Supporting Information

Construction of Novel Mn-based Metal-Organic Frameworks for Regioselective Cross-Dehydrogenative Coupling of Coumarins and Dimethylanilines

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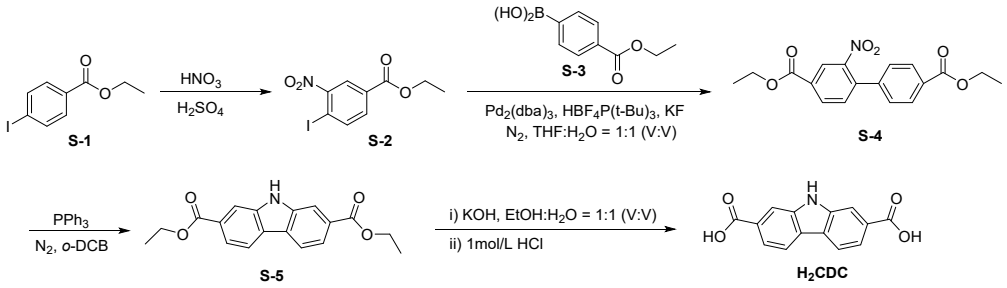
Contents

1. General information

Unless specifically emphasized, all reagents were purchased from commercial sources and used without further purification. Various gases required for experiments were supplied by Hangzhou Jingong Special Gases. ^{1}H NMR spectra and ^{13}C NMR spectra were recorded at 25 ^{o}C on Bruker AVANCE NEO (400 MHz) spectrometer and Bruker AVANCE NEO (100 MHz) spectrometer, respectively. The single-crystal X-ray diffraction (SCXRD) data were collected using a Bruker D8 Venture single-crystal diffractometer, equipped with a Cu Kα radiation source (λ = 1.54178 Å) at a temperature of 193 K. Power X-ray diffraction (PXRD) patterns were recorded with a PANalytical Empyrean powder diffractometer using Cu Kα radiation (λ= 0.1541 nm). The working voltage was 40 kV and the working current was 40 mA. The patterns were collected with a 2θ range from 2^{o} to 50^{o} at a step of 0.026^{o}. The BET surface area was determined with ASAP 2460 specific surface analyzer and a predetermined quantity of the sample was subjected to a degassing process at 120 °C for 6 h. The infrared spectra of the materials were recorded by Nexus 670 (Thermo Nicolet, USA) instrument at the range of 400-4000 cm^{-1} using KBr pellet technique. The morphology and size of the as-prepared Mn-CDC were characterized by Zeiss Sigma 300 VP scanning electron microscope (SEM). High resolution mass spectra (HRMS) were measured with an Agilent 6230 TOF instrument.

2. General procedure for the synthesis of 9*H*-carbazole-2,7-dicarboxylic acid



9*H*-carbazole-2,7-dicarboxylic acid (**H_2CDC**) was synthesized in our laboratory according to the literatures.[1,2] Firstly, ethyl 4-iodo-3-nitrobenzoate (**S-2**) was synthesized form ethyl 4-iodobenzoate (**S-1**) through a typical nitration reaction. Secondly, **S-2** reacted with (4-(ethoxycarbonyl)phenyl)boronic acid (**S-3**) via Suzuki-Miyaura cross coupling reaction to generate diethyl 2-nitro-[1,1'-biphenyl]-4,4'-dicarboxylate (**S-4**). Then, the resulting **S-4** and triphenylphosphine (PPh_3) were put in 1,2-dichlorobenzene (*o*-DCB) and was heated to reflux with vigorous stirring. Diethyl

9*H*-carbazole-2,7-dicarboxylate (**S-5**) was synthesized via Cadogan nitrene insertion. Finally, hydrolysis reaction of **S-5** produced the corresponding target product **H_2CDC**. In the whole process, all the products were characterized by NMR.

3. General procedure for the synthesis of Mn-CDC

H_2CDC (25.5 mg, 0.10 mmol) and $MnCl_2 \cdot 4H_2O$ (19.8 mg, 0.10 mmol) were dissolved in DMF (2 mL). Subsequently, deionized water (80 μL) was added, followed by sonication for 5 min. The resulting mixture was sealed in a glass vial and placed in a preheated oven at 100 °C for 24 h. After completion of the reaction, the mixture was cooled to room temperature and light-yellow flaky crystals were collected. The synthesized crystals were washed three times with DMF and MeOH. Following this, they were immersed in MeOH, with the new MeOH solution being replaced every eight hours for a period of three days. Subsequently, the crystals were subjected to vacuum drying at 60 °C for a duration of 10-12 h.

4. Characterization of Mn-CDC

Table S1. Crystallographic data and structure refinement parameters of Mn-CDC

Empirical formula	$C_{51}H_{44}Mn_3N_6O_{16}$
Formula weight	1161.0955
Temperature/K	193.00
Crystal system	Triclinic
Space group	*P*-1
a/Å	14.2545(7)
b/Å	18.0400(8)
c/Å	30.3498(14)
α/°	91.749(3)
β/°	96.795(3)
γ/°	100.827(3)
Volume/ Å^3	7600.6(6)
Z	2
ρ_{calc} g/cm^3	1.111
μ/mm^{-1}	4.497
F(000)	2620.0
Crystal size/mm^3	0.13 × 0.12 × 0.1
Radiation	CuKα (λ = 1.54178)
2θ range for data collection/°	4.994 to 133.19
Index ranges	-16 ≤ h ≤ 16, -21 ≤ k ≤ 21, -36 ≤ l ≤ 34
Reflections collected	94533
Independent reflections	26693 [R_{int} = 0.0990, R_{sigma} = 0.0857]
Data/restraints/parameters	26693/28/1525
Goodness-of-fit on F^2	1.081
Final R indexes [I>=2σ (I)]	R_1 = 0.0986, wR_2 = 0.2722
Final R indexes [all data]	R_1 = 0.1151, wR_2 = 0.2907
Largest diff. peak/hole / e Å^{-3}	0.98/-0.62

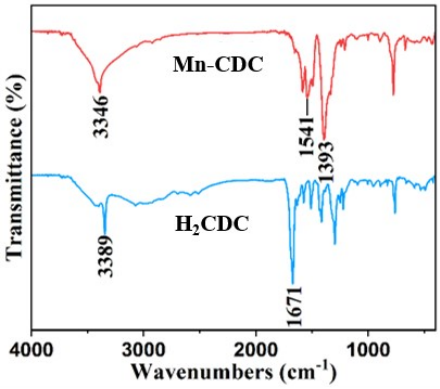


Fig. S1. FT-IR spectra of Mn-CDC and H_2CDC.

The absorption peaks at 3346 and 3389 cm^{-1}, were attributed to N-H stretching vibration of H_2CDC and Mn-CDC respectively, indicating that carbazole skeleton remained intact following the MOF synthesis reaction. In the FTIR spectrum of H_2CDC, the strong absorption peak at 1671 cm^{-1} was attributed to stretching vibration of the -COOH group, which significantly weakened in the FTIR spectrum of Mn-CDC due to the coordination of carboxylic group with Mn^{2+}. In the FTIR spectrum of Mn-CDC, the peaks at 1541 and 1393 cm^{-1} were assigned to vibrations of carboxylate.

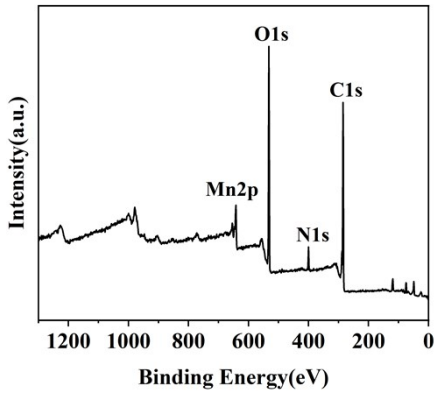


Fig. S2. XPS survey spectrum of Mn-CDC.

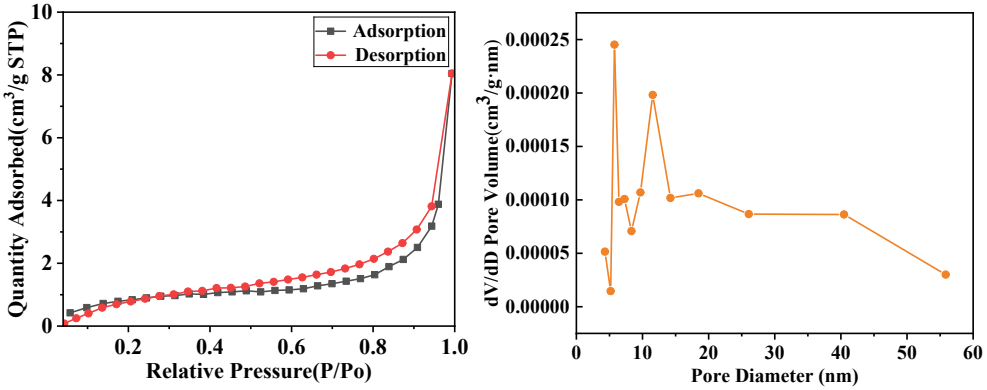


Fig. S3. BET surface area measurement and pore size distribution pattern of Mn-CDC.

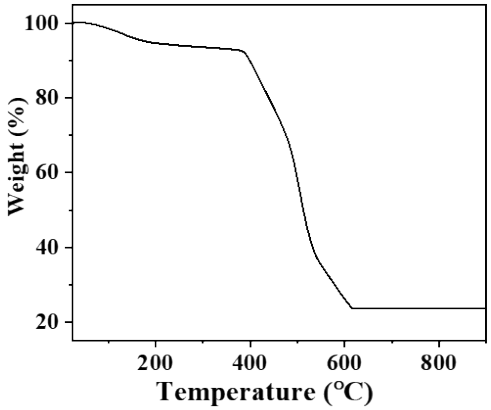


Fig. S4. TGA curve of Mn-CDC.

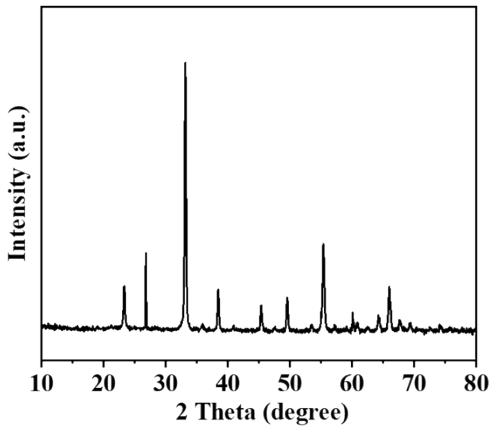


Fig S5. PXRD pattern of the residue obtained after the TGA test of Mn-CDC.

5. General procedure for the synthesis of Mn/Co-CDC

H_2CDC (25.5 mg, 0.10 mmol), $MnCl_2 \cdot 4H_2O$ (9.9 mg, 0.05 mmol) and $CoCl_2 \cdot 6H_2O$ (11.9 mg, 0.05 mmol) were dissolved in DMF (2 mL). Subsequently, deionized water (80 μL) was added, followed by sonication for 5 min. The resulting mixture was sealed in a glass vial and placed in a preheated oven at 100 °C for 24 h. After completion of the reaction, the mixture was cooled to room temperature and purple flaky crystals were collected. The synthesized crystals were washed three times with DMF and MeOH. Following this, they were immersed in MeOH, with the new MeOH solution being replaced every eight hours for a period of three days. Subsequently, the crystals were subjected to vacuum drying at 60 °C for a duration of 10-12 h.

6. Characterization of Mn/Co-CDC

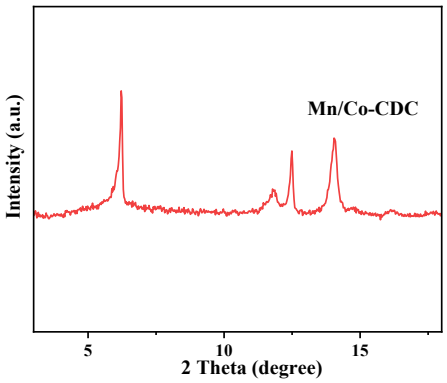


Fig. S6. PRXD pattern of Mn/Co-CDC.

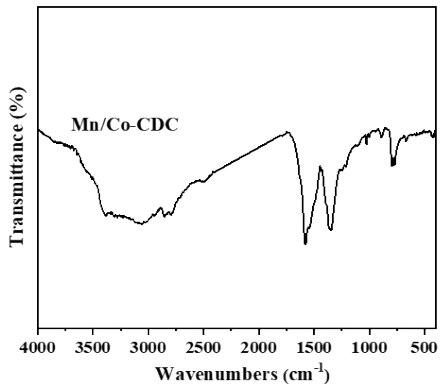


Fig. S7. FT-IR spectrum of Mn/Co-CDC.

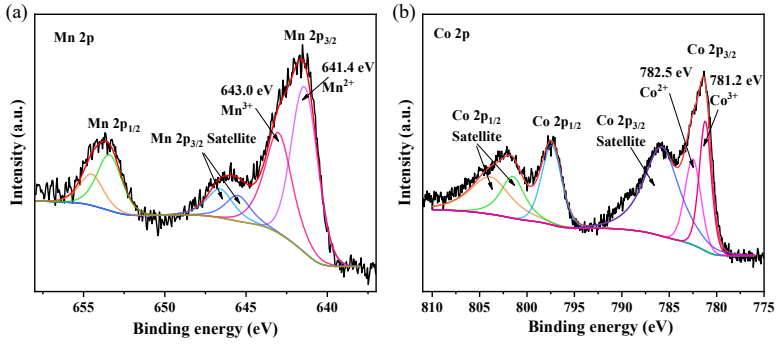


Fig. S8. (a) Mn 2p and (b) Co 2p XPS spectra of Mn/Co-CDC.

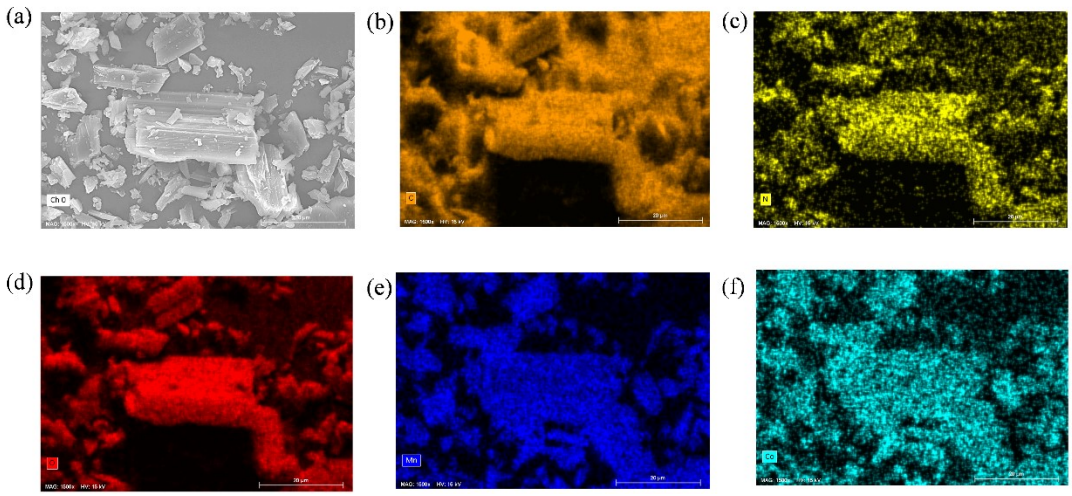
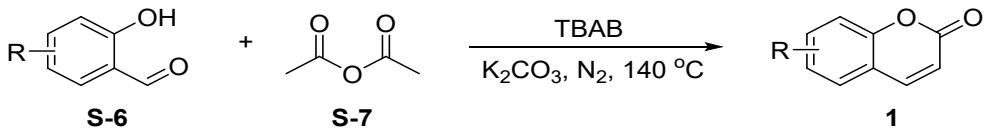


Fig. S9. (a) SEM images of Mn/Co-CDC; (b-f) EDX-mapping of C, N, O, Mn, and Co elements in Mn/Co-CDC.

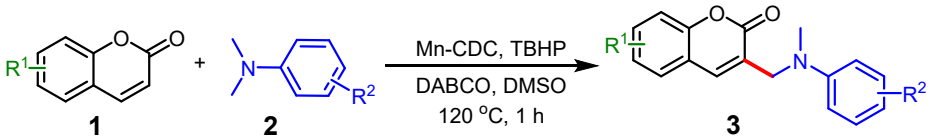
7. General procedure for the synthesis of coumarins 1b-1m



S-6 **S-7** **1**

Coumarins **1** were synthesized according to the literature procedure.[3] Salicylaldehyde (**S-6**, 8.00 mmol), acetic anhydride (**S-7**, 8.00 mmol), anhydrous potassium carbonate (2.00 mmol) and tetrabutylammonium bromide (TBAB, 0.32 mmol) were added into a reaction bottle and then stirred at 140°C for 1 h. Subsequently, a portion of the acetic acid formed in reaction was evaporated, and another portion of **S-7** (16.00 mmol) was added dropwise to the mixture, which continued to be stirred at 140 °C for 6 h. After completion of the reaction, the pH of reaction mixture was adjusted to 8 with a saturated Na_2CO_3 solution. The resulting mixture was extracted with ethyl acetate. The combined organic phase was dried with anhydrous Na_2SO_4, and evaporated under vacuum. The crude products were purified by silica column chromatography with petroleum ether/ethyl acetate as the eluent to afford coumarins **1b-1m**.

8. General procedure for coupling reactions of coumarins with dimethylanilines



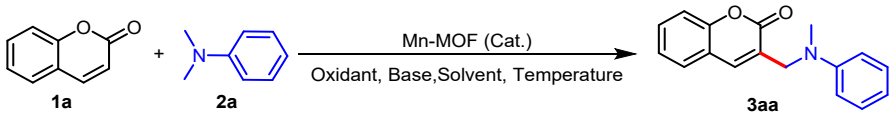
1 **2** **3**

Coumarins (**1**, 0.2 mmol), *N,N*-dimethylanilines (**2**, 5.0 equiv.), TBHP (4.0 equiv.), DABCO (1.5 equiv.), Mn-CDC (5.0 mg) and DMSO (0.5 mL) were added to

a reaction tube and the mixture was stirred at 120 °C for 1 h. After completion of the reaction, the mixture was concentrated in vacuo and the residue was purified by column chromatography using petroleum ether/ethyl acetate as the eluent to afford products **3**, which were characterized by NMR.

9. Optimization of coupling reaction conditions of coumarin with dimethylaniline

Table S2. Optimization of the reaction conditions [a]



Entry	Variation from the standard conditions	Yield (%) [b]
1	none	73
2	MeCN instead of DMSO	48
3	1,4-Dioxane, THF, Acetone or MeOH instead of DMSO	trace
4	Mn-CDC (10 mg, about 0.043 mol%)	73
5	**2a** (4.0 equiv.) instead of **2a** (5.0 equiv.)	48
6	**2a** (6.0 equiv.) instead of **2a** (5.0 equiv.)	73
7	O_2, H_2O_2 or DTBP instead of TBHP	trace
8	TEA instead of DABCO	trace
9	NaOAc instead of DABCO	44
10	K_2CO_3 instead of DABCO	74
11	110 °C instead of 120 °C	57
12	130 °C instead of 120 °C	72
13	0.5 h instead of 1 h	65
14	1.5 h instead of 1 h	71
15	TBHP (3.0 equiv.) instead of TBHP (4.0 equiv.)	58
16	TBHP (5.0 equiv.) instead of TBHP (4.0 equiv.)	67
17	DABCO (1.0 equiv.) instead of DABCO (1.5 equiv.)	58
18	DABCO (2.0 equiv.) instead of DABCO (1.5 equiv.)	73
19	Without Mn-CDC	9

[a] Standard conditions: **1a** (0.2 mmol), **2a** (5.0 equiv.), Mn-CDC (5 mg, about 0.022 mol%), TBHP (4.0 equiv.), DABCO (1.5 equiv.), DMSO, 120 °C, 1 h. The concentration of **1a** and **2a** in DMSO were 0.4 M and 2.0 M. [b] Isolated yield.

10. A comparison of the current methodology with the reported methods

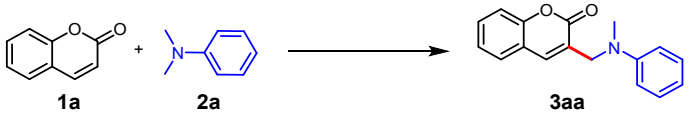


Table S3. Coupling reactions of coumarin **1a** with *N*,*N*-dimethylaniline **2a**.

Catalyst	Oxidant	Additive	Yield (%)	Reference
$^{n}Bu_4NI$	TBHP	DBU	80	[7]
$Ru(bpy)_3Cl_2·6H_2O$	O_2	DBU	82	[8]
$Fe_3(BTC)(NDC)_2·6.65H_2O$	TBHP	DABCO	89	[20]
$Mn_6(CDC)_6(DMF)_6(H_2O)_2$	TBHP	DABCO	73	This work

11. Recycle experiments results of Mn-CDC

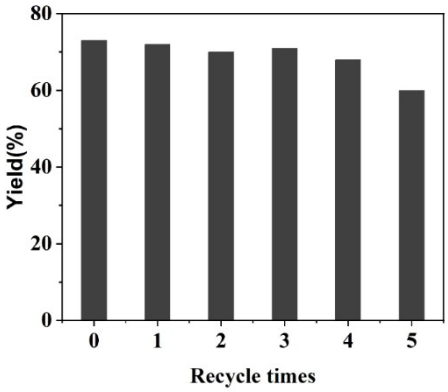


Fig. S10. Recycle experiments results of Mn-CDC.

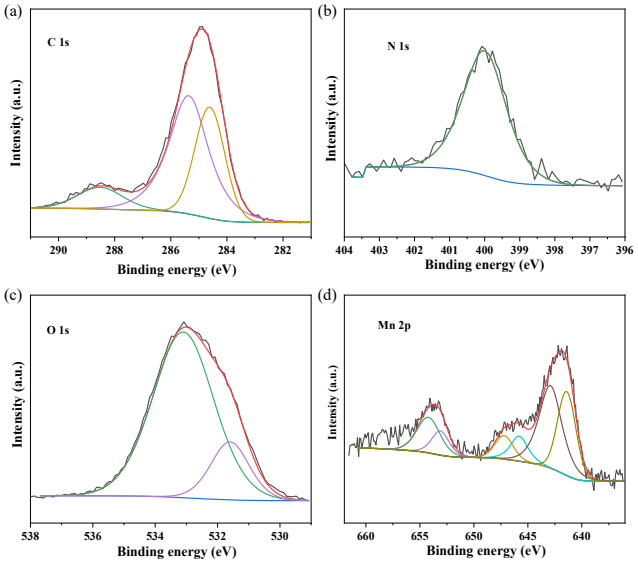


Fig. S11. XPS spectra of recovered Mn-CDC after cycles.

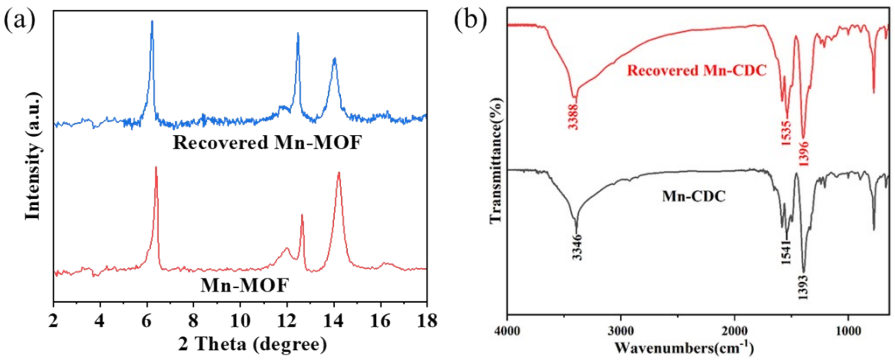
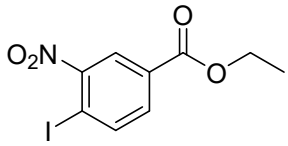
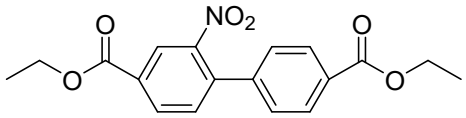


Fig. S12. (a) Comparison of PXRD patterns of Mn-CDC and recovered Mn-CDC. (b) Comparison of FT-IR spectra of Mn-CDC and recovered Mn-CDC.

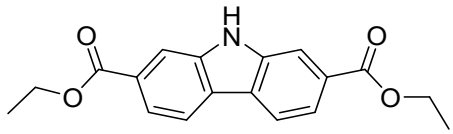
12. Characterization of the compounds involved in the synthesis of CDC



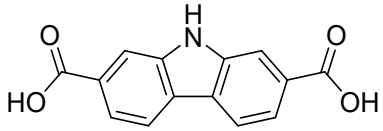
Ethyl 4-iodo-3-nitrobenzoate (S-2): Yellow solid; ^{1}H NMR (400 MHz, $CDCl_3$): δ 8.44 (s, 1H), 8.14 (d, J = 8.2 Hz, 1H),7.88 (dd, J = 8.2, 2.0 Hz, 1H), 4.44-4.39 (m, 2H), 1.41 (t, J = 7.2 Hz, 3H); ^{13}C NMR (100 MHz, $CDCl_3$): δ 164.1, 153.2, 142.3, 133.5, 132.0, 126.0, 92.0, 62.2, 14.3. NMR data is consistent with literature values.[4]



Diethyl 2-nitro-[1,1'-biphenyl]-4,4'-dicarboxylate (S-4): Yellow solid; ^{1}H NMR (400 MHz, $CDCl_3$): δ 8.54 (d, J = 1.7 Hz, 1H), 8.29 (dd, J = 8.0, 1.7 Hz, 1H), 8.12 (d, J = 8.3 Hz, 2H), 7.53 (d, J = 8.0 Hz, 1H), 7.39 (d, J = 8.3 Hz, 2H), 4.48-4.37 (m, 4H), 1.45-1.39 (m, 6H); ^{13}C NMR (100 MHz, $CDCl_3$): δ 166.0, 164.2, 149.0, 141.0, 139.4, 133.1, 132.0, 131.4, 130.8, 130.0, 127.8, 125.4, 62.0, 61.2, 14.3 (d, J = 4.7 Hz). NMR data is consistent with literature values.[1]

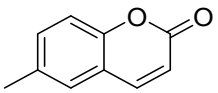


Diethyl 9*H*-carbazole-2,7-dicarboxylate (S-5): White solid; ^{1}H NMR (400 MHz, DMSO-d_6): δ 8.29 (d, J = 8.2 Hz,2H), 8.16 (s, 2H), 7.80 (d, J = 8.2 Hz, 2H), 4.38-4.33 (m, 4H), 1.36 (t, J = 7.1 Hz, 6H); ^{13}C NMR (100 MHz, DMSO-d_6): δ 166.3, 140.4, 127.9, 125.2, 121.2, 119.7, 112.8, 60.3, 14.3. NMR data is consistent with literature values.[1]

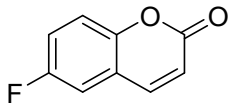


9*H*-Carbazole-2,7-dicarboxylic acid (CDC): Yellow solid; ^{1}H NMR (400 MHz, DMSO-d_6): δ 8.28 (d, *J* = 8.2 Hz, 2H), 8.16 (s, 2H), 7.81(d, *J* = 8.1 Hz, 2H); ^{13}C NMR (100 MHz, DMSO-d_6): δ 167.9, 140.4, 128.8, 125.1, 120.9, 120.0, 112.9. NMR data is consistent with literature values.[1]

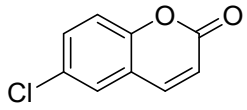
13. Characterization of coumarins 1b-1m



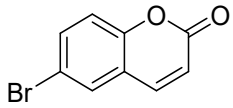
6-Methyl-2*H*-chromen-2-one (1b): Yellow solid; ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.66 (d, *J* = 9.6 Hz, 1H), 7.33 (dd, *J* = 8.5, 2.1 Hz, 1H), 7.27 (d, *J* = 2.1 Hz, 1H), 7.22 (d, *J* = 8.4 Hz, 1H), 6.40 (d, *J* = 9.5 Hz, 1H), 2.40 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 161.1, 152.1, 143.4, 134.1, 132.8, 127.7, 118.5, 116.5 (d, *J* = 2.1 Hz), 20.7. NMR data is consistent with literature values.[5]



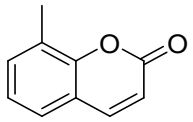
6-Fluoro-2*H*-chromen-2-one (1c): White solid; ^{1}H NMR (400 MHz, $CDCl_3$): 7.69 (d, *J* = 9.6 Hz, 1H), 7.34-7.30 (m, 1H), 7.28-7.26 (m, 1H),7.20 (dd, *J* = 7.9, 2.9 Hz, 1H), 6.49 (d, *J* = 9.6 Hz, 1H); ^{13}C NMR (100 MHz, $CDCl_3$): δ 160.3, 158.7 (d, *J* = 244.3 Hz), 150.2 (d, *J* = 2.1 Hz), 142.5 (d, *J* = 2.8 Hz), 119.5 (d, *J* = 9.0 Hz), 119.2 (d, *J* = 24.5 Hz), 118.4 (d, *J* = 8.4 Hz), 117.9, 113.2 (d, *J* = 23.8 Hz). NMR data is consistent with literature values.[5]



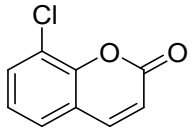
6-Chloro-2*H*-chromen-2-one (1d): White solid; ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.66 (d, *J* = 9.6 Hz, 1H), 7.50-7.47 (m, 2H), 7.30-7.26 (m, 1H), 6.48 (d, *J* = 9.6 Hz, 1H); ^{13}C NMR (100 MHz, $CDCl_3$): δ 160.0, 152.4, 142.2, 131.8, 129.7, 127.1, 119.18, 118.3, 117.8. NMR data is consistent with literature values.[5]



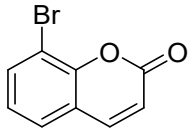
6-Bromo-2*H*-chromen-2-one (1e): White solid; ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.64-7.59 (m, 3H), 7.21 (d, *J* = 8.5 Hz, 1H), 6.45 (d, *J* = 9.6 Hz, 1H); ^{13}C NMR (100 MHz, $CDCl_3$): δ 160.0, 152.9, 142.2, 134.6, 130.2, 120.3, 118.7, 117.9, 117.0. NMR data is consistent with literature values.[5]



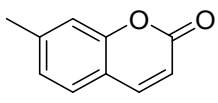
8-Methyl-2*H*-chromen-2-one (1f): White solid; ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.68 (d, *J* = 9.5 Hz, 1H), 7.37 (d, *J* = 7.4 Hz, 1H), 7.31 (d, *J* = 7.6 Hz, 1H), 7.16 (t, *J* = 7.6 Hz, 1H), 6.39 (d, *J* = 9.5 Hz, 1H), 2.44 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$): δ 161.0, 152.4, 143.8, 133.2, 126.3, 125.6, 124.0, 118.5, 116.3, 15.4. NMR data is consistent with literature values.[5]



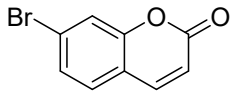
8-Chloro-2*H*-chromen-2-one (1g): White solid; ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.70 (d, *J* = 9.6 Hz, 1H), 7.59-7.56 (m, 1H), 7.41-7.39 (m, 1H), 7.21 (t, *J* = 7.9 Hz, 1H), 6.45 (d, *J* = 9.6 Hz, 1H); ^{13}C NMR (100 MHz, $CDCl_3$): δ 159.5, 149.7, 143.1, 132.2, 126.4, 124.7, 121.7, 120.1, 117.3. NMR data is consistent with literature values.[5]



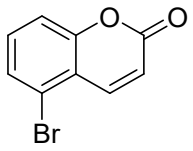
8-Bromo-2*H*-chromen-2-one (1h): White solid; ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.75 (d, *J* = 8.0 Hz, 1H), 7.68 (d, *J* = 9.6 Hz, 1H), 7.44 (dd, *J* = 7.8, 1.5 Hz, 1H), 7.16 (t, *J* = 7.8 Hz, 1H), 6.45 (dd, *J* = 9.5, 1.4 Hz, 1H); ^{13}C NMR (100 MHz, $CDCl_3$): δ 159.7, 150.8, 143.2, 135.4, 127.2, 125.2, 120.1, 117.3, 110.4. NMR data is consistent with literature values.[5]



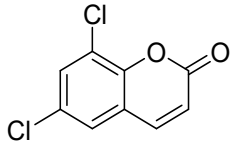
7-Methyl-2*H*-chromen-2-one (1i): White solid; ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.65 (d, *J* = 9.5 Hz, 1H), 7.34 (d, *J* = 7.8 Hz, 1H), 7.11 (s, 1H), 7.13-7.04 (m, 2H),6.33 (d, *J* = 9.5 Hz, 1H), 2.43 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$): δ 161.1, 154.2, 143.4, 143.1, 127.5, 125.6, 117.0, 116.5, 115.4, 21.7. NMR data is consistent with literature values.[5]



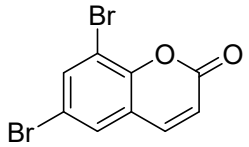
7-Bromo-2*H*-chromen-2-one (1j): White solid; ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.66 (d, *J* = 9.6 Hz, 1H), 7.49 (d, *J* = 1.9 Hz, 1H), 7.42-7.39 (m, 1H), 7.34 (d, *J* = 8.3 Hz, 1H), 6.42 (d, *J* = 9.6 Hz, 1H); ^{13}C NMR (100 MHz, $CDCl_3$): δ 159.9, 154.3, 142.8, 128.8, 127.9, 125.8, 120.2, 117.8, 116.9. NMR data is consistent with literature values.[5]



5-Bromo-2*H*-chromen-2-one (1k): White solid; ^{1}H NMR (400 MHz, $CDCl_3$): δ 8.07 (d, *J* = 9.8 Hz, 1H), 7.52-7.50 (m, 1H), 7.38 (t, *J* = 8.1 Hz, 1H), 7.29 (d, *J* = 8.4 Hz, 1H), 6.50 (d, *J* = 9.8 Hz, 1H); ^{13}C NMR (100 MHz, $CDCl_3$): δ 159.9, 154.8, 142.2, 132.2, 128.5, 122.4, 118.8, 117.8, 116.5. NMR data is consistent with literature values.[6]

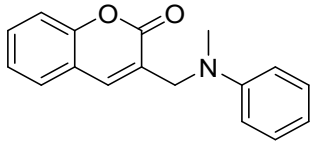


6,8-Dichloro-2*H*-chromen-2-one (1l): Yellow solid; ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.64 (d, *J* = 9.6 Hz, 1H), 7.57 (d, *J* = 2.3 Hz, 1H), 7.39 (d, *J* = 2.3 Hz, 1H), 6.51 (d, *J* = 9.6 Hz, 1H); ^{13}C NMR (100 MHz, $CDCl_3$): δ 158.8, 148.4, 142.0, 131.8, 129.6, 125.8, 122.7, 120.6, 118.5. NMR data is consistent with literature values.[5]

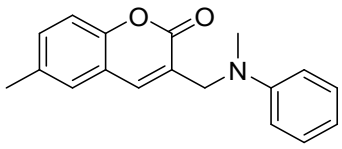


6,8-Dibromo-2*H*-chromen-2-one (1m): Yellow solid; ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.87 (d, *J* = 2.2 Hz, 1H), 7.62-7.57 (m, 2H), 6.49 (d, *J* = 9.5 Hz, 1H); ^{13}C NMR (100 MHz, $CDCl_3$): δ 158.9, 150.0, 141.9, 137.4, 129.5, 121.1, 118.5, 117.0, 111.5. NMR data is consistent with literature values.[7]

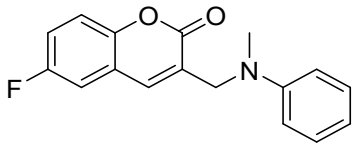
14. Characterization of coupling products 3



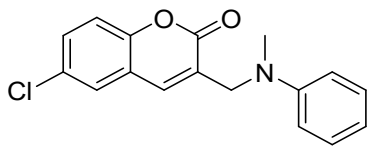
3-((Methyl(phenyl)amino)methyl)-2*H*-chromen-2-one (3aa): Yellow solid; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.50-7.45 (m, 2H), 7.39-7.33 (m, 2H), 7.25-7.22 (m, 3H), 6.77-6.70 (m, 3H), 4.43 (d, *J* = 1.8 Hz, 2H), 3.11 (s, 1H); ^{13}C NMR (100 MHz, $CDCl_3$): δ 161.2, 153.1, 148.9, 137.7, 131.0, 129.4, 127.7, 125.4, 124.4, 119.2, 117.0, 116.5, 112.0, 52.7, 38.9. NMR data is consistent with literature values.[8]



6-Methyl-3-((methyl(phenyl)amino)methyl)-2*H*-chromen-2-one (3ba): Yellow solid; ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.36 (d, *J* = 2.0 Hz, 1H), 7.26-7.19 (m, 4H), 7.12 (s, 1H), 6.73-6.67 (m, 3H), 4.39 (d, *J* = 2.1 Hz, 2H), 3.08 (d, *J* = 1.7 Hz, 3H), 2.32 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$): δ 161.4, 151.1, 148.8, 137.7, 134.0, 132.0, 129.3, 127.5, 125.0, 118.9, 116.9, 116.1, 111.9, 52.6, 38.9, 20.7. NMR data is consistent with literature values.[8]

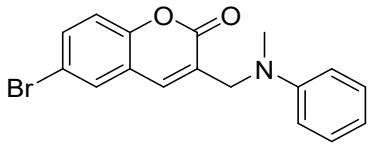


6-Fluoro-3-((methyl(phenyl)amino)methyl)-2*H*-chromen-2-one (3ca): Yellow solid; ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.40 (s, 1H), 7.33-7.30 (m, 1H), 7.26-7.16 (m, 3H), 7.07 (dd, *J* = 8.0, 3.0 Hz, 1H), 6.76 (t, *J* = 7.3 Hz, 1H), 6.69 (d, *J* = 8.2 Hz, 2H), 4.43 (s, 2H), 3.11 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$): δ 160.8, 158.7 (d, *J* = 244.1 Hz), 149.2 (d, *J* = 2.1 Hz), 148.8, 136.7 (d, *J* = 2.9 Hz), 129.4, 126.8, 120.0 (d, *J* = 9.1 Hz), 118.4 (d, *J* = 24.4 Hz), 118.0 (d, *J* = 8.5 Hz), 117.2, 113.0 (d, *J* = 23.8 Hz), 112.0, 52.8, 39.0. NMR data is consistent with literature values.[9]

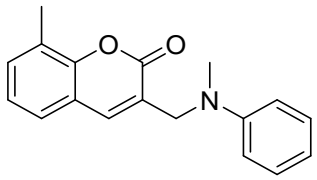


6-Chloro-3-((methyl(phenyl)amino)methyl)-2*H*-chromen-2-one (3da): Yellow solid; ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.42 (dd, *J* = 8.8, 2.4 Hz, 1H), 7.37 (t, *J* = 1.9 Hz,

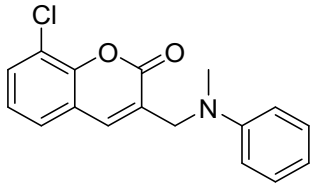
2H), 7.30-7.22 (m, 3H), 6.76 (t, J = 7.3 Hz, 1H), 6.71-6.68 (m, 2H), 4.43 (d, J = 1.8 Hz, 2H), 3.11 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$): δ 160.6, 151.4, 148.7, 136.5, 130.9, 129.7, 129.5, 127.0, 126.8, 120.3, 117.9, 117.3, 112.0, 52.7, 39.0. NMR data is consistent with literature values.[8]



6-Bromo-3-((methyl(phenyl)amino)methyl)-2*H*-chromen-2-one (3ea): Yellow solid; ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.57 (dd, J = 8.8, 2.1 Hz, 1H), 7.53 (d, J = 2.5 Hz, 1H), 7.39 (s, 1H), 7.28-7.23 (m, 3H), 6.78 (t, J = 7.3 Hz, 1H), 6.71 (d, J = 8.1 Hz, 2H), 4.45 (s, 2H), 3.13 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$): δ 160.5, 151.9, 148.7, 136.4, 133.7, 130.0, 129.4, 126.7, 120.8, 118.2, 117.2, 117.0, 112.0, 52.7, 39.0. NMR data is consistent with literature values.[8]

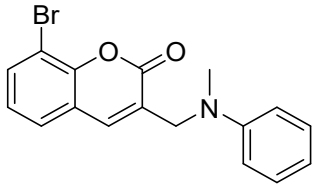


8-Methyl-3-((methyl(phenyl)amino)methyl)-2*H*-chromen-2-one (3fa): Yellow solid; ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.44 (s, 1H), 7.33 (d, J = 7.3 Hz, 1H), 7.26-7.21 (m, 3H), 7.13 (t, J = 7.5 Hz, 1H), 6.77-6.70 (m, 3H), 4.44 (d, J = 1.8 Hz, 2H), 3.11 (s, 3H), 2.47 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$): δ 161.4, 151.4, 148.9, 138.1, 132.3, 129.4, 125.9, 125.4, 124.9, 124.0, 118.9, 116.9, 111.9, 52.6, 38.9, 15.5; HRMS (ESI): m/z calcd for $C_{18}H_{17}NO_2$ $[M+H]^+$ 280.1332 Found 280.1336.

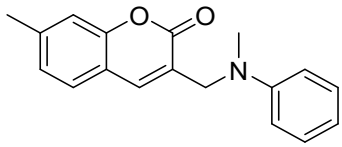


8-Chloro-3-((methyl(phenyl)amino)methyl)-2*H*-chromen-2-one (3ga): Yellow solid; ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.53 (dd, J = 7.9, 1.5 Hz, 1H), 7.44 (t, J = 1.8 Hz, 1H), 7.29 (dd, J = 7.8, 1.5 Hz, 1H), 7.26-7.22 (m, 2H), 7.17 (t, J = 7.8 Hz, 1H), 6.77-6.74

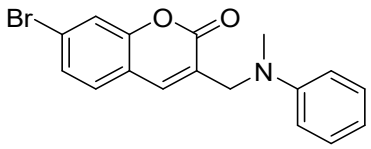
(m, 1H), 6.70 (d, J = 7.7 Hz, 1H), 4.44 (d, J = 1.9 Hz, 2H), 3.11 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$): δ 160.0, 148.8, 137.3, 131.4, 129.4, 126.4, 126.2, 124.6, 121.4, 120.5, 117.2, 112.0, 52.7, 39.0. NMR data is consistent with literature values.[9]



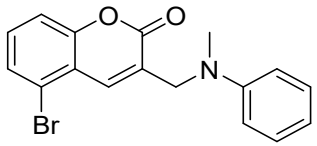
8-Bromo-3-((methyl(phenyl)amino)methyl)-2*H*-chromen-2-one (3ha): Yellow solid; ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.70 (dd, J = 7.9, 1.4 Hz, 1H), 7.42 (d, J = 1.8 Hz, 1H), 7.33 (dd, J = 7.8, 1.4 Hz, 1H), 7.26-7.22 (m, 2H), 7.11 (t, J = 7.8 Hz, 1H), 6.76 (t, J = 7.3 Hz, 1H), 6.70 (d, J = 8.1 Hz, 2H), 4.44 (d, J = 1.8 Hz, 2H), 3.12 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$): δ 160.1, 149.8, 148.8, 137.3, 134.5, 129.4, 127.0, 126.3, 125.1, 120.5, 117.2, 112.0, 110.0, 52.6, 39.0; HRMS (ESI): m/z calcd for $C_{17}H_{14}BrNO_2$ $[M+H]^+$ 344.0281 Found 344.0278.



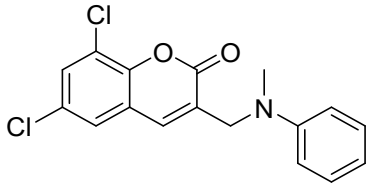
7-Methyl-3-((methyl(phenyl)amino)methyl)-2*H*-chromen-2-one (3ia): Yellow solid; ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.42 (s, 1H), 7.26-7.22 (m, 3H), 7.15 (s, 1H), 7.04 (dd, J = 7.9, 1.6 Hz, 1H), 6.76-6.70 (m, 3H), 4.41 (d, J = 1.8 Hz, 2H), 3.10 (s, 3H), 2.43 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$): δ 161.4, 153.1, 148.9 142.2, 137.7, 129.3, 127.4, 125.6, 124.0, 116.9, 116.8, 116.6, 111.9, 52.6, 38.9, 21.7; HRMS (ESI): m/z calcd for $C_{18}H_{17}NO_2$ $[M+H]^+$ 280.1332 Found 280.1342.



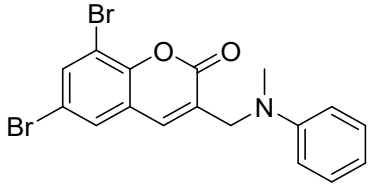
7-Bromo-3-((methyl(phenyl)amino)methyl)-2*H*-chromen-2-one (3ja): Yellow solid; ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.51 (d, J = 1.8 Hz, 1H), 7.41 (d, J = 1.9 Hz, 1H), 7.36 (dd, J = 8.3, 1.9 Hz, 1H), 7.26-7.22 (m, 3H), 6.78-6.74 (m, 1H), 6.71-6.69 (m, 2H), 4.40 (d, J = 1.8 Hz, 2H), 3.11 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$): δ 160.4, 153.3, 148.8, 137.0, 129.4, 128.7, 127.9, 125.8, 124.8, 119.8, 118.2, 117.2, 112.0, 52.8, 39.0; HRMS (ESI): m/z calcd for $C_{17}H_{14}BrNO_2$ $[M+H]^+$ 344.0281 Found 344.0278.



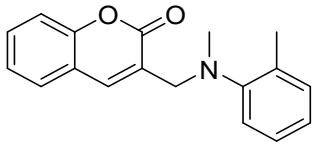
5-Bromo-3-((methyl(phenyl)amino)methyl)-2*H*-chromen-2-one (3ka): White solid; ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.80 (s, 1H), 7.45 (dd, *J* = 7.0, 2.1 Hz, 1H), 7.33-7.28 (m, 2H), 7.23 (d, *J* = 7.3 Hz, 2H), 6.77-6.73 (m, 3H), 4.44 (d, *J* = 1.9 Hz, 2H), 311 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$): δ 160.5, 153.6, 149.0, 136.8, 131.4, 129.4, 128.5, 126.9, 122.1, 119.3, 117.4, 116.1, 112.4, 52.9, 39.0; HRMS (ESI): m/z calcd for $C_{17}H_{14}BrNO_2$ $[M+H]^+$ 344.0281 Found 344.0277.



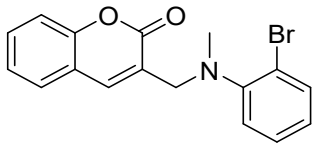
6,8-Dichloro-3-((methyl(phenyl)amino)methyl)-2*H*-chromen-2-one (3la): Yellow solid; ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.52 (d, *J* = 2.3 Hz, 1H), 7.36 (d, *J* = 1.8 Hz, 1H), 7.29 (d, *J* = 2.4 Hz, 1H), 7.26-7.22 (m, 2H), 6.76 (t, *J* = 7.3 Hz, 1H), 6.68 (d, *J* = 8.7 Hz, 2H), 4.44 (d, *J* = 1.8 Hz, 2H), 3.11 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$): δ 159.5, 148.6, 147.4, 136.2, 131.0, 129.5 (d, *J* = 4.6 Hz), 127.8, 125.6, 122.4, 121.1, 117.4, 112.0, 52.7, 39.1; HRMS (ESI): m/z calcd for $C_{17}H_{13}Cl_2NO_2$ $[M+H]^+$ 334.0396 Found 334.0392.



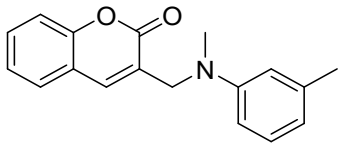
6,8-Dibromo-3-((methyl(phenyl)amino)methyl)-2*H*-chromen-2-one (3ma): Yellow solid; ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.82 (d, *J* = 2.2 Hz, 1H), 7.48 (d, *J* = 2.2 Hz, 1H), 7.33 (s, 1H), 7.26-7.22 (m, 2H), 6.76 (t, *J* = 7.3 Hz, 1H), 6.68 (d, *J* = 8.2 Hz, 2H), 4.44 (d, *J* = 1.8 Hz, 2H), 3.11 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$): δ 159.5, 149.0, 148.6, 136.5, 136.2, 129.5, 129.3, 127.7, 121.6, 117.4, 116.9, 112.0, 111.0, 52.7, 39.1; HRMS (ESI): m/z calcd for $C_{17}H_{13}Br_2NO_2$ $[M+H]^+$ 421.9386 Found 421.9382.



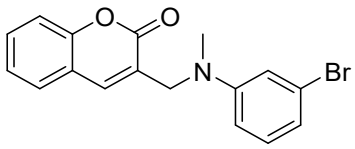
3-((Methyl(o-tolyl)amino)methyl)-2*H*-chromen-2-one (3ab): Yellow solid; ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.49 (d, *J* = 2.0 Hz, 2H), 7.41-7.35 (m, 2H), 7.26-7.22 (m, 1H), 7.06 (d, *J* = 8.1 Hz, 2H), 6.65 (d, *J* = 8.5 Hz, 2H), 4.41 (s, 2H), 3.09 (s, 3H), 2.26 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$): δ 161.2, 153.1, 146.9, 137.8, 131.0, 130.0, 127.7, 126.3, 125.6, 124.4, 119.3, 116.5, 112.2, 52.9, 39.1, 20.2. NMR data is consistent with literature values.[8]



3-(((2-Bromophenyl)(methyl)amino)methyl)-2*H*-chromen-2-one (3ac): Yellow solid; ^{1}H NMR (400 MHz, $CDCl_3$): δ 8.04 (s, 1H), 7.59 (dd, *J* = 7.9, 1.5 Hz, 1H), 7.53-7.47 (m, 2H), 7.34 (d, *J* = 8.2 Hz, 1H), 7.30-7.26 (m, 2H), 7.21 (dd, *J* = 8.0, 1.7 Hz, 1H), 6.96-6.92 (m, 1H), 4.15 (d, *J* = 1.7 Hz, 2H), 2.81 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$): δ 161.4, 153.0, 150.7, 139.6, 133.9, 131.0, 128.4, 127.8, 125.7, 124.8, 124.4, 122.1, 120.1, 119.5, 116.5, 54.7, 41.5. NMR data is consistent with literature values.[9]

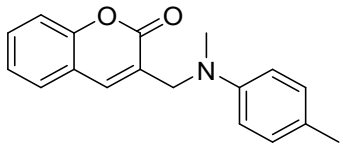


3-((Methyl(m-tolyl)amino)methyl)-2*H*-chromen-2-one (3ad): Yellow solid; ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.51-7.47 (m, 2H), 7.41-7.34 (m, 2H), 7.26-7.22 (m, 1H), 7.14 (dd, *J* = 9.0, 7.4 Hz, 1H), 6.59 (d, *J* = 7.4 Hz, 1H), 6.54-6.53 (m, 2H), 4.42 (d, *J* = 1.8 Hz, 2H), 3.10 (s, 3H), 2.31 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$): δ 161.2, 153.1, 149.0, 139.2, 137.6, 131.0, 129.3, 127.7, 125.5, 124.4, 119.3, 118.0, 116.5, 112.6, 109.2, 52.7, 38.9, 21.9. NMR data is consistent with literature values.[9]

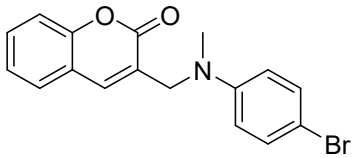


3-(((3-Bromophenyl)(methyl)amino)methyl)-2*H*-chromen-2-one (3ae): Yellow solid; ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.52-7.48 (m, 1H), 7.42-7.34 (m, 3H), 7.25 (t, *J*

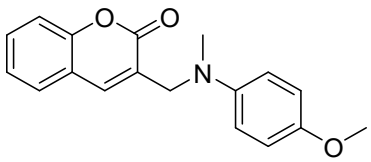
= 7.4 Hz, 1H), 7.07 (t, *J* = 8.1 Hz, 1H), 6.85 (d, *J* = 8.6 Hz, 2H), 6.60 (dd, *J* = 7.5, 2.2 Hz, 1H), 4.42 (s, 2H), 3.10 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$): δ 161.0, 153.1, 150.0, 137.7, 131.2, 130.6, 127.8, 124.6, 124.5, 123.6, 119.8, 119.0, 116.5, 114.6, 110.5, 52.5, 38.9. NMR data is consistent with literature values.[9]



3-((Methyl(p-tolyl)amino)methyl)-2*H*-chromen-2-one (3af): Yellow solid; ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.51-7.47 (m, 2H), 7.37 (dd, *J* = 15.2, 8.0 Hz, 2H), 7.24 (t, *J* = 7.3 Hz, 1H), 7.06 (d, *J* = 8.1 Hz, 2H), 6.65 (d, *J* = 8.2 Hz, 2H), 4.41 (s, 2H), 3.09 (s, 3H), 2.27 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$): δ 161.2, 153.0, 146.8, 137.7, 131.0, 129.9, 127.7, 126.2, 125.6, 124.4, 119.3, 116.5, 112.1, 52.9, 39.1, 20.2. NMR data is consistent with literature values.[8]

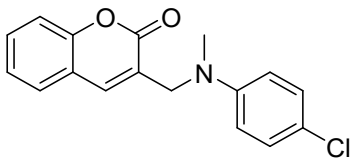


3-(((4-Bromophenyl)(methyl)amino)methyl)-2*H*-chromen-2-one (3ag): Yellow solid; ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.51-7.47 (m, 1H), 7.40-7.37 (m, 2H), 7.34 (d, *J* = 8.3 Hz, 1H), 7.30-7.28 (m, 2H), 7.25-7.22 (m, 1H), 6.57 (d, *J* = 8.9 Hz, 2H), 4.40 (d, *J* = 1.7 Hz, 2H), 3.09 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$): δ 161.1, 153.1, 147.8, 137.8, 132.0, 131.2, 127.8, 124.8, 124.5, 119.1, 116.5, 113.6, 109.1, 52.7, 39.1. NMR data is consistent with literature values.[8]

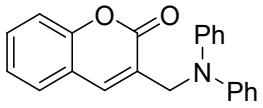


3-(((4-Methoxyphenyl)(methyl)amino)methyl)-2*H*-chromen-2-one (3ah): Yellow solid; ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.52-7.46 (m, 2H), 7.40 (dd, *J* = 7.8, 1.6 Hz, 1H), 7.35 (d, *J* = 8.3 Hz, 1H), 7.24 (dd, *J* = 7.5, 6.3 Hz, 1H), 6.85-6.83 (m, 2H), 6.71-6.68 (m, 2H), 4.36 (d, *J* = 1.8 Hz, 2H), 3.75 (s, 3H), 3.05 (s, 3H); ^{13}C NMR (100 MHz,

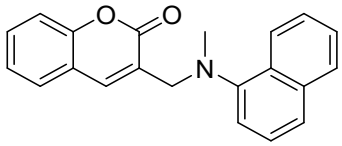
$CDCl_3$): δ 161.2, 153.1, 151.9, 143.8, 138.0, 131.0, 127.7, 125.8, 124.4, 119.3, 116.5, 114.9, 113.7, 55.8, 53.5, 39.5. NMR data is consistent with literature values.[8]



3-(((4-Chlorophenyl)(methyl)amino)methyl)-2*H*-chromen-2-one (3ai): Yellow solid; ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.52-7.48 (m, 1H), 7.41-7.39 (m, 2H), 7.35 (d, *J* = 8.3 Hz, 1H), 7.27-7.23 (m, 1H), 7.18-7.16 (m, 2H), 6.62 (d, *J* = 9.0 Hz, 2H), 4.41 (d, *J* = 1.7 Hz, 2H), 3.10 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$): δ 161.1, 153.1, 147.4, 137.8, 131,2, 129.2, 127.8, 124.9, 124.5, 122.0, 119.1, 116.5, 113.1, 52.7, 39.1. NMR data is consistent with literature values.[8]



3-((Diphenylamino)methyl)-2*H*-chromen-2-one (3aj): Yellow solid; ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.69 (s, 1H), 7.47 (t, *J* = 7.8 Hz, 1H), 7.38 (d, *J* = 7.7 Hz, 1H), 7.32 (d, *J* = 8.4 Hz, 1H), 7.28 (t, *J* = 7.7 Hz, 4H), 7.22 (t, *J* = 7.5 Hz, 1H), 7.08 (d, *J* = 8.0 Hz, 4H), 6.98 (t, *J* = 7.3 Hz, 2H), 4.90 (s, 2H); ^{13}C NMR (100 MHz, $CDCl_3$): δ 161.0, 153.0, 147.3, 138.2, 131.1, 129.5, 127.8, 125.5, 124.4, 122.0, 120.5, 119.2, 116.5, 52.1. NMR data is consistent with literature values.[8]



3-((Methyl(naphthalen-1-yl)amino)methyl)-2*H*-chromen-2-one (3ak): Yellow solid; ^{1}H NMR (400 MHz, $CDCl_3$): δ 8.24-8,21 (m, 1H), 7.93 (d, *J* = 1.7 Hz, 1H), 7.85-7.83 (m, 1H), 7.56 (d, *J* = 8.2, 1H), 7.51-7.44 (m, 4H), 7.39 (t, *J* = 7.8 Hz, 1H), 7.34 (d, *J* = 8.3 Hz, 1H), 7.27-7.23 (m, 1H), 7.20 (d, *J* = 7.4 Hz, 1H), 4.26 (d, *J* = 1.7 Hz, 2H), 2.93 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$): δ 161.4, 153.1, 149.2, 139.0, 134.9, 131.0, 129.1, 128.6, 127.8, 126.2, 125.9, 125.8, 125.6, 124.4, 123.8, 123.2, 119.4, 116.5, 115.6, 55.5, 42.6. NMR data is consistent with literature values.[8]

15. References

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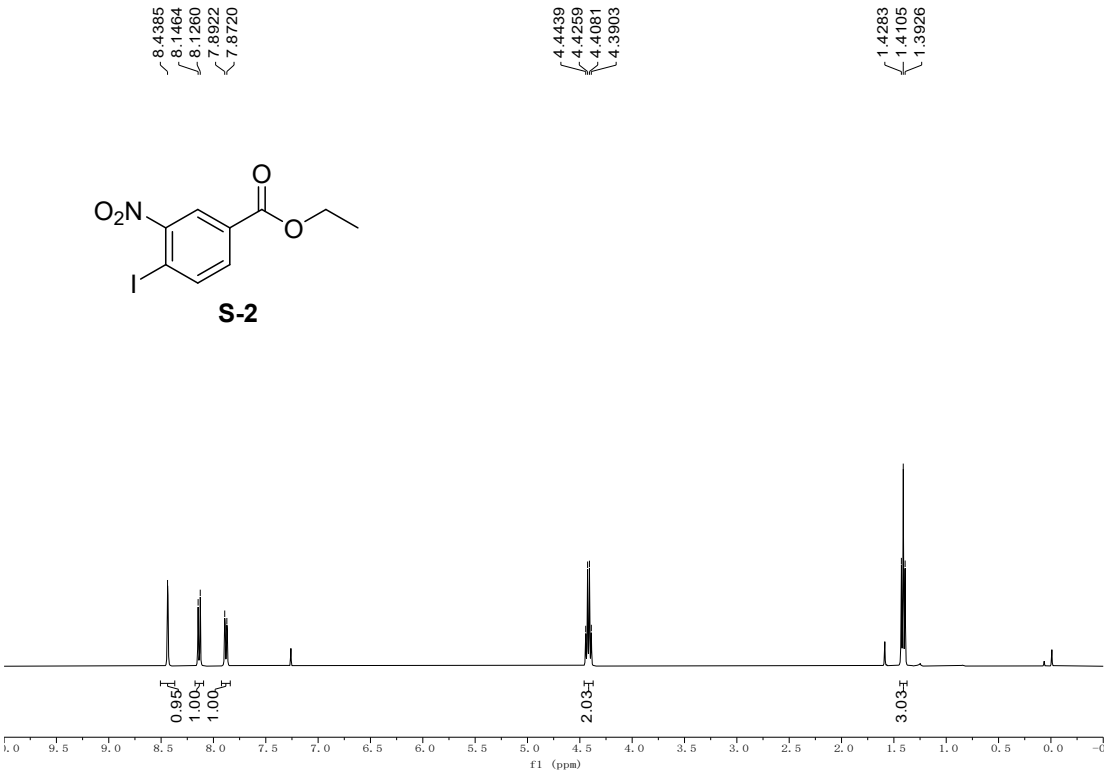
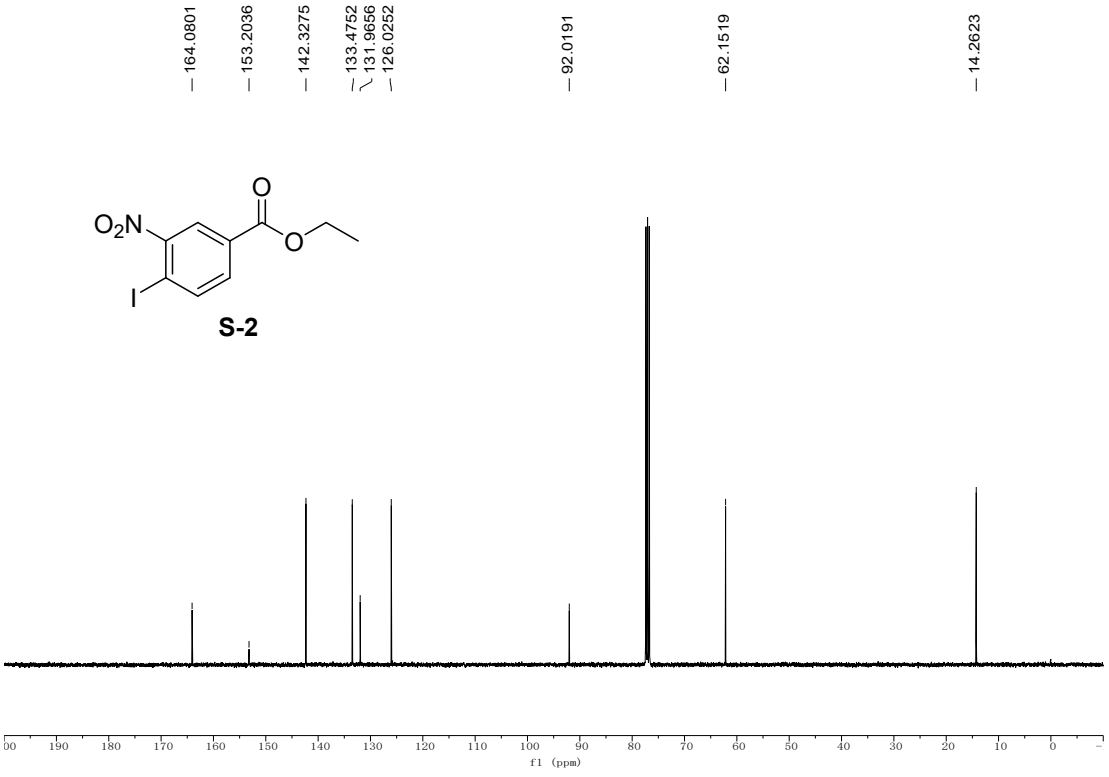
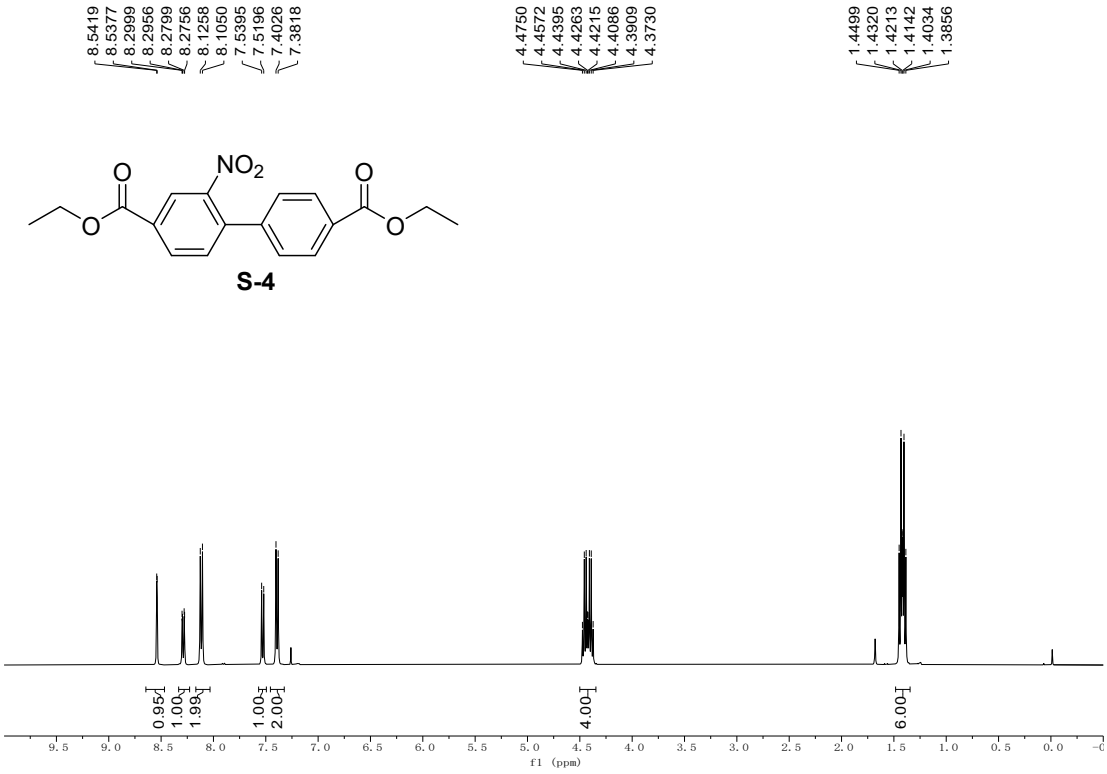
16. Spectra of compounds



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1.4499
1.4320
1.4213
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1.4034
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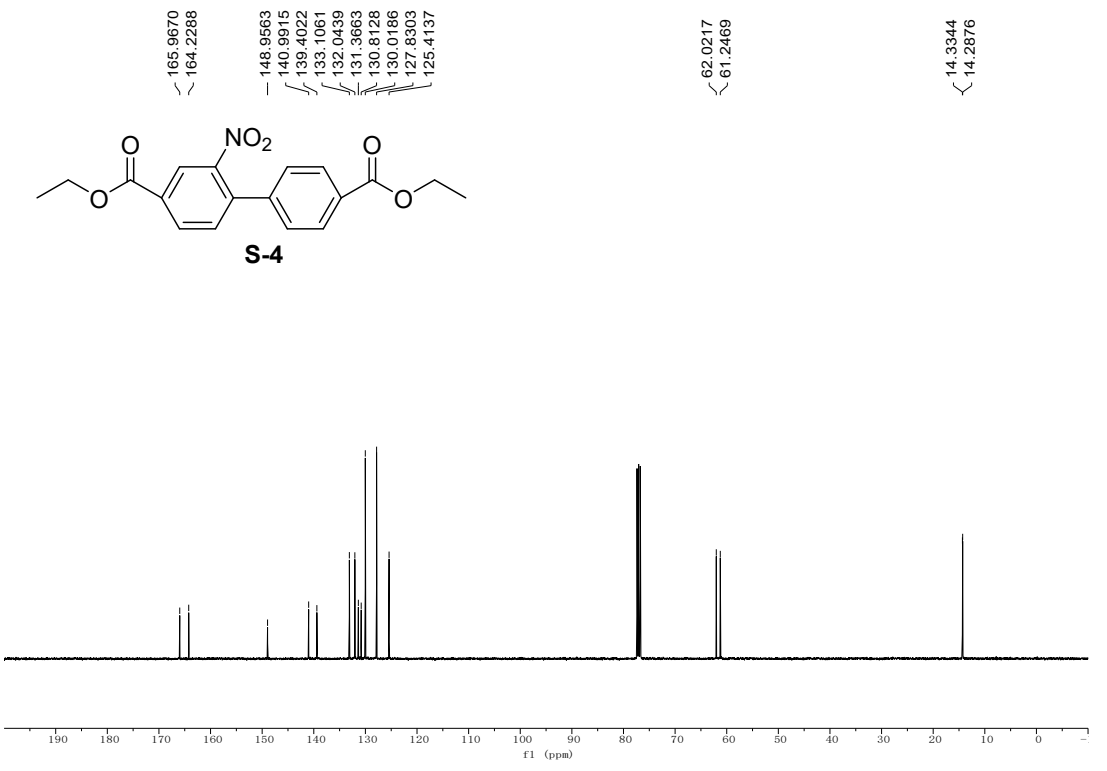
6.00
f1 (ppm)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O
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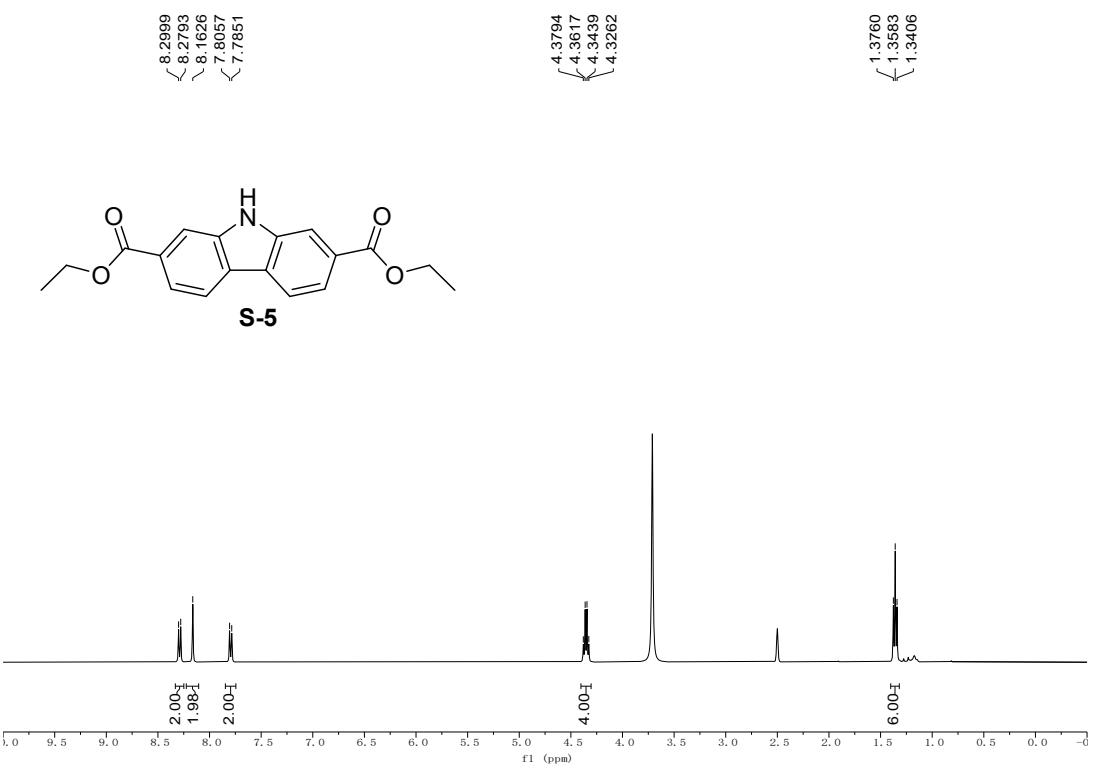
S-4
f1 (ppm)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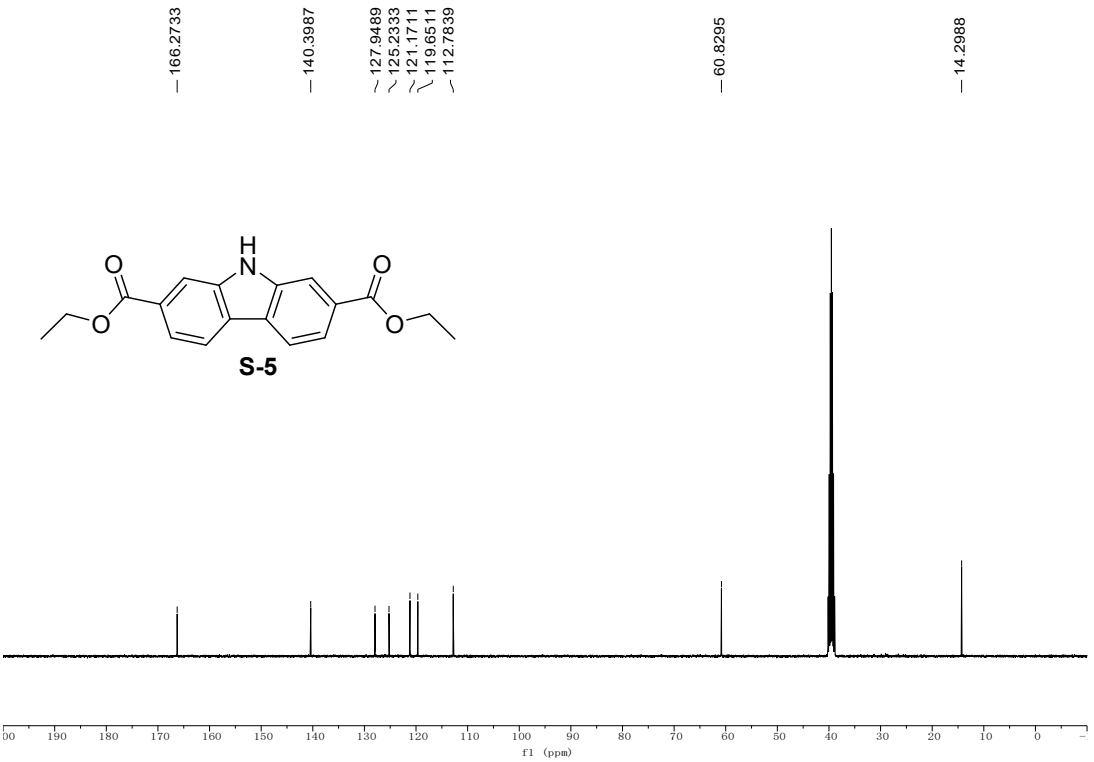
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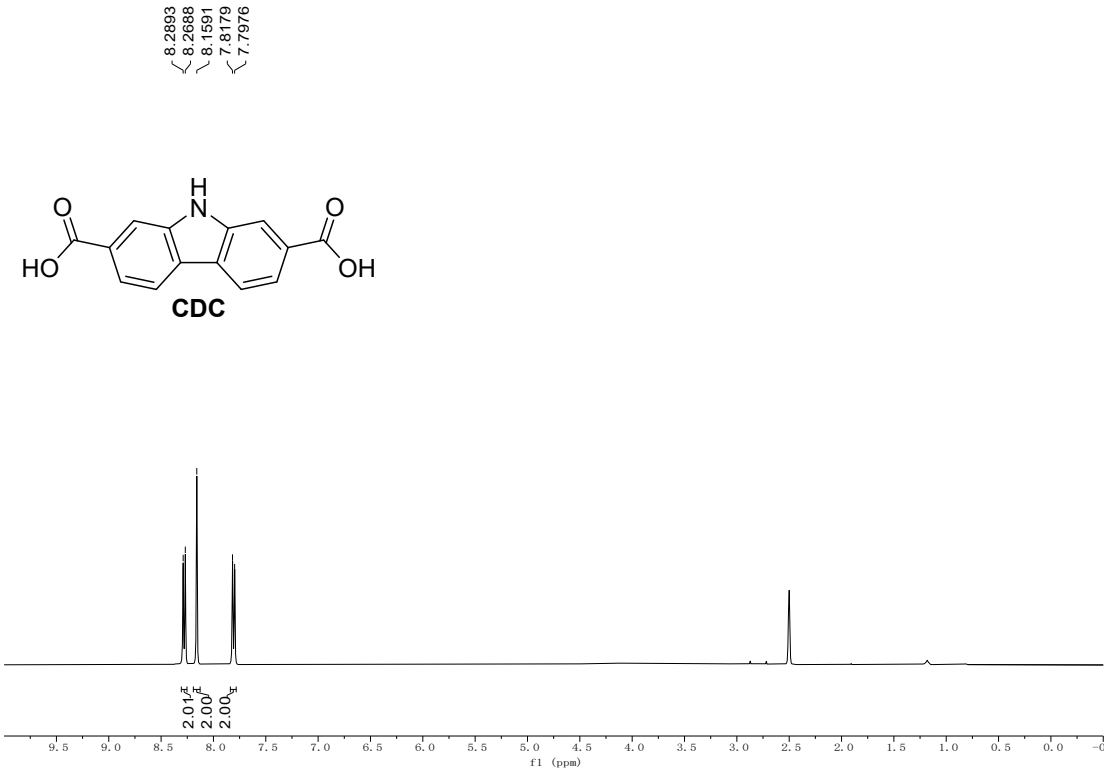
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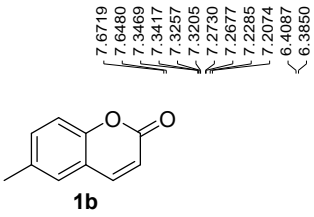
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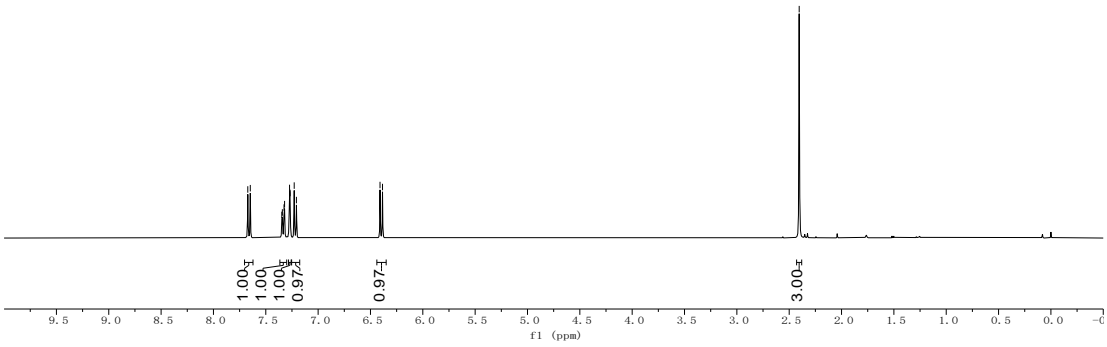
1b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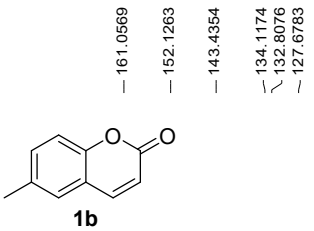
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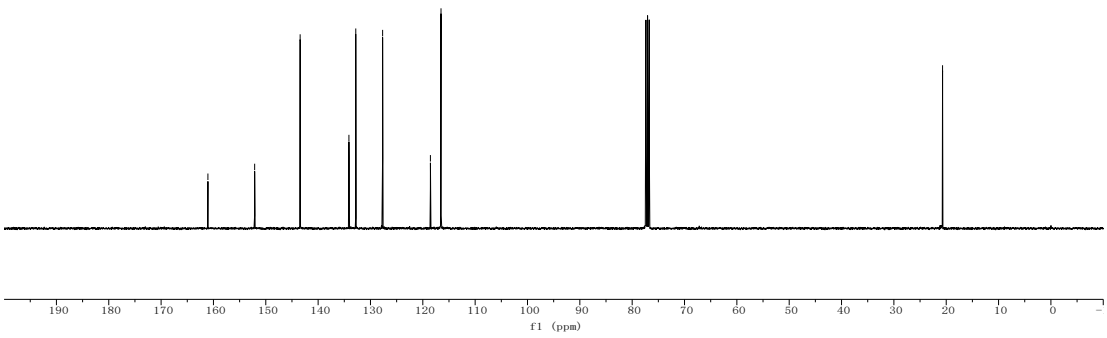
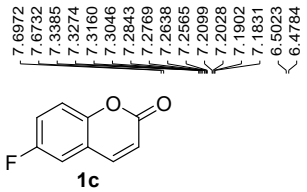
O

1b


f1 (ppm)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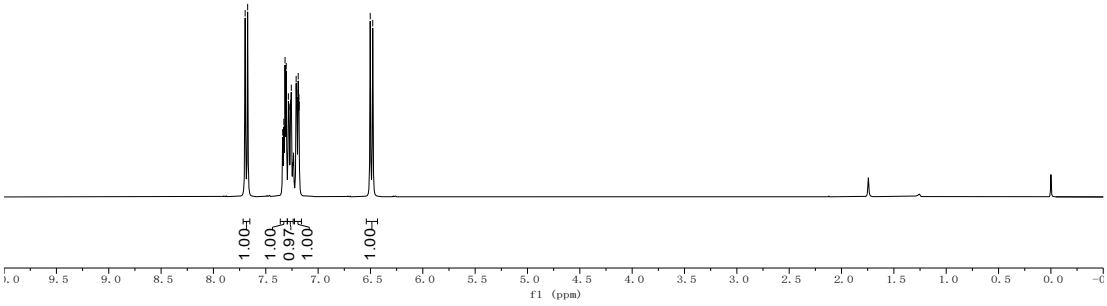
7.3385
7.3274
7.3160
7.3046
7.2843
7.2769
7.2638
7.2565
7.2099
7.2028
7.1902
7.1831
6.5023
6.4784
O
O
F

1c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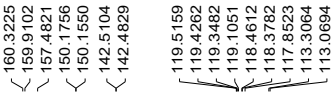
1.00
1.00
f1 (ppm)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150.1756
150.1550
142.5104
142.4829
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119.4262
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118.4612
118.3782
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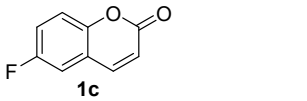
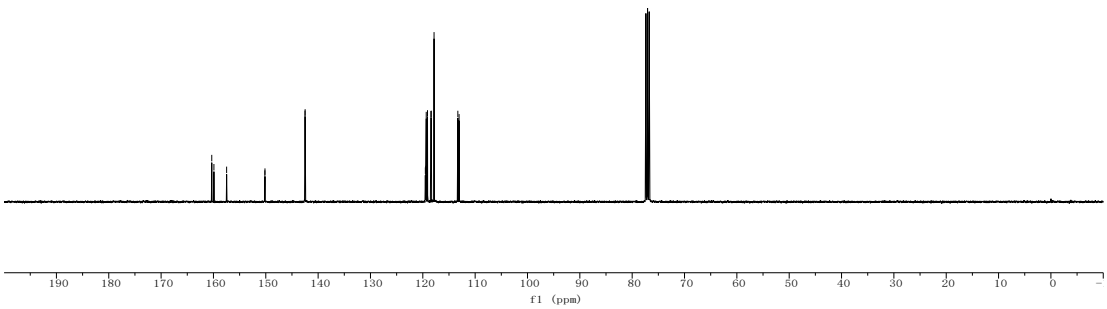
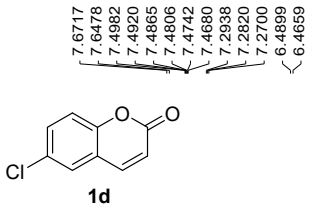
113.3064
113.0694


O
O
F

1c


f1 (ppm)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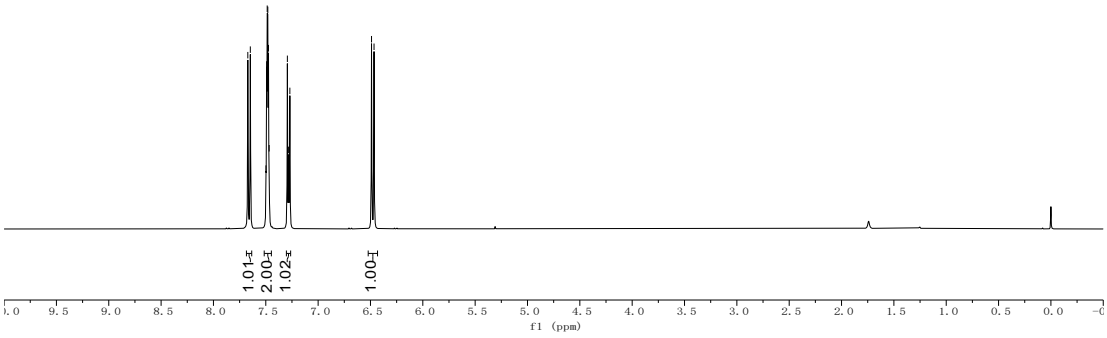
7.6478
7.4982
7.4920
7.4865
7.4806
7.4742
7.4680
7.2938
7.2820
7.2700
6.4899
6.4659
O
O
Cl

1d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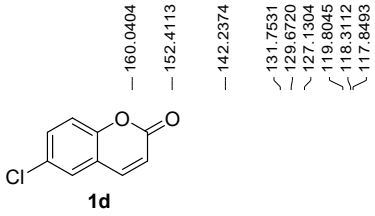
2.00
1.02
1.00
f1 (ppm)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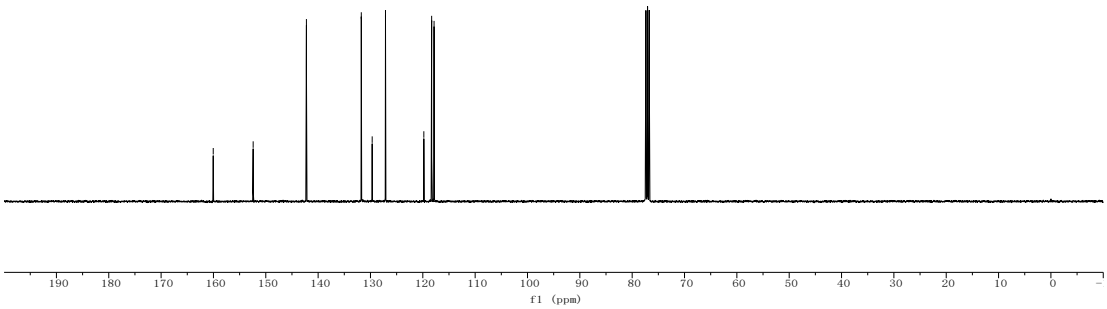
142.2374
131.7531
129.6720
127.1304
119.8045
118.3112
117.8493
O
O
Cl

1d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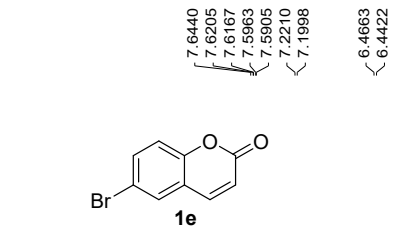
7.6440
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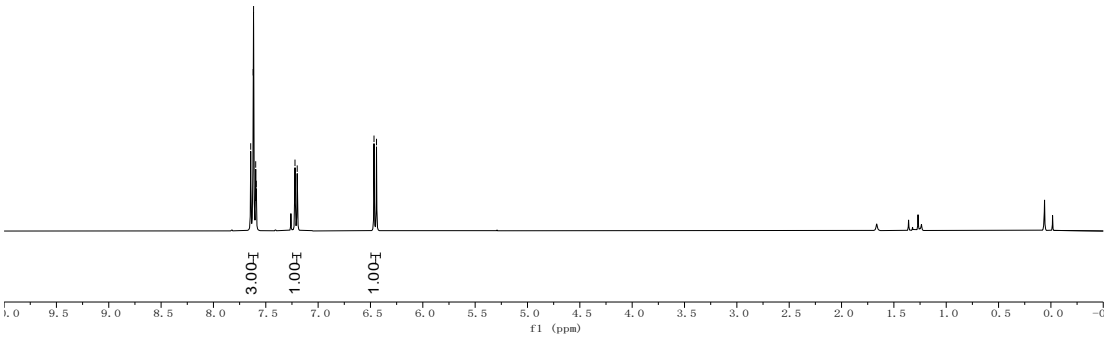
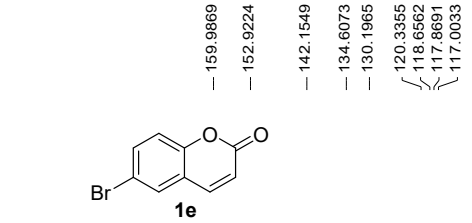
7.6167
7.5963
7.5905
7.2210
7.1998
6.4663
6.4422
O
O
Br

1e


3.00
1.00
1.00
f1 (ppm)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142.1549
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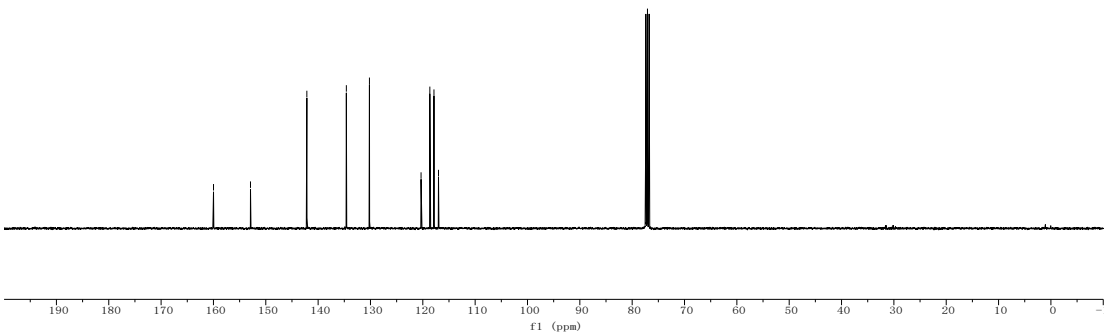
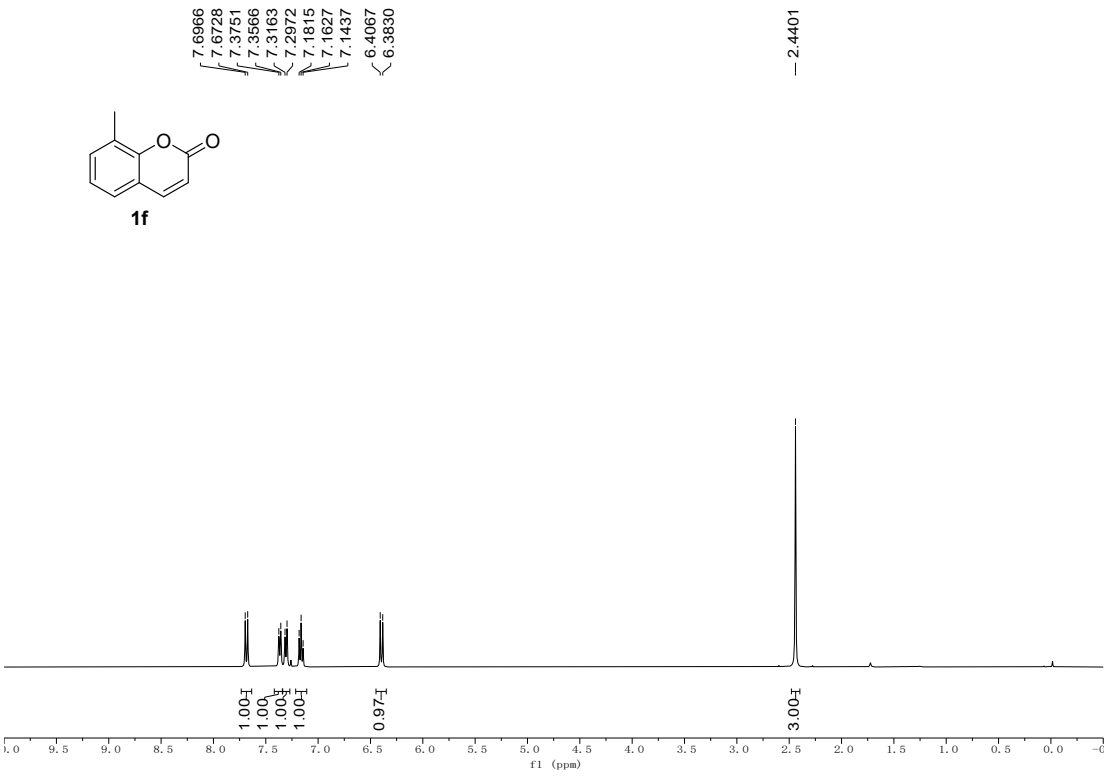
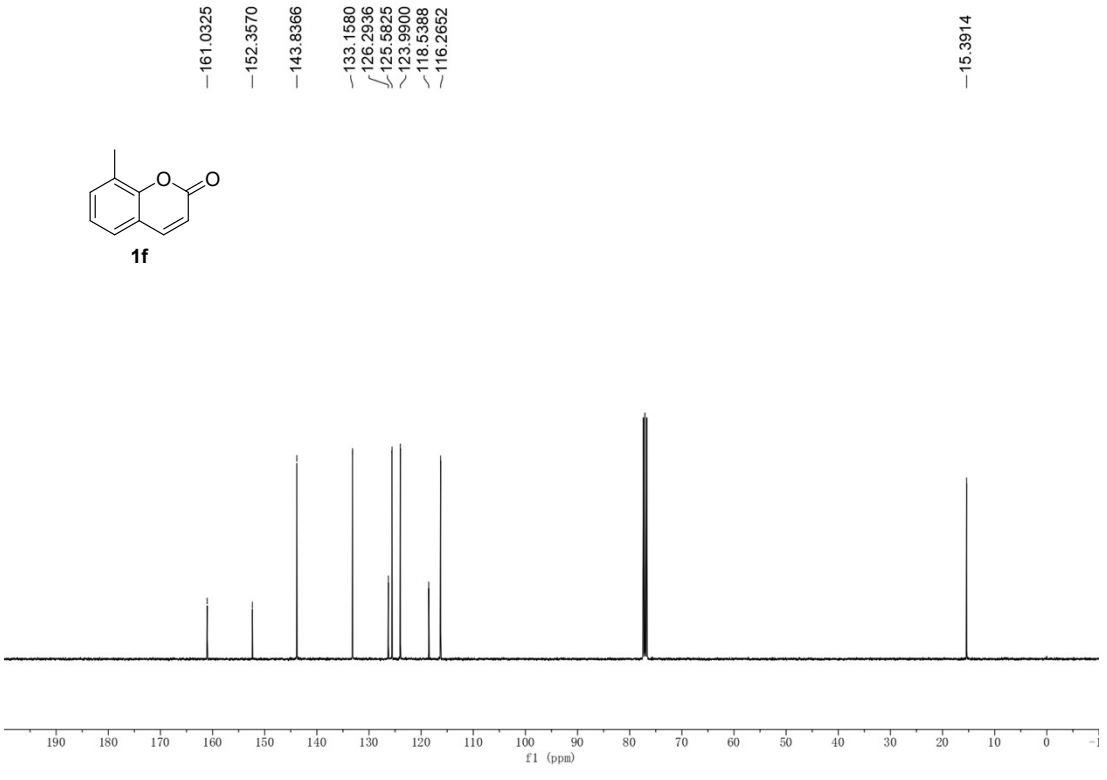
130.1965
120.3355
118.6562
117.8691
117.0033
O
O
Br

1e


f1 (ppm)


7.6966
7.6728
7.3751
7.3566
7.3163
7.2972
7.1815
7.1627
7.1437
6.4067
6.3830
2.4401
1f
1.00
1.00
1.00
1.00
0.97
3.00
f1 (ppm)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152.3570
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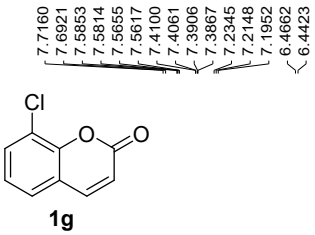
123.9900
118.5388
116.2652
15.3914
1f
f1 (ppm)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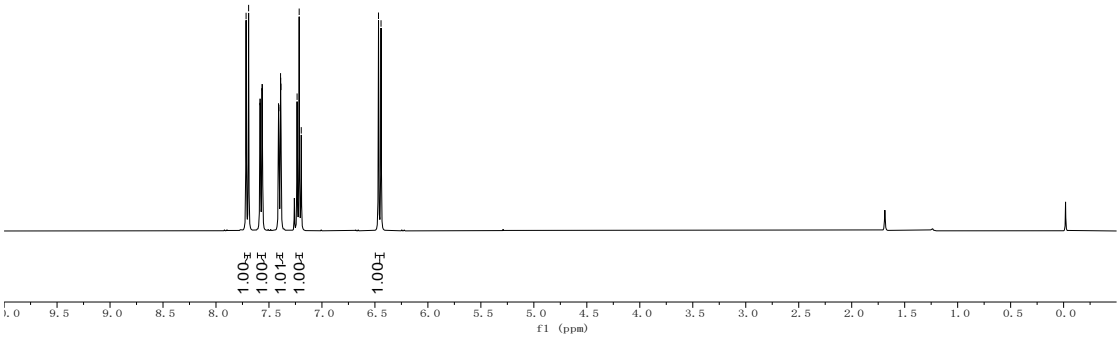
7.6921
7.5853
7.5814
7.5655
7.5617
7.4100
7.4061
7.3906
7.3867
7.2345
7.2148
7.1952
6.4662
6.4423
Cl
O
O

1g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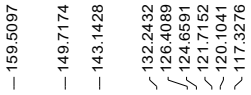
1.00
1.01
1.00
1.00
f1 (ppm)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126.4089
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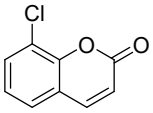
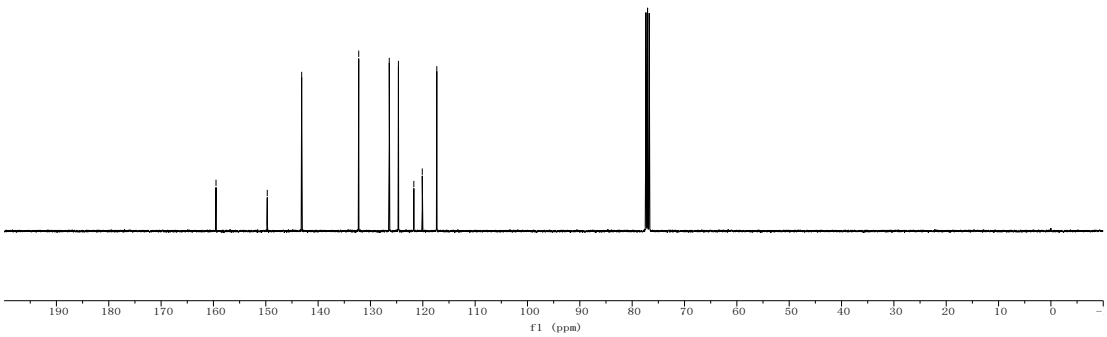
121.7152
120.1041
117.3276


Cl
O
O

1g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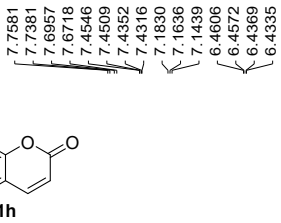
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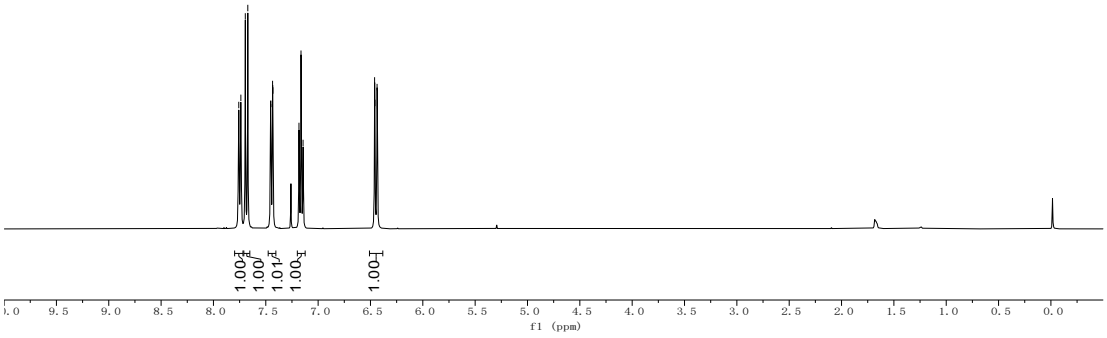
7.6957
7.6718
7.4546
7.4509
7.4352
7.4316
7.1830
7.1636
7.1439
6.4606
6.4572
6.4369
6.4335
Br
O
O
1h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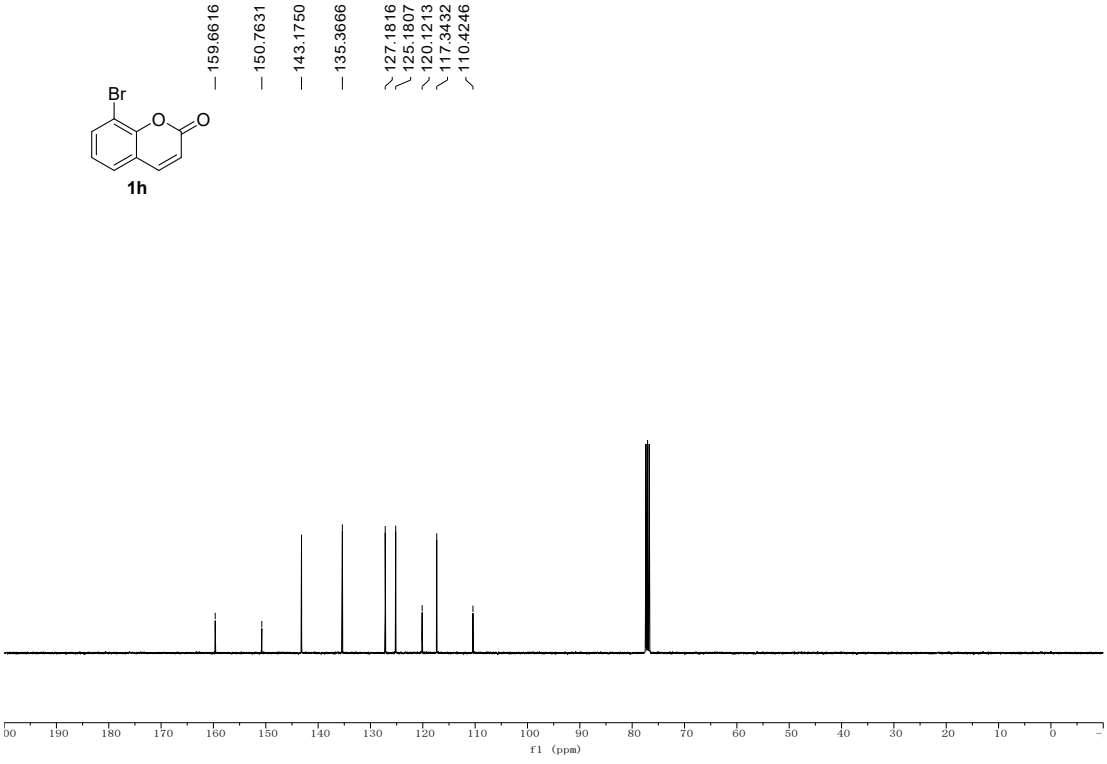
1.00
1.01
1.00
1.00
f1 (ppm)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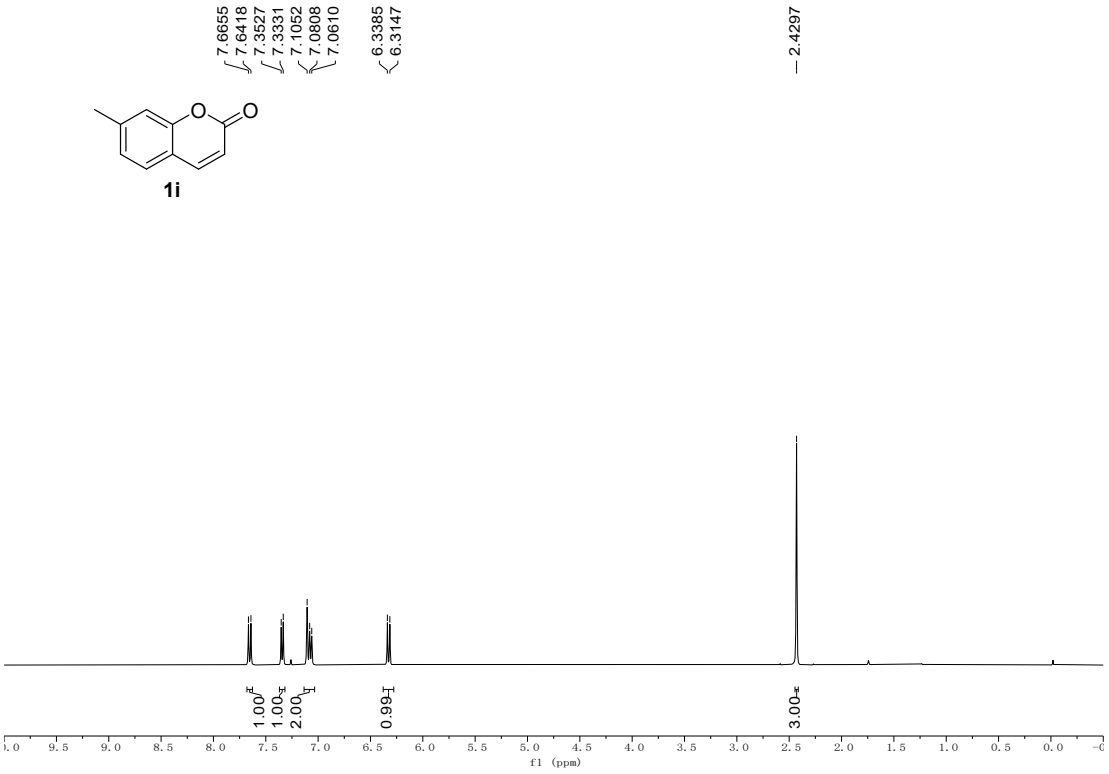
127.1816
125.1807
120.1213
117.3432
110.4246
Br
O
O
1h
f1 (ppm)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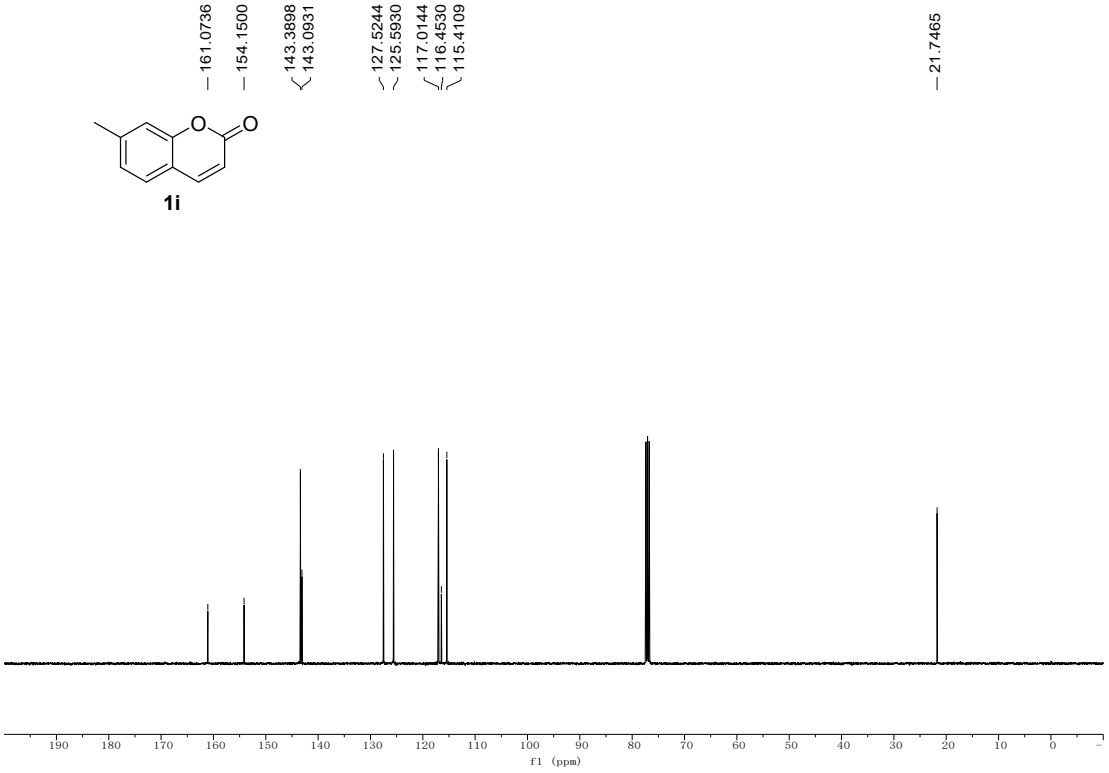
7.6418
7.3527
7.3331
7.1052
7.0808
7.0610
6.3385
6.3147
2.4297
1i
1.00
1.00
2.00
0.99
3.00
f1 (ppm)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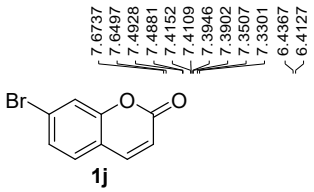
143.0931
127.5244
125.5930
117.0144
116.4530
115.4109
21.7465
1i
f1 (ppm)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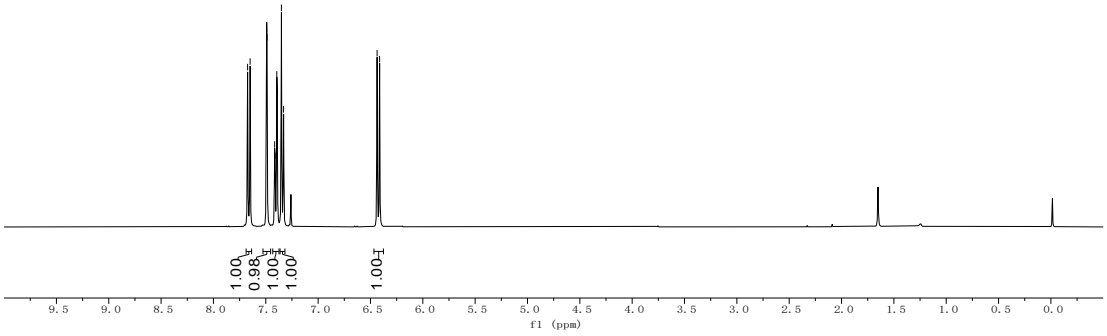
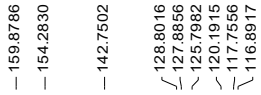
7.6497
7.4928
7.4881
7.4152
7.4109
7.3946
7.3902
7.3507
7.3301
6.4367
6.4127
Br
O
O

1j


1.00
0.98
1.00
1.00
1.00
9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0
f1 (ppm)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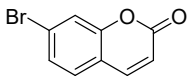
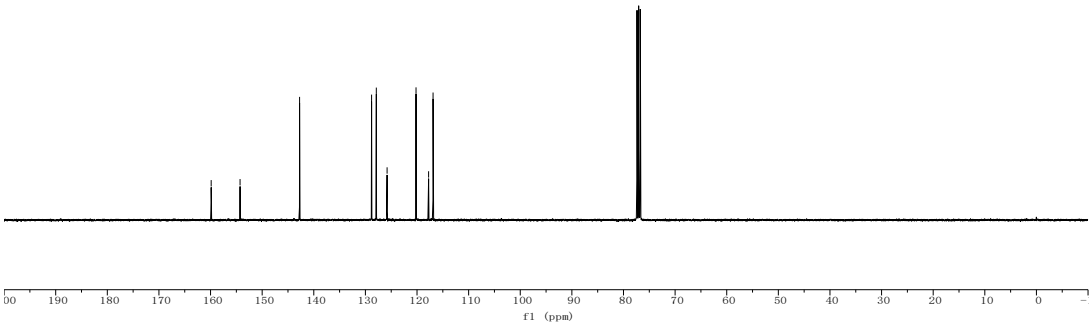
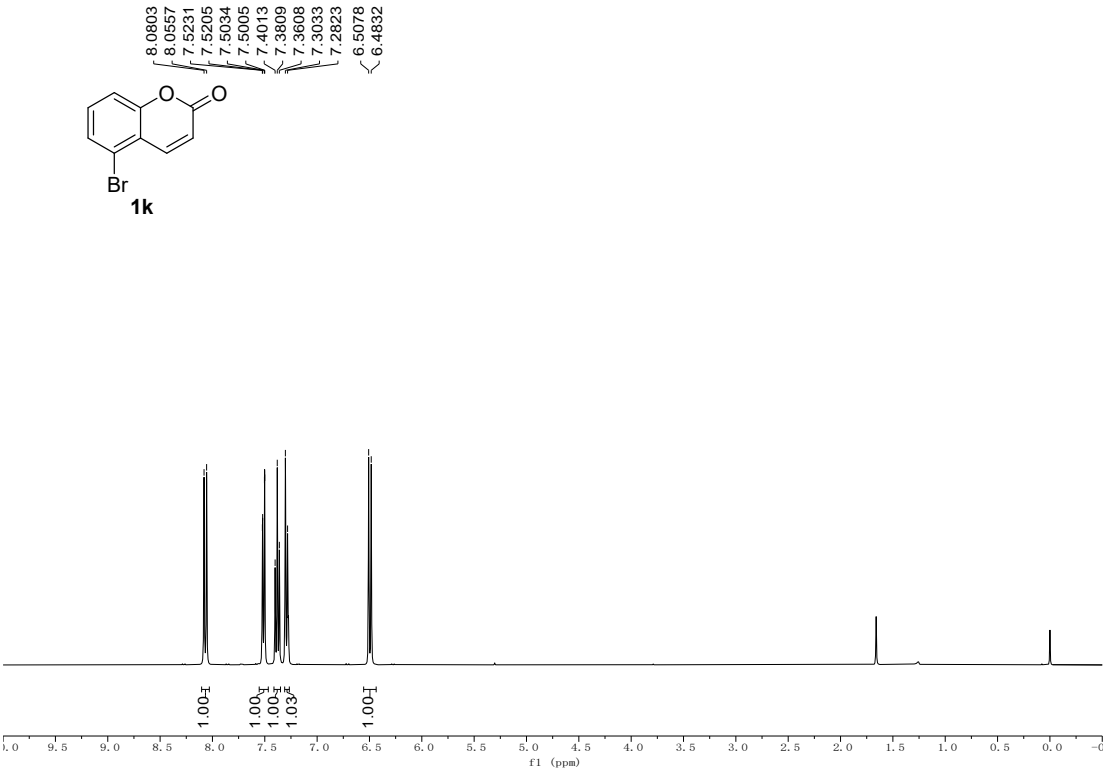
120.1915
117.7556
116.8917


Br
O
O

1j


190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0
f1 (ppm)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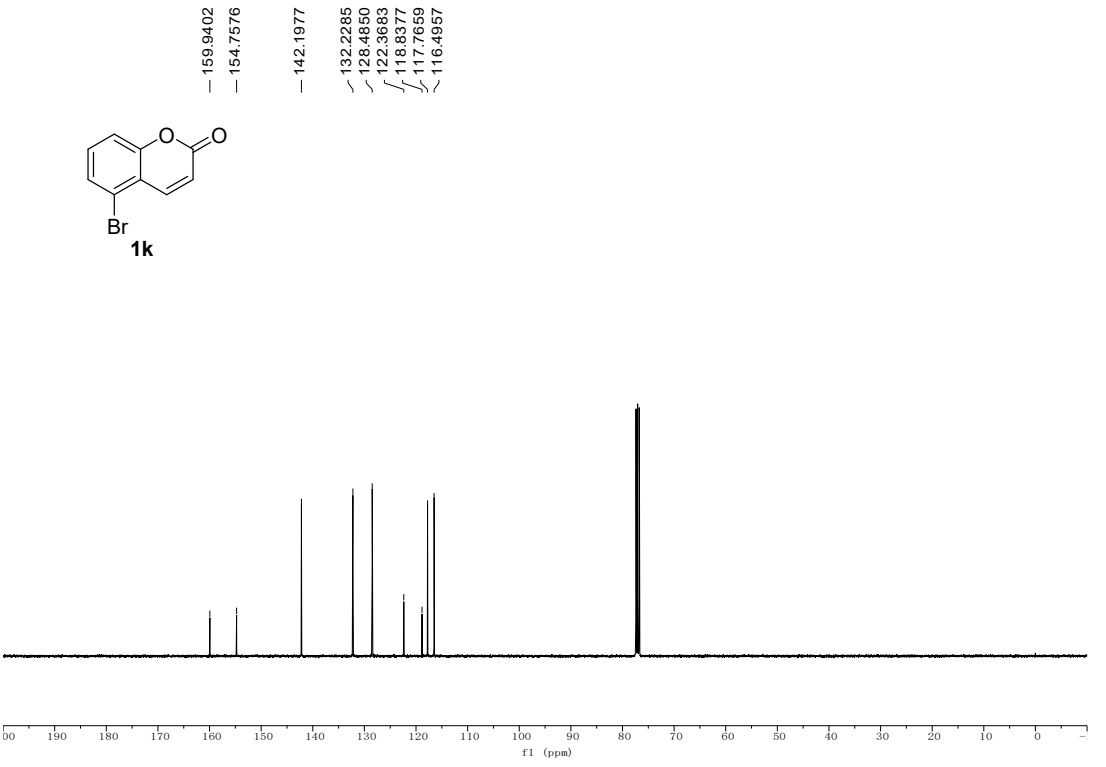
7.5231
7.5205
7.5034
7.5005
7.4013
7.3809
7.3608
7.3033
7.2823
6.5078
6.4832
O
O
Br
1k
1.00
1.00
1.00
1.03
1.00
f1 (ppm)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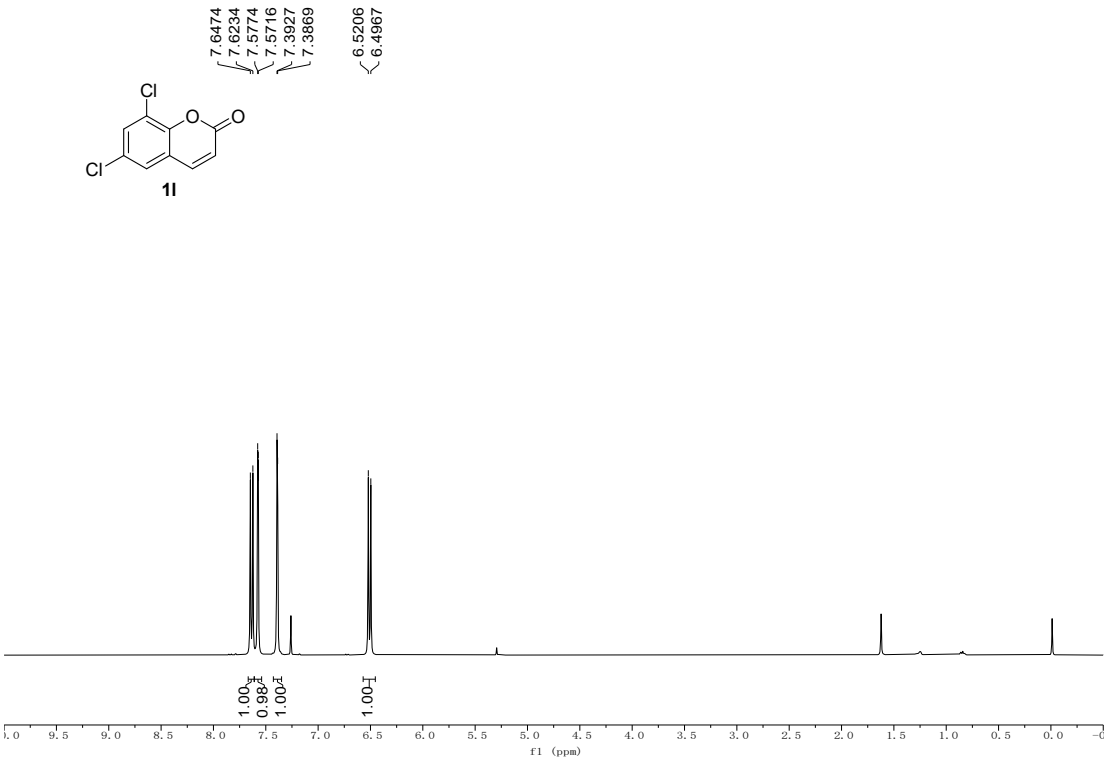
128.4850
122.3683
118.8377
117.7659
116.4957
O
O
Br
1k
f1 (ppm)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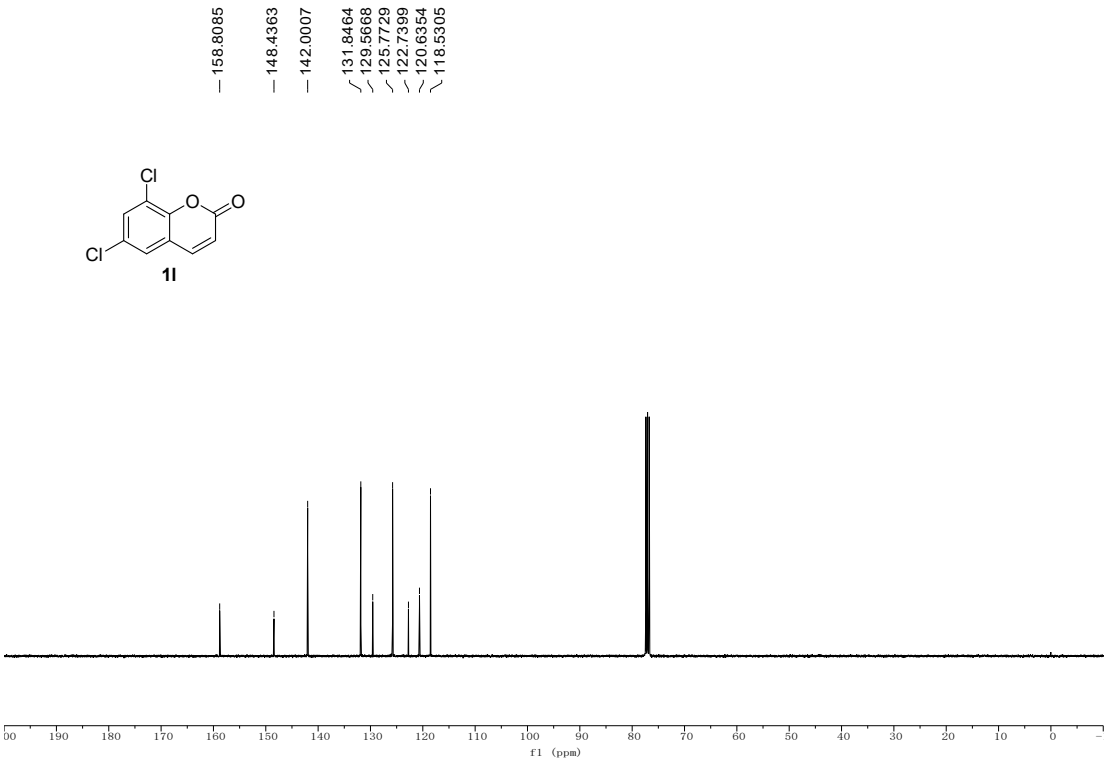
7.6234
7.5774
7.5716
7.3927
7.3869
6.5206
6.4967
Cl
O
O
Cl
1l
1.00
0.98
1.00
1.00
f1 (ppm)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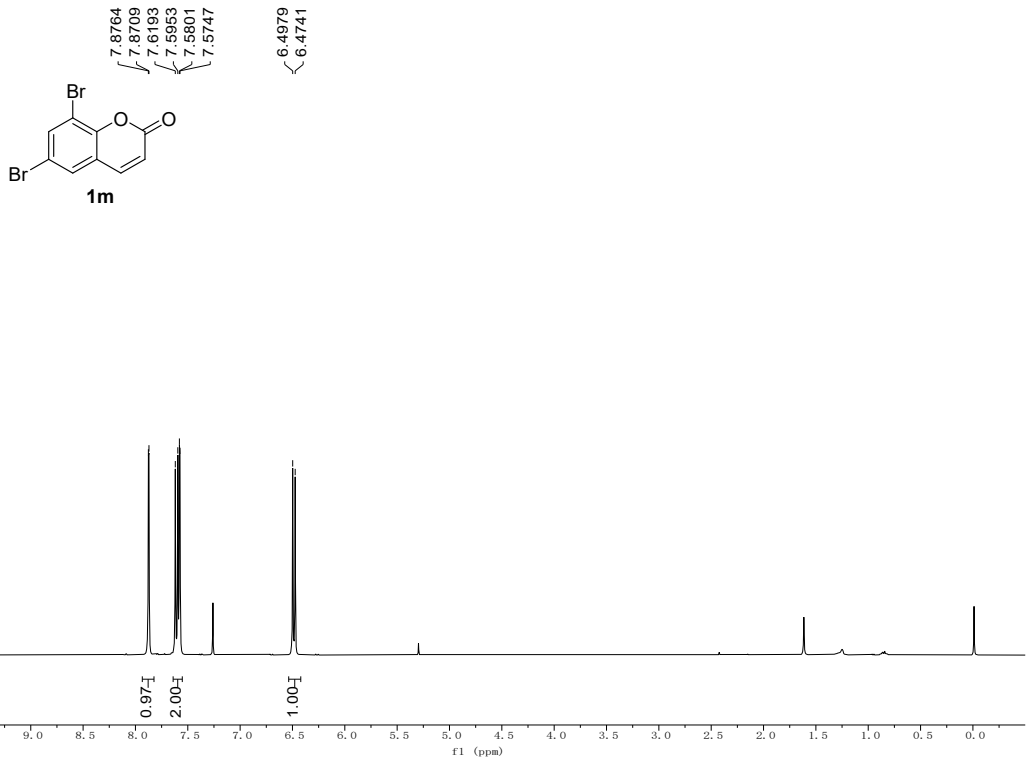
148.4363
142.0007
131.8464
129.5668
125.7729
122.7399
120.6354
118.5305
Cl
O
O
Cl
1l
f1 (ppm)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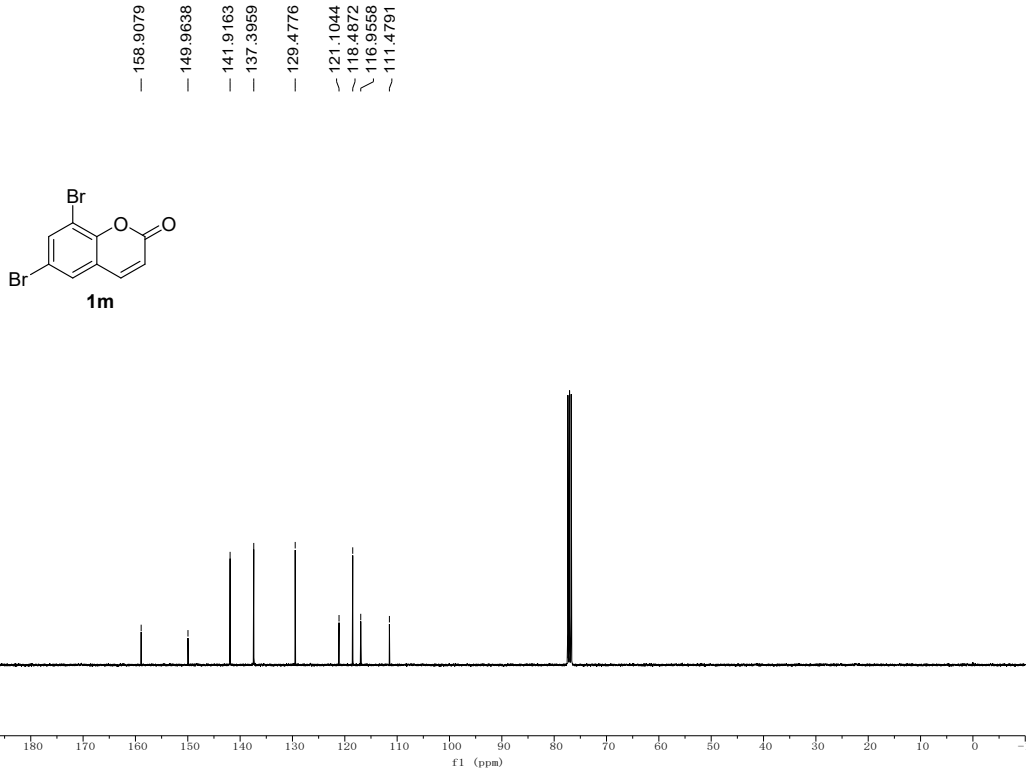
7.6193
7.5953
7.5801
7.5747
6.4979
6.4741
Br
O
O
Br
1m
0.97
2.00
1.00
f1 (ppm)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141.9163
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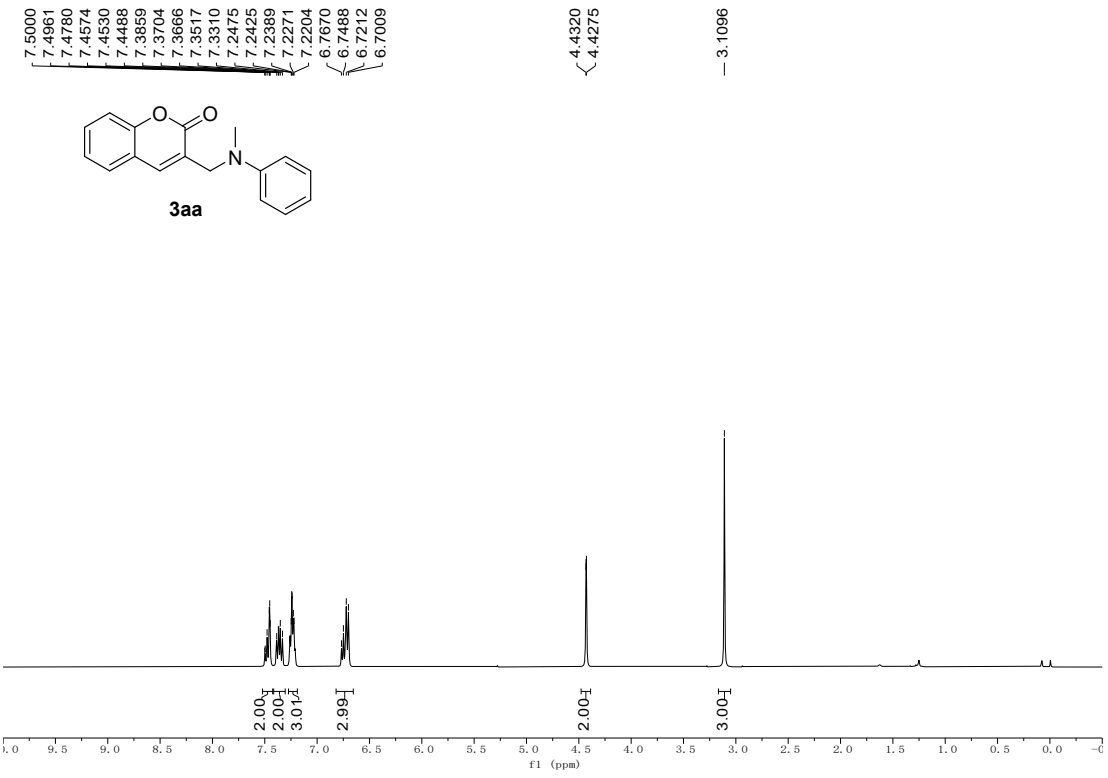
121.1044
118.4872
116.9558
111.4791
Br
O
O
Br
1m
f1 (ppm)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7.4961
7.4780
7.4574
7.4530
7.4488
7.3859
7.3704
7.3666
7.3517
7.3310
7.2475
7.2425
7.2389
7.2271
7.2204
6.7670
6.7488
6.7212
6.7009
4.4320
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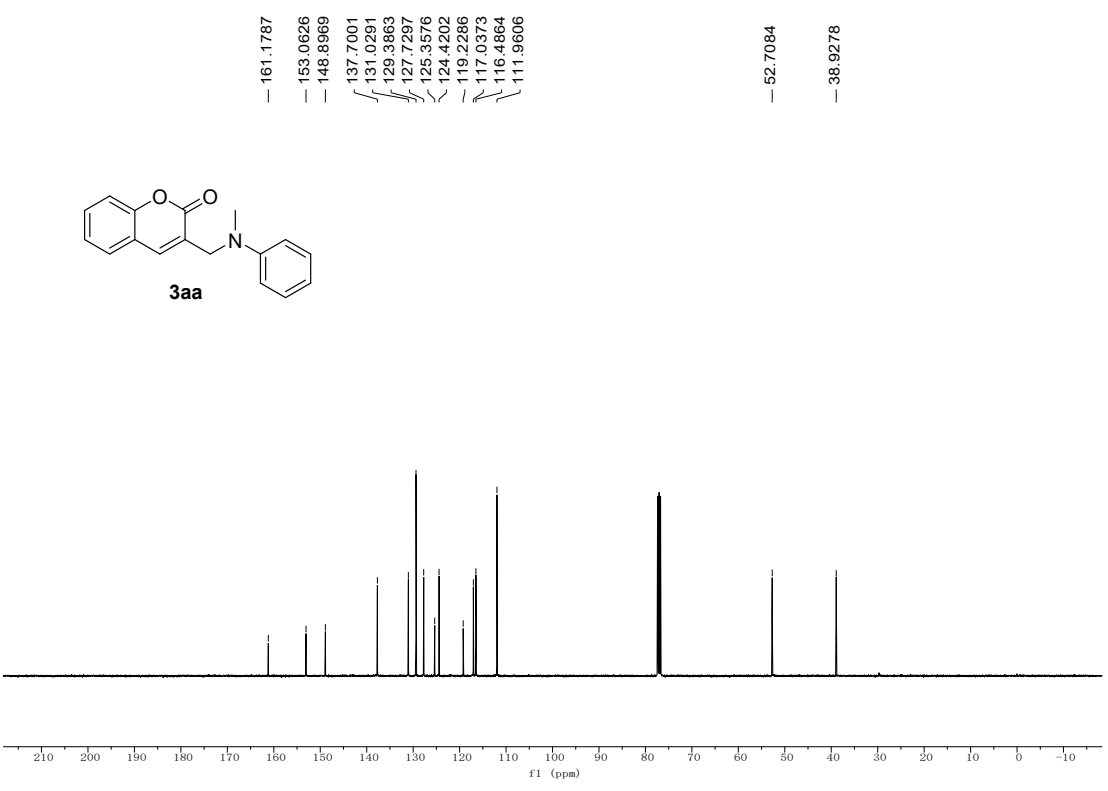
3.1096
O
O
N
3aa
2.00
2.00
3.01
2.99
2.00
3.00
f1 (ppm)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148.8969
137.7001
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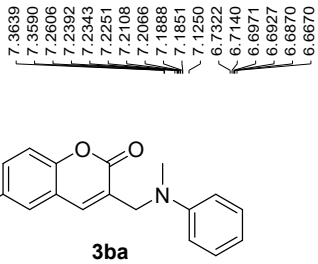
129.3863
127.7297
125.3576
124.4202
119.2286
117.0373
116.4864
111.9606
52.7084
38.9278
O
O
N
3aa
f1 (ppm)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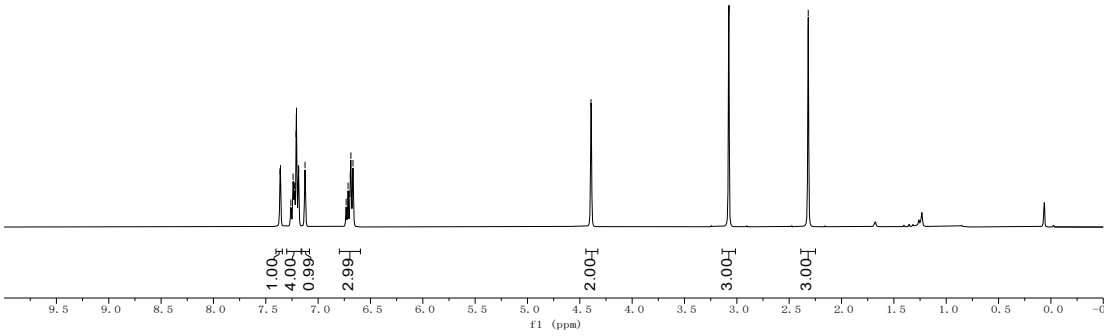
7.3590
7.2606
7.2392
7.2343
7.2251
7.2108
7.2066
7.1888
7.1851
7.1250
6.7322
6.7140
6.6971
6.6927
6.6870
6.6670
4.3934
3.0793
3.0751
2.3182
O
O
N

3ba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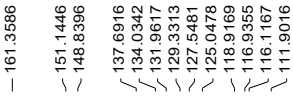
4.00
0.99
2.99
2.00
3.00
3.00
f1 (ppm)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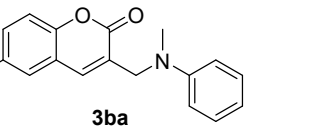
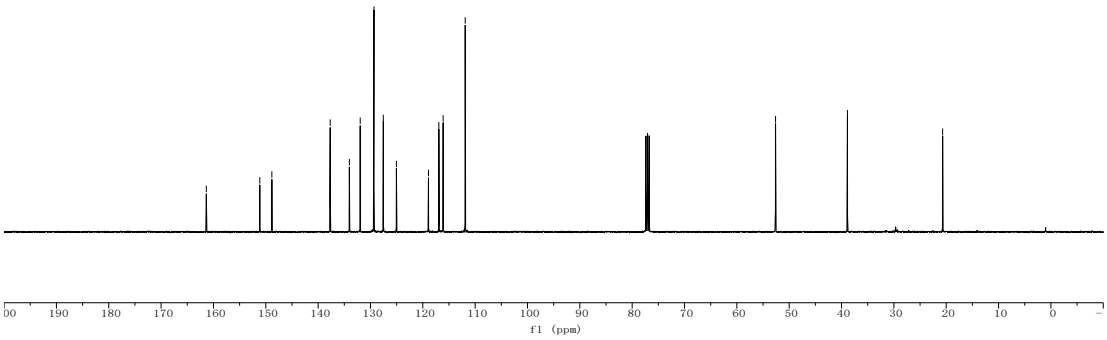
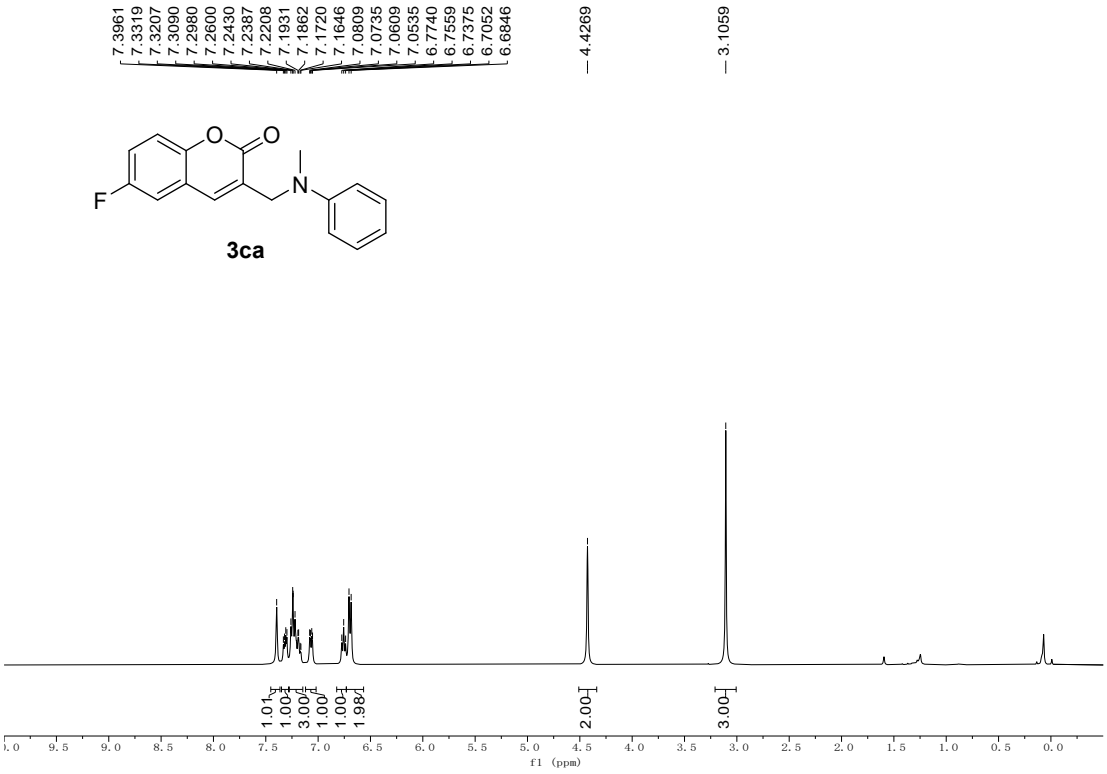
148.8396
137.6916
134.0342
131.9617
129.3313
127.5481
125.0478
118.9169
116.9355
116.1167
111.9016
52.6094
38.8723
20.6835


O
O
N

3ba


f1 (ppm)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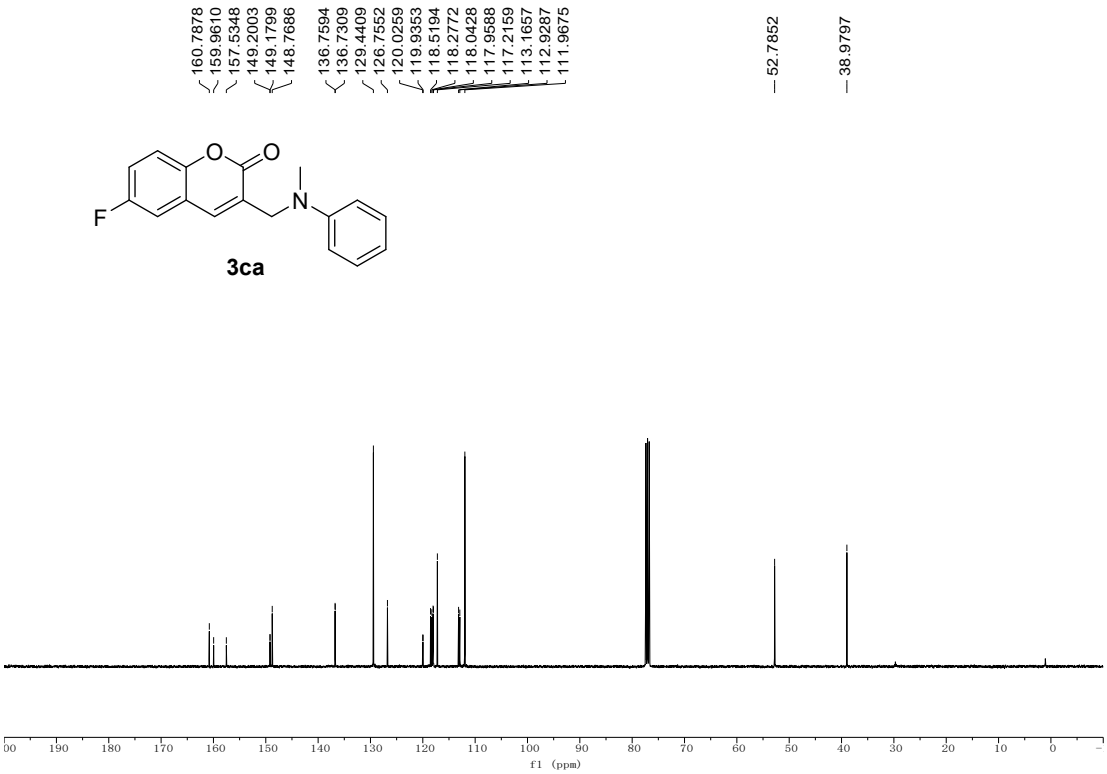
7.3207
7.3090
7.2980
7.2600
7.2430
7.2387
7.2208
7.1931
7.1862
7.1720
7.1646
7.0809
7.0735
7.0609
7.0535
6.7740
6.7559
6.7375
6.7052
6.6846
4.4269
3.1059
O
O
N
F
3ca
1.01
1.00
3.00
1.00
1.00
1.98
2.00
3.00
f1 (ppm)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157.5348
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148.7686
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129.4409
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120.0259
119.9353
118.5194
118.2772
118.0428
117.9588
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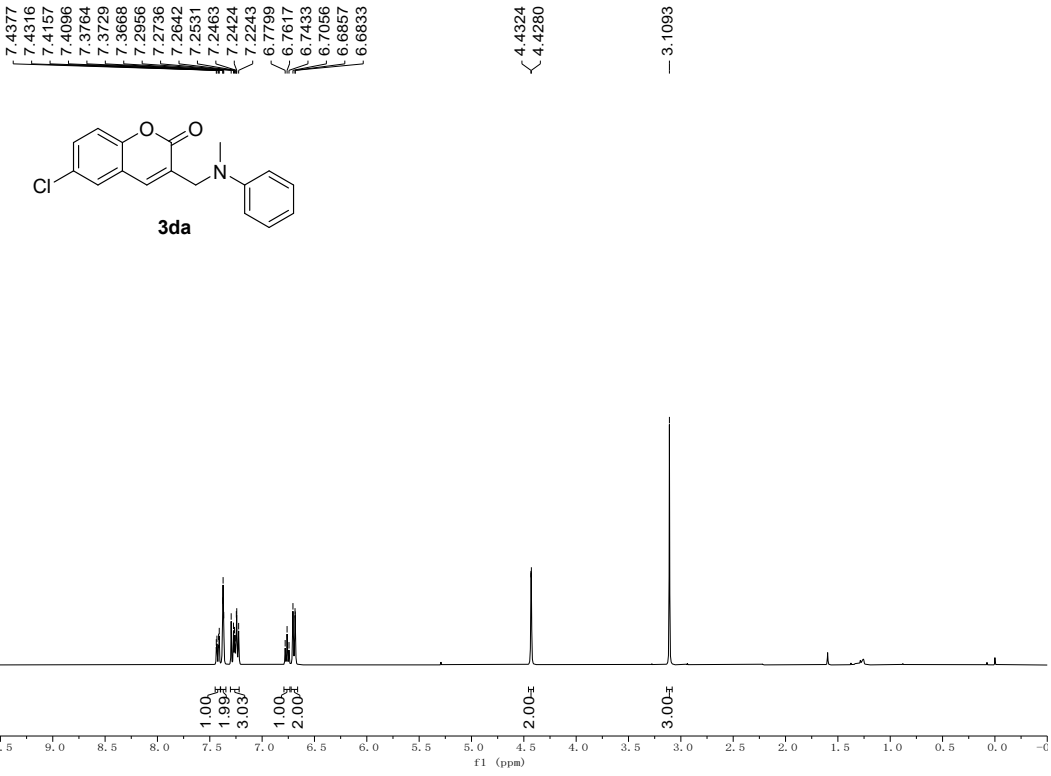
112.9287
111.9675
52.7852
38.9797
O
O
N
F
3ca
f1 (ppm)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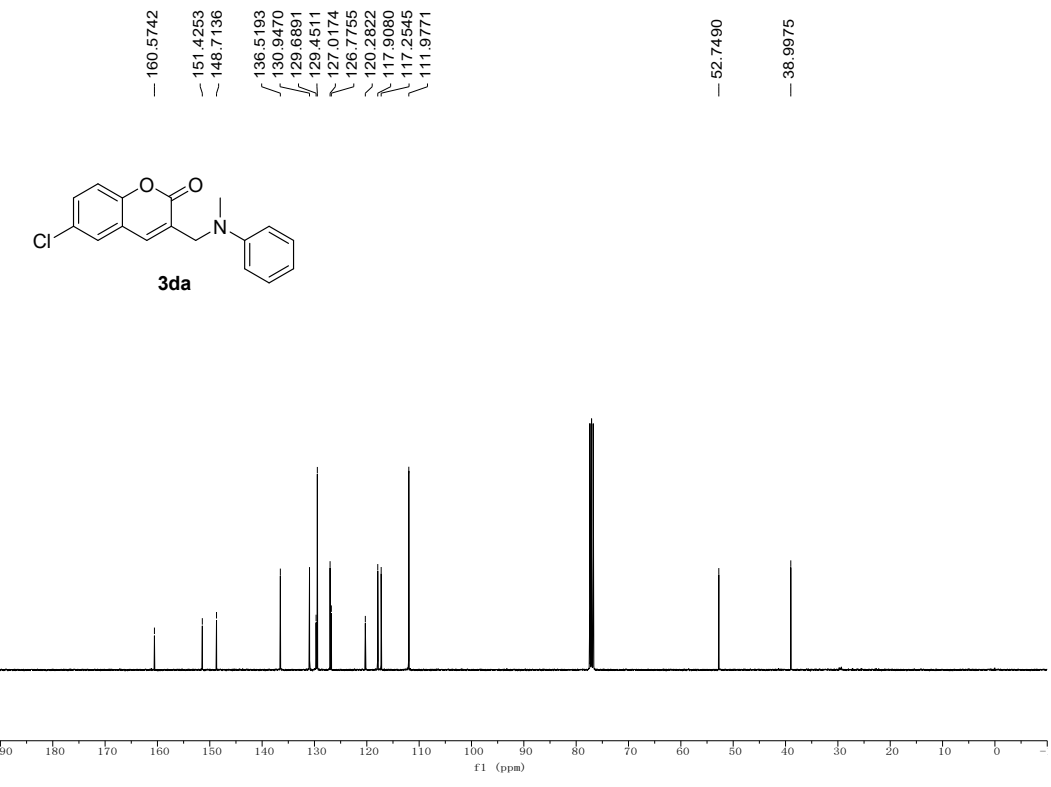
7.4316
7.4157
7.4096
7.3764
7.3729
7.3668
7.2956
7.2736
7.2642
7.2531
7.2463
7.2424
7.2243
6.7799
6.7617
6.7433
6.7056
6.6857
6.6833
4.4324
4.4280
3.1093
Cl
O
O
N
1.00
1.99
3.03
1.00
2.00
2.00
3.00
f1 (ppm)

3da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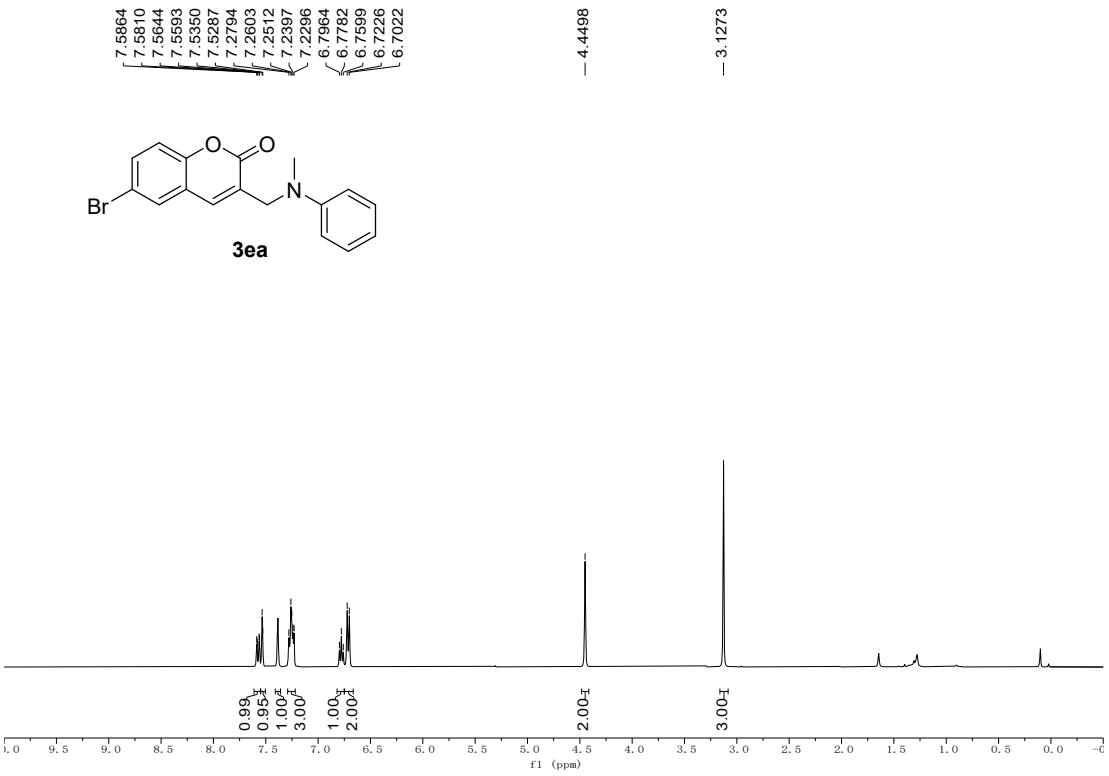
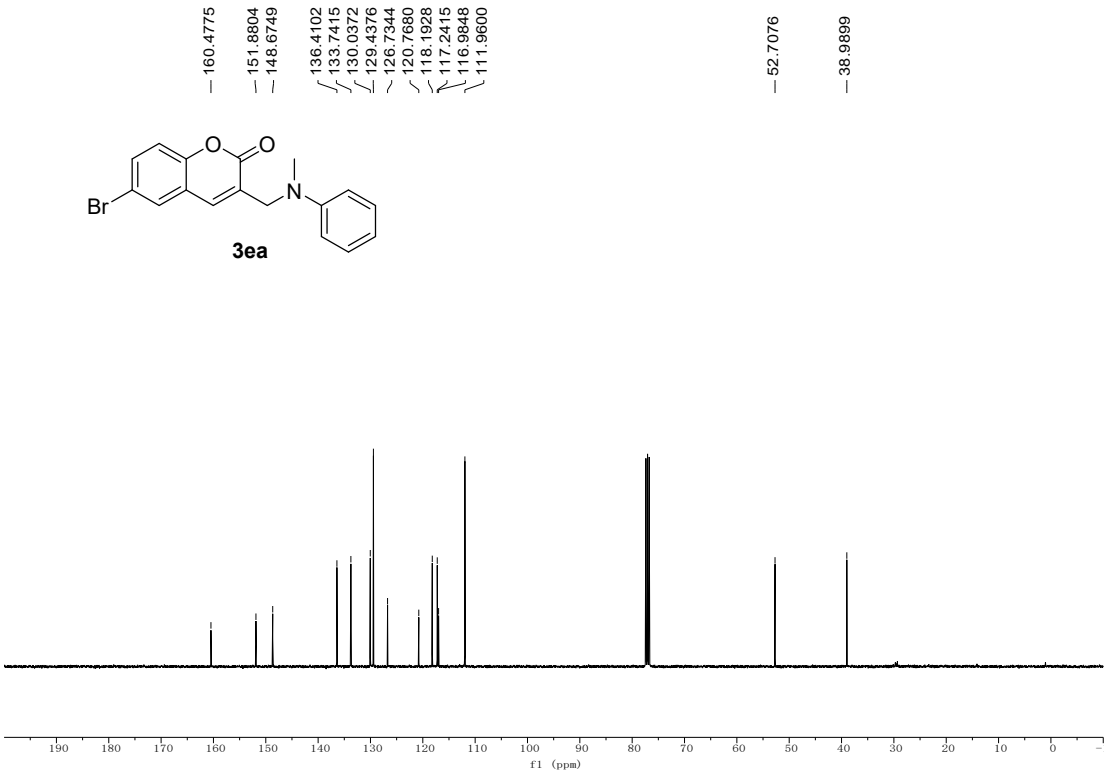
151.4253
148.7136
136.5193
130.9470
129.6891
129.4511
127.0174
126.7755
120.2822
117.9080
117.2545
111.9771
52.7490
38.9975
Cl
O
O
N
f1 (ppm)

3da


7.5864
7.5810
7.5644
7.5593
7.5350
7.5287
7.2794
7.2603
7.2512
7.2397
7.2296
6.7964
6.7782
6.7599
6.7226
6.7022
4.4498
3.1273
Br
O
O
N
3ea
0.99
0.95
1.00
3.00
1.00
2.00
2.00
3.00
f1 (ppm)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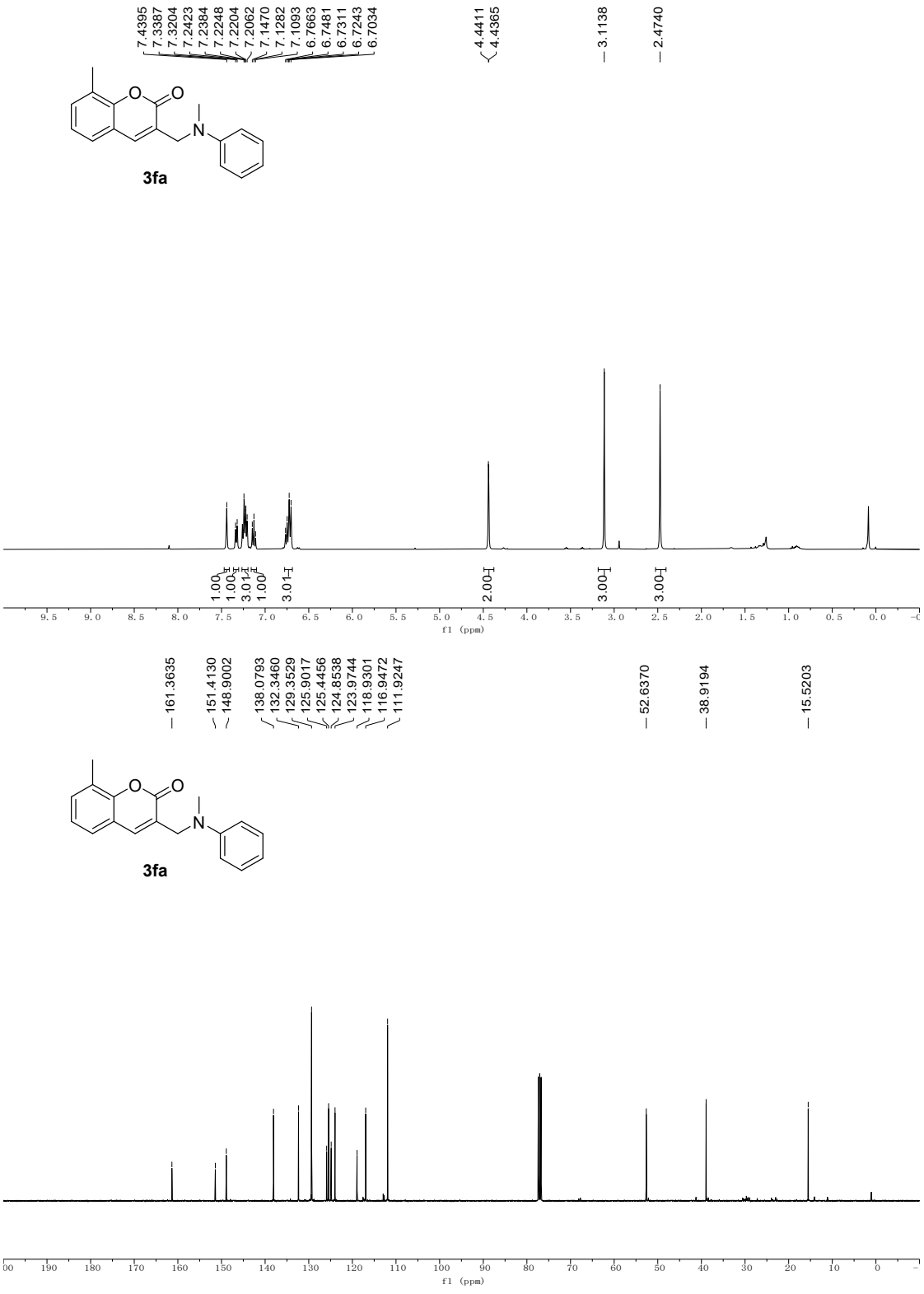
148.6749
136.4102
133.7415
130.0372
129.4376
126.7344
120.7680
118.1928
117.2415
116.9848
111.9600
52.7076
38.9899
Br
O
O
N
3ea
f1 (ppm)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7.3204
7.2423
7.2384
7.2248
7.2204
7.2062
7.1470
7.1282
7.1093
6.7663
6.7481
6.7311
6.7243
6.7034
4.4411
4.4365
3.1138
2.4740
O
O
N
3fa
1.00
1.00
3.01
1.00
3.01
2.00
3.00
3.00
f1 (ppm)
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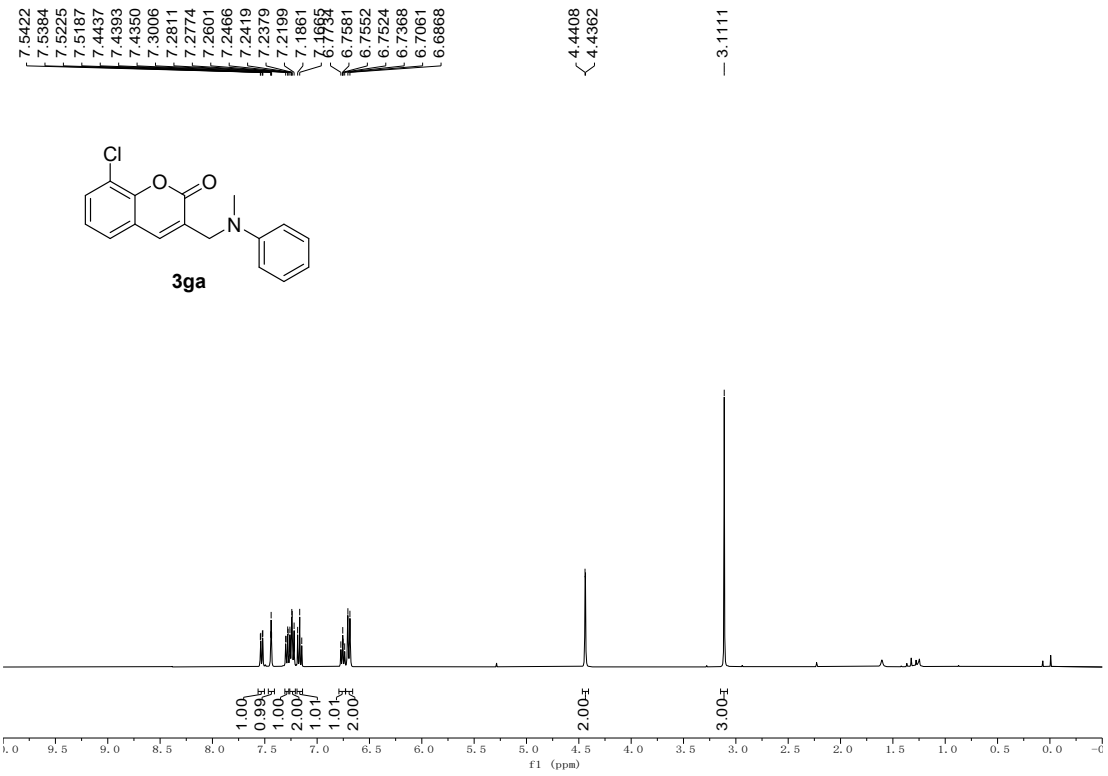
151.4130
148.9002
138.0793
132.3460
129.3529
125.9017
125.4456
124.8538
123.9744
118.9301
116.9472
111.9247
52.6370
38.9194
15.5203
O
O
N
3fa
f1 (ppm)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7.5225
7.5187
7.4437
7.4393
7.4350
7.3006
7.2811
7.2774
7.2601
7.2466
7.2419
7.2379
7.2199
7.1861
7.1665
7.1634
6.7581
6.7552
6.7524
6.7368
6.7061
6.6868
4.4408
4.4362
3.1111
Cl
O
O
N
3ga
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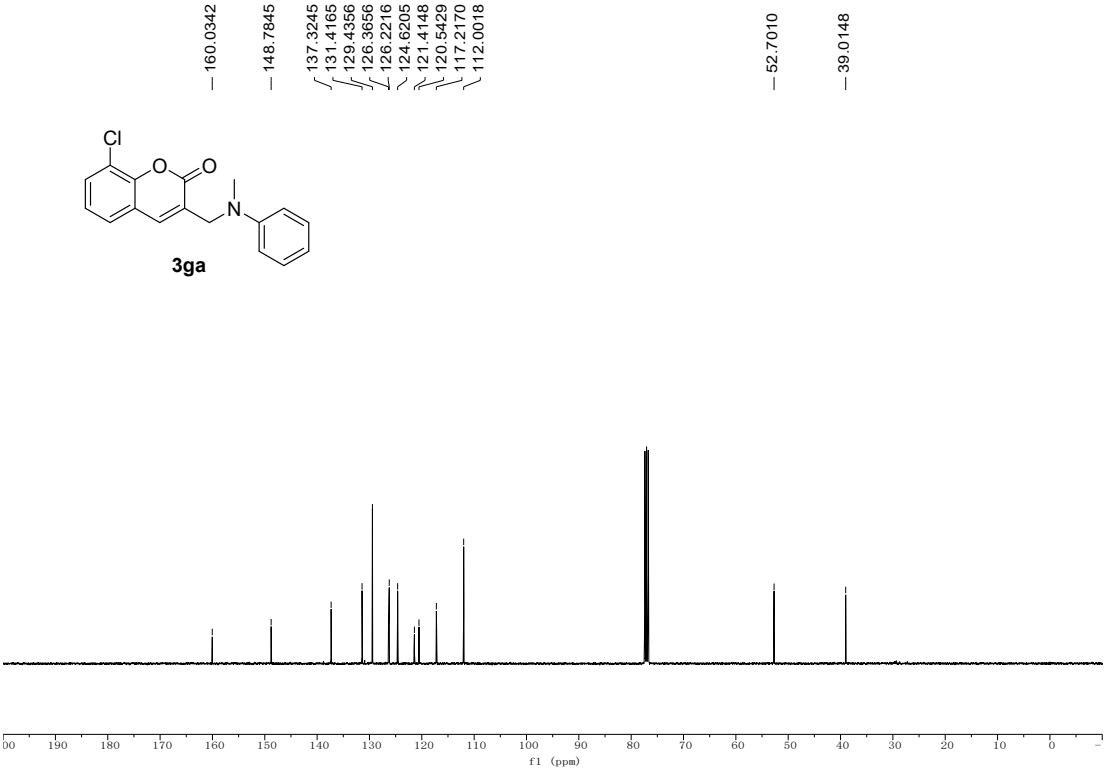
0.99
1.00
2.00
1.01
1.01
2.00
2.00
3.00
f1 (ppm)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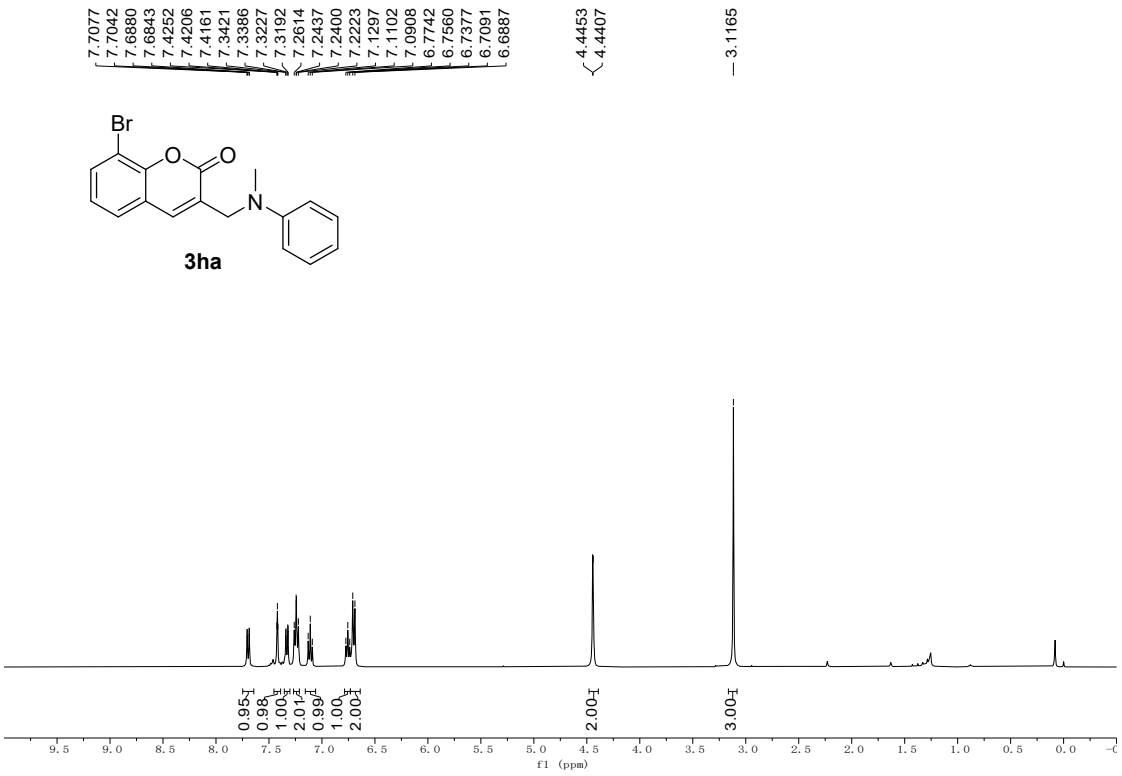
137.3245
131.4165
129.4356
126.3656
126.2216
124.6205
121.4148
120.5429
117.2170
112.0018
52.7010
39.0148
Cl
O
O
N
3ga
f1 (ppm)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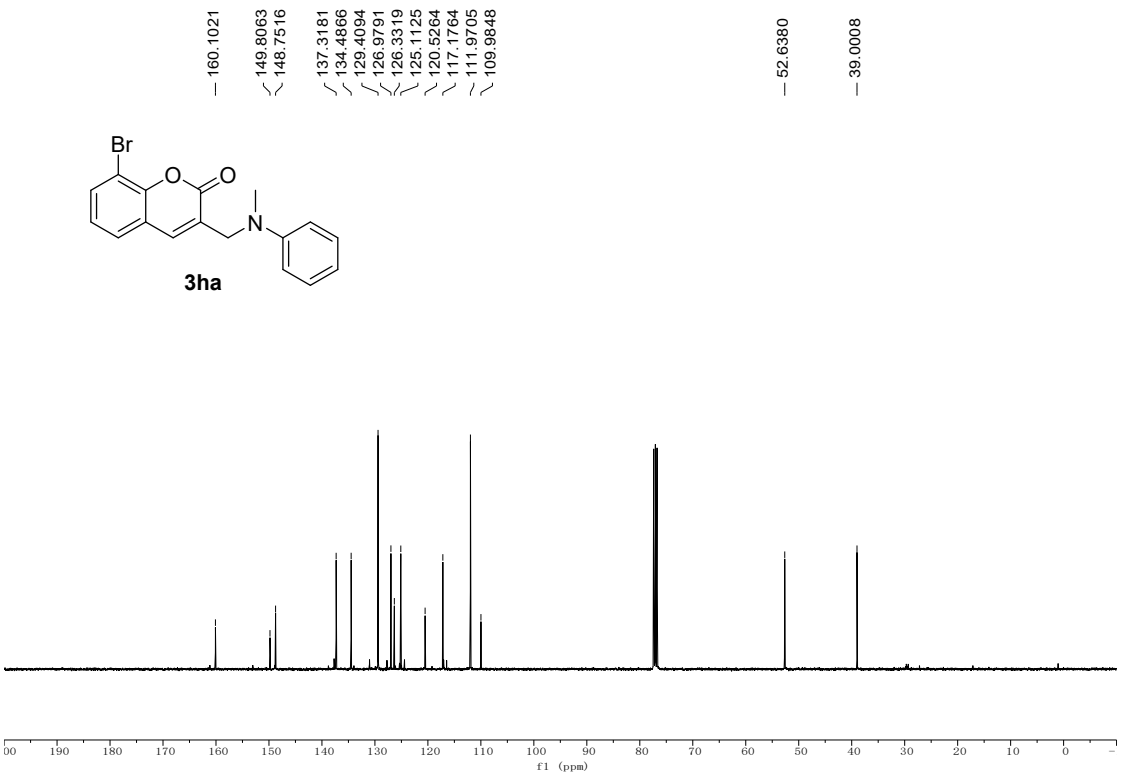
7.7042
7.6880
7.6843
7.4252
7.4206
7.4161
7.3421
7.3386
7.3227
7.3192
7.2614
7.2437
7.2400
7.2223
7.1297
7.1102
7.0908
6.7742
6.7560
6.7377
6.7091
6.6887
4.4453
4.4407
3.1165
Br
O
O
N
0.95
0.98
1.00
2.01
0.99
1.00
2.00
2.00
3.00
f1 (ppm)

3ha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148.7516
137.3181
134.4866
129.4094
126.9791
126.3319
125.1125
120.5264
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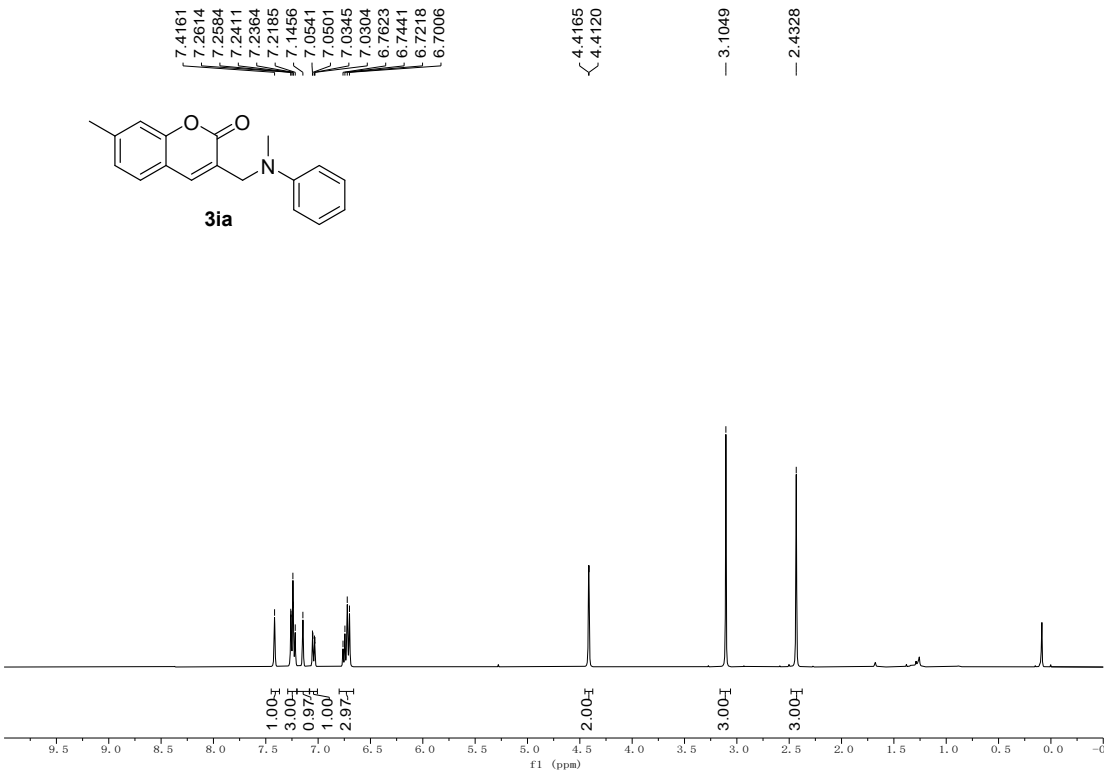
111.9705
109.9848
52.6380
39.0008
Br
O
O
N
f1 (ppm)

3ha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7.2614
7.2584
7.2411
7.2364
7.2185
7.1456
7.0541
7.0501
7.0345
7.0304
6.7623
6.7441
6.7218
6.7006
4.4165
4.4120
3.1049
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3ia
1.00
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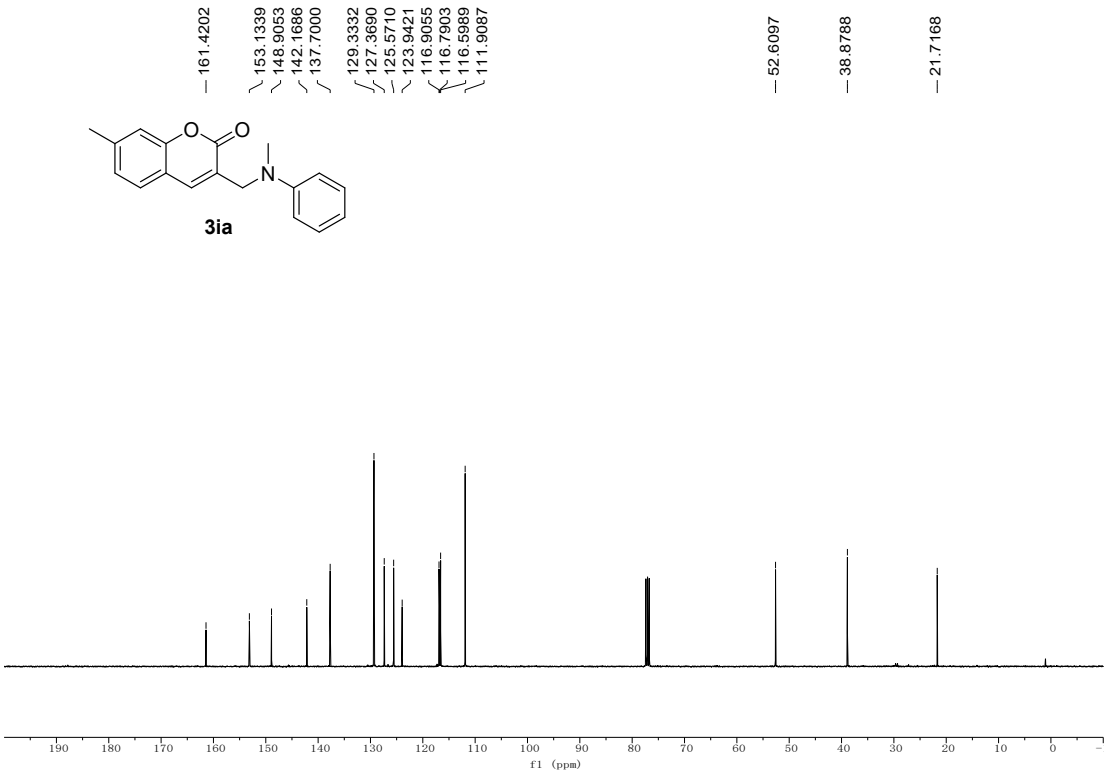
1.00
2.97
2.00
3.00
3.00
f1 (ppm)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127.3690
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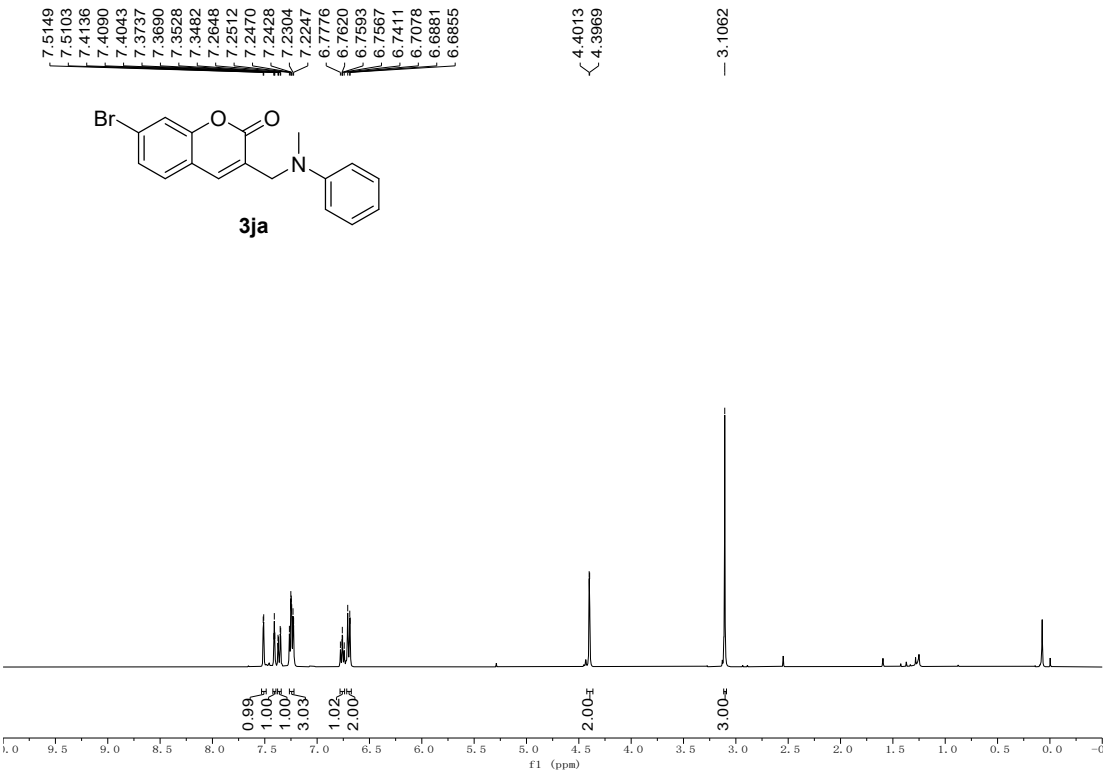
38.8788
21.7168
3ia
f1 (ppm)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7.4136
7.4090
7.4043
7.3737
7.3690
7.3528
7.3482
7.2648
7.2512
7.2470
7.2428
7.2304
7.2247
6.7776
6.7620
6.7593
6.7567
6.7411
6.7078
6.6881
6.6855
4.4013
4.3969
3.1062
Br
O
O
N
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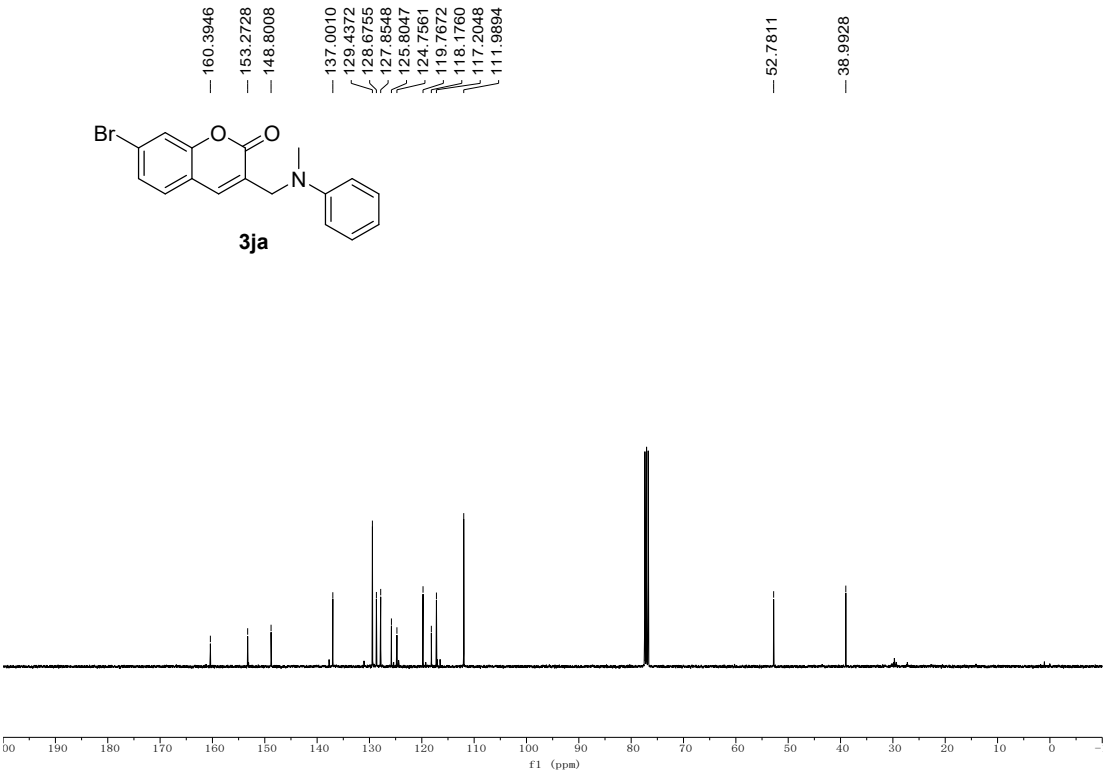
1.00
1.00
3.03
1.02
2.00
2.00
3.00
f1 (ppm)

3ja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127.8548
125.8047
124.7561
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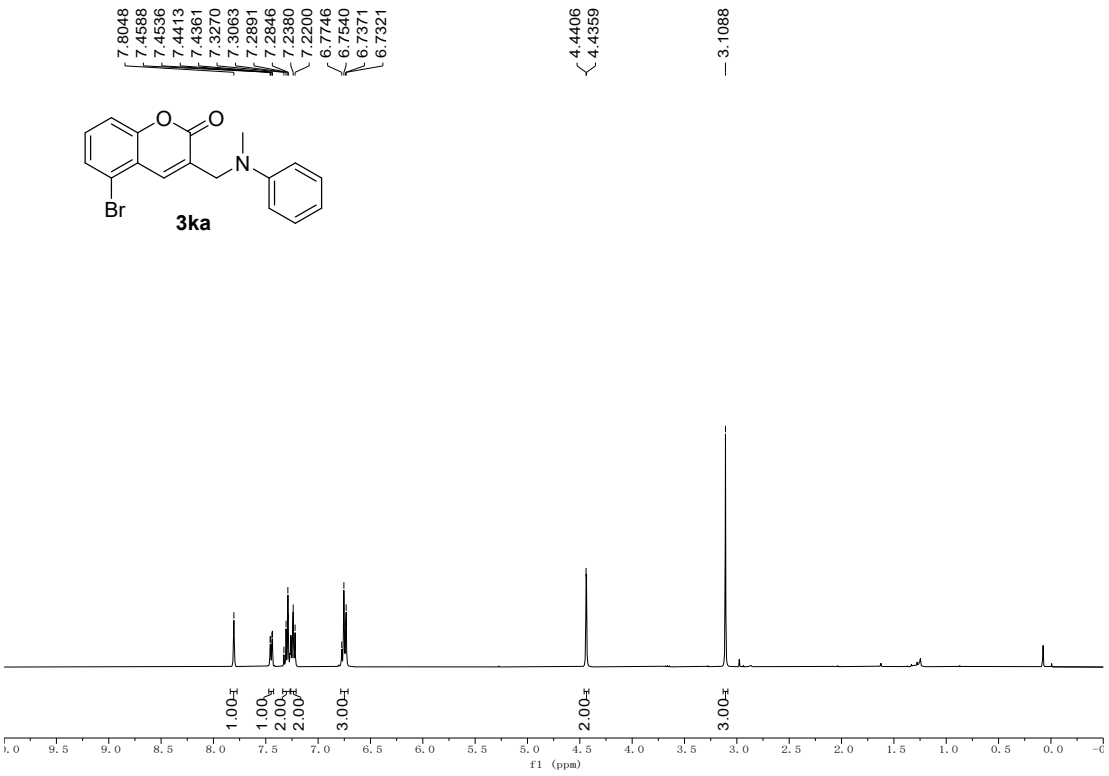
117.2048
111.9894
52.7811
38.9928
Br
O
O
N
f1 (ppm)

3ja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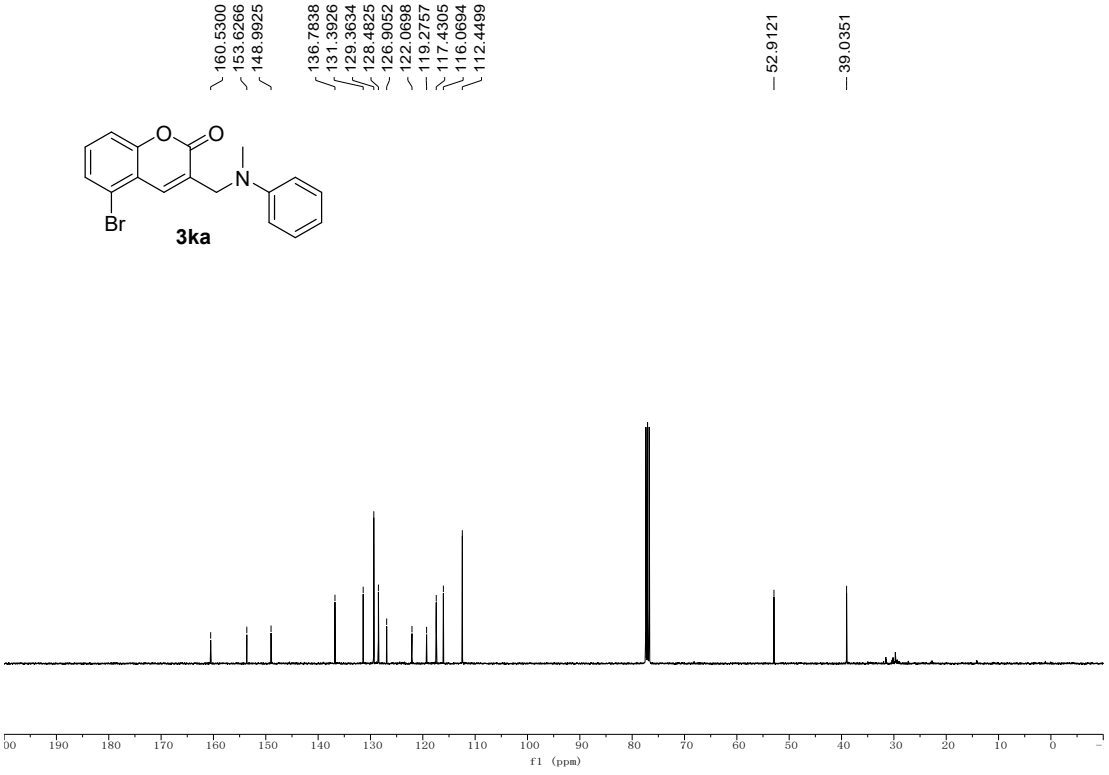
7.3270
7.3063
7.2891
7.2846
7.2380
7.2200
6.7746
6.7540
6.7371
6.7321
4.4406
4.4359
3.1088
O
O
N
Br
3ka
1.00
1.00
2.00
2.00
3.00
2.00
3.00
f1 (ppm)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128.4825
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122.0698
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116.0694
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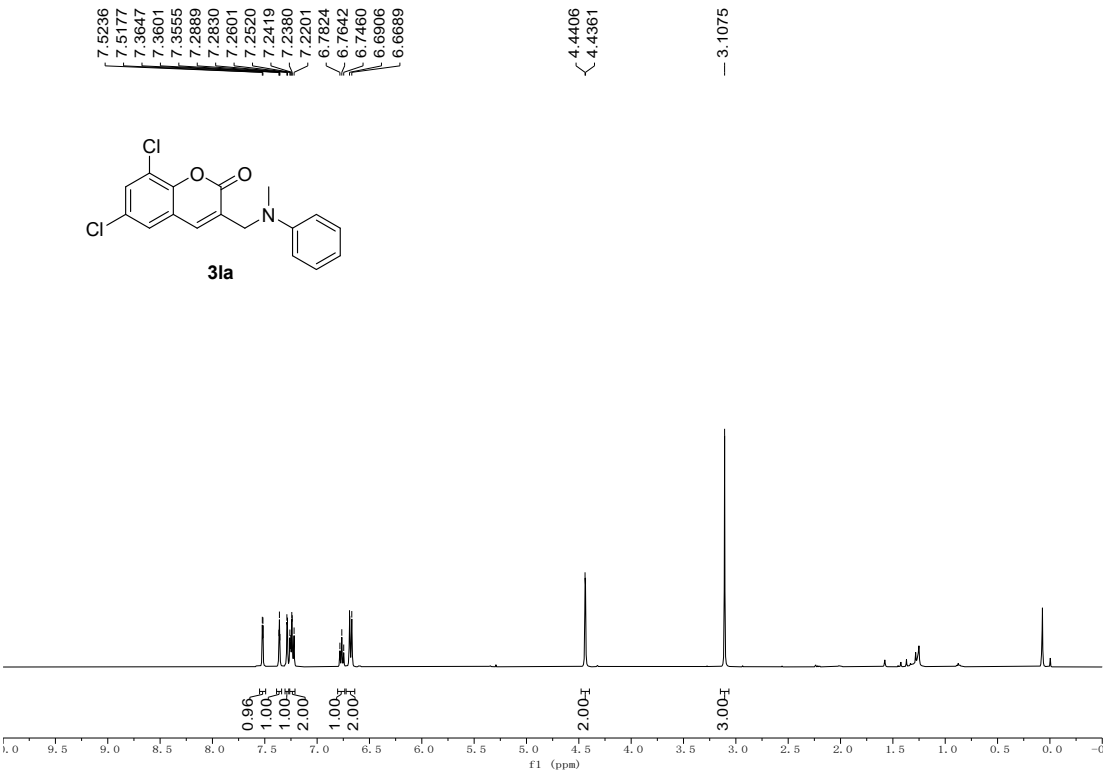
52.9121
39.0351
O
O
N
Br
3ka
f1 (ppm)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7.5177
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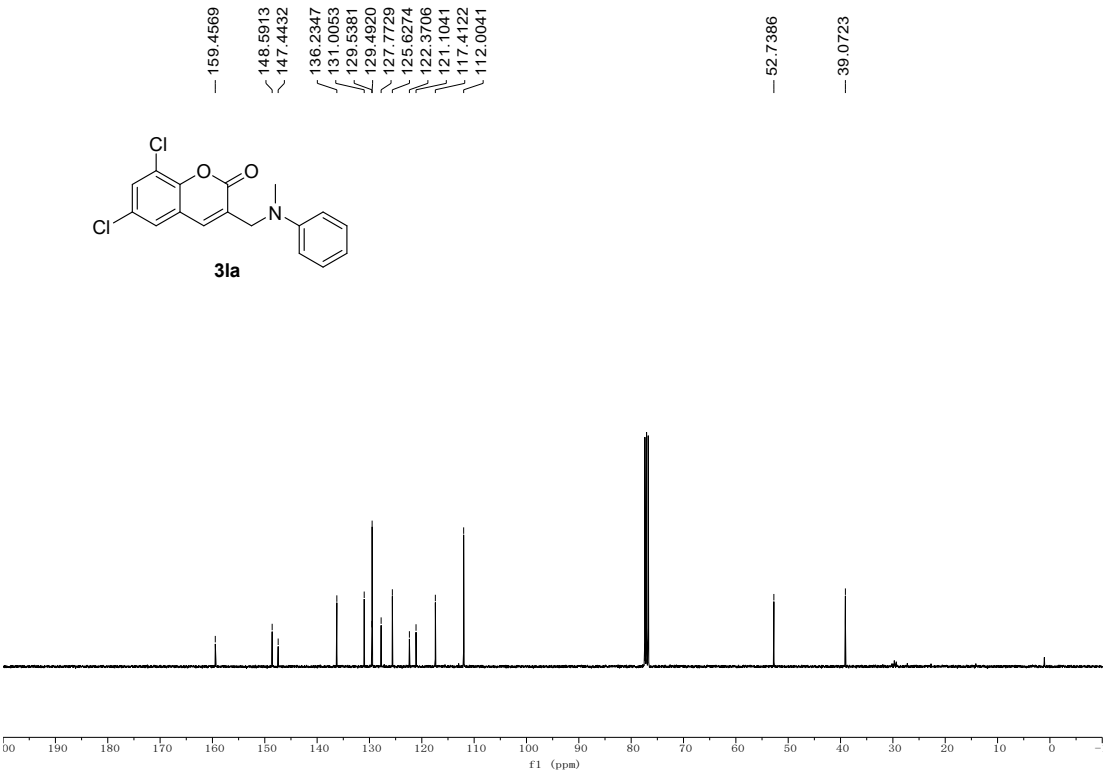
7.3601
7.3555
7.2889
7.2830
7.2601
7.2520
7.2419
7.2380
7.2201
6.7824
6.7642
6.7460
6.6906
6.6689
4.4406
4.4361
3.1075
Cl
O
O
N
Cl
3la
0.96
1.00
1.00
2.00
1.00
2.00
2.00
3.00
f1 (ppm)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131.0053
129.5381
129.4920
127.7729
125.6274
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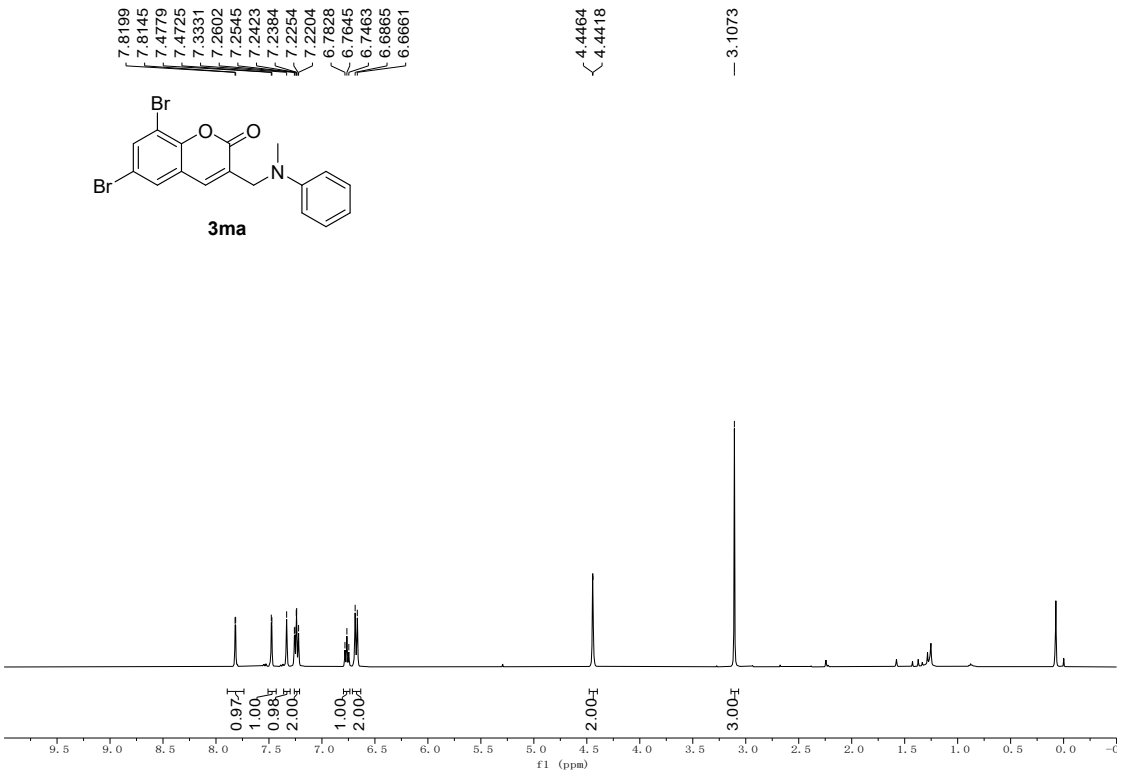
117.4122
112.0041
52.7386
39.0723
Cl
O
O
N
Cl
3la
f1 (ppm)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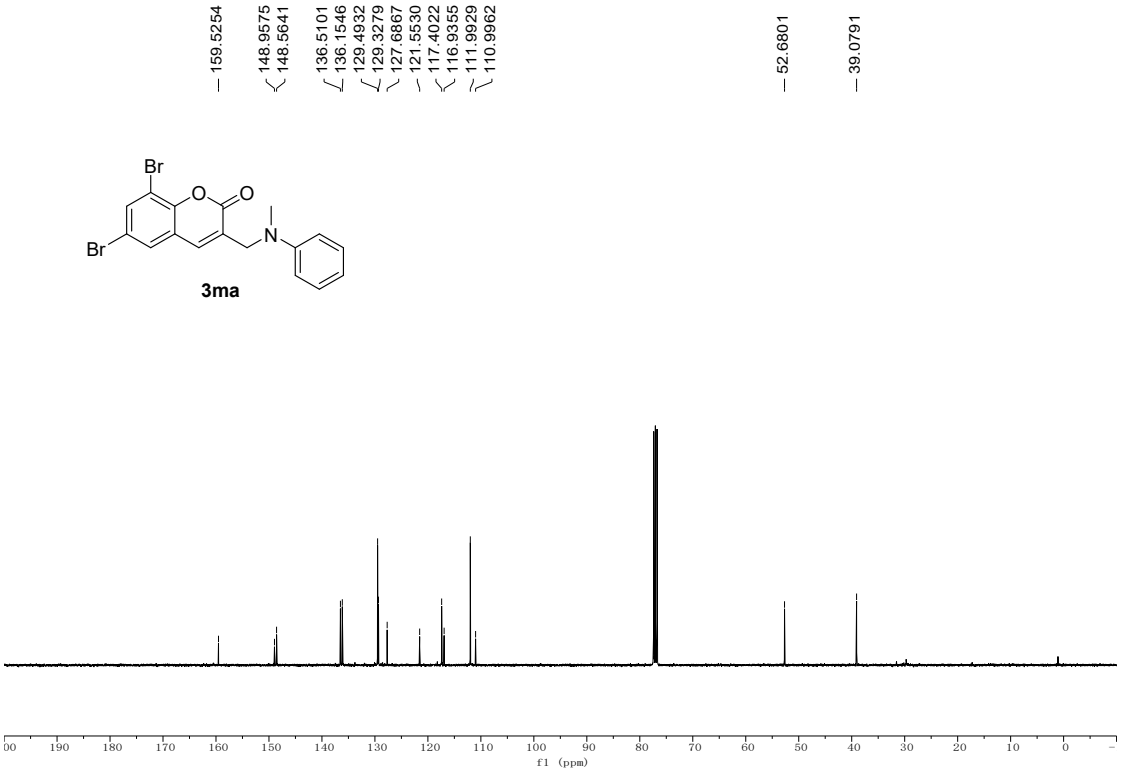
7.8145
7.4779
7.4725
7.3331
7.2602
7.2545
7.2423
7.2384
7.2254
7.2204
6.7828
6.7645
6.7463
6.6865
6.6661
4.4464
4.4418
3.1073
Br
O
O
Br
N
3ma
0.97
1.00
0.98
2.00
1.00
2.00
2.00
3.00
f1 (ppm)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148.5641
136.5101
136.1546
129.4932
129.3279
127.6867
121.5530
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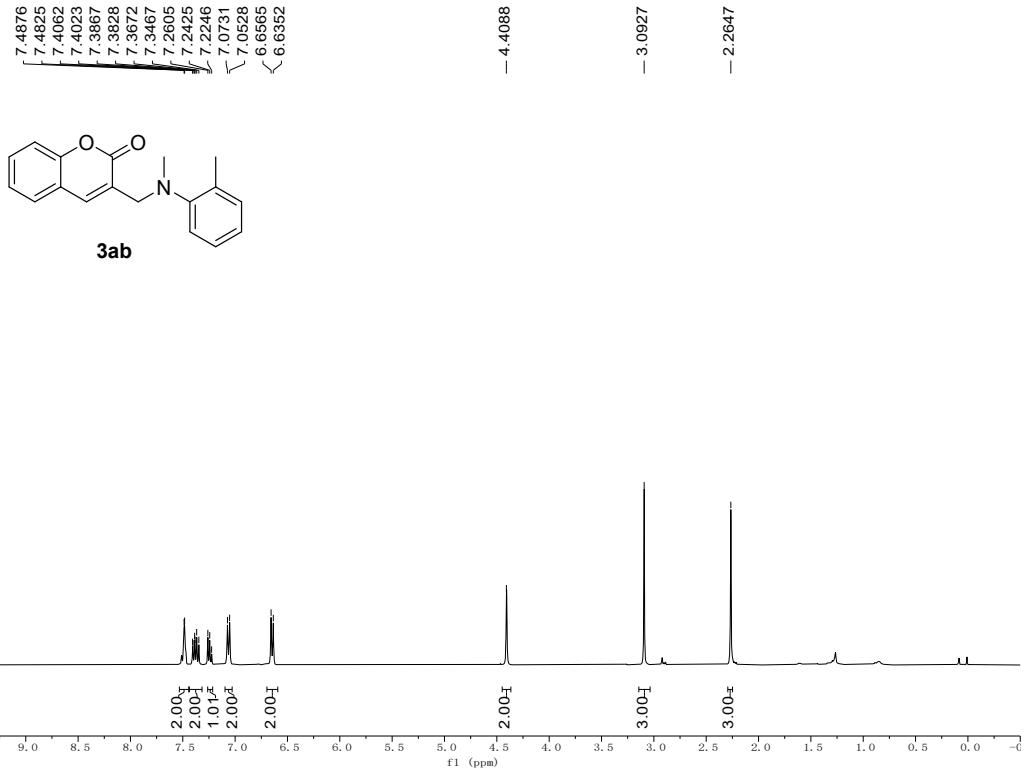
116.9355
111.9929
110.9962
52.6801
39.0791
Br
O
O
Br
N
3ma
f1 (ppm)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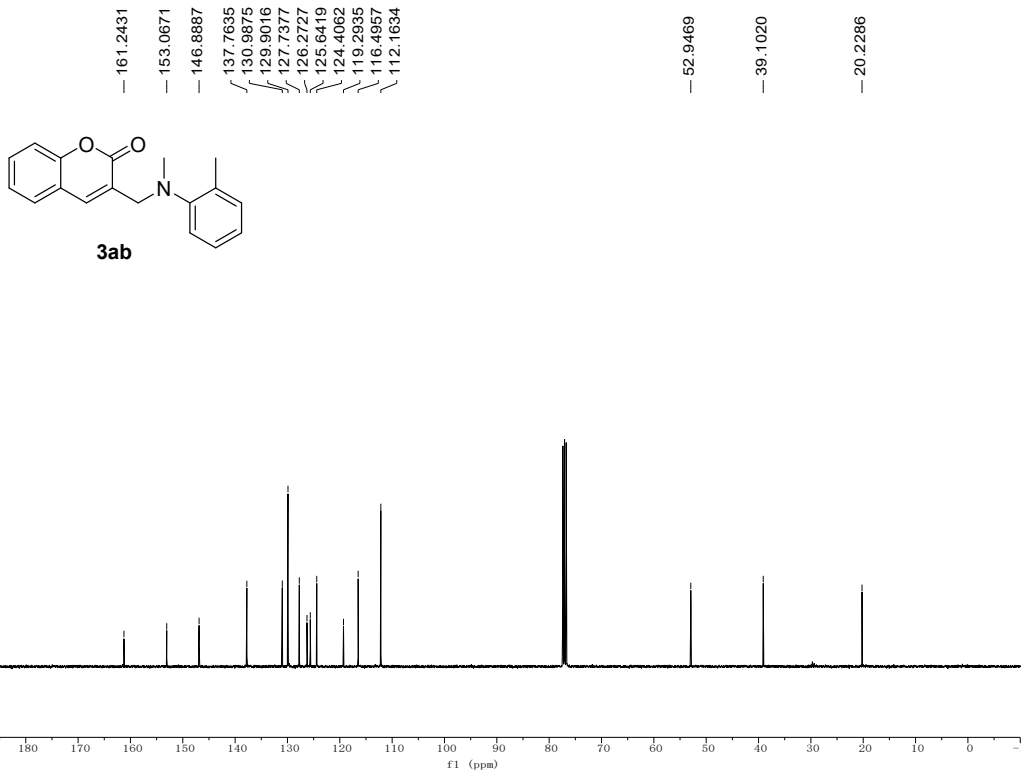
7.4825
7.4062
7.4023
7.3867
7.3828
7.3672
7.3467
7.2605
7.2425
7.2246
7.0731
7.0528
6.6565
6.6352
4.4088
3.0927
2.2647
O
O
N
2.00
2.00
1.01
2.00
2.00
2.00
3.00
3.00
f1 (ppm)

3ab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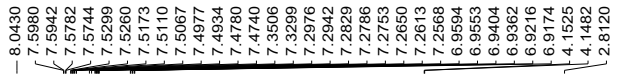
130.9875
129.9016
127.7377
126.2727
125.6419
124.4062
119.2935
116.4957
112.1634
52.9469
39.1020
20.2286
O
O
N
f1 (ppm)

3ab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7.5942
7.5782
7.5744
7.5299
7.5260
7.5173
7.5110
7.5067
7.4977
7.4934
7.4780
7.4740
7.3506
7.3299
7.2976
7.2942
7.2829
7.2786
7.2753
7.2650
7.2613
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6.9553
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6.9216
6.9174
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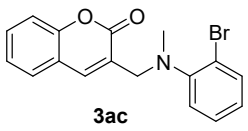
4.1482
2.8120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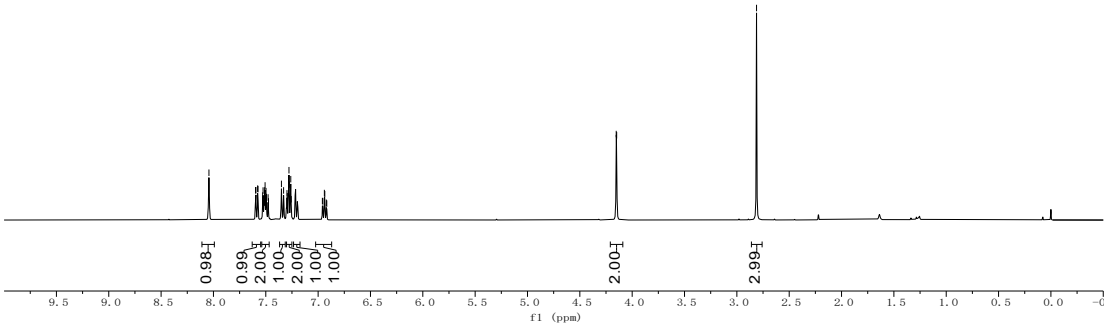
O
Br
N

3ac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2.00
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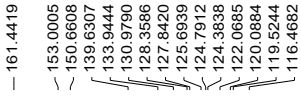
1.00
2.00
2.99
f1 (ppm)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128.3586
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120.0884
119.5244
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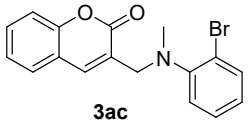
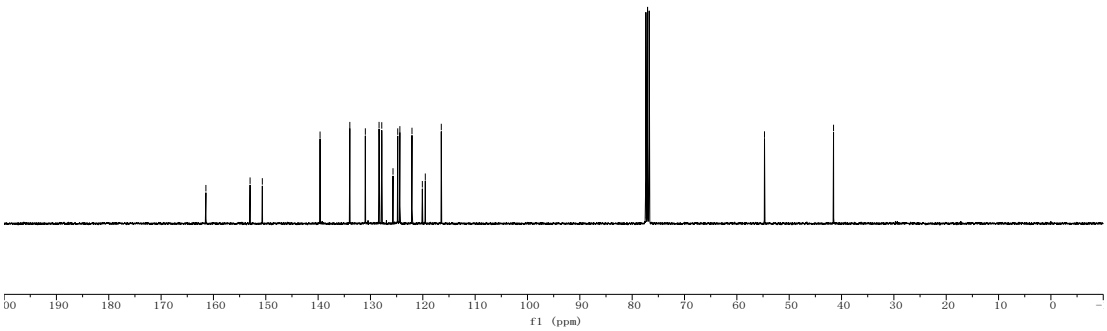
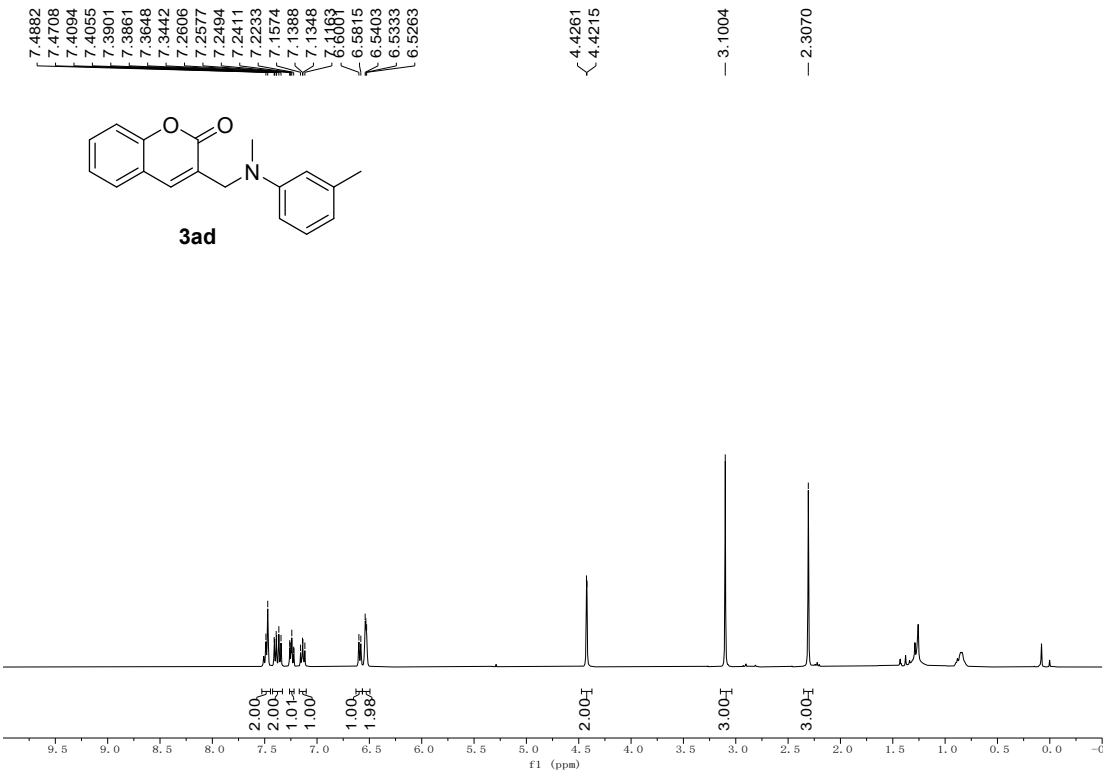
54.7194
41.5290


O
O
Br
N

3ac


f1 (ppm)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7.4055
7.3901
7.3861
7.3648
7.3442
7.2606
7.2577
7.2494
7.2411
7.2233
7.1574
7.1388
7.1348
7.1163
7.1001
6.5815
6.5403
6.5333
6.5263
4.4261
4.4215
3.1004
2.3070
O
O
N
3ad
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2.00
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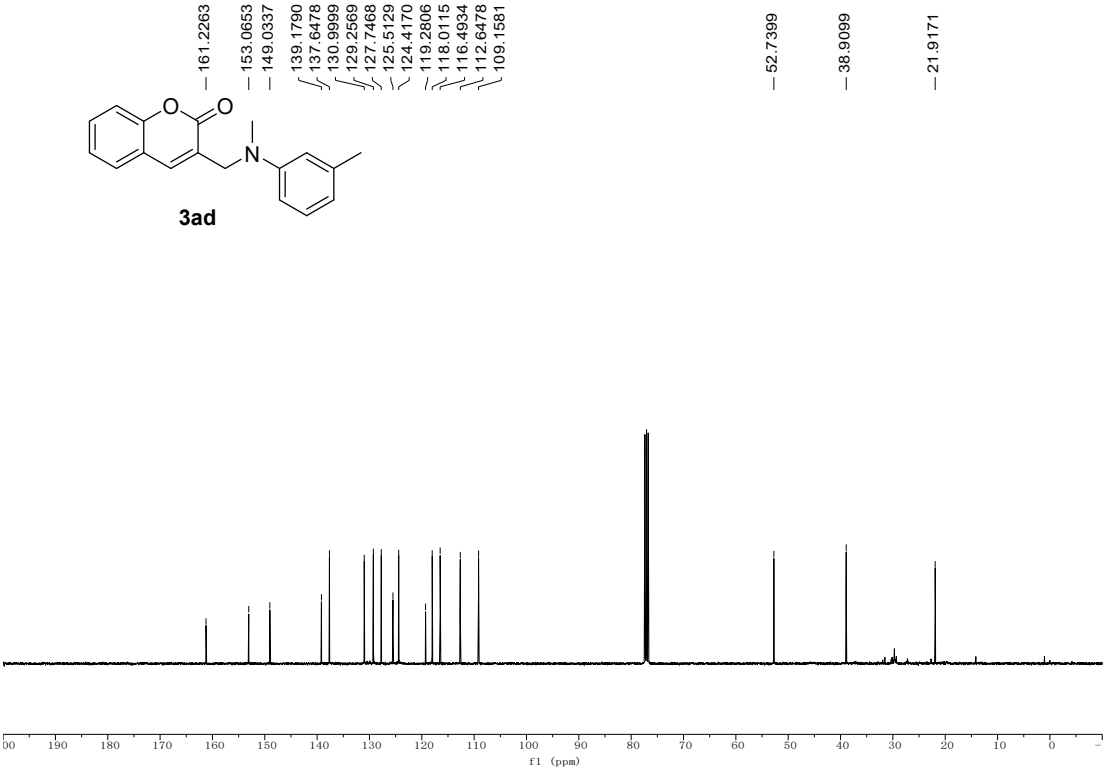
1.00
1.00
1.98
2.00
3.00
3.00
f1 (ppm)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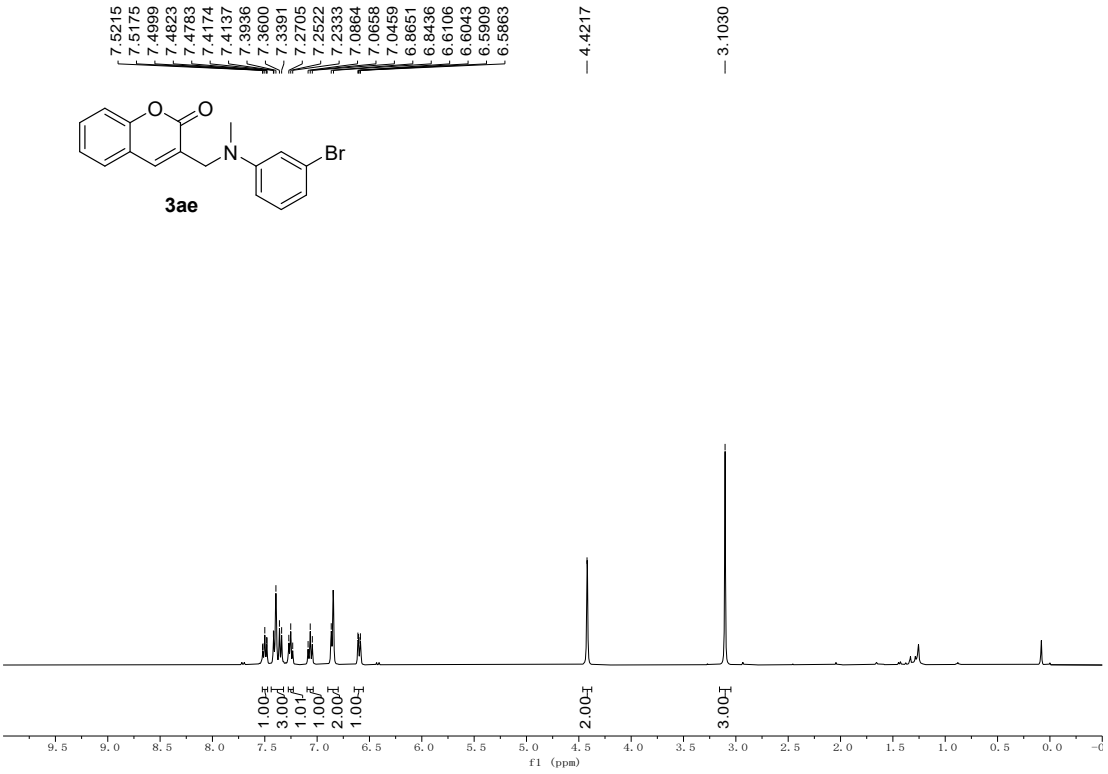
149.0337
139.1790
137.6478
130.9999
129.2569
127.7468
125.5129
124.4170
119.2806
118.0115
116.4934
112.6478
109.1581
52.7399
38.9099
21.9171
O
O
N
3ad
f1 (ppm)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7.4999
7.4823
7.4783
7.4174
7.4137
7.3936
7.3600
7.3391
7.2705
7.2522
7.2333
7.0864
7.0658
7.0459
6.8651
6.8436
6.6106
6.6043
6.5909
6.5863
4.4217
3.1030
O
O
N
Br
3ae
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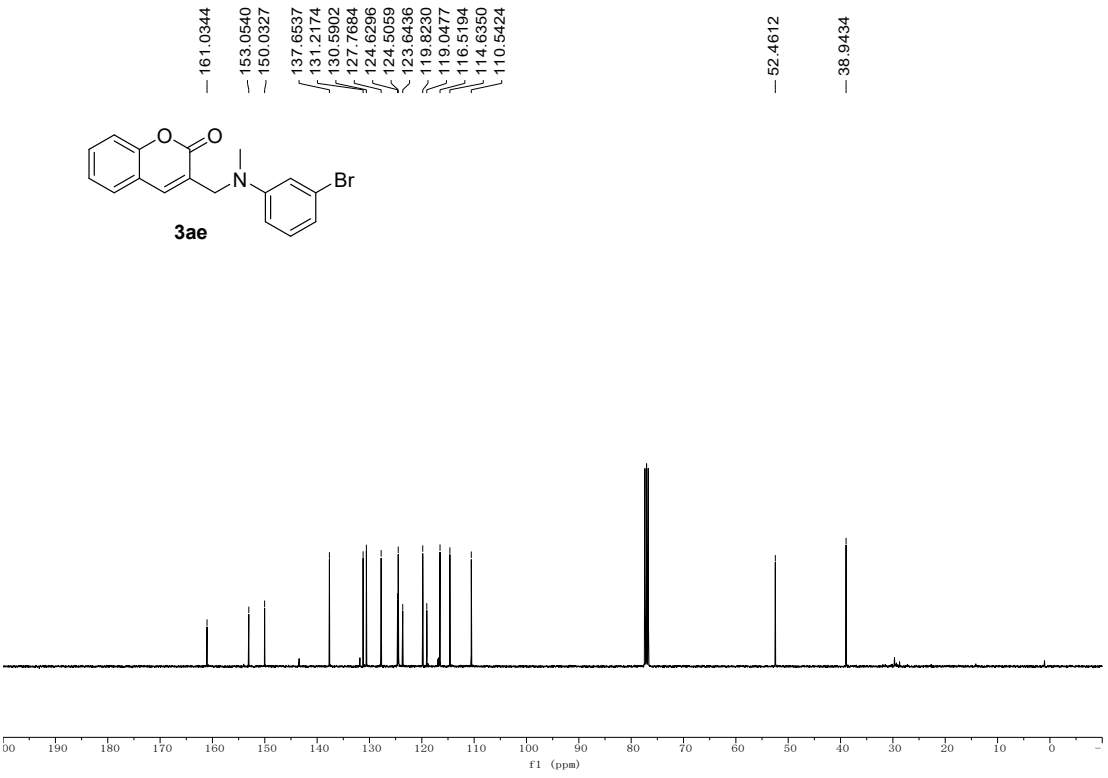
3.00
1.01
1.00
2.00
1.00
2.00
3.00
f1 (ppm)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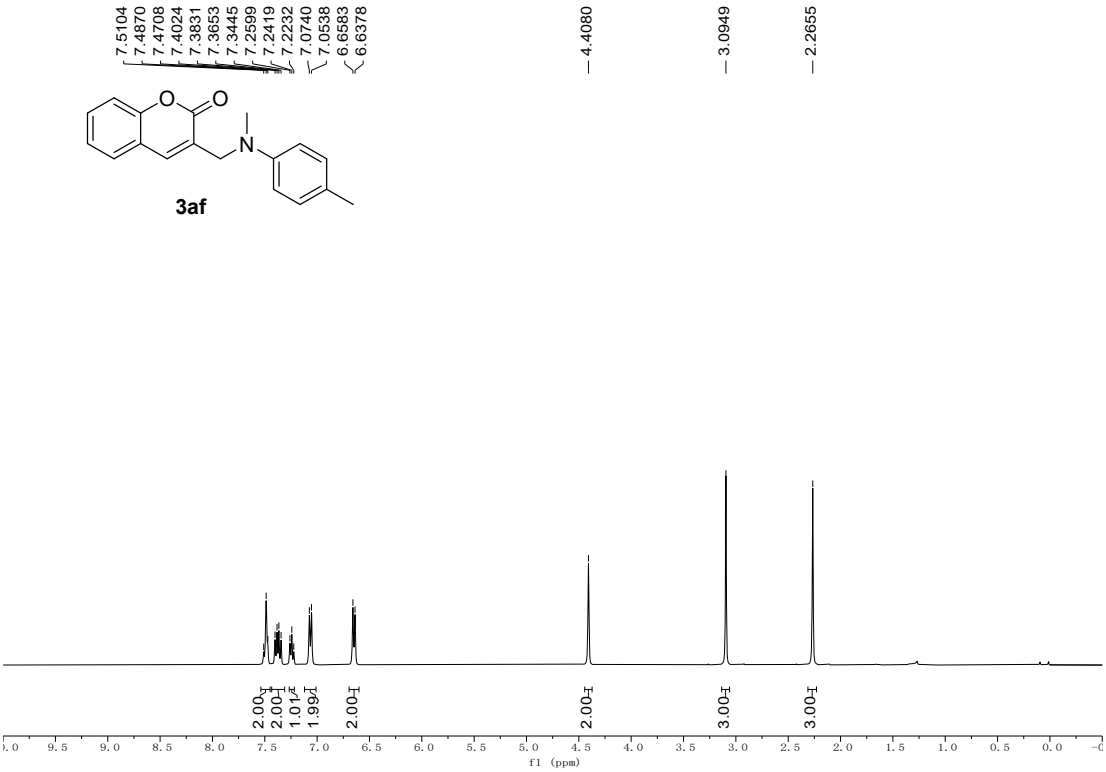
137.6537
131.2174
130.5902
127.7684
124.6296
124.5059
123.6436
119.8230
119.0477
116.5194
114.6350
110.5424
52.4612
38.9434
O
O
N
Br
3ae
f1 (ppm)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7.4870
7.4708
7.4024
7.3831
7.3653
7.3445
7.2599
7.2419
7.2232
7.0740
7.0538
6.6583
6.6378
4.4080
3.0949
2.2655
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O
N
3af
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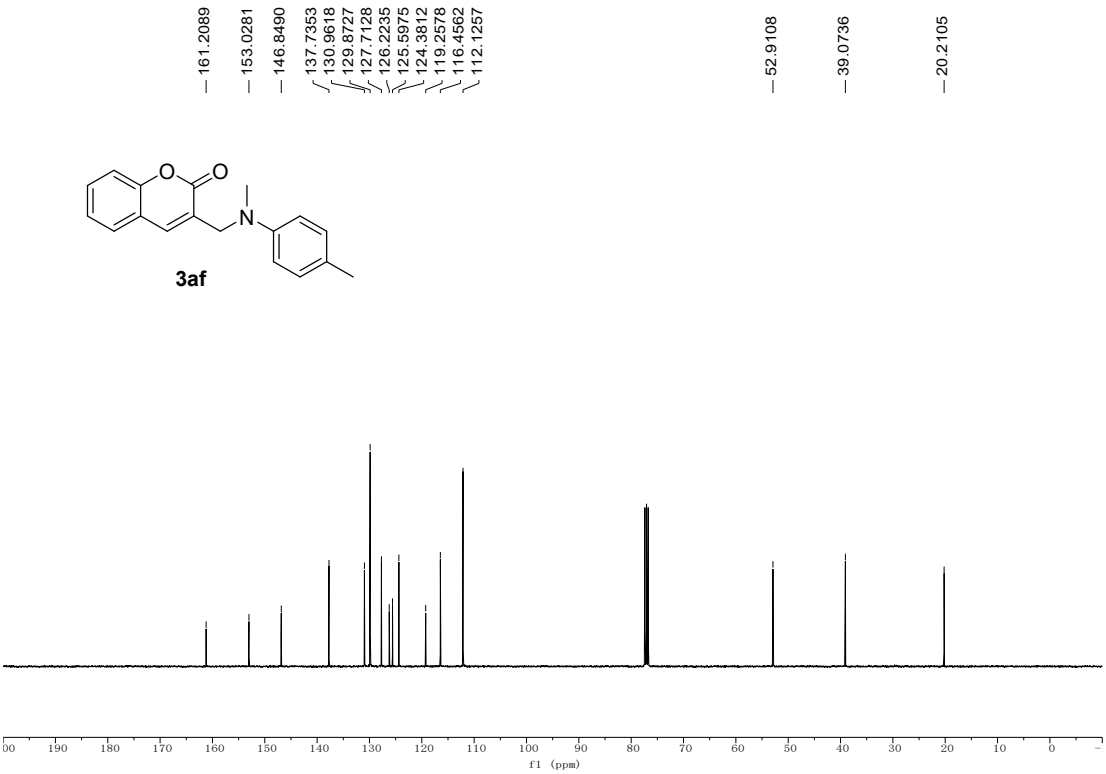
2.00
1.01
1.99
2.00
2.00
3.00
3.00
f1 (ppm)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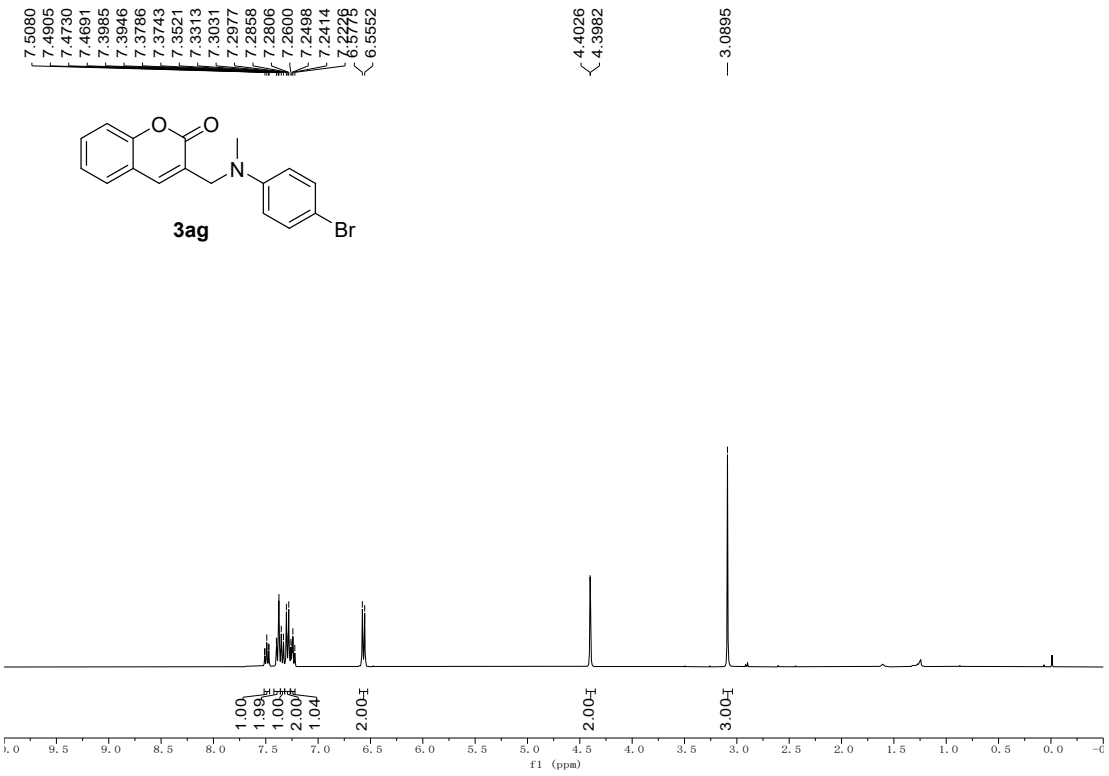
146.8490
137.7353
130.9618
129.8727
127.7128
126.2235
125.5975
124.3812
119.2578
116.4562
112.1257
52.9108
39.0736
20.2105
O
O
N
3af
f1 (ppm)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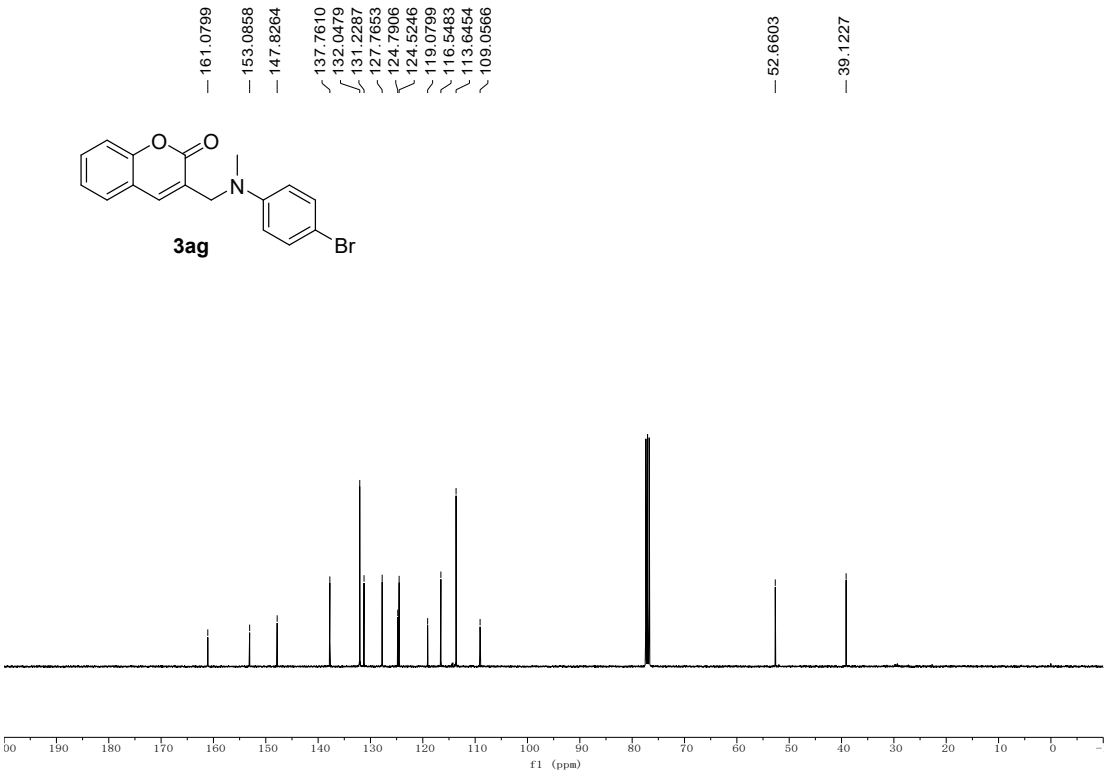
7.4730
7.4691
7.3985
7.3946
7.3786
7.3743
7.3521
7.3313
7.3031
7.2977
7.2858
7.2806
7.2600
7.2498
7.2414
6.5775
6.5552
4.4026
4.3982
3.0895
3ag
Br
1.00
1.99
1.00
2.00
1.04
2.00
2.00
3.00
f1 (ppm)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131.2287
127.7653
124.7906
124.5246
119.0799
116.5483
113.6454
109.0566
52.6603
39.1227
3ag
Br
f1 (ppm)


7.5196
7.5151
7.4897
7.4863
7.4828
7.4688
7.4115
7.4075
7.3921
7.3881
7.3576
7.3369
7.2613
7.2582
7.2425
6.8453
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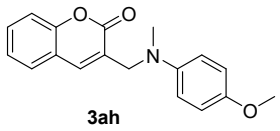
4.3543
3.7533
3.0504



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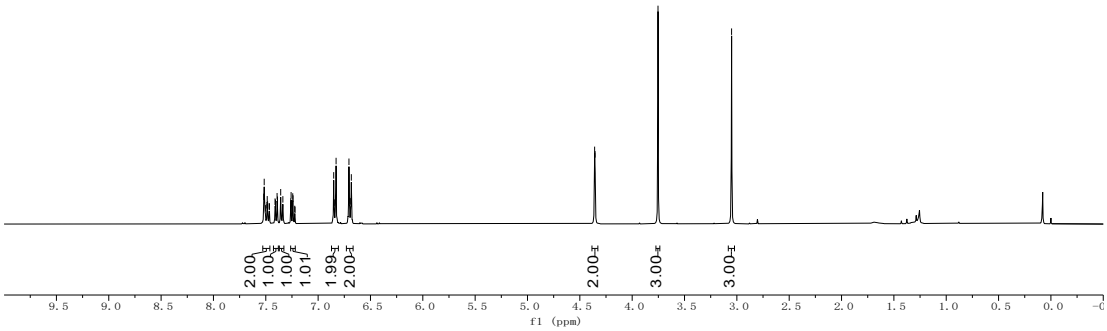
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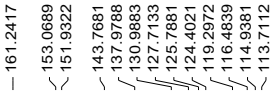
1.01
1.99
2.00
2.00
3.00
3.00
f1 (ppm)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143.7681
137.9788
130.9883
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124.4021
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116.4839
114.9381
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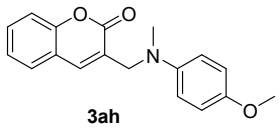
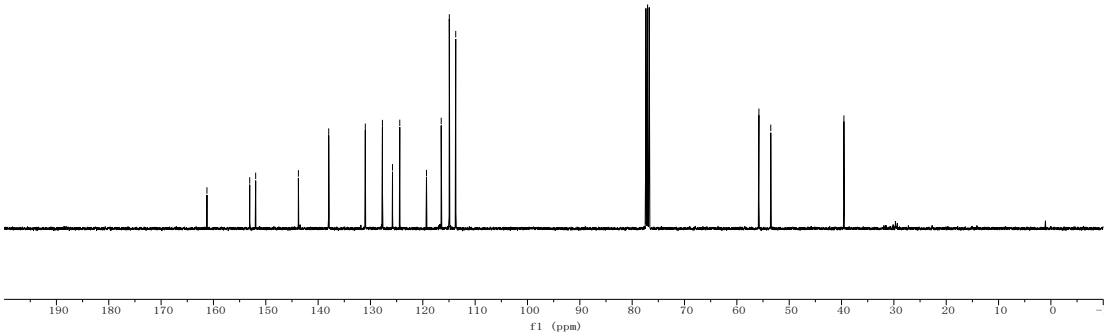
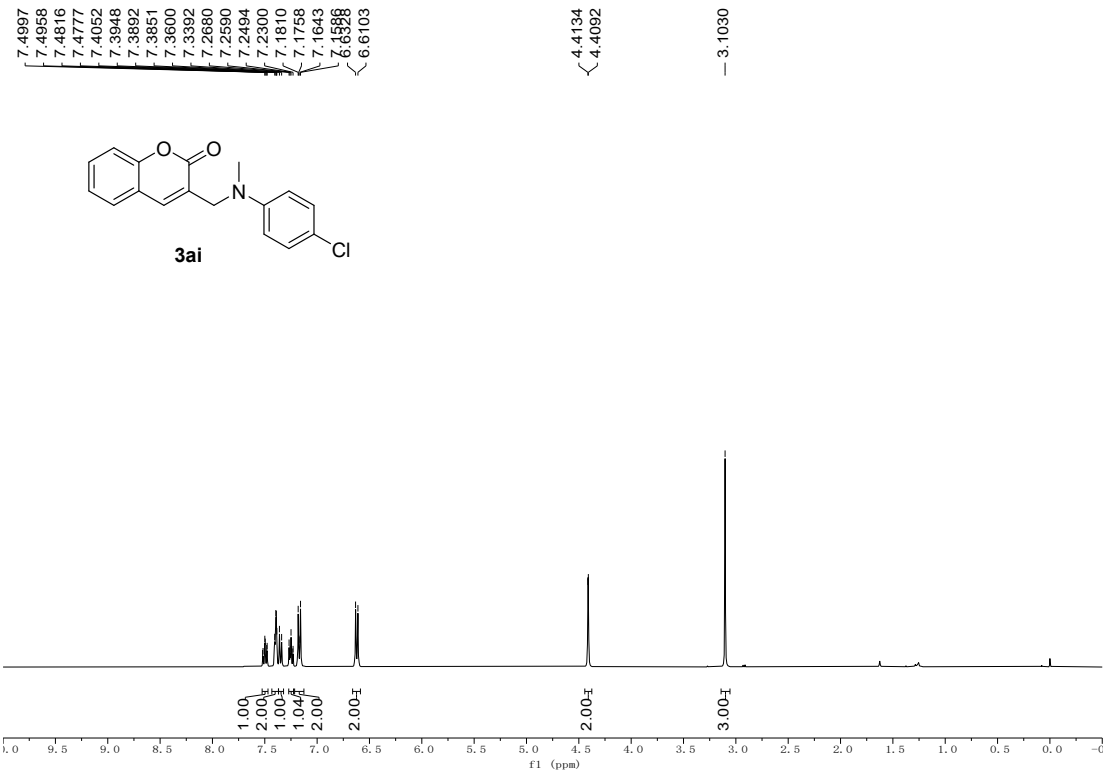
55.7870
53.5202
39.5480



3ah


f1 (ppm)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7.3892
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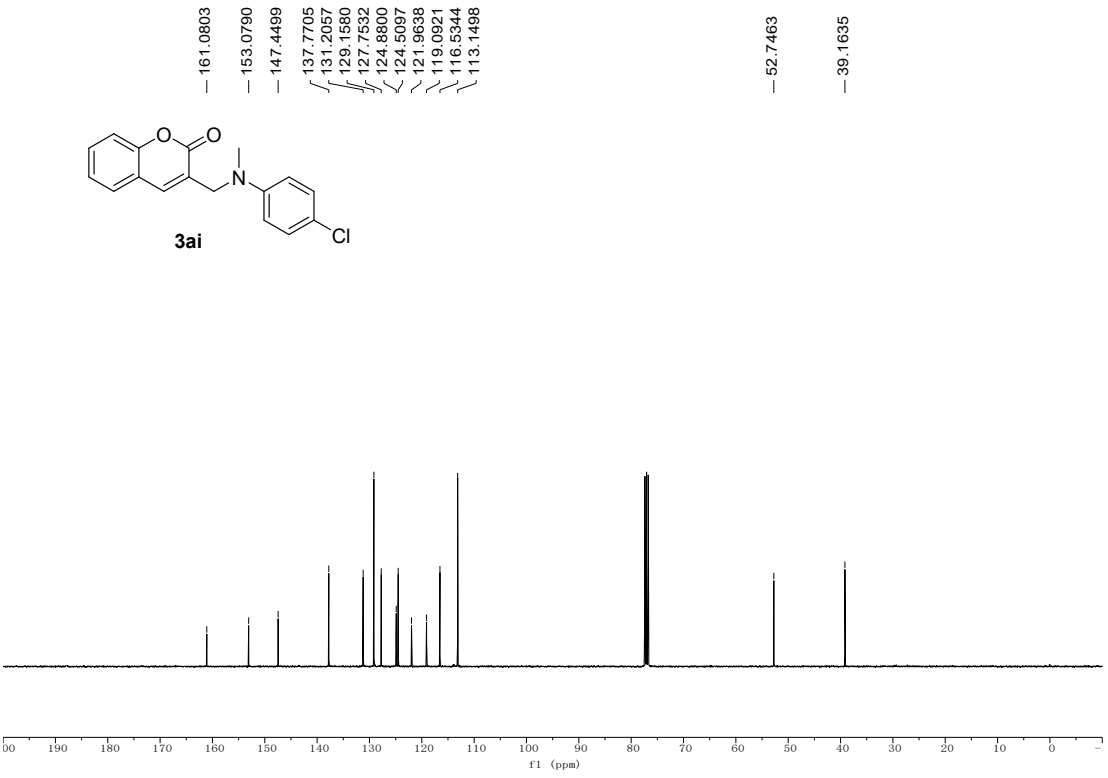
7.3600
7.3392
7.2680
7.2590
7.2494
7.2300
7.1810
7.1758
7.1643
7.1586
6.6328
6.6103
4.4134
4.4092
3.1030
O
O
N
Cl
3ai
1.00
2.00
1.00
1.04
2.00
2.00
2.00
3.00
f1 (ppm)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127.7532
124.8800
124.5097
121.9638
119.0921
116.5344
113.1498
52.7463
39.1635
O
O
N
Cl
3ai
f1 (ppm)


7.6944
7.4869
7.4671
7.4476
7.3927
7.3733
7.3348
7.3138
7.2948
7.2758
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7.0717
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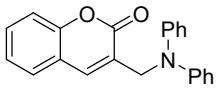
6.9791
6.9608
4.9035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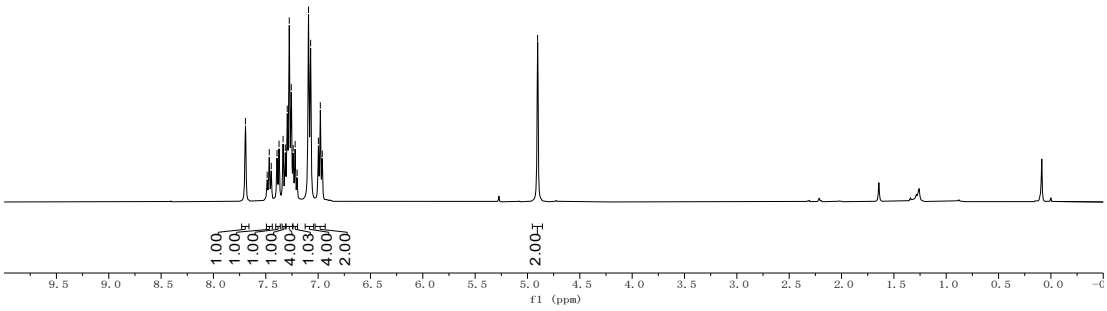
O
Ph
N
Ph

3aj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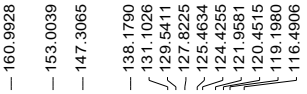
4.00
1.03
4.00
2.00
2.00
f1 (ppm)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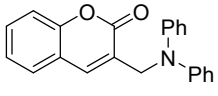
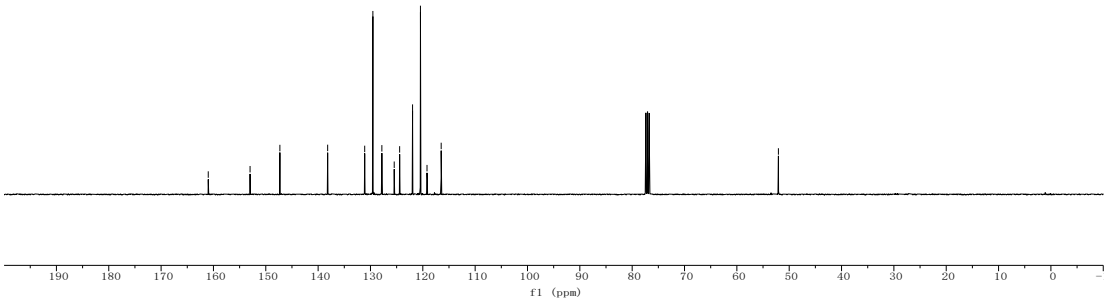
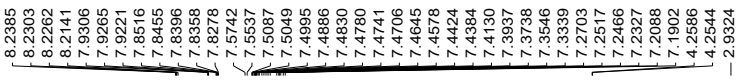
120.4515
119.1980
116.4906
52.0625


O
O
Ph
N
Ph

3aj


f1 (ppm)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7.8396
7.8358
7.8278
7.5742
7.5537
7.5087
7.5049
7.4995
7.4886
7.4830
7.4780
7.4741
7.4706
7.4645
7.4578
7.4424
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7.3738
7.3546
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7.2088
7.1902
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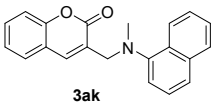
4.2544
2.9324



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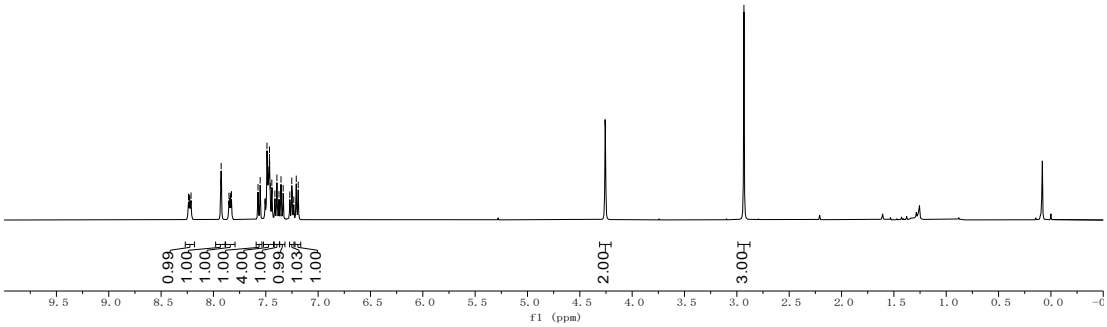
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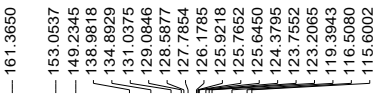
1.00
4.00
1.00
0.99
1.03
1.00
2.00
3.00
f1 (ppm)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131.0375
129.0846
128.5877
127.7854
126.1785
125.9218
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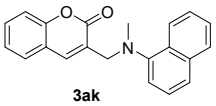
116.5080
115.6002
55.5331
42.6384



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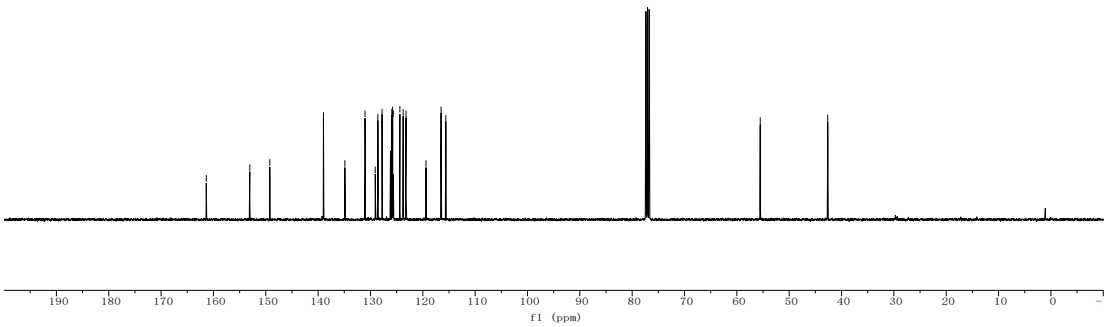
f1 (ppm)