The ESI for *Org. Biomol. Chem.*, 2022, **20**, 5575–5581, DOI: 10.1039/D2OB00639A, originally published on 22nd June 2022, was updated on 20th November 2024. Corrected structures for compounds **3ia** and **3ib** have been included.

Supporting Information

Cu(II)-mediated aerobic oxidative synthesis of sulfonated chromeno[4,3-*c*] pyrazol-4(2*H*)-ones

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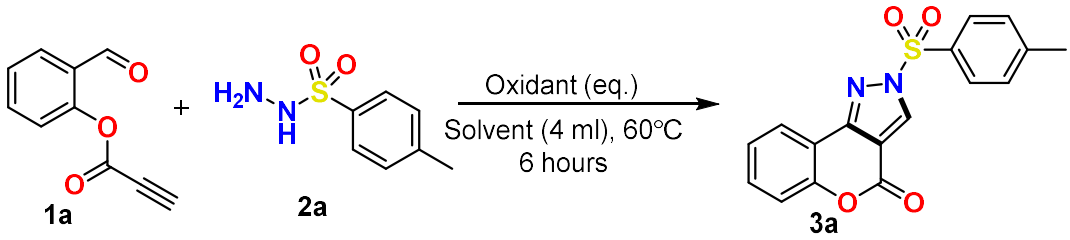
1. General consideration

Unless otherwise noted, chemicals and materials were purchased from commercial suppliers and used without further purification. All the solvents were treated according to the general methods. All ^{1}H NMR, ^{13}C NMR and ^{19}F NMR spectra were recorded on a 400 MHz Bruker FT-NMR spectrometer (400/100/376 MHz, respectively). Chemical shifts for protons are reported in parts per million downfield from tetramethylsilane and are referenced to residual in the NMR solvent. Chemical shifts for carbon are reported in parts per million downfield from tetramethylsilane and are referenced to the carbon resonances of the solvent ($CDCl_3$ = δ 77.0; DMSO = δ 39.5). The peak patterns are indicated as follows: s, singlet; d, doublet; t, triplet; m, multiplet; q, quartet; br, broad. The coupling constants, *J*, are reported in Hertz (Hz). High resolution mass spectroscopy data of the product were collected on an Agilent Technologies 6540 UHD Accurate-Mass Q-TOF LC/MS (ESI). Products were purified by flash chromatography on 200–300 mesh silica gels, SiO_2.

2. Further optimization of the reaction conditions

Table S1. Further optimization of the reaction conditions [a]



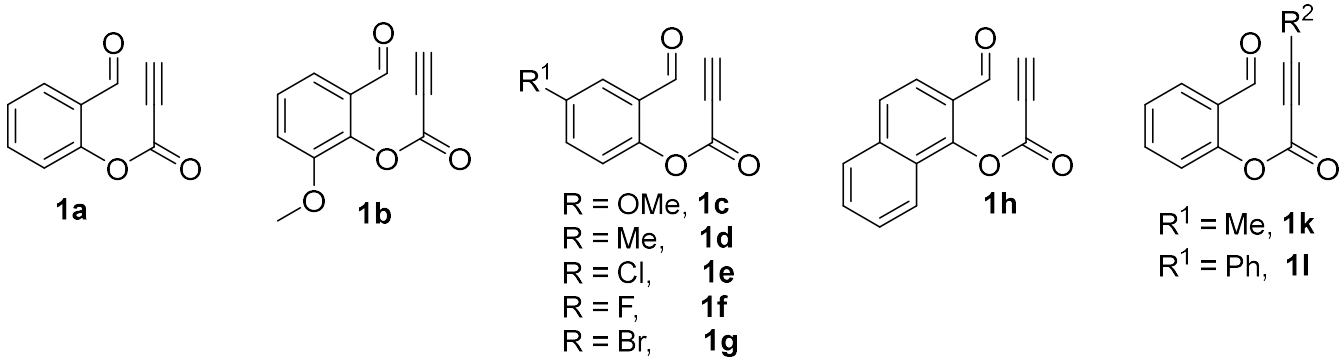
Entry	Oxidant/Lewis acid (eq.)	Solvent	Yield of **3a** (%)[b]
1	$ZnCl_2$ (1.0)	DCE	trace
2	$AlCl_3$ (1.0)	DCE	trace
3	$CuCl_2$ (1.0)	DCE	20
4	$Cu(OAc)_2$ (1.0)	DCE	74
5	$Cu(OAc)_2$ (0.5)	DCE	40
6	$Cu(OAc)_2$ (0.2)	DCE	41[c]
7	Ag_2O (1.0)	DCE	20
8	$(NH_4)_2Ce(NO_3)_6$ (1.0)	DCE	15
9	Cu_2O (1.0)	DCE	45
10	CuI (1.0)	DCE	30
11	$CuSO_4$ (1.0)	DCE	trace
12	$Co(OAc)_2$ (1.0)	DCE	trace
13	SeO_2 (1.0)	DCE	trace
14	^tBuOOH (1.0)	DCE	trace
15	$Cu(OAc)_2$ (1.0)	DCE	trace[d]
16	$Cu(OAc)_2$ (1.0)	DCE	25[e]
17	$Cu(OAc)_2$ (1.0)	DME	30[f]
18	$Cu(OAc)_2$ (1.0)	DCM	15[f]
19	$Cu(OAc)_2$ (1.0)	DMF	28[f]
20	$Cu(OAc)_2$ (1.0)	DMSO	37[f]
21	$Cu(OAc)_2$ (1.0)	THF	33[f]
22	$Cu(OAc)_2$ (1.0)	DCE	73[g] (10[h])

[a]*Reaction conditions*: **1a** (0.30 mmol), **2a** (0.33 mmol), oxidant/Lewis acid (1.00 equiv.), solvent (6.0 mL), 60 °C, 6 h, air; [b] Isolated yield based on **1a**; [c] 12 h; [d] at 30 °C; [e] at 90 °C; [f] 1,2-Dimethoxy ethane (DME); *N*,*N*-dimethyl formaldehyde (DMF); Dimethylsulfoxide (DMSO); Tetrahydrogenfuran (THF); [g] under 1 atm O_2; [h] under Ar.

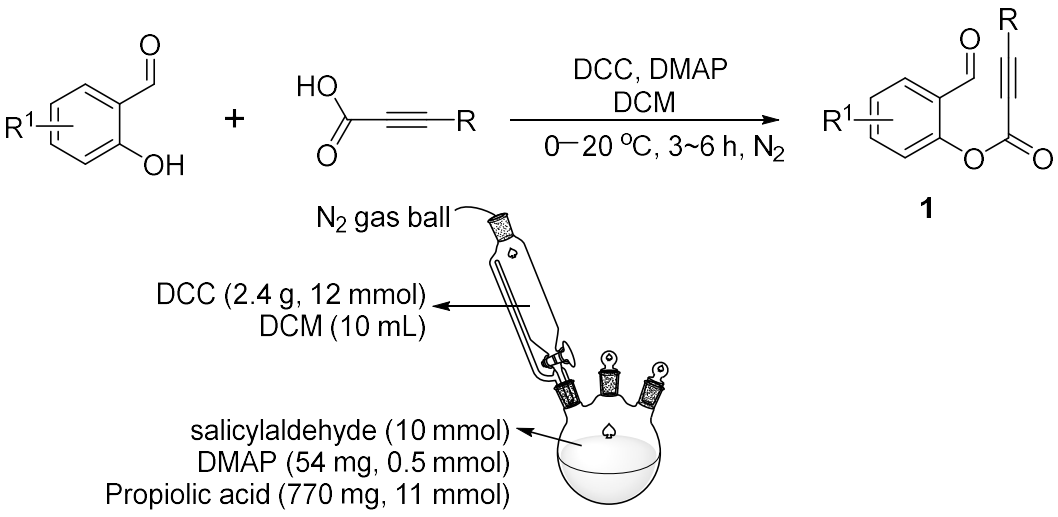
3. Synthesis of substrates 1

3.1 General procedure for the synthesis of substrates (1a–1h, and 1k–1l)

The synthesis of the substrates (**1a–1h**, **1k**, and **1l,** shown in the following Scheme S1**)** was according to reported method (Vagh, S. S.; Hou, B.-J. *Org. Lett.,* **2021**, *23*, 842–846; Chen, Y.-S.; Zheng, Y.; Chen, Z.-J.; Xie, Z.-Z.; He, X.-C.; Xiao, J.-A.; Chen, K.; Xiang, H.-Y.; Yang, H. *Org. Biomol. Chem.,* **2021**, *19*, 7074–7080).

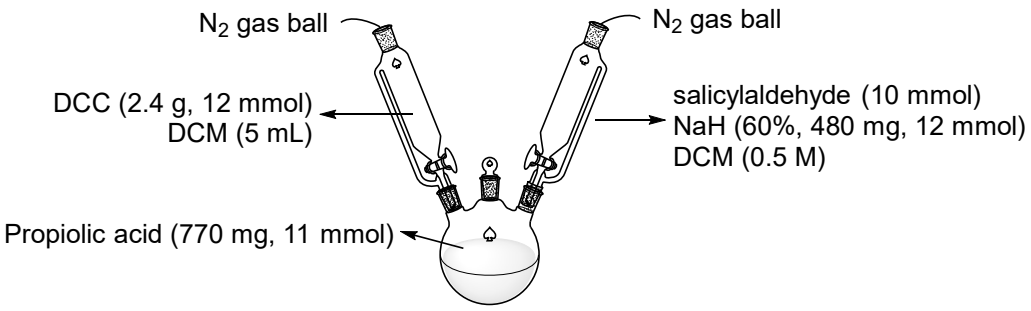


Scheme S1: The structure of substrates



Scheme S2: Apparatus of method **A** for substrate synthesis

The general **method A** for the synthesis of substrates: Into a three-neck round bottle, salicylaldehyde (1.04 mL, 10 mmol, 1.0 equiv.), prop-2-ynoic acid derivative (840 mg, 1.1 equiv.), and DMAP (36.7 mg, 0.03 equiv.) in anhydrous CH_2Cl_2 (10 mL) cooled to 0 °C, and a solution of DCC (2.06 g, 1.0 equiv) in CH_2Cl_2 (10 mL) was added dropwise in 20 min. The reaction mixture was then stirred for 10 minutes at 0 ºC and allowed to 30 ºC for 1-5 h (monitored by TLC). Precipitated urea was then filtered off and the filtrate was evaporated in vacuum. The crude residue was subjected to flash column chromatography on silica gel to obtain the pure product alkynoate **1**.

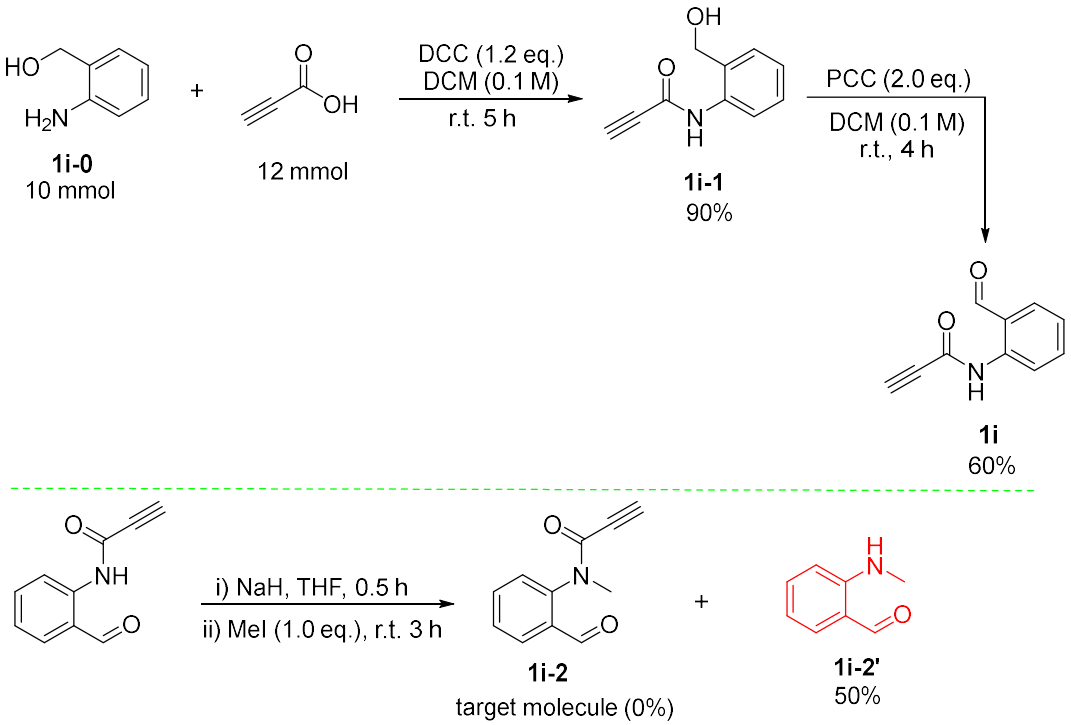


Scheme S3: Apparatus of method **B** for substrate synthesis

The general **method B** for the synthesis of substrates: Under standard Schleck manual, firstly, into one Shlenck tube 1.0 equivalent NaH was slowly added into substituted salicylaldehyde dichloromethane solution under 0 ºC and the mixture was stirred and kept under nitrogen protection. In another three necked round bottle, DCC (1.2 eq.) in DCM (0.5 M) were added dropwise into propiolic

acid (1.1 eq.) dichloromethane (0.1M) solution under 0 °C, after addition, then the deprotonated salicylaldehyde was added into activated propiolic acid ester solution via constant pressure dropping funnel (with PTFE gate), after addition, the solution was warmed to room temperature for another several hours, reaction procession was monitored by TLC.

3.2 Procedure for the synthesis of 1i

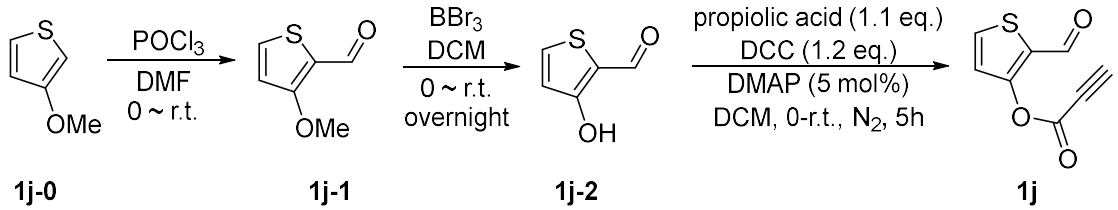


Scheme S4: Synthetic route to **1i**

According to the reported literature (Ming Lang, Jian Wang, *Org. Chem. Front.*, 2019, *6*, 1367-1371), **1i** was synthesized by two steps as shown in the Scheme S2. Dicyclohexylmethanediimine (DCC) was used to promote amidation

and pyridinium chlorochromate (PCC) was involved in the oxidation. Furthermore, we have tried to synthesize the **1i-2** to exclude the impact of free hydrogen bonding effect on this oxidative cyclolization, however, no target **1i**–**2** was obtained, only **1i**–**2'** was isolated.

3.3 Procedure for the synthesis of 1j



1j-0 **1j-1** **1j-2** **1j**

Scheme S5: Synthesis route for **1j**

Substrate **1j** was synthesized via three steps from commercial available starting material 3-methoxy thiophene as shown in Scheme S5.

(I) DMF as the selective 2-position electrophilic formylation of 3-methoxy thiophene (5 g, 44 mmol) under ice-bath and stirred at room temperature for several hours. After finished, the reaction mixture was poured into ice-water. Precipitation was filtrated, washed with water/petroleum and dried under vaccum (4.5 g grey solid, 72 % yield), which afforded the desired **1j-1**.

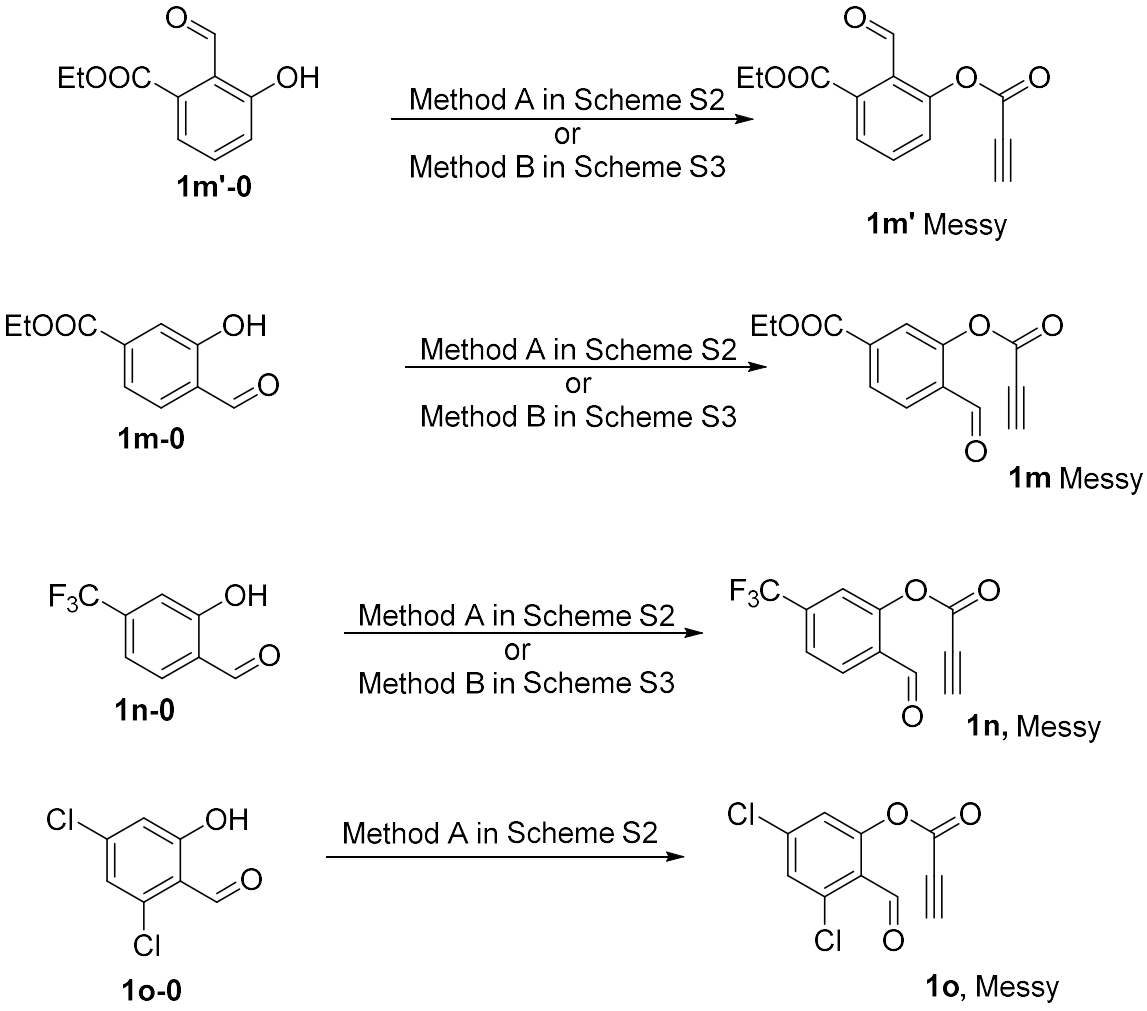
(II) Demethylation: Into an oven-dried, 150 mL three-necked round bottle layered with **1j-1** (2.13 g, 15 mmol), stir bar and anhydrous DCM (50 mL). The

mixture was stirred and cooled to 0 ℃. BBr_3 (2 M, 10 mL, 1.33 eq.) was added into the mixture via constant pressure dropping funnel (with PTFE gate) under nitrogen gas protected. After addition finished, the mixture was slowly warmed to room temperature (25 centigrade), stirred, and monitored by TLC. Precipitation slowly grew as the reaction proceeded. After nearly 16 hours, the starting material was exhausted. The reaction mixture was quenched with saturated NH_4Cl (10 mL), diluted with DCM (50 mL), washed with brine (20 mL×2), dried over anhydrous magnesium sulfate, concentrated under reduced pressure, purified through silica-gel chromatography (PE/EA, 10/1 ~ 4/1), which afforded the desired product **1j-2** in quasi-white solid (1.3 g, 67.6%). (Yuan, Zhao; Younes, Ali H.; Allen, John R.; Davidson, Michael W.; Zhu, Lei, *J. Org. Chem.*, 2015, *80*, 5600 –5610).

(III) Into an oven-dried, 100 mL three-necked round bottle layered with **1j-2** (384 mg, 3 mmol), 4-*N*, *N'*-dimethylamino-pyridine (18.3 mg, 0.05 eq.), propiolic acid (233 mg, 1.1 eq.), anhydrous dichloromethane (10 mL). The mixture was stirred and cooled under 0 ℃ cooling bath. Then dicyclohexylmethanediimine (DCC, 730 mg, 1.2 eq.) was dissolved in 10 mL anhydrous dichloromethane and dropped wisely through constant pressure dropping funnel under nitrogen gas protection from moisture. After DCC addition finished, the reaction round bottle was warmed to room temperature, stirred, and monitored by TLC. After nearly 5 hours, **1j-2** was nearly disappeared, then the reaction was filtrated to remove the urea, concentrated under reduced pressure and purified

through silica-gel chromatography (20/1, R_f = 0.3), which afforded the desired product **1j** in yellow oil (240 mg, 44%). ^{1}H NMR (400 MHz, $CDCl_3$) δ 10.00 (s, 1H), 7.72 (dd, J = 5.4, 1.0 Hz, 1H), 7.21 (d, J = 5.4 Hz, 1H), 3.25 (s, 1H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 180.6, 151.2, 148.9, 133.9, 128.8, 122.7, 78.8, 73.3. HR-MS (ESI) ([M+H]$^+$) Calcd. for $[C_8H_5O_3S]^+$: 180.9954 (100%), Found: 180.9952 (100.0%).

3.4 Other substrates (1m, 1m', 1n, 1o) were synthesized, but failed



Scheme S6: synthesis attempt for substrates **1m'**, **1m**, **1n**, **1o**

Starting material (salicylaldehyde with various electron-withdrawing groups

or multi-substituents) of **1m'-0**, **1m-0** (BIDE PHARMATECH - CN110407697, 2019, A), **1n-0** (H. LUNDBECK A/S - WO2017/197192, 2017, A1) as shown in Scheme S6, were synthesized according to corresponding reference. While utilizing the various substituted salicylaldehyde en route to salicylaldehyde propiolates, several methods we have tried, however no corresponding substrate was obtained.

4. General procedure for the synthesis of product 3

4.1 Sulfonylated chromeno[4,3-*c*]pyrazol-4(2*H*)-ones

Into a φ20×180mm glass tube equipped with a magnetic stirrer bar was charged with salicylaldehyde propiolate (**1a**, 0.30 mmol), sulfonohydrazide (**2**, 0.33 mmol), $Cu(OAc)_2$ (1.0 equiv.), 1,2-dichloroethane (6.0 mL). The reaction vessel was stirred at 60 ºC for 6 h. After completion of the reaction, the mixture was concentrated under reduced pressure. The resulting crude product was further purified by flash chromatography (silica gel, petroleum ether/ethyl acetate), which afforded the desired product 2-sulfonylated chromeno[4,3-*c*]pyrazol-4(2*H*)-one (**3a**–**3h**, **3h**–**3s**).

4.2 *N*-Sulfonated Quinolin-2(1H)-one-3-Carboxamides

Into a φ20×180mm glass tube equipped with a magnetic stirrer bar was charged with *N*-(2-formylphenyl)propiolamide (**1i**, 0.30 mmol), sulfonohydrazide (**2**, 0.33 mmol), $Cu(OAc)_2$ (1.0 eq.), 1,2-dichloroethane (6.0 mL), trifluoroacetic

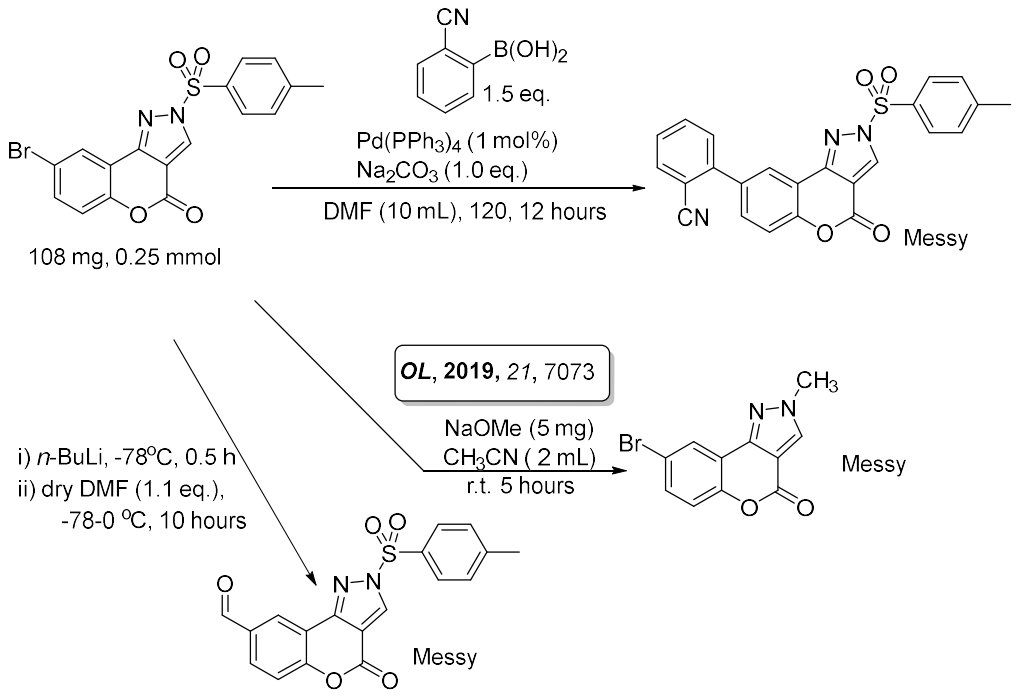
acid (15 μL). The reaction vessel was stirred at 60 ºC for 6 h. After completion of the reaction, the mixture was concentrated under reduced pressure. The resulting crude product was further purified by flash chromatography (silica gel, dichloromethane/methanol), which afforded *N*-Sulfonated Quinolin-2(1*H*)-one-3-Carboxamides (**3ia**, **3ib**).

4.3 General procedure for the synthesis of product 3g in 4.0 mmol

Into a 100 mL round bottle equipped with a magnetic stirrer bar was charged with 4-bromo-2-formylphenyl propiolate (**1g**, 1.04 g, 4.0 mmol), sulfonohydrazide (**2**, 714 mg, 4 mmol), $Cu(OAc)_2$ (744 mg, 4.0 mmol, 1.0 equiv.), 1,2-dichloroethane (60 mL). The reaction vessel was stirred at 60 ºC under air/*oxygen* for 12 h. TLC monitored, **1g** or Schiff intermediate disappeared, stop reaction, the mixture was filtrated through a short pad of silica gel to remove the undissolved Cu^X salts, washed with ethyl acetate, concentrated the filtrate under reduced pressure. The resulting residue was further purified by flash chromatography (silica gel, dichloromethane/methanol), which afforded the desired product **3g** (415 mg, 25%)/ *(752 mg, 45%)*.

4.4 The further late-stage transformations

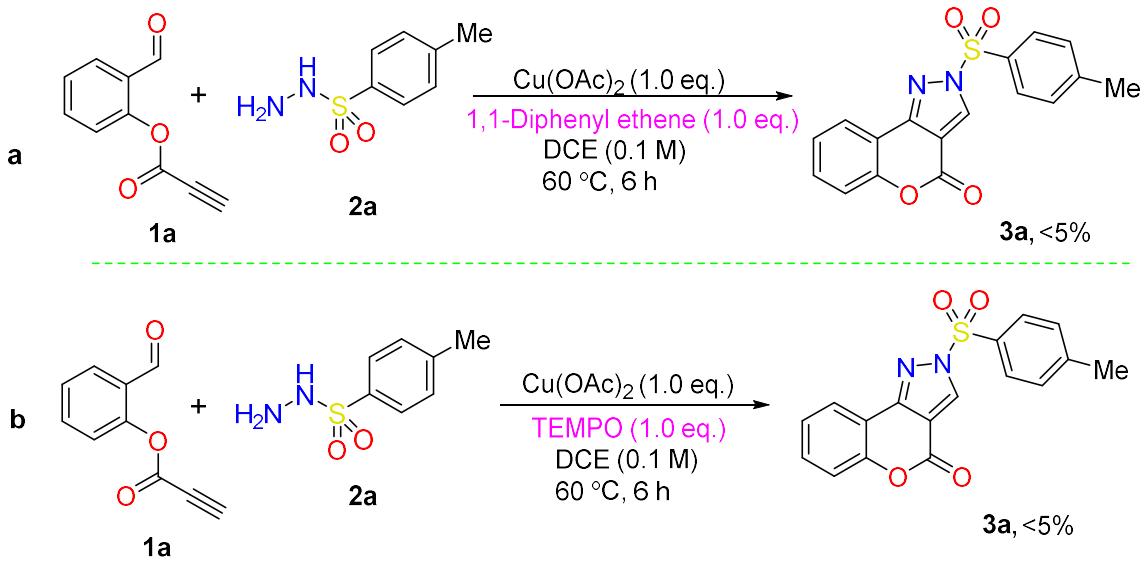
The further late-stage transformations were outlined in Scheme 7. However, no satisfactory results were obtained, shown in the following Scheme 7.



Scheme S7: Attempts of late stage transformations

5. Mechanism studies

5.1. Free-radical quenching experiments



Scheme S8: Free-radical trapping experiments

Into a 15 mL reaction vessel equipped with a magnetic stirrer bar was charged with salicylaldehyde propiolate (**1a**, 0.30 mmol), sulfonyl hydrazide (**2a**, 0.33 mmol), $Cu(OAc)_2$ (1.0 equiv.), 1,2-dichloroethane (3.0 mL), radical quenching reagent [0.3 mmol, 1.0 equiv of 1,1-diphenylethene (54 mg), and 1.0 equiv of TEMPO (57.5 mg), respectively. The reaction vessel was sealed and stirred at 60 °C for 6 h. After the reaction stirring for 6 h, the mixture was concentrated under reduced pressure. The resulting crude product was further purified by flash chromatography (silica gel, petroleum ether/ethyl acetate), which afforded the desired product. As the radical quenching reagent addition, no observable target product was forged, the reaction procession was significantly ceased. Furthermore, the reaction solution was applied on HR-MS for *in-situ* detection of intermediate. Satisfying we had observed the intermediate signal of **3a-TEMPO**.

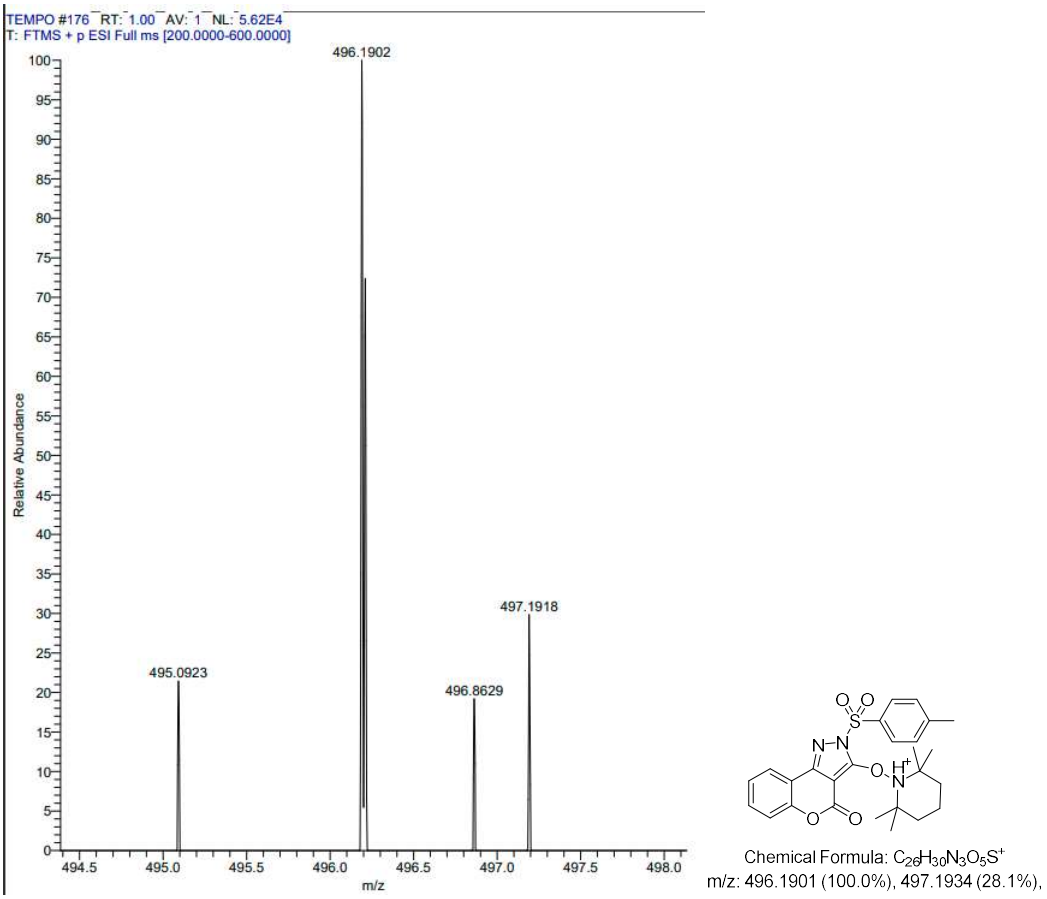
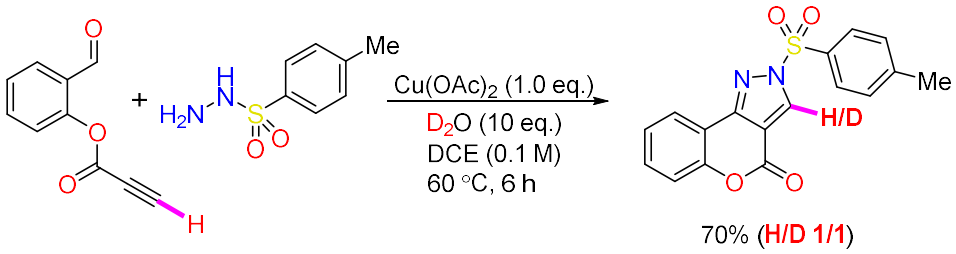


Figure S1: HRMS spectra of m/z for [(**3a**-H˙+TEMPO)+H+]

5.2 H/D isotopic exchange experiment



Scheme S9: H-D exchange experiment

Into a 15 mL reaction vessel equipped with a magnetic stirrer bar was charged with salicylaldehyde propiolate (**1a**, 0.30 mmol), sulfonyl hydrazide (**2a**, 0.33 mmol), $Cu(OAc)_2$ (1.0 equiv.), 1, 2-dichloroethane (3.0 mL), D_2O (60 mg, 3 mmol, 10 equiv.). The reaction vessel was sealed and stirred at 60 ºC for 6 h. After the reaction stirring for 6 hours, the mixture was concentrated under reduced

pressure. The resulting crude product was further purified by flash chromatography (silica gel, PE/EA, 1/10), providing a mixture of **3a** and **3a-D1** in 70% yield. ^{1}H NMR data analysis found 50% deuterium was obtained (Figure S2), which was confirmed by HRMS (Figure S3).

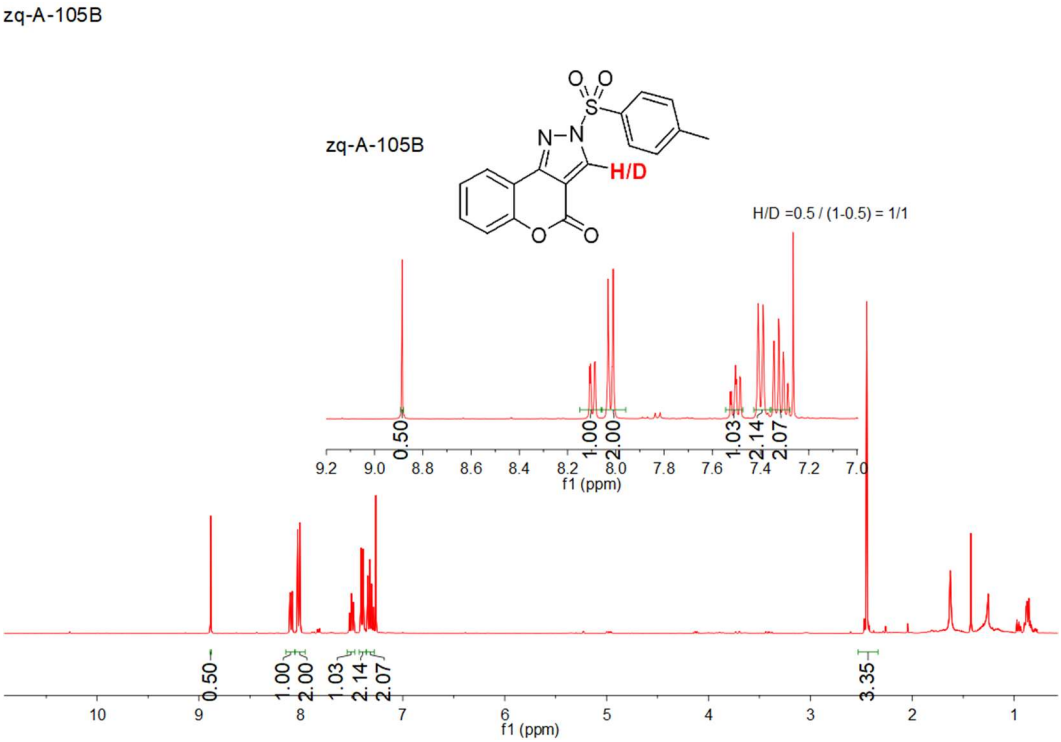


Figure S2: ^{1}H NMR analysis for the products from H/D isotopic exchange experiment

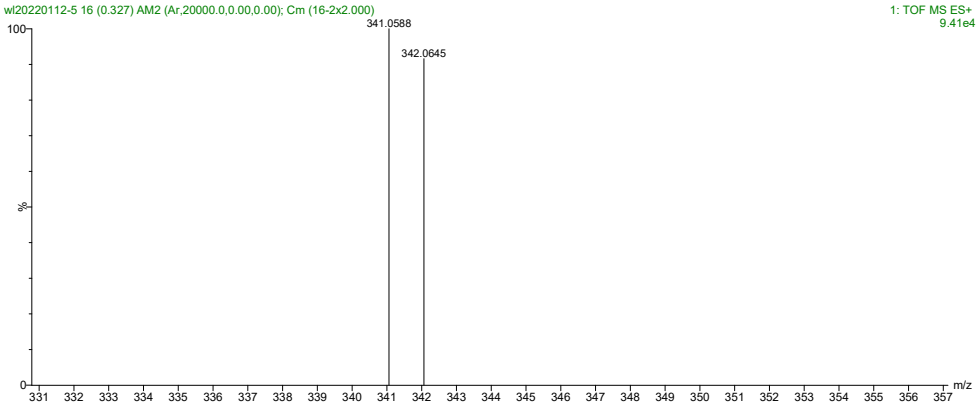
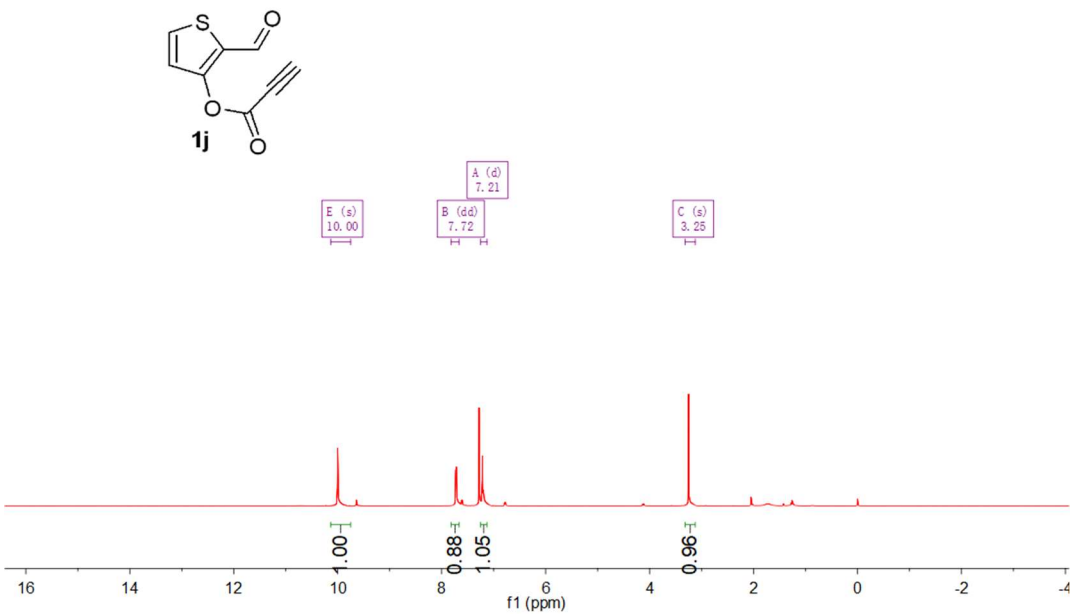
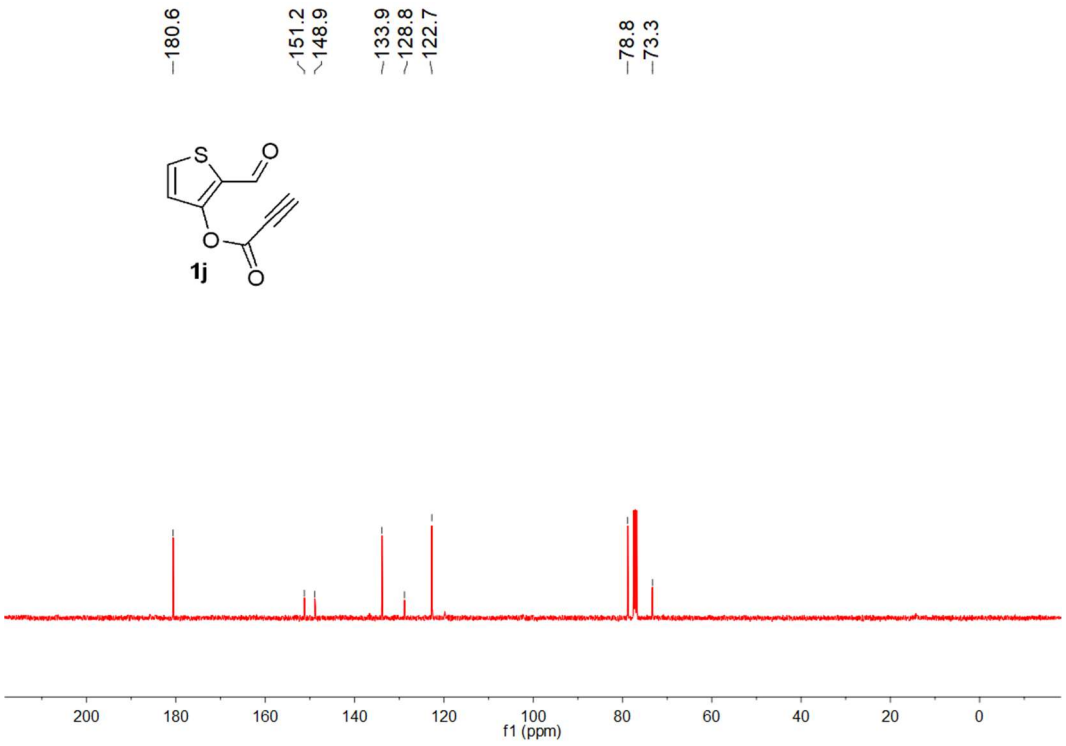


Figure S3: HR-MS analysis for **M+H^{+}** of **3a-H** [341.0591 (100.0%)] found 341.0588 & **3a-D$_1$** [342.0653 (100.0%)] found 342.0645.

6. Copies NMR spectra of the products





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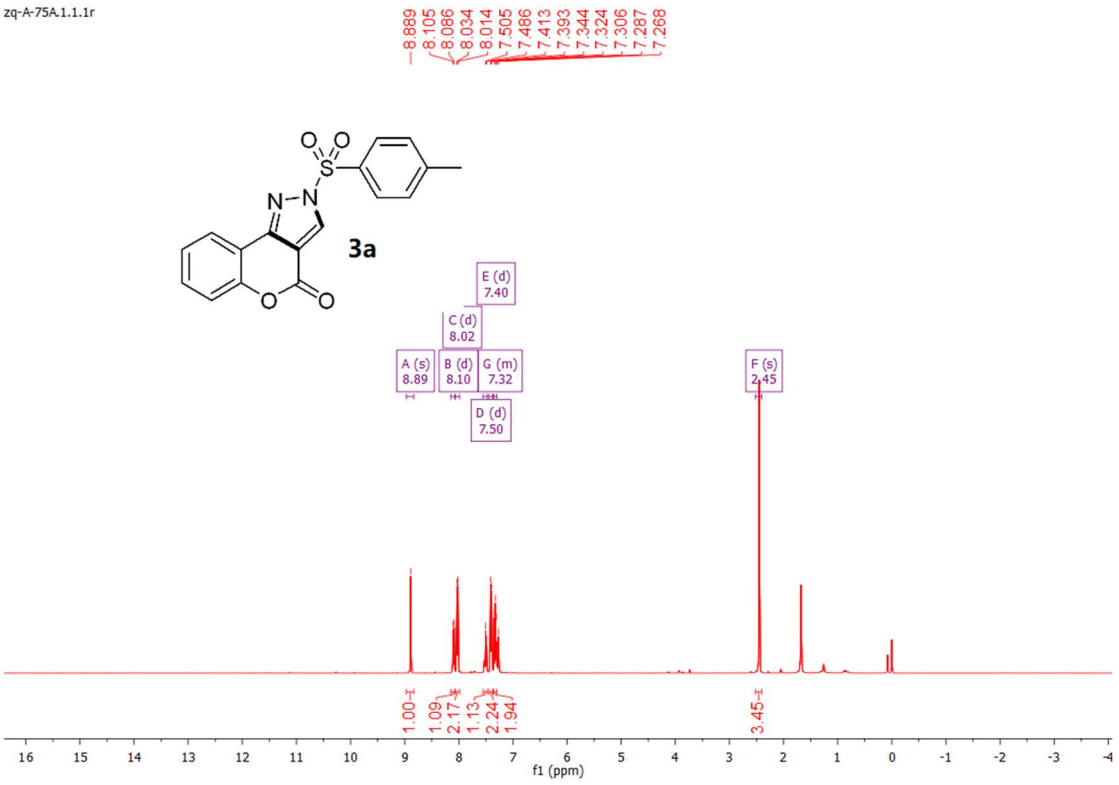

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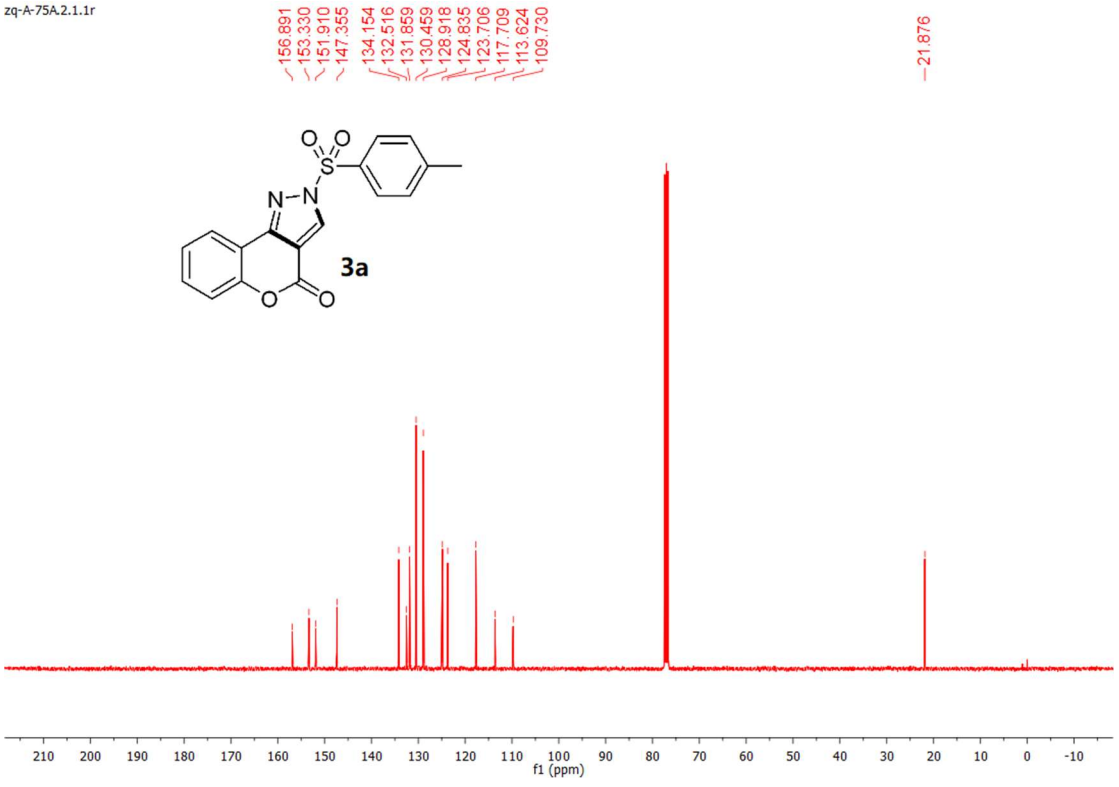
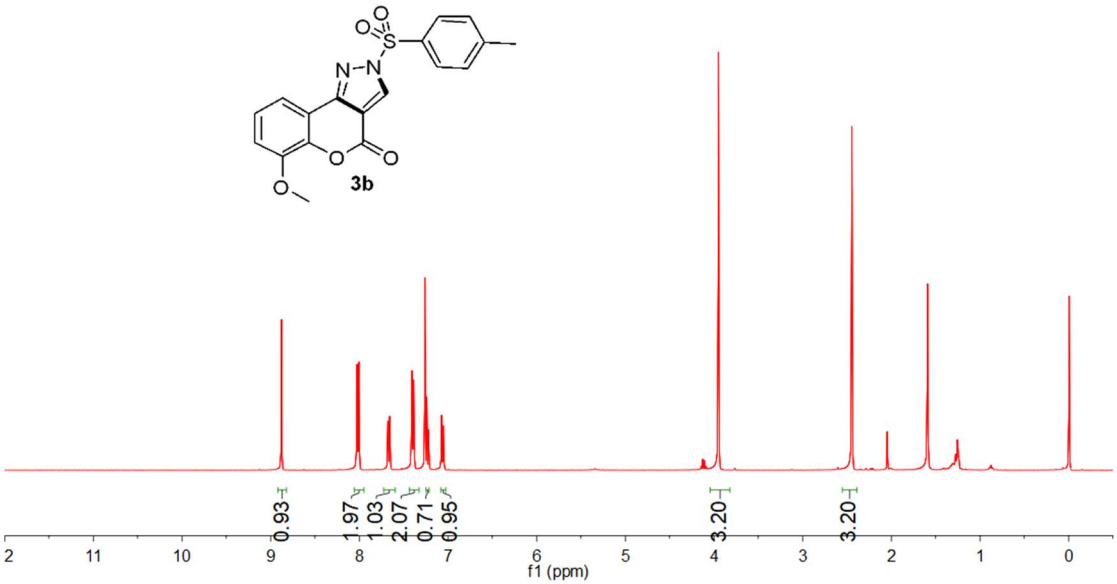
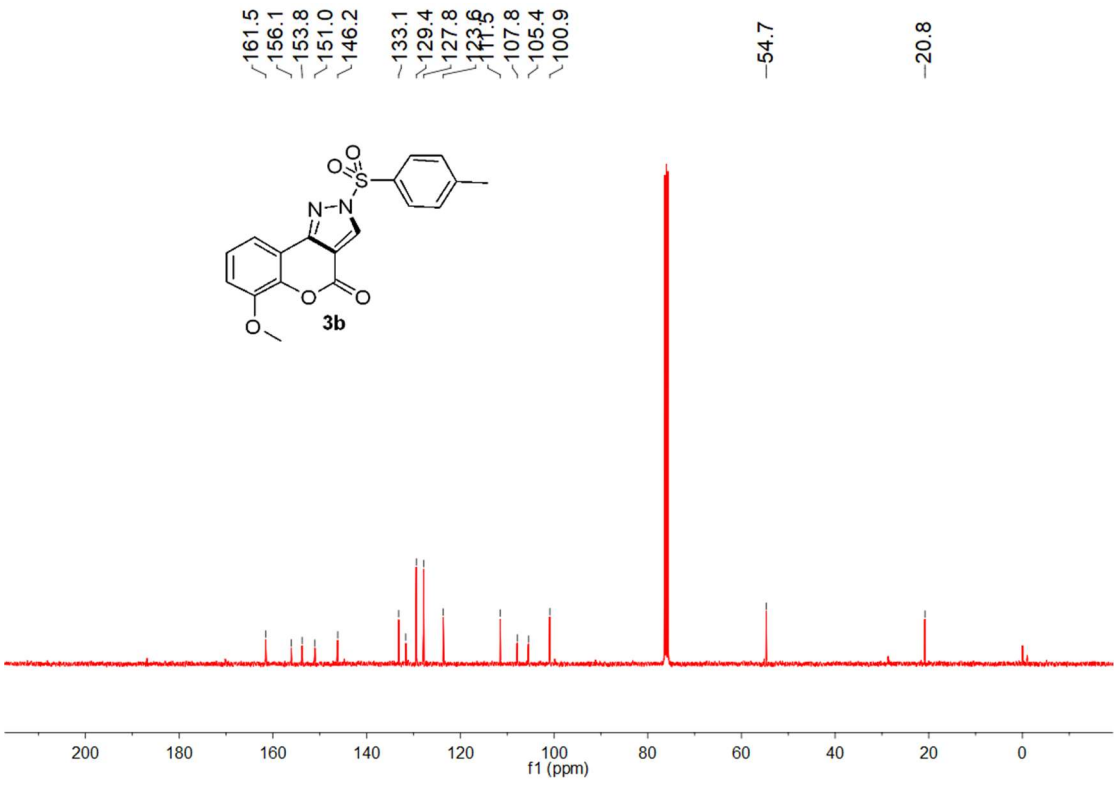
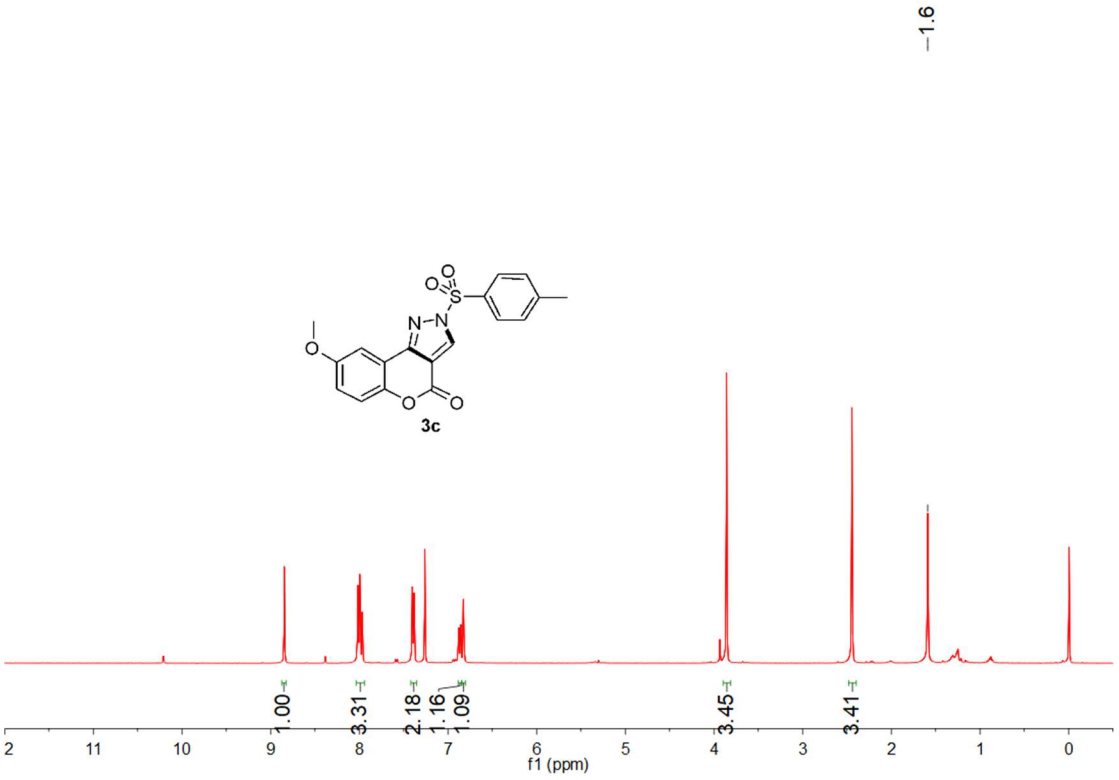



3b
0.93
1.97
1.03
2.07
0.71
0.95
3.20
3.20
f1 (ppm)


161.5
156.1
153.8
151.0
146.2
133.1
129.4
127.8
123.6
111.5
107.8
105.4
100.9
54.7
20.8
3b
f1 (ppm)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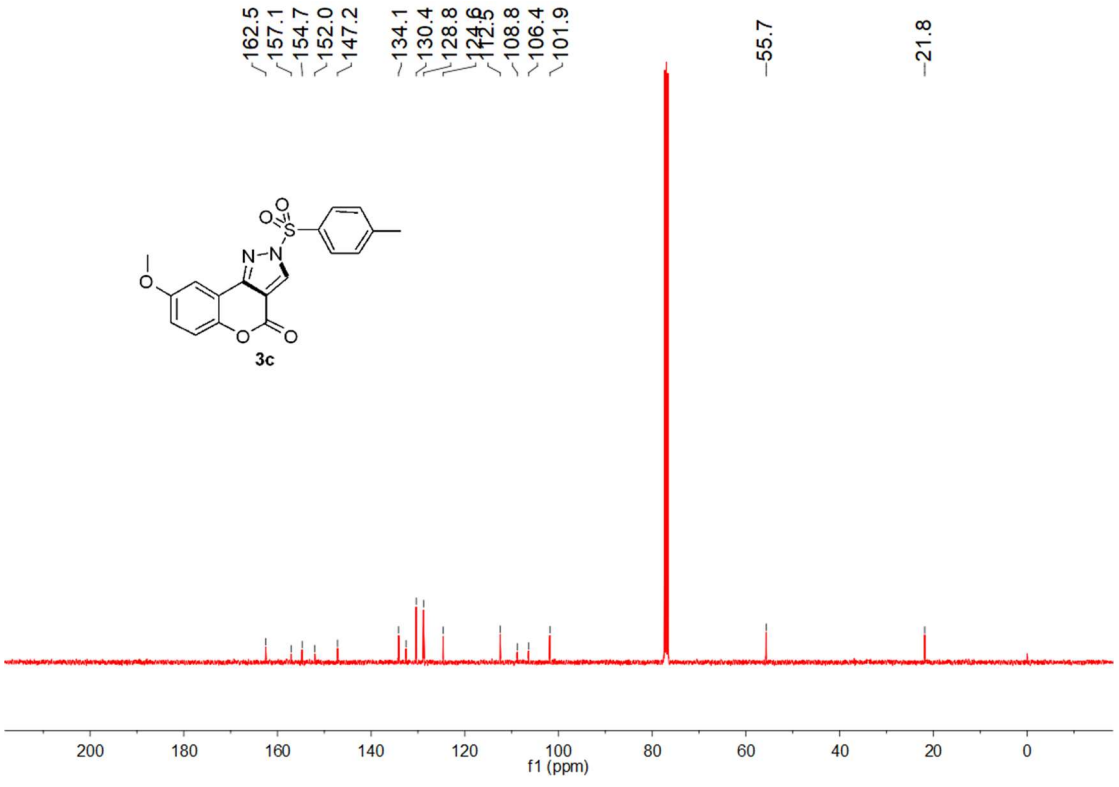
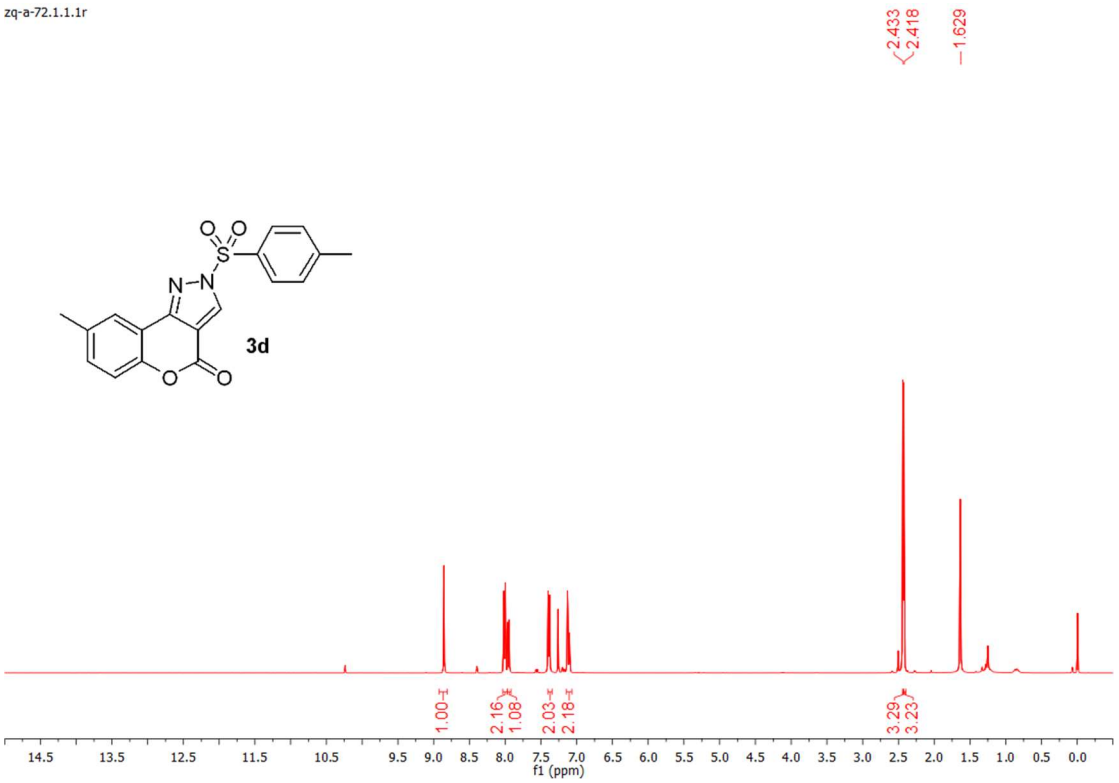
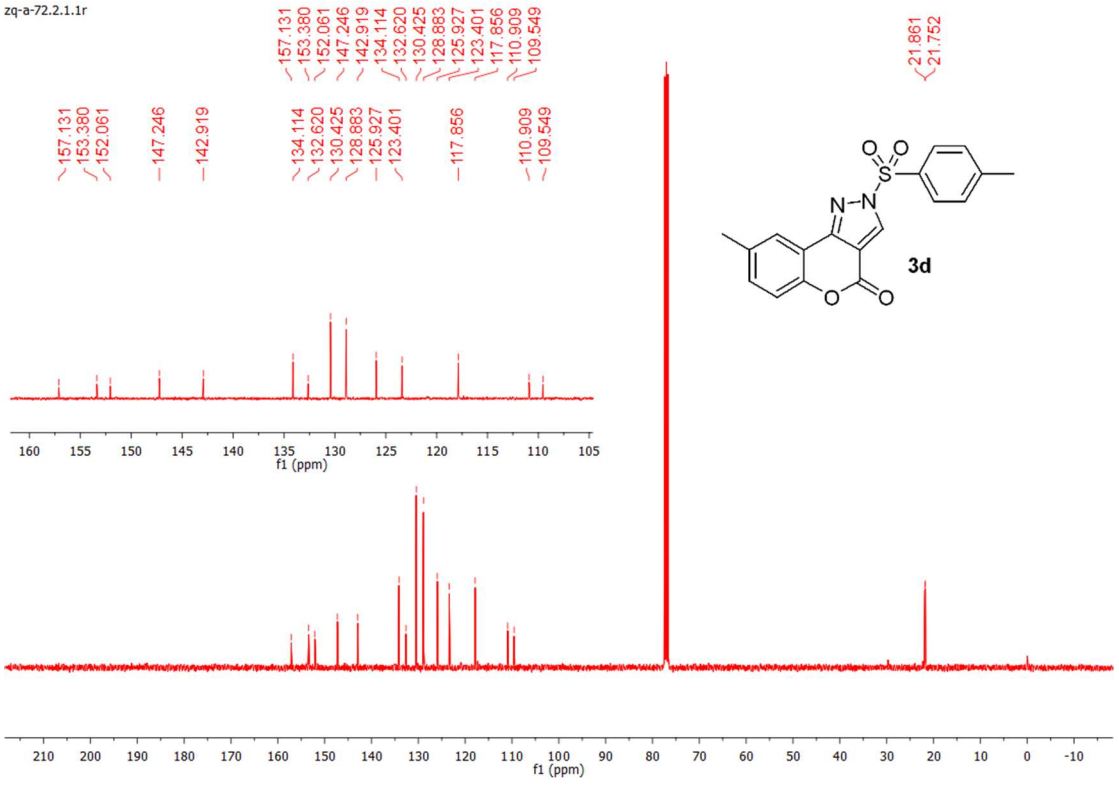
3c
1.00
3.31
2.18
1.16
1.09
3.45
3.41
f1 (ppm)

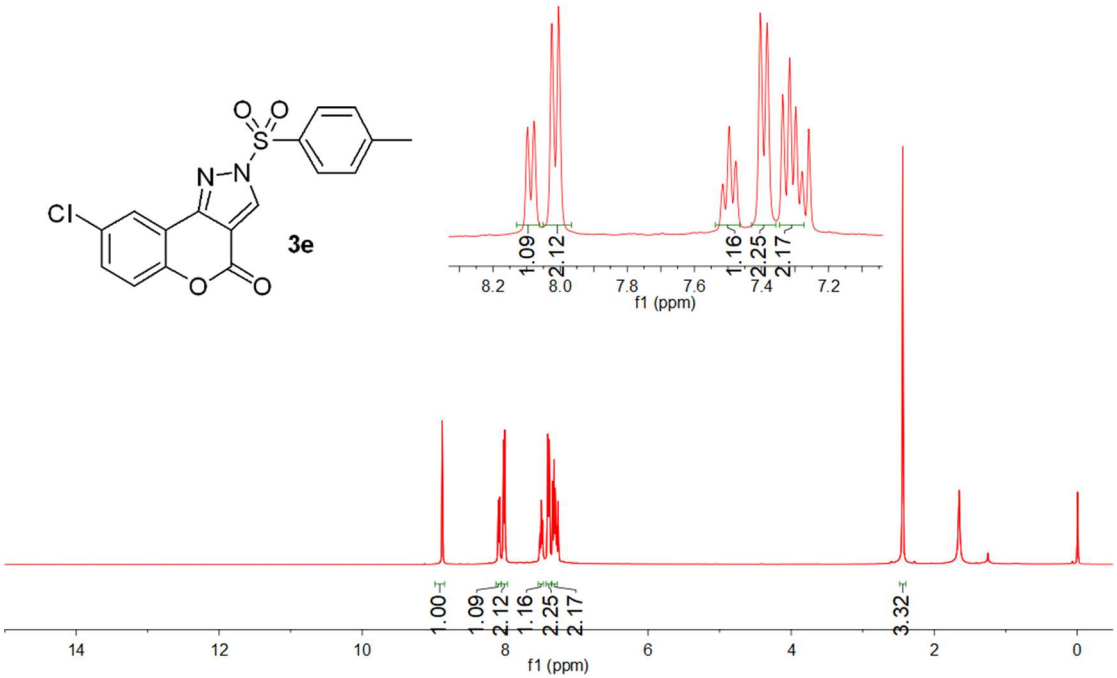

162.5
157.1
154.7
152.0
147.2
134.1
130.4
128.8
124.6
112.5
108.8
106.4
101.9
55.7
21.8
3c
f1 (ppm)

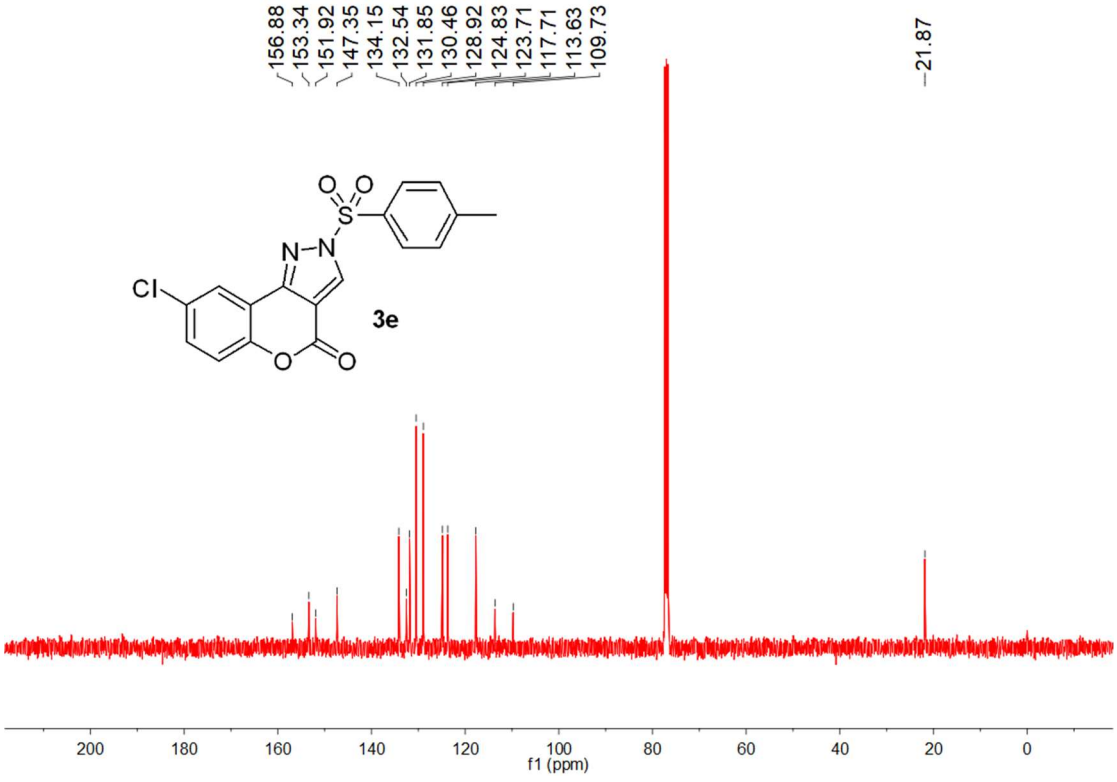
zq-a-72.1.1.1r

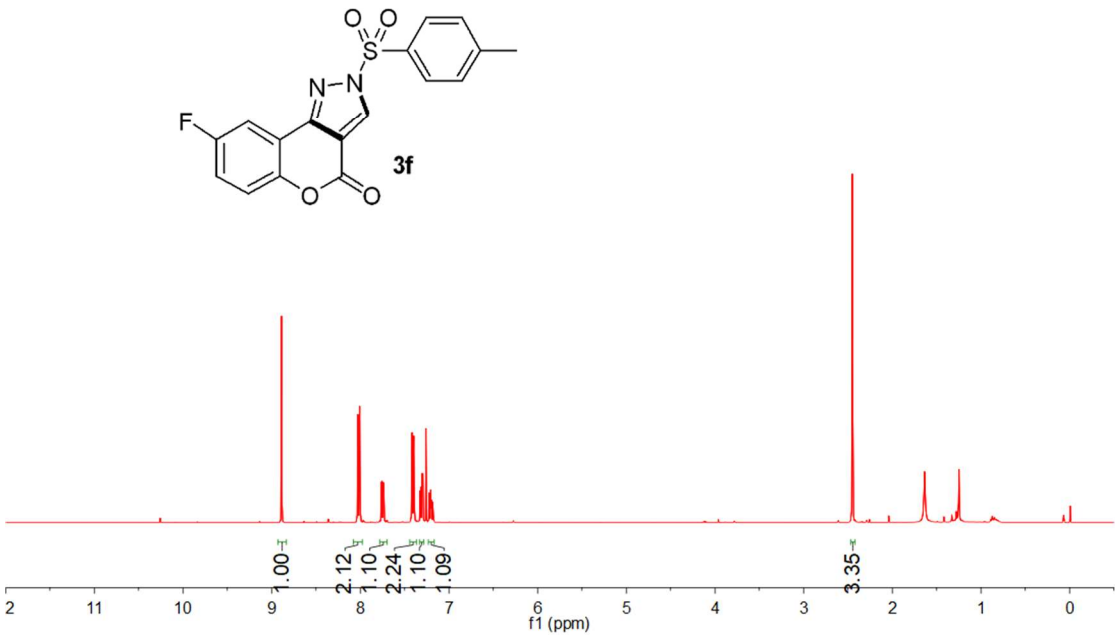


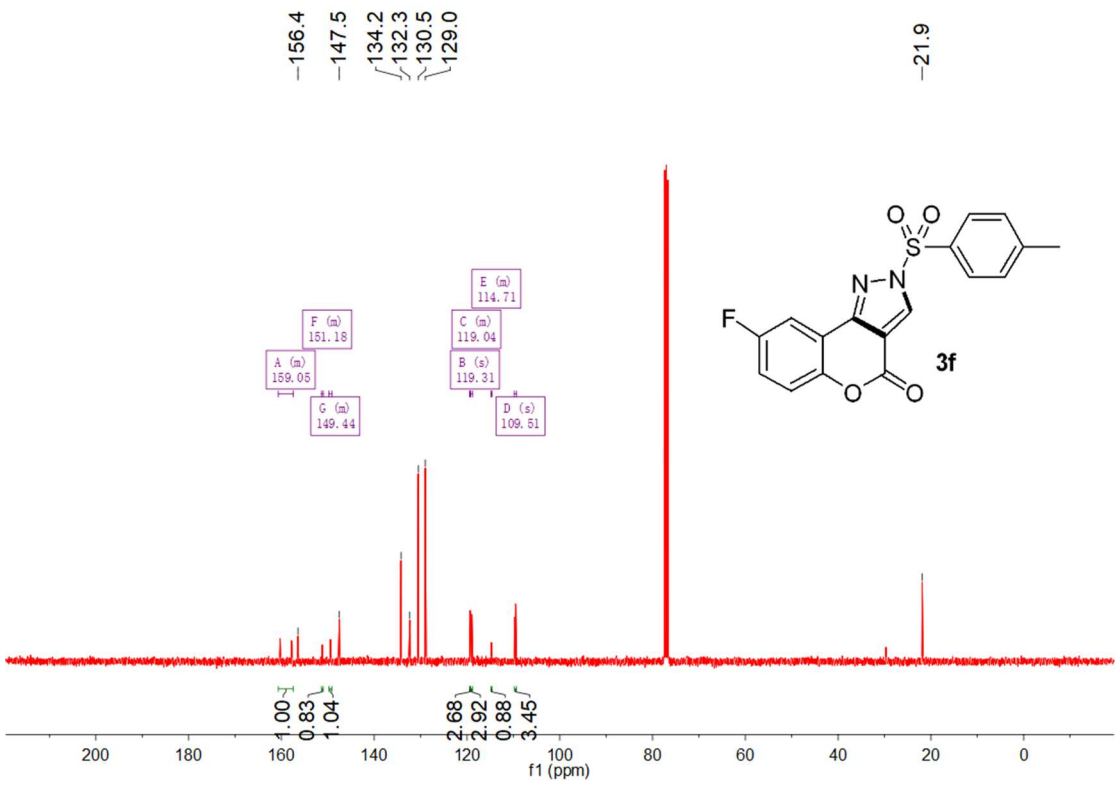
zq-a-72.2.1.1r



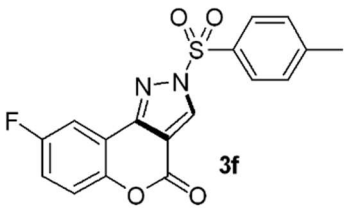

3e
1.09
2.12
1.16
2.25
2.17
8.2
8.0
7.8
7.6
7.4
7.2
f1 (ppm)
1.00
1.09
2.12
1.16
2.25
2.17
3.32
14
12
10
8
6
4
2
0
f1 (ppm)


156.88
153.34
151.92
147.35
134.15
132.54
131.85
130.46
128.92
124.83
123.71
117.71
113.63
109.73
21.87
3e
200
180
160
140
120
100
80
60
40
20
0
f1 (ppm)

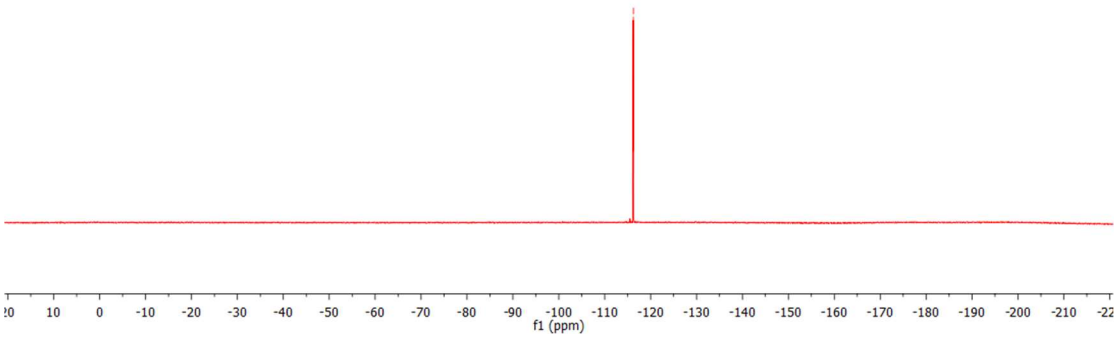

3f
1.00
2.12
1.10
2.24
1.10
1.09
3.35
f1 (ppm)

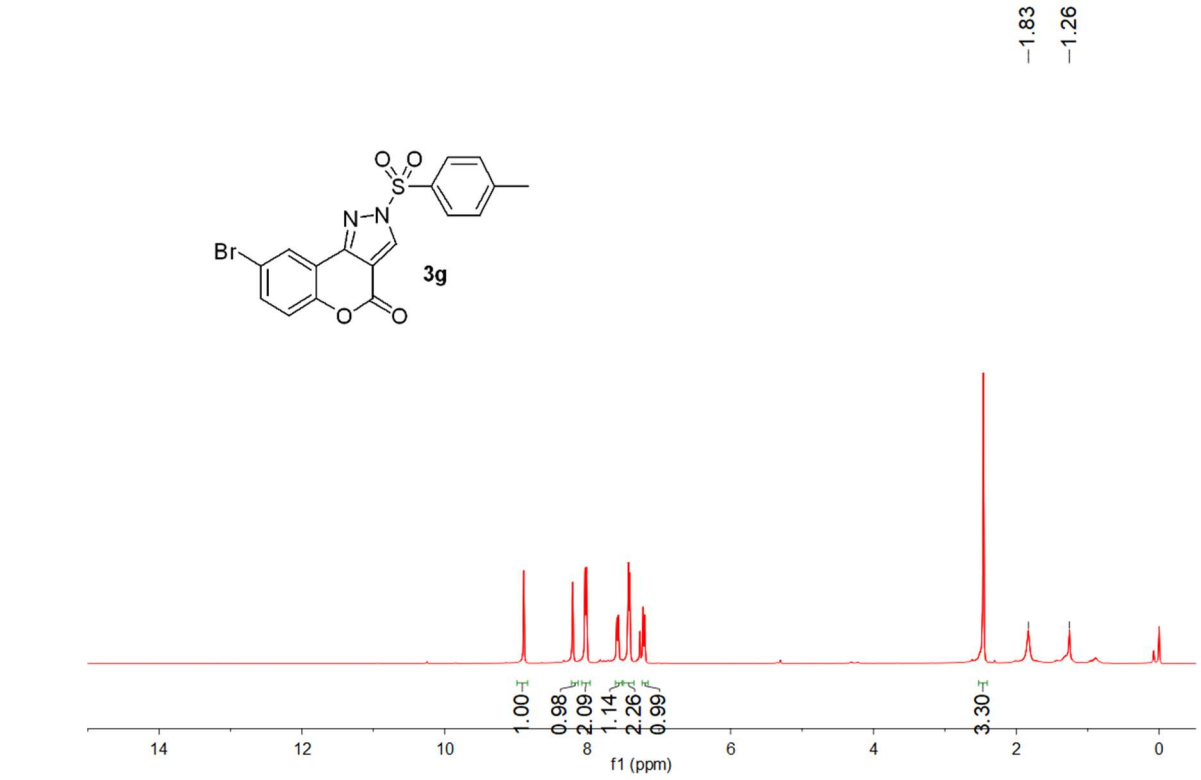

156.4
147.5
134.2
132.3
130.5
129.0
21.9
F (m) 151.18
A (m) 159.05
G (m) 149.44
E (m) 114.71
C (m) 119.04
B (s) 119.31
D (s) 109.51
3f
1.00
0.83
1.04
2.68
2.92
0.88
3.45
f1 (ppm)

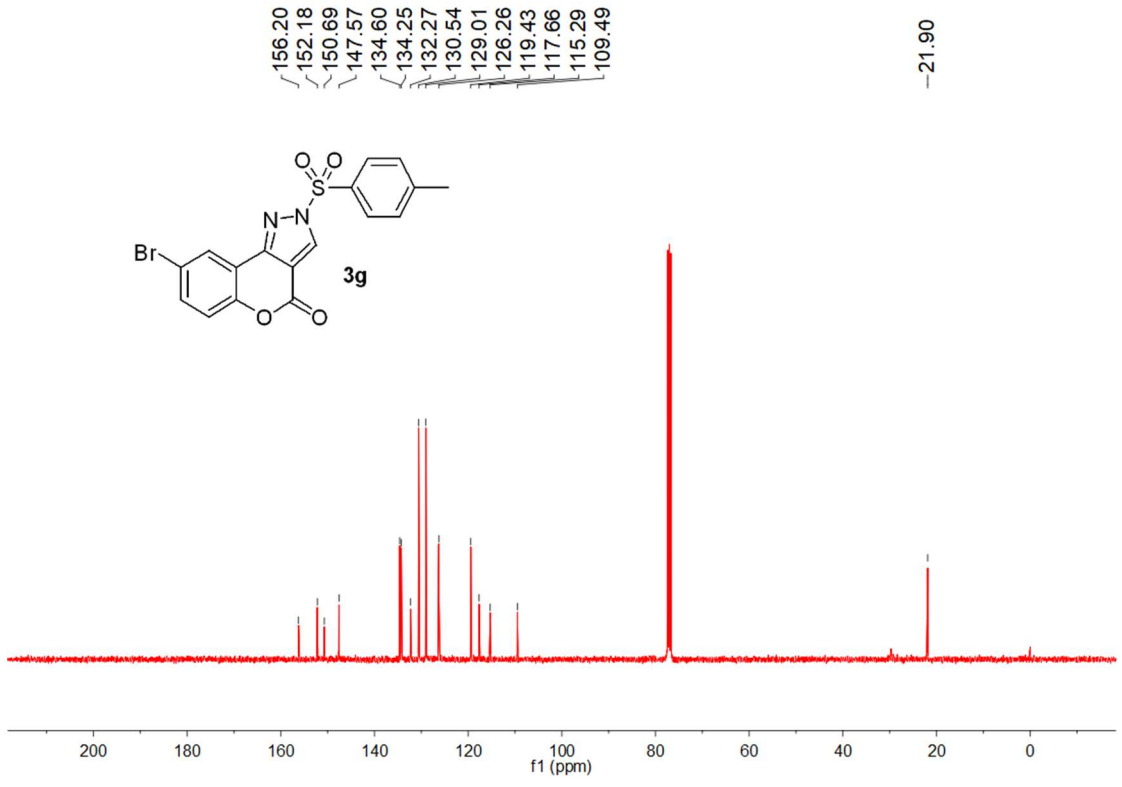
zq-A-98A.3.1.1r

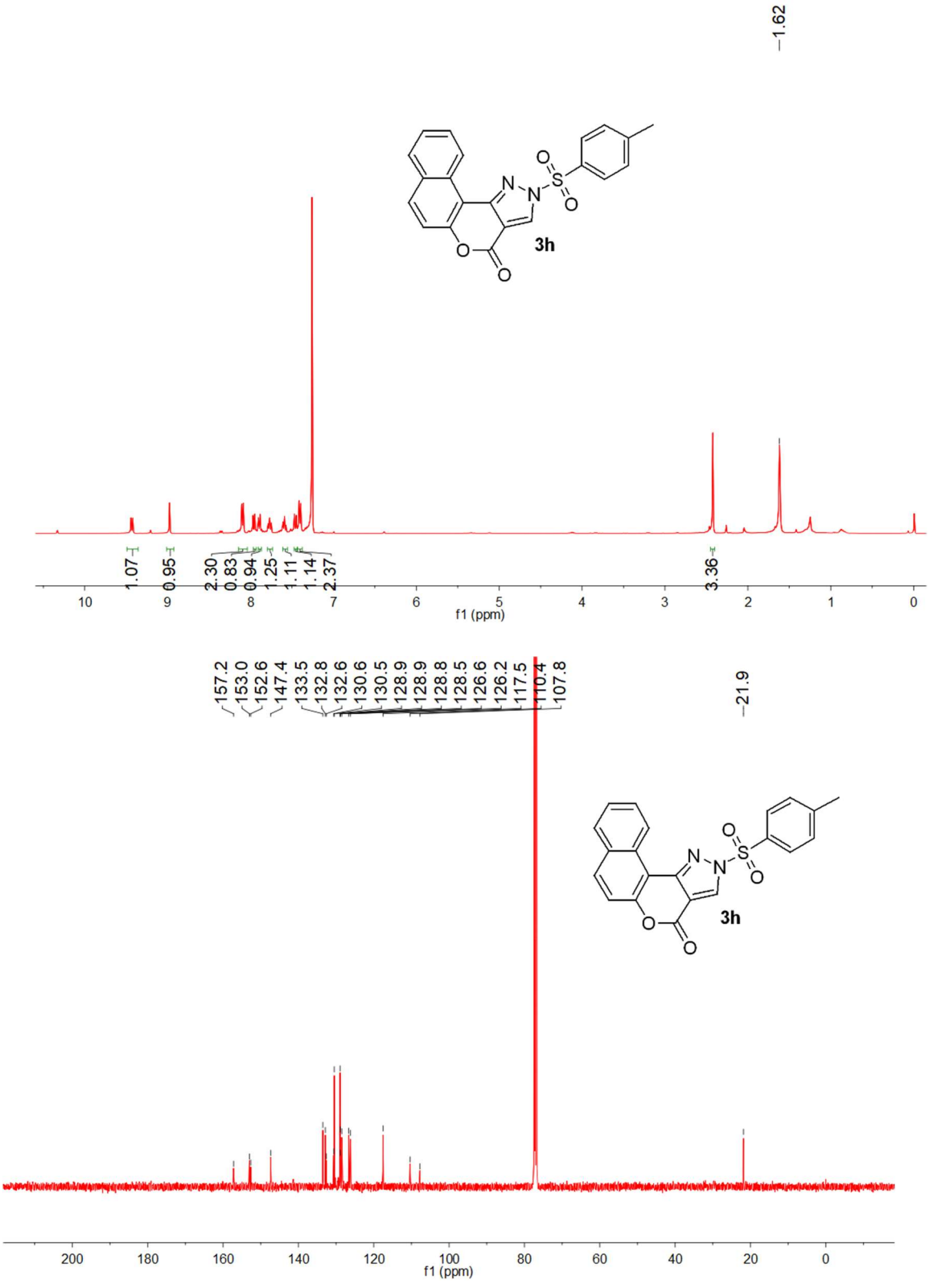


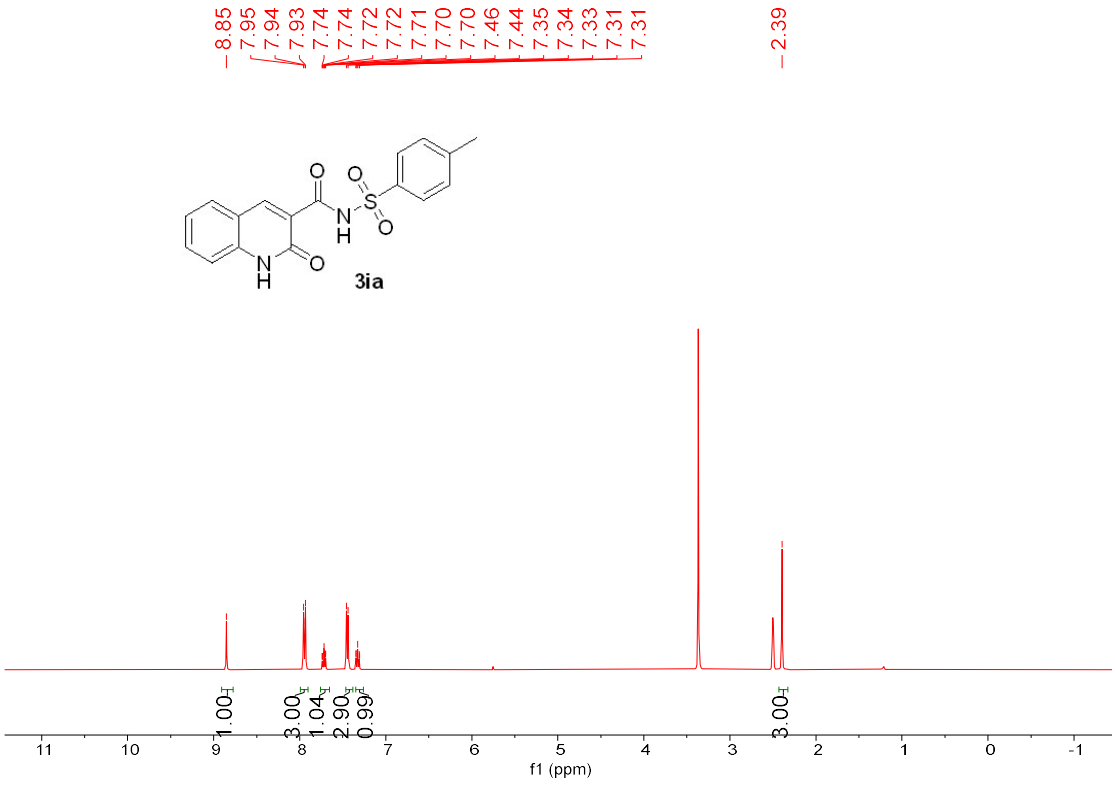
3f

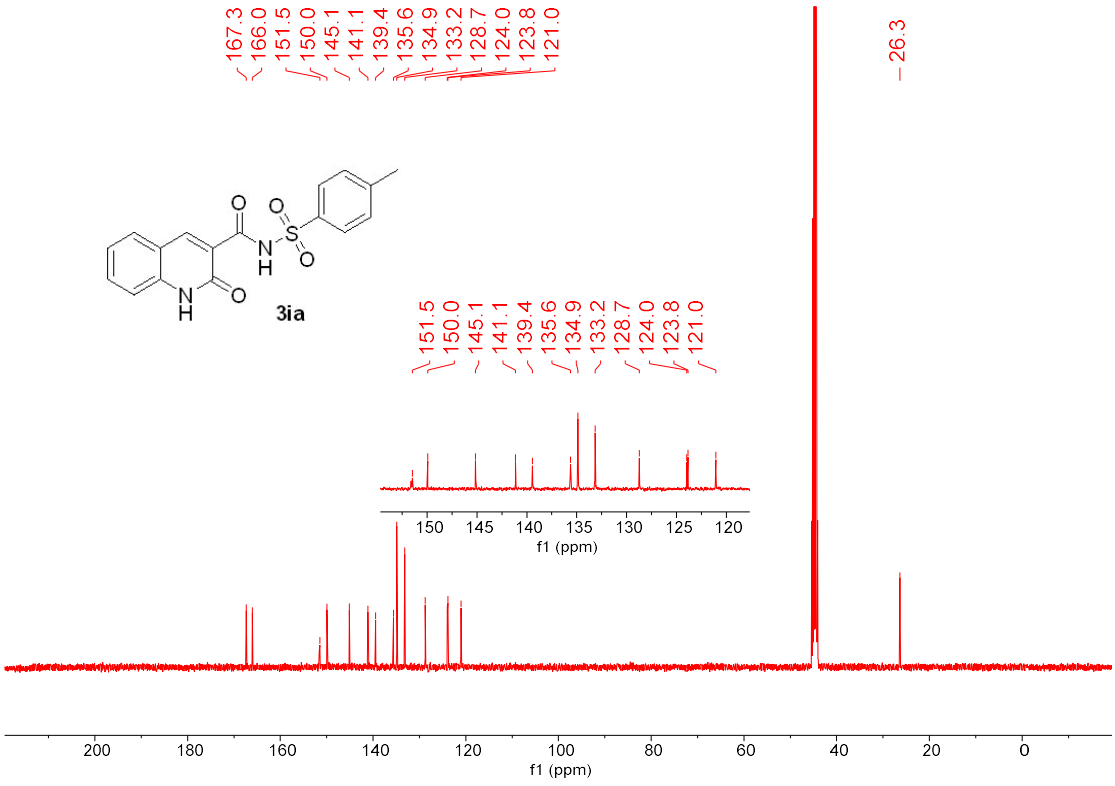


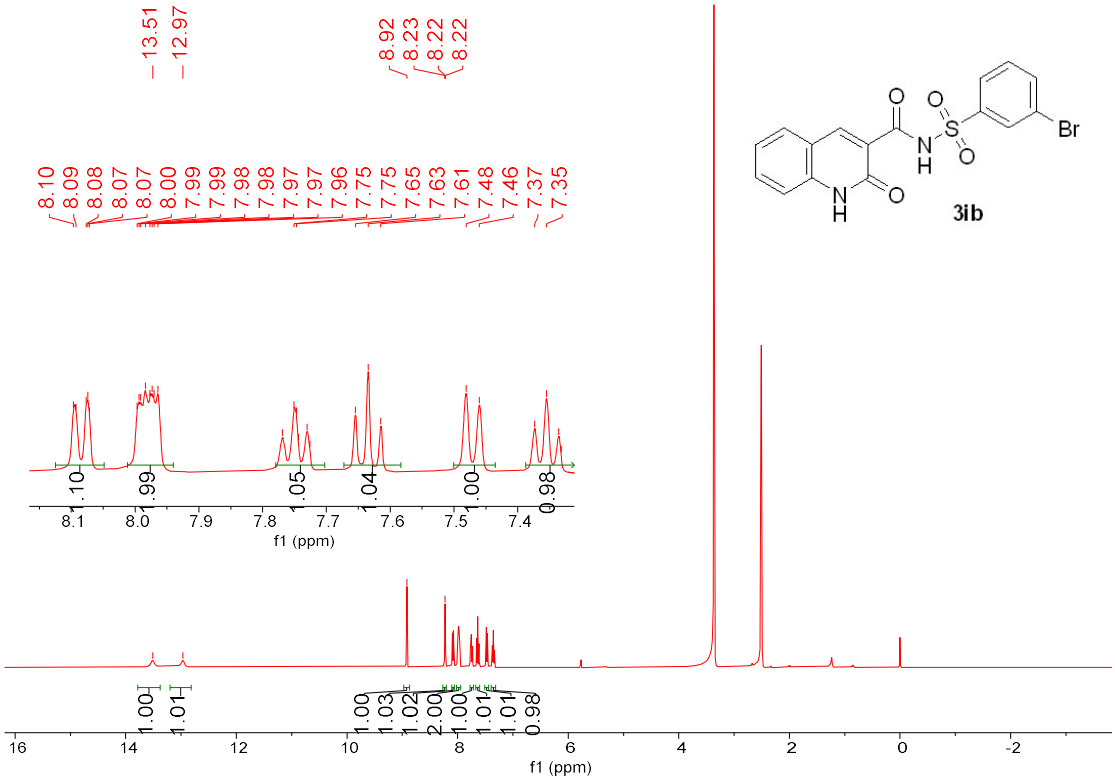

2.83
2.26
Br
3g
1.00
0.98
2.09
1.14
2.26
0.99
3.30
14
12
10
8
6
4
2
0
f1 (ppm)

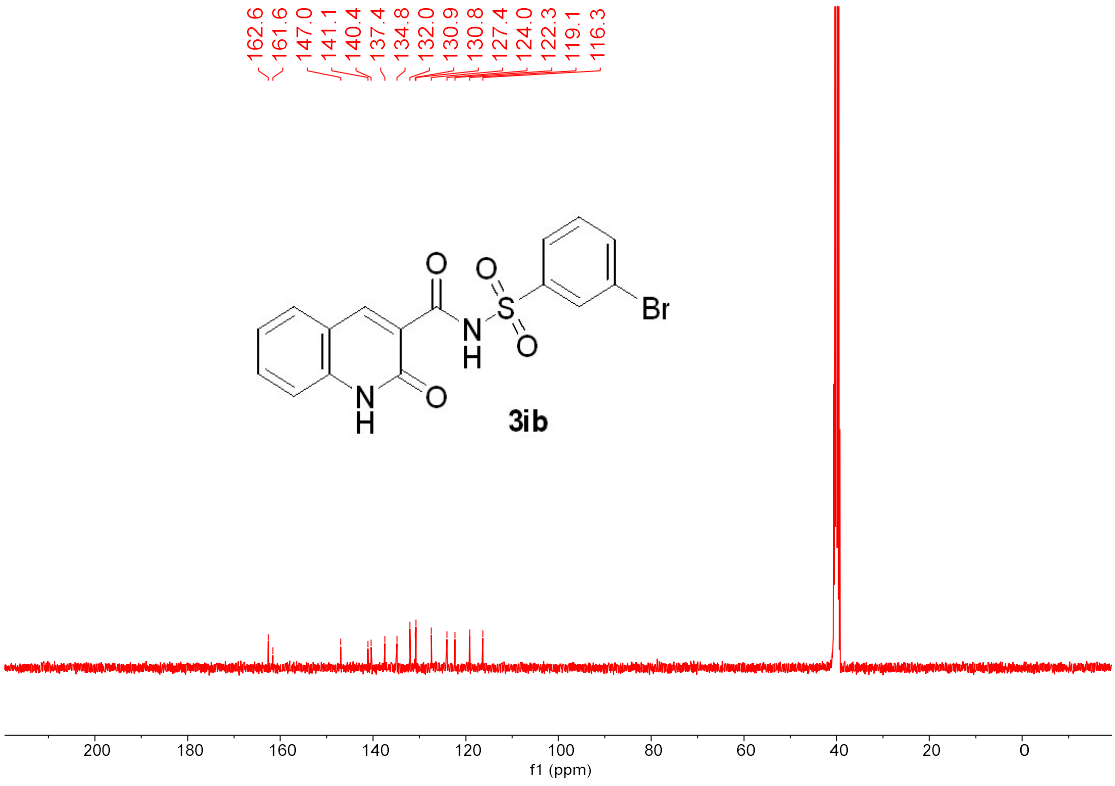

156.20
152.18
150.69
147.57
134.60
134.25
132.27
130.54
129.01
126.26
119.43
117.66
115.29
109.49
21.90
Br
3g
200
180
160
140
120
100
80
60
40
20
0
f1 (ppm)

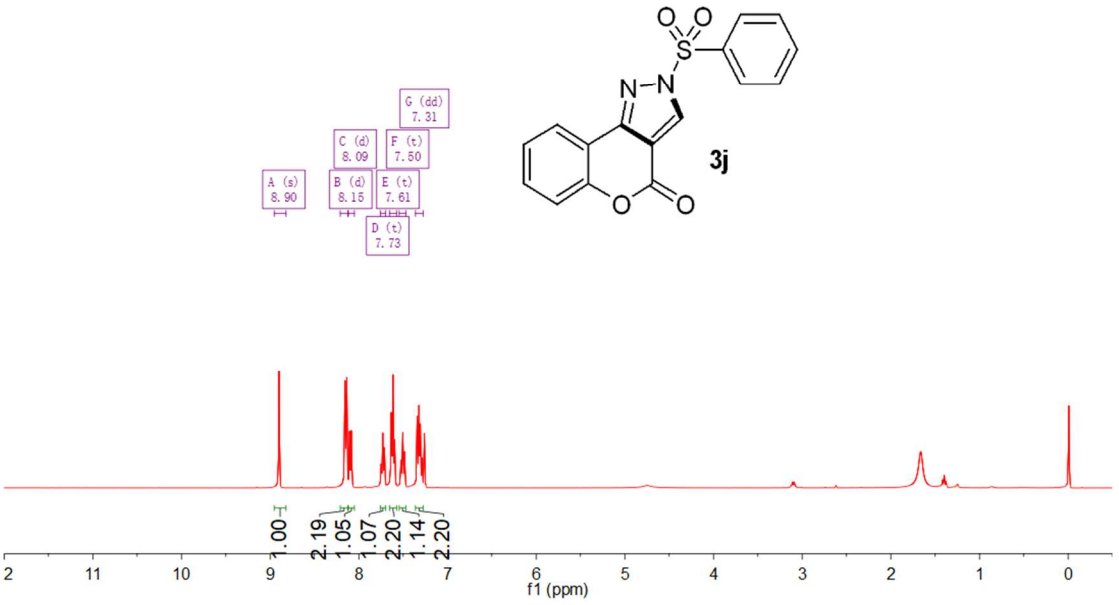

2.62
3h
1.07
0.95
2.30
0.83
0.94
1.25
1.11
1.14
2.37
3.36
f1 (ppm)
157.2
153.0
152.6
147.4
133.5
132.8
132.6
130.6
130.5
128.9
128.9
128.8
128.5
126.6
126.2
117.5
110.4
107.8
21.9
3h
f1 (ppm)

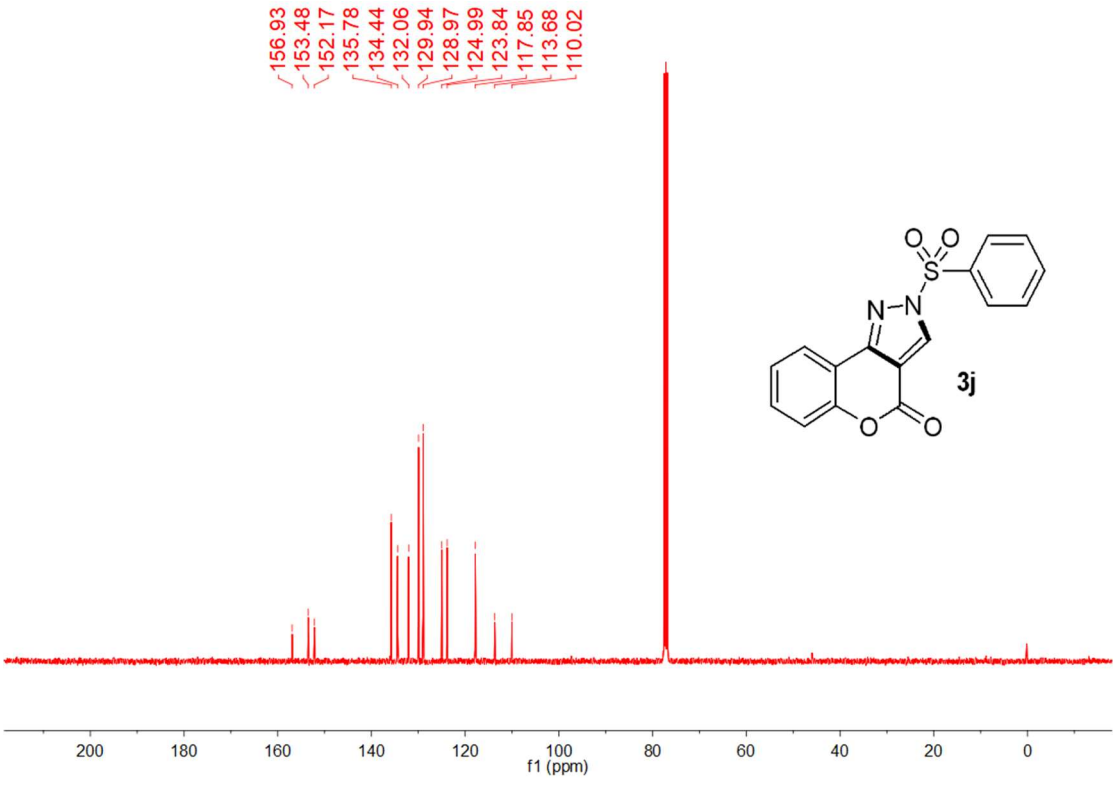

8.85
7.95
7.94
7.93
7.74
7.74
7.72
7.72
7.71
7.70
7.70
7.46
7.44
7.35
7.34
7.33
7.31
7.31
2.39
3ia
1.00
3.00
1.04
2.90
0.99
3.00
f1 (ppm)


167.3
166.0
151.5
150.0
145.1
141.1
139.4
135.6
134.9
133.2
128.7
124.0
123.8
121.0
26.3
3ia
151.5
150.0
145.1
141.1
139.4
135.6
134.9
133.2
128.7
124.0
123.8
121.0
f1 (ppm)
f1 (ppm)

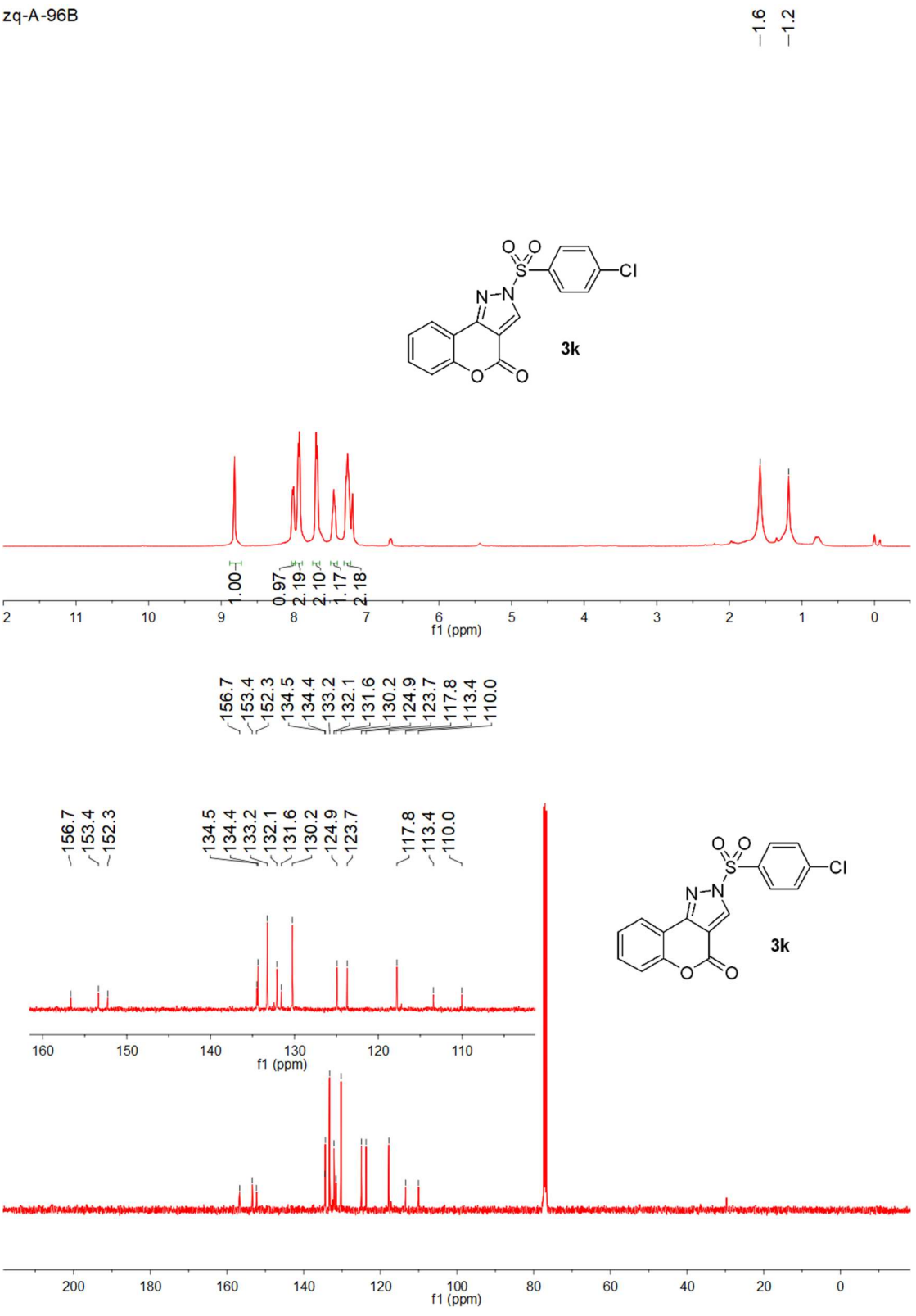

13.51
12.97
8.92
8.23
8.22
8.22
8.10
8.09
8.08
8.07
8.07
8.00
7.99
7.99
7.98
7.98
7.97
7.97
7.96
7.75
7.75
7.65
7.63
7.61
7.48
7.46
7.37
7.35
Br
3ib
1.10
1.99
1.05
1.04
1.00
0.98
f1 (ppm)
1.00
1.01
1.00
1.03
1.02
2.00
1.00
1.01
1.01
0.98
f1 (ppm)

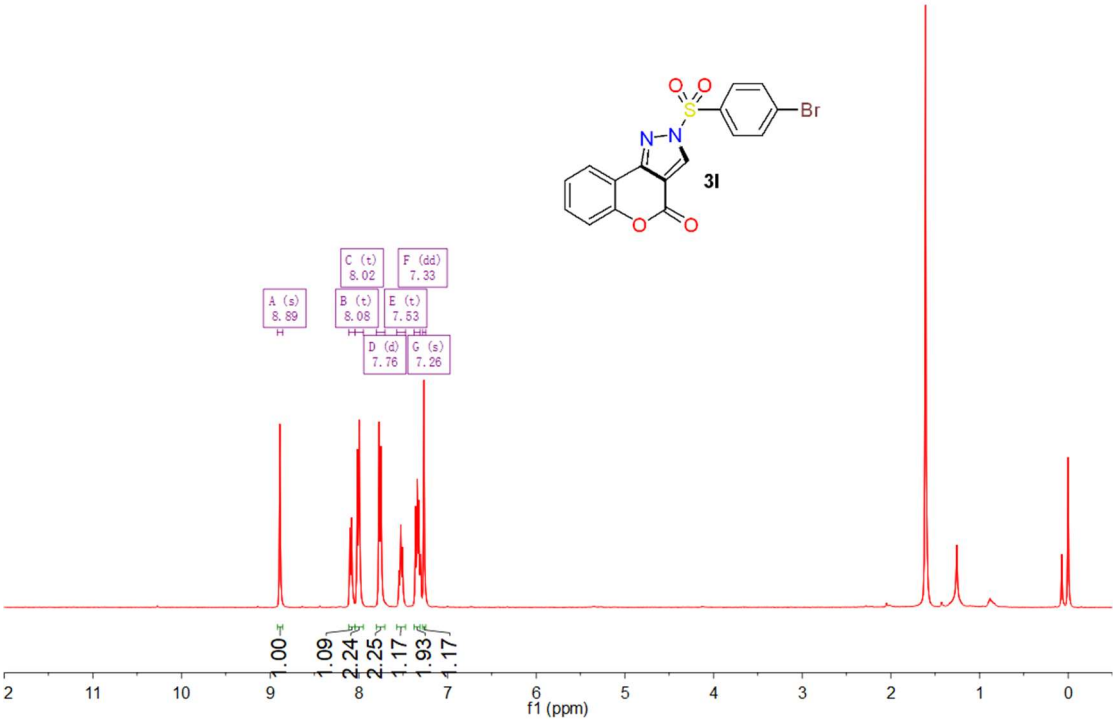

162.6
161.6
147.0
141.1
140.4
137.4
134.8
132.0
130.9
130.8
127.4
124.0
122.3
119.1
116.3
Br
3ib
f1 (ppm)

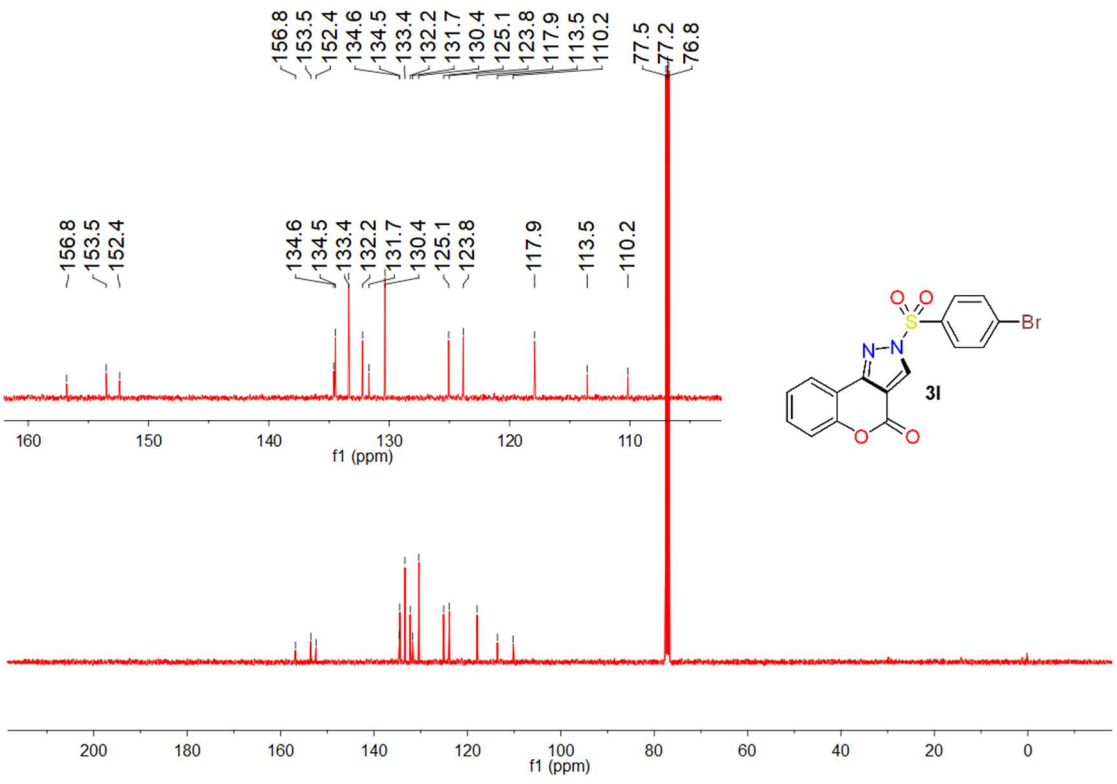

A (s)
8.90
B (d)
8.15
C (d)
8.09
D (t)
7.73
E (t)
7.61
F (t)
7.50
G (dd)
7.31
3j
1.00
2.19
1.05
1.07
2.20
1.14
2.20
f1 (ppm)

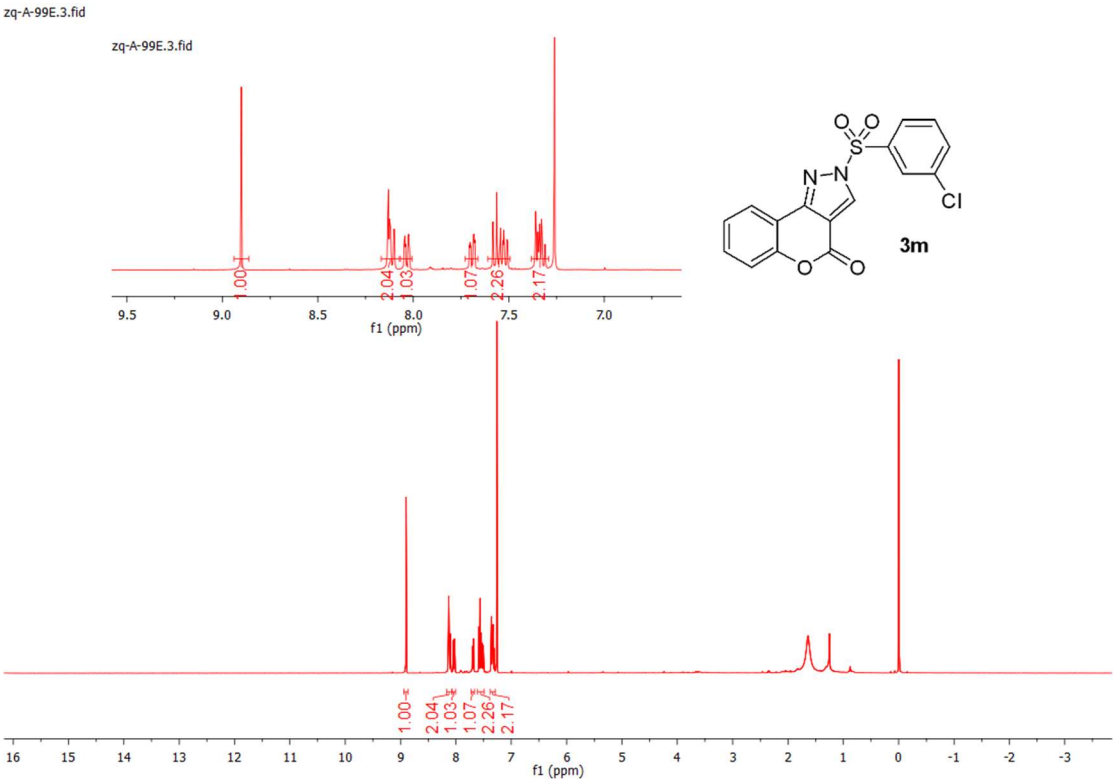

156.93
153.48
152.17
135.78
134.44
132.06
129.94
128.97
124.99
123.84
117.85
113.68
110.02
3j
f1 (ppm)

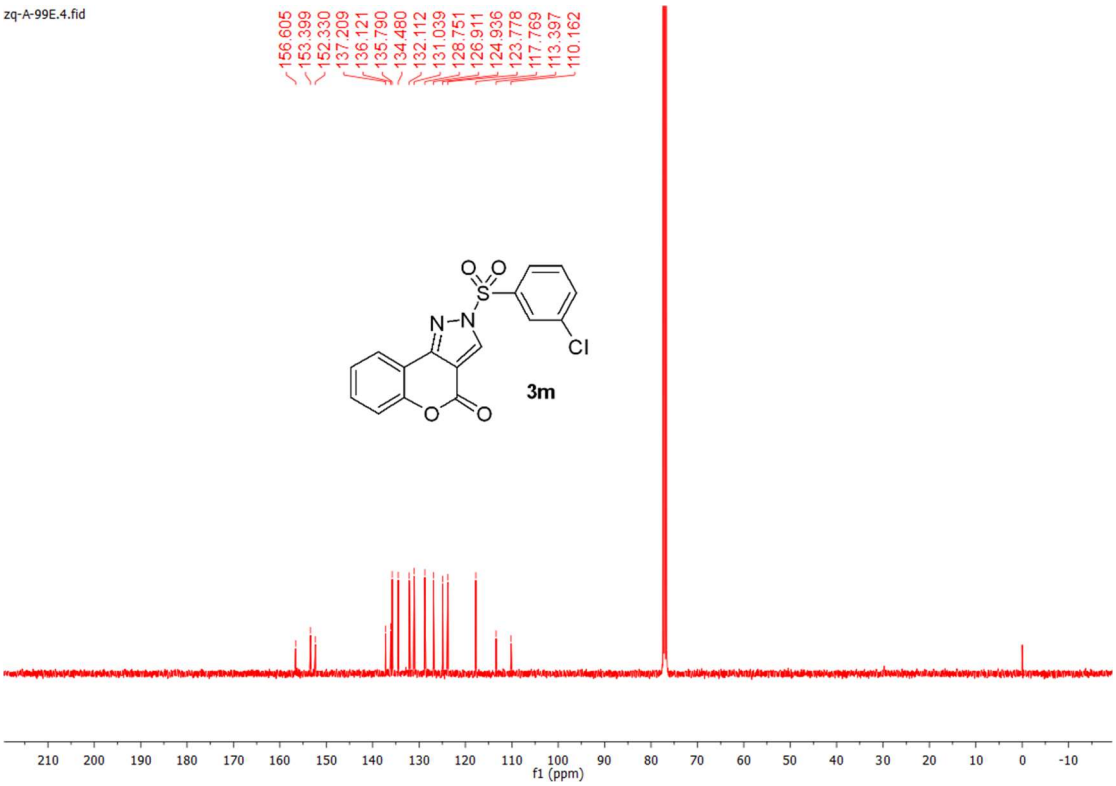
zq-A-96B

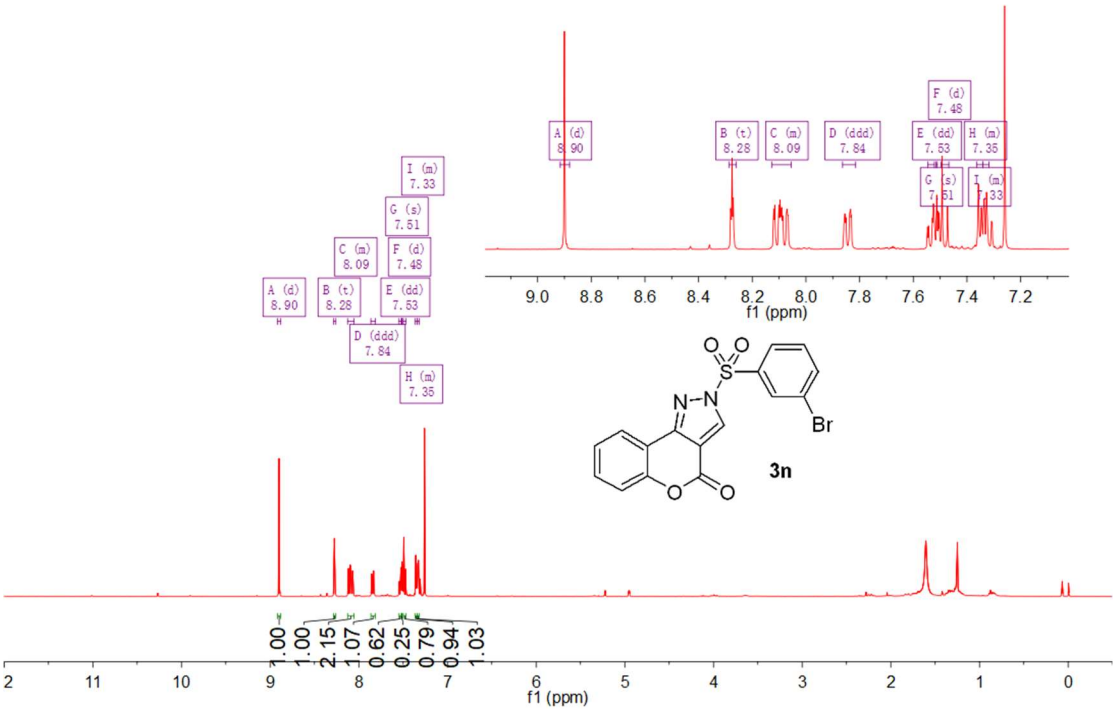

1.6
1.2
3k
1.00
0.97
2.19
2.10
1.17
2.18
f1 (ppm)
156.7
153.4
152.3
134.5
134.4
133.2
132.1
131.6
130.2
124.9
123.7
117.8
113.4
110.0
3k
f1 (ppm)
f1 (ppm)

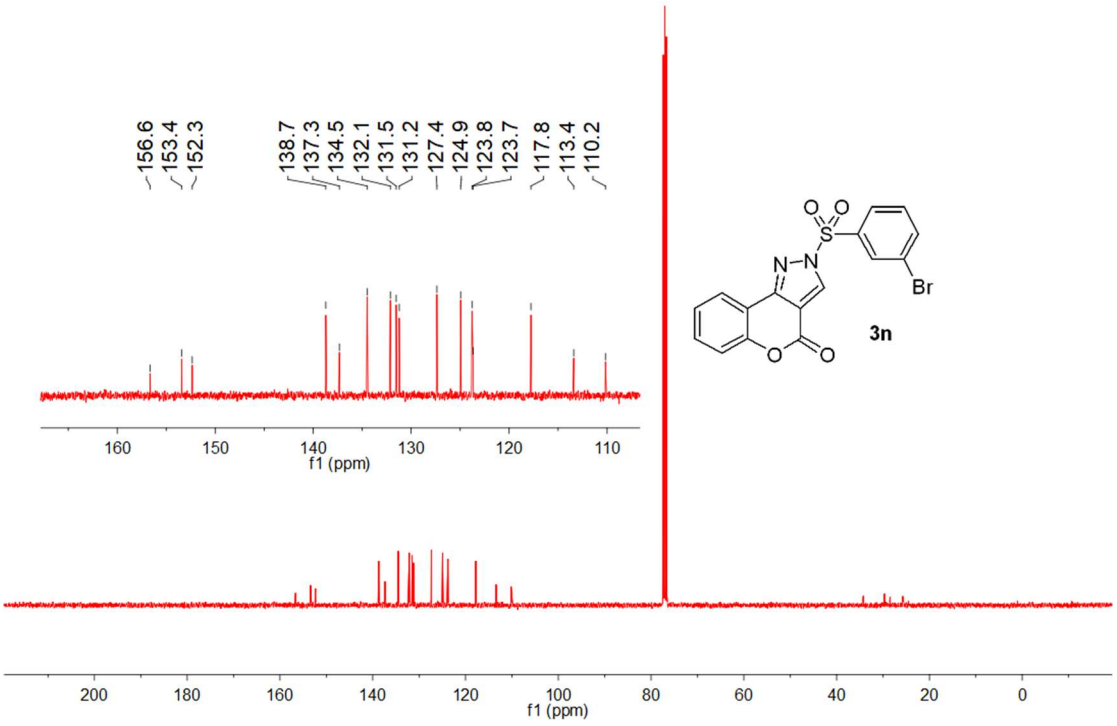

A (s)
8.89
B (t)
8.08
C (t)
8.02
D (d)
7.76
E (t)
7.53
F (dd)
7.33
G (s)
7.26
1.00
1.09
2.24
2.25
1.17
1.93
1.17
f1 (ppm)
Br
3l

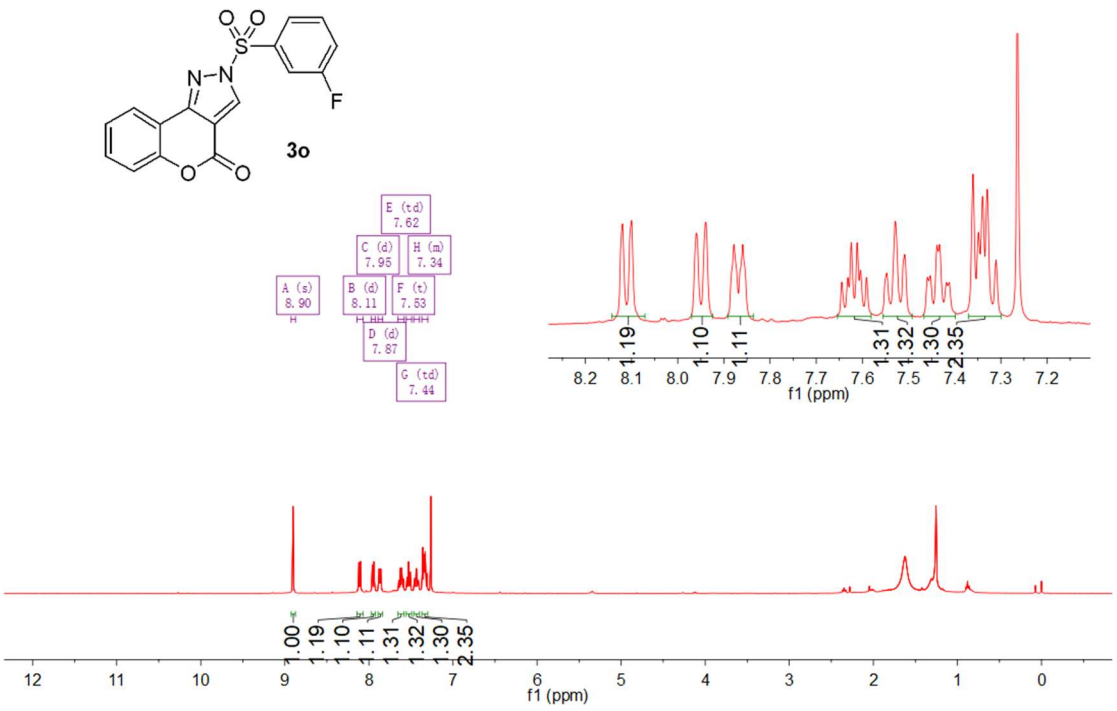

156.8
153.5
152.4
134.6
134.5
133.4
132.2
131.7
130.4
125.1
123.8
117.9
113.5
110.2
77.5
77.2
76.8
f1 (ppm)
Br
3l

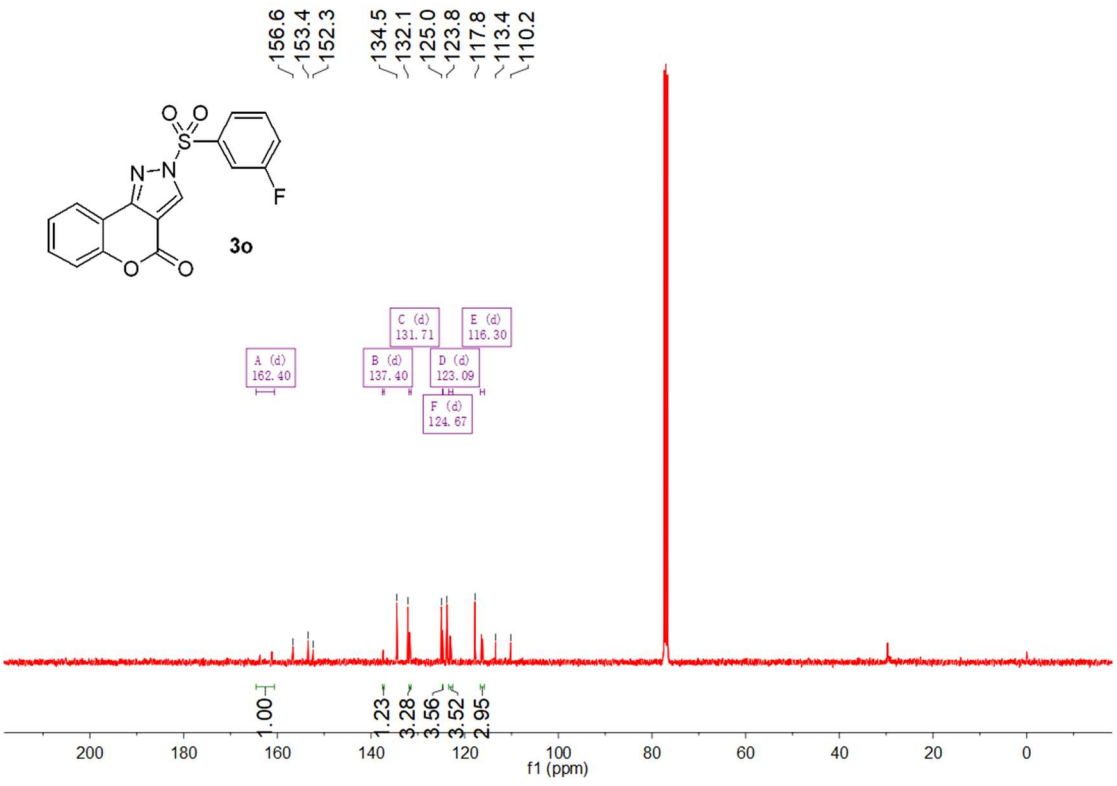

zq-A-99E.3.fid
zq-A-99E.3.fid
1.00
2.04
1.03
1.07
2.26
2.17
f1 (ppm)
3m
1.00
2.04
1.03
1.07
2.26
2.17
f1 (ppm)

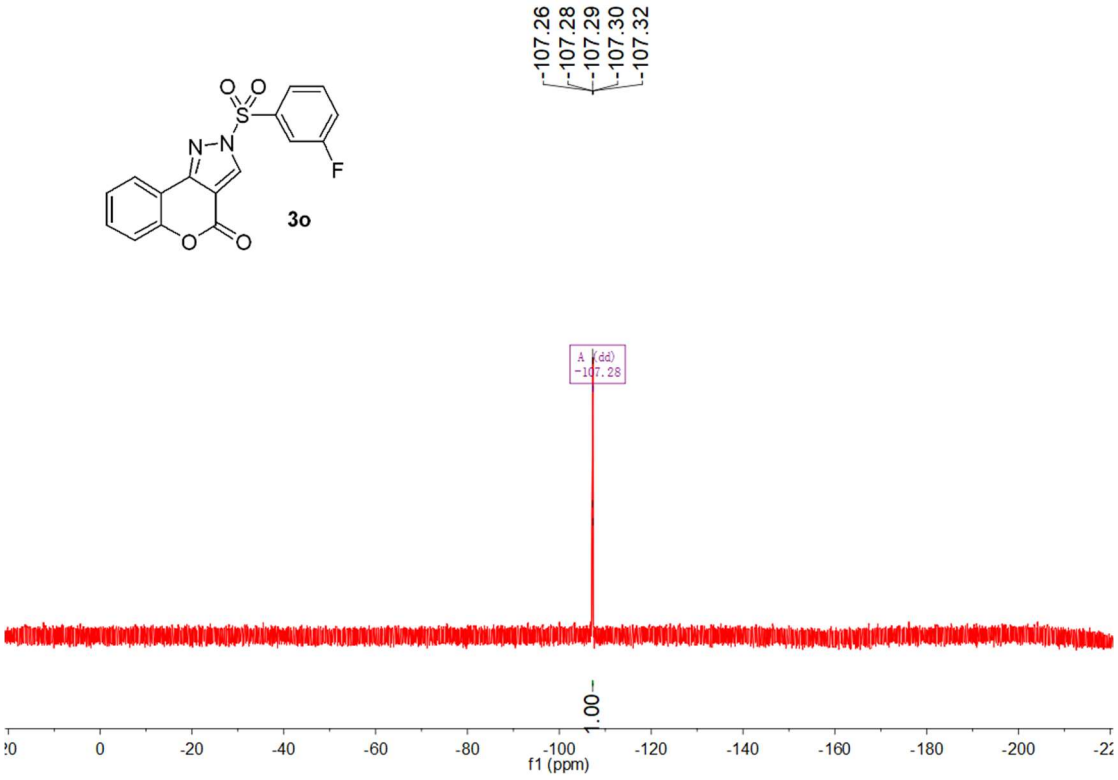

zq-A-99E.4.fid
156.605
153.399
152.330
137.209
136.121
135.790
134.480
132.112
131.039
128.751
126.911
124.936
123.778
117.769
113.397
110.162
3m
f1 (ppm)

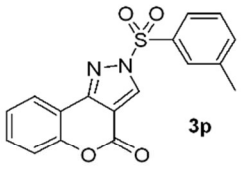

A (d) 8.90
B (t) 8.28
C (m) 8.09
D (ddd) 7.84
E (dd) 7.53
F (d) 7.48
G (s) 7.51
H (m) 7.35
I (m) 7.33
1.00
1.00
2.15
1.07
0.62
0.25
0.79
0.94
1.03
f1 (ppm)
Br
3n


156.6
153.4
152.3
138.7
137.3
134.5
132.1
131.5
131.2
127.4
124.9
123.8
123.7
117.8
113.4
110.2
f1 (ppm)
Br
3n

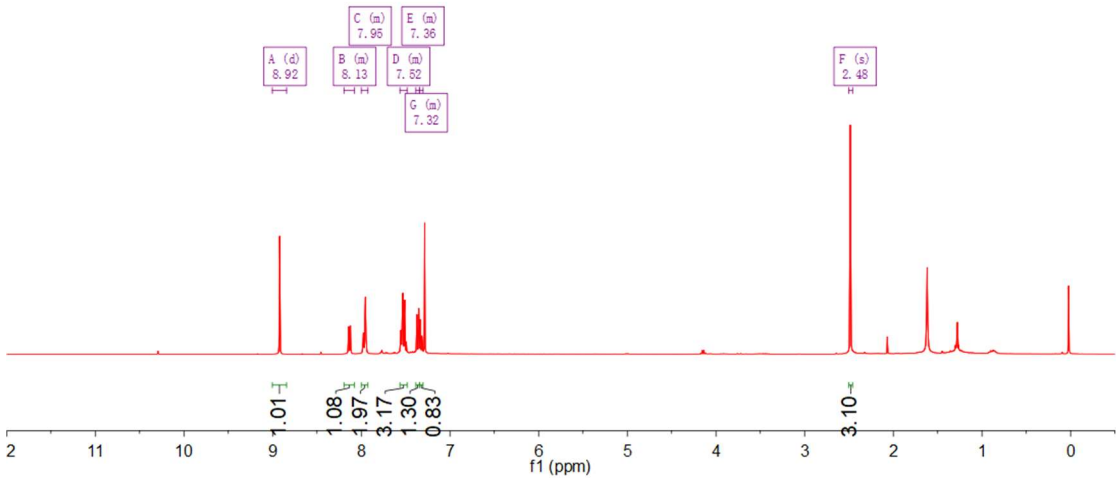

3o
E (td) 7.62
C (d) 7.95
H (m) 7.34
A (s) 8.90
B (d) 8.11
F (t) 7.53
D (d) 7.87
G (td) 7.44
1.19
1.10
1.11
1.31
1.32
1.30
2.35
f1 (ppm)
1.00
1.19
1.10
1.11
1.31
1.32
1.30
2.35
f1 (ppm)

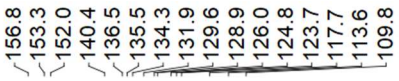

156.6
153.4
152.3
134.5
132.1
125.0
123.8
117.8
113.4
110.2
3o
C (d) 131.71
E (d) 116.30
A (d) 162.40
B (d) 137.40
D (d) 123.09
F (d) 124.67
1.00
1.23
3.28
3.56
3.52
2.95
f1 (ppm)

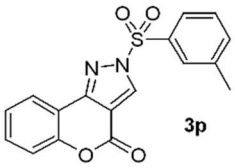

-107.26
-107.28
-107.29
-107.30
-107.32
O
O
S
N
N
F
O
O
3o
A (dd)
-107.28
1.00
0
-20
-40
-60
-80
-100
-120
-140
-160
-180
-200
f1 (ppm)



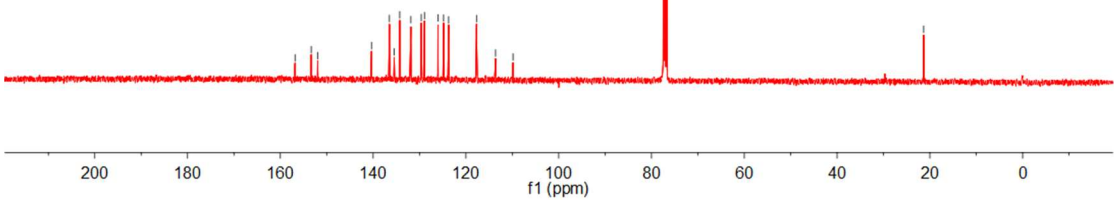
3p

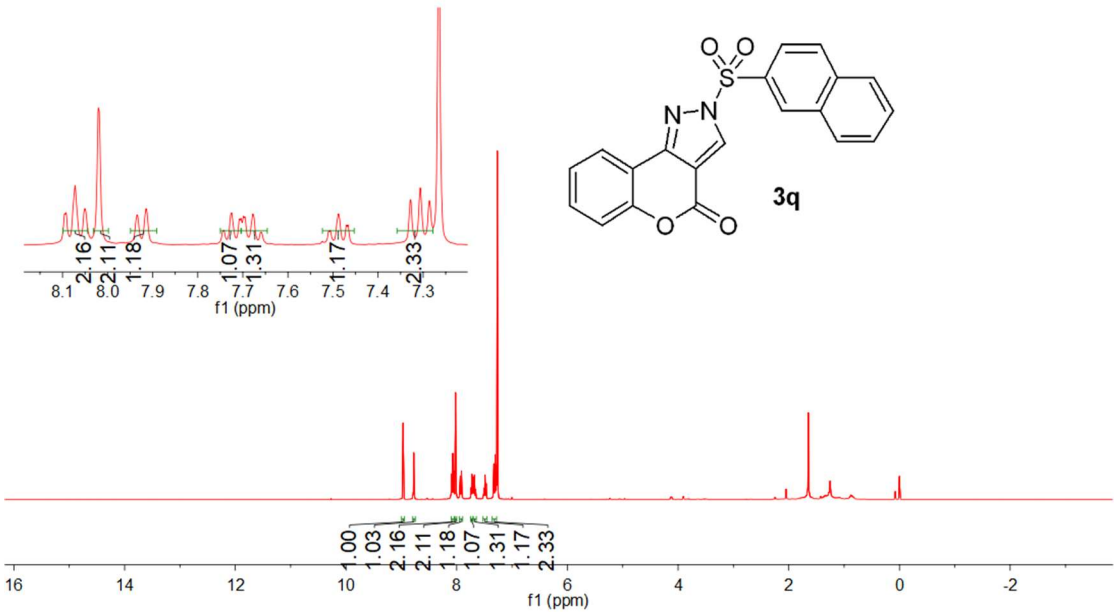

A (d) 8.92
B (m) 8.13
C (m) 7.95
D (m) 7.52
E (m) 7.36
G (m) 7.32
F (s) 2.48
1.01
1.08
1.97
3.17
1.30
0.83
3.10
f1 (ppm)

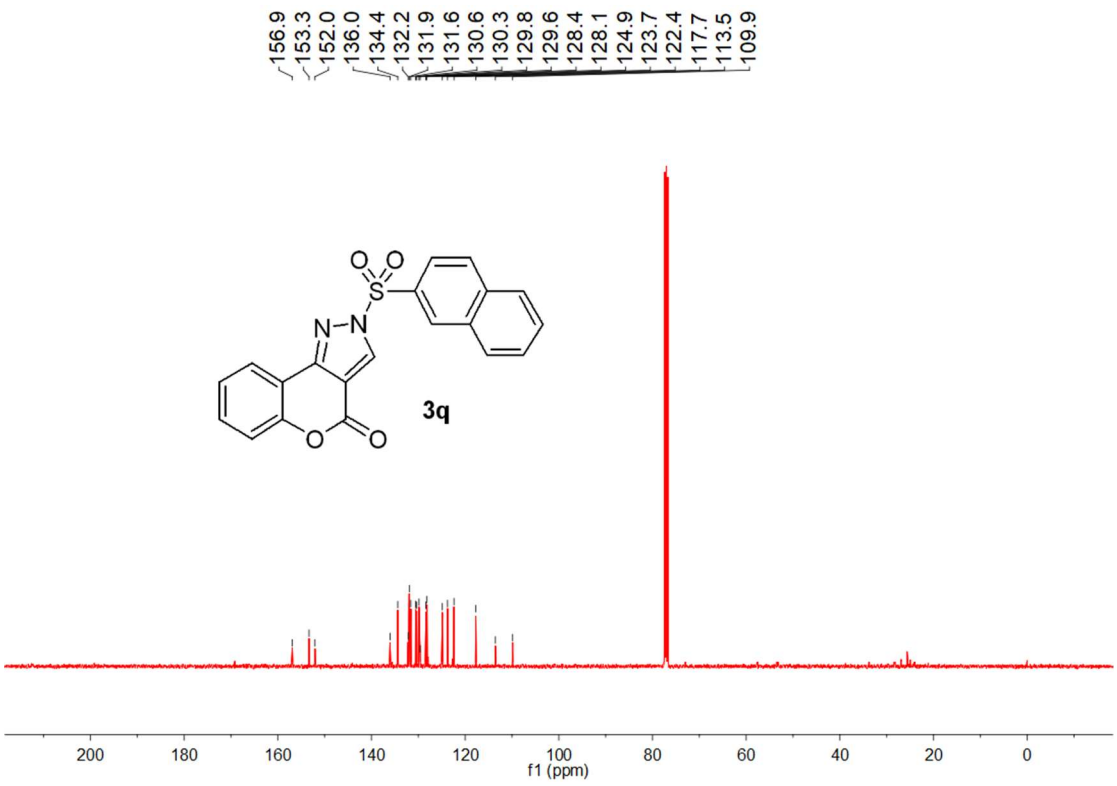

156.8
153.3
152.0
140.4
136.5
135.5
134.3
131.9
129.6
128.9
126.0
124.8
123.7
117.7
113.6
109.8
21.3

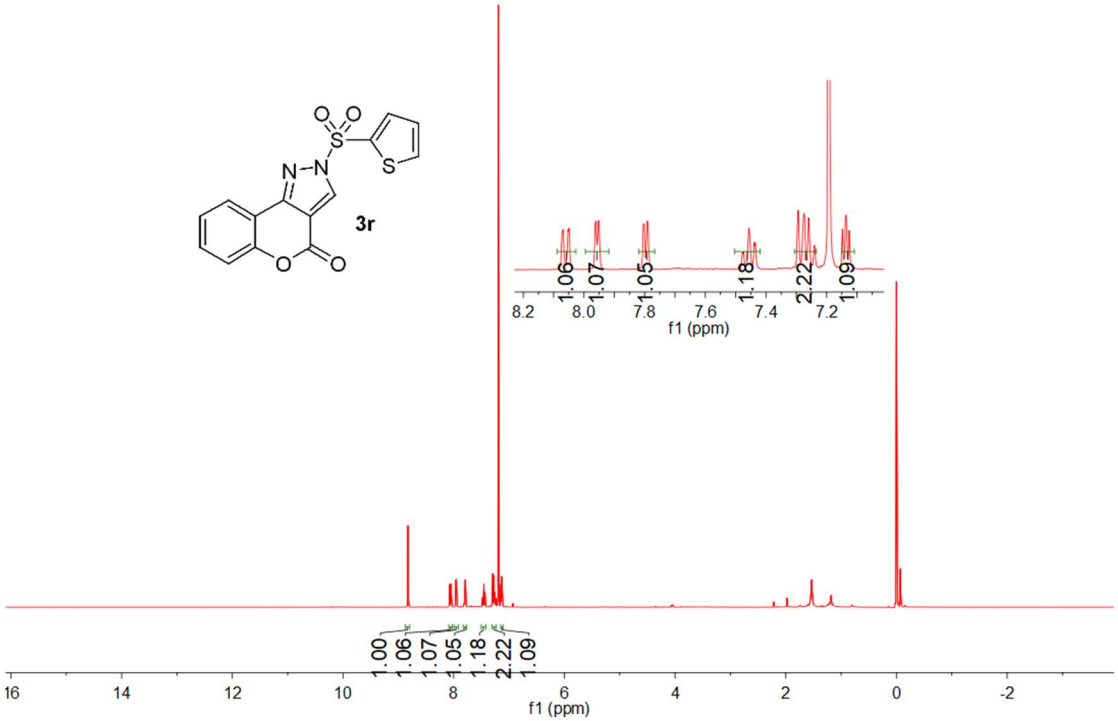


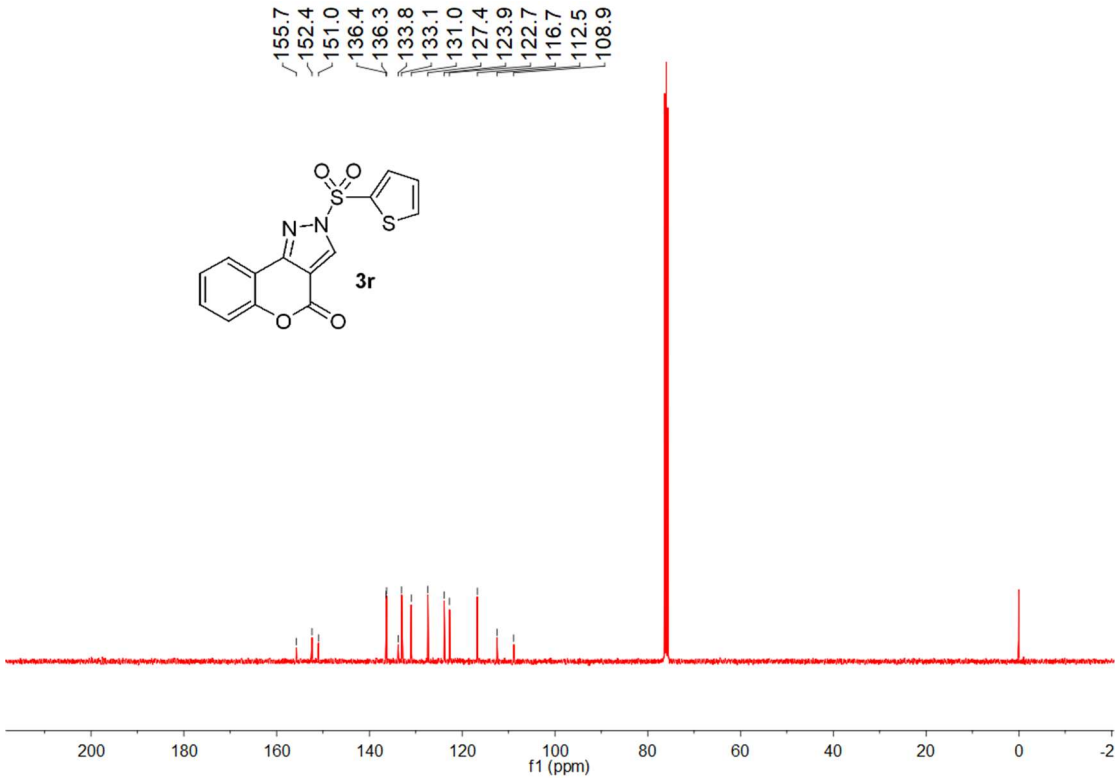
3p

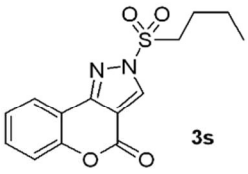

f1 (ppm)


2.16
2.11
1.18
1.07
1.31
1.17
2.33
8.1
8.0
7.9
7.8
7.7
7.6
7.5
7.4
7.3
f1 (ppm)
3q
1.00
1.03
2.16
2.11
1.18
1.07
1.31
1.17
2.33
16
14
12
10
8
6
4
2
0
-2
f1 (ppm)

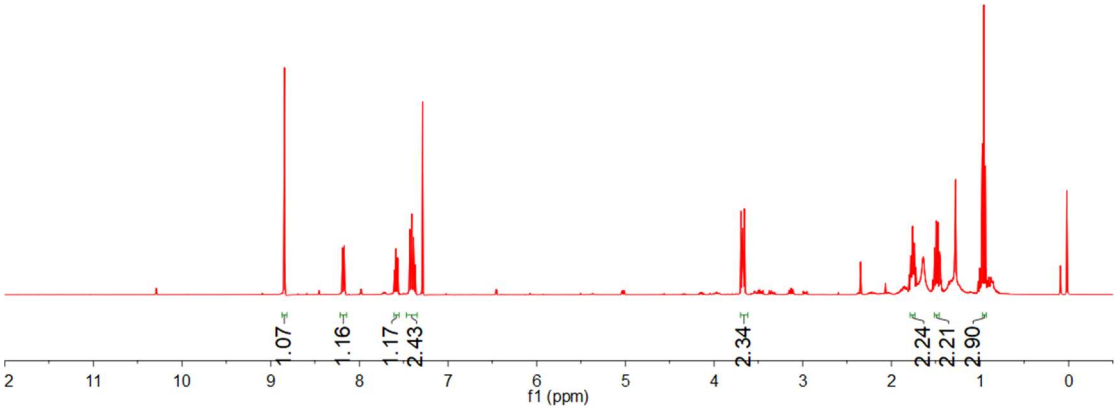

156.9
153.3
152.0
136.0
134.4
132.2
131.9
131.6
130.6
130.3
129.8
129.6
128.4
128.1
124.9
123.7
122.4
117.7
113.5
109.9
3q
200
180
160
140
120
100
80
60
40
20
0
f1 (ppm)

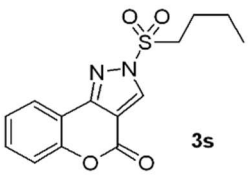

3r
1.06
1.07
1.05
1.18
2.22
1.09
8.2
8.0
7.8
7.6
7.4
7.2
f1 (ppm)
1.00
1.06
1.07
1.05
1.18
2.22
1.09
16
14
12
10
8
6
4
2
0
-2
f1 (ppm)


155.7
152.4
151.0
136.4
136.3
133.8
133.1
131.0
127.4
123.9
122.7
116.7
112.5
108.9
3r
200
180
160
140
120
100
80
60
40
20
0
-2
f1 (ppm)



3s


1.07
1.16
1.17
2.43
2.34
2.24
2.21
2.90
2
11
10
9
8
7
6
5
4
3
2
1
0
f1 (ppm)



3s

156.7
153.4
152.1
134.8
132.1
125.0
123.7
117.8
113.5
109.6
53.8
24.8
21.1
13.3
200
180
160
140
120
100
80
60
40
20
0
f1 (ppm)