Electronic Supplementary Material (ESI) for ChemComm.
This journal is © The Royal Society of Chemistry 2017

Supporting Information

Access to Thiopyrano[2,3-b]indole via Tertiary Amine-Catalyzed Formal (3+3) Annulations of β'-Acetoxy Allenaotes with Indoline-2-thiones

Chunjie Ni, Yuwen Zhang, Yading Hou and Xiaofeng Tong*

Table of Contents

1. General Information...……..... S2

2. Optimization of Reaction Conditions...…… S3

3. General Procedure and Date for Compounds 4 ....…….…… S4

4. Synthetic Transformations .....…….…….....…...…… S14

5. NMR and HPLC Spectra …….. S17

6. X-ray Analysis of Compound 4aa …….……..…….. S56

1. General Information

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

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

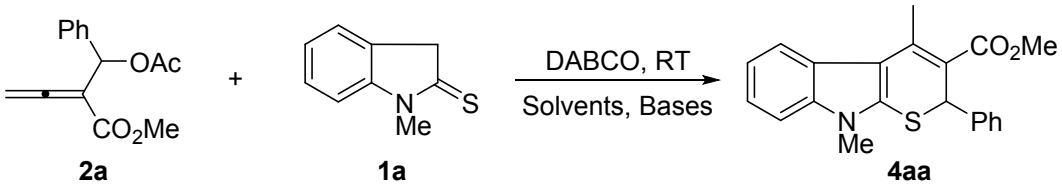
Mass spectroscopy: Mass spectra were in general recorded on an AMD 402/3 or a HP 5989A mass selective detector.

High Performance Liquid Chromatography: HPLC analysis was performed on Waters equipment using Daicel ChiralpakOD-H column.

Spectropolarimeter: Optical rotations were measured on a JASCOP-1030 polarimeter.

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

2. Optimization of Reaction Conditions[a]

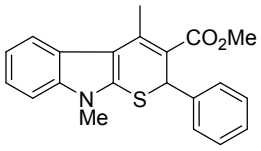


Entry	Solvent	Base	Yield%[b]
1	THF	K_2CO_3	77
2	CH_3CN	K_2CO_3	86
3	Acetone	K_2CO_3	23
4	PhMe	K_2CO_3	97
5	1,4-Dioxane	K_2CO_3	61
6	EtOAc	K_2CO_3	82
7	CH_2Cl_2	K_2CO_3	79
8	$ClCH_2CH_2Cl$	K_2CO_3	82
9	DMF	K_2CO_3	trace
10	DMSO	K_2CO_3	trace
11	PhMe	Na_2CO_3	92
12	PhMe	Cs_2CO_3	85
13	PhMe	K_3PO_4	81
14	PhMe	NaOH	86
15	PhMe	$NaHCO_3$	94
16	PhMe	DIPEA	91
17	PhMe	Et_3N	89
18	PhMe	DBU	62

[a]Reaction conditions: to the solution of **2a** (16.3 mg, 0.1 mmol), Base (0.11 mmol) and DABCO (1.1 mg, 0.01 mmol) in solvent (1 mL) was slowly added the relevant solution (1mL) of **1a** (29.6 mg, 0.12 mmol). [b]Isolated yield.

3. General Procedure and the Date for Compounds 4

To a 10 mL Schlenk tubewas added indoline-2-thione**2**(0.1 mmol), K_2CO_3 (15.2 mg, 0.11mmol), DABCO (1.1 mg, 0.01mmol), and toluene (1.0 mL) with stirring at room temperature. To the mixture, the solution of ellenoate **1** (0.1 mmol) in toluene (1.0 mL) was added. 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 **4**.



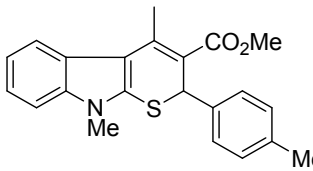
4aa, 33.9 mg, 97% yield, yellow solid, M.p: 159-163 °C.

^{1}H NMR (400 MHz, $CDCl_3$): δ 7.87-7.85 (m, 1H), 7.32 (d, *J* = 6.8 Hz, 2H), 7.20-7.15 (m, 6H), 5.58 (s, 1H), 3.76 (s, 3H), 3.58 (s, 3H), 3.00 (s, 3H).

^{13}C NMR (100 MHz, $CDCl_3$): δ 167.8, 147.4, 140.9, 138.4, 135.8, 128.1, 127.3, 127.2, 126.2, 121.4, 120.9, 119.8, 114.5, 109.9, 109.0, 51.5, 43.4, 30.6, 19.7.

HRMS (ESI) Calcd for $C_{21}H_{20}NO_2S[M+H^+]$ 350.1209, found 350.1211.

HPLC Parameters for **4aa**: Daicel Chiralpak OD-H column, n-hexane/i-propanol = 97/3, flow rate: 0.8 mL/min, UV = 254 nm.

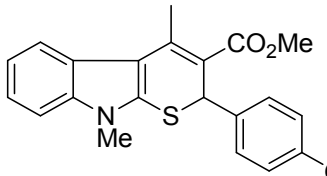


4ab, 33.1 mg, 91% yield, yellow solid, M.p: 141-146 °C.

^{1}H NMR (400 MHz, $CDCl_3$): δ 7.87-7.84 (m, 1H), 7.22-7.17 (m, 5H), 6.97 (d, *J* = 8.0 Hz, 2H), 5.55 (s, 1H), 3.75 (s, 3H), 3.58 (s, 3H), 3.00 (s, 3H), 2.24 (s, 3H).

^{13}C NMR (100 MHz, $CDCl_3$): δ 167.8, 147.2, 138.4, 137.9, 137.1, 135.8, 128.8, 127.1, 126.2, 121.3, 120.8, 119.8, 114.5, 110.0, 109.0, 51.5, 43.3, 30.6, 21.0, 19.7.

HRMS (ESI) Calcd for $C_{22}H_{22}NO_2S[M+H^+]$ 364.1366, found 364.1364.



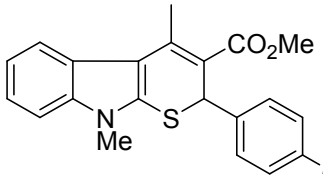
4ac, 27.7 mg, 73% yield, yellow solid, M.p: 144-150 °C.

^{1}H NMR (400 MHz, $CDCl_3$): δ 7.90 (d, *J* = 4.8 Hz, 1H), 7.28-7.22 (m, 5H), 6.72 (d,

J= 8.0 Hz, 2H), 5.58 (s, 1H), 3.79 (s, 3H), 3.71 (s, 3H), 3.60 (s, 3H), 3.03 (s, 3H).

^{13}C NMR (100 MHz, $CDCl_3$): δ 167.8, 158.8, 147.0, 138.4, 135.8, 132.8, 128.3, 126.1, 121.3, 120.8, 119.7, 114.4, 113.4, 110.2, 109.0, 55.0, 51.5, 43.1, 30.5, 19.6.

HRMS (ESI) Calcd for $C_{22}H_{22}NO_3S[M+H^+]$ 380.1315, found 380.1312.

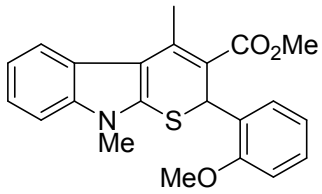


4ad, 31.4 mg, 80% yield, yellow solid, M.p: 181-187 °C.

^{1}H NMR (400 MHz, $CDCl_3$): δ 7.74 (d, *J* = 6.8 Hz, 1H), 7.13-7.06 (m, 5H), 6.91 (d, *J* = 8.0 Hz, 2H), 5.45 (s, 1H), 3.64 (s, 3H), 3.45 (s, 3H), 2.87 (s, 3H), 2.72-2.64 (m, 1H), 1.04 (d, *J* = 6.8 Hz, 6H).

^{13}C NMR (100 MHz, $CDCl_3$): δ 167.9, 147.8, 147.0, 138.4, 138.2, 136.0, 127.1, 126.2, 121.3, 120.8, 119.8, 114.5, 110.0, 109.0, 51.5, 43.2, 33.5, 30.6, 23.8, 19.7.

HRMS (ESI) Calcd for $C_{24}H_{26}NO_2S[M+H^+]$ 392.1679, found 392.1682.

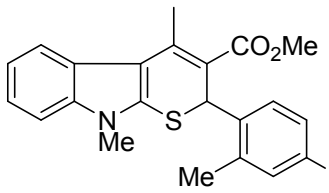


4ae, 26.2 mg, 69% yield, yellow oil.

^{1}H NMR (400 MHz, $CDCl_3$): δ 7.89 (d, *J* = 7.6 Hz, 1H), 7.21-7.12 (m, 4H), 7.05 (d, *J* = 7.2 Hz, 1H), 6.87 (d, *J* = 8.0 Hz, 1H), 6.66 (d, *J* = 8.0 Hz, 1H), 5.96 (s, 1H), 3.97 (s, 3H), 3.72 (s, 3H), 3.50 (s, 3H), 3.01 (s, 3H).

^{13}C NMR (100 MHz, $CDCl_3$): δ 167.9, 155.8, 147.8, 138.4, 137.3, 128.4, 128.3, 127.9, 126.2, 121.1, 120.7, 120.0, 119.7, 113.4, 110.5, 108.9, 108.9, 55.6, 51.4, 36.9, 30.4, 19.7.

HRMS (ESI) Calcd for $C_{22}H_{22}NO_3S[M+H^+]$ 380.1315, found 380.1316.



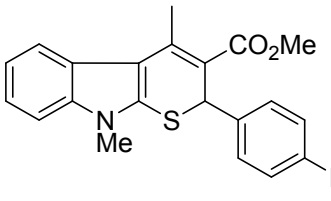
4af, 30.2 mg, 80% yield, yellow oil.

^{1}H NMR (400 MHz, $CDCl_3$): δ7.92-7.89 (m, 1H), 7.23-7.19 (m, 3H), 7.00 (t, *J* = 3.6 Hz, 2H), 6.71 (d, *J* = 8.0 Hz, 1H), 5.72 (s, 1H), 3.71 (s, 3H), 3.51 (s, 3H), 3.02 (s, 3H),

2.54 (s, 3H), 2.22 (s, 3H).

^{13}C NMR (100 MHz, $CDCl_3$): δ 167.7, 147.6, 138.5, 137.1, 135.7, 134.9, 134.6, 131.5, 127.5, 126.6, 126.2, 121.3, 120.8, 119.8, 114.0, 110.4, 109.0, 51.5, 39.8, 30.5, 20.9, 19.8, 19.7.

HRMS (ESI) Calcd for $C_{23}H_{24}NO_2S[M+H^+]$ 378.1522, found 378.1523.

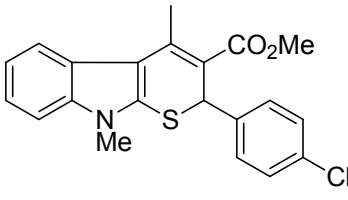


4ag, 34.9 mg, 95% yield, yellow solid, M.p: 165-169 °C.

^{1}H NMR (400 MHz, $CDCl_3$): δ 7.75-7.73 (m, 1H), 7.18-7.08 (m, 5H), 5.98 (s, 1H), 5.89 (s, 1H), 5.58 (s, 1H), 3.69 (s, 3H), 3.52 (s, 3H), 2.85 (s, 3H).

^{13}C NMR (100 MHz, $CDCl_3$): δ 167.8, 163.3, 160.9, 147.5, 138.6, 136.7 (d, J = 3.0 Hz), 135.6, 128.9 (d, J = 10.2 Hz), 126.2, 121.6, 121.1, 119.9, 115.0 (d, J = 21.4 Hz), 114.6, 110.1, 109.2, 51.7, 42.9, 30.8, 19.8.

HRMS (ESI) Calcd for $C_{21}H_{19}FNO_2S[M+H^+]$ 368.1115, found 368.1117.

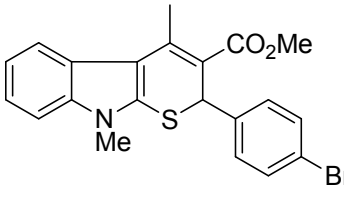


4ah, 34.6 mg, 90% yield, yellow solid, M.p: 195-198°C.

^{1}H NMR (400 MHz, $CDCl_3$): δ 7.75 (s, 1H), 7.15-7.01 (m, 7H), 5.42 (s, 1H), 3.66 (s, 3H), 3.48 (s, 3H), 2.89 (s, 3H).

^{13}C NMR (100 MHz, $CDCl_3$): δ 167.6, 147.6, 139.4, 138.4, 135.4, 133.0, 128.6, 128.2, 126.0, 121.6, 121.0, 119.8, 114.5, 109.6, 109.1, 51.6, 42.9, 30.7, 19.6.

HRMS (ESI) Calcd for $C_{21}H_{19}ClNO_2S[M+H^+]$ 384.0820, found 384.0821.



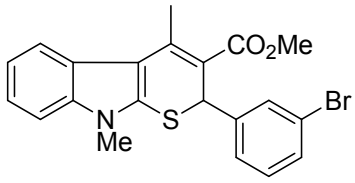
4ai, 39.4mg, 92% yield, yellow solid, M.p: 163-168 °C.

^{1}H NMR (400 MHz, $CDCl_3$): δ 7.75 (s, 1H), 7.19-7.07 (m, 7H), 5.40 (s, 1H), 3.67 (s, 3H), 3.51 (s, 3H), 2.89 (s, 3H).

^{13}C NMR (100 MHz, $CDCl_3$): δ 167.7, 147.7, 139.9, 138.5, 135.4, 131.2, 129.0, 126.1,

121.6, 121.3, 121.0, 119.8, 114.6, 109.5, 109.1, 51.6, 43.0, 30.7, 19.6.

HRMS (ESI) Calcd for $C_{21}H_{18}BrNNaO_2S$[M+Na$^+$] 450.0134, found 450.0131.

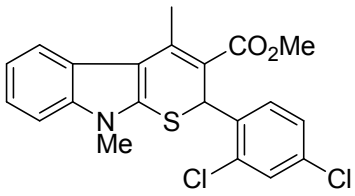


4aj, 39.8 mg, 93% yield, yellow solid, M.p: 169-175 °C.

^{1}H NMR (400 MHz, $CDCl_3$): δ7.87-7.84 (m, 1H), 7.48 (s, 1H), 7.28-7.25 (m, 1H), 7.22-7.18 (m, 4H), 7.00 (t, *J* = 8.0 Hz, 1H), 5.53 (s, 1H), 3.77 (s, 3H), 3.60 (s, 3H), 3.00 (s, 3H).

^{13}C NMR (100 MHz, $CDCl_3$): δ 167.6, 147.9, 143.3, 138.5, 135.5, 130.4, 130.4, 129.6, 126.1, 125.9, 122.1, 121.6, 121.0, 119.9, 114.6, 109.1, 109.0, 51.6, 42.9, 30.7, 19.6.

HRMS (ESI) Calcd for $C_{21}H_{18}BrNNaO_2S$[M+Na$^+$] 450.0134, found 450.0133.

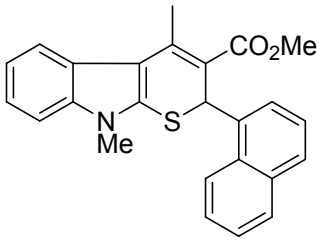


4ak, 40.1 mg, 96% yield, yellow solid, M.p: 171-175 °C.

^{1}H NMR (400 MHz, $CDCl_3$): δ 7.90 (d, *J* = 6.0 Hz, 1H), 7.40 (s, 1H), 7.27-7.22 (m, 3H), 7.07 (d, *J* = 8.4 Hz, 1H),6.94 (d, *J* = 8.0 Hz, 1H), 5.90 (s, 1H), 3.74 (s, 3H), 3.55 (s, 3H), 3.04 (s, 3H).

^{13}C NMR (100 MHz, $CDCl_3$): δ 167.3, 148.9, 138.5, 135.8, 135.7, 133.7, 133.0, 129.7, 129.6, 126.8, 126.0, 121.6, 121.1, 119.7, 113.7, 109.2, 108.7, 51.6, 39.8, 30.6, 19.6.

HRMS (ESI) Calcd for $C_{21}H_{18}Cl_2NO_2S$[M+H$^+$] 418.0430, found 418.0435.



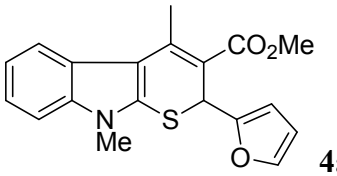
4al, 34.8 mg, 87% yield, yellow oil.

^{1}H NMR (400 MHz, $CDCl_3$): δ 8.30 (d, *J* = 8.8 Hz, 1H), 7.94 (d, *J* = 8.0 Hz, 1H), 7.86 (d, *J* = 8.0 Hz, 1H), 7.68-7.63 (m, 2H), 7.55-7.51 (m, 1H), 7.32 (d, *J* = 7.2 Hz, 1H), 7.24-7.11 (m, 4H), 6.43 (s, 1H), 3.67 (s, 3H), 3.39 (s, 3H), 3.09 (s, 3H).

^{13}C NMR (100 MHz, $CDCl_3$): δ 167.9, 148.3, 138.6, 136.6, 134.4, 134.0, 129.8, 129.3, 128.4, 126.3, 126.3, 126.2, 125.5, 125.3, 123.1, 121.4, 121.0, 119.9, 113.4, 110.0,

109.2, 51.7, 39.3, 30.6, 20.0.

HRMS (ESI) Calcd for $C_{25}H_{22}NO_2S[M+H^+]$ 400.1366, found 400.1367.

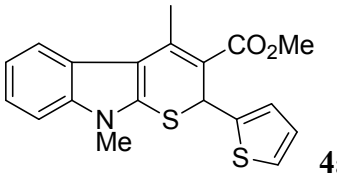


4am, 21.4 mg, 63% yield, yellow oil.

^{1}H NMR (400 MHz, $CDCl_3$): δ7.85-7.82 (m, 1H), 7.25-7.15 (m, 4H), 6.81 (t, *J* = 8.4 Hz, 2H), 5.51 (s, 1H), 3.74 (s, 3H), 3.57 (s, 3H), 2.96 (s, 3H).

^{13}C NMR (100 MHz, $CDCl_3$): δ 167.3, 152.2, 147.9, 142.2, 138.4, 135.8, 126.2, 121.4, 120.9, 119.8, 114.1, 110.3, 109.1, 108.8, 108.0, 51.6, 38.2, 30.7, 19.6.

HRMS (ESI) Calcd for $C_{19}H_{18}NO_3S[M+H^+]$ 340.1002, found 340.1002.

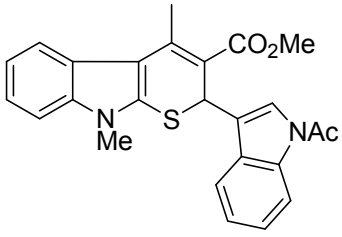


4an, 27.0 mg, 76% yield, yellow oil.

^{1}H NMR (400 MHz, $CDCl_3$): δ 7.87-7.84 (m, 1H), 7.28-7.20 (m, 3H), 6.96 (dd, *J* = 5.2 Hz, *J* = 1.2 Hz, 1H), 6.93-6.91 (m, 1H),6.75 (dd, *J* = 4.8 Hz, *J* = 3.6 Hz, 1H), 5.84 (s, 1H), 3.82 (s, 3H), 3.66 (s, 3H), 2.96 (s, 3H).

^{13}C NMR (100 MHz, $CDCl_3$): δ 167.4, 147.1, 145.7, 138.5, 135.7, 126.1, 126.0, 125.5, 124.1, 121.6, 121.0, 119.9, 114.6, 111.3, 109.1, 51.6, 40.0, 30.7, 19.5.

HRMS (ESI) Calcd for $C_{19}H_{18}NO_2S_2[M+H^+]$ 356.0773, found 356.0774.

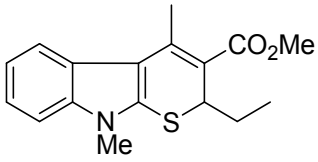


4ao, 40.1 mg, 93% yield, yellow oil.

^{1}H NMR (400 MHz, $CDCl_3$): δ8.34 (d, *J* = 6.0 Hz, 1H), 7.89-7.86 (m, 1H), 7.82-7.79 (m, 1H), 7.37-7.30 (m, 1H), 7.23-7.17 (m, 3H), 5.89 (s, 1H), 3.78 (s, 3H), 3.51 (s, 3H), 3.03 (s, 3H), 2.34 (s, 3H).

^{13}C NMR (100 MHz, $CDCl_3$): δ 168.2, 167.3, 147.2, 138.4, 136.3, 128.2, 126.1, 125.2, 125.0, 123.3, 121.5, 121.0, 119.6, 119.5, 119.3, 116.7, 113.8, 109.1, 109.0, 51.6, 36.5, 30.7, 23.7, 19.6.

HRMS (ESI) Calcd for $C_{25}H_{23}N_2O_3S[M+H^+]$ 431.1424, found 431.1420.

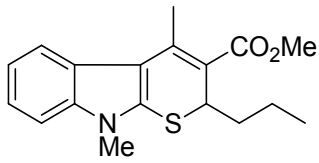


4ap, 28.8 mg, 96% yield, yellow oil.

^{1}H NMR (400 MHz, $CDCl_3$): δ7.83-7.80 (m, 1H), 7.31-7.26 (m, 1H), 7.24-7.16 (m, 2H), 4.22 (dd, *J* = 8.4 Hz, *J* = 6.8 Hz, 1H), 3.83 (s, 3H), 3.72 (s, 3H), 2.84 (s, 3H), 1.73-1.65 (m, 2H), 0.92 (t, *J* = 7.2 Hz, 3H).

^{13}C NMR (100 MHz, $CDCl_3$): δ 168.1, 145.1, 138.3, 136.3, 126.2, 121.2, 120.8, 119.7, 113.8, 112.4, 108.9, 51.3, 43.9, 30.6, 25.7, 19.5, 11.1.

HRMS (ESI) Calcd for $C_{17}H_{20}NO_2S[M+H^+]$ 302.1209, found 302.1210.

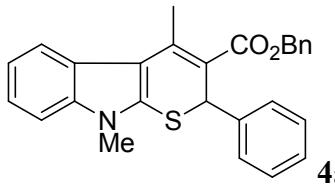


4aq, 28.4 mg, 90% yield, yellow solid, M.p: 90-94 °C.

^{1}H NMR (400 MHz, $CDCl_3$): δ 7.72-7.69 (m, 1H), 7.20-7.15 (m, 1H), 7.13-7.05 (m, 2H), 4.21 (dd, *J* = 8.4 Hz, *J* = 6.4 Hz, 1H), 3.72 (s, 3H), 3.60 (s, 3H), 2.72 (s, 3H), 1.59-1.48 (m, 2H), 1.40-1.31 (m, 1H), 1.26-1.17 (m, 1H), 0.74 (t, *J* = 7.2 Hz, 3H).

^{13}C NMR (100 MHz, $CDCl_3$): δ 168.0, 145.0, 138.3, 136.4, 126.2, 121.1, 120.8, 119.7, 113.7, 112.5, 108.9, 51.3, 41.6, 34.9, 30.7, 19.5, 19.4, 13.4.

HRMS (ESI) Calcd for $C_{18}H_{22}NO_2S[M+H^+]$ 316.1366, found 316.1364.

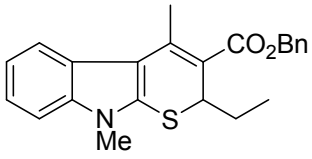


4ar, 39.2 mg, 92% yield, yellow oil.

^{1}H NMR (400 MHz, $CDCl_3$): δ 7.91-7.88 (m, 1H), 7.37-7.28 (m, 7H), 7.25-7.18 (m, 6H), 5.65 (s, 1H), 5.28 (d, *J* = 12.8 Hz, 1H), 5.24 (d, *J* = 12.8 Hz, 1H), 3.61 (s, 3H), 3.05 (s, 3H).

^{13}C NMR (100 MHz, $CDCl_3$): δ 167.0, 147.8, 141.1, 138.5, 136.4, 135.8, 128.4, 128.2, 127.8, 127.8, 127.4, 127.2, 126.1, 121.4, 120.9, 119.8, 114.5, 110.0, 109.0, 66.0, 43.5, 30.6, 19.8.

HRMS (ESI) Calcd for $C_{27}H_{24}NO_2S[M+H^+]$ 426.1522, found 426.1521.

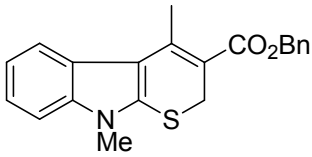


4as, 34.7 mg, 92% yield, yellow oil.

^{1}H NMR (400 MHz, $CDCl_3$): δ7.69 (d, *J* = 8.0 Hz, 1H), 7.35-7.23 (m, 5H), 7.17 (d, *J* = 7.6 Hz, 1H), 7.12-7.04 (m, 2H), 5.20 (d, *J* = 12.4 Hz, 1H), 5.14 (d, *J* = 12.4 Hz, 1H), 4.15 (dd, *J* = 8.4 Hz, *J* = 6.0 Hz, 1H), 3.59 (s, 3H), 2.74 (s, 3H), 1.63-1.53 (m, 3H), 0.78 (t, *J* = 7.2 Hz, 3H).

^{13}C NMR (100 MHz, $CDCl_3$): δ 167.3, 145.6, 138.3, 136.5, 128.5, 128.0, 127.9, 126.2, 121.3, 120.8, 119.7, 113.8, 112.3, 109.0, 66.0, 43.9, 30.7, 25.9, 19.7, 11.1.

HRMS (ESI) Calcd for $C_{23}H_{24}NO_2S[M+H^+]$ 378.1522, found 378.1523.

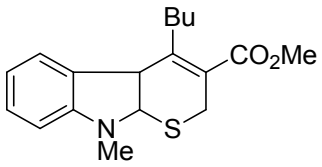


4at, 31.7 mg, 91% yield, yellow oil.

^{1}H NMR (400 MHz, $CDCl_3$): δ 7.66-7.63 (m, 1H), 7.35-7.21 (m, 5H), 7.16-7.04 (m, 3H), 5.17 (s, 2H), 3.84 (s, 2H), 3.56 (s, 3H), 2.72 (s, 3H).

^{13}C NMR (100 MHz, $CDCl_3$): δ 166.8, 148.3, 140.5, 138.2, 136.5, 128.5, 128.1, 128.0, 126.3, 121.6, 121.0, 119.8, 115.5, 109.0, 105.9, 66.0, 31.0, 29.4, 19.3.

HRMS (ESI) Calcd for $C_{21}H_{20}NO_2S[M+H^+]$ 350.1209, found 350.1211.

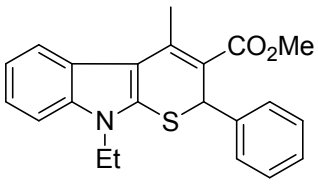


4au, 19.4 mg, 61% yield, yellow oil.

^{1}H NMR (400 MHz, $CDCl_3$): δ7.71-7.68 (m, 1H), 7.29-7.26 (m, 1H), 7.24-7.16 (m, 2H), 3.91 (s, 2H), 3.81 (s, 3H), 3.72 (s, 3H), 3.27-3.22 (m, 2H), 1.65-1.47 (m, 6H), 0.96 (t, *J* = 7.2 Hz, 3H).

^{13}C NMR (75 MHz, $CDCl_3$): δ 167.3, 152.9, 141.1, 138.2, 126.1, 121.6, 121.2, 119.4, 114.4, 109.1, 105.1, 51.3, 31.9, 31.3, 31.1, 29.6, 23.1, 14.0.

HRMS (ESI) Calcd for $C_{18}H_{24}NO_2S[M+H^+]$ 318.1522, found 318.1523.

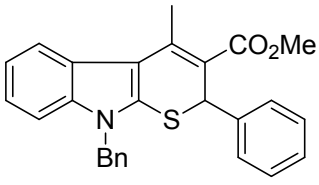


4ba, 33.8 mg, 93% yield, yellow solid, M.p: 154-158 °C.

^{1}H NMR (400 MHz, $CDCl_3$): δ7.88-7.86 (m, 1H), 7.31 (d, *J* = 7.6 Hz, 2H), 7.26-7.23 (m, 1H), 7.20-7.14 (m, 5H), 5.59 (s, 1H), 4.17-4.07 (m, 1H), 4.04-3.94 (m, 1H), 3.77 (s, 3H), 3.00 (s, 3H), 1.25 (t, *J* = 7.2 Hz, 3H).

^{13}C NMR (100 MHz, $CDCl_3$): δ 167.8, 147.3, 140.8, 137.3, 134.7, 128.1, 127.3, 127.1, 126.4, 121.3, 120.8, 119.9, 114.8, 110.1, 109.1, 51.5, 43.5, 39.3, 19.7, 15.0.

HRMS (ESI) Calcd for $C_{22}H_{22}NO_2S[M+H^+]$ 364.1366, found 364.1363.

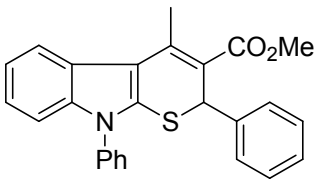


4ca, 40.0 mg, 94% yield, yellow solid, M.p: 147-150 °C.

^{1}H NMR (400 MHz, $CDCl_3$): δ7.88 (d, *J* = 8.0 Hz, 1H), 7.31-7.30 (m, 2H), 7.18-7.10 (m, 9H), 6.86 (d, *J* = 7.2 Hz, 2H), 5.57 (s, 1H), 5.31 (d, *J* = 16.4 Hz, 1H), 5.07 (d, *J* = 16.4 Hz, 1H), 3.76 (s, 3H), 3.02 (s, 3H).

^{13}C NMR (100 MHz, $CDCl_3$): δ 167.7, 147.4, 140.4, 137.8, 135.9, 135.0, 128.7, 128.1, 127.6, 127.3, 126.4, 121.6, 121.0, 119.8, 115.2, 110.8, 109.7, 51.6, 48.1, 43.7.

HRMS (ESI) Calcd for $C_{27}H_{24}NO_2S[M+H^+]$ 426.1522, found 426.1521.

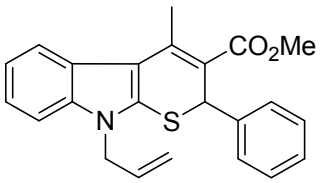


4da, 33.8 mg, 82% yield, yellow solid, M.p: 157-161 °C.

^{1}H NMR (400 MHz, $CDCl_3$): δ7.95 (d, *J* = 8.0 Hz, 1H), 7.57-7.47 (m, 3H), 7.34-7.27 (m, 5H), 7.24-7.17 (m, 5H), 5.55 (s, 1H), 3.61 (s, 3H), 3.07 (s, 3H).

^{13}C NMR (100 MHz, $CDCl_3$): δ 167.7, 146.8, 140.8, 138.8, 136.3, 135.5, 129.5, 128.4, 128.1, 127.3, 127.1, 127.0, 126.3, 121.9, 121.4, 119.9, 115.8, 111.7, 110.2, 51.6, 43.7, 19.7.

HRMS (ESI) Calcd for $C_{26}H_{22}NO_2S[M+H^+]$ 412.1366, found 412.1362.

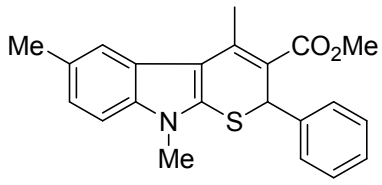


4ea, 34.5 mg, 92% yield, yellow solid, M.p: 136-141 °C.

^{1}H NMR (400 MHz, $CDCl_3$): δ7.88 (d, *J* = 6.8 Hz, 1H), 7.31 (d, *J* = 5.6 Hz, 2H), 7.20-7.14 (m, 6H), 5.84-5.76 (m, 1H), 5.57 (s, 1H),5.07 (d, *J* = 10.0 Hz, 1H), 4.79 (d, *J* = 16.8 Hz, 1H), 4.69 (d, *J* = 16.8 Hz, 1H), 4.52 (dd, *J* = 17.2 Hz, *J*= 3.6 Hz, 1H), 3.77 (s, 3H), 3.01 (s, 3H).

^{13}C NMR (100 MHz, $CDCl_3$): δ 167.8, 147.2, 140.6, 137.7, 135.1, 131.7, 128.0, 127.3, 127.2, 126.2, 121.5, 120.9, 119.9, 117.3, 115.0, 110.5, 109.4, 51.5, 46.5, 43.5, 19.7.

HRMS (ESI) Calcd for $C_{23}H_{22}NO_2S[M+H^+]$ 376.1366, found 376.1363.

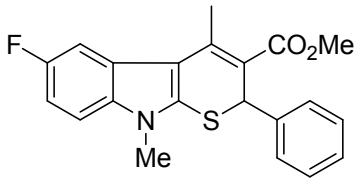


4fa, 30.8 mg, 85% yield, yellow oil.

^{1}H NMR (400 MHz, $CDCl_3$): δ7.64 (s, 1H), 7.32-7.29 (m, 2H), 7.19-7.13 (m, 3H), 7.09 (d, *J* = 8.0 Hz, 1H), 7.00 (d, *J* = 8.0 Hz, 1H), 5.56 (s, 1H), 3.75 (s, 3H), 3.55 (s, 3H), 2.98 (s, 3H), 2.48 (s, 3H).

^{13}C NMR (100 MHz, $CDCl_3$): δ 167.9, 147.7, 141.0, 136.9, 135.7, 130.3, 128.1, 127.3, 127.2, 126.4, 122.7, 119.9, 114.2, 109.5, 108.7, 51.5, 43.4, 30.7, 21.7, 19.7.

HRMS (ESI) Calcd for $C_{22}H_{22}NO_2S[M+H^+]$ 364.1366, found 364.1367.

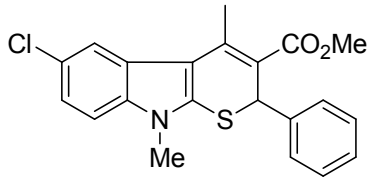


4ga, 33.0 mg, 90%yield, yellow oil.

^{1}H NMR (400 MHz, $CDCl_3$): δ7.49 (dd, *J* = 10.4 Hz, *J* = 2.0 Hz, 1H), 7.29 (d, *J* = 6.4 Hz, 2H), 7.20-7.14 (m, 3H), 7.09 (dd, *J* = 8.8 Hz, *J* = 4.4 Hz, 1H), 6.93-6.87 (m, 1H), 5.57 (s, 1H), 3.75 (s, 3H), 3.56 (s, 3H), 2.93 (s, 3H).

^{13}C NMR (100 MHz, $CDCl_3$): δ 167.7, 159.6, 157.3, 146.8, 140.7, 137.3, 135.0, 128.2, 127.4, 127.2, 126.5 (d, *J* = 10.2 Hz), 114.3 (d, *J* = 4.1 Hz), 110.2, 109.5 (d, *J* = 9.9Hz), 109.2 (d, *J* = 25.7 Hz), 105.5 (d, *J* = 25.2 Hz), 51.6, 43.5, 30.9, 19.3.

HRMS (ESI) Calcd for $C_{21}H_{19}FNO_2S[M+H^+]$ 368.1115, found 364.1116.



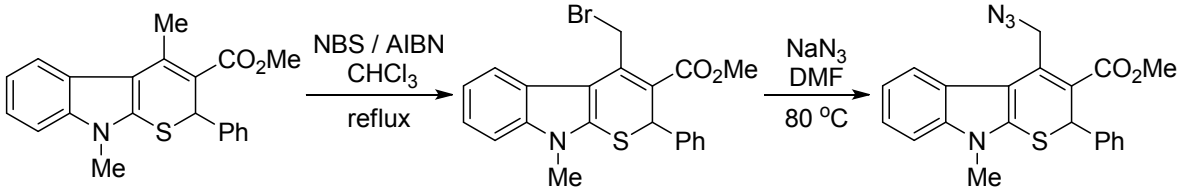
4ha, 31.1 mg, 81%yield, yellow oil.

^{1}H NMR (400 MHz, $CDCl_3$): δ7.82 (s, 1H), 7.32-7.29 (m, 2H), 7.22-7.19 (m, 3H), 7.14 (s, 2H), 5.59 (s, 1H), 3.78 (s, 3H), 3.59 (s, 3H), 2.96 (s, 3H).

^{13}C NMR (100 MHz, $CDCl_3$): δ 167.7, 146.6, 140.6, 137.1, 136.9, 128.2, 127.5, 127.2, 127.0, 126.7, 121.5, 119.3, 114.0, 110.6, 109.9, 51.6, 43.5, 30.9, 19.6.

HRMS (ESI) Calcd for $C_{21}H_{19}ClNO_2S[M+H^+]$ 384.0820, found 384.0823.

4. Synthetic Transformations of 4aa



4aa **5** **6**

To a solution of **4aa** (174.5 mg, 0.5 mmol) in $CHCl_3$(5 mL) was added NBS (106.8 mg, 0.6 mmol) and AIBN (8.3 mg, 0.05 mmol) at room temperature. The mixture was refluxed for 16h. After completion, the reaction solution was cooled down to room temperature and diluted with diethyl ether. The mixture was filtrated and filtrate was concentrated under reduce pressure. The residue was purified by silica gel column chromatography(petroleum ether/ethyl acetate) to afford **5**.

5, 175.5 mg, 82% yield, yellow foam.

^{1}H NMR (300 MHz, $CDCl_3$): δ8.12-8.07 (m, 1H), 7.41-7.37 (m, 2H), 7.25-7.16 (m, 6H), 5.80 (d, *J* = 9.3 Hz, 1H), 5.59 (s, 1H), 4.85 (d, *J* = 9.0 Hz, 1H), 3.80 (s, 3H), 3.60 (s, 3H).

^{13}C NMR (75 MHz, $CDCl_3$): δ 166.4, 146.0, 139.9, 138.5, 137.8, 128.3, 127.6, 127.2, 125.0, 122.0, 121.6, 120.0, 112.5, 109.5, 109.2, 52.0, 42.9, 30.9, 29.5.

HRMS (ESI) Calcd for $C_{21}H_{18}BrNNaO_2S$[M+Na^+] 450.0134, found 450.0131.

Compound **5** (85.6 mg, 0.2 mmol) was dissolved in DMF (2 mL). To the solution was added sodium azide (26.0 mg, 0.4 mmol) and heated at 80 °C for two hour. After finished reaction, water was added and exacted by ethyl acetate (30 mL). The organic layer was concentrated and the residue was directly subjected to silica gel column chromatography (petroleum ether/ethyl acetate as eluent) to give product **6**.

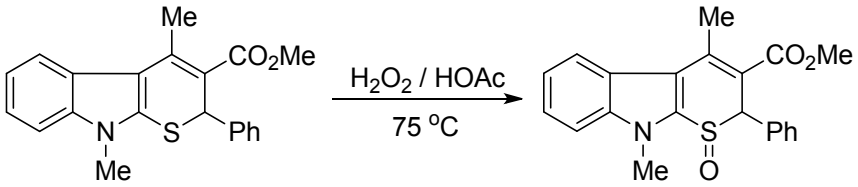
6, 57.7 mg, 74% yield, yellow oil.

^{1}H NMR (300 MHz, $CDCl_3$): δ7.92-7.87 (m, 1H), 7.39-7.35 (m, 2H), 7.24-7.17 (m, 6H), 5.64 (s, 1H), 5.44 (d, *J* = 12.3 Hz, 1H), 4.51 (d, *J* = 12.3 Hz, 1H), 3.81 (s, 3H), 3.61 (s, 3H).

^{13}C NMR (75 MHz, $CDCl_3$): δ 166.9, 142.5, 139.7, 138.5, 137.3, 128.4, 127.7, 127.1,

125.4, 122.1, 121.6, 119.6, 112.9, 112.2, 109.2, 52.1, 49.1, 43.3, 30.9.

HRMS (ESI) Calcd for $C_{21}H_{19}N_4O_2S[M+H^+]$ 391.1223, found 391.1225.



4aa **7**

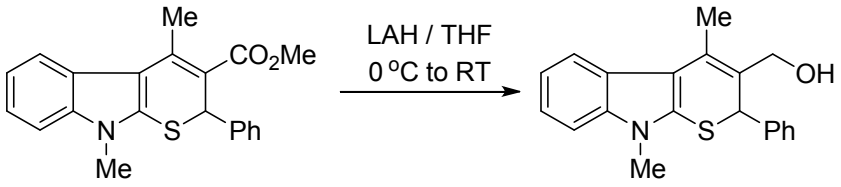
To a solution of **4aa** (34.9 mg, 0.1 mmol) was added 30% H_2O_2 (0.6 mL) and HOAc (0.4 mL). The mixture was heated at 75 °C for 10h. After completion, the reaction solution was cooled down to room temperature and then diluted by diethyl ether (30 mL). The mixture liquid was washed respectively by saturated sodium bicarbonate solution and brine. The organic phase was dried over anhydrous Na_2SO_4 and concentrated under reduce pressure. The residue was purified by silica gel column chromatography(petroleum ether/ethyl acetate) to afford **7**.

7, 16.8 mg, 46% yield, yellow oil.

^{1}H NMR (300 MHz, $CDCl_3$): δ8.15 (d, *J* = 8.1 Hz, 1H), 7.43-7.40 (m, 2H), 7.36-7.29 (m, 1H), 7.20-7.14 (m, 5H), 6.08 (s, 1H), 3.86 (s, 3H), 3.75 (s, 3H), 3.12 (s, 3H).

^{13}C NMR (75 MHz, $CDCl_3$): δ 167.0, 145.3, 138.8, 132.4, 128.9, 128.8, 128.4, 125.1, 124.4, 122.8, 122.2, 116.6, 114.3, 110.8, 66.1, 52.0, 30.5, 20.0.

HRMS (ESI) Calcd for $C_{21}H_{20}NO_3S[M+H^+]$ 366.1158, found 366.1158.



4aa **8**

To solution of **4aa** (69.8 mg, 0.2 mmol) in THF (2 mL) was added $LiAlH_4$ (9.2 mg, 0.24 mmol) below 0℃. Then the mixture was stirred at room temperature for one hour. After completion, the reaction was quenched with saturated ammonium chloride solution. The organic phase was separated and aqueous phase was extracted with

ethyl acetate (3×15 mL). Combined the organic layers, which was dried over anhydrous Na_2SO_4 and concentrated under reduce pressure. The residue was purified by silica gel column chromatography(petroleum ether/ethyl acetate) to afford **8**.

8, 58.5 mg, 91% yield, yellow foam.

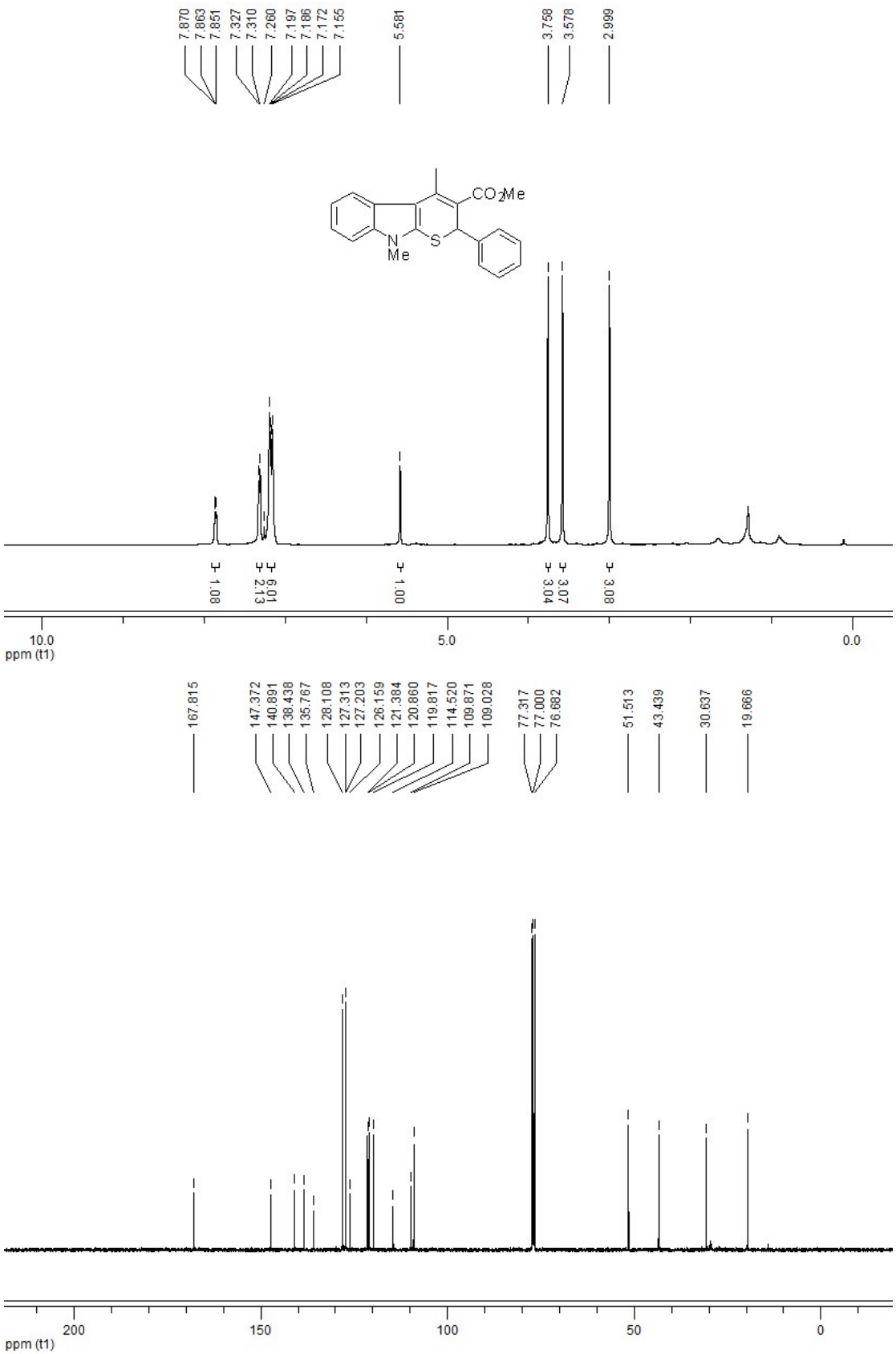
^{1}H NMR (300 MHz, $CDCl_3$): δ7.83-7.78 (m, 1H), 7.29-7.27 (m, 1H), 7.26-7.20 (m, 2H), 7.19-7.13 (m, 5H), 4.95 (s, 1H), 4.68 (d, *J* = 12.3 Hz, 1H), 4.07 (d, *J* = 12.3 Hz, 1H), 3.55 (s, 3H), 2.57 (s, 3H).

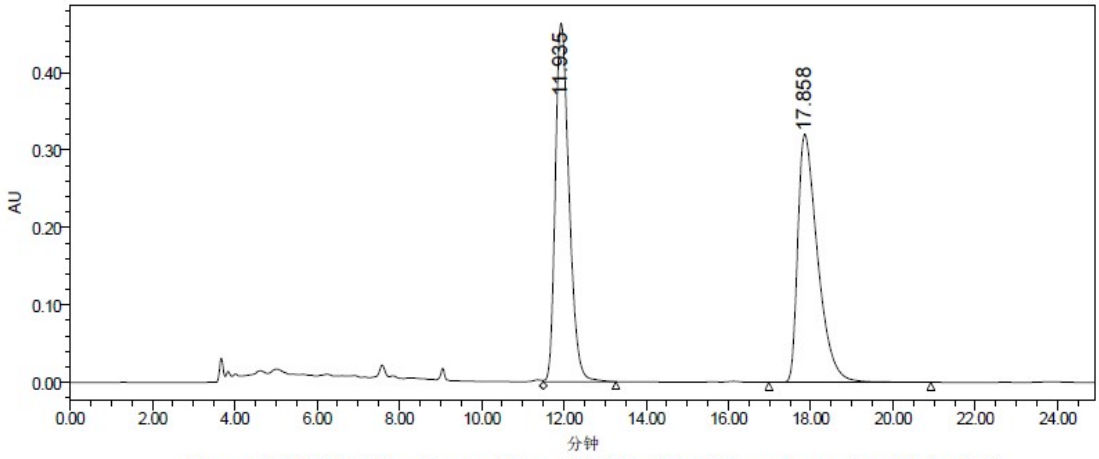
^{13}C NMR (75 MHz, $CDCl_3$): δ 141.4, 138.0, 131.8, 130.5, 128.4, 127.6, 127.4, 125.8, 120.5, 120.1, 120.0, 119.1, 112.4, 108.8, 61.6, 45.7, 30.3, 16.7.

HRMS (ESI) Calcd for $C_{20}H_{20}NOS[M+H^+]$ 322.1260, found 322.1261.

5. NMR and HPLC Spectra

4aa

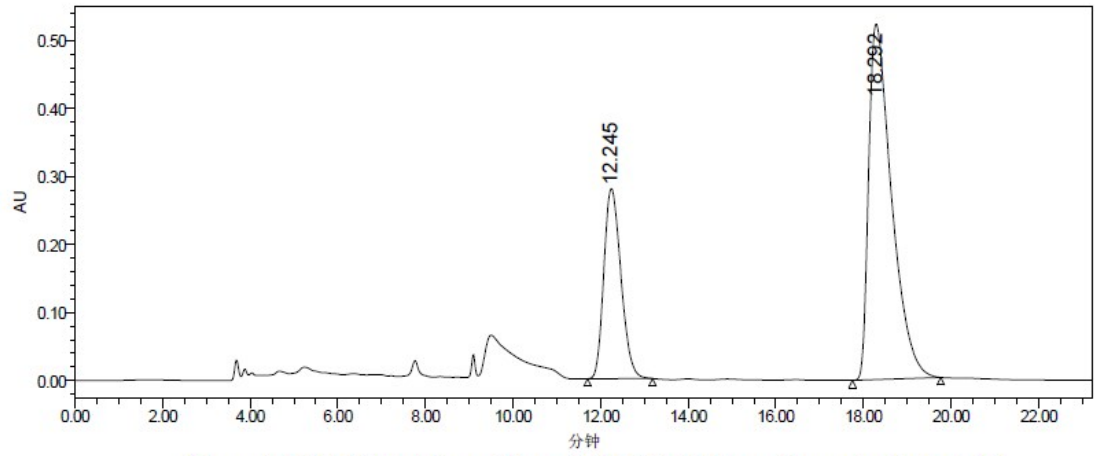




Channel: W2489 ChA; Channel Desc.: W2489 ChA 254nm; Processing Method: 01

	Channel Description	RT (min)	Area (礦*sec)	% Area	Height (礦)
1	W2489 ChA 254nm	11.935	10713293	49.97	462903
2	W2489 ChA 254nm	17.858	10725230	50.03	320318

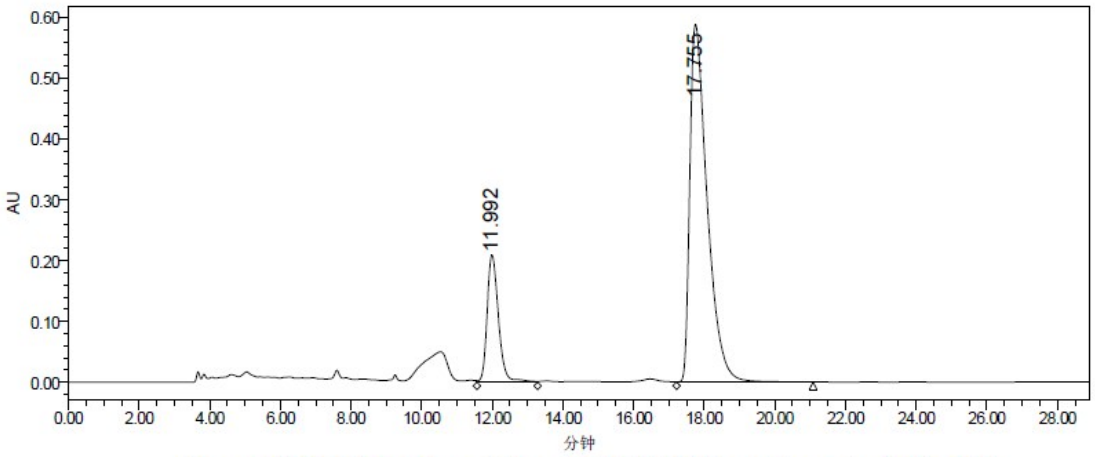
9a as chiral Lewis base catalyst



Channel: W2489 ChA; Channel Desc.: W2489 ChA 254nm; Processing Method: 01

	Channel Description	RT (min)	Area (礦*sec)	% Area	Height (礦)
1	W2489 ChA 254nm	12.245	7580302	28.52	279662
2	W2489 ChA 254nm	18.292	18998486	71.48	523475

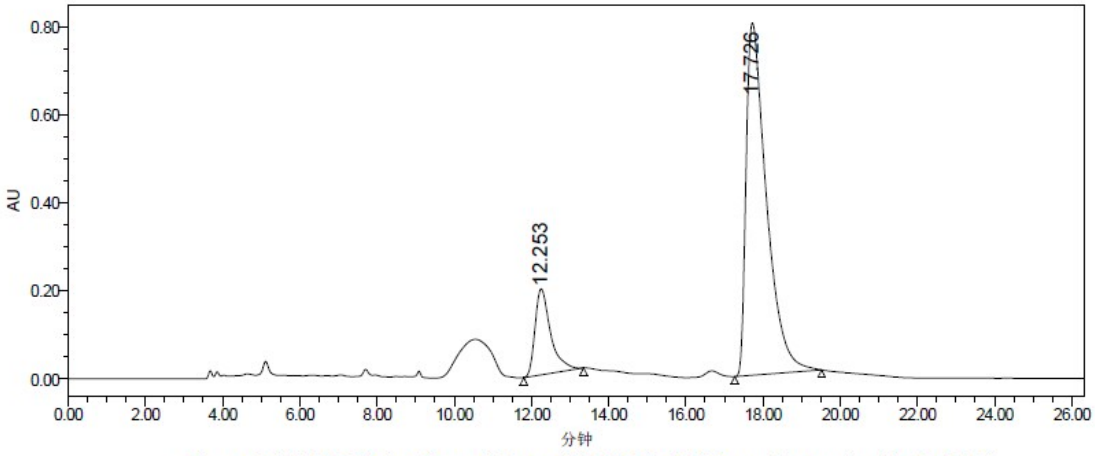
9b as chiral Lewis base catalyst



Channel: W2489 ChA; Channel Desc.: W2489 ChA 254nm; Processing Method: 01

	Channel Description	RT (min)	Area (礦*sec)	% Area	Height (礦)
1	W2489 ChA 254nm	11.992	4670118	18.85	209409
2	W2489 ChA 254nm	17.755	20108883	81.15	588913

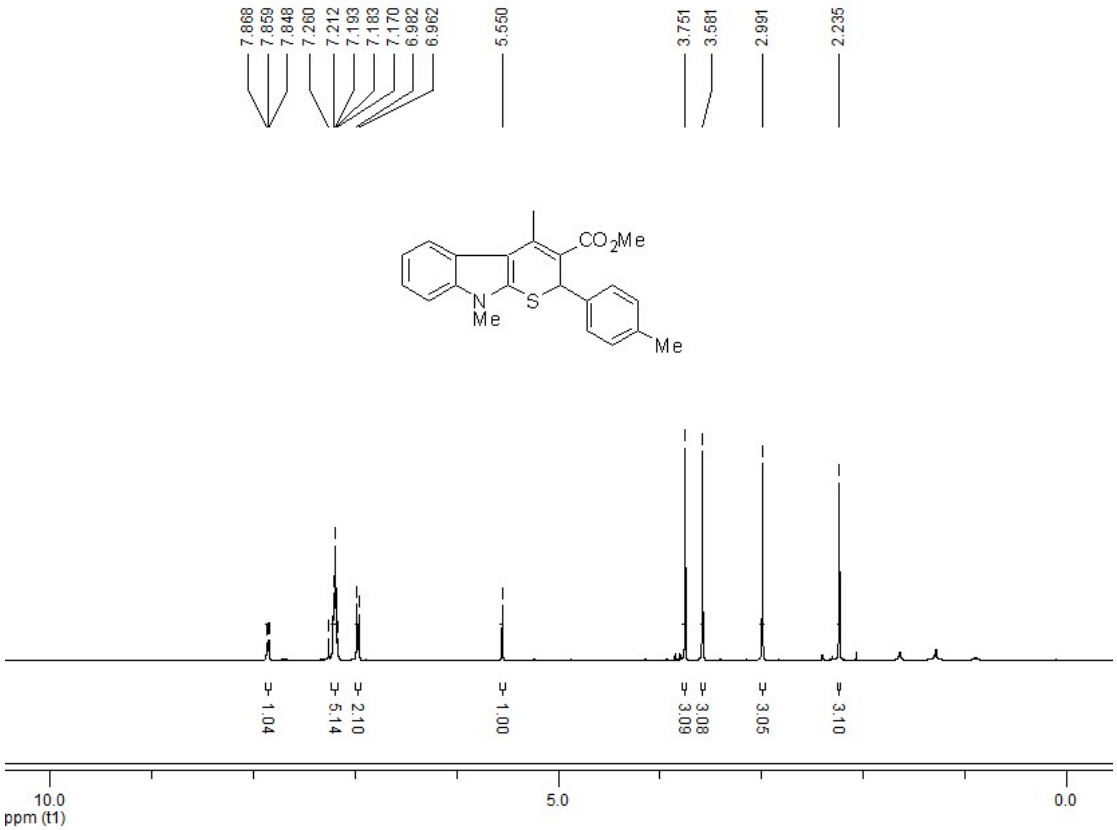
9c as chiral Lewis base catalyst

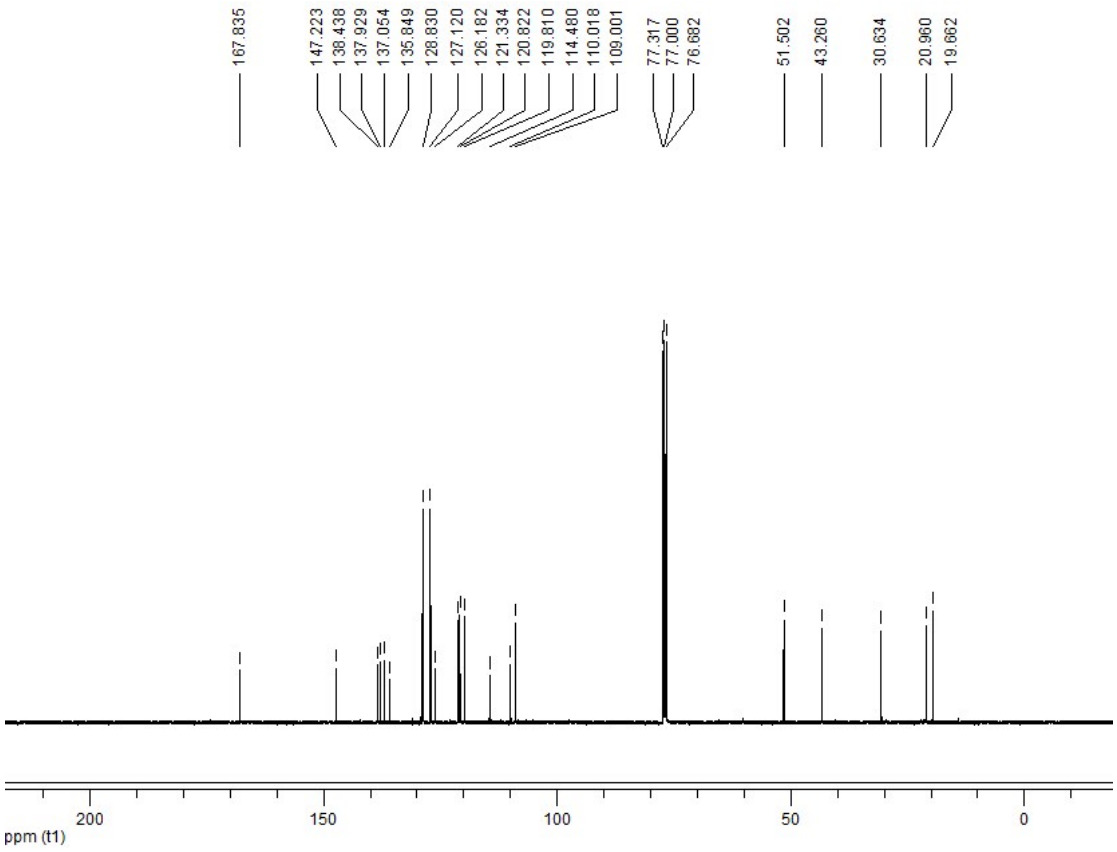


Channel: W2489 ChA; Channel Desc.: W2489 ChA 254nm; Processing Method: 01

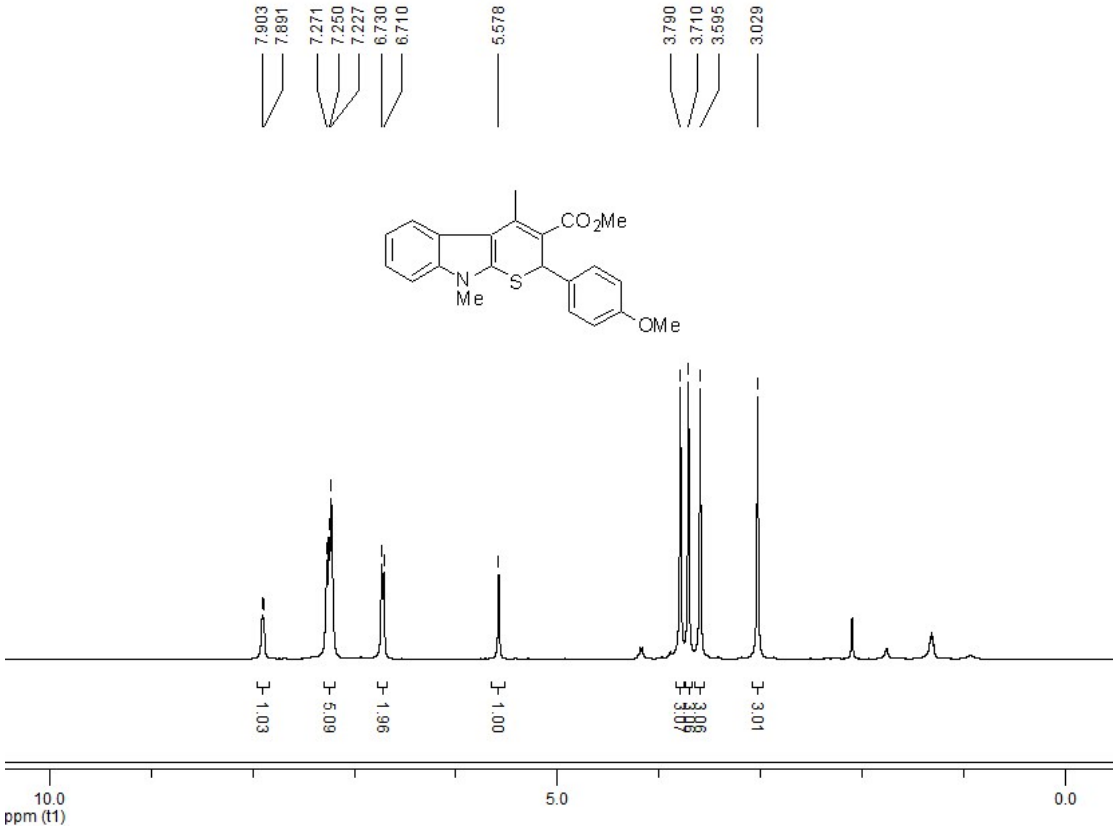
	Channel Description	RT (min)	Area (礦*sec)	% Area	Height (礦)
1	W2489 ChA 254nm	12.253	5468982	15.74	195230
2	W2489 ChA 254nm	17.726	29285209	84.26	801394

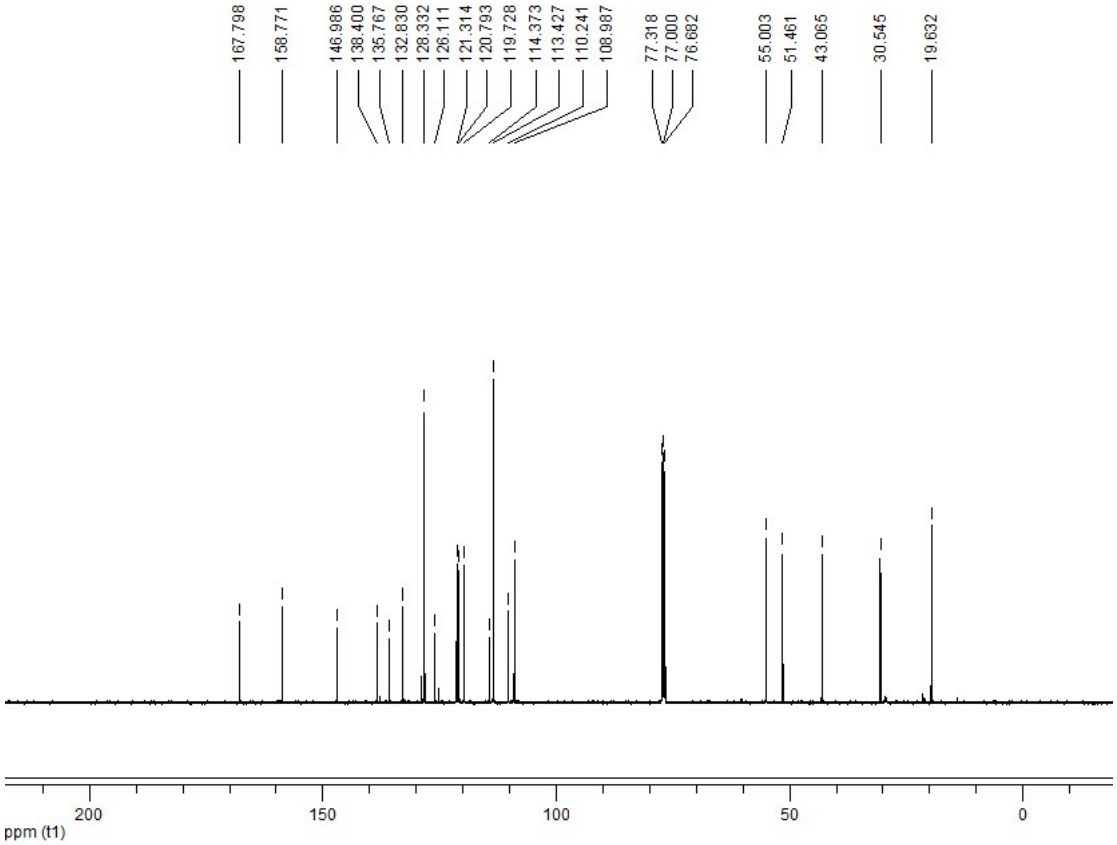
4ab


7.868
7.859
7.848
7.260
7.212
7.193
7.183
7.170
6.982
6.962
5.550
3.751
3.581
2.991
2.235
CO2Me
N
Me
S
Me
1.04
5.14
2.10
1.00
3.09
3.08
3.05
3.10
10.0
ppm (t1)
5.0
0.0

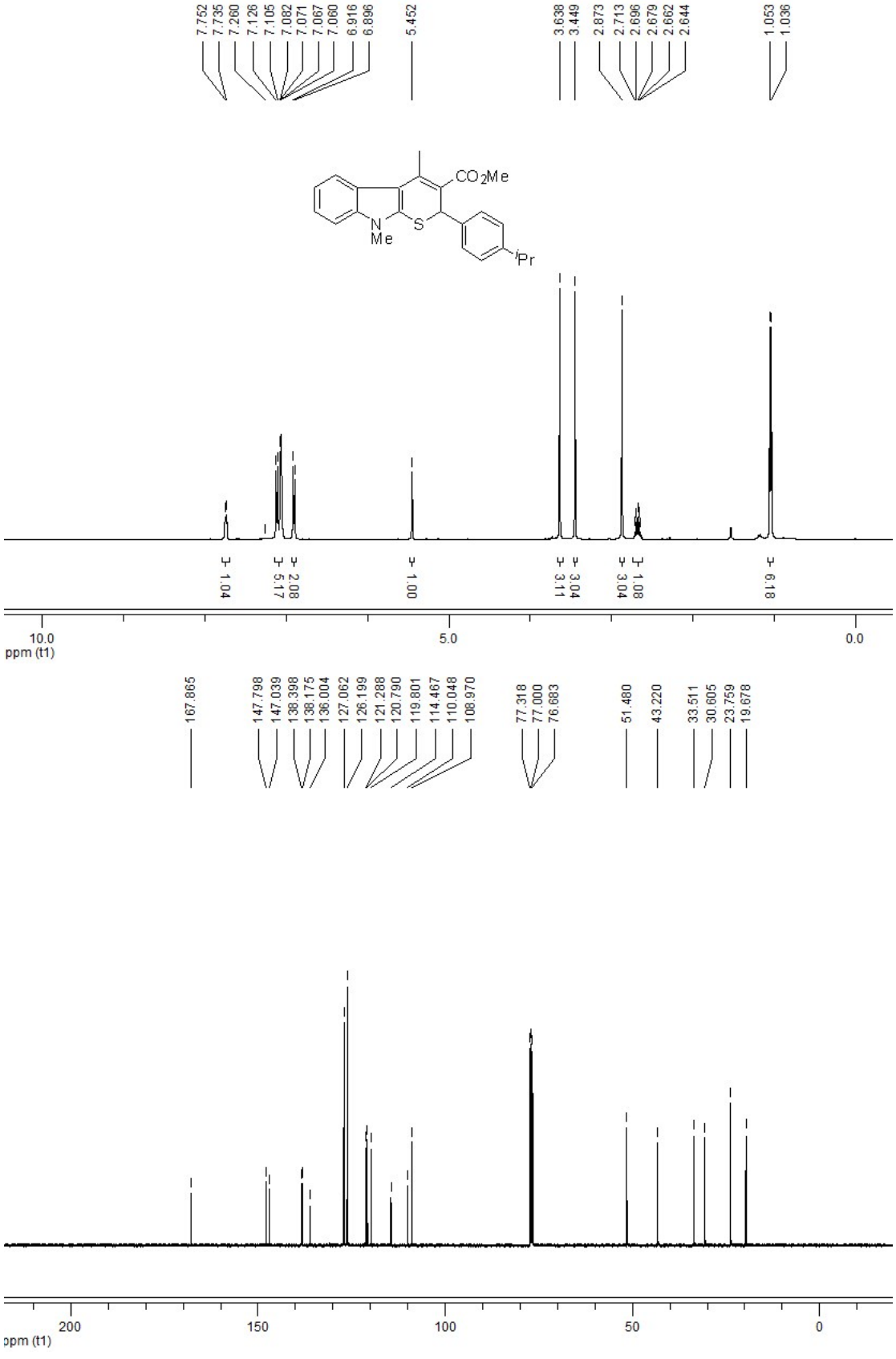

167.835
147.223
138.438
137.929
137.054
135.849
128.830
127.120
126.182
121.334
120.822
119.810
114.480
110.018
109.001
77.317
77.000
76.682
51.502
43.260
30.634
20.960
19.662
200
150
100
50
0
ppm (t1)

4ac

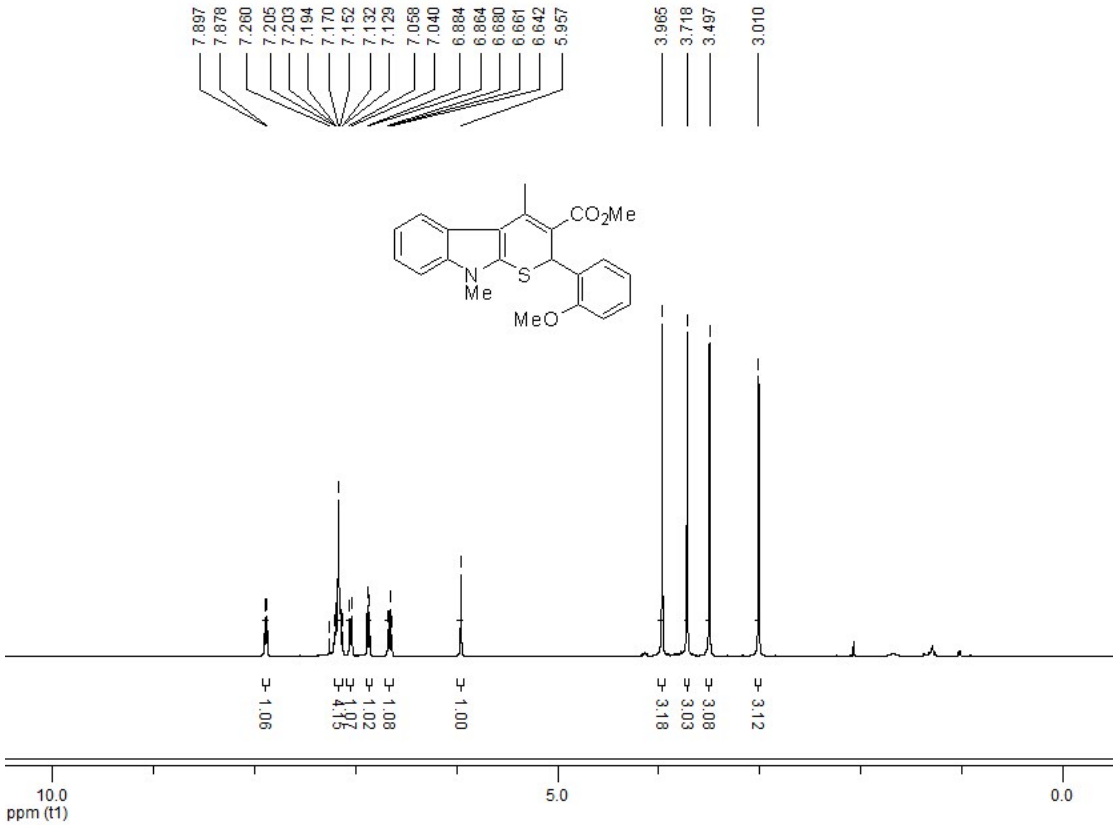

7.903
7.891
7.271
7.250
7.227
6.730
6.710
5.578
3.790
3.710
3.595
3.029
CO2Me
N
Me
S
OMe
1.03
6.09
1.96
1.00
3.08
3.01
10.0
5.0
0.0
ppm (t1)

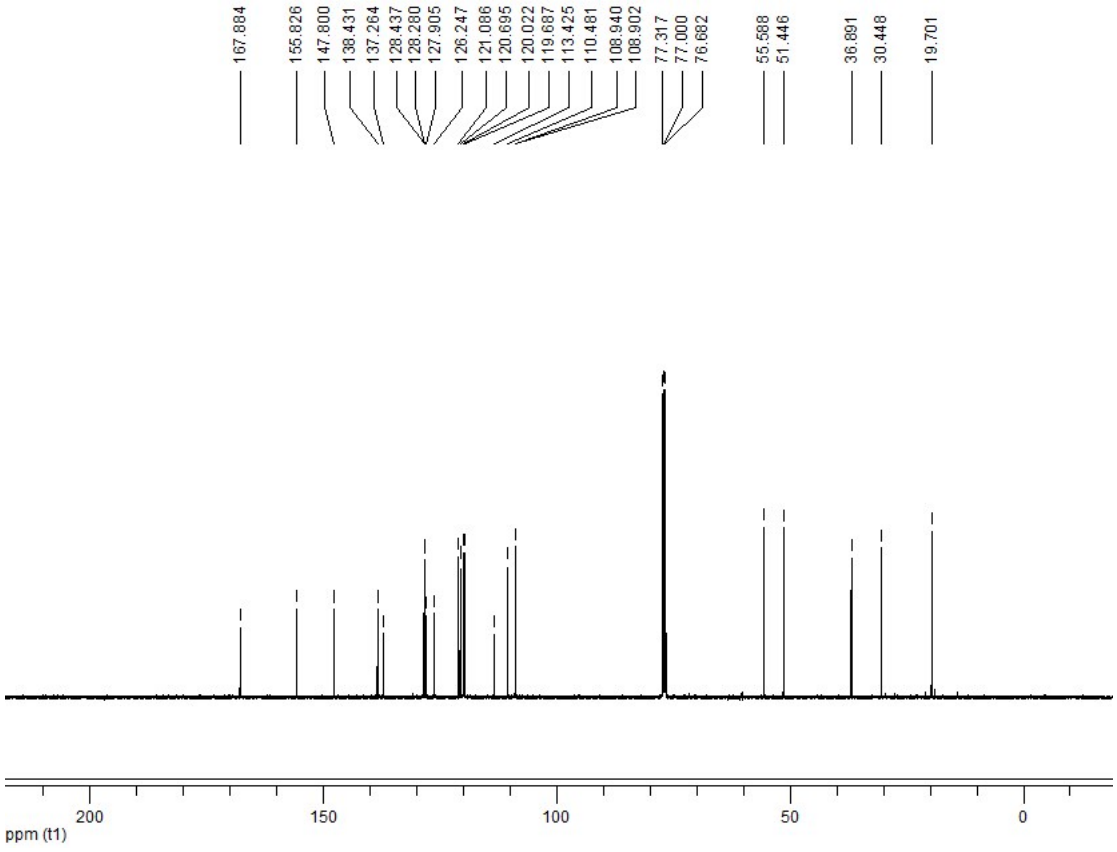

167.798
158.771
146.986
138.400
135.767
132.830
128.332
126.111
121.314
120.793
119.728
114.373
113.427
110.241
108.987
77.318
77.000
76.682
55.003
51.461
43.065
30.545
19.632
200
150
100
50
0
ppm (t1)

4ad

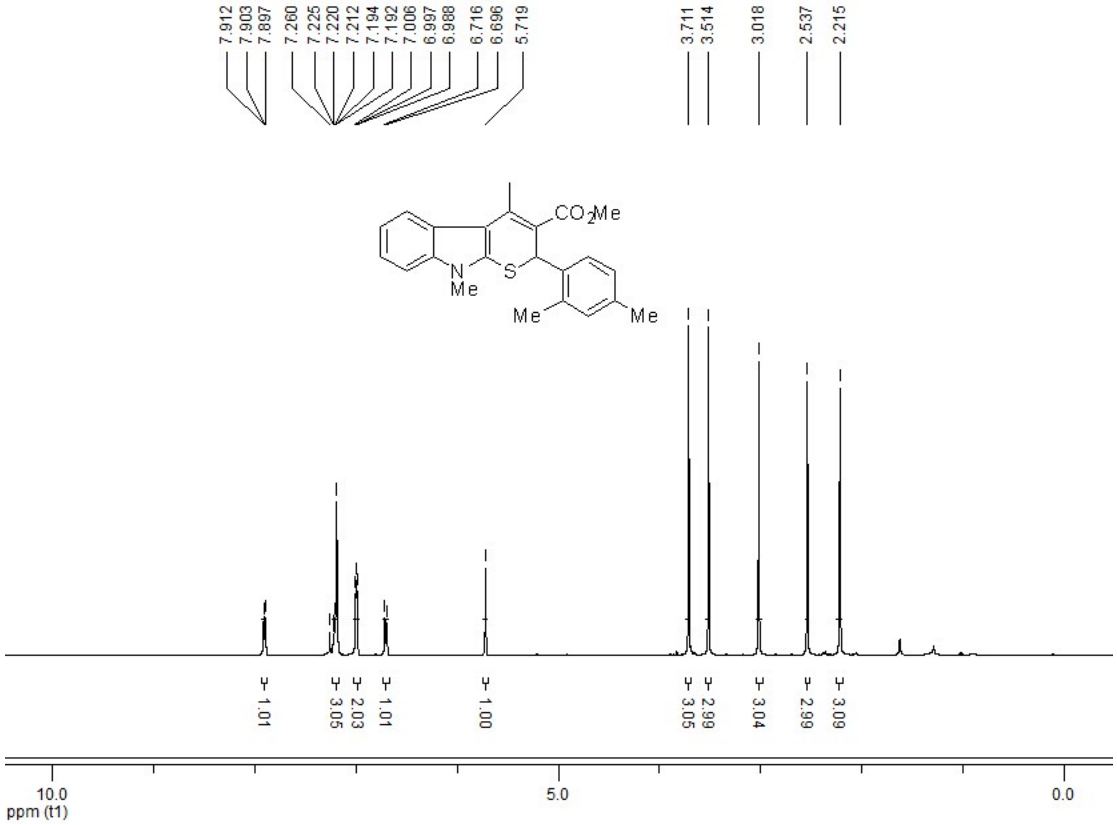

7.752
7.735
7.260
7.126
7.105
7.082
7.071
7.067
7.060
6.916
6.896
5.452
3.638
3.449
2.873
2.713
2.696
2.679
2.662
2.644
1.053
1.036
CO2Me
N
Me
S
iPr
1.04
5.17
2.08
1.00
3.11
3.04
3.04
1.08
6.18
10.0
ppm (t1)
5.0
0.0
167.865
147.798
147.039
138.398
138.175
136.004
127.062
126.199
121.288
120.790
119.801
114.467
110.048
108.970
77.318
77.000
76.683
51.480
43.220
33.511
30.605
23.759
19.678
200
150
100
50
0
ppm (t1)

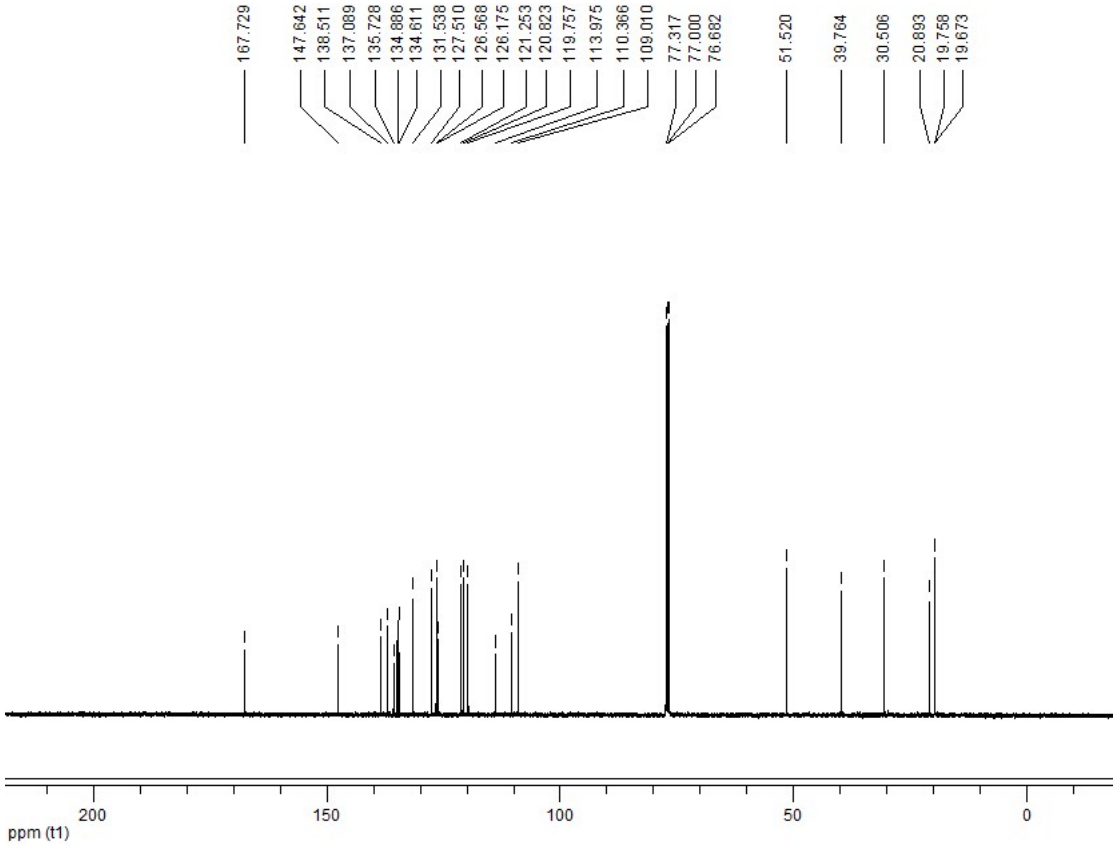
4ae


7.897
7.878
7.260
7.205
7.203
7.194
7.170
7.152
7.132
7.129
7.058
7.040
6.884
6.864
6.680
6.661
6.642
5.957
3.965
3.718
3.497
3.010
CO2Me
N
Me
S
MeO
1.06
4.75
4.73
1.07
1.02
1.08
1.00
3.18
3.03
3.08
3.12
10.0
5.0
0.0
ppm (t1)

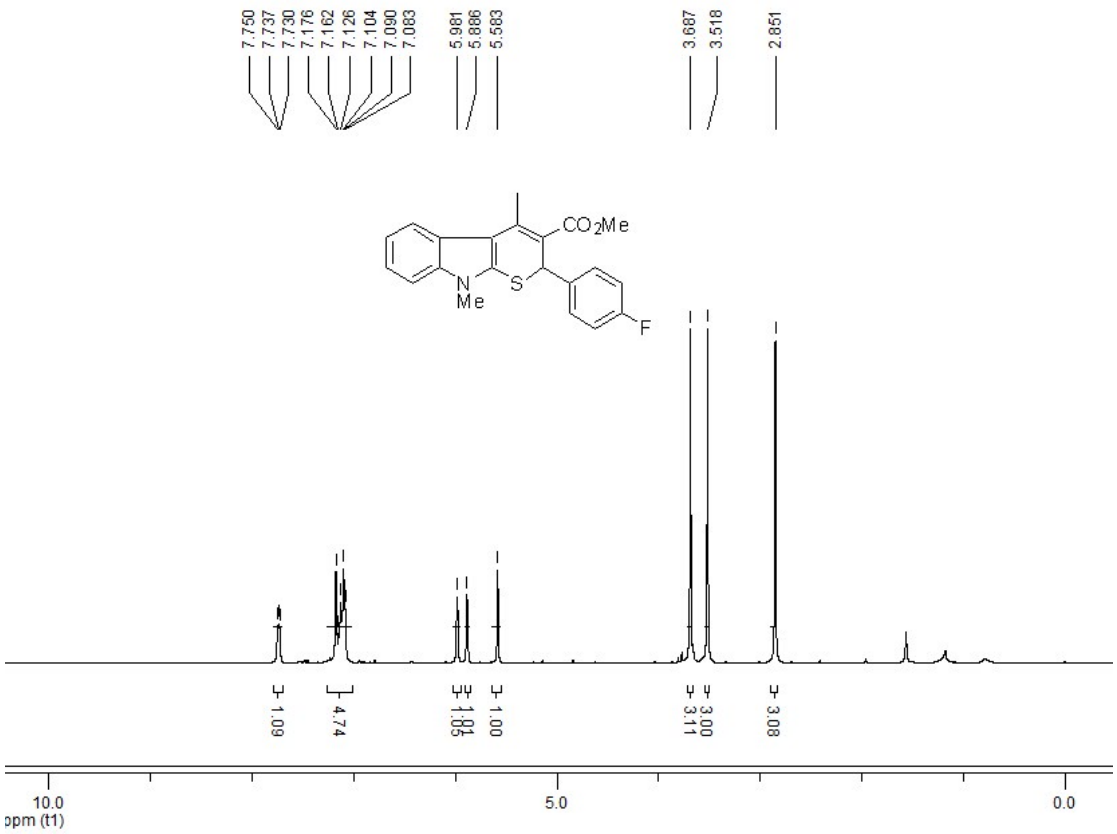

167.884
155.826
147.800
138.431
137.264
128.437
128.280
127.905
126.247
121.086
120.695
120.022
119.687
113.425
110.481
108.940
108.902
77.317
77.000
76.682
55.588
51.446
36.891
30.448
19.701
200
150
100
50
0
ppm (t1)

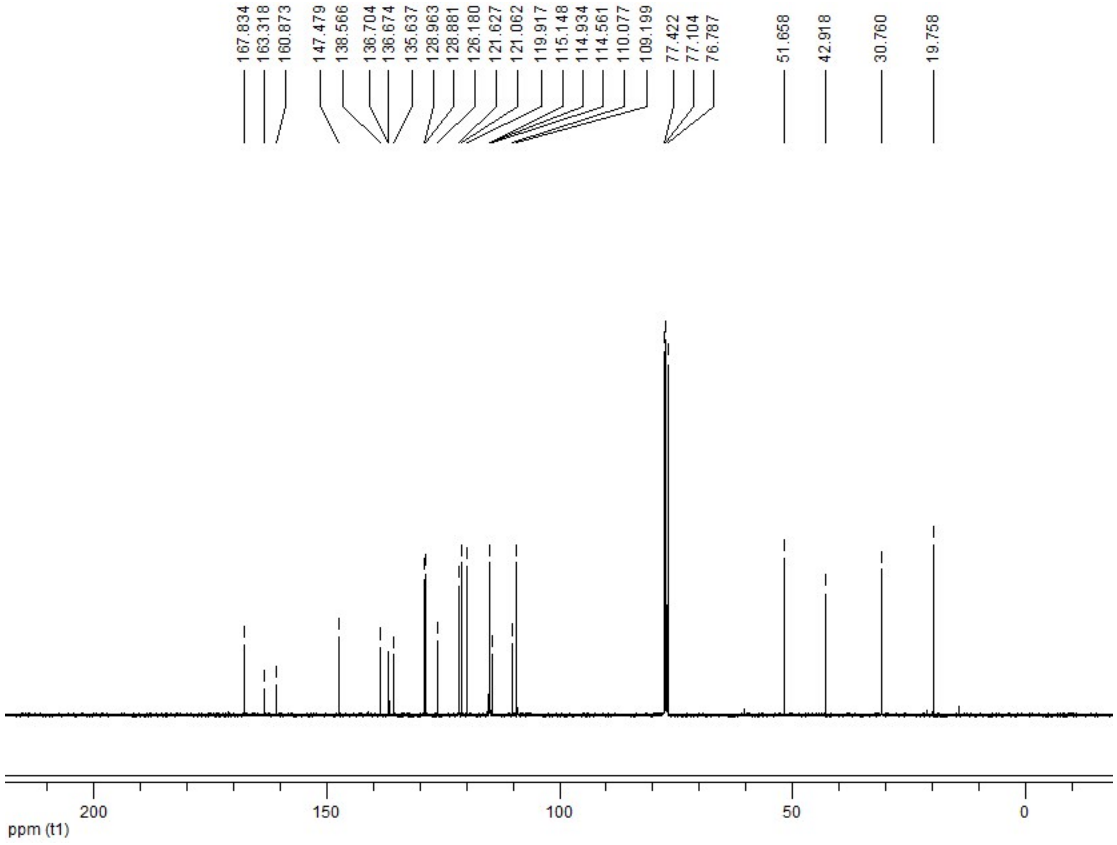
4af


7.912
7.903
7.897
7.260
7.225
7.220
7.212
7.194
7.192
7.006
6.997
6.988
6.716
6.696
5.719
3.711
3.514
3.018
2.537
2.215
CO2Me
N
Me
S
Me
Me
1.01
3.05
2.03
1.01
1.00
3.05
2.99
3.04
2.99
3.09
10.0
5.0
0.0
ppm (t1)

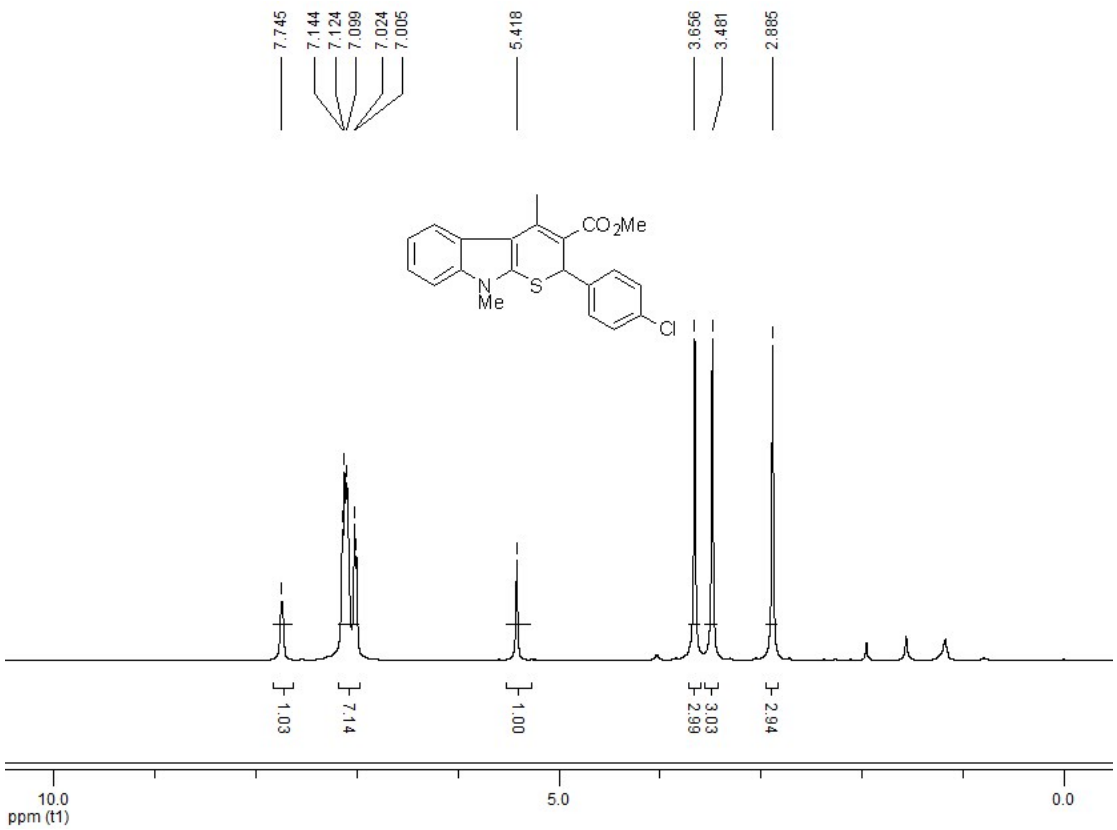

167.729
147.642
138.511
137.089
135.728
134.886
134.611
131.538
127.510
126.568
126.175
121.253
120.823
119.757
113.975
110.366
109.010
77.317
77.000
76.682
51.520
39.764
30.506
20.893
19.758
19.673
200
150
100
50
0
ppm (t1)

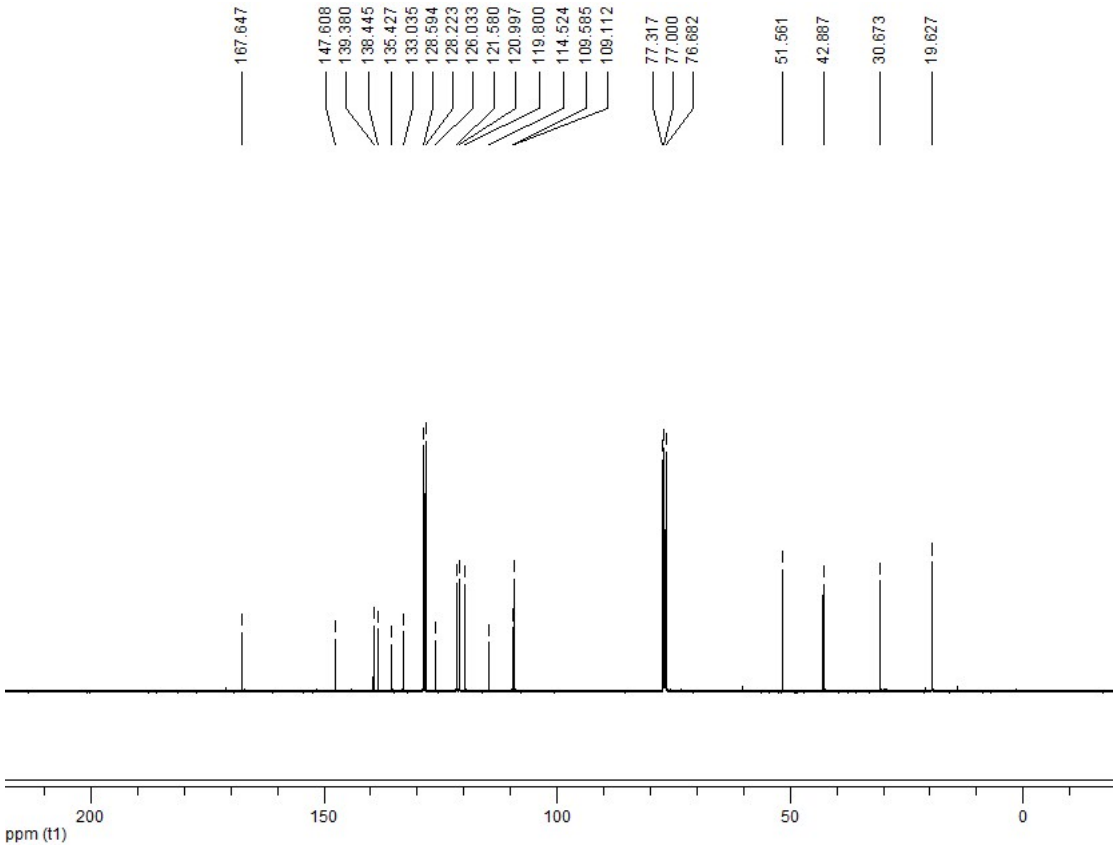
4ag


7.750
7.737
7.730
7.176
7.162
7.126
7.104
7.090
7.083
5.981
5.886
5.583
3.687
3.518
2.851
CO2Me
N
Me
S
F
1.09
4.74
1.05
1.00
3.11
3.00
3.08
10.0
ppm (t1)
5.0
0.0

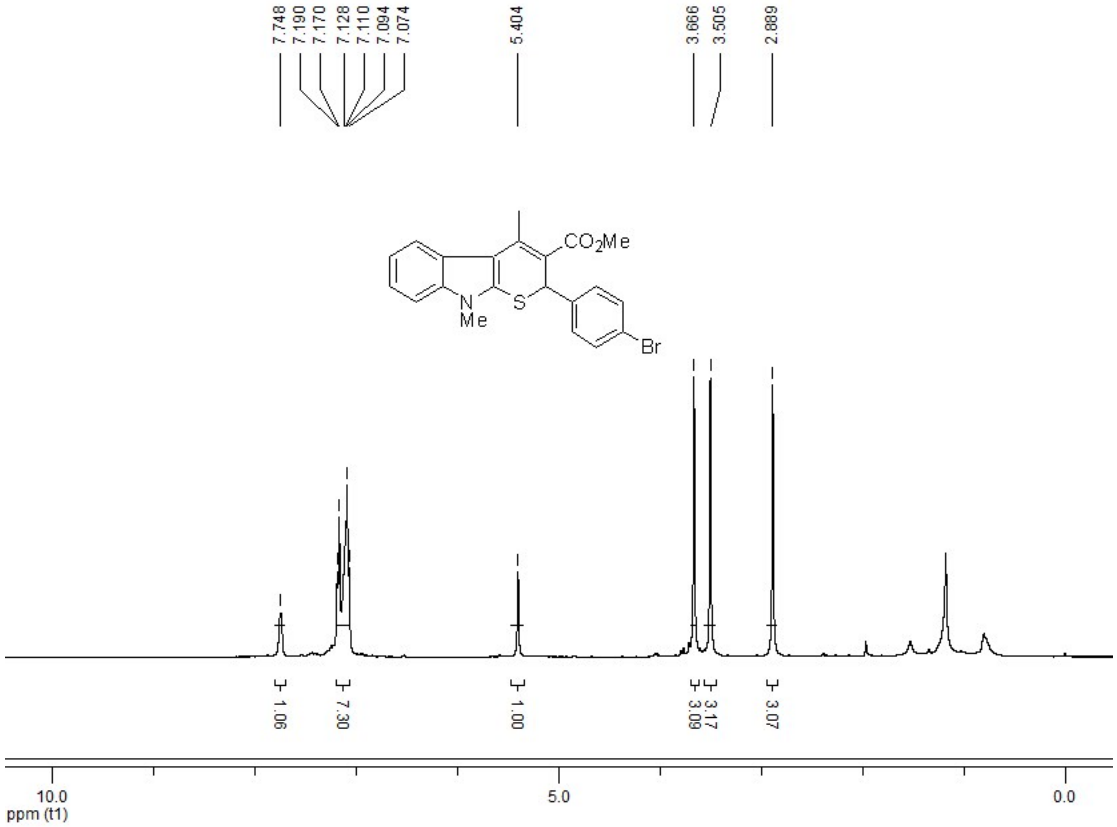

167.834
163.318
160.873
147.479
138.566
136.704
136.674
135.637
128.963
128.881
126.180
121.627
121.062
119.917
115.148
114.934
114.561
110.077
109.199
77.422
77.104
76.787
51.658
42.918
30.760
19.758
200
150
100
50
0
ppm (t1)

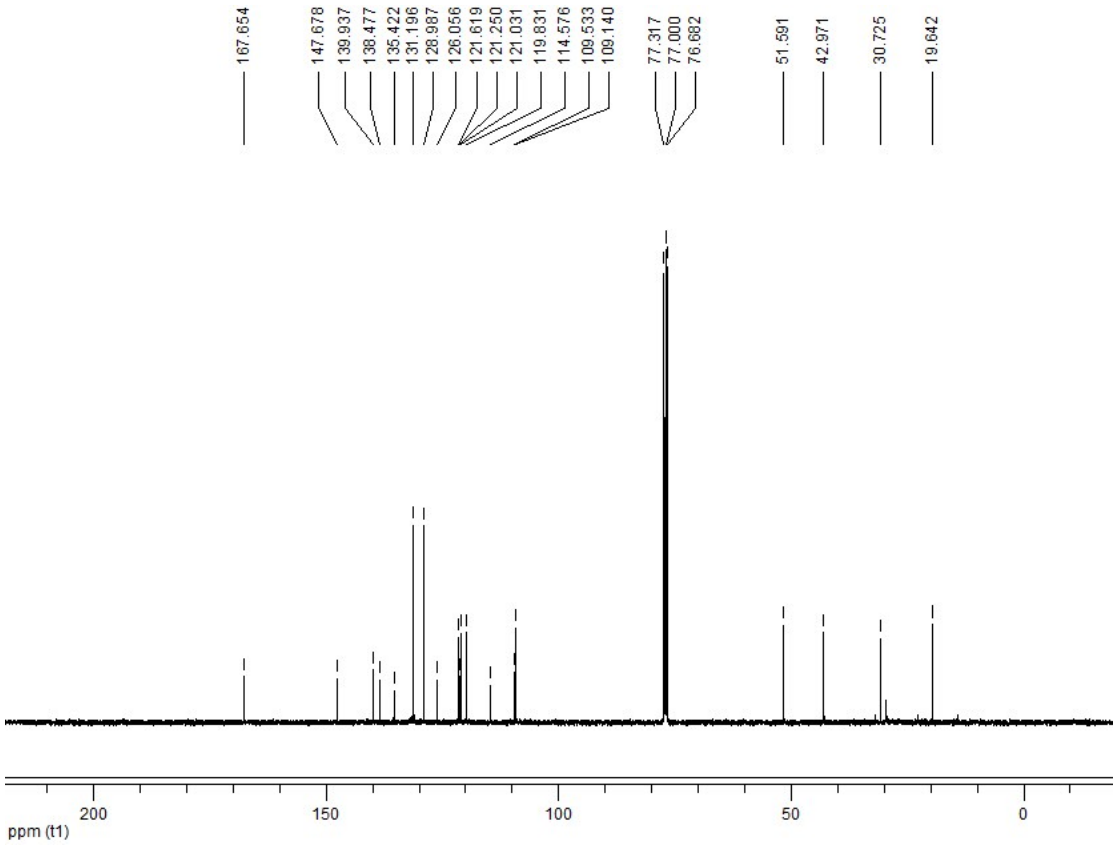
4ah


7.745
7.144
7.124
7.099
7.024
7.005
5.418
3.656
3.481
2.885
CO2Me
N
Me
S
Cl
1.03
7.14
1.00
3.03
2.99
2.94
10.0
ppm (t1)
5.0
0.0

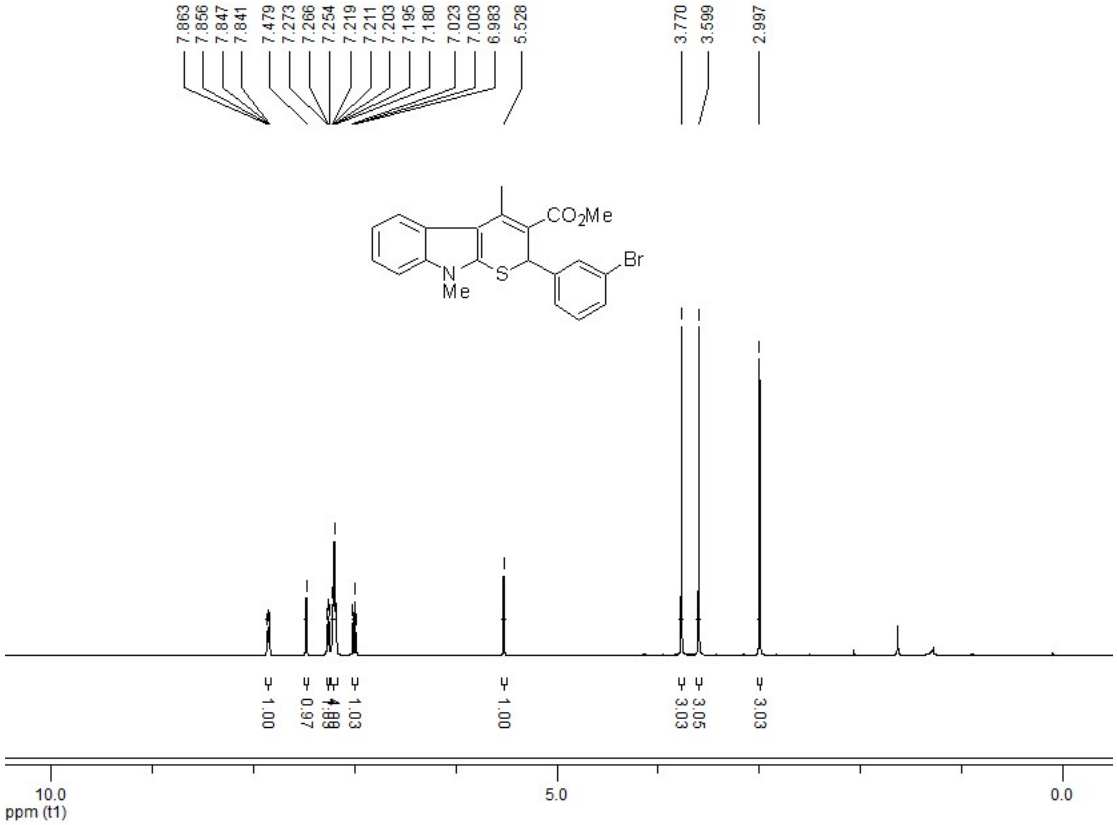

167.647
147.608
139.380
138.445
135.427
133.035
128.594
128.223
126.033
121.580
120.997
119.800
114.524
109.585
109.112
77.317
77.000
76.682
51.561
42.887
30.673
19.627
200
150
100
50
0
ppm (t1)

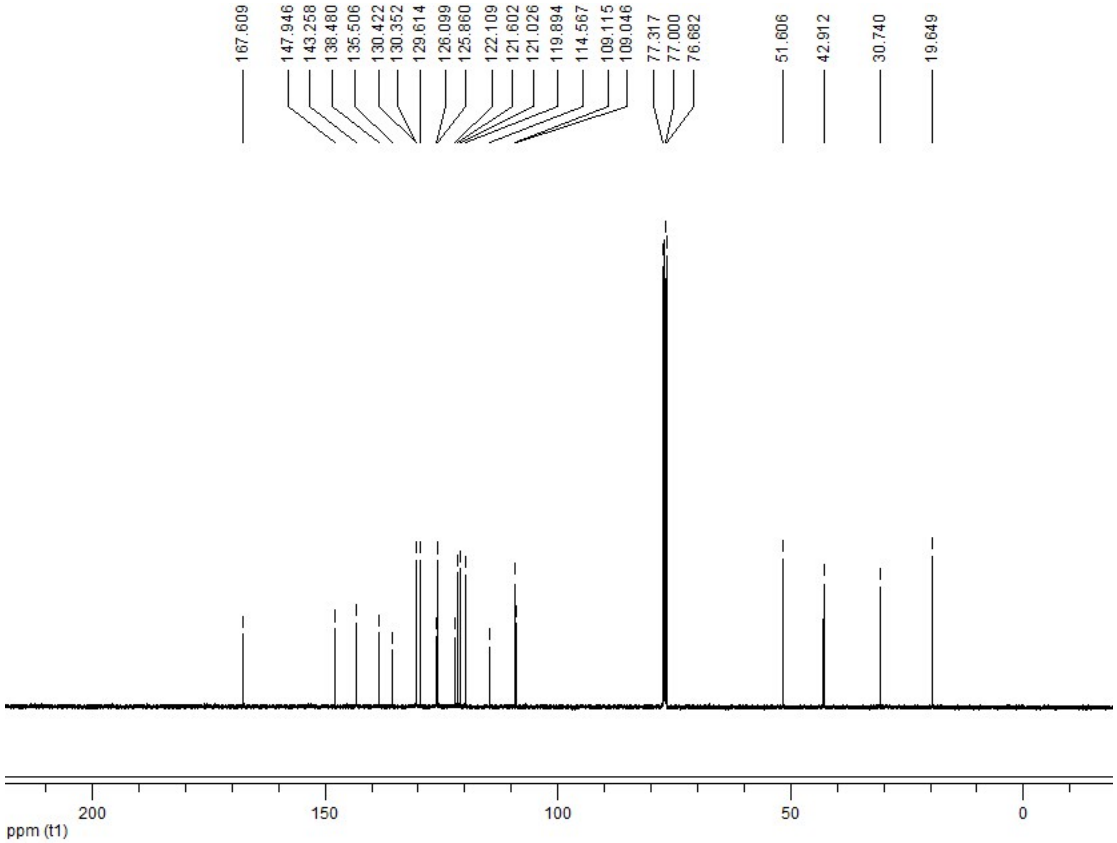
4ai


7.748
7.190
7.170
7.128
7.110
7.094
7.074
5.404
3.666
3.505
2.889
CO2Me
N
Me
S
Br
1.06
7.30
1.00
3.09
3.17
3.07
10.0
ppm (t1)
5.0
0.0

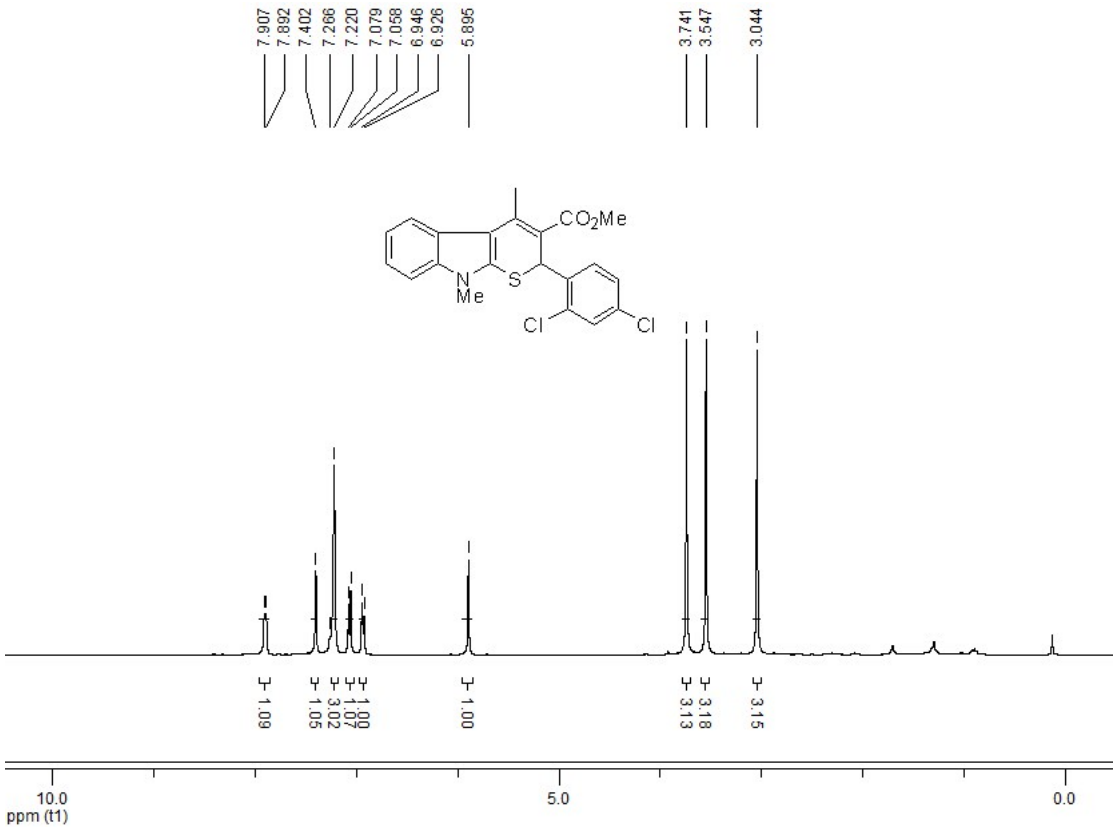

167.654
147.678
139.937
138.477
135.422
131.196
128.987
126.056
121.619
121.250
121.031
119.831
114.576
109.533
109.140
77.317
77.000
76.682
51.591
42.971
30.725
19.642
200
150
100
50
0
ppm (t1)

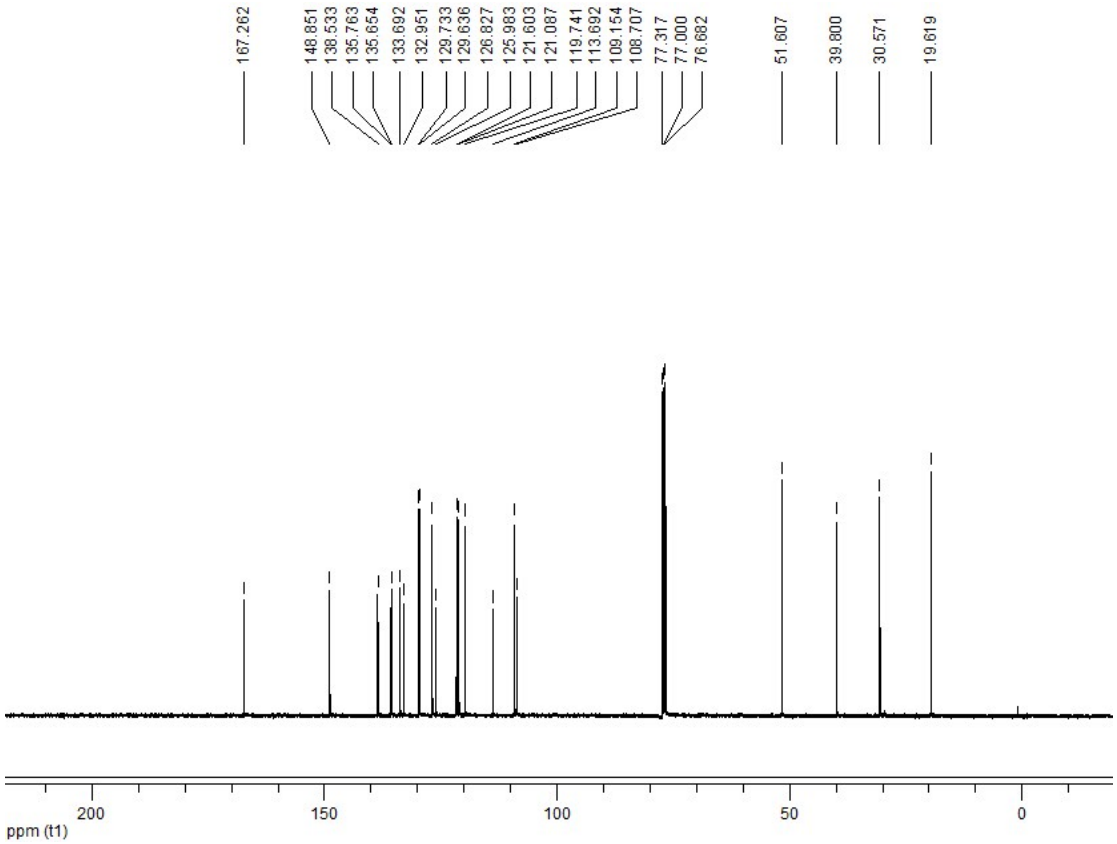
4aj


7.863
7.856
7.847
7.841
7.479
7.273
7.266
7.254
7.219
7.211
7.203
7.195
7.180
7.023
7.003
6.983
5.528
3.770
3.599
2.997
CO2Me
Br
N
Me
S
1.00
0.97
1.03
1.00
3.03
3.05
3.03
10.0
5.0
0.0
ppm (t1)

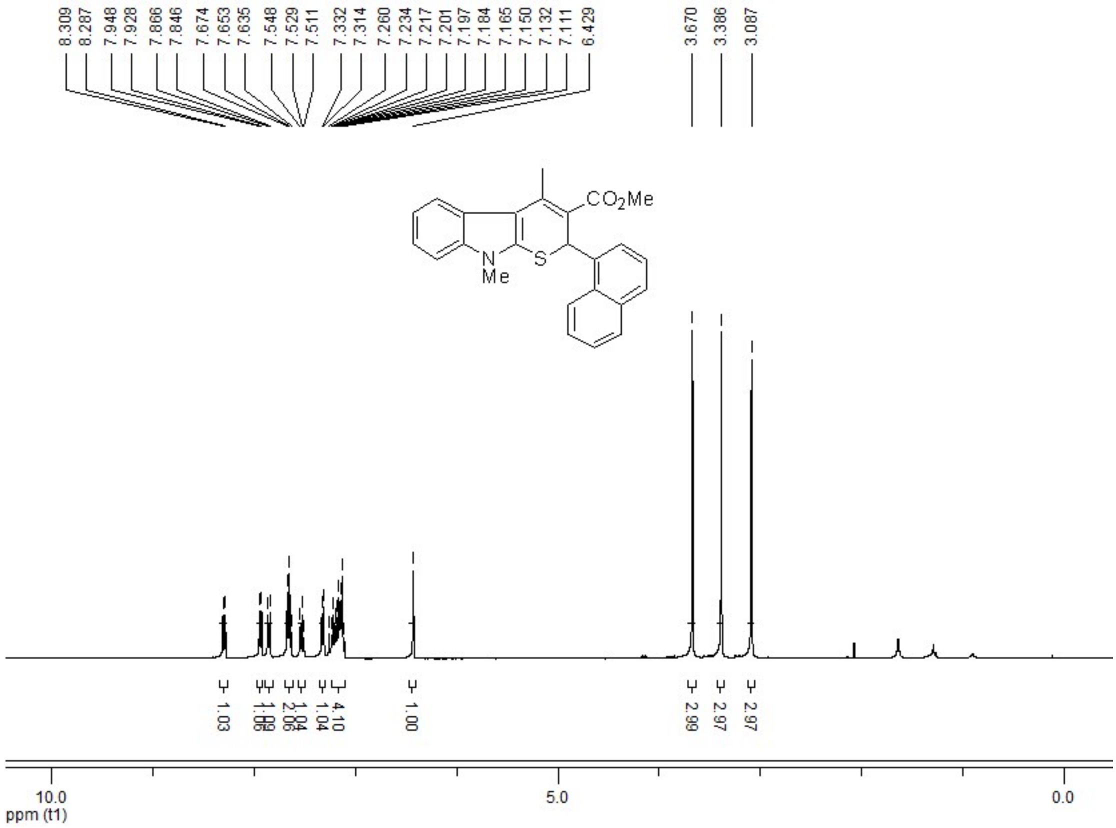

167.609
147.946
143.258
138.480
135.506
130.422
130.352
129.614
126.099
125.860
122.109
121.602
121.026
119.894
114.567
109.115
109.046
77.317
77.000
76.682
51.606
42.912
30.740
19.649
200
150
100
50
0
ppm (t1)

4ak

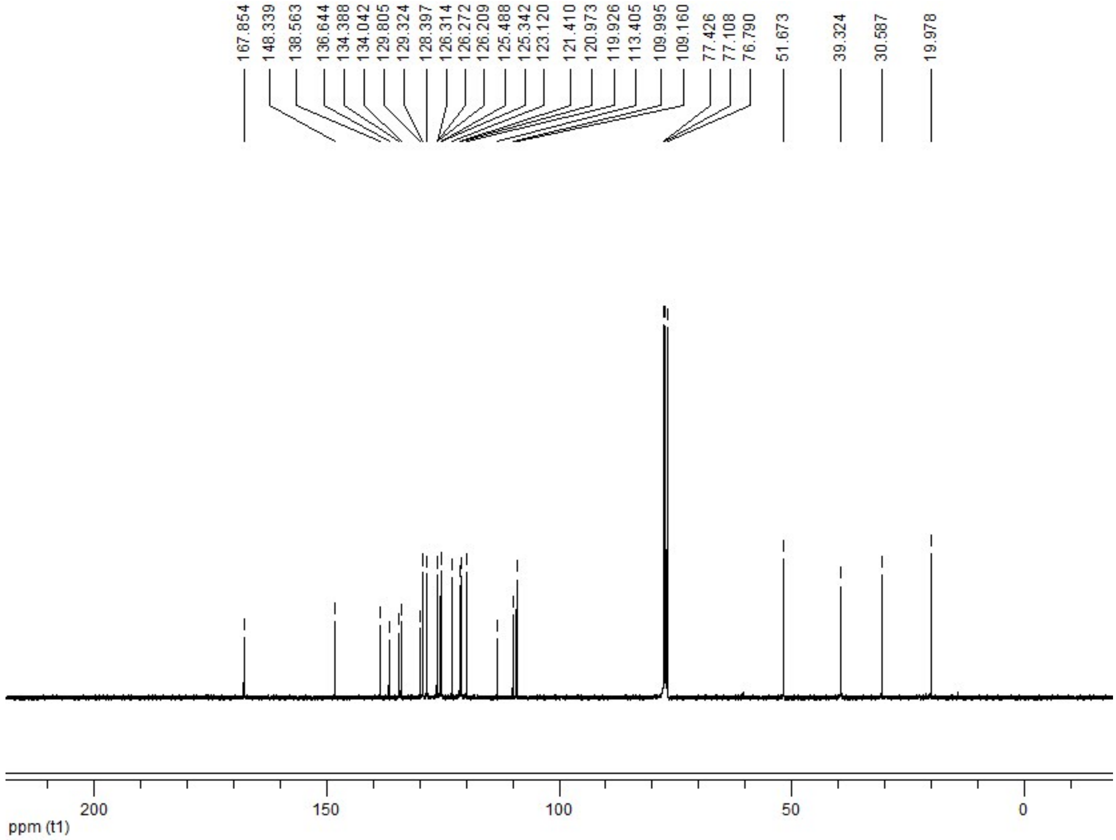

7.907
7.892
7.402
7.266
7.220
7.079
7.058
6.946
6.926
5.895
3.741
3.547
3.044
CO2Me
N
Me
S
Cl
Cl
1.09
1.05
3.02
3.07
1.00
3.13
3.18
3.15
10.0
5.0
0.0
ppm (t1)


167.262
148.851
138.533
135.763
135.654
133.692
132.951
129.733
129.636
126.827
125.983
121.603
121.087
119.741
113.692
109.154
108.707
77.317
77.000
76.682
51.607
39.800
30.571
19.619
200
150
100
50
0
ppm (t1)

4al

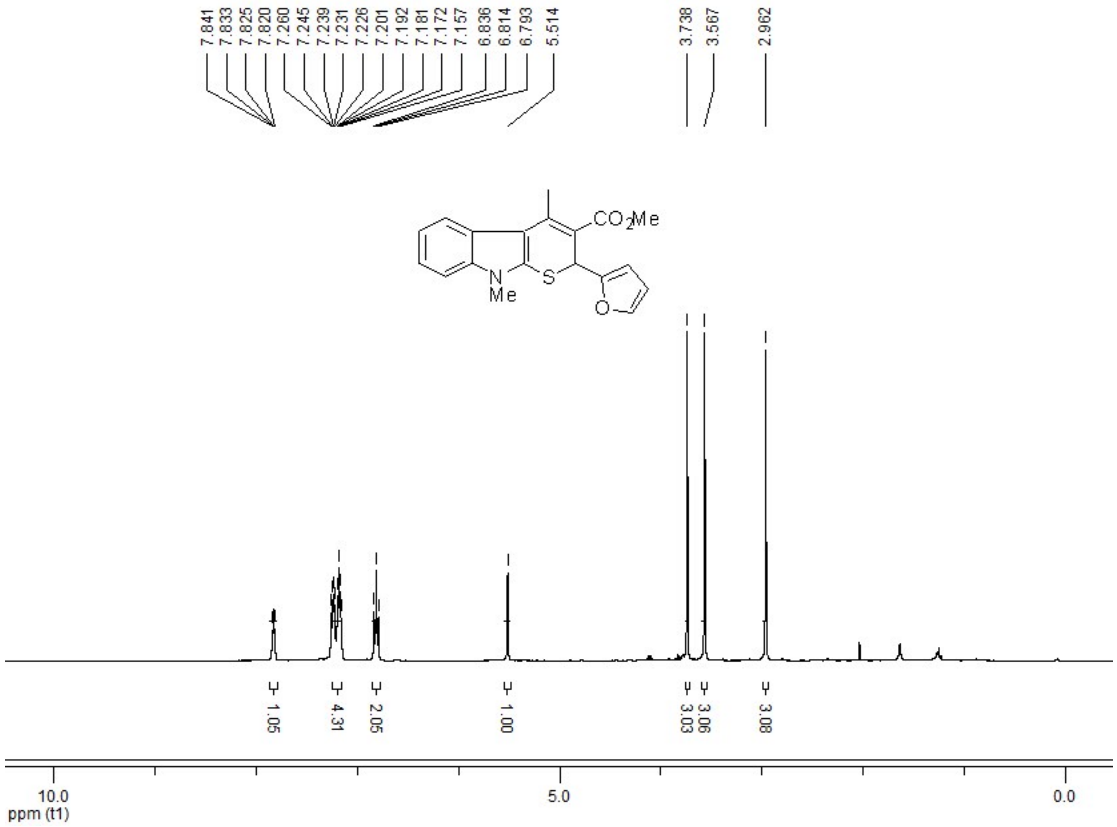


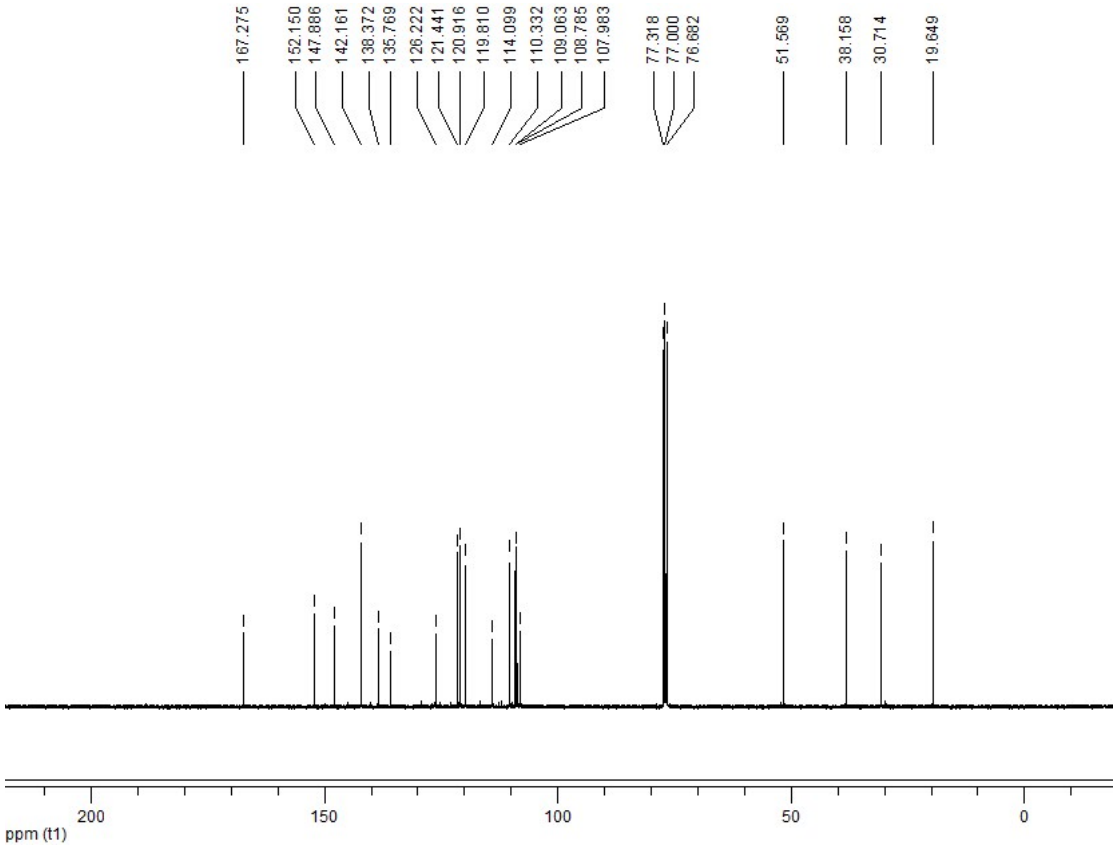
8.309 8.287 7.948 7.928 7.866 7.846 7.674 7.653 7.635 7.548 7.529 7.511 7.332 7.314 7.260 7.234 7.217 7.201 7.197 7.184 7.165 7.150 7.132 7.111 6.429
3.670 3.386 3.087
CO2Me
N
Me
S
1.03 1.00 1.06 2.04 2.06 1.04 4.10 1.00 2.99 2.97 2.97
10.0
5.0
0.0
ppm (t1)



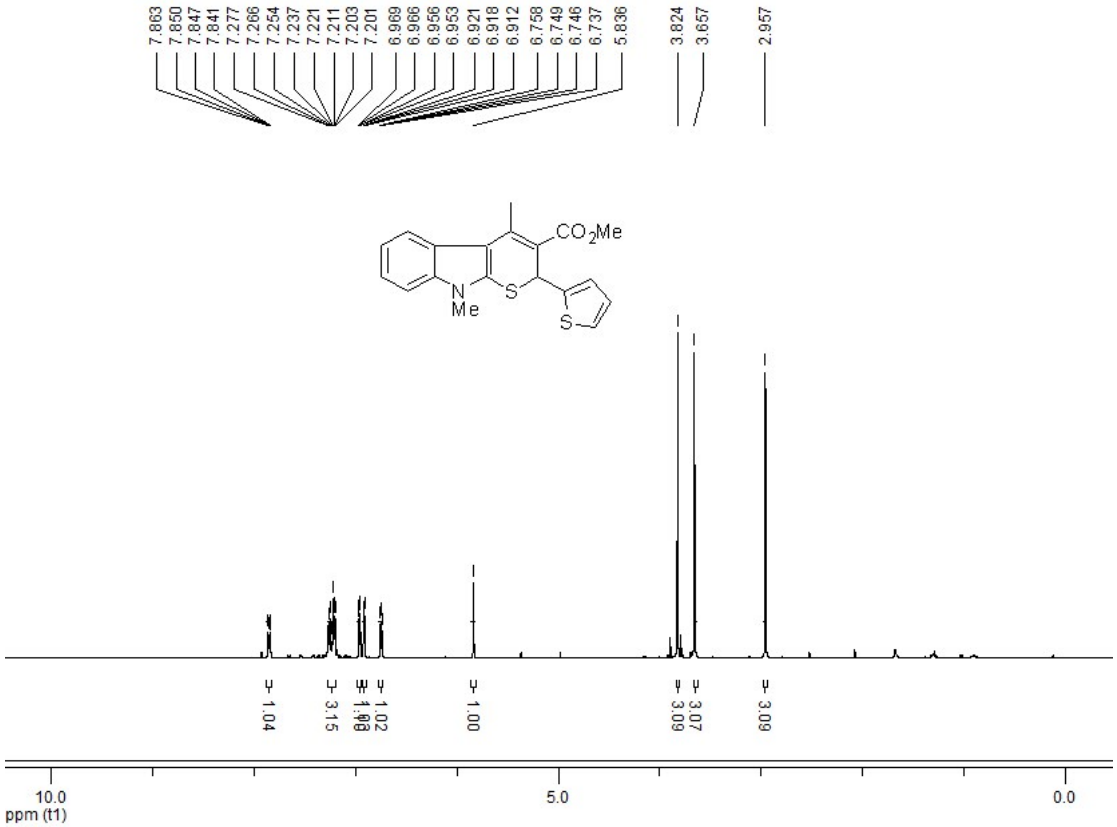
167.854 148.339 138.563 136.644 134.388 134.042 129.805 129.324 128.397 126.314 126.272 126.209 125.488 125.342 123.120 121.410 120.973 119.926 113.405 109.995 109.160 77.426 77.108 76.790 51.673 39.324 30.587 19.978
200
150
100
50
0
ppm (t1)

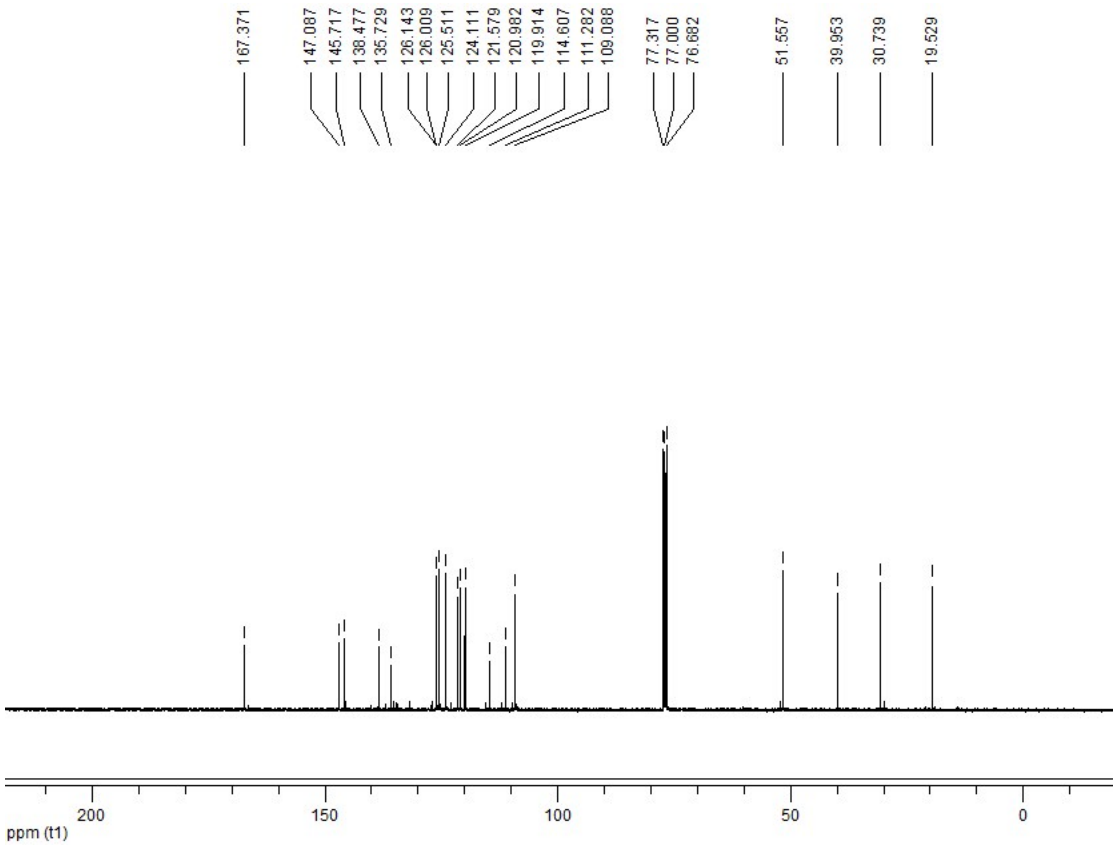
4am


7.841
7.833
7.825
7.820
7.260
7.245
7.239
7.231
7.226
7.201
7.192
7.181
7.172
7.157
6.836
6.814
6.793
5.514
3.738
3.567
2.962
CO2Me
N
Me
S
O
1.06
4.31
2.06
1.00
3.03
3.06
3.08
10.0
5.0
0.0
ppm (t1)

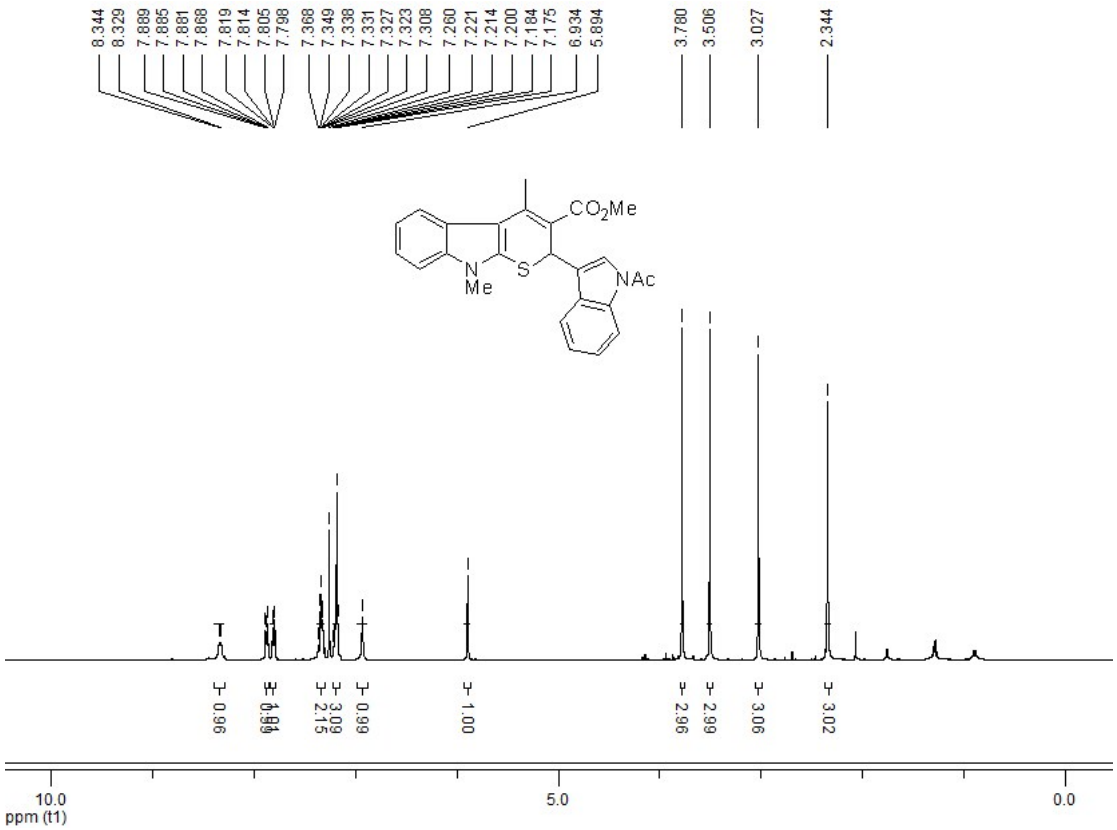

167.275
152.150
147.886
142.161
138.372
135.769
126.222
121.441
120.916
119.810
114.099
110.332
109.063
108.785
107.983
77.318
77.000
76.682
51.569
38.158
30.714
19.649
200
150
100
50
0
ppm (t1)

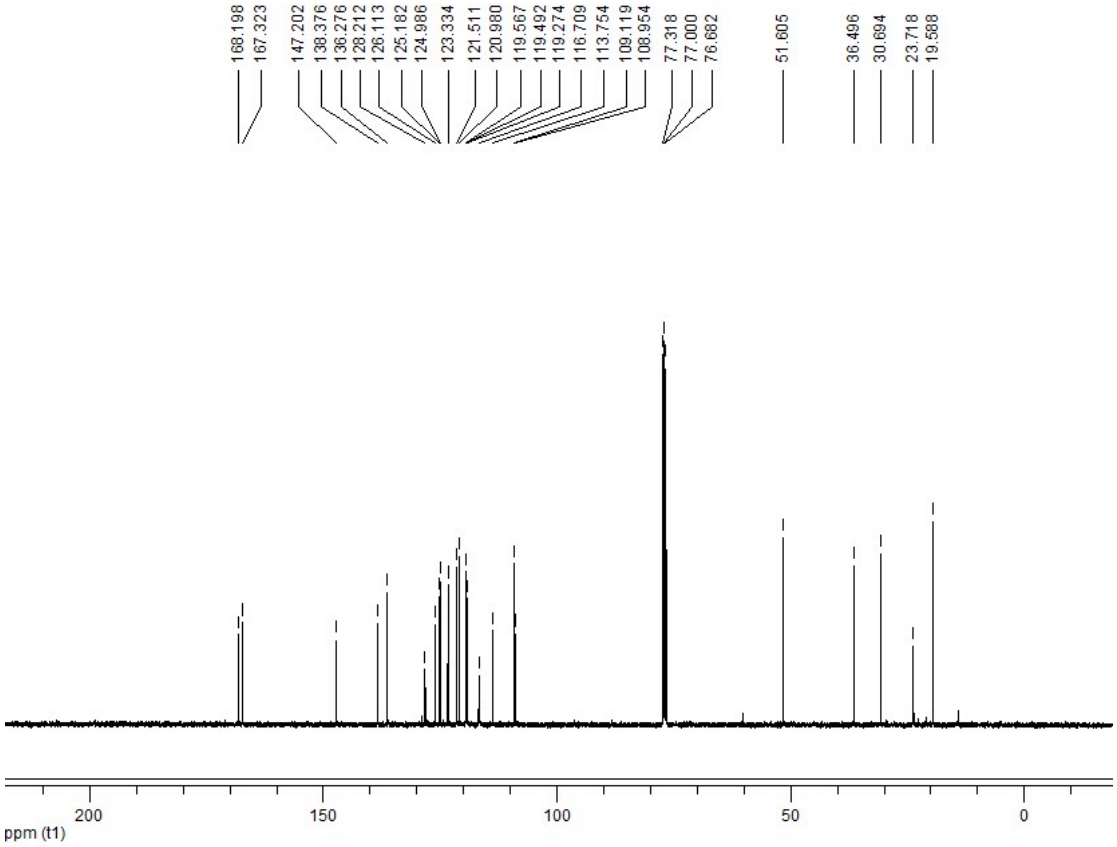
4an


7.863
7.850
7.847
7.841
7.277
7.266
7.254
7.237
7.221
7.211
7.203
7.201
6.969
6.966
6.956
6.953
6.921
6.918
6.912
6.758
6.749
6.746
6.737
5.836
3.824
3.657
2.957
CO2Me
N
Me
S
S
1.04
3.15
1.02
1.00
3.09
3.07
3.09
10.0
5.0
0.0
ppm (t1)

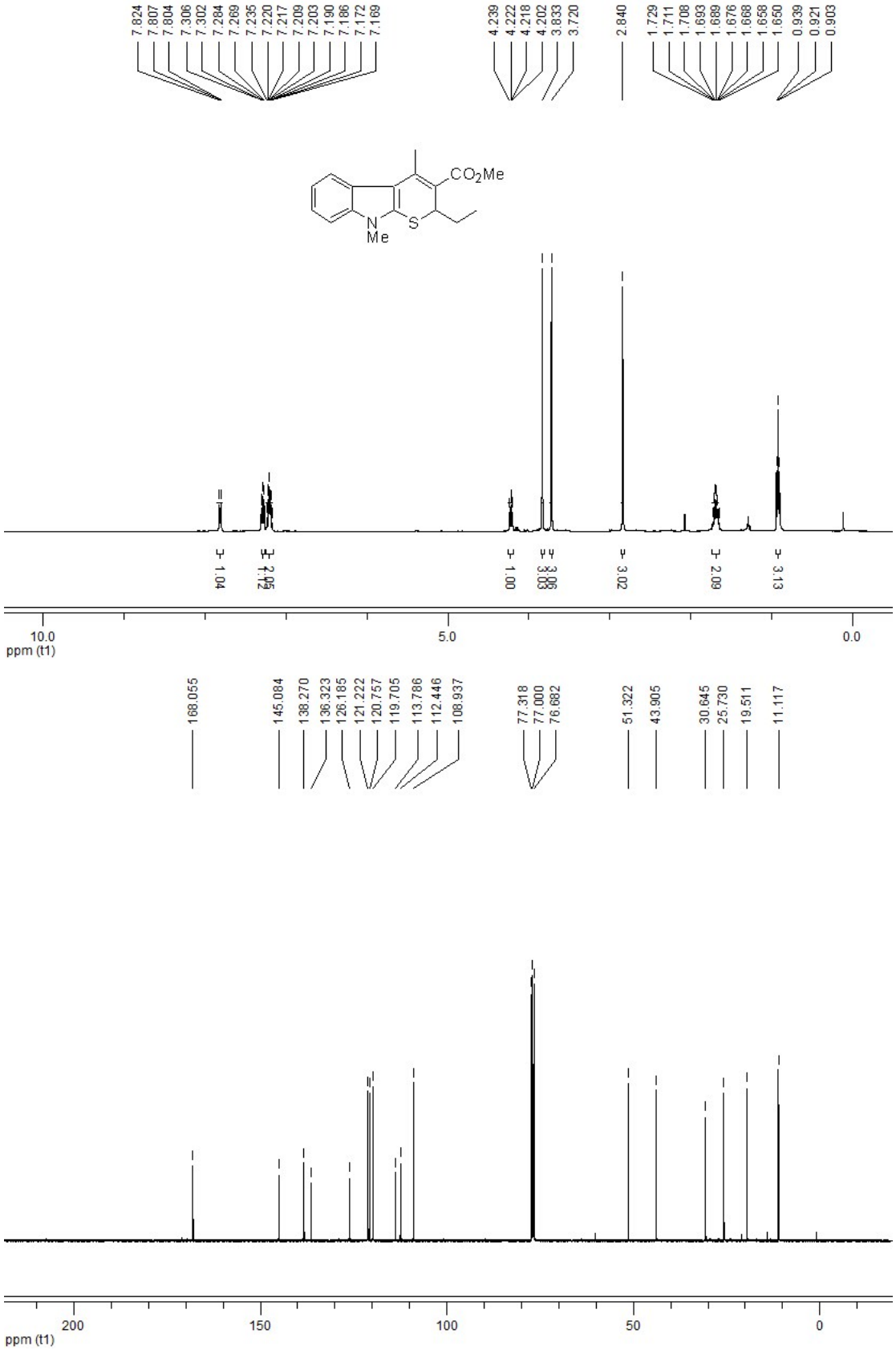

167.371
147.087
145.717
138.477
135.729
126.143
126.009
125.511
124.111
121.579
120.982
119.914
114.607
111.282
109.088
77.317
77.000
76.682
51.557
39.953
30.739
19.529
200
150
100
50
0
ppm (t1)

4ao

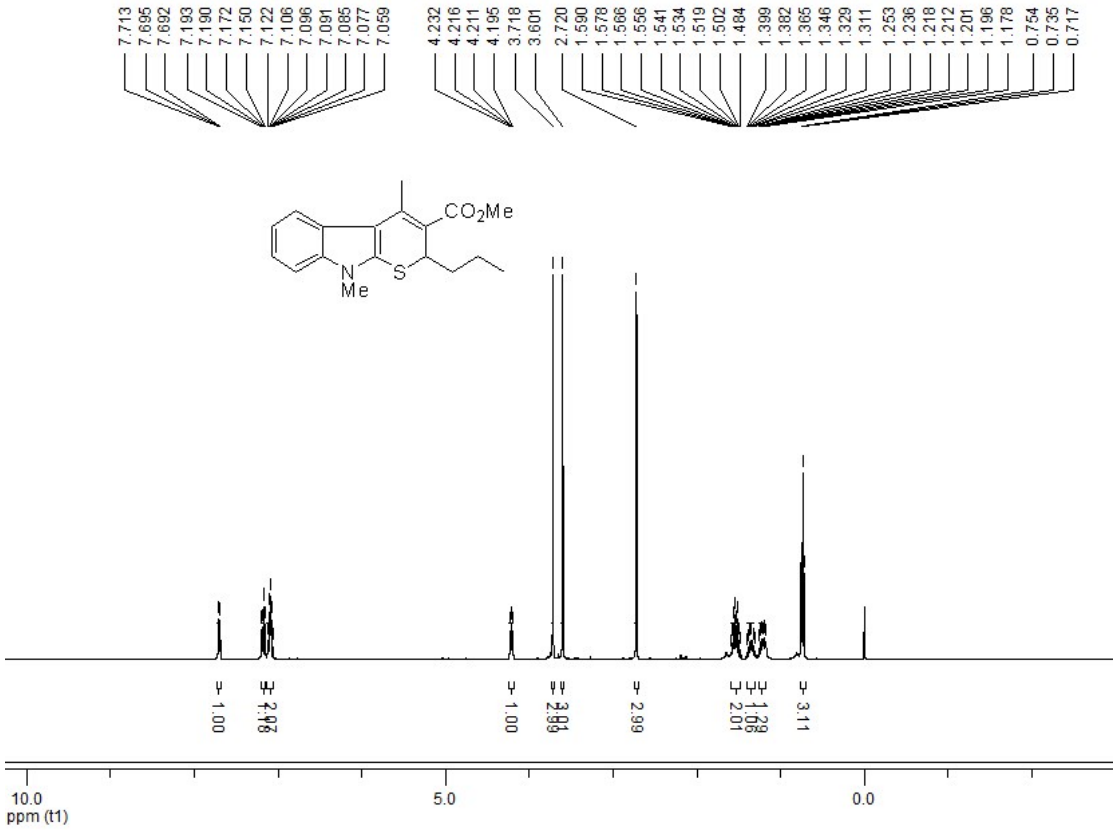

8.344
8.329
7.889
7.885
7.881
7.868
7.819
7.814
7.805
7.798
7.368
7.349
7.338
7.331
7.327
7.323
7.308
7.260
7.221
7.214
7.200
7.184
7.175
6.934
5.894
3.780
3.506
3.027
2.344
CO2Me
N
Me
S
NAc
0.96
0.99
3.09
2.15
0.99
1.00
2.96
2.99
3.06
3.02
10.0
5.0
0.0
ppm (t1)

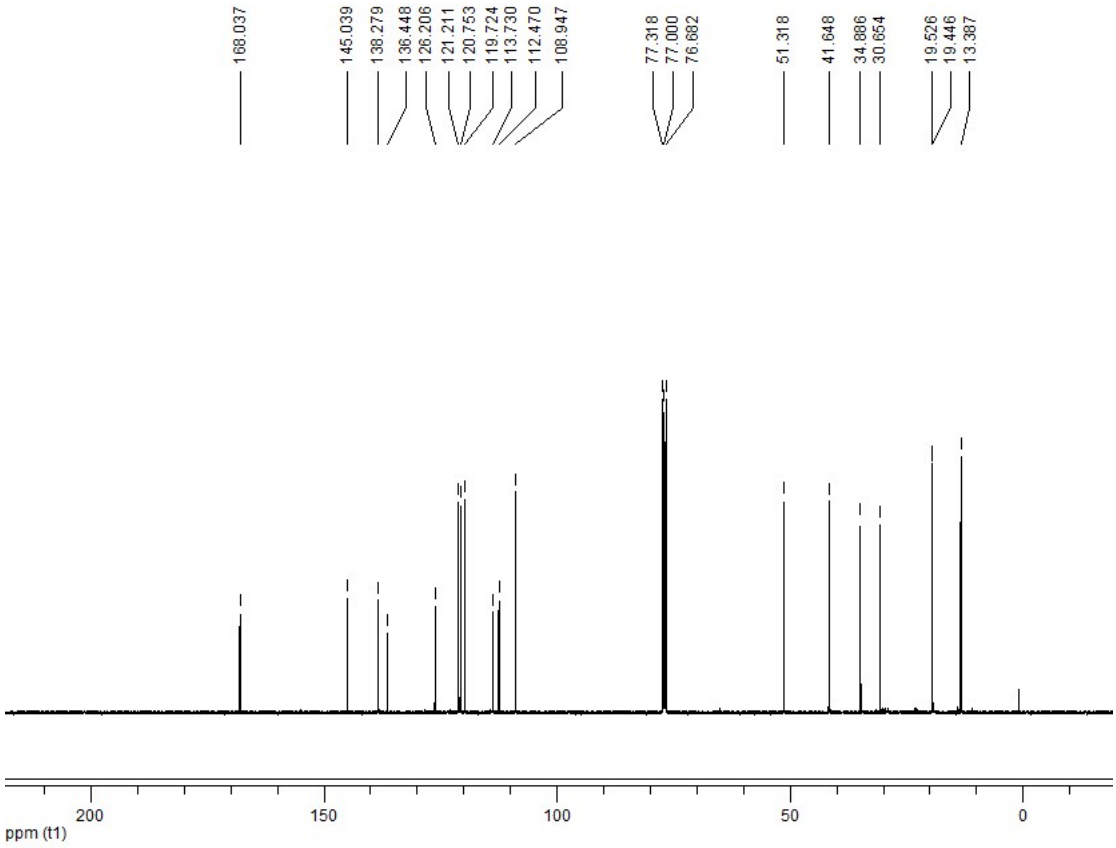

168.198
167.323
147.202
138.376
136.276
128.212
126.113
125.182
124.986
123.334
121.511
120.980
119.567
119.492
119.274
116.709
113.754
109.119
108.954
77.318
77.000
76.682
51.605
36.496
30.694
23.718
19.588
200
150
100
50
0
ppm (t1)

4ap

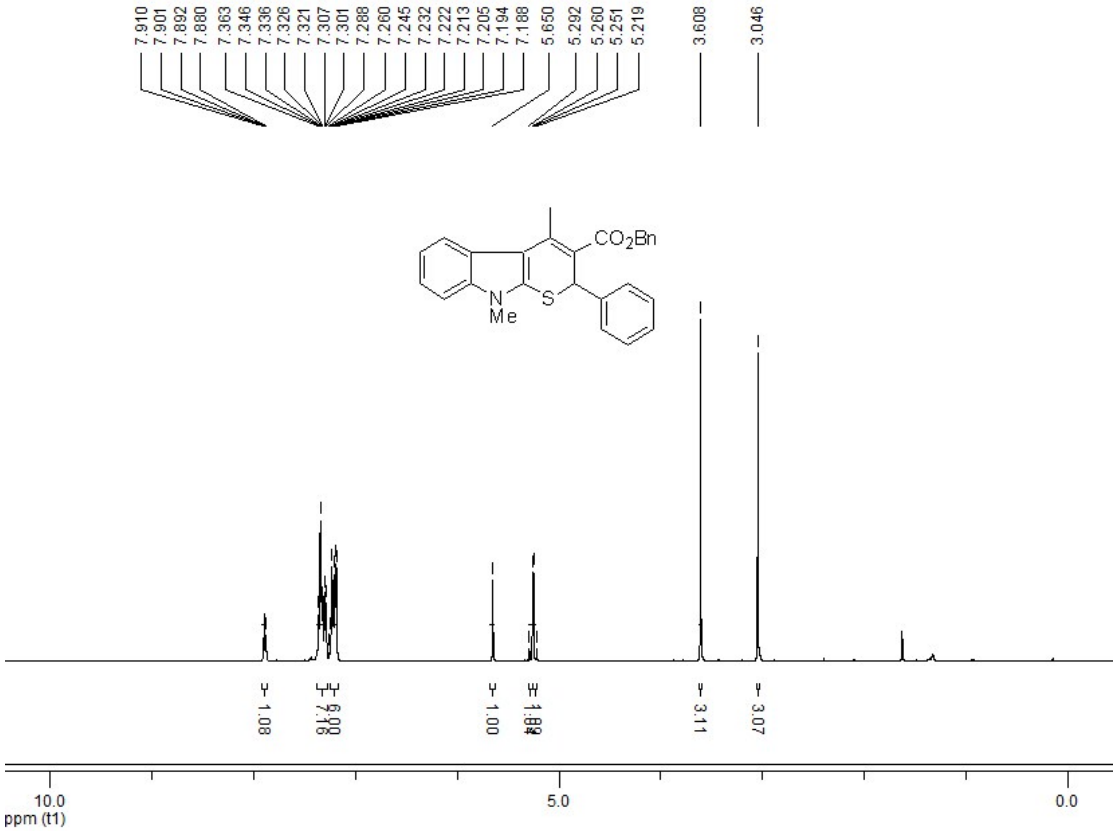

7.824
7.807
7.804
7.306
7.302
7.284
7.269
7.235
7.220
7.217
7.209
7.203
7.190
7.186
7.172
7.169
4.239
4.222
4.218
4.202
3.833
3.720
2.840
1.729
1.711
1.708
1.693
1.689
1.676
1.668
1.658
1.650
0.939
0.921
0.903
CO2Me
N
Me
S
1.04
2.05
1.00
3.06
3.02
2.09
3.13
10.0
5.0
0.0
ppm (t1)
168.055
145.084
138.270
136.323
126.185
121.222
120.757
119.705
113.786
112.446
108.937
77.318
77.000
76.682
51.322
43.905
30.645
25.730
19.511
11.117
200
150
100
50
0
ppm (t1)

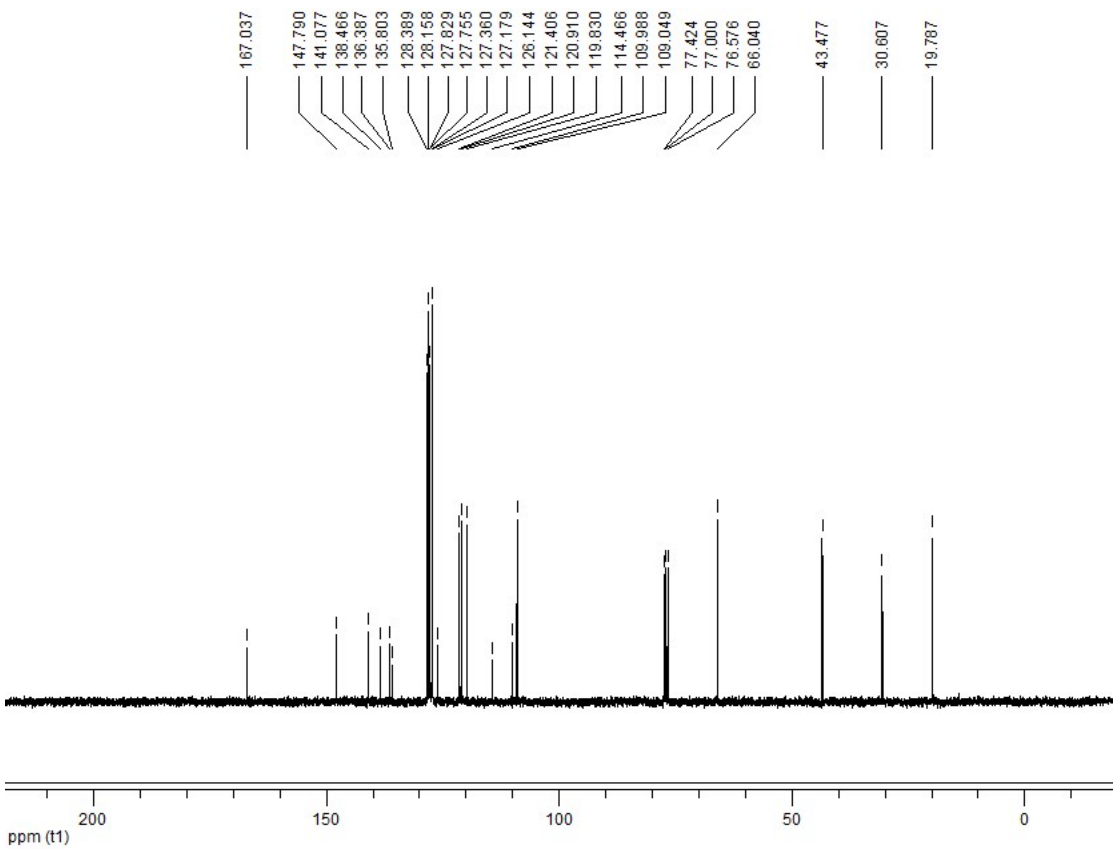
4aq


7.713
7.695
7.692
7.193
7.190
7.172
7.150
7.122
7.106
7.096
7.091
7.085
7.077
7.059
4.232
4.216
4.211
4.195
3.718
3.601
2.720
1.590
1.578
1.566
1.556
1.541
1.534
1.519
1.502
1.484
1.399
1.382
1.365
1.346
1.329
1.311
1.253
1.236
1.218
1.212
1.201
1.196
1.178
0.754
0.735
0.717
CO2Me
N
Me
S
1.00
2.08
1.00
2.01
2.99
2.01
1.08
1.09
3.11
10.0
5.0
0.0
ppm (t1)

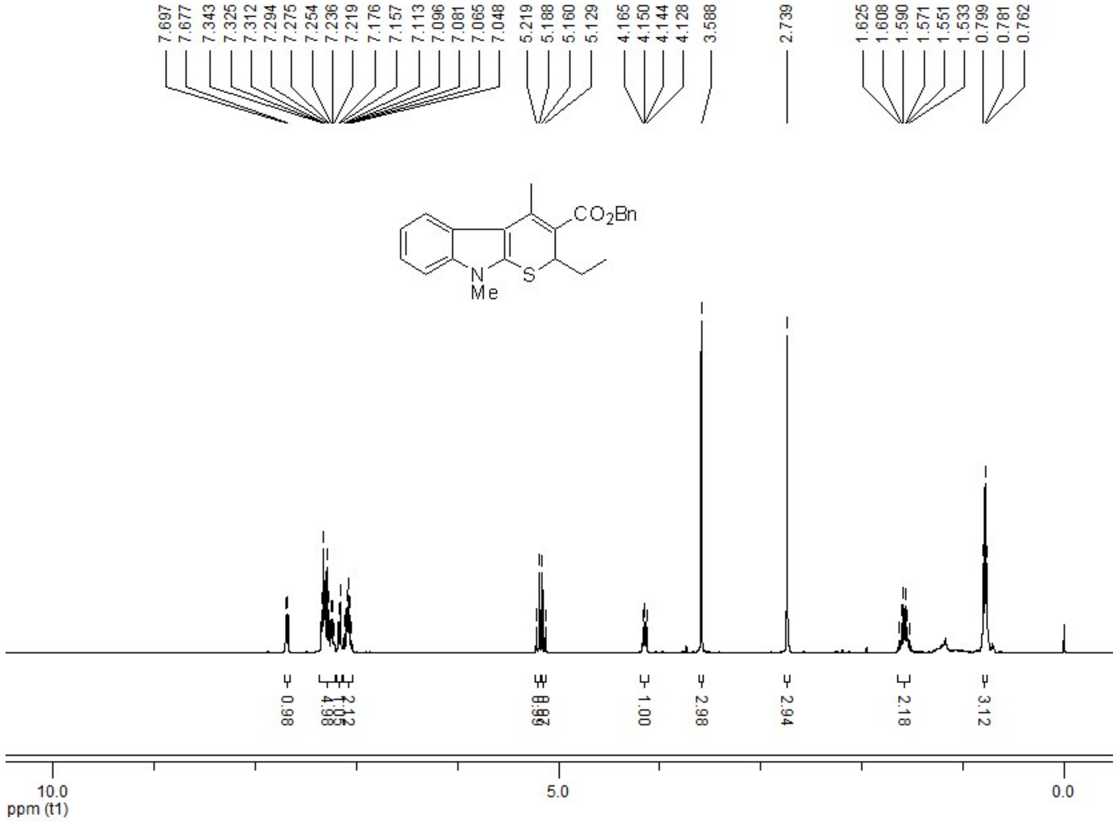

168.037
145.039
138.279
136.448
126.206
121.211
120.753
119.724
113.730
112.470
108.947
77.318
77.000
76.682
51.318
41.648
34.886
30.654
19.526
19.446
13.387
200
150
100
50
0
ppm (t1)

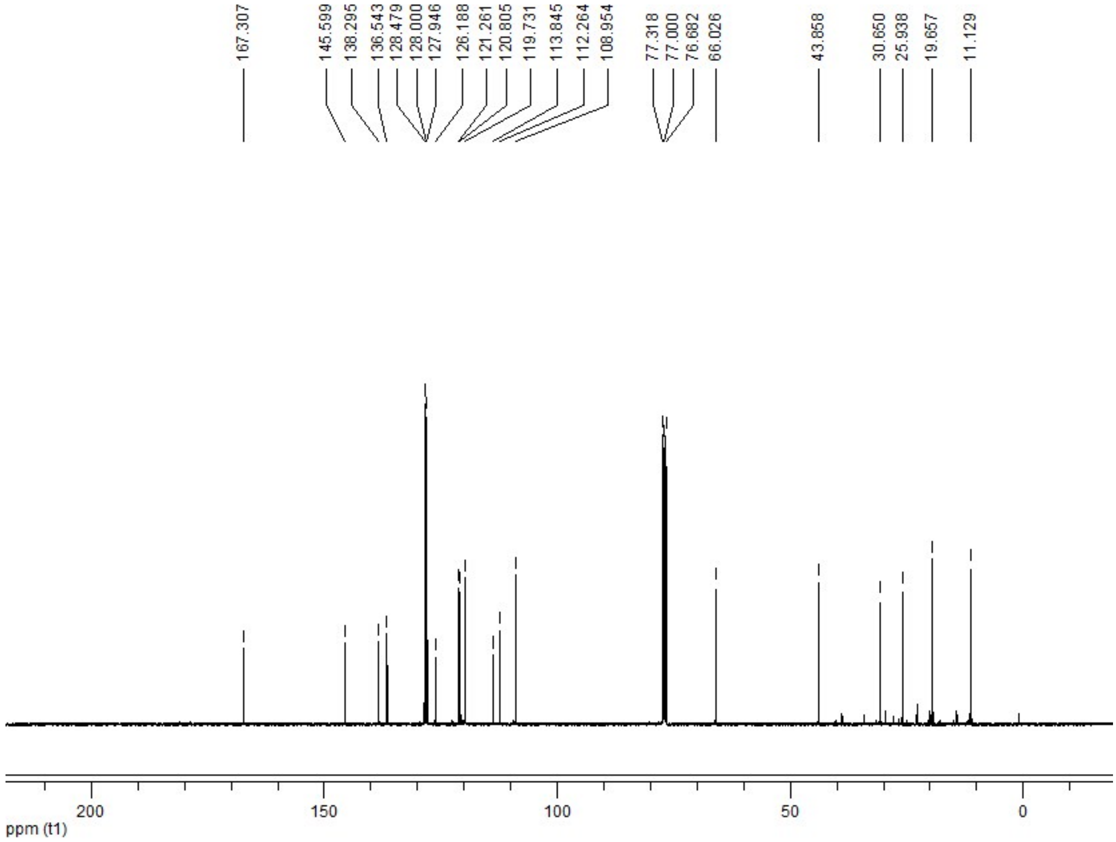
4ar


7.910
7.901
7.892
7.880
7.363
7.346
7.336
7.326
7.321
7.307
7.301
7.288
7.260
7.245
7.232
7.222
7.213
7.205
7.194
7.188
5.650
5.292
5.260
5.251
5.219
3.608
3.046
CO2Bn
N
Me
S
1.08
7.18
1.00
1.88
3.11
3.07
10.0
5.0
0.0
ppm (t1)

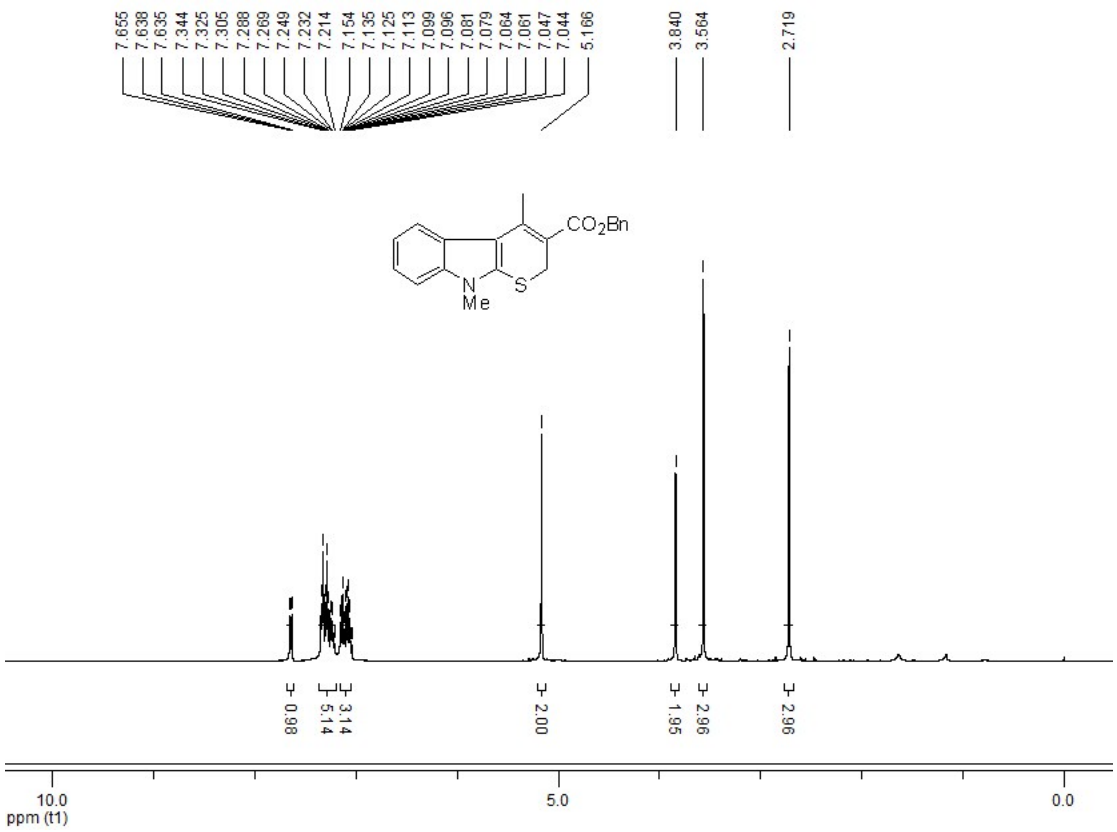

167.037
147.790
141.077
138.466
136.387
135.803
128.389
128.158
127.829
127.755
127.360
127.179
126.144
121.406
120.910
119.830
114.466
109.988
109.049
77.424
77.000
76.576
66.040
43.477
30.607
19.787
200
150
100
50
0
ppm (t1)

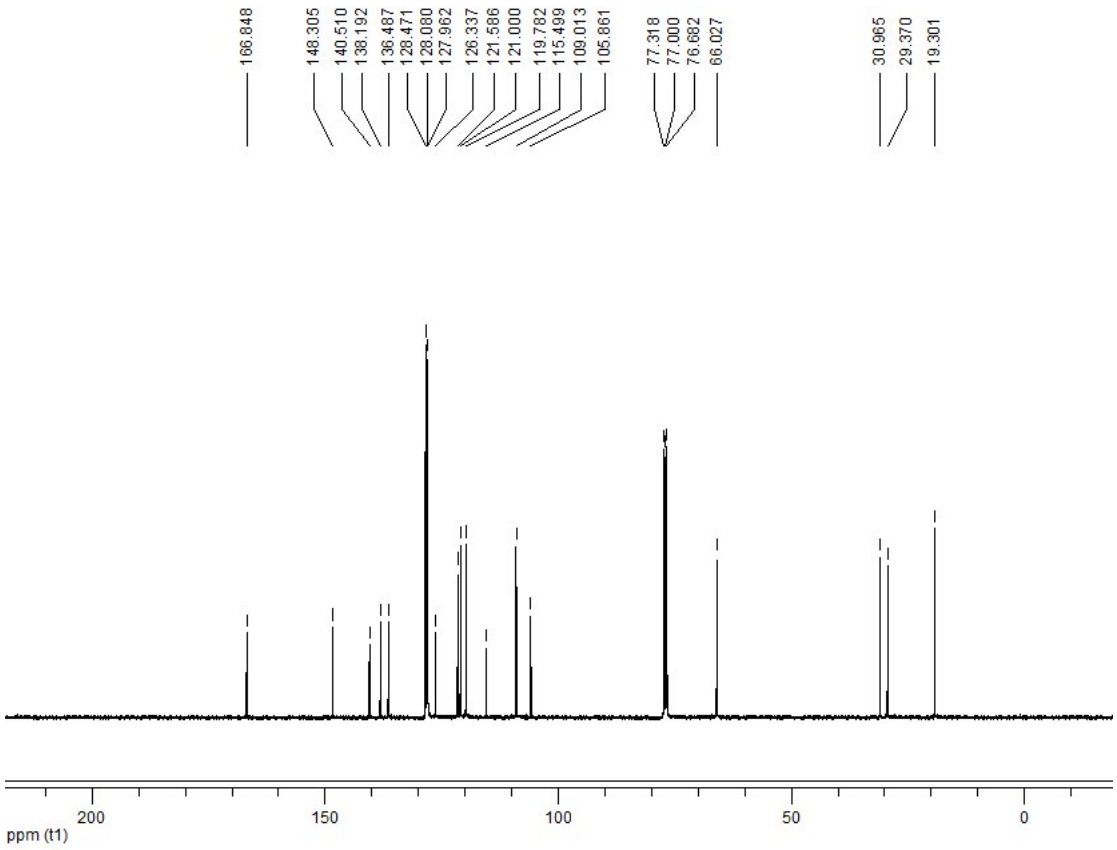
4as


7.697
7.677
7.343
7.325
7.312
7.294
7.275
7.254
7.236
7.219
7.176
7.157
7.113
7.096
7.081
7.065
7.048
5.219
5.188
5.160
5.129
4.165
4.150
4.144
4.128
3.588
2.739
1.625
1.608
1.590
1.571
1.551
1.533
0.799
0.781
0.762
CO2Bn
N
S
Me
0.98
4.98
1.05
2.12
0.99
0.92
1.00
2.98
2.94
2.18
3.12
10.0
5.0
0.0
ppm (t1)

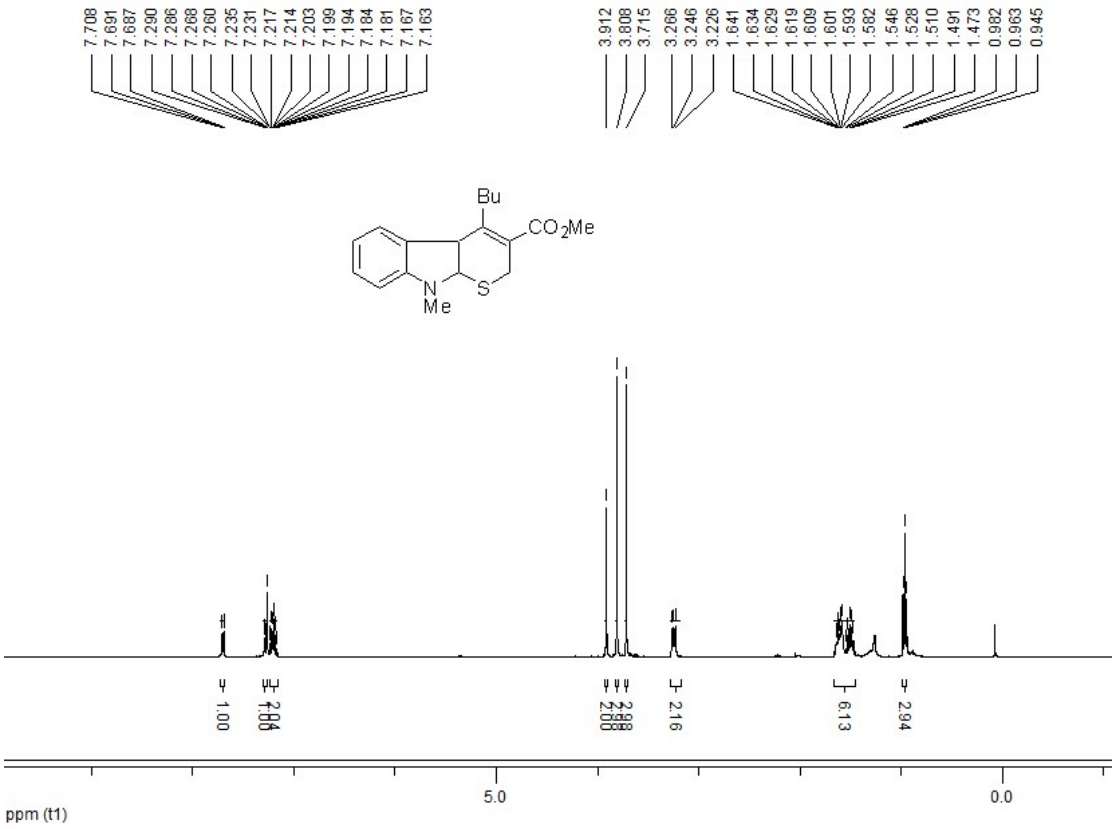

167.307
145.599
138.295
136.543
128.479
128.000
127.946
126.188
121.261
120.805
119.731
113.845
112.264
108.954
77.318
77.000
76.682
66.026
43.858
30.650
25.938
19.657
11.129
200
150
100
50
0
ppm (t1)

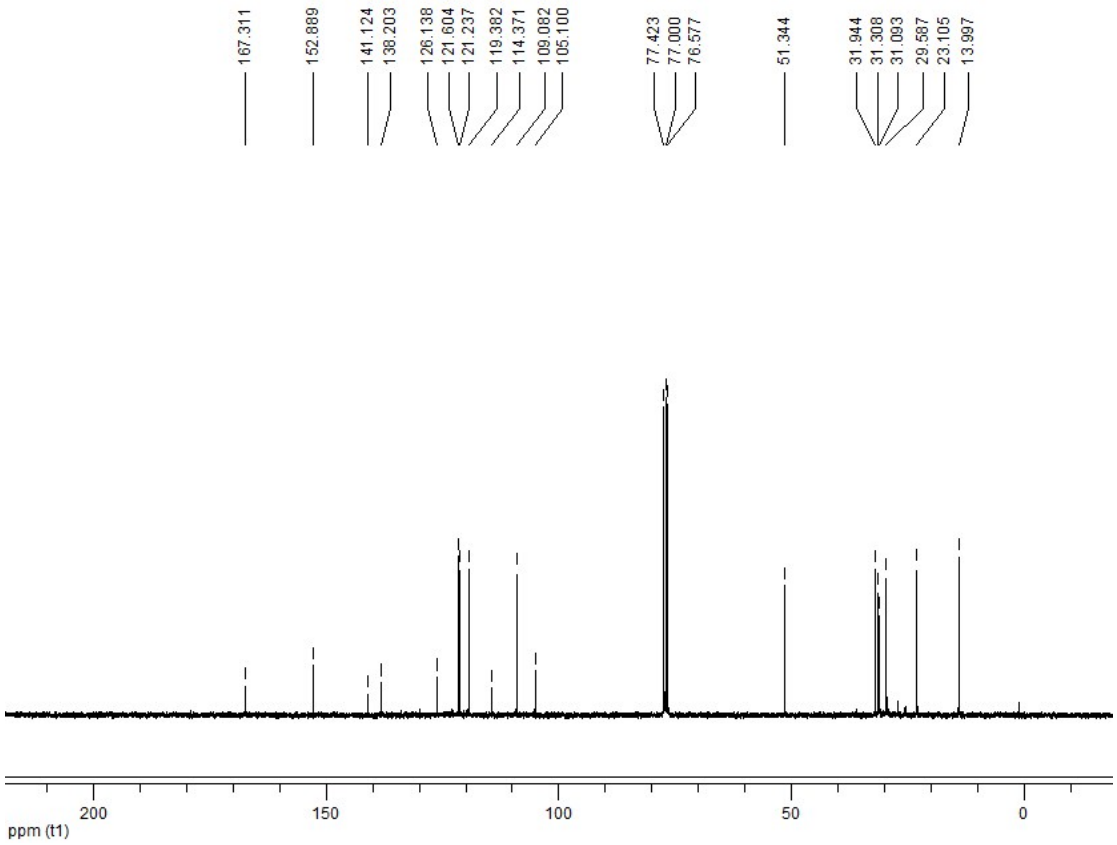
4at


7.655
7.638
7.635
7.344
7.325
7.305
7.288
7.269
7.249
7.232
7.214
7.154
7.135
7.125
7.113
7.099
7.096
7.081
7.079
7.064
7.061
7.047
7.044
5.166
3.840
3.564
2.719
CO2Bn
N
Me
S
0.98
6.14
3.14
2.00
1.95
2.96
2.96
10.0
5.0
0.0
ppm (t1)

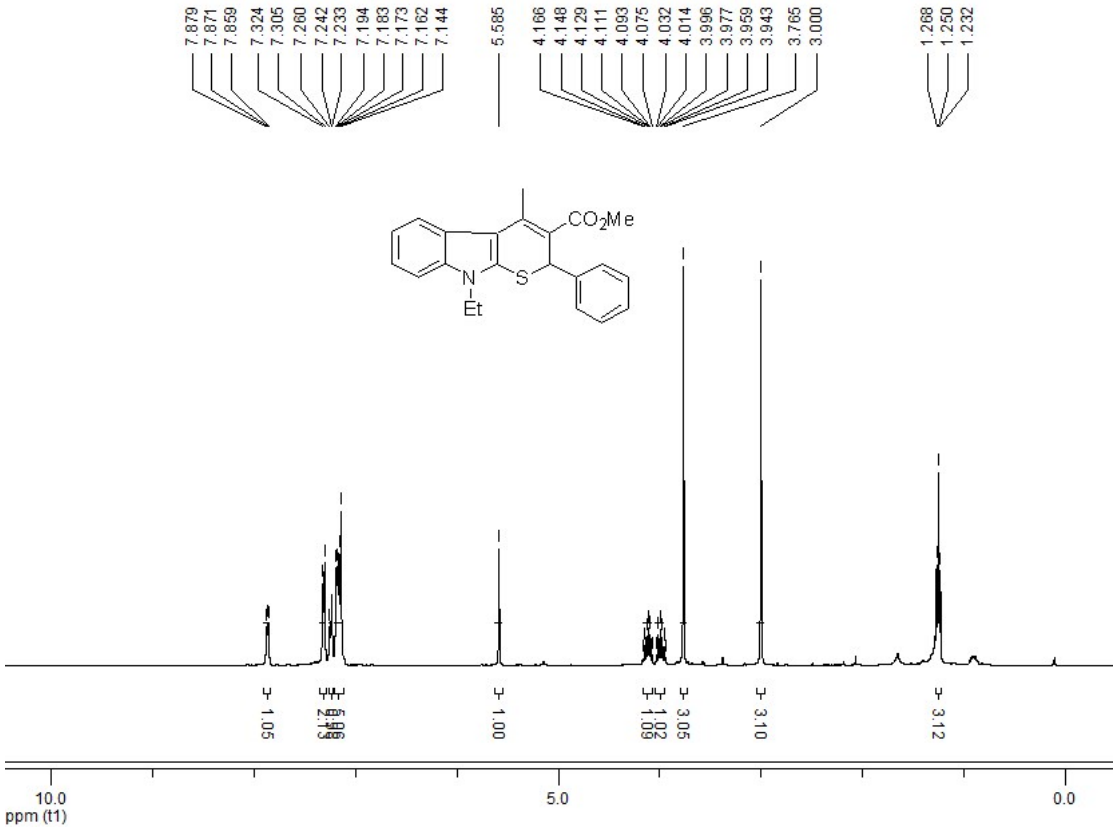

166.848
148.305
140.510
138.192
136.487
128.471
128.080
127.962
126.337
121.586
121.000
119.782
115.499
109.013
105.861
77.318
77.000
76.682
66.027
30.965
29.370
19.301
200
150
100
50
0
ppm (t1)

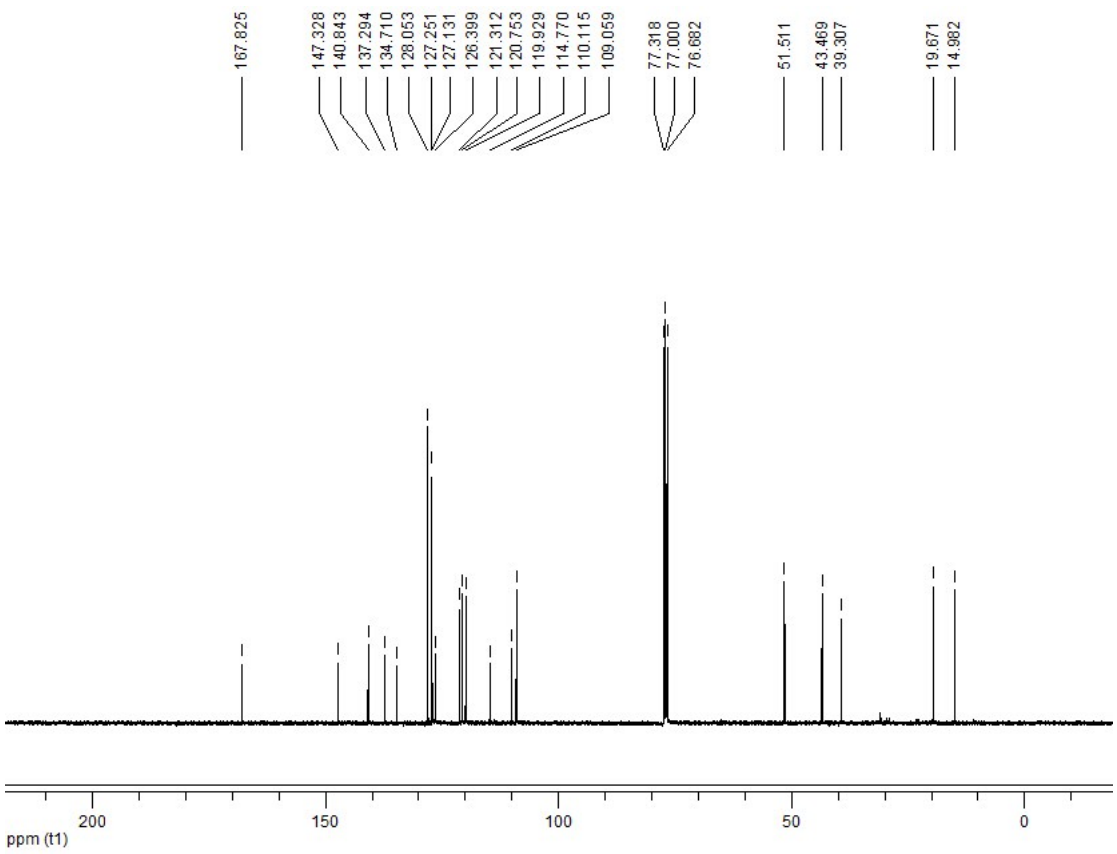
4au


7.708
7.691
7.687
7.290
7.286
7.268
7.260
7.235
7.231
7.217
7.214
7.203
7.199
7.194
7.184
7.181
7.167
7.163
3.912
3.808
3.715
3.266
3.246
3.226
1.641
1.634
1.629
1.619
1.609
1.601
1.593
1.582
1.546
1.528
1.510
1.491
1.473
0.982
0.963
0.945
Bu
CO2Me
N
Me
S
1.00
2.04
2.16
6.13
2.94
5.0
0.0
ppm (t1)

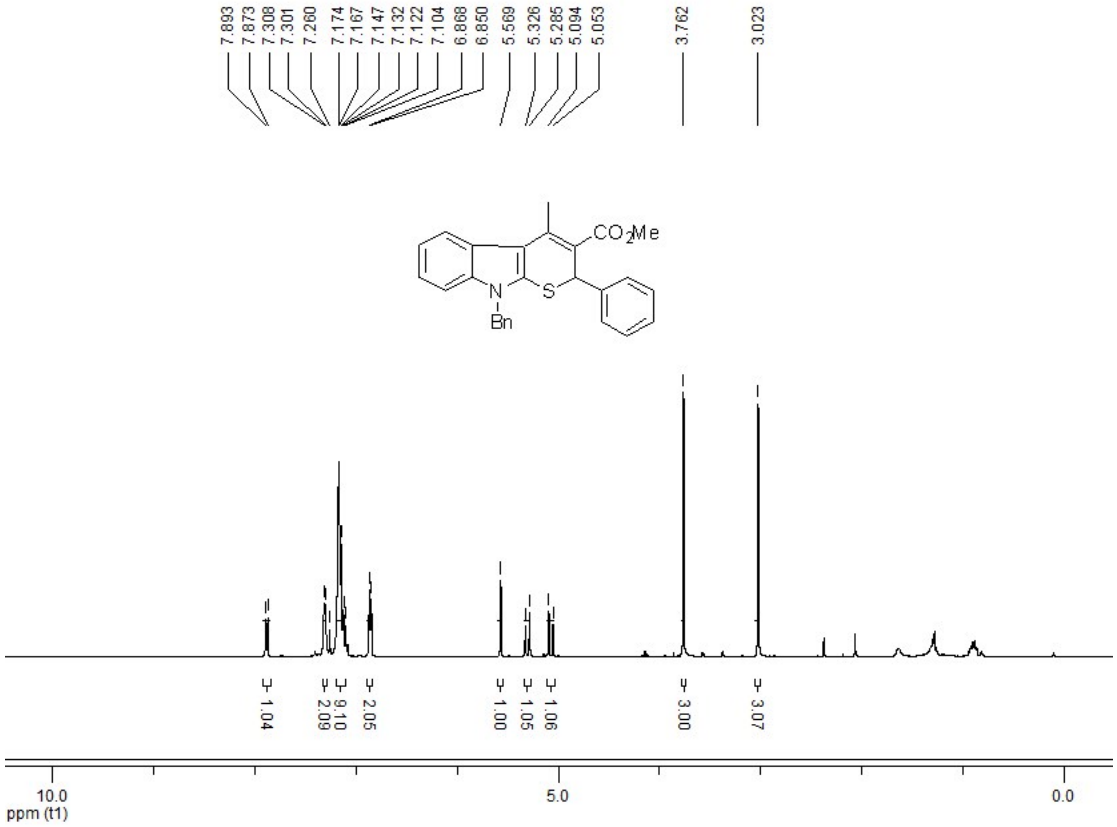

167.311
152.889
141.124
138.203
126.138
121.604
121.237
119.382
114.371
109.082
105.100
77.423
77.000
76.577
51.344
31.944
31.308
31.093
29.587
23.105
13.997
200
150
100
50
0
ppm (t1)

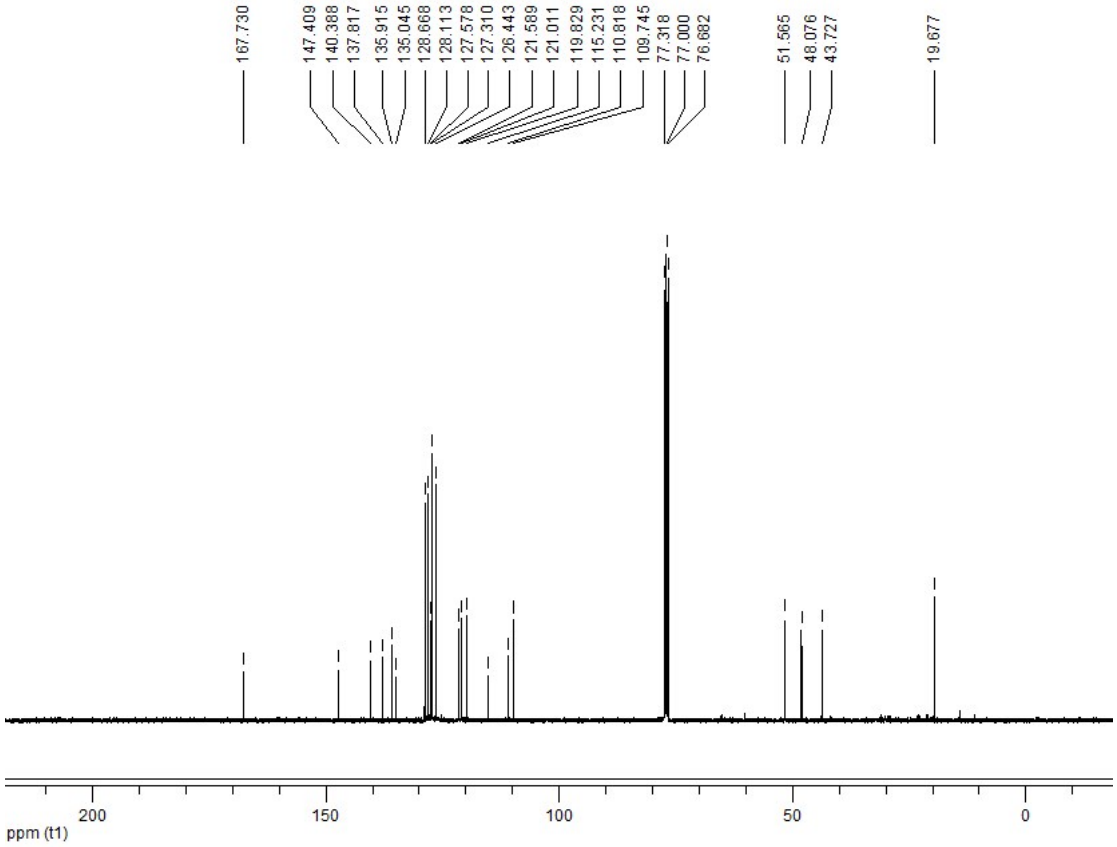
4ba


7.879
7.871
7.859
7.324
7.305
7.260
7.242
7.233
7.194
7.183
7.173
7.162
7.144
5.585
4.166
4.148
4.129
4.111
4.093
4.075
4.032
4.014
3.996
3.977
3.959
3.943
3.765
3.000
1.268
1.250
1.232
CO2Me
N
S
Et
1.05
1.00
3.05
3.10
3.12
10.0
5.0
0.0
ppm (t1)

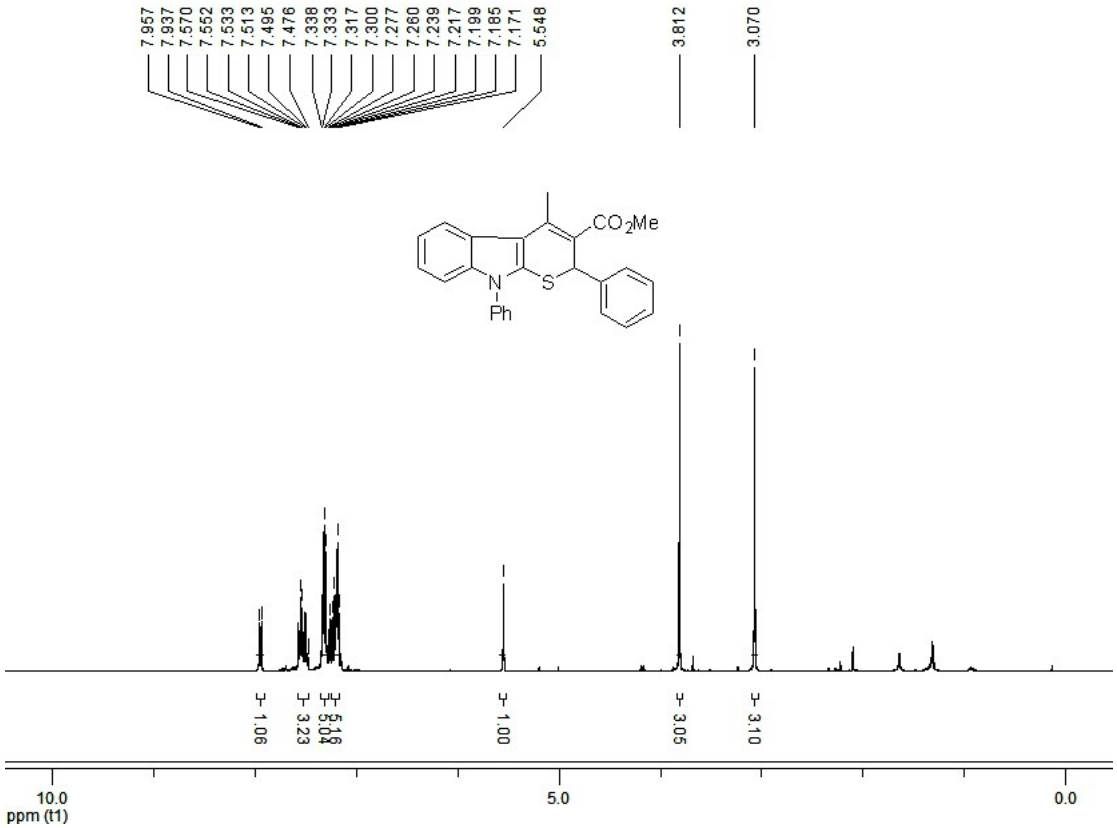

167.825
147.328
140.843
137.294
134.710
128.053
127.251
127.131
126.399
121.312
120.753
119.929
114.770
110.115
109.059
77.318
77.000
76.682
51.511
43.469
39.307
19.671
14.982
200
150
100
50
0
ppm (t1)

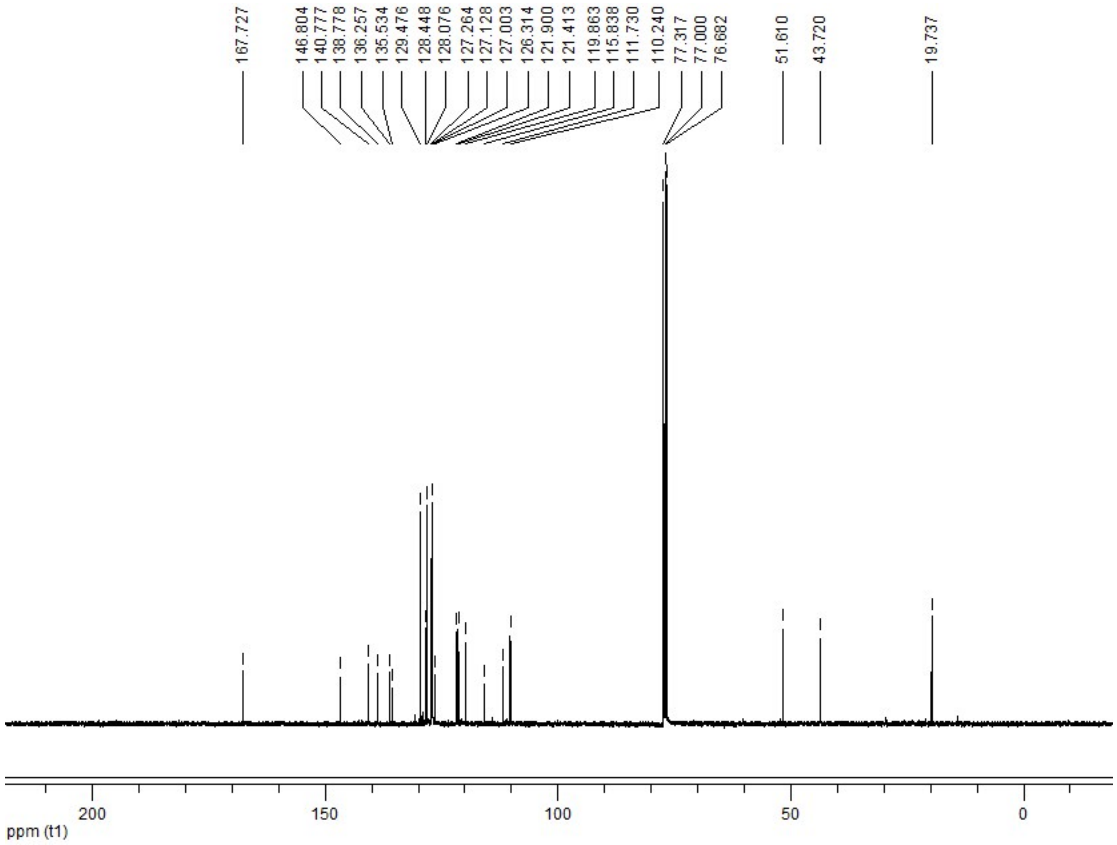
4ca


7.893
7.873
7.308
7.301
7.260
7.174
7.167
7.147
7.132
7.122
7.104
6.868
6.850
5.569
5.326
5.285
5.094
5.053
3.762
3.023
CO2Me
N
S
Bn
1.04
2.09
2.05
1.00
1.05
1.06
3.00
3.07
10.0
5.0
0.0
ppm (t1)

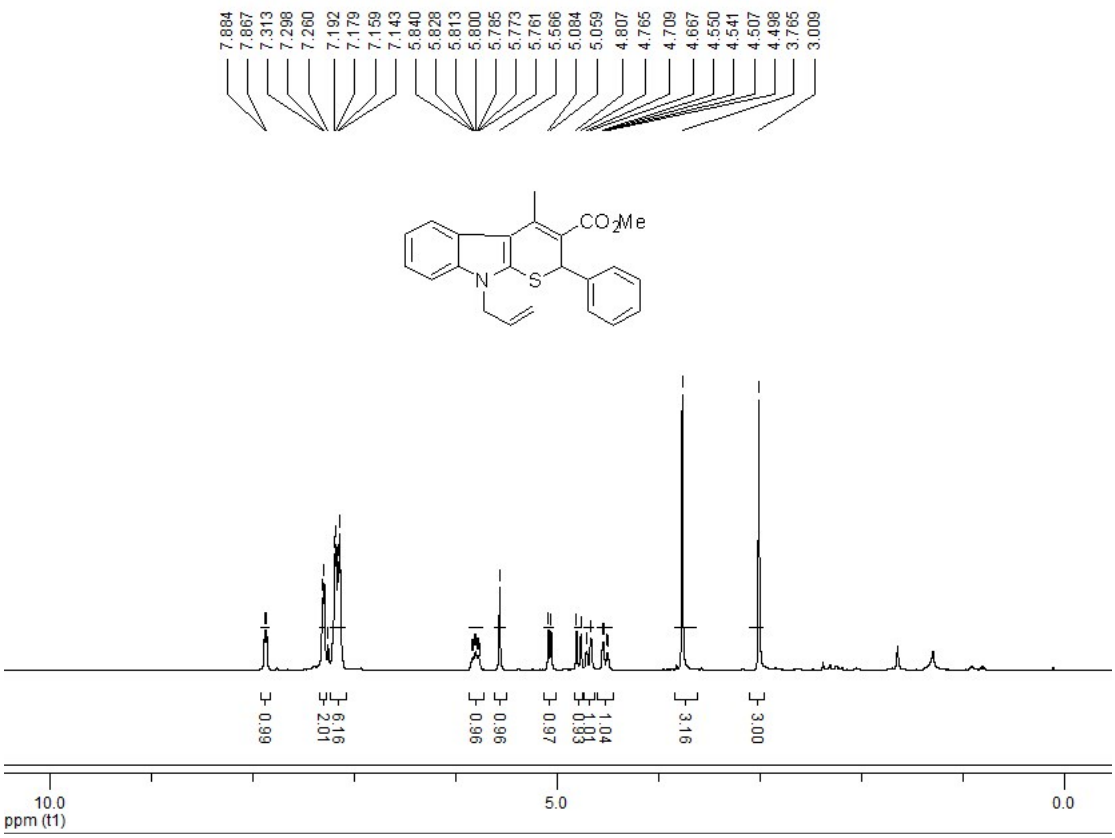

167.730
147.409
140.388
137.817
135.915
135.045
128.668
128.113
127.578
127.310
126.443
121.589
121.011
119.829
115.231
110.818
109.745
77.318
77.000
76.682
51.565
48.076
43.727
19.677
200
150
100
50
0
ppm (t1)

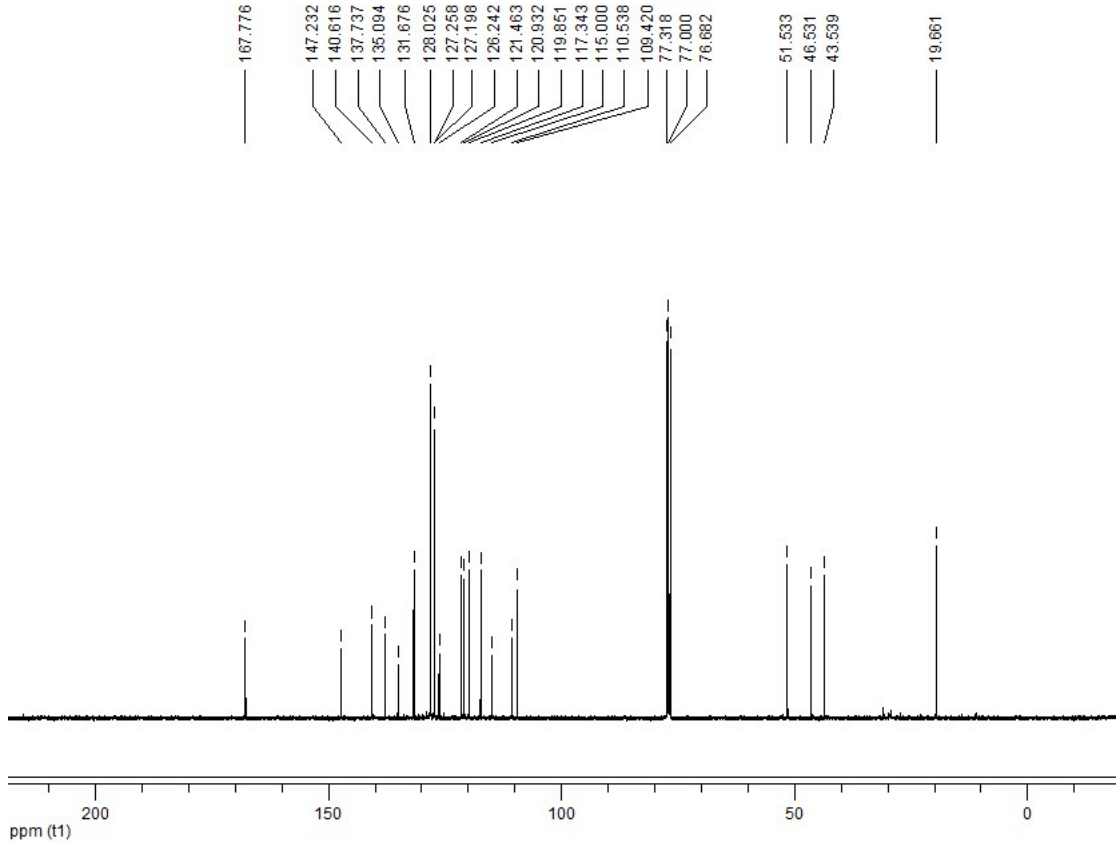
4da


7.957
7.937
7.570
7.552
7.533
7.513
7.495
7.476
7.338
7.333
7.317
7.300
7.277
7.260
7.239
7.217
7.199
7.185
7.171
5.548
3.812
3.070
CO2Me
N
S
Ph
1.06
3.23
5.08
1.00
3.05
3.10
10.0
5.0
0.0
ppm (t1)

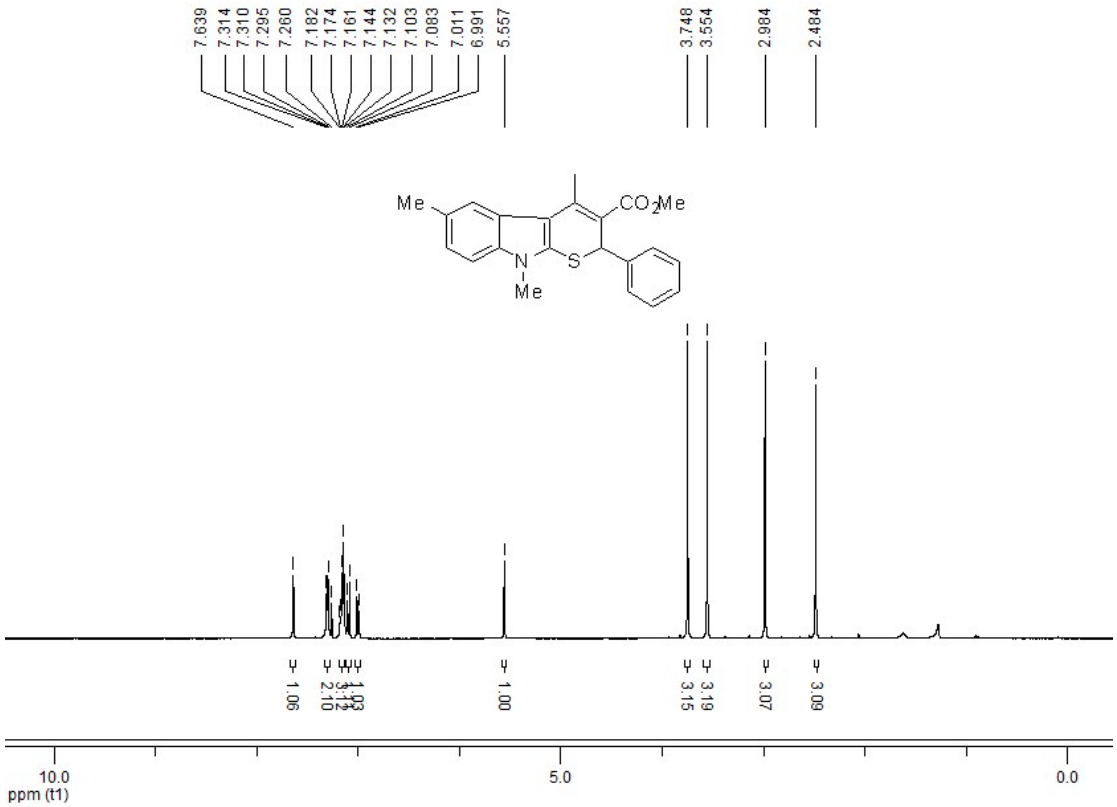

167.727
146.804
140.777
138.778
136.257
135.534
129.476
128.448
128.076
127.264
127.128
127.003
126.314
121.900
121.413
119.863
115.838
111.730
110.240
77.317
77.000
76.682
51.610
43.720
19.737
200
150
100
50
0
ppm (t1)

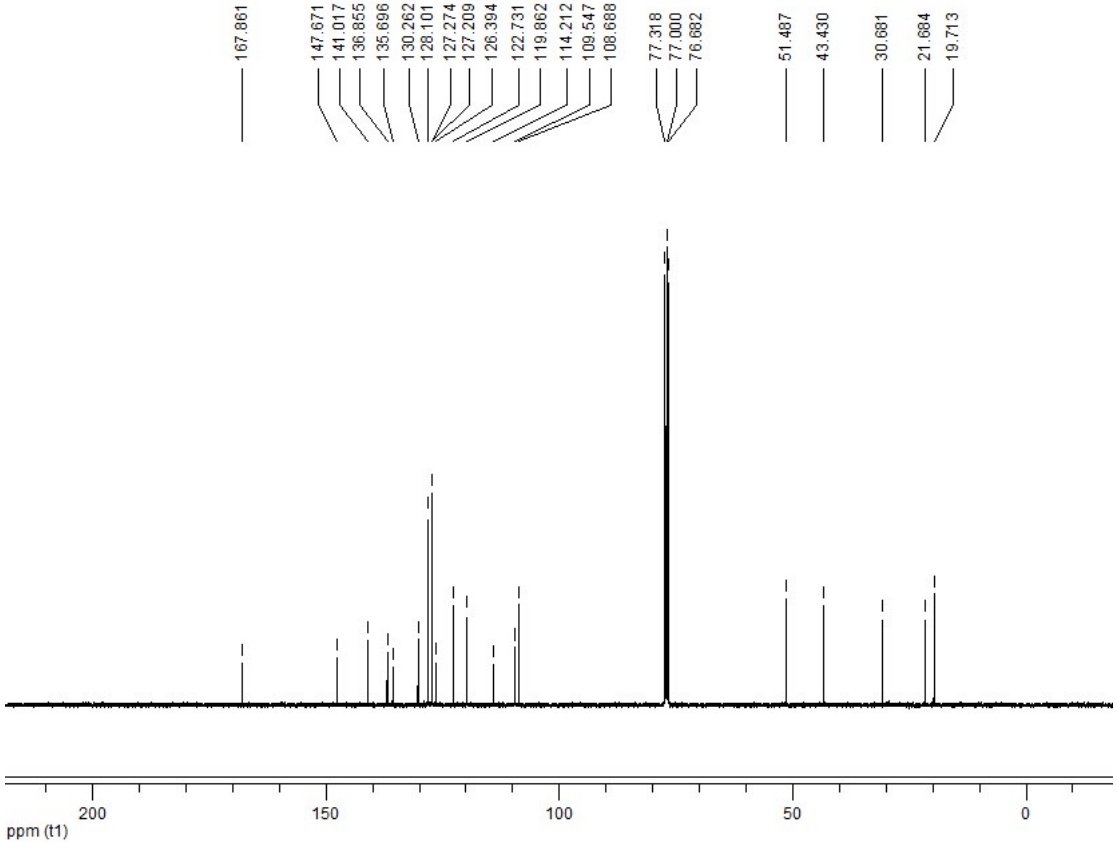
4ea


7.884
7.867
7.313
7.298
7.260
7.192
7.179
7.159
7.143
5.840
5.828
5.813
5.800
5.785
5.773
5.761
5.566
5.084
5.059
4.807
4.765
4.709
4.667
4.550
4.541
4.507
4.498
3.765
3.009
CO2Me
N
S
0.99
2.01
1.16
0.96
0.96
0.97
0.93
1.01
1.04
3.16
3.00
10.0
5.0
0.0
ppm (t1)

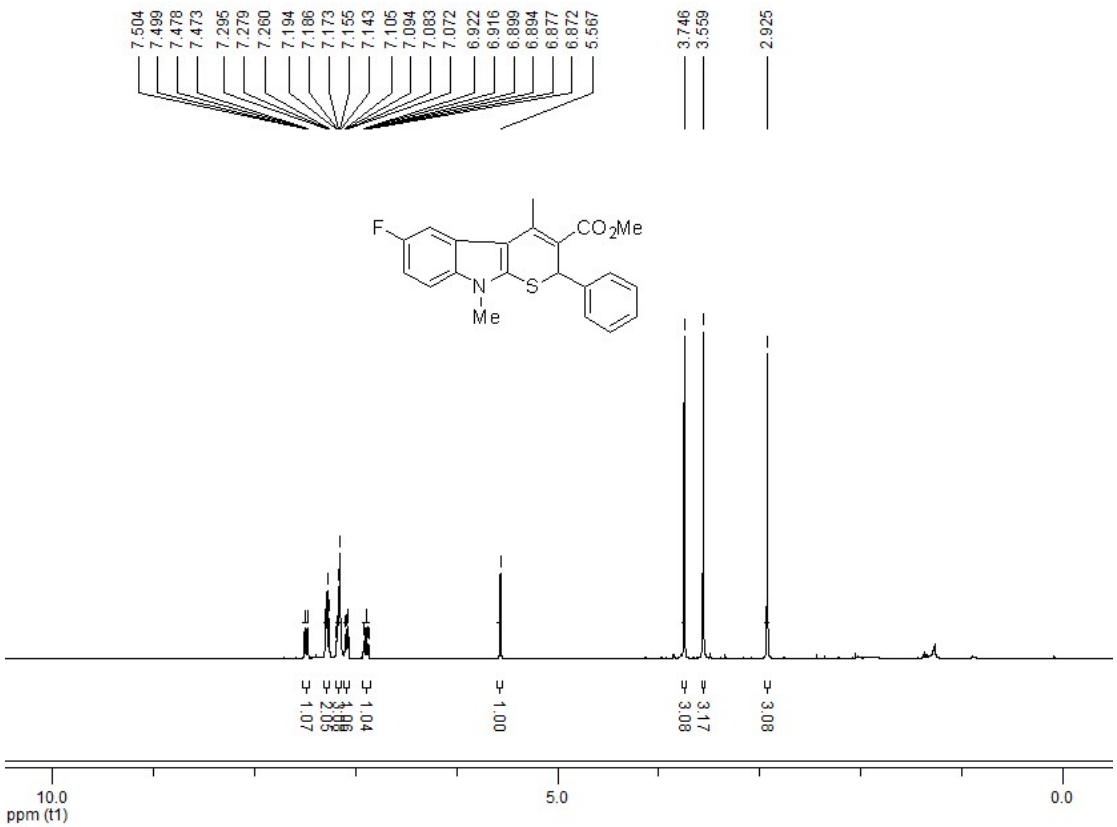

167.776
147.232
140.616
137.737
135.094
131.676
128.025
127.258
127.198
126.242
121.463
120.932
119.851
117.343
115.000
110.538
109.420
77.318
77.000
76.682
51.533
46.531
43.539
19.661
200
150
100
50
0
ppm (t1)

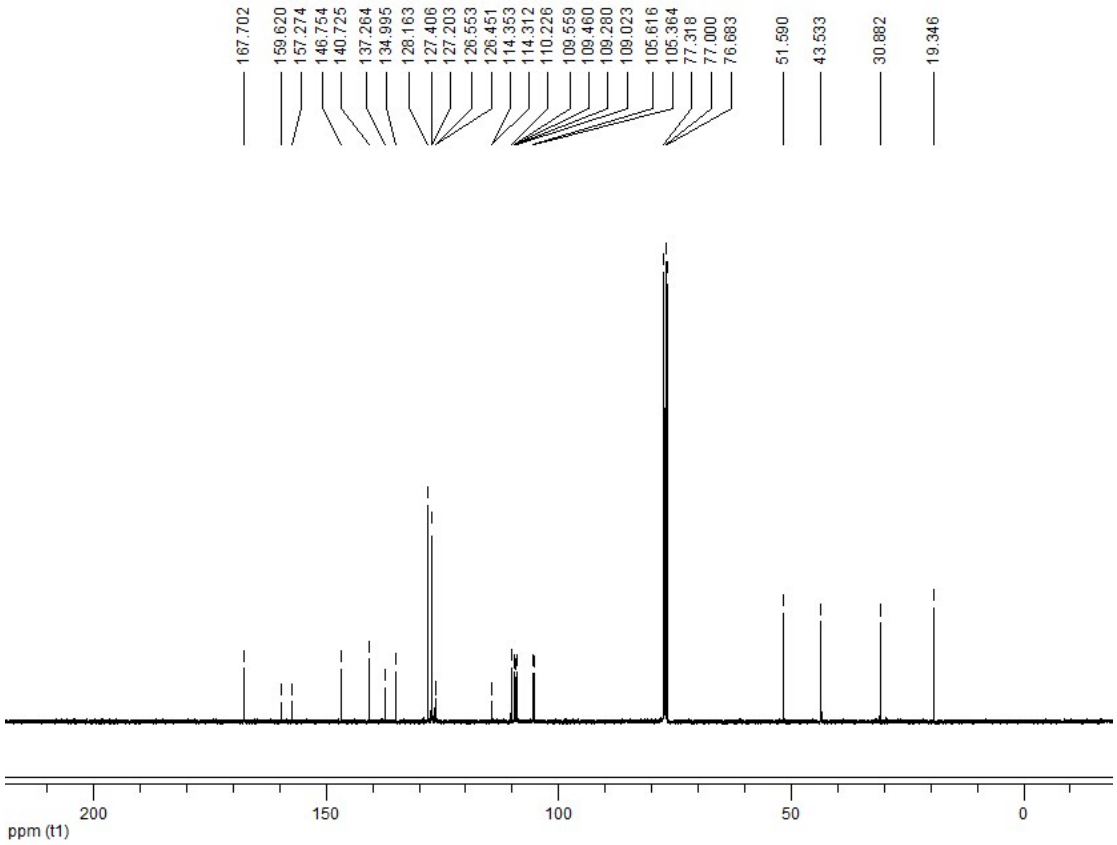
4fa


7.639
7.314
7.310
7.295
7.260
7.182
7.174
7.161
7.144
7.132
7.103
7.083
7.011
6.991
5.557
3.748
3.554
2.984
2.484
Me
CO2Me
N
S
Me
1.06
2.10
1.00
3.15
3.19
3.07
3.09
10.0
5.0
0.0
ppm (t1)

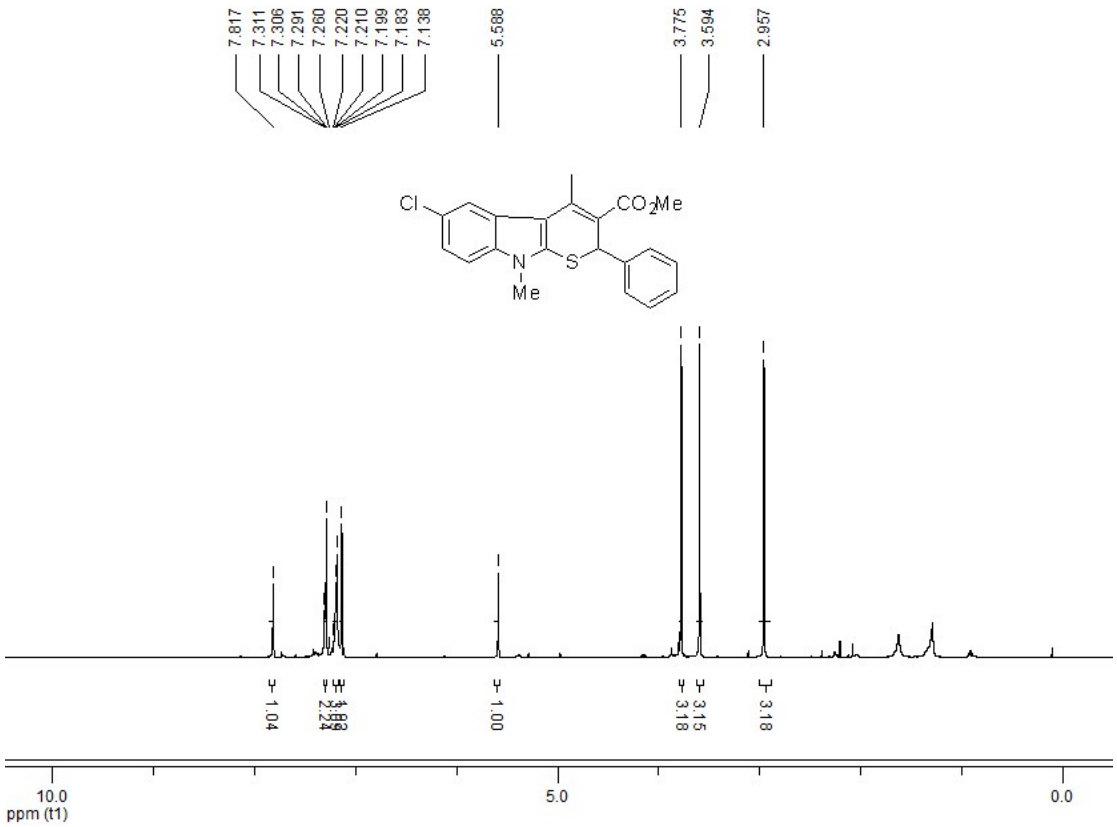

167.861
147.671
141.017
136.855
135.696
130.262
128.101
127.274
127.209
126.394
122.731
119.862
114.212
109.547
108.688
77.318
77.000
76.682
51.487
43.430
30.681
21.684
19.713
200
150
100
50
0
ppm (t1)

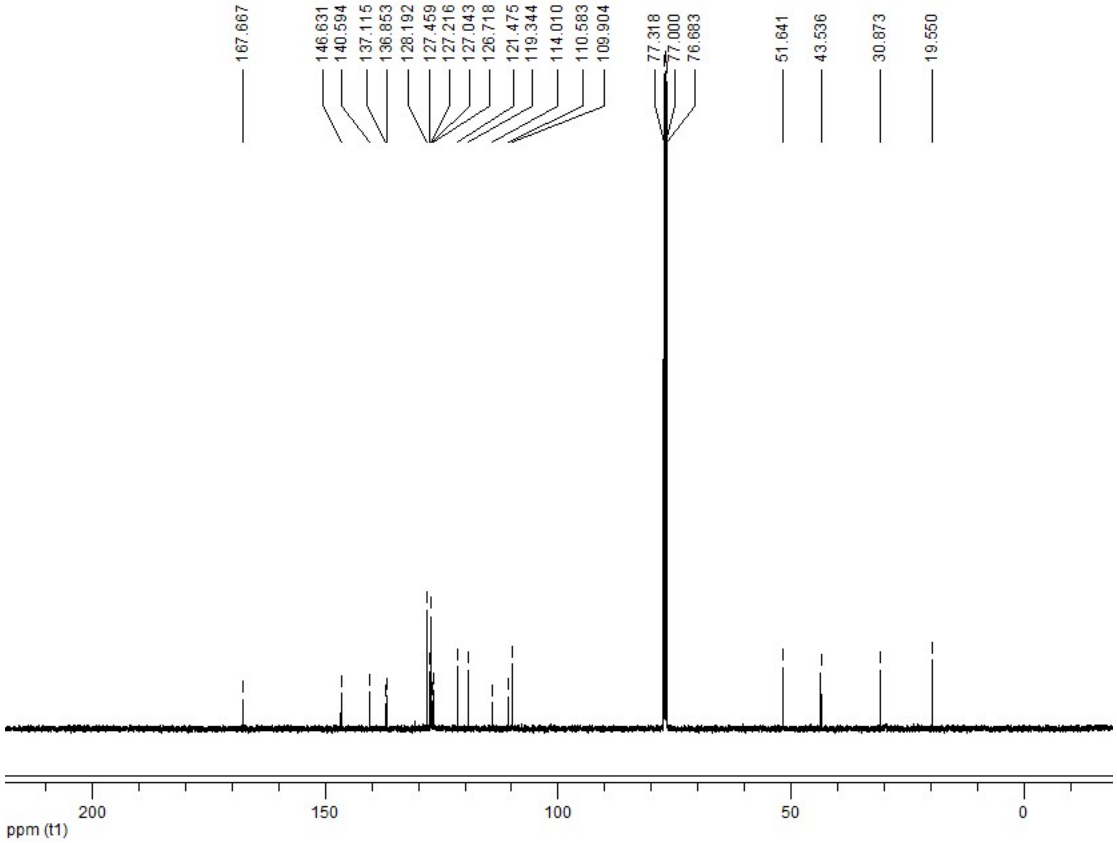
4ga


7.504
7.499
7.478
7.473
7.295
7.279
7.260
7.194
7.186
7.173
7.155
7.143
7.105
7.094
7.083
7.072
6.922
6.916
6.899
6.894
6.877
6.872
5.567
3.746
3.559
2.925
F
CO2Me
N
Me
S
1.07
2.05
3.08
1.04
1.00
3.08
3.17
3.08
10.0
ppm (t1)
5.0
0.0

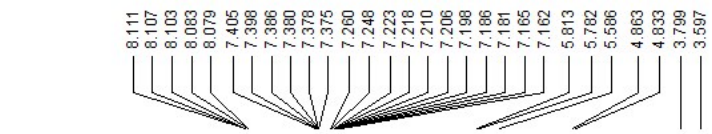

167.702
159.620
157.274
146.754
140.725
137.264
134.995
128.163
127.406
127.203
126.553
126.451
114.353
114.312
110.226
109.559
109.460
109.280
109.023
105.616
105.364
77.318
77.000
76.683
51.590
43.533
30.882
19.346
200
150
100
50
0
ppm (t1)

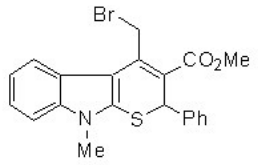
4ha

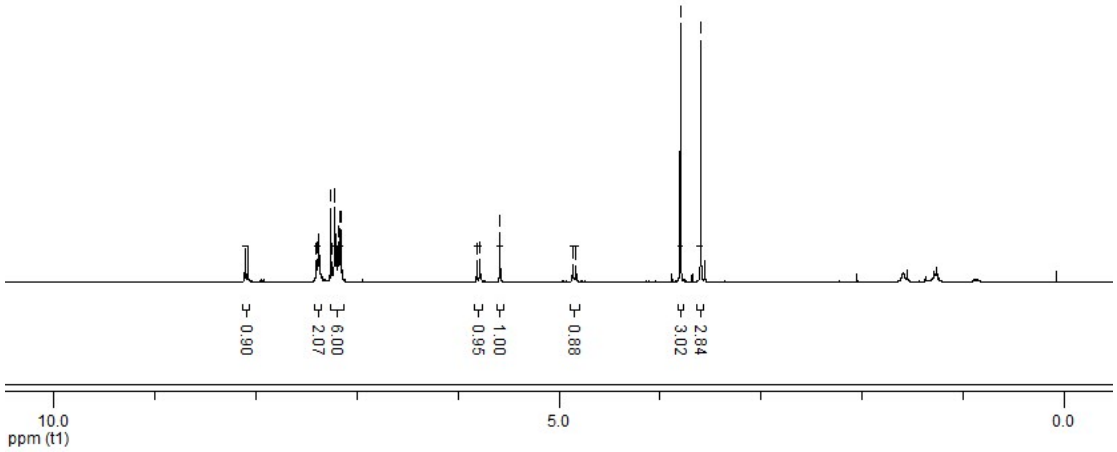

7.817
7.311
7.306
7.291
7.260
7.220
7.210
7.199
7.183
7.138
5.588
3.775
3.594
2.957
Cl
CO2Me
N
Me
S
1.04
2.27
2.88
1.00
3.18
3.15
3.18
10.0
5.0
0.0
ppm (t1)

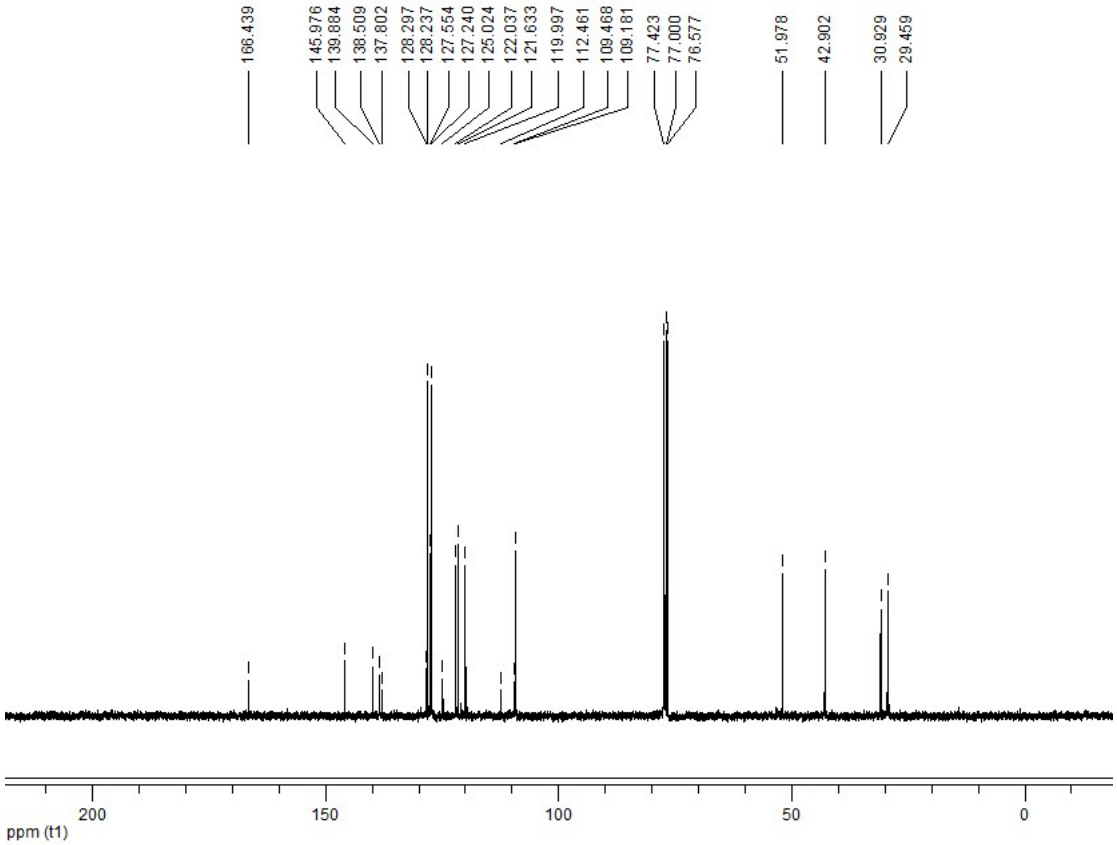

167.667
146.631
140.594
137.115
136.853
128.192
127.459
127.216
127.043
126.718
121.475
119.344
114.010
110.583
109.904
77.318
77.000
76.683
51.641
43.536
30.873
19.550
200
150
100
50
0
ppm (t1)

5

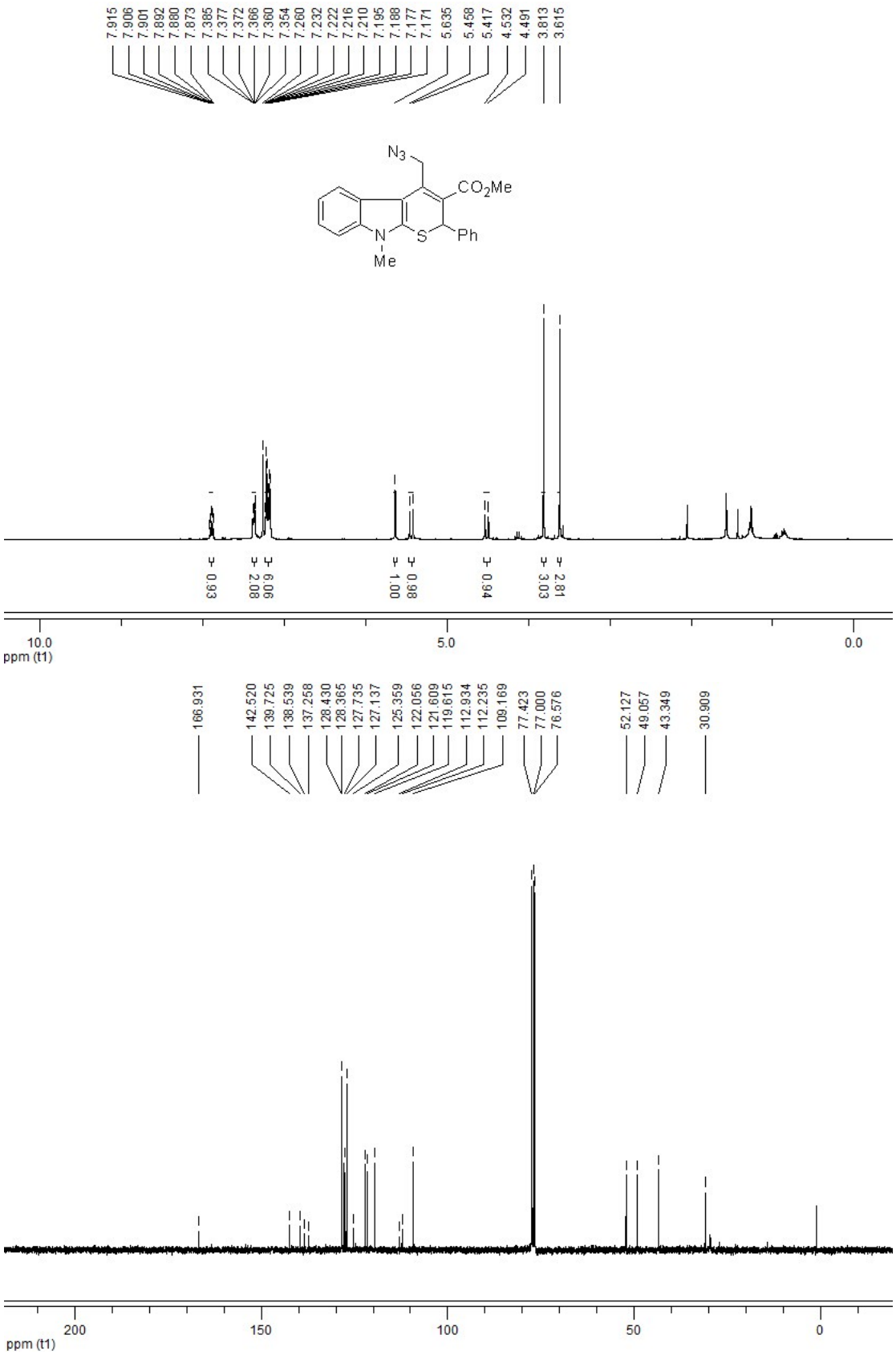

8.111
8.107
8.103
8.083
8.079
7.405
7.398
7.386
7.380
7.378
7.375
7.260
7.248
7.223
7.218
7.210
7.206
7.198
7.186
7.181
7.165
7.162
5.813
5.782
5.586
4.863
4.833
3.799
3.597


Br
CO2Me
N
S
Ph
Me

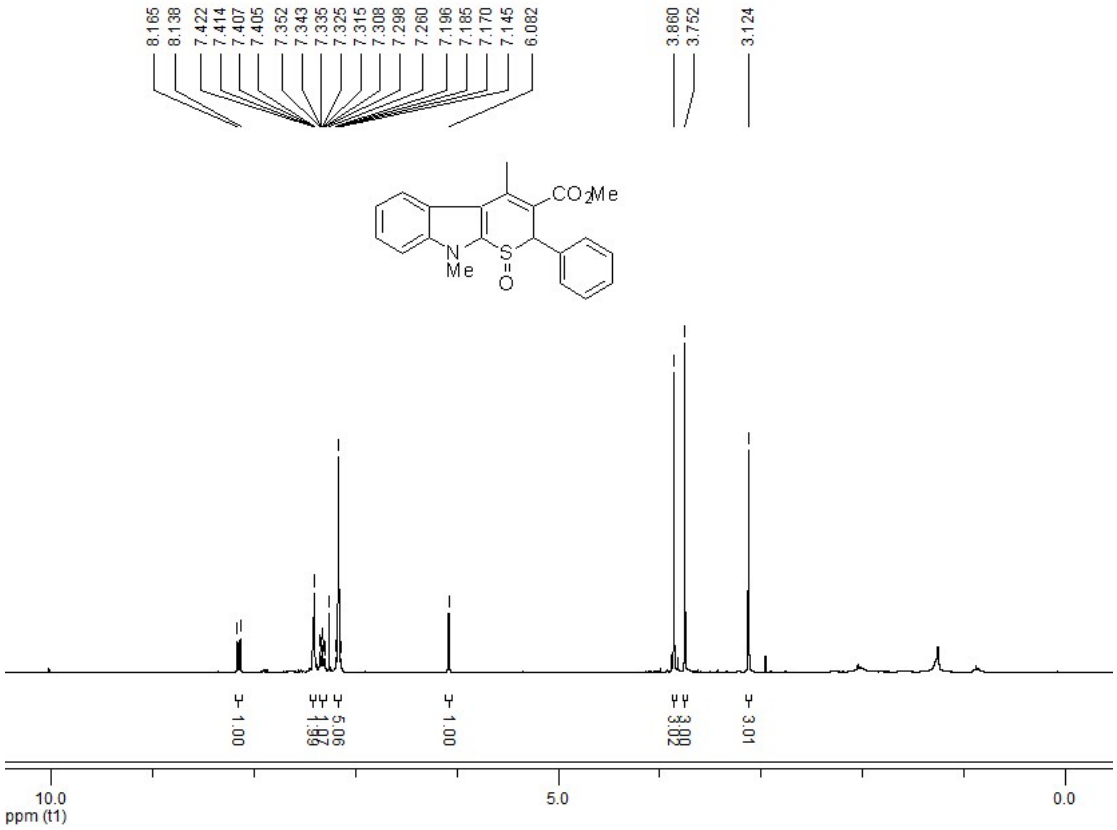

0.90
2.07
6.00
0.95
1.00
0.88
3.02
2.84
10.0
5.0
0.0
ppm (t1)

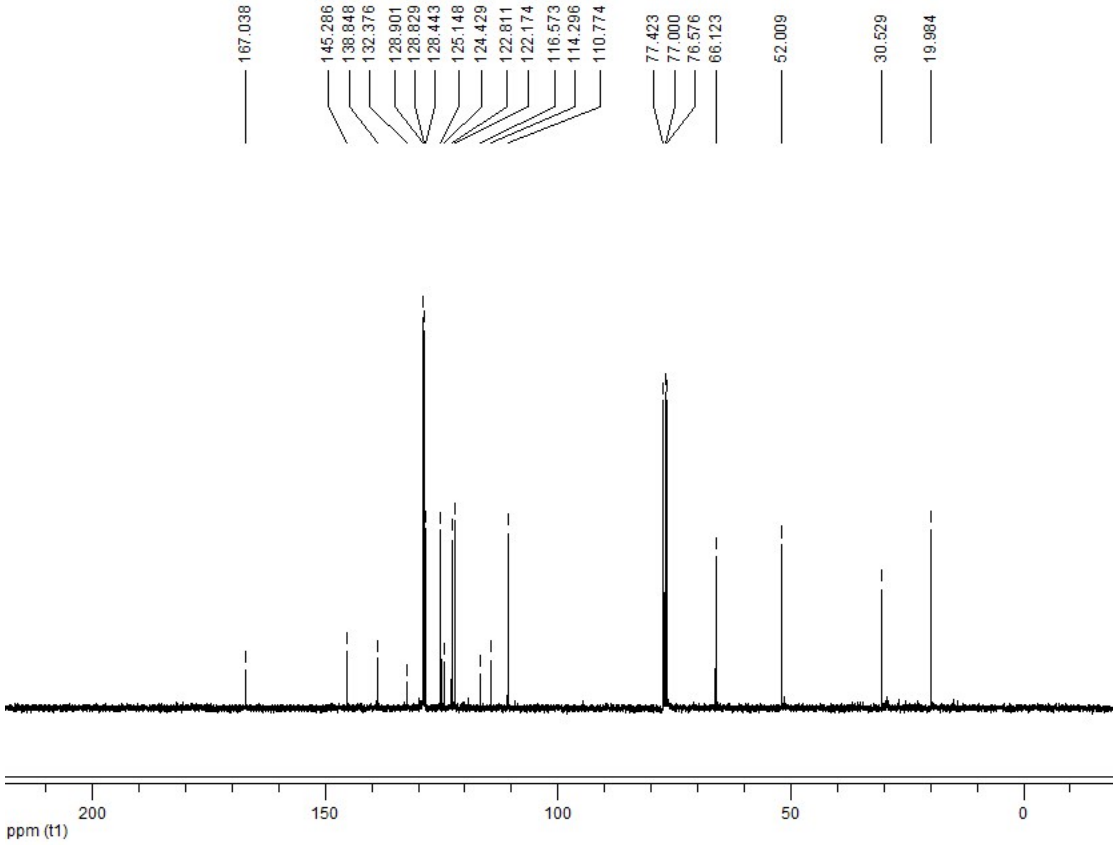

166.439
145.976
139.884
138.509
137.802
128.297
128.237
127.554
127.240
125.024
122.037
121.633
119.997
112.461
109.468
109.181
77.423
77.000
76.577
51.978
42.902
30.929
29.459
200
150
100
50
0
ppm (t1)

6

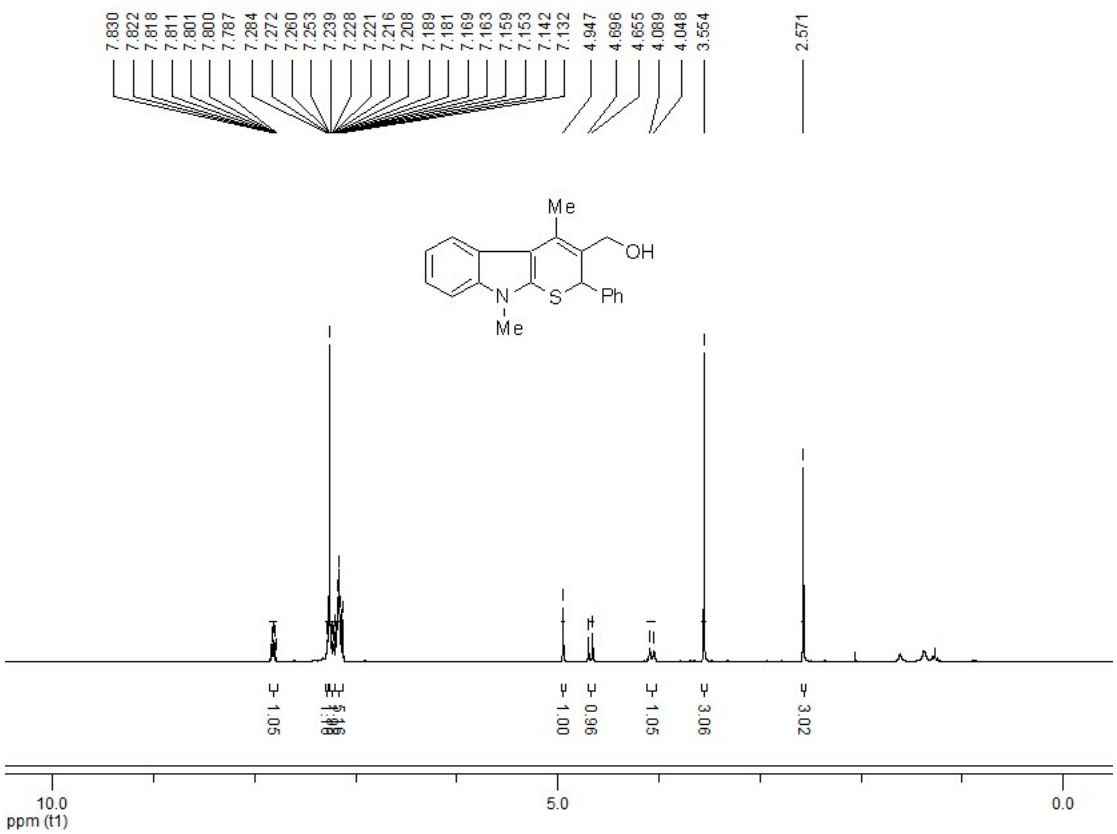

7.915
7.906
7.901
7.892
7.880
7.873
7.385
7.377
7.372
7.366
7.360
7.354
7.260
7.232
7.222
7.216
7.210
7.195
7.188
7.177
7.171
5.635
5.458
5.417
4.532
4.491
3.813
3.615
N3
CO2Me
Ph
N
S
Me
0.93
2.08
6.06
1.00
0.98
0.94
3.03
2.81
10.0
5.0
0.0
ppm (t1)
166.931
142.520
139.725
138.539
137.258
128.430
128.365
127.735
127.137
125.359
122.056
121.609
119.615
112.934
112.235
109.169
77.423
77.000
76.576
52.127
49.057
43.349
30.909
200
150
100
50
0
ppm (t1)

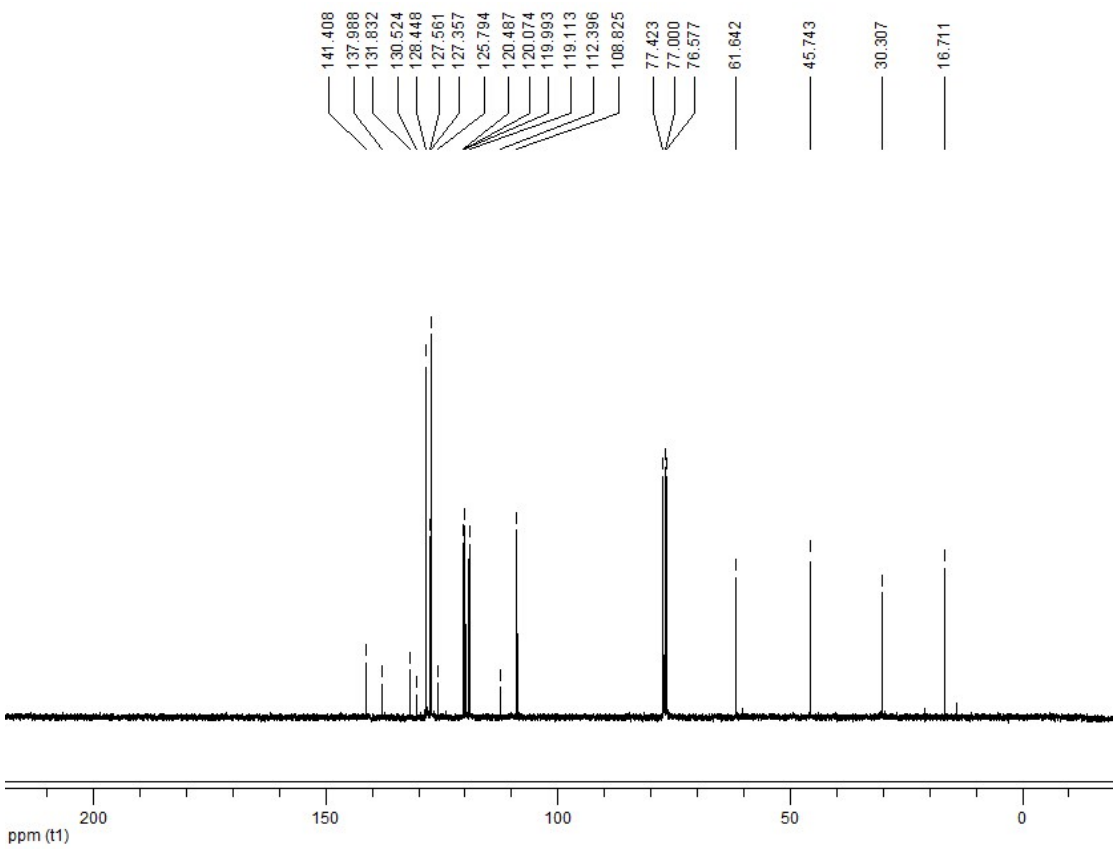
7


8.165
8.138
7.422
7.414
7.407
7.405
7.352
7.343
7.335
7.325
7.315
7.308
7.298
7.260
7.196
7.185
7.170
7.145
6.082
3.860
3.752
3.124
CO2Me
N
Me
S
O
1.00
1.92
1.97
5.06
1.00
3.02
3.00
3.01
10.0
5.0
0.0
ppm (t1)

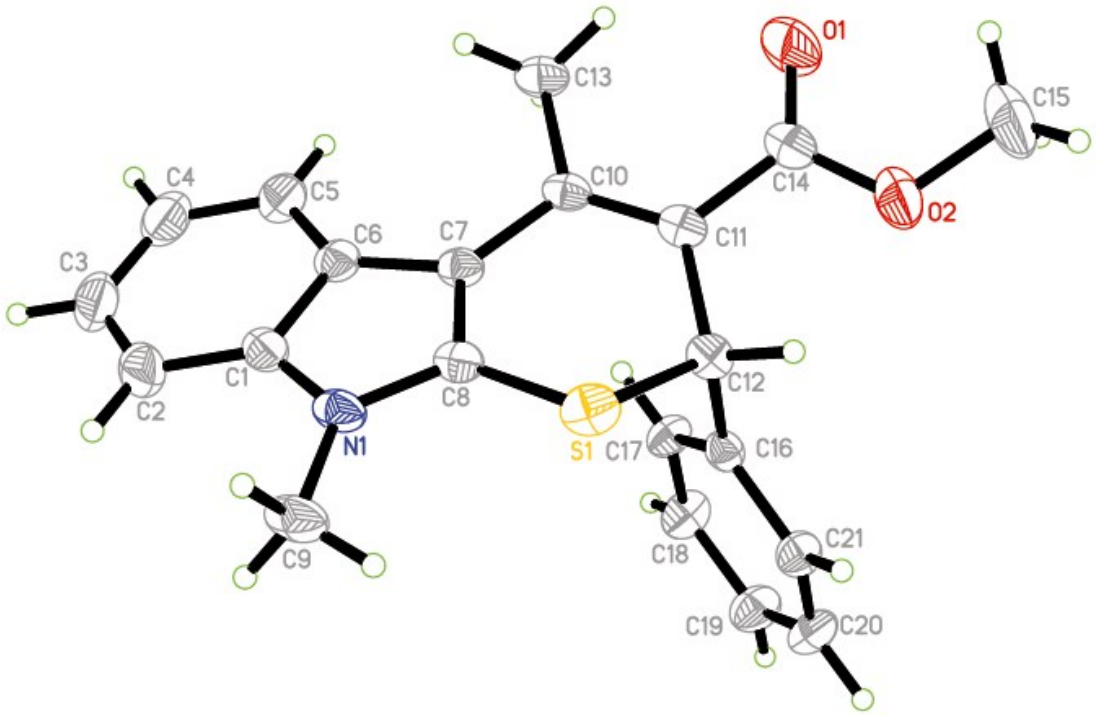

167.038
145.286
138.848
132.376
128.901
128.829
128.443
125.148
124.429
122.811
122.174
116.573
114.296
110.774
77.423
77.000
76.576
66.123
52.009
30.529
19.984
200
150
100
50
0
ppm (t1)

8


7.830
7.822
7.818
7.811
7.801
7.800
7.787
7.284
7.272
7.260
7.253
7.239
7.228
7.221
7.216
7.208
7.189
7.181
7.169
7.163
7.159
7.153
7.142
7.132
4.947
4.696
4.655
4.089
4.048
3.554
2.571
Me
OH
N
S
Ph
Me
1.05
5.16
1.00
0.99
1.05
3.00
3.02
10.0
ppm (t1)
5.0
0.0


141.408
137.988
131.832
130.524
128.448
127.561
127.357
125.794
120.487
120.074
119.993
119.113
112.396
108.825
77.423
77.000
76.577
61.642
45.743
30.307
16.711
200
150
100
50
0
ppm (t1)

6. X-ray Analysis of Compound 4aa



Crystal data and structure refinement for 160428d.

Identification code	160428d	
Empirical formula	C21 H19 N O2 S	
Formula weight	349.43	
Temperature	295(2) K	
Wavelength	0.71073 Å	
Crystal system	Triclinic	
Space group	P-1	
Unit cell dimensions	a = 7.754(3) Å	α= 97.693(9)°.
	b = 10.149(5) Å	β= 108.065(8)°.
	c = 11.964(5) Å	γ = 95.123(9)°.
Volume	878.5(7) $Å^3$	
Z	2	
Density (calculated)	1.321 Mg/m^3	
Absorption coefficient	0.198 mm^{-1}	
F(000)	368	
Crystal size	0.240 x 0.220 x 0.200 mm^3	
Theta range for data collection	2.045 to 25.248°.	
Index ranges	-9<=h<=9, -12<=k<=8, -14<=l<=14	
Reflections collected	4777	

Independent reflections	3093 [R(int) = 0.0218]
Completeness to theta = 25.242°	97.0 %
Absorption correction	None
Refinement method	Full-matrix least-squares on F^2
Data / restraints / parameters	3093 / 0 / 229
Goodness-of-fit on F^2	1.073
Final R indices [I>2sigma(I)]	R1 = 0.0500, wR2 = 0.1351
R indices (all data)	R1 = 0.0598, wR2 = 0.1565
Extinction coefficient	n/a
Largest diff. peak and hole	0.274 and -0.264 e.$Å^{-3}$