Supporting information

Annulation of β-naphthols and 1,4-hydroxycoumarins with vinylsulfonium salts: Synthesis of dihydrofuran derivatives

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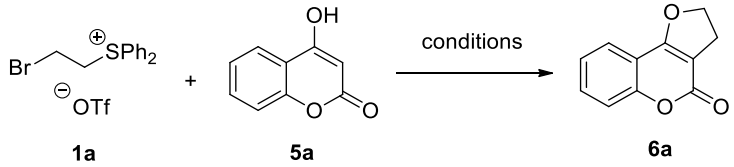
1. General Information

^{1}H NMR and ^{13}C NMR spectra were recorded on Bruker AVANCE 400 or 500 spectrometer. Chemical shifts of protons are reported in parts per million downfield from tetramethylsilane and are referenced to residual deuterium in the NMR solvent ($CDCl_3$: δ 7.26; *d*-DMSO: δ 2.50). Chemical shifts of carbon are referenced to the carbon resonances of the solvent ($CDCl_3$: δ 77.16 ppm; *d*-DMSO: δ 39.52 ppm). Peaks are labeled as singlet (s), doublet (d), triplet (t), quartet (q) and multiplet (m). Infrared data were recorded on a Nicolet 6700-Contium spectrometer. Melting points were measured on a WRS-2A melting point apparatus and are uncorrected. All products were further characterized by HRMS (high resolution mass spectra). Copies of their ^{1}H NMR, ^{19F} NMR and ^{13}C NMR spectra were provided.

2. Optimization of reaction conditions

Table 1. Optimization of the conditions for the reaction of 4-hydroxycoumarin (5a) and sufonium salt (1a)



1a **5a** **6a**

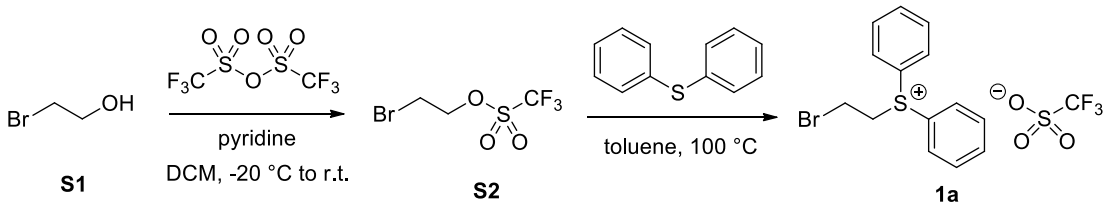
Entry[a]	Solvent	Base	Yield (%)[b]
1	MeCN	K_2CO_3	18
2	acetone	K_2CO_3	30
3	DMF	K_2CO_3	59
4	DMSO	K_2CO_3	24
5	1,4-dioxane	K_2CO_3	12
6	MeCN	DBU	52
7	1,4-dioxane	DBU	67
8	DMF	DBU	53
9[c]	1,4-dioxane	DBU	83

[a] Reaction conditions: **1a** (0.3 mmol), **5a** (0.2 mmol), base (0.6 mmol), solvent (4.0 mL), under an argon atmosphere at 0 °C, 24 h. [b] Isolated Yields. [c] The reaction was carried out at room temperature.

3. **Experiment procedures and characterization data**

3.1 Synthesis and characterization data of the starting materials

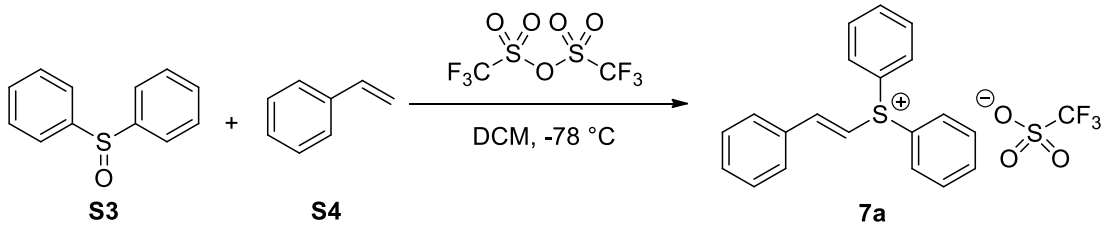
(2-Bromoethyl)diphenylsulfonium trifluoromethanesulfonate (1a)[1]



To a solution of pyridine (2.9 g, 36.8 mmol) in anhydrous DCM (35.0 mL) was added trifluoromethanesulfonic anhydride (10.0 g, 35.4 mmol) dropwise at -20 °C. After stirring for 5 min, 2-bromoethanol **S1** (4.2 g, 33.6 mmol) was added dropwise and the reaction was stirred at room temperature for 10 min. The resulting suspension was filtered. The filtrate was concentrated (using a rotary evaporator, keeping the water bath temperature below 20 °C). Then petroleum ether (30.0 mL) was added while stirring. The petroleum ether layer was separated and evaporated under vacuum to afford 2-bromoethyl trifluoromethanesulfonate **S2** (4.2 g, 49% yield) as pale brown liquid, which was used in the next step without further purification.

To a solution of 2-bromoethyl trifluoromethanesulfonate **S2** (3.3 g, 12.8 mmol) in anhydrous toluene was added diphenyl sulfide (2.9 g, 15.6 mmol) at room temperature. Then the mixture was stirred at 100 °C overnight under an argon atmosphere. After being cooled down to room temperature, Et_2O (30.0 mL) was added to precipitate the product **1a**. The precipitation was filtrated, washed with Et_2O and dried under vacuum. **1a** (4.5 g, 86% yield) was obtained as a white solid. **^{1}H NMR** (400 MHz, DMSO) δ 8.16–8.11 (m, 4H), 7.86–7.79 (m, 2H), 7.79–7.73 (m, 4H), 5.00–4.92 (m, 2H), 3.85–3.77 (m, 2H) ppm. **^{19}F NMR** (376 MHz, DMSO) δ -77.71 ppm. **^{13}C NMR** (100 MHz, DMSO) δ 134.4, 131.2, 130.9, 124.8, 45.4, 24.9 ppm. The data are consistent with that reported in the literature.[1]

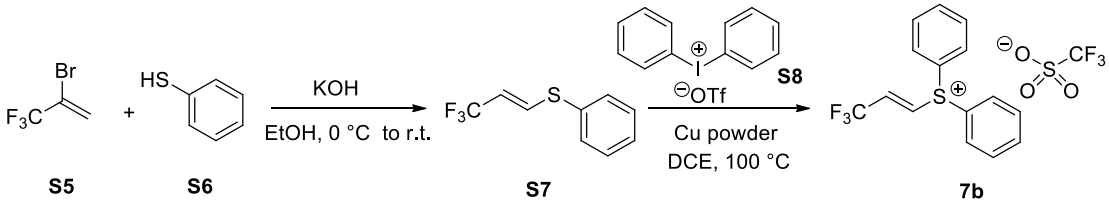
(*E*)-diphenyl(styryl)sulfonium trifluoromethanesulfonate (7a)[2]



S3 S4 7a

A solution of phenyl sulfoxide **S3** (2.2 g, 11.0 mmol) in anhydrous DCM (200.0 mL) was cooled down to -78 °C. Trifluoromethanesulfonic anhydride (2.8 g, 10.0 mmol) was slowly added to the solution while stirring. After 30 min, a solution of styrene **S4** (1.0 g, 10.0 mmol) in anhydrous DCM (25.0 mL) was slowly added and the mixture was stirred overnight. The solvent was removed and the crude product was purified by column chromatography (DCM/MeOH = 10:1) to give **7a** (2.2 g, 49% yield) as a white solid. **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.96–7.75 (m, 8H), 7.69–7.60 (m, 6H), 7.46–7.36 (m, 3H) ppm. **^{19}F NMR** (376 MHz, $CDCl_3$) δ -78.16 ppm. **^{13}C NMR** (100 MHz, $CDCl_3$) δ 153.5, 134.4, 132.8, 132.2, 131.6, 130.6, 129.8, 129.4, 127.4, 121.0 (q, $^1J_{CF}$ = 320.4 Hz), 110.0 ppm. The data are consistent with that reported in the literature.[2]

(*E*)-Diphenyl-*β*-(trifluoromethyl)vinylsulfonium trifluoromethanesulfonate (7b)[3]



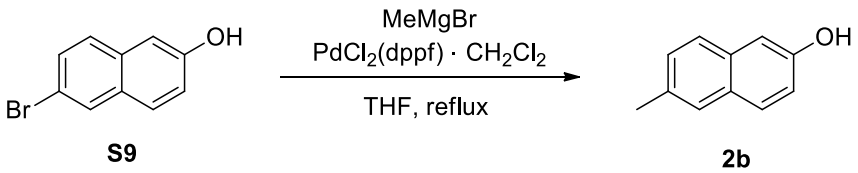
S5 S6 S7 S8 7b

To a mixture of KOH (544.3 mg, 9.7 mmol) in EtOH (10.0 mL) were added thiophenol **S6** (892.5 mg, 8.1 mmol) and 3,3,3-trifluoro-2-bromoprop-1-ene **S5** (1.7 g, 9.7 mmol) at 0 °C. The mixture was gradually warmed to room temperature and stirred overnight. The reaction was quenched with saturated aqueous NH_4Cl (10 mL) and the water layer was extracted with hexane (10 mL × 2). The combined organic layer was dried over anhydrous Na_2SO_4 and concentrated under vacuum. The resulting residue was purified by column chromatography (petroleum ether as eluent) to give (*E*)-phenyl *β*-(trifluoromethyl)vinyl sulfide **S7** (785.9 mg, 48% yield) as colorless liquid.

To a mixture of diphenyliodonium triflate **S8** (1.6 g, 3.9 mmol) and Cu powder (1.3 g, 19.3 mmol) in DCE (10.0 mL) was added (*E*)-phenyl *β*-(trifluoromethyl)vinyl sulfide

S7 (785.9 mg, 3.8 mmol) under an argon atmosphere. The mixture was stirred at 100 °C for 5 h. After being cooled down to room temperature, the mixture was filtered through Celite and the filtrate was concentrated under vacuum. The resulting residue was purified by column chromatography (DCM/acetone = 5:2) to give **7b** (643.9 mg, 38% yield) as a pale yellow solid. **^{1}H NMR** (400 MHz, $CDCl_3$) δ 8.05–7.92 (m, 5H), 7.80–7.65 (m, 6H), 7.12–7.02 (m, 1H) ppm. **^{19}F NMR** (376 MHz, $CDCl_3$) δ -64.59, -78.45 ppm. **^{13}C NMR** (100 MHz, $CDCl_3$) δ 137.5 (q, $^2J_{CF}$ = 37.4 Hz), 135.4, 132.1, 131.2, 127.2 (q, $^3J_{CF}$ = 6.8 Hz), 123.8, 120.8 (q, $^1J_{CF}$ = 320.1 Hz), 120.2 (q, $^1J_{CF}$ = 237.4 Hz) ppm. The data are consistent with that reported in the literature.[3]

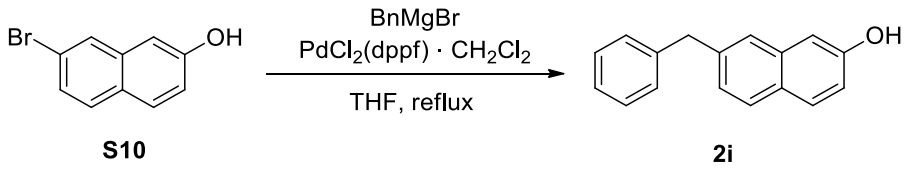
6-Methylnaphthalen-2-ol (2b)[4]



S9 **2b**

To a solution of 6-bromo-2-naphthol **S9** (446.1 mg, 2.0 mmol) and $PdCl_2(dppf)\cdot CH_2Cl_2$ (163.3 mg, 10 mol%) in anhydrous THF (15.0 mL) was added methyl magnesium bromide (10.0 mL, 1 M in THF) with constant stirring at 0 °C. The mixture was then heated to reflux for 5 h. The mixture was cooled down to room temperature, quenched with saturated aqueous NH_4Cl (10 mL) and extracted with ethyl acetate (10 mL × 2). The combined organic layer was washed with brine and dried over anhydrous Na_2SO_4. The solvent was removed and the residue was purified by column chromatography (petroleum ether/ethyl acetate = 5:1) to give **2b** (153.3 mg, 48% yield) as a white solid. **M.p.**: 127.5-129.5 °C. **^{1}H NMR** (400 MHz, DMSO) δ 9.58 (br, 1H), 7.64 (d, J = 8.8 Hz, 1H), 7.57 (d, J = 8.4 Hz, 1H), 7.53–7.51 (m, 1H), 7.22 (dd, J = 8.4, 1.5 Hz, 1H), 7.08–7.06 (m, 1H), 7.04 (dd, J = 8.8, 2.4 Hz, 1H), 2.39 (s, 3H) ppm. **^{13}C NMR** (100 MHz, DMSO) δ 154.6, 132.7, 131.5, 128.5, 128.3, 127.9, 126.4, 125.9, 118.5, 108.5, 21.0 ppm. The data are consistent with that reported in the literature.[4]

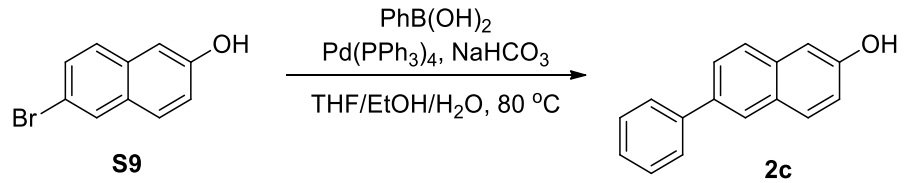
7-Benzylnaphthalen-2-ol (2i)



S10 **2i**

2i (157.2 mg, 67% yield) was obtained as a white solid via a similar procedure for the synthesis of **2b**. **M.p.**: 94.5-95.8 °C. **^{1}H NMR** (400 MHz, DMSO) δ 9.68 (br, 1H), 7.70–7.64 (m, 2H), 7.53–7.50 (m, 1H), 7.31–7.24 (m, 4H), 7.20–7.15 (m, 1H), 7.11 (dd, J = 8.4, 1.6 Hz, 1H), 7.06–7.04 (m, 1H), 7.01 (dd, J = 8.4, 2.4 Hz, 1H), 4.03 (s, 2H) ppm. **^{13}C NMR** (100 MHz, DMSO) δ 155.5, 141.3, 139.0, 134.8, 129.0, 128.8, 128.4, 127.7, 126.3, 125.9, 124.9, 124.3, 117.9, 108.4, 41.4 ppm. **IR (thin film)**: ν (cm^{-1}) 3234, 3026, 2917, 1633, 1515. **HRMS (ESI)** calculated for $C_{17}H_{13}O$ $[M-H]^-$: 233.0972, found: 233.0976.

6-Phenylnaphthalen-2-ol (2c)[5]

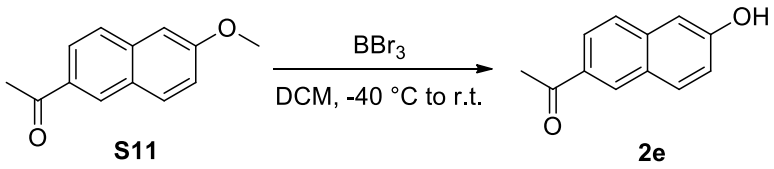


S9 **2c**

To a solution of 6-bromo-2-naphthol **S9** (334.7 mg, 1.5 mmol), $Pd(PPh_3)_4$ (86.7 mg, 5 mol %) in toluene (15.0 mL) was added a solution of $NaHCO_3$ (378.0 mg, 4.5 mmol) in water (4.0 mL). The mixture was stirred at room temperature under an argon atmosphere. A solution of phenyl boronic acid (243.9 mg, 2.0 mmol) in ethanol (4.5 mL) was added and the mixture was stirred for 10 min. Then the reaction mixture was heated to 80 °C and stirred overnight. The mixture was cooled down to room temperature and extracted with ethyl acetate (10 mL × 2). The combined organic layer was washed with water, brine and dried over anhydrous Na_2SO_4. The solvent was removed and the residue was purified by column chromatography (petroleum ether/ethyl acetate = 10:1) to give **2c** (237.9 mg, 72% yield) as a white solid. **M.p.**: 175.3-176.1 °C. **^{1}H NMR** (400 MHz, DMSO) δ 9.78 (br, 1H), 8.09–8.06 (m, 1H), 7.84 (d, J = 8.8 Hz, 1H), 7.79–7.69 (m, 4H), 7.51–7.45 (m, 2H), 7.38–7.33 (m, 1H),7.15 (d, J = 2.0 Hz, 1H), 7.12 (dd, J = 8.8, 2.4 Hz, 1H) ppm. **^{13}C NMR** (100 MHz, DMSO) δ

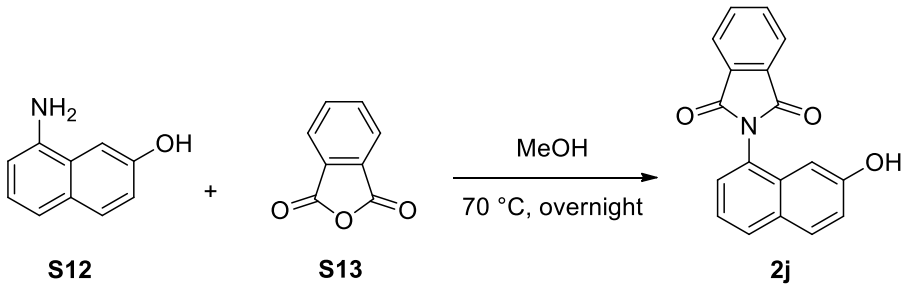
155.5, 140.3, 134.3, 133.8, 129.8, 128.9, 127.9, 127.0, 126.7, 126.6, 125.2, 125.1, 119.0, 108.4 ppm. The data are consistent with that reported in the literature.[5]

1-(6-Hydroxynaphthalen-2-yl)ethanone (2e)[6]



To a solution of 1-(6-methoxynaphthalen-2-yl)ethanone (600.0 mg, 3.0 mmol) in anhydrous DCM (10.0 mL) was added boron tribromide (3.8 g, 15.2 mmol) at -40 °C under an argon atmosphere. Then the mixture was allowed to stir at room temperature for 1 h. The reaction was quenched with water and saturated $NaHCO_3$. The mixture was extracted with DCM and the solvent was removed to give the crude product which was purified by column chromatography (petroleum ether/ethyl acetate = 5:1) to give **2e** (156.4 mg, 28% yield) as a white solid. **M.p.**: 175.0-176.0 °C. **^{1}H NMR** (400 MHz, DMSO) δ 10.16 (br, 1H), 8.52 (d, J = 0.9 Hz, 1H), 7.99–7.94 (m, 1H), 7.87 (dd, J = 8.6, 1.7 Hz, 1H), 7.75 (d, J = 8.7 Hz, 1H), 7.20–7.14 (m, 2H), 2.64 (s, 3H) ppm. **^{13}C NMR** (100 MHz, DMSO) δ 197.3, 157.8, 137.1, 131.4, 131.4, 130.4, 126.5, 126.2, 123.9, 119.5, 108.8, 26.4 ppm. **IR (thin film)**: ν (cm^{-1}) 3357, 1660, 1626, 1483, 1433. **HRMS** (ESI) calculated for $C_{12}H_{10}O_2Na$ $[M+Na]^+$: 209.0573, found: 209.0578.

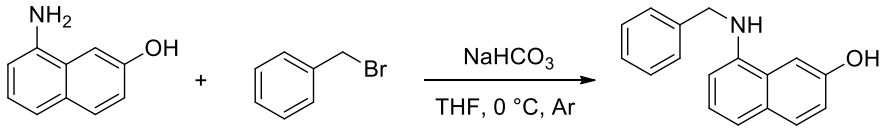
2-(7-Hydroxynaphthalen-1-yl)isoindoline-1,3-dione (2j)



A mixture of 8-aminonaphthalen-2-ol **S12** (477.5 mg, 3.0 mmol) and phthalic anhydride **S13** (615.7 mg, 3.6 mmol) in methanol (25.0 mL) was stirred at 70 °C overnight. After completion, the solvent was removed to give the crude product which

was purified by column chromatography (petroleum ether/ethyl acetate = 5:2) to give **2j** (224.4 mg, 30% yield) as a yellow solid. **M.p.**: 204.6–207.1 °C. **^{1}H NMR** (400 MHz, DMSO) δ 9.80 (br, 1H), 8.08–8.02 (m, 2H), 8.00–7.94 (m, 3H), 7.92 (d, J = 8.9 Hz, 1H), 7.57–7.53 (m, 1H), 7.45–7.38 (m, 1H), 7.15 (dd, J = 8.8, 2.3 Hz, 1H), 6.85 (d, J = 2.1 Hz, 1H) ppm. **^{13}C NMR** (100 MHz, DMSO) δ 167.5, 156.4, 134.9, 131.8, 131.6, 130.2, 129.2, 128.5, 127.7, 126.7, 123.6, 122.1, 119.2, 103.5 ppm. **IR (thin film)**: ν (cm^{-1}) 3306, 1076, 1631, 1511, 1607, 1382. **HRMS** (ESI) calculated for $C_{18}H_{10}NO_3$ $[M-H]^-$: 288.0666, found: 288.0657.

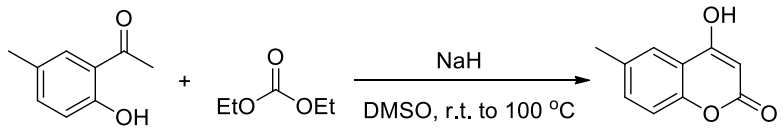
8-(Benzylamino)naphthalen-2-ol (2k)



S12 **2k**

To a mixture of 8-aminonaphthalen-2-ol **S12** (795.9 mg, 5.0 mmol) and $NaHCO_3$ (1.3 g, 15.5 mmol) in THF (20.0 mL) was added benzyl bromide (940.5 mg, 5.5 mmol) at 0 °C under an argon atmosphere. The mixture was allowed to stir at room temperature overnight. After completion, the solvent was removed to give the residue which was purified by column chromatography (petroleum ether/ethyl acetate = 5:1) to give **2k** (560.1 mg, 45% yield) as a white solid. **M.p.**: 125.4-126.8 °C. **^{1}H NMR** (400 MHz, DMSO) δ 9.45 (br, 1H), 7.60 (d, J = 8.8 Hz, 1H), 7.44 (d, J = 2.0 Hz, 1H), 7.42–7.37 (m, 2H), 7.33–7.27 (m, 2H), 7.23–7.17 (m, 1H), 7.05 (dd, J = 8.8, 2.4 Hz, 1H), 7.00–6.90 (m, 2H), 6.46–6.40 (m, 1H), 6.30–6.26 (m, 1H), 4.48–4.42 (m, 2H) ppm. **^{13}C NMR** (100 MHz, DMSO) δ 154.2, 142.3, 140.3, 129.4, 128.4, 128.2, 126.9, 126.4, 124.7, 123.1, 117.7, 115.8, 103.9, 103.9, 46.6 ppm. **IR (thin film)**: ν (cm^{-1}) 3439, 3026, 1623, 1485, 1438, 1345, 1223, 821. **HRMS (ESI)** calculated for $C_{17}H_{16}NO$ $[M+H]^+$: 250.1226, found: 250.1225.

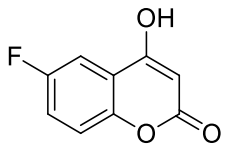
4-Hydroxy-6-methyl-2*H*-chromen-2-one (5b)



S14 **S15** **5b**

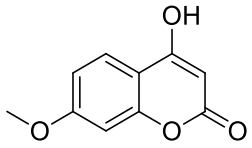
To a solution of 5-methyl-1-(2-hydroxyphenyl)ethanone **S14** (1.5 g, 10.0 mmol) and diethyl carbonate **S15** (1.8 g, 15.0 mmol) in DMSO (15.0 mL) was added NaH (60%, 1.2 g, 50.0 mmol) in portions while stirring at 0 °C. Then the mixture was allowed to stir at 100 °C for 2 h. After completion, the mixture was cooled down to room temperature. Water (30.0 mL) was added and the solution was acidified to pH = 6-7 by adding saturated aqueous NH_4Cl. The water layer was extracted with ethyl acetate. The combined organic layer was dried over Na_2SO_4 and the solvent was removed under vacuum. The residue was purified by recrystallization with 70% EtOH (aq.) to afford **5b** (423.6 mg, 24% yield) as a pale brown solid. **M.p.**: 260.9-262.3 °C. **^{1}H NMR** (400 MHz, DMSO) δ 12.46 (br, 1H), 7.61 (d, J = 1.1 Hz, 1H), 7.45 (dd, J = 8.4, 1.9 Hz, 1H), 7.26 (d, J = 8.4 Hz, 1H), 5.58 (s, 1H), 2.37 (s, 3H) ppm. **^{13}C NMR** (100 MHz, DMSO) δ 165.7, 162.1, 151.7, 133.5, 133.1, 122.8, 116.2, 115.5, 90.9, 20.3 ppm. **IR (thin film)**: ν(cm^{-1}) 3082, 2929, 2734, 2604, 1687, 1634, 1606. **HRMS (ESI)** calculated for $C_{10}H_8O_3Na$ $[M+Na]^+$: 199.0366, found: 199.0362.

6-Fluoro-4-hydroxy-2*H*-chromen-2-one (5c)



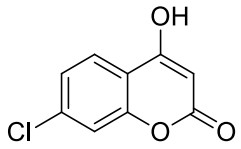
5c (340.2 mg, 29% yield) was obtained as a white solid following the similar procedure for the synthesis of **5b**. **M.p.**: 247.0-248.0 °C. **^{1}H NMR** (400 MHz, DMSO) δ 12.75 (br, 1H), 7.54–7.47 (m, 2H), 7.45–7.40 (m, 1H), 5.67 (s, 1H) ppm. **^{19}F NMR** (376 MHz, DMSO) δ -118.07 ppm. **^{13}C NMR** (100 MHz, DMSO) δ 164.8 (d, $^4J_{CF}$ = 2.5 Hz), 161.6, 157.9 (d, $^1J_{CF}$ = 240.8 Hz), 149.8 (d, $^4J_{CF}$ = 1.6 Hz), 119.9 (d, $^2J_{CF}$ = 24.5 Hz), 118.5 (d, $^3J_{CF}$ = 8.5 Hz), 117.0 (d, $^3J_{CF}$ = 9.0 Hz), 108.6 (d, $^2J_{CF}$ = 25.1 Hz), 91.6 ppm. **IR (thin film)**: ν (cm^{-1}) 3088, 2962, 1703, 1617, 1574, 1309. **HRMS (ESI)** calculated for $C_9H_5FO_3Na$ $[M+Na]^+$: 203.0115, found: 203.0121.

4-Hydroxy-7-methoxy-2*H*-chromen-2-one (5e)



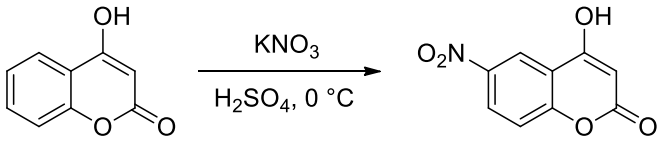
5e (341.8 mg, 16% yield) was obtained as a pink solid following the similar procedure for the synthesis of **5b**. **M.p.**: 252.3-253.3 °C. **^{1}H NMR** (400 MHz, DMSO) δ 12.31 (br, 1H), 7.71 (d, J = 8.9 Hz, 1H), 6.95–6.90 (m, 2H), 5.44 (s, 1H), 3.85 (s, 3H) ppm. **^{13}C NMR** (100 MHz, DMSO) δ 166.0, 163.0, 162.3, 155.4, 124.3, 111.9, 108.9, 100.5, 88.5, 55.9 ppm. **IR (thin film)**: ν (cm^{-1}) 3072, 2988, 2748, 2595, 1697, 1614. **HRMS (ESI)** calculated for $C_{10}H_8O_4Na$ $[M+Na]^+$: 215.0315, found: 215.0325.

7-Chloro-4-hydroxy-2*H*-chromen-2-one (5g)



5g (300.2 mg, 15% yield) was obtained as a pink solid following the similar procedure for the synthesis of **5b**. **M.p.**: 227.3-229.5 °C. **^{1}H NMR** (400 MHz, DMSO) δ 7.81 (d, J = 8.4 Hz, 1H), 7.55 (d, J = 2.0 Hz, 1H), 7.40 (dd, J = 8.4, 2.0 Hz, 1H), 5.59 (s, 1H) ppm. **^{13}C NMR** (100 MHz, DMSO) δ 165.2, 161.5, 154.0, 136.9, 124.8, 124.2, 116.5, 114.9, 91.0 ppm. **IR (thin film)**: ν (cm^{-1}) 3406, 3094, 2929, 1679, 1624, 1602, 777. **HRMS** (ESI) calculated for $C_9H_5{}^{35}ClO_3Na$ $[M+Na]^+$: 218.9819, found: 218.9822. **HRMS** (ESI) calculated for $C_9H_5{}^{37}ClO_3Na$ $[M+Na]^+$: 220.9793, found: 220.9804.

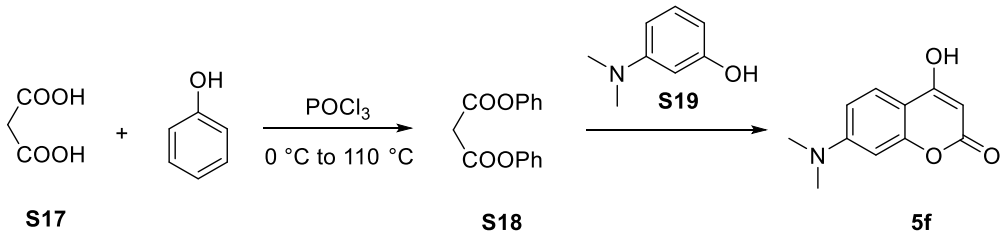
4-Hydroxy-6-nitro-2*H*-chromen-2-one (5d)[7]



S16 **5d**

To a solution of potassium nitrate (687.5 mg, 6.8 mmol) in sulphuric acid at 0 °C was added 4-hydroxy-2*H*-chromen-2-one **S16** (1.0 g, 6.2 mmol) in portions. After being stirred at 0 °C for 1 h, the solution was poured into cold water. The produced solid was filtered and purified by recrystallization with ethanol to give **5d** (834.8 mg, 65% yield) as a pale yellow solid. **M.p.**: 237.2-238.5 °C. **^{1}H NMR** (400 MHz, DMSO) δ 8.52 (d, J = 2.4 Hz, 1H), 8.44 (dd, J = 9.0, 2.5 Hz, 1H), 7.60 (d, J = 9.0 Hz, 1H), 5.70 (s, 1H) ppm. **^{13}C NMR** (100 MHz, DMSO) δ 164.5, 160.8, 157.1, 143.2, 127.3, 119.1, 118.1, 116.4, 92.0 ppm. The data are consistent with that reported in the literature.[7]

7-(Dimethylamino)-4-hydroxy-2*H*-chromen-2-one (5f)[8]

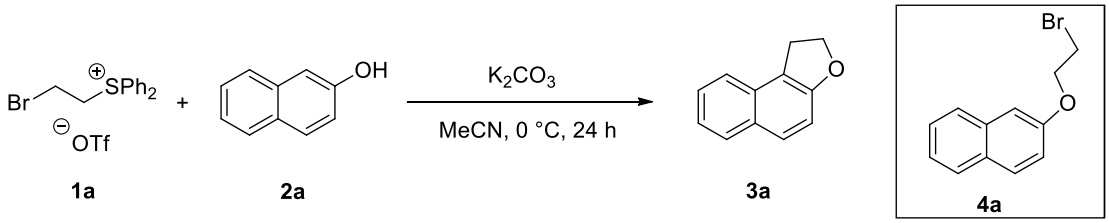


To a mixture of malonic acid **S17** (5.2 g, 49.9 mmol) and phenol (9.4 g, 100 mmol) was slowly added $POCl_3$ (9.3 mL, 100.0 mmol) at 0 °C. Then the mixture was stirred at 110 °C until the release of HCl was ceased. The upper layer of the reaction mixture was poured into water (150.0 mL). The mixture was extracted with ethyl acetate, dried over anhydrous Na_2SO_4 and evaporated under vacuum. Diphenyl malonate **S18** (12.3 g, 90% yield) was obtained as pale brown oil, which was used in the next step without further purification.

To a solution of diphenyl malonate **S18** (1.5 g, 5.9 mmol) in toluene (20.0 mL) was added 3-*N,N*-dimethylaminophenol **S19** (685.9 mg, 5.0 mmol). The mixture was heated to reflux and stirred for 7 h. The precipitation was filtered and recrystallized from 70% EtOH (aq.) to give **5f** (719 mg, 70% yield) as a purple solid. **M.p.**: 252.3-253.6 °C. **^{1}H NMR** (400 MHz, DMSO) δ 7.56 (d, J = 8.8 Hz, 1H), 7.72–7.65 (m, 1H), 6.51–6.45 (m, 1H), 5.28 (s, 1H), 3.00 (s, 6H) ppm. **^{13}C NMR** (100 MHz, DMSO) δ 166.5, 162.8, 155.8, 153.4, 123.8, 108.6, 104.1, 97.9, 86.5, 39.7 ppm. The data are consistent with that reported in the literature.[8]

3.2 Experiment procedures and characterization data of products 3a-3l and 6a-6h

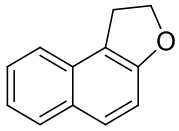
3.2.1 General procedure for the synthesis of 3a-3l



1a 2a 3a 4a

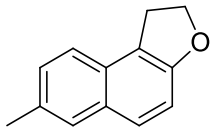
A solution of **2a** (28.8 mg, 0.2 mmol), **1a** (122.2 mg, 0.3 mmol) and K_2CO_3 (82.9 mg, 0.6 mmol) in MeCN (4.0 mL) was stirred at 0 °C under an argon atmosphere for 24 h. Then piperazine (17.2 mg, 0.2 mmol) was added and the reaction mixture was stirred at 60 °C for 5 h to remove the side product **4a**. After being cooled down to room temperature, water (10 mL) was added. Then mixture was extracted with ethyl acetate (10 mL × 2). The combined organic layer was dried over anhydrous Na_2SO_4, filtered and evaporated under vacuum. The residue was purified by column chromatography to give the product **3a**.

1,2-Dihydronaphtho[2,1-*b*]furan (3a)



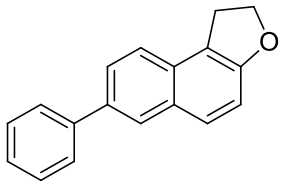
The product **3a** (31.0 mg, 91% yield) was obtained as colorless liquid following the general procedure. **R*f*** = 0.3 (petroleum ether). **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.83 (d, J = 8.2 Hz, 1H), 7.69 (d, J = 8.7 Hz, 1H), 7.61 (d, J = 8.3 Hz, 1H), 7.51–7.46 (m, 1H), 7.35–7.29 (m, 1H), 7.14 (d, J = 8.7 Hz, 1H), 4.81–4.73 (m, 2H), 3.54–3.46 (m, 2H) ppm. **^{13}C NMR** (100 MHz, $CDCl_3$) δ 157.8, 131.0, 129.3, 129.0, 128.8, 126.8, 122.9, 122.9, 118.7, 112.2, 71.9, 28.8 ppm. **IR (thin film)**: ν (cm^{-1}) 3057, 2966, 2894, 1631, 1521, 1463, 1259, 1244. **HRMS** (EI) calculated for $C_{12}H_{10}O$ $[M]^+$: 170.0726, found: 170.0727.

7-Methyl-1,2-dihydronaphtho[2,1-*b*]furan (3b)



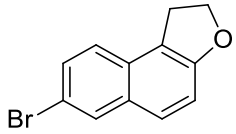
The product **3b** (33.9 mg, 92% yield) was obtained as a white solid following the general procedure. **M.p.**: 70.2–71.3 °C. **R*f*** = 0.2 (petroleum ether). **^{1}H NMR** (400 MHz, CDCl3) δ 7.61–7.58 (m, 2H), 7.52 (d, J = 8.4 Hz, 1H), 7.35–7.30 (m, 1H), 7.10 (d, J = 8.8 Hz, 1H), 4.78–4.72 (m, 2H), 3.51–3.44 (m, 2H), 2.49 (s, 3H) ppm. **^{13}C NMR** (100 MHz, $CDCl_3$) δ 157.2, 132.3, 129.6, 129.1, 129.0, 128.2, 127.8, 122.7, 118.6, 112.1, 71.7, 28.8, 21.6 ppm. **IR (thin film)**: ν (cm^{-1}) 2967, 2894, 1602, 1479, 1356, 1243, 1160, 811. **HRMS** (EI) calculated for $C_{13}H_{12}O$ $[M]^+$: 184.0883, found: 184.0882.

7-Phenyl-1,2-dihydronaphtho[2,1-*b*]furan (3c)



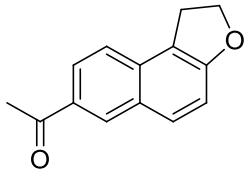
The product **3c** (42.4 mg, 86% yield) was obtained as a white solid following the general procedure. **M.p.**: 133.1–134.6 °C. **R*f*** = 0.8 (petroleum ether/ethyl acetate = 10:1). **^{1}H NMR** (400 MHz, $CDCl_3$) δ 8.04 (d, J = 1.5 Hz, 1H), 7.79–7.66 (m, 5H), 7.53–7.47 (m, 2H), 7.41–7.36 (m, 1H), 7.17 (d, J = 8.7 Hz, 1H), 4.83–4.76 (m, 2H), 3.55–3.48 (m, 2H) ppm. **^{13}C NMR** (100 MHz, $CDCl_3$) δ 158.0, 141.4, 135.7, 130.1, 129.6, 129.4, 129.0, 127.3, 127.2, 126.8, 126.5, 123.5, 118.7, 112.6, 72.0, 28.8 ppm. **IR (thin film)**: ν (cm^{-1}) 3062, 2956, 2890, 1601, 1496, 1241. **HRMS** (EI) calculated for $C_{18}H_{14}O$ $[M]^+$: 246.1039, found: 246.1037.

7-Bromo-1,2-dihydronaphtho[2,1-*b*]furan (3d)



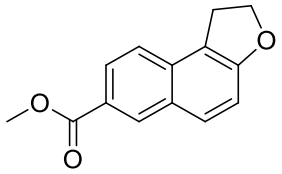
The product **3d** (46.3 mg, 93% yield) was obtained as a white solid following the general procedure. **M.p.**: 63.1–64.9 °C. **R*f*** = 0.7 (petroleum ether/ethyl acetate = 10:1). **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.94 (d, J = 1.9 Hz, 1H), 7.56 (d, J = 8.8 Hz, 1H), 7.52 (dd, J = 8.8, 1.9 Hz, 1H), 7.43 (d, J = 8.8 Hz, 1H), 7.13 (d, J = 8.8 Hz, 1H), 4.79–4.72 (m, 2H), 3.48–3.40 (m, 2H) ppm. **^{13}C NMR** (100 MHz, $CDCl_3$) δ 158.2, 130.7, 130.4, 130.0, 129.4, 128.2, 124.6, 119.0, 116.4, 113.2, 71.9, 28.7 ppm. **IR (thin film):** ν (cm^{-1}) 2963, 2895, 1620, 1586, 1347, 1243, 811. **HRMS (EI)** calculated for $C_{12}H_9{}^{79}BrO$ $[M]^+$: 247.9831, found: 247.9833. **HRMS (EI)** calculated for $C_{12}H_9{}^{81}BrO$ $[M]^+$: 249.9816, found: 249.9814.

1-(1,2-Dihydronaphtho[2,1-*b*]furan-7-yl)ethanone (3e)



The product **3e** (35.7 mg, 84% yield) was as a white solid obtained following the general procedure. **M.p.**: 101.8–103.0 °C. **R*f*** = 0.4 (petroleum ether/ethyl acetate = 10:1). **^{1}H NMR** (400 MHz, CDCl3) δ 8.42 (d, J = 1.5 Hz, 1H), 8.03 (dd, J = 8.7, 1.7 Hz, 1H), 7.79 (d, J = 8.7 Hz, 1H), 7.61 (d, J = 8.7 Hz, 1H), 7.17 (d, J = 8.8 Hz, 1H), 4.85–4.76 (m, 2H), 3.54–3.46 (m, 2H), 2.69 (s, 3H) ppm. **^{13}C NMR** (100 MHz, $CDCl_3$) δ 197.8, 160.2, 133.2, 132.0, 131.3, 131.2, 128.1, 125.0, 123.2, 119.2, 113.1, 72.3, 28.4, 26.5 ppm. **IR (thin film)**: ν (cm^{-1}) 2947, 2912, 2854, 1663, 1624, 1476, 1357, 1242, 1187. **HRMS** (ESI) calculated for $C_{14}H_{12}O_2Na$ $[M+Na]^+$: 235.0730, found: 235.0723.

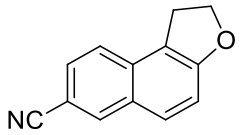
Methyl 1,2-dihydronaphtho[2,1-*b*]furan-7-carboxylate (3f)



The product **3f** (36.1 mg, 79% yield) was obtained as a white solid following the general procedure. **M.p.**: 93.7–94.8 °C. **R*f*** = 0.5 (petroleum ether/ethyl acetate = 10:1). **^{1}H**

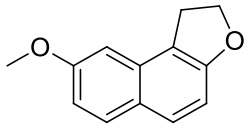
NMR (400 MHz, CDCl3) δ 8.54 (d, J = 1.3 Hz, 1H), 8.03 (dd, J = 8.7, 1.6 Hz, 1H), 7.77 (d, J = 8.8 Hz, 1H), 7.57 (d, J = 8.7 Hz, 1H), 7.15 (d, J = 8.8 Hz, 1H), 4.81–4.74 (m, 2H), 3.94 (s, 3H), 3.50–3.42 (m, 2H) ppm. **^{13}C NMR** (100 MHz, $CDCl_3$) δ 167.5, 160.0, 133.2, 132.1, 130.9, 128.2, 126.3, 124.5, 122.9, 119.0, 113.0, 72.2, 52.2, 28.5 ppm. **IR (thin film)**: ν (cm^{-1}) 2948, 2911, 2855, 1709, 1624, 1479, 1280, 1241, 1197. **HRMS** (ESI) calculated for $C_{14}H_{12}O_3Na$ $[M+Na]^+$: 251.0679, found: 251.0684.

1,2-Dihydronaphtho[2,1-*b*]furan-7-carbonitrile (3g)



The product **3g** (21.1 mg, 54% yield) was obtained as a white solid following the general procedure. **M.p.**: 115.6–117.9 °C. **R*f*** = 0.4 (petroleum ether/ethyl acetate = 10:1). **^{1}H NMR** (400 MHz, CDCl3) δ 8.19–8.16 (m, 1H), 7.73 (d, J = 8.8 Hz, 1H), 7.64 (d, J = 8.6 Hz, 1H), 7.58 (dd, J = 8.6, 1.4 Hz, 1H), 7.22 (d, J = 8.8 Hz, 1H), 4.87–4.78 (m, 2H), 3.54–3.46 (m, 2H) ppm. **^{13}C NMR** (100 MHz, $CDCl_3$) δ 160.6, 135.0, 132.4, 130.1, 128.0, 127.3, 124.0, 119.8, 119.44, 114.0, 106.0, 72.4, 28.3 ppm. **IR (thin film)**: ν (cm^{-1}) 3052, 2921, 2853, 2221, 1625, 1473, 1359, 1264, 1243, 1159. **HRMS** (ESI) calculated for $C_{13}H_9NONa$ $[M+Na]^+$: 218.0568, found: 218.0576.

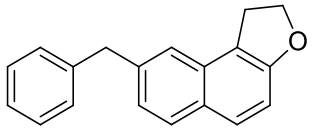
8-Methoxy-1,2-dihydronaphtho[2,1-*b*]furan (3h)



The product **3h** (31.2 mg, 78% yield) was obtained as a white solid following the general procedure. **M.p.**: 133.2–134.2 °C. **R*f*** = 0.7 (petroleum ether/ethyl acetate = 10:1). **^{1}H NMR** (400 MHz, CDCl3) δ 7.70 (d, J = 9.0 Hz, 1H), 7.60 (d, J = 8.7 Hz, 1H), 7.00–6.95 (m, 2H), 6.83 (d, J = 2.4 Hz, 1H), 4.79–4.72 (m, 2H), 3.93 (s, 3H), 3.47–3.39 (m, 2H) ppm. **^{13}C NMR** (100 MHz, $CDCl_3$) δ 158.6, 158.4, 132.2, 130.4, 128.8, 124.8, 117.8, 115.5, 109.6, 101.4, 71.8, 55.4, 28.8 ppm. **IR (thin film)**: ν (cm^{-1}) 3010, 2965,

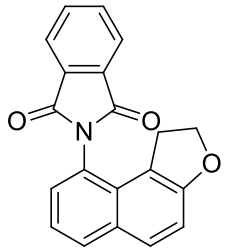
2022, 1629, 1516, 1472, 1244, 1224. **HRMS** (EI) calculated for $C_{13}H_{12}O_2$ $[M]^+$: 200.0832, found: 200.0831.

8-Benzyl-1,2-dihydronaphtho[2,1-*b*]furan (3i)



The product **3i** (32.8 mg, 63% yield) was obtained as a white solid following the general procedure. **M.p.**: 98.1–99.3 °C. **R*f*** = 0.1 (petroleum ether). **^{1}H NMR** (400 MHz, CDCl3) δ 7.69 (d, J = 8.4 Hz, 1H), 7.60 (d, J = 8.7 Hz, 1H), 7.40–7.37 (m, 1H), 7.30–7.25 (m, 2H), 7.23–7.16 (m, 3H), 7.12 (dd, J = 8.4, 1.5 Hz, 1H), 7.05 (d, J = 8.7 Hz, 1H), 4.75–4.67 (m, 2H), 4.11 (s, 2H), 3.45–3.37 (m, 2H) ppm. **^{13}C NMR** (100 MHz, $CDCl_3$) δ 158.0, 141.2, 139.6, 131.2, 129.1, 129.0, 128.8, 128.6, 128.0, 126.3, 124.8, 122.3, 118.4, 111.6, 72.0, 42.5, 28.8 ppm. **IR (thin film)**: ν (cm^{-1}) 3039, 2965, 2924, 2904, 2847, 1633, 1601, 1512, 1453, 1245. **HRMS** (EI) calculated for $C_{19}H_{16}O$ $[M]^+$: 260.1196, found: 260.1194.

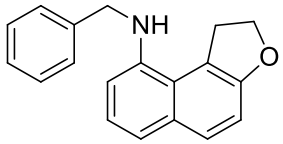
2-(1,2-Dihydronaphtho[2,1-*b*]furan-9-yl)isoindoline-1,3-dione (3j)



The product **3j** (44.1 mg, 70% yield) was obtained as a yellow solid following the general procedure. **M.p.**: 213.8.1–215.8 °C. **R*f*** = 0.6 (petroleum ether/ethyl acetate/DCM = 5:1:1). **^{1}H NMR** (400 MHz, CDCl3) δ 8.05–7.99 (m, 2H), 7.94 (dd, J = 8.3, 1.2 Hz, 1H), 7.86–7.81 (m, 2H), 7.77 (d, J = 8.8 Hz, 1H), 7.41–7.36 (m, 1H), 7.34 (dd, J = 7.2, 1.4 Hz, 1H), 7.15 (d, J = 8.8 Hz, 1H), 4.57–4.50 (m, 2H), 3.24–3.16 (m, 2H) ppm. **^{13}C NMR** (100 MHz, $CDCl_3$) δ 168.2, 159.9, 134.6, 132.5, 131.4, 131.2, 130.5, 129.9, 129.2, 125.6, 124.3, 122.6, 115.2, 113.22, 71.5, 29.8 ppm. **IR (thin film)**:

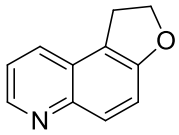
ν (cm^{-1}) 2960, 2921, 2852, 1719, 1378, 1247, 1111, 1084. **HRMS** (ESI) calculated for $C_{20}H_{13}NO_3Na$ $[M+Na]^+$: 338.0788, found: 338.0784.

_N_-benzyl-1,2-dihydronaphtho[2,1-*b*]furan-9-amine (3k)



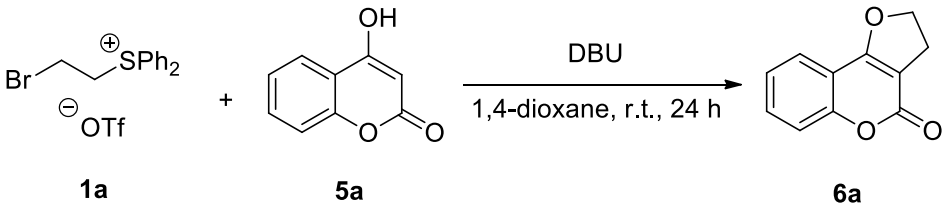
The product **3k** (33.0 mg, 60% yield) was obtained as a yellow solid following the general procedure. **M.p.**: 136.7–138.6 °C. **R*f*** = 0.7 (petroleum ether/ethyl acetate = 10:1). **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.59 (d, J = 8.7 Hz, 1H), 7.47–7.43 (m, 2H), 7.42–7.36 (m, 2H), 7.35–7.30 (m, 1H), 7.23–7.19 (m, 1H), 7.16–7.10 (m, 1H), 7.06 (d, J = 8.7 Hz, 1H), 6.58 (d, J = 7.4 Hz, 1H), 4.69–4.59 (m, 2H), 4.39 (s, 2H), 3.86–3.78 (m, 2H) ppm. **^{13}C NMR** (100 MHz, $CDCl_3$) δ 157.8, 143.7, 139.3, 131.1, 129.9, 128.9, 127.8, 127.5, 123.8, 123.3, 119.3, 115.8, 112.1, 106.4, 71.0, 49.3, 32.7 ppm. **IR (thin film)**: ν (cm^{-1}) 3390, 2921, 2895, 1591, 1525, 1429, 1282, 1248. **HRMS** (ESI) calculated for $C_{19}H_{18}NO$ $[M+H]^+$: 276.1384, found: 276.1383.

1,2-Dihydrofuro[3,2-*f*]quinoline (3l)



The product **3l** (21.2 mg, 62% yield) was obtained as a yellow solid following the general procedure. **M.p.**: 83.4–86.9 °C. **R*f*** = 0.2 (petroleum ether/ethyl acetate = 10:1). **^{1}H NMR** (400 MHz, CDCl3) δ 8.77–8.72 (m, 1H), 7.97–7.89 (m, 2H), 7.37–7.29 (m, 2H), 4.84–4.79 (m, 2H), 3.51–3.42 (m, 2H) ppm. **^{13}C NMR** (100 MHz, $CDCl_3$) δ 158.0, 147.5, 144.8, 131.0, 130.5, 126.0, 121.5, 118.5, 115.4, 72.3, 28.4 ppm. **IR (thin film)**: ν (cm^{-1}) 2970, 2905, 2852, 1618, 1510, 1474, 1254, 1232. **HRMS** (ESI) calculated for $C_{11}H_{10}NO$ $[M+H]^+$: 172.0757, found: 172.0757.

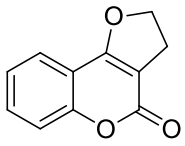
3.2.2 General procedure for the synthesis of 6a-6h



1a 5a 6a

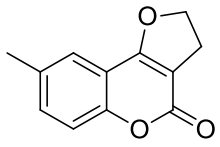
To a solution of **5a** (32.4 mg, 0.2 mmol) and **1a** (122.2 mg, 0.3 mmol) in 1,4-dioxane (4.0 mL) was added DBU (91.3 mg, 0.6 mmol). The mixture was stirred at room temperature for 24 h. Water (10 mL) was added and the mixture was extracted with ethyl acetate (10 mL × 2). The combined organic layer was dried over anhydrous Na_2SO_4, filtered and evaporated under vacuum. The residue was purified by column chromatography to give **6a**.

2*H*-furo[3,2-*c*]chromen-4(3*H*)-one (6a)



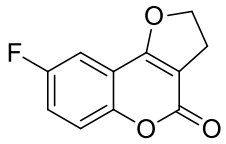
The product **6a** (31.2 mg, 83% yield) was obtained as a white solid following the general procedure. **M.p.**: 143.3–145.5 °C. **R*f*** = 0.2 (petroleum ether/ethyl acetate = 5:1). **^{1}H NMR** (400 MHz, CDCl3) δ 7.64 (dd, J = 7.8, 1.6 Hz, 1H), 7.58–7.52 (m, 1H), 7.39–7.35 (m, 1H), 7.30–7.25 (m, 1H), 4.92–4.84 (m, 2H), 3.24–3.16 (m, 2H) ppm. **^{13}C NMR** (100 MHz, $CDCl_3$) δ 167.5, 160.9, 155.0, 132.5, 124.1, 122.8, 117.1, 112.7, 102.5, 74.5, 27.0 ppm. **IR (thin film)**: ν (cm^{-1}) 2916, 1708, 1644, 1640, 1500, 1419, 1328, 1275, 1249. **HRMS** (ESI) calculated for $C_{11}H_8O_3Na$ $[M+Na]^+$: 211.0358, found: 211.0366.

8-Methyl-2*H*-furo[3,2-*c*]chromen-4(3*H*)-one (6b)



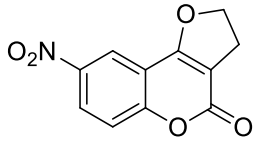
The product **6b** (25.1 mg, 62% yield) was obtained as a white solid following the general procedure. **M.p.**: 154.1–155.7 °C. **R*f*** = 0.4 (petroleum ether/ethyl acetate = 5:1). **^{1}H NMR** (400 MHz, CDCl3) δ 7.44–7.42 (m, 1H), 7.37 (dd, J = 8.5, 1.9 Hz, 1H), 7.29–7.27 (m, 1H), 4.92–4.84 (m, 2H), 3.25–3.16 (m, 2H), 2.42 (s, 3H) ppm. **^{13}C NMR** (100 MHz, $CDCl_3$) δ 167.4, 161.0, 153.2, 133.8, 133.5, 122.4, 116.7, 112.4, 102.4, 74.5, 27.0, 20.9 ppm. **IR (thin film)**: ν (cm^{-1}) 2977, 2954, 2925, 2866, 1714, 1646, 1491, 1206, 1097, 1437, 1401, 1375. **HRMS** (ESI) calculated for $C_{12}H_{10}O_3Na$ $[M+Na]^+$: 225.0517, found: 225.0522.

8-Fluoro-2*H*-furo[3,2-*c*]chromen-4(3*H*)-one (6c)



The product **6c** (35.9 mg, 87% yield) was obtained as a white solid following the general procedure. **M.p.**: 161.6–163.7 °C. **R*f*** = 0.2 (petroleum ether/ethyl acetate = 5:1). **^{1}H NMR** (400 MHz, CDCl3) δ 7.40–7.25 (m, 3H), 4.96–4.87 (m, 2H), 3.28–3.19 (m, 2H) ppm. **^{19}F NMR** (376 MHz, DMSO) δ -117.12 ppm. **^{13}C NMR** (100 MHz, $CDCl_3$) δ 166.7 (d, $^4J_{CF}$ = 2.8 Hz), 160.5, 158.5 (d, $^1J_{CF}$ = 244.6 Hz), 151.1 (d, $^4J_{CF}$ = 2.1 Hz), 120.0 (d, $^2J_{CF}$ = 24.6 Hz), 118.7 (d, $^3J_{CF}$ = 8.3 Hz), 113.4 (d, $^3J_{CF}$ = 9.3 Hz), 108.4 (d, $^2J_{CF}$ = 25.2 Hz), 103.5, 74.7, 27.0 ppm. **IR (thin film)**: ν (cm^{-1}) 3070, 2921, 2852, 1714, 1647, 1575, 1499, 1445, 1259, 1185, 1033. **HRMS** (ESI) calculated for $C_{11}H_8FO_3$ $[M+H]^+$: 207.0450, found: 207.0452.

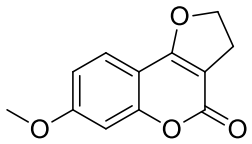
8-Nitro-2*H*-furo[3,2-*c*]chromen-4(3*H*)-one (6d)



The product **6d** (31.7 mg, 68% yield) was obtained as a pale yellow solid following the general procedure. **M.p.**: 189.2–191.8 °C. **R*f*** = 0.2 (petroleum ether/ethyl acetate = 5:1). **^{1}H NMR** (400 MHz, $CDCl_3$) δ 8.55 (d, J = 2.5 Hz, 1H), 8.41 (dd, J = 9.2, 2.6 Hz,

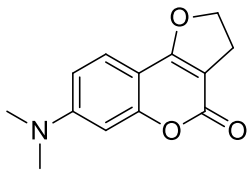
1H), 7.49 (d, *J* = 9.2 Hz, 1H), 5.01–4.91 (m, 2H), 3.30–3.20 (m, 2H) ppm. **^{13}C NMR** (100 MHz, $CDCl_3$) δ 166.3, 159.1, 158.2, 143.8, 127.1, 119.3, 118.2, 113.0, 104.3, 75.1, 27.1 ppm. **IR (thin film)**: ν (cm^{-1}) 3082, 2975, 2919, 2851,1726, 1648, 1620, 1528, 1492, 1433, 1403, 1336, 1265, 1126, 1072. **HRMS** (EI) calculated for $C_{11}H_7NO_5$ $[M]^+$: 233.0320, found: 233.0324.

7-Methoxy-2*H*-furo[3,2-*c*]chromen-4(3*H*)-one (6e)



The product **6e** (34.9 mg, 80% yield) was obtained as a white solid following the general procedure. **M.p.**: 144.1–146.4 °C. **R*f*** = 0.2 (petroleum ether/ethyl acetate = 5:1). **^{1}H NMR** (400 MHz, CDCl3) δ 7.52–7.46 (m, 1H), 6.86–6.77 (m, 2H), 4.86–4.77 (m, 2H), 3.84 (s, 3H), 3.18–3.09 (m, 2H) ppm. **^{13}C NMR** (100 MHz, $CDCl_3$) δ 167.8, 163.4, 161.1, 156.9, 123.7, 112.4, 106.0, 100.8, 99.5, 74.5, 55.8, 26.7 ppm. **IR (thin film)**: ν (cm^{-1}) 3009, 2976, 2910, 1738, 1643, 1614, 1419, 1275, 1156, 1090. **HRMS** (ESI) calculated for $C_{12}H_{10}O_4Na$ $[M+Na]^+$: 241.0459, found: 241.0471.

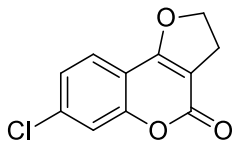
7-(Dimethylamino)-2*H*-furo[3,2-*c*]chromen-4(3*H*)-one (6f)



The product **6f** (30.1 mg, 65% yield) was obtained as a pink solid following the general procedure. **M.p.**: 171.8–173.7 °C. **R*f*** = 0.4 (petroleum ether/ethyl acetate = 5:2). **^{1}H NMR** (400 MHz, CDCl3) δ 7.41 (d, *J* = 8.8 Hz, 1H), 6.58 (dd, *J* = 8.8, 2.3 Hz, 1H), 6.52 (d, *J* = 2.3 Hz, 1H), 4.83–4.73 (m, 2H), 3.15–3.06 (m, 2H), 3.03 (s, 6H) ppm. **^{13}C NMR** (100 MHz, $CDCl_3$) δ 168.3, 161.8, 157.3, 153.5, 123.3, 108.8, 101.5, 98.1, 97.1, 74.3, 40.2, 26.6 ppm. **IR (thin film)**: ν (cm^{-1}) 2918, 2875, 2852, 1693, 1622, 1545,

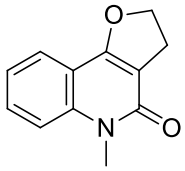
1527, 1425, 1327, 1272, 1248, 1092. **HRMS** (ESI) calculated for $C_{13}H_{13}NO_3Na$ $[M+Na]^+$: 254.0787, found: 254.0788.

7-Chloro-2*H*-furo[3,2-*c*]chromen-4(3*H*)-one (6g)



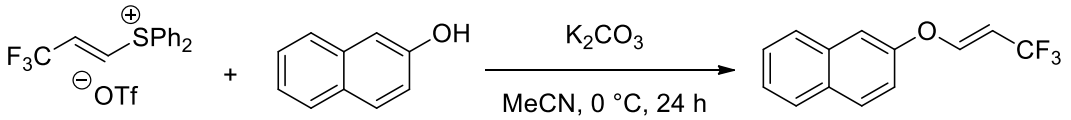
The product **6g** (16.9 mg, 38% yield) was obtained as a white solid following the general procedure. **M.p.**: 201.6–204.1 °C. **R*f*** = 0.3 (petroleum ether/ethyl acetate = 5:1). **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.55 (d, J = 8.4 Hz, 1H), 7.36 (d, J = 1.8 Hz, 1H), 7.25 (dd, J = 7.2, 1.8 Hz, 1H), 4.93–4.83 (m, 2H), 3.24–3.13 (m, 2H) ppm. **^{13}C NMR** (100 MHz, $CDCl_3$) δ 166.9, 160.2, 155.2, 138.5, 124.7, 123.7, 117.4, 111.3, 102.5, 74.7, 26.9 ppm. **IR (thin film)**: ν (cm^{-1}) 3084, 2920, 2851, 1723, 1641, 1419, 1104, 1026, 741. **HRMS** (ESI) calculated for $C_{11}H_7{}^{35}ClO_3Na$ $[M+Na]^+$: 244.9976, found: 244.9974. **HRMS** (ESI) calculated for $C_{11}H_7{}^{37}ClO_3Na$ $[M+Na]^+$: 246.9950, found: 246.9946.

5-Methyl-2,3-dihydrofuro[3,2-*c*]quinolin-4(5*H*)-one (6h)



The product **6h** (13.7 mg, 34% yield) was obtained as a white solid following the general procedure. **M.p.**: 130.2–132.7 °C. **R*f*** = 0.2 (petroleum ether/ethyl acetate = 5:3). **^{1}H NMR** (400 MHz, CDCl3) δ 7.73 (dd, J = 7.9, 1.4 Hz, 1H), 7.56 (ddd, J = 8.7, 7.3, 1.5 Hz, 1H), 7.38–7.36 (d, J = 8.6 Hz, 1H), 7.24–7.19 (m, 1H), 4.86–4.75 (m, 2H), 3.70 (s, 3H), 3.29–3.18 (m, 2H) ppm. **^{13}C NMR (**100 MHz, $CDCl_3$) δ 163.1, 161.6, 140.7, 131.0, 123.1, 121.7, 114.6, 112.7, 108.5, 73.5, 29.2, 28.1 ppm. **IR (thin film)**: ν (cm^{-1}) 2970, 2921, 2860, 1657, 1621, 1576, 1424, 1106, 752. **HRMS** (ESI) calculated for $C_{12}H_{11}NO_2Na$ $[M+Na]^+$: 224.0684, found: 224.0682.

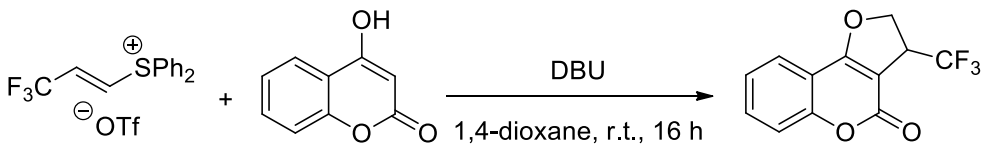
3.3 Reaction of (*E*)-diphenyl-*β*-(trifluoromethyl)vinylsulfonium triflate 7b with β-naphthol 2a



7b **2a** **8a**

The solution of **2a** (28.8 mg, 0.2 mmol), K_2CO_3 (82.9 mg, 0.6 mmol) and (*E*)-diphenyl-*β*-(trifluoromethyl)vinylsulfonium triflate **7b** (129.1 mg, 0.3 mmol) in MeCN (4.0 mL) was stirred at 0 °C under an argon atmosphere for 24 h. Water (10 mL) was added and the mixture was extracted with ethyl acetate (10 mL × 2). The combined organic layer was dried over anhydrous Na_2SO_4, filtered and evaporated under vacuum. The residue was purified by column chromatography to give (*E*)-2-((3,3,3-trifluoroprop-1-en-1-yl)oxy)naphthalene (**8a**) as a colorless liquid (11.9 mg, 25% yield). **R*f*** = 0.5 (petroleum ether/DCM = 10:1). **^{1}H NMR** (400 MHz, CDCl3) *δ* 7.88–7.81 (m, 2H), 7.81–7.76 (m, 1H), 7.54–7.43 (m, 2H), 7.42–7.39 (m, 1H), 7.30–7.26 (m, 1H), 6.91–6.87 (m, 1H), 5.14–5.03 (m, 1H) ppm. **^{19}F NMR** (376 MHz, $CDCl_3$) *δ* -57.60 ppm. **^{13}C NMR** (100 MHz, $CDCl_3$) *δ* 154.5, 149.3 (q, $^3J_{CF}$ = 5.3 Hz), 134.1, 130.9, 130.4, 128.0, 127.4, 127.2, 125.5, 123.0 (q, $^1J_{CF}$ = 269.4 Hz), 118.4, 112.6, 99.8 (q, $^2J_{CF}$ = 35.3 Hz) ppm. **IR (thin film)**: ν (cm^{-1}) 2924, 2853, 1678, 1630, 1598, 1248. **HRMS** (EI) calculated for $C_{13}H_9F_3O$ $[M]^+$: 238.0600, found: 238.0601.

3.4 Reaction of (*E*)-diphenyl-*β*-(trifluoromethyl)vinylsulfonium triflate 7b with 4-hydroxycoumarin 5a

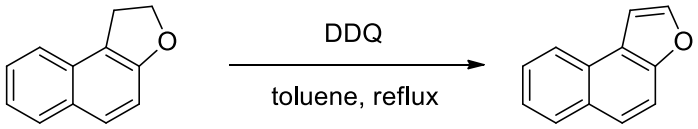


7b **5a** **8b**

A solution of 4-hydroxycoumarin **5a** (32.4 mg, 0.2 mmol), (*E*)-diphenyl-*β*-(trifluoromethyl)vinylsulfonium triflate **7b** (129.1 mg, 0.3 mmol) and DBU (91.3 mg, 0.6 mmol) in 1,4-dioxane (4.0 mL) was stirred at room temperature for 16 h. Water (10 mL) was added and the mixture was extracted with ethyl acetate (10 mL × 2). The

combined organic layer was dried over anhydrous Na_2SO_4, filtered and evaporated under vacuum. The residue was purified by column chromatography to give 3-(Trifluoromethyl)-2*H*-furo[3,2-*c*]chromen-4(3*H*)-one (**8b**) as a white solid (19.0 mg, 37% yield). **M.p.**: 127.9–131.2 °C. **R*f*** = 0.6 (petroleum ether/ethyl acetate = 5:2). **^{1}H NMR** (400 MHz, CDCl3) δ 7.74–7.57 (m, 2H), 7.39 (d, J = 8.4 Hz, 1H), 7.35–7.27 (m, 1H), 5.09–4.99 (m, 1H), 4.96–4.86 (m, 1H), 4.26–4.14 (m, 1H) ppm. **^{19}F NMR** (376 MHz, $CDCl_3$) δ -71.37 ppm. **^{13}C NMR** (100 MHz, $CDCl_3$) δ 170.2, 158.9, 155.6, 133.9, δ 125.5 (q, $^1J_{CF}$ = 280.4 Hz), 124.4, 123.3, 117.3, 111.8, 97.5 (q, $^3J_{CF}$ = 2.0 Hz), 74.1 (q, $^3J_{CF}$ = 3.0 Hz), 45.1 (q, $^2J_{CF}$ = 31.7 Hz) ppm. **IR (thin film)**: ν (cm^{-1}) 3098, 2975, 2923, 1706, 1646, 1271. **HRMS** (ESI) calculated for $C_{12}H_7F_3O_3Na$ $[M+Na]^+$: 279.0239, found: 279.0240.

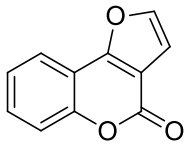
3.5 Synthesis of furans 9a and 9b



3a **9a**

To a solution of **3a** (34.0 mg, 0.2 mmol) in toluene (4.0 mL) was added DDQ (49.9 mg, 0.22 mmol). The solution was heated to reflux overnight. The precipitation was filtered and the filtrate was evaporated under vacuum. The residue The residue was purified by column chromatography to give naphtho[2,1-*b*]furan **9a** (36.9 mg, 99% yield) as a white solid. **M.p.**: 60.4-61.5 °C. **^{1}H NMR** (400 MHz, $CDCl_3$) δ 8.17 (d, J = 8.2 Hz, 1H), 7.98 (d, J = 8.1 Hz, 1H), 7.79 (d, J = 1.9 Hz, 1H), 7.78–7.68 (m, 2H), 7.65–7.59 (m, 1H), 7.55–7.49 (m, 1H), 7.29 (d, J = 1.9 Hz, 1H). **^{13}C NMR** (100 MHz, $CDCl_3$) δ 152.6, 144.2, 130.4, 128.8, 127.9, 126.3, 125.2, 124.5, 123.5, 122.7, 112.6, 105.6. **IR (thin film)**: ν (cm^{-1}) 3144, 3052, 2922, 2852, 1622, 1510, 810, 749. HRMS (EI) calculated for $C_{12}H_8O$ $[M]^+$: 168.0570, found: 168.0570.

4*H*-furo[3,2-*c*]chromen-4-one (9b)



The product **9b** (27.9 mg, 75% yield) was obtained as a pink solid via a similar procedure except DDQ (68.1 mg, 0.3 mmol) was used. **M.p.**: 96.8-98.7 °C. **^{1}H NMR** (500 MHz, $CDCl_3$) δ 7.86 (d, J = 7.7 Hz, 1H), 7.66–7.62 (m, 1H), 7.54–7.48 (m, 1H), 7.45–7.41 (m, 1H), 7.37–7.31 (m, 1H), 7.01–7.98 (m, 1H). **^{13}C NMR** (125 MHz, $CDCl_3$) δ 158.4, 157.8, 152.7, 144.9, 130.9, 124.7, 121.0, 117.4, 112.9, 110.8, 108.7. **IR (thin film)**: ν (cm^{-1}) 3125, 3079, 1738, 1630, 1495, 753, 727. HRMS (EI) calculated for $C_{11}H_6O_3$ $[M]^+$: 186.0311, found: 186.0312.

4. **References**

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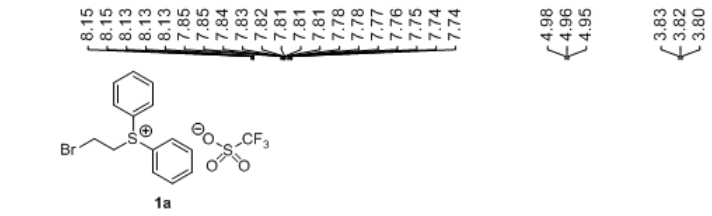
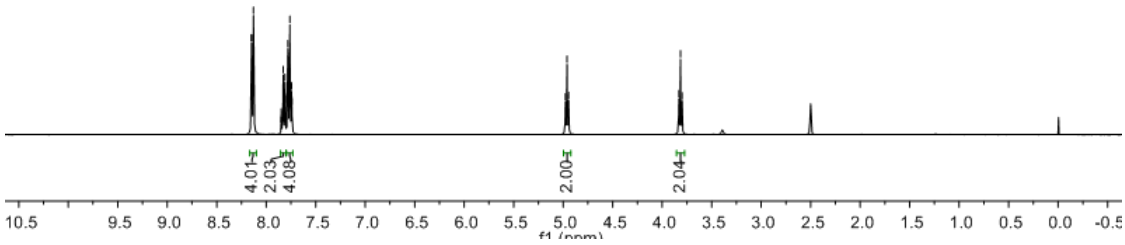
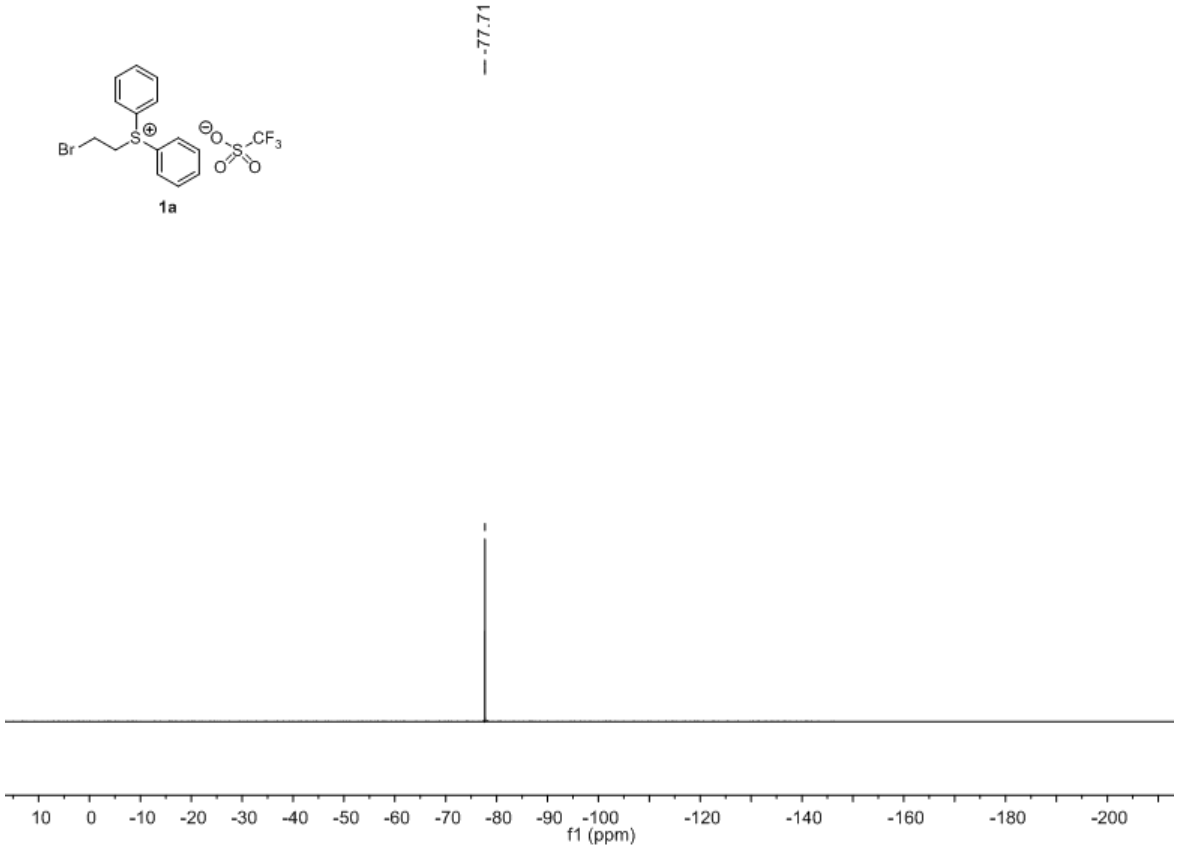
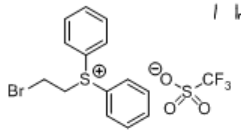
5. NMR Spectra





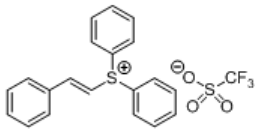



Br
S
O
O
O
S
O
CF3

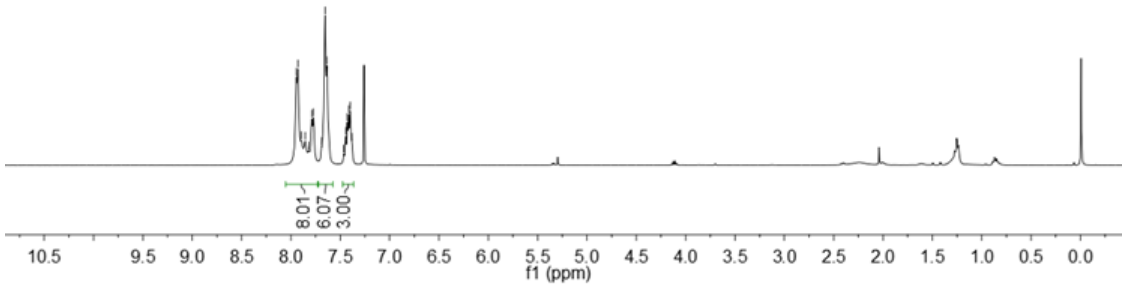
1a

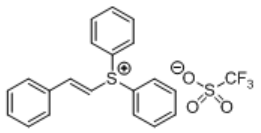
134.4
131.2
130.9
124.8
45.4
24.9
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0


7.95
7.93
7.90
7.86
7.82
7.79
7.77
7.69
7.65
7.64
7.46
7.45
7.43
7.42
7.40
7.38


S
O
O
O
S
O
CF3

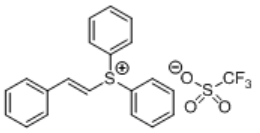
7a


8.01
6.07
3.00
10.5
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)



7a

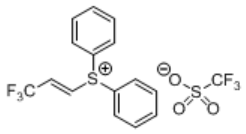
-78.16
10
0
-10
-20
-30
-40
-50
-60
-70
-80
-90
-100
-120
-140
-160
-180
-200
f1 (ppm)



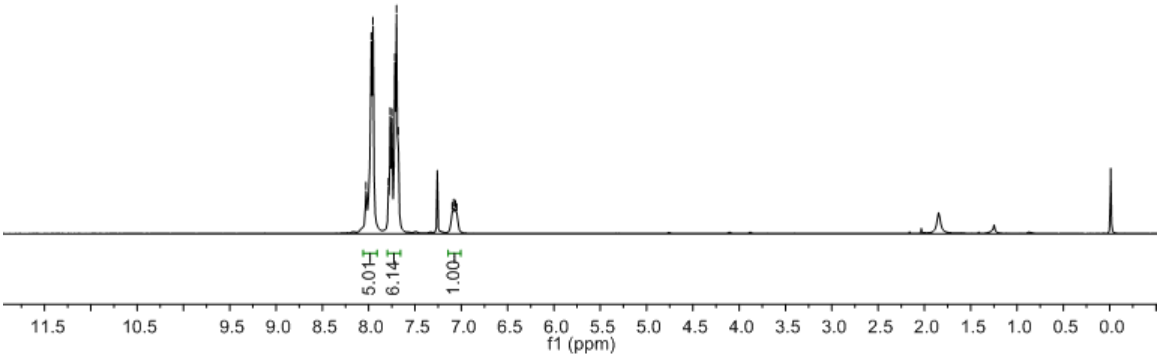
7a

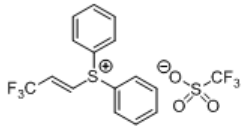
153.5
134.4
132.8
132.2
131.6
130.1
129.8
129.4
127.4
122.6
119.4
110.0
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
f1 (ppm)


8.03
7.97
7.95
7.79
7.77
7.75
7.72
7.70
7.68
7.10
7.08
7.06
7.05


F3C
S
O
S
CF3
O
O

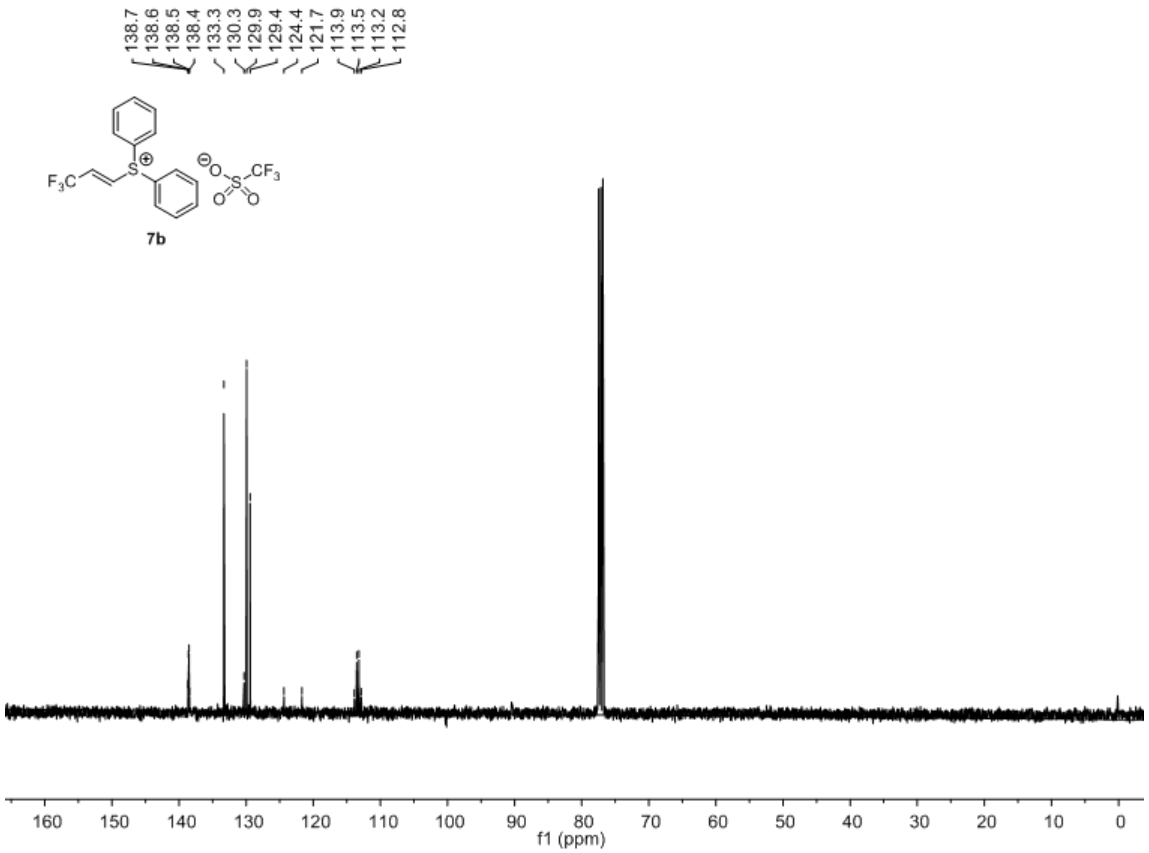
7b

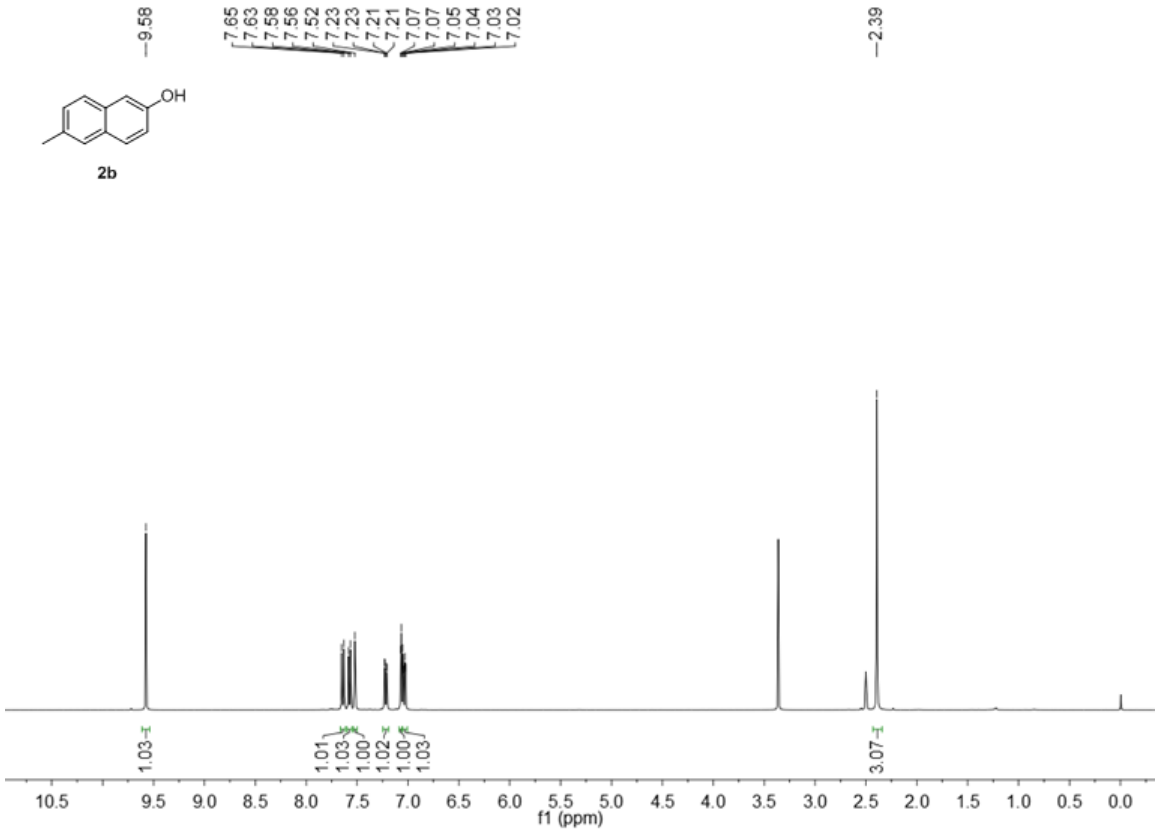

5.01
6.14
1.00
11.5
10.5
9.5
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
f1 (ppm)

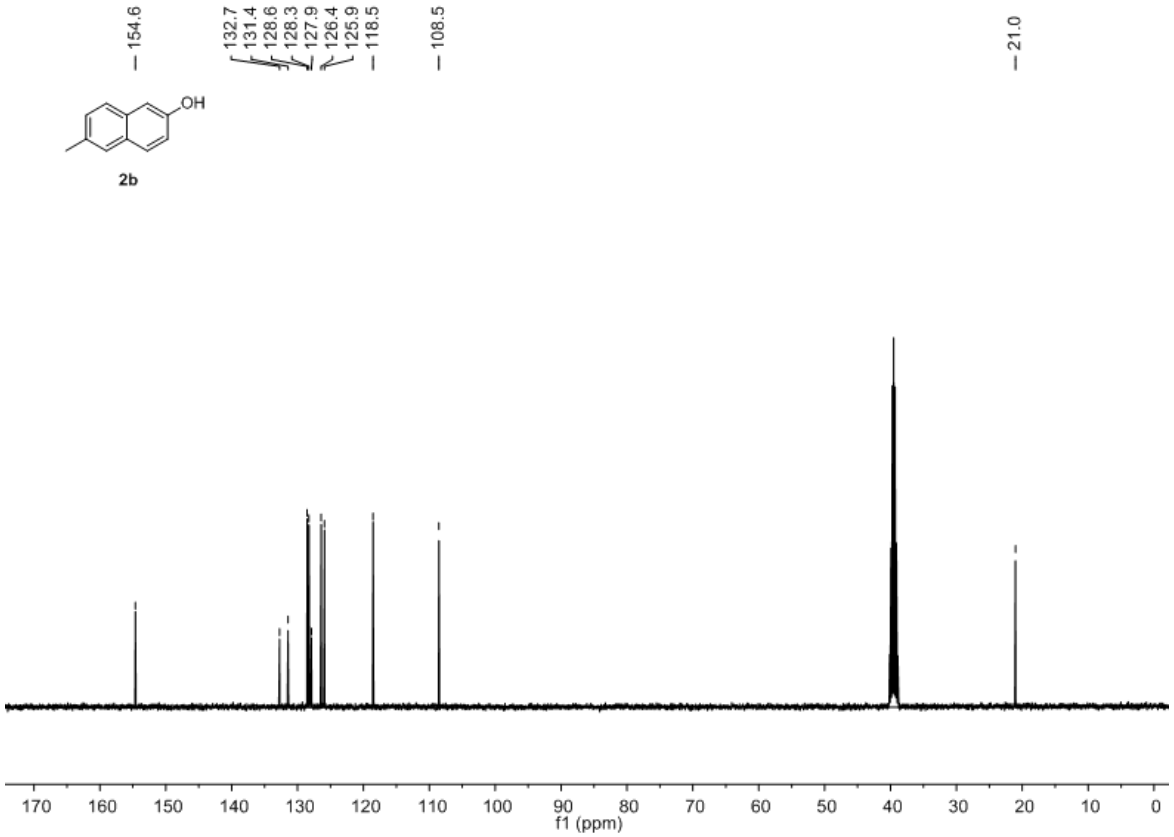

F3C
S
O
S
CF3
O
O

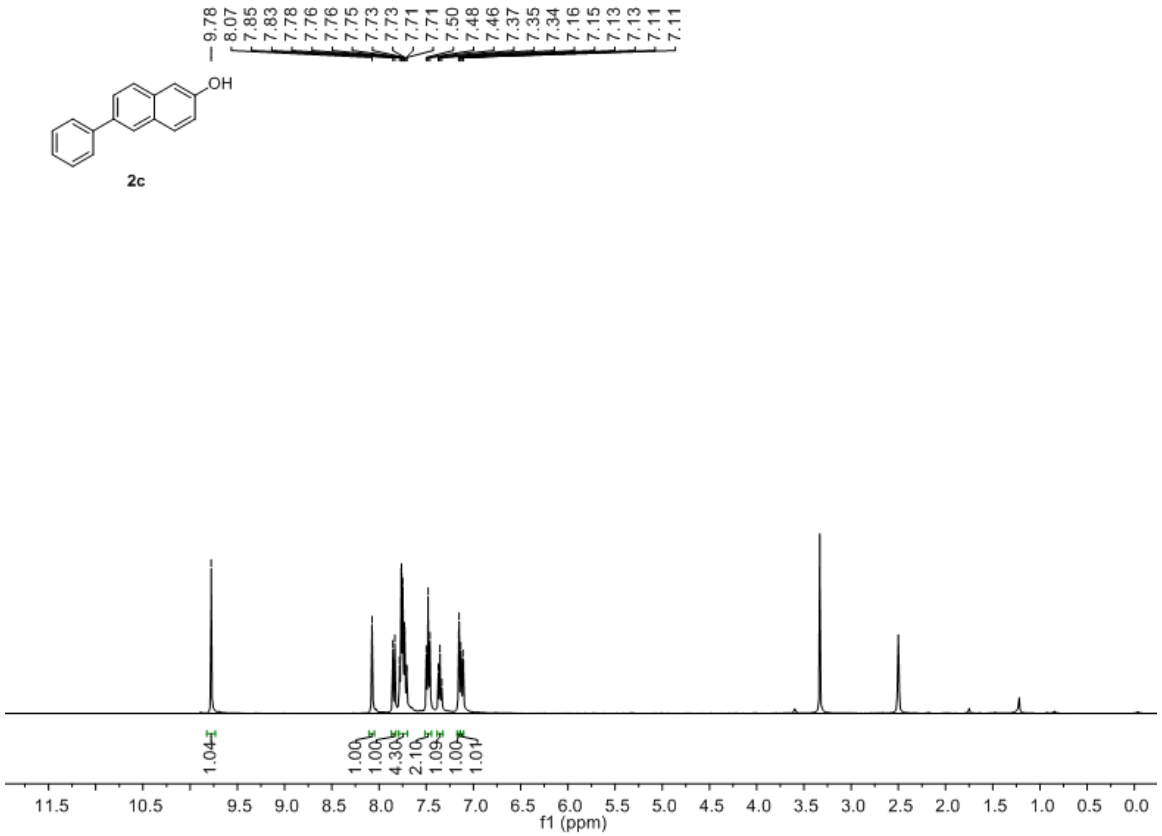
7b

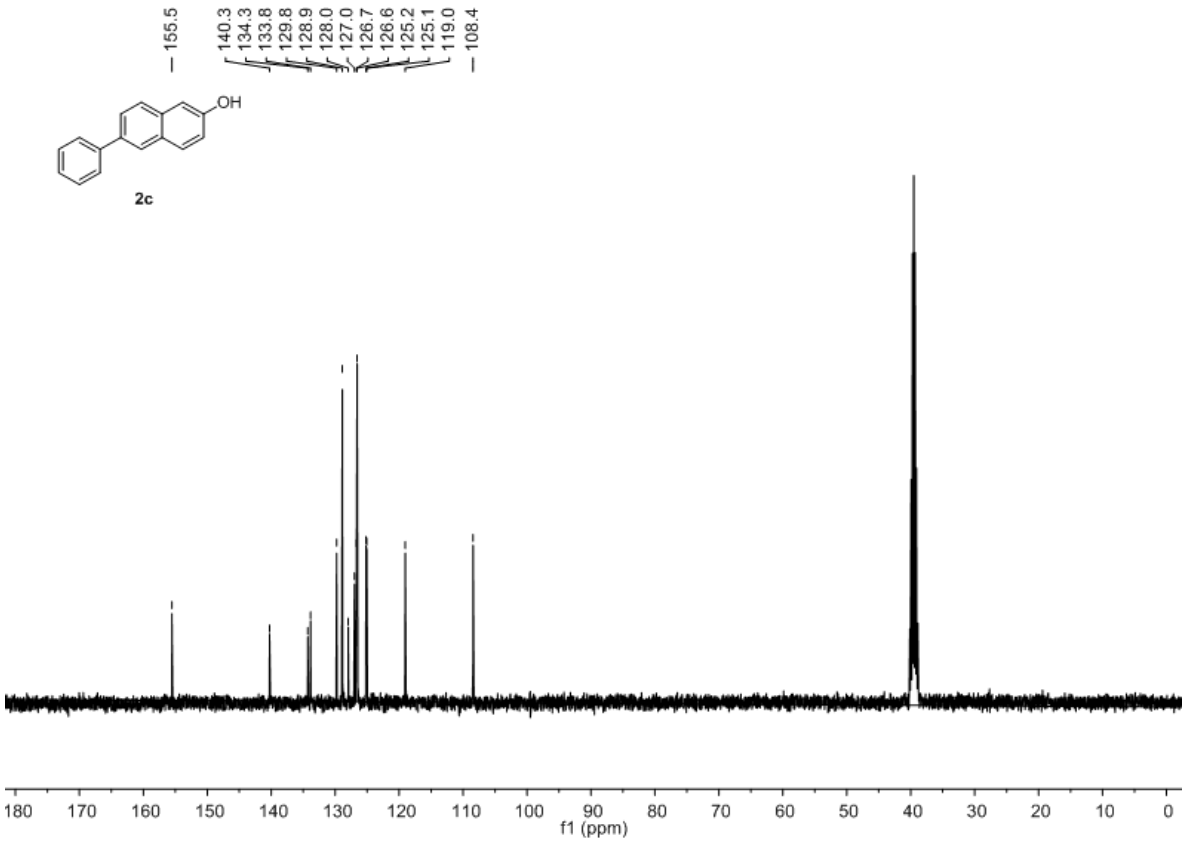
-64.59
-78.45
10
0
-10
-20
-30
-40
-50
-60
-70
-80
-90
-100
-120
-140
-160
-180
-200
f1 (ppm)

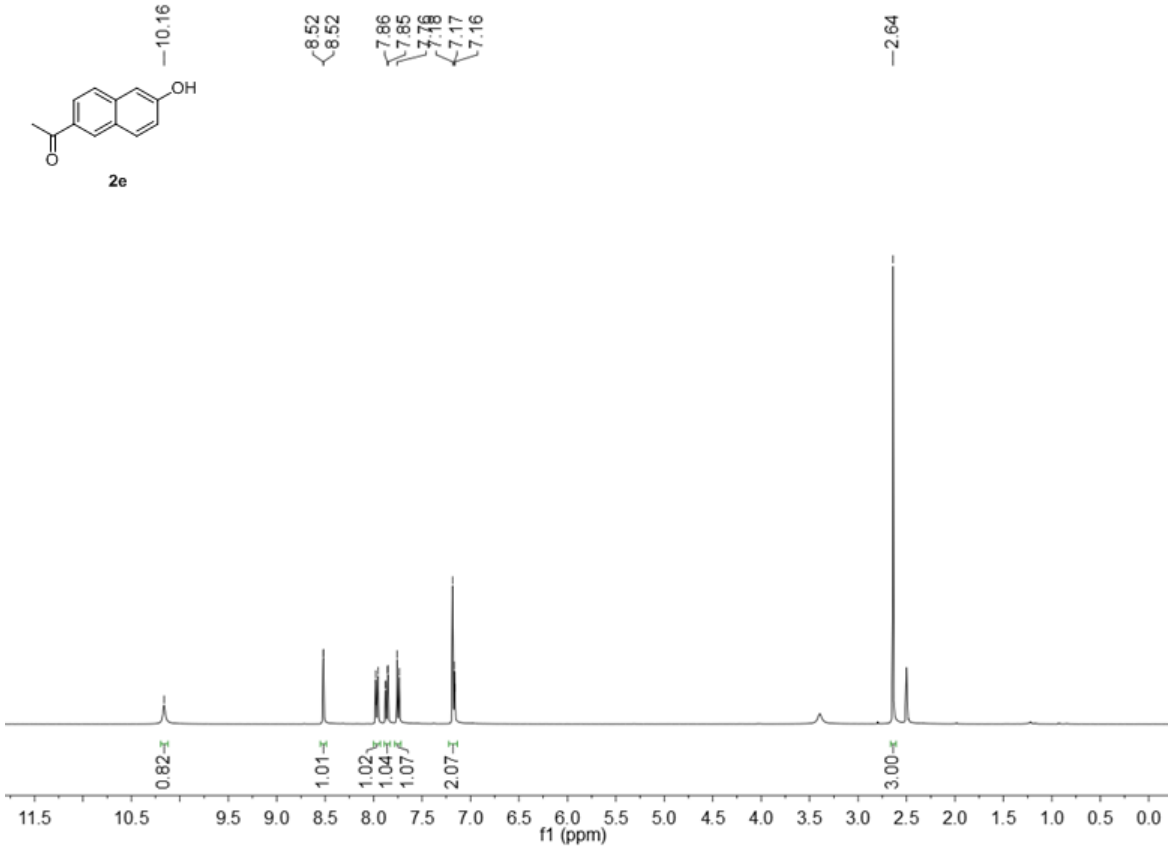

138.7
138.6
138.5
138.4
133.3
130.3
129.9
129.4
124.4
121.7
113.9
113.5
113.2
112.8
F3C
S
O
O
S
CF3
O
O
7b
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
f1 (ppm)

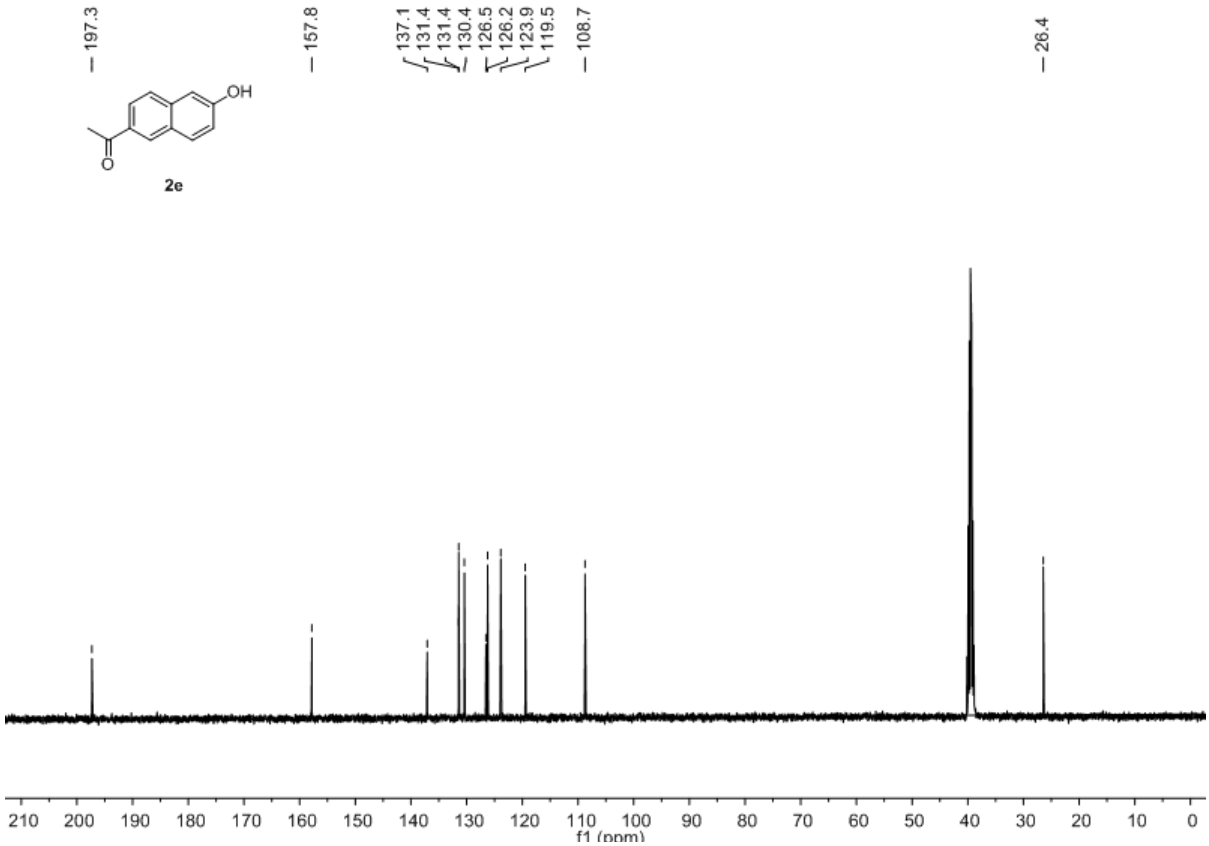

9.58
7.65
7.63
7.58
7.56
7.52
7.23
7.23
7.21
7.21
7.07
7.07
7.05
7.04
7.03
7.02
2.39
OH
2b
1.03
1.01
1.03
1.00
1.02
1.00
1.03
3.07
10.5
9.5
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
f1 (ppm)

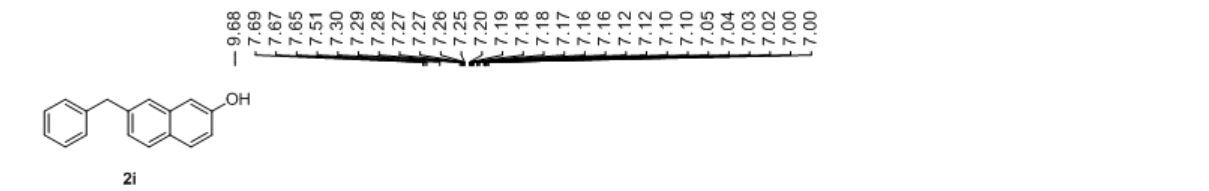

154.6
132.7
131.4
128.6
128.3
127.9
126.4
125.9
118.5
108.5
21.0
OH
2b
170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0
f1 (ppm)

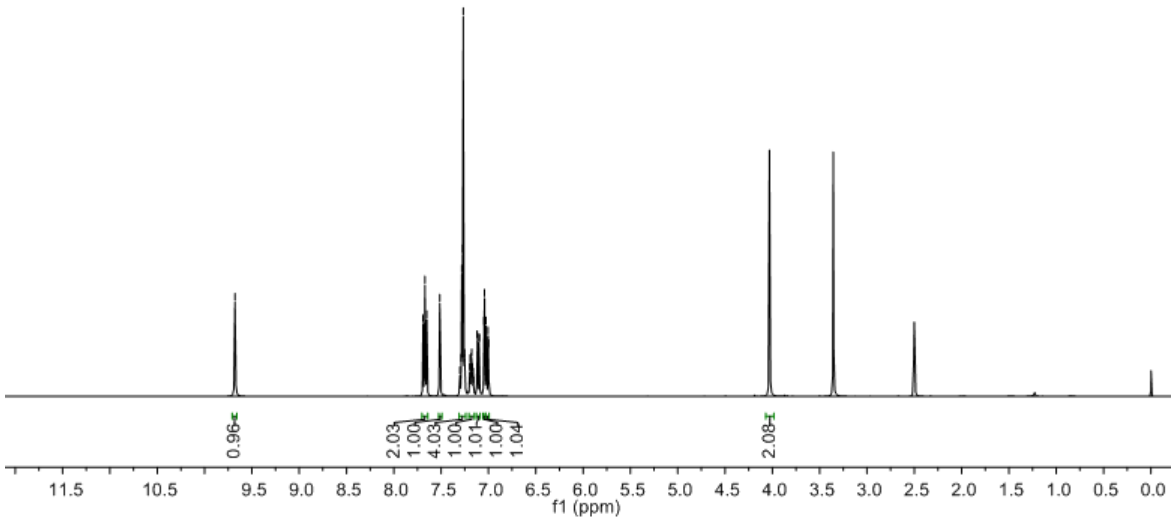

9.78
8.07
7.85
7.83
7.78
7.76
7.76
7.75
7.73
7.73
7.71
7.71
7.50
7.48
7.46
7.37
7.35
7.34
7.16
7.15
7.13
7.13
7.11
7.11
OH
2c
1.04
1.00
1.00
4.30
2.10
1.09
1.00
1.01
11.5 10.5 9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0
f1 (ppm)

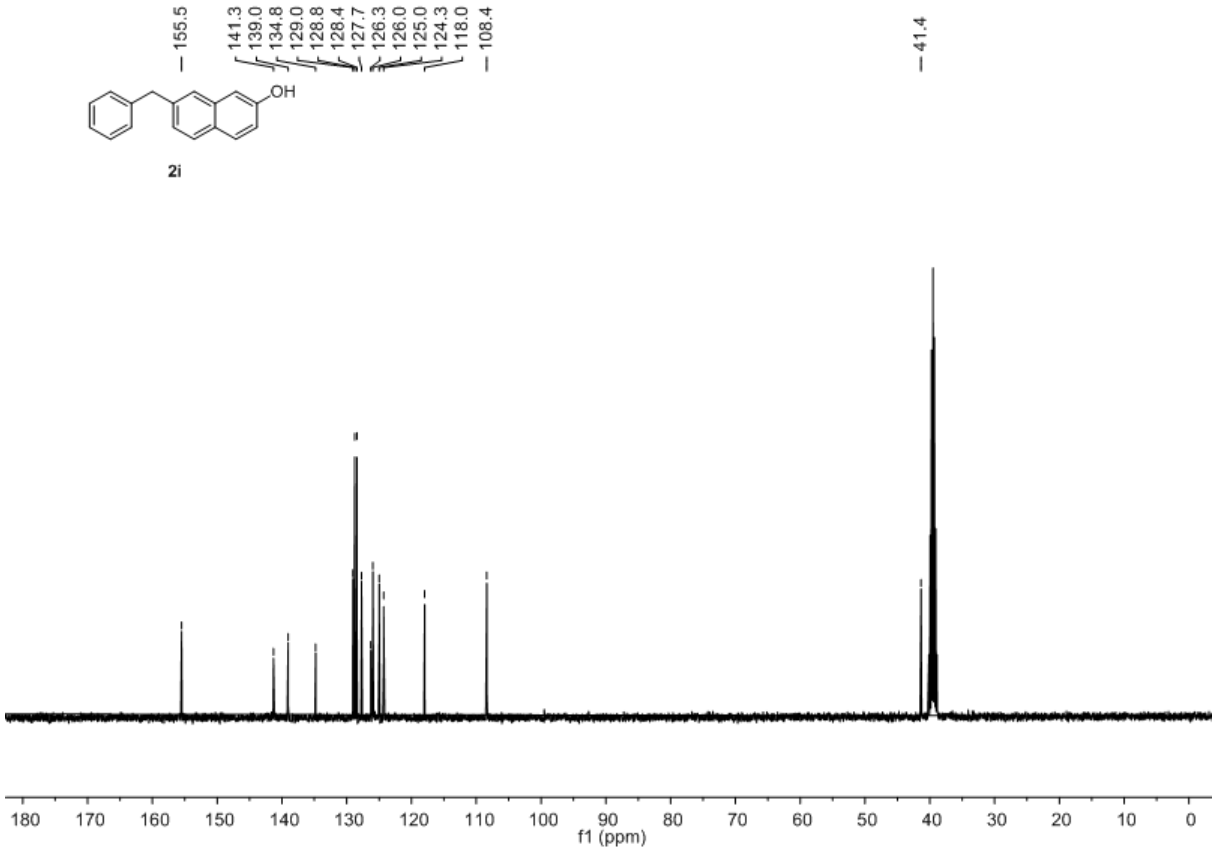

155.5
140.3
134.3
133.8
129.8
128.9
128.0
127.0
126.7
126.6
125.2
125.1
119.0
108.4
OH
2c
180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0
f1 (ppm)

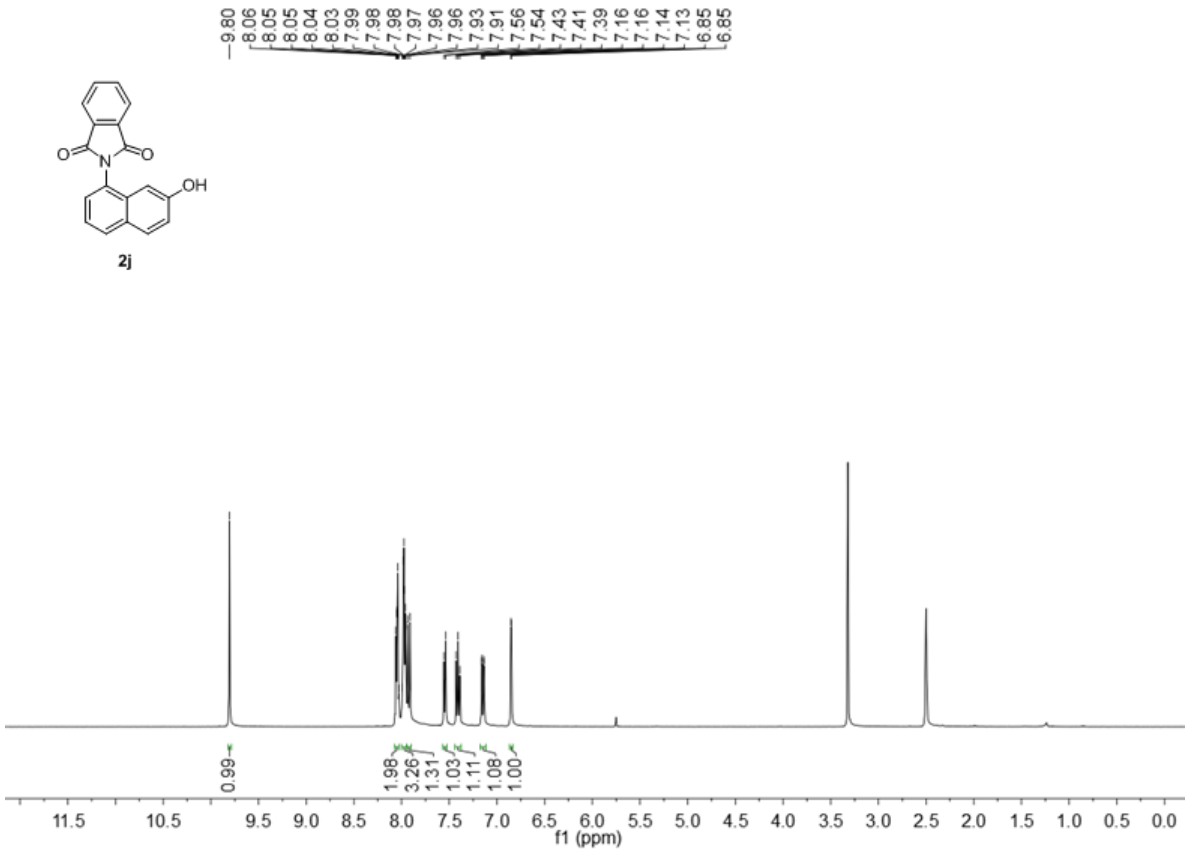

10.16
8.52
8.52
7.86
7.85
7.17
7.16
2.64
OH
O
2e
0.82
1.01
1.02
1.04
1.07
2.07
3.00
11.5 10.5 9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0
f1 (ppm)

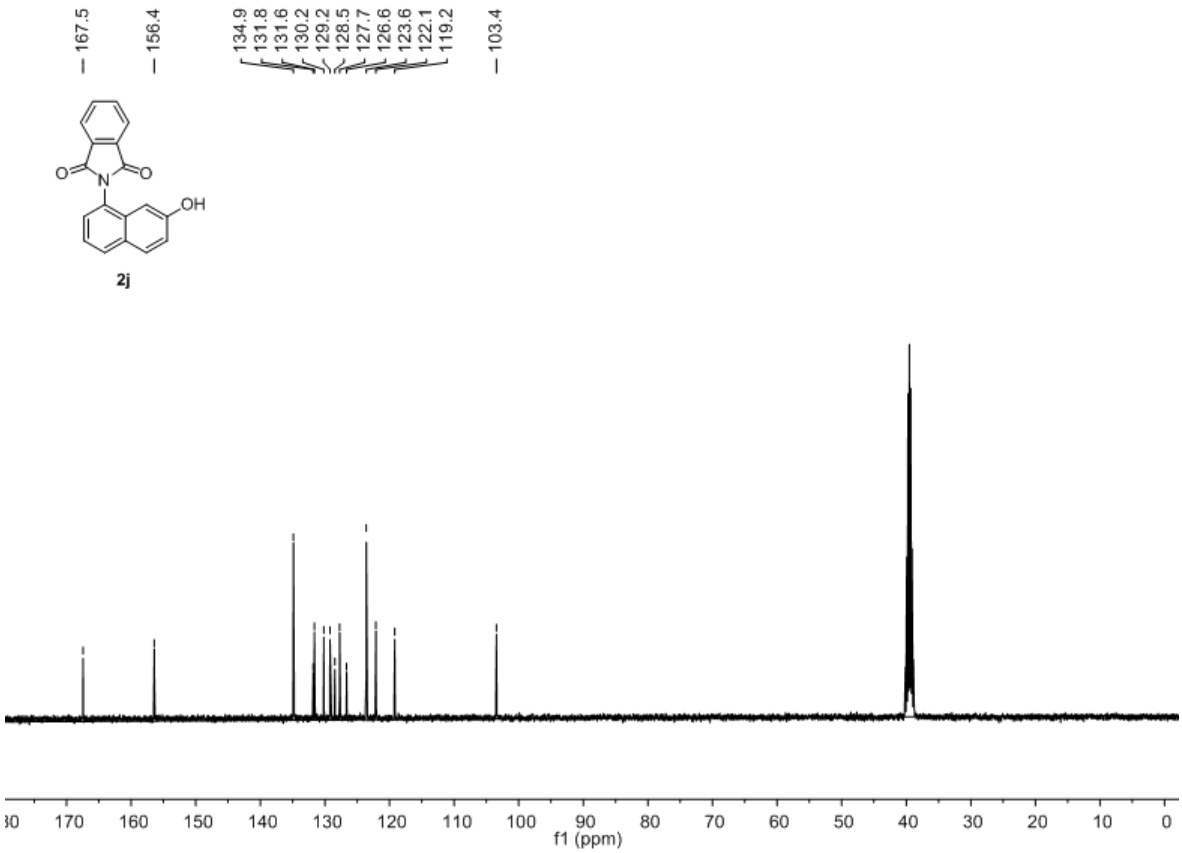

197.3
157.8
137.1
131.4
131.4
130.4
126.5
126.2
123.9
119.5
108.7
26.4
OH
O
2e
f1 (ppm)

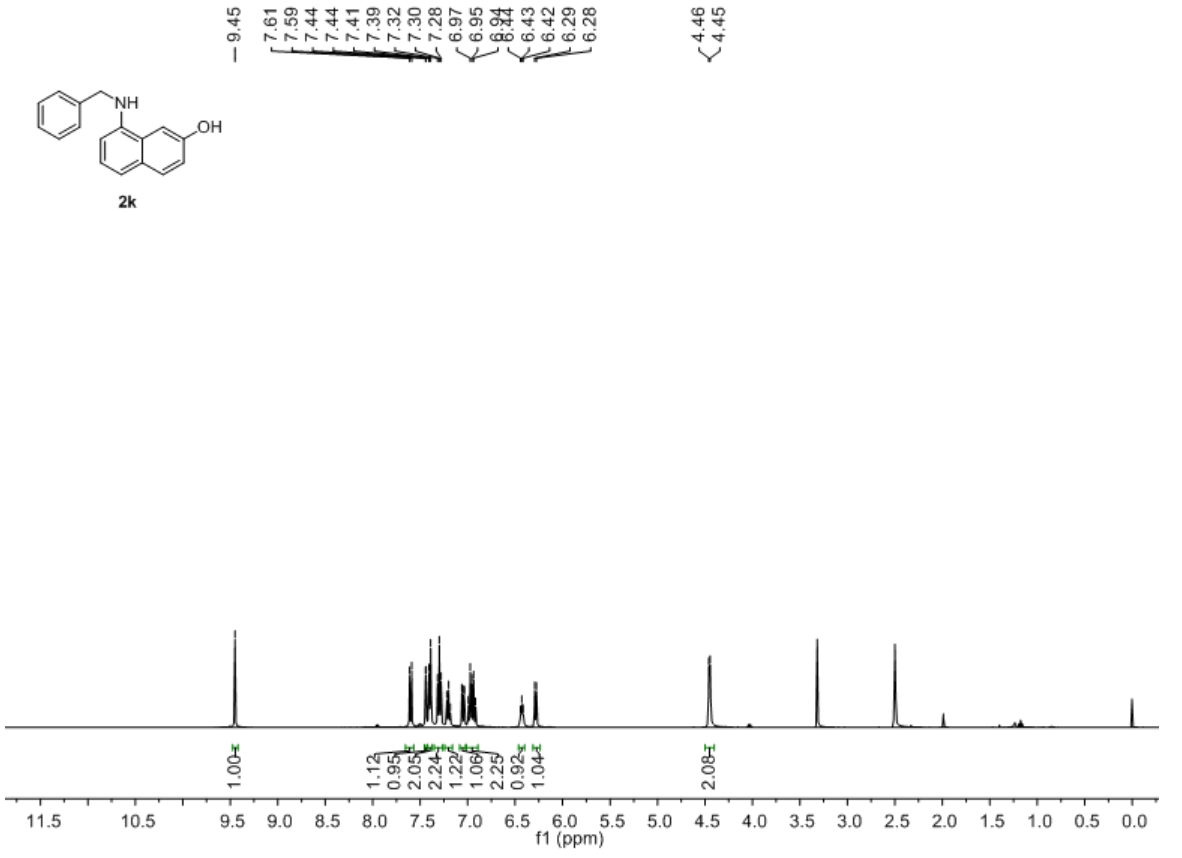

9.68
7.69
7.67
7.65
7.51
7.30
7.29
7.28
7.27
7.27
7.26
7.25
7.20
7.19
7.18
7.18
7.17
7.16
7.16
7.12
7.12
7.10
7.10
7.05
7.04
7.03
7.02
7.00
7.00
OH
2i

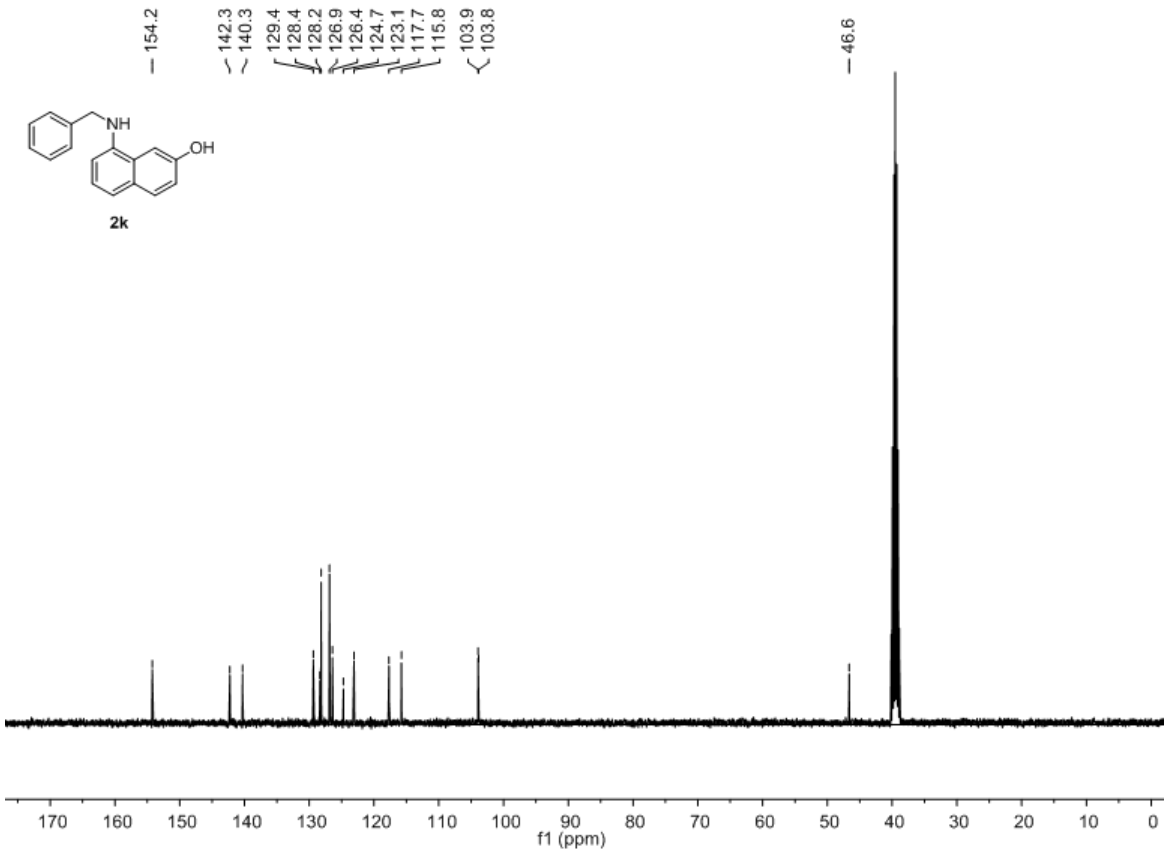

0.96
2.03
1.00
4.03
1.00
1.01
1.00
1.04
2.08
f1 (ppm)

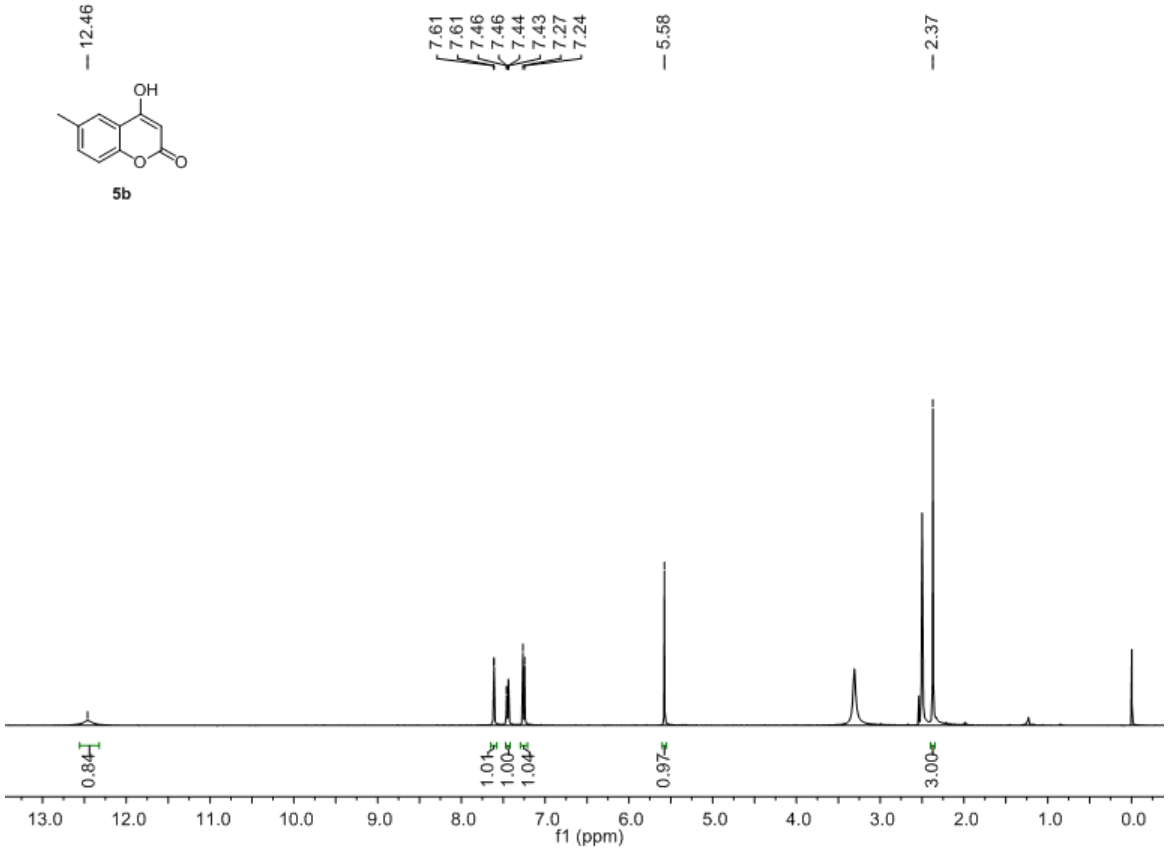

155.5
141.3
139.0
134.8
129.0
128.8
128.4
127.7
126.3
126.0
125.0
124.3
118.0
108.4
41.4
OH
2i
180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0
f1 (ppm)

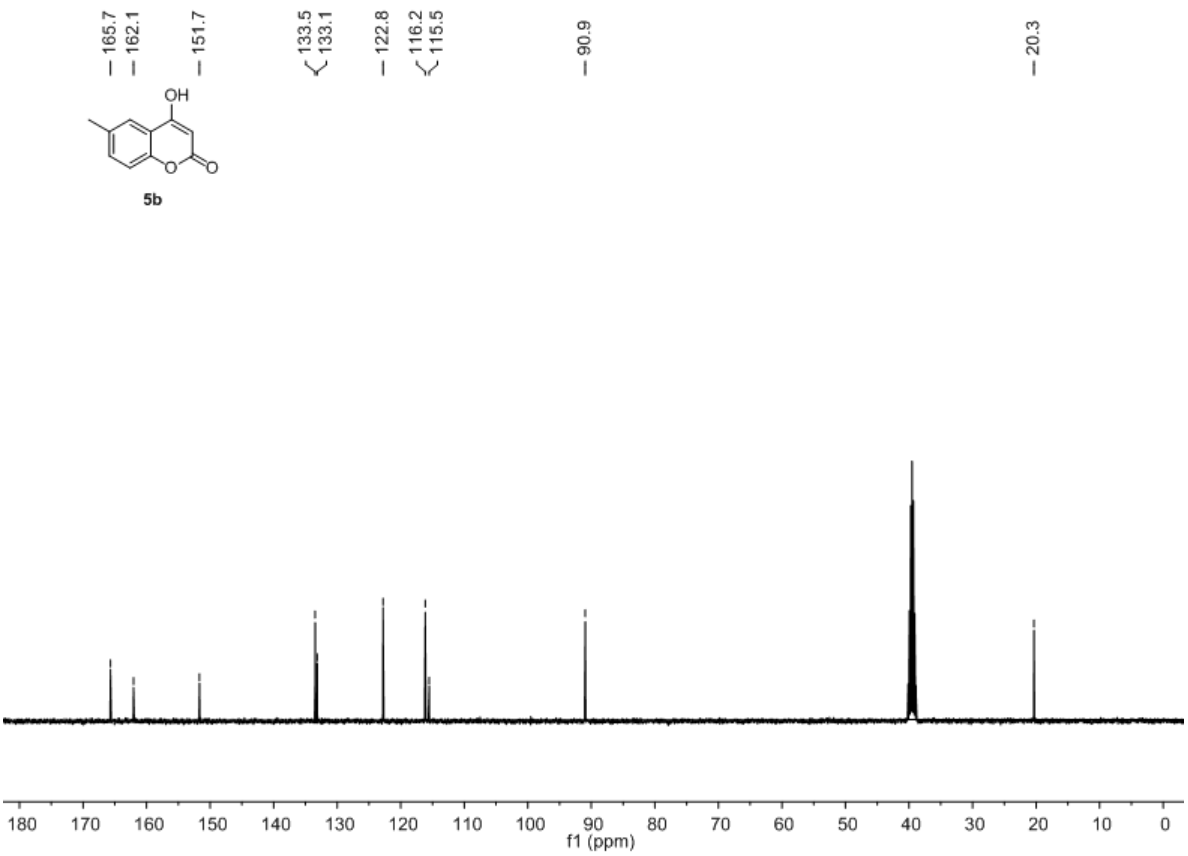

9.80
8.06
8.05
8.05
8.04
8.03
7.99
7.98
7.98
7.97
7.96
7.96
7.93
7.91
7.56
7.54
7.43
7.41
7.39
7.16
7.16
7.14
7.13
6.85
6.85
O
N
O
OH
2j
0.99
1.98
3.26
1.31
1.03
1.11
1.08
1.00
11.5 10.5 9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0
f1 (ppm)

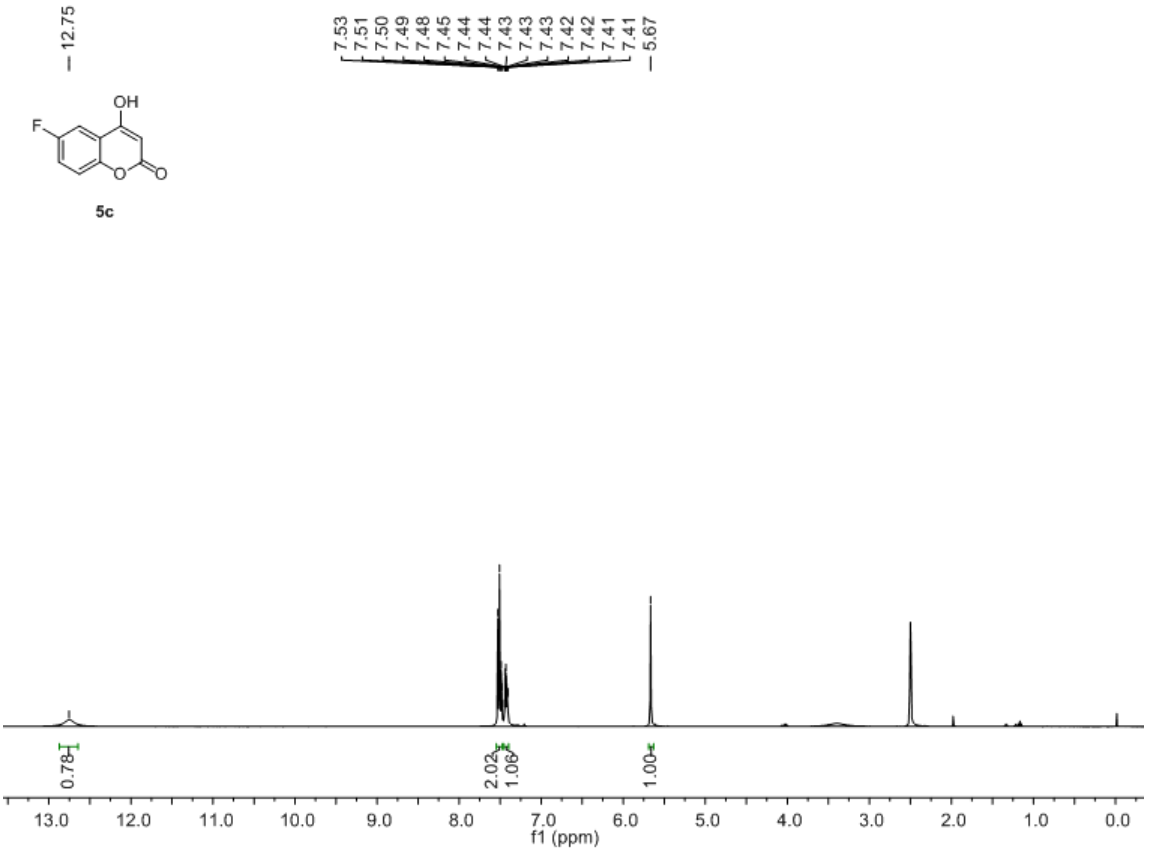

167.5
156.4
134.9
131.8
131.6
130.2
129.2
128.5
127.7
126.6
123.6
122.1
119.2
103.4
O
N
O
OH
2j
f1 (ppm)

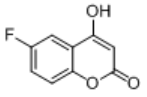

9.45
7.61
7.59
7.44
7.44
7.41
7.39
7.32
7.30
7.28
6.97
6.95
6.44
6.43
6.42
6.29
6.28
4.46
4.45
NH
OH
2k
1.00
1.12
0.95
2.05
2.24
1.22
1.06
2.25
0.92
1.04
2.08
f1 (ppm)


154.2
142.3
140.3
129.4
128.4
128.2
126.9
126.4
124.7
123.1
117.7
115.8
103.9
103.8
46.6
NH
OH
2k
170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0
f1 (ppm)


12.46
7.61
7.61
7.46
7.46
7.44
7.43
7.27
7.24
5.58
2.37
OH
O
O
5b
0.84
1.01
1.00
1.04
0.97
3.00
13.0 12.0 11.0 10.0 9.0 8.0 7.0 6.0 5.0 4.0 3.0 2.0 1.0 0.0
f1 (ppm)

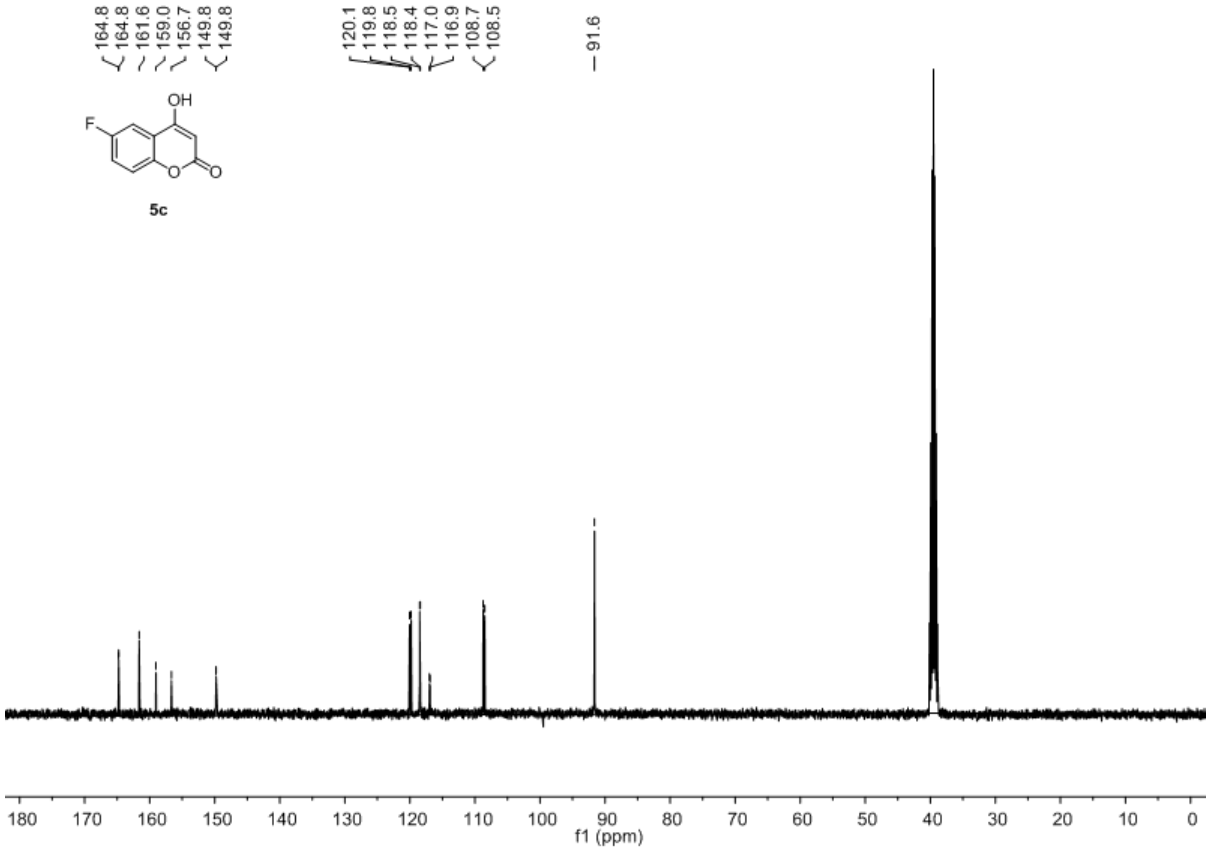

165.7
162.1
151.7
133.5
133.1
122.8
116.2
115.5
90.9
20.3
OH
O
O
5b
180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0
f1 (ppm)


12.75
7.53
7.51
7.50
7.49
7.48
7.45
7.44
7.44
7.43
7.43
7.43
7.42
7.42
7.41
7.41
5.67
OH
F
O
O
5c
0.78
2.02
1.06
1.00
13.0 12.0 11.0 10.0 9.0 8.0 7.0 6.0 5.0 4.0 3.0 2.0 1.0 0.0
f1 (ppm)


OH
F
O
O

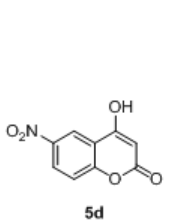
5c

-118.07
10
0
-10
-20
-30
-40
-50
-60
-70
-80
-90
-100
-120
-140
-160
-180
-200
f1 (ppm)


164.8
164.8
161.6
159.0
156.7
149.8
149.8
120.1
119.8
118.5
118.4
117.0
116.9
108.7
108.5
91.6
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
f1 (ppm)

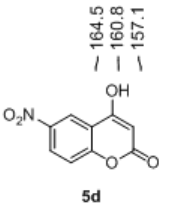
OH
F
O
O

5c


OH
O_2N
O
O

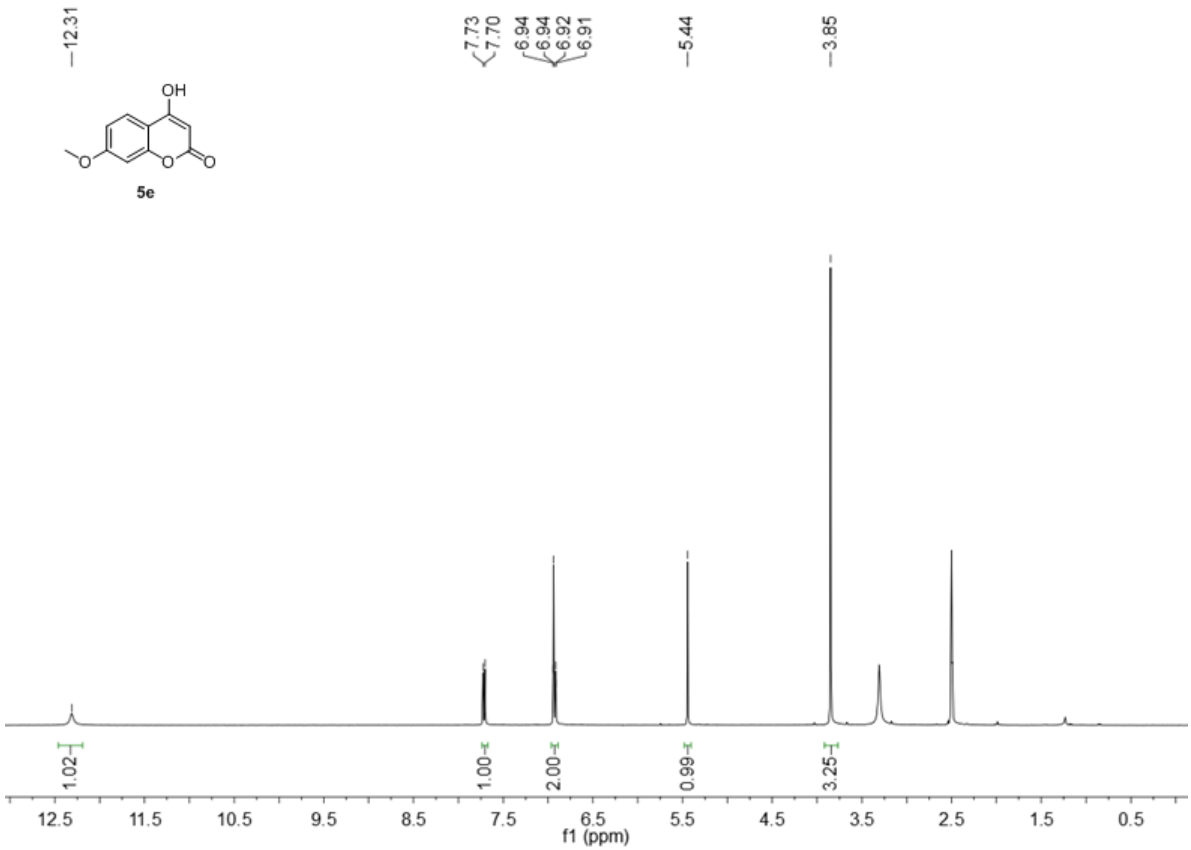
5d

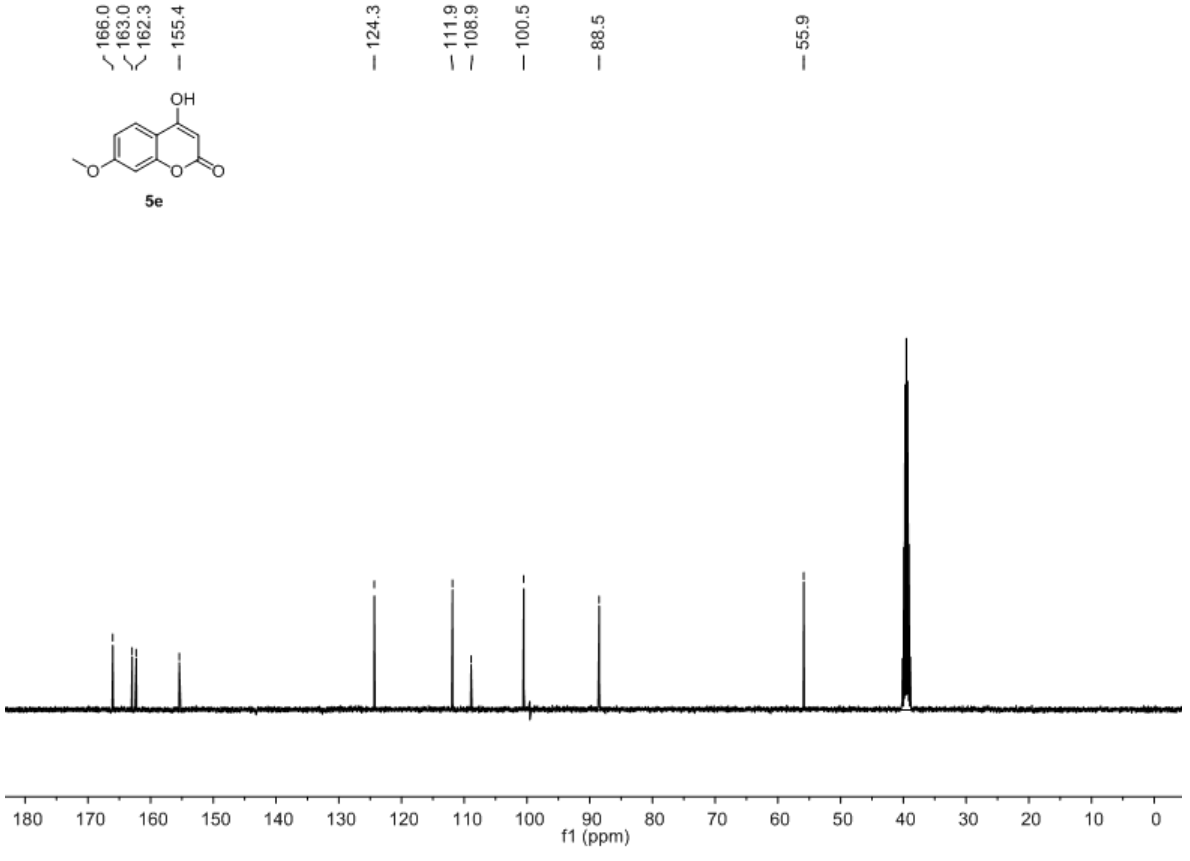
8.52
8.52
8.45
8.44
8.43
8.42
7.61
7.58
5.70
1.00
1.02
1.03
1.07
11.5
10.5
9.5
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
f1 (ppm)

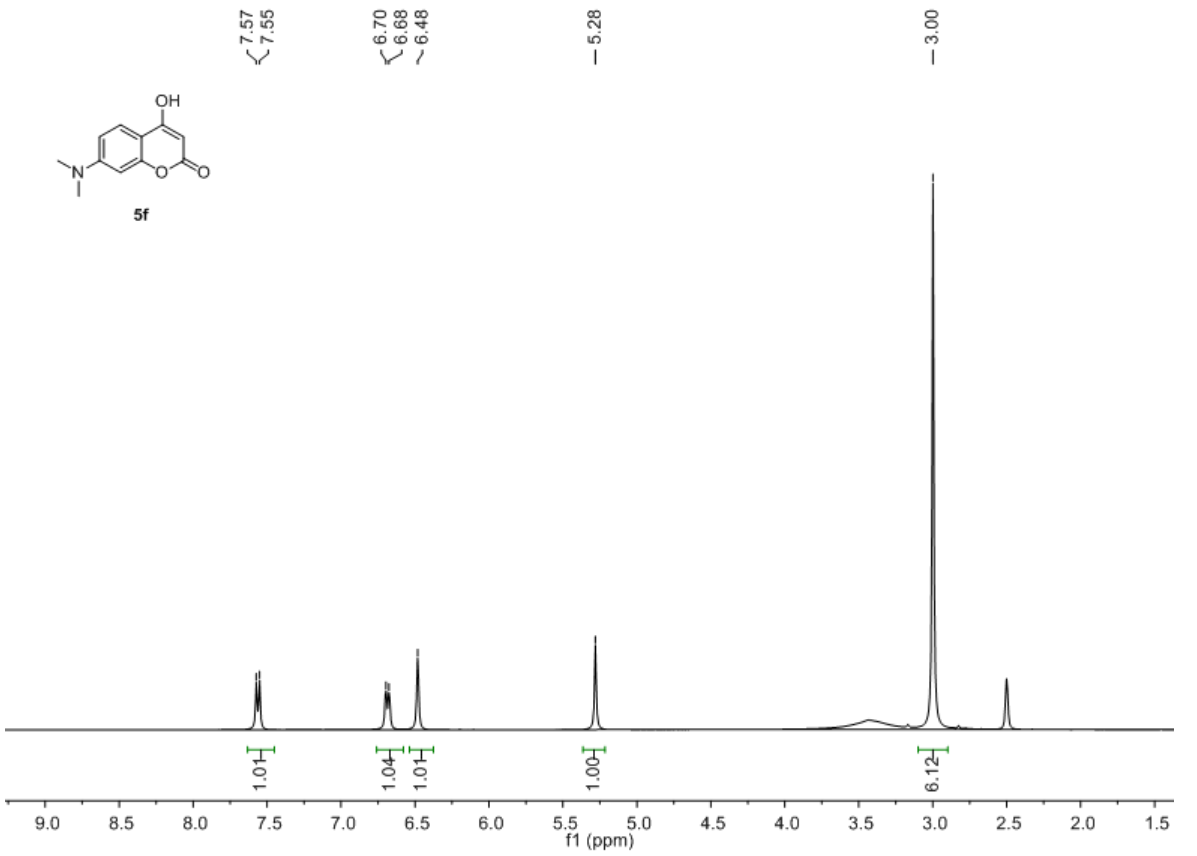

OH
O_2N
O
O

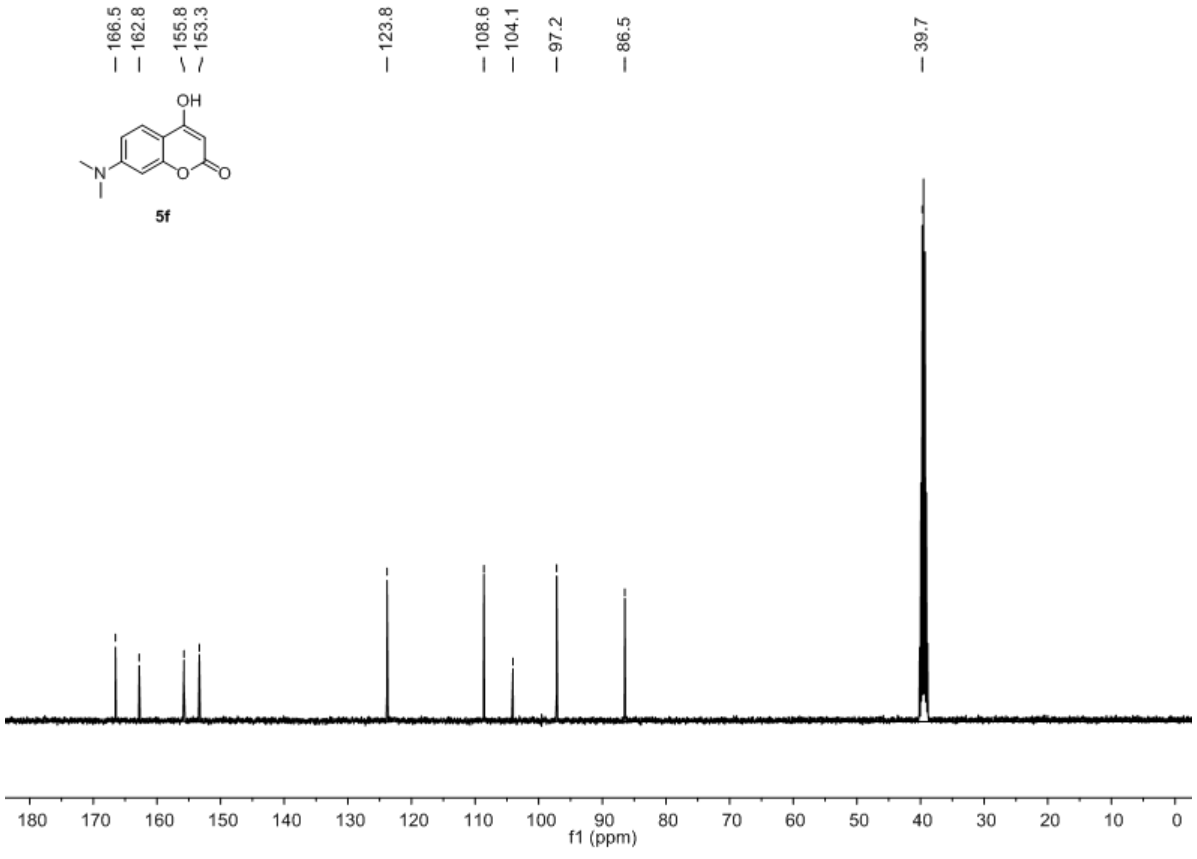
5d

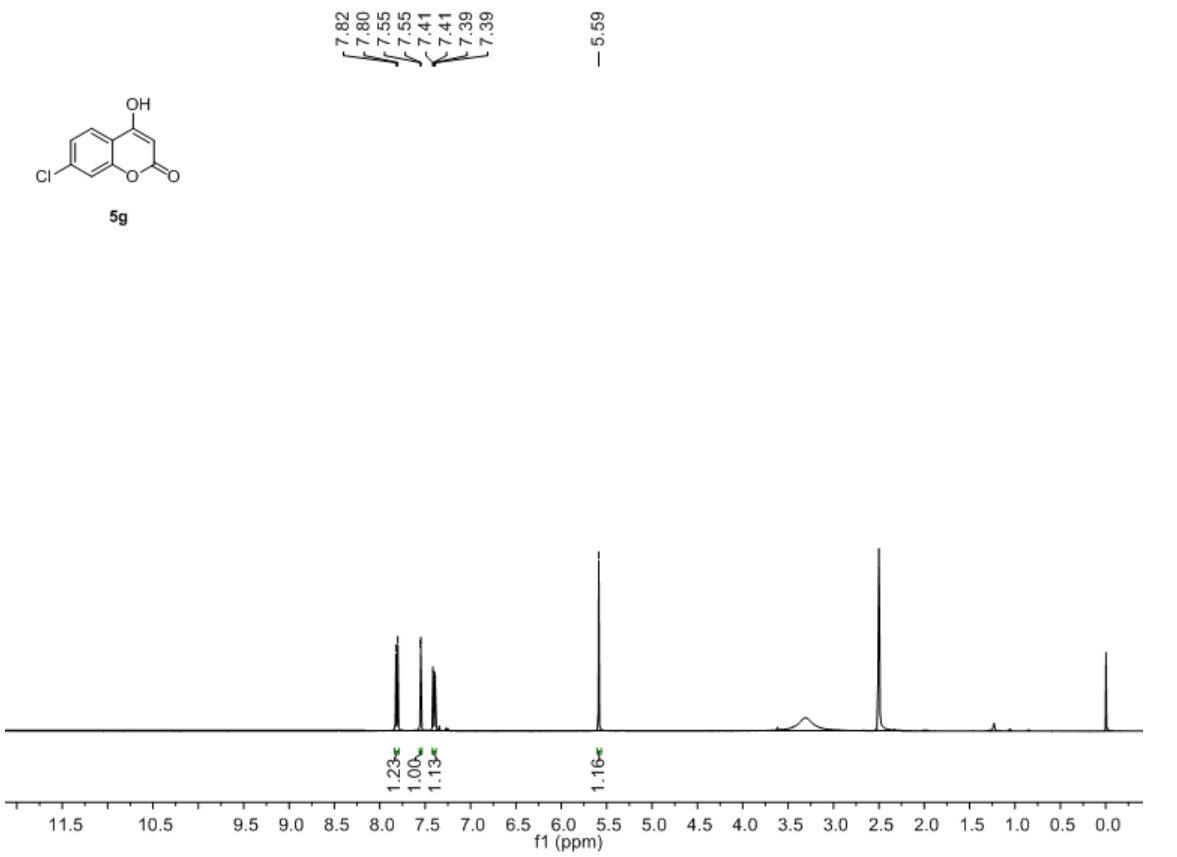
164.5
160.8
157.1
143.2
127.3
119.1
118.1
116.4
92.0
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
f1 (ppm)


12.31
7.73
7.70
6.94
6.94
6.92
6.91
5.44
3.85
OH
O
O
O
5e
1.02
1.00
2.00
0.99
3.25
12.5
11.5
10.5
9.5
8.5
7.5
6.5
5.5
4.5
3.5
2.5
1.5
0.5
f1 (ppm)

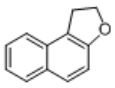

166.0
163.0
162.3
155.4
124.3
111.9
108.9
100.5
88.5
55.9
OH
O
O
O
5e
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
f1 (ppm)


7.57
7.55
6.70
6.68
6.48
5.28
3.00
OH
N
O
O
5f
1.01
1.04
1.01
1.00
6.12
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
f1 (ppm)

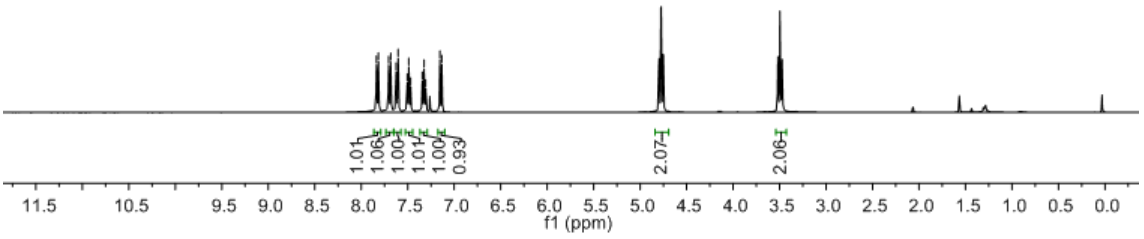

166.5
162.8
155.8
153.3
123.8
108.6
104.1
97.2
86.5
39.7
OH
N
O
O
5f
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
f1 (ppm)

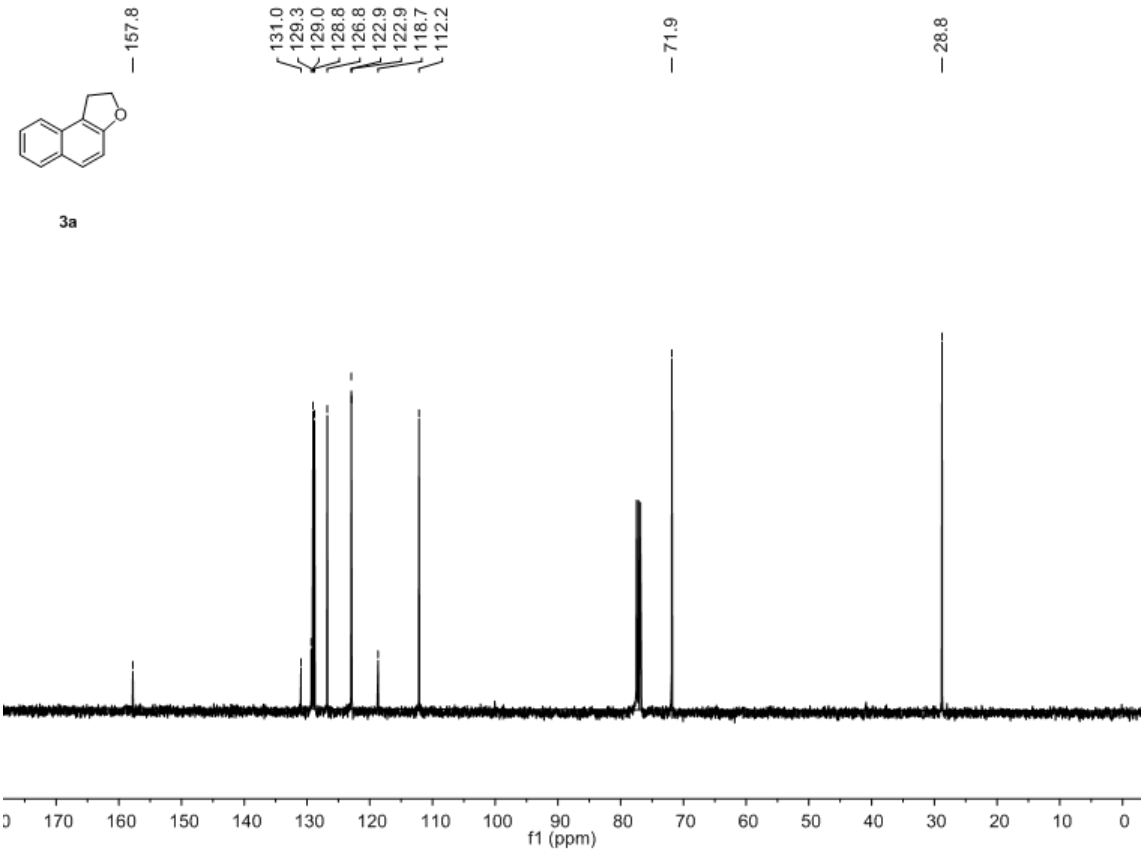

7.82
7.80
7.55
7.55
7.41
7.41
7.39
7.39
5.59
OH
Cl
O
O
5g
1.23
1.00
1.13
1.16
11.5 10.5 9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0
f1 (ppm)
165.2
161.4
154.0
136.9
124.8
124.2
116.5
114.9
90.9
OH
Cl
O
O
5g
180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0
f1 (ppm)


7.84
7.82
7.71
7.68
7.63
7.60
7.51
7.49
7.47
7.34
7.32
7.31
7.16
7.13



3a

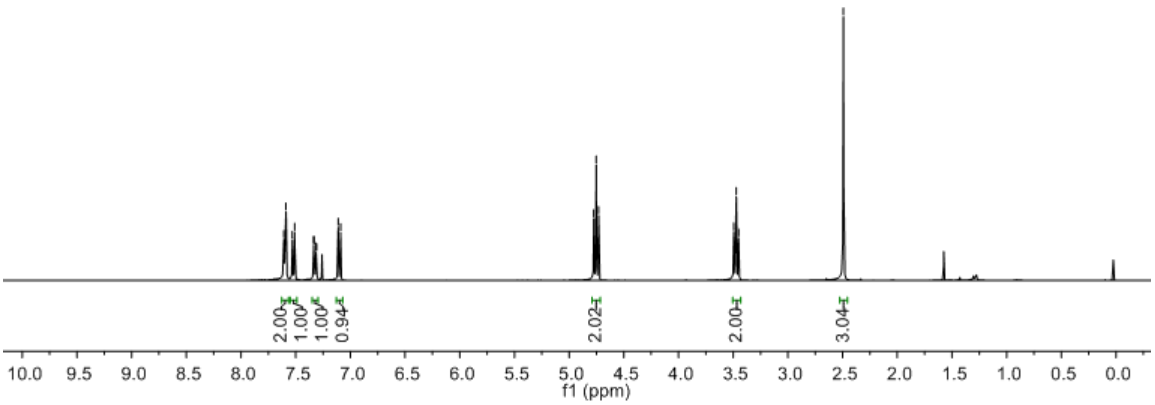

1.01
1.06
1.00
1.01
1.00
0.93
2.07
2.06
11.5
10.5
9.5
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
f1 (ppm)


157.8
131.0
129.3
129.0
128.8
126.8
122.9
122.9
118.7
112.2
71.9
28.8
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
f1 (ppm)

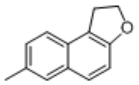
3a


7.61
7.59
7.53
7.51
7.34
7.33
7.31
7.31
7.11
7.09
4.77
4.75
4.73
3.50
3.47
3.45
2.49

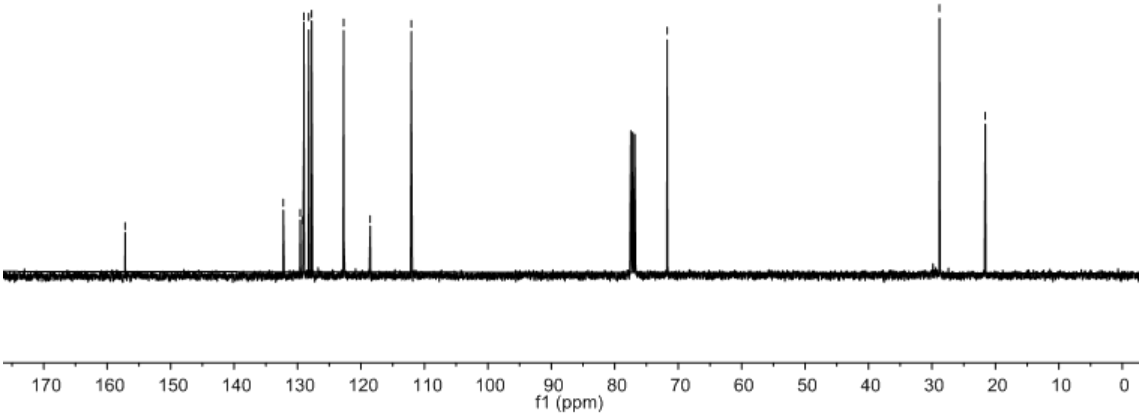
3b

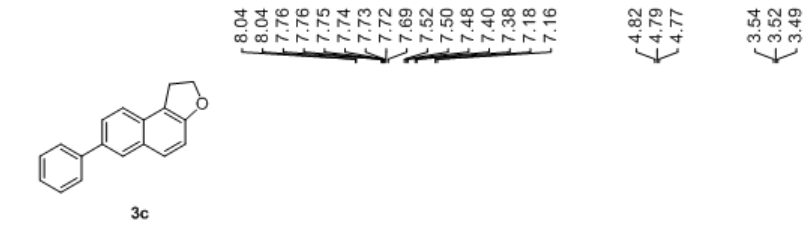

2.00
1.00
1.00
0.94
2.02
2.00
3.04
10.0 9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0
f1 (ppm)


157.2
132.2
129.6
129.1
129.0
128.2
127.8
122.7
118.5
112.1
71.7
28.8
21.6

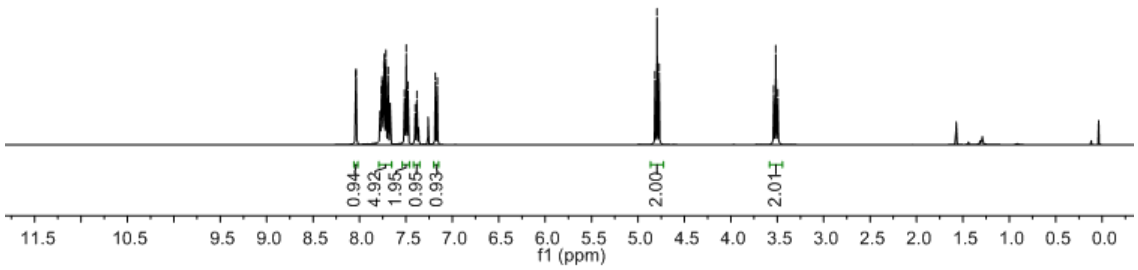


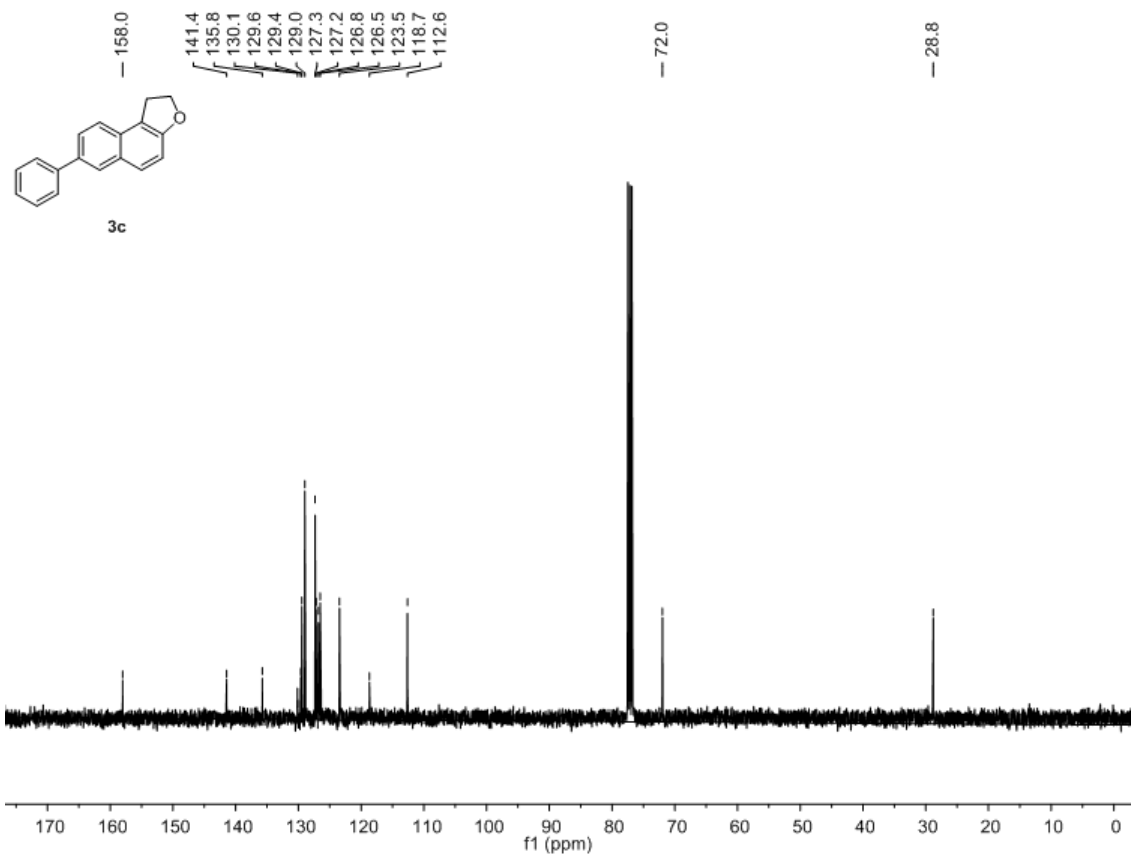
3b


170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0
f1 (ppm)

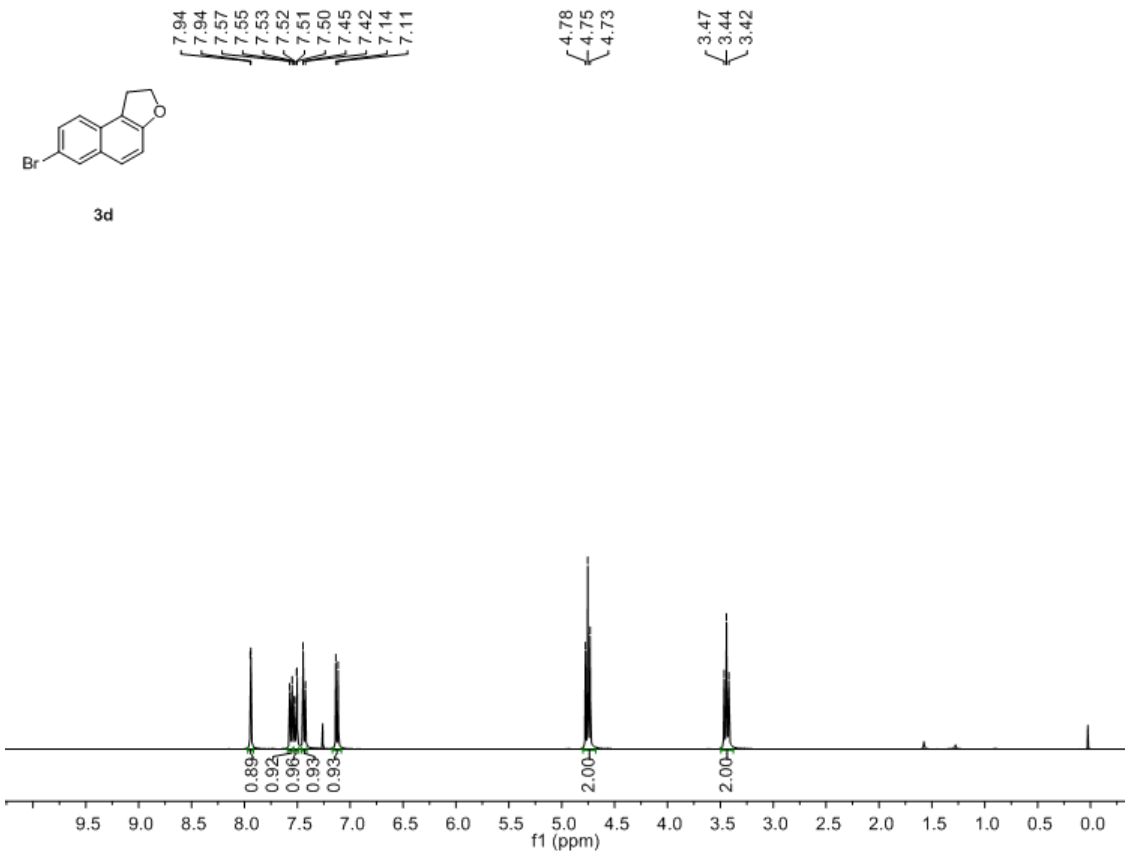

8.04
8.04
7.76
7.76
7.75
7.74
7.73
7.72
7.69
7.52
7.50
7.48
7.40
7.38
7.18
7.16
4.82
4.79
4.77
3.54
3.52
3.49

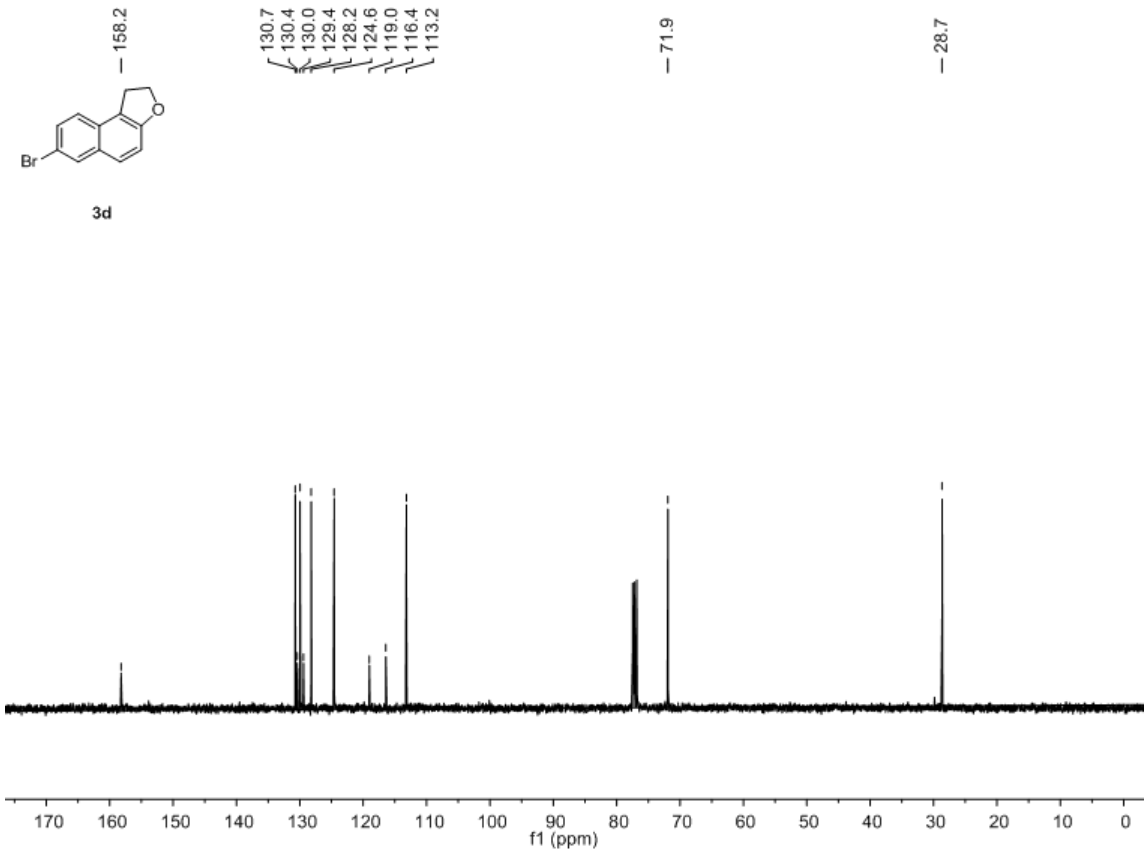
3c

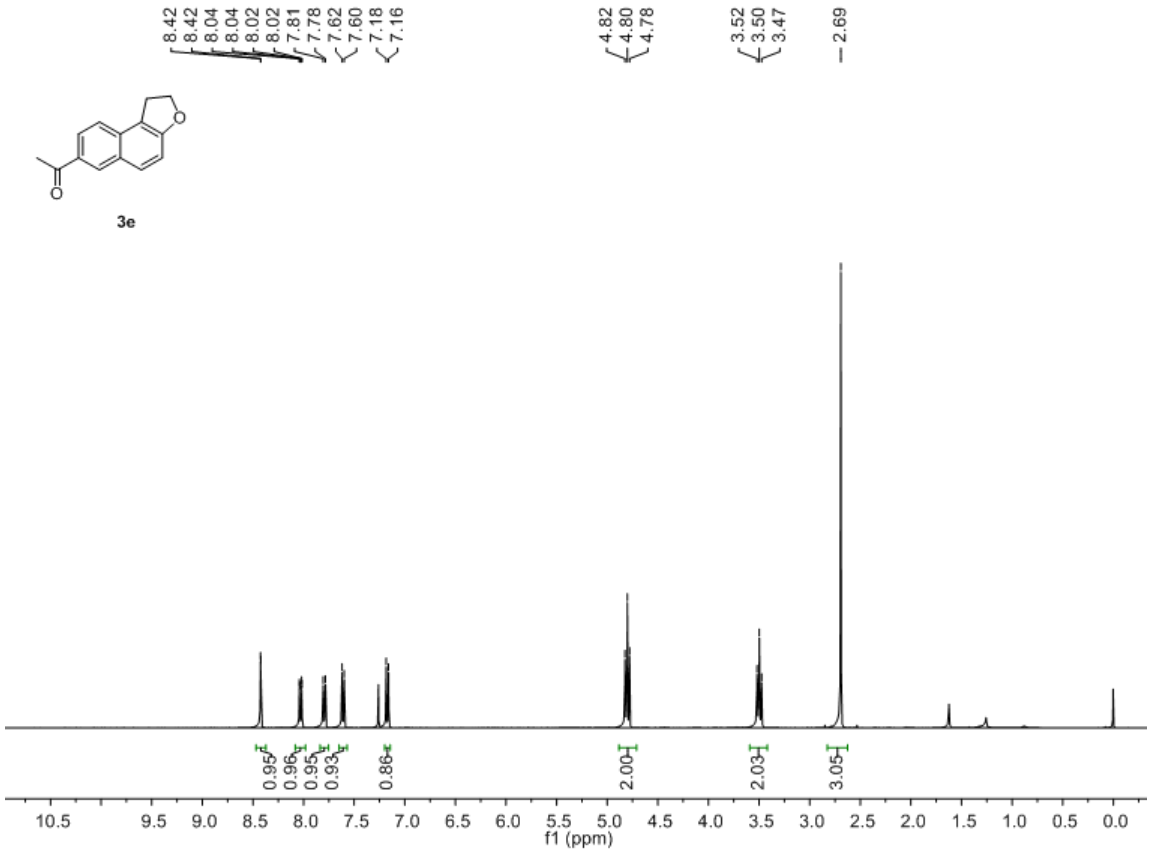

0.94
4.92
1.95
0.95
0.93
2.00
2.01
11.5
10.5
9.5
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
f1 (ppm)

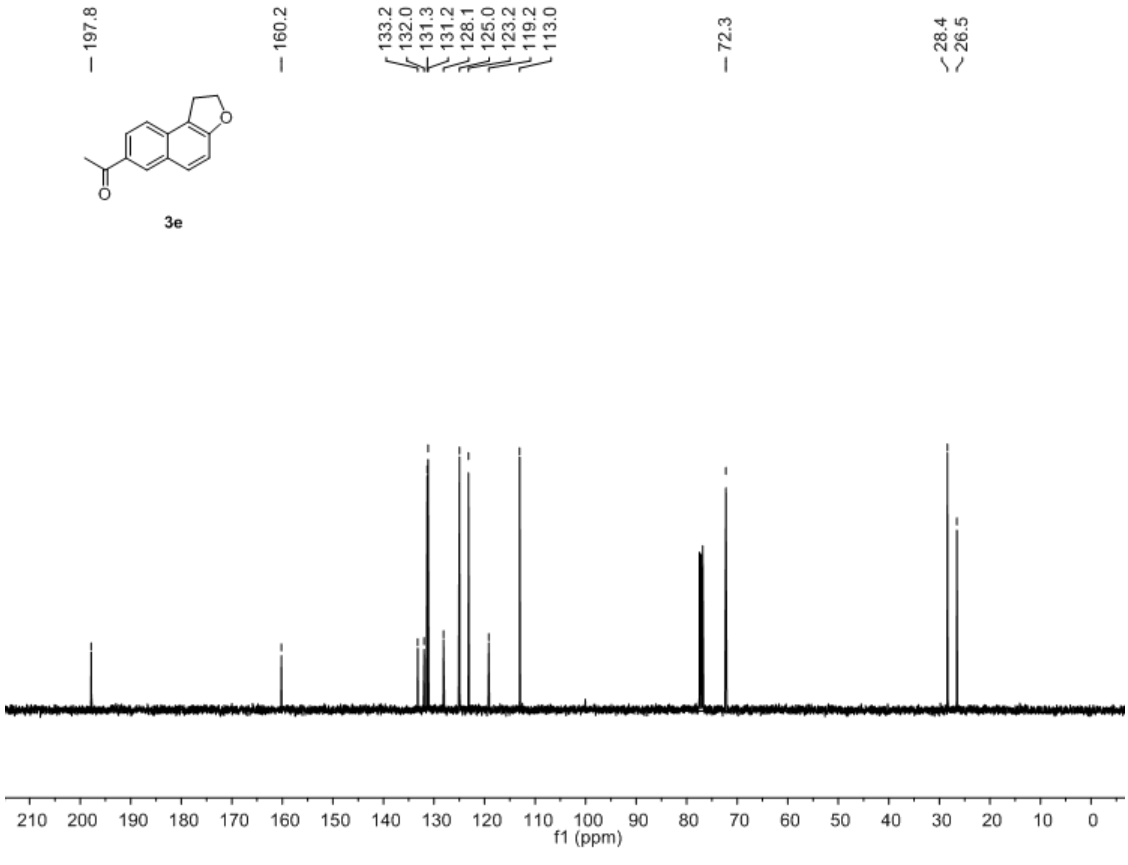

158.0
141.4
135.8
130.1
129.6
129.4
129.0
127.3
127.2
126.8
126.5
123.5
118.7
112.6
72.0
28.8
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
f1 (ppm)

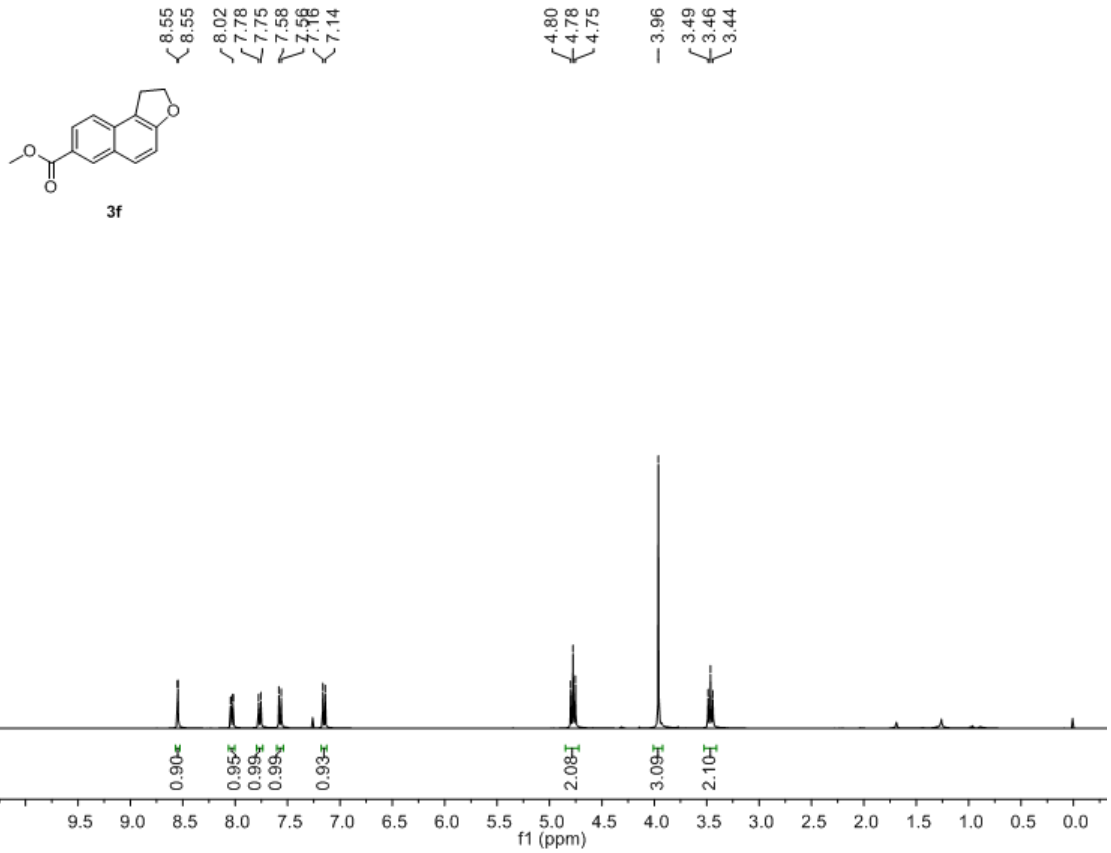
3c

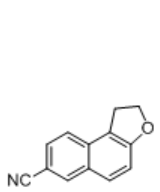

7.94
7.94
7.57
7.55
7.53
7.52
7.51
7.50
7.45
7.42
7.14
7.11
4.78
4.75
4.73
3.47
3.44
3.42
Br
O
3d
0.89
0.92
0.96
0.93
0.93
2.00
2.00
9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0
f1 (ppm)


158.2
130.7
130.4
130.0
129.4
128.2
124.6
119.0
116.4
113.2
71.9
28.7
Br
O
3d
170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0
f1 (ppm)


8.42
8.42
8.04
8.04
8.02
8.02
7.81
7.78
7.62
7.60
7.18
7.16
4.82
4.80
4.78
3.52
3.50
3.47
2.69
O
O
3e
0.95
0.96
0.95
0.93
0.86
2.00
2.03
3.05
10.5
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)

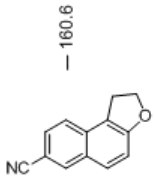

197.8
160.2
133.2
132.0
131.3
131.2
128.1
125.0
123.2
119.2
113.0
72.3
28.4
26.5
O
O
3e
210
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
f1 (ppm)


8.55
8.55
8.02
7.78
7.75
7.58
7.56
7.16
7.14
4.80
4.78
4.75
3.96
3.49
3.46
3.44
3f
0.90
0.95
0.99
0.99
0.93
2.08
3.09
2.10
f1 (ppm)
167.5
160.0
133.2
132.1
130.9
128.2
126.3
124.5
122.9
119.0
113.0
72.2
52.2
28.5
3f
f1 (ppm)


NC
O

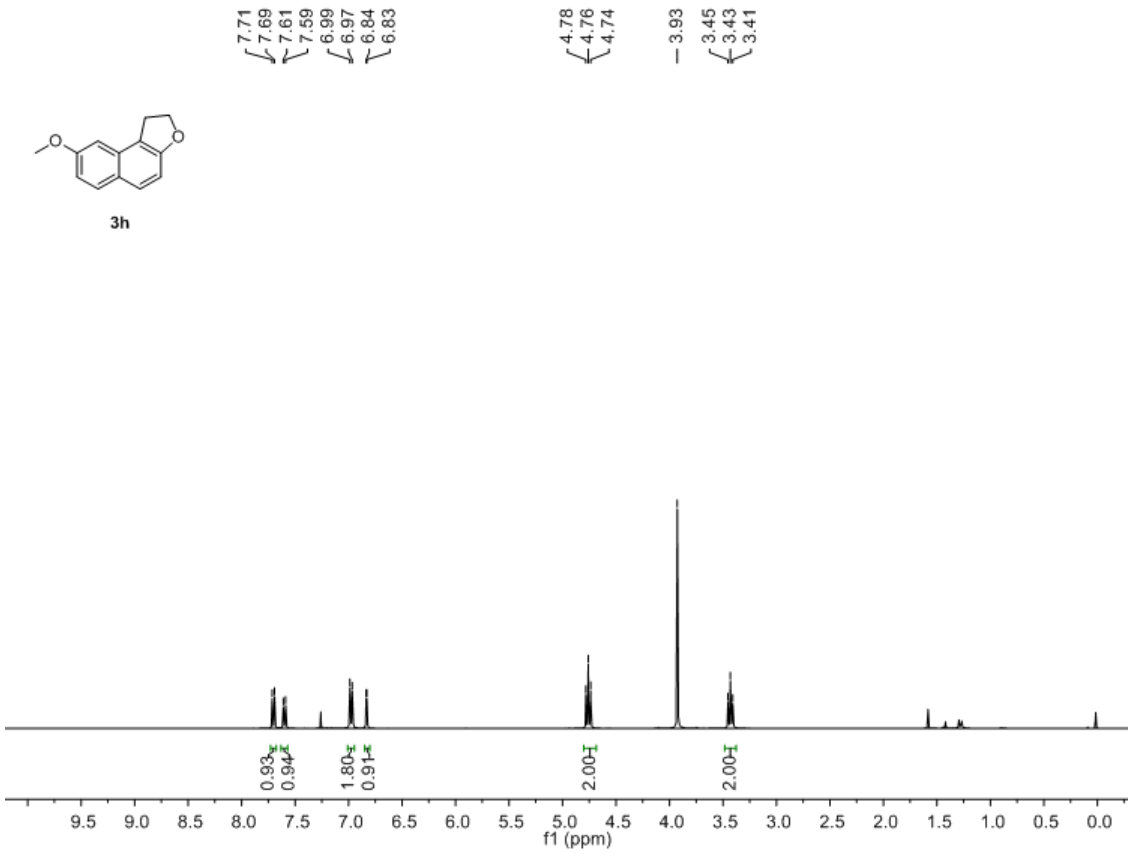
3g

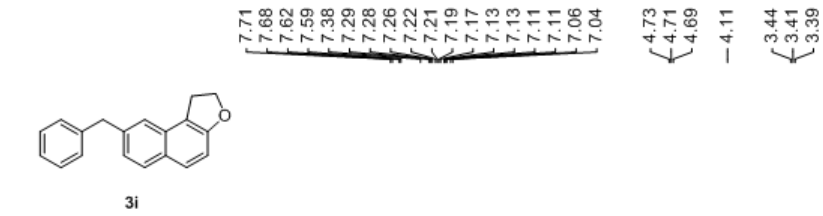
8.17
7.74
7.72
7.65
7.63
7.59
7.59
7.57
7.57
7.23
7.21
4.85
4.82
4.80
3.53
3.50
3.48
1.00
0.99
1.01
0.97
0.95
2.05
2.09
10.5
9.5
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
f1 (ppm)


NC
O

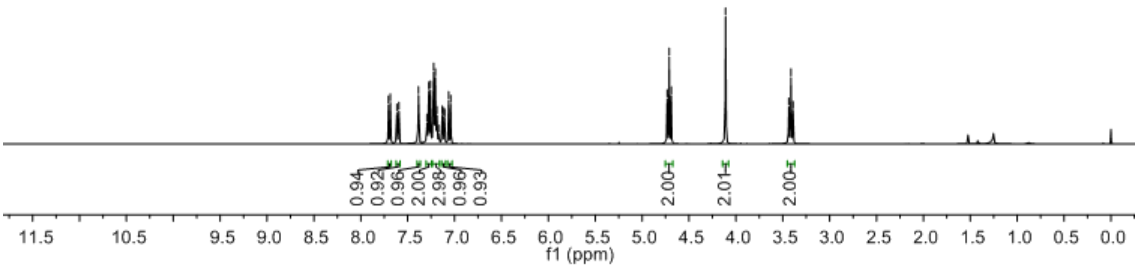
3g

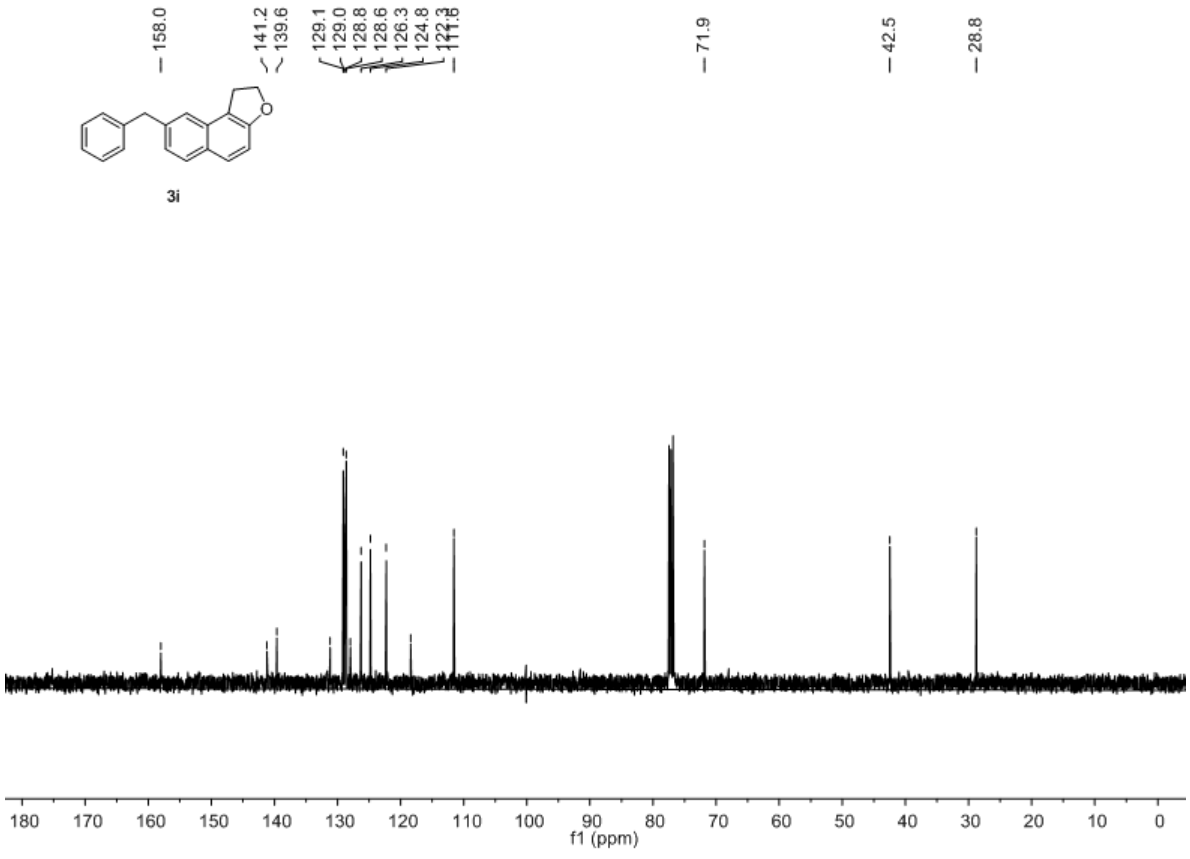
160.6
135.0
132.4
130.1
128.0
127.3
124.0
119.8
119.4
114.0
106.0
72.4
28.3
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
f1 (ppm)


7.71
7.69
7.61
7.59
6.99
6.97
6.84
6.83
4.78
4.76
4.74
3.93
3.45
3.43
3.41
3h
0.93
0.94
1.80
0.91
2.00
2.00
f1 (ppm)
158.6
158.4
132.2
130.4
128.8
124.8
117.8
115.5
109.6
101.4
71.8
55.4
28.8
3h
f1 (ppm)

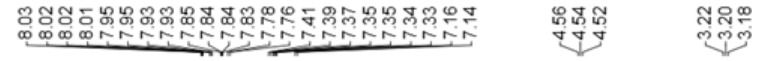

7.71
7.68
7.62
7.59
7.38
7.29
7.28
7.26
7.22
7.21
7.19
7.17
7.13
7.13
7.11
7.11
7.06
7.04
4.73
4.71
4.69
4.11
3.44
3.41
3.39

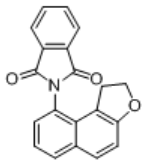
3i


0.94
0.92
0.96
2.00
2.98
0.96
0.93
2.00
2.01
2.00
11.5
10.5
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)

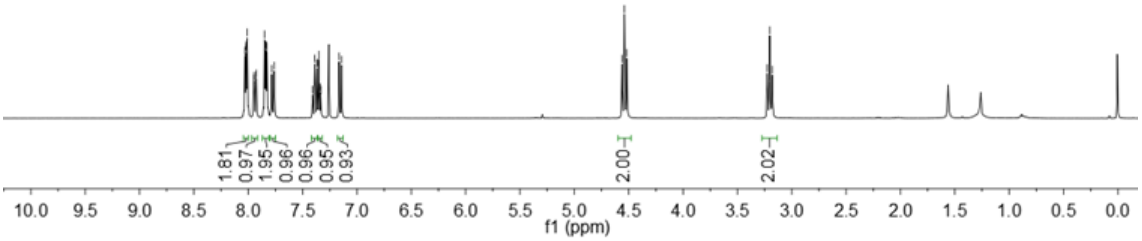

158.0
141.2
139.6
129.1
129.0
128.8
128.6
126.3
124.8
122.3
111.8
71.9
42.5
28.8
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
f1 (ppm)

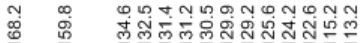
3i

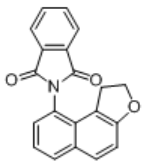

8.03
8.02
8.02
8.01
7.95
7.95
7.93
7.93
7.85
7.84
7.84
7.83
7.78
7.76
7.41
7.39
7.37
7.35
7.35
7.34
7.33
7.16
7.14
4.56
4.54
4.52
3.22
3.20
3.18



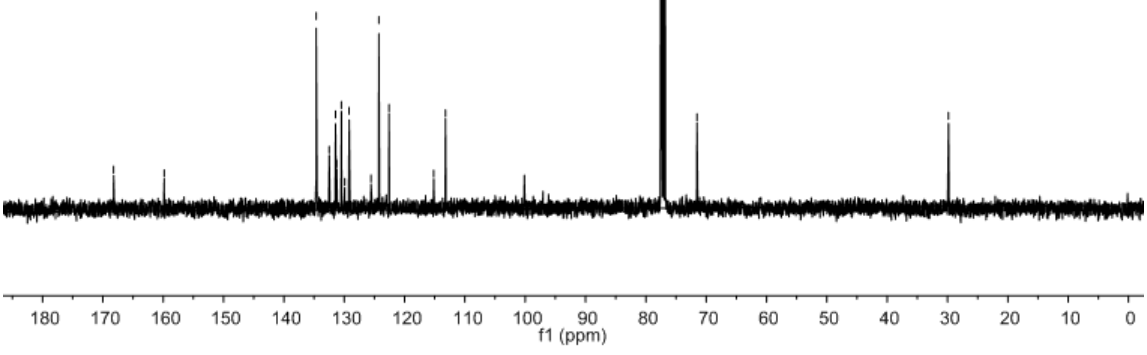
3j

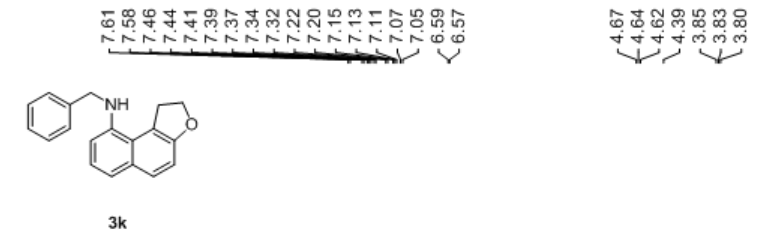

1.81
0.97
1.95
0.96
0.96
0.95
0.93
2.00
2.02
10.0 9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0
f1 (ppm)


168.2
159.8
134.6
132.5
131.4
131.2
130.5
129.9
129.2
125.6
124.2
122.6
115.2
113.2
71.5
29.8

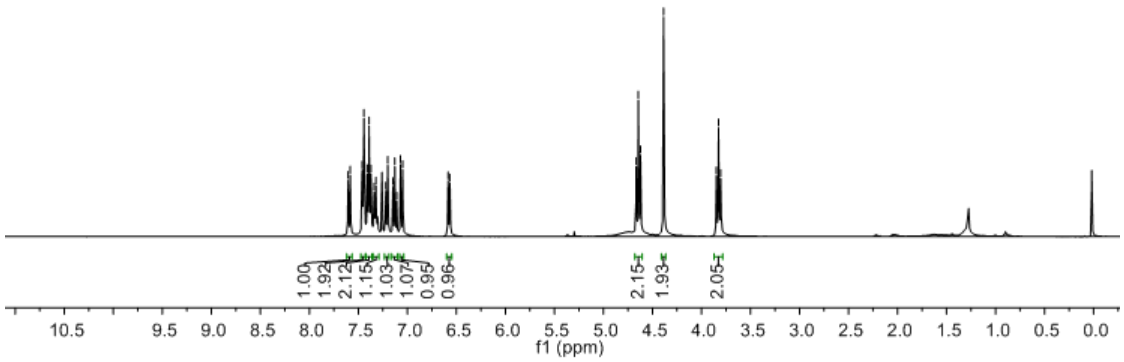


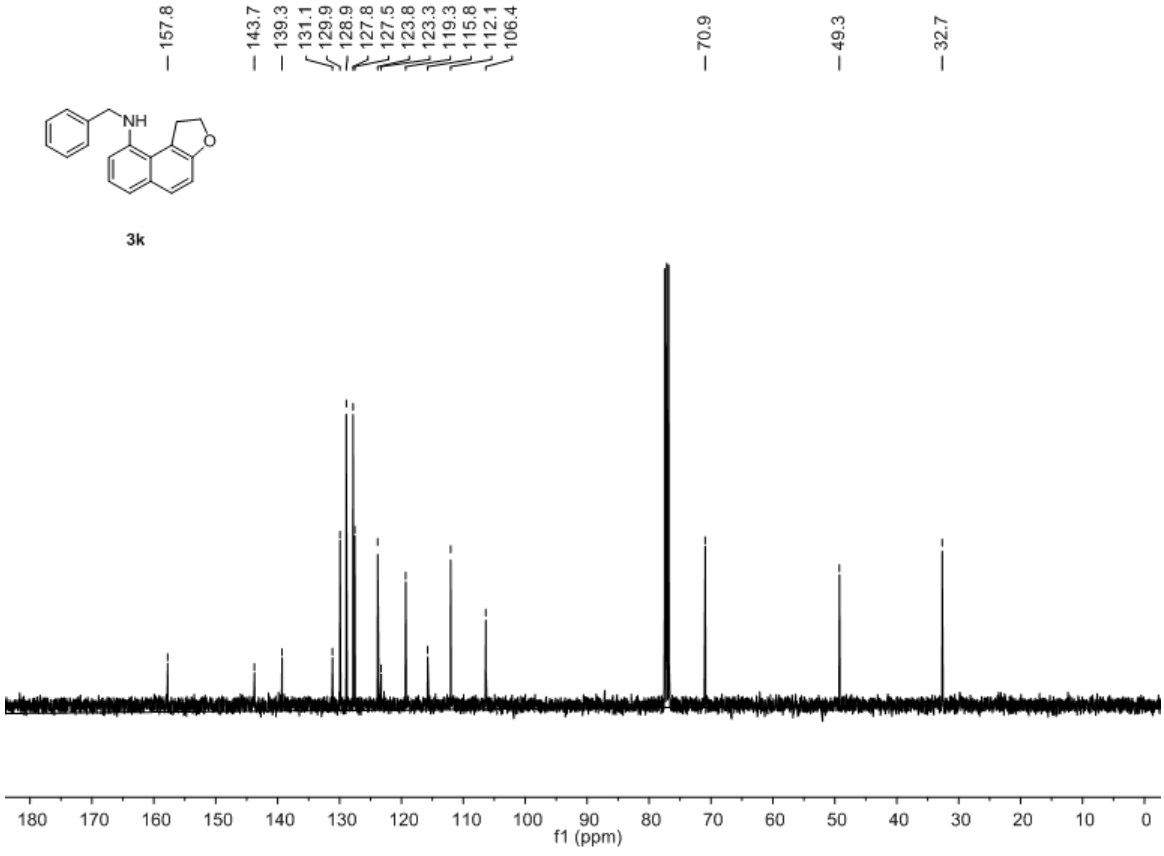
3j


180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0
f1 (ppm)

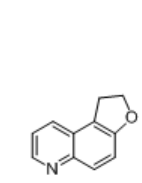

7.61
7.58
7.46
7.44
7.41
7.39
7.37
7.34
7.32
7.22
7.20
7.15
7.13
7.11
7.07
7.05
6.59
6.57
4.67
4.64
4.62
4.39
3.85
3.83
3.80
NH
O

3k


1.00
1.92
2.12
1.15
1.03
1.07
0.95
0.96
2.15
1.93
2.05
10.5
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)

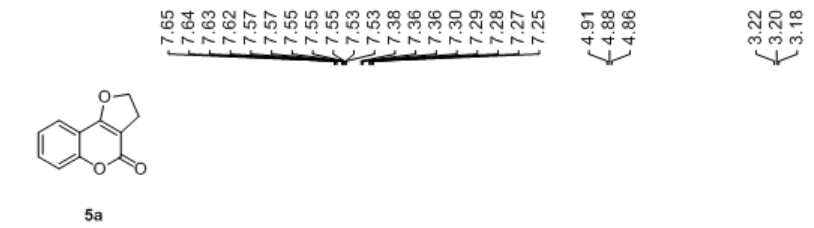

157.8
143.7
139.3
131.1
129.9
128.9
127.8
127.5
123.8
123.3
119.3
115.8
112.1
106.4
70.9
49.3
32.7
NH
O
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
f1 (ppm)

3k

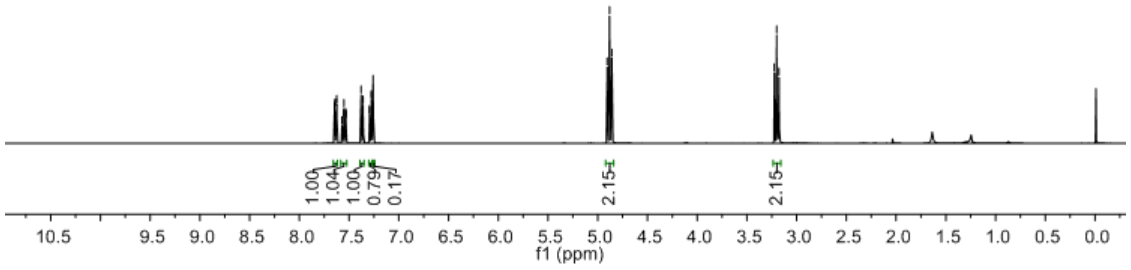


3l

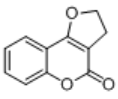
3l


7.65
7.64
7.63
7.62
7.57
7.57
7.55
7.55
7.55
7.53
7.53
7.38
7.36
7.36
7.30
7.29
7.28
7.27
7.25
4.91
4.88
4.86
3.22
3.20
3.18

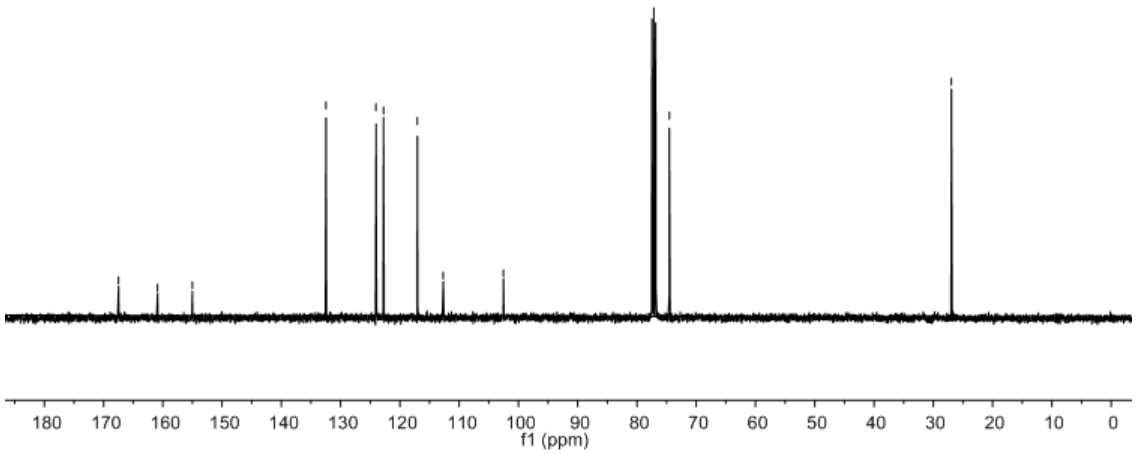
5a

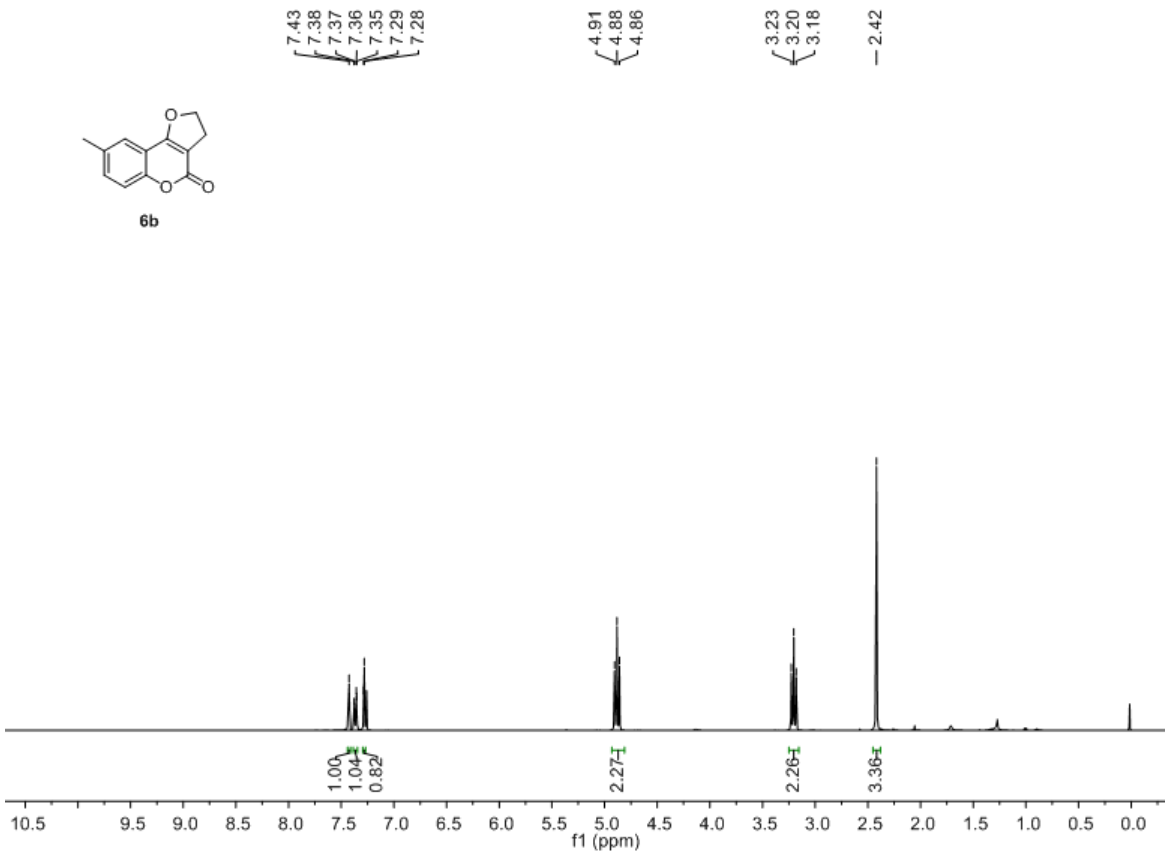

1.00
1.04
1.00
0.79
0.17
2.15
2.15
10.5
9.5
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
f1 (ppm)

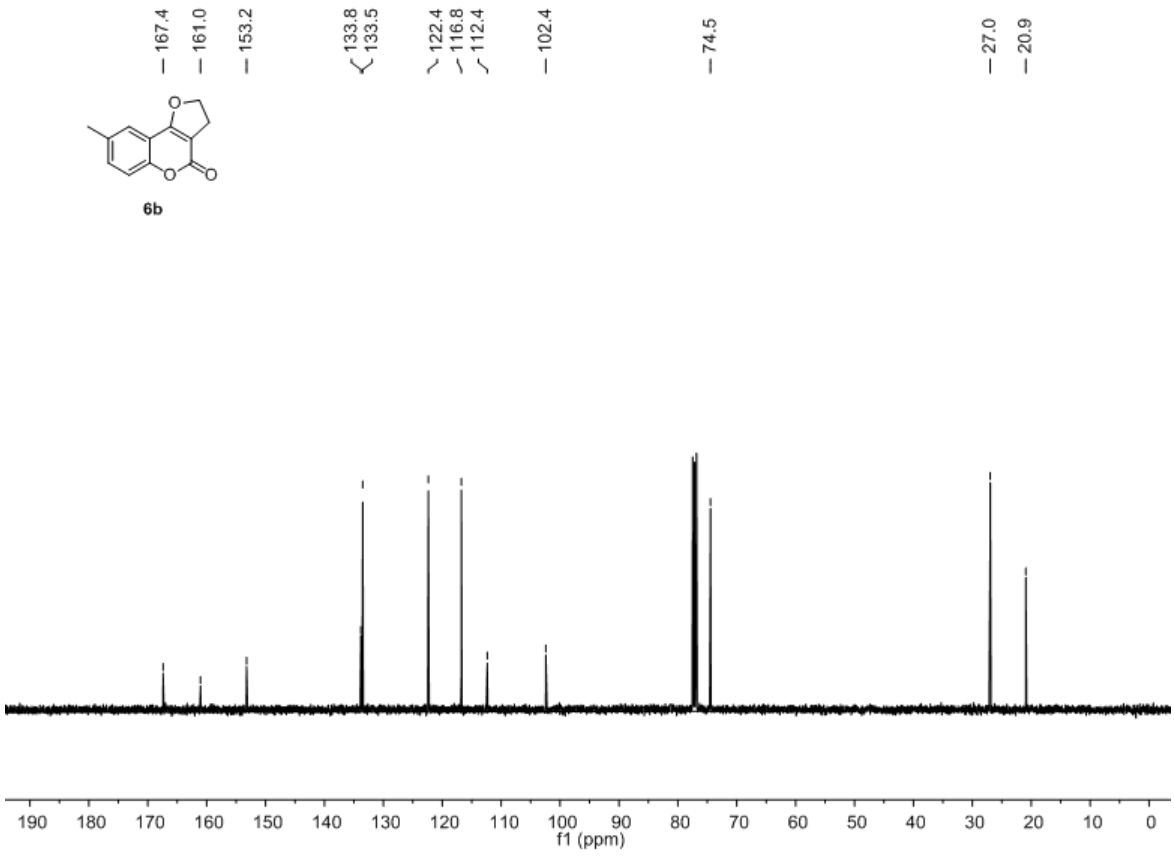

167.5
160.9
155.0
132.5
124.0
122.8
117.1
112.7
102.5
74.5
27.0

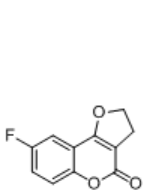


5a


180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
f1 (ppm)

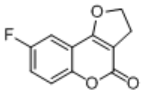

7.43
7.38
7.37
7.36
7.35
7.29
7.28
4.91
4.88
4.86
3.23
3.20
3.18
2.42
6b
1.00
1.04
0.82
2.27
2.26
3.36
f1 (ppm)


167.4
161.0
153.2
133.8
133.5
122.4
116.8
112.4
102.4
74.5
27.0
20.9
6b
f1 (ppm)



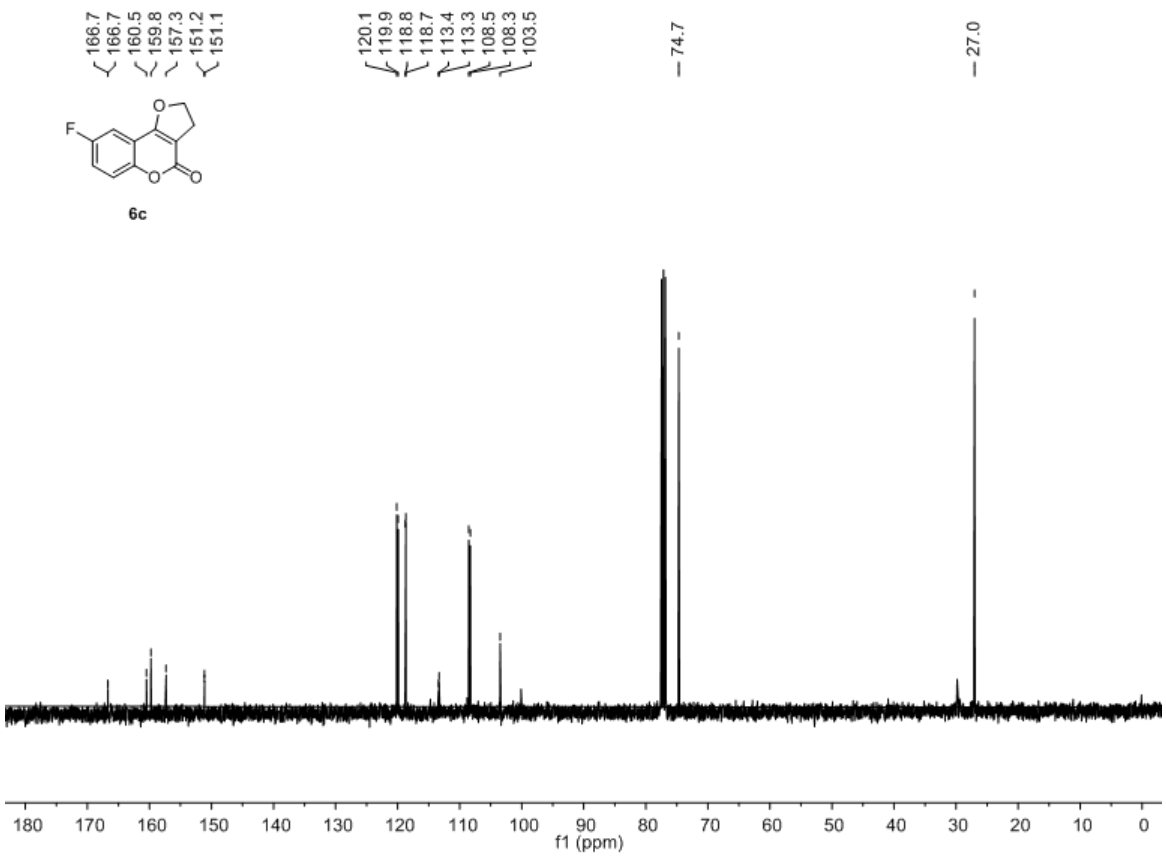
6c

7.39
7.38
7.36
7.35
7.33
7.33
7.31
7.29
7.27
7.26
4.94
4.92
4.89
3.26
3.23
3.21
3.01
2.06
2.11
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)

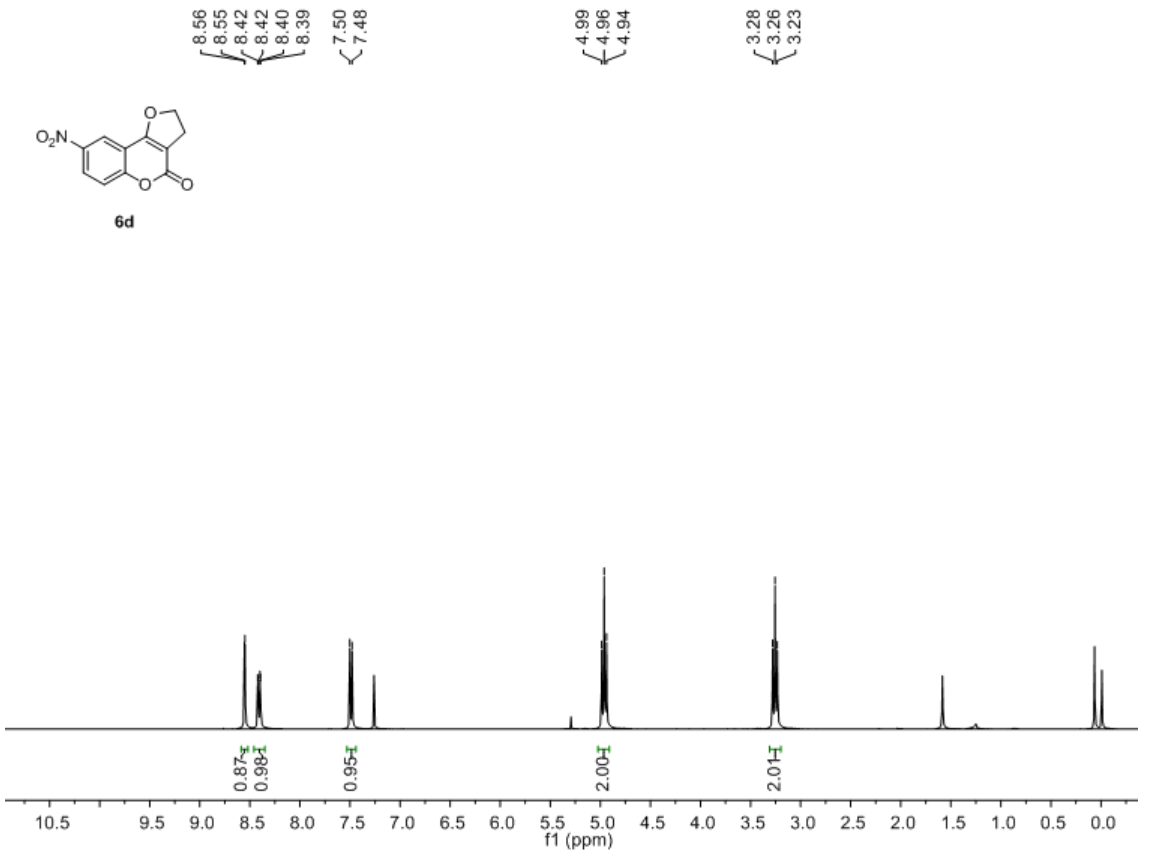


6c

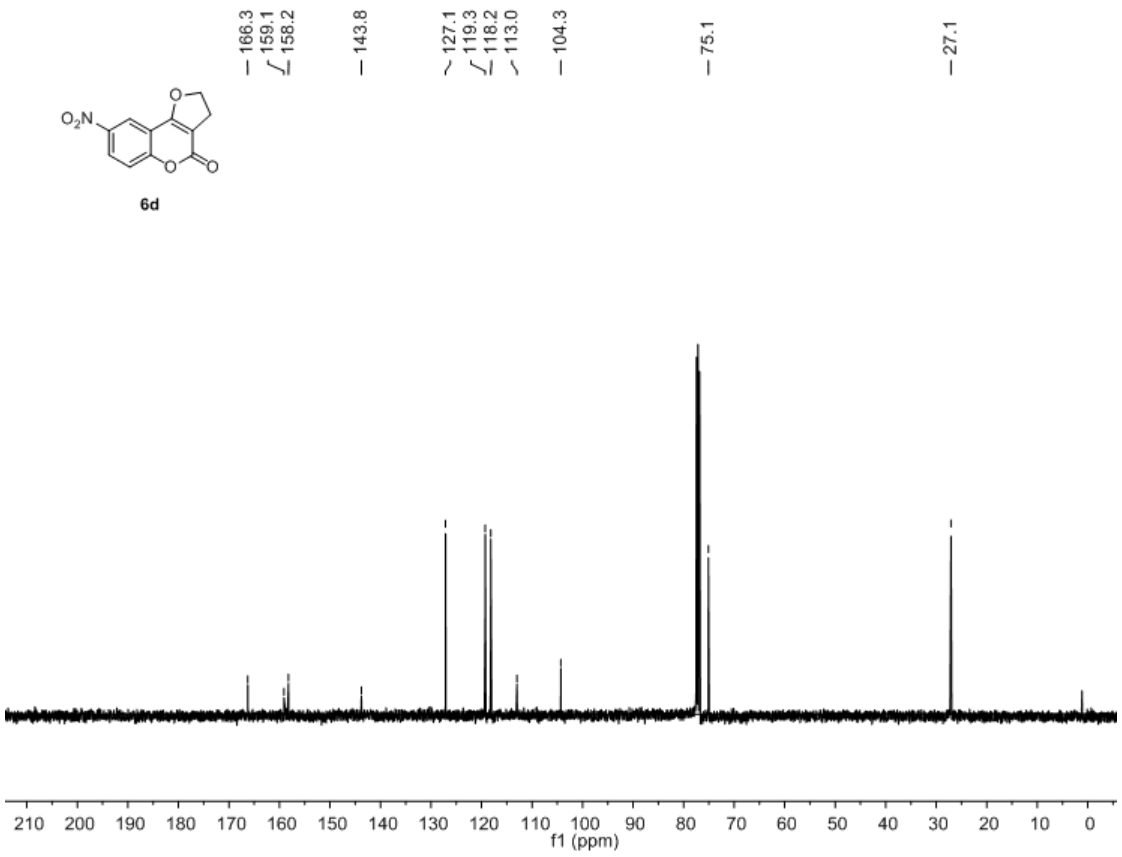
-117.12
10 0 -10 -20 -30 -40 -50 -60 -70 -80 -90 -100 -120 -140 -160 -180 -200
f1 (ppm)

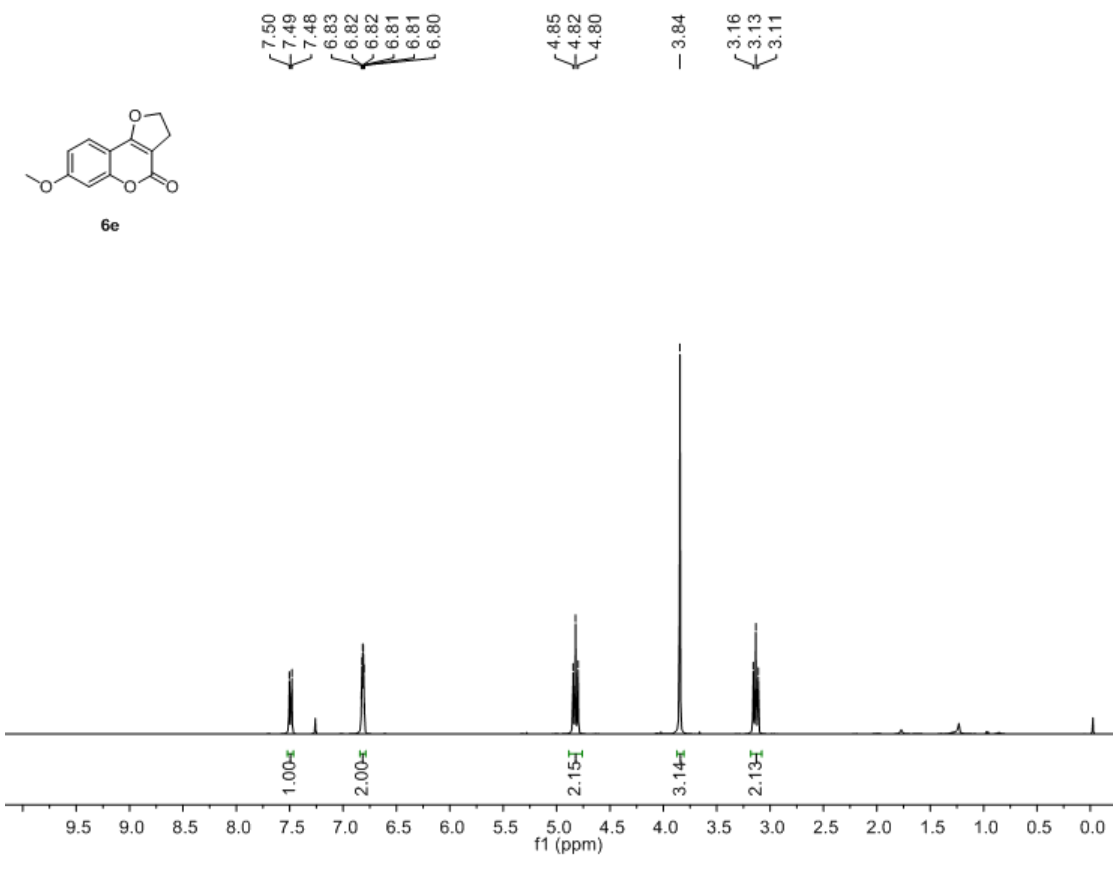

166.7
166.7
160.5
159.8
157.3
151.2
151.1
120.1
119.9
118.8
118.7
113.4
113.3
108.5
108.3
103.5
74.7
27.0
F
O
O
O
f1 (ppm)

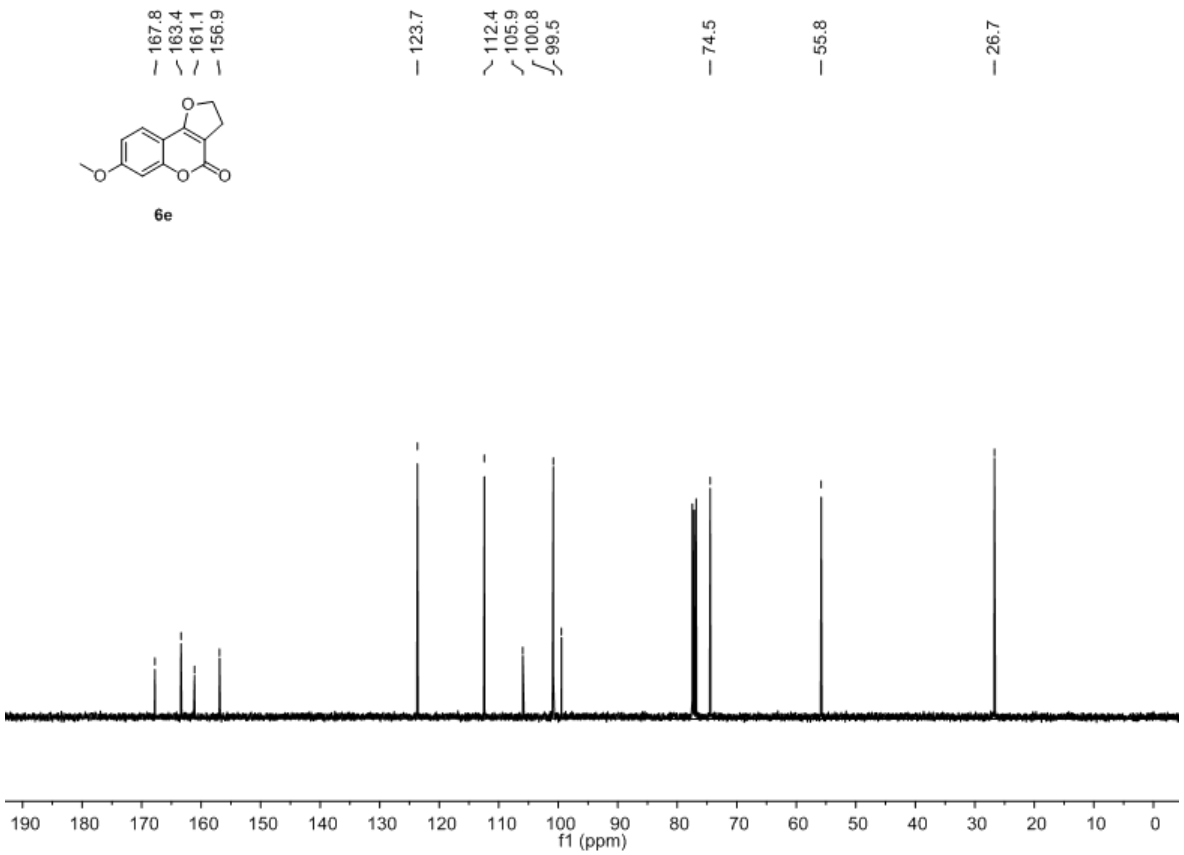
6c

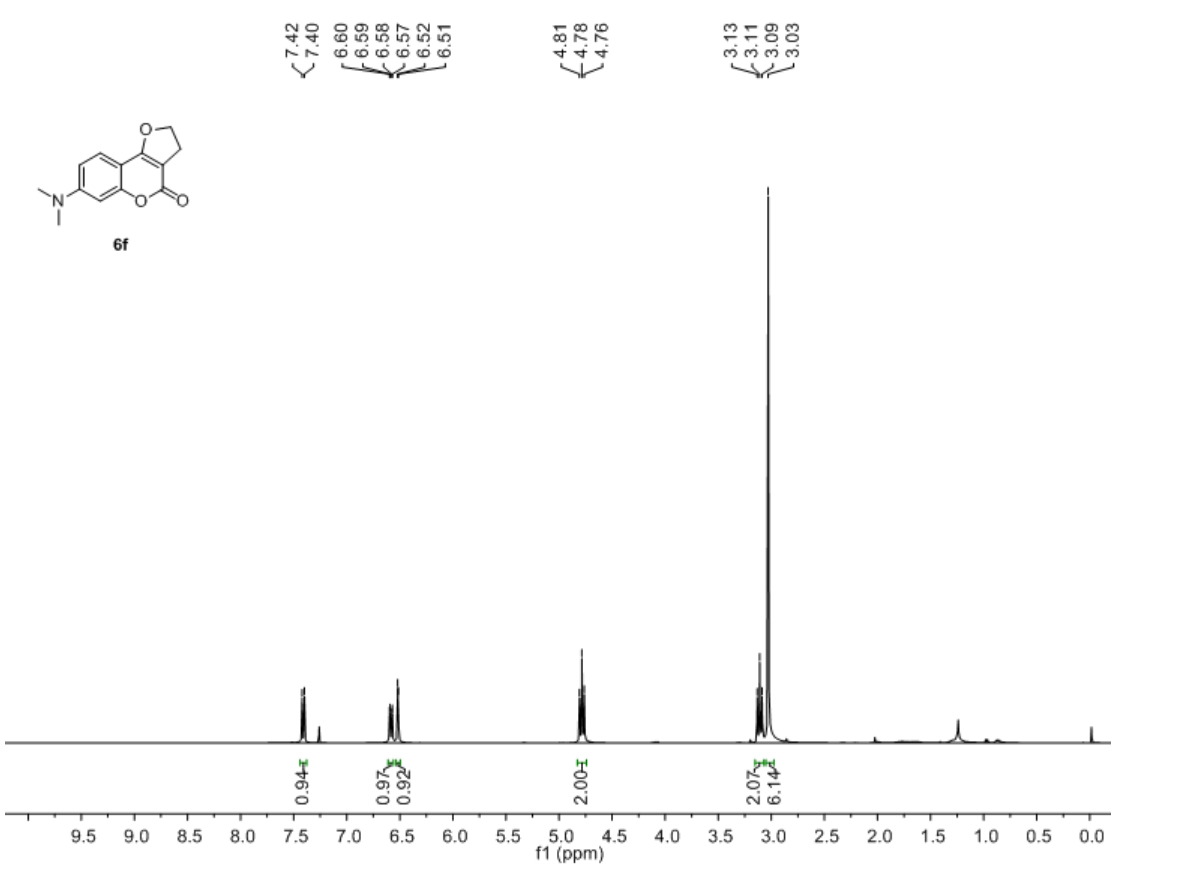

8.56
8.55
8.42
8.42
8.40
8.39
7.50
7.48
4.99
4.96
4.94
3.28
3.26
3.23
O2N
O
O
O
0.87
0.98
0.95
2.00
2.01
f1 (ppm)

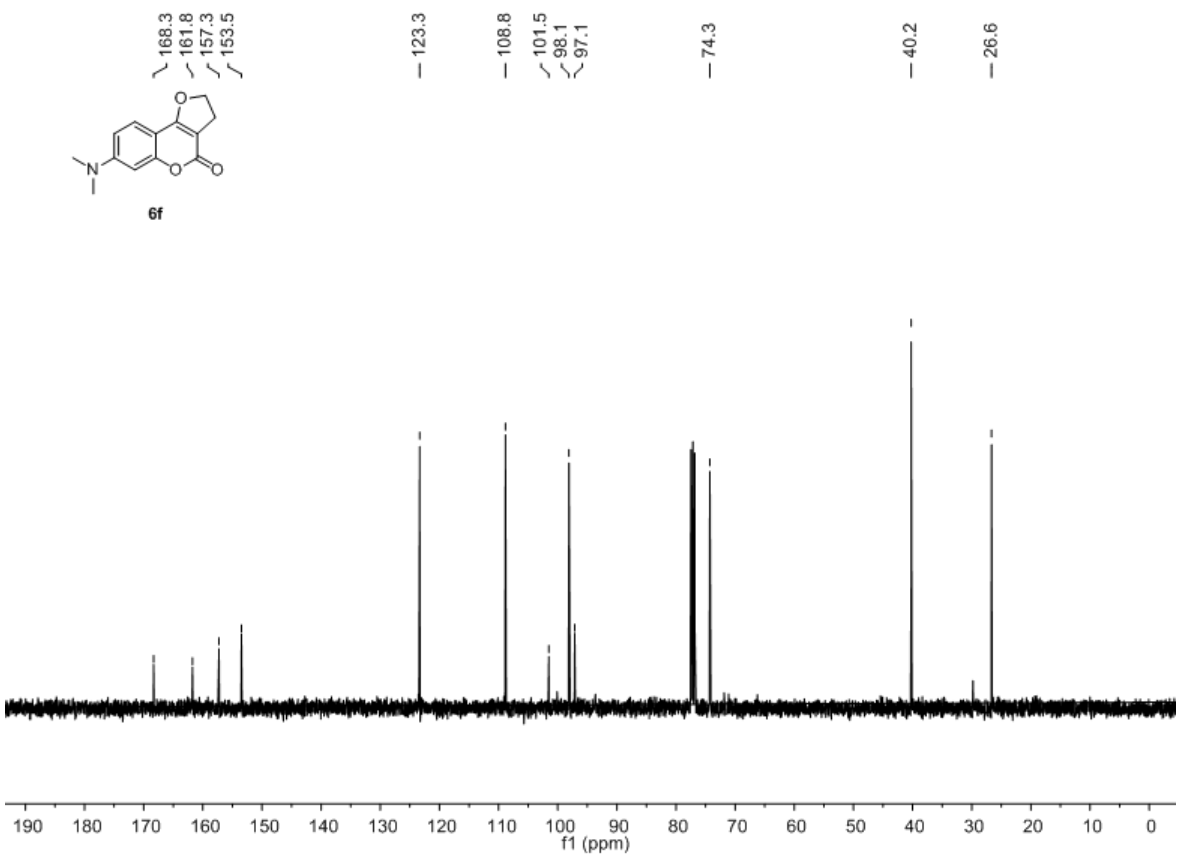
6d


166.3
159.1
158.2
143.8
127.1
119.3
118.2
113.0
104.3
75.1
27.1
O2N
O
O
O
6d
210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0
f1 (ppm)

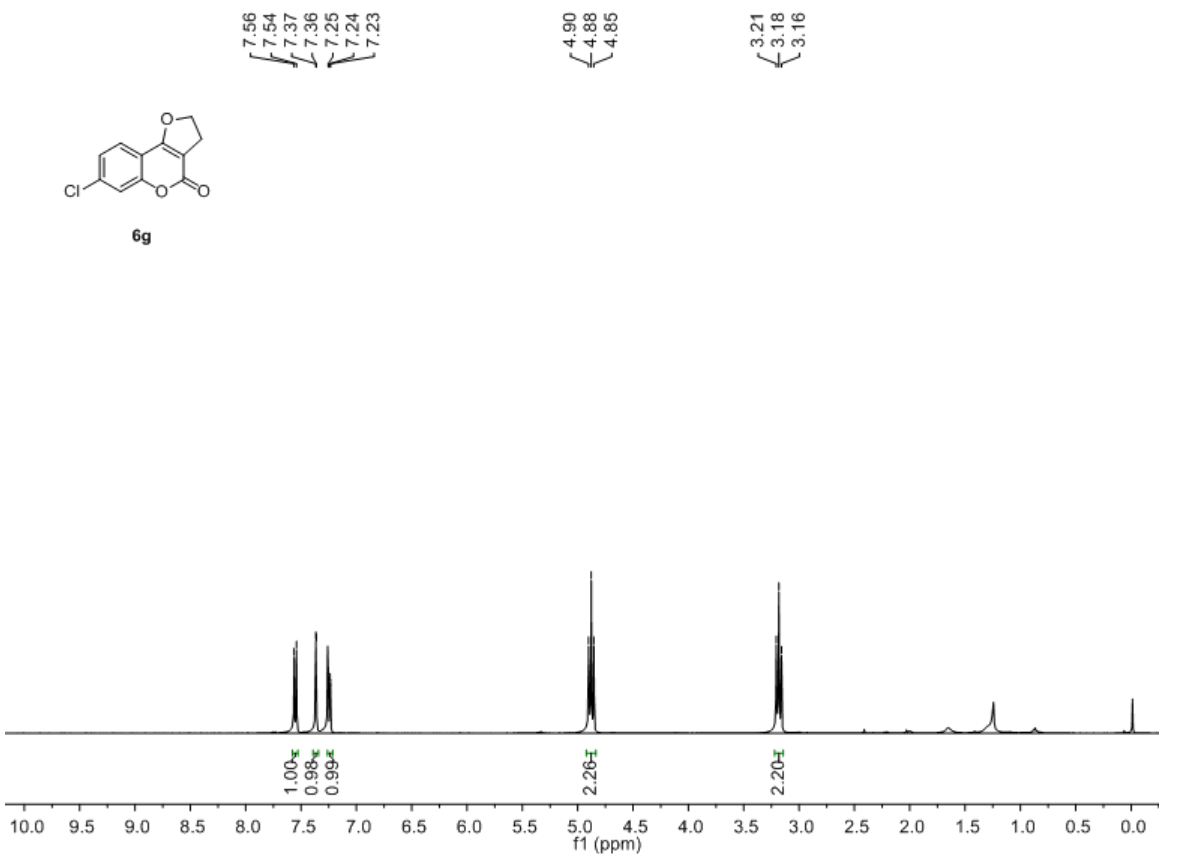

7.50
7.49
7.48
6.83
6.82
6.82
6.81
6.81
6.80
4.85
4.82
4.80
3.84
3.16
3.13
3.11
O
O
O
6e
1.00
2.00
2.15
3.14
2.13
9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0
f1 (ppm)


167.8
163.4
161.1
156.9
123.7
112.4
105.9
100.8
99.5
74.5
55.8
26.7
6e
f1 (ppm)

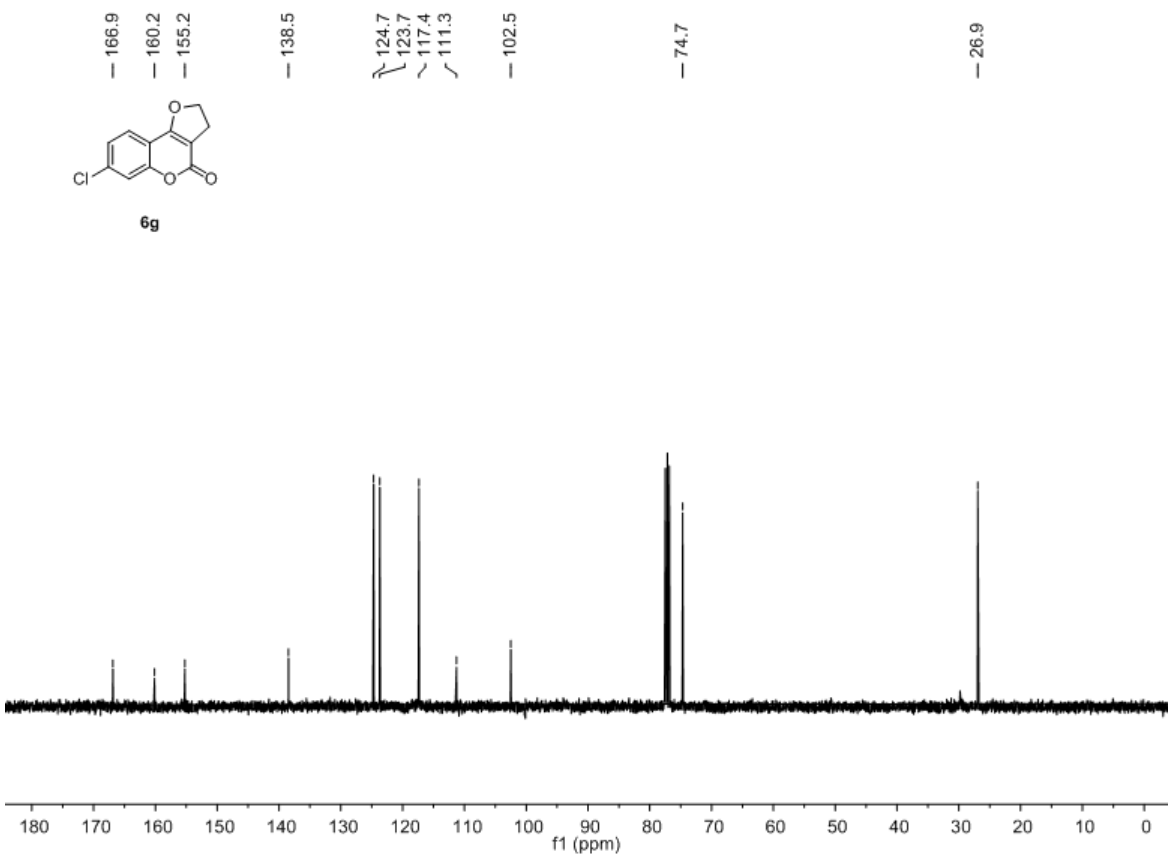

7.42
7.40
6.60
6.59
6.58
6.57
6.52
6.51
4.81
4.78
4.76
3.13
3.11
3.09
3.03
6f
0.94
0.97
0.92
2.00
2.07
6.14
f1 (ppm)

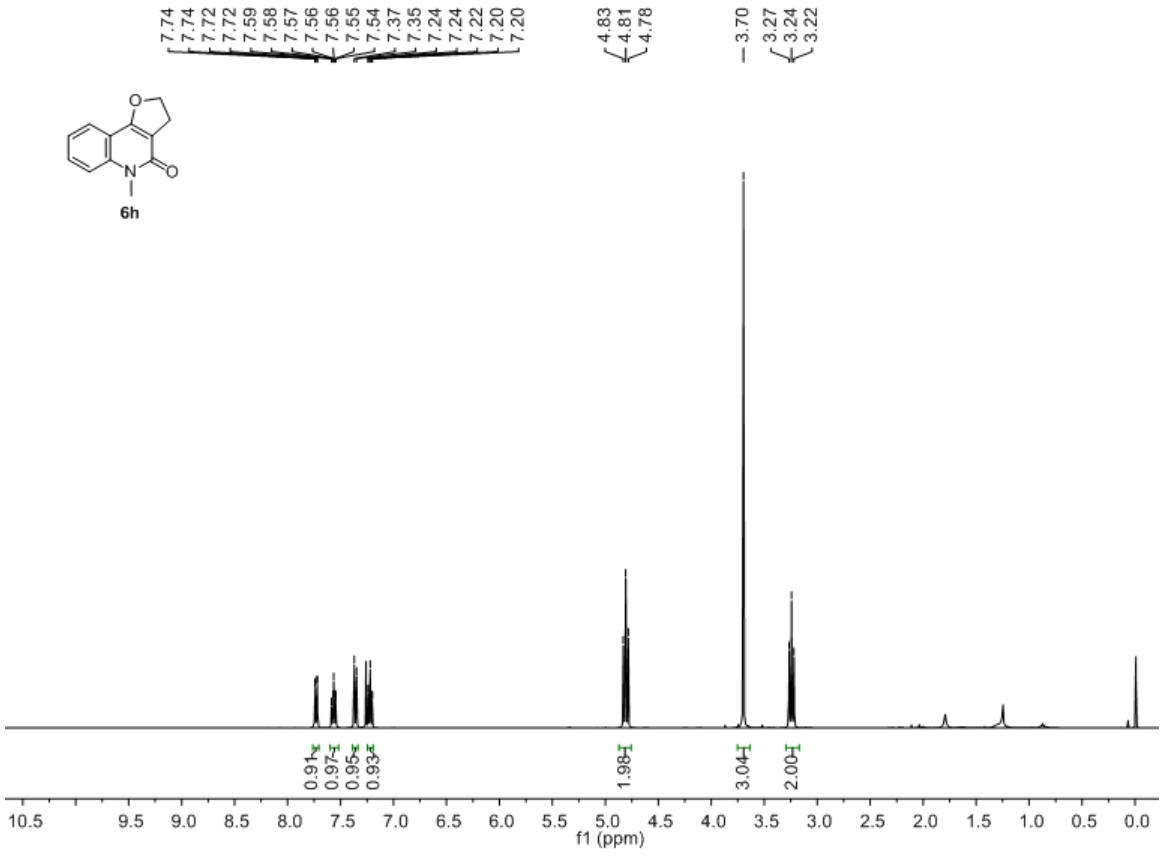

168.3
161.8
157.3
153.5
123.3
108.8
101.5
98.1
97.1
74.3
40.2
26.6
f1 (ppm)

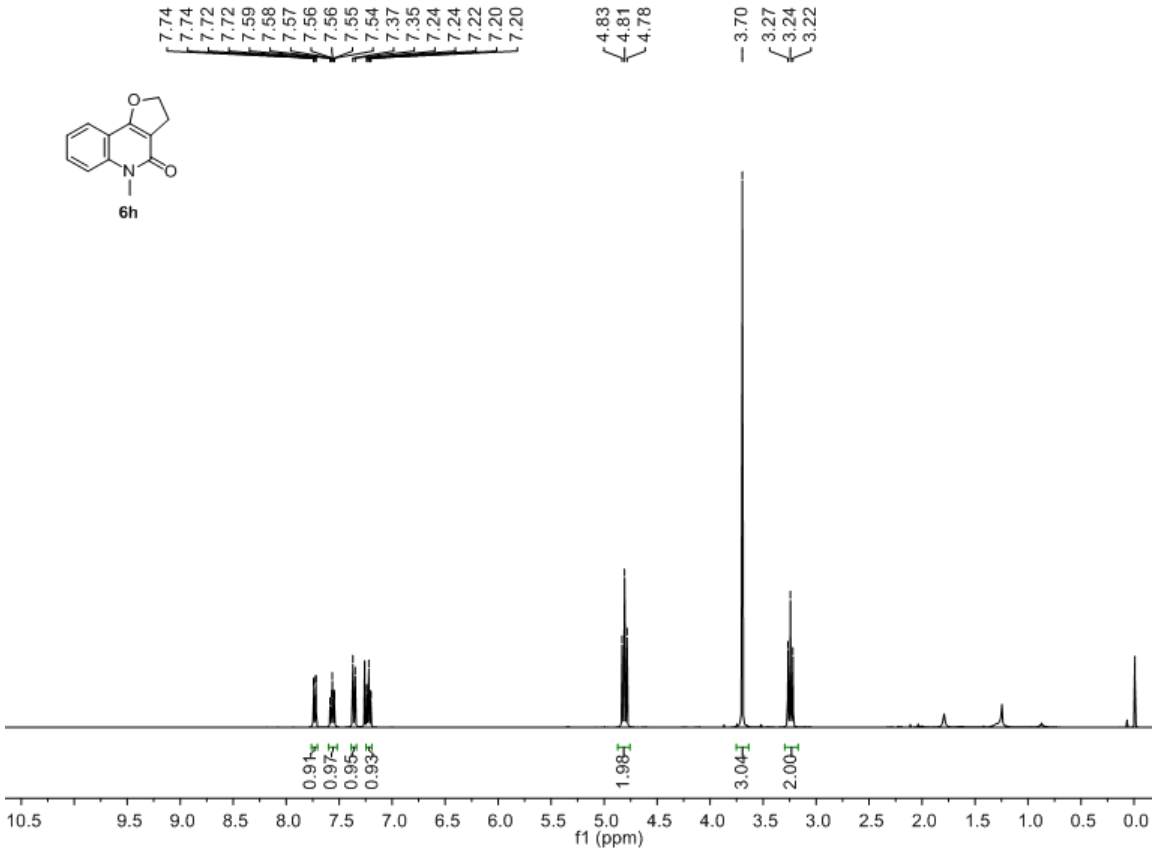
6f

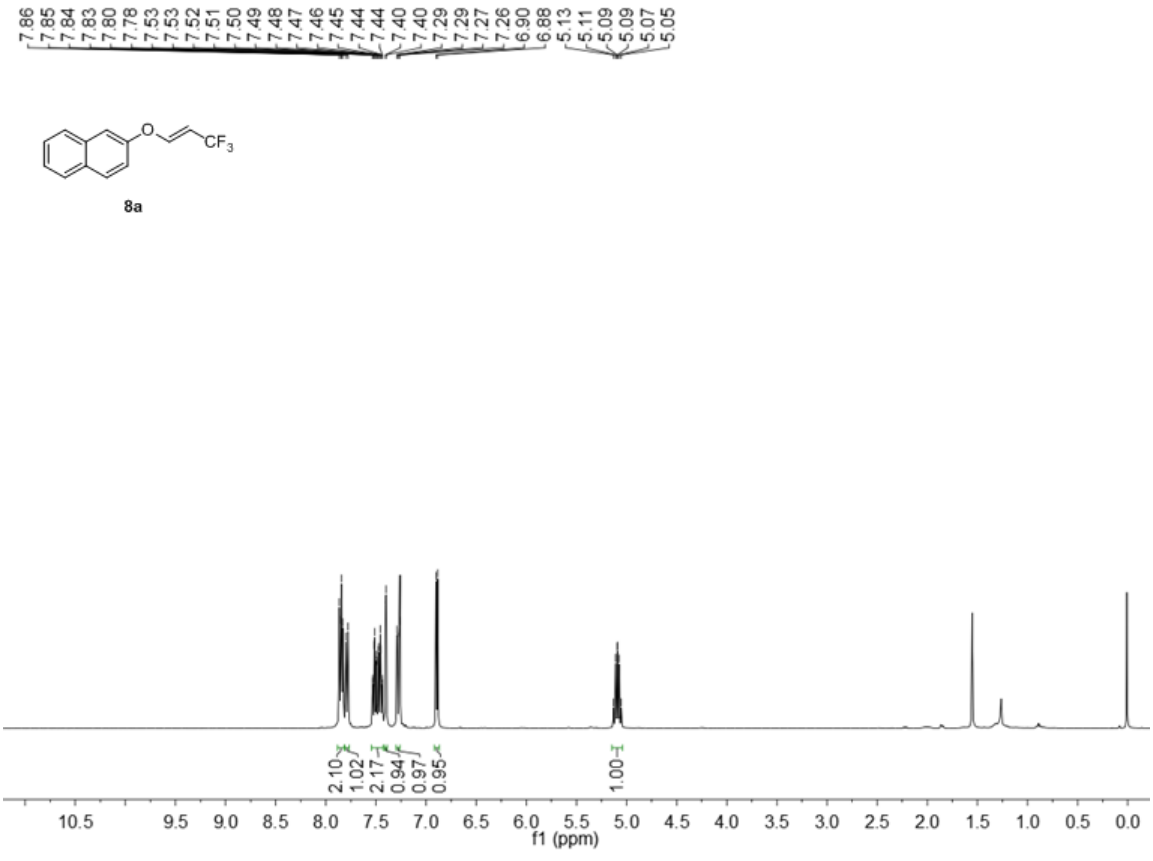

7.56
7.54
7.37
7.36
7.25
7.24
7.23
4.90
4.88
4.85
3.21
3.18
3.16
1.00
0.98
0.99
2.26
2.20
f1 (ppm)

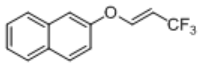
6g


166.9
160.2
155.2
138.5
124.7
123.7
117.4
111.3
102.5
74.7
26.9
Cl
O
O
O
6g
180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0
f1 (ppm)


7.74
7.74
7.72
7.72
7.59
7.58
7.57
7.56
7.56
7.55
7.54
7.37
7.35
7.24
7.24
7.22
7.20
7.20
4.83
4.81
4.78
3.70
3.27
3.24
3.22
O
N
O
6h
0.91
0.97
0.95
0.93
1.98
3.04
2.00
10.5 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)

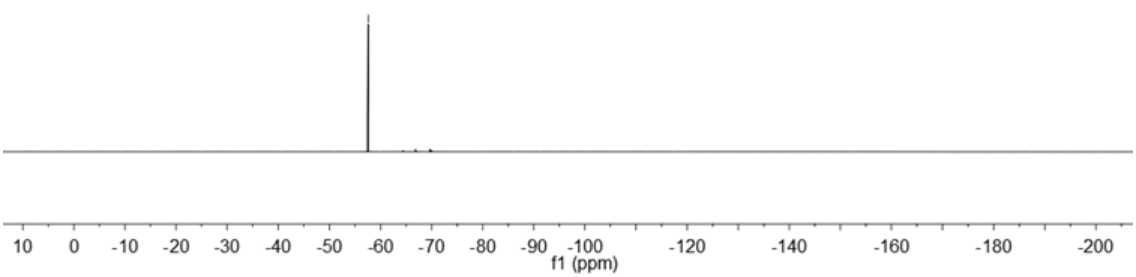

7.74
7.74
7.72
7.72
7.59
7.58
7.57
7.56
7.56
7.55
7.54
7.37
7.35
7.24
7.24
7.22
7.20
7.20
4.83
4.81
4.78
3.70
3.27
3.24
3.22
O
N
O
6h
0.91
0.97
0.95
0.93
1.98
3.04
2.00
10.5
9.5
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
f1 (ppm)


7.86
7.85
7.84
7.83
7.80
7.78
7.53
7.53
7.52
7.51
7.50
7.49
7.48
7.47
7.46
7.45
7.44
7.44
7.40
7.40
7.29
7.27
7.26
6.90
6.88
5.13
5.11
5.09
5.09
5.07
5.05
O
CF3
8a
2.10
1.02
2.17
0.94
0.97
0.95
1.00
10.5
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)

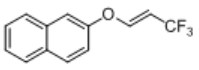


8a

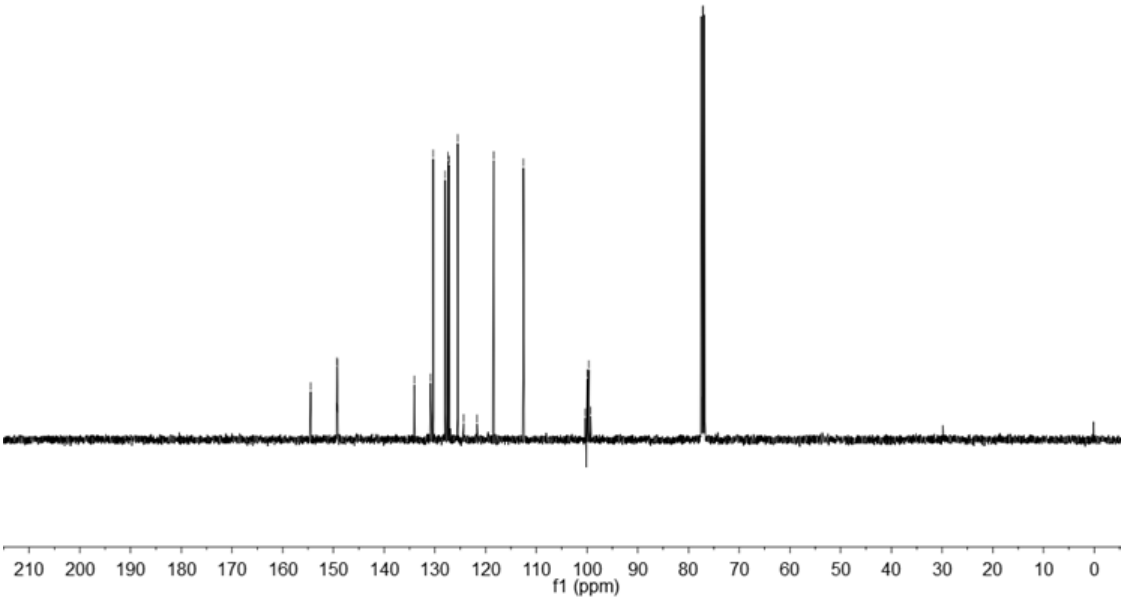

57.60

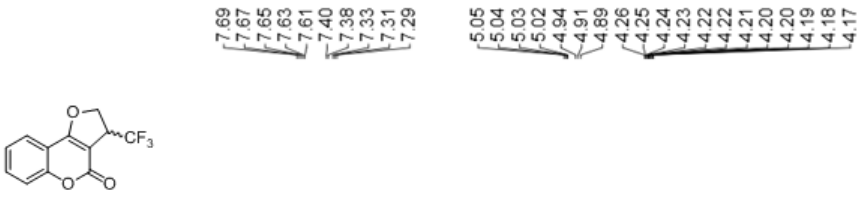

10 0 -10 -20 -30 -40 -50 -60 -70 -80 -90 -100 -120 -140 -160 -180 -200
f1 (ppm)


154.5
149.3
149.3
149.2
149.2
130.9
130.4
128.0
127.4
127.2
125.5
118.4
112.6
100.3
100.0
99.6
99.3



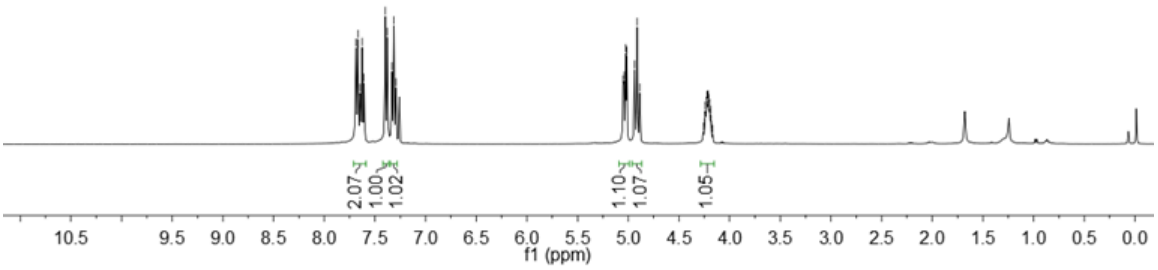
8a

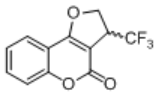

210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0
f1 (ppm)


7.69
7.67
7.65
7.63
7.61
7.40
7.38
7.33
7.31
7.29
5.05
5.04
5.03
5.02
4.94
4.91
4.89
4.26
4.25
4.24
4.23
4.22
4.22
4.21
4.20
4.20
4.19
4.18
4.17

O
CF3
O
O

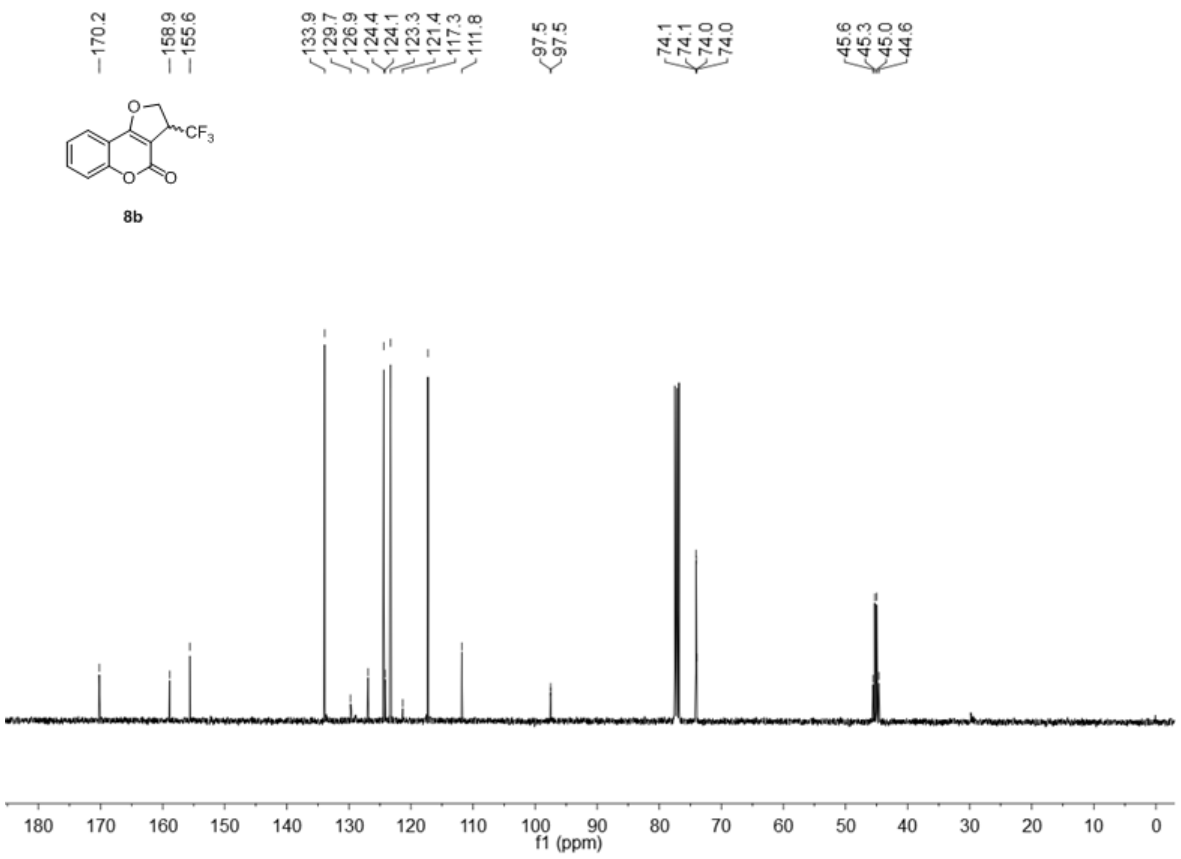
8b

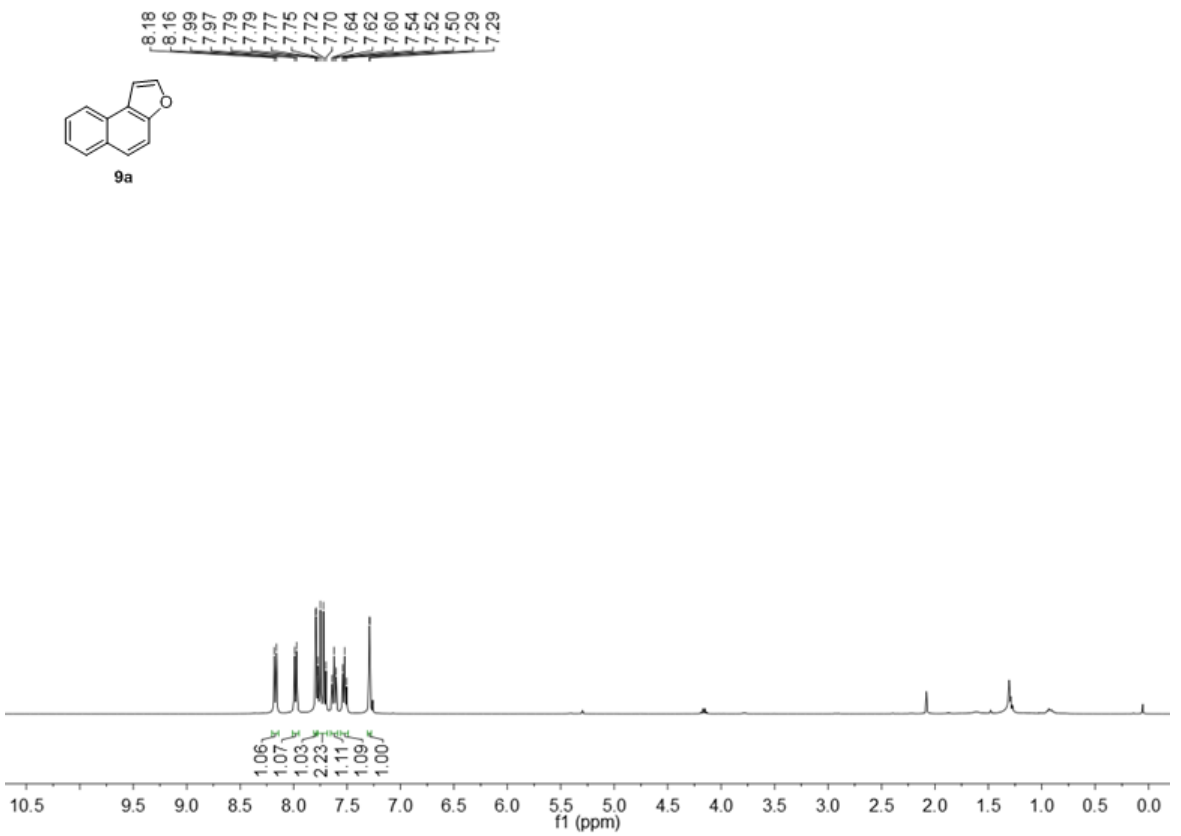

2.07
1.00
1.02
1.10
1.07
1.05
10.5
9.5
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
f1 (ppm)

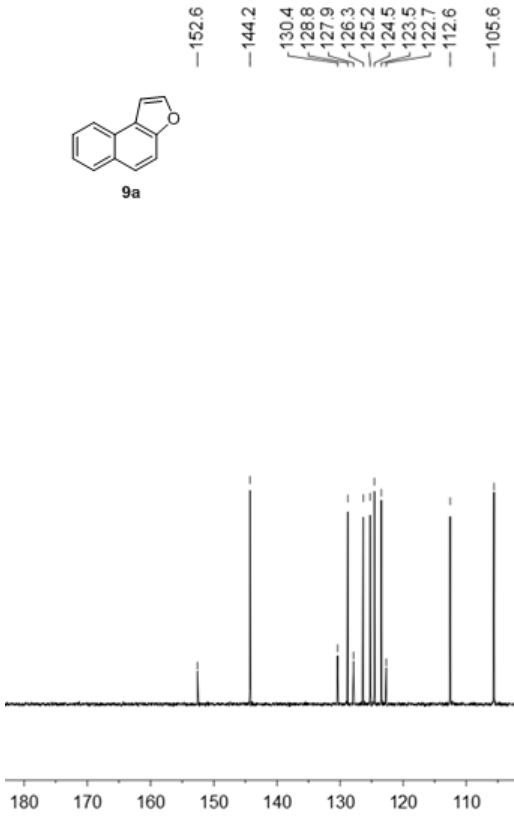

O
CF3
O
O

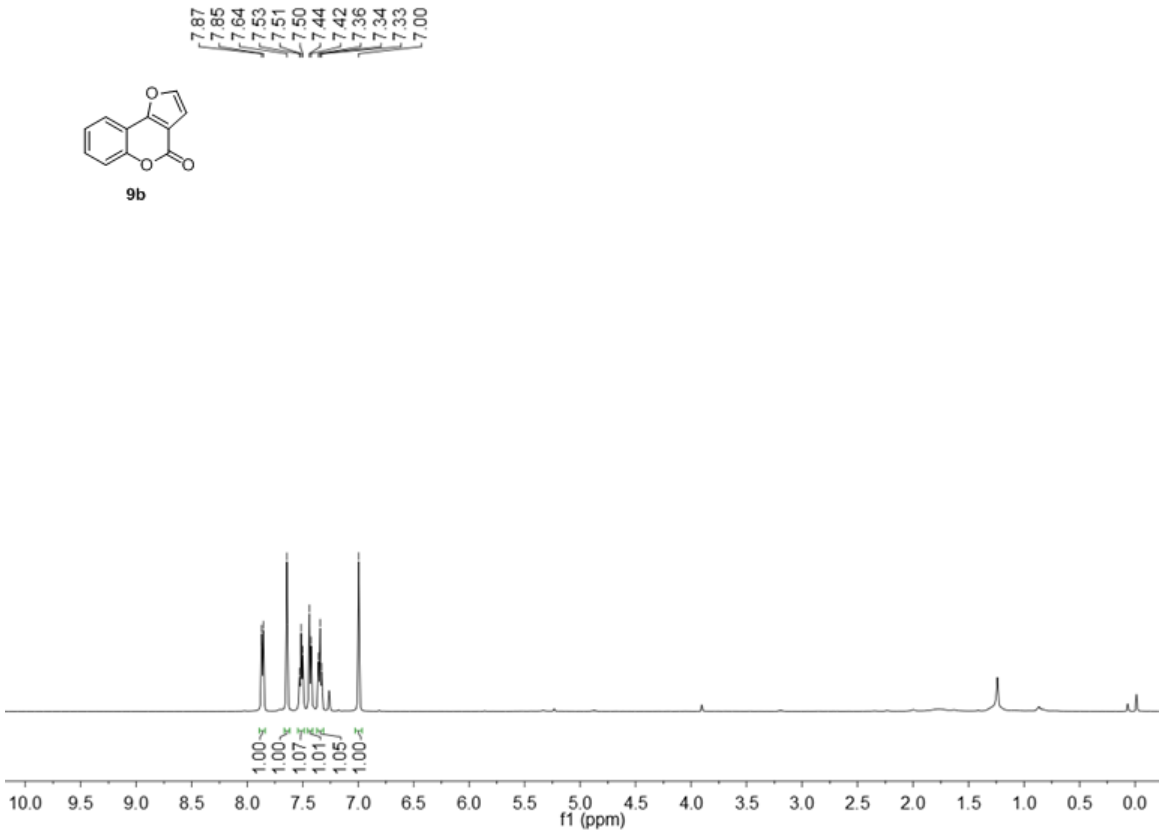
8b

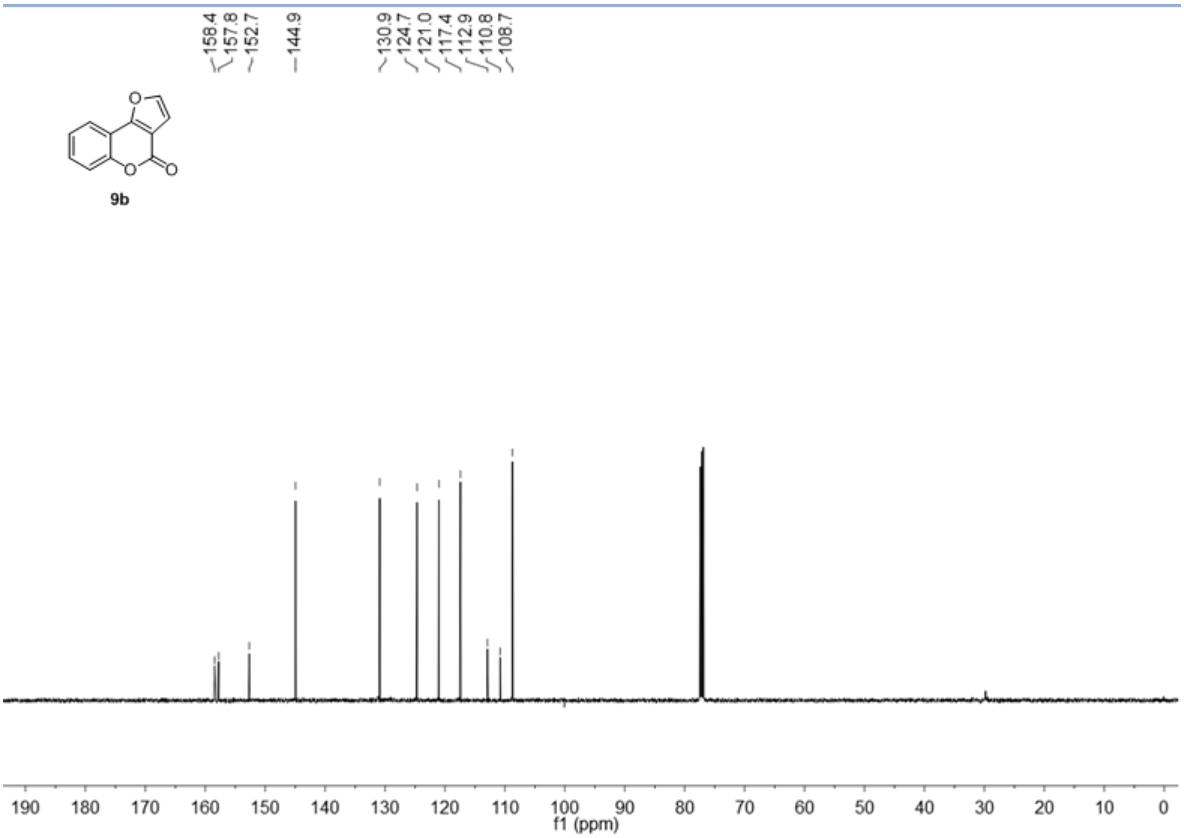
-71.37
10
0
-10
-20
-30
-40
-50
-60
-70
-80
-90
-100
-120
-140
-160
-180
-200
f1 (ppm)


170.2
158.9
155.6
133.9
129.7
126.9
124.4
124.1
123.3
121.4
117.3
111.8
97.5
97.5
74.1
74.1
74.0
74.0
45.6
45.3
45.0
44.6
O
CF3
O
O
8b
180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0
f1 (ppm)


8.18
8.16
7.99
7.97
7.79
7.79
7.77
7.75
7.72
7.70
7.64
7.62
7.60
7.54
7.52
7.50
7.29
7.29
O
9a
1.06
1.07
1.03
2.23
1.11
1.09
1.00
10.5 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)


152.6
144.2
130.4
128.8
127.9
126.3
125.2
124.5
123.5
122.7
112.6
105.6
9a
180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0
f1 (ppm)


7.87
7.85
7.64
7.53
7.51
7.50
7.44
7.42
7.36
7.34
7.33
7.00
9b
1.00
1.00
1.07
1.01
1.05
1.00
10.0 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)


158.4
157.8
152.7
144.9
130.9
124.7
121.0
117.4
112.9
110.8
108.7
O
O
O
9b
190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0
f1 (ppm)