

Synthesis of Polycyclic Spiroindolines via the Cascade Reaction of 3-(2-isocyanoethyl)Indoles

Haizhen Li, Jinyu Wu, Jianfeng Zheng* and Wei-Dong Z. Li*

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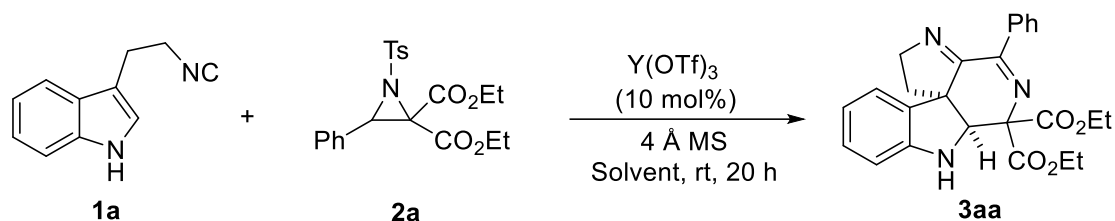
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1. General Information

Reactions were carried out using commercial reagents in over-dried apparatus. CH_2Cl_2 was dried over powdered CaH_2 and distilled under nitrogen just before use. ^1H NMR spectra were recorded on commercial instruments (400 MHz). Chemical shifts are recorded in ppm relative to tetramethylsilane and with the solvent resonance as the internal standard (CDCl_3 , $\delta = 7.26$). Spectra are reported as follows: chemical shift, multiplicity (s = singlet, d = doublet, t = triplet, m = multiplet), coupling constants (Hz), integration and assignment. ^{13}C NMR data were collected on commercial instruments (101 MHz) with complete proton decoupling. Chemical shifts are reported in ppm from the tetramethylsilane with the solvent resonance as internal standard (CDCl_3 , $\delta = 77.0$). Melting points (m. p.) were measured on the electrothermal digital melting point apparatus. HRMS was recorded on a commercial apparatus (ESI Source). All 2-isocyanoethylindoles¹ and 2,2-diester aziridines² were prepared according to the literature.

2. Optimization of Reaction Conditions

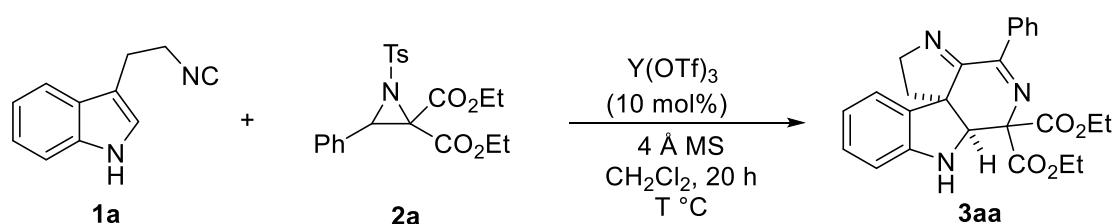
2.1 Screening of reaction solvents



Entry ^a	Solvent	Yield (%) ^b
1	CH ₂ Cl ₂	78%
2	ClCH ₂ CH ₂ Cl	73%
3	CHCl ₃	73%
4	CH ₃ CN	22%
5	1,4-Dioxane	13%
6	THF	trace
7	Toluene	trace
8	DMF	N.R

^aUnless otherwise noted, the reactions were performed with Y(OTf)₃ (10 mol%), 4 Å MS (50 mg), **1a** (0.2 mmol) and **2a** (0.3 mmol) in solvent (1.0 mL) at rt for 20 h. ^bYield of isolated product.

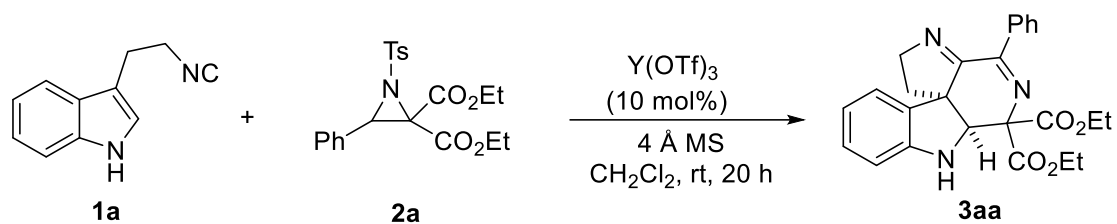
2.2 Screening of reaction temperature



Entry ^a	T	yield (%) ^b
1	0 °C	54%
2	rt	78%
3	30 °C	42%

^aUnless otherwise noted, the reactions were performed with Y(OTf)₃ (10 mol%), 4 Å MS (50 mg), **1a** (0.2 mmol) and **2a** (0.3 mmol) in CH₂Cl₂ (1.0 mL) at rt for 20 h. ^bYield of isolated product.

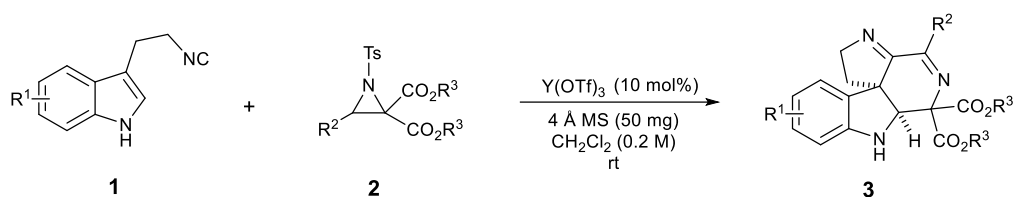
2.3 Screening of concentration of reaction



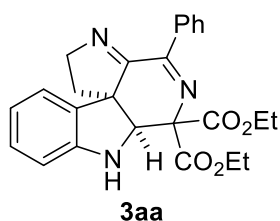
Entry ^a	Concentration (mol/L)	Yield (%) ^b
1	0.40	76%
2	0.20	78%
3	0.13	64%

^aUnless otherwise noted, the reactions were performed with Y(OTf)₃ (10 mol%), 4 Å MS (50 mg), **1a** (0.2 mmol) and **2a** (0.3 mmol) in CH₂Cl₂ at rt for 20 h. ^bYield of isolated product

3. General Procedure and Spectral Data of Products 3



A dry reaction tube was charged with 2-isocyanoethylindoles **1** (0.2 mmol), aziridines **2** (0.3 mmol) and 4 ÅMS (50 mg). Under N_2 atmosphere, CH_2Cl_2 (0.5 mL) was added. The mixture was stirred at room temperature for 15 min, then $Y(OTf)_3$ (0.02 mmol, 10.8 mg) and dry CH_2Cl_2 (0.5 mL) was added in the tube. The reaction mixture continued stirring at room temperature for indicated time. The residue was directly purified by flash chromatography on silica gel using petroleum ether/ethyl acetate/dichloromethane = 5/1/1 as eluent to afford the desired products **3**.



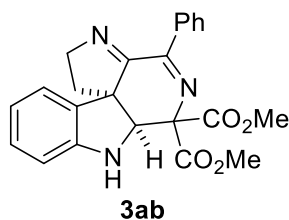
diethyl 4-phenyl-1,2,6a,7-tetrahydro-6H-pyrrolo[3',2':4,5]pyrido[3,4-b]indole-6,6-dicarboxylate **3aa**

The reaction was run at rt for 20 h, affording product **3aa** in 78% yield (67.4 mg) as a yellow solid. $R_f = 0.3$ (PE:EA:DCM = 5:1:1), m.p. 123-125 °C.

1H NMR (400 MHz, $CDCl_3$) δ 7.91 – 7.82 (m, 2H), 7.36 – 7.21 (m, 3H), 6.95 – 6.85 (m, 2H), 6.57 (td, $J = 7.5, 0.8$ Hz, 1H), 6.40 (d, $J = 7.8$ Hz, 1H), 5.16 (d, $J = 5.0$ Hz, 1H), 4.38 (qd, $J = 7.1, 2.5$ Hz, 2H), 4.30 (td, $J = 9.2, 4.5$ Hz, 1H), 4.22 – 4.15 (m, 2H), 4.13 – 4.02 (m, 2H), 2.67 – 2.49 (m, 2H), 1.33 (t, $J = 7.2$ Hz, 3H), 1.12 (t, $J = 7.2$ Hz, 3H).

^{13}C NMR (101 MHz, $CDCl_3$) δ 169.0, 168.5, 167.9, 166.5, 149.1, 134.8, 131.4, 131.0, 129.1, 128.6, 128.2, 122.6, 119.6, 110.0, 76.0, 70.8, 62.7, 62.6, 62.4, 60.4, 41.3, 14.2, 13.9.

HRMS (ESI) calcd for $C_{25}H_{26}N_3O_4$ ($[M+H]^+$) = 432.1923, Found 432.1920.



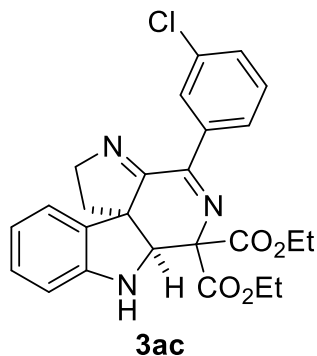
dimethyl 4-phenyl-1,2,6a,7-tetrahydro-6H-pyrrolo[3',2':4,5]pyrido[3,4-b]indole-6,6-dicarboxylate **3ab**

The reaction was run at rt for 24 h, affording product **3ab** in 49% yield (39.5 mg) as a yellow solid. $R_f = 0.2$ (PE:EA:DCM = 5:1:1), m.p.

153-155 °C. 1H NMR (400 MHz, $CDCl_3$) δ 7.96 – 7.94 (m, 2H), 7.43 – 7.38 (m, 1H), 7.35 – 7.31 (m, 2H), 7.00 – 6.94 (m, 2H), 6.66 (td, $J = 7.5, 0.8$ Hz, 1H), 6.49 (d, $J = 7.8$ Hz, 1H), 5.27 (d, $J = 5.3$ Hz, 1H), 4.43 – 4.35 (m, 1H), 4.30 – 4.24 (m, 2H), 4.00 (s, 3H), 3.68 (s, 3H), 2.73 – 2.57 (m, 2H).

^{13}C NMR (101 MHz, CDCl_3) δ 169.8, 168.8, 167.8, 166.9, 149.0, 134.5, 131.6, 131.0, 129.1, 128.6, 128.3, 122.6, 119.8, 110.2, 76.1, 71.2, 62.7, 60.5, 53.6, 53.5, 41.3.

HRMS (ESI) calcd for $\text{C}_{23}\text{H}_{22}\text{N}_3\text{O}_4$ ($[\text{M}+\text{H}^+]$) = 404.1610, Found 404.1606.



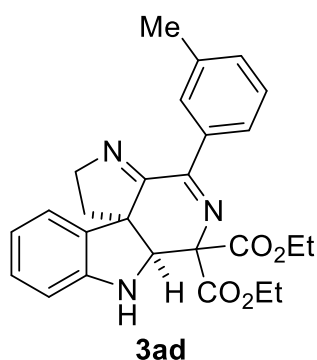
diethyl 4-(3-chlorophenyl)-1,2,6a,7-tetrahydro-6H-pyrrolo[3',2':4,5]pyrido[3,4-b] indole-6,6-dicarboxylate 3ac

The reaction was run at rt for 18 h, affording product **3ac** in 91% yield (84.6 mg) as a yellow solid. R_f = 0.2 (PE:EA:DCM = 5:1:1), m.p. 155-157 °C.

^1H NMR (400 MHz, CDCl_3) δ 8.02 (t, J = 1.8 Hz, 1H), 7.82 (td, J = 8.0 Hz, 1.2 Hz, 1H), 7.38 – 7.36 (m, 1H), 7.28 – 7.24 (m, 1H), 6.99 – 6.95 (m, 2H), 6.65 (td, J = 7.5, 0.9 Hz, 1H), 6.50 – 6.48 (m, 1H), 5.23 (d, J = 4.0 Hz, 1H), 4.49 – 4.43 (m, 2H), 4.41 – 4.34 (m, 1H), 4.30 – 4.23 (m, 2H), 4.20 – 4.10 (m, 2H), 2.70 – 2.56 (m, 2H), 1.42 (t, J = 7.2 Hz, 3H), 1.20 (t, J = 7.2 Hz, 3H).

^{13}C NMR (101 MHz, CDCl_3) δ 168.8, 167.5, 167.2, 166.2, 149.0, 136.3, 134.5, 131.5, 130.8, 129.5, 129.2, 128.2, 127.0, 122.6, 119.8, 110.1, 76.2, 70.8, 62.7, 62.7, 62.6, 60.5, 41.2, 14.2, 13.9.

HRMS (ESI) calcd for $\text{C}_{25}\text{H}_{25}\text{ClN}_3\text{O}_4$ ($[\text{M}+\text{H}^+]$) = 466.1534, Found 466.1512.



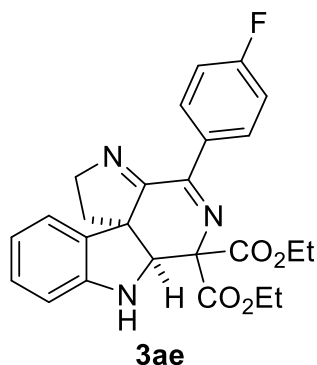
diethyl 4-(m-tolyl)-1,2,6a,7-tetrahydro-6H-pyrrolo[3',2':4,5]pyrido[3,4-b] indole-6,6-dicarboxylate 3ad

The reaction was run at rt for 24 h, affording product **3ad** in 92% yield (82.0 mg) as a yellow solid. R_f = 0.2 (PE:EA:DCM = 5:1:1), m.p. 158-160 °C.

^1H NMR (400 MHz, CDCl_3) δ 7.82 (s, 1H), 7.69 (td, J = 4.0, 1.2 Hz, 1H), 7.21 – 7.19 (m, 2H), 6.99 – 6.93 (m, 2H), 6.64 (td, J = 7.2, 0.8 Hz, 1H), 6.47 (d, J = 8.0 Hz, 1H), 5.23 (d, J = 2.0 Hz, 1H), 4.46 (qd, J = 7.2, 2.8 Hz, 2H), 4.40 – 4.34 (m, 1H), 4.29 – 4.22 (m, 2H), 4.17 – 4.10 (m, 2H), 2.71 – 2.56 (m, 2H), 2.32 (s, 3H), 1.41 (t, J = 7.2 Hz, 3H), 1.19 (t, J = 7.2 Hz, 3H).

^{13}C NMR (101 MHz, CDCl_3) δ 169.0, 168.7, 167.9, 166.5, 149.1, 137.9, 134.6, 132.4, 131.0, 129.1, 128.5, 128.1, 126.2, 122.6, 119.6, 110.1, 76.0, 70.9, 62.8, 62.6, 62.5, 60.4, 41.3, 21.3, 14.2, 13.9.

HRMS (ESI) calcd for C₂₆H₂₈N₃O₄ ([M+H⁺]) = 446.2080, Found 446.2076.



diethyl 4-((4-fluorophenyl))-1,2,6a,7-tetrahydro-6H-pyrrolo[3',2':4,5]pyrido[3,4-b] indole-6,6-dicarboxylate 3ae

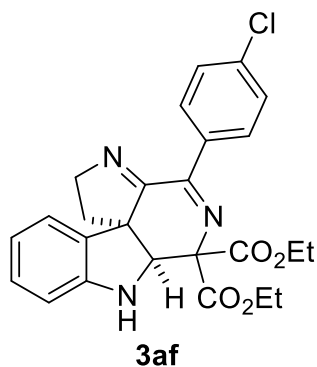
The reaction was run at rt for 40 h, affording product **3ae** in 61% yield (54.5 mg) as a yellow solid. *R_f* = 0.2 (PE:EA:DCM = 5:1:1), m.p. 149-151 °C.

¹H NMR (400 MHz, CDCl₃) δ 8.00 – 7.97 (m, 2H), 7.03 – 6.94 (m, 4H), 6.64 (td, *J* = 7.6, 1.2 Hz, 1H), 6.49 (dd, *J* = 8.0, 0.8 Hz, 1H), 5.22 (s, 1H),

4.49 – 4.42 (m, 2H), 4.40 – 4.34 (m, 1H), 4.30 – 4.22 (m, 2H), 4.20 – 4.10 (m, 2H), 2.71 – 2.56 (m, 2H), 1.41 (t, *J* = 7.2 Hz, 3H), 1.19 (t, *J* = 7.2 Hz, 3H).

¹³C NMR (101 MHz, CDCl₃) δ 168.9, 167.8, 167.2, 166.2, 165.1 (d, *J* = 253 Hz), 149.0, 131.0 (d, *J* = 3 Hz), 130.9, 130.8, 129.2, 122.5, 119.7, 115.3 (d, *J* = 20 Hz), 110.1, 76.0, 70.7, 62.7, 62.7, 62.5, 60.4, 41.3, 14.2, 13.9.

HRMS (ESI) calcd for C₂₅H₂₅FN₃O₄ ([M+H⁺]) = 450.1829, Found 450.1825.



diethyl 4-(4-chlorophenyl)-1,2,6a,7-tetrahydro-6H-pyrrolo[3',2':4,5]pyrido[3,4-b] indole-6,6-dicarboxylate 3af

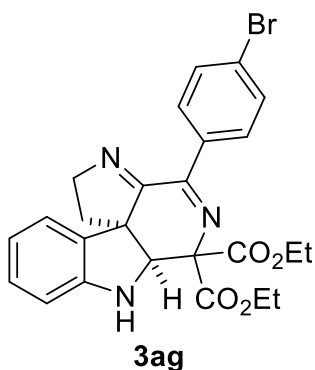
The reaction was run at rt for 33 h, affording product **3af** in 71% yield (66.0 mg) as a yellow solid. *R_f* = 0.2 (PE:EA:DCM = 5:1:1), m.p. 107-109 °C.

¹H NMR (400 MHz, CDCl₃) δ 7.95 (d, *J* = 8.4 Hz, 2H), 7.31 (d, *J* = 8.0 Hz, 2H), 6.99 – 6.96 (m, 2H), 6.66 (t, *J* = 7.2 Hz, 1H), 6.50 (d, *J* = 8.0 Hz,

1H), 5.24 (s, 1H), 4.50 – 4.43 (m, 2H), 4.41 – 4.35 (m, 1H), 4.32 – 4.27 (m, 2H), 4.21 – 4.11 (m, 2H), 2.72 – 2.57 (m, 2H), 1.42 (t, *J* = 7.2 Hz, 3H), 1.21 (t, *J* = 7.2 Hz, 3H).

¹³C NMR (101 MHz, CDCl₃) δ 168.8, 167.6, 167.3, 166.3, 149.0, 137.8, 133.1, 130.8, 129.9, 129.2, 128.5, 122.5, 119.7, 110.1, 76.1, 70.7, 62.7, 62.7, 62.5, 60.5, 41.2, 14.2, 13.9.

HRMS (ESI) calcd for C₂₅H₂₅ClN₃O₄ ([M+H⁺]) = 466.1534, Found 466.1532.



diethyl 4-(4-bromophenyl)-1,2,6a,7-tetrahydro-6H-pyrrolo[3',2':4,5]pyrido[3,4-b] indole-6,6-dicarboxylate 3ag

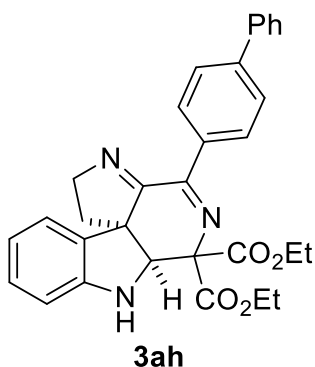
The reaction was run at rt for 33 h, affording product **3ag** in 77% yield (78.0 mg) as a yellow solid. $R_f = 0.2$ (PE:EA:DCM = 5:1:1), m.p. 137-139 °C.

$^1\text{H NMR}$ (400 MHz, CDCl_3) δ 7.90 – 7.86 (m, 2H), 7.50 – 7.47 (m, 2H), 7.00 - 6.96 (m, 2H), 6.66 (td, $J = 7.6, 1.2$ Hz, 1H), 6.50 (d, $J = 7.6$ Hz,

1H), 5.24 (d, $J = 3.6$ Hz, 1H), 4.52 – 4.44 (m, 2H), 4.42 – 4.36 (m, 1H), 4.32 – 4.24 (m, 2H), 4.22 – 4.12 (m, 2H), 2.70 – 2.60 (m, 2H), 1.43 (t, $J = 7.2$ Hz, 3H), 1.21 (t, $J = 7.2$ Hz, 3H).

$^{13}\text{C NMR}$ (101 MHz, CDCl_3) δ 168.8, 167.6, 167.4, 166.2, 149.0, 133.5, 131.5, 130.8, 130.1, 129.2, 126.5, 122.5, 119.7, 110.1, 76.1, 70.7, 62.7, 62.7, 62.5, 60.5, 41.2, 14.2, 13.9.

HRMS (ESI) calcd for $\text{C}_{25}\text{H}_{25}\text{BrN}_3\text{O}_4$ ($[\text{M}+\text{H}^+]$) = 510.1028, Found 510.1027.



diethyl 4-(4-[1,1'-biphenyl]-4-yl)-1,2,6a,7-tetrahydro-6H-pyrrolo[3',2':4,5]pyrido[3,4-b] indole-6,6-dicarboxylate 3ah

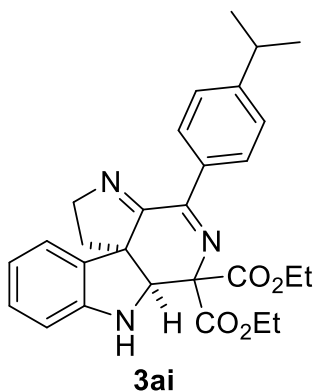
The reaction was run at rt for 40 h, affording product **3ah** in 74% yield (75.4 mg) as a yellow solid. $R_f = 0.2$ (PE:EA:DCM = 5:1:1), m.p. 148-150 °C.

$^1\text{H NMR}$ (400 MHz, CDCl_3) δ 8.05 – 8.02 (m, 2H), 7.57 – 7.55 (m, 4H), 7.44 – 7.40 (m, 2H), 7.36 – 7.32 (m, 1H), 7.01 – 6.94 (m, 2H), 6.66 (td, J

= 7.6, 0.8 Hz, 1H), 6.49 (d, $J = 8.0$ Hz, 1H), 5.25 (s, 1H), 4.51 – 4.42 (m, 2H), 4.40 – 4.36 (m, 1H), 4.32 – 4.23 (m, 2H), 4.18 – 4.11 (m, 2H), 2.73 – 2.58 (m, 2H), 1.42 (t, $J = 7.2$ Hz, 3H), 1.21 (t, $J = 7.2$ Hz, 3H).

$^{13}\text{C NMR}$ (101 MHz, CDCl_3) δ 169.0, 168.0, 167.9, 166.5, 149.1, 144.1, 140.5, 133.6, 131.0, 129.1, 129.1, 128.8, 127.7, 127.2, 127.0, 122.6, 119.7, 110.1, 76.1, 70.8, 62.7, 62.6, 62.5, 60.5, 41.3, 14.3, 13.9.

HRMS (ESI) calcd for $\text{C}_{31}\text{H}_{30}\text{N}_3\text{O}_4$ ($[\text{M}+\text{H}^+]$) = 508.2236, Found 508.2233.



**diethyl 4-(4-isopropylphenyl)-1,2,6a,7-tetrahydro-6H-pyrrolo
[3',2':4,5]pyrido[3,4-b] indole-6,6-dicarboxylate 3ai**

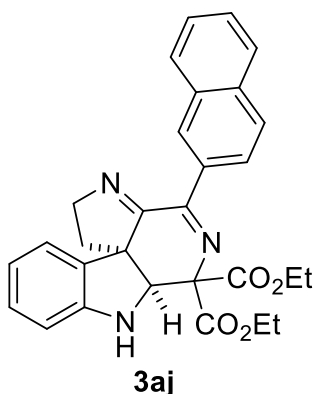
The reaction was run at rt for 40 h, affording product **3ai** in 83% yield (78.5 mg) as a yellow solid. $R_f = 0.3$ (PE:EA:DCM = 5:1:1), m.p. 156-158 °C.

^1H NMR (400 MHz, CDCl_3) δ 7.87 (d, $J = 8.4$ Hz, 2H), 7.20 (d, $J = 8.4$ Hz, 2H), 7.02 – 6.96 (m, 2H), 6.69 – 6.65 (m, 1H), 6.50 (d, $J = 8.0$ Hz,

1H), 5.24 (d, $J = 4.8$ Hz, 1H), 4.52 – 4.43 (m, 2H), 4.42 – 4.35 (m, 1H), 4.31 – 4.25 (m, 2H), 4.21 – 4.12 (m, 2H), 2.93 – 2.86 (m, 1H), 2.74 – 2.58 (m, 2H), 1.43 (t, $J = 7.2$ Hz, 3H), 1.23 – 1.20 (m, 9H).

^{13}C NMR (101 MHz, CDCl_3) δ 169.0, 168.3, 167.9, 166.6, 152.7, 149.1, 132.5, 131.1, 129.0, 128.7, 126.4, 122.6, 119.6, 110.0, 75.9, 70.7, 62.6, 62.5, 62.4, 60.3, 41.4, 34.1, 23.8, 23.6, 14.2, 13.9.

HRMS (ESI) calcd for $\text{C}_{28}\text{H}_{32}\text{N}_3\text{O}_4$ ($[\text{M}+\text{H}^+]$) = 474.2393, Found 474.2389.



**diethyl 4-(4-(naphthalen-2-yl)-1,2,6a,7-tetrahydro-6H-pyrrolo
[3',2':4,5]pyrido[3,4-b] indole-6,6-dicarboxylate 3aj**

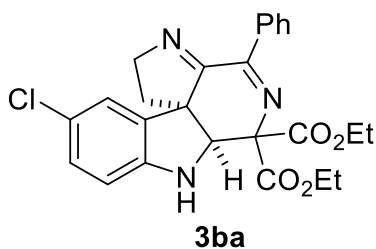
The reaction was run at rt for 28 h, affording product **3aj** in 47% yield (45.3 mg) as a yellow solid. $R_f = 0.2$ (PE:EA:DCM = 5:1:1), m.p. 155-157 °C.

^1H NMR (400 MHz, CDCl_3) δ 8.30 (d, $J = 8.4$ Hz, 1H), 7.83 (dd, $J = 6.8$, 2.4 Hz, 1H), 7.77 (d, $J = 8.0$ Hz, 2H), 7.41 – 7.31 (m, 4H), 7.07 – 7.04

(m, 2H), 6.73 (td, $J = 7.2$, 0.8 Hz, 1H), 6.56 – 6.54 (m, 1H), 5.32 (s, 1H), 4.50 – 4.37 (m, 3H), 4.33 – 4.11 (m, 4H), 2.65 – 2.62 (m, 2H), 1.39 (t, $J = 7.2$ Hz, 3H), 1.29 (t, $J = 7.2$ Hz, 3H).

^{13}C NMR (101 MHz, CDCl_3) δ 171.1, 169.4, 168.9, 166.5, 149.3, 133.9, 133.0, 131.1, 131.0, 130.8, 129.5, 129.1, 128.1, 126.8, 126.0, 125.9, 124.7, 123.1, 119.4, 109.9, 76.2, 70.1, 62.8, 62.5, 62.2, 60.2, 41.0, 14.2, 14.0.

HRMS (ESI) calcd for $\text{C}_{29}\text{H}_{28}\text{N}_3\text{O}_4$ ($[\text{M}+\text{H}^+]$) = 482.2080, Found 482.2076.



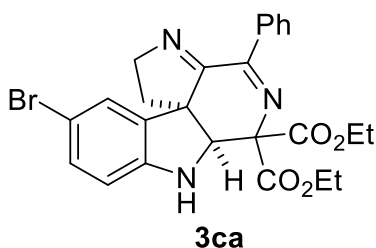
**diethyl 10-chloro-4-phenyl-1,2,6a,7-tetrahydro-6H-pyrrolo
[3',2':4,5]pyrido[3,4-b] indole-6,6-dicarboxylate 3ba**

The reaction was run at rt for 28 h, affording product **3ba** in 65% yield (60.4 mg) as a yellow solid. $R_f = 0.2$ (PE:EA:DCM = 5:1:1), m.p. 156-158 °C.

$^1\text{H NMR}$ (400 MHz, CDCl_3) δ 8.00 – 7.98 (dd, $J = 8.4, 1.3$ Hz, 2H), 7.48 – 7.43 (m, 1H), 7.40 – 7.36 (m, 2H), 6.95 – 6.92 (m, 2H), 6.42 – 6.40 (m, 1H), 5.27 (s, 1H), 4.50 – 4.46 (m, 2H), 4.44 – 4.35 (m, 1H), 4.32 – 4.26 (m, 2H), 4.22 – 4.12 (m, 2H), 2.73 – 2.58 (m, 2H), 1.43 (t, $J = 7.2$ Hz, 3H), 1.22 (t, $J = 7.2$ Hz, 3H).

$^{13}\text{C NMR}$ (101 MHz, CDCl_3) δ 168.9, 168.3, 167.2, 166.3, 147.7, 134.5, 132.7, 131.6, 129.1, 128.5, 128.3, 123.8, 122.7, 110.7, 75.8, 71.2, 62.7, 62.6, 62.6, 60.4, 41.2, 14.2, 13.9.

HRMS (ESI) calcd for $\text{C}_{25}\text{H}_{25}\text{ClN}_3\text{O}_4$ ($[\text{M}+\text{H}^+]$) = 466.1534, Found 466.1531.



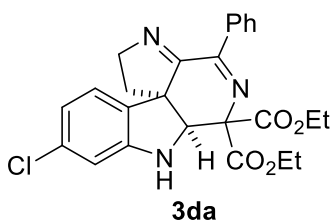
**diethyl 10-bromo-4-phenyl-1,2,6a,7-tetrahydro-6H-pyrrolo
[3',2':4,5]pyrido[3,4-b] indole-6,6-dicarboxylate 3ca**

The reaction was run at rt for 31 h, affording product **3ca** in 85% yield (86.6 mg) as a yellow solid. $R_f = 0.2$ (PE:EA:DCM = 5:1:1), m.p. 115-117°C.

$^1\text{H NMR}$ (400 MHz, CDCl_3) δ 7.98 – 7.95 (m, 2H), 7.45 – 7.41 (m, 1H), 7.38 – 7.34 (m, 2H), 7.04 – 7.02 (m, 2H), 6.34 (dd, $J = 8.0, 1.2$ Hz, 1H), 5.24 (s, 1H), 4.47 – 4.41 (m, 2H), 4.39 – 4.23 (m, 3H), 4.19 – 4.09 (m, 2H), 2.69 – 2.54 (m, 2H), 1.40 (t, $J = 7.2$ Hz, 3H), 1.19 (t, $J = 7.2$ Hz, 3H).

$^{13}\text{C NMR}$ (101 MHz, CDCl_3) δ 168.9, 168.3, 167.2, 166.3, 148.2, 134.5, 133.2, 131.9, 131.7, 128.6, 128.4, 125.5, 111.2, 110.6, 75.8, 71.1, 62.7, 62.6, 62.5, 60.4, 41.2, 14.2, 13.9.

HRMS (ESI) calcd for $\text{C}_{25}\text{H}_{25}\text{BrN}_3\text{O}_4$ ($[\text{M}+\text{H}^+]$) = 510.1028, Found 510.1030.



**diethyl 9-chloro-4-phenyl-1,2,6a,7-tetrahydro-6H-pyrrolo
[3',2':4,5]pyrido[3,4-b] indole-6,6-dicarboxylate 3da**

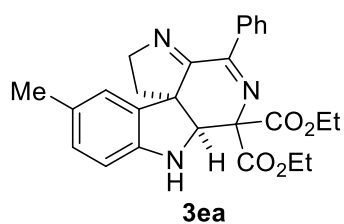
The reaction was run at rt for 18 h, affording product **3da** in 82% yield (76 mg) as a yellow solid. $R_f = 0.2$ (PE:EA:DCM = 5:1:1), m.p.

186-188 °C.

^1H NMR (400 MHz, CDCl_3) δ 7.96 – 7.93 (m, 2H), 7.44 – 7.39 (m, 1H), 7.36 – 7.32 (m, 2H), 6.85 (d, $J = 8.0$ Hz, 1H), 6.58 (dd, $J = 8.0, 2.0$ Hz, 1H), 6.42 (d, $J = 2.0$ Hz, 1H), 5.24 (d, $J = 4.8$ Hz, 1H), 4.48 – 4.39 (m, 3H), 4.37 – 4.22 (m, 2H), 4.19 – 4.09 (m, 2H), 2.67 – 2.51 (m, 2H), 1.39 (t, $J = 7.2$ Hz, 3H), 1.19 (t, $J = 7.2$ Hz, 3H).

^{13}C NMR (101 MHz, CDCl_3) δ 168.9, 168.4, 167.3, 166.3, 150.2, 134.8, 134.6, 131.6, 129.5, 128.5, 128.3, 123.3, 119.3, 109.9, 75.8, 71.1, 62.7, 62.6, 62.0, 60.4, 41.1, 14.2, 13.9.

HRMS (ESI) calcd for $\text{C}_{25}\text{H}_{25}\text{ClN}_3\text{O}_4$ ($[\text{M}+\text{H}^+]$) = 466.1534, Found 466.1531.



**diethyl 10-methyl-4-phenyl-1,2,6a,7-tetrahydro-6H-pyrrolo
[3',2':4,5]pyrido[3,4-b] indole-6,6-dicarboxylate 3ea**

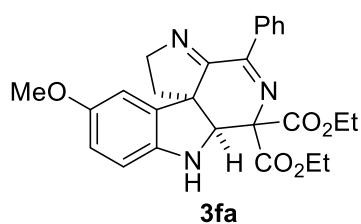
The reaction was run at rt for 24 h, affording product **3ea** in 56% yield (49.8 mg) as a yellow solid. $R_f = 0.2$ (PE:EA:DCM = 5:1:1), m.p.

136-138 °C.

^1H NMR (400 MHz, CDCl_3) δ 8.00 – 7.97 (m, 2H), 7.44 – 7.40 (m, 1H), 7.38 – 7.33 (m, 2H), 6.80 – 6.77 (m, 2H), 6.41 (d, $J = 8.0$ Hz, 1H), 5.24 (s, 1H), 4.51 – 4.44 (m, 2H), 4.43 – 4.36 (m, 1H), 4.33 – 4.24 (m, 1H), 4.21 – 4.11 (m, 3H), 2.73 – 2.57 (m, 2H), 2.20 (s, 3H), 1.43 (t, $J = 7.2$ Hz, 3H), 1.21 (t, $J = 7.2$ Hz, 3H).

^{13}C NMR (101 MHz, CDCl_3) δ 168.9, 168.3, 168.1, 166.5, 146.8, 134.8, 131.4, 129.6, 129.1, 128.6, 128.2, 123.1, 110.1, 76.1, 71.1, 62.8, 62.5, 62.4, 60.4, 41.3, 20.8, 14.2, 13.9.

HRMS (ESI) calcd for $\text{C}_{26}\text{H}_{28}\text{N}_3\text{O}_4$ ($[\text{M}+\text{H}^+]$) = 446.2080, Found 446.2076.



**diethyl 10-methoxyl-4-phenyl-1,2,6a,7-tetrahydro-6H-pyrrolo
[3',2':4,5]pyrido[3,4-b] indole-6,6-dicarboxylate 3fa**

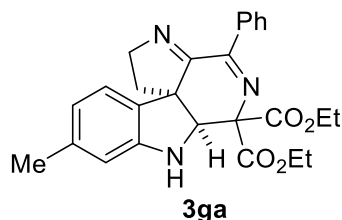
The reaction was run at rt for 37 h, affording product **3fa** in 57% yield (52.3 mg) as a yellow solid. $R_f = 0.2$ (PE:EA:DCM = 5:1:1), m.p.

121-123 °C.

^1H NMR (400 MHz, CDCl_3) δ 7.98 – 7.96 (m, 2H), 7.43 – 7.38 (m, 1H), 7.35 – 7.31 (m, 2H), 6.57 – 6.54 (m, 2H), 6.44 (d, $J = 8.4$ Hz, 1H), 5.23 (s, 1H), 4.49 – 4.41 (m, 2H), 4.39 – 4.33 (m, 1H), 4.30 – 4.23 (m, 1H), 4.15 – 4.07 (m, 3H), 3.68 (s, 3H), 2.74 – 2.57 (m, 2H), 1.41 (t, $J = 7.2$ Hz, 3H), 1.19 (t, $J = 7.2$ Hz, 3H).

^{13}C NMR (101 MHz, CDCl_3) δ 168.8, 168.2, 167.9, 166.6, 154.2, 143.1, 134.7, 132.7, 131.5, 128.6, 128.2, 114.1, 111.1, 109.3, 76.1, 71.4, 63.2, 62.6, 62.4, 60.4, 56.0, 41.2, 14.3, 13.9.

HRMS (ESI) calcd for $\text{C}_{26}\text{H}_{28}\text{N}_3\text{O}_5$ ($[\text{M}+\text{H}^+]$) = 462.2029, Found 462.2028.



**diethyl 9-methyl-4-phenyl-1,2,6a,7-tetrahydro-6H-pyrrolo
[3',2':4,5]pyrido[3,4-b] indole-6,6-dicarboxylate **3ga****

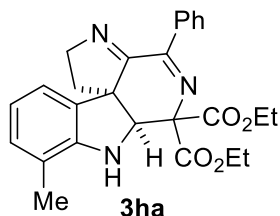
The reaction was run at rt for 27 h, affording product **3ga** in 81% yield (72.0 mg) as a yellow solid. R_f = 0.3 (PE:EA:DCM = 5:1:1), m.p.

167-169 °C.

^1H NMR (400 MHz, CDCl_3) δ 7.96 – 7.94 (m, 2H), 7.41 – 7.31 (m, 3H), 6.86 (d, J = 7.6 Hz, 1H), 6.46 (d, J = 7.6 Hz, 1H), 6.30 (s, 1H), 5.22 (s, 1H), 4.49 – 4.40 (m, 2H), 4.38– 4.32 (m, 1H), 4.28 – 4.09 (m, 4H), 2.69 – 2.53 (m, 2H), 2.14 (s, 3H), 1.41 (t, J = 7.2 Hz, 3H), 1.19 (t, J = 7.2 Hz, 3H).

^{13}C NMR (101 MHz, CDCl_3) δ 169.0, 168.4, 168.0, 166.5, 149.3, 139.2, 134.8, 131.4, 128.6, 128.2, 122.3, 120.5, 110.9, 76.1, 71.0, 62.6, 62.4, 62.4, 60.3, 41.2, 21.4, 14.2, 13.9.

HRMS (ESI) calcd for $\text{C}_{26}\text{H}_{28}\text{N}_3\text{O}_4$ ($[\text{M}+\text{H}^+]$) = 446.2080, Found 446.2079.



**diethyl 8-methyl-4-phenyl-1,2,6a,7-tetrahydro-6H-pyrrolo
[3',2':4,5]pyrido[3,4-b] indole-6,6-dicarboxylate **3ha****

The reaction was run at rt for 37 h, affording product **3ha** in 63% yield (55.8 mg) as a yellow solid. R_f = 0.3 (PE:EA:DCM = 5:1:1), m.p.

145-147 °C.

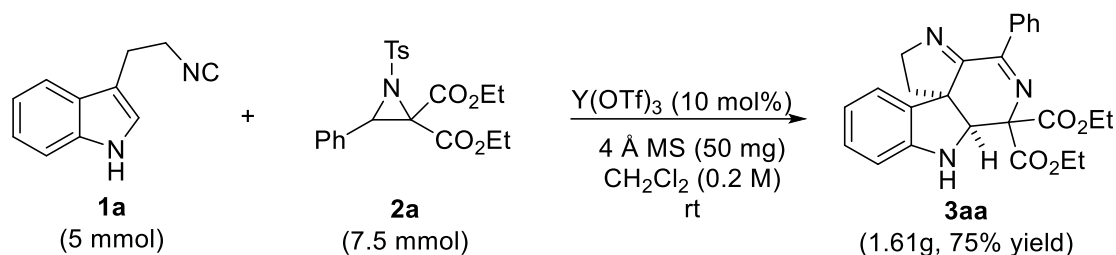
^1H NMR (400 MHz, CDCl_3) δ 7.92 – 7.90 (m, 2H), 7.42 – 7.37 (m, 1H), 7.35 – 7.31 (m, 2H), 6.85 (d, J = 7.6 Hz, 1H), 6.80 (d, J = 7.6 Hz, 1H), 6.61 (t, J = 7.6 Hz, 1H), 5.24 (d, J = 4.8 Hz, 1H), 4.47 (q, J = 6.8 Hz, 2H), 4.41– 4.33 (m, 1H), 4.18 – 4.11 (m, 3H), 4.00 (d, J = 4.8 Hz, 1H), 2.70 – 2.55 (m, 2H), 2.00 (s, 3H), 1.40 (t, J = 7.2 Hz, 3H), 1.20 (t, J = 7.2 Hz, 3H).

^{13}C NMR (101 MHz, CDCl_3) δ 169.1, 168.5, 168.0, 166.5, 147.9, 134.9, 131.4, 130.4, 129.9, 128.7, 128.2, 120.0, 120.0, 119.6, 119.6, 76.3, 70.7, 62.9, 62.6, 62.4, 60.3, 41.5, 16.7, 14.3, 13.9.

HRMS (ESI) calcd for $\text{C}_{26}\text{H}_{28}\text{N}_3\text{O}_4$ ($[\text{M}+\text{H}^+]$) = 446.2080, Found 446.2079

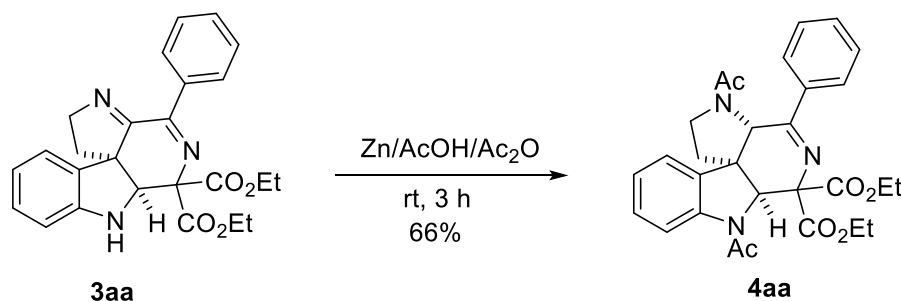
4. Experimental procedure for the scale-up reaction and transformation of the product

a) Scale-up version of the reaction

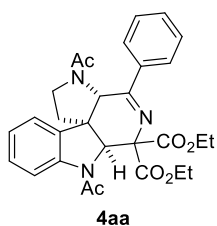


Procedure: A dry reaction tube was charged with **1a** (5 mmol, 0.85 g), **2a** (7.5 mmol, 3.13 g) and 4 Å MS (1.25 g). Under N₂ atmosphere, CH₂Cl₂ (12.5 mL) was added. The mixture was stirred at room temperature for 15 min, then Y(OTf)₃ (0.5 mmol, 267 mg) and dry CH₂Cl₂ (12.5 mL) was added in the tube. The reaction mixture continued stirring at room temperature for 20 h. The solvent was removed under reduced pressure and the residue was directly purified by flash chromatography on silica gel using petroleum ether/ethyl acetate/dichloromethane = 5/1/1 as eluent to afford the desired product **3aa** in 75% yield (1.61g).

b) Transformations of the product **3aa**



Procedure: A dry round-bottom flask was charged with **3aa** (0.5 mmol, 216 mg), AcOH (4 mL) and Ac₂O (4 mL). Then Zn power (2.5 mmol, 162.5 mg) was slowly added to the reaction mixture. The reaction mixture was stirred at room temperature for 3 h. The precipitate was filtered out and the solvent was removed under reduced pressure. Saturated aqueous Na₂CO₃ was added to the mixture to adjust the pH of solution to 8.0-9.0. Then the solution was diluted with ethyl acetate, washed with water, dried with Na₂SO₄, and concentrated under reduced pressure. The residue was directly purified by flash chromatography on silica gel using petroleum ether/ethyl acetate = 1/4 as eluent to afford the desired product **4aa** in 66% yield.



diethyl-3,7-diacetyl-4-phenyl-1,2,3,3a,6a,7-hexahydro-6H-pyrrolo[3',2':4,5]pyrido[3,4-b]indole-6,6-dicarboxylate **4aa**

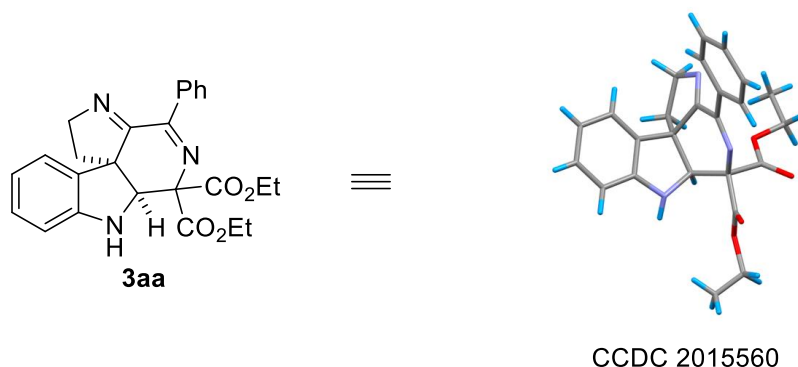
The reaction was run at rt for 3 h, affording product **4aa** in 66% yield (171 mg) as a white solid. $R_f = 0.3$ (PE:EA = 1:4), m.p. 143-145 °C.

$^1\text{H NMR}$ (400 MHz, CDCl_3) δ 7.64 (s, 2H), 7.44 – 7.39 (m, 1H), 7.34 – 7.28 (m, 3H), 7.23 (t, $J = 7.6$ Hz, 1H), 7.02 – 6.97 (m, 1H), 6.94 – 6.88 (m, 1H), 5.28 (s, 1H), 5.09 (s, 1H), 4.32 – 4.15 (m, 2H), 4.08 – 4.00 (m, 1H), 3.92 – 3.84 (m, 1H), 3.73 – 3.66 (m, 1H), 3.61 – 3.51 (m, 1H), 2.43 (s, 3H), 2.27 – 2.18 (m, 2H), 1.97 (s, 3H), 1.26 (t, $J = 7.2$ Hz, 3H), 1.11 (t, $J = 7.2$ Hz, 3H).

$^{13}\text{C NMR}$ (101 MHz, CDCl_3) δ 170.2, 169.9, 169.6, 168.6, 143.0, 130.3, 129.8, 129.1, 128.9, 128.6, 127.9, 127.8, 127.5, 124.8, 121.9, 65.0, 63.0, 62.8, 62.6, 62.2, 46.1, 39.9, 23.9, 21.8, 13.9, 13.8.

HRMS (ESI) calcd for $\text{C}_{29}\text{H}_{32}\text{N}_3\text{O}_6$ ($[\text{M}+\text{H}^+]$) = 518.2291, Found 518.2299.

5. X-ray Structures of **3aa** and **4aa**.

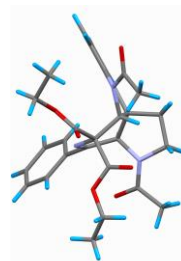
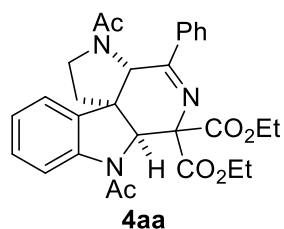


Single crystal of compound **3aa** [C₂₅H₂₅N₃O₄] was obtained in PE and EtOAc. CCDC 2015560 contains the supplementary crystallographic data which can be obtained free of charge from the Cambridge Crystallographic Data Center via <https://www.ccdc.cam.ac.uk/structures/>.

Crystal data

Empirical formula	C ₂₅ H ₂₅ N ₃ O ₄
Formula weight	431.48
Temperature/K	293.15
Crystal system	orthorhombic
Space group	P2 ₁ 2 ₁ 2 ₁
a/Å	11.3360(4)
b/Å	11.9463(3)
c/Å	16.0968(7)
α/°	90
β/°	90
γ/°	90
Volume/Å ³	2179.89(14)
Z	4
ρ _{calc} /cm ³	1.315
μ/mm ⁻¹	0.090
F(000)	912.0
Crystal size/mm ³	0.35 × 0.3 × 0.25
Radiation	MoKα (λ = 0.71073)
2θ range for data collection/°	6.104 to 52.738
Index ranges	-14 ≤ h ≤ 13, -14 ≤ k ≤ 9, -11 ≤ l ≤ 20
Reflections collected	6852
Independent reflections	3988 [R _{int} = 0.0220, R _{sigma} = 0.0485]
Data/restraints/parameters	3988/1/295
Goodness-of-fit on F ²	1.028

Final R indexes [$I \geq 2\sigma(I)$] $R_1 = 0.0567$, $wR_2 = 0.1245$
 Final R indexes [all data] $R_1 = 0.0834$, $wR_2 = 0.1399$
 Largest diff. peak/hole / $e \text{ \AA}^{-3}$ 0.41/-0.31
 Flack parameter 0.4(9)



CCDC 2104294

Single crystal of compound **4aa** [$C_{29}H_{31}N_3O_6$] was obtained in PE and EtOAc. CCDC 2104294 contains the supplementary crystallographic data which can be obtained free of charge from the Cambridge Crystallographic Data Center via <https://www.ccdc.cam.ac.uk/structures/>.

Crystal data

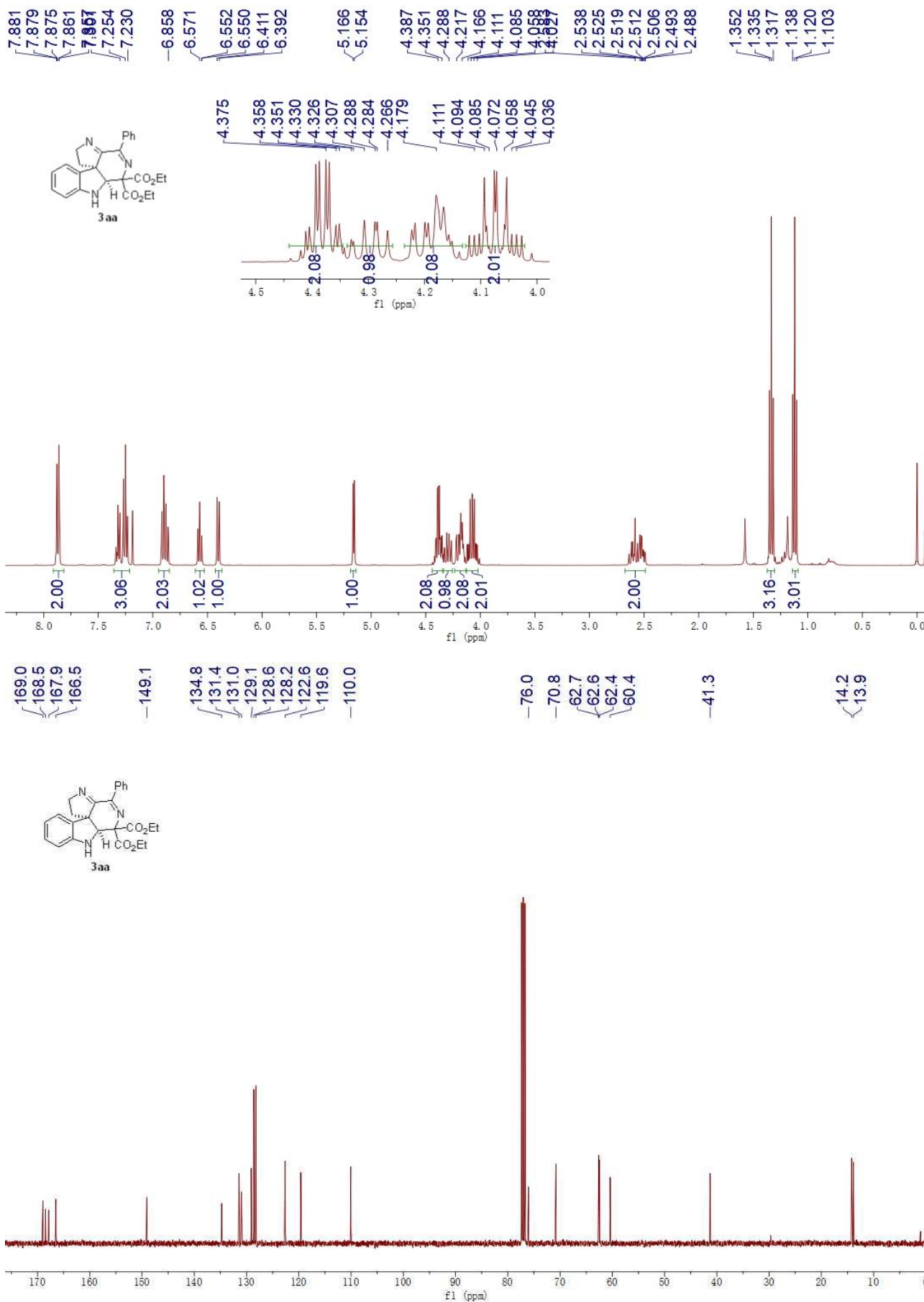
Empirical formula	$C_{29}H_{31}N_3O_6$
Formula weight	517.57
Temperature/K	293.15
Crystal system	monoclinic
Space group	$I2/a$
$a/\text{\AA}$	15.8169(18)
$b/\text{\AA}$	16.0922(13)
$c/\text{\AA}$	23.146(2)
$\alpha/^\circ$	90
$\beta/^\circ$	105.329(13)
$\gamma/^\circ$	90
Volume/ \AA^3	5681.8(10)
Z	8
$\rho_{\text{calc}}/\text{cm}^3$	1.210
μ/mm^{-1}	0.085
$F(000)$	2192.0
Crystal size/ mm^3	$0.35 \times 0.3 \times 0.25$
Radiation	$\text{MoK}\alpha$ ($\lambda = 0.71073$)
2θ range for data collection/ $^\circ$	6.032 to 52.742
Index ranges	$-19 \leq h \leq 11$, $-16 \leq k \leq 20$, $-24 \leq l \leq 28$
Reflections collected	13458
Independent reflections	5791 [$R_{\text{int}} = 0.0296$, $R_{\text{sigma}} = 0.0642$]

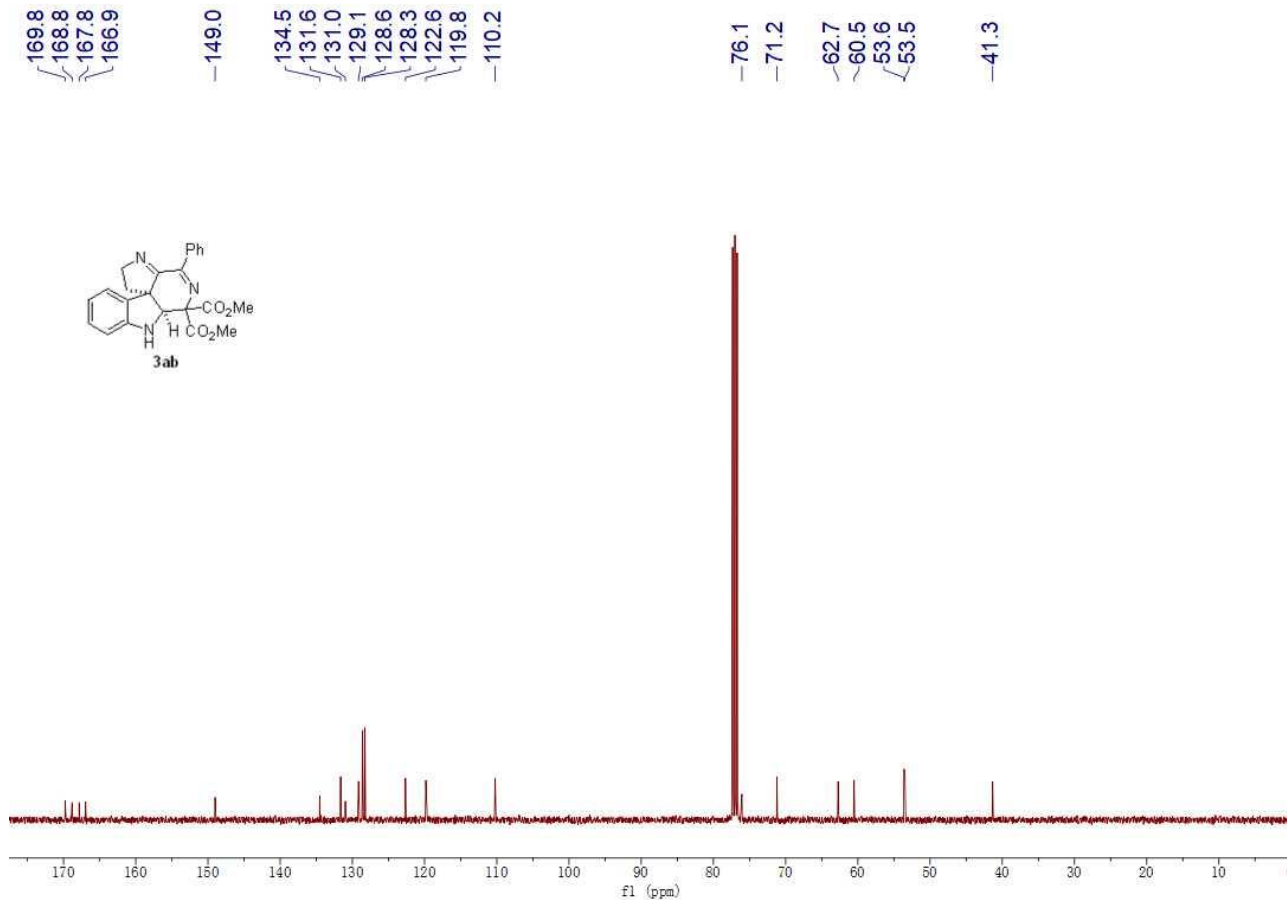
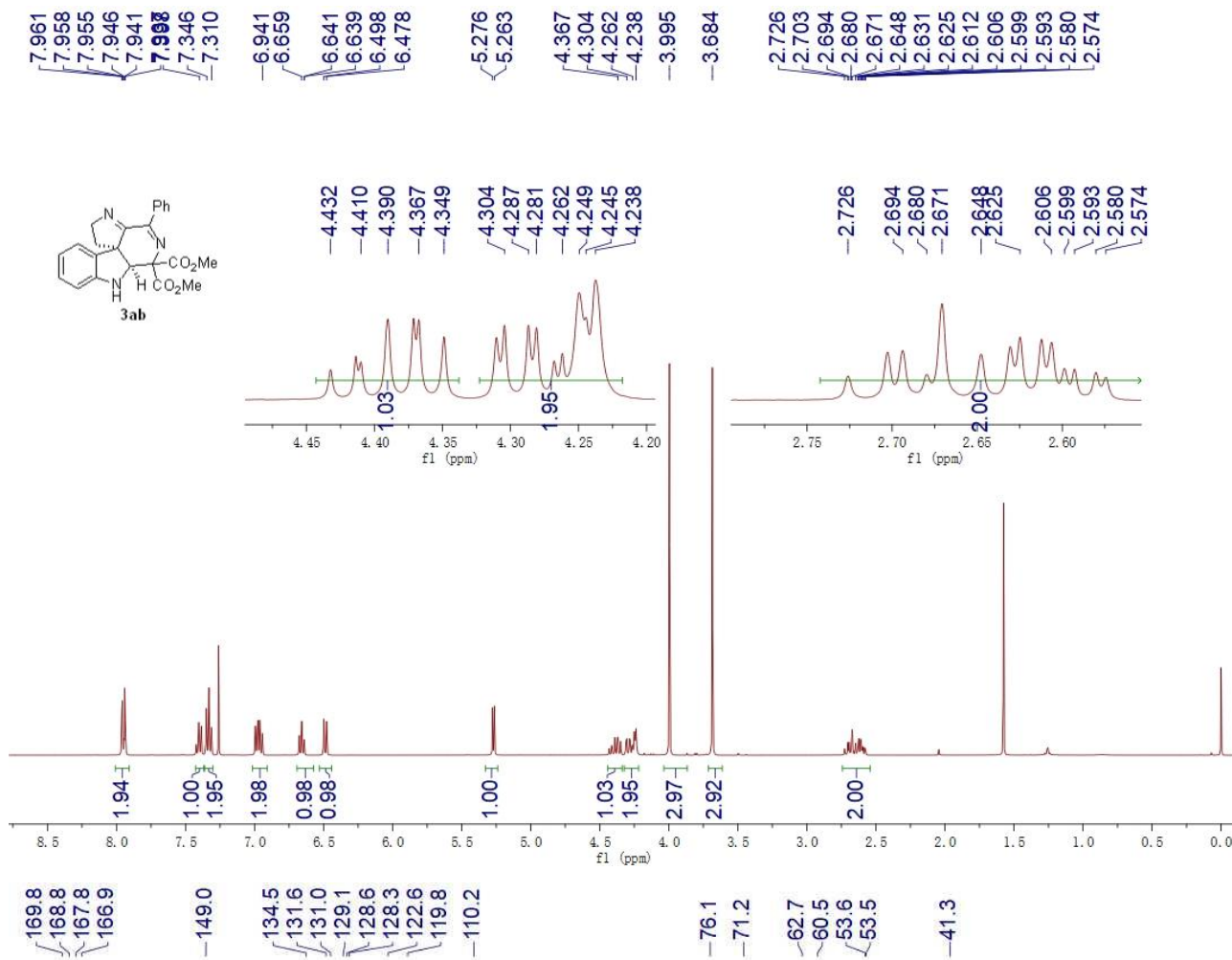
Data/restraints/parameters 5791/4/351
Goodness-of-fit on F^2 1.049
Final R indexes [$I \geq 2\sigma(I)$] $R_1 = 0.0639$, $wR_2 = 0.1670$
Final R indexes [all data] $R_1 = 0.1098$, $wR_2 = 0.1906$
Largest diff. peak/hole / $e \text{ \AA}^{-3}$ 0.36/-0.24

6. References

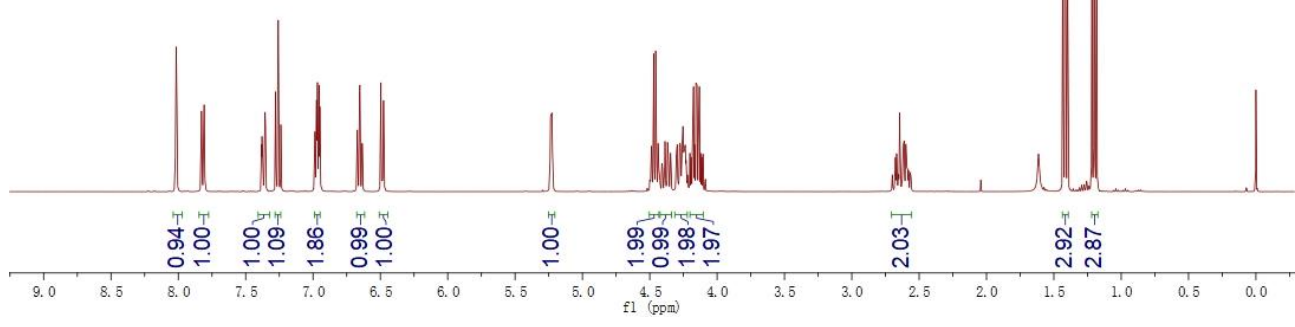
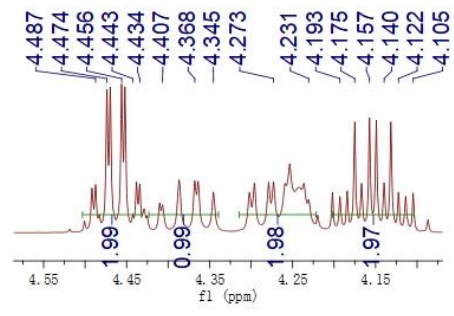
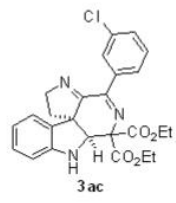
1. H. Liu, A. Domling, *J. Org. Chem.*, **2009**, *74*, 6895-6898.
2. X. W, L. Li, J. L. Zhang, *Adv. Synth. Catal.* **2012**, *354*, 3485-34

7. Copy of ^1H NMR and ^{13}C NMR Spectra

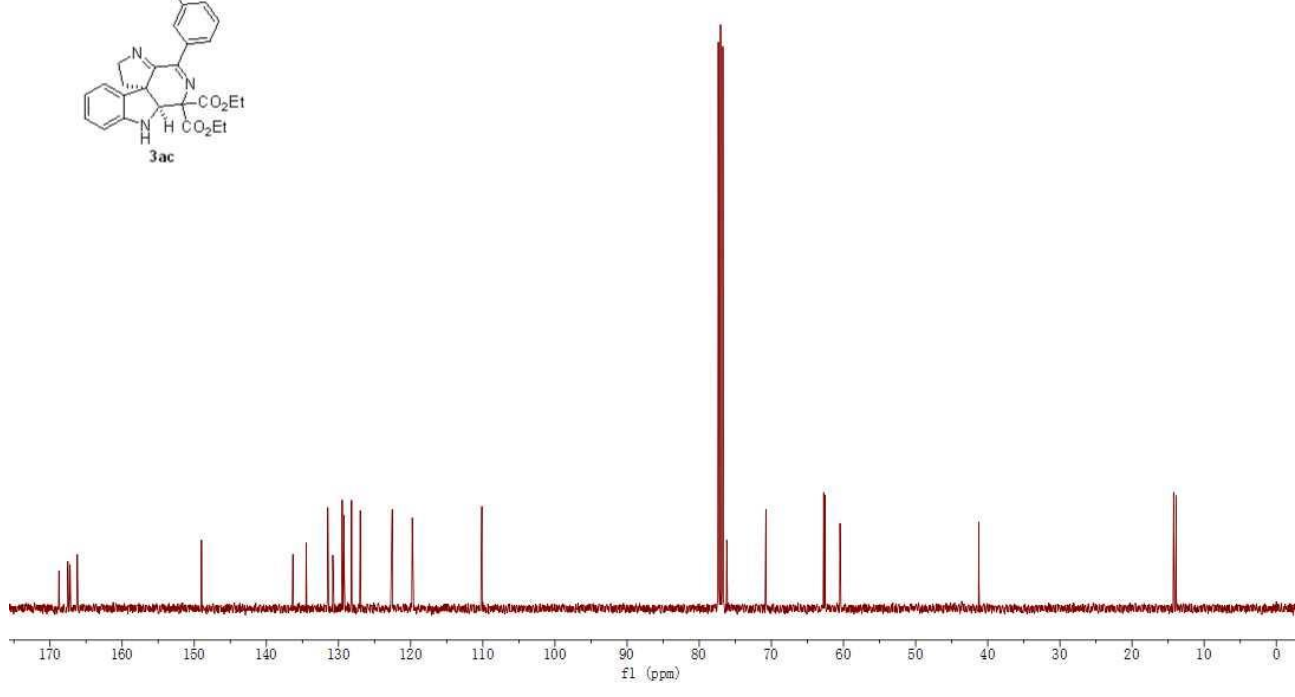
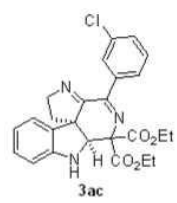


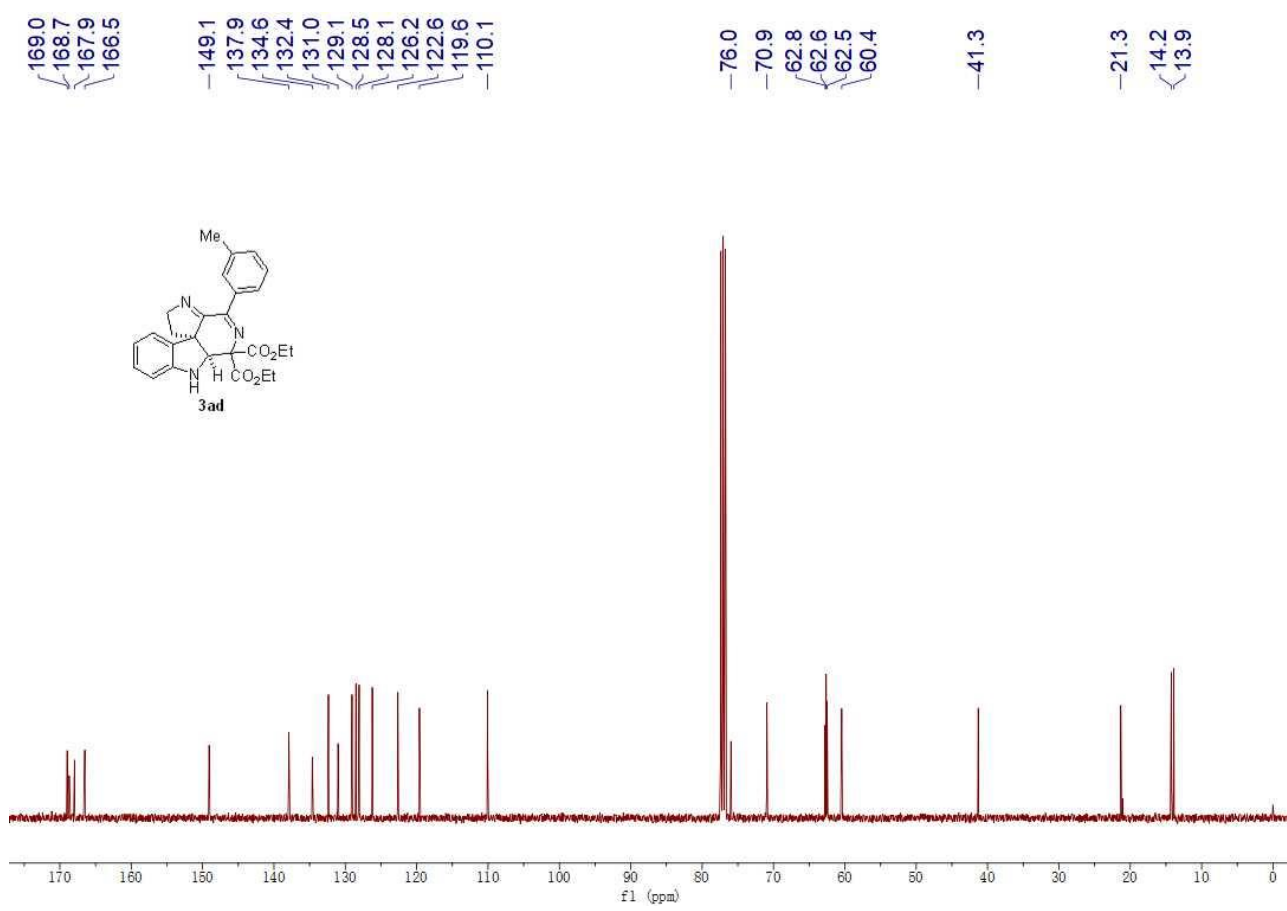
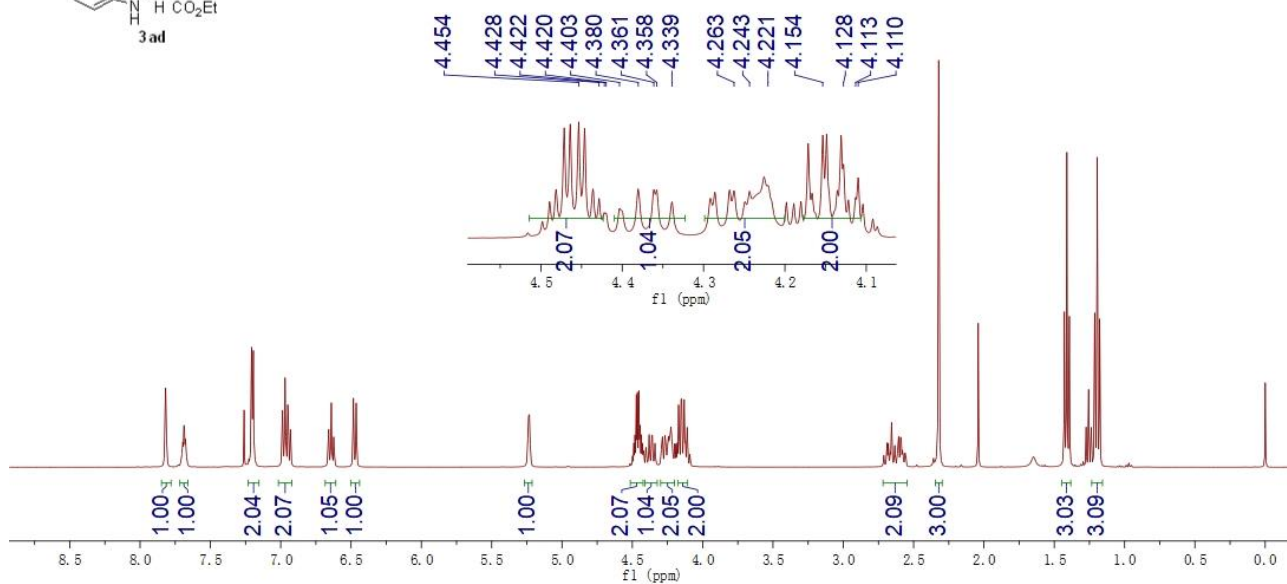
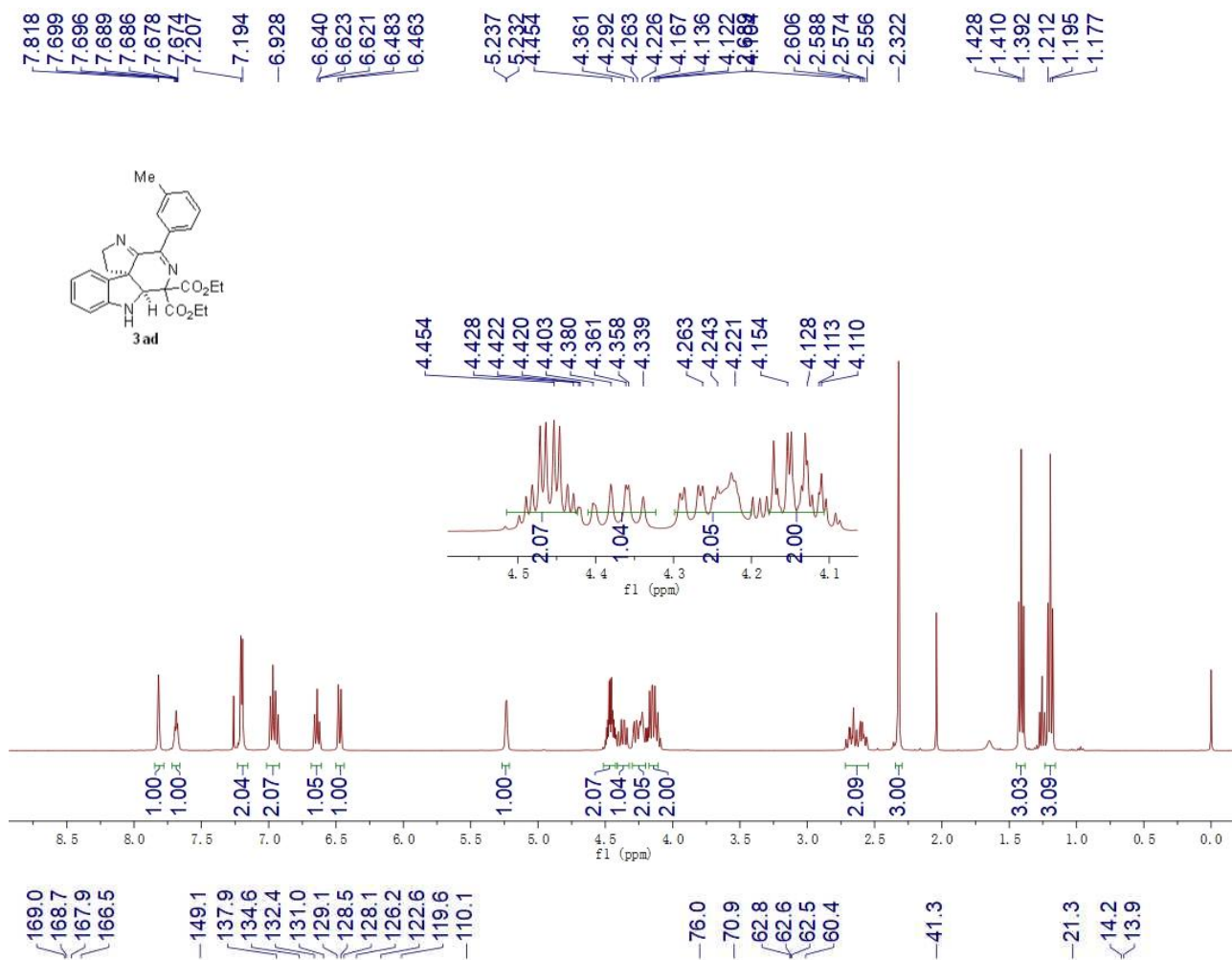


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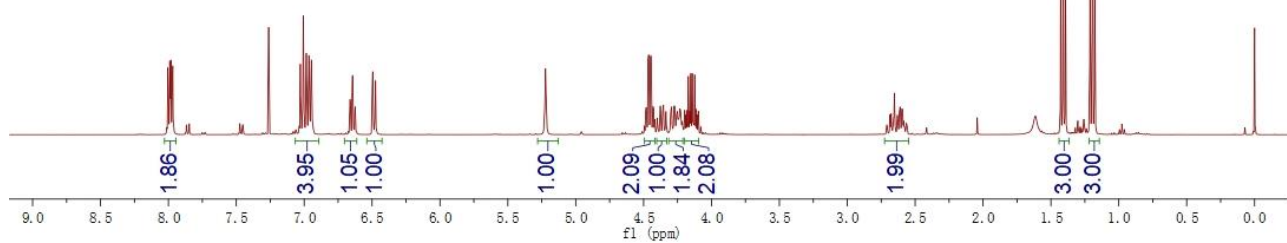
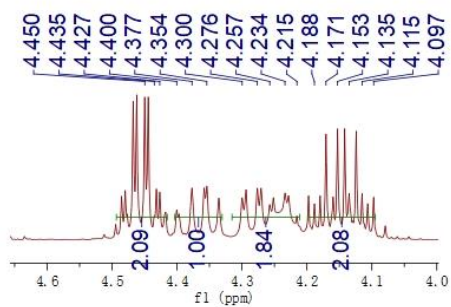
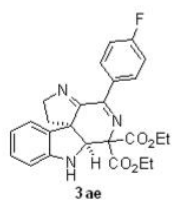
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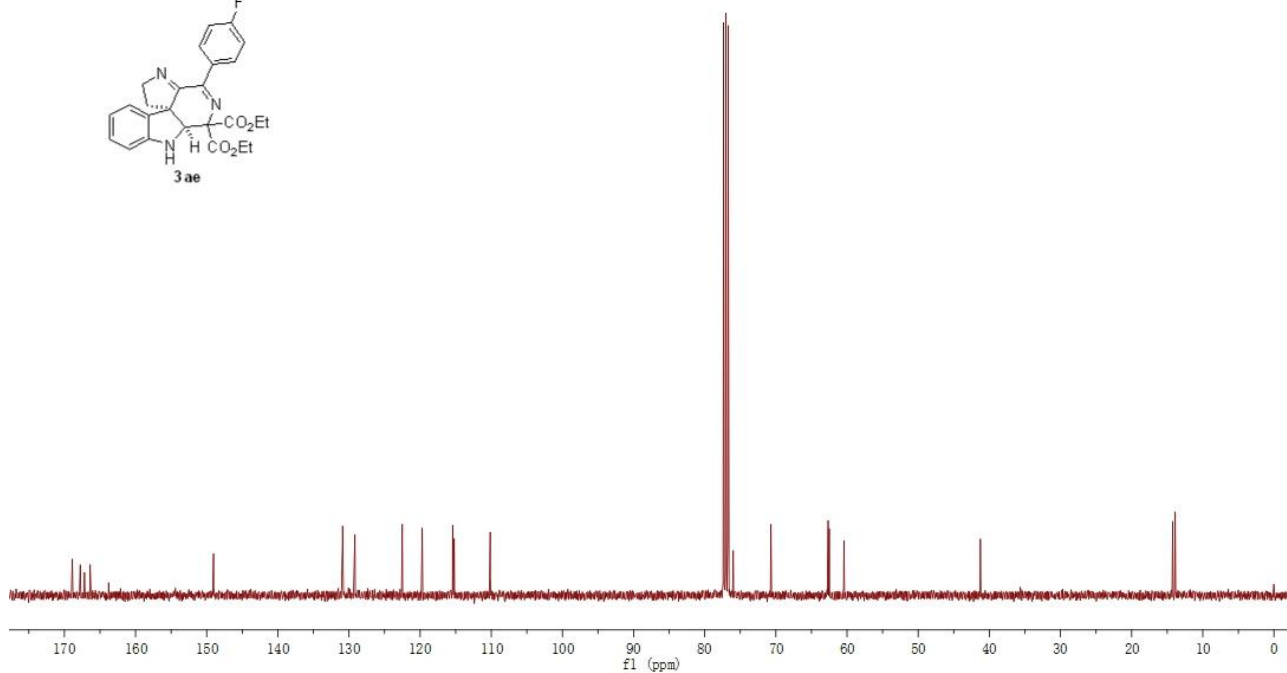
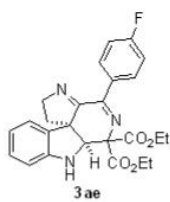
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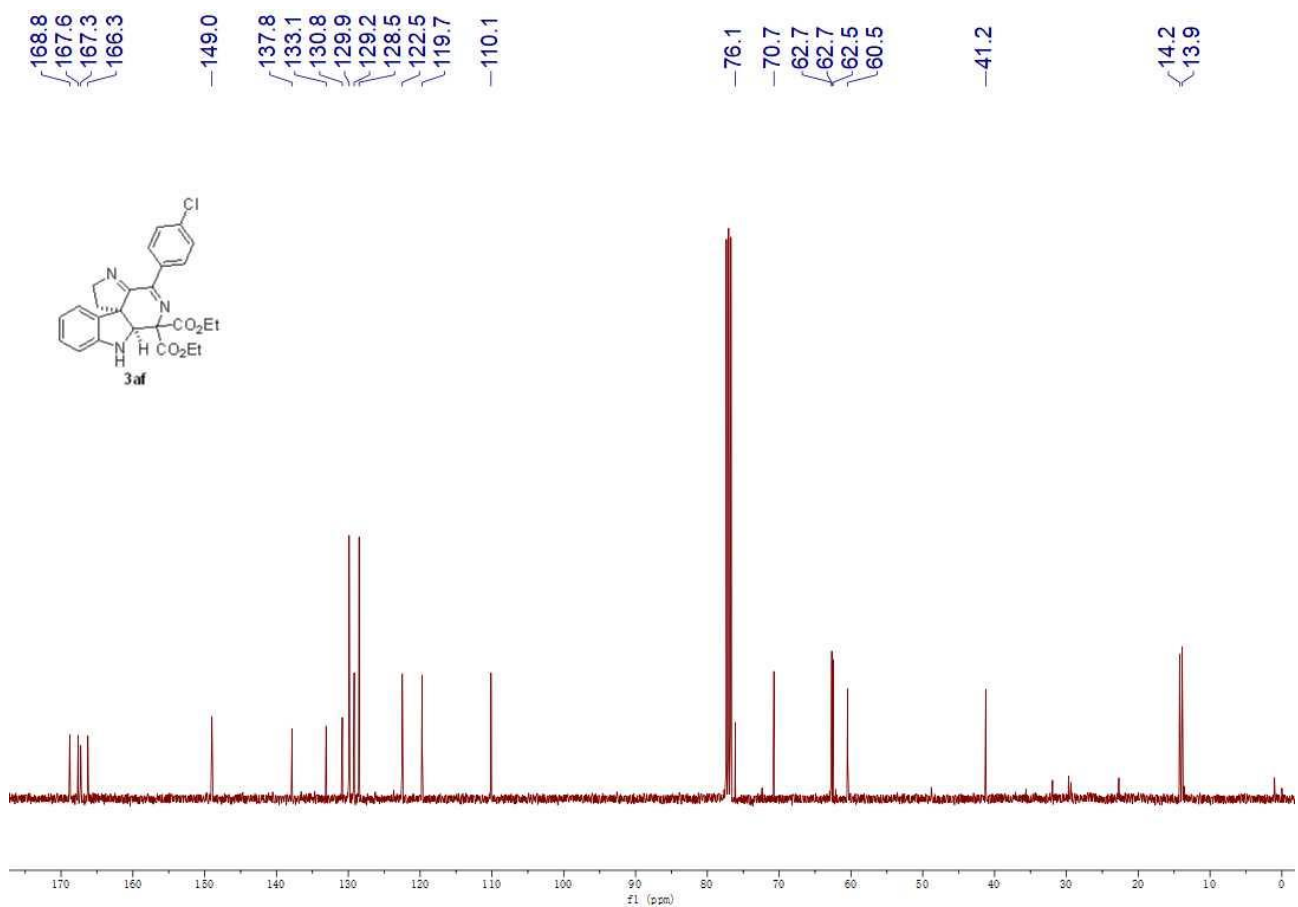
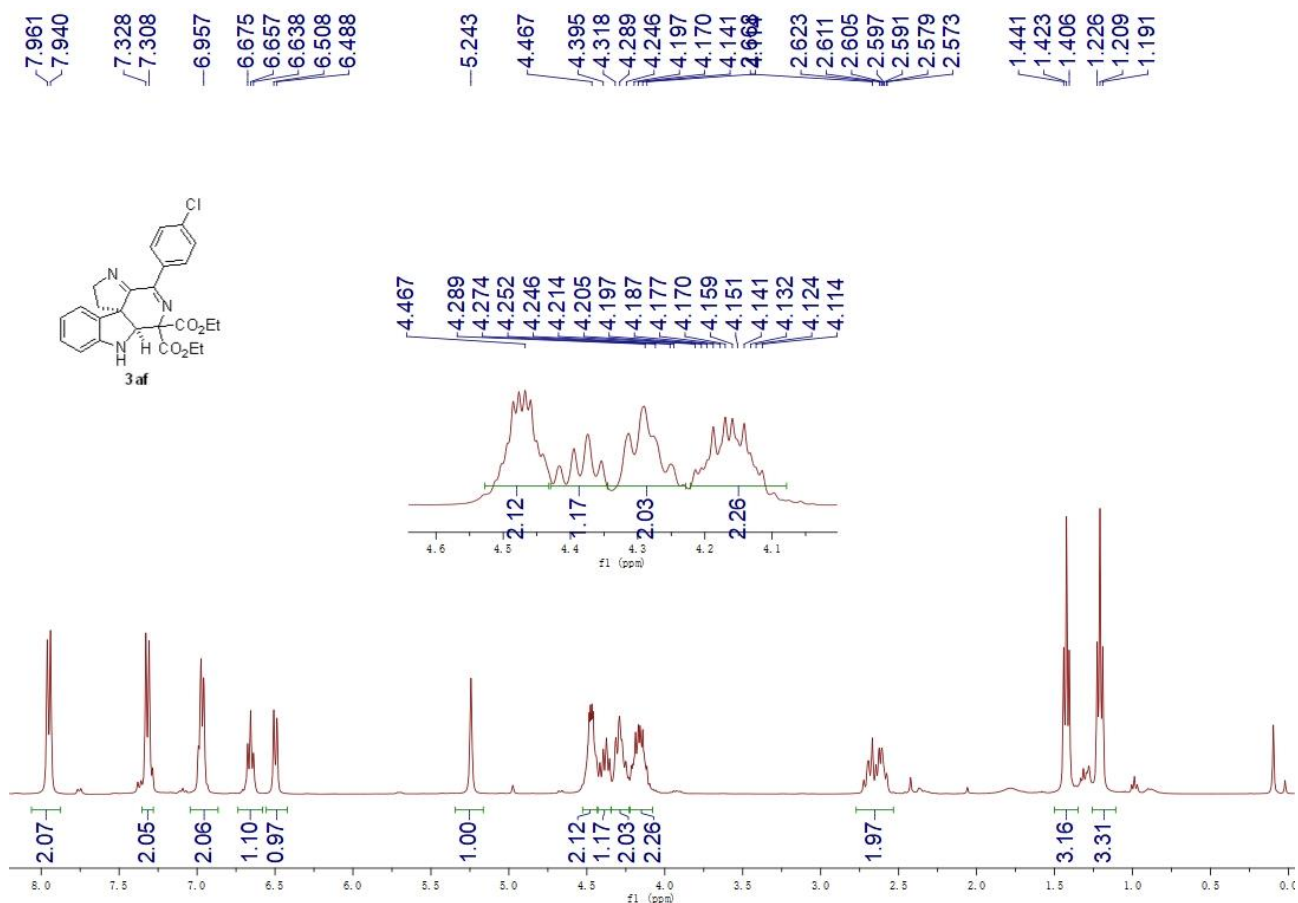
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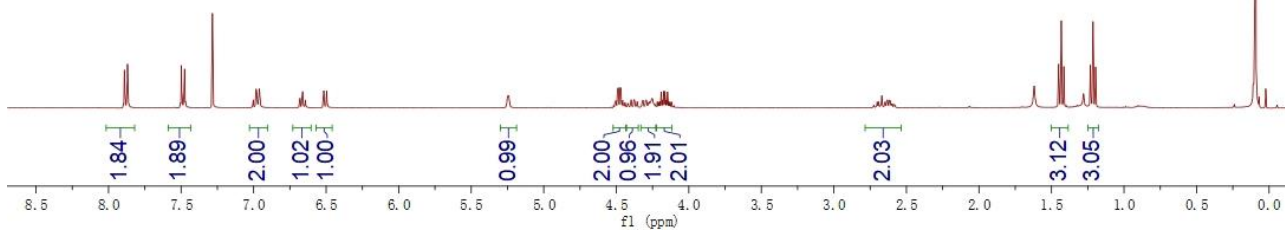
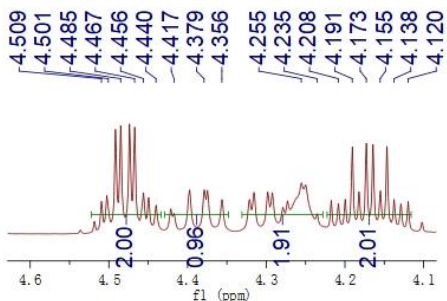
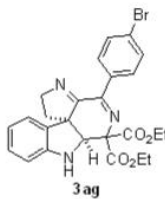
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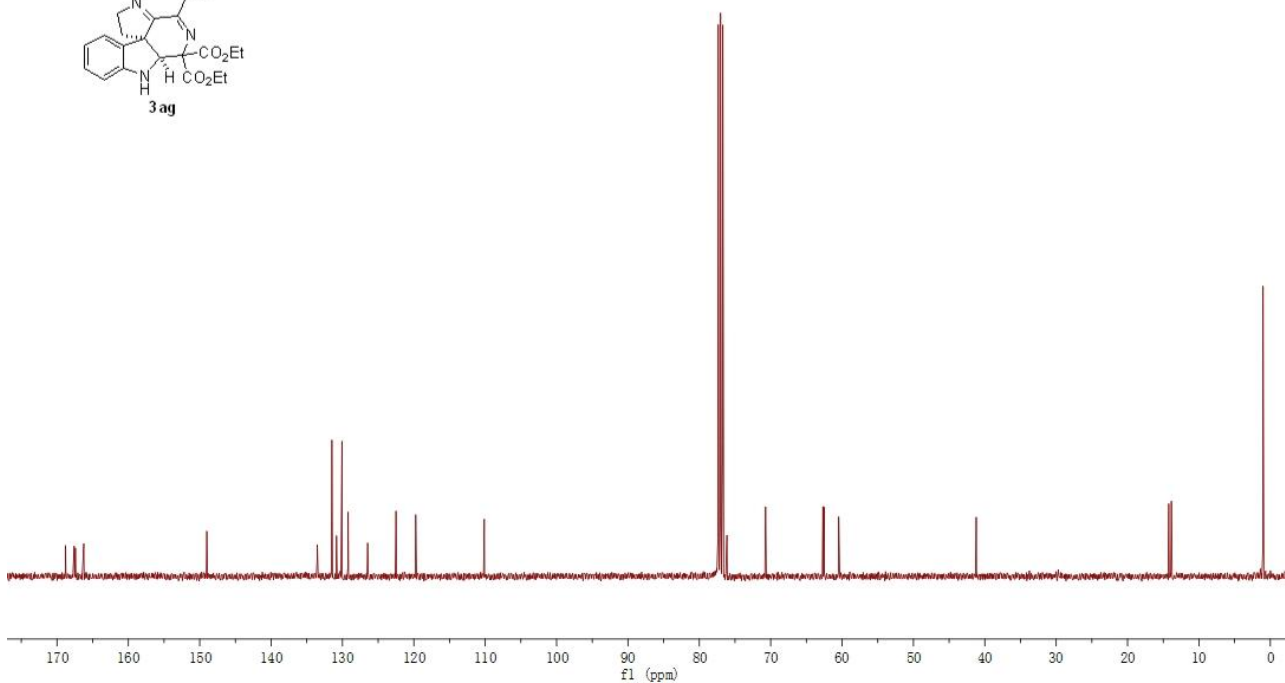
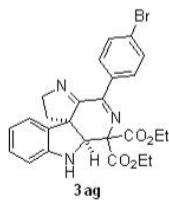
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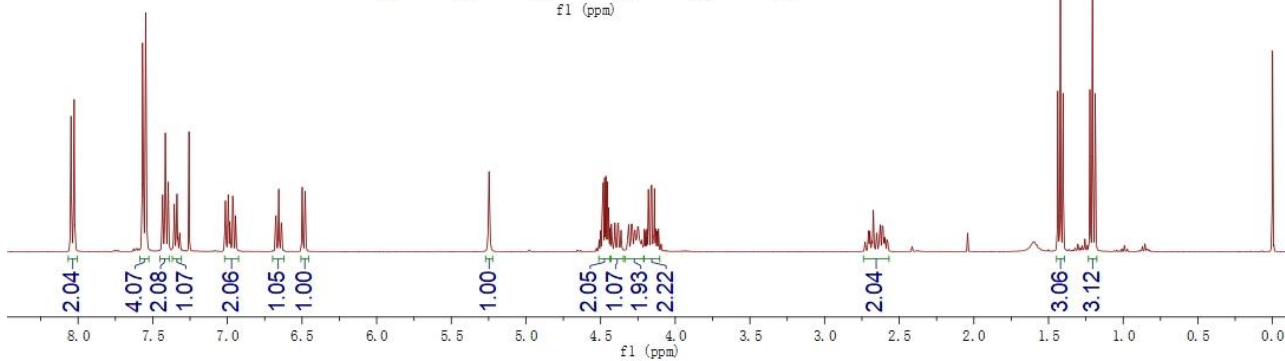
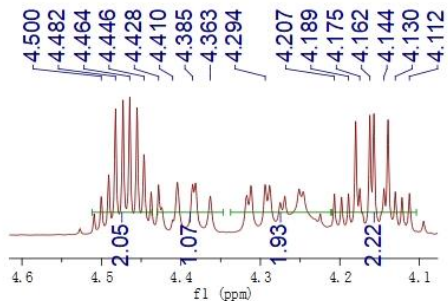
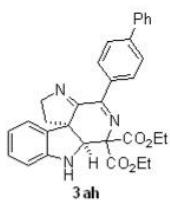
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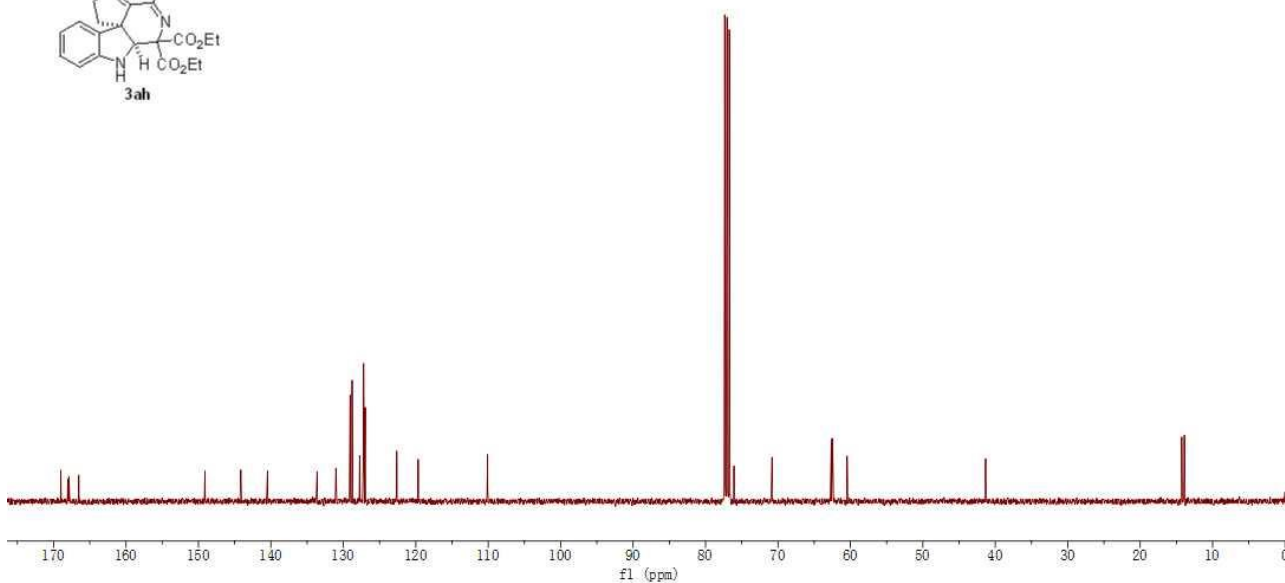
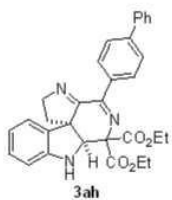
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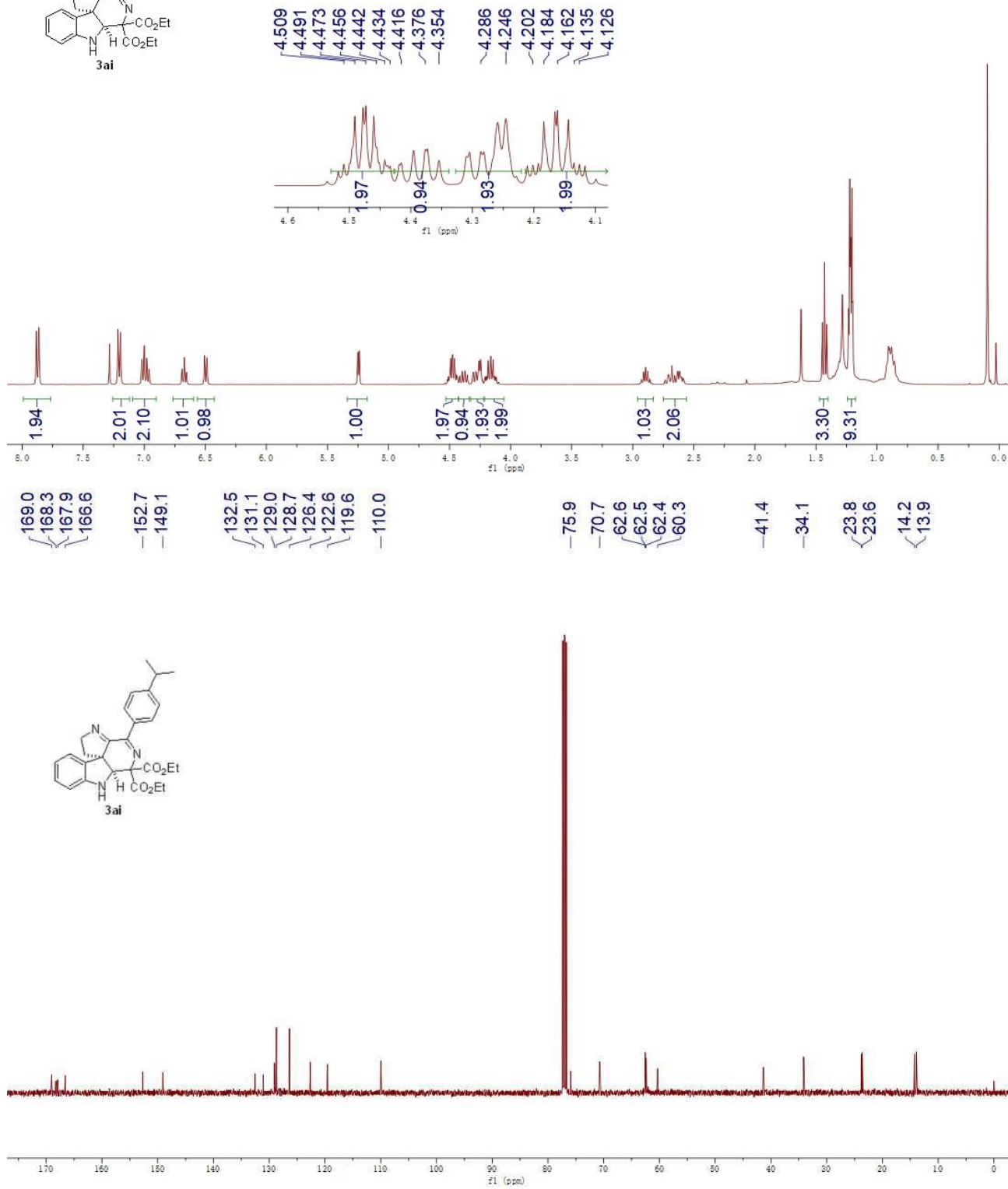
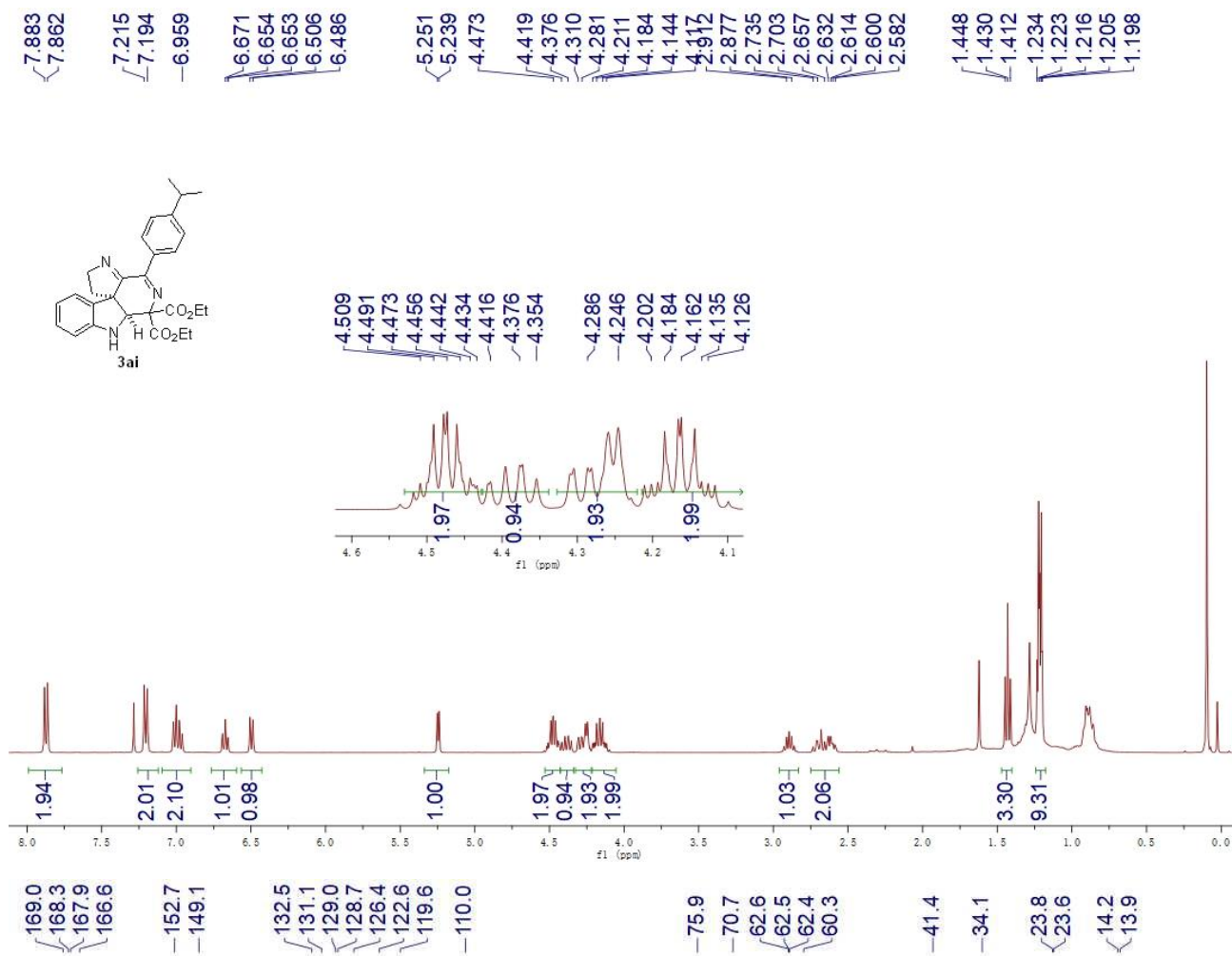


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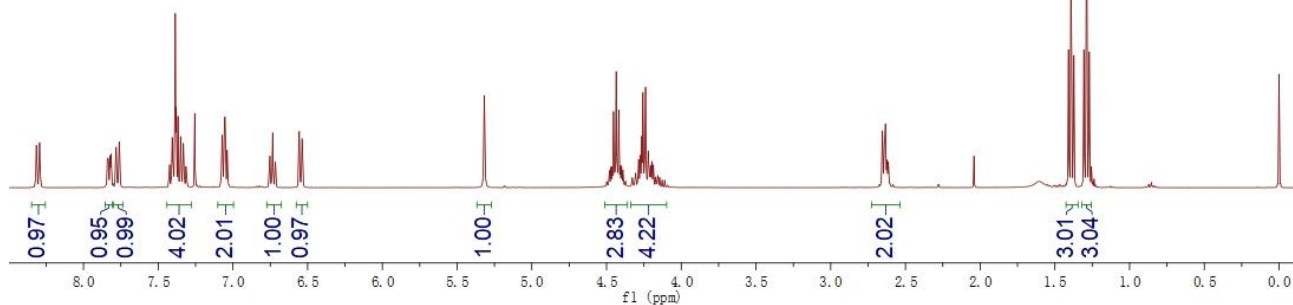
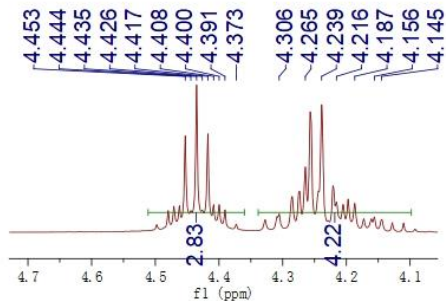
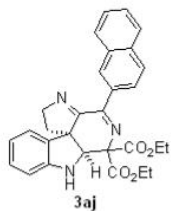


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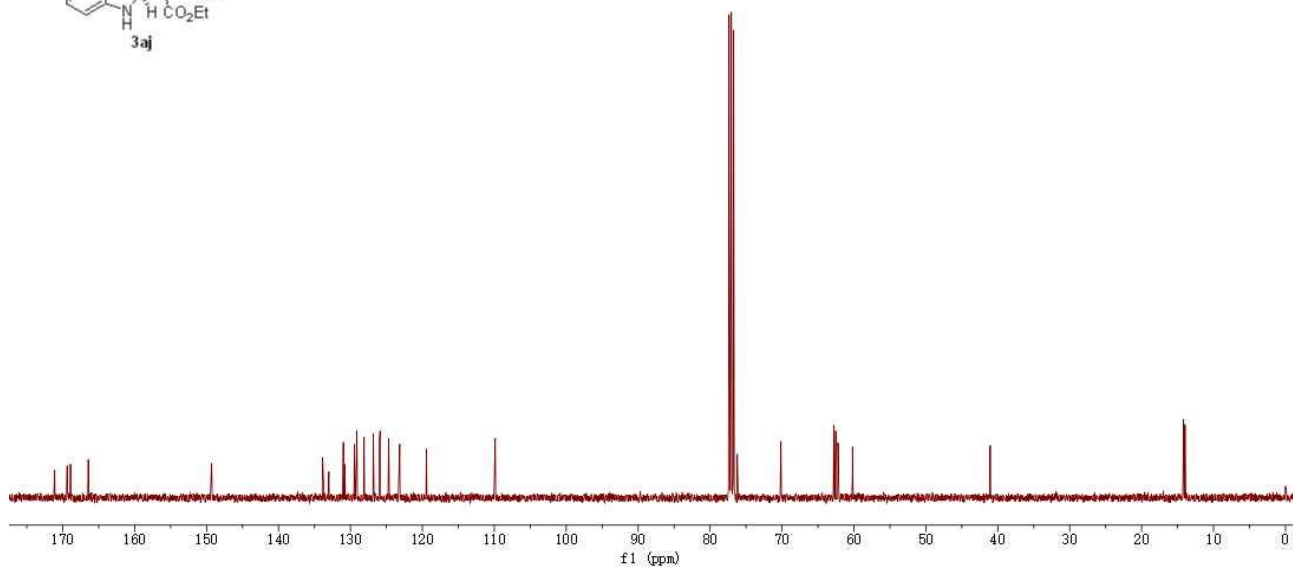
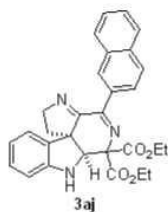




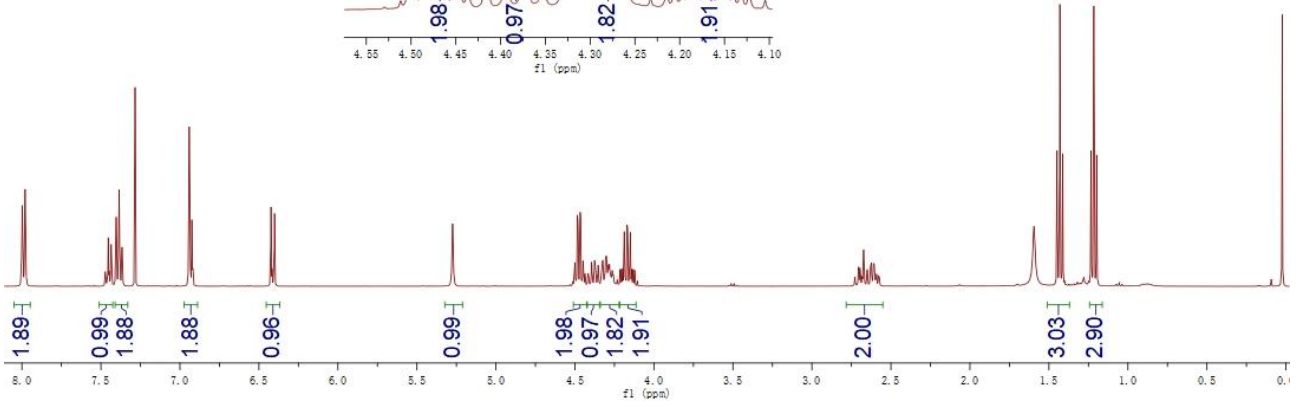
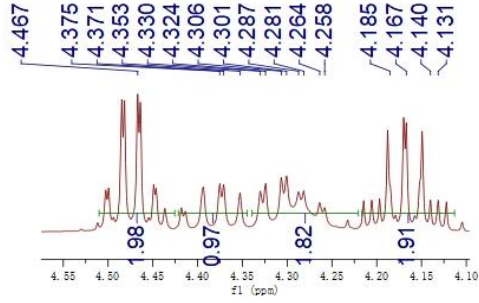
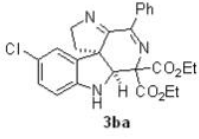
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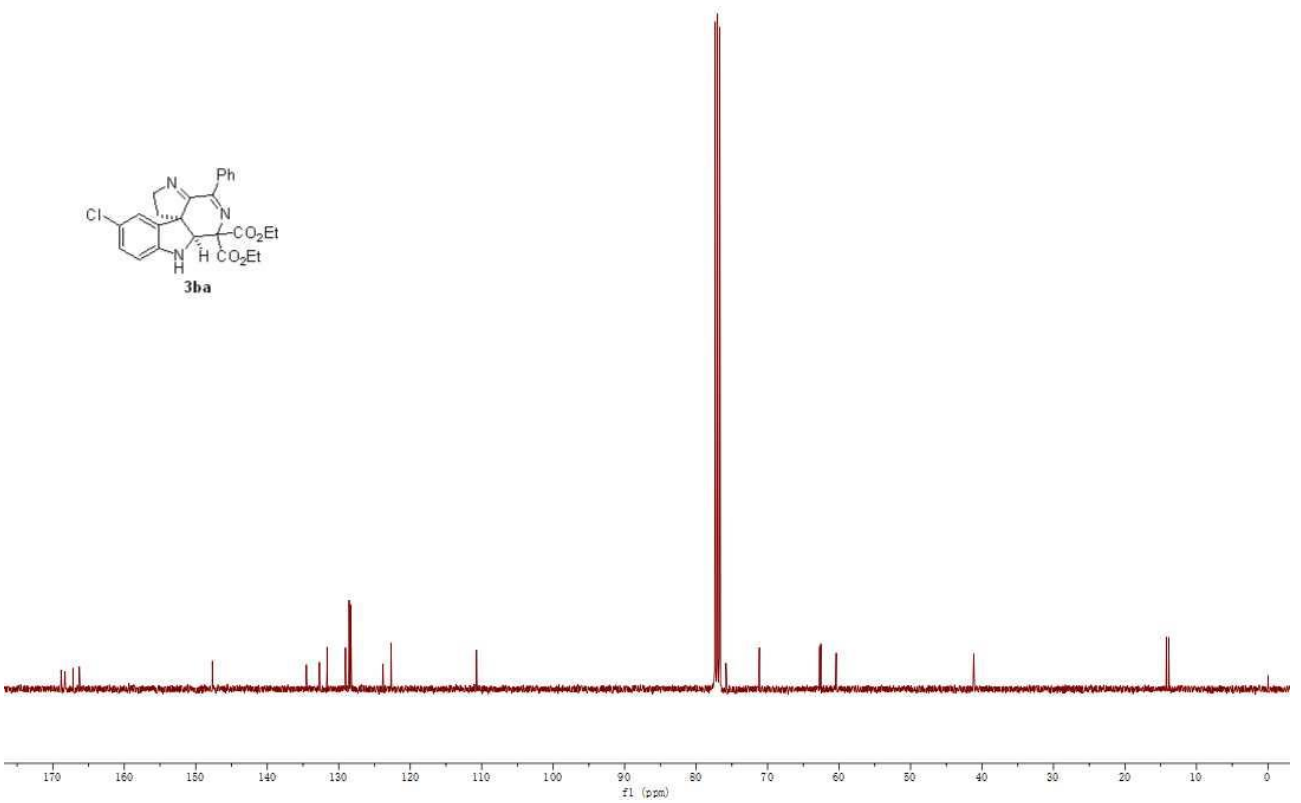
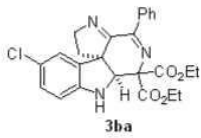
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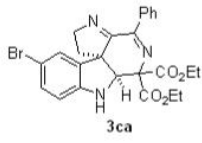


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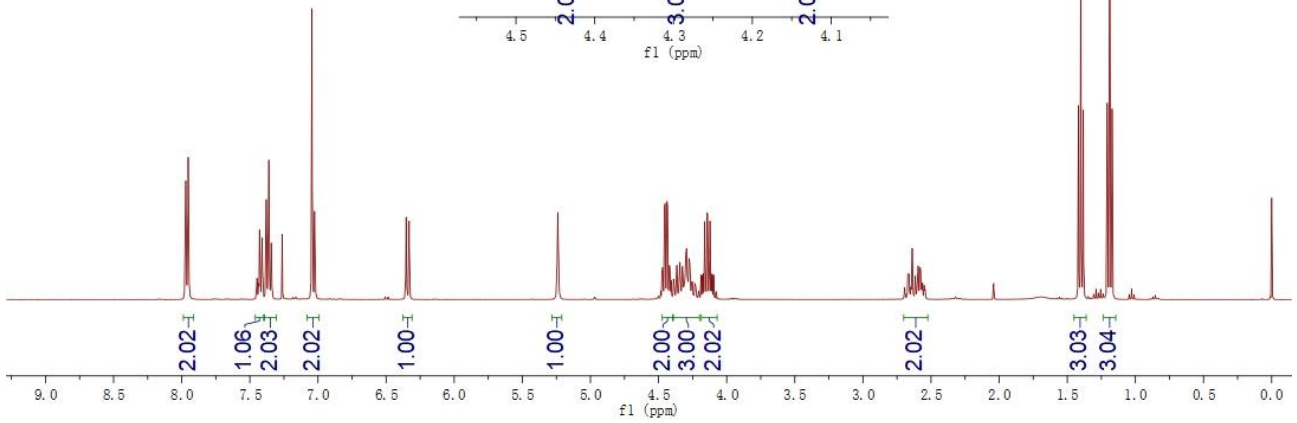
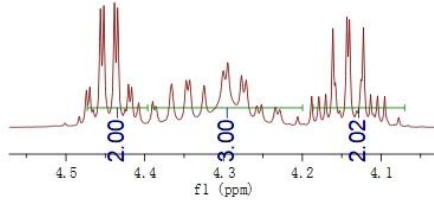
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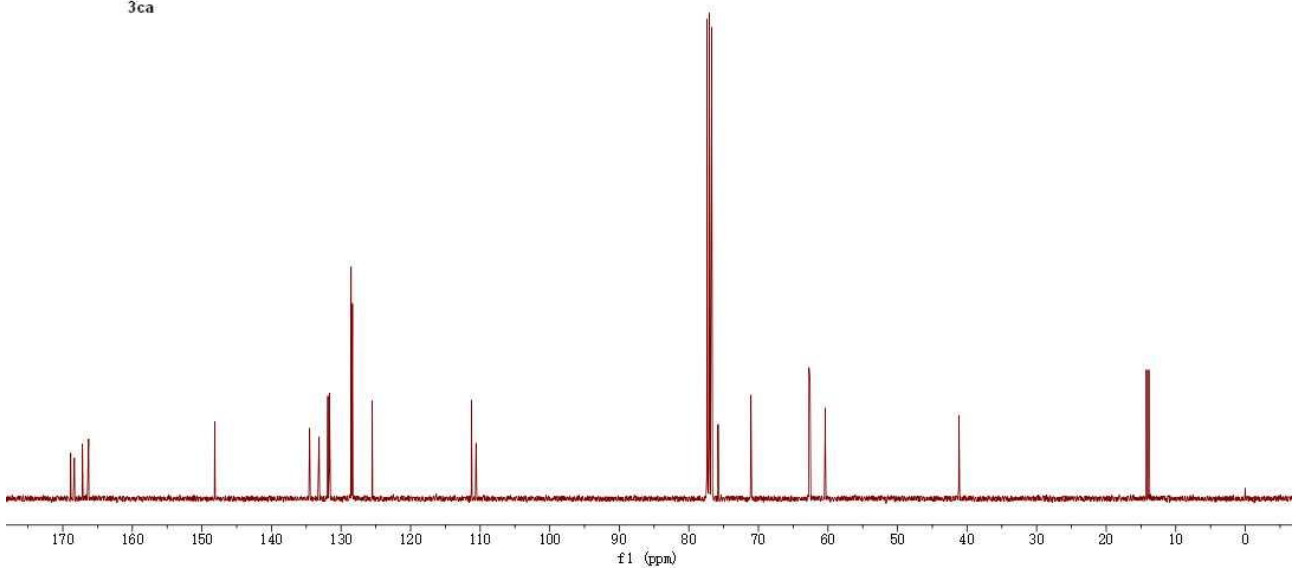


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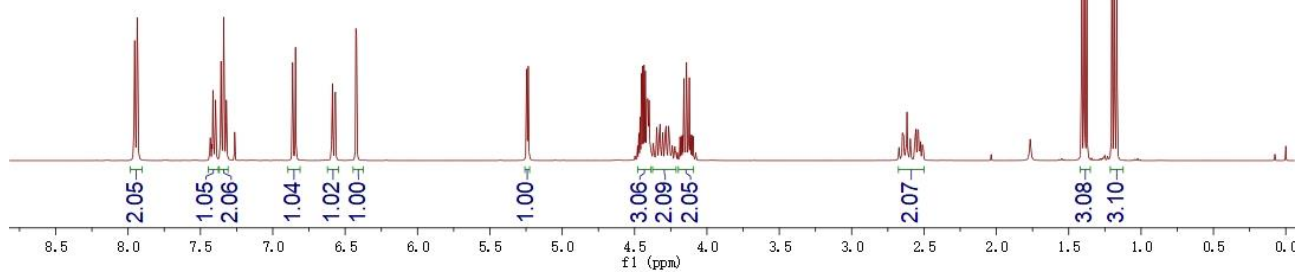
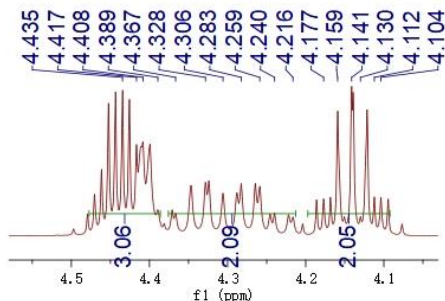
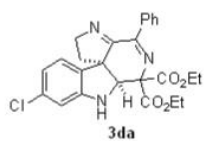
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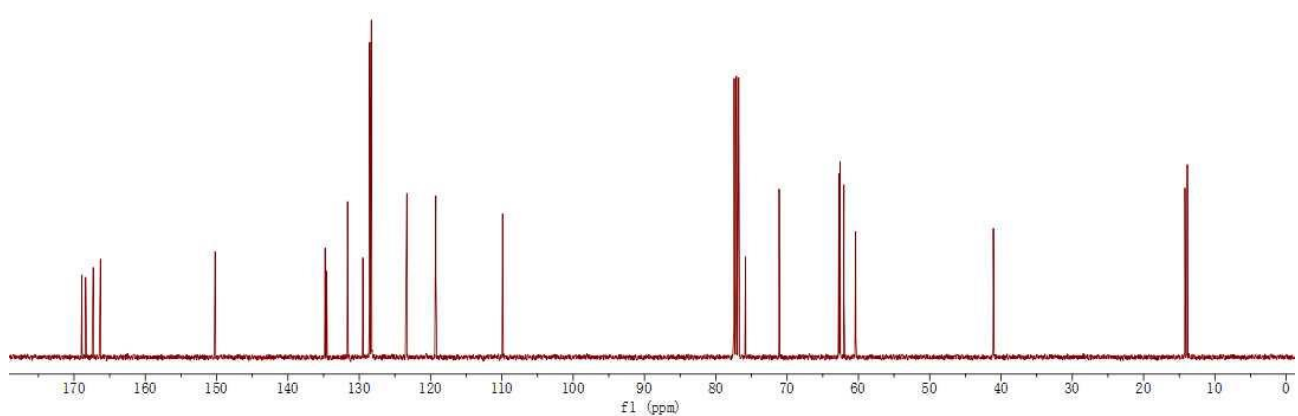
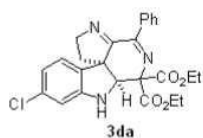
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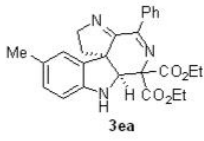
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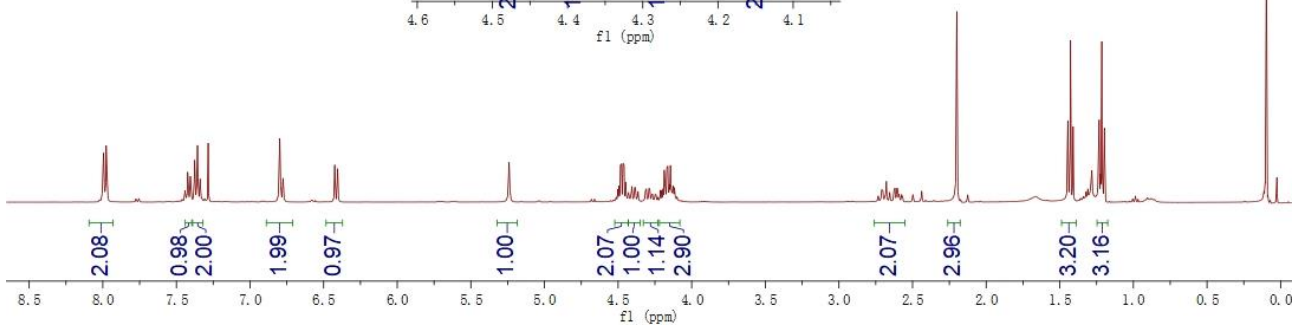
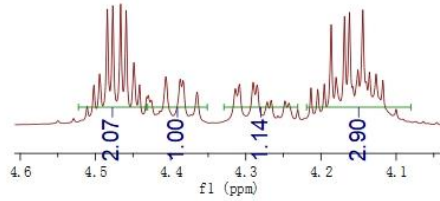


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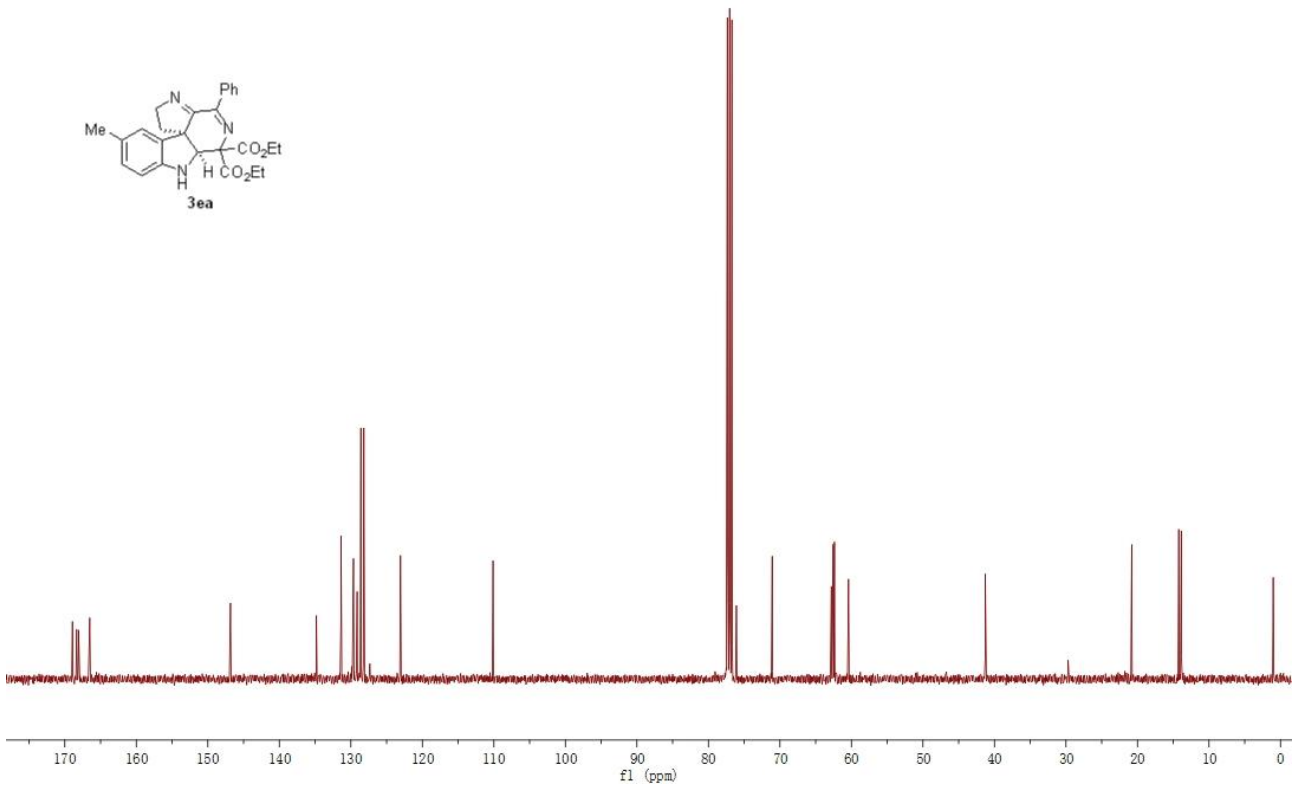
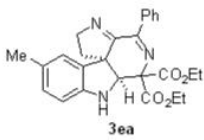


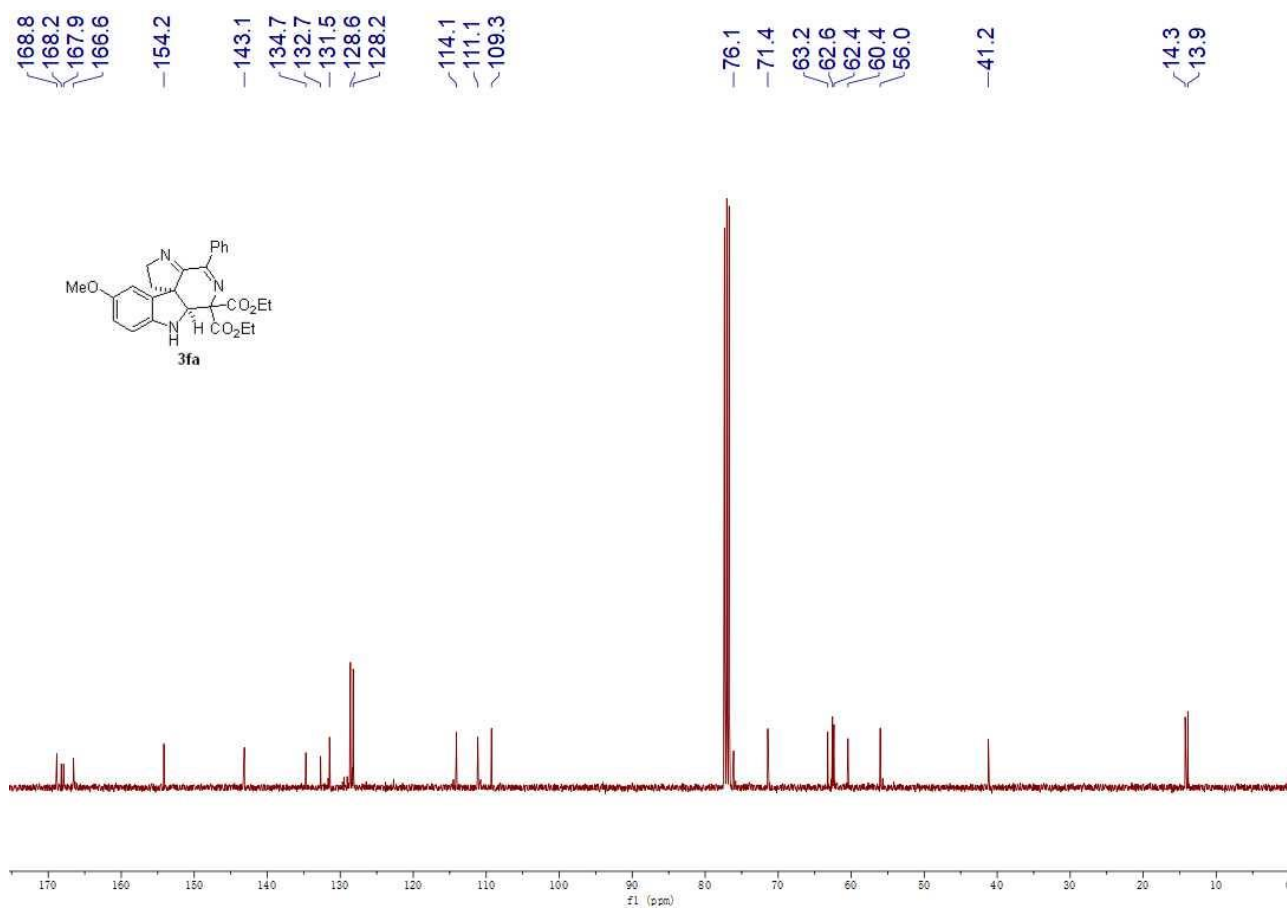
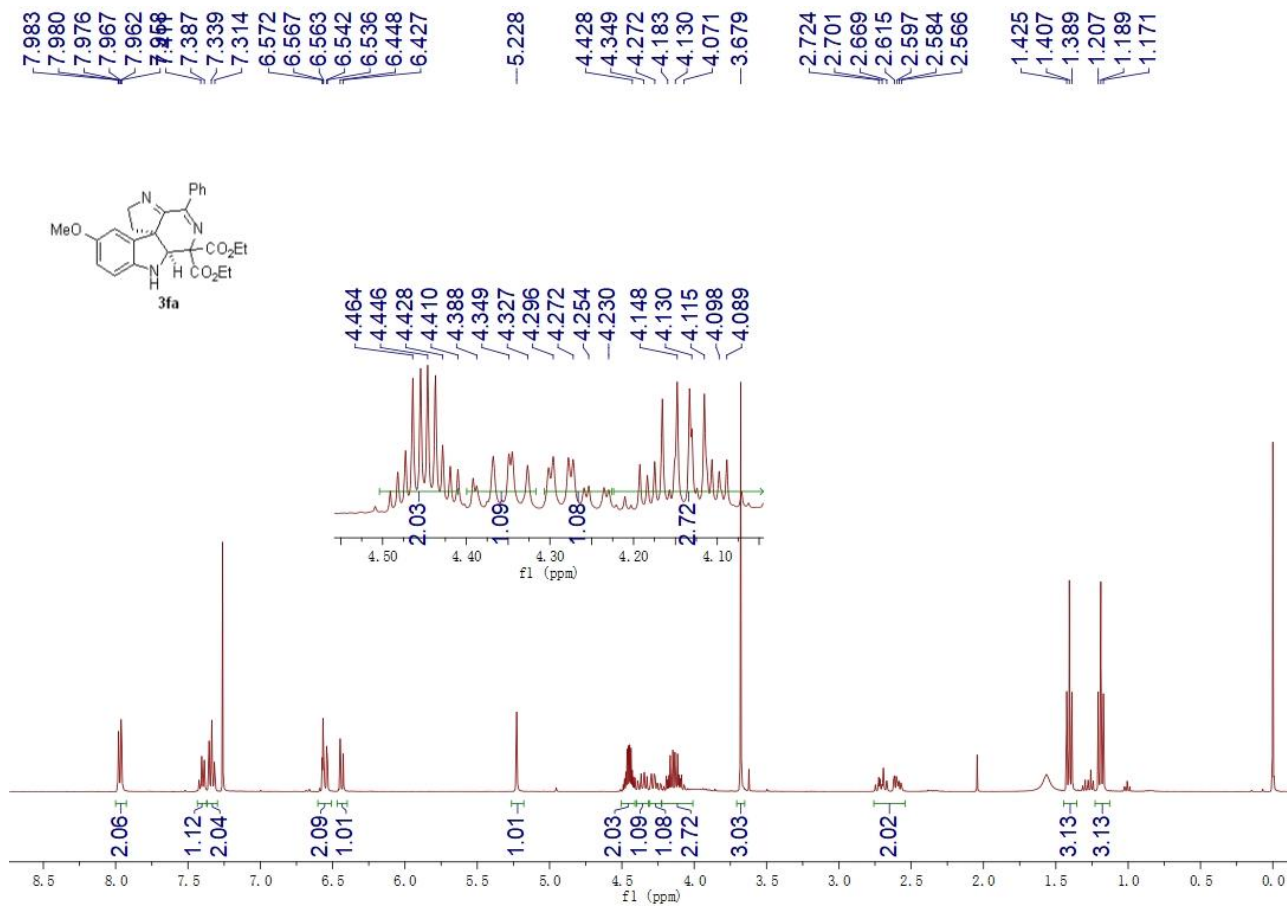
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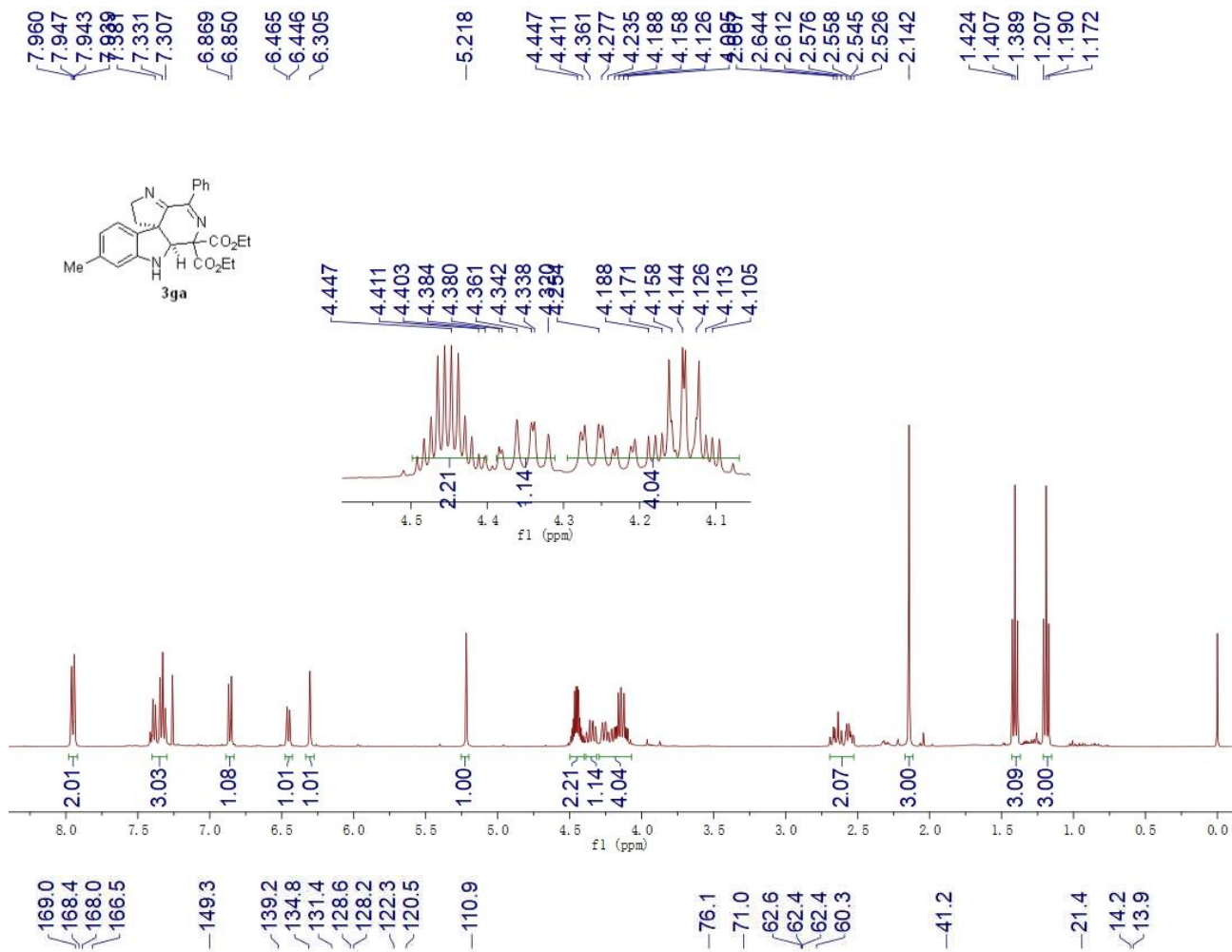
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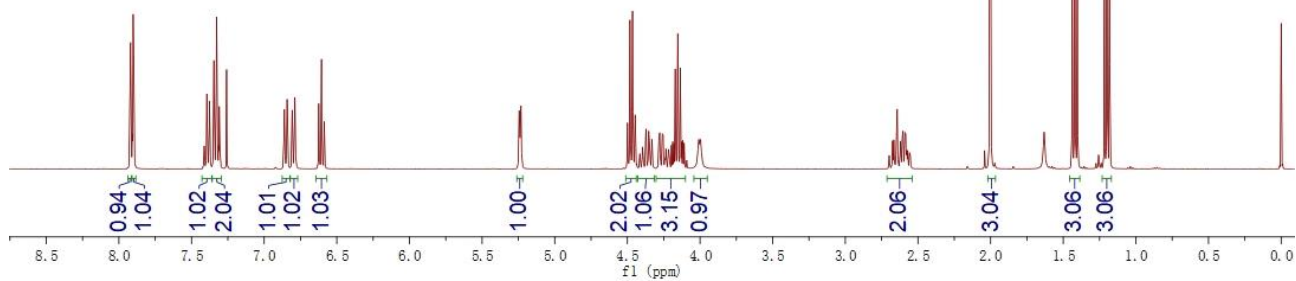
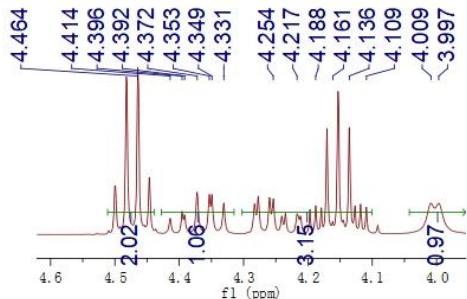
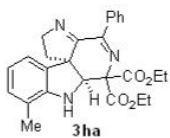
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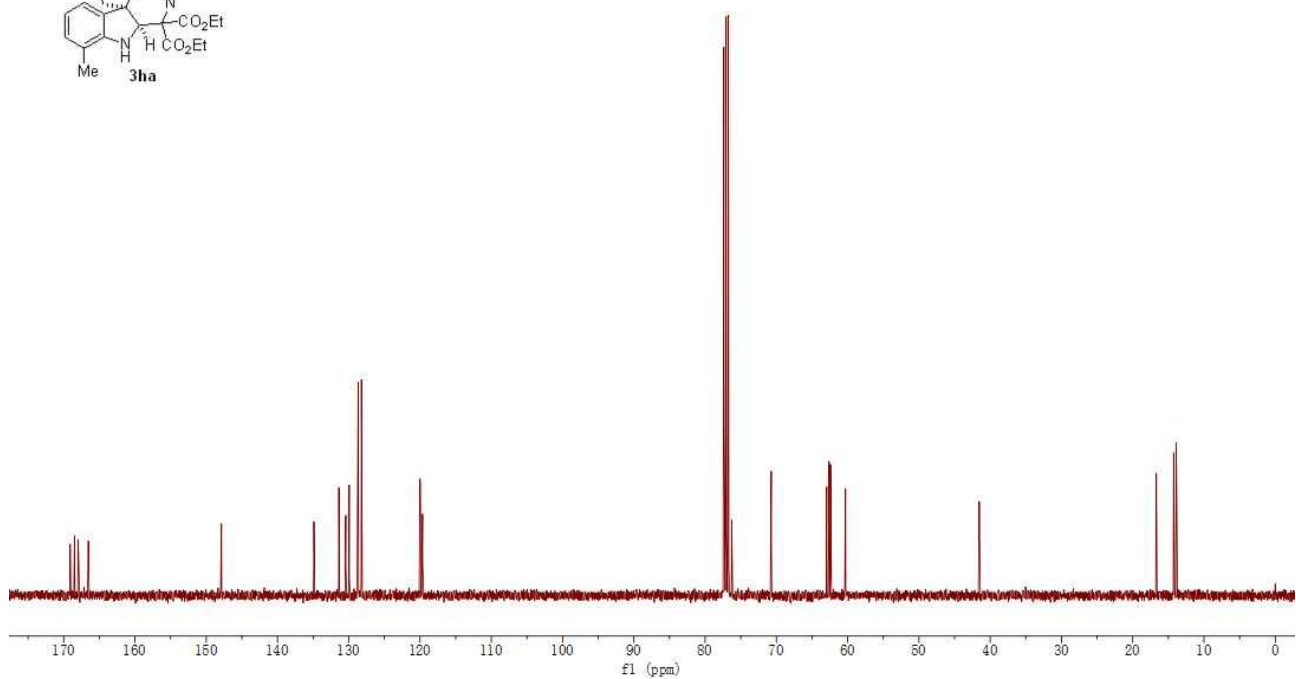
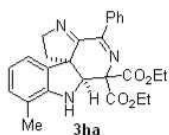




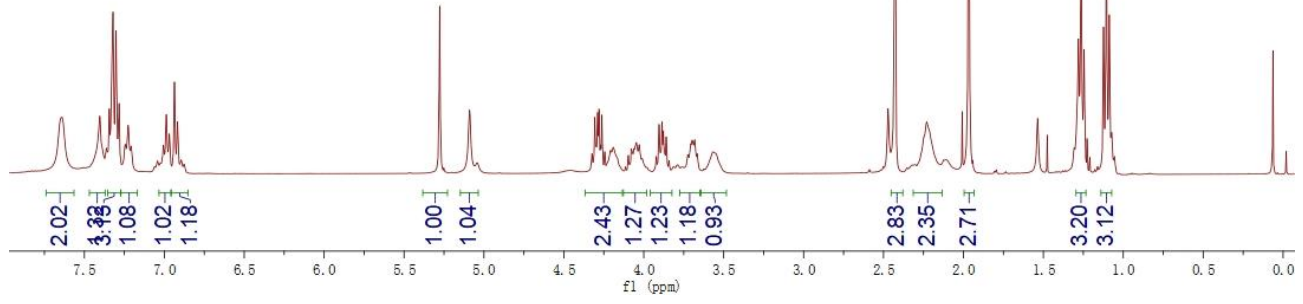
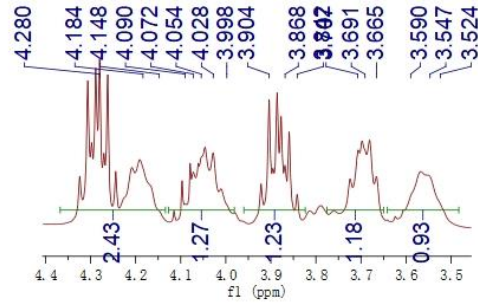
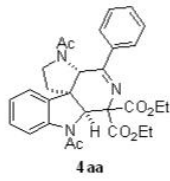
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