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Rh^{III}-catalyzed dual directing group assisted sterically hindered C-H bond activation: a unique route to *meta* and *ortho* substituted benzofurans

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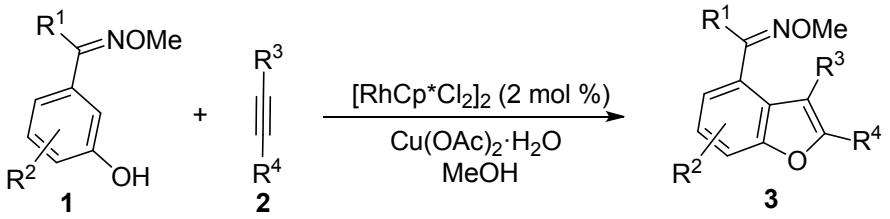
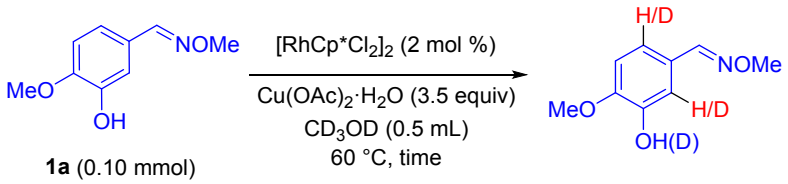
General Methods.

General Procedure for the Rh(III)–Catalyzed Synthesis of Benzofurans



A seal tube initially fitted with a rubber septum containing a magnetic stir bar, oxime **1 (**0.20 mmol**)**, alkyne **2 (**0.30 mmol**)**, $[RhCp^*Cl_2]_2$ (0.0040 mmol, 2.0 mol %) and $Cu(OAc)_2 \cdot H_2O$ (0.70 mmol) was evacuated and purged with nitrogen gas three times. Then, MeOH (1.0 mL) was added to the system via syringe under a stream of nitrogen and the septum was replaced with a screw cap. The reaction mixture was allowed to stir at the indicated temperature for 12 to 48 h. When the reaction was complete, the mixture was cooled to room temperature, diluted with EtOAc and filtered through a Celite pad. The filtrate was concentrated and the residue was purified by flash column chromatography (silica gel, hexane/EtOAc) to give the corresponding product **3**.

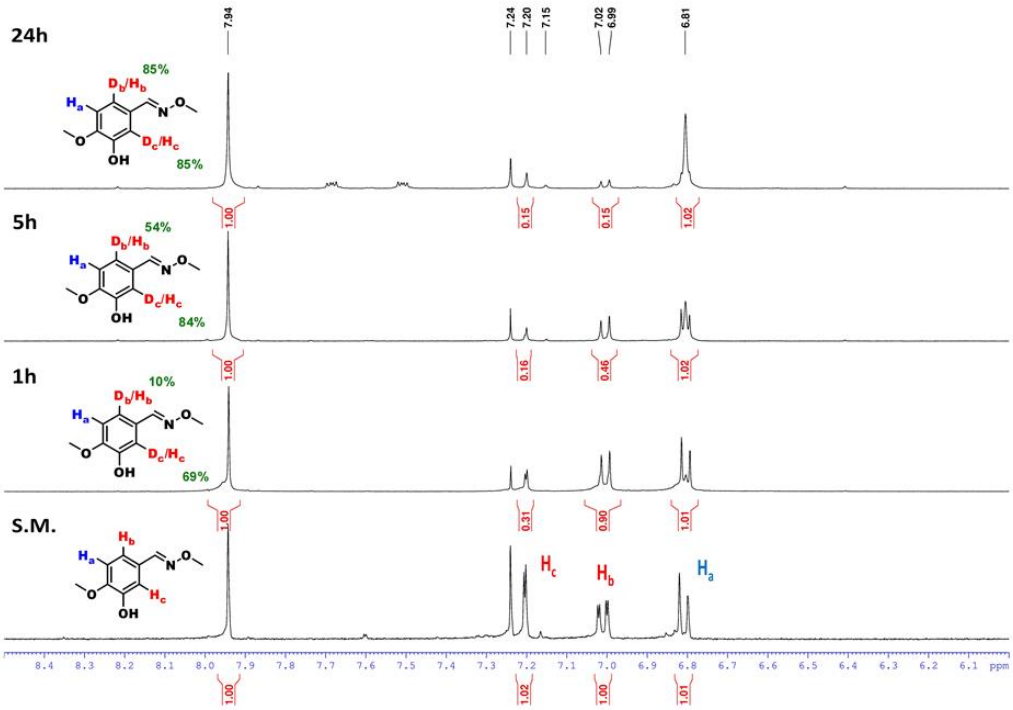
Deuterium Labeling Study of 1a



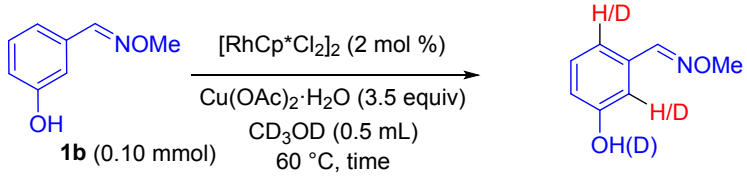
1a (0.10 mmol)

A seal tube initially fitted with a rubber septum containing a magnetic stir bar, oxime **1a** (0.1 mmol), $[RhCp^*Cl_2]_2$ (0.0020 mmol, 2.0 mol %), and $Cu(OAc)_2 \cdot H_2O$ (0.35 mmol) was evacuated and purged with nitrogen gas three times. Then, CD_3OD (0.5 mL) was added to the system via syringe under a stream of nitrogen and the septum was replaced with a screw cap. The reaction mixture was allowed to stir at 60 °C for 1, 5, and 24 h. When the reaction was complete, the mixture was cooled to room temperature, diluted with EtOAc and filtered through a Celite pad. The filtrate was evaporated in vacuum and the H/D exchange ratio was determined by ^1H NMR integration.

^1H NMR Spectra for Deuterium Labeling Study of Compound **1a**

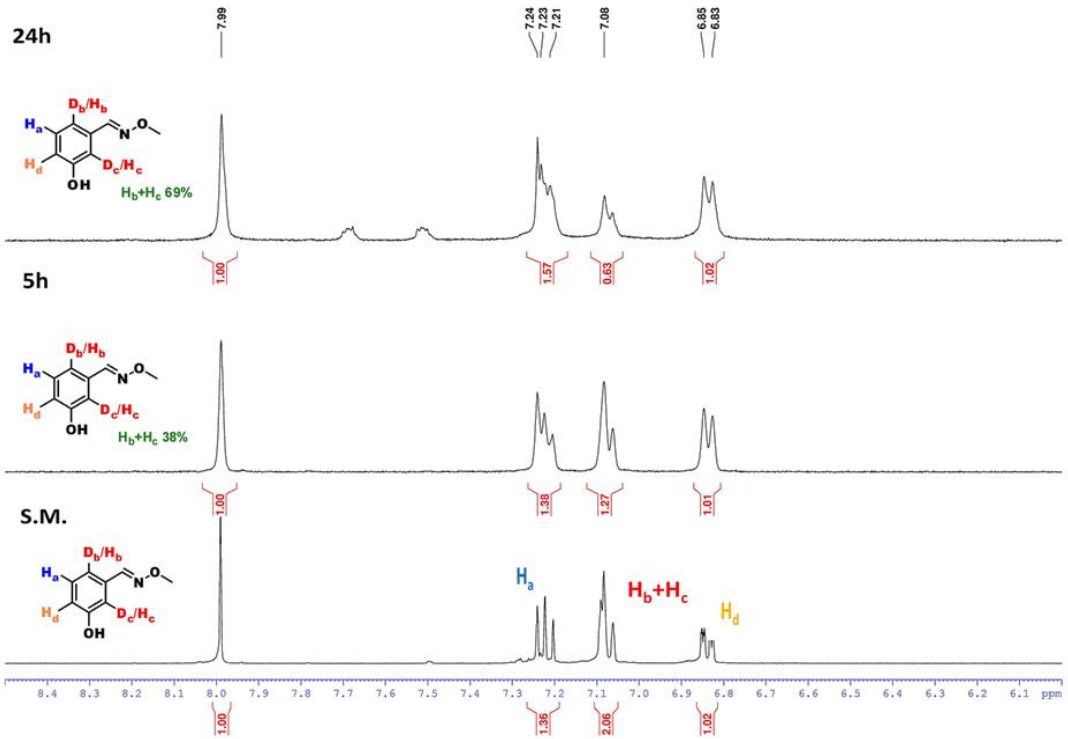


Deuterium Labeling Study of 1b

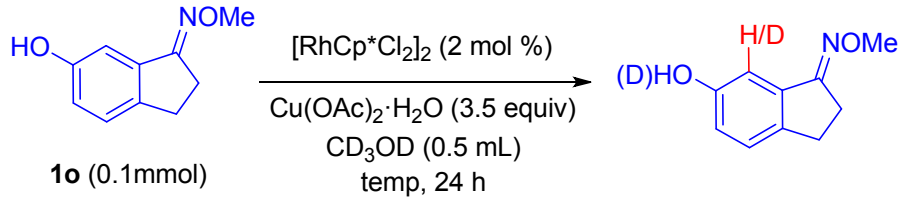


A seal tube initially fitted with a rubber septum containing a magnetic stir bar, oxime **1b (**0.10 mmol**)**, $[RhCp^*Cl_2]_2$ (0.002 mmol, 2.0 mol %), and $Cu(OAc)_2 \cdot H_2O$ (0.350 mmol) was evacuated and purged with nitrogen gas three times. Then, CD_3OD (0.50 mL) was added to the system via syringe under a stream of nitrogen and the septum was replaced with a screw cap. The reaction mixture was allowed to stir at 60 ˚C for 1, 5, and 24 h. When the reaction was complete, the mixture was cooled to room temperature, diluted with EtOAc and filtered through a Celite pad. The filtrate was evaporated in vacuum and the H/D exchange ratio was confirmed by ^{1}H NMR.

^{1}H NMR Spectra for Deuterium Labeling Study of Compound **1b**



Deuterium Labeling Study of 1o



A seal tube initially fitted with a rubber septum containing magnetic stir bar, oxime **1o** (0.1 mmol), $[RhCp^*Cl_2]_2$ (0.002 mmol, 2.0 mol %) and $Cu(OAc)_2·H_2O$ (0.35 mmol) was evacuated and purged with nitrogen gas three times. Then, CD_3OD (0.5 mL) was added to the system via syringe under a stream of nitrogen and the septum was replaced with a screw cap. The reaction mixture was allowed to stir at 60 and 100 °C for 24 h. When the reaction was complete, the mixture was cooled to room temperature, diluted with EtOAc and filtered through a Celite pad. The filtrate was evaporated in vacuum and confirmed by ^1H NMR.

^1H NMR Spectra for Deuterium Labeling Study of Compound **1o**

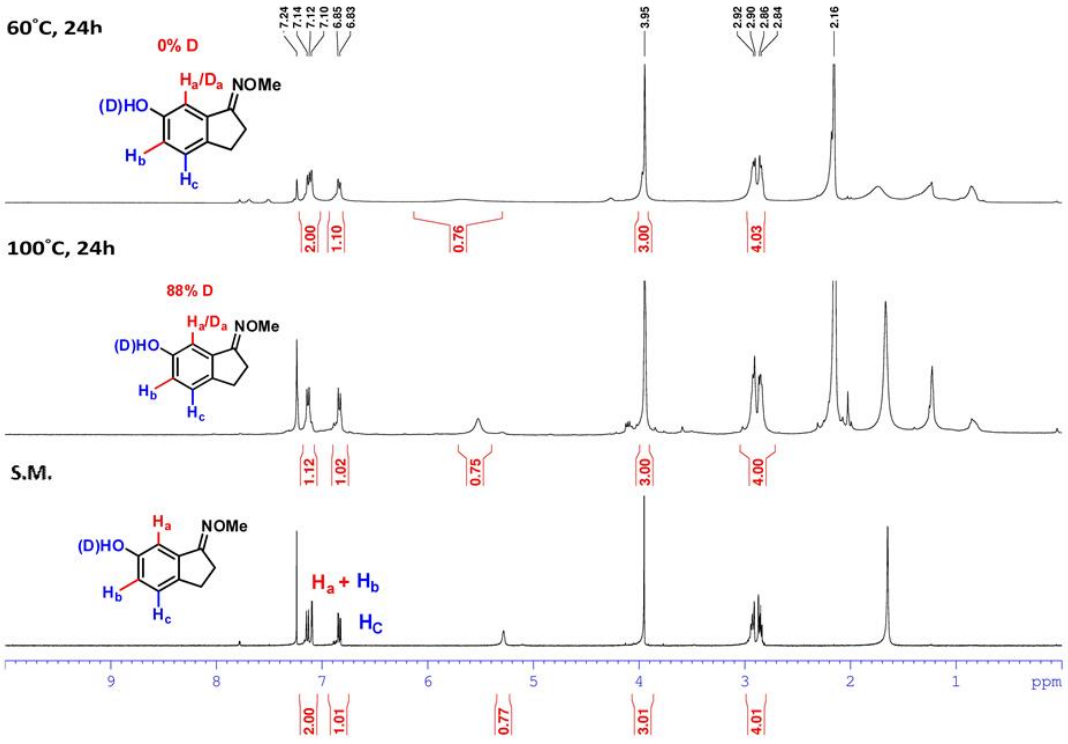
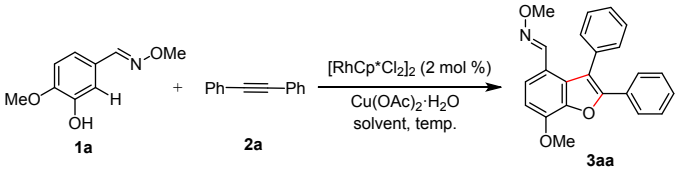


Table S1. Optimization Studies for the Synthesis of Benzofuran **3aa**[a]

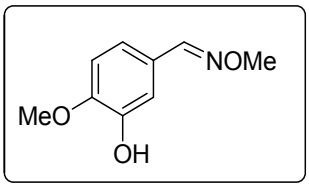


Entry	Additive	**2a** (mmol)	Solvent	*T* (°C)	Yield/Conv. (%)[b,c]
1[d]		2.0	*t*-amylOH	100	55/60
2		2.0	*t*-amylOH	100	56/69
3[e]	O_2 (1 atm)	2.0	*t*-amylOH	100	13/90
4[d]		2.0	1,4-dioxane	100	43/59
5[d]		2.0	EtOH	80	62/86
6		1.5	MeOH	80	52/65
7		2.0	MeOH	80	79/90
8	$AgSbF_6$ (0.02 mmol)	1.5	MeOH	80	53/88
9	$AgBF_4$ (0.02 mmol)	1.5	MeOH	80	52/89
10	AcOH (0.02 mmol)	1.5	MeOH	80	5/90
11[f]		**1.5**	**MeOH**	**60**	**83/95**
12		2.0	toluene	100	65/65
13		2.0	toluene	130	51/70
14		2.0	*O*-xylene	130	43/50
15		2.0	benzene	100	62/73
16		2.0	hexane	100	36/66
17		2.0	decane	130	38/75
18		2.0	chlorobenzene	100	68/74
19		2.0	chlorobenzene	130	45/77
20		2.0	fluorobenzene	100	58/80

[a] Conditions: **1a** (0.1 mmol), $Cu(OAc)_2·H_2O$ (0.35 mmol) and $[RhCp^*Cl_2]_2$ (2 mol %) in solvent (0.5 mL) under N_2 for 20 h, unless otherwise noted. [b] Yields were determined by NMR integration method using mesitylene as internal standard. [c] Conversions of **1a** were determined by crude ^1H NMR. [d] $Cu(OAc)_2·H_2O$ (0.20 mmol) was used. [e] $Cu(OAc)_2·H_2O$ (0.05 mmol) was used. [f] Reaction time: 30 h.

Synthesis and Characterization of Starting Materials

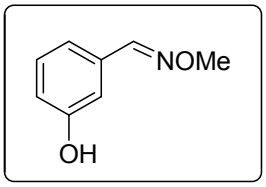
3-Hydroxy-4-methoxybenzaldehyde *O*-methyl oxime (1a)



Compound **1a** was prepared using modified procedure from reported method:[1] 3-hydroxy-4-methoxybenzaldehyde (1.5 g, 10 mmol, 1.0 equiv) was added to the solution of $MeONH_2 \cdot HCl$ (1.0 g, 12 mmol, 1.2 equiv), and pyridine (3.2 g, 40 mmol, 4.0 equiv) in CH_2Cl_2 (1 M, 10 mL). The solution was stirred for 24 h at room temperature. After completion of the reaction, the solvent was removed under vacuo. The remaining residue was dissolved in CH_2Cl_2 and filtered through a short pad of silica gel. The filtrate was concentrated and purified by silica flash chromatography (hexane–EtOAc) to give the corresponding product as white solid (1.6 g, 88%).

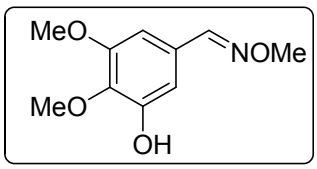
R_f = 0.61 (50% ethyl acetate in *n*-hexane); mp: 50-52 ˚C; **^{1}H NMR (400 MHz, $CDCl_3$):** δ = 7.96 (s, 1H), 7.22 (d, J = 2.0 Hz, 1H), 7.02 (dd, J = 8.4, 2.0 Hz, 1H), 6.82 (d, J = 8.4 Hz, 1H), 5.71 (s, OH), 3.94 (s, 3H), 3.90 (s, 3H); **^{13}C NMR (100 MHz, $CDCl_3$):** δ = 148.2, 148.1, 145.8, 125.6, 120.1, 112.3, 110.4, 61.8, 55.9; **HRMS (EI^+):** calcd for $C_9H_{11}NO_3$ 181.0739, found 181.0735; **IR (KBr, cm^{-1}):** 3450, 2938 and 1612.

3-Hydroxybenzaldehyde *O*-methyl oxime (1b)



Compound **1b** was prepared from 3-hydroxybenzaldehyde using the synthetic procedure for **1a**; R_f = 0.29 (20% ethyl acetate in *n*-hexane); white solid; mp: 62-64 ˚C; **^{1}H NMR (400 MHz, $CDCl_3$):** δ = 8.01(s, 1H), 7.26-7.08 (m, 3H), 6.87-6.85 (m, 1H), 5.69 (s, OH), 3.97 (s, 3H); **^{13}C NMR (100 MHz, $CDCl_3$):** δ = 155.8, 148.6, 135.5, 130.0, 120.2, 117.2, 113.0, 62.0; **HRMS (EI^+):** calcd for $C_8H_9NO_2$ 151.0633, found 151.0630; **IR (KBr, cm^{-1}):** 3363, 2938 and 1581.

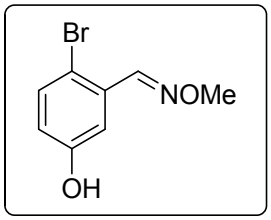
3-Hydroxy-4,5-dimethoxybenzaldehyde *O*-methyl oxime (1c)



This product was prepared from 3-hydroxy-4,5-dimethoxybenzaldehyde by following the synthetic procedure for **1a**; R_f = 0.38 (30% ethyl acetate in *n*-hexane); brown oil; **^{1}H NMR (400 MHz, $CDCl_3$):** δ = 7.91 (s, 1H), 6.78 (s, 1H), 6.74 (s, 1H), 5.79 (s, 1H), 3.94 (s, 3H), 3.89 (s, 3H), 3.88 (s, 3H); **^{13}C NMR (100 MHz, $CDCl_3$):** δ = 152.6, 149.4, 148.2, 136.9, 128.1, 108.0, 101.9, 62.0,

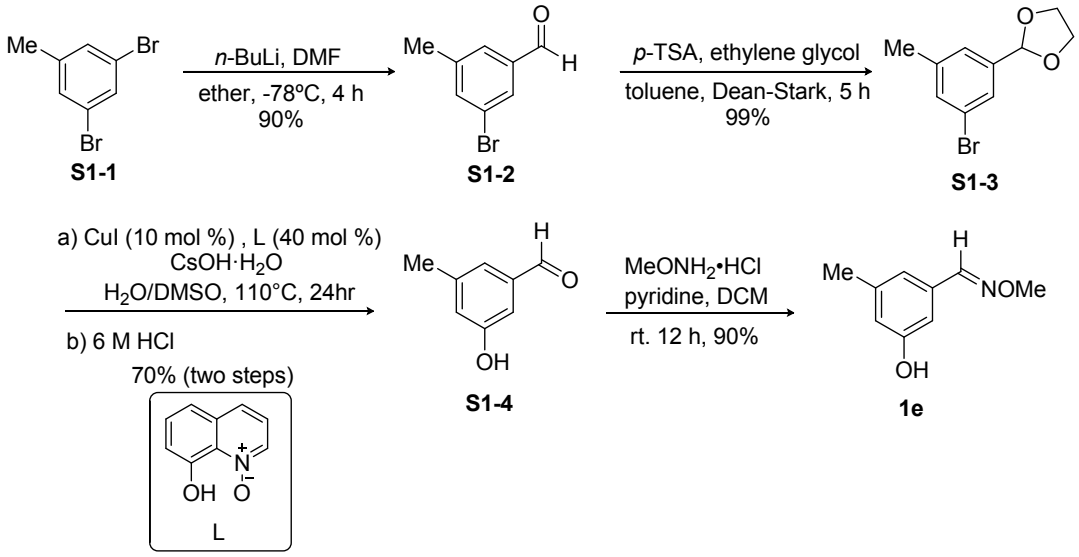
61.0, 55.9; **HRMS (EI$^+$):** calcd for $C_{10}H_{13}NO_4$ 211.0845, found 211.0847; **IR (KBr, cm^{-1}):** 3402, 2939 and 1581.

2-Bromo-5-hydroxybenzaldehyde *O*-methyl oxime (1d)



Compound **1d** was prepared from 2-bromo-5-hydroxybenzaldehyde using the the synthetic procedure of **1a**.[2] R_f = 0.45 (30% ethyl acetate in *n*-hexane); white solid; mp: 81-83 ˚C; **^{1}H NMR (400 MHz, $CDCl_3$):** δ = 8.37 (s, 1H), 7.37 (d, J = 8.8 Hz, 1H), 7.30 (d, J = 2.8 Hz, 1H), 6.73 (dd, J = 8.8, 3.2 Hz, 1H), 5.92 (s, OH), 3.96 (s, 3H); **^{13}C NMR (100 MHz, $CDCl_3$):** δ =154.9, 148.1, 134.0, 132.0, 119.1, 114.5, 113.6, 62.2; **HRMS (EI$^+$):** calcd for $C_8H_8BrNO_2$ 228.9738, found 228.9732; **IR (KBr, cm^{-1}):** 3394, 2939, 1566 and 1435.

3-Hydroxy-5-methylbenzaldehyde *O*-methyl oxime (1e)

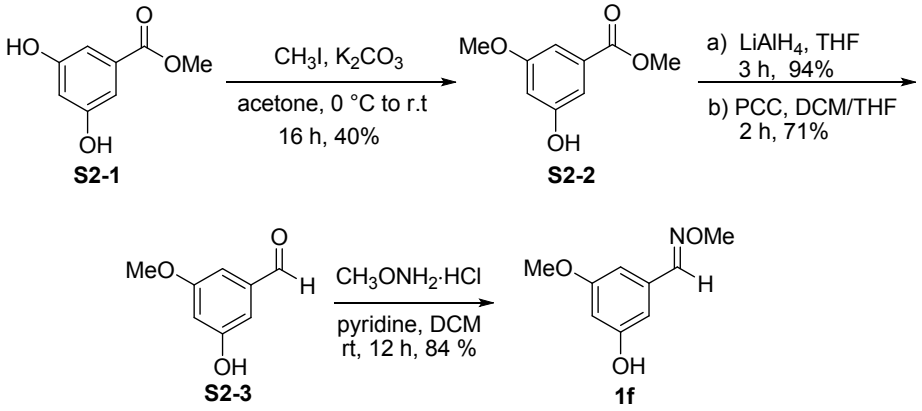


Scheme S1. Synthesis of 3-Hydroxy-5-methylbenzaldehyde *O*-methyl oxime (1e).

Compound **1e** was prepared starting from 3,5-dibromotoluene (**S1-1**), followed by formylation,[3] acetalization,[4] hydroxylation of the aryl bromide and hydrolysis to get 3-hydroxy-5-methylbenzaldehyde (**S1-4**).[5] Then, condensation with $MeONH_2 \cdot HCl$ to give oxime **1e**. (**Note**: hydroxylation reaction does not work in the absense of acetal protection) R_f = 0.67 (50% ethyl acetate in *n*-hexane); white solid; mp: 91-92 ˚C; **^{1}H NMR (400 MHz, $CDCl_3$):** δ = 7.95 (s, 1H), 6.92 (s, 1H), 6.87 (s, 1H), 6.66 (s, 1H), 3.94 (s, 3H), 2.29 (s, 3H); **^{13}C NMR (100 MHz, $CDCl_3$):** δ = 155.8, 148.5, 140.3, 133.4, 120.9, 117.8, 110.4, 62.0, 21.2; **HRMS (EI$^+$):** calcd for $C_9H_{11}NO_2$ 165.0790,

found 165.0789; **IR (KBr, cm^{-1}):** 3232 and 1589.

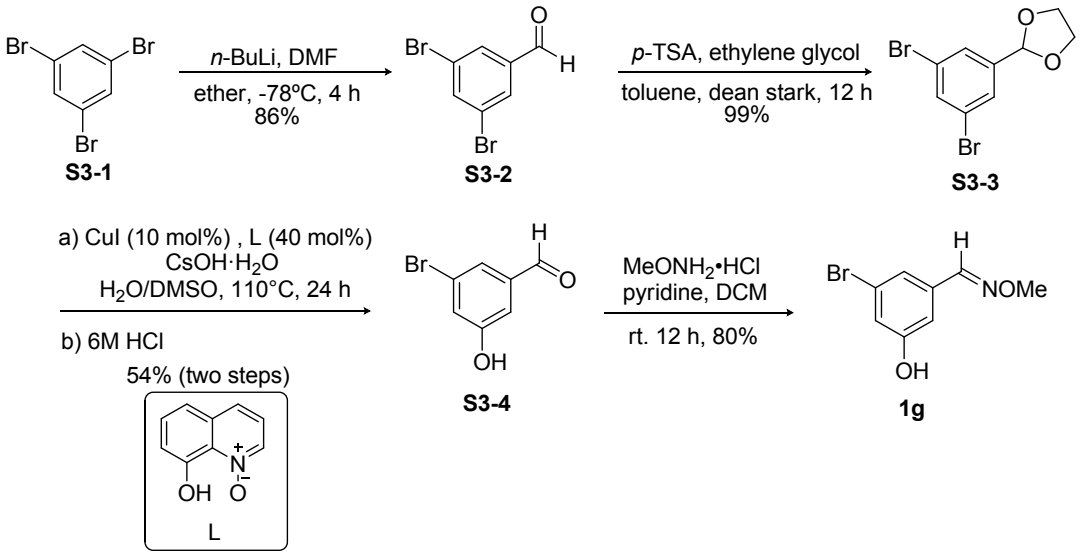
3-Hydroxy-5-methoxybenzaldehyde *O*-methyl oxime (1f)



Scheme S2. Synthesis of 3-Hydroxy-5-methoxybenzaldehyde *O*-methyl oxime (**1f**)

Compound **1f** was prepared starting from methyl 3,5-dihydroxybenzoate (**S2-1**), followed by methylation,[6] reduction,[7] oxidation,[8] and condensation with $MeONH_2 \cdot HCl$ to give oxime **1f** (Scheme S2). R_f = 0.31 (30% ethyl acetate in *n*-hexane); white solid; mp: 92-94 ˚C; **^{1}H NMR (400 MHz, $CDCl_3$):** δ = 7.93 (s, 1H), 6.68-6.64 (m, 2H), 6.41 (m, 1H), 5.61 (s, OH), 3.94 (s, 3H), 3.77 (s, 3H); **^{13}C NMR (100 MHz, $CDCl_3$):** δ = 161.1, 156.9, 148.5, 134.1, 106.5, 105.1, 103.4, 62.1, 55.5; **HRMS (EI$^+$):** calcd for $C_9H_{11}NO_3$ 181.0739, found 181.0737; **IR (KBr, cm^{-1}):** 2947 and 1589.

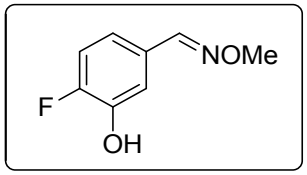
3-Bromo-5-hydroxybenzaldehyde *O*-methyl oxime (1g)



Scheme S3. Synthesis of 3-Bromo-5-hydroxybenzaldehyde *O*-methyl oxime **(1g)**

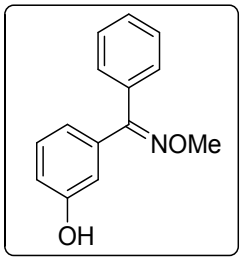
Compound **1g** was prepared starting from 1,3,5-dibromotoluene (**S3-1**), followed by formylation,[3] acetalization,[4] hydroxylation of aryl bromide and hydrolysis to get 3-hydroxy-5-methylbenzaldehyde (**S1-4**).[5] Then, condensation with $MeONH_2 \cdot HCl$ to give oxime **1g**. (**Note**: hydroxylation reaction does not work in the absense of acetal protection) R_f = 0.26 (30% ethyl acetate in *n*-hexane); white solid; mp: 71-73 °C; **^{1}H NMR (400 MHz, $CDCl_3$):** δ = 7.90 (s, 1H), 7.25 (m, 1H), 7.00-6.98 (m, 2H), 5.47 (s, OH), 3.95 (s, 3H); **^{13}C NMR (100 MHz, $CDCl_3$):** δ = 156.4, 146.8, 135.1, 123.1, 122.8, 120.0, 112.2, 62.3; **HRMS (EI$^+$):** calcd for $C_8H_8BrNO_2$ 405.0364, found 405.0364; **IR (KBr, cm^{-1}):** 2353, 1566 and 1435.

4-Fluoro-3-hydroxybenzaldehyde *O*-methyl oxime (1h)



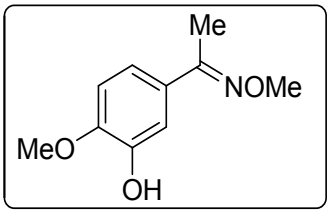
Compound **1h** was prepared from 4-fluoro-3-hydroxybenzaldehyde by following the synthetic procedure for **1a**; R_f = 0.70 (50% ethyl acetate in *n*-hexane); white solid; mp: 77-79 ˚C; **^{1}H NMR (400 MHz, $CDCl_3$):** δ = 7.95 (s, 1H), 7.26-7.24 (m, 1H), 7.04 (m, 1H), 7.03 (m, 1H), 5.49 (brs, OH), 3.94 (s, 3H); **^{13}C NMR (100 MHz, $CDCl_3$):** δ = 153.2, 150.8, 147.5, 143.9, 143.8, 129.3, 120.1, 120.1, 116.0, 115.8, 115.4, 62.1; **HRMS (EI$^+$):** calcd for $C_8H_8FNO_2$ 169.0539, found 169.0538; **IR (KBr, cm^{-1}):** 3116, 1597, 1519 and 1435.

(3-Hydroxyphenyl)(phenyl)methanone *O*-methyl oxime (1i); mixture of *E* and *Z* isomers



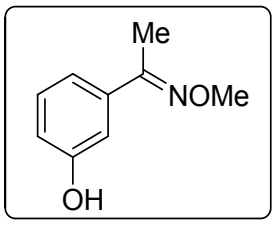
3-Hydroxybenzophenone (0.4 g, 2.0 mmol, 1.0 equiv) was added to a solution of $MeONH_2 \cdot HCl$ (0.17 g, 2.4 mmol, 1.2 equiv), and pyridine (0.63 g, 8.0 mmol, 4.0 equiv) in MeOH (4 mL). The solution was heated to reflux for 24 h, the reaction was then cooled to room temperature and concentrated in vacuo. The remaining residue was dissolved in CH_2Cl_2 and filtered through a short pad of silica gel. The filtrate was purified by silica flash chromatography (*n*-hexane–EtOAc) to give the corresponding product as colorless oil (0.45 g, 99%); R_f = 0.67 (50% ethyl acetate in *n*-hexane); **^{1}H NMR for mixture of *E* and *Z* isomers (400 MHz, $CDCl_3$):** δ = 7.55-7.27 (m, 5H), 7.18 (t, *J* = 7.6 Hz, 1H), 7.07-6.84 (m, 3H), 4.00 (s, 3H); **^{13}C NMR for mixture of *E* and *Z* isomers (100 MHz, $CDCl_3$):** δ = 157.1, 157.0, 155.7, 155.6, 137.4, 135.8, 134.4, 132.9, 129.3, 129.0, 128.9, 128.1, 128.0, 127.7, 121.0, 120.3, 116.7, 116.1, 114.6; **HRMS (EI$^+$):** calcd for $C_{14}H_{13}NO_2$ 227.0946, found 227.0948; **IR (KBr, cm^{-1}):** 3400, 2938 and 1589.

1-(3-Hydroxy-4-methoxyphenyl)ethanone *O*-methyl oxime (1j)



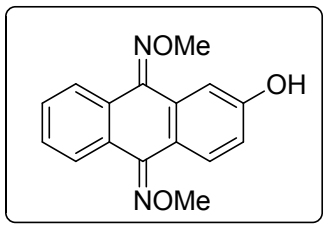
Compound **1j** was prepared from 3'-hydroxy-4'-methoxyacetophenone by following the synthetic procedure for **1i**; R_f = 0.58 (50% ethyl acetate in *n*-hexane); colorless oil; **^{1}H NMR (400 MHz, $CDCl_3$):** δ = 7.26 (d, *J* = 2.0 Hz, 1H), 7.13 (dd, *J* = 8.4, 2.0 Hz, 1H), 6.80 (d, *J* = 8.4 Hz, 1H), 3.97 (s, 3H), 3.86 (s, 3H), 2.17 (s, 3H); **^{13}C NMR (100 MHz, $CDCl_3$):** δ = 154.1, 147.5, 145.4, 129.9, 118.1,112.3, 110.2, 61.7, 55.8, 12.4; **HRMS (EI^+):** calcd for $C_{10}H_{13}NO_3$ 195.0895, found 195.0895; **IR (KBr, cm^{-1}):** 3450, 2939 and 1619.

1-(3-Hydroxyphenyl)ethanone *O*-methyl oxime (1k)



Compound **1k** was prepared from 3'-hydroxyacetophenone using the synthetic procedure of **1i;** R_f = 0.64 (50% ethyl acetate in *n*-hexane); colorless oil; **^{1}H NMR (400 MHz, $CDCl_3$):** δ = 7.20 (t, *J* = 8.0 Hz, 1H), 7.14-7.11 (m, 2H), 6.88-6.77(m, 1H), 3.98 (s, 3H), 2.19 (s, 3H); **^{13}C NMR (100 MHz, $CDCl_3$):** δ = 155.8, 155.4, 137.8, 129.7, 118.5, 116.5, 113.0, 61.8, 13.0; **HRMS (EI^+):** calcd for $C_9H_{11}NO_2$ 165.0790, found 165.0790; **IR (KBr, cm^{-1}):** 3394, 2938 and 1581.

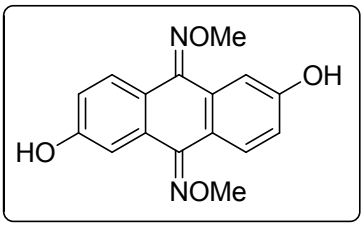
2-Hydroxyanthracene-9,10-dione *O*,*O*-dimethyl dioxime (1l; mixture of isomers**)**



The solution containing 2-hydroxyanthraquinone (0.90 g, 4.0 mmol, 1.0 equiv), and $MeONH_2{\cdot}HCl$ (0.70 g, 10.0 mmol, 2.5 equiv) in pyridine (4 mL) as solvent, was heated to reflux for 24 h. The reaction was then cooled to room temperature and the mixture was dissolved in CH_2Cl_2 (20 mL). The mixture was washed with $NH_4Cl_{(aq)}$ (10 mL) and organic layer was evaporated in vacuo. The residue was filtered through a short pad of silica gel and washed with CH_2Cl_2. The filtrate was purification by silica flash chromatography (hexane–EtOAc) to give the corresponding product as brown foam (0.53 g, 47%); R_f = 0.61 (50% ethyl acetate in *n*-hexane); **^{1}H NMR (400 MHz, $CDCl_3$):** δ = 9.00 (s, OH), 8.55-8.49 (m, 1H), 8.10-7.89 (m, 2H), 7.54-7.40 (m, 3H), 7.04-6.98 (m, 1H), 4.09-4.05 (m, 6H); **^{13}C NMR (100 MHz, $CDCl_3$):** δ = 159.2, 158.9, 158.6, 158.2, 149.4, 146.7, 146.6, 146.5, 146.3, 146.2, 136.2, 134.4, 134.2, 134.1, 132.9, 132.8, 132.4, 130.8, 130.7, 130.6, 130.4, 130.4, 130.3, 129.8, 129.7, 129.4, 129.2, 126.1, 125.6, 124.8, 124.6, 120.7, 119.3, 118.4, 117.8, 117.4, 117.2, 116.9, 116.7, 111.6, 110.6, 63.2, 63.1;

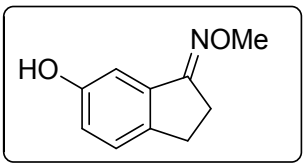
HRMS (EI$^+$): calcd for $C_{16}H_{14}N_2O_3$ 282.1004, found 282.1003; **IR (KBr, cm^{-1}):** 3300, 2938 and 1604.

2,6-Dihydroxyanthracene-9,10-dione *O*,*O*-dimethyl dioxime (1m)



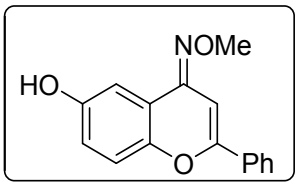
Followed the synthesis of **1l** and started from anthraflavic acid; R_f = 0.48 (50% ethyl acetate in *n*-hexane); pale yellow solid; mp: 198-200 ˚C; **^{1}H NMR (400 MHz, $(CD_3)_2CO$)** for the major isomer: δ = 8.92 (s, OH), 8.45 (d, J = 8.8 Hz, 2H), 7.53 (d, J = 2.4 Hz, 2H), 6.98-6.95 (m, 2H), 4.05 (s, 6H); **^{13}C NMR (100 MHz, $(CD_3)_2CO$):** δ = 158.7, 158.4, 158.1, 146.1, 145.9, 145.8, 136.1, 134.0, 132.4, 132.2, 130.2, 126.9, 126.3, 124.1, 120.4, 118.9, 117.7, 117.1, 117.0, 116.5, 116.0, 111.1, 110.0, 62.6; **HRMS (EI$^+$):** calcd for $C_9H_{11}NO_3$ 298.0954, found 298.0952; **IR (KBr, cm^{-1}):** 3355 and 1566.

6-Hydroxy-2,3-dihydro-1*H*-inden-1-one *O*-methyl oxime (1n)



Compound **1n** was prepared from 6-hydroxy-1-indanone by following the synthetic procedure for **1i;** R_f = 0.26 (50% ethyl acetate in *n*-hexane); yellow solid; mp: 172-175 ˚C; **^{1}H NMR (400 MHz, $CDCl_3$):** δ = 7.16 (d, J = 8.0 Hz, 1H), 7.11 (d, J = 2.4 Hz, 1H), 6.86 (dd, J = 8.0, 2.4 Hz, 1H), 5.25 (s, OH), 3.97 (s, 3H), 2.96-2.86 (m, 4H); **^{13}C NMR (100 MHz, $CDCl_3$):** δ = 162.8, 155.0, 140.6, 137.3, 126.4, 118.5, 107.2, 62.0, 27.8, 27.0; **HRMS (EI$^+$):** calcd for $C_{10}H_{11}NO_2$ 177.0790, found 177.0785; **IR (KBr, cm^{-1}):** 3394, 2915 and 1604.

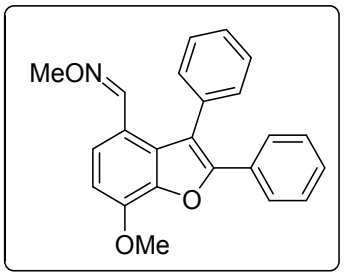
6-Hydroxy-2-phenyl-4*H*-chromen-4-one *O*-methyl oxime (1o)



Followed the synthesis of **1i** and started from 6-hydroxyflavone; R_f = 0.47 (50% ethyl acetate in *n*-hexane); yellow solid; mp: 153-156 ˚C; **^{1}H NMR (400 MHz, $CDCl_3$):** δ = 7.84-7.83 (m, 2H), 7.44-7.40 (m, 4H), 7.18 (d, J = 8.8 Hz, 1H), 7.00 (s, 1H), 6.95 (dd, J = 8.8, 3.2 Hz, 1H), 5.93(s, OH), 3.98(s, 3H); **^{13}C NMR (100 MHz, $CDCl_3$):** δ = 155.4, 152.8, 146.3, 144.6, 132.8, 130.2, 128.6, 125.7, 119.2, 119.0, 118.5, 107.3, 92.9, 61.7; **HRMS (EI$^+$):** calcd for $C_{16}H_{13}NO_3$ 267.0895, found 267.0900; **IR (KBr, cm^{-1}):** 3170 and 1627.

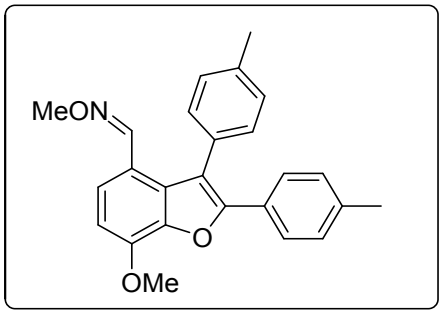
Characterization data of Benzofuran Derivatives

7-Methoxy-2,3-diphenylbenzofuran-4-carbaldehyde *O*-methyl oxime (3aa)



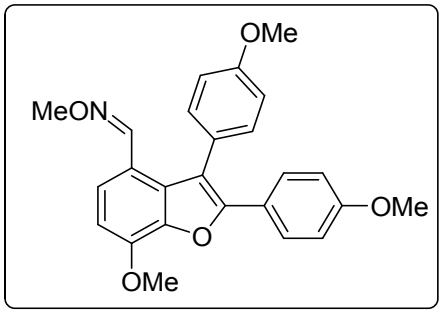
R_f = 0.54 (20% ethyl acetate in *n*-hexane); yellow solid; mp: 140-143 °C; **^{1}H NMR (400 MHz, $CDCl_3$):** δ = 7.73 (d, *J* = 8.4 Hz, 1H), 7.70 (s, 1H), 7.59-7.26 (m, 10H), 6.85 (d, *J* = 8.4 Hz, 1H), 4.08 (s, 3H), 3.85 (s, 3H); **^{13}C NMR (100 MHz, $CDCl_3$):** δ = 151.4, 146.1, 145.2, 142.8, 133.4, 130.4, 130.0, 130.0, 129.3, 128.4, 128.3, 128.2, 126.6, 121.4, 118.0, 117.5, 107.1, 61.5, 56.1; **HRMS (EI$^+$):** calcd for $C_{23}H_{19}NO_3$ 357.1365, found 357.1365; **IR (KBr, cm^{-1}):** 2938 and 1596.

7-Methoxy-2,3-di-*p*-tolylbenzofuran-4-carbaldehyde *O*-methyl oxime (3ab)



R_f = 0.69 (30% ethyl acetate in *n*-hexane); white solid; mp: 143-145 °C; **^{1}H NMR (400 MHz, $CDCl_3$):** δ = 7.71 (s, 1H), 7.66 (d, *J* = 8.0 Hz, 1H), 7.40 (d, *J* = 8.4 Hz, 2H), 7.26 (s, 4H), 7.04 (d, *J* = 8.0 Hz, 2H), 6.81 (d, *J* = 8.4 Hz, 1H), 4.07 (s, 3H), 3.81 (s, 3H), 2.44 (s, 3H), 2.29 (s, 3H); **^{13}C NMR (100 MHz, $CDCl_3$):** δ = 151.8, 146.2, 145.6, 142.8, 138.4, 138.0, 130.4, 130.3, 130.0, 129.0, 127.4, 126.6, 121.3, 118.1, 116.9, 107.0, 61.6, 56.3, 21.5, 21.3; **HRMS (EI$^+$):** calcd for $C_{25}H_{23}NO_3$ 385.1678, found 385.1673; **IR (KBr, cm^{-1}):** 2931, 2360, 1597 and 1512.

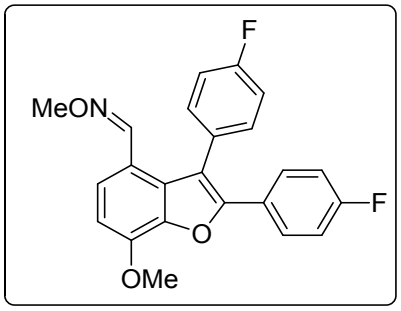
7-Methoxy-2,3-bis(4-methoxyphenyl)benzofuran-4-carbaldehyde *O*-methyl oxime (3ac)



R_f = 0.47 (30% ethyl acetate in *n*-hexane); white solid; mp: 141-143 °C; **^{1}H NMR (400 MHz, $CDCl_3$):** δ = 7.75 (s, 1H), 7.66 (d, *J* = 8.0 Hz, 1H), 7.46-7.44 (m, 2H), 7.30-7.28 (m, 2H), 7.00 (m, 2H), 6.80-6.76 (m, 3H), 4.06 (s, 3H), 3.88 (s, 3H), 3.81 (s, 3H), 3.76 (s, 3H); **^{13}C NMR (100 MHz, $CDCl_3$):** δ = 159.7, 159.6, 152.0, 146.2, 145.6, 131.7, 130.6, 128.2, 125.6, 123.0, 121.3, 118.0, 115.7, 114.8, 113.8, 106.9, 61.6, 56.3, 55.3, 55.2; **HRMS (EI$^+$):** calcd for $C_{25}H_{23}NO_5$ 417.1576, found 417.1578; **IR (KBr,**

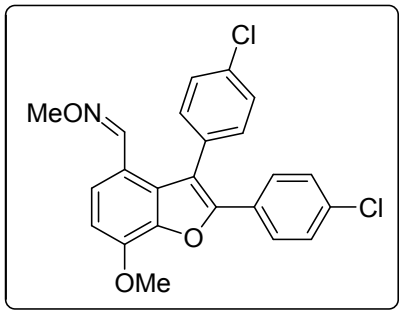
cm^{-1}): 2939, 2839, 1612 and 1512.

2,3-Bis(4-fluorophenyl)-7-methoxybenzofuran-4-carbaldehyde *O*-methyl oxime (3ad)



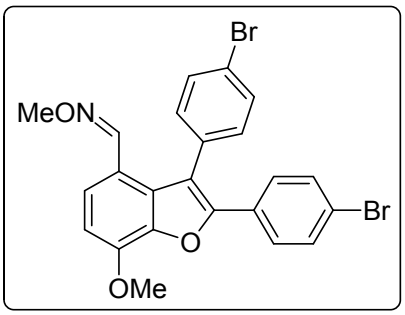
R_f = 0.66 (30% ethyl acetate in *n*-hexane); pale yellow solid; mp: 142-144 ˚C; **^{1}H NMR (400 MHz, $CDCl_3$):** δ = 7.67 (s, 1H), 7.66 (d, *J* = 8.6 Hz, 1H), 7.48-7.44 (m, 2H), 7.37-7.34 (m, 2H), 7.21-7.17 (m, 2H), 6.97-6.92 (m, 2H), 6.83 (d, *J* = 8.6 Hz, 1H), 4.06 (s, 3H), 3.80 (s, 3H); **^{13}C NMR (100 MHz, $CDCl_3$):** δ = 164.1, 163.9, 161.6, 161.5, 151.1, 146.3, 145.1, 142.9, 132.3, 132.2, 129.8, 129.3, 128.8, 128.7, 126.2, 121.9, 118.1, 116.7, 116.5, 116.3, 115.7, 115.4, 107.3, 61.7, 56.3; **HRMS (EI$^+$):** calcd for $C_{23}H_{17}F_2NO_3$ 393.1176, found 393.1179; **IR (KBr, cm^{-1}):** 2939, 2399, 1597 and 1512.

2,3-Bis(4-chlorophenyl)-7-methoxybenzofuran-4-carbaldehyde *O*-methyl oxime (3ae)



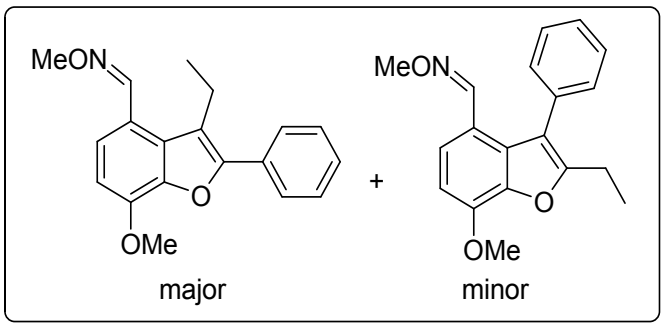
R_f = 0.66 (30% ethyl acetate in *n*-hexane); yellow solid; mp: 125-128 ˚C; **^{1}H NMR (400 MHz, $CDCl_3$):** δ = 7.69 (s, 1H), 7.65 (d, *J* = 8.4 Hz, 1H), 7.49-7.45 (m, 2H), 7.41-7.38 (m, 2H), 7.33-7.31 (m, 2H), 7.24-7.21 (m, 2H), 6.84 (d, *J* = 8.4 Hz, 1H), 4.06 (s, 3H), 3.80 (s, 3H); **^{13}C NMR (100 MHz, $CDCl_3$):** δ =150.8, 146.3,145.1, 143.1, 134.7, 134.6, 132.8, 131.8, 129.8, 129.5, 128.8, 128.5, 128.3, 128.1, 122.1, 118.2, 116.9, 107.5, 61.7, 56.3; **HRMS (EI$^+$):** calcd for $C_{23}H_{17}Cl_2NO_3$ 425.0585, found 425.0586; **IR (KBr, cm^{-1}):** 2931, 2399, 1728 and 1597.

2,3-Bis(4-bromophenyl)-7-methoxybenzofuran-4-carbaldehyde *O*-methyl oxime (3af)



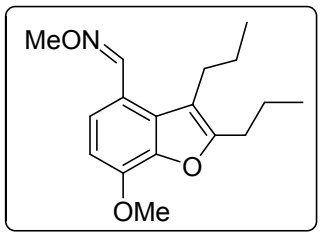
R_f = 0.50 (20% ethyl acetate in *n*-hexane); yellow solid; mp: 161-164 ˚C; **^{1}H NMR (400 MHz, $CDCl_3$):** δ = 7.72 (s, 1H), 7.66 (d, *J* = 8.4 Hz, 1H), 7.63 (d, *J* = 8. 0 Hz, 2H), 7.40 (d, *J* = 8.4 Hz, 2H), 7.33 (d, *J* = 8.4 Hz, 2H), 7.27 (d, *J* = 8.0 Hz, 2H), 6.85 (d, *J* = 8.4 Hz, 1H), 4.07 (s, 3H), 3.82 (s, 3H); **^{13}C NMR (100 MHz, $CDCl_3$):** δ = 150.8, 146.3, 145.0, 143.1, 132.7, 132.3, 132.1, 131.7, 129.3, 128.7, 128.2, 122.9, 122.1, 118.1, 117.0, 107.5, 61.7, 56.2; **HRMS (EI$^+$):** calcd for $C_{23}H_{17}Br_2NO_3$ 512.9575, found 512.9561; **IR (KBr, cm^{-1}):** 2931 and 1596.

3ag (mixture of isomers)



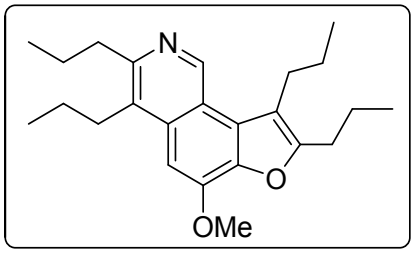
R_f = 0.51 (20% ethyl acetate in *n*-hexane); yellow solid; mp: 129-132 ˚C; **^{1}H NMR for major isomer (400 MHz, $CDCl_3$):** δ = 8.62 (s, 1H), 7.74 (d, *J* = 7.2 Hz, 2H), 7.65 (d, *J* = 8.4 Hz, 1H), 7.50-7.38 (m, 3H), 6.82 (d, *J* = 8.4 Hz, 1H), 4.04 (s, 3H), 4.01 (s, 3H), 2.98 (q, *J* = 7.2 Hz, 2H), 1.35 (t, *J* = 7.2 Hz, 3H); **^{13}C NMR for major isomer (100 MHz, $CDCl_3$):** δ = 146.8, 146.7, 146.0, 130.6, 129.5, 128.9, 128.8, 128.1, 127.9, 122.3, 121.5, 118.4, 107.0, 62.1, 56.4, 29.9, 20.2, 18.7, 15.4; **HRMS (EI$^+$):** calcd for $C_{19}H_{19}NO_3$ 309.1365, found 309.1358; **IR (KBr, cm^{-1}):** 2931 and 1604.

7-Methoxy-2,3-dipropylbenzofuran-4-carbaldehyde *O*-methyl oxime (3ah)



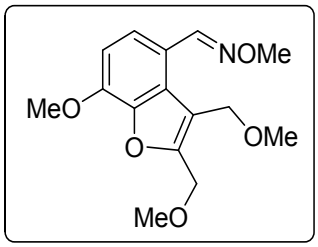
R_f = 0.57 (20% ethyl acetate in *n*-hexane); yellow solid; mp: 57-59 ˚C; **^{1}H NMR (400 MHz, $CDCl_3$):** δ = 8.49 (s, 1H), 7.58 (d, *J* = 8.4 Hz, 1H), 6.73 (d, *J* = 8.4, 1H), 4.00 (s, 3H), 3.99 (s, 3H), 2.73-2.65 (m, 4H), 1.78-1.56 (m, 4H), 0.97 (t, *J* = 7.6 Hz, 6H); **^{13}C NMR (100 MHz, $CDCl_3$):** δ = 156.2, 146.6, 146.1, 143.2, 128.9, 121.6, 117.4, 114.9, 105.6, 61.8, 56.0, 28.2, 26.8, 23.7, 21.8, 13.9, 13.8; **HRMS (EI$^+$):** calcd for $C_{17}H_{23}NO_3$ 289.1678, found 289.1683; **IR (KBr, cm^{-1}):** 2962 and 1596.

6-Methoxy-3,4,8,9-tetrapropylfuro[2,3-*h*]isoquinoline (3ah')



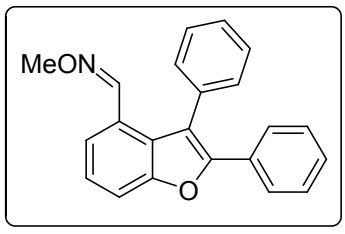
R_f = 0.41 (20% ethyl acetate in *n*-hexane); brown solid; mp: 78-81 ˚C; **^{1}H NMR (400 MHz, $CDCl_3$):** δ = 9.35 (s, 1H), 7.02 (s, 1H), 4.13 (s, 3H), 3.01-2.85 (m, 6H), 2.78 (t, *J* = 7.6 Hz, 2H), 1.83-1.67 (m, 8H), 1.11-0.95 (m, 12H); **^{13}C NMR (100 MHz, $CDCl_3$):** δ = 155.8, 151.9, 148.4, 144.2, 142.5, 134.7, 128.2, 124.9, 118.3, 116.7, 96.8, 55.7, 37.6, 30.7, 28.2, 27.4, 23.7, 23.5, 23.1, 22.1, 14.7, 14.4, 14.0, 13.8; **HRMS (EI$^+$):** calcd for $C_{24}H_{33}NO_2$ 367.2511, found 367.2510; **IR (KBr, cm^{-1}):** 3178 and 1612.

7-Methoxy-2,3-bis(methoxymethyl)benzofuran-4-carbaldehyde *O*-methyl oxime (3ai)



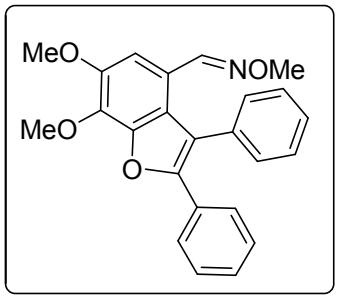
R_f = 0.30 (30% ethyl acetate in *n*-hexane); yellow solid; mp: 110-112 ˚C; **^{1}H NMR (400 MHz, $CDCl_3$):** δ = 9.18 (s, 1H), 7.64 (d, *J* = 8.0 Hz, 1H), 6.65 (d, *J* = 8.0 Hz, 1H), 4.67 (s, 2H), 4.35 (s, 2H), 4.12 (s, 3H), 3.89 (s, 3H), 3.47 (s, 3H), 3.34 (s, 3H); **^{13}C NMR (100 MHz, $CDCl_3$):** δ = 154.3, 151.6, 141.0, 140.5, 132.3, 126.9, 121.6, 121.0, 66.9, 63.8, 63.5, 58.2, 57.9, 56.1; **HRMS (EI$^+$):** calcd for $C_{15}H_{19}NO_5$ 293.1263, found 293.1260; **IR (KBr, cm^{-1}):** 2924, 2854, 1589 and 1458.

2,3-Diphenylbenzofuran-4-carbaldehyde *O*-methyl oxime (3ba)



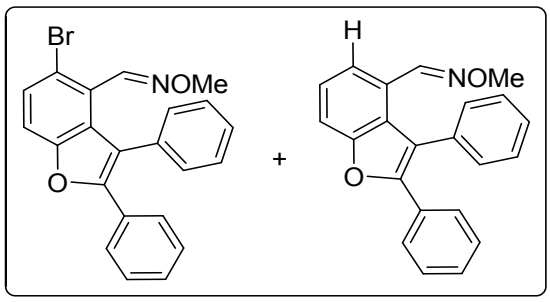
R_f = 0.54 (20% ethyl acetate in *n*-hexane); yellow solid; mp: 115-118 ˚C; **^{1}H NMR (400 MHz, $CDCl_3$):** δ = 7.75 (d, *J* = 7.6 Hz, 1H), 7.74 (s, 1H), 7.59-7.27 (m, 12H), 3.86 (s, 3H); **^{13}C NMR (100 MHz, $CDCl_3$):** δ = 154.0, 151.4, 145.5, 133.7, 130.4, 130.2, 129.4, 128.5, 128.4 (2C), 126.6, 125.7, 124.6, 120.4, 117.3, 112.1, 61.8; **HRMS (EI$^+$):** calcd for $C_{22}H_{17}NO_2$ 327.1259, found 327.1266; **IR (KBr, cm^{-1}):** 2938 and 1596.

6,7-Dimethoxy-2,3-diphenylbenzofuran-4-carbaldehyde *O*-methyl oxime (3ca)



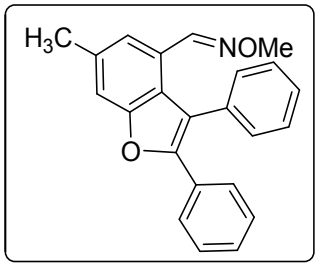
R_f = 0.59 (30% ethyl acetate in *n*-hexane); orange solid; mp: 112-114 ˚C; **^{1}H NMR (400 MHz, $CDCl_3$):** δ = 7.60 (s, 1H), 7.50-7.44 (m, 5H), 7.41-7.38 (m, 3H), 7.24-7.21 (m, 3H), 4.30 (s, 3H), 3.95 (s, 3H), 3.80 (s, 3H); **^{13}C NMR (100 MHz, $CDCl_3$):** δ = 151.1, 148.9, 145.5, 145.1, 135.6, 133.6, 130.4, 130.2, 129.5, 128.6, 128.4, 128.3, 126.3, 125.5, 118.5, 117.3, 105.8, 61.8, 61.0, 57.0; **HRMS (EI$^+$):** calcd for $C_{24}H_{21}NO_4$ 387.1471, found 387.1470; **IR (KBr, cm^{-1}):** 2939, 1604, 1512 and 1250.

3da (with 60% debromination product)



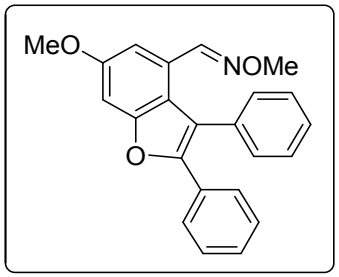
R_f = 0.54 (20 % ethyl acetate in *n*-hexane); **^{1}H NMR (400 MHz, $CDCl_3$):** δ = 7.98 (s, 1H), 7.52-7.23 (m, 12H), 3.40 (s, 3H); **^{13}C NMR (100 MHz, $CDCl_3$):** δ =153.2, 153.0, 145.5, 133.5, 130.7, 130.1, 129.9, 128.7, 128.4, 127.7, 127.2, 125.2, 117.9, 117.8, 113.1, 61.6; **HRMS (EI$^+$):** calcd for $C_{22}H_{16}BrNO_2$ 405.0364, found 405.0358; **IR (KBr, cm^{-1}):** 3055, 2938 and 1604.

6-Methyl-2,3-diphenylbenzofuran-4-carbaldehyde *O*-methyl oxime (3ea)



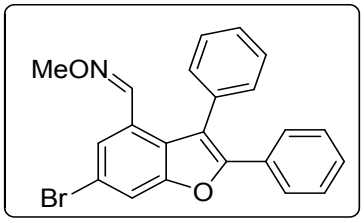
R_f = 0.85 (50% ethyl acetate in *n*-hexane); pale yellow solid; mp: 111-113 ˚C; **^{1}H NMR (400 MHz, $CDCl_3$):** δ = 7.69 (s, 1H), 7.56 (s, 1H), 7.50-7.47 (m, 5H), 7.41-7.39 (m, 2H), 7.37 (s, 1H), 7.25-7.22 (m, 3H), 3.83 (s, 3H), 2.48 (s, 3H); **^{13}C NMR (100 MHz, $CDCl_3$):** δ = 154.5, 150.8, 145.7, 135.1, 133.9, 130.4, 129.4, 128.4, 128.2, 126.5, 125.0, 121.4, 117.3, 112.6, 61.8, 21.6; **HRMS (EI$^+$):** calcd for $C_{23}H_{19}NO_2$ 341.1416, found 341.1416; **IR (KBr, cm^{-1}):** 2939 and 1604.

6-Methoxy-2,3-diphenylbenzofuran-4-carbaldehyde *O*-methyl oxime (3fa)



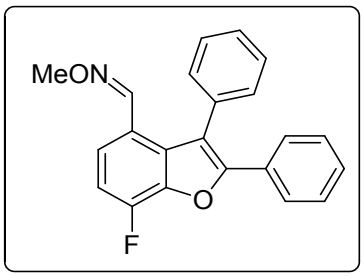
R_f = 0.68 (30% Ethyl acetate in *n*-hexane); white solid; mp: 100-102 ˚C; **^{1}H NMR (400 MHz, $CDCl_3$):** δ = 7.68 (s, 1H), 7.51-7.46 (m, 5H), 7.43-7.40 (m, 2H), 7.38 (d, *J* = 2.4 Hz, 1H), 7.26-7.23 (m, 3H), 7.13 (d, *J* = 2.4 Hz, 1H), 3.90 (s, 3H), 3.84 (s, 3H); **^{13}C NMR (100 MHz, $CDCl_3$):** δ =157.9, 155.1, 150.5, 145.1, 133.8, 130.4, 130.3, 129.3, 128.4, 128.3, 127.9, 126.2, 125.6, 122.9, 117.1, 107.3, 98.0, 61.9, 55.9; **HRMS (EI^+):** calcd for $C_{23}H_{19}NO_3$ 357.1365, found 357.1363; **IR (KBr, cm^{-1}):** 3062, 2939 and 1620.

6-Bromo-2,3-diphenylbenzofuran-4-carbaldehyde *O*-methyl oxime (3ga)



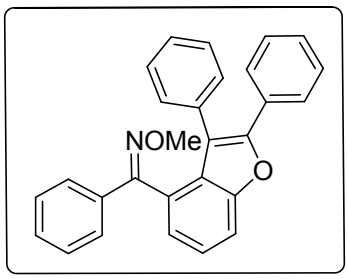
R_f = 0.81 (30% ethyl acetate in *n*-hexane); white solid; mp: 112-115 ˚C; **^{1}H NMR (400 MHz, $CDCl_3$):** δ = 7.87 (d, *J* = 1.6 Hz, 1H), 7.69 (d, *J* = 1.6 Hz, 1H), 7.60 (s, 1H), 7.51-7.46 (m, 5H), 7.39-7.37 (m, 2H), 7.26-7.24 (m, 3H), 3.83 (s, 3H); **^{13}C NMR (100 MHz, $CDCl_3$):** δ = 154.3, 152.0, 144.1, 133.1, 130.4, 129.8, 129.5, 128.7, 128.5, 127.8, 126.7, 123.3, 118.0, 117.2, 115.2, 62.1; **HRMS (EI^+):** calcd for $C_{22}H_{16}BrNO_2$ 405.0364, found 405.0364; **IR (KBr, cm^{-1}):** 2276, 1736 and 1604.

7-Fluoro-2,3-diphenylbenzofuran-4-carbaldehyde *O*-methyl oxime (3ha)



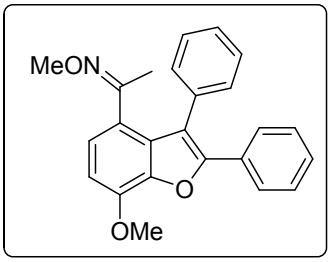
R_f = 0.82 (30% ethyl acetate in *n*-hexane); yellow solid; mp: 160-162 ˚C; **^{1}H NMR (400 MHz, $CDCl_3$):** δ = 7.66 (quart, *J* = 4.4 Hz, 1H), 7.60 (s, 1H), 7.53-7.47 (m, 5H), 7.41-7.38 (m, 2H), 7.28-7.25 (m, 3H), 7.04 (m, 1H), 3.80 (s, 3H); **^{13}C NMR (100 MHz, $CDCl_3$):** δ = 152.4, 149.8, 147.3, 144.7, 141.0, 132.9, 131.9, 130.4, 129.7, 129.5, 128.9, 128.8, 128.5, 126.8, 121.7, 121.4, 121.3, 117.7, 111.4, 111.3, 61.9; **HRMS (EI^+):** calcd for $C_{22}H_{16}FNO_2$ 345.1165, found 345.1162; **IR (KBr, cm^{-1}):** 2337, 1581 and 1396.

(2,3-Diphenylbenzofuran-4-yl)(phenyl)methanone *O*-methyl oxime (3ia)



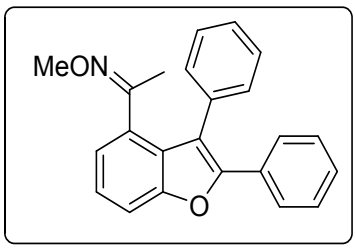
R_f = 0.63 (20% ethyl acetate in *n*-hexane); white solid; mp: 128-131˚C; **^{1}H NMR (400 MHz, $CDCl_3$):** δ = 7.63 (d, J = 8.0 Hz, 1H), 7.48-7.11 (m, 17H), 3.76 (s, 3H); **^{13}C NMR (100 MHz, $CDCl_3$):** δ = 154.3, 154.0, 151.5, 133.3, 133.1, 130.9, 130.4, 130.3, 129.9, 128.8, 128.4, 128.3, 128.2, 127.5, 127.1, 127.0, 125.6, 124.2, 117.9, 111.7, 62.1; **HRMS (EI$^+$):** calcd for $C_{28}H_{21}NO_2$ 403.1572, found 403.1563; **IR (KBr, cm^{-1}):** 2931 and 1604.

1-(7-Methoxy-2,3-diphenylbenzofuran-4-yl)ethanone *O*-methyl oxime (3ja)



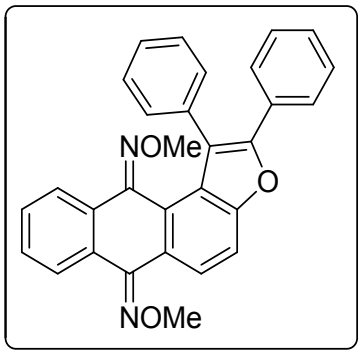
R_f = 0.49 (20% ethyl acetate in *n*-hexane); white solid; mp: 129-131 ˚C; **^{1}H NMR (400 MHz, $CDCl_3$):** δ = 7.58-7.25 (m, 10H), 7.07 (d, J = 8.0 Hz, 1H), 6.83 (d, J = 8.0 Hz, 1H), 4.07 (s, 3H), 3.72 (s, 3H), 1.53 (s, 3H); **^{13}C NMR (100 MHz, $CDCl_3$):** δ = 155.6, 151.4, 145.7, 143.5, 133.4, 130.6, 130.4, 129.0, 128.5, 128.3, 128.2, 127.6, 127.2, 124.3, 124.0, 117.9, 106.5, 61.4, 56.3, 16.8; **HRMS (EI$^+$):** calcd for $C_{24}H_{21}NO_3$ 371.1521, found 371.1511; **IR (KBr, cm^{-1}):** 2931 and 1619.

1-(2,3-Diphenylbenzofuran-4-yl)ethanone *O*-methyl oxime (3ka)



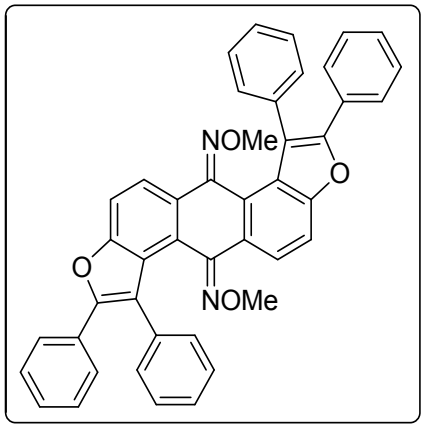
R_f = 0.64 (20% ethyl acetate in *n*-hexane); colorless oil; **^{1}H NMR (400 MHz, $CDCl_3$):** δ = 7.59-7.54 (m, 3H), 7.43-7.27 (m, 9H), 7.13 (d, J = 7.2 Hz, 1H), 3.72 (s, 3H), 1.59 (s, 3H); **^{13}C NMR (100 MHz, $CDCl_3$):** δ = 155.6, 154.3, 133.6, 131.8, 130.6, 130.5, 128.5, 128.3, 127.6, 127.5, 127.0, 124.4, 123.2, 117.6, 111.5, 61.5, 16.7; **HRMS (EI$^+$):** calcd for $C_{23}H_{19}NO_2$ 341.1416, found 341.1407; **IR (KBr, cm^{-1}):** 2931 and 1604.

1,2-Diphenylanthra[2,1-*b*]furan-6,11-dione *O*,*O*-dimethyl dioxime (**3la**; mixture of isomers)



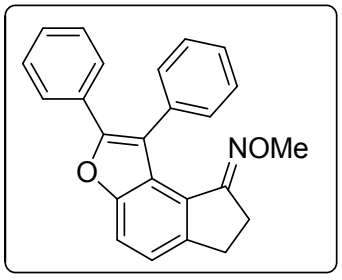
R_f = 0.51 (20% ethyl acetate in *n*-hexane); pale yellow oil; **^{1}H NMR for major isomer (400 MHz, $CDCl_3$):** δ = 8.60 (t, *J* = 8.8 Hz, 1H), 8.02 (d, *J* = 8.8 Hz, 1H), 7.67-7.26 (m, 14H), 4.17 (s, 3H), 3.28 (s, 3H); **^{13}C NMR (100 MHz, $CDCl_3$):** δ = 155.3, 155.1, 152.8, 147.2, 147.0, 145.0, 144.9, 134.9, 134.8, 134.2, 131.5, 130.5, 130.4, 130.3 (2C), 130.0, 129.8, 129.5, 129.2, 128.7, 128.6, 128.5, 128.4, 128.2, 128.1, 128.0, 127.7, 127.6, 127.0, 126.9, 126.7, 126.3, 124.9, 124.8, 124.2, 121.4, 118.5, 118.4, 112.0, 110.9, 63.0, 62.9, 62.09, 62.04; **HRMS (EI$^+$):** calcd for $C_{30}H_{22}N_2O_3$ 458.1630, found 458.1629; **IR (KBr, cm^{-1}):** 2931 and 1565.

1,2,7,8-Tetraphenylanthra[2,1-*b*:6,5-*b′*]difuran-6,12-dione *O,O*-dimethyl dioxime (3ma)



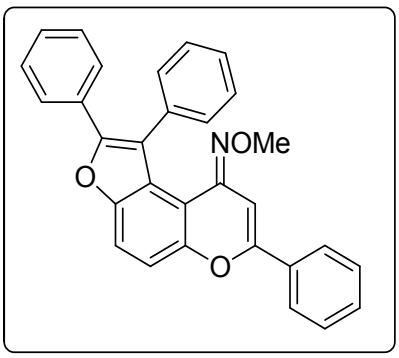
R_f = 0.43 (20% ethyl acetate in *n*-hexane); yellow solid; mp: 311-314 ˚C; **^{1}H NMR (400 MHz, $CDCl_3$):** δ = 8.03 (d, *J* = 8.4 Hz, 2H), 7.62 (d, *J* = 8.4 Hz, 2H), 7.54-7.29 (m, 20H), 3.28 (s, 6H); **^{13}C NMR (100 MHz, $CDCl_3$):** δ = 154.9, 152.7, 145.2, 134.8, 130.5, 130.4, 128.9, 128.4, 128.3, 128.2, 127.7, 127.1, 125.3, 125.0, 118.4, 110.5, 62.1; **HRMS (EI$^+$):** calcd for $C_{44}H_{30}N_2O_4$ 650.2206, found 650.2215; **IR (KBr, cm^{-1}):** 2933 and 1573.

1,2-Diphenyl-6*H*-indeno[5,4-b]furan-8(7*H*)-one *O*-methyl oxime (3na)



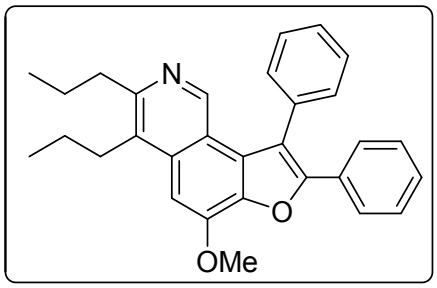
R_f = 0.66 (20% ethyl acetate in *n*-hexane); yellow solid; mp: 150-153 ˚C; **^{1}H NMR (400 MHz, $CDCl_3$):** δ = 7.56-7.51 (m, 4H), 7.43-7.42 (m, 4H), 7.27-7.22 (m, 4H), 3.31 (s, 3H), 3.08 (t, *J*=6.4 Hz, 2H), 2.85-2.82 (m, 2H); **^{13}C NMR (100 MHz, $CDCl_3$):** δ = 162.2, 153.7, 144.2, 135.3, 131.4, 130.7, 129.2, 128.2, 128.1, 127.9, 127.3, 126.8, 125.3, 125.1, 121.2, 118.9, 112.8, 61.4, 28.8, 26.3; **HRMS (EI$^+$):** calcd for $C_{24}H_{19}NO_2$ 353.1416, found 353.1417; **IR (KBr, cm^{-1}):** 2931 and 1604.

1,2,7-Triphenyl-9*H*-furo[3,2-*f*]chromen-9-one *O*-methyl oxime (3oa)



R_f = 0.68 (20% ethyl acetate in *n*-hexane); white solid; mp: 199-202 ˚C; **^{1}H NMR (400 MHz, $CDCl_3$):** δ = 7.89-7.87 (m, 2H), 7.64 (d, *J* = 8.8 Hz, 1H), 7.47-7.34 (m, 10H), 7.31 (d, *J* = 8.4 Hz, 1H), 7.26-7.25 (m, 3H), 7.02 (s, 1H), 3.16 (s, 3H); **^{13}C NMR (100 MHz, $CDCl_3$):** δ = 153.8, 153.7, 151.5, 149.8, 143.1, 136.7, 132.7, 130.8, 129.9, 128.5, 128.2, 128.1, 127.8, 127.7, 127.5, 126.8, 125.4, 124.9, 123.6, 114.7, 113.3, 112.4, 93.8, 60.7; **HRMS (EI$^+$):** calcd for $C_{30}H_{21}NO_3$ 443.1521, found 443.1520; **IR (KBr, cm^{-1}):** 2931 and 1643.

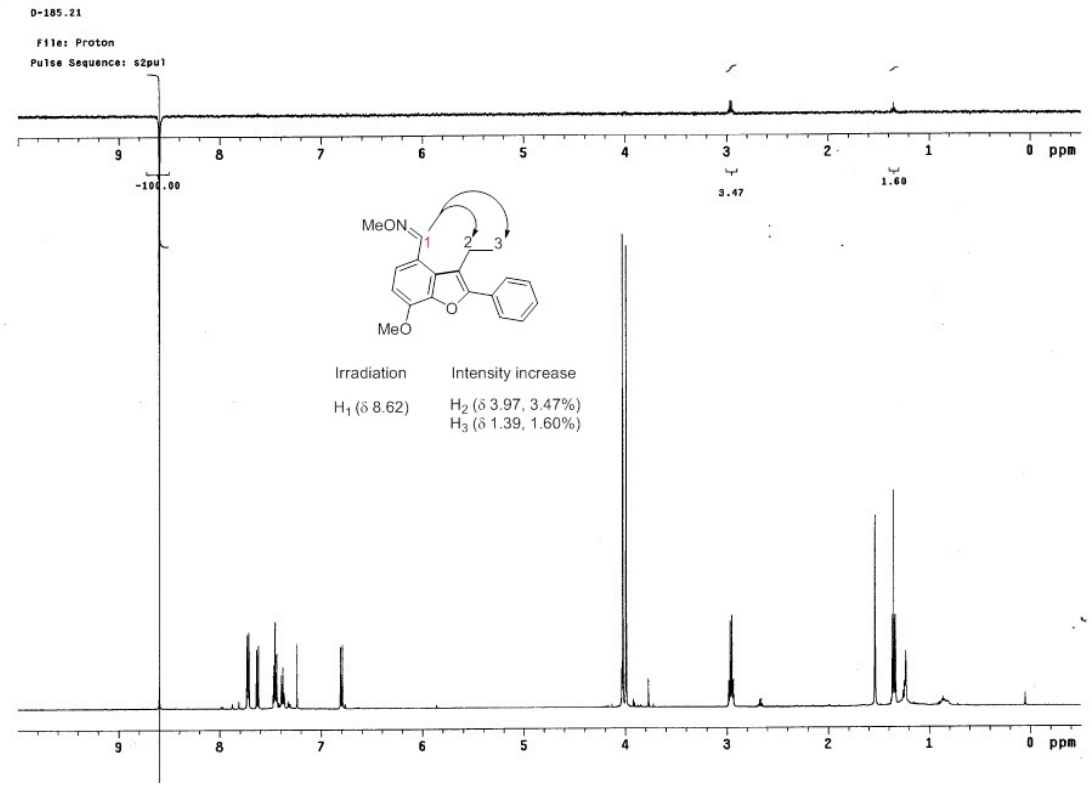
6-Methoxy-8,9-diphenyl-3,4-dipropylfuro[2,3-*h*]isoquinoline (4)

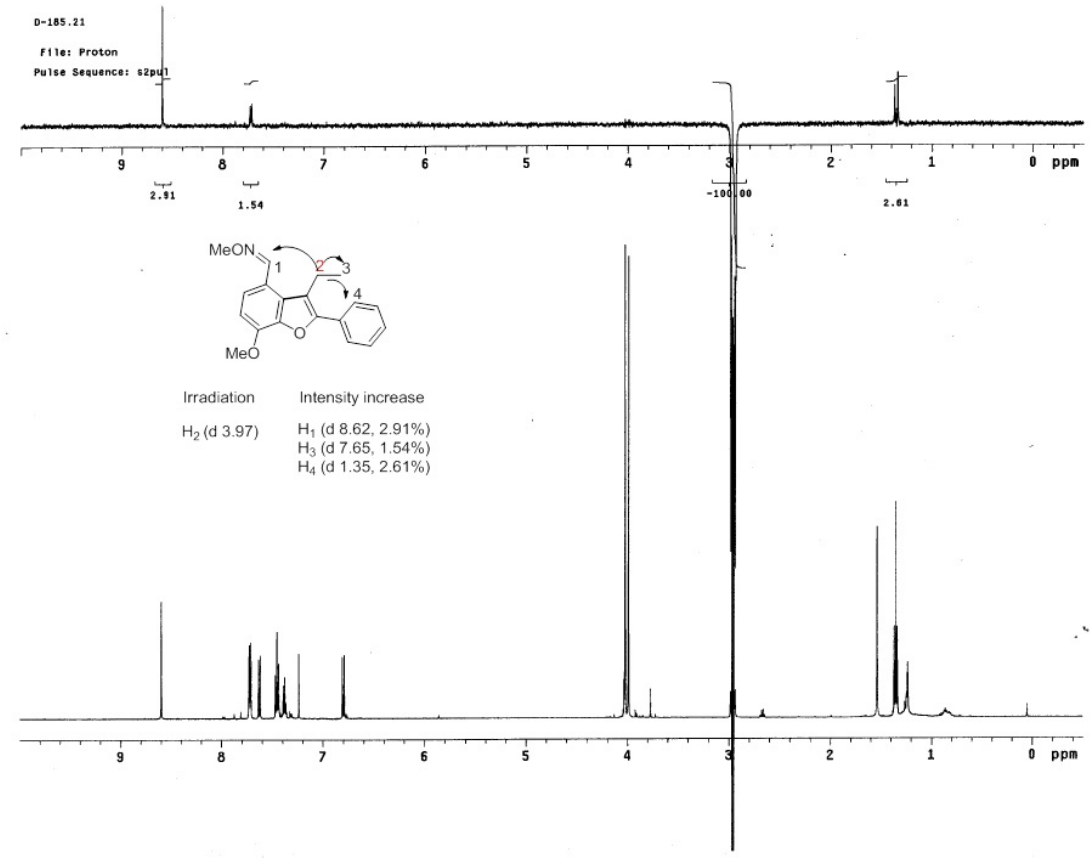


R_f = 0.23 (20 % ethyl acetate in *n*-hexane); yellow solid; mp: 155-158 ˚C; **^{1}H NMR (400 MHz, $CDCl_3$):** δ = 8.65 (s, 1H), 7.59-7.50 (m, 7H), 7.28-7.24 (m, 3H), 7.14 (s, 1H), 4.19 (s, 3H), 3.03-2.86 (m, 4H), 1.77-1.70 (m, 4H), 1.12 (t, *J* = 7.2 Hz, 3H), 1.01 (t, *J* = 7.2 Hz, 3H); **^{13}C NMR (100 MHz, $CDCl_3$):** δ = 152.5, 151.4, 148.4, 144.2, 142.5, 135.0, 133.8, 130.3, 129.7, 128.5, 128.4, 128.2, 128.1, 126.4, 126.2, 119.3, 118.1, 55.9, 37.6, 30.7, 23.7, 23.6, 14.7, 14.4; **HRMS (EI$^+$):** calcd for $C_{30}H_{29}NO_2$ 435.2198, found 435.2196; **IR (KBr, cm^{-1}):** 2962 and 1612.

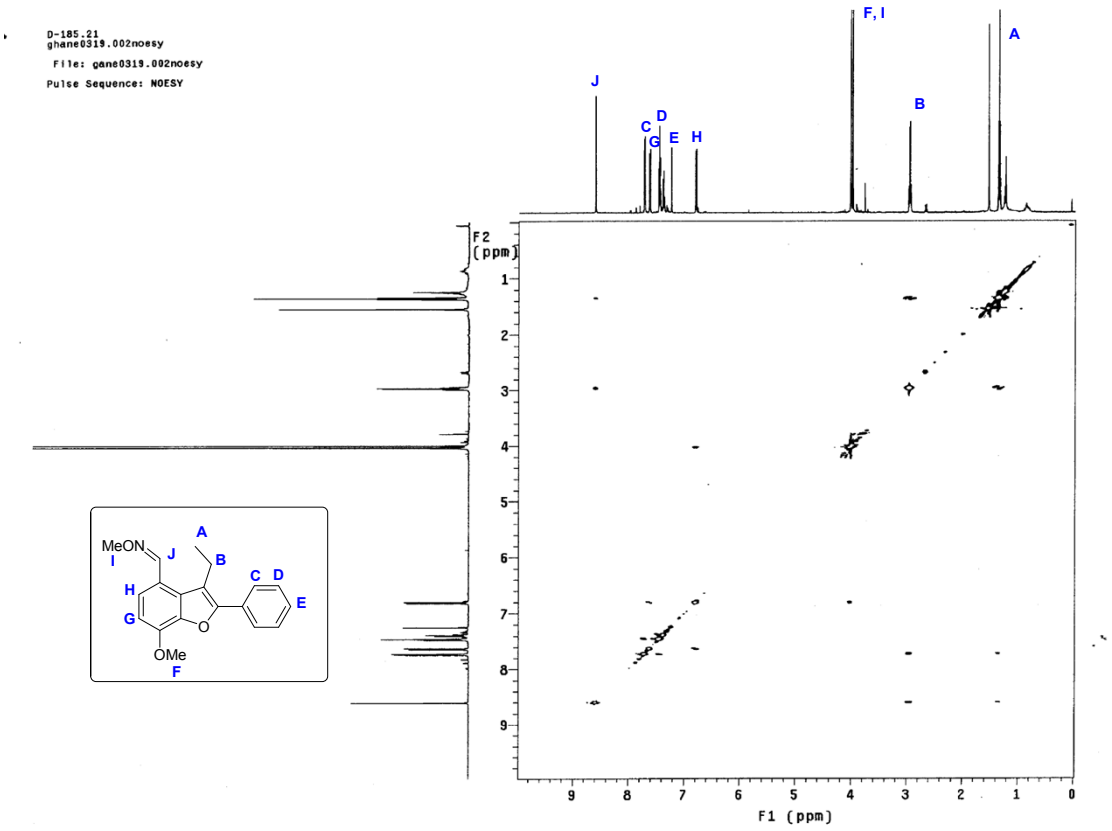
NOE and NOESY spectra of 3ag

NOE spectra of compound **3ag**





NOESY spectra of compound **3ag**



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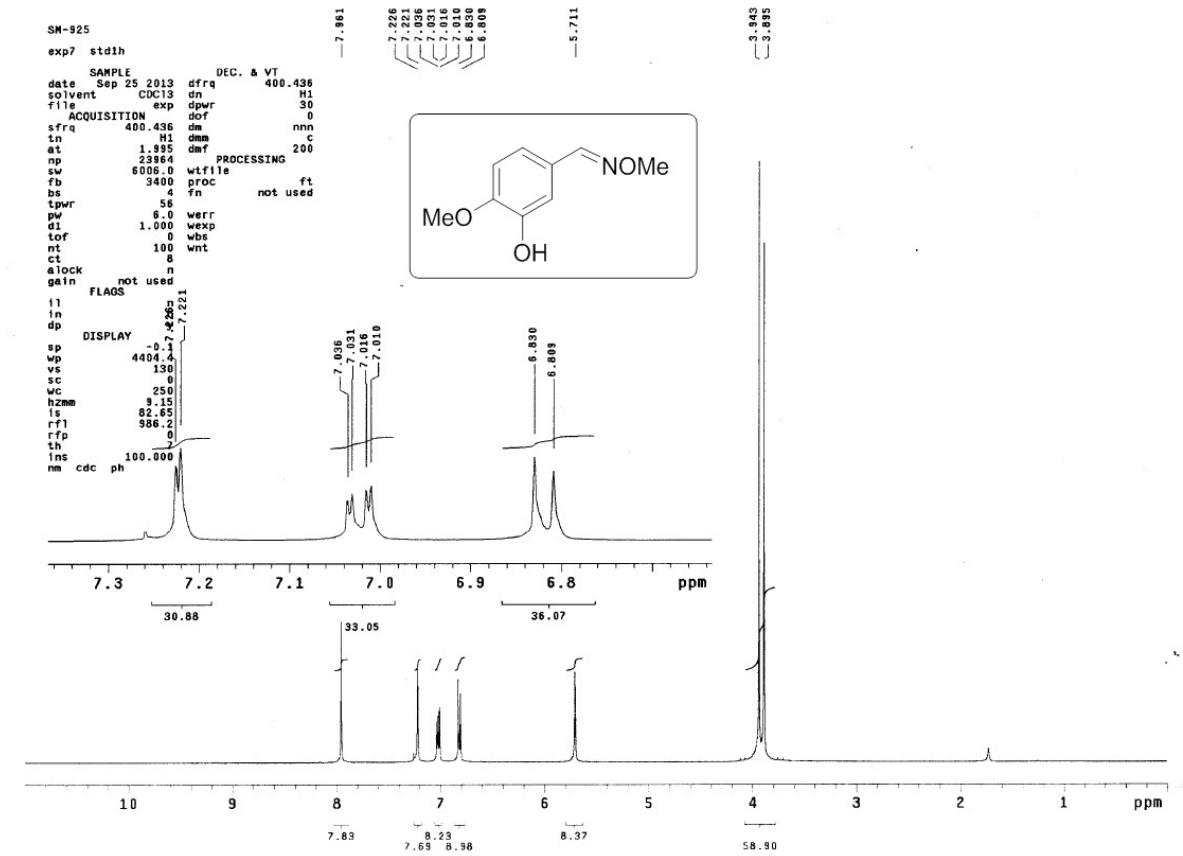
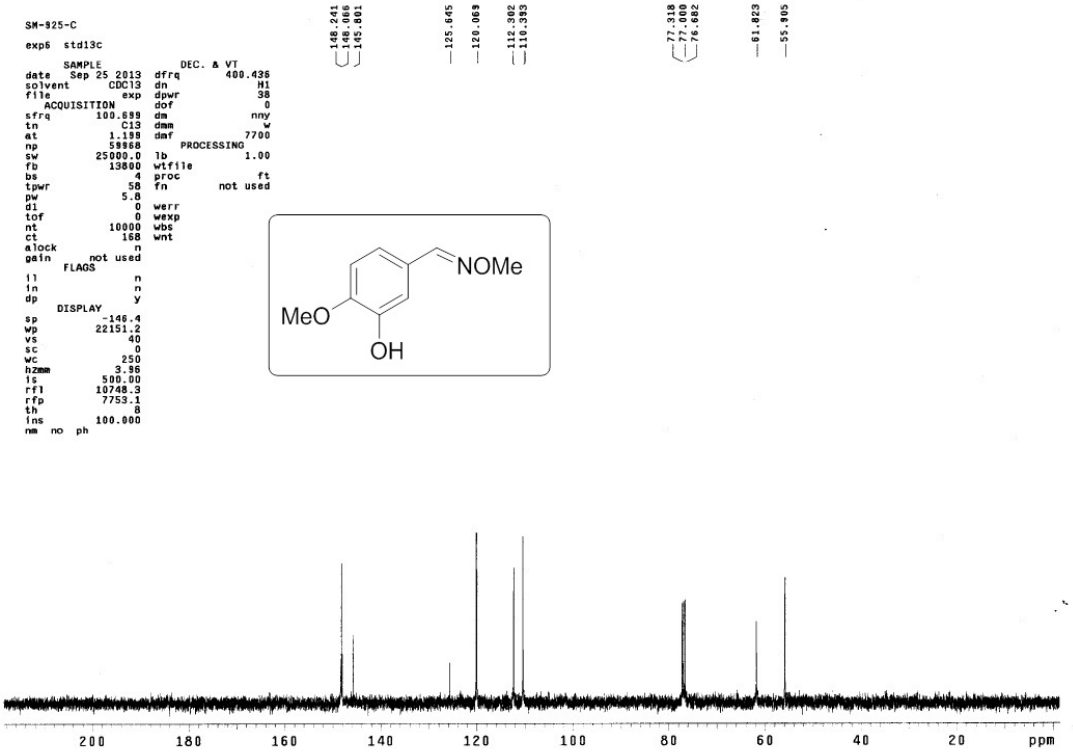
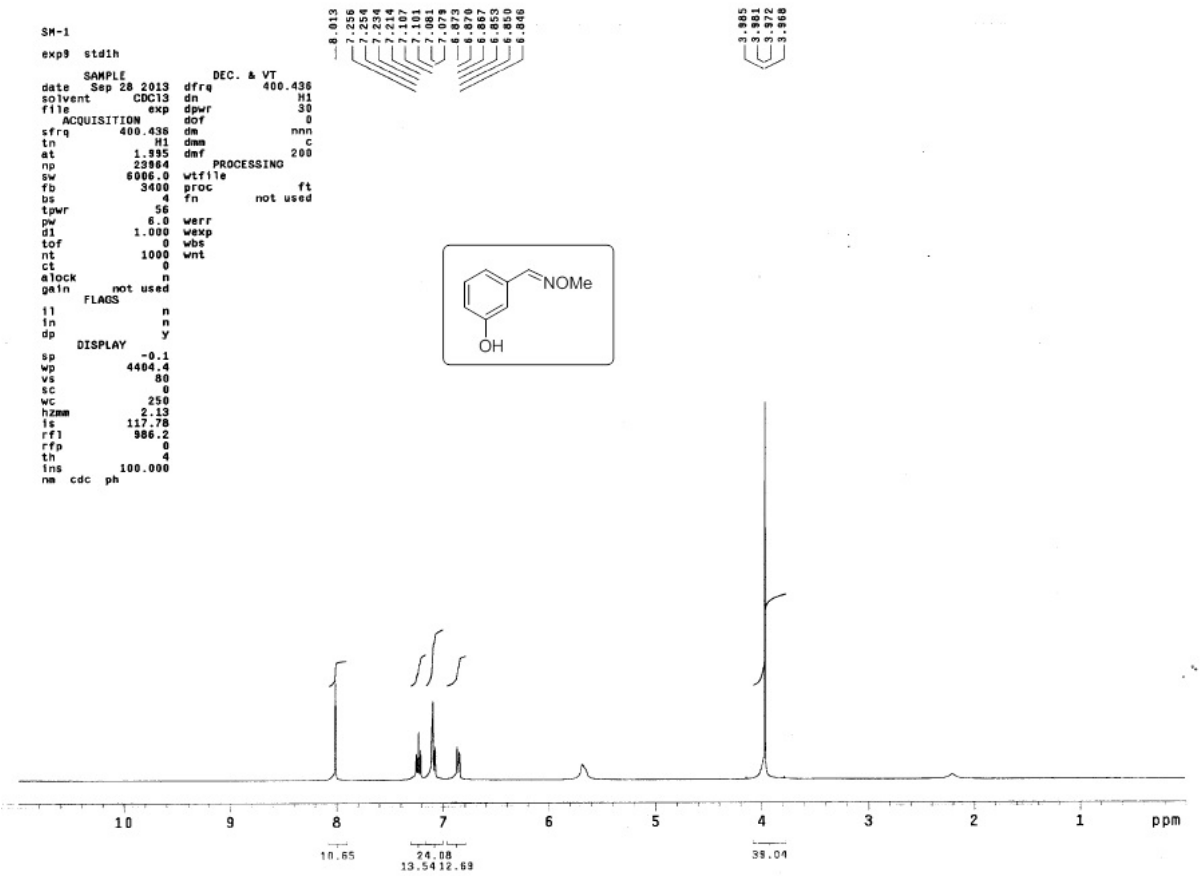
1H and 13C NMR Spectra

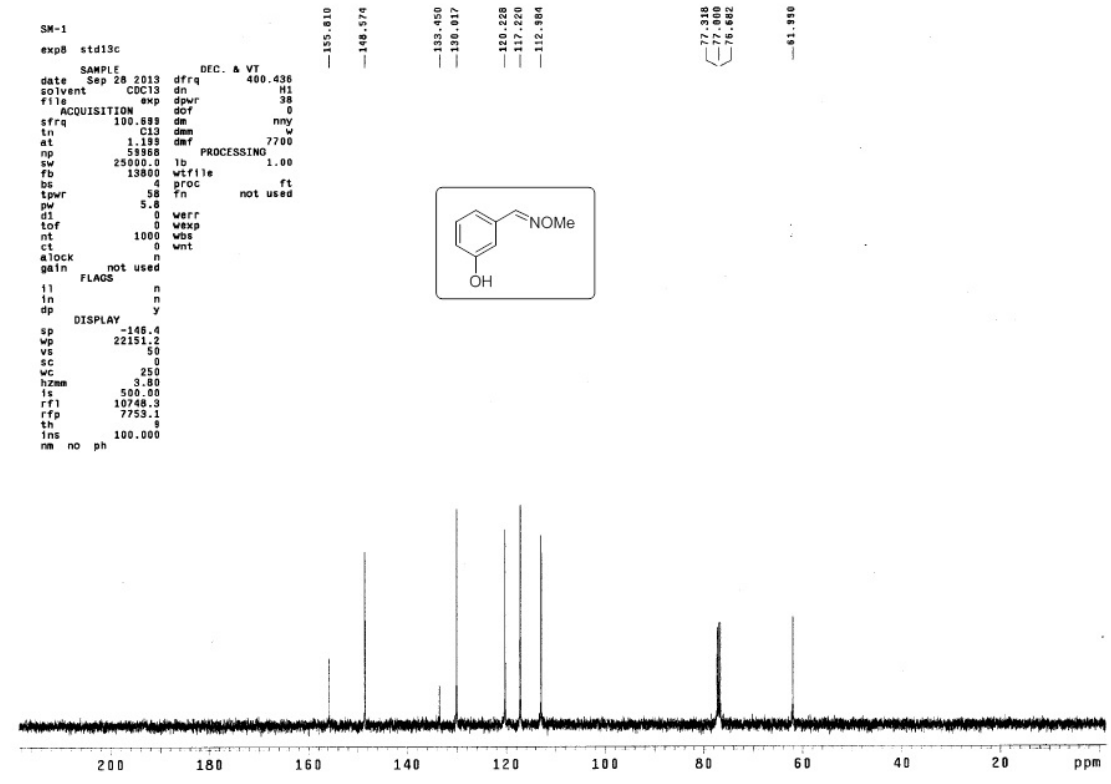
^{1}H and ^{13}C spectra of compound **1a**



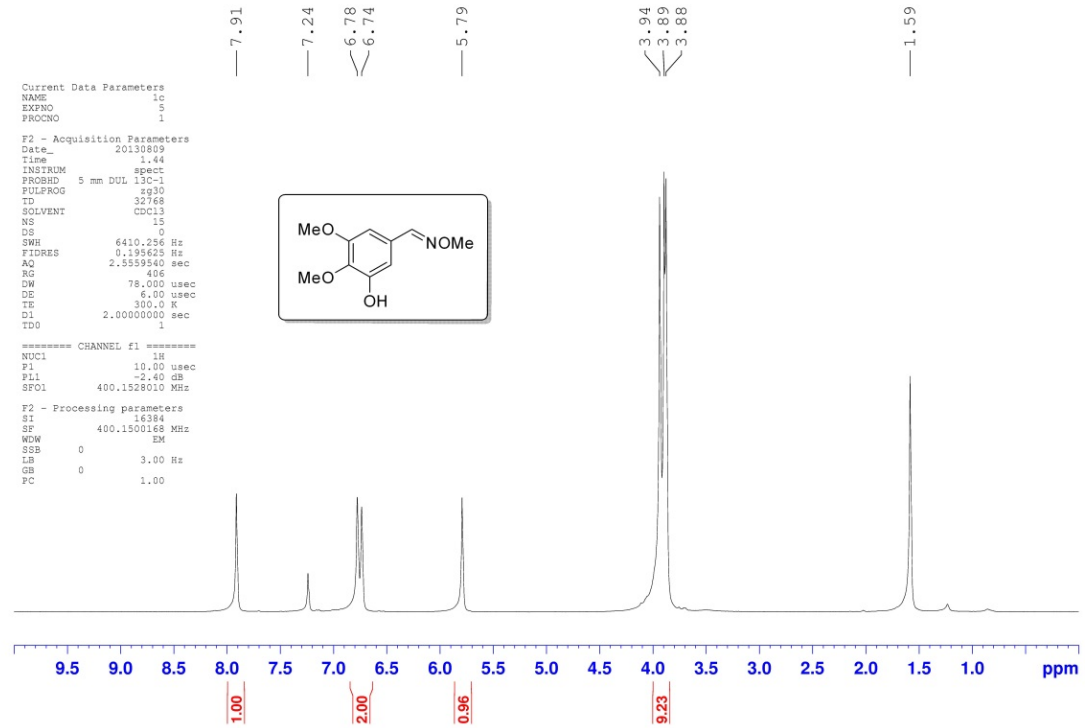


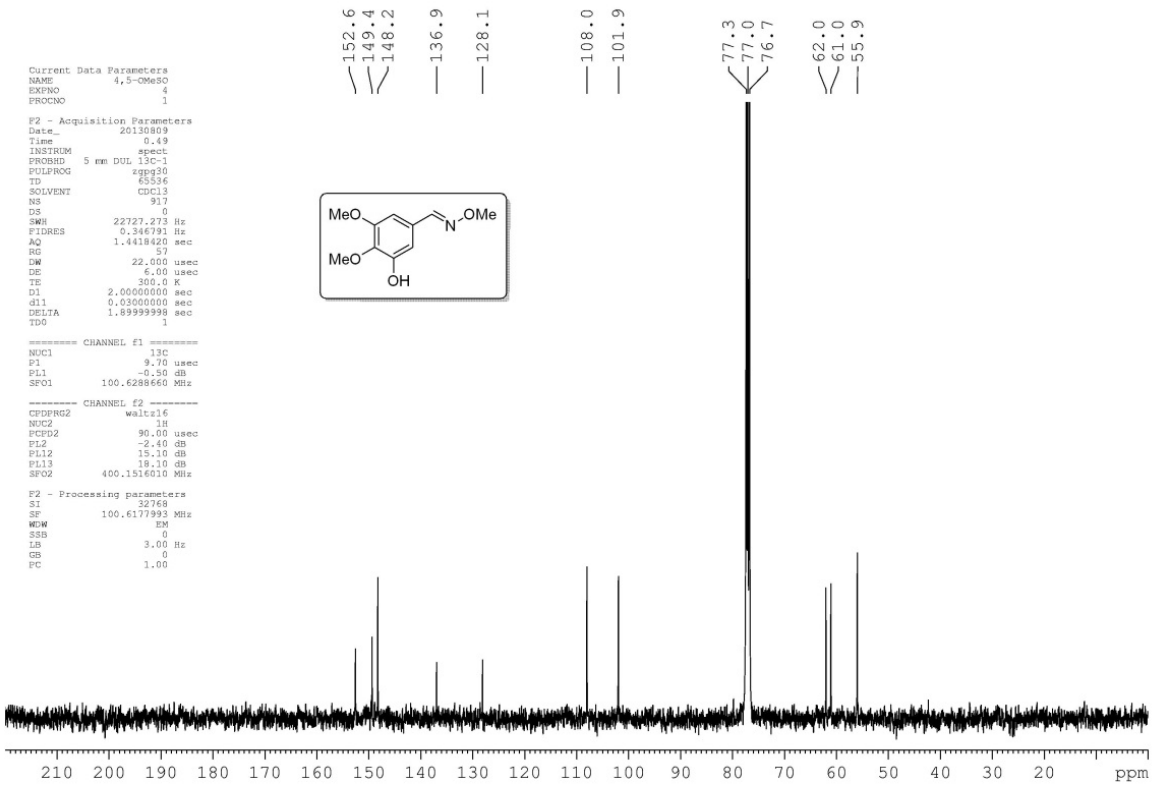
^{1}H and ^{13}C spectra of compound **1b**



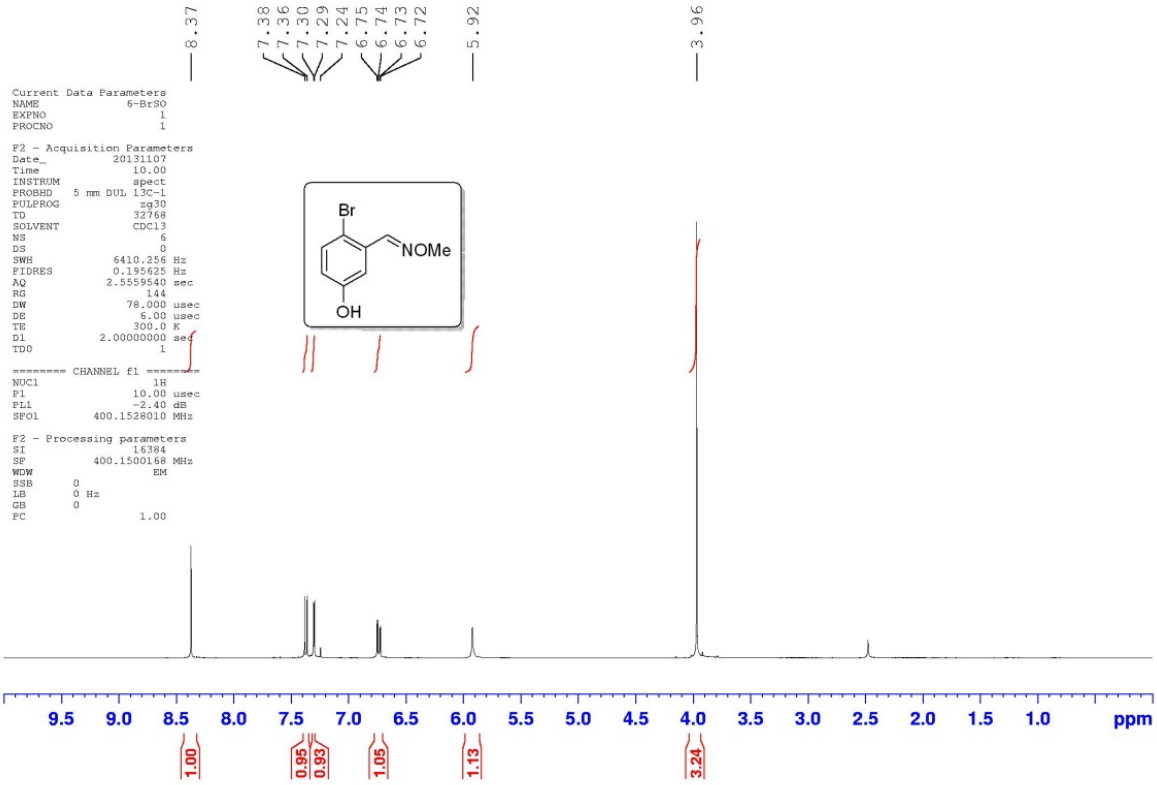


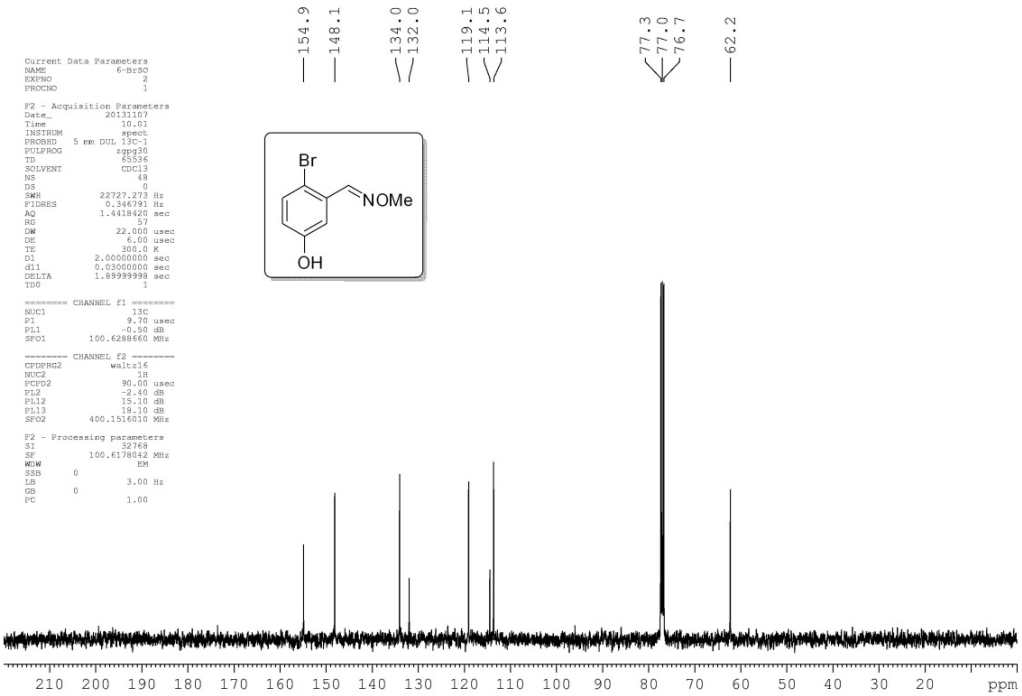
^{1}H and ^{13}C spectra of compound **1c**



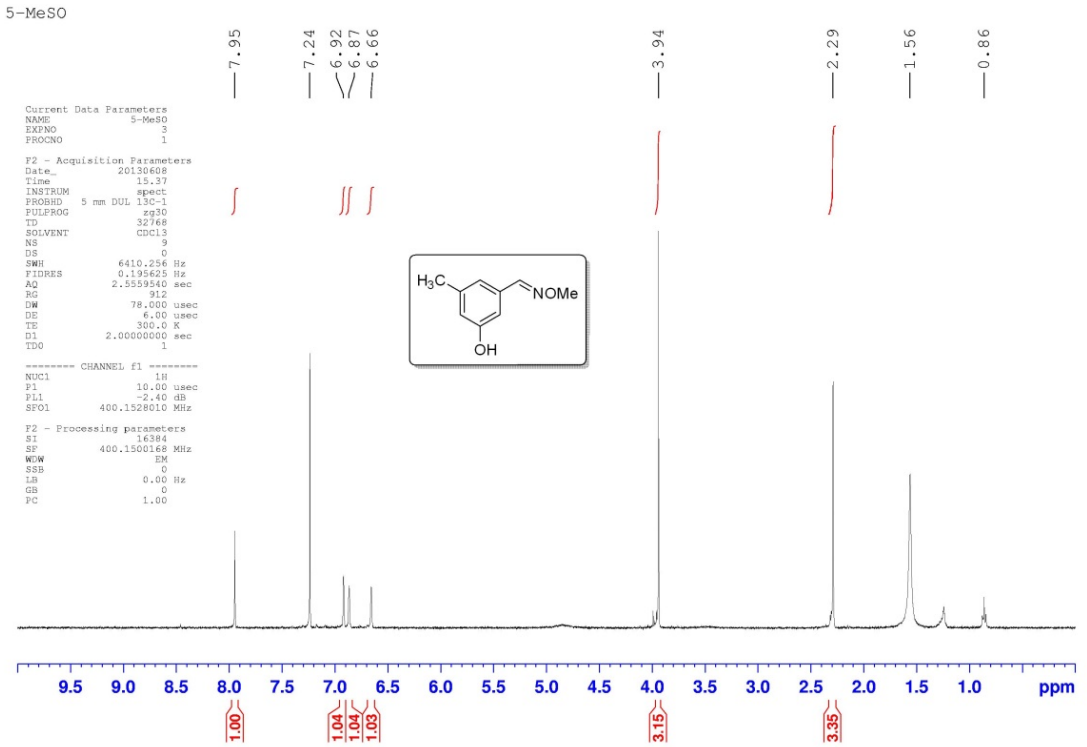


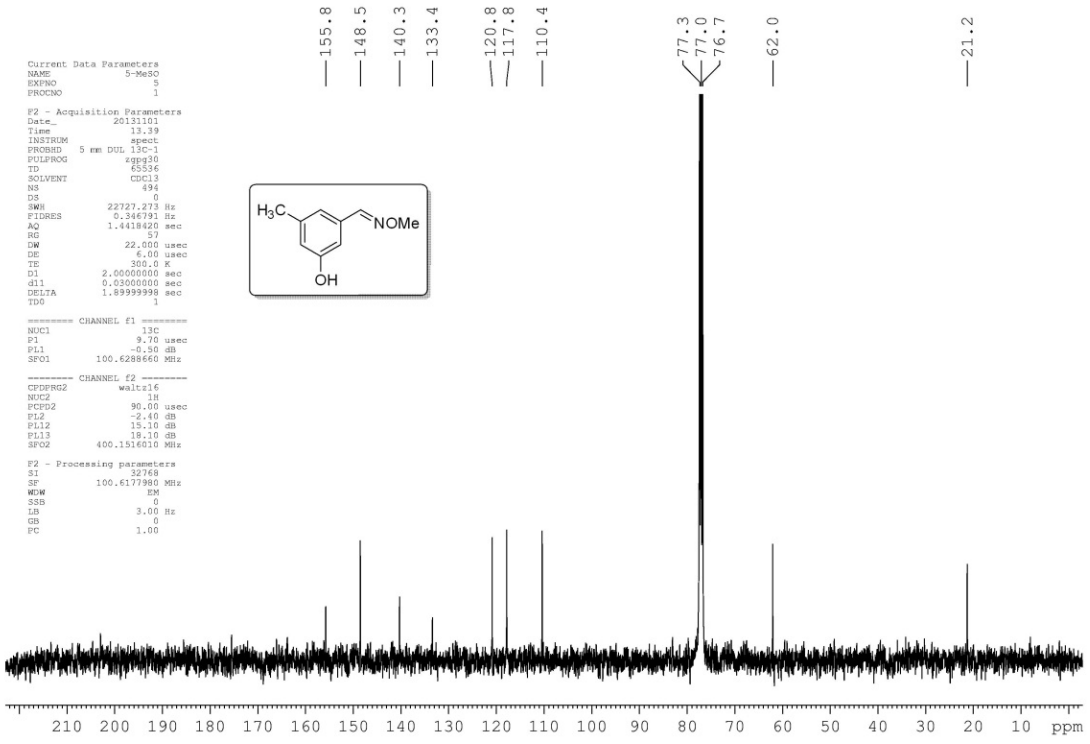
^{1}H and ^{13}C spectra of compound **1d**



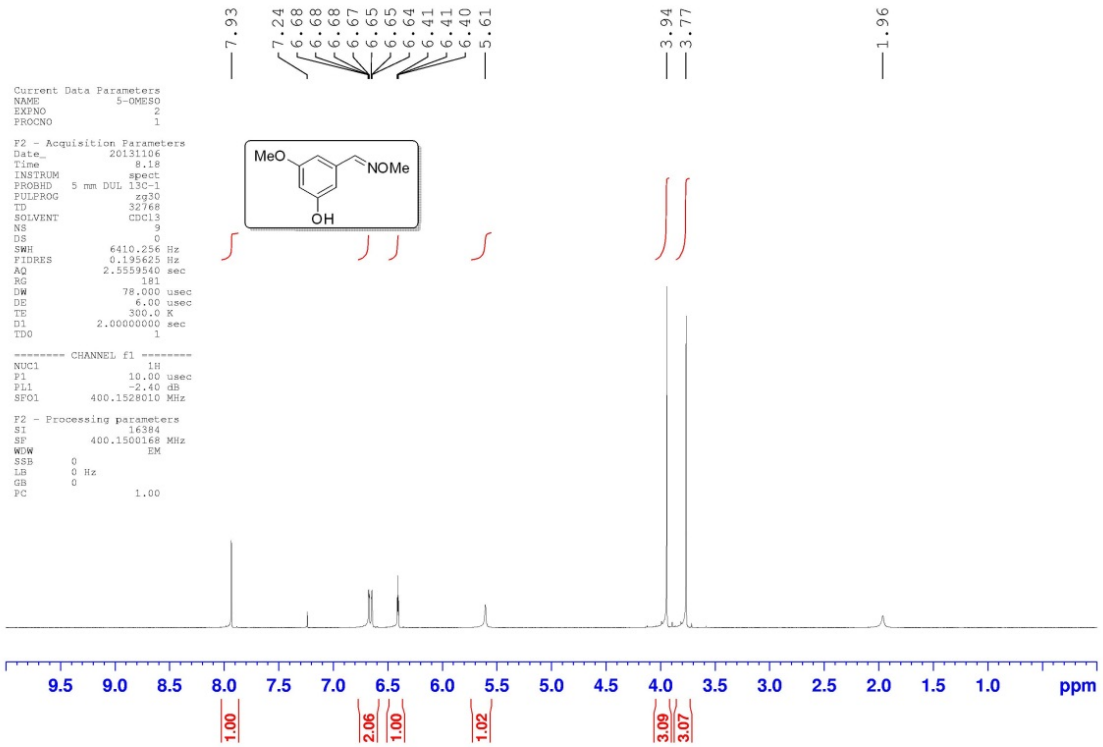


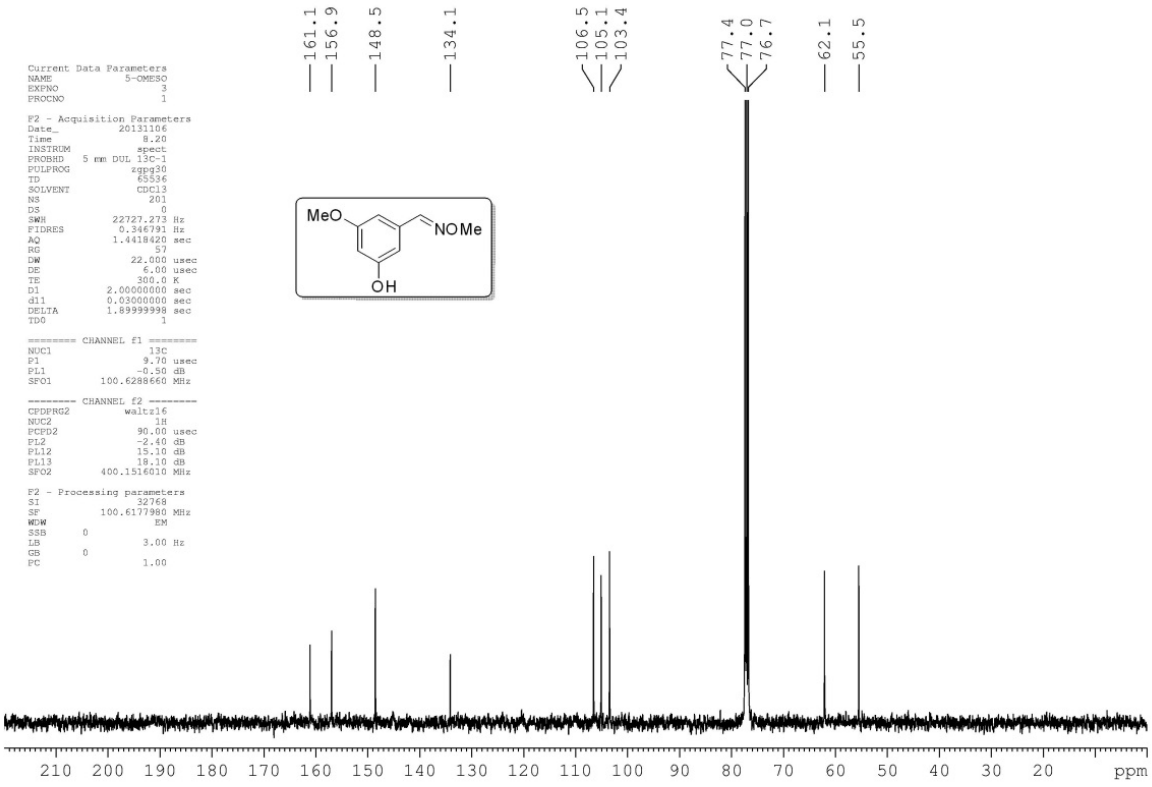
^{1}H and ^{13}C spectra of compound **1e**



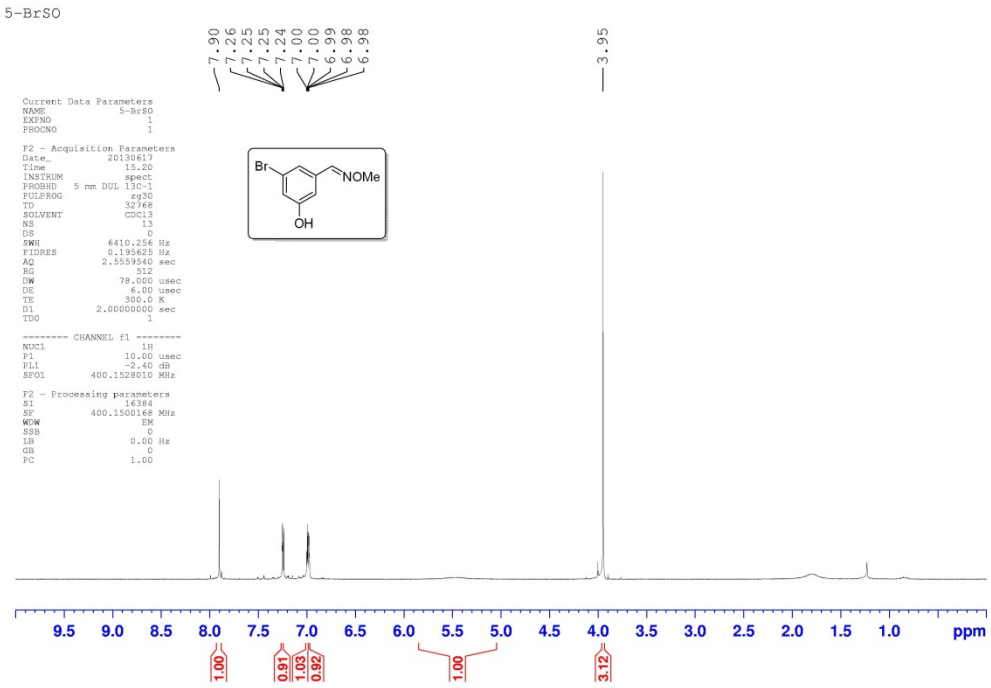


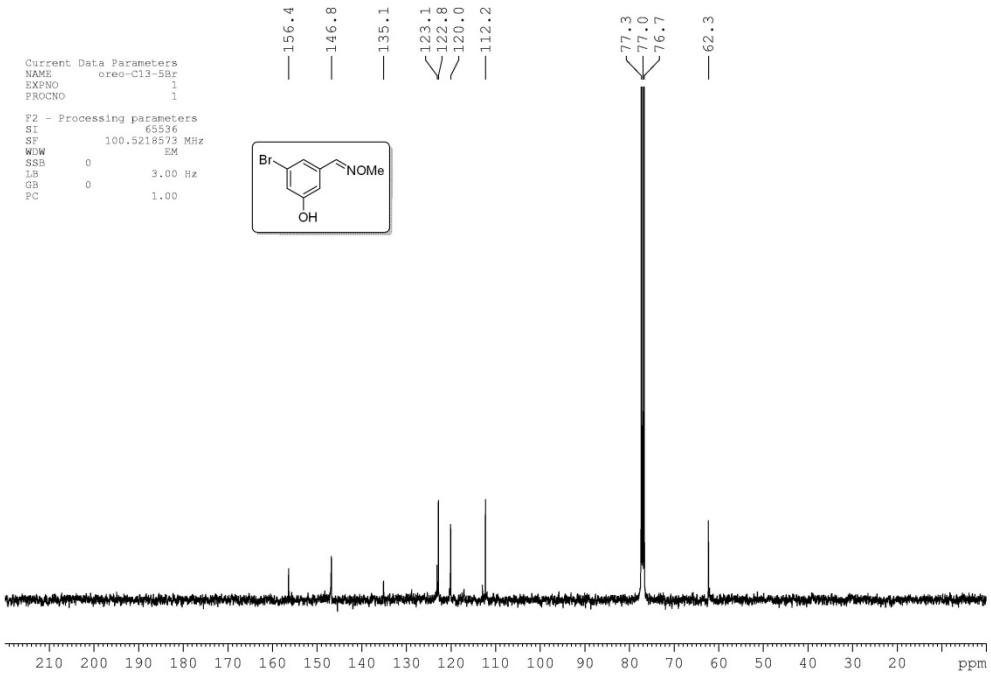
^{1}H and ^{13}C spectra of compound **1f**



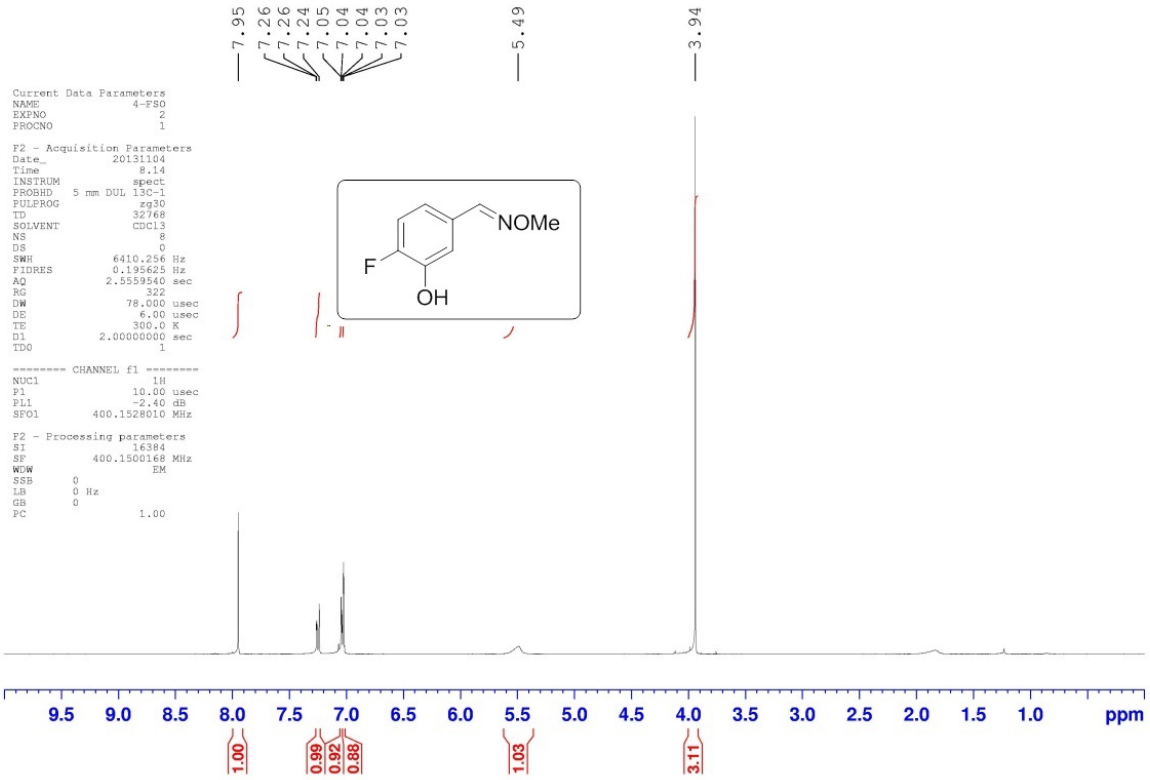


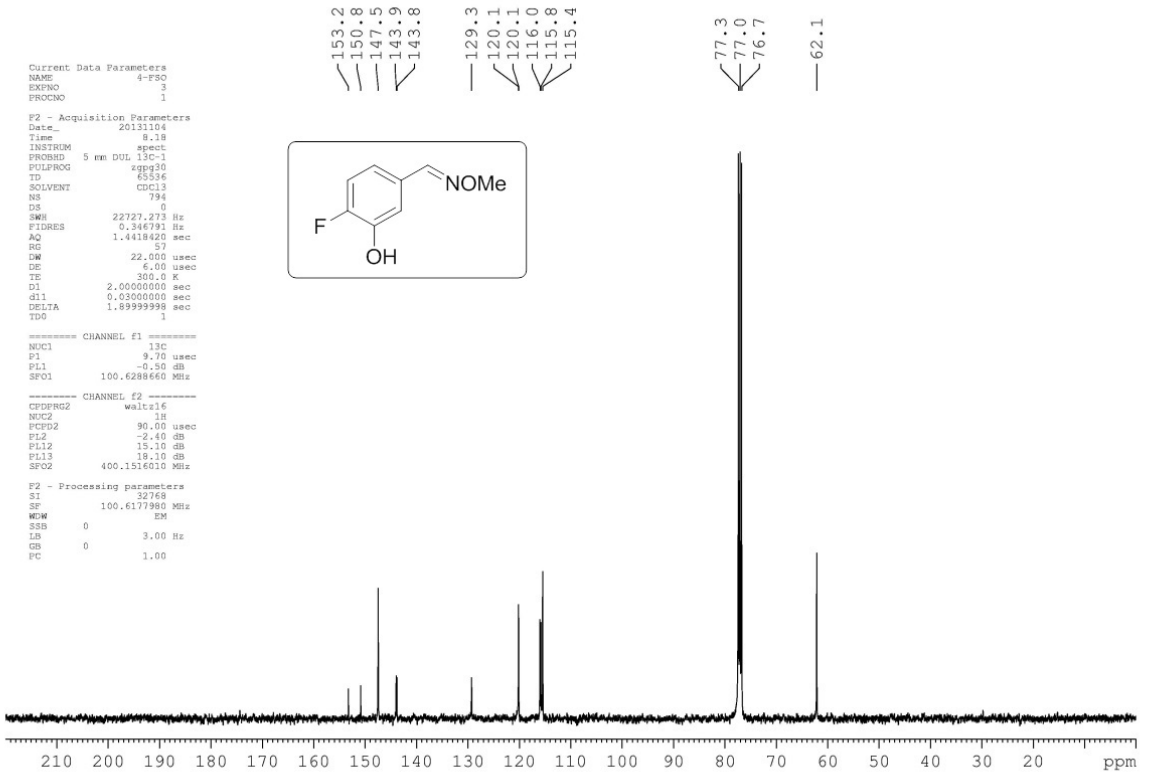
^{1}H and ^{13}C spectra of compound **1g**



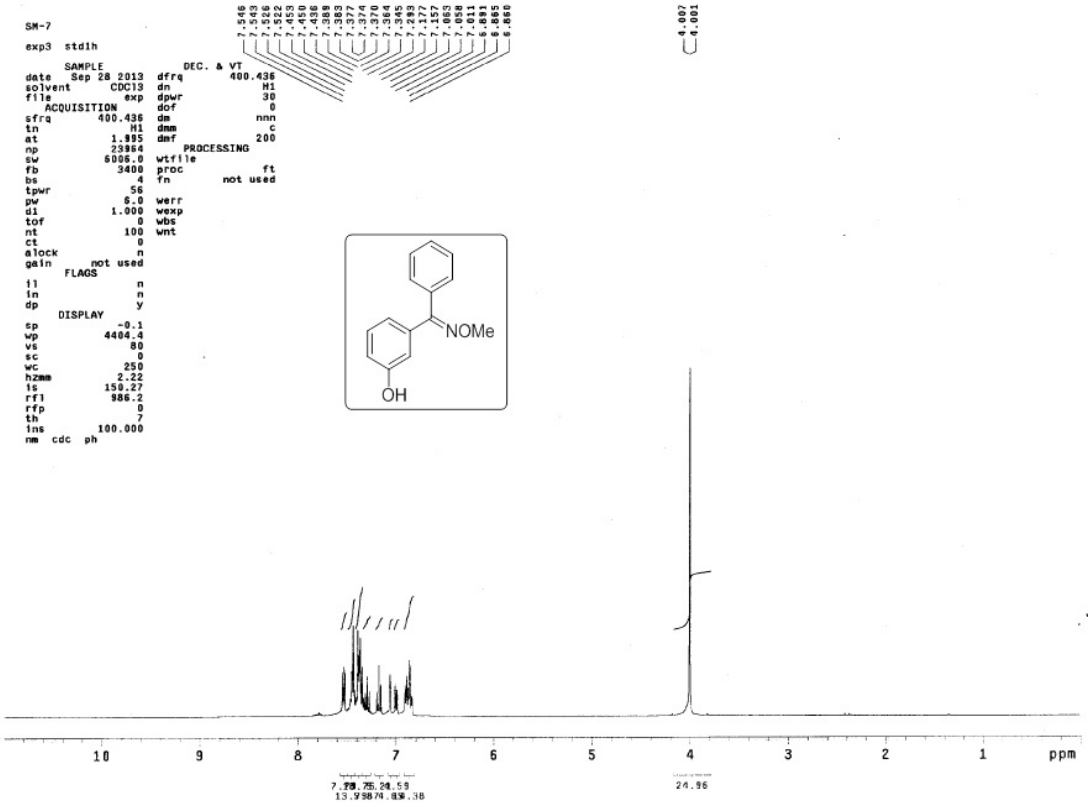


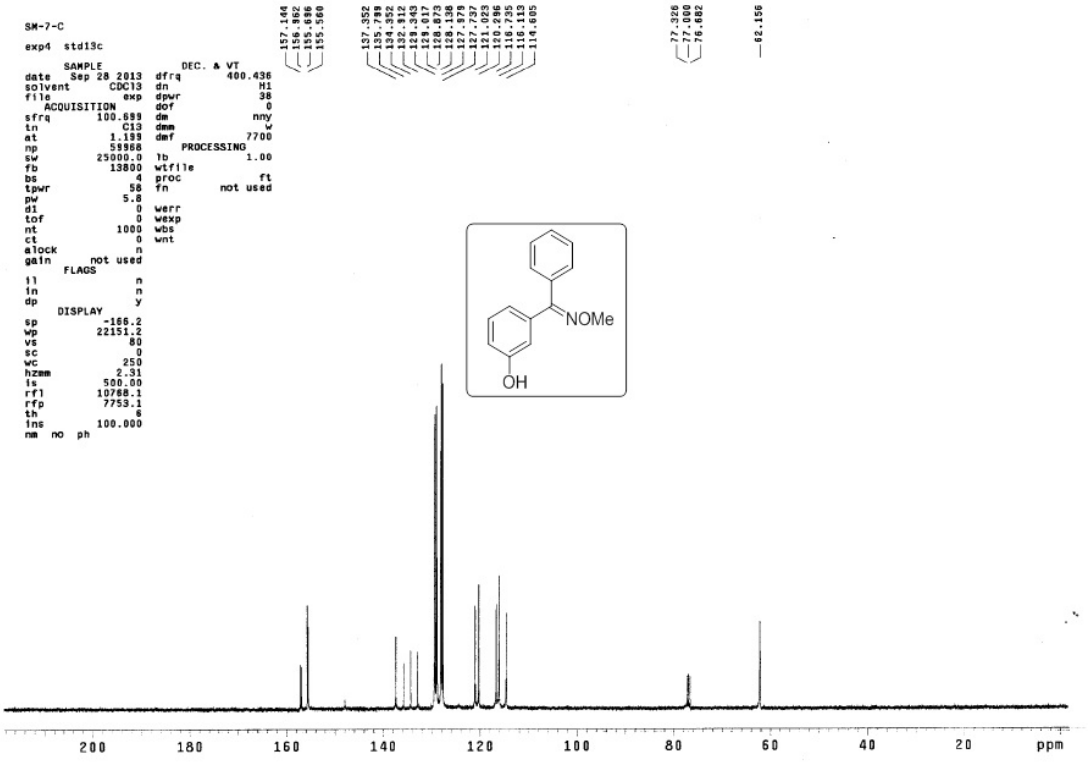
^{1}H and ^{13}C spectra of compound **1h**



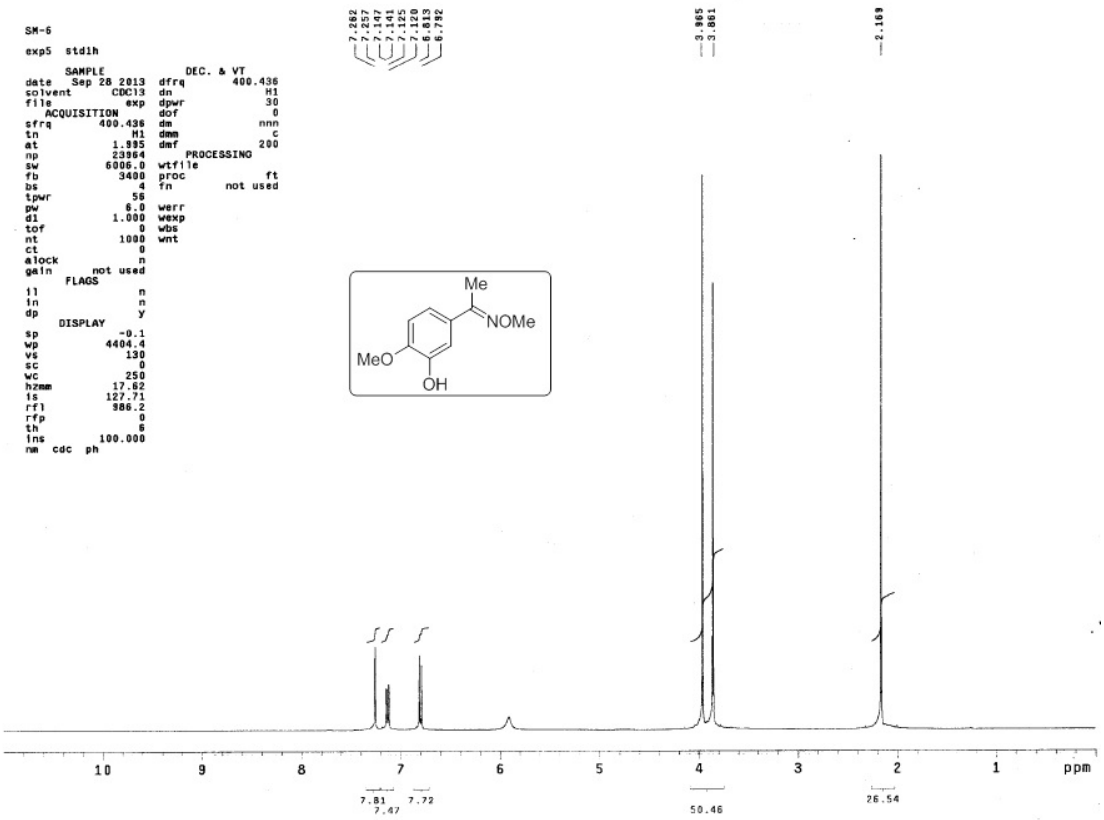


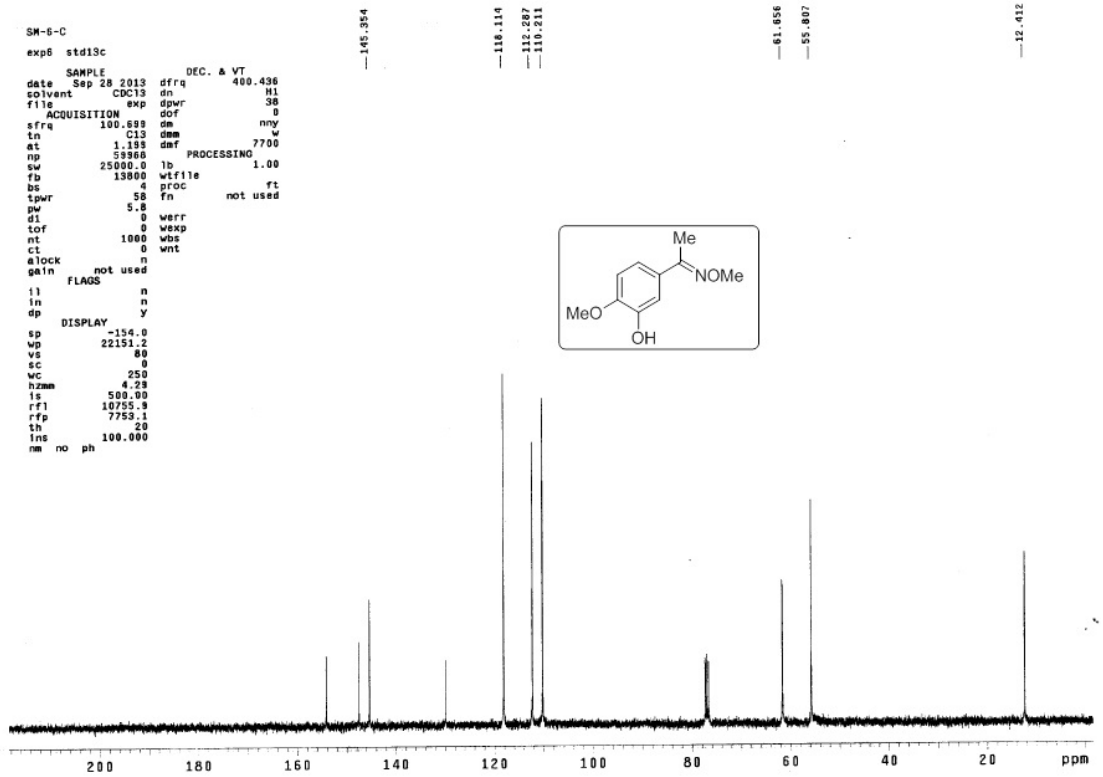
^{1}H and ^{13}C spectra of compound **1i**



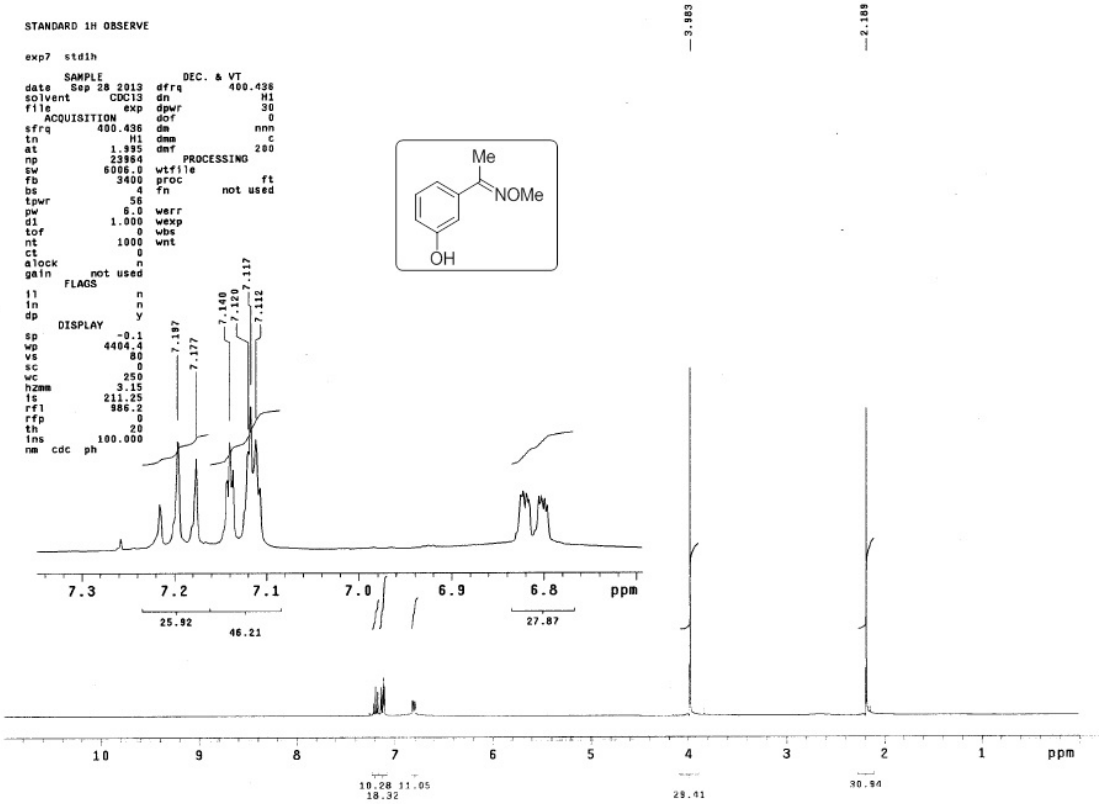


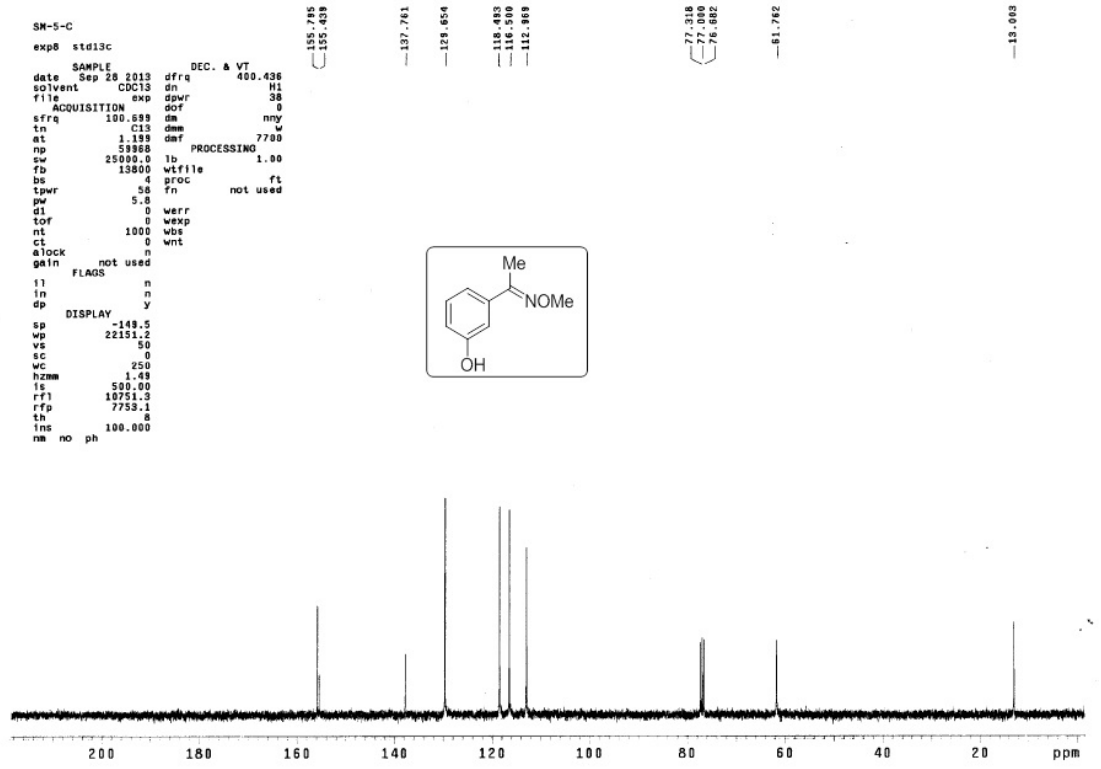
^{1}H and ^{13}C spectra of compound **1j**



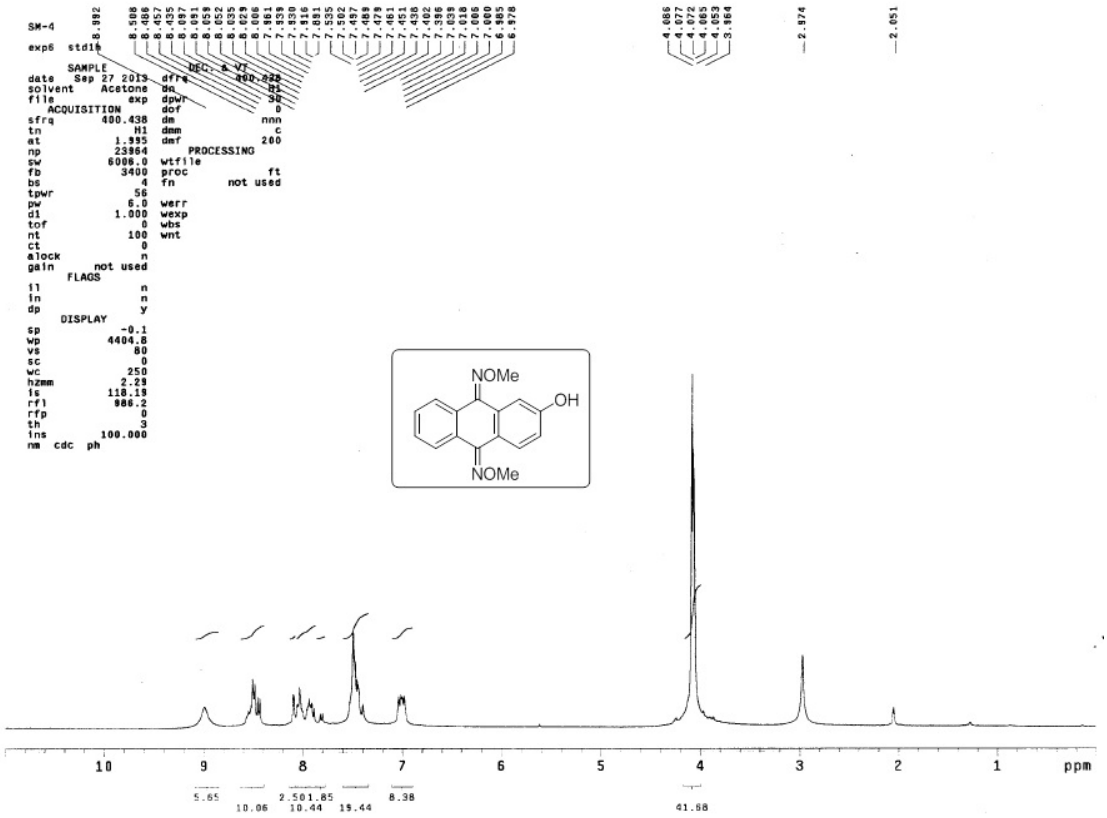


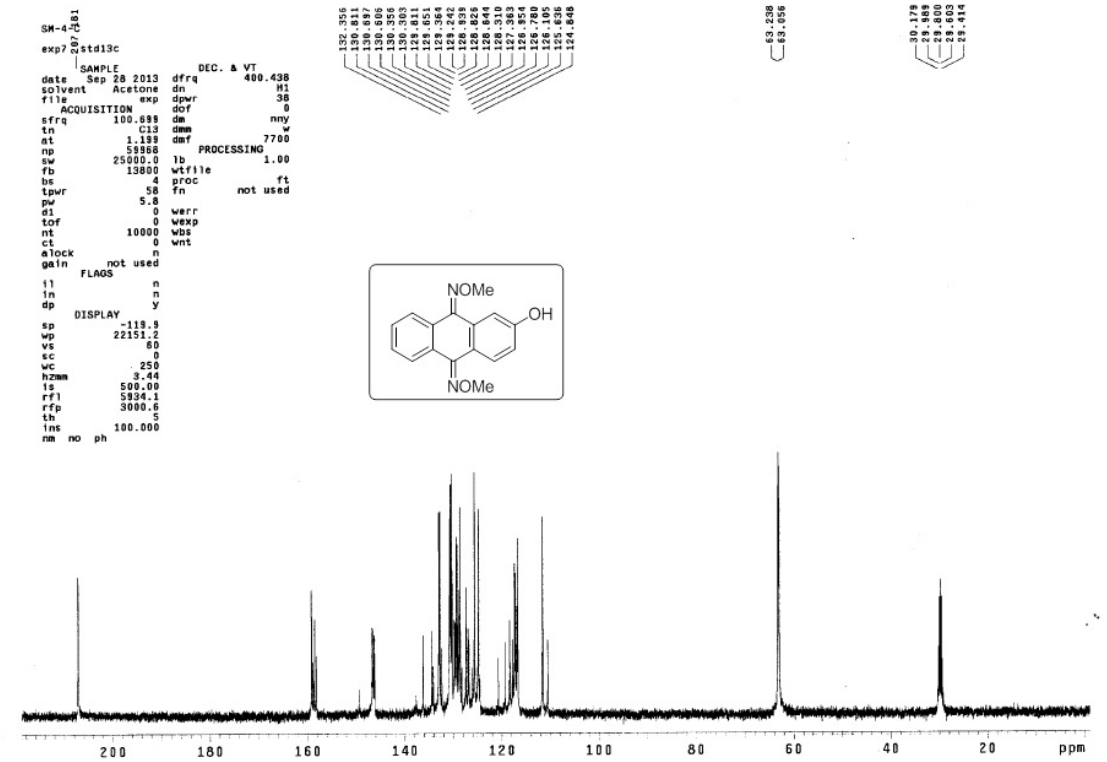
^{1}H and ^{13}C spectra of compound **1k**



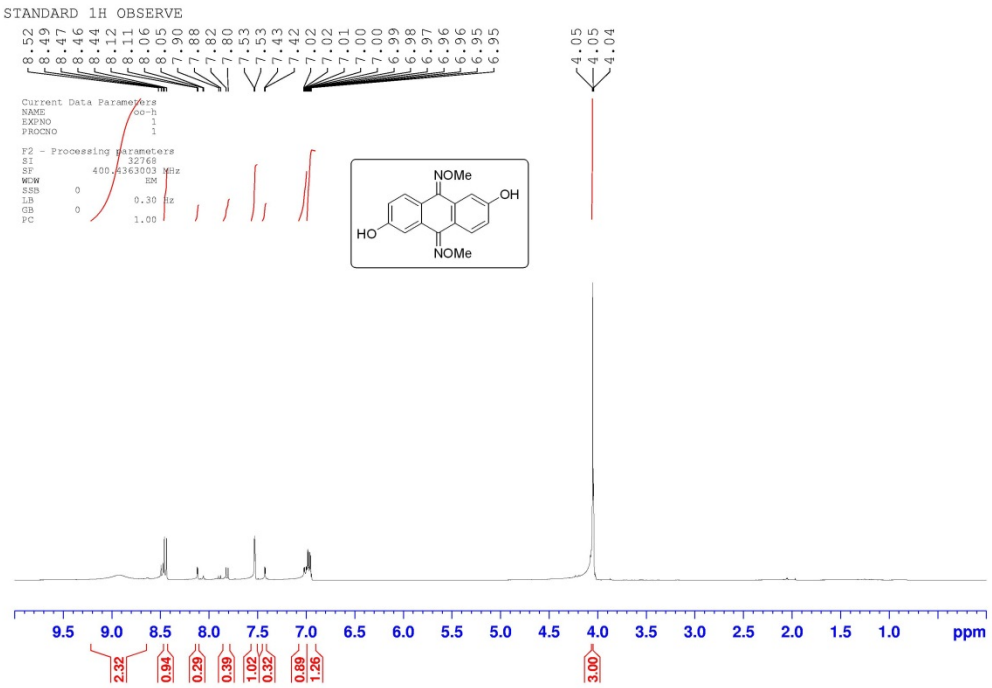


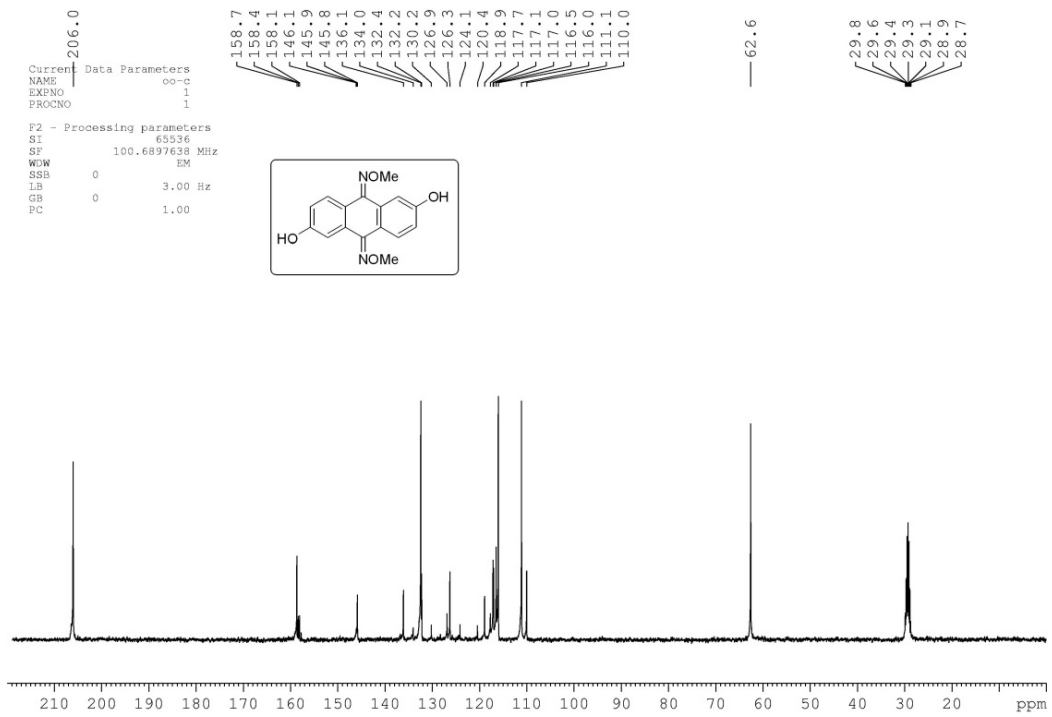
^{1}H and ^{13}C spectra of compound **1l**



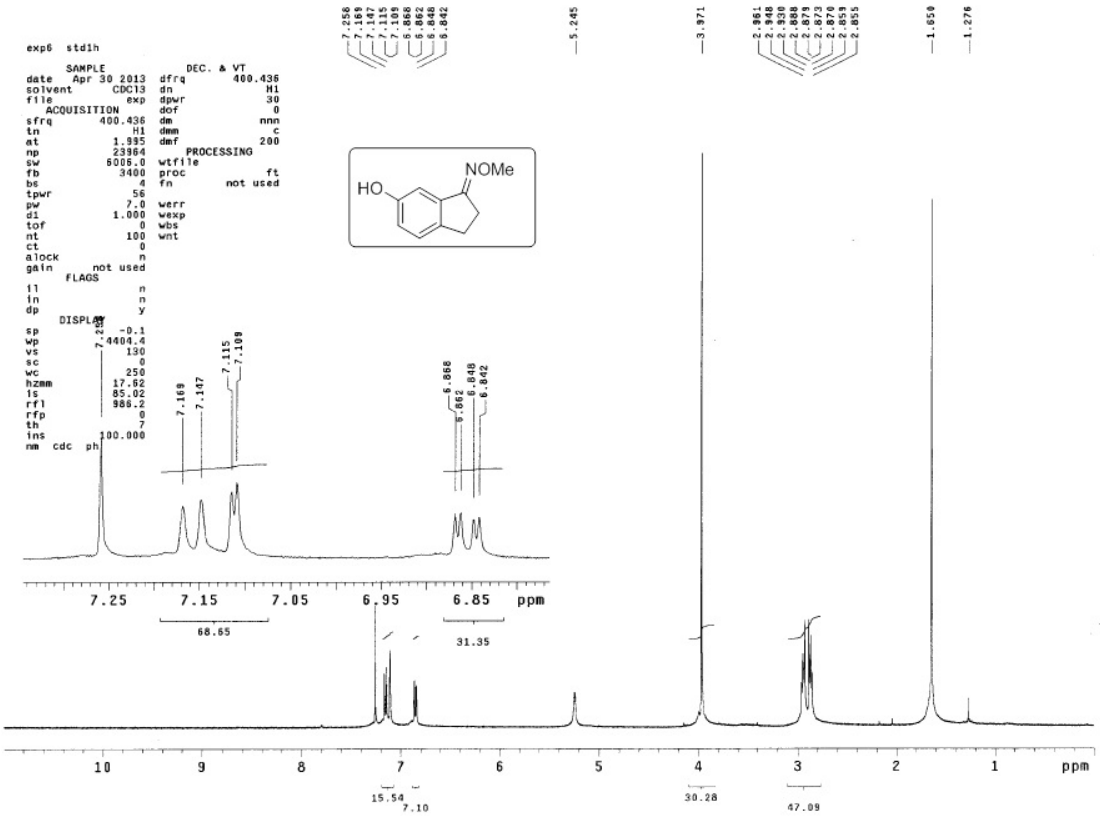


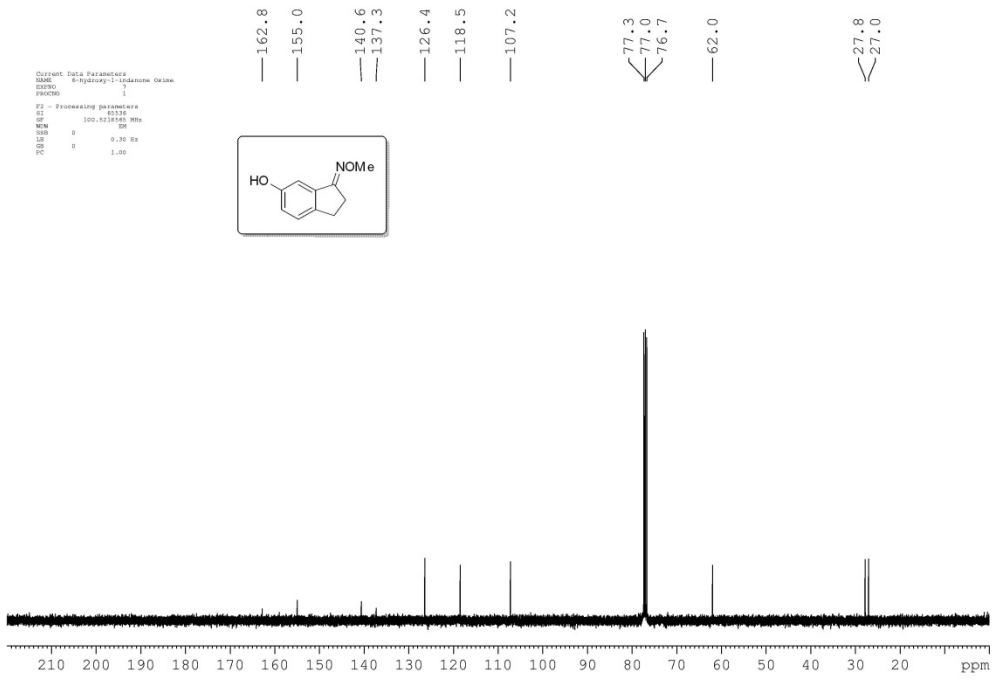
^{1}H and ^{13}C spectra of compound **1m**



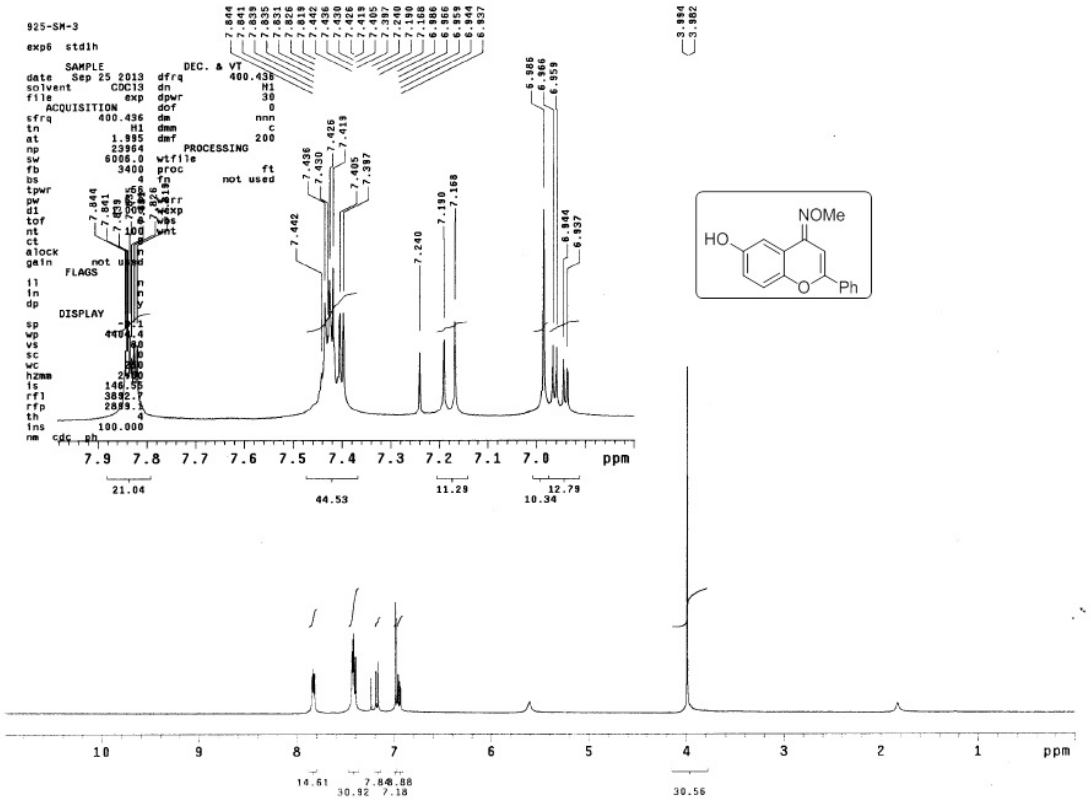


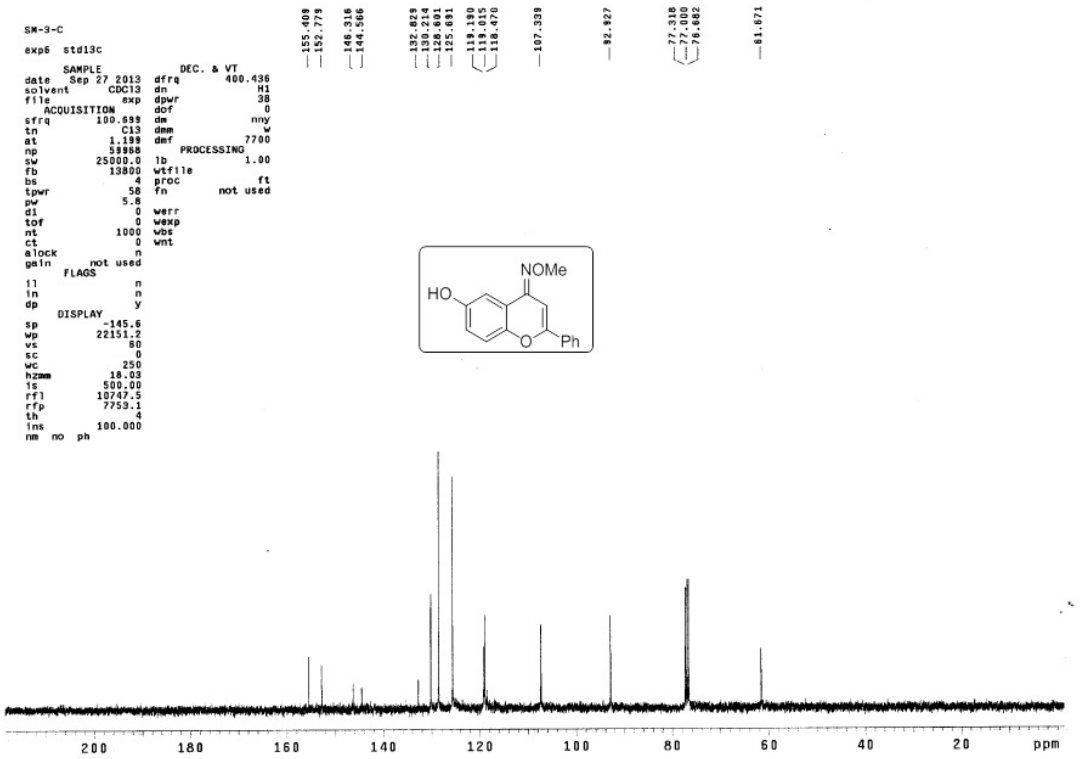
^{1}H and ^{13}C spectra of compound **1n**



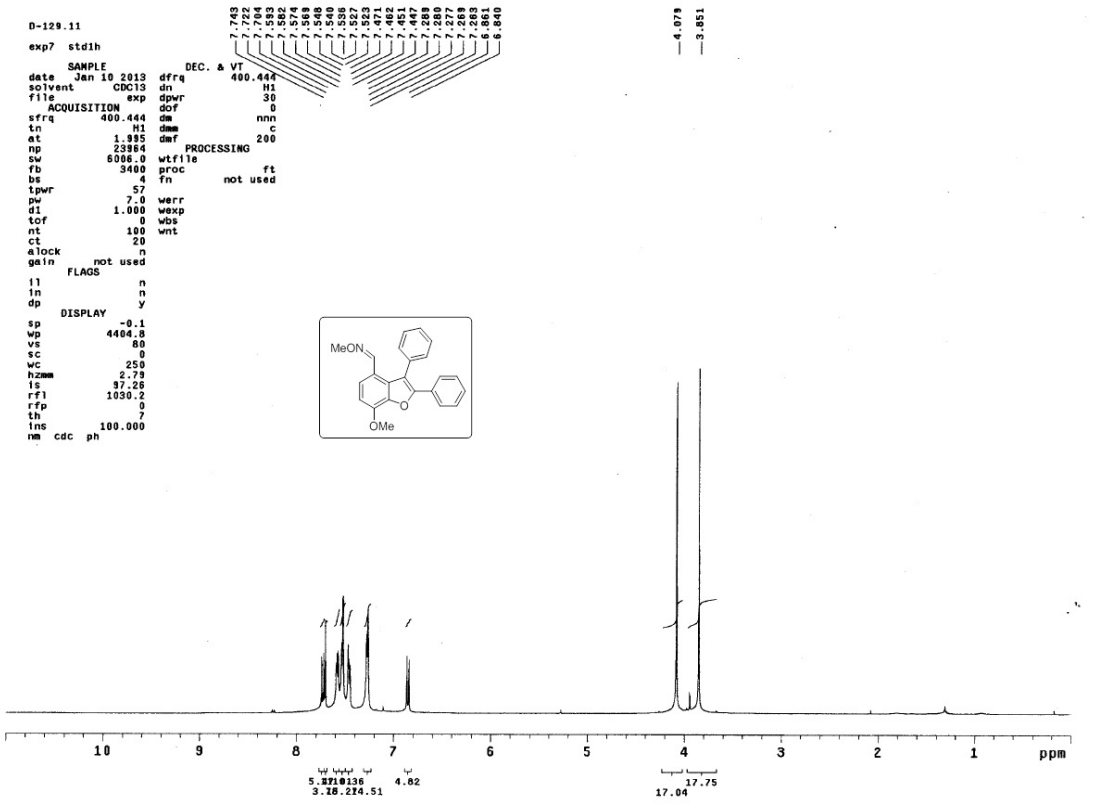


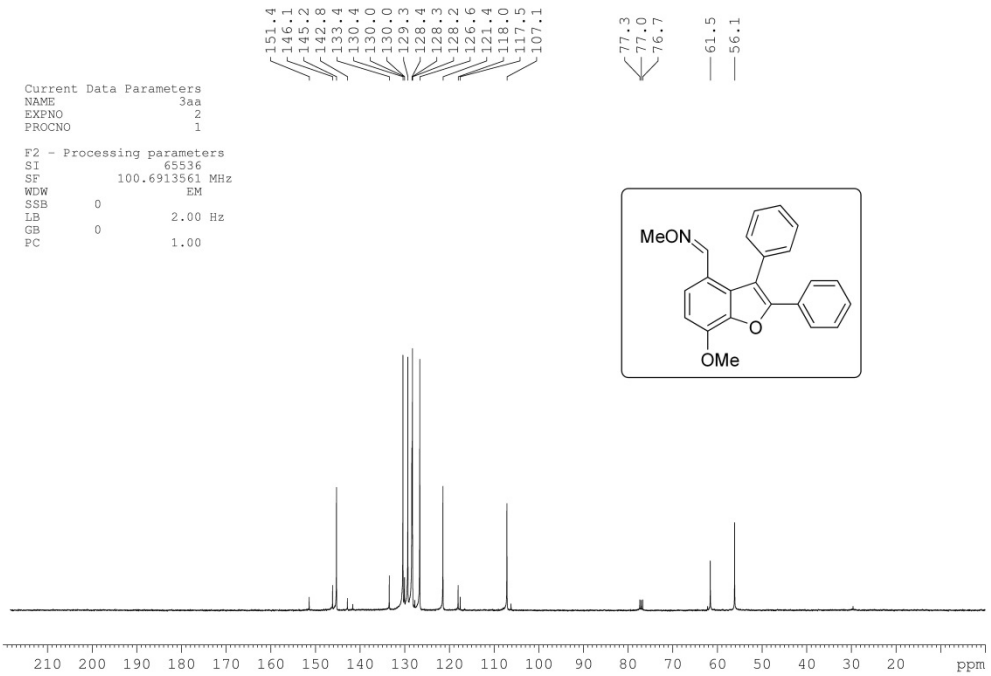
^{1}H and ^{13}C spectra of compound **1o**



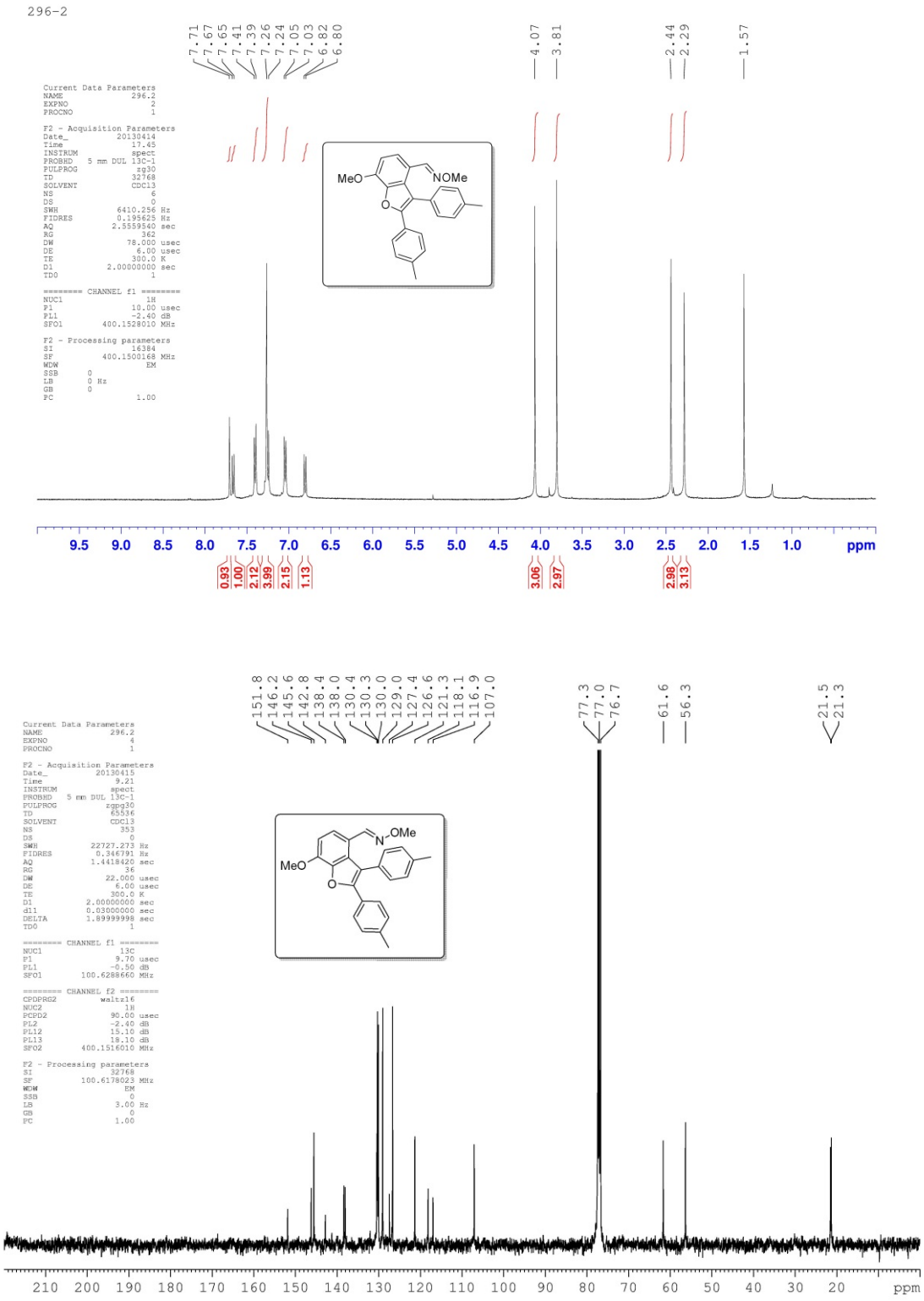


H and ^{13}C spectra of compound **3aa**

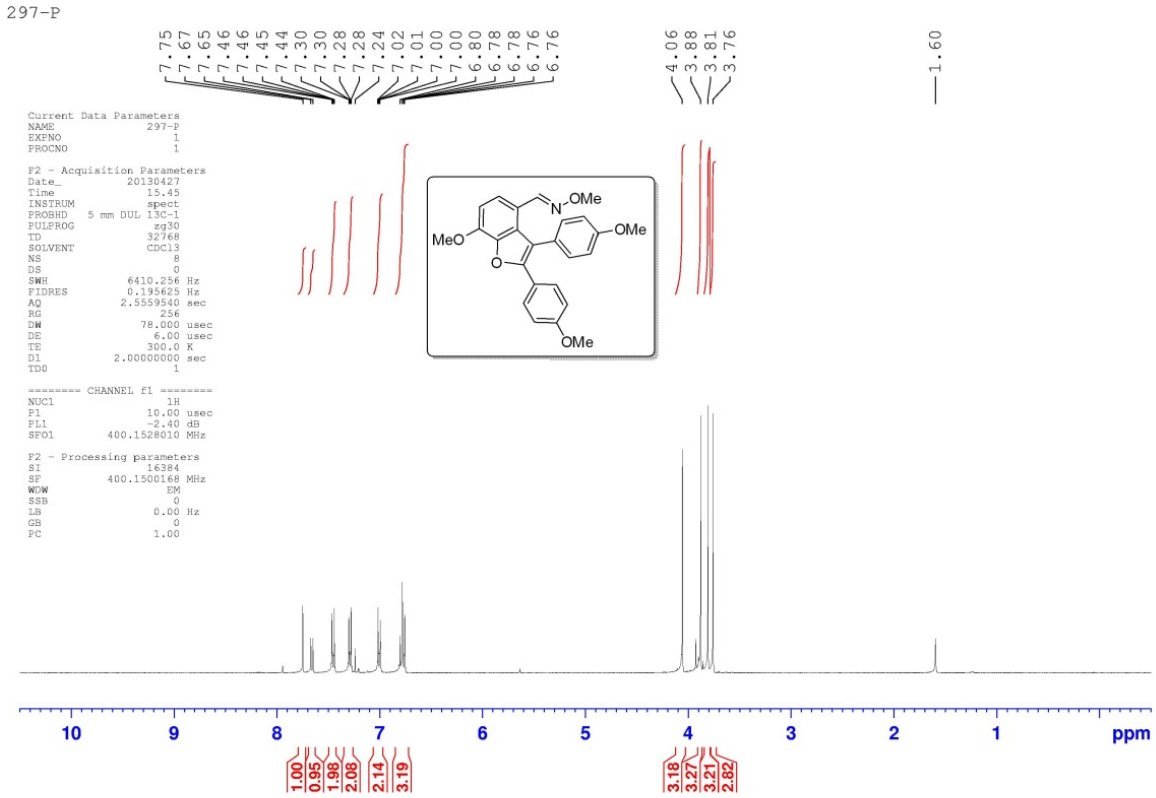


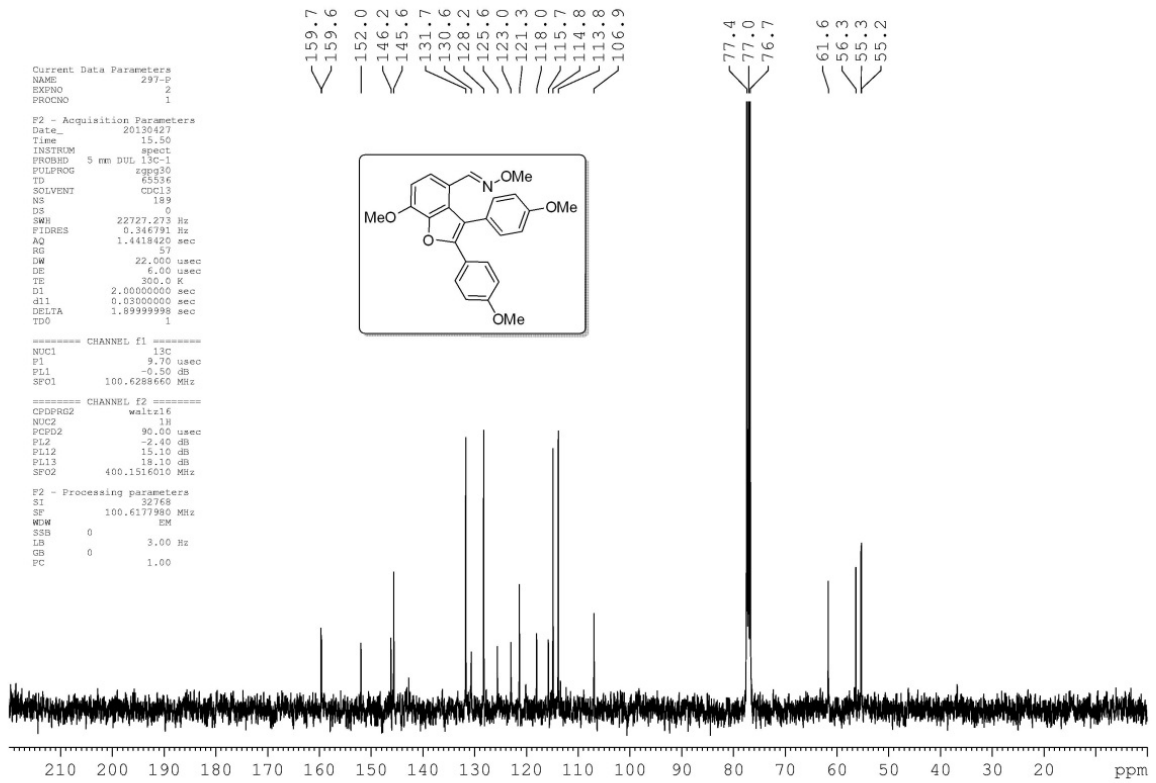


^{1}H and ^{13}C spectra of compound **3ab**

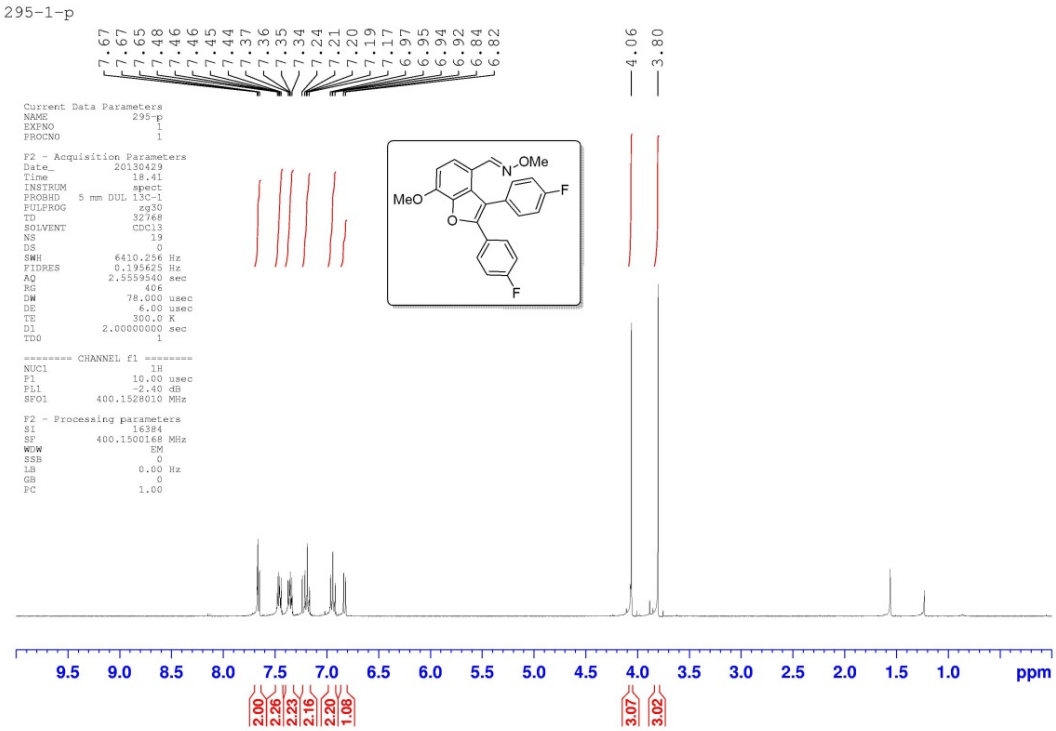


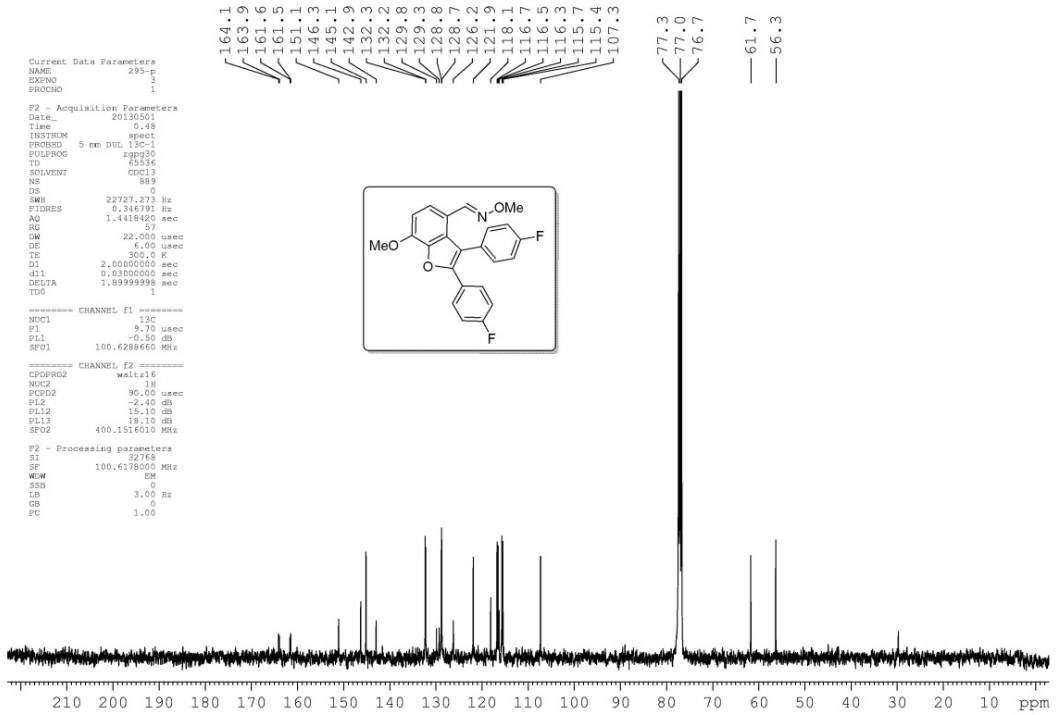
^{1}H and ^{13}C spectra of compound **3ac**



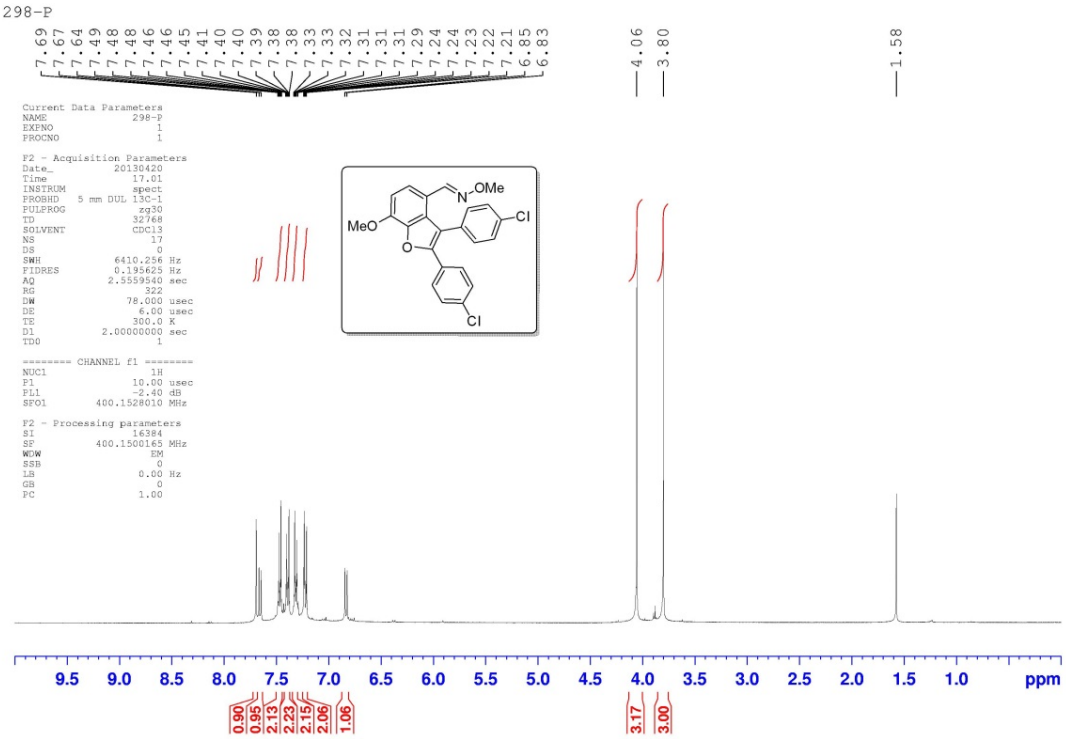


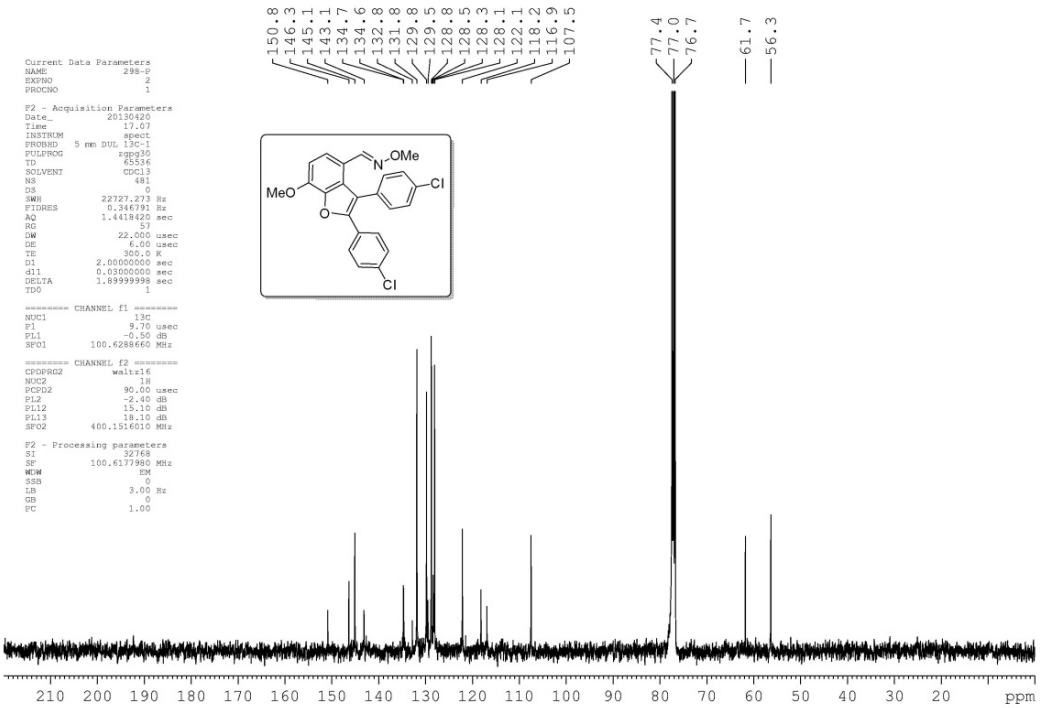
^{1}H and ^{13}C spectra of compound **3ad**



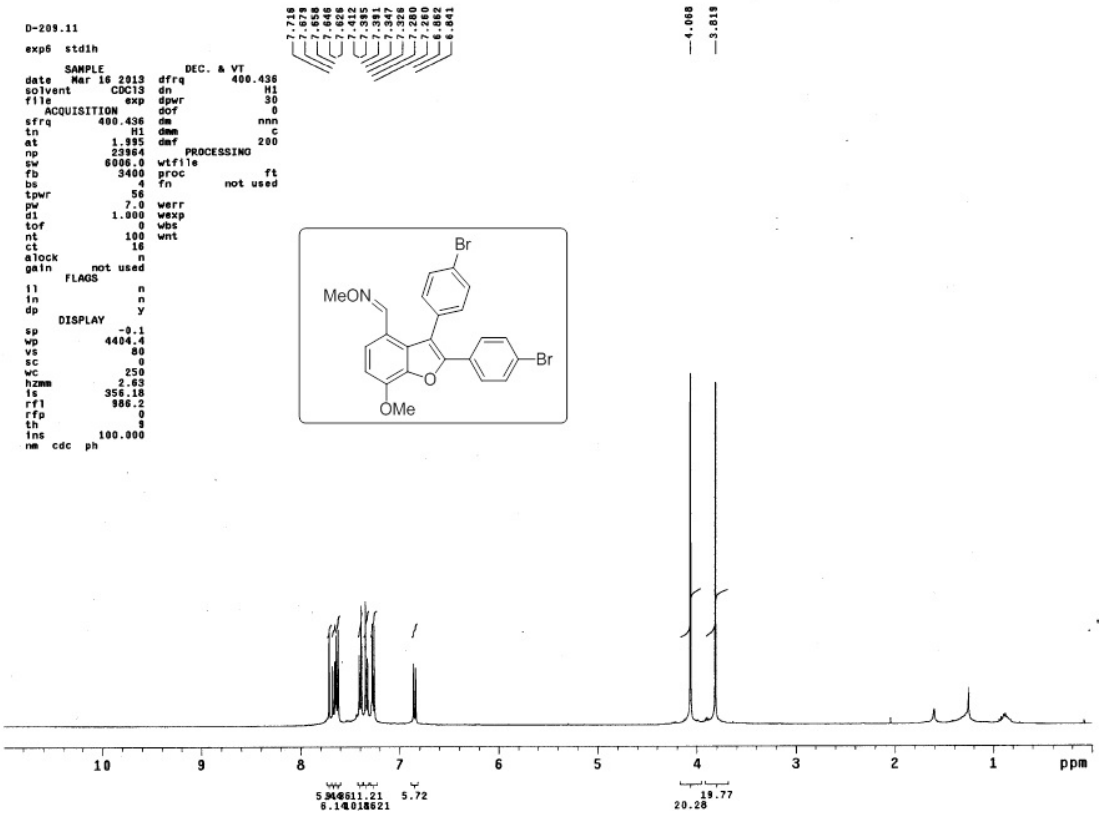


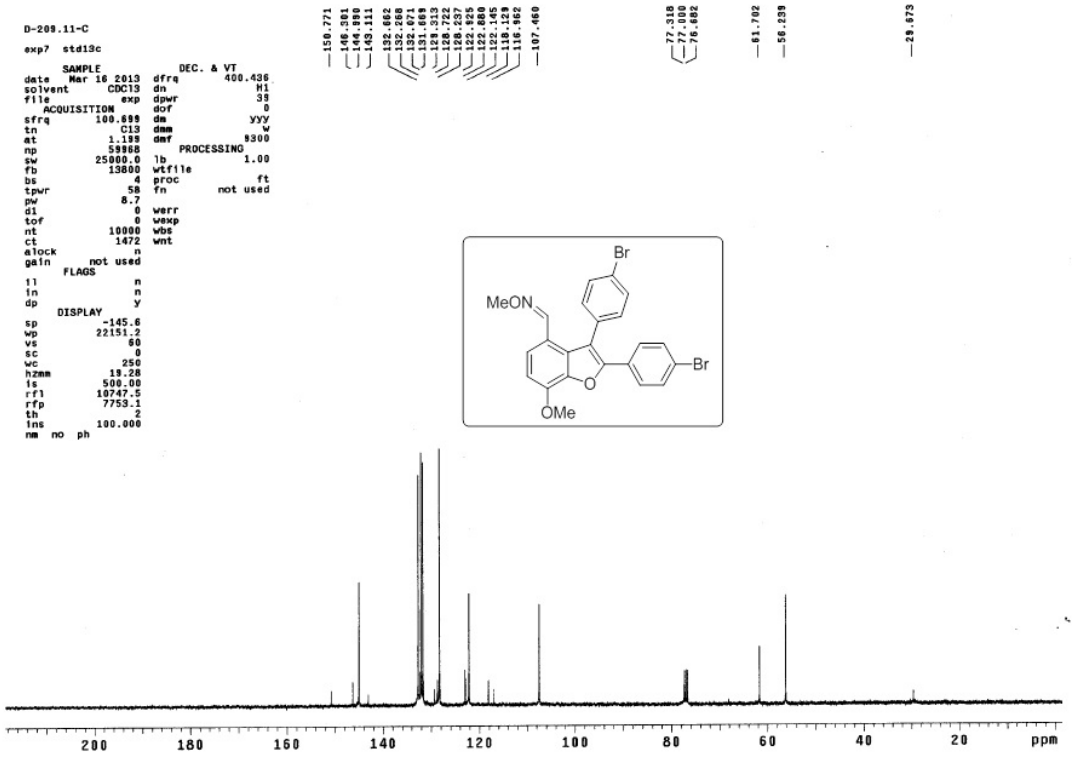
^{1}H and ^{13}C spectra of compound **3ae**



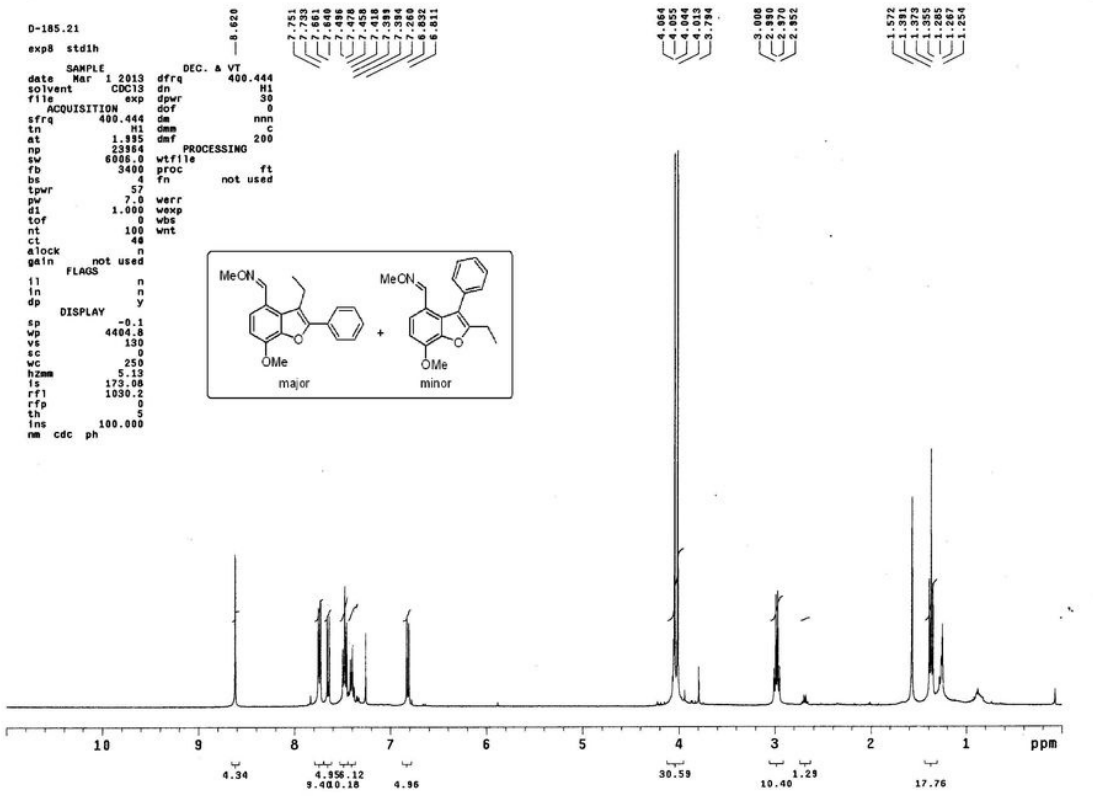


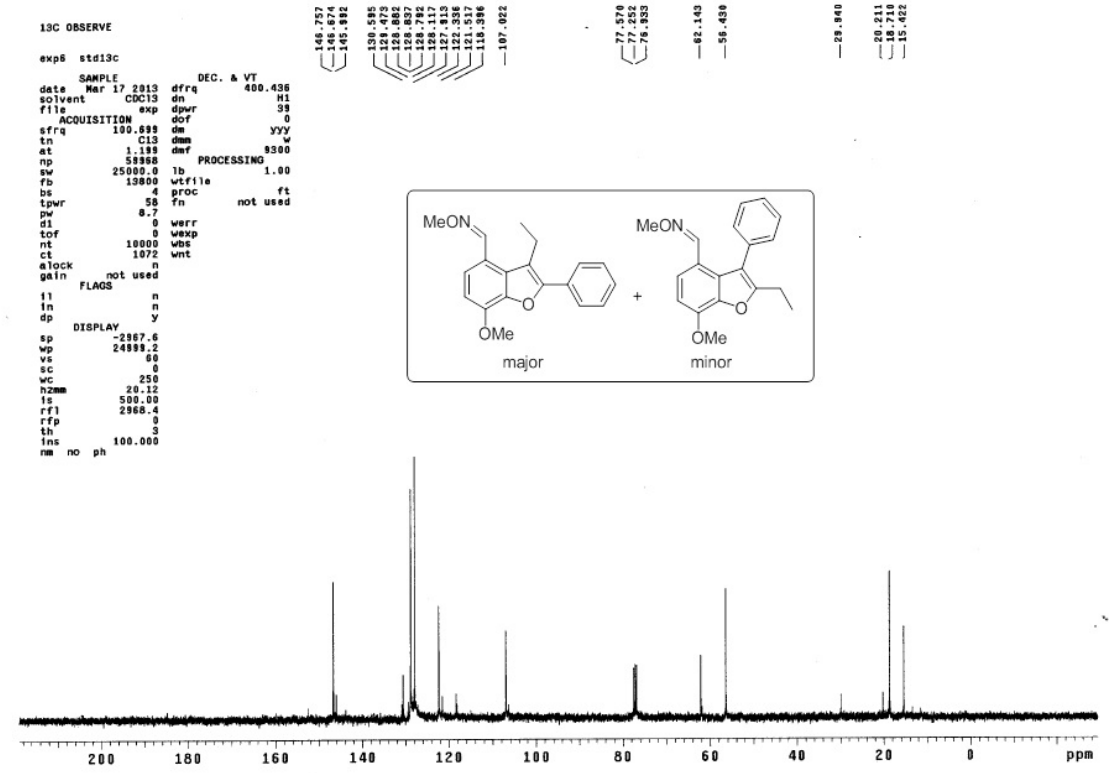
^{1}H and ^{13}C spectra of compound **3af**



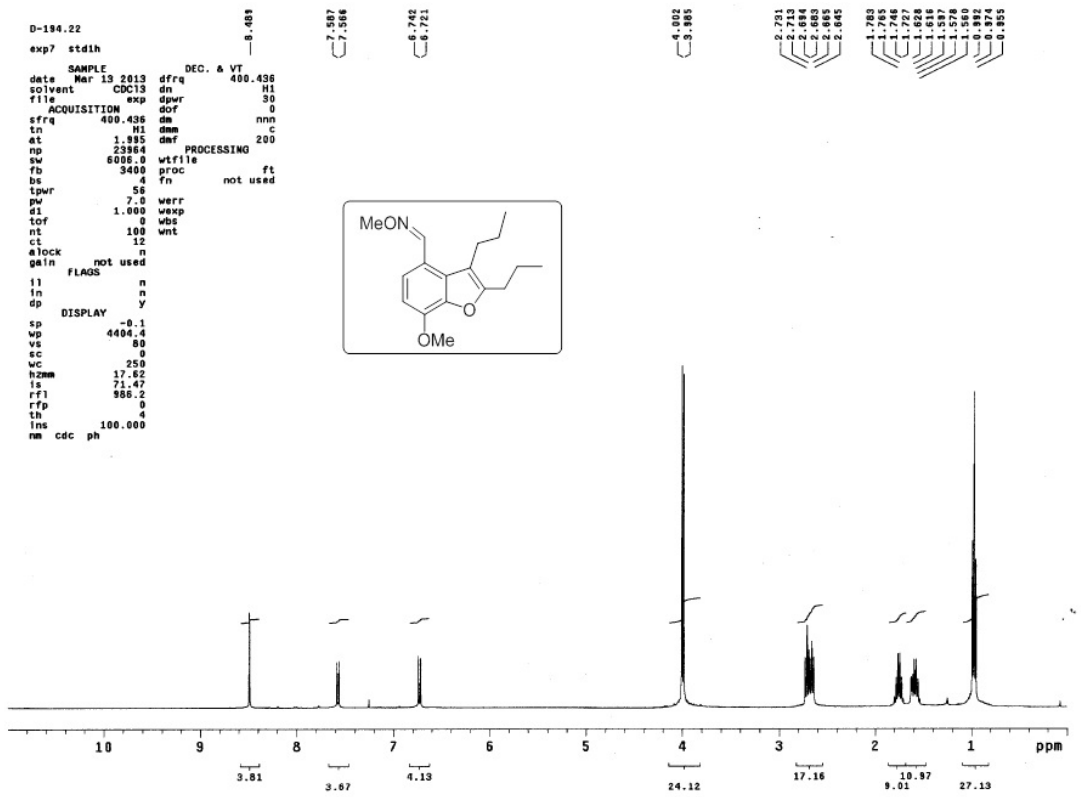


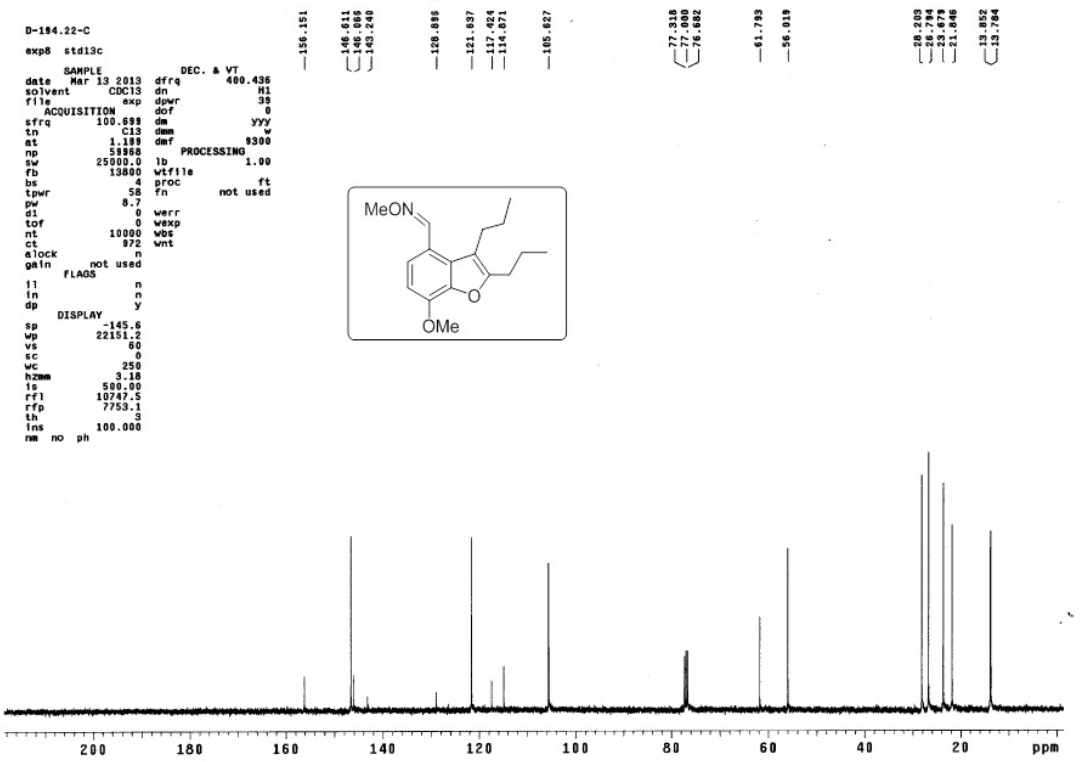
^{1}H and ^{13}C spectra of compound **3ag**



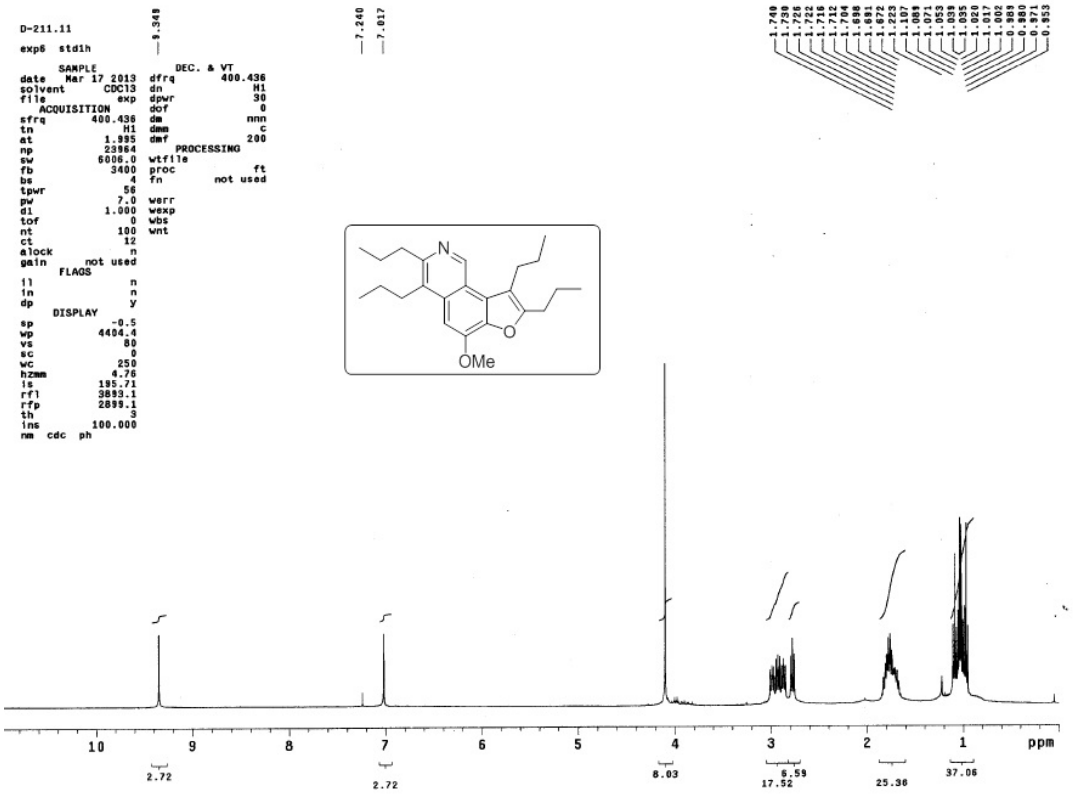


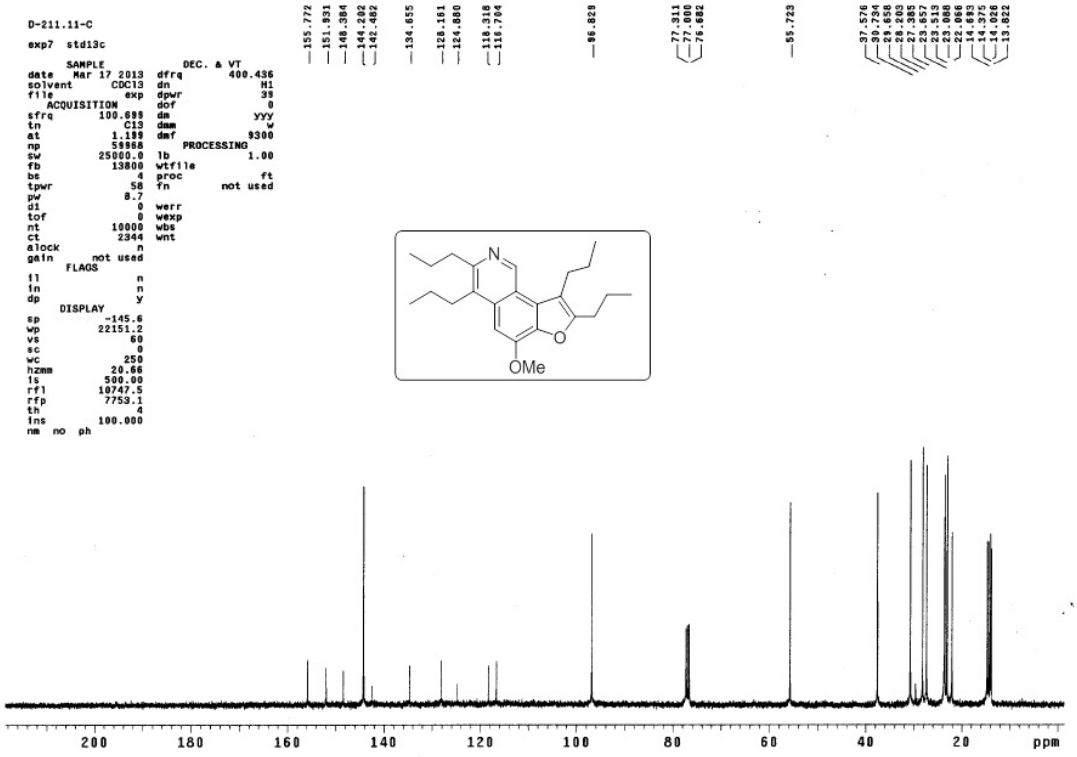
^{1}H and ^{13}C spectra of compound **3ah**



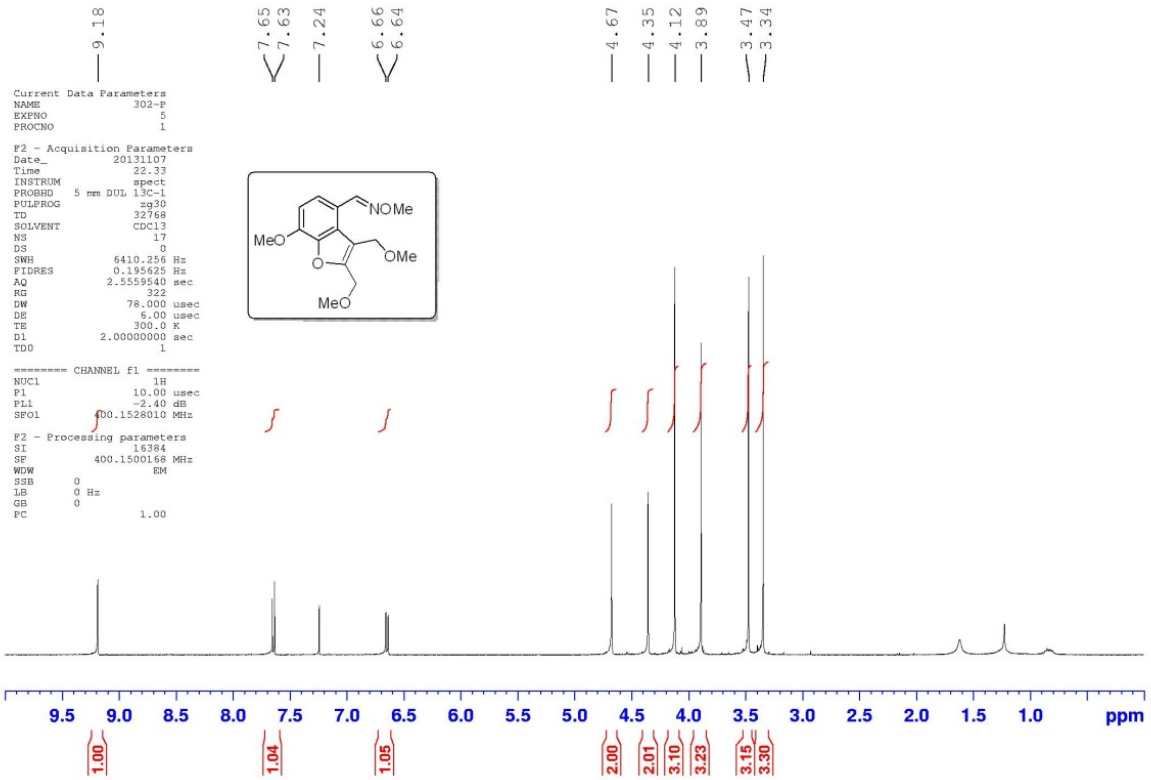


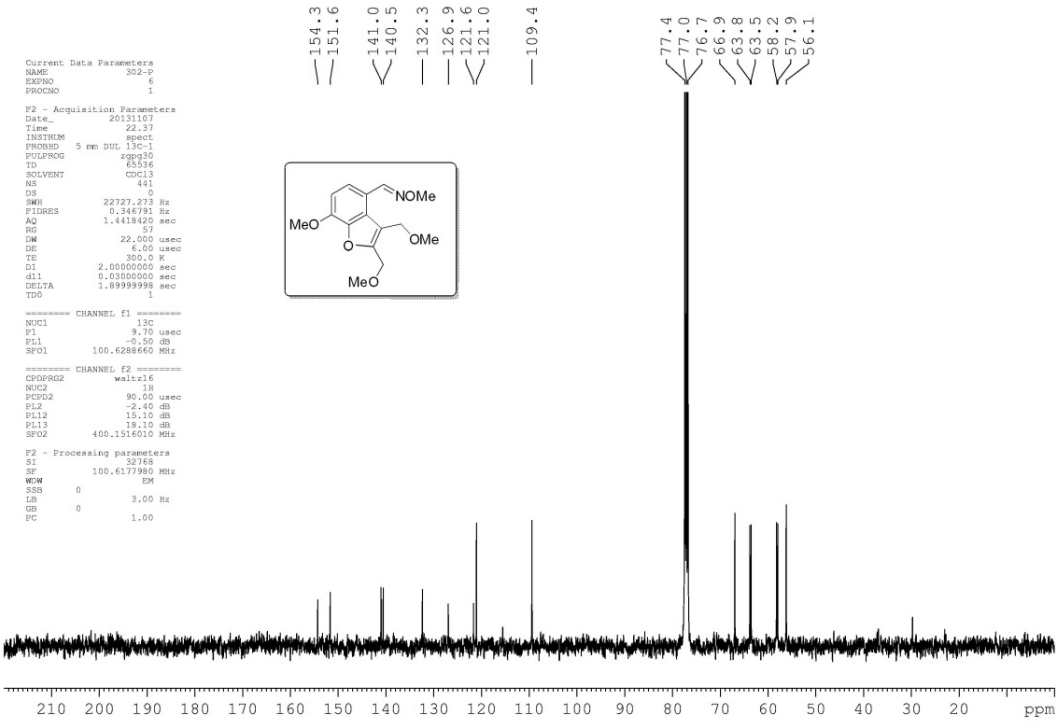
^{1}H and ^{13}C spectra of compound **3ah'**



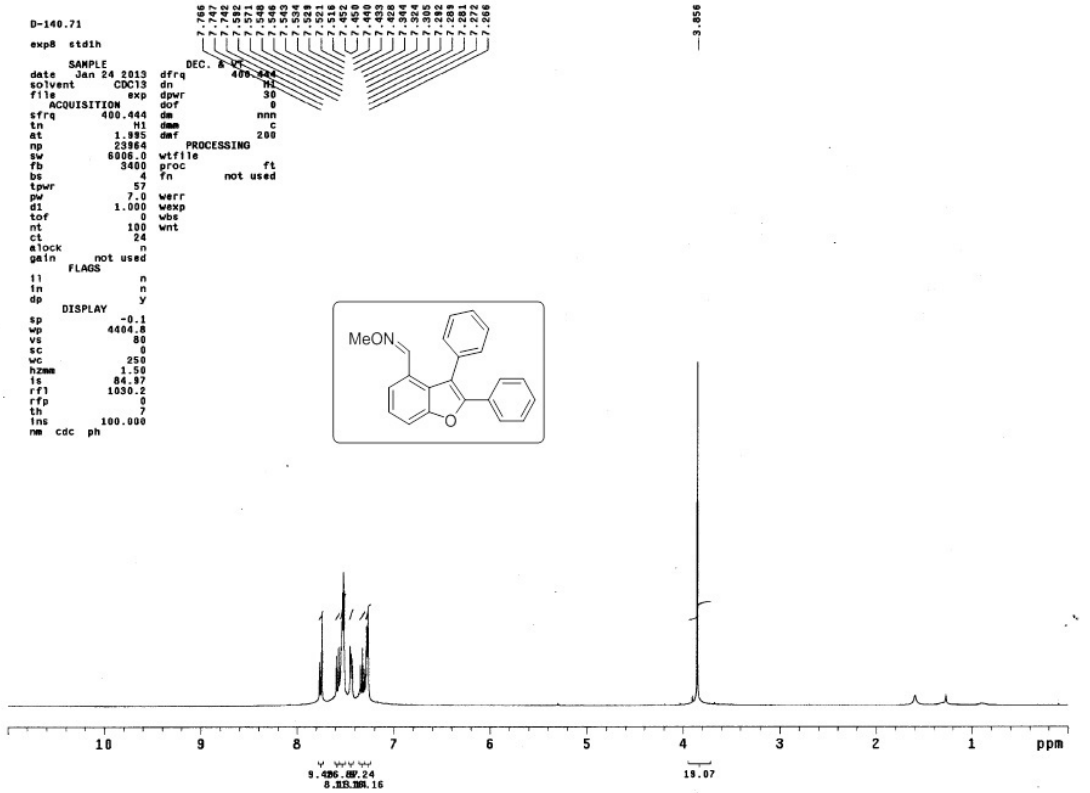


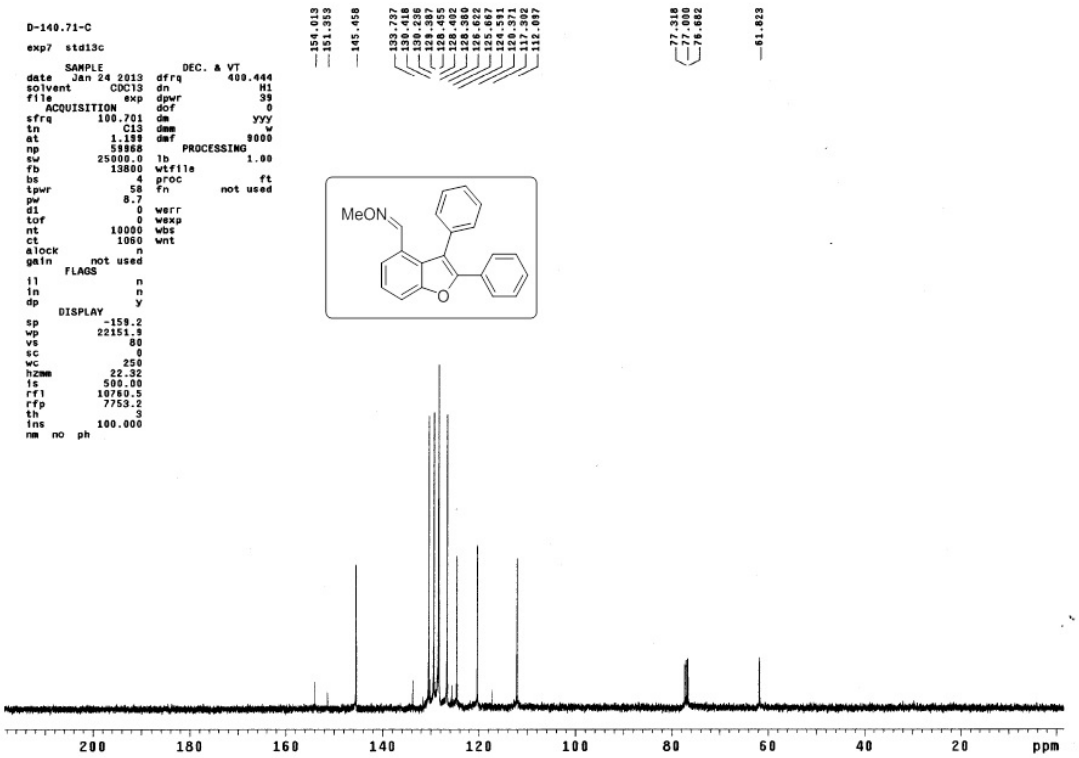
^{1}H and ^{13}C spectra of compound **3ai**



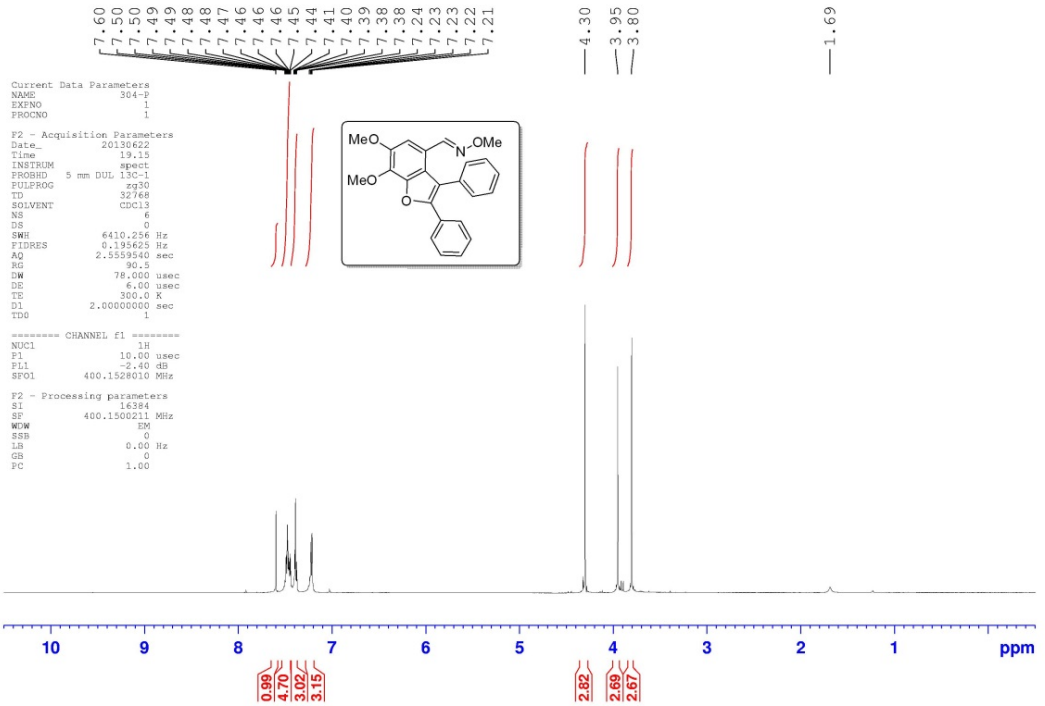


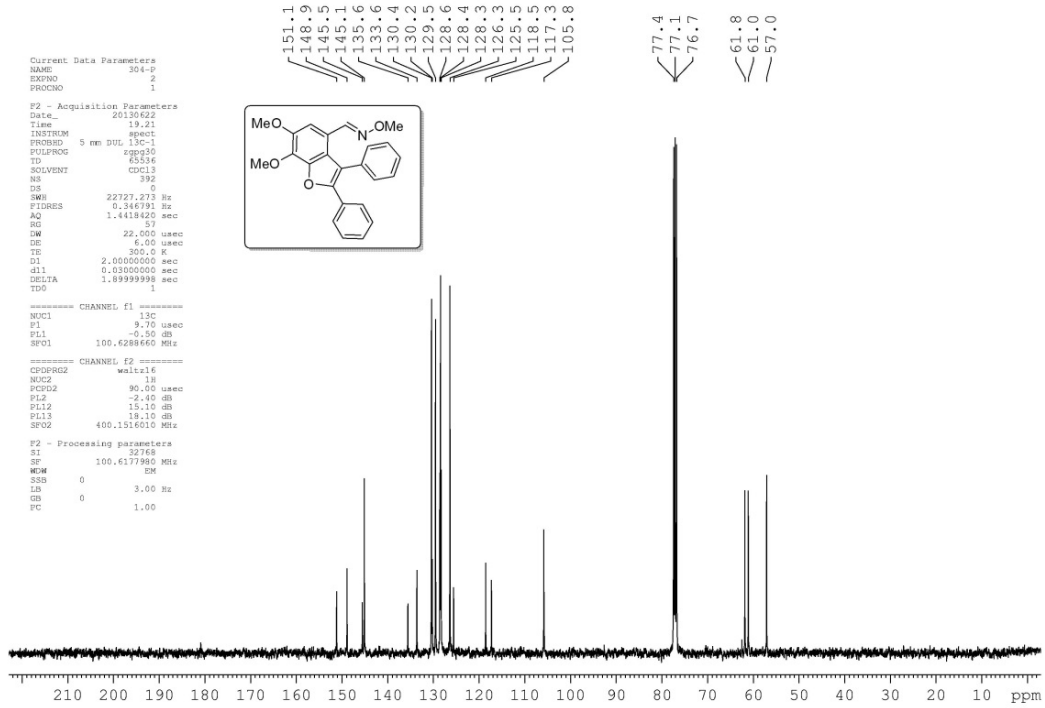
^{1}H and ^{13}C spectra of compound **3ba**



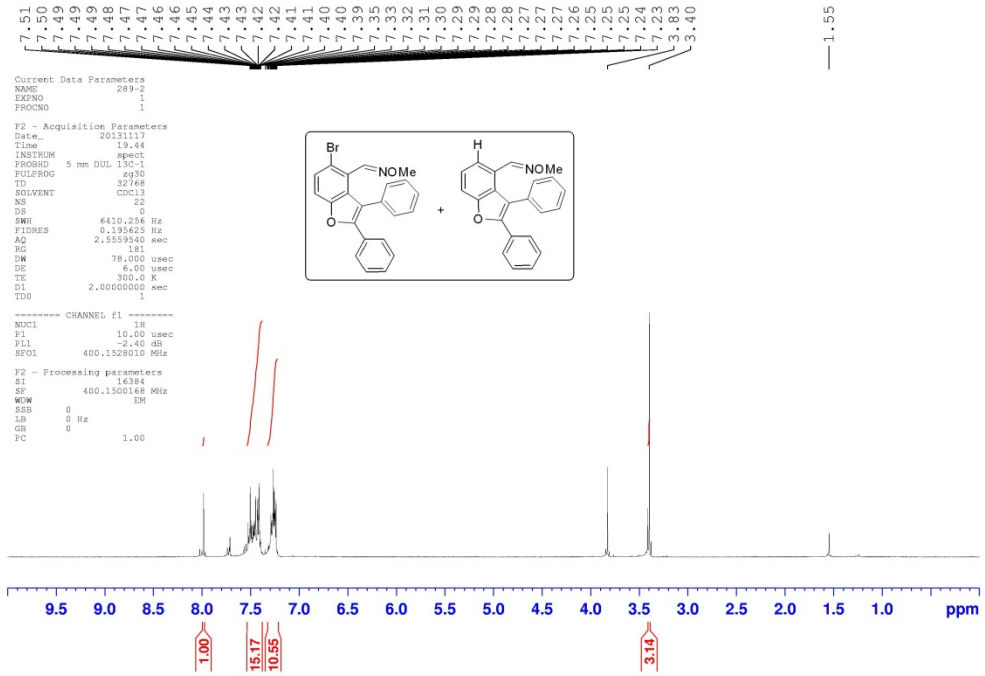


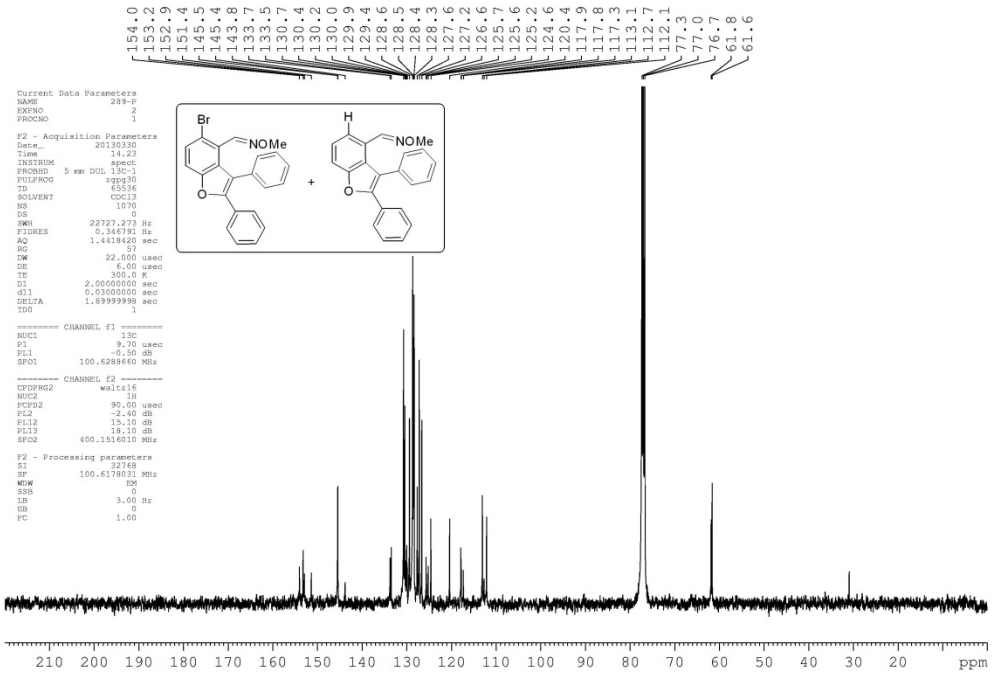
^{1}H and ^{13}C spectra of compound **3ca**



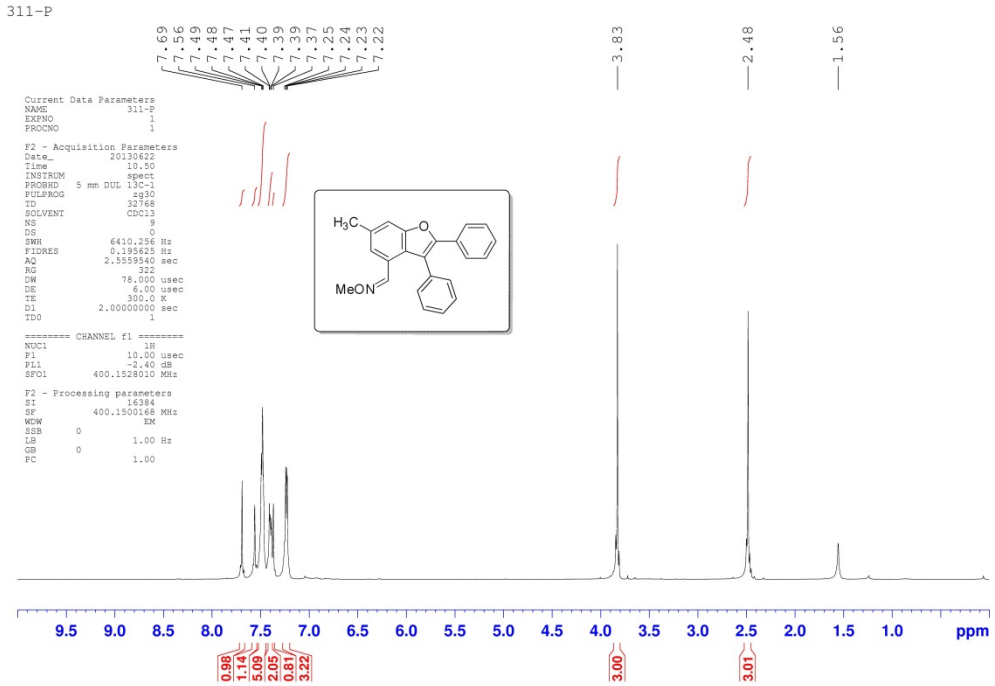


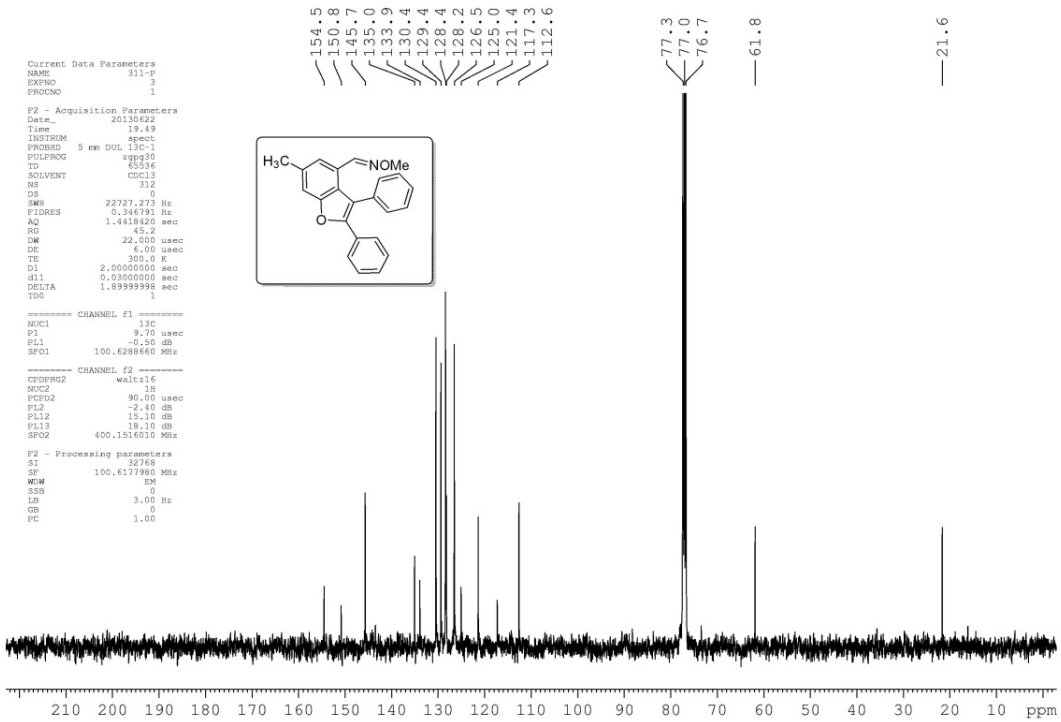
^{1}H and ^{13}C spectra of compound **3da**



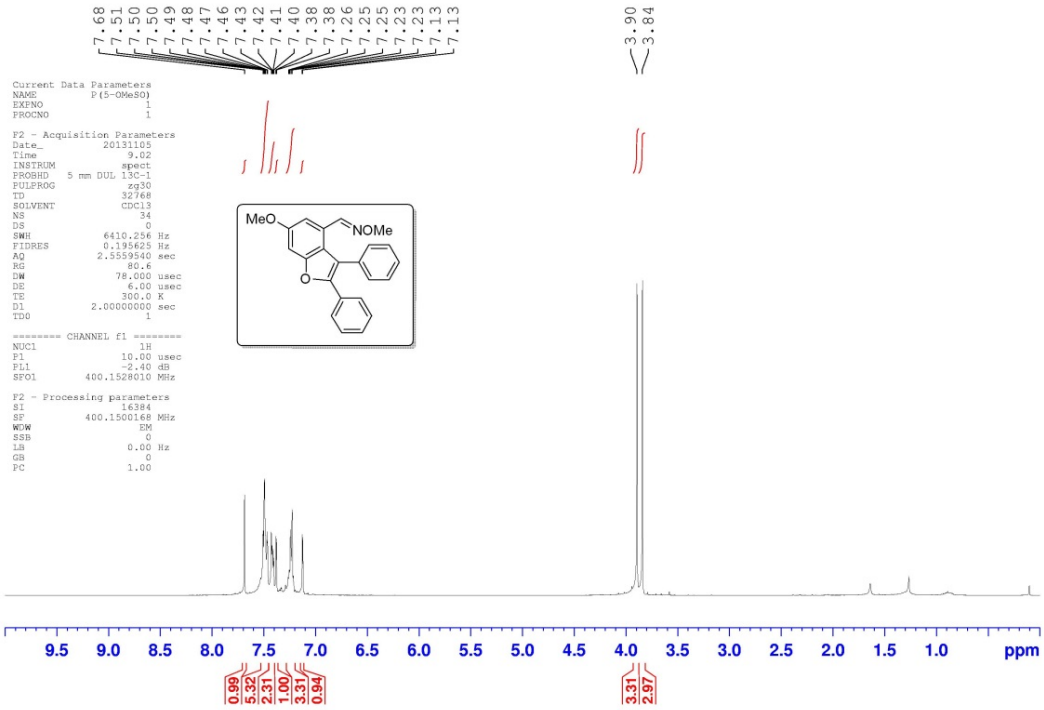


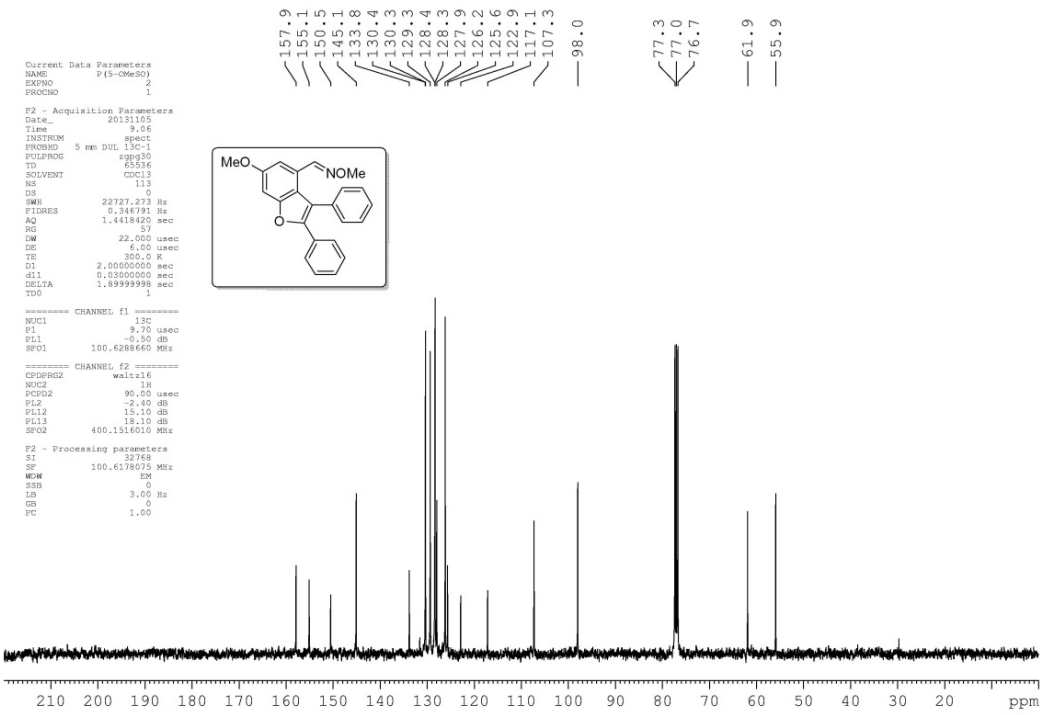
^{1}H and ^{13}C spectra of compound **3ea**



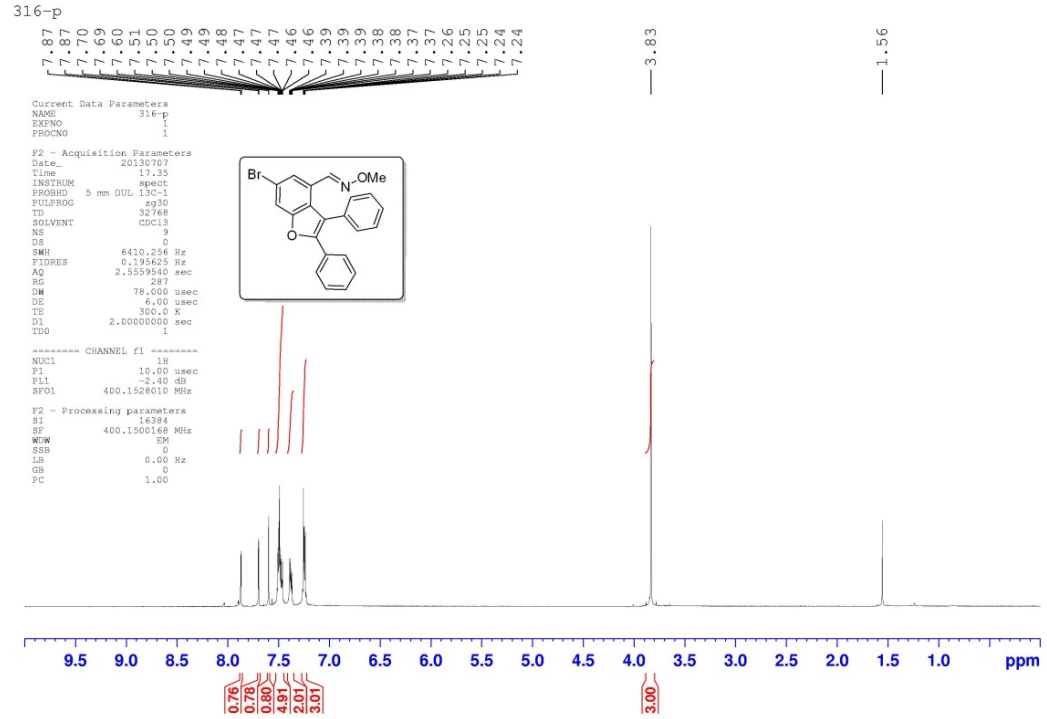


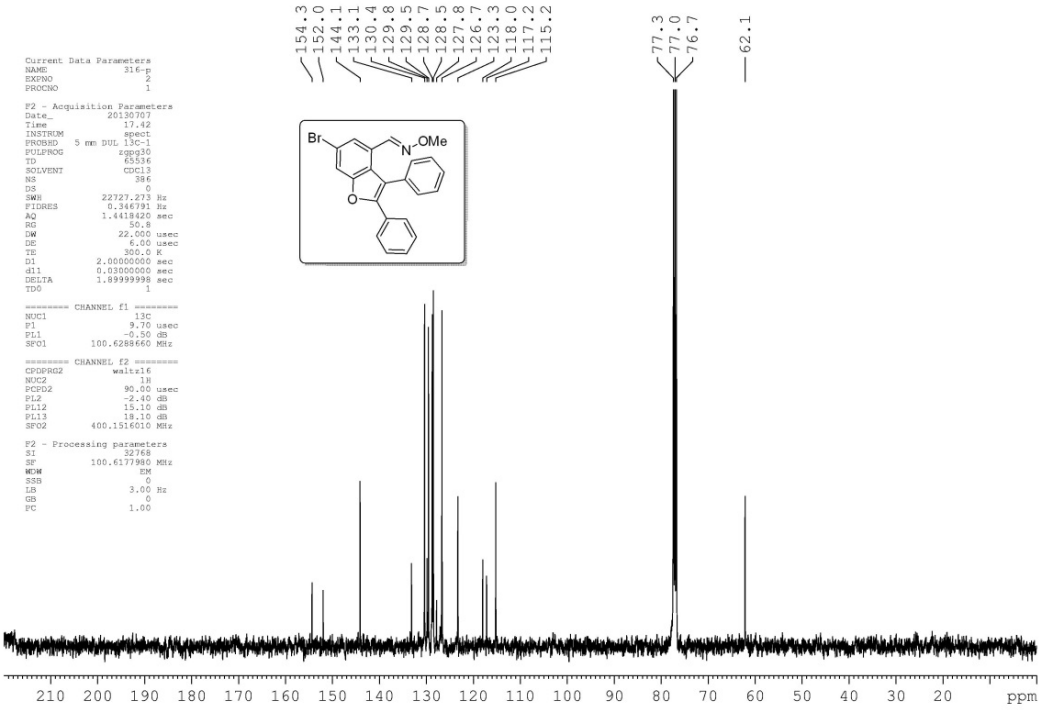
^{1}H and ^{13}C spectra of compound **3fa**



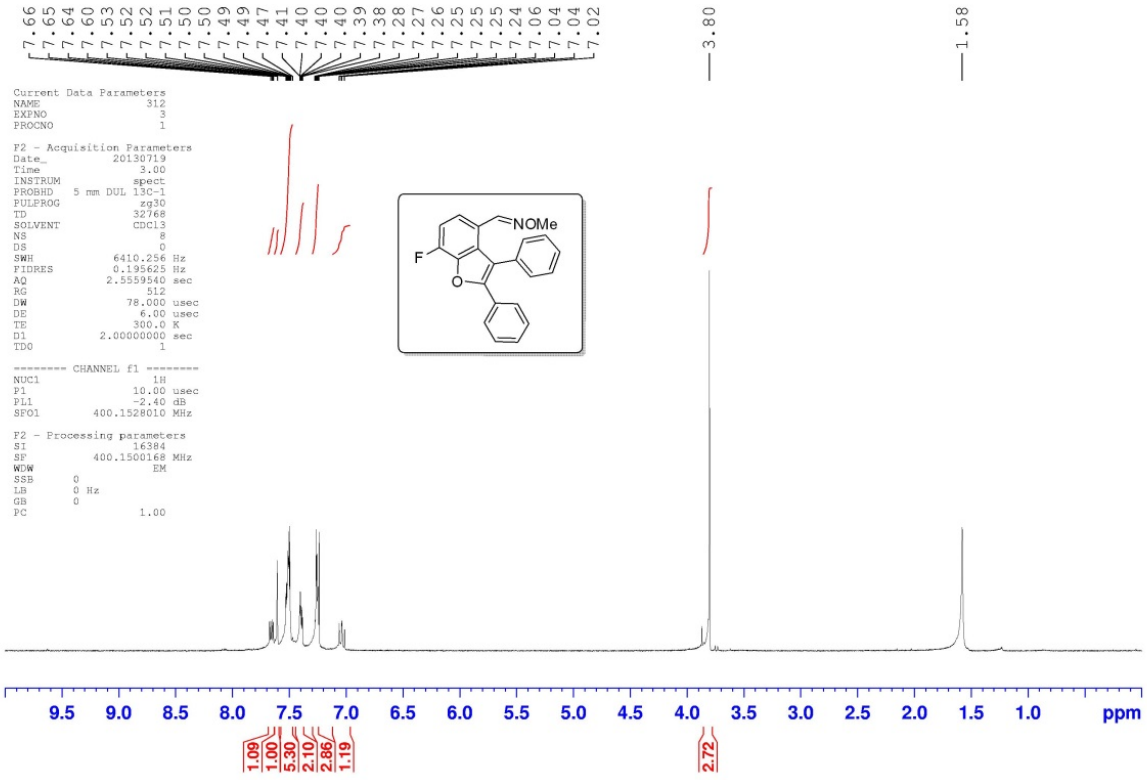


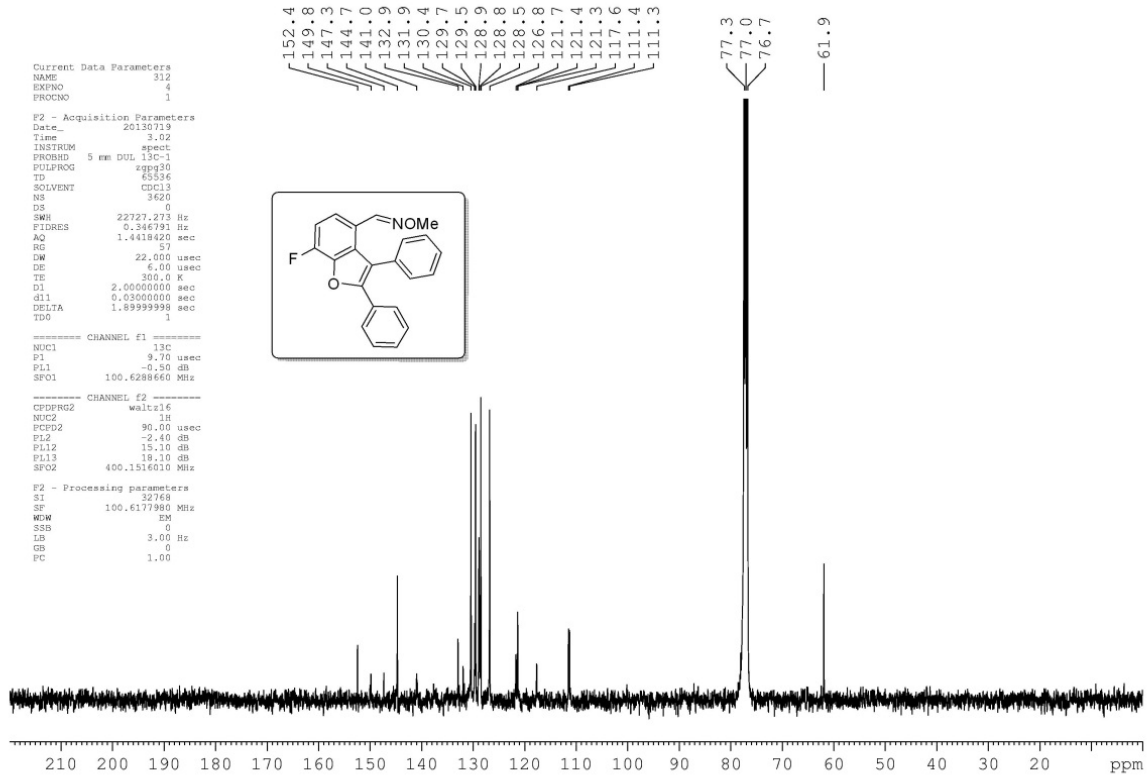
^{1}H and ^{13}C spectra of compound **3ga**



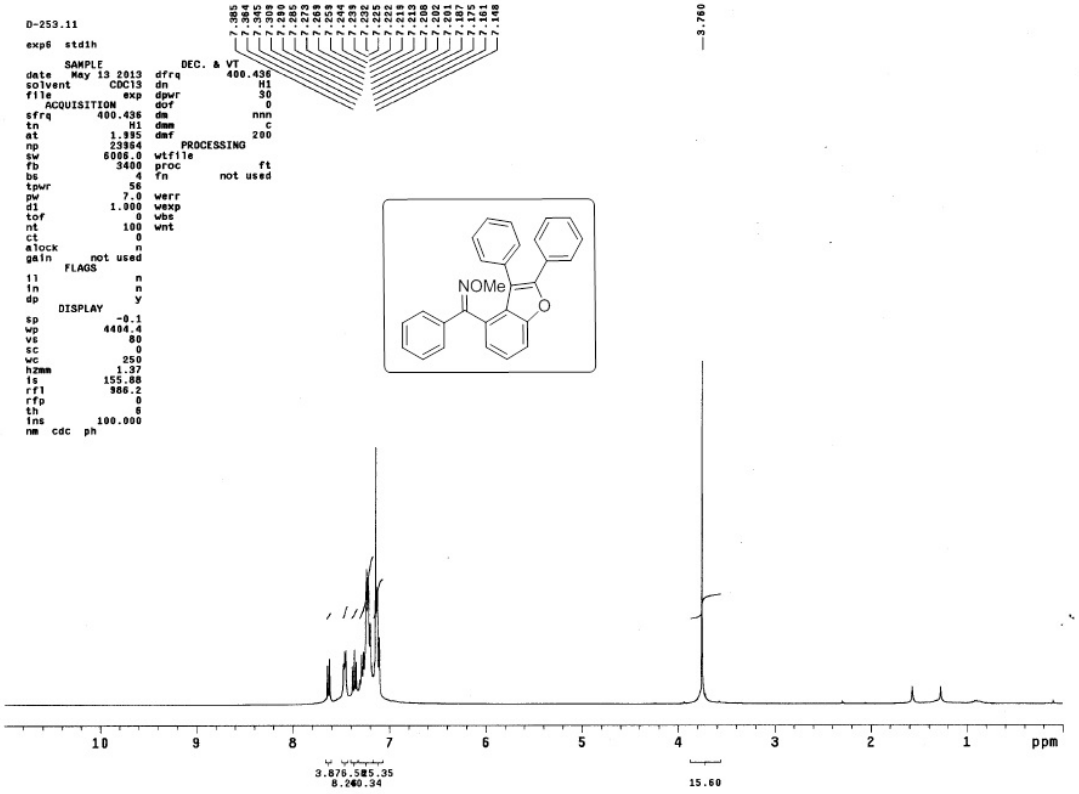


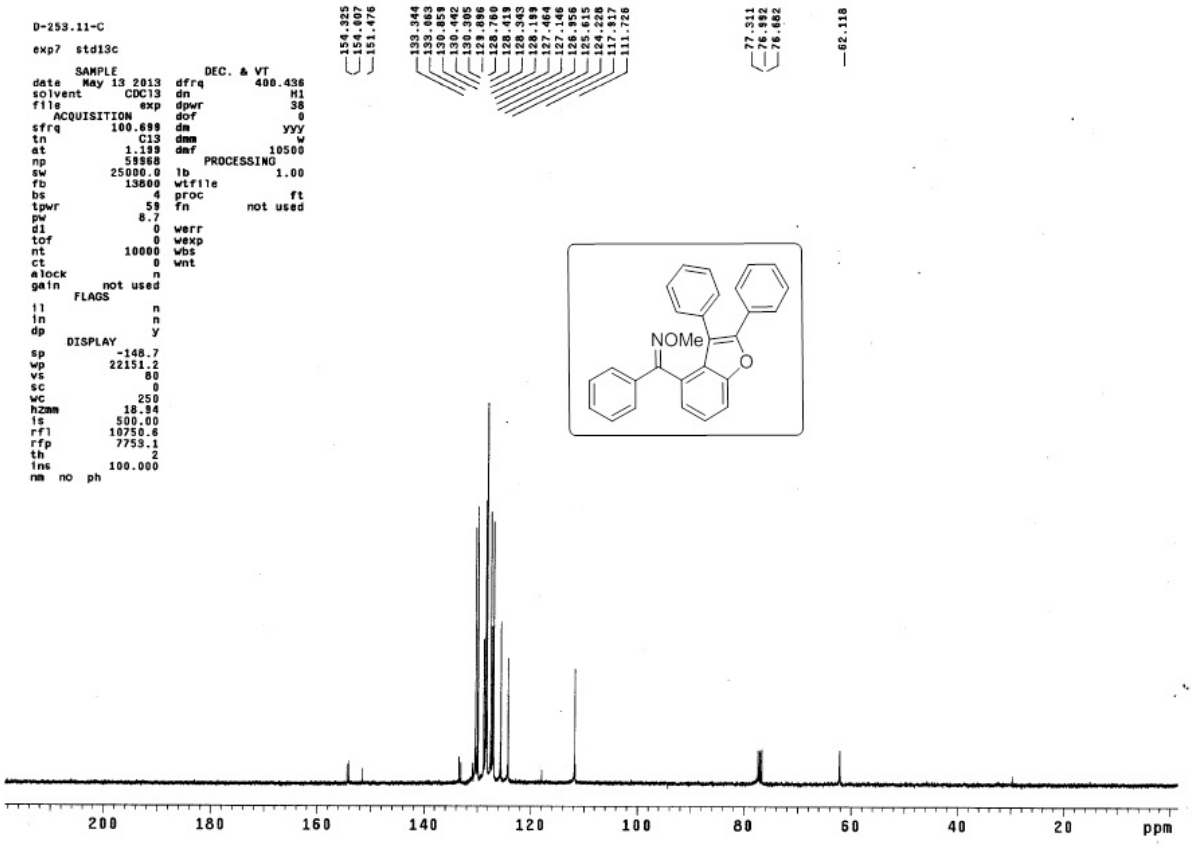
^{1}H and ^{13}C spectra of compound **3ha**



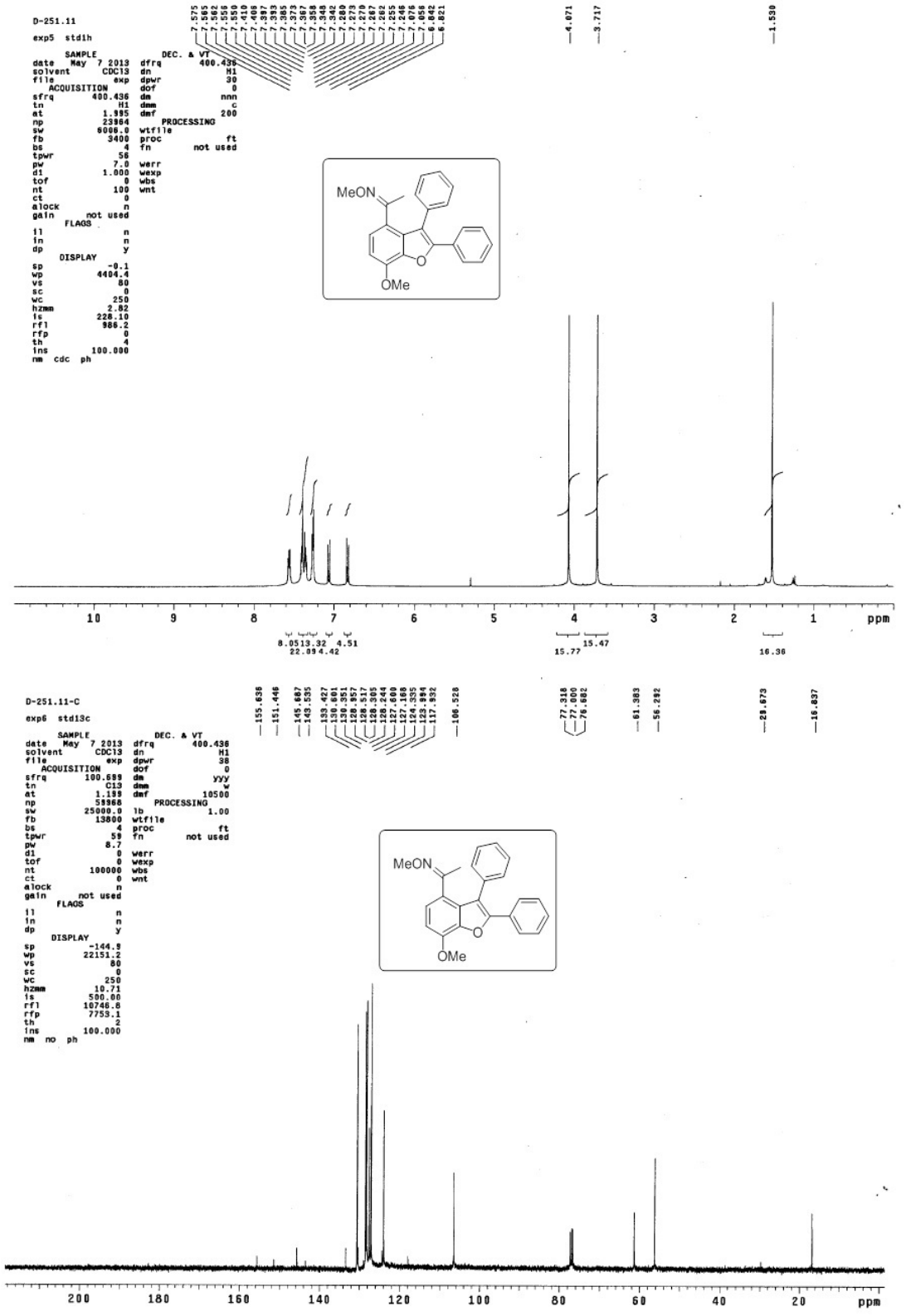


^{1}H and ^{13}C spectra of compound **3ia**

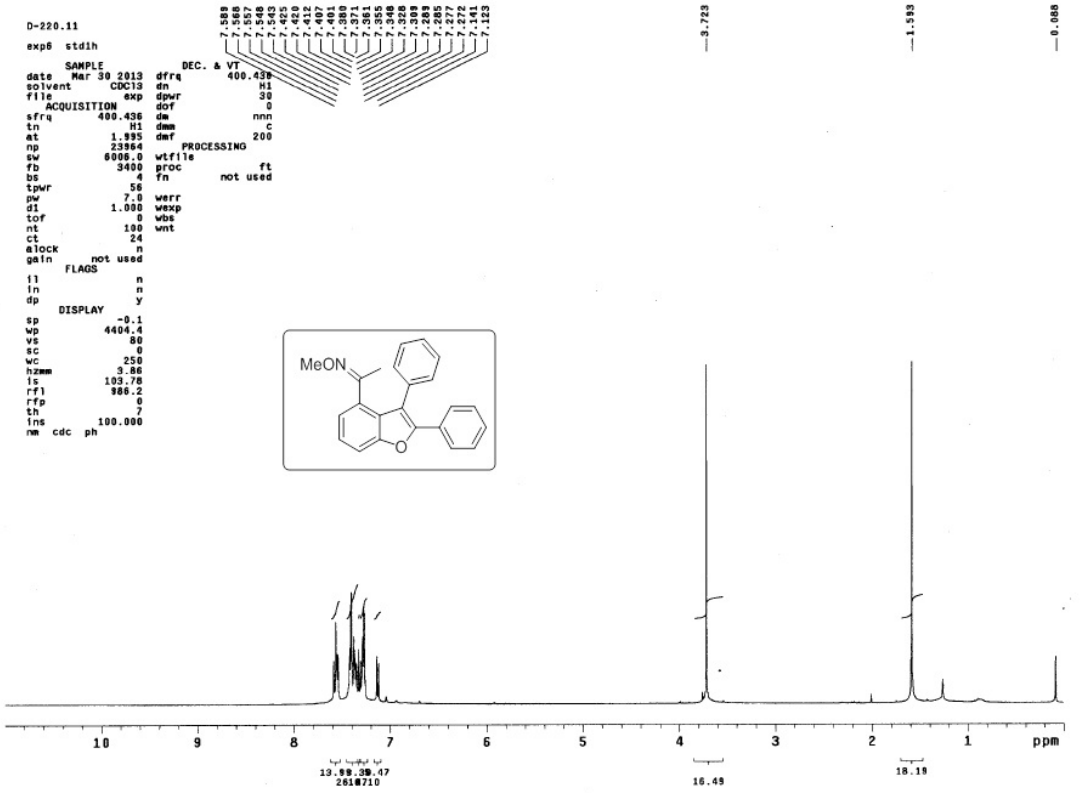


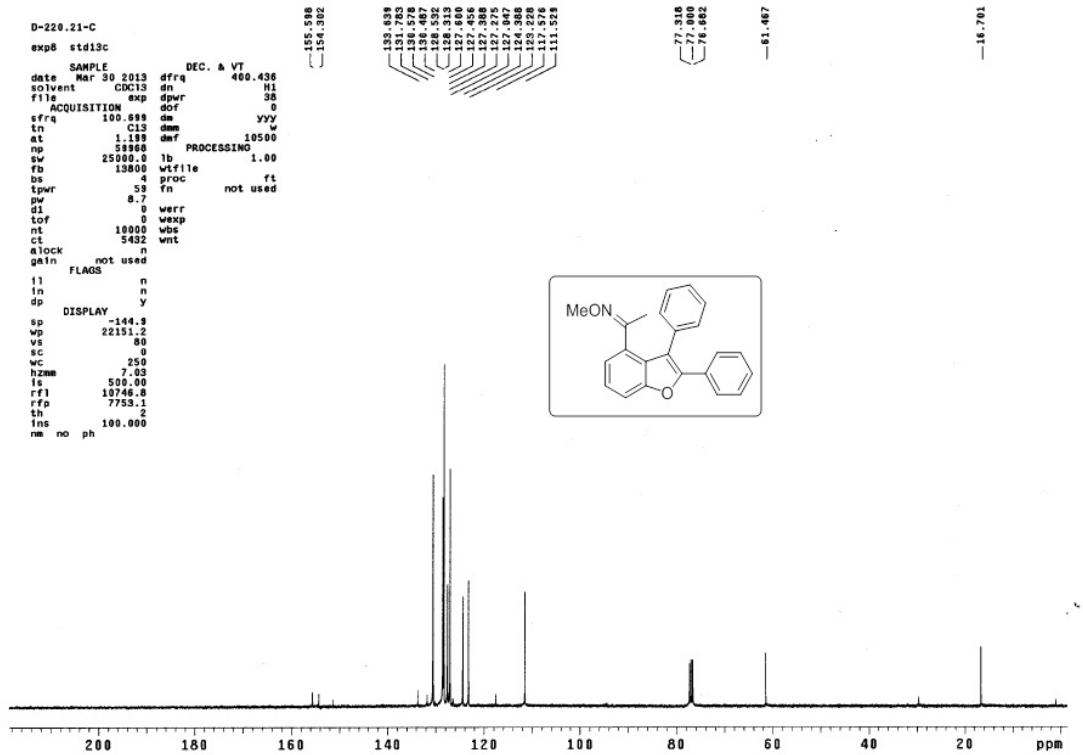


^{1}H and ^{13}C spectra of compound **3ja**

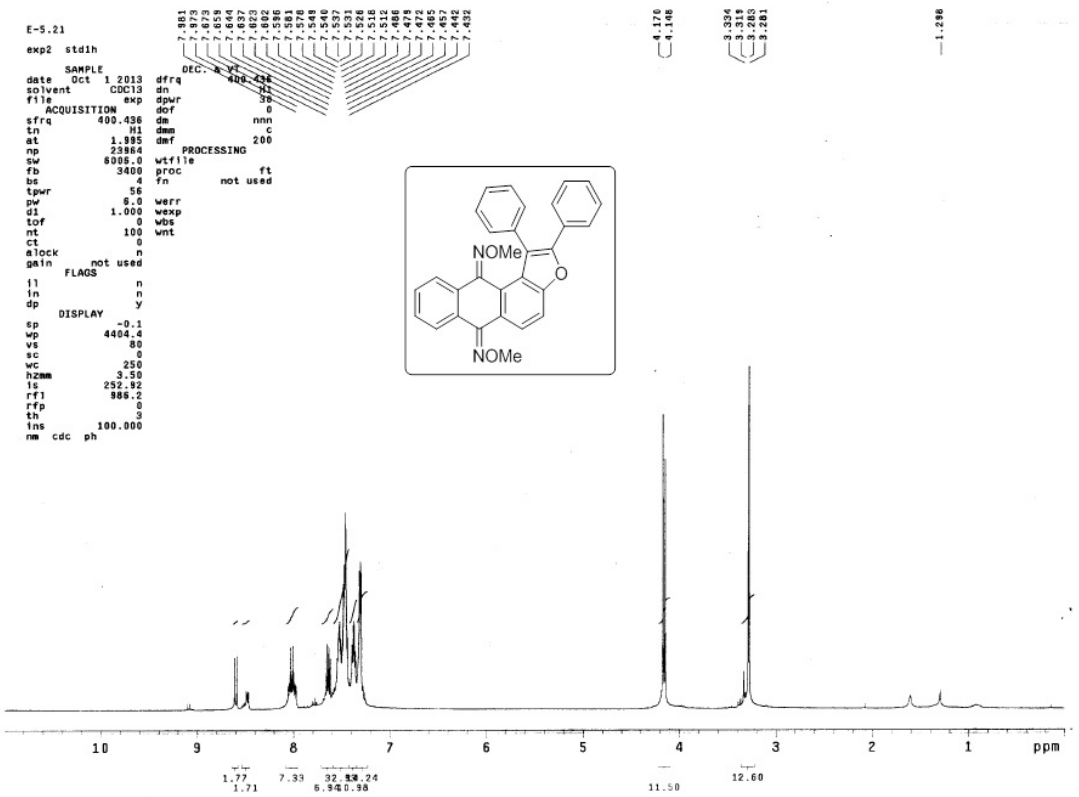


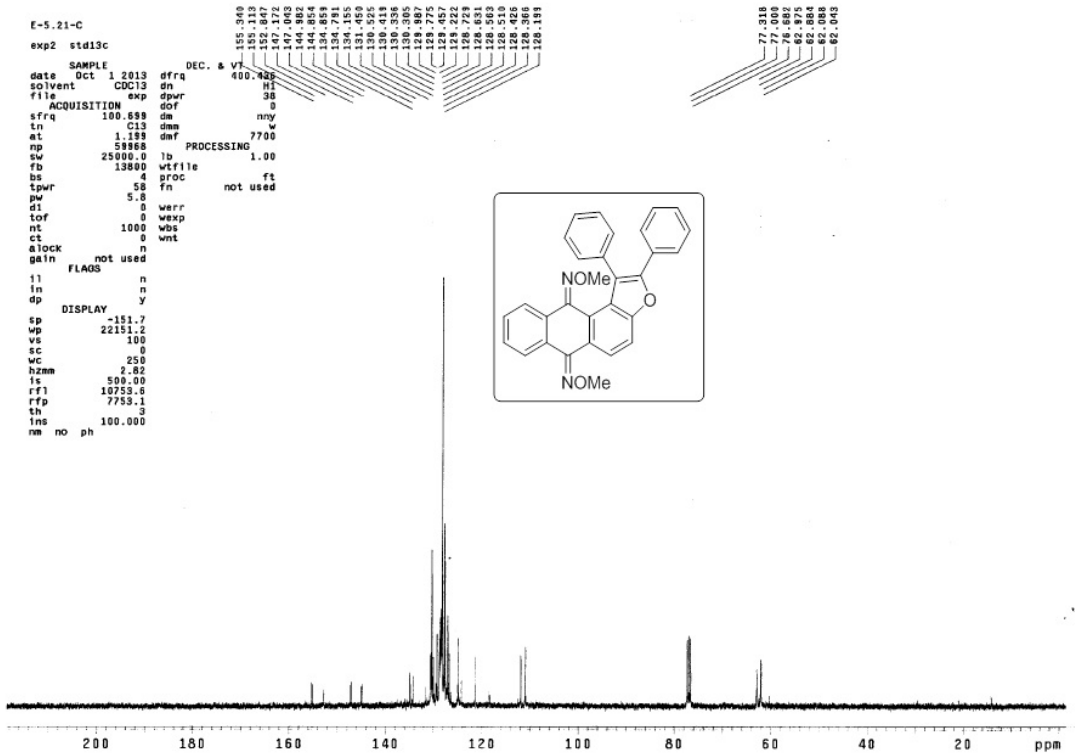
^{1}H and ^{13}C spectra of compound **3ka**



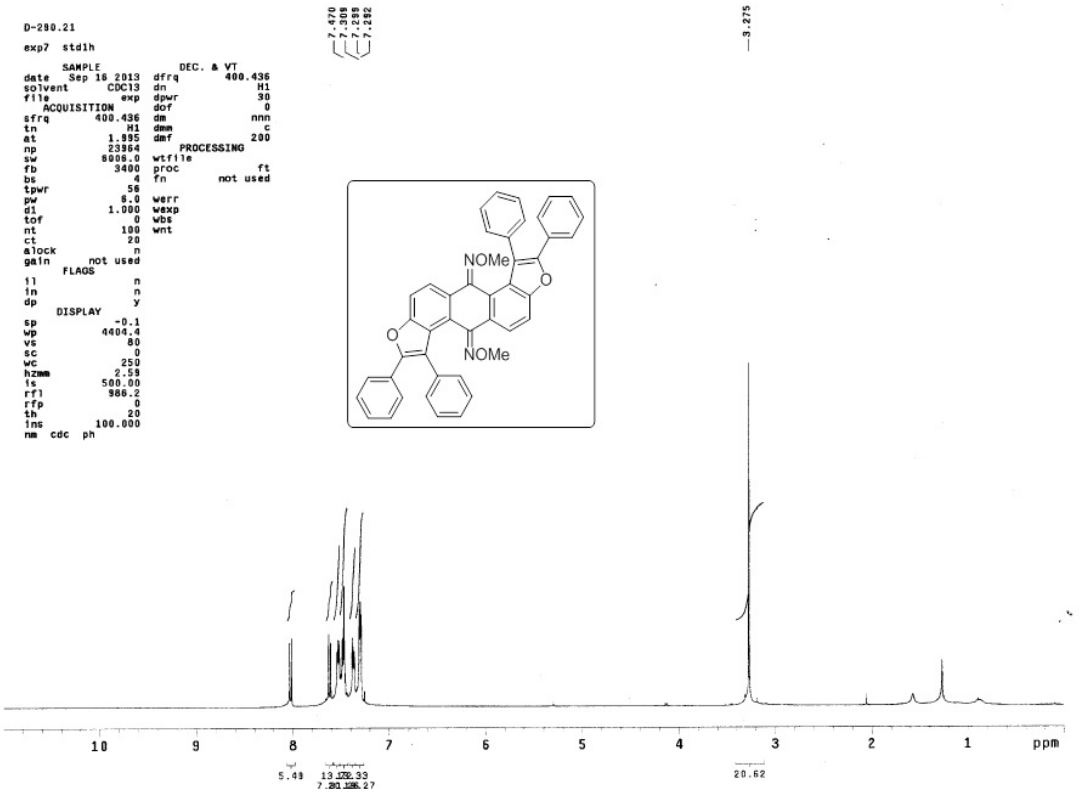


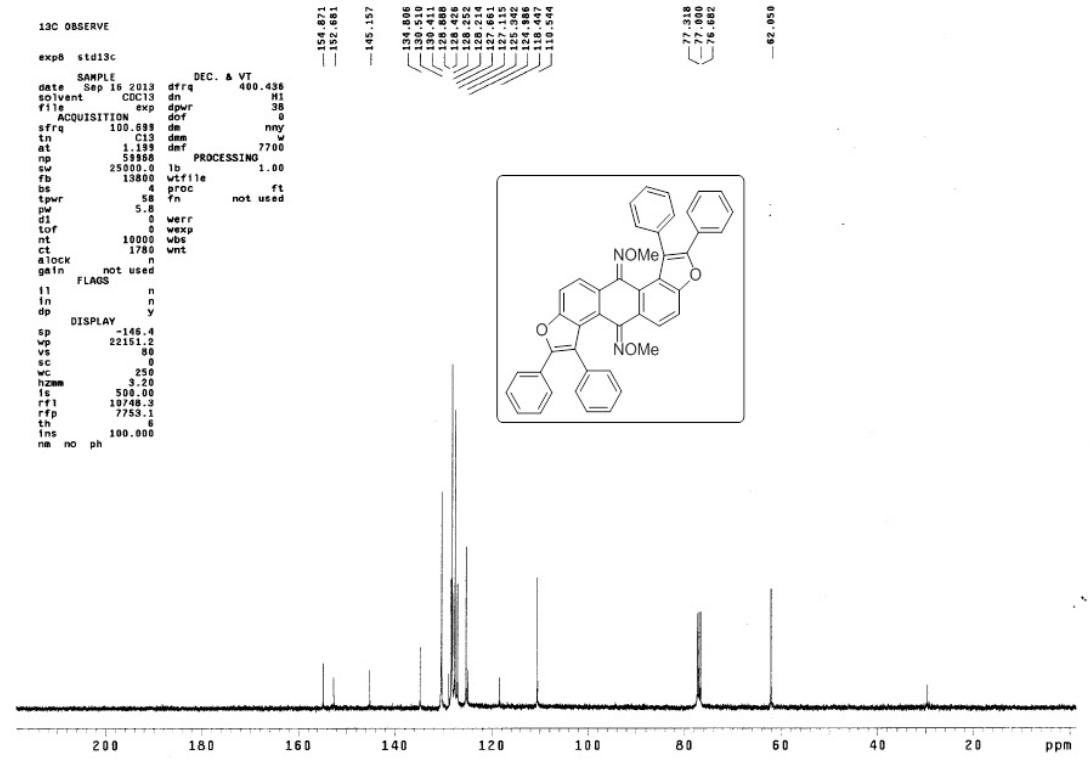
^{1}H and ^{13}C spectra of compound **3la**



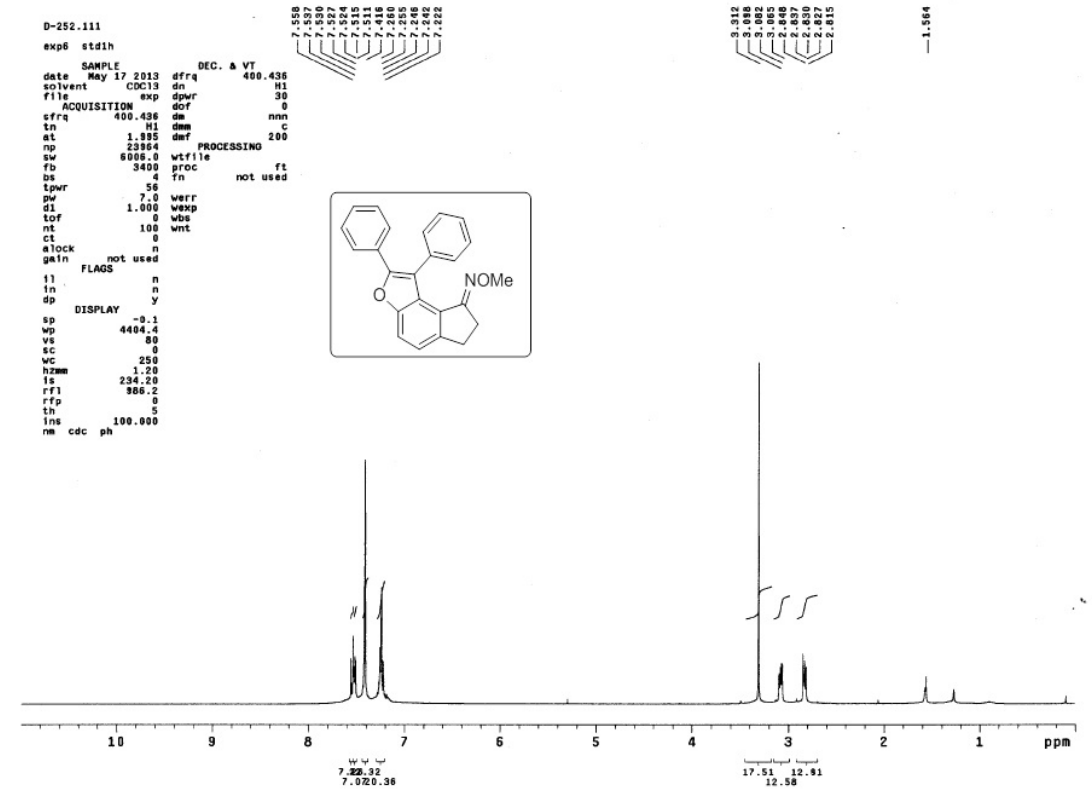


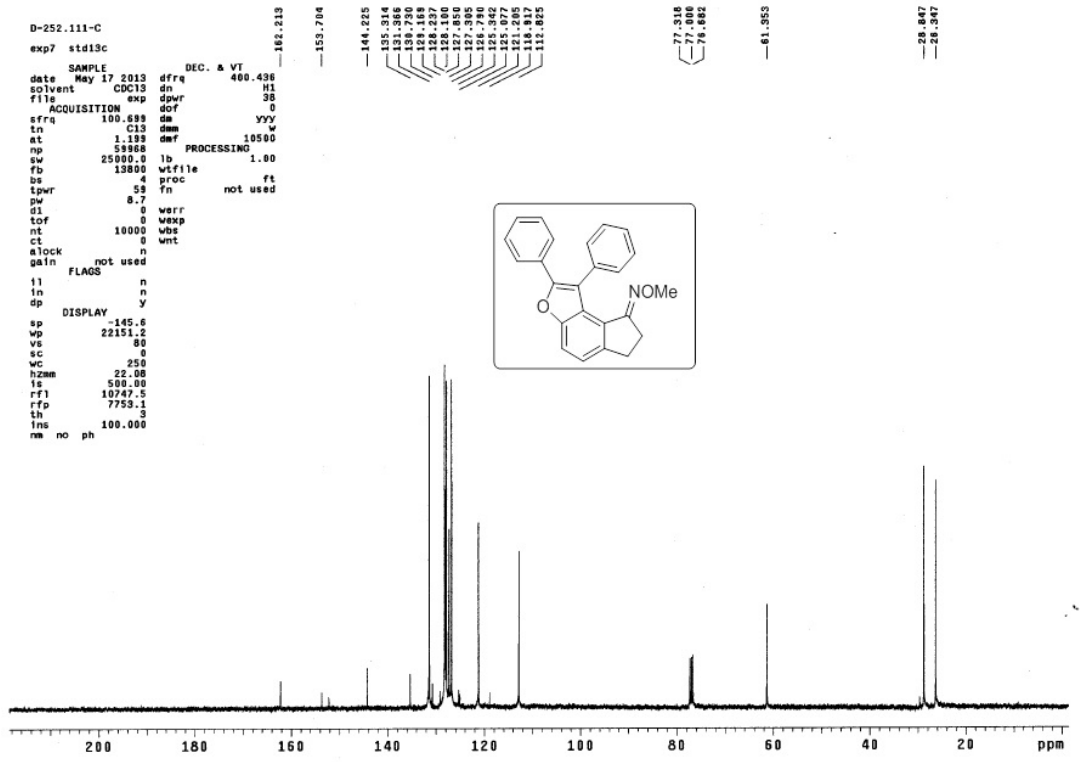
^{1}H and ^{13}C spectra of compound **3ma**



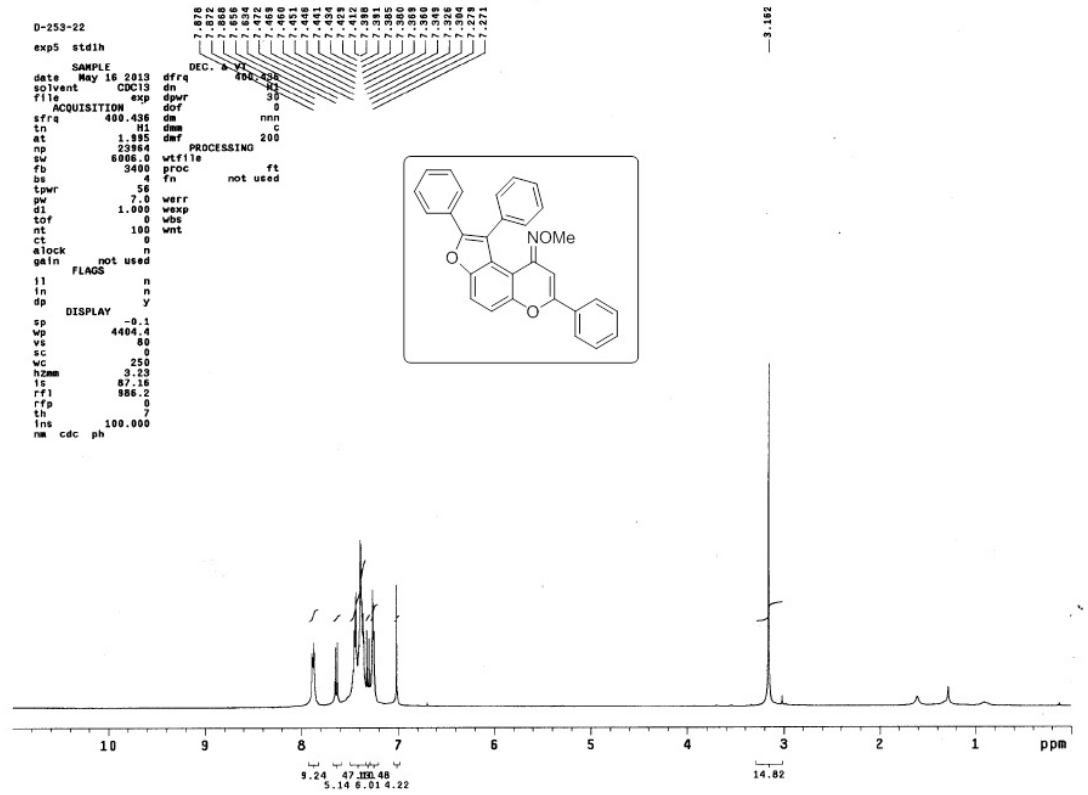


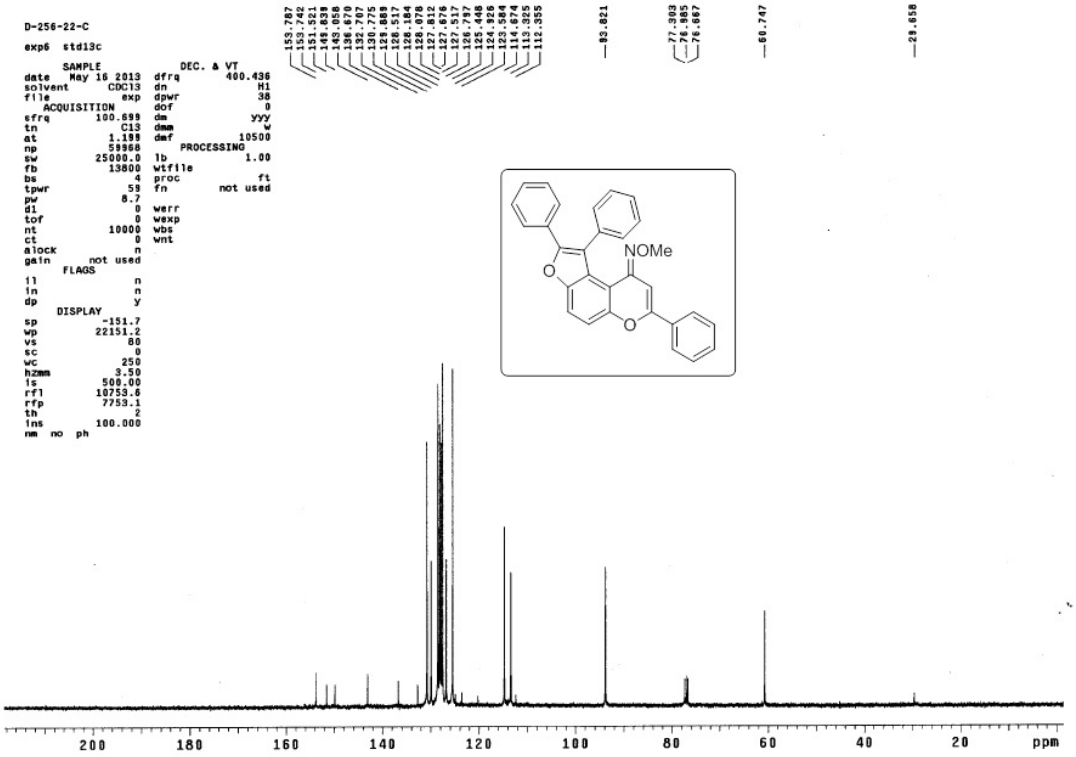
^{1}H and ^{13}C spectra of compound **3na**



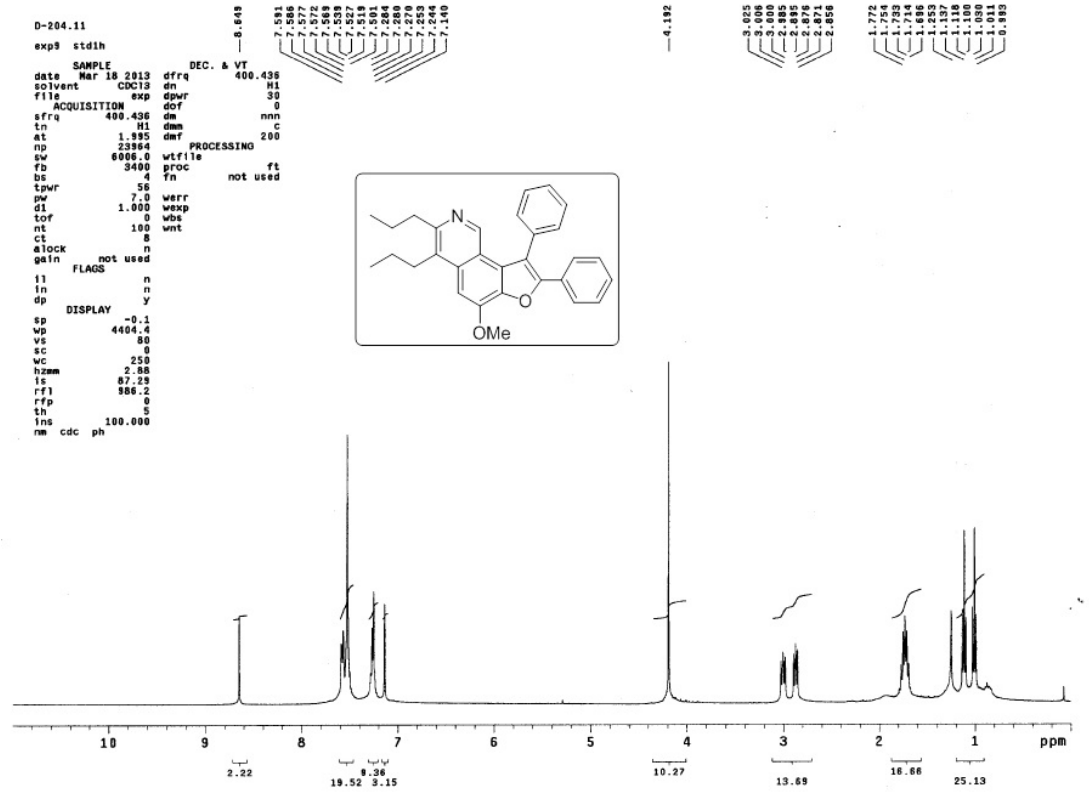


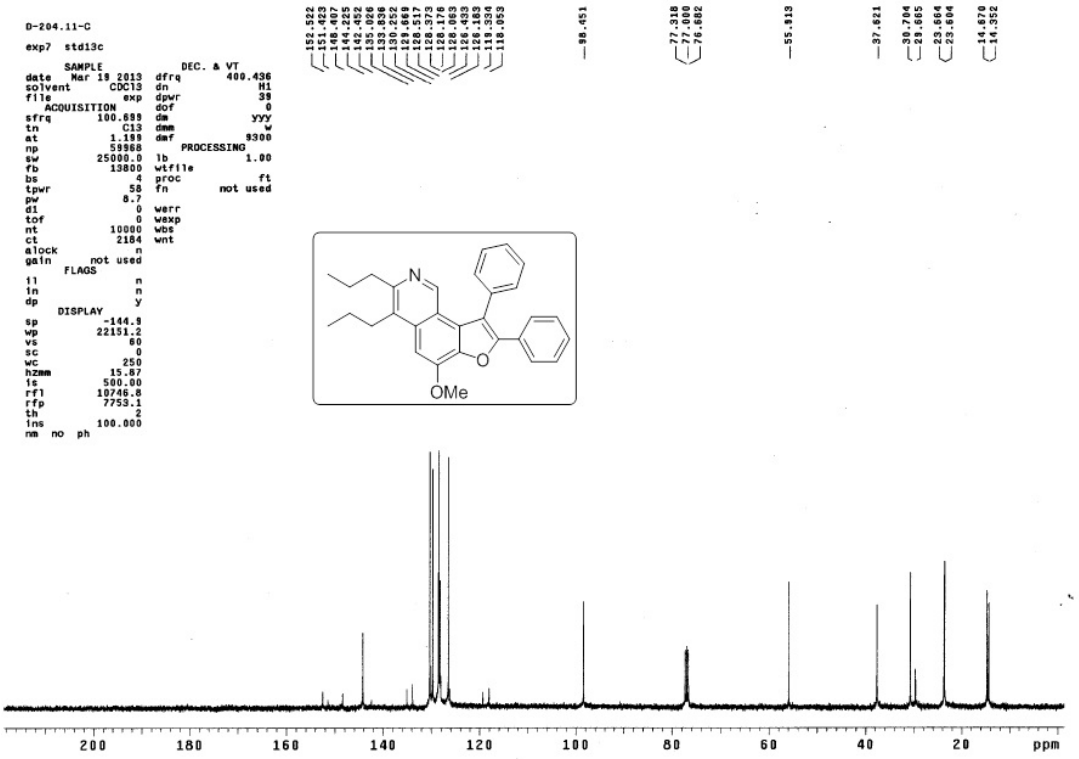
^{1}H and ^{13}C spectra of compound **3oa**





^{1}H and ^{13}C spectra of compound **4**





The X-ray structure

X-ray structure of **3aa**

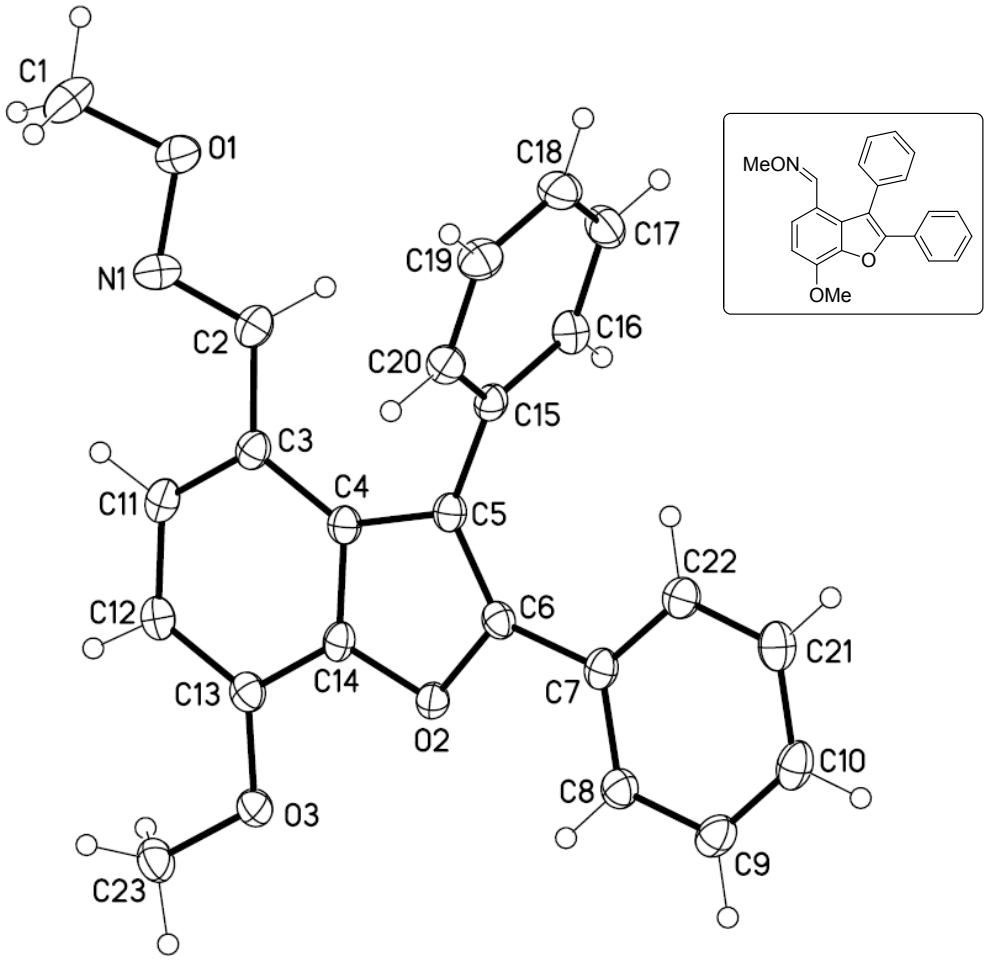


Table 1. Crystal data and structure refinement for mo_130319lt_0m (**3aa**).

Identification code	mo_130319lt_0m	
Empirical formula	C23 H19 N O3	
Formula weight	357.39	
Temperature	100(2) K	
Wavelength	0.71073 Å	
Crystal system	Monoclinic	
Space group	P 1 21/c 1	
Unit cell dimensions	a = 11.2184(5) Å	α= 90°.
	b = 11.0939(5) Å	β= 103.1300(10)°.
	c = 15.1186(7) Å	γ = 90°.
Volume	1832.41(14) $Å^3$	
Z	4	
Density (calculated)	1.295 Mg/m^3	
Absorption coefficient	0.086 mm^{-1}	

F(000)	752
Crystal size	0.30 x 0.28 x 0.26 mm^3
Theta range for data collection	1.86 to 26.42°.
Index ranges	-14<=h<=8, -13<=k<=13, -16<=l<=18
Reflections collected	14922
Independent reflections	3747 [R(int) = 0.0289]
Completeness to theta = 26.42°	99.6 %
Absorption correction	Semi-empirical from equivalents
Max. and min. transmission	0.9486 and 0.8897
Refinement method	Full-matrix least-squares on F^2
Data / restraints / parameters	3747 / 0 / 246
Goodness-of-fit on F^2	1.019
Final R indices [I>2sigma(I)]	R1 = 0.0400, wR2 = 0.0983
R indices (all data)	R1 = 0.0506, wR2 = 0.1053
Largest diff. peak and hole	0.576 and -0.210 $e.Å^{-3}$

X-ray structure of **3ga**

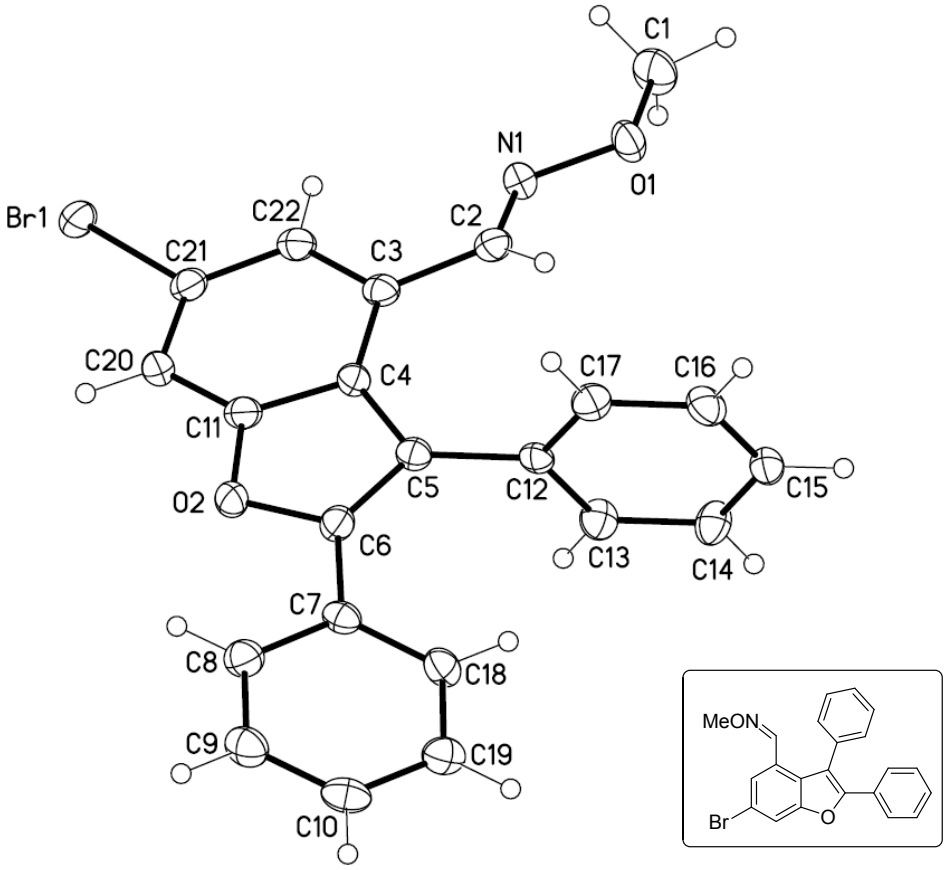
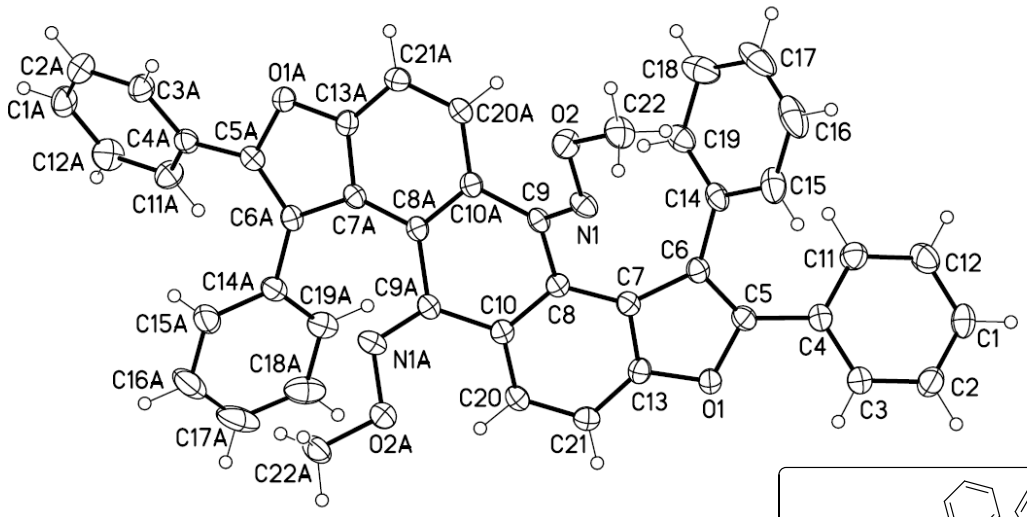


Table 1. Crystal data and structure refinement for 130931LT (**3ga**).

Identification code	130931lt	
Empirical formula	C22 H16 Br N O2	
Formula weight	406.27	
Temperature	100(2) K	
Wavelength	0.71073 Å	
Crystal system	Monoclinic	
Space group	P 1 21/c 1	
Unit cell dimensions	a = 17.3636(16) Å	α= 90°.
	b = 10.3459(9) Å	β= 92.111(2)°.
	c = 9.9494(10) Å	γ = 90°.
Volume	1786.1(3) $Å^3$	
Z	4	
Density (calculated)	1.511 Mg/m^3	
Absorption coefficient	2.317 mm^{-1}	
F(000)	824	
Crystal size	0.25 x 0.20 x 0.20 mm^3	

Theta range for data collection	1.17 to 26.42°.
Index ranges	-21<=h<=21, -12<=k<=12, -12<=l<=12
Reflections collected	14119
Independent reflections	3664 [R(int) = 0.0353]
Completeness to theta = 26.42°	99.6 %
Absorption correction	Semi-empirical from equivalents
Max. and min. transmission	0.9486 and 0.7854
Refinement method	Full-matrix least-squares on F^2
Data / restraints / parameters	3664 / 0 / 236
Goodness-of-fit on F^2	1.130
Final R indices [I>2sigma(I)]	R1 = 0.0256, wR2 = 0.0615
R indices (all data)	R1 = 0.0388, wR2 = 0.0786
Largest diff. peak and hole	0.344 and -0.289 e.$Å^{-3}$

X-ray structure of **3ma**



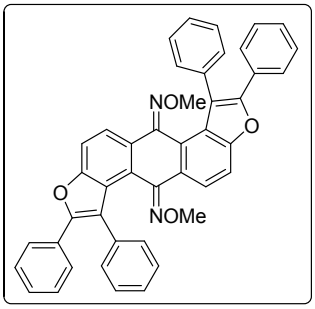


Table 1. Crystal data and structure refinement for mo_130940lt_0m(**3ma**).

Identification code	mo_130940lt_0m	
Empirical formula	C44 H30 N2 O4	
Formula weight	650.70	
Temperature	100(2) K	
Wavelength	0.71073 Å	
Crystal system	Monoclinic	
Space group	C 1 2/c 1	
Unit cell dimensions	a = 25.919(3) Å	α= 90°.
	b = 11.2554(14) Å	β= 101.271(2)°.
	c = 11.6261(14) Å	γ = 90°.
Volume	3326.3(7) $Å^3$	
Z	4	
Density (calculated)	1.299 Mg/m^3	
Absorption coefficient	0.083 mm^{-1}	
F(000)	1360	
Crystal size	0.25 x 0.22 x 0.15 mm^3	
Theta range for data collection	1.60 to 26.48°.	
Index ranges	-32<=h<=32, -14<=k<=13, -14<=l<=14	
Reflections collected	13500	
Independent reflections	3428 [R(int) = 0.0487]	
Completeness to theta = 26.48°	99.6 %	
Absorption correction	Semi-empirical from equivalents	
Max. and min. transmission	0.9486 and 0.8035	
Refinement method	Full-matrix least-squares on F^2	

Data / restraints / parameters	3428 / 0 / 227
Goodness-of-fit on F^2	1.031
Final R indices [I>2sigma(I)]	R1 = 0.0494, wR2 = 0.1252
R indices (all data)	R1 = 0.0723, wR2 = 0.1394
Largest diff. peak and hole	0.835 and -0.249 e.$Å^{-3}$