

Electronic Supplementary Information

**Nickel–Catalyzed Tandem Reaction of Cyclic Esterification/C–S Bond
Formation For Synthesis of 5-Oxa-11-thia-benzofluoren-6-ones**

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Experimental Details

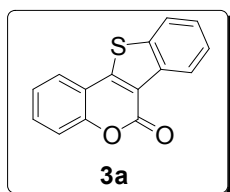
Materials

All reagents used in the experiment were obtained from commercial sources and used without further purification. Solvents for chromatography were of technical grade and distilled prior to use. Solvent mixtures were understood as volume/volume. Chemical yields refer to pure isolated substances. Catalysts were purchased from Alfa Aesar (analytical reagent). Thin layer chromatography (TLC) employed glass 0.25 mm silica gel plates with an F-254 indicator, visualized by irradiation with UV light. The NMR spectra were recorded on a Bruker AVANCE III-400 spectrometer at 400 MHz and 100 MHz for ^1H and ^{13}C NMR in CDCl_3 , respectively. The NMR chemical shift was reported in ppm relative to 7.26 and 77 ppm of CDCl_3 as the standards of ^1H and ^{13}C NMR, respectively. The mass spectra were performed on a Bruker Esquire 3000 plus mass spectrometer equipped with an ESI interface and ion trap analyzer. The ESI-HRMS was tested on a Bruker 7-tesla FT-ICR MS equipped with an electrospray source.

General Synthesis Methods of 3a–5f

A solution of 3-(2-hydroxy-phenyl)-acrylic acids **1** (0.5 mmol), 2-halide-benzenethiols **2** or **4** (0.6 mmol), $\text{Ni}(\text{CO})_4$ (10 mol%, 8.5 mg), and NaOEt (2 equiv, 68 mg) in DMSO (5 mL) was stirred under air. After stirred at 90 °C for 10 h, it was cooled to room temperature. Then the reaction mixture was quenched with saturated salt water (10 mL). After that, the solution was extracted with ethyl acetate (3 × 10 mL), and then washed with saturated Na_2CO_3 solution. The organic layers were combined and dried by Na_2SO_4 and concentrated in vacuo. The pure product **3** or **5** (69-89% yield) was afforded by flash column chromatography on silica gel (cyclohexane/ethyl acetate).

Analytical Datas



Benzo[4,5]furo[3,2-c]chromen-6-one (3a) white solid, mp 181-182 °C, was afforded by flash column chromatography on silica gel (cyclohexane/ethyl acetate = 5:1);

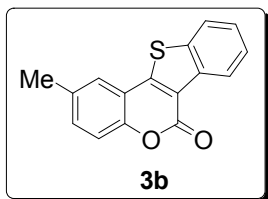
^1H NMR (500 MHz, CDCl_3): δ 8.15 (dd, $J_1 = 2.4$ Hz, $J_2 = 6.6$ Hz, 1H), 8.05 (dd, $J_1 = 1.5$ Hz, $J_2 = 7.8$ Hz,

1H), 7.68 (dd, $J_1 = 1.7$ Hz, $J_2 = 6.9$ Hz, 1H), 7.60-7.64 (m, 1H), 7.41-7.52 (m, 4H);

^{13}C NMR (125 MHz, CDCl_3): δ 160.0, 158.1, 155.6, 153.7, 131.9, 126.8, 125.2, 124.7, 123.5, 121.9, 117.5, 112.7, 111.8, 105.9 (one peak is missing due to overlap);

IR (CHCl_3): 2918, 2849, 1736, 1628, 1498, 1452, 1371, 1320, 1192, 1096, 1083, 1032, 972, 912, 889, 780, 744 cm^{-1} ;

HRMS (+ESI) Calcd for $\text{C}_{15}\text{H}_9\text{O}_2\text{S}$ $[\text{M}+\text{H}]^+$: 253.0320, found 253.0325.



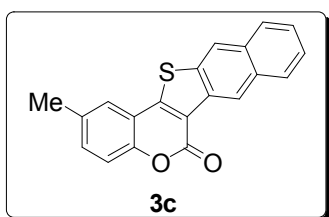
2-Methyl-5-oxa-11-thia-benzo[a]fluoren-6-one (3b) yellow solid, mp 151-153 °C, was afforded by flash column chromatography on silica gel (cyclohexane/ethyl acetate = 5:1);

^1H NMR (500 MHz, CDCl_3): δ 8.07-8.18 (m, 1H), 7.80 (br s, 1H), 7.59-7.70 (m, 1H), 7.32-7.51 (m, 4H), 2.48 (s, 3H);

^{13}C NMR (125 MHz, CDCl_3): δ 160.0, 158.2, 155.5, 151.9, 134.5, 133.0, 126.6, 125.1, 123.5, 121.8, 121.5, 117.2, 112.3, 111.7, 105.8, 20.9;

IR (CHCl_3): 2920, 2850, 1713, 1635, 1570, 1447, 1358, 1320, 1161, 1097, 1077, 1009, 982, 817, 776, 748, 737, 669, 656 cm^{-1} ;

HRMS (+ESI) Calcd for $\text{C}_{16}\text{H}_{11}\text{O}_2\text{S}$ $[\text{M}+\text{H}]^+$: 266.0403, found 266.0404.



2-Methyl-5-oxa-13-thia-dibenzo[a,h]fluoren-6-one (3c) yellow solid, mp 151-153 °C, was afforded by flash column chromatography on silica gel (cyclohexane/ethyl acetate = 5:1);

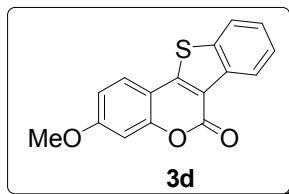
^1H NMR (500 MHz, CDCl_3): δ 8.59 s, 1H), 7.94-8.06 (m, 3H), 7.86 (s, 1H), 7.42-7.56 (m, 4H), 2.51 (s, H);

^{13}C NMR (125 MHz, CDCl_3): δ 162.4, 158.3, 153.9, 152.4, 35.7, 134.7, 133.7, 132.1, 128.5, 127.9, 126.2, 125.3, 123.4, 121.8, 20.4, 117.3, 112.1, 107.7, 105.2, 20.9 ;

IR (CHCl_3): 2923, 2853, 1729, 714, 1613, 1594, 1506, 1464, 1456, 1367, 1261, 1210, 805, 771, 666,

45 cm⁻¹;

HRMS (+ESI) Calcd for C₂₀H₁₃O₂S [M+H]⁺: 316.6560, Found 316.6562.



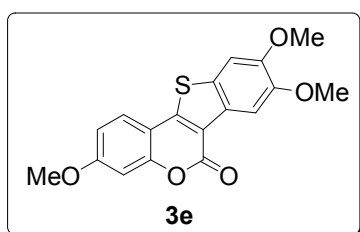
3-Methoxy-5-oxa-11-thia-benzo[a]fluoren-6-one (3d) yellow solid, mp 188-189 °C, was afforded by flash column chromatography on silica gel (cyclohexane/ethyl acetate = 5:1);

¹H NMR (500 MHz, CDCl₃): δ 8.04–8.14 (m, 1H), 7.91 (dd, *J*₁ = 1.9 Hz, *J*₂ = 7.3 Hz, 1H), 7.57-7.67 (m, H), 7.39-7.47 (m, 2H), 6.94-7.02 (m, 2H), 3.91 (s, 3H);

¹³C NMR 125 MHz, CDCl₃): δ 163.0, 160.6, 158.3, 155.5, 155.2, 126.0, 125.0, 23.5, 122.8, 121.4, 113.0, 111.4, 105.8, 103.3, 101.3, 55.7;

IR (CHCl₃): 2921, 2851, 1729, 1613, 1600, 1447, 1427, 1367, 1275, 254, 1095, 1023, 986, 945, 855, 774, 753, 746 cm⁻¹;

HRMS (+ESI) calcd for C₁₆H₁₁O₃S [M+H]⁺: 282.0353, found 282.0355.



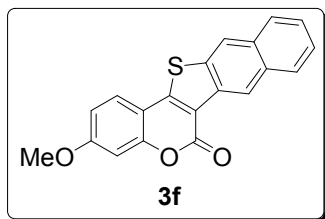
3,8,9-Trimethoxy-5-oxa-11-thia-benzo[a]fluoren-6-one (3e) yellow solid, mp 230-233 °C, was afforded by flash column chromatography on silica gel (cyclohexane/ethyl acetate = 5:1);

¹H NMR (500 MHz, CDCl₃): δ 7.85 (d, *J* = 8.4 Hz, 1H), 7.51 (s, 1H), 7.13 (s, 1H), 6.94–7.04 (m 2H), 4.00 (s, 3H), 3.96 (s, 3H), 3.90 (s, 3H);

¹³C NMR (125 MHz, CDCl₃): δ 162.4, 159.7, 158.8, 154.9, 149.9, 149.0, 147.9, 122.3, 115.5, 113.0, 106.3, 103.8, 102.2, 101.4, 95.5, 56.5, 56.4, 55.8;

IR (CHCl₃): 2924, 2853, 1741, 1628, 1608, 1494, 1464, 1411, 1278, 1214, 1024, 837, 804, 765 cm⁻¹;

HRMS (+ESI) Calcd for C₁₈H₁₅O₅S [M+H]⁺: 342.0564, found 342.0566.



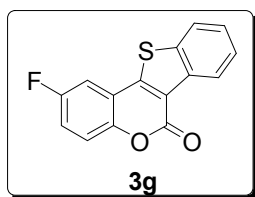
3-Methoxy-5-oxa-13-thia-dibenzo[a,h]fluoren-6-one (3f) yellow solid, mp: 197-200 °C m, was afforded by flash column chromatography on silica gel (cyclohexane/ethyl acetate = 5:1);

¹H NMR (500 MHz, CDCl₃): δ 8.55 (s, 1H), 7.87-8.12 (m, 4H), 7.43-7.60 (m, 2H), 6.92-7.10 (m, 2H), 3.93 (s, 3H);

¹³C NMR (125 MHz, CDCl₃): δ 163.5, 162.9, 158.2, 156.1, 153.8, 131.8, 131.4, 128.3, 127.9, 125.9, 125.2, 123.4, 123.2, 119.8, 113.2, 107.5, 105.6, 102.6, 101.4, 55.8 ;

IR (CHCl₃): 3419, 2922, 2851, 1743, 1613, 1465, 1206, 1161, 1025, 937, 768, 746, 702 cm⁻¹;

HRMS (+ESI) Calcd for C₂₀H₁₃O₃S [M+H]⁺: 332.0507, found 332.0512.



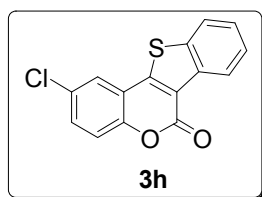
2-Fluoro-5-oxa-11-thia-benzo[a]fluoren-6-one (3g) yellow solid, mp 198-201 °C, was afforded by flash column chromatography on silica gel (cyclohexane/ethyl acetate = 5:1);

¹H NMR (500 MHz, CDCl₃): δ 8.15 (d, *J* = 7.4 Hz, 1H), 7.62-7.74 (m, 2H), 7.45-7.55 (m, 3H), 7.29-7.34 (m, 1H);

¹³C NMR (125 MHz, CDCl₃): δ 159.0 (d, *J* = 2.8 Hz), 158.9 (d, *J* = 245.7 Hz), 157.6, 155.7, 149.8 (d, *J* = 1.6 Hz), 127.2, 126.4, 123.2, 122.0, 119.4 (d, *J* = 34.7 Hz), 119.3, 113.4 (d, *J* = 9.8 Hz), 111.8, 107.4 (d, *J* = 25.8 Hz), 106.6;

IR (CHCl₃): 2920, 2850, 1763, 1734, 1567, 1451, 1401, 1257, 1157, 1094, 1066, 996, 861, 821, 774, 748, 667 cm⁻¹;

HRMS (+ESI) Calcd for C₁₅H₈FO₂S [M+H]⁺: 270.0153, found 270.0151.



2-Chloro-5-oxa-11-thia-benzo[a]fluoren-6-one (3h) yellow solid, mp 219-220 °C, was afforded by

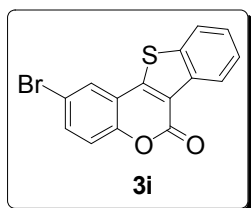
flash column chromatography on silica gel (cyclohexane/ethyl acetate = 5:1);

^1H NMR (500 MHz, CDCl_3): δ 8.14 (dd, $J_1 = 1.2$ Hz, $J_2 = 7.9$ Hz, 1H), 8.01 (d, $J = 2.5$ Hz, 1H), 7.68 (d, $J = 7.6$ Hz, 1H), 7.55 (dd, $J_1 = 2.5$ Hz, $J_2 = 8.9$ Hz, 1H), 7.47-7.52 (m, 2H), 7.45 (d, $J = 8.9$ Hz, 1H);

^{13}C NMR (125 MHz, CDCl_3): δ 158.5, 157.4, 155.6, 151.8, 131.8, 130.2, 127.1, 125.4, 123.1, 121.9, 121.2, 118.8, 113.6, 111.8, 106.5;

IR (CHCl_3): 2919, 2850, 1760, 1732, 1556, 1447, 1416, 1162, 1094, 1068, 981, 870, 822, 774, 750, 662 cm^{-1} ;

HRMS (+ESI) Calcd for $\text{C}_{15}\text{H}_8\text{ClO}_2\text{S}$ [$\text{M}+\text{H}$] $^+$: 285.9857, found 285.9862



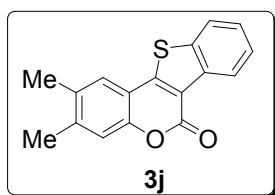
2-Bromo-5-oxa-11-thia-benzo[a]fluoren-6-one (3i) yellow solid, mp 215-217 $^{\circ}\text{C}$, was afforded by flash column chromatography on silica gel (cyclohexane/ethyl acetate = 5:1);

^1H NMR (500 MHz, CDCl_3): δ 8.18 (d, $J = 2.3$ Hz, 1H), 8.13-8.16 (m, 1H), 7.67-7.71 (m, 2H), 7.46-7.55 (m, 2H), 7.40 (d, $J = 8.8$ Hz, 1H);

^{13}C NMR (125 MHz, CDCl_3): δ 158.4, 157.3, 155.6, 152.3, 134.6, 127.2, 125.4, 124.3, 123.1, 121.9, 119.1, 117.4, 114.1, 111.8, 106.5;

IR (CHCl_3): 2921, 2851, 1757, 1734, 1447, 1162, 979, 872, 820, 775, 750, 665 cm^{-1} ;

HRMS (+ESI) Calcd for $\text{C}_{15}\text{H}_8\text{BrO}_2\text{S}$ [$\text{M}+\text{H}$] $^+$: 329.9352, found 329.9348.



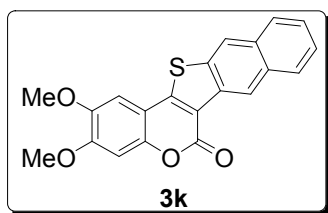
2,3-Dimethyl-5-oxa-11-thia-benzo[a]fluoren-6-one (3j) yellow solid, mp 208-210 $^{\circ}\text{C}$, was afforded by flash column chromatography on silica gel (cyclohexane/ethyl acetate = 5:1);

^1H NMR (500 MHz, CDCl_3): δ 8.03-8.14 (m, 1H), 7.67 (s, 1H), 7.56-7.64 (m, 1H), 7.36-7.50 (m, 2H), 7.21 (s, 1H), 2.34 (s, 6H);

^{13}C NMR (125 MHz, CDCl_3): δ 160.2, 158.3, 155.2, 152.1, 142.1, 133.5, 126.2, 124.9, 123.6, 121.6, 121.5, 117.8, 111.5, 109.9, 104.8, 20.4, 19.2;

IR (CHCl_3): 2917, 2849, 1741, 1638, 1448, 1375, 1177, 1095, 1055, 866, 776, 749, 737 cm^{-1} ;

HRMS (+ESI) Calcd for $C_{17}H_{13}O_2S$ $[M+H]^+$: 280.0560, found 286.0558.



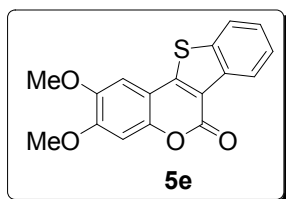
2,3-Dimethoxy-5-oxa-13-thia-dibenzo[a,h]fluoren-6-one (3k) yellow solid, was afforded by flash column chromatography on silica gel (cyclohexane/ethyl acetate = 5:1);

1H NMR (500 MHz, $CDCl_3$): δ 8.54 (s, 1H), 7.94-8.05 (m, 3H), 7.50-7.55 (m, 2H), 7.39 (s, 1H), 7.00 (s, 1H), 4.04 (s, 3H), 3.99 (s, 3H);

^{13}C NMR (125 MHz, $CDCl_3$): δ 162.9, 158.5, 153.8, 153.6, 150.4, 146.9, 131.8, 131.5, 128.4, 127.9, 126.0, 125.3, 123.6, 119.9, 114.1, 107.5, 104.4, 102.0, 100.6, 56.6, 56.6;

IR ($CHCl_3$): 2960, 2925, 2854, 138, 1732, 1519, 1456, 1276, 1261, 1095, 1020, 800, 675, 664 cm^{-1} ;

HRMS (+ESI) Calcd for $C_{21}H_{15}O_4S$ $[M+H]^+$: 362.0615, found 362.0617.



2,3-Dimethoxy-5-oxa-11-thia-benzo[a]fluoren-6-one (5e) yellow solid, mp 227-230 $^{\circ}C$, was afforded by flash column chromatography on silica gel (cyclohexane/ethyl acetate = 5:1);

1H NMR (500 MHz, $CDCl_3$): δ 8.09 (dd, $J_1 = 3.4$ Hz, $J_2 = 5.7$ Hz, 1H), 7.62 (dd, $J_1 = 3.0$ Hz, $J_2 = 6.2$ Hz, 1H), 7.44 (d, $J = 3.3$ Hz, 1H), 7.43 (d, $J = 3.1$ Hz, 1H), 7.35 (s, 1H), 6.99 (s, 1H), 4.02 (s, 3H), 3.97 (s, 3H);

^{13}C NMR (125 MHz, $CDCl_3$): δ 160.5, 158.4, 155.1, 152.9, 149.6, 146.7, 126.1, 125.0, 123.6, 121.5, 111.3, 104.5, 103.6, 101.7, 100.5, 56.3, 56.3;

IR ($CHCl_3$): 2917, 2849, 1722, 1515, 1459, 1444, 1270 cm^{-1} ;

HRMS (+ESI) Calcd for $C_{17}H_{13}O_4S$ $[M+H]^+$: 299.0380, found 299.0382.

Spectrums

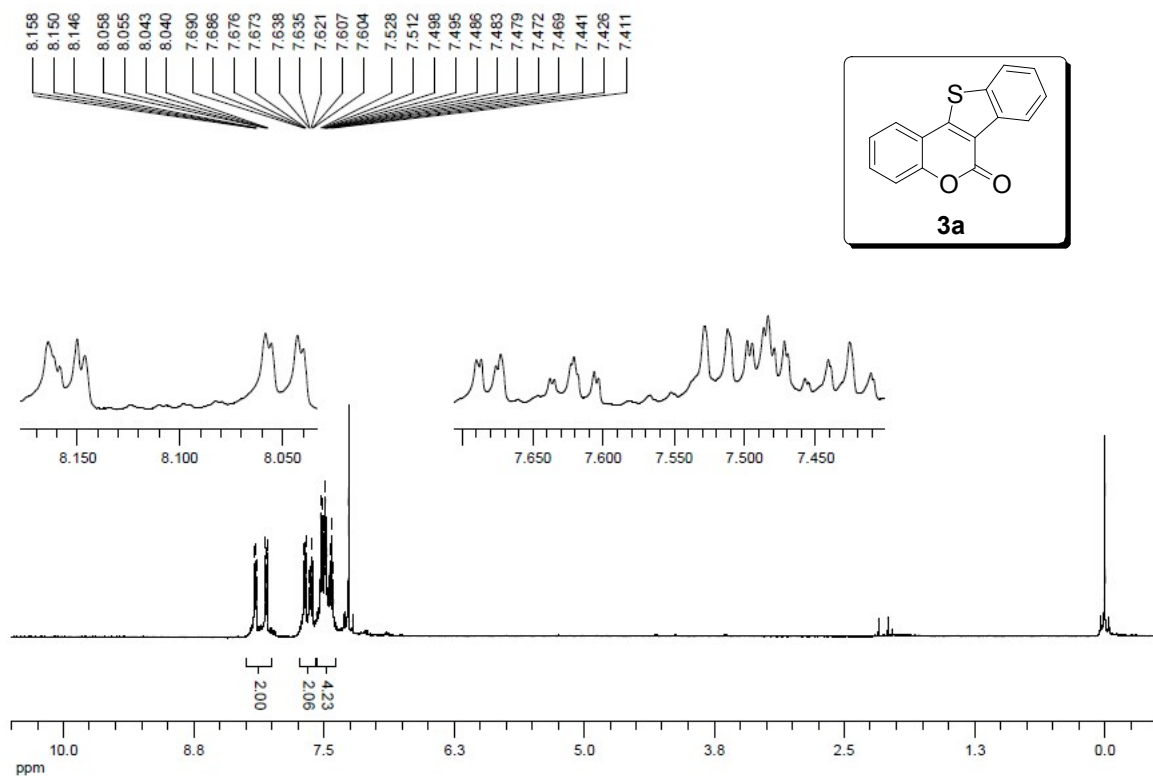


Figure 1. **3a** ^1H NMR

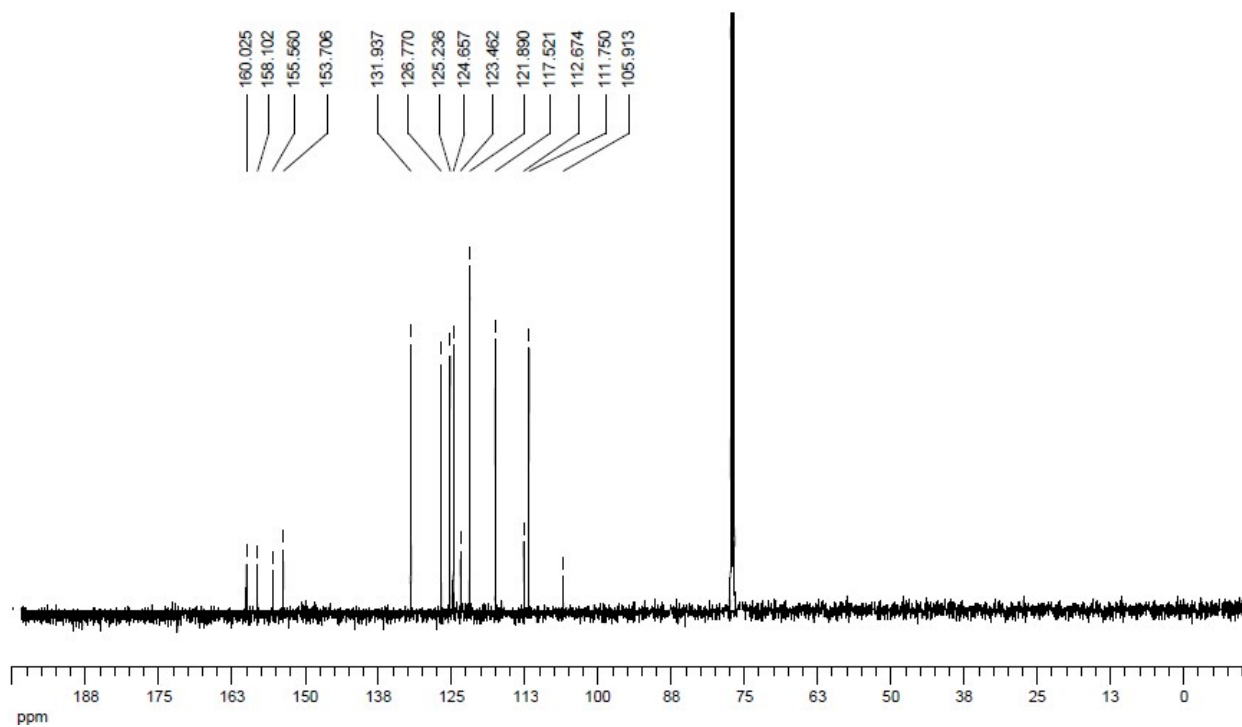


Figure 2. **3a** ^{13}C NMR

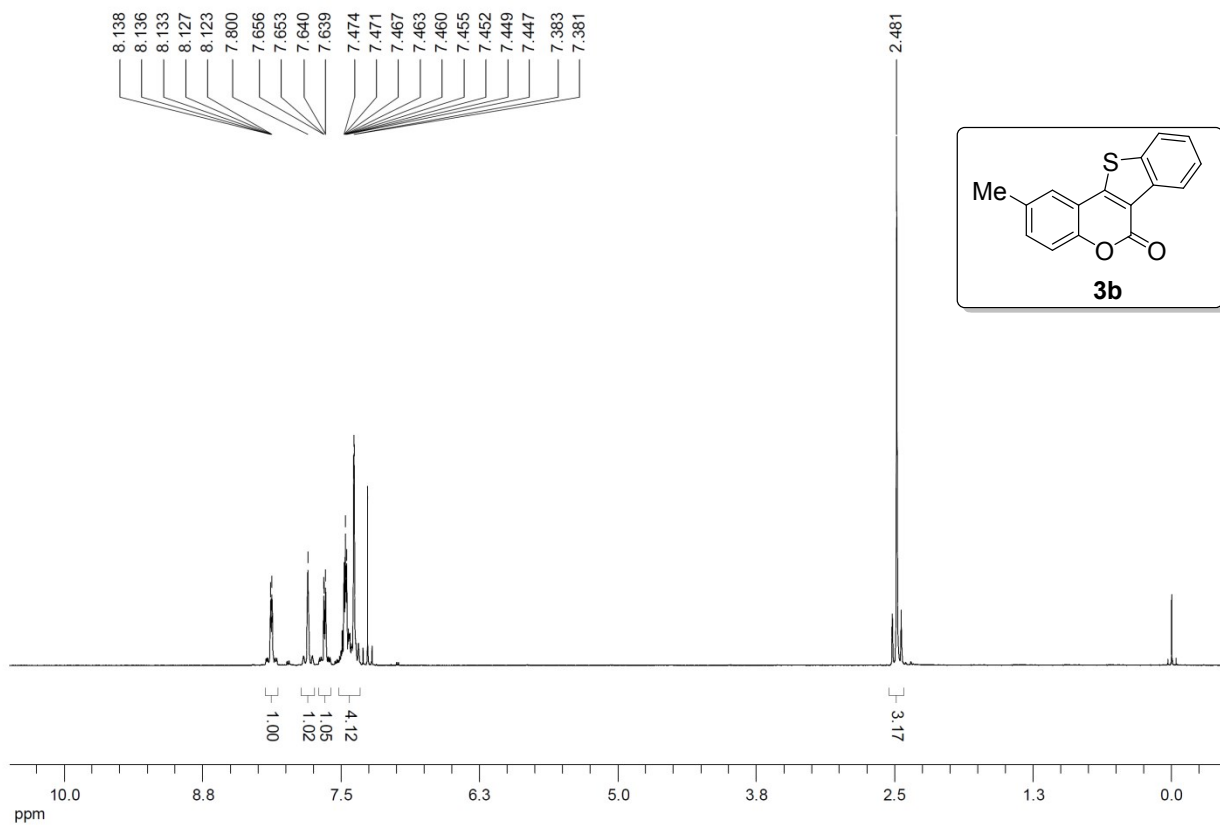


Figure 3. **3b** ^1H NMR

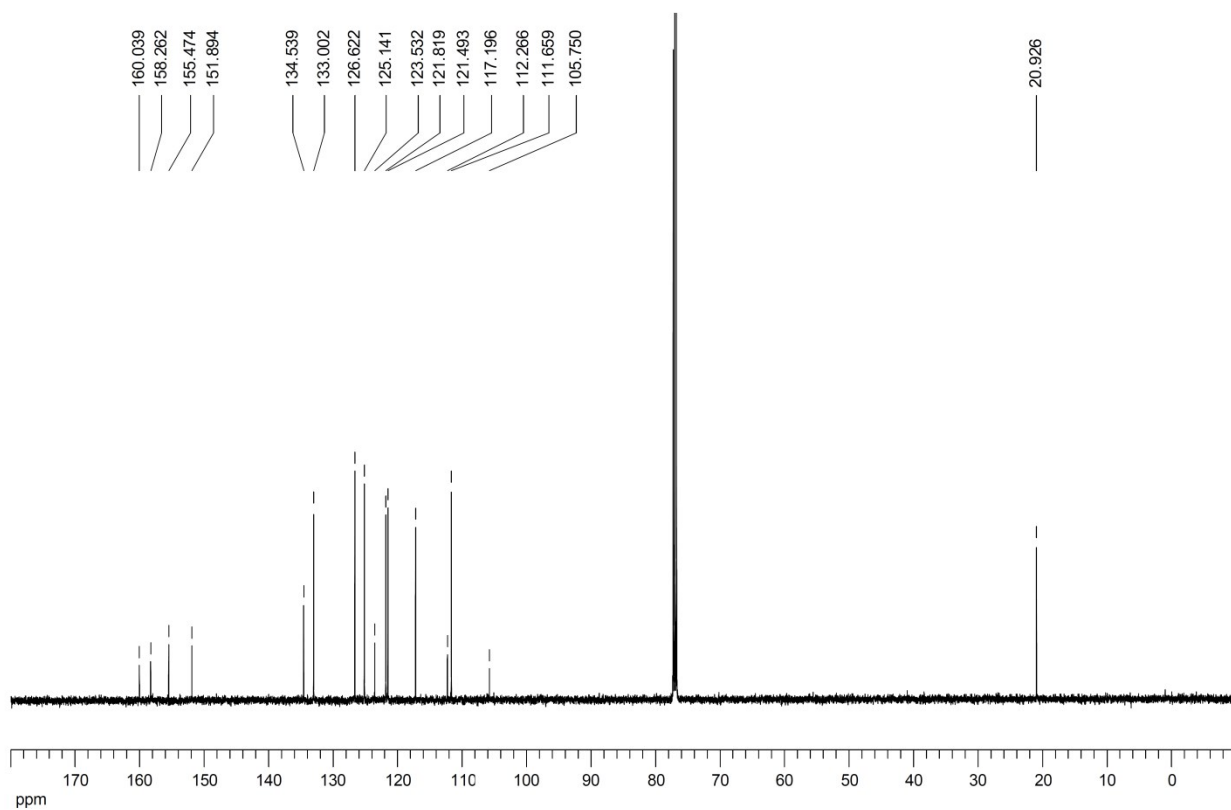


Figure 4. **3b** ^{13}C NMR

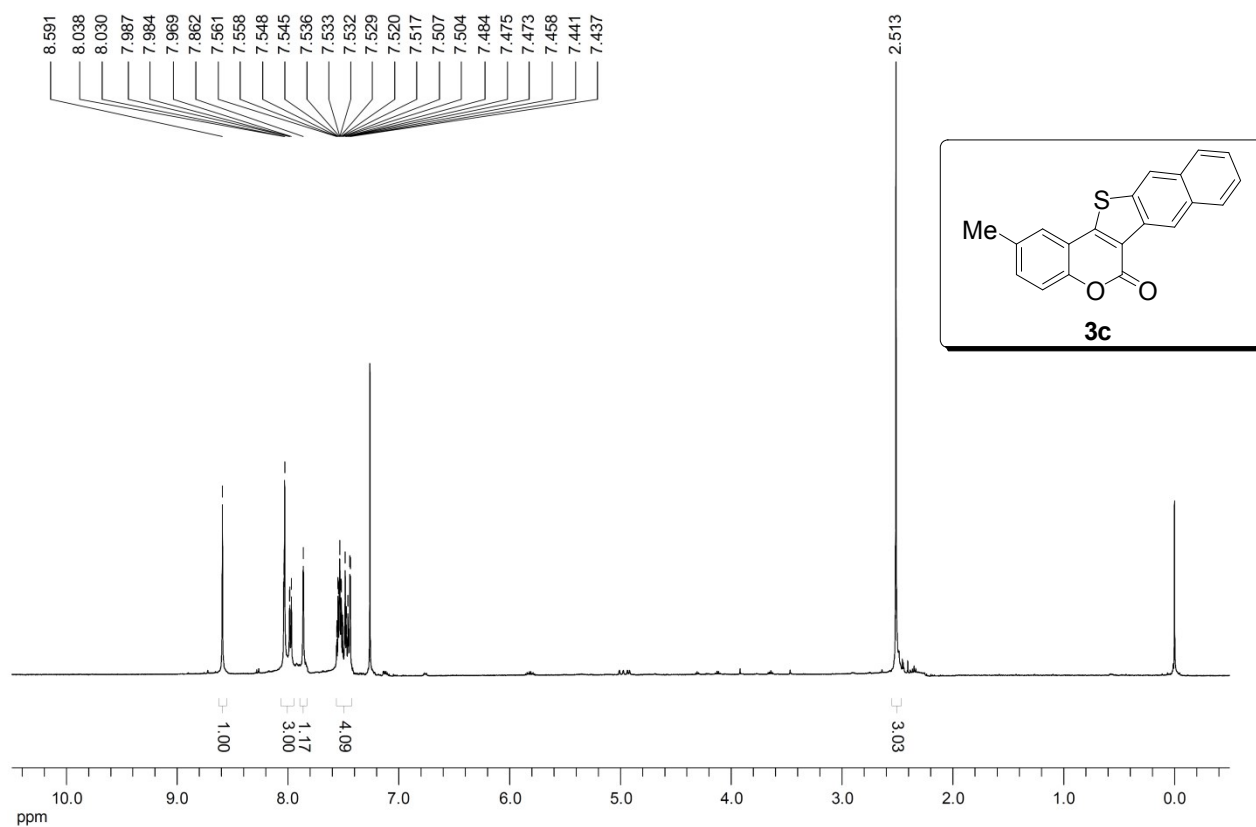


Figure 5. **3c** ¹H NMR

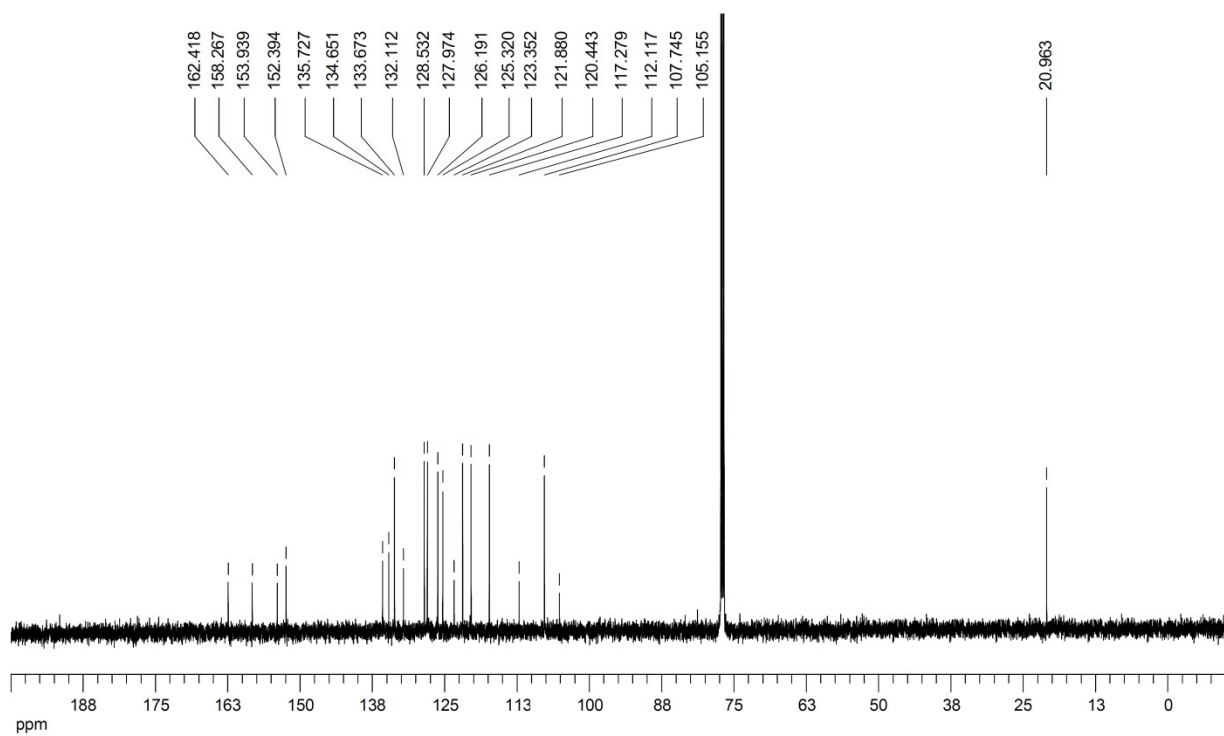


Figure 6. **3c** ¹³C NMR

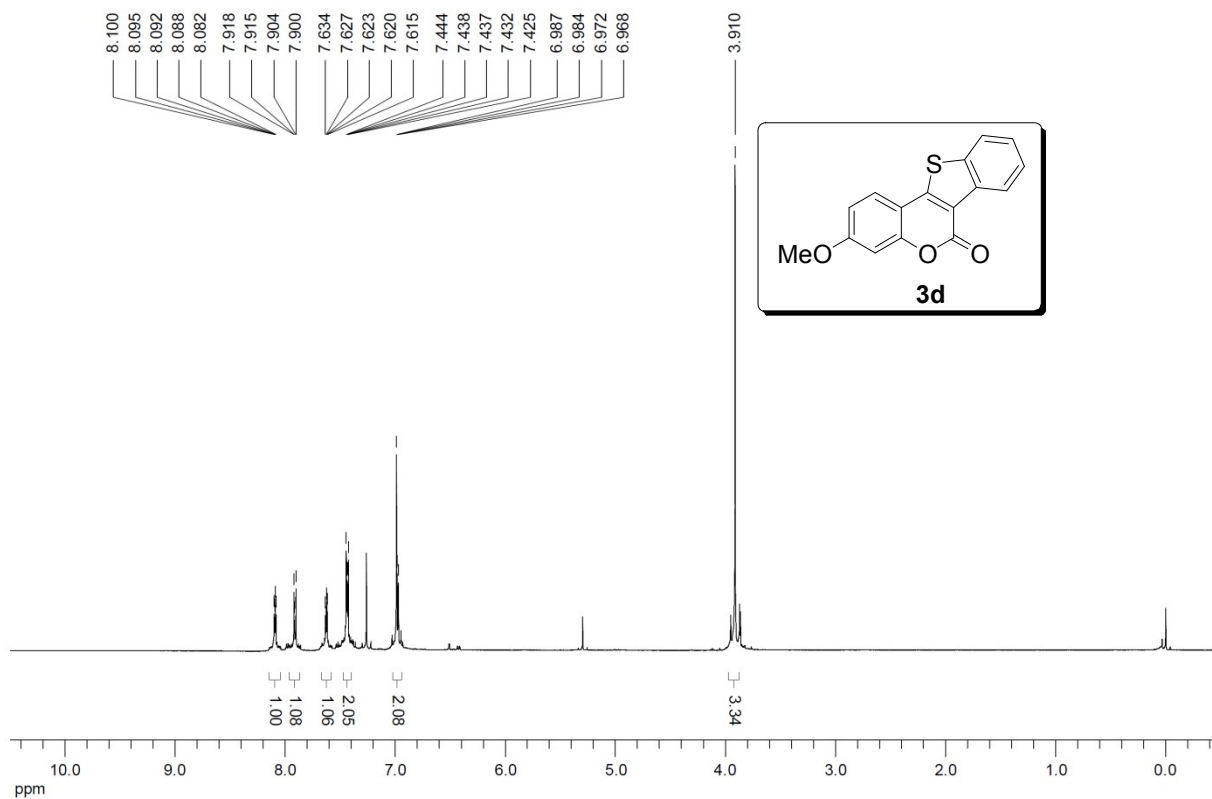


Figure 7. **3d** ^1H NMR

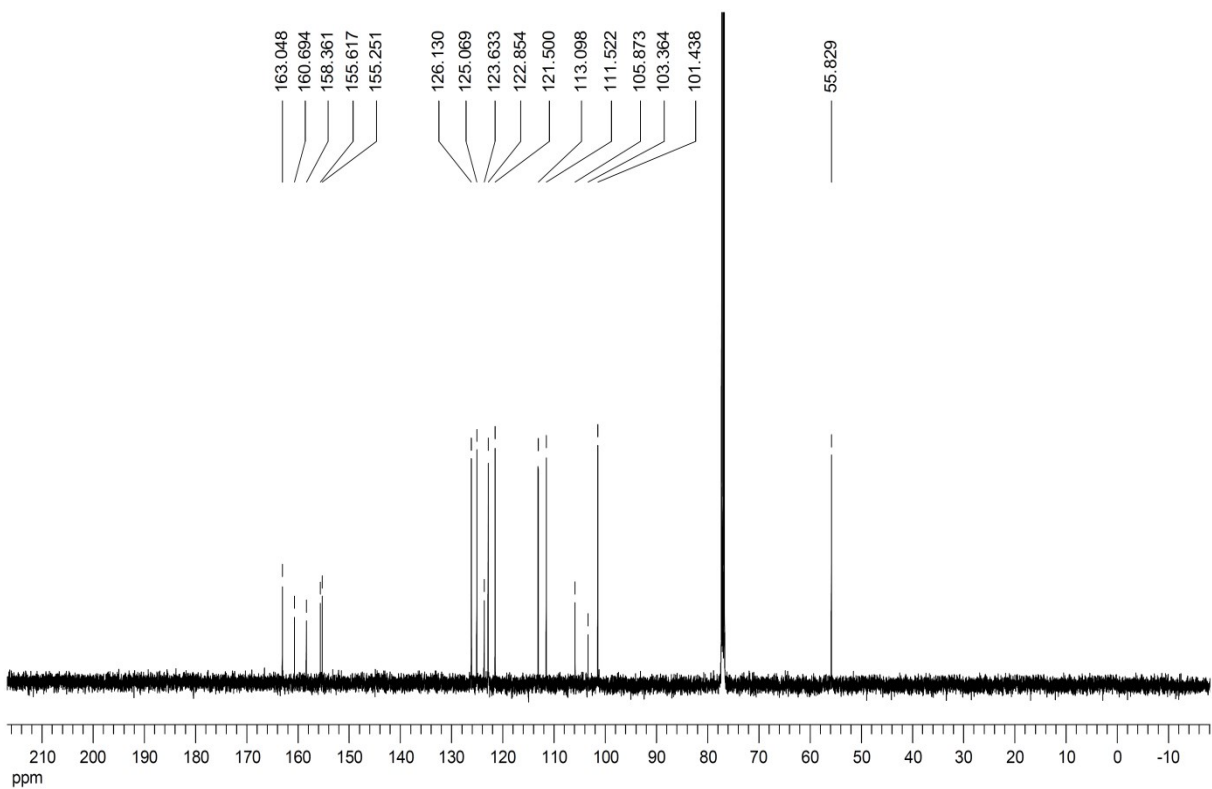


Figure 8. **3d** ^{13}C NMR

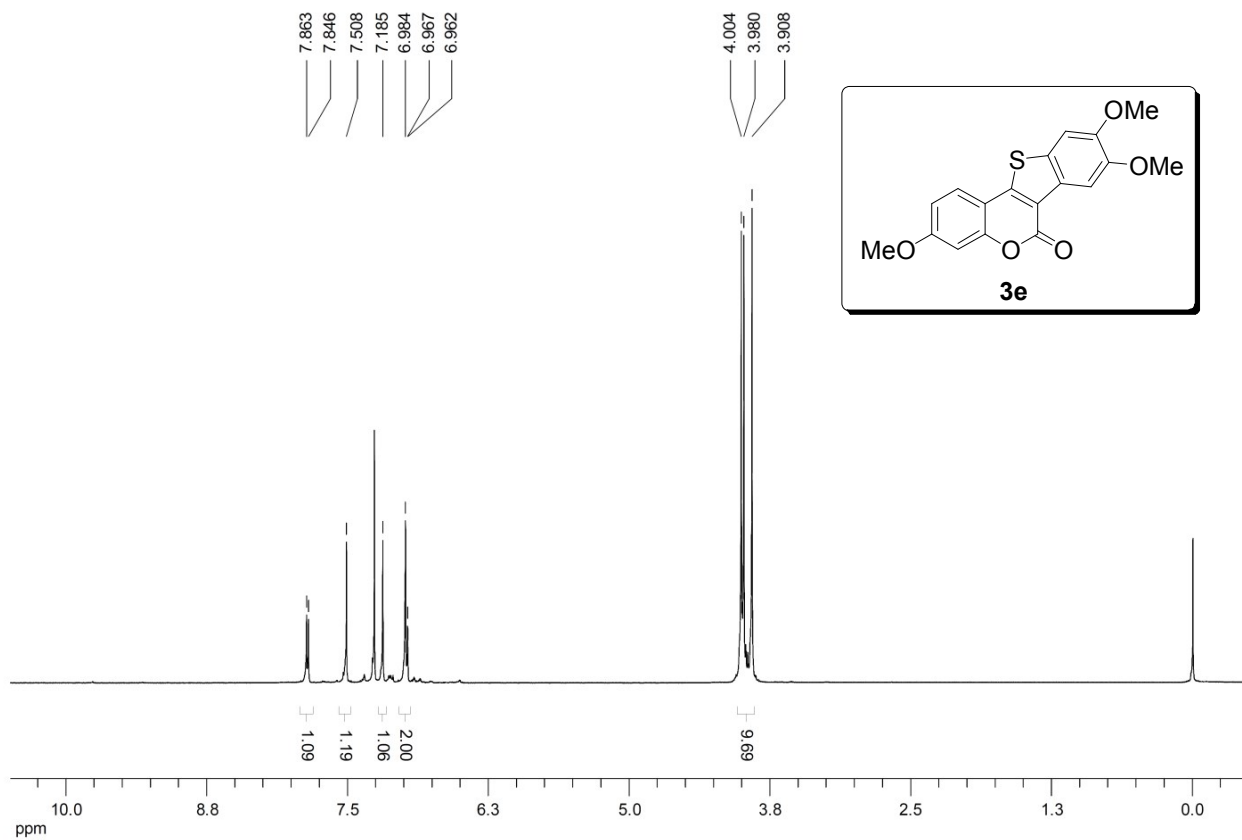


Figure 9. **3e** ^1H NMR

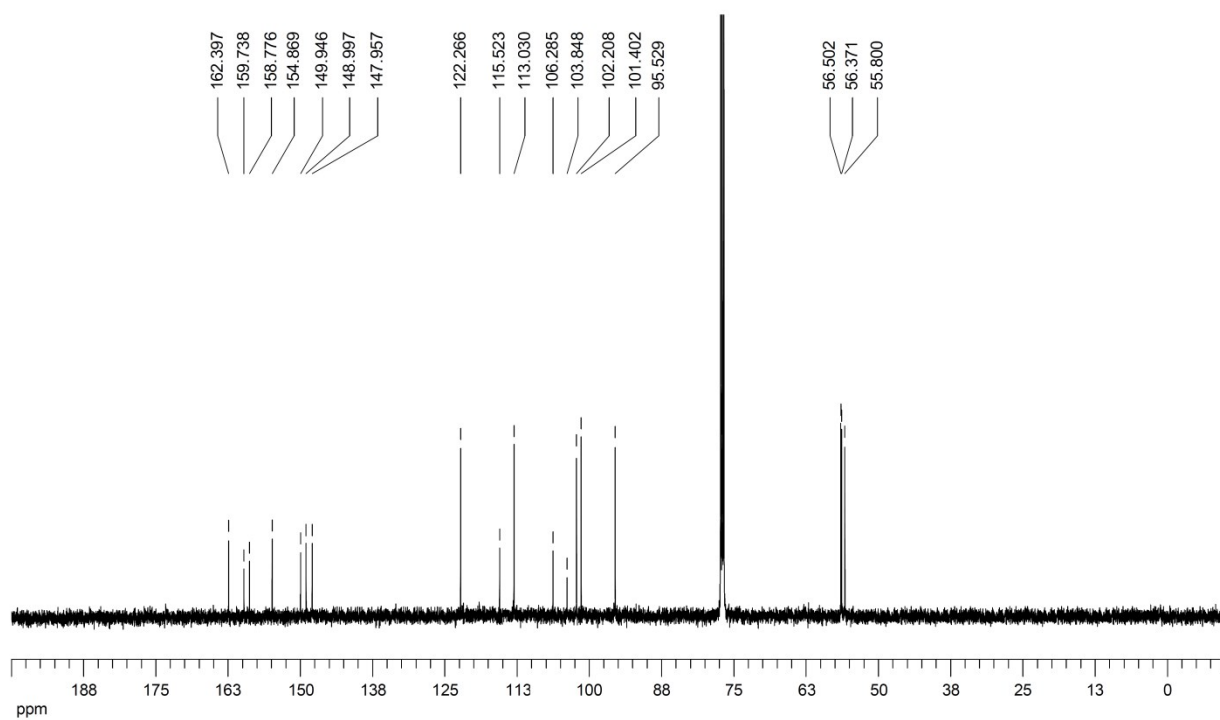


Figure 10. **3e** ^{13}C NMR

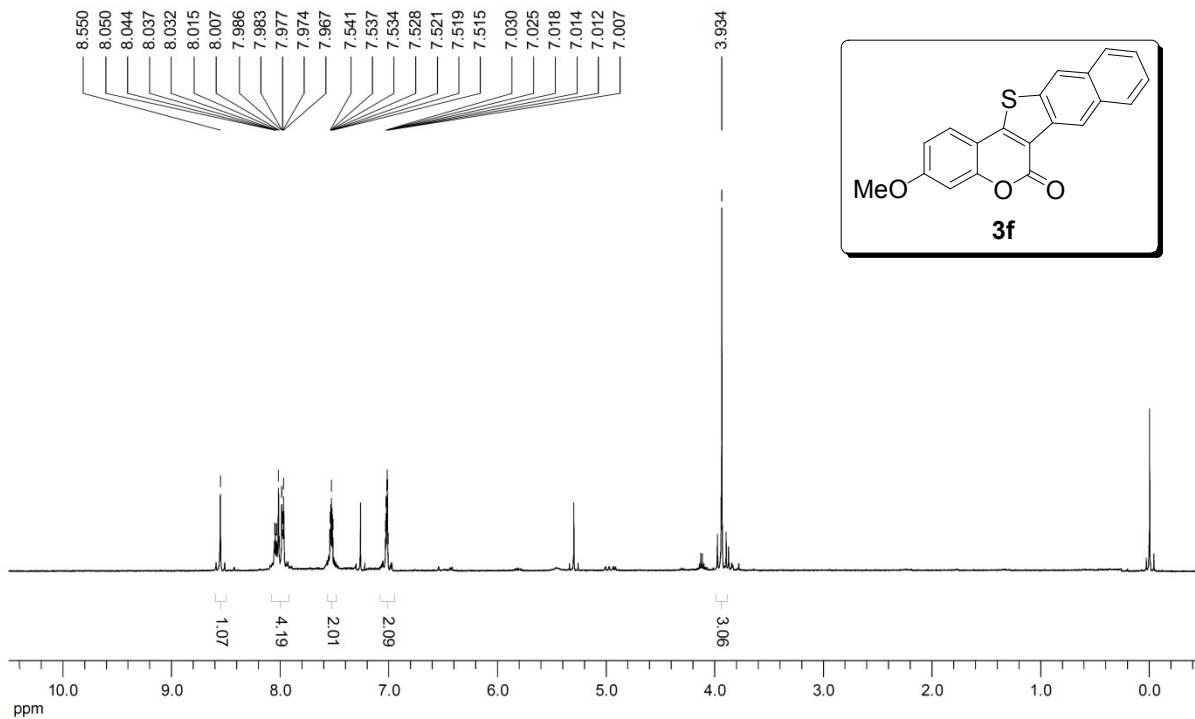


Figure 11. **3f** ¹H NMR

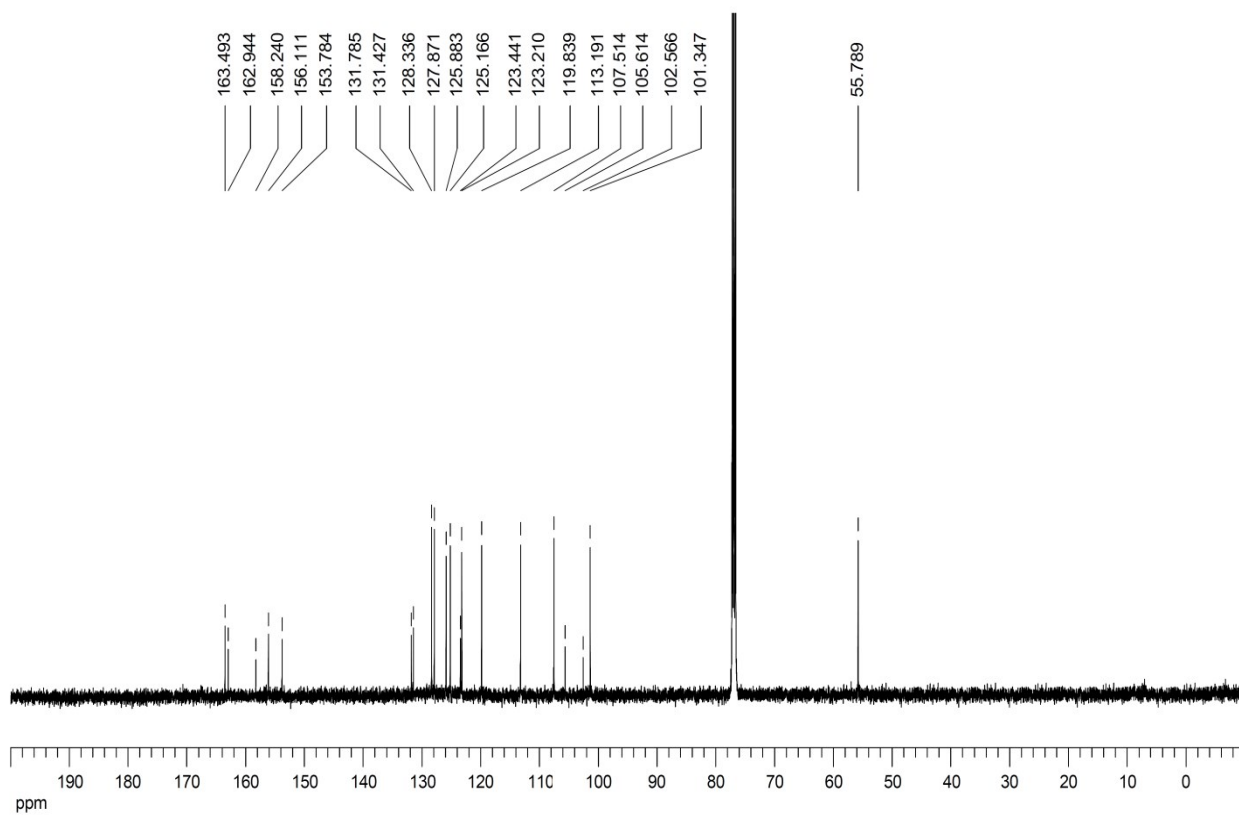


Figure 12. **3f** ¹³C NMR

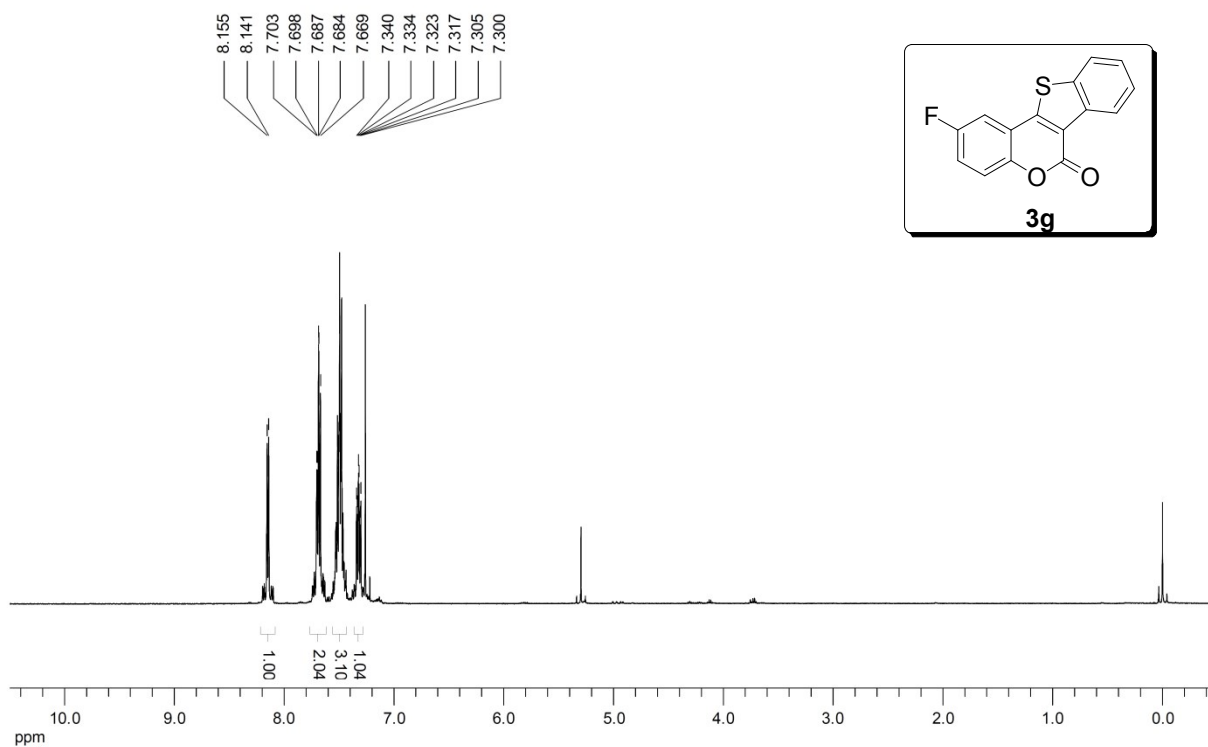


Figure 13. **3g** ¹H NMR

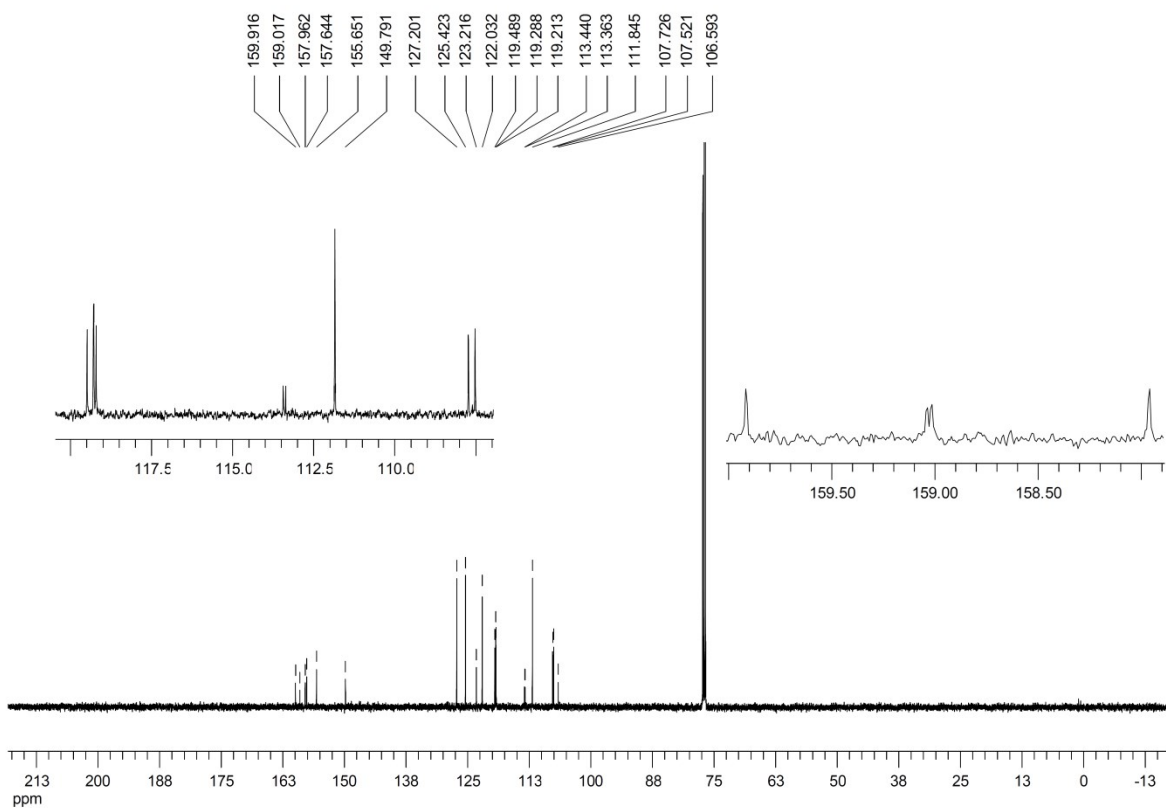


Figure 14. **3g** ¹³C NMR

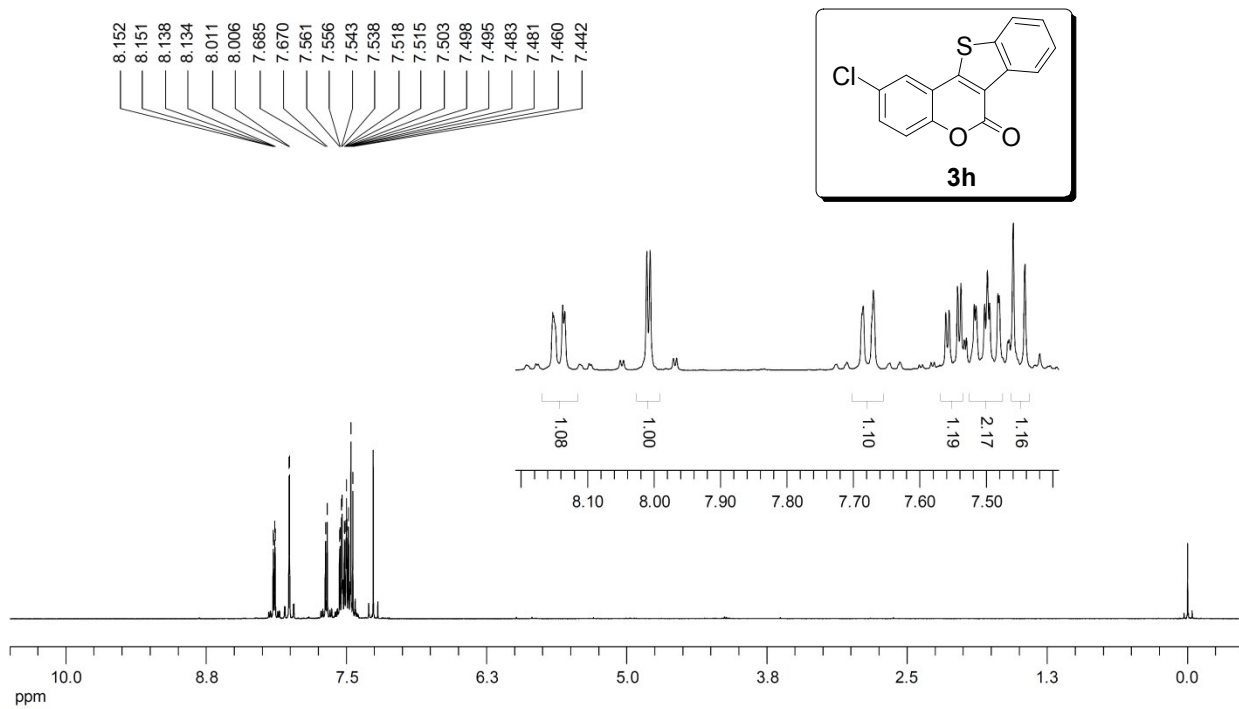


Figure 15. **3h** ¹H NMR

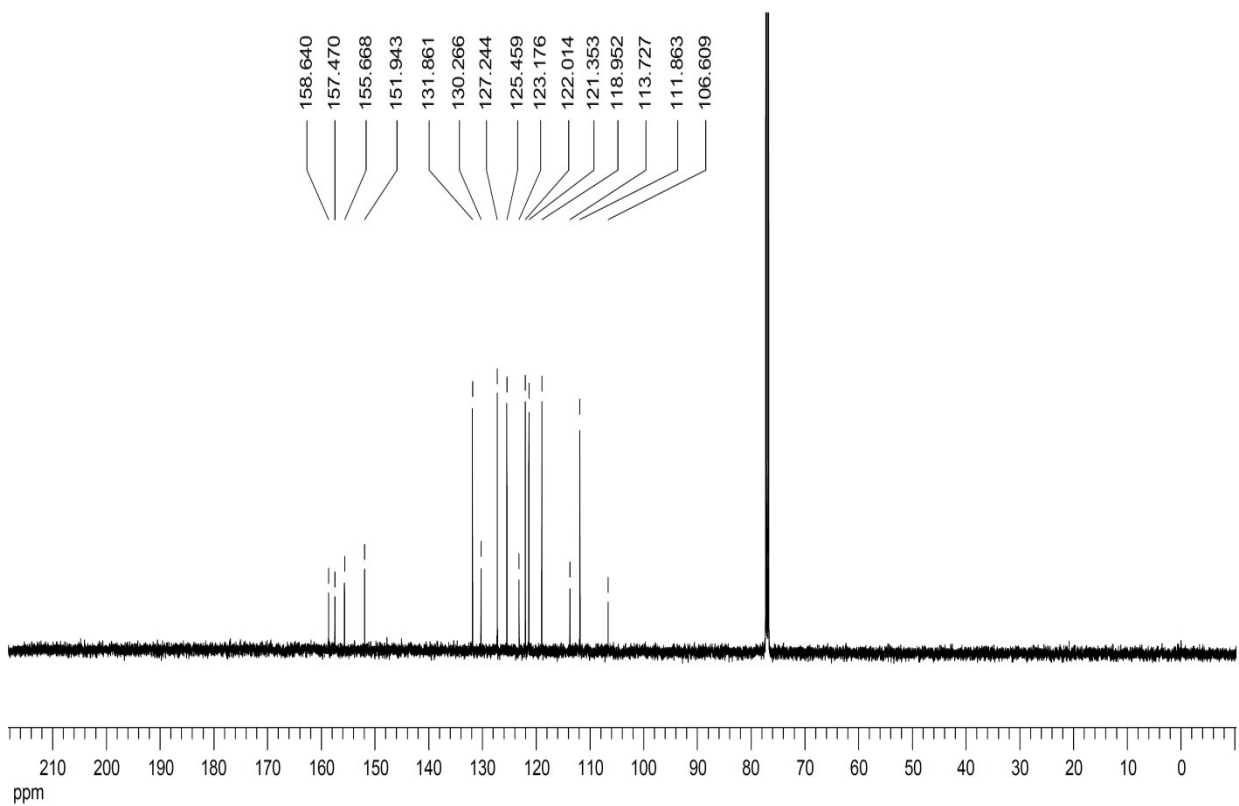


Figure 16. **3h** ¹³C NMR

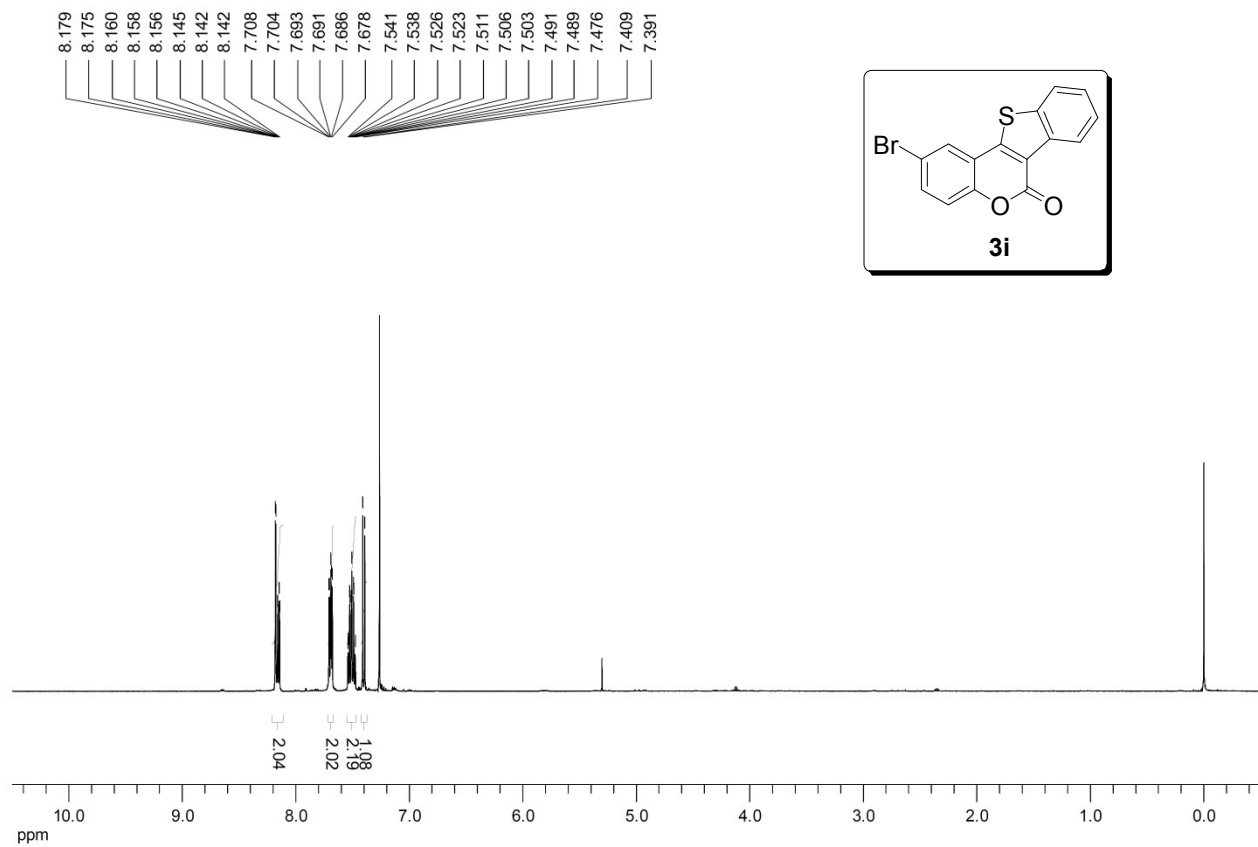


Figure 17. **3i** ¹H NMR

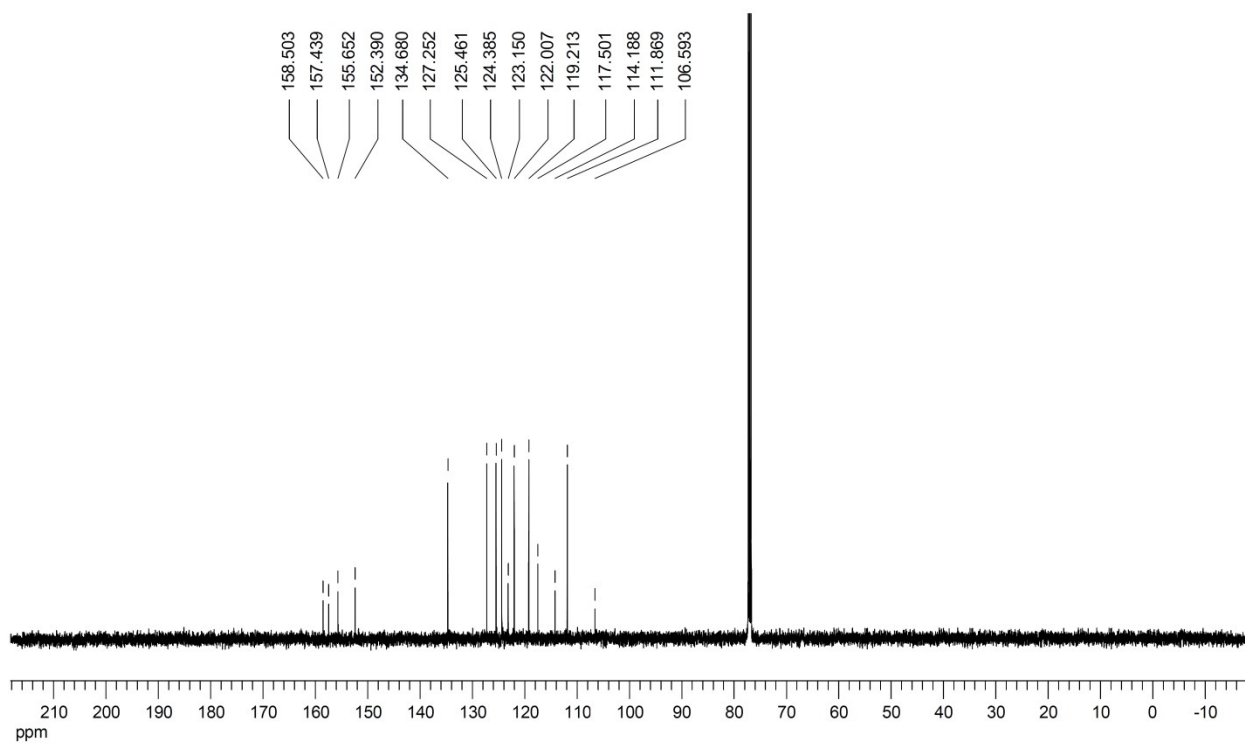


Figure 18. **3i** ¹³C NMR

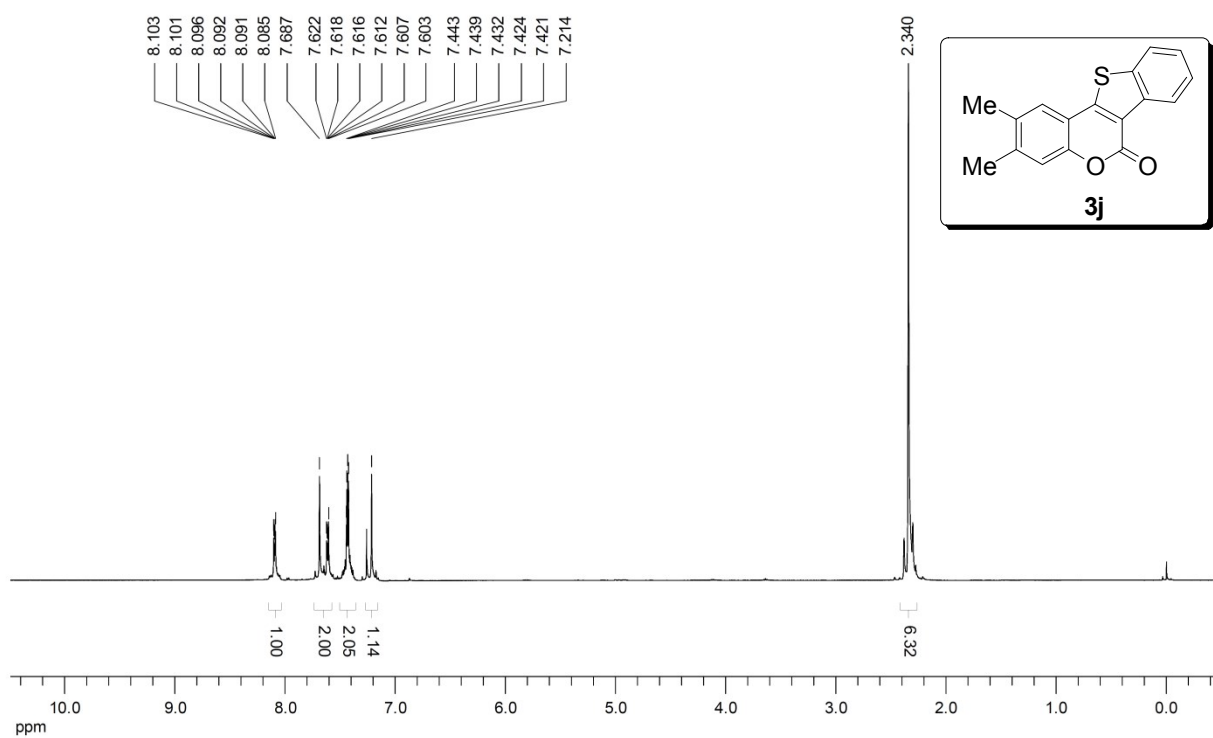


Figure 19. **3j** ^1H NMR

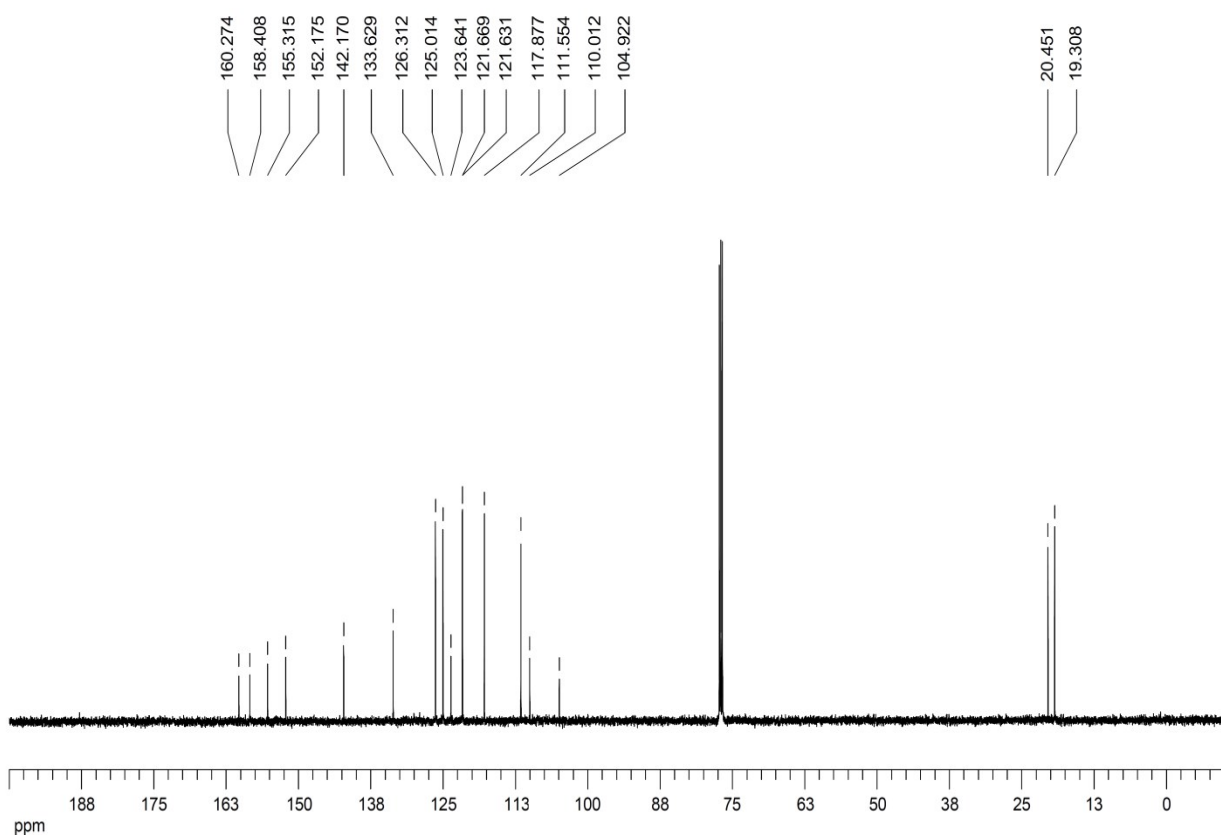


Figure 20. **3j** ^{13}C NMR

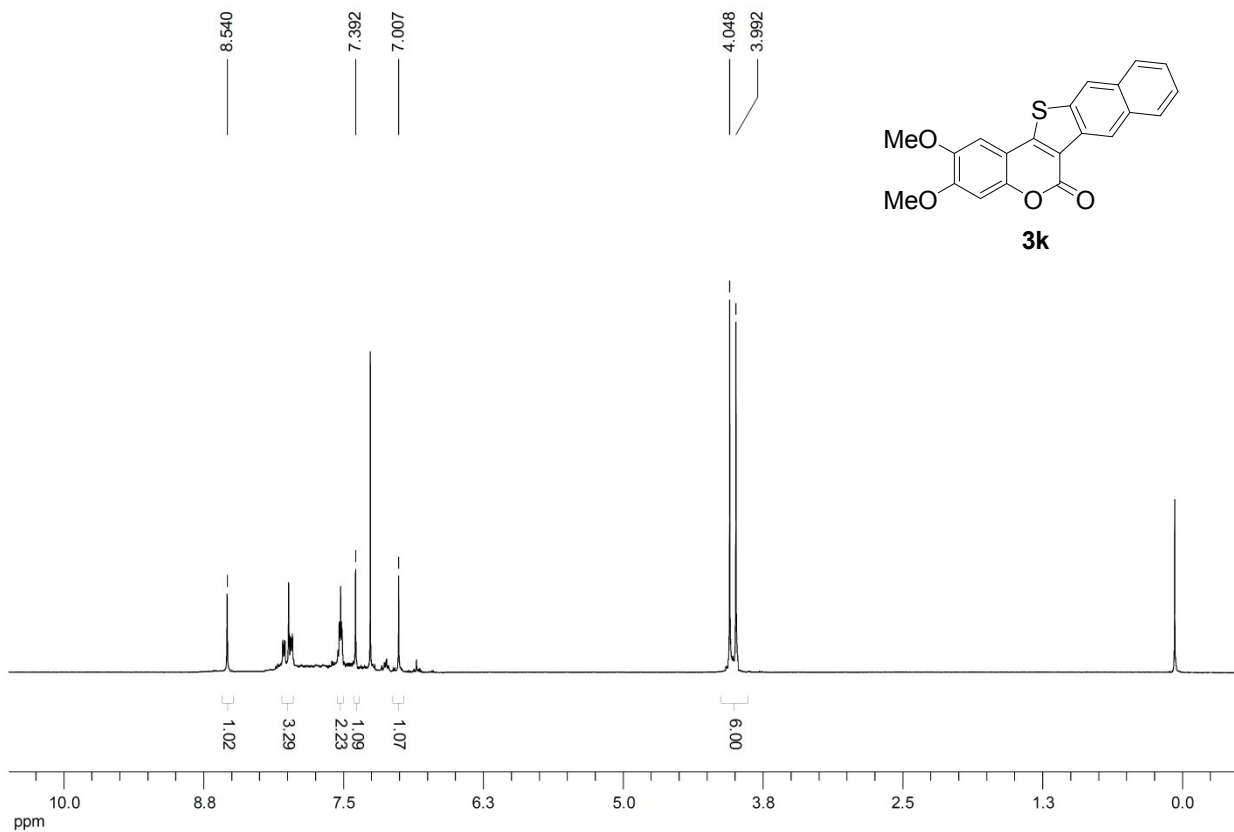


Figure 21. **3k** ¹H NMR

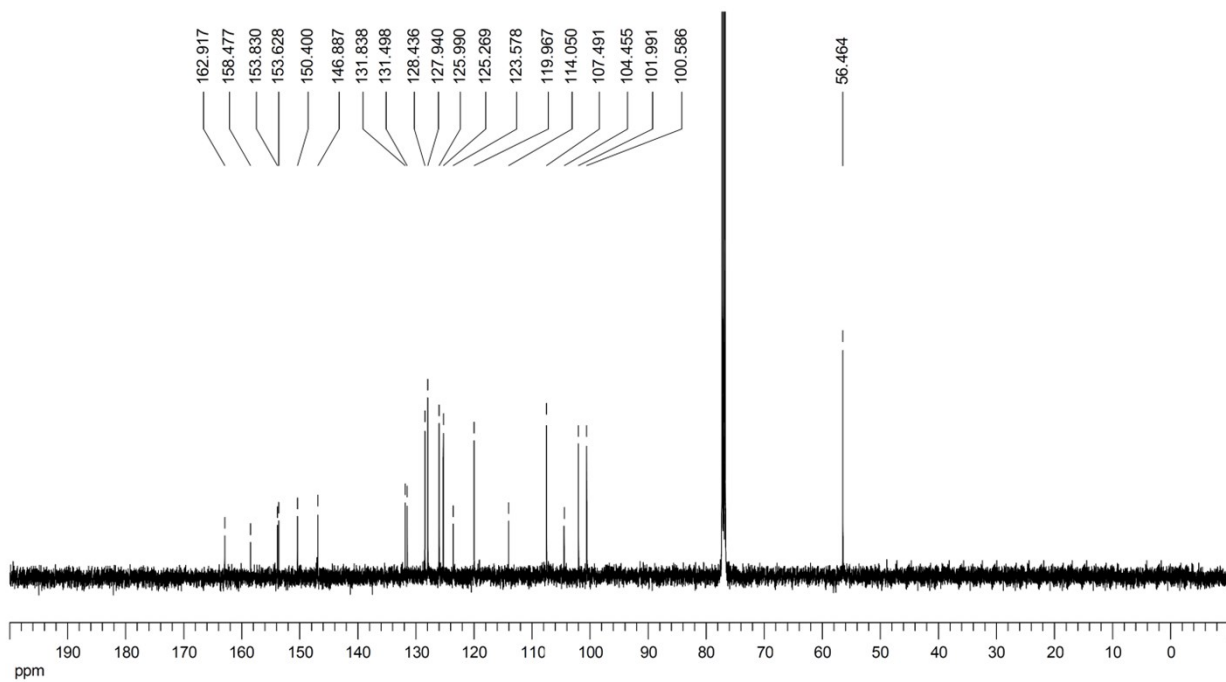


Figure 22. **3k** ¹³C NMR

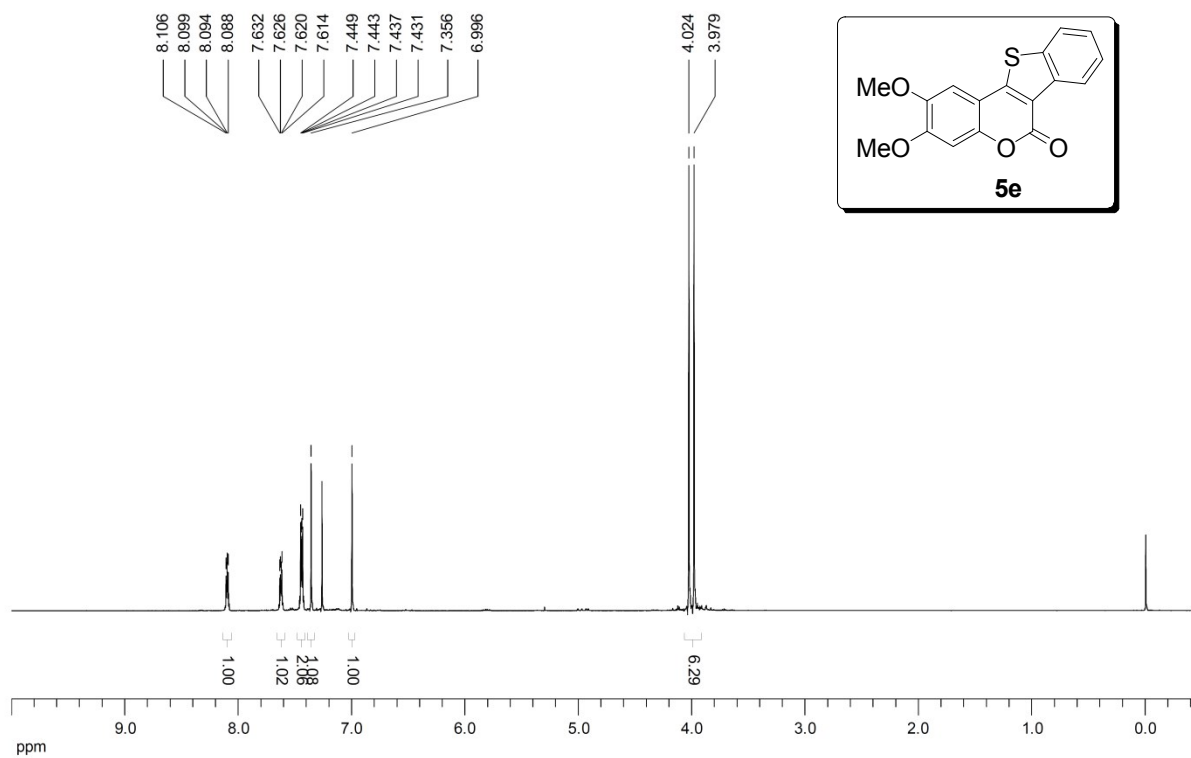


Figure 23. **5e** ^1H NMR

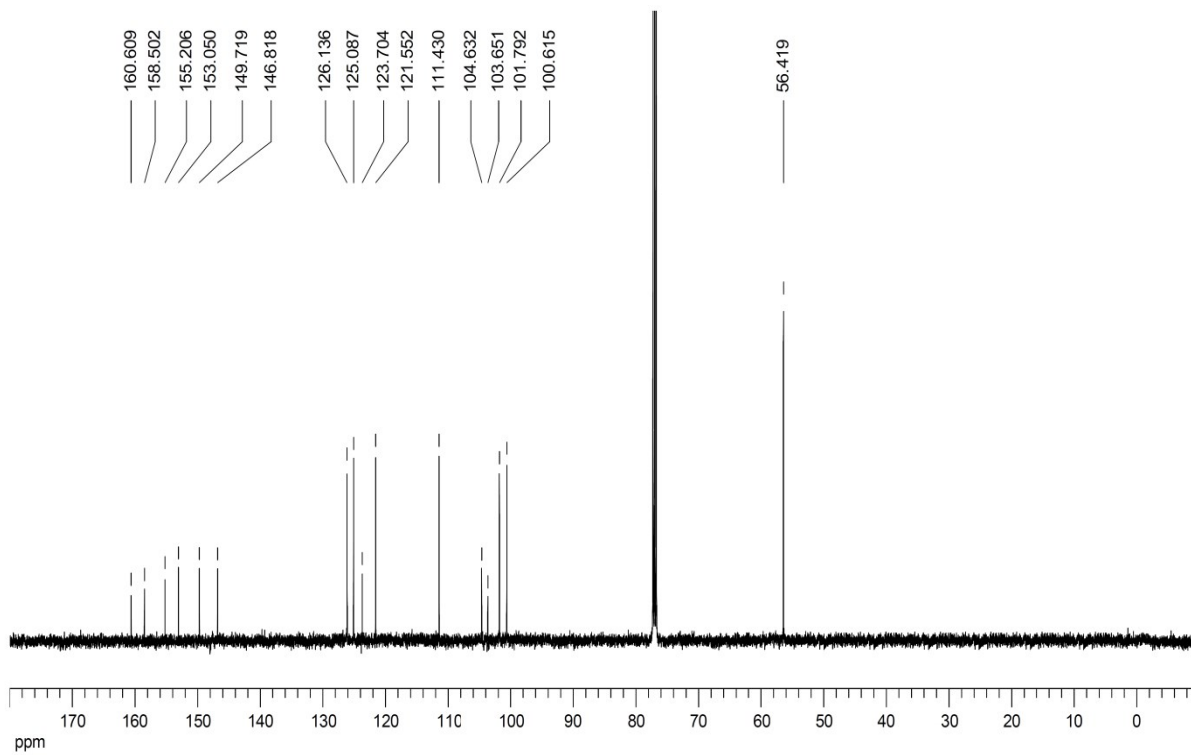


Figure 24. **5e** ^{13}C NMR