Electronic Supplementary Material (ESI) for RSC Advances.

Supporting Information

DTBP-mediated Cross-Dehydrogenative Coupling of 3-Aryl Benzofuran-2(3*H*)-ones with Toluenes/Phenols for All Carbon Quaternary Centers

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S1. General Method

Instrumentation

All the reactions were carried out under an N_2 atmosphere using standard Schlenk techniques. Glassware was dried in an oven (150 °C) and heated under reduced pressure before use. Flash column chromatography was performed using Qingdao Haiyang silica gel (300−400) with distilled solvents. ^1H NMR (400MHz) spectra were recorded on Bruker Avance 400 spectrometers in $CDCl_3$ [using $(CH_3)_4Si$ (for ^1H, $\delta = 0.00$) as internal standard]. ^{13}C NMR (100MHz) spectra on Bruker Avance 400 spectrometers in $CDCl_3$ [using $CDCl_3$ (for ^{13}C, $\delta = 77.00$) as an internal standard]. The following abbreviations were used to explain the multiplicities: s = singlet, d = doublet, t = triplet, q = quartet, m = multiple. Chemical shifts (δ) are in parts per million relatives to $CDCl_3$ at 7.26 ppm for ^1H and at 77.16 ppm for $^{13}C\{1H\}$, respectively. Melting points were measured using a melting point instrument and are uncorrected. HRMS was carried out on a high-resolution mass spectrometer (LCMS-IT-TOF). TLC was performed using commercially available 100−400 mesh silica gel plates (GF254). X-ray single crystal diffraction analysis was performed using the SMART-APEX and RASA-7A equipment at Shanghai Institute Organic Chemistry, China Academy of Science. Caution: After the reaction system is completed, it must be quenched with a reducing agent. When peroxides are used in large amounts, there is a risk of explosion.

Chemicals

Unless otherwise noted, all the solvents and commercially available reagents were purchased from commercial sources and used directly without further purification.

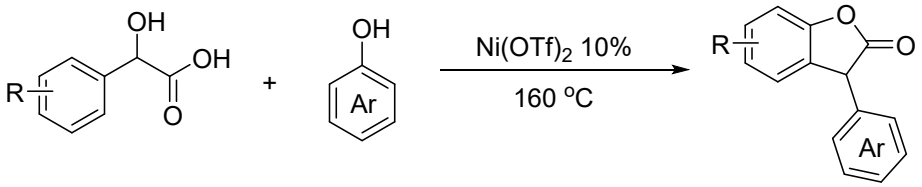
S2. Experimental Section

The starting materials of Benzofuranones derivatives was synthesized according to reported procedure.[1]

2.1 Typical Experimental Procedure for the Preparation of Starting Materials 3-phenylbenzofuran-2(3*H*)-ones Derivatives (1a-1n)

To a flask was added Mandelic acid (3.04 g, 20 mmol), phenol (1.9 mL, 20 mmol) and $Ni(OTf)_2$ (712 mg, 2 mmol). Then put the flask to the reaction system in 160 oC and stirred for 12 h. The reaction mixture was dissolved in 2.0 mL ethyl acetate . Dried by rotary evaporator, the residue was purified by columnchromatography (petroleum ether/ethyl acetate =20/1) to obtain the product.[1]

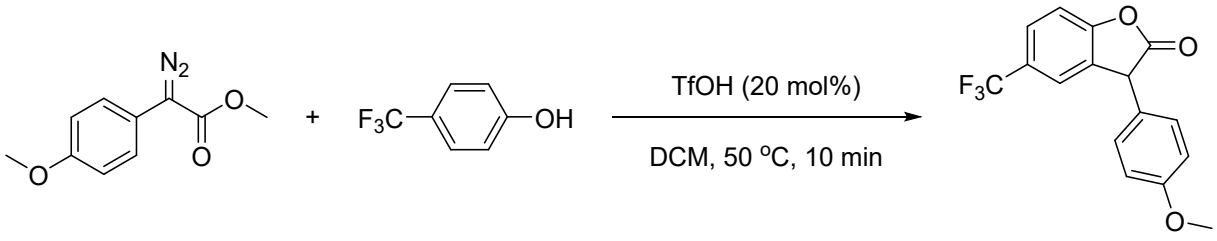
Scheme S1. Synthesis of Starting Materials 3-Phenylbenzofuran-2(3H)-ones Derivatives



2.2 Experimental Procedure for the Preparation of Starting Materials 3-(4-methoxyphenyl)-5-(trifluoromethyl)benzofuran-2(3H)-one (1o)

To a flask was added 4-trifluoromethylphenol (34 mg, 0.24 mmol), methyl 2-diazo-2-(4-methoxyphenyl)acetate (41.2 mg, 0.2 mmol) and TfOH (5 ul, 0.04 mmol) in 0.7 mL of DCM, Then put the flask to the reaction system in50 °C and stirred for 10 min. Then, excess solid sodium bicarbonate was added to neutralize the acid. After filtration, the solvent was removed under reduced pressure. The crude product was then purified by flash chromatography on silica gel to afford the corresponding products. [2]

Scheme S2. Synthesis of Starting Materials 3-(4-methoxyphenyl)-5-(trifluoromethyl)benzofuran-2(3H)-one (1o)



2.3 Optimization of Reaction Conditions.

A 10 mL oven-dried Schlenk tube equipped with a magnetic stirring bar, 5-methyl-3-phenylbenzofuran-2(*3H*)-one (**1a**) (0.2 mmol, 1.0 equiv.), catalst (0.02 mmol, 10 mol %), oxidant (0.1 mmol, 0.5 equiv.), and solvent (1.0 mL) was vigorously stirred at 140 °C for 12 h under air. Then the mixture was cooled to room temperature, added water (15 mL), extracted with EtOAc (15 mL×3). The combined organic phases were dried over anhydrous Na_2SO_4, filtered and concentrated in vacuo. Further purification by flash column chromatography on silica gel (eluting with petroleum ether/ethyl acetate) provided the desired product.

2.4 Typical procedure for the synthesis of products 3 ,4 and 5

A 10 mL oven-dried Schlenk tube equipped with a magnetic stirring bar, benzofuran-2(3*H*)-ones **1** (0.2 mmol，1.0 equiv.), DTBP (0.1 mmol, 0.5 equiv., 19 uL, peroxide is explosive at high temperature), and toluene (1.0 mL) was vigorously stirred at 140 °C for 12 h under N_2. Then the mixture was cooled to room temperature, and saturated $NaHSO_3$ (aq) and water (15 mL) were added to quench the reaction mixture. After it was examined by potassium iodide-starch test paper, the mixture was extracted with EtOAc (15 mL×3). The combined organic phases were dried over anhydrous Na_2SO_3, filtered and concentrated in vacuo. Further purification by flash column chromatography on silica gel (eluting with petroleum ether/ethyl acetate = 50/1) provided the product **3**.

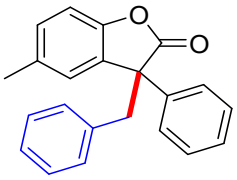
A 10 mL oven-dried Schlenk tube equipped with a magnetic stirring bar, benzofuran-2(3*H*)-ones **1** (0.2 mmol，1.0 equiv.), DTBP (0.1 mmol, 0.5 equiv., 19 uL, peroxide is explosive at high temperature), and toluene analogues (0.5 mL) was vigorously stirred at 140 °C for 12 h under N_2. Then the mixture was cooled to room temperature, and saturated $NaHSO_3$ (aq) and water (15 mL) were added to quench the reaction mixture. After it was examined by potassium iodide-starch test paper, the mixture was extracted with EtOAc (15 mL×3). The combined organic phases were dried over anhydrous Na_2SO_4, filtered and concentrated in vacuo. Further purification by flash column chromatography on silica gel (eluting with petroleum ether/ethyl acetate = 50/1) provided the product **4**.

A 10 mL oven-dried Schlenk tube equipped with a magnetic stirring bar, benzofuran-2(3*H*)-ones **1** (0.2 mmol，1.0 equiv.), phenol (0.4 mmol, 2.0 equiv.), and DTBP (0.1 mmol, 0.5 equiv., 19 uL) was vigorously stirred at 140 °C for 12 h under N_2. Then the mixture was cooled to room temperature, and saturated $NaHSO_3$ (aq) and water (15 mL) were added to quench the reaction mixture. After it was examined by potassium iodide-starch test paper, the mixture was extracted with EtOAc (15 mL×3). The combined organic phases were dried over anhydrous Na_2SO_4, filtered and concentrated in vacuo. Further

purification by flash column chromatography on silica gel (eluting with petroleum ether/ethyl acetate = 10/1) provided the product **5**.

S3. Analysis Data for the Products

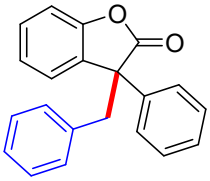
3-Benzyl-5-methyl-3-phenylbenzofuran-2(3H)-one(3a)[3]



The representative general procedure mentioned above was followed. Purification by PTLC on silica gel (petroleum ether/ethyl acetate = 200/1) yielded the title compound **3a** in 88% (55.3 mg) as a White solid; mp: 120 – 122 °C; R_f = 0.35 (petroleum ether/ethyl acetate = 200/1); ^{1}H NMR (400 MHz, Chloroform-*d*) δ 7.51 (d, *J* = 7.1 Hz, 2H), 7.40 – 7.28 (m, 3H), 7.12 – 6.98 (m, 5H), 6.86 (d, *J* = 6.7 Hz,2H), 6.79 (d, *J* = 7.9 Hz, 1H), 3.70 (d, *J* = 13.1 Hz, 1H), 3.51 (d, *J* = 13.1 Hz, 1H), 2.35 (s, 3H). ^{13}C NMR (101 MHz, Chloroform-*d*) δ177.8, 150.9, 138.6, 134.8, 133.4, 130.0, 129.5, 129.0, 128.8, 127.9, 127.8, 127.0, 126.9, 126.1, 110.3, 57.5, 44.7, 21.2.

HRMS (EI) *m/z*: $[M+H]^+$ calcd for $C_{22}H_{19}O_2^+$ 315.1380 found: 315.1376.

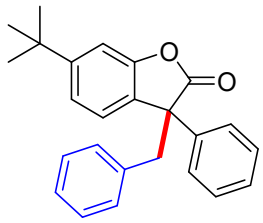
3-Benzyl-3-phenylbenzofuran-2(3H)-one(3b) [3]



The representative general procedure mentioned above was followed. Purification by PTLC on silica gel (petroleum ether/ethyl acetate = 200/1) yielded the title compound **3b** in 91% (54.6 mg) as a white solid; mp: 120 – 122 °C; R_f = 0.29 (petroleum ether/ethyl acetate = 200/1); ^{1}H NMR (400 MHz, Chloroform-*d*) δ 7.58 (d, *J* = 7.5 Hz, 2H), 7.45 – 7.36 (m, 3H), 7.32 – 7.27 (m, 2H), 7.26 – 7.21 (m, 1H), 7.20 – 7.10 (m, 3H), 6.99 (d, *J* = 8.0 Hz, 1H), 6.92 (d, *J* = 7.1 Hz, 2H), 3.79 (d, *J* = 13.1 Hz, 1H), 3.58 (d, *J* = 13.1 Hz, 1H). ^{13}C NMR (101 MHz, Chloroform-*d*) δ 177.5, 153.1, 138.5, 134.8, 130.1, 129.1, 128.8, 128.0, 128.0, 127.1, 127.0, 125.9, 123.9, 110.8, 57.4, 44.9.

HRMS (EI) *m/z*: $[M+H]^+$ calcd for $C_{21}H_{17}O_2^+$ 313.1223, Found 313.1231.

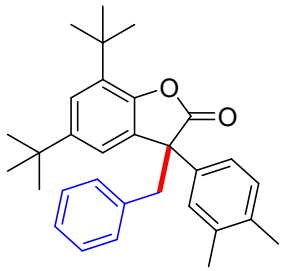
3-Benzyl-6-(tert-butyl)-3-phenylbenzofuran-2(3H)-one(3c)



The representative general procedure mentioned above was followed. Purification by PTLC on silica gel (petroleum ether/ethyl acetate = 200/1) yielded the title compound **3c** in 96% (68.3 mg) as a white solid; mp: 98 – 100 °C; R_f = 0.29 (petroleum ether/ethyl acetate = 200/1); ^{1}H NMR (400 MHz, Chloroform-*d*) δ 7.62 – 7.57 (m, 2H), 7.47 – 7.34 (m, 3H), 7.27 – 7.23 (m, 1H), 7.20 – 7.09 (m, 4H), 7.01 (d, *J* = 1.6 Hz, 1H), 6.91 – 6.86 (m, 2H), 3.70 (d, *J* = 13.1 Hz, 1H), 3.57 (d, *J* = 13.1 Hz, 1H), 1.34 (s, 9H). ^{13}C NMR (101 MHz, Chloroform-*d*) δ 178.0, 151.0, 138.5, 137.4, 133.5, 133.3, 130.4, 129.7, 129.5, 128.8, 128.7, 127.9, 127.3, 127.2, 126.7, 125.4, 110.4, 56.7, 41.0, 21.2, 19.9.

HRMS (EI) *m/z*: $[M+H]^+$ calcd for $C_{25}H_{25}O_2^+$ 357.1849, Found 357.1851.

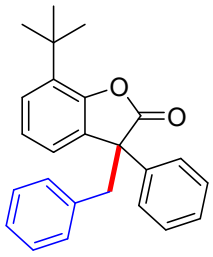
3-Benzyl-5,7-di-tert-butyl-3-(3,4-dimethylphenyl)benzofuran-2(3H)-one(3d)



The representative general procedure mentioned above was followed. Purification by PTLC on silica gel (petroleum ether/ethyl acetate = 200/1) yielded the title compound **3d** in 88% (77.1 mg) as a white solid; mp: 130 – 132 °C; R_f = 0.31 (petroleum ether/ethyl acetate = 200/1); ^{1}H NMR (400 MHz, Chloroform-*d*) δ 7.39 (s, 1H), 7.29 – 7.23 (m, 1H), 7.23 – 7.19 (m, 2H), 7.12 – 7.04 (m, 4H), 6.87 – 6.81 (m, 2H), 3.80 (d, *J* = 12.8 Hz, 1H), 3.46 (d, *J* = 12.8 Hz, 1H), 2.33 (d, *J* = 6.4 Hz, 6H), 1.38 (s, 9H), 1.21 (s, 9H). ^{13}C NMR (101 MHz, Chloroform-*d*) δ 178.4, 148.9, 146.5, 137.0, 136.4, 136.2, 135.1, 133.2, 130.0, 129.9, 129.2, 128.5, 127.8, 126.8, 124.7, 122.5, 120.4, 56.9, 45.4, 34.8, 34.2, 31.7, 29.3, 20.1, 19.4.

HRMS (EI) *m/z*: $[M+H]^+$ calcd for $C_{31}H_{37}O_2^+$ 441.2788, Found 441.2797.

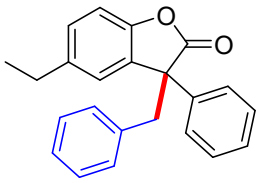
3-Benzyl-7-(tert-butyl)-3-phenylbenzofuran-2(3H)-one(3e)



The representative general procedure mentioned above was followed. Purification by PTLC on silica gel (petroleum ether/ethyl acetate = 200/1) yielded the title compound **3e** in 94% (66.9 mg) as white solid; mp: 138 – 140 °C; R_f = 0.27 (petroleum ether/ethyl acetate = 200/1); ^{1}H NMR (400 MHz, Chloroform-*d*) δ 7.53 (d, *J* = 7.7 Hz, 2H), 7.39 (t, *J* = 7.4 Hz, 2H), 7.35 (d, *J* = 7.8 Hz, 2H), 7.15 (d, *J* = 1.9 Hz, 1H), 7.07 (q, *J* = 6.5 Hz, 3H), 6.88 – 6.82 (m, 3H), 3.69 (d, *J* = 13.2 Hz, 1H), 3.55 (d, *J* = 13.2 Hz, 1H), 1.32 (s, 9H). ^{13}C NMR (101 MHz, Chloroform-*d*) δ 178.1, 150.9, 146.9, 138.5, 135.0, 130.1, 128.8, 128.0, 127.9, 127.2, 127.1, 126.6, 125.7, 123.4, 110.0, 57.5, 45.1, 34.7, 31.5.

HRMS (EI) *m/z*: $[M+H]^+$ calcd for $C_{25}H_{25}O_2^+$ 357.1849, Found 357.1851.

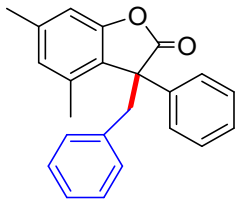
3-Benzyl-5-ethyl-3-phenylbenzofuran-2(3H)-one(3f) [3]



The representative general procedure mentioned above was followed. Purification by PTLC on silica gel (petroleum ether/ethyl acetate = 200/1) yielded the title compound **3f** in 97% (63.6 mg) as white solid; mp: 53 – 54 °C; R_f = 0.32 (petroleum ether/ethyl acetate = 200/1); ^{1}H NMR (400 MHz, Chloroform-*d*) δ 7.56 – 7.50 (m, 2H), 7.42 – 7.31 (m, 3H), 7.15 – 7.05 (m, 4H), 7.01 (d, *J* = 1.4 Hz, 1H), 6.87 – 6.81 (m, 3H), 3.71 (d, *J* = 13.1 Hz, 1H), 3.54 (d, *J* = 13.1 Hz, 1H), 2.71 – 2.61(m, 2H), 1.24 (t, *J* = 7.6 Hz, 3H). ^{13}C NMR (101 MHz, Chloroform-*d*) δ 177.9, 151.1, 140.0, 138.6, 134.9, 130.1, 128.9, 128.8, 128.4, 128.0, 127.9, 127.1, 127.1, 125.3, 110.4, 57.5, 44.9, 28.7, 16.1.

HRMS (EI) *m/z*: $[M+Na]^+$ calcd for $C_{23}H_{20}O_2Na^+$ 351.1356, Found 351.1359.

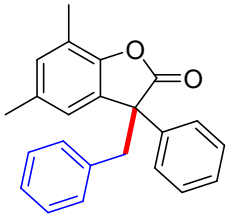
3-Benzyl-4,6-dimethyl-3-phenylbenzofuran-2(3H)-one(3g)



The representative general procedure mentioned above was followed. Purification by PTLC on silica gel (petroleum ether/ethyl acetate = 200/1) yielded the title compound **3g** in 72% (47.2 mg) as white solid; mp: 108 – 110 °C; R_f = 0.26 (petroleum ether/ethyl acetate = 200/1); ^{1}H NMR (400 MHz, Chloroform-*d*) δ 7.41 – 7.31 (m, 5H), 7.10 (d, *J* = 6.2 Hz, 3H), 6.96 – 6.91 (m, 2H), 6.77 (s, 1H), 6.56 (s, 1H), 3.95 (d, *J* = 13.0 Hz, 1H), 3.59 (d, *J* = 12.9 Hz, 1H), 2.29 (s, 3H), 2.15 (s, 3H). ^{13}C NMR (101 MHz, Chloroform-*d*) δ 178.1, 153.4, 139.4, 138.2, 135.1, 134.9, 129.5, 128.9, 128.1, 128.0, 127.0, 127.0, 126.9, 124.8, 108.8, 57.9, 40.4, 21.5, 18.3.

HRMS (EI) *m/z*: $[M+H]^+$ calcd for $C_{23}H_{21}O_2^+$ 329.1536, Found 329.1538

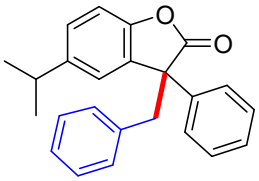
3-Benzyl-5,7-dimethyl-3-phenylbenzofuran-2(3H)-one(3h)



The representative general procedure mentioned above was followed. Purification by PTLC on silica gel (petroleum ether/ethyl acetate = 200/1) yielded the title compound **3h** in 85% (55.7 mg) as white solid; mp: 98 – 100 °C; R_f = 0.36 (petroleum ether/ethyl acetate = 200/1); ^{1}H NMR (400 MHz, Chloroform-*d*) δ 7.54 (d, *J* = 7.5 Hz, 2H), 7.42 – 7.30 (m, 3H), 7.17 – 7.06 (m, 3H), 6.88 (d, *J* = 6.1 Hz, 3H), 6.83 (s, 1H), 3.70 (d, *J* = 13.1 Hz, 1H), 3.53 (d, *J* = 13.1 Hz, 1H), 2.34 (s, 3H), 2.13 (s, 3H). ^{13}C NMR (101 MHz, Chloroform-*d*) δ 178.0, 149.6, 138.8, 135.0, 133.2, 131.1, 130.1, 128.8, 128.5, 127.9, 127.9, 127.1, 127.0, 123.5, 120.5, 57.9, 44.9, 21.2, 14.9.

HRMS (EI) *m/z*: $[M+H]^+$ calcd for $C_{23}H_{21}O_2^+$ 329.1536, Found 329.1539.

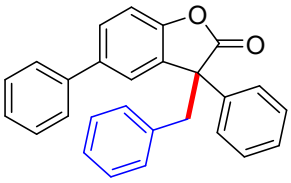
3-Benzyl-5-isopropyl-3-phenylbenzofuran-2(3H)-one(3i) [3]



The representative general procedure mentioned above was followed. Purification by PTLC on silica gel (petroleum ether/ethyl acetate = 200/1) yielded the title compound **3i** in 95% (64.9 mg) as white solid; mp: 74 – 76 °C; R_f = 0.33 (petroleum ether/ethyl acetate = 200/1); ^{1}H NMR (400 MHz, Chloroform-*d*) δ 7.57 – 7.51 (m, 2H), 7.43 – 7.38 (m, 2H), 7.36 – 7.33 (m, 1H), 7.13 – 7.05 (m, 4H), 7.02 (d, *J* = 1.8 Hz, 1H), 6.88 – 6.82 (m, 3H), 3.71 (d, *J* = 13.1 Hz, 1H), 3.54 (d, *J* = 13.1 Hz, 1H), 2.95 – 2.87 (m, 1H), 1.27 – 1.24 (m, 6H). ^{13}C NMR (101 MHz, Chloroform-*d*) δ 177.9, 151.2, 144.7, 138.5, 134.9, 130.1, 128.8, 128.7, 128.0, 127.9, 127.1, 127.1, 127.0, 124.0, 110.4, 57.5, 45.0, 33.9, 24.5, 23.9.

HRMS (EI) *m/z*: $[M+H]^+$ calcd for $C_{24}H_{23}O_2^+$ 343.1693, Found 343.1697.

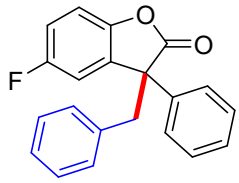
3-Benzyl-3,5-diphenylbenzofuran-2(3H)-one(3j)



The representative general procedure mentioned above was followed. Purification by PTLC on silica gel (petroleum ether/ethyl acetate = 200/1) yielded the title compound **3j** in 82% (61.7 mg) as a color-less liquid; R_f = 0.27 (petroleum ether/ethyl acetate = 200/1); ^{1}H NMR (400 MHz, Chloroform-*d*) δ 7.59 – 7.52 (m, 4H), 7.52 – 7.44 (m, 3H), 7.42 – 7.34 (m, 5H), 7.16 – 7.08 (m, 3H), 7.03 (d, *J* = 8.3 Hz, 1H), 6.91 (d, *J* = 7.2 Hz, 2H), 3.75 (d, *J* = 13.2 Hz, 1H), 3.62 (d, *J* = 13.2 Hz, 1H). ^{13}C NMR (101 MHz, Chloroform-*d*) δ 177.6, 152.6, 140.4, 138.3, 137.4, 134.8, 130.2, 129.6, 129.0, 128.2, 128.1, 128.0, 127.5, 127.2, 127.1, 127.0, 124.8, 111.0, 57.6, 45.1.

HRMS (EI) *m/z*: $[M+Na]^+$ calcd for $C_{27}H_{20}O_2Na^+$ 399.1356, Found 399.1360.

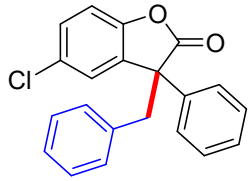
3-Benzyl-5-fluoro-3-phenylbenzofuran-2(3H)-one(3k) [3]



The representative general procedure mentioned above was followed. Purification by PTLC on silica gel (petroleum ether/ethyl acetate = 200/1) yielded the title compound **3k** in 73% (46.4 mg) as white solid; mp: 131 – 132 °C; R_f = 0.35 (petroleum ether/ethyl acetate = 200/1); ^{1}H NMR (400 MHz, Chloroform-*d*) δ 7.53 (d, *J* = 7.3 Hz, 2H), 7.48 – 7.39 (m, 3H), 7.32 – 7.23 (m, 2H), 7.17 (q, *J* = 6.1 Hz, 3H), 6.92 (d, *J* = 8.2 Hz, 3H), 3.79 (d, *J* = 13.2 Hz, 1H), 3.56 (d, *J* = 13.2 Hz, 1H). ^{13}C NMR (101 MHz, Chloroform-*d*) δ 177.3, 160.4, 158.0, 148.9, 137.9, 134.4, 130.8, 130.7, 130.0, 129.0, 128.3, 128.2, 127.3, 126.9, 116.0, 115.7, 113.3, 113.0, 111.8, 111.7, 58.2, 44.8. ^{19}F NMR (376 MHz, Chloroform-*d*) δ -117.69.

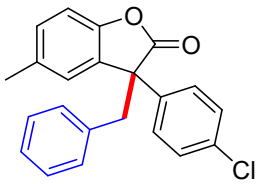
HRMS (EI) *m/z*: $[M+H]^+$ calcd for $C_{21}H_{16}FO_2^+$ 319.1129, Found 319.1131.

3-Benzyl-5-chloro-3-phenylbenzofuran-2(3H)-one(3l) [3]



The representative general procedure mentioned above was followed. Purification by PTLC on silica gel (petroleum ether/ethyl acetate = 200/1) yielded the title compound **3l** in 82% (54.8 mg) as white solid; mp: 108 – 111 °C; R_f = 0.37 (petroleum ether/ethyl acetate = 200/1); ^{1}H NMR (400 MHz, Chloroform-*d*) δ 7.60 – 7.51 (m, 2H), 7.49 – 7.38 (m, 3H), 7.22 – 7.13 (m, 3H), 7.06 – 6.98 (m, 3H), 6.98 – 6.90 (m, 3H), 3.80 (d, *J* = 13.2 Hz, 1H), 3.57 (d, *J* = 13.2 Hz, 1H). ^{13}C NMR (101 MHz, Chloroform-*d*) δ 176.8, 151.5, 137.8, 134.3, 131.1, 130.0, 129.3, 129.2, 129.1, 128.3, 128.2, 127.4, 126.9, 126.0, 112.0, 57.9, 44.8. HRMS (EI) *m/z*: $[M+Na]^+$ calcd for $C_{21}H_{15}ClO_2Na^+$ 357.0653, Found 357.0659.

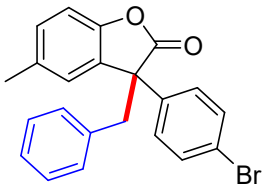
3-Benzyl-3-(4-chlorophenyl)-5-methylbenzofuran-2(3H)-one(3m)



The representative general procedure mentioned above was followed. Purification by PTLC on silica gel (petroleum ether/ethyl acetate = 200/1) yielded the title compound **3m** in 53% (36.9 mg) as white solid; mp: 93 – 95 °C; R_f = 0.37 (petroleum ether/ethyl acetate = 200/1); ^{1}H NMR (400 MHz, Chloroform-*d*) δ 7.54 – 7.47 (m, 2H), 7.44 – 7.36 (m, 2H), 7.21 – 7.07 (m, 4H), 7.01 (s, 1H), 6.92 – 6.85 (m, 3H), 3.69 (d, *J* = 13.1 Hz, 1H), 3.52 (d, *J* = 13.1 Hz, 1H), 2.42 (s, 3H). ^{13}C NMR (101 MHz, Chloroform-*d*) δ 177.4, 151.0, 137.1, 134.5, 134.1, 133.7, 130.1, 129.8, 129.0, 128.6, 128.5, 128.0, 127.2, 126.2, 110.6, 57.1, 45.0, 21.3.

HRMS (EI) *m/z*: $[M+H]^+$ calcd for $C_{22}H_{18}ClO_2^+$ 349.0990, Found 349.0991.

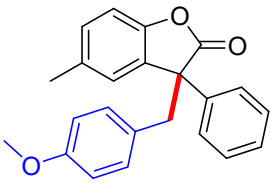
3-Benzyl-3-(4-bromophenyl)-5-methylbenzofuran-2(3H)-one(3n)



The representative general procedure mentioned above was followed. Purification by PTLC on silica gel (petroleum ether/ethyl acetate = 200/1) yielded the title compound **3n** in 76% (59.7 mg) as white solid; mp: 90 – 92 °C; R_f = 0.32 (petroleum ether/ethyl acetate = 200/1); ^{1}H NMR (400 MHz, Chloroform-*d*) δ 7.56 (d, *J* = 8.6 Hz, 2H), 7.45 (d, *J* = 8.7 Hz, 2H), 7.24 – 7.03 (m, 4H), 7.01 (s, 1H), 6.89 – 6.86 (m, 3H), 3.70 (d, *J* = 13.1 Hz, 1H), 3.52 (d, *J* = 13.1 Hz, 1H), 2.42 (s, 3H). ^{13}C NMR (101 MHz, Chloroform-*d*) δ 177.4, 151.0, 137.7, 134.5, 133.7, 131.9, 130.1, 129.8, 129.7, 128.9, 128.4, 128.3, 128.0, 127.2, 126.2, 124.8, 122.3, 110.8, 110.6, 57.1, 44.9, 21.3.

HRMS (EI) *m/z*: $[M+H]^+$ calcd for $C_{22}H_{18}BrO_2^+$ 393.0485, Found 393.0492.

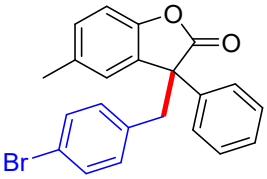
3-(4-Methoxybenzyl)-5-methyl-3-phenylbenzofuran-2(3H)-one(4a)



The representative general procedure mentioned above was followed. Purification by PTLC on silica gel (petroleum ether/ethyl acetate = 200/1) yielded the title compound **4a** in 91% (62.6 mg) as a white solid; mp: 98 – 100 °C; R_f = 0.34 (petroleum ether/ethyl acetate = 200/1); ^{1}H NMR (400 MHz, Chloroform-*d*) δ 7.57 (d, *J* = 7.6 Hz, 2H), 7.45 – 7.36 (m, 3H), 7.14 – 7.07 (m, 2H), 6.89 (d, *J* = 8.1 Hz, 1H), 6.82 (d, *J* = 8.4 Hz, 2H), 6.67 (d, *J* = 8.4 Hz, 2H), 3.76 (s, 3H), 3.71 (d, J = 13.3 Hz, 1H), 3.52 (d, *J* = 13.2 Hz, 1H), 2.43 (s, 3H). ^{13}C NMR (101 MHz, Chloroform-*d*) δ 177.9, 158.6, 151.1, 138.7, 133.5, 131.1, 129.5, 129.3, 128.8, 127.9, 127.1, 126.9, 126.1, 113.4, 110.4, 57.8, 55.1, 44.1, 21.3.

HRMS (EI) *m/z*: $[M+Na]^+$ calcd for $C_{23}H_{20}O_3Na^+$ 367.1305, Found 367.1304.

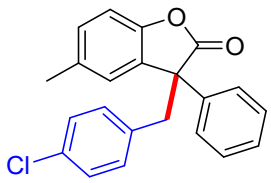
3-(4-Bromobenzyl)-5-methyl-3-phenylbenzofuran-2(3H)-one(4b)



The representative general procedure mentioned above was followed. Purification by PTLC on silica gel (petroleum ether/ethyl acetate = 200/1) yielded the title compound **4b** in 82% (63.3 mg) as a white solid; mp:112 – 114 °C; R_f = 0.35 (petroleum ether/ethyl acetate = 200/1); ^{1}H NMR (400 MHz, Chloroform-*d*) δ 7.50 (d, *J* = 7.6 Hz,2H), 7.44 – 7.33 (m, 3H), 7.22 (d, *J* = 8.0 Hz, 2H), 7.08 (d, *J* = 8.2 Hz, 1H), 7.04 (s, 1H), 6.86 (d, *J* = 8.2 Hz, 1H), 6.74 (d, *J* = 8.2 Hz, 2H), 3.67 (d, *J* = 13.1 Hz, 1H), 3.46 (d, *J* = 13.1 Hz, 1H), 2.39 (s,3H). ^{13}C NMR (101 MHz, Chloroform-*d*) δ 177.6, 151.0, 138.4, 133.9, 133.7, 131.8, 131.1, 129.8, 128.9, 128.8, 128.1, 127.0, 126.0, 121.4, 110.7, 57.4, 44.1, 21.3.

HRMS (EI) *m/z*: $[M+H]^+$ calcd for $C_{22}H_{18}BrO^+$ 393.0485, Found 393.0488.

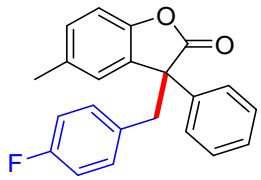
3-(4-Chlorobenzyl)-5-methyl-3-phenylbenzofuran-2(3H)-one(4c)



The representative general procedure mentioned above was followed. Purification by PTLC on silica gel (petroleum ether/ethyl acetate = 100/1) yielded the title compound **4c** in 86% (59.8 mg) as a white solid; mp:116 – 118 °C; R_f = 0.31 (petroleum ether/ethyl acetate = 100/1); ^{1}H NMR (400 MHz, Chloroform-*d*) δ 7.50 (d, *J* = 8.0 Hz, 2H), 7.41 – 7.32 (m, 3H), 7.11 – 7.01 (m, 4H), 6.85 (d, *J* = 8.2 Hz, 1H), 6.80 (d, *J* = 7.5 Hz, 2H), 3.68 (d, *J* = 13.1 Hz, 1H), 3.47 (d, *J* = 13.2 Hz, 1H), 2.38 (s, 3H). ^{13}C NMR (101 MHz, Chloroform-*d*) δ 177.6, 151.0, 138.4, 133.7, 133.4, 133.1, 131.4, 129.8, 128.9, 128.8, 128.2, 128.1, 127.0, 126.0, 110.6, 57.5, 44.0, 21.3.

HRMS (EI) *m/z*: $[M+H]^+$ calcd for $C_{22}H_{18}ClO_2^+$ 349.0990, Found 349.0996.

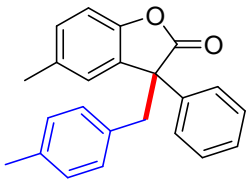
3-(4-Fluorobenzyl)-5-methyl-3-phenylbenzofuran-2(3H)-one(4d)



The representative general procedure mentioned above was followed. Purification by PTLC on silica gel (petroleum ether/ethyl acetate = 200/1) yielded the title compound **4d** in 62% (41.2 mg) as a white solid; mp:98 – 100 °C; R_f = 0.33 (petroleum ether/ethyl acetate = 200/1); ^{1}H NMR (400 MHz, Chloroform-*d*) δ 7.96 (d, *J* = 8.1 Hz, 2H), 7.50 (d, *J* = 7.7 Hz, 2H), 7.42 – 7.34 (m, 3H), 7.10 – 7.04 (m, 4H), 6.85 (d, *J* = 8.1 Hz, 1H), 3.84 (d, *J* = 13.0 Hz, 1H), 3.59 (d, *J* = 13.0 Hz, 1H), 2.40 (s, 3H). ^{13}C NMR (101 MHz, Chloroform-*d*) δ 177.7, 162.0 (d, *J* = 246.7 Hz), 151.0, 138.5, 133.6, 131.6 (d, *J* = 8.1 Hz), 130.6 (d, *J* = 3.2 Hz), 129.7, 128.9, 128.9, 128.1, 127.0, 126.0, 114.9 (d, *J* = 21.4 Hz), 110.5, 57.6, 43.9, 21.3. ^{19}F NMR (376 MHz, Chloroform-d) δ -115.4.

HRMS (EI) *m/z*: $[M^+]$ calcd for $C_{22}H_{17}FO_2$ 332.1213, Found 332.1214.

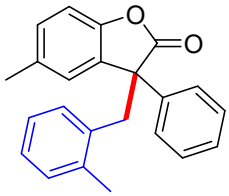
5-Methyl-3-(4-methylbenzyl)-3-phenylbenzofuran-2(3H)-one(4e)



The representative general procedure mentioned above was followed. Purification by PTLC on silica gel (petroleum ether/ethyl acetate = 200/1) yielded the title compound **4e** in 73% (47.8 mg) as a white solid; mp:102 – 104 °C; R_f = 0.33 (petroleum ether/ethyl acetate = 200/1); ^{1}H NMR (400 MHz, Chloroform-*d*) δ 7.52 (d, *J* = 7.7 Hz, 2H), 7.40 – 7.26 (m, 3H), 7.09 – 7.02 (m, 2H), 6.89 (d, *J* = 7.7 Hz,2H), 6.83 (d, *J* = 8.1 Hz, 1H), 6.75 (d, *J* = 7.8 Hz, 2H), 3.68 (d, *J* = 13.1 Hz, 1H), 3.49 (d, *J* = 13.1 Hz, 1H), 2.38 (s, 3H), 2.22 (s, 3H). ^{13}C NMR (101 MHz, Chloroform-*d*) δ 177.8, 151.1, 138.8, 136.6, 133.4, 131.7, 130.0, 129.5, 129.3, 128.8, 128.7, 127.9, 127.1, 126.2, 110.4, 57.7 44.4, 21.3, 21.0.

HRMS (EI) *m/z*: $[M+H]^+$ calcd for $C_{23}H_{21}O_2^+$ 329.1536, Found 329.1531.

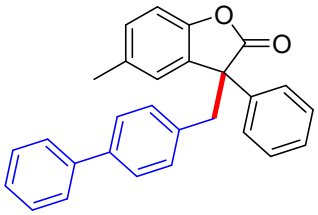
5-Methyl-3-(2-methylbenzyl)-3-phenylbenzofuran-2(3H)-one(4f)



The representative general procedure mentioned above was followed. Purification by PTLC on silica gel (petroleum ether/ethyl acetate = 200/1) yielded the title compound **4f** in 70% (45.9 mg) as a colorle-ss liquid; R_f = 0.34 (petroleum ether/ethyl acetate = 200/1); ^{1}H NMR (400 MHz, Chloroform-*d*) δ 7.61 (d, *J* = 7.5 Hz, 2H), 7.46 – 7.37 (m, 3H), 7.18 – 7.06 (m, 3H), 6.97 – 6.91 (m, 2H), 6.84 (s, 1H), 6.66 (d, *J* = 7.7 Hz, 1H), 3.76 (d, *J* = 13.7 Hz, 1H), 3.66 (d, *J* = 13.8 Hz, 1H), 2.37 (s, 3H), 2.11 (s, 3H). ^{13}C NMR (101 MHz, Chloroform-*d*) δ 177.6, 153.6, 153.1, 137.0, 134.6, 134.0, 130.2, 128.9, 128.7, 127.9, 127.2, 125.4, 125.2, 120.9, 108.2, 56.8, 45.4, 35.1, 31.3.

HRMS (EI) *m/z*: $[M+Na]^+$calcd for $C_{23}H_{20}O_2Na^+$ 351.1356, Found 351.1354.

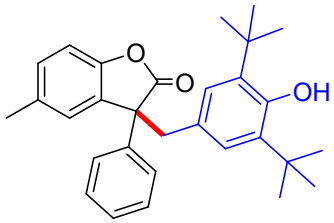
3-([1,1'-Biphenyl]-4-ylmethyl)-5-methyl-3-phenylbenzofuran-2(3H)-one(4g)



The representative general procedure mentioned above was followed. Purification by PTLC on silica gel (petroleum ether/ethyl acetate = 200/1) yielded the title compound **4g** in 82% (64 mg) as a white solid; mp:134 – 136 °C; R_f = 0.36 (petroleum ether/ethyl acetate = 200/1); ^{1}H NMR (400 MHz, Chloroform-*d*) δ 7.56 – 7.48 (m, 4H), 7.42 – 7.37 (m, 4H), 7.33 (q, *J* = 7.7, 7.1 Hz, 4H), 7.08 – 7.04 (m, 2H), 6.93 (d, *J* = 8.1 Hz, 2H), 6.84 (d, *J* = 8.7 Hz, 1H), 3.75 (d, *J* = 13.1 Hz, 1H), 3.56 (d, *J* = 13.1 Hz, 1H), 2.39 (s, 3H). ^{13}C NMR (101 MHz, Chloroform-*d*) δ 177.8, 151.1, 140.6, 139.8, 138.7, 134.0, 133.6, 130.5, 129.6, 129.1, 128.9, 128.7, 128.0, 127.2, 127.1, 126.9, 126.6, 126.2, 110.5, 57.6, 44.5, 29.7, 21.3.

HRMS (EI) *m/z*: $[M+Na]^+$ calcd for $C_{28}H_{22}O_2Na^+$ 413.1512, Found 413.1508.

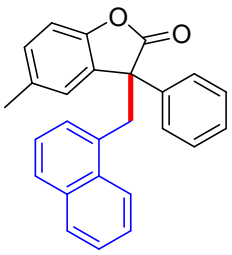
3-(3,5-Di-tert-butyl-4-hydroxybenzyl)-5-methyl-3-phenylbenzofuran-2(3H)-one(4h)



The representative general procedure mentioned above was followed. Purification by PTLC on silica gel (petroleum ether/ethyl acetate = 50/1) yielded the title compound **4h** in 61% (53.9 mg) as a white solid; mp:101 – 102 °C; R_f = 0.67 (petroleum ether/ethyl acetate = 50/1); ^{1}H NMR (400 MHz, Chloroform-*d*) δ 7.54 (d, *J* = 7.9 Hz, 2H), 7.40 – 7.30 (m, 3H), 7.05 (d, *J* = 8.3 Hz, 1H), 6.99 (s, 1H), 6.82 (d, *J* = 8.1 Hz, 1H), 6.62 (s, 2H), 5.02 (s, 1H), 3.57 (d, *J* = 13.1 Hz, 1H), 3.44 (d, *J* = 13.1 Hz, 1H), 2.38 (s, 3H), 1.27 (s, 18H). ^{13}C NMR (101 MHz, Chloroform-*d*) δ 177.9, 152.8, 151.1, 138.6, 135.1, 133.2, 129.4, 129.3, 128.7, 127.8, 127.2, 126.8, 126.6, 125.2, 110.3, 57.8, 45.3, 34.1, 30.1, 21.2.

HRMS (EI) *m/z*: $[M^+]$ calcd for $C_{30}H_{34}O_3$ 442.2508, Found 442.2512.

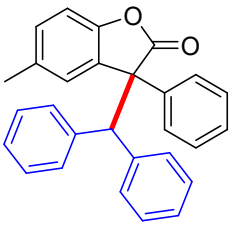
5-Methyl-3-(naphthalen-1-ylmethyl)-3-phenylbenzofuran-2(3H)-one(4i)



The representative general procedure mentioned above was followed. Purification by PTLC on silica gel (petroleum ether/ethyl acetate = 200/1) yielded the title compound **4i** in 54% (39.3 mg) as a white solid; mp:107 – 109 °C; R_f = 0.28 (petroleum ether/ethyl acetate = 200/1); ^{1}H NMR (400 MHz, Chloroform-*d*) δ 7.93 (d, *J* = 7.3 Hz, 1H), 7.77 (d, *J* = 7.7 Hz, 1H), 7.69 (d, *J* = 8.1 Hz, 1H), 7.65 (d, *J* = 7.3 Hz, 2H), 7.49 – 7.38 (m, 5H), 7.25 (t, *J* = 7.6 Hz, 1H), 7.10 (d, *J* = 7.0 Hz, 1H), 6.94 (d, *J* = 8.1 Hz, 1H), 6.85 (s, 1H), 6.79 (d, *J* = 8.1 Hz, 1H), 4.28 (d, *J* = 13.9 Hz, 1H), 4.11 (d, *J* = 13.9 Hz, 1H), 2.16 (s, 3H). ^{13}C NMR (101 MHz, Chloroform-*d*) δ 178.2, 150.9, 138.7, 133.6, 133.1, 132.3, 131.4, 129.3, 128.8, 128.5, 128.0, 128.0, 127.9, 127.2, 125.3, 125.2, 124.9, 124.1, 110.1, 57.3, 40.2, 20.9.

HRMS (EI) *m/z*: $[M+H]^+$ calcd for $C_{26}H_{21}O_2^+$ 366.1614, Found 366.1619.

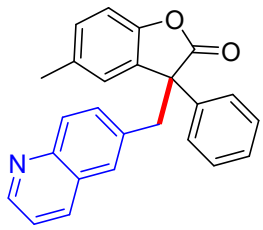
3-Benzhydryl-5-methyl-3-phenylbenzofuran-2(3H)-one(4j)



The representative general procedure mentioned above was followed. Purification by PTLC on silica gel (petroleum ether/ethyl acetate = 50/1) yielded the title compound **4j** in 34% (26.5 mg) as a white solid; mp:108 – 110 °C; R_f = 0.61 (petroleum ether/ethyl acetate = 50/1); ^{1}H NMR (400 MHz, Chloroform-*d*) δ 7.69 – 7.61 (m, 2H), 7.38 (q, *J* = 6.9, 6.4 Hz, 3H), 7.25 – 7.19 (m, 5H), 7.14 (t, *J* = 7.5 Hz, 2H), 7.07 – 6.99 (m, 3H), 6.85 (d, *J* = 7.7 Hz, 2H), 6.71 (s, 1H), 5.34 (s, 1H), 2.39 (s, 3H). ^{13}C NMR (101 MHz, Chloroform-*d*) δ 176.9, 151.4, 139.4, 138.2, 138.0, 133.1, 130.1, 129.9, 129.6, 128.6, 128.4, 128.2, 128.1, 128.0, 127.9, 127.8, 127.5, 127.2, 127.0, 110.6, 60.2, 60.0, 21.4.

HRMS (EI) *m/z*: $[M^+]$ calcd for $C_{18}H_{22}O_2$ 390.1620, Found 390.1611.

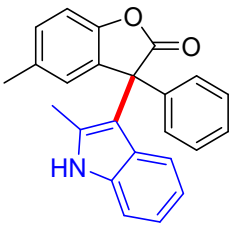
5-Methyl-3-phenyl-3-(quinolin-6-ylmethyl)benzofuran-2(3H)-one(4k)



The representative general procedure mentioned above was followed. Purification by PTLC on silica gel (petroleum ether/ethyl acetate = 50/1) yielded the title compound **4k** in 43% (31.4 mg) as a yellow liquid; R_f = 0.62 (petroleum ether/ethyl acetate = 20/1); ^{1}H NMR (400 MHz, Chloroform-*d*) δ 8.91 (d, *J* = 2.4 Hz, 1H), 8.05 (d, *J* = 8.3 Hz, 1H), 7.85 (d, *J* = 8.7 Hz, 1H), 7.62 (d, *J* = 7.6 Hz, 2H), 7.48 – 7.38 (m , 5H), 7.23 – 7.07 (m, 3H), 6.83 (d, *J* = 8.1 Hz, 1H), 3.98 (d, *J* = 13.1 Hz, 1H), 3.77 (d, *J* = 13.1 Hz, 1H), 2.45 (s, 3H). ^{13}C NMR (101 MHz, Chloroform-*d*) δ 177.6, 150.9, 150.3, 147.3, 138.4, 135.9, 133.7, 133.4, 131.7, 129.8, 129.0, 128.9, 128.8, 128.8, 128.1, 127.8, 127.0, 126.1, 121.2, 110.6, 57.6, 44.6, 21.3.

HRMS (EI) *m/z*: $[M+H]^+$ calcd for $C_{25}H_{20}NO_2^+$ 366.1494, Found 366.1484.

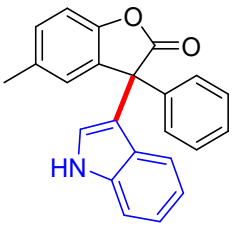
5-Methyl-3-(2-methyl-1H-indol-3-yl)-3-phenylbenzofuran-2(3H)-one(4l)



The representative general procedure mentioned above was followed. Purification by PTLC on silica gel (petroleum ether/ethyl acetate = 20/1) yielded the title compound **4l** in 45% (31.8 mg) as a white solid; mp: 263 – 265 °C; R_f = 0.33 (petroleum ether/ethyl acetate = 20/1); ^{1}H NMR (400 MHz, Chloroform-*d*) δ 7.89 (s, 1H), 7.44 (s, 2H), 7.34 (s, 3H), 7.24 (s, 1H), 7.12 (q, *J* = 8.4 Hz, 2H), 7.08 – 7.02 (m, 2H), 6.83 (t, *J* = 7.6 Hz, 1H), 6.52 (d, *J* = 8.1 Hz, 1H), 2.28 (s, 3H), 2.05 (s, 3H). ^{13}C NMR (101 MHz, Chloroform-*d*) δ 177.5, 150.3, 139.7, 134.9, 134.2, 133.1, 131.5, 129.5, 128.7, 127.9, 127.3, 126.4, 121.2, 119.8, 119.6, 110.8, 110.6, 110.3, 60.4, 56.3, 21.2, 21.1, 14.2, 13.6.

HRMS (EI) *m/z*: $[M+Na]^+$ calcd for $C_{24}H_{19}NO_2Na^+$ 376.1313, Found 376.1309.

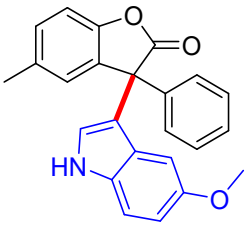
3-(1H-indol-3-yl)-5-methyl-3-phenylbenzofuran-2(3H)-one(4m)



The representative general procedure mentioned above was followed. Purification by PTLC on silica gel (petroleum ether/ethyl acetate = 20/1) yielded the title compound **4m** in 76% (51.5 mg) as a white solid; mp: 260 – 261 °C; R_f = 0.35 (petroleum ether/ethyl acetate = 20/1); ^{1}H NMR (400 MHz, Chloroform-*d*) δ 8.14 (s, 1H), 7.39 – 7.30 (m, 6H), 7.21 – 7.09 (m, 5H), 6.98 (t, *J* = 7.5 Hz, 1H), 6.89 (d, *J* = 2.3 Hz, 1H), 2.31 (s, 3H). ^{13}C NMR (101 MHz, Chloroform-*d*) δ 177.0, 150.5, 139.2, 137.1, 134.1, 131.8, 129.5, 128.7, 127.8, 127.6, 125.9, 125.2, 124.4, 122.6, 121.3, 120.0, 115.7, 111.4, 110.6, 56.4, 21.2.

HRMS (EI) *m/z*: $[M+H]^+$ calcd for $C_{23}H_{18}NO_2^+$ 340.1338, Found 376.1328.

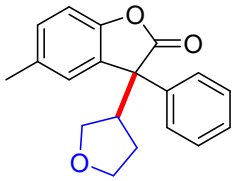
3-(5-methoxy-1H-indol-3-yl)-5-methyl-3-phenylbenzofuran-2(3H)-one(4n)



The representative general procedure mentioned above was followed. Purification by PTLC on silica gel (petroleum ether/ethyl acetate = 20/1) yielded the title compound **4n** in 55% (40.6 mg) as a white solid; mp: 255 – 257 °C; R_f = 0.32 (petroleum ether/ethyl acetate = 20/1); ^{1}H NMR (400 MHz, Chloroform-*d*) δ 8.05 (s, 1H), 7.39 (d, *J* = 6.3 Hz, 2H), 7.32 (d, *J* = 6.7 Hz, 3H), 7.23 (d, *J* = 8.8 Hz, 1H), 7.11 (t, *J* = 6.4 Hz, 3H), 6.82 (d, *J* = 9.2 Hz, 2H), 6.59 (s, 1H), 3.60 (s, 3H), 2.31 (s, 3H). ^{13}C NMR (101 MHz, Chloroform-*d*) δ 177.0, 154.0, 150.6, 139.1, 134.1, 132.2, 131.8, 129.5, 128.7, 127.7, 127.7, 126.0, 125.8, 125.1, 115.3, 112.9, 112.0, 110.6, 103.1, 56.4, 55.6, 21.3.

HRMS (EI) *m/z*: $[M+H]^+$ calcd for $C_{24}H_{20}NO_3^+$ 370.1443, Found 370.1438.

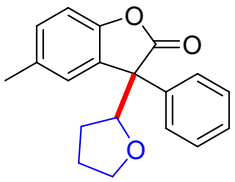
5-Methyl-3-phenyl-3-(tetrahydrofuran-3-yl)benzofuran-2(3H)-one(4o)



The representative general procedure mentioned above was followed. Purification by PTLC on silica gel (petroleum ether/ethyl acetate = 10/1) yielded the title compound **4o** in 32% (18.8 mg) as a colorless liquid; R_f = 0.41 (petroleum ether/ethyl acetate = 10/1); ^{1}H NMR (400 MHz, Chloroform-*d*) δ 7.52 (d, *J* = 7.5 Hz, 2H), 7.37 (t, *J* = 7.3 Hz, 2H), 7.33 – 7.26 (m, 3H), 7.17 (d, *J* = 7.8 Hz, 1H), 7.07 (d, *J* = 7.9 Hz, 1H), 4.88 (t, *J* = 7.3 Hz, 1H), 3.81 (t, *J* = 6.5 Hz, 2H), 2.39 (s, 3H), 2.06 – 2.00 (m , 1H), 1.93 – 1.79 (m, 1H), 1.79 – 1.68 (m, 1H), 1.56 – 1.49 (m, 1H). ^{13}C NMR (101 MHz, Chloroform-*d*) δ 176.1, 151.4, 137.6, 133.9, 129.7, 128.8, 128.5, 127.8, 127.1, 126.8, 110.2, 83.5, 69.5, 59.1, 27.8, 26.0, 21.2.

HRMS (EI) *m/z*: $[M+H]^+$ calcd for $C_{19}H_{19}O_3^+$ 295.1334, Found 360.1325.

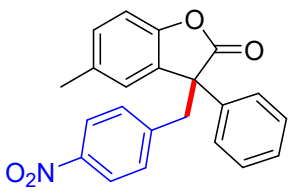
5-Methyl-3-phenyl-3-(tetrahydrofuran-2-yl)benzofuran-2(3H)-one(4o')



The representative general procedure mentioned above was followed. Purification by PTLC on silica gel (petroleum ether/ethyl acetate = 10/1) yielded the title compound **4o'** in 39% (23.0 mg) as a colorless liquid; R_f = 0.40 (petroleum ether/ethyl acetate = 10/1); ^{1}H NMR (400 MHz, Chloroform-*d*) δ 7.51 (s, 2H), 7.39 – 7.27 (m, 3H), 7.24 (s, 1H), 7.18 (d, *J* = 7.5 Hz, 1H), 7.07 (d, *J* = 7.5 Hz, 1H), 4.89 (s, 1H), 3.71 (s, 1H), 3.49 (d, *J* = 6.5 Hz, 1H), 2.41 (s, 3H), 2.03 – 1.69 (m, 4H). ^{13}C NMR (101 MHz, Chloroform-*d*) δ 177.0, 151.9, 136.0, 133.3, 1298, 128.7, 127.9, 127.5, 127.4, 126.5, 110.6, 84.0, 69.2, 59.2, 27.4, 25.8, 21.3.

HRMS (EI) *m/z*: $[M+Na]^+$ calcd for $C_{19}H_{18}O_3Na^+$ 317.1154, Found 317.1147.

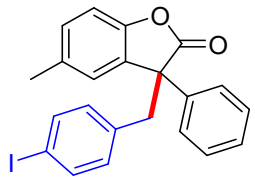
5-Methyl-3-(4-nitrobenzyl)-3-phenylbenzofuran-2(3H)-one(4p)



The representative general procedure mentioned above was followed. Purification by PTLC on silica gel (petroleum ether/ethyl acetate = 20/1) yielded the title compound **4p** in 34% (24.4 mg) as a yellow solid; mp:142 – 144 °C; R_f = 0.41 (petroleum ether/ethyl acetate = 20/1); ^{1}H NMR (400 MHz, Chloroform-*d*) δ 8.00 (d, *J* = 8.1 Hz, 2H), 7.55 (d, *J* = 7.7 Hz, 2H), 7.48 – 7.39 (m, 3H), 7.14 – 7.08 (m, 4H), 6.89 (d, *J* = 8.1 Hz, 1H), 3.88 (d, *J* = 13.0 Hz, 1H), 3.63 (d, *J* = 13.0 Hz, 1H), 2.44 (s, 3H). ^{13}C NMR (101 MHz, Chloroform-*d*) δ 177.2, 150.9, 147.1, 142.5, 138.0, 134.0, 131.0, 130.1, 129.0, 128.3, 126.9, 125.8, 123.1, 110.8, 57.2, 44.2, 21.3.

HRMS (EI) *m/z*: $[M+H]^+$ calcd for $C_{22}H_{18}NO_4^+$ 360.1230, Found 360.1235.

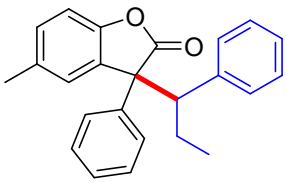
3-(4-Iodobenzyl)-5-methyl-3-phenylbenzofuran-2(3H)-one(4q)



The representative general procedure mentioned above was followed. Purification by PTLC on silica gel (petroleum ether/ethyl acetate = 200/1) yielded the title compound **4q** in 55% (48.4 mg) as a white solid; mp:100 – 103 °C; R_f = 0.36 (petroleum ether/ethyl acetate = 200/1); ^{1}H NMR (400 MHz, Chloroform-*d*) δ 7.49 (d, *J* = 8.2 Hz, 2H), 7.45 – 7.32 (m, 5H), 7.08 (d, *J* = 8.1 Hz, 1H), 7.02 (s, 1H), 6.86 (d, *J* = 8.2 Hz, 1H), 6.61 (d, *J* = 8.0 Hz, 2H), 3.65 (d, *J* = 13.1 Hz, 1H), 3.44 (d, *J* = 13.1 Hz, 1H), 2.38 (s, 3H). ^{13}C NMR (101 MHz, Chloroform-*d*) δ 177.5, 151.0, 138.4, 137.1, 134.5, 133.7, 132.0, 129.8, 128.9, 128.8, 128.1, 126.9, 126.0, 110.6, 93.0, 57.3, 44.2, 21.3.

HRMS (EI) *m/z*: $[M+H]^+$ calcd for $C_{22}H_{18}IO_2^+$ 441.0346, Found 441.0349.

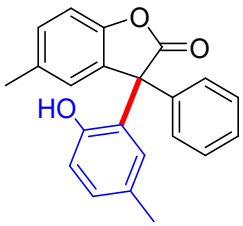
5-Methyl-3-phenyl-3-((R)-1-phenylpropyl)benzofuran-2(3H)-one (4r)



The representative general procedure mentioned above was followed. Purification by PTLC on silica gel (petroleum ether/ethyl acetate = 50/1) yielded the title compound **4r** in 75% (51.3 mg) as a white solid; mp:120 – 122 °C; R_f = 0.54 (petroleum ether/ethyl acetate = 50/1); ^{1}H NMR (400 MHz, Chloroform-*d*) δ 7.60 – 7.52 (m, 2H), 7.39 – 7.30 (m, 2H), 7.32 – 7.25 (m, 1H), 7.19 – 7.07 (m, 3H), 7.08 – 7.01 (m, 1H), 6.97 – 6.85 (m, 4H), 3.66 (d, *J* = 11.9, 3.3 Hz, 1H), 2.35 (s, 3H), 1.91 – 1.69 (m, 2H), 0.73 (t, *J* = 7.2 Hz, 3H). ^{13}C NMR (101 MHz, Chloroform-*d*) δ 177.9, 150.7, 137.7, 137.0, 132.9, 129.9, 129.1, 128.6, 128.4, 127.6, 127.5, 127.2, 127.1, 127.1, 110.2, 60.9, 56.4, 22.2, 21.3, 12.3.

HRMS (EI) *m/z*: [M^+] calcd for $C_{24}H_{22}O_2$ 342.1620, Found 342.1620.

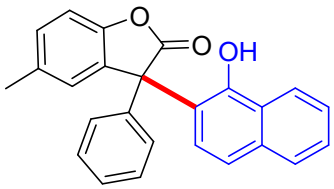
3-(2-Hydroxyphenyl)-5-methyl-3-phenylbenzofuran-2(3H)-one(5a)



The representative general procedure mentioned above was followed. Purification by PTLC on silica gel (petroleum ether/ethyl acetate = 5/1) yielded the title compound **5a** in 86% (54.4 mg) as white solid; mp:98 – 100 °C; R_f = 0.42 (petroleum ether/ethyl acetate = 5/1); ^{1}H NMR (400 MHz, DMSO) δ 9.76 (s, 1H), 7.46 – 7.41 (m, 5H), 7.19 (q, *J* = 8.3 Hz, 2H), 6.97 (d, *J* = 5.8 Hz, 2H), 6.66 (d, *J* = 8.1 Hz, 1H), 6.49 (s, 1H), 2.31 (s, 3H), 2.11 (s, 3H). ^{13}C NMR (101 MHz, DMSO) δ 177.5, 152.6, 151.4, 137.6, 133.6, 130.5, 129.8, 129.7, 129.2, 129.1, 128.8, 128.6, 127.7, 126.6, 115.8, 110.3, 79.6, 58.0, 21.1, 20.8.

HRMS (EI) m/z: [M^+] calcd for $C_{22}H_{18}O_3$ 330.1256, Found 330.1260.

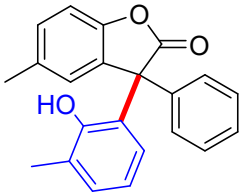
3-(1-Hydroxynaphthalen-2-yl)-5-methyl-3-phenylbenzofuran-2(3H)-one(5b)



The representative general procedure mentioned above was followed. Purification by PTLC on silica gel (petroleum ether/ethyl acetate = 5/1) yielded the title compound **5b** in 75% (54.9 mg) as white solid; mp:124 – 125 °C; R_f = 0.43 (petroleum ether/ethyl acetate = 5/1); ^{1}H NMR (400 MHz, DMSO) δ 9.75 (s, 1H), 8.11 (d, *J* = 8.8 Hz, 1H), 8.04 (d, *J* = 8.2 Hz, 1H), 7.63 (d, *J* = 8.8 Hz, 1H), 7.43 – 7.35 (m, 6H), 7.06 – 6.93 (m, 2H), 6.62 (d, *J* = 8.0 Hz, 1H), 2.20 (s, 3H). ^{13}C NMR (101 MHz, DMSO) δ 177.8, 152.8, 151.1, 136.6, 130.8, 130.8, 130.3, 129.7, 129.6, 129.6, 129.3, 128.7, 128.5, 127.5, 127.4, 127.1, 124.4, 122.6, 121.1, 115.6, 111.6, 58.6, 20.6.

HRMS (EI) m/z: [M^+] calcd for $C_{25}H_{18}O_3$ 366.1256, Found 366.1254.

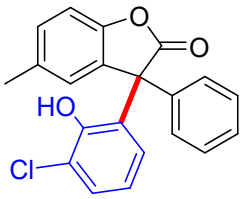
3-(2-Hydroxy-3-methylphenyl)-5-methyl-3-phenylbenzofuran-2(3H)-one(5c)



The representative general procedure mentioned above was followed. Purification by PTLC on silica gel (petroleum ether/ethyl acetate = 5/1) yielded the title compound **5c** in 44% (29.0 mg) as white solid; mp:100 – 101 °C; R_f = 0.44 (petroleum ether/ethyl acetate = 5/1); ^{1}H NMR (400 MHz, DMSO) δ 9.74 (s, 1H), 7.42 – 7.33 (m, 5H), 7.21 (d, *J* = 7.6 Hz, 1H), 7.08 (t, *J* = 7.6 Hz, 1H), 6.93 (d, *J* = 7.0 Hz, 2H), 6.60 (d, *J* = 8.1 Hz, 1H), 6.45 (d, *J* = 1.3 Hz, 1H), 2.29 (s, 3H), 2.07 (s, 3H). ^{13}C NMR (101 MHz, DMSO) δ 176.9, 152.2, 151.5, 137.3, 130.2, 129.8, 129.4, 129.4, 128.7, 128.7, 128.3, 128.2, 127.4, 123.8, 123.3, 119.7, 115.3, 57.8, 20.4, 14.8.

HRMS (EI) m/z: [M^+] calcd for $C_{22}H_{18}O_3$ 330.1256, Found 330.1257.

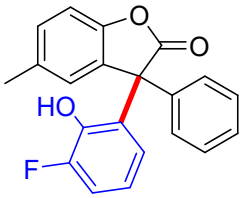
3-(3-Chloro-2-hydroxyphenyl)-5-methyl-3-phenylbenzofuran-2(3H)-one(5d)



The representative general procedure mentioned above was followed. Purification by PTLC on silica gel (petroleum ether/ethyl acetate = 5/1) yielded the title compound **5d** in 60% (42.0 mg) as white solid; mp:107 – 109 °C; R_f = 0.38 (petroleum ether/ethyl acetate = 5/1); ^{1}H NMR (400 MHz, Chloroform-*d*) δ 7.42 – 7.34 (m, 3H), 7.29 – 7.26 (m, 2H), 7.21 – 7.19 (m, 1H), 7.16 – 7.11 (m, 2H), 7.08 (s, 1H), 7.01 (d, *J* = 8.6 Hz, 1H), 5.72 (s, 1H), 2.39 (s, 3H). ^{13}C NMR (101 MHz, Chloroform-*d*)) δ 177.0, 151.1, 150.4, 140.6, 134.5, 133.7, 130.6, 130.0, 128.9, 128.8, 128.5, 128.0, 127.9, 126.3, 120.1, 116.4, 110.9, 60.6, 21.3.

HRMS (EI) m/z: [M^+] calcd for $C_{21}H_{15}ClO_3$ 350.0710, Found 350.0713.

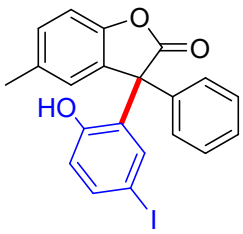
3-(3-Fluoro-2-hydroxyphenyl)-5-methyl-3-phenylbenzofuran-2(3H)-one(5e)



The representative general procedure mentioned above was followed. Purification by PTLC on silica gel (petroleum ether/ethyl acetate = 5/1) yielded the title compound **5e** in 69% (46.1 mg) as white solid; mp:103 – 104 °C; R_f = 0.38 (petroleum ether/ethyl acetate = 5/1); ^{1}H NMR (400 MHz, Chloroform-*d*) δ 7.37 – 7.29 (m, 3H), 7.26 – 7.23 (m, 2H), 7.15 (d, *J* = 8.2 Hz, 1H), 7.09 (d, *J* = 8.2 Hz, 1H), 7.05 (s, 1H), 7.03 – 6.99 (m, 1H), 6.98 – 6.91 (m, 2H), 5.62 (s, 1H), 2.35 (s, 3H). ^{13}C NMR (101 MHz, Chloroform-*d*) δ 177.17, 150.8 (d, *J* = 239.4 Hz), 150.41, 143.4 (d, *J* = 14.1 Hz), 140.60, 134.45, 133.1 (d, *J* = 7.1 Hz), 130.72, 129.91, 128.84, 127.96, 127.94, 126.36, 124.8 (d, *J* = 3.0 Hz), 117.3 (d, *J* = 2.0 Hz), 116.0 (d, *J* = 20.2 Hz), 110.91, 60.72, 21.25. ^{19}F NMR (376 MHz, Chloroform-*d*) δ -138.81.

HRMS (EI) m/z: [M^+] calcd for $C_{21}H_{15}FO_3$ 334.1005, Found 334.0999.

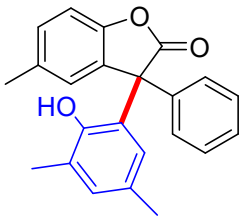
3-(2-Hydroxy-5-iodophenyl)-5-methyl-3-phenylbenzofuran-2(3H)-one(5f)



The representative general procedure mentioned above was followed. Purification by PTLC on silica gel (petroleum ether/ethyl acetate = 5/1) yielded the title compound **5f** in 45% (39.8 mg) as yellow liquid; R_f = 0.39 (petroleum ether/ethyl acetate = 5/1); ^{1}H NMR (400 MHz, Chloroform-*d*) δ 7.40 – 7.30 (m, 5H), 7.20 – 7.11 (m, 4H), 7.09 (s, 1H), 6.85 – 6.79 (m, 2H), 5.48 (s, 1H), 2.38 (s, 3H). ^{13}C NMR (101 MHz, Chloroform-*d*) δ 177.7, 155.4, 150.4, 141.1, 134.23, 132.6, 131.3, 129.7, 129.6, 128.7, 128.0, 127.8, 126.4, 115.6, 110.8, 60.9, 21.2.

HRMS (EI) m/z: [M^+] calcd for $C_{21}H_{15}IO_3$ 442.0066, Found 442.0060.

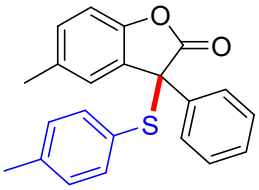
3-(2-Hydroxy-3,5-dimethylphenyl)-5-methyl-3-phenylbenzofuran-2(3H)-one(5g)



The representative general procedure mentioned above was followed. Purification by PTLC on silica gel (petroleum ether/ethyl acetate = 5/1) yielded the title compound **5g** in 78% (53.1 mg) as white solid; mp:100 – 101 °C; R_f = 0.42 (petroleum ether/ethyl acetate = 5/1); ^{1}H NMR (400 MHz, DMSO-d_6) δ 9.74 (s, 1H), 7.47 – 7.36 (m, 5H), 7.04 (d, *J* = 1.7 Hz, 1H), 6.96 (dd, *J* = 8.1, 2.1 Hz, 1H), 6.76 (d, *J* = 1.7 Hz, 1H), 6.63 (d, *J* = 8.1 Hz, 1H), 6.46 (d, *J* = 2.0 Hz, 1H), 2.27 (d, *J* = 3.4 Hz, 6H), 2.10 (s, 3H). ^{13}C NMR (101 MHz, DMSO-d_6) δ 177.4, 152.6, 149.9, 137.8, 133.3, 131.1, 130.1, 129.8, 129.2, 129.0, 128.8, 128.6, 127.7, 123.9, 119.7, 115.7, 58.4, 21.0, 20.8, 15.1.

HRMS (EI) m/z: [M^+] calcd for $C_{23}H_{20}O_3$ 344.1412, Found 344.1415.

5-Methyl-3-phenyl-3-(p-tolylthio)benzofuran-2(3H)-one(6a)



The representative general procedure mentioned above was followed. Purification by PTLC on silica gel (petroleum ether/ethyl acetate = 50/1) yielded the title compound **6a** in 30% (20.6 mg) as colorless liquid; R_f = 0.46 (petroleum ether/ethyl acetate = 50/1); ^{1}H NMR (400 MHz, Chloroform-*d*) δ 7.79 – 7.69 (m, 2H), 7.45 – 7.33 (m, 3H), 7.27 (d, *J* = 1.6 Hz, 1H), 7.10 – 7.02 (m, 3H), 6.95 (d, *J* = 7.8 Hz, 2H), 6.76 (d, *J* = 8.1 Hz, 1H), 2.40 (s, 3H), 2.27 (s, 3H). ^{13}C NMR (101 MHz, Chloroform-*d*) δ 174.8, 150.4, 140.4, 136.4, 135.2, 134.0, 130.2, 129.5, 128.8, 128.7, 128.1, 128.0, 126.6, 126.0, 110.4, 61.5, 21.3, 21.2.

HRMS (EI) m/z: [M^+] calcd for $C_{22}H_{18}O_2S$ 346.1028, Found 346.1027.

4. X-ray Crystallographic Data

Compounds **3a** were collected at 100 K on a Rigaku Oxford Diffraction Supernova Dual Source, Cu at Zero equipped with an AtlasS2 CCD using Cu Kα radiation. Data reduction was carried out with the diffractometer's software. The structures were solved by direct methods using Olex2 software and the non-hydrogen atoms were located from the trial structure and then refined anisotropically with SHELXL-2014 using a full-matrix least squares procedure based on F2. The weighted R factor, wR and goodness-of-fit S values were obtained based on F2.The hydrogen atom positions were fixed geometrically at the calculated distances and allowed to ride on their parent atoms. Crystallographic data for the structure reported in this paper have been deposited at the Cambridge Crystallographic Data Center and allocated with the deposition numbers: CCDC 1949691 for **3a**.

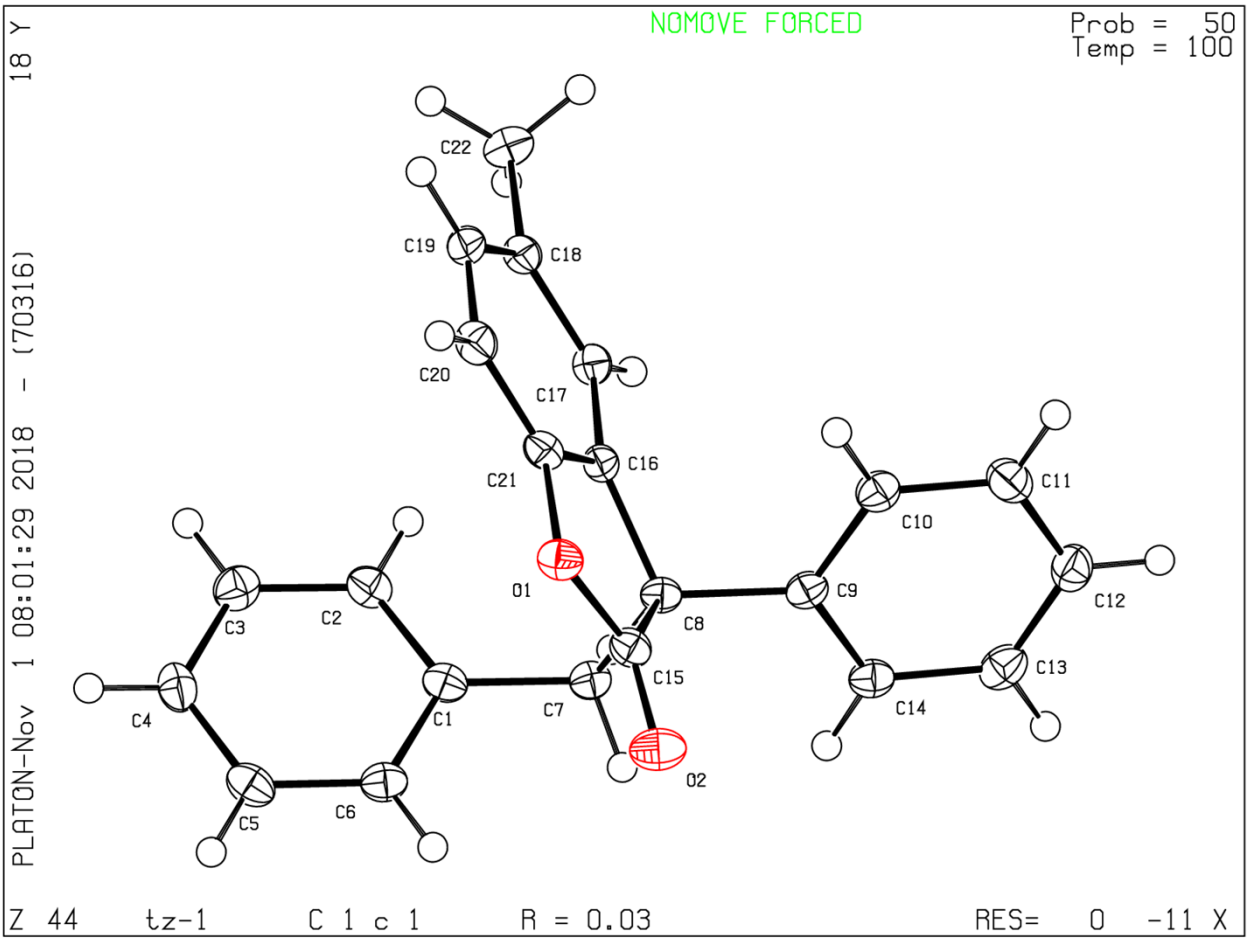


Table S1 Cystal data and structure refinement for **1a**

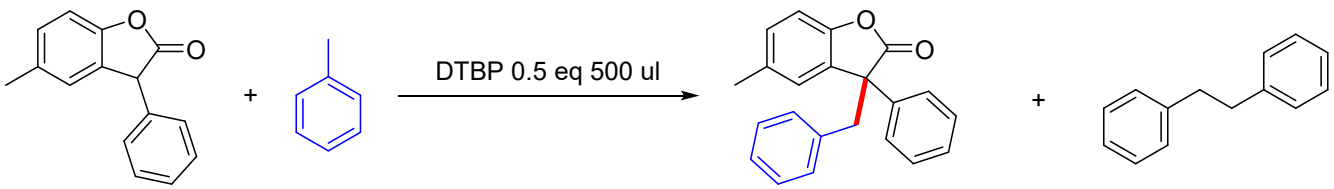
Identification code	TZ-1

Empirical formula	$C_{22}H_{18}O_2$
Formula weight	314.36
Temperature/K	100.01(10)
Crystal system	monoclinic
Space group	Cc
a/Å	16.6597(9)
b/Å	9.1073(4)
c/Å	10.5974(6)
α/°	90
β/°	94.571(5)
γ/°	90
Volume/Å^3	1602.78(14)
Z	4
ρ_{calc}g/cm^3	1.303
μ/mm^{-1}	0.082
F(000)	664.0
Crystal size/mm^3	0.15 × 0.13 × 0.12
Radiation	MoKα (λ = 0.71073)
2Θ range for data collection/°	4.906 to 58.602
Index ranges	-20 ≤ h ≤ 20, -11 ≤ k ≤ 9, -13 ≤ l ≤ 8

Reflections collected	5926
Independent reflections	2822 [R_{int} = 0.0197, R_{sigma} = 0.0278]
Data/restraints/parameters	2822/2/218
Goodness-of-fit on F^2	1.059
Final R indexes [I>=2σ (I)]	R_1 = 0.0322, wR_2 = 0.0750
Final R indexes [all data]	R_1 = 0.0331, wR_2 = 0.0758
Largest diff. peak/hole / e $Å^{-3}$	0.19/-0.20

5. Gram Scale Experiment and Transformation

Scheme S2. Gram Scale Experiment of **3a**



1a, 5.0 mmol, 1.12g **Tol, 25 ml** **3a, 1.02 g, 65%** **Detected by GC-MS**

Procedures

To a flask was added **1a** (1.12 g, 5 mmol), DTBP (500 uL, 2.5 mmol) and toluene 25 ml. Then put the flask to the reaction system in 140 °C and stirred for 24 h. The reaction mixture was dissolved in 2.0 mL ethyl acetate. Then the mixture was cooled to room temperature, added $NaHSO_3$ and water (50 mL), extracted with EtOAc (25 mL×3). The combined organic phases were dried over anhydrous Na_2SO_4, filtered and concentrated in vacuo. Dried by rotary evaporator, the residue was purified by columnchromatography (petroleum ether/ethyl acetate =50/1) to obtain the product **3a**.

Result

Get **3a** 1.02 g, yield is 65%. And detected toluene homo-coupling product by GC-MS.

Scheme S3. Gram Scale Experiment of **5a**

1a, 5.0 mmol, 1.12g **10.0 mmol, 1.0 ml** **5a, 1.17 g, 71%**

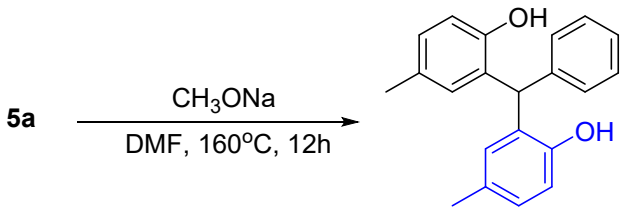
Procedures

To a flask was added **1a** (1.12 g, 5 mmol), DTBP (500 uL, 2.5 mmol) and 4-methylphenol 1.0 ml. Then put the flask to the reaction system in 140 °C and stirred for 24 h. The reaction mixture was dissolved in 2.0 mL ethyl acetate. Then the mixture was cooled to room temperature, added $NaHSO_3$ and water (15 mL), extracted with EtOAc (15 mL×3). The combined organic phases were dried over anhydrous Na_2SO_4, filtered and concentrated in vacuo. Dried by rotary evaporator, the residue was purified by columnchromatography (petroleum ether/ethyl acetate =50/1) to obtain the product **5a**.

Result

Get **4a** 1.17 g, yield is 71%.

Scheme S4. Decarboxylation of **5a**



Procedures

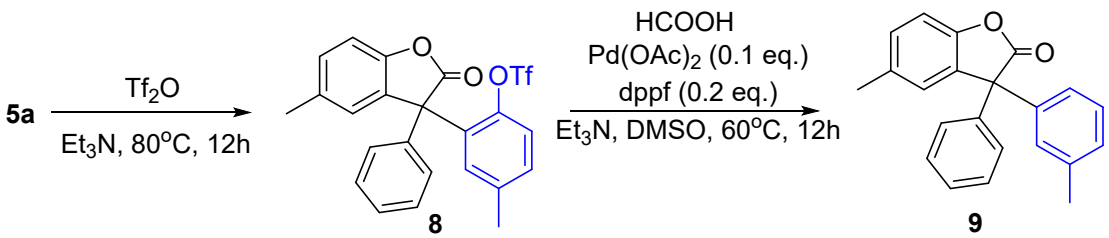
To a flask was added **5a** (66.0 mg, 0.2 mmol), CH_3ONa (10.8 mg, 0.2 mmol) and DMF 1.0 ml. Then put the flask to the reaction system in 160 °C and stirred for 24 h. The reaction mixture was dissolved in 2.0 mL ethyl acetate. Dried by rotary evaporator, the residue was purified by columnchromatography (petroleum ether/ethyl acetate = 5/1) to obtain the product.[4]

Result

Get **7** 51.7 mg, yield is 85%.

Purification by PTLC on silica gel (petroleum ether/ethyl acetate = 5/1) yielded the title compound **7** in 85 % (51.7 mg) as a white solid. ^{1}H NMR (400 MHz, DMSO-d_6) δ 9.03 (s, 2H), 7.26 (t, J = 7.4 Hz, 2H), 7.17 (t, J = 7.3 Hz, 1H), 7.04 – 6.97 (m, 2H), 6.87 – 6.80 (m, 2H), 6.70 (d, J = 8.0 Hz, 2H), 6.48 (d, J = 2.2 Hz, 2H), 6.01 (s, 1H), 2.10 (s, 6H). ^{13}C{^{1}H} NMR (101 MHz, DMSO-d_6) δ 153.0, 144.6, 130.5, 130.4, 129.5, 128.3, 127.7, 126.9, 126.0, 115.3, 43.1, 21.0.

Scheme S4. Dehydroxylation of **5a**



Procedures

To a flask was added **5a** (0.66 g, 2 mmol), Tf_2O (0.67 mL, 4 mmol), Et_3N (0.6 mL, 4 mmol), and DCM 1.0 mL. Then put the flask to the reaction system in 80 °C and stirred for 12 h. The reaction mixture was

dissolved in 2.0 mL ethyl acetate. Dried by rotary evaporator, the residue was purified by columnchromatography (petroleum ether/ethyl acetate =50/1) to obtain the product **8**.

Result

Get **8** 0.55 g, yield is 60%.

Procedures

To a flask was added **8** (0.66 g, 0.2 mmol), $Pd(OAc)_2$ (2.2 mg, 0.01 mmol), DPPF(5.5 mg, 0.01 mmol), HCOOH(15 uL, 0.4 mmol), Et_3N (56 ul, 0.4 mmol), and DMSO 1.0 mL. Then put the flask to the reaction system in 80 °C and stirred for 12 h. The reaction mixture was dissolved in 2.0 mL ethyl acetate. Dried by rotary evaporator, the residue was purified by columnchromatography (petroleum ether/ethyl acetate =50/1) to obtain the product **9**.[4]

Result

Get **9** 52.1 mg, yield is 83%.

Purification by PTLC on silica gel (petroleum ether/ethyl acetate = 20/1) yielded the title compound **8** in 60 % (0.55 g) as a colorless liquid. ^{1}H NMR (400 MHz, Chloroform-*d*) δ 7.42 (s, 5H), 7.32 (d, *J* = 8.6 Hz, 1H), 7.26 – 7.22 (m, 2H), 7.15 (d, *J* = 8.2 Hz, 1H), 7.00 (d, *J* = 1.7 Hz, 1H), 6.89 (d, *J* = 2.1 Hz, 1H), 2.40 (s, 3H), 2.32 (s, 3H). ^{13}C NMR (101 MHz, Chloroform-*d*) δ 176.0, 151.1, 146.3, 137.6, 136.9, 134.2, 132.6, 132.0, 130.4, 130.3, 128.9, 128.8, 128.6, 126.2, 123.0, 119.9, 118.2 (q, *J* = 322.1 Hz), 111.35, 58.46, 21.19, 21.00. ^{19}F NMR (376 MHz, Chloroform-d) δ -73.95.

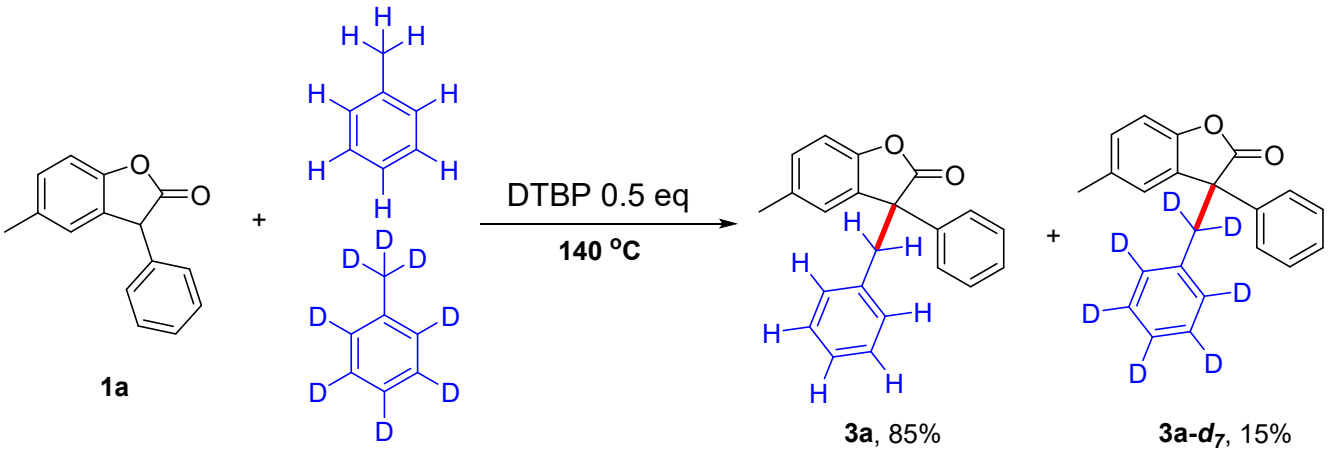
HRMS (EI) m/z: [M+] calcd for C23H17F3O5S 462.0749, Found 462.0748.

Purification by PTLC on silica gel (petroleum ether/ethyl acetate = 20/1) yielded the title compound **9** in 83 % (52.1 mg) as a colorless liquid. ^{1}H NMR (400 MHz, Chloroform-*d*) δ 7.38 – 7.28 (m, 3H), 7.29 – 7.26 (m, 2H), 7.22 (t, *J* = 7.6 Hz, 1H), 7.16 – 7.02 (m, 6H), 2.35 (s, 3H), 2.31 (s, 3H). ^{13}C NMR (101 MHz, Chloroform-*d*)) δ 177.3, 150.5, 140.8, 140.8, 138.5, 134.2, 131.1, 129.6, 128.7, 128.7, 128.6, 128.5, 128.3, 127.8, 126.5, 125.3, 110.7, 61.5, 21.5, 21.3.

HRMS (EI) m/z: [M^+] calcd for $C_{22}H_{18}O_2$ 314.1307, Found 314.1380.

6. Control Experiments

Scheme S5. KIE Experiment

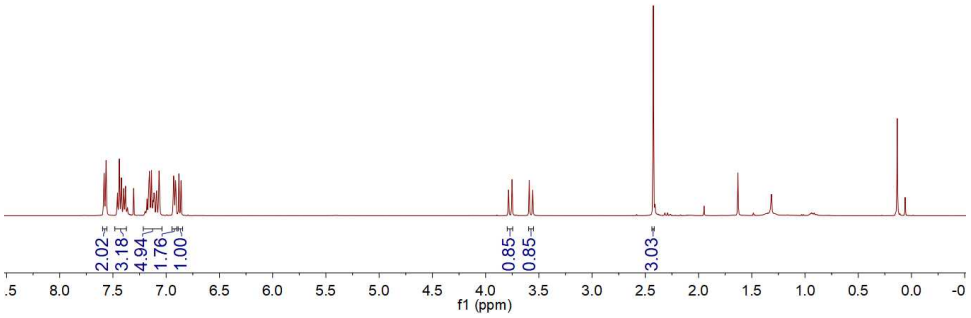


Procedures

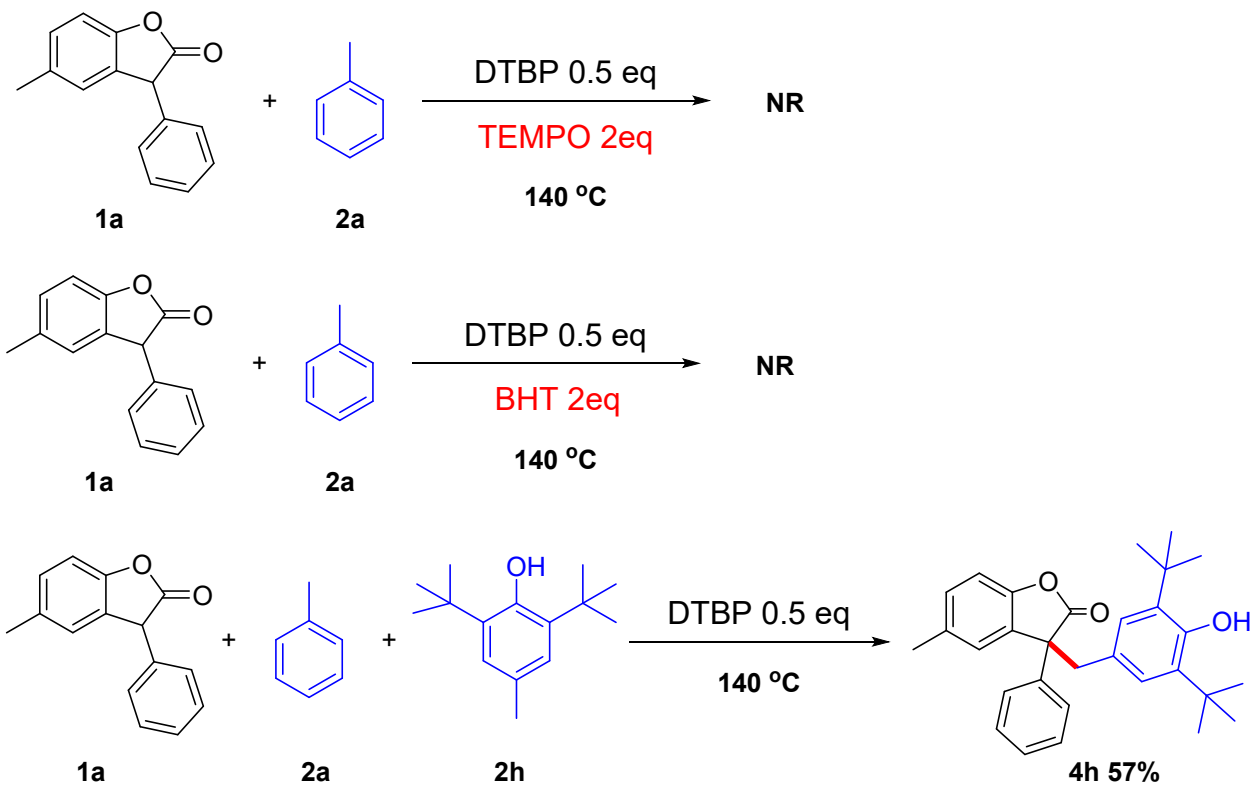
To a flask was added **1a** (44.8 mg, 0.2 mmol), DTBP (19 ul, 0.1 mmol) and toluene 0.5 ml and toluene-d_7 0.5 ml. Then put the flask to the reaction system in 140 °C and stirred for 12 h. The reaction mixture was dissolved in 2.0 mL ethyl acetate. Dried by rotary evaporator, the residue was purified by columnchromatography (petroleum ether/ethyl acetate =50/1) to obtain the product **3a**.

Result

K_H/K_D = 5.7



Scheme S6. Radical Trapping Experiments



Procedures

To a flask was added **1a** (44.8 mg, 0.2 mmol), DTBP (19 ul, 0.1 mmol), TEMPO (62.4 mg, 0.4 mmol) and toluene 1.0 ml. Then put the flask to the reaction system in 140 °C and stirred for 12 h. The reaction mixture was dissolved in 2.0 mL ethyl acetate.

To a flask was added **1a** (44.8 mg, 0.2 mmol), DTBP (19 ul, 0.1 mmol), BQ (43.2 mg, 0.4 mmol) and toluene 1.0 ml. Then put the flask to the reaction system in 140 °C and stirred for 12 h. The reaction mixture was dissolved in 2.0 mL ethyl acetate.

To a flask was added **1a** (44.8 mg, 0.2 mmol), DTBP (19 ul, 0.1 mmol), **2h** (88.1 mg, 0.4 mmol) and toluene 1.0 ml. Then put the flask to the reaction system in 140 °C and stirred for 12 h. The reaction mixture was dissolved in 2.0 mL ethyl acetate.

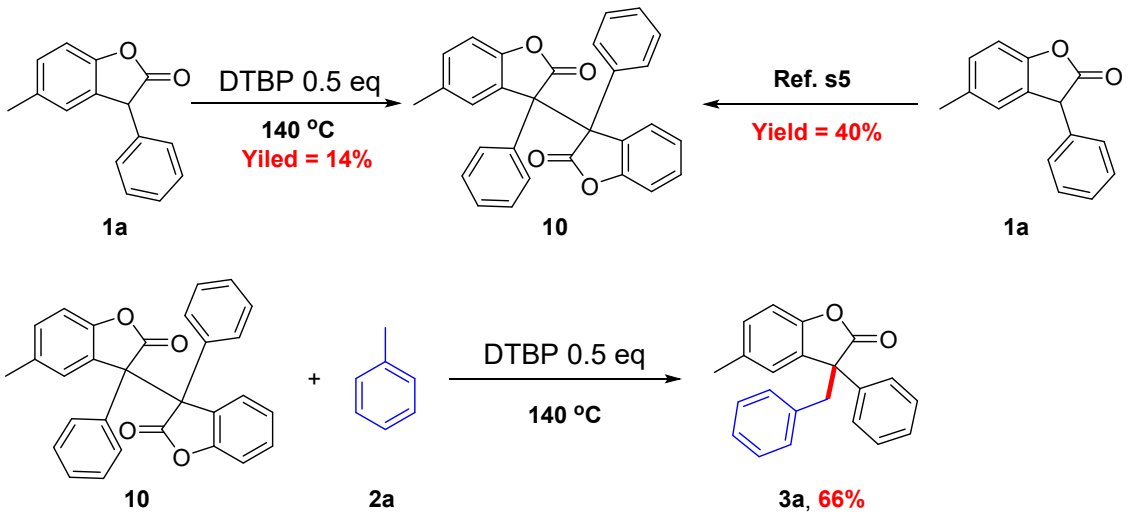
Result

No Reaction.

No Reaction.

Get **4h** 50.2 mg, yield is 57%.

Scheme S7. Homo-coupling Experiments



Procedures

To a flask was added **1a** (44.8 mg, 0.2 mmol), DTBP (19 ul, 0.1 mmol). Then put the flask to the reaction system in 140 °C and stirred for 12 h. The reaction mixture was dissolved in 2.0 mL ethyl acetate . Dried by rotary evaporator, the residue was purified by columnchromatography (petroleum ether/ethyl acetate =20/1) to obtain the product **10**.[5]

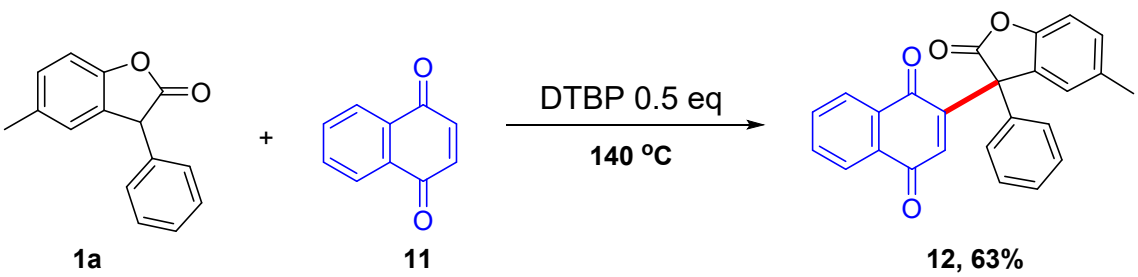
Procedures

To a flask was added **10** (43.2 mg, 0.1 mmol), DTBP (10 ul, 0.05 mmol) and toluene 1.0 ml. Then put the flask to the reaction system in 140 °C and stirred for 12 h. The reaction mixture was dissolved in 2.0 mL ethyl acetate . Dried by rotary evaporator, the residue was purified by columnchromatography (petroleum ether/ethyl acetate =50/1) to obtain the product **3a**.

Result

Get **10** 13.2 mg, yield is 14%. Get **3a** 41.2 mg, yield is 88%.

Scheme S7. 1,4-Naphthoquinone Experiments



Procedures

To a flask was added **1a** (44.8 mg, 0.2 mmol), **11** (63.2 mg, 0.4 mmol), DTBP (19 ul, 0.1 mmol). Then put the flask to the reaction system in 140 °C and stirred for 12 h. The reaction mixture was dissolved in 2.0 mL ethyl acetate . Dried by rotary evaporator, the residue was purified by columnchromatography (petroleum ether/ethyl acetate =20/1) to obtain the product **12**.

Result

Get **12** 47.9 mg, yield is 63%.

Purification by PTLC on silica gel (petroleum ether/ethyl acetate = 10/1) yielded the title compound **11** in 63 % (47.5 mg) as a yellow solid. ^{1}H NMR (400 MHz, Chloroform-*d*) δ 8.05 (d, *J* = 6.9 Hz, 1H), 8.01 (d, *J* = 8.5 Hz, 1H), 7.79 – 7.70 (m, 2H), 7.46 (d, *J* = 3.7 Hz, 2H), 7.42 – 7.36 (m, 3H), 7.21 (d, *J* = 8.2 Hz, 1H), 7.16 (d, *J* = 8.2 Hz, 1H), 6.99 (s, 1H), 6.62 (s, 1H), 2.35 (s, 3H). ^{13}C NMR (101 MHz, Chloroform-*d*) δ 184.6, 183.0, 175.8, 152.1, 151.6, 138.0, 134.6, 134.3, 134.2, 133.7, 131.8, 131.6, 130.6, 129.1, 129.0, 128.8, 128.2, 127.4, 126.3, 125.8, 111.2, 57.7, 21.2.

7. References

[1] Z. Tang, Z. Tong, Z. Xu, C.-T. Au, R. Qiu, S.-F. Yin, *Green Chem*. **2019**, *21*, 2015.

[2] Hu, S.; Lu, Z.; Liu, M.; Xu, H.; Wu, J.; Chen, F. *J. Org. Chem.* **2020**, *85*, 14916.

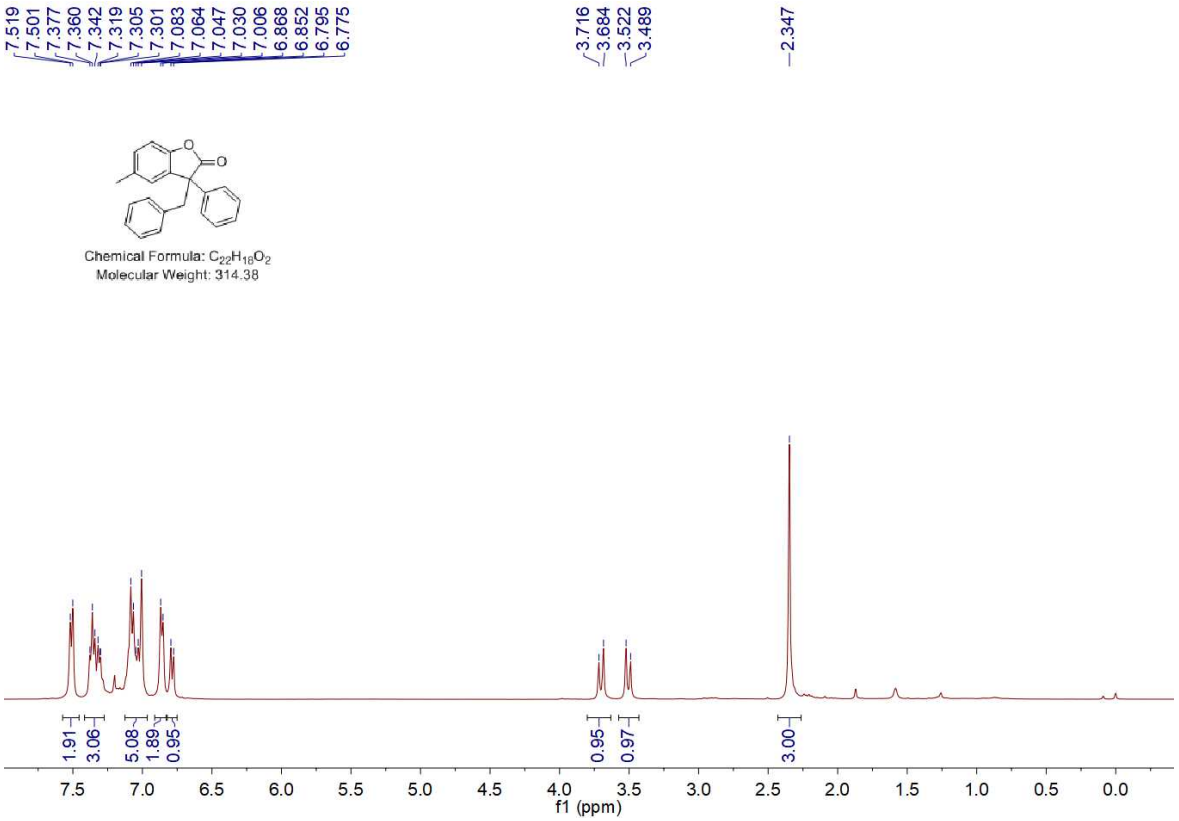
[3] G. Hong, P. D. Nahide, U. K. Neelam, P. Amadeo, A. Vijeta, J. M. Curto, C. E. Hendrick, K. F. VanGelder, M. C. Kozlowski, *ACS Catal.* **2019**, *9*, 3716.

[4] Z. Tang, L. Peng, Y. Yuan, T. Li, R. Qiu, N. Kambe, *J. Org. Chem.* **2020**, *85*, 5300.

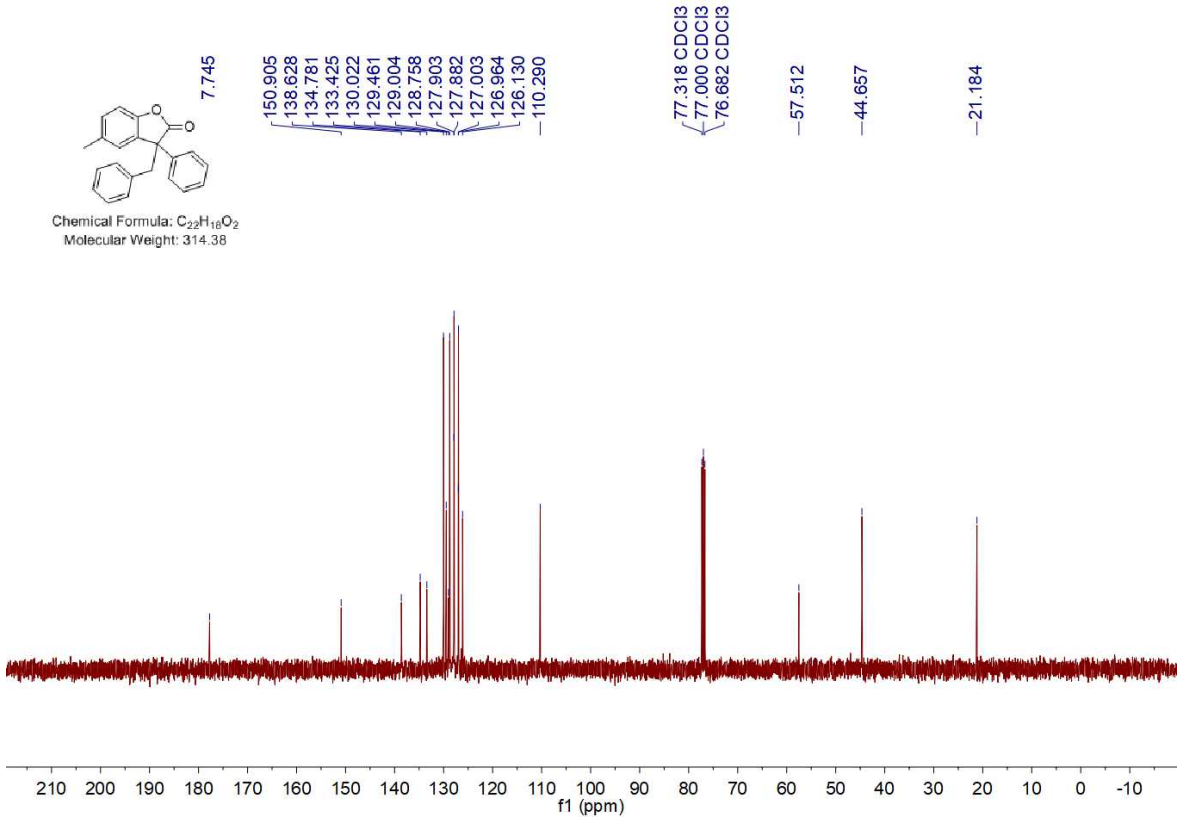
[5] Z. Tang, Z. Liu, Z. Tong, Z. Xu, C. T. Au, R. Qiu, N. Kambe, *Org. Lett.* **2019**, *21*, 5152.

8. NMR Spectra of All Compounds

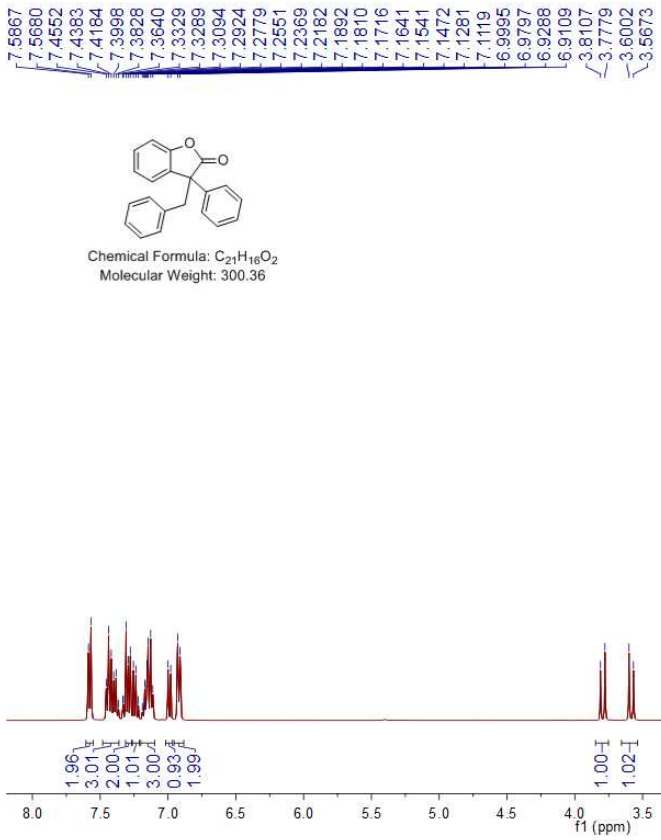
^{1}H NMR (400 MHz, Chloroform-d) spectrum for 3a



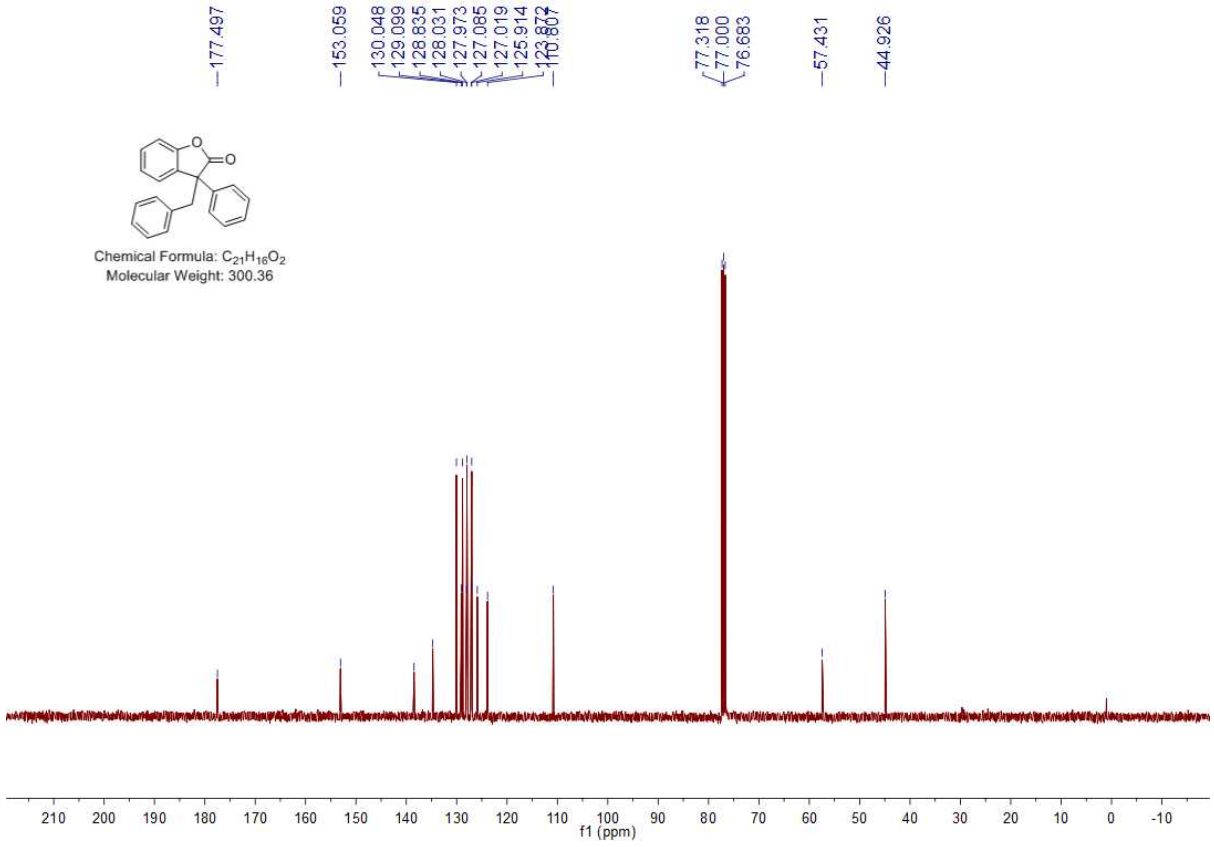
^{13}C NMR (101 MHz, Chloroform-d) spectrum for 3a



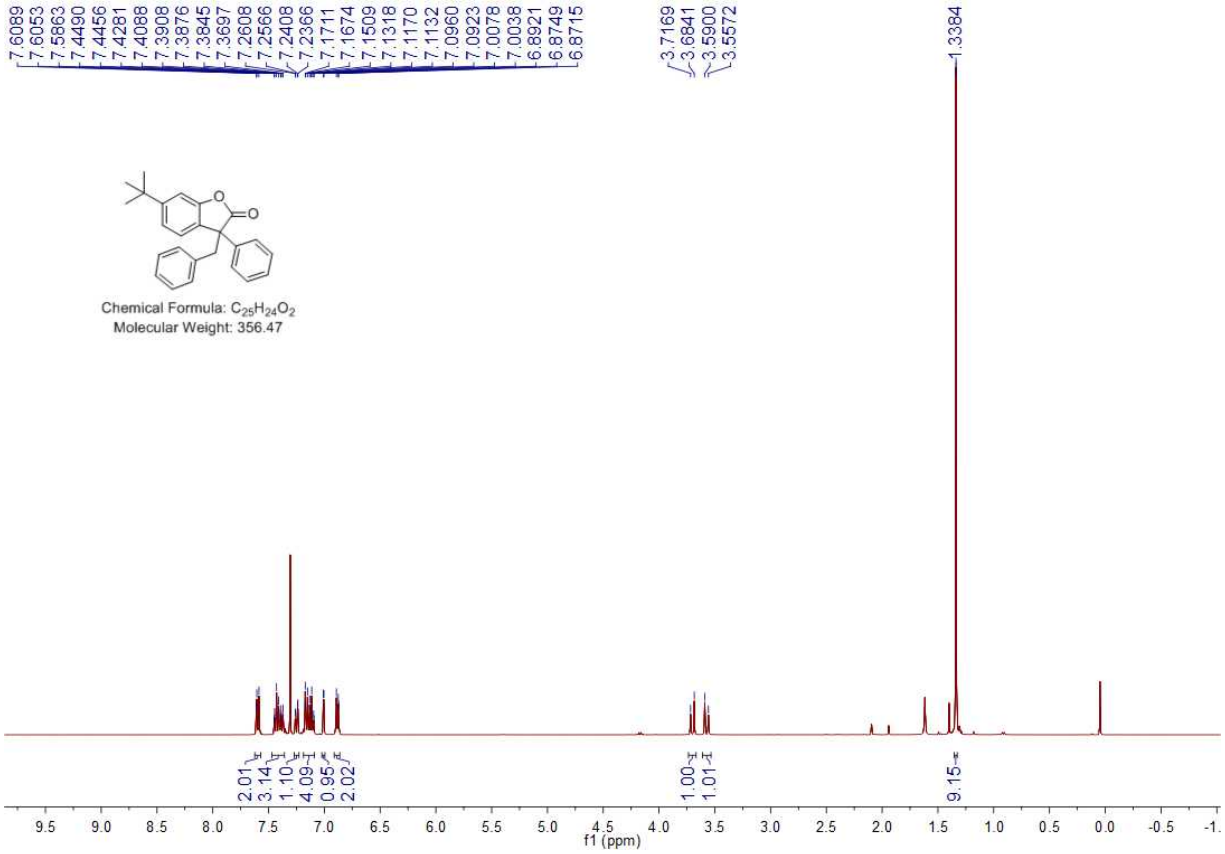
^{1}H NMR (400 MHz, Chloroform-d) spectrum for 3b



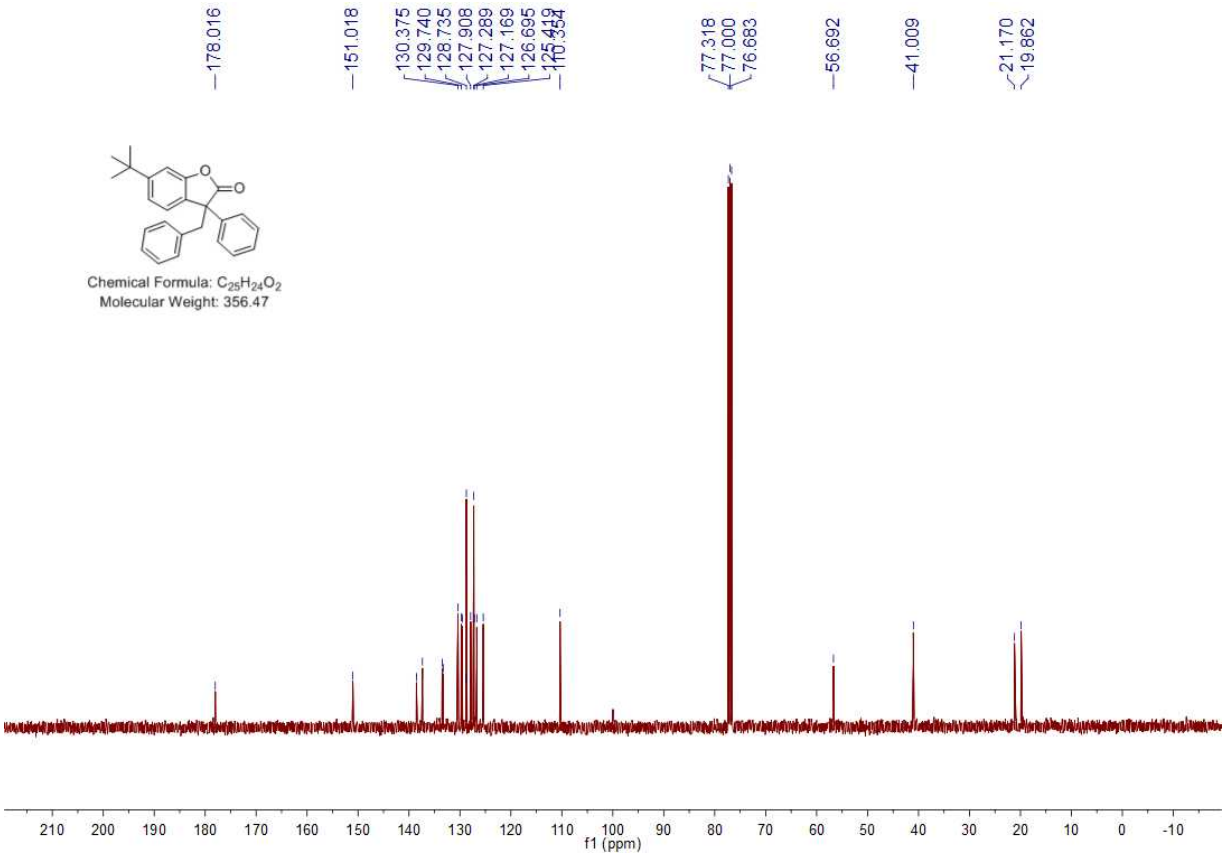
^{13}C NMR (101 MHz, Chloroform-d) spectrum for 3b



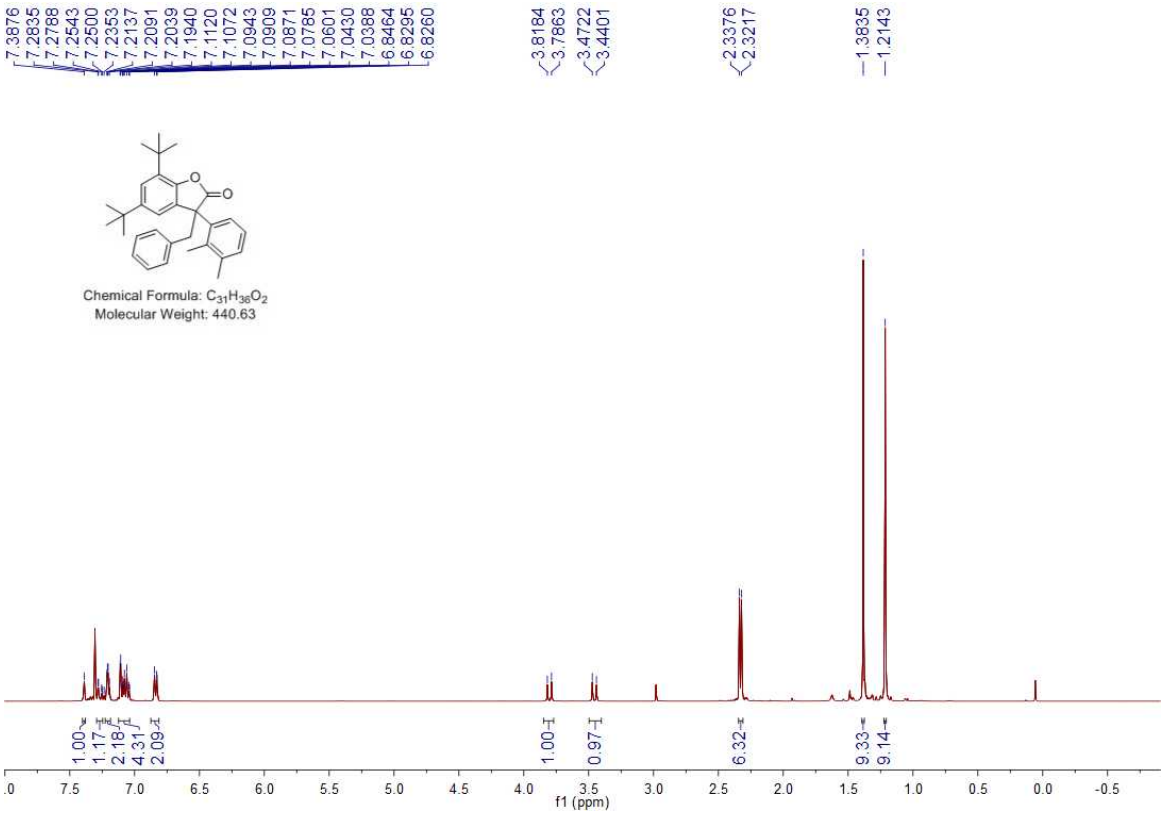
^{1}H NMR (400 MHz, Chloroform-d) spectrum for 3c



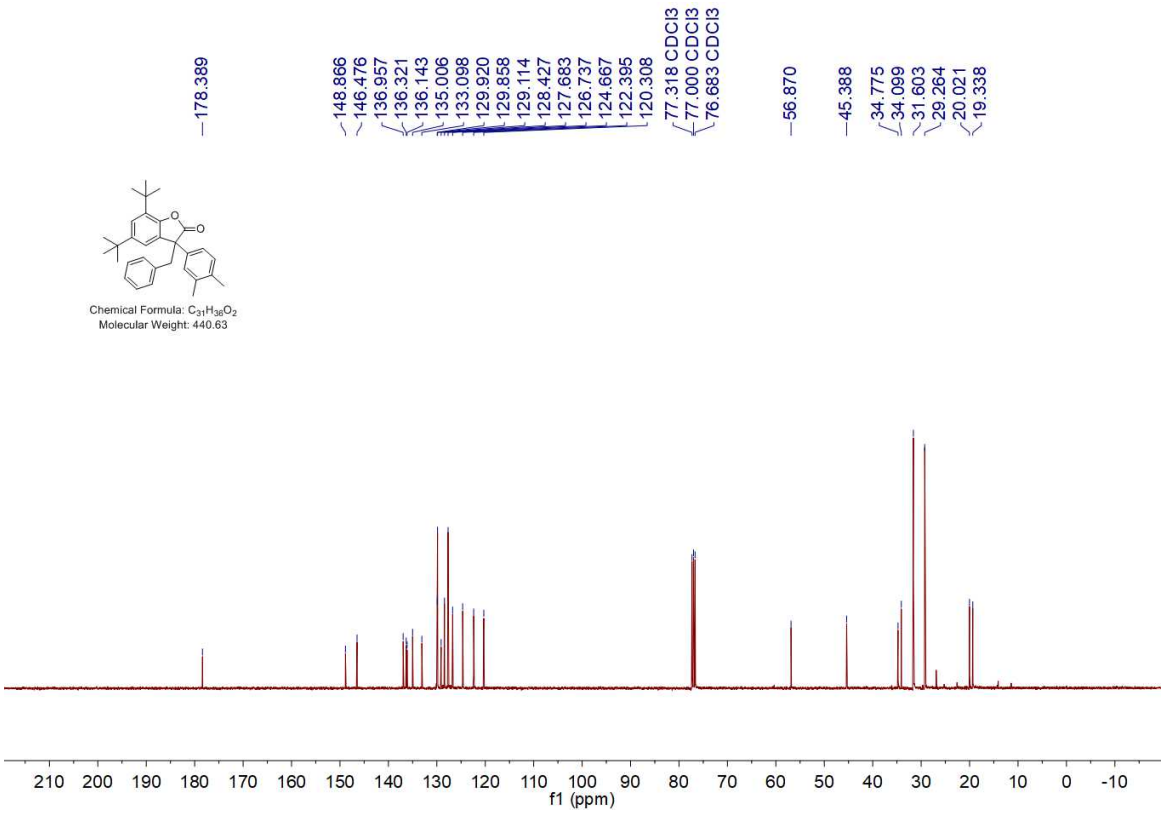
^{13}C NMR (101 MHz, Chloroform-d) spectrum for 3c



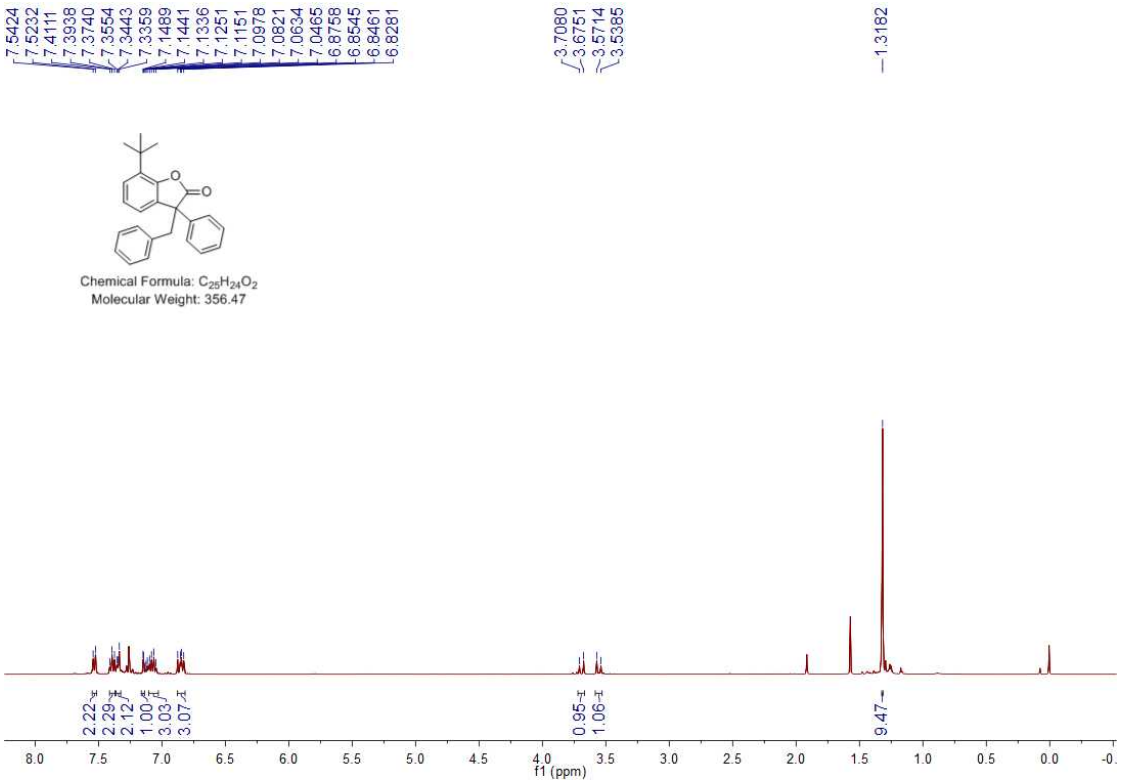
^{1}H NMR (400 MHz, Chloroform-d) spectrum for 3d



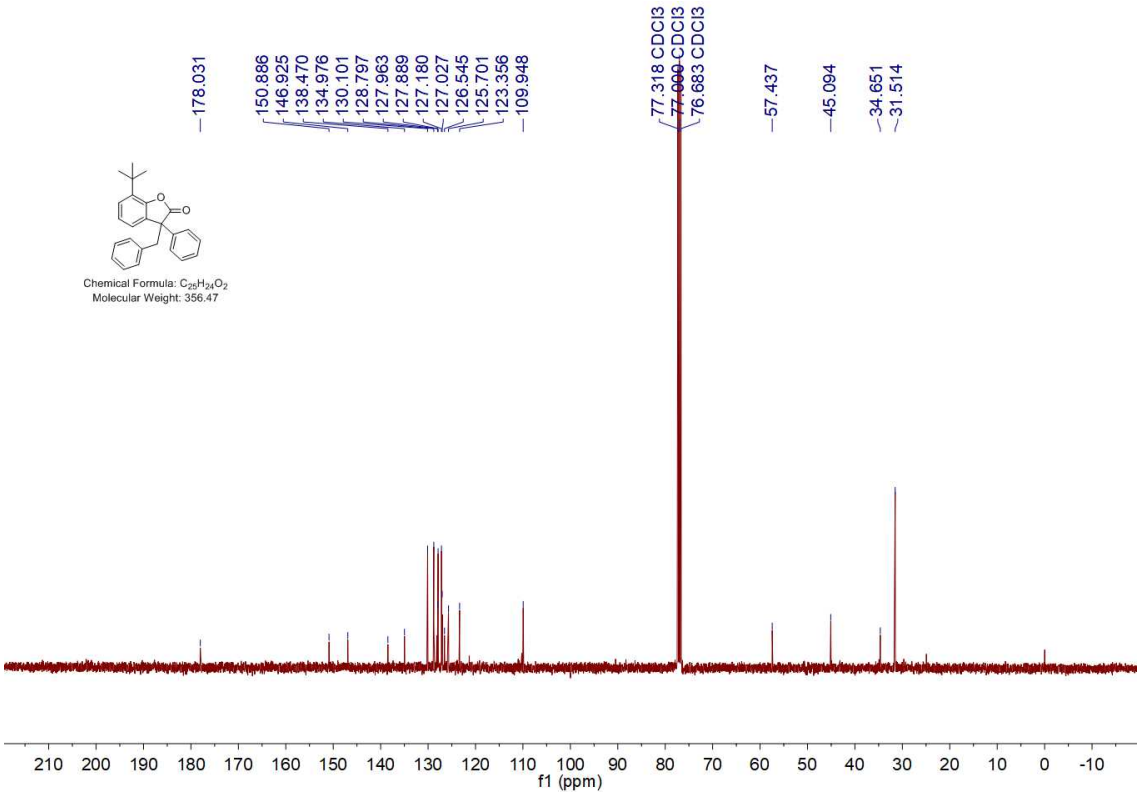
^{13}C NMR (101 MHz, Chloroform-d) spectrum for 3d



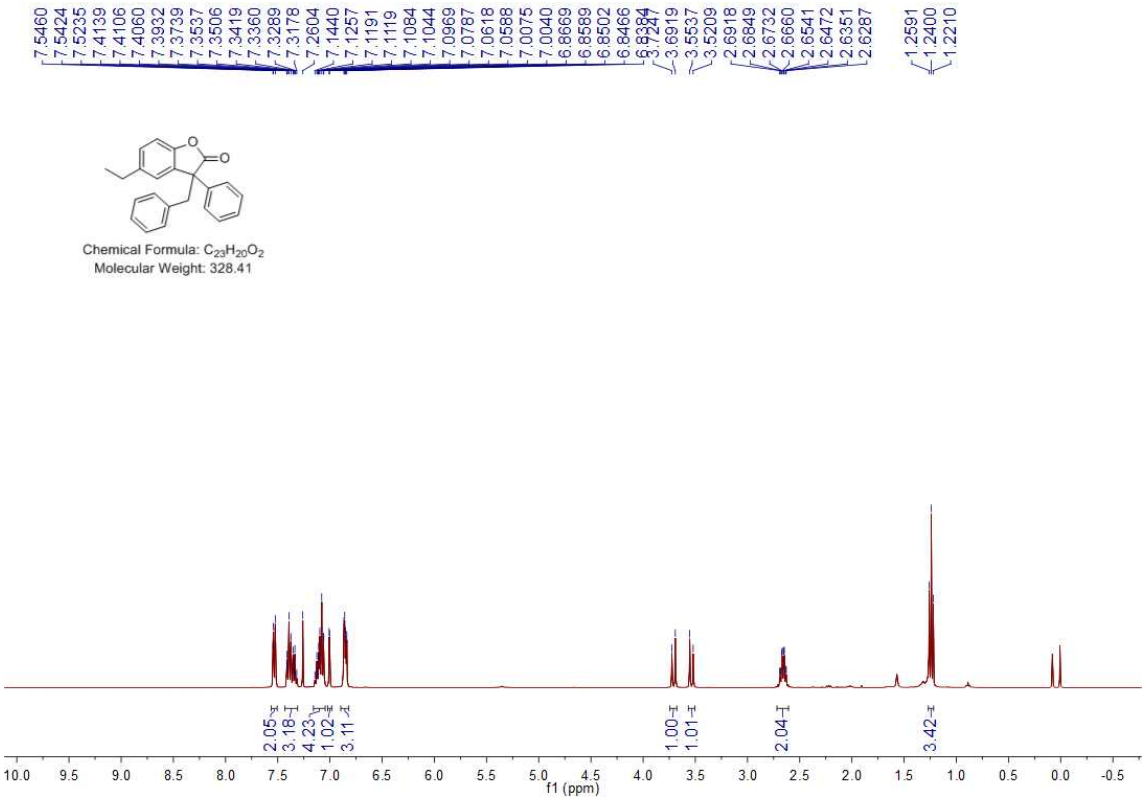
^{1}H NMR (400 MHz, Chloroform-d) spectrum for 3e



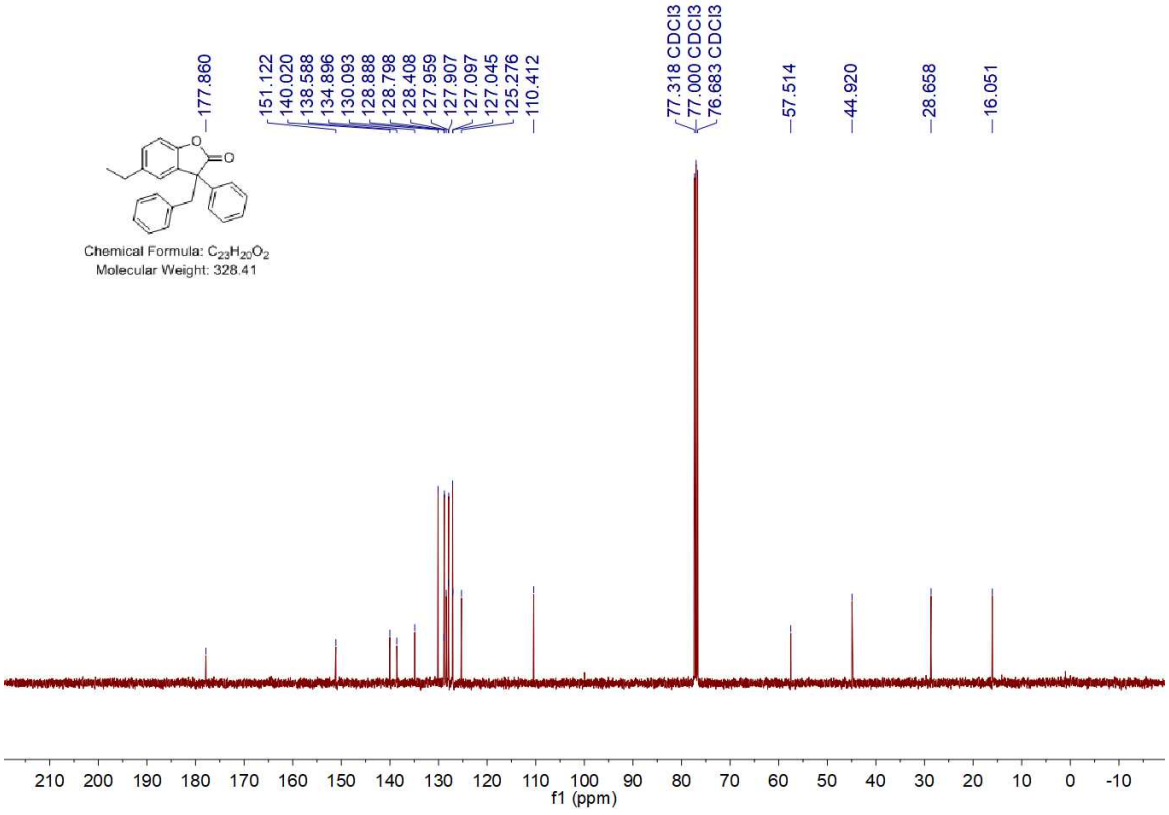
^{13}C NMR (101 MHz, Chloroform-d) spectrum for 3e



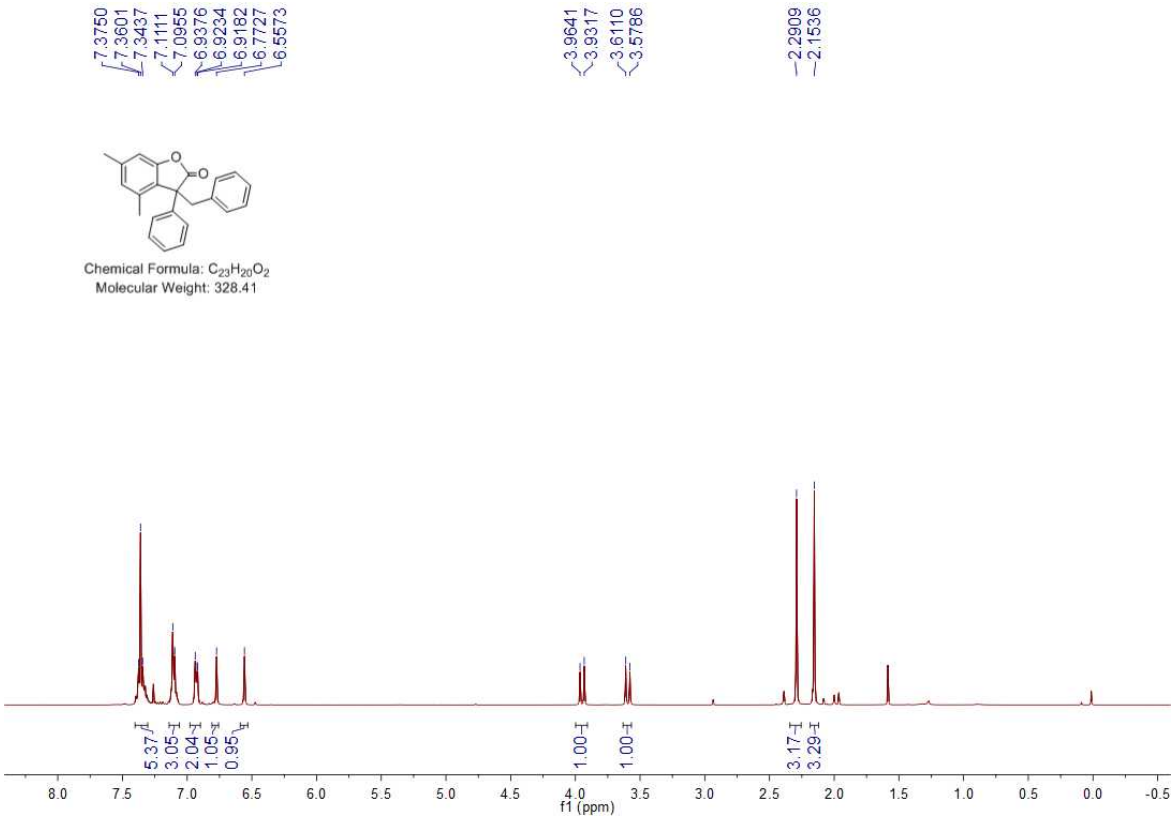
^{1}H NMR (400 MHz, Chloroform-d) spectrum for 3f



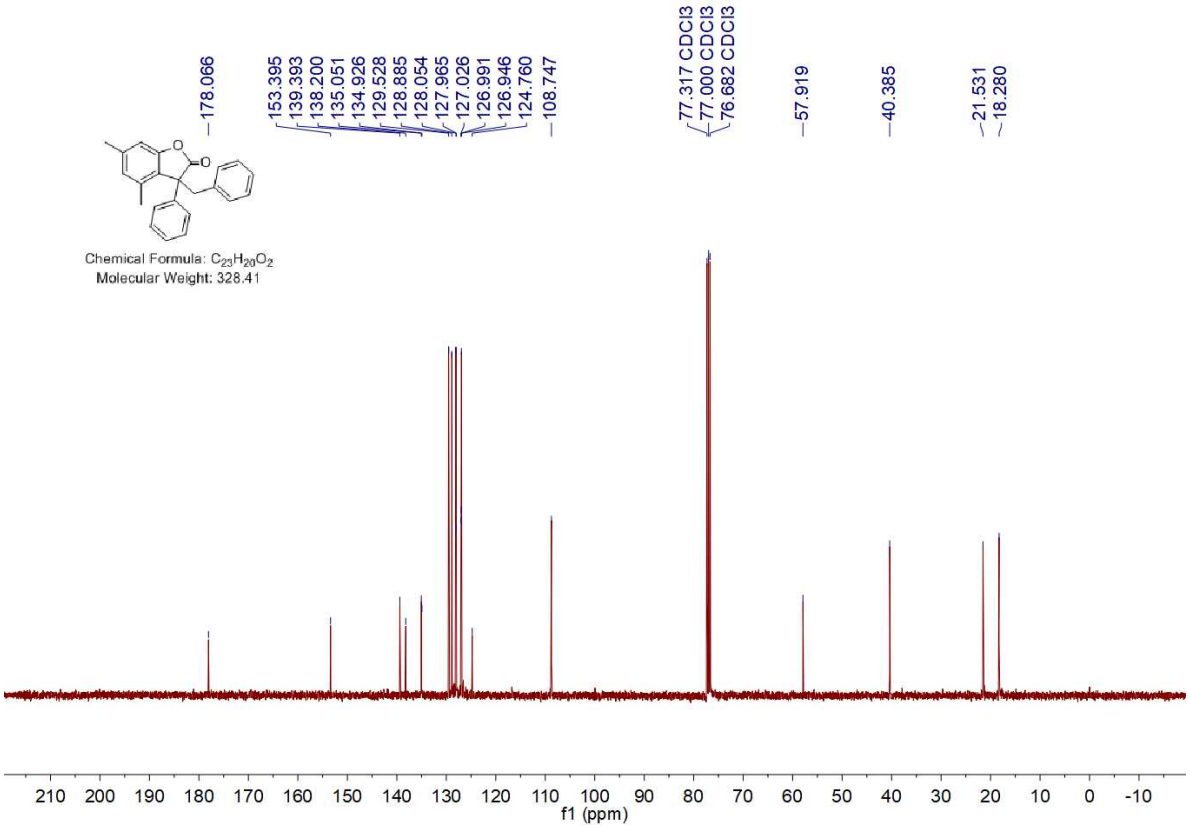
^{13}C NMR (101 MHz, Chloroform-d) spectrum for 3f



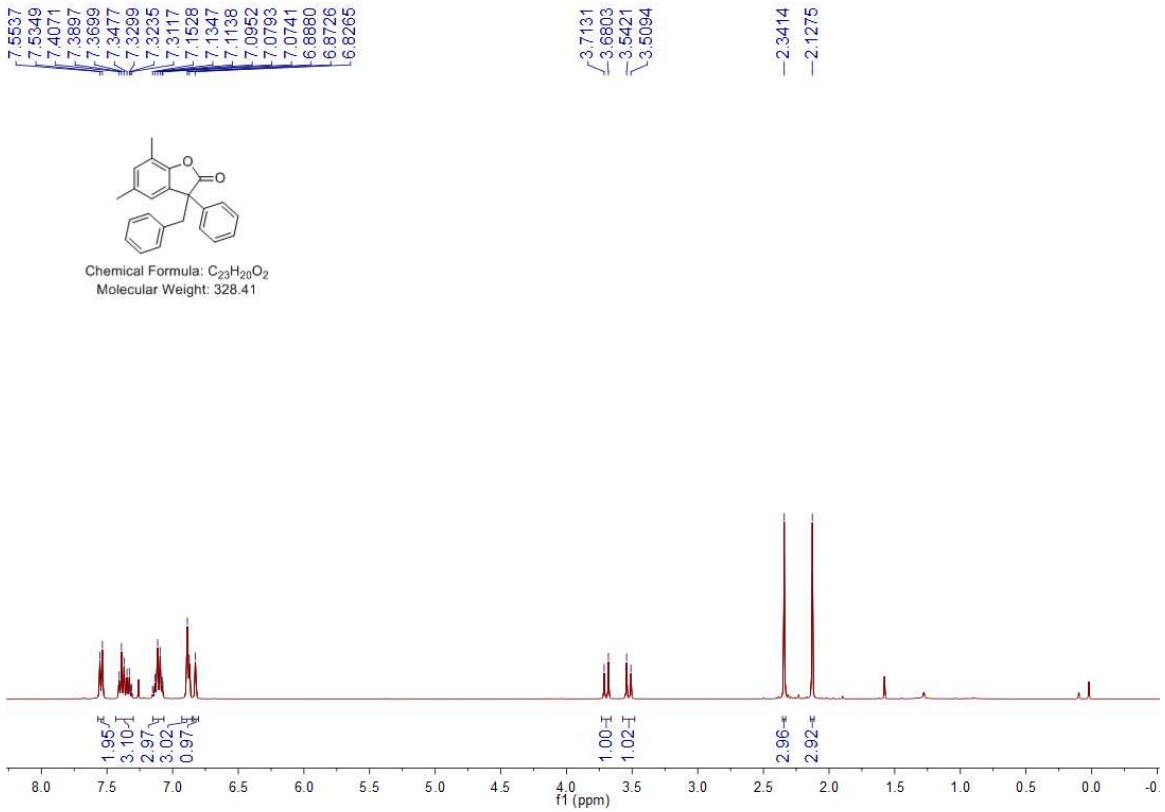
^{1}H NMR (400 MHz, Chloroform-d) spectrum for 3g



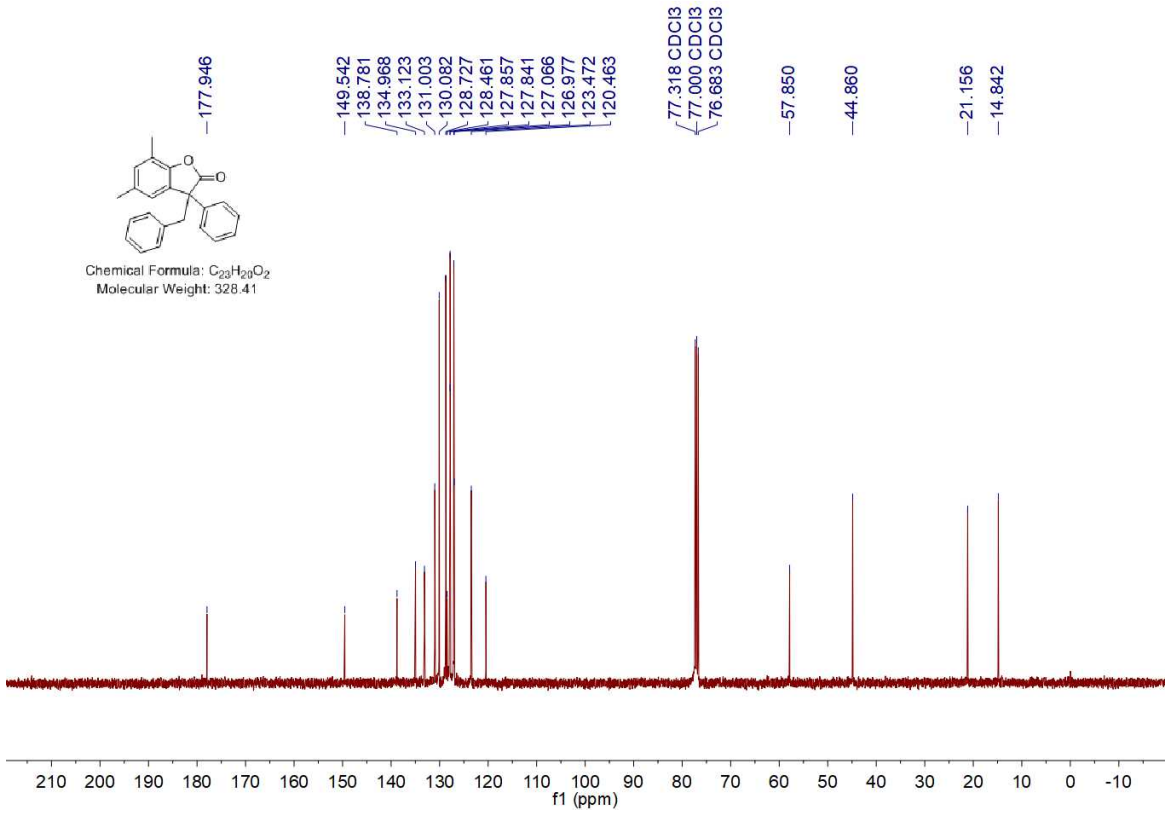
^{13}C NMR (101 MHz, Chloroform-d) spectrum for 3g



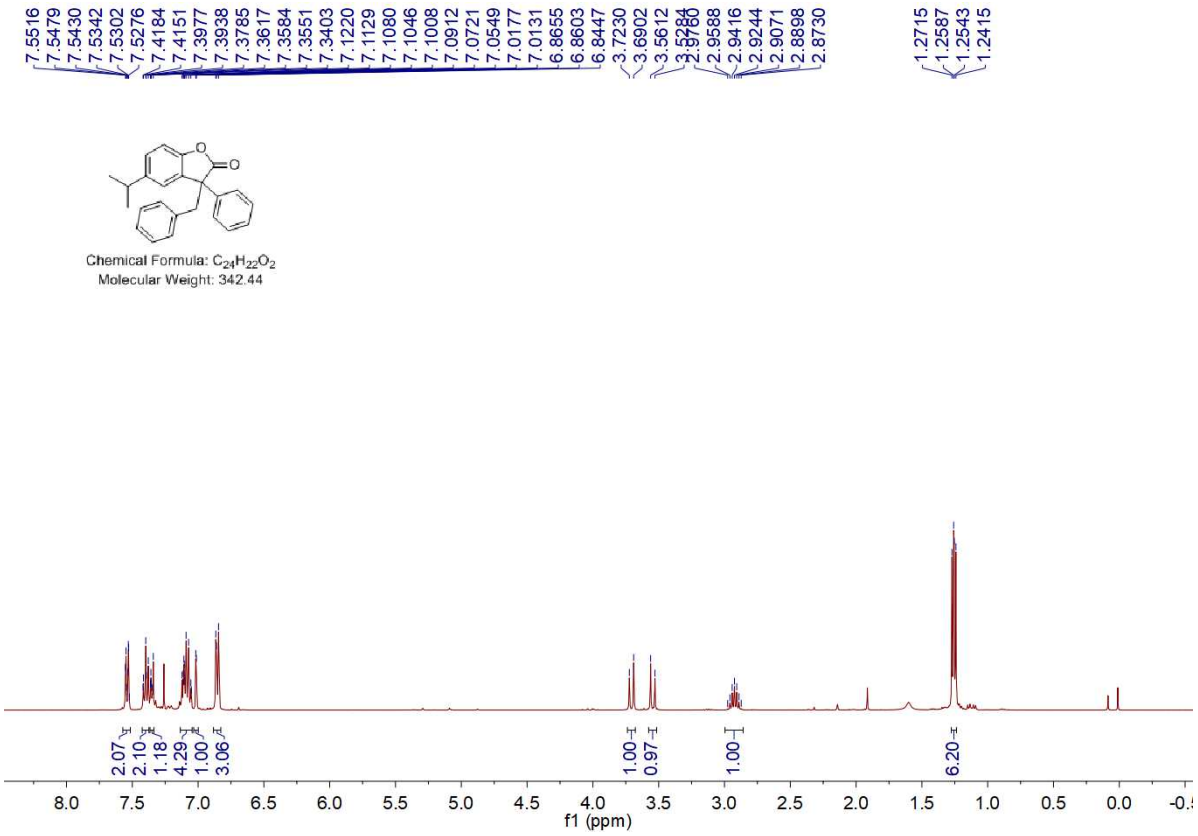
^{1}H NMR (400 MHz, Chloroform-d) spectrum for 3h



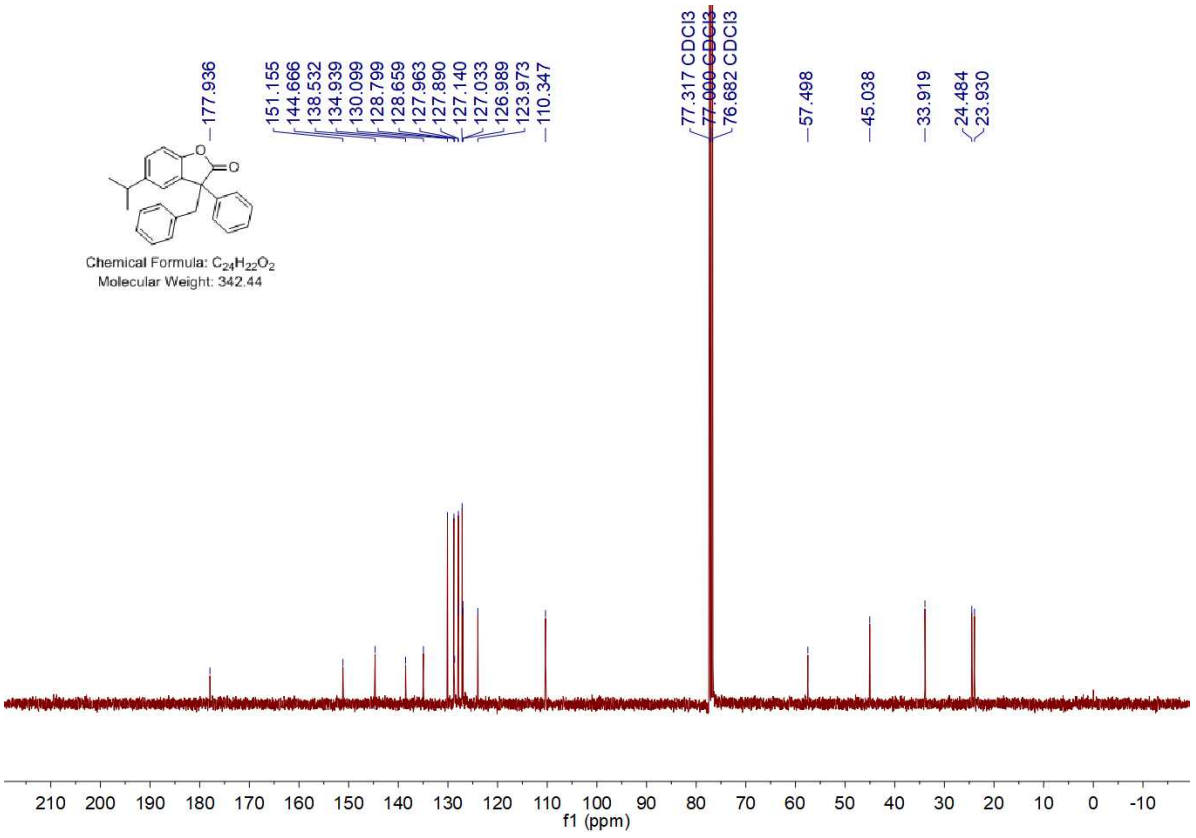
^{13}C NMR (101 MHz, Chloroform-d) spectrum for 3h



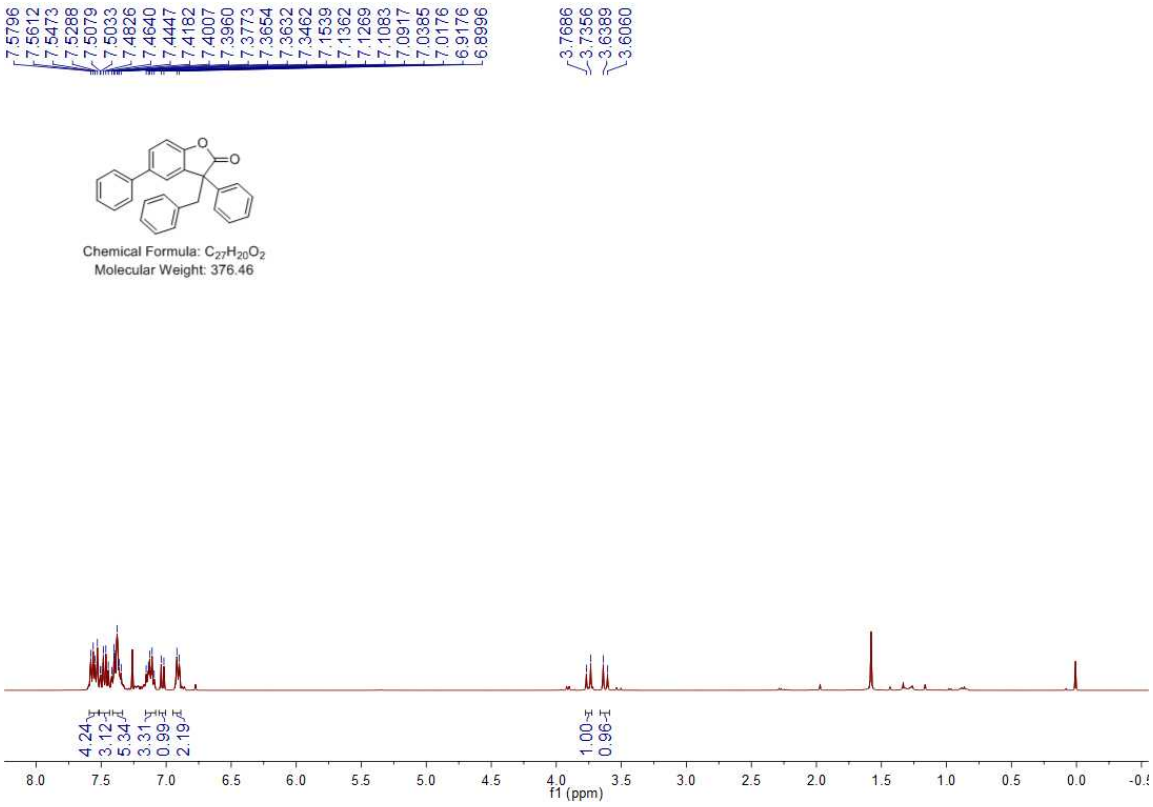
^{1}H NMR (400 MHz, Chloroform-d) spectrum for 3i



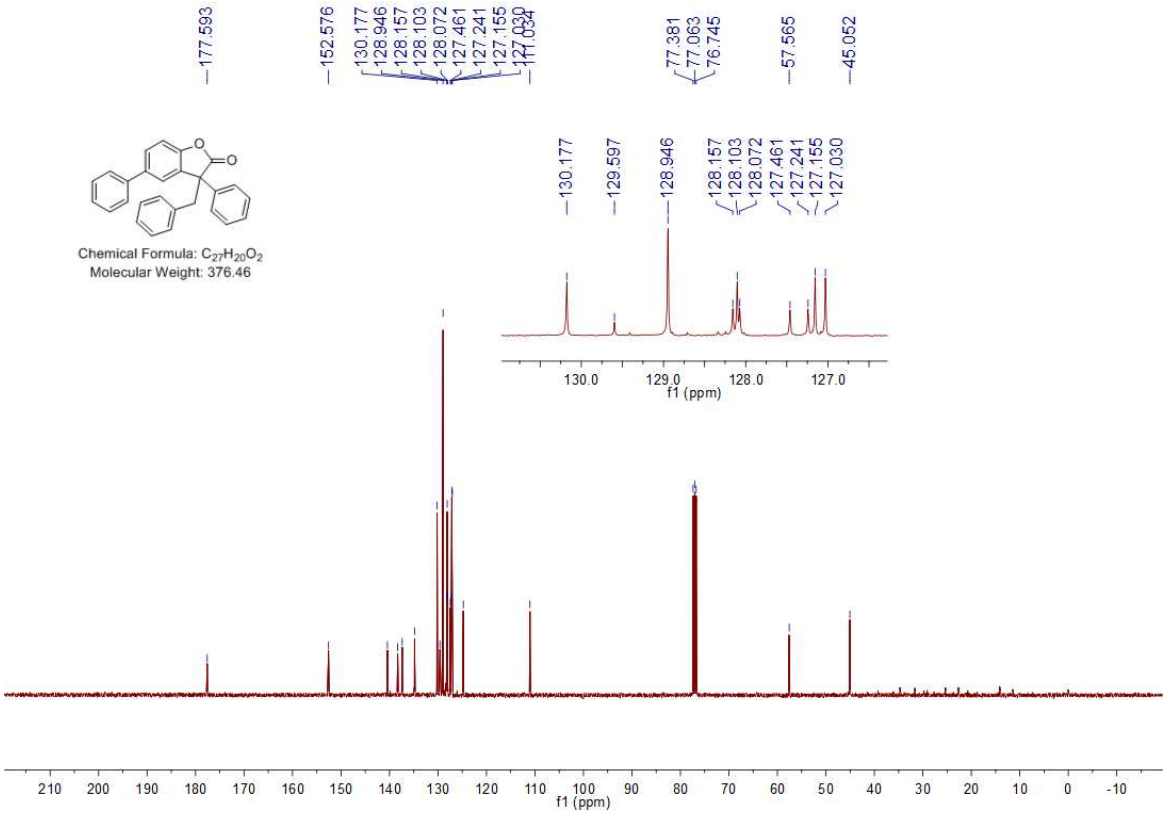
^{13}C NMR (101 MHz, Chloroform-d) spectrum for 3i



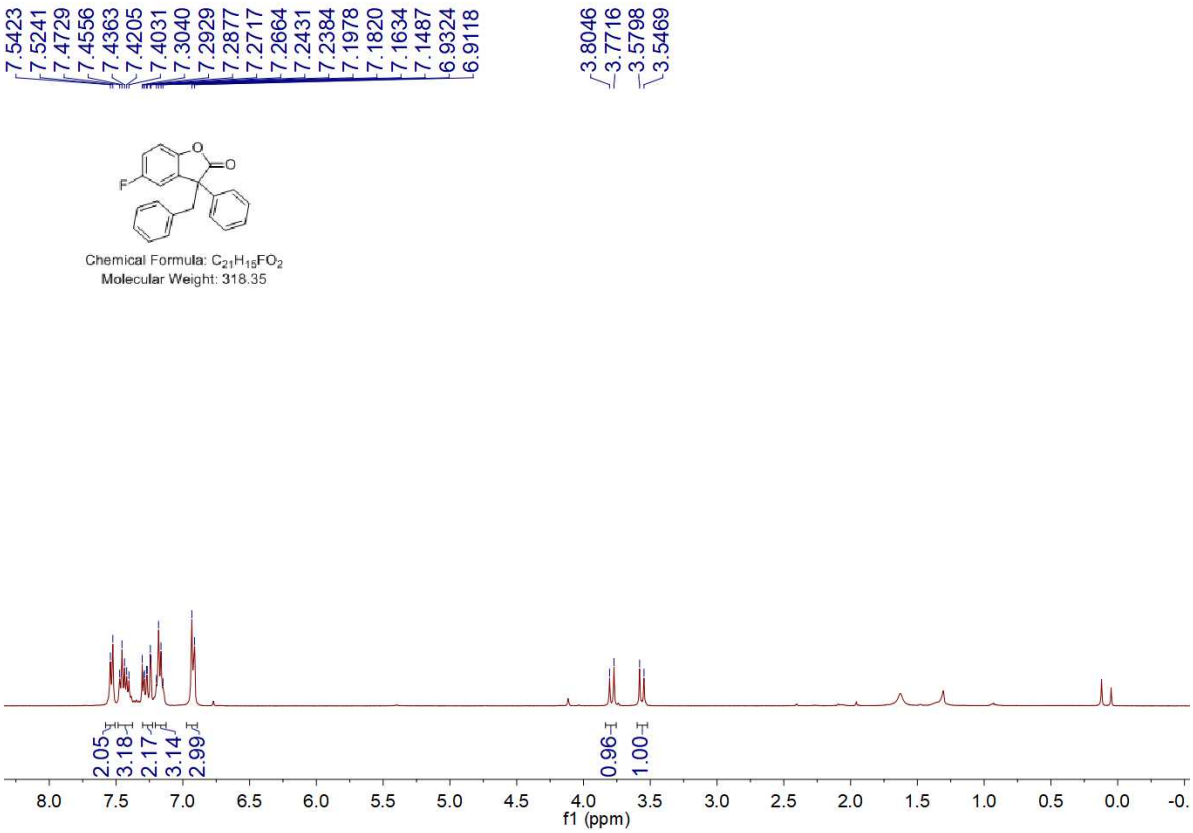
^{1}H NMR (400 MHz, Chloroform-d) spectrum for 3j



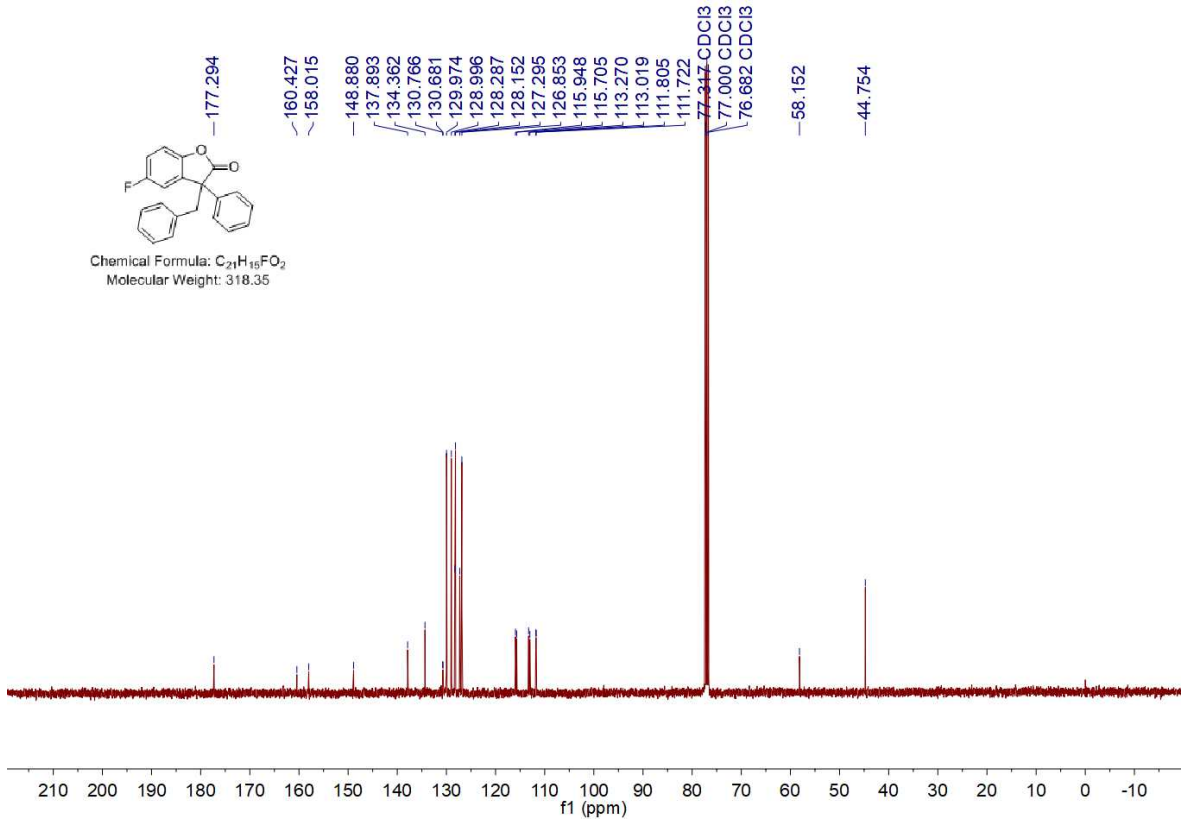
^{13}C NMR (101 MHz, Chloroform-d) spectrum for 3j



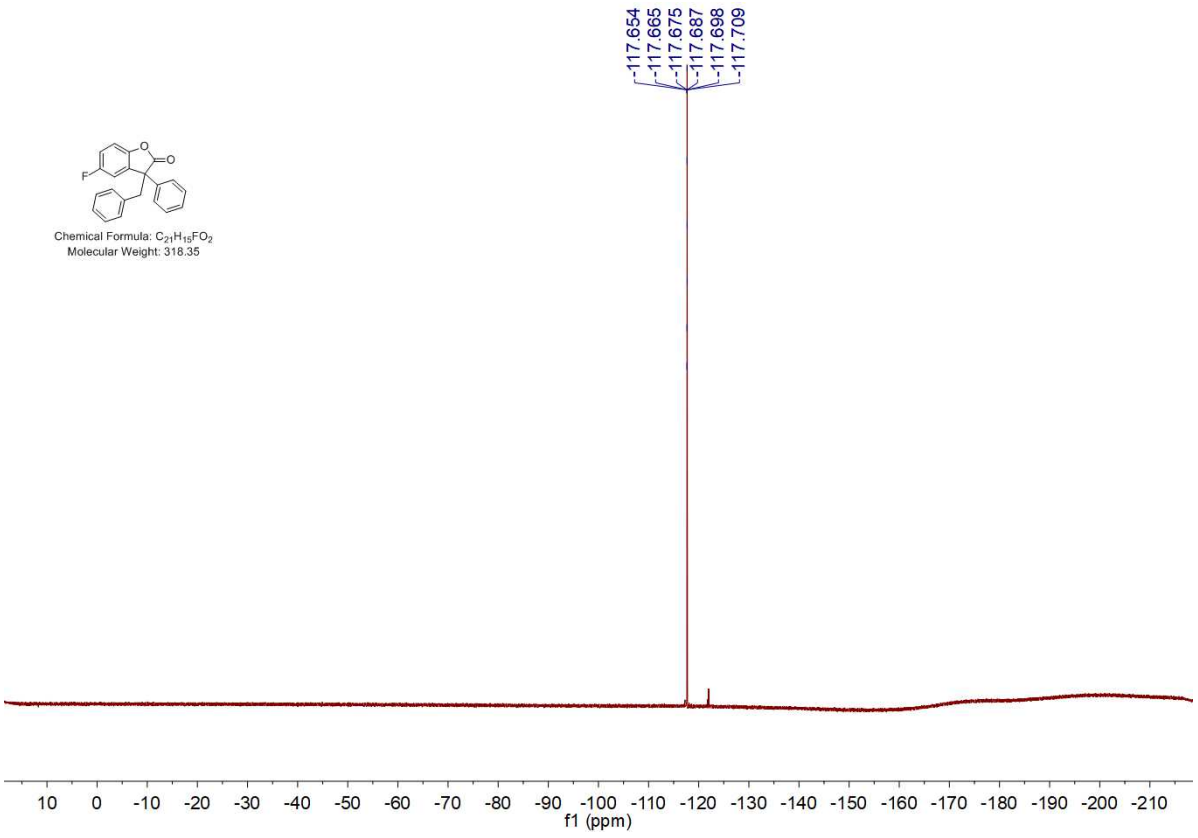
^{1}H NMR (400 MHz, Chloroform-d) spectrum for 3k



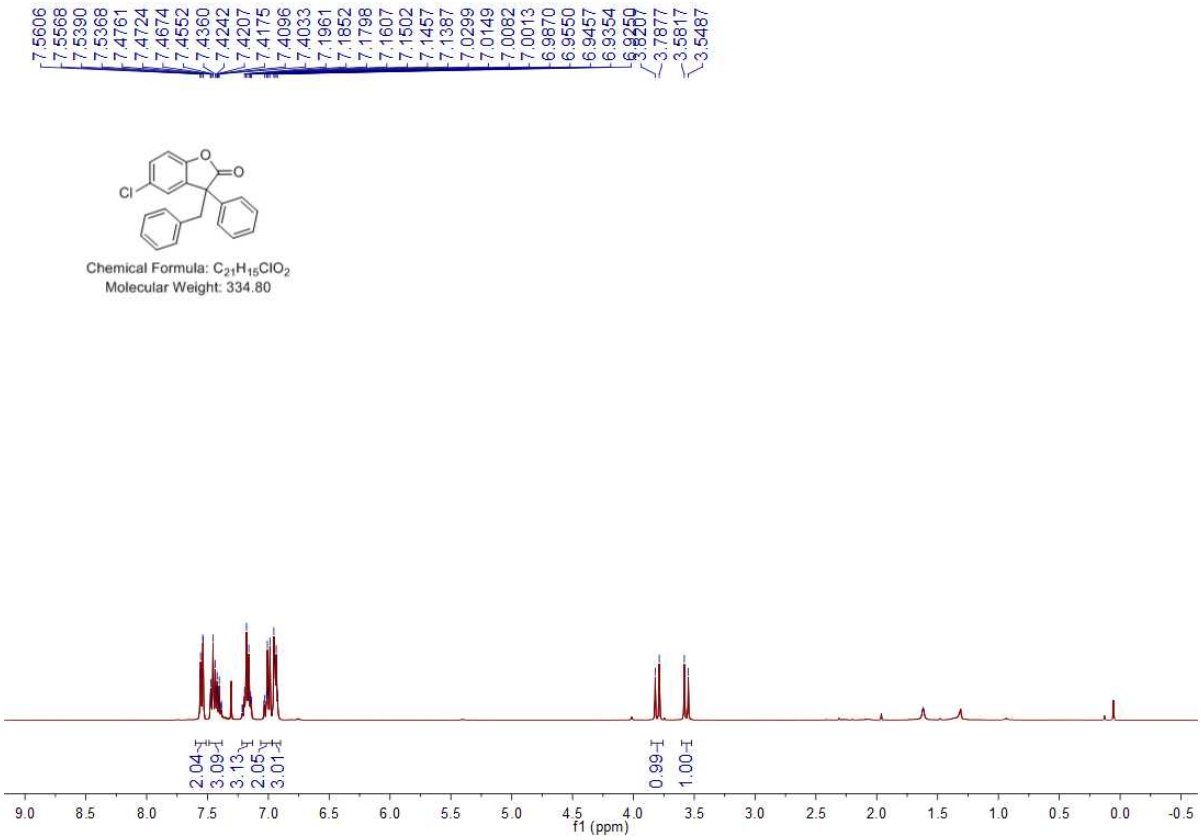
^{13}C NMR (101 MHz, Chloroform-d) spectrum for 3k



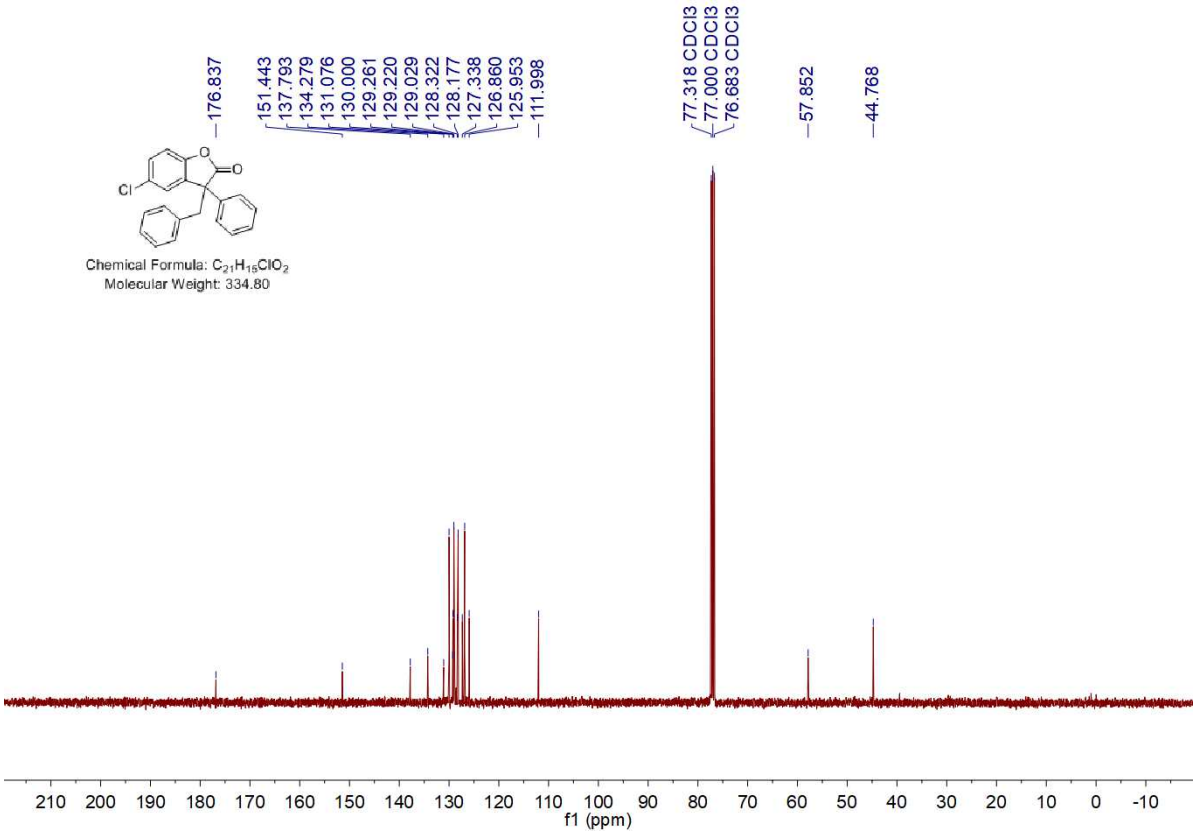
^{19}F NMR (376 MHz, Chloroform-d) spectrum for 3k



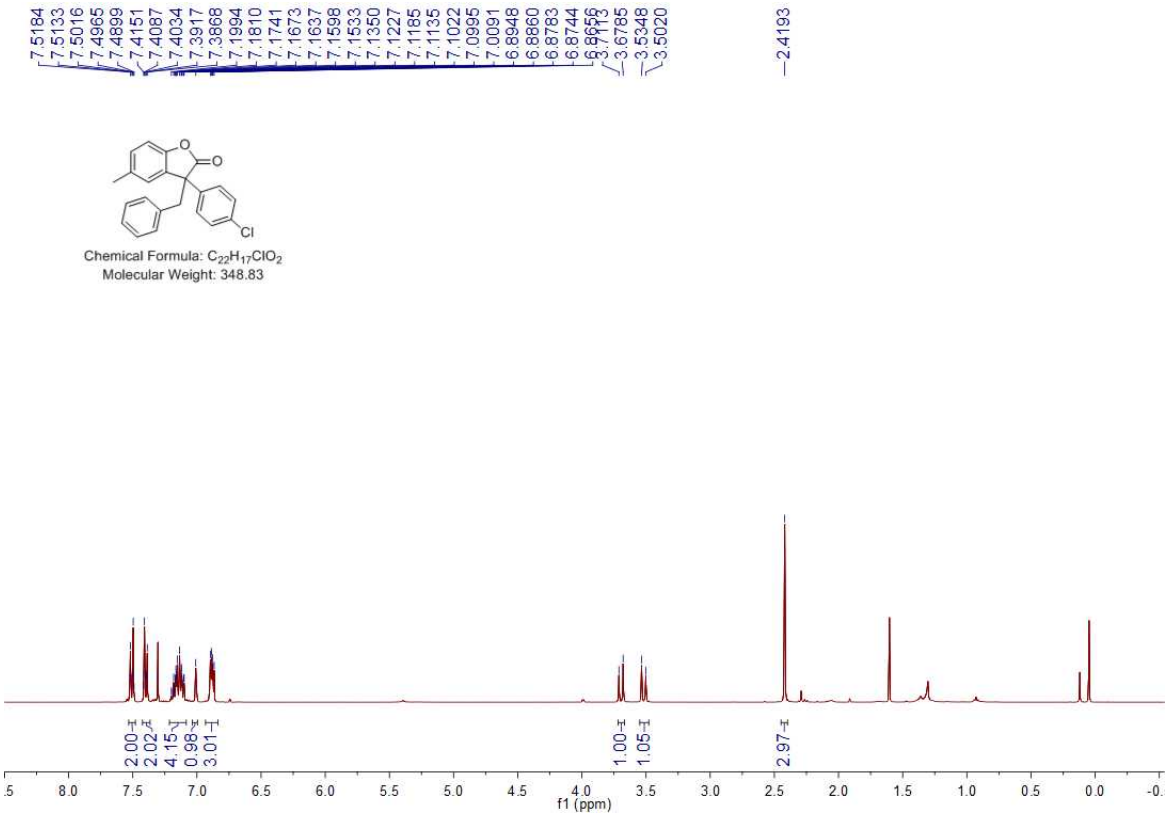
^{1}H NMR (400 MHz, Chloroform-d) spectrum for 3l



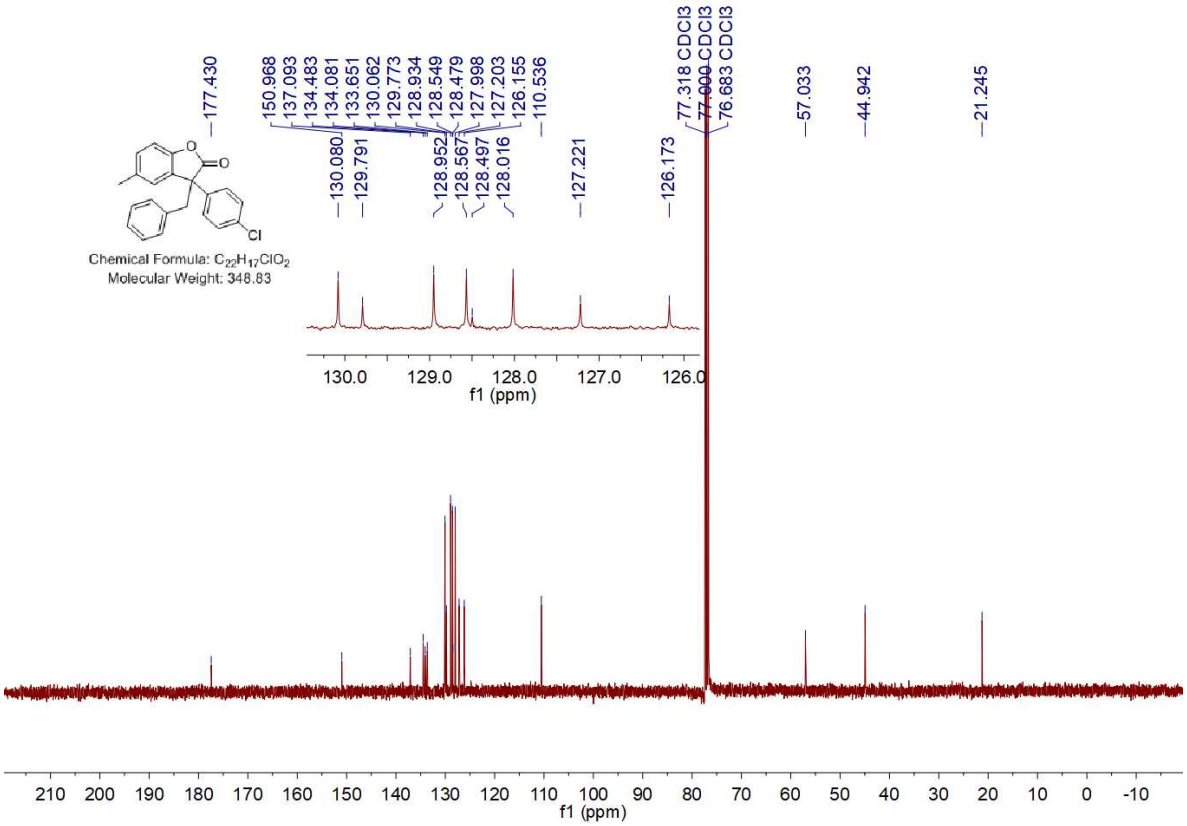
^{13}C NMR (101 MHz, Chloroform-d) spectrum for 3l



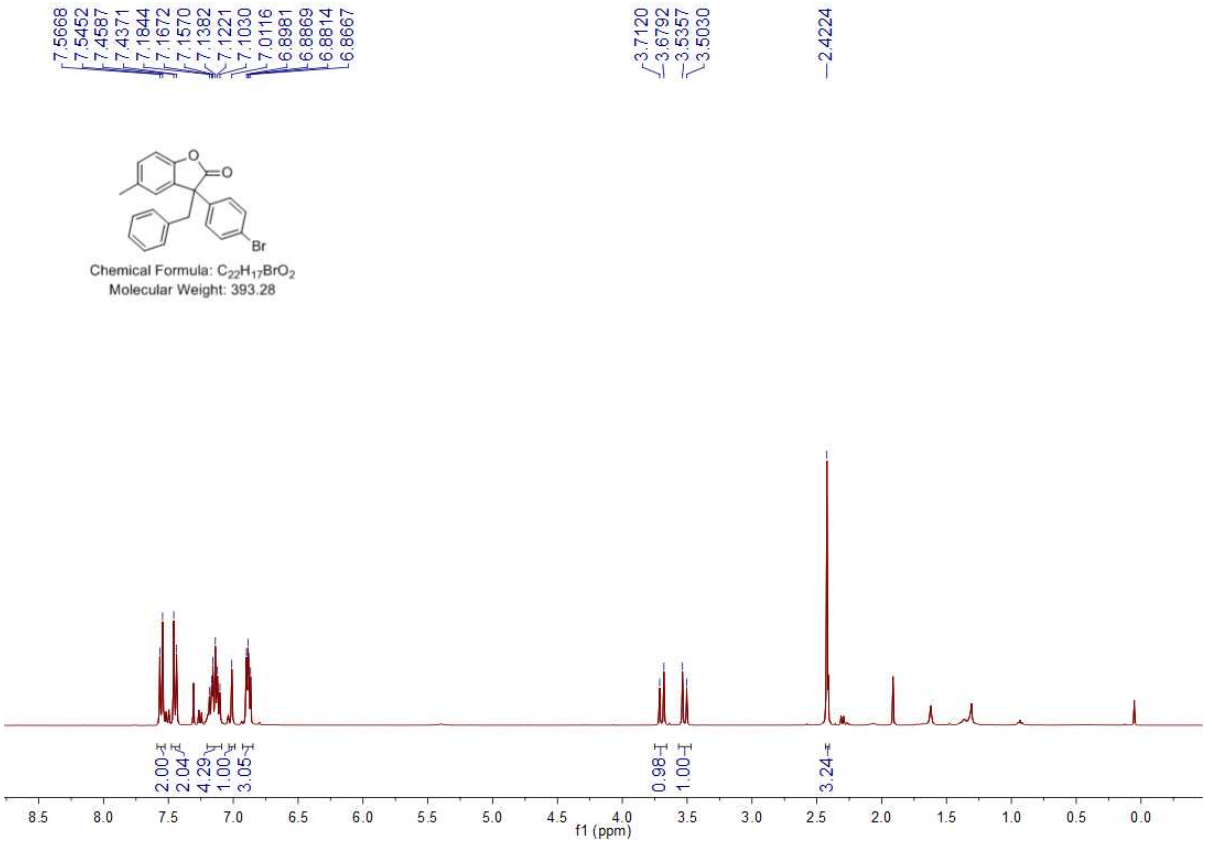
^{1}H NMR (400 MHz, Chloroform-d) spectrum for 3m



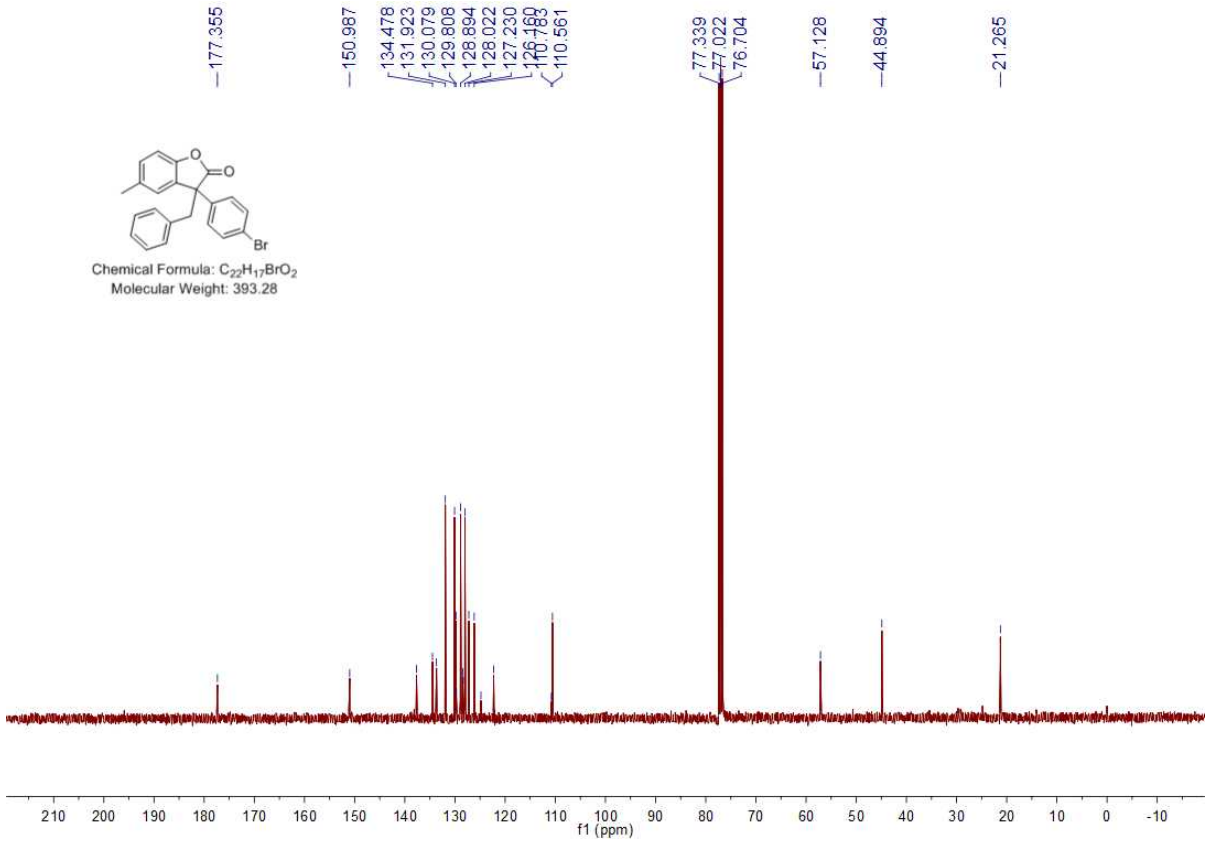
^{13}C NMR (101 MHz, Chloroform-d) spectrum for 3m



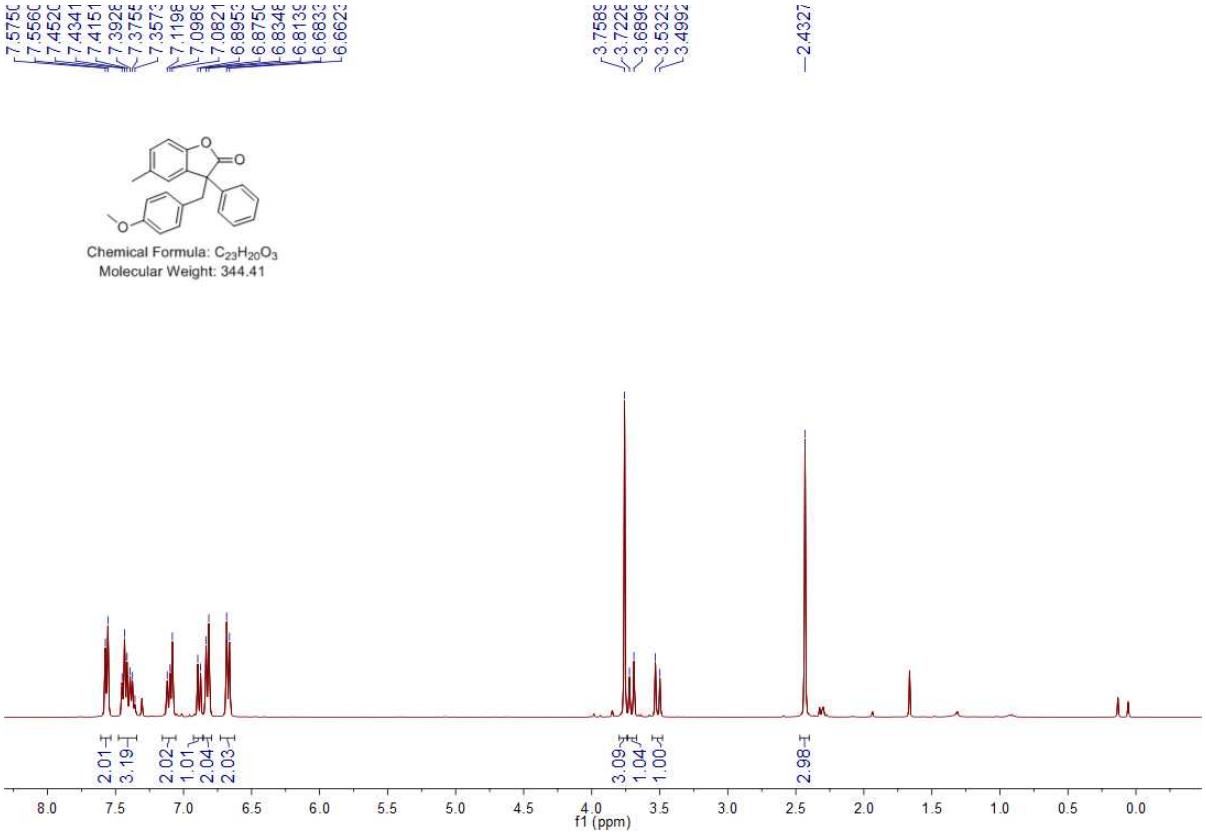
^{1}H NMR (400 MHz, Chloroform-d) spectrum for 3n



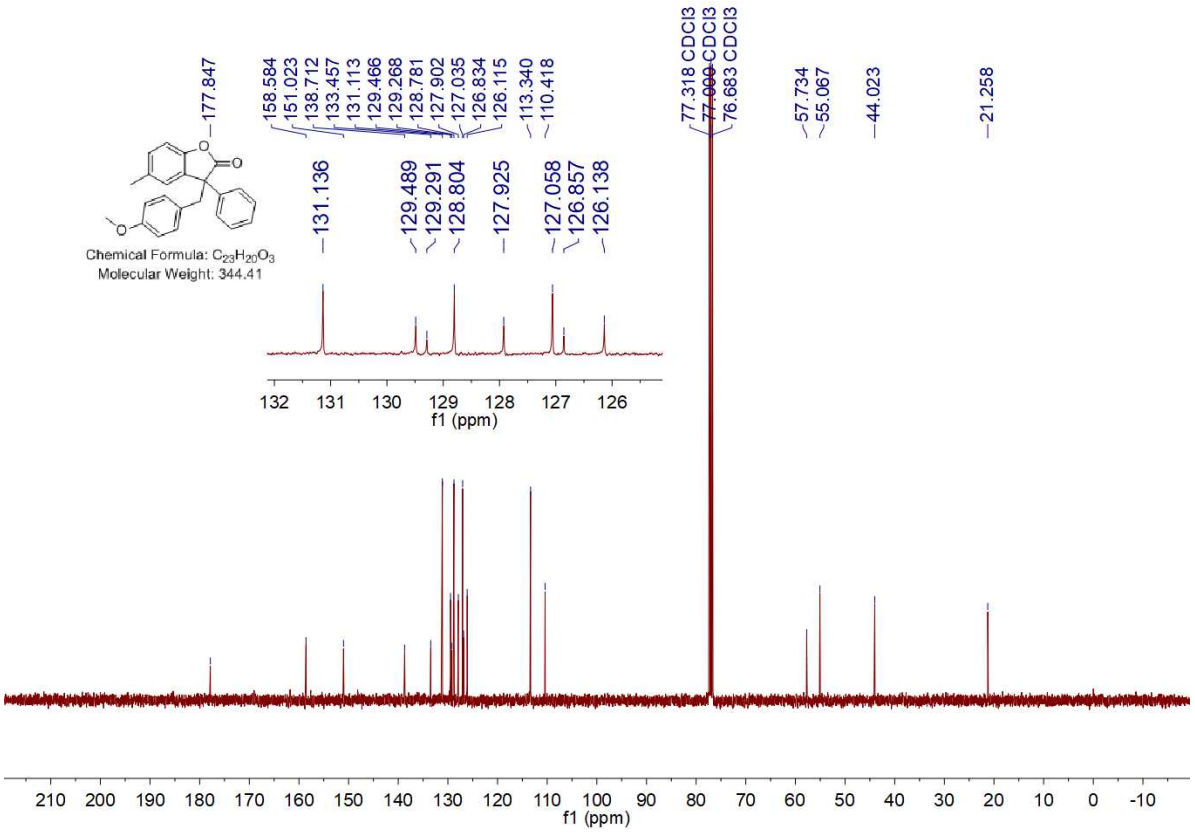
^{13}C NMR (101 MHz, Chloroform-d) spectrum for 3n



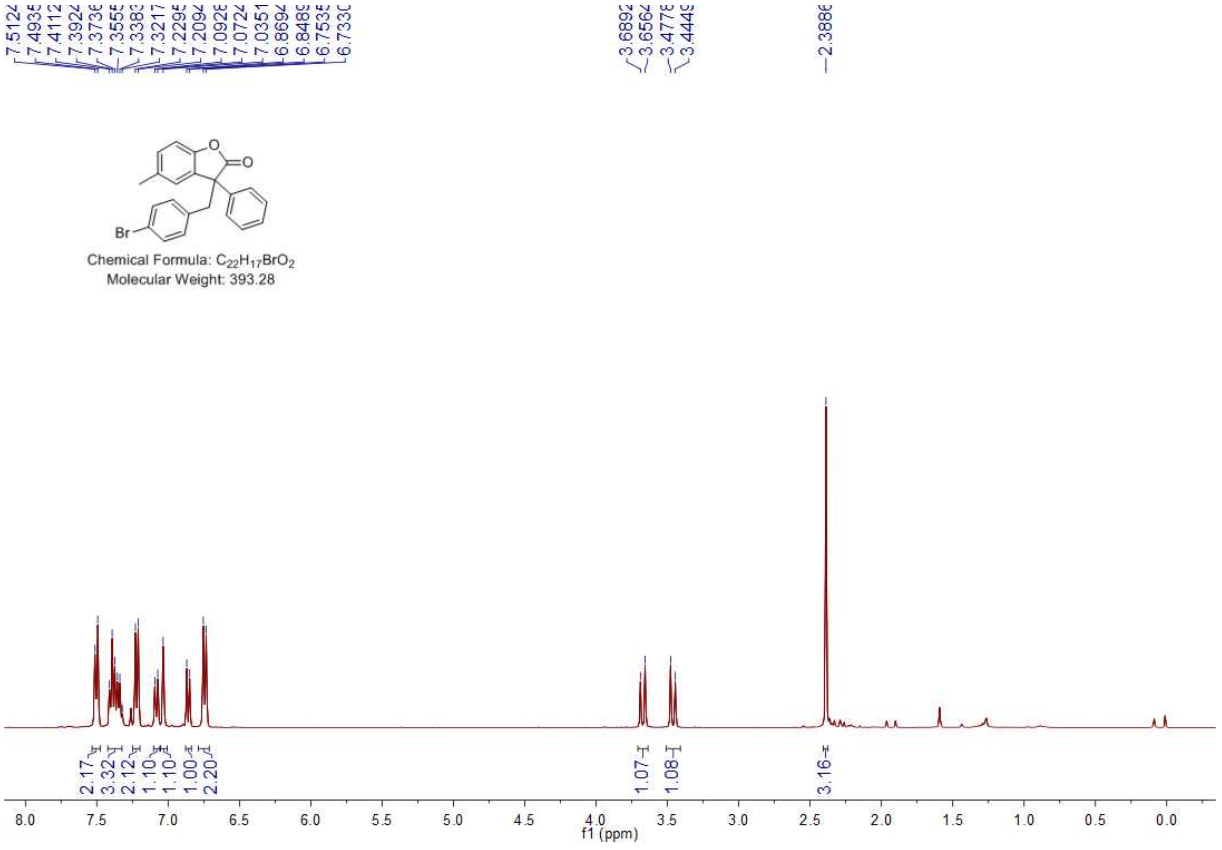
^{1}H NMR (400 MHz, Chloroform-d) spectrum for 4a



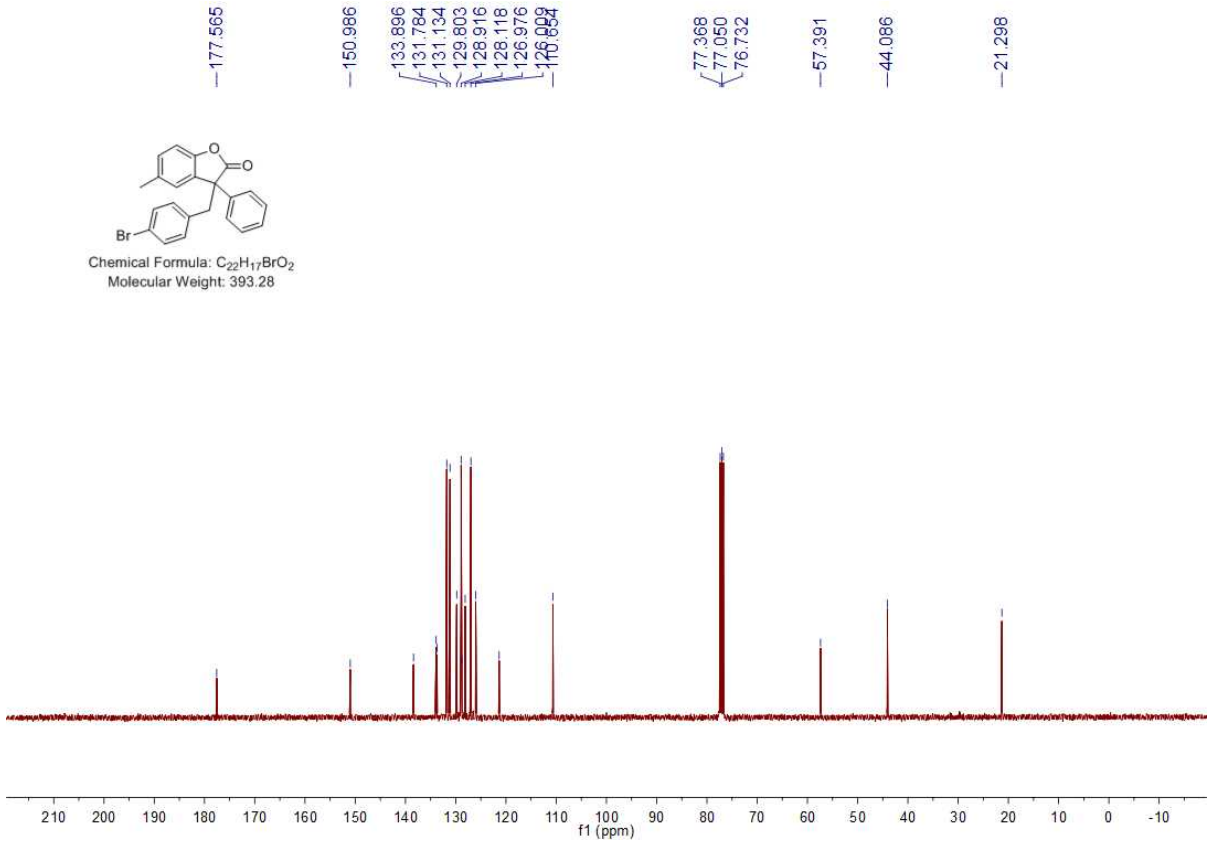
^{13}C NMR (101 MHz, Chloroform-d) spectrum for 4a



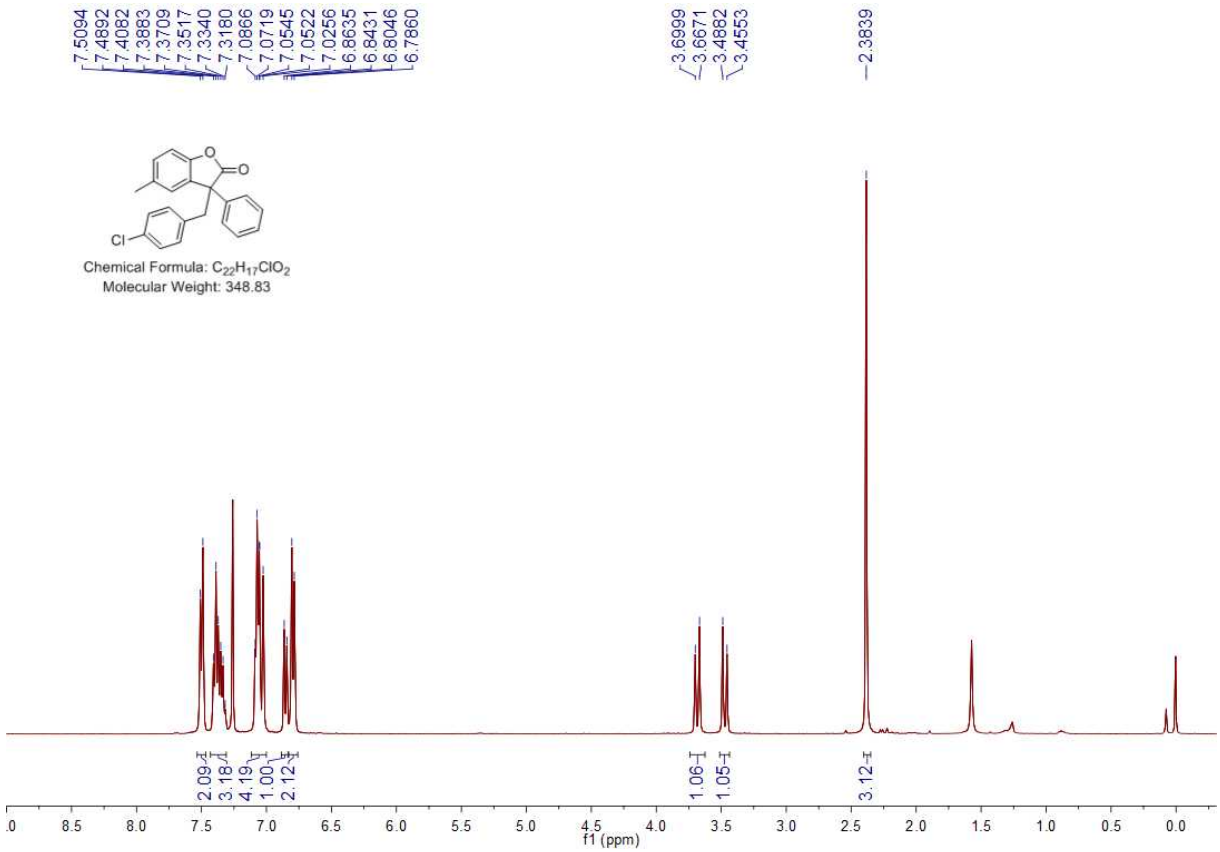
^{1}H NMR (400 MHz, Chloroform-d) spectrum for 4b



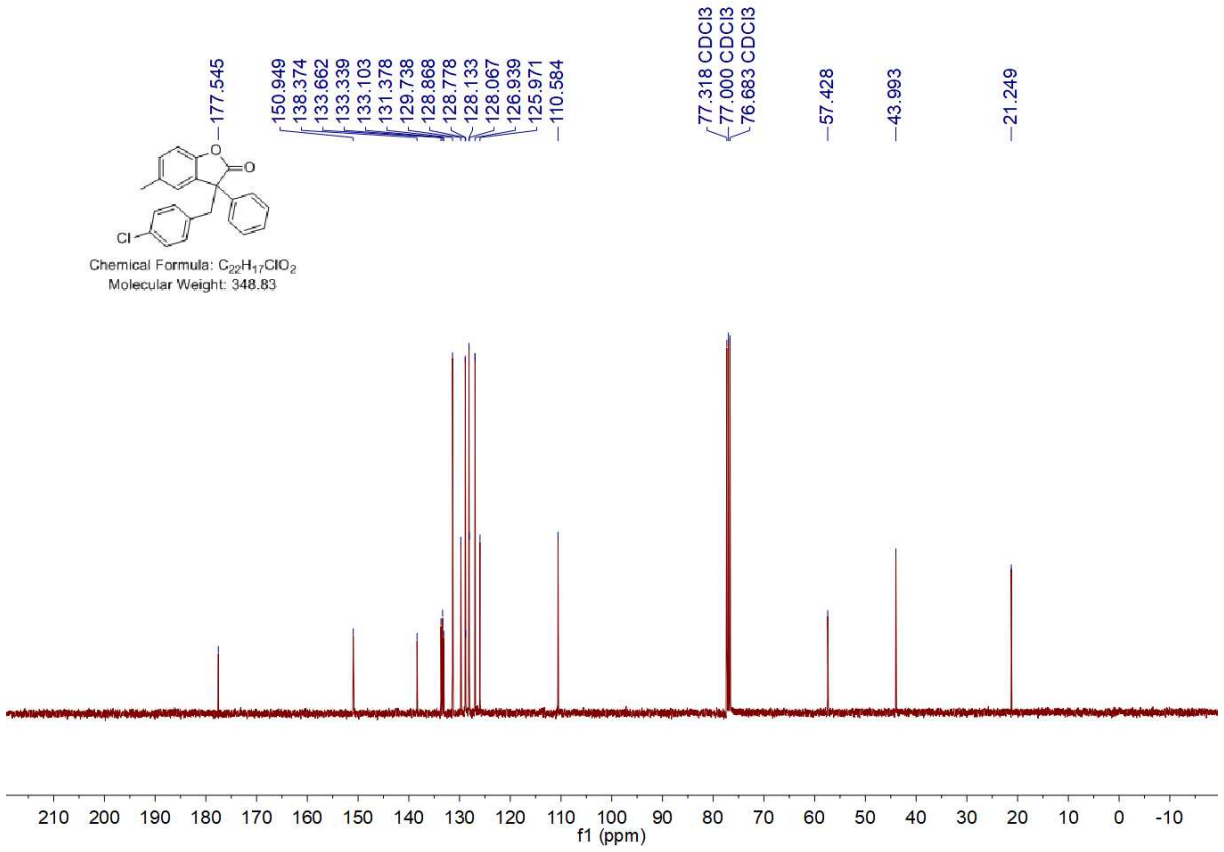
^{13}C NMR (101 MHz, Chloroform-d) spectrum for 4b



^{1}H NMR (400 MHz, Chloroform-d) spectrum for 4c



^{13}C NMR (101 MHz, Chloroform-d) spectrum for 4c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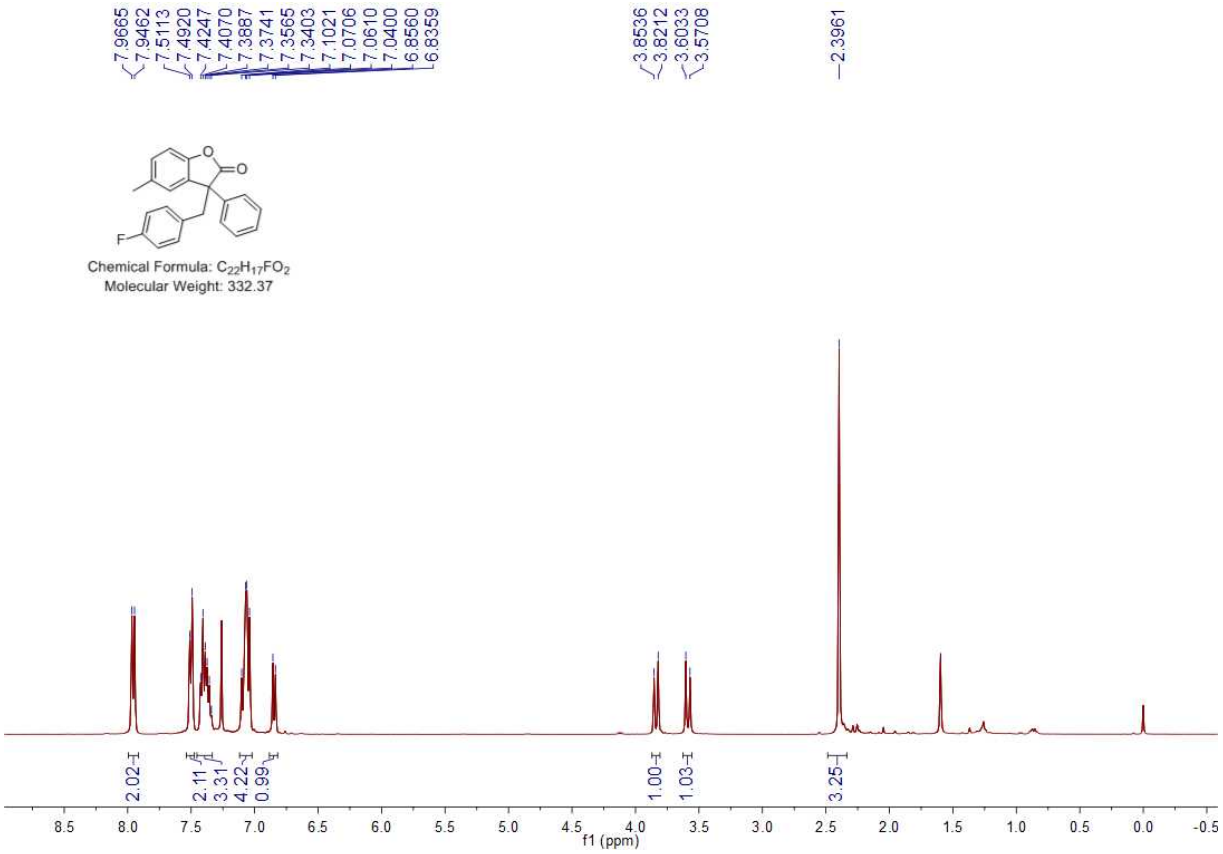
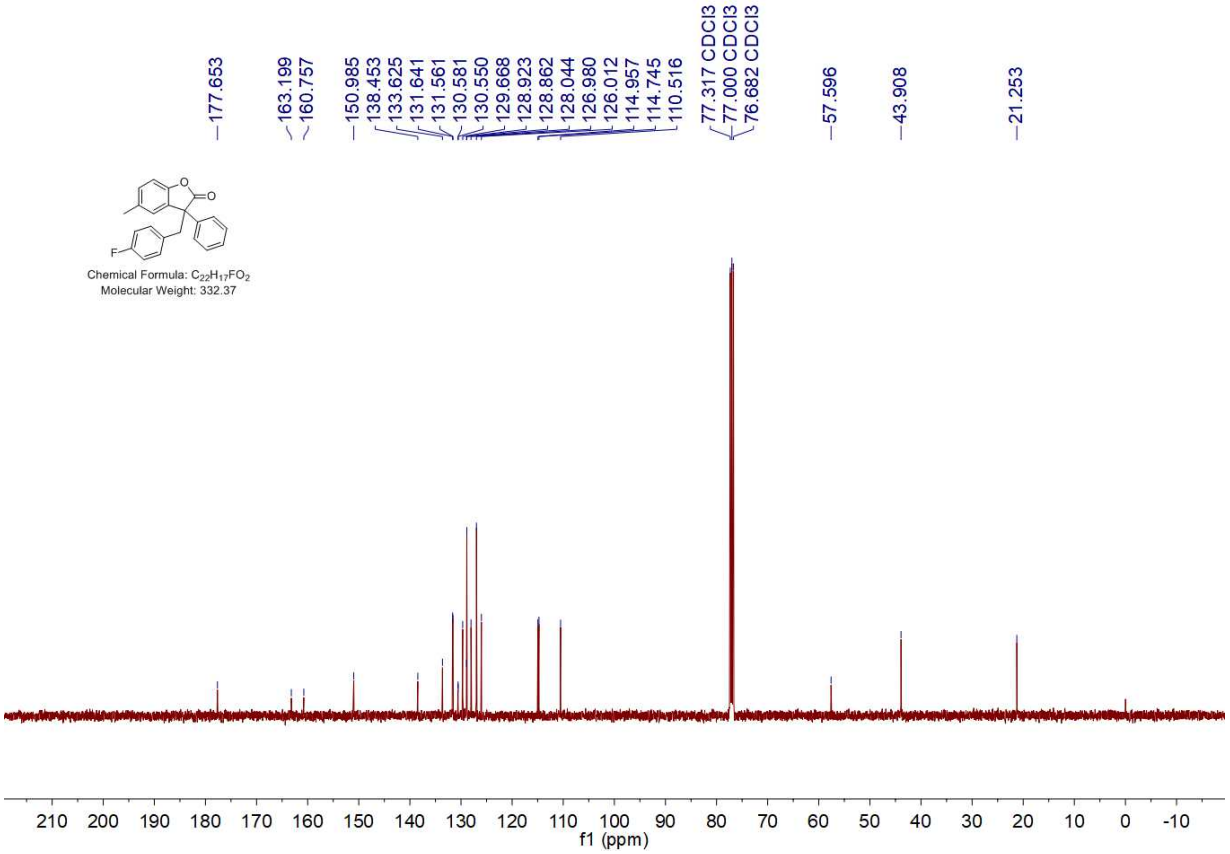
150.949
138.374
133.662
133.339
133.103
131.378
129.738
128.868
128.778
128.133
128.067
126.939
125.971
110.584
77.318 CDCl3
77.000 CDCl3
76.683 CDCl3
57.428
43.993
21.249
O
O
Cl
Chemical Formula: C22H17ClO2
Molecular Weight: 348.83
210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 -10
f1 (ppm)

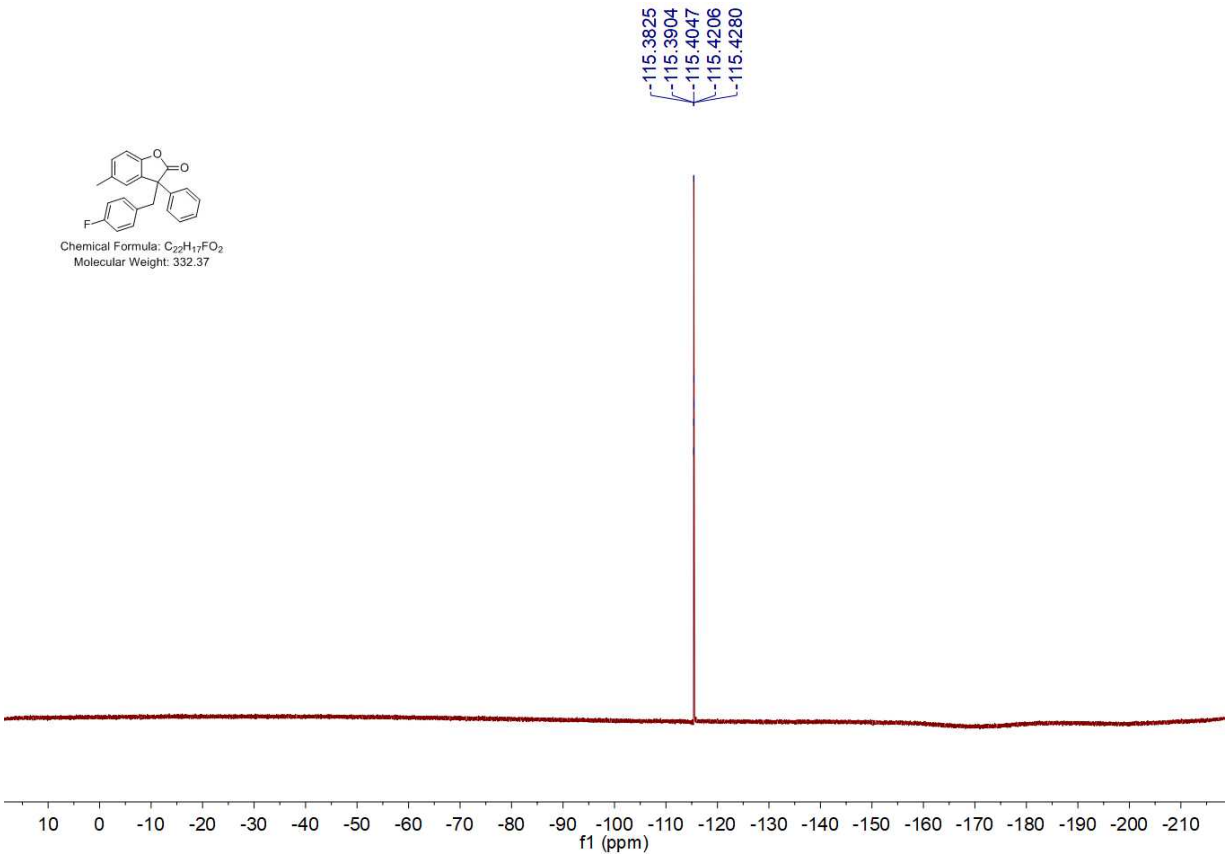
^{1}H NMR (400 MHz, Chloroform-d) spectrum for 4d



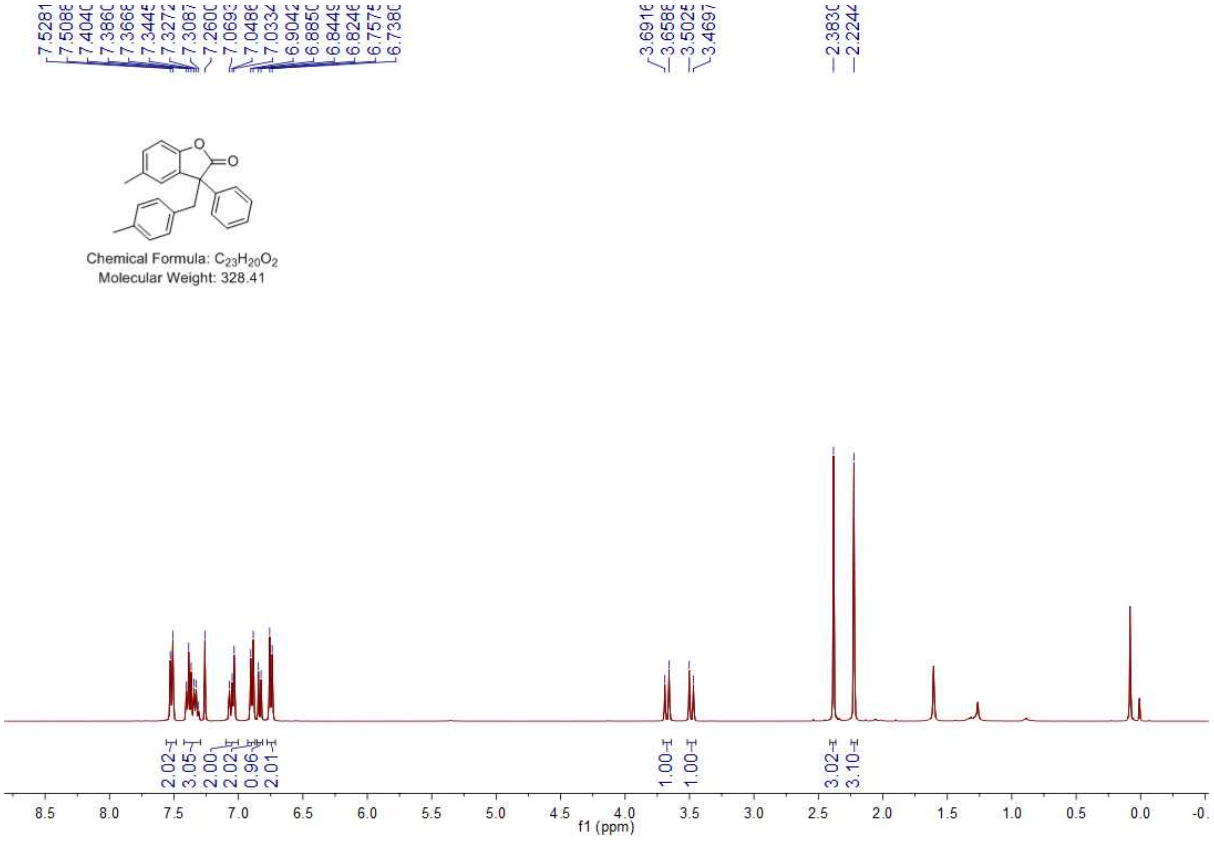
^{13}C NMR (101 MHz, Chloroform-d) spectrum for 4d



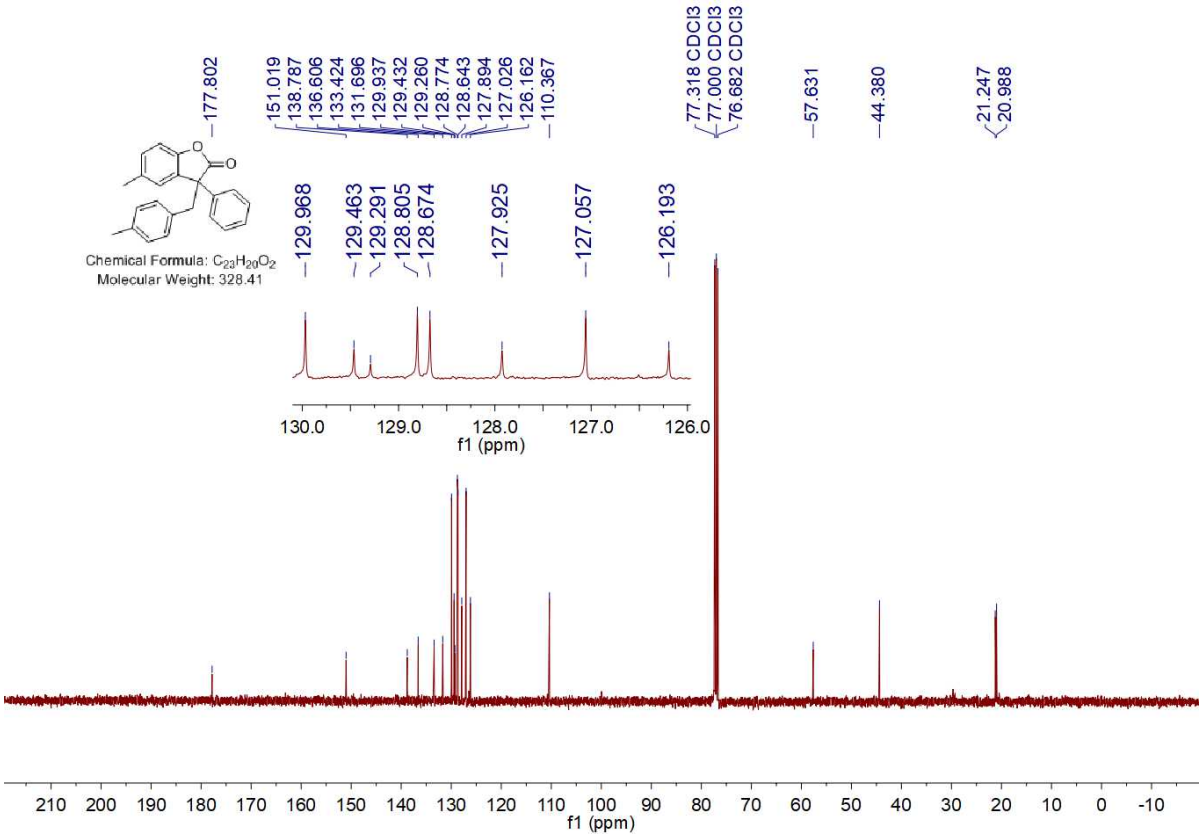
^{19}F NMR (376 MHz, Chloroform-d) spectrum for 4d



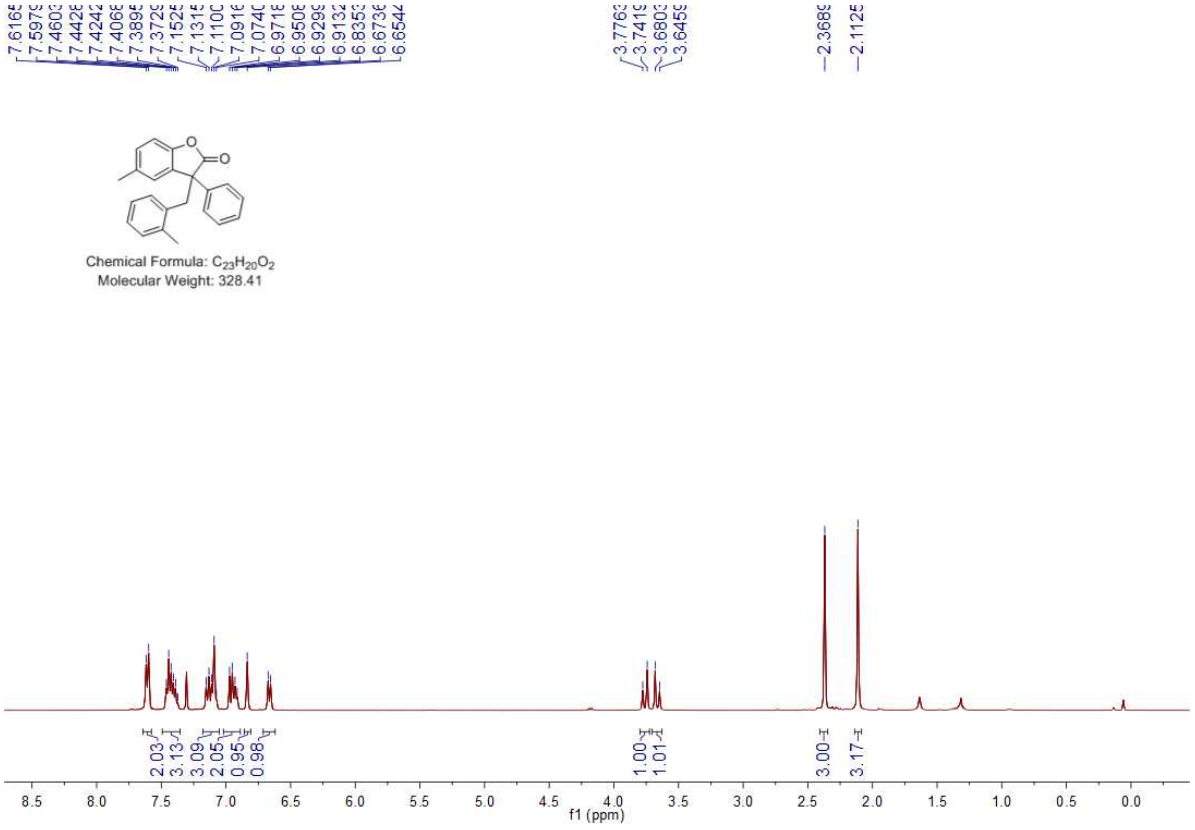
^{1}H NMR (400 MHz, Chloroform-d) spectrum for 4e



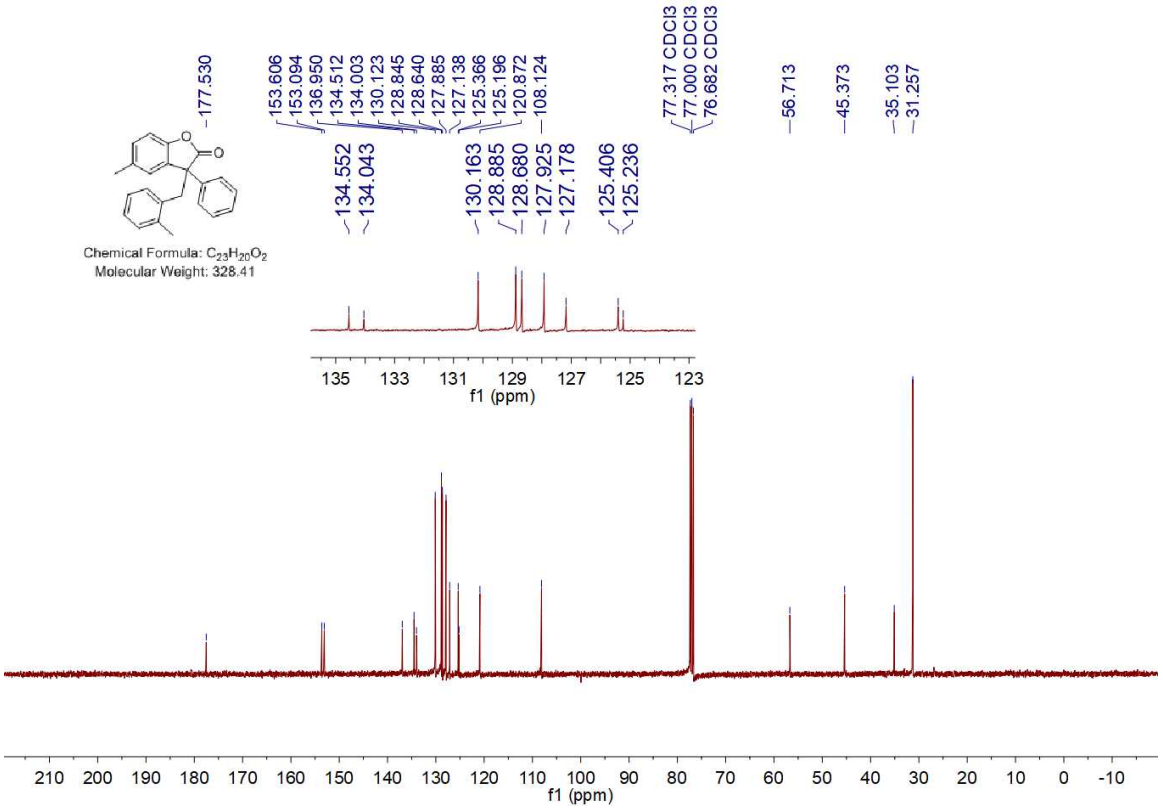
^{13}C NMR (101 MHz, Chloroform-d) spectrum for 4e



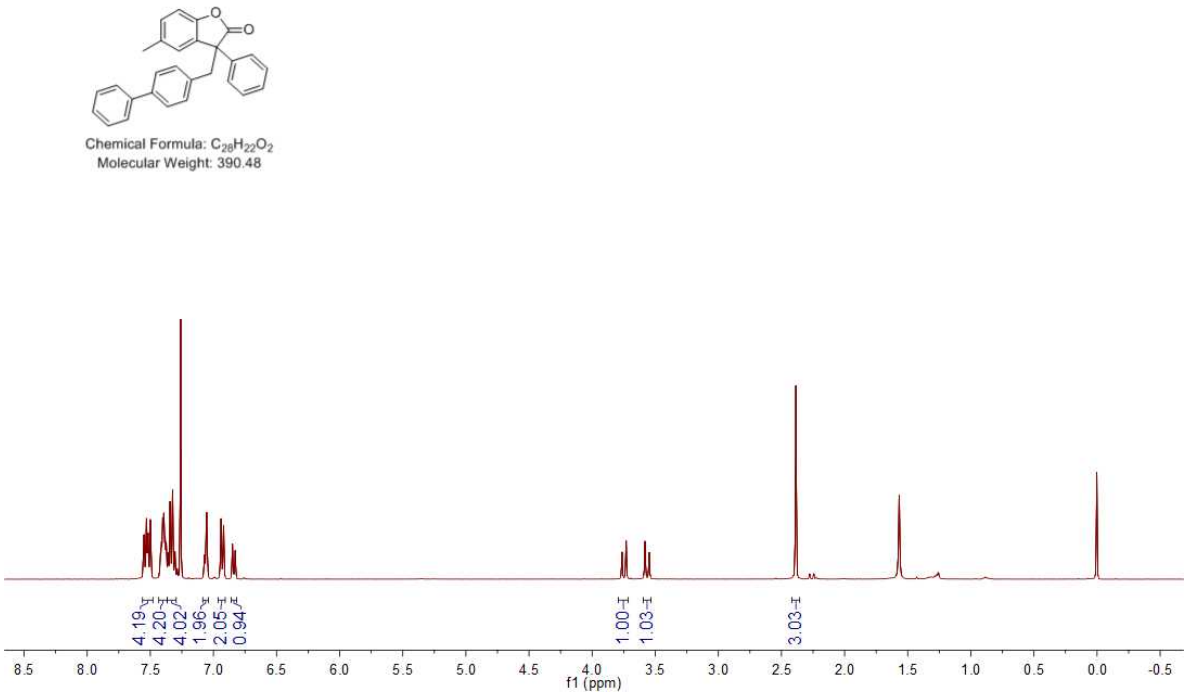
^{1}H NMR (400 MHz, Chloroform-d) spectrum for 4f



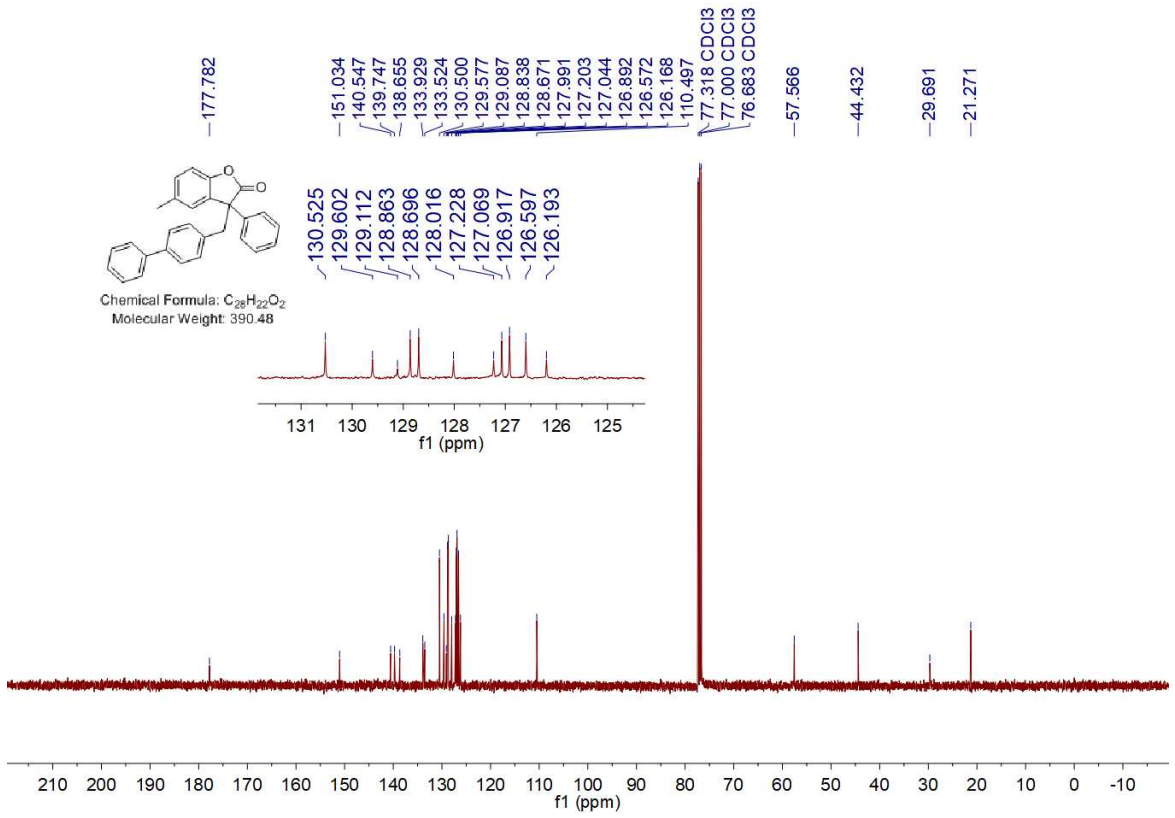
^{13}C NMR (101 MHz, Chloroform-d) spectrum for 4f



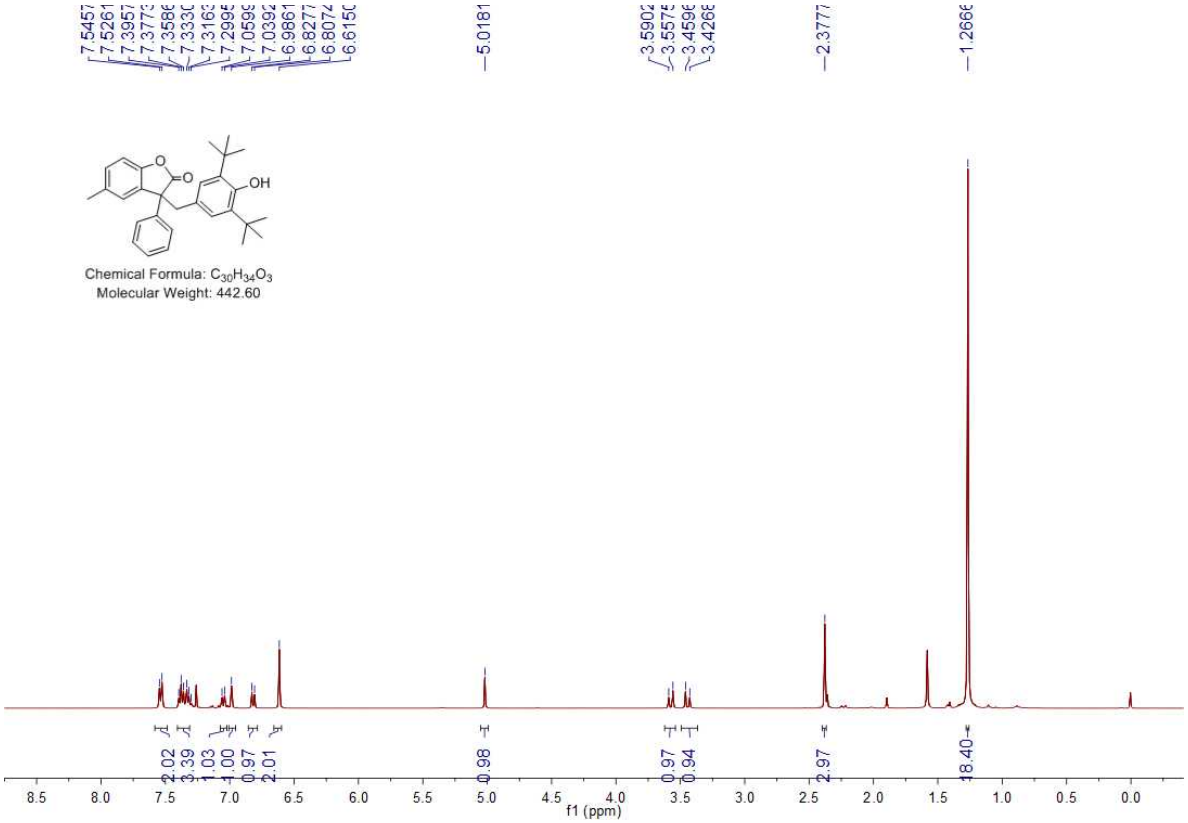
^{1}H NMR (400 MHz, Chloroform-d) spectrum for 4g



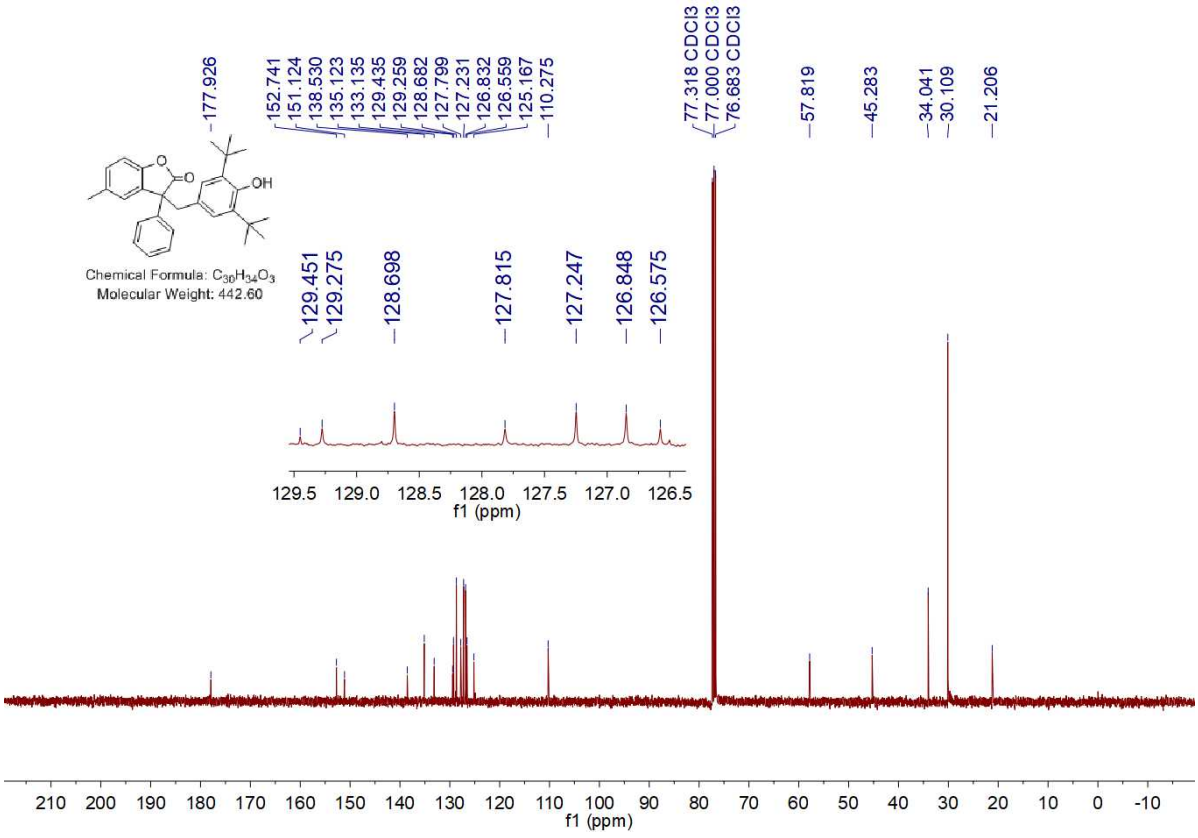
^{13}C NMR (101 MHz, Chloroform-d) spectrum for 4g



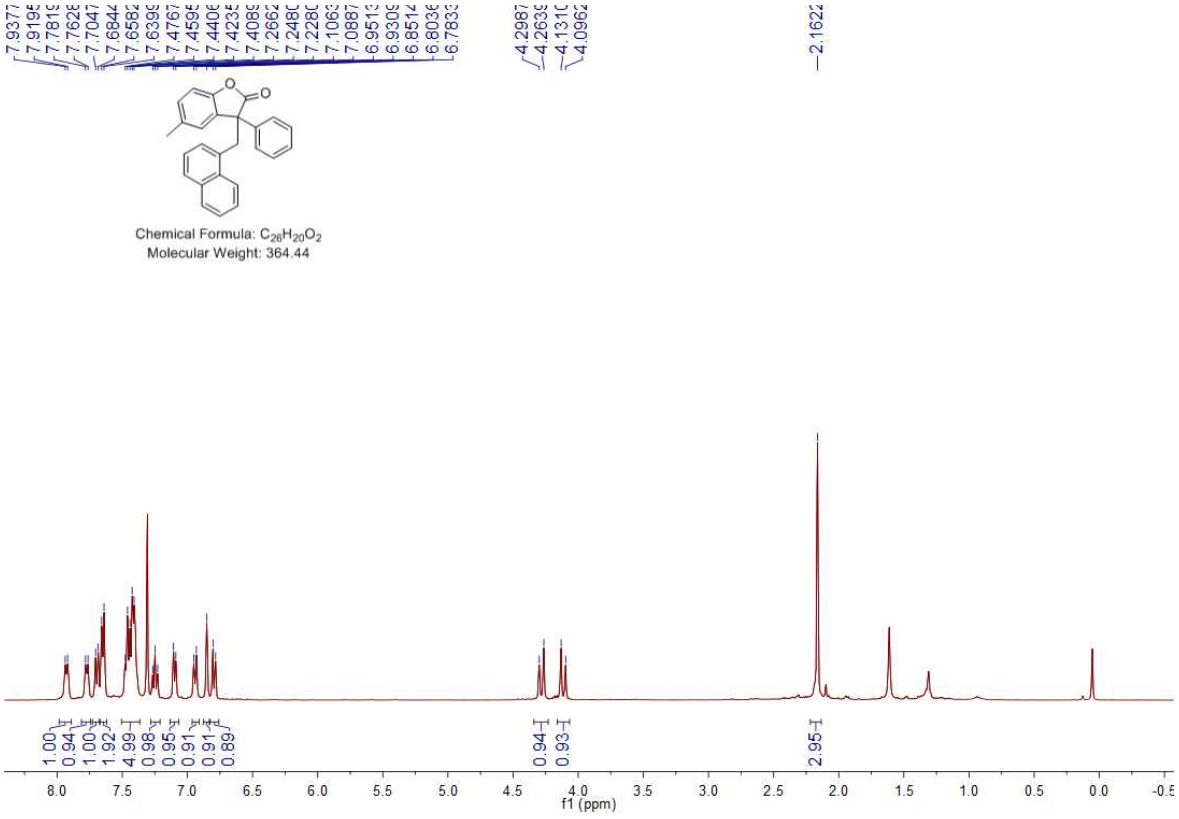
^{1}H NMR (400 MHz, Chloroform-d) spectrum for 4h



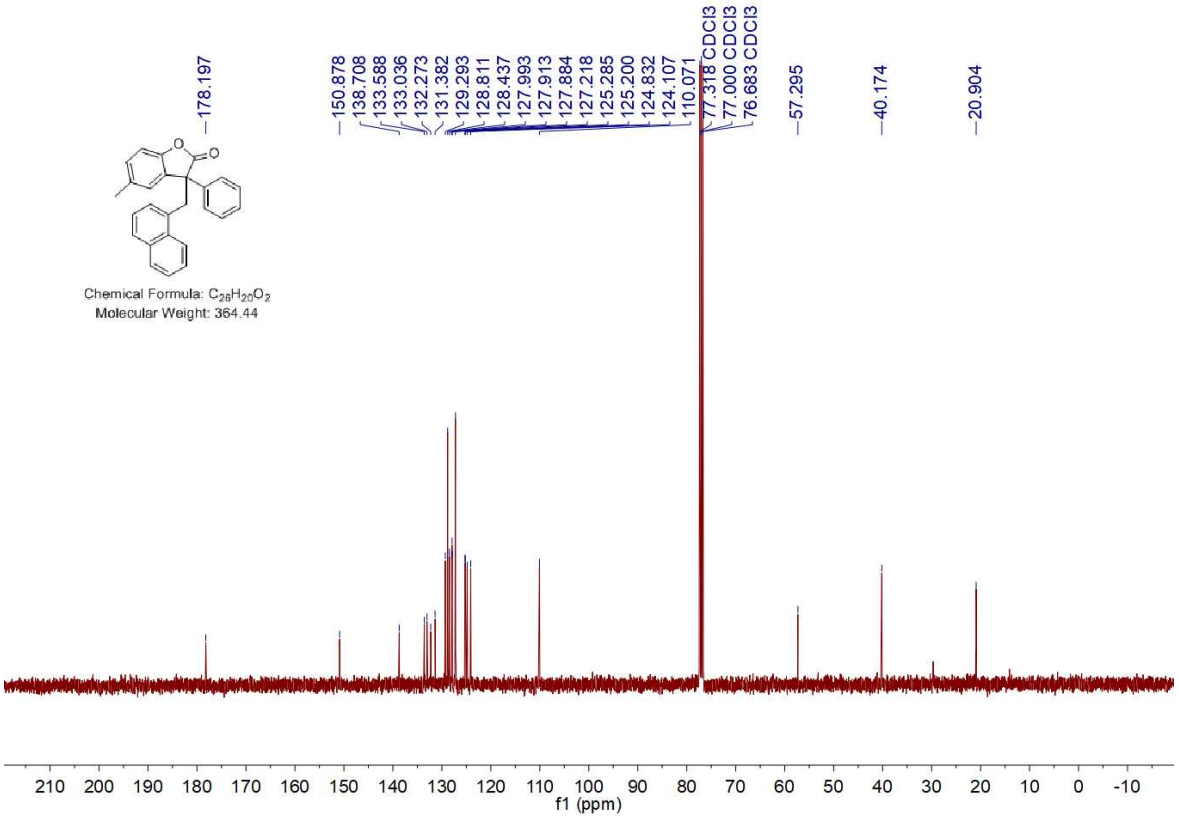
^{13}C NMR (101 MHz, Chloroform-d) spectrum for 4h



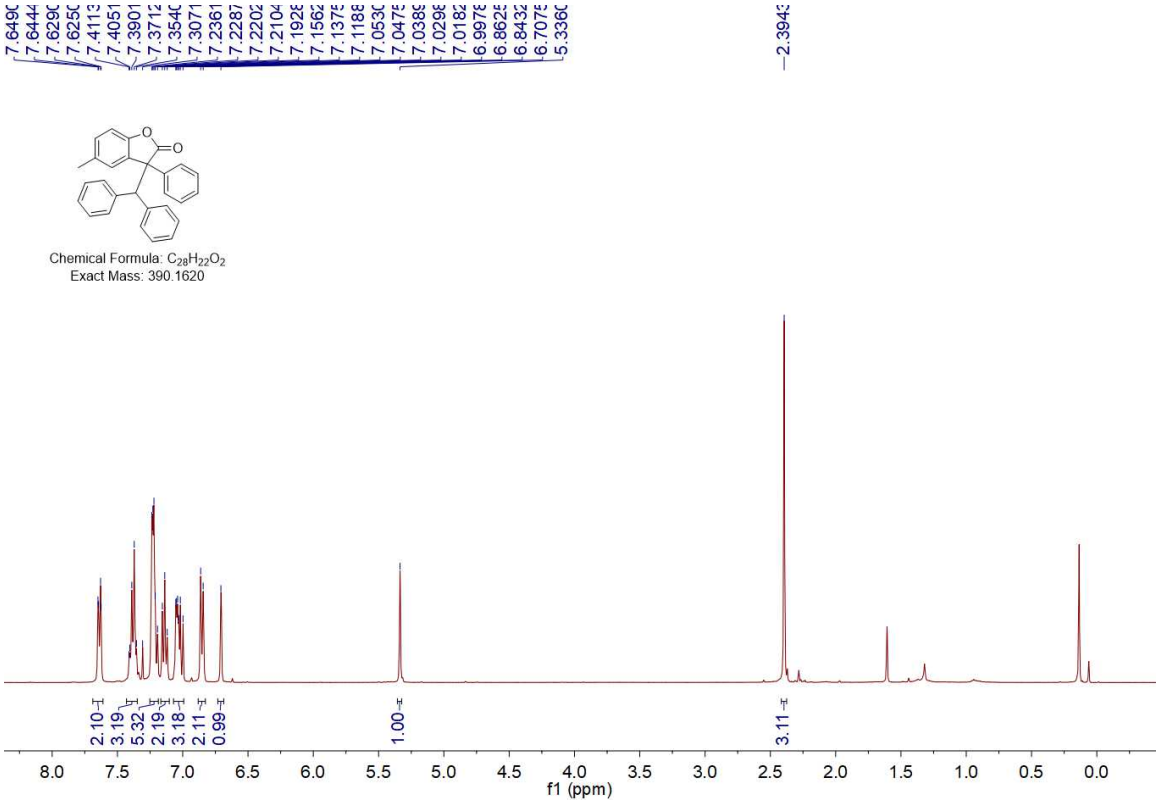
^{1}H NMR (400 MHz, Chloroform-d) spectrum for 4i



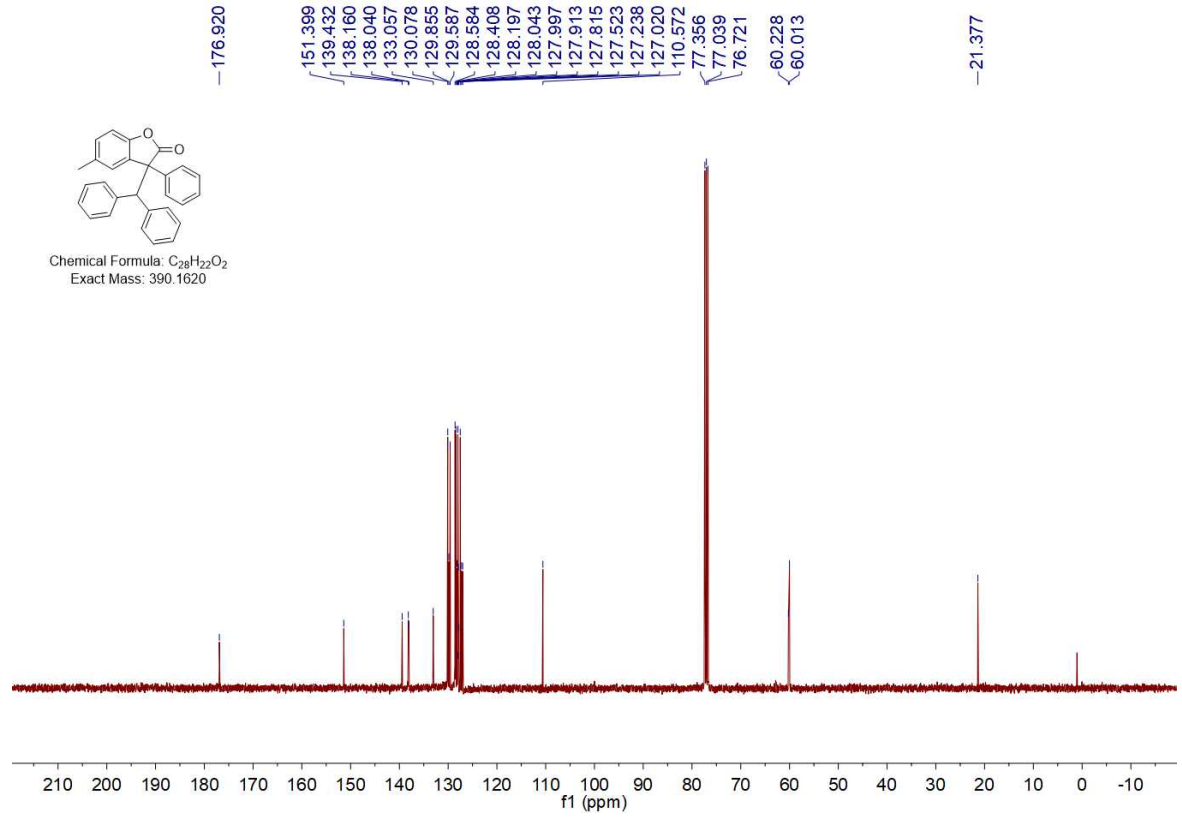
^{13}C NMR (101 MHz, Chloroform-d) spectrum for 4i



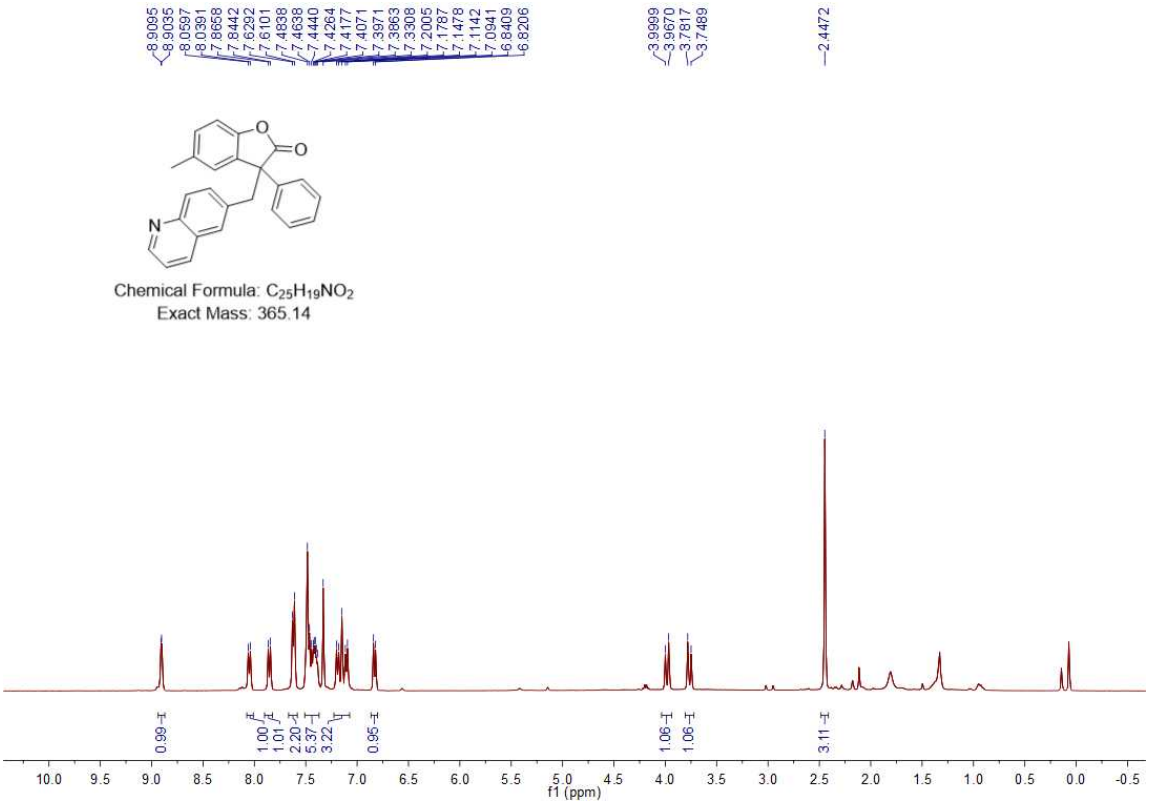
^{1}H NMR (400 MHz, Chloroform-d) spectrum for 4j



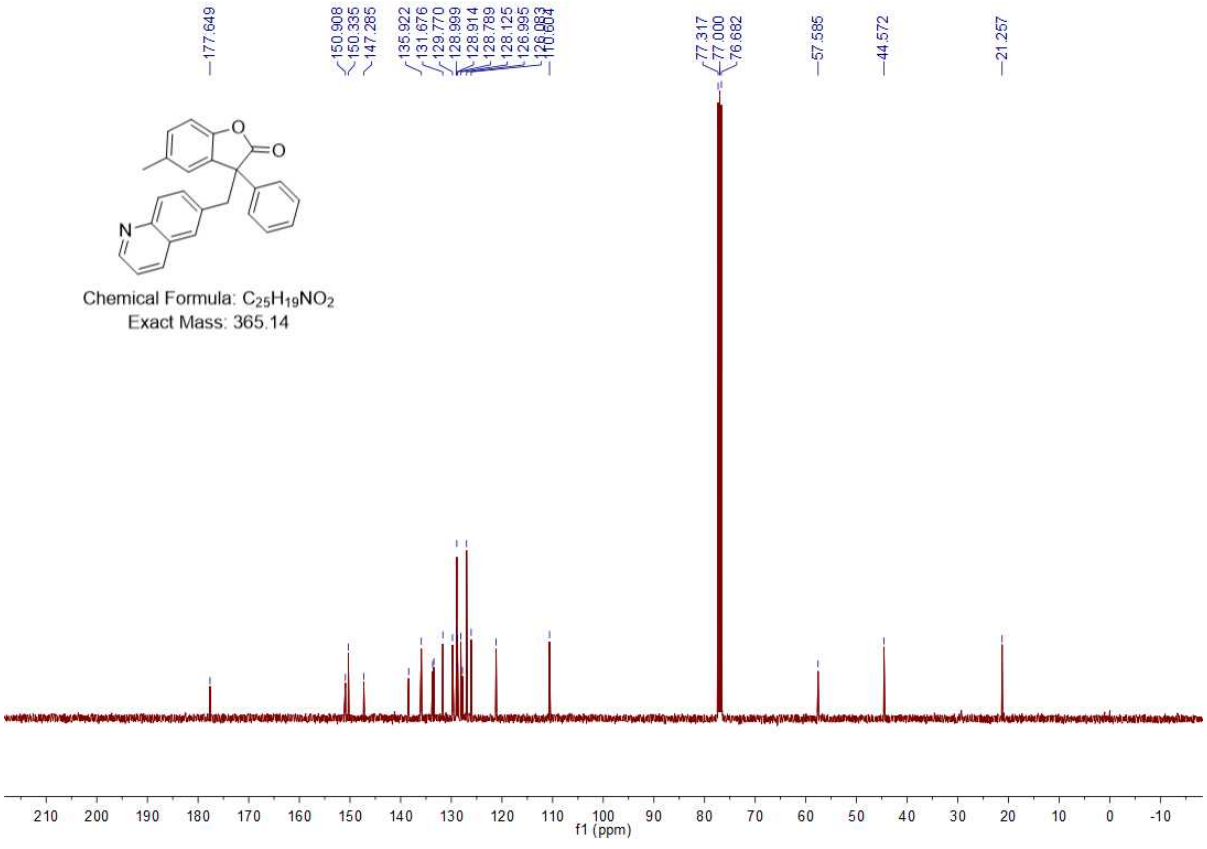
^{13}C NMR (101 MHz, Chloroform-d) spectrum for 4j



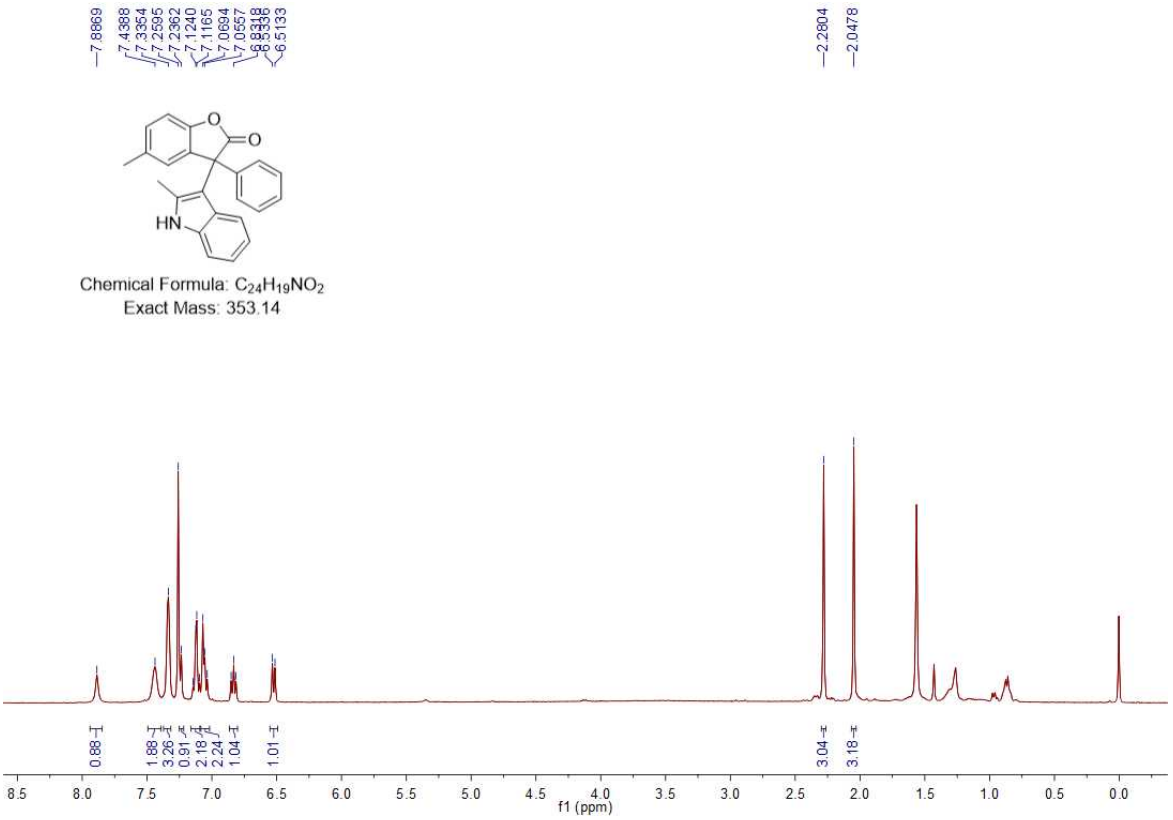
^{1}H NMR (400 MHz, Chloroform-d) spectrum for 4k



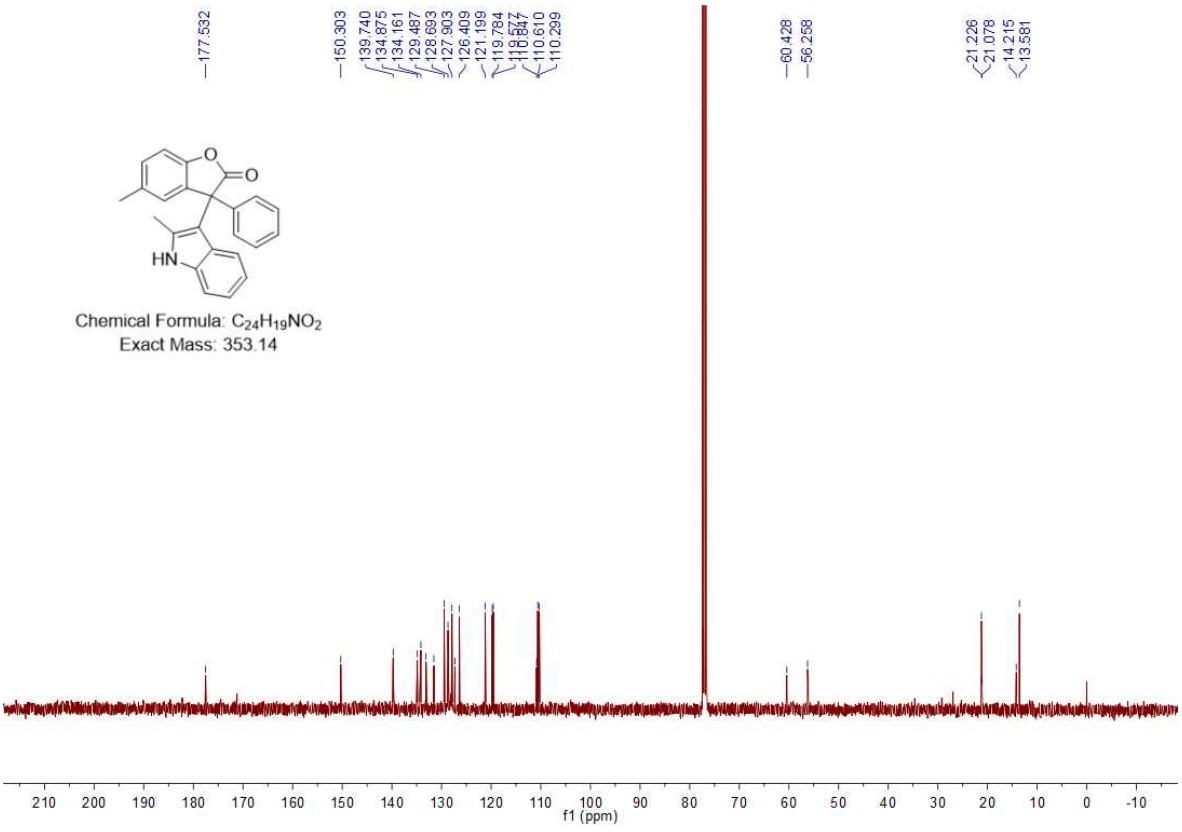
^{13}C NMR (101 MHz, Chloroform-d) spectrum for 4k



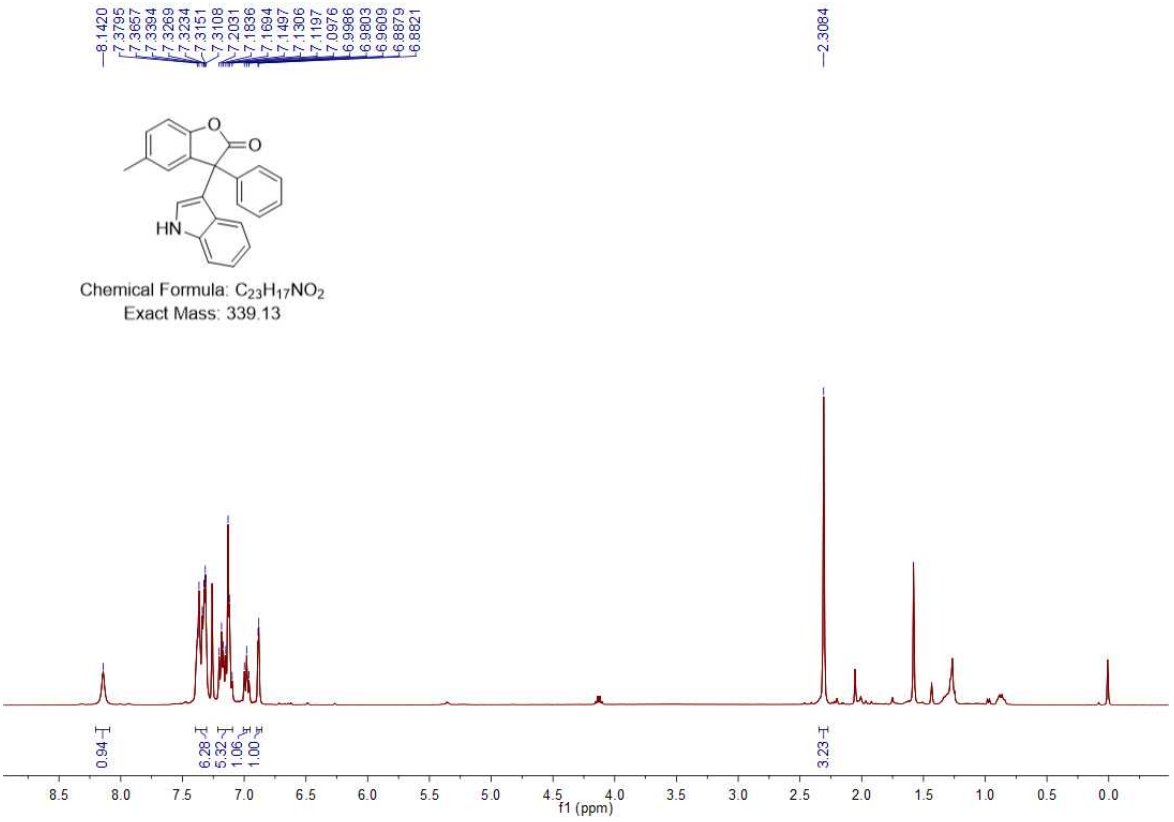
^{1}H NMR (400 MHz, Chloroform-d) spectrum for 4l



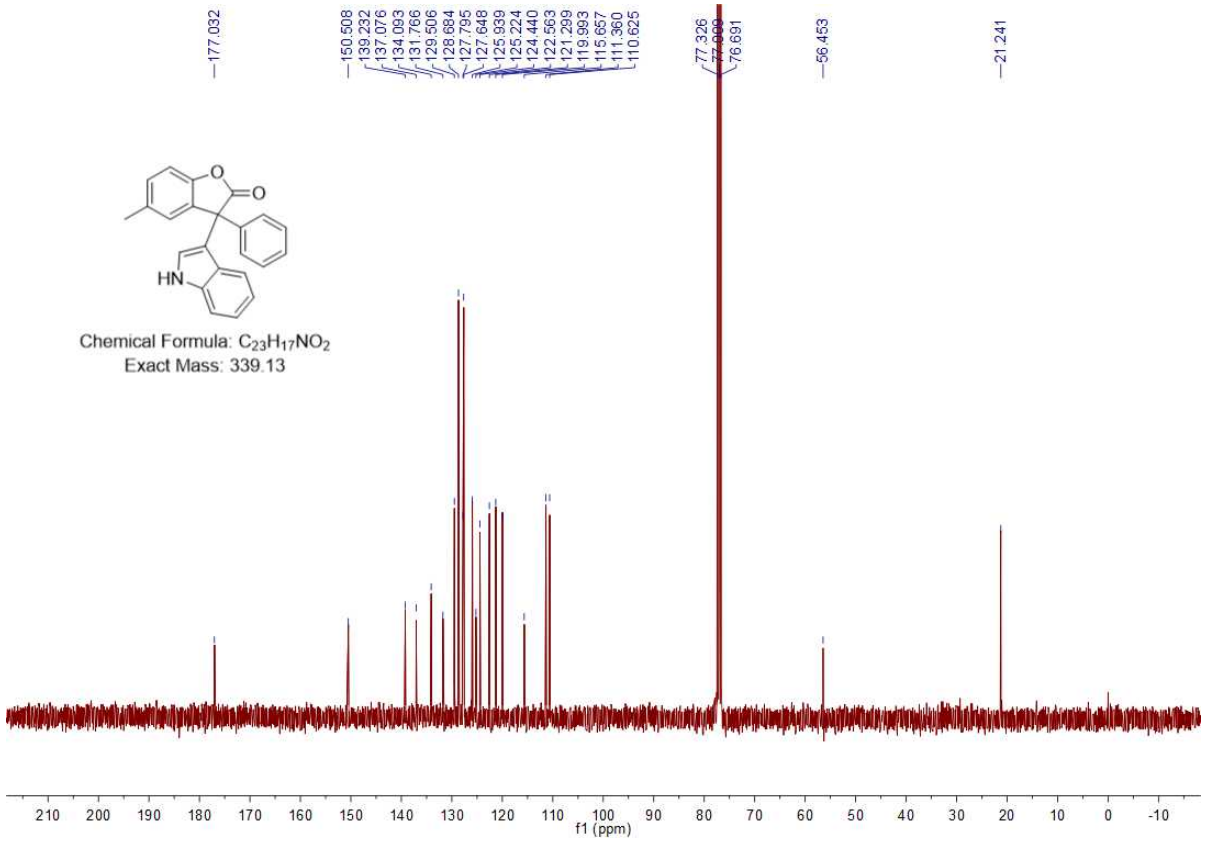
^{13}C NMR (101 MHz, Chloroform-d) spectrum for 4l



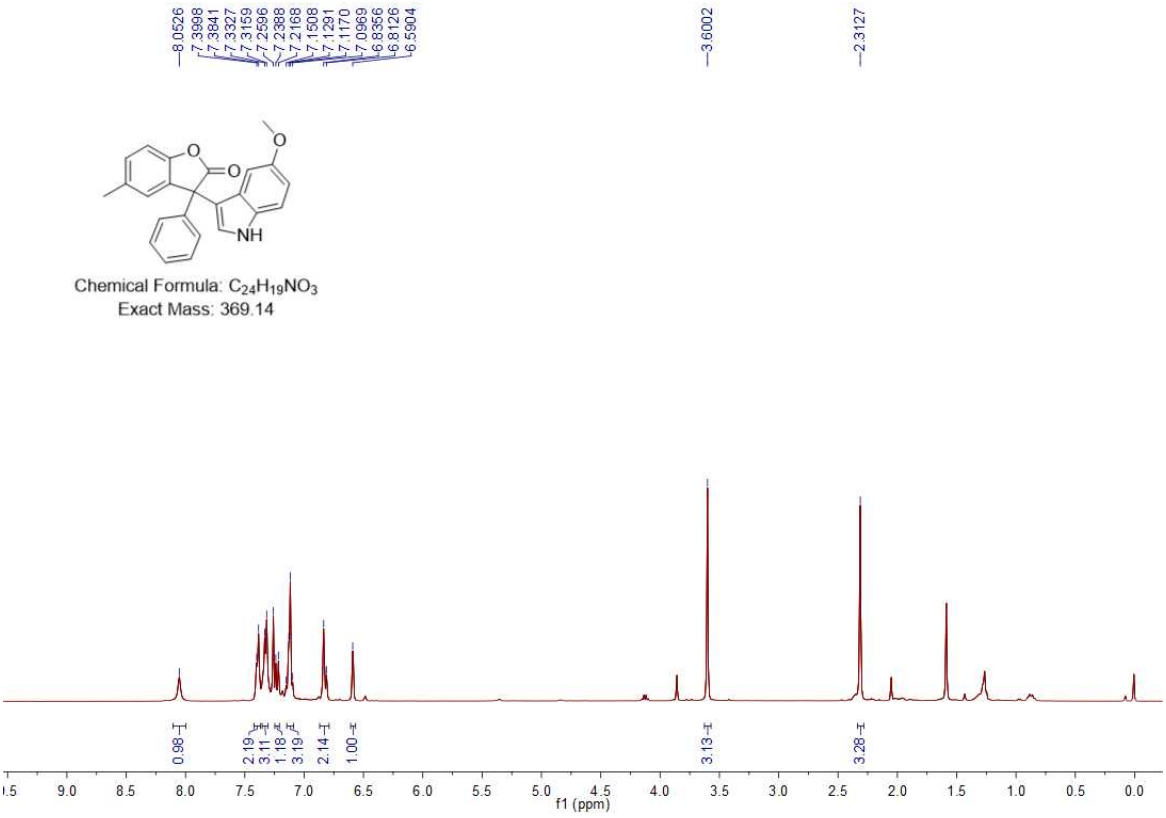
^{1}H NMR (400 MHz, Chloroform-d) spectrum for 4m



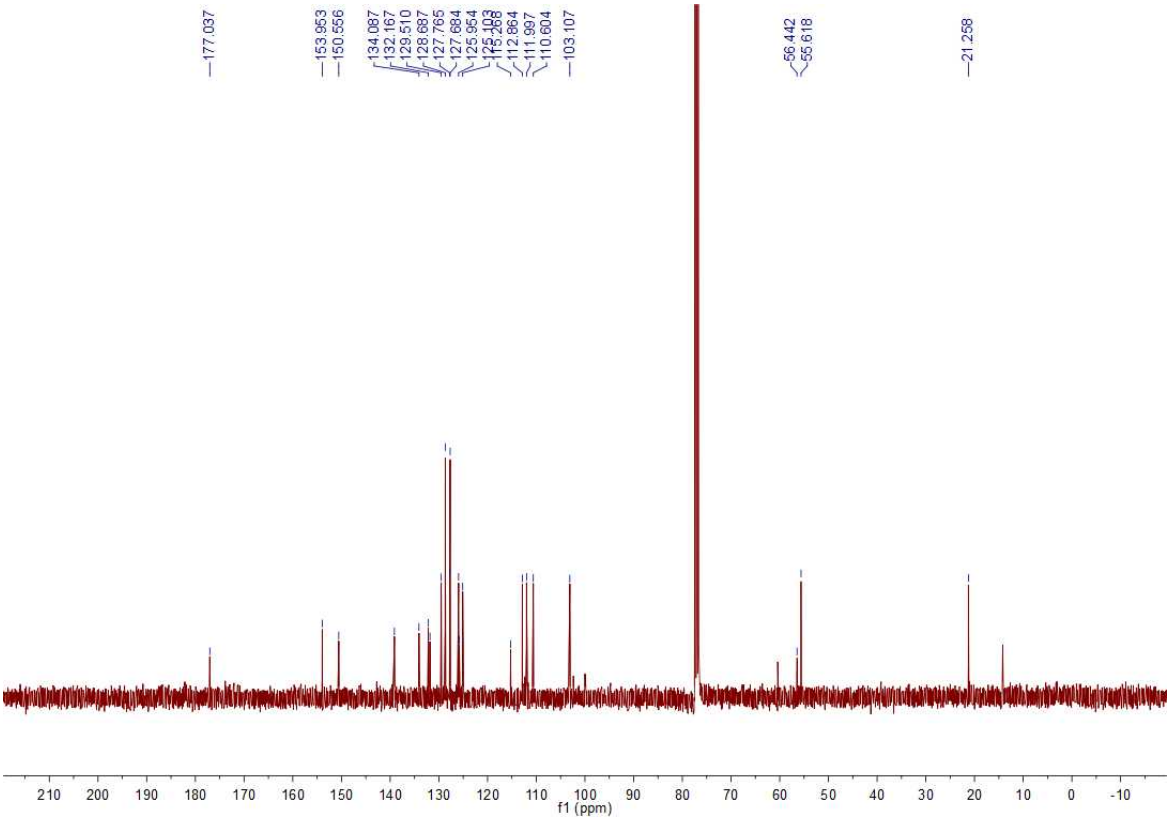
^{13}C NMR (101 MHz, Chloroform-d) spectrum for 4m



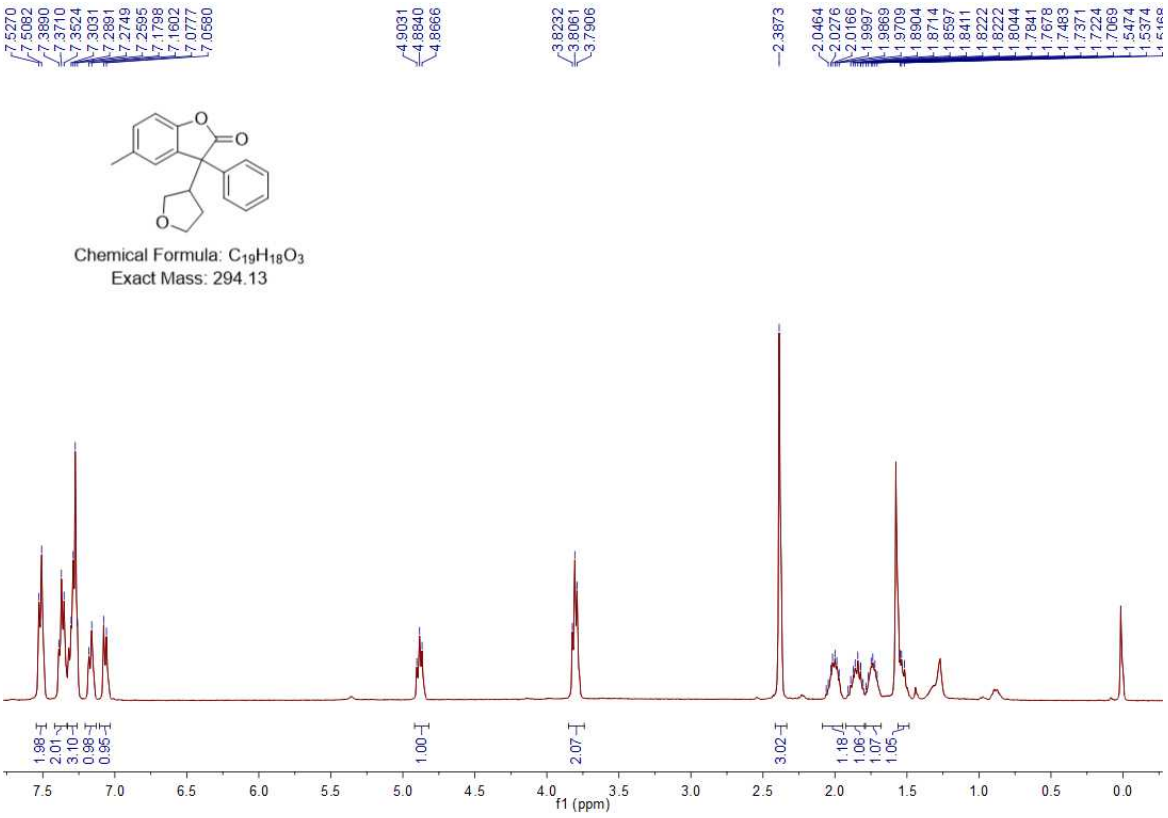
^{1}H NMR (400 MHz, Chloroform-d) spectrum for 4n



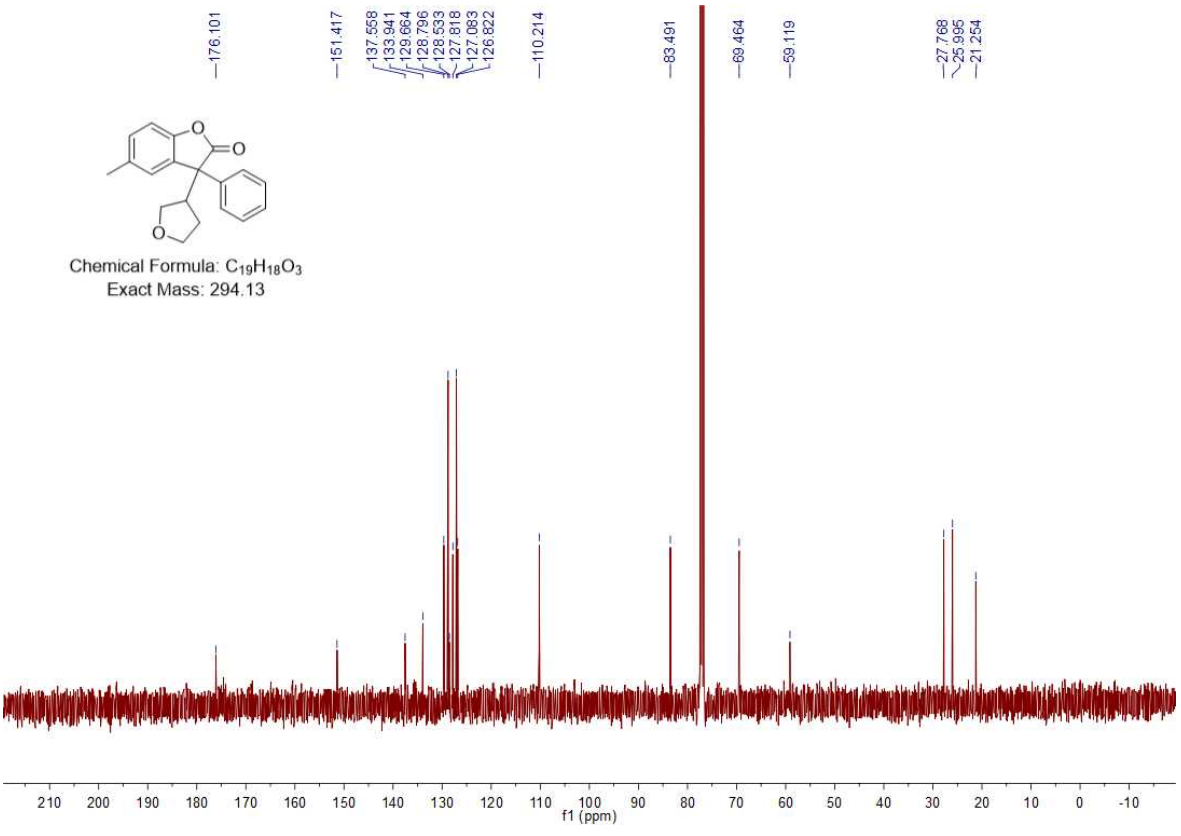
^{13}C NMR (101 MHz, Chloroform-d) spectrum for 4n



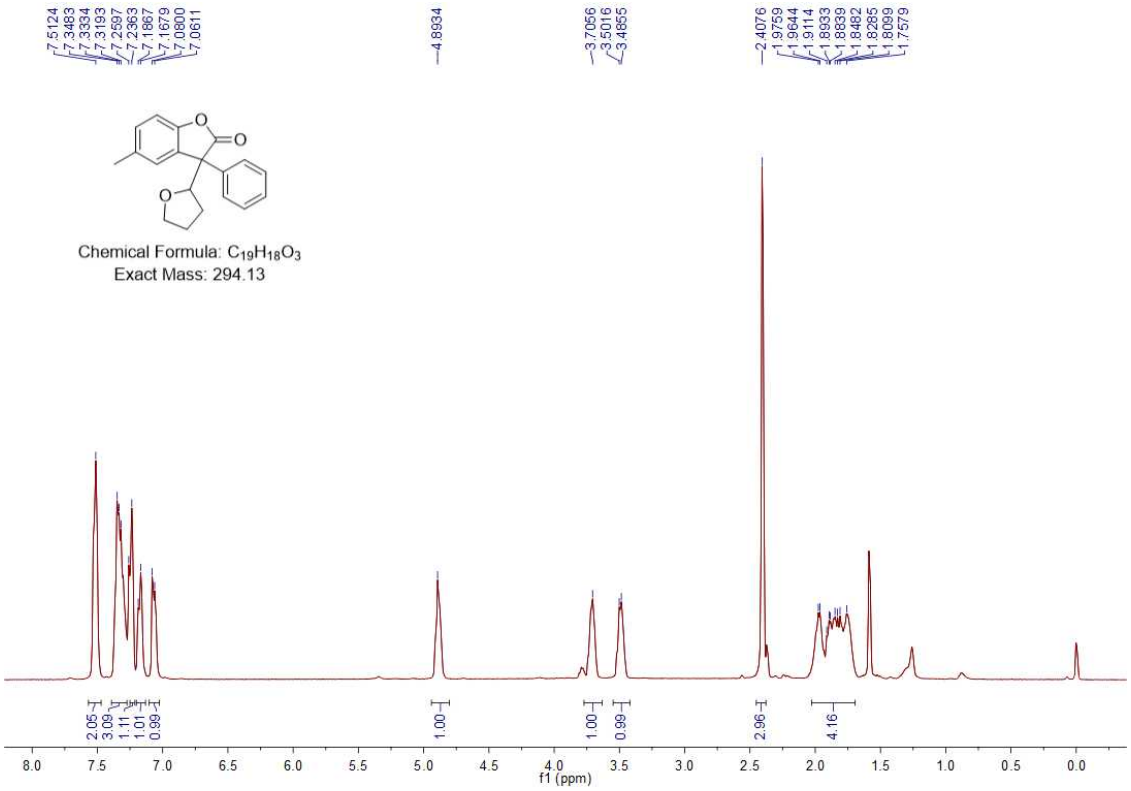
^{1}H NMR (400 MHz, Chloroform-d) spectrum for 4o



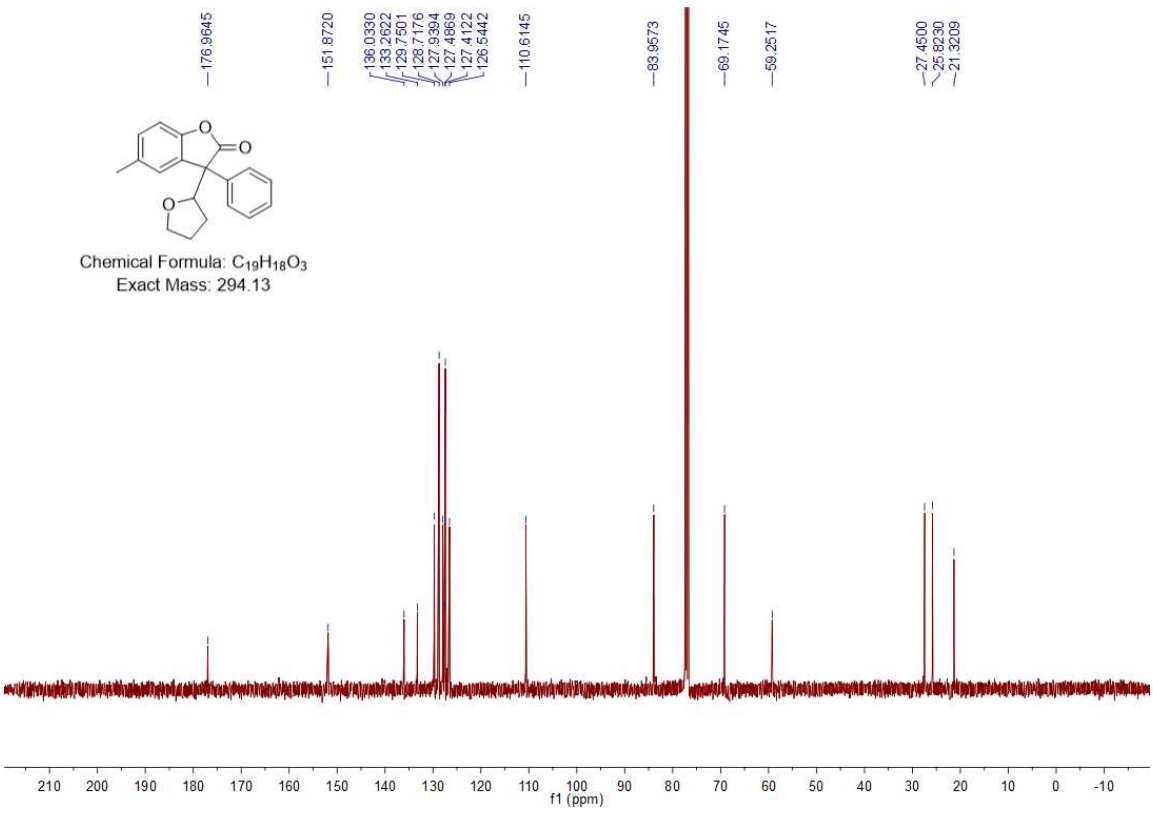
^{13}C NMR (101 MHz, Chloroform-d) spectrum for 4o



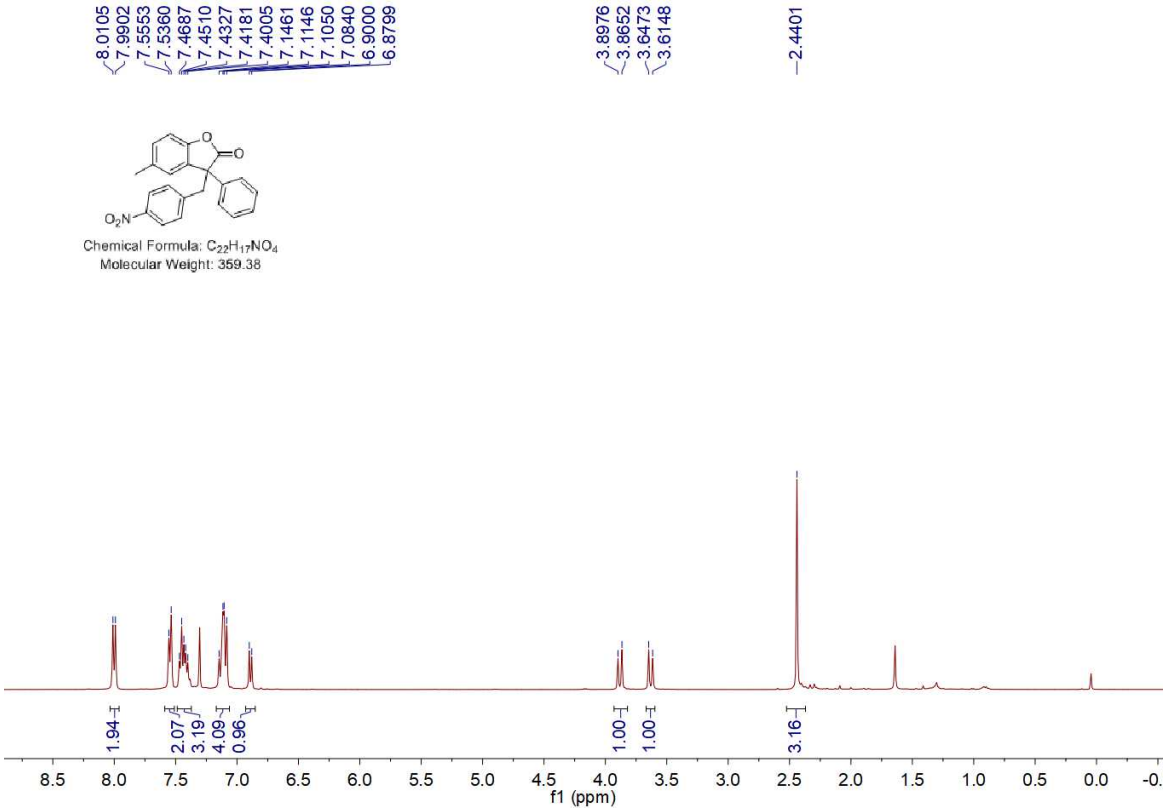
^{1}H NMR (400 MHz, Chloroform-d) spectrum for 4o'



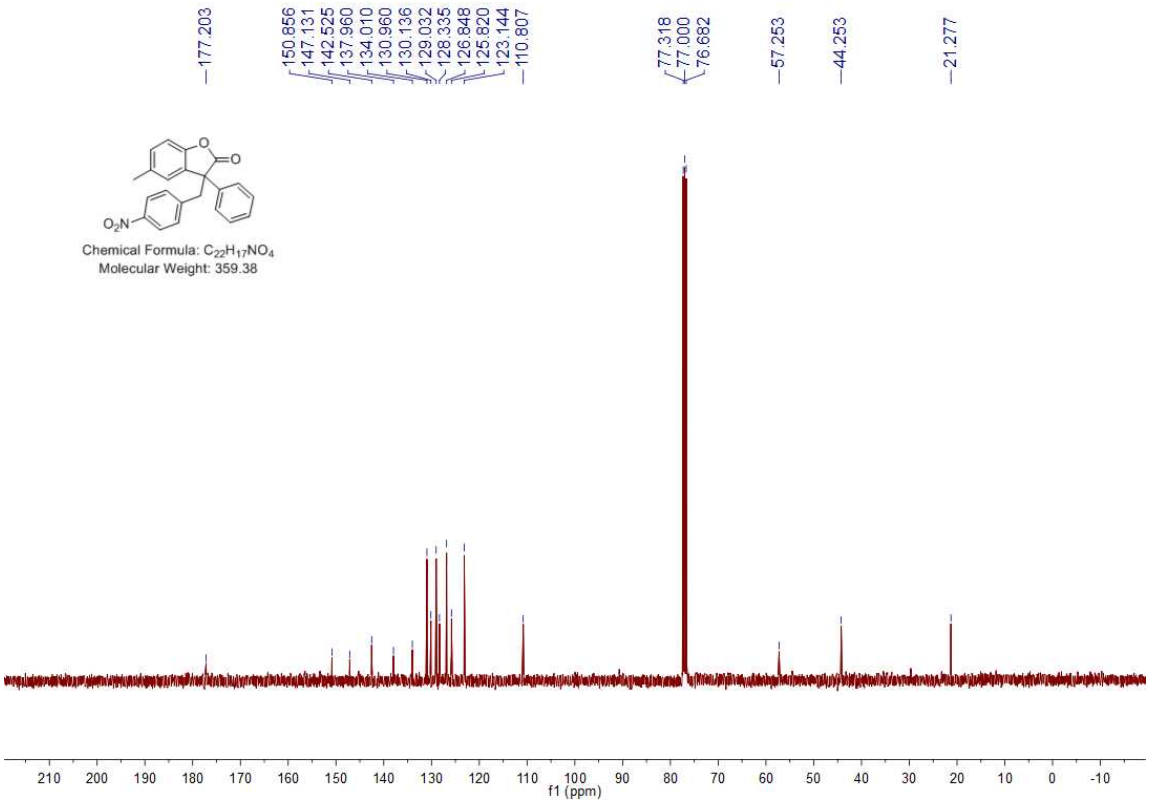
^{13}C NMR (101 MHz, Chloroform-d) spectrum for 4o'



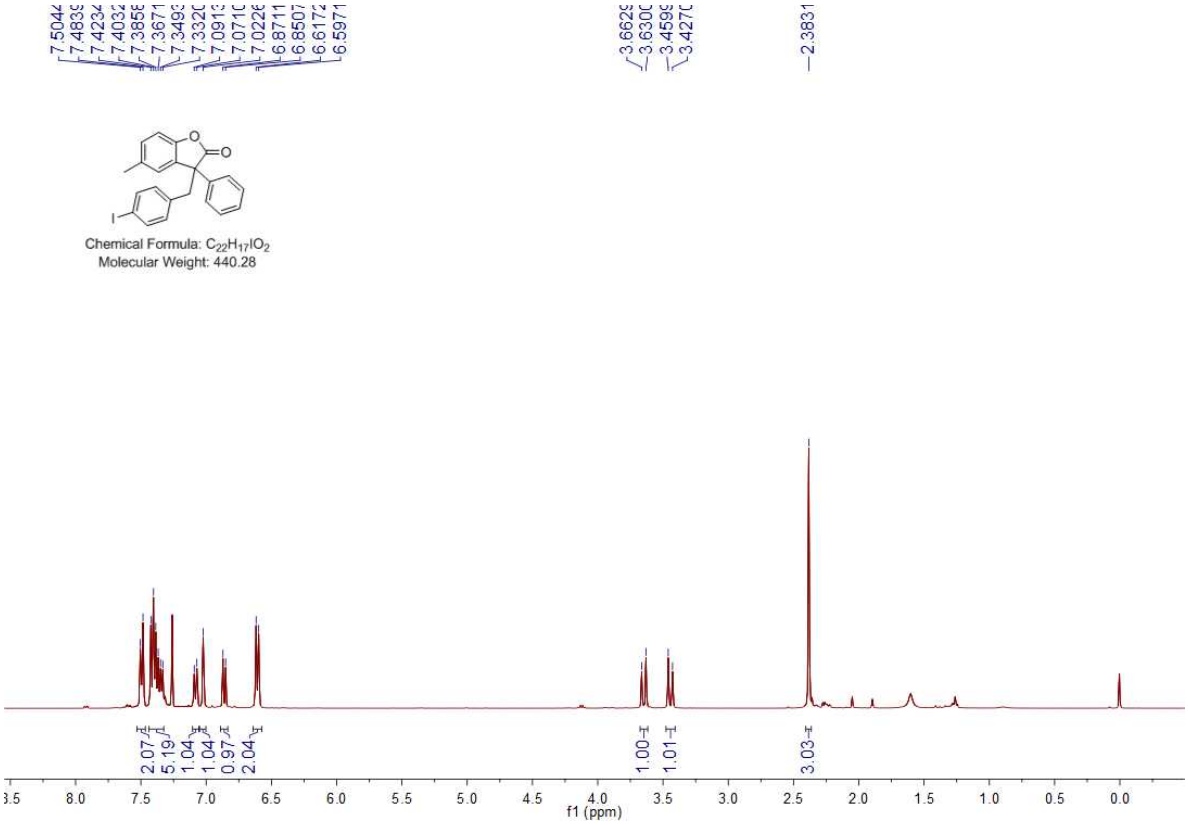
^{1}H NMR (400 MHz, Chloroform-d) spectrum for 4p



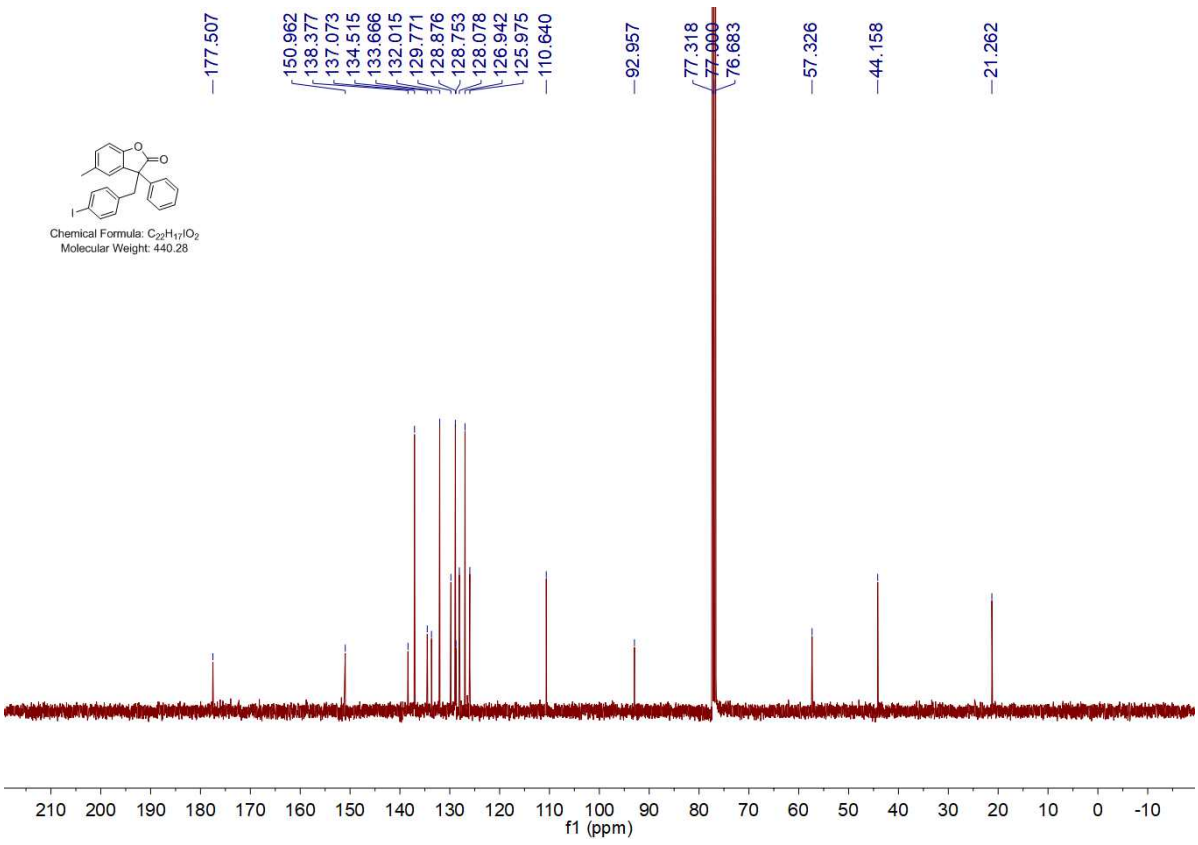
^{13}C NMR (101 MHz, Chloroform-d) spectrum for 4p



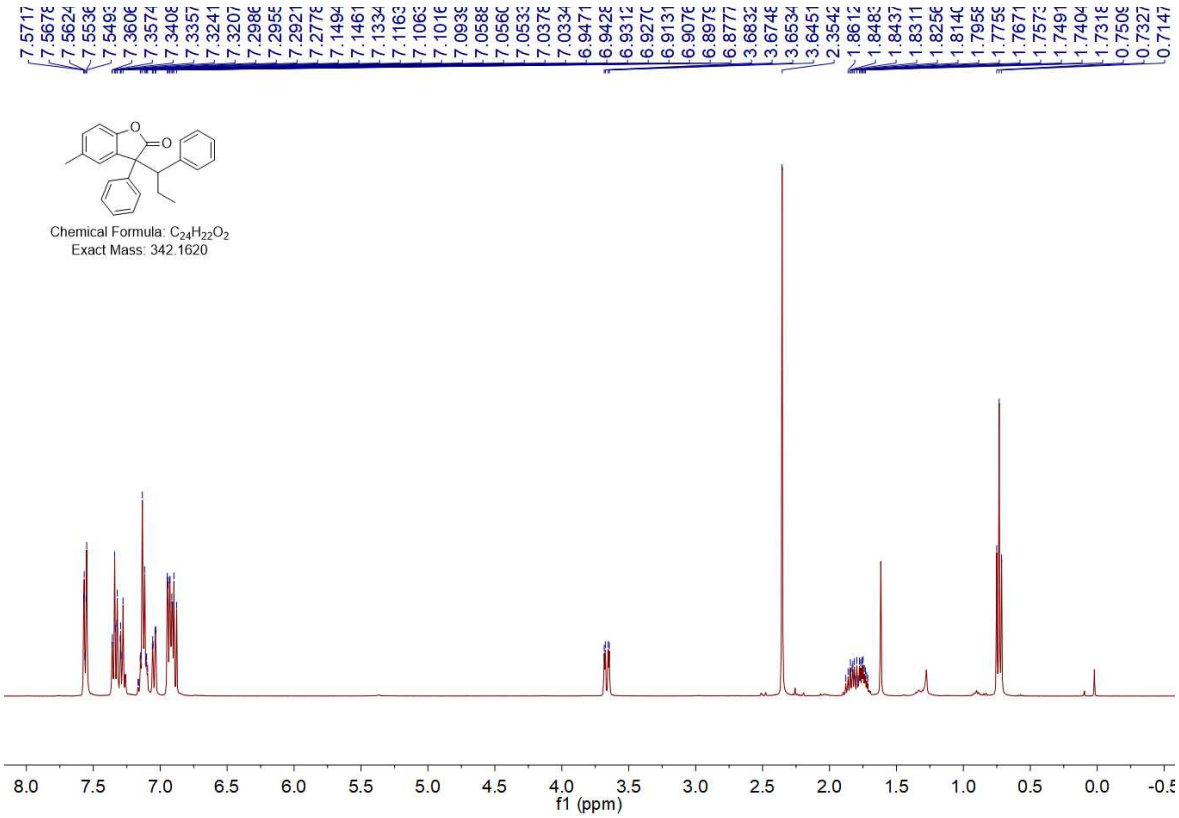
^{1}H NMR (400 MHz, Chloroform-d) spectrum for 4q



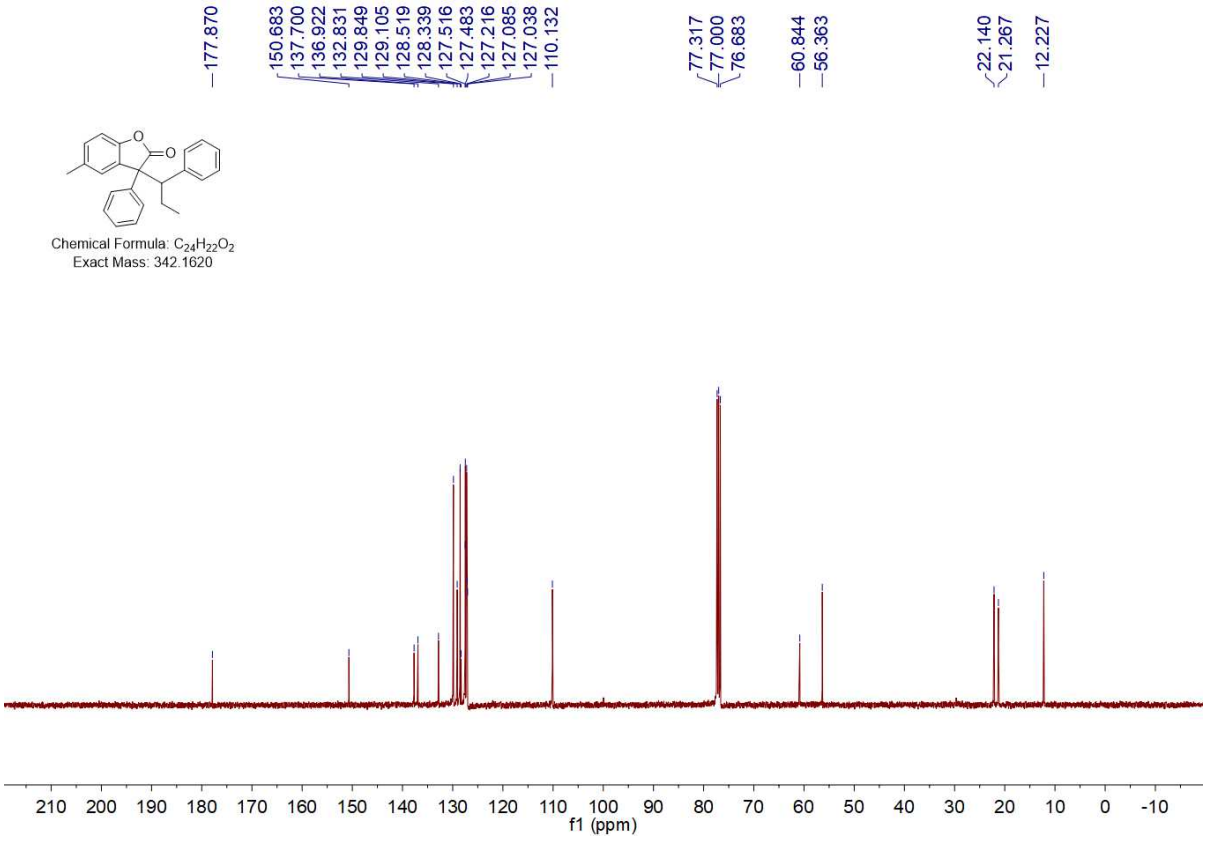
^{13}C NMR (101 MHz, Chloroform-d) spectrum for 4q



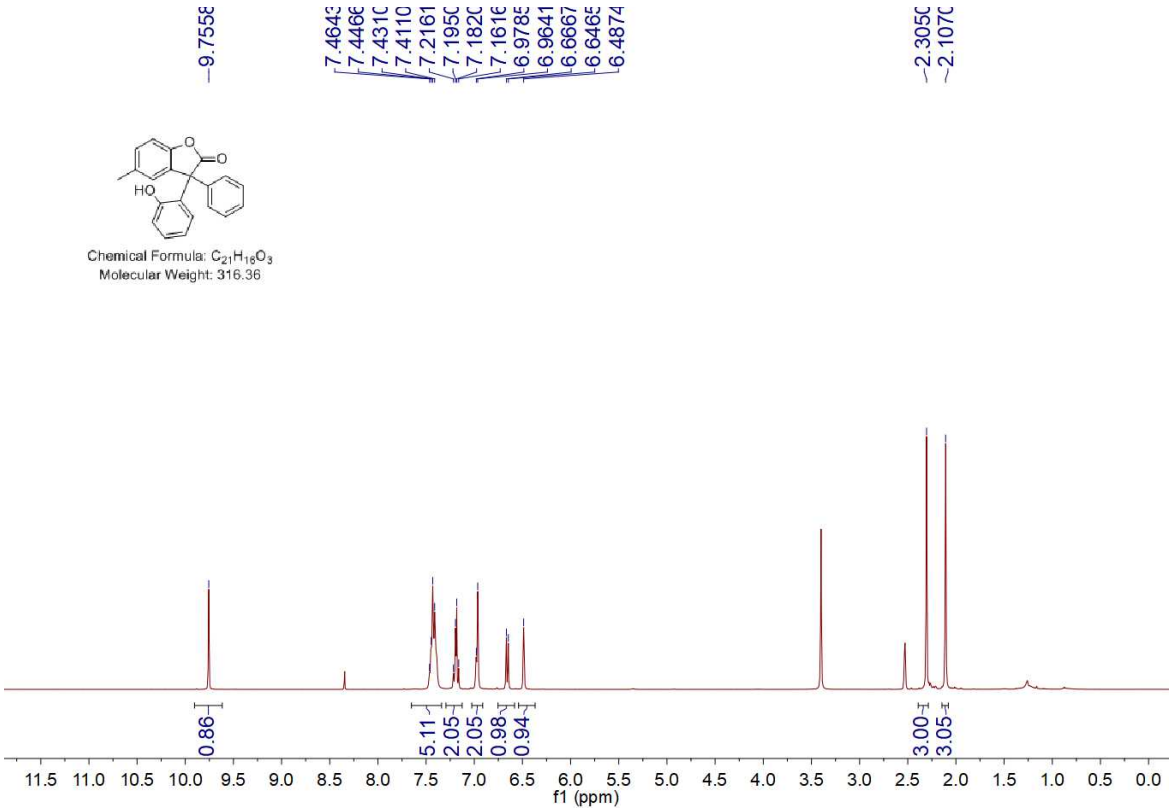
^{1}H NMR (400 MHz, Chloroform-d) spectrum for 4r



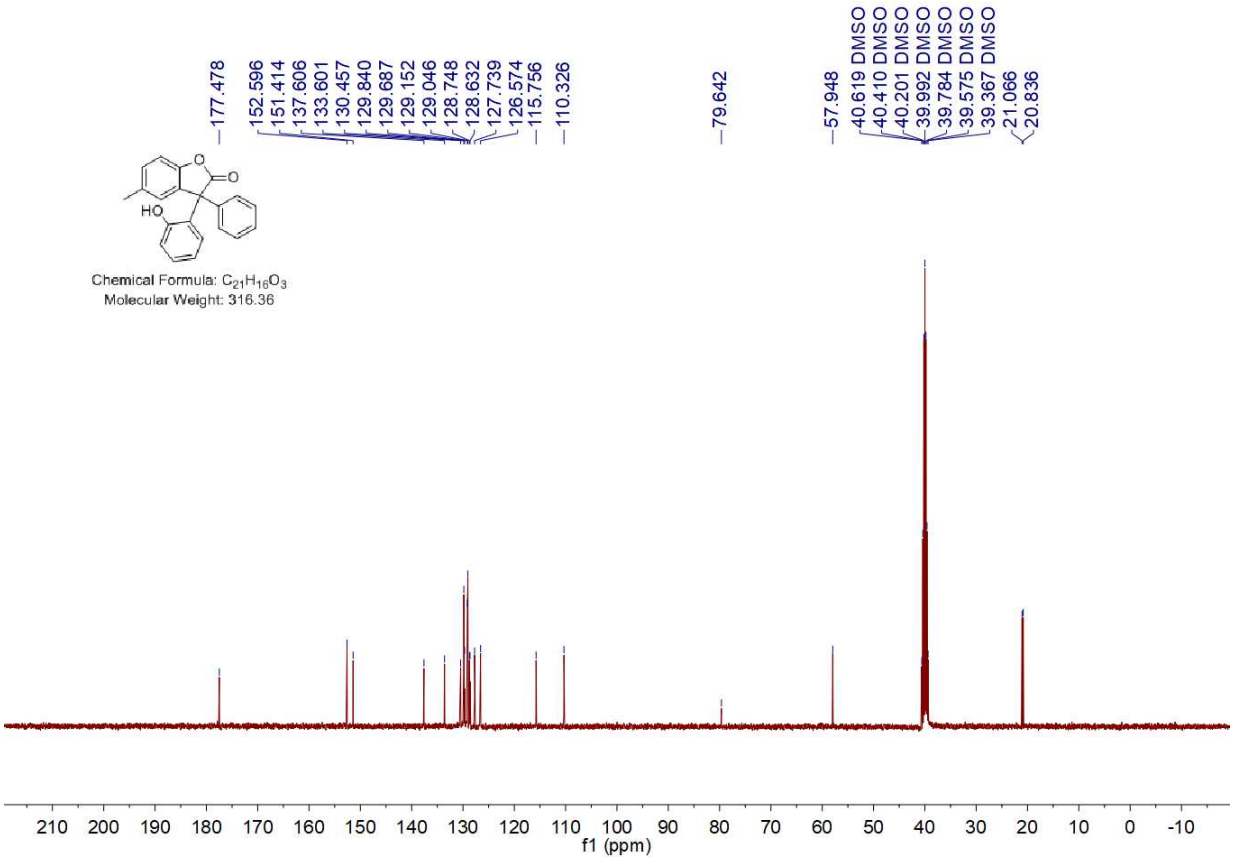
^{13}C NMR (101 MHz, Chloroform-d) spectrum for 4r



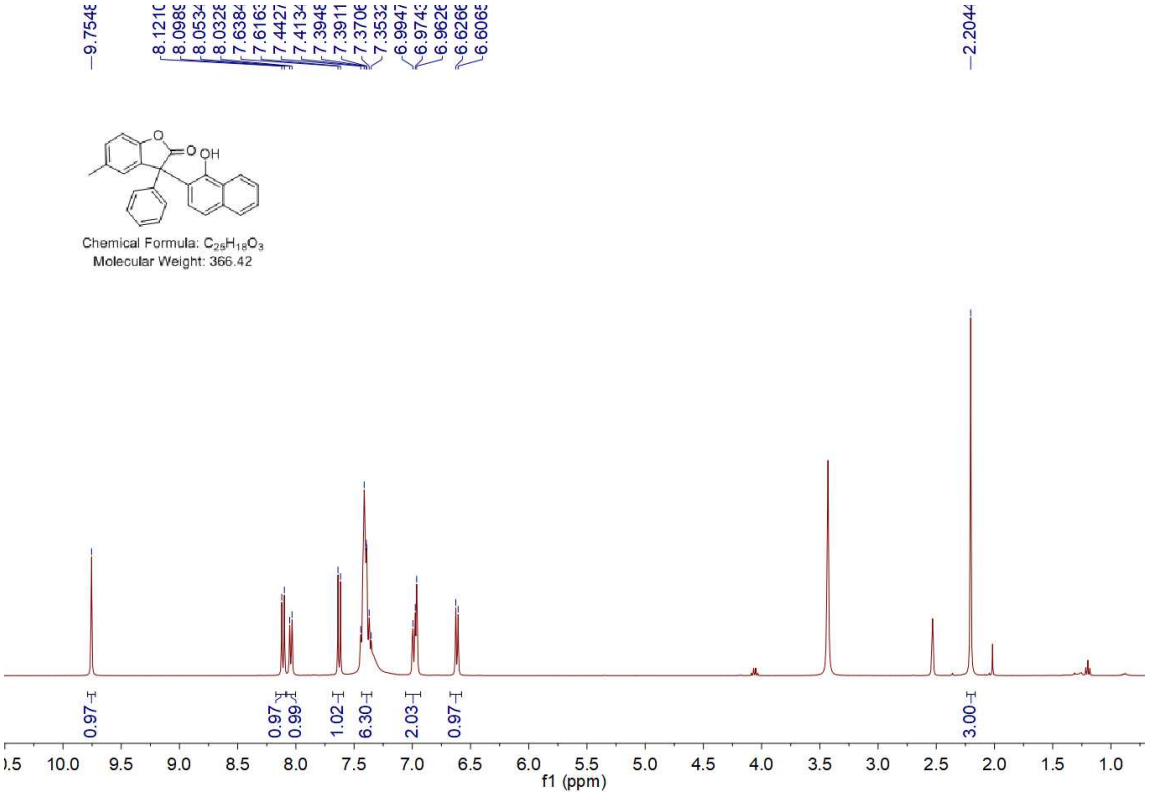
^{1}H NMR (400 MHz, DMSO-d) spectrum for 5a



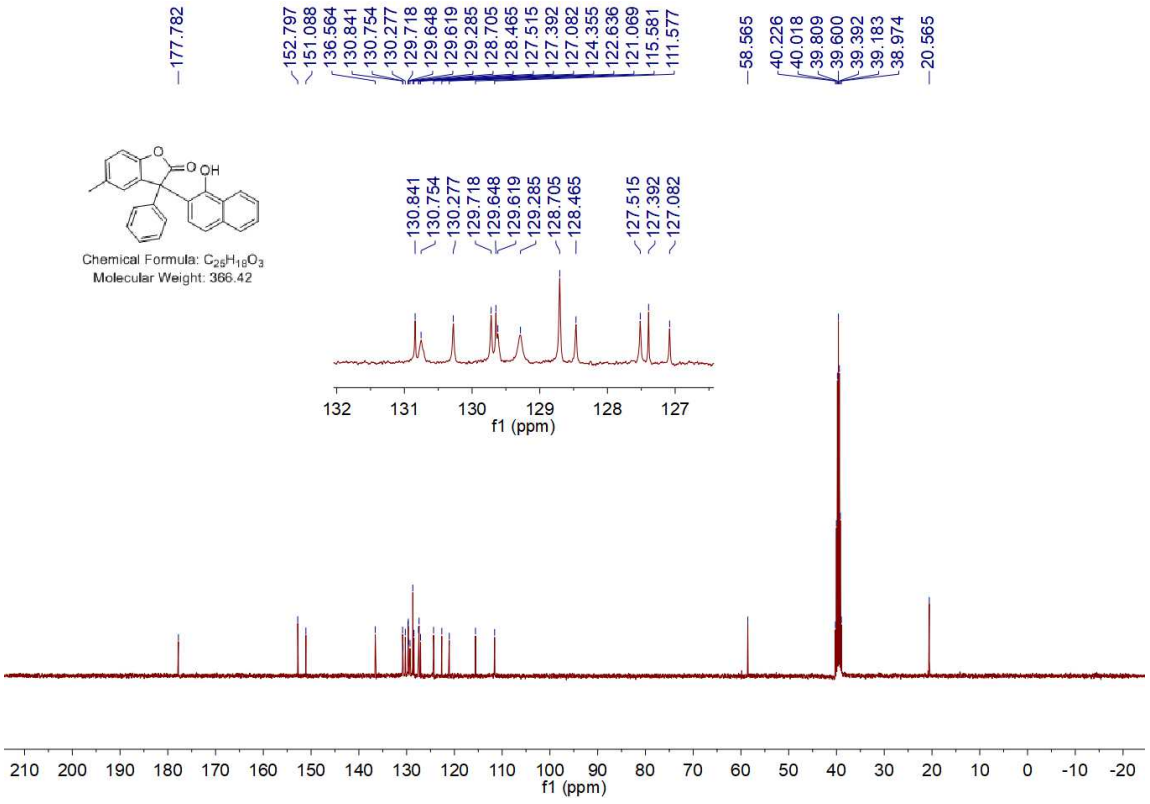
^{13}C NMR (101 MHz, DMSO-d) spectrum for 5a



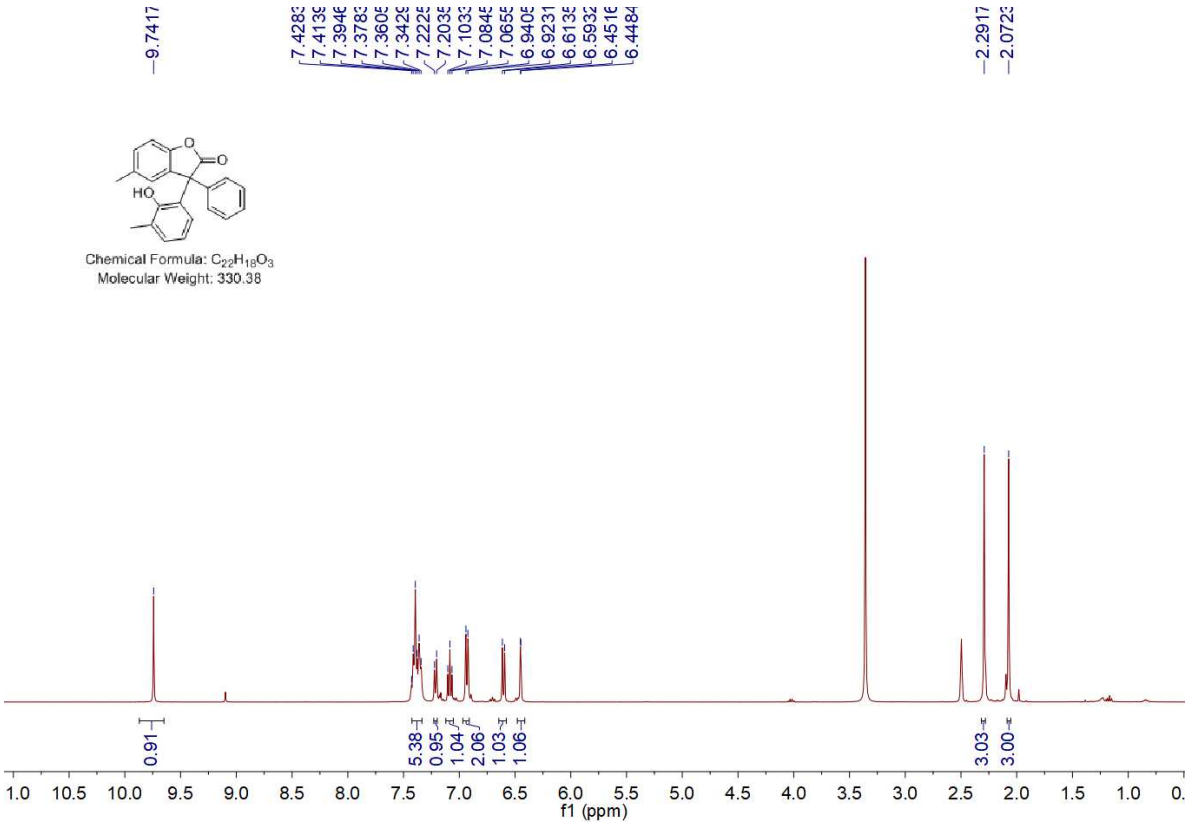
^{1}H NMR (400 MHz, DMSO-d) spectrum for 5b



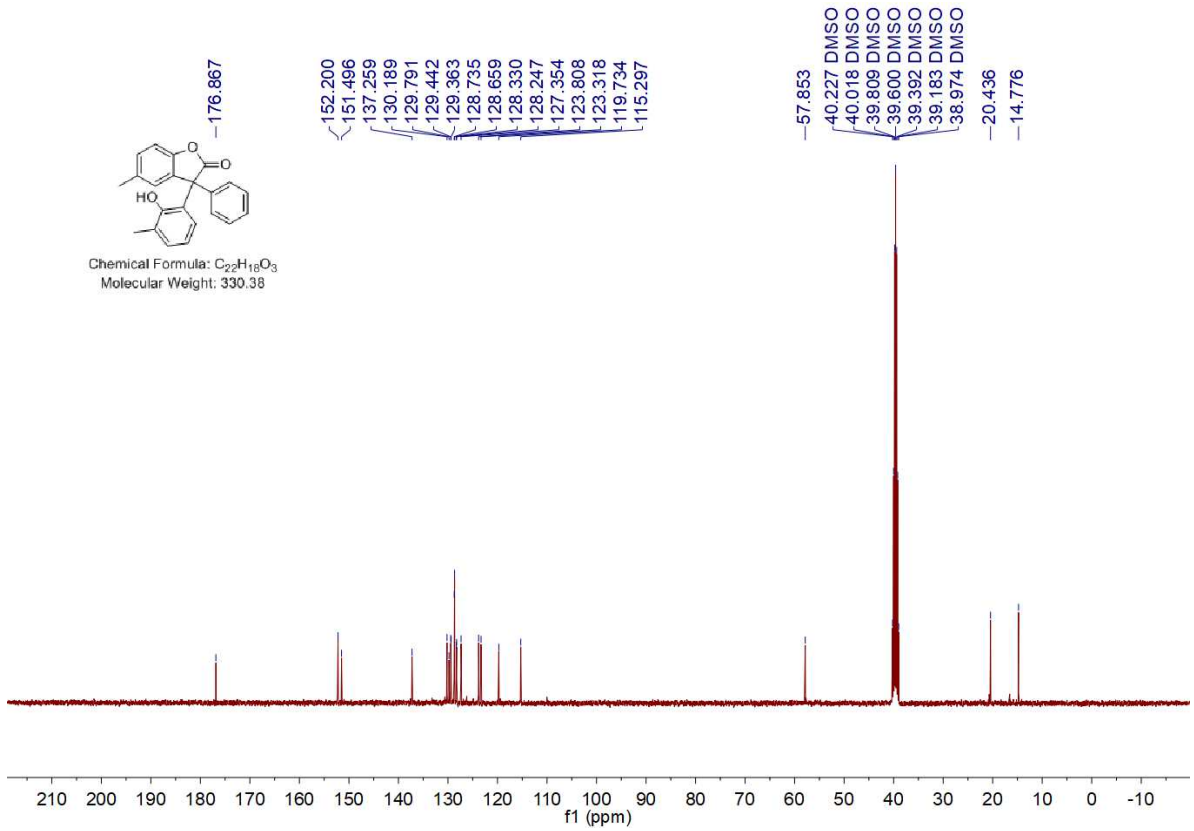
^{13}C NMR (101 MHz, DMSO-d) spectrum for 5b



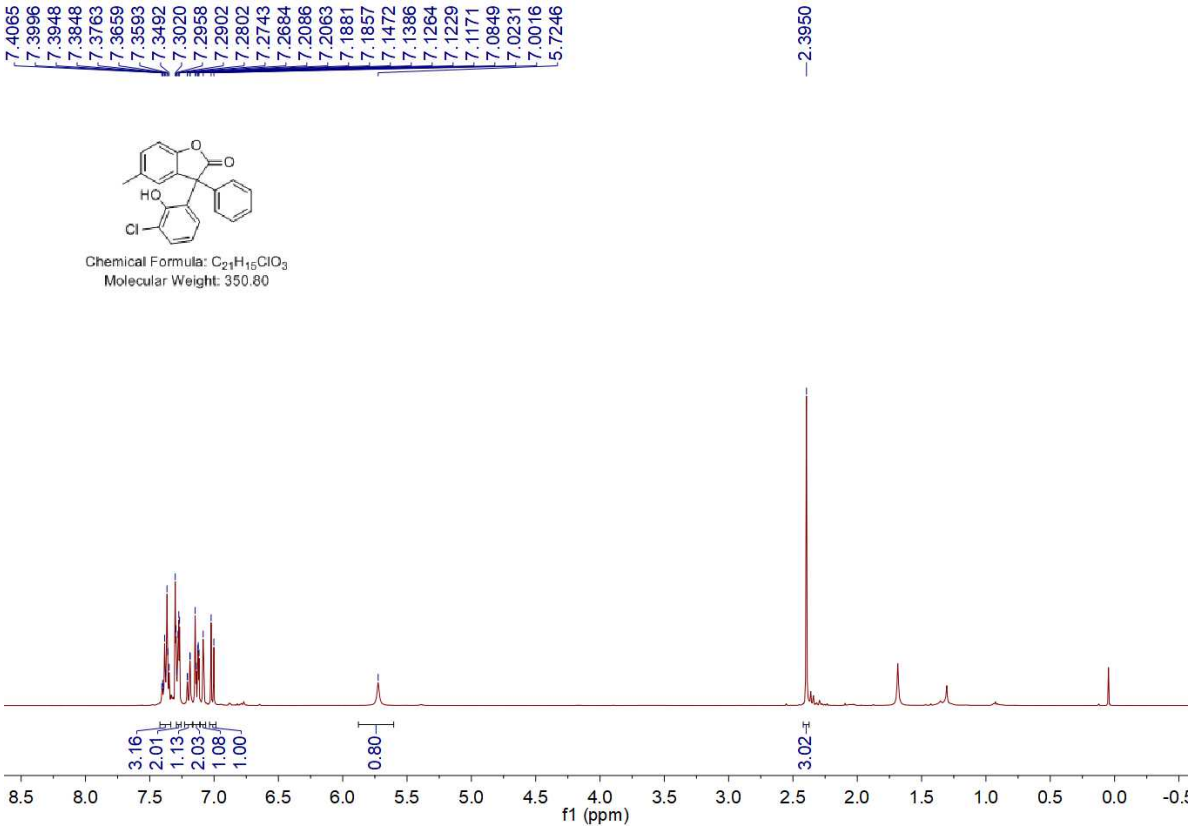
^{1}H NMR (400 MHz, DMSO-d) spectrum for 5c



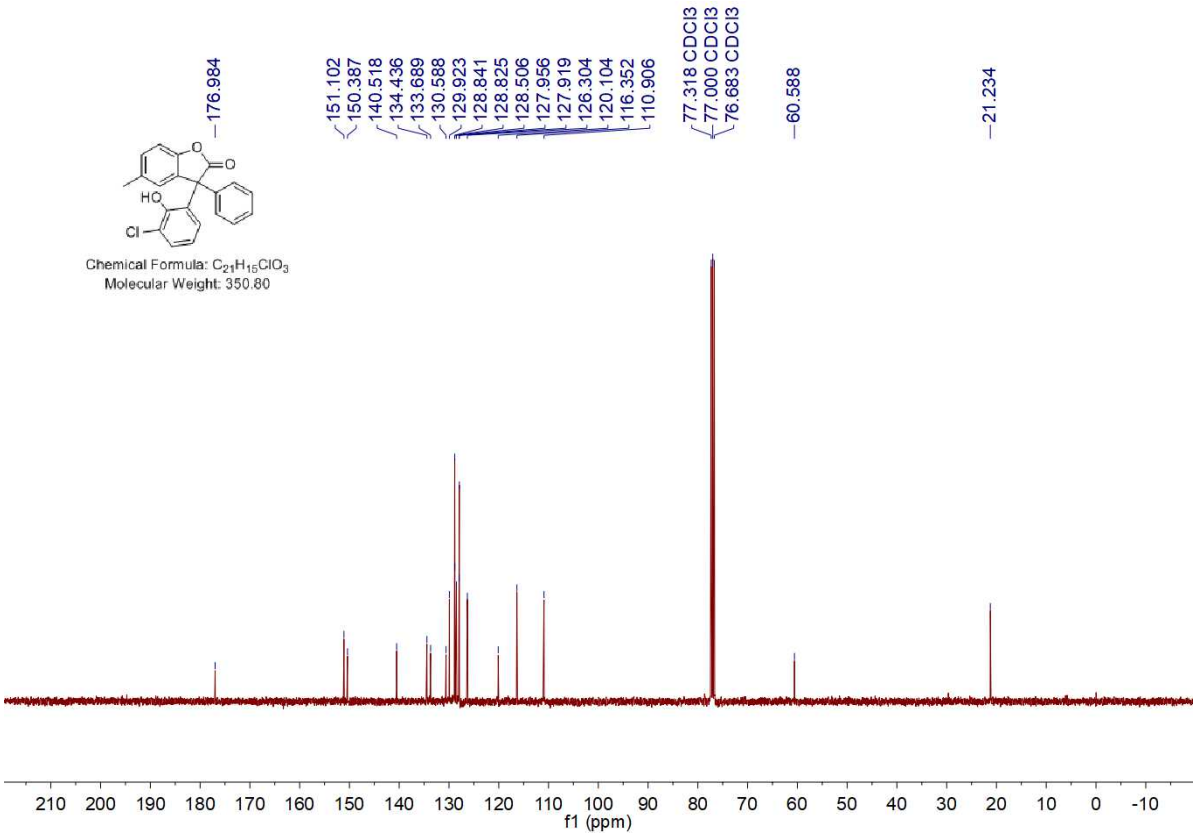
^{13}C NMR (101 MHz, DMSO-d) spectrum for 5c



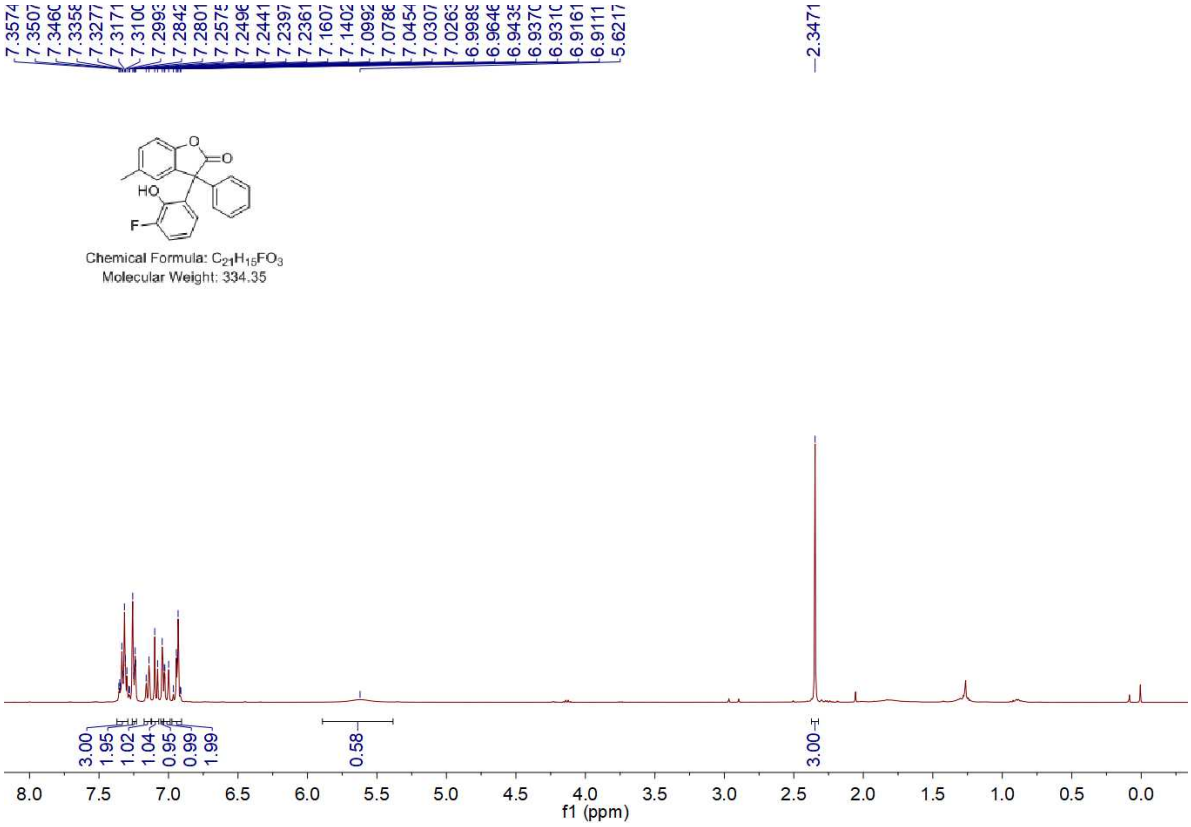
^{1}H NMR (400 MHz, Chloroform-d) spectrum for 5d



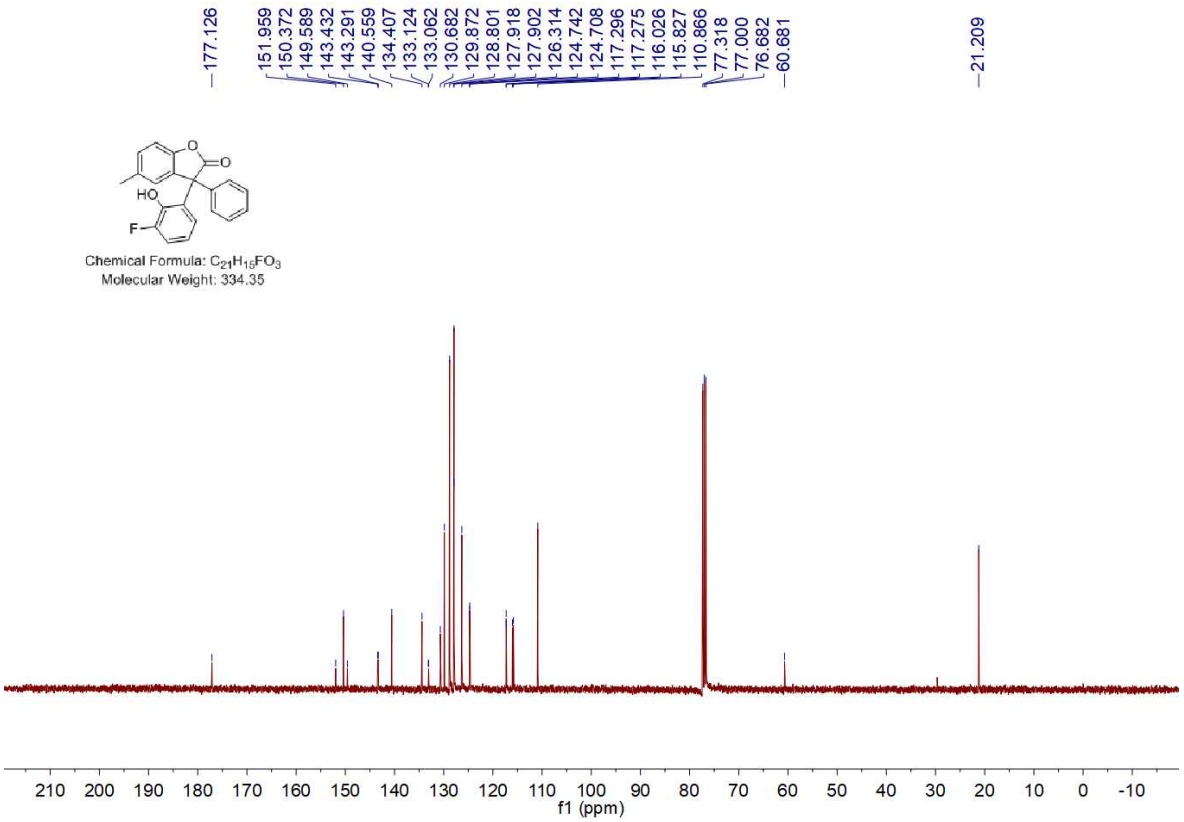
^{13}C NMR (101 MHz, Chloroform-d) spectrum for 5d



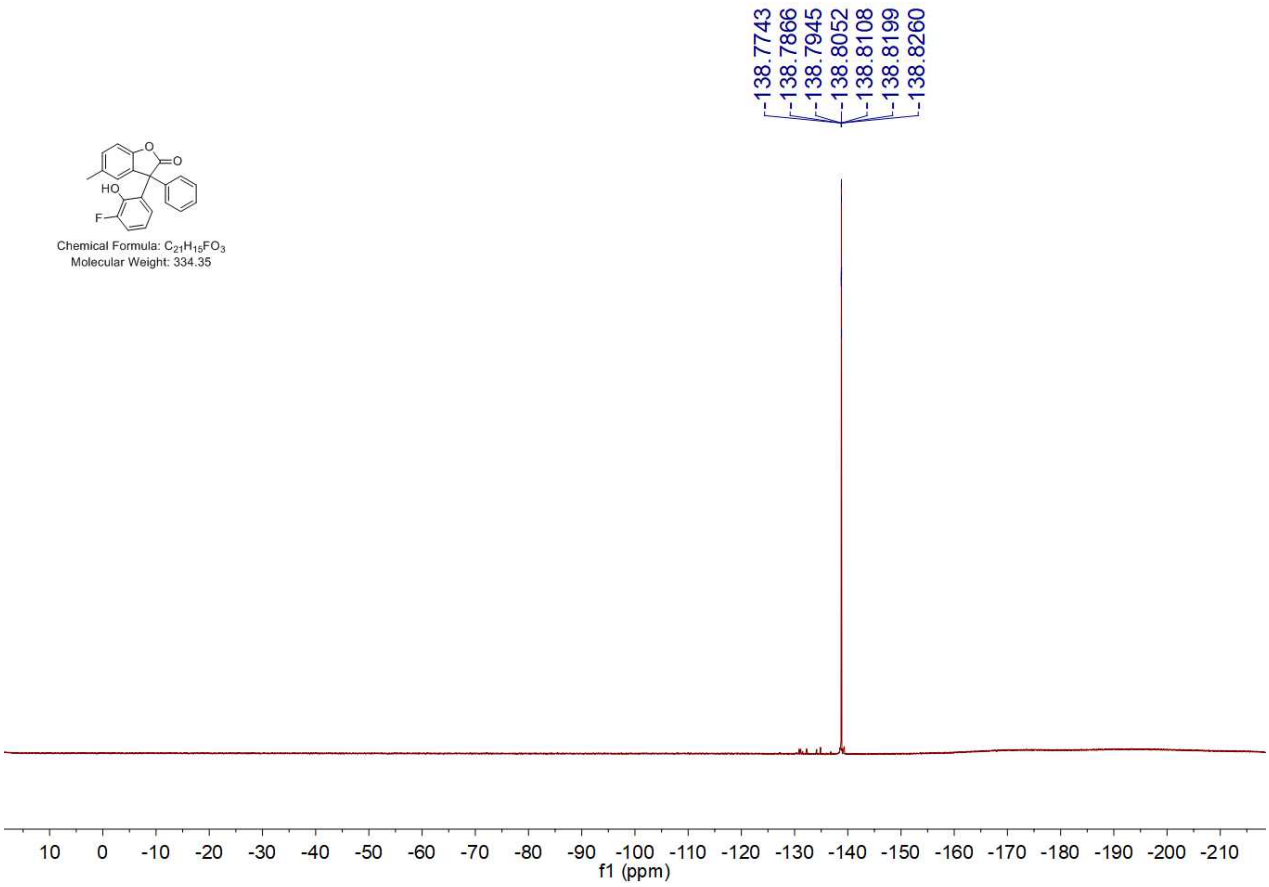
^{1}H NMR (400 MHz, DMSO-d) spectrum for 5e



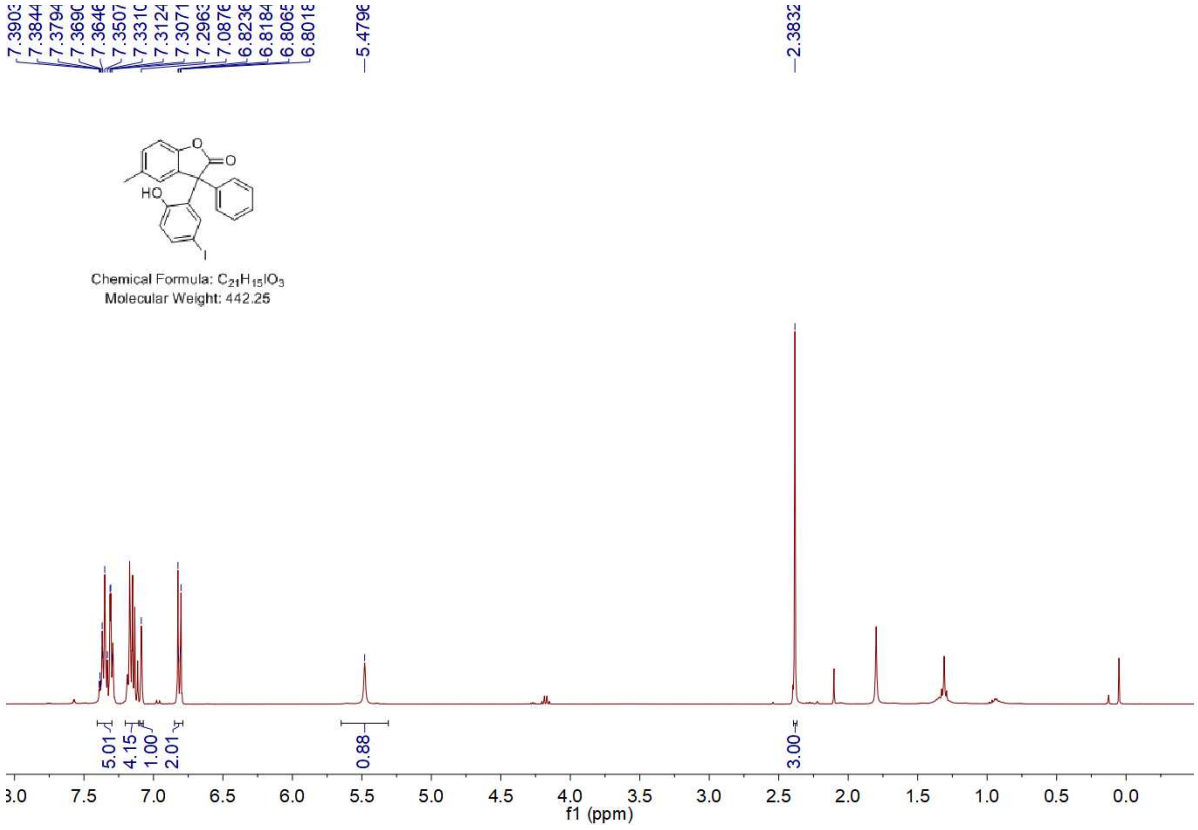
^{13}C NMR (101 MHz, DMSO-d) spectrum for 5e



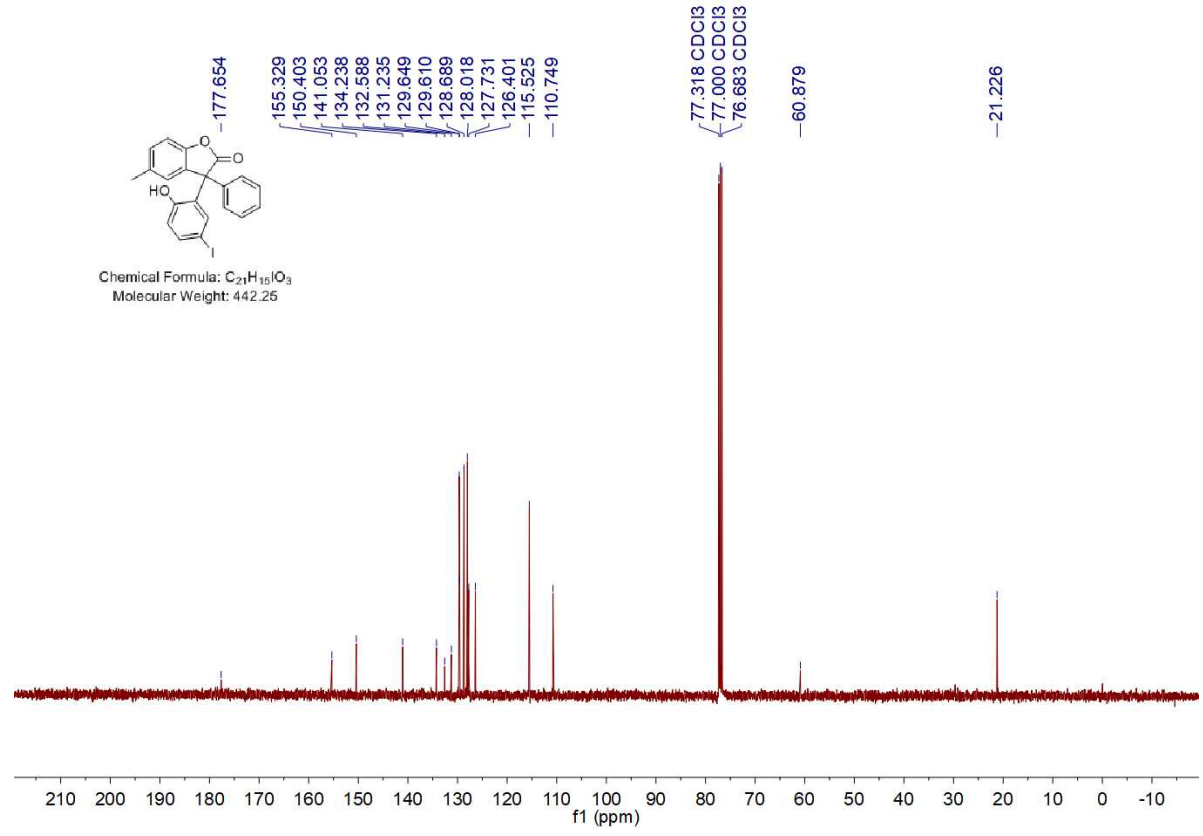
^{19}F NMR (376 MHz, DMSO-d) spectrum for 5e



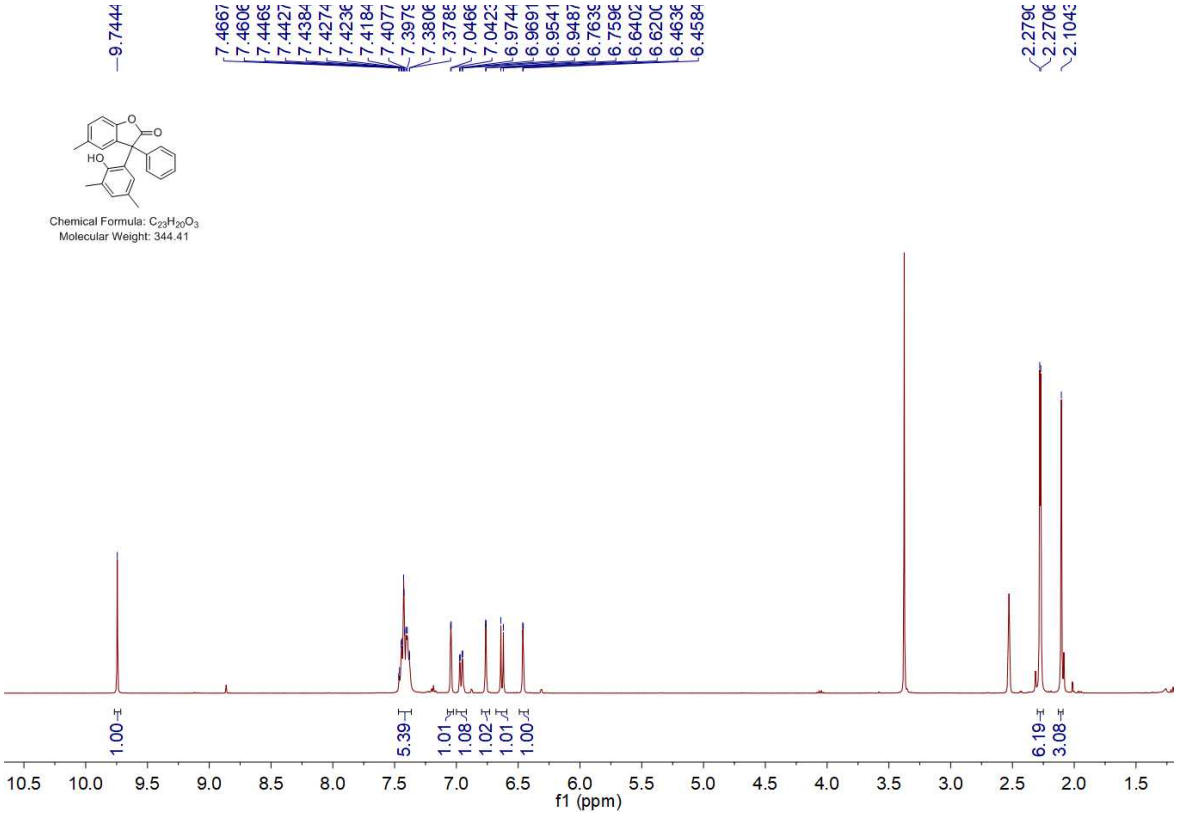
^{1}H NMR (400 MHz, Chloroform-d) spectrum for 5f



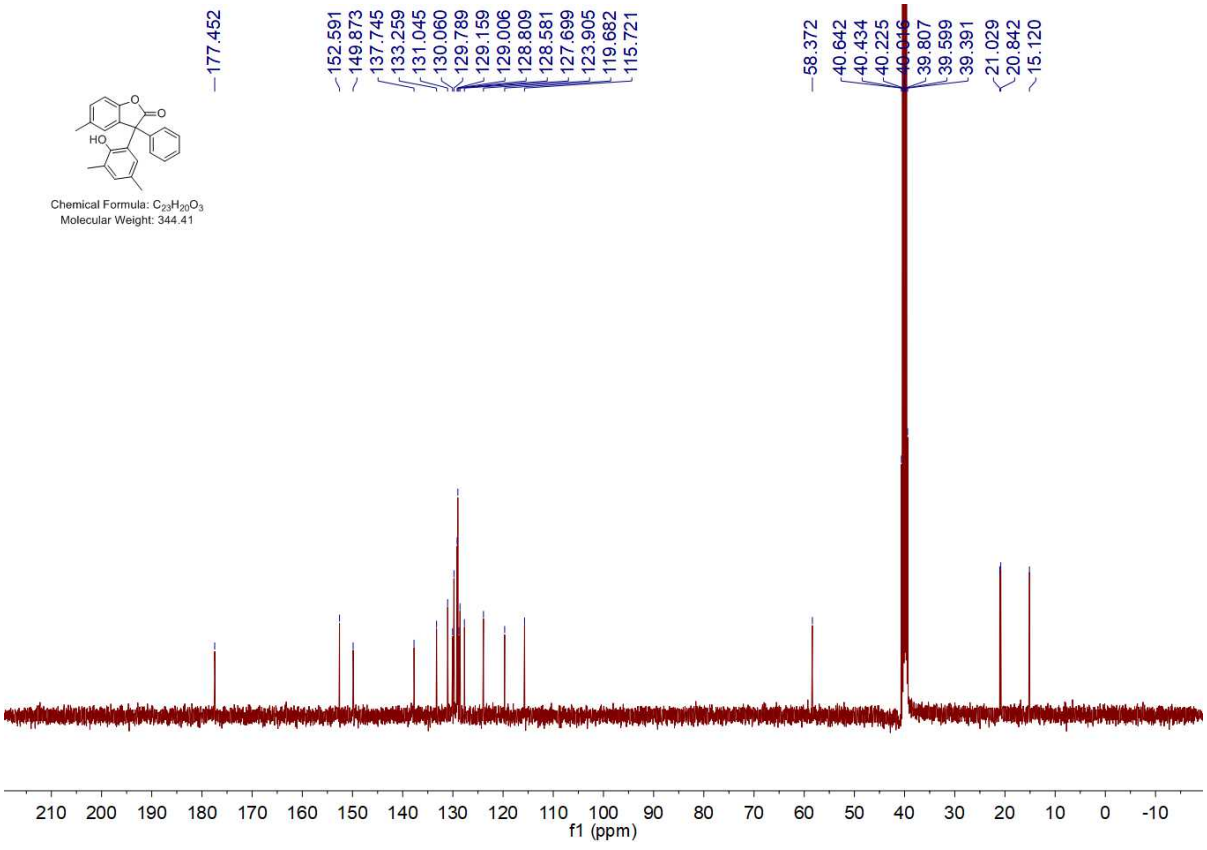
^{13}C NMR (101 MHz, Chloroform-d) spectrum for 5f



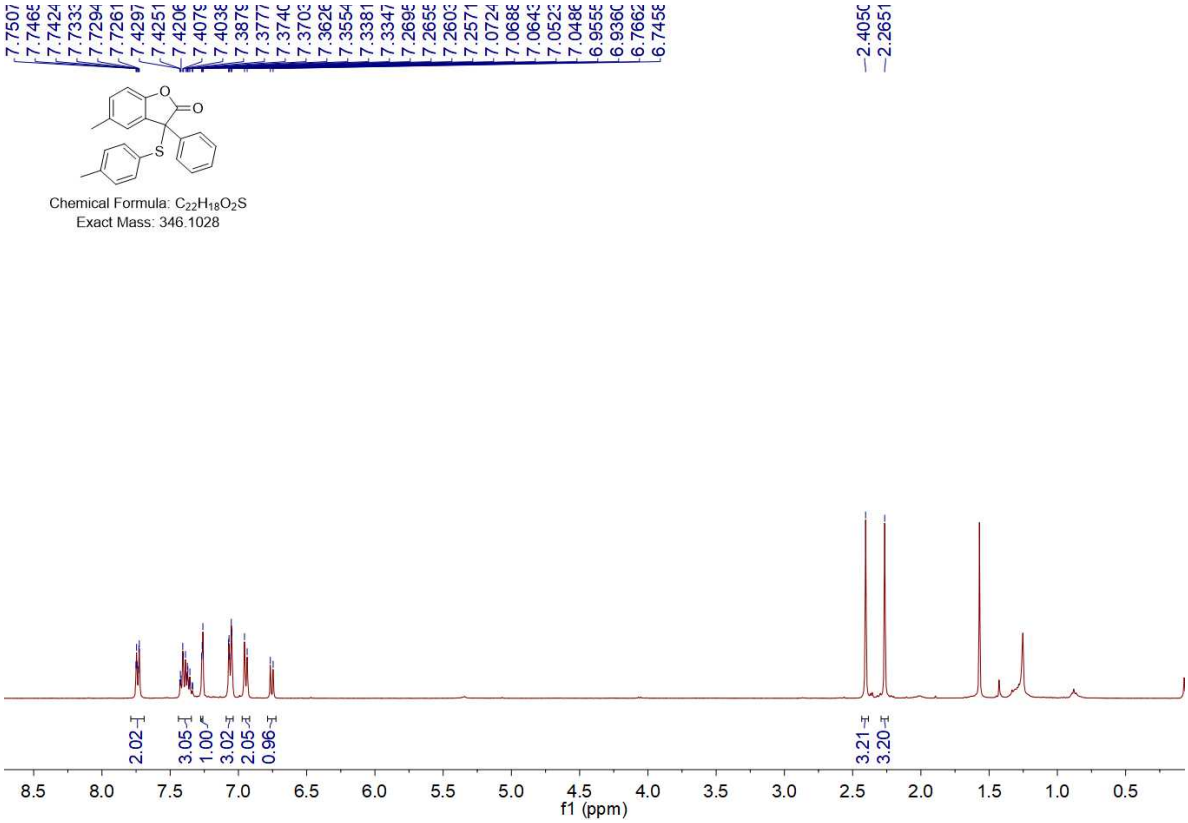
^{1}H NMR (400 MHz, DMSO-d) spectrum for 5g



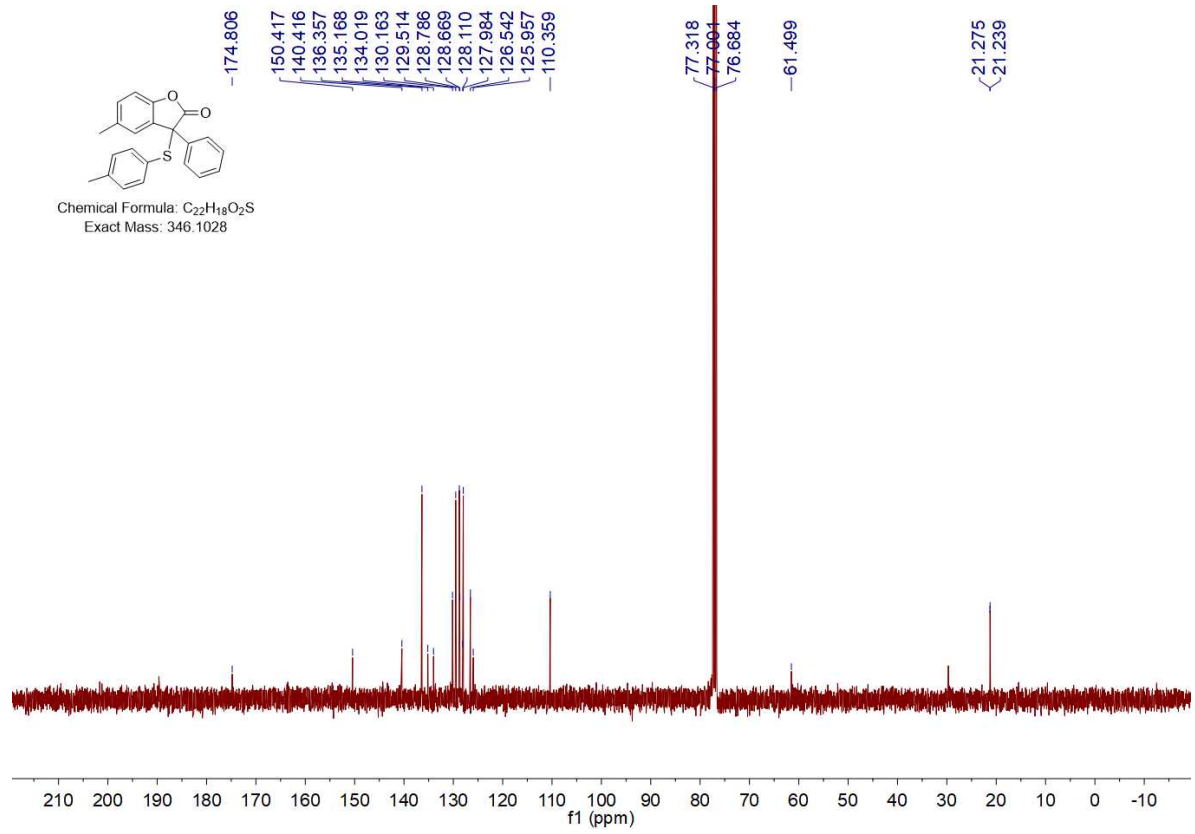
^{13}C NMR (101 MHz, DMSO-d) spectrum for 5g



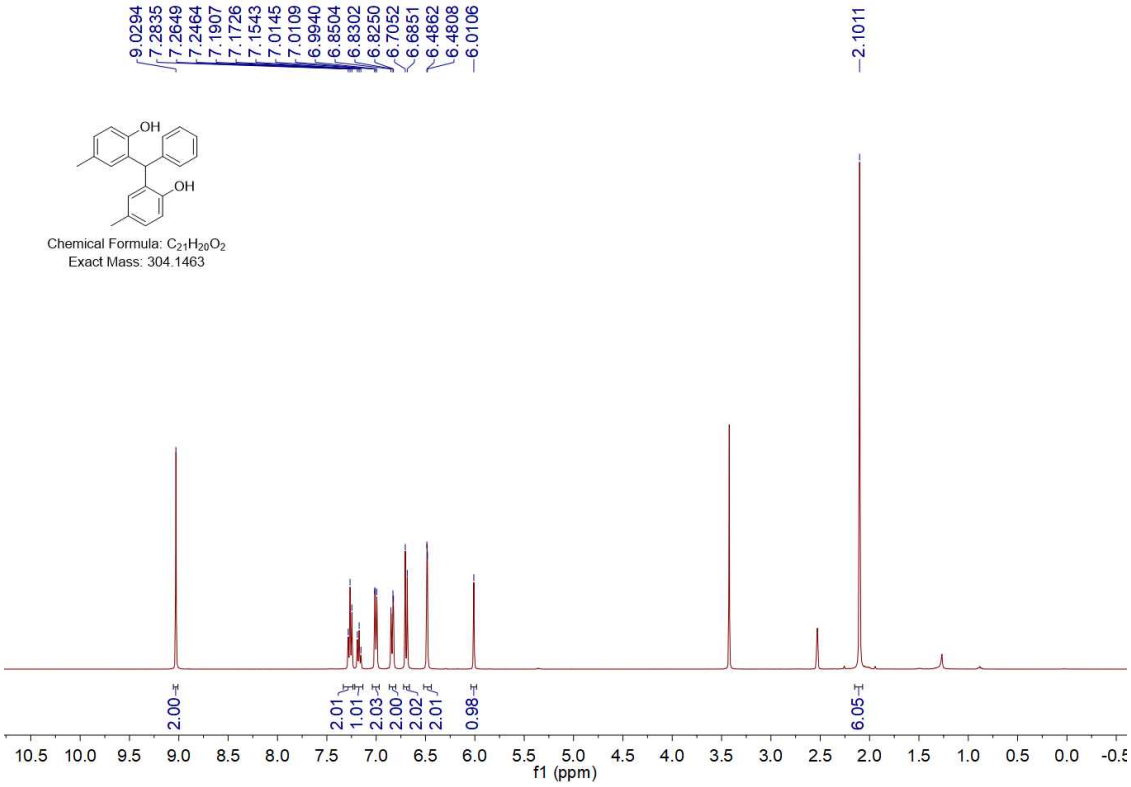
^{1}H NMR (400 MHz, Chloroform-d) spectrum for 6a



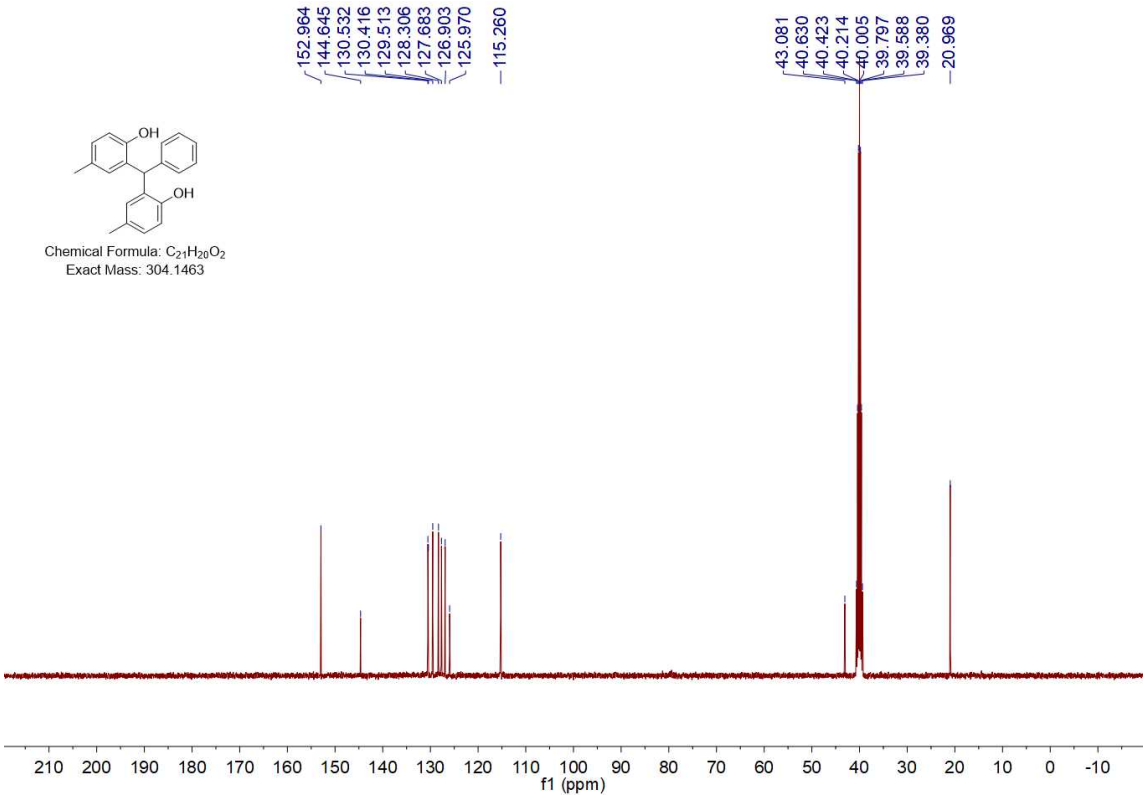
^{13}C NMR (101 MHz, Chloroform-d) spectrum for 6a



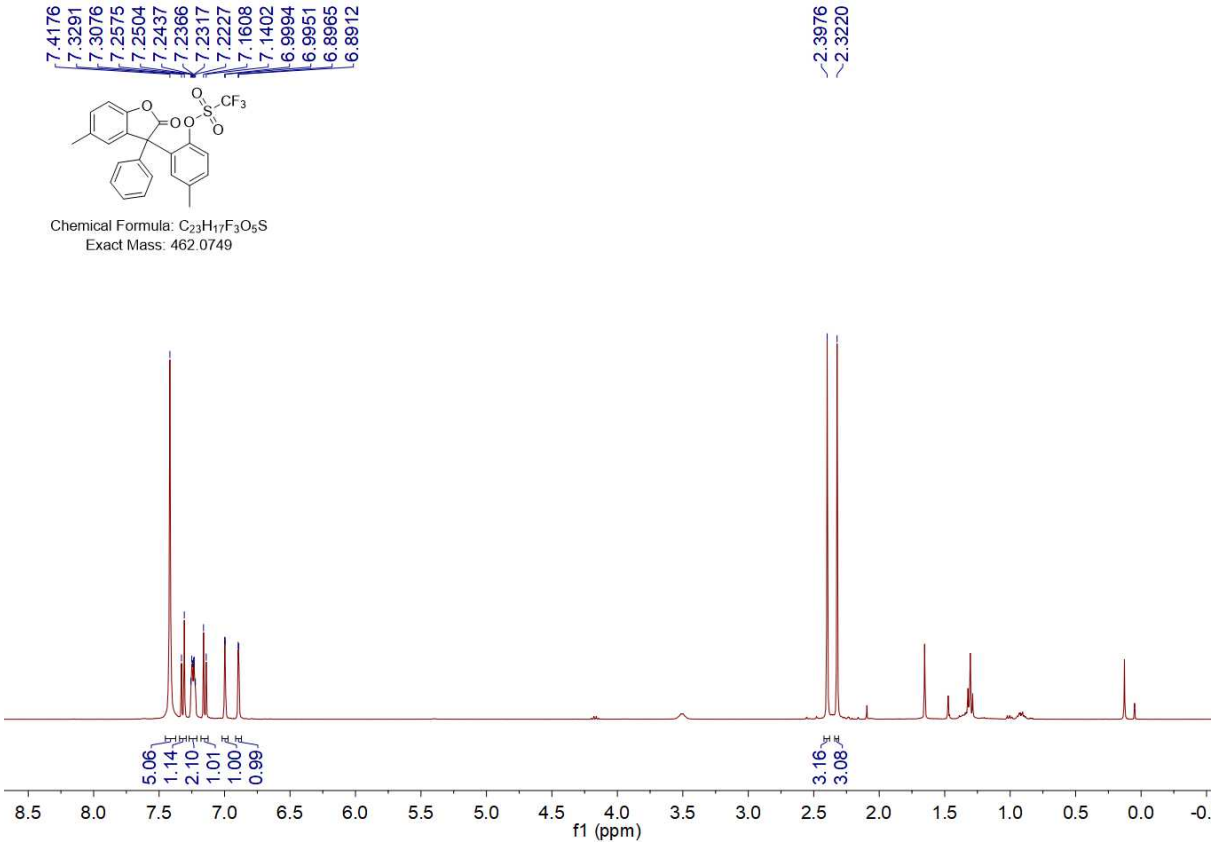
^{1}H NMR (400 MHz, DMSO-d) spectrum for 7



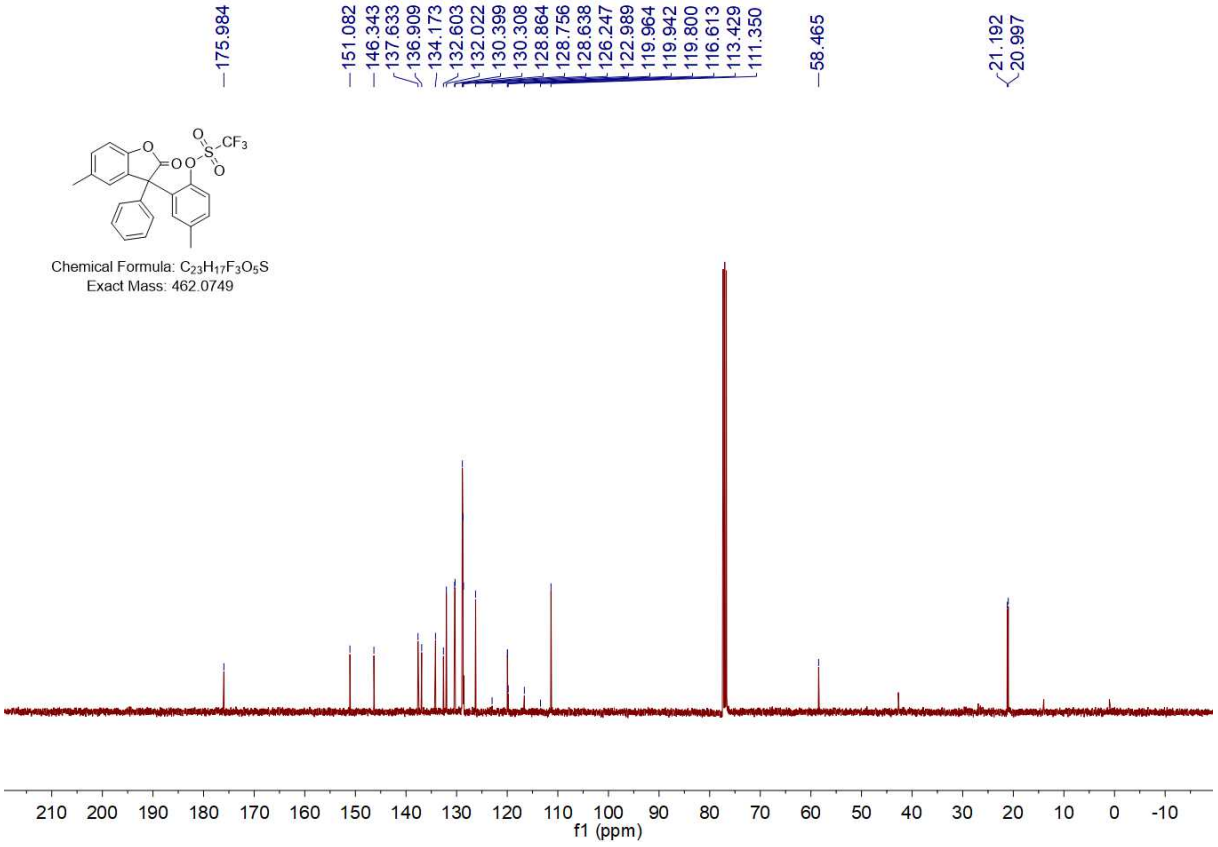
^{13}C NMR (101 MHz, DMSO-d) spectrum for 7



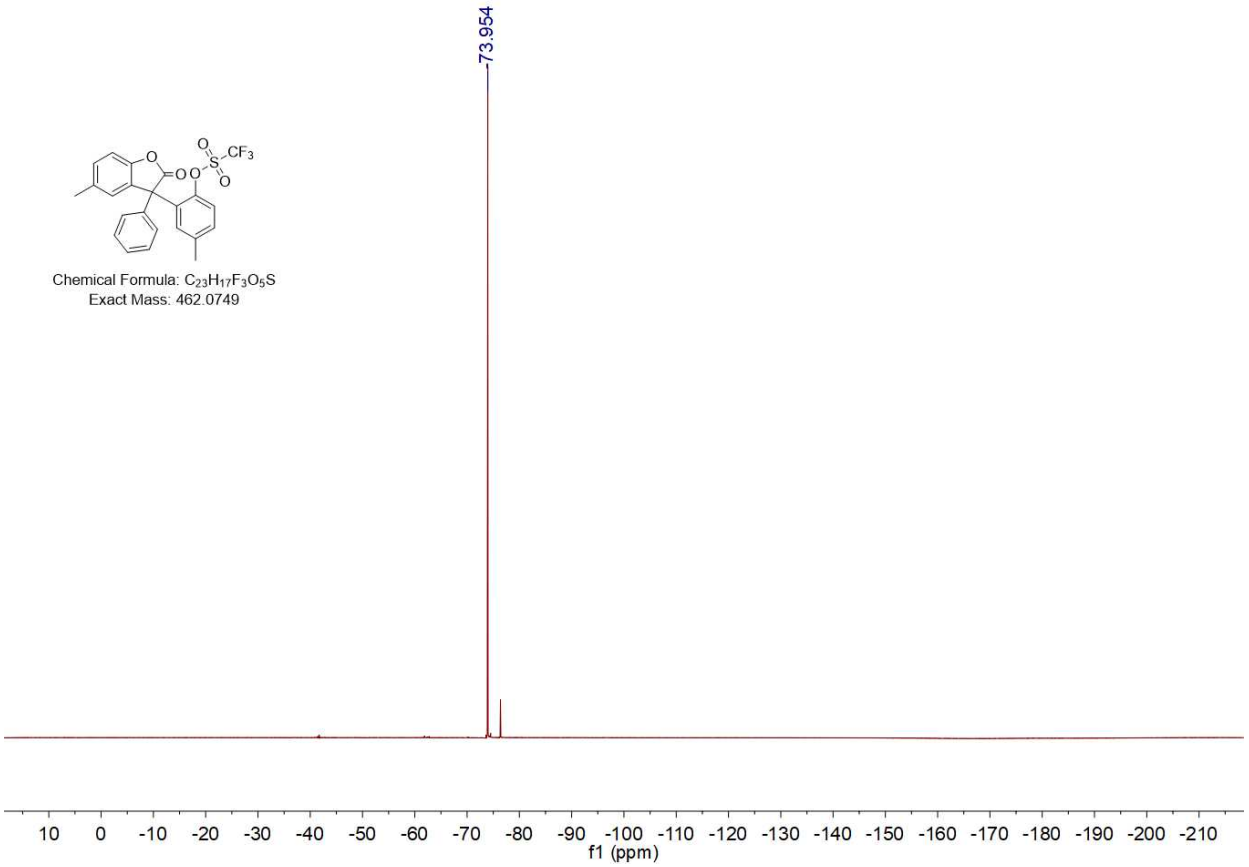
^{1}H NMR (400 MHz, Chloroform-d) spectrum for 8



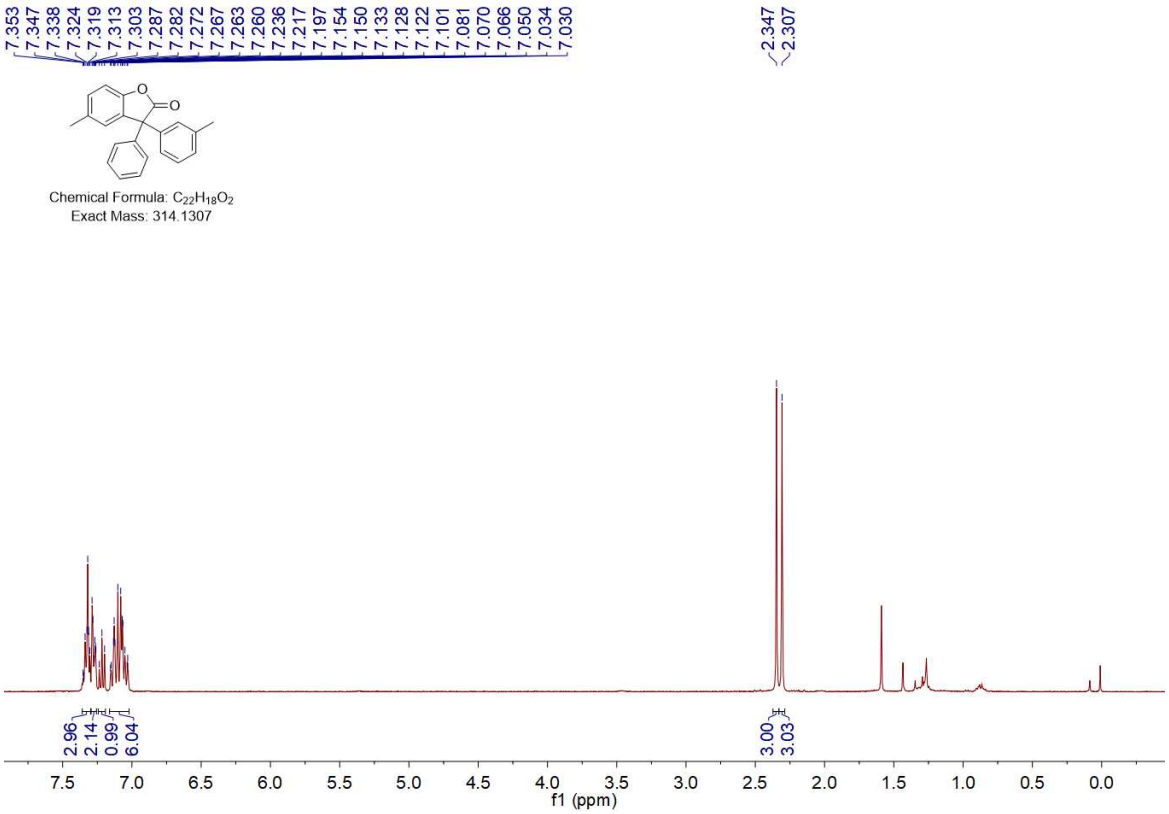
^{13}C NMR (101 MHz, Chloroform-d) spectrum for 8



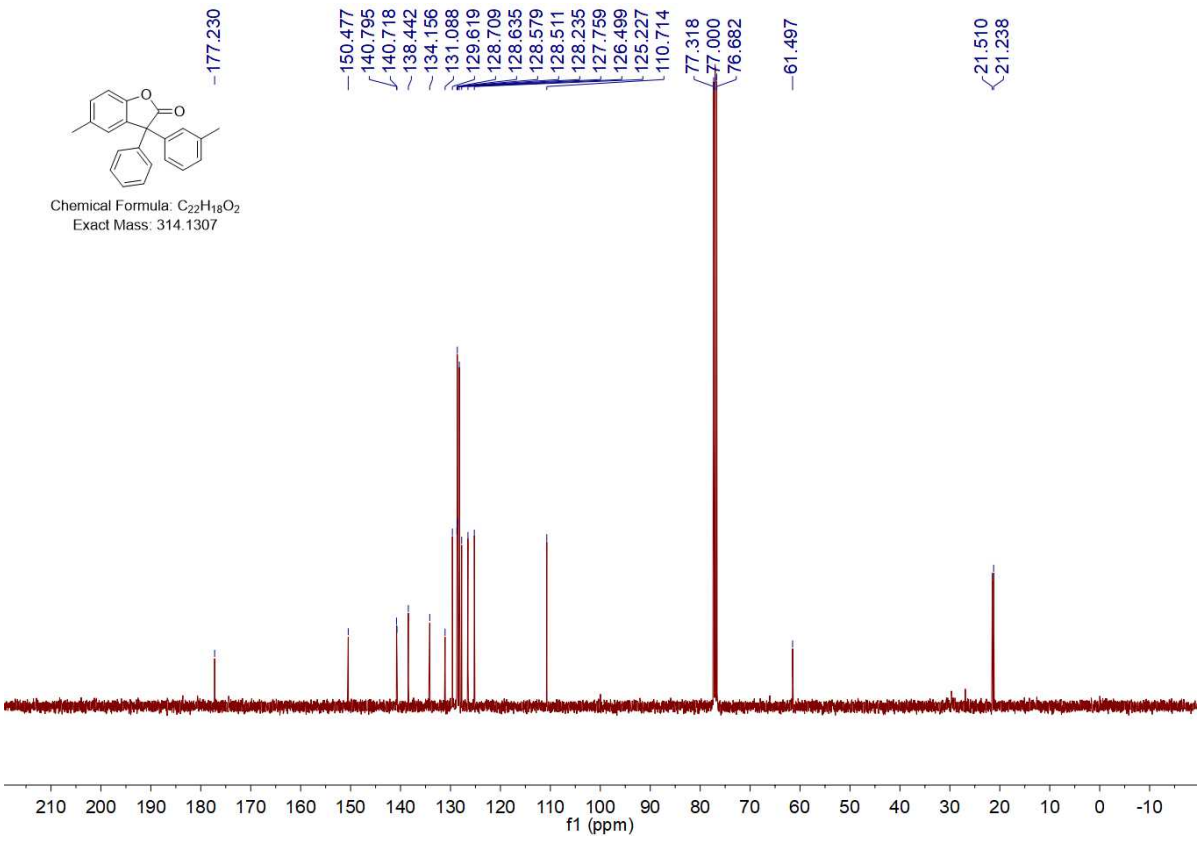
^{19}F NMR (376 MHz, Chloroform-d) spectrum for 8



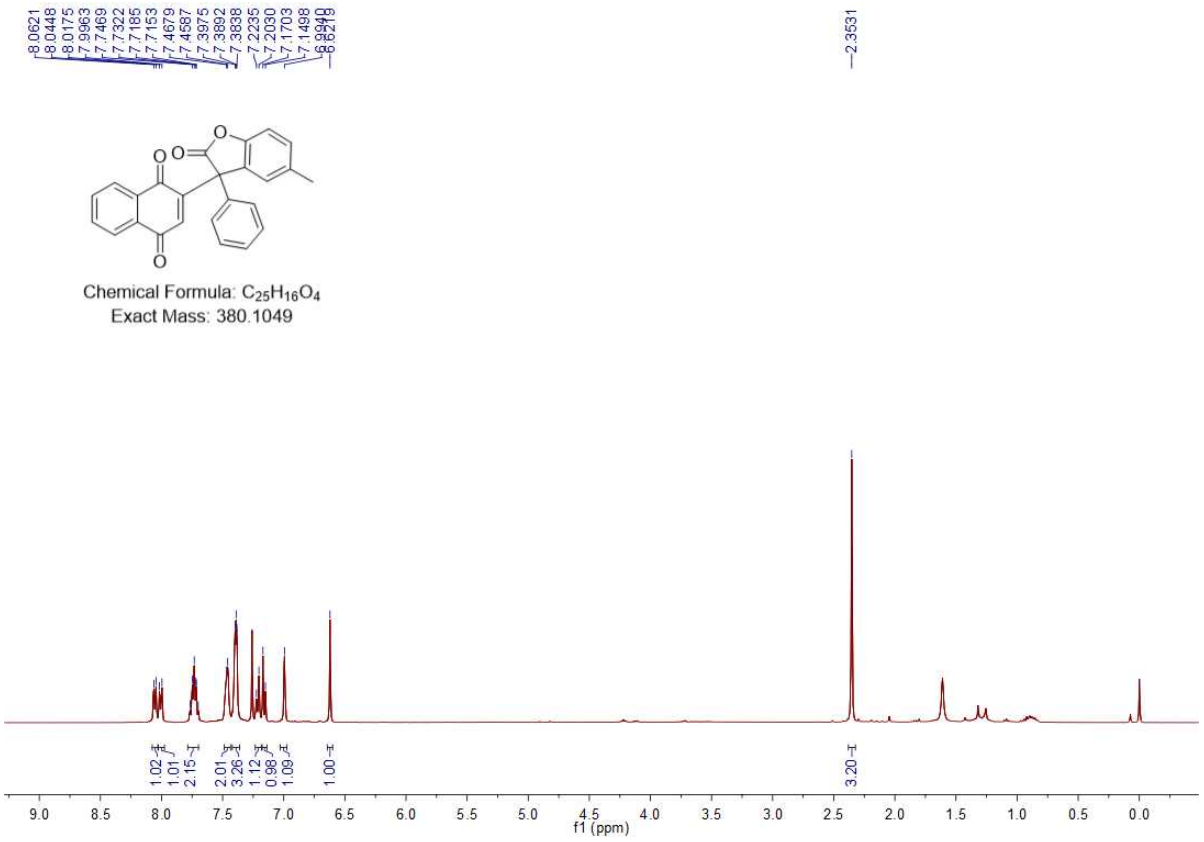
^{1}H NMR (400 MHz, Chloroform-d) spectrum for 9



^{13}C NMR (101 MHz, Chloroform-d) spectrum for 9



^{1}H NMR (400 MHz, Chloroform-d) spectrum for 11



^{13}C NMR (101 MHz, Chloroform-d) spectrum for 11