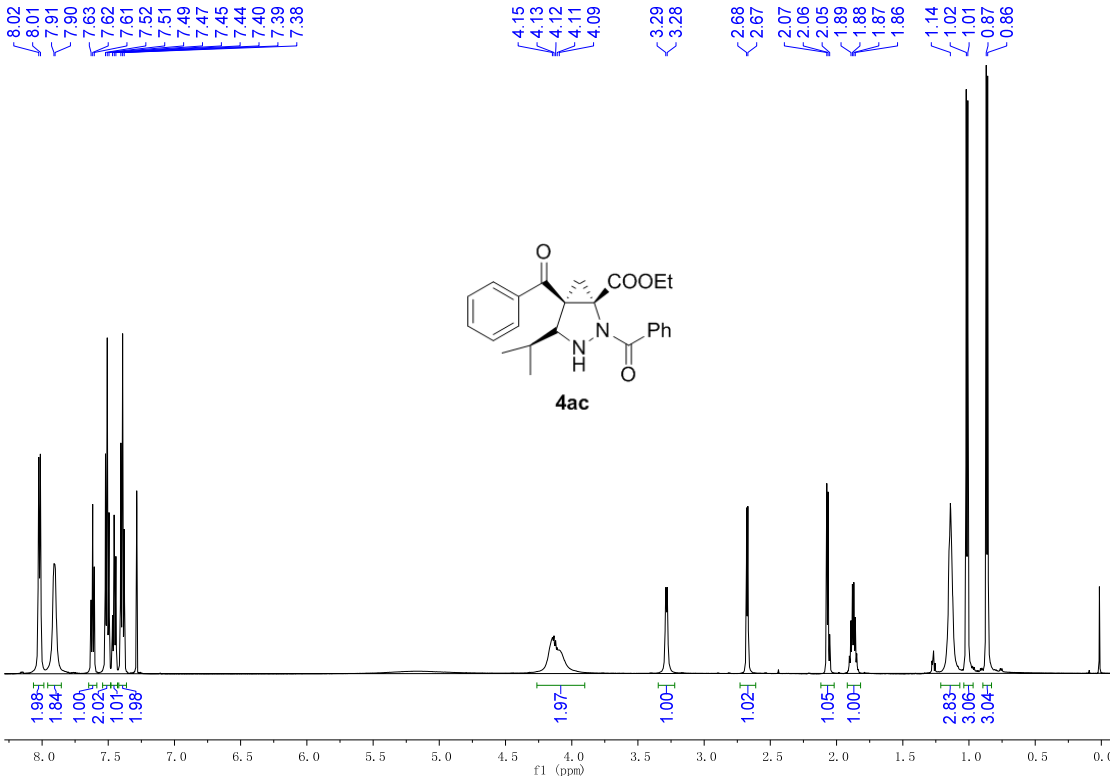
13. 4ab

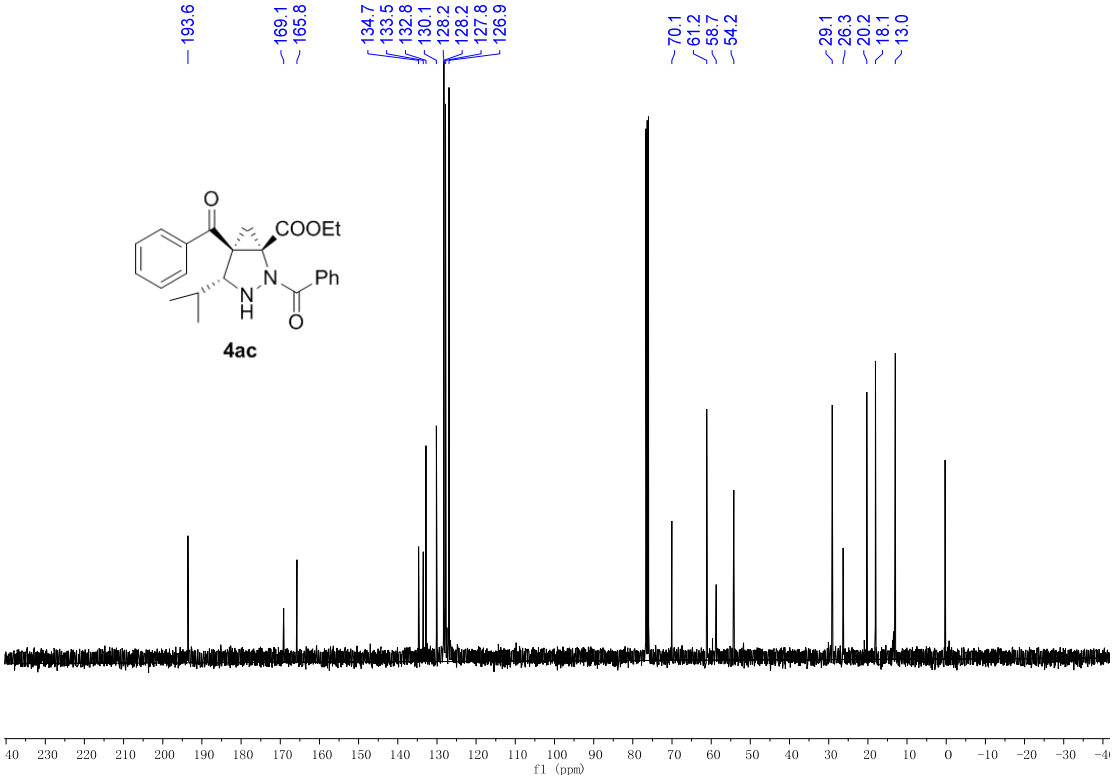

8.02
8.01
7.86
7.85
7.64
7.63
7.62
7.53
7.52
7.50
7.47
7.46
7.45
7.41
7.40
7.38
4.17
4.13
4.12
3.44
2.70
2.70
2.10
2.09
1.56
1.55
1.54
1.20
1.18
1.17
0.89
0.88
0.87
O
COOEt
N
Ph
N
H
O
4ab
2.10
1.98
1.15
2.22
1.17
2.07
2.14
1.06
1.00
1.04
2.26
3.15
3.18
8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0
f1 (ppm)


8.02
8.00
7.86
7.85
7.63
7.62
7.61
7.52
7.51
7.50
7.46
7.45
7.44
7.40
7.38
7.37
4.17
4.13
4.11
3.44
3.44
2.68
2.67
2.10
2.09
1.56
1.54
1.53
1.18
1.17
0.89
0.87
0.86
COOEt
Ph
N
H
O
4ab
2.02
1.95
1.04
2.09
1.03
2.00
2.03
1.00
1.00
1.02
2.06
2.95
3.10
f1 (ppm)
192.9
169.0
167.1
135.8
134.1
134.0
131.0
129.2
128.9
127.7
70.0
61.9
55.9
53.6
33.4
23.3
14.0
11.6
f1 (ppm)

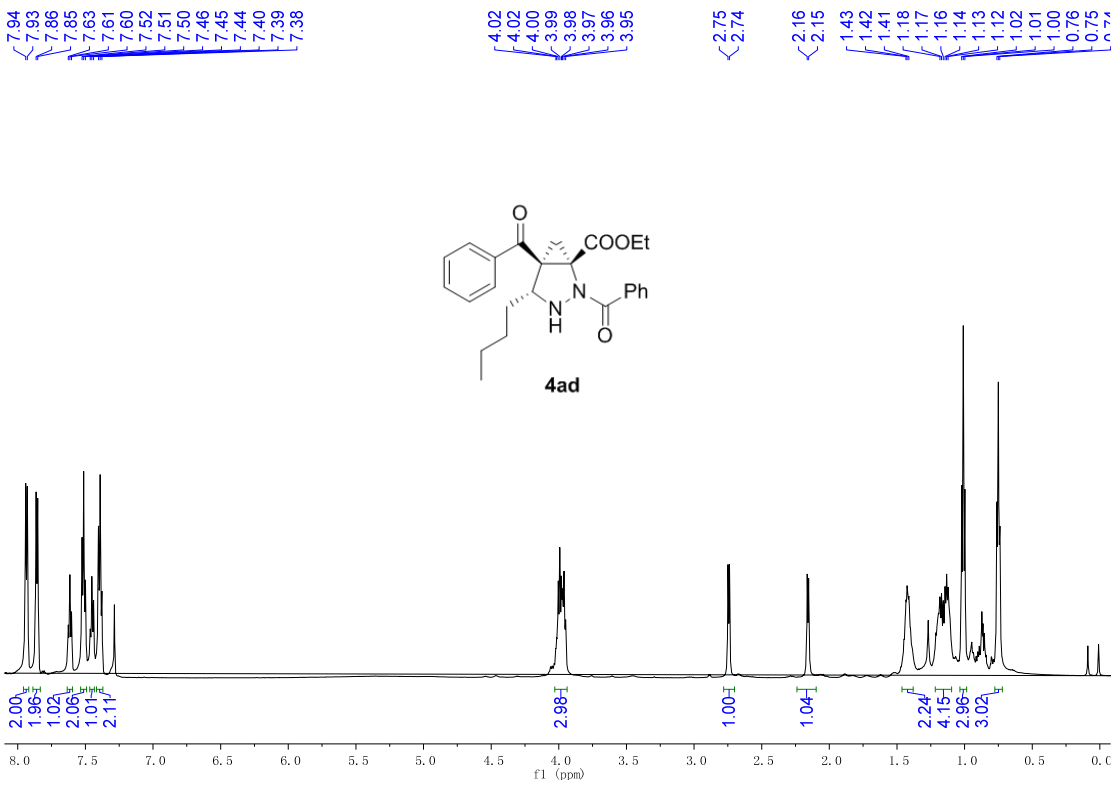
14.4ac

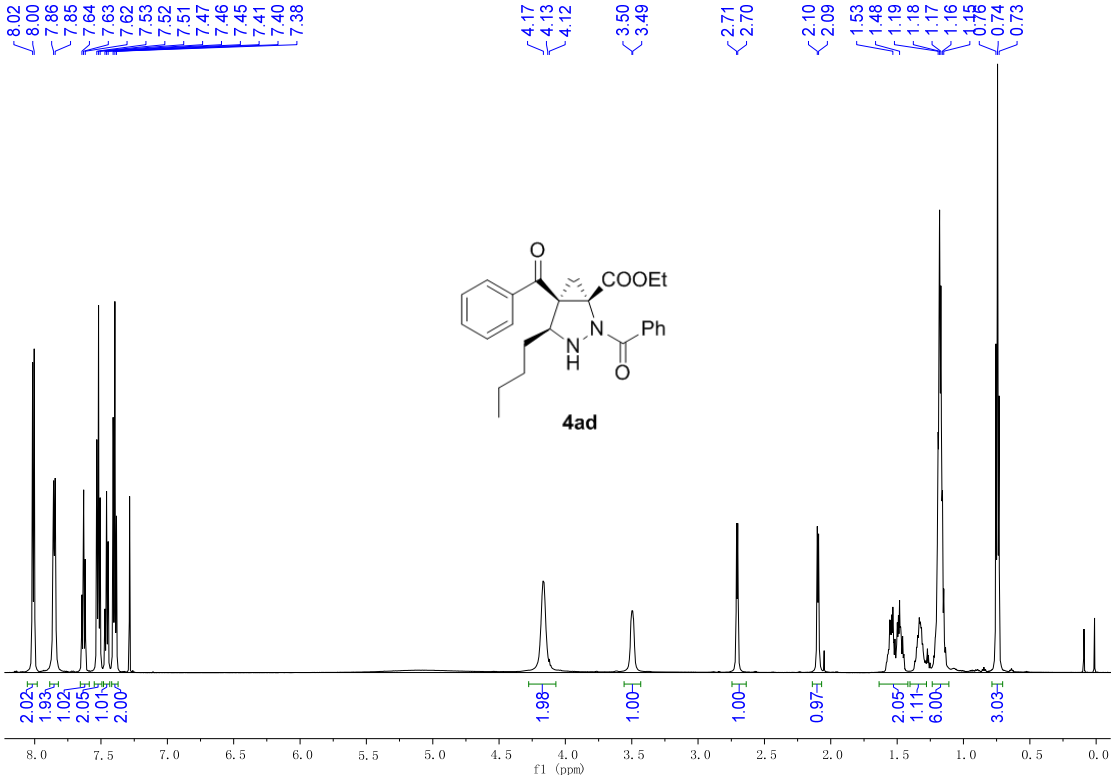

7.95
7.93
7.93
7.86
7.84
7.84
7.62
7.60
7.60
7.54
7.52
7.50
7.45
7.45
7.44
7.43
7.43
7.41
7.39
7.39
7.37
3.96
3.95
3.94
3.93
3.93
3.91
3.90
3.89
3.88
3.57
3.54
2.90
2.89
2.08
2.07
2.05
1.55
1.54
1.53
0.93
0.91
0.84
0.82
0.80
0.79
O
COOEt
N
N
H
Ph
O
4ac
1.92
1.99
1.06
2.14
1.13
1.93
2.00
0.97
1.00
1.21
0.97
2.88
2.72
2.92
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
f1 (ppm)

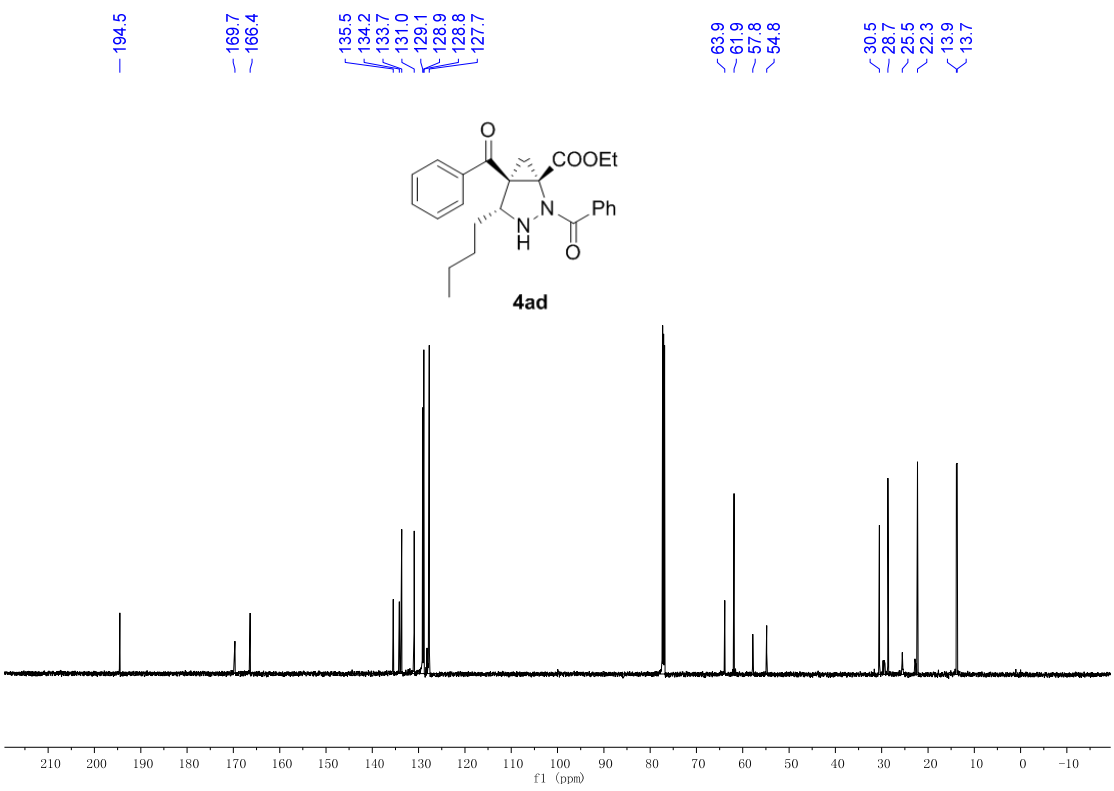

8.02
8.01
7.91
7.90
7.63
7.62
7.61
7.52
7.51
7.49
7.47
7.45
7.44
7.40
7.39
7.38
4.15
4.13
4.12
4.11
4.09
3.29
3.28
2.68
2.67
2.07
2.06
2.05
1.89
1.88
1.87
1.86
1.14
1.02
1.01
0.87
0.86
O
COOEt
N
N
H
Ph
O
4ac
1.98
1.84
1.00
2.02
1.01
1.98
1.97
1.00
1.02
1.05
1.00
2.83
3.06
3.04
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
f1 (ppm)


193.6
169.1
165.8
134.7
133.5
132.8
130.1
128.2
128.2
127.8
126.9
70.1
61.2
58.7
54.2
29.1
26.3
20.2
18.1
13.0
O
COOEt
N
Ph
N
H
O
4ac
f1 (ppm)

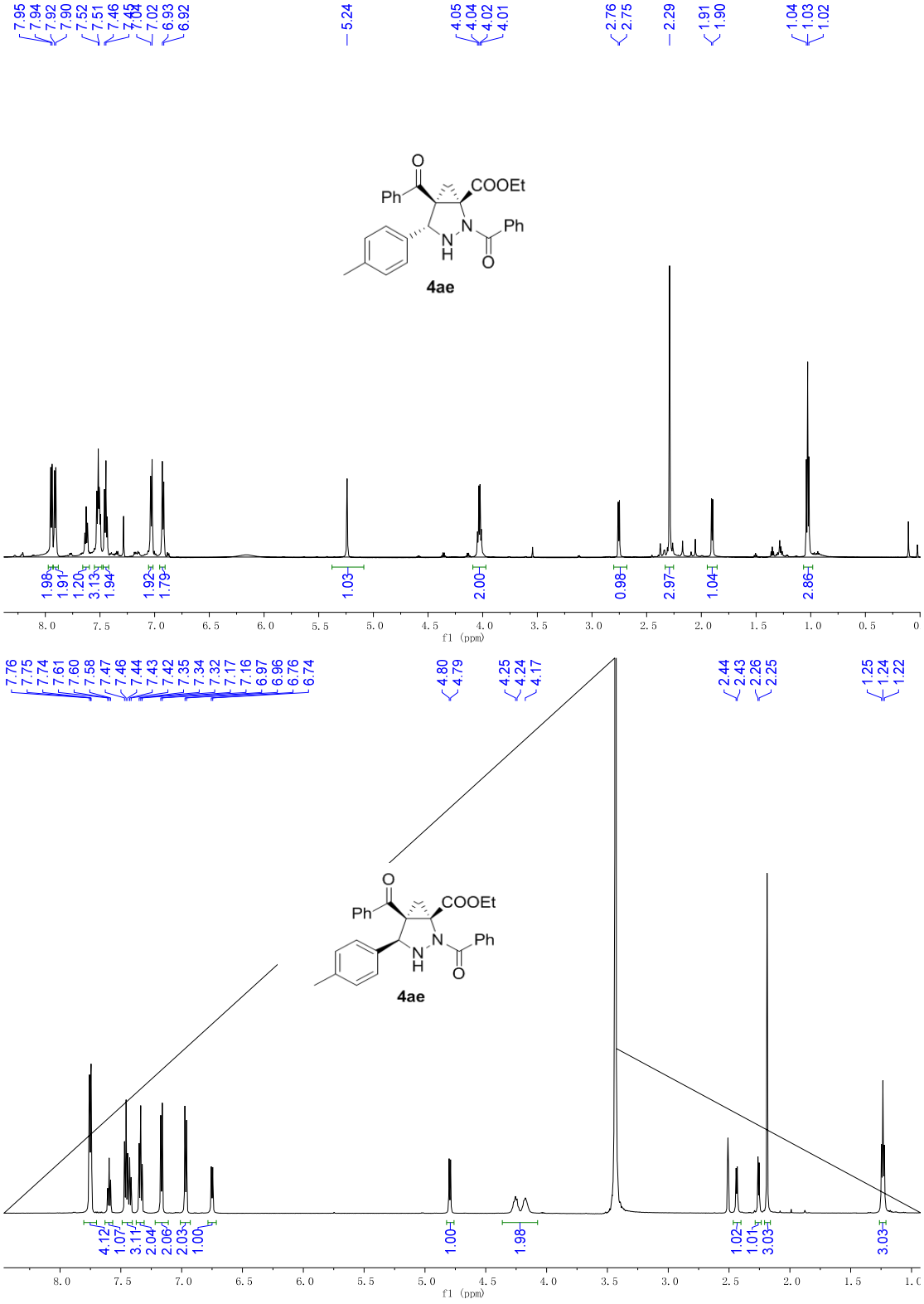
15. 4ad

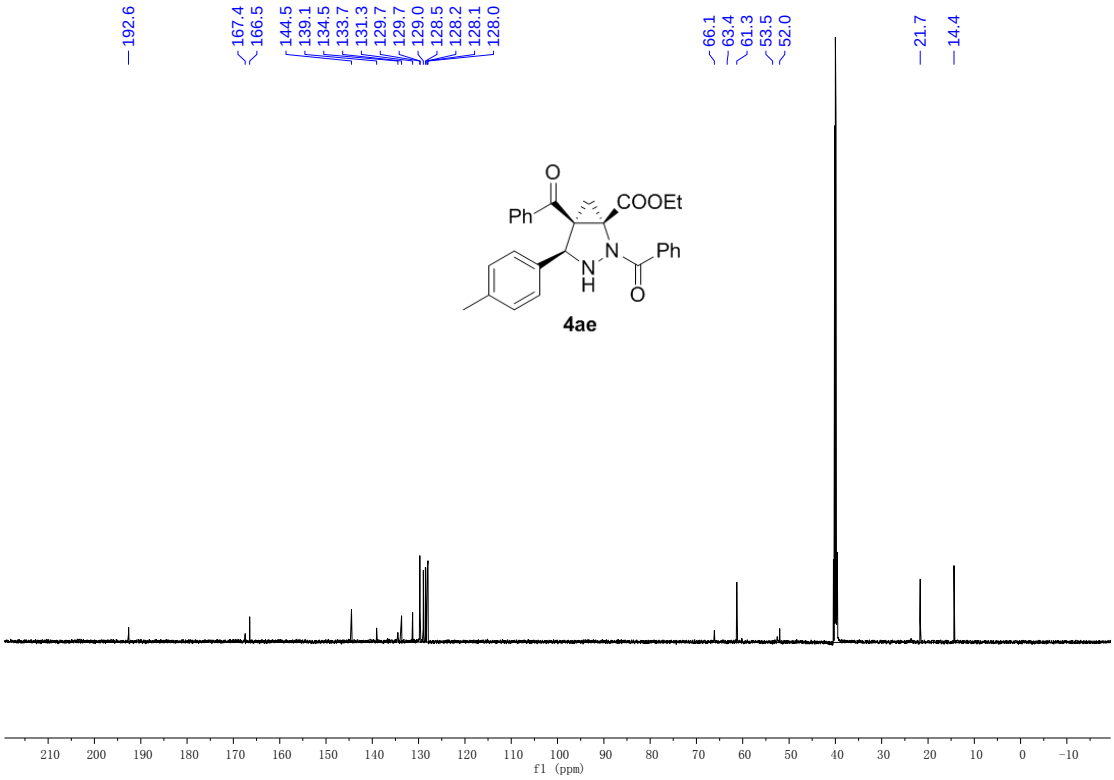

7.94
7.93
7.86
7.85
7.63
7.61
7.60
7.52
7.51
7.50
7.46
7.45
7.44
7.40
7.39
7.38
4.02
4.02
4.00
3.99
3.98
3.97
3.96
3.95
2.75
2.74
2.16
2.15
1.43
1.42
1.41
1.18
1.17
1.16
1.14
1.13
1.12
1.02
1.01
1.00
0.76
0.75
O
COOEt
N
Ph
N
H
O
4ad
2.00
1.96
1.02
2.06
1.01
2.11
2.98
1.00
1.04
2.24
4.15
2.96
3.02
f1 (ppm)


8.02
8.00
7.86
7.85
7.64
7.63
7.62
7.53
7.52
7.51
7.47
7.46
7.45
7.41
7.40
7.38
4.17
4.13
4.12
3.50
3.49
2.71
2.70
2.10
2.09
1.53
1.48
1.19
1.18
1.17
1.16
0.75
0.74
0.73
O
COOEt
N
Ph
N
H
O
4ad
2.02
1.93
1.02
2.05
1.01
2.00
1.98
1.00
1.00
0.97
2.05
1.11
6.00
3.03
f1 (ppm)

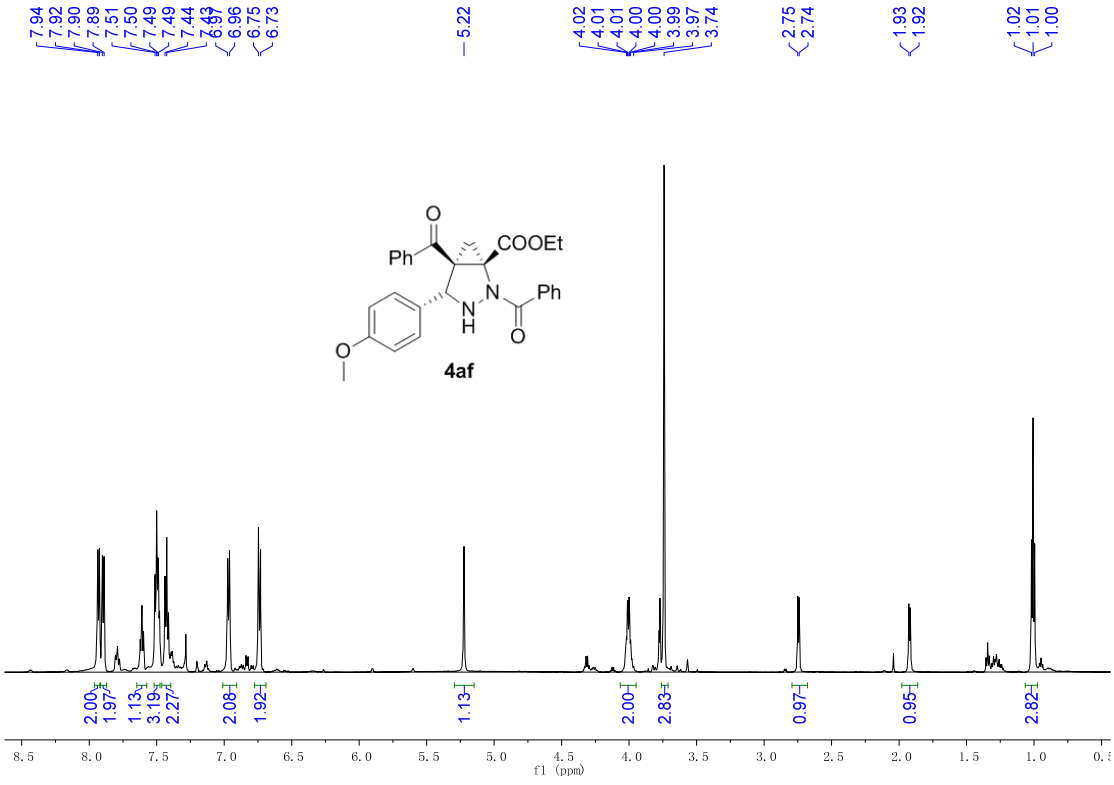

194.5
169.7
166.4
135.5
134.2
133.7
131.0
129.1
128.9
128.8
127.7
63.9
61.9
57.8
54.8
30.5
28.7
25.5
22.3
13.9
13.7
O
COOEt
N
Ph
N
H
O
4ad
f1 (ppm)

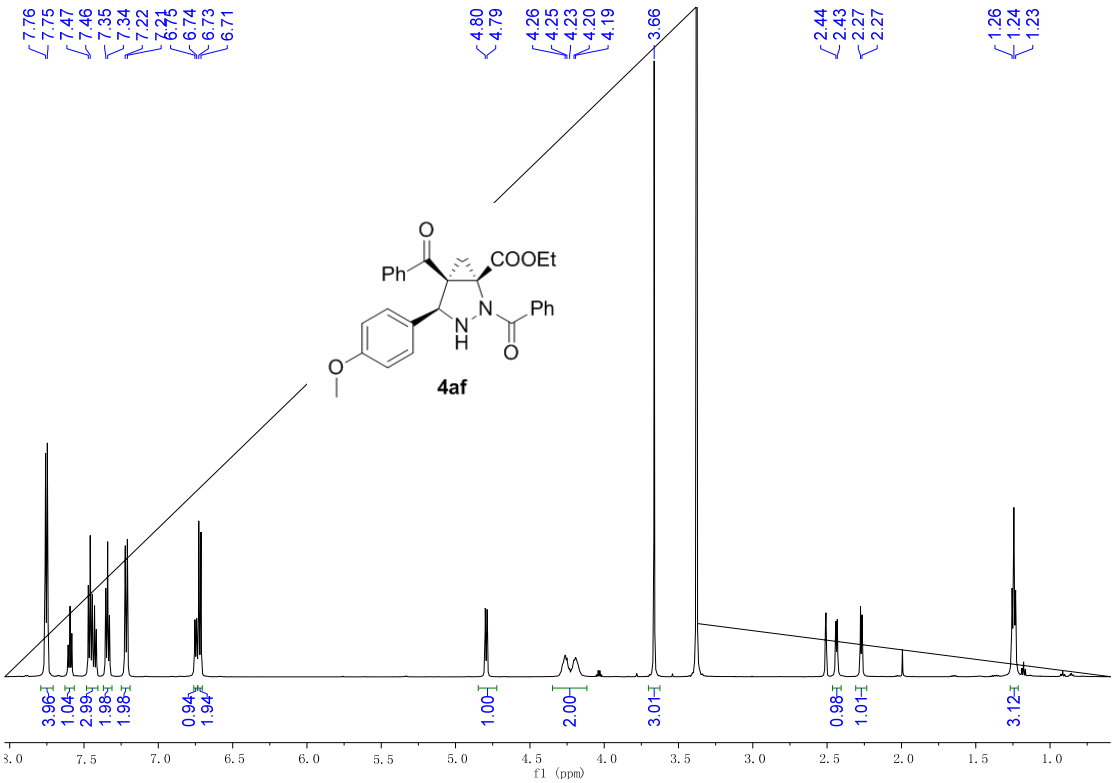
16. 4ae

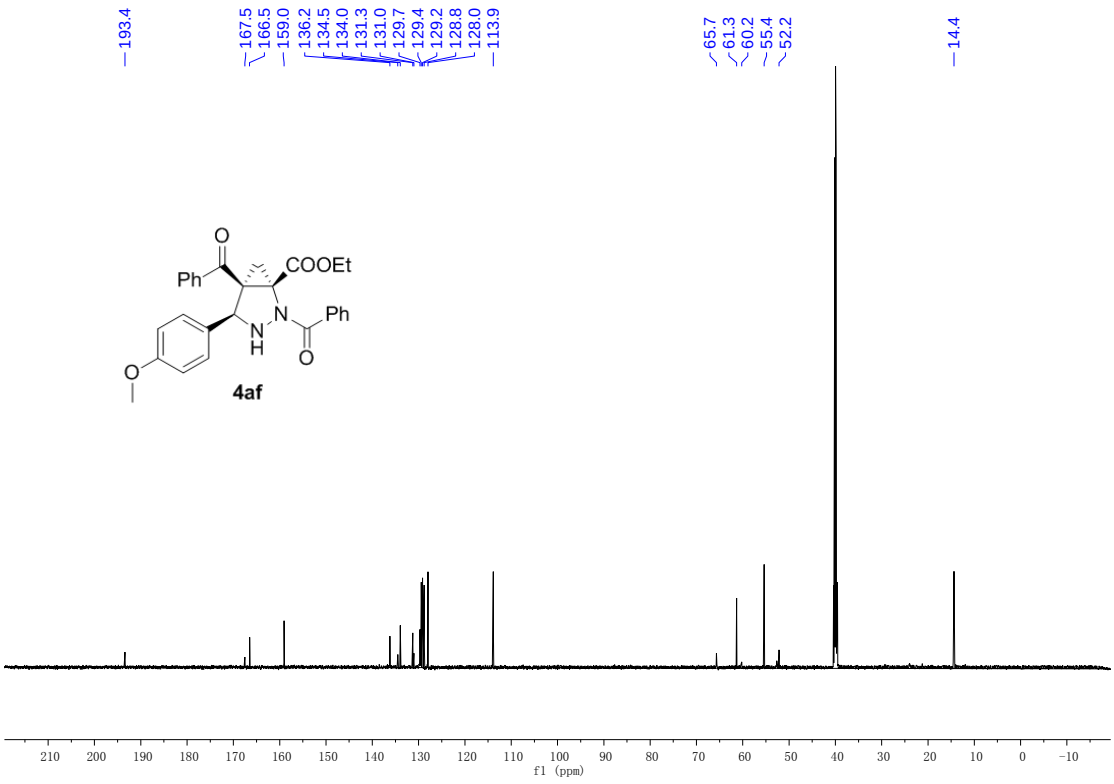

7.95
7.94
7.92
7.90
7.52
7.51
7.46
7.45
7.44
7.02
6.93
6.92
5.24
4.05
4.04
4.02
4.01
2.76
2.75
2.29
1.91
1.90
1.04
1.03
1.02
O
Ph
COOEt
N
N
H
Ph
O
4ae
1.98
1.91
1.20
3.15
1.94
1.92
1.79
1.03
2.00
0.98
2.97
1.04
2.86
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0
f1 (ppm)
7.76
7.75
7.74
7.61
7.60
7.58
7.47
7.46
7.44
7.43
7.42
7.35
7.34
7.32
7.17
7.16
6.97
6.96
6.76
6.74
4.80
4.79
4.25
4.24
4.17
2.44
2.43
2.26
2.25
1.25
1.24
1.22
O
Ph
COOEt
N
N
H
Ph
O
4ae
4.12
1.07
3.11
2.04
2.06
2.03
1.00
1.00
1.98
1.02
1.01
3.03
3.03
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
f1 (ppm)


192.6
167.4
166.5
144.5
139.1
134.5
133.7
131.3
129.7
129.7
129.0
128.5
128.2
128.1
128.0
66.1
63.4
61.3
53.5
52.0
21.7
14.4
O
Ph
COOEt
N
N
H
Ph
O
4ae
f1 (ppm)

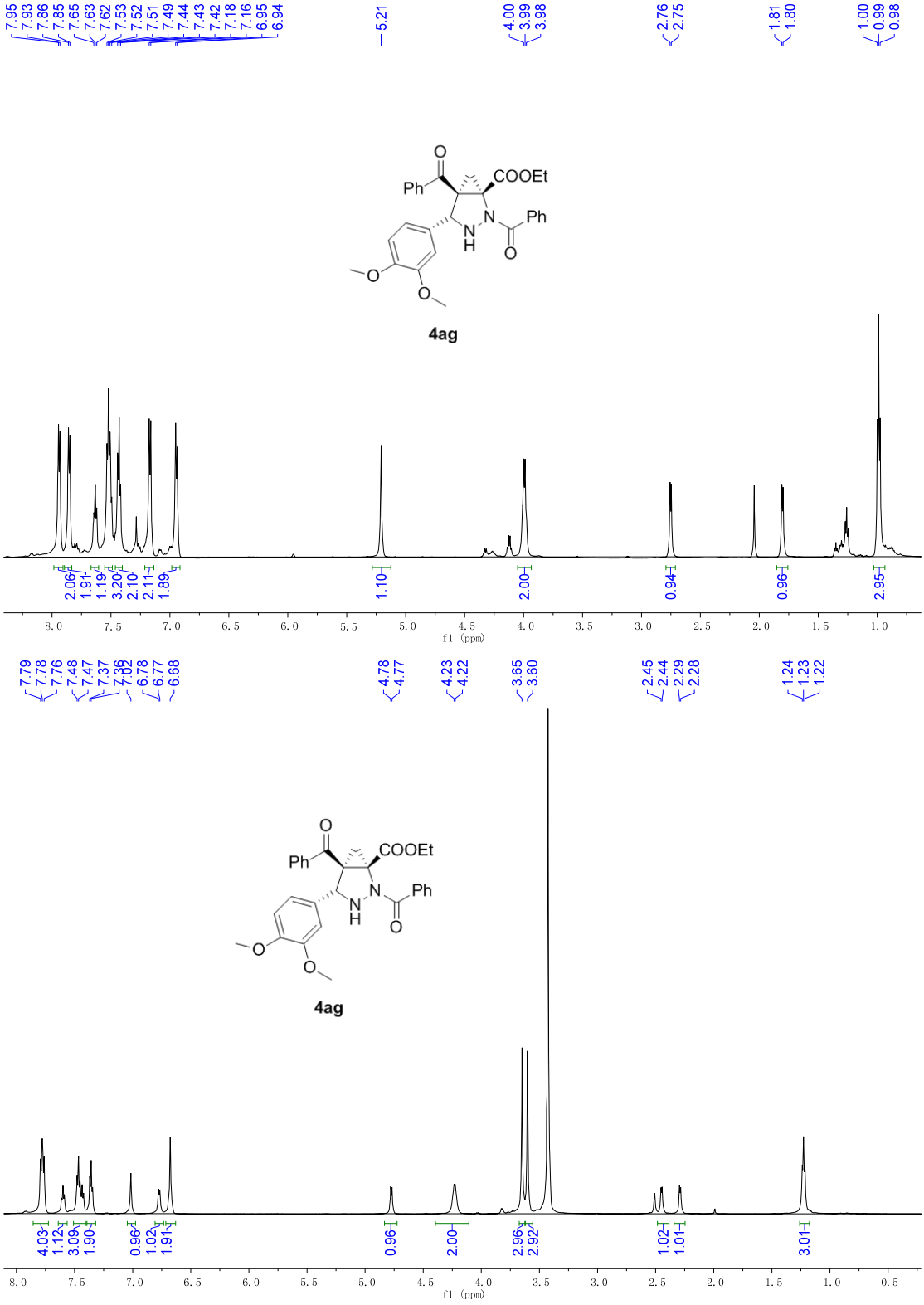
17. 4af

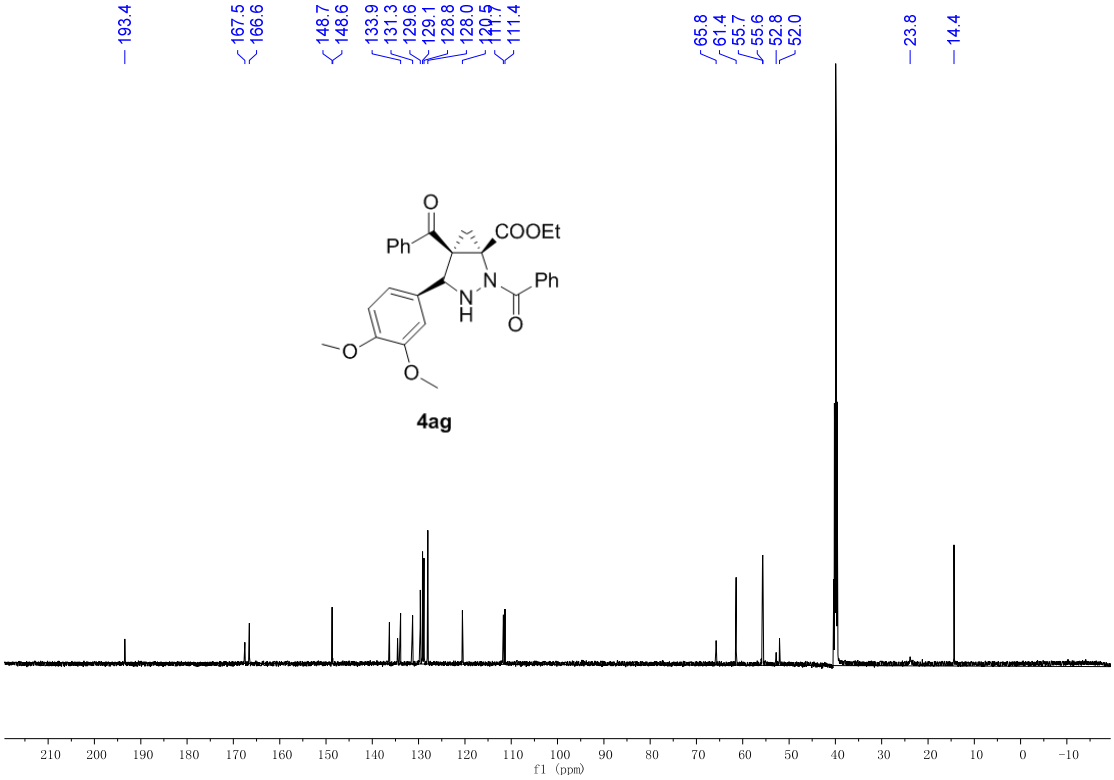

7.94
7.92
7.90
7.89
7.51
7.50
7.49
7.49
7.44
6.96
6.75
6.73
5.22
4.02
4.01
4.01
4.00
4.00
3.99
3.97
3.74
2.75
2.74
1.93
1.92
1.02
1.01
1.00
O
Ph
COOEt
N
N
H
Ph
O
O
4af
2.00
1.97
1.13
3.19
2.27
2.08
1.92
1.13
2.00
2.83
0.97
0.95
2.82
f1 (ppm)


7.76
7.75
7.47
7.46
7.35
7.34
7.22
7.21
6.75
6.74
6.73
6.71
4.80
4.79
4.26
4.25
4.23
4.20
4.19
3.66
2.44
2.43
2.27
2.27
1.26
1.24
1.23
3.96
1.04
2.99
1.98
1.98
0.94
1.94
1.00
2.00
3.01
0.98
1.01
3.12
f1 (ppm)
O
Ph
COOEt
N
N
H
Ph
O
O
4af

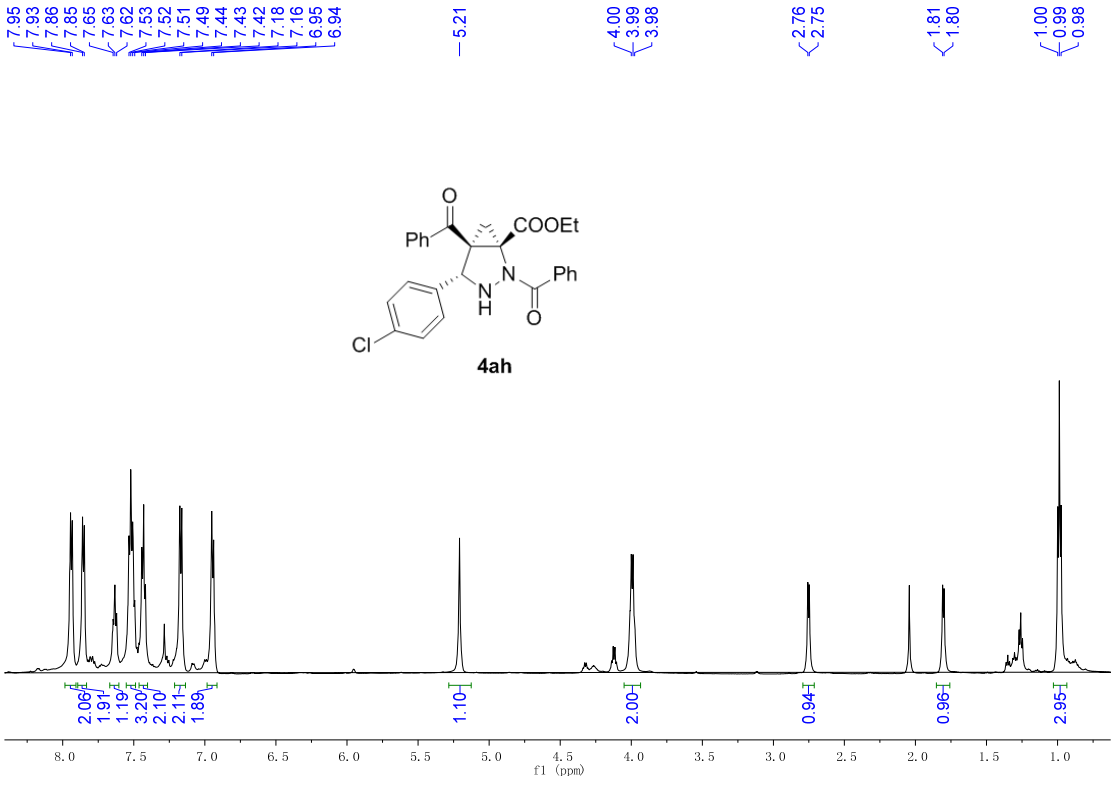

193.4
167.5
166.5
159.0
136.2
134.5
134.0
131.3
131.0
129.7
129.4
129.2
128.8
128.0
113.9
65.7
61.3
60.2
55.4
52.2
14.4
f1 (ppm)
O
Ph
COOEt
N
N
H
Ph
O
O
4af

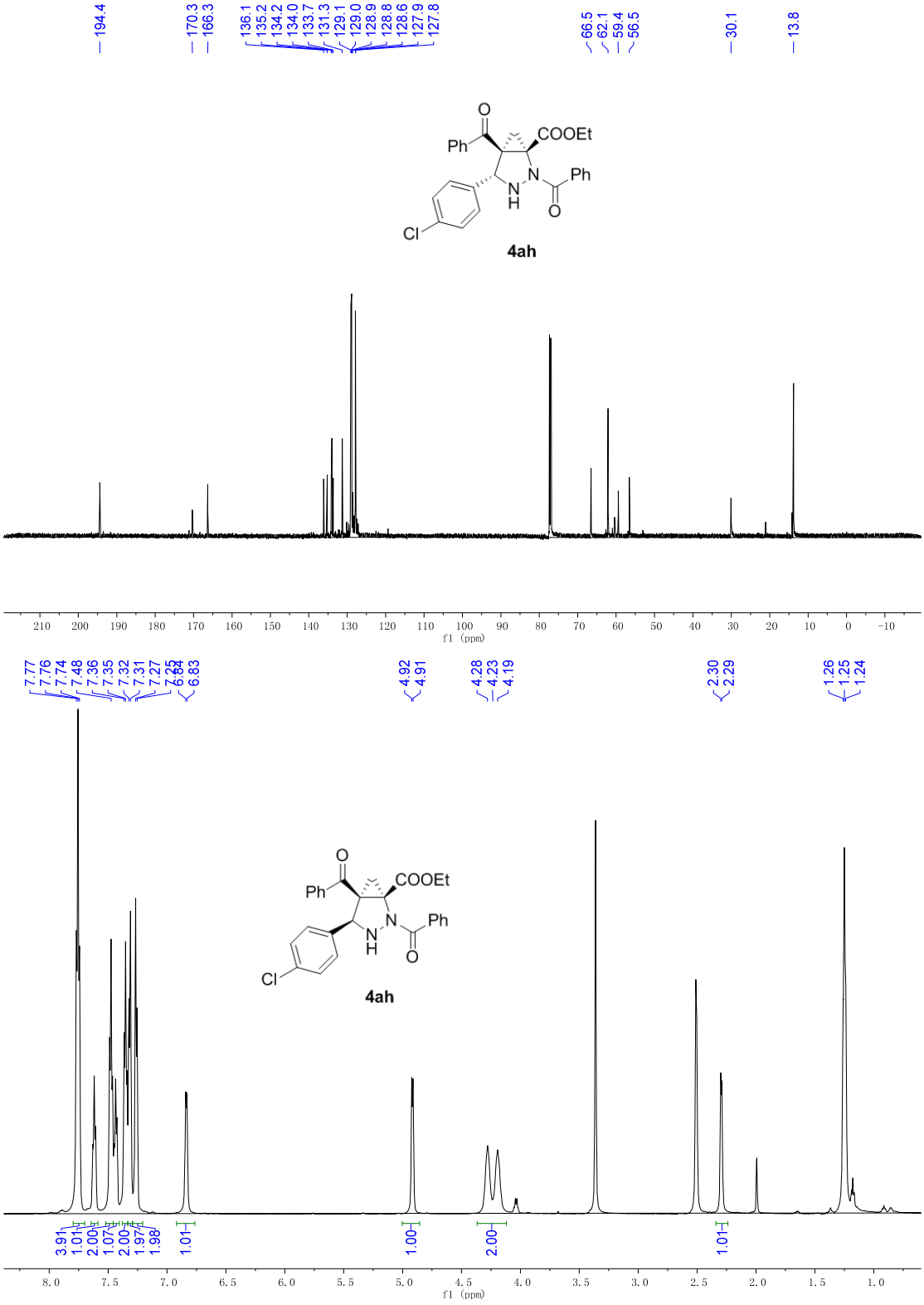
18.4ag


7.95
7.93
7.86
7.85
7.65
7.63
7.62
7.53
7.52
7.51
7.49
7.44
7.43
7.42
7.18
7.16
6.95
6.94
5.21
4.00
3.99
3.98
2.76
2.75
1.81
1.80
1.00
0.99
0.98
O
Ph
COOEt
N
N
H
Ph
O
O
O
4ag
2.06
1.91
1.19
3.20
2.10
2.11
1.89
1.10
2.00
0.94
0.96
2.95
f1 (ppm)
7.79
7.78
7.76
7.48
7.47
7.37
6.78
6.77
6.68
4.78
4.77
4.23
4.22
3.65
3.60
2.45
2.44
2.29
2.28
1.24
1.23
1.22
4ag
4.03
1.12
3.09
1.90
0.96
1.02
1.91
0.96
2.00
2.96
2.92
1.02
1.01
3.01
f1 (ppm)

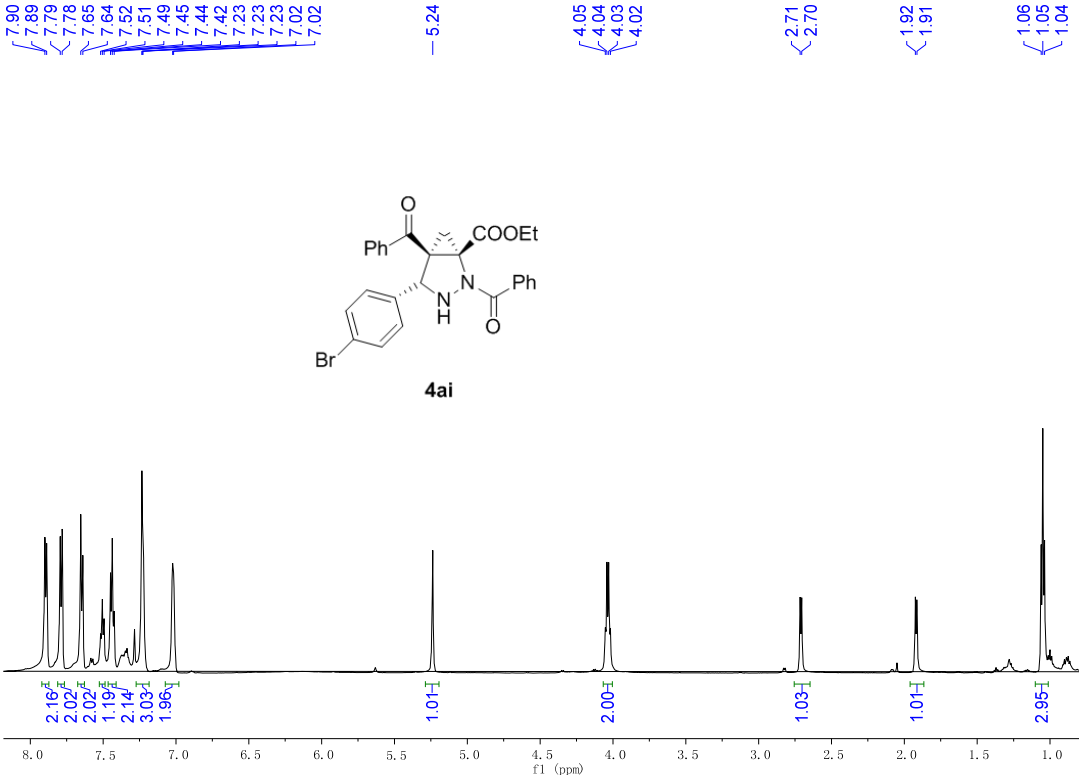

193.4
167.5
166.6
148.7
148.6
133.9
131.3
129.6
129.1
128.8
128.0
120.5
111.7
111.4
65.8
61.4
55.7
55.6
52.8
52.0
23.8
14.4
O
Ph
COOEt
N
N
H
Ph
O
O
O
4ag
210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 -10
f1 (ppm)

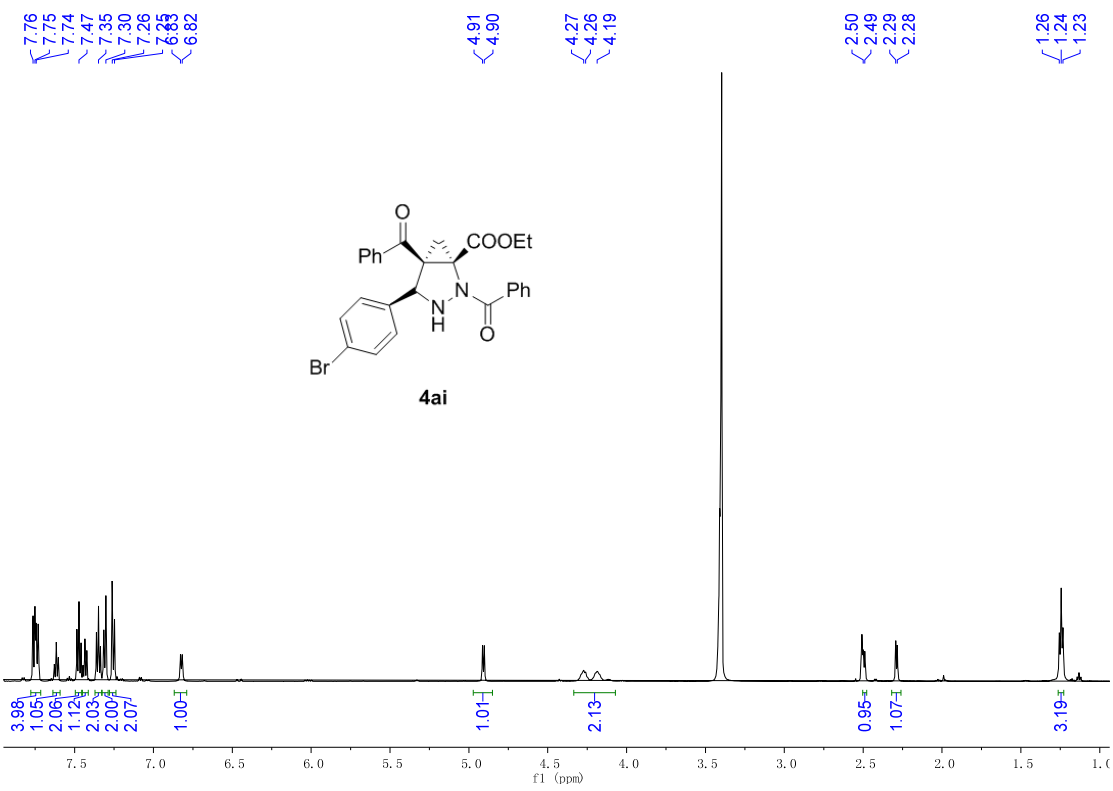
19. 4ah

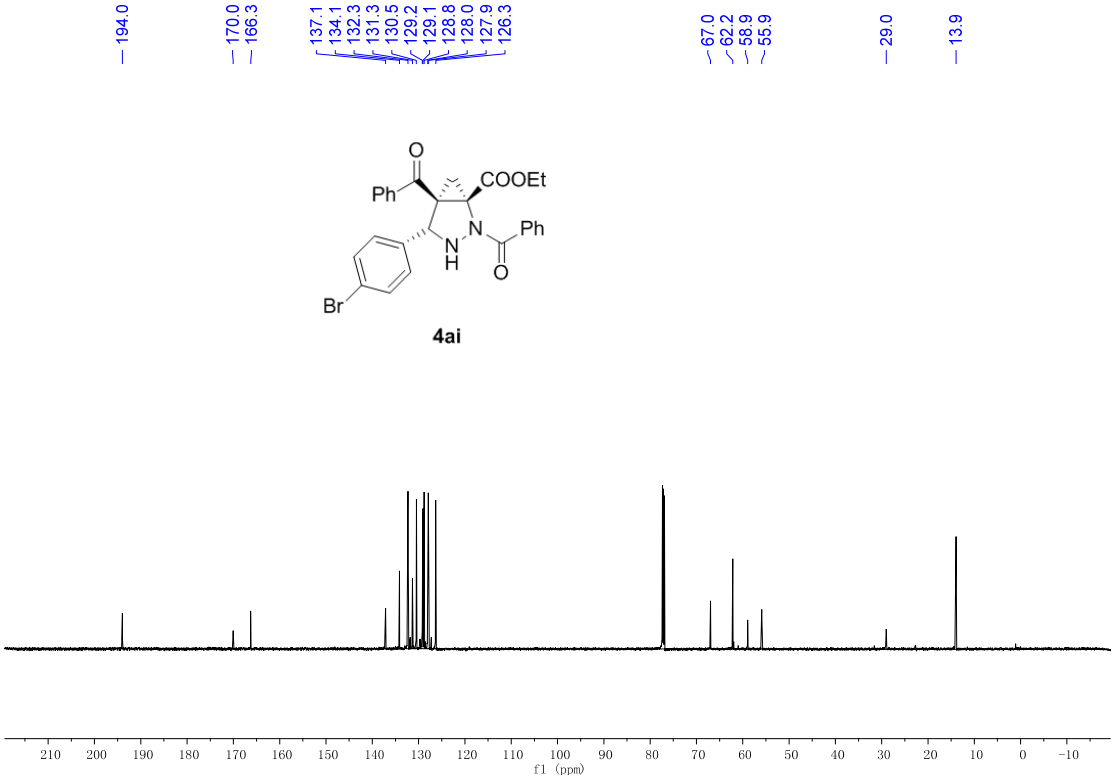

7.95
7.93
7.86
7.85
7.65
7.63
7.62
7.53
7.52
7.51
7.49
7.44
7.43
7.42
7.18
7.16
6.95
6.94
5.21
4.00
3.99
3.98
2.76
2.75
1.81
1.80
1.00
0.99
0.98
O
Ph
COOEt
N
N
H
Ph
O
Cl
4ah
2.06
1.91
1.19
3.20
2.10
2.11
1.89
1.10
2.00
0.94
0.96
2.95
8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0
f1 (ppm)


194.4
170.3
166.3
136.1
135.2
134.2
134.0
133.7
131.3
129.1
129.0
128.9
128.8
128.6
127.9
127.8
66.5
62.1
59.4
56.5
30.1
13.8
O
Ph
COOEt
N
N
H
Ph
O
Cl
4ah
f1 (ppm)
7.77
7.76
7.74
7.48
7.36
7.35
7.32
7.31
7.27
6.84
6.83
4.92
4.91
4.28
4.23
4.19
2.30
2.29
1.26
1.25
1.24
3.91
1.01
2.00
1.07
2.00
1.97
1.98
1.01
1.00
2.00
1.01
4ah
f1 (ppm)

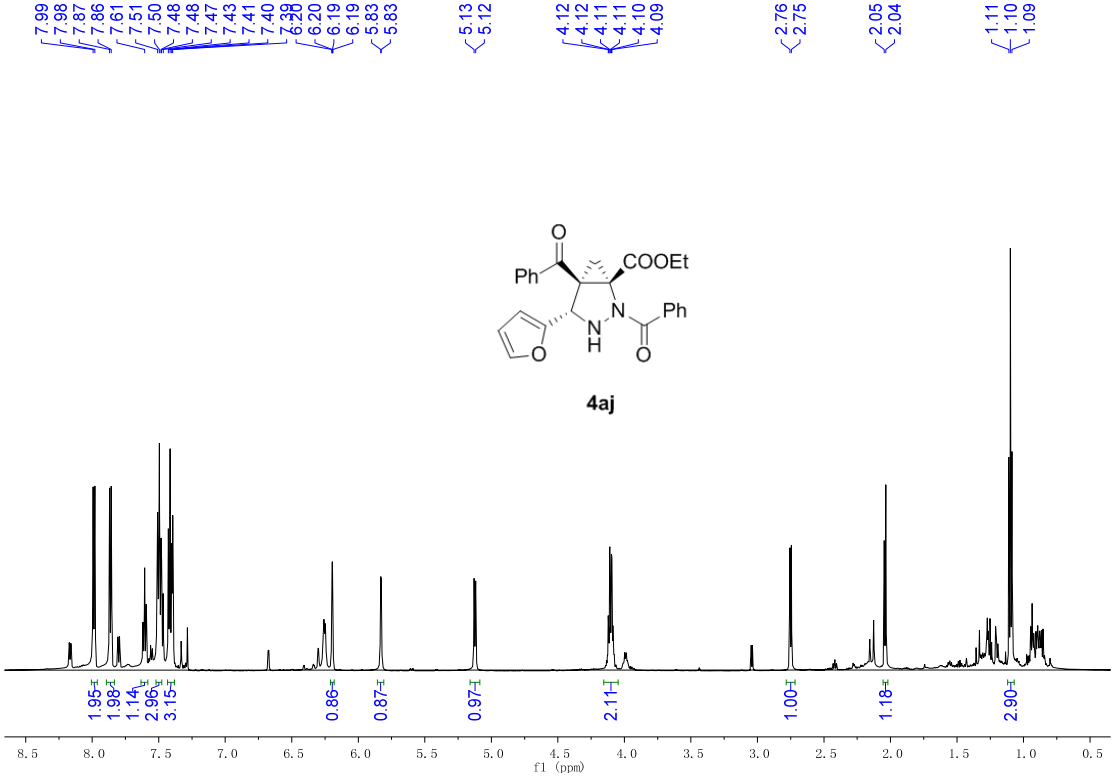
20. 4ai

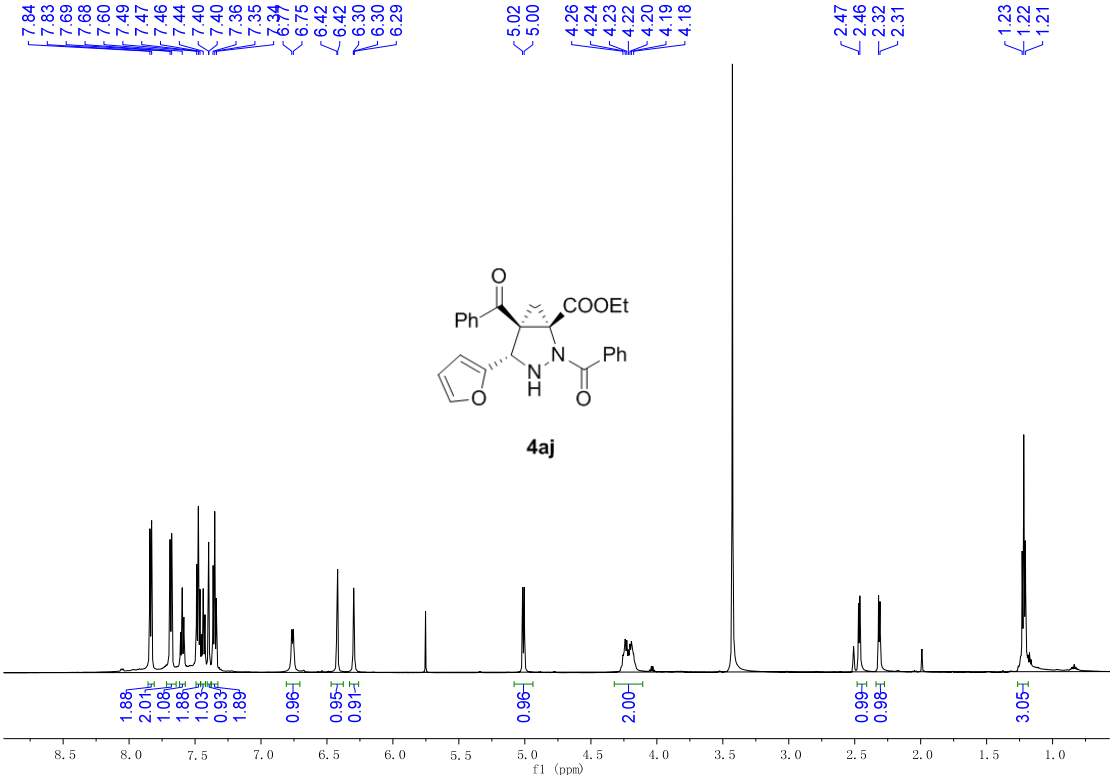

7.90
7.89
7.79
7.78
7.65
7.64
7.52
7.51
7.49
7.45
7.44
7.42
7.23
7.23
7.23
7.02
7.02
5.24
4.05
4.04
4.03
4.02
2.71
2.70
1.92
1.91
1.06
1.05
1.04
O
Ph
COOEt
N
N
H
Ph
O
Br
4ai
2.16
2.02
2.02
1.19
2.14
3.03
1.96
1.01
2.00
1.03
1.01
2.95
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
f1 (ppm)

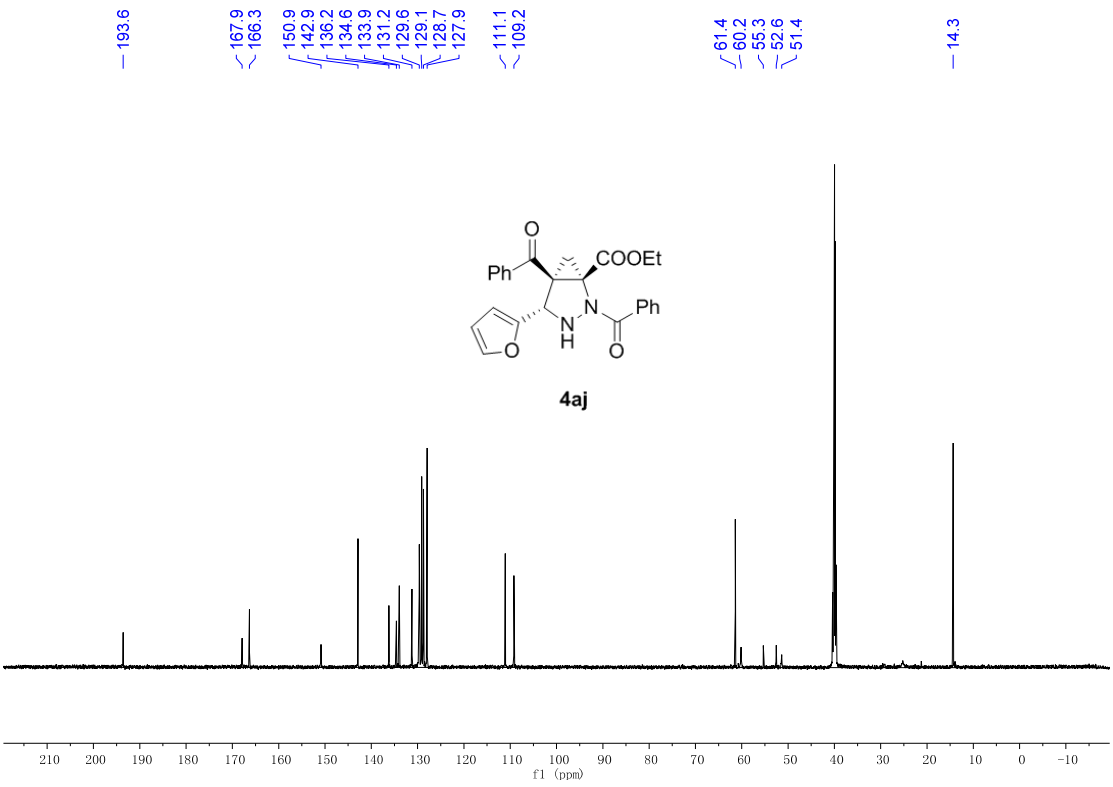

7.76
7.75
7.74
7.47
7.35
7.30
7.26
6.83
6.82
4.91
4.90
4.27
4.26
4.19
2.50
2.49
2.29
2.28
1.26
1.24
1.23
O
Ph
COOEt
N
N
H
Ph
O
Br
4ai
3.98
1.05
2.06
1.12
2.03
2.00
2.07
1.00
1.01
2.13
0.95
1.07
3.19
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
f1 (ppm)


194.0
170.0
166.3
137.1
134.1
132.3
131.3
130.5
129.2
129.1
128.8
128.0
127.9
126.3
67.0
62.2
58.9
55.9
29.0
13.9
O
Ph
COOEt
N
Ph
N
H
O
Br
4ai
210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 -10
f1 (ppm)

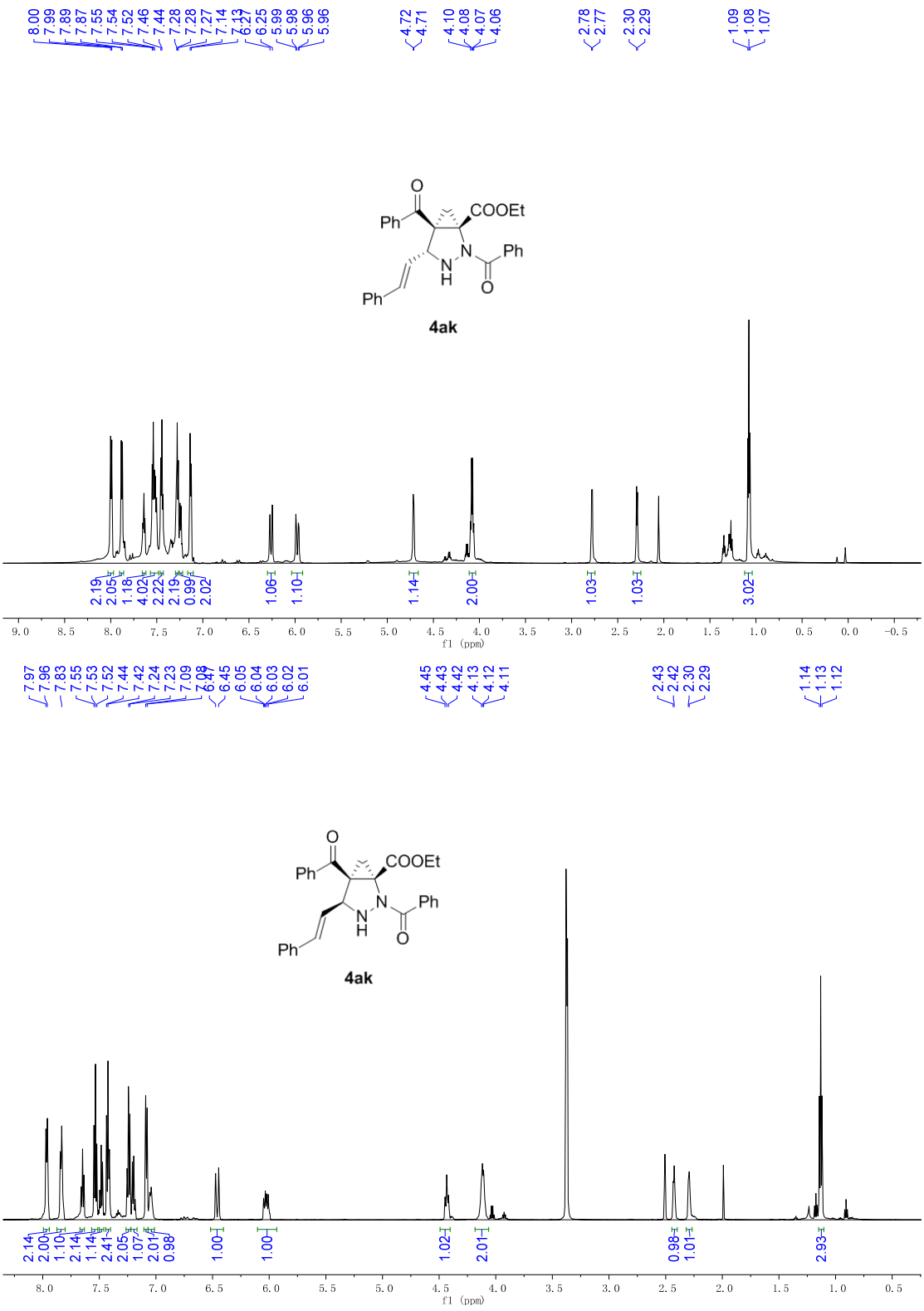
21. 4aj

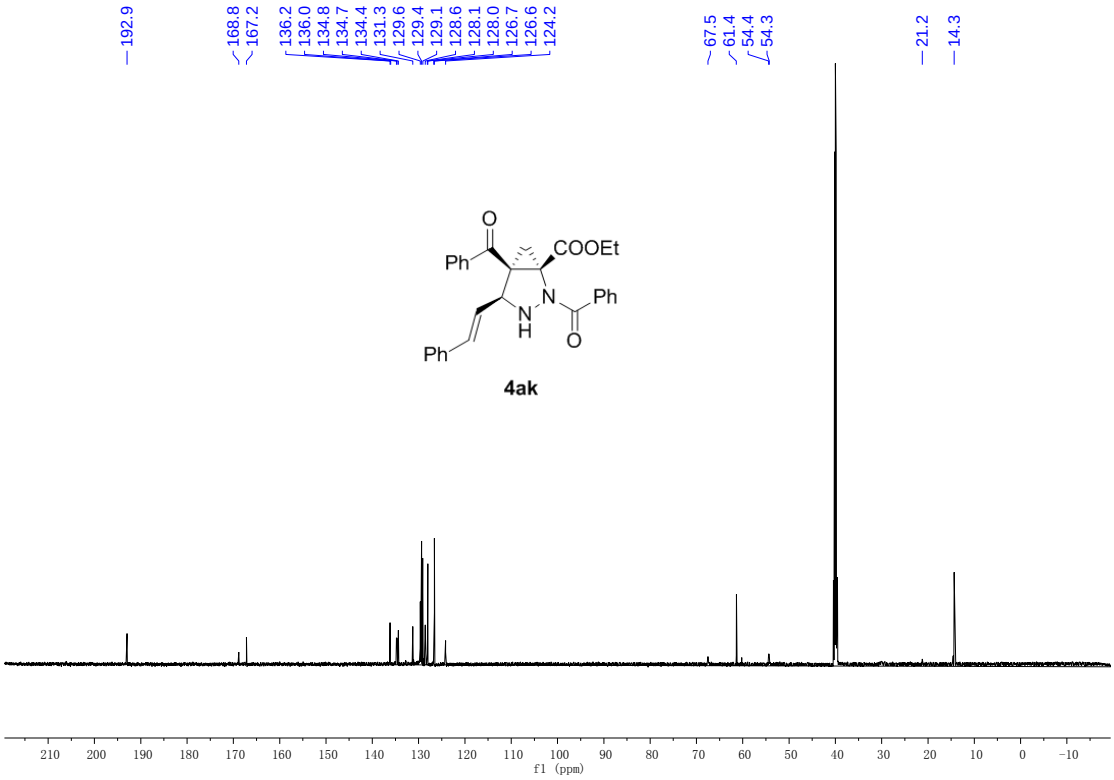

7.99
7.98
7.87
7.86
7.61
7.51
7.50
7.48
7.48
7.47
7.43
7.41
7.40
6.20
6.20
6.19
6.19
5.83
5.83
5.13
5.12
4.12
4.12
4.11
4.11
4.10
4.09
2.76
2.75
2.05
2.04
1.11
1.10
1.09
O
Ph
COOEt
N
Ph
N
H
O
O
4aj
1.95
1.98
1.14
2.96
3.15
0.86
0.87
0.97
2.11
1.00
1.18
2.90
8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5
f1 (ppm)


7.84
7.83
7.69
7.68
7.60
7.49
7.47
7.46
7.44
7.40
7.40
7.36
7.35
7.34
6.77
6.75
6.42
6.42
6.30
6.30
6.29
5.02
5.00
4.26
4.24
4.23
4.22
4.20
4.19
4.18
2.47
2.46
2.32
2.31
1.23
1.22
1.21
O
Ph
COOEt
N
Ph
N
H
O
O
4aj
1.88
2.01
1.08
1.88
1.03
0.93
1.89
0.96
0.95
0.91
0.96
2.00
0.99
0.98
3.05
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
f1 (ppm)

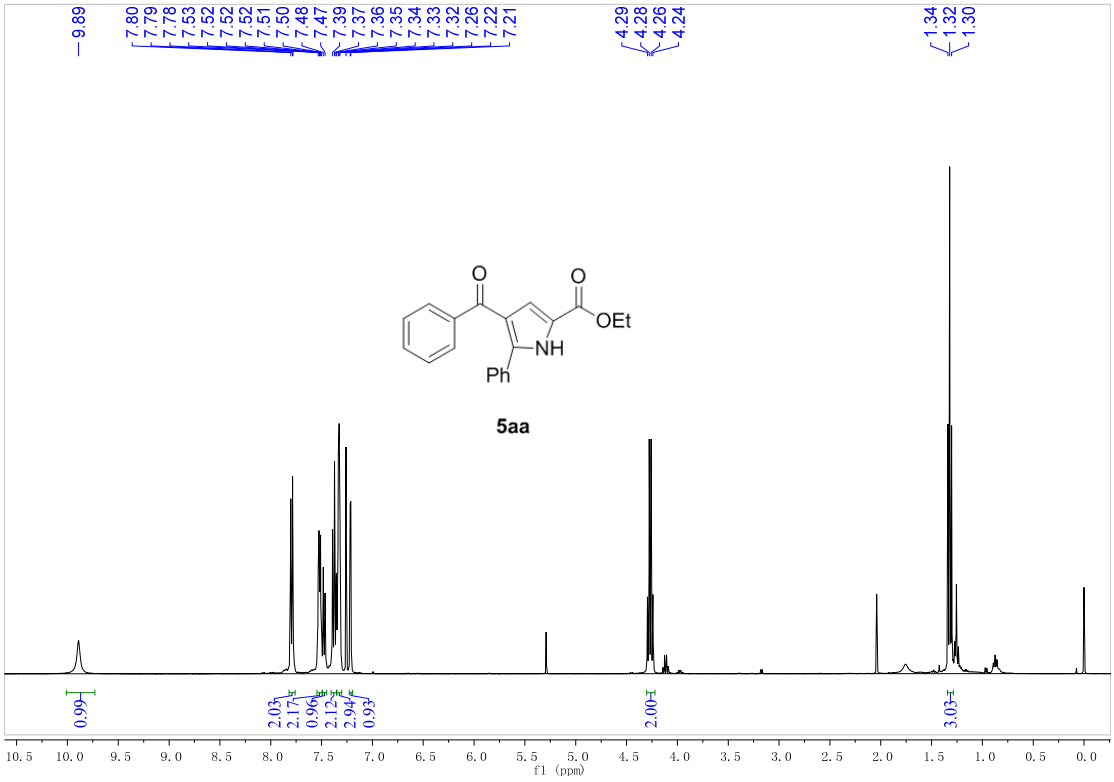

193.6
167.9
166.3
150.9
142.9
136.2
134.6
133.9
131.2
129.6
129.1
128.7
127.9
111.1
109.2
61.4
60.2
55.3
52.6
51.4
14.3
O
Ph
COOEt
N
Ph
N
H
O
O
4aj
210
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
−10
f1 (ppm)

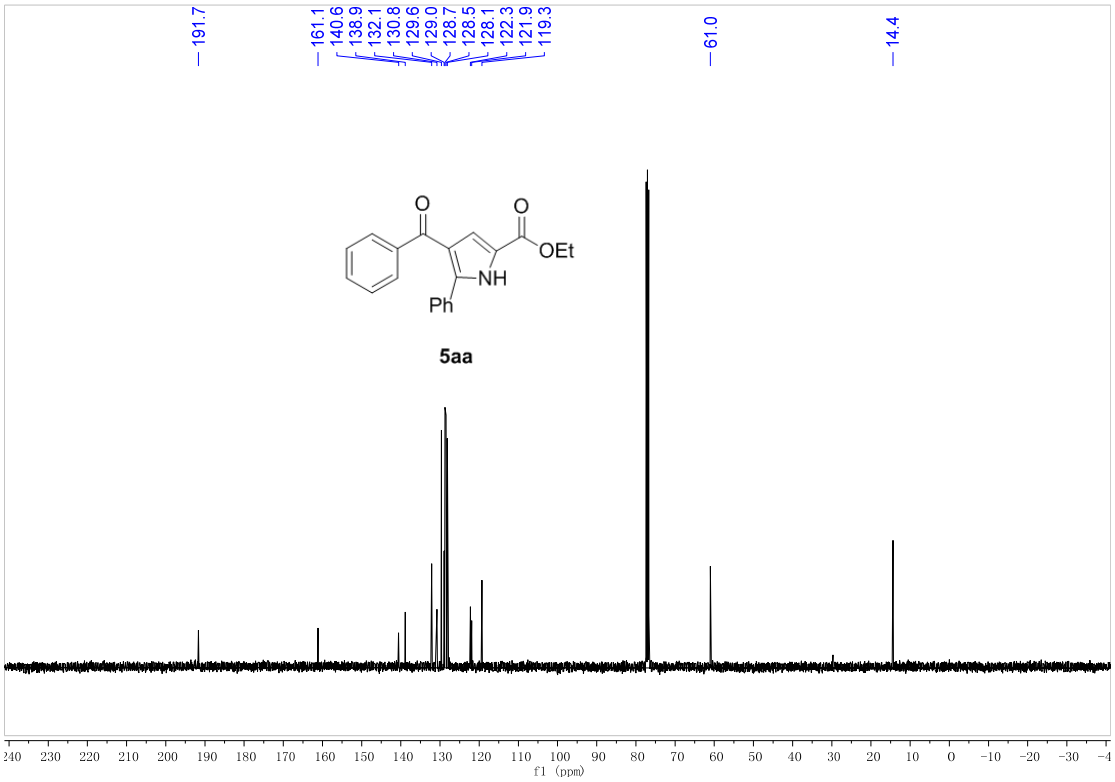
22. 4ak


8.00
7.99
7.89
7.87
7.55
7.54
7.52
7.46
7.44
7.28
7.28
7.27
7.14
7.13
6.27
6.25
5.99
5.98
5.96
5.96
4.72
4.71
4.10
4.08
4.07
4.06
2.78
2.77
2.30
2.29
1.09
1.08
1.07
O
Ph
COOEt
N
H
N
Ph
O
Ph
4ak
2.19
2.05
1.18
4.02
2.22
2.19
0.99
2.02
1.06
1.10
1.14
2.00
1.03
1.03
3.02
9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0 -0.5
f1 (ppm)
7.97
7.96
7.83
7.55
7.53
7.52
7.44
7.42
7.24
7.23
7.09
6.45
6.05
6.04
6.03
6.02
6.01
4.45
4.43
4.42
4.13
4.12
4.11
2.43
2.42
2.30
2.29
1.14
1.13
1.12
O
Ph
COOEt
N
H
N
Ph
O
Ph
4ak
2.14
2.00
1.10
2.14
1.14
2.41
2.05
1.07
2.01
0.98
1.00
1.00
1.02
2.01
0.98
1.01
2.93
8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5
f1 (ppm)

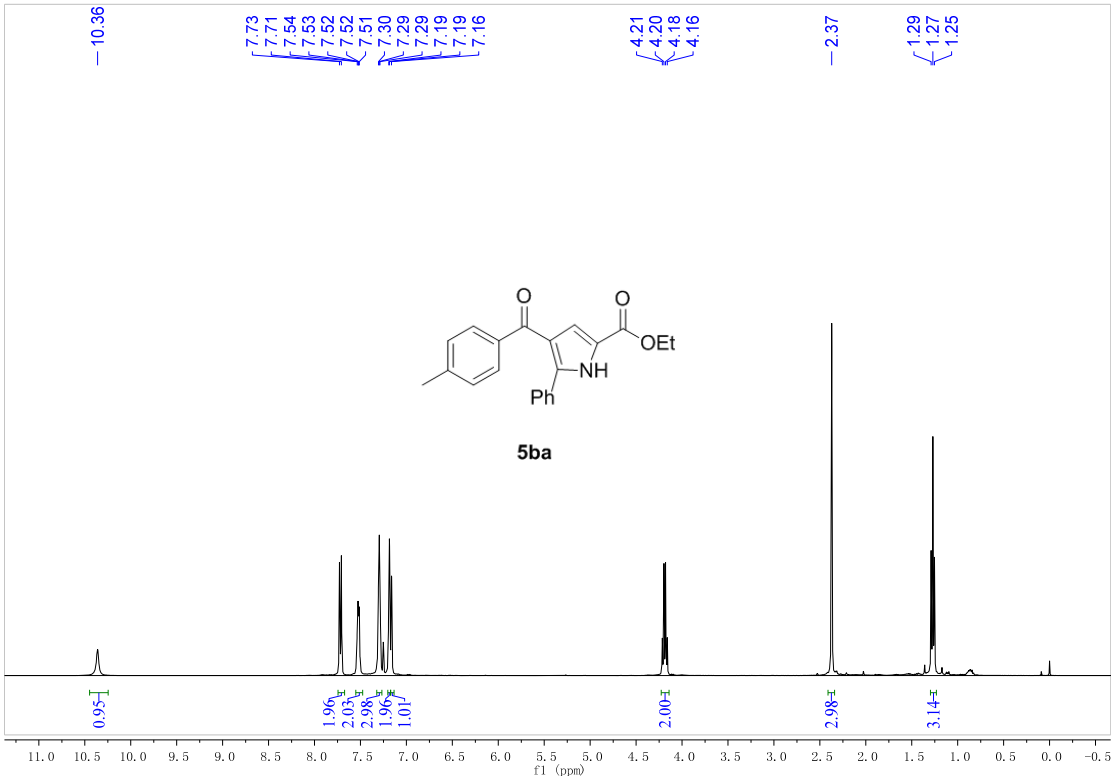

192.9
168.8
167.2
136.2
136.0
134.8
134.7
134.4
131.3
129.6
129.4
129.1
128.6
128.1
128.0
126.7
126.6
124.2
67.5
61.4
54.4
54.3
21.2
14.3
O
Ph
COOEt
N
N
H
Ph
O
Ph
4ak
210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 −10
f1 (ppm)

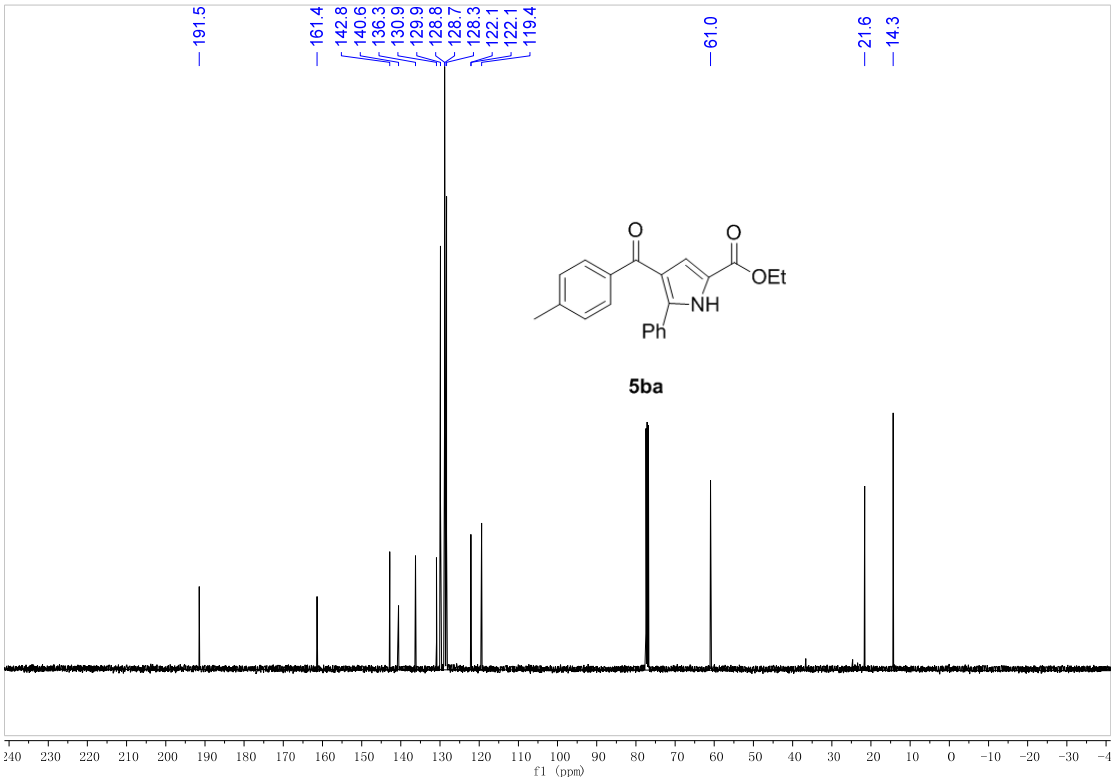
23. 5aa


9.89
7.80
7.79
7.78
7.53
7.52
7.52
7.52
7.51
7.50
7.48
7.47
7.39
7.37
7.36
7.35
7.34
7.33
7.32
7.26
7.22
7.21
4.29
4.28
4.26
4.24
1.34
1.32
1.30
O
O
OEt
NH
Ph
5aa
0.99
2.03
2.17
0.96
2.12
2.94
0.93
2.00
3.03
10.5 10.0 9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0
f1 (ppm)

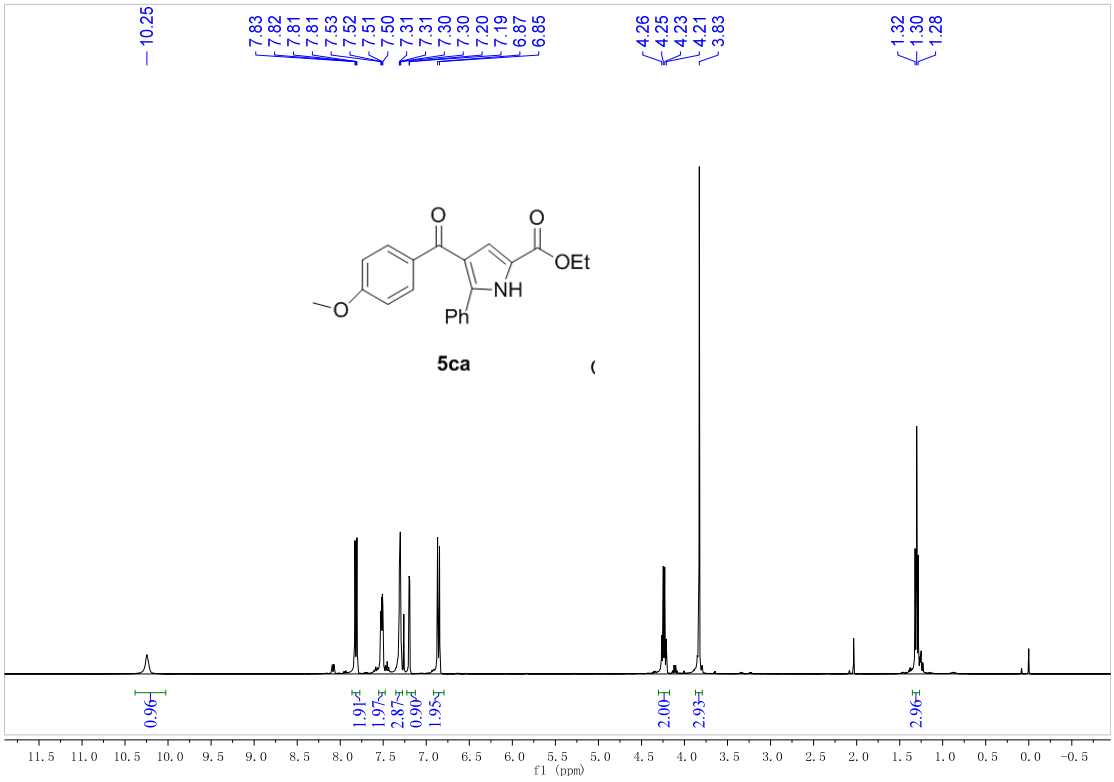

191.7
161.1
140.6
138.9
132.1
130.8
129.6
129.0
128.7
128.5
128.1
122.3
121.9
119.3
61.0
14.4
O
O
OEt
NH
Ph
5aa
f1 (ppm)

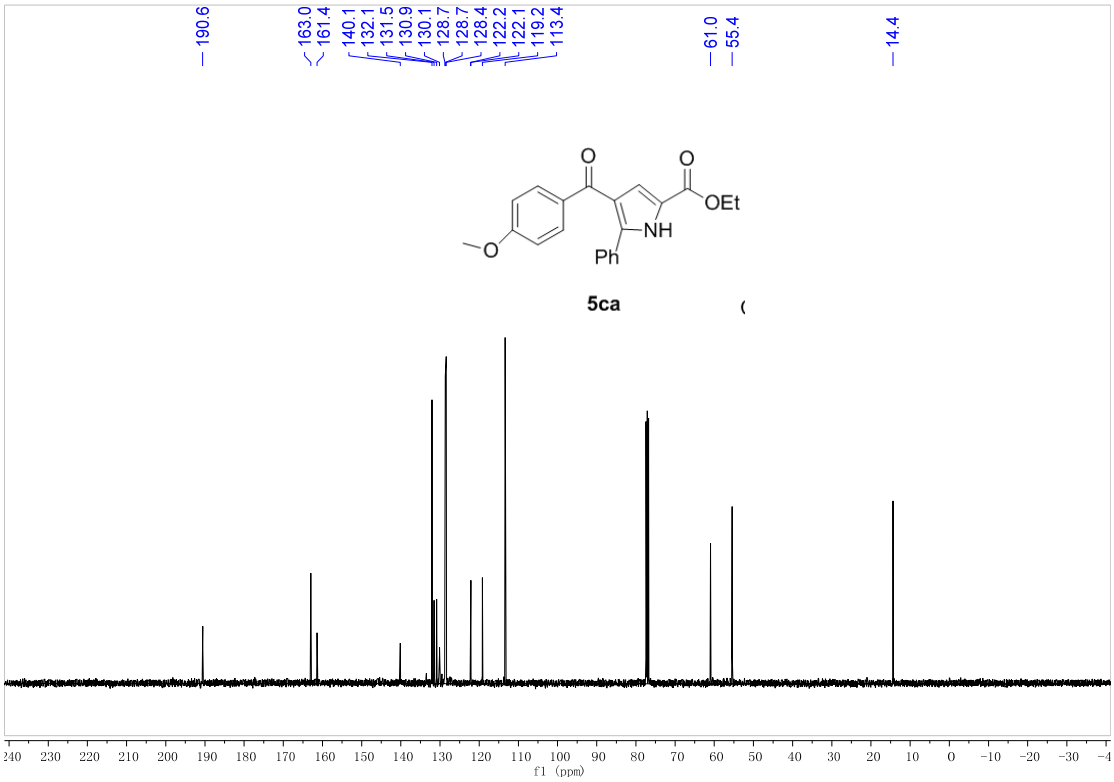
24. 5ba


10.36
7.73
7.71
7.54
7.53
7.52
7.52
7.51
7.30
7.29
7.29
7.19
7.19
7.16
4.21
4.20
4.18
4.16
2.37
1.29
1.27
1.25
O
O
OEt
NH
Ph
5ba
0.95
1.96
2.03
2.98
1.96
1.01
2.00
2.98
3.14
f1 (ppm)

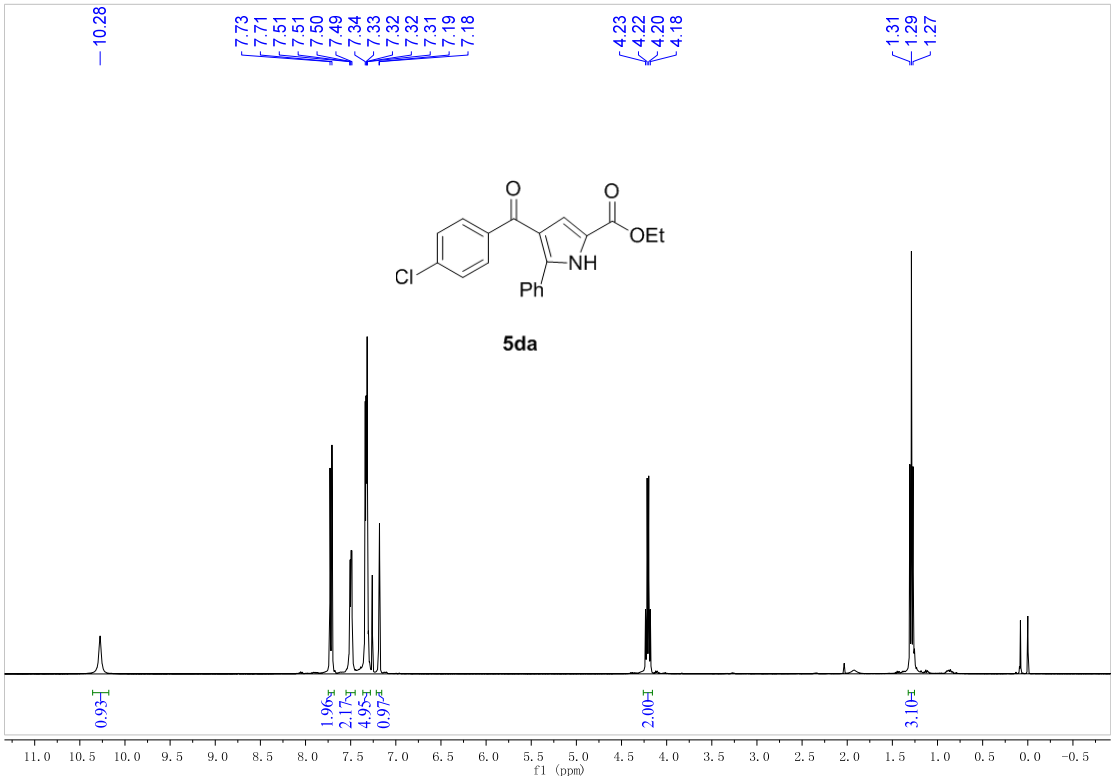

191.5
161.4
142.8
140.6
136.3
130.9
129.9
128.8
128.7
128.3
122.1
122.1
119.4
61.0
21.6
14.3
O
O
OEt
NH
Ph
5ba
f1 (ppm)

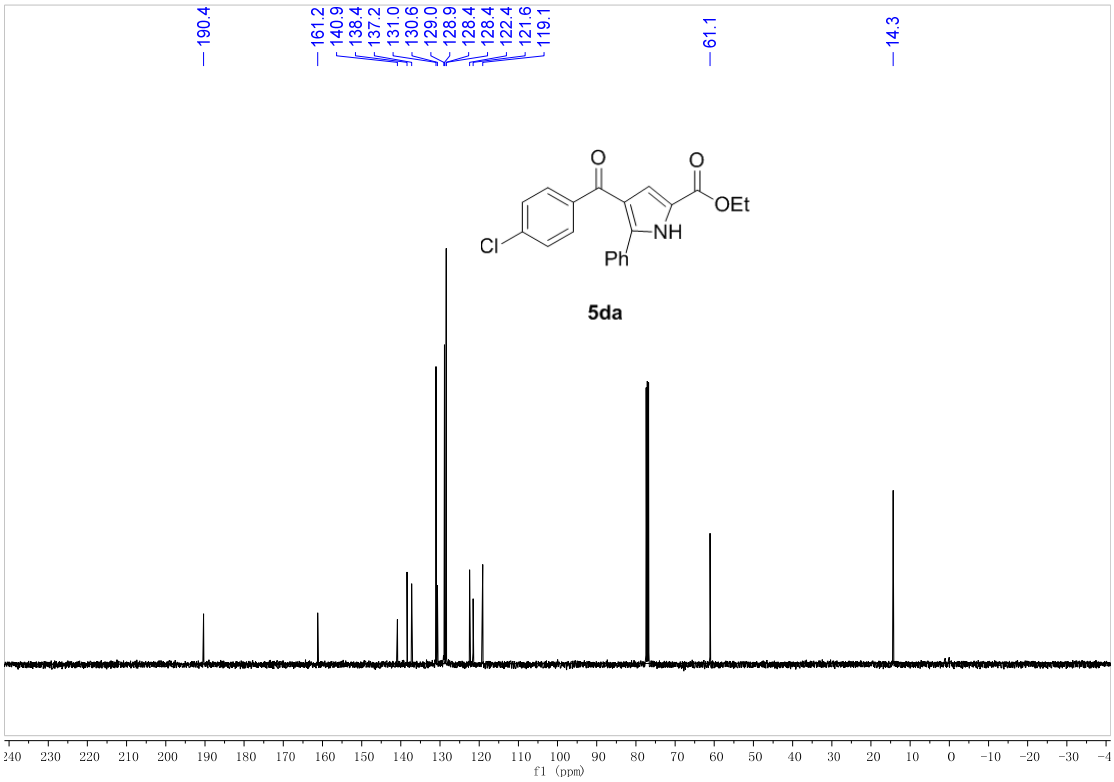
25. 5ca


10.25
7.83
7.82
7.81
7.81
7.53
7.52
7.51
7.50
7.31
7.31
7.30
7.30
7.20
7.19
6.87
6.85
4.26
4.25
4.23
4.21
3.83
1.32
1.30
1.28
O
O
OEt
NH
Ph
O
5ca
0.96
1.91
1.97
2.87
0.90
1.95
2.00
2.93
2.96
f1 (ppm)

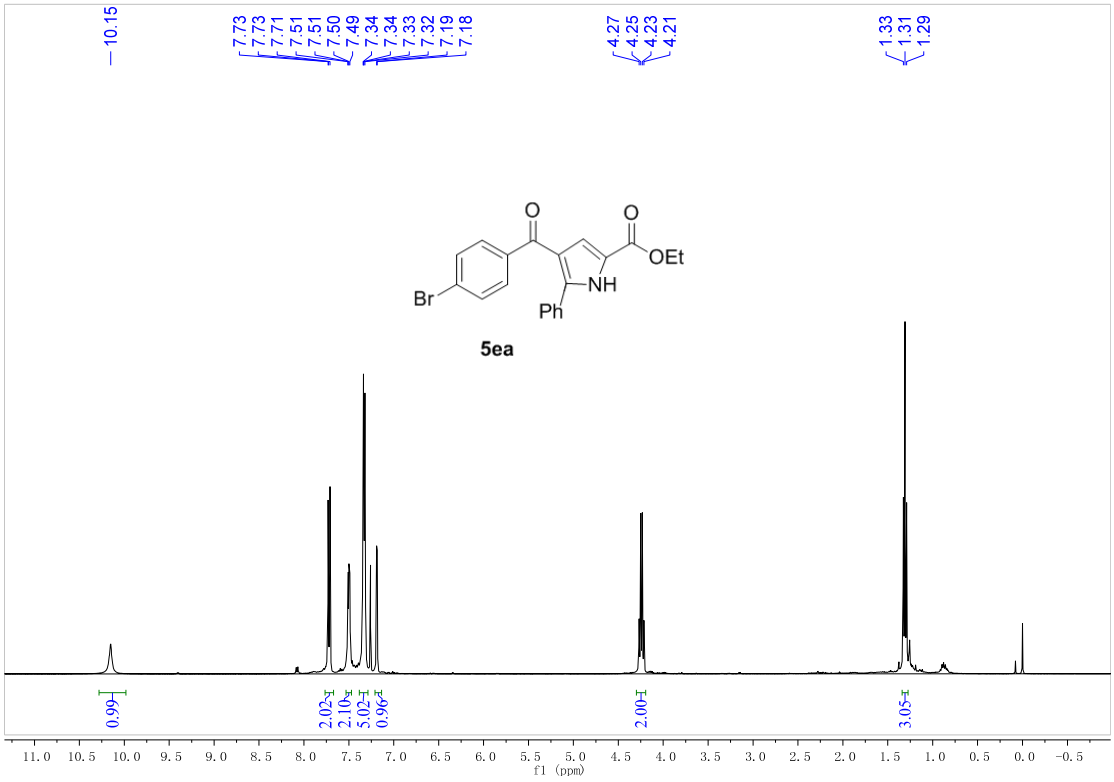

190.6
163.0
161.4
140.1
132.1
131.5
130.9
130.1
128.7
128.4
122.2
122.1
119.2
113.4
61.0
55.4
14.4
O
O
OEt
NH
Ph
O
5ca
f1 (ppm)

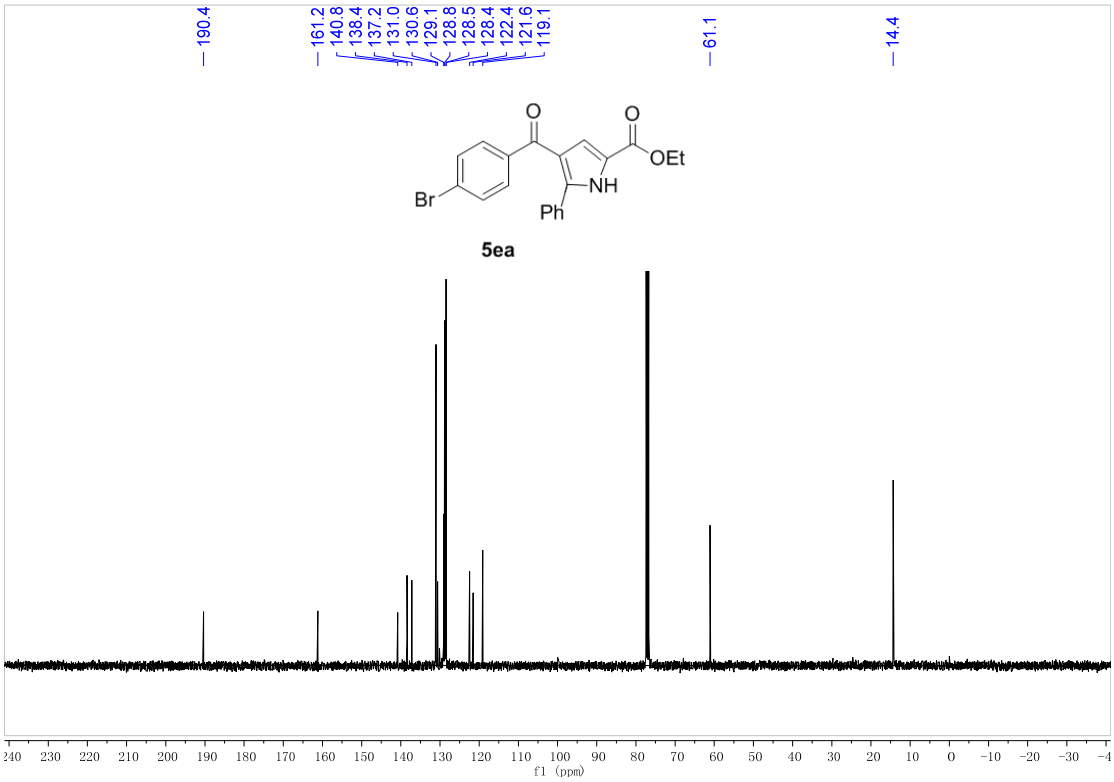
26. 5da


10.28
7.73
7.71
7.51
7.51
7.50
7.49
7.34
7.33
7.32
7.32
7.31
7.19
7.18
4.23
4.22
4.20
4.18
1.31
1.29
1.27
O
O
OEt
NH
Cl
Ph
5da
0.93
1.96
2.17
4.95
0.97
2.00
3.10
f1 (ppm)

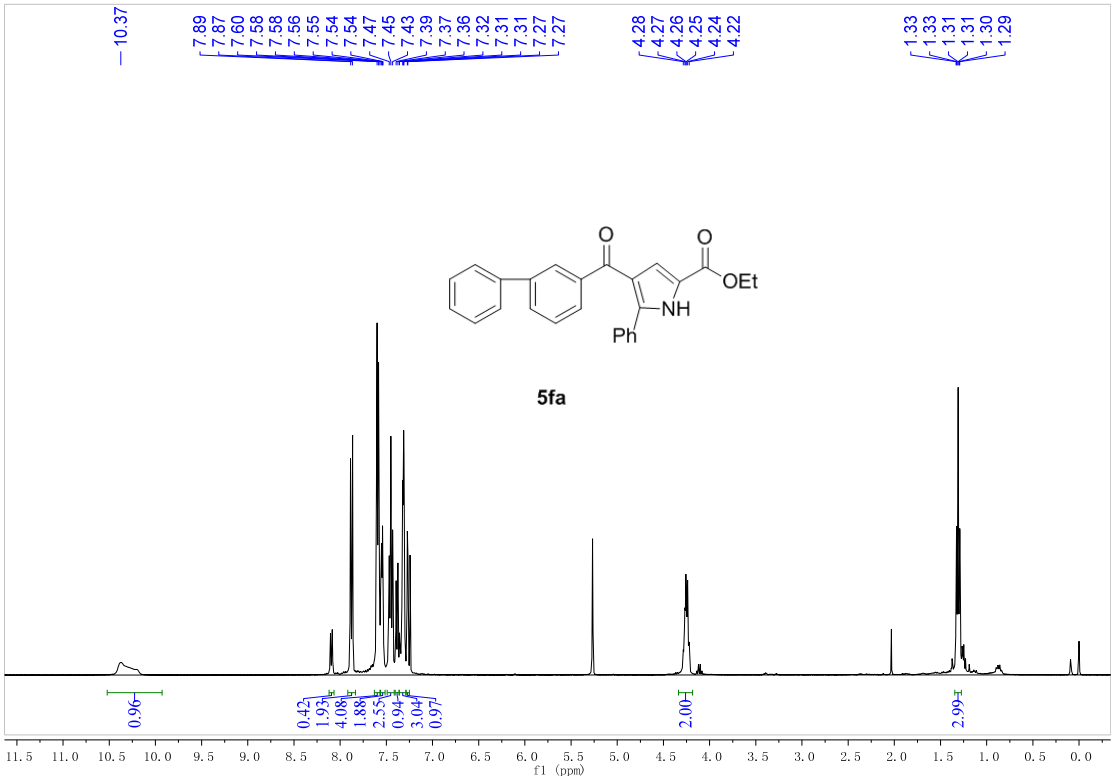

190.4
161.2
140.9
138.4
137.2
131.0
130.6
129.0
128.9
128.4
128.4
122.4
121.6
119.1
61.1
14.3
O
O
OEt
NH
Cl
Ph
5da
f1 (ppm)

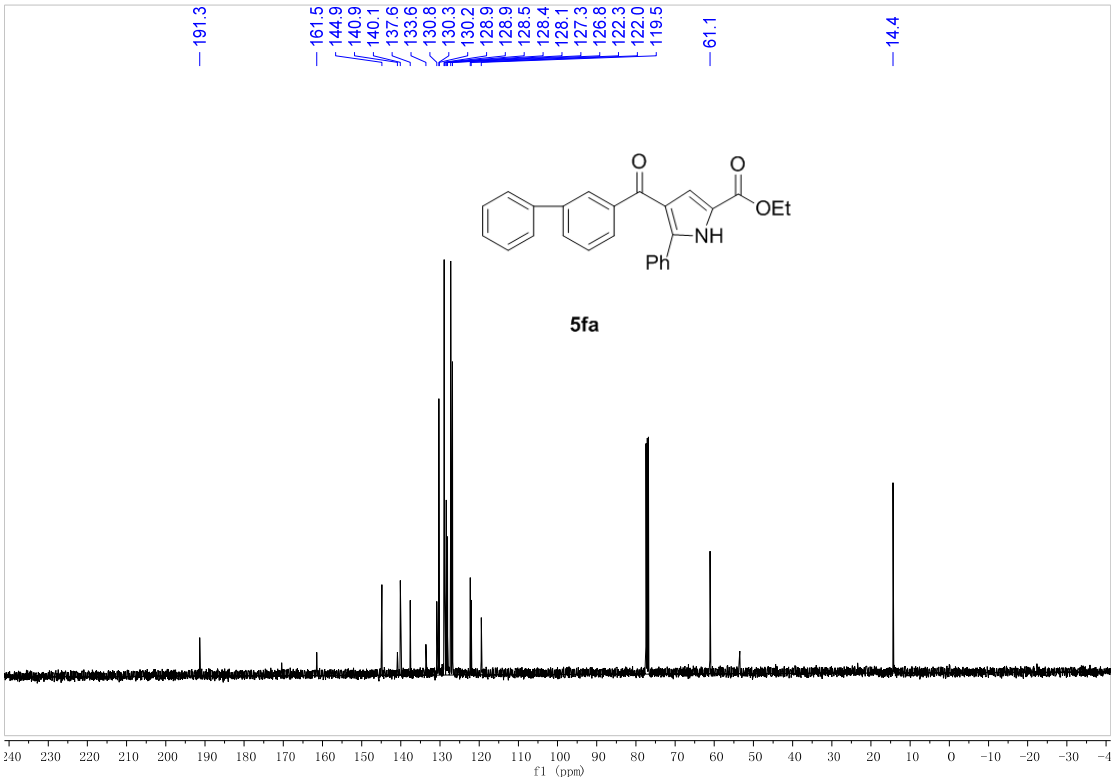
27. 5ea


10.15
7.73
7.73
7.71
7.51
7.51
7.50
7.49
7.34
7.34
7.33
7.32
7.19
7.18
4.27
4.25
4.23
4.21
1.33
1.31
1.29
O
O
OEt
NH
Br
Ph
5ea
0.99
2.02
2.10
5.02
0.96
2.00
3.05
f1 (ppm)

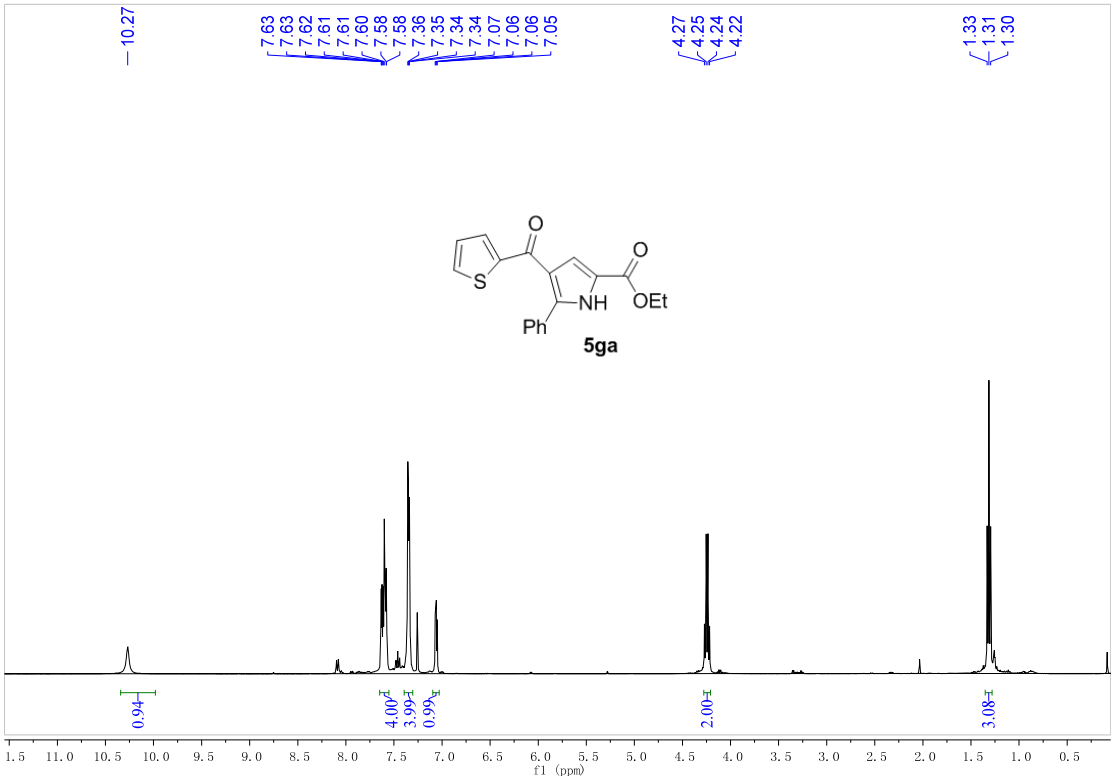

190.4
161.2
140.8
138.4
137.2
131.0
130.6
129.1
128.8
128.5
128.4
122.4
121.6
119.1
61.1
14.4
O
O
OEt
NH
Ph
Br
5ea
f1 (ppm)

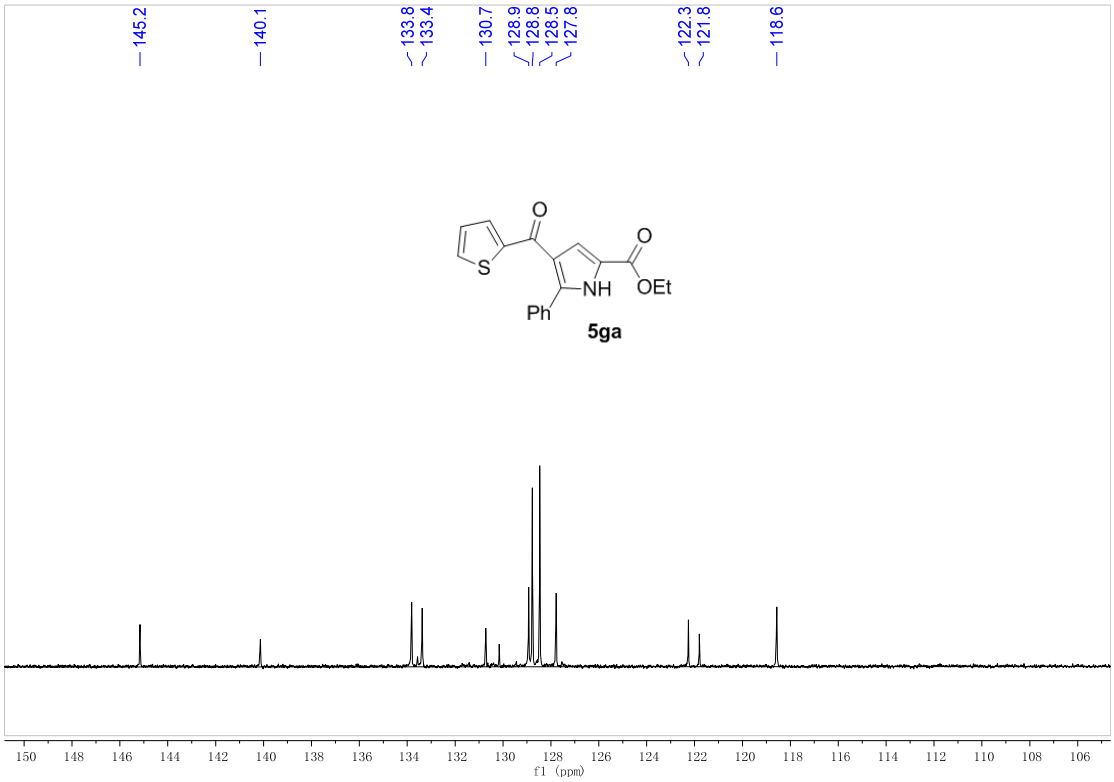
28. 5fa


10.37
7.89
7.87
7.60
7.58
7.58
7.56
7.55
7.54
7.54
7.47
7.45
7.43
7.39
7.37
7.36
7.32
7.31
7.31
7.27
7.27
4.28
4.27
4.26
4.25
4.24
4.22
1.33
1.33
1.31
1.31
1.30
1.29
O
O
OEt
NH
Ph
5fa
0.96
0.42
1.93
4.08
1.88
2.55
0.94
3.04
0.97
2.00
2.99
f1 (ppm)

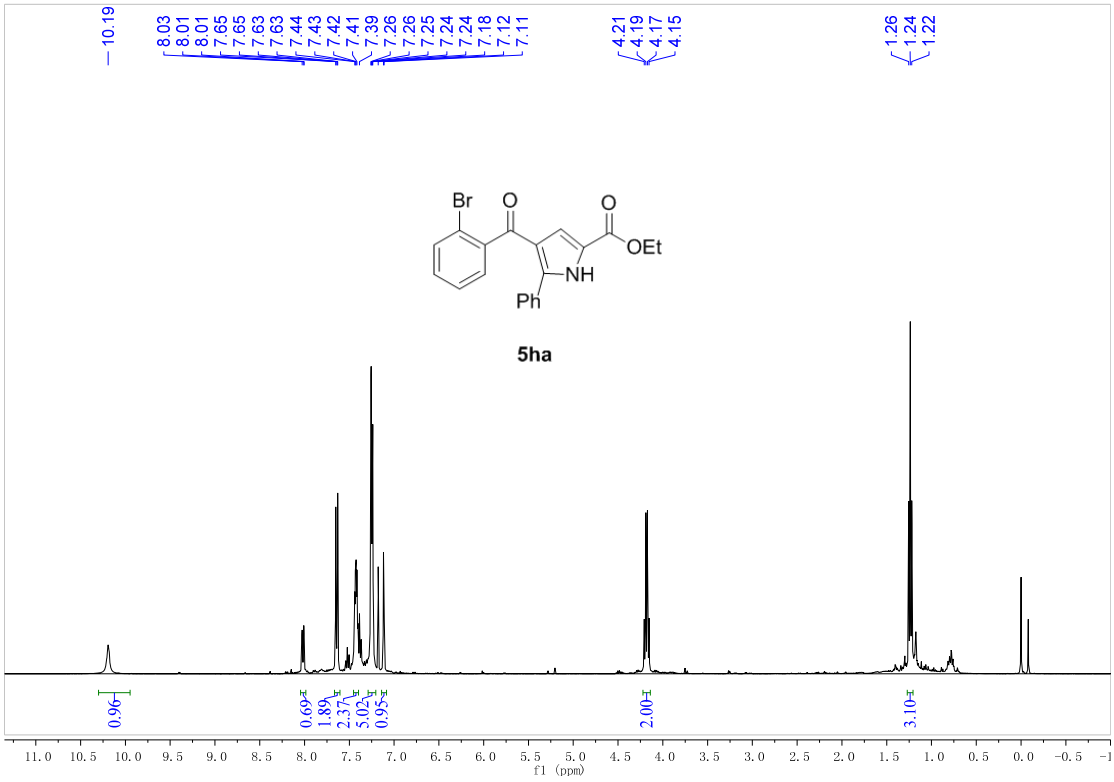

191.3
161.5
144.9
140.9
140.1
137.6
133.6
130.8
130.3
130.2
128.9
128.9
128.5
128.4
128.1
127.3
126.8
122.3
122.0
119.5
61.1
14.4
O
O
OEt
NH
Ph
5fa
f1 (ppm)

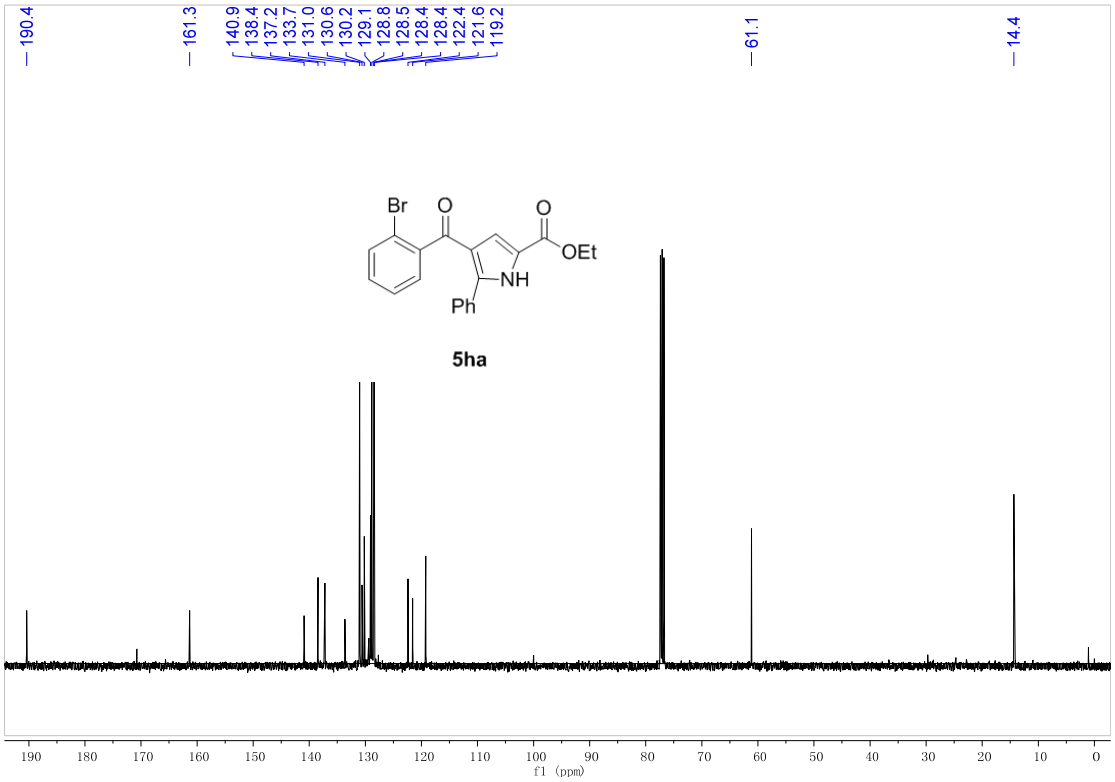
29. 5ga


10.27
7.63
7.63
7.62
7.61
7.61
7.60
7.58
7.58
7.36
7.35
7.34
7.34
7.07
7.06
7.06
7.05
4.27
4.25
4.24
4.22
1.33
1.31
1.30
O
O
S
NH
OEt
Ph
5ga
0.94
4.00
3.99
0.99
2.00
3.08
f1 (ppm)

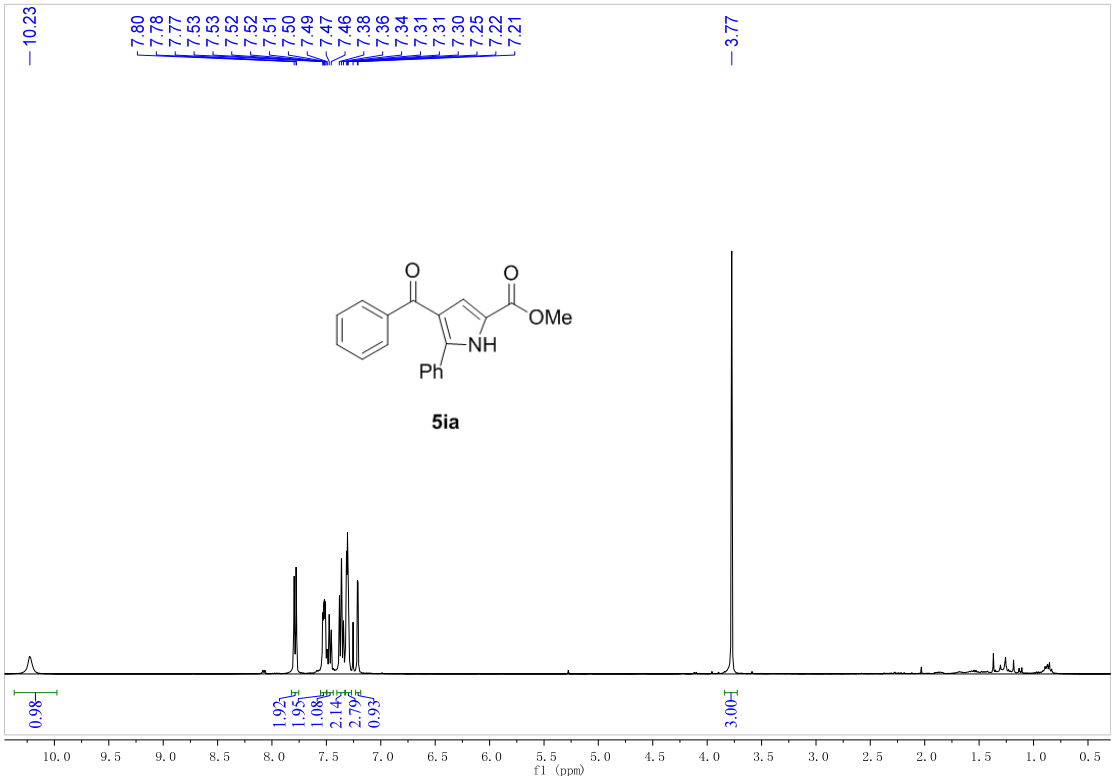

145.2
140.1
133.8
133.4
130.7
128.9
128.8
128.5
127.8
122.3
121.8
118.6
O
O
S
NH
OEt
Ph
5ga
150 148 146 144 142 140 138 136 134 132 130 128 126 124 122 120 118 116 114 112 110 108 106
f1 (ppm)

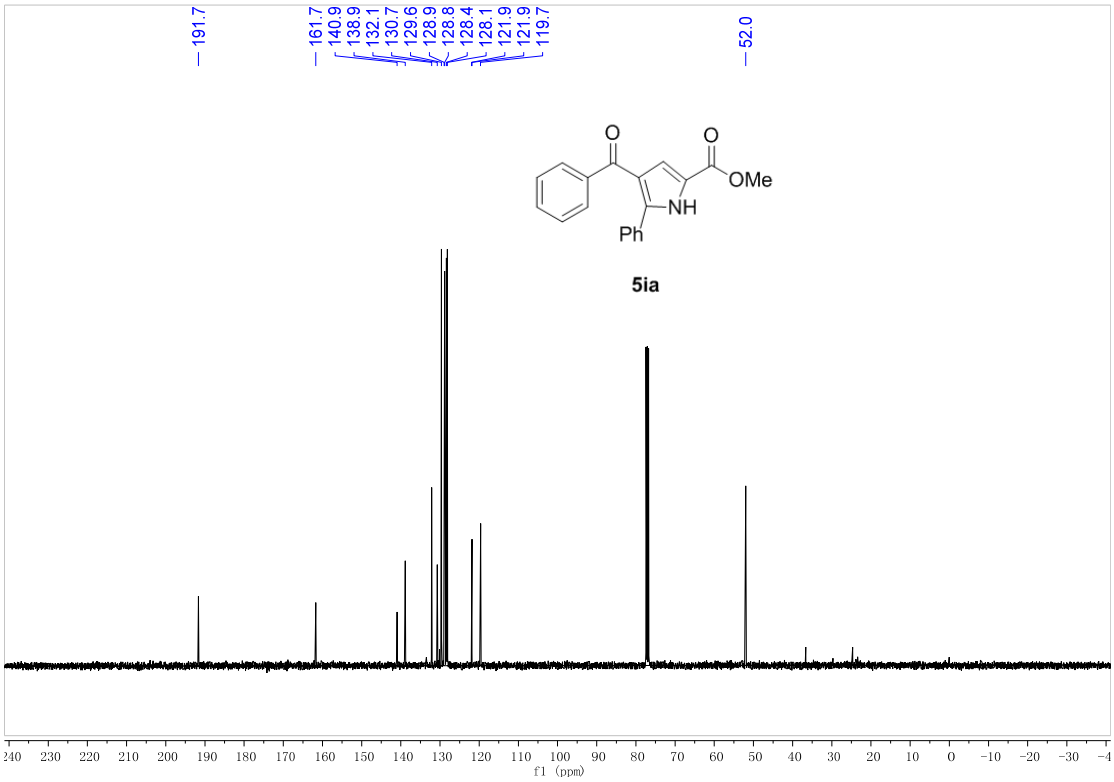
30. 5ha


10.19
8.03
8.01
8.01
7.65
7.65
7.63
7.63
7.44
7.43
7.42
7.41
7.39
7.26
7.26
7.25
7.24
7.24
7.18
7.12
7.11
4.21
4.19
4.17
4.15
1.26
1.24
1.22
Br
O
O
OEt
NH
Ph
5ha
0.96
0.69
1.89
2.37
5.02
0.95
2.00
3.10
11.0 10.5 10.0 9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0 -0.5 -1
f1 (ppm)

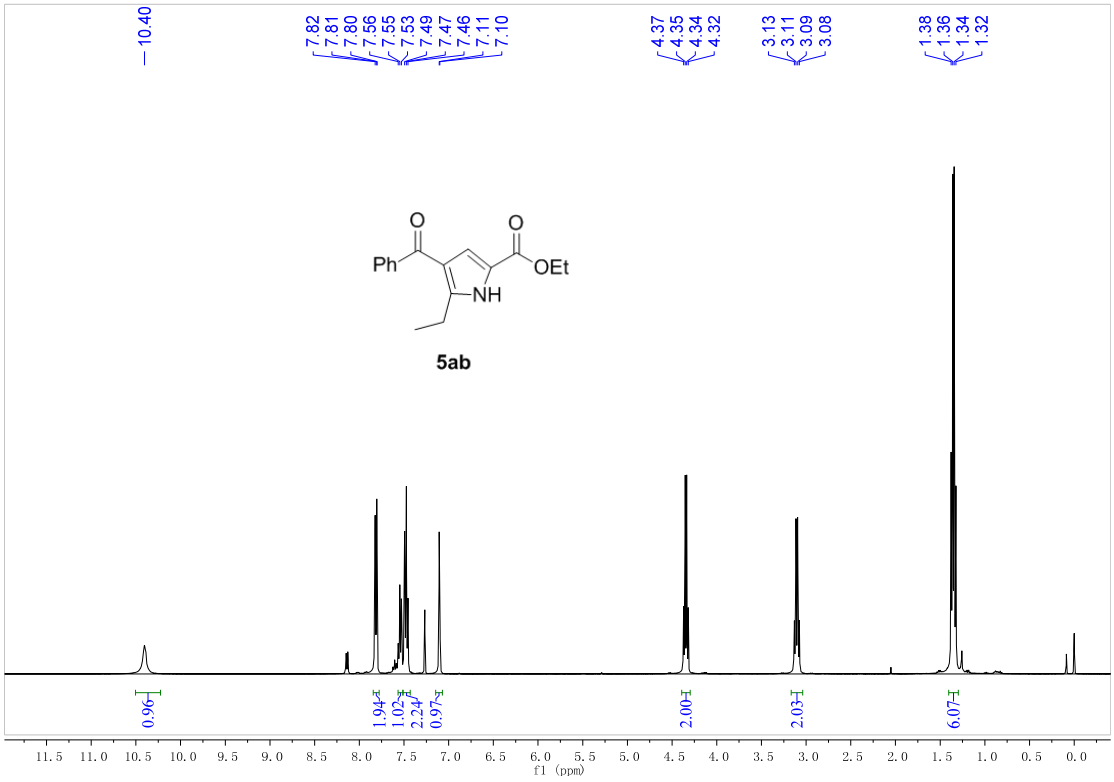

190.4
161.3
140.9
138.4
137.2
133.7
131.0
130.6
130.2
129.1
128.8
128.5
128.4
128.4
122.4
121.6
119.2
61.1
14.4
Br
O
O
OEt
NH
Ph
5ha
f1 (ppm)

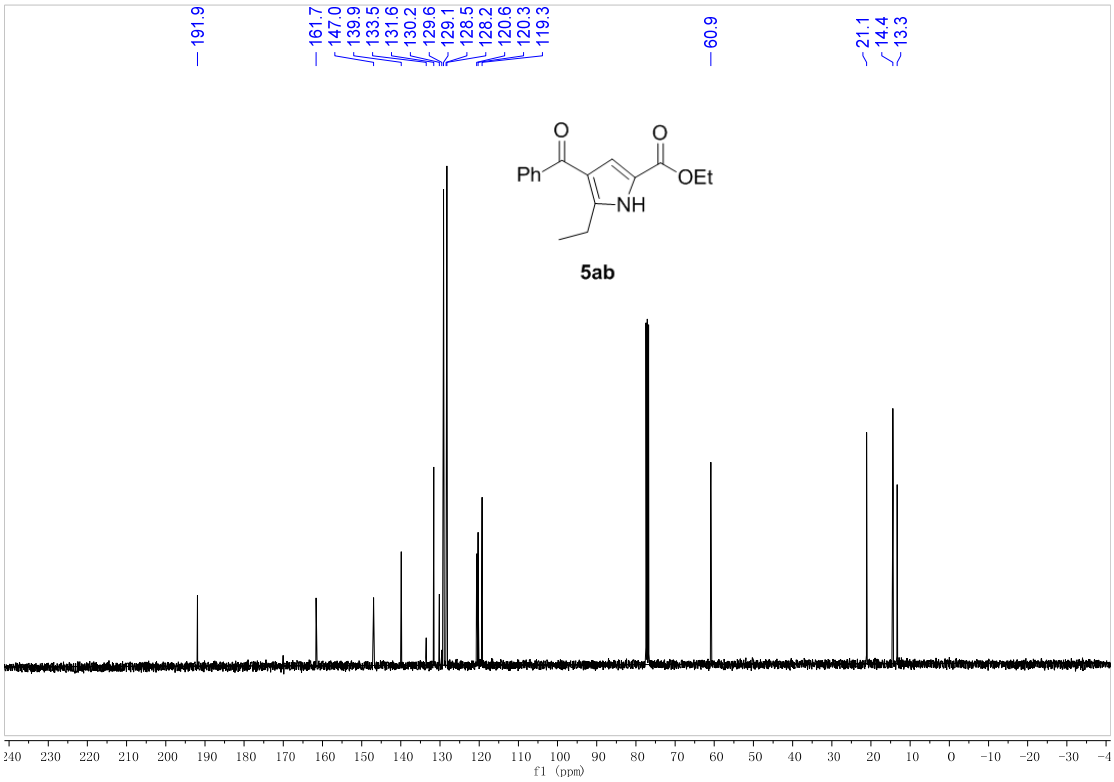
31.5ia


10.23
7.80
7.78
7.77
7.53
7.53
7.52
7.52
7.51
7.50
7.49
7.47
7.46
7.38
7.36
7.34
7.31
7.31
7.30
7.25
7.22
7.21
3.77
O
O
OMe
NH
Ph
5ia
0.98
1.92
1.95
1.08
2.14
2.79
0.93
3.00
f1 (ppm)

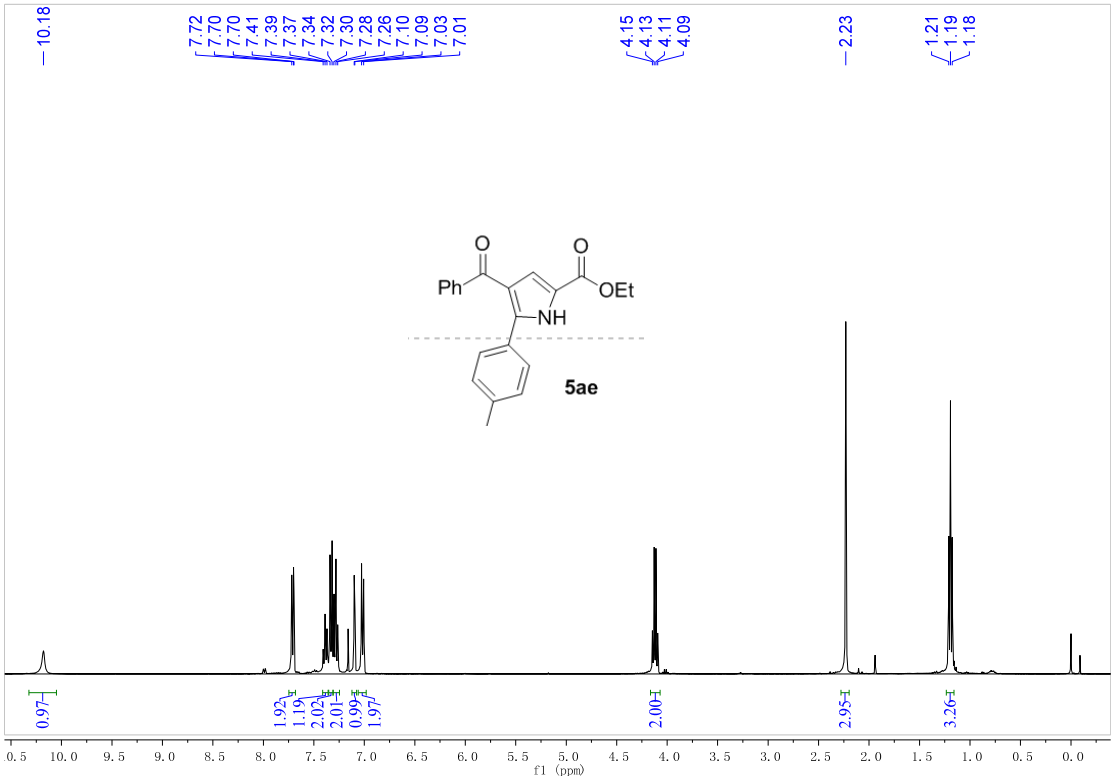

191.7
161.7
140.9
138.9
132.1
130.7
129.6
128.9
128.8
128.4
128.1
121.9
121.9
119.7
52.0
O
O
OMe
NH
Ph
5ia
f1 (ppm)

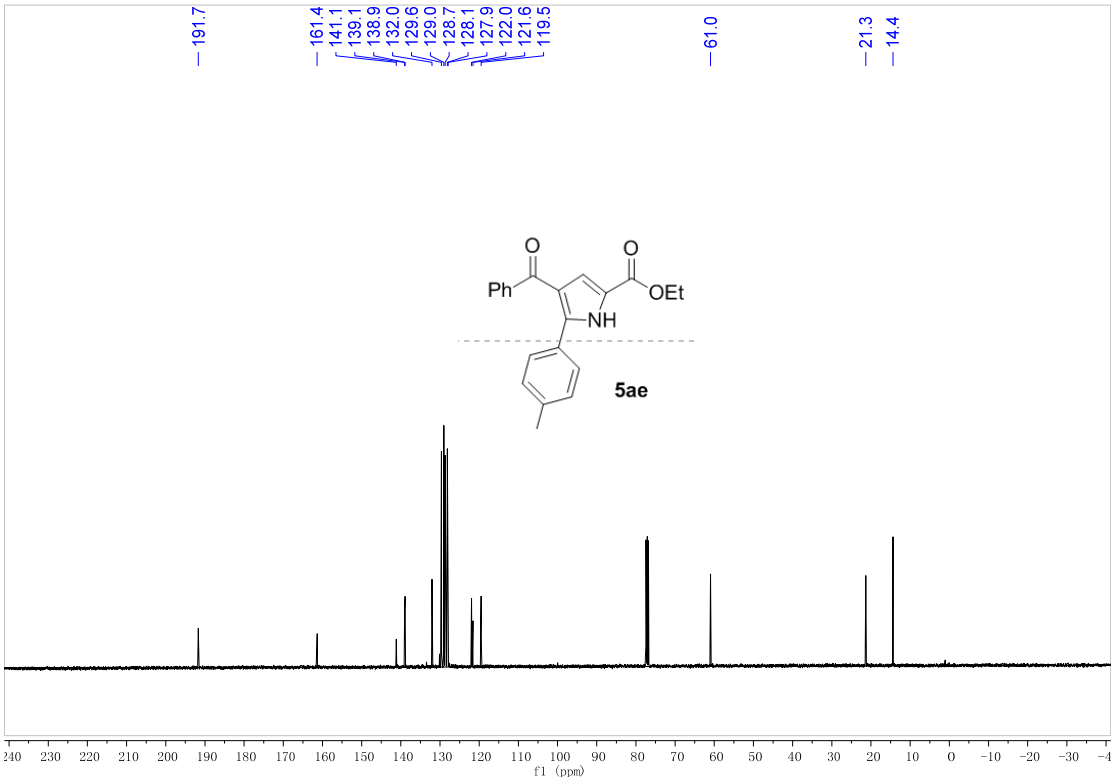
32. 5ab


10.40
7.82
7.81
7.80
7.56
7.55
7.53
7.49
7.47
7.46
7.11
7.10
4.37
4.35
4.34
4.32
3.13
3.11
3.09
3.08
1.38
1.36
1.34
1.32
O
O
Ph
OEt
NH
5ab
0.96
1.94
1.02
2.24
0.97
2.00
2.03
6.07
f1 (ppm)

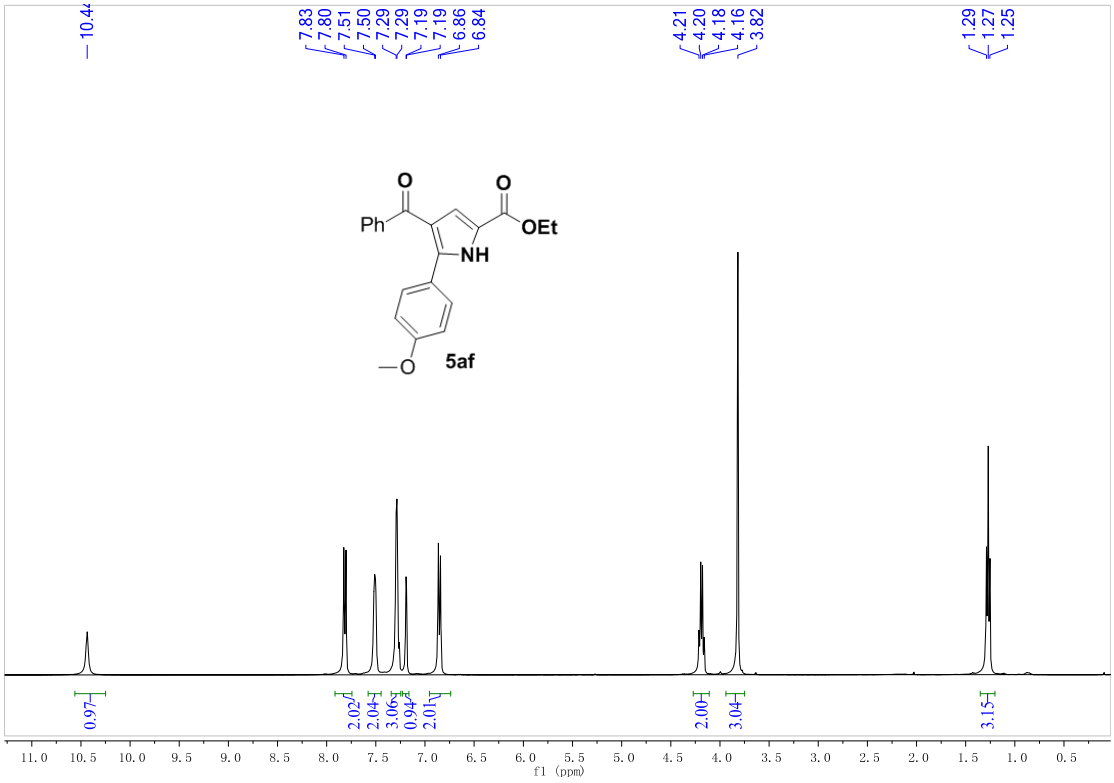

191.9
161.7
147.0
139.9
133.5
131.6
130.2
129.6
129.1
128.5
128.2
120.6
120.3
119.3
60.9
21.1
14.4
13.3
O
O
Ph
OEt
NH
5ab
f1 (ppm)

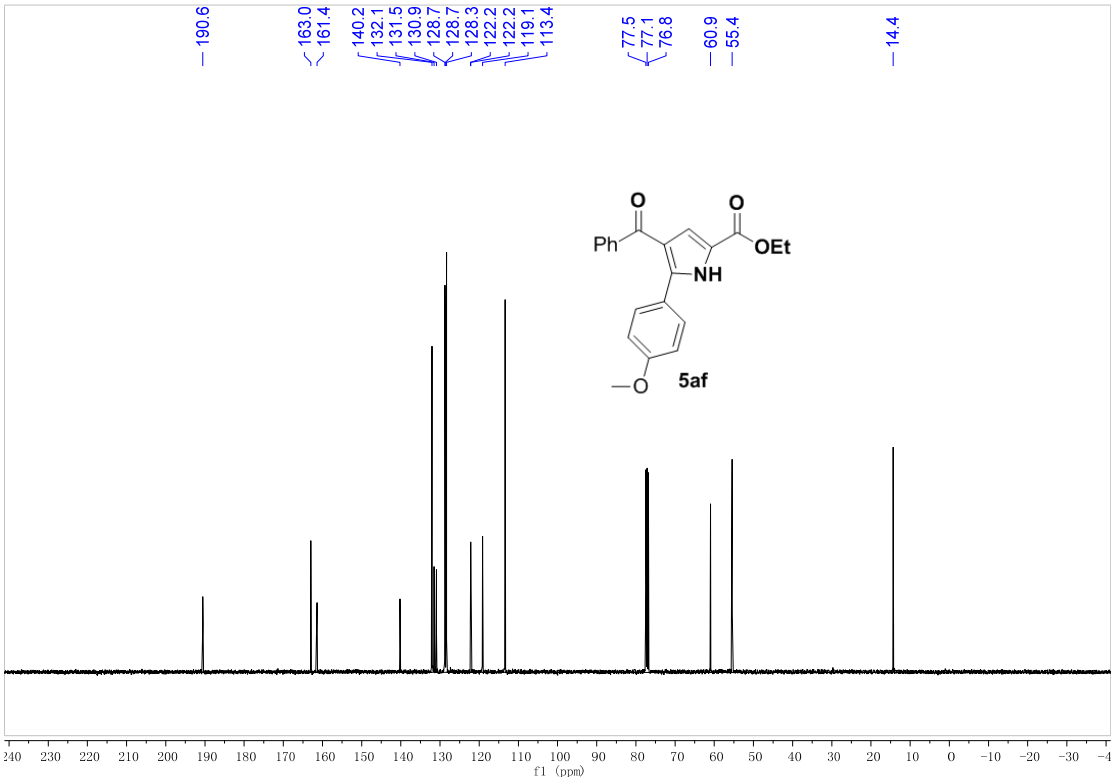
33. 5ae


10.18
7.72
7.70
7.70
7.41
7.39
7.37
7.34
7.32
7.30
7.28
7.26
7.10
7.09
7.03
7.01
4.15
4.13
4.11
4.09
2.23
1.21
1.19
1.18
O
O
Ph
OEt
NH
5ae
0.97
1.92
1.19
2.02
2.01
0.99
1.97
2.00
2.95
3.26
f1 (ppm)

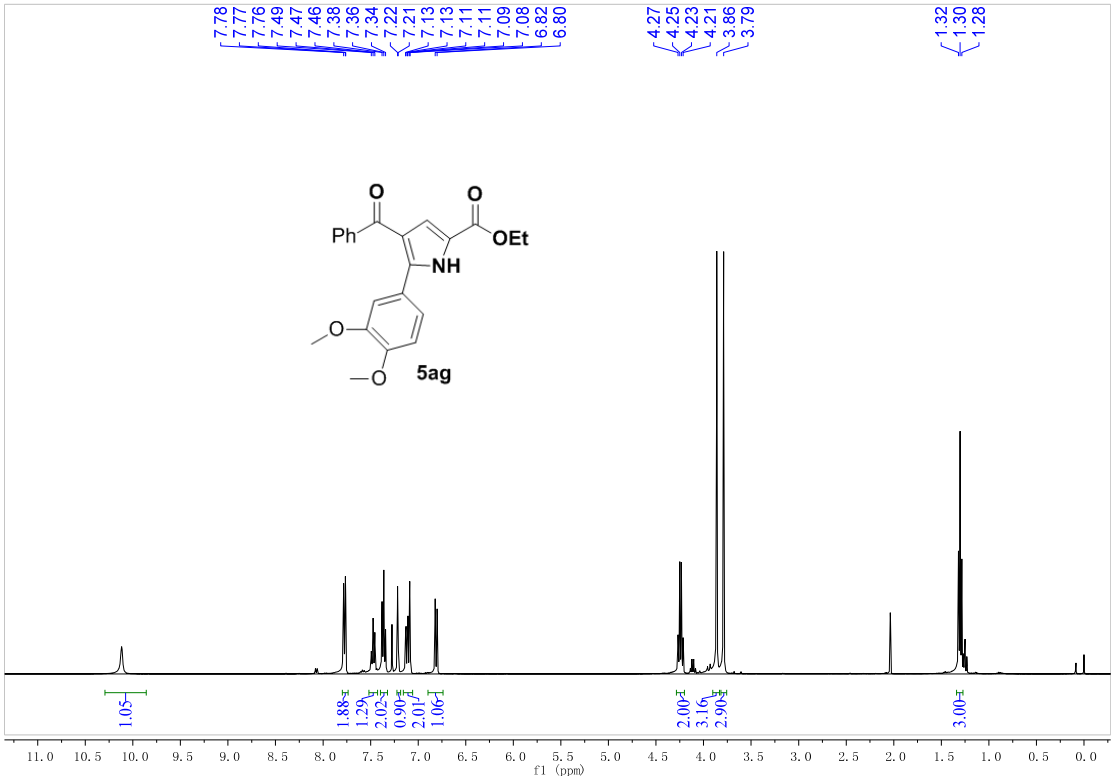

191.7
161.4
141.1
139.1
138.9
132.0
129.6
129.0
128.7
128.1
127.9
122.0
121.6
119.5
61.0
21.3
14.4
Ph
O
O
OEt
NH
5ae
f1 (ppm)

34. 5af


10.44
7.83
7.80
7.51
7.50
7.29
7.29
7.19
7.19
6.86
6.84
4.21
4.20
4.18
4.16
3.82
1.29
1.27
1.25
Ph
O
O
OEt
NH
O
5af
0.97
2.02
2.04
3.06
0.94
2.01
2.00
3.04
3.15
f1 (ppm)


190.6
163.0
161.4
140.2
132.1
131.5
130.9
128.7
128.7
128.3
122.2
122.2
119.1
113.4
77.5
77.1
76.8
60.9
55.4
14.4
Ph
O
O
OEt
NH
O
5af
f1 (ppm)

35. 5ag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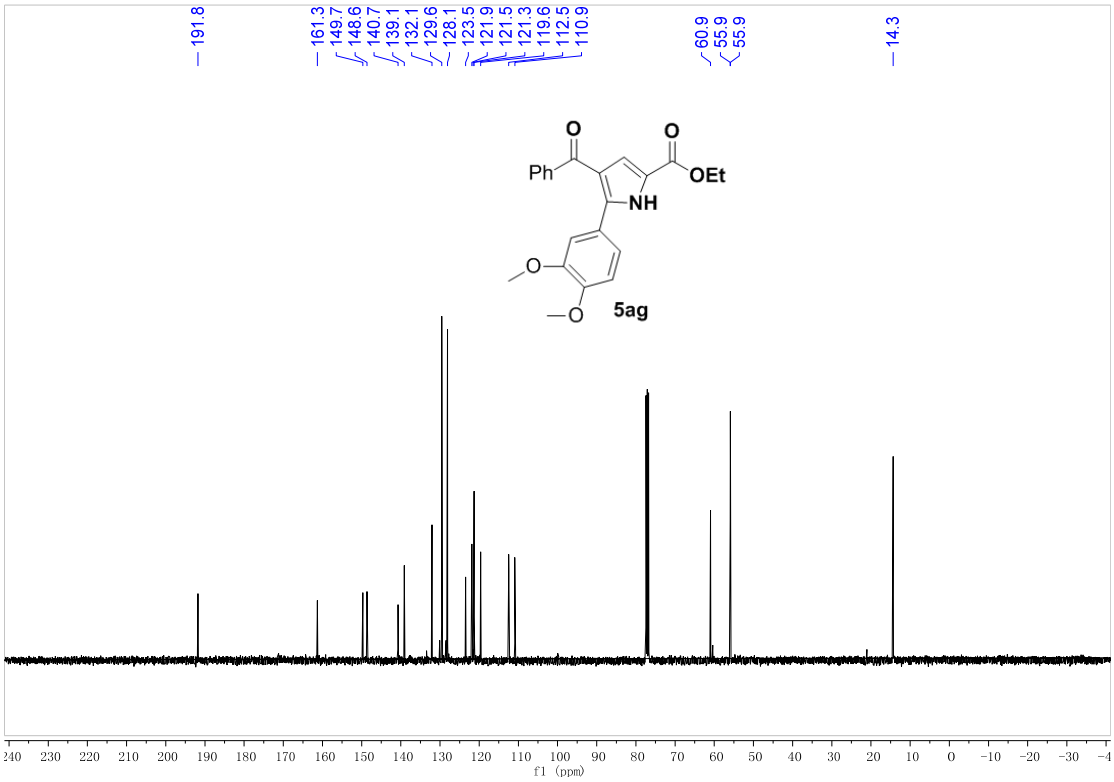
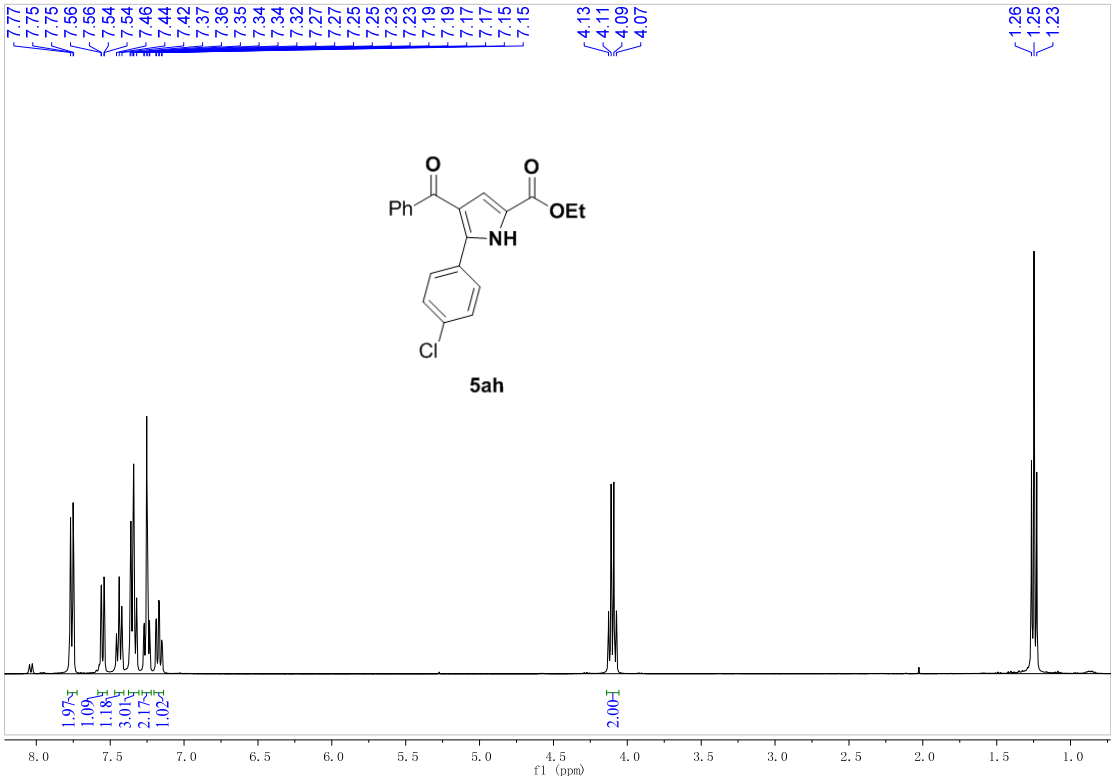
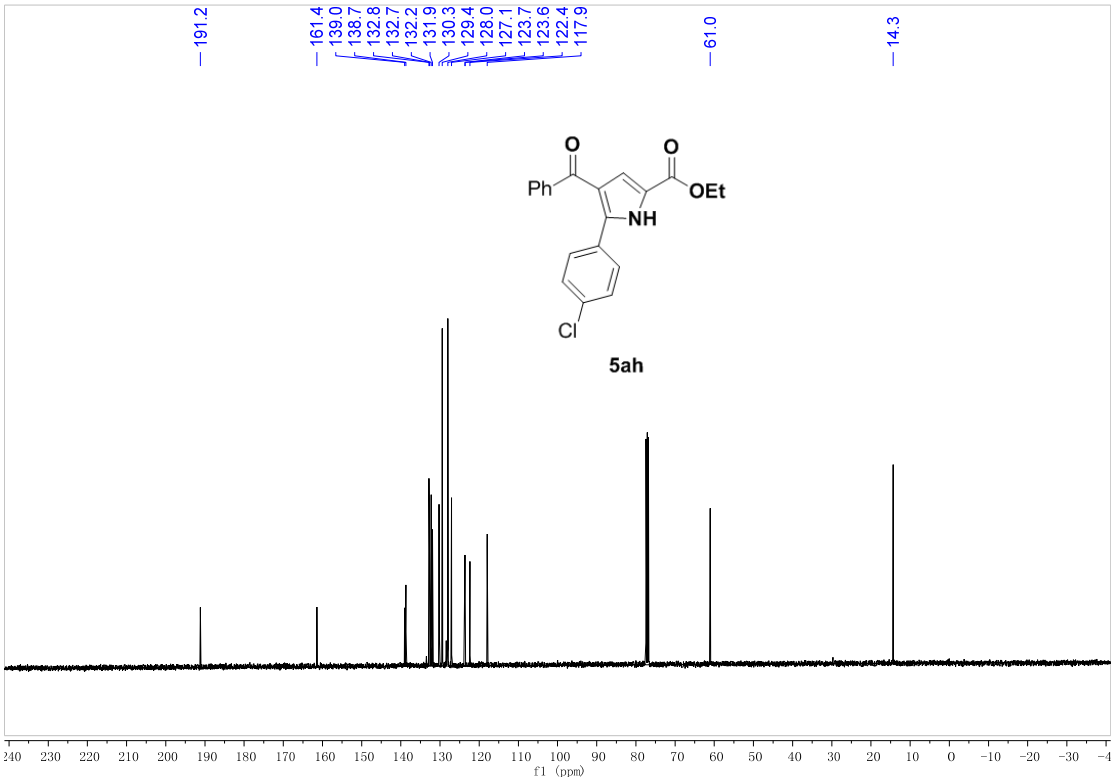
7.77
7.76
7.49
7.47
7.46
7.38
7.36
7.34
7.22
7.21
7.13
7.13
7.11
7.11
7.09
7.08
6.82
6.80
4.27
4.25
4.23
4.21
3.86
3.79
1.32
1.30
1.28
Ph
O
O
OEt
NH
O
O
5ag
1.05
1.88
1.29
2.02
0.90
2.01
1.06
2.00
3.16
2.90
3.00
f1 (ppm)

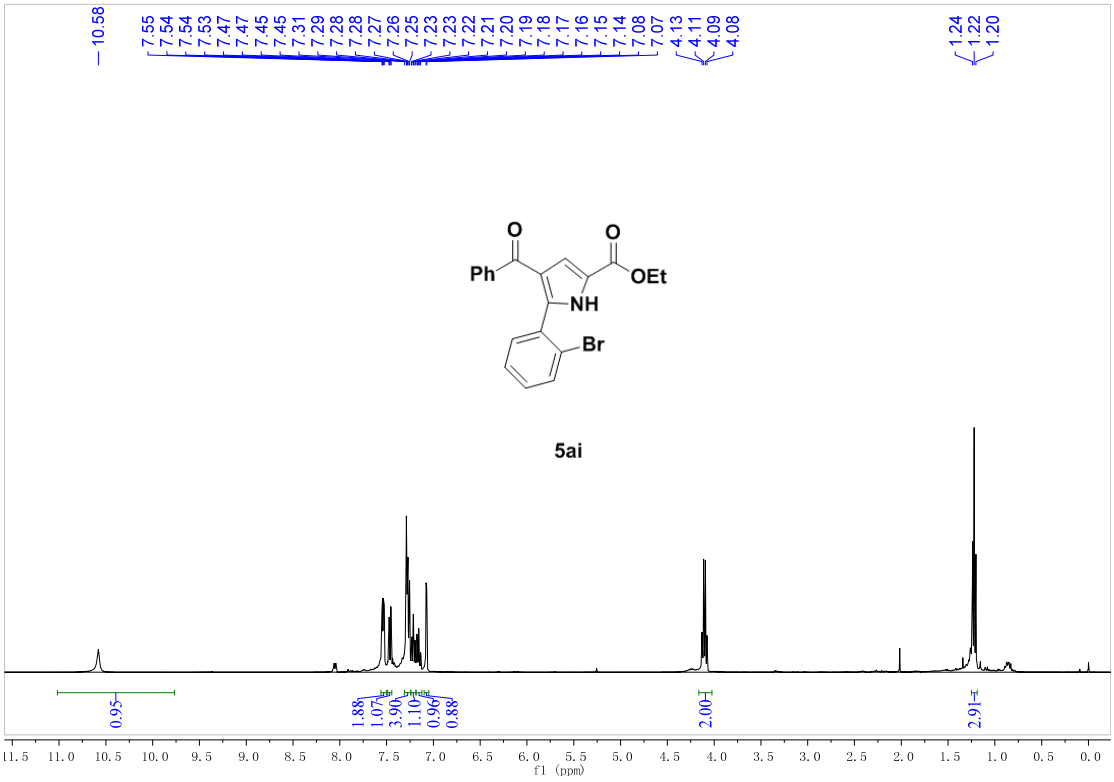

191.8
161.3
149.7
148.6
140.7
139.1
132.1
129.6
128.1
123.5
121.9
121.5
121.3
119.6
112.5
110.9
60.9
55.9
55.9
14.3
Ph
O
O
OEt
NH
O
O
5ag
f1 (ppm)

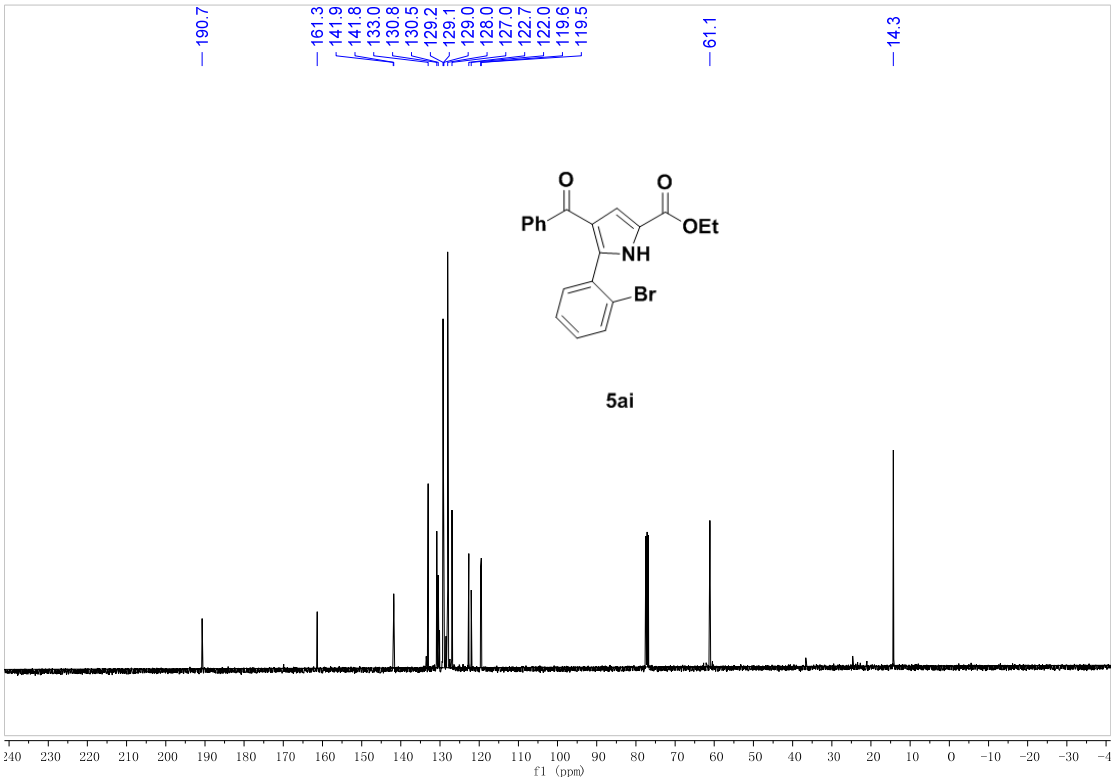
36. 5ah


7.77
7.75
7.75
7.56
7.56
7.54
7.54
7.46
7.44
7.42
7.37
7.36
7.35
7.34
7.34
7.32
7.27
7.27
7.25
7.25
7.23
7.23
7.19
7.19
7.17
7.17
7.15
7.15
4.13
4.11
4.09
4.07
1.26
1.25
1.23
Ph
O
O
OEt
NH
Cl
5ah
1.97
1.09
1.18
3.01
2.17
1.02
2.00
f1 (ppm)

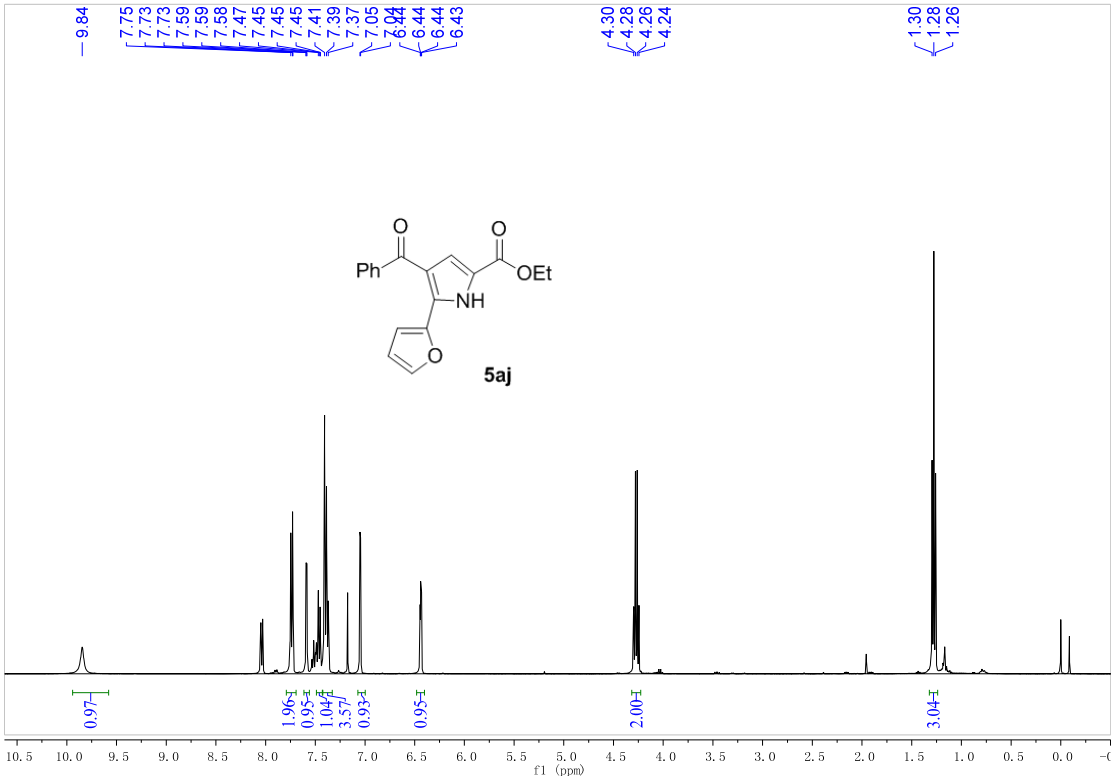

191.2
161.4
139.0
138.7
132.8
132.7
132.2
131.9
130.3
129.4
128.0
127.1
123.7
123.6
122.4
117.9
61.0
14.3
O
O
Ph
OEt
NH
Cl
5ah
f1 (ppm)

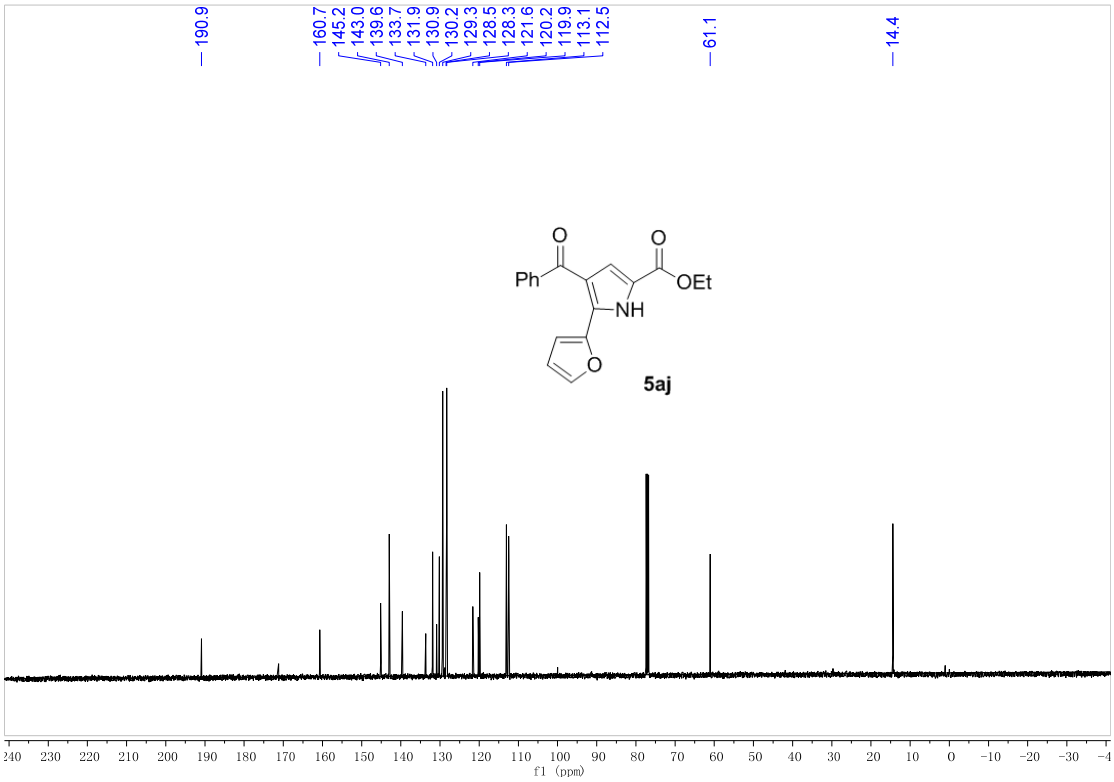
37.5ai


10.58
7.55
7.54
7.54
7.53
7.47
7.45
7.45
7.31
7.29
7.28
7.28
7.27
7.26
7.25
7.23
7.23
7.22
7.21
7.20
7.19
7.18
7.17
7.16
7.15
7.14
7.08
7.07
4.13
4.11
4.09
4.08
1.24
1.22
1.20
O
O
Ph
OEt
NH
Br
5ai
0.95
1.88
1.07
3.90
1.10
0.96
0.88
2.00
2.91
f1 (ppm)

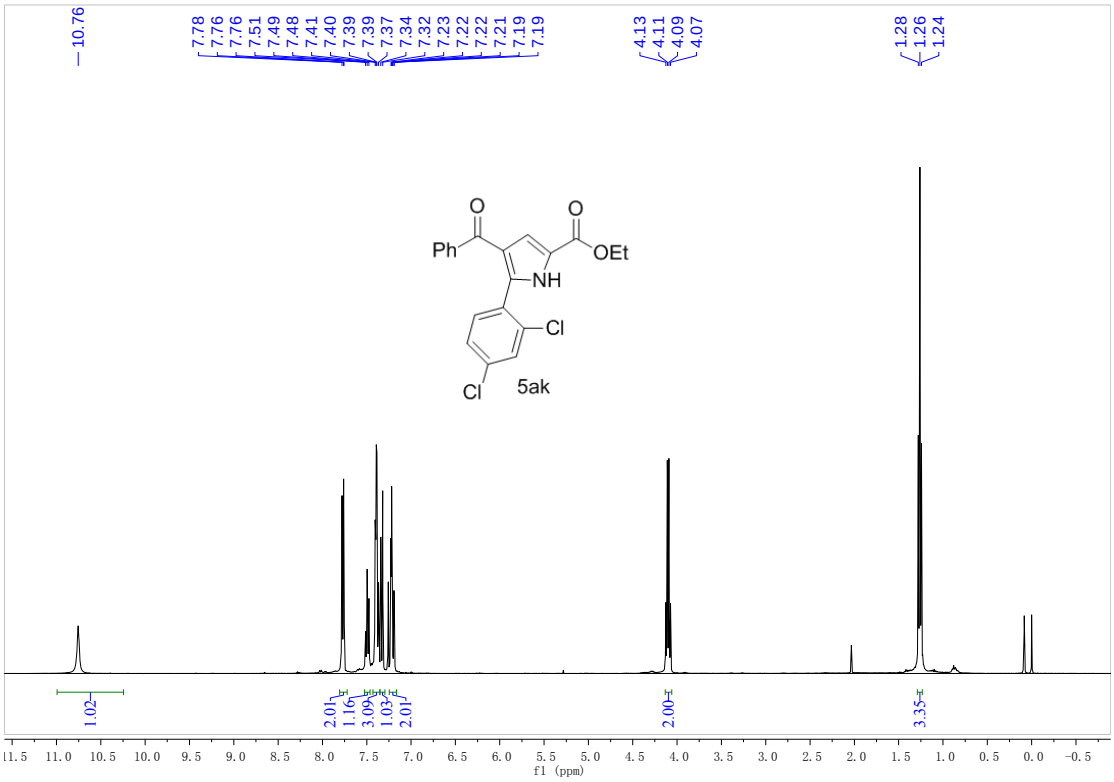

190.7
161.3
141.9
141.8
133.0
130.8
130.5
129.2
129.1
129.0
128.0
127.0
122.7
122.0
119.6
119.5
61.1
14.3
O
O
Ph
OEt
NH
Br
5ai
f1 (ppm)

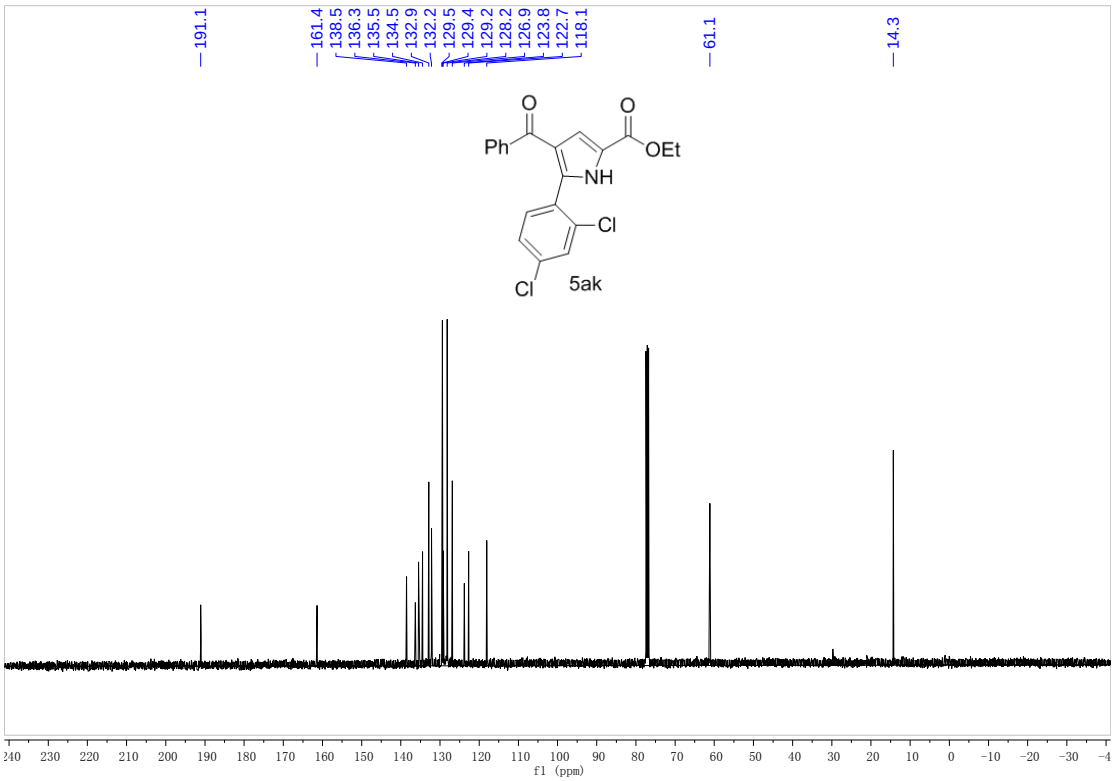
38.5aj


9.84
7.75
7.73
7.73
7.59
7.59
7.58
7.47
7.45
7.45
7.45
7.41
7.39
7.37
7.05
6.44
6.44
6.43
4.30
4.28
4.26
4.24
1.30
1.28
1.26
O
O
Ph
OEt
NH
O
5aj
0.97
1.96
0.95
1.04
3.57
0.93
0.95
2.00
3.04
f1 (ppm)


190.9
160.7
145.2
143.0
139.6
133.7
131.9
130.9
130.2
129.3
128.5
128.3
121.6
120.2
119.9
113.1
112.5
61.1
14.4
Ph
O
O
OEt
NH
O
5aj
f1 (ppm)

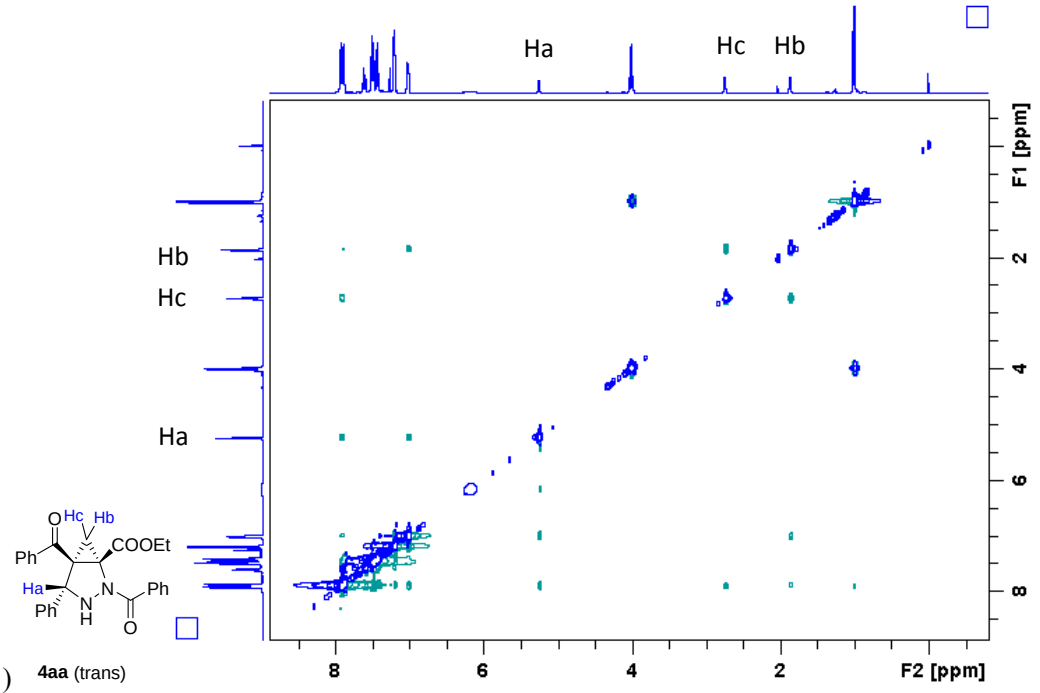
39. 5ak


10.76
7.78
7.76
7.76
7.51
7.49
7.48
7.41
7.40
7.39
7.39
7.37
7.34
7.32
7.23
7.22
7.22
7.21
7.19
7.19
4.13
4.11
4.09
4.07
1.28
1.26
1.24
Ph
O
O
OEt
NH
Cl
Cl
5ak
1.02
2.01
1.16
3.09
1.03
2.01
2.00
3.35
f1 (ppm)



(4) NOE spectra for 4aa、4af、4ag and 4ab.

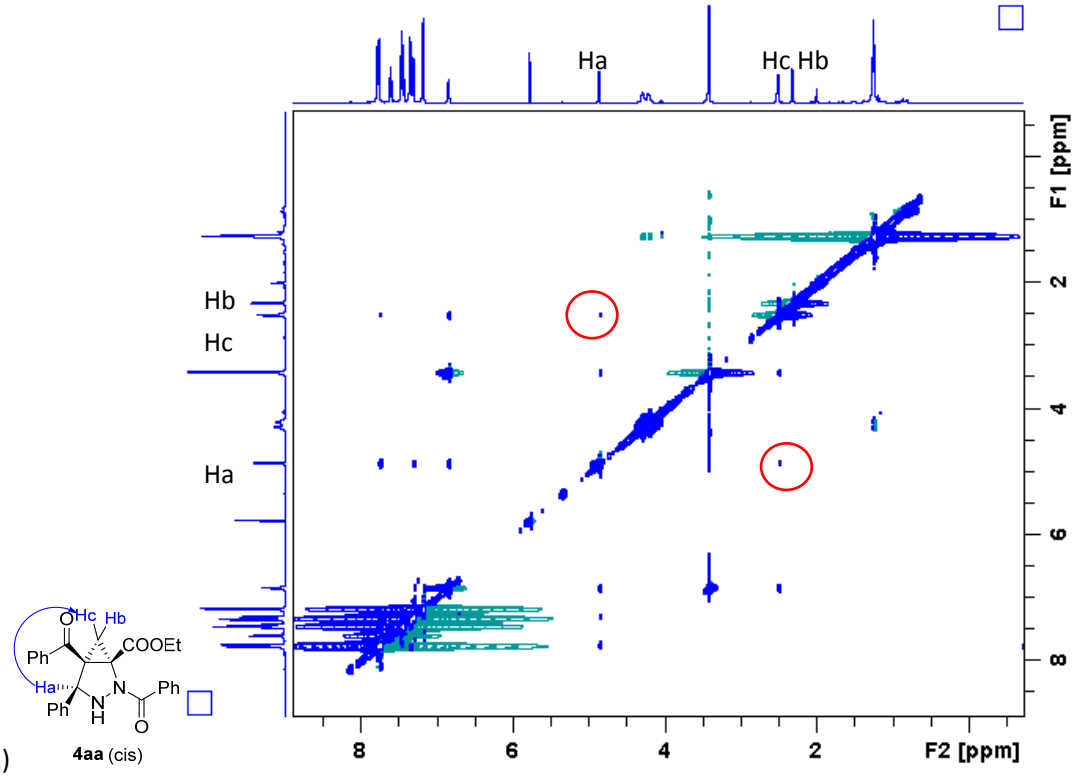
NOESY spectra for **4aa**(trans)、**4aa** (cis)、**4af**(trans)、**4af** (cis)、 **4aj**(cis) **and 4ab**(cis), where H_b is easily distinguished with H_c due to their different chemical shifts. Since H_c locates on the same side with aroyl group on the cyclopropane ring, the resonance absorption peak of H_c appears in the low field relative to that of H_b for the deshielding effect.



(1) **4aa** (trans)

Note: the trans isomers can be confirmed as there has no relevence between **Ha** and **Hb** or **Hc**.

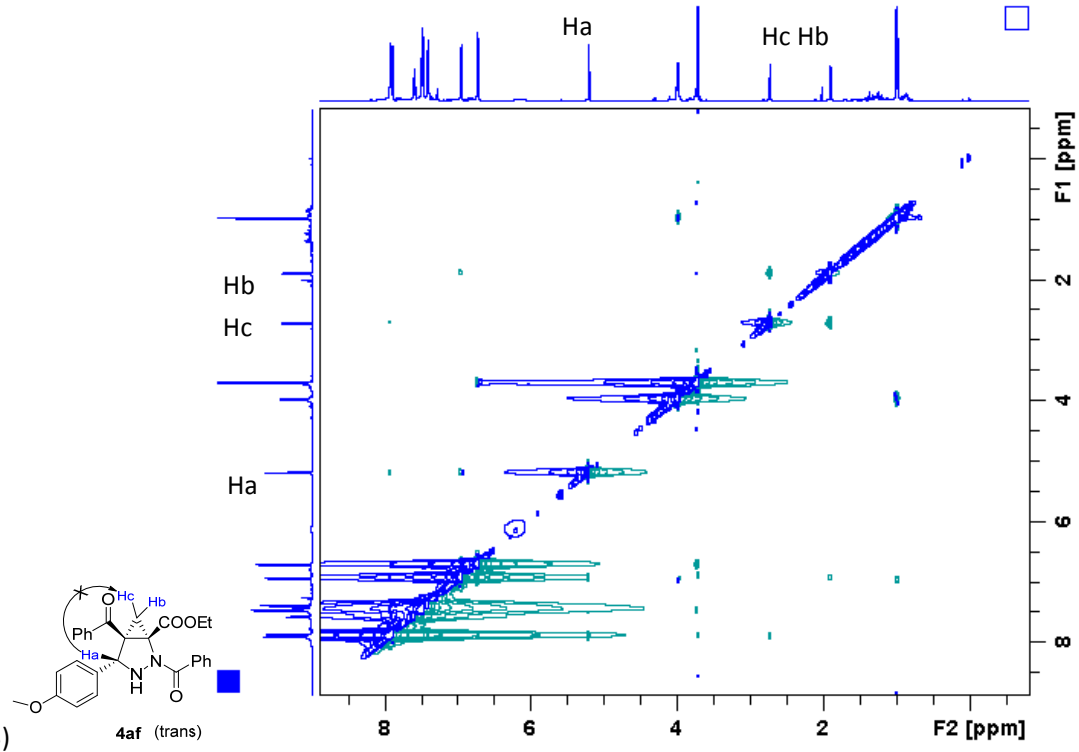
(2)



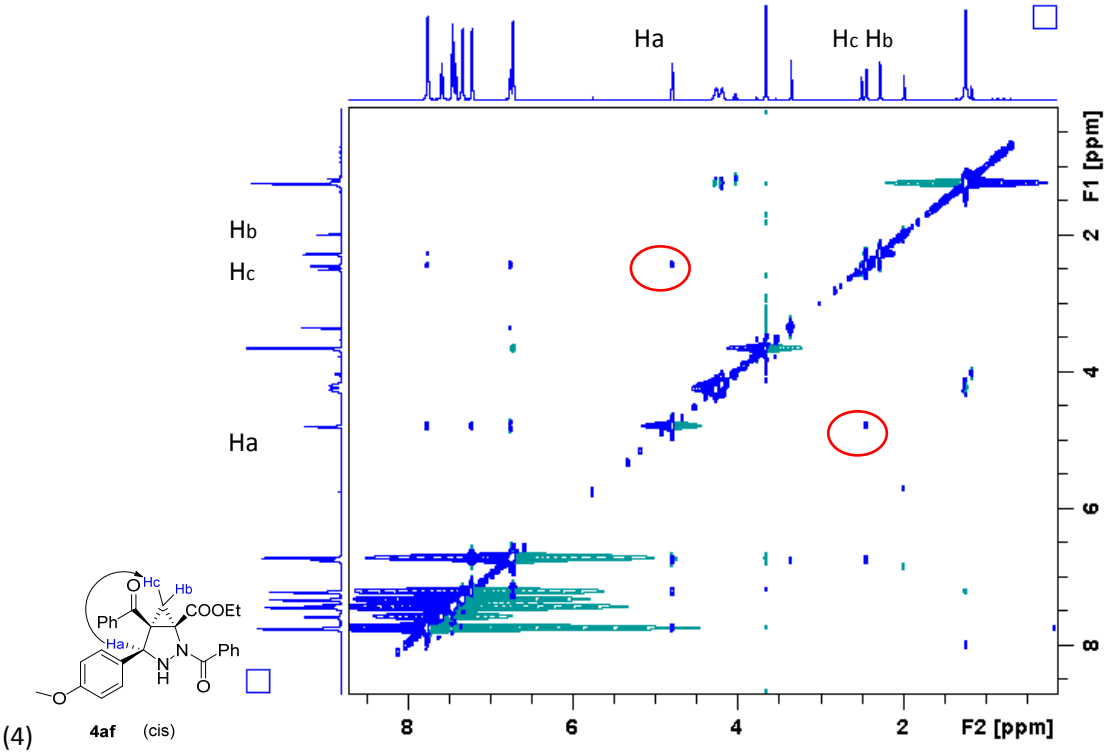
4aa (cis)

Note: the cis isomers can be confirmed as there has obvious relevance between **Ha** and **Hc**

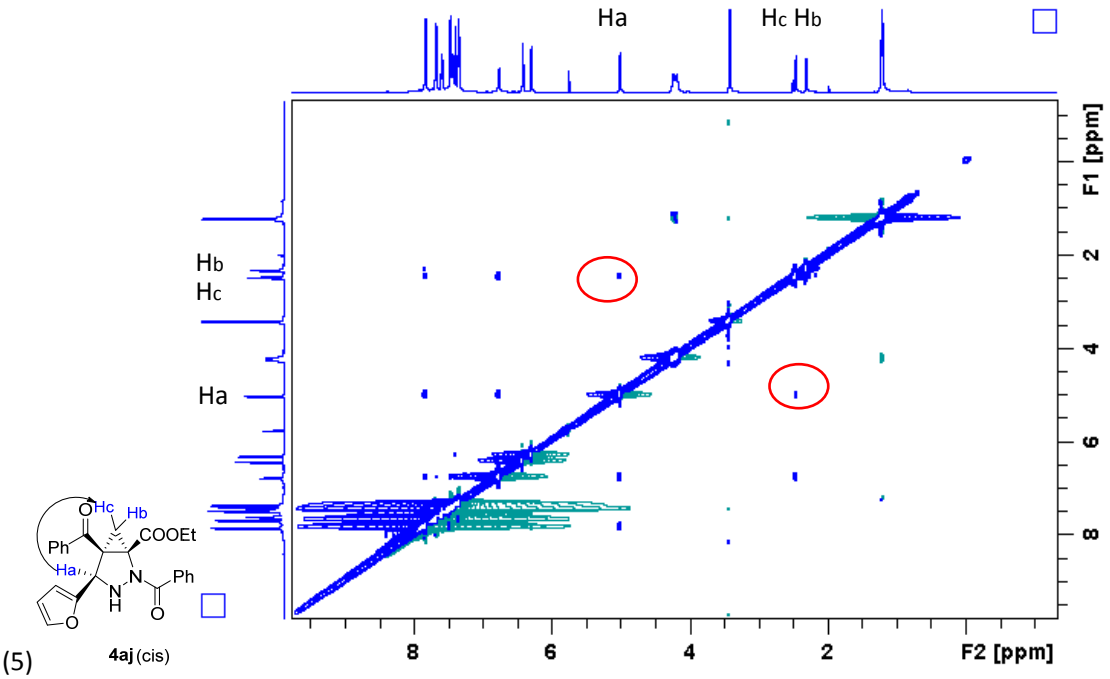
(3)



4af (trans)

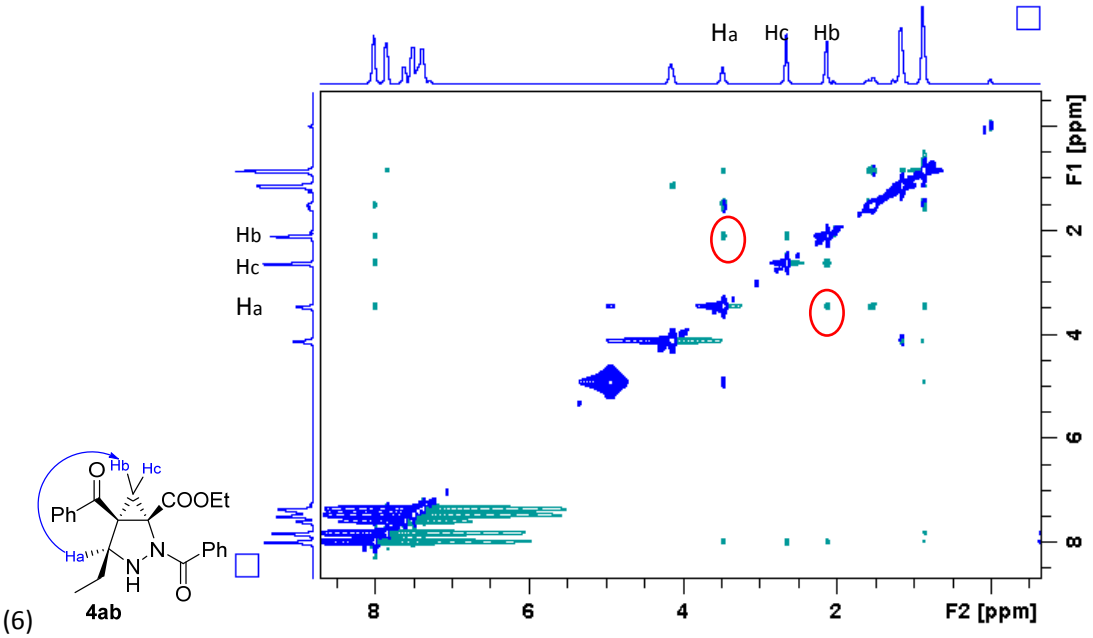


(4) **4af** (cis)



(5) **4aj** (cis)

(6)



(5) Crystallographic information for compound 4aa

CCDC (1404398), Formula: $C_{27}H_{24}N_2O_4$, Unit Cell Parameters: (1) a 10.919 (2) b 21.054 (3) c21.054 (4) Pca21

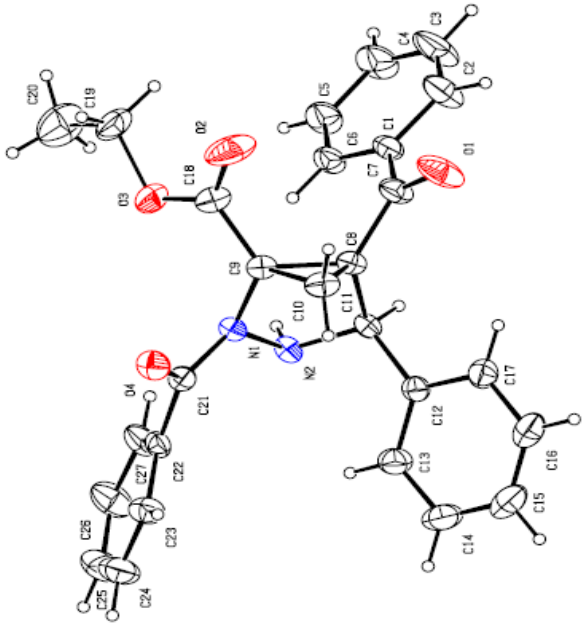


Figure 1 Crystal structure of 4aa (trans)

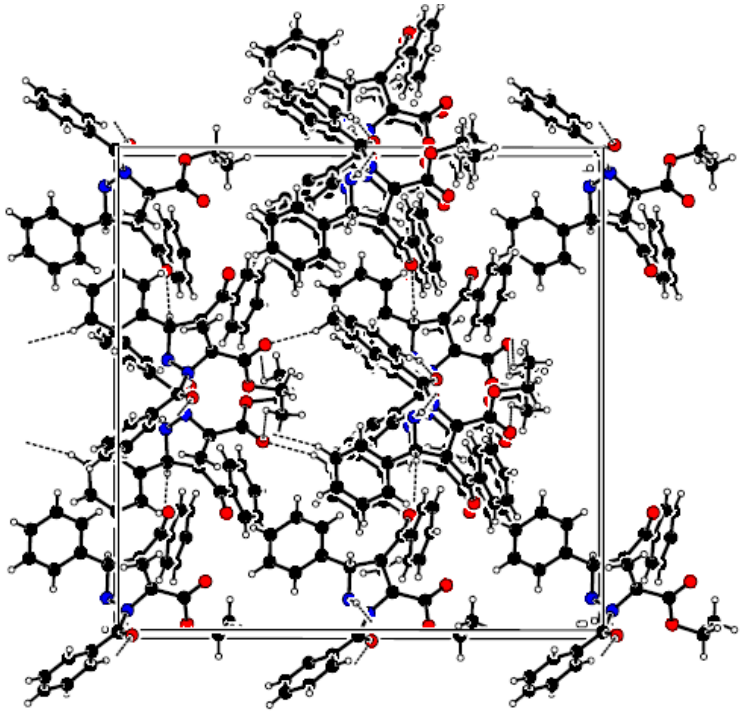


Figure 2 Projection of one unit cell