Electronic Supplementary Material (ESI) for Green Chemistry.

Supporting Information

For

p-TsOH Promoted Synthesis of Benzo-Fused O-Heterocycles from Alkynols via Ring Contraction and C-O Scission Strategy

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(1) General Information

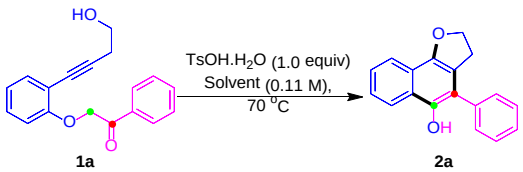
^{1}H, ^{13}C and DEPT NMR spectra were recorded on a 400 MHz Varian Unity Plus or Varian Mercury plus spectrometer or JEOL ECS-400. The chemical shift (δ) values are reported in parts per million (ppm), and the coupling constants (J) are given in Hz. The spectra were recorded using $CDCl_3$ as a solvent. ^{1}H NMR chemical shifts are referenced to tetramethylsilane (TMS) (0 ppm). ^{13}C NMR was referenced to $CDCl_3$ (77.0 ppm) or d-acetone (29.92 ppm). The abbreviations used are as follows: s, singlet; d, doublet; t, triplet; q, quartet; dd, doublet of doublet; ddd, doublet of doublet of doublet; dt, doublet of triplets; td, triplet of doublet; m, multiplet. Mass spectra and high resolution mass spectra (HRMS) were measured using the ESI (FT-MS solariX) at National Sun Yat-Sen University, Kaohsiung, Taiwan and LTQ Orbitrap XL (Thermo Fischer Scientific) at National Chung Hsing University. Melting points were determined on an EZ-Melt (Automated melting point apparatus). All products reported showed ^{1}H NMR spectra in agreement with the assigned structures. Reaction progress and product mixtures were routinely monitored by TLC using Merck TLC aluminum sheets (silica gel 60 F254). Column chromatography was carried out with 230–400 mesh silica gel 60 (Merck) and a mixture of hexane/ethyl acetate or hexane as an eluent. Preparative TLC was run on a Merck TLC aluminum sheets (silica gel 60 F254).

(2) Studies on reaction parameters

Initially, the reaction was performed using **1a** as the model substrate to optimize the reaction conditions. Control reactions establish that the desired product **2a** was not formed in the absence of TsOH (Table S1, entry 1). Similarly, the reaction gave <10% of product formation in the presence of Lewis acids such as $AuCl(PPh_3)$, AgOTf, $AgSbF_6$ and $FeCl_3$ (Table S1, entries 2-5). Subsequent investigation of reaction under catalytic “iodo” sources like I_2, NIS and TBAI gave trace amount of **2a** (Table S1, entries 6-8). The desired product **2a** was obtained in 60% yield when

the reaction was performed with 20% of TsOH.H_2O for 16 h (Table S1, entry 9). By increasing the equivalents of TsOH to 0.5 and 1.0 resulted in a higher yields than that of catalytic version (Table 1, entry 10-11). Replacing TsOH with other acids such as BF_3-Et_2O, TfOH, TFA and

Table S1. Studies on reaction parameters[a]



1a **2a**

entry	reagents (equiv)	solvent	time, h	Yield (%)[b]
1	-	1,2-DCE	16	0
2	5% AuCl(PPh_3) (0.05)	1,2-DCE	16	<10
3	5% AgOTf (0.05)	1,2-DCE	16	<10
4	5% $AgSbF_6$ (0.05)	1,2-DCE	16	<10
5	5% $FeCl_3$ (0.05)	1,2-DCE	16	<10
6	I_2 (0.2)	1,2-DCE	16	<10
7	NIS (0.2)	1,2-DCE	16	<10
8	TBAI (0.2)	1,2-DCE	16	0
9	TsOH (0.2)	1,2-DCE	16	60
10	TsOH (0.5)	1,2-DCE	8	71
11	TsOH (1.0)	1,2-DCE	6	91
12	BF_3-Et_2O (1.0)	1,2-DCE	6	40
13	TfOH (1.0)	1,2-DCE	6	35
14	TFA (1.0)	1,2-DCE	6	<10
15	CH_3COOH (1.0)	1,2-DCE	6	trace
16	TsOH (1.0)	H_2O:1-butanol (9:1)	6	20[c]
17	TsOH (1.0)	Acetone	6	58[c]
18	TsOH (1.0)	Ethanol	6	83(88)[c]
19	TsOH (1.0)	2-propanol	6	75
20	TsOH (1.0)	Ethyl acetate	6	87(92)[c]
21	TsOH (1.0)	Methanol	6	45[c]
22	TsOH (1.0)	Methyl ethyl ketone (MEK)	6	30[c]
23	TsOH (1.0)	1-butanol	6	54[c]
25	TsOH (1.0)	Toluene	6	90(94)[c]
25	TsOH (1.0)	Acetonitrile	6	82[c]
26	TsOH (1.0)	THF	6	74[c]
27	TsOH (1.0)	DMSO	6	60[c,d]
28	TsOH (1.0)	Ethylene glycol	6	20[c]
29	TsOH (1.0)	DMSO	6	-[e]

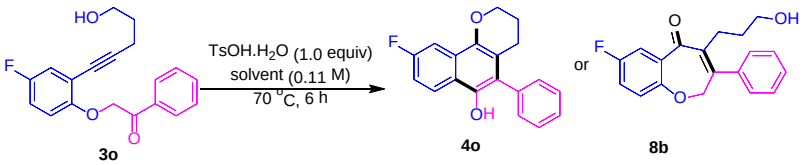
[a]All reactions were performed with 0.25 mmol of **1a** in 0.11 M of solvent. [b]Isolated yields. [c]Yields were determined by NMR spectra using 1,3,5-trimethoxy benzene as an internal standard. [d]20% of 2-(2-hydroxyethyl)-3-phenylnaphthalene-1,4-dione **12a** was also observed. [e]After 24 h of heating at 100 °C, compound **12a** has been completely converted to **12a** in 80% yields.

CH_3COOH also failed to improve the yield of **2a** (Table S1, entries 12-15). With the optimized reagent in hand, we next focused on identifying the greener solvent to replace 1,2-dichloroethane.

In this context, preferred and usable green solvents[1] such as water, acetone, ethanol, 2-propanol, ethylacetate, methanol, methyl ethyl ketone, 1-butanol, toluene, acetonitrile, tetrahydrofuran, dimethylsulfoxide and ethylene glycol were tested using 0.25 mmol of **1a** with 1.0 equiv of $TsOH.H_2O$ at 70 °C for 6 h as shown in Table S1. The reaction proceeded smoothly with ethanol (Table S1, entry 18), ethyl acetate (Table S1, entry 20) and toluene (Table S1, entry 25) in 83-90% yields respectively as compared with other solvents (Table S1, 16-28). While using DMSO as a solvent, 20% of 2-(2-hydroxyethyl)-3-phenylnaphthalene-1,4-dione **12a** was observed as by-product (Table S1, entry 27). When the reaction time and temperature was increased to 100 °C and 24h, the expected **12a** was obtained in 80% yield thus suggesting the role of DMSO also as an oxidant (Table S1, 29).

To finalize the optimum solvent, random reaction was performed with substrate **3o** with ethanol, ethyl acetate and toluene as shown in Table S2. Unfortunately, the reaction gave compound **8b** rather than the desired product **4o** in ethanol and ethylacetate. In case of toluene, the required product in 53% yield. Thus, 1.0 equiv of $TsOH.H_2O$ in 0.11M of Toluene at 70 °C (Table S2, entry 9) was considered as the optimum reaction conditions.

Table S2. Solvent finalization study

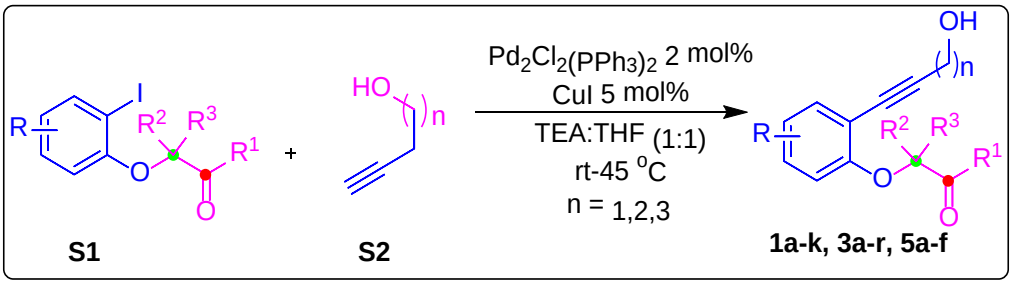


entry	product	ethanol	ethylacetate	toluene
1	**4o**	0%	0%	51%
2	**8b**	82%	91%	0%

[a]All reactions were performed with 0.25 mmol of **1a** in 0.11 M of solvents.

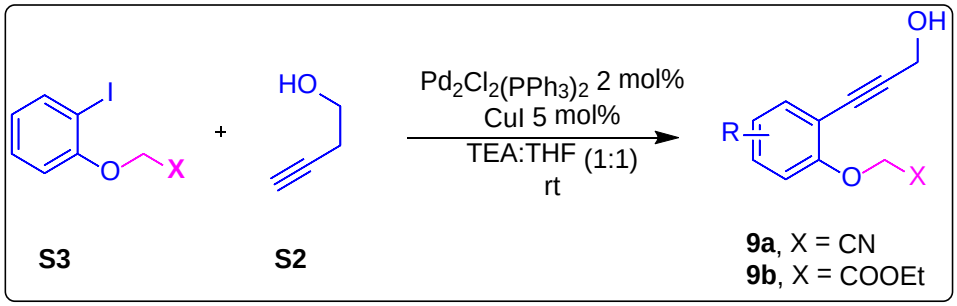
(3) Experimental procedures

General procedure A for the synthesis of starting materials 1a-k, 3a-r and 5a-f



To a stirred solution of **S1 (**1.0 equiv) in 1:1 mixture of triethylamine (TEA) and THF were added alkynol (**S2**, 1.5 equiv), $PdCl_2(PPh_3)_2$ catalyst (2.0 mol %) at rt under N_2 atmosphere. After stirring at room temperature for 5 minutes CuI (5.0 mol %) was added and the resultant reaction mixture was allowed to stir at rt-45 °C. The completion of the reaction was monitored with the help of TLC. After completion, the reaction mixture was concentrated under vacuum to remove excess solvent and then diluted using water followed by extraction with ethyl acetate. Combined ethyl acetate layer was washed with water, brine, dried over sodium sulfate and evaporated under reduced pressure. The obtained crude compound was purified by column chromatography (hexane to 25% EA/Hex) to obtain pure starting materials respectively. The structure of compounds **3a**, **3b**, **3c**, **3d**, **3f**, **3g**, **3h**, **3i**, **3l**, **3n**, **3o**, **3p**, **3q**, **5b**, **5c**, **5d** and **5e** were matched with our previous reported literature data.[2]

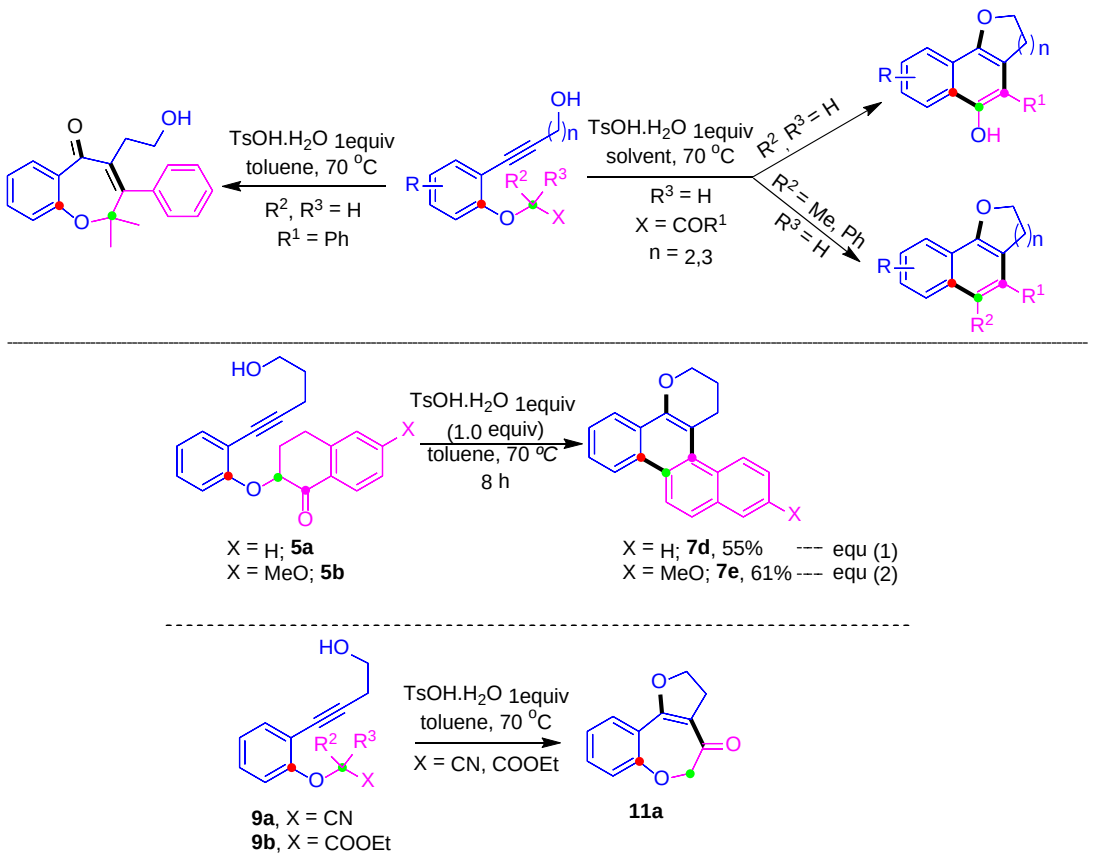
Procedure for the synthesis of starting materials 9a and 9b



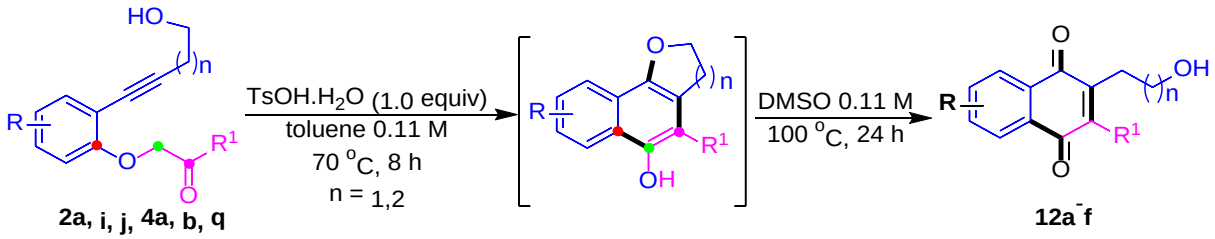
To the stirred solution of **S3 (**1.0 equiv) in 1:1 mixture of triethylamine (TEA) and THF were added 3-butyn-1-ol (**S2**, 1.5 equiv), $PdCl_2(PPh_3)_2$ catalyst (2.0 mol %) at rt under N_2 atmosphere. After stirring at room temperature for 5 minutes CuI (5.0 mol %) was added and the resultant reaction mixture was allowed to stir at rt. The completion of the reaction was monitored with the help of TLC. After completion, the reaction mixture was concentrated under vacuum to remove excess solvent and then diluted using water followed by extraction with ethyl acetate. Combined ethyl acetate layer was washed with water, brine, dried over sodium sulfate and evaporated under reduced pressure. The obtained crude compound was purified by column chromatography (hexane to 25% EA/Hex) to obtain pure starting material **9a** and **9b**.

General procedure B for the TsOH promoted cyclization

To the stirred solution of **1, 3, 5** and **9 (**0.25 mmol, 1.0 equiv) in 0.11 M of toluene or 1,2-dichloroethane (1,2-DCE) was added TsOH. H_2O (0.25 mmol, 1.0 equiv) at room temperature and allowed to stir at 70 ^oC until the completion of reaction was analysed by TLC. After completion, the reaction mixture was diluted using water followed by extraction with dichloromethane or ethylacetate. Combined organic layer was washed with water, brine, dried over sodium sulfate and evaporated under reduced pressure. The obtained crude products were purified by column chromatography (hexane to hexane to 0.25% EA/Hexane) to afford the pure compounds respectively.



General procedure C for the synthesis of 1,4-naphthaquinone derivatives



To the stirred solution of **2a, i, j 4a, b, q (**0.25 mmol, 1.0 equiv) in 0.11M of toluene was added TsOH. H_2O (0.25 mmol, 1.0 equiv) at room temperature and allowed to stir at 70 °C until the completion of reaction was analysed by TLC. After completion of the reaction, excess toluene was removed under vacuum followed by the addition of DMSO (0.11 M) and continued stirring under air for another 24 h at 100 °C. After completion of the reaction monitored by TLC, the reaction mixture was diluted using water followed by extraction with ethyl acetate. Combined ethyl acetate layer was washed with water followed by brine, dried over sodium sulfate and evaporated under

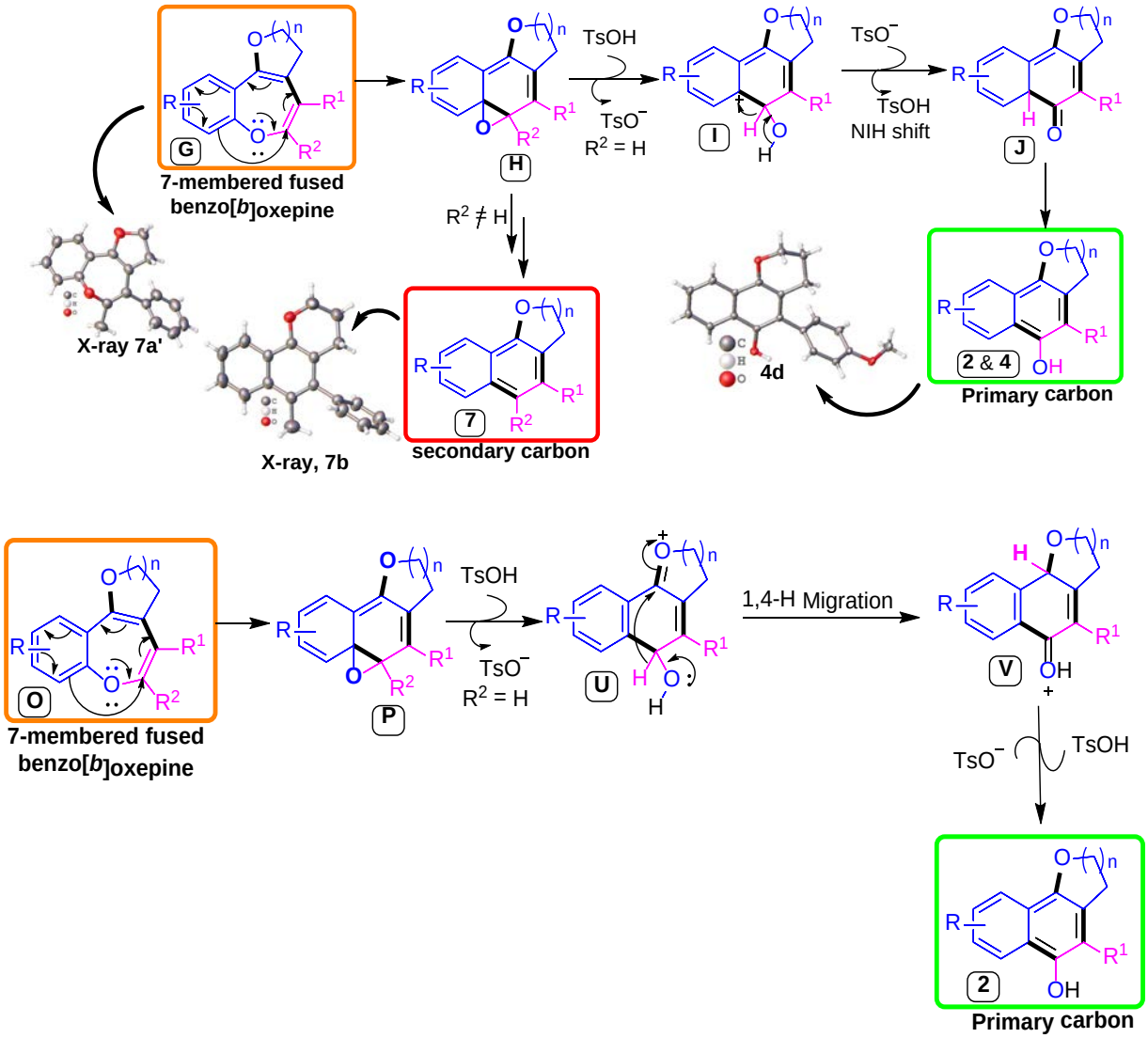
reduced pressure. The crude products were purified by column chromatography (hexane to 25% EA/Hex) to afford the pure compounds **12a-f**.

(4) References

1. K. Alfonsi, J. Colberg, P. J. Dunn, T. Fevig, S. Jennings, T. A. Johnson, H. P. Kleine, C. Knight, M. A. Nagy, D. A. Perry and M. Stefaniakc, *Green Chem*. 2008, **10**, 31-36.

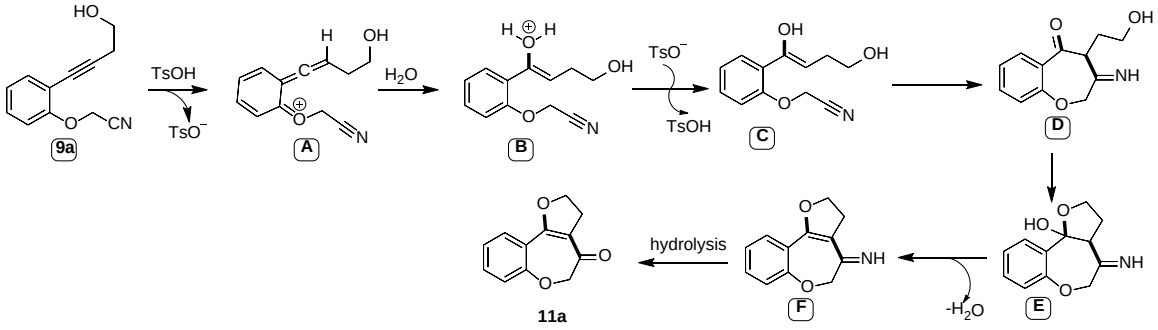
2. A. M. Garkhedkar, G. C. Senadi and J. –J. Wang, *Org. Lett*. 2017, **19**, 488-491.

(5) Alternative mechanisms from intermediate G

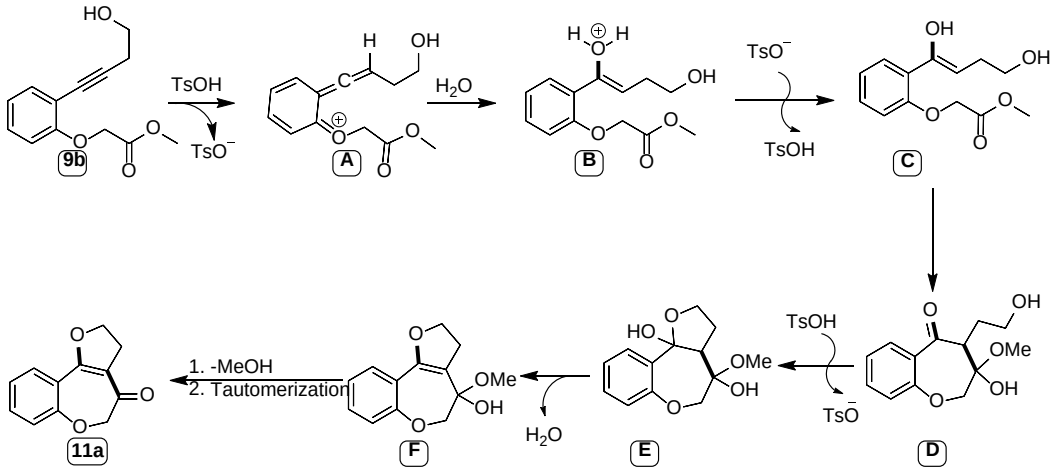


(6) Mechanism for product 11a and 7d, e

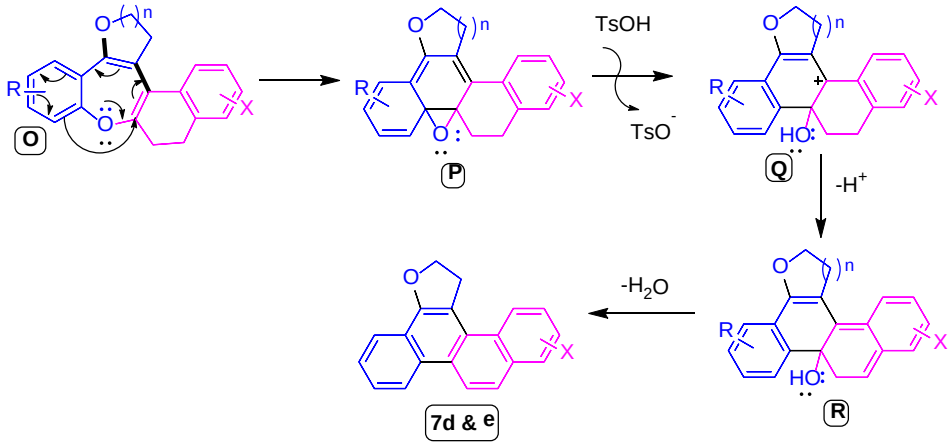
(i) From nitrile starting material 9a:



(ii) From ester starting material 9b:

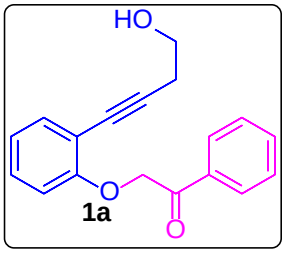


(iii) From tetralone derivatives 5d and e:



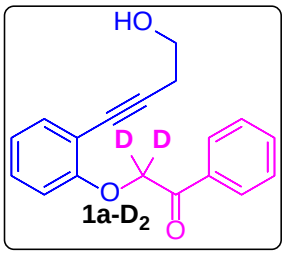
(7) Spectral Characterization

2-(2-(4-hydroxybut-1-yn-1-yl)phenoxy)-1-phenylethan-1-one (1a): The title compound was



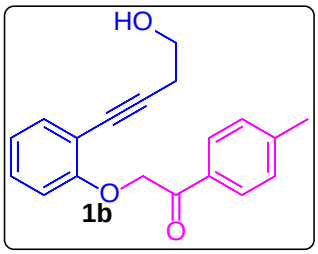
prepared according to the general procedure A as a yellow solid; M.P. 55 °C ~ 57 °C; ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.02 (dt, *J* = 8.5, 1.6 Hz, 2H), 7.61 (tt, *J* = 7.2, 2.4 Hz, 1H), 7.53 – 7.47 (m, 2H), 7.39 (dd, *J* = 7.6, 1.7 Hz, 1H), 7.23 (ddd, *J* = 9.2, 7.7, 3.6 Hz, 1H), 6.93 (td, *J* = 7.5, 1.0 Hz, 1H), 6.82 (d, *J* = 8.3 Hz, 1H), 5.33 (s, 2H), 3.82 (q, *J* = 6.0 Hz, 2H), 2.84 (t, *J* = 6.4 Hz, 1H), 2.71 (t, *J* = 5.9 Hz, 2H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 193.81, 158.46, 134.32, 133.91, 133.17, 129.07, 128.77, 128.07, 121.45, 113.40, 112.18, 91.75, 78.37, 71.05, 60.96, 24.23; HR-MS (ESI): m/z = 281.1176, calcd. for $C_{18}H_{17}O_3$ $[M+H]^+$: 281.1172.

2-(2-(4-hydroxybut-1-yn-1-yl)phenoxy)-1-phenylethan-1-one-2,2-d$_2$ (1a-D$_2$): The title

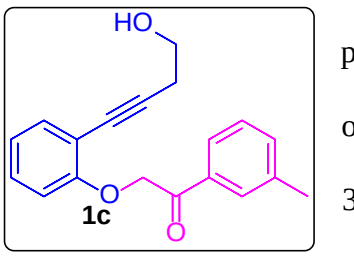


compound was prepared using 1.0 mmol of **1a** and 10 mol% of NaOH in a 1:1 mixture of D_2O/THF (5.6 mL) at room temperature for 16 h. Then the reaction mixture was diluted with ethylacetate and layers were separated, dried over sodium sulfate. The crude product obtained after evaporation was purified by column chromatography (hexane to 20% EA/Hex) to afford the pure compound as an off-white sticky mass (142 mg, 50% yield). ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.04 – 8.00 (m, 2H), 7.66 – 7.58 (m, 1H), 7.54 – 7.47 (m, 2H), 7.40 (dd, *J* = 7.6, 1.7 Hz, 1H), 7.26 – 7.19 (m, 2H), 6.94 (td, *J* = 7.5, 1.0 Hz, 1H), 6.82 (dd, *J* = 8.3, 0.8 Hz, 1H), 3.82 (d, *J* = 5.3 Hz, 2H), 2.71 (t, *J* = 5.9 Hz, 3H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 193.96, 158.53, 134.42, 133.95, 133.24, 129.12, 128.81, 128.14, 121.50, 113.45, 112.23, 91.72, 78.47, 61.00, 24.28.; HR-MS (ESI): m/z = 305.1117, calcd. for $C_{18}H_{14}NaD_2O_3$ $[M+Na]^+$: 305.1116.

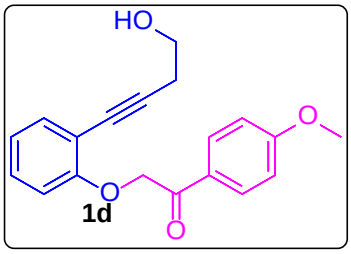
2-(2-(4-hydroxybut-1-yn-1-yl)phenoxy)-1-(*p*-tolyl)ethan-1-one (1b): The title compound was prepared according to the general procedure A as a yellow viscous oil; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.86 (dt, *J* = 8.4, 1.6 Hz 2H), 7.34 (dd, *J* = 7.6, 1.7 Hz, 1H), 7.23 (dd, *J* = 8.5, 0.6 Hz, 2H), 7.16 (ddd, *J* = 8.3, 7.5, 1.7 Hz, 1H), 6.87 (td, *J* = 7.5, 1.0 Hz, 1H), 6.77 (dd, *J* = 8.4, 0.7 Hz, 1H), 5.24 (s, 2H), 3.80 (t, *J* = 6.1 Hz, 2H), 3.46 – 3.27 (m, 1H), 2.67 (t, *J* = 6.1 Hz, 2H), 2.36 (s, 3H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 193.37, 158.32, 144.65, 132.97, 131.60, 129.22, 128.80, 127.93, 121.11, 113.23, 112.15, 91.69, 78.05, 70.77, 60.74, 23.98, 21.47; HR-MS (ESI): m/z = 317.1148, calcd. for $C_{19}H_{18}NaO_3$ $[M+Na]^+$: 317.1147.



2-(2-(4-hydroxybut-1-yn-1-yl)phenoxy)-1-(*m*-tolyl)ethan-1-one (1c): The title compound was prepared according to the general procedure A as a yellow viscous oil; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.84 – 7.78 (m, 2H), 7.45 – 7.34 (m, 3H), 7.23 (ddd, *J* = 8.3, 7.6, 1.7 Hz, 1H), 6.93 (td, *J* = 7.5, 1.0 Hz, 1H), 6.82 (dd, *J* = 8.3, 0.7 Hz, 1H), 5.32 (s, 2H), 3.83 (t, *J* = 5.4 Hz, 2H), 2.88 (s, 1H), 2.71 (t, *J* = 5.9 Hz, 2H), 2.42 (s, 3H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 193.92, 158.53, 138.71, 134.70, 134.36, 133.16, 129.06, 128.64, 128.54, 125.19, 121.42, 113.45, 112.23, 91.77, 78.42, 71.06, 60.97, 24.27, 21.30; HR-MS (ESI): m/z = 317.1148, calcd. for $C_{19}H_{18}NaO_3$ $[M+Na]^+$: 317.1146.

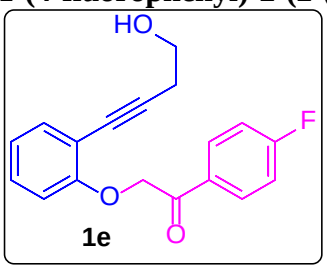


2-(2-(4-hydroxybut-1-yn-1-yl)phenoxy)-1-(4-methoxyphenyl)ethan-1-one (1d): The title compound was prepared according to the general procedure A as a yellow viscous oil; ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.01 (dt, *J* = 9.2, 2.8 Hz, 2H), 7.38 (dd, *J* = 7.6, 1.7 Hz, 1H), 7.21 (ddd, *J* = 8.3, 7.6, 1.7 Hz, 1H), 6.95 (dt, J = 8.0, 2.8 Hz, 2H), 6.92 (td, J = 7.6, 0.8 Hz, 1H), 6.81 (dd, *J* = 8.3, 0.7 Hz, 1H), 5.27 (s, 2H), 3.86 (s, 3H), 3.85 – 3.78 (m, 2H), 3.05 (s, 1H), 2.70 (t, *J* = 6.0 Hz, 2H); ^{13}C



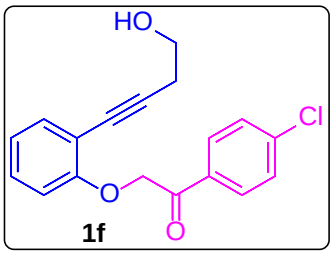
NMR (101 MHz, $CDCl_3$) δ 192.42, 164.01, 158.52, 133.12, 130.44, 129.02, 127.31, 121.31, 113.91, 113.34, 112.20, 91.73, 78.34, 70.89, 60.92, 55.45, 24.19; HR-MS (ESI): m/z = 333.1097, calcd. for $C_{19}H_{18}NaO_4$ $[M+Na]^+$: 333.1094.

1-(4-fluorophenyl)-2-(2-(4-hydroxybut-1-yn-1-yl)phenoxy)ethan-1-one (1e): The title compound was prepared according to the general procedure A as a yellow viscous oil; ^1H NMR (400 MHz, $CDCl_3$) δ 8.08 – 8.01 (m, 2H), 7.36 (dd, *J* = 7.6, 1.7 Hz, 1H), 7.23 – 7.09 (m, 3H), 6.90 (td, *J* = 7.5, 1.0 Hz, 1H), 6.79 (dd, *J* = 8.4, 0.8 Hz, 1H), 5.26 (s, 2H), 3.80 (t, *J* = 6.0 Hz, 2H), 3.08 (s, 1H), 2.68 (t, *J* = 6.1 Hz, 2H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 192.61, 165.95 (d, J_F = 254.7 Hz) 158.24, 133.20, 130.88 (d, J_F = 9.2 Hz), 130.69 (d, J_F = 3.1 Hz), 128.99, 121.46, 115.88 (d, J_F = 21.8 Hz), 113.32, 112.22, 91.77, 78.14, 71.04, 60.83, 24.05; HR-MS (ESI): m/z = 321.0897, calcd. for $C_{18}H_{15}FNaO_3$ $[M+Na]^+$: 321.0894.



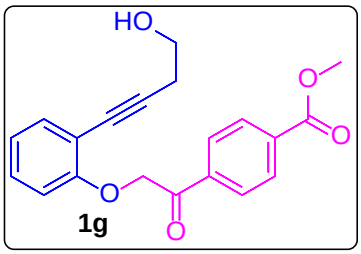
1e

1-(4-chlorophenyl)-2-(2-(4-hydroxybut-1-yn-1-yl)phenoxy)ethan-1-one (1f): The title compound was prepared using the general procedure A as a yellow viscous oil; ^1H NMR (400 MHz, $CDCl_3$) δ 7.94 (dt, *J* = 8.8, 2.4 Hz, 2H), 7.43 (dt, *J* = 6.8, 2.4 Hz, 2H), 7.36 (dd, *J* = 7.6, 1.6 Hz, 1H), 7.19 (ddd, *J* = 8.4, 7.6, 1.6 Hz, 1H), 6.90 (td, *J* = 7.2, 0.8 Hz, 1H), 6.78 (d, *J* = 8.4 Hz, 1H), 5.25 (s, 2H), 3.80 (t, *J* = 6.0 Hz, 2H), 2.68 (t, *J* = 6.0 Hz, 1H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 193.14, 158.26, 140.35, 133.30, 132.61, 129.60, 129.06, 121.60, 113.41, 112.28, 91.8, 78.23, 71.15, 60.89, 24.11; HR-MS (ESI): m/z = 315.0779, calcd. for $C_{18}H_{16}O_3Cl$ $[M+H]^+$: 315.0782.



1f

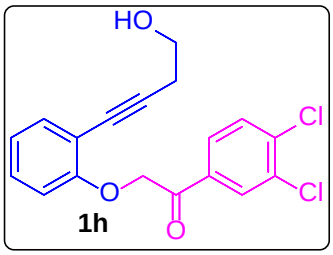
Methyl 4-(2-(2-(4-hydroxybut-1-yn-1-yl)phenoxy)acetyl)benzoate (1g): The title compound



1g

was prepared using the general procedure A as a yellow solid; M.P. 99 °C ~ 101 °C; ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.13-8.04 (m, 4H), 7.37 (dd, *J* = 7,6, 2.0 Hz, 1H), 7.22 (ddd, *J* = 8.4, 7.6, 1.2 Hz, 1H), 6.92 (tt, *J* = 7.6, 0.8 Hz, 1H), 6.81 (d, *J* = 8.4 Hz, 1H); 5.31 (s, 2H), 3.93 (s, 3H), 3.80 (t, *J* = 6.0 Hz, 1H), 2.68 (t, *J* = 6.0 Hz, 2H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 193.84, 166.01, 158.29, 137.53, 134.50, 133.31, 129.88, 129.10, 128.15, 121.67, 113.50, 112.34, 91.82, 71.40, 60.94, 52.51, 24.17; HR-MS (ESI): m/z = 339.1226, calcd. for $C_{20}H_{19}O_5$ $[M+H]^+$: 339.1227.

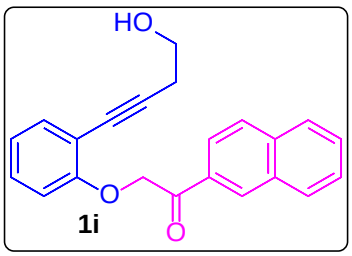
1-(3,4-dichlorophenyl)-2-(2-(4-hydroxybut-1-yn-1-yl)phenoxy)ethan-1-one (1h): The title



1h

compound was prepared according to the general procedure A as a yellow viscous oil; ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.15 – 8.11 (m, 1H), 7.86 (dd, *J* = 8.4, 2.0 Hz, 1H), 7.56 (d, *J* = 8.4 Hz, 1H), 7.38 (dd, *J* = 7.6, 1.7 Hz, 1H), 7.23 (ddd, *J* = 8.3, 7.5, 1.7 Hz, 1H), 6.94 (td, *J* = 7.5, 1.0 Hz, 1H), 6.81 (dd, *J* = 8.4, 0.8 Hz, 1H), 5.24 (s, 2H), 3.82 (t, *J* = 6.0 Hz, 22H), 2.71 (t, *J* = 6.0 Hz, 2H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 192.44, 158.07, 138.53, 133.81, 133.45, 133.39, 130.88, 130.32, 129.14, 127.32, 121.78, 113.44, 112.24, 91.82, 78.19, 71.29, 60.94, 24.16; HR-MS (ESI): m/z = 371.0212, calcd. for $C_{18}H_{14}Cl_2NaO_3$ $[M+Na]^+$: 371.0211.

2-(2-(4-hydroxybut-1-yn-1-yl)phenoxy)-1-(naphthalen-2-yl)ethan-1-one (1i): The title

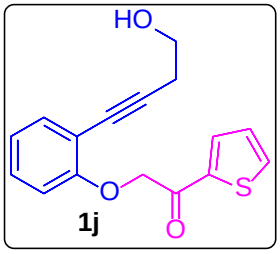


1i

compound was prepared according to the general procedure A as a yellow viscous oil; ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.56 (d, *J* = 1.1 Hz, 1H), 8.04 (dd, *J* = 8.6, 1.8 Hz, 1H), 7.97 (dd, *J* = 8.0, 0.6 Hz, 1H), 7.93 – 7.85 (m, 2H), 7.59 (dddd, *J* = 22.1, 8.1, 6.9, 1.3 Hz, 2H), 7.39 (dd, *J* = 7.6, 1.7 Hz, 1H), 7.27 – 7.19 (m, 1H), 6.93 (td, *J* = 7.5, 1.0 Hz, 1H), 6.87 (dd, *J* = 8.3, 0.7 Hz, 1H), 5.43 (s,

2H), 3.79 (t, *J* = 5.9 Hz, 2H), 2.85 (s, 1H), 2.67 (t, J = 5.9 Hz, 2H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 193.90, 158.51, 135.86, 133.21, 132.32, 131.64, 130.06, 129.61, 129.09, 128.87, 128.67, 127.80, 126.96, 123.52, 121.47, 113.45, 112.27, 91.79, 78.41, 71.26, 60.94, 24.22; HR-MS (ESI): m/z = 353.11482, calcd. for $C_{22}H_{18}NaO_3$ $[M+Na]^+$: 353.11482.

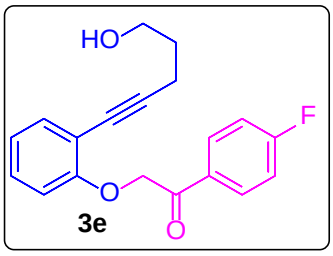
2-(2-(4-hydroxybut-1-yn-1-yl)phenoxy)-1-(thiophen-2-yl)ethan-1-one (1j): The title



1j

compound was prepared according to the general procedure A as a brown viscous oil; ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.09 (dd, *J* = 3.9, 1.1 Hz, 1H), 7.72 (dd, *J* = 4.9, 1.1 Hz, 1H), 7.41 (dd, *J* = 7.6, 1.7 Hz, 1H), 7.27 – 7.21 (m, 1H), 7.17 (dd, *J* = 4.9, 3.9 Hz, 1H), 6.95 (td, *J* = 7.5, 1.0 Hz, 1H), 6.85 (dd, *J* = 8.4, 0.7 Hz, 1H), 5.15 (s, 2H), 3.83 (m, 2H), 2.73 (t, *J* = 6.0 Hz, 2H), 2.51 (s, 1H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 187.73, 158.37, 134.75, 133.44, 133.39, 129.26, 128.32, 121.65, 112.14, 91.63, 78.53, 71.78, 61.00, 24.21; HR-MS (ESI): m/z = 309.05559, calcd. for $C_{16}H_{14}NaO_3S$ $[M+Na]^+$: 309.05552.

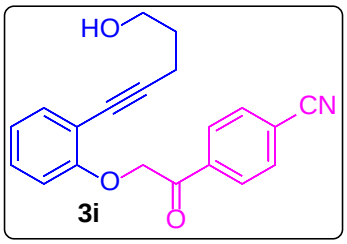
1-(4-fluorophenyl)-2-(2-(5-hydroxypent-1-yn-1-yl)phenoxy)ethan-1-one (3e): The title



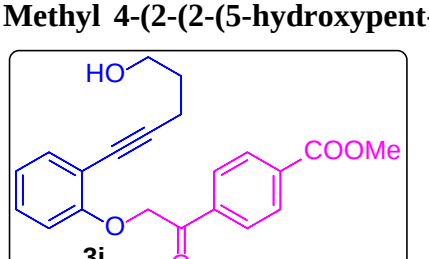
3e

compound was prepared according to the general procedure A as a yellow viscous oil; ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.13 – 8.04 (m, 2H), 7.37 (dd, *J* = 7.6, 1.7 Hz, 1H), 7.24 – 7.11 (m, 3H), 6.92 (td, *J* = 7.5, 1.0 Hz, 1H), 6.79 (dd, *J* = 8.4, 0.9 Hz, 1H), 5.26 (s, 2H), 3.83 (t, *J* = 5.9 Hz, 2H), 2.57 (t, *J* = 6.8 Hz, 2H), 2.17 (s, 1H), 1.84 (quin, *J* = 6.8 Hz, 2H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 193.08, 167.58 (d, J_F = 254.3 Hz), 158.34, 133.47, 131.18 (d, J_F = 9.5 Hz), 130.95 (d, J_F = 2.7 Hz), 128.92, 121.63, 115.92 (d, J_F = 21.7 Hz), 113.67, 112.43, 94.26, 71.60, 61.84, 31.08, 16.49; HR-MS (ESI): m/z = 335.10539, calcd. for $C_{19}H_{17}FNaO_3$ $[M+Na]^+$: 335.10536.

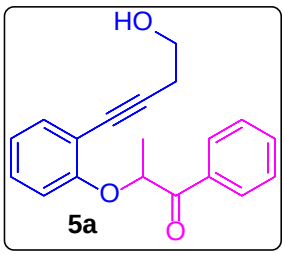
4-(2-(2-(5-hydroxypent-1-yn-1-yl)phenoxy)acetyl)benzonitrile (3i): The title compound was prepared according to the general procedure A as a yellow viscous oil; ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.20 – 8.13 (m, 2H), 7.83 – 7.77 (m, 2H), 7.38 (dd, *J* = 7.6, 1.7 Hz, 1H), 7.22 (ddd, *J* = 8.3, 7.5, 1.7 Hz, 1H), 6.95 (td, *J* = 7.5, 1.0 Hz, 1H), 6.79 (dd, *J* = 8.3, 0.8 Hz, 1H), 5.27 (s, 2H), 3.83 (t, *J* = 5.9 Hz, 2H), 2.56 (t, *J* = 6.8 Hz, 2H), 1.87 – 1.79 (quin, *J* = 6.8 Hz, 2H), 1.61 (s, 1H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 193.99, 158.03, 137.47, 133.66, 132.51, 129.04, 121.97, 117.75, 117.00, 113.72, 112.42, 94.41, 71.93, 61.96, 31.11, 17.27, 16.55; HR-MS (ESI): m/z = 342.11006, calcd. for $C_{20}H_{17}NNaO_3$ $[M+Na]^+$: 342.11002.



Methyl 4-(2-(2-(5-hydroxypent-1-yn-1-yl)phenoxy)acetyl)benzoate (3j): The title compound was prepared according to the general procedure A as a yellow solid; M.P. 82 °C ~ 84 °C; ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.17 – 8.07 (m, 4H), 7.37 (dd, *J* = 7.6, 1.7 Hz, 1H), 7.24 – 7.16 (m, 1H), 6.93 (td, *J* = 7.5, 1.0 Hz, 1H), 6.82 – 6.78 (m, 1H), 5.30 (d, *J* = 4.5 Hz, 2H), 3.96 (s, 3H), 3.82 (t, *J* = 6.0 Hz, 2H), 2.56 (t, *J* = 6.8 Hz, 2H), 2.09 (s, 1H), 1.83 (quin, *J* = 6.4 Hz, 2H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 194.34, 166.09, 158.25, 137.68, 134.43, 133.54, 129.86, 128.93, 128.37, 121.73, 113.74, 112.47, 94.34, 71.80, 61.88, 52.55, 31.11, 16.50.; HR-MS (ESI): m/z = 389.1359, calcd. for $C_{22}H_{22}NaO_5$ $[M+Na]^+$: 389.1356.

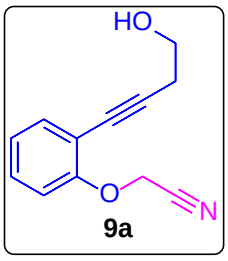


2-(2-(4-hydroxybut-1-yn-1-yl)phenoxy)-1-phenylpropan-1-one (5a): The title compound was prepared according to the general procedure A as a yellow solid; M.P. 59 °C ~ 61 °C; ^{1}H NMR (400 MHz, $CDCl_3$) 8.10-8.08 (m, 2H), 7.58 (tt, *J* = 7.6, 1.2 Hz, 1H), 7.48-7.43 (m, 2H), 7.36 (dd, *J* = 7.6, 1.6 Hz), 7.14 (ddd, *J* = 8.4, 7.6, 2.0 Hz, 1H), 6.88 (td, *J* = 7.2, 0.8 Hz, 1H), 6.77 (d, *J* = 8.0 Hz, 1 H), 5.55 (q, *J*



= 6.8 Hz, 1H), 3.97-3.78 (m, 2H), 2.69 (t, *J* = 6.0 Hz, 2H), 2.50 (s, 1H), 1.73 (d, *J* = 6.8 Hz, 3H) ; ^{13}C NMR (101 MHz, $CDCl_3$) δ; 198.55, 158.08, 134.00, 133.66, 133.34, 129.09, 128.90, 128.68, 121.48, 113.83, 113.66, 91.21, 78.88, 60.97, 24.14, 18.79; HR-MS (ESI): m/z = 295.1335, calcd. for $C_{19}H_{19}O_3$ $[M+H]^+$: 295.1329.

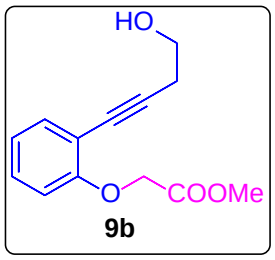
2-(2-(4-hydroxybut-1-yn-1-yl)phenoxy)acetonitrile (9a): The title compound was



9a

prepared according to the general procedure A as a red viscous oil; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.44 (dd, *J* = 7.6, 1.6 Hz, 1H), 7.29 (t, *J* = 7.2 Hz, 1H), 7.07 (t, *J* = 7.2 Hz, 1H), 6.99 (d, *J* = 7.6 Hz, 1H), 4.85 (s, 2H), 3.83 (q, *J* = 6.0 Hz, 2H), 2.73 (t, *J* = 6.8 Hz, 2H); 2.1 (t, *J* = 6.0 Hz. 1H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 157.02, 134.01, 129.42, 123.46, 115.03, 114.37, 114.26, 92.19, 60.96, 54.82, 24.03; HR-MS (ESI): m/z = 202.0861, calcd. for $C_{12}H_{12}O_2N$ $[M+H]^+$: 202.0863.

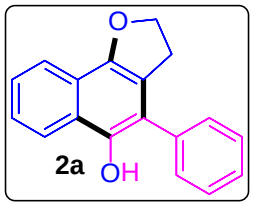
Methyl 2-(2-(4-hydroxybut-1-yn-1-yl)phenoxy)acetate (9b): The title compound was



9b

prepared according to the general procedure A as a red viscous oil; **1**H NMR (400 MHz, $CDCl_3$) δ 7.36 (d, *J* = 7.5 Hz, 1H), 7.18 (dd, *J* = 11.5, 4.3 Hz, 1H), 6.89 (t, *J* = 7.5 Hz, 1H), 6.73 (d, *J* = 8.4 Hz, 1H), 4.64 (s, 2H), 4.21 (q, *J* = 7.1 Hz, 2H), 3.77 (t, *J* = 6.4 Hz, 2H), 2.66 (t, *J* = 6.4 Hz, 2H), 1.23 (t, *J* = 7.1 Hz, 3H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 168.24, 157.67, 132.79, 128.44, 120.94, 112.89, 111.74, 91.40, 65.18, 60.83, 60.25, 23.44, 13.50; HR-MS (ESI): m/z = 249.1123, calcd. for $C_{14}H_{17}O_4N$ $[M+H]^+$: 249.1121.

4-phenyl-2,3-dihydronaphtho[1,2-*b*]furan-5-ol (2a): The title compound was

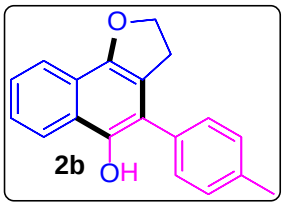


2a

prepared according to the general procedure B on a 0.25 mmol of **1a** to afford an off-white solid (59 mg, 90% yield); M.P. 101 °C ~ 103 °C; ^{1}H NMR (400 MHz, D-ACETONE) δ 8.39 – 8.15 (m, 1H), 7.97 – 7.77 (m, 1H),

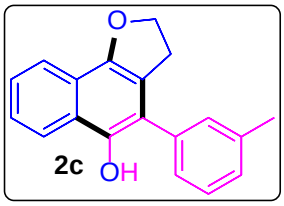
7.50 – 7.34 (m, 8H), 4.65 (t, *J* = 8.8 Hz, 2H), 3.15 (t, *J* = 8.8 Hz, 2H); ^{13}C NMR (101 MHz, D-ACETONE) δ 149.90, 144.09, 138.17, 131.51, 130.10, 128.81, 126.97, 126.94, 126.26, 124.54, 122.58, 122.49, 121.78, 121.17, 72.60, 32.34; HR-MS (ESI): m/z = 261.0920, calcd. for $C_{18}H_{13}O_2$ $[M-H]^-$: 261.0910.

4-(*p*-tolyl)-2,3-dihydronaphtho[1,2-*b*]furan-5-ol (2b): The title compound was



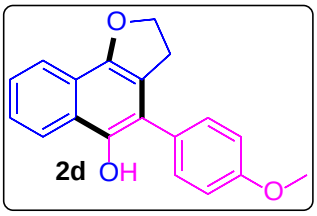
prepared according to the general procedure B on a 0.25 mmol of **1b** to afford an off-white solid (57 mg, 85% yield); M.P. 120 °C ~ 122 °C; ^{1}H NMR (400 MHz, D-ACETONE) δ 8.27 – 8.22 (m, 1H), 7.88 – 7.82 (m, 1H), 7.49 – 7.40 (m, 2H), 7.38 – 7.34 (m, 2H), 7.29 (m, *J* = 3H), 4.65 (t, *J* = 8.8 Hz, 2H), 3.16 (t, *J* = 8.8 Hz, 2H), 2.39 (s, 3H); ^{13}C NMR (101 MHz, D-ACETONE) δ 149.83, 144.15, 138.32, 135.08, 131.40, 130.81, 126.88, 126.85, 126.20, 124.54, 122.48, 122.39, 121.71, 121.28, 72.59, 32.39, 21.91; HR-MS (EI) calcd for $C_{19}H_{16}O_2$ 276.1150, found 276.1148.

4-(*m*-tolyl)-2,3-dihydronaphtho[1,2-*b*]furan-5-ol (2c): The title compound was



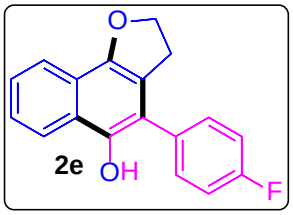
prepared according to the general procedure B on a 0.25 mmol of **1c** to afford a pale-yellow viscous gel (47 mg, 69% yield); ^{1}H NMR (400 MHz, D-ACETONE) δ 8.24 (dd, *J* = 6.8, 2.4 Hz, 1H), 7.89 – 7.81 (m, 1H), 7.49 – 7.41 (m, 2H), 7.36 (t, *J* = 7.5 Hz, 1H), 7.28 (ddd, *J* = 8.1, 4.4, 0.9 Hz, 2H), 7.20 (d, *J* = 7.5 Hz, 1H), 4.66 (t, *J* = 8.8 Hz, 2H), 3.16 (t, *J* = 8.8 Hz, 2H), 2.39 (s, 3H); ^{13}C NMR (101 MHz, D-ACETONE) δ 149.84, 144.11, 139.61, 138.02, 132.09, 130.13, 129.57, 128.51, 126.90, 126.22, 124.57, 122.49, 121.77, 121.18, 72.61, 32.39, 22.16; HR-MS (EI) calcd for $C_{19}H_{16}O_2$ 276.1150, found 276.1143.

4-(3-methoxyphenyl)-2,3-dihydronaphtho[1,2-*b*]furan-5-ol (2d): The title compound was



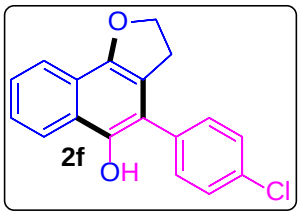
prepared according to the general procedure B on a 0.25 mmol of **1d** to afford an off-white solid (67 mg, 92% yield); M.P. 144 °C ~ 146 °C; ^{1}H NMR (400 MHz, D-ACETONE) δ 8.24 (dd, *J* = 6.7, 3.0 Hz, 1H), 7.88 – 7.82 (m, 1H), 7.48 – 7.36 (m, 4H), 7.06 – 7.00 (m, 2H), 4.65 (t, *J* = 8.8 Hz, 2H), 3.85 (s, 3H), 3.16 (t, *J* = 8.8 Hz, 2H); ^{13}C NMR (101 MHz, D-ACETONE) δ 160.61, 149.77, 144.23, 132.66, 130.02, 126.82, 126.78, 126.16, 124.52, 122.46, 122.13, 121.64, 121.44, 115.57, 72.57, 56.19, 32.40; HR-MS (EI) calcd for $C_{19}H_{16}O_3$ 292.1099, found 292.1093.

4-(4-fluorophenyl)-2,3-dihydronaphtho[1,2-*b*]furan-5-ol (2e): The title compound was



prepared according to the general procedure B on a 0.25 mmol of **1e** to afford an off-white solid (49 mg, 71% yield); M.P. 138 °C ~ 140 °C; ^{1}H NMR (400 MHz, D-ACETONE) δ 8.25 (dd, *J* = 6.8, 2.5 Hz, 1H), 7.91 – 7.78 (m, 1H), 7.57 – 7.39 (m, 5H), 7.24 (ddd, *J* = 8.9, 5.9, 2.5 Hz, 2H), 4.66 (t, *J* = 8.8 Hz, 2H), 3.16 (t, *J* = 8.8 Hz, 2H); ^{13}C NMR (101 MHz, D-ACETONE) δ 164.10 (d, J_F = 242 Hz), 149.96, 144.26, 134.42, 133.58 (d, J_F = 8.2 Hz), 127.03, 126.34, 124.52, 122.53, 121.85, 121.72, 121.66, 121.19, 116.80 (d, J_F = 21.2 Hz), 72.63; HR-MS (EI) calcd for $C_{18}H_{13}FO_2$ 280.0900, found 280.0909.

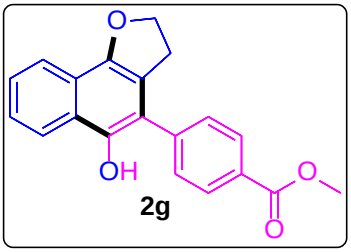
4-(4-chlorophenyl)-2,3-dihydronaphtho[1,2-*b*]furan-5-ol (2f): The title compound was



prepared according to the general procedure B on a 0.25 mmol of **1f** to afford an off-white solid (55mg, 75% yield); M.P. 93 °C ~ 95 °C; ^{1}H NMR (400 MHz, D-ACETONE) δ 8.25 (dd, *J* = 7.2, 2.4 Hz 1H), 7.86 (dd, *J* = 6.8, 2.0 Hz, 1H), 7.58 (s, 1H), 7.55 – 7.43 (m, 6H), 4.68 (t, *J* = 8.8 Hz, 2H), 3.19 (t, *J* = 8.8 Hz, 2H); ^{13}C NMR (101 MHz, D-ACETONE) δ 150.06, 144.24, 137.16, 134.15, 133.39,

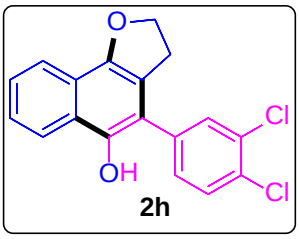
130.12, 127.14, 127.09, 126.41, 124.53, 122.55, 121.94, 121.55, 120.96, 72.66, 32.25, 31.07; HR-MS (ESI): m/z = 295.05313, calcd. for $C_{18}H_{12}ClO_2$ $[M-H]^-$: 295.05291.

Methyl 4-(5-hydroxy-2,3-dihydronaphtho[1,2-*b*]furan-4-yl)benzoate (2g): The title compound



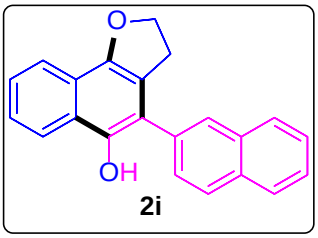
was prepared according to the general procedure B on a 0.25 mmol of **1g** to afford an off-white solid (50 mg, 63% yield); M.P. 168 °C ~ 170 °C; ^{1}H NMR (400 MHz, D-ACETONE) δ 8.27 (dd, *J* = 7.1, 2.1 Hz, 1H), 8.10 (d, *J* = 8.3 Hz, 2H), 7.88 (dd, *J* = 6.9, 2.2 Hz, 1H), 7.69 – 7.59 (m, 3H), 7.52 – 7.44 (m, 2H), 4.68 (t, *J* = 8.8 Hz, 2H), 3.92 (s, 3H), 3.19 (t, *J* = 8.8 Hz, 2H); ^{13}C NMR (101 MHz, D-ACETONE) δ 167.81, 150.23, 144.19, 143.47, 131.88, 130.97, 130.50, 127.28, 127.18, 126.50, 124.53, 122.60, 122.07, 121.99, 120.73, 72.69, 53.04, 32.26; HR-MS (ESI): m/z = 321.1113, calcd. for $C_{20}H_{17}O_4$ $[M+H]^+$: 321.1121.

4-(3,4-dichlorophenyl)-2,3-dihydronaphtho[1,2-*b*]furan-5-ol (2h): The title compound was



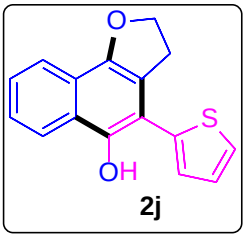
prepared according to the general procedure B on a 0.25 mmol of **1h** to afford an off-white solid (55 mg, 67% yield); M.P. 140 °C ~ 142 °C; ^{1}H NMR (400 MHz, D-ACETONE) δ 8.30 – 8.17 (m, 1H), 7.93 – 7.78 (m, 1H), 7.76 (s, 1H), 7.68 (dd, *J* = 10.3, 5.1 Hz, 2H), 7.56 – 7.39 (m, 3H), 4.68 (t, *J* = 8.8 Hz, 2H), 3.21 (t, *J* = 8.8 Hz, 2H); ^{13}C NMR (101 MHz, D-ACETONE) δ 150.20, 144.36, 144.25, 139.14, 133.67, 133.29, 132.15, 131.84, 127.39, 127.12, 126.56, 124.54, 122.60, 122.14, 120.70, 120.49, 72.73, 32.13; HR-MS (EI) calcd for $C_{18}H_{12}Cl_2O_2$ 280.0900, found 330.0207.

4-(naphthalen-2-yl)-2,3-dihydronaphtho[1,2-*b*]furan-5-ol (2i): The title compound was prepared according to the general procedure B on a 0.25 mmol of **1i** to afford a pale yellow solid (62 mg, 80% yield); M.P. 123 °C ~ 125 °C; ^{1}H NMR (400 MHz, D-ACETONE) δ 8.29 (dd, *J* = 7.2, 2.4 Hz, 1H), 8.03 – 7.93 (m, 4H), 7.89 (dd, *J* = 6.8, 2.3 Hz, 1H), 7.58 (m, 4H), 7.53 – 7.44 (m, 2H), 4.69 (t, *J* = 8.8 Hz, 2H), 3.23 (t, *J* = 8.8 Hz, 2H); ^{13}C NMR (101 MHz, D-ACETONE) δ 149.91, 144.45, 135.75, 135.25, 134.28, 130.48, 129.74, 129.67, 129.59, 129.17, 127.66, 127.60, 127.04, 126.98, 126.30, 124.63, 122.52, 122.27, 121.90, 121.28, 111.52, 72.66, 32.37; HR-MS (EI) calcd for $C_{22}H_{16}O_2$ 312.1150, found 312.1158.



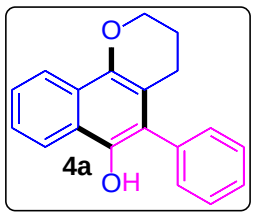
2i

4-(thiophen-2-yl)-2,3-dihydronaphtho[1,2-*b*]furan-5-ol (2j): The title compound was prepared according to the general procedure B on a 0.25 mmol of **1j** to afford an off-white solid (43mg, 64% yield) ^{1}H NMR (400 MHz, D-ACETONE) δ 8.25 (s, 1H), 7.91 – 7.70 (m, 2H), 7.65 – 7.40 (m, 3H), 7.33 (s, 1H), 7.19 (dd, *J* = 5.1, 3.6 Hz, 10H), 4.70 (m, , 20H), 3.39 (m, 2H); HR-MS (ESI): m/z = 267.04852, calcd. for $C_{16}H_{11}O_2S$ [M-H]$^{-}$: 267.04855.

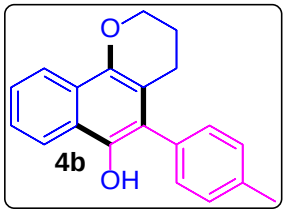


2j

5-phenyl-3,4-dihydro-2*H*-benzo[*h*]chromen-6-ol (4a): The title compound was prepared according to the general procedure B on a 0.25 mmol of **3a** to afford a yellow sticky mass (56 mg, 83% yield)**;** ^{1}H NMR (400 MHz, D-ACETONE) δ 8.23 – 8.09 (m, 2H), 7.51 – 7.36 (m, 5H), 7.33 – 7.30 (m, 2H), 6.91 (s, 1H), 4.24 (t, *J* = 5.2 Hz, 2H), 2.39 (t, *J* = 6.5 Hz, 2H), 1.97 – 1.90 (m, 2H); ^{13}C NMR (101 MHz, D-ACETONE) δ 144.93, 143.53, 137.83, 132.16, 130.28, 128.98, 126.93, 126.76, 126.34, 126.16, 124.67, 123.66, 122.57, 116.46, 67.20, 25.69, 24.00; HR-MS (ESI): m/z = 275. 1066, calcd. for $C_{19}H_{15}O_2$ [M-H]$^{-}$: 275.1066.

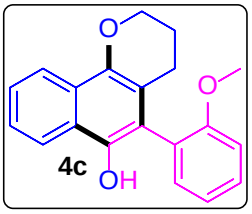


5-(*p*-tolyl)-3,4-dihydro-2*H*-benzo[*h*]chromen-6-ol (4b): The title compound was



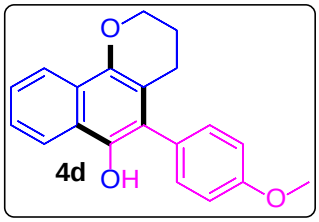
prepared according to the general procedure B on a 0.25 mmol of **3b** to afford an off-white solid (62 mg, 85% yield); M.P. 142 °C ~ 144 °C; ^{1}H NMR (400 MHz, D-ACETONE) δ 8.22 – 8.15 (m, 1H), 8.11 (ddd, *J* = 4.8, 2.3, 0.5 Hz, 1H), 7.49 – 7.41 (m, 2H), 7.34 – 7.27 (m, 2H), 7.23 – 7.17 (m, 2H), 6.83 (s, 1H), 4.25 (t, *J* = 5.2 Hz, 2H), 2.44 – 2.37 (m, 5H), 1.99 – 1.91 (m, 2H); ^{13}C NMR (101 MHz, D-ACETONE) δ 144.89, 143.65, 138.48, 134.67, 132.07, 131.01, 126.89, 126.70, 126.30, 126.08, 124.44, 124.36, 123.68, 122.56, 116.66, 67.22, 25.73, 24.06, 21.94; HR-MS (ESI): m/z = 289,1224, calcd. for $C_{20}H_{17}O_2$ $[M-H]^-$: 289.1223.

5-(2-methoxyphenyl)-3,4-dihydro-2H-benzo[h]chromen-6-ol (4c): The title compound was



prepared according to the general procedure B on a 0.25 mmol of **3c** to afford an off-white solid (58 mg, 76% yield); M.P. 106 °C ~ 107 °C; ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.26 – 8.05 (m, 2H), 7.51 – 7.40 (m,3H), 7.25 (dd, *J* = 7.6, 1.6 Hz, 1H), 7.14 – 7.05 (m, 2H), 4.96 (s, 1H), 4.34-4.25 (m, 2H), 3.78 (s, 3H), 2.51 – 2.36 (m, 2H), 2.04 – 1.95 (m, 2H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 157.61, 143.72, 141.56, 132.37, 130.04, 125.61, 125.45, 125.04, 123.52, 123.29, 122.07, 121.41, 121.14, 118.42, 115.19, 111.63, 66.01, 55.64, 23.61, 22.61; HR-MS (ESI): m/z = 307.1327, calcd. for $C_{20}H_{19}O_3$ $[M+H]^+$: 307.1329.

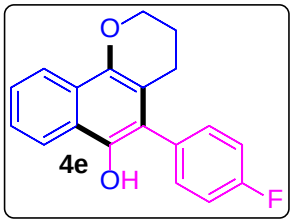
5-(4-methoxyphenyl)-3,4-dihydro-2*H*-benzo[*h*]chromen-6-ol (4d): The title compound was



prepared according to the general procedure B on a 0.25 mmol of **3d** to afford as light yellow solid (66 mg, 87% yield); M.P. 175 °C ~ 177 °C; ^{1}H NMR (400 MHz, D-ACETONE) δ 8.19 (ddd, *J* = 4.1, 2.4, 0.6 Hz, 1H), 8.14 – 8.07 (m, 1H), 7.49 – 7.40 (m, 2H), 7.23 (dt, *J* = 8.8, 2.8 Hz, 2H), 7.04 (dt, *J* = 8.8,

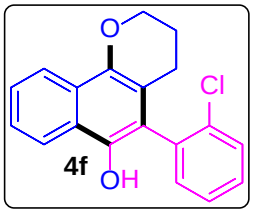
2.8 Hz, 2H), 4.25 (t, *J* = 5.2 Hz, 2H), 3.86 (s, 3H), 2.41 (t, *J* = 6.5 Hz, 2H), 1.99 – 1.90 (m, 2H); ^{13}C NMR (101 MHz, D-ACETONE) δ 160.80, 144.83, 143.88, 133.32, 129.49, 126.87, 126.68, 126.27, 125.99, 124.08, 123.69, 122.55, 116.91, 115.79, 67.20, 56.20, 25.74, 24.08; HR-MS (ESI): m/z = 307.1324, calcd. for $C_{20}H_{19}O_3$ $[M+H]^+$: 307.1329.

5-(4-fluorophenyl)-3,4-dihydro-2*H*-benzo[*h*]chromen-6-ol (4e): The title compound was



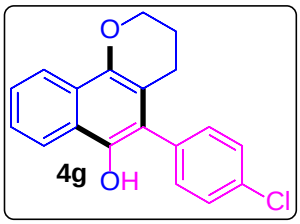
prepared according to the general procedure B on a 0.25 mmol of **3e** to afford an off-white solid (49 mg, 68% yield); M.P. 127 °C ~ 129 °C; ^{1}H NMR (400 MHz, D-ACETONE) δ 8.16 (dddd, *J* = 7.7, 4.3, 1.8, 0.6 Hz, 2H), 7.50 – 7.43 (m, 2H), 7.38 – 7.32 (m, 2H), 7.25 (ddd, *J* = 8.9, 5.8, 2.5 Hz, 2H), 7.10 (s, 1H), 4.25 (t, *J* = 5.2 Hz, 2H), 2.40 (t, *J* = 6.5 Hz, 2H), 1.99 – 1.92 (m, 2H); ^{13}C NMR (101 MHz, D-ACETONE) δ 163.83 (d, J_{CF} = 242 Hz), 144.97, 143.85, 134.18 (d, J_{CF} = 8.1 Hz), 134.04, 127.03, 126.88, 126.42, 126.21, 123.67, 122.59, 117.01 (d, J_{CF} = 21.0 Hz), 116.51, 67.21, 25.68, 24.02; HR-MS (ESI): m/z = 295.1130, calcd. for $C_{19}H_{16}O_2F$ $[M+H]^+$: 295.1129.

5-(2-chlorophenyl)-3,4-dihydro-2*H*-benzo[*h*]chromen-6-ol (4f): The title compound was



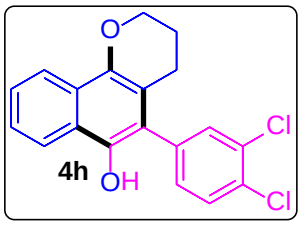
prepared according to the general procedure B on a 0.25 mmol of **3f** to afford an off-white solid (56 mg, 73% yield); M.P. 63 °C ~ 65 °C; ^{1}H NMR (400 MHz, D-ACETONE) δ 8.25 – 8.19 (m, 1H), 8.16 – 8.11 (m, 1H), 7.59 – 7.53 (m, 1H), 7.52 – 7.45 (m, 2H), 7.45 – 7.39 (m, 2H), 7.36 (dt, *J* = 4.9, 3.1 Hz, 1H), 7.32 (s, 1H), 4.26 (t, *J* = 4.8 Hz, 2H), 2.34 (t, *J* = 6.5 Hz, 2H), 2.02 – 1.93 (m, 2H); ^{13}C NMR (101 MHz, D-ACETONE) δ 144.95, 143.89, 136.97, 136.32, 134.25, 131.15, 130.99, 128.91, 127.30, 126.96, 126.34, 126.29, 123.69, 122.62, 122.15, 116.45, 67.26, 24.90, 23.93; HR-MS (ESI): m/z = 311.0825, calcd. for $C_{19}H_{16}O_2Cl$ $[M+H]^+$: 311.0833.

5-(4-chlorophenyl)-3,4-dihydro-2*H*-benzo[*h*]chromen-6-ol (4g): The title compound was



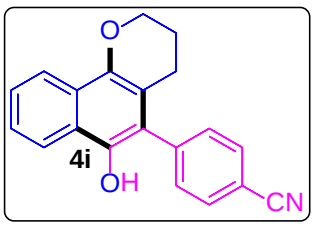
prepared according to the general procedure B on a 0.25 mmol of **3g** to afford an off-white solid (60 mg, 78% yield); M.P. 150 °C ~ 152 °C; ^{1}H NMR (400 MHz, D-ACETONE) δ 8.23 – 8.17 (m, 1H), 8.14 – 8.09 (m, 1H), 7.53 – 7.43 (m, 4H), 7.34 (dt, *J* = 8.4, 2.4 Hz, 2H), 7.21 (s, 1H), 4.26 (t, *J* = 5.2 Hz, 2H), 2.40 (t, *J* = 6.5 Hz, 2H), 2.01 – 1.92 (m, 2H); ^{13}C NMR (101 MHz, D-ACETONE) δ 145.04, 143.75, 143.64, 136.89, 134.41, 134.09, 130.32, 127.10, 126.96, 126.48, 126.30, 123.69, 123.58, 123.51, 122.63, 116.24, 111.55, 67.23, 25.68, 24.01; HR-MS (ESI): m/z = 309.0687, calcd. for $C_{19}H_{14}O_2Cl$ $[M-H]^-$: 309.0677.

5-(3,4-dichlorophenyl)-3,4-dihydro-2*H*-benzo[*h*]chromen-6-ol (4h): The title compound was



prepared according to the general procedure B on a 0.25 mmol of **3h** to afford an off-white solid (59 mg, 69% yield); M.P. 158 °C ~ 162 °C; ^{1}H NMR (400 MHz, D-ACETONE) δ 8.23 – 8.09 (m, 2H), 7.67 (d, *J* = 8.2 Hz, 1H), 7.54 (d, *J* = 2.0 Hz, 1H), 7.53 – 7.44 (m, 3H), 7.32 (dd, *J* = 8.2, 2.0 Hz, 1H), 4.27 (dd, *J* = 5.7, 4.5 Hz, 2H), 2.44 (t, *J* = 6.5 Hz, 2H), 2.02 – 1.94 (m, 2H); ^{13}C NMR (101 MHz, D-ACETONE) δ 145.08, 143.86, 138.98, 134.37, 133.47, 132.61, 132.36, 132.31, 127.26, 127.17, 126.59, 126.34, 123.70, 122.64, 122.55, 115.93, 67.23, 25.60, 23.94; HR-MS (ESI): m/z = 345.0438, calcd. for $C_{19}H_{15}O_2Cl_2$ $[M+H]^+$: 345.0444.

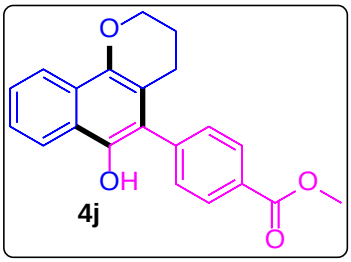
4-(6-hydroxy-3,4-dihydro-2*H*-benzo[*h*]chromen-5-yl)benzonitrile (4i): The title compound



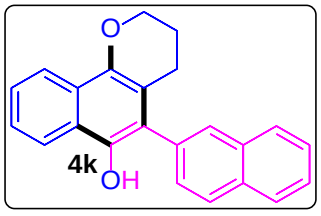
was prepared according to the general procedure B on a 0.25 mmol of **3i** to afford an off-white solid (47 mg, 63% yield); M.P. 218 °C ~ 220 °C; ^{1}H NMR (400 MHz, D-ACETONE) δ 8.21 (ddd, *J* = 6.4, 2.2, 0.6 Hz, 1H), 8.16 – 8.09 (m, 1H), 7.88 (dt, *J* = 8.4, 1.6 Hz, 2H), 7.57 (dt, *J* = 8.4, 1.6 Hz, 2H), 7.54

– 7.45 (m, 2H), 7.42 (s, 1H), 4.29 (t, J = 5.2 Hz, 2H), 2.41 (t, *J* = 6.5 Hz, 2H), 2.01 – 1.93 (m, 2H); ^{13}C NMR (101 MHz, D-ACETONE) δ 145.27, 144.72, 143.76, 138.96, 133.85, 133.53, 129.39, 127.29, 127.20, 126.68, 126.51, 125.36, 123.83, 123.64, 123.12, 122.73, 121.80, 120.16, 115.72, 114.95, 112.58, 112.49, 111.56, 67.28, 25.63, 23.92; HR-MS (ESI): m/z = 300.1030, calcd. for $C_{20}H_{14}NO_2$ $[M-H]^-$: 300.1031.

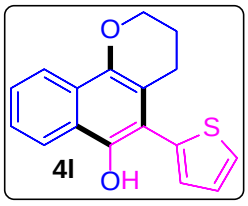
Methyl 4-(6-hydroxy-3,4-dihydro-2*H*-benzo[*h*]chromen-5-yl)benzoate (4j) : The title compound was prepared according to the general procedure B on a 0.25 mmol of **3j** to afford an off-white solid (51 mg, 62% yield); M.P. 170 °C ~ 173 °C; ^{1}H NMR (400 MHz, D-ACETONE) δ 8.24 – 8.19 (m, 1H), 8.16 – 7.99 (m, 3H), 7.53 – 7.45 (m, 4H), 7.24 (s, 1H), 4.27 (t, *J* = 5.2 Hz, 2H), 3.93 (s, 3H), 2.42 (t, *J* = 6.5 Hz, 2H), 2.01 – 1.91 (m, 21H); ^{13}C NMR (101 MHz, D-ACETONE) δ 167.88, 145.13, 143.41, 132.61, 131.14, 130.79, 127.15, 127.03, 126.55, 126.41, 124.17, 123.65, 122.67, 115.95, 111.54, 67.25, 53.06, 25.65, 23.95; HR-MS (ESI): m/z = 334. 1200, calcd. for $C_{21}H_{18}O_4$ $[M+H]^+$: 334.1200.



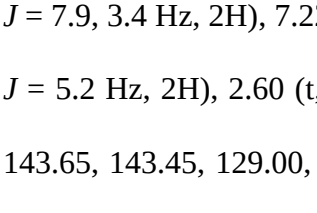
5-(naphthalen-2-yl)-3,4-dihydro-2*H*-benzo[*h*]chromen-6-ol (**4k**): The title compound was prepared according to the general procedure B on a 0.25 mmol of **3k** to afford an off-white solid (65 mg, 80% yield); M.P. 157 °C ~ 159 °C; ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.18 (dd, *J* = 6.5, 2.2 Hz, 2H), 7.99 (d, *J* = 8.4 Hz, 1H), 7.94 – 7.84 (m, 3H), 7.58 – 7.47 (m, 4H), 7.43 (dd, *J* = 8.3, 1.6 Hz, 1H), 5.00 (s, 1H), 4.35 – 4.23 (m, 2H), 2.48 (qt, *J* = 17.0, 6.5 Hz, 2H), 2.04 – 1.92 (m, 2H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 143.80, 141.45, 133.69, 132.88, 132.58, 129.52, 129.29, 128.29, 127.94, 127.84, 126.62, 126.61, 125.84, 125.42, 125.33, 123.37, 122.03, 121.44, 121.18, 114.42, 66.00, 24.28, 22.59; HR-MS (ESI): m/z = 327.1382, calcd. for $C_{23}H_{19}O_2$ $[M+H]^+$: 327.1380.



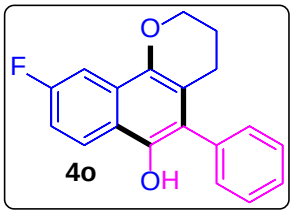
5-(thiophen-2-yl)-3,4-dihydro-2*H*-benzo[*h*]chromen-6-ol (4l): The title compound was prepared according to the general procedure B on a 0.25 mmol of **3l** to afford an off-white solid (44 mg, 61% yield); M.P. 82 °C ~ 84 °C; ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.19 – 8.12 (m, 2H), 7.54 (dd, *J* = 5.2, 0.8 Hz, 1H), 7.49 (tt, *J* = 7.9, 3.4 Hz, 2H), 7.22 (dd, *J* = 5.2, 3.4 Hz, 1H), 7.08 (d, *J* = 2.6 Hz, 1H), 5.33 (s, 8H), 4.29 (t, *J* = 5.2 Hz, 2H), 2.60 (t, *J* = 6.5 Hz, 2H), 2.06 – 1.97 (m, 2H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 143.65, 143.45, 129.00, 128.00, 127.92, 126.39, 125.42, 122.27, 121.19, 115.12, 113.37, 65.98, 24.00, 22.56; HR-MS (ESI): m/z = 283.0788, calcd. for $C_{17}H_{15}O_2S$ $[M+H]^+$: 283.0787.



9-methyl-5-phenyl-3,4-dihydro-2*H*-benzo[*h*]chromen-6-ol (4n): The title compound was prepared according to the general procedure B on a 0.25 mmol of **3n** to afford an off-white solid (57 mg, 79% yield); M.P. 124 °C ~ 127 °C; ^{1}H NMR (400 MHz, D-ACETONE) δ 8.09 (d, *J* = 8.5 Hz, 1H), 7.90 (s, 1H), 7.51 – 7.44 (m, 2H), 7.42 – 7.38 (tt, *J* = 6.8, 2.8 Hz, 1H), 7.32- 7.28 (m, 3H), 6.82 (s, 1H), 4.25 (dd, *J* = 10.1, 5.0 Hz, 2H), 2.50 (s, 3H), 2.39 (t, *J* = 6.5 Hz, 2H), 1.97 – 1.90 (m, 2H); ^{13}C NMR (101 MHz, D-ACETONE) δ 144.57, 143.60, 137.98, 136.27, 132.26, 130.26, 128.92, 128.38, 127.15, 124.44, 123.77, 123.70, 121.74, 116.50, 67.15, 25.74, 24.09, 22.55; HR-MS (ESI): m/z = 289.1234, calcd. for $C_{20}H_{17}O_2$ $[M-H]^-$: 289.1235.

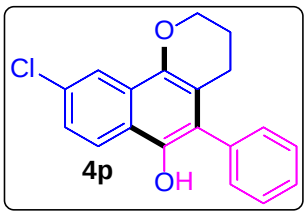


9-fluoro-5-phenyl-3,4-dihydro-2*H*-benzo[*h*]chromen-6-ol (4o): The title compound was prepared according to the general procedure B on a 0.25 mmol of **3n** to afford an off-white sticky mass (36 mg, 51% yield); ^{1}H NMR (400 MHz, D-ACETONE) δ 8.25 (dd, *J* = 9.2, 5.8 Hz, 1H), 7.69 (dd, *J* = 11.0, 2.6 Hz, 1H), 7.51 – 7.46 (m, 2H), 7.41 (dt, *J* = 9.6, 4.4 Hz, 1H), 7.35 – 7.31 (m, 2H), 7.28 (ddd, *J* = 9.1, 8.5, 2.7 Hz, 1H), 7.09 (s, 1H), 4.26 (t, *J* = 5.2 Hz, 2H), 2.40 (t, *J* = 6.5 Hz, 2H), 1.97 – 1.91



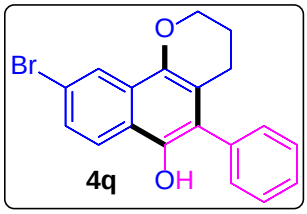
(m, 2H); ^{13}C NMR (101 MHz, D-ACETONE) δ 162.46 (d, J_F = 241.2 Hz), 144.44 (d, J_F = 5.0 Hz), 143.80, 137.50, 132.21, 130.35, 129.13, 127.76 (d, J_F = 8.8 Hz), 126.91 (d, J_F = 9.1 Hz), 124.17, 123.28, 118.29, 115.96 (d, J_F = 25.2 Hz), 106.27, 106.05, 67.33, 25.71, 23.92; HR-MS (ESI): m/z = 293.0982, calcd. for $C_{29}H_{14}FO_2$ $[M-H]^-$: 293.0983.

9-chloro-5-phenyl-3,4-dihydro-2*H*-benzo[*h*]chromen-6-ol (4p): The title compound was



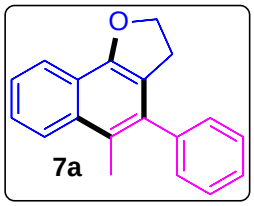
prepared according to the general procedure B on a 0.25 mmol of **3p** to afford an off-white solid (52 mg, 67% yield); M.P. 116 °C ~ 118 °C; ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.14 (s, 1H), 8.09 (d, *J* = 8.9 Hz, 1H), 7.54 (t, *J* = 7.2 Hz, 2H), 7.47 (d, *J* = 7.3 Hz, 1H), 7.39 (d, *J* = 10.0 Hz, 1H), 7.34 (d, *J* = 7.2 Hz, 2H), 4.90 (s, 1H), 4.28 (t, *J* = 4.8 Hz, 2H), 2.44 (t, *J* = 6.4 Hz, 2H), 2.03 – 1.93 (m, 2H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 143.02, 141.36, 134.64, 131.96, 130.49, 129.58, 128.44, 125.99, 123.96, 121.94, 121.58, 120.51, 115.82, 66.04, 24.21, 22.50; HR-MS (ESI): m/z = 311.0832, calcd. for $C_{19}H_{16}O_2Cl$ $[M+H]^+$: 311.0833.

9-bromo-5-phenyl-3,4-dihydro-2*H*-benzo[*h*]chromen-6-ol (4q): The title compound was

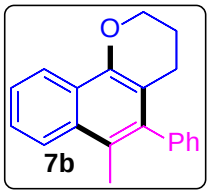


prepared according to the general procedure B on a 0.25 mmol of **3q** to afford an off-white solid (62 mg, 71% yield); M.P. 153 °C ~ 154 °C; ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.32 (d, *J* = 1.6 Hz, 1H), 8.02 (d, *J* = 8.9 Hz, 1H), 7.52 (ddd, *J* = 19.6, 14.8, 7.3 Hz, 4H), 7.34 (d, *J* = 7.0 Hz, 2H), 4.89 (s, 1H), 4.27 (t, *J* = 5.2 Hz, 2H), 2.44 (t, *J* = 6.5 Hz, 2H), 2.05 – 1.91 (m, 2H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 142.90, 141.37, 134.60, 130.43, 129.58, 128.49, 128.45, 126.37, 124.03, 123.76, 122.08, 121.75, 120.26, 115.81, 66.02, 24.19, 22.46; HR-MS (ESI): m/z = 327.1382, calcd. for $C_{19}H_{14}O_2Br$ $[M-H]^-$: 327.1380.

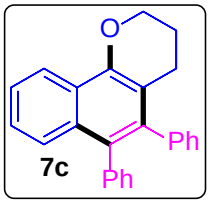
5-methyl-4-phenyl-2,3-dihydronaphtho[1,2-*b*]furan (7a): The title compound was prepared according to the general procedure B on a 0.25 mmol of **5a** to afford a light yellow solid (42 mg, 65% yield); M.P. 128 °C ~ 130 °C; ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.01 (td, *J* = 8.3, 1.4 Hz, 2H), 7.54 – 7.41 (m, 4H), 7.41 – 7.33 (m, 1H), 7.32 – 7.26 (m, 2H), 4.71 (t, *J* = 8.9 Hz, 2H), 3.10 (t, *J* = 8.9 Hz, 2H), 2.42 (s, 3H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 153.14, 140.68, 136.54, 132.96, 129.24, 128.20, 126.86, 125.83, 124.87, 124.86, 123.04, 121.79, 120.03, 119.59, 71.55, 31.02, 15.69; HR-MS (ESI): m/z = 261.12740, calcd. for $C_{19}H_{17}O$ $[M+H]^+$: 261.12739.



6-methyl-5-phenyl-3,4-dihydro-2*H*-benzo[*h*]chromene (7b): The title compound was prepared according to the general procedure B on a 0.25 mmol of **5b** to aford a yellow viscous oil (38 mg, 55% yield); ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.28 – 8.21 (m, 1H), 8.01 – 7.94 (m, 1H), 7.53 – 7.46 (m, 2H), 7.43 (d, *J* = 7.5 Hz, 2H), 7.37 (d, *J* = 7.4 Hz, 1H), 7.21 – 7.17 (m, 2H), 4.29 (t, *J* = 5.2 Hz, 2H), 2.38 (t, *J* = 6.5 Hz, 2H), 2.28 (s, 3H), 1.96 (dd, *J* = 11.1, 5.9 Hz, 2H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 141.09, 139.81, 131.91, 129.41, 128.27, 126.67, 125.81, 124.79, 124.13, 121.71, 114.87, 66.10, 24.66, 22.68, 15.91; HR-MS (ESI): m/z = 275.1422, calcd. for $C_{20}H_{19}O$ $[M+H]^+$: 275.1430.

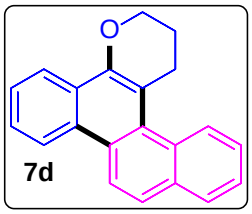


5,6-diphenyl-3,4-dihydro-2H-benzo[h]chromene (7c) : The title compound was prepared according to the general procedure B on a 0.25 mmol of **5c** to afford a yellow viscous oil (37 mg, 45% yield); ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.90 – 7.84 (m, 1H), 7.73 (d, *J* = 7.9 Hz, 1H), 7.59 (td, *J* = 7.6, 1.3 Hz, 1H), 7.28 – 7.24 (m, 11H), 4.19 (t, *J* = 5.2 Hz, 2H), 2.02 – 1.92 (m, 2H), 1.69 (t, *J* = 6.4 Hz, 2H): ^{13}C NMR (101 MHz, $CDCl_3$) δ 144.00, 141.08, 135.25, 134.24, 129.84, 128.83, 128.11, 127.87, 127.34, 127.17, 121.52,

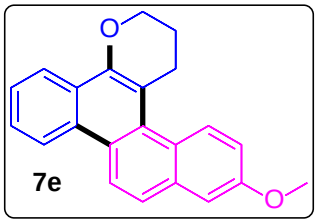


114.15, 65.83, 23.61, 22.62; HR-MS (ESI): m/z = 336.1522, calcd. for $C_{25}H_{20}O$ $[M+H]^+$: 336.1509.

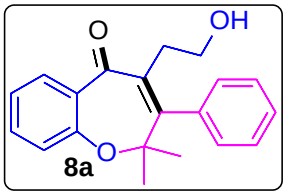
12,13-dihydro-11*H*-benzo[*h*]naphtho[1,2-*f*]chromene (7d): The title compound was prepared according to the general procedure B on a 0.25 mmol of **5d** to afford a yellow viscous oil (36 mg, 51% yield); ^{1}H NMR (400 MHz, $CDCl_3$) δ 9.00 (dd, *J* = 9.4, 3.0 Hz, 2H), 8.43 – 8.36 (m, 1H), 7.98 (dd, *J* = 7.9, 1.5 Hz, 1H), 7.90 (s, 2H), 7.67 – 7.57 (m, 3H), 7.54 (ddd, *J* = 7.9, 6.9, 1.1 Hz, 1H), 4.43 (t, *J* = 5.2 Hz, 2H), 3.17 (t, *J* = 6.6 Hz, 2H), 2.35 – 2.23 (m, 2H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 148.74, 131.89, 131.02, 130.33, 129.87, 128.23, 127.91, 127.77, 127.52, 126.54, 125.96, 125.71, 125.61, 124.76, 122.22, 121.67, 120.88, 110.68, 66.22, 29.68, 22.64, 22.24; HR-MS (ESI): m/z = 285.1268, calcd. for $C_{21}H_{17}O$ $[M+H]^+$: 285.1274.



8-methoxy-12,13-dihydro-11*H*-benzo[*h*]naphtho[1,2-*f*]chromene (**7e**): The title compound was prepared according to the general procedure B on a 0.25 mmol of **5e** to afford a yellow viscous oil (44 mg, 57% yield); ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.97 – 8.85 (m, 2H), 8.42 – 8.35 (m, 1H), 7.87 (dd, *J* = 25.2, 8.9 Hz, 2H), 7.63 – 7.58 (m, 2H), 7.33 (d, *J* = 2.8 Hz, 1H), 7.28 (dd, *J* = 9.3, 2.8 Hz, 1H), 4.43 (t, *J* = 5.2, Hz 2H), 4.00 (s, 3H), 3.17 (t, *J* = 6.6 Hz, 2H), 2.33 – 2.24 (m, 2H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 156.71, 148.03, 133.30, 129.64, 129.34, 127.88, 126.82, 126.64, 125.63, 125.57, 125.22, 124.28, 122.61, 121.64, 121.48, 117.11, 110.70, 107.44, 66.18, 55.37, 22.69, 22.24; HR-MS (ESI): m/z = 315.1372, calcd. for $C_{22}H_{19}O_2$ $[M+H]^+$: 315.1380.

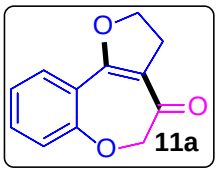


4-(2-hydroxyethyl)-2,2-dimethyl-3-phenylbenzo[*b*]oxepin-5(2*H*)-one (8a): The title compound



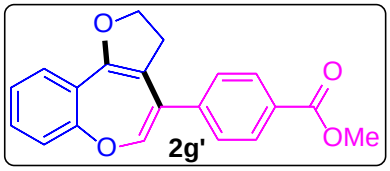
was prepared according to the general procedure B on a 0.25 mmol of **5f** to afford a yellow viscous oil (46 mg, 73% yield); ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.93 (dd, *J* = 8.0, 1.7 Hz, 1H), 7.47 (ddd, *J* = 8.3, 7.2, 1.8 Hz, 1H), 7.38 (tt, *J* = 8.0, 1.8 Hz, 2H), 7.36 – 7.29 (m, 1H), 7.13 – 7.06 (m, 3H), 7.00 (dd, *J* = 8.2, 1.0 Hz, 1H), 3.49 – 3.41 (m, 2H), 2.74 (s, 1H), 2.33 (t, *J* = 6.2 Hz, 2H), 1.39 (s, 6H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 195.43, 155.95, 155.16, 139.21, 138.70, 135.19, 130.24, 128.55, 128.54, 128.53, 127.75, 127.63, 122.43, 122.26, 81.72, 62.37, 35.29, 28.85; HR-MS (ESI): m/z = 309.1487, calcd. for $C_{20}H_{21}O_3$ $[M+H]^+$: 309.1485.

2,3-dihydrobenzo[*b*]furo[2,3-*d*]oxepin-4(5*H*)-one (11a): The title compound was prepared



according to the general procedure B on a 0.25 mmol of **9a** to afford a yellow viscous oil (31 mg, 62% yield); M.P. 109 °C ~ 111 °C; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.72 (dd, *J* = 7.9, 1.7 Hz, 1H), 7.44 – 7.37 (m, 1H), 7.22 – 7.14 (m, 2H), 4.63 (t, *J* = 9.7 Hz, 2H), 4.52 (s, 2H), 3.16 (t, *J* = 9.7 Hz, 2H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 192.50, 164.36, 158.49, 132.81, 128.52, 124.28, 121.58, 121.19, 115.68, 70.97, 29.38; HR-MS (ESI): m/z = 203.0699, calcd. for $C_{12}H_{11}O_3$ $[M+H]^+$: 203.0703.

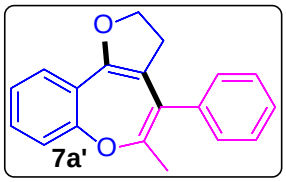
Methyl 4-(2,3-dihydrobenzo[*b*]furo[2,3-*d*]oxepin-4-yl)benzoate (2c'): The title compound



was prepared according to the general procedure B on a 0.25 mmol of **1g** to afford a light yellow viscous oil (38 mg, 48% yield); ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.03 – 7.91 (m, 2H), 7.49 (dd, *J* = 7.7, 1.7 Hz, 1H), 7.36 (td, *J* = 7.7, 1.7 Hz, 1H), 7.33 – 7.28 (m, 2H), 7.18 (td, *J* = 7.5, 0.7 Hz, 1H), 7.07 – 7.01 (m, 1H), 6.22 (s, 1H), 4.55 (t, *J* = 9.4 Hz, 2H), 3.90 (s, 3H), 2.82 (t, *J* = 9.4 Hz, 2H); ^{13}C NMR (101 MHz,) δ 166.91, 155.09, 154.84, 140.97, 138.58, 131.66, 129.75, 129.42, 128.53, 125.62 , 124.92, 121.05,

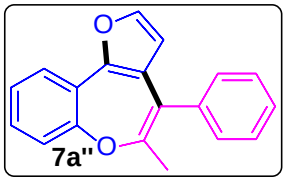
109.53, 69.64, 52.22, 32.26; HR-MS (ESI): m/z = 321.1120, calcd. for $C_{20}H_{17}O_4$ $[M+H]^+$: 321.1121.

5-methyl-4-phenyl-2,3-dihydrobenzo[*b*]furo[2,3-*d*]oxepine (7a'): The title compound was



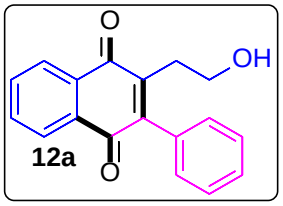
prepared according to the general procedure B on a 0.25 mmol of **5a** to afford a light yellow solid (41 mg, 60% yield); M.P. 81 °C ~ 83 °C; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.49 (dd, *J* = 7.7, 1.7 Hz, 1H), 7.40 – 7.34 (m, 1H), 7.32 (ddd, *J* = 6.6, 4.3, 1.1 Hz, 2H), 7.26 (dt, *J* = 7.3, 1.7 Hz, 1H), 7.19 (td, *J* = 7.5, 1.2 Hz, 1H), 7.16 – 7.12 (m, 2H), 7.04 (dd, *J* = 8.1, 1.0 Hz, 1H), 4.45 (t, *J* = 9.4 Hz, 2H), 2.63 (t, *J* = 9.4 Hz, 2H), 1.95 (s, 3H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 153.18, 152.04, 145.51, 137.92, 130.83, 129.51, 128.17, 127.00, 125.19, 124.85, 124.60, 123.04, 121.23, 112.39, 69.16, 32.99, 18.21; HR-MS (ESI): m/z = 277.1222, calcd. for $C_{19}H_{17}O_2$ $[M+H]^+$: 277.1223.

5-methyl-4-phenylbenzo[*b*]furo[2,3-*d*]oxepine (7a''): The title compound was prepared using



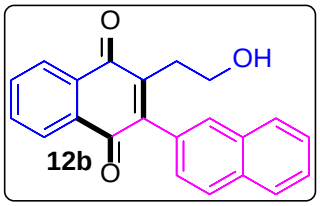
0.1 mmol of **7a'** in 0.11M of 1,2-DCE at 70 °C for about 16 h. After completion, the reaction mixture was diluted using water followed by extraction with dichloromethane. Combined dichloromethane layer was washed with water, brine, dried over sodium sulfate and evaporated under reduced pressure. The obtained crude products were purified by column chromatography (hexane to 0.25% EA/HEX) to afford the pure compound **7a''** in (7 mg) 40% yield as an off-white sticky mass. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.63 (dd, *J* = 7.7, 1.7 Hz, 1H), 7.38 (d, *J* = 1.9 Hz, 1H), 7.37 – 7.19 (m, 7H), 7.10 (dd, *J* = 8.0, 1.2 Hz, 1H), 6.03 (d, *J* = 1.9 Hz, 1H), 2.06 (s, 30H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 152.84, 149.15, 147.72, 141.74, 138.10, 129.97, 129.83, 128.21, 127.27, 125.10, 125.03, 124.51, 122.85, 121.62, 121.21, 111.61, 109.98, 18.68; HR-MS (ESI): m/z = 297.0886, calcd. for $C_{19}H_{14}NaO_2$ $[M+Na]^+$: 297.0888.

2-(2-hydroxyethyl)-3-phenylnaphthalene-1,4-dione (12a):The title compound was prepared



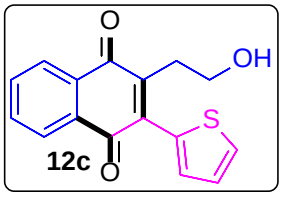
according to the general procedure C on a 0.25 mmol of **1a** to afford a yellow viscous oil (46 mg, 82% yield); ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.12 (dddd, *J* = 6.8, 5.0, 3.3, 0.5 Hz, 2H), 7.84 – 7.65 (m, 2H), 7.52 – 7.39 (m, 3H), 7.25 – 7.19 (m, 2H), 3.73 (t, *J* = 6.4 Hz, 2H), 2.78 (t, *J* = 6.4 Hz, 2H), 2.33 (t, *J* = 6.8 Hz, 1H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 186.29, 184.28, 148.03, 144.55, 133.89, 133.63, 133.23, 131.97, 131.94, 128.96, 128.54, 128.21, 126.58, 126.33, 61.83, 31.65; HR-MS (ESI): m/z = 301.08352, calcd. for $C_{18}H_{14}NaO_3$ $[M+Na]^+$: 301.08350.

3-(2-hydroxyethyl)-[2,2'-binaphthalene]-1,4-dione (**12b**): The title compound was prepared



according to the general procedure C on a 0.25 mmol of **1i** to afford a yellow viscous oil (35 mg, 72% yield); ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.20 – 8.06 (m, 2H), 7.96 – 7.80 (m, 3H), 7.80 – 7.68 (m, 3H), 7.56 – 7.48 (m, 2H), 7.31 (dd, *J* = 8.5, 2.3 Hz, 2H), 3.71 (t, *J* = 6.4 Hz, 2H), 2.81 (t, *J* = 6.7 Hz, 2H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 186.45, 184.51, 148.23, 145.05, 134.05, 133.81, 128.34, 127.99, 127.88, 126.84, 126.81, 126.76, 126.60, 126.54, 62.01, 31.84; HR-MS (ESI): m/z = 329.1179, calcd. for $C_{22}H_{17}O_3$ $[M+H]^+$: 329.1172.

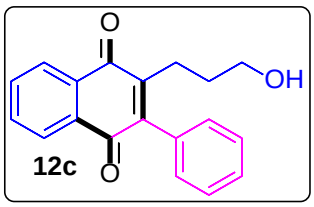
2-(2-hydroxyethyl)-3-(thiophen-2-yl)naphthalene-1,4-dione (**12c**): The title compound was



prepared according to the general procedure C on a 0.25 mmol of **1j** to afford a yellow viscous oil (44 mg, 63% yield); ^{1}H NMR (400 MHz, $CDCl_3$) 8.15 – 8.04 (m, 2H), 7.79 – 7.71 (m, 2H), 7.59 (dd, *J* = 5.1, 1.2 Hz, 1H), 7.28 – 7.24 (m, 1H), 7.16 (dd, *J* = 5.1, 3.6 Hz, 1H), 3.89 (t, *J* = 6.4 Hz, 2H), 3.01 (t, *J* = 6.4 Hz, 2H), 2.15 (s, 1H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 185.78, 183.64, 145.24, 141.28, 133.95,

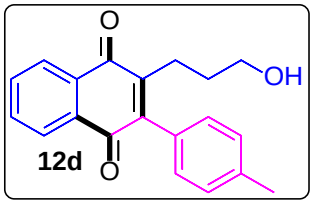
133.79, 132.58, 131.93, 131.86, 130.42, 129.24, 126.86, 126.80, 126.39, 62.26, 32.14; HR-MS (ESI): m/z = 307.0399, calcd. for $C_{16}H_{12}NaO_3S$ $[M+Na]^+$: 307.0422.

2-(3-hydroxypropyl)-3-phenylnaphthalene-1,4-dione (**12d**): The title compound was prepared



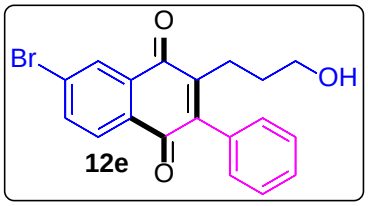
according to the general procedure C on a 0.25 mmol of **3a** to afford a yellow viscous oil (33 mg, 76% yield); ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.15 – 8.06 (m, 2H), 7.76 – 7.71 (m, 2H), 7.48 – 7.40 (m, 3H), 7.22 – 7.17 (m, 2H), 3.51 (t, *J* = 6.2 Hz, 2H), 2.60 – 2.53 (m, 2H), 1.74 (s, 1H), 1.67 (ddd, *J* = 13.4, 8.7, 6.3 Hz, 2H); ^{13}C NMR (101 MHz,) δ 185.94, 184.50, 147.61, 147.10, 133.94, 133.74, 133.53, 132.26, 132.15, 128.90, 128.65, 128.38, 126.69, 126.48, 62.05, 32.50, 24.20; HR-MS (ESI): m/z = 293.1173, calcd. for $C_{19}H_{17}O_3$ $[M+H]^+$: 293.1172.

2-(3-hydroxypropyl)-3-(*p*-tolyl)naphthalene-1,4-dione (12e): The title compound was prepared



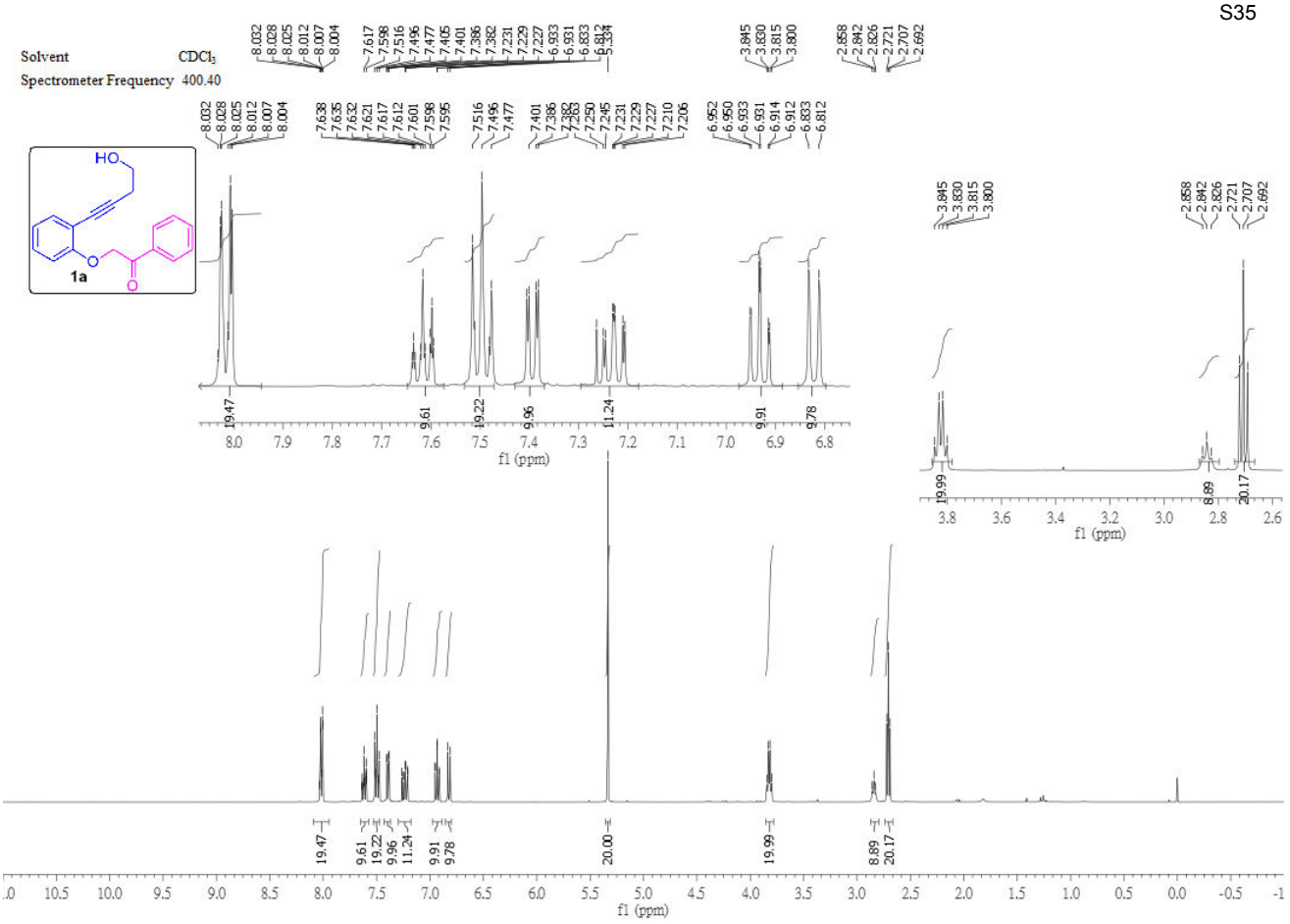
using according to the general procedure C on a 0.25 mmol of **3b** to afford a yellow viscous oil (33 mg, 73% yield); ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.10 (ddd, *J* = 8.7, 6.6, 4.0 Hz, 2H), 7.73 (dd, *J* = 5.3, 3.4 Hz, 2H), 7.17 (dd, *J* = 68.0, 7.8 Hz, 4H), 3.51 (t, *J* = 6.1 Hz, 2H), 2.58 (t, *J* = 7.4 Hz, 2H), 2.40 (s, 3H), 1.84 – 1.53 (m, 3H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 186.01, 184.60, 147.46, 147.21, 138.57, 133.88, 133.68, 132.28, 132.19, 130.51, 129.11, 128.84, 126.69, 126.44, 62.05, 32.53, 24.18, 21.44; HR-MS (ESI): m/z = 307.1335, calcd. for $C_{20}H_{19}O_3$ $[M+H]^+$: 307.1329.

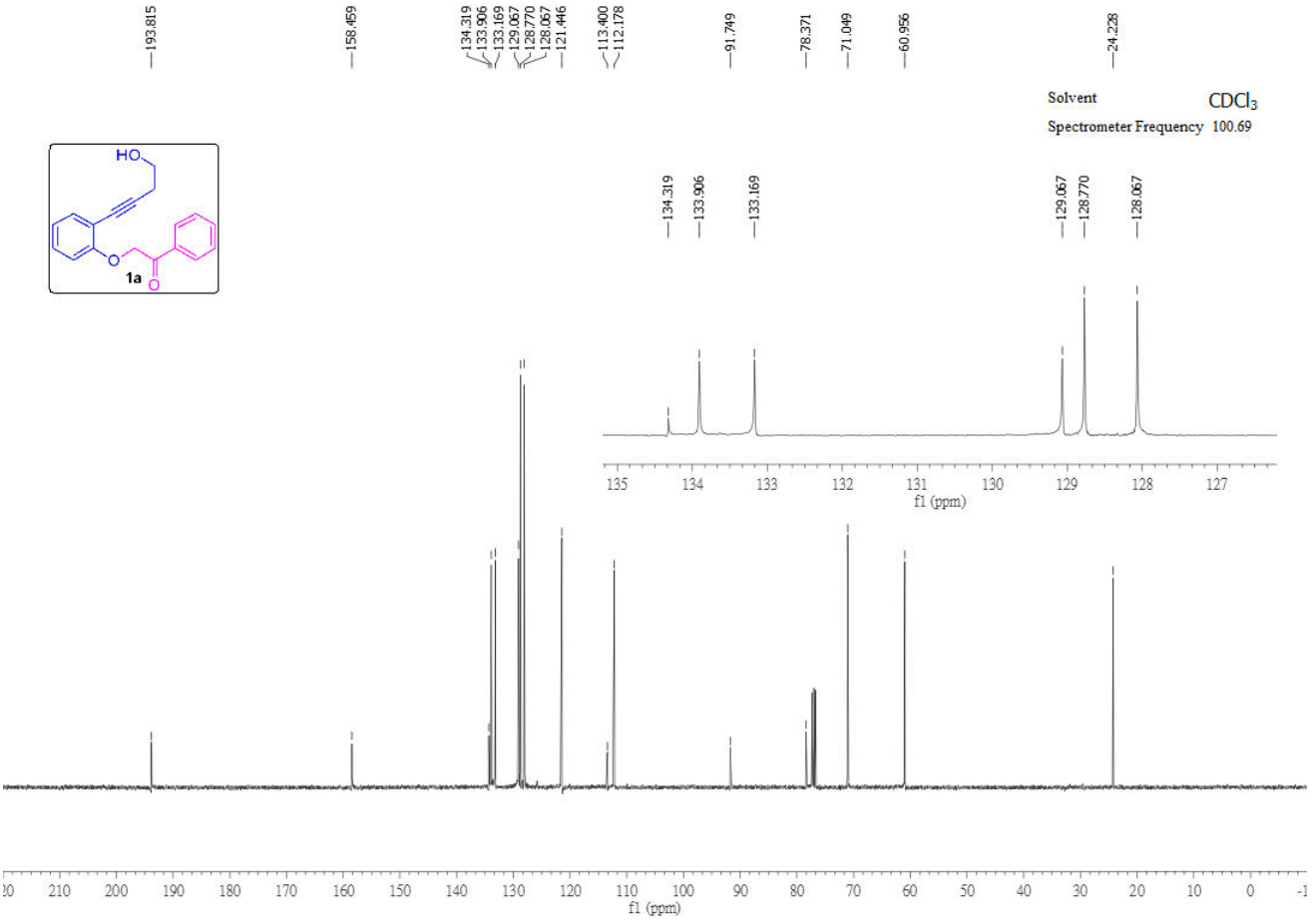
6-bromo-3-(3-hydroxypropyl)-2-phenylnaphthalene-1,4-dione (**12f**) : The title compound was



prepared according to the general procedure C on a 0.25 mmol of **3q** to afford a yellow viscous oil (39 mg, 71% yield); ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.26 (d, *J* = 2.0 Hz, 1H), 7.96 (d, *J* = 8.3 Hz, 1H), 7.86 (dd, *J* = 8.3, 2.0 Hz, 1H), 7.49 – 7.41 (m, 3H), 7.21 – 7.16 (m, 2H), 3.51 (t, *J* = 6.2 Hz, 2H),

2.60 – 2.52 (m, 2H), 1.67 (dt, *J* = 13.5, 6.3 Hz, 3H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 184.78, 183.75, 147.62, 147.20, 136.92, 133.29, 133.20, 130.70, 129.50, 129.24, 128.86, 128.82, 128.49, 128.43, 62.09, 32.43, 24.35; HR-MS (ESI): m/z = 371.0284, calcd. for $C_{19}H_{16}O_3Br$ $[M+H]^+$: 371.0277.


Solvent CDCl3
Spectrometer Frequency 400.40
HO
O
O
1a
f1 (ppm)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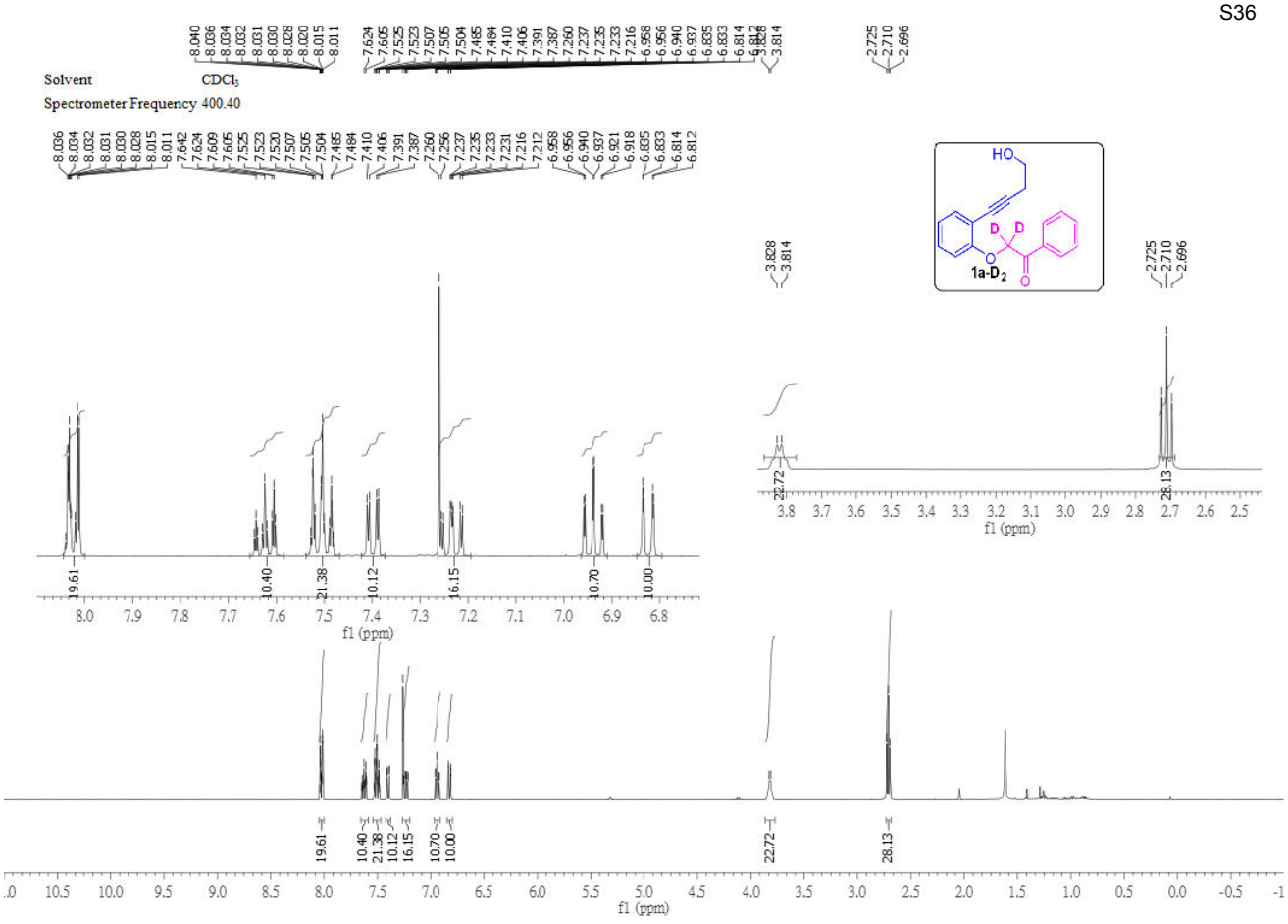
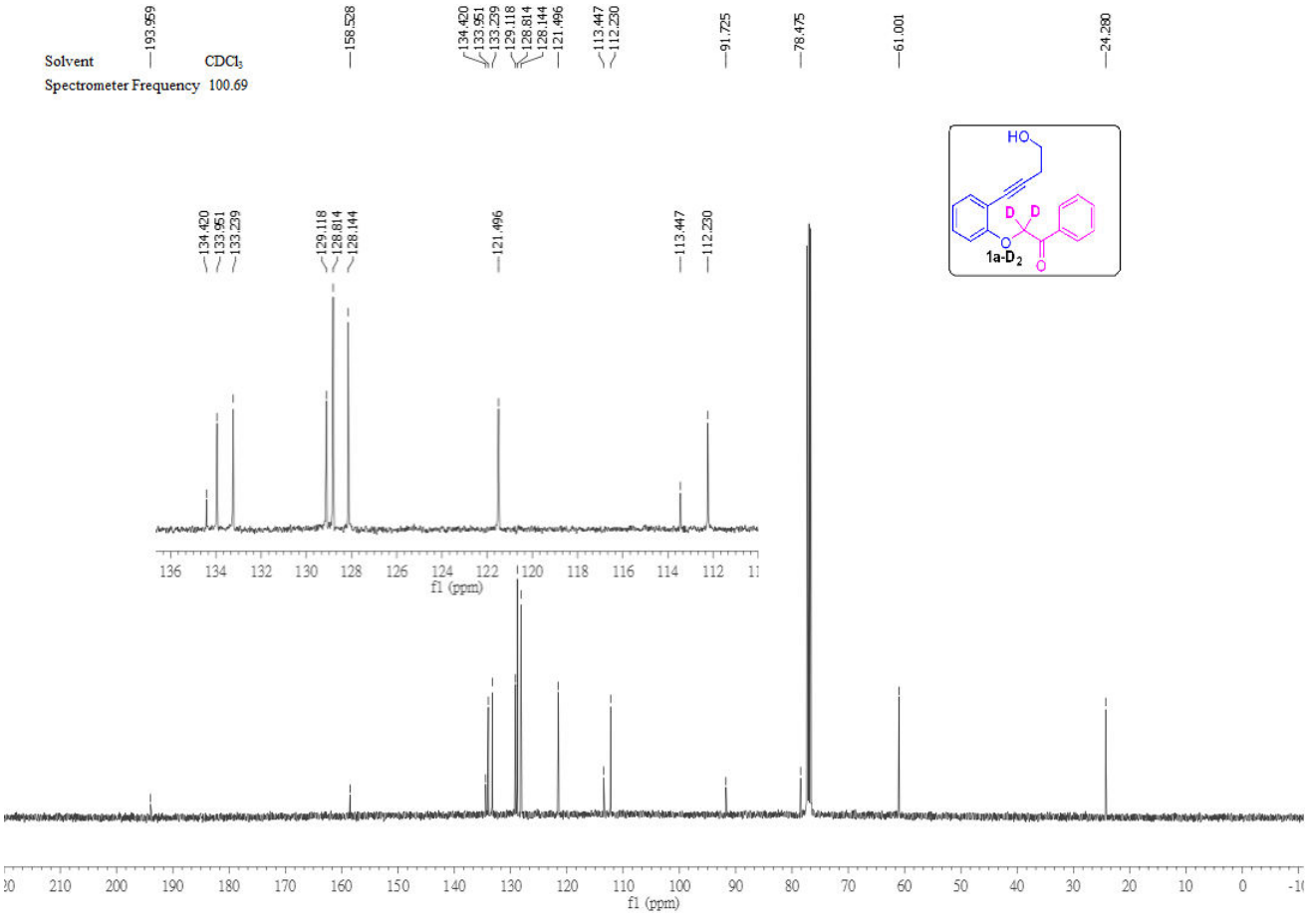
Spectrometer Frequency 100.69
HO
O
O
1a
f1 (ppm)


Solvent CDCl3
Spectrometer Frequency 400.40
HO
D D
O
1a-D2
f1 (ppm)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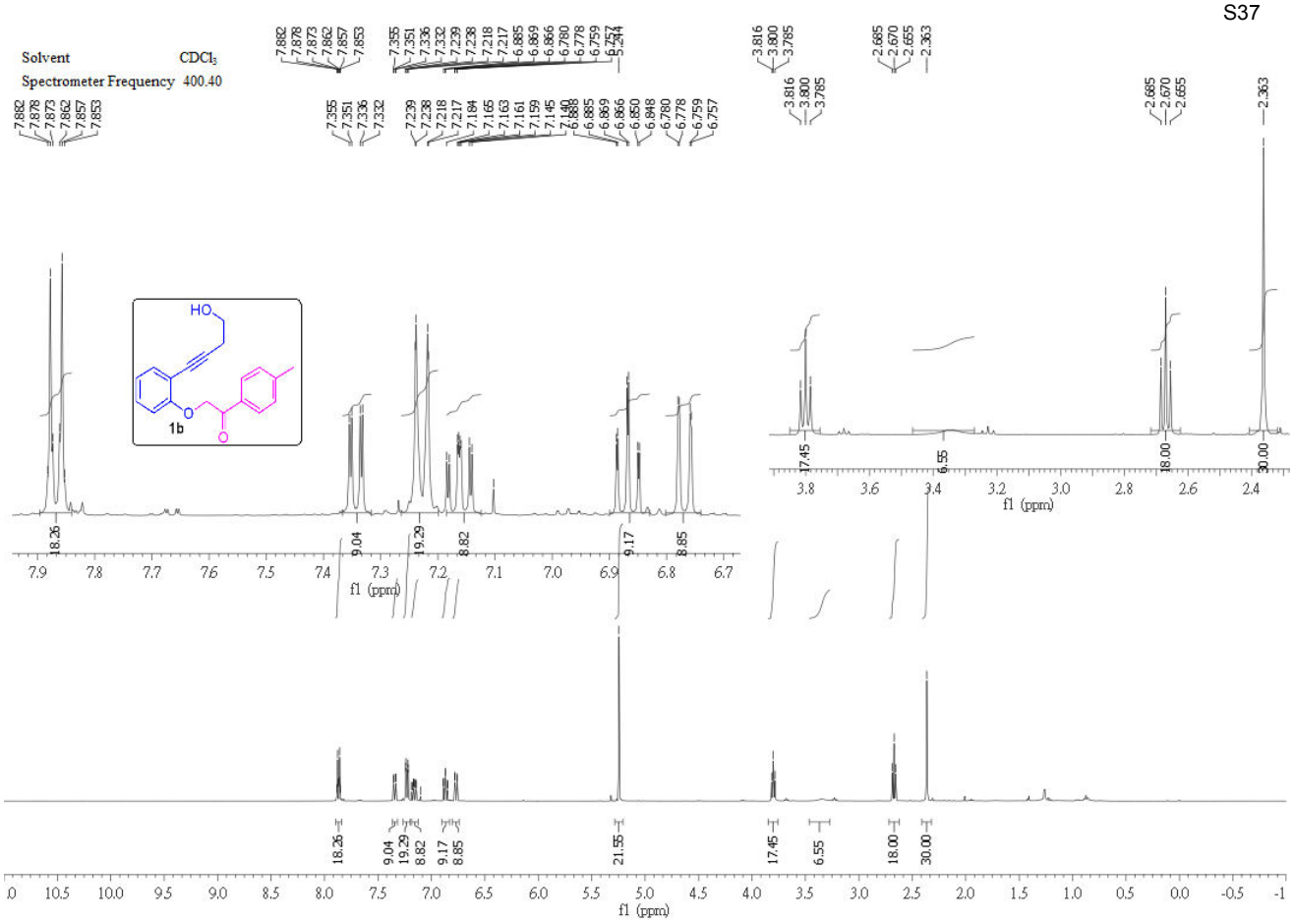
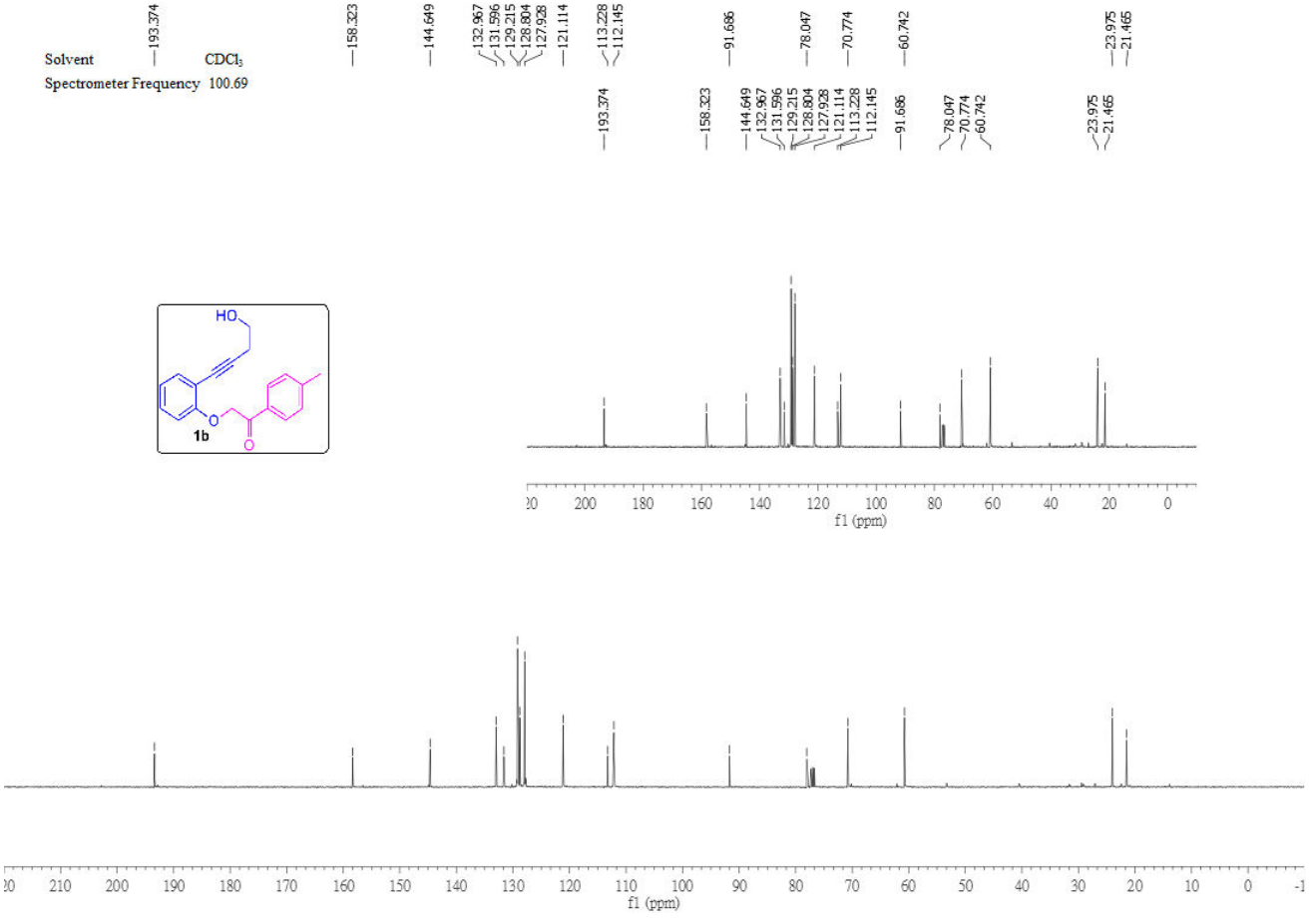
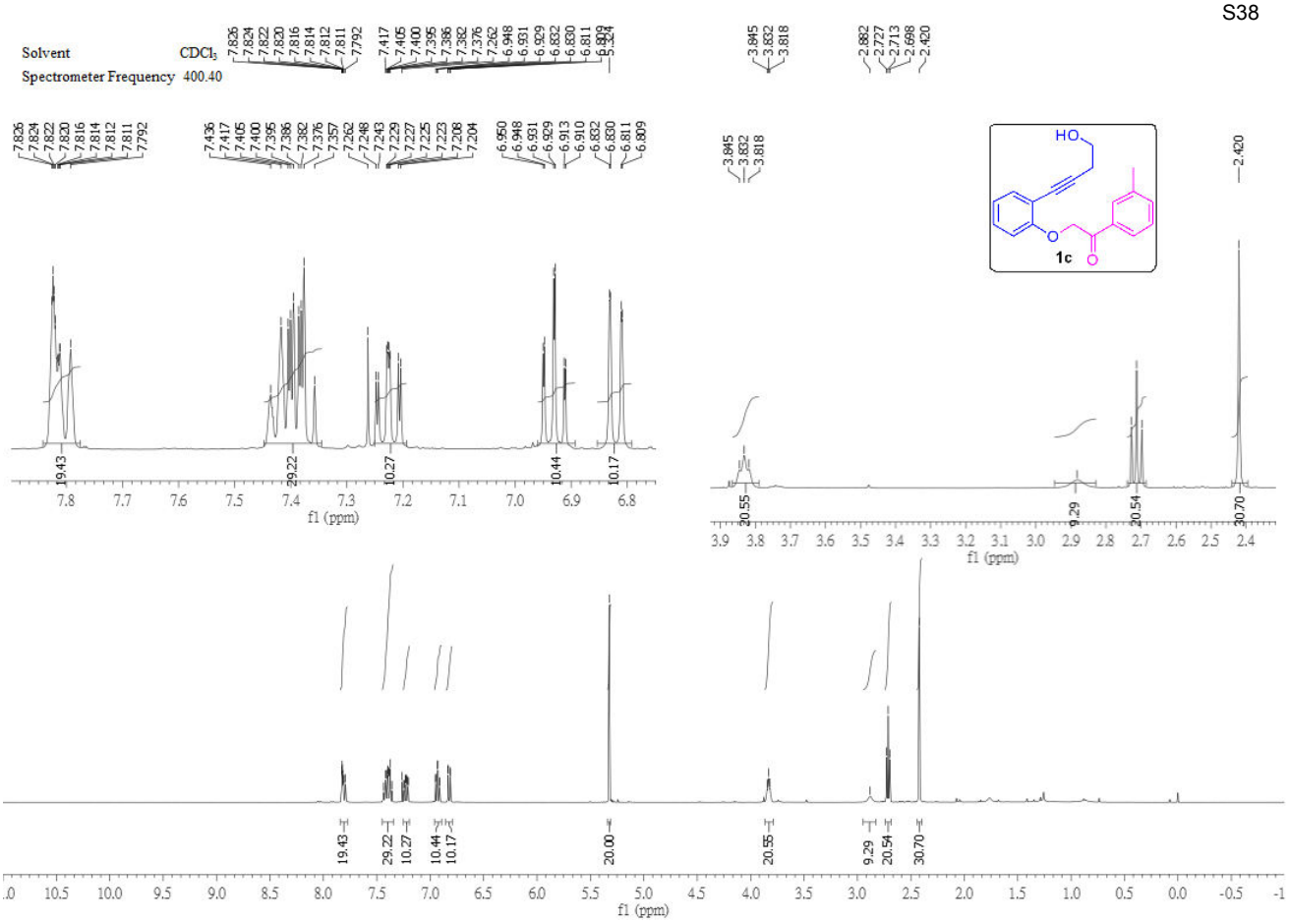
Spectrometer Frequency 100.69
HO
D D
O
1a-D2
f1 (ppm)


Solvent CDCl3
Spectrometer Frequency 400.40
HO
O
O
1b
f1 (ppm)


Solvent CDCl3
Spectrometer Frequency 100.69
HO
O
O
1b
f1 (ppm)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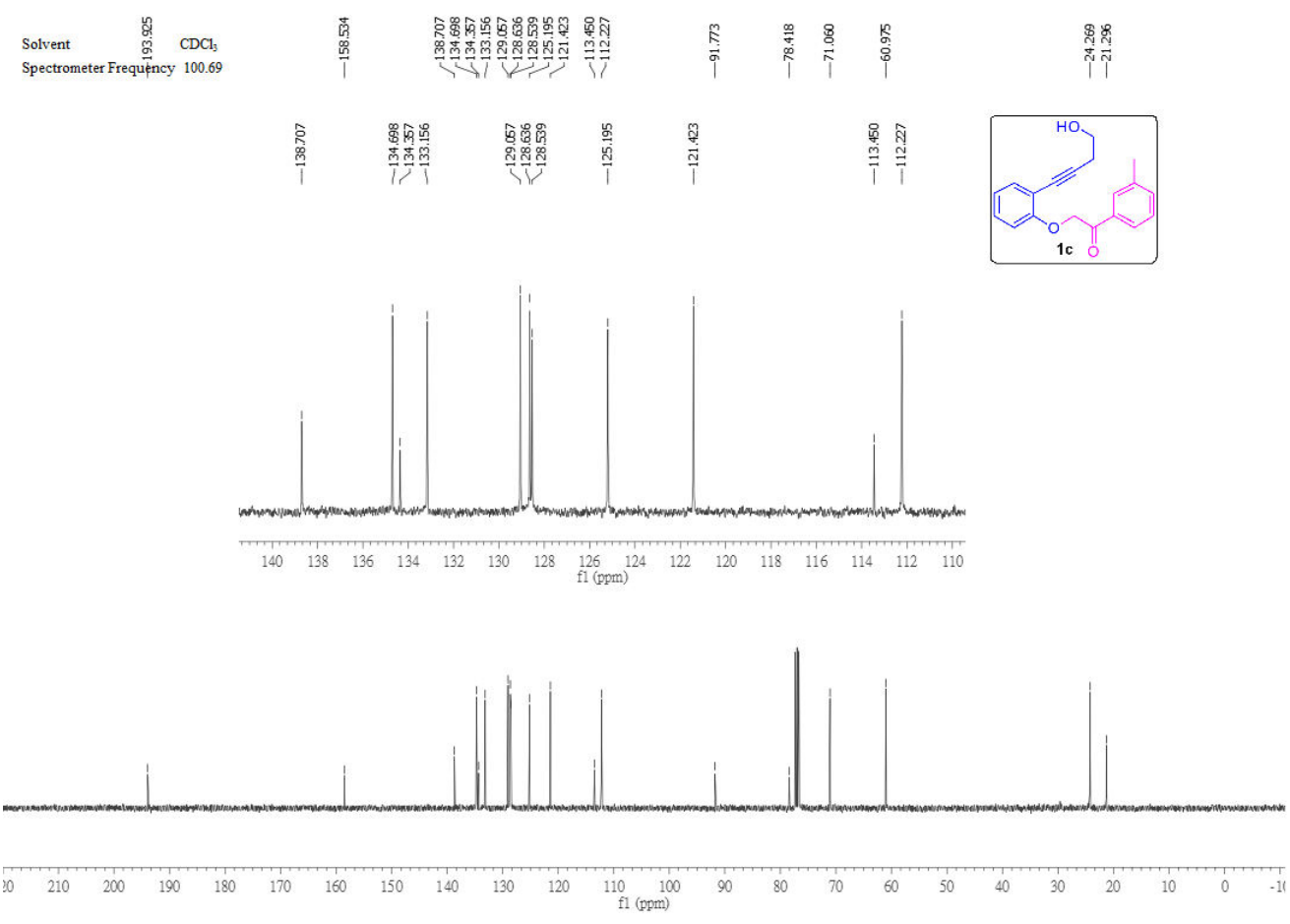
Spectrometer Frequency 400.40
1c
f1 (ppm)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Spectrometer Frequency 100.69
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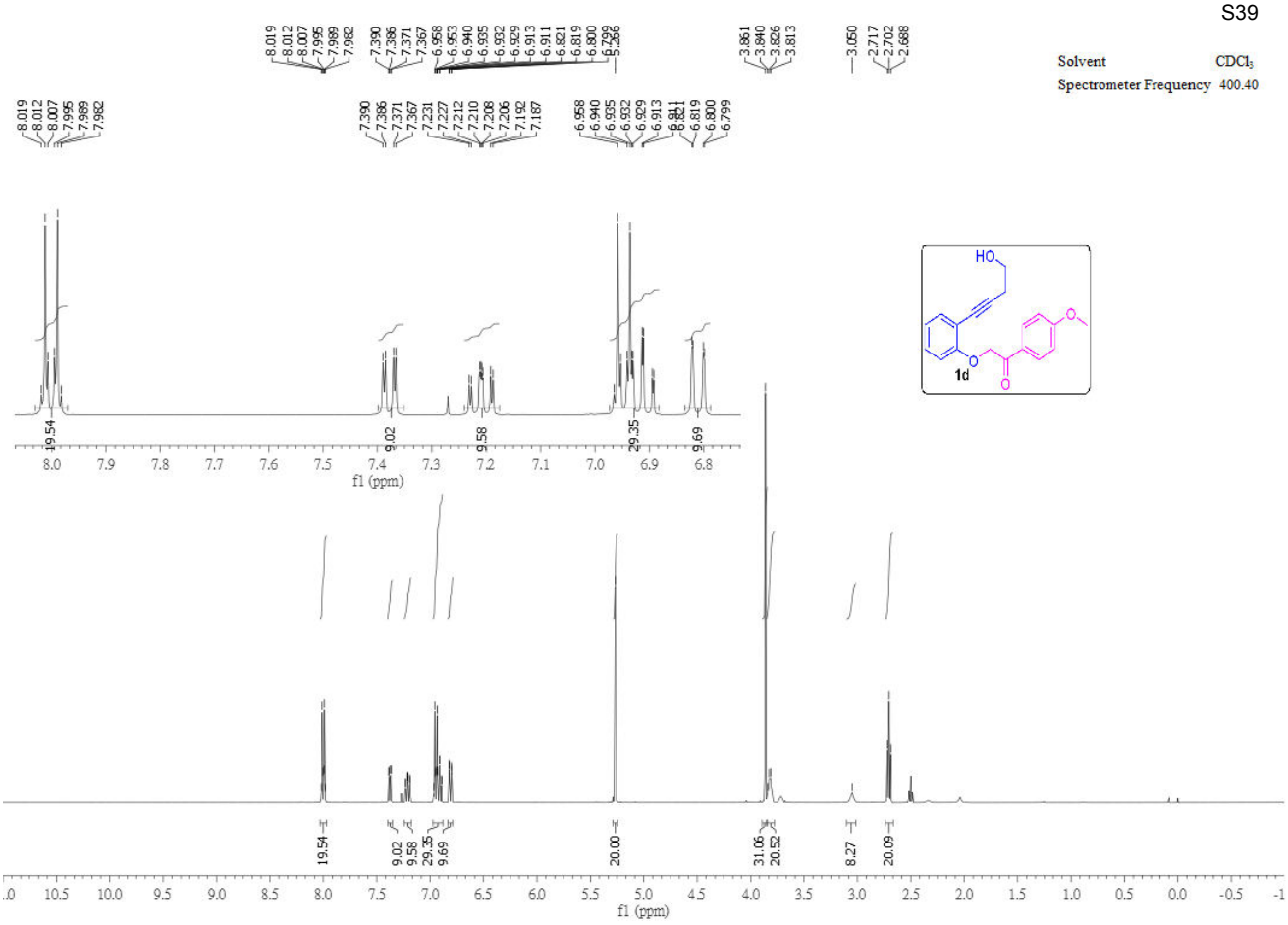
f1 (ppm)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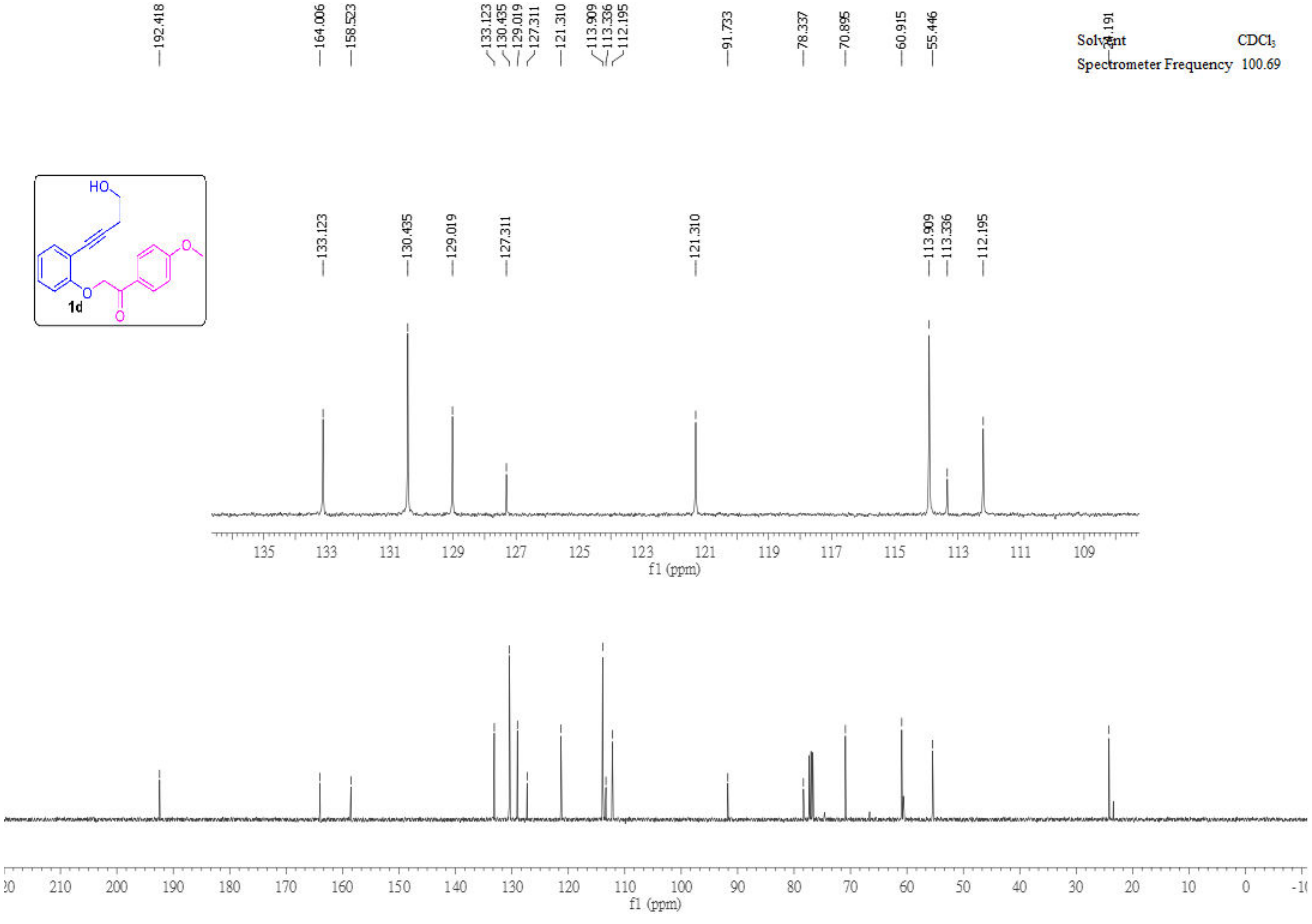
Spectrometer Frequency 400.40
1d
f1 (ppm)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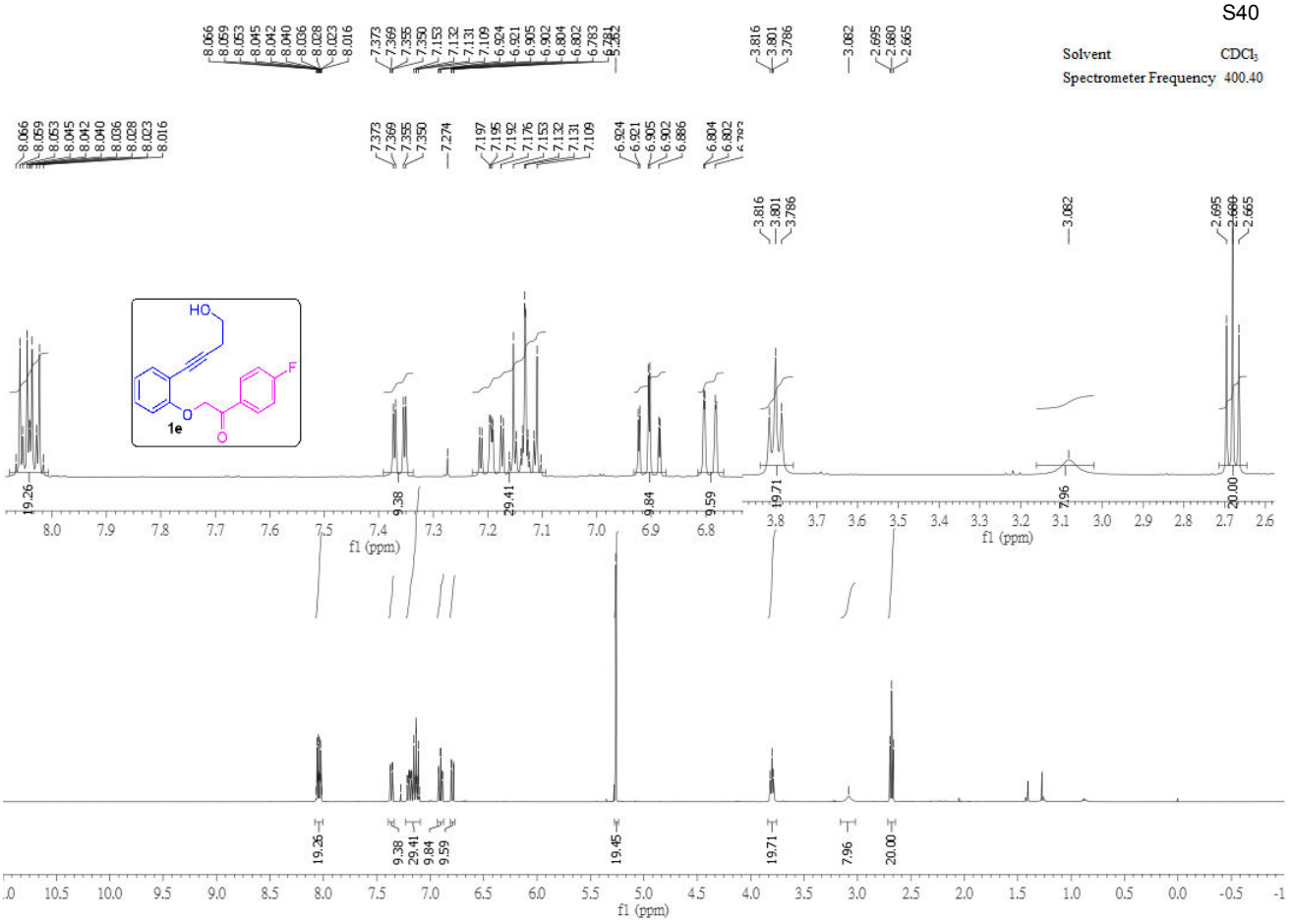
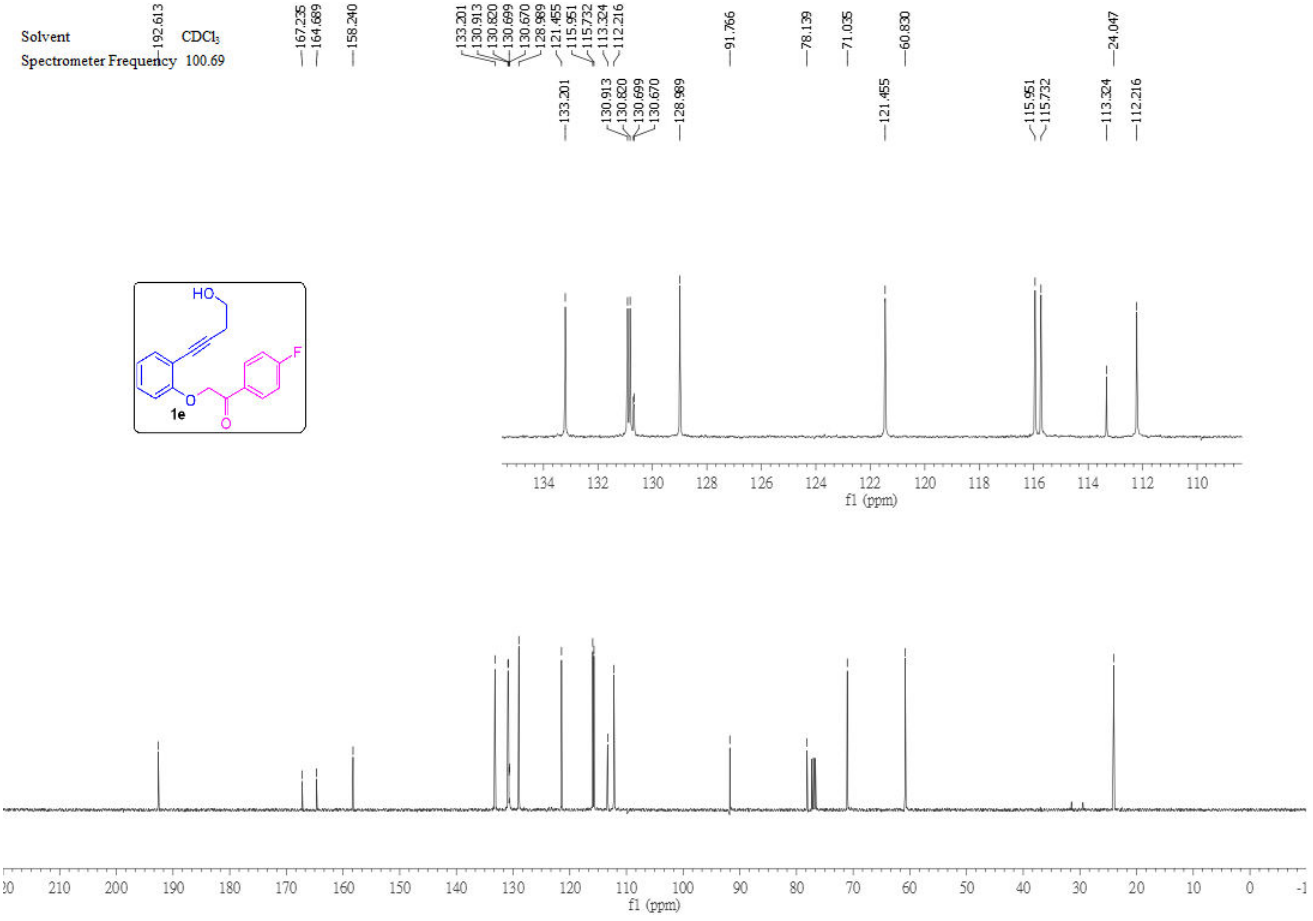
Spectrometer Frequency 100.69
1d
f1 (ppm)

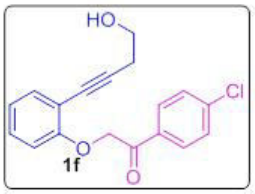

Solvent CDCl3
Spectrometer Frequency 400.40
1e
f1 (ppm)

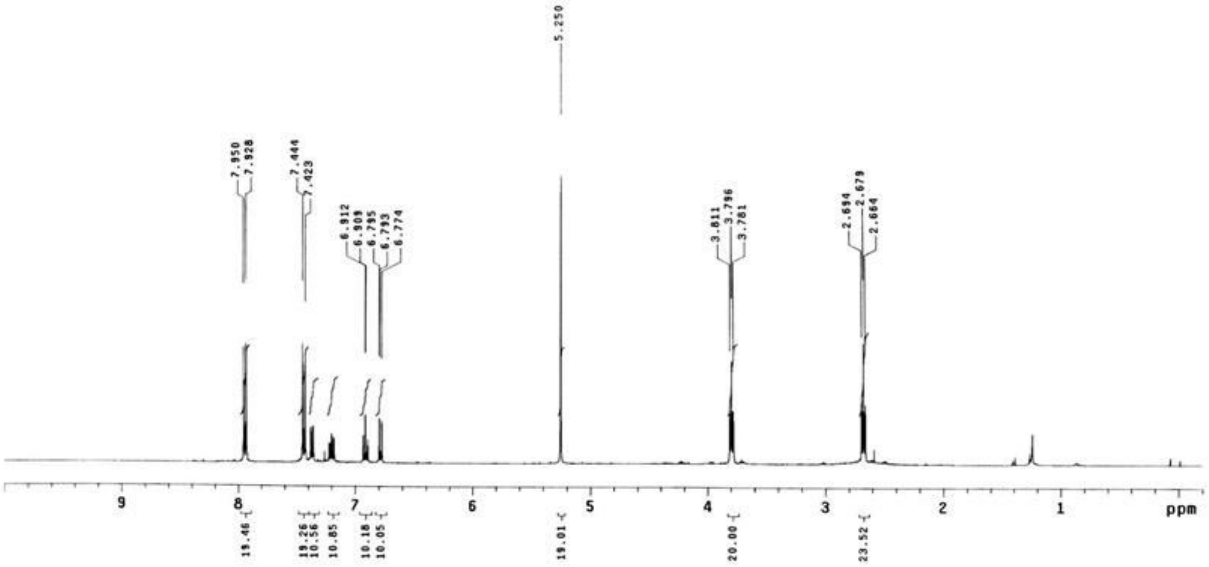

Solvent CDCl3
Spectrometer Frequency 100.69
1e
f1 (ppm)

SGC/RP8/sm-3

Pulse Sequence: s2pul

Mercury-400BB "MercuryPlus400"
Date: Apr 28 2016
Solvent: CDCl3
Ambient temperature
Total 64 repetitions

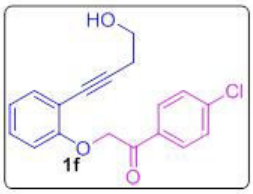


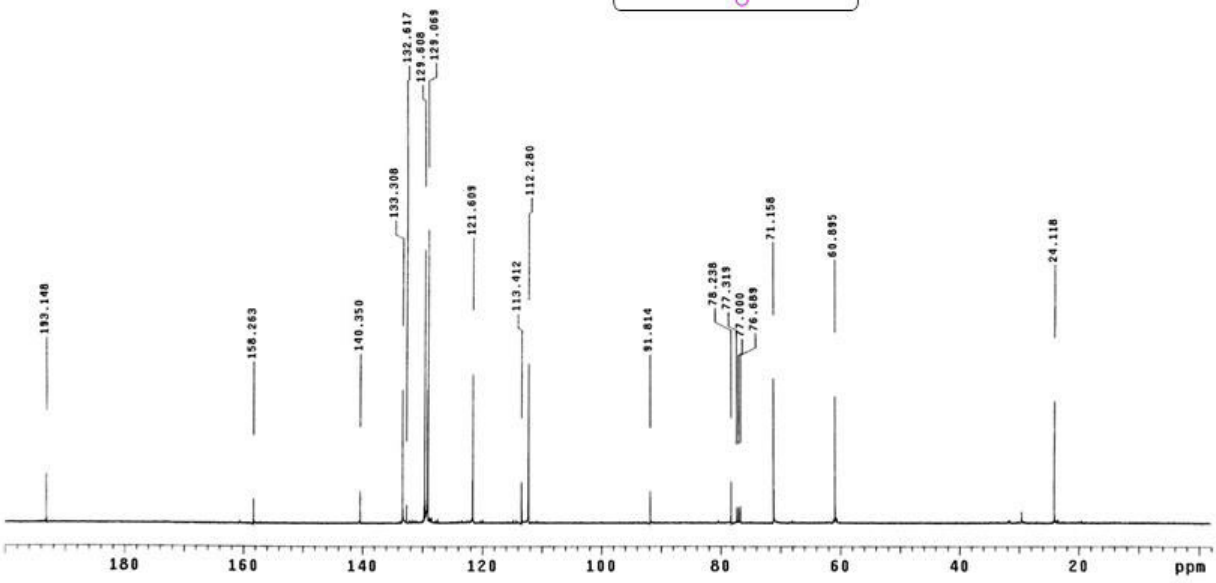


SGC/RP8/sm-3

Pulse Sequence: s2pul

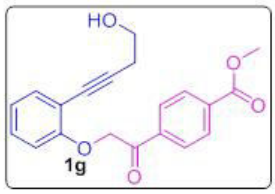
Mercury-400BB "MercuryPlus400"
Date: Apr 28 2016
Solvent: CDCl3
Ambient temperature
Total 64000 repetitions

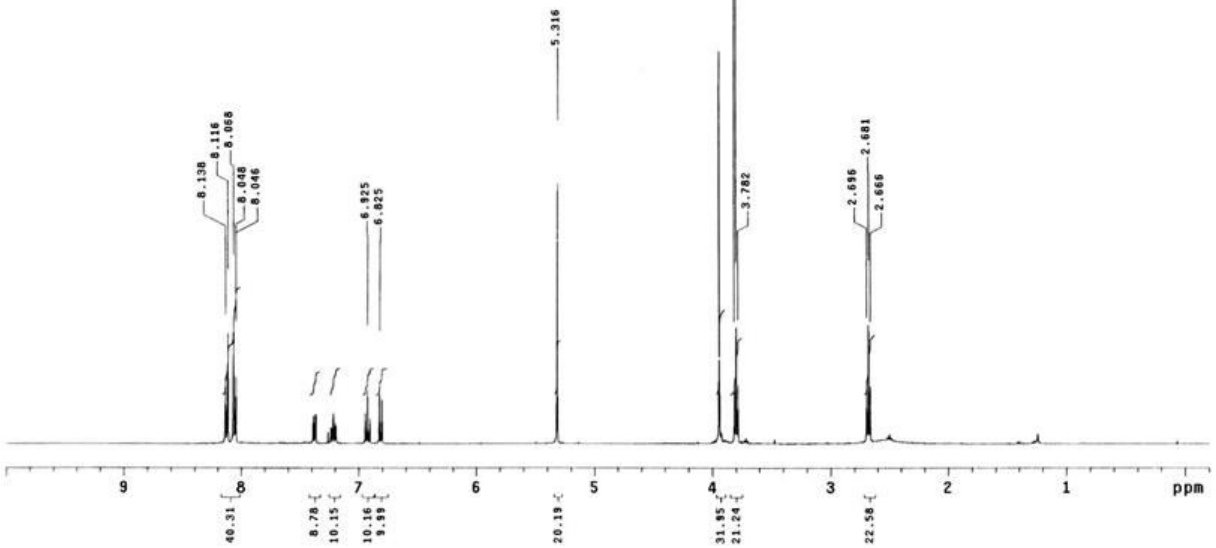




SGC/RP8/sm-5

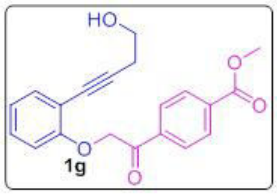
Pulse Sequence: s2pul
Mercury-400BB "MercuryPlus400"
Date: May 12 2016
Solvent: CDCl3
Ambient temperature
Total 32 repetitions

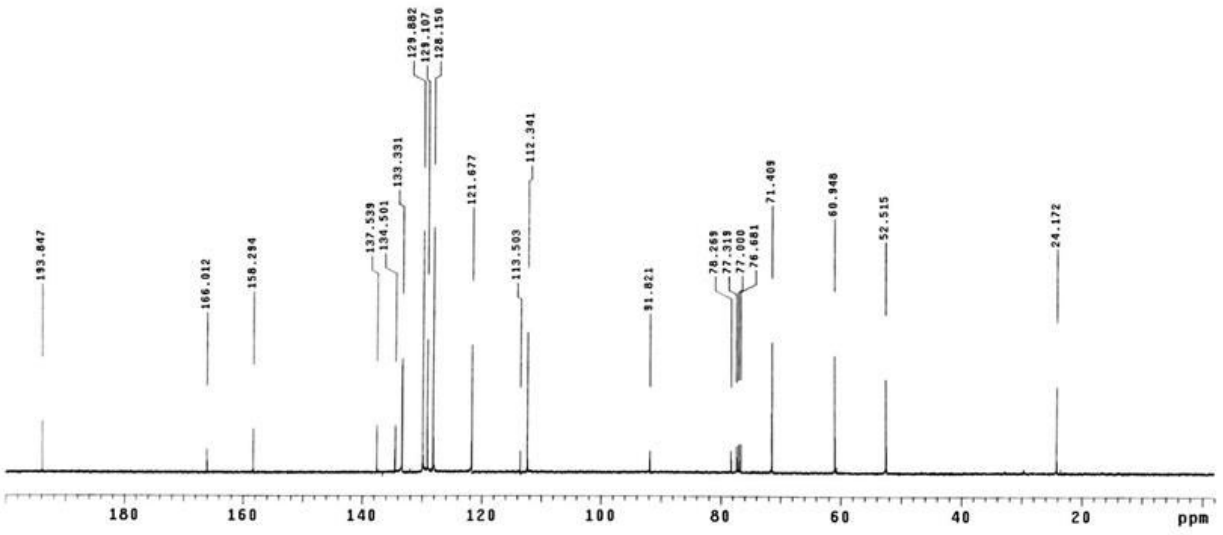


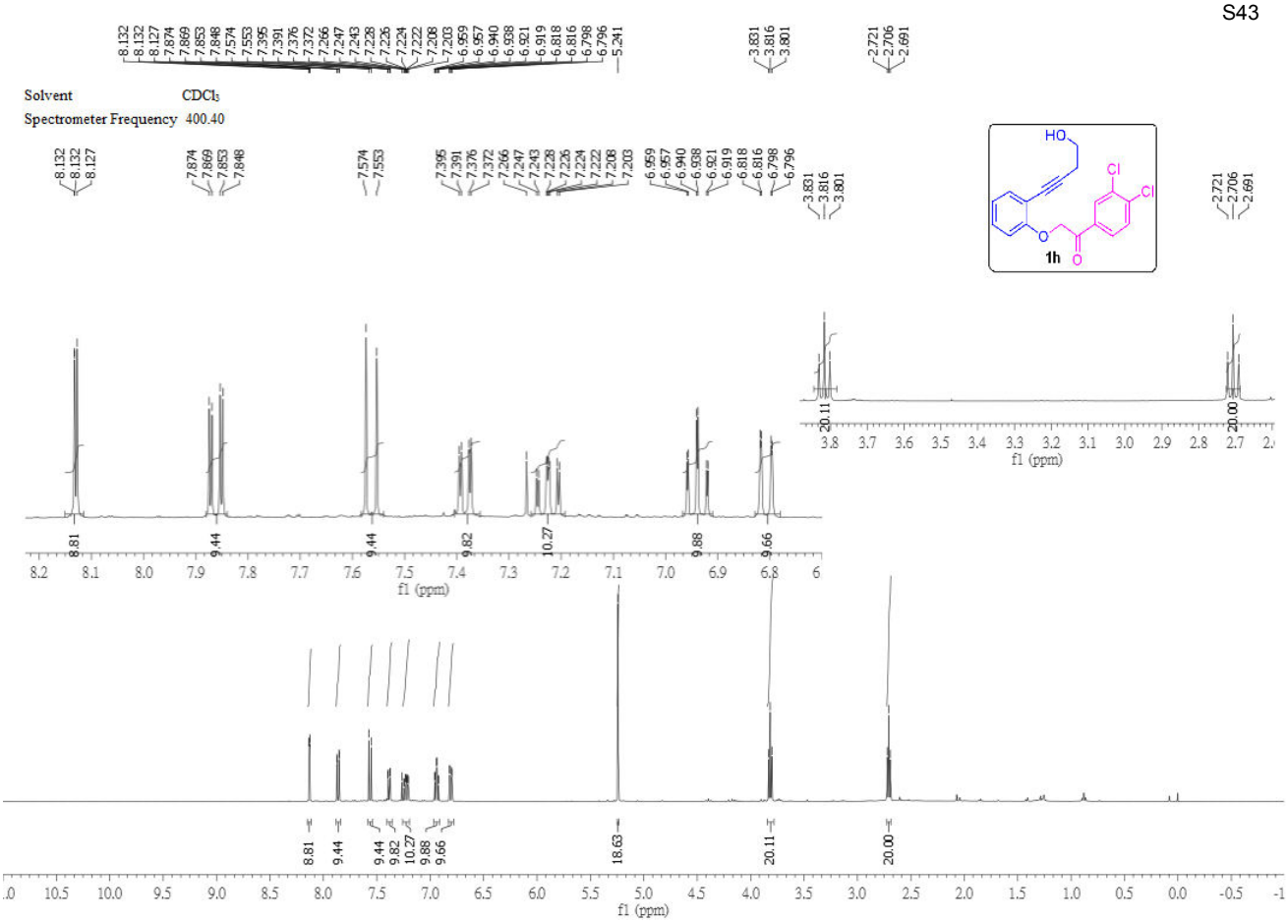


SGC/RP8/sm-5

Pulse Sequence: s2pul
Mercury-400BB "MercuryPlus400"
Date: May 12 2016
Solvent: CDCl3
Ambient temperature
Total 1680 repetitions



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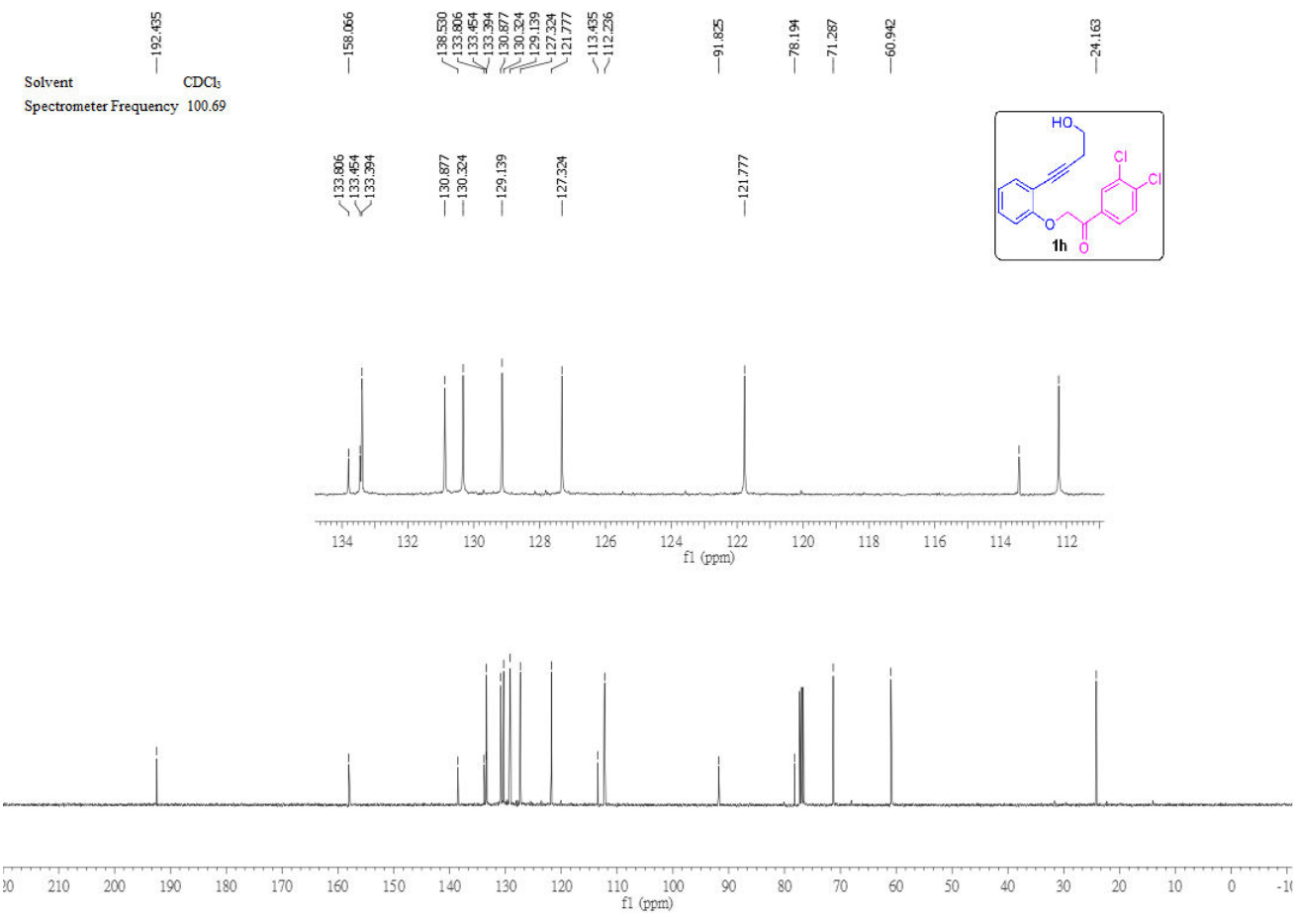
1h
f1 (ppm)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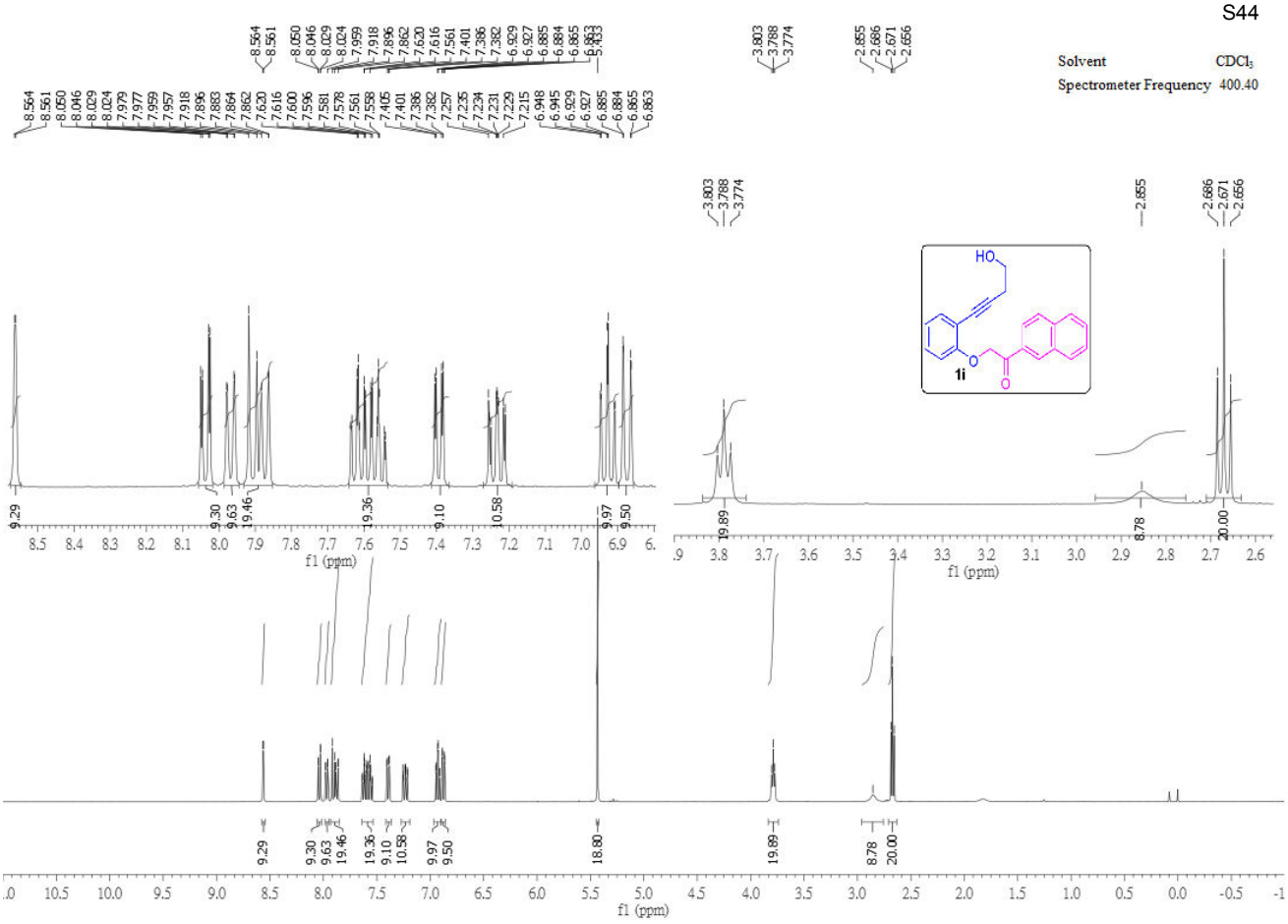
Spectrometer Frequency 100.69
1h
f1 (ppm)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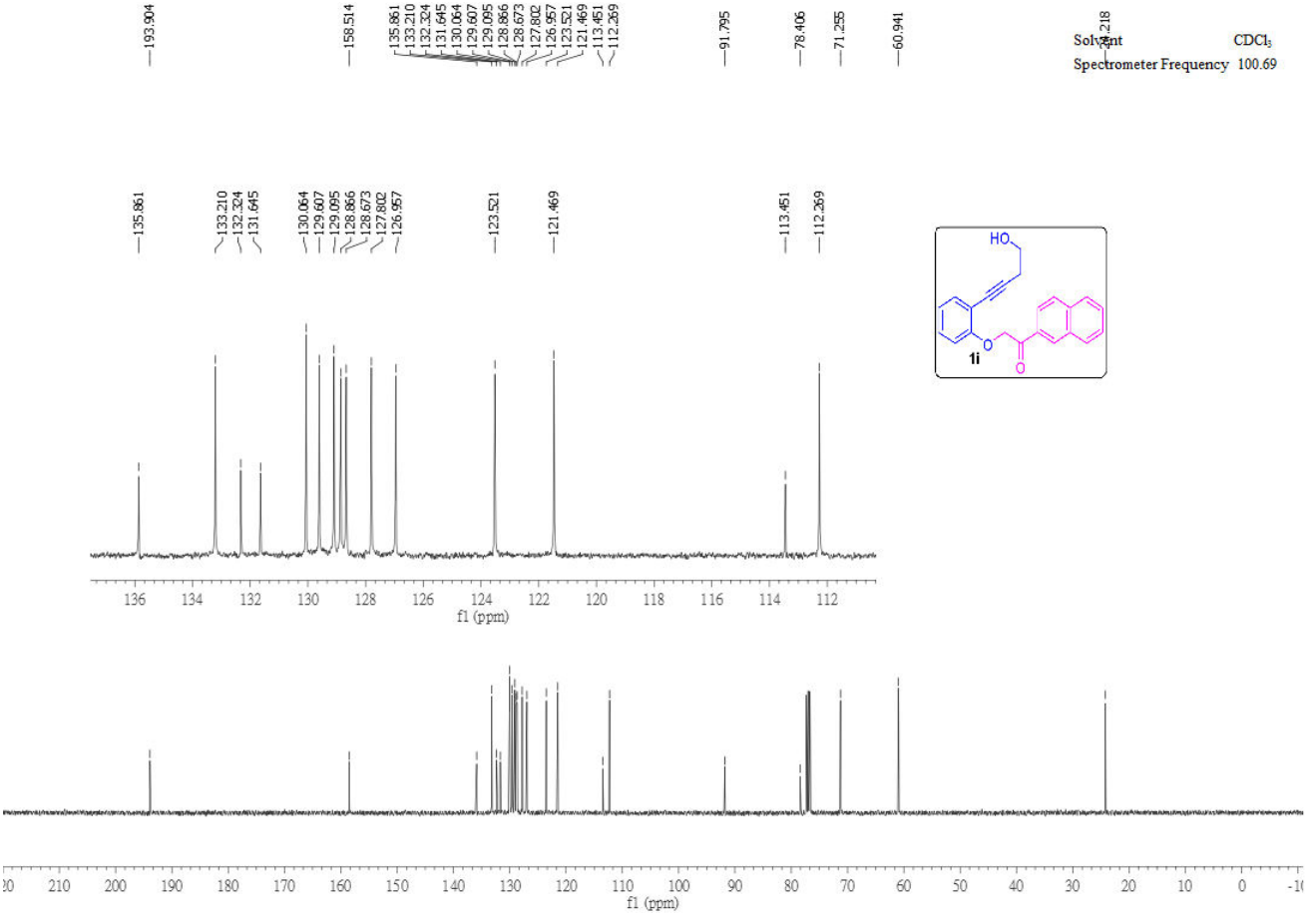
Spectrometer Frequency 400.40
1i
f1 (ppm)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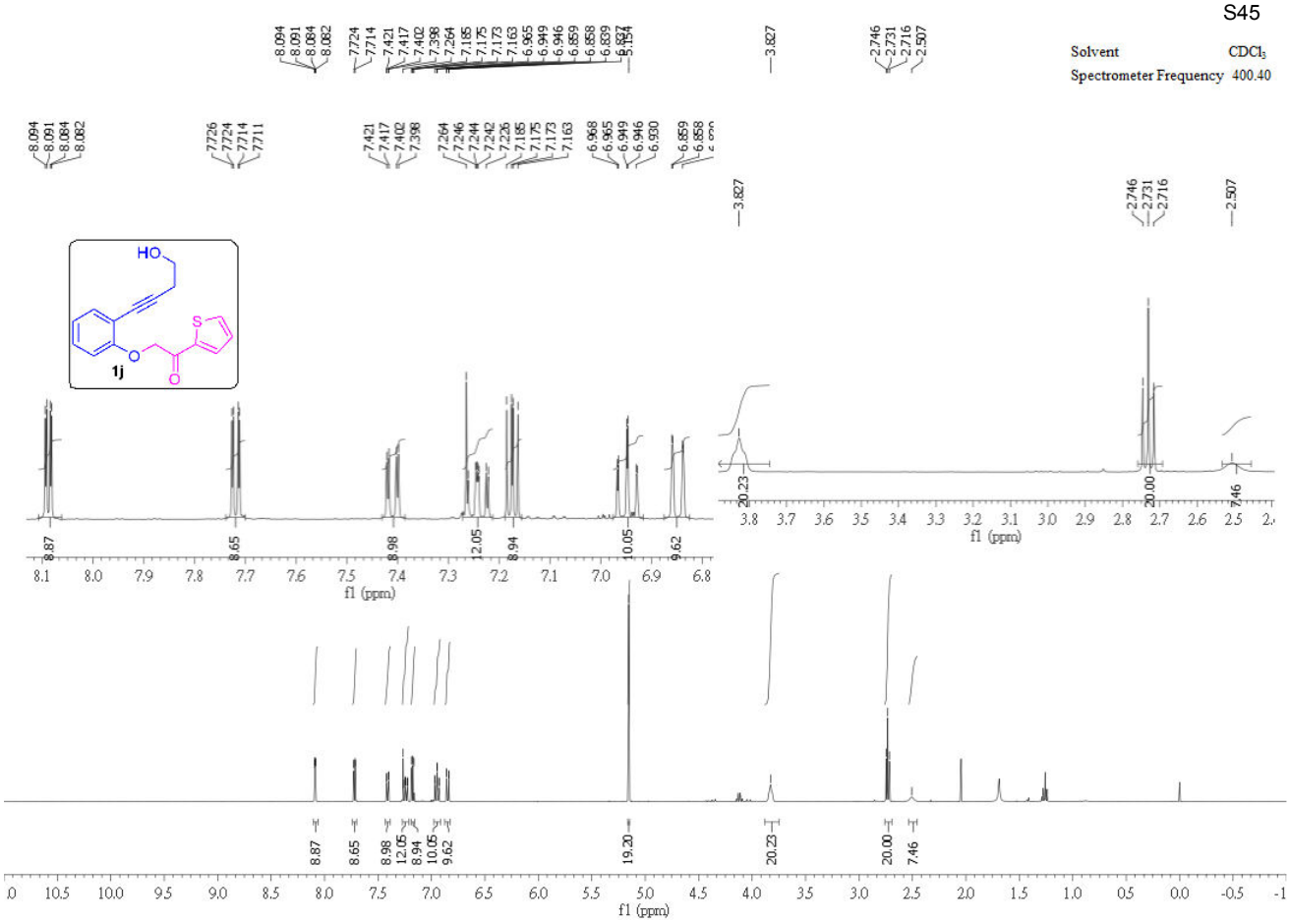
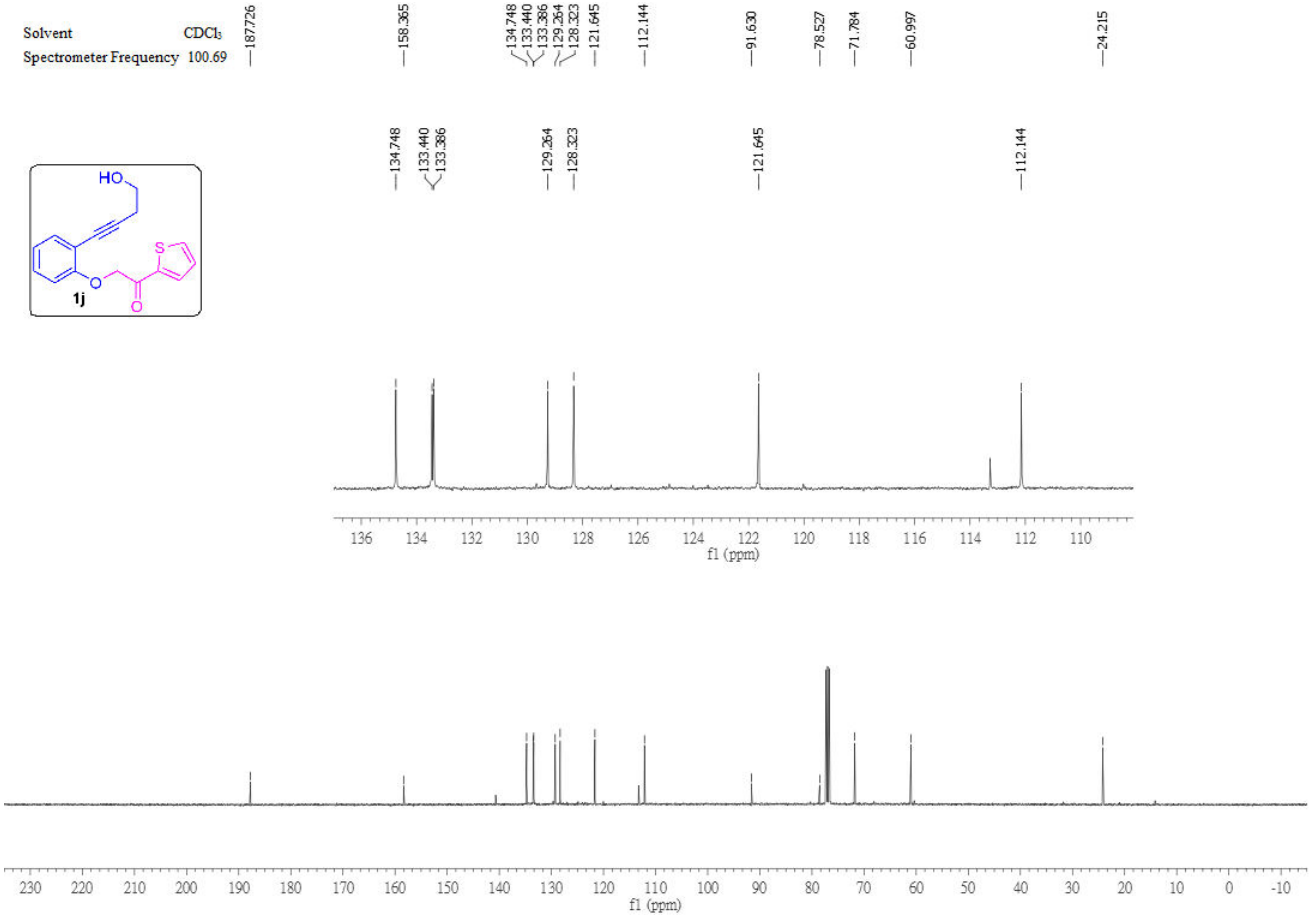
Spectrometer Frequency 100.69
1i
f1 (ppm)


Solvent CDCl3
Spectrometer Frequency 400.40
HO
S
O
O
1j
f1 (ppm)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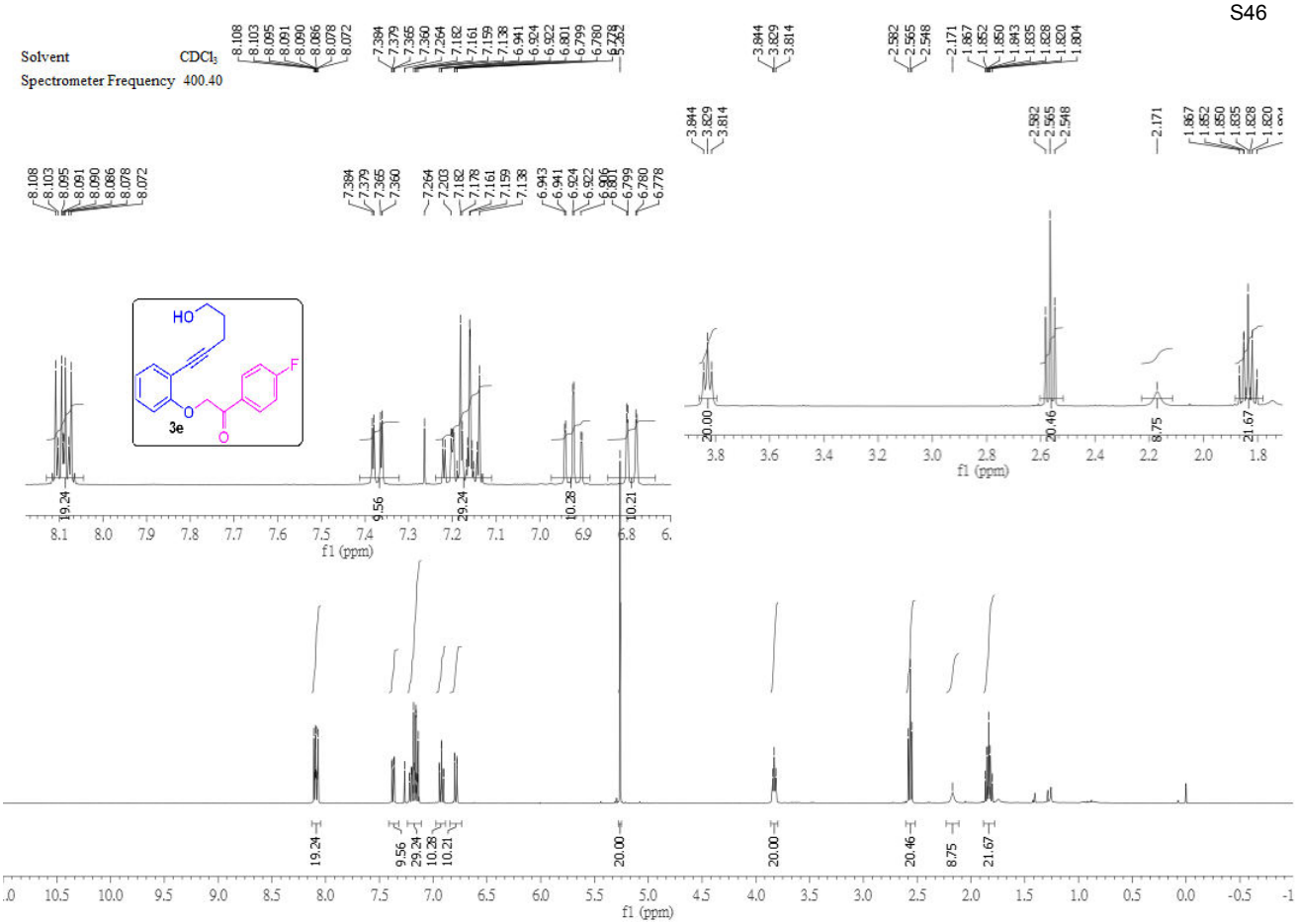
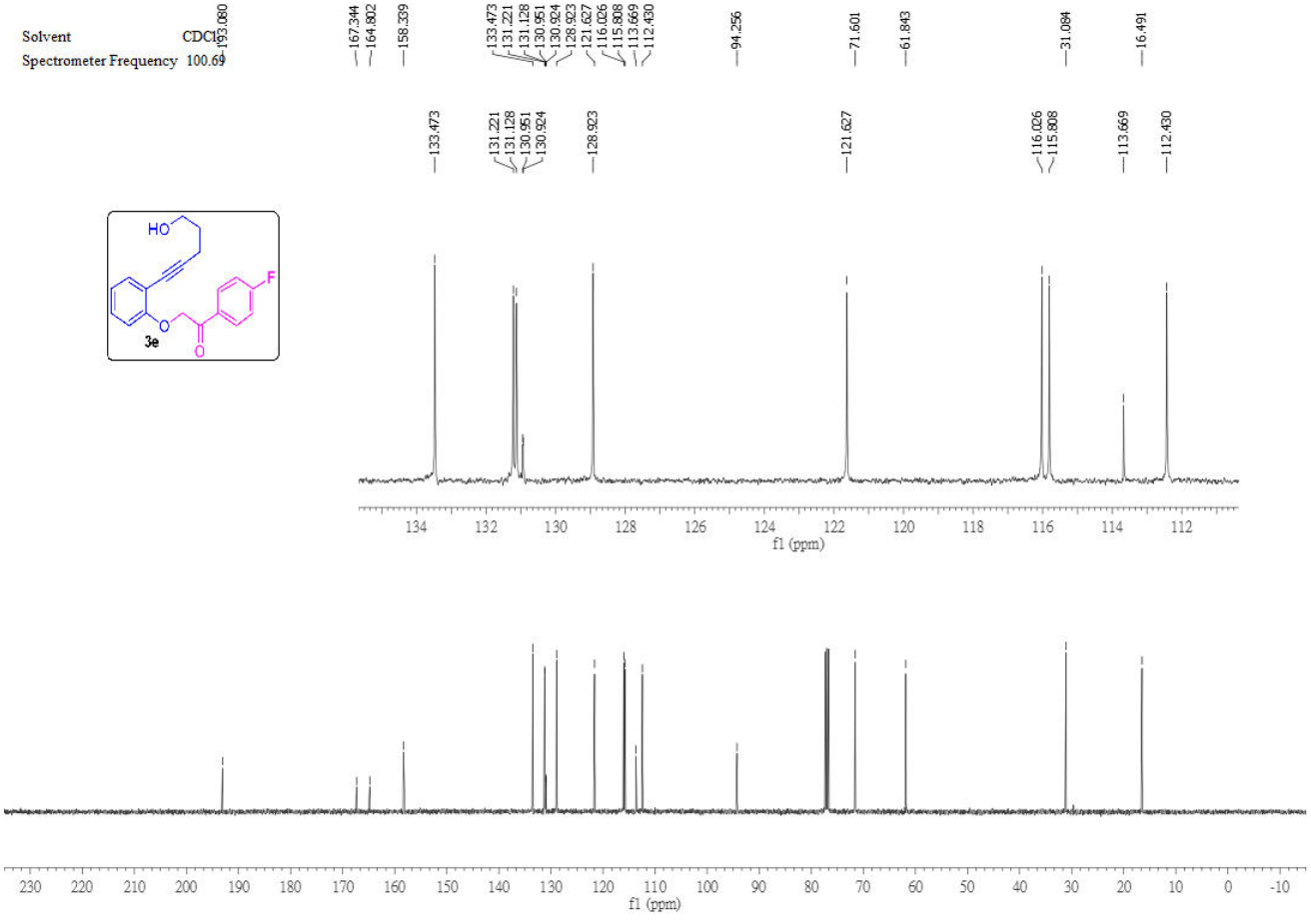
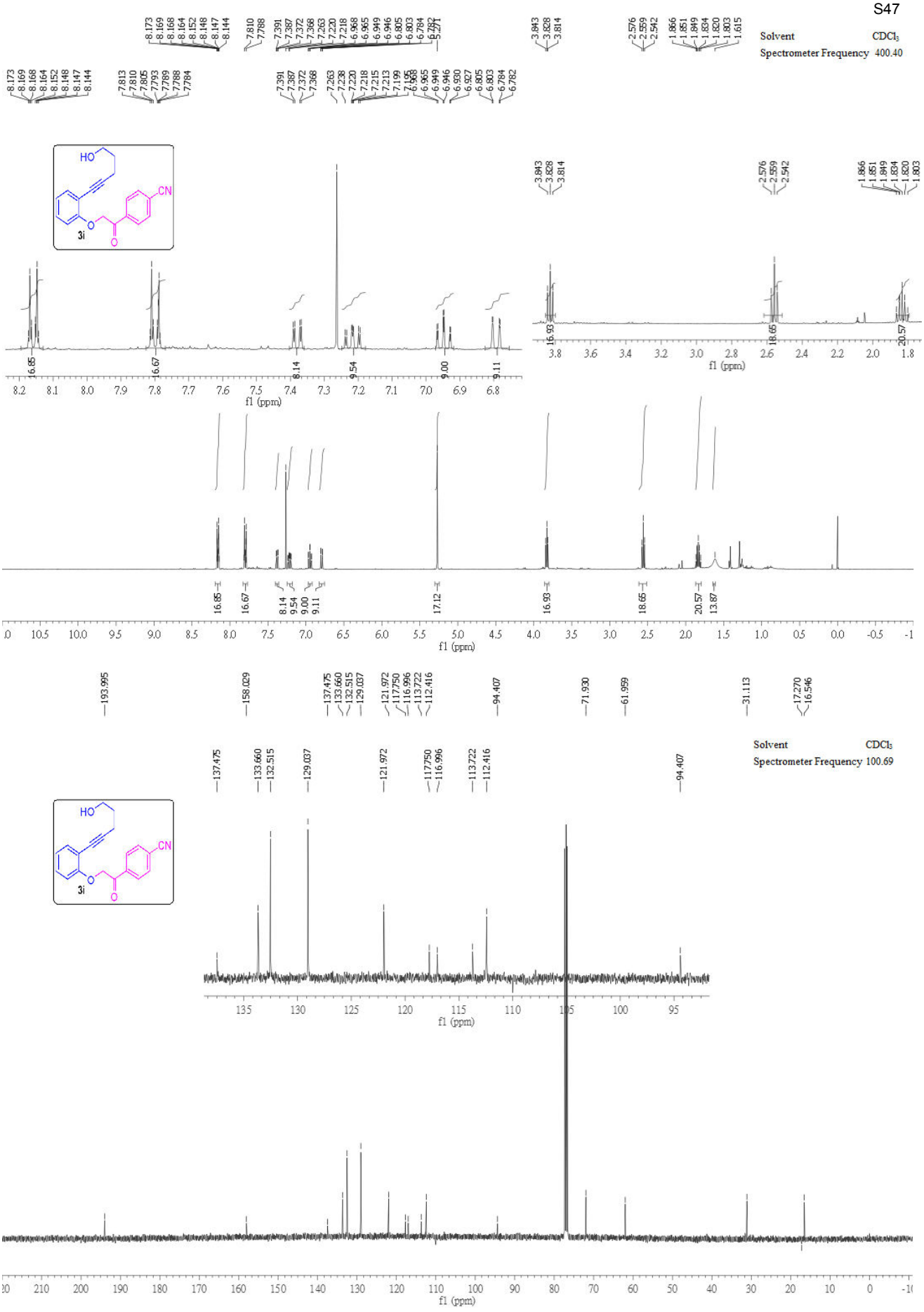
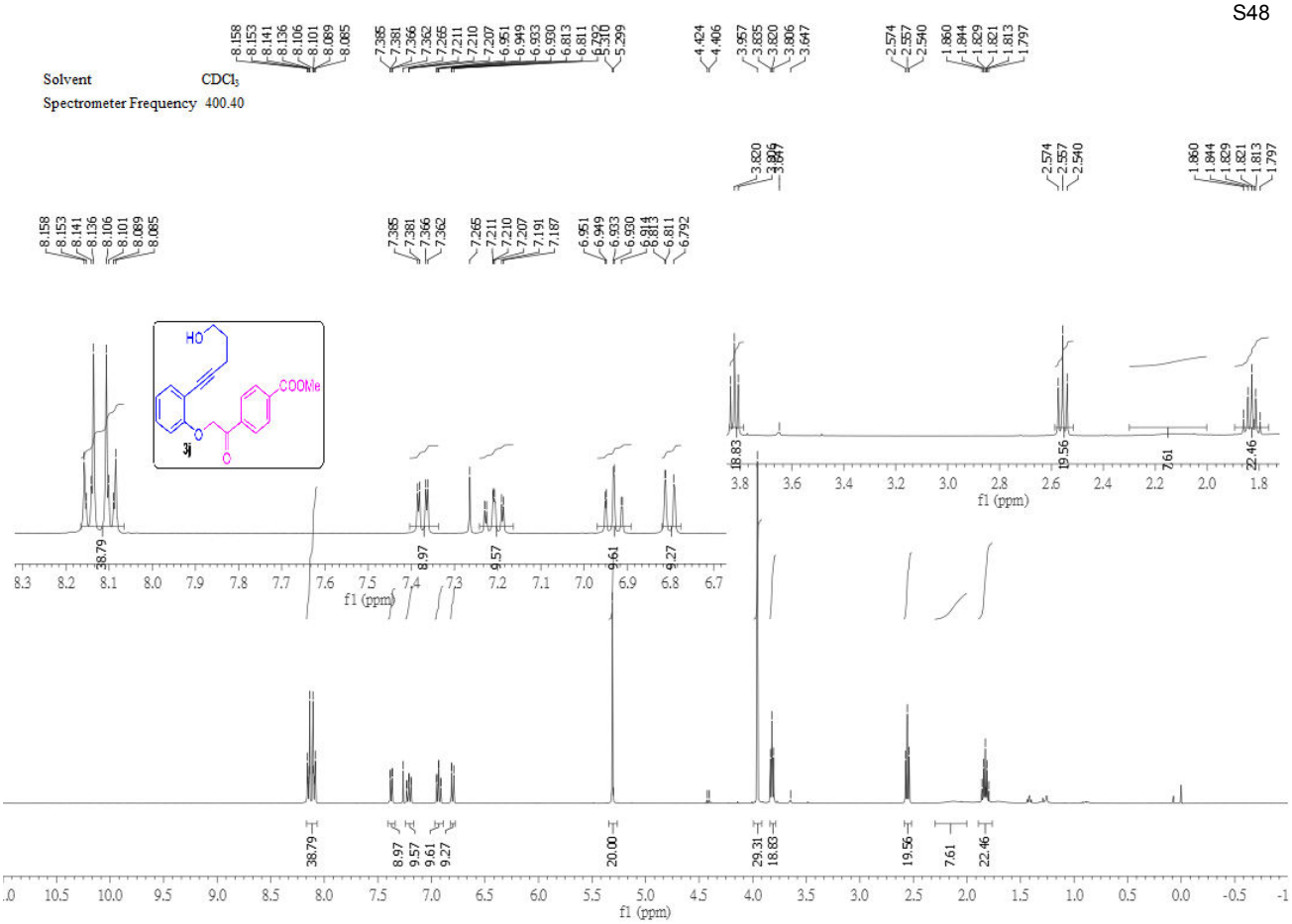
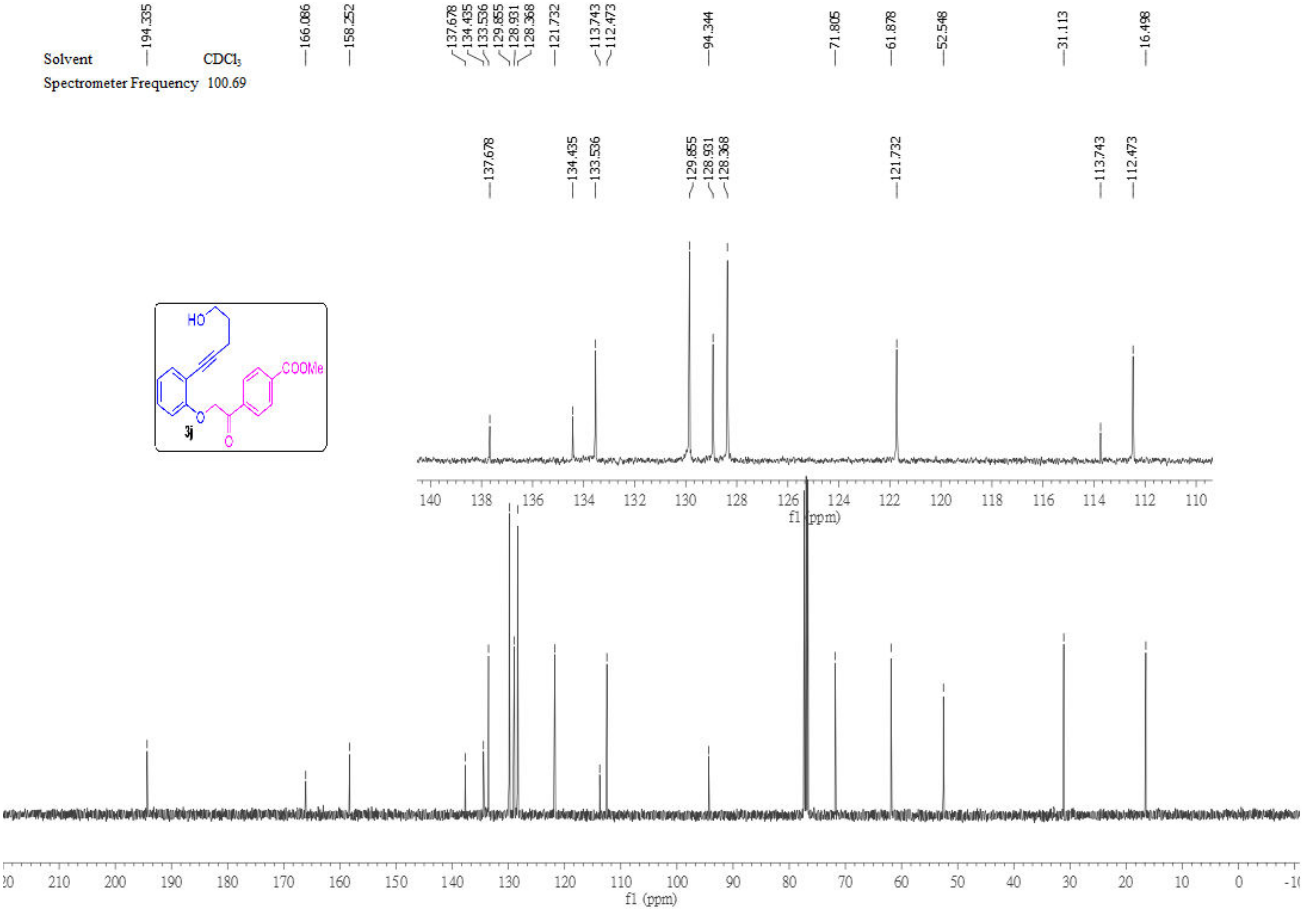
Spectrometer Frequency 100.69
HO
S
O
O
1j
f1 (ppm)


Solvent CDCl3
Spectrometer Frequency 400.40
HO
F
O
O
3e
f1 (ppm)


Solvent CDCl3
Spectrometer Frequency 100.69
HO
F
O
O
3e
f1 (ppm)


Solvent CDCl3
Spectrometer Frequency 400.40
Solvent CDCl3
Spectrometer Frequency 100.69
f1 (ppm)

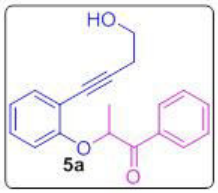

Solvent CDCl3
Spectrometer Frequency 400.40
HO
COOMe
O
O
3j
f1 (ppm)

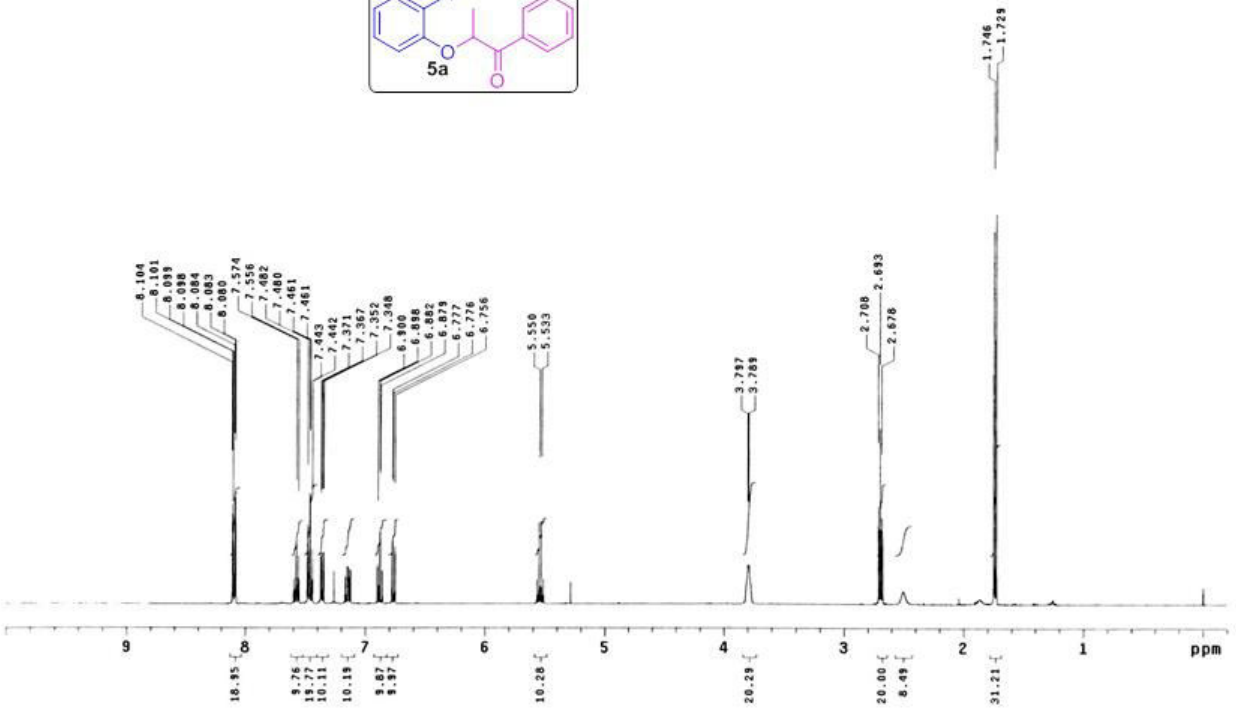

Solvent CDCl3
Spectrometer Frequency 100.69
HO
COOMe
O
O
3j
f1 (ppm)

SGC/RP8/sm-4

Pulse Sequence: s2pul

Mercury-400BB "MercuryPlus400"
Date: Apr 28 2016
Solvent: CDCl3
Ambient temperature
Total 32 repetitions

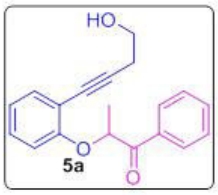


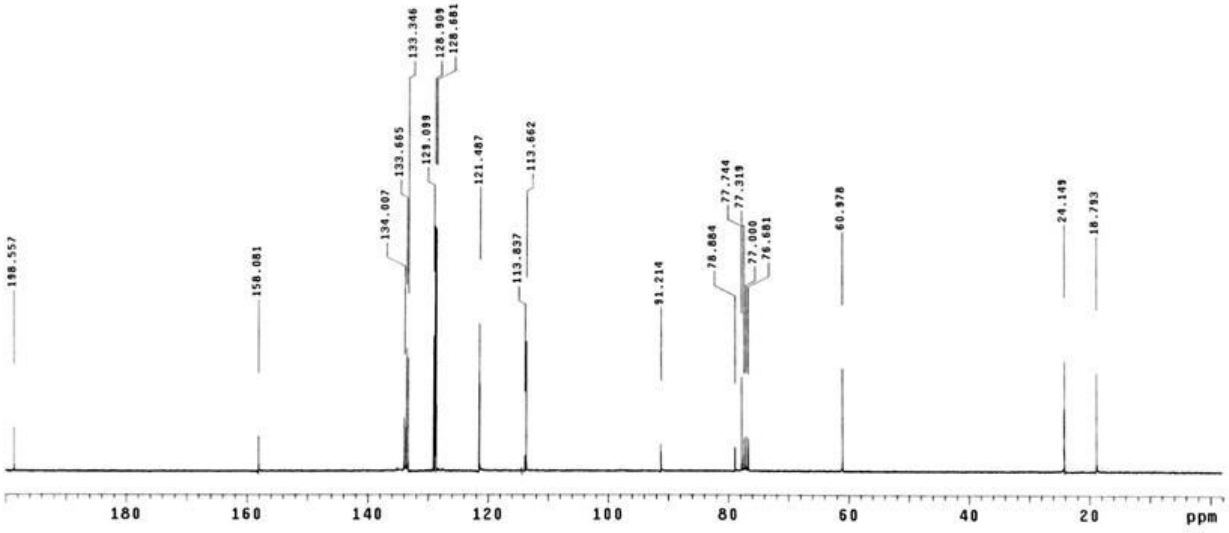


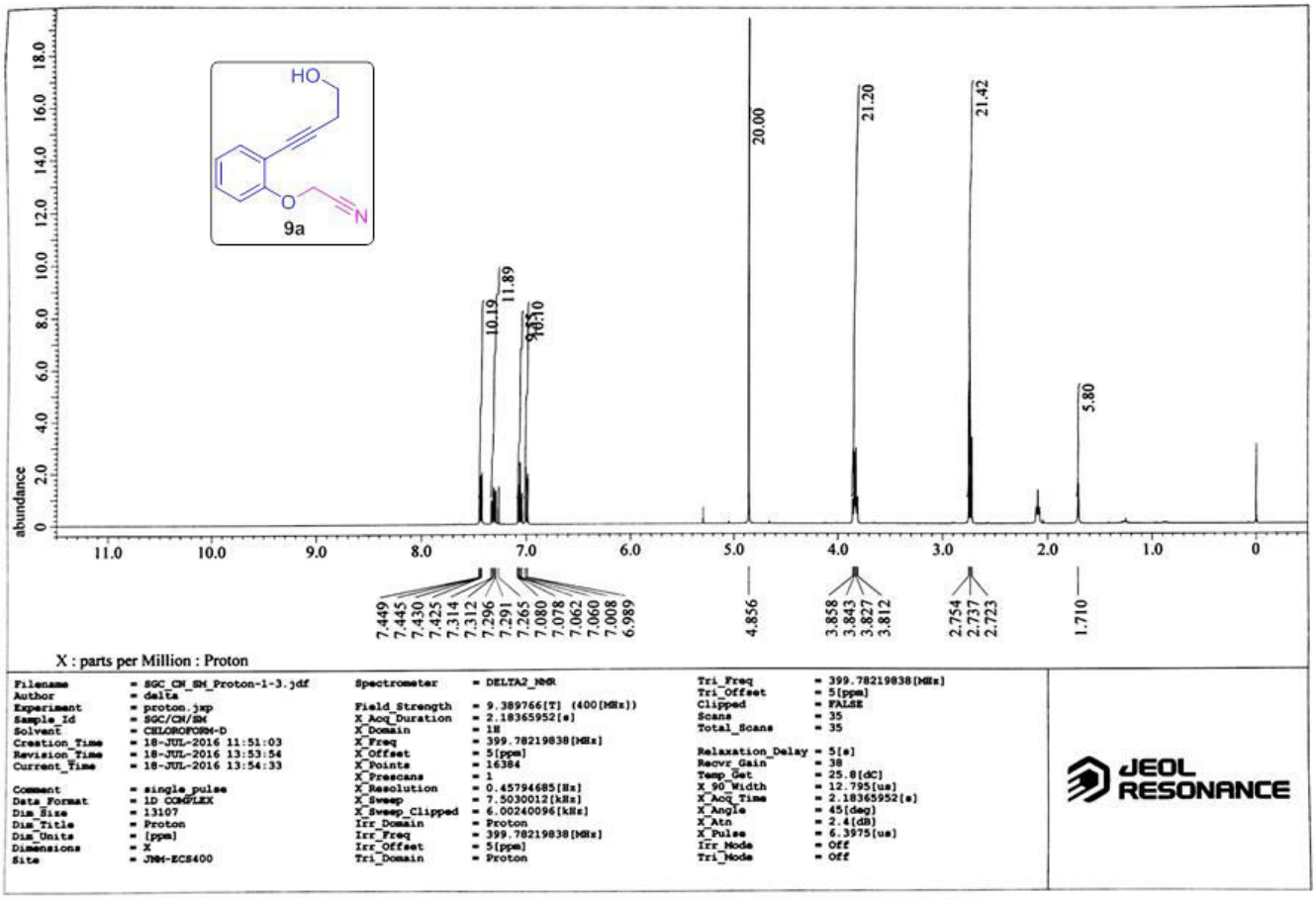
SGC/RP8/sm-4

Pulse Sequence: s2pul

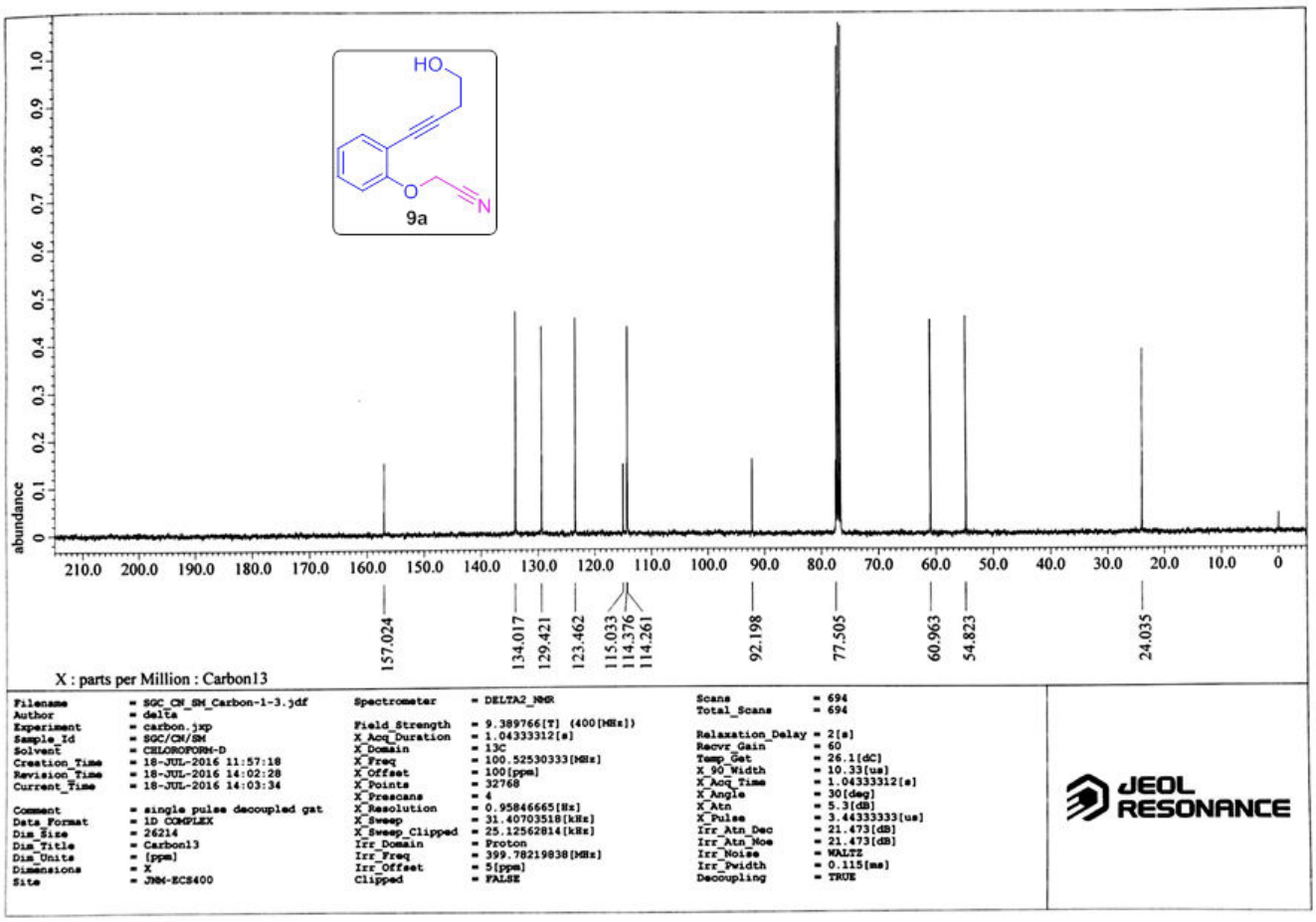
Mercury-400BB "MercuryPlus400"
Date: Apr 28 2016
Solvent: CDCl3
Ambient temperature
Total 1680 repetitions



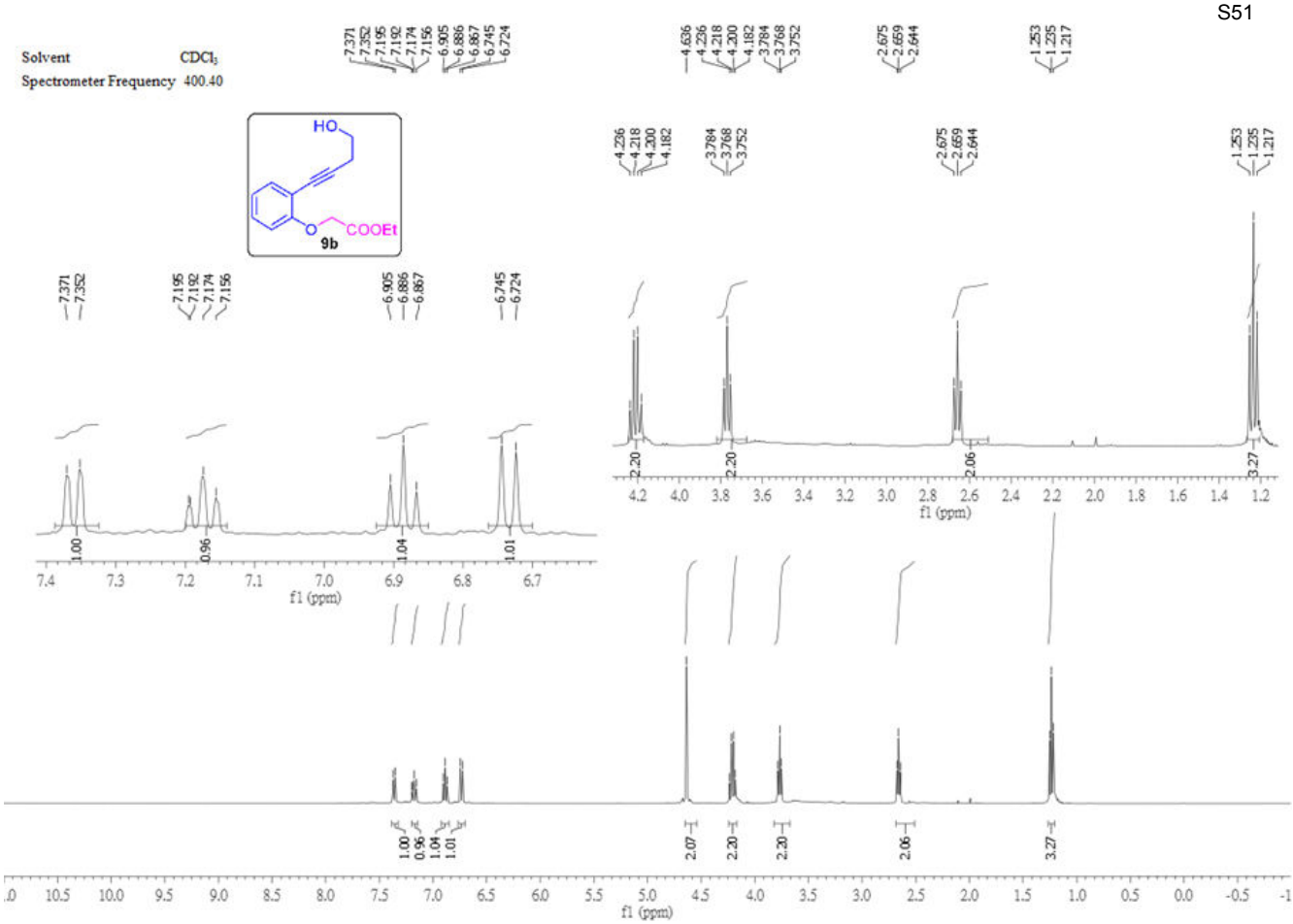


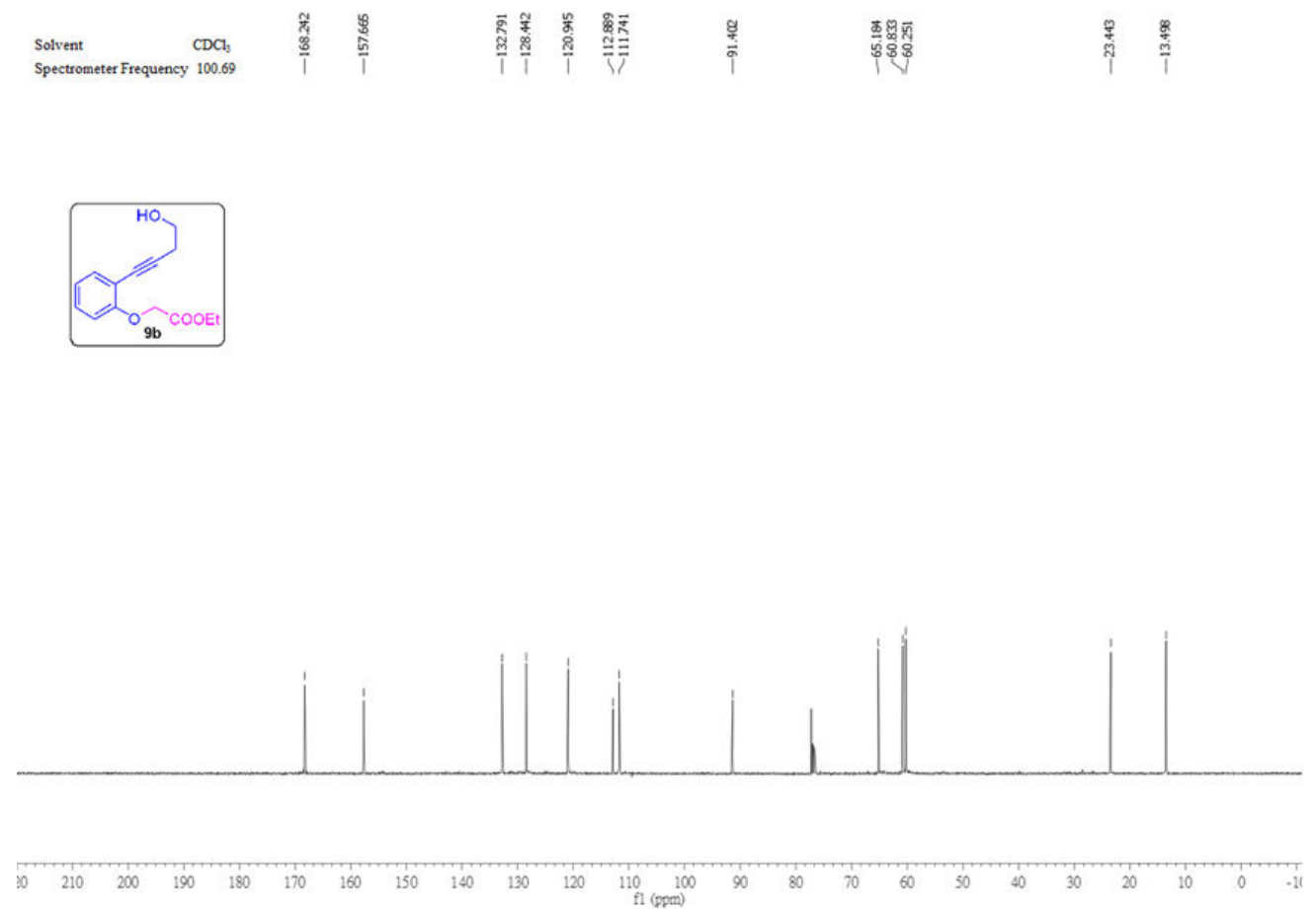


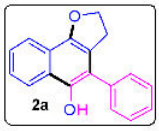
Filename	= SGC_CN_SM_Proton-1-3.jdf	Spectrometer	= DELTA2_NMR			Tri_Freq	= 399.78219838[MHz]
Author	= delta					Tri_Offset	= 5[ppm]
Experiment	= proton.jxp	Field_Strength	= 9.389766[T] (400[MHz])			Clipped	= FALSE
Sample_Id	= SGC/CN/SM	X_Acq_Duration	= 2.18365952[s]			Scans	= 35
Solvent	= CHLOROFORM-D	X_Domain	= 1H			Total_Scans	= 35
Creation_Time	= 18-JUL-2016 11:51:03	X_Freq	= 399.78219838[MHz]				
Revision_Time	= 18-JUL-2016 13:53:54	X_Offset	= 5[ppm]			Relaxation_Delay	= 5[s]
Current_Time	= 18-JUL-2016 13:54:33	X_Points	= 16384			Recvr_Gain	= 38
		X_Prescans	= 1			Temp_Get	= 25.8[dC]
Comment	= single_pulse	X_Resolution	= 0.45794685[Hz]			X_90_Width	= 12.795[us]
Data_Format	= 1D COMPLEX	X_Sweep	= 7.5030012[kHz]			X_Acq_Time	= 2.18365952[s]
Dim_Size	= 13107	X_Sweep_Clipped	= 6.00240096[kHz]			X_Angle	= 45[deg]
Dim_Title	= Proton	Irr_Domain	= Proton			X_Atn	= 2.4[dB]
Dim_Units	= [ppm]	Irr_Freq	= 399.78219838[MHz]			X_Pulse	= 6.3975[us]
Dimensions	= X	Irr_Offset	= 5[ppm]			Irr_Mode	= Off
Site	= JNM-ECS400	Tri_Domain	= Proton			Tri_Mode	= Off



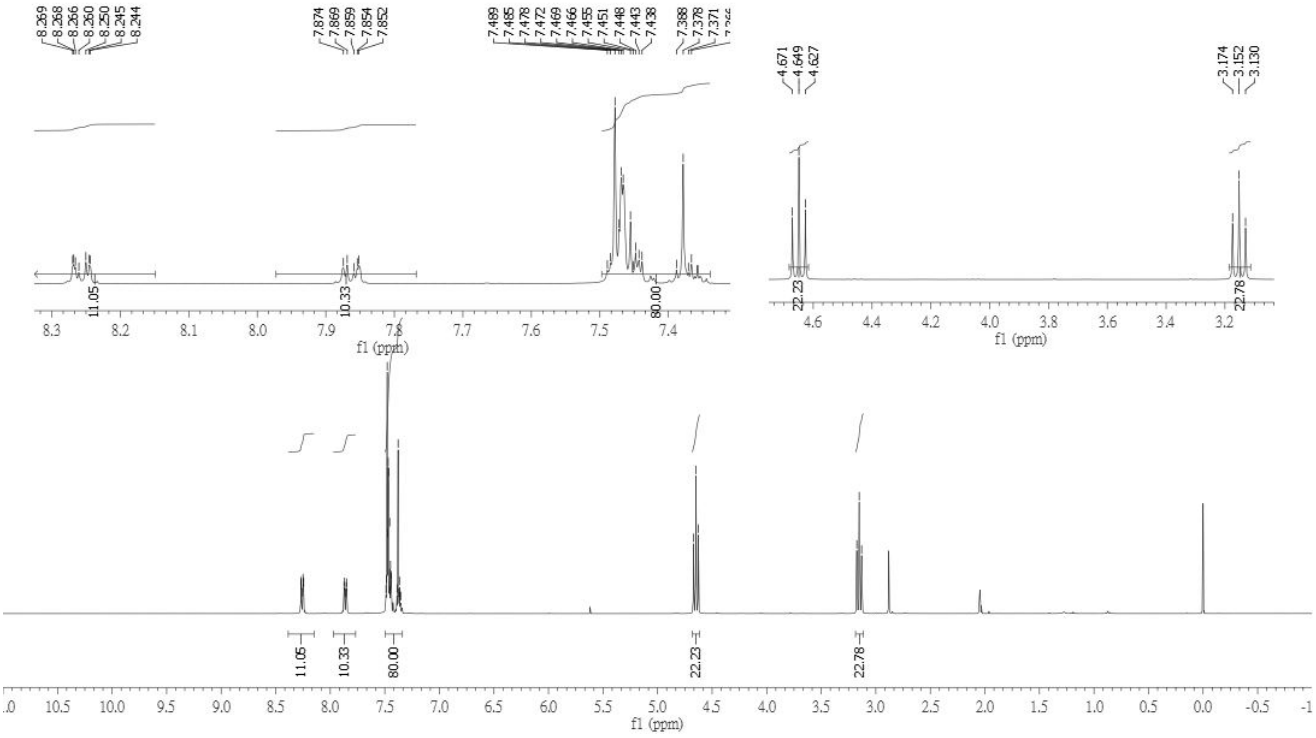
Filename	= SGC_CN_SM_Carbon-1-3.jdf	Spectrometer	= DELTA2_NMR			Scans	= 694
Author	= delta					Total_Scans	= 694
Experiment	= carbon.jxp	Field_Strength	= 9.389766[T] (400[MHz])				
Sample_Id	= SGC/CN/SM	X_Acq_Duration	= 1.04333312[s]			Relaxation_Delay	= 2[s]
Solvent	= CHLOROFORM-D	X_Domain	= 13C			Recvr_Gain	= 60
Creation_Time	= 18-JUL-2016 11:57:18	X_Freq	= 100.52530333[MHz]			Temp_Get	= 26.1[dC]
Revision_Time	= 18-JUL-2016 14:02:28	X_Offset	= 100[ppm]			X_90_Width	= 10.33[us]
Current_Time	= 18-JUL-2016 14:03:34	X_Points	= 32768			X_Acq_Time	= 1.04333312[s]
		X_Prescans	= 4			X_Angle	= 30[deg]
Comment	= single pulse decoupled gat	X_Resolution	= 0.95846665[Hz]			X_Atn	= 5.3[dB]
Data_Format	= 1D COMPLEX	X_Sweep	= 31.40703518[kHz]			X_Pulse	= 3.44333333[us]
Dim_Size	= 26214	X_Sweep_Clipped	= 25.12562814[kHz]			Irr_Atn_Dec	= 21.473[dB]
Dim_Title	= Carbon13	Irr_Domain	= Proton			Irr_Atn_Noe	= 21.473[dB]
Dim_Units	= [ppm]	Irr_Freq	= 399.78219838[MHz]			Irr_Noise	= WALTZ
Dimensions	= X	Irr_Offset	= 5[ppm]			Irr_Pwidth	= 0.115[ms]
Site	= JNM-ECS400	Clipped	= FALSE			Decoupling	= TRUE


Solvent CDCl3
Spectrometer Frequency 400.40
HO
COOEt
9b
f1 (ppm)

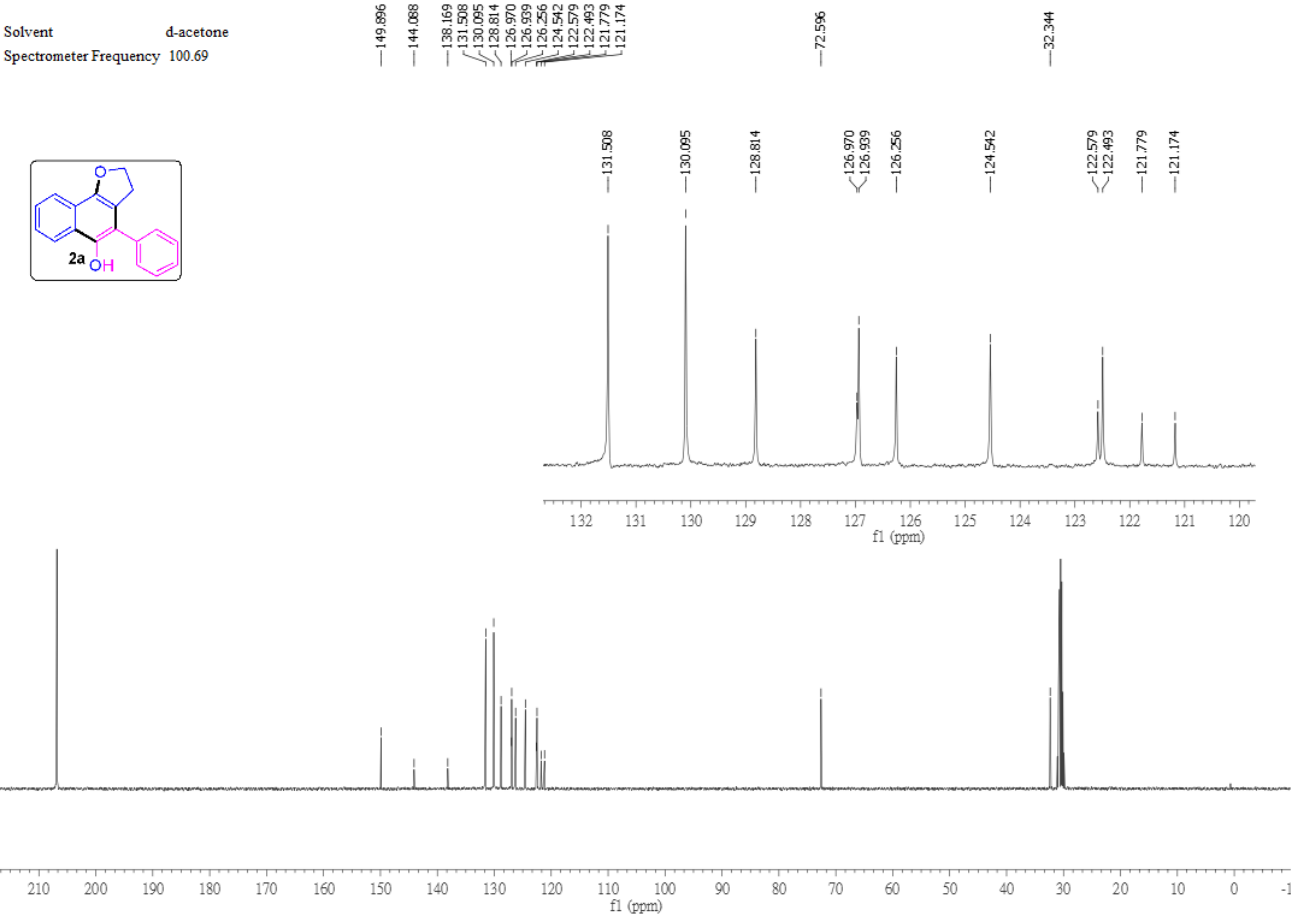

Solvent CDCl3
Spectrometer Frequency 100.69
HO
COOEt
9b
f1 (ppm)

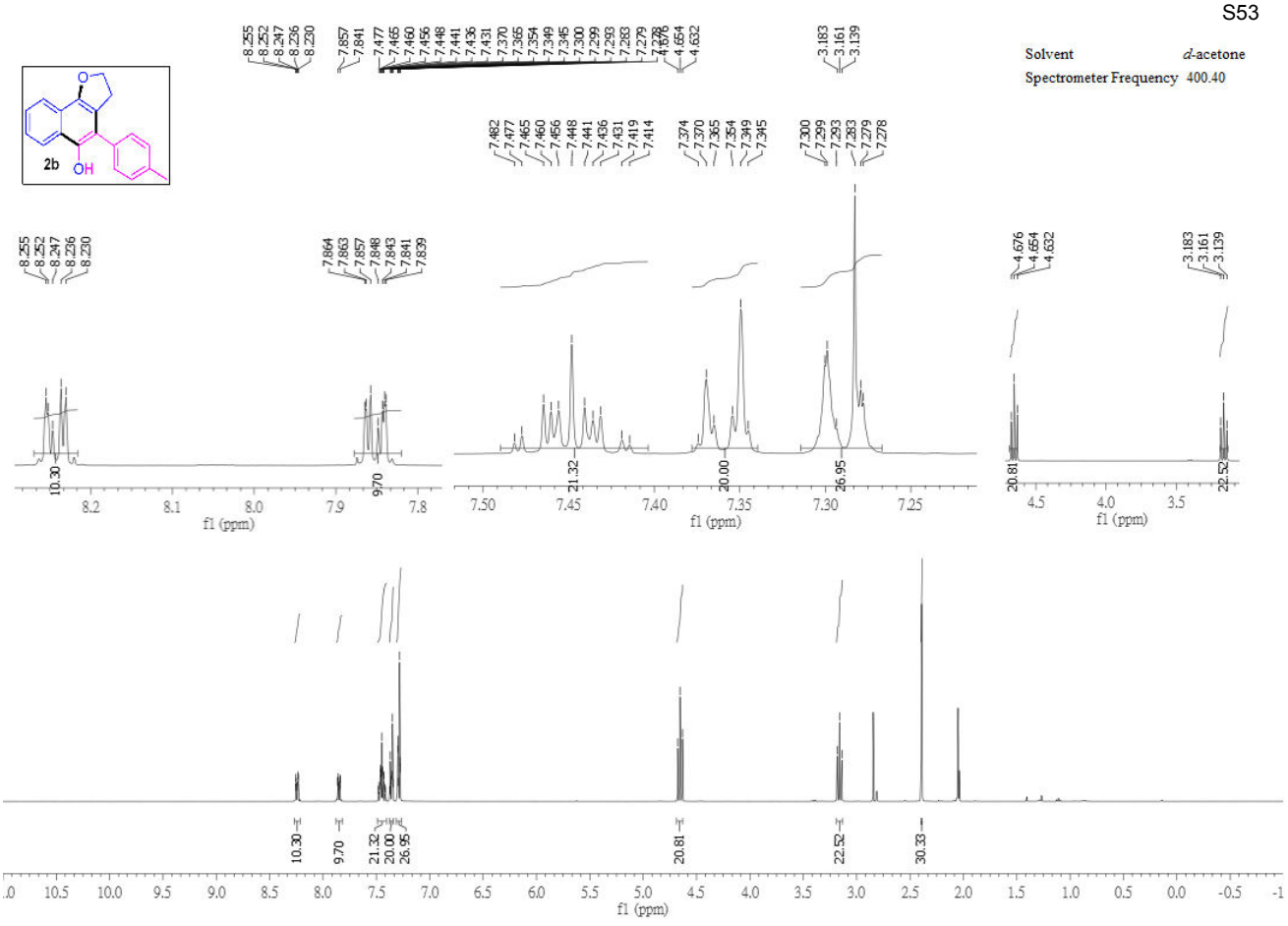


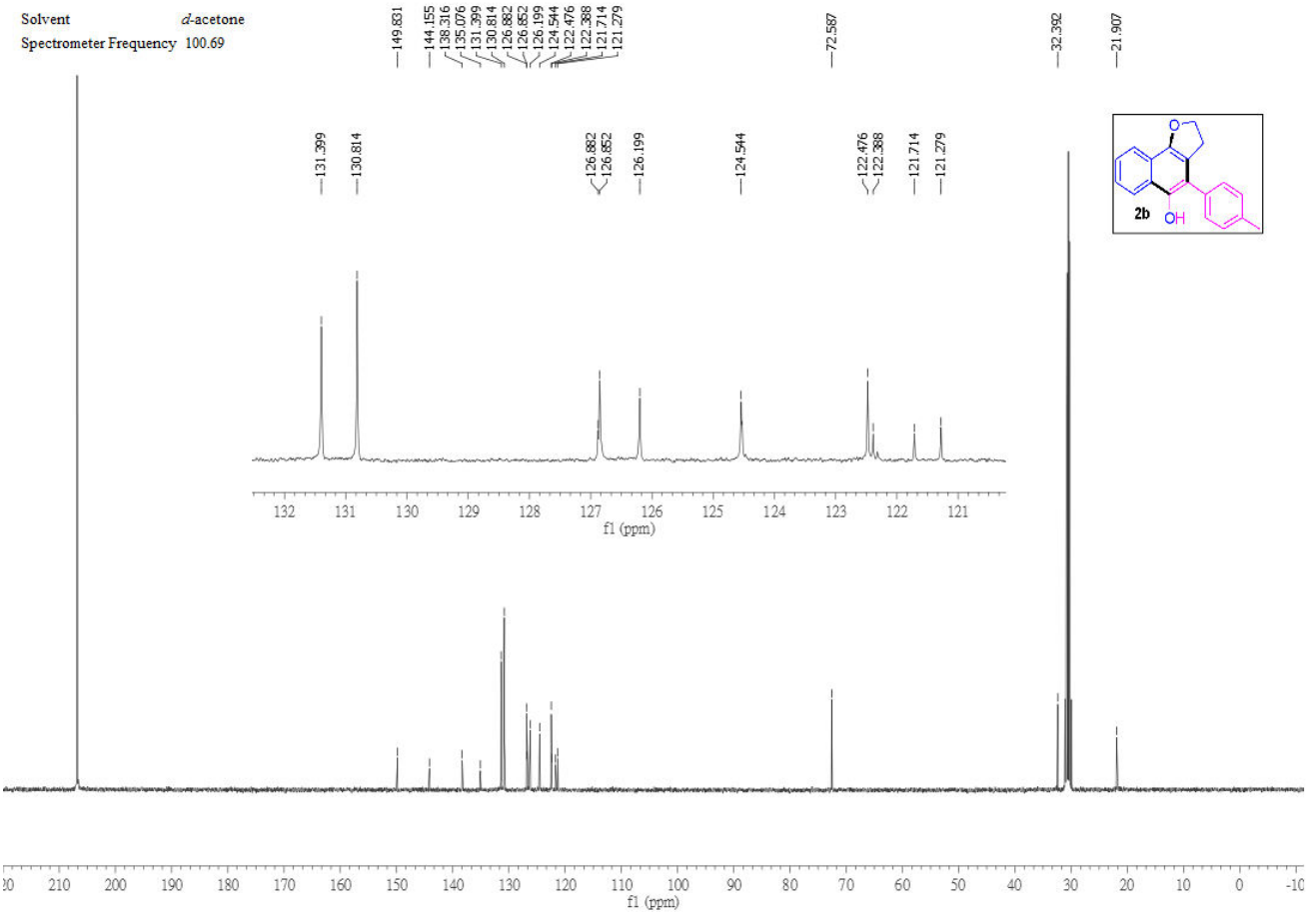
Solvent d-acetone
Spectrometer Frequency 400.40

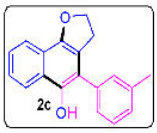


Solvent d-acetone
Spectrometer Frequency 100.69

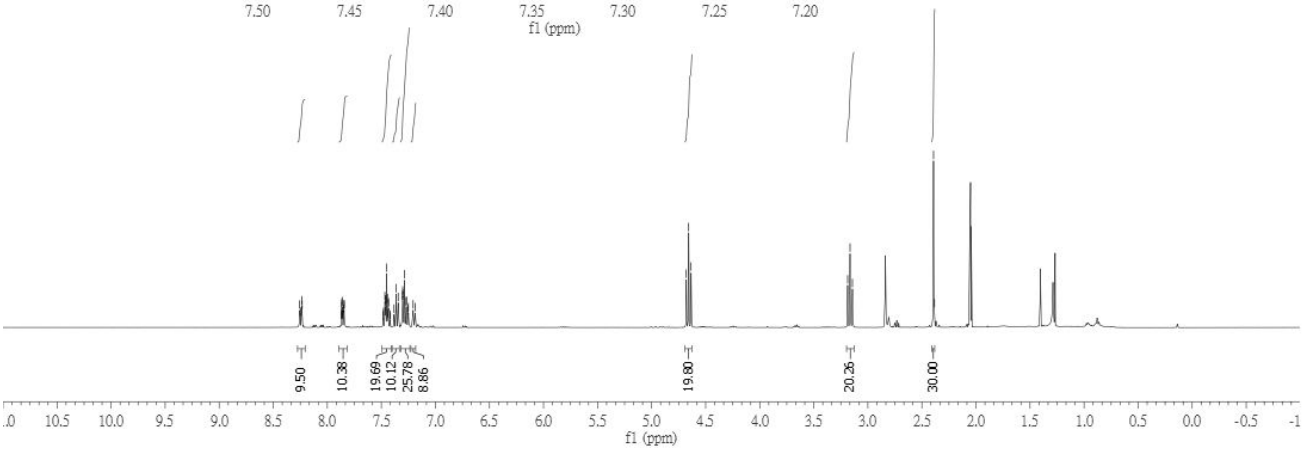



Solvent d-acetone
Spectrometer Frequency 400.40
2b
OH
f1 (ppm)

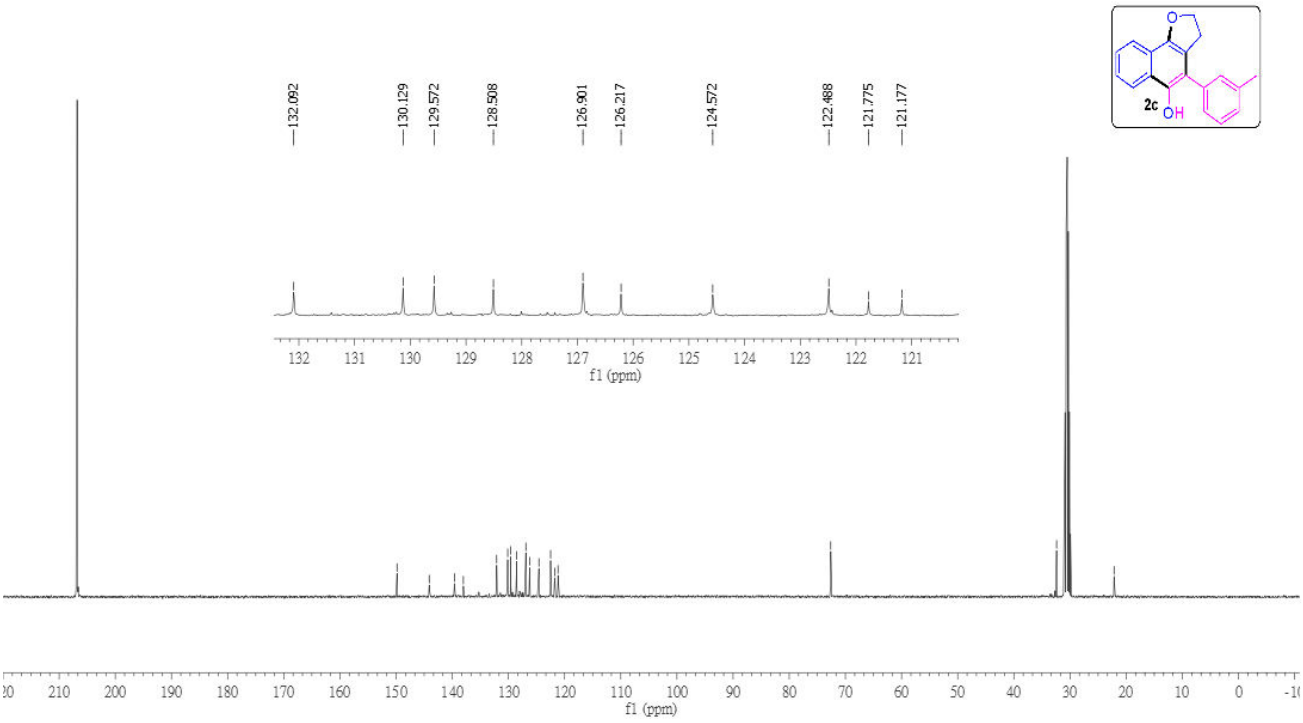

Solvent d-acetone
Spectrometer Frequency 100.69
2b
OH
f1 (ppm)

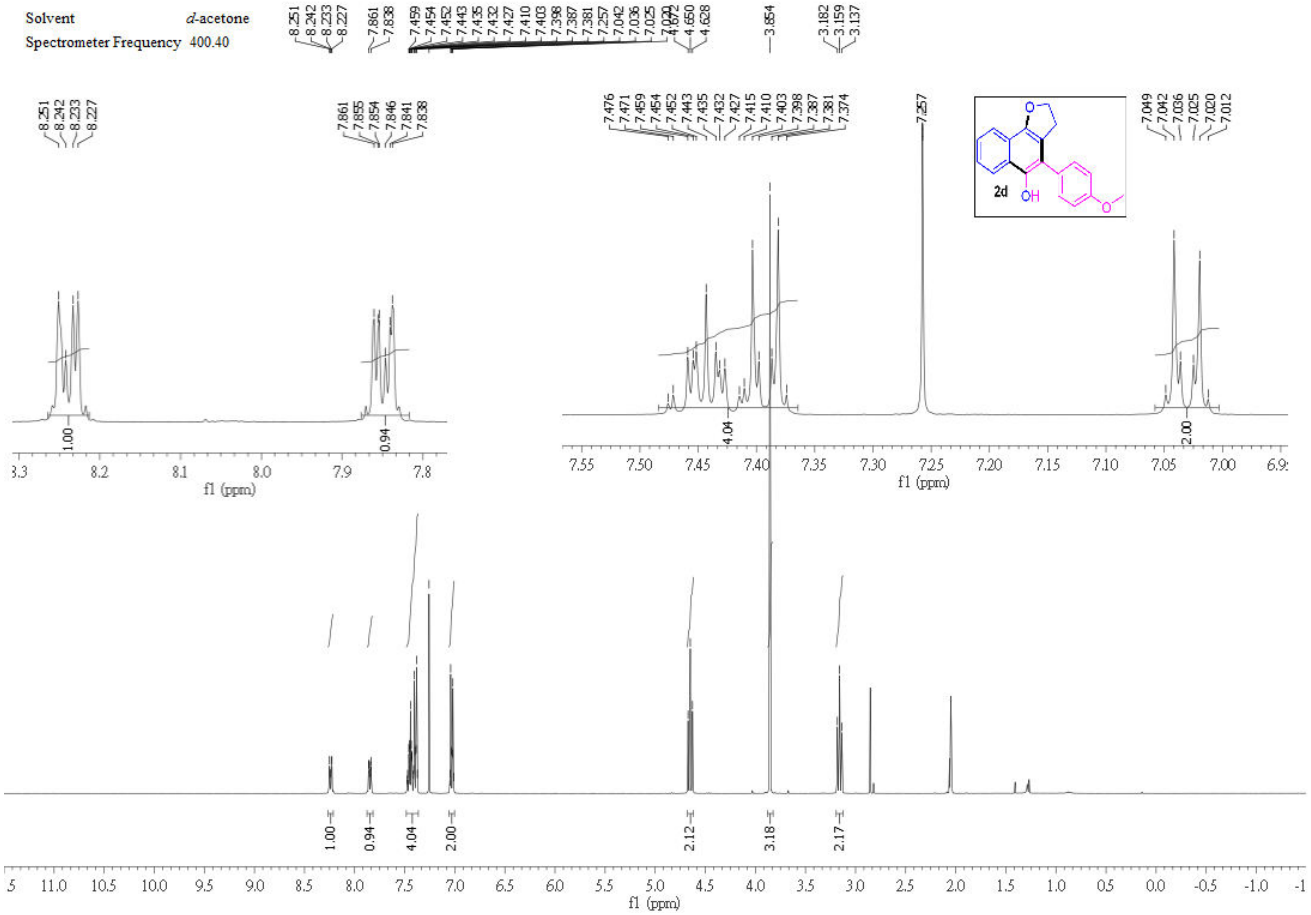


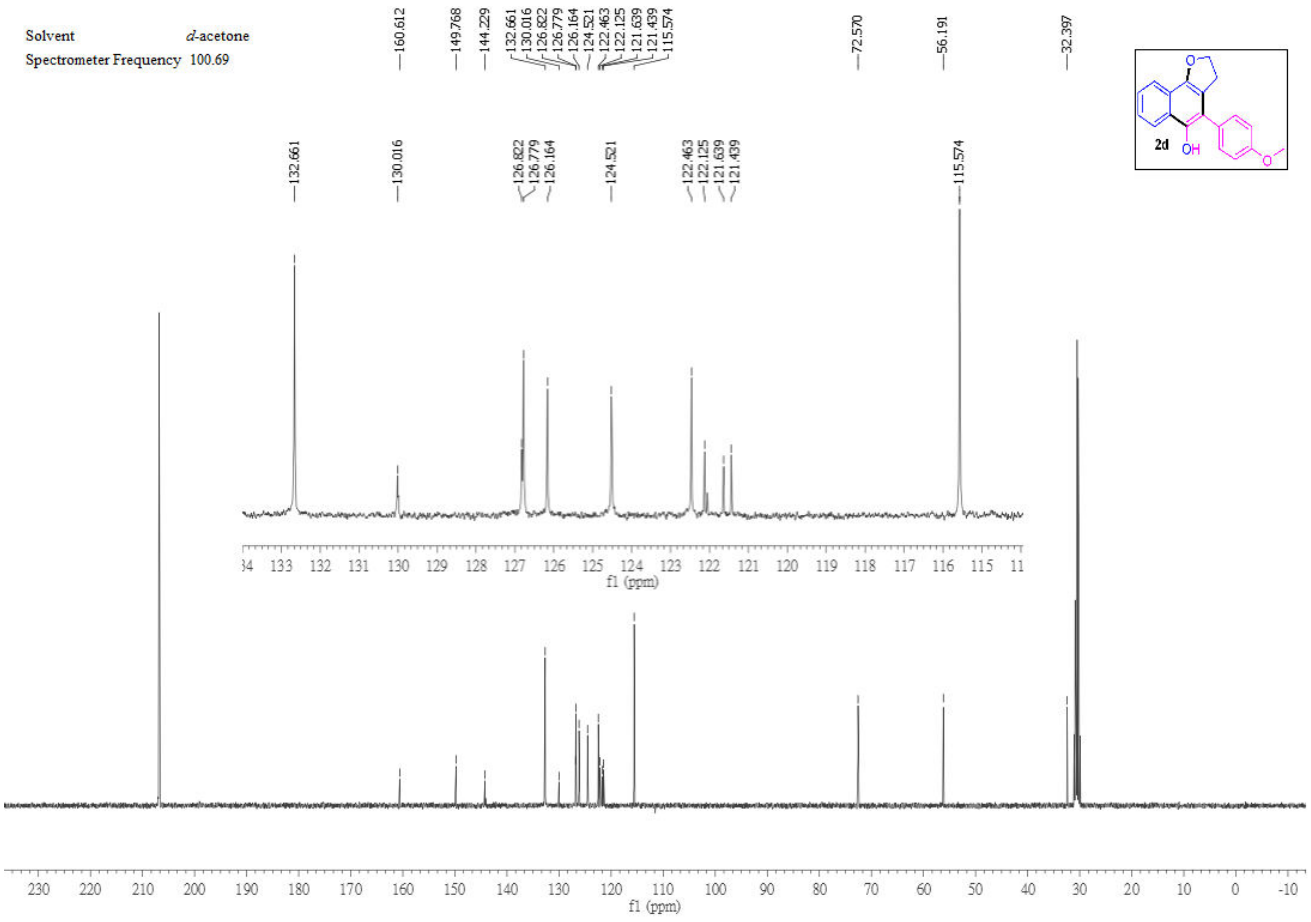
Solvent d-acetone
Spectrometer Frequency 400.40

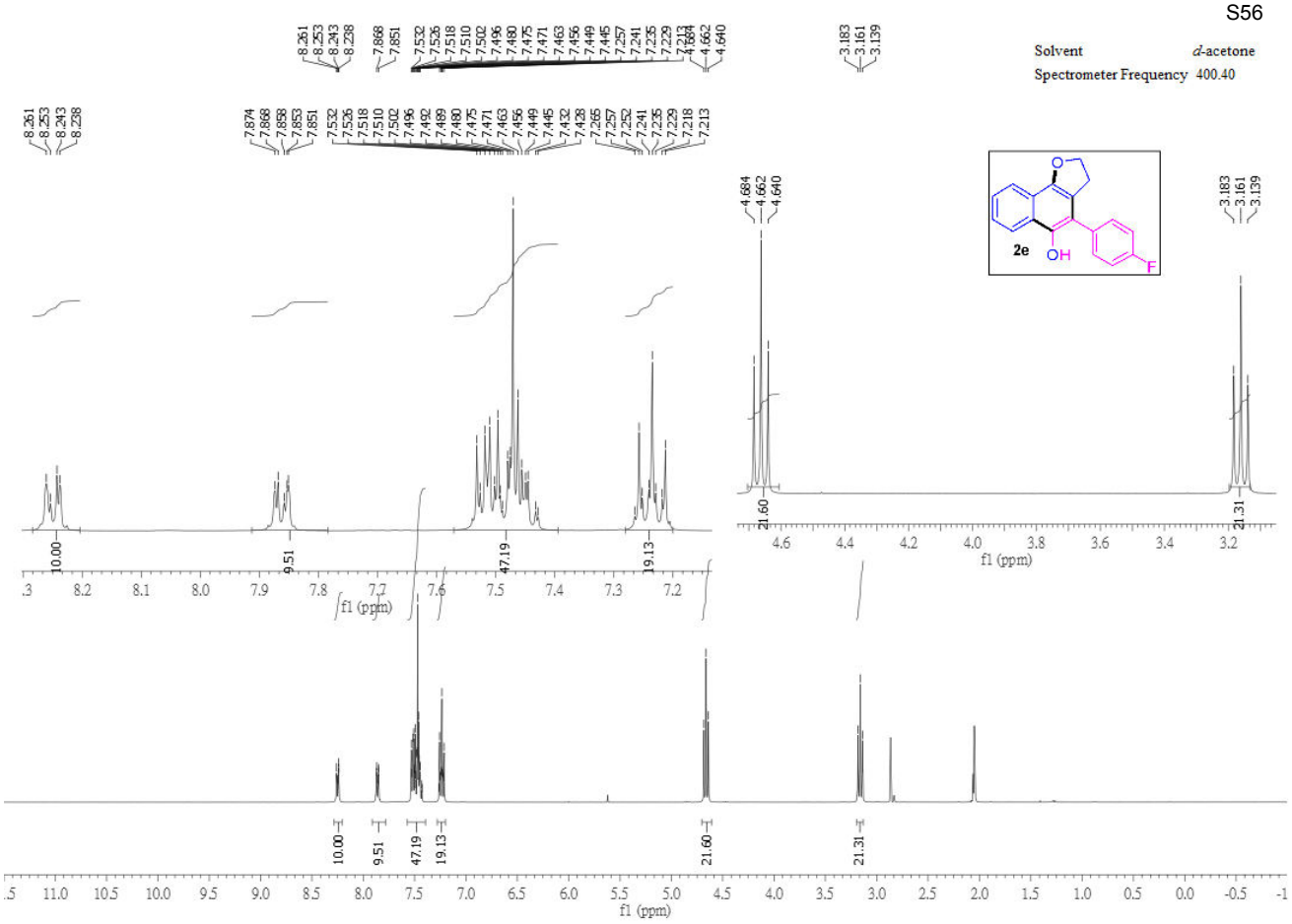


Solvent d-acetone
Spectrometer Frequency 100.69




Solvent d-acetone
Spectrometer Frequency 400.40
2d
f1 (ppm)


Solvent d-acetone
Spectrometer Frequency 100.69
2d
f1 (ppm)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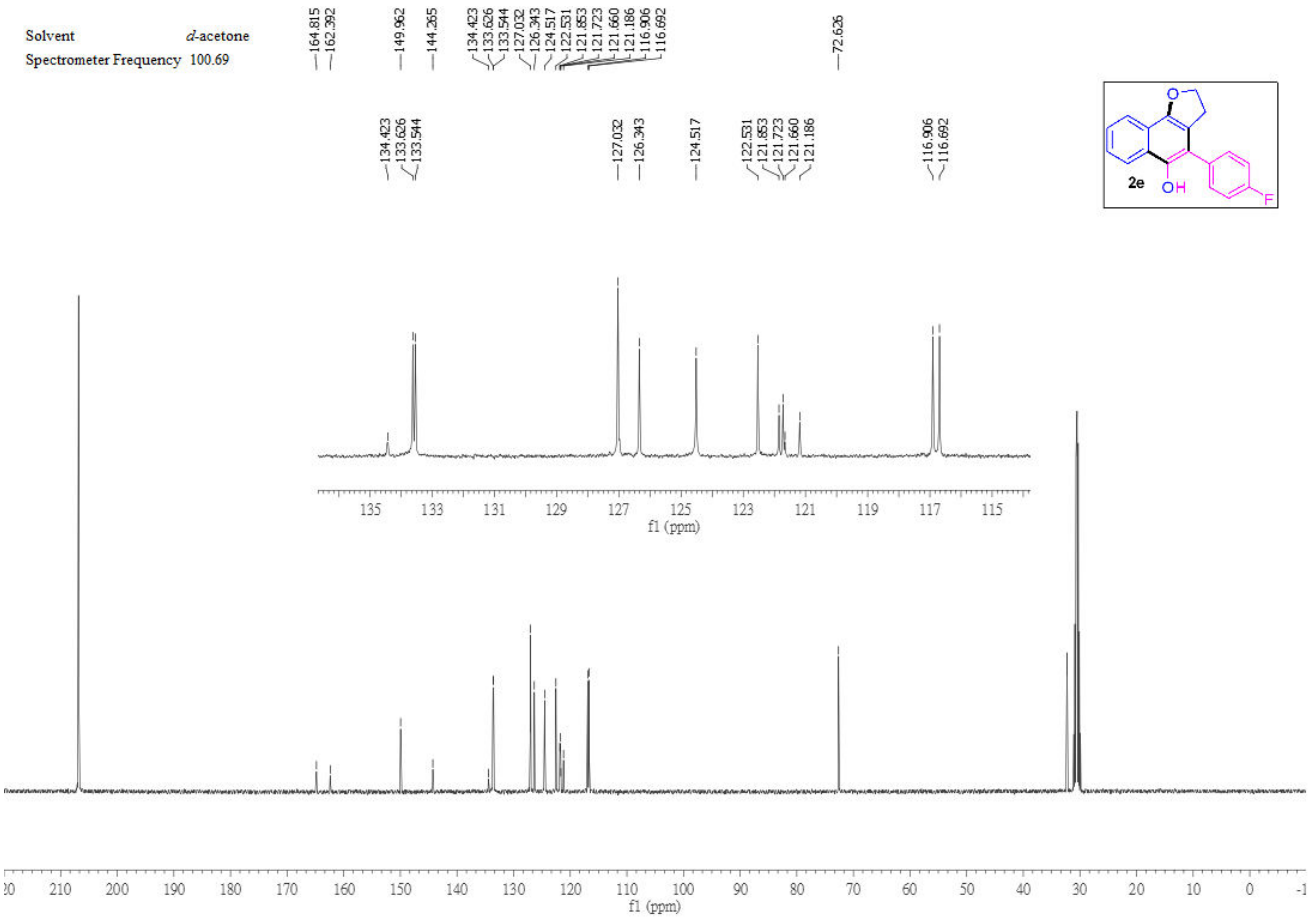
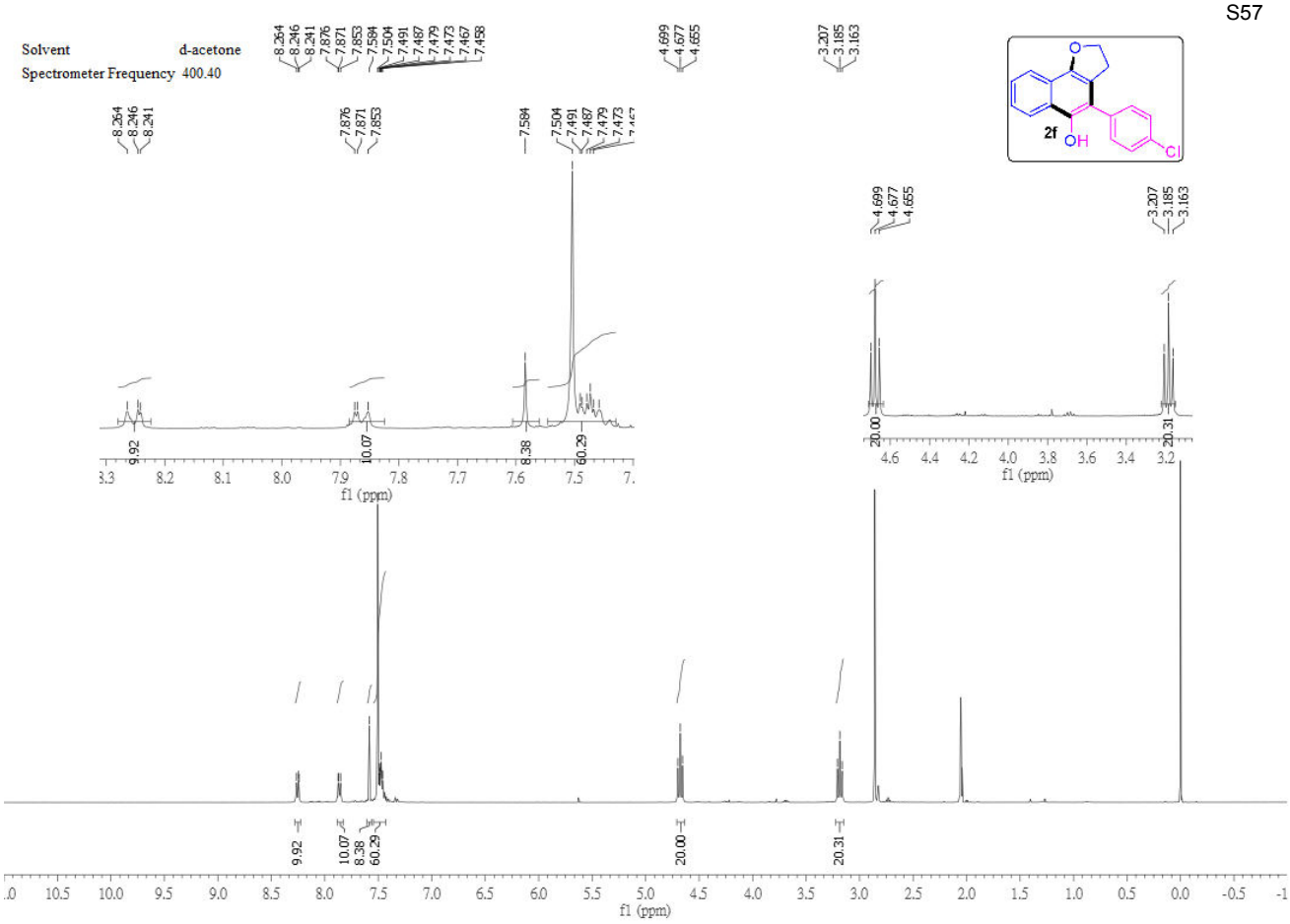
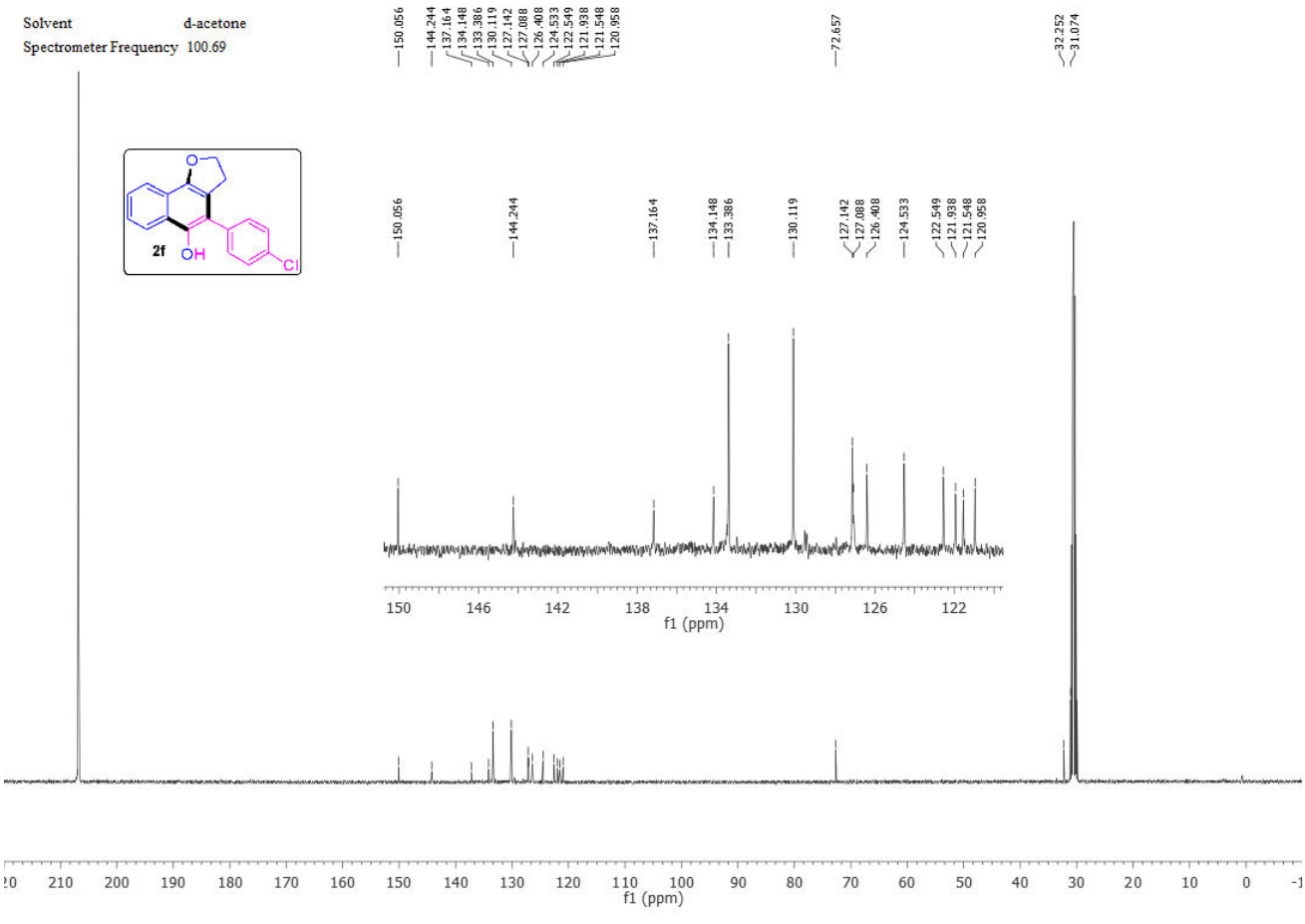
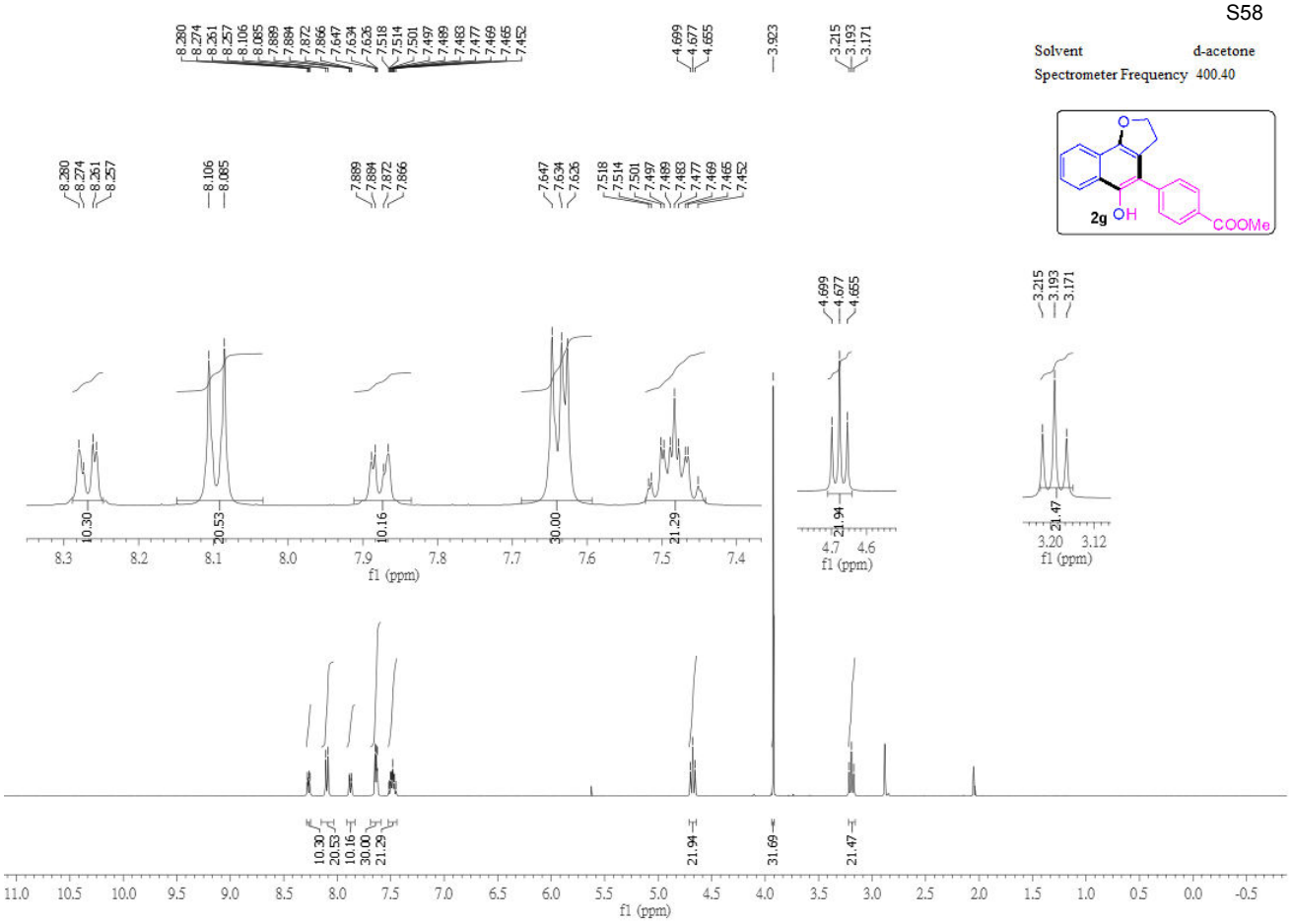
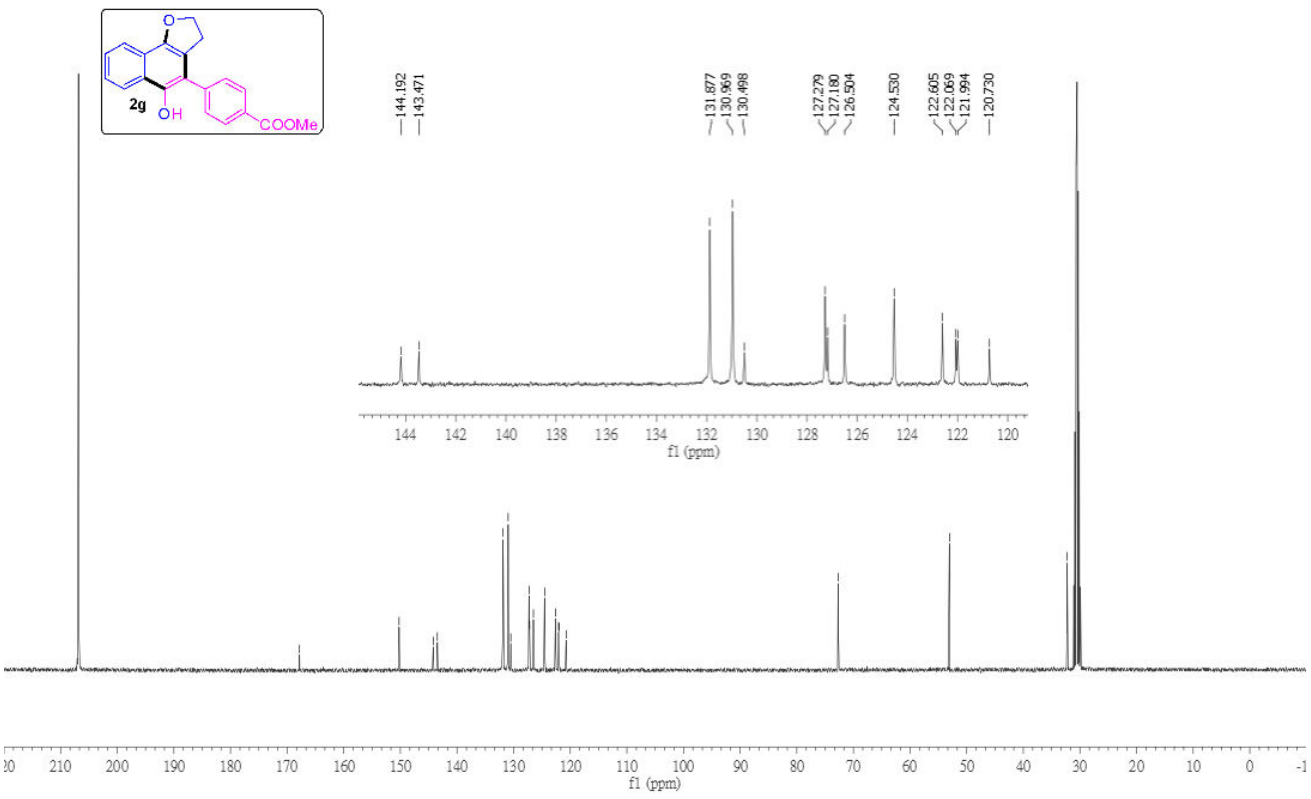
Spectrometer Frequency 400.40
2e
f1 (ppm)

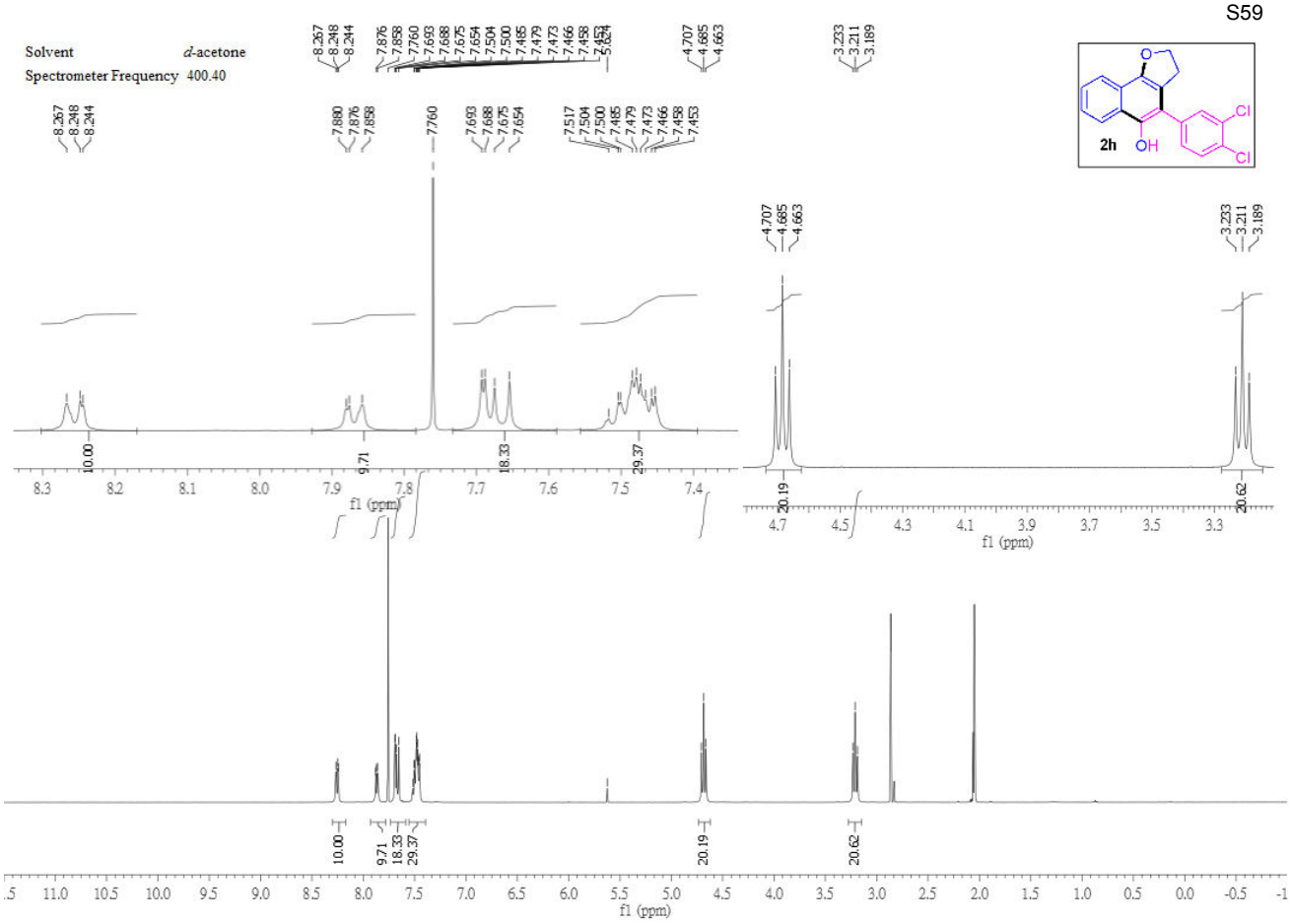

Solvent d-acetone
Spectrometer Frequency 100.69
2e
f1 (ppm)

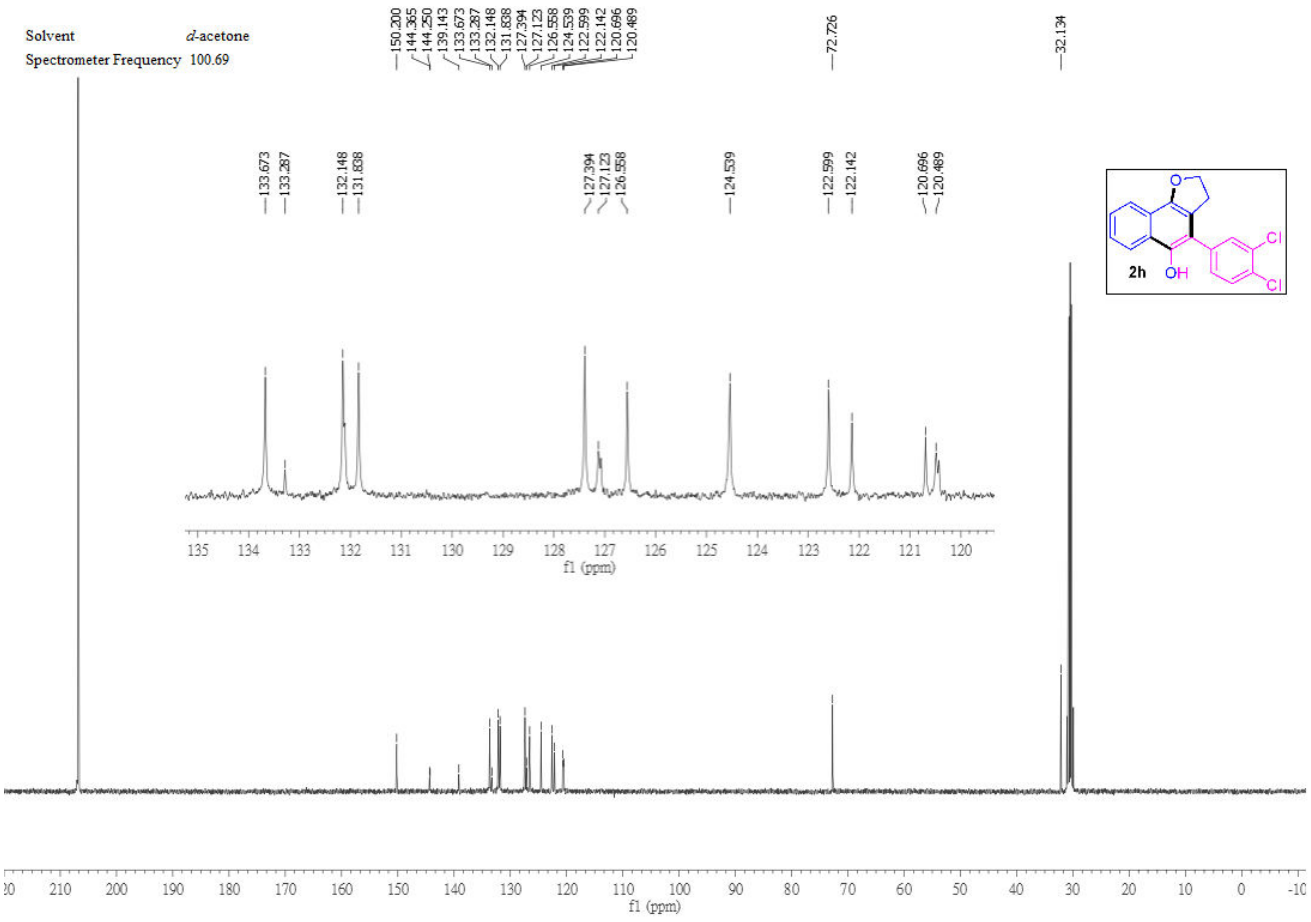

Solvent d-acetone
Spectrometer Frequency 400.40
8.264
8.246
8.241
7.876
7.871
7.853
7.584
7.504
7.491
7.487
7.479
7.473
7.467
7.458
4.699
4.677
4.655
3.207
3.185
3.163
2f
OH
Cl
9.92
10.07
8.38
60.29
20.00
20.31
f1 (ppm)

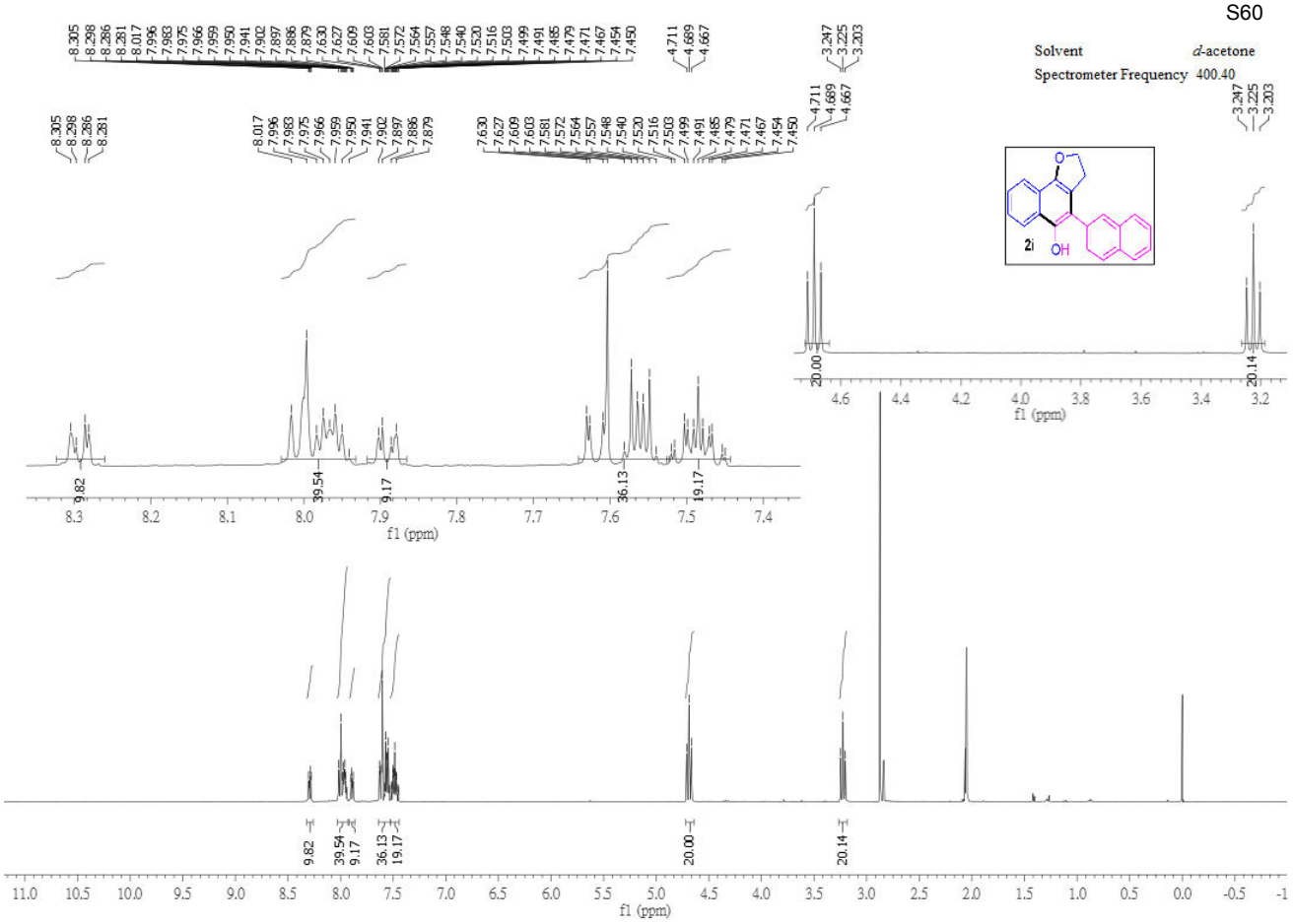

Solvent d-acetone
Spectrometer Frequency 100.69
150.056
144.244
137.164
134.148
133.386
130.119
127.142
127.088
126.408
124.533
122.549
121.938
121.548
120.958
72.657
32.252
31.074
2f
OH
Cl
f1 (ppm)

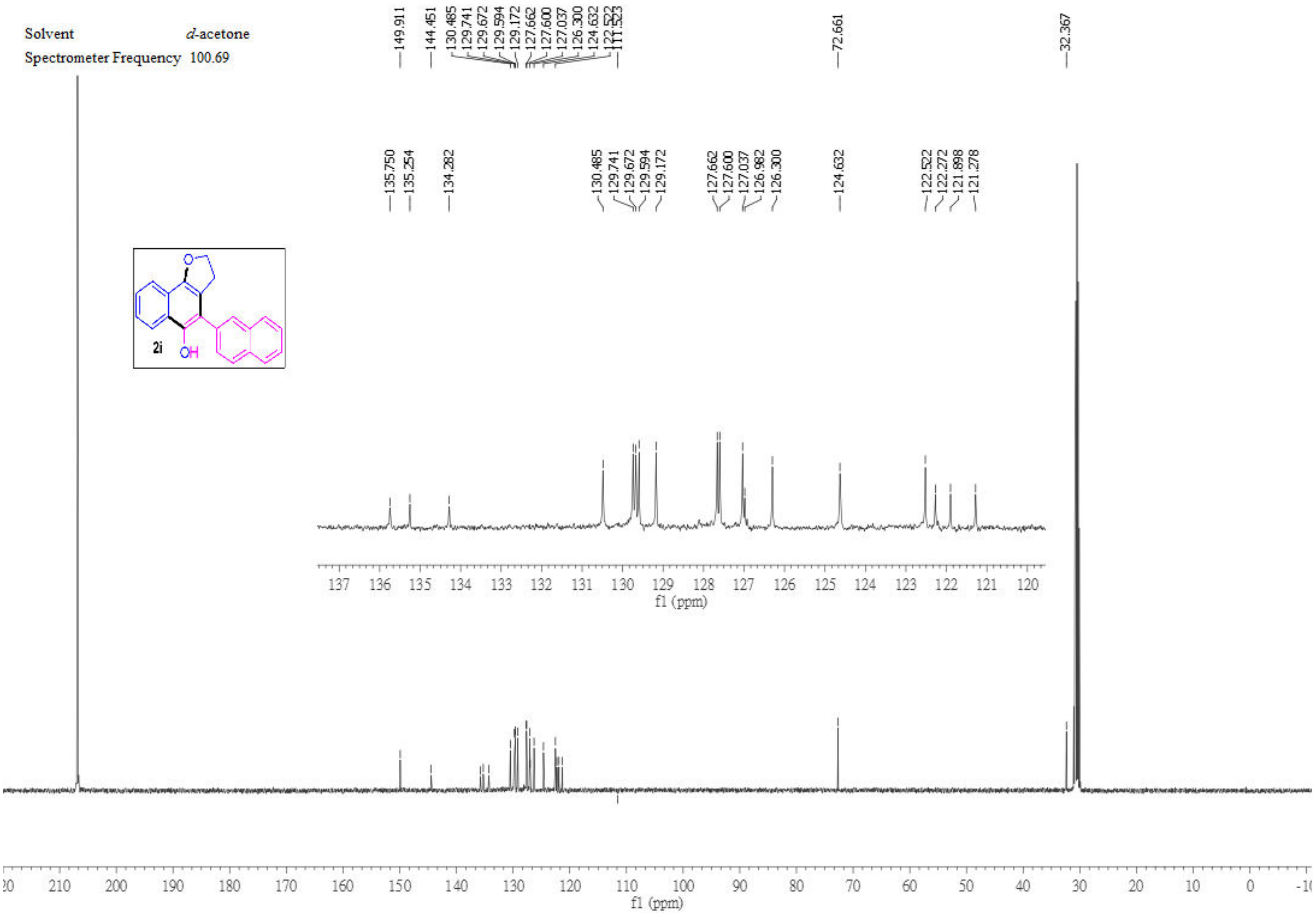

Solvent d-acetone
Spectrometer Frequency 400.40
2g
f1 (ppm)

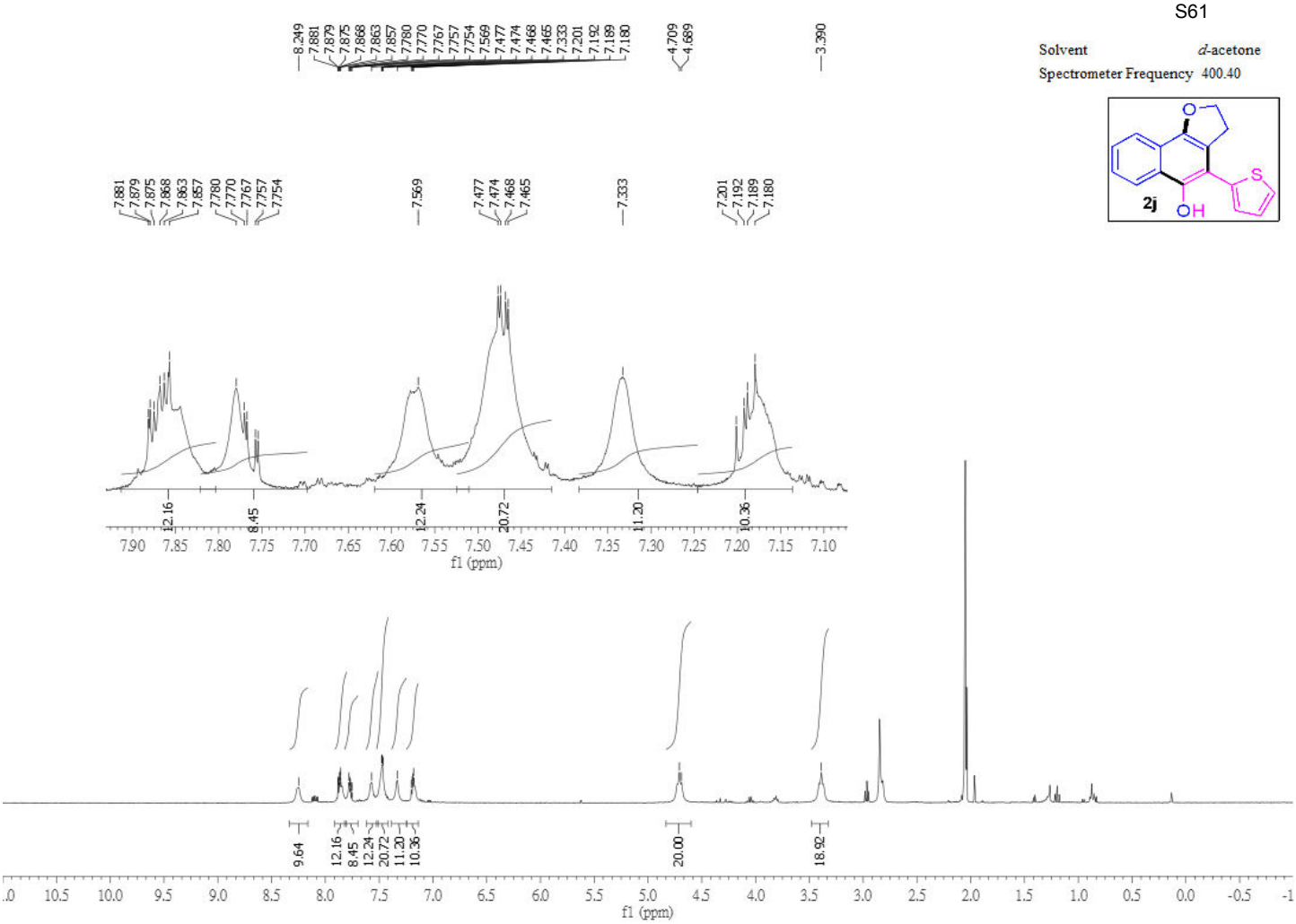

Solvent d-acetone
Spectrometer Frequency 100.69
2g
f1 (ppm)

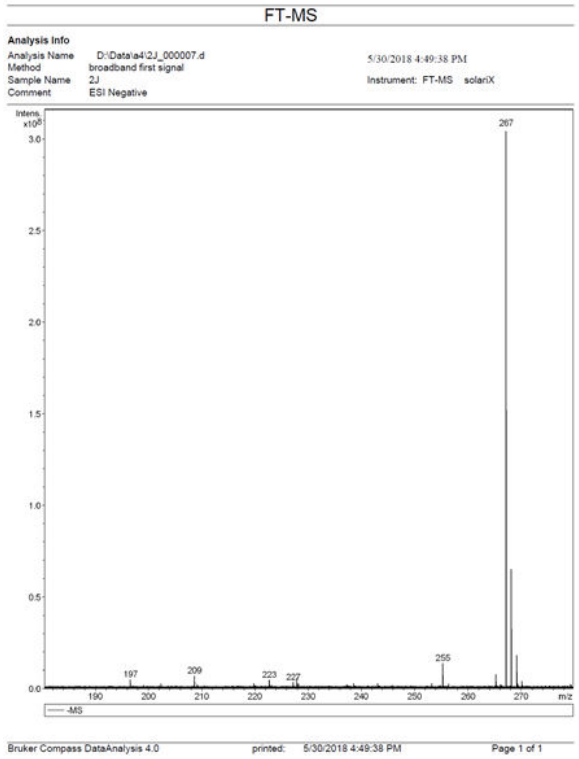

Solvent d-acetone
Spectrometer Frequency 400.40
2h
f1 (ppm)

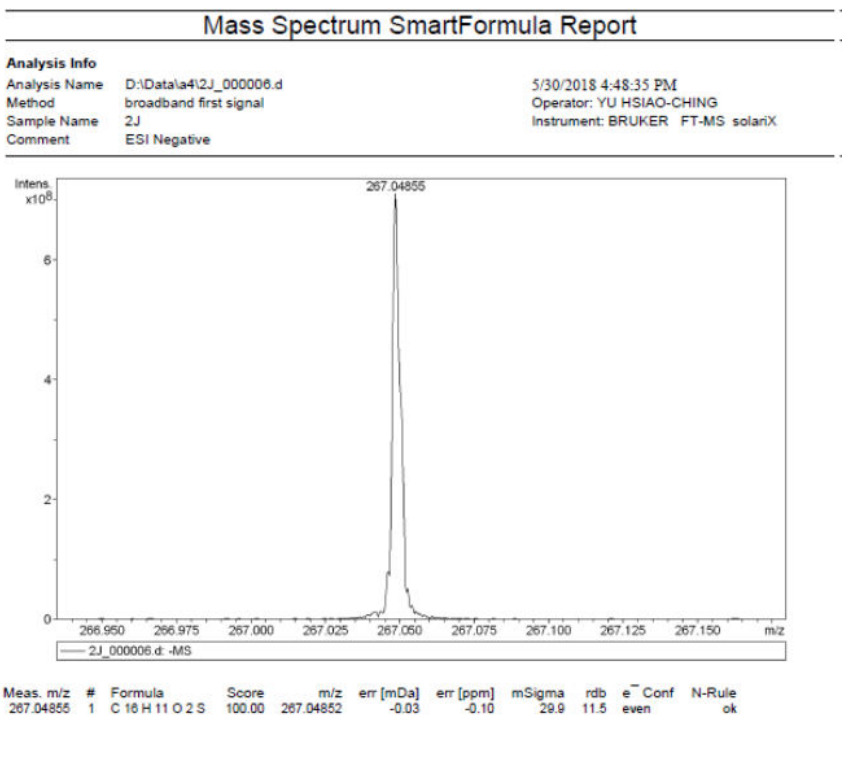

Solvent d-acetone
Spectrometer Frequency 100.69
2h
f1 (ppm)


Solvent d-acetone
Spectrometer Frequency 400.40
2i
OH
f1 (ppm)

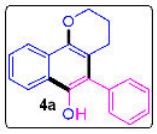

Solvent d-acetone
Spectrometer Frequency 100.69
2i
OH
f1 (ppm)

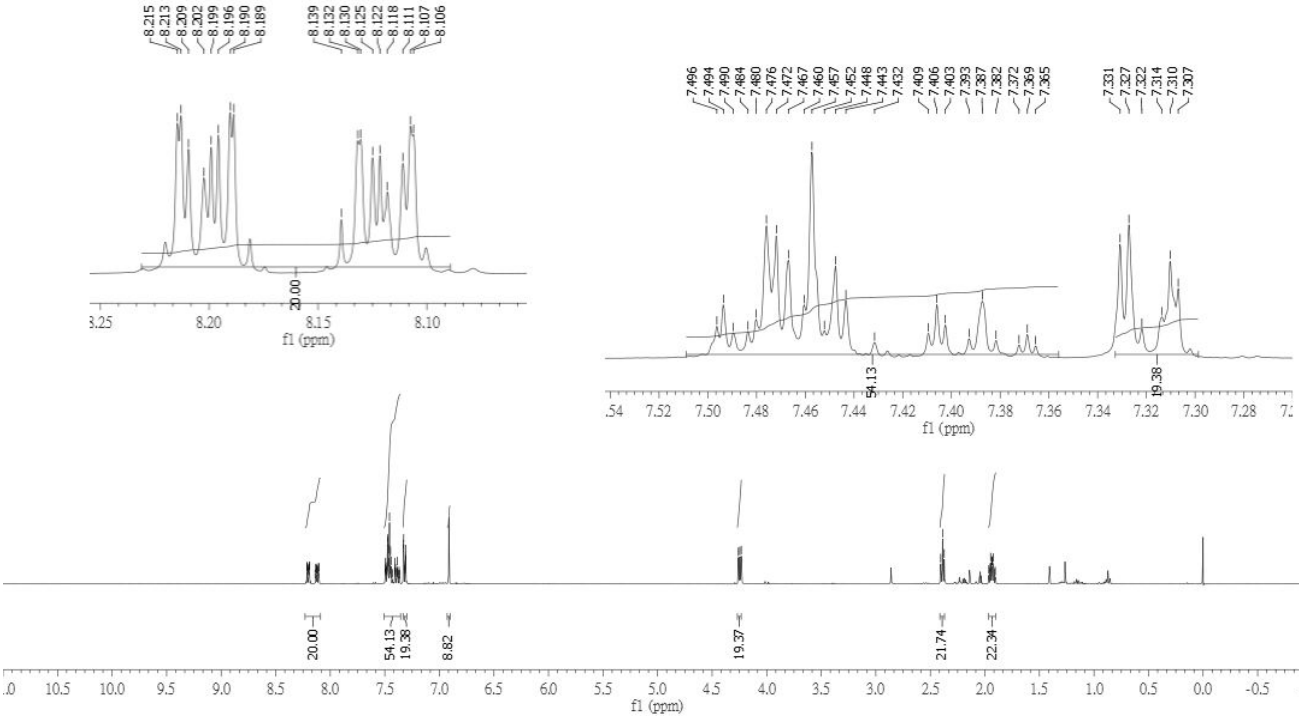

8.249
7.881
7.879
7.875
7.868
7.863
7.857
7.780
7.770
7.767
7.757
7.754
7.569
7.477
7.474
7.468
7.465
7.333
7.201
7.192
7.189
7.180
4.709
4.689
3.390
Solvent d-acetone
Spectrometer Frequency 400.40
2j
12.16
8.45
12.24
20.72
11.20
10.36
f1 (ppm)
9.64
12.16
8.45
12.24
20.72
11.20
10.36
20.00
18.92
f1 (ppm)


FT-MS
Analysis Info
Analysis Name D:\Data\a4\2J_000007.d
Method broadband first signal
Sample Name 2J
Comment ESI Negative
5/30/2018 4:49:38 PM
Instrument: FT-MS solariX
Intens.
x10^8
267
255
197
209
223
227
m/z
-MS
Bruker Compass DataAnalysis 4.0
printed: 5/30/2018 4:49:38 PM
Page 1 of 1

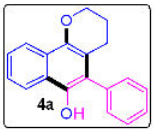

Mass Spectrum SmartFormula Report
Analysis Info
Analysis Name D:\Data\a4\2J_000006.d
Method broadband first signal
Sample Name 2J
Comment ESI Negative
5/30/2018 4:48:35 PM
Operator: YU HSIAO-CHING
Instrument: BRUKER FT-MS solariX
Intens.
x10^8
267.04855
m/z
2J_000006.d: -MS
Meas. m/z # Formula Score m/z err [mDa] err [ppm] mSigma rdb e¯ Conf N-Rule
267.04855 1 C 16 H 11 O 2 S 100.00 267.04852 -0.03 -0.10 29.9 11.5 even ok

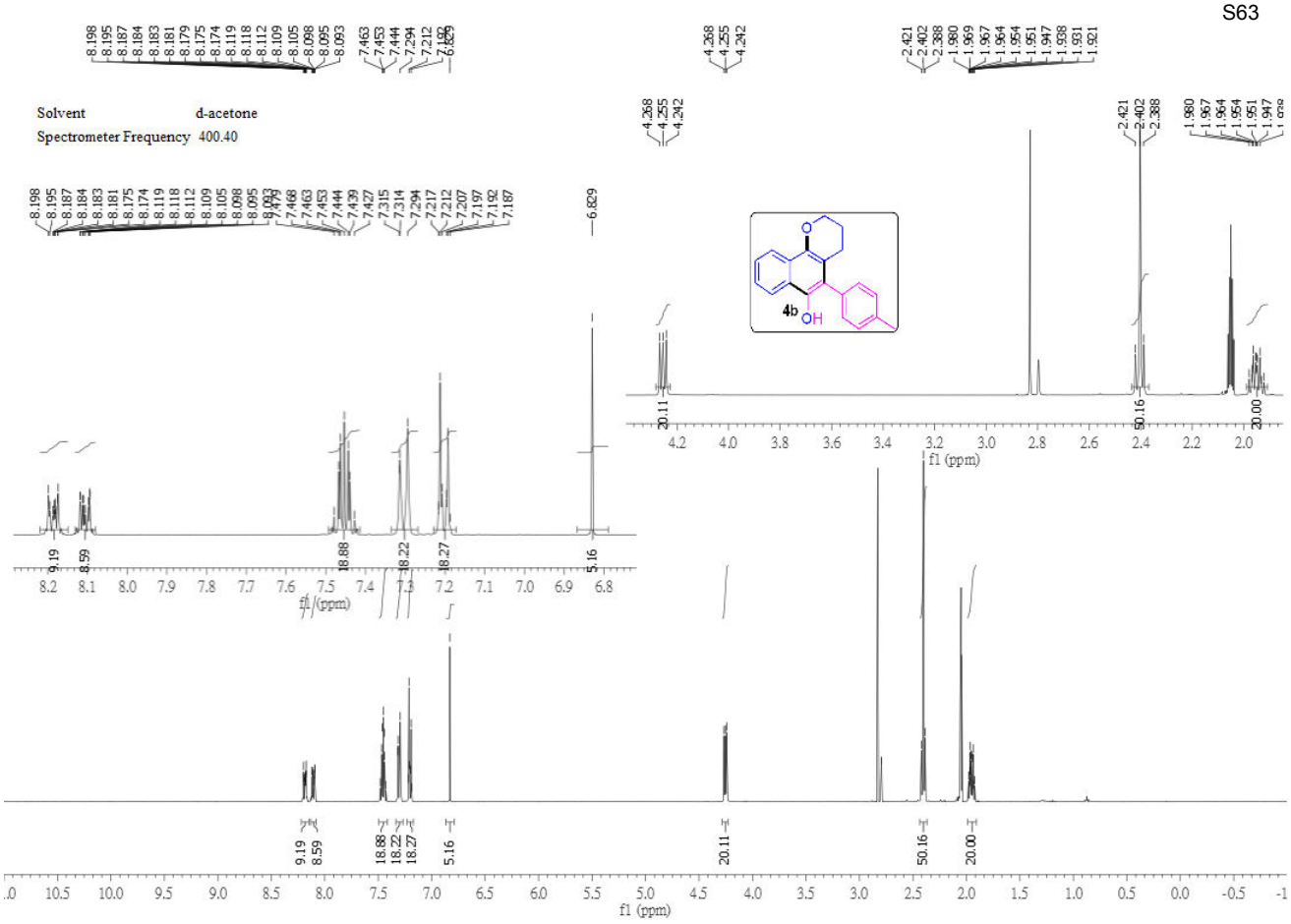
Solvent d-acetone
Spectrometer Frequency 400.40

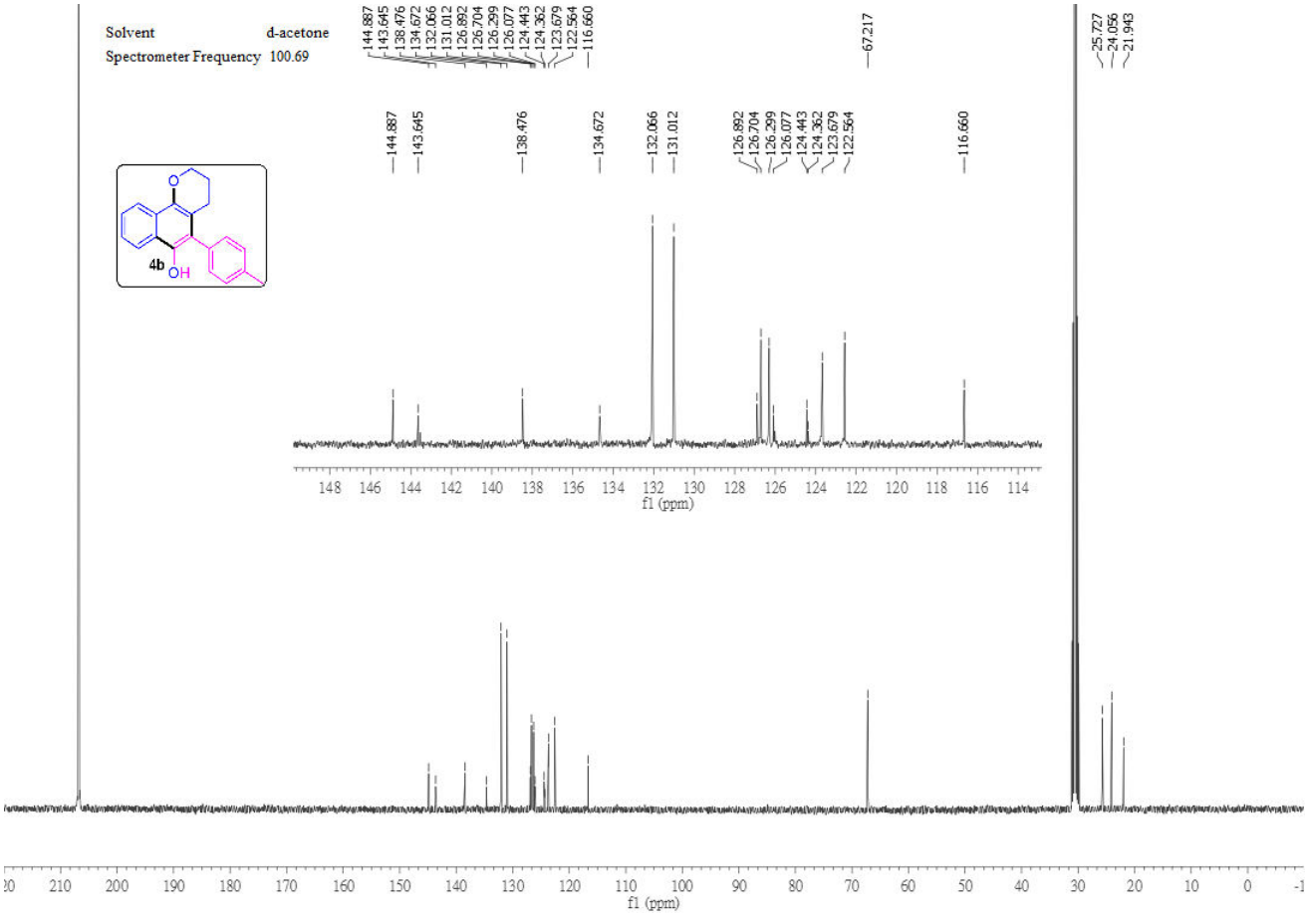


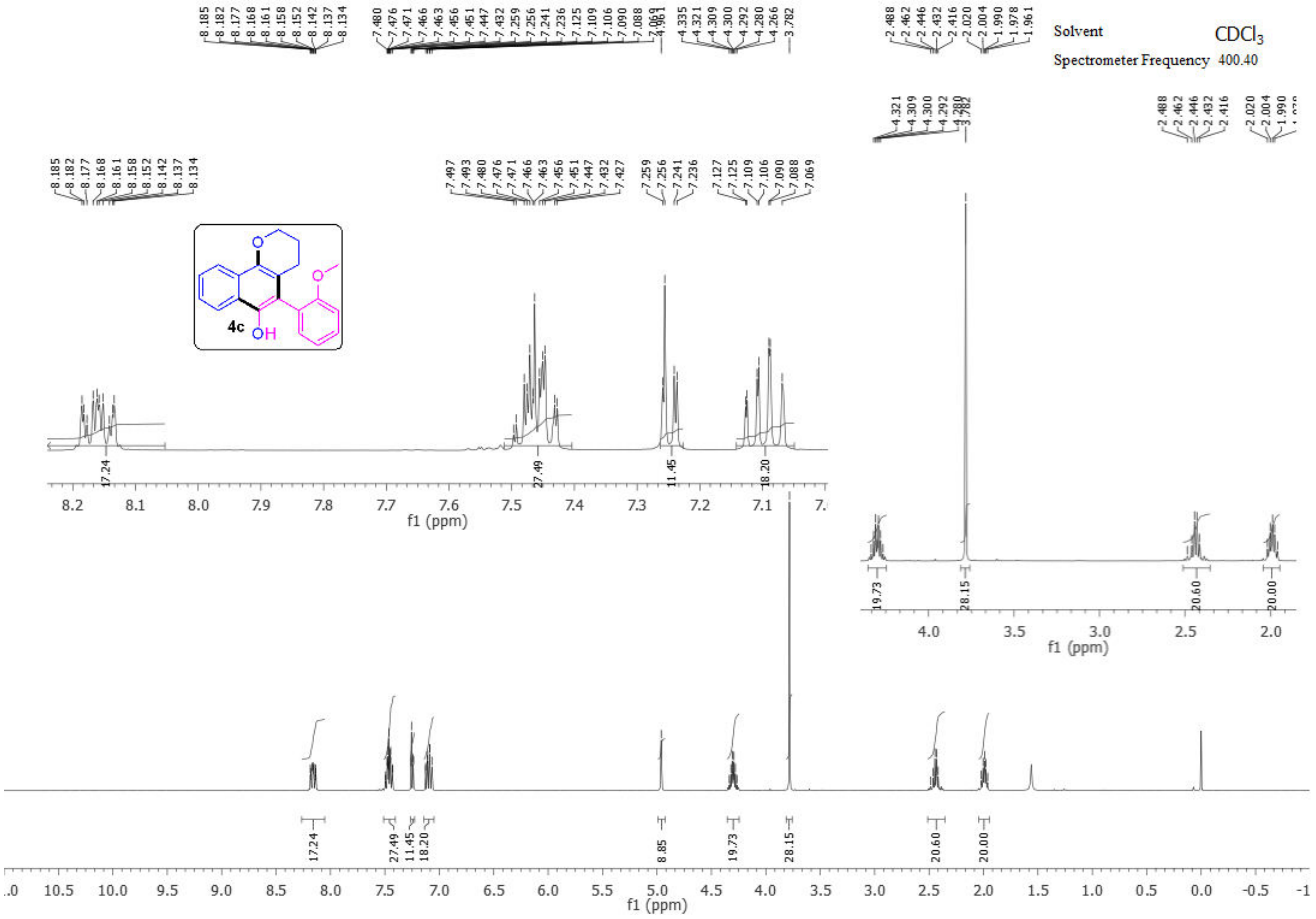


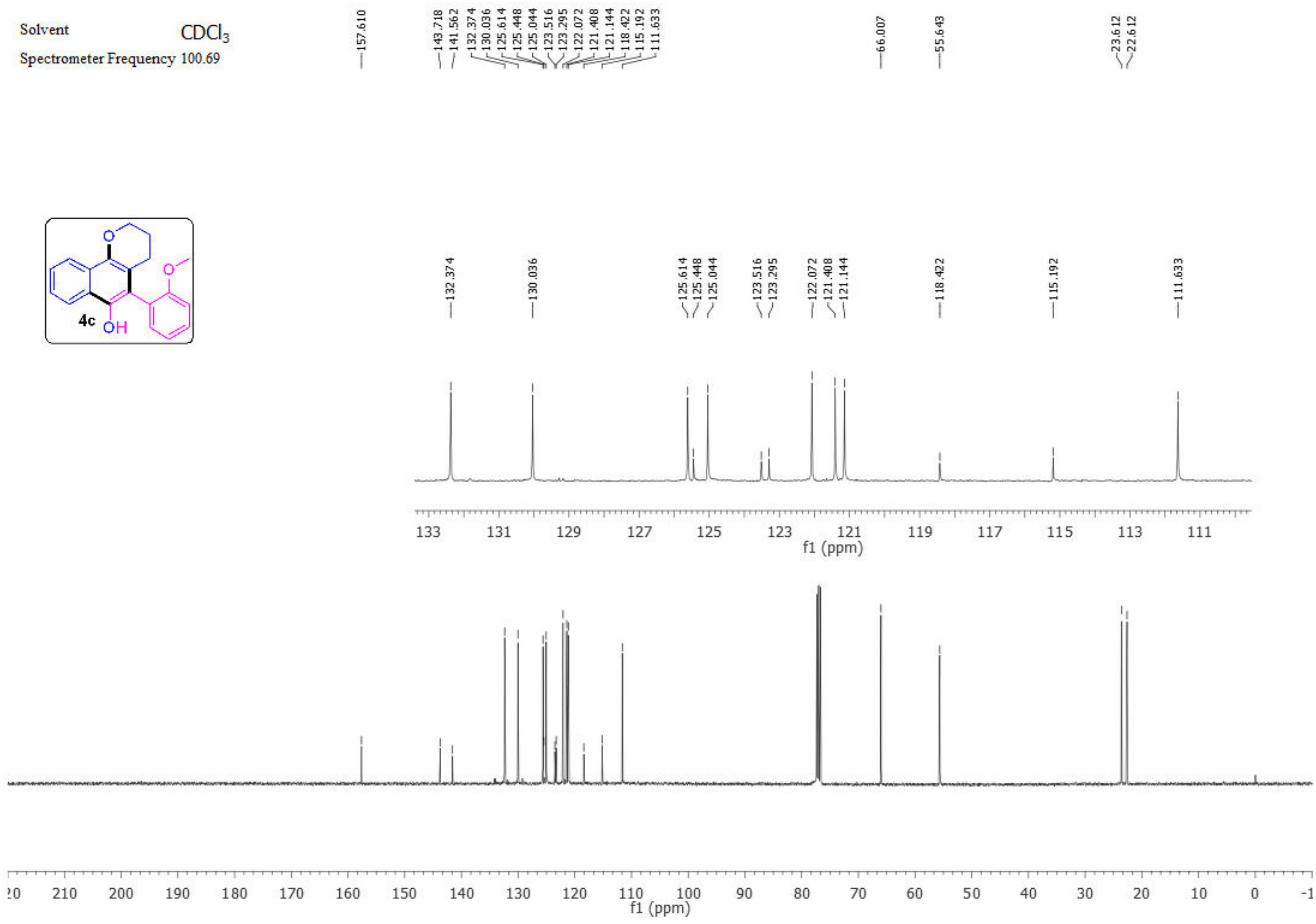
Solvent d-acetone
Spectrometer Frequency 100.69

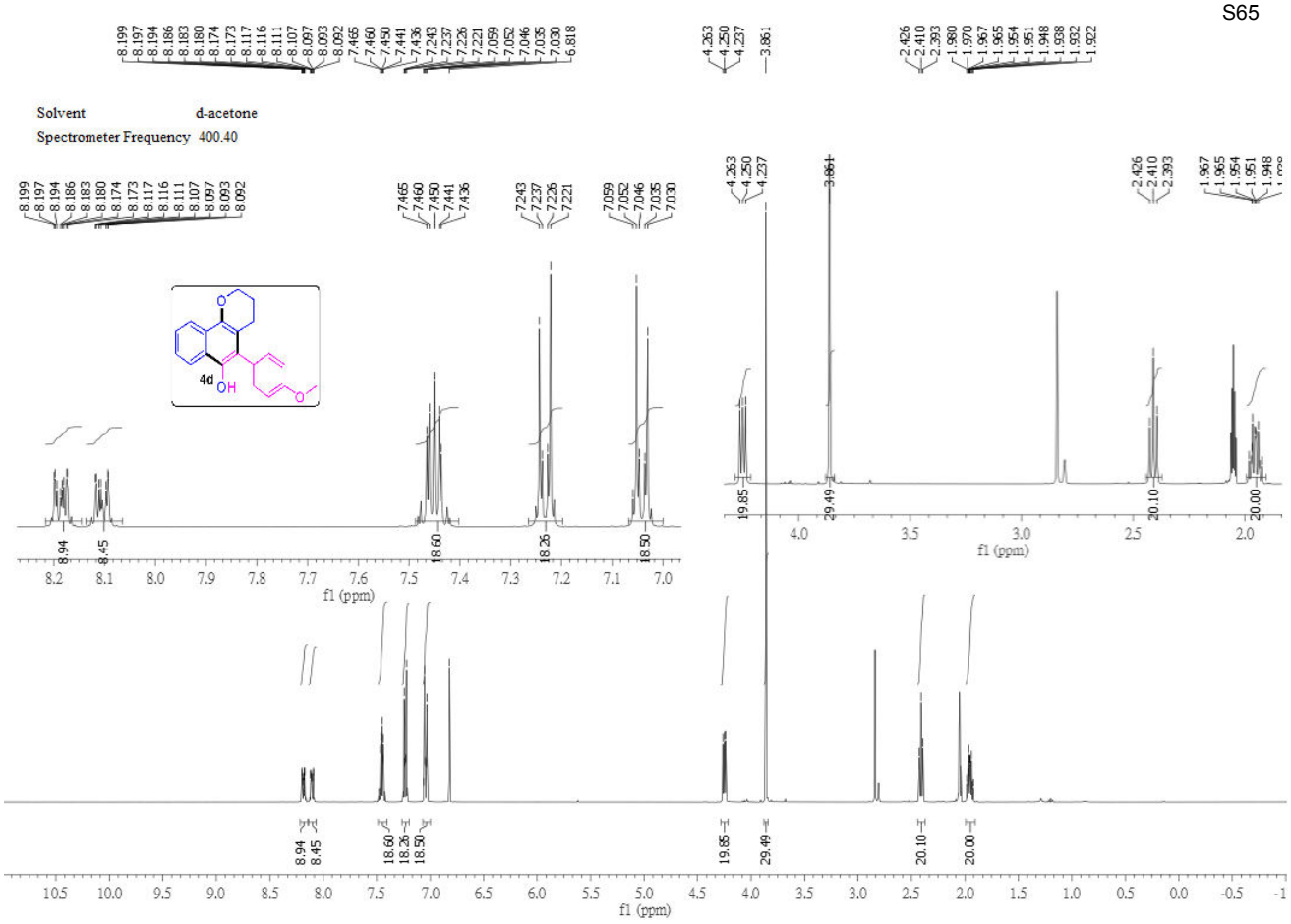


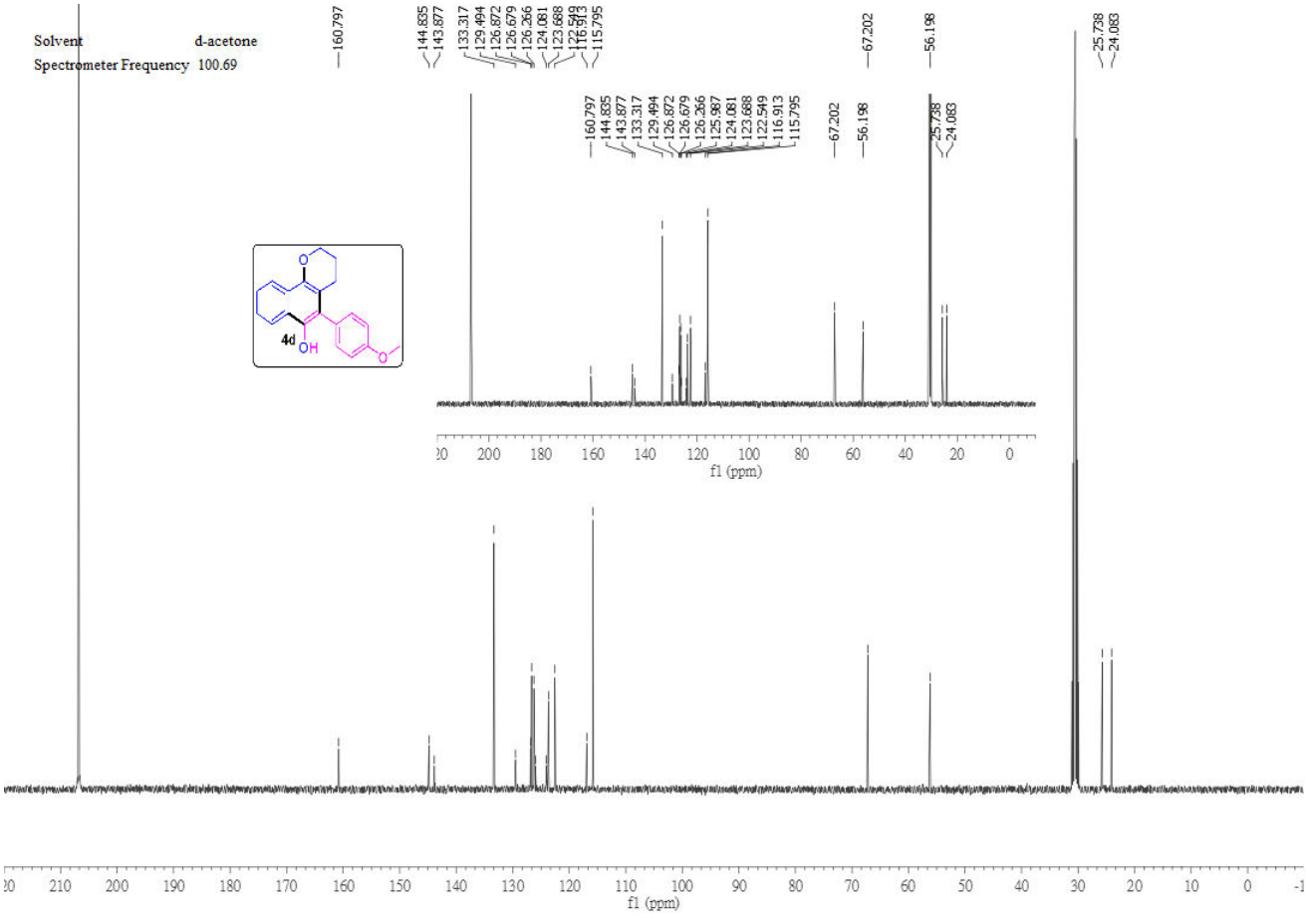

Solvent d-acetone
Spectrometer Frequency 400.40
4b
OH
f1 (ppm)

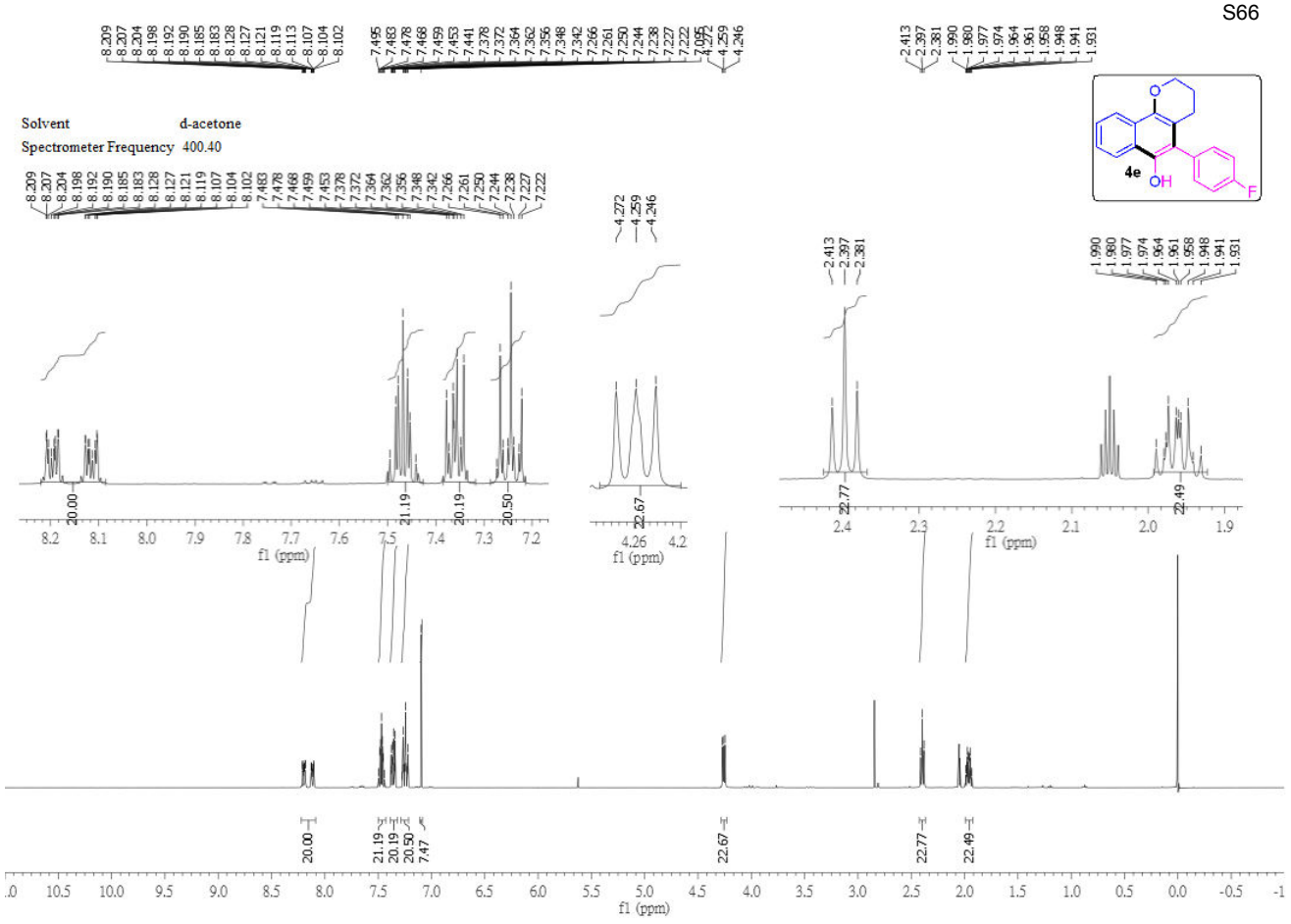

Solvent d-acetone
Spectrometer Frequency 100.69
4b
OH
f1 (ppm)

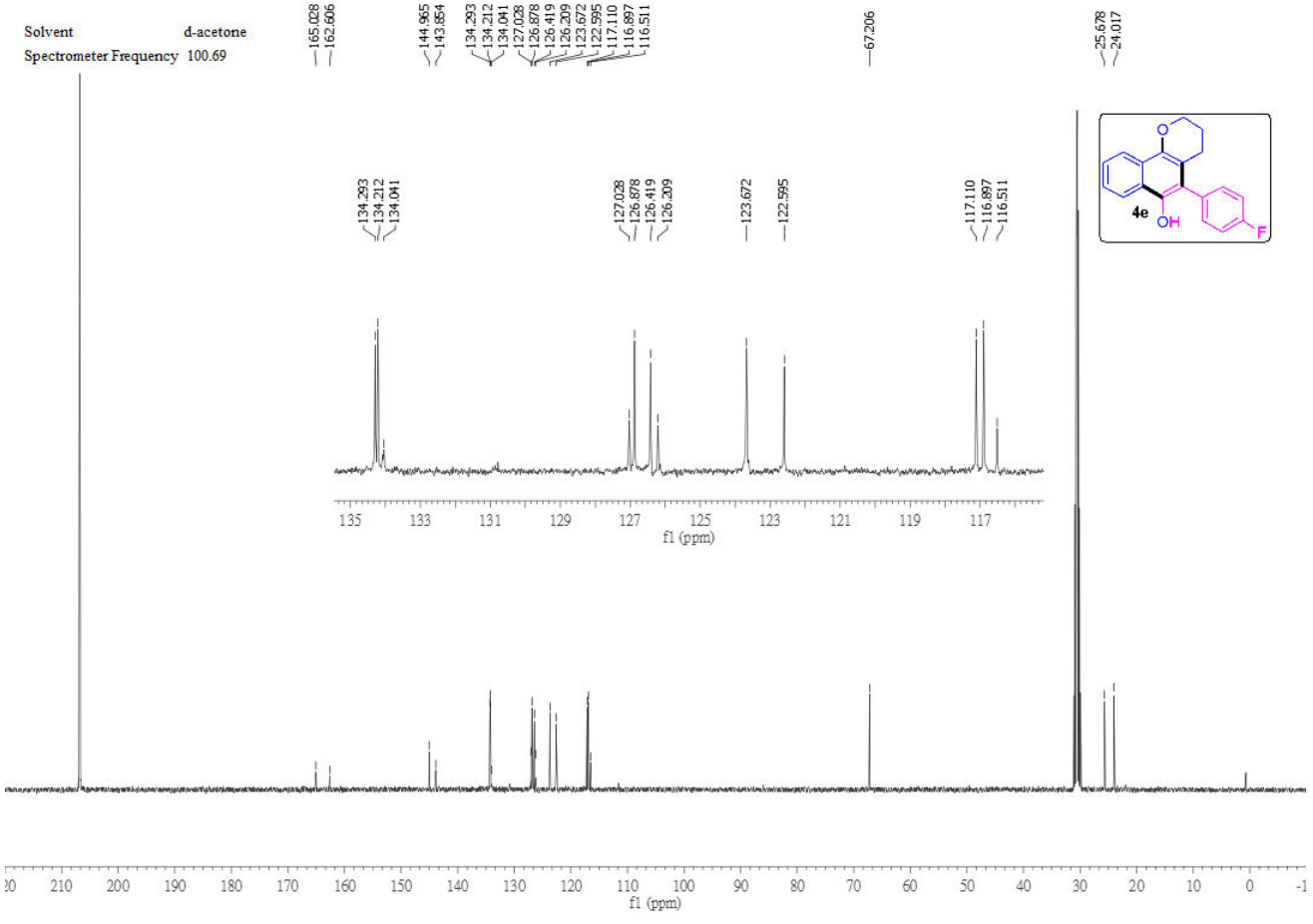

Solvent CDCl3
Spectrometer Frequency 400.40
4c
f1 (ppm)

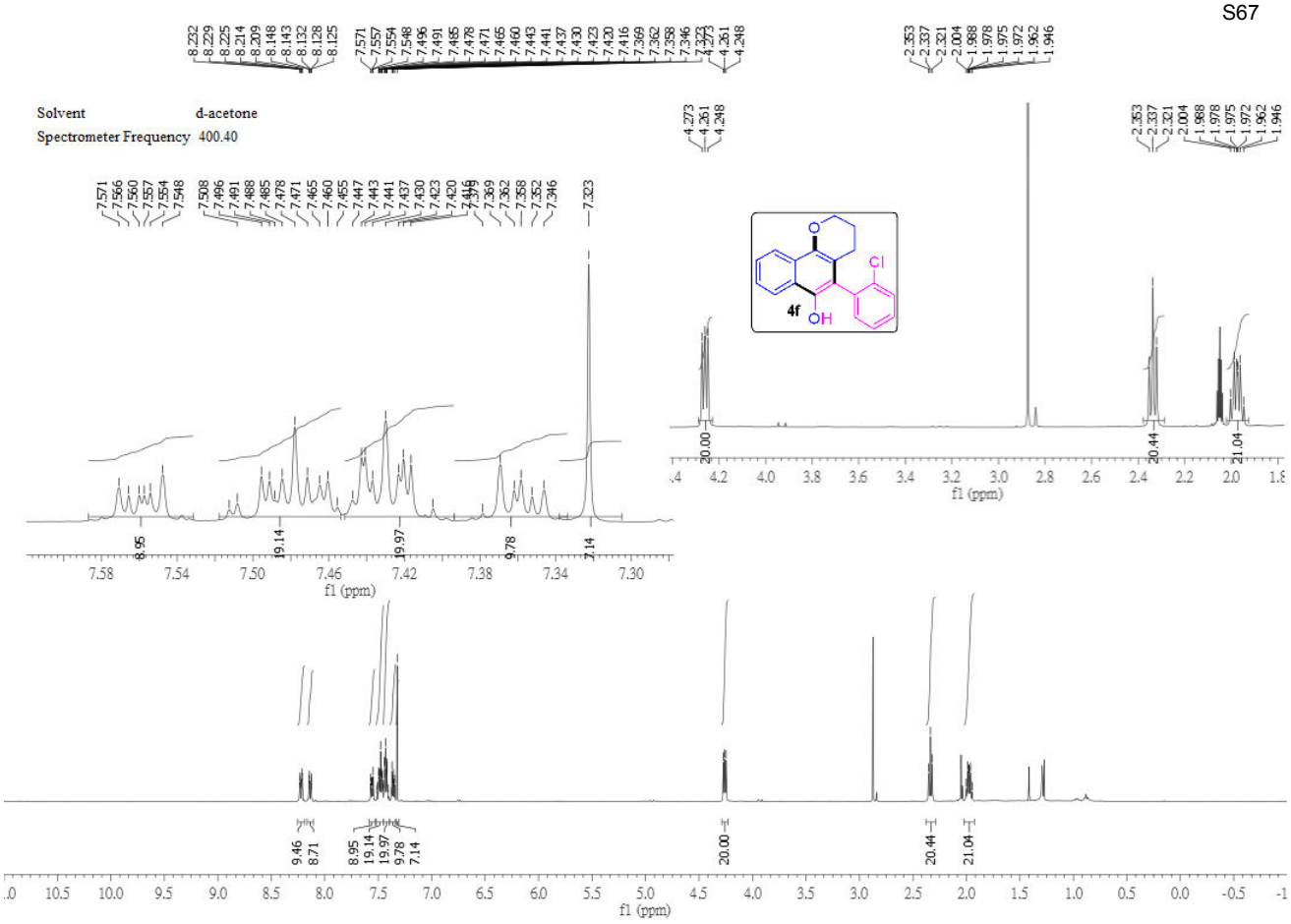

Solvent CDCl3
Spectrometer Frequency 100.69
4c
f1 (ppm)

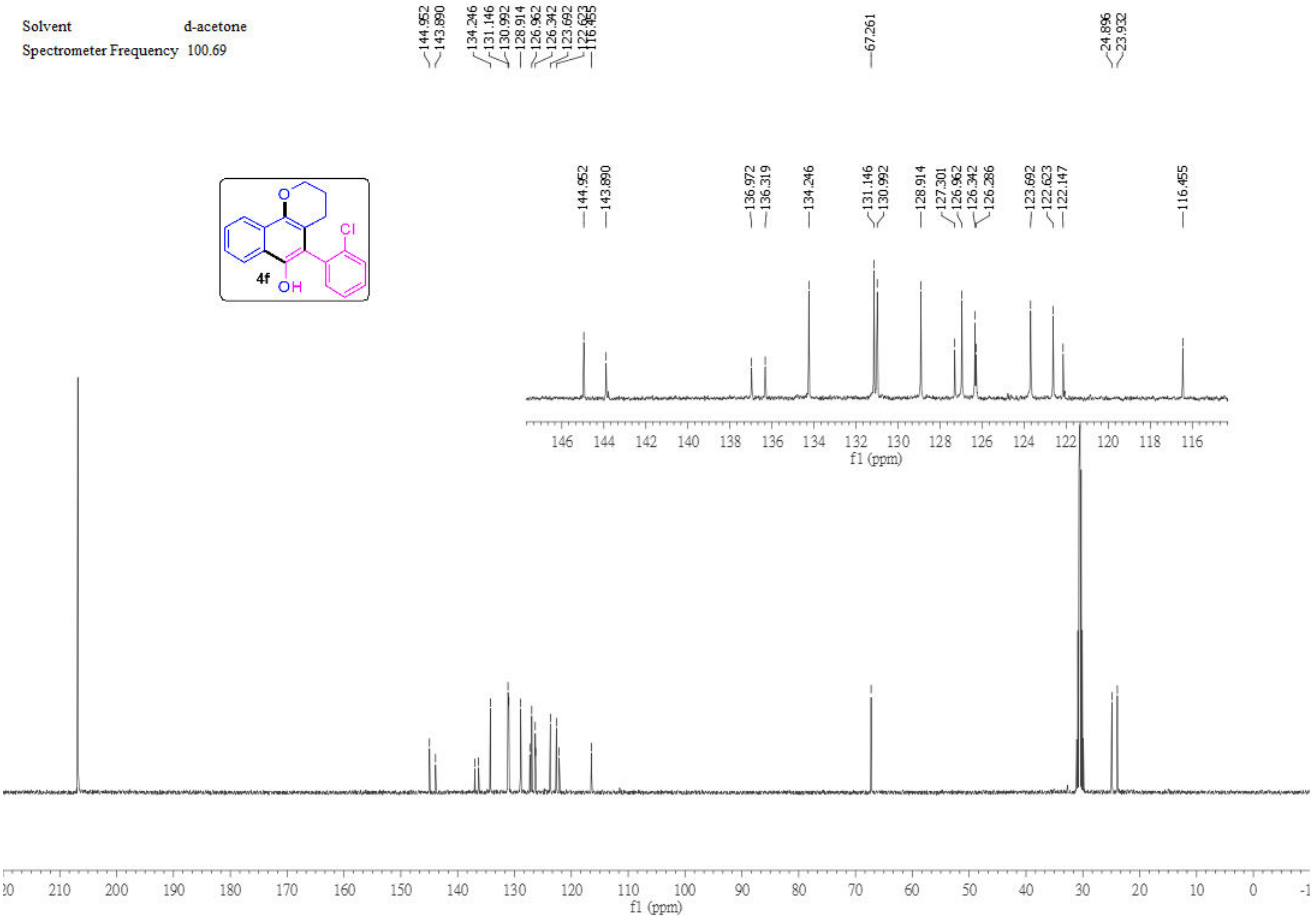

Solvent d-acetone
Spectrometer Frequency 400.40
4d
f1 (ppm)

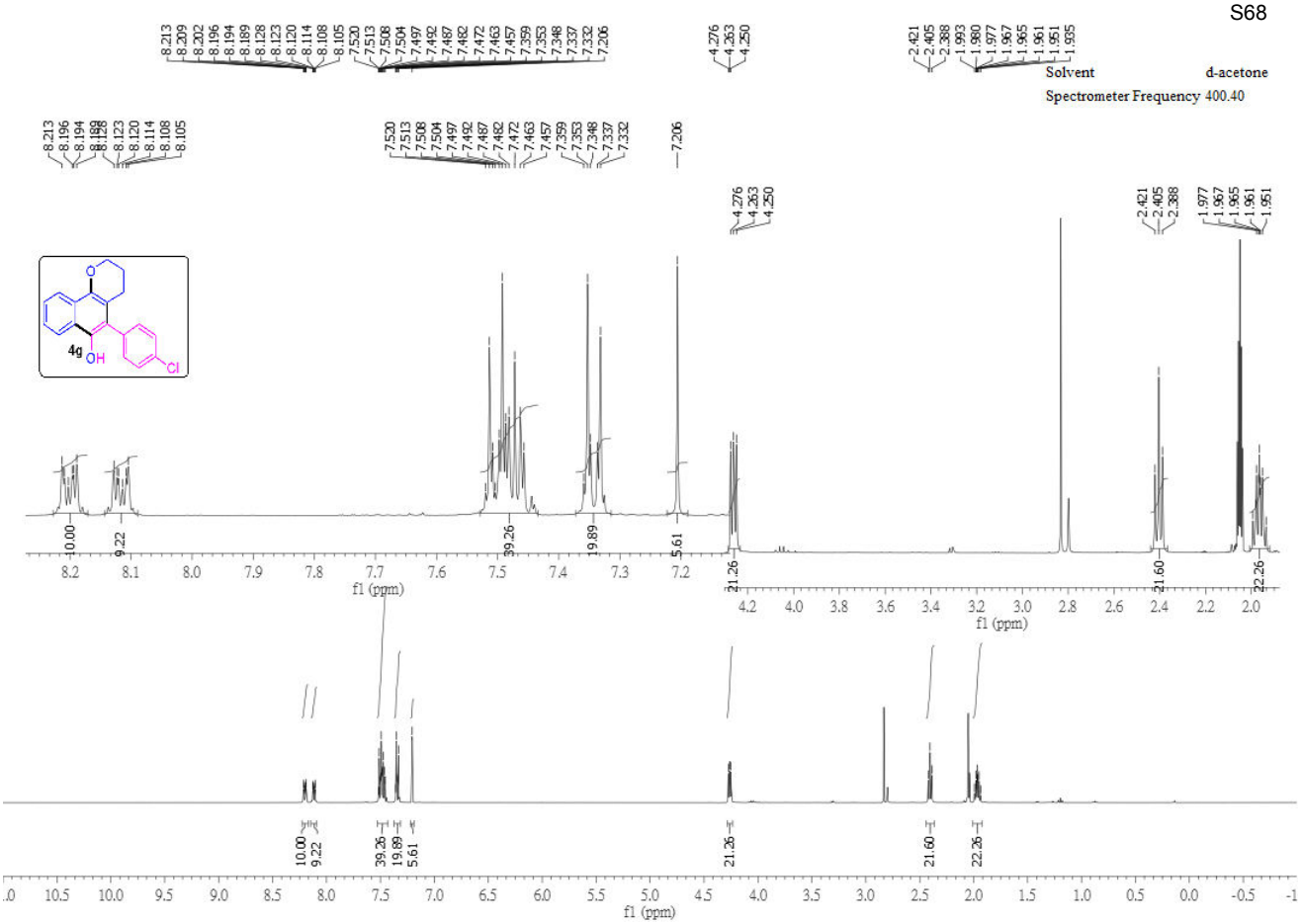

Solvent d-acetone
Spectrometer Frequency 100.69
4d
f1 (ppm)

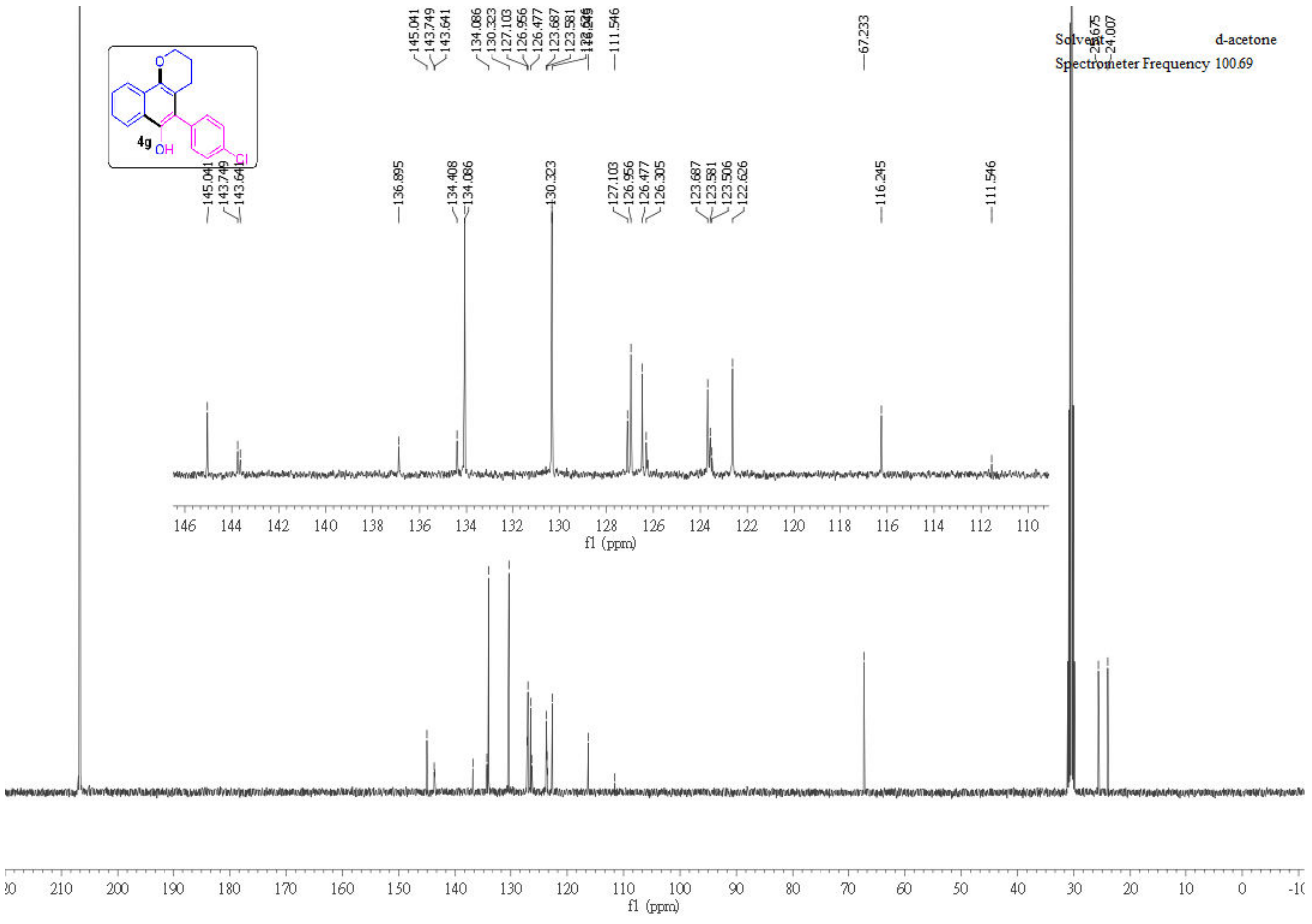

Solvent d-acetone
Spectrometer Frequency 400.40
4e
OH
F
f1 (ppm)

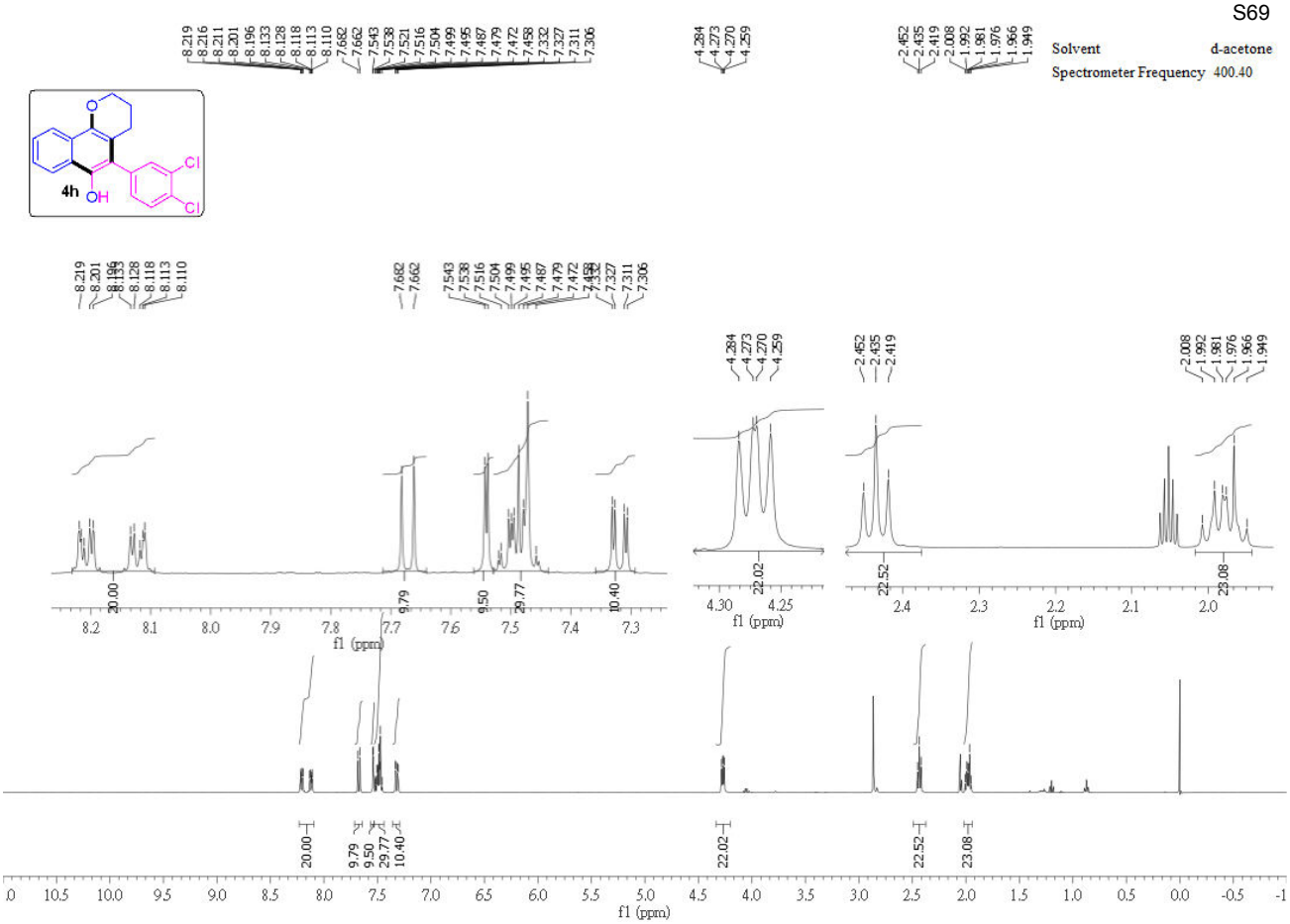

Solvent d-acetone
Spectrometer Frequency 100.69
4e
OH
F
f1 (ppm)

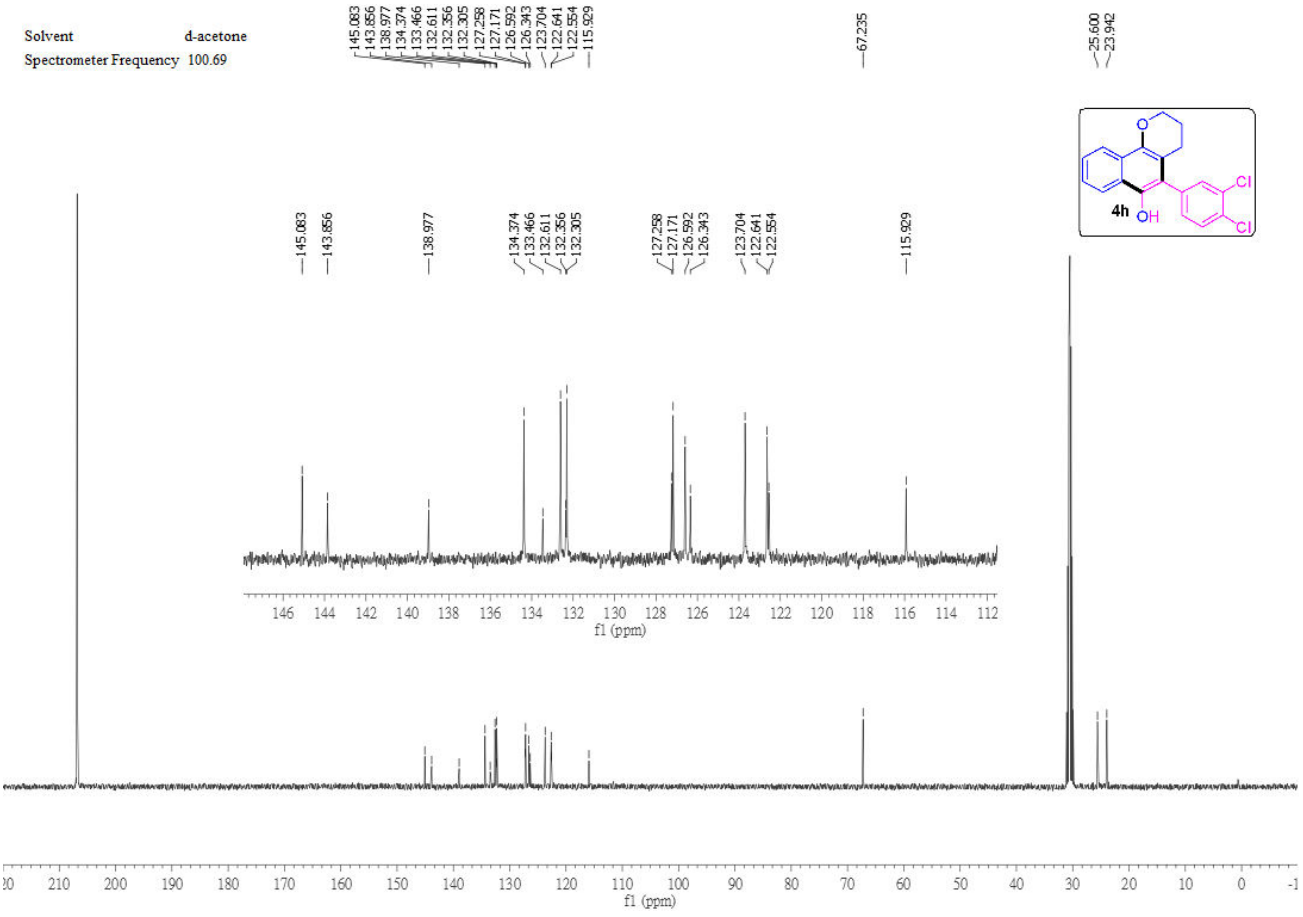

Solvent d-acetone
Spectrometer Frequency 400.40
4f
f1 (ppm)

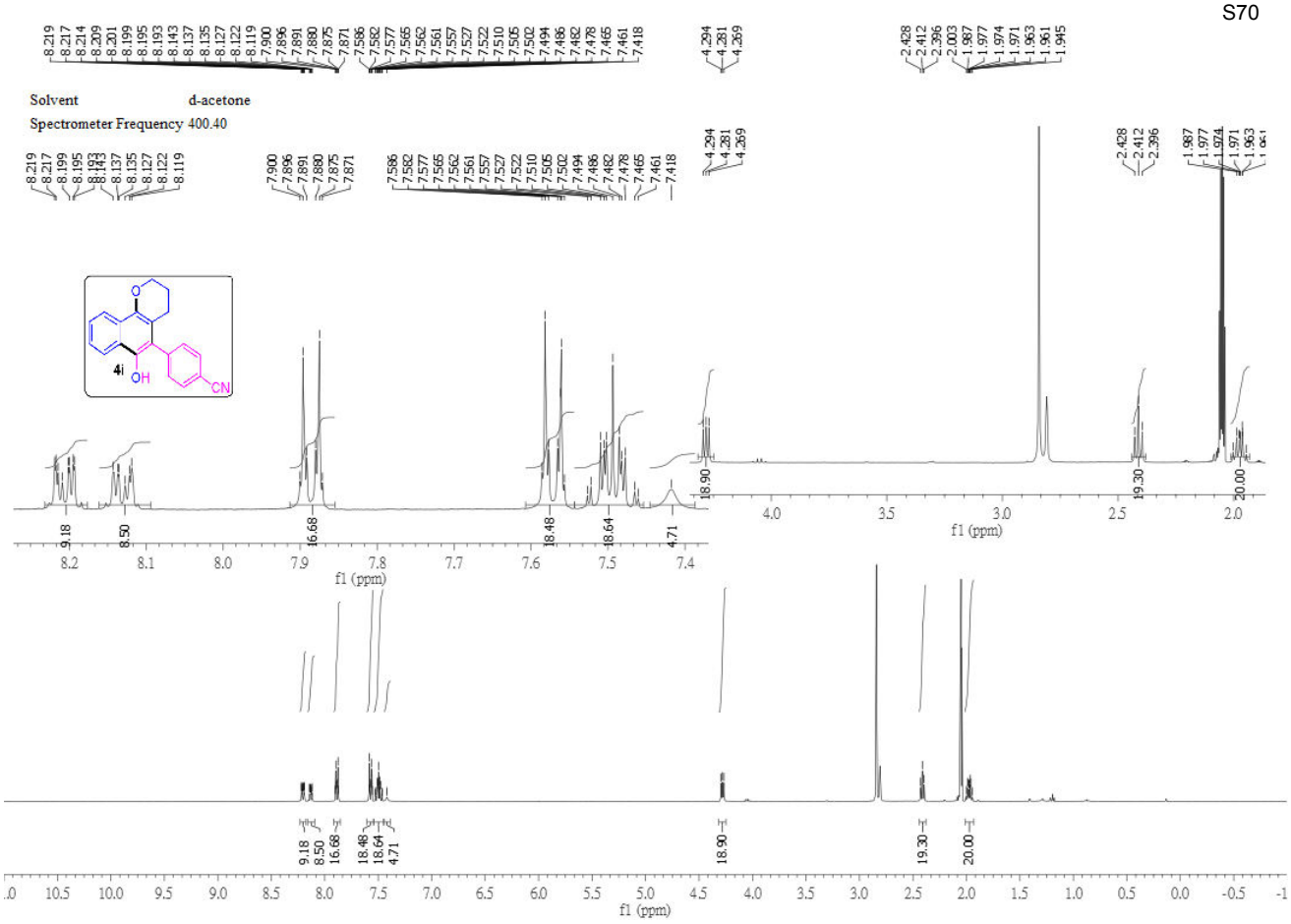

Solvent d-acetone
Spectrometer Frequency 100.69
4f
f1 (ppm)

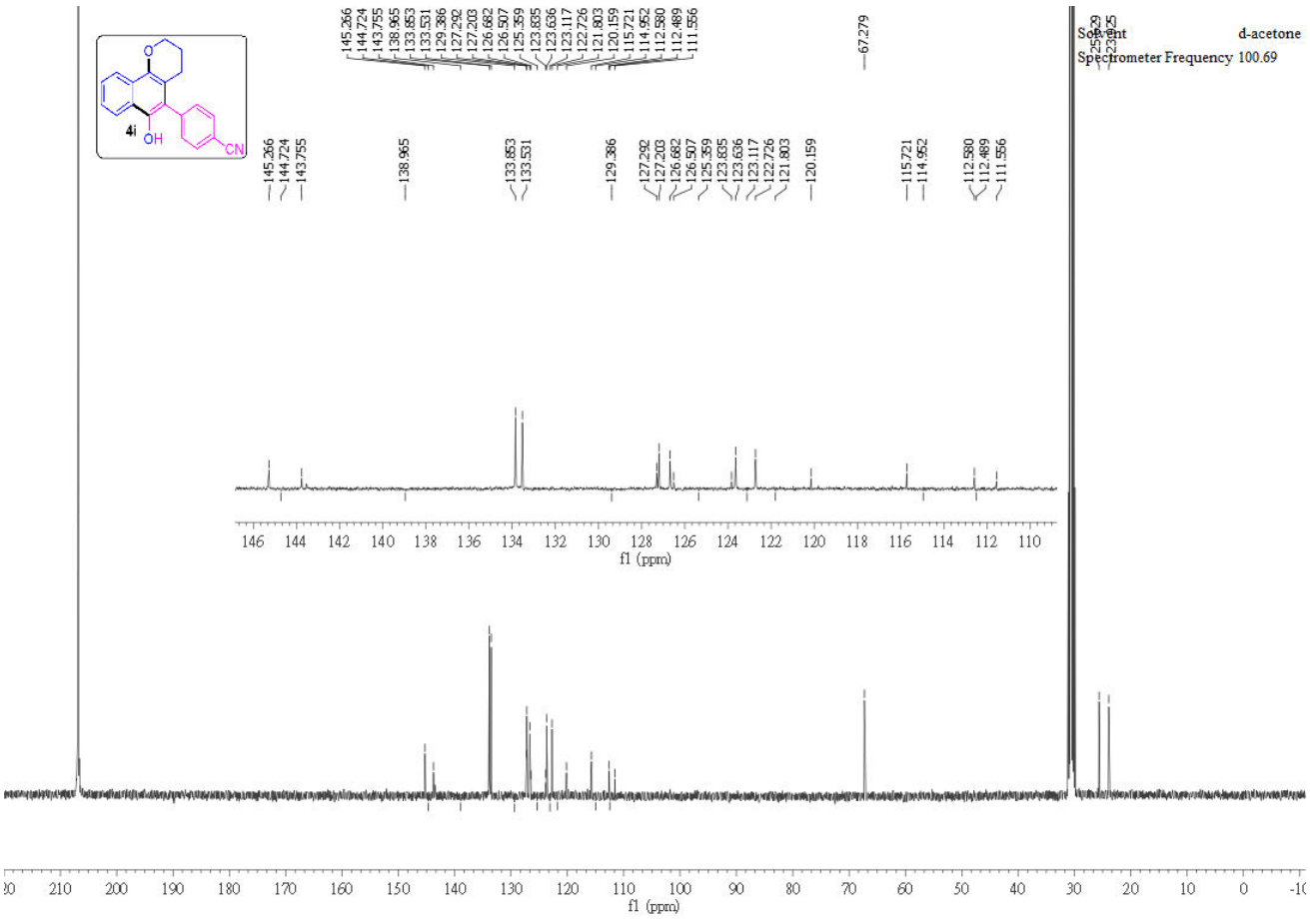

Solvent
d-acetone
Spectrometer Frequency 400.40
4g
OH
Cl
f1 (ppm)

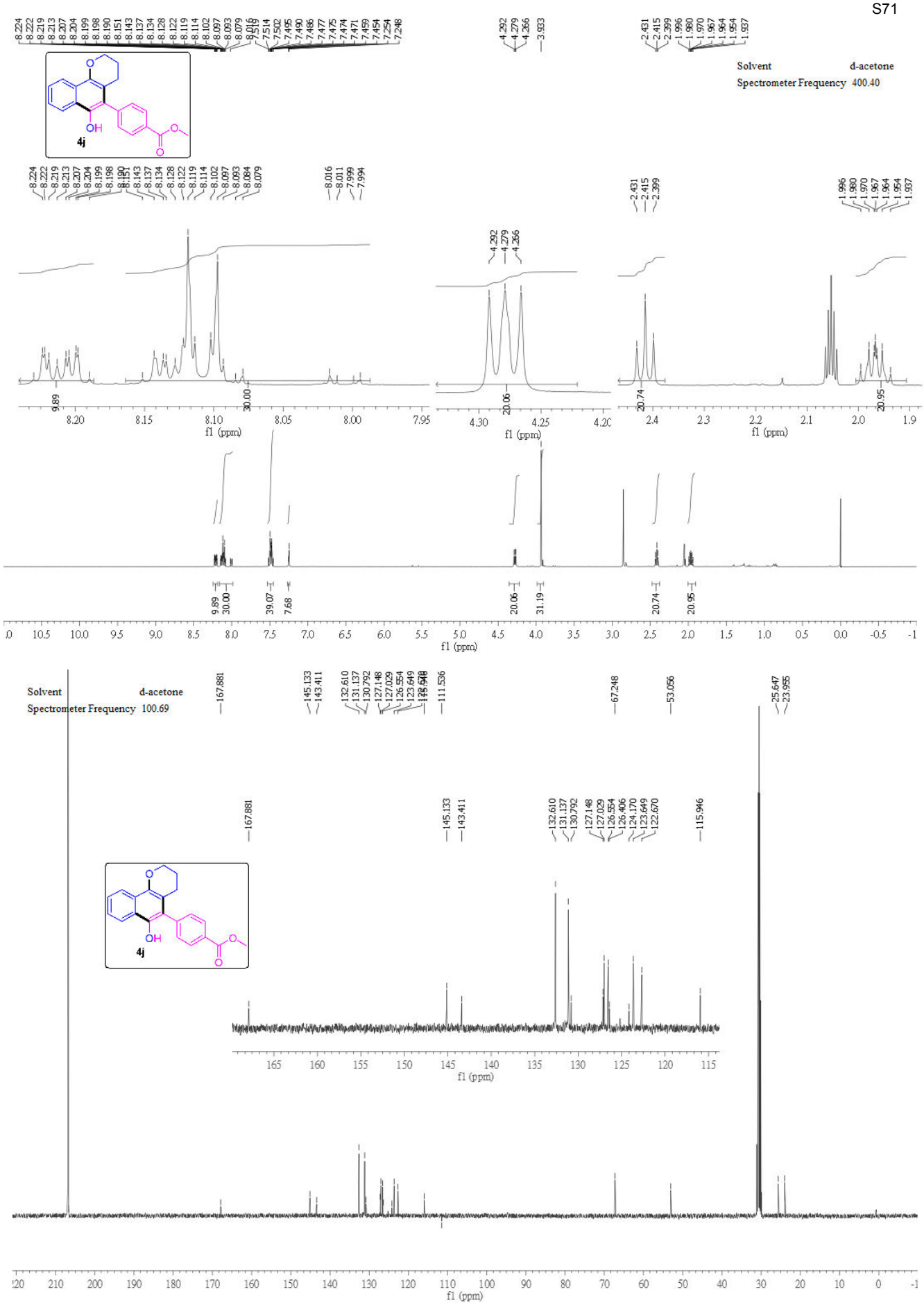

Solvent
d-acetone
Spectrometer Frequency 100.69
4g
OH
Cl
f1 (ppm)


Solvent d-acetone
Spectrometer Frequency 400.40
4h
f1 (ppm)

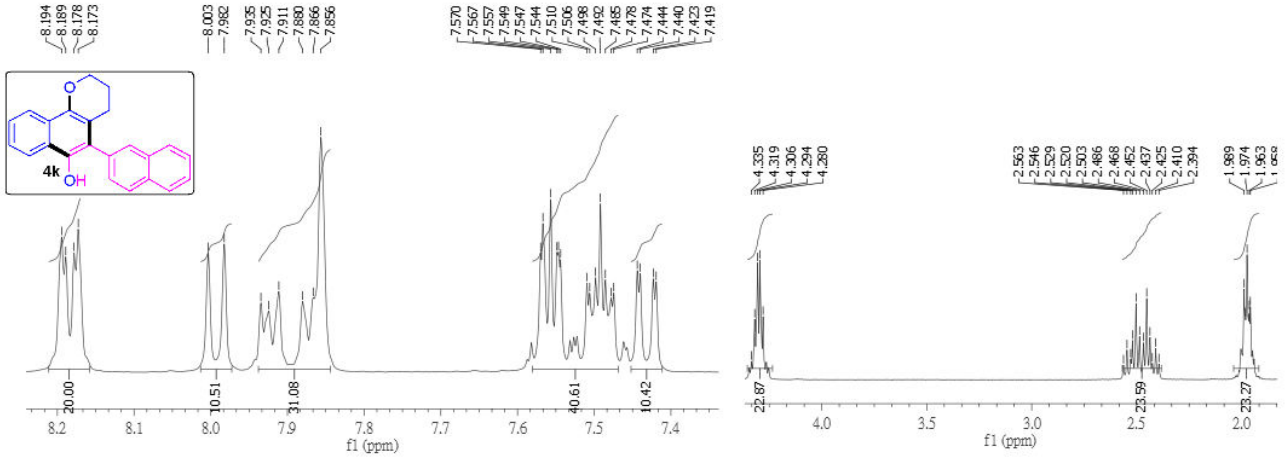

Solvent d-acetone
Spectrometer Frequency 100.69
4h
f1 (ppm)

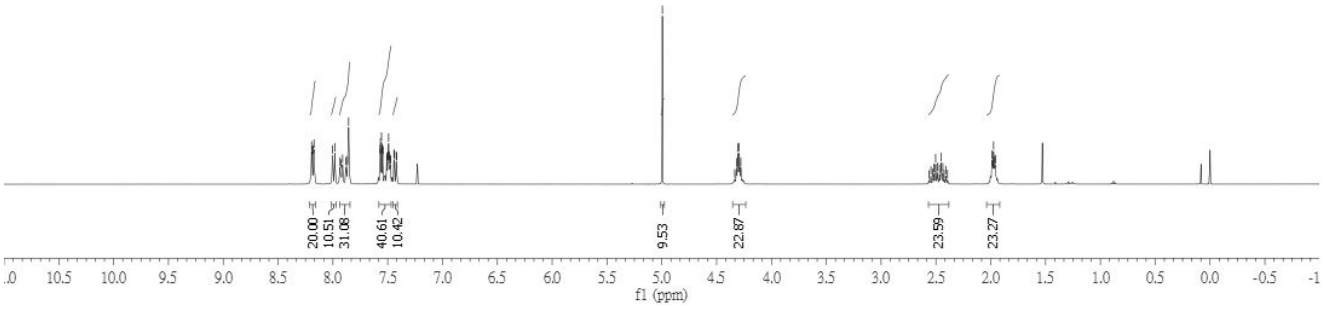

Solvent d-acetone
Spectrometer Frequency 400.40
4i
f1 (ppm)


Solvent d-acetone
Spectrometer Frequency 100.69
4i
f1 (ppm)

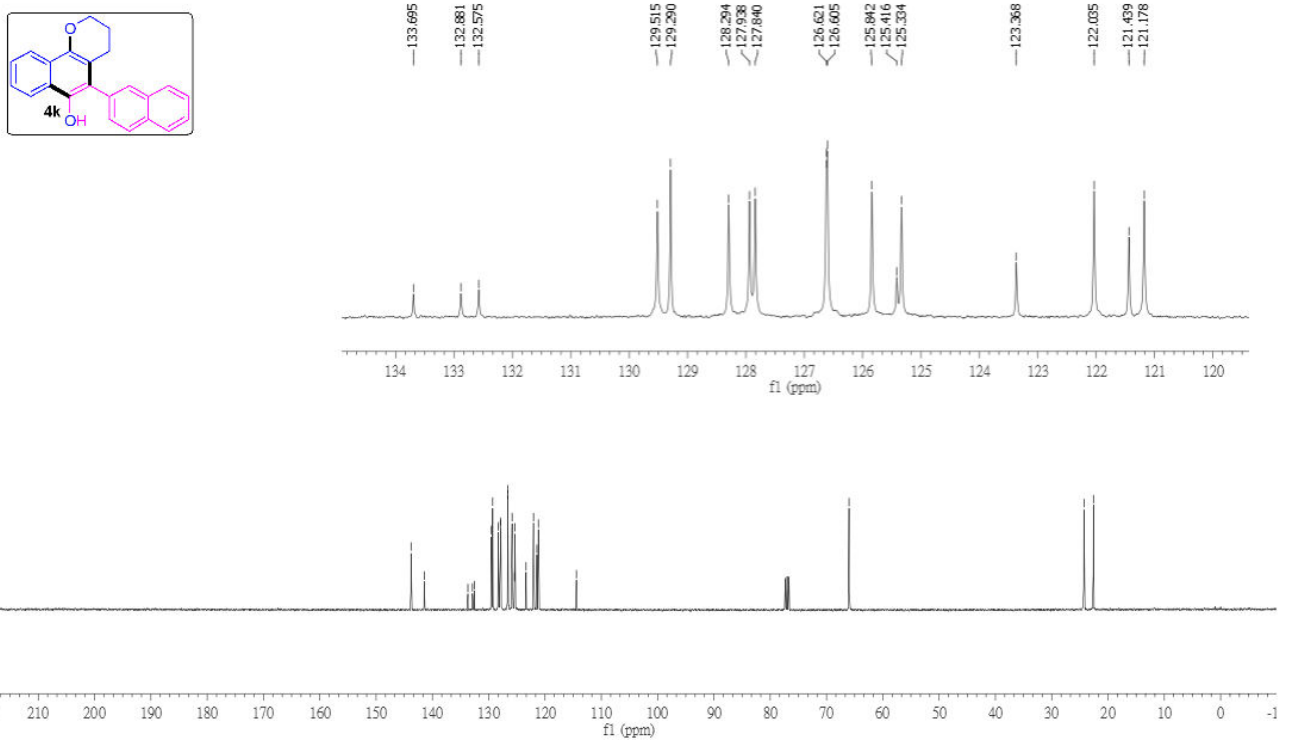

Solvent d-acetone
Spectrometer Frequency 400.40
4j
f1 (ppm)
Solvent d-acetone
Spectrometer Frequency 100.69
4j
f1 (ppm)

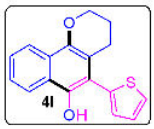

Solvent CDCl3
Spectrometer Frequency 400.40


4k
f1 (ppm)


f1 (ppm)


Solvent CDCl3
Spectrometer Frequency 100.69


4k
f1 (ppm)

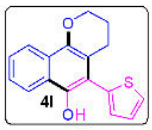


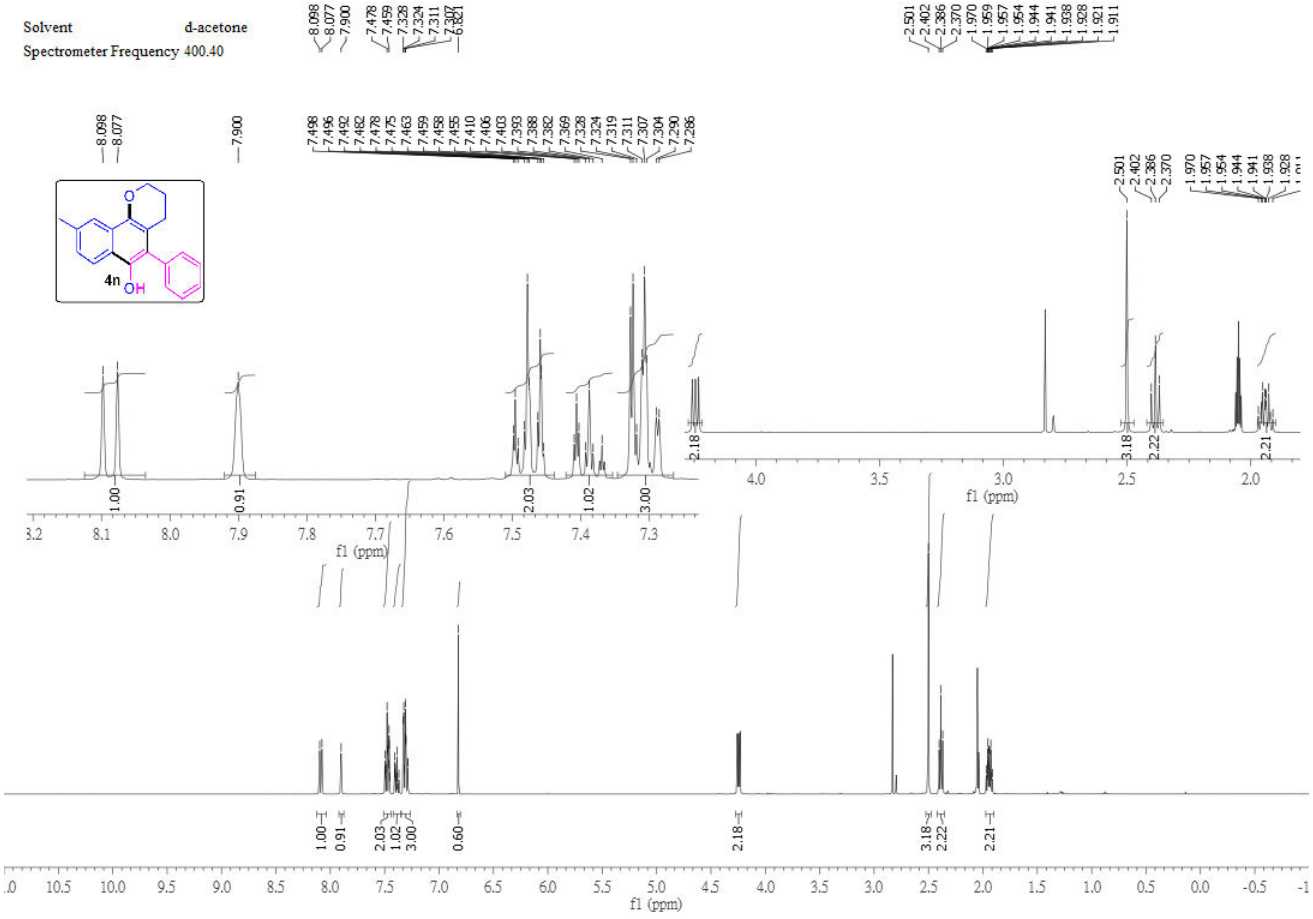
Solvent $CDCl_3$

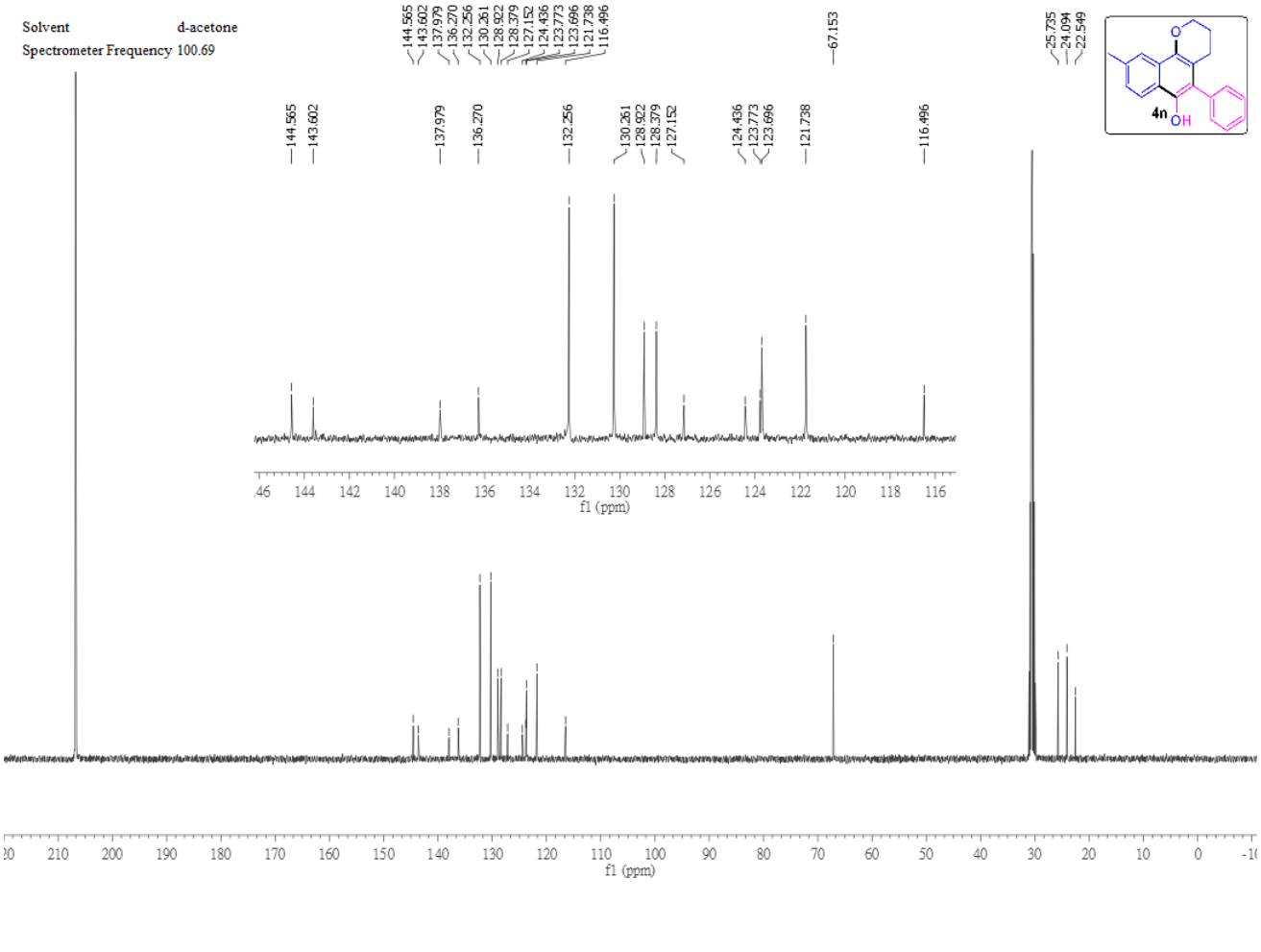
Spectrometer Frequency 400.40

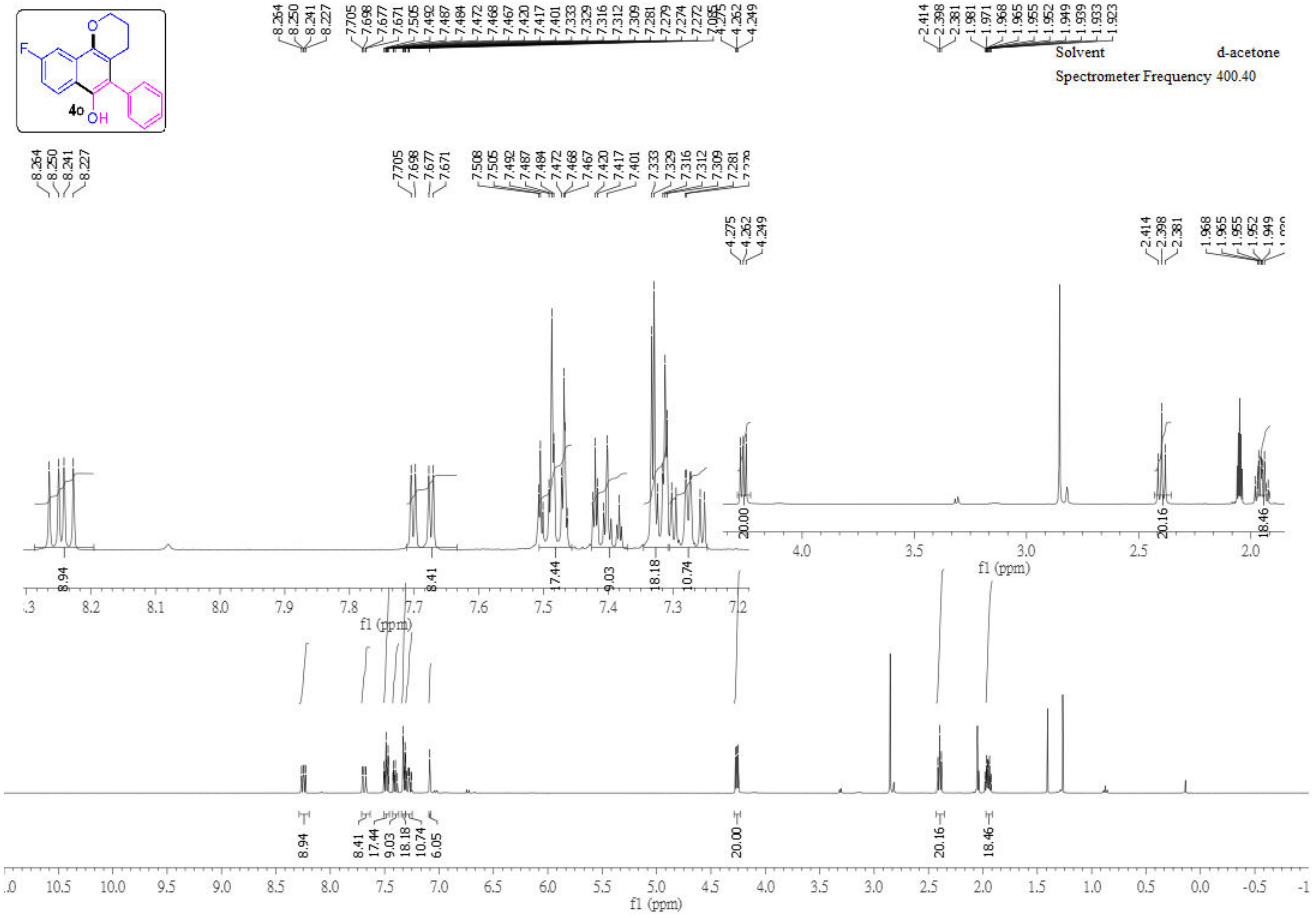
Solvent $CDCl_3$

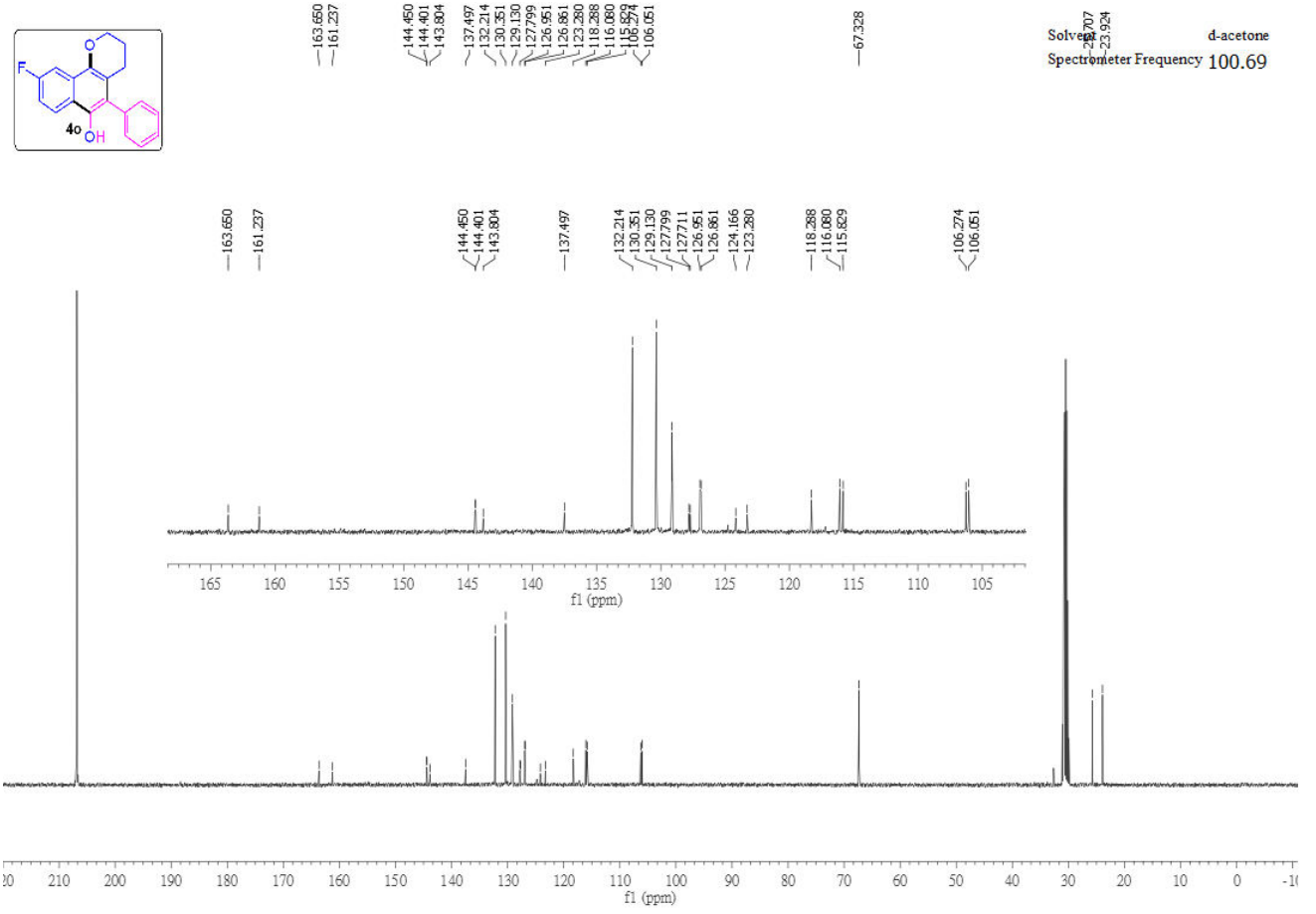
Spectrometer Frequency 100.69

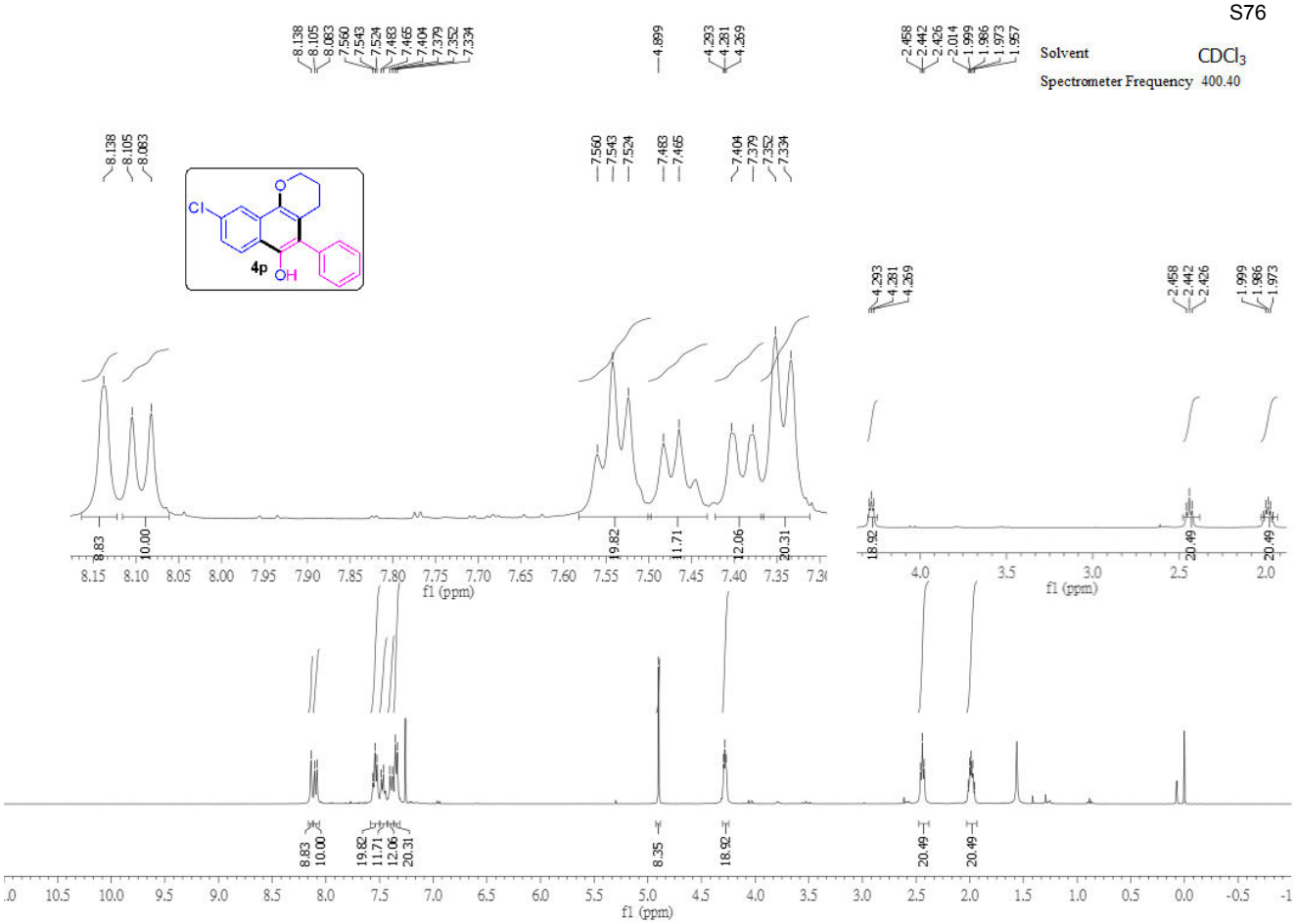


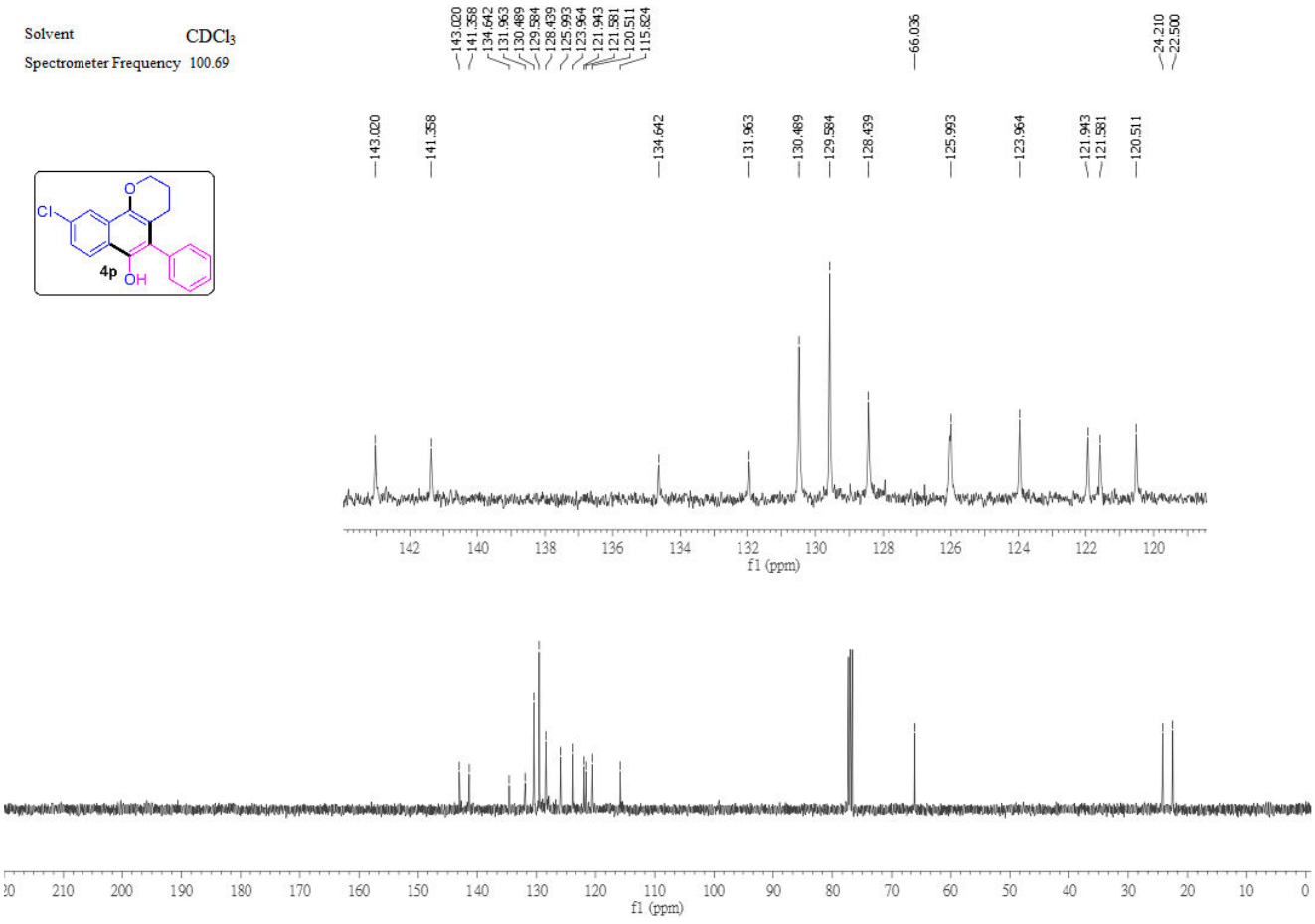

Solvent d-acetone
Spectrometer Frequency 400.40
8.098
8.077
7.900
7.478
7.459
7.328
7.324
7.311
7.307
6.821
2.501
2.402
2.386
2.370
1.970
1.959
1.957
1.954
1.944
1.941
1.938
1.928
1.921
1.911
4n
OH
f1 (ppm)

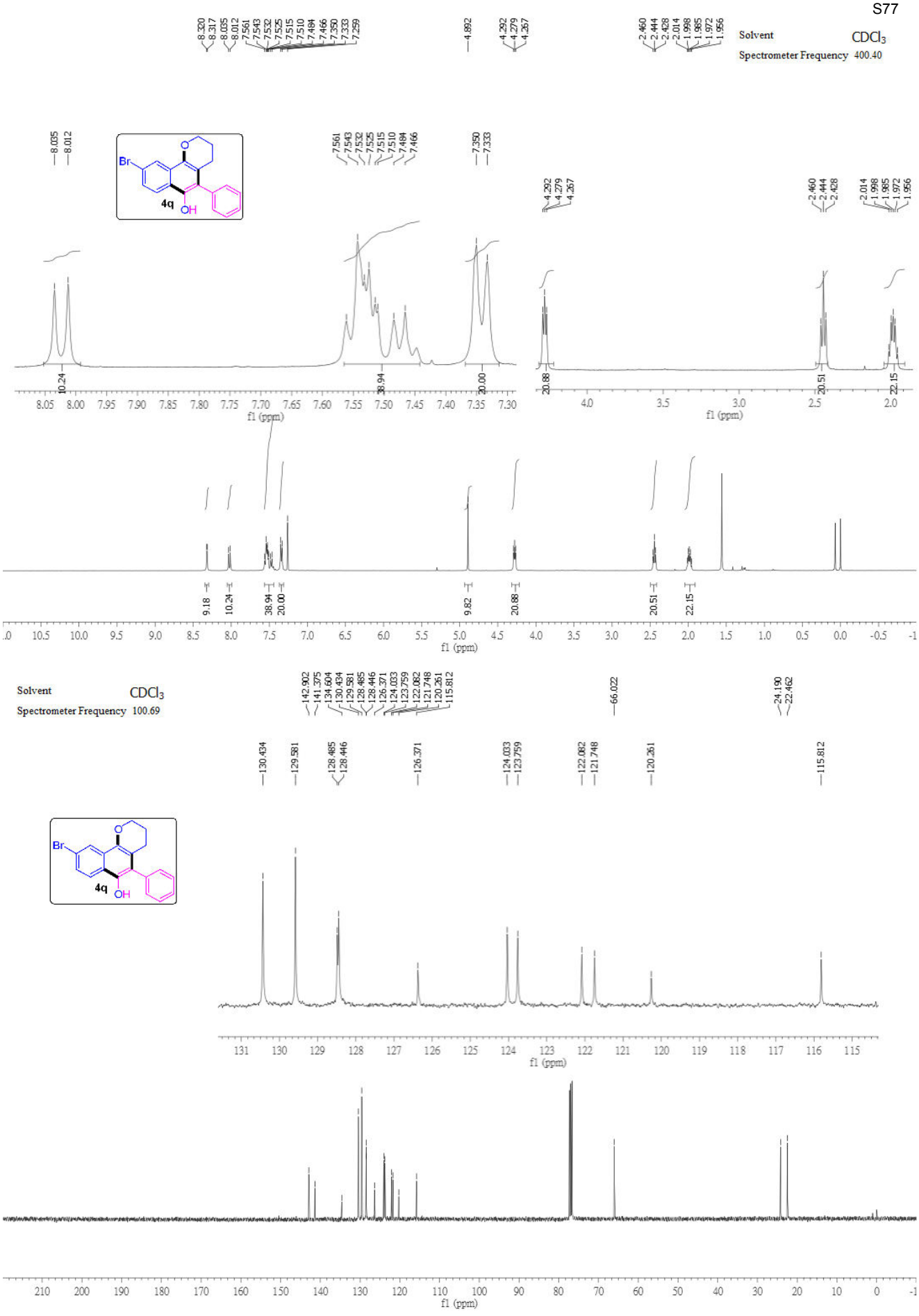

Solvent d-acetone
Spectrometer Frequency 100.69
144.565
143.602
137.979
136.270
132.256
130.261
128.922
128.379
127.152
124.436
123.773
123.696
121.738
116.496
67.153
25.735
24.094
22.549
4n
OH
f1 (ppm)


4o
Solvent d-acetone
Spectrometer Frequency 400.40
f1 (ppm)


4o
Solvent d-acetone
Spectrometer Frequency 100.69
f1 (ppm)

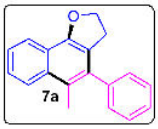

Solvent CDCl3
Spectrometer Frequency 400.40
4p
f1 (ppm)

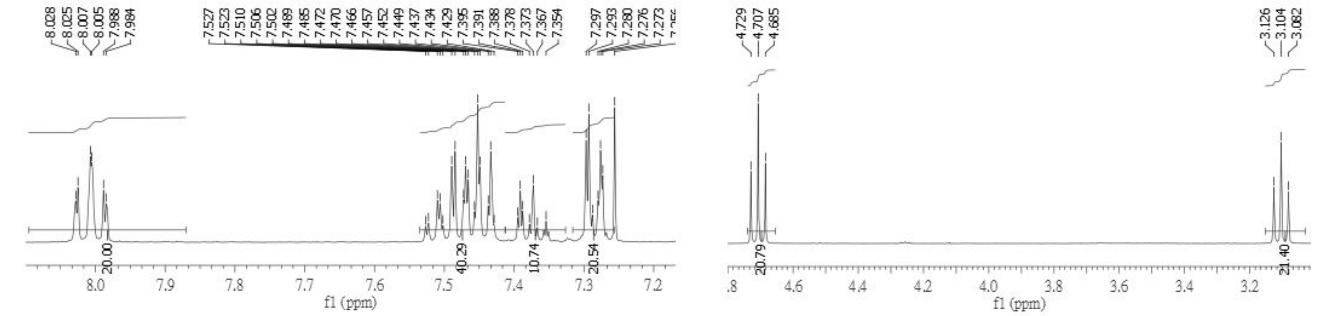

Solvent CDCl3
Spectrometer Frequency 100.69
4p
f1 (ppm)

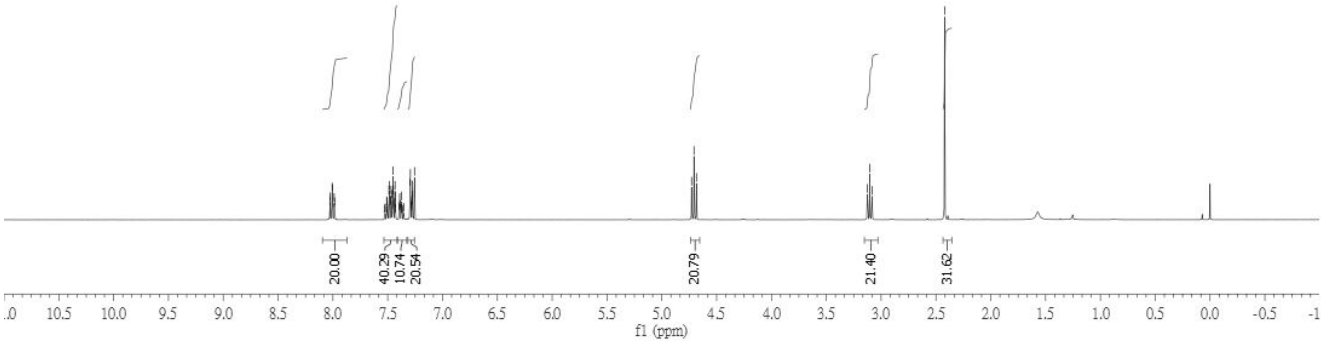

Solvent CDCl3
Spectrometer Frequency 400.40
4q
f1 (ppm)
Solvent CDCl3
Spectrometer Frequency 100.69
4q
f1 (ppm)

Solvent $CDCl_3$

Spectrometer Frequency 400.40

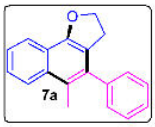


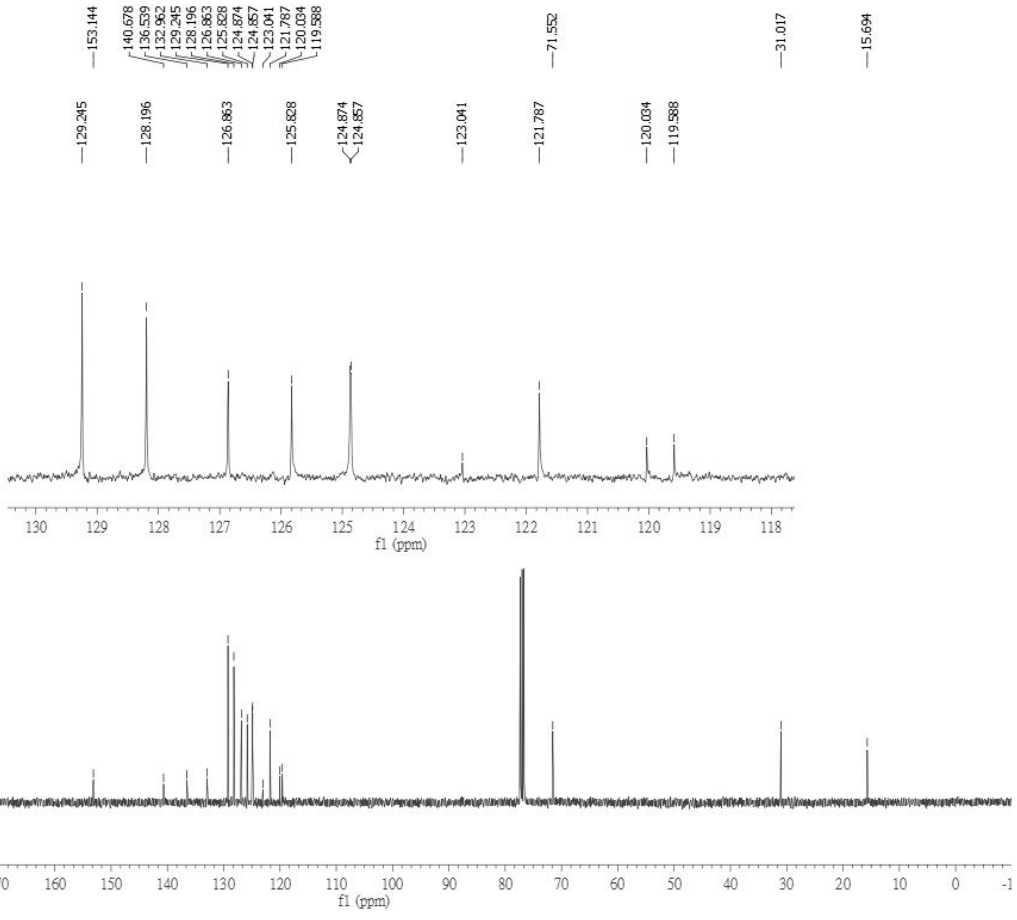




Solvent $CDCl_3$

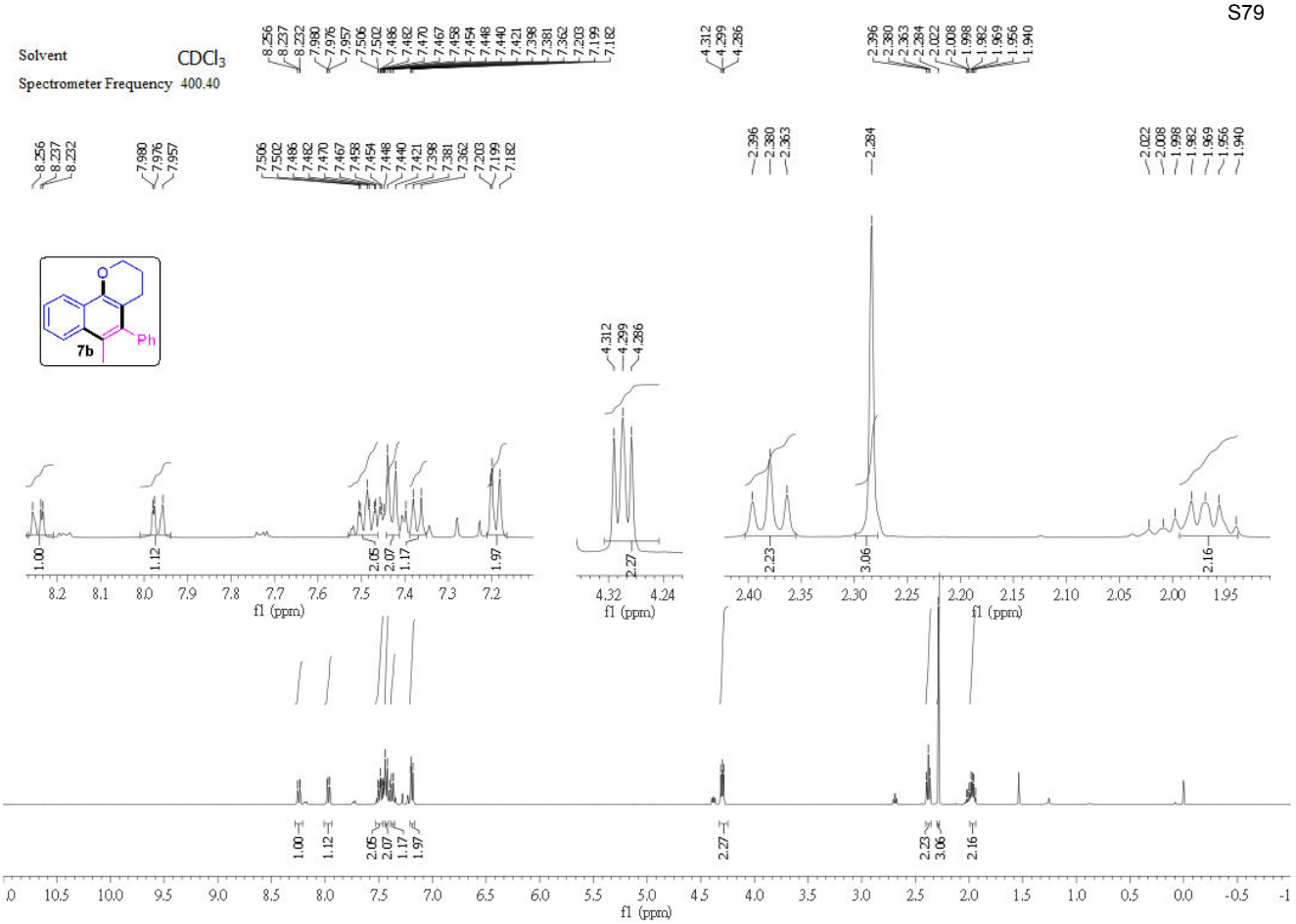
Spectrometer Frequency 400.40





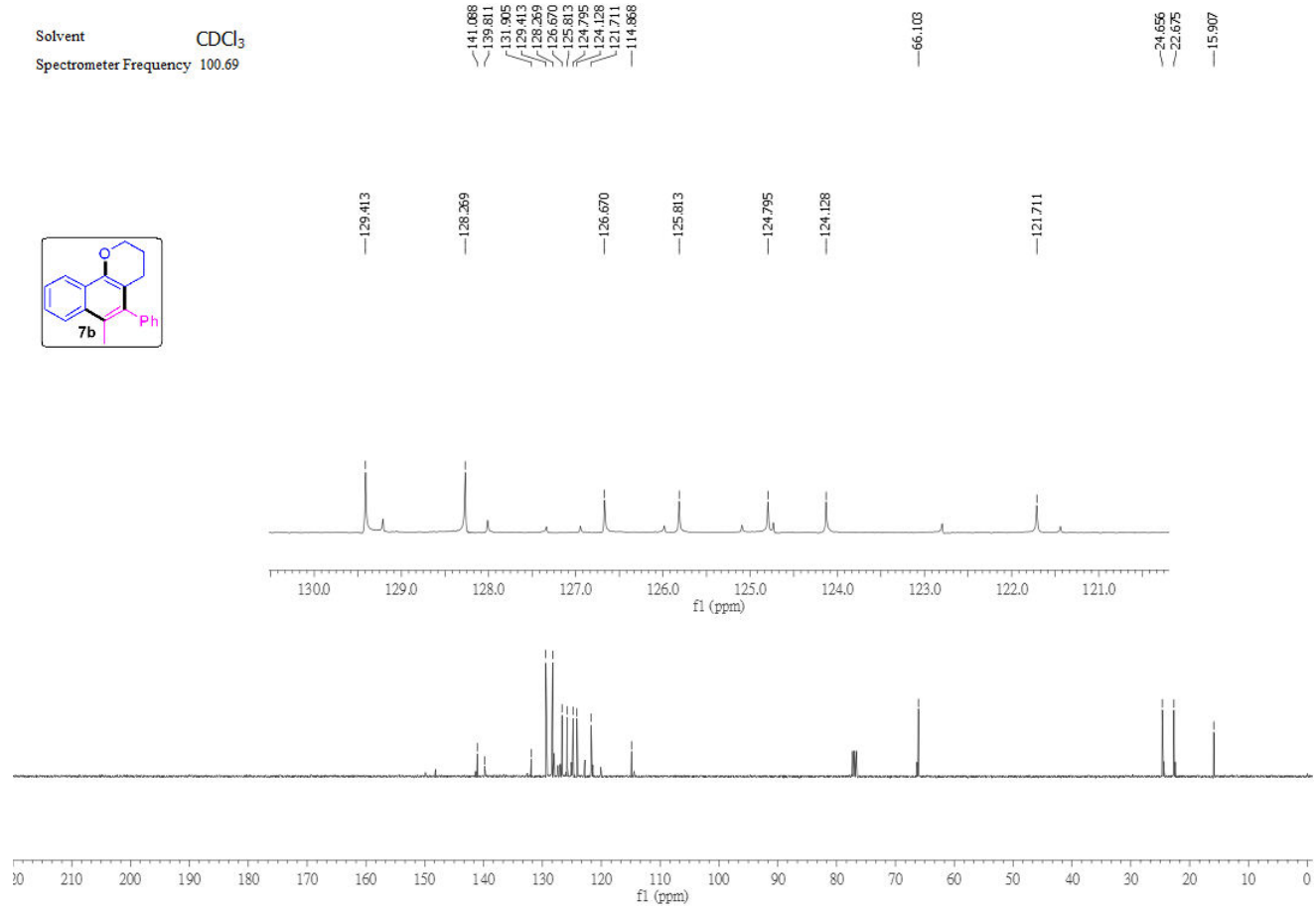
Solvent $CDCl_3$

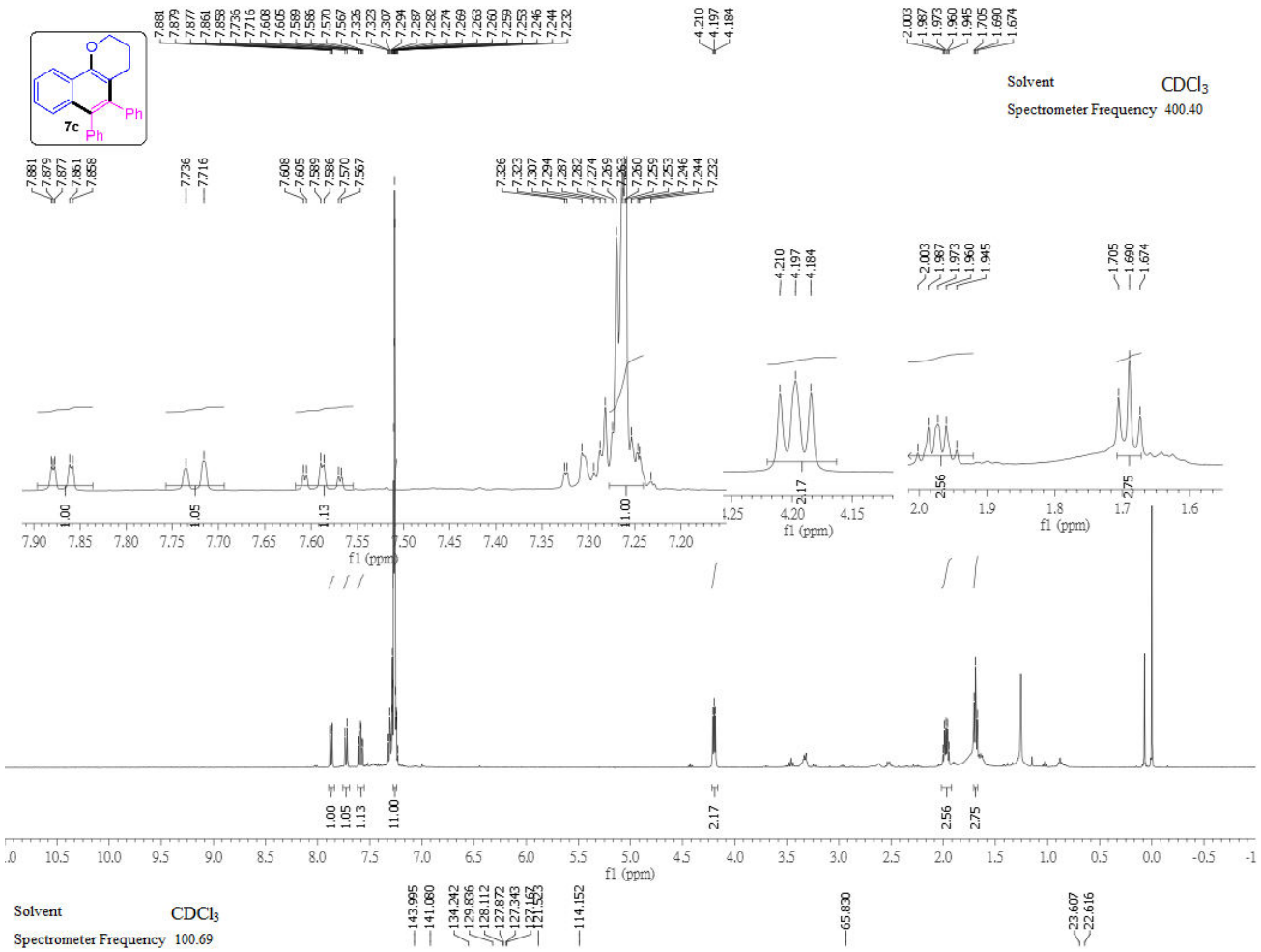
Spectrometer Frequency 400.40

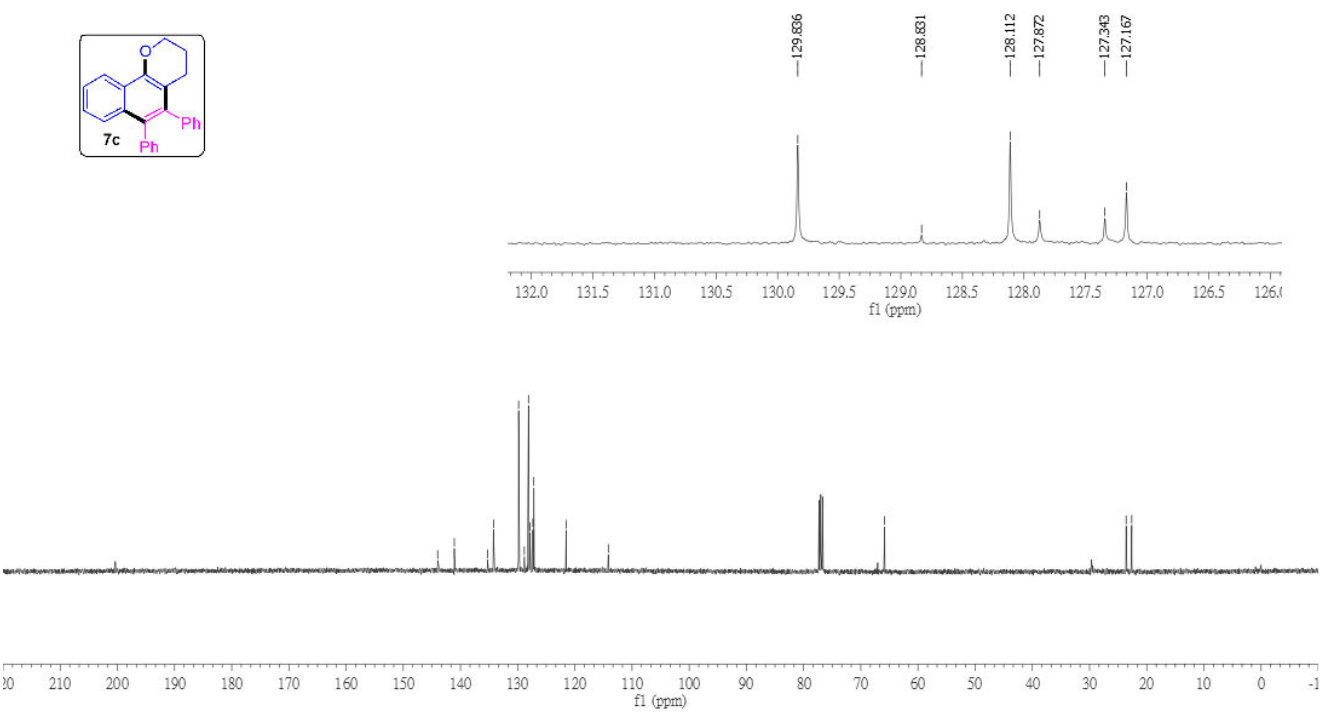


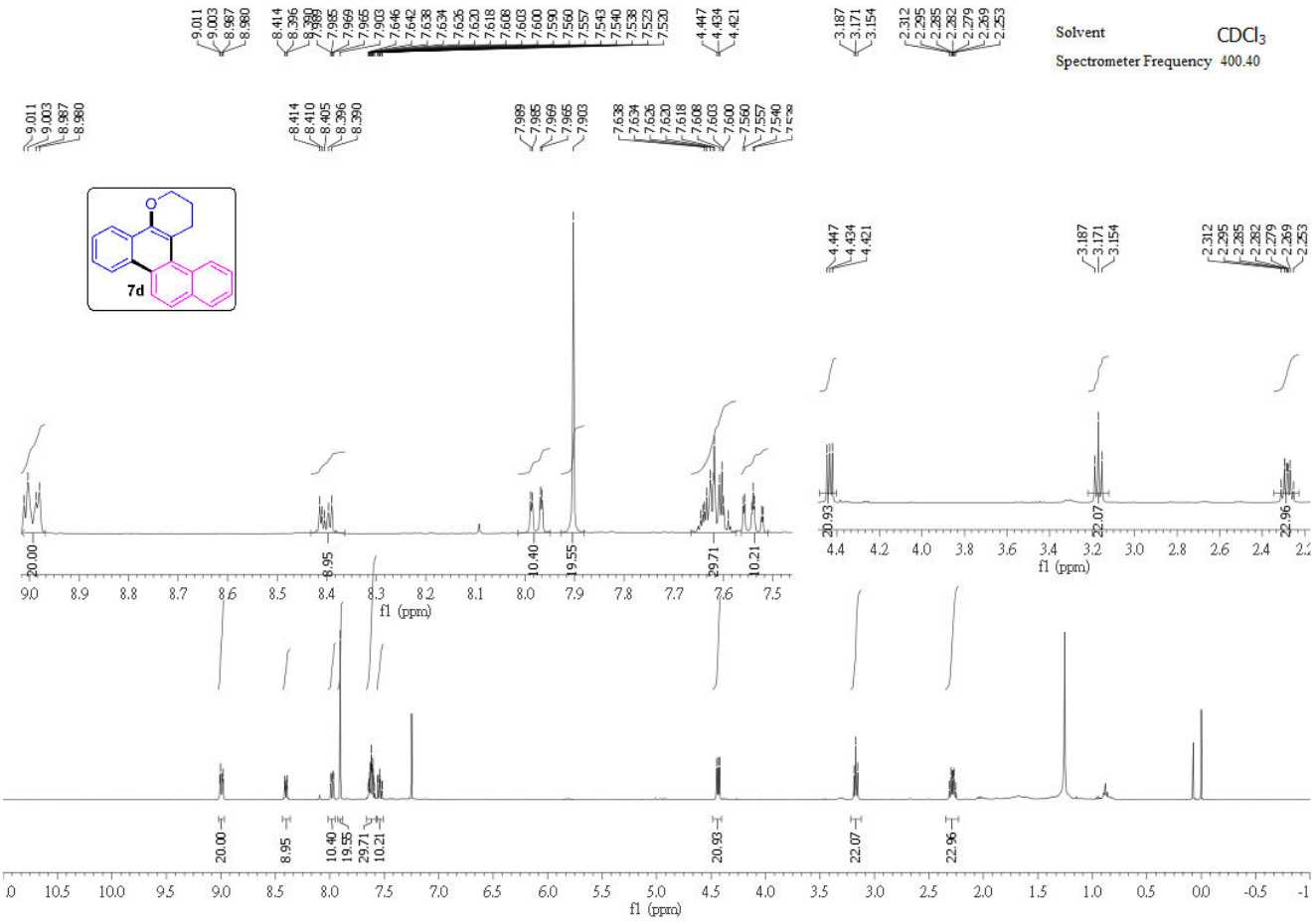
Solvent $CDCl_3$

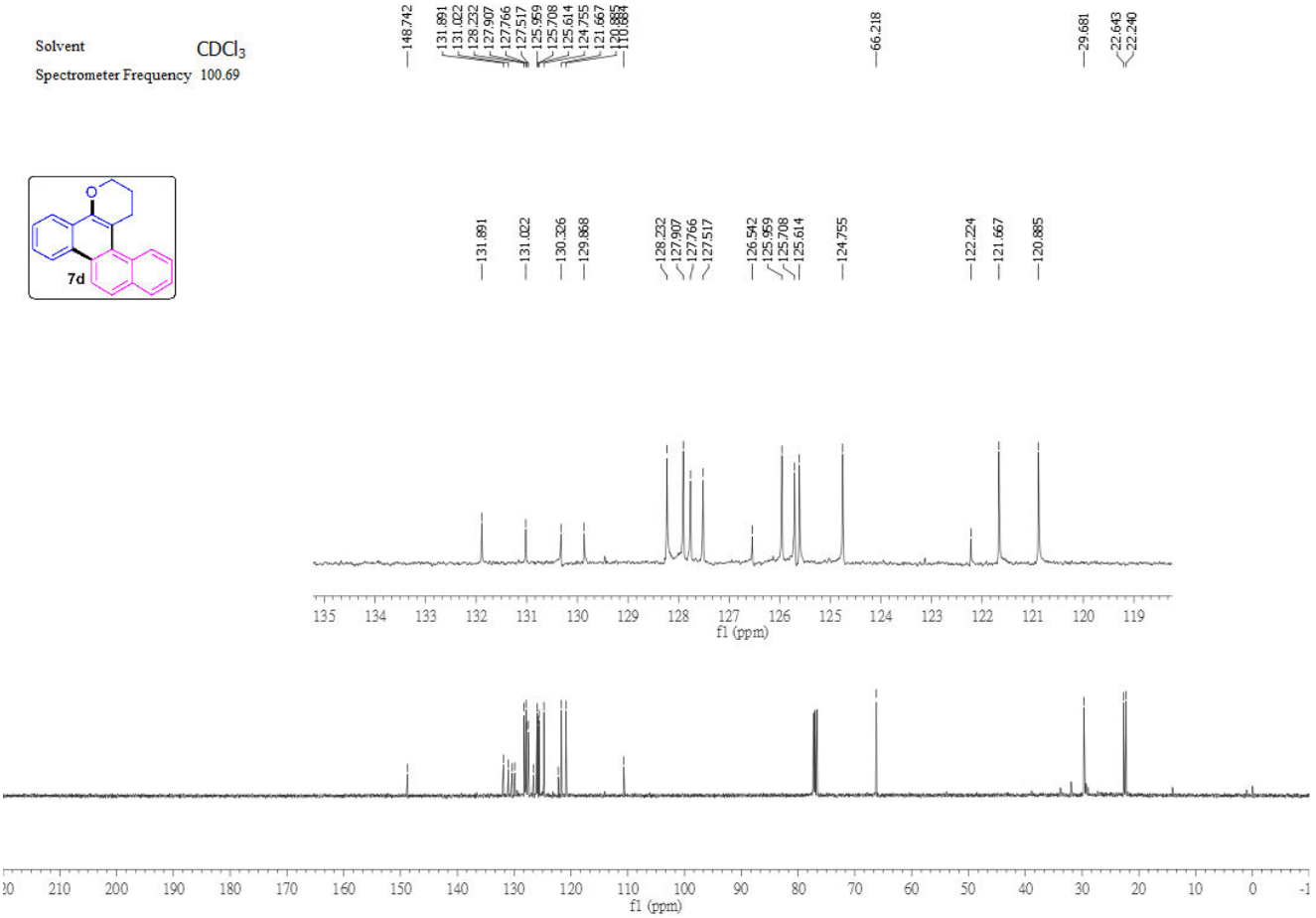
Spectrometer Frequency 100.69

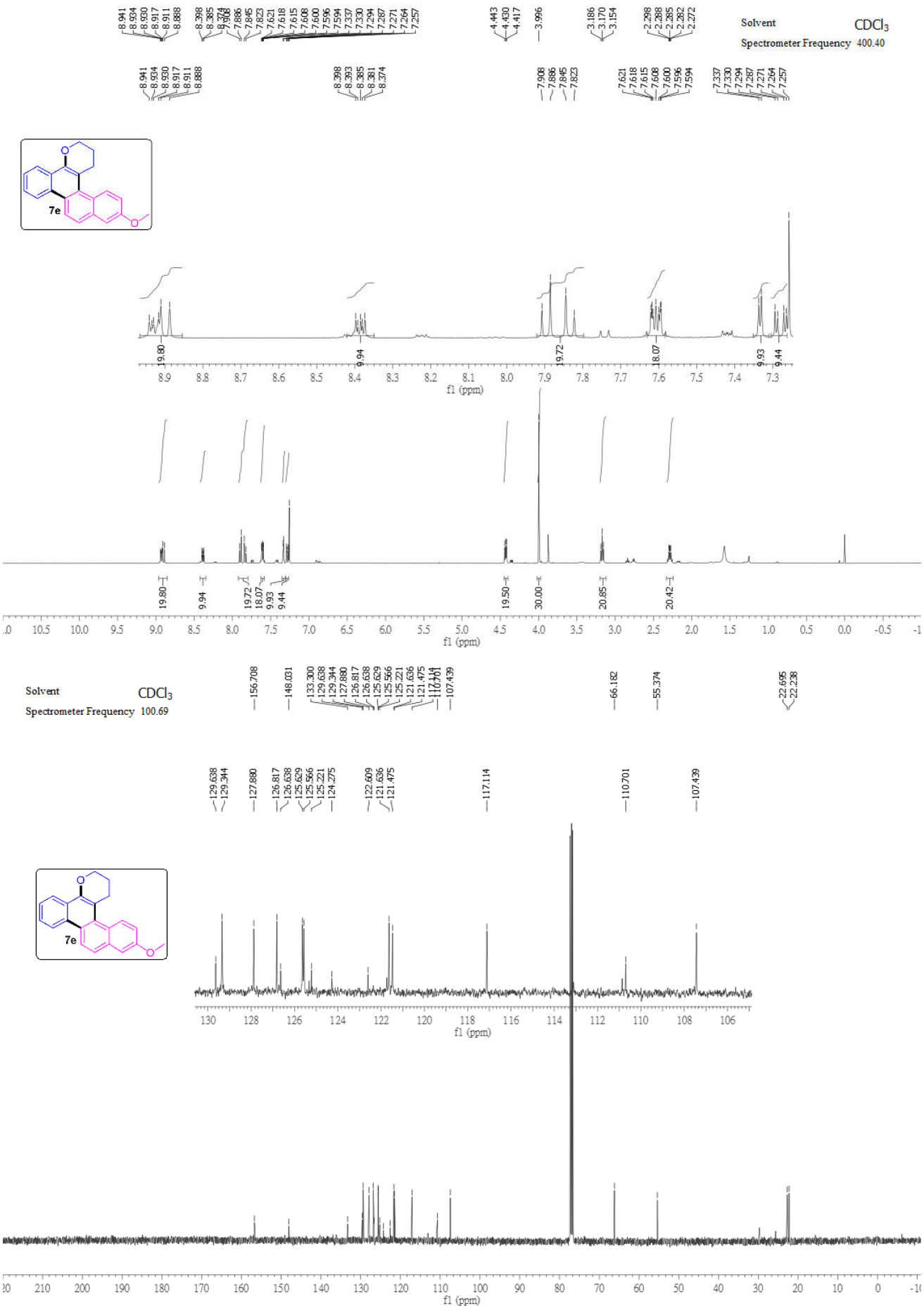


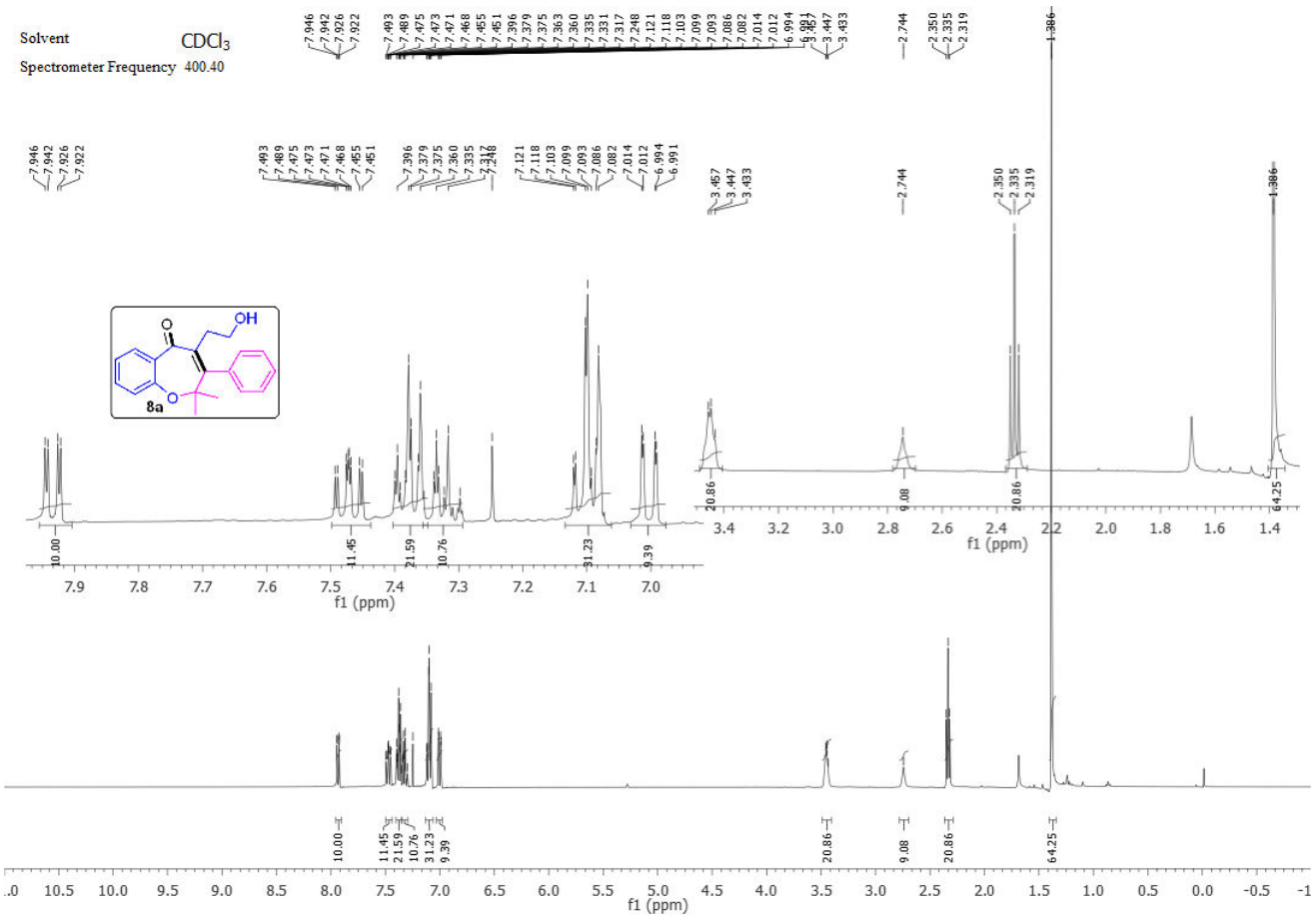

7c
Ph
Ph
Solvent CDCl3
Spectrometer Frequency 400.40
f1 (ppm)

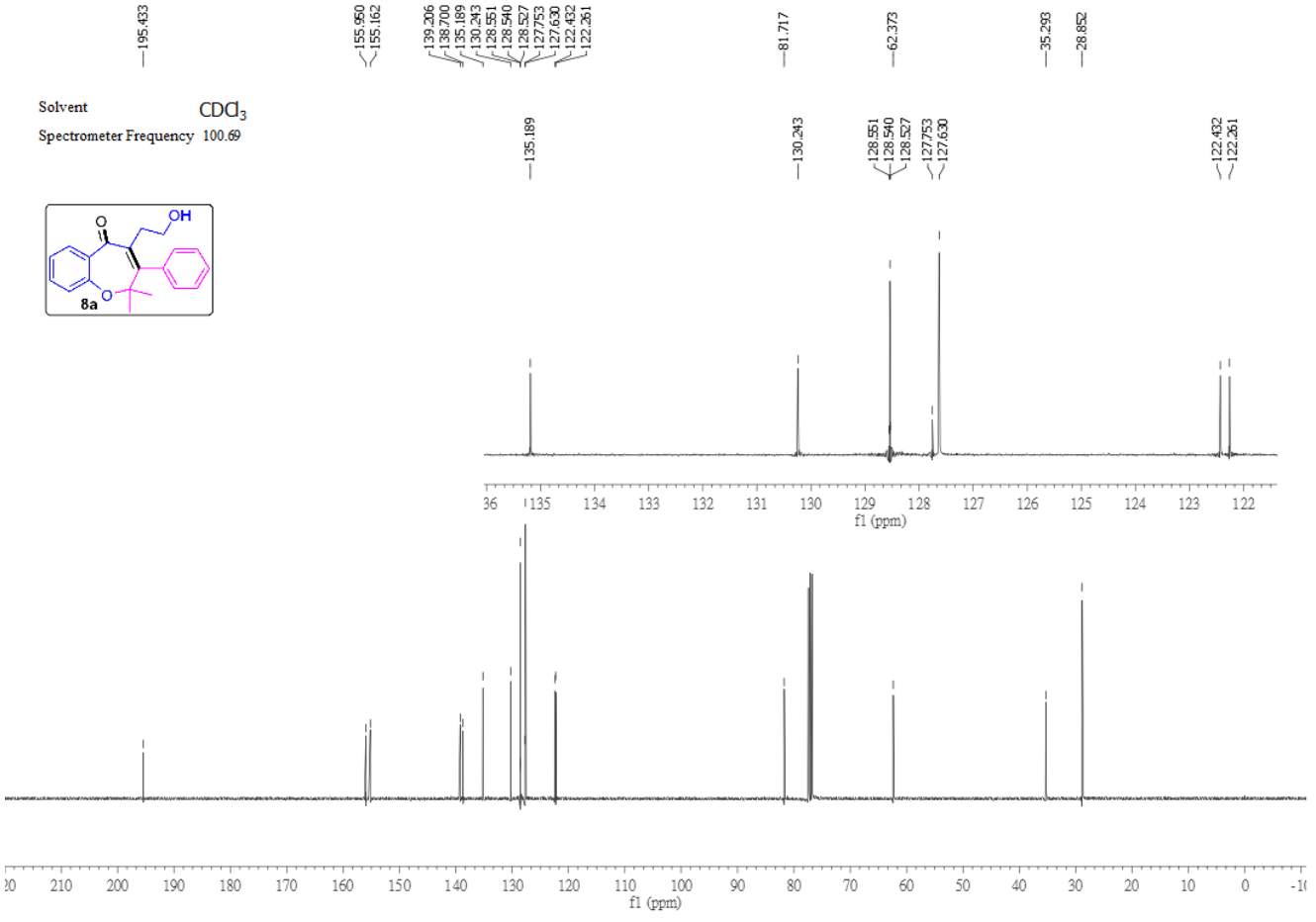

7c
Ph
Ph
Solvent CDCl3
Spectrometer Frequency 100.69
f1 (ppm)

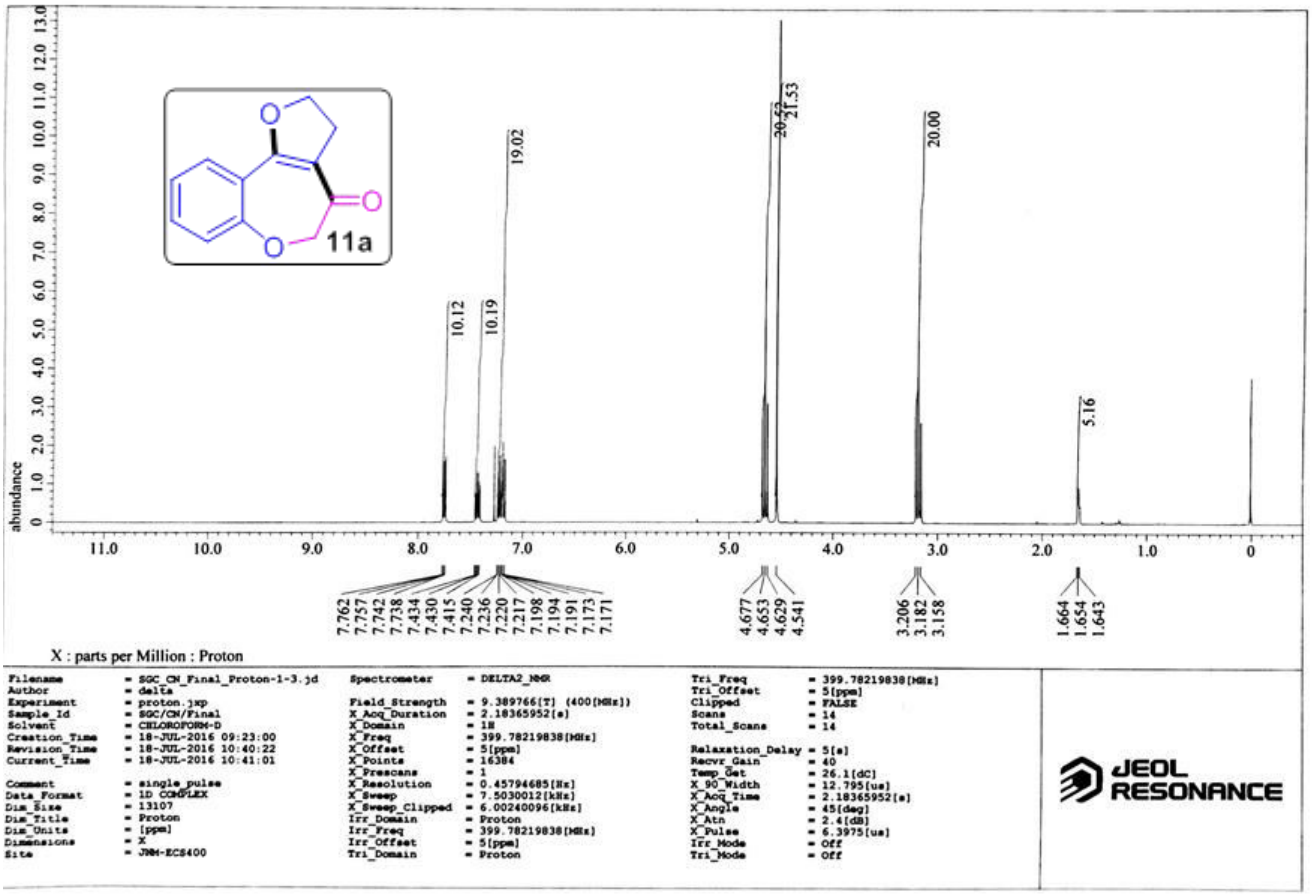

Solvent CDCl3
Spectrometer Frequency 400.40
7d
f1 (ppm)


Solvent CDCl3
Spectrometer Frequency 100.69
7d
f1 (ppm)

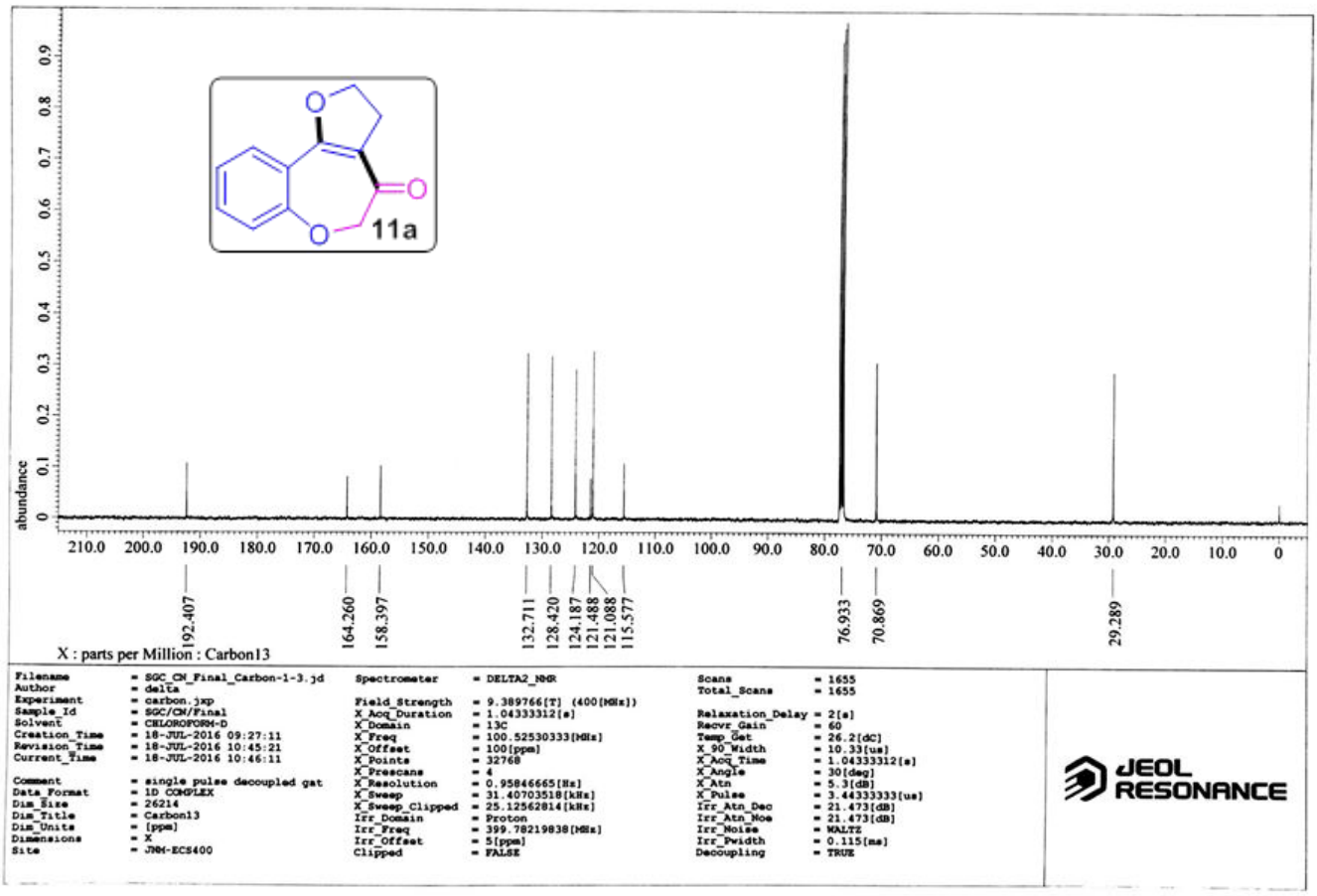

Solvent CDCl3
Spectrometer Frequency 400.40
7e
f1 (ppm)
Solvent CDCl3
Spectrometer Frequency 100.69
7e
f1 (ppm)


Solvent CDCl3
Spectrometer Frequency 400.40
8a
f1 (ppm)

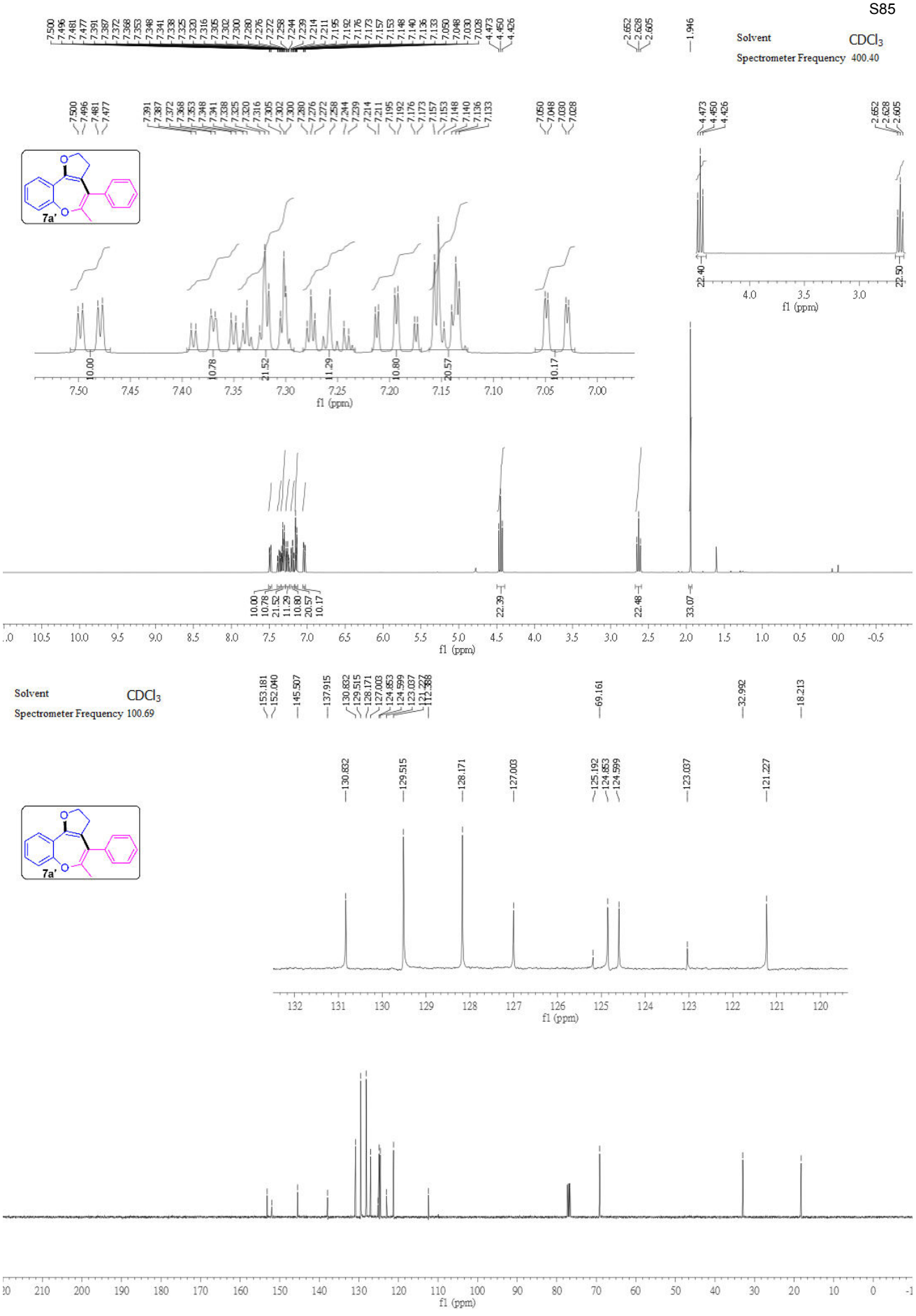

Solvent CDCl3
Spectrometer Frequency 100.69
8a
f1 (ppm)

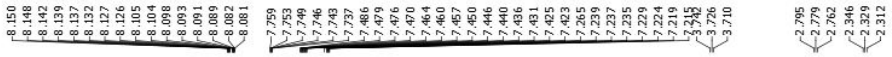


Filename	= SGC_CN_Final_Proton-1-3.jd	Spectrometer	= DELTA2_NMR	Tri_Freq	= 399.78219838[MHz]
Author	= delta			Tri_Offset	= 5[ppm]
Experiment	= proton.jxp	Field_Strength	= 9.389766[T] (400[MHz])	Clipped	= FALSE
Sample_Id	= SGC/CN/Final	X_Acq_Duration	= 2.18365952[s]	Scans	= 14
Solvent	= CHLOROFORM-D	X_Domain	= 1H	Total_Scans	= 14
Creation_Time	= 18-JUL-2016 09:23:00	X_Freq	= 399.78219838[MHz]		
Revision_Time	= 18-JUL-2016 10:40:22	X_Offset	= 5[ppm]	Relaxation_Delay	= 5[s]
Current_Time	= 18-JUL-2016 10:41:01	X_Points	= 16384	Recvr_Gain	= 40
		X_Prescans	= 1	Temp_Get	= 26.1[dC]
Comment	= single_pulse	X_Resolution	= 0.45794685[Hz]	X_90_Width	= 12.795[us]
Data_Format	= 1D COMPLEX	X_Sweep	= 7.5030012[kHz]	X_Acq_Time	= 2.18365952[s]
Dim_Size	= 13107	X_Sweep_Clipped	= 6.00240096[kHz]	X_Angle	= 45[deg]
Dim_Title	= Proton	Irr_Domain	= Proton	X_Atn	= 2.4[dB]
Dim_Units	= [ppm]	Irr_Freq	= 399.78219838[MHz]	X_Pulse	= 6.3975[us]
Dimensions	= X	Irr_Offset	= 5[ppm]	Irr_Mode	= Off
Site	= JNM-ECS400	Tri_Domain	= Proton	Tri_Mode	= Off

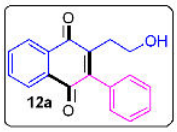


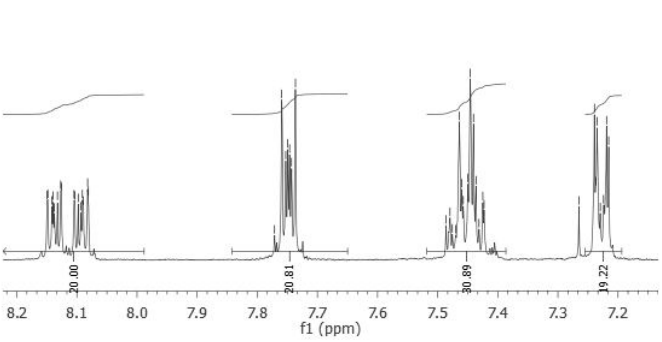
Filename	= SGC_CN_Final_Carbon-1-3.jd	Spectrometer	= DELTA2_NMR	Scans	= 1655
Author	= delta			Total_Scans	= 1655
Experiment	= carbon.jxp	Field_Strength	= 9.389766[T] (400[MHz])		
Sample_Id	= SGC/CN/Final	X_Acq_Duration	= 1.04333312[s]	Relaxation_Delay	= 2[s]
Solvent	= CHLOROFORM-D	X_Domain	= 13C	Recvr_Gain	= 60
Creation_Time	= 18-JUL-2016 09:27:11	X_Freq	= 100.52530333[MHz]	Temp_Get	= 26.2[dC]
Revision_Time	= 18-JUL-2016 10:45:21	X_Offset	= 100[ppm]	X_90_Width	= 10.33[us]
Current_Time	= 18-JUL-2016 10:46:11	X_Points	= 32768	X_Acq_Time	= 1.04333312[s]
		X_Prescans	= 4	X_Angle	= 30[deg]
Comment	= single pulse decoupled gat	X_Resolution	= 0.95846665[Hz]	X_Atn	= 5.3[dB]
Data_Format	= 1D COMPLEX	X_Sweep	= 31.40703518[kHz]	X_Pulse	= 3.44333333[us]
Dim_Size	= 26214	X_Sweep_Clipped	= 25.12562814[kHz]	Irr_Atn_Dec	= 21.473[dB]
Dim_Title	= Carbon13	Irr_Domain	= Proton	Irr_Atn_Noe	= 21.473[dB]
Dim_Units	= [ppm]	Irr_Freq	= 399.78219838[MHz]	Irr_Noise	= WALTZ
Dimensions	= X	Irr_Offset	= 5[ppm]	Irr_Pwidth	= 0.115[ms]
Site	= JNM-ECS400	Clipped	= FALSE	Decoupling	= TRUE

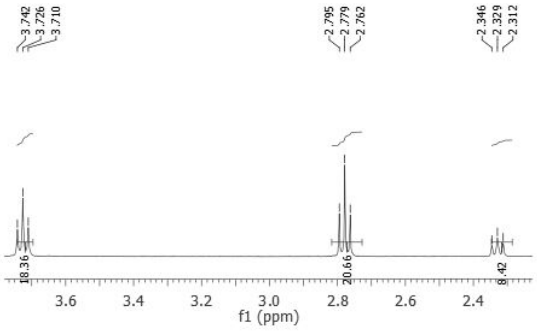

Solvent CDCl3
Spectrometer Frequency 400.40
7a'
f1 (ppm)
Solvent CDCl3
Spectrometer Frequency 100.69
7a'
f1 (ppm)

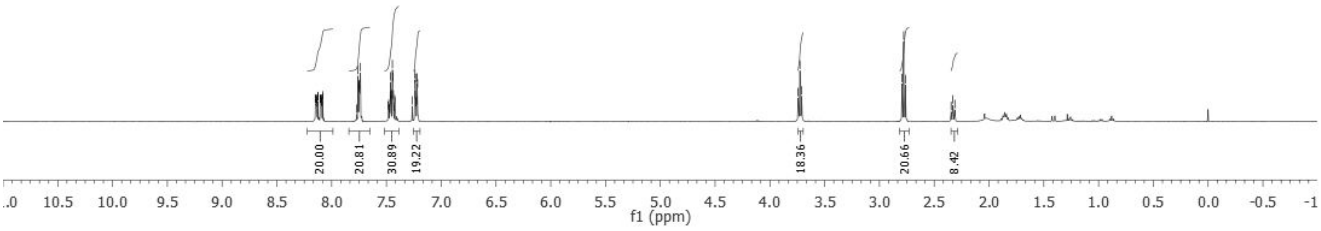


Solvent $CDCl_3$
Spectrometer Frequency 400.40

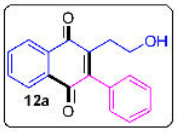


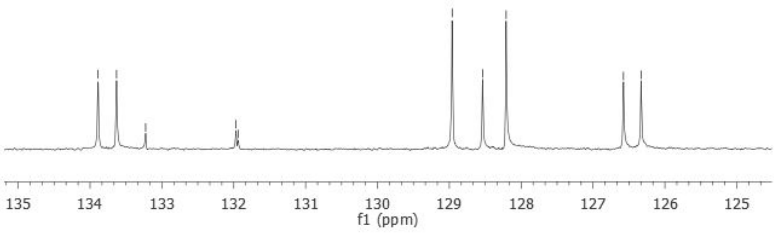


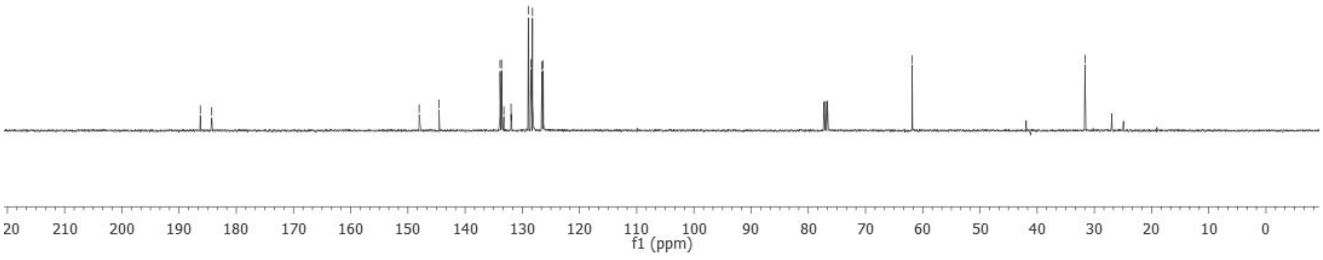


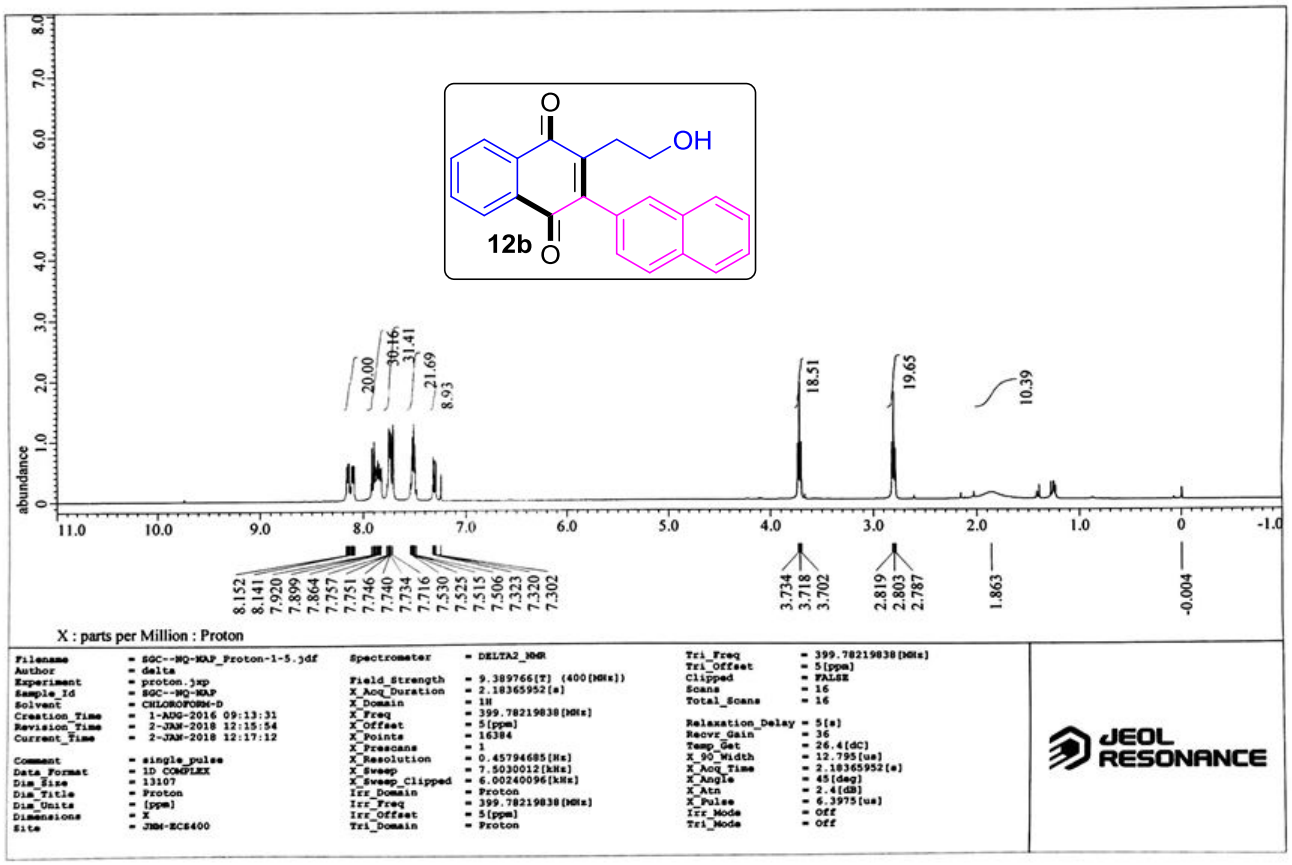


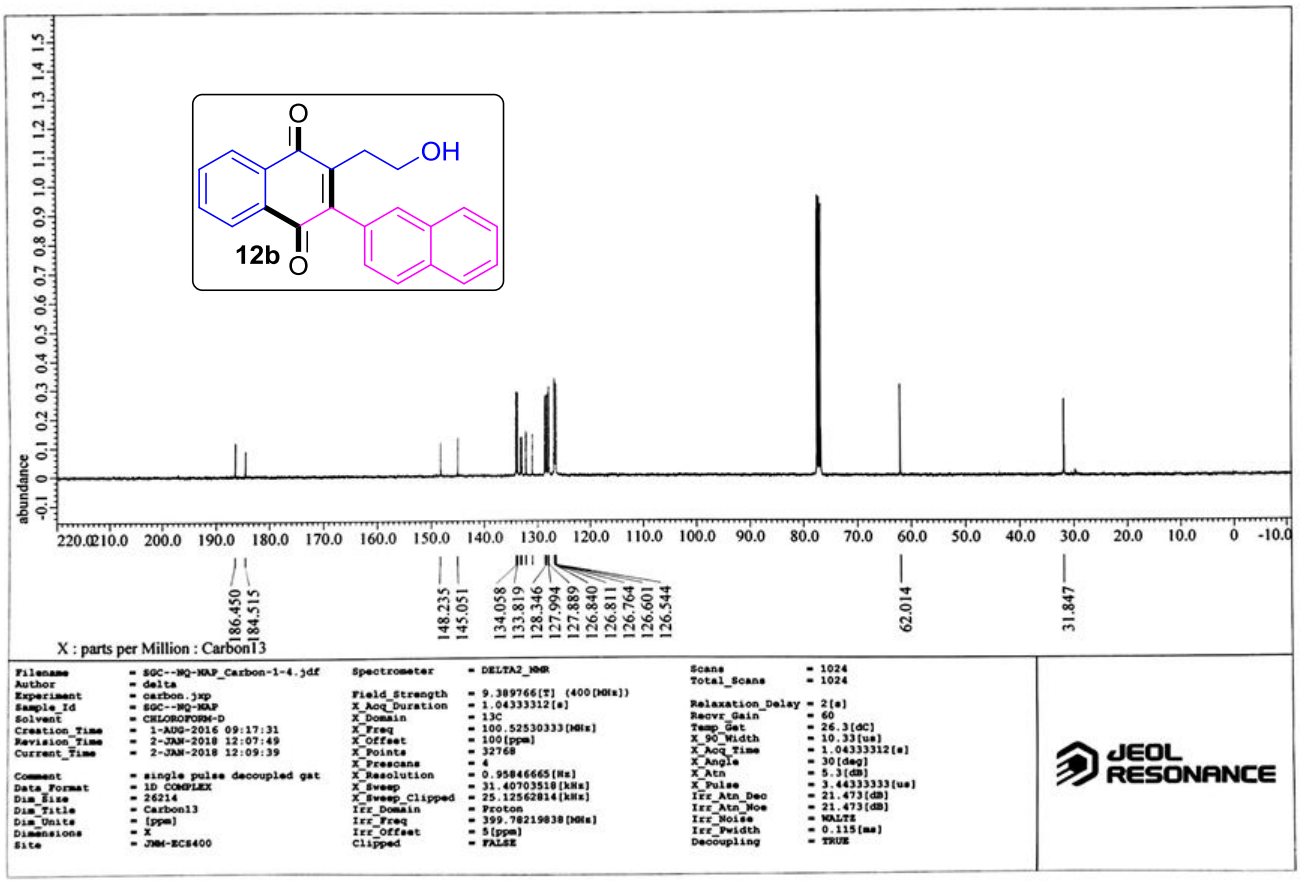
Solvent $CDCl_3$
Spectrometer Frequency 100.69

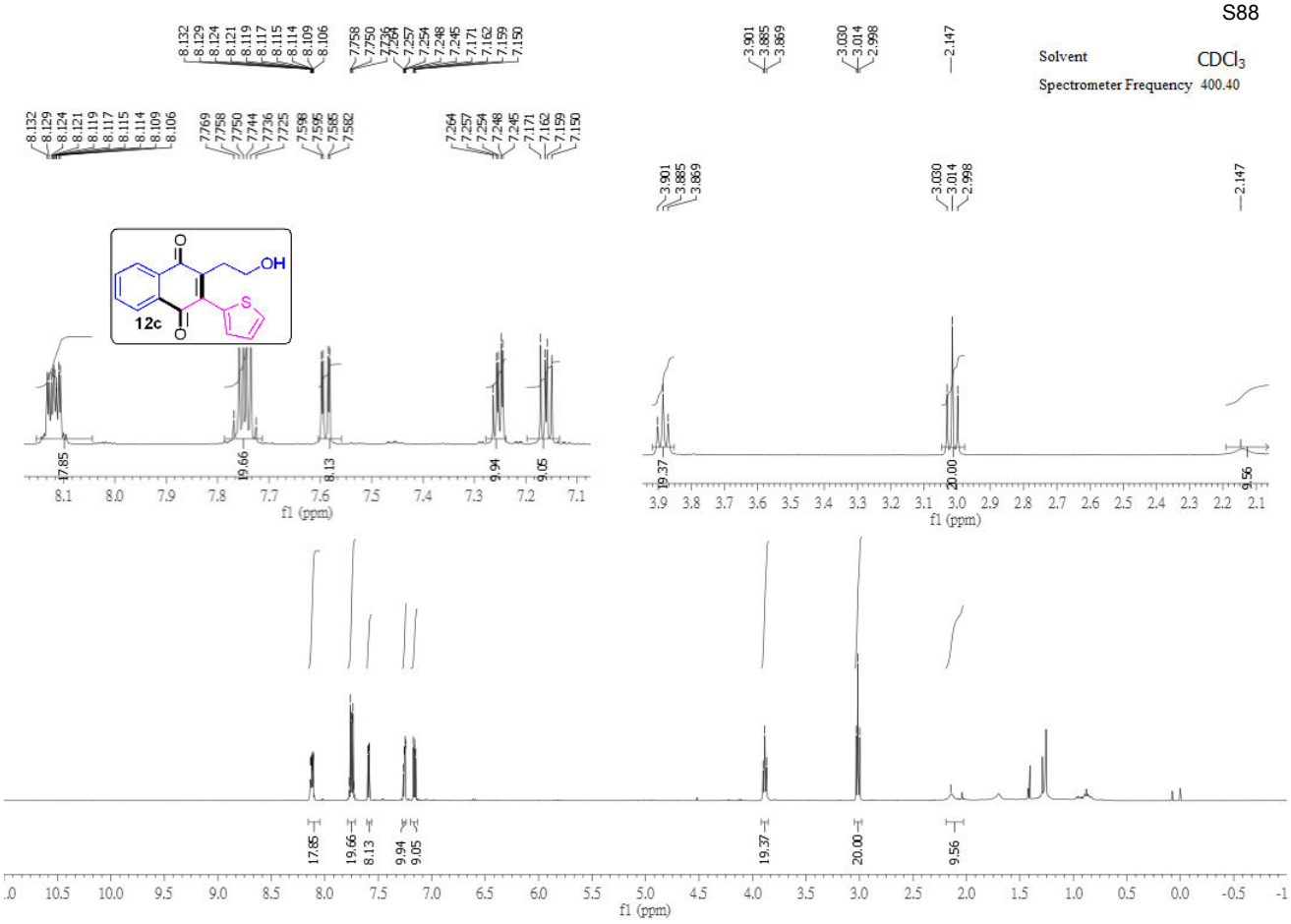


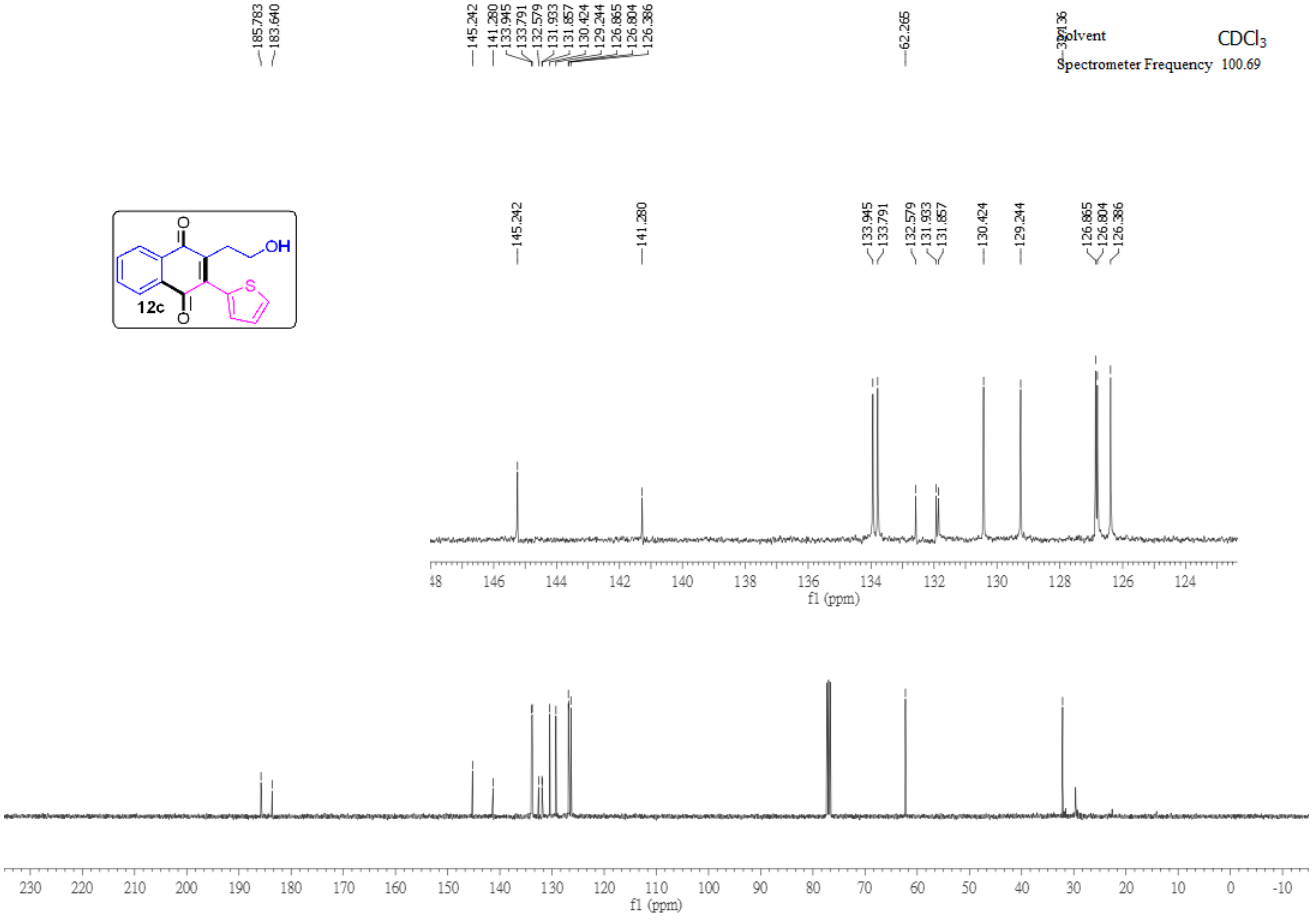


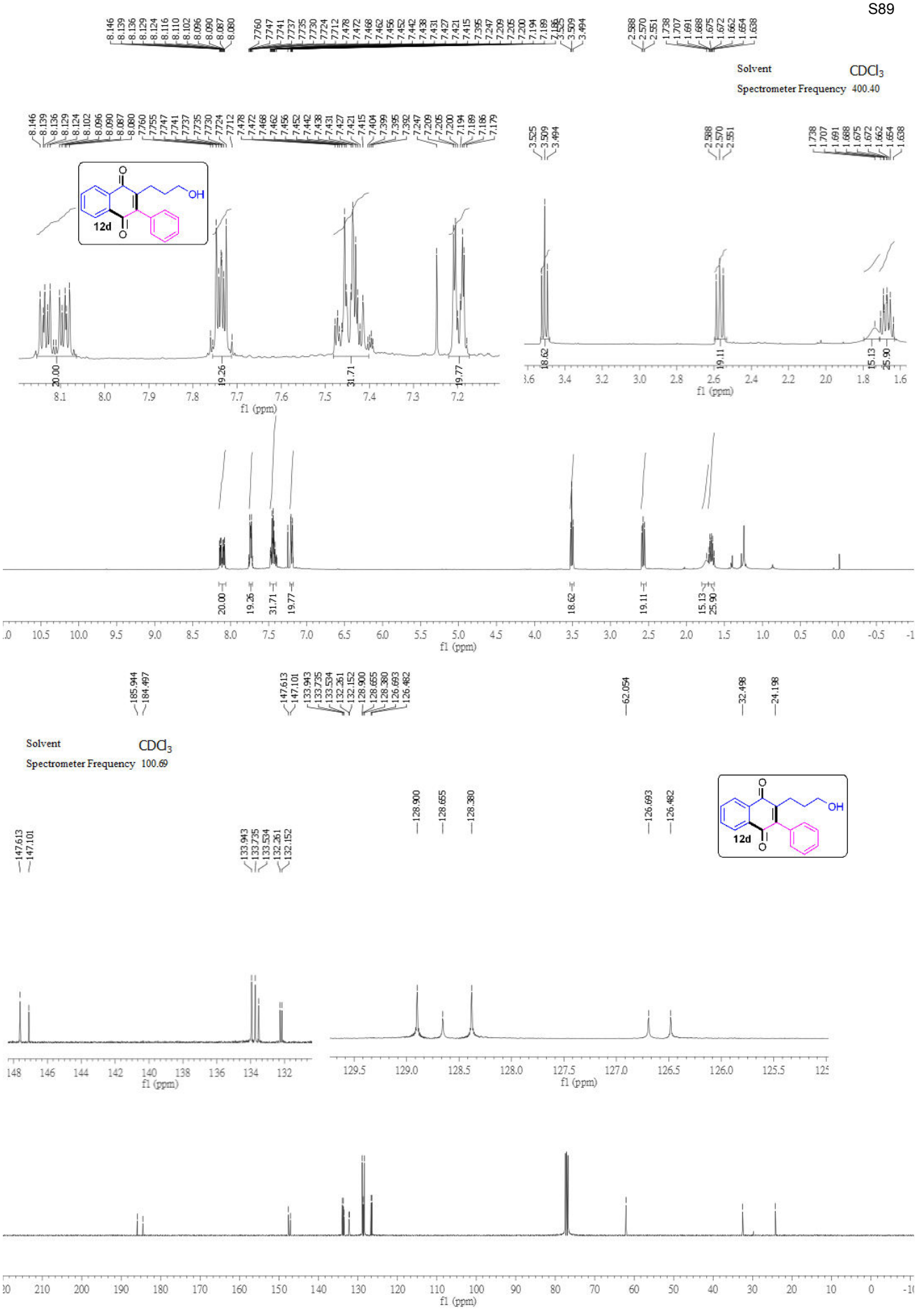


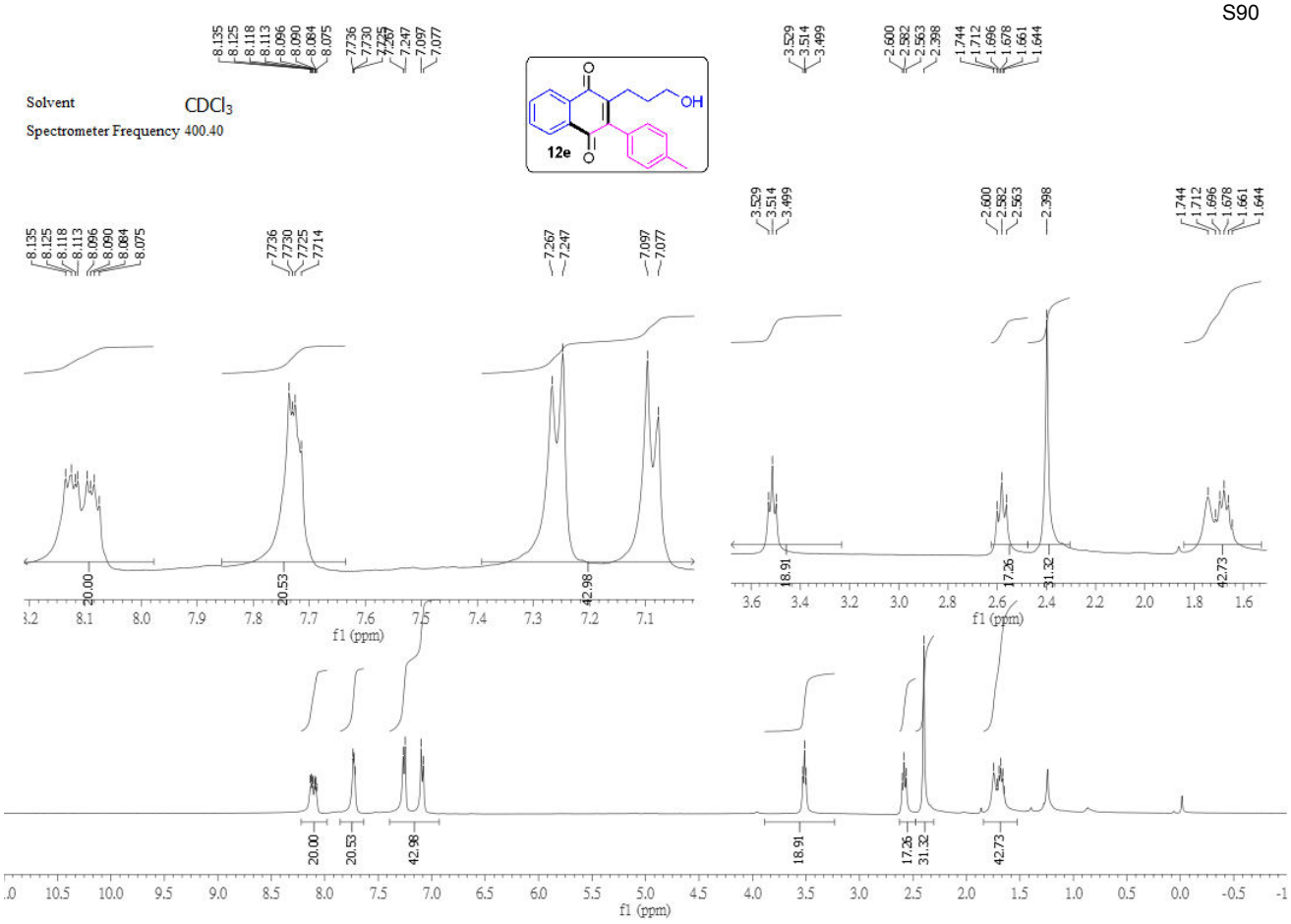

O
OH
12b
O
20.00
30.46
31.41
21.69
8.93
18.51
19.65
10.39
abundance
8.152
8.141
7.920
7.899
7.864
7.757
7.751
7.746
7.740
7.734
7.716
7.530
7.525
7.515
7.506
7.323
7.320
7.302
3.734
3.718
3.702
2.819
2.803
2.787
1.863
-0.004
X : parts per Million : Proton
Filename = SGC--MQ-MAP_Proton-1-5.jdf
Author = delta
Experiment = proton.jxp
Sample_Id = SGC--MQ-MAP
Solvent = CHLOROFORM-D
Creation_Time = 1-AUG-2016 09:13:31
Revision_Time = 2-JAN-2018 12:15:54
Current_Time = 2-JAN-2018 12:17:12
Comment = single_pulse
Data_Format = 1D COMPLEX
Dim_Size = 13107
Dim_Title = Proton
Dim_Units = [ppm]
Dimensions = X
Site = JNM-ECS400
Spectrometer = DELTA2_NMR
Field_Strength = 9.389766[T] (400[MHz])
X_Acq_Duration = 2.18365952[s]
X_Domain = 1H
X_Freq = 399.78219838[MHz]
X_Offset = 5[ppm]
X_Points = 16384
X_Prescans = 1
X_Resolution = 0.45794685[Hz]
X_Sweep = 7.5030012[kHz]
X_Sweep_Clipped = 6.00240096[kHz]
Irr_Domain = Proton
Irr_Freq = 399.78219838[MHz]
Irr_Offset = 5[ppm]
Tri_Domain = Proton
Tri_Freq = 399.78219838[MHz]
Tri_Offset = 5[ppm]
Clipped = FALSE
Scans = 16
Total_Scans = 16
Relaxation_Delay = 5[s]
Recvr_Gain = 36
Temp_Get = 26.4[dC]
X_90_Width = 12.795[us]
X_Acq_Time = 2.18365952[s]
X_Angle = 45[deg]
X_Atn = 2.4[dB]
X_Pulse = 6.3975[us]
Irr_Mode = Off
Tri_Mode = Off
JEOL RESONANCE

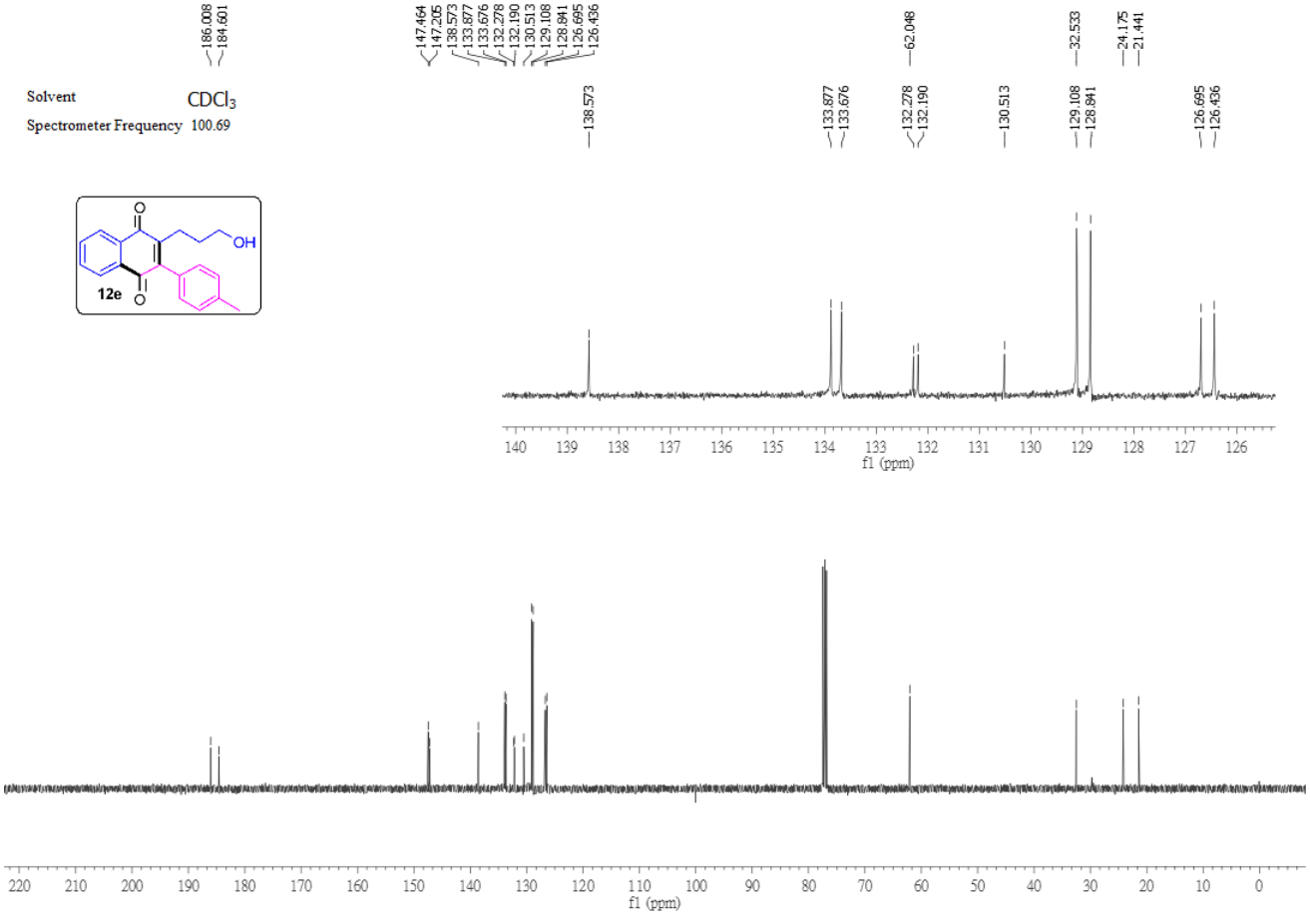

O
OH
12b
O
abundance
186.450
184.515
148.235
145.051
134.058
133.819
128.346
127.994
127.889
126.840
126.811
126.764
126.601
126.544
62.014
31.847
X : parts per Million : Carbon13
Filename = SGC--MQ-MAP_Carbon-1-4.jdf
Author = delta
Experiment = carbon.jxp
Sample_Id = SGC--MQ-MAP
Solvent = CHLOROFORM-D
Creation_Time = 1-AUG-2016 09:17:31
Revision_Time = 2-JAN-2018 12:07:49
Current_Time = 2-JAN-2018 12:09:39
Comment = single pulse decoupled gat
Data_Format = 1D COMPLEX
Dim_Size = 26214
Dim_Title = Carbon13
Dim_Units = [ppm]
Dimensions = X
Site = JNM-ECS400
Spectrometer = DELTA2_NMR
Field_Strength = 9.389766[T] (400[MHz])
X_Acq_Duration = 1.04333312[s]
X_Domain = 13C
X_Freq = 100.52530333[MHz]
X_Offset = 100[ppm]
X_Points = 32768
X_Prescans = 4
X_Resolution = 0.95846665[Hz]
X_Sweep = 31.40703518[kHz]
X_Sweep_Clipped = 25.12562814[kHz]
Irr_Domain = Proton
Irr_Freq = 399.78219838[MHz]
Irr_Offset = 5[ppm]
Clipped = FALSE
Scans = 1024
Total_Scans = 1024
Relaxation_Delay = 2[s]
Recvr_Gain = 60
Temp_Get = 26.3[dC]
X_90_Width = 10.33[us]
X_Acq_Time = 1.04333312[s]
X_Angle = 30[deg]
X_Atn = 5.3[dB]
X_Pulse = 3.44333333[us]
Irr_Atn_Dec = 21.473[dB]
Irr_Atn_Noe = 21.473[dB]
Irr_Noise = WALTZ
Irr_Pwidth = 0.115[ms]
Decoupling = TRUE
JEOL RESONANCE


Solvent CDCl3
Spectrometer Frequency 400.40
12c
f1 (ppm)


Solvent CDCl3
Spectrometer Frequency 100.69
12c
f1 (ppm)

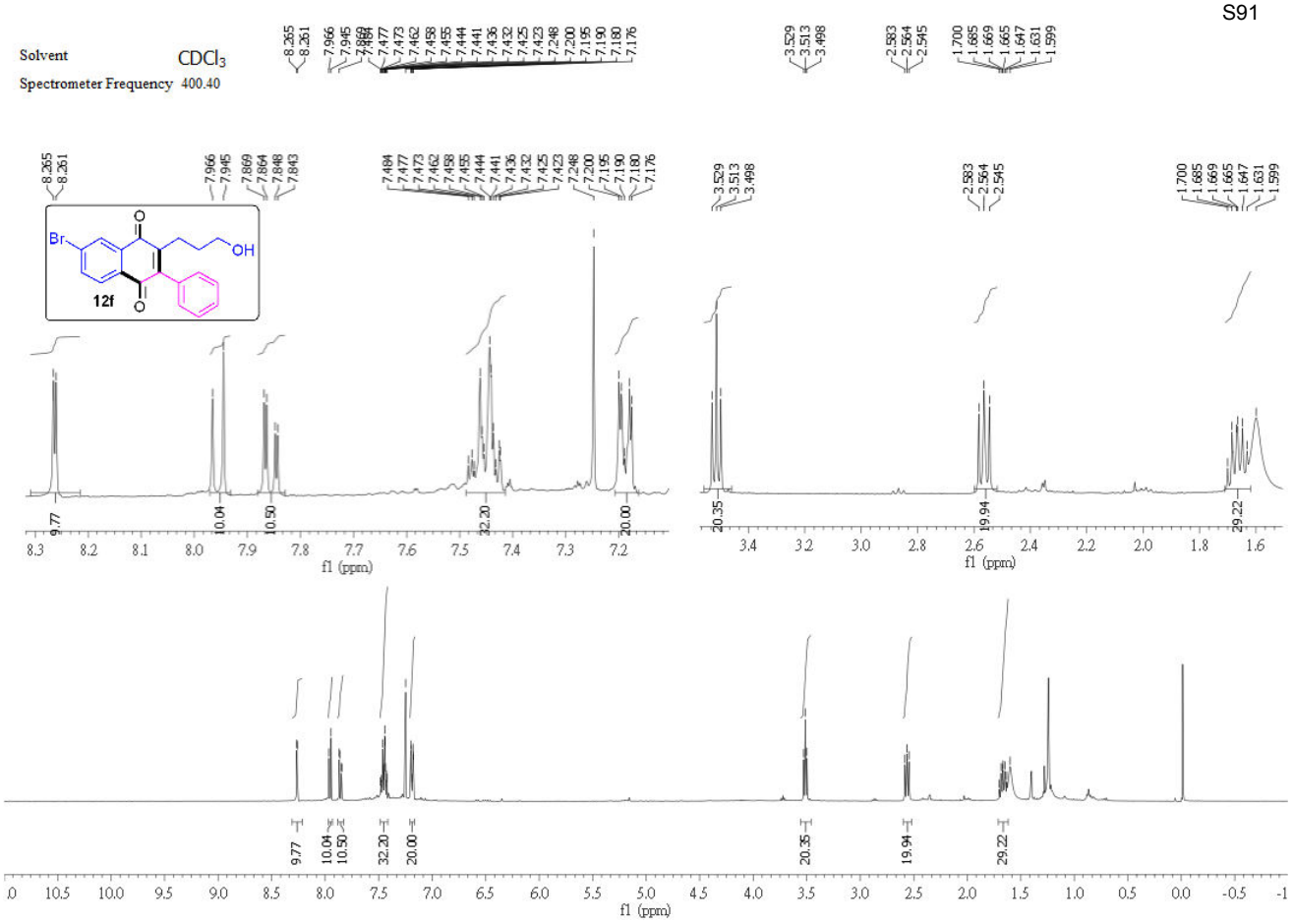

Solvent CDCl3
Spectrometer Frequency 400.40
12d
OH
f1 (ppm)
Solvent CDCl3
Spectrometer Frequency 100.69
12d
OH
f1 (ppm)

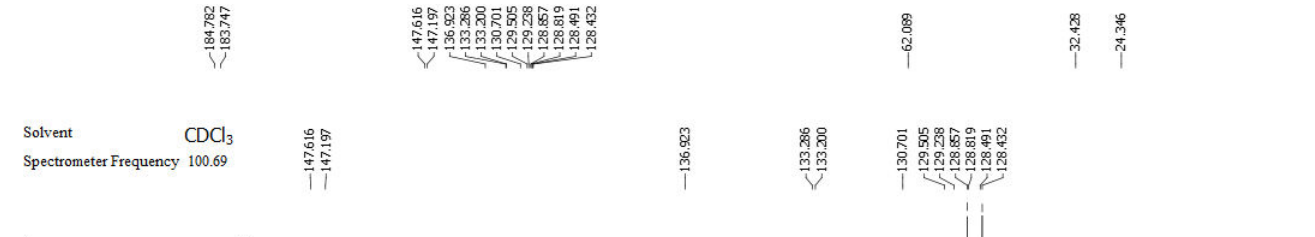

Solvent CDCl3
Spectrometer Frequency 400.40
12e
f1 (ppm)


Solvent CDCl3
Spectrometer Frequency 100.69
12e
f1 (ppm)

Solvent $CDCl_3$

Spectrometer Frequency 400.40



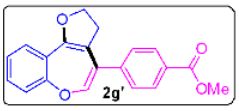


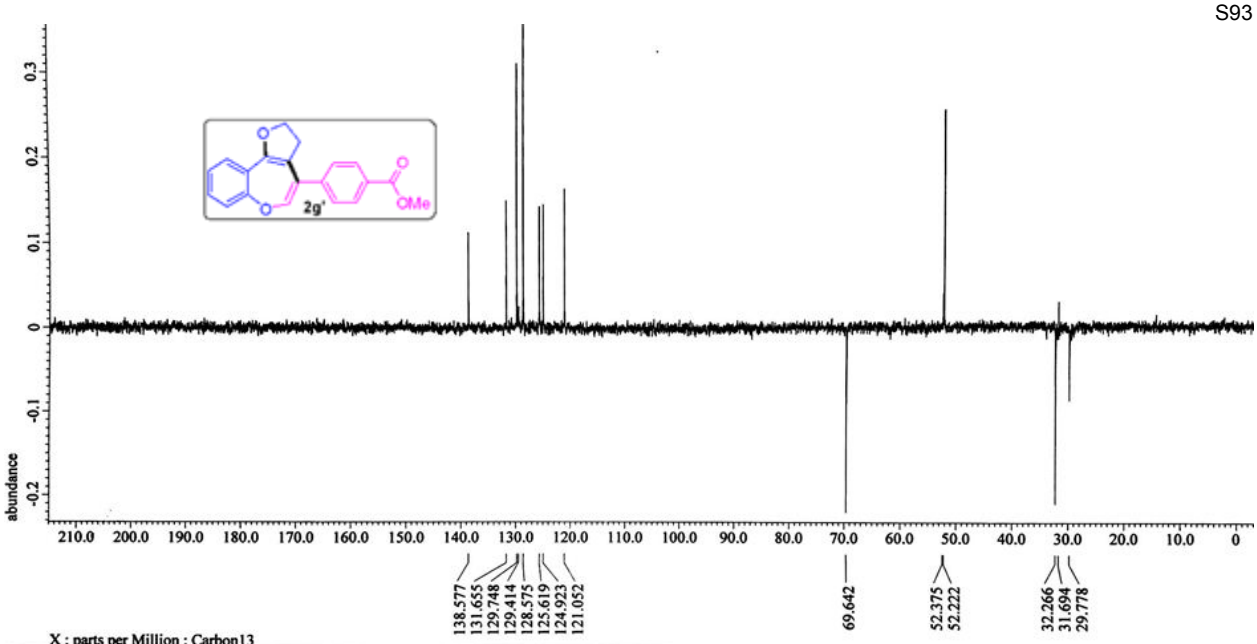
Solvent $CDCl_3$

Spectrometer Frequency 100.69

Solvent $CDCl_3$
Spectrometer Frequency 400.40

Solvent $CDCl_3$
Spectrometer Frequency 100.69

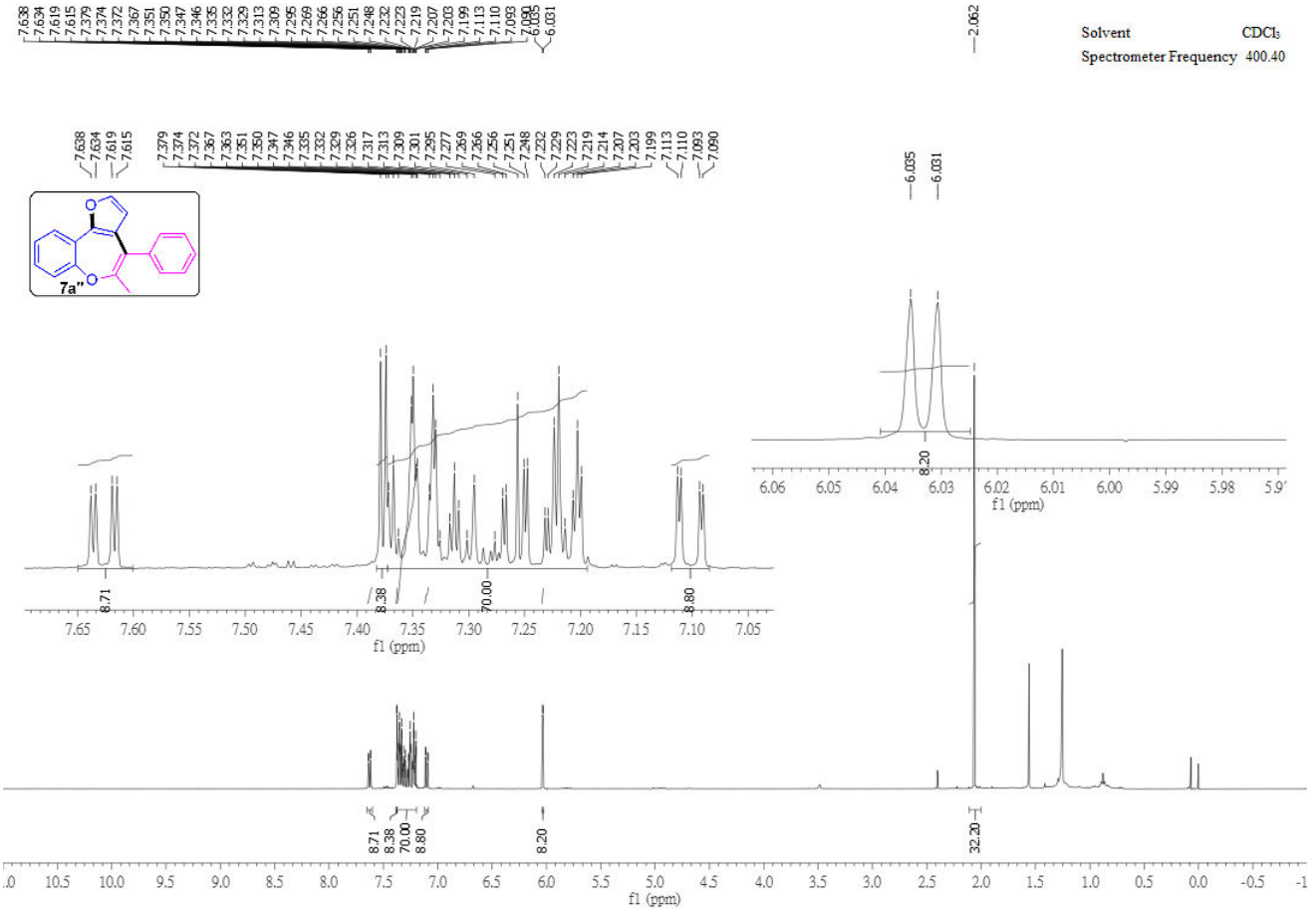




X : parts per Million : Carbon13

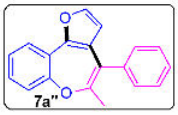
Filename	= SGC_COOMe_gnt_DEPT135deg-	Spectrometer	= DELTA2_NMR	Scans	= 512
Author	= delta			Total_Scans	= 512
Experiment	= dept.jxp	Field_Strength	= 9.389766[T] (400[MHz])		
Sample_Id	= SGC/COOMe/gnt	X_Acq_Duration	= 1.04333312[s]	Relaxation_Delay	= 2[s]
Solvent	= CHLOROFORM-D	X_Domain	= 13C	Recvr_Gain	= 60
Creation_Time	= 13-JUL-2016 12:29:06	X_Freq	= 100.52530333[MHz]	Temp_Get	= 24.9[dC]
Revision_Time	= 13-JUL-2016 12:47:38	X_Offset	= 100[ppm]	X_Acq_Time	= 1.04333312[s]
Current_Time	= 13-JUL-2016 12:49:43	X_Points	= 32768	X_Atn	= 5.3[dB]
		X_Prescans	= 4	X_Pulse	= 10.33[us]
Comment	= DEPT with decoupling	X_Resolution	= 0.95846665[Hz]	Irr_Atn	= 2.4[dB]
Data_Format	= 1D COMPLEX	X_Sweep	= 31.40703518[kHz]	Irr_Atn_Dec	= 21.473[dB]
Dim_Size	= 26214	X_Sweep_Clipped	= 25.12562814[kHz]	Irr_Noise	= WALTZ
Dim_Title	= Carbon13	Irr_Domain	= Proton	Irr_Pulse	= 12.795[us]
Dim_Units	= [ppm]	Irr_Freq	= 399.78219838[MHz]	Irr_Pwidth	= 0.115[ms]
Dimensions	= X	Irr_Offset	= 5[ppm]	Base_Line_Correct	= TRUE
Site	= JNM-ECS400	Clipped	= FALSE	Decoupling	= TRUE

JEOL RESONANCE

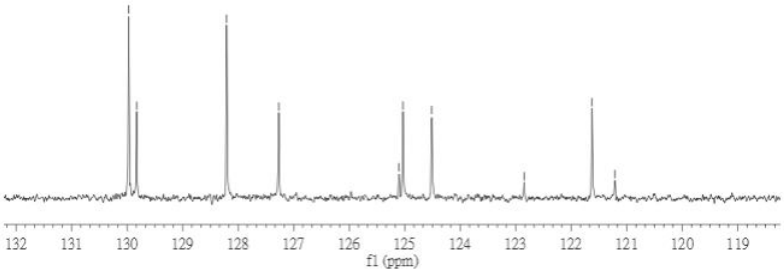


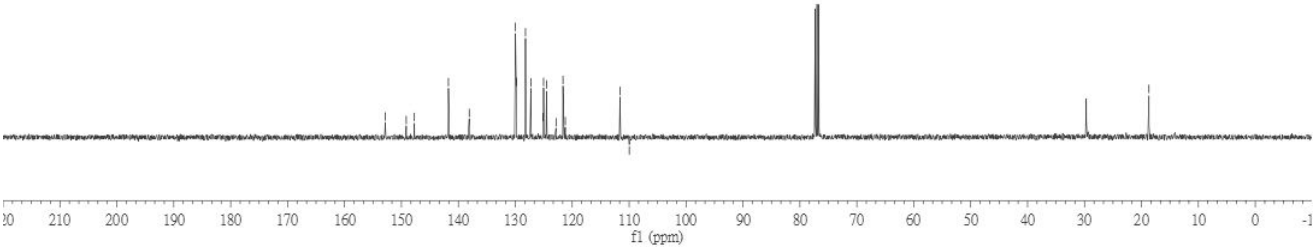
Solvent $CDCl_3$
Spectrometer Frequency 100.69

152.842
149.155
147.718
141.742
138.096
129.970
129.828
128.206
127.267
125.101
125.031
124.512
121.625
121.806
109.979
18.679



129.970
129.828
128.206
127.267
125.101
125.031
124.512
122.847
121.625
121.211





checkCIF/PLATON report

Structure factors have been supplied for datablock(s) agau4ome

THIS REPORT IS FOR GUIDANCE ONLY. IF USED AS PART OF A REVIEW PROCEDURE FOR PUBLICATION, IT SHOULD NOT REPLACE THE EXPERTISE OF AN EXPERIENCED CRYSTALLOGRAPHIC REFEREE.

No syntax errors found. CIF dictionary Interpreting this report

Datablock: agau4ome

```
Bond precision:  C-C = 0.0026 A          Wavelength=0.71073

Cell:          a=9.9142(7)       b=9.9565(8)      c=15.2208(13)
               alpha=87.468(7)   beta=86.546(6)   gamma=88.917(6)
Temperature:   150 K
```

	Calculated	Reported
Volume	1498.1(2)	1498.1(2)
Space group	P -1	P -1
Hall group	-P 1	-P 1
Moiety formula	C20 H18 O3	C20 H18 O3
Sum formula	C20 H18 O3	C20 H18 O3
Mr	306.34	306.34
Dx,g cm-3	1.358	1.358
Z	4	4
Mu (mm-1)	0.090	0.090
F000	648.0	648.0
F000’	648.32	
h,k,lmax	13,13,21	13,13,20
Nref	8322	6914
Tmin,Tmax	0.955,0.965	0.997,1.000
Tmin’	0.952	

```
Correction method= # Reported T Limits: Tmin=0.997 Tmax=1.000
AbsCorr = MULTI-SCAN

Data completeness= 0.831          Theta(max)= 29.467

R(reflections)= 0.0545( 4920)     wR2(reflections)= 0.1413( 6914)

S = 1.032                 Npar= 450
```

The following ALERTS were generated. Each ALERT has the format
test-name_ALERT_alert-type_alert-level.
Click on the hyperlinks for more details of the test.

Alert level A

PLAT183_ALERT_1_A Missing _cell_measurement_reflns_used Value .... Please Do !
PLAT184_ALERT_1_A Missing _cell_measurement_theta_min Value ..... Please Do !
PLAT185_ALERT_1_A Missing _cell_measurement_theta_max Value ..... Please Do !

Alert level C

PLAT410_ALERT_2_C Short Intra H...H Contact H23B ..H22D . 1.90 Ang.
PLAT906_ALERT_3_C Large K Value in the Analysis of Variance ..... 3.084 Check
PLAT910_ALERT_3_C Missing # of FCF Reflection(s) Below Theta(Min). 8 Note

Alert level G

PLAT301_ALERT_3_G Main Residue Disorder .....(Resd 1) 9% Note
PLAT898_ALERT_4_G Second Reported H-M Symbol in CIF Ignored ..... ! Check
PLAT912_ALERT_4_G Missing # of FCF Reflections Above STh/L= 0.600 1397 Note
PLAT913_ALERT_3_G Missing # of Very Strong Reflections in FCF .... 1 Note
PLAT978_ALERT_2_G Number C-C Bonds with Positive Residual Density. 7 Info

3 **ALERT level A** = Most likely a serious problem - resolve or explain
0 **ALERT level B** = A potentially serious problem, consider carefully
3 **ALERT level C** = Check. Ensure it is not caused by an omission or oversight
5 **ALERT level G** = General information/check it is not something unexpected

3 ALERT type 1 CIF construction/syntax error, inconsistent or missing data
2 ALERT type 2 Indicator that the structure model may be wrong or deficient
4 ALERT type 3 Indicator that the structure quality may be low
2 ALERT type 4 Improvement, methodology, query or suggestion
0 ALERT type 5 Informative message, check

It is advisable to attempt to resolve as many as possible of the alerts in all categories. Often the minor alerts point to easily fixed oversights, errors and omissions in your CIF or refinement strategy, so attention to these fine details can be worthwhile. In order to resolve some of the more serious problems it may be necessary to carry out additional measurements or structure refinements. However, the purpose of your study may justify the reported deviations and the more serious of these should normally be commented upon in the discussion or experimental section of a paper or in the "special_details" fields of the CIF. checkCIF was carefully designed to identify outliers and unusual parameters, but every test has its limitations and alerts that are not important in a particular case may appear. Conversely, the absence of alerts does not guarantee there are no aspects of the results needing attention. It is up to the individual to critically assess their own results and, if necessary, seek expert advice.

Publication of your CIF in IUCr journals

A basic structural check has been run on your CIF. These basic checks will be run on all CIFs submitted for publication in IUCr journals (*Acta Crystallographica, Journal of Applied Crystallography, Journal of Synchrotron Radiation*); however, if you intend to submit to *Acta Crystallographica Section C* or *E* or *IUCrData*, you should make sure that full publication checks are run on the final version of your CIF prior to submission.

Publication of your CIF in other journals

Please refer to the *Notes for Authors* of the relevant journal for any special instructions relating to CIF submission.

Validation response form

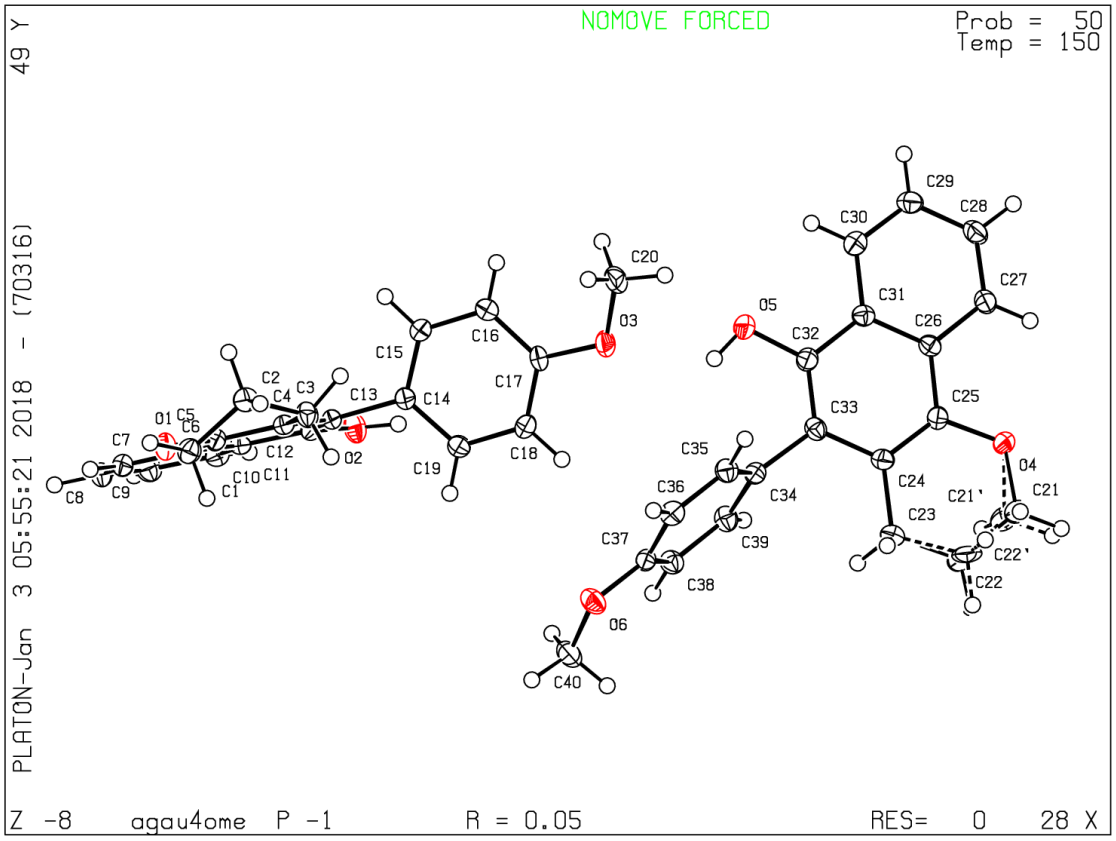
Please find below a validation response form (VRF) that can be filled in and pasted into your CIF.

```
# start Validation Reply Form
_vrf_PLAT183_agau4ome
;
PROBLEM: Missing _cell_measurement_reflns_used Value ....     Please Do !
RESPONSE: ...
;
_vrf_PLAT184_agau4ome
;
PROBLEM: Missing _cell_measurement_theta_min Value ......     Please Do !
RESPONSE: ...
;
_vrf_PLAT185_agau4ome
;
PROBLEM: Missing _cell_measurement_theta_max Value ......     Please Do !
RESPONSE: ...
;
_vrf_PLAT410_agau4ome
;
PROBLEM: Short Intra H...H Contact H23B     ..H22D      .       1.90 Ang.
RESPONSE: ...
;
_vrf_PLAT906_agau4ome
;
PROBLEM: Large K Value in the Analysis of Variance ......      3.084 Check
RESPONSE: ...
;
_vrf_PLAT910_agau4ome
```

```
;
PROBLEM: Missing # of FCF Reflection(s) Below Theta(Min).          8 Note
RESPONSE: ...
;
# end Validation Reply Form
```

PLATON version of 13/12/2017; check.def file version of 12/12/2017

Datablock agau4ome - ellipsoid plot



checkCIF/PLATON report

Structure factors have been supplied for datablock(s) agptsme

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No syntax errors found. CIF dictionary Interpreting this report

Datablock: agptsme

Bond precision: C-C = 0.0038 A Wavelength=0.71073

Cell: a=14.0810(14) b=14.4862(11) c=16.1120(15)
alpha=90 beta=113.689(12) gamma=90
Temperature: 297 K

	Calculated	Reported
Volume	3009.6(5)	3009.6(5)
Space group	C 2/c	C 2/c
Hall group	-C 2yc	-C 2yc
Moiety formula	C20 H18 O	C20 H18 O
Sum formula	C20 H18 O	C20 H18 O
Mr	274.34	274.34
Dx,g cm-3	1.211	1.211
Z	8	8
Mu (mm-1)	0.073	0.073
F000	1168.0	1168.0
F000’	1168.47	
h,k,lmax	19,20,22	18,19,21
Nref	4148	3514
Tmin,Tmax	0.966,0.978	0.975,1.000
Tmin’	0.966	

Correction method= # Reported T Limits: Tmin=0.975 Tmax=1.000
AbsCorr = MULTI-SCAN

Data completeness= 0.847 Theta(max)= 29.389

R(reflections)= 0.0714(2080) wR2(reflections)= 0.2261(3514)

S = 1.030 Npar= 191

The following ALERTS were generated. Each ALERT has the format
test-name_ALERT_alert-type_alert-level.
Click on the hyperlinks for more details of the test.

Alert level C

```
PLAT230_ALERT_2_C Hirshfeld Test Diff for   C2       --C3        .        5.5 s.u.
PLAT906_ALERT_3_C Large K Value in the Analysis of Variance ......      9.949 Check
PLAT906_ALERT_3_C Large K Value in the Analysis of Variance ......      2.234 Check
```

Alert level G

```
PLAT003_ALERT_2_G Number of Uiso or Uij Restrained non-H Atoms ...          2 Report
PLAT072_ALERT_2_G SHELXL First  Parameter in WGHT  Unusually Large       0.10 Report
PLAT177_ALERT_4_G The CIF-Embedded .res File Contains DELU Records          1 Report
PLAT860_ALERT_3_G Number of Least-Squares Restraints .............         1 Note
PLAT898_ALERT_4_G Second Reported H-M Symbol in CIF Ignored ......         ! Check
PLAT910_ALERT_3_G Missing # of FCF Reflection(s) Below Theta(Min).         4 Note
PLAT912_ALERT_4_G Missing # of FCF Reflections Above STh/L=  0.600        608 Note
PLAT978_ALERT_2_G Number C-C Bonds with Positive Residual Density.         2 Info
```

```
   0 ALERT level A = Most likely a serious problem - resolve or explain
   0 ALERT level B = A potentially serious problem, consider carefully
   3 ALERT level C = Check. Ensure it is not caused by an omission or oversight
   8 ALERT level G = General information/check it is not something unexpected

   0 ALERT type 1 CIF construction/syntax error, inconsistent or missing data
   4 ALERT type 2 Indicator that the structure model may be wrong or deficient
   4 ALERT type 3 Indicator that the structure quality may be low
   3 ALERT type 4 Improvement, methodology, query or suggestion
   0 ALERT type 5 Informative message, check
```

Validation response form

Please find below a validation response form (VRF) that can be filled in and pasted into your CIF.

```
# start Validation Reply Form
_vrf_PLAT230_agptsme
;
PROBLEM: Hirshfeld Test Diff for   C2       --C3        .        5.5 s.u.
RESPONSE: ...
;
_vrf_PLAT906_agptsme
;
PROBLEM: Large K Value in the Analysis of Variance ......      9.949 Check
RESPONSE: ...
;
# end Validation Reply Form
```

It is advisable to attempt to resolve as many as possible of the alerts in all categories. Often the minor alerts point to easily fixed oversights, errors and omissions in your CIF or refinement strategy, so attention to these fine details can be worthwhile. In order to resolve some of the more serious problems it may be necessary to carry out additional measurements or structure refinements. However, the purpose of your study may justify the reported deviations and the more serious of these should normally be commented upon in the discussion or experimental section of a paper or in the "special_details" fields of the CIF. checkCIF was carefully designed to identify outliers and unusual parameters, but every test has its limitations and alerts that are not important in a particular case may appear. Conversely, the absence of alerts does not guarantee there are no aspects of the results needing attention. It is up to the individual to critically assess their own results and, if necessary, seek expert advice.

Publication of your CIF in IUCr journals

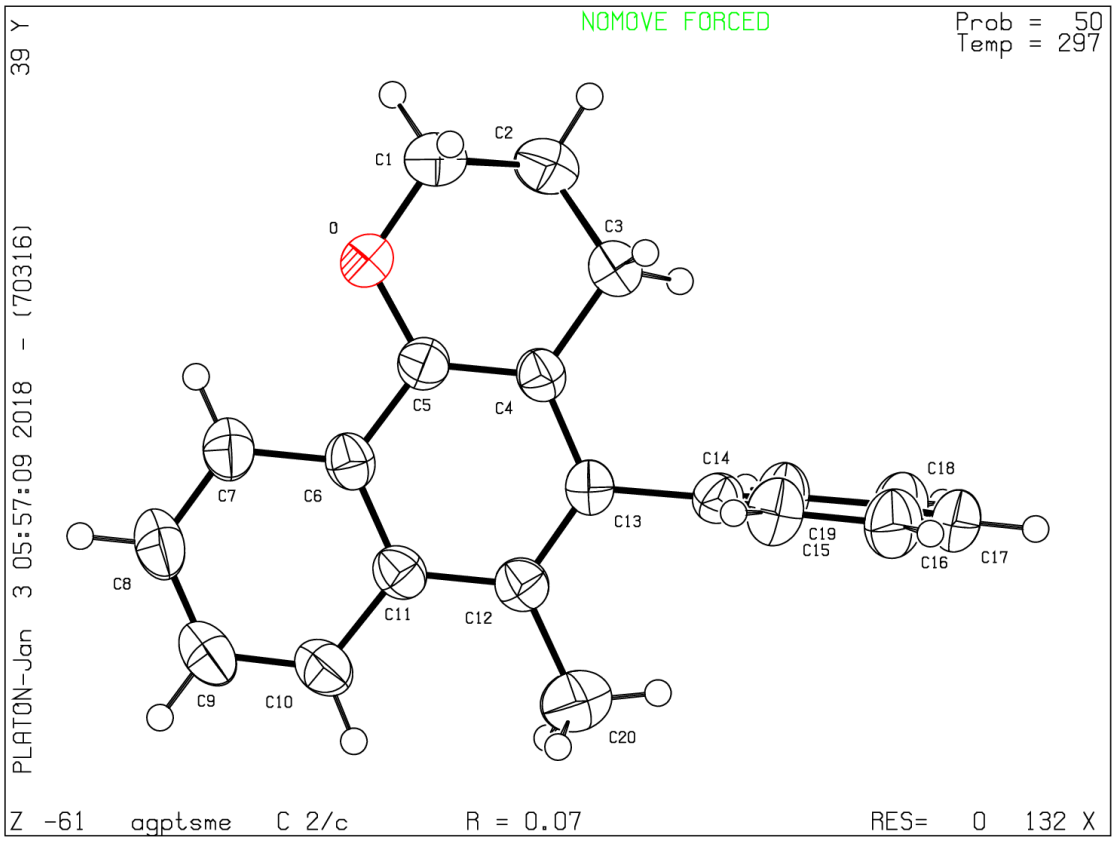
A basic structural check has been run on your CIF. These basic checks will be run on all CIFs submitted for publication in IUCr journals (*Acta Crystallographica, Journal of Applied Crystallography, Journal of Synchrotron Radiation*); however, if you intend to submit to *Acta Crystallographica Section C* or *E* or *IUCrData*, you should make sure that full publication checks are run on the final version of your CIF prior to submission.

Publication of your CIF in other journals

Please refer to the *Notes for Authors* of the relevant journal for any special instructions relating to CIF submission.

PLATON version of 13/12/2017; check.def file version of 12/12/2017

Datablock agptsme - ellipsoid plot



checkCIF/PLATON report

Structure factors have been supplied for datablock(s) pmeint

THIS REPORT IS FOR GUIDANCE ONLY. IF USED AS PART OF A REVIEW PROCEDURE FOR PUBLICATION, IT SHOULD NOT REPLACE THE EXPERTISE OF AN EXPERIENCED CRYSTALLOGRAPHIC REFEREE.

No syntax errors found. CIF dictionary Interpreting this report

Datablock: pmeint

```
Bond precision:  C-C = 0.0045 A          Wavelength=0.71073

Cell:         a=6.3828(8)        b=10.3101(16)     c=11.896(2)
              alpha=104.198(14)  beta=100.779(12)  gamma=97.652(12)
Temperature:  297 K
```

	Calculated	Reported
Volume	732.3(2)	732.2(2)
Space group	P -1	P -1
Hall group	-P 1	-P 1
Moiety formula	C19 H16 O2	C19 H16 O2
Sum formula	C19 H16 O2	C19 H16 O2
Mr	276.32	276.32
Dx,g cm-3	1.253	1.253
Z	2	2
Mu (mm-1)	0.080	0.080
F000	292.0	292.0
F000’	292.13	
h,k,lmax	8,14,16	8,14,15
Nref	3949	3328
Tmin,Tmax	0.960,0.984	0.929,1.000
Tmin’	0.951	

```
Correction method= # Reported T Limits: Tmin=0.929 Tmax=1.000
AbsCorr = MULTI-SCAN

Data completeness= 0.843          Theta(max)= 29.156

R(reflections)= 0.0636( 1834)     wR2(reflections)= 0.2617( 3328)

S = 0.867                 Npar= 191
```

The following ALERTS were generated. Each ALERT has the format
test-name_ALERT_alert-type_alert-level.
Click on the hyperlinks for more details of the test.

Alert level C

```
PLAT084_ALERT_3_C High wR2 Value (i.e. > 0.25) ...................       0.26 Report
PLAT340_ALERT_3_C Low Bond Precision on  C-C Bonds ...............    0.00455 Ang.
PLAT906_ALERT_3_C Large K Value in the Analysis of Variance ......      4.389 Check
PLAT978_ALERT_2_C Number C-C Bonds with Positive Residual Density.          0 Info
```

Alert level G

```
PLAT063_ALERT_4_G Crystal Size Likely too Large for Beam Size ....       0.63 mm
PLAT072_ALERT_2_G SHELXL First  Parameter in WGHT  Unusually Large       0.17 Report
PLAT380_ALERT_4_G Incorrectly? Oriented X(sp2)-Methyl Moiety .....        C13 Check
PLAT398_ALERT_2_G Deviating  C-O-C    Angle From 120 for O2            106.2 Degree
PLAT898_ALERT_4_G Second Reported H-M Symbol in CIF Ignored ......          ! Check
PLAT910_ALERT_3_G Missing # of FCF Reflection(s) Below Theta(Min).          3 Note
PLAT912_ALERT_4_G Missing # of FCF Reflections Above STh/L=  0.600        604 Note
```

```
   0 ALERT level A = Most likely a serious problem - resolve or explain
   0 ALERT level B = A potentially serious problem, consider carefully
   4 ALERT level C = Check. Ensure it is not caused by an omission or oversight
   7 ALERT level G = General information/check it is not something unexpected

   0 ALERT type 1 CIF construction/syntax error, inconsistent or missing data
   3 ALERT type 2 Indicator that the structure model may be wrong or deficient
   4 ALERT type 3 Indicator that the structure quality may be low
   4 ALERT type 4 Improvement, methodology, query or suggestion
   0 ALERT type 5 Informative message, check
```

Validation response form

Please find below a validation response form (VRF) that can be filled in and pasted into your CIF.

```
# start Validation Reply Form
_vrf_PLAT084_pmeint
;
PROBLEM: High wR2 Value (i.e. > 0.25) ...................       0.26 Report
RESPONSE: ...
;
_vrf_PLAT340_pmeint
;
PROBLEM: Low Bond Precision on  C-C Bonds ...............    0.00455 Ang.
RESPONSE: ...
;
_vrf_PLAT906_pmeint
;
PROBLEM: Large K Value in the Analysis of Variance ......      4.389 Check
RESPONSE: ...
;
_vrf_PLAT978_pmeint
;
PROBLEM: Number C-C Bonds with Positive Residual Density.          0 Info
RESPONSE: ...
;
# end Validation Reply Form
```

It is advisable to attempt to resolve as many as possible of the alerts in all categories. Often the minor alerts point to easily fixed oversights, errors and omissions in your CIF or refinement strategy, so attention to these fine details can be worthwhile. In order to resolve some of the more serious problems it may be necessary to carry out additional measurements or structure refinements. However, the purpose of your study may justify the reported deviations and the more serious of these should normally be commented upon in the discussion or experimental section of a paper or in the "special_details" fields of the CIF. checkCIF was carefully designed to identify outliers and unusual parameters, but every test has its limitations and alerts that are not important in a particular case may appear. Conversely, the absence of alerts does not guarantee there are no aspects of the results needing attention. It is up to the individual to critically assess their own results and, if necessary, seek expert advice.

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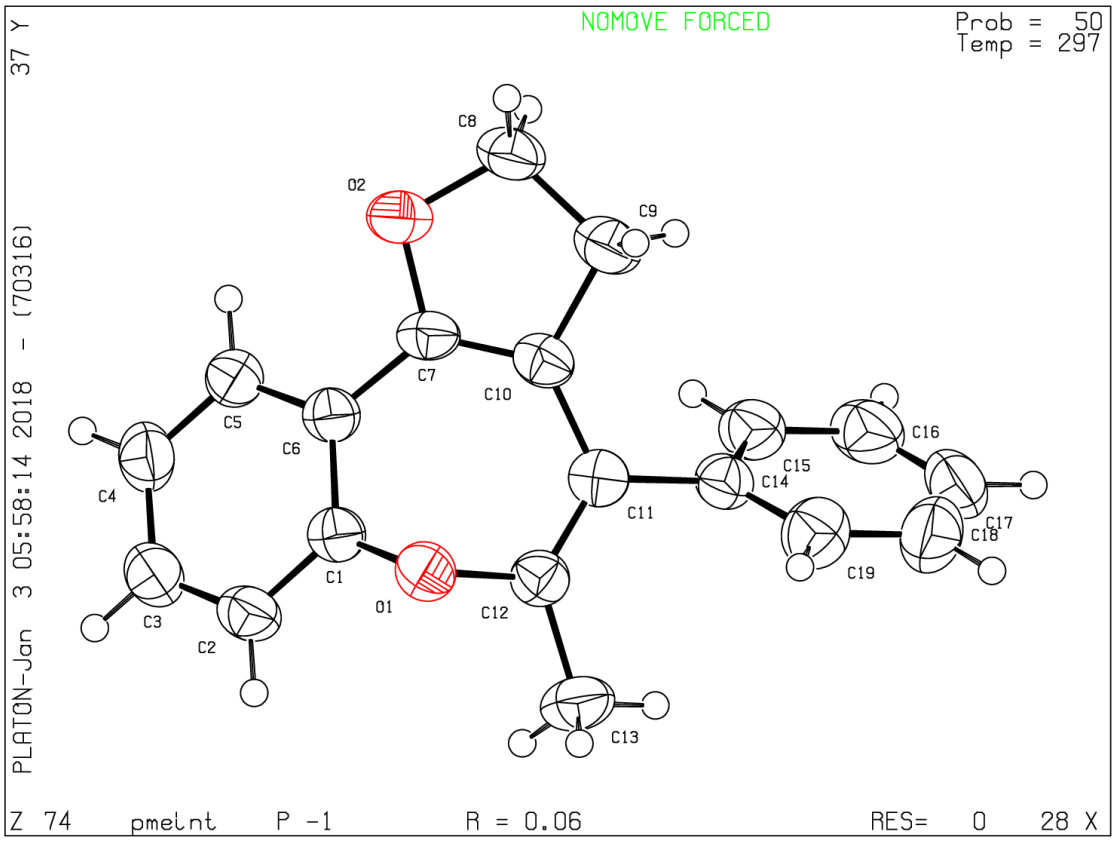
A basic structural check has been run on your CIF. These basic checks will be run on all CIFs submitted for publication in IUCr journals (*Acta Crystallographica, Journal of Applied Crystallography, Journal of Synchrotron Radiation*); however, if you intend to submit to *Acta Crystallographica Section C* or *E* or *IUCrData*, you should make sure that full publication checks are run on the final version of your CIF prior to submission.

Publication of your CIF in other journals

Please refer to the *Notes for Authors* of the relevant journal for any special instructions relating to CIF submission.

PLATON version of 13/12/2017; check.def file version of 12/12/2017

Datablock pmeint - ellipsoid plot



checkCIF/PLATON report

Structure factors have been supplied for datablock(s) rp12173

THIS REPORT IS FOR GUIDANCE ONLY. IF USED AS PART OF A REVIEW PROCEDURE FOR PUBLICATION, IT SHOULD NOT REPLACE THE EXPERTISE OF AN EXPERIENCED CRYSTALLOGRAPHIC REFEREE.

No syntax errors found. CIF dictionary Interpreting this report

Datablock: rp12173

```
Bond precision:  C-C = 0.0033 A          Wavelength=0.71073

Cell:           a=9.5200(17)    b=13.201(2)          c=8.3853(14)
                alpha=90        beta=112.716(19)     gamma=90
Temperature:    297 K

                Calculated                Reported
Volume          972.1(3)                  972.1(3)
Space group     P 21/c                    P 21/c
Hall group      -P 2ybc                   -P 2ybc
Moiety formula  C12 H10 O3                C12 H10 O3
Sum formula     C12 H10 O3                C12 H10 O3
Mr              202.20                    202.20
Dx,g cm-3       1.382                     1.382
Z               4                         4
Mu (mm-1)       0.099                     0.099
F000            424.0                     424.0
F000'           424.24
h,k,lmax        12,17,11                  12,17,11
Nref            2578                      2225
Tmin,Tmax       0.977,0.982               0.876,1.000
Tmin'           0.940

Correction method= # Reported T Limits: Tmin=0.876 Tmax=1.000
AbsCorr = MULTI-SCAN

Data completeness= 0.863          Theta(max)= 28.974

R(reflections)= 0.0549( 1352)     wR2(reflections)= 0.1454( 2225)

S = 1.046                 Npar= 137
```

The following ALERTS were generated. Each ALERT has the format
test-name_ALERT_alert-type_alert-level.
Click on the hyperlinks for more details of the test.

Alert level C

```
PLAT906_ALERT_3_C Large K Value in the Analysis of Variance ......     12.177 Check
PLAT906_ALERT_3_C Large K Value in the Analysis of Variance ......      2.432 Check
```

Alert level G

```
PLAT063_ALERT_4_G Crystal Size Likely too Large for Beam Size ....       0.62 mm
PLAT398_ALERT_2_G Deviating  C-O-C    Angle From 120 for O1            108.2 Degree
PLAT898_ALERT_4_G Second Reported H-M Symbol in CIF Ignored ......         ! Check
PLAT910_ALERT_3_G Missing # of FCF Reflection(s) Below Theta(Min).         1 Note
PLAT912_ALERT_4_G Missing # of FCF Reflections Above STh/L=  0.600        351 Note
PLAT978_ALERT_2_G Number C-C Bonds with Positive Residual Density.         1 Info
```

```
   0 ALERT level A = Most likely a serious problem - resolve or explain
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   0 ALERT type 1 CIF construction/syntax error, inconsistent or missing data
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   3 ALERT type 3 Indicator that the structure quality may be low
   3 ALERT type 4 Improvement, methodology, query or suggestion
   0 ALERT type 5 Informative message, check
```

Validation response form

Please find below a validation response form (VRF) that can be filled in and pasted into your CIF.

```
# start Validation Reply Form
_vrf_PLAT906_rp12173
;
PROBLEM: Large K Value in the Analysis of Variance ......     12.177 Check
RESPONSE: ...
;
# end Validation Reply Form
```

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PLATON version of 13/12/2017; check.def file version of 12/12/2017

Datablock rp12173 - ellipsoid plot