

Supporting Information

Polycycle Construction via DMAP-Catalyzed Tandem Addition-(4+2)

Annulation Sequence of δ -Acetoxy Allenolate

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1. General Information

Unless otherwise noted, all reagents were obtained commercially and used without further purification.

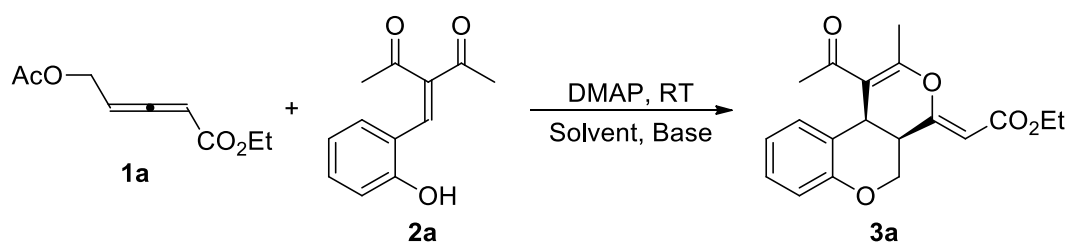
NMR spectrum: ^1H and ^{13}C spectra are recorded on the Bruker AVANCE spectrometer, operating at 400 MHz (300MHz or 500 MHz) for ^1H NMR and 100 MHz (75 MHz or 125 MHz) for ^{13}C NMR. Chemical shifts are reported in parts per million (ppm). Chemical shifts are reported downfield from CDCl_3 (δ : 7.26 ppm) and DMSO-d_6 (δ : 2.5 ppm) for ^1H NMR. Chemical shifts of ^{13}C NMR are reported in the scale relative to the solvent of CDCl_3 (δ : 77.0 ppm) and DMSO-d_6 (δ : 40.0 ppm) used as an internal reference. Multiplicities are recorded as follows: s (singlet), d (doublet), t (triplet), dd (doublet of doublet), q (quartet), m (multiplet). Coupling constants are reported in Hertz (Hz).

Mass spectroscopy: Mass spectra were in general recorded on an AMD 402/3 or a HP 5989A mass selective detector.

Chromatography: Column chromatography was performed with silica gel (200-300 mesh ASTM).

2. Optimization of Reaction Conditions

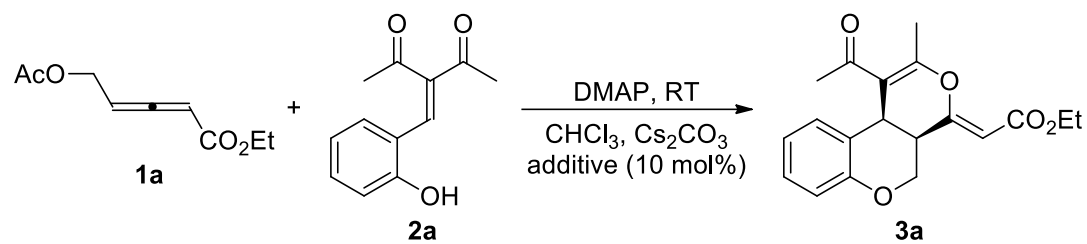
Table S1: Screening of solvents and Bases^a



Entry	Solvent	Base	Yield ^b
1	PhMe	Cs ₂ CO ₃	32%
2	CHCl ₃	Cs ₂ CO ₃	72%
3	CH ₃ CN	Cs ₂ CO ₃	trace
4	dioxane	Cs ₂ CO ₃	trace
5	CH ₂ Cl ₂	Cs ₂ CO ₃	50%
7	CH ₂ ClCH ₂ Cl	Cs ₂ CO ₃	38%
8	CCl ₄	Cs ₂ CO ₃	trace
9	THF	Cs ₂ CO ₃	trace
10	EtOAc	Cs ₂ CO ₃	29%
11	EtOH	Cs ₂ CO ₃	ND
12	DMF	Cs ₂ CO ₃	ND
13	DMSO	Cs ₂ CO ₃	ND
14	DMPU	Cs ₂ CO ₃	ND
15	CHCl ₃	K ₂ CO ₃	55%
16	CHCl ₃	Na ₂ CO ₃	38%
17	CHCl ₃	NaOH	22%
18	CHCl ₃	K ₃ PO ₄ ·3H ₂ O	65%
19	CHCl ₃	TMG	35%
20	CHCl ₃	Et ₃ N	ND
21	CHCl ₃	DBU	ND
22	CHCl ₃	DIEA	trace

^aReaction conditions: to the solution of **2a** (40.8 mg, 0.2 mmol), Base (0.24 mmol) and DABCO (4.5 mg, 0.04 mmol) in solvent (1.5 mL) was slowly added the relevant solution (1.5 mL) of **1a** (47.8 mg, 0.26 mmol). ^bIsolated yield.

Table S2: Screening of Lewis Acids^a

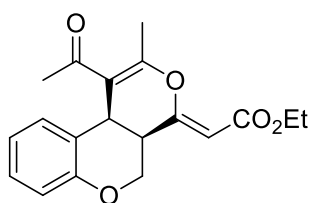


Entry	Additive	Yield ^b	Entry	Additive	Yield ^b
1	$\text{Mg}(\text{OTf})_2$	40%	4	$\text{Bi}(\text{OTf})_3$	40%
2	$\text{Sm}(\text{OTf})_3$	28%	5	$\text{Ce}(\text{OTf})_4$	28%
3	$\text{Sc}(\text{OTf})_3$	40%	6	$\text{Zn}(\text{OAc})_2 \cdot 2\text{H}_2\text{O}$	47%

^aReaction conditions: to the solution of **2a** (40.8 mg, 0.2 mmol), Cs_2CO_3 (78.2 mg, 0.24 mmol) and DABCO (4.5 mg, 0.04 mmol) in CHCl_3 (1.5 mL) was slowly added the CHCl_3 solution (1 mL) of **1a** (47.8 mg, 0.26 mmol). ^bIsolated yield.

3. General Procedure and the Date for Compounds 3

To a 10 mL Schlenk tube was added compound **2** (0.2 mmol), Cs₂CO₃ (78.2 mg, 0.24 mmol), DMAP (4.5 mg, 0.04 mmol), and chloroform (1.5 mL) with stirring. To the mixture, the solution of allenolate **1a** (47.8 mg, 0.26 mmol) in chloroform (1.5 mL) was slowly added over half an hour. After completion of the reaction (monitored by TLC), the solvent was removed and the residue was directly subjected to silica gel column chromatography (petroleum ether/ethyl acetate as eluent) to give the product **3**.

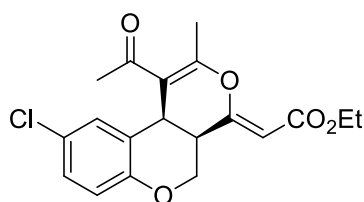


3a, 47.3 mg, 72% yield, yellow oil.

¹H NMR (400 MHz, DMSO-d₆): δ 7.19-7.14 (m, 1H), 6.89-6.84 (m, 2H), 6.77 (d, *J* = 7.6 Hz, 1H), 5.03 (d, *J* = 1.2 Hz, 1H), 4.61 (dd, *J* = 10.4 Hz, *J* = 4.8 Hz, 1H), 4.24 (t, *J* = 10.4 Hz, 1H), 4.13-4.06 (m, 3H), 2.98-2.89 (m, 1H), 2.32 (s, 3H), 2.10 (d, *J* = 2.0 Hz, 3H), 1.21 (t, *J* = 7.2 Hz, 3H)。

¹³C NMR (100 MHz, DMSO-d₆): δ 201.3, 163.8, 158.9, 154.4, 153.7, 128.8, 125.6, 125.1, 120.8, 117.6, 115.3, 97.0, 66.7, 60.0, 37.6, 35.3, 31.2, 18.0, 14.7.

HRMS (ESI) Calcd for C₁₉H₂₁O₅[M+H⁺] 329.1384, found 329.1386.

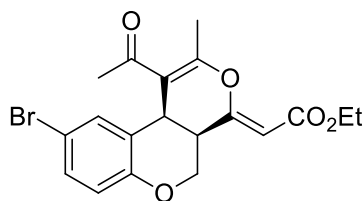


3b, 43.6 mg, 60% yield, yellow oil.

¹H NMR (400 MHz, DMSO-d₆): δ 7.23 (dd, *J* = 8.8 Hz, *J* = 2.8 Hz, 1H), 6.92 (d, *J* = 8.8 Hz, 1H), 6.70-6.69 (m, 1H), 5.05 (d, *J* = 1.2 Hz, 1H), 4.62 (dd, *J* = 10.0 Hz, *J* = 4.4 Hz, 1H), 4.27 (t, *J* = 10.4 Hz, 1H), 4.14-4.06 (m, 3H), 3.00-2.93 (m, 1H), 2.26 (s, 3H), 2.11 (d, *J* = 1.6 Hz, 3H), 1.21 (t, *J* = 7.2 Hz, 3H)

¹³C NMR (100 MHz, DMSO-d₆): δ 201.1, 163.7, 158.4, 154.5, 153.4, 128.5, 127.4, 125.2, 124.4, 119.3, 114.6, 97.4, 67.0, 60.0, 37.2, 35.2, 31.2, 31.2, 18.2, 14.6.

HRMS (ESI) Calcd for C₁₉H₂₀ClO₅[M+H⁺] 363.0994, found 363.0998.

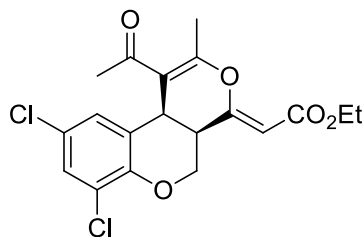


3c, 51.3 mg, 63% yield, yellow oil.

^1H NMR (400 MHz, DMSO- d_6): δ 7.35 (dd, J = 8.4 Hz, J = 1.6 Hz, 1H), 6.87 (d, J = 7.6 Hz, 1H), 6.83-6.81 (m, 1H), 5.05 (d, J = 1.6 Hz, 1H), 4.62 (dd, J = 10.4 Hz, J = 4.8 Hz, 1H), 4.26 (t, J = 10.8 Hz, 1H), 4.15-4.06 (m, 3H), 3.01-2.93 (m, 1H), 2.25 (s, 3H), 2.11 (d, J = 2.0 Hz, 3H), 1.21 (t, J = 7.2 Hz, 3H)

^{13}C NMR (100 MHz, DMSO- d_6): δ 201.1, 163.7, 158.4, 154.6, 153.9, 131.4, 128.1, 127.9, 119.8, 114.6, 112.0, 97.4, 67.0, 60.0, 37.1, 35.2, 31.2, 18.2, 14.7.

HRMS (ESI) Calcd for $\text{C}_{19}\text{H}_{19}\text{BrNaO}_5[\text{M}+\text{Na}^+]$ 429.0308, found 429.0312.

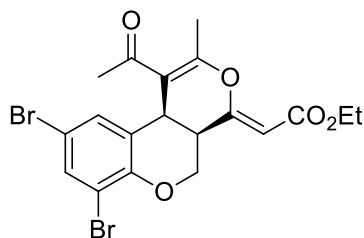


3d, 40.5 mg, 51% yield, yellow oil.

^1H NMR (300 MHz, DMSO- d_6): δ 7.52 (d, J = 2.1 Hz, 1H), 6.64 (dd, J = 2.1 Hz, J = 1.2 Hz, 1H), 5.09 (d, J = 1.5 Hz, 1H), 4.73 (dd, J = 10.2 Hz, J = 4.8 Hz, 1H), 4.39 (t, J = 10.5 Hz, 1H), 4.17 (d, J = 11.1 Hz, 1H), 4.11 (q, J = 7.2 Hz, 2H), 3.09-3.00 (m, 1H), 2.26 (s, 3H), 2.14 (d, J = 1.8 Hz, 3H), 1.22 (t, J = 7.2 Hz, 3H)

^{13}C NMR (100 MHz, DMSO- d_6): δ 200.9, 163.7, 157.9, 155.4, 149.3, 129.4, 128.4, 124.3, 124.1, 122.6, 114.0, 97.8, 68.0, 60.1, 36.9, 35.4, 31.1, 18.4, 14.7

HRMS (ESI) Calcd for $\text{C}_{19}\text{H}_{18}\text{Cl}_2\text{NaO}_5[\text{M}+\text{Na}^+]$ 419.0424, found 419.0425.

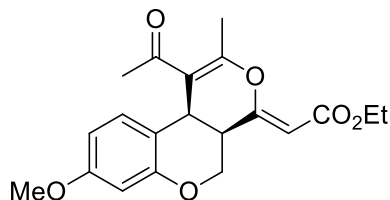


3e, 45.7mg, 47% yield, yellow oil.

^1H NMR (400 MHz, DMSO- d_6): δ 7.73 (s, 1H), 6.79 (s, 1H), 5.10 (s, 1H), 4.71 (dd, J = 10.0 Hz, J = 4.8 Hz, 1H), 4.39 (t, J = 10.8 Hz, 1H), 4.18 (d, J = 12.4 Hz, 1H), 4.10 (q, J = 7.2 Hz, 2H), 3.08-3.00 (m, 1H), 2.25 (s, 3H), 2.13 (s, 3H), 1.21 (t, J = 7.2 Hz, 3H)

^{13}C NMR (100 MHz, DMSO- d_6): δ 200.8, 163.7, 157.9, 155.4, 150.7, 133.7, 129.8, 127.5, 113.9, 112.3, 112.1, 97.8, 68.1, 60.1, 36.9, 35.5, 31.1, 18.4, 14.7.

HRMS (ESI) Calcd for $\text{C}_{19}\text{H}_{18}\text{Br}_2\text{NaO}_5[\text{M}+\text{Na}^+]$ 506.9413, found 506.9418.

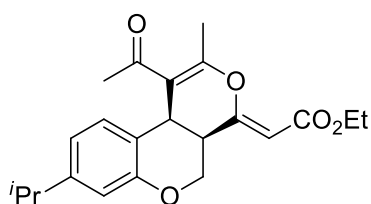


3f, 46.6 mg, 65% yield, yellow oil.

^1H NMR (400 MHz, CDCl_3): δ 6.80 (d, $J = 4.8$ Hz, 1H), 6.46 (d, $J = 2.8$ Hz, 1H), 6.43 (dd, $J = 8.4$ Hz, $J = 2.4$ Hz, 1H), 4.86 (d, $J = 2.0$ Hz, 1H), 4.54 (dd, $J = 10.0$ Hz, $J = 4.8$ Hz, 1H), 4.23-4.15 (m, 3H), 3.83 (d, $J = 11.6$ Hz, 1H), 3.75 (s, 3H), 2.89-2.81 (m, 1H), 2.24 (s, 3H), 2.21 (d, $J = 2.0$ Hz, 3H), 1.30 (t, $J = 7.2$ Hz, 3H).

^{13}C NMR (100 MHz, CDCl_3): δ 207.0, 201.2, 164.0, 160.0, 158.5, 155.0, 154.2, 126.1, 116.1, 115.1, 107.0, 102.9, 96.7, 66.5, 60.2, 55.3, 38.3, 35.3, 31.0, 30.9, 17.8, 14.2.

HRMS (ESI) Calcd for $\text{C}_{20}\text{H}_{23}\text{O}_6[\text{M}+\text{H}^+]$ 359.1489, found 359.1487.

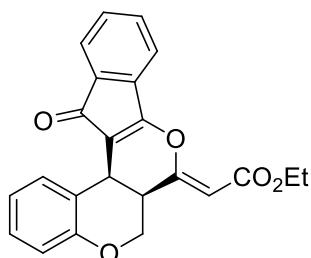


3g, 51.8 mg, 70% yield, yellow oil.

^1H NMR (400 MHz, CDCl_3): δ 6.82 (d, $J = 8.0$ Hz, 1H), 6.77 (d, $J = 2.0$ Hz, 1H), 6.72 (dd, $J = 8.0$ Hz, $J = 2.0$ Hz, 1H), 4.87 (d, $J = 2.0$ Hz, 1H), 4.54 (dd, $J = 10.0$ Hz, $J = 4.8$ Hz, 1H), 4.24-4.16 (m, 3H), 3.85 (d, $J = 12.0$ Hz, 1H), 2.89-2.79 (m, 2H), 2.25 (s, 3H), 2.22 (d, $J = 2.0$ Hz, 3H), 1.30 (t, $J = 7.2$ Hz, 3H), 1.21-1.18 (d, $J = 6.8$ Hz, 6H).

^{13}C NMR (100 MHz, CDCl_3): δ 201.1, 164.0, 158.5, 154.6, 153.9, 150.0, 125.2, 121.5, 119.2, 115.2, 114.7, 96.8, 66.4, 60.2, 38.2, 35.7, 33.6, 30.9, 30.9, 23.8, 17.8, 14.2

HRMS (ESI) Calcd for $\text{C}_{22}\text{H}_{27}\text{O}_5[\text{M}+\text{H}^+]$ 371.1853, found 371.1853.



3i, 39.7 mg, 53% yield, yellow oil.

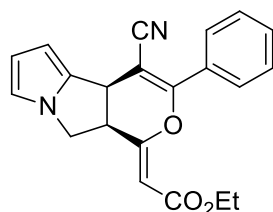
^1H NMR (400 MHz, DMSO- d_6): δ 7.55-7.42 (m, 3H), 7.25-7.21 (m, 2H), 7.13-7.08 (m, 1H), 6.88-6.83 (m, 1H), 6.79 (dd, $J = 8.4$ Hz, $J = 1.2$ Hz, 1H), 5.86 (d, $J = 1.6$ Hz, 1H), 4.70 (dd, $J = 12.4$ Hz, $J = 3.6$ Hz, 1H), 4.32 (dd, $J = 12.0$ Hz, $J = 2.8$ Hz, 1H), 4.28 (d, $J = 6.4$ Hz, 1H), 4.13 (q, $J = 6.8$ Hz, 2H), 1.24 (t, $J = 6.8$ Hz, 3H).

^{13}C NMR (100 MHz, DMSO- d_6): δ 192.6, 169.2, 163.6, 159.0, 152.9, 136.1, 133.7, 132.1, 131.5, 130.3, 128.8, 122.3, 121.8, 121.3, 118.9, 117.1, 111.4, 102.9, 64.3, 60.5, 33.3, 28.5, 14.6.

HRMS (ESI) Calcd for $\text{C}_{23}\text{H}_{19}\text{O}_5[\text{M}+\text{H}^+]$ 375.1227, found 375.1227.

4. General Procedure and the Date for Compounds 5

To a 10 mL Schlenk tube was added compound **4** (0.2 mmol), Cs₂CO₃ (78.2 mg, 0.24 mmol), DMAP (4.5 mg, 0.04 mmol), and chloroform (1.5 mL) with stirring. To the mixture, the solution of allenolate **1a** (47.8 mg, 0.26 mmol) in chloroform (1.5 mL) was slowly added over half an hour. After completion of the reaction (monitored by TLC), the solvent was removed and the residue was directly subjected to silica gel column chromatography (petroleum ether/ethyl acetate as eluent) to give the product **5**.

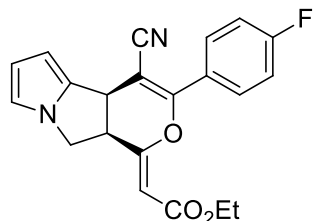


5a, 56.8 mg, 82% yield, yellow foam.

¹H NMR (400 MHz, CDCl₃): δ 8.08-8.04 (m, 2H), 7.51-7.43 (m, 3H), 6.65 (dd, *J* = 2.8 Hz, *J* = 1.2 Hz, 1H), 6.30-6.25 (m, 2H), 5.48 (s, 1H), 4.29-4.20 (m, 3H), 4.14-4.03 (m, 2H), 3.97-3.89 (m, 1H), 1.34 (t, *J* = 7.2 Hz, 3H).

¹³C NMR (100 MHz, CDCl₃): δ 163.4, 159.2, 133.6, 131.5, 130.5, 128.5, 128.4, 117.8, 114.9, 113.3, 102.9, 102.5, 87.1, 60.5, 48.9, 44.7, 36.1, 14.2.

HRMS (ESI) Calcd for C₂₁H₁₉N₂O₃[M+H⁺] 347.1390, found 347.1391.

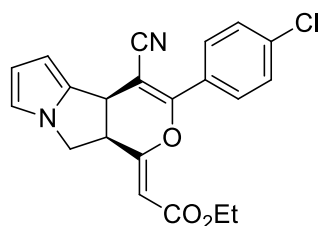


5b, 52.5 mg, 72% yield, yellow solid, M.p: 123-126 °C.

¹H NMR (400 MHz, CDCl₃): δ 8.13-8.08 (m, 2H), 7.18-7.11 (m, 2H), 6.65 (dd, *J* = 2.8 Hz, *J* = 1.2 Hz, 1H), 6.30-6.24 (m, 2H), 5.50 (s, 1H), 4.28-4.21 (m, 3H), 4.14-4.03 (m, 2H), 3.97-3.90 (m, 1H), 1.33 (t, *J* = 7.2 Hz, 3H).

¹³C NMR (100 MHz, CDCl₃): δ 165.6, 163.2 (d, *J* = 68.4 Hz), 158.1, 156.2, 133.5, 130.8 (d, *J* = 8.9 Hz), 126.6 (d, *J* = 12.4 Hz), 117.7, 115.7 (d, *J* = 21.9 Hz), 114.9, 113.3, 103.0, 102.4, 87.0, 60.5, 48.9, 44.6, 36.1, 14.2.

HRMS (ESI) Calcd for C₂₁H₁₈N₂O₃[M+H⁺] 365.1296, found 365.1291.

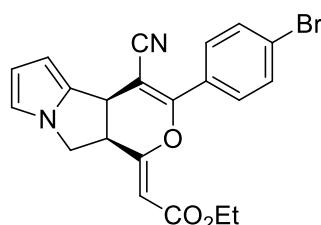


5c, 70.0 mg, 80% yield, yellow foam.

^1H NMR (400 MHz, DMSO- d_6): δ 7.96 (d, J = 8.4 Hz, 2H), 7.64 (d, J = 8.4 Hz, 2H), 6.75 (s, 1H), 6.12 (s, 1H), 5.99 (d, J = 2.8 Hz, 1H), 5.74 (s, 1H), 4.30-4.05 (m, 6H), 1.22 (t, J = 7.2 Hz, 3H).

^{13}C NMR (100 MHz, DMSO- d_6): δ 163.7, 157.7, 157.4, 136.8, 134.0, 130.4, 130.1, 129.3, 118.3, 115.8, 112.6, 102.6, 101.8, 88.5, 60.4, 48.9, 43.4, 35.5, 14.7.

HRMS (ESI) Calcd for $\text{C}_{21}\text{H}_{18}\text{ClN}_2\text{O}_3[\text{M}+\text{H}^+]$ 381.1000, found 381.1003.

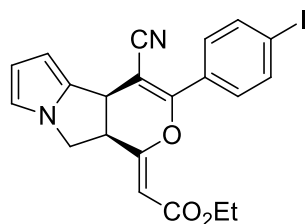


5d, 71.5 mg, 84% yield, brown solid, M.p: 144-147 °C.

^1H NMR (400 MHz, DMSO- d_6): δ 7.91-7.86 (m, 2H), 7.79-7.75 (m, 2H), 6.75 (dd, J = 2.4 Hz, J = 1.2 Hz, 1H), 6.12 (t, J = 2.8 Hz, 1H), 5.99 (dd, J = 3.2 Hz, J = 1.2 Hz, 1H), 5.73 (s, 1H), 4.28-4.05 (m, 6H), 1.22 (t, J = 7.2 Hz, 3H).

^{13}C NMR (100 MHz, DMSO- d_6): δ 163.6, 157.8, 157.3, 133.9, 132.2, 130.5, 130.4, 125.7, 118.3, 115.7, 112.6, 101.8, 88.5, 60.4, 48.9, 43.4, 35.5, 14.6.

HRMS (ESI) Calcd for $\text{C}_{21}\text{H}_{18}\text{BrN}_2\text{O}_3[\text{M}+\text{H}^+]$ 425.0495, found 425.0497.

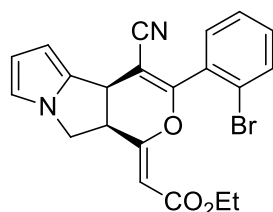


5e, 62.4 mg, 66% yield, yellow solid, M.p: 162-167 °C.

^1H NMR (400 MHz, DMSO- d_6): δ 7.95-7.91 (m, 2H), 7.73-7.69 (m, 2H), 6.74 (dd, J = 2.8 Hz, J = 1.2 Hz, 1H), 6.11 (t, J = 3.2 Hz, 1H), 5.99 (dd, J = 3.2 Hz, J = 1.2 Hz, 1H), 5.72 (s, 1H), 4.30-4.23 (m, 1H), 4.22-4.11 (m, 4H), 4.08-4.03 (m, 1H), 1.22 (t, J = 7.2 Hz, 3H).

^{13}C NMR (100 MHz, DMSO- d_6): δ 163.6, 158.1, 157.3, 138.0, 133.9, 130.7, 130.3, 118.3, 115.7, 112.6, 102.6, 101.8, 99.7, 88.4, 60.4, 48.9, 43.4, 35.5, 14.7.

HRMS (ESI) Calcd for $C_{21}H_{17}IN_2NaO_3[M+Na^+]$ 495.0176, found 495.0179.

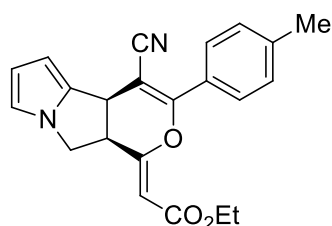


5f, 46.8 mg, 55% yield, brown solid, M.p: 155-157 °C.

1H NMR (400 MHz, DMSO- d_6): δ 7.96-7.93 (m, 2H), 7.56-7.53 (m, 2H), 6.75 (d, J = 1.2 Hz, 1H), 6.12 (t, J = 2.8 Hz, 1H), 5.99 (d, J = 2.8 Hz, 1H), 5.73 (s, 1H), 4.31-4.12 (m, 5H), 4.09-4.01 (m, 1H), 1.22 (t, J = 7.2 Hz, 3H).

^{13}C NMR (100 MHz, DMSO- d_6): δ 163.9, 158.9, 157.5, 134.2, 132.1, 131.2, 129.1, 128.6, 118.6, 115.7, 112.6, 102.5, 101.8, 88.0, 60.4, 48.9, 43.5, 35.5, 14.7.

HRMS (ESI) Calcd for $C_{21}H_{18}BrN_2O_3[M+H^+]$ 425.0495, found 425.0496.

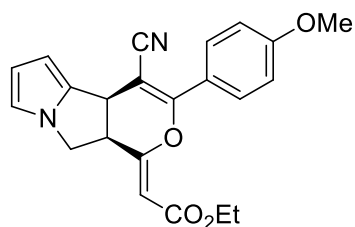


5g, 46.2 mg, 64% yield, yellow oil.

1H NMR (400 MHz, DMSO- d_6): δ 7.85 (d, J = 8.0 Hz, 2H), 7.34 (d, J = 8.0 Hz, 2H), 6.74 (s, 1H), 6.11 (t, J = 3.2 Hz, 1H), 5.99 (d, J = 3.2 Hz, 1H), 5.72 (s, 1H), 4.30-4.23 (m, 1H), 4.22-4.12 (m, 4H), 4.06-4.00 (m, 1H), 2.36 (s, 3H), 1.22 (t, J = 7.2 Hz, 3H).

^{13}C NMR (100 MHz, DMSO- d_6): δ 163.7, 158.9, 157.5, 142.3, 134.3, 129.6, 128.5, 128.4, 118.7, 115.7, 112.6, 102.5, 101.7, 87.2, 60.4, 49.0, 43.6, 35.6, 21.6, 14.7.

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

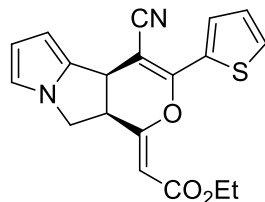


5h, 50.5 mg, 67% yield, yellow oil.

1H NMR (400 MHz, DMSO- d_6): δ 7.97-7.92 (m, 2H), 7.11-7.06 (m, 2H), 6.73 (dd, J = 2.4 Hz, J = 1.2 Hz, 1H), 6.12 (t, J = 3.2 Hz, 1H), 5.98 (dd, J = 3.6 Hz, J = 0.8 Hz, 1H), 5.71 (s, 1H), 4.30-4.24 (m, 1H), 4.21-4.12 (m, 4H), 4.05-4.00 (m, 1H), 3.82 (s, 3H), 1.23 (t, J = 7.2 Hz, 3H).

^{13}C NMR (100 MHz, DMSO- d_6): δ 163.7, 162.2, 158.6, 157.7, 134.4, 130.3, 123.2, 118.9, 115.6, 114.5, 112.6, 102.3, 101.6, 85.9, 60.3, 56.0, 48.9, 43.6, 35.6, 14.7.

HRMS (ESI) Calcd for $\text{C}_{22}\text{H}_{21}\text{N}_2\text{O}_4[\text{M}+\text{H}^+]$ 377.1496, found 377.1493.

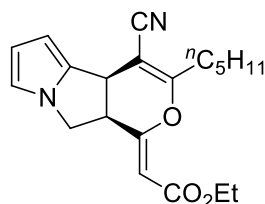


5i, 48.0 mg, 68% yield, yellow oil.

^1H NMR (500 MHz, DMSO- d_6): δ 7.98 (d, J = 2.8 Hz, 1H), 7.90 (d, J = 3.6 Hz, 1H), 7.25 (t, J = 3.6 Hz, 1H), 6.73 (s, 1H), 6.11 (t, J = 2.0 Hz, 1H), 5.99 (d, J = 2.0 Hz, 1H), 5.70 (s, 1H), 4.30-4.15 (m, 5H), 4.02 (t, J = 7.6 Hz, 1H), 1.25 (t, J = 5.6 Hz, 3H).

^{13}C NMR (125 MHz, DMSO- d_6): δ 163.5, 156.8, 153.0, 134.1, 133.1, 132.1, 131.3, 128.4, 118.4, 115.6, 112.6, 102.6, 101.7, 84.8, 60.3, 49.0, 43.1, 35.1, 14.7.

HRMS (ESI) Calcd for $\text{C}_{19}\text{H}_{17}\text{N}_2\text{O}_3\text{S}[\text{M}+\text{H}^+]$ 353.0954, found 353.0954.

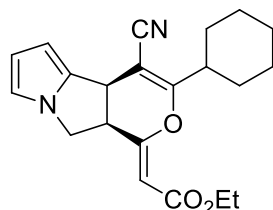


5j, 53.1 mg, 78% yield, yellow oil.

^1H NMR (400 MHz, DMSO- d_6): δ 6.72 (d, J = 0.8 Hz, 1H), 6.09 (t, J = 2.8 Hz, 1H), 5.92 (d, J = 2.8 Hz, 1H), 5.60 (s, 1H), 4.26-4.20 (m, 1H), 4.14-4.01 (m, 4H), 3.90 (t, 10.0 Hz, 1H), 2.47 (t, J = 6.8 Hz, 2H), 1.70-1.62 (m, 2H), 1.34-1.26 (m, 4H), 1.22 (t, J = 7.2 Hz, 3H), 0.87 (t, J = 6.8 Hz, 3H).

^{13}C NMR (100 MHz, DMSO- d_6): δ 163.8, 163.5, 157.0, 134.4, 117.8, 115.5, 112.5, 102.2, 101.5, 88.3, 60.2, 48.9, 43.3, 34.0, 32.8, 30.8, 25.7, 22.2, 14.6, 14.3.

HRMS (ESI) Calcd for $\text{C}_{20}\text{H}_{25}\text{N}_2\text{O}_3[\text{M}+\text{H}^+]$ 341.1860, found 341.1861.



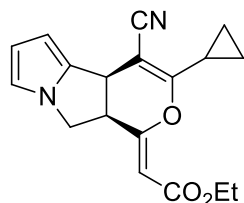
5k, 49.4 mg, 70% yield, white solid, M.p: 157-158 °C.

^1H NMR (400 MHz, DMSO- d_6): δ 6.71 (dd, J = 2.4 Hz, J = 0.8 Hz, 1H), 6.07 (t, J =

2.8 Hz, 1H), 5.90 (d, $J = 2.8$ Hz, 1H), 5.57 (s, 1H), 4.22 (dd, $J = 10.4$ Hz, $J = 8.0$ Hz, 1H), 4.16-3.98 (m, 4H), 3.82 (t, $J = 10.0$ Hz, 1H), 2.62-2.54 (m, 1H), 1.80-1.64 (m, 6H), 1.59-1.48 (m, 1H), 1.34-1.21 (m, 5H), 1.78-1.10 (m, 1H).

^{13}C NMR (100 MHz, DMSO- d_6): δ 166.9, 163.6, 157.0, 134.3, 117.6, 115.5, 112.4, 102.2, 101.5, 86.3, 60.3, 48.9, 43.3, 42.6, 33.9, 29.7, 29.1, 25.7, 25.6, 25.6, 14.8.

HRMS (ESI) Calcd for $\text{C}_{21}\text{H}_{25}\text{N}_2\text{O}_3[\text{M}+\text{H}^+]$ 353.1860, found 353.1861.

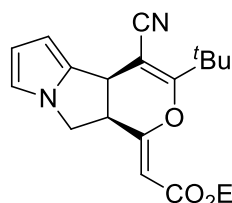


5l, 37.3 mg, 60% yield, yellow oil.

^1H NMR (400 MHz, DMSO- d_6): δ 6.70 (s, 1H), 6.09 (t, $J = 2.8$ Hz, 1H), 5.90 (d, $J = 2.8$ Hz, 1H), 5.57 (s, 1H), 4.23-4.17 (m, 1H), 4.13-3.99 (m, 4H), 3.86 (t, $J = 10.0$ Hz, 1H), 2.00-1.93 (m, 1H), 1.31-1.27 (m, 1H), 1.21 (t, $J = 7.2$ Hz, 3H), 1.06-1.02 (m, 1H), 0.96-0.88 (m, 2H).

^{13}C NMR (100 MHz, DMSO- d_6): δ 163.5, 163.5, 157.0, 134.7, 118.4, 115.4, 112.6, 102.2, 101.4, 86.1, 60.3, 49.0, 43.3, 34.2, 14.6, 13.6, 7.3, 7.3.

HRMS (ESI) Calcd for $\text{C}_{18}\text{H}_{19}\text{N}_2\text{O}_3[\text{M}+\text{H}^+]$ 311.1390, found 311.1396.

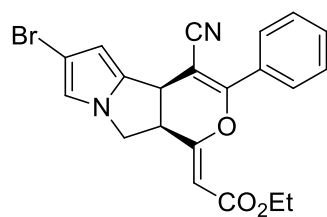


5m, 50.9 mg, 78% yield, yellow oil.

^1H NMR (400 MHz, DMSO- d_6): δ 6.72 (dd, $J = 2.8$ Hz, $J = 1.2$ Hz, 1H), 6.07 (t, $J = 3.2$ Hz, 1H), 5.93 (d, $J = 3.6$ Hz, 1H), 5.57 (s, 1H), 4.22 (dd, $J = 10.8$ Hz, $J = 8.0$ Hz, 1H), 4.11 (q, $J = 7.2$ Hz, 2H), 4.06-3.99 (m, 2H), 3.86 (t, $J = 10.0$ Hz, 1H), 1.32 (s, 9H), 1.21 (t, $J = 7.2$ Hz, 3H).

^{13}C NMR (100 MHz, DMSO- d_6): δ 169.0, 163.6, 157.1, 134.5, 118.0, 115.5, 112.3, 101.9, 85.4, 60.2, 48.9, 43.2, 38.5, 35.7, 28.6, 14.7.

HRMS (ESI) Calcd for $\text{C}_{19}\text{H}_{23}\text{N}_2\text{O}_3[\text{M}+\text{H}^+]$ 327.1703, found 327.1703.

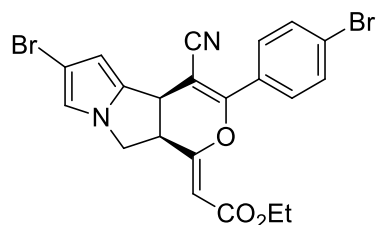


5n, 57.9 mg, 68% yield, yellow solid, M.p: 129-133 °C.

^1H NMR (400 MHz, DMSO- d_6): δ 7.95 (d, J = 6.8 Hz, 2H), 7.58-7.51 (m, 3H), 6.96 (d, J = 0.8 Hz, 1H), 6.08 (s, 1H), 5.74 (s, 1H), 4.34-4.26 (m, 2H), 4.20-4.07 (m, 4H), 1.22 (t, J = 6.8 Hz, 3H)

^{13}C NMR (100 MHz, DMSO- d_6): δ 163.6, 159.3, 156.9, 134.8, 132.2, 131.1, 129.1, 128.7, 118.4, 116.1, 104.3, 102.9, 97.1, 87.2, 60.4, 49.9, 42.6, 36.1, 14.7.

HRMS (ESI) Calcd for $\text{C}_{21}\text{H}_{18}\text{BrN}_2\text{O}_3[\text{M}+\text{H}^+]$ 425.0495, found 425.0493.

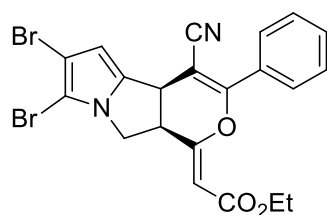


5o, 63.5 mg, 63% yield, yellow solid, M.p: 167-171 °C.

^1H NMR (400 MHz, DMSO- d_6): δ 7.88 (d, J = 8.4 Hz, 2H), 7.78 (d, J = 8.4 Hz, 2H), 6.96 (d, J = 1.2 Hz, 1H), 6.08 (s, 1H), 5.74 (s, 1H), 4.32-4.25 (m, 2H), 4.21-4.08 (m, 4H), 1.22 (t, J = 7.2 Hz, 3H)

^{13}C NMR (100 MHz, DMSO- d_6): δ 163.6, 158.3, 156.8, 134.6, 132.2, 130.6, 130.3, 125.8, 118.2, 116.1, 104.3, 103.0, 97.1, 87.7, 60.4, 49.9, 42.5, 36.1, 14.7.

HRMS (ESI) Calcd for $\text{C}_{21}\text{H}_{16}\text{Br}_2\text{N}_2\text{NaO}_3[\text{M}+\text{Na}^+]$ 524.9420, found 524.9426.

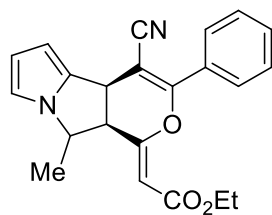


5p, 39.4 mg, 39% yield, brown foam.

^1H NMR (400 MHz, DMSO- d_6): δ 7.95 (d, J = 6.8 Hz, 2H), 7.58-7.52 (m, 3H), 6.24 (s, 1H), 5.71 (s, 1H), 4.37 (d, J = 7.2 Hz, 1H), 4.31-4.12 (m, 5H), 1.22 (t, J = 7.2 Hz, 3H)

^{13}C NMR (100 MHz, DMSO- d_6): δ 163.5, 159.6, 156.4, 135.4, 132.2, 131.2, 129.1, 128.7, 118.3, 105.7, 103.2, 99.3, 97.8, 86.8, 60.5, 50.1, 41.9, 37.0, 14.7.

HRMS (ESI) Calcd for $\text{C}_{21}\text{H}_{17}\text{Br}_2\text{N}_2\text{O}_3[\text{M}+\text{H}^+]$ 502.9600, found 502.9603.



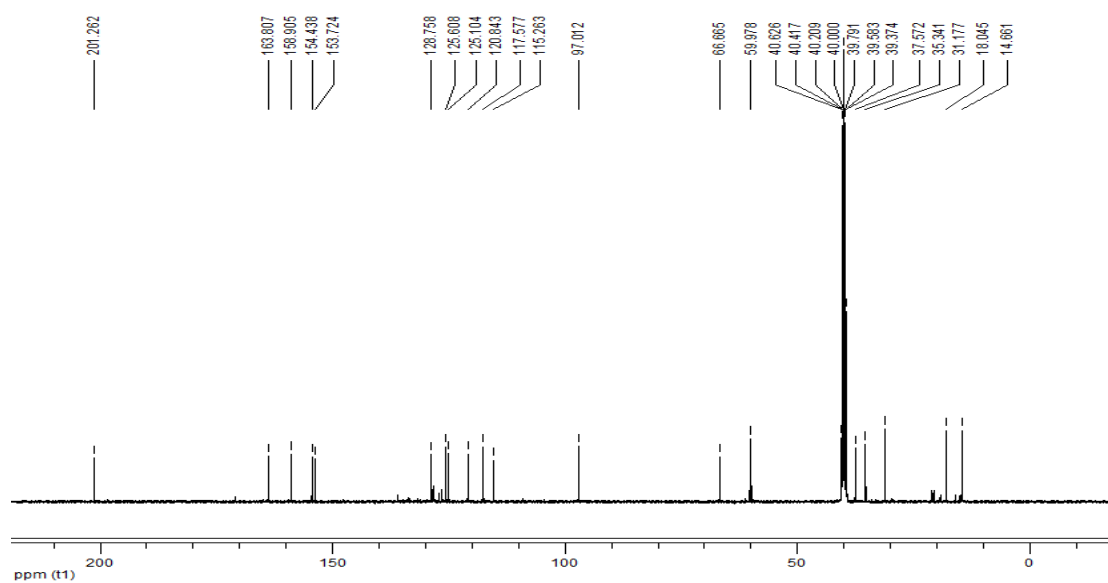
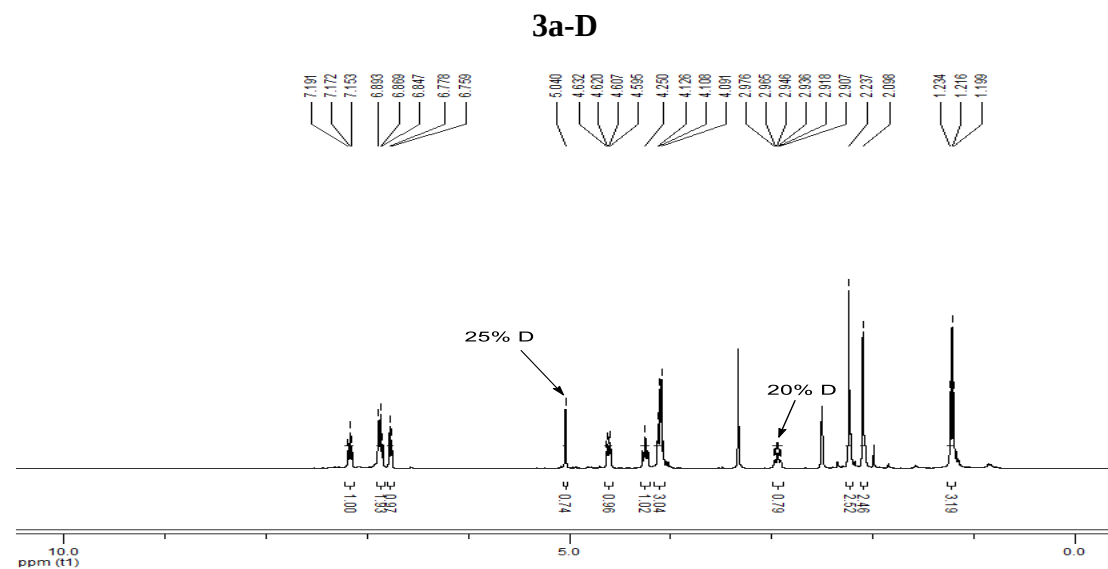
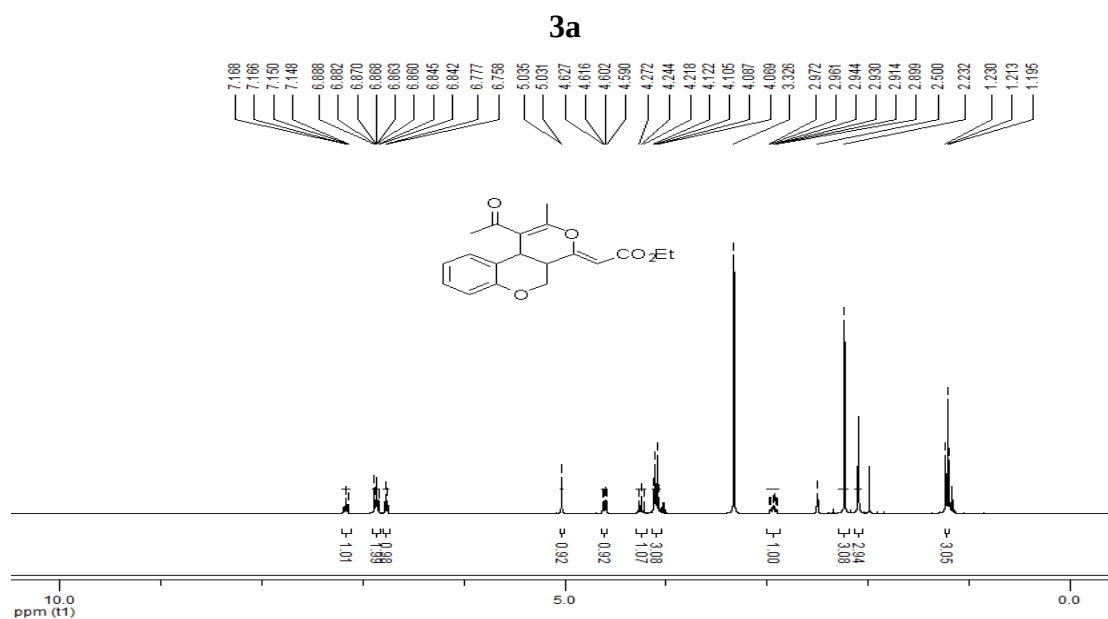
5ba, 41.8 mg, 58% yield, yellow oil.

^1H NMR (400 MHz, DMSO-d_6): δ 8.01-7.97 (m, 0.64 H), 7.95-7.91 (m, 2H), 7.60-7.50 (m, 4.38 H), 6.90-6.88 (m, 0.35H), 6.80-6.78 (m, 1H), 6.16-6.12 (m, 1.33H), 6.04-5.99 (m, 1.31 H), 5.68 (s, 1H), 5.32 (s, 0.33 H), 4.38-4.11 (m, 5.69 H), 3.67 (dd, $J = 9.2$ Hz, $J = 8.0$ Hz, 1H), 1.60 (dd, $J = 6.0$ Hz, 1H), 1.50 (d, $J = 6.0$ Hz, 3H), 1.24 (t, $J = 7.2$ Hz, 4H).

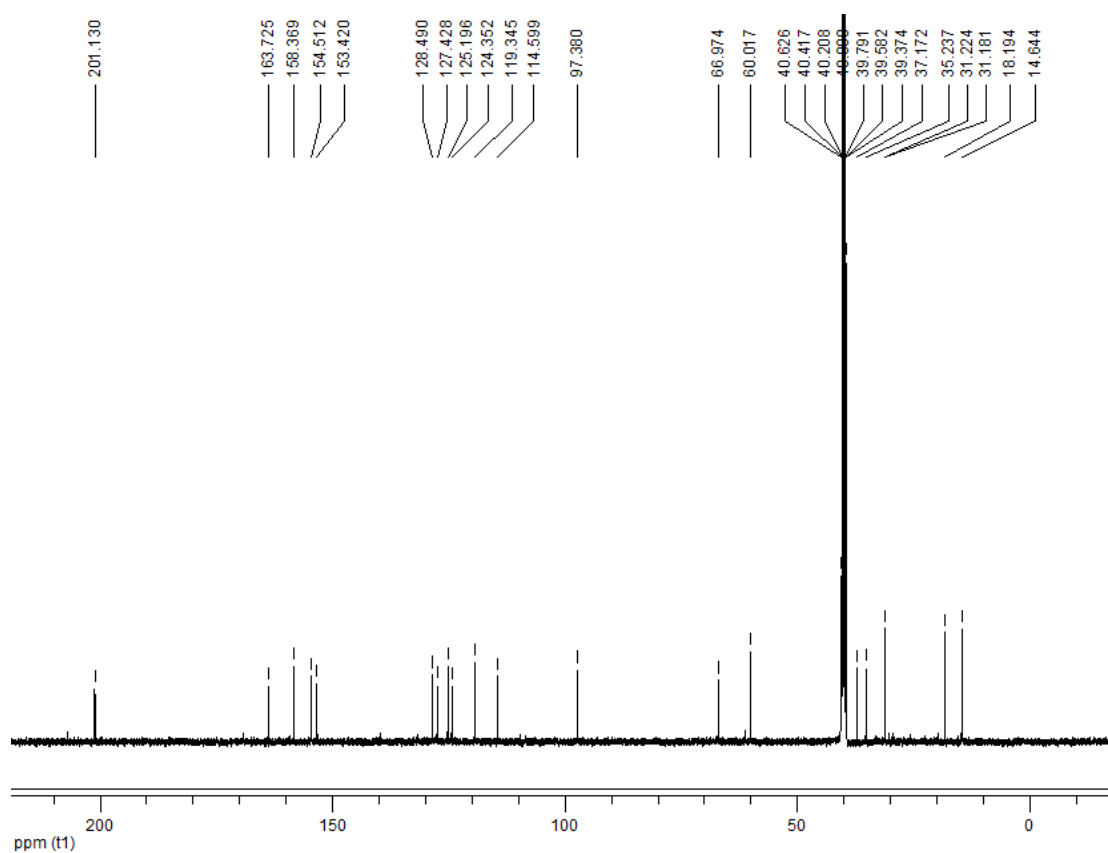
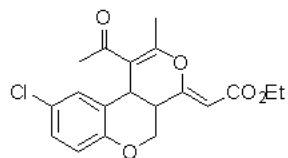
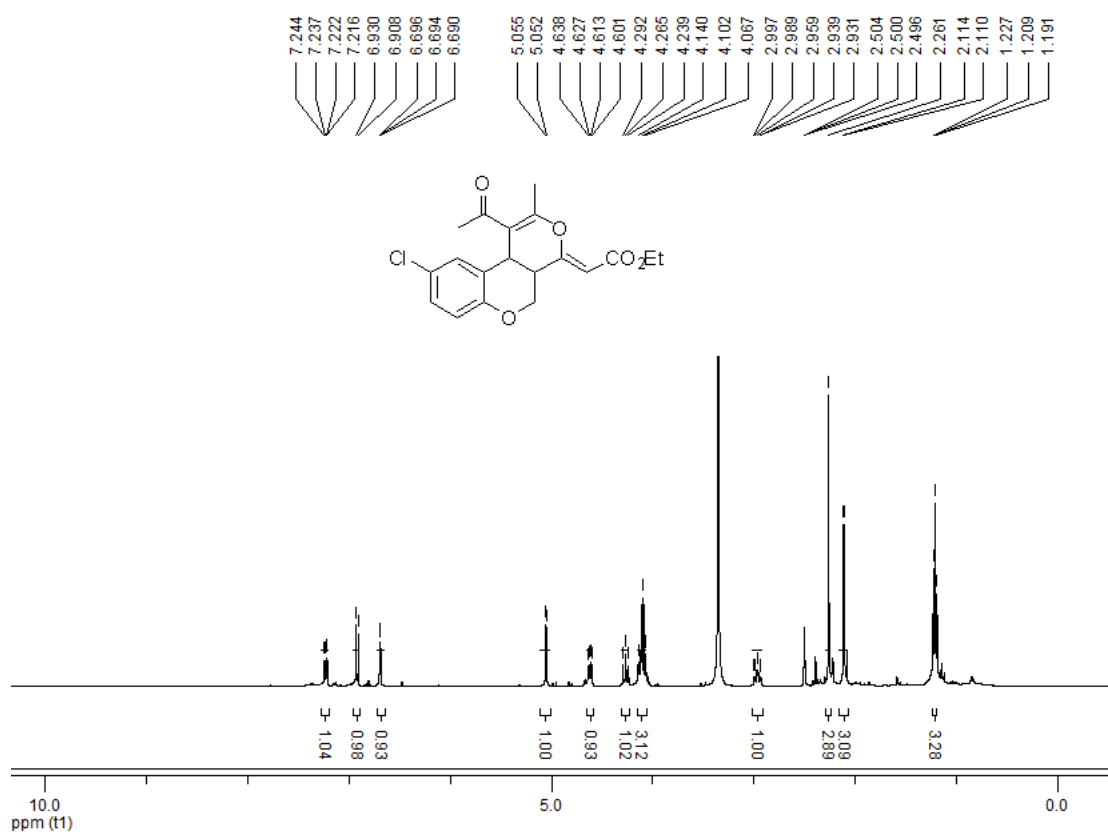
^{13}C NMR (100 MHz, DMSO-d_6): δ 163.6, 163.5, 160.9, 160.0, 158.8, 156.8, 132.6, 132.1, 132.0, 131.2, 131.1, 130.3, 129.2, 129.0, 128.5, 128.1, 118.4, 114.5, 114.1, 112.5, 111.2, 102.9, 101.8, 100.4, 96.1, 89.6, 88.2, 60.4, 60.3, 55.9, 53.9, 53.8, 51.4, 37.2, 35.4, 18.0, 17.7, 14.7, 14.6.

HRMS (ESI) Calcd for $\text{C}_{22}\text{H}_{21}\text{N}_2\text{O}_3[\text{M}+\text{H}^+]$ 361.1547, found 361.1548.

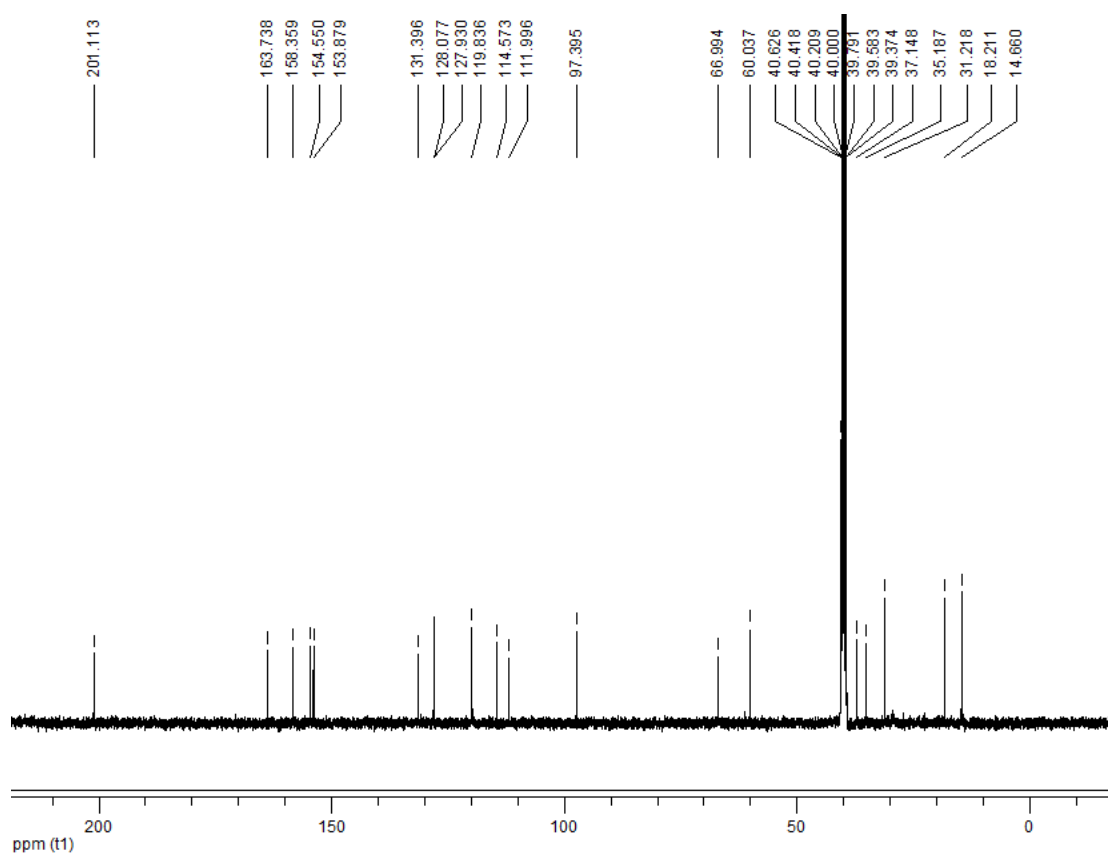
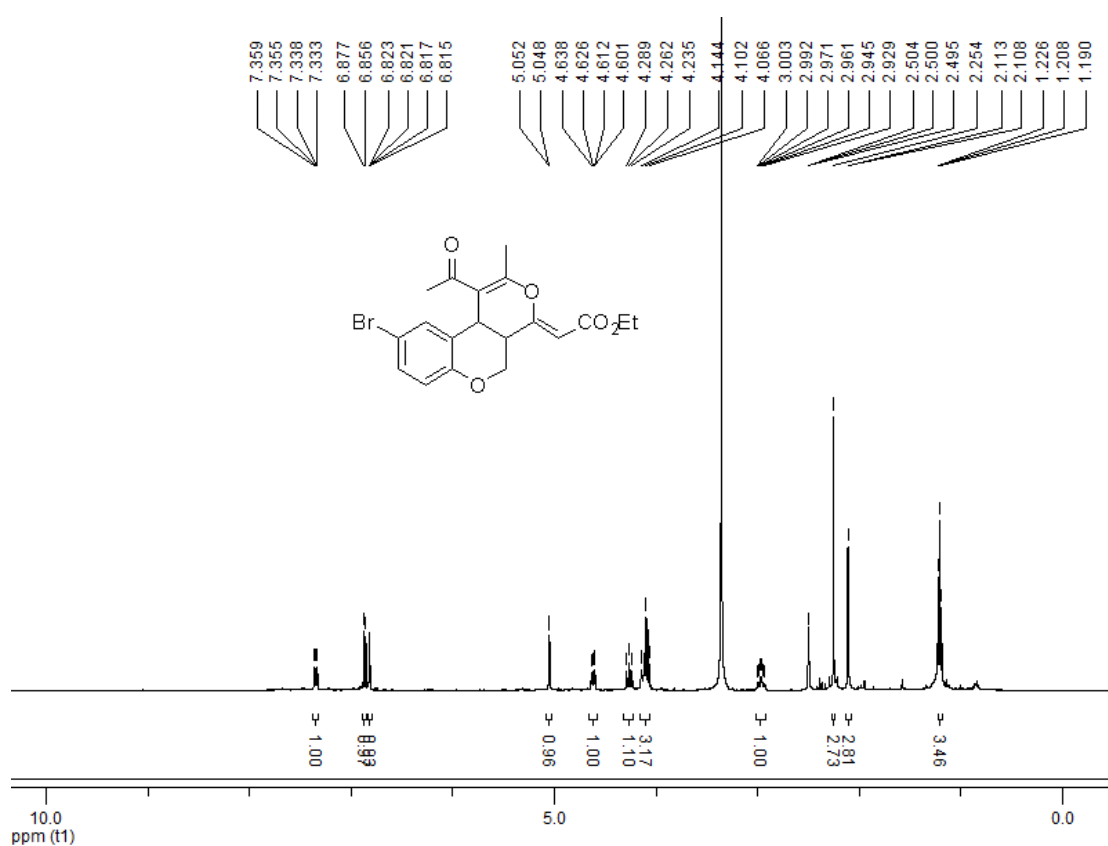
5. NMR Spectra



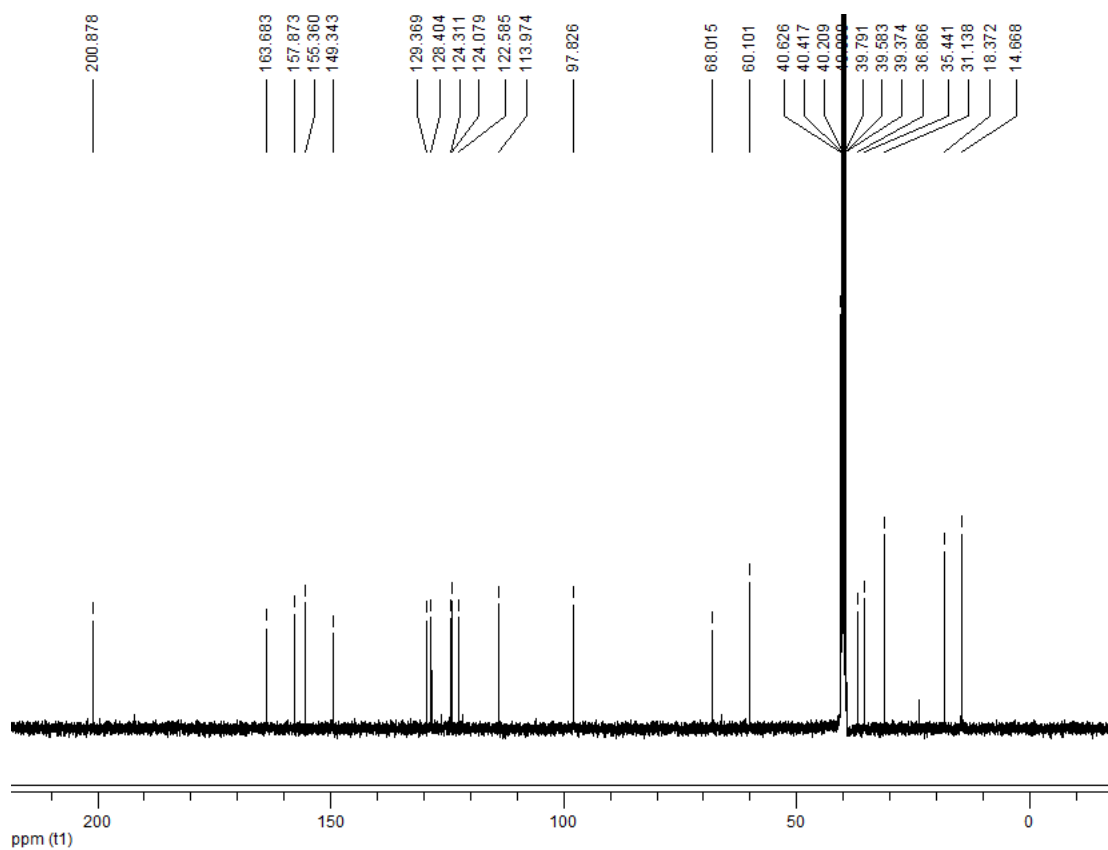
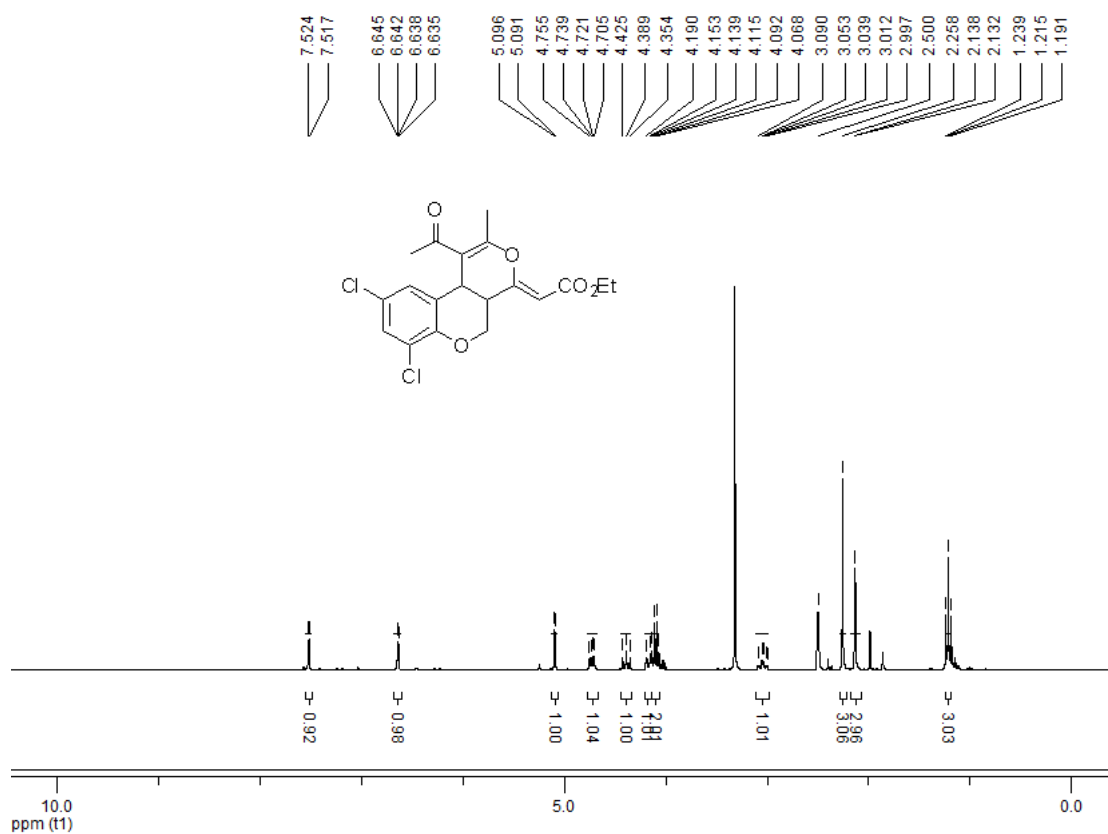
3b



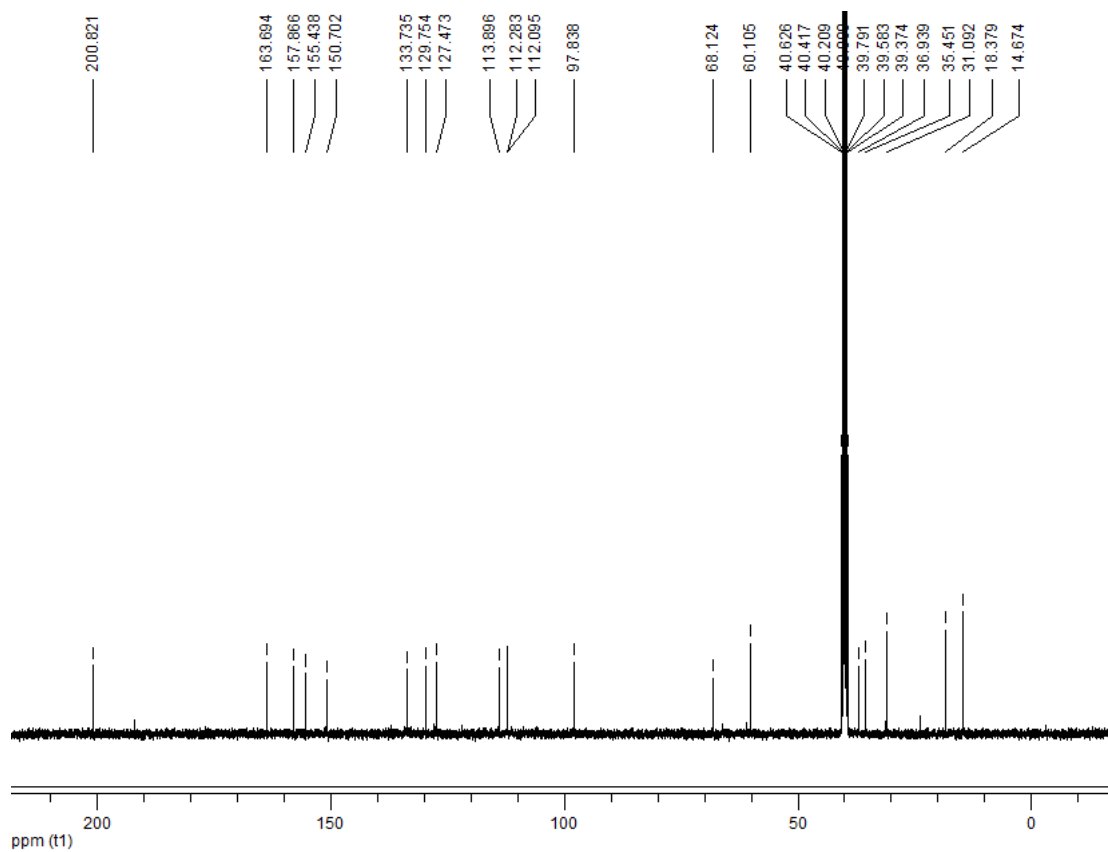
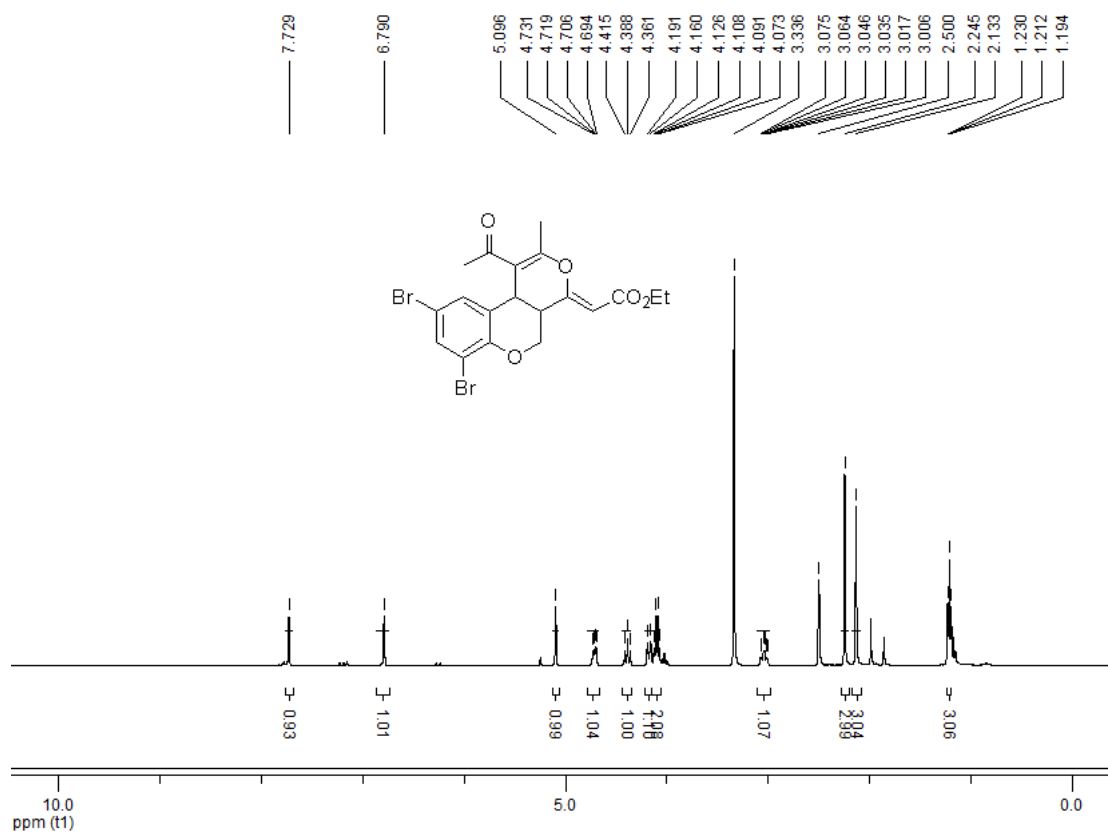
3c



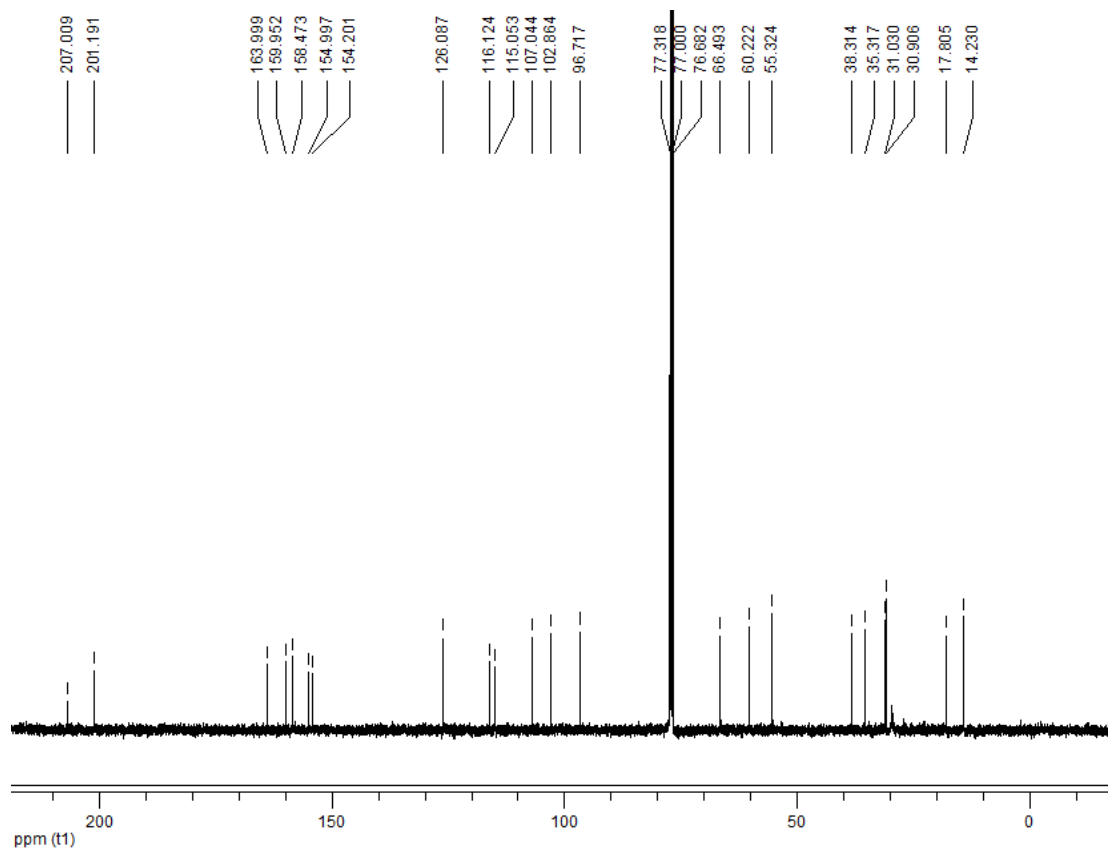
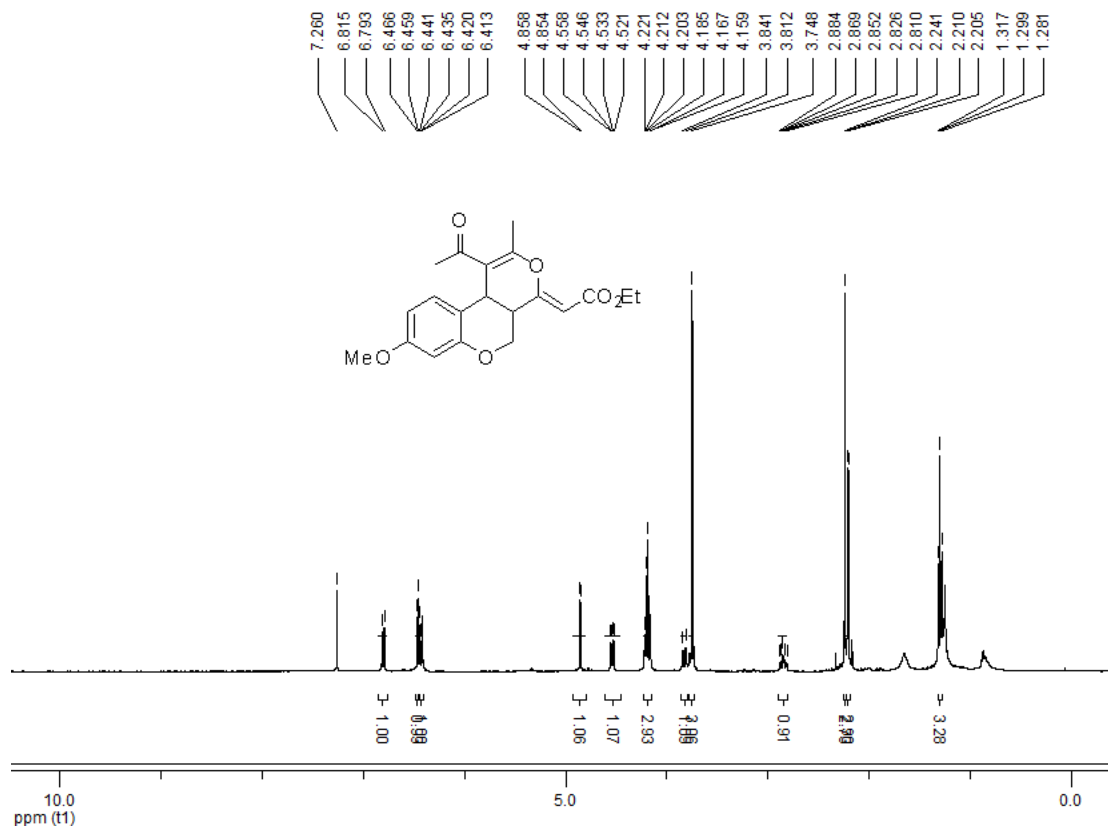
3d

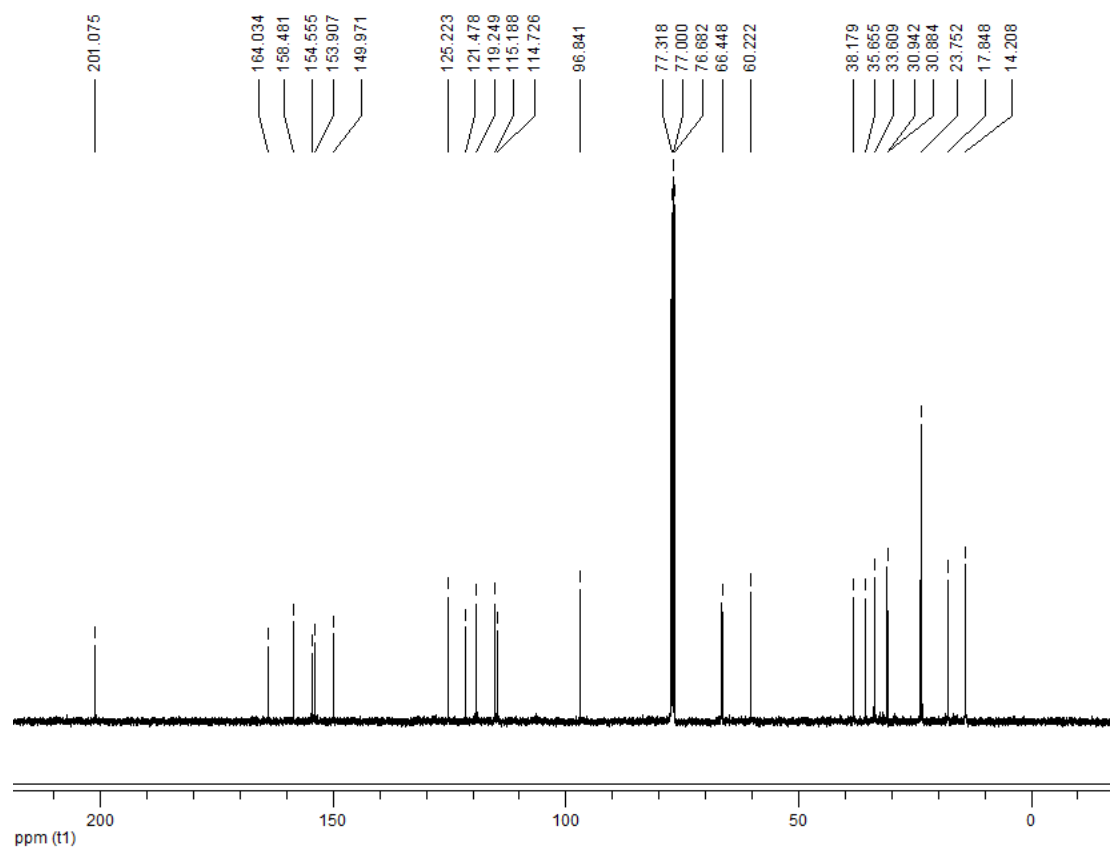
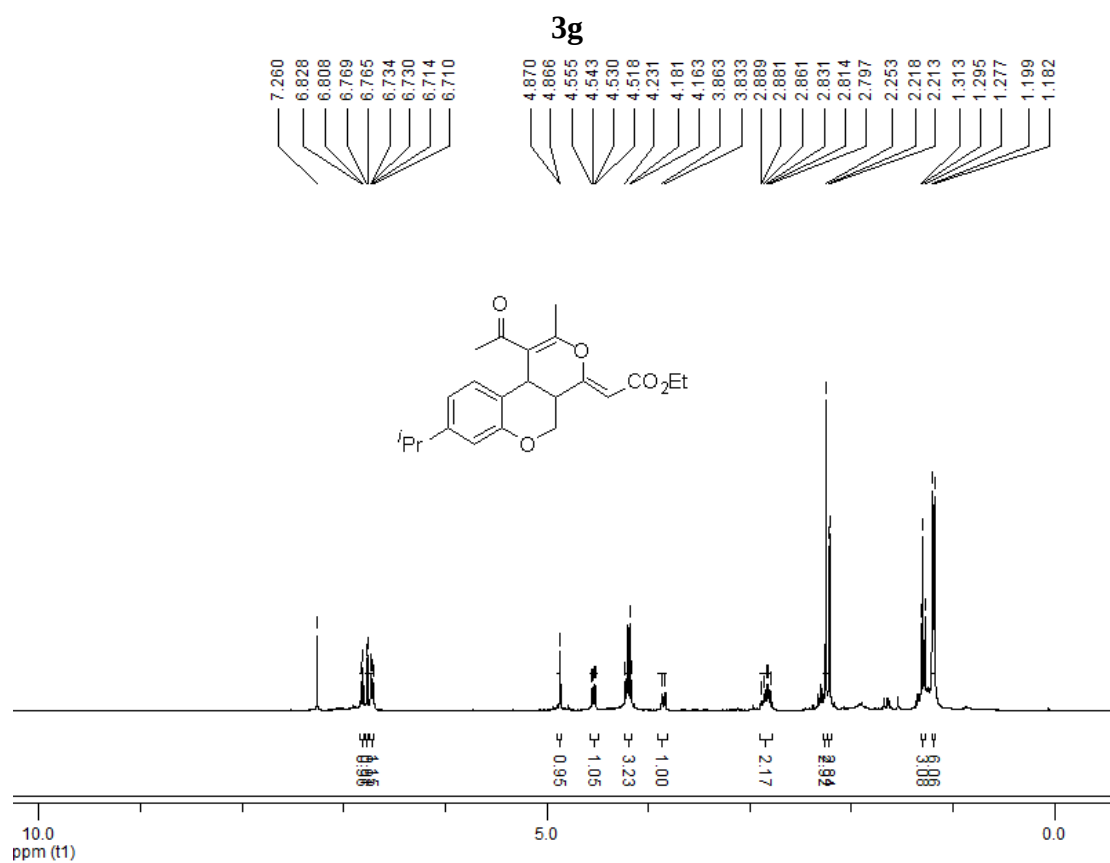


3e

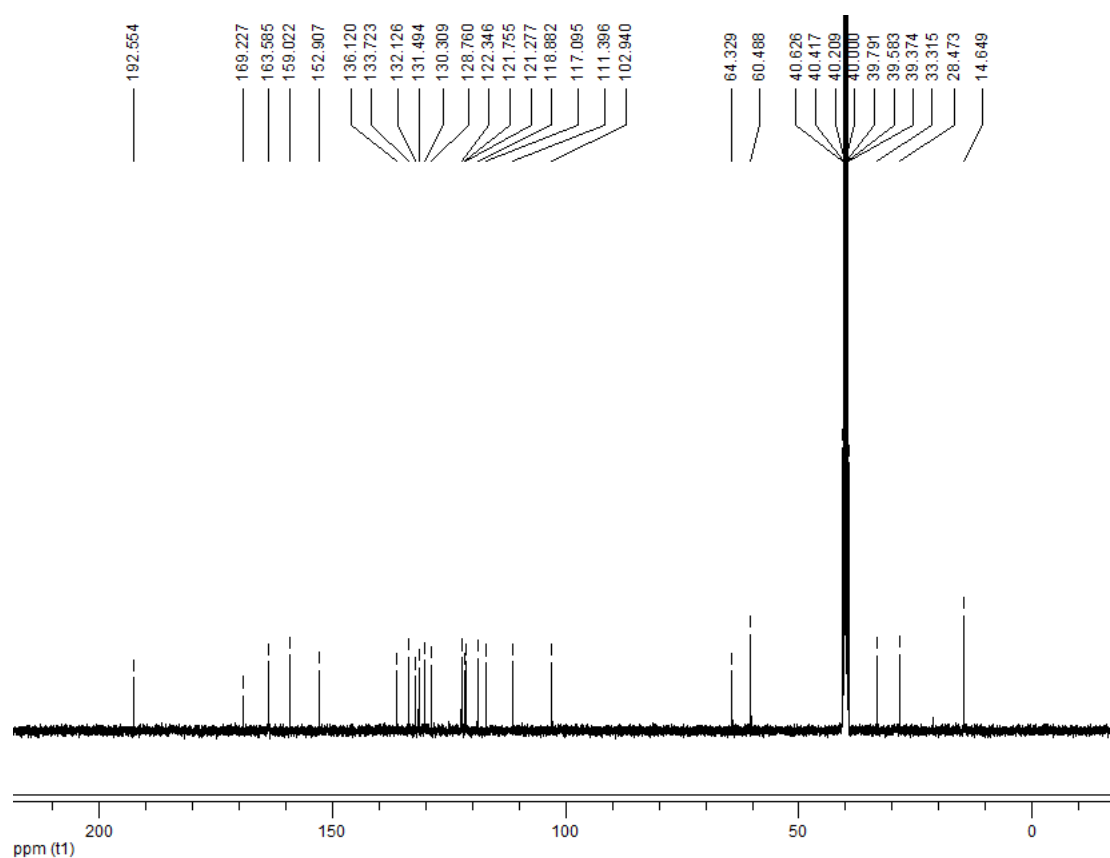
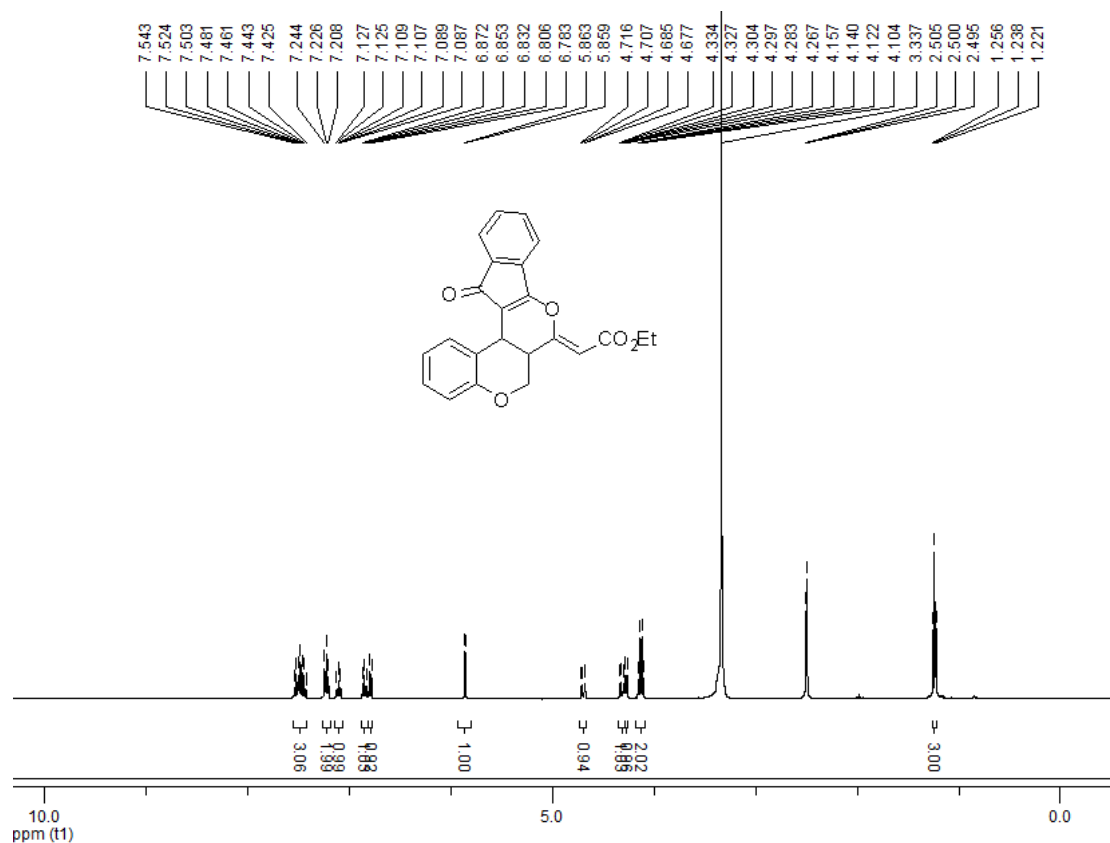


3f



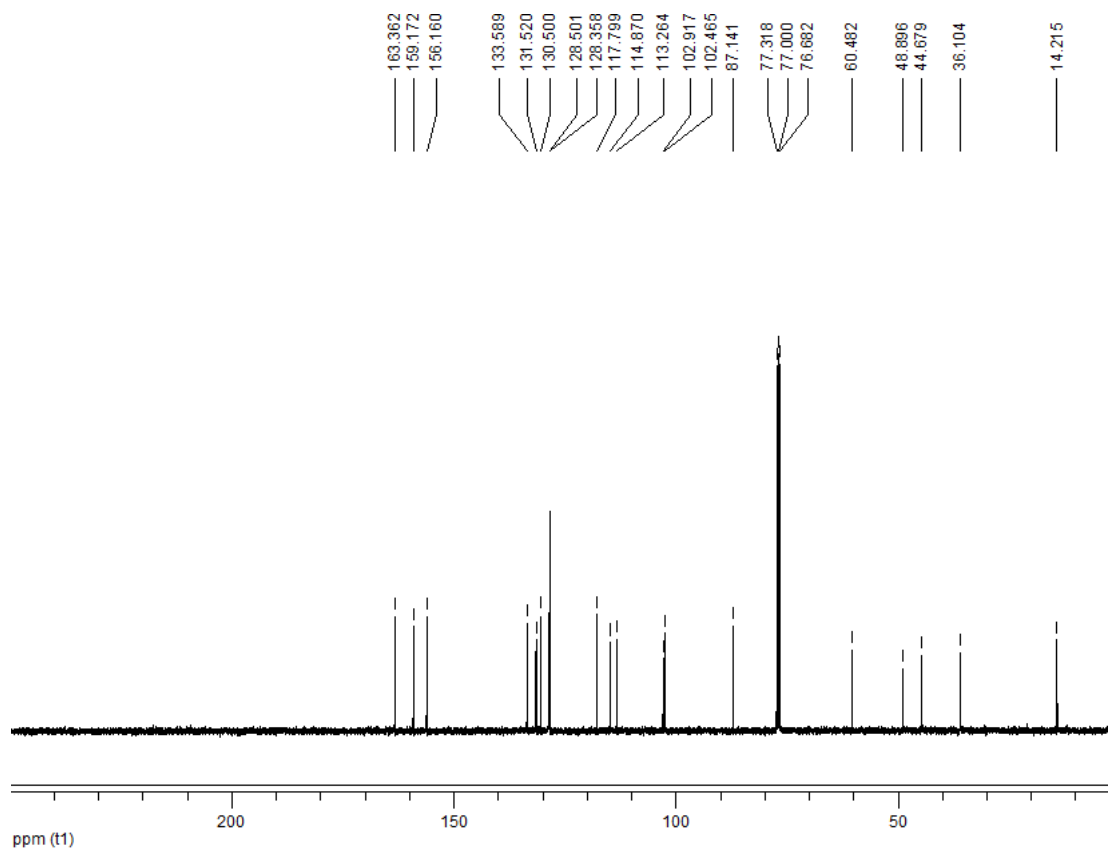
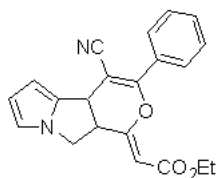
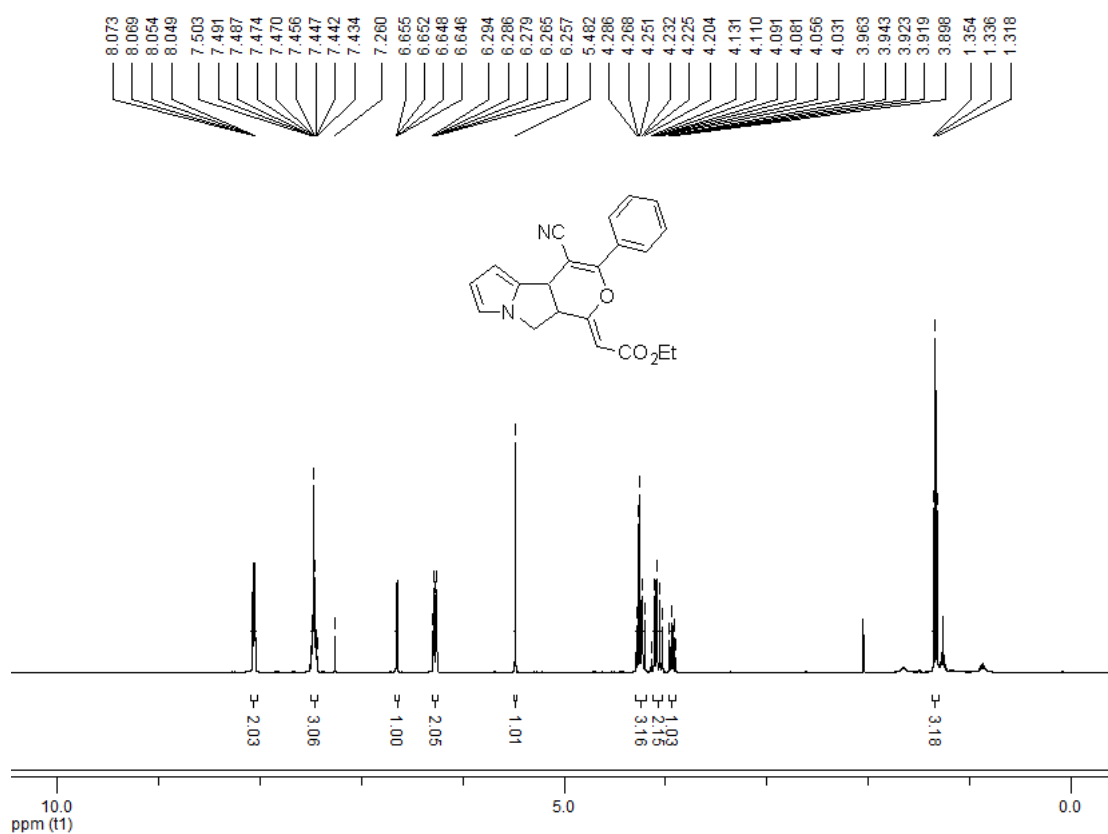


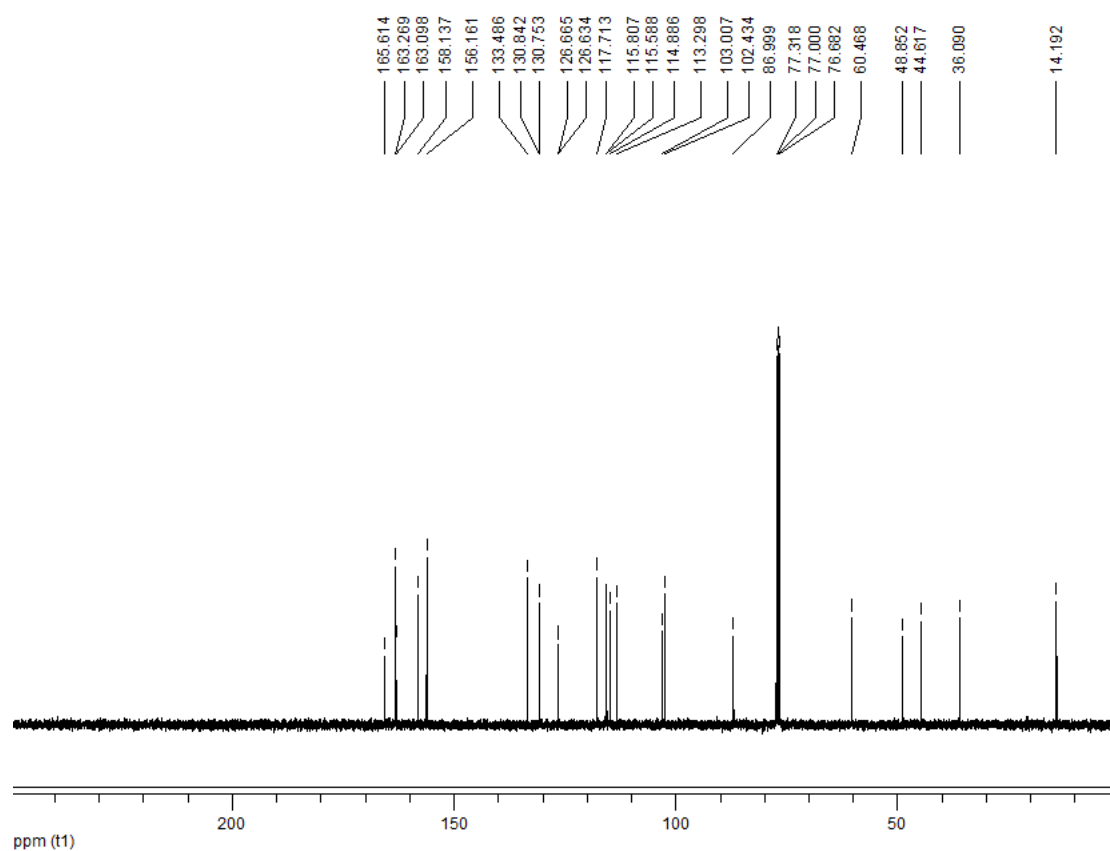
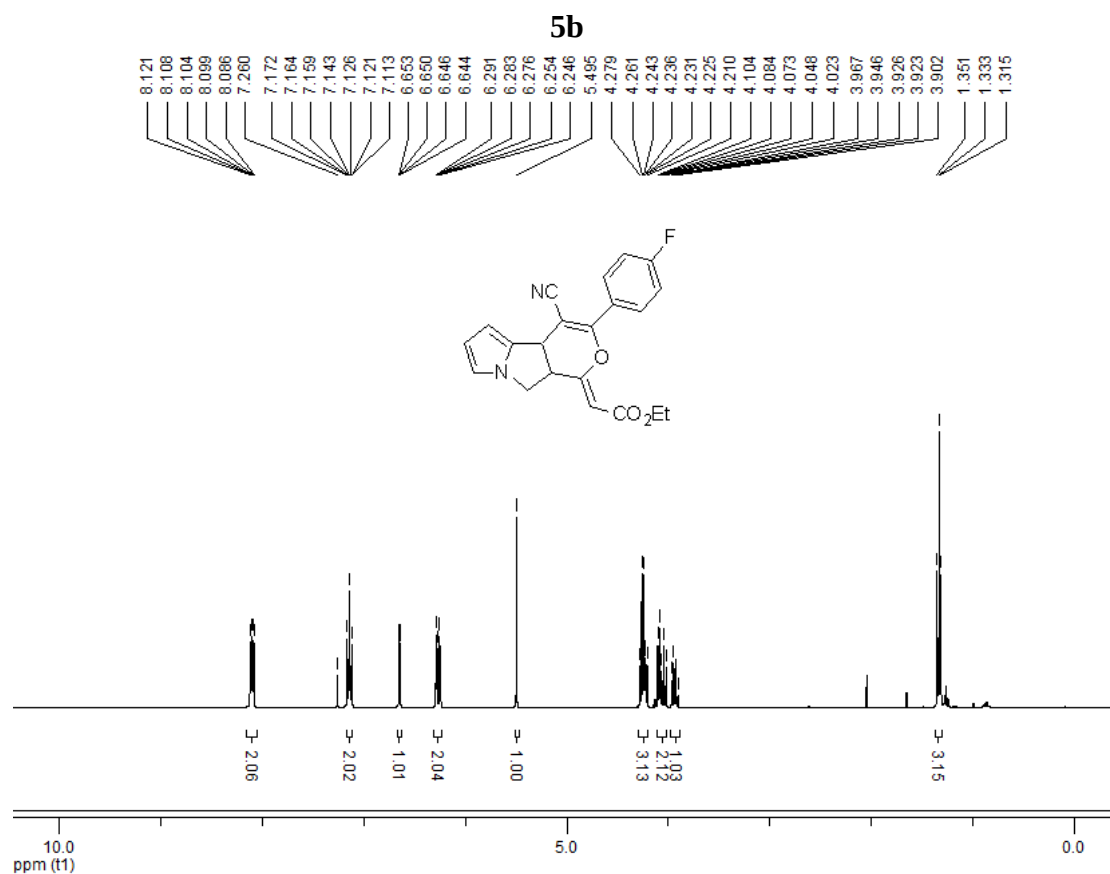
3i



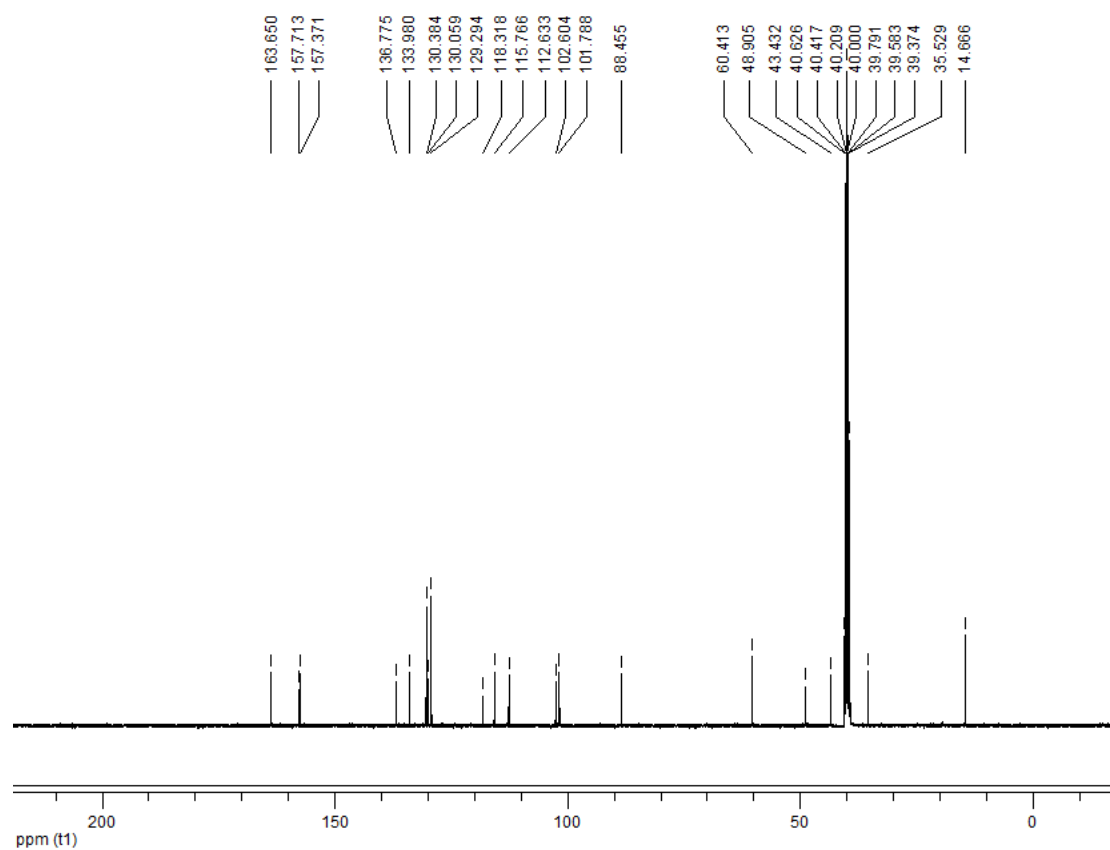
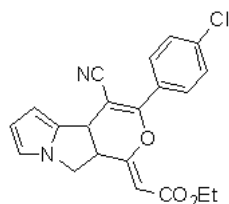
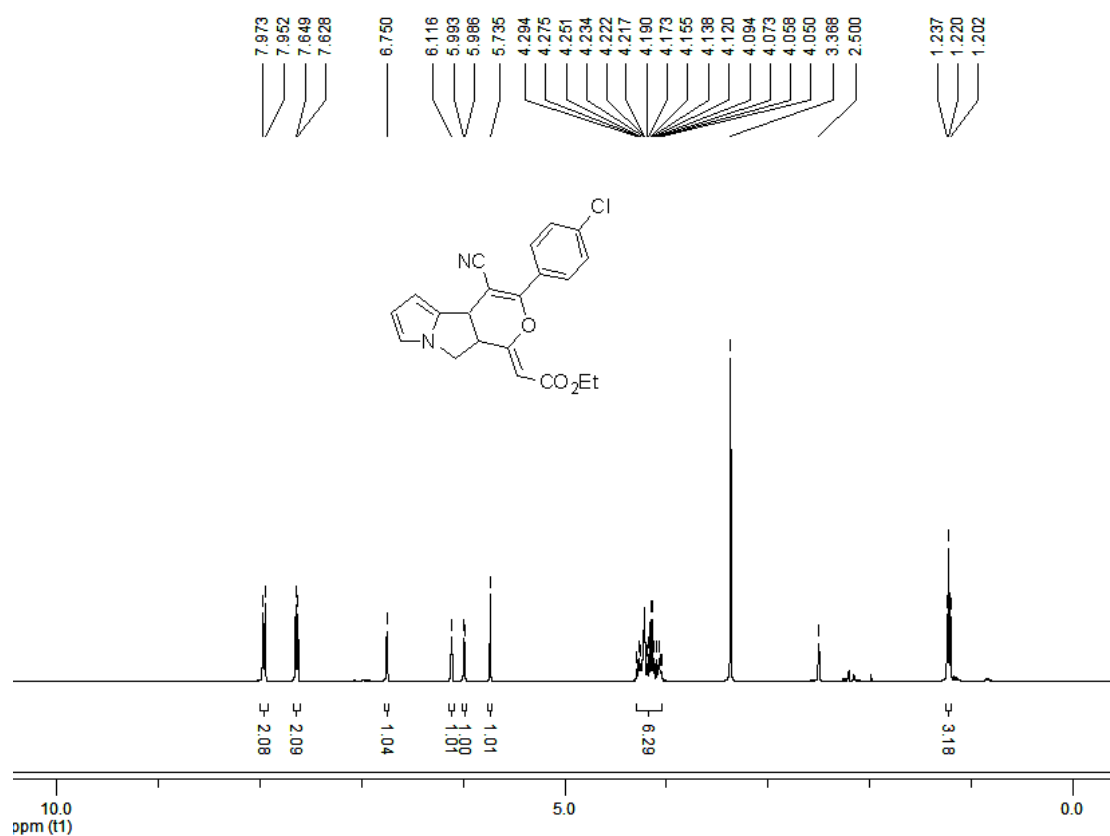
S23

5a

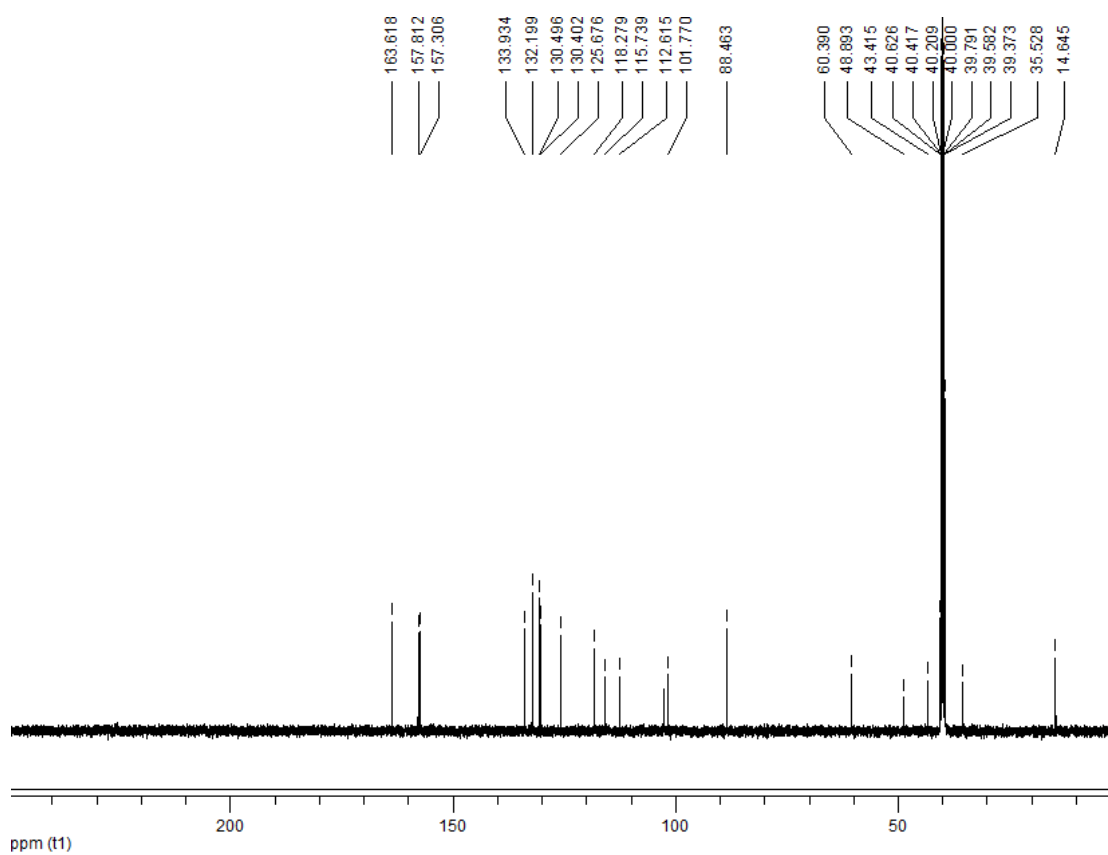
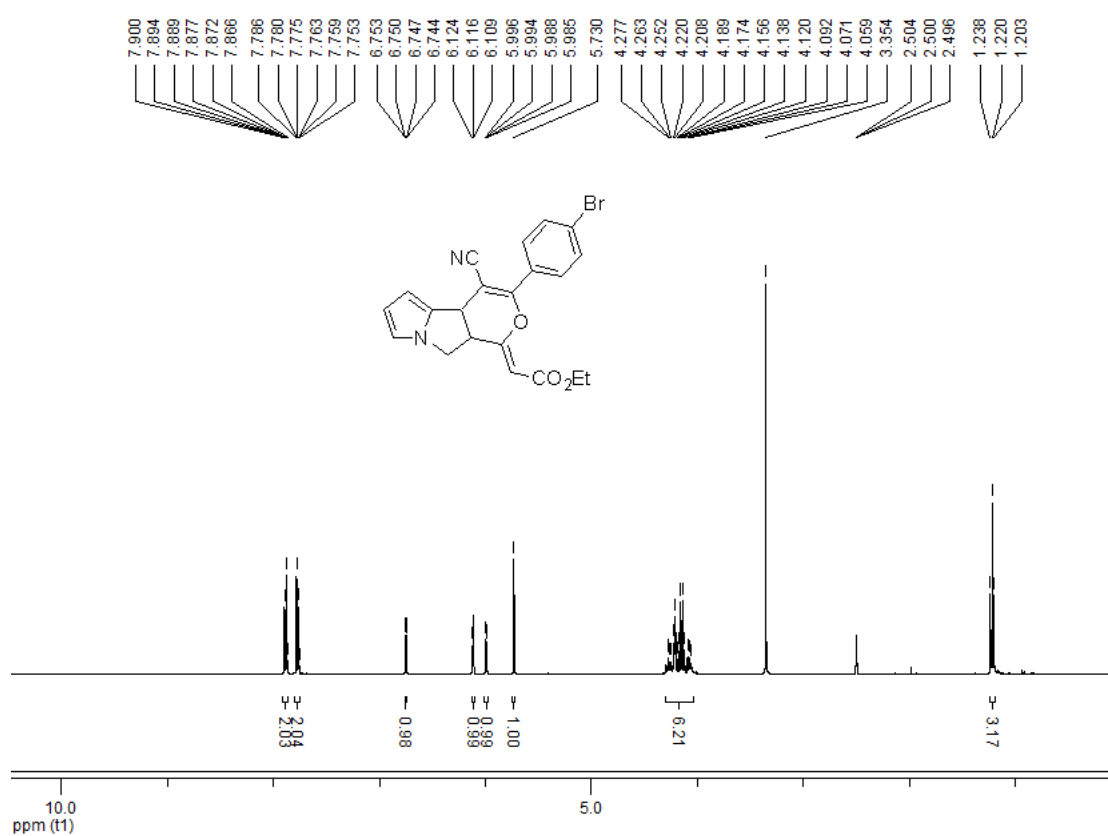




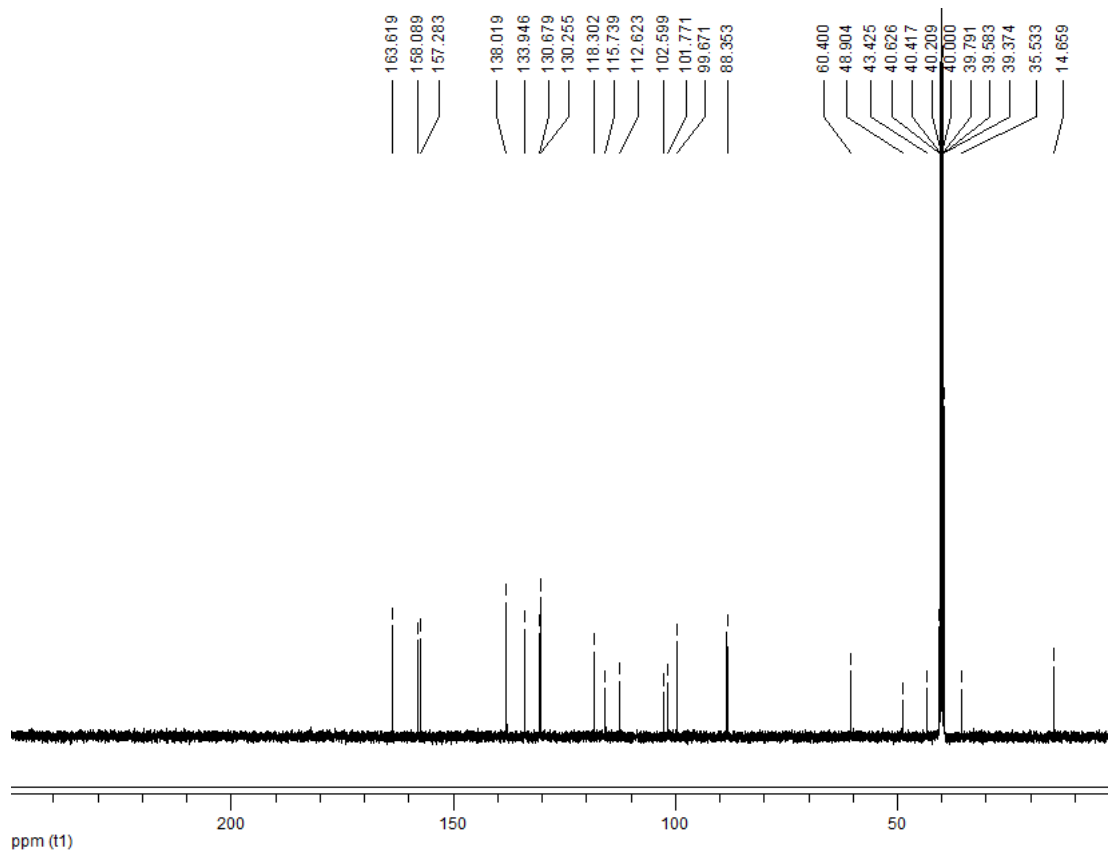
5c

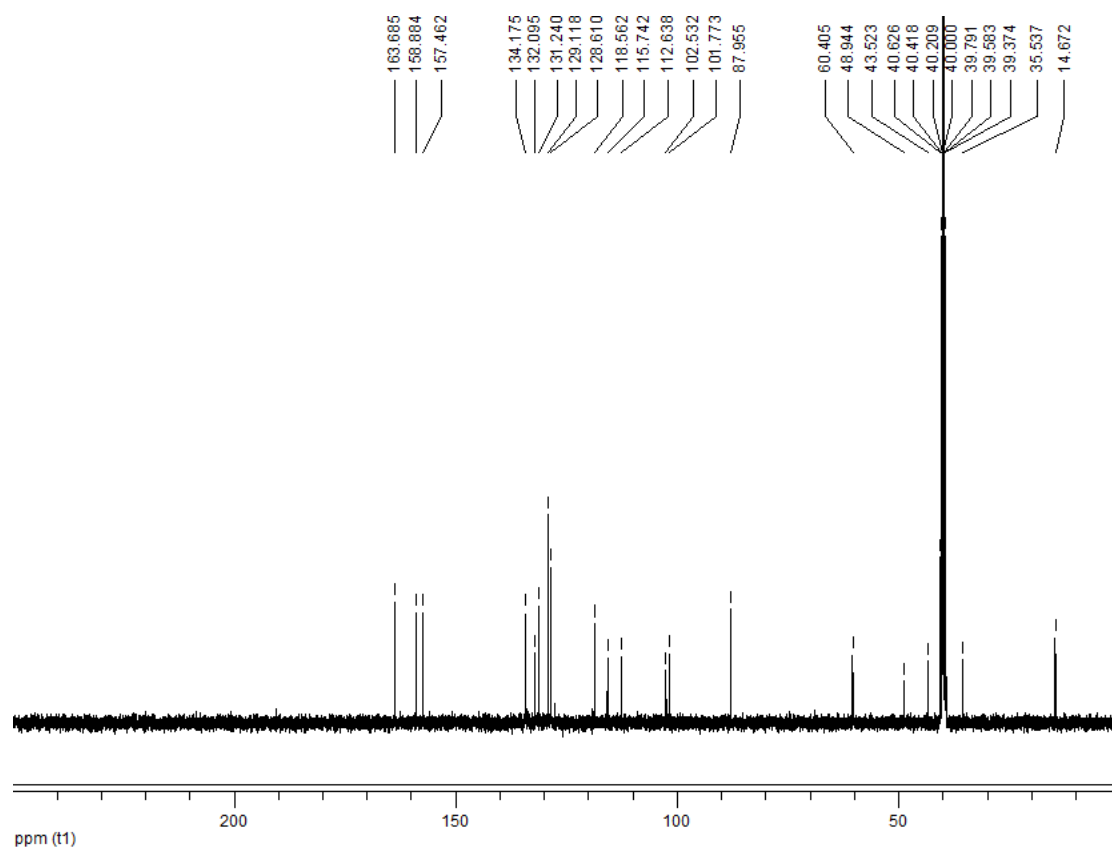
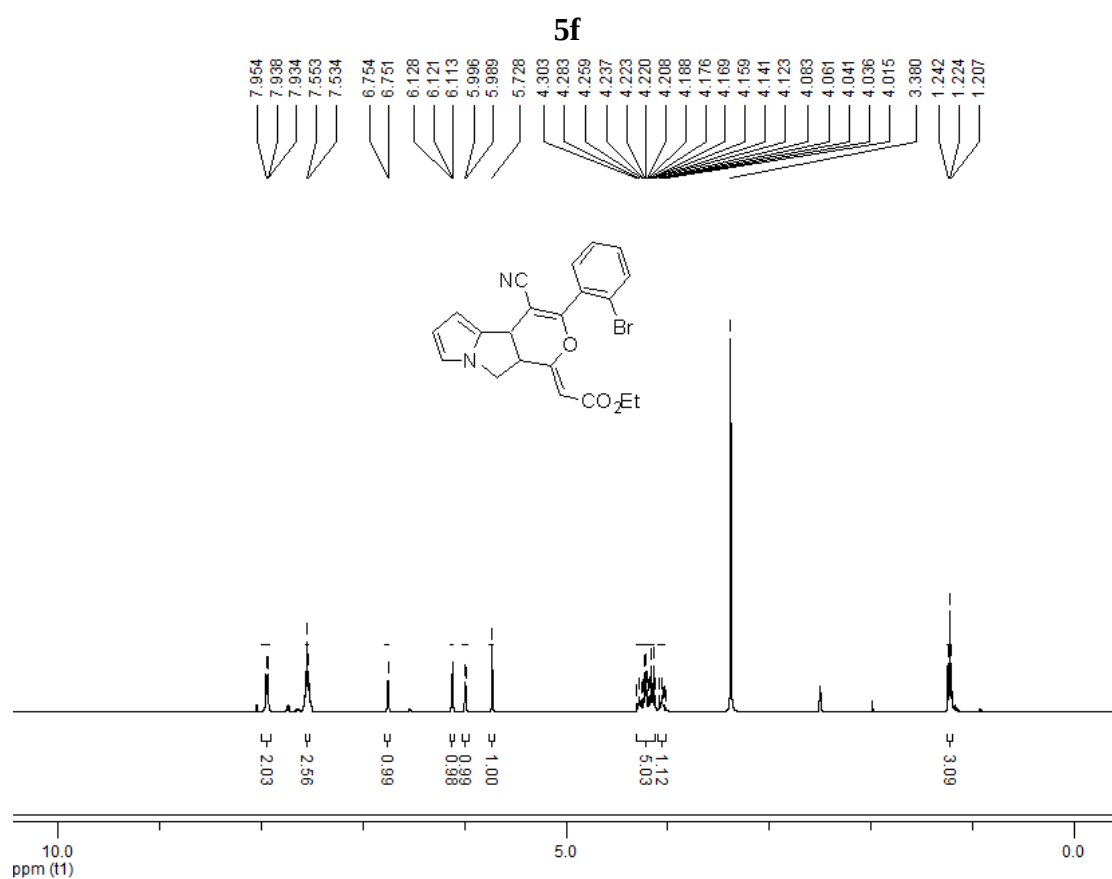


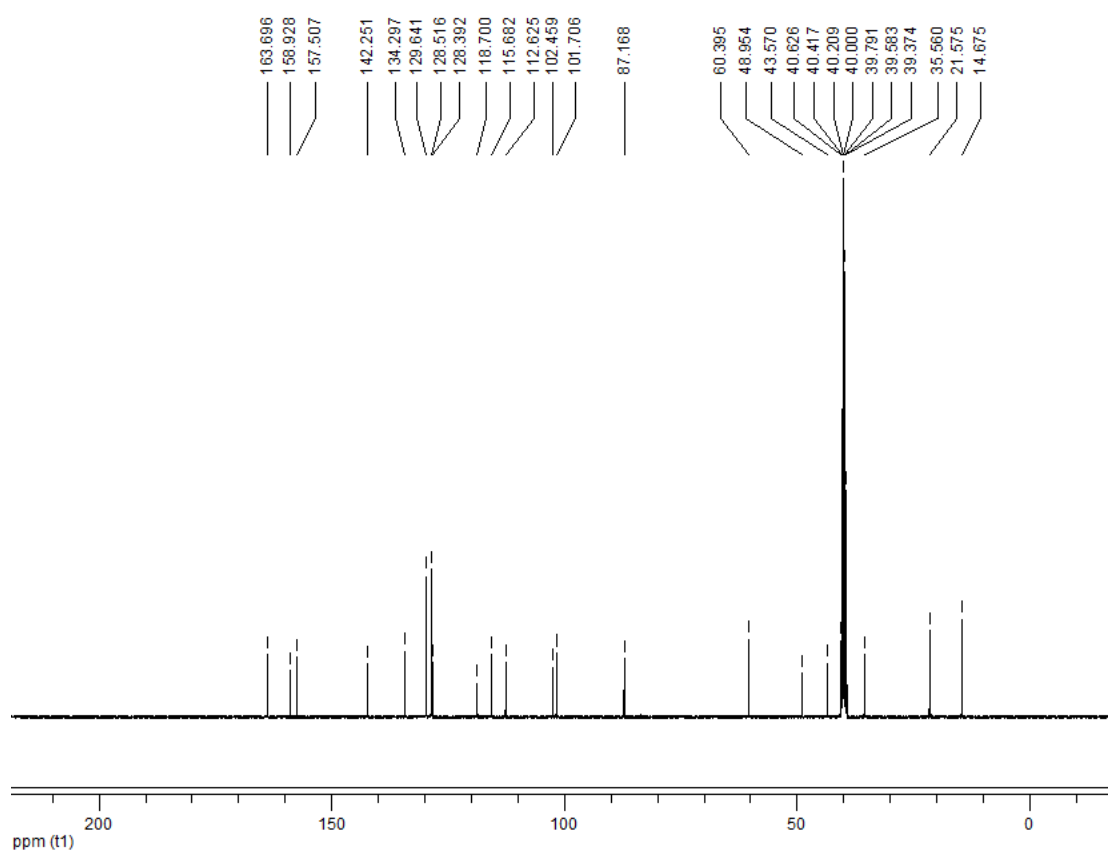
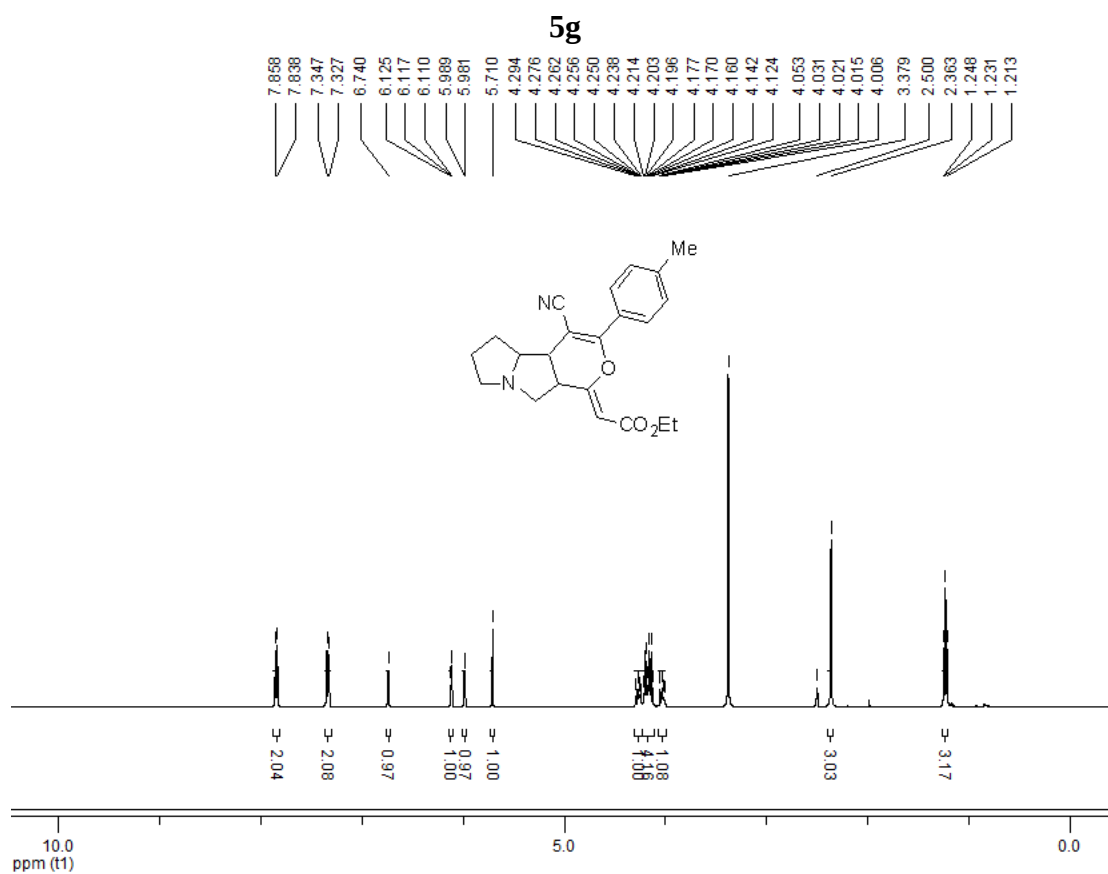
5d



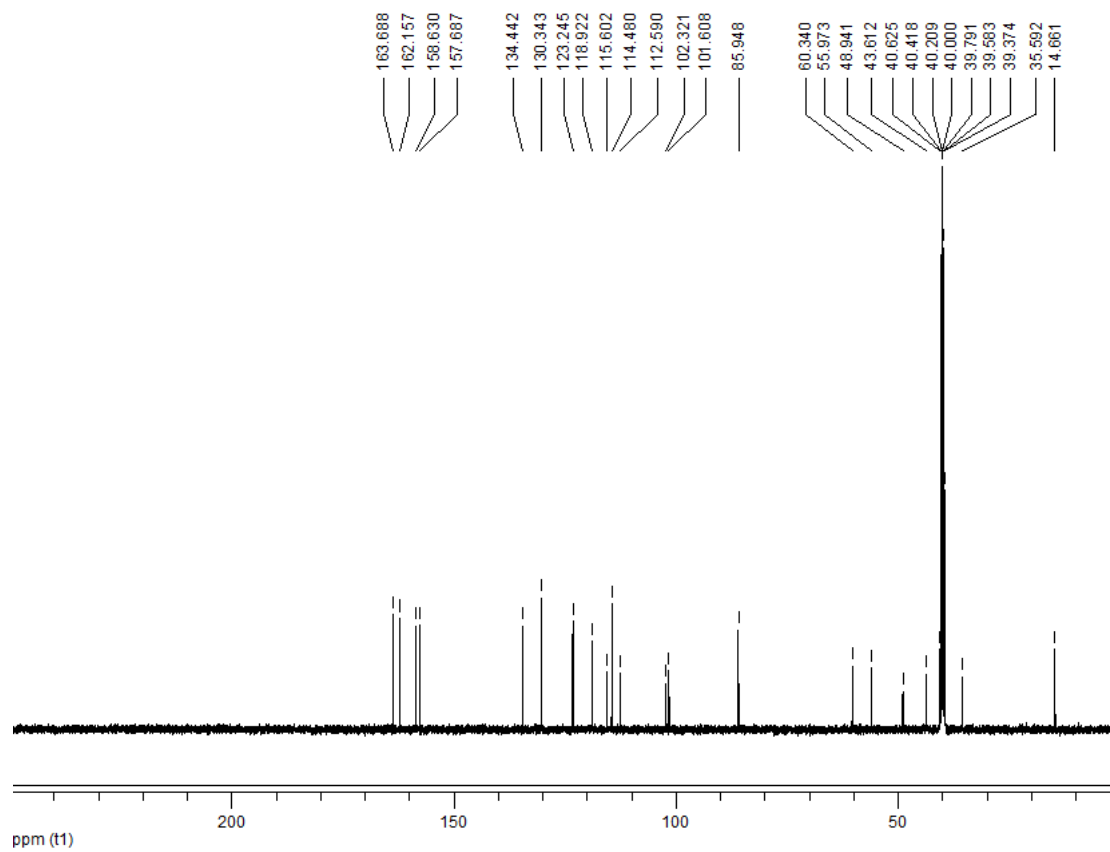
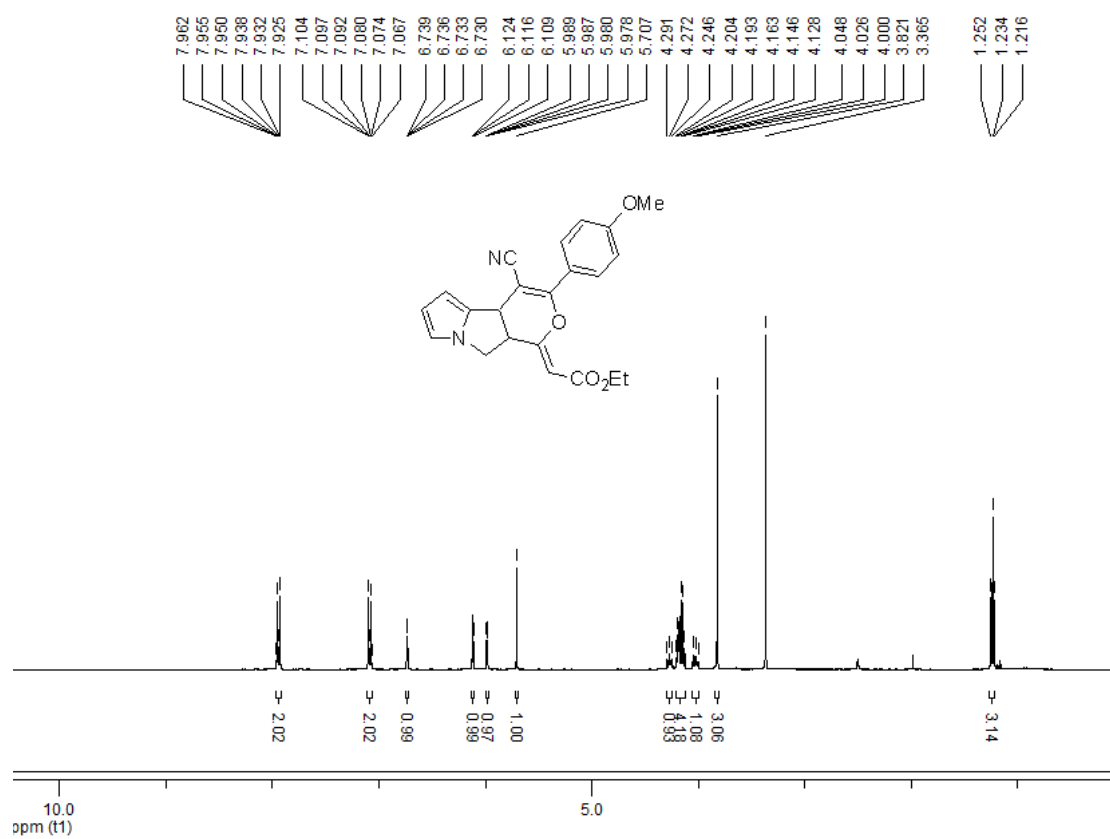
S28



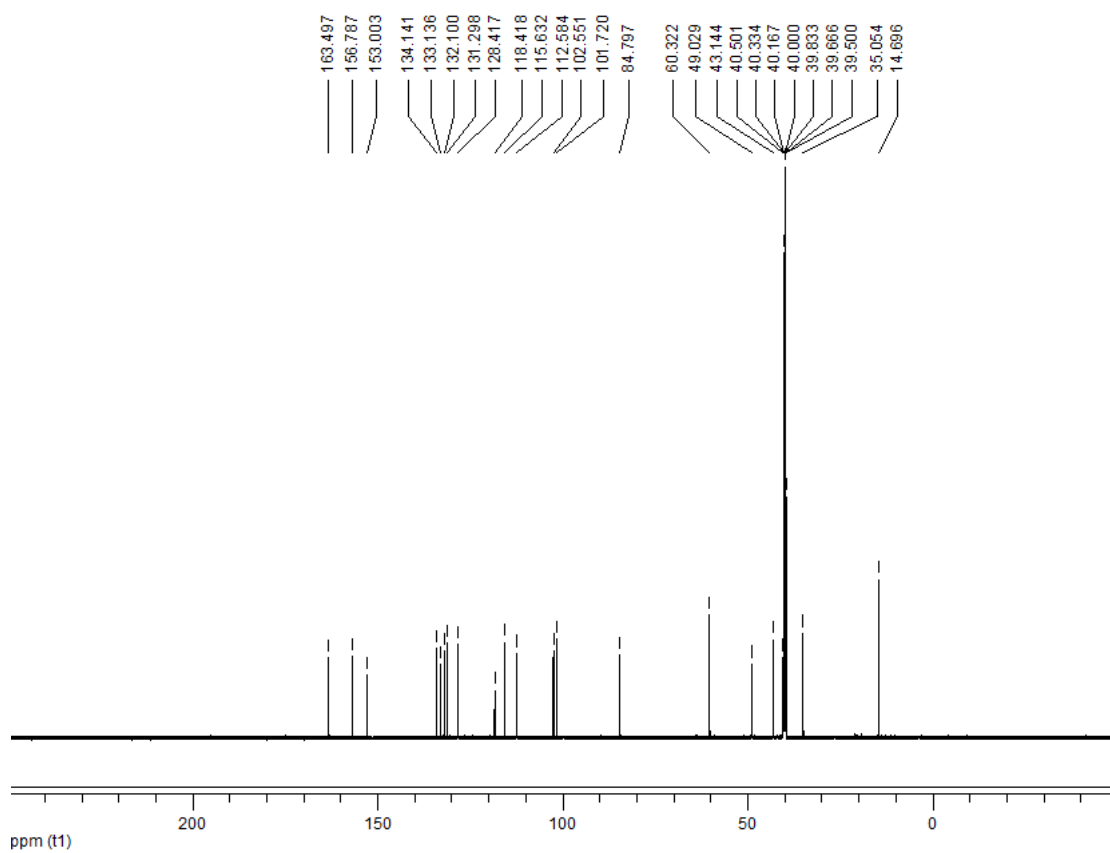
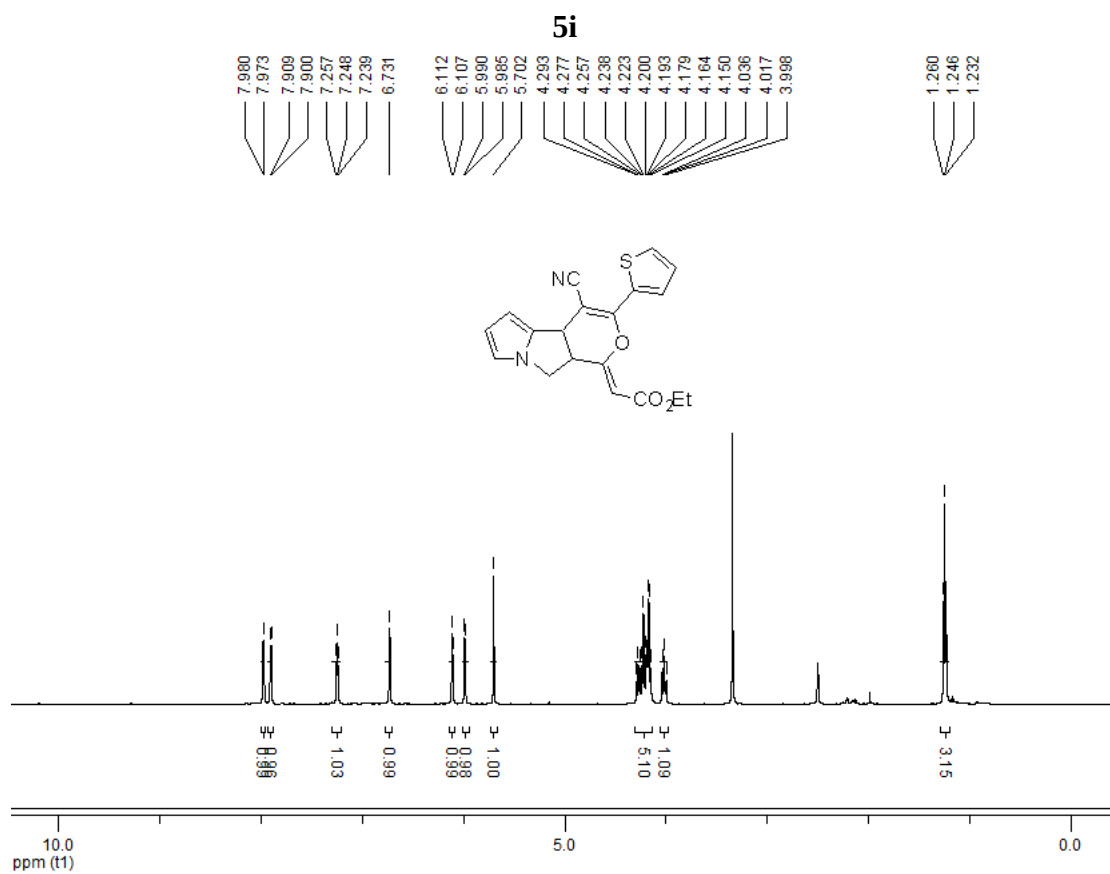




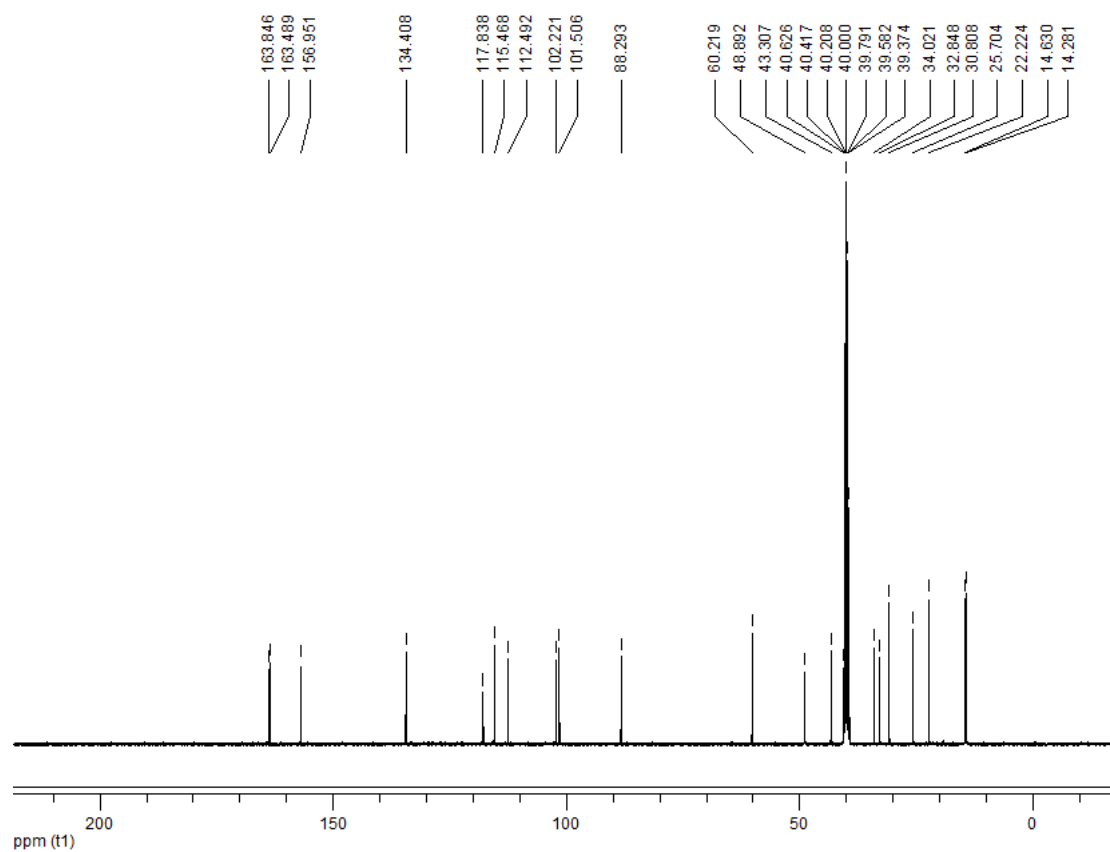
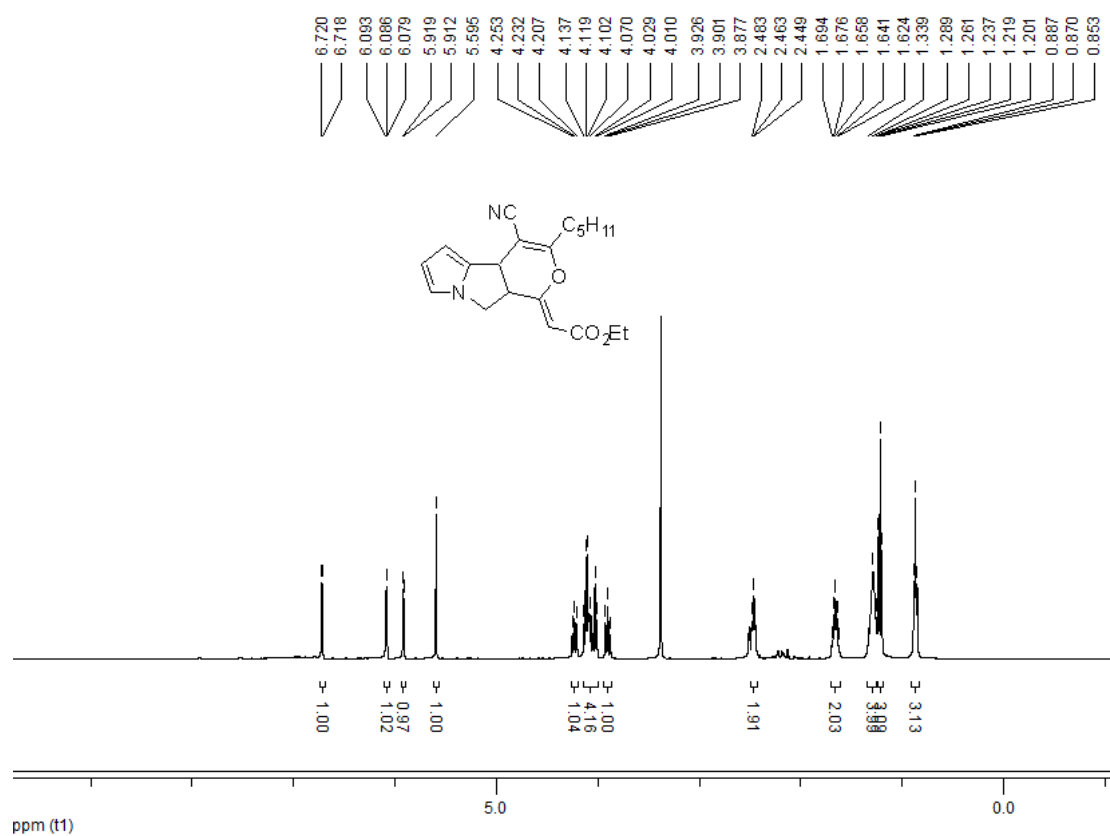
5h



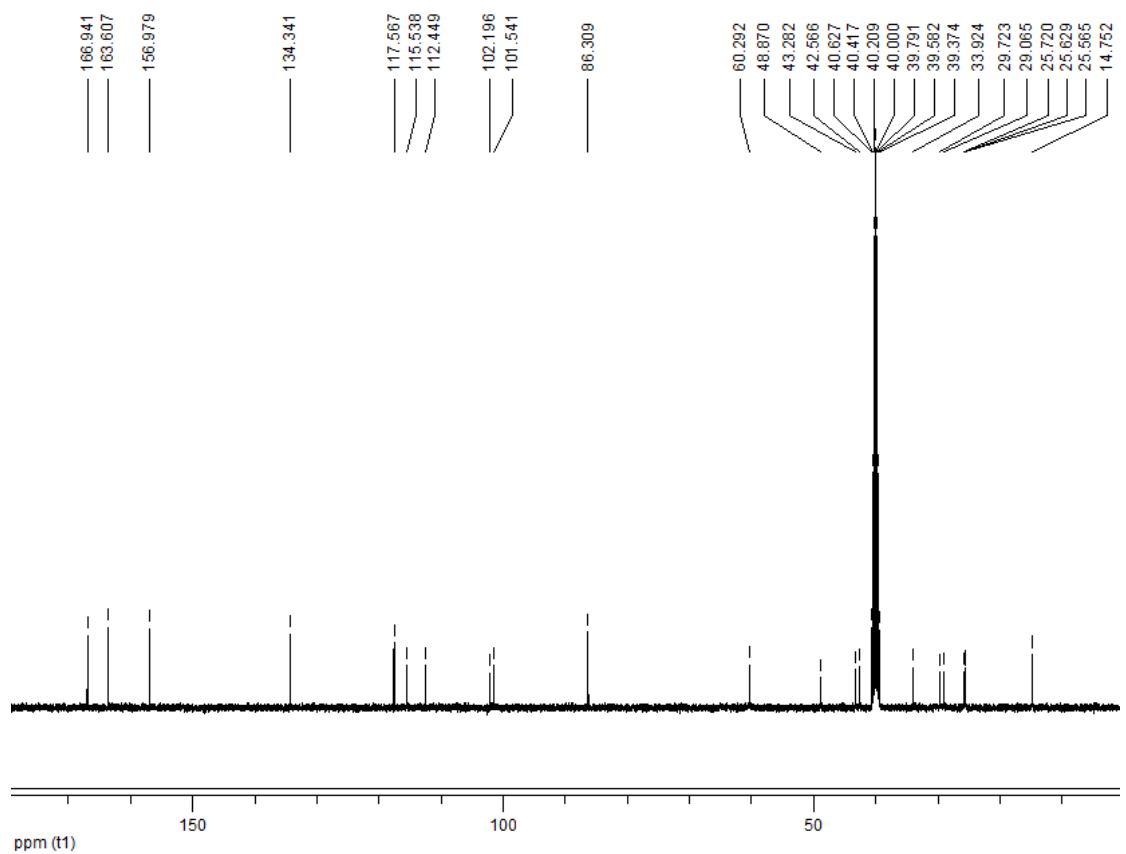
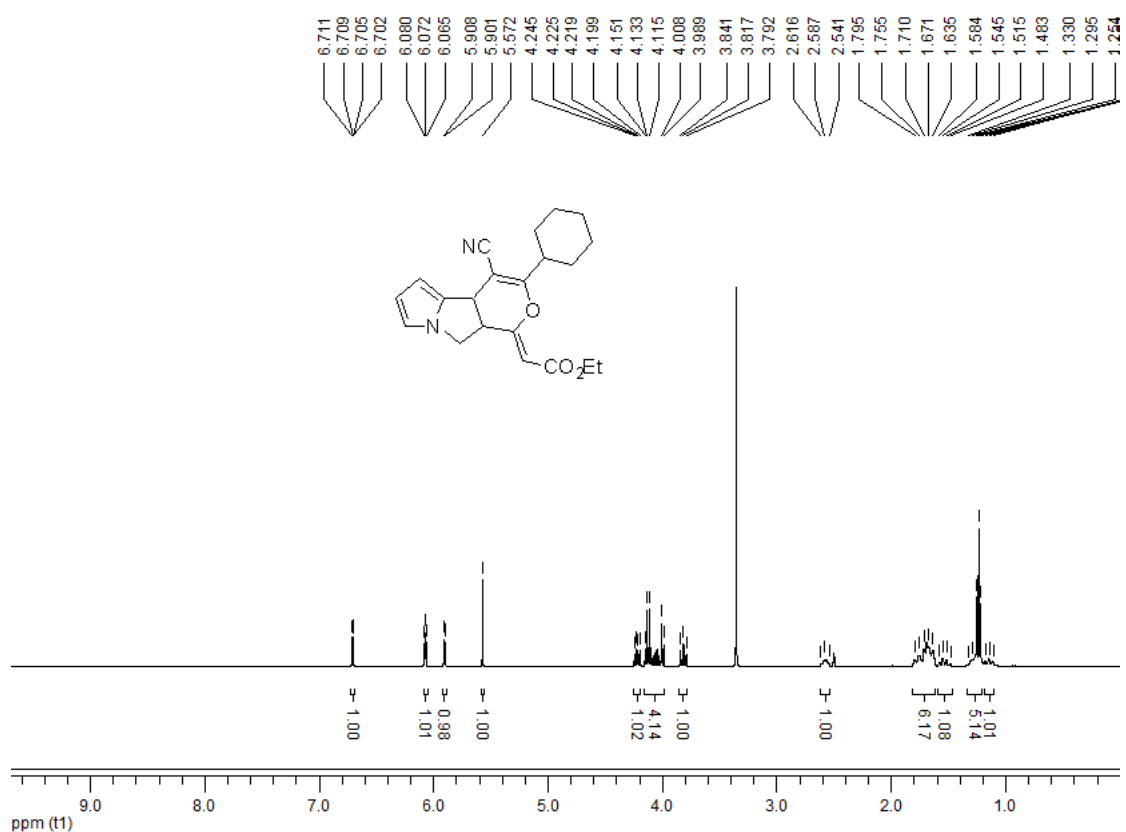
S31



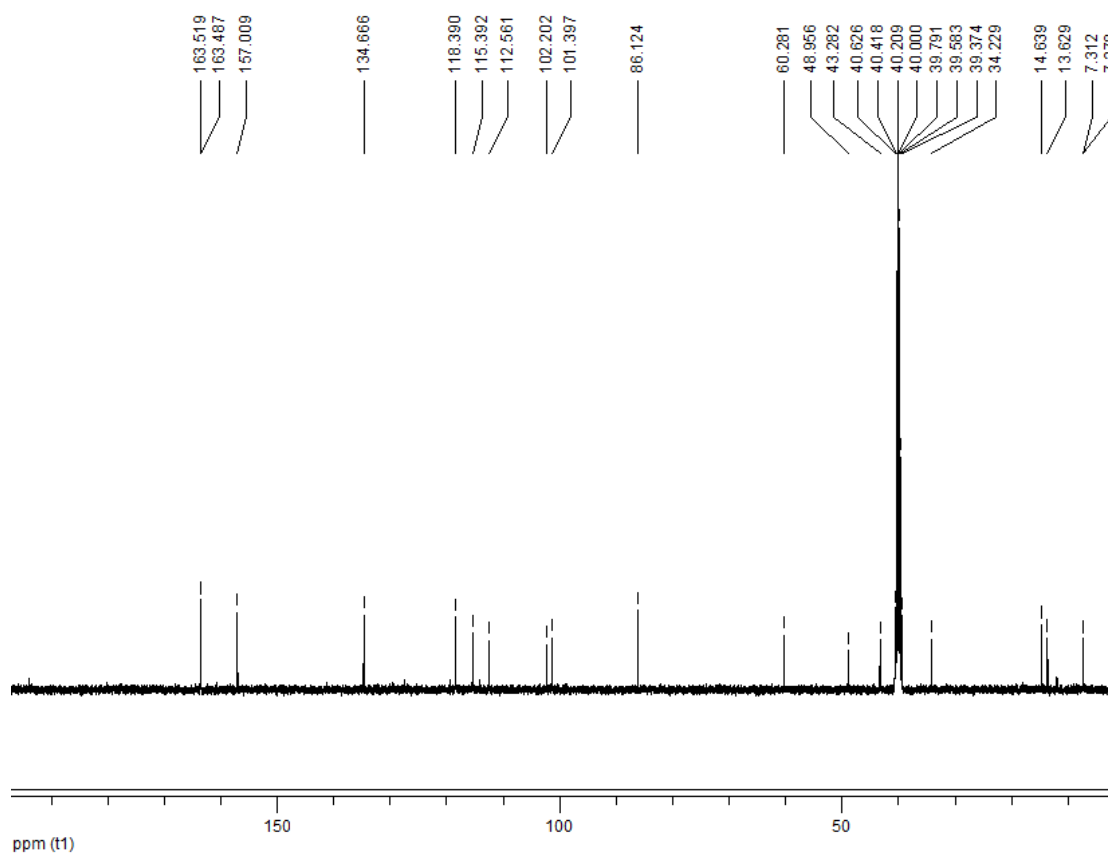
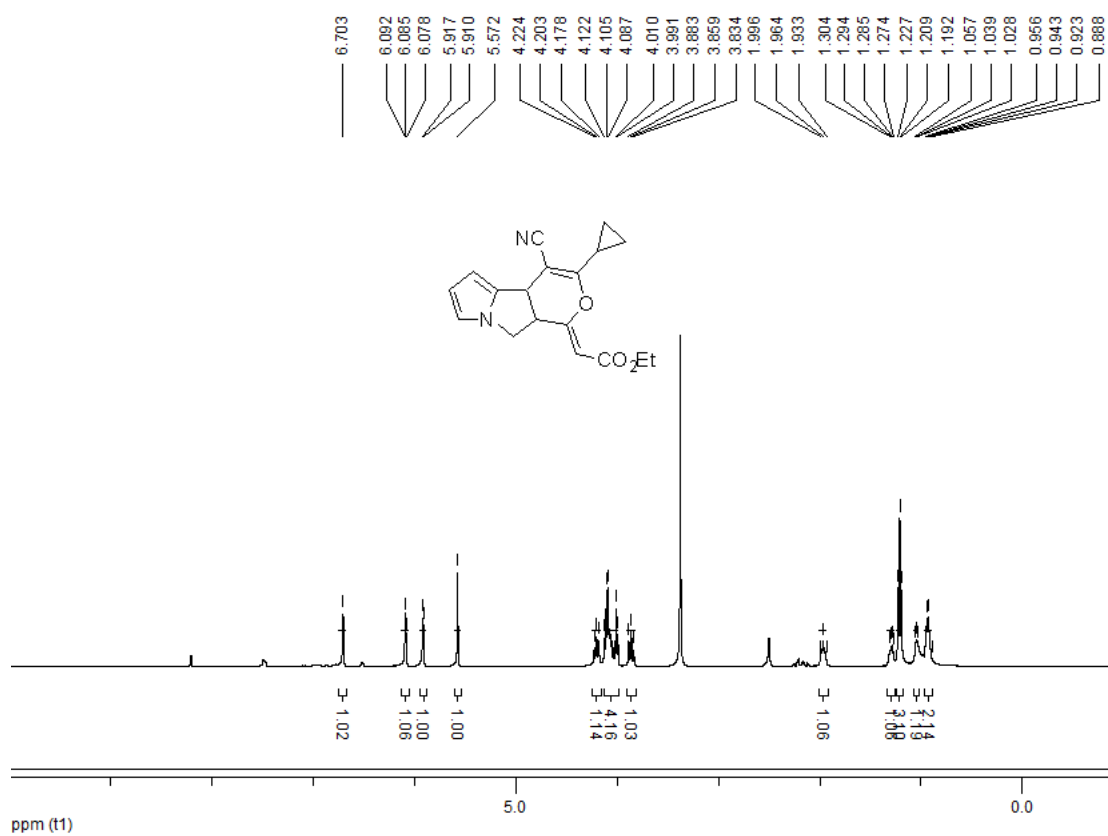
5j



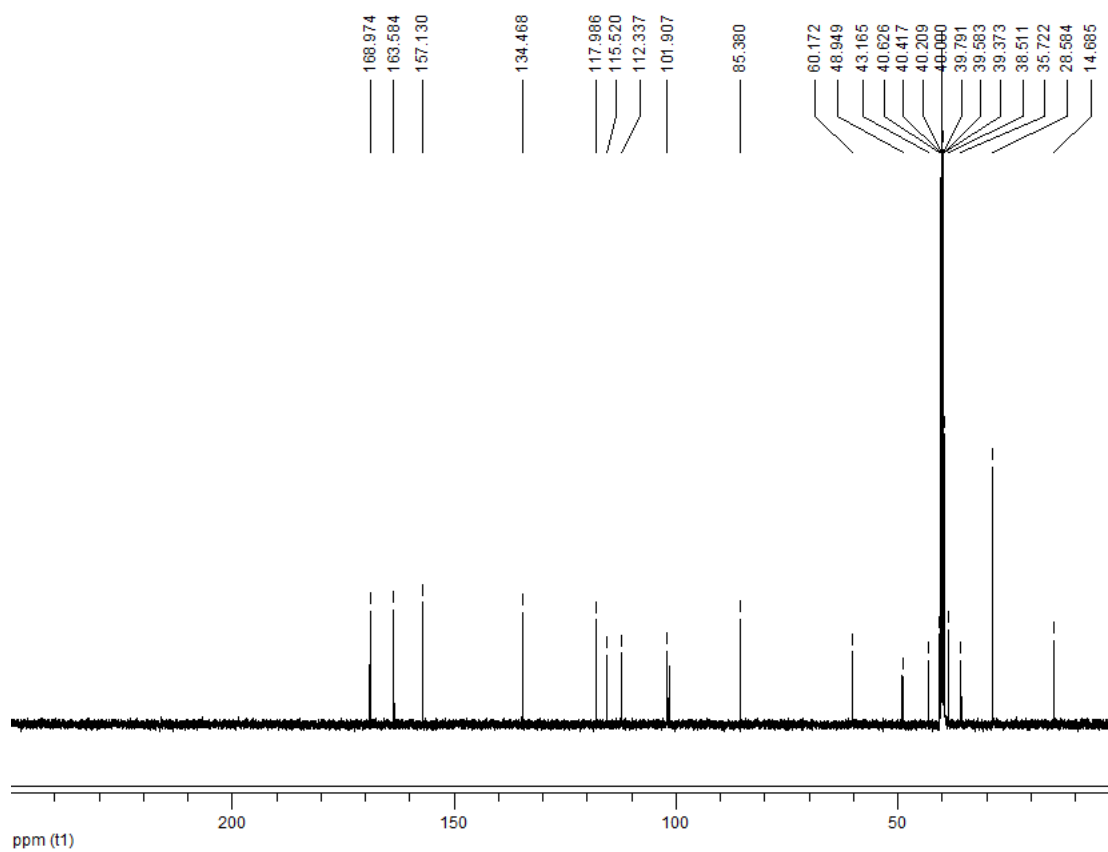
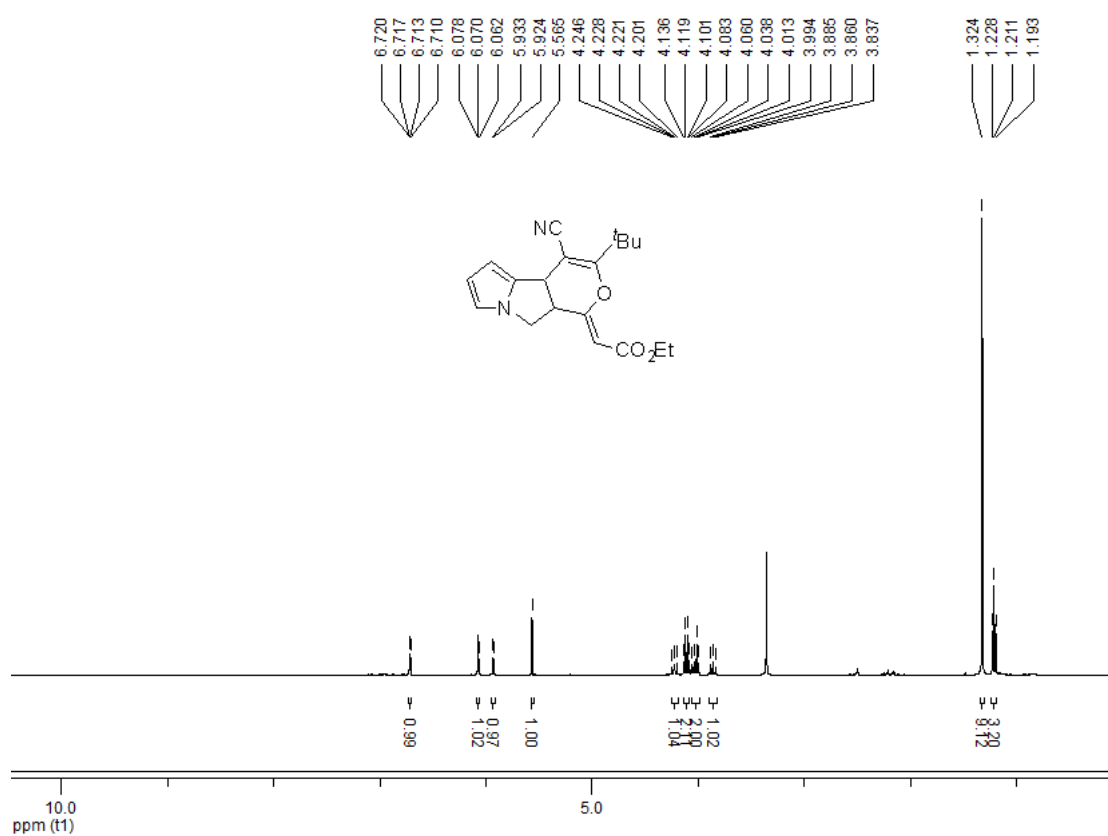
5k



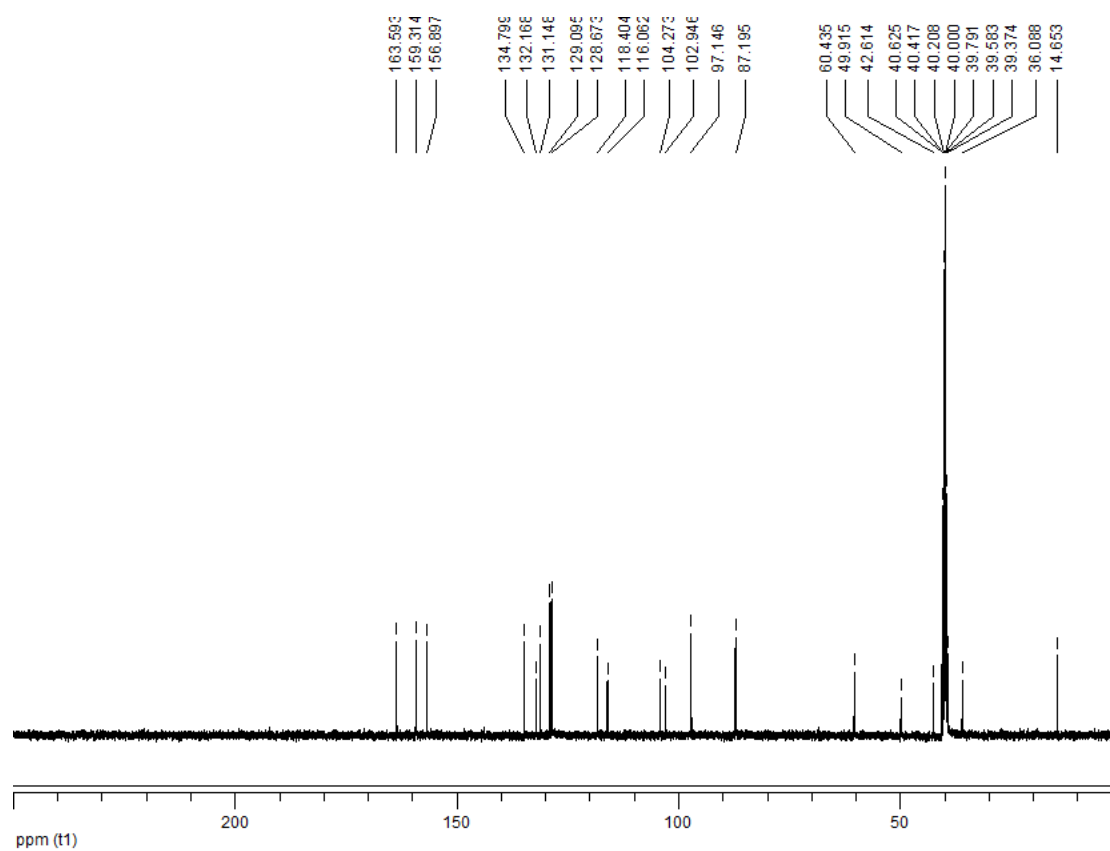
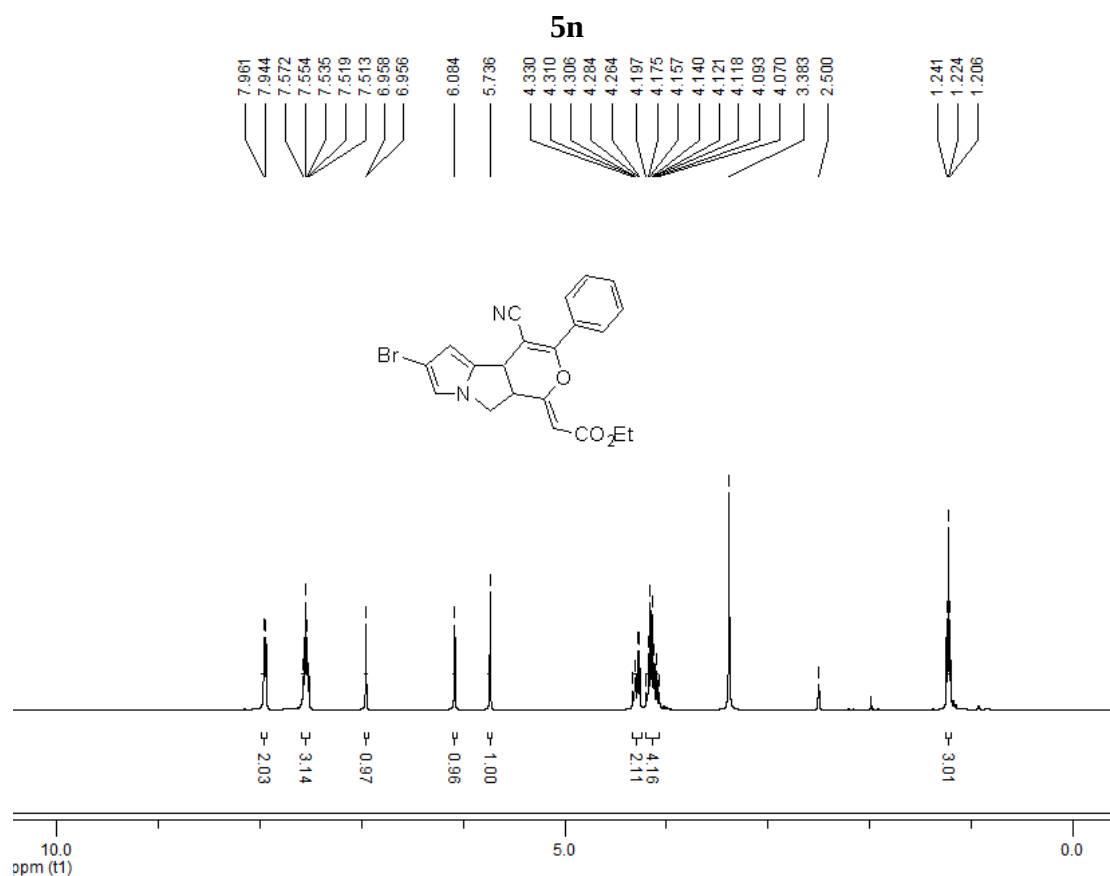
5l

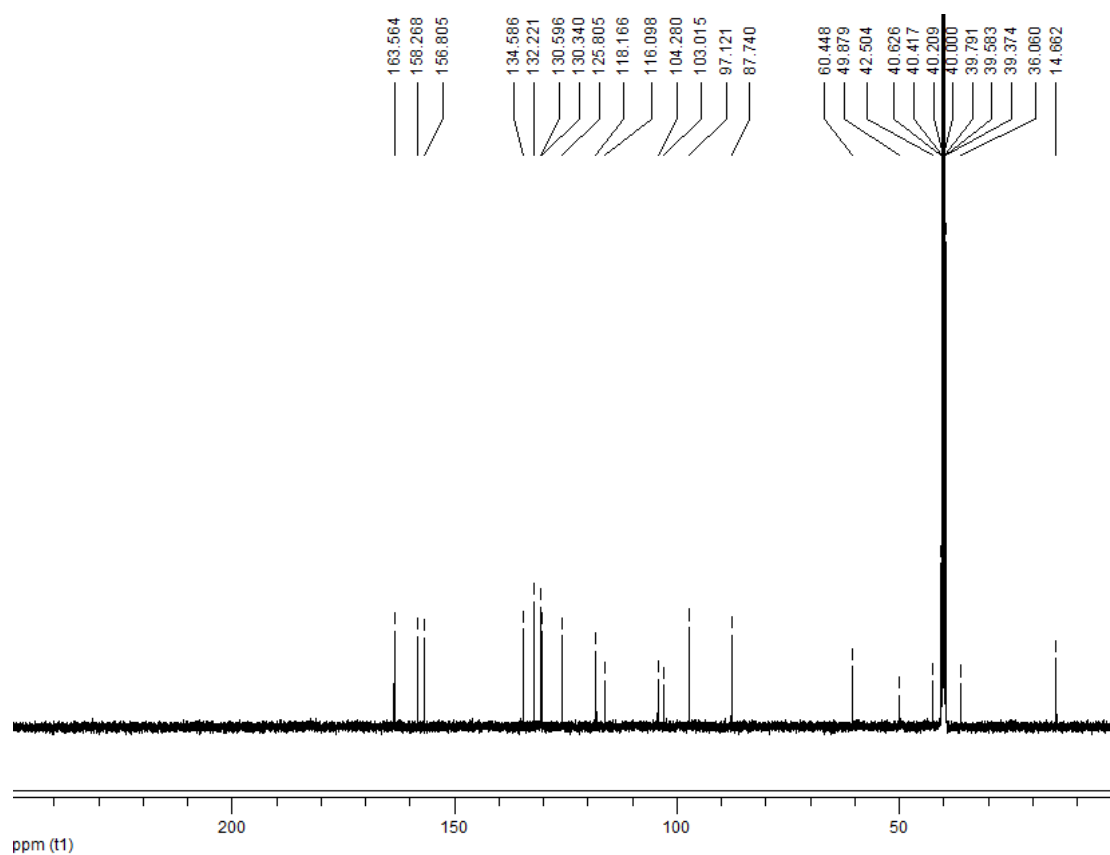
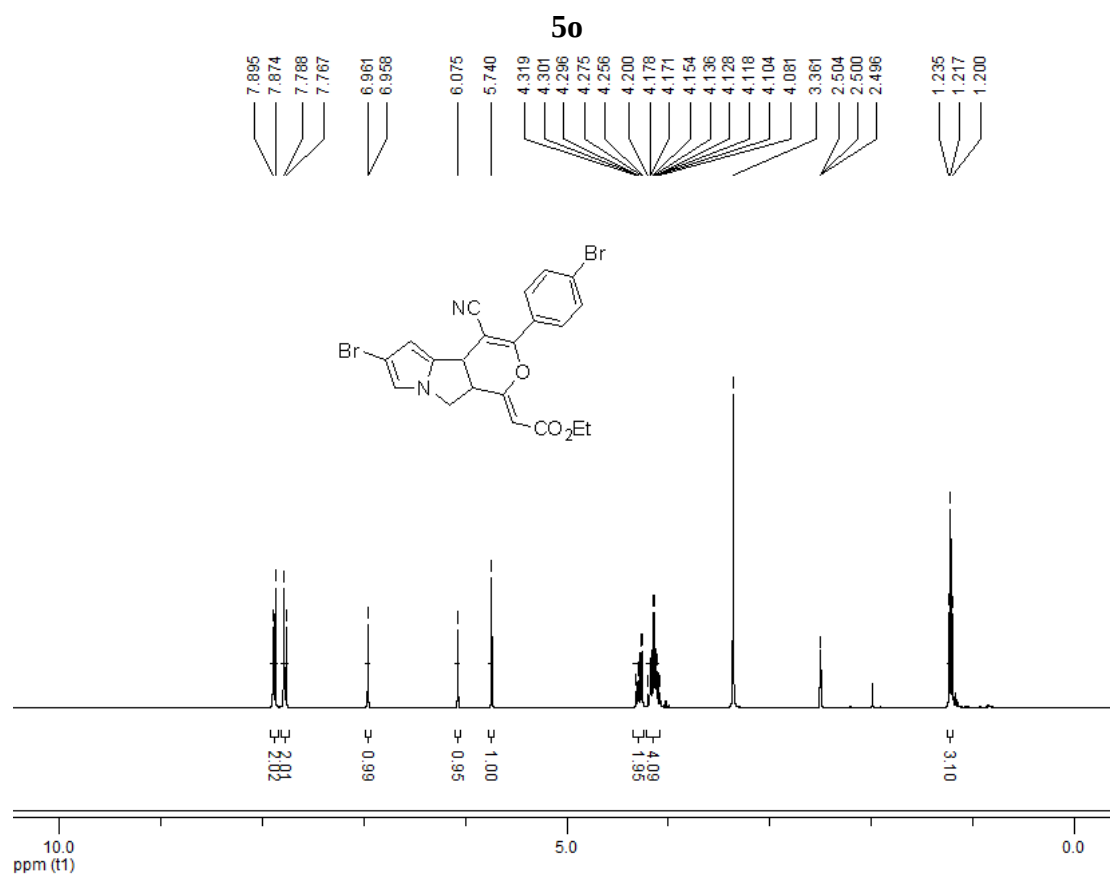


5m

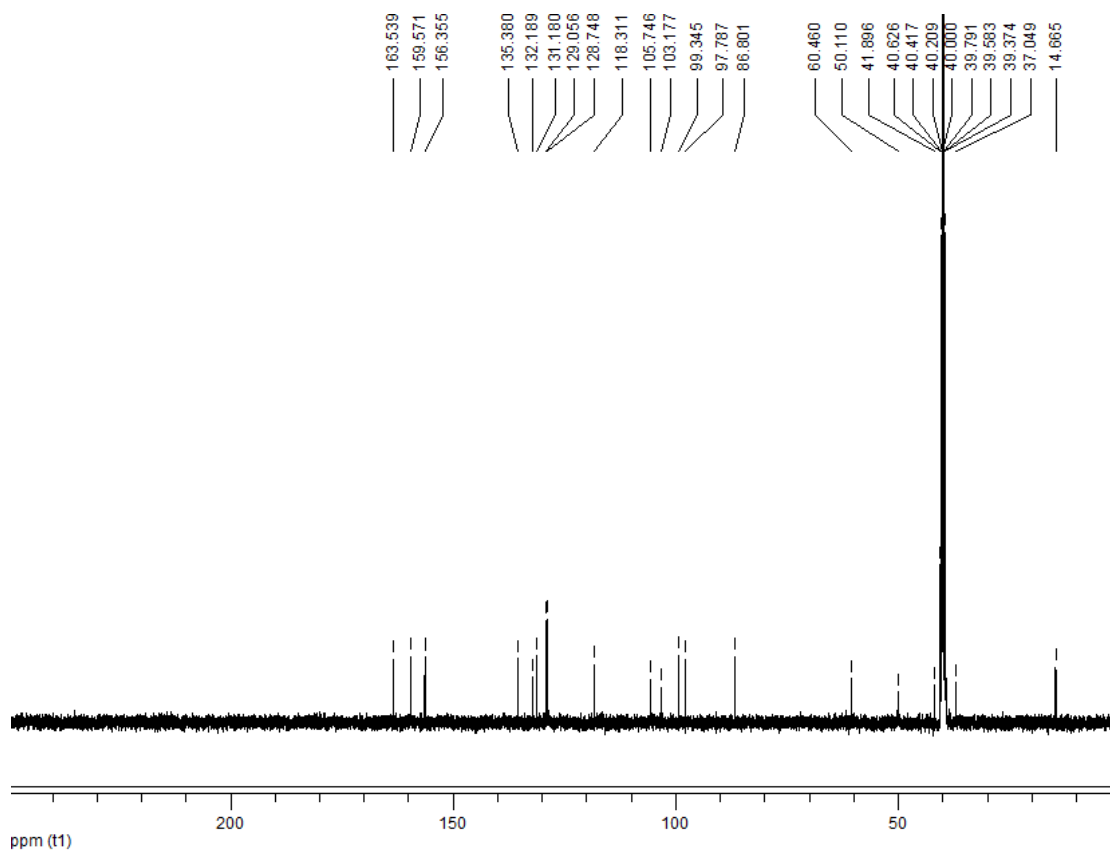
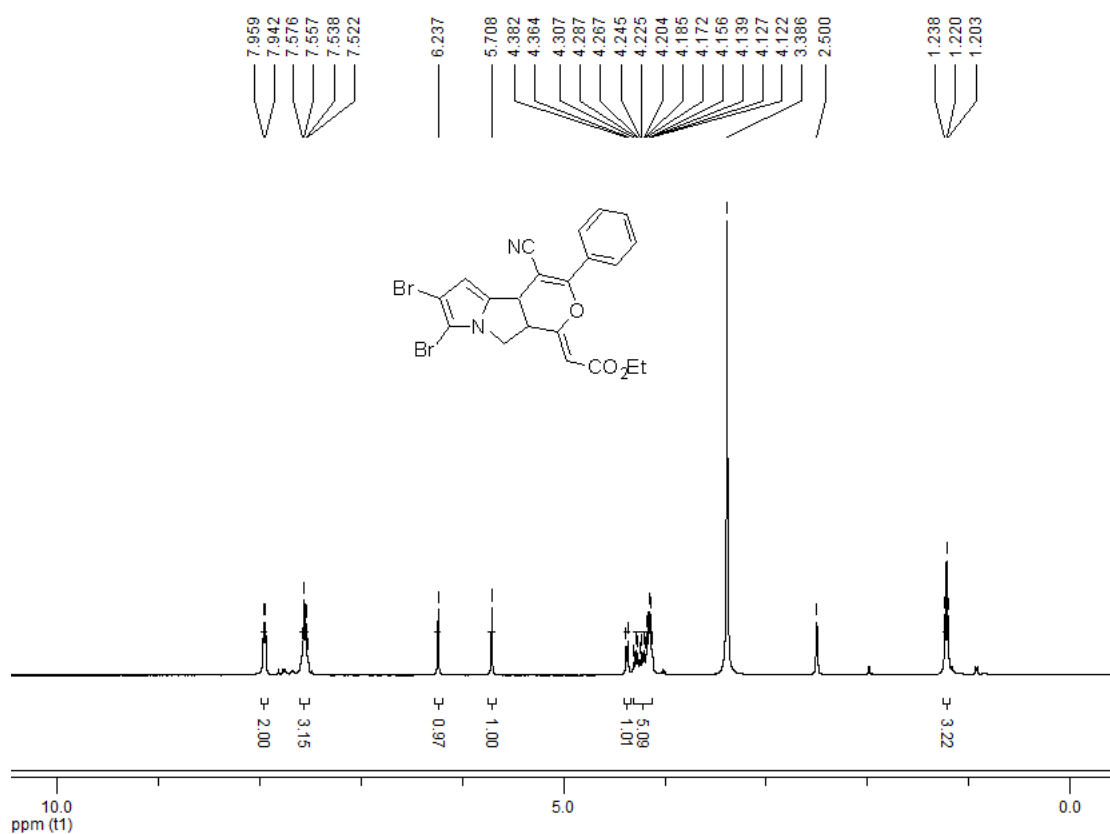


S36

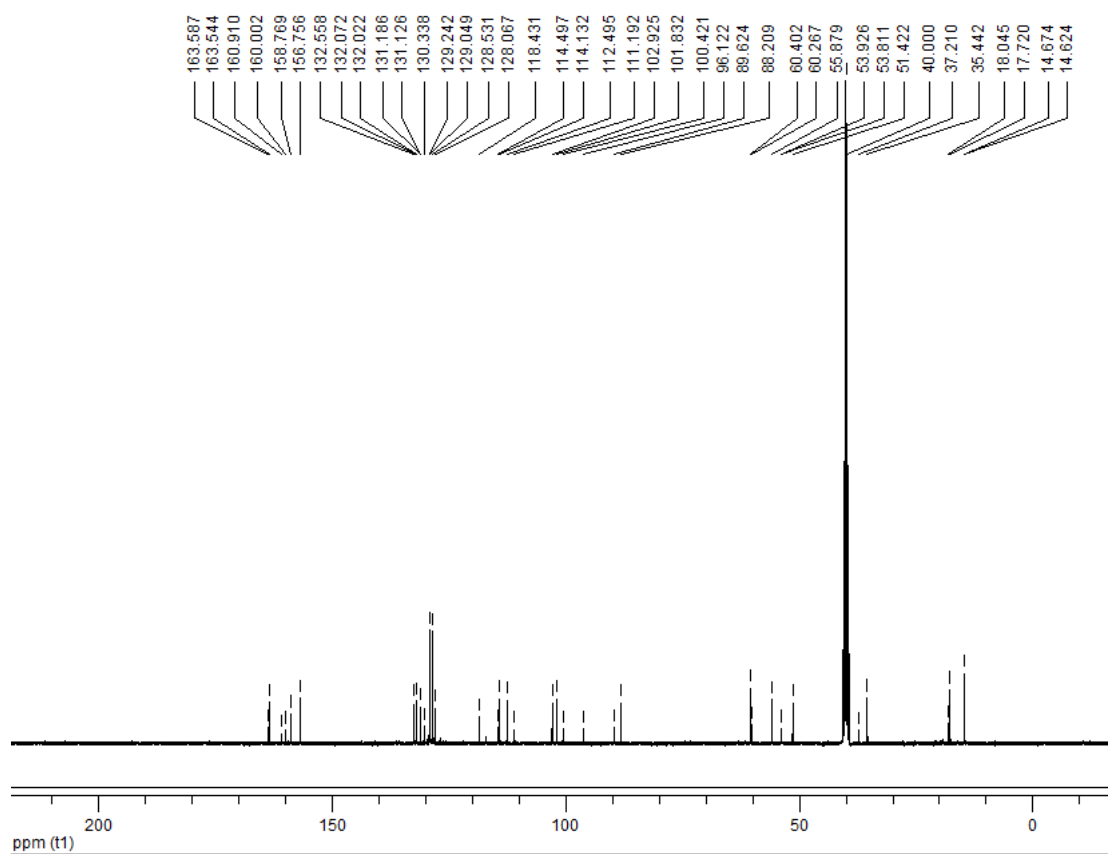
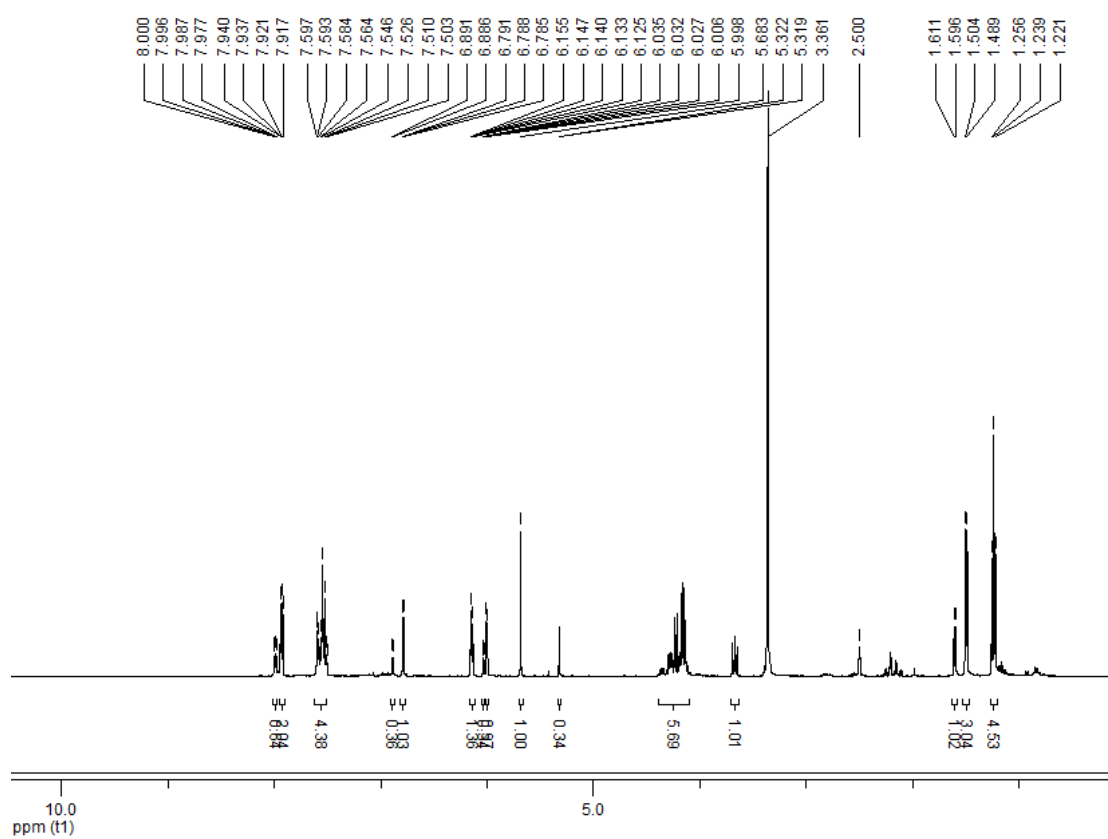




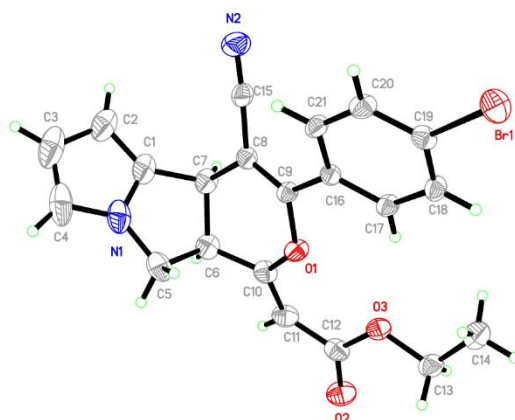
5p



5ba



6. X-ray Analysis of Compound 5d



Bond precision: C-C = 0.0061 Å

Wavelength=0.71073

Cell: a=12.869 (2) b=14.380 (3) c=10.957 (2)

alpha=90

beta=108.813 (4)

gamma=90

Temperature: 296 K

	Calculated	Reported
Volume	1919.3 (6)	1919.2 (7)
Space group	P 21/c	P2 (1) /c
Hall group	-P 2ybc	?
Moiety formula	C21 H17 Br N2 O3	?
Sum formula	C21 H17 Br N2 O3	C21 H17 Br N2 O3
Mr	425.27	425.28
Dx, g cm ⁻³	1.472	1.472
Z	4	4
Mu (mm ⁻¹)	2.165	2.165
F000	864.0	864.0
F000'	863.20	
h,k,lmax	15,17,13	15,17,13
Nref	3574	3567
Tmin,Tmax	0.627,0.677	0.647,0.697
Tmin'	0.615	

Correction method= # Reported T Limits: Tmin=0.647 Tmax=0.697

AbsCorr = MULTI-SCAN

Data completeness= 0.998

Theta(max)= 25.500

R(reflections)= 0.0486 (2486)

wR2(reflections)= 0.1561 (3567)

S = 0.963

Npar= 245