Diversity-oriented synthesis of benzofuro[3,2-*b*]pyridine derivatives from aurone-derived α,β-unsaturated imines and activated terminal alkynes

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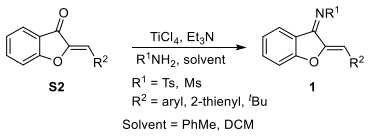
1. General Information

All isolated compounds were characterized on JEOL 400 MHz spectrometer in $CDCl_3$. Chemical shifts were reported as δ values relative to internal chloroform (δ 7.26 for ^{1}H NMR and 77.16 for ^{13}C NMR). ^{19}F NMR chemical shifts were determined as δ values relative to external standard $PhCF_3$ at −63.0. High-resolution mass spectra (HRMS) were obtained on a 4G mass spectrometer using electrospray ionization (ESI) analyzed by a quadrupole time-of-flight (QTof). All melting points were measured with the samples after column chromatography and uncorrected. Column chromatography was performed on silica gel. All solvents and reagents were used as obtained from commercial sources without further purification. Azadienes were all known and prepared according to the literature.[1]

2. Experimental Procedure

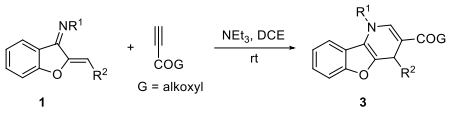
(1) General Procedure for the Synthesis of Azadienes 1

Step 1: To a solution of benzofuran-3(2*H*)-one (**S1**, 4 mmol) and aldehyde (8 mmol, 2.0 equiv) in dichloromethane (30 mL) was added basic aluminium oxide (13 g). The mixture was violently stirred at room temperature under argon atmosphere. After completion of the condensation reaction as monitored by TLC, the suspension was filtered off and the residue was washed with dichloromethane. The filtrates were combined and concentrated. The resulting residue was purified by silica gel column chromatography to afford the corresponding aurone **S2**.



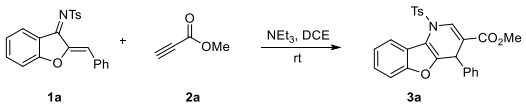
Step 2: To a solution of sulfamide (4.5 mmol, 1.5 equiv) and aurone **S2** (3.0 mmol) in toluene (40 mL) at 0 °C were added successively Et_3N (0.84 mL, 6.0 mmol, 2.0 equiv) and $TiCl_4$ (1.0 M in toluene, 3.6 mmol, 1.2 equiv). The reaction mixture was heated to reflux overnight. It was cooled to room temperature, quenched with icy water and extracted with DCM. The combined organic phases were combined, dried over Na_2SO_4, and concentrated. The residue was purified by silica gel column chromatography to afford the corresponding azadiene **1**. When R^2 was ^{t}Bu group, DCM as the solvent and heating at 45 ^{o}C was adopted instead.

(2) General procedure for the synthesis of 1,4-dihydrobenzofuro[3,2-*b*]pyridines 3a−3p



To a solution of aurone-derived α,β-unsaturated imine **1** (0.2 mmol, 1.0 equiv) in DCE (2 mL) were

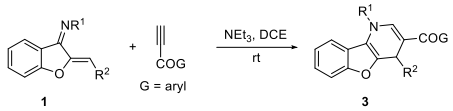
added terminal alkyne (0.24 mmol, 1.2 equiv) and NEt_3 (0.24 mmol, 1.2 equiv), and then the mixture was stirred at rt. After completion of the annulation reaction as monitored by TLC, the solvent was evaporated and the resulting residue was purified directly by silica gel column chromatography to afford the corresponding 1,4-dihydrobenzofuro[3,2-*b*]pyridines **3a−3p**. For the synthesis of **3i**, **3k**, and **3p**, the terminal alkyne (0.2 mmol, 1.0 equiv) was added first and another portion of terminal alkyne (0.2 mmol, 1.0 equiv) was added after 4 h.



1a **2a** **3a**

Scale-up experiment of 3a: To a solution of aurone-derived α,β-unsaturated imine **1a** (1.0 g, 2.66 mmol, 1.0 equiv) in DCE (27 mL) were added methyl propiolate **2a** (0.28 mL, 3.2 mmol, 1.2 equiv) and NEt_3 (4.4 mL, 3.2 mmol, 1.2 equiv), and then the mixture was stirred at rt. After completion of the annulation reaction as monitored by TLC, the solvent was evaporated and the resulting residue was purified directly by silica gel column chromatography to afford **3a** (880 mg, 72%) as a yellow solid.

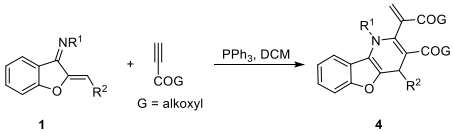
(3) General procedure for the synthesis of 1,4-dihydrobenzofuro[3,2-*b*]pyridines 3q−3t



1 **3**

To a solution of aurone-derived α,β-unsaturated imine **1** (0.2 mmol, 1.0 equiv) in DCE (2 mL) were added terminal alkyne (0.4 mmol, 2.0 equiv) and NEt_3 (0.24 mmol, 1.2 equiv), and then the mixture was stirred at rt. After completion of the annulation reaction as monitored by TLC, the solvent was evaporated and the resulting residue was purified directly by silica gel column chromatography to afford the corresponding 1,4-dihydrobenzofuro[3,2-*b*]pyridines **3q−3t**. For the synthesis of **3s**, the terminal alkyne (0.4 mmol, 2.0 equiv) was added first and another portion of terminal alkyne (0.2 mmol, 1 equiv) was added after 4 h.

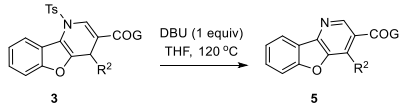
(4) General procedure for the synthesis of 1,4-dihydrobenzofuro[3,2-*b*]pyridines 4a−4f



1 **4**

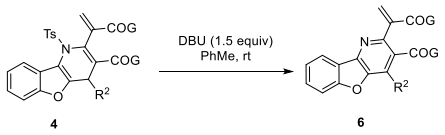
To a solution of aurone-derived α,β-unsaturated imine **1** (0.2 mmol, 1.0 equiv) in DCM (3 mL) were added terminal alkyne (0.6 mmol, 3.0 equiv) and PPh_3 (0.2 mmol, 1.0 equiv), then the mixture was stirred at rt. After completion of the annulation reaction as monitored by TLC, the solvent was evaporated and the resulting residue was purified by silica gel column chromatography to afford the corresponding 1,4-dihydrobenzofuro[3,2-*b*]pyridines (**4a−4f**).

(5) General procedure for the synthesis of benzofuro[3,2-*b*]pyridines 5a−5l



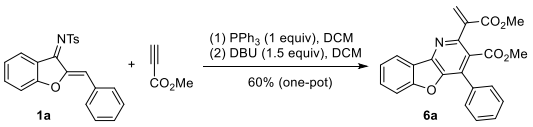
To a solution of 1,4-dihydrobenzofuro[3,2-*b*]pyridine **3** (0.12 mmol, 1.0 equiv) in THF (1.5 mL) was added DBU (0.12 mmol, 1.0 equiv), and then the mixture was stirred at 120 °C. After completion of the aromatization reaction as monitored by TLC, the solvent was evaporated and the resulting residue was purified directly by silica gel column chromatography to afford the corresponding benzofuro[3,2-*b*]pyridines **5a−5l**.

(6) General procedure for the synthesis of benzofuro[3,2-*b*]pyridines 6a−6c



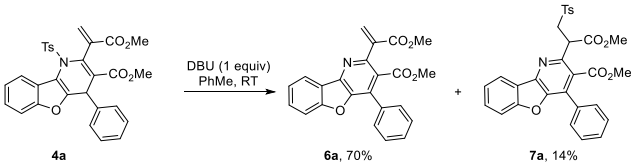
To a solution of 1,4-dihydrobenzofuro[3,2-*b*]pyridine **4** (0.2 mmol, 1.0 equiv) in PhMe (2 mL) was added DBU (0.3 mmol, 1.5 equiv), and then the mixture was stirred at rt. After completion of the aromatization reaction as monitored by TLC, the solvent was evaporated and the resulting residue was purified directly by silica gel column chromatography to afford the corresponding benzofuro[3,2-*b*]pyridines **6a−6c**.

(7) One-pot synthesis of benzofuro[3,2-*b*]pyridine 6a



To a solution of aurone-derived α,β-unsaturated imine **1a** (113 mg, 0.3 mmol, 1.0 equiv) in DCM (3 mL) were added methyl propiolate (0.08 mL, 0.9 mmol, 3.0 equiv) and PPh_3 (79 mg, 0.3 mmol, 1.0 equiv), and then the mixture was stirred at rt. After completion of the first step as monitored by TLC, DBU (68 mg, 0.45 mmol, 1.5 equiv) was added directly into the mixture. After an hour, the solvent was evaporated and the resulting residue was purified directly by silica gel column chromatography to afford **6a** (70 mg, 60%) as a yellow oil.

(8) Synthesis of benzofuro[3,2-*b*]pyridine 7a



4a **6a**, 70% **7a**, 14%

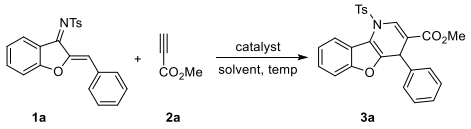
To a solution of 1,4-dihydrobenzofuro[3,2-*b*]pyridine **4a** (0.2 mmol, 1.0 equiv) in PhMe (2 mL) was added DBU (0.2 mmol, 1.0 equiv), and then the mixture was stirred at rt. After completion of the reaction as monitored by TLC, the solvent was evaporated and the resulting residue was purified by silica gel column chromatography to afford **6a** (54 mg, 70%) and **7a** (15 mg, 14%).

3. References

1. (a) M. Espinosa, G. Blay, L. Cardona and J. R. Pedro, *Chem. Eur. J.*, 2013, **19**, 14861; (b) H. Ni, X. Tang, W. Zheng, W. Yao, N. Ullah and Y. Lu, *Angew. Chem. Int. Ed.*, 2017, **56**, 14222; (c) K. Verma and P. Banerjee, *Adv. Synth. Catal.*, 2018, **360**, 3687; (d) B. M. Trost and Z. Zuo, *Angew. Chem. Int. Ed.*, 2020, **59**, 1243.

4. Optimization Conditions

Table S1 Optimization of the reaction conditions for the formation of **3a**.[a]



Entry	**1a**:**2a:** Initiator	Initiator	Solvent	Temp	Time (h)	**3a** Yield (%)[b]
1	1:3:3	NEt_3	DCE	rt	2	72[d]
2	1:3:0	-	DCE	rt to 80 °C	24 (rt); 24 (80 °C)	NP
3	1:1.5:1.5	NEt_3	DCE	rt	2	83
4	1:1.5:0.2	NEt_3	DCE	rt	16	82
5	**1:1.2:1.2**	**NEt_3**	**DCE**	**rt**	**3**	**83 (75)**[d]
6	1:1.2:1.2	DABCO	DCE	rt to 80 °C	24 (rt); 24 (80 °C)	NP
7[c]	1:1.2:1.2	PPh_3	DCE	rt	24	NP
8	1:1.2:1.2	DMAP	DCE	rt	24	NP
9	1:1.2:1.2	CsF	DCE	rt to 60 °C	24 (rt); 24 (60 °C)	NP
10	1:1.2:1.2	DBU	DCE	rt	24	NP
11	1:1.2:1.2	Cs_2CO_3	DCE	rt	24	NP
12	1:1.2:1.2	NEt_3	CH_3CN	rt	2	31
13	1:1.2:1.2	NEt_3	Dioxane	rt	36	36
14	1:1.2:1.2	NEt_3	THF	rt	22	42
15	1:1.2:1.2	NEt_3	$CHCl_3$	rt	24	NP
16	1:1.2:1.2	NEt_3	DMF	rt	1.5	53
17	1:1.2:1.2	NEt_3	Acetone	rt	24	10

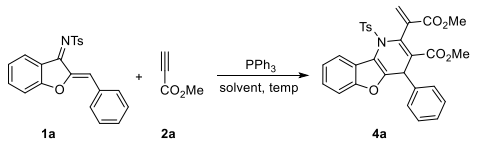
[a] Reaction conditions: **1a** (0.2 mmol), **2a** and initiator in solvent (2 mL) in air.

[b] The yield was determined by ^{1}H-NMR spectra using 1,3,5-trimethoxybenzene as the internal standard.

[c] **4a** was obtained instead.

[d] Isolated yield

Table S2 Optimization of the reaction conditions for the formation of **4a**.[a]



Entry	**1a**: **2a:** Initiator	Initiator	Solvent	Temp	Time (h)	**4a** Yield (%)[b]
1	1:3:2	PPh_3	DCE	rt to 50 °C	24 (rt), 24 (50 °C)	54
2	1:3:2	PPh_3	DCE	50 °C	2	62
3	1:3:2	PPh_3	DCM	rt	1	72[d]
4	1:3:2	PPh_3	DMF	rt	2	63
5	1:3:2	PPh_3	MeCN	rt	1	56
6	1:3:2	PPh_3	Toluene	rt to 50 °C	24 (rt), 24 (50 °C)	13
7	1:3:2	PPh_3	$CHCl_3$	rt to 50 °C	24 (rt), 24 (50 °C)	ND
8	1:3:2	PPh_3	MeOH	rt	5	35
9	1:3:2	PPh_3	Acetone	rt to 50 °C	24 (rt), 24 (50 °C)	ND
10	1:3:2	PPh_3	THF	rt to 50 °C	24 (rt), 24 (50 °C)	ND
11	1:3:2	PPh_3	HFIP	rt to 50 °C	24 (rt), 24 (50 °C)	ND
12[c]	1:3:0.2	PPh_3	DCM	rt	1	16
13[c]	1:3:0.5	PPh_3	DCM	rt	3	64
14	1:3:1	PPh_3	DCM	rt	1	81[d]

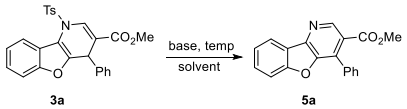
[a] Reaction conditions: **1a** (0.2 mmol), **2a** and PPh_3, in solvent (2 mL) in air.

[b] The yield was determined by ^{1}H-NMR spectra using 1,3,5-trimethoxybenzene as the internal standard.

[c] Large amount of **1a** was retained and there was no PPh_3 detected after the indicated reaction time. The yield will not be increased if the reaction time was prolonged. Instead, the yield will decrease owing to the instability of the product **4**.

[d] Isolated yield.

Table S3 Optimization of the aromatization reaction conditions of **5a**.[a]



Entry	**3a**:Base	Base	Solvent	Temp	Time (h)	**5a** Yield (%)[b]
1	1:5	DBU	DCE	120 °C	48	-[c]
2	1:2	DBU	DMF	120 °C	3	81
3	1:2	DBU	Toluene	120 °C	3	80
4	1:2	DBU	THF	120 °C	3	93[d]
5	1:2	DBU	Acetone	120 °C	3	86
6	1:2	NaOH	Ethanol	120 °C	3	trace
7	1:1	DBU	THF	120 °C	3	95[d]
8	1:2	DBU	THF	rt	48	93[d]
9	1:1.5	DBU	THF	120 °C	3	95[d]

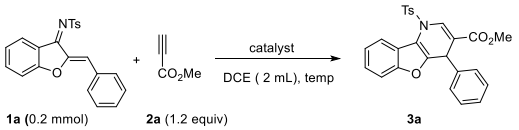
[a] Reaction conditions: **3a** (0.1 mmol) and base in solvent in air.

[b] The yield was determined by ^{1}H-NMR spectra using 1,3,5-trimethoxybenzene as the internal standard.

[c] Large amount of **3a** was retained, although the amount of base of DBU has been increased to 5 equiv with prolonged time.

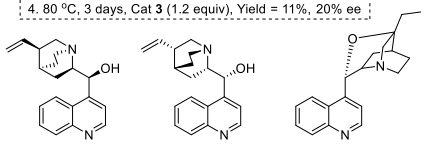
[d] Isolated yield.

Asymmetric Versions for the Formation of 3a and 4a

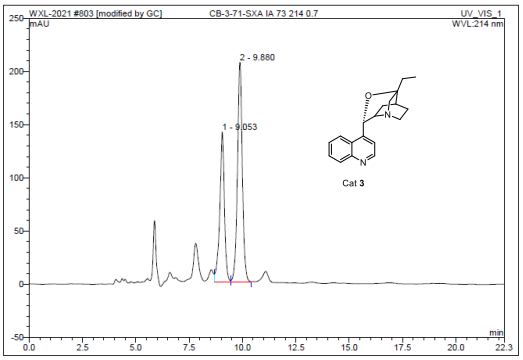


1a (0.2 mmol) **2a** (1.2 equiv) **3a**

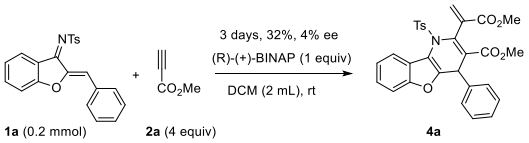
1. rt to 80 °C, Cat **1** (1.2 equiv), no product
2. rt to 80 °C, Cat **2** (1.2 equiv), no product
3. rt, Cat **3** (1.2 equiv), no product
4. 80 °C, 3 days, Cat **3** (1.2 equiv), Yield = 11%, 20% ee



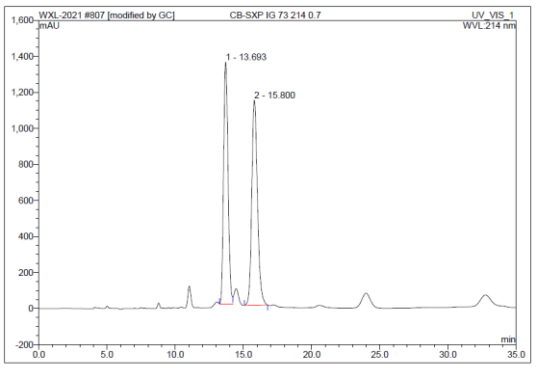
Cat **1** Cat **2** Cat **3**



No.	Ret.Time min	Peak Name	Height mAU	Area mAU*min	Rel.Area %	Amount	Type
1	9.05	n.a.	140.712	36.111	39.81	n.a.	M *
2	9.88	n.a.	206.376	54.599	60.19	n.a.	MB*
Total:			347.088	90.711	100.00	0.000	

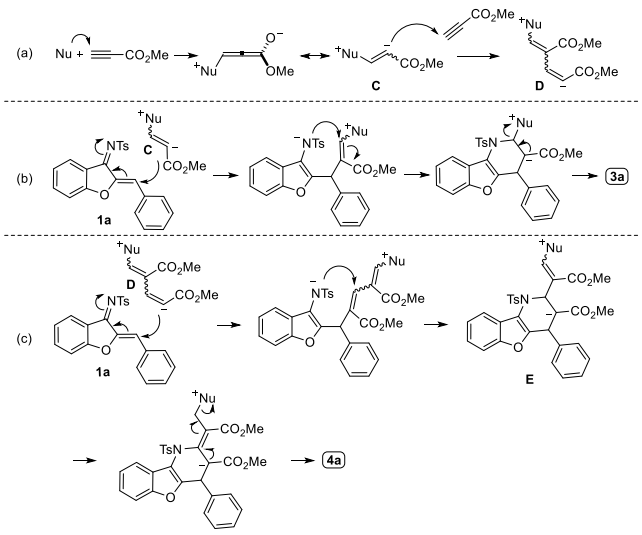


1a (0.2 mmol) **2a** (4 equiv) **4a**

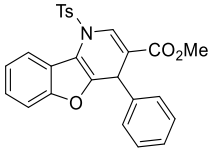


No.	Ret.Time min	Peak Name	Height mAU	Area mAU*min	Rel.Area %	Amount	Type
1	13.69	n.a.	1340.534	506.587	47.96	n.a.	BM *
2	15.80	n.a.	1138.632	549.669	52.04	n.a.	BMB*
Total:			2479.167	1056.256	100.00	0.000	

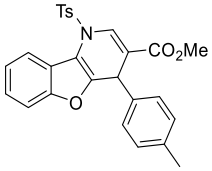
5. Proposed mechanisms for the Formation of 3a and 4a



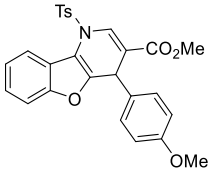
6. **Characterization Data**



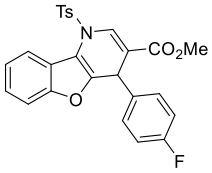
Methyl 4-phenyl-1-tosyl-1,4-dihydrobenzofuro[3,2-*b*]pyridine-3-carboxylate. Compound **3a** (69 mg, Yield = 75%, R_f = 0.56 (PE/EA = 5:1)) was isolated as a yellow solid; mp 161–162 °C. ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.43–8.39 (m, 1H), 8.10 (s, 1H), 7.62 (d, J = 8.4 Hz, 2H), 7.37–7.26 (m, 5H), 7.11 (t, J = 7.6 Hz, 1H), 7.00 (t, J = 7.6 Hz, 2H), 6.52 (d, J = 4.4 Hz, 2H), 5.16 (s, 1H), 3.70 (s, 3H), 2.46 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 165.9, 154.4, 146.7, 145.3, 140.4, 135.3, 132.8, 130.4, 128.2, 128.0 (2C), 127.2, 125.0, 123.7, 122.5, 121.4, 116.0, 114.8, 111.7, 52.1, 40.5, 21.8; ESI-HRMS *m/z* calcd for $C_{26}H_{22}NO_5S$ $[M + H]^+$ 460.1213, found 460.1215.



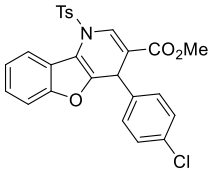
Methyl 4-(*p*-tolyl)-1-tosyl-1,4-dihydrobenzofuro[3,2-*b*]pyridine-3-carboxylate. Compound **3b** (77 mg, Yield = 81%, R_f = 0.32 (PE/EA = 10:1)) was isolated as a yellow solid; mp 194–195 °C. ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.44–8.39 (m, 1H), 8.09 (s, 1H), 7.63 (d, J = 8.0 Hz, 2H), 7.37–7.26 (m, 5H), 6.82 (d, J = 8.0 Hz, 2H), 6.42 (d, J = 8.0 Hz, 2H), 5.13 (s, 1H), 3.71 (s, 3H), 2.48 (s, 3H), 2.25 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 165.9, 154.3, 146.8, 145.3, 137.5, 136.8, 135.1, 132.6, 130.3, 129.0, 128.0, 127.8, 124.9, 123.6, 122.4, 121.4, 116.2, 114.6, 111.7, 52.1, 40.1, 21.8, 21.2; ESI-HRMS *m/z* calcd for $C_{27}H_{24}NO_5S$ $[M + H]^+$ 474.1370, found 474.1372.



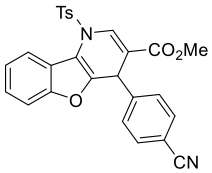
Methyl 4-(4-methoxyphenyl)-1-tosyl-1,4-dihydrobenzofuro[3,2-*b*]pyridine-3-carboxylate. Compound **3c** (80 mg, Yield = 82%, R_f = 0.33 (PE/EA = 5:1)) was isolated as a yellow solid; mp 201–202 °C. ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.43–8.38 (m, 1H), 8.07 (s, 1H), 7.62 (d, J = 8.0 Hz, 2H), 7.38–7.26 (m, 5H), 6.53 (d, J = 8.8 Hz, 2H), 6.42 (d, J = 8.8 Hz, 2H), 5.10 (s, 1H), 3.72 (s, 3H), 3.71 (s, 3H), 2.47 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 165.9, 158.5, 154.3, 146.9, 145.2, 135.0, 132.7, 132.6, 130.3, 129.0, 128.0, 125.0, 123.6, 122.4, 121.4, 116.3, 114.6, 113.5, 111.6, 55.2, 52.1, 39.6, 21.8; ESI-HRMS *m/z* calcd for $C_{27}H_{23}NO_6SNa$ $[M + Na]^+$ 512.1138, found 512.1140.



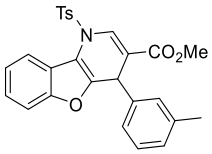
Methyl 4-(4-fluorophenyl)-1-tosyl-1,4-dihydrobenzofuro[3,2-*b*]pyridine-3-carboxylate. Compound **3d** (78 mg, Yield = 82%, R_f = 0.55 (PE/EA = 5:1)) was isolated as a yellow oil. ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.42–8.38 (m, 1H), 8.09 (s, 1H), 7.62 (d, J = 8.4 Hz, 2H), 7.37–7.30 (m, 3H), 7.28 (d, J = 8.0 Hz, 2H), 6.68 (t, J = 8.4 Hz, 2H), 6.52–6.45 (m, 2H), 5.14 (s, 1H), 3.71 (s, 3H), 2.46 (s, 3H); ^{13}C{^{1}H} NMR (100 MHz, $CDCl_3$) δ 165.8, 161.8 (d, $^1J_{C\text{-}F}$ = 244.8 Hz), 154.3, 146.3, 145.4, 136.3 (d, $^4J_{C\text{-}F}$ = 3.2 Hz), 135.4, 132.7, 130.4, 129.5 (d, $^3J_{C\text{-}F}$ = 8.1 Hz), 128.0, 125.2, 123.8, 122.5, 121.3, 115.9, 115.1 (d, $^2J_{C\text{-}F}$ = 21.5 Hz), 114.8, 111.7, 52.2, 39.7, 21.8; ^{19}F{^{1}H} NMR (376 MHz, $CDCl_3$) δ -115.2 (s, 1F); ESI-HRMS *m/z* calcd for $C_{26}H_{21}FNO_5S$ $[M + H]^+$ 478.1119, found 478.1121.



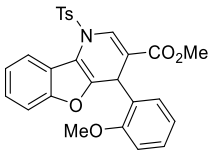
Methyl 4-(4-chlorophenyl)-1-tosyl-1,4-dihydrobenzofuro[3,2-*b*]pyridine-3-carboxylate. Compound **3e** (85 mg, Yield = 86%, R_f = 0.29 (PE/EA = 10:1)) was isolated as a yellow solid; mp 192–193 °C. ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.42–8.37 (m, 1H), 8.09 (s, 1H), 7.61 (d, J = 8.0 Hz, 2H), 7.38–7.24 (m, 5H), 6.96 (d, J = 8.4 Hz, 2H), 6.46 (d, J = 8.4 Hz, 2H), 5.14 (s, 1H), 3.72 (s, 3H), 2.46 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 165.7, 154.3, 146.0, 145.5, 139.0, 135.6, 133.0, 132.6, 130.4, 129.2, 128.4, 128.0, 125.2, 123.8, 122.5, 121.2, 115.6, 114.9, 111.7, 52.2, 39.8, 21.8; ESI-HRMS *m/z* calcd for $C_{26}H_{21}ClNO_5S$ $[M + H]^+$ 494.0823, found 494.0826.



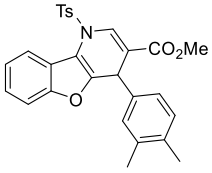
Methyl 4-(4-cyanophenyl)-1-tosyl-1,4-dihydrobenzofuro[3,2-*b*]pyridine-3-carboxylate. Compound **3f** (64 mg, Yield = 66%, R_f = 0.34 (PE/EA = 5:1)) was isolated as a yellow solid; mp 94–95 °C. ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.43–8.37 (m, 1H), 8.13 (s, 1H), 7.61 (d, J = 8.4 Hz, 2H), 7.38–7.32 (m, 3H), 7.31–7.26 (m, 4H), 6.67 (d, J = 8.4 Hz, 2H), 5.22 (s, 1H), 3.71 (s, 3H), 2.47 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 165.5, 154.4, 145.6 (2C), 144.9, 136.1, 132.7, 132.1, 130.4, 128.7, 128.0, 125.5, 123.9, 122.6, 121.0, 118.6, 115.3, 114.6, 111.7, 111.1, 52.3, 40.5, 21.8; ESI-HRMS *m/z* calcd for $C_{27}H_{21}N_2O_5S$ $[M + H]^+$ 485.1166, found 485.1168.



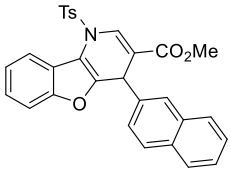
Methyl 4-(*m*-tolyl)-1-tosyl-1,4-dihydrobenzofuro[3,2-*b*]pyridine-3-carboxylate. Compound **3g** (76 mg, Yield = 80%, R_f = 0.42 (PE/EA = 5:1)) was isolated as a yellow oli. ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.48–8.41 (m, 1H), 8.14 (s, 1H), 7.65 (d, *J* = 8.4 Hz, 2H), 7.37–7.25 (m, 5H), 6.94 (d, *J* = 7.6 Hz, 1H), 6.85 (t, *J* = 7.6 Hz, 1H), 6.78 (br s, 1H), 6.13 (d, *J* = 7.8 Hz, 1H), 5.14 (s, 1H), 3.71 (s, 3H), 2.43 (s, 3H), 2.20 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 165.9, 154.3, 146.6, 145.3, 140.4, 138.0, 135.2, 133.0, 130.3, 129.0, 128.1, 127.9, 124.9, 124.7, 123.6, 122.4, 121.2, 115.5, 114.5, 111.7, 52.1, 40.4, 21.8, 21.5, (1C peak is merged with other peaks); ESI-HRMS *m/z* calcd for $C_{27}H_{23}NO_5SNa$ $[M + Na]^+$ 496.1189, found 496.1191.



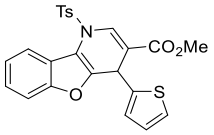
Methyl 4-(2-methoxyphenyl)-1-tosyl-1,4-dihydrobenzofuro[3,2-*b*]pyridine-3-carboxylate. Compound **3h** (81 mg, Yield = 83%, R_f = 0.41 (PE/EA = 5:1)) was isolated as a yellow solid; mp 122–123 °C. ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.36 (dd, *J* = 7.2, 1.6 Hz, 1H), 8.14 (s, 1H), 7.61 (d, *J* = 8.4 Hz, 2H), 7.34–7.22 (m, 5H), 7.10–7.03 (m, 1H), 6.85 (d, *J* = 8.0 Hz, 1H), 6.36 (td, *J* = 7.6, 1.2 Hz, 1H), 5.74 (s, 1H), 5.70 (dd, *J* = 7.6, 1.6 Hz, 1H), 3.91 (s, 3H), 3.64 (s, 3H), 2.42 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 165.8, 157.0, 154.1, 147.4, 145.2, 135.9, 132.8, 130.3, 129.6, 128.2, 128.0 (2C), 124.7, 123.4, 122.3, 121.3, 120.3, 116.0, 114.4, 111.7, 111.2, 56.3, 52.0, 32.4, 21.8; ESI-HRMS *m/z* calcd for $C_{27}H_{23}NO_6SNa$ $[M + Na]^+$ 512.1138, found 512.1140.



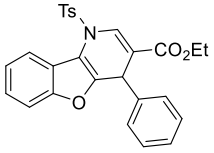
Methyl 4-(3,4-dimethylphenyl)-1-tosyl-1,4-dihydrobenzofuro[3,2-*b*]pyridine-3-carboxylate. Compound **3i** (74 mg, Yield = 76%, R_f = 0.22 (PE/EA = 10:1)) was isolated as a yellow solid; mp 180–181 °C. ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.44–8.40 (m, 1H), 8.12 (s, 1H), 7.65 (d, *J* = 8.4 Hz, 2H), 7.36–7.26 (m, 5H), 6.75 (d, *J* = 2.0 Hz, 1H), 6.71 (d, *J* = 7.6 Hz, 1H), 6.03 (dd, *J* = 8.0, 2.0 Hz, 1H), 5.12 (s, 1H), 3.71 (s, 3H), 2.44 (s, 3H), 2.15 (s, 3H), 2.10 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 166.0, 154.3, 146.8, 145.3, 138.0, 136.6, 135.6, 135.1, 133.0, 130.3, 129.6, 128.0, 124.9 (2C), 123.6, 122.4, 121.3, 115.7, 114.5, 111.7, 52.1, 40.1, 21.8, 19.8, 19.6, (1C peak is merged with other peaks); ESI-HRMS *m/z* calcd for $C_{28}H_{26}NO_5S$ $[M + H]^+$ 488.1526, found 488.1528.



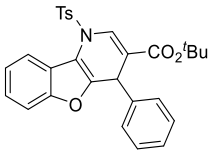
Methyl 4-(naphthalen-2-yl)-1-tosyl-1,4-dihydrobenzofuro[3,2-*b*]pyridine-3-carboxylate. Compound **3j** (70 mg, Yield = 69%, R_f = 0.48 (PE/EA = 5:1)) was isolated as a yellow solid; mp 194–195 °C. ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.46 (dt, *J* = 8.0, 1.2 Hz, 1H), 8.20 (s, 1H), 7.75–7.68 (m, 1H), 7.68 (d, *J* = 8.4 Hz, 2H), 7.60–7.56 (m, 1H), 7.47–7.39 (m, 3H), 7.38–7.27 (m, 6H), 6.59 (dd, *J* = 8.6, 1.6 Hz, 1H), 5.37 (s, 1H), 3.69 (s, 3H), 2.45 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 165.9, 154.4, 146.4, 145.4, 137.8, 135.5, 133.2, 133.0, 132.5, 130.4, 128.0 (3C), 127.6, 127.0, 126.1, 126.0, 125.6, 125.1, 123.7, 122.5, 121.2, 115.4, 114.8, 111.7, 52.1, 40.6, 21.8; ESI-HRMS *m/z* calcd for $C_{30}H_{24}NO_5S$ $[M + H]^+$ 510.1371, found 510.1371.



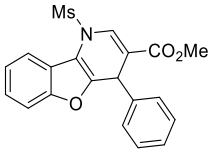
Methyl 4-(thiophen-2-yl)-1-tosyl-1,4-dihydrobenzofuro[3,2-*b*]pyridine-3-carboxylate. Compound **3k** (76 mg, Yield = 82%, R_f = 0.47 (PE/EA = 5:1)) was isolated as a yellow solid; mp 106–107 °C. ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.43–8.36 (m, 1H), 8.09 (s, 1H), 7.58 (d, *J* = 8.4 Hz, 2H), 7.41–7.29 (m, 3H), 7.20 (d, *J* = 8.0 Hz, 2H), 7.01 (dd, *J* = 5.0, 1.2 Hz, 1H), 6.68 (dd, *J* = 5.0, 3.6 Hz, 1H), 6.13 (dd, *J* = 4.0, 1.2 Hz, 1H), 5.46 (s, 1H), 3.77 (s, 3H), 2.39 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 165.8, 154.3, 145.6, 145.3, 144.9, 135.3, 132.9, 130.4, 127.8, 126.6, 125.2, 124.7, 123.7, 122.5, 121.2, 115.5, 114.7, 111.8, 52.2, 35.0, 21.7, (1C peak is merged with other peaks); ESI-HRMS *m/z* calcd for $C_{24}H_{19}NO_5S_2Na$ $[M + Na]^+$ 488.0597, found 488.0597.



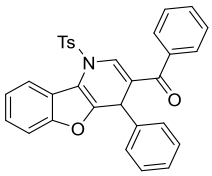
Ethyl 4-phenyl-1-tosyl-1,4-dihydrobenzofuro[3,2-*b*]pyridine-3-carboxylate. Compound **3m** (64 mg, Yield = 68%, R_f = 0.57 (PE/EA = 5:1)) was isolated as a yellow oil. ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.44–8.38 (m, 1H), 8.10 (s, 1H), 7.63 (d, *J* = 8.0 Hz, 2H), 7.37–7.26 (m, 5H), 7.11 (t, *J* = 7.6 Hz, 1H), 7.00 (t, *J* = 7.6 Hz, 2H), 6.52 (d, *J* = 6.8 Hz, 2H), 5.16 (s, 1H), 4.24–4.04 (m, 2H), 2.46 (s, 3H), 1.22 (t, *J* = 7.2 Hz, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 165.4, 154.3, 146.8, 145.3, 140.5, 135.1, 132.7, 130.3, 128.2, 128.0 (2C), 127.2, 125.0, 123.6, 122.5, 121.4, 116.4, 114.8, 111.6, 61.1, 40.5, 21.8, 14.2; ESI-HRMS *m/z* calcd for $C_{27}H_{24}NO_5S$ $[M + H]^+$ 474.1370, found 474.1373.



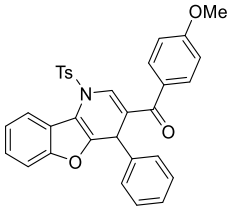
tert-Butyl 4-phenyl-1-tosyl-1,4-dihydrobenzofuro[3,2-*b*]pyridine-3-carboxylate. Compound **3n** (64 mg, Yield = 64%, R_f = 0.53 (PE/EA = 5:1)) was isolated as a yellow solid; mp 169–170 °C. ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.41–8.36 (m, 1H), 8.02 (s, 1H), 7.61 (d, J = 8.4 Hz, 2H), 7.35–7.24 (m, 5H), 7.14–7.08 (m, 1H), 7.01 (t, J = 8.0 Hz, 2H), 6.53 (d, J = 6.8 Hz, 2H), 5.10 (s, 1H), 2.45 (s, 3H), 1.34 (s, 9H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 164.6, 154.4, 146.9, 145.2, 140.8, 134.7, 132.8, 130.3, 128.1, 128.0, 127.9, 127.1, 124.9, 123.6, 122.5, 121.5, 117.8, 114.7, 111.6, 81.6, 40.8, 28.1, 21.8; ESI-HRMS *m/z* calcd for $C_{29}H_{27}NO_5SNa$ $[M + Na]^+$ 524.1502, found 524.1506.



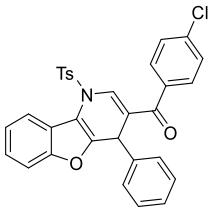
Methyl 1-(methylsulfonyl)-4-phenyl-1,4-dihydrobenzofuro[3,2-*b*]pyridine-3-carboxylate. Compound **3p** (65 mg, Yield = 84%, R_f = 0.32 (PE/EA = 5:1)) was isolated as a yellow solid; mp 201–202 °C. ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.19–8.14 (m, 1H), 8.13 (s, 1H), 7.41–7.38 (m, 1H), 7.34–7.28 (m, 6H), 7.27–7.21 (m, 1H), 5.36 (s, 1H), 3.70 (s, 3H), 3.24 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 166.0, 154.3, 144.8, 141.3, 134.4, 128.8, 128.0, 127.6, 125.2, 123.8, 121.4, 119.6, 114.2, 112.4, 112.1, 52.1, 40.3 (2C); ESI-HRMS *m/z* calcd for $C_{20}H_{17}NO_5SNa$ $[M + Na]^+$ 406.0720, found 406.0717.



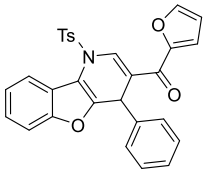
Phenyl(4-phenyl-1-tosyl-1,4-dihydrobenzofuro[3,2-*b*]pyridin-3-yl)methanone. Compound **3q** (55 mg, Yield = 54%, R_f = 0.40 (PE/EA = 5:1)) was isolated as a yellow solid; mp 164–165 °C. ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.45–8.39 (m, 1H), 7.69–7.62 (m, 3H), 7.60–7.54 (m, 3H), 7.51–7.45 (m, 2H), 7.41–7.30 (m, 5H), 7.11 (t, J = 7.6 Hz, 1H), 7.03 (t, J = 7.6 Hz, 2H), 6.66 (d, J = 7.2 Hz, 2H), 5.54 (s, 1H), 2.49 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 194.3, 154.4, 146.8, 145.6, 140.2, 138.0, 137.7, 132.9, 132.4, 130.4, 128.8, 128.6, 128.4, 128.0, 127.9, 127.2, 125.1, 124.6, 123.7, 122.4, 121.3, 114.9, 111.7, 40.1, 21.8; ESI-HRMS *m/z* calcd for $C_{31}H_{24}NO_4S$ $[M + H]^+$ 506.1421, found 506.1424.



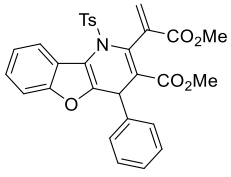
(4-Methoxyphenyl)(4-phenyl-1-tosyl-1,4-dihydrobenzofuro[3,2-*b*]pyridin-3-yl)methanone. Compound **3r** (87 mg, Yield = 81%, R_f = 0.34 (PE/EA = 5:1)) was isolated as a yellow solid; mp 191–192 °C. ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.43–8.38 (m, 1H), 7.67–7.62 (m, 3H), 7.60 (d, *J* = 8.8 Hz, 2H), 7.39–7.29 (m, 5H), 7.12–7.06 (m, 1H), 7.05–6.99 (m, 2H), 6.96 (d, *J* = 8.8 Hz, 2H), 6.67–6.62 (m, 2H), 5.53 (s, 1H), 3.88 (s, 3H), 2.48 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 193.0, 163.2, 154.4, 146.8, 145.6, 140.2, 136.1, 132.9, 131.3, 130.4, 130.3, 128.4, 128.0, 127.9, 127.2, 125.0, 124.7, 123.7, 122.4, 121.7, 115.0, 113.9, 111.7, 55.6, 40.4, 21.8; ESI-HRMS *m/z* calcd for $C_{32}H_{26}NO_5S$ $[M + H]^+$ 536.1526, found 536.1528.



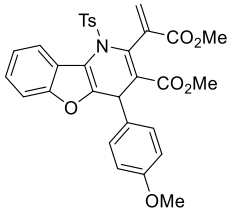
(4-Chlorophenyl)(4-phenyl-1-tosyl-1,4-dihydrobenzofuro[3,2-*b*]pyridin-3-yl)methanone. Compound **3s** (50 mg, Yield = 46%, R_f = 0.61 (PE/EA = 5:1)) was isolated as a yellow solid; mp 208–209 °C. ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.40 (dd, *J* = 7.2, 2.0 Hz, 1H), 7.64 (s, 1H), 7.63 (d, *J* = 8.0 Hz, 2H), 7.54–7.43 (m, 4H), 7.40–7.30 (m, 5H), 7.14–7.07 (m, 1H), 7.02 (t, *J* = 8.0 Hz, 2H), 6.64 (d, *J* = 7.2 Hz, 2H), 5.49 (s, 1H), 2.49 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 193.0, 154.4, 146.6, 145.8, 140.1, 138.8, 137.7, 136.3, 132.9, 130.4, 130.2, 129.0, 128.5, 128.0, 127.9, 127.3, 125.2, 124.3, 123.8, 122.4, 121.2, 114.9, 111.8, 40.1, 21.9; ESI-HRMS *m/z* calcd for $C_{31}H_{23}ClNO_4S$ $[M + H]^+$ 540.1031, found 540.1033.



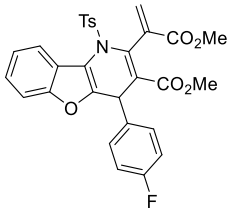
Furan-2-yl(4-phenyl-1-tosyl-1,4-dihydrobenzofuro[3,2-*b*]pyridin-3-yl)methanone. Compound **3t** (59 mg, Yield = 60%, R_f = 0.53 (PE/EA = 5:1)) was isolated as a yellow oil. ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.48 (s, 1H), 8.44–8.40 (m, 1H), 7.71–7.66 (m, 3H), 7.38–7.26 (m, 5H), 7.20 (dd, *J* = 4.0, 0.8 Hz, 1H), 7.10–7.05 (m, 1H), 7.02–6.96 (m, 2H), 6.63–6.59 (m, 2H), 6.57 (dd, *J* = 3.6, 1.6 Hz, 1H), 5.48 (s, 1H), 2.45 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 179.0, 154.3, 152.4, 146.8, 146.4, 145.5, 140.2, 137.0, 132.8, 130.4, 128.3, 128.0 (2C), 127.1, 125.0, 123.7, 123.5, 122.4, 121.3, 119.0, 114.6, 112.4, 111.7, 39.9, 21.8; ESI-HRMS *m/z* calcd for $C_{29}H_{22}NO_5S$ $[M + H]^+$ 496.1213, found 496.1216.



Methyl
2-(3-methoxy-3-oxoprop-1-en-2-yl)-4-phenyl-1-tosyl-1,4-dihydrobenzofuro[3,2-*b*]pyridine-3-carboxyl ate. Compound **4a** (88 mg, Yield = 81%, R_f = 0.48 (PE/EA = 3:1)) was isolated as a yellow oil. ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.20–8.15 (m, 1H), 7.46–7.40 (m, 1H), 7.39–7.30 (m, 4H), 7.15–7.04 (m, 3H), 6.96–6.84 (m, 4H), 6.66 (s, 1H), 6.09 (s, 1H), 5.08 (br s, 1H), 3.94 (s, 3H), 3.53 (s, 3H), 2.25 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 165.9, 165.6, 154.8, 149.4, 144.9, 140.0, 139.5, 131.9, 129.3, 129.1, 128.7, 128.4, 127.2, 126.3, 124.8, 123.6, 123.4, 122.1, 117.4, 111.6, 52.3, 52.2, 41.0, 21.7, (2C peaks are merged with other peaks); HRMS (ESI) *m*/*z*: $[M + Na]^+$ calcd for $C_{30}H_{25}NO_7SNa$ 566.1244, found 566.1245.

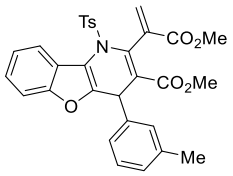


Methyl
2-(3-methoxy-3-oxoprop-1-en-2-yl)-4-(4-methoxyphenyl)-1-tosyl-1,4-dihydrobenzofuro[3,2-*b*]pyridin e-3-carboxylate. Compound **4b** (89 mg, Yield = 78%, R_f = 0.39 (PE/EA = 3:1)) was isolated as a yellow oil. ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.19–8.14 (m, 1H), 7.45–7.40 (m, 1H), 7.39–7.29 (m, 4H), 6.95 (d, J = 8.0 Hz, 2H), 6.82 (d, J = 8.5 Hz, 2H), 6.67–6.56 (m, 3H), 6.08 (s, 1H), 4.95 (br s, 1H), 3.93 (s, 3H), 3.75 (s, 3H), 3.52 (s, 3H), 2.28 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 165.9, 165.6, 158.2, 154.7, 149.6, 145.0, 139.4, 132.3, 131.8, 129.3, 129.1, 128.7, 128.4, 124.7, 123.6, 123.4, 122.1, 117.2, 113.8, 111.6, 55.2, 52.3, 52.1, 40.4, 21.6, (2C peaks are merged with other peaks); HRMS (ESI) *m*/*z*: $[M + Na]^+$ calcd for $C_{31}H_{27}NO_8SNa$ 596.1350, found 596.1351.

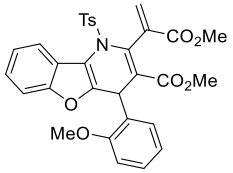


Methyl
4-(4-fluorophenyl)-2-(3-methoxy-3-oxoprop-1-en-2-yl)-1-tosyl-1,4-dihydrobenzofuro[3,2-*b*]pyridine-3 -carboxylate. Compound **4c** (101 mg, Yield = 90%, R_f = 0.56 (PE/EA = 3:1)) was isolated as a yellow oil. ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.20–8.14 (m, 1H), 7.48–7.42 (m, 1H), 7.39–7.28 (m, 4H), 6.94–6.85 (m, 4H), 6.75 (t, J = 8.4 Hz, 2H), 6.66 (s, 1H), 6.08 (s, 1H), 5.10 (br s, 1H), 3.94 (s, 3H), 3.55 (s, 3H), 2.26 (s, 3H); ^{13}C{^{1}H} NMR (100 MHz, $CDCl_3$) δ 165.8, 165.6, 161.4 (d, $^1J_{C\text{-}F}$ = 243.7 Hz), 154.9, 149.2, 145.1, 139.4, 136.3, 132.1, 129.2, 129.1, 128.7, 124.9, 123.7, 123.3, 122.2, 117.5, 115.2 (d, $^2J_{C\text{-}F}$ = 21.3 Hz), 111.6, 52.4, 52.2, 40.2, 21.6, (3C peaks are merged with other peaks); ^{19}F{^{1}H} NMR (376 MHz, $CDCl_3$): δ –116.4 (s, 1F); HRMS (ESI) *m*/*z*: $[M + Na]^+$ calcd for $C_{30}H_{24}FNO_7SNa$

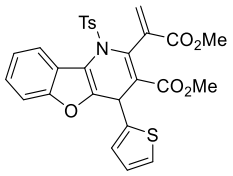
584.1150, found 584.1153.



Methyl
2-(3-methoxy-3-oxoprop-1-en-2-yl)-4-(*m*-tolyl)-1-tosyl-1,4-dihydrobenzofuro[3,2-*b*]pyridine-3-carboxylate. Compound **4d** (97 mg, Yield = 87%, R_f = 0.53 (PE/EA = 3:1)) was isolated as a yellow oil. ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.19–8.14 (m, 1H), 7.47–7.42 (m, 1H), 7.39–7.30 (m, 4H), 7.00–6.82 (m, 5H), 6.69–6.63 (m, 2H), 6.10 (s, 1H), 4.99 (br s, 1H), 3.94 (s, 3H), 3.53 (s, 3H), 2.26 (s, 3H), 2.25 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 165.9, 165.5, 154.8, 149.6, 144.7, 140.0, 139.4, 137.7, 131.9, 129.3, 129.2, 128.6, 128.4, 128.1, 127.3, 124.7, 124.2, 123.6, 123.4, 122.0, 117.4, 111.7, 52.3, 52.1, 40.8, 21.7, 21.6, (2C peaks are merged with other peaks); HRMS (ESI) *m*/*z*: $[M + Na]^+$ calcd for $C_{31}H_{27}NO_7SNa$ 580.1400, found 580.1401.

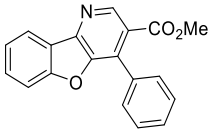


Methyl
2-(3-methoxy-3-oxoprop-1-en-2-yl)-4-(2-methoxyphenyl)-1-tosyl-1,4-dihydrobenzofuro[3,2-*b*]pyridine-3-carboxylate. Compound **4e** (108 mg, Yield = 94%, R_f = 0.36 (PE/EA = 3:1)) was isolated as a yellow oil. ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.11 (d, *J* = 8.0 Hz, 1H), 7.48 (d, *J* = 8.4 Hz, 2H), 7.37–7.25 (m, 3H), 7.19–7.09 (m, 3H), 6.80 (d, *J* = 8.0 Hz, 1H), 6.65–6.48 (m, 3H), 6.14 (s, 1H), 4.96 (br s, 1H), 3.88 (s, 3H), 3.79 (s, 3H), 3.38 (s, 3H), 2.39 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 166.0, 165.5, 157.0, 154.4, 149.8, 145.1, 138.9, 131.4, 129.5, 129.3, 129.0, 128.8, 128.4, 127.4, 124.5, 123.3, 123.4, 121.8, 120.8, 117.4, 111.6, 111.0, 56.0, 52.3, 51.8, 35.7, 21.8, (2C peaks are merged with other peaks); HRMS (ESI) *m*/*z*: $[M + Na]^+$ calcd for $C_{31}H_{27}NO_8SNa$ 596.1350, found 596.1350.

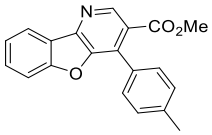


Methyl
2-(3-methoxy-3-oxoprop-1-en-2-yl)-4-(thiophen-2-yl)-1-tosyl-1,4-dihydrobenzofuro[3,2-*b*]pyridine-3-carboxylate. Compound **4f** (90s mg, Yield = 82%, R_f = 0.52 (PE/EA = 3:1)) was isolated as a yellow oil. ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.23–8.16 (m, 1H), 7.49–7.44 (m, 1H), 7.40–7.30 (m, 4H), 7.02 (d, *J* =

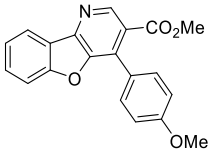
4.8 Hz, 1H), 6.87 (d, *J* = 8.0 Hz, 2H), 6.65 (s, 1H), 6.62–6.56 (m, 1H), 6.18 (s, 1H), 6.03 (s, 1H), 5.40 (s, 1H), 3.93 (s, 3H), 3.65 (s, 3H), 2.25 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 165.5, 165.4, 154.8, 148.2, 144.8, 143.6, 139.5, 132.1, 129.3, 129.1, 128.5, 126.5, 125.0, 124.6, 124.1, 123.7, 123.2, 122.2, 117.7, 111.8, 52.3, 36.5, 21.7, (3C peaks are merged with other peaks); HRMS (ESI) *m/z*: $[M + Na]^+$ calcd for $C_{28}H_{23}NO_7S_2Na$ 572.0808, found 572.0811.



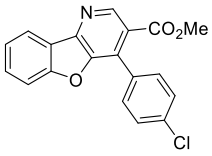
Methyl 4-phenylbenzofuro[3,2-*b*]pyridine-3-carboxylate. Compound **5a** (34 mg, Yield = 94%, R_f = 0.41 (PE/EA = 5:1)) was isolated as a yellow solid; mp 170–171 °C. ^{1}H NMR (400 MHz, $CDCl_3$) δ 9.14 (s, 1H), 8.29 (d, *J* = 8.0 Hz, 1H), 7.62–7.44 (m, 8H), 3.75 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 167.1, 158.8, 147.4 (2C), 146.9, 134.2, 132.7, 130.4, 129.3, 129.1, 128.4, 124.1, 123.8, 123.0, 122.0, 112.7, 52.5; ESI-HRMS *m/z* calcd for $C_{19}H_{14}NO_3$ $[M + H]^+$ 304.0968, found 304.0967.



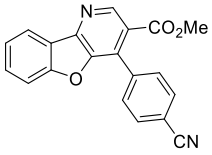
Methyl 4-(*p*-tolyl)benzofuro[3,2-*b*]pyridine-3-carboxylate. Compound **5b** (34 mg, Yield = 89%, R_f = 0.36 (PE/EA = 5:1)) was isolated as a white solid; mp 140–141 °C. ^{1}H NMR (400 MHz, $CDCl_3$) δ 9.12 (s, 1H), 8.28 (d, *J* = 7.6 Hz, 1H), 7.63–7.55 (m, 2H), 7.49–7.40 (m, 3H), 7.36 (d, *J* = 8.0 Hz, 2H), 3.78 (s, 3H), 2.47 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 167.2, 158.7, 147.5, 147.3, 146.7, 139.2, 134.3, 130.4, 129.5, 129.3, 129.2, 124.1, 123.7, 123.0, 122.0, 112.6, 52.5, 21.6; ESI-HRMS *m/z* calcd for $C_{20}H_{16}NO_3$ $[M + H]^+$ 318.1125, found 318.1125.



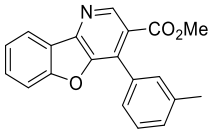
Methyl 4-(4-methoxyphenyl)benzofuro[3,2-*b*]pyridine-3-carboxylate. Compound **5c** (37 mg, Yield = 92%, R_f = 0.28 (PE/EA = 5:1)) was isolated as a yellow solid; mp 128–129 °C. ^{1}H NMR (400 MHz, $CDCl_3$) δ 9.09 (s, 1H), 8.28 (d, *J* = 8.0 Hz, 1H), 7.63–7.56 (m, 2H), 7.54–7.44 (m, 3H), 7.07 (d, *J* = 8.8 Hz, 2H), 3.90 (s, 3H), 3.78 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 167.4, 160.3, 158.7, 147.5, 147.3, 146.6, 133.9, 130.8, 130.3, 124.5, 124.0, 123.7, 123.0, 122.0, 114.0, 112.6, 55.4, 52.5; ESI-HRMS *m/z* calcd for $C_{20}H_{16}NO_4$ $[M + H]^+$ 334.1074, found 334.1075.



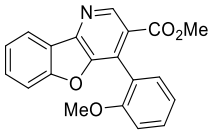
Methyl 4-(4-chlorophenyl)benzofuro[3,2-*b*]pyridine-3-carboxylate. Compound **5d** (38 mg, Yield = 94%, R_f = 0.41 (PE/EA = 5:1)) was isolated as a white solid; mp 130–131 °C. ^{1}H NMR (400 MHz, $CDCl_3$) δ 9.15 (s, 1H), 8.27 (d, *J* = 8.0 Hz, 1H), 7.64–7.43 (m, 7H), 3.78 (s, 1H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 166.7, 158.8, 147.5, 147.2, 147.0, 135.2, 133.0, 131.0, 130.6 (2C), 128.8, 124.2, 123.2, 122.8, 122.0, 112.6, 52.6; ESI-HRMS *m/z* calcd for $C_{19}H_{13}ClNO_3$ $[M + H]^+$ 338.0578, found 338.0579.



Methyl 4-(4-cyanophenyl)benzofuro[3,2-*b*]pyridine-3-carboxylate. Compound **5e** (35 mg, Yield = 90%, R_f = 0.21 (PE/EA = 5:1)) was isolated as a white solid; mp 197–198 °C. ^{1}H NMR (400 MHz, $CDCl_3$) δ 9.24 (s, 1H), 8.29 (d, *J* = 7.6 Hz, 1H), 7.84 (d, *J* = 8.0 Hz, 2H), 7.67–7.58 (m, 3H), 7.56 (d, *J* = 8.1 Hz, 1H), 7.49 (t, *J* = 7.4 Hz, 1H), 3.79 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 166.2, 158.9, 147.8, 147.5, 147.0, 137.7, 132.3, 132.1, 131.0, 130.1, 124.5, 122.6, 122.5, 122.2, 118.7, 112.8, 112.6, 52.7; ESI-HRMS *m/z* calcd for $C_{20}H_{13}N_2O_3$ $[M + H]^+$ 329.0921, found 329.0920.

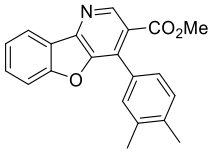


Methyl 4-(*m*-tolyl)benzofuro[3,2-*b*]pyridine-3-carboxylate. Compound **5f** (30 mg, Yield = 79%, R_f = 0.39 (PE/EA = 5:1)) was isolated as a yellow solid; mp 145–146 °C. ^{1}H NMR (400 MHz, $CDCl_3$) δ 9.13 (s, 1H), 8.29 (d, *J* = 7.6 Hz, 1H), 7.63–7.56 (m, 2H), 7.50–7.41 (m, 2H), 7.36–7.29 (m, 3H), 3.76 (s, 3H), 2.47 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 167.2, 158.8, 147.5, 147.2, 146.7, 138.1, 134.3, 132.6, 130.4, 129.9, 129.8, 128.4, 126.3, 124.1, 123.9, 123.0, 122.0, 112.7, 52.5, 21.7; ESI-HRMS *m/z* calcd for $C_{20}H_{16}NO_3$ $[M + H]^+$ 318.1125, found 318.1125.

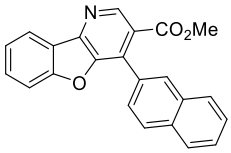


Methyl 4-(2-methoxyphenyl)benzofuro[3,2-*b*]pyridine-3-carboxylate. Compound **5g** (38 mg, Yield = 95%, R_f = 0.30 (PE/EA = 5:1)) was isolated as a yellow solid; mp 141–142 °C. ^{1}H NMR (400 MHz, $CDCl_3$) δ 9.16 (s, 1H), 8.28 (d, *J* = 7.6 Hz, 1H), 7.62–7.42 (m, 5H), 7.16 (t, *J* = 7.2 Hz, 1H), 7.04 (d, *J* = 8.0 Hz, 1H), 3.75 (s, 3H), 3.74 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 166.9, 158.6, 156.4, 147.7,

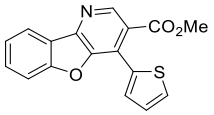
147.0, 146.9, 130.8, 130.7, 130.6, 130.2, 124.5, 123.9, 123.1, 121.9, 121.6, 120.7, 112.6, 110.8, 55.5, 52.2; ESI-HRMS *m/z* calcd for $C_{20}H_{16}NO_4$ $[M + H]^+$ 334.1074, found 334.1073.



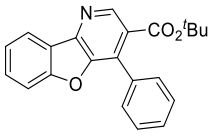
Methyl 4-(3,4-dimethylphenyl)benzofuro[3,2-*b*]pyridine-3-carboxylate. Compound **5h** (36 mg, Yield = 90%, R_f = 0.28 (PE/EA = 10:1)) was isolated as a yellow solid; mp 133–134 °C. ^{1}H NMR (400 MHz, $CDCl_3$) δ 9.10 (s, 1H), 8.28 (d, J = 7.6 Hz, 1H), 7.62–7.56 (m, 2H), 7.50-7.42 (m, 1H), 7.34–7.24 (m, 3H), 3.78 (s, 3H), 2.37 (s, 6H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 167.2, 158.7, 147.5, 147.2, 146.6, 137.8, 136.8, 134.4, 130.3, 129.9, 129.8, 126.7, 124.0, 123.8, 123.0, 121.9, 112.7, 52.5, 20.0, 19.9, (1C peak is merged with other peaks); ESI-HRMS *m/z* calcd for $C_{21}H_{18}NO_3$ $[M + H]^+$ 332.1281, found 332.1283.



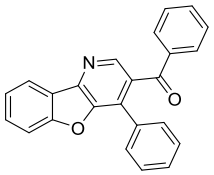
Methyl 4-(naphthalen-2-yl)benzofuro[3,2-*b*]pyridine-3-carboxylate. Compound **5i** (40 mg, Yield = 94%, R_f = 0.39 (PE/EA = 5:1)) was isolated as a yellow solid; mp 168–169 °C. ^{1}H NMR (400 MHz, $CDCl_3$) δ 9.20 (s, 1H), 8.32 (d, J = 7.6 Hz, 1H), 8.07 (d, J = 1.6 Hz, 1H), 8.00 (d, J = 8.4 Hz, 1H), 7.97–7.92 (m, 2H), 7.63–7.53 (m, 5H), 7.51–7.45 (m, 1H), 3.72 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 167.1, 158.8, 147.6, 147.5, 146.9, 134.2, 133.4, 133.1, 130.5, 130.1, 128.8, 128.6, 128.0, 127.0, 126.8, 126.7, 124.1, 123.8, 123.0, 122.0, 112.7, 52.5, (1C peak is merged with other peaks); ESI-HRMS *m/z* calcd for $C_{23}H_{16}NO_3$ $[M + H]^+$ 354.1125, found 354.1125.



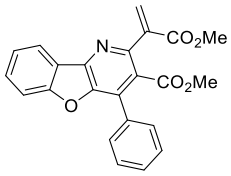
Methyl 4-(thiophen-2-yl)benzofuro[3,2-*b*]pyridine-3-carboxylate. Compound **5j** (36 mg, Yield = 97%, R_f = 0.33 (PE/EA = 5:1)) was isolated as a yellow solid; mp 145–146 °C. ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.99 (s, 1H), 8.26 (d, J = 7.6 Hz, 1H), 7.64–7.58 (m, 3H), 7.52 (dd, J = 3.6, 1.2 Hz, 1H), 7.49–7.44 (m, 1H), 7.24 (dd, J = 5.2, 3.6 Hz, 1H), 3.86 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 167.4, 158.6, 146.8, 146.7, 146.6, 132.1, 130.4, 130.3, 128.9, 127.6, 126.4, 124.2, 124.0, 122.9, 122.0, 112.6, 52.8; ESI-HRMS *m/z* calcd for $C_{17}H_{12}NO_3S$ $[M + H]^+$ 310.0532, found 310.0532.



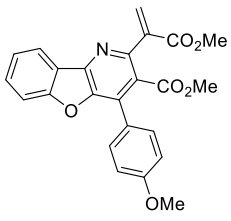
tert-Butyl 4-phenylbenzofuro[3,2-*b*]pyridine-3-carboxylate. Compound **5k** (37 mg, Yield = 90%, R_f = 0.45 (PE/EA = 10:1)) was isolated as a yellow solid; mp 120–121 °C. ^{1}H NMR (400 MHz, $CDCl_3$) δ 9.09 (s, 1H), 8.28 (d, J = 8.0 Hz, 1H), 7.61–7.42 (m, 8H), 1.30 (s, 9H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 166.0, 158.7, 147.4, 147.3, 146.2, 133.5, 133.3, 130.2, 129.4, 128.8, 128.4, 126.0, 124.0, 123.0, 121.9, 112.6, 82.4, 27.7; ESI-HRMS *m/z* calcd for $C_{22}H_{20}NO_3$ $[M + H]^+$ 346.1438, found 346.1437.



Phenyl(4-phenylbenzofuro[3,2-*b*]pyridin-3-yl)methanone. Compound **5l** (35 mg, Yield = 84%, R_f = 0.31 (PE/EA = 5:1)) was isolated as a yellow solid; mp 163–164 °C. ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.80 (s, 1H), 8.32 (d, J = 8.0 Hz, 1H), 7.71 (dd, J = 8.6, 1.6 Hz, 2H), 7.62 (d, J = 3.6 Hz, 2H), 7.56–7.43 (m, 4H), 7.38–7.28 (m, 5H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 196.1, 158.6, 147.0, 146.1, 145.8, 137.4, 133.5, 132.6, 132.2, 131.9, 130.2, 130.1, 130.0, 129.3, 128.7, 128.5, 124.2, 123.1, 121.9, 112.6; ESI-HRMS *m/z* calcd for $C_{24}H_{16}NO_2$ $[M + H]^+$ 350.1176, found 350.1177.

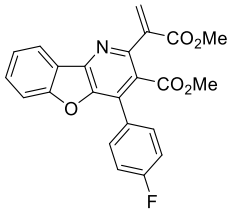


Methyl 2-(3-methoxy-3-oxoprop-1-en-2-yl)-4-phenylbenzofuro[3,2-*b*]pyridine-3-carboxylate. Compound **6a** (64 mg, Yield = 83%, R_f = 0.45 (PE/EA = 3:1)) was isolated as a yellow oil. ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.30 (dt, J = 7.6, 1.2 Hz, 1H), 7.62–7.41 (m, 8H), 6.72 (d, J = 1.4 Hz, 1H), 6.22 (d, J = 1.4 Hz, 1H), 3.79 (s, 3H), 3.56 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 168.1, 166.3, 158.7, 150.4, 146.6, 144.9, 140.9, 132.7, 132.6, 130.9, 130.2, 129.3, 129.1, 128.7, 125.9, 124.0, 122.9, 122.0, 112.5, 52.4, 52.3; HRMS (ESI) *m/z*: $[M + H]^+$ calcd for $C_{23}H_{18}NO_5$ 388.1179, found 388.1178.

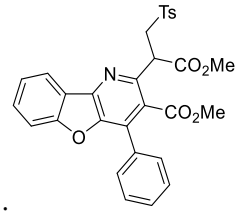


Methyl
2-(3-methoxy-3-oxoprop-1-en-2-yl)-4-(4-methoxyphenyl)benzofuro[3,2-*b*]pyridine-3-carboxylate. Compound **6b** (77 mg, Yield = 92%, R_f = 0.33 (PE/EA = 3:1)) was isolated as a yellow oil. ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.29 (dt, J = 8.0, 1.2 Hz, 1H), 7.60–7.52 (m, 4H), 7.48–7.40 (m, 1H), 7.09–7.03 (m, 2H), 6.70 (d, J = 1.2 Hz, 1H), 6.18 (d, J = 1.2 Hz, 1H), 3.89 (s, 3H), 3.78 (s, 3H), 3.61 (s, 3H); ^{13}C

NMR (100 MHz, $CDCl_3$) δ 168.3, 166.3, 160.4, 158.6, 150.4, 146.7, 144.7, 140.9, 132.3, 130.8, 130.6, 130.1, 125.8, 124.7, 124.0, 123.0, 122.0, 114.2, 112.5, 55.4, 52.5, 52.4; HRMS (ESI) *m*/*z*: $[M + H]^+$ calcd for $C_{24}H_{20}NO_6$ 418.1285, found 418.1283.



Methyl 4-(4-fluorophenyl)-2-(3-methoxy-3-oxoprop-1-en-2-yl)benzofuro[3,2-*b*]pyridine-3-carboxylate. Compound **6c** (75 mg, Yield = 92%, R_f = 0.49 (PE/EA = 3:1)) was isolated as a yellow oil. ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.28 (d, *J* = 8.0, 1H), 7.60–7.53 (m, 4H), 7.48–7.39 (m, 1H), 7.25–7.19 (m, 2H), 6.71 (s, 1H), 6.21 (s, 1H), 3.78 (s, 3H), 3.59 (s, 3H); ^{13}C{^{1}H} NMR (100 MHz, $CDCl_3$) δ 167.9, 166.2, 163.2 (d, $^1J_{C\text{-}F}$ = 248.2 Hz), 158.7, 150.5, 146.5, 144.9, 140.8, 131.5, 131.1 (d, $^3J_{C\text{-}F}$ = 8.4 Hz), 130.8, 130.3, 128.6 (d, $^4J_{C\text{-}F}$ = 3.5 Hz), 125.7, 124.1, 122.8, 122.1, 115.9 (d, $^2J_{C\text{-}F}$ = 21.8 Hz), 112.4, 52.4, 52.3; ^{19}F{^{1}H} NMR (376 MHz, $CDCl_3$): δ –111.7 (s, 1F); HRMS (ESI) *m*/*z*: $[M + H]^+$ calcd for $C_{23}H_{17}FNO_5$ 406.1085, found 406.1086.



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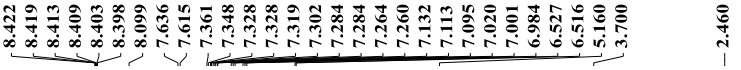
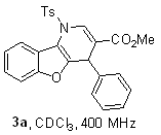
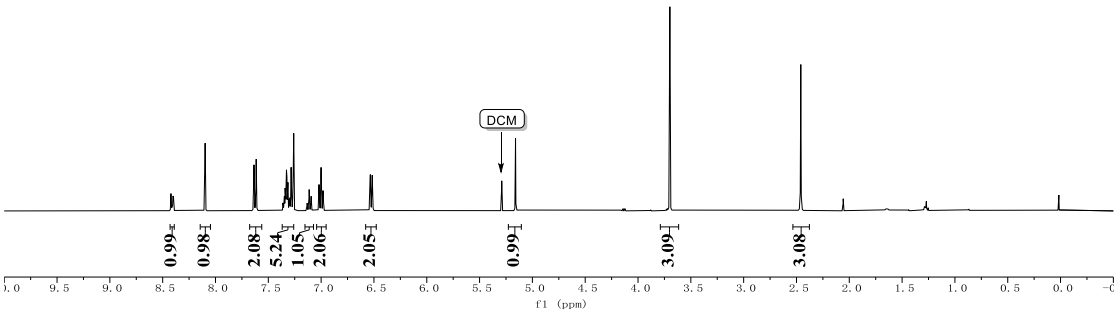
Methyl 2-(1-methoxy-1-oxo-3-tosylpropan-2-yl)-4-phenylbenzofuro[3,2-*b*]pyridine-3-carboxylate. Compound **7a** (15 mg, Yield = 14%, R_f = 0.35 (PE/EA = 3:1)) was isolated as a yellow solid; mp 163–164 ℃. ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.05 (d, *J* = 7.6 Hz, 1H), 7.61–7.50 (m, 9H), 7.48–7.42 (m, 1H), 6.86 (d, *J* = 7.6 Hz, 2H), 5.01 (dd, *J* = 8.8, 4.4 Hz, 1H), 4.55 (dd, *J* = 14.8, 8.8 Hz, 1H), 4.11 (dd, *J* = 14.8, 4.4 Hz, 1H), 3.67 (s, 3H), 3.65 (s, 3H), 1.86 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 170.4, 168.1, 158.6, 147.6, 145.9, 144.5, 144.1, 136.4, 132.6, 132.2, 130.2, 129.5, 129.1, 129.0, 128.9, 128.1, 126.9, 124.0, 122.6, 122.2, 112.4, 56.6, 53.1, 52.8, 45.3, 21.1; HRMS (ESI) *m*/*z*: $[M + Na]^+$ calcd for $C_{30}H_{25}NO_7SNa$ 566.1244, found 566.1245.

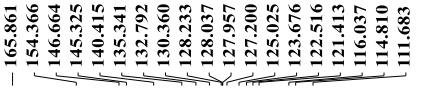
7. NMR Spectra

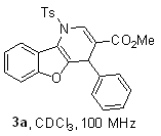




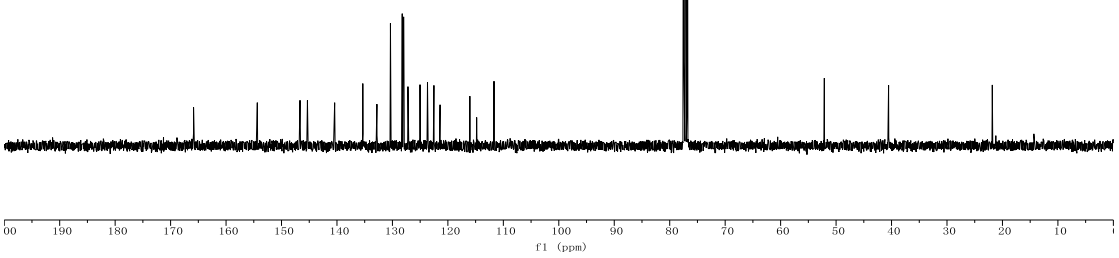
3a, $CDCl_3$, 400 MHz

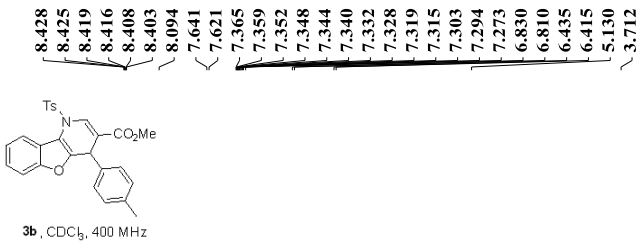




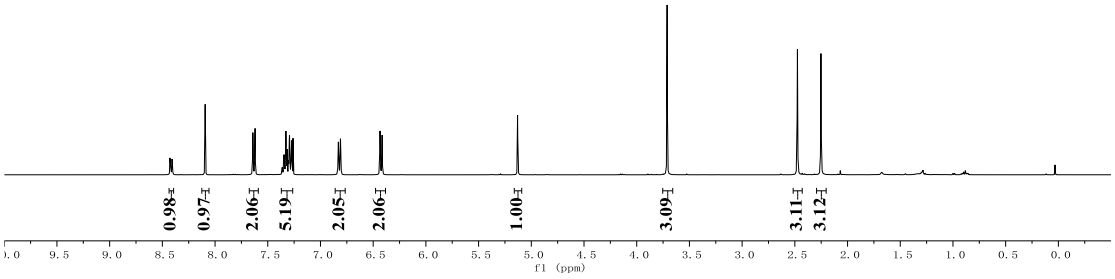


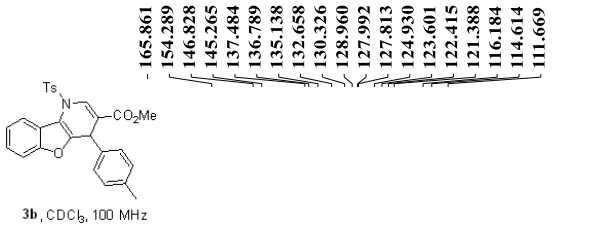
3a, $CDCl_3$, 100 MHz



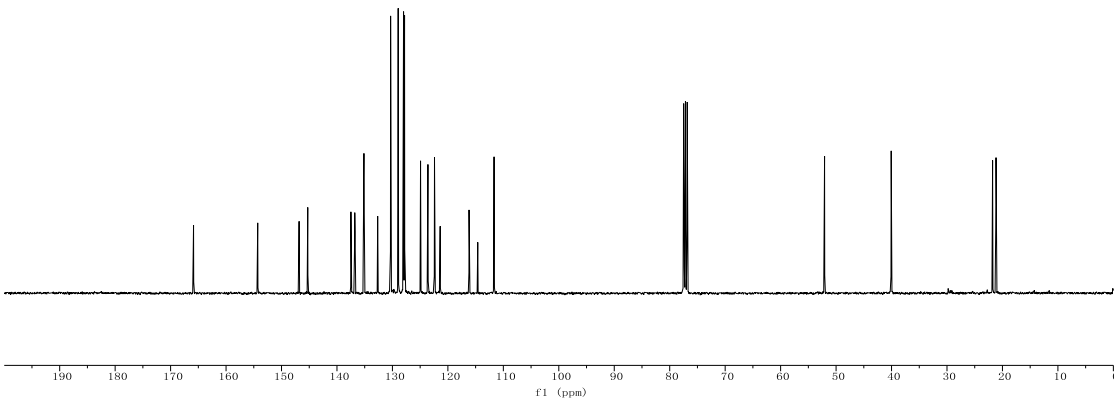


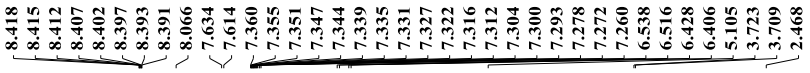
3b, $CDCl_3$, 400 MHz

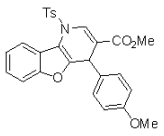




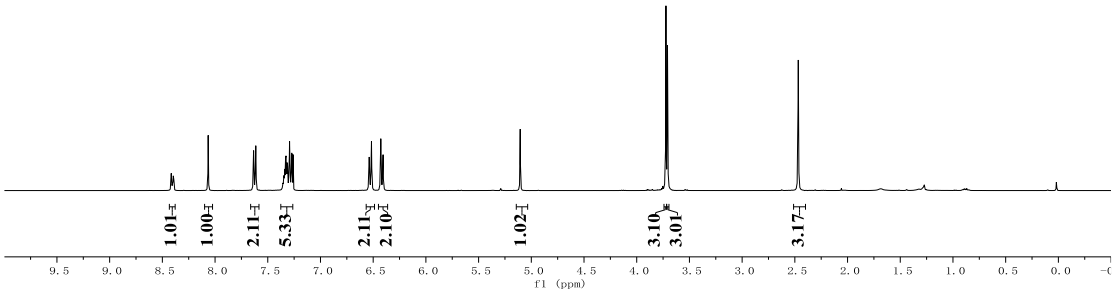
3b, $CDCl_3$, 100 MHz

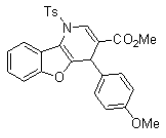




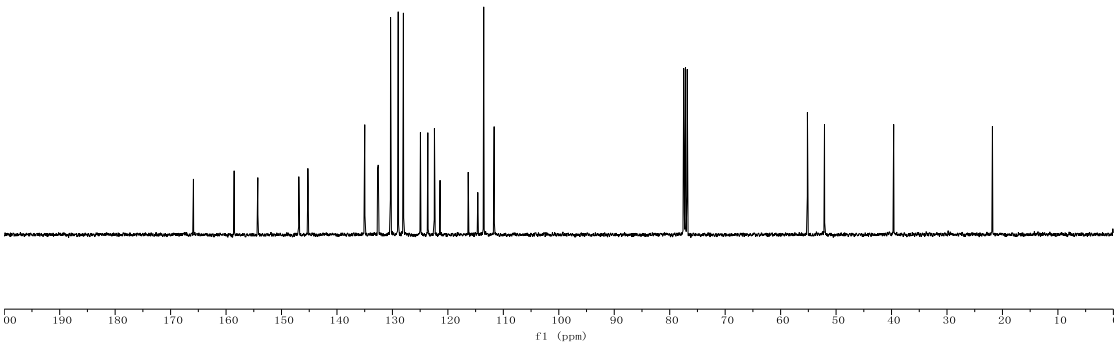


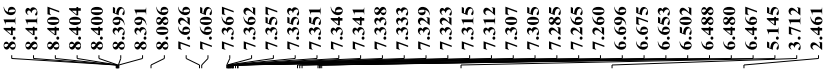
3c, $CDCl_3$, 400 MHz

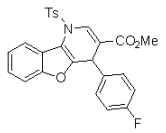




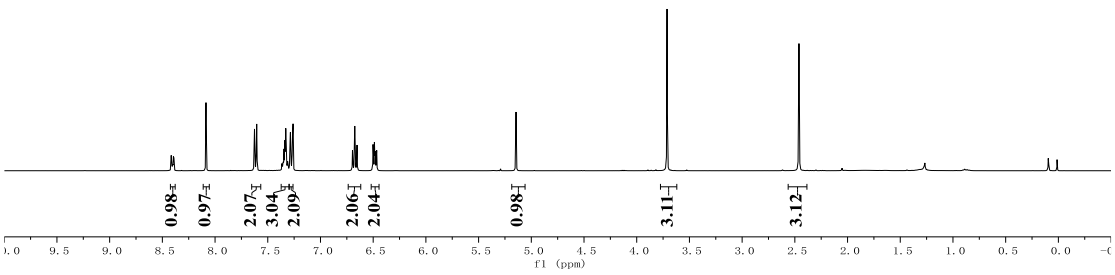
3c, $CDCl_3$, 100 MHz

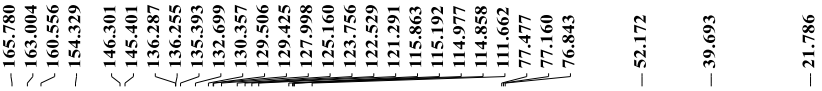


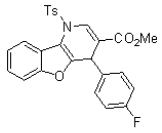




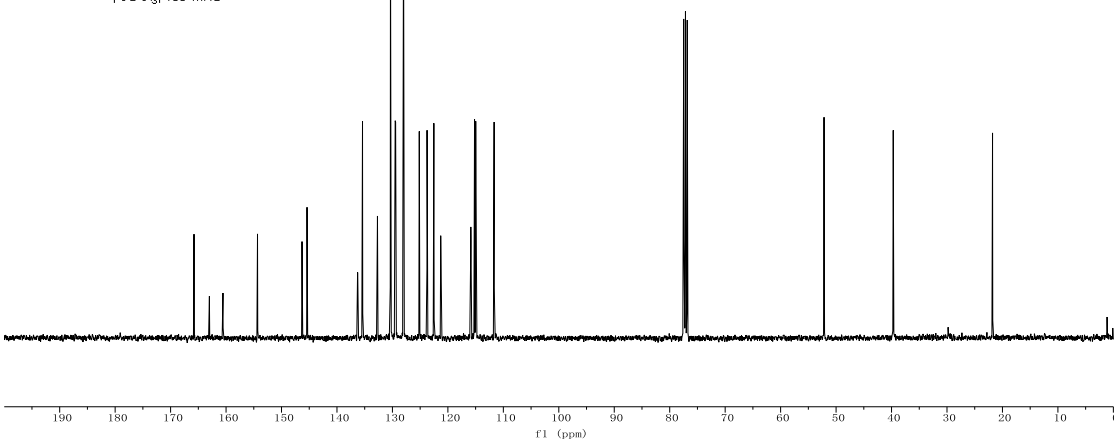
3d, $CDCl_3$, 400 MHz

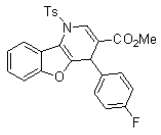




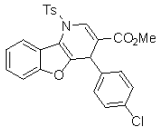


3d, $CDCl_3$, 100 MHz

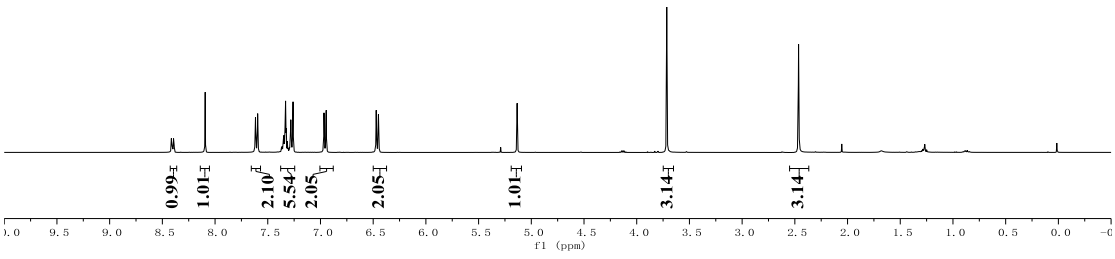


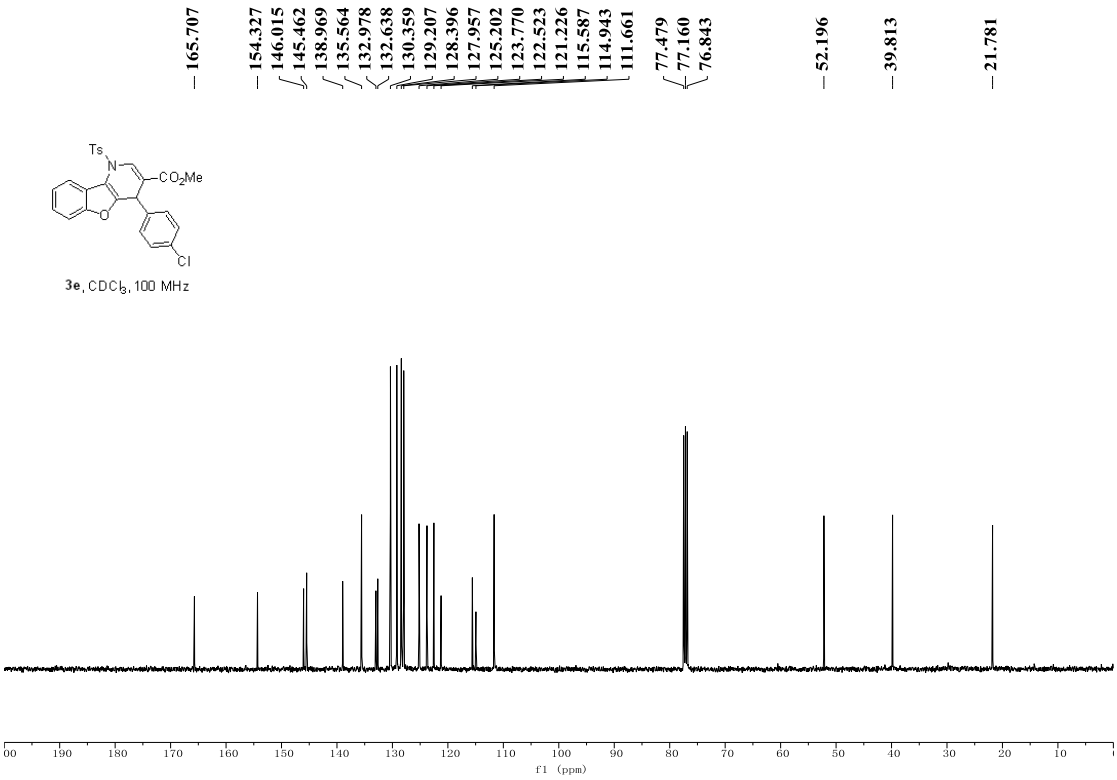


3d, $CDCl_3$, 376 MHz

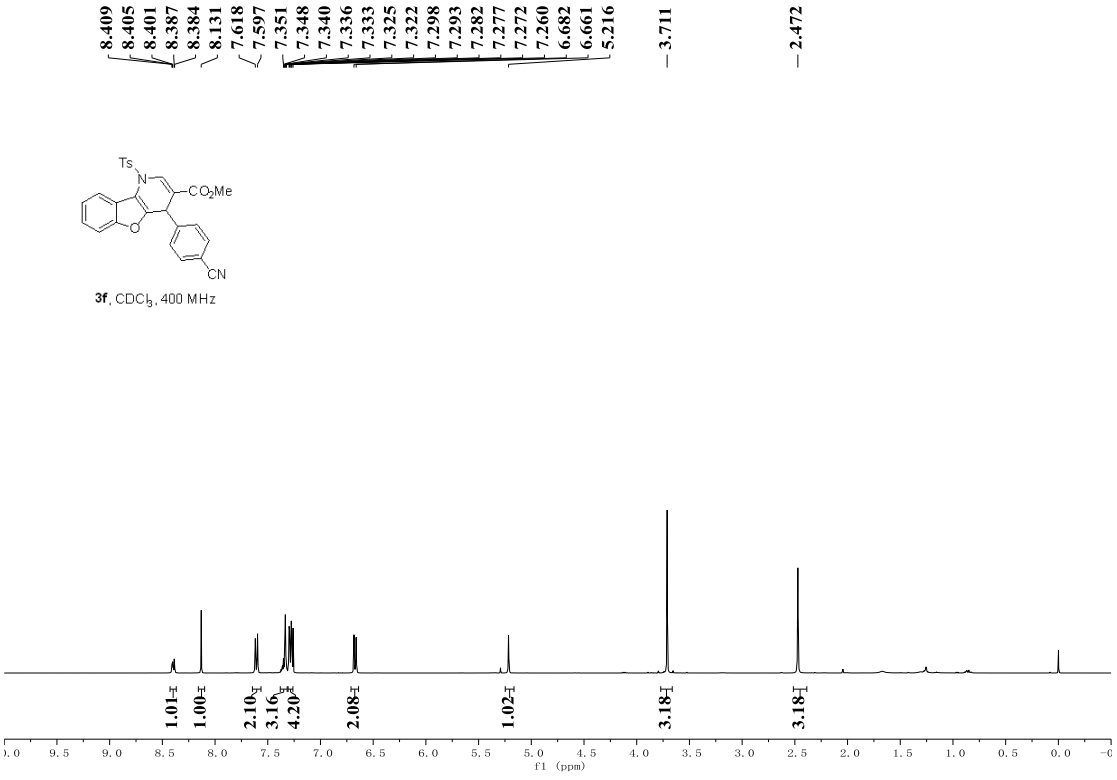


3e, $CDCl_3$, 400 MHz

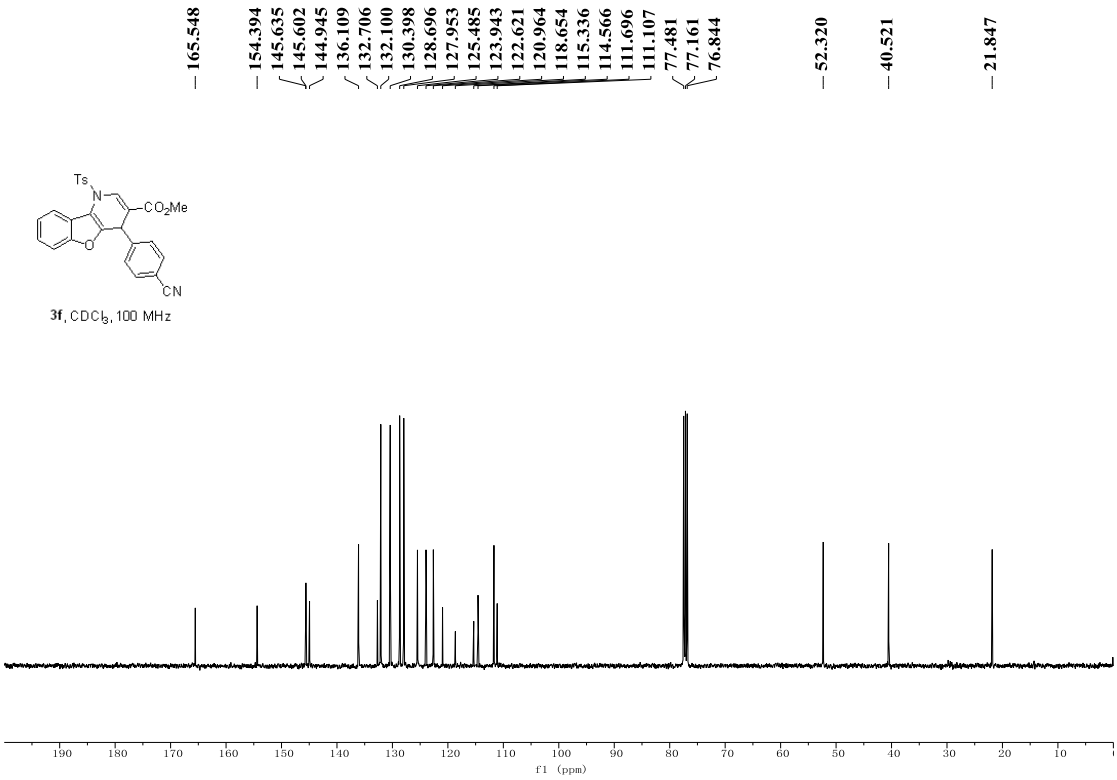




3e, $CDCl_3$, 100 MHz



3f, $CDCl_3$, 400 MHz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122.621
120.964
118.654
115.336
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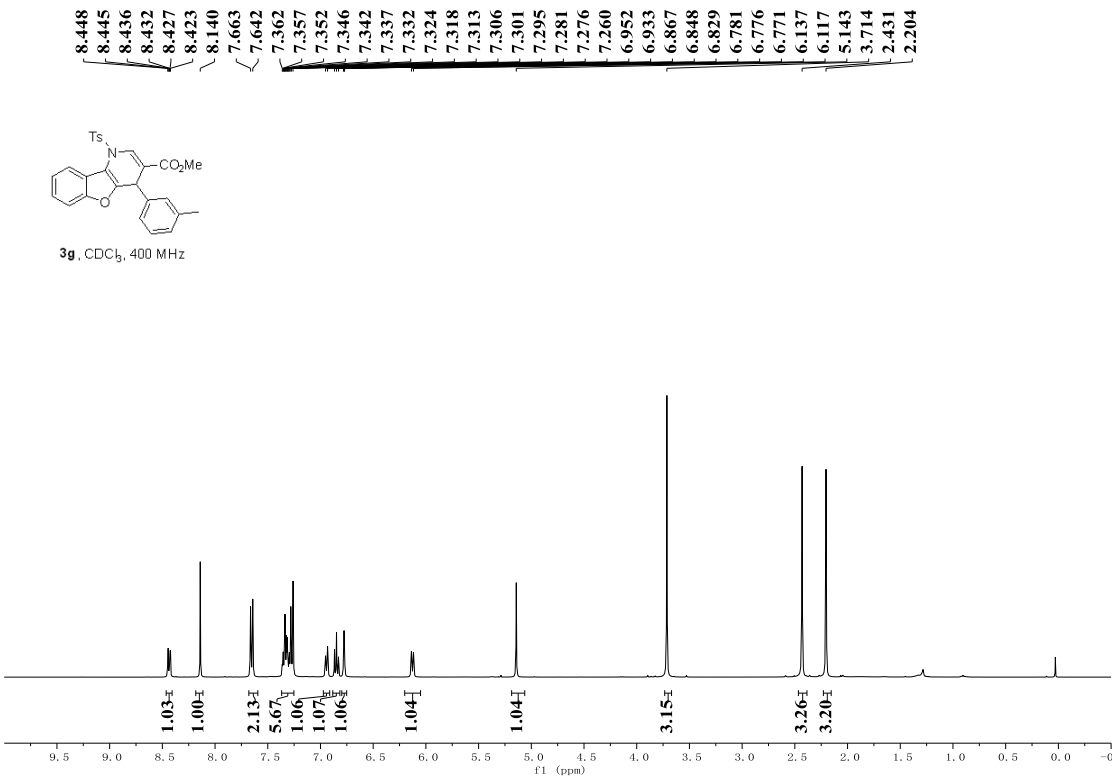
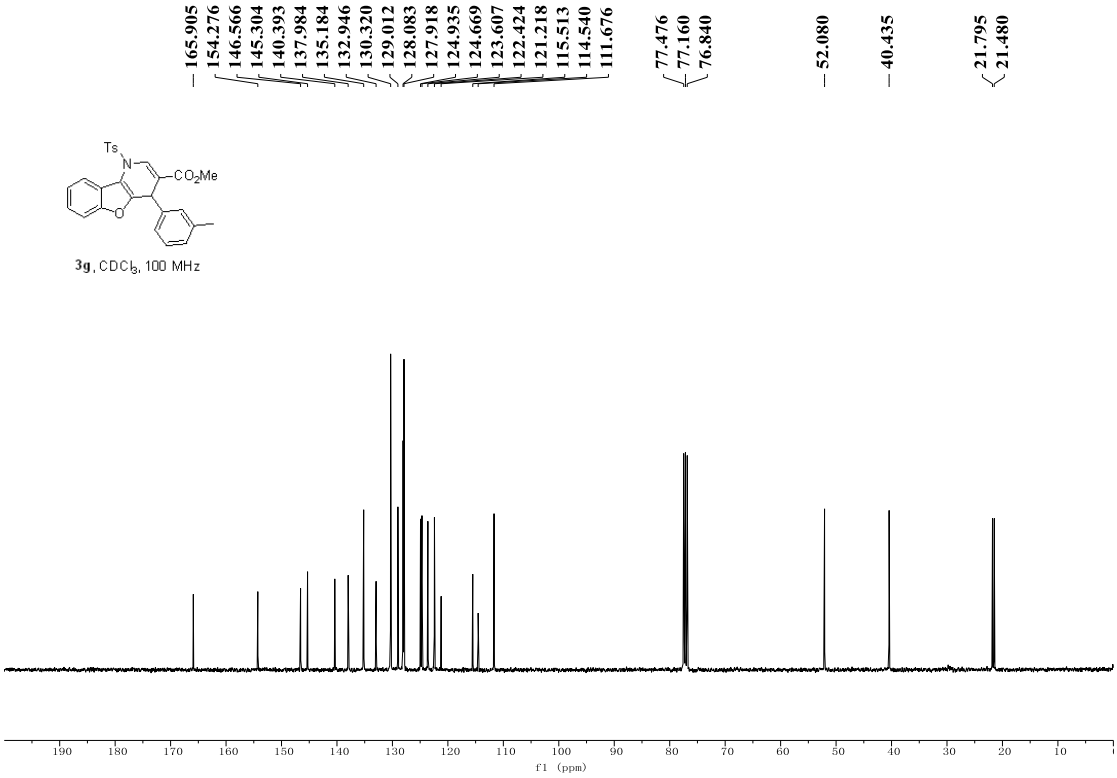
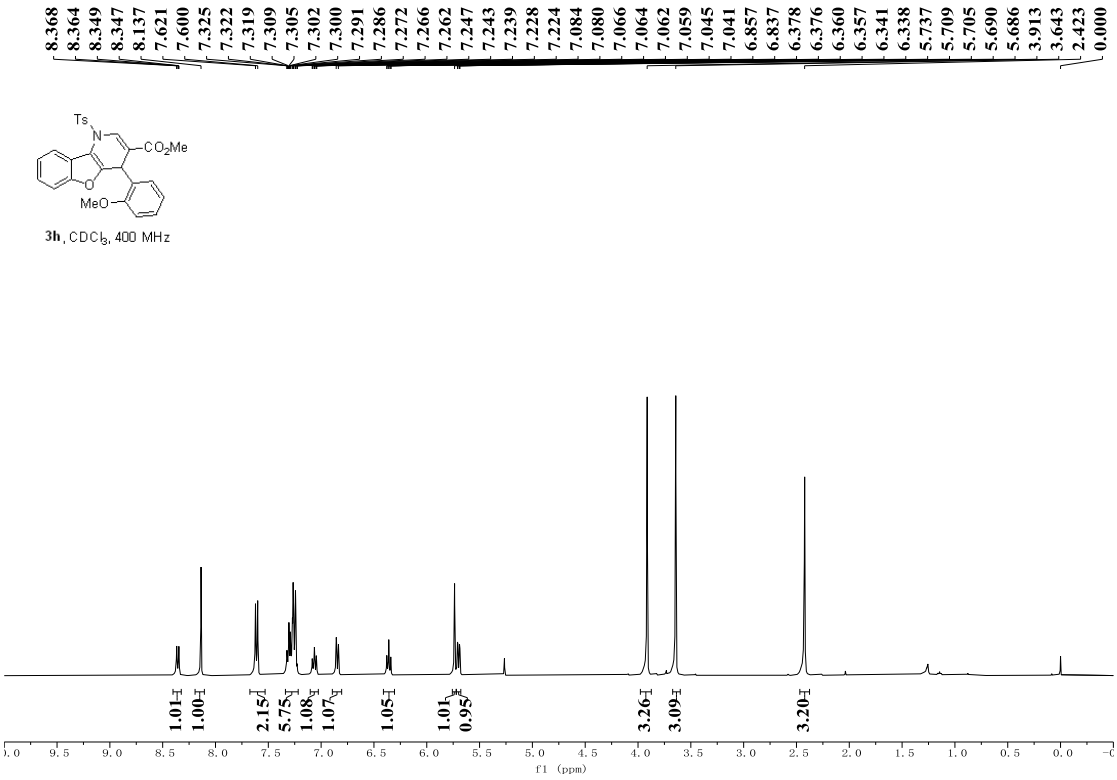
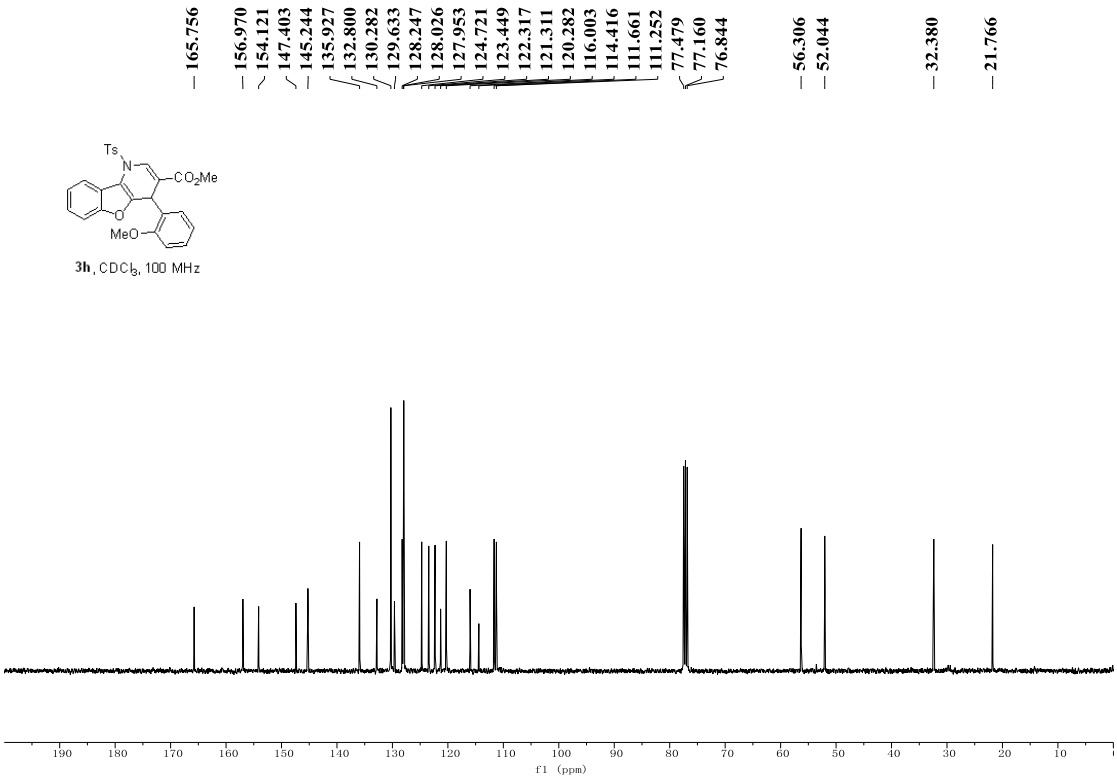
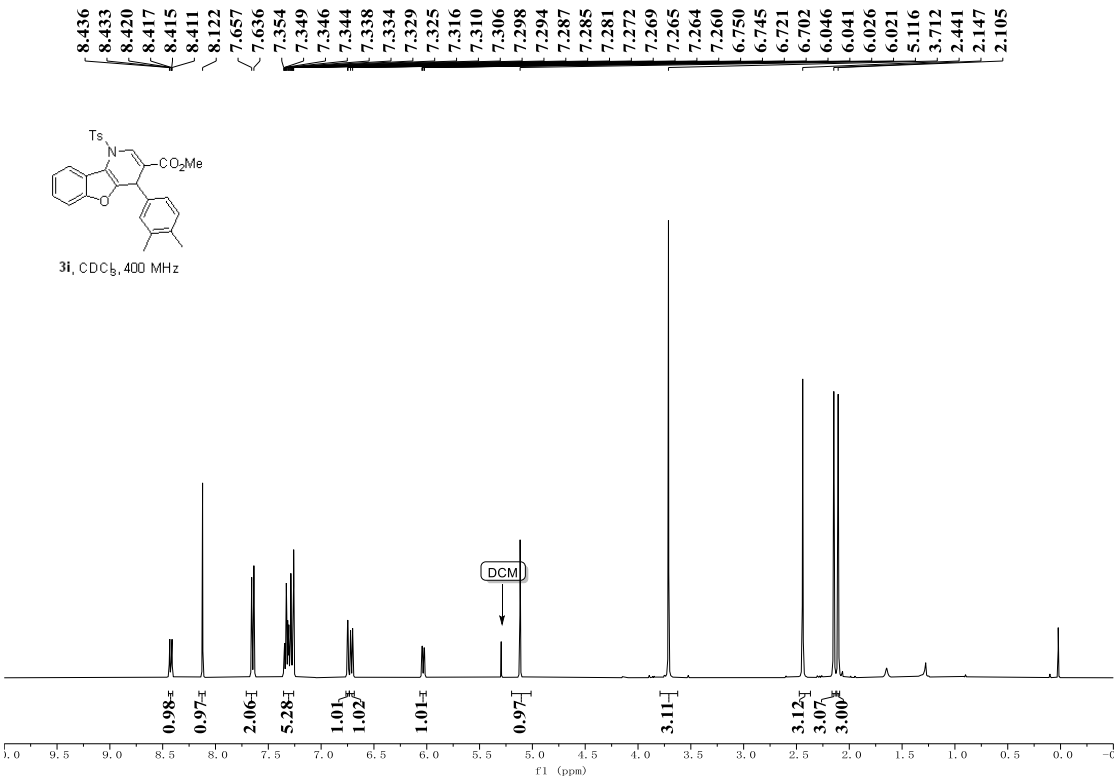
111.696
111.107
77.481
77.161
76.844
52.320
40.521
21.847
Ts
N
CO2Me
O
CN
3f, CDCl3, 100 MHz
f1 (ppm)

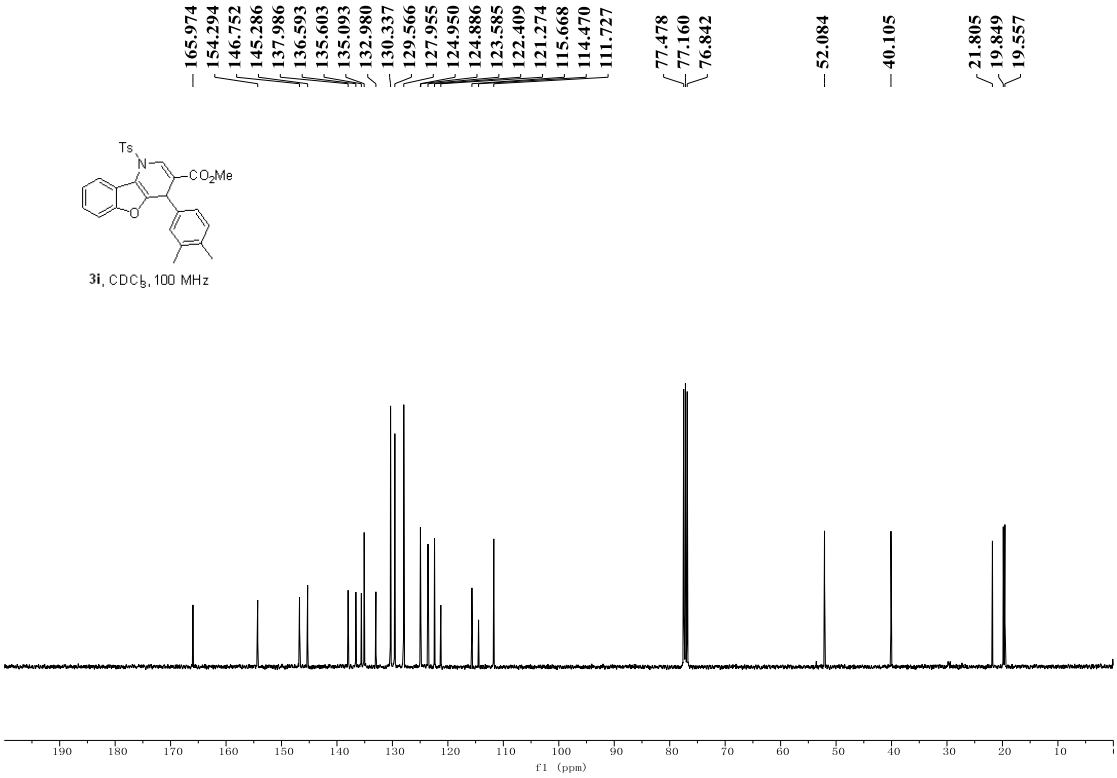

8.448
8.445
8.436
8.432
8.427
8.423
8.140
7.663
7.642
7.362
7.357
7.352
7.346
7.342
7.337
7.332
7.324
7.318
7.313
7.306
7.301
7.295
7.281
7.276
7.260
6.952
6.933
6.867
6.848
6.829
6.781
6.776
6.771
6.137
6.117
5.143
3.714
2.431
2.204
Ts
N
CO2Me
O
3g, CDCl3, 400 MHz
1.03
1.00
2.13
5.67
1.06
1.07
1.06
1.04
1.04
3.15
3.26
3.20
f1 (ppm)

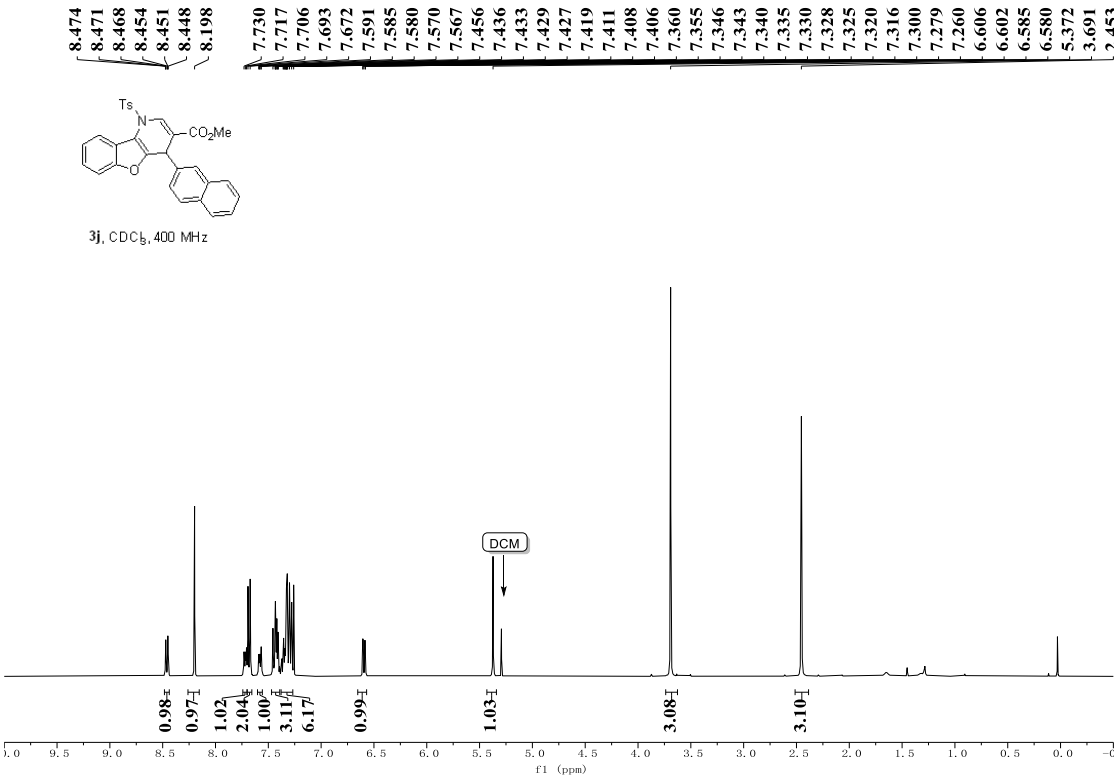

165.905
154.276
146.566
145.304
140.393
137.984
135.184
132.946
130.320
129.012
128.083
127.918
124.935
124.669
123.607
122.424
121.218
115.513
114.540
111.676
77.476
77.160
76.840
52.080
40.435
21.795
21.480
Ts
N
CO2Me
O
3g, CDCl3, 100 MHz
f1 (ppm)

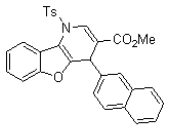

8.368
8.364
8.349
8.347
8.137
7.621
7.600
7.325
7.322
7.319
7.309
7.305
7.302
7.300
7.291
7.286
7.272
7.266
7.262
7.247
7.243
7.239
7.228
7.224
7.084
7.080
7.066
7.064
7.062
7.059
7.045
7.041
6.857
6.837
6.378
6.376
6.360
6.357
6.341
6.338
5.737
5.709
5.705
5.690
5.686
3.913
3.643
2.423
0.000
Ts
N
CO2Me
O
MeO
3h, CDCl3, 400 MHz
1.01
1.00
2.15
5.75
1.08
1.07
1.05
1.01
0.95
3.26
3.09
3.20
f1 (ppm)


165.756
156.970
154.121
147.403
145.244
135.927
132.800
130.282
129.633
128.247
128.026
127.953
124.721
123.449
122.317
121.311
120.282
116.003
114.416
111.661
111.252
77.479
77.160
76.844
56.306
52.044
32.380
21.766
Ts
N
CO2Me
O
MeO
3h, CDCl3, 100 MHz
f1 (ppm)

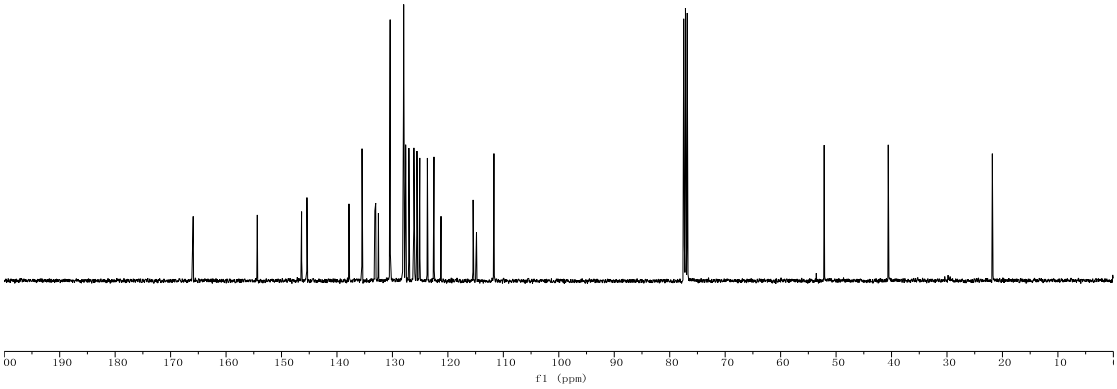

8.436
8.433
8.420
8.417
8.415
8.411
8.122
7.657
7.636
7.354
7.349
7.346
7.344
7.338
7.334
7.329
7.325
7.316
7.310
7.306
7.298
7.294
7.287
7.285
7.281
7.272
7.269
7.265
7.264
7.260
6.750
6.745
6.721
6.702
6.046
6.041
6.026
6.021
5.116
3.712
2.441
2.147
2.105
Ts
N
CO2Me
O
3i, CDCl3, 400 MHz
DCM
0.98
0.97
2.06
5.28
1.01
1.02
1.01
0.97
3.11
3.12
3.07
3.00
f1 (ppm)

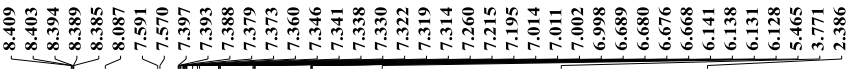

165.974
154.294
146.752
145.286
137.986
136.593
135.603
135.093
132.980
130.337
129.566
127.955
124.950
124.886
123.585
122.409
121.274
115.668
114.470
111.727
77.478
77.160
76.842
52.084
40.105
21.805
19.849
19.557
Ts
N
CO2Me
O
3i, CDCl3, 100 MHz
f1 (ppm)

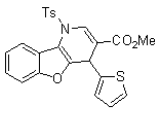

8.474
8.471
8.468
8.454
8.451
8.448
8.198
7.730
7.717
7.706
7.693
7.672
7.591
7.585
7.580
7.570
7.567
7.456
7.436
7.433
7.429
7.427
7.419
7.411
7.408
7.406
7.360
7.355
7.346
7.343
7.340
7.335
7.330
7.328
7.325
7.320
7.316
7.300
7.279
7.260
6.606
6.602
6.585
6.580
5.372
3.691
Ts
N
CO2Me
O
3j, CDCl3, 400 MHz
DCM
0.98
0.97
1.02
2.04
1.00
3.11
6.17
0.99
1.03
3.08
3.10
f1 (ppm)



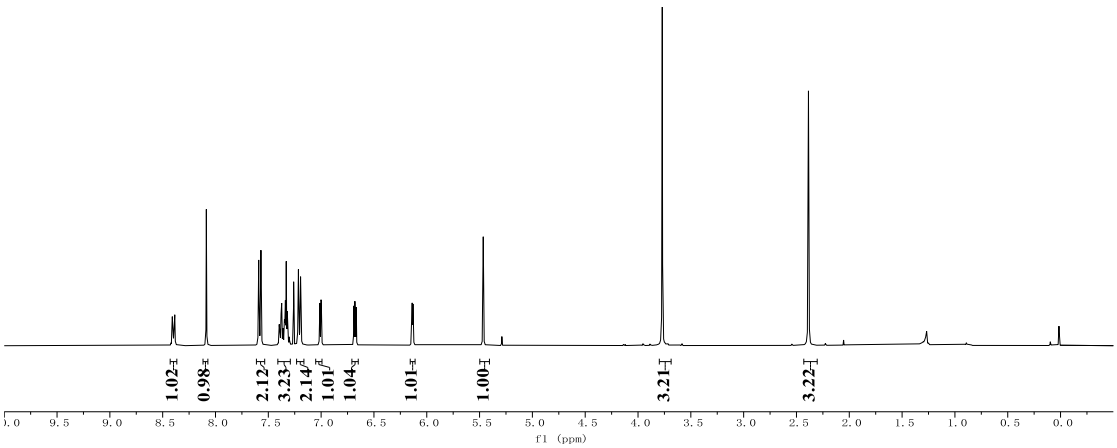
3j, $CDCl_3$, 100 MHz

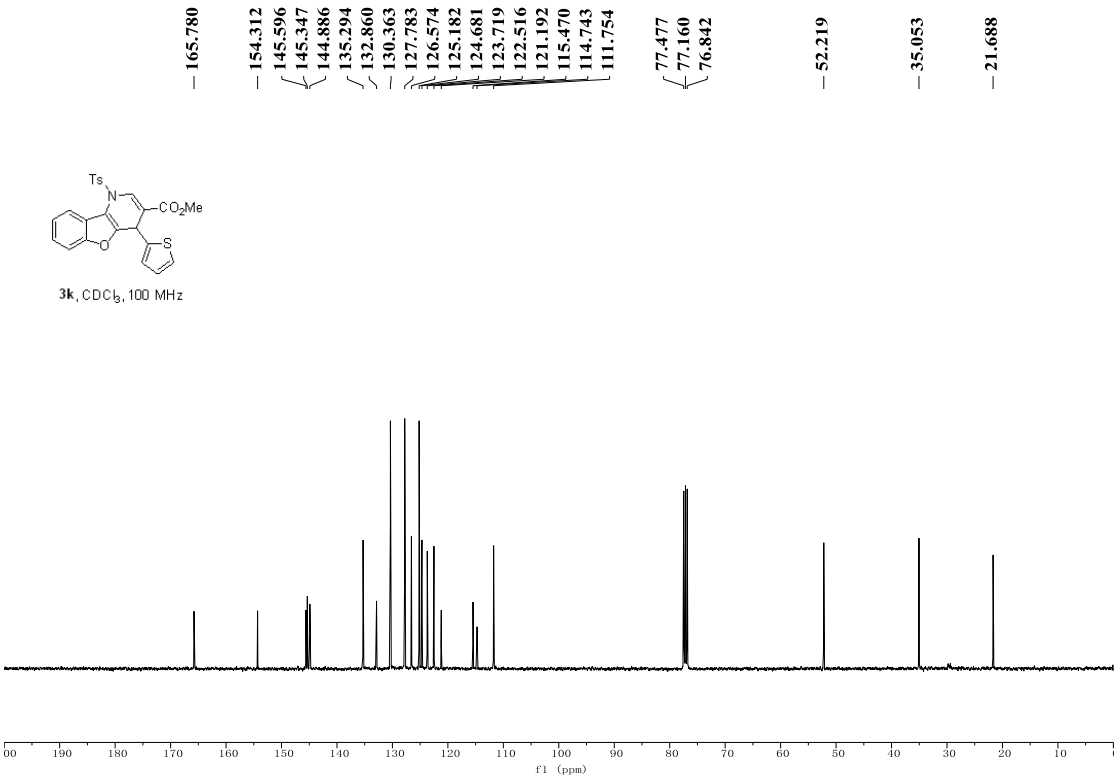




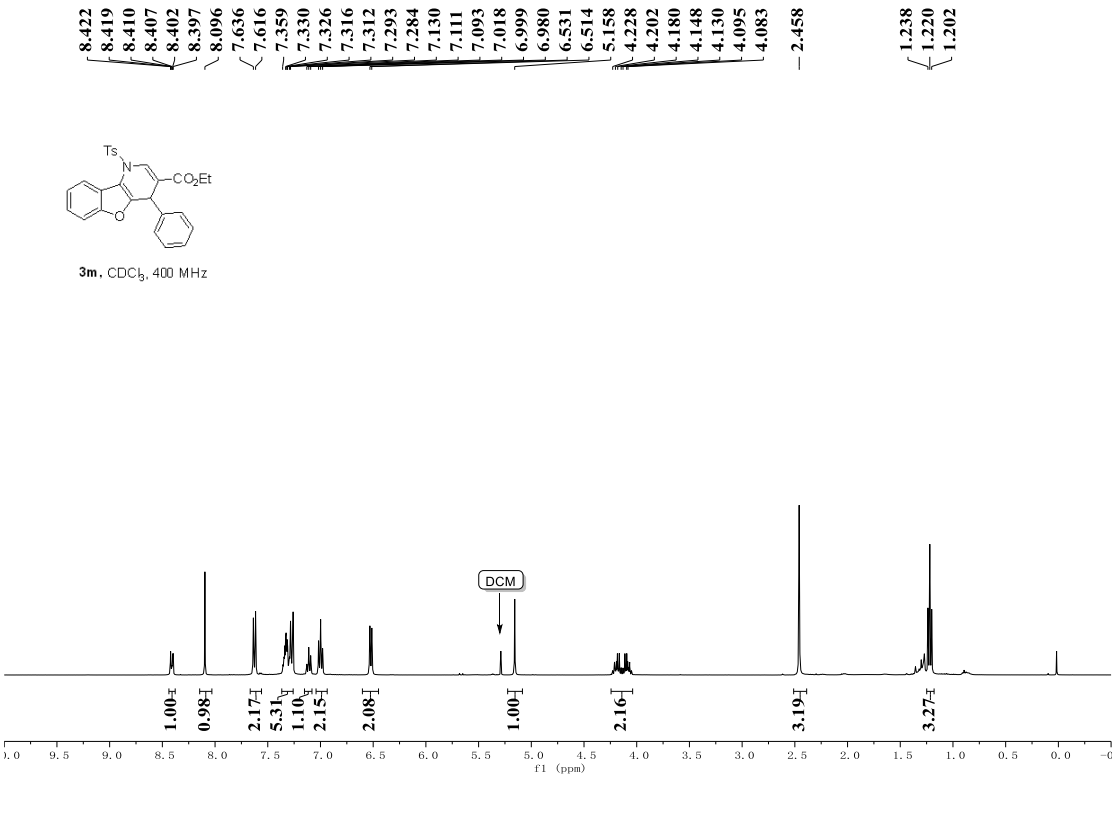


3k, $CDCl_3$, 400 MHz

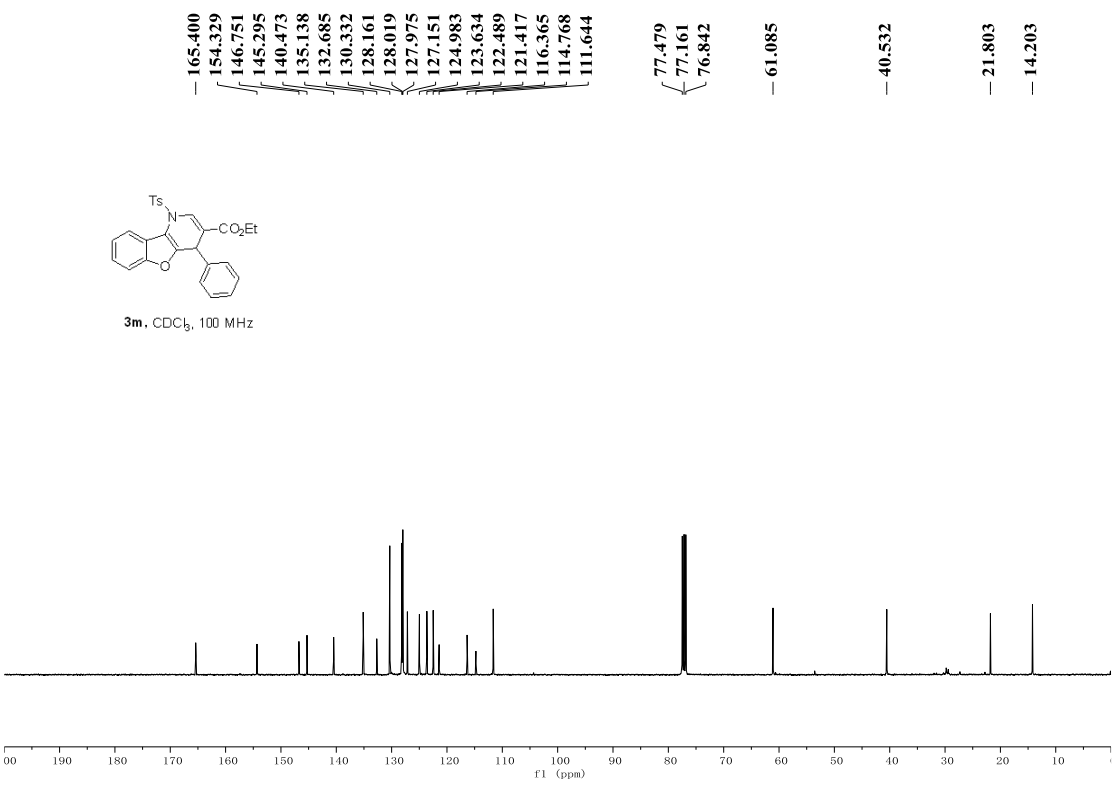


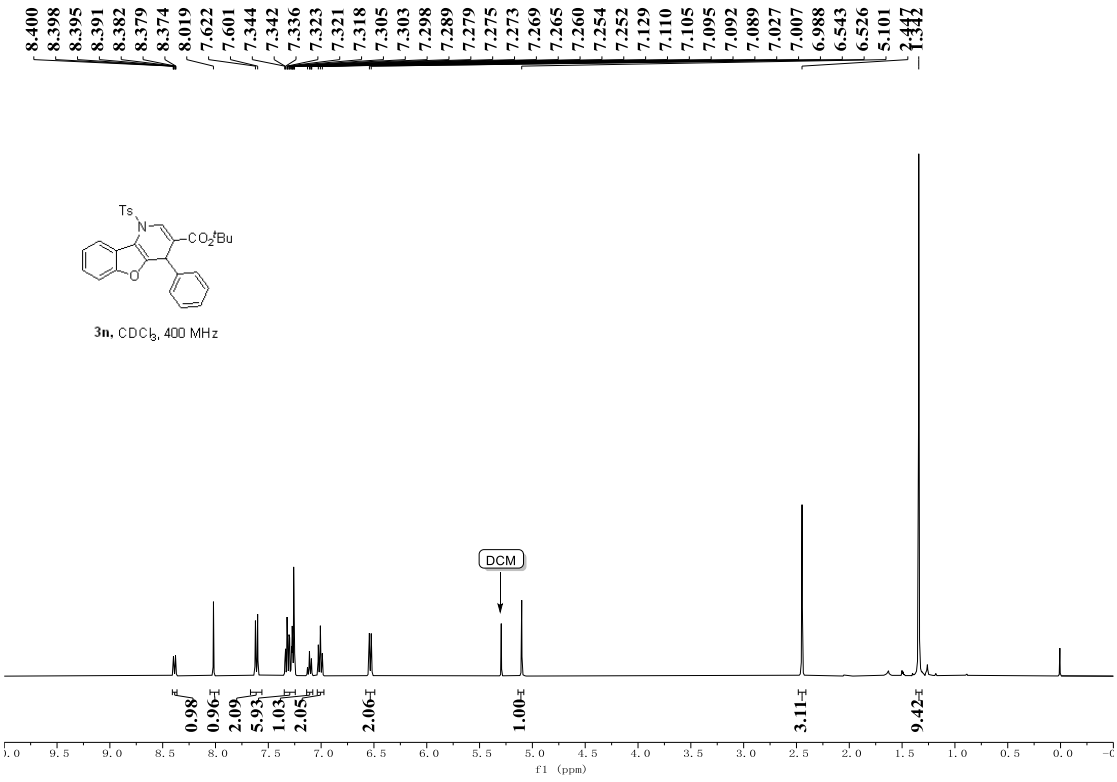


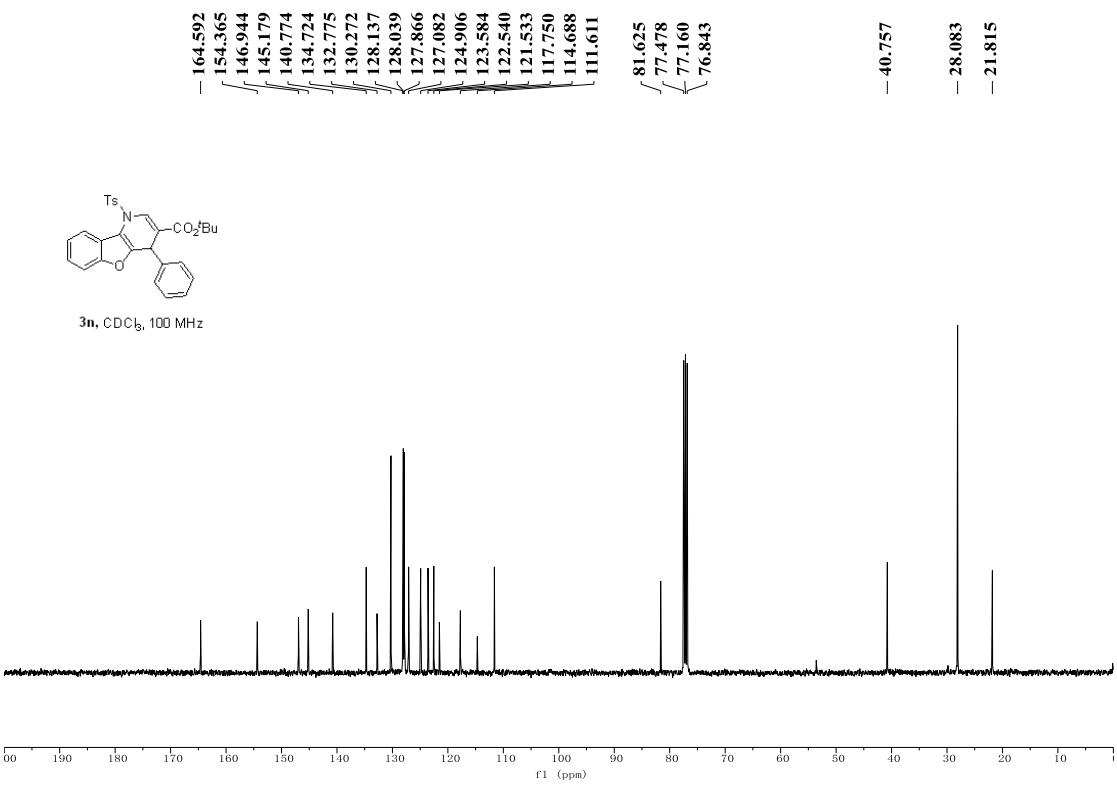
3k, $CDCl_3$, 100 MHz

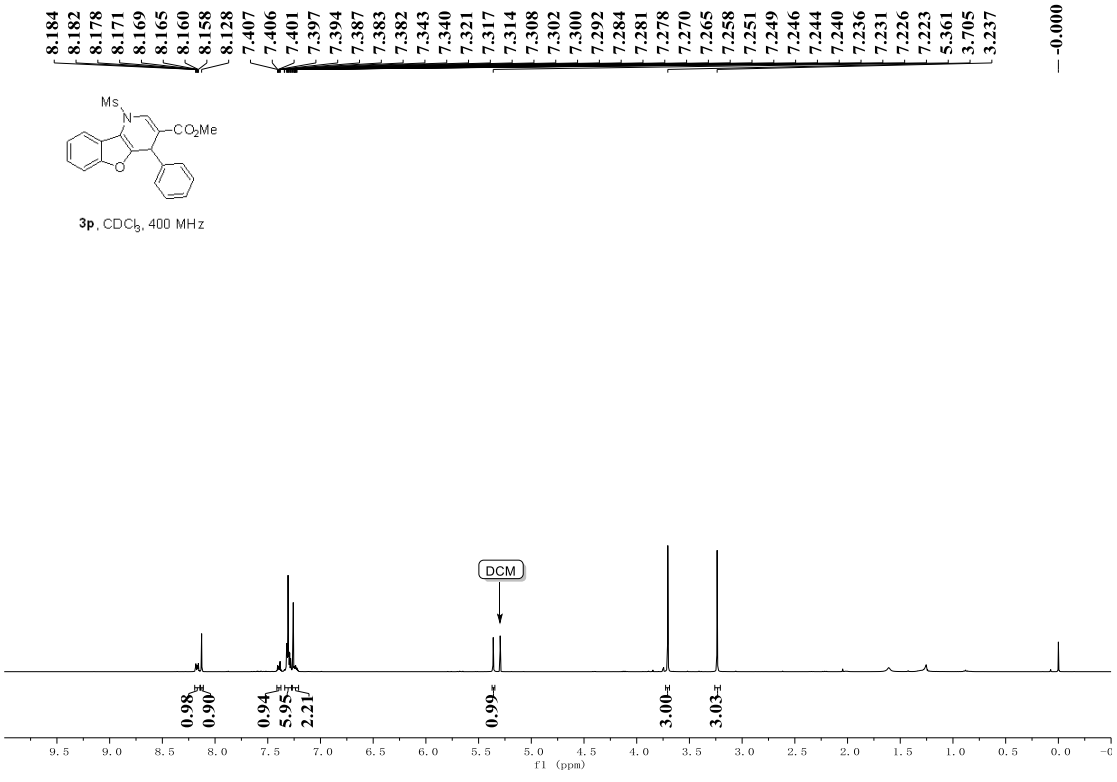


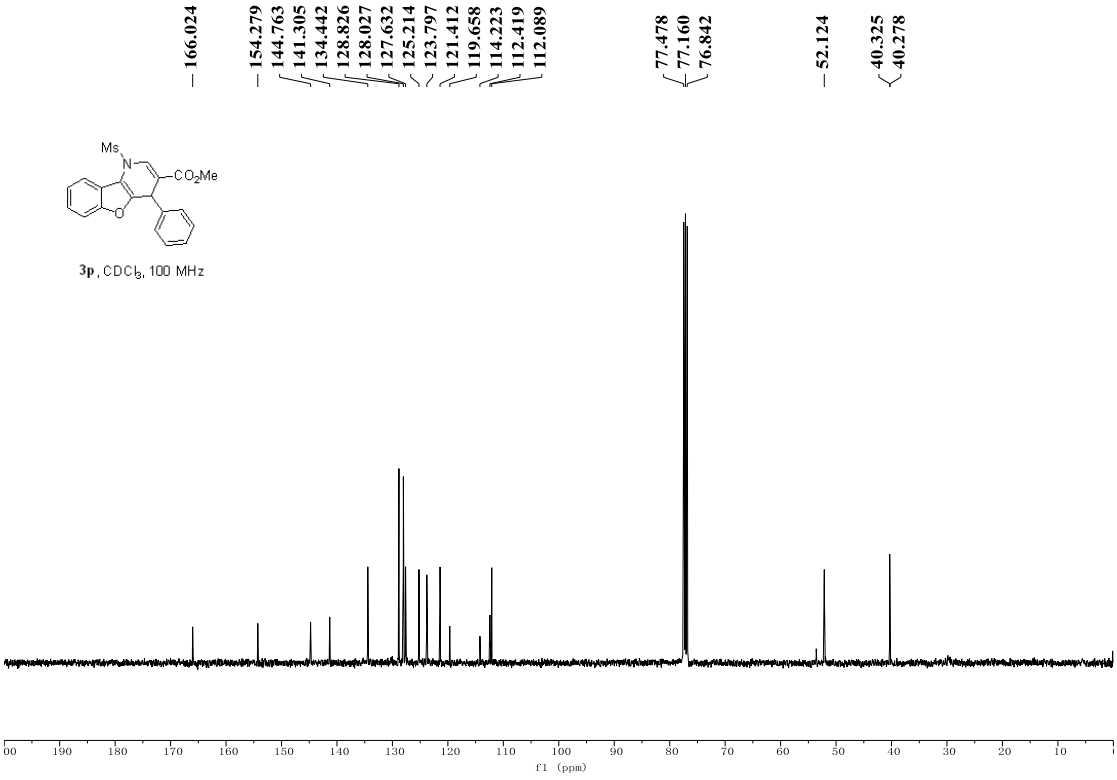
3m, $CDCl_3$, 400 MHz


165.400
154.329
146.751
145.295
140.473
135.138
132.685
130.332
128.161
128.019
127.975
127.151
124.983
123.634
122.489
121.417
116.365
114.768
111.644
77.479
77.161
76.842
61.085
40.532
21.803
14.203
Ts
N
CO2Et
3m, CDCl3, 100 MHz
f1 (ppm)

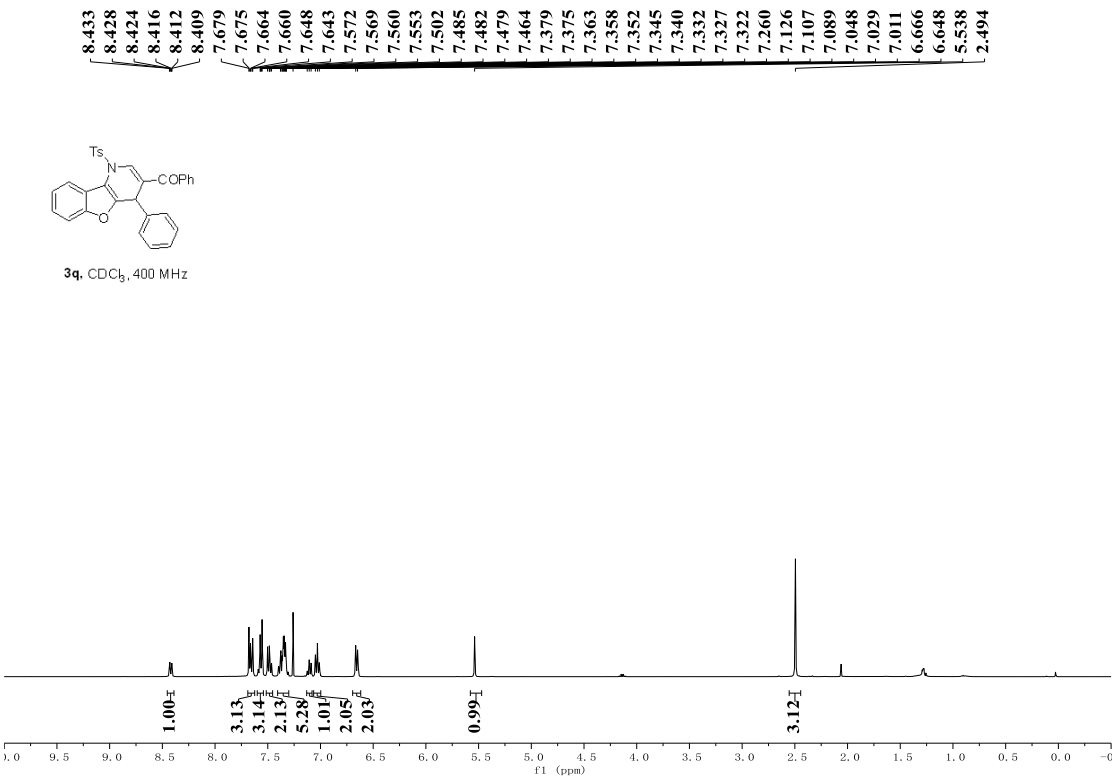

8.400
8.398
8.395
8.391
8.382
8.379
8.374
8.019
7.622
7.601
7.344
7.342
7.336
7.323
7.321
7.318
7.305
7.303
7.298
7.289
7.279
7.275
7.273
7.269
7.265
7.260
7.254
7.252
7.129
7.110
7.105
7.095
7.092
7.089
7.027
7.007
6.988
6.543
6.526
5.101
2.447
1.342
Ts
N
CO2tBu
3n, CDCl3, 400 MHz
DCM
0.98
0.96
2.09
5.93
1.03
2.05
2.06
1.00
3.11
9.42
f1 (ppm)


164.592
154.365
146.944
145.179
140.774
134.724
132.775
130.272
128.137
128.039
127.866
127.082
124.906
123.584
122.540
121.533
117.750
114.688
111.611
81.625
77.478
77.160
76.843
40.757
28.083
21.815
Ts
N
CO2tBu
O
3n, CDCl3, 100 MHz
f1 (ppm)

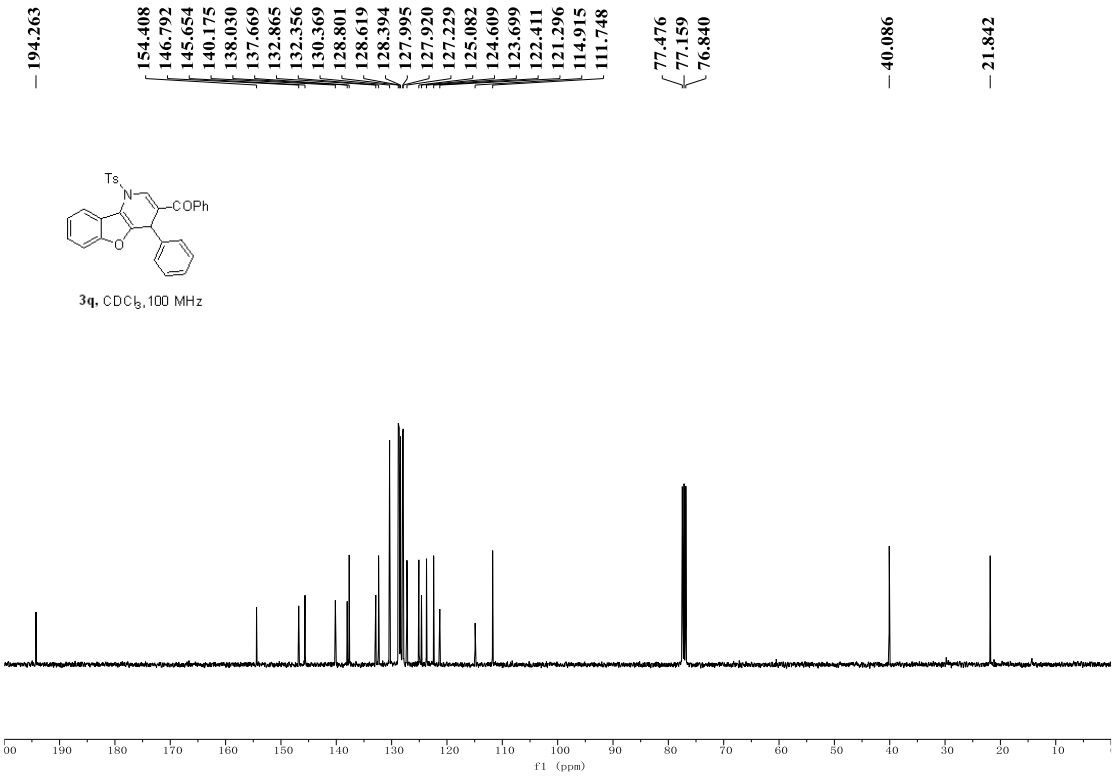

8.184
8.182
8.178
8.171
8.169
8.165
8.160
8.158
8.128
7.407
7.406
7.401
7.397
7.394
7.387
7.383
7.382
7.343
7.340
7.321
7.317
7.314
7.308
7.302
7.300
7.292
7.284
7.281
7.278
7.270
7.265
7.258
7.251
7.249
7.246
7.244
7.240
7.236
7.231
7.226
7.223
5.361
3.705
3.237
-0.000
Ms
N
CO2Me
O
3p, CDCl3, 400 MHz
DCM
0.98
0.90
0.94
5.95
2.21
0.99
3.00
3.03
f1 (ppm)



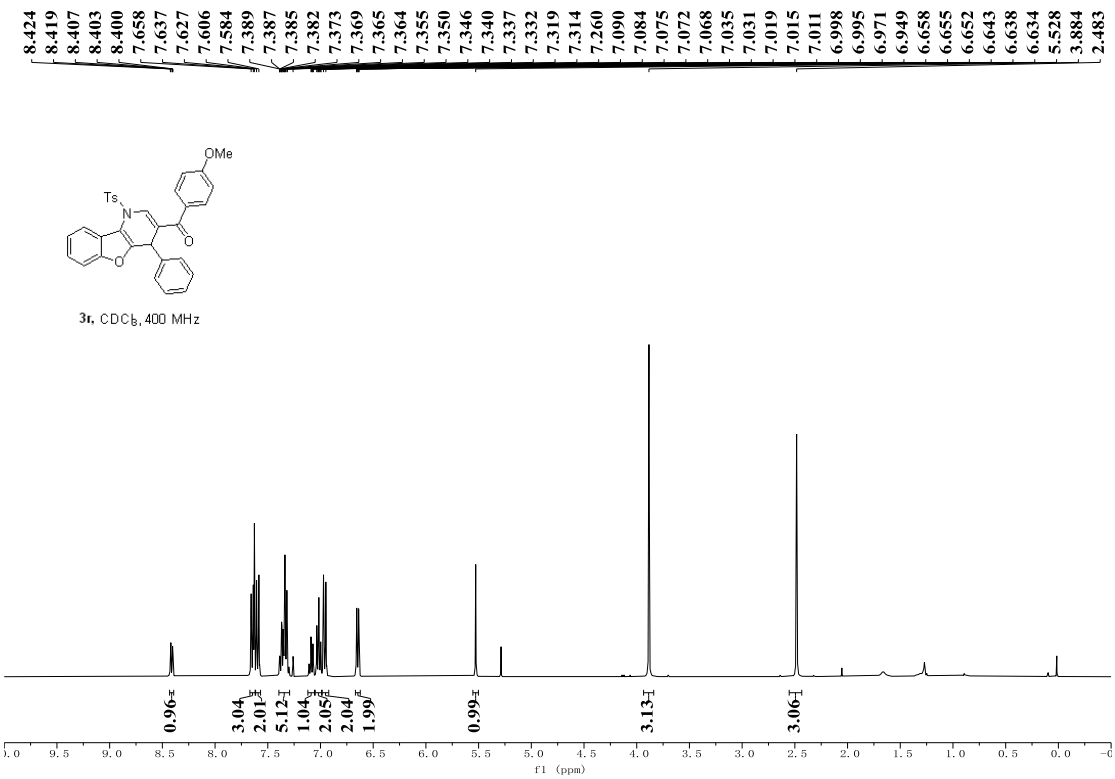
3p, $CDCl_3$, 100 MHz



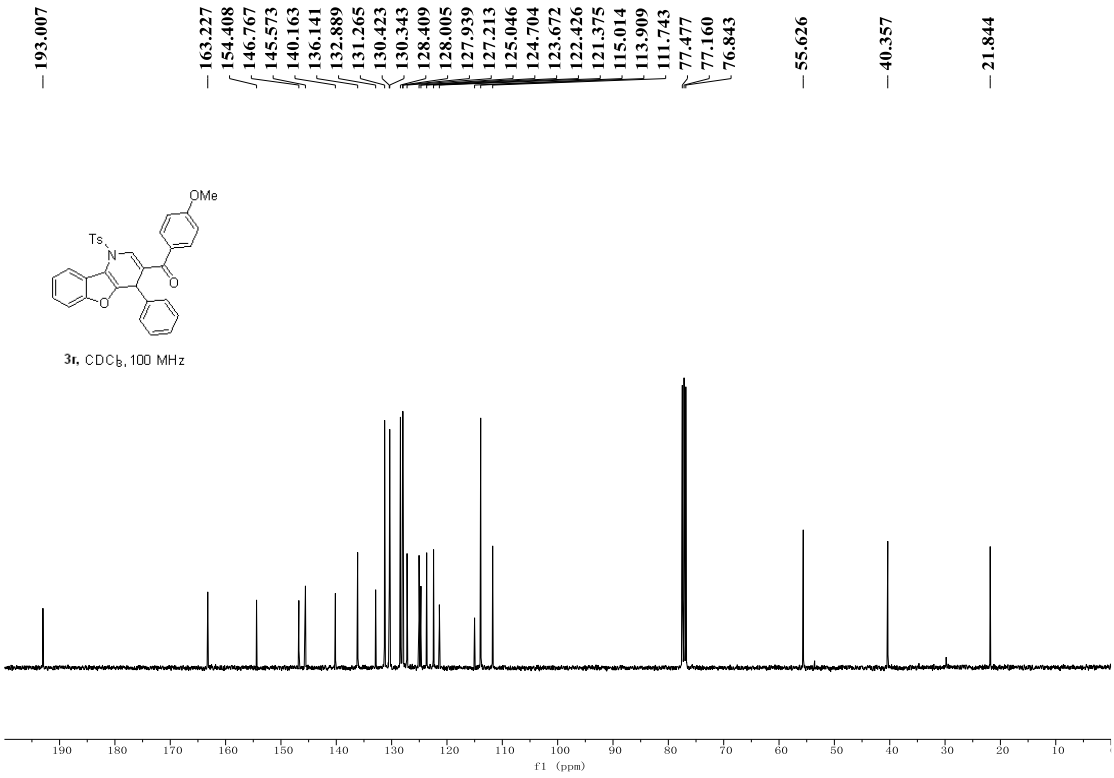
3q, $CDCl_3$, 400 MHz

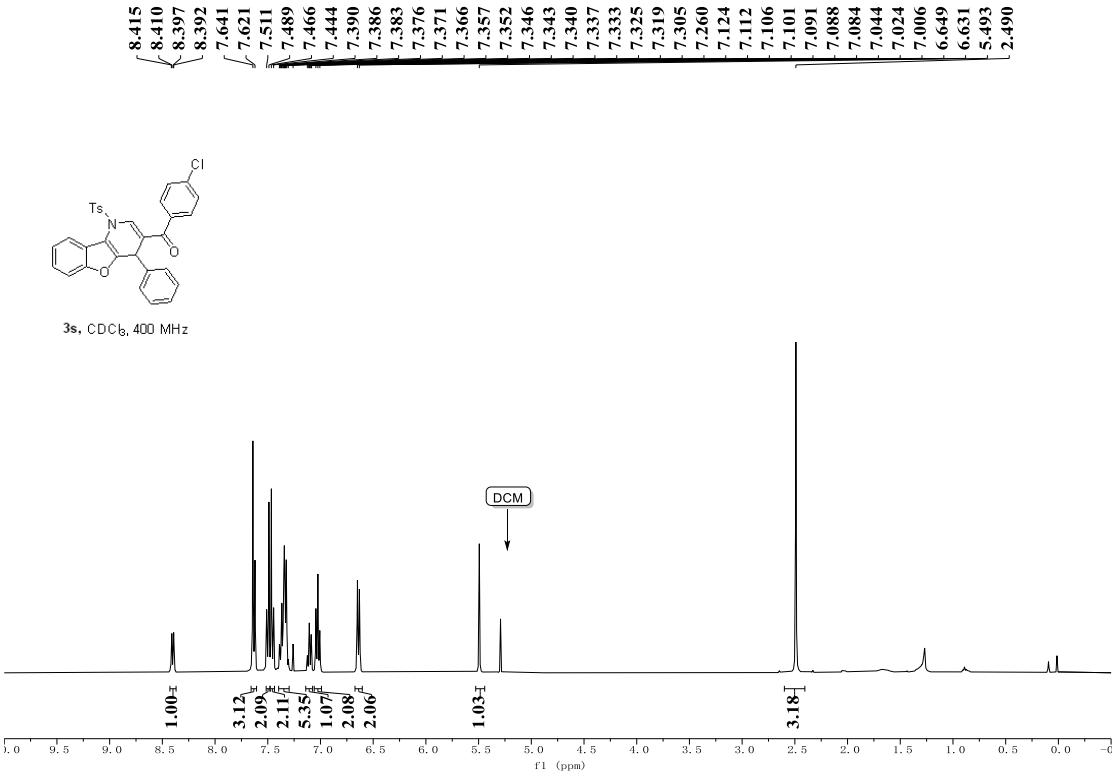


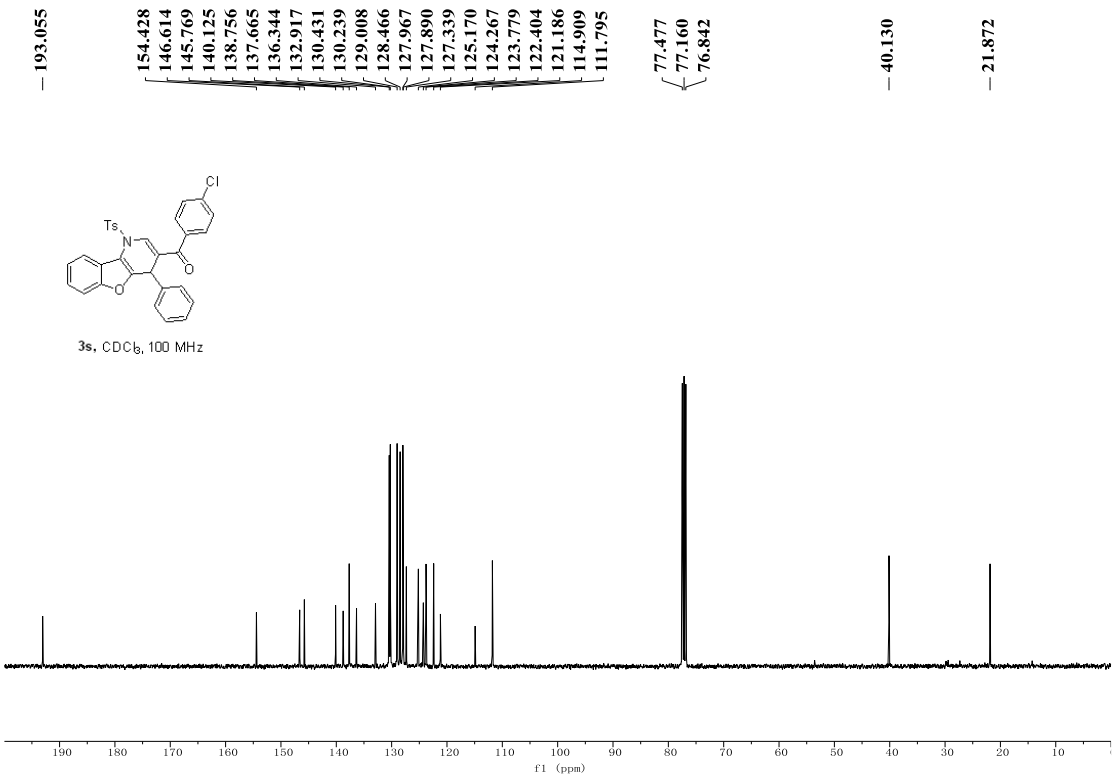
3q, $CDCl_3$, 100 MHz



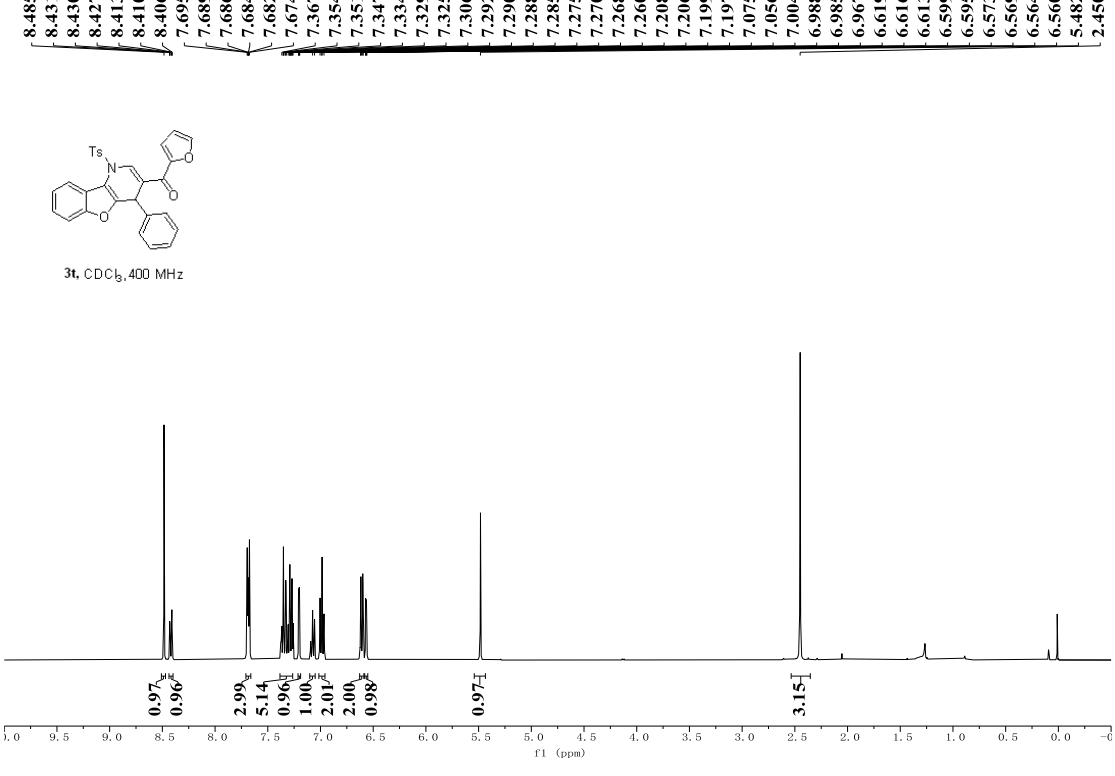
3r, $CDCl_3$, 400 MHz


193.007
163.227
154.408
146.767
145.573
140.163
136.141
132.889
131.265
130.423
130.343
128.409
128.005
127.939
127.213
125.046
124.704
123.672
122.426
121.375
115.014
113.909
111.743
77.477
77.160
76.843
55.626
40.357
21.844
OMe
Ts
N
O
O
3r, CDCl3, 100 MHz
f1 (ppm)

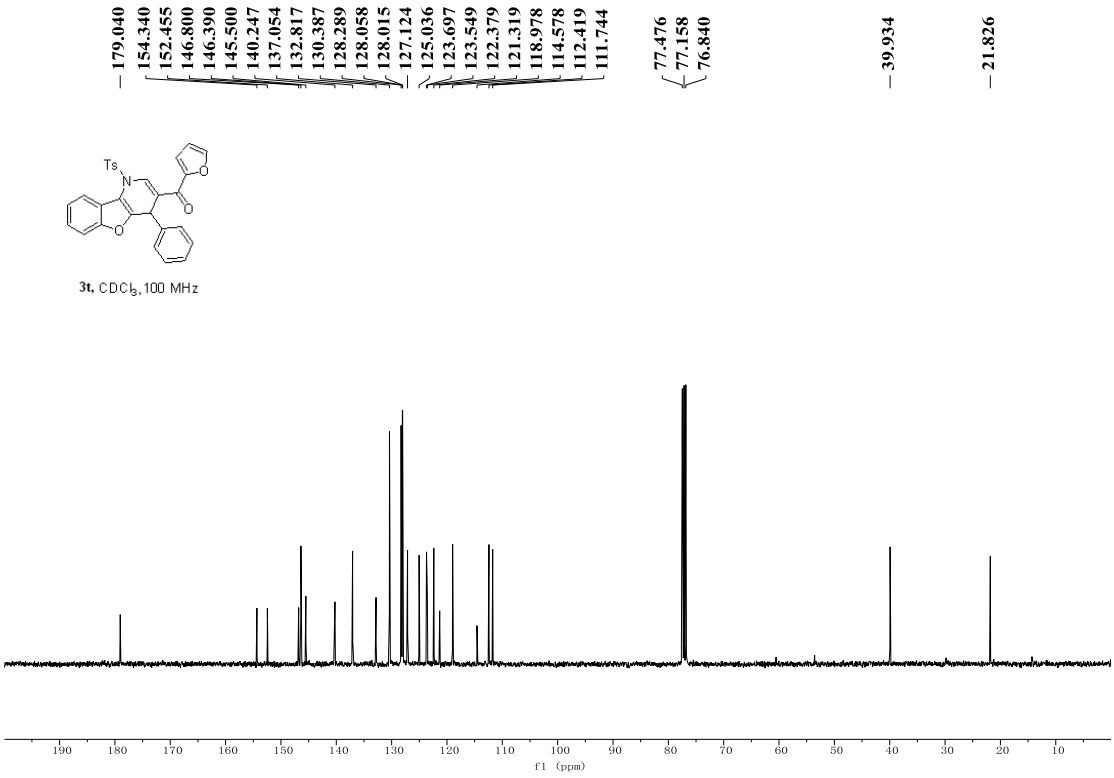

8.415
8.410
8.397
8.392
7.641
7.621
7.511
7.489
7.466
7.444
7.390
7.386
7.383
7.376
7.371
7.366
7.357
7.352
7.346
7.343
7.340
7.337
7.333
7.325
7.319
7.305
7.260
7.124
7.112
7.106
7.101
7.091
7.088
7.084
7.044
7.024
7.006
6.649
6.631
5.493
2.490
Cl
Ts
N
O
O
3s, CDCl3, 400 MHz
DCM
1.00
3.12
2.09
2.11
5.35
1.07
2.08
2.06
1.03
3.18
f1 (ppm)

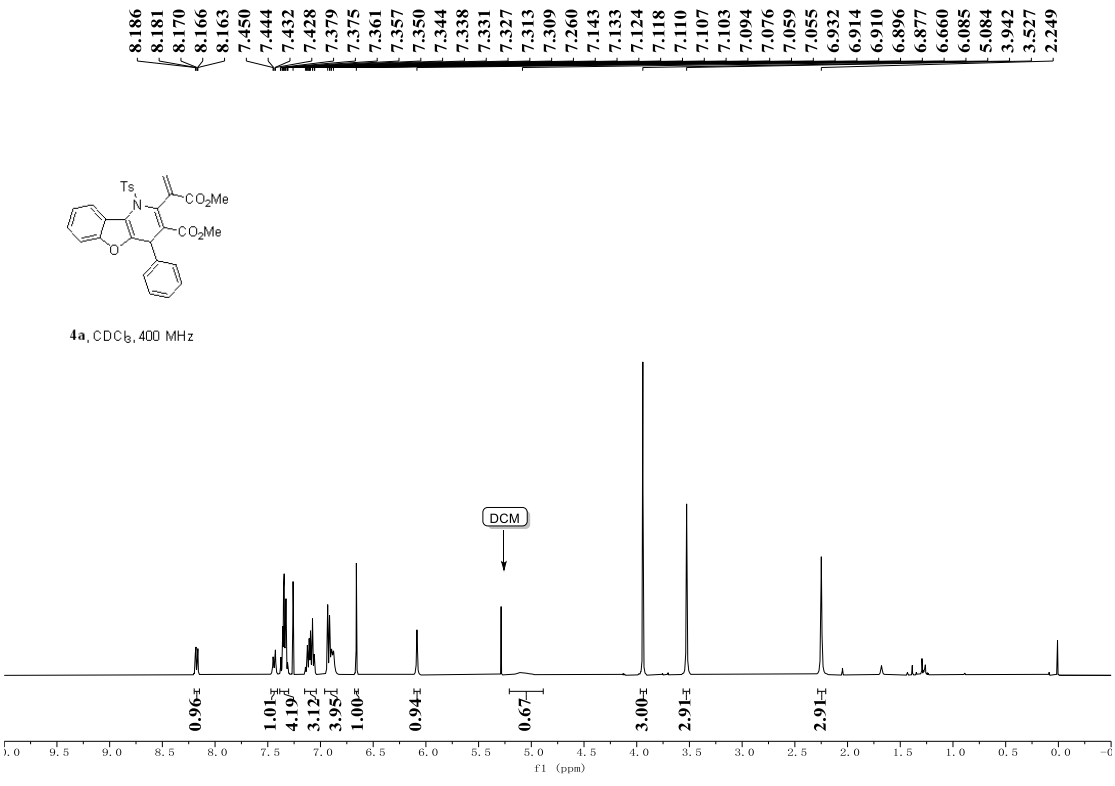


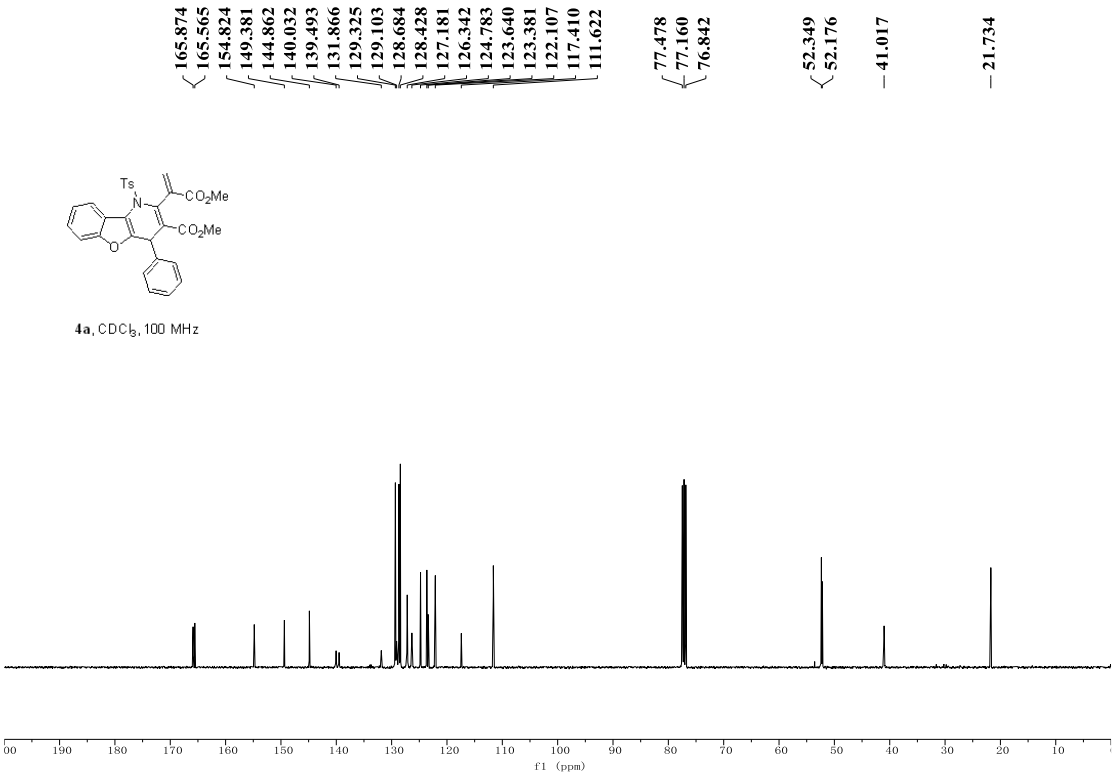
3s, $CDCl_3$, 100 MHz



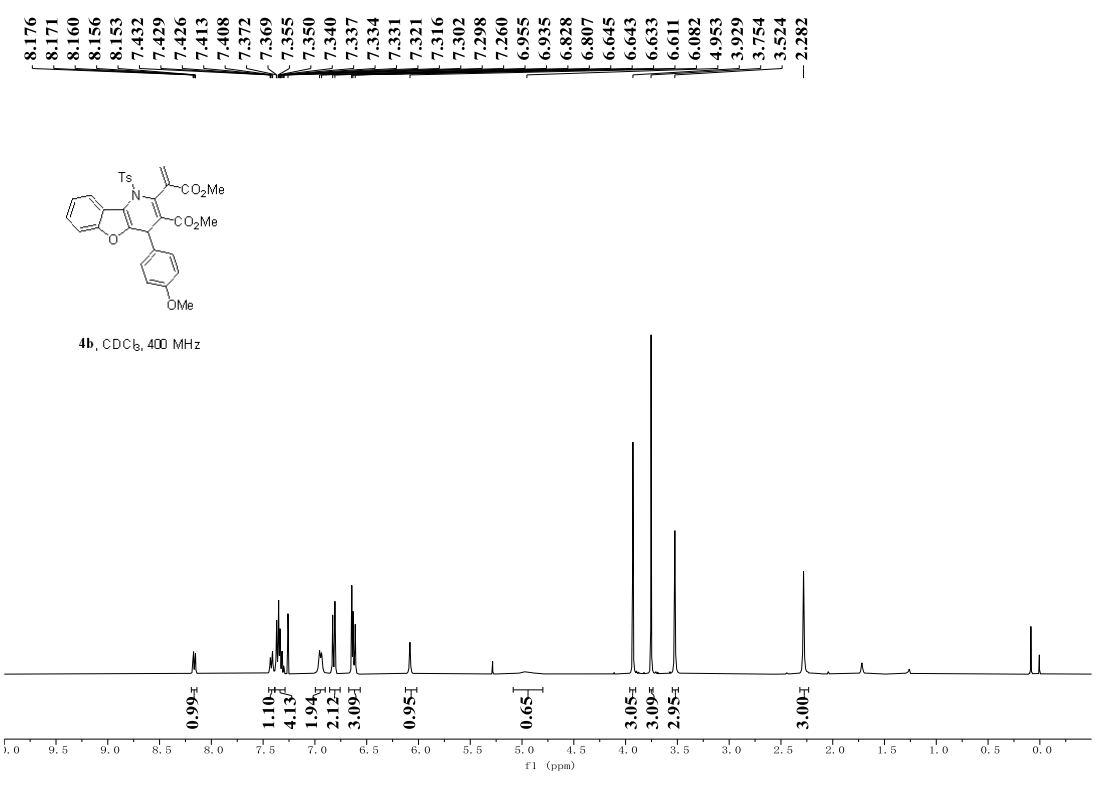
3t, $CDCl_3$, 400 MHz


179.040
154.340
152.455
146.800
146.390
145.500
140.247
137.054
132.817
130.387
128.289
128.058
128.015
127.124
125.036
123.697
123.549
122.379
121.319
118.978
114.578
112.419
111.744
77.476
77.158
76.840
39.934
21.826
Ts
N
O
O
O
3t, CDCl3, 100 MHz
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
f1 (ppm)

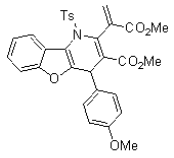

8.186
8.181
8.170
8.166
8.163
7.450
7.444
7.432
7.428
7.379
7.375
7.361
7.357
7.350
7.344
7.338
7.331
7.327
7.313
7.309
7.260
7.143
7.133
7.124
7.118
7.110
7.107
7.103
7.094
7.076
7.059
7.055
6.932
6.914
6.910
6.896
6.877
6.660
6.085
5.084
3.942
3.527
2.249
Ts
N
CO2Me
CO2Me
O
4a, CDCl3, 400 MHz
DCM
0.96
1.01
4.19
3.12
3.95
1.00
0.94
0.67
3.00
2.91
2.91
f1 (ppm)



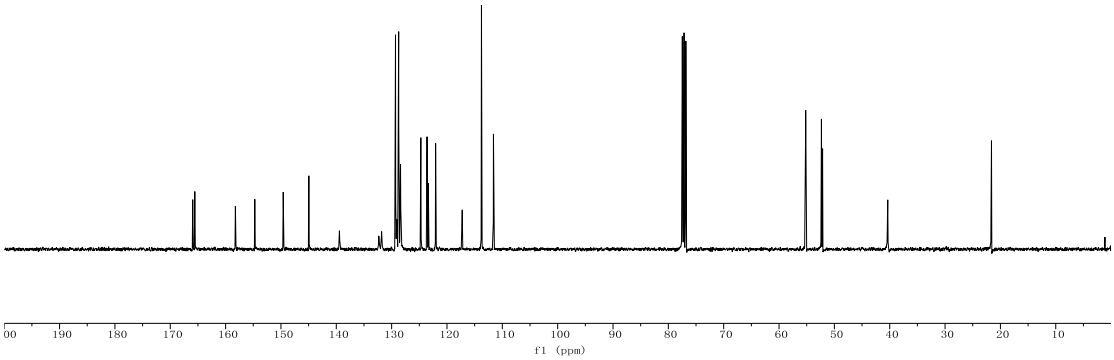
4a, $CDCl_3$, 100 MHz

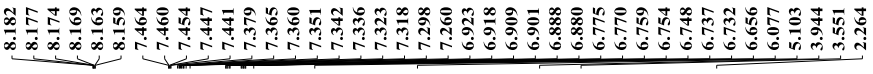


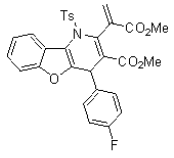
4b, $CDCl_3$, 400 MHz



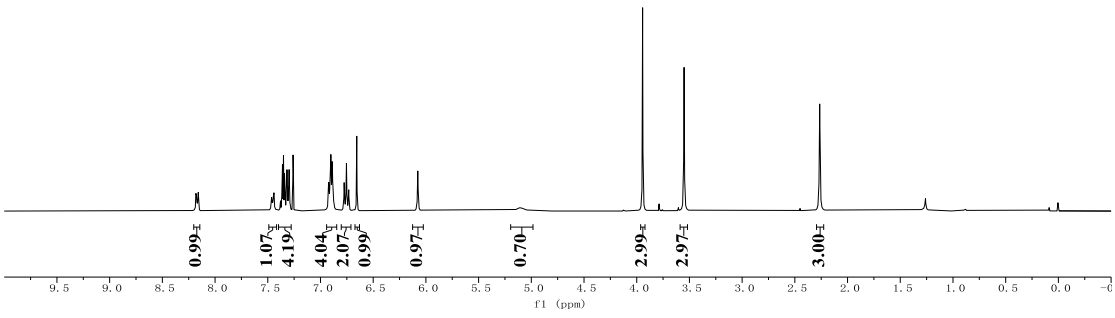
4b, $CDCl_3$, 100 MHz

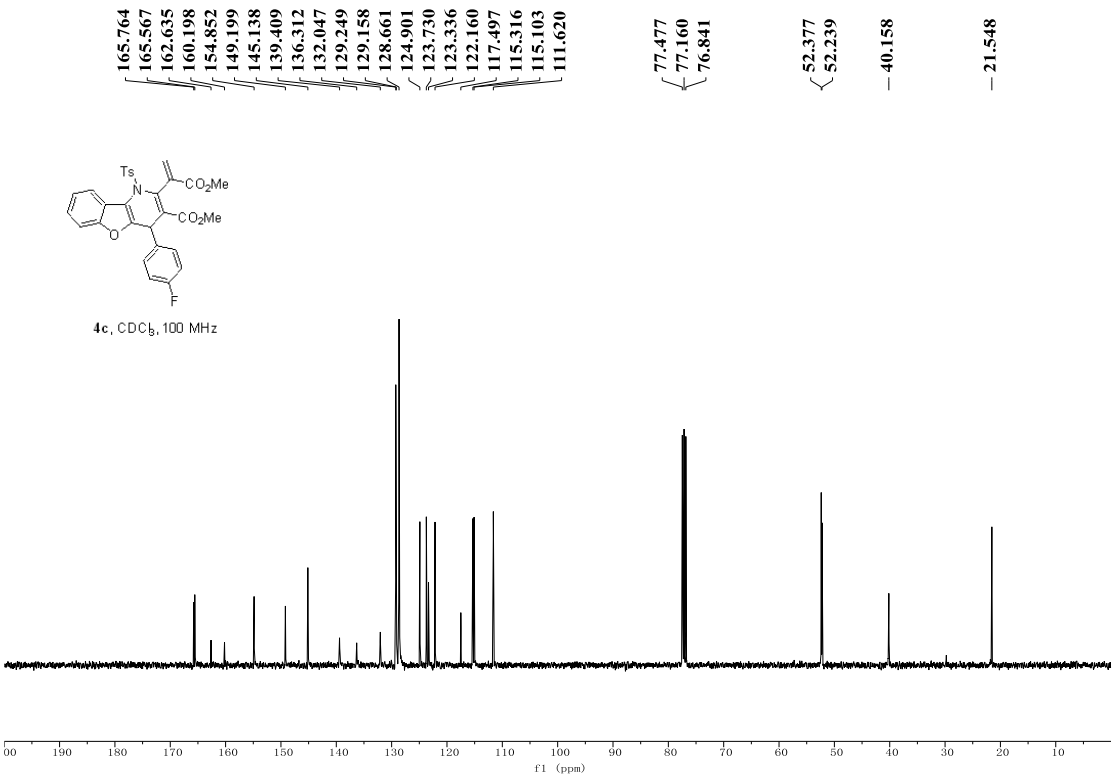


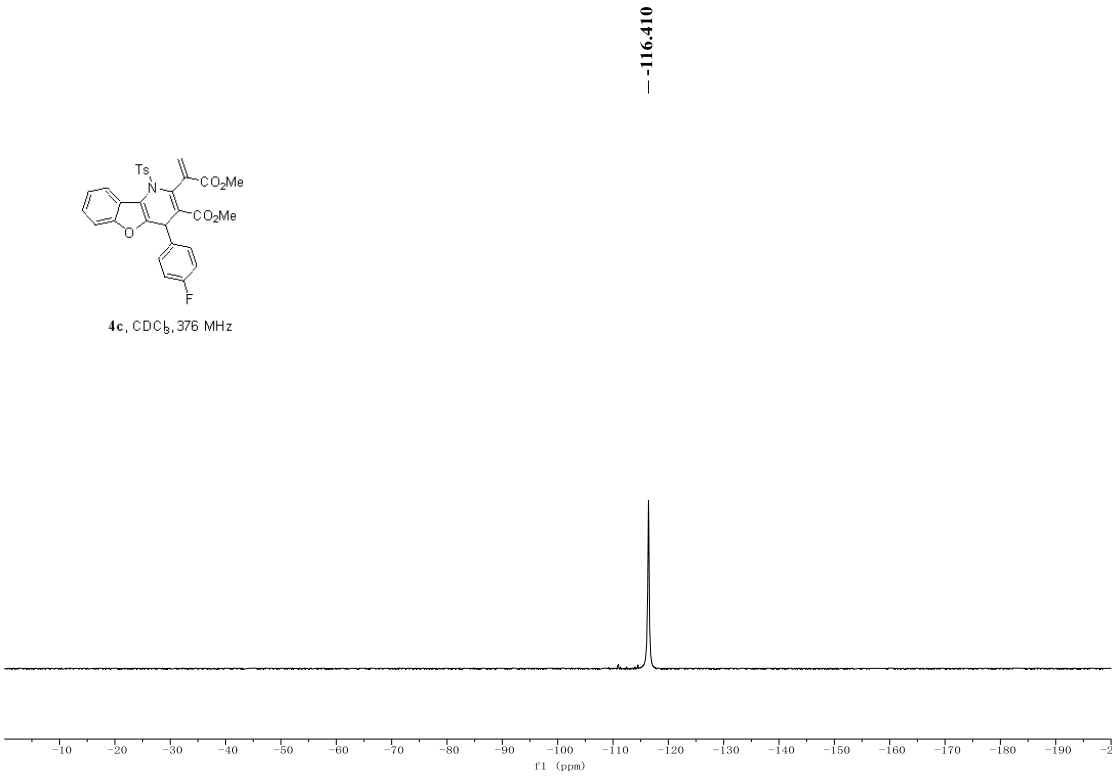


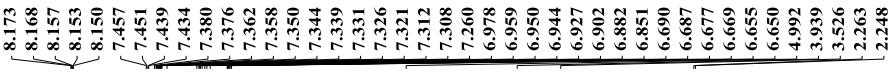


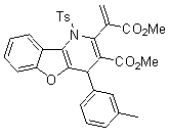
4c, $CDCl_3$, 400 MHz



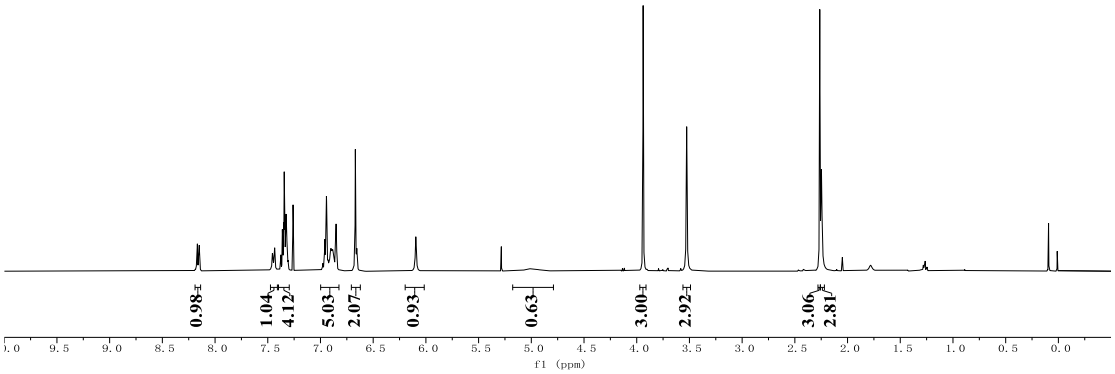

165.764
165.567
162.635
160.198
154.852
149.199
145.138
139.409
136.312
132.047
129.249
129.158
128.661
124.901
123.730
123.336
122.160
117.497
115.316
115.103
111.620
77.477
77.160
76.841
52.377
52.239
40.158
21.548
Ts
N
CO2Me
CO2Me
O
F
4c, CDCl3, 100 MHz
f1 (ppm)

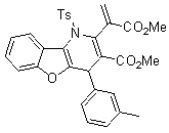

-116.410
Ts
N
CO2Me
CO2Me
O
F
4c, CDCl3, 376 MHz
f1 (ppm)



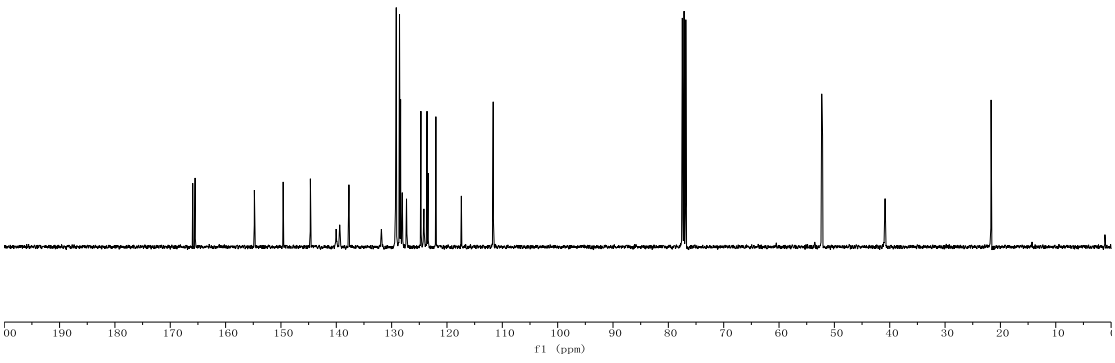


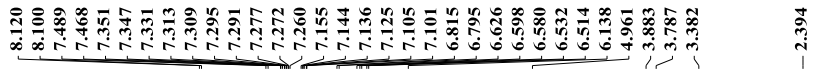
4d, $CDCl_3$, 400 MHz

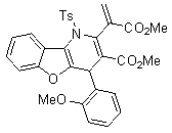




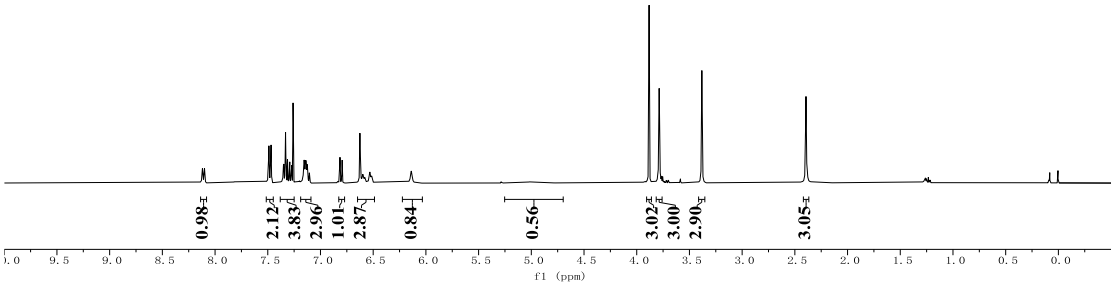
4d, $CDCl_3$, 100 MHz

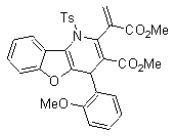




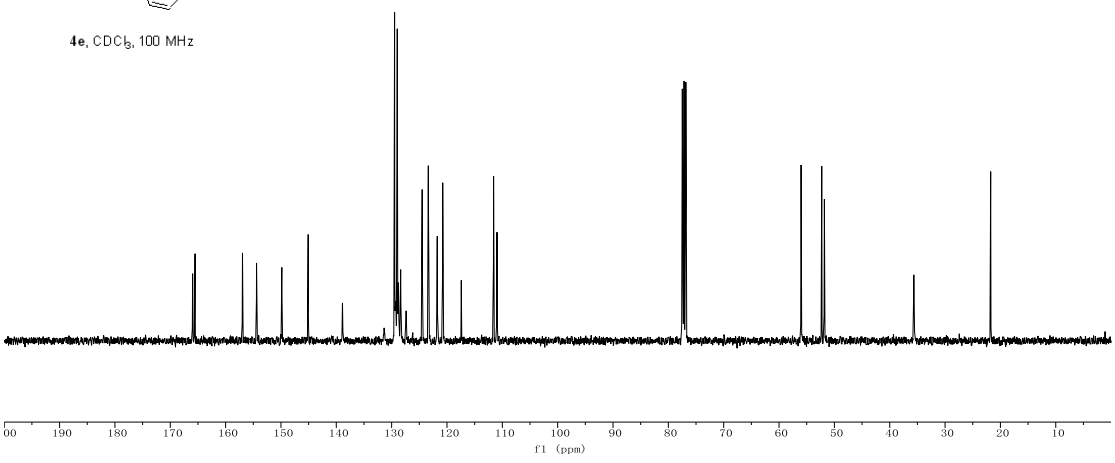


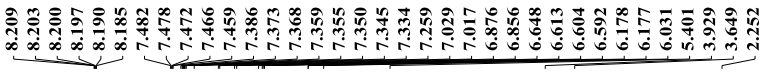
4e, $CDCl_3$, 400 MHz

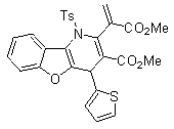




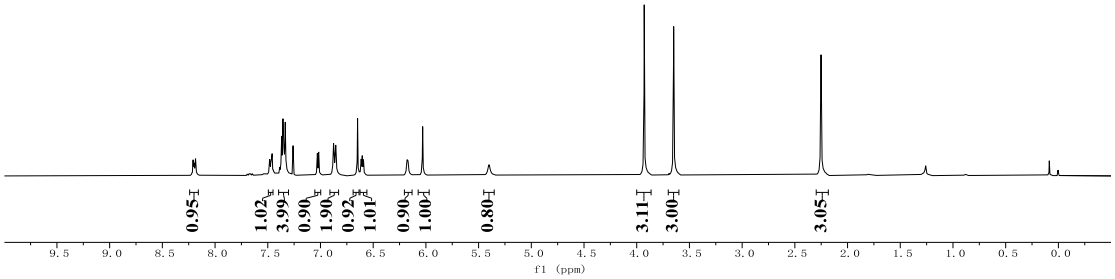
4e, $CDCl_3$, 100 MHz

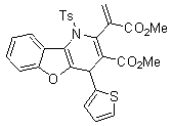




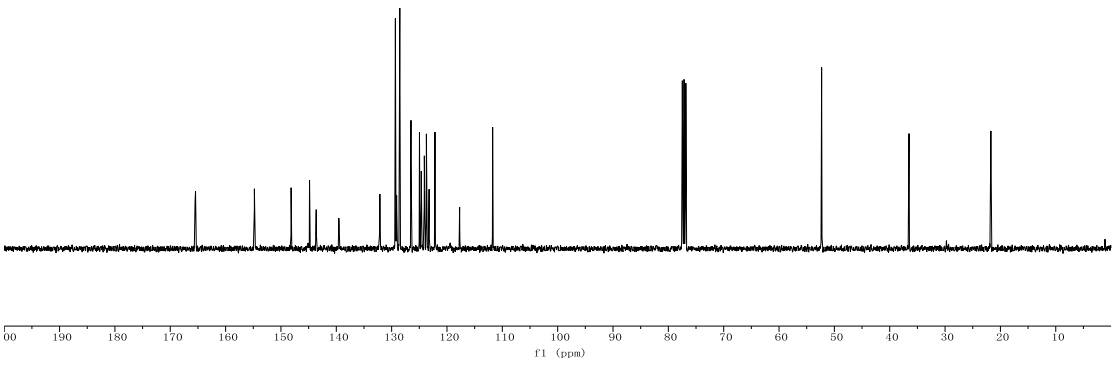


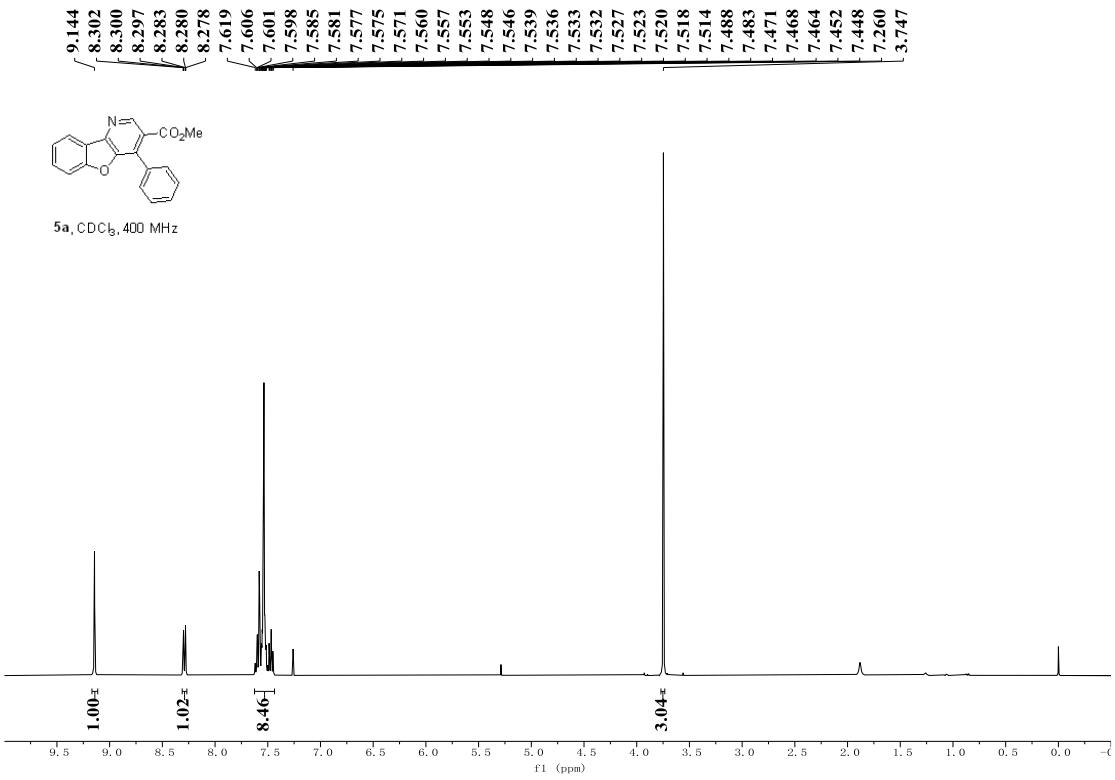
4f, $CDCl_3$, 400 MHz

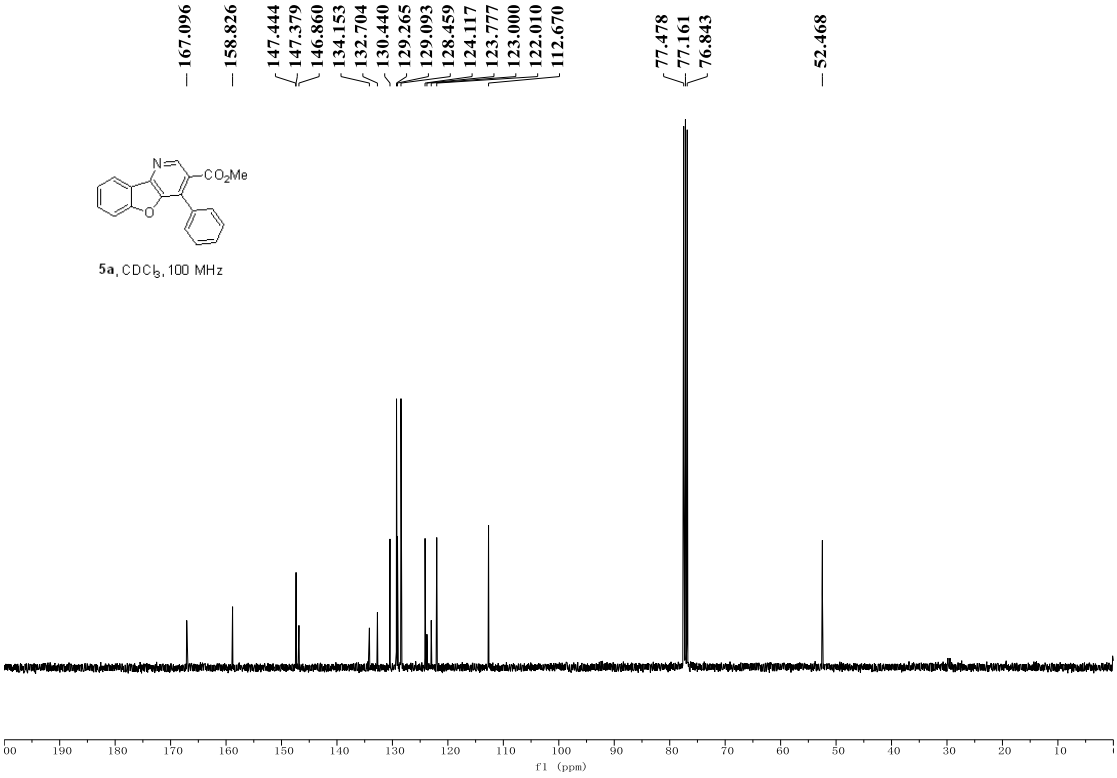


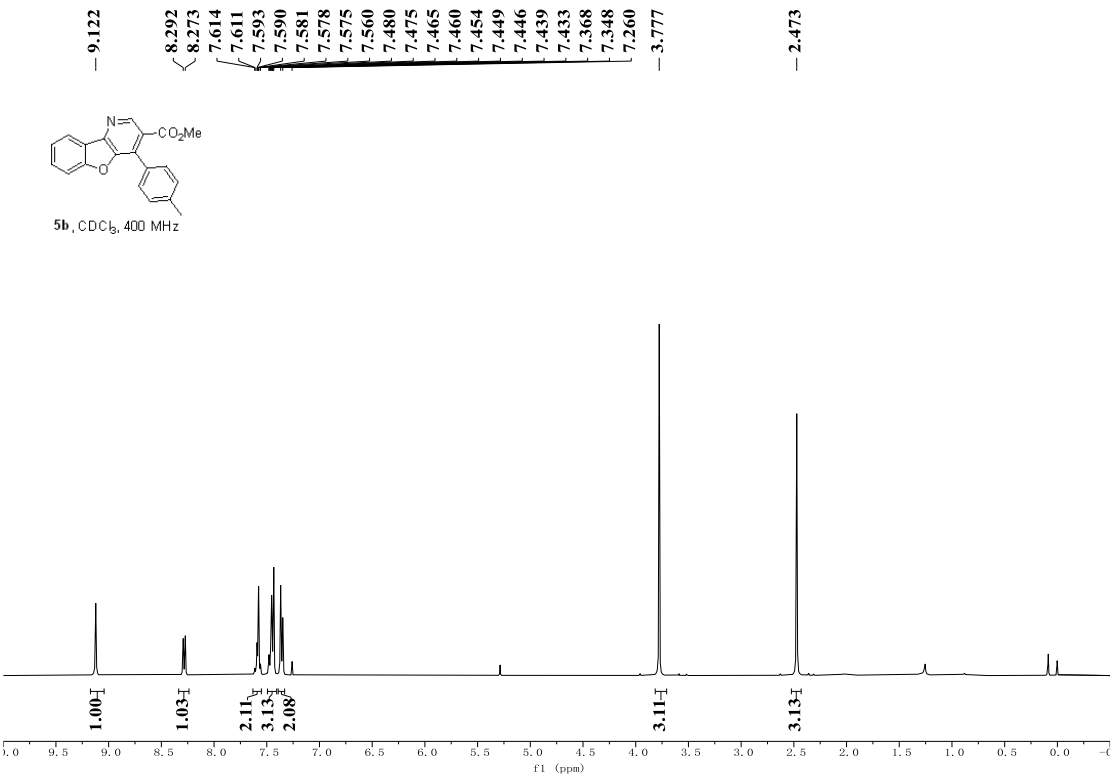


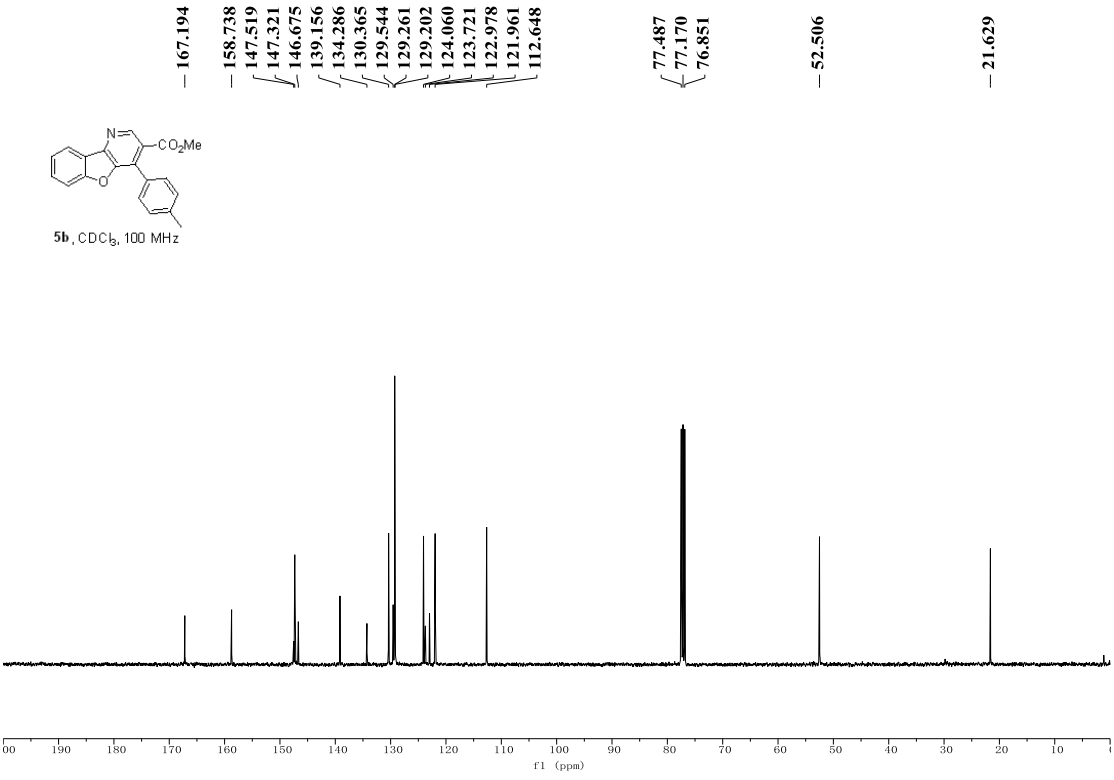
4f, $CDCl_3$, 100 MHz

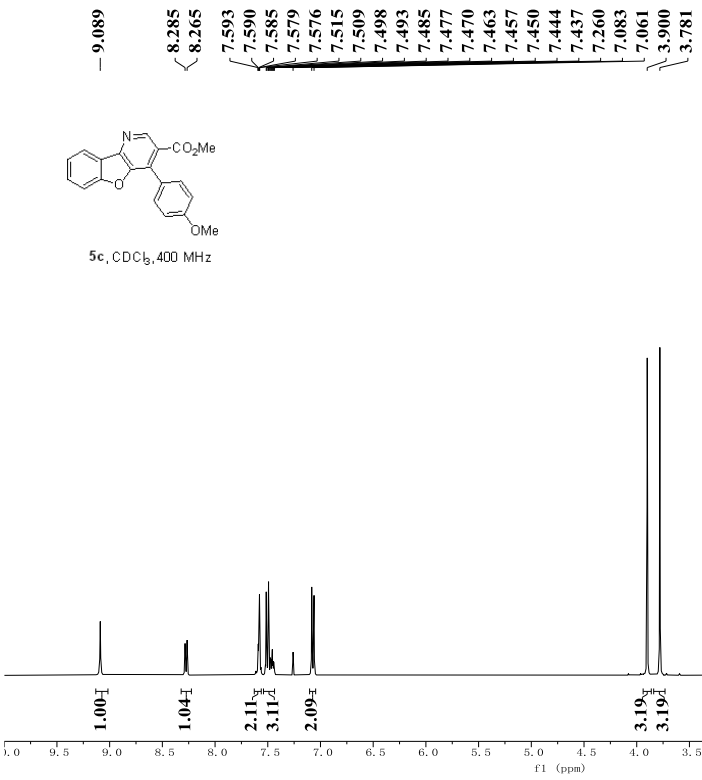



9.144
8.302
8.300
8.297
8.283
8.280
8.278
7.619
7.606
7.601
7.598
7.585
7.581
7.577
7.575
7.571
7.560
7.557
7.553
7.548
7.546
7.539
7.536
7.533
7.532
7.527
7.523
7.520
7.518
7.514
7.488
7.483
7.471
7.468
7.464
7.452
7.448
7.260
3.747
CO2Me
5a, CDCl3, 400 MHz
1.00
1.02
8.46
3.04
f1 (ppm)

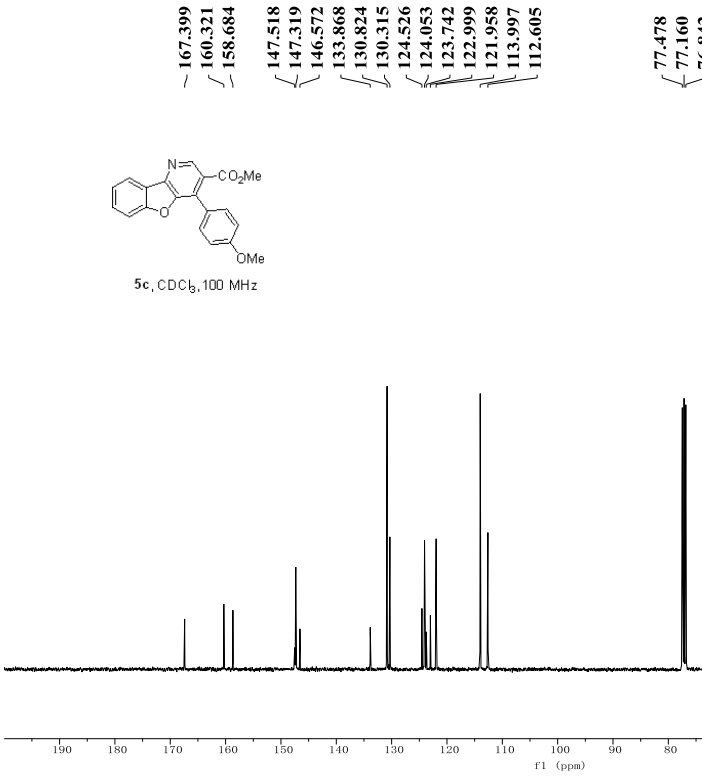

167.096
158.826
147.444
147.379
146.860
134.153
132.704
130.440
129.265
129.093
128.459
124.117
123.777
123.000
122.010
112.670
77.478
77.161
76.843
52.468
CO2Me
5a, CDCl3, 100 MHz
f1 (ppm)


9.122
8.292
8.273
7.614
7.611
7.593
7.590
7.581
7.578
7.575
7.560
7.480
7.475
7.465
7.460
7.454
7.449
7.446
7.439
7.433
7.368
7.348
7.260
3.777
2.473
CO2Me
5b, CDCl3, 400 MHz
1.00
1.03
2.11
3.13
2.08
3.11
3.13
f1 (ppm)

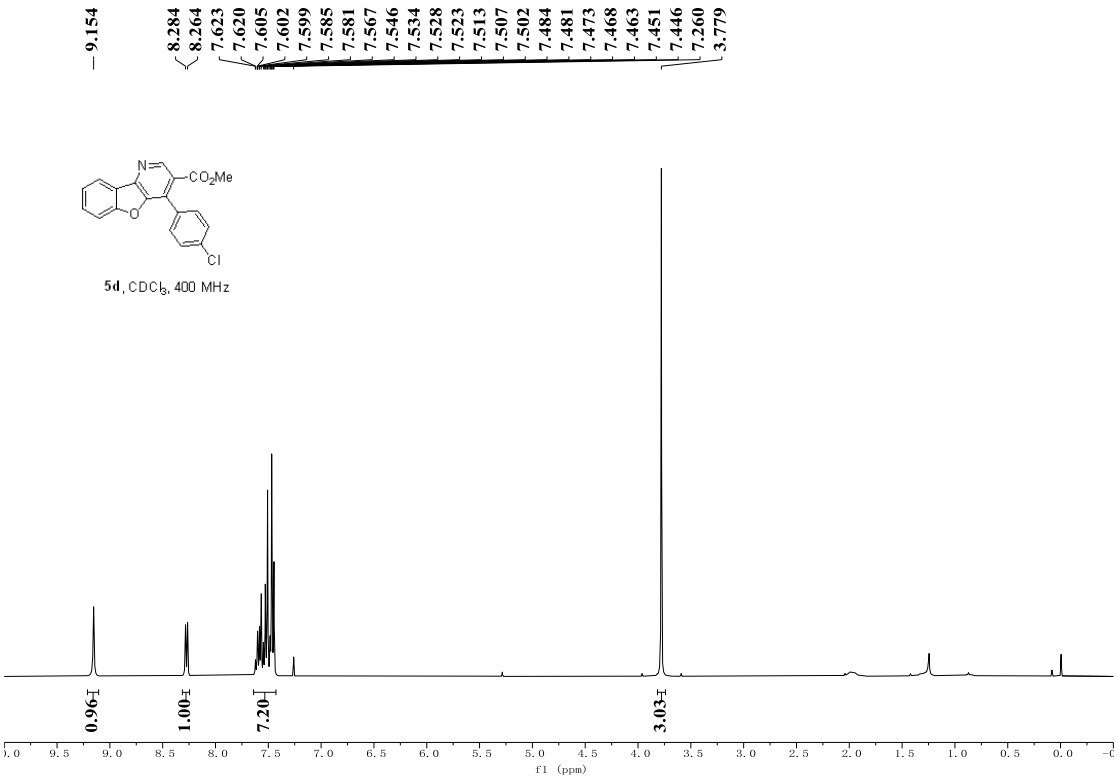

167.194
158.738
147.519
147.321
146.675
139.156
134.286
130.365
129.544
129.261
129.202
124.060
123.721
122.978
121.961
112.648
77.487
77.170
76.851
52.506
21.629
CO2Me
5b, CDCl3, 100 MHz
f1 (ppm)

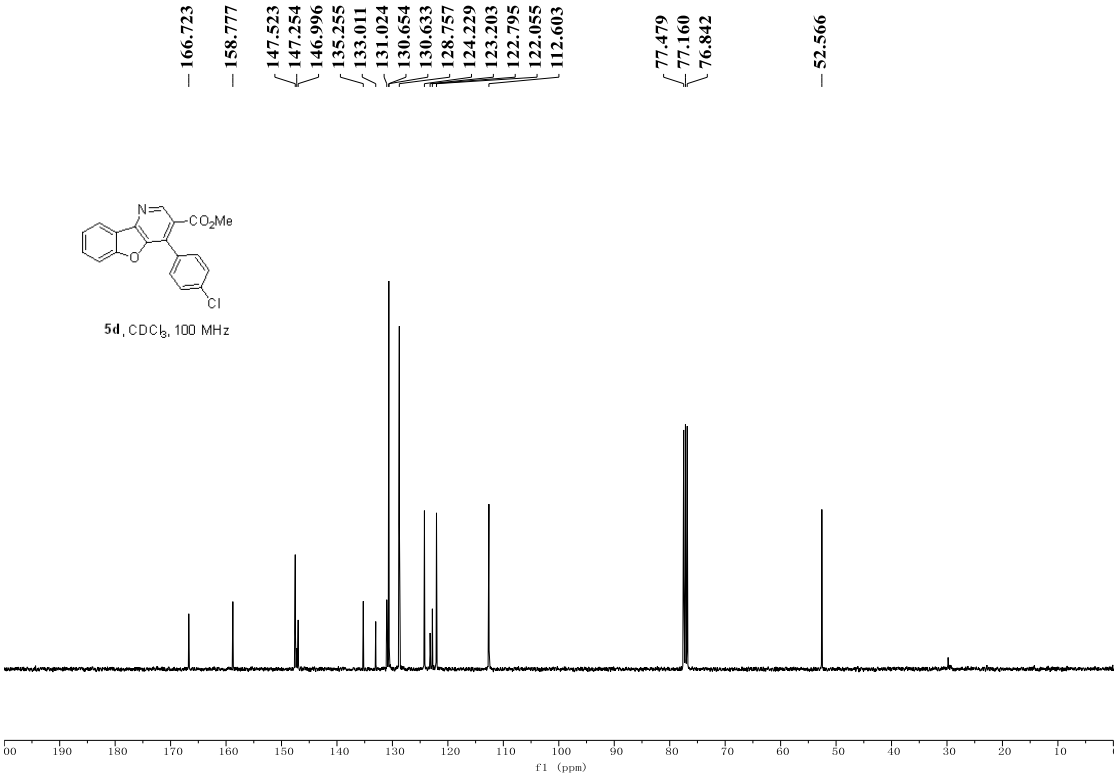


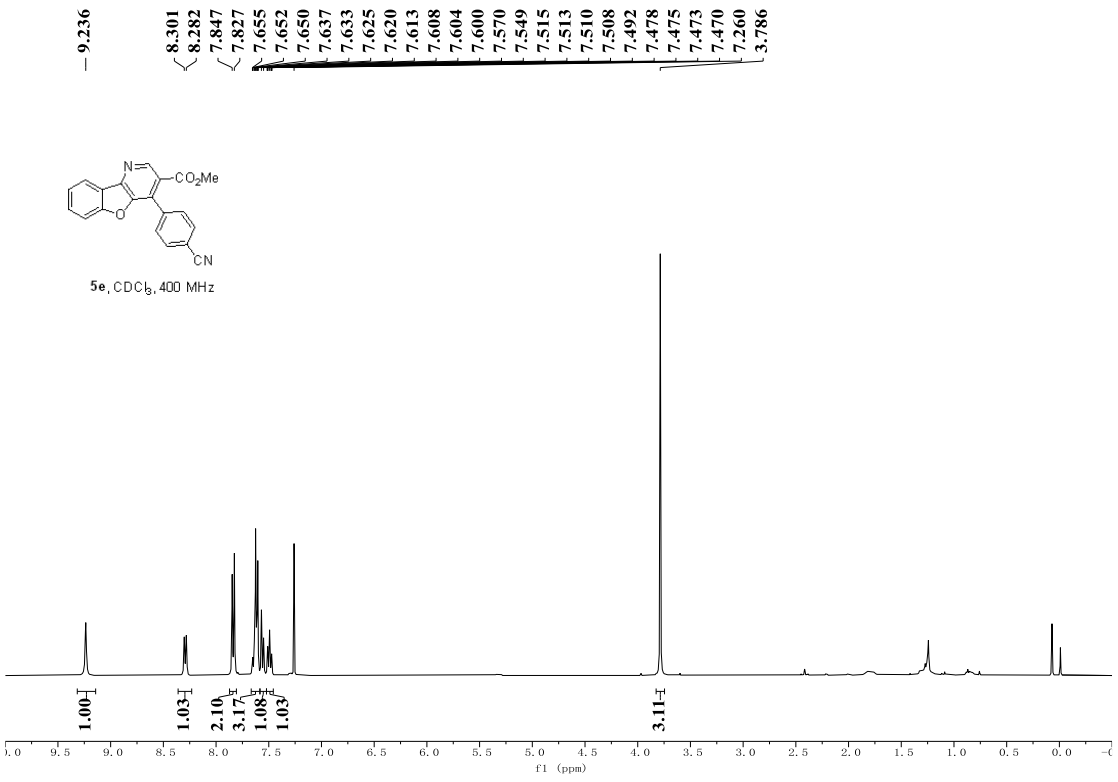
5c, $CDCl_3$, 400 MHz

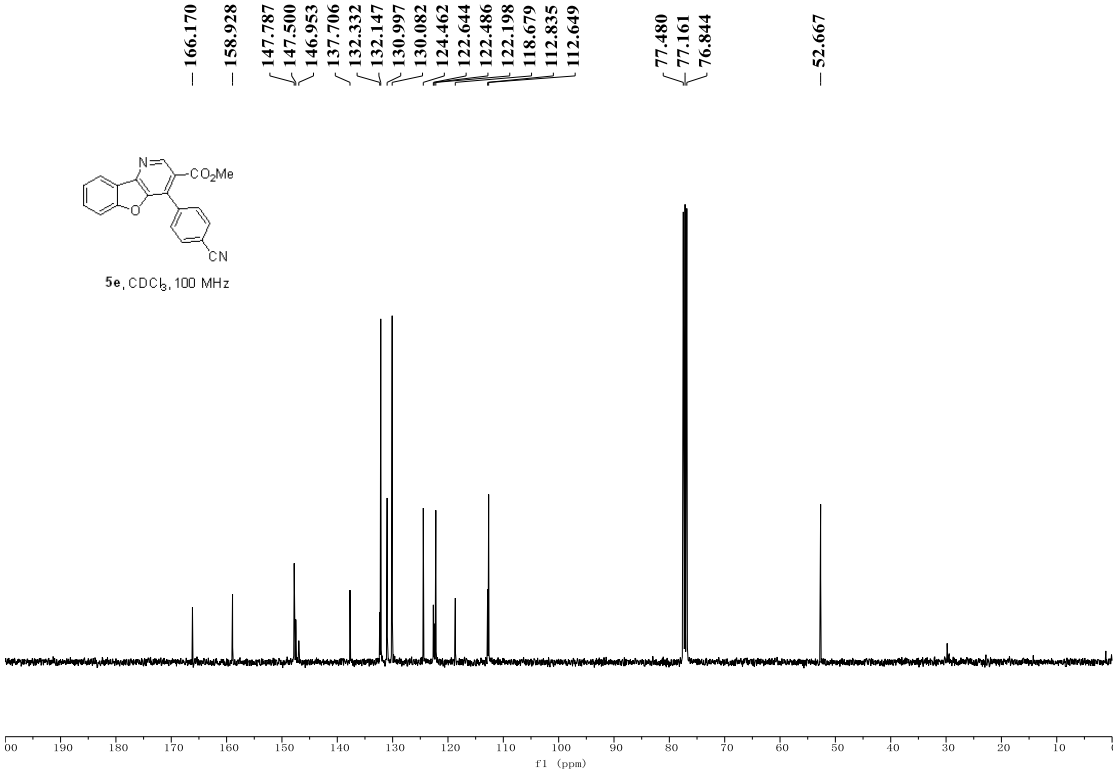


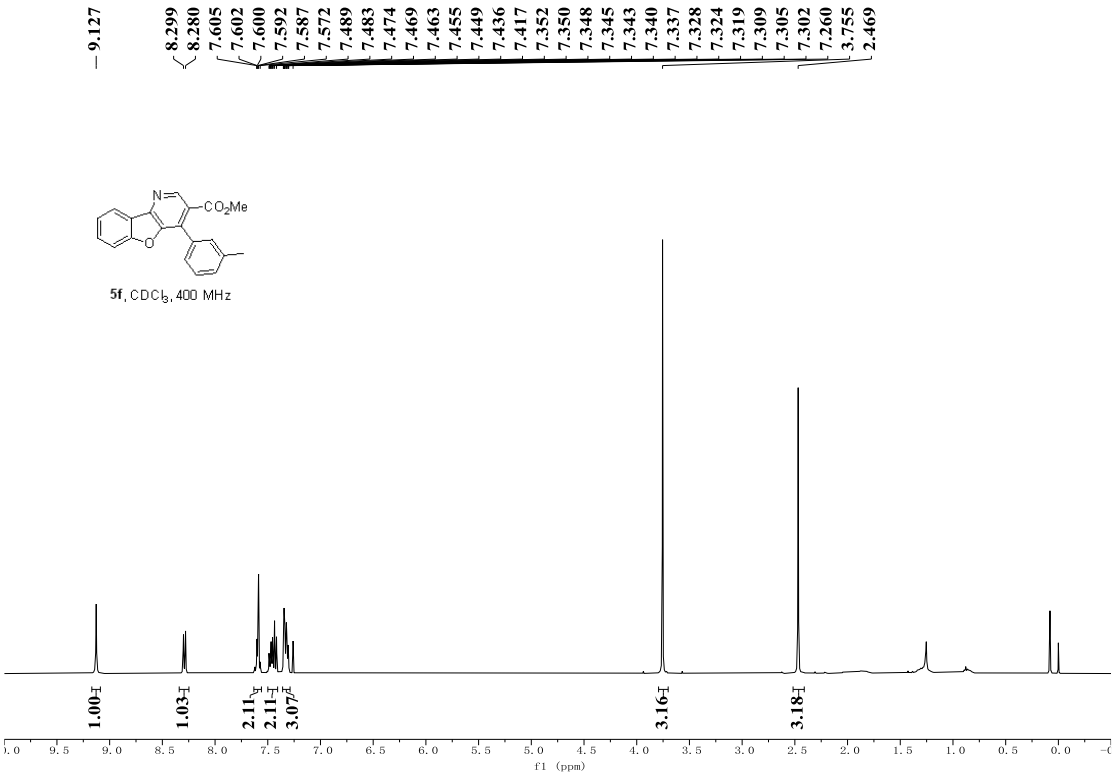
5c, $CDCl_3$, 100 MHz

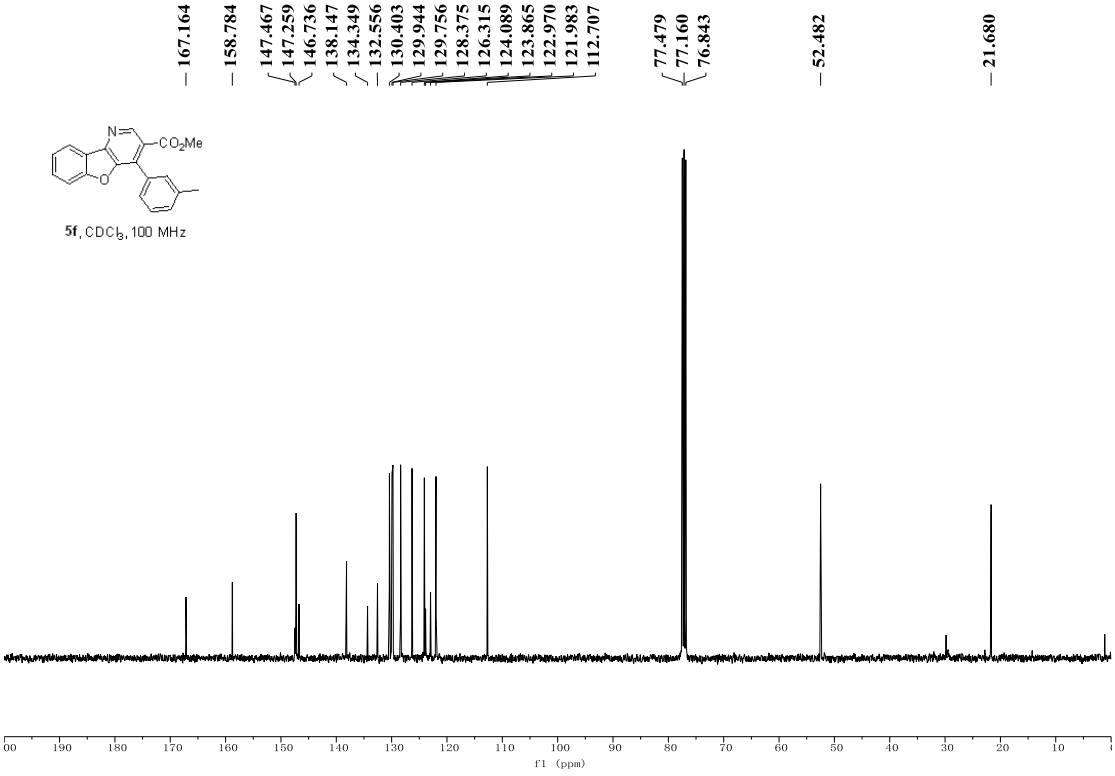

9.154
8.284
8.264
7.623
7.620
7.605
7.602
7.599
7.585
7.581
7.567
7.546
7.534
7.528
7.523
7.513
7.507
7.502
7.484
7.481
7.473
7.468
7.463
7.451
7.446
7.260
3.779
CO2Me
Cl
5d, CDCl3, 400 MHz
0.96
1.00
7.20
3.03
f1 (ppm)

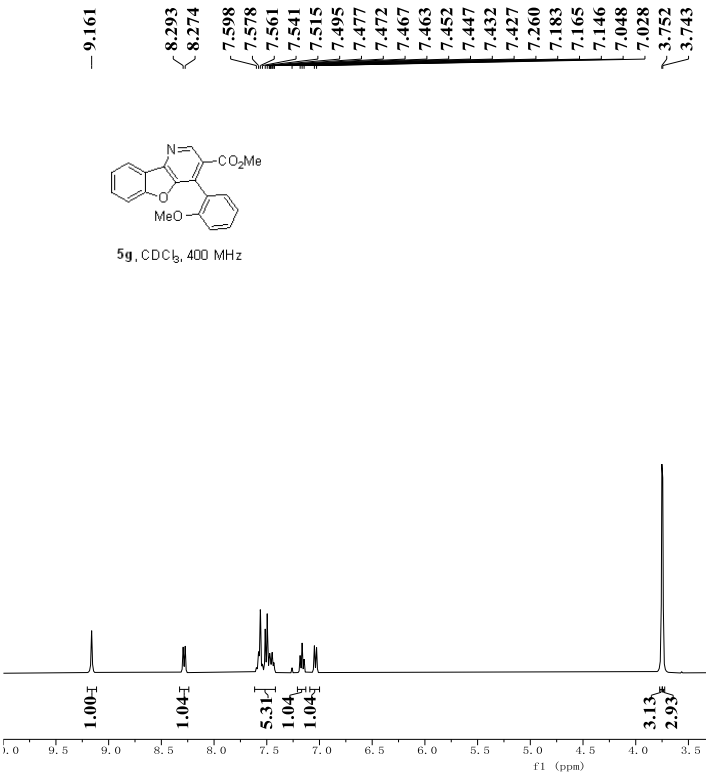

166.723
158.777
147.523
147.254
146.996
135.255
133.011
131.024
130.654
130.633
128.757
124.229
123.203
122.795
122.055
112.603
77.479
77.160
76.842
52.566
CO2Me
Cl
5d, CDCl3, 100 MHz
f1 (ppm)


9.236
8.301
8.282
7.847
7.827
7.655
7.652
7.650
7.637
7.633
7.625
7.620
7.613
7.608
7.604
7.600
7.570
7.549
7.515
7.513
7.510
7.508
7.492
7.478
7.475
7.473
7.470
7.260
3.786
CO2Me
CN
5e, CDCl3, 400 MHz
1.00
1.03
2.10
3.17
1.08
1.03
3.11
f1 (ppm)

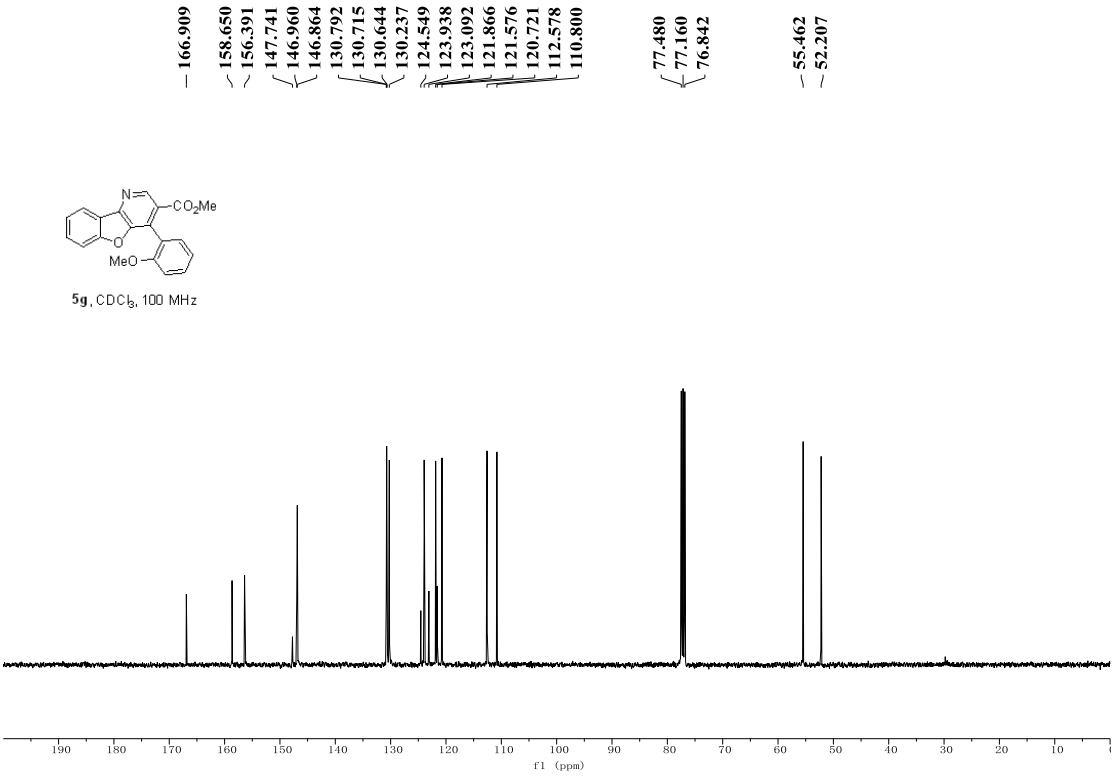

166.170
158.928
147.787
147.500
146.953
137.706
132.332
132.147
130.997
130.082
124.462
122.644
122.486
122.198
118.679
112.835
112.649
77.480
77.161
76.844
52.667
CO2Me
CN
5e, CDCl3, 100 MHz
f1 (ppm)


9.127
8.299
8.280
7.605
7.602
7.600
7.592
7.587
7.572
7.489
7.483
7.474
7.469
7.463
7.455
7.449
7.436
7.417
7.352
7.350
7.348
7.345
7.343
7.340
7.337
7.328
7.324
7.319
7.309
7.305
7.302
7.260
3.755
2.469
CO2Me
5f, CDCl3, 400 MHz
1.00
1.03
2.11
2.11
3.07
3.16
3.18
f1 (ppm)

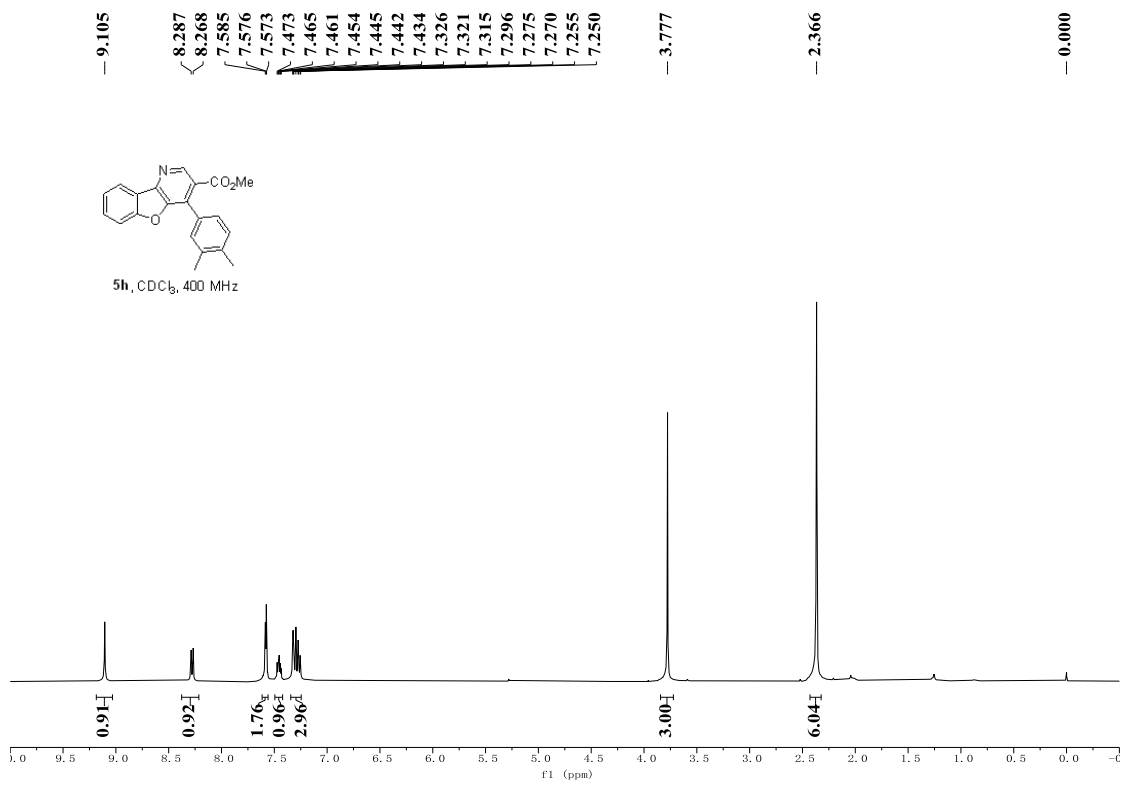

167.164
158.784
147.467
147.259
146.736
138.147
134.349
132.556
130.403
129.944
129.756
128.375
126.315
124.089
123.865
122.970
121.983
112.707
77.479
77.160
76.843
52.482
21.680
CO2Me
5f, CDCl3, 100 MHz
f1 (ppm)

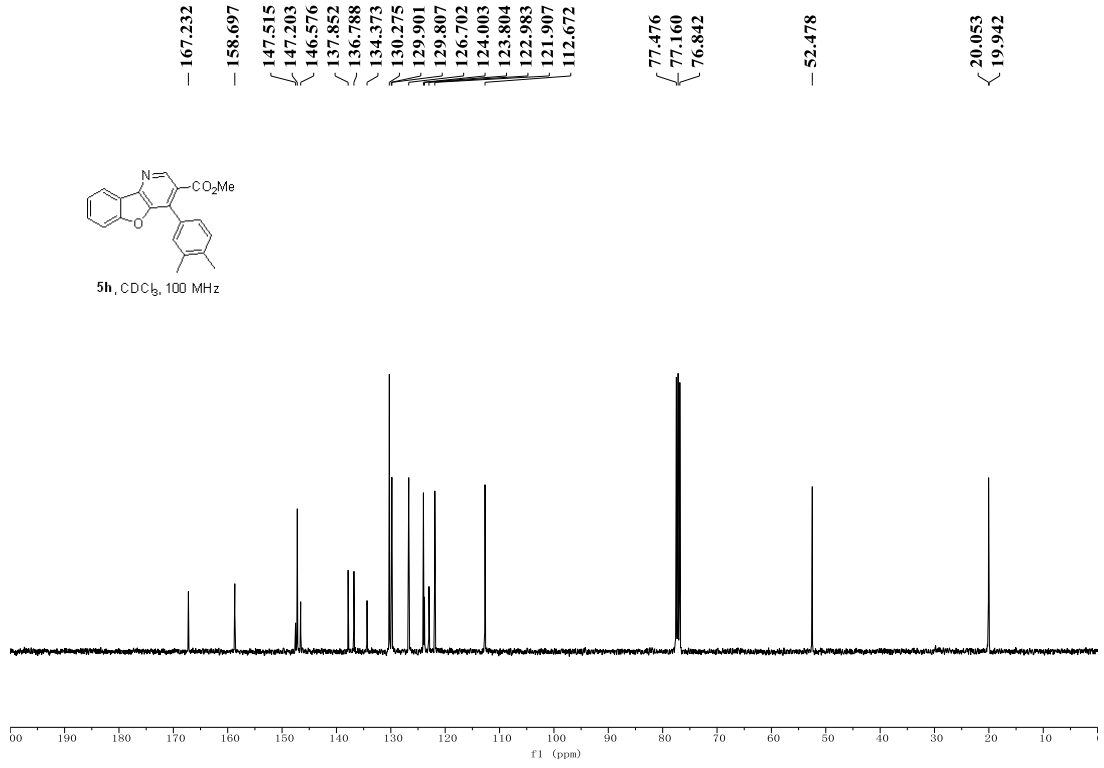


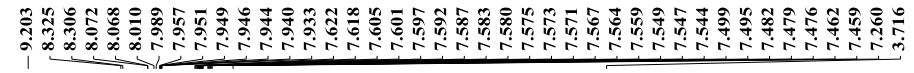
5g, $CDCl_3$, 400 MHz

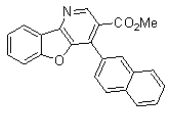


5g, $CDCl_3$, 100 MHz

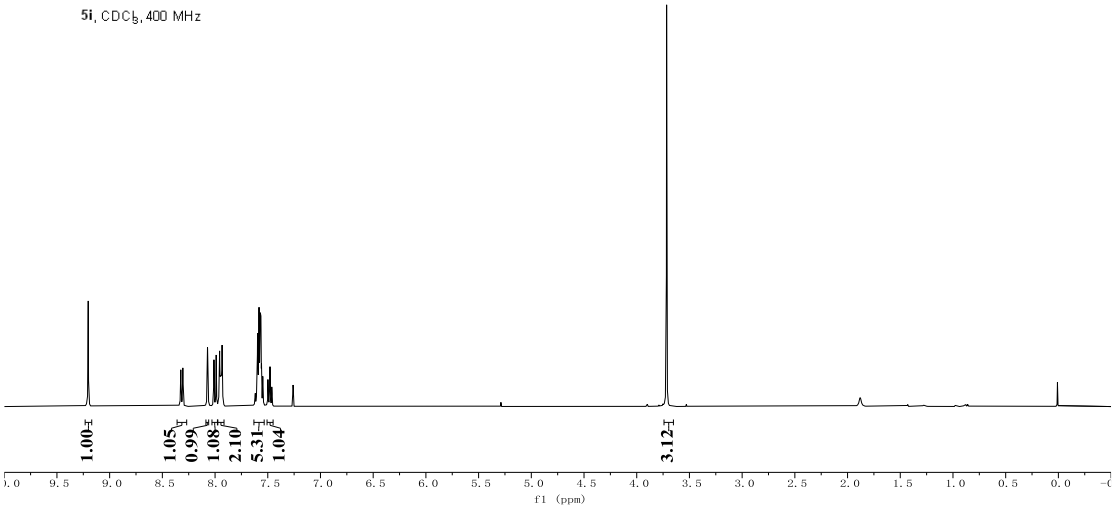

9.105
8.287
8.268
7.585
7.576
7.573
7.473
7.465
7.461
7.454
7.445
7.442
7.434
7.326
7.321
7.315
7.296
7.275
7.270
7.255
7.250
3.777
2.366
0.000
CO2Me
5h, CDCl3, 400 MHz
0.91
0.92
1.76
0.96
2.96
3.00
6.04
f1 (ppm)

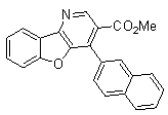

167.232
158.697
147.515
147.203
146.576
137.852
136.788
134.373
130.275
129.901
129.807
126.702
124.003
123.804
122.983
121.907
112.672
77.476
77.160
76.842
52.478
20.053
19.942
CO2Me
5h, CDCl3, 100 MHz
f1 (ppm)



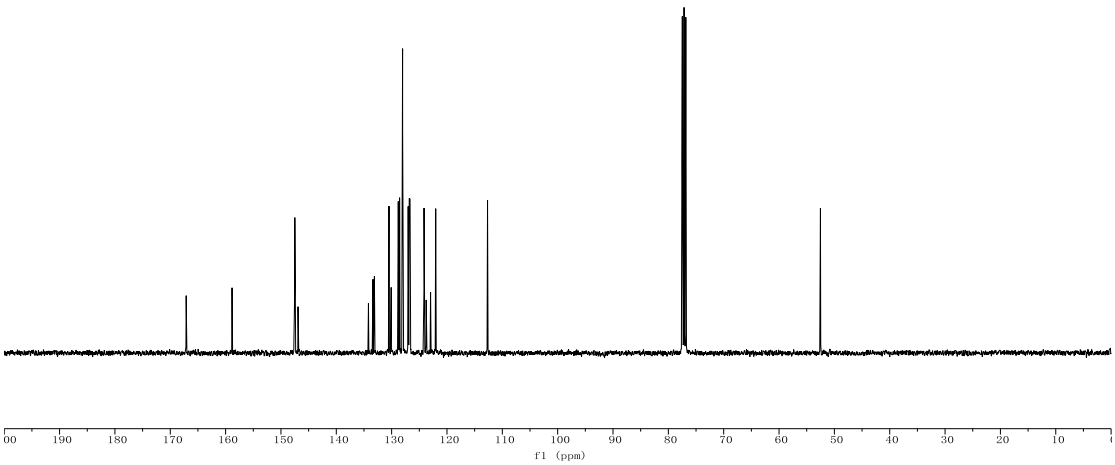


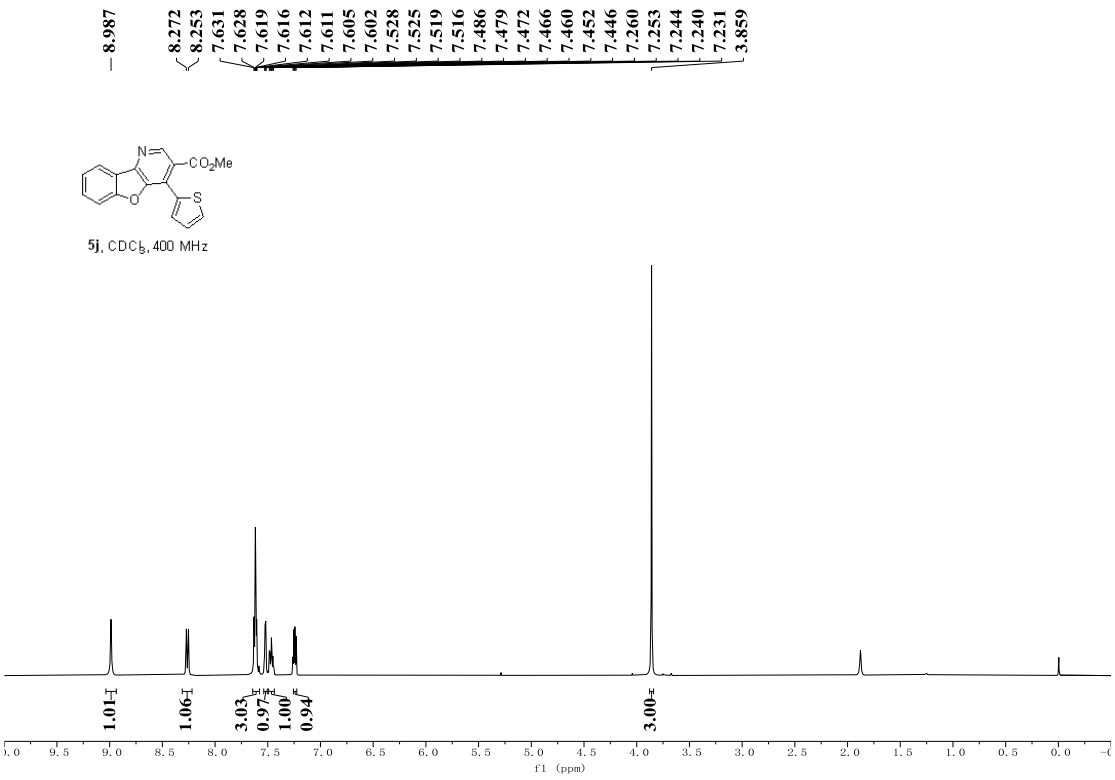
5i, $CDCl_3$, 400 MHz

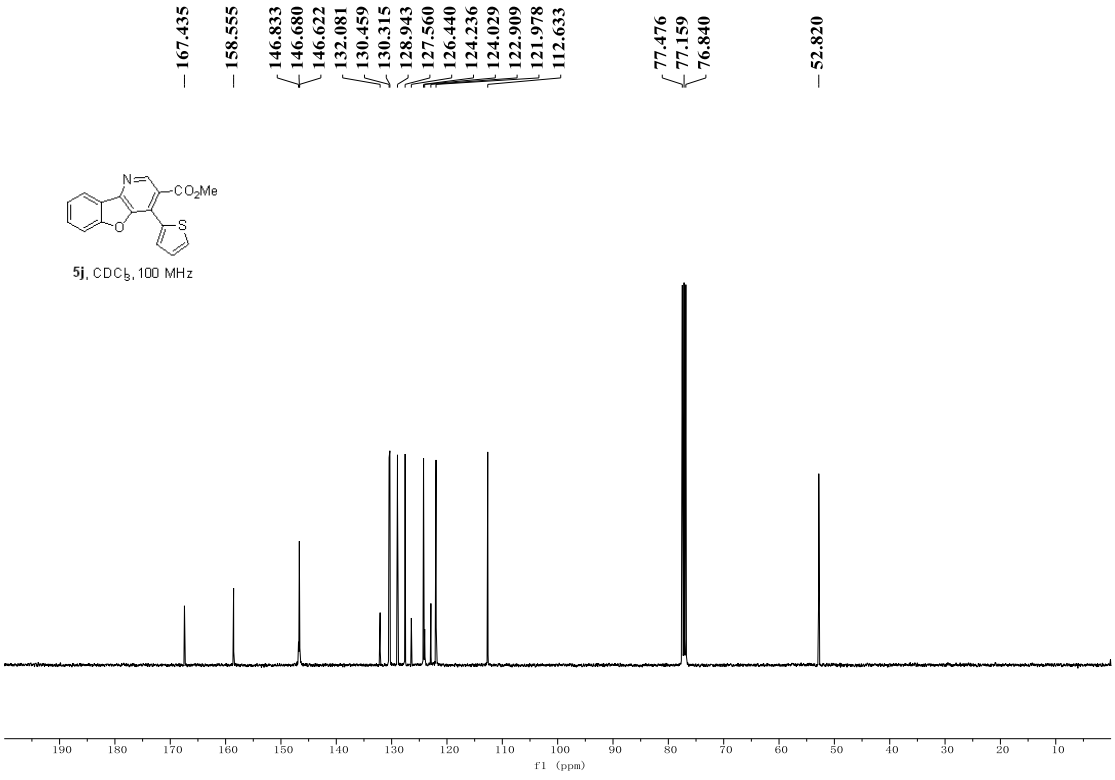


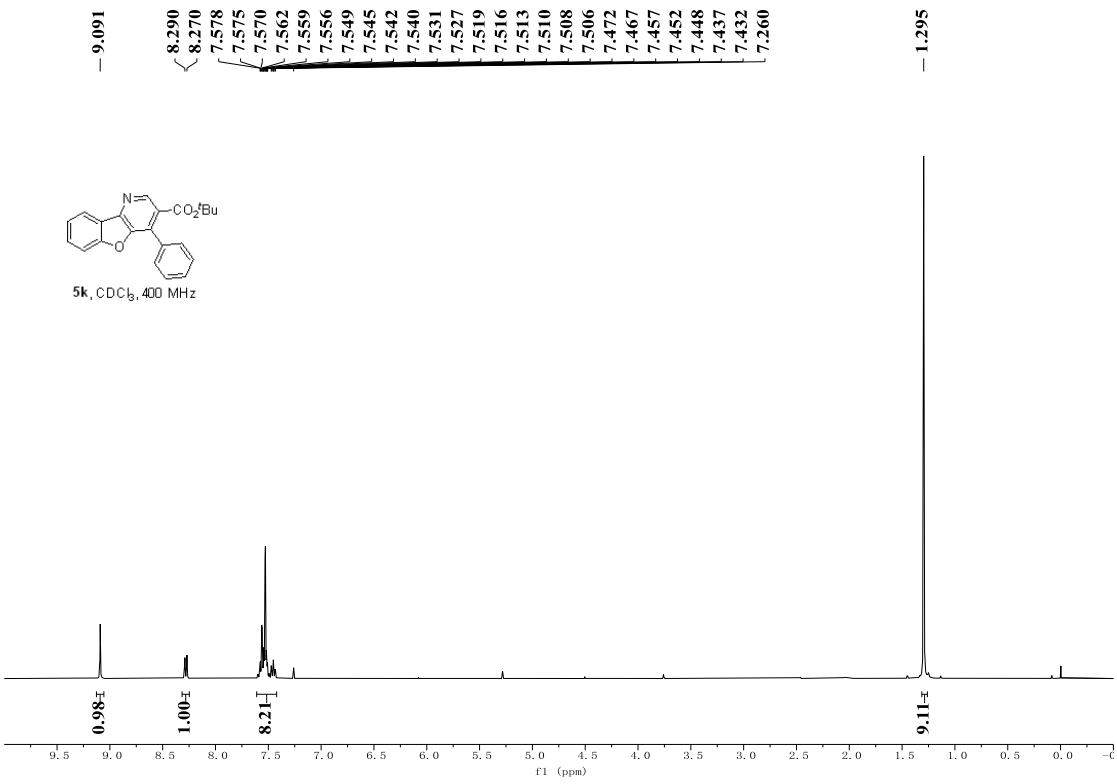


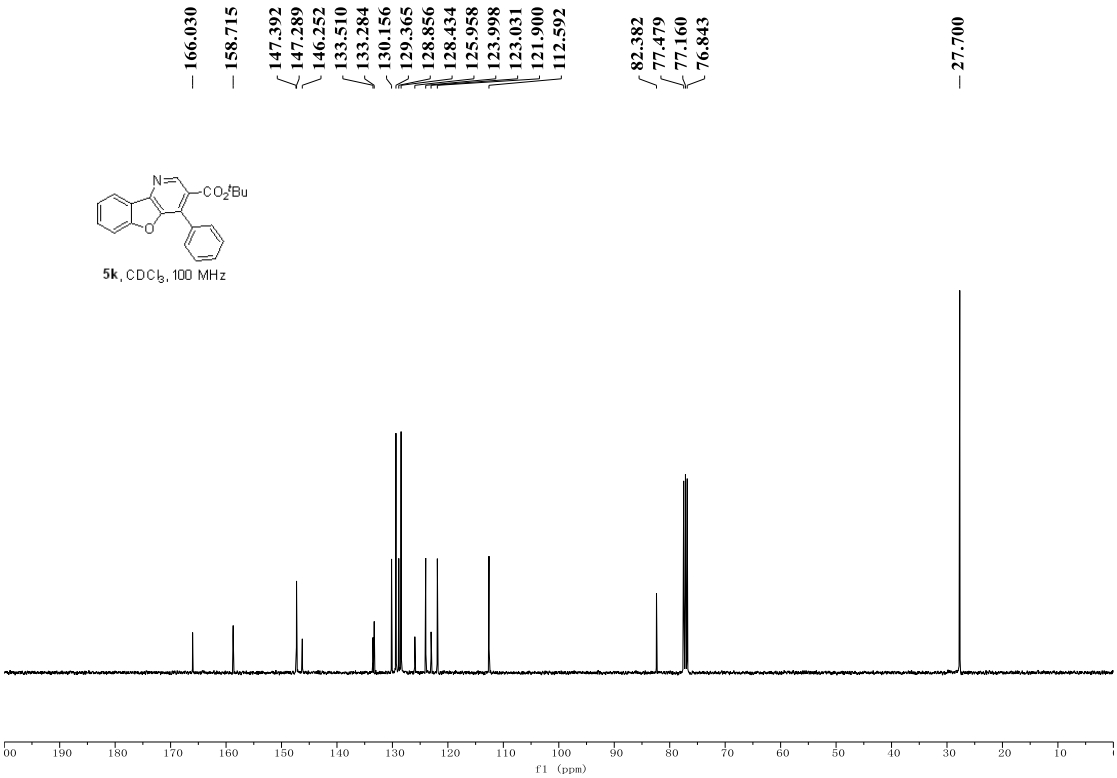
5i, $CDCl_3$, 100 MHz

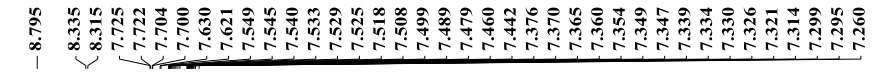


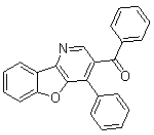

8.987
8.272
8.253
7.631
7.628
7.619
7.616
7.612
7.611
7.605
7.602
7.528
7.525
7.519
7.516
7.486
7.479
7.472
7.466
7.460
7.452
7.446
7.260
7.253
7.244
7.240
7.231
3.859
CO2Me
N
O
S
5j, CDCl3, 400 MHz
1.01
1.06
3.03
0.97
1.00
0.94
3.00
f1 (ppm)


167.435
158.555
146.833
146.680
146.622
132.081
130.459
130.315
128.943
127.560
126.440
124.236
124.029
122.909
121.978
112.633
77.476
77.159
76.840
52.820
CO2Me
N
O
S
5j, CDCl3, 100 MHz
f1 (ppm)

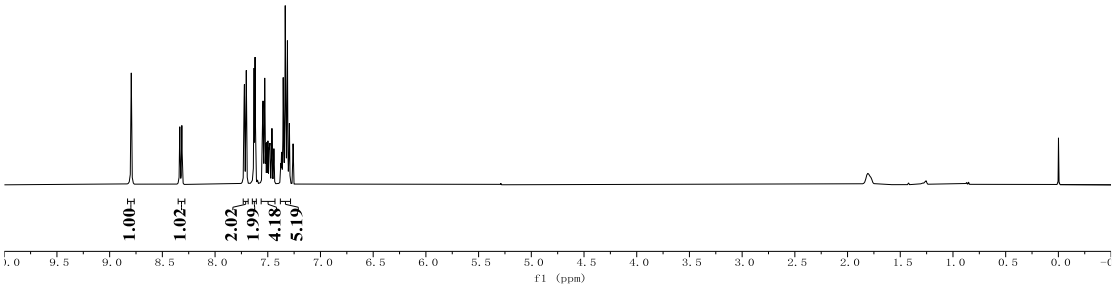

9.091
8.290
8.270
7.578
7.575
7.570
7.562
7.559
7.556
7.549
7.545
7.542
7.540
7.531
7.527
7.519
7.516
7.513
7.510
7.508
7.506
7.472
7.467
7.457
7.452
7.448
7.437
7.432
7.260
1.295
CO2tBu
5k, CDCl3, 400 MHz
0.98
1.00
8.21
9.11
f1 (ppm)

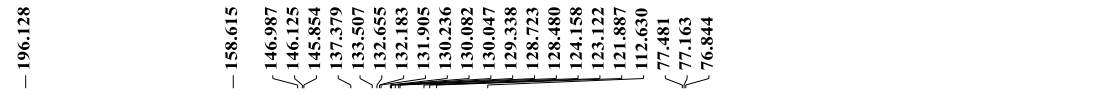

166.030
158.715
147.392
147.289
146.252
133.510
133.284
130.156
129.365
128.856
128.434
125.958
123.998
123.031
121.900
112.592
82.382
77.479
77.160
76.843
27.700
CO2tBu
5k, CDCl3, 100 MHz
f1 (ppm)

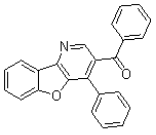




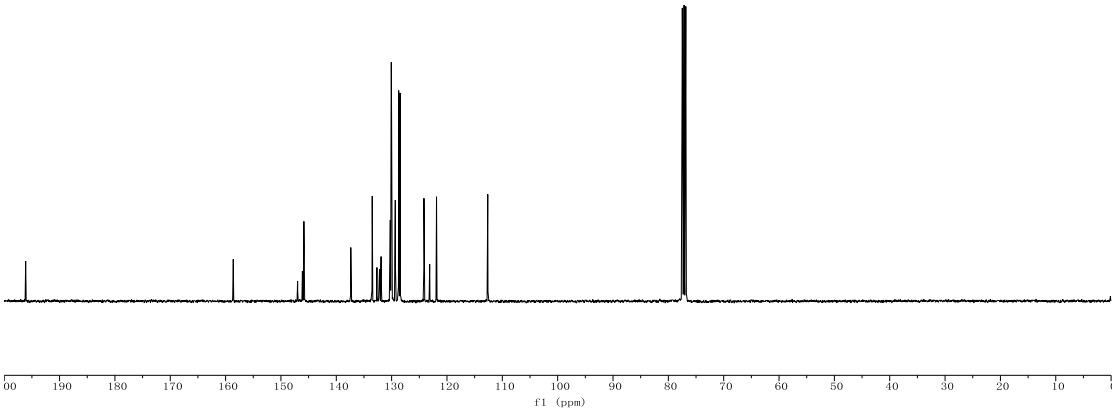
5l, $CDCl_3$, 400 MHz

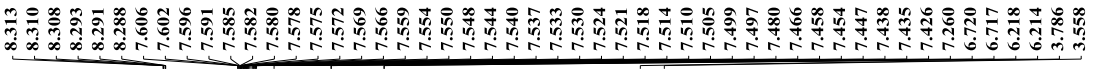


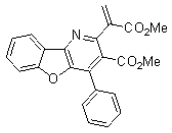




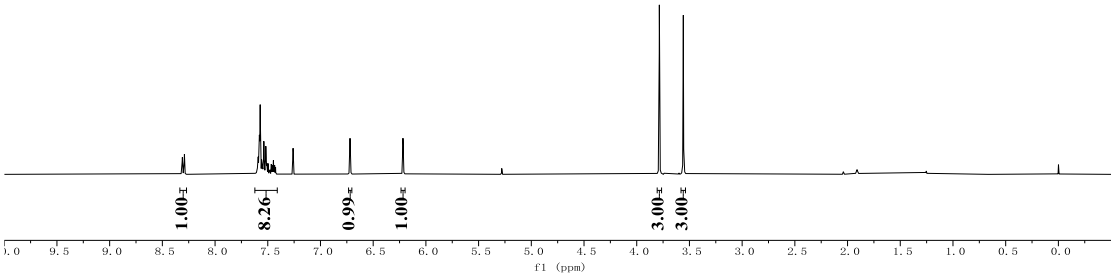
5l, $CDCl_3$, 100 MHz

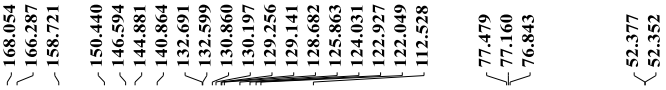


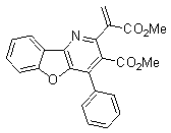




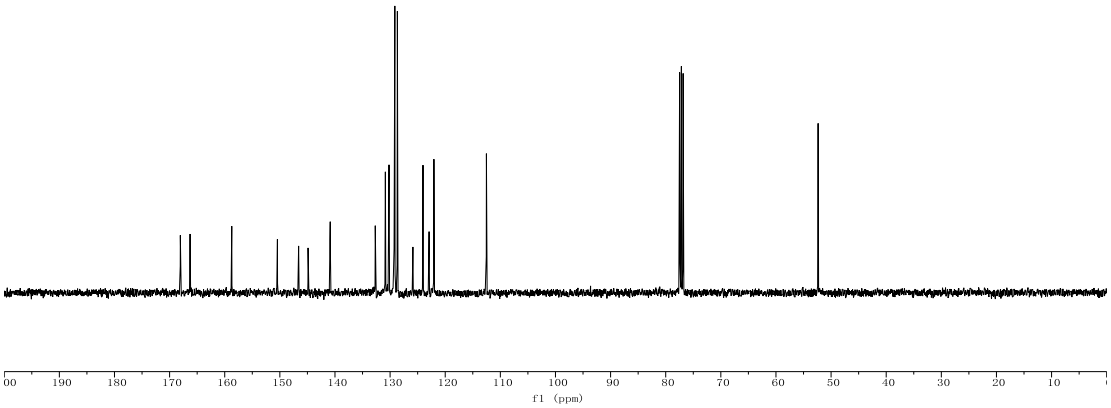
6a, $CDCl_3$, 400 MHz

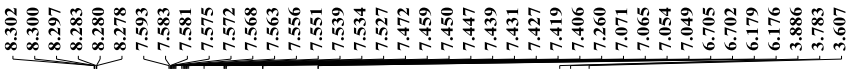


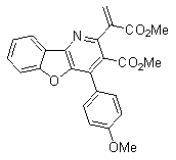




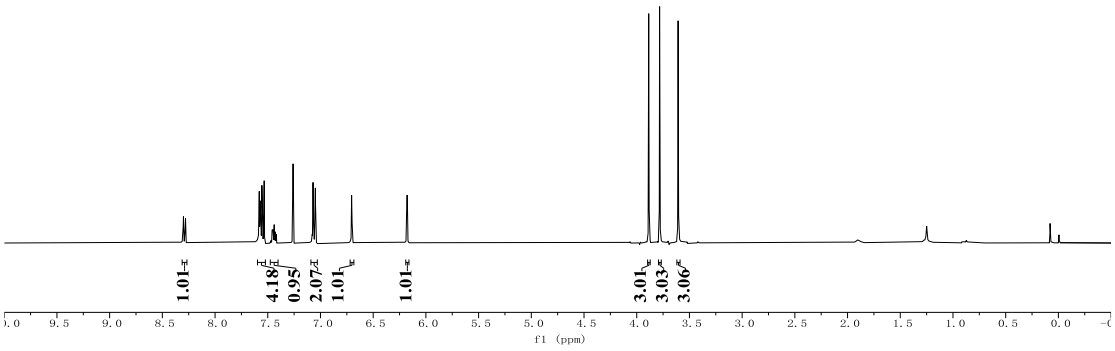
6a, $CDCl_3$, 100 MHz

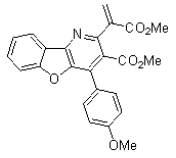




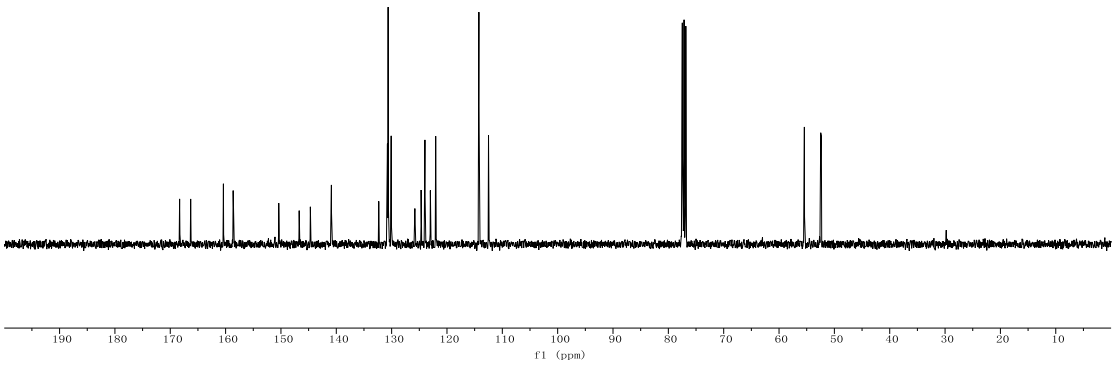


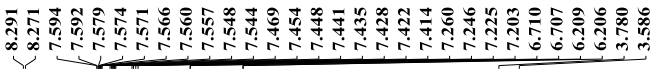
6b, $CDCl_3$, 400 MHz

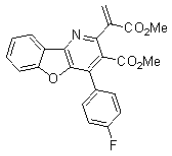




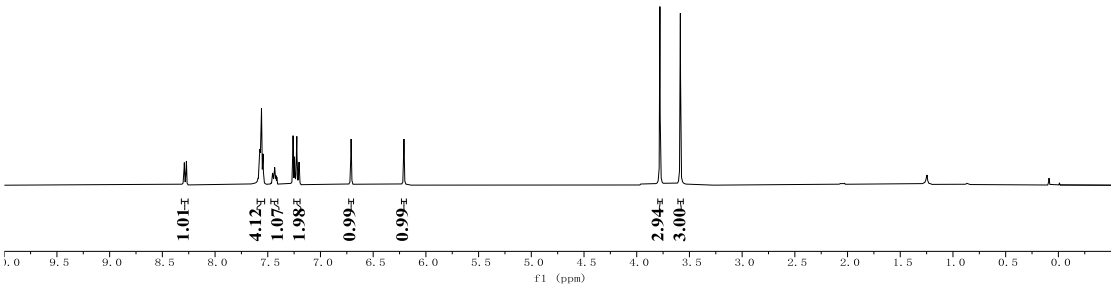
6b, $CDCl_3$, 100 MHz

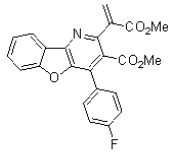




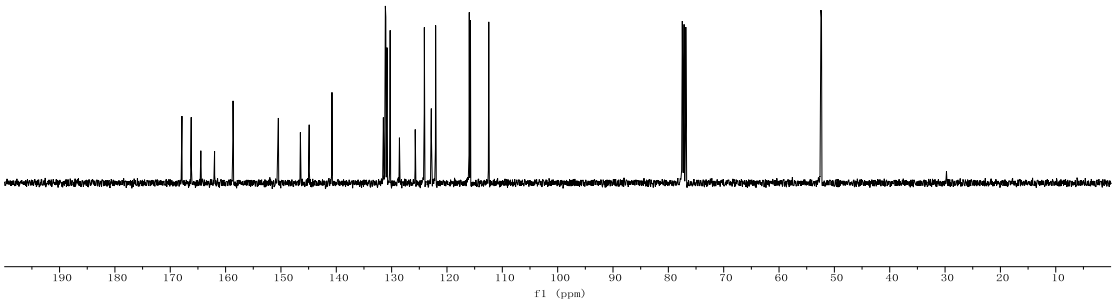


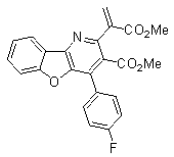
6c, $CDCl_3$, 400 MHz



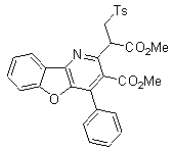


6c, $CDCl_3$, 100 MHz

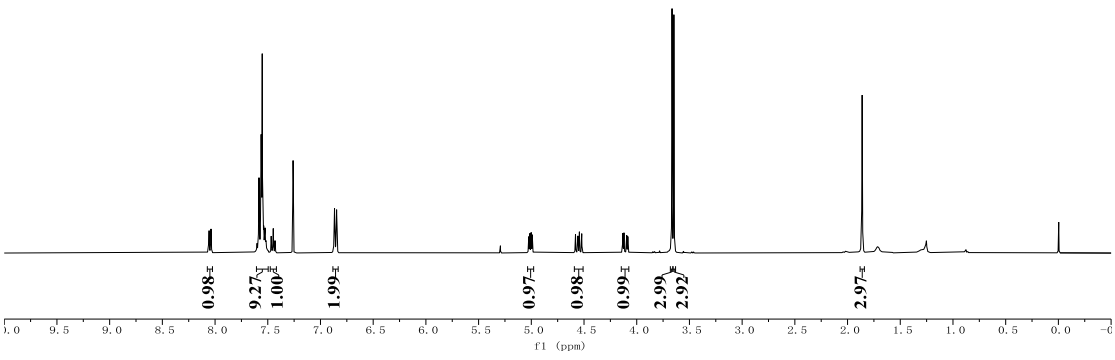


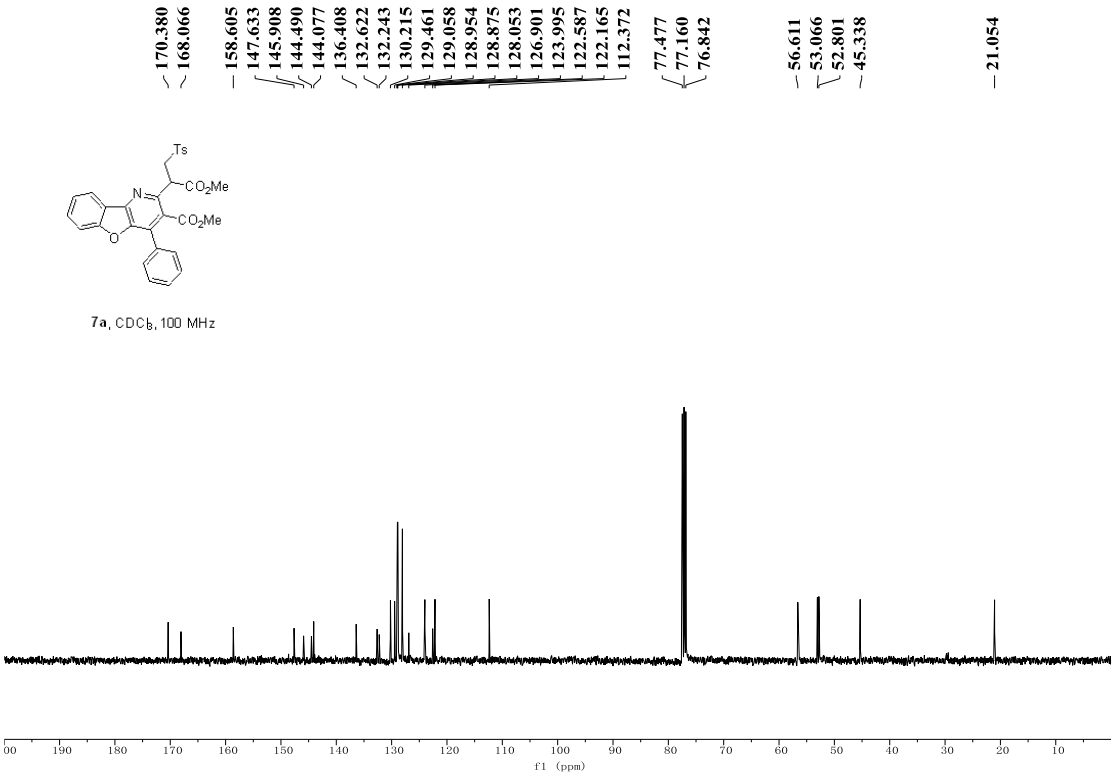


6c, $CDCl_3$, 376 MHz



7a, $CDCl_3$, 400 MHz





7a, $CDCl_3$, 100 MHz