

Supporting Information

KMnO₄/AcOH-mediated C3-selective Direct Arylation of coumarins with Arylboronic acids

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1. Screening of the reaction conditions

Table S1 The yields of 3-phenylcoumarin was affected by the amount of KMnO_4 ^a

Entry	KMnO_4 (eq.)	Yields ^b (%)
1	0.2	30
2	1.0	60
3	2.0	75
4	3.0	76
5	4.0	75

^a Reaction conditions: a solution of KMnO_4 (1.0 mmol, 158 mg) in 20 mL AcOH was stirred under reflux until the purple color of KMnO_4 turn brown (20 min). After the reaction was cooled to room temperature, coumarins **1a** (0.5 mmol, 73 mg) and phenylboronic acid **2a** (1.0 mmol, 122 mg) were added and the reaction was continued at 120 °C for 1.0 h.

^b Isolated yield.

Table S2 The yields of 3-phenylcoumarin was affected by the molar ratio of coumarin **1a** and phenylboronic acid **2a**^a

Entry	The molar ratio of 1a and 2a	Yields ^b (%)
1	2:1	35
2	1:1	65
3	1:2	75
4	1:3	72
5	1:4	70

^a Reaction conditions: a solution of KMnO_4 (1.0 mmol, 158 mg) in 20 mL AcOH was stirred under reflux until the purple color of KMnO_4 turn brown (20 min). After the reaction was cooled to room temperature, coumarins **1a** (0.5 mmol, 73 mg) and phenylboronic acid **2a** were added and the reaction was continued at 120 °C for 1.0 h.

^b Isolated yield.

2. Copies of spectra of products

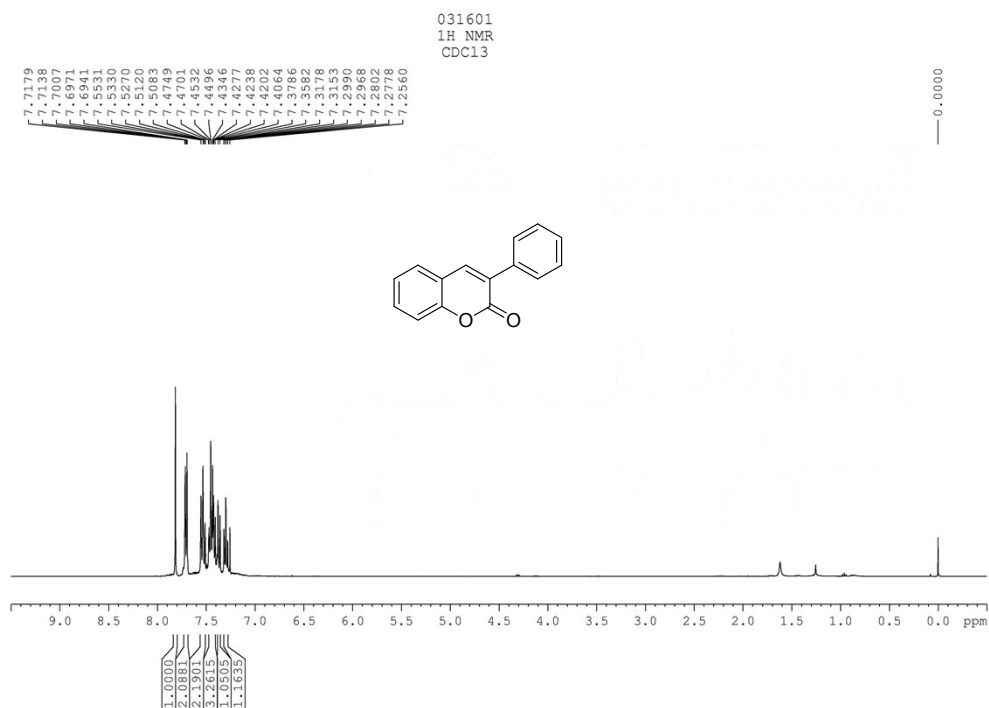


Fig. S1 ¹H NMR spectrum of **3a**

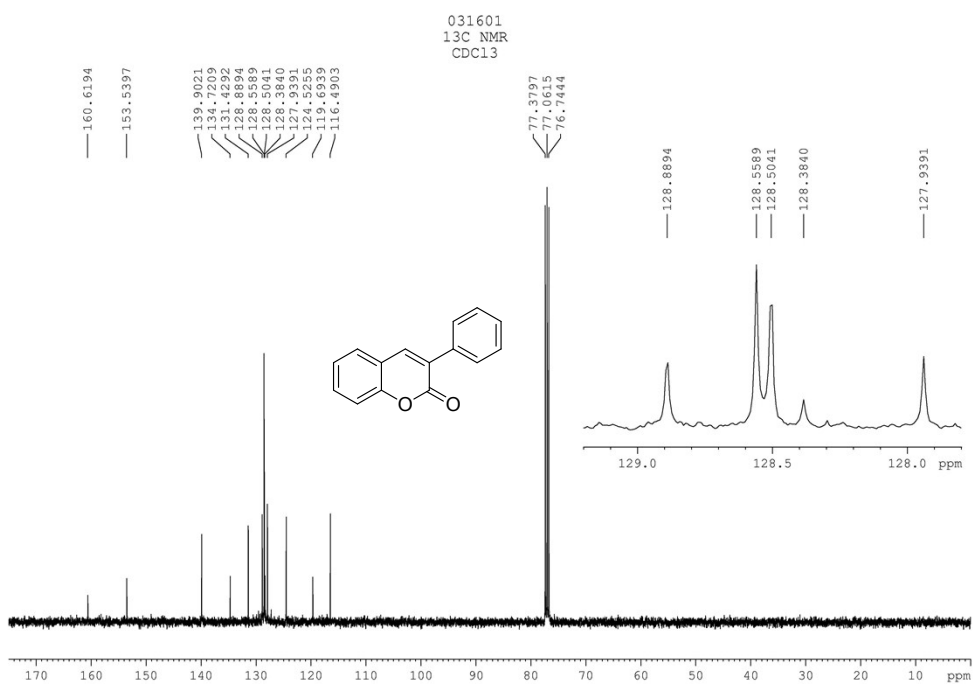


Fig. S2 ¹³C NMR spectrum of **3a**

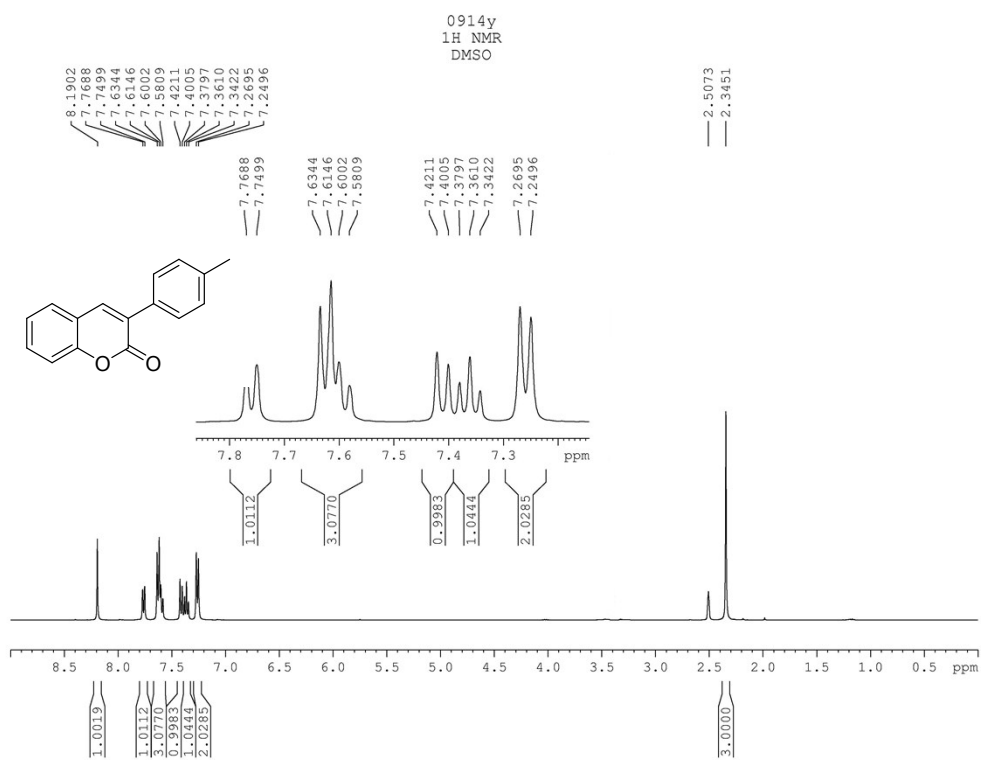


Fig. S3 ¹H NMR spectrum of 3b

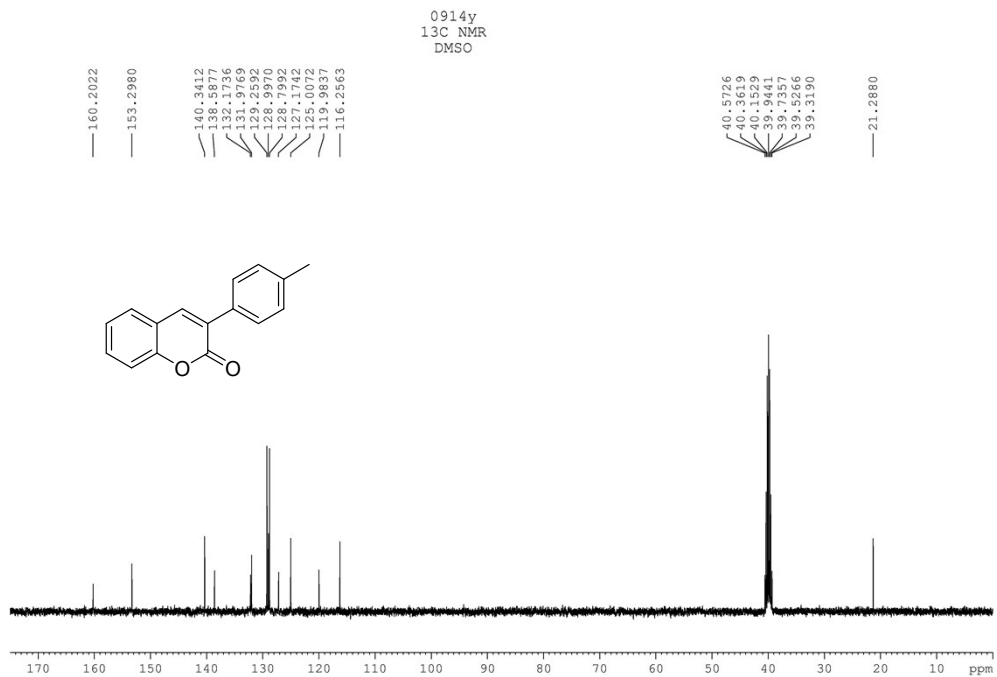


Fig. S4 ¹³C NMR spectrum of 3b

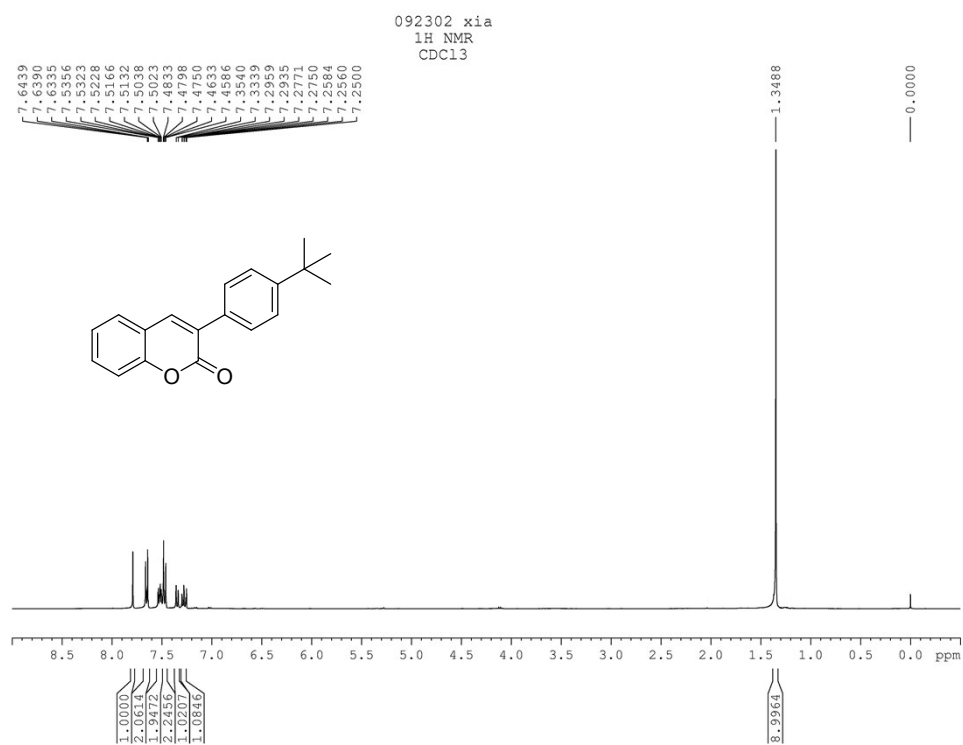


Fig. S5 ^1H NMR spectrum of **3c**

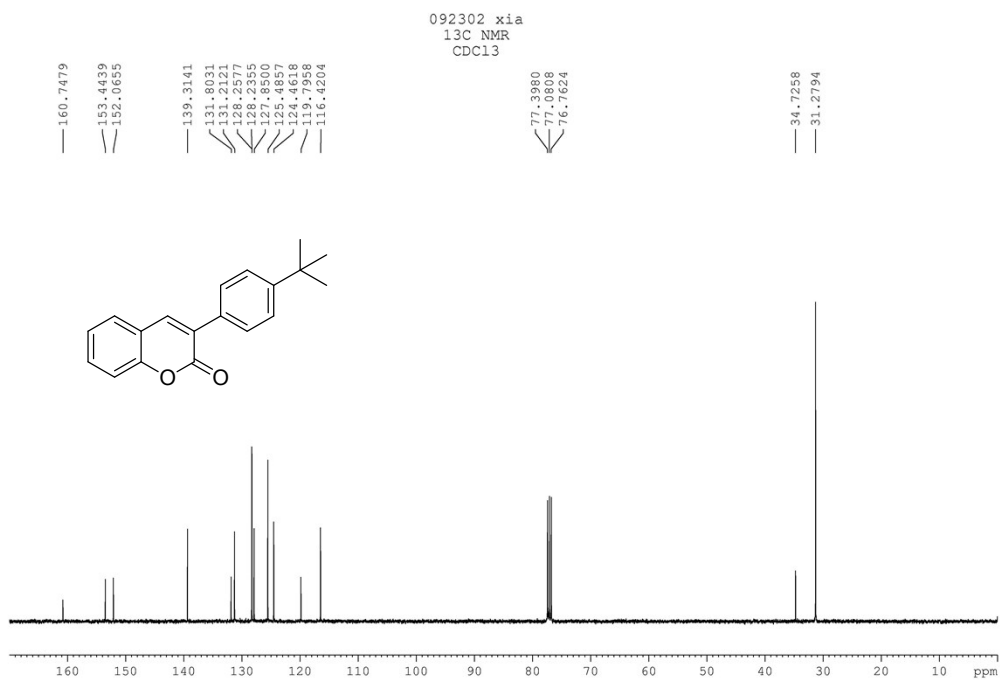


Fig. S6 ^{13}C NMR spectrum of **3c**

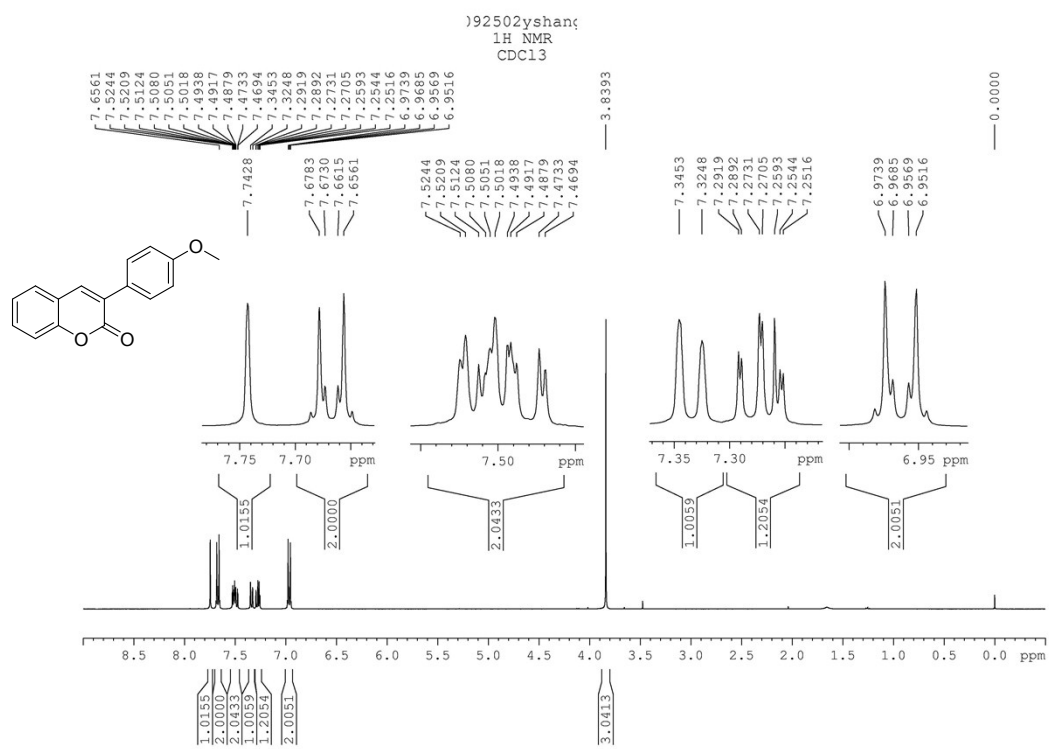


Fig. S7 ¹H NMR spectrum of 3d

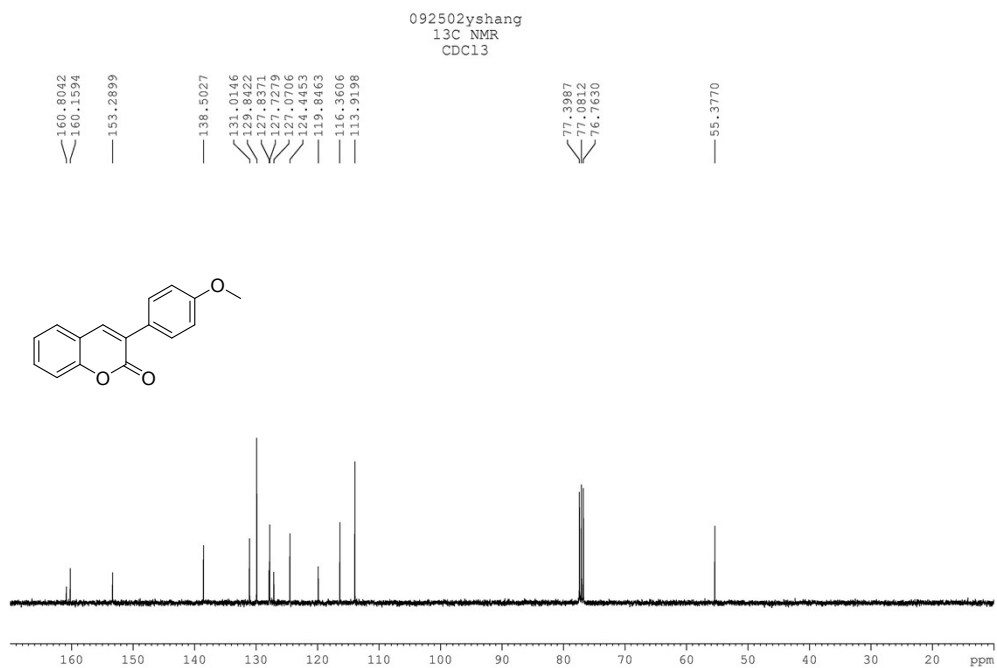


Fig. S8 ¹³C NMR spectrum of 3d

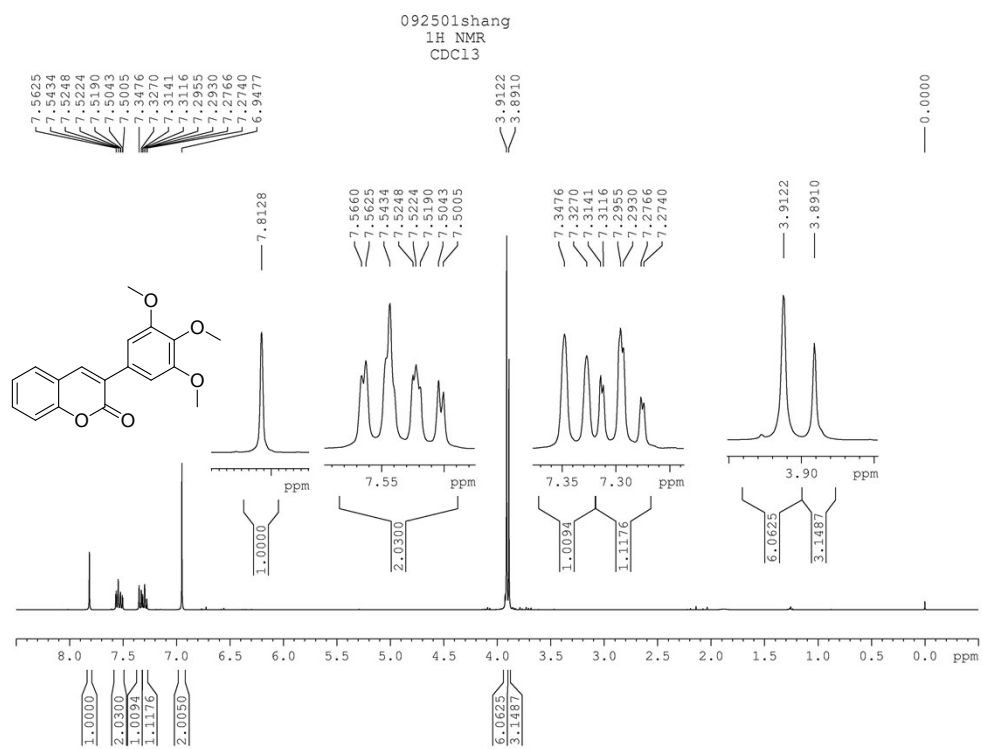


Fig. S9 ¹H NMR spectrum of **3e**

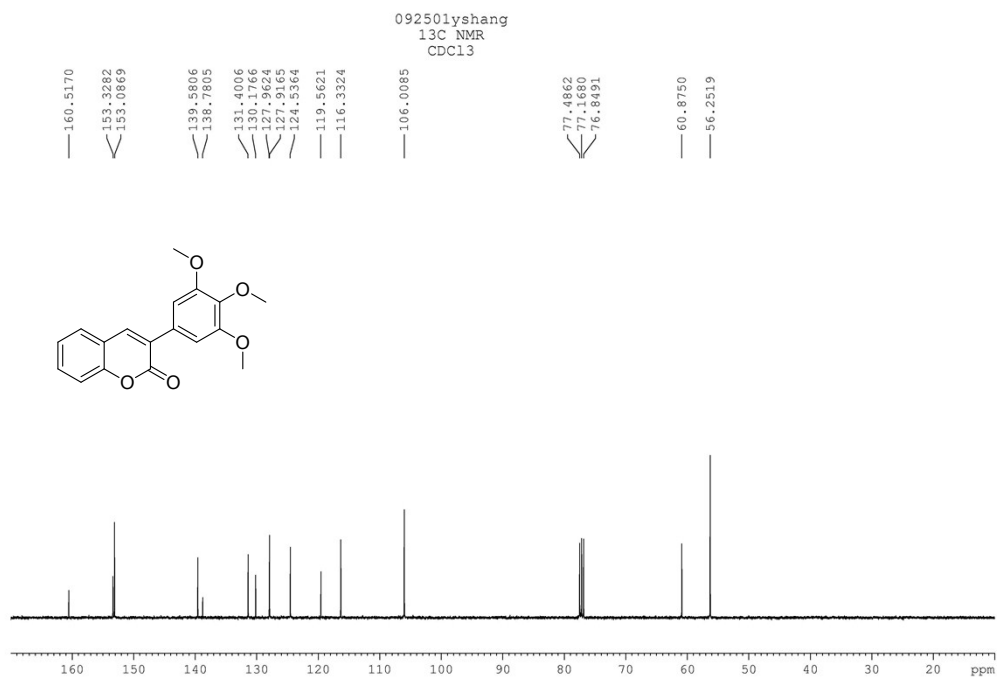


Fig. S10 ¹³C NMR spectrum of **3e**

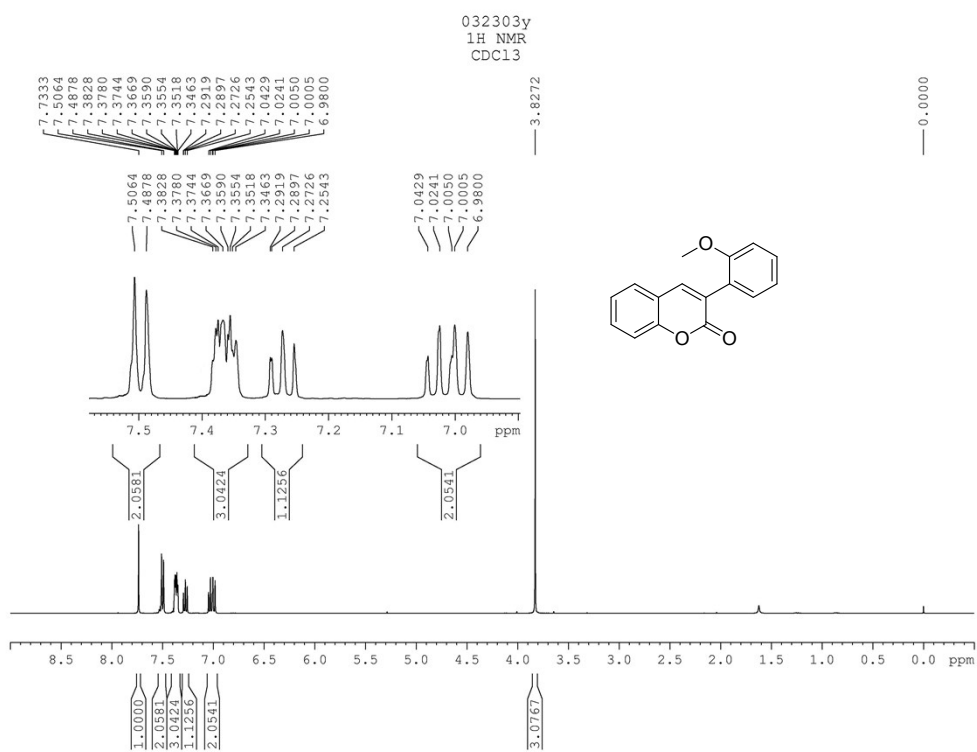


Fig. S11 ¹H NMR spectrum of 3f

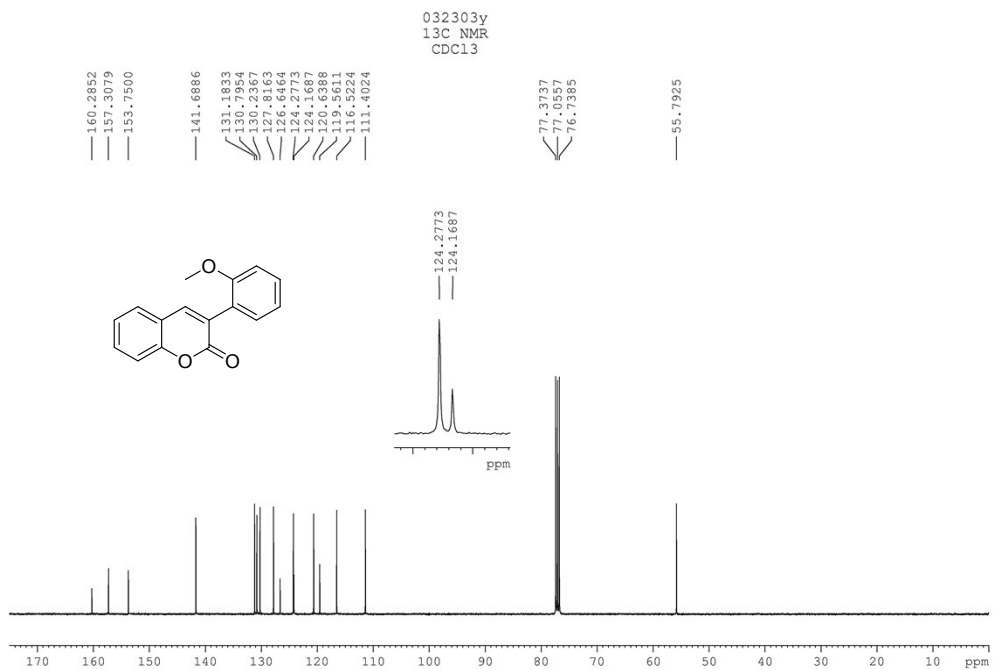


Fig. S12 ¹³C NMR spectrum of 3f

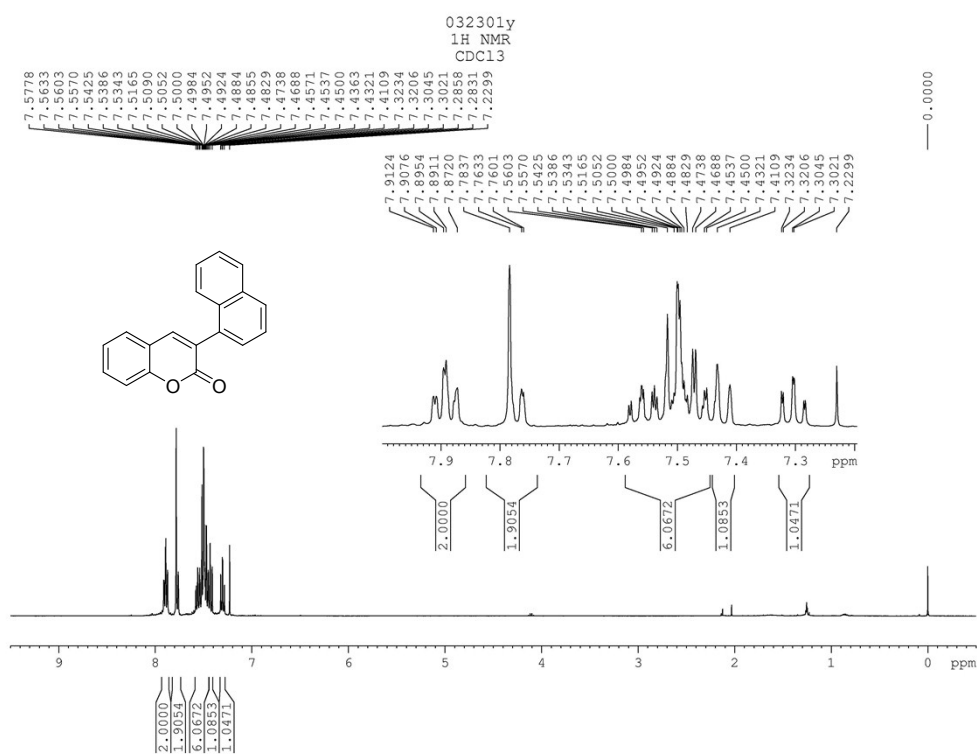


Fig. S13 ¹H NMR spectrum of 3g

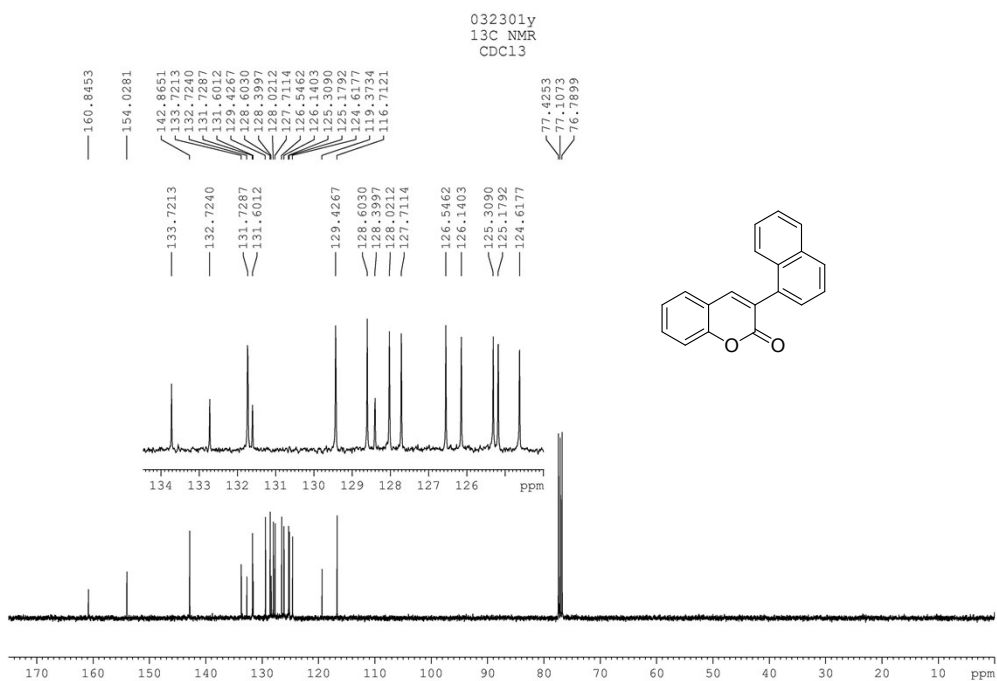


Fig. S14 ¹³C NMR spectrum of 3g

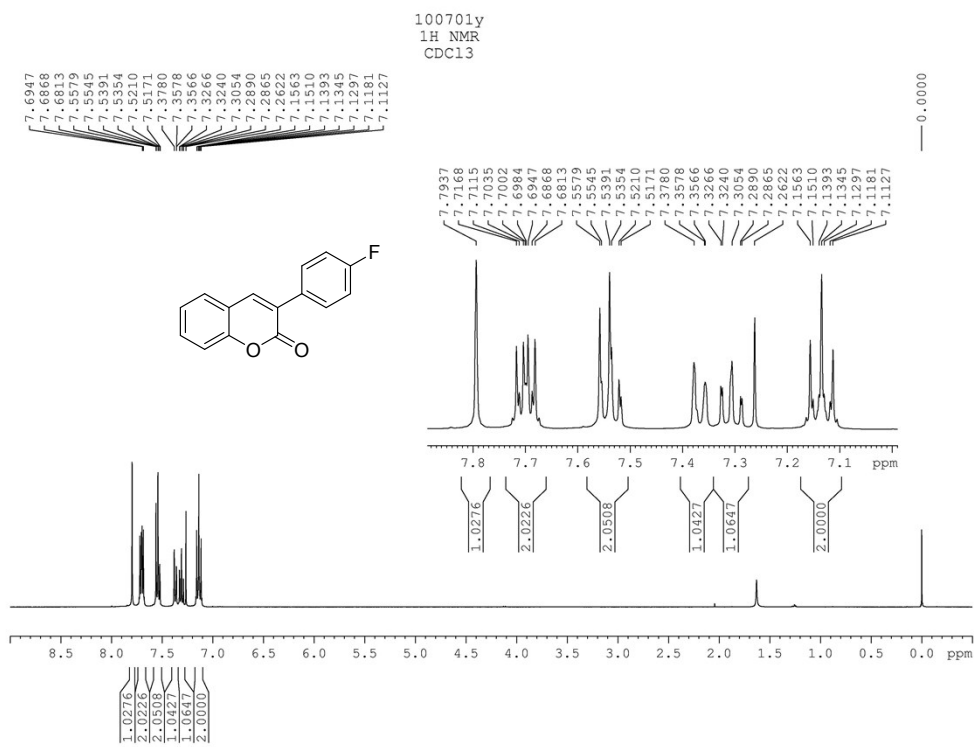


Fig. S15 ^1H NMR spectrum of 3h

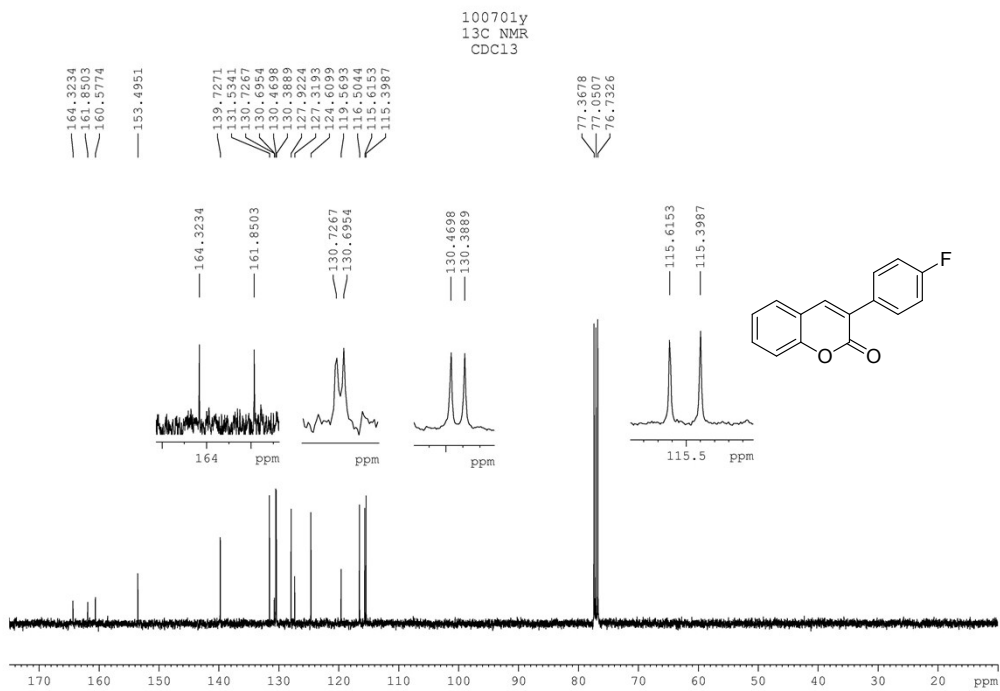


Fig. S16 ^{13}C NMR spectrum of 3h

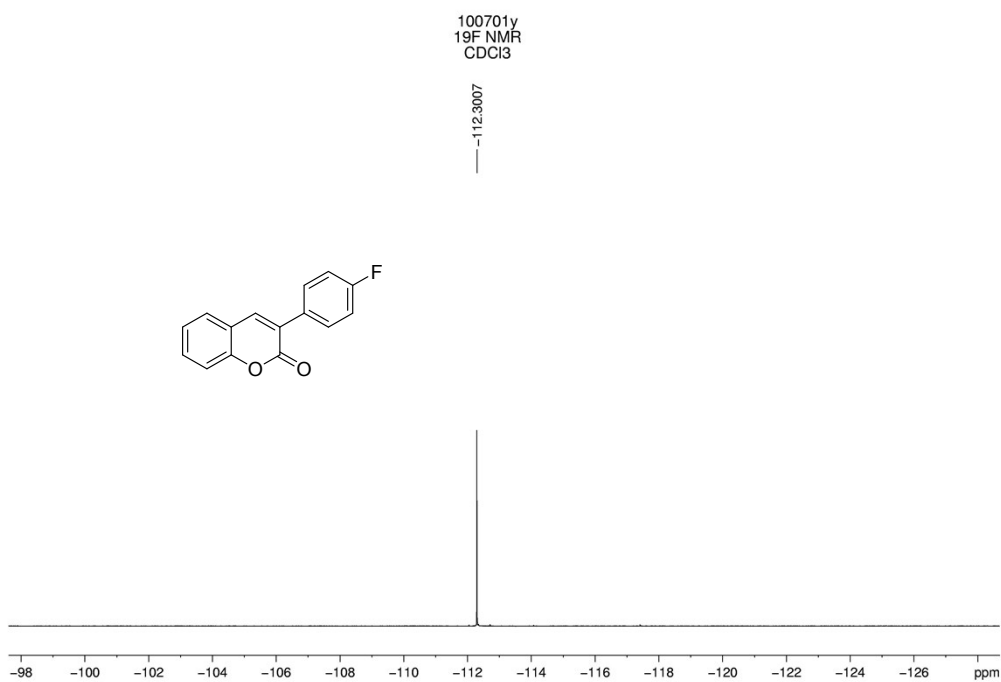


Fig. S17 ¹⁹F NMR spectrum of 3h

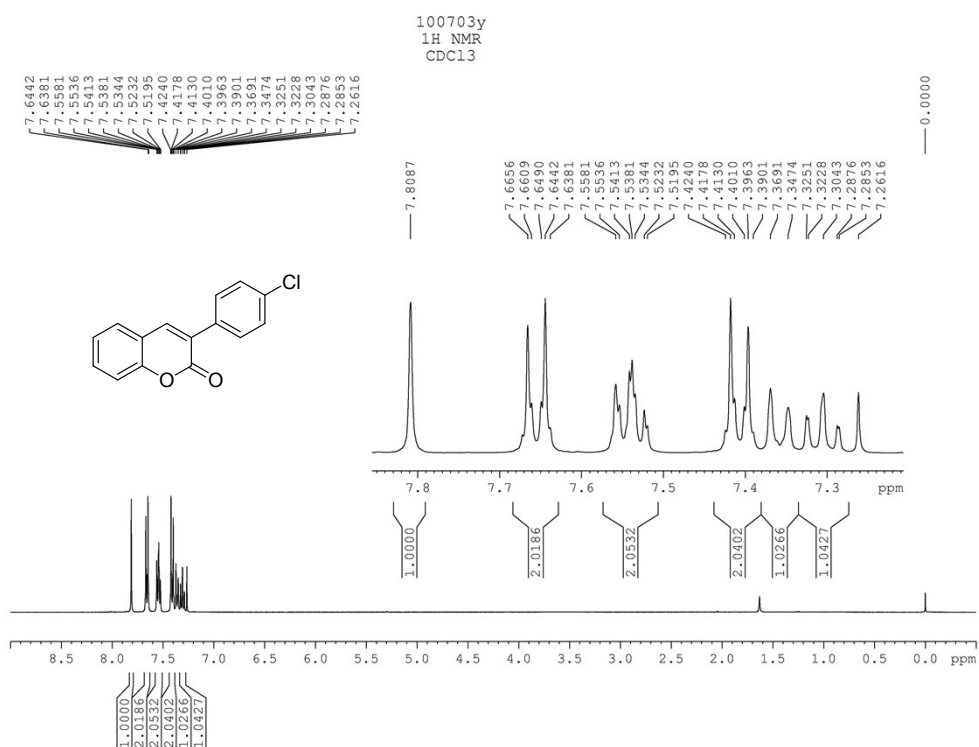


Fig. S18 ¹H NMR spectrum of 3i

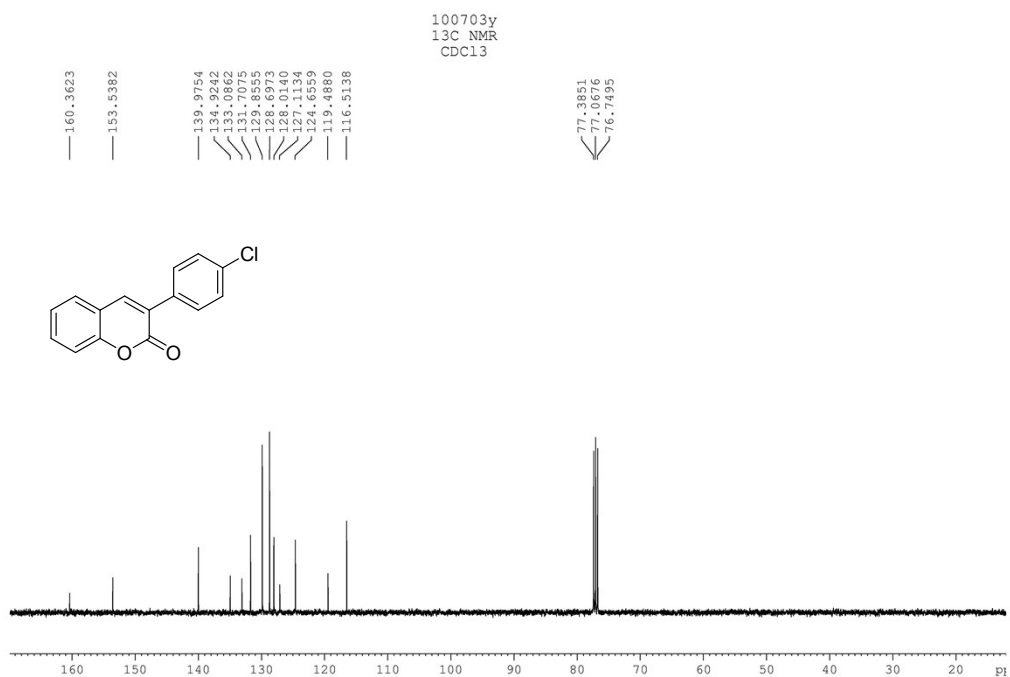


Fig. S19 ¹³C NMR spectrum of **3i**

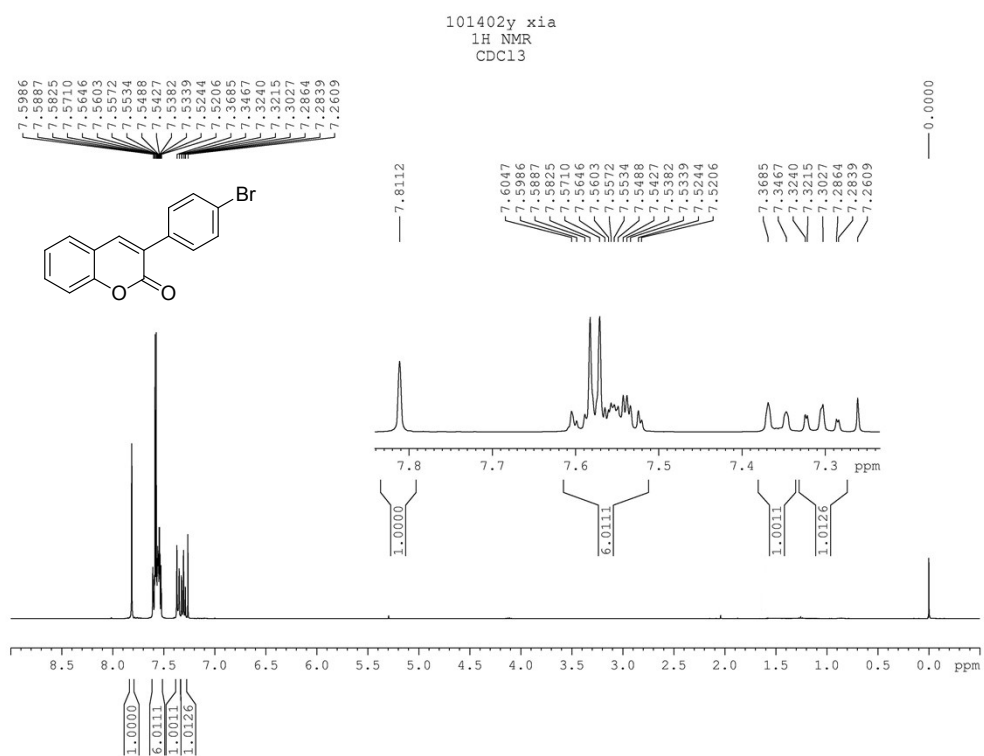


Fig. S20 ¹H NMR spectrum of **3j**

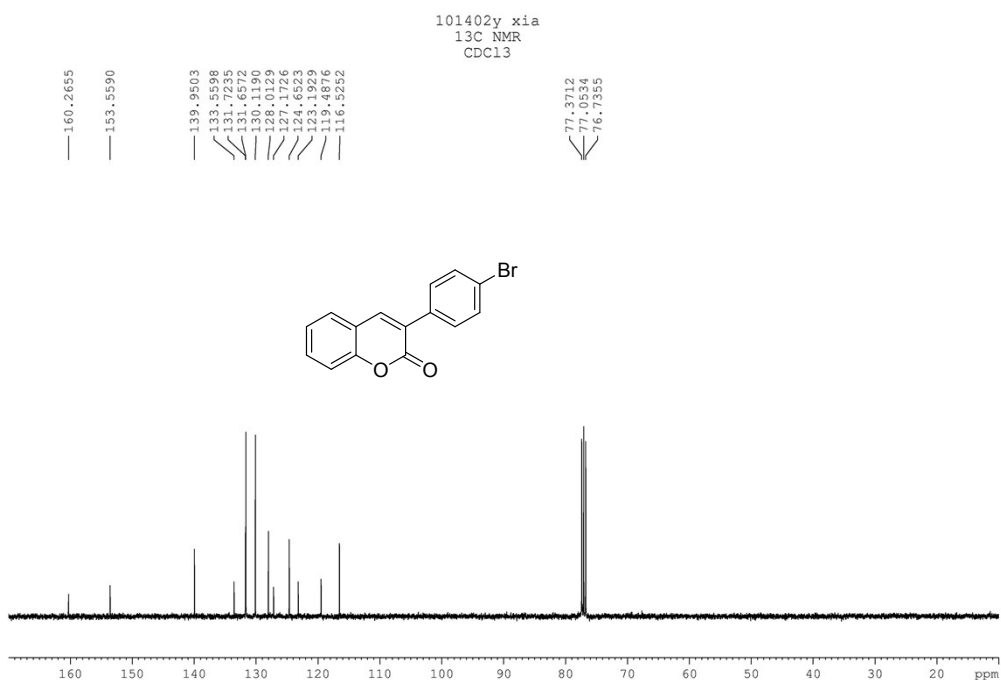


Fig. S21 ¹³C NMR spectrum of 3j

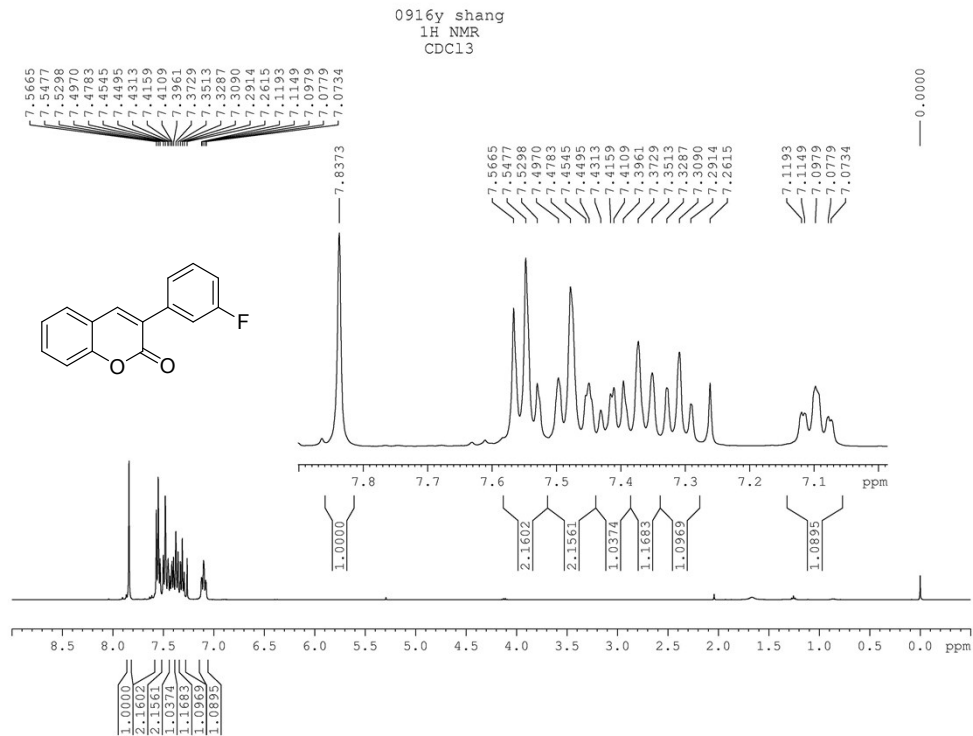


Fig. S22 ¹H NMR spectrum of 3k

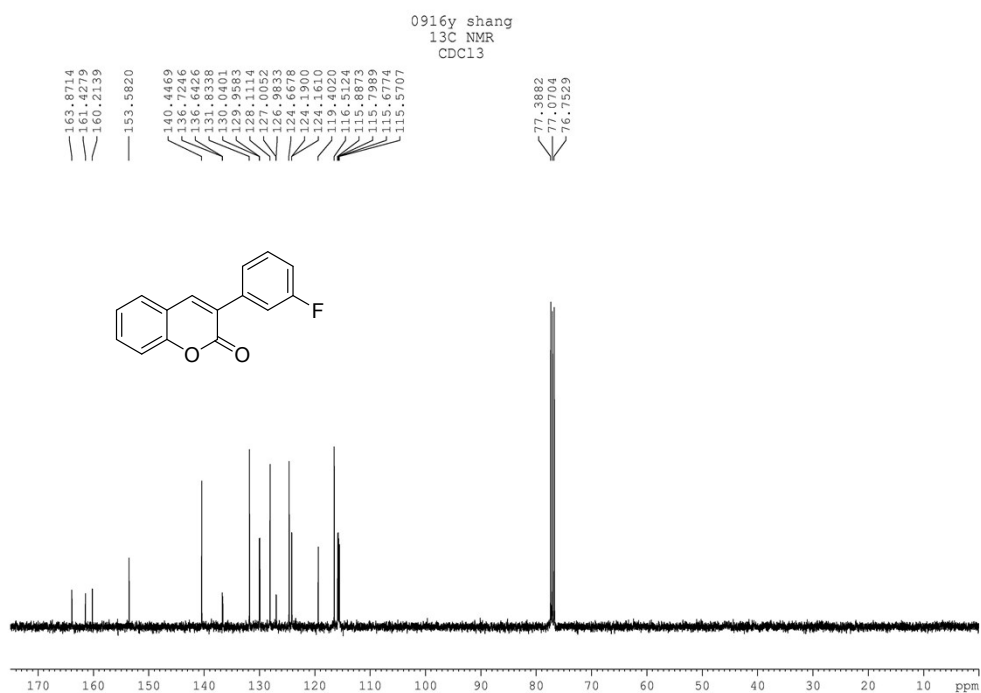


Fig. S23 ¹³C NMR spectrum of 3k

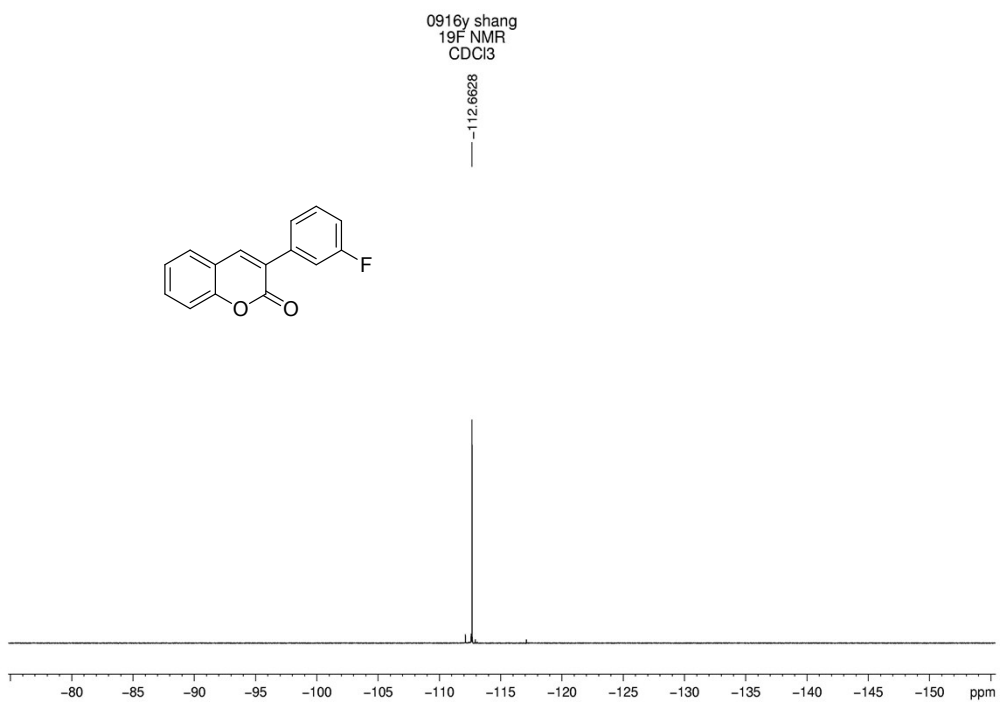


Fig. S24 ¹⁹F NMR spectrum of 3k

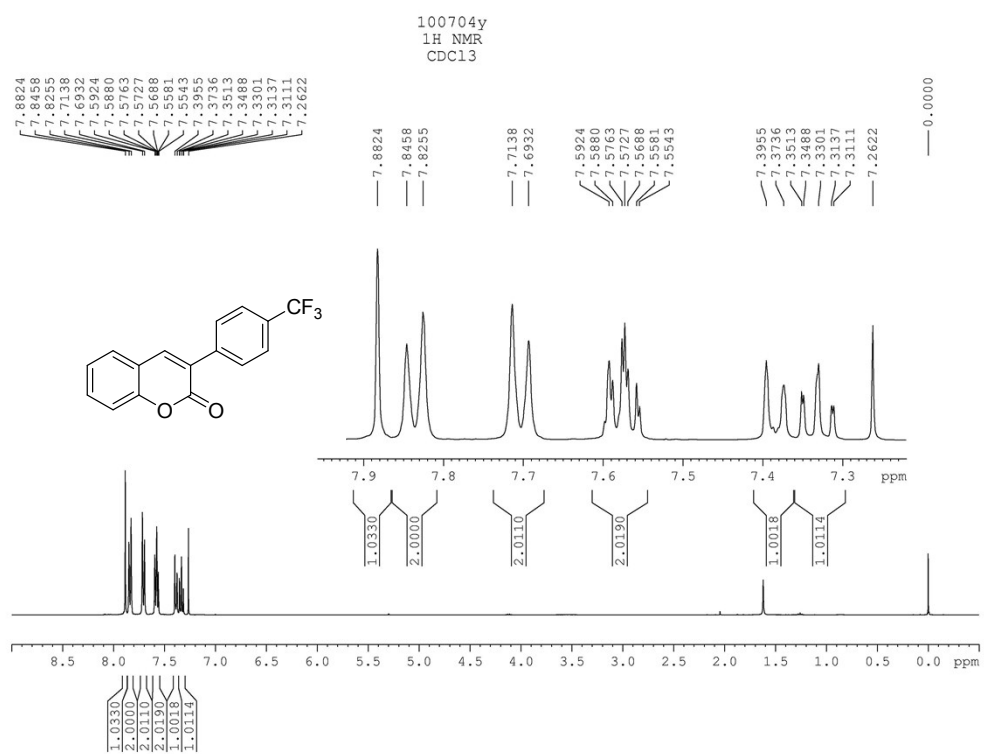


Fig. S25 ¹H NMR spectrum of 3I

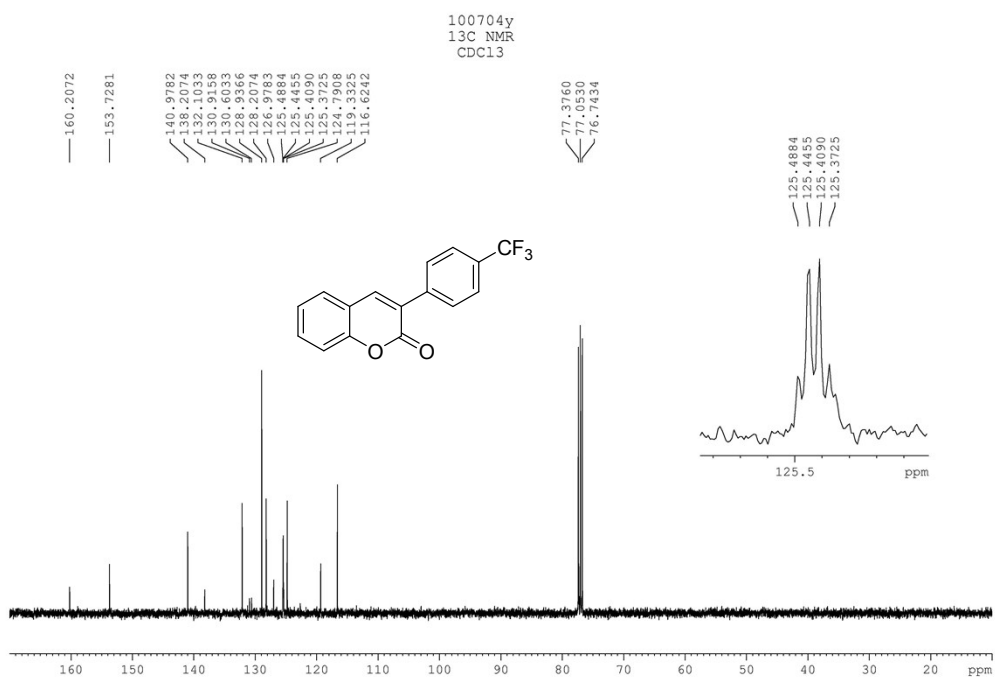


Fig. S26 ¹³C NMR spectrum of 3I

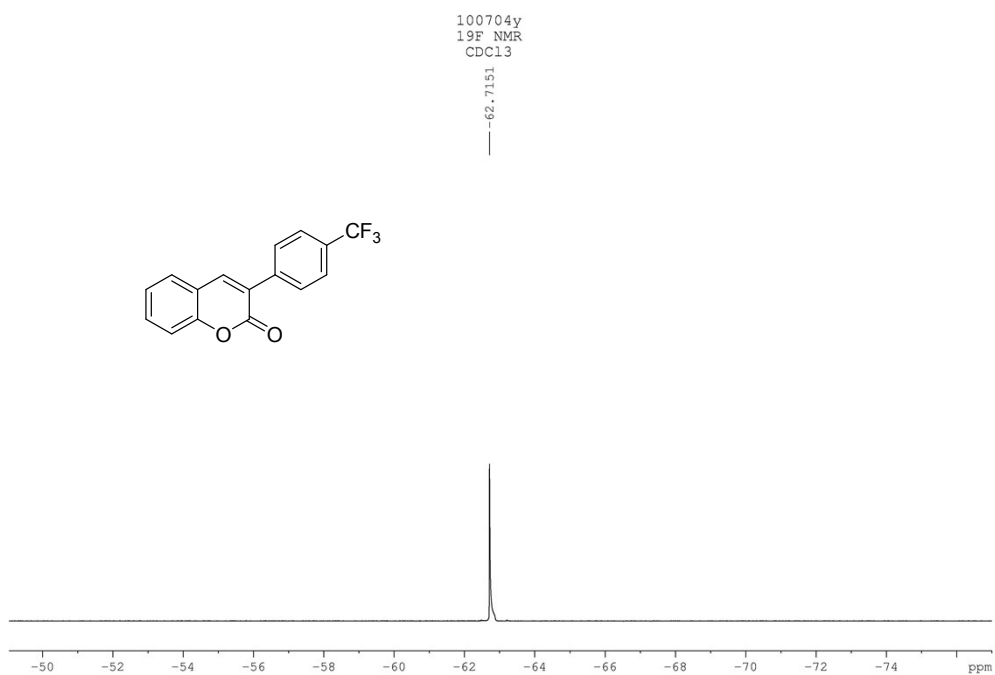


Fig. S27 ¹⁹F NMR spectrum of **31**

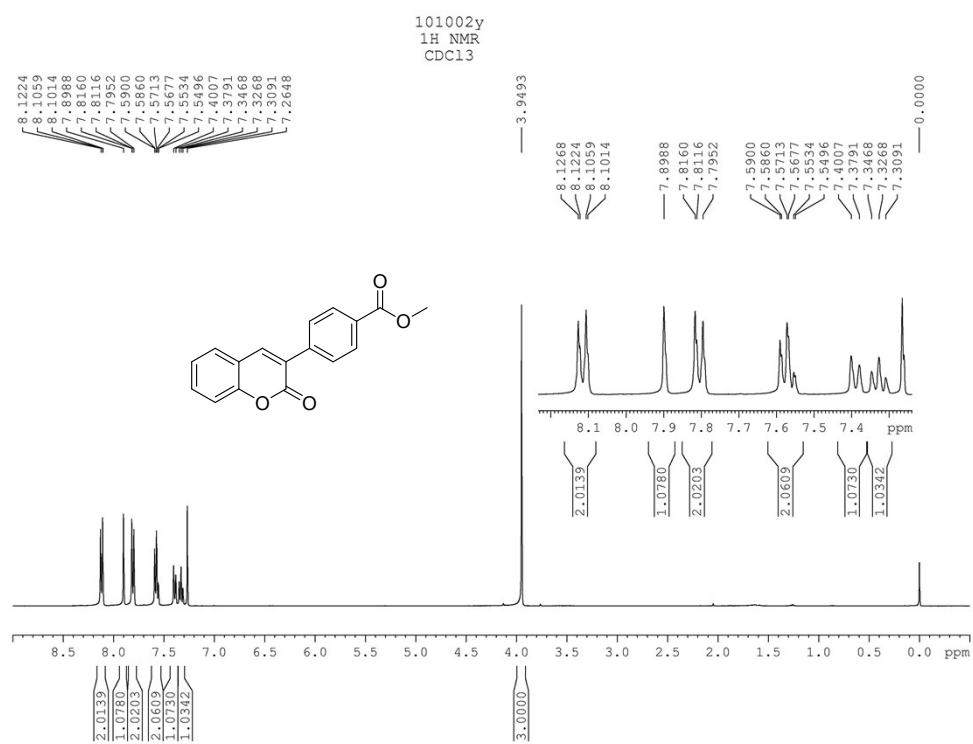


Fig. S28 ¹H NMR spectrum of **3m**

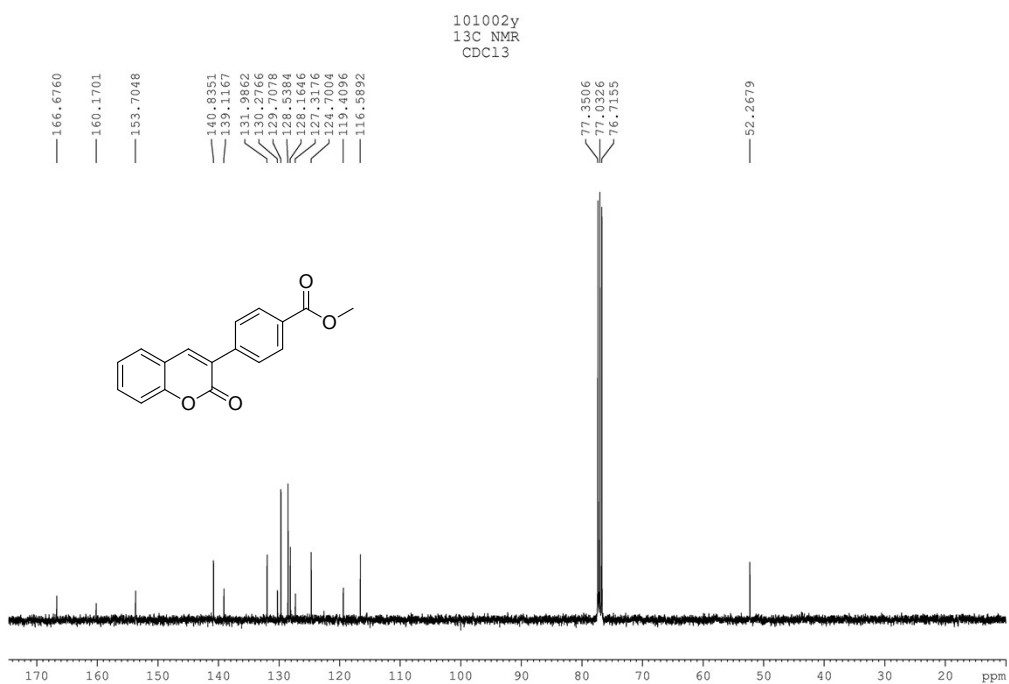


Fig. S29 ¹³C NMR spectrum of 3m

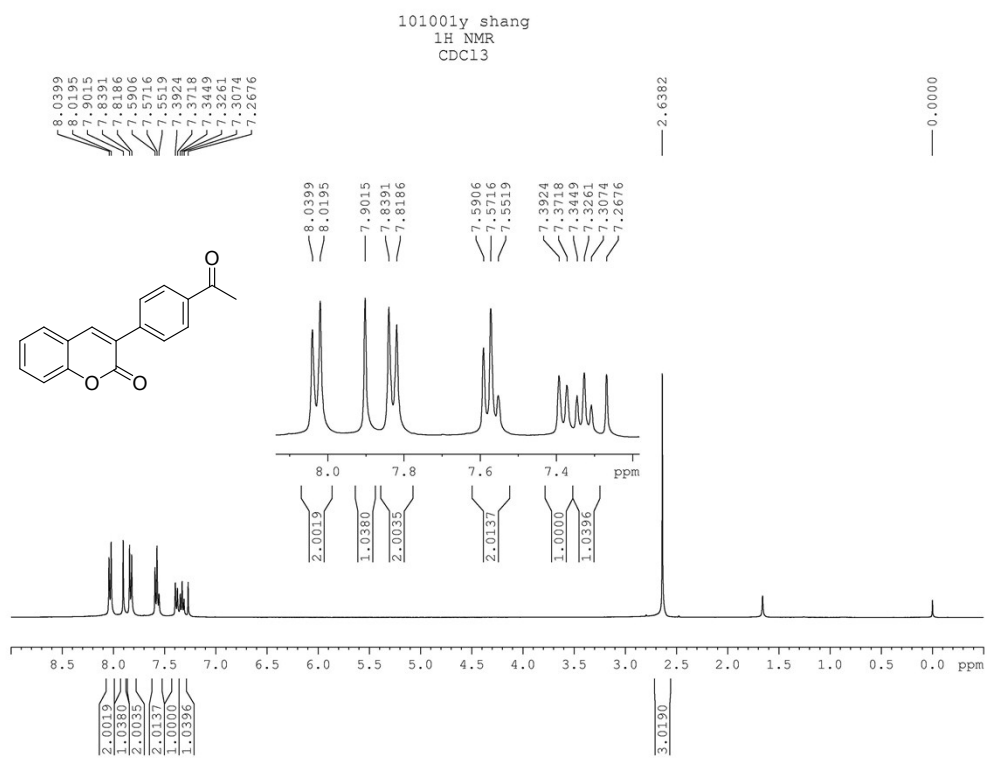


Fig. S30 ¹H NMR spectrum of 3n

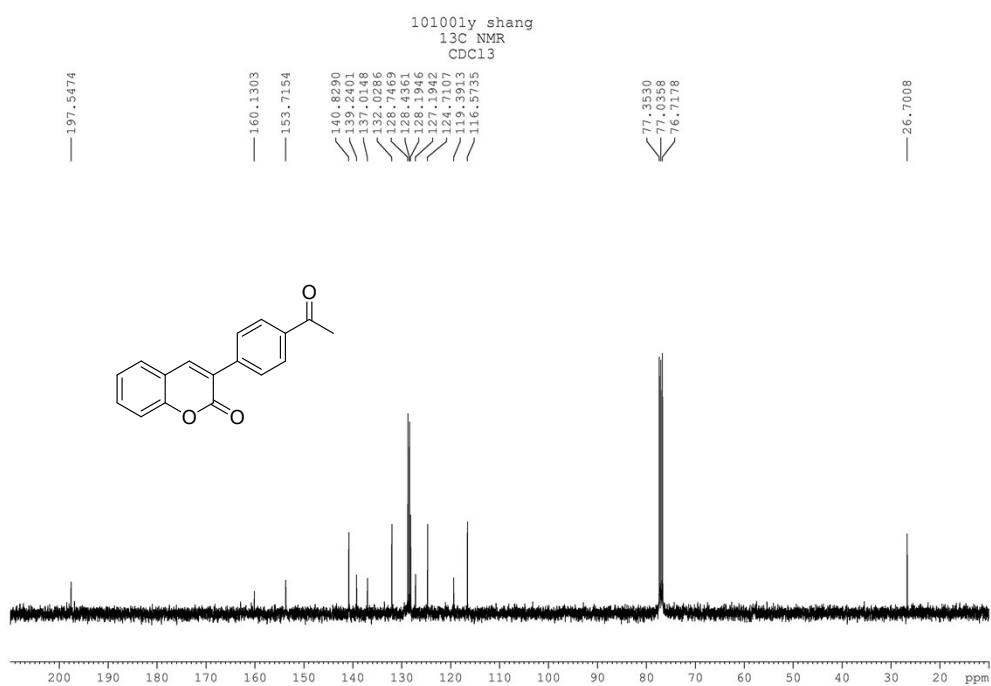


Fig. S31 ¹³C NMR spectrum of 3n

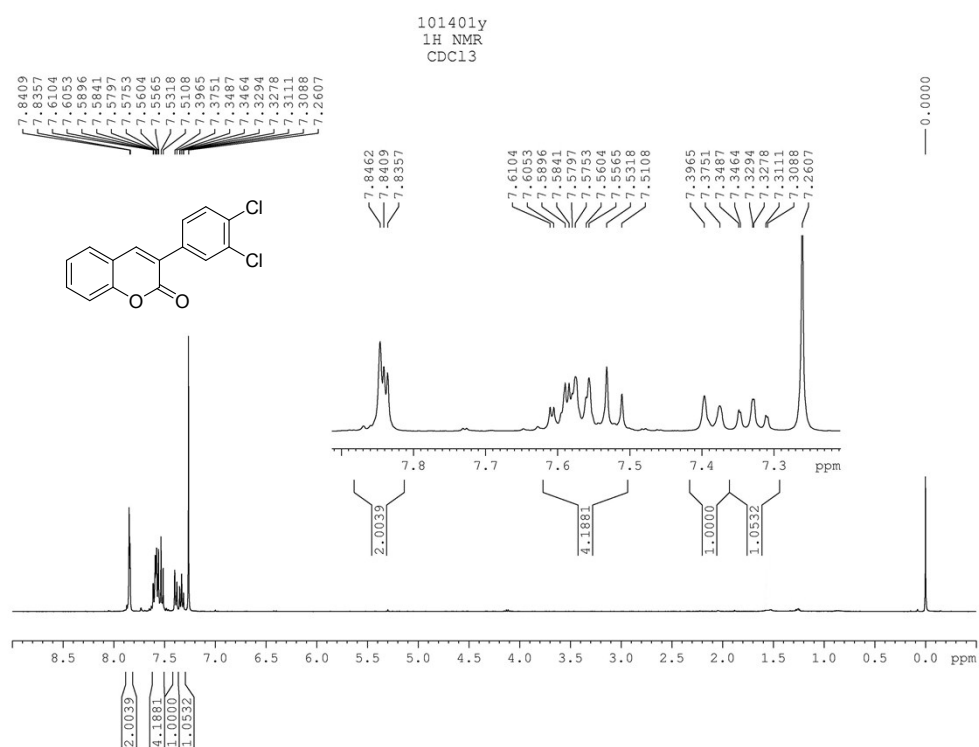


Fig. S32 ¹H NMR spectrum of 3o

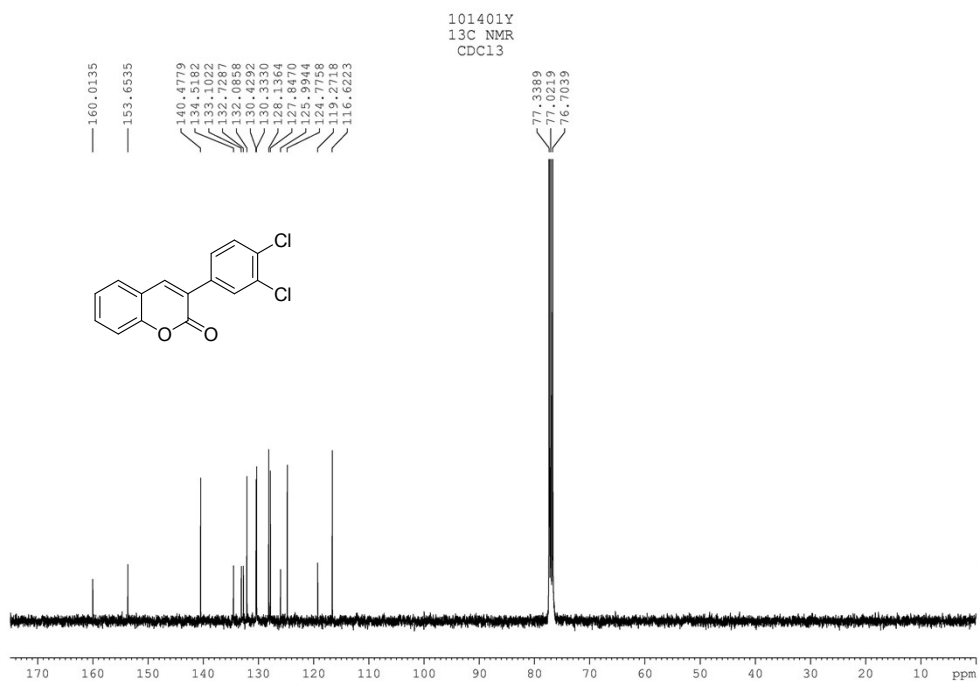


Fig. S33 ¹³C NMR spectrum of **3o**

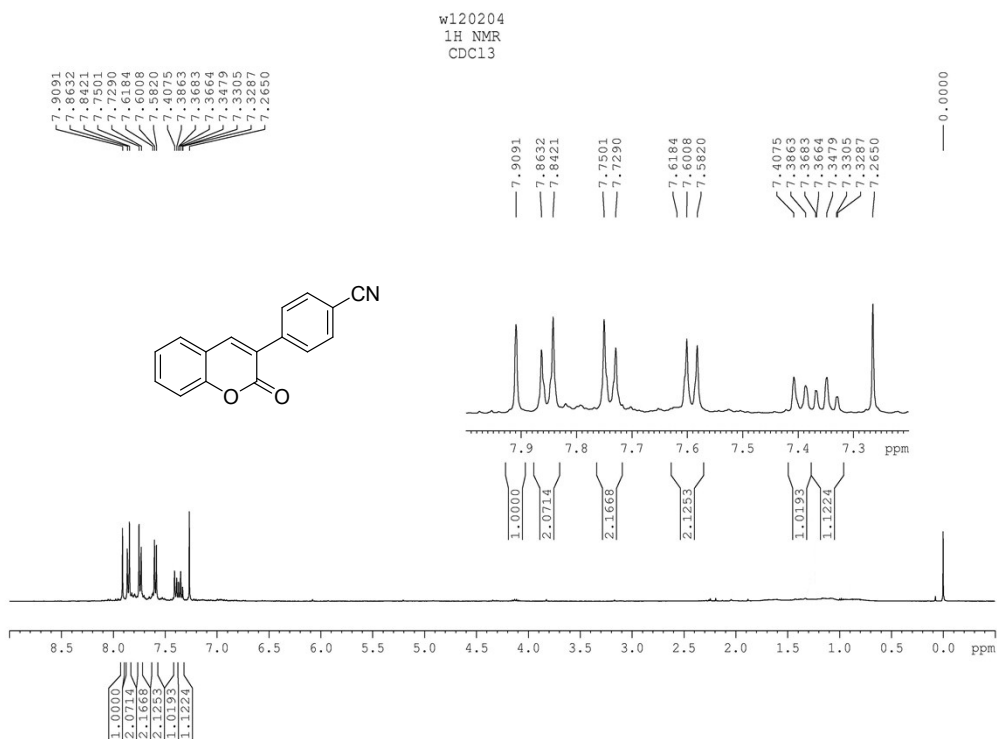


Fig. S34 ¹H NMR spectrum of **3p**

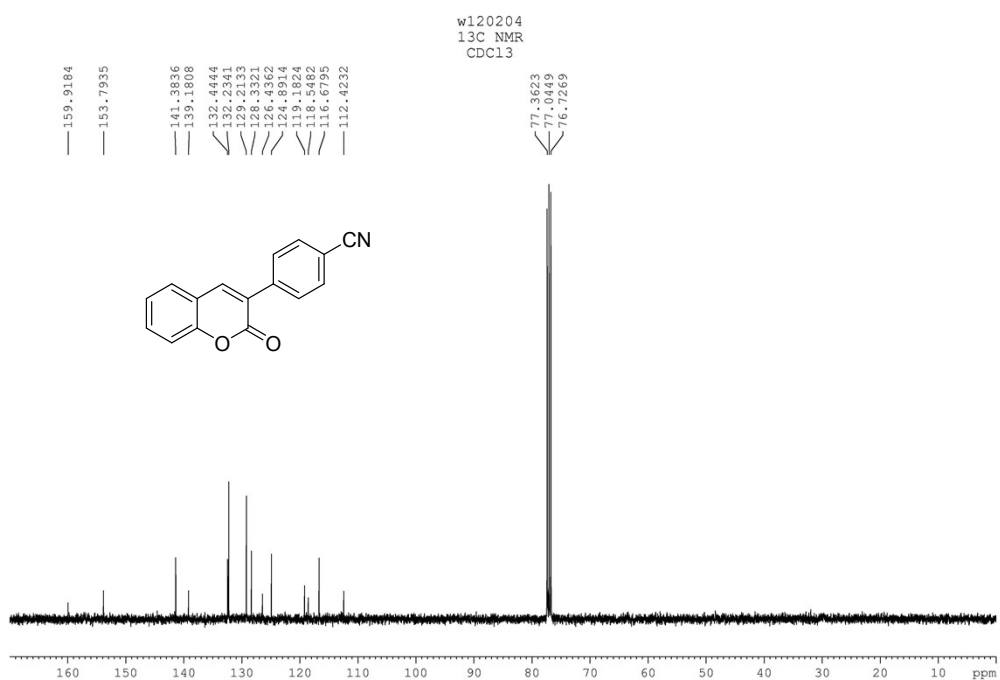


Fig. S35 ¹³C NMR spectrum of 3p

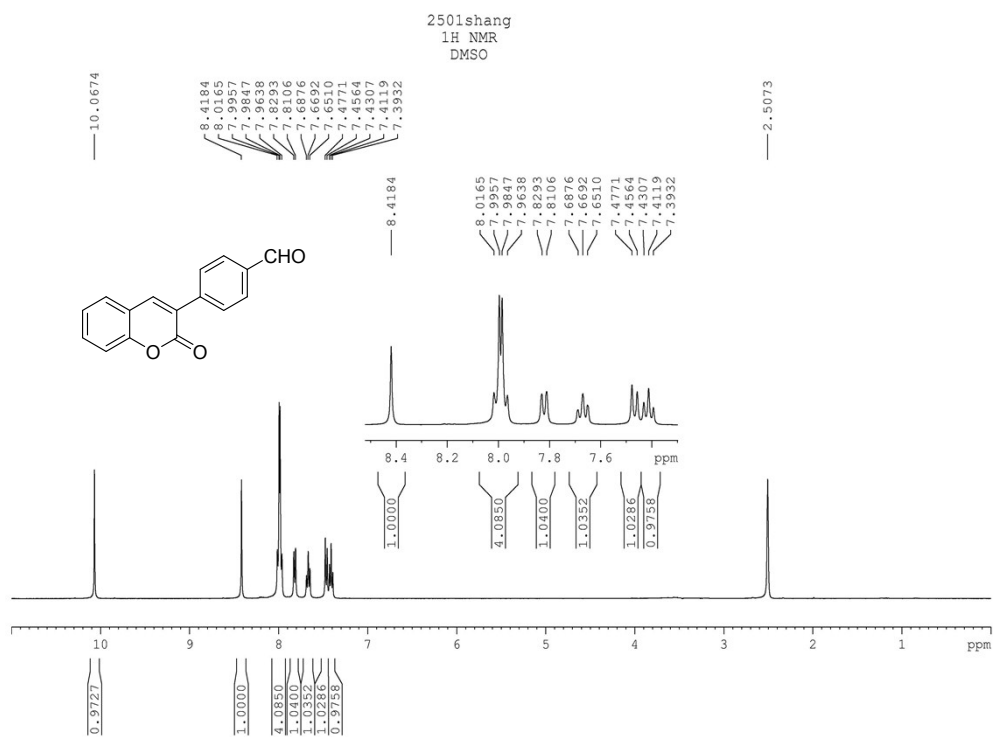


Fig. S36 ¹H NMR spectrum of 3q

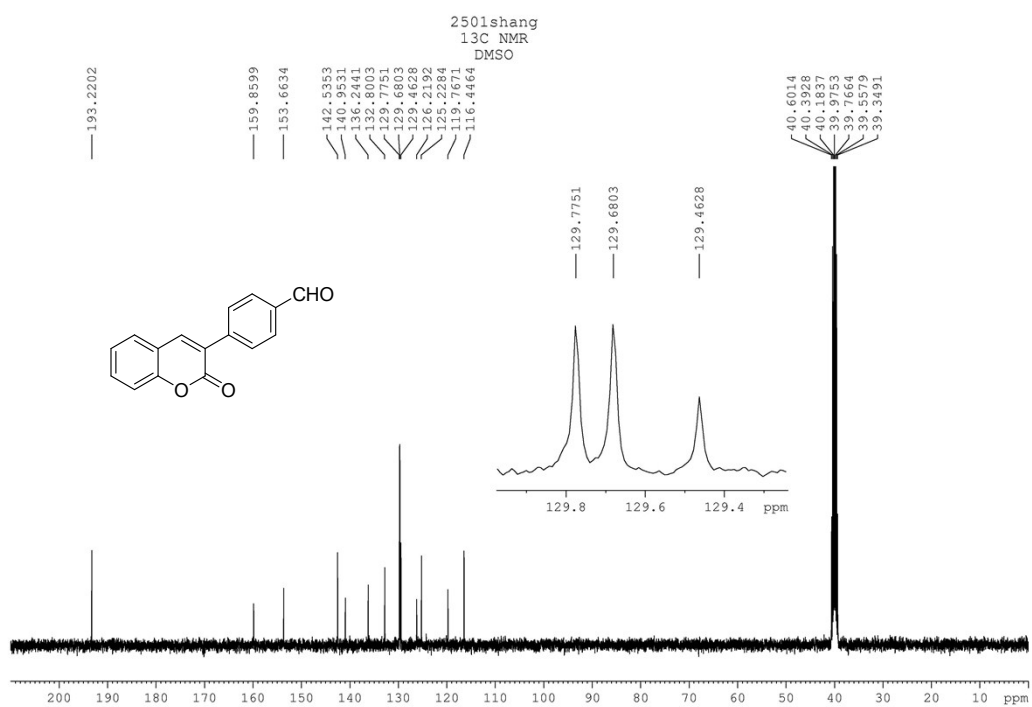


Fig. S37 ¹³C NMR spectrum of 3q

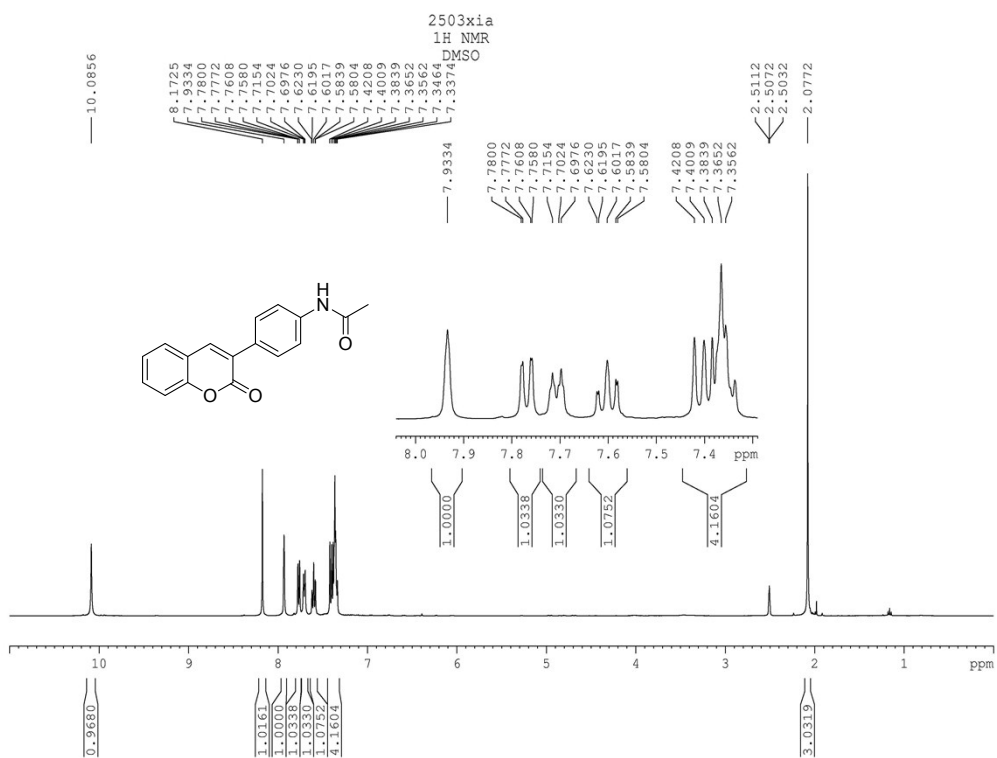


Fig. S38 ¹H NMR spectrum of 3r

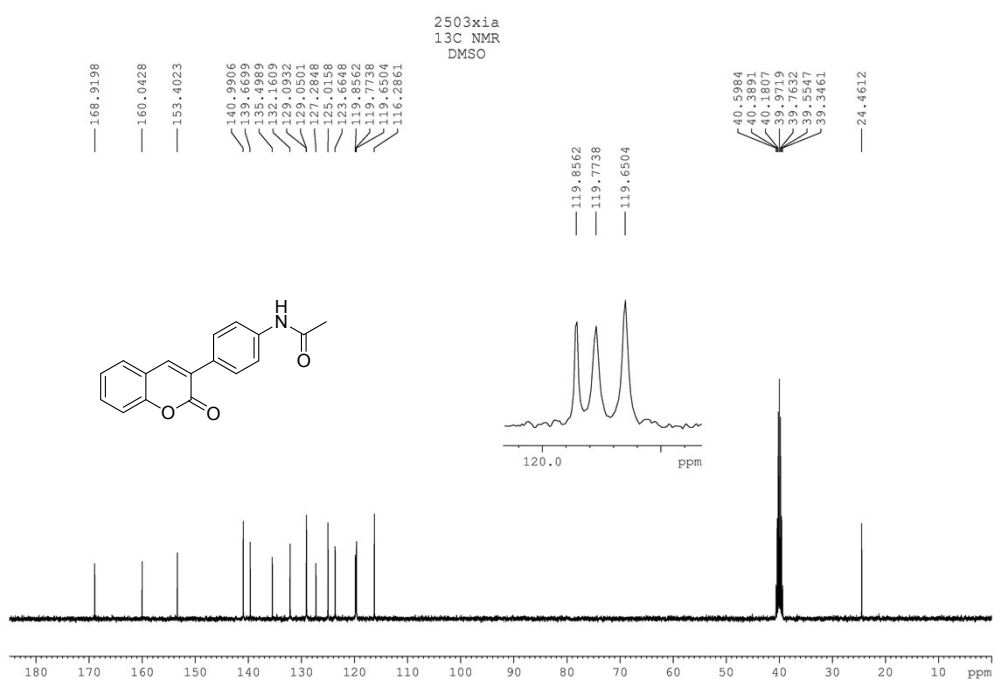


Fig. S39 ¹³C NMR spectrum of 3r

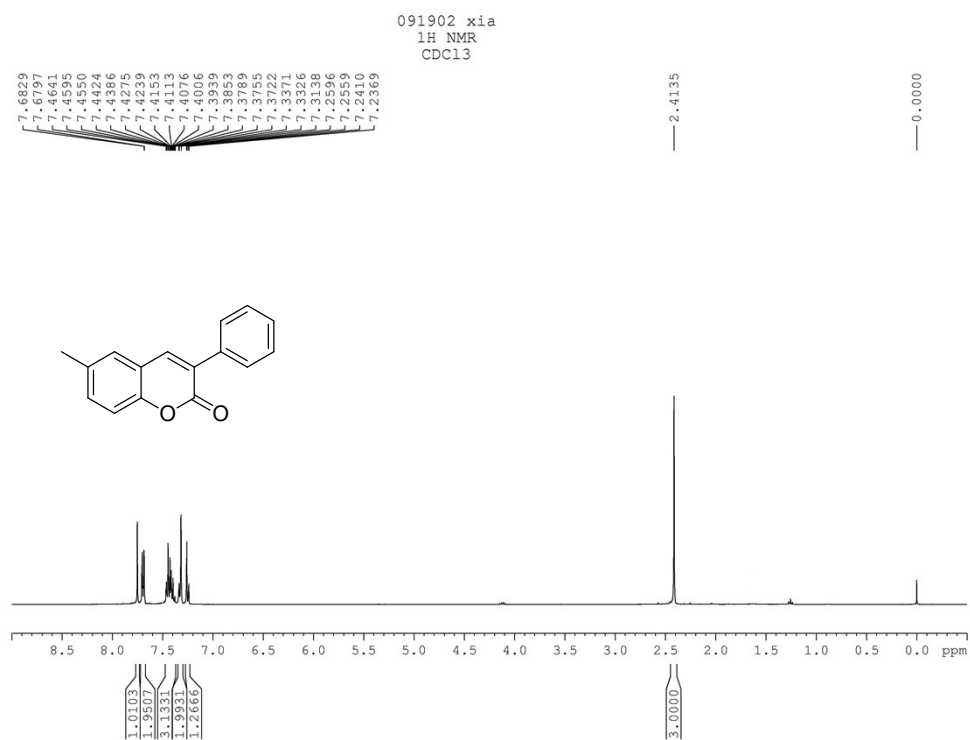


Fig. S40 ¹H NMR spectrum of 3s

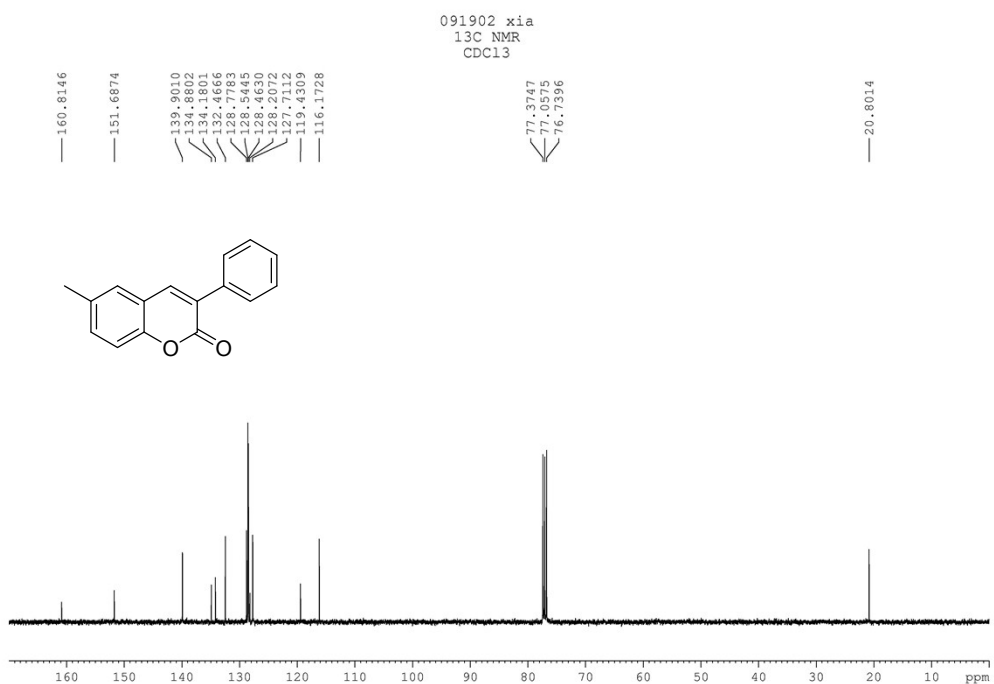


Fig. S41 ¹³C NMR spectrum of 3s

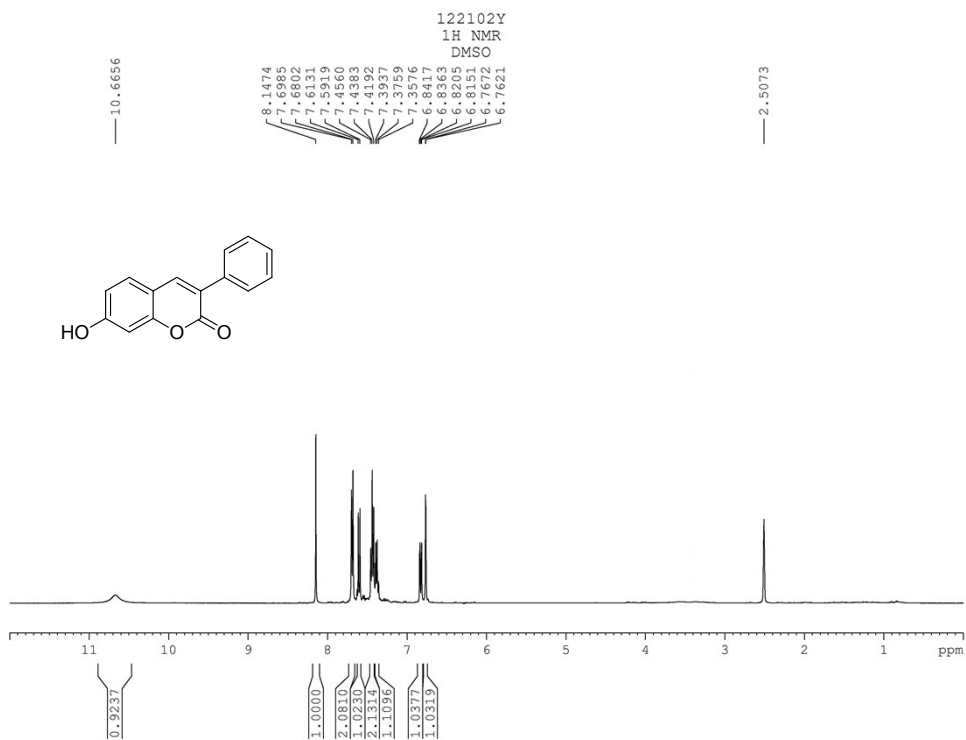


Fig. S42 ¹H NMR spectrum of 3t

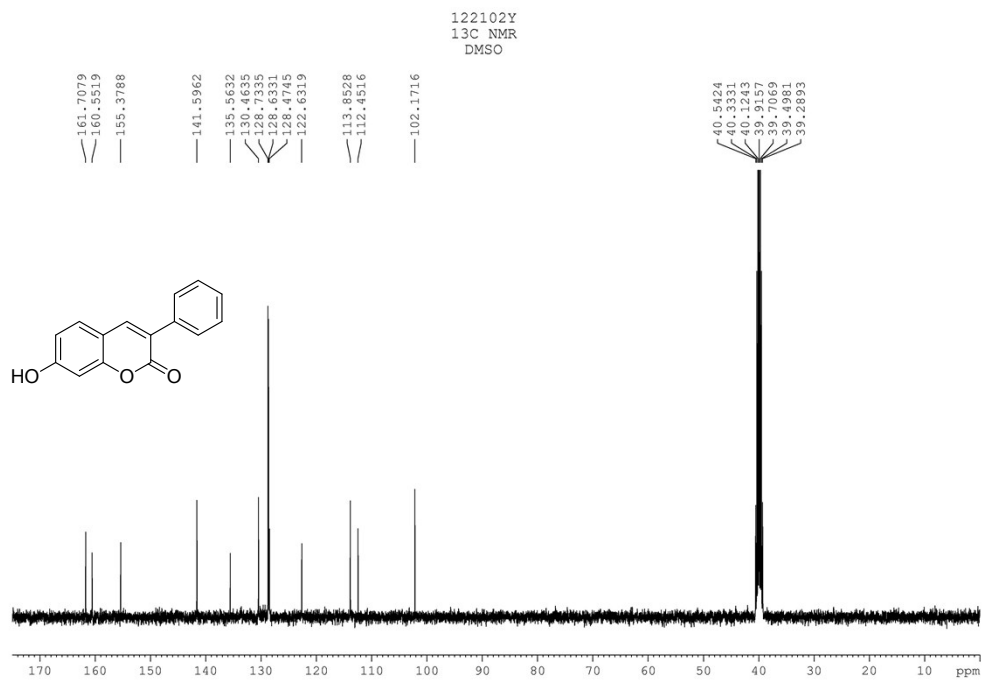


Fig. S43 ¹³C NMR spectrum of 3t

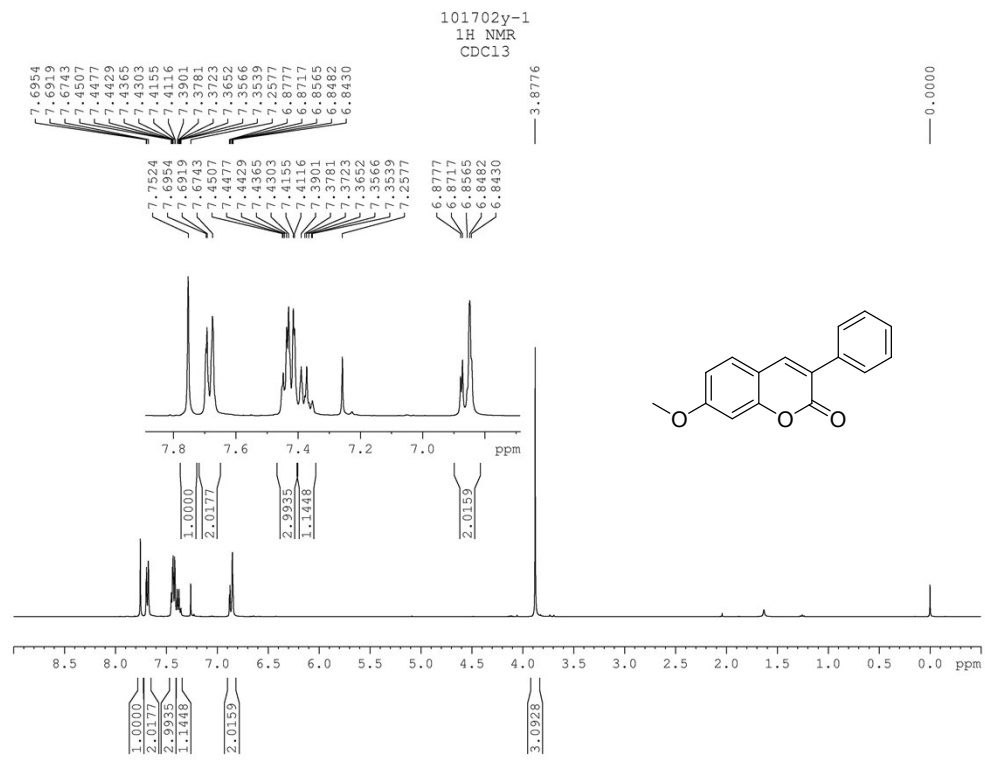


Fig. S44 ¹H NMR spectrum of 3u

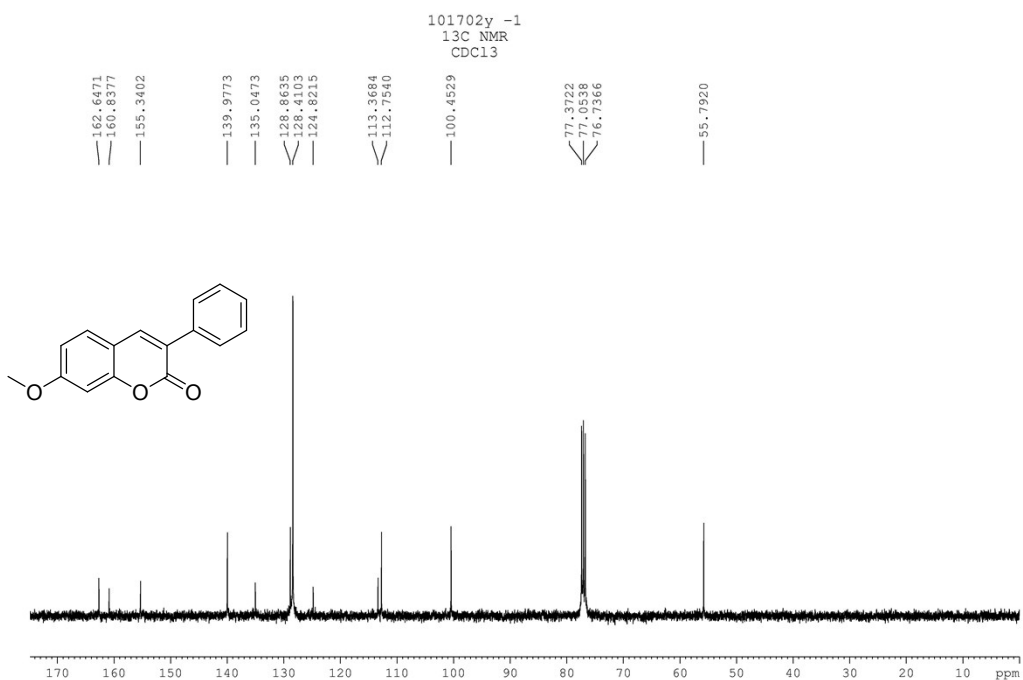


Fig. S45 ¹³C NMR spectrum of 3u

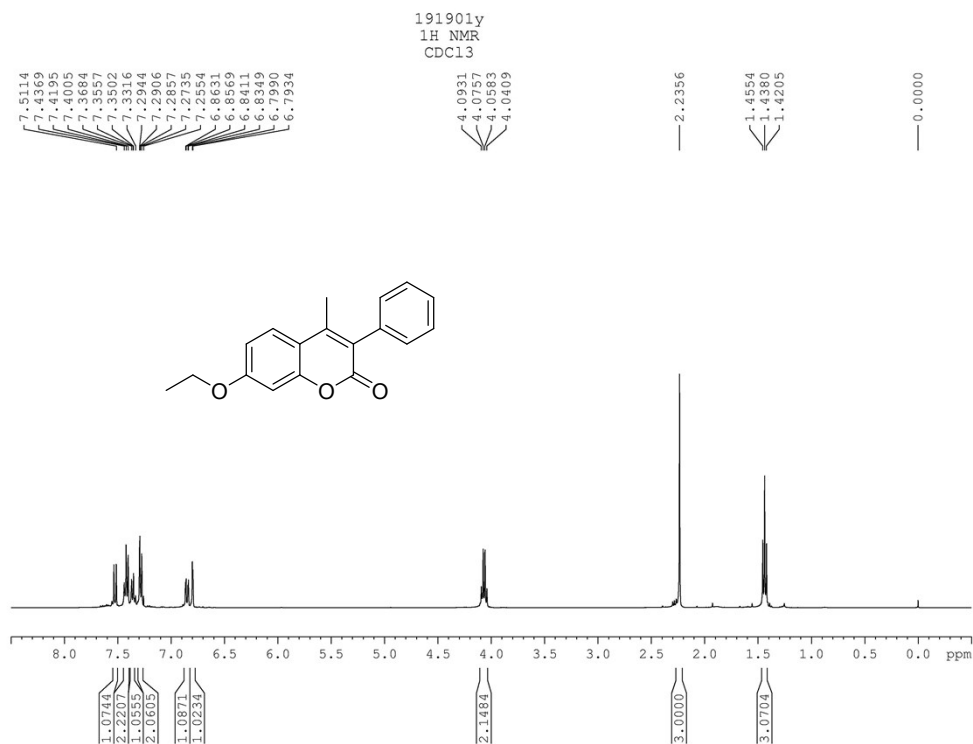


Fig. S46 ¹H NMR spectrum of 3w

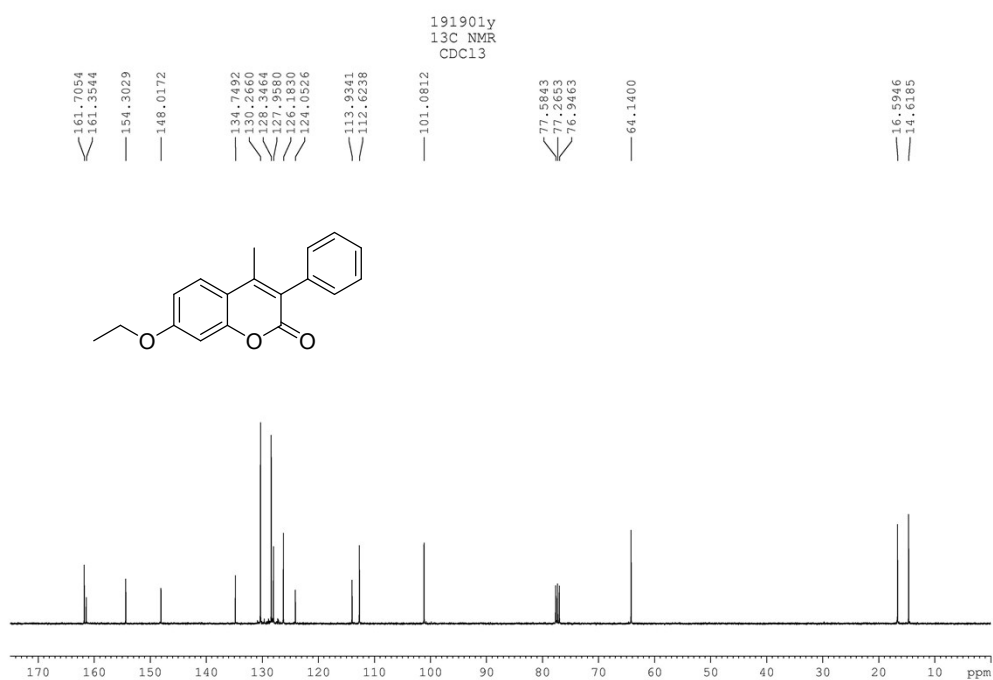


Fig. S47 ¹³C NMR spectrum of **3w**

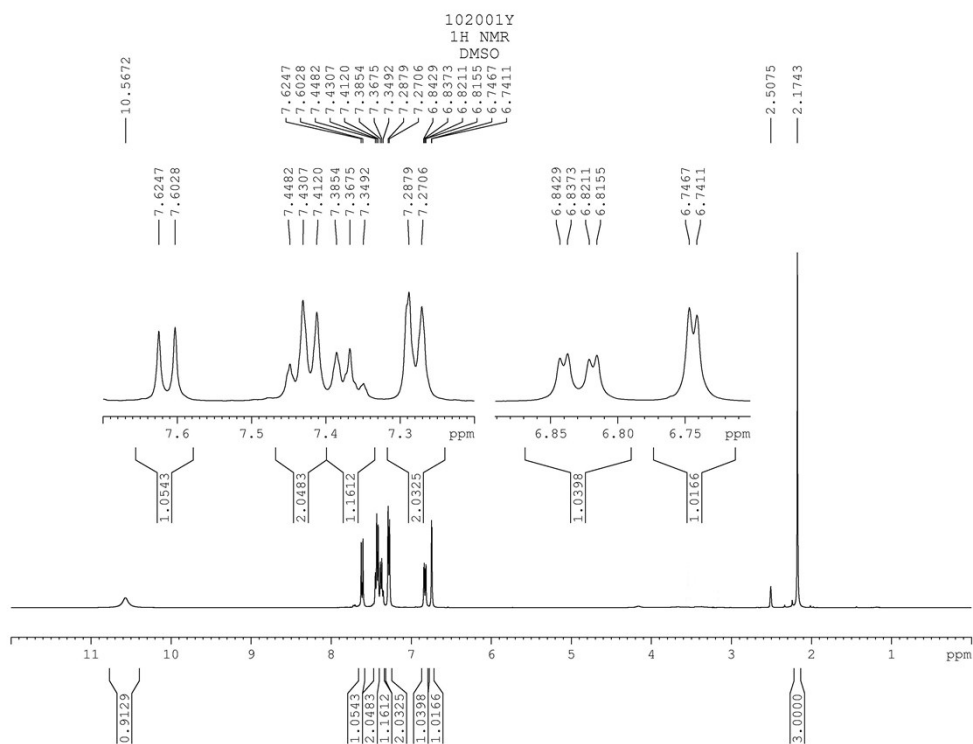


Fig. S48 ¹H NMR spectrum of **3x**

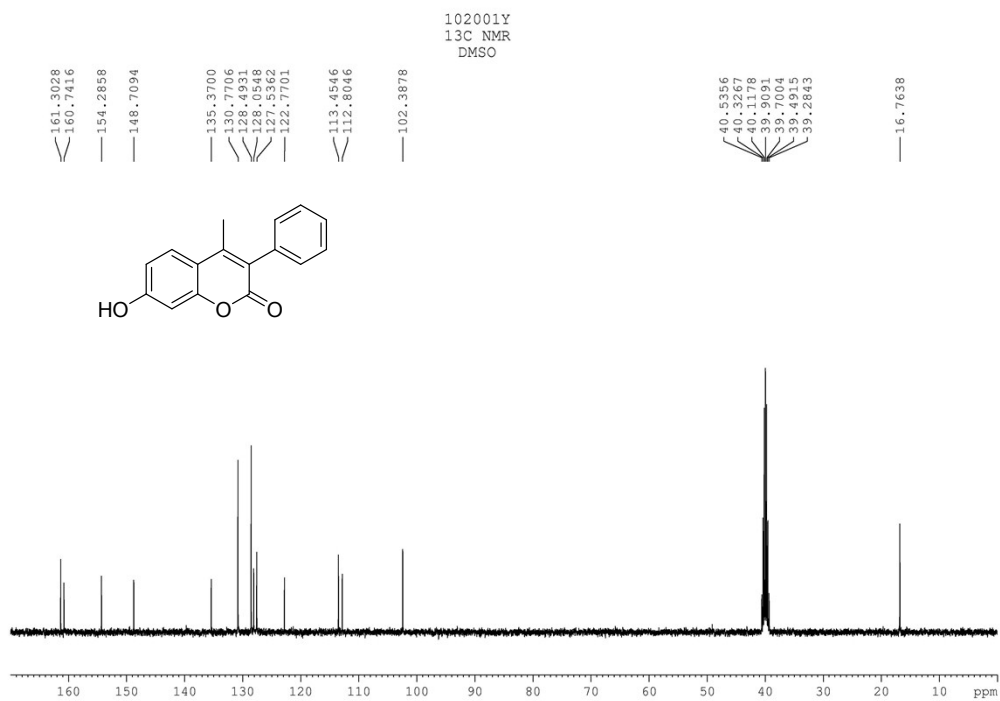


Fig. S49 ¹³C NMR spectrum of 3x

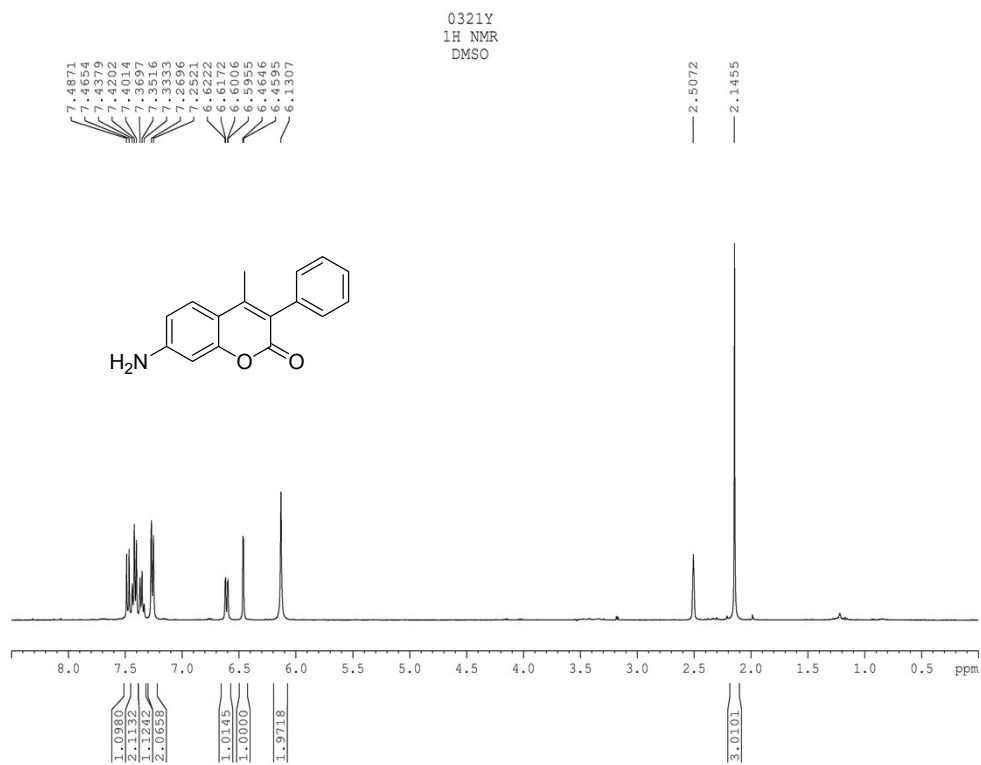


Fig. S50 ¹H NMR spectrum of 3y

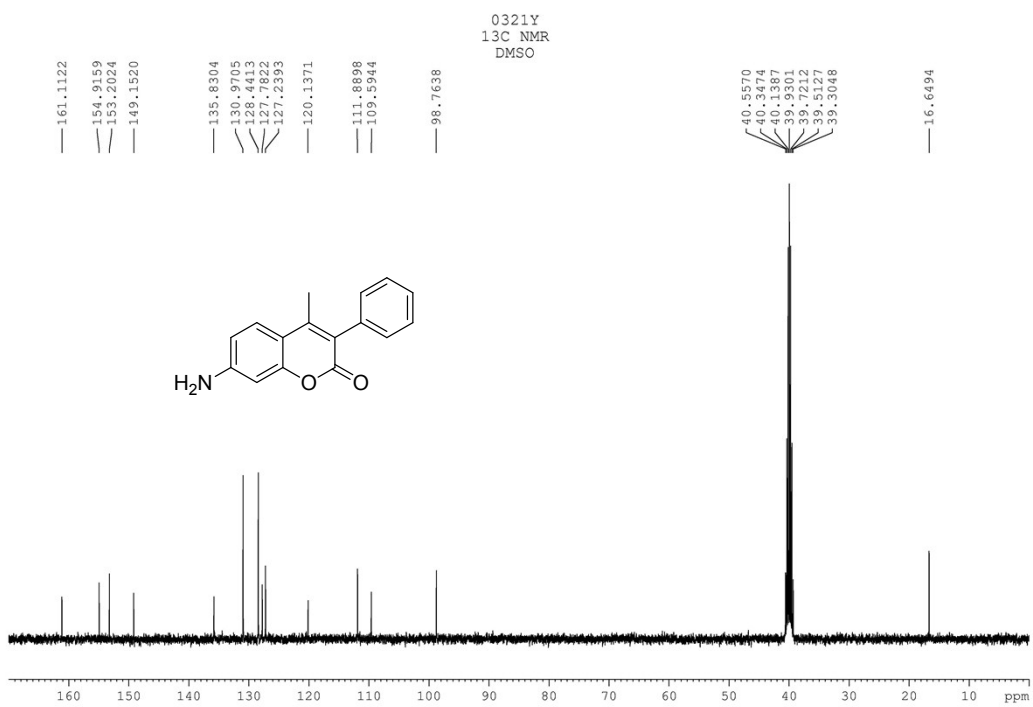


Fig. S51 ¹³C NMR spectrum of **3y**

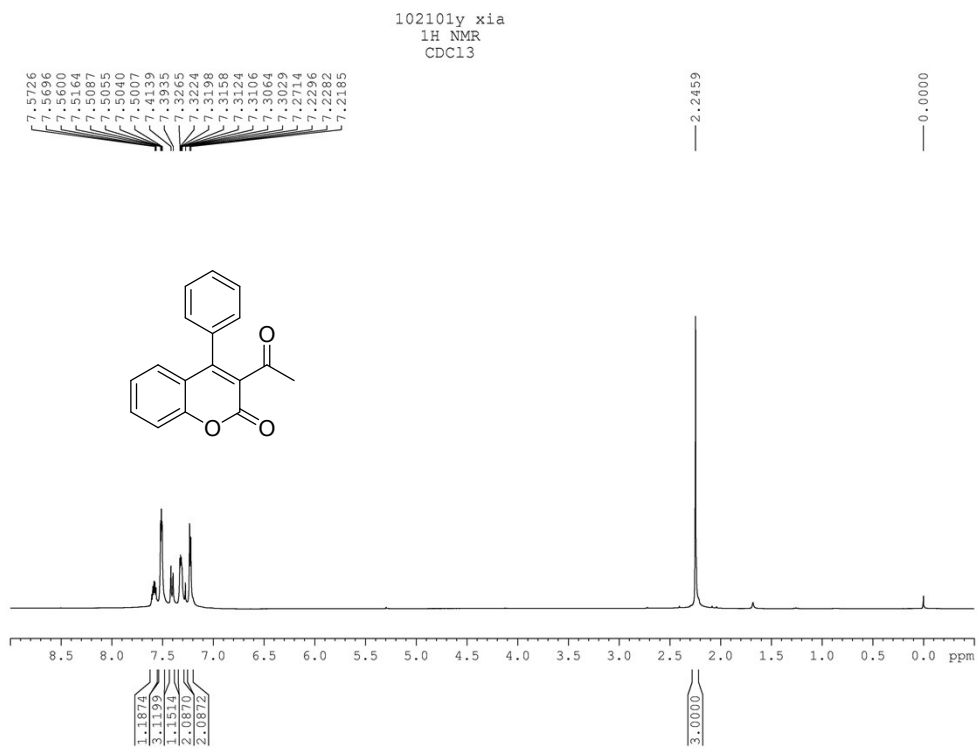


Fig. S52 ¹H NMR spectrum of **3z**

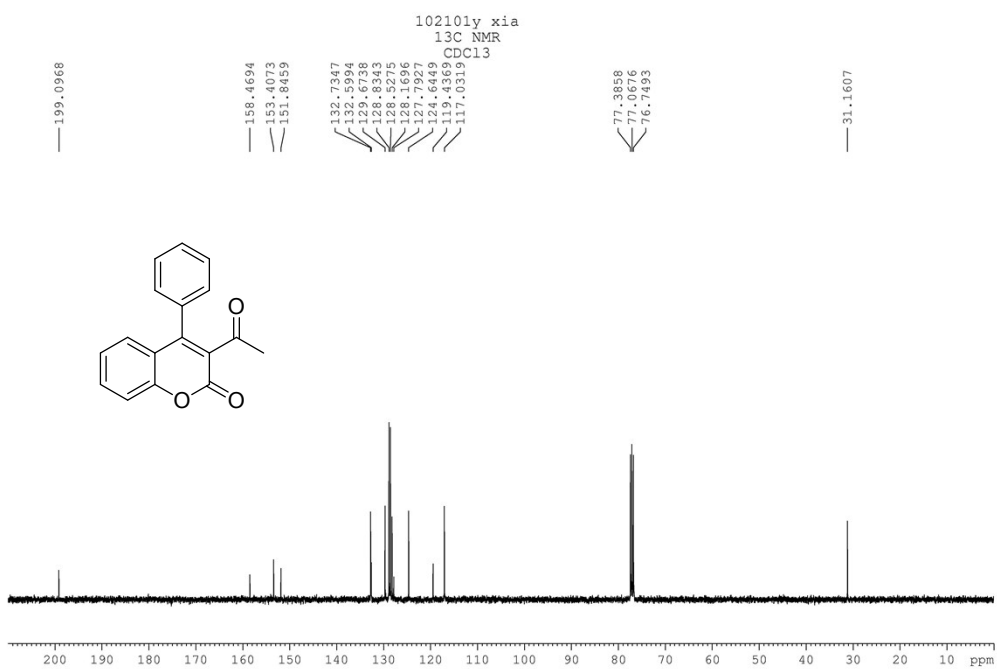


Fig. S53 ¹³C NMR spectrum of 3z

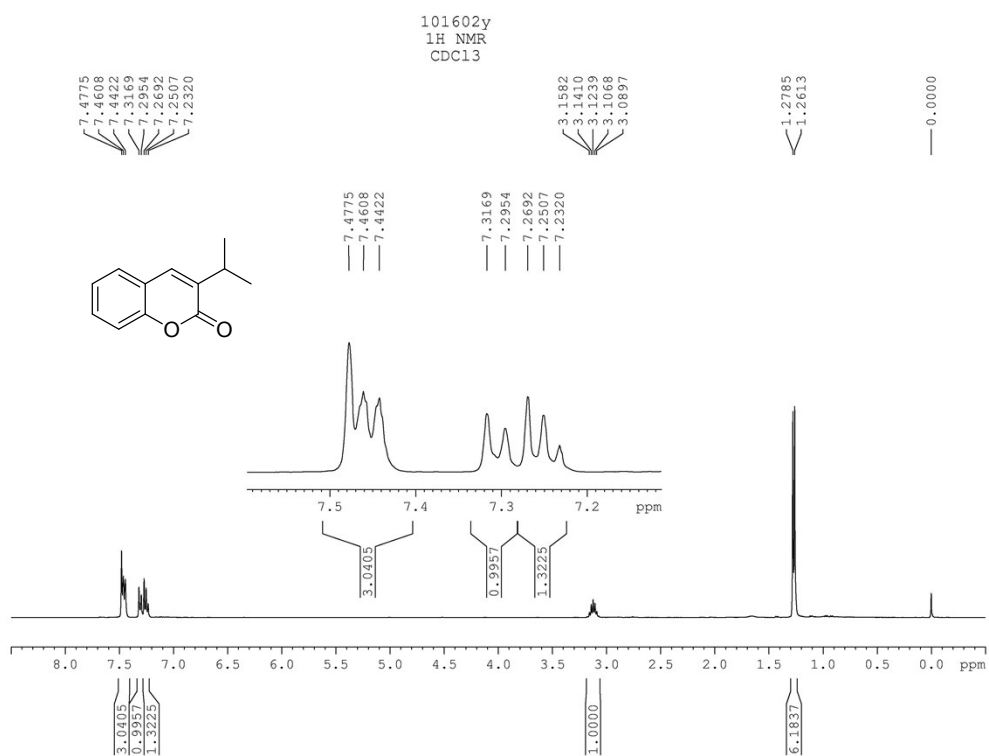


Fig. S54 ¹H NMR spectrum of 3zz

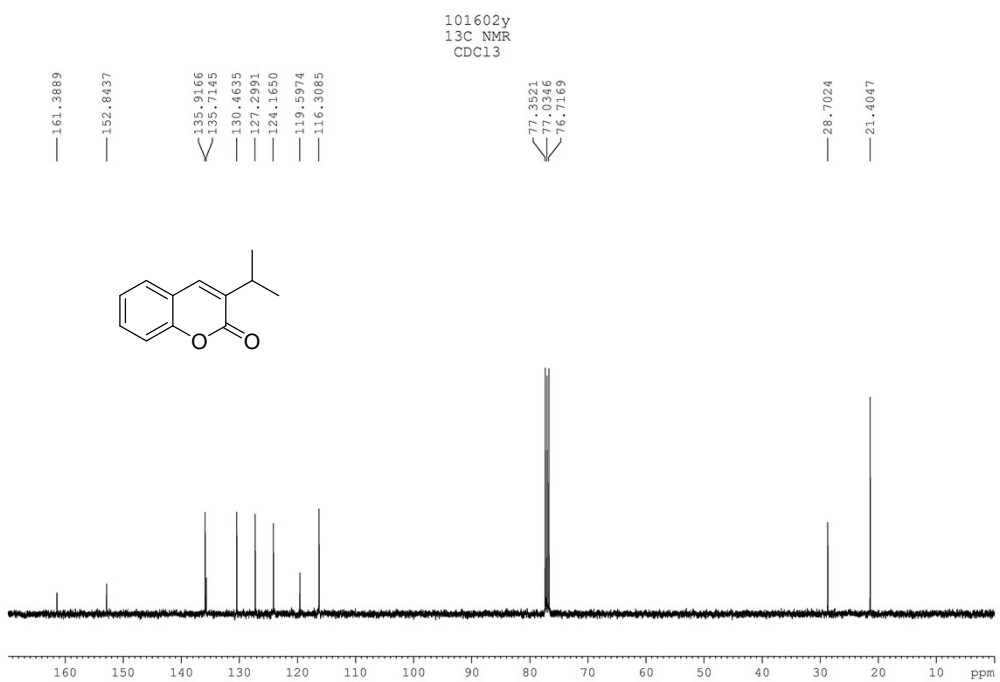


Fig. S55 ¹³C NMR spectrum of 3zz

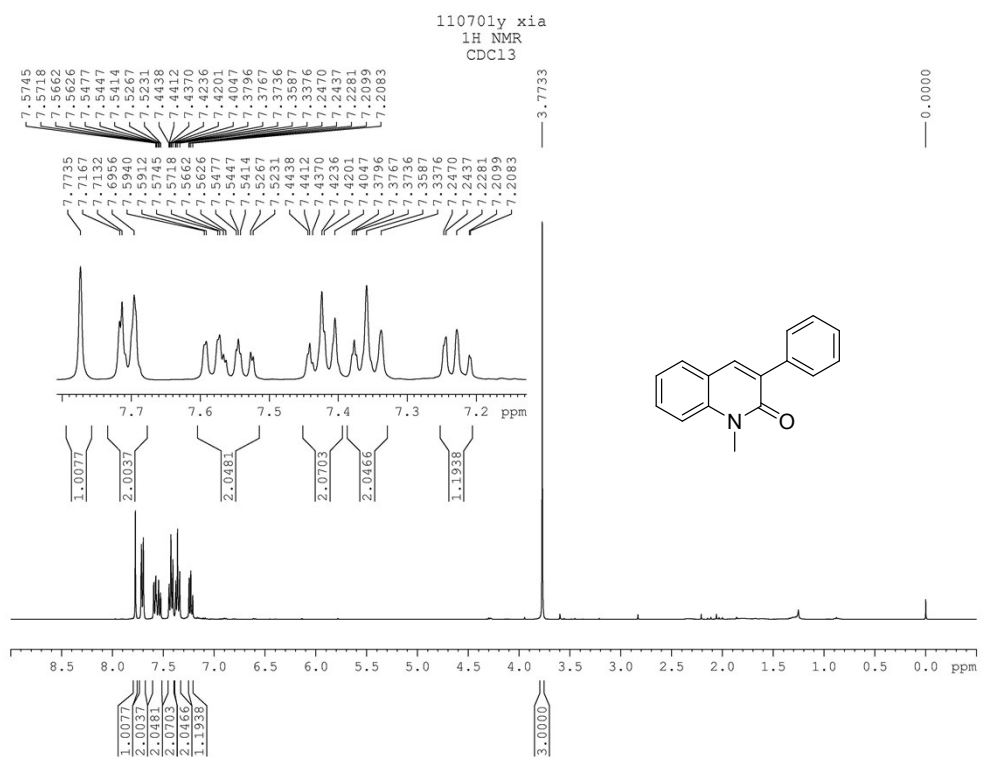


Fig. S56 ¹H NMR spectrum of 5a

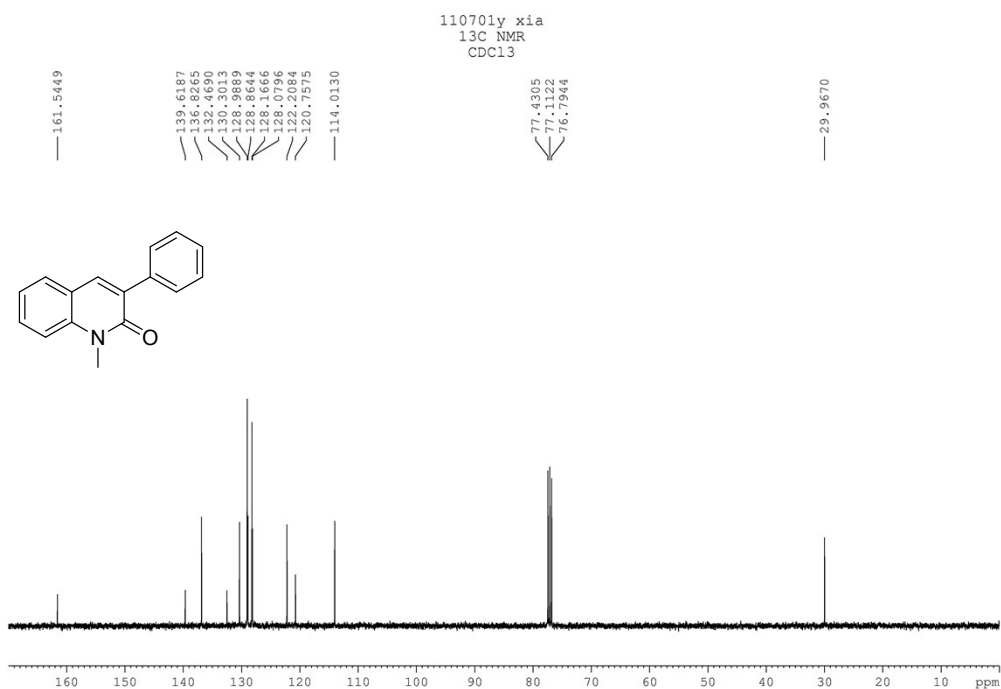


Fig. S57 ¹³C NMR spectrum of 5a

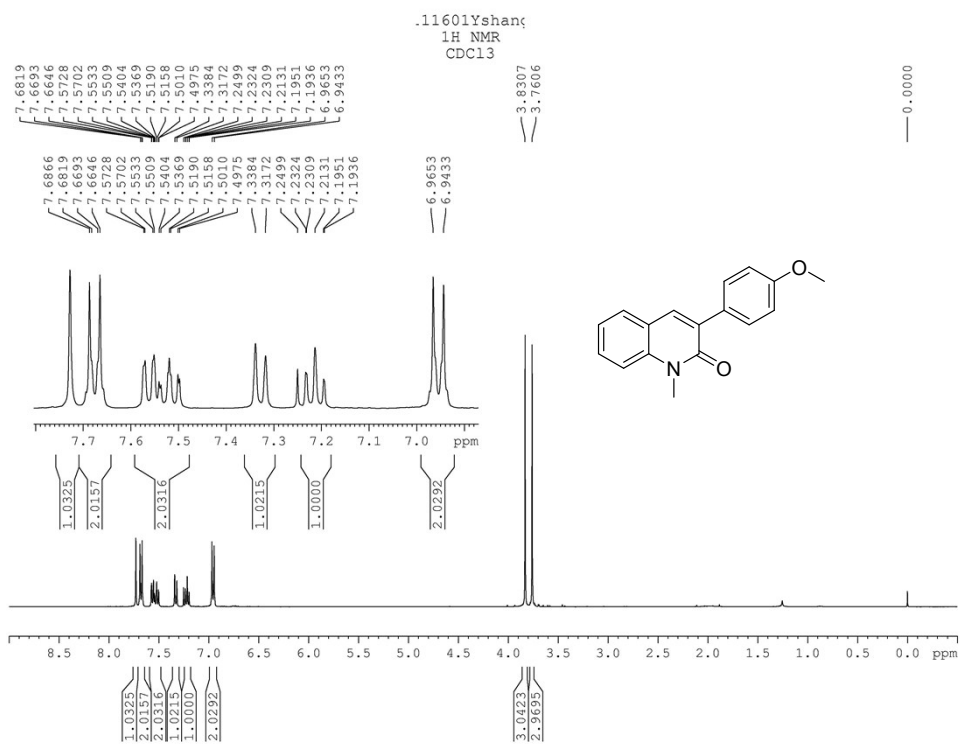


Fig. S58 ¹H NMR spectrum of 5b

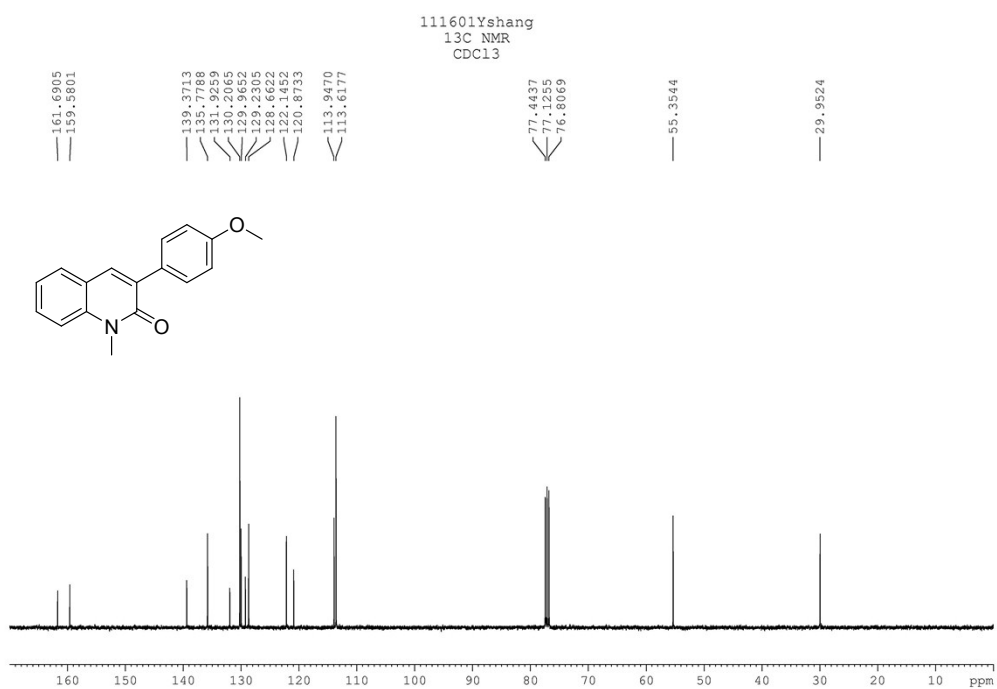


Fig. S59 ¹³C NMR spectrum of 5b

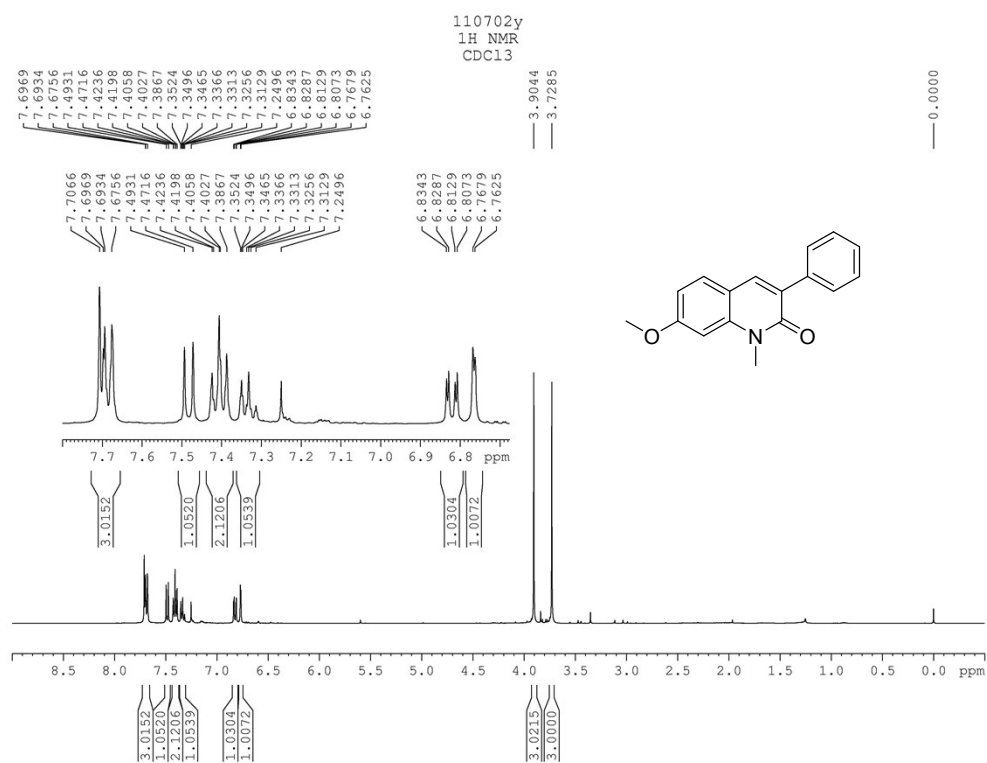


Fig. S60 ¹H NMR spectrum of 5c

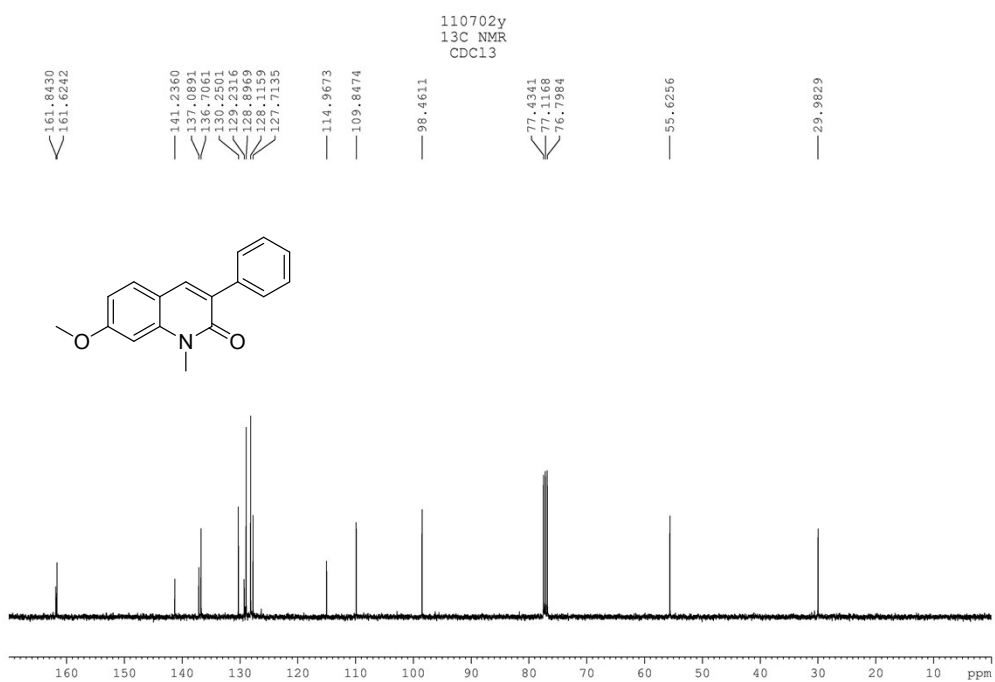


Fig. S61 ¹³C NMR spectrum of 5c

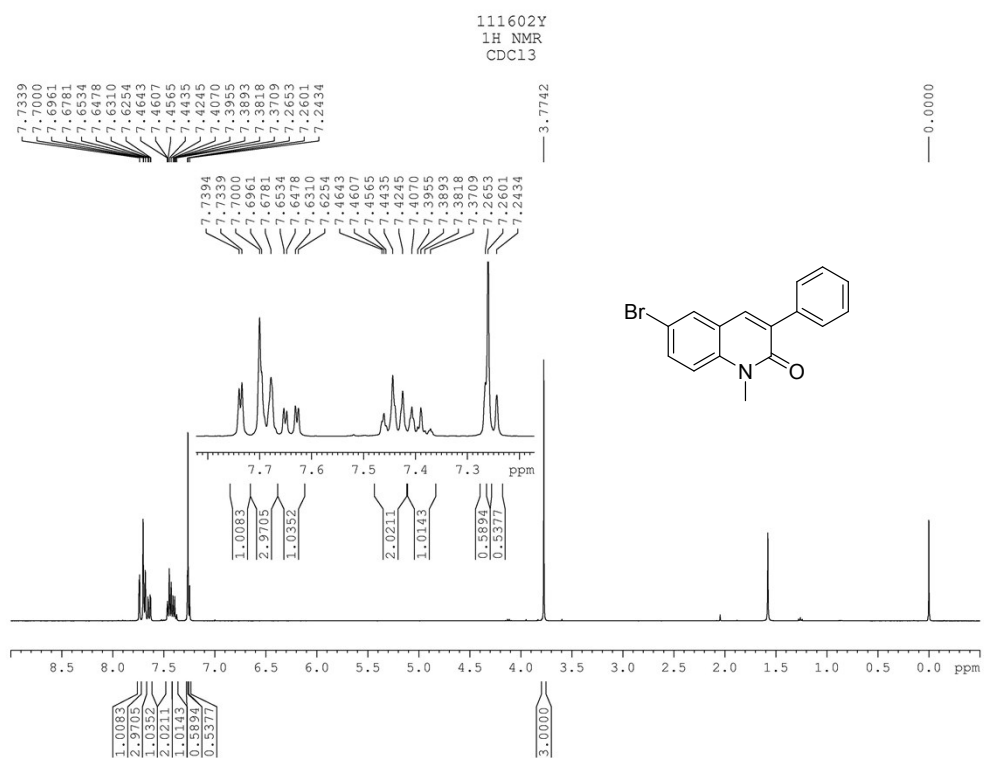


Fig. S62 ¹H NMR spectrum of 5d

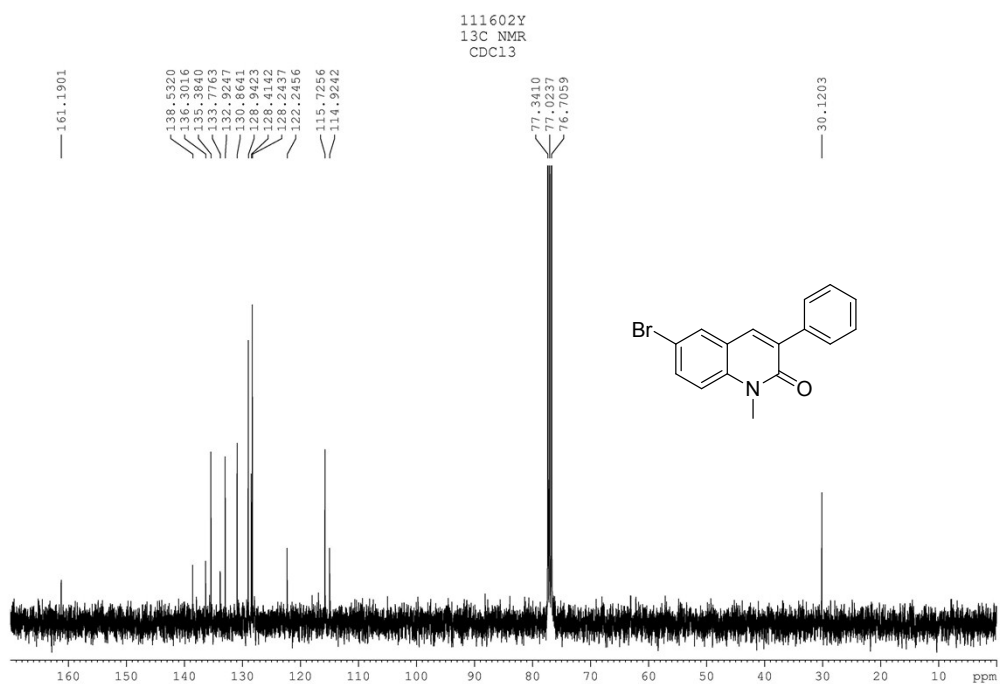


Fig. S63 ¹³C NMR spectrum of 5d

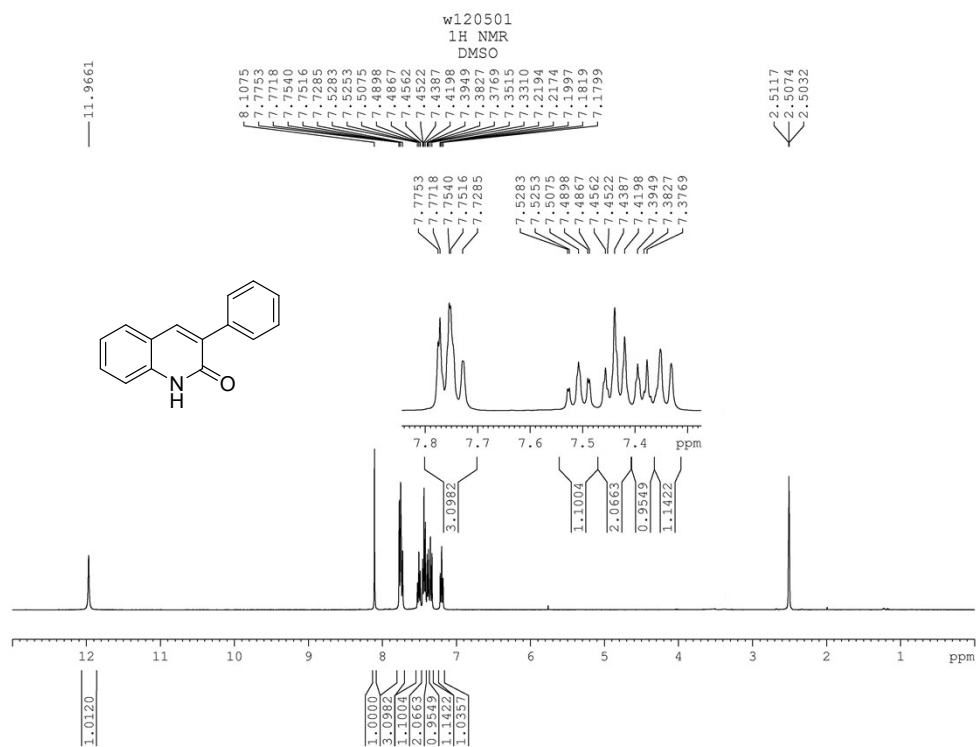


Fig. S64 ¹H NMR spectrum of 5e

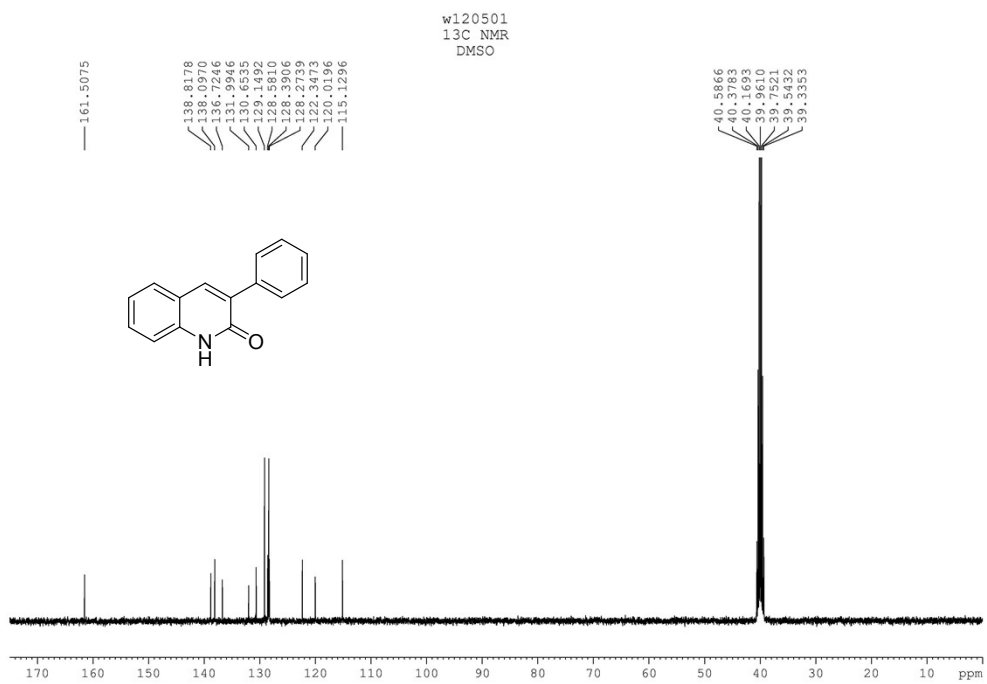


Fig. S65 ¹³C NMR spectrum of 5e