Supporting Information

A one-pot Synthesis of 2,3-Dihydrobenzofurans, Benzofuran-2(3H)-ones, and Indoles via [4 + 1] Annulation Reaction of *ortho*-substituted *para*-Quinone Methides and Bromonitromethane

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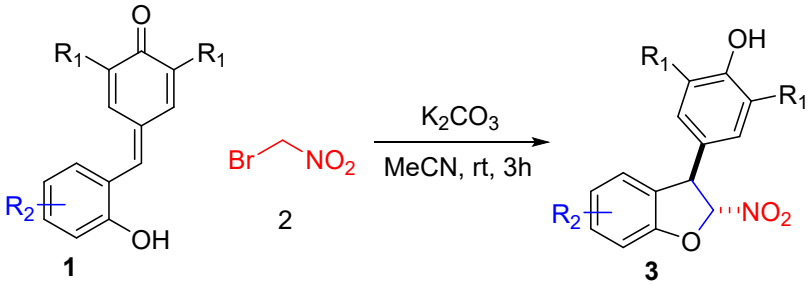
1. General Information

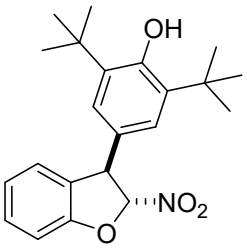
Unless otherwise noted, all commercially available components, as well as reagents, and solvents, were obtained from suppliers and used without further purification. Analytical thin layer chromatography (TLC) was performed using a Merck 60 F_{254} precoated silica gel plate (0.2 mm thickness). After elution, plates were visualized using UV radiation (254 nm). Further visualization was possible by staining with a basic solution of potassium permanganate or an acidic solution of ceric molybdate. Column chromatography was carried out through silica gel (100-200 mesh) using EtOAc/n-Hexane as an eluent. ^{1}H NMR (400 MHz) and ^{13}CNMR (100MHz) spectra were measured on Bruker AMX 400 spectrometers with $CDCl_3$ as solvent and tetramethylsilane (TMS) as internal standard. Chemical shifts were reported in units (ppm) by assigning TMS resonance in the ^{1}H spectrum as 0.00 ppm and $CDCl_3$ resonance in the ^{13}C spectrum as 77.00 ppm. All coupling constants (J values) were reported in Hertz (Hz). Multiplicities were given as: s (singlet); d (doublet); t (triplet); q (quartet); dd (doublets of doublet); ddd (doublets of doublets of doublet); dt (doublets of triplet); or m (multiplets), coupling constants (Hz) and integration. Chemical shifts of common trace ^{1}H NMR impurities (ppm): H_2O: 1.56, $CHCl_3$: 7.26. HRMS (ESI) spectra were recorded using a Bruker Impact HD quadrupole plus ion trap at the CIF S. P. Pune University. Melting points were determined with a Buchi B-540 capillary melting point apparatus in open capillaries and were uncorrected. Oil bath was used as a heating source. The starting compounds **1a−1k**[1], **5a-5k**[2], and **11**[3] have been synthesized using the reported procedure.

2. General experimental procedures and characterization data for the synthesis of compounds 3:

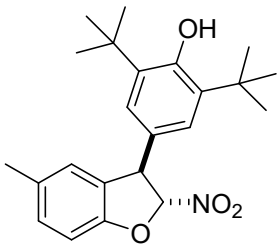


General experimental procedure: To an oven-dried 50 mL round bottom flask was added *ortho*-hydroxyphenyl-substituted *p*-QM (0.32 mmol, 1.0 equiv), bromonitromethane (0.39 mmol, 1.2 equiv.), and K_2CO_3 (0.81 mmol, 2.5 equiv.) in anhydrous MeCN (1.5 mL), and the resulting solution was stirred at room temperature until starting completely consumed (based on TLC analysis). After completion of the reaction, the mixture was diluted with water (10 mL) and extracted with EtOAc (3×10 mL). The organic layer was collected and dried over anhydrous Na_2SO_4. The combined organic layer was concentrated under reduced pressure. The resultant crude material was purified by column chromatography on silica gel using *n*-hexane /EtOAc as an eluent.

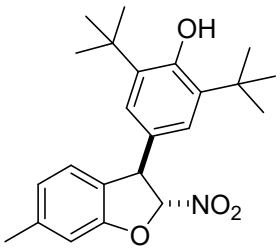
Characterization of the products:



2,6-di-tert-butyl-4-((2R*,3R*)-2-nitro-2,3-dihydrobenzofuran-3-yl)phenol (3a); Pale yellow solid, 77 mg, 65% yield, R_f = 0.6, column chromatography on silica gel (*n*-Hexane/EtOAc 90:10), mp 167−169°C; **^{1}H NMR (400 MHz, $CDCl_3$):** δ 7.34 (ddd, *J* = 8.2, 7.6, 0.9 Hz, 1H), 7.18 (m, 2H), 7.07 (td, *J* = 7.4, 0.9 Hz, 1H), 6.90 (s, 2H), 6.02 (d, *J* = 1.8 Hz, 1H), 5.24 (s, 1H), 4.86 (s, 1H), 1.38 (s, 18H); **^{13}C {^{1}H}NMR (101 MHz, $CDCl_3$):** δ 158.3, 153.8, 136.8, 129.8, 129.7, 126.6, 125.7, 124.1, 123.6, 112.5, 110.8, 55.7, 34.5, 30.3; **HRMS (ESI)** calcd for: $C_{22}H_{27}NO_4Na$: $[M + Na]^+$, 392.1832 found: 392.1838.

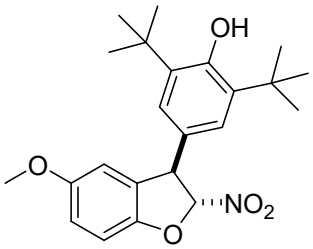


2,6-di-tert-butyl-4-(-((2R*,3R*)-5-methyl-2-nitro-2,3-dihydrobenzo-furan-3-yl)phenol (3b); Pale yellow solid, 80 mg, 68% yield, R_f = 0.6, column chromatography on silica gel (*n*-Hexane/EtOAc 90:10), mp 164−166°C; **^{1}H NMR (400 MHz, $CDCl_3$):** δ 7.12 (dd, *J* = 8.3, 1.6 Hz, 1H), 7.04 (d, *J* = 8.2 Hz, 1H), 6.98 (s, 1H), 6.90 (s, 2H), 5.99 (d, *J* = 1.7 Hz, 1H), 5.24 (s, 1H), 4.80 (s, 1H), 2.30 (s, 3H), 1.39 (s, 18H**); ^{13}C {^{1}H}NMR (101 MHz, $CDCl_3$)**: δ 156.1, 153.7, 136.7, 133.1, 130.1, 129.8, 126.6, 125.9, 124.0, 112.6, 110.2, 55.7, 3.4, 30.2, 20.9; **HRMS (ESI)** calcd for: $C_{23}H_{30}NO_4$: $[M + H]^+$, 384.2169 found: 384.2187.

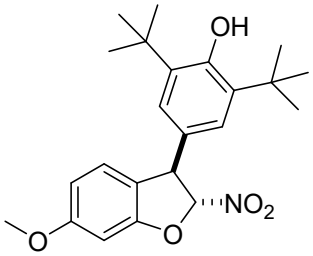


2,6-di-tert-butyl-4-((2R*,3R*)-6-methyl-2-nitro-2,3-dihydrobenzo-furan -3-yl) phenol (3c); Pale yellow solid, 80 mg, 68% yield, R_f = 0.6, column chromatography on silica gel (*n*-Hexane/EtOAc 90:10), mp

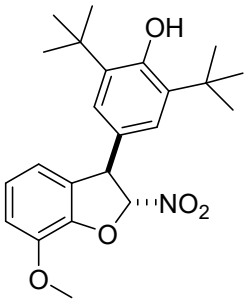
174−176°C; **^{1}H NMR (400 MHz, $CDCl_3$):** δ 7.05 (d, *J* = 7.6 Hz, 1H), 6.98 (s, 1H), 6.93 – 6.84 (m, 3H), 6.01 (d, *J* = 1.8 Hz, 1H), 5.23 (s, 1H), 4.81 (s, 1H), 2.40 (s, 3H), 1.39 (s, 18H); **^{13}C {^{1}H}NMR (101 MHz, $CDCl_3$)**: δ 158.6, 153.8, 140.2, 136.8, 129.9, 125.2, 124.4, 124.1, 123.5, 112.8, 111.4, 55.6, 34.5, 30.3, 21.8; **HRMS (ESI)** calcd for: $C_{23}H_{30}NO_4$: $[M + H]^+$, 384.2169 found: 384.2177.



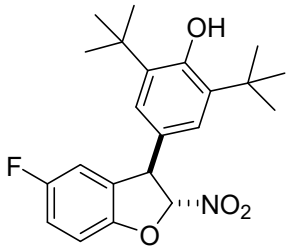
2,6-di-tert-butyl-4-((2R*,3R*)-5-methoxy-2-nitro-2,3-dihydrobenzo furan-3-yl)phenol phenol (3d); Pale orange solid, 83 mg, 71% yield, R_f = 0.6, column chromatography on silica gel (*n*-Hexane/EtOAc 90:10), mp 176−178°C; **^{1}H NMR (400 MHz, $CDCl_3$):** ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.07 (d, *J* = 8.8 Hz, 1H), 6.91 (s, 2H), 6.86 (dd, *J* = 8.8, 2.7 Hz, 1H), 6.73 (d, *J* = 2.6 Hz, 1H), 5.98 (d, *J* = 1.7 Hz, 1H), 5.25 (s, 1H), 4.82 (s, 1H), 3.74 (s, 3H), 1.39 (s, 18H); **^{13}C {^{1}H}NMR (101 MHz, $CDCl_3$)**: δ 156.3, 153.9, 152.3, 136.8, 129.5, 127.6, 124.1, 115.2, 112.9, 111.1, 111.0, 56.1, 34.5, 30.3; **HRMS (ESI)** calcd for: $C_{23}H_{29}NNaO_5$: $[M + Na]^+$, 422.1938 found: 422.1928.



2,6-di-tert-butyl-4-((2R*,3R*)-6-methoxy-2-nitro-2,3-dihydrobenzofuran-3-yl)phenol (3e); Pale orange solid, 82 mg, 70% yield, R_f = 0.6, column chromatography on silica gel (*n*-Hexane/EtOAc 90:10), mp 172−174°C; **^{1}H NMR (400 MHz, $CDCl_3$):** δ 7.06 (d, *J* = 8.3 Hz, 1H), 6.91 (s, 2H), 6.74 (d, *J* = 2.2 Hz, 1H), 6.62 (dd, *J* = 8.3, 2.3 Hz, 1H), 6.01 (d, *J* = 1.8 Hz, 1H), 5.23 (s, 1H), 4.79 (s, 1H), 3.84 (s, 3H), 1.39 (s, 18H)); **^{13}C {^{1}H}NMR (101 MHz, $CDCl_3$)**: δ 161.4, 159.7, 153.8, 136.8, 130.0, 125.9, 124.1, 118.2, 113.2, 109.8, 97.0, 55.8, 55.3, 34.5, 30.3; **HRMS (ESI)** calcd for: $C_{23}H_{29}NNaO_5$: $[M + Na]^+$, 422.1938 found: 422.1928.

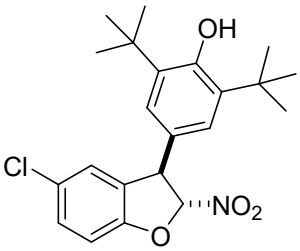


2,6-di-tert-butyl-4-((2R*,3R*)-7-methoxy-2-nitro-2,3-dihydrobenzofuran-3-yl)phenol (3f); Pale yellow solid, 82 mg, 70% yield, R_f = 0.6, column chromatography on silica gel (*n*-Hexane/EtOAc 90:10), mp 110−112°C; **^{1}H NMR (400 MHz, $CDCl_3$):** δ 7.08 – 6.99 (m, 1H), 6.97 – 6.87 (m, 3H), 6.79 (d, *J* = 7.5 Hz, 1H), 6.06 (d, *J* = 1.9 Hz, 1H), 5.24 (s, 1H), 4.88 (s, 1H), 4.00 (s, 3H), 1.39 (s, 18H).; **^{13}C {^{1}H}NMR (101 MHz, $CDCl_3$)**: δ 153.9, 146.6, 144.9, 136.8, 129.4, 128.0, 124.5, 124.1, 117.5, 113.2, 112.5, 56.6, 56.3, 34.5, 30.3; **HRMS (ESI)** calcd for: $C_{23}H_{29}NNaO_5$: $[M + Na]^+$, 422.1938 found: 422.1928.

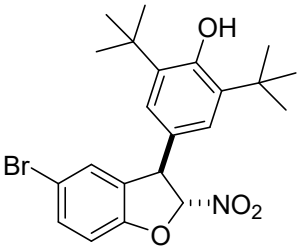


2,6-di-tert-butyl-4-((2R*,3R*)-5-fluoro-2-nitro-2,3-dihydrobenzofuran-3-yl)phenol (3g); Pale yellow solid, 75 mg, 64% yield, R_f = 0.6, column chromatography on silica gel (*n*-Hexane/EtOAc 90:10), mp 170−172°C; **^{1}H NMR (400 MHz, $CDCl_3$):** δ 7.10 (dd, *J* = 8.8, 4.1 Hz, 1H), 7.03 (td, *J* = 8.7, 2.7 Hz, 1H), 6.90 (d, *J* = 2.6 Hz, 1H), 6.88 (s, 2H), 6.23 – 5.75 (m, 1H), 5.27 (s, 1H), 4.83 (s, 1H), 1.39 (s, 18H); **^{13}C {^{1}H}NMR (101 MHz, $CDCl_3$)**: δ 159.30 (d, *J* = 241.1 Hz),

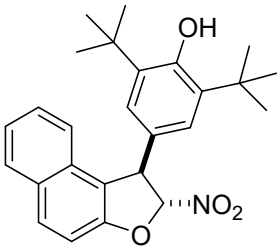
154.2 (d, J = 1.5 Hz), 137.0, 129.0, 128.4 (d, J = 9.0 Hz), 124.0, 116.4 (d, J = 24.7 Hz), 112.9, 112.7 (d, J = 24.0 Hz), 111.4 (d, J = 8.7 Hz), 55.9, 34.5, 30.2; **^{19}F{^{1}H} NMR (377 MHz, $CDCl_3$):** δ -119.96 (s); **HRMS (ESI)** calcd for: $C_{22}H_{27}FNO_4$: $[M + H]^+$, 388.1919 found: 388.1923.



2,6-di-tert-butyl-4-((2R*,3R*)-5-chloro-2-nitro-2,3-dihydrobenzo furan-3-yl)phenol (3h); Pale yellow solid, 76 mg, 65% yield, R_f = 0.6, column chromatography on silica gel (*n*-Hexane/EtOAc 90:10), mp 180−182°C; **^{1}H NMR (400 MHz, $CDCl_3$):** δ 7.30 (dd, J = 8.6, 2.2 Hz, 1H), 7.21 – 7.14 (m, 1H), 7.10 (d, J = 8.6 Hz, 1H), 6.88 (s, 2H), 6.15 – 5.96 (m, 1H), 5.28 (s, 1H), 4.81 (s, 1H), 1.39 (s, 18H); **^{13}C {^{1}H}NMR (101 MHz, $CDCl_3$)**: δ 156.8, 154.1, 137.1, 129.8, 129.0, 128.9, 128.7, 125.8, 124.0, 112.5, 111.9, 55.7, 34.6, 30.2; **HRMS (ESI)** calcd for: $C_{22}H_{27}ClNO_4$: $[M + H]^+$, 404.1623 found: 404.1637.



4-((2R*,3R*)-5-bromo-2-nitro-2,3-dihydrobenzofuran-3-yl)-2,6-di-tert-butylphenol (3i); Pale yellow solid, 73 mg, 63% yield, R_f = 0.6, column chromatography on silica gel (*n*-Hexane/EtOAc 90:10), mp 174−176°C; **^{1}H NMR (400 MHz, $CDCl_3$):** ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.44 (ddd, J = 8.6, 2.1, 0.5 Hz, 1H), 7.30 (d, J = 1.4 Hz, 1H), 7.06 (d, J = 8.6 Hz, 1H), 6.87 (s, 2H), 6.03 (d, J = 1.8 Hz, 1H), 5.28 (s, 1H), 4.81 (s, 1H), 1.39 (s, 18H); **^{13}C {^{1}H}NMR (101 MHz, $CDCl_3$)**: δ 157.3, 154.1, 137.1, 132.7, 129.4, 129.0, 128.6, 124.0, 115.9, 112.4, 55.6, 34.6, 30.2; **HRMS (ESI)** calcd for: $C_{22}H_{27}BrNO_4$: $[M + H]^+$, 448.1118 found: 448.1138.

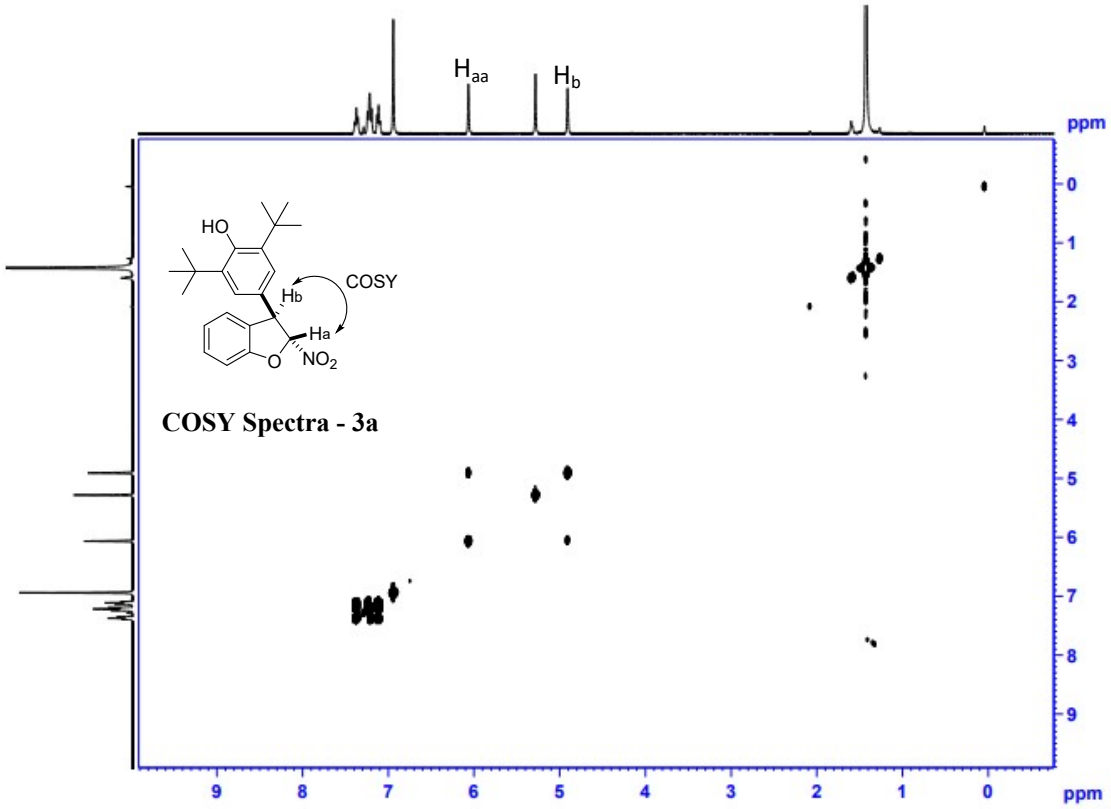


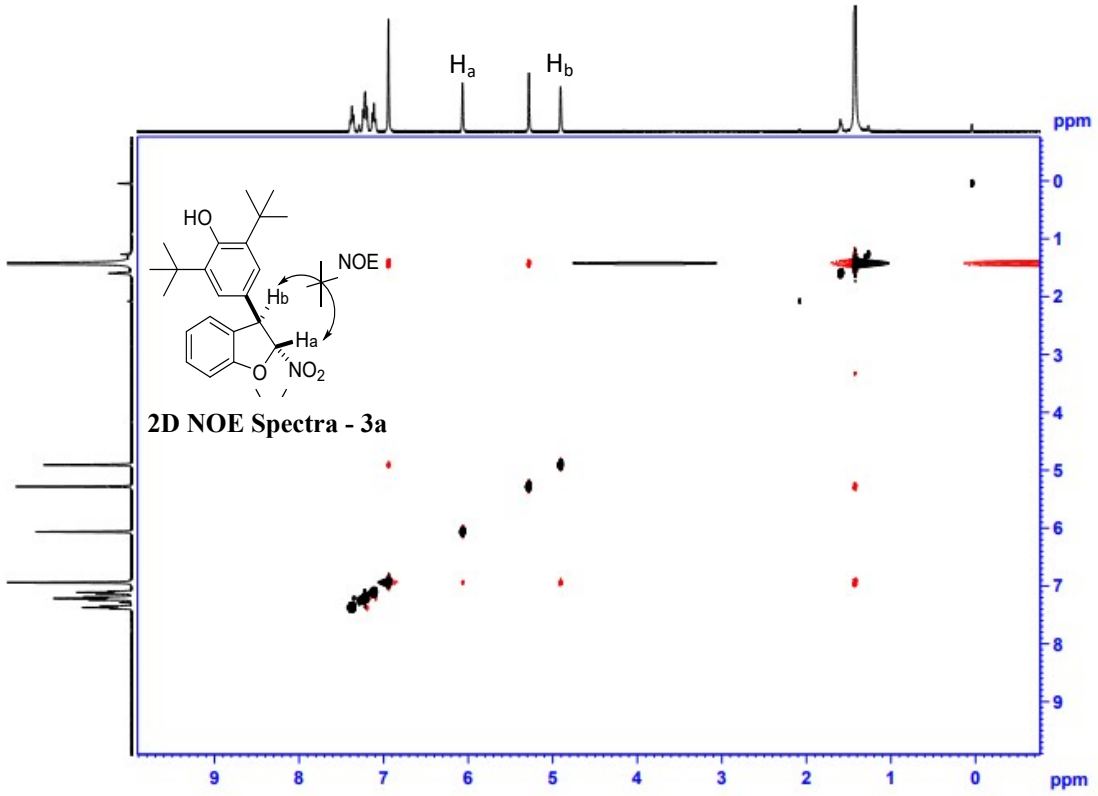
2,6-di-tert-butyl-4-((1R*,2R*)-2-nitro-1,2-dihydronaphtho[2,1-b]furan-1-yl)phenol (3j); Pale brown solid, 84 mg, 72% yield, R_f = 0.6, column chromatography on silica gel (*n*-Hexane/EtOAc 90:10), mp 157−159°C; **^{1}H NMR (400 MHz, $CDCl_3$):** δ 7.88 (dd, J = 13.1, 5.4 Hz, 2H), 7.42 (t, J = 6.0 Hz, 2H), 7.37 (ddt, J = 9.6, 8.3, 3.4 Hz, 2H), 6.94 (s, 2H), 6.13 (d, J = 1.6 Hz, 1H), 5.24 (s, 1H), 5.20 (s, 1H), 1.33 (s, 18H); **^{13}C {^{1}H}NMR (101 MHz, $CDCl_3$)**: 156.1, 153.8, 136.8, 131.3, 130.9, 130.0, 129.1, 128.7, 127.5, 124.5, 124.2, 123.5, 118.9, 113.2, 111.9, 55.5, 34.5, 30.3; **HRMS (ESI)** calcd for: $C_{26}H_{29}NNaO_4$: $[M + Na]^+$, 420.2169 found: 420.2156.

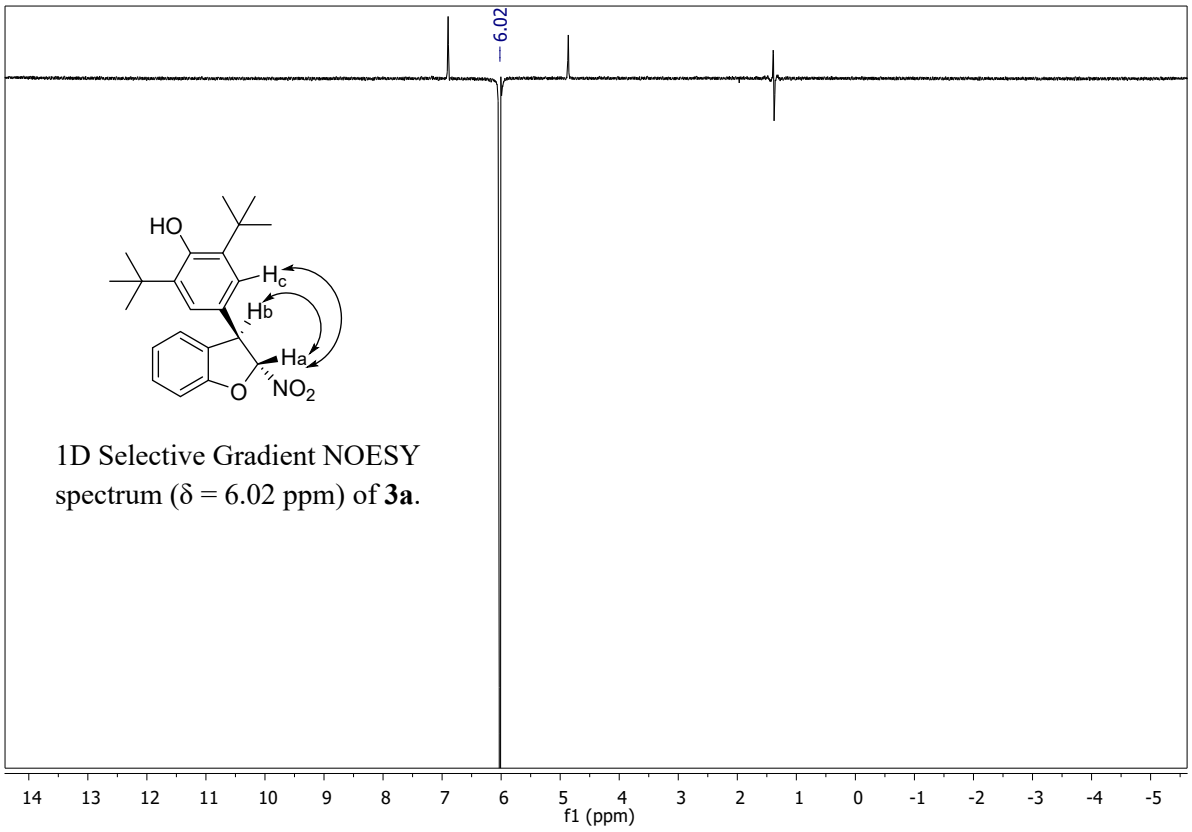
3. Relative configuration determination

The relative configuration of major diastereomer **3a** (isolated from mixture dr = 20:1) was determined by 2D NOE spectra of its isolated compound. For major diastereomer (**3a**), there are no significant cross-peaks between Ha-Hb as shown in 2D NOE spectra. Also, the relative configuration of the major

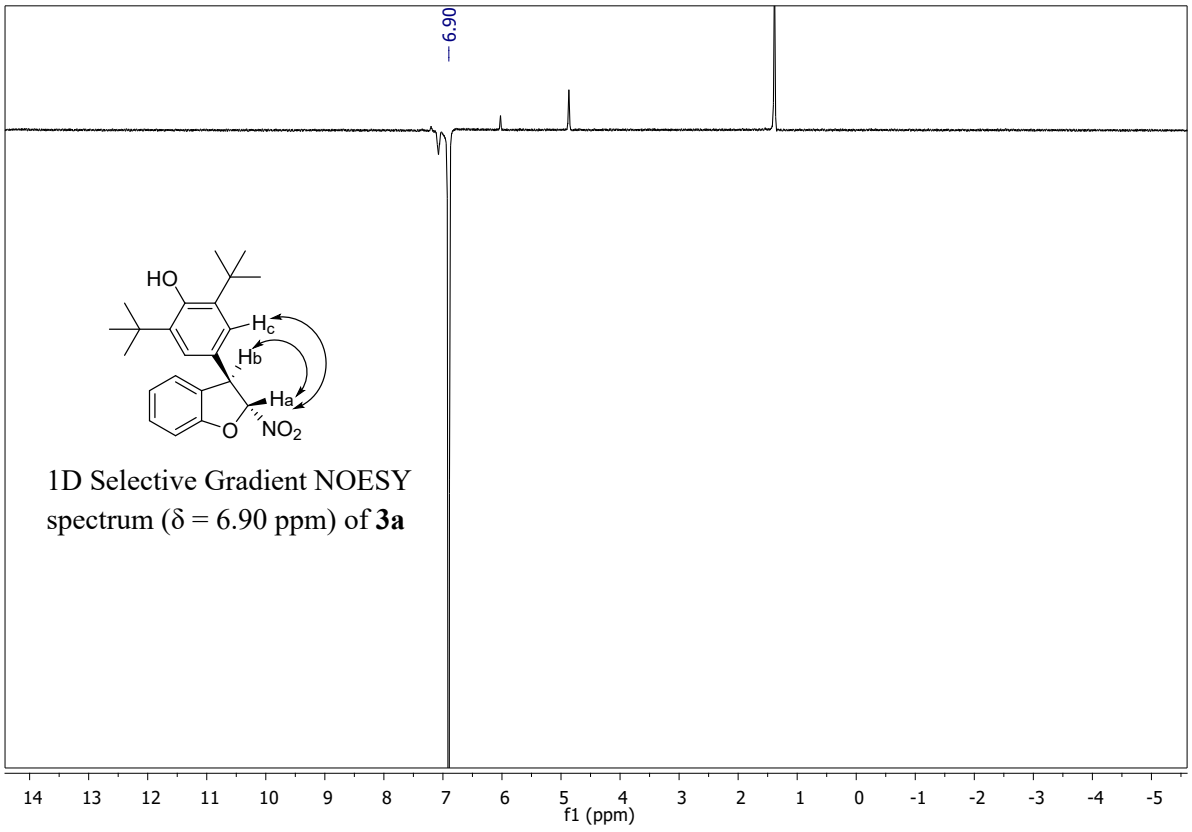
diastereomer **3a** (isolated from mixture dr = 20:1) was determined by 1D NOE spectra and it shows significant cross-peaks between Ha-Hc and Ha-Hb.





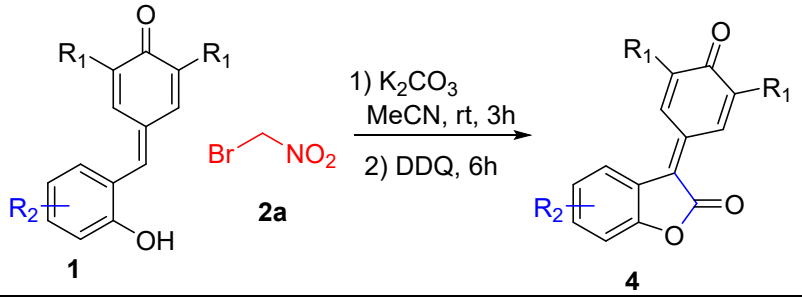


1D Selective Gradient NOESY spectrum (δ = 6.02 ppm) of **3a**.



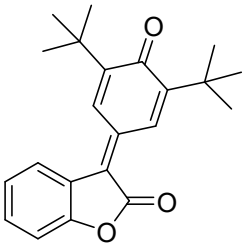
1D Selective Gradient NOESY spectrum (δ = 6.90 ppm) of **3a**

4. General experimental procedure and characterization data for the synthesis of compounds 4:

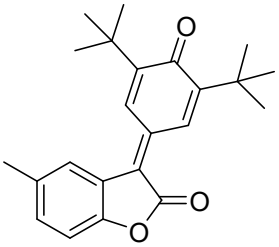


General experimental procedure: To an oven-dried 50 mL round bottom flask was added *ortho*-hydroxyphenyl-subsituted *p*-QM (0.32 mmol, 1.0 equiv), bromonitromethane (0.39 mmol, 1.2 equiv.), and K_2CO_3 (0.81 mmol, 2.5 equiv.) in anhydrous MeCN (1.5 mL), and it was stirred at room temperature. After the consumption of **1** (based on TLC analysis), DDQ (2.0 equiv.) was added and the reaction mixture was stirred at room temperature until the former reaction product was completely consumed (based on TLC analysis). The residue was filtered through a pad of celite, and the filtrate was then concentrated under reduced pressure. The residue was purified by column chromatography on silica gel using *n*-hexane/EtOAc as an eluent.

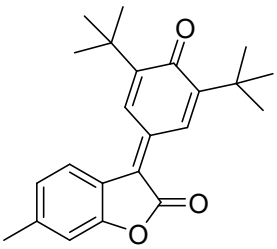
Characterization of the products:



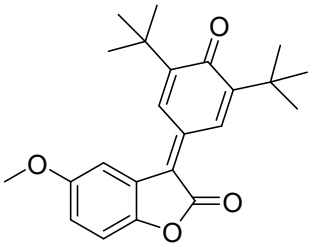
3-(3,5-di-tert-butyl-4-oxocyclohexa-2,5-dien-1-ylidene)benzofuran-2(3H)-one (4a).Red brown solid, 74 mg, 68% yield, R_f = 0.7, column chromatography on silica gel (*n*-Hexane/EtOAc 90:10), mp 154−156°C; **^{1}H NMR (400 MHz, $CDCl_3$):** δ 8.75 (d, *J* = 2.5 Hz, 1H), 7.81 (d, *J* = 2.5 Hz, 1H), 7.76 (d, *J* = 7.9 Hz, 1H), 7.48 – 7.37 (m, 1H), 7.23 (td, *J* = 7.8, 1.0 Hz, 1H), 7.15 (d, *J* = 8.1 Hz, 1H), 1.39 (s, 9H), 1.35 (s, 9H); **^{13}C {^{1}H} NMR (101 MHz, $CDCl_3$):** δ 186.7, 167.0, 154.8, 153.4, 152.4, 140.1, 132.3, 127.8, 127.5, 125.5, 124.8, 124.0, 123.8, 111.7, 36.3, 36.2, 29.9, 29.9; **HRMS (ESI)** calcd for: $C_{22}H_{25}O_3$: $[M + H]^+$, 337.1798 found: 337.1794.



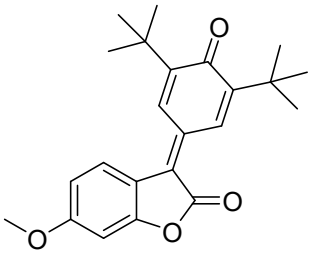
3-(3,5-di-tert-butyl-4-oxocyclohexa-2,5-dien-1-ylidene)-5-methylbenzofuran-2(3H)-one (4b). Red brown solid, 76 mg, 70% yield, R_f = 0.7, column chromatography on silica gel (*n*-Hexane/EtOAc 90:10), mp 180−182°C; **^{1}H NMR (400 MHz, $CDCl_3$):** δ 8.74 (d, *J* = 2.5 Hz, 1H), 7.81 (d, *J* = 2.5 Hz, 1H), 7.55 (s, 1H), 7.23 (d, *J* = 8.2 Hz, 1H), 7.03 (d, *J* = 8.2 Hz, 1H), 2.41 (s, 3H), 1.39 (s, 9H), 1.35 (s, 9H); **^{13}C {^{1}H} NMR (101 MHz, $CDCl_3$):** δ 186.7, 167.3, 153.1, 153.0, 152.2, 139.7, 134.2, 133.1, 127.9, 127.6, 125.9, 124.1, 123.8, 111.3, 36.4, 36.3, 29.9, 29.9, 21.7; **HRMS (ESI)** calcd for: $C_{23}H_{27}O_3$: $[M + H]^+$, 351.1955 found: 351.1960.



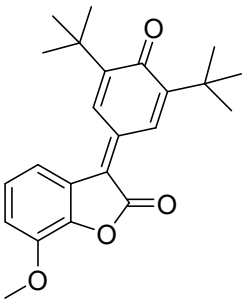
3-(3,5-di-tert-butyl-4-oxocyclohexa-2,5-dien-1-ylidene)-6-methylbenzofuran-2(3H)-one (4c); Red brown solid, 75 mg, 69% yield, R_f = 0.7, column chromatography on silica gel (*n*-Hexane/EtOAc 90:10), mp 158−160°C; **^{1}H NMR (400 MHz, $CDCl_3$):** δ 8.81 – 8.59 (m, 1H), 7.78 (d, *J* = 2.3 Hz, 1H), 7.63 (d, *J* = 8.1 Hz, 1H), 7.03 (dd, *J* = 8.1, 0.6 Hz, 1H), 6.96 (s, 1H), 2.44 (s, 3H), 1.38 (s, 9H), 1.35 (s, 9H); **^{13}C NMR (101 MHz, $CDCl_3$):** δ 186.7, 167.4, 155.1, 152.9, 151.8, 144.0, 138.8, 127.9, 127.6, 125.8, 125.2, 124.1, 121.4, 112.3, 36.4, 36.3, 29.9, 29.9, 22.4 ; **HRMS (ESI)** calcd for: $C_{23}H_{27}O_3$: $[M + H]^+$, 351.1955 found: 351.1960.



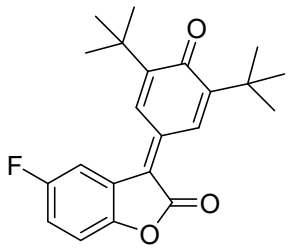
3-(3,5-di-tert-butyl-4-oxocyclohexa-2,5-dien-1-ylidene)-5-methoxybenzofuran-2(3H)-one (4d); Red brown solid, 77 mg, 71% yield, R_f = 0.7, column chromatography on silica gel (*n*-Hexane/EtOAc 90:10), mp 154−156°C; **^{1}H NMR (400 MHz, $CDCl_3$):** δ 8.74 (d, *J* = 2.5 Hz, 1H), 7.78 (d, *J* = 2.5 Hz, 1H), 7.27 (d, *J* = 2.5 Hz, 1H), 7.06 (d, *J* = 8.8 Hz, 1H), 6.98 (dd, *J* = 8.8, 2.5 Hz, 1H), 3.85 (s, 3H), 1.39 (s, 9H), 1.35 (s, 9H); **^{13}C NMR (101 MHz, $CDCl_3$):** δ 186.7, 167.5, 156.6, 153.2, 152.4, 149.3, 140.0, 127.8, 127.4, 124.4, 124.2, 118.5, 112.1, 110.5, 56.0, 36.4, 36.3, 29.9, 29.9 ; **HRMS (ESI)** calcd for: $C_{23}H_{27}O_4$: $[M + H]^+$, 367.1904 found: 367.1900.



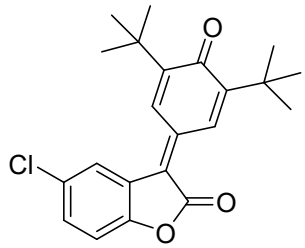
3-(3,5-di-tert-butyl-4-oxocyclohexa-2,5-dien-1-ylidene)-6-methoxybenzofuran-2(3H)-one (4e); Red brown solid, 77 mg, 71% yield, R_f = 0.7, column chromatography on silica gel (*n*-Hexane/EtOAc 90:10), mp 174−176°C; **^{1}H NMR (400 MHz, $CDCl_3$):** δ 8.69 (d, *J* = 2.5 Hz, 1H), 7.73 (d, *J* = 2.4 Hz, 1H), 7.67 (d, *J* = 8.8 Hz, 1H), 6.77 (dd, *J* = 8.8, 2.4 Hz, 1H), 6.68 (d, *J* = 2.4 Hz, 1H), 3.90 (s, 3H), 1.38 (s, 9H), 1.35 (s, 9H); **^{13}C NMR (101 MHz, $CDCl_3$):** δ 186.6, 167.4, 163.5, 156.7, 152.6, 151.4, 137.1, 127.9, 127.7, 126.7, 123.8, 117.0, 111.8, 97.4, 56.1, 36.3, 36.2, 29.9, 29.8; **HRMS (ESI)** calcd for: $C_{23}H_{27}O_4$: $[M + H]^+$, 367.1904 found: 367.1909.



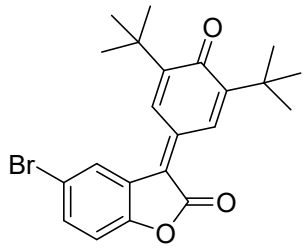
3-(3,5-di-tert-butyl-4-oxocyclohexa-2,5-dien-1-ylidene)-7-methoxybenzofuran-2(3H)-one (4f); Red brown solid, 78 mg, 72% yield, R_f = 0.7, column chromatography on silica gel (*n*-Hexane/EtOAc 90:10), mp 156−158°C; **^{1}H NMR (400 MHz, $CDCl_3$):** δ 8.75 (d, *J* = 2.4 Hz, 1H), 7.81 (d, *J* = 2.4 Hz, 1H), 7.36 (d, *J* = 7.9 Hz, 1H), 7.16 (t, *J* = 8.1 Hz, 1H), 7.01 (d, *J* = 8.3 Hz, 1H), 3.97 (s, 3H), 1.38 (s, 9H), 1.35 (s, 9H); **^{13}C NMR (101 MHz, $CDCl_3$):** δ 186.8, 166.6, 153.3, 152.4, 144.6, 143.7, 140.4, 127.8, 127.5, 125.1, 124.9, 124.0, 117.5, 115.5, 56.6, 36.4, 36.3, 29.9; **HRMS (ESI)** calcd for: $C_{23}H_{27}O_4$: $[M + H]^+$, 367.1904 found: 367.1909.



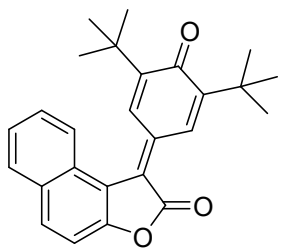
3-(3,5-di-tert-butyl-4-oxocyclohexa-2,5-dien-1-ylidene)-5-fluorobenzofuran-2(3H)-one (4g); Red brown solid, 70 mg, 65% yield, R_f = 0.7, column chromatography on silica gel (*n*-Hexane/EtOAc 90:10), mp 156−158°C; **^{1}H NMR (400 MHz, $CDCl_3$):** δ 8.74 (d, *J* = 2.5 Hz, 1H), 7.67 (d, *J* = 2.5 Hz, 1H), 7.43 (dd, *J* = 8.6, 2.3 Hz, 1H), 7.19 – 7.08 (m, 2H), 1.39 (s, 9H), 1.35 (s, 9H); **^{13}C NMR (101 MHz, $CDCl_3$):** δ 186.7, 166.9, δ 159.4 (d, *J* = 242.3 Hz), 154.0, 153.0, 150.8 (d, *J* = 1.7 Hz), 141.2, 127.6, 126.8, 124.5 (d, *J* = 9.2 Hz), 123.3 (d, *J* = 3.6 Hz), 119.0 (d, *J* = 24.9 Hz), 112.6 (d, *J* = 8.5 Hz), 112.2 (d, *J* = 27.0 Hz), 36.5, 36.4, 29.9, 29.9; **^{19}F{^{1}H} NMR (377 MHz, $CDCl_3$):** δ -116.76 (s); **HRMS (ESI)** calcd for: $C_{22}H_{24}FO_3$: $[M + H]^+$, 355.1704 found: 355.1714.



5-chloro-3-(3,5-di-tert-butyl-4-oxocyclohexa-2,5-dien-1-ylidene)benzofuran-2(3H)-one (4h); Red brown solid, 68 mg, 68% yield, R_f = 0.7, column chromatography on silica gel (*n*-Hexane/EtOAc 90:10), mp 180−182°C; **^{1}H NMR (400 MHz, $CDCl_3$):** δ 8.72 (d, *J* = 2.5 Hz, 1H), 7.71 (d, *J* = 2.0 Hz, 1H), 7.68 (d, *J* = 2.5 Hz, 1H), 7.39 (dd, *J* = 8.6, 2.1 Hz, 1H), 7.10 (d, *J* = 8.6 Hz, 1H), 1.39 (s, 9H), 1.35 (s, 9H); **^{13}C NMR (101 MHz, $CDCl_3$):** δ 186.7, 166.5, 154.1, 153.1, 153.0, 141.3, 131.9, 130.0, 127.6, 126.9, 125.3, 125.1, 122.5, 112.8, 36.5, 36.4, 29.9; **HRMS (ESI)** calcd for: $C_{22}H_{24}ClO_3$: $[M + H]^+$, 371.1408 found: 371.1401.



5-bromo-3-(3,5-di-tert-butyl-4-oxocyclohexa-2,5-dien-1-ylidene) benzofuran-2(3H)-one (4i); Red brown solid, 56 mg, 53% yield, R_f = 0.7, column chromatography on silica gel (*n*-Hexane/EtOAc 90:10), mp 180−182°C; **^{1}H NMR (400 MHz, $CDCl_3$):** δ 8.71 (d, *J* = 2.5 Hz, 1H), 7.87 (d, *J* = 1.9 Hz, 1H), 7.68 (d, *J* = 2.5 Hz, 1H), 7.53 (dd, *J* = 8.6, 1.9 Hz, 1H), 7.06 (d, *J* = 8.6 Hz, 1H), 1.39 (s, 9H), 1.35 (s, 9H); **^{13}C NMR (101 MHz, $CDCl_3$):** δ 186.6, 166.4, 154.1, 153.4, 153.1, 141.4, 134.7, 128.3, 127.5, 127.0, 125.7, 122.3, 117.3, 113.2, 36.5, 36.4, 29.9, 29.8; **HRMS (ESI)** calcd for: $C_{22}H_{24}BrO_3$: $[M + H]^+$, 414.0831 found: 414.0835.

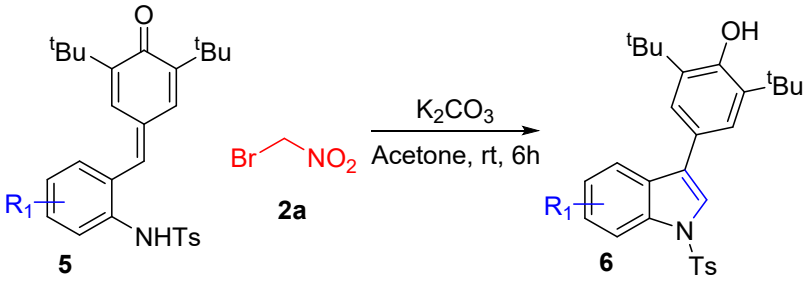


1-(3,5-di-tert-butyl-4-oxocyclohexa-2,5-dien-1-ylidene)naphtho[2,1-b]furan-2(1H)-one (4j); Red brown solid, 77 mg, 72% yield, R_f = 0.7, column chromatography on silica gel (*n*-Hexane/EtOAc 90:10), mp 174−176°C; **^{1}H NMR (400 MHz, $CDCl_3$):** δ 8.84 (t, 1H), 8.68 (d, *J* = 2.3 Hz, 1H), 8.15 (d, *J* = 8.9 Hz, 1H), 7.89 (d, *J* = 8.2 Hz, 1H), 7.72 (ddd, *J* = 8.3, 7.0, 1.2 Hz, 1H), 7.60 (d, *J* = 2.3 Hz, 1H), 7.53 (ddd, *J* = 8.2, 7.0, 1.2 Hz, 1H), 7.44 (d, *J* = 8.9 Hz, 1H), 1.39 (s, 9H), 1.38 (s, 9H); **^{13}C NMR (101 MHz, $CDCl_3$):**) δ 186.7, 184.7, 166.6, 152.8, 152.3, 147.6, 139.6, 130.6, 130.5, 129.3, 129.0, 126.3, 126.3, 125.7, 123.6, 121.1, 115.4, 112.8, 36.3, 36.1, 29.8, 29.8; **HRMS (ESI)** calcd for: $C_{26}H_{27}O_3$: $[M + H]^+$, 387.1955 found: 387.1948.

5. Experimental procedure for gram scale synthesis of 4:

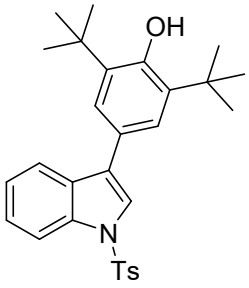
To an oven-dried 50 mL round bottom flask was added *ortho*-hydroxyphenyl-subsituted *p*-QM (3.22 mmol, 1.0 equiv), bromonitromethane (3.87 mmol, 1.2 equiv.), and K_2CO_3 (8.05 mmol, 2.5 equiv.) in anhydrous MeCN (10 mL), and the resulting solution was stirred 6 h at room temperature. After the reaction was complete (based on TLC analysis), DDQ (6.44 mmol, 2.0 equiv.) was added and the reaction mixture was stirred at room temperature until the former reaction product was completely consumed (based on TLC analysis). The residue was filtered through a pad of celite, and the filtrate was then concentrated under reduced pressure. The residue was purified by column chromatography on silica gel using EtOAc/n-hexane as an eluent. (n-hexane/EtOAc, 90:10) (0.68 g, 63% yield).

6. General experimental procedures and characterization data for synthesis of compounds 6:

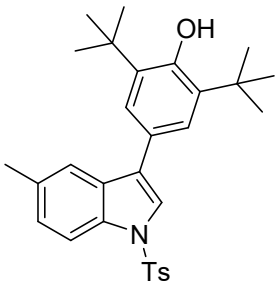


General experimental procedures: To an oven-dried 50 mL round bottom flask was added *ortho*-tosylaminophenyl-subsituted *p*-QM (0.22 mmol, 1.0 equiv), bromonitromethane (0.26 mmol, 1.2 equiv.), and K_2CO_3 (0.54 mmol, 2.5 equiv.) in anhydrous acetone (1.5 mL), and the resulting solution was stirred at room temperature until *ortho*-tosylaminophenyl-subsituted *p*-QM was completely consumed (based on TLC analysis). After completion of the reaction, the mixture was diluted with water (10 mL) and extracted with EtOAc (3×10 mL). The organic layer was collected and dried over anhydrous Na_2SO_4. The combined organic layer was concentrated under reduced pressure. The resultant crude material was purified by column chromatography on silica gel using *n*-hexane/EtOAc as an eluent.

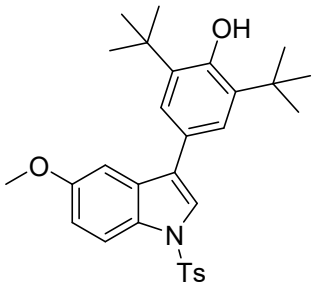
Characterization of the products:



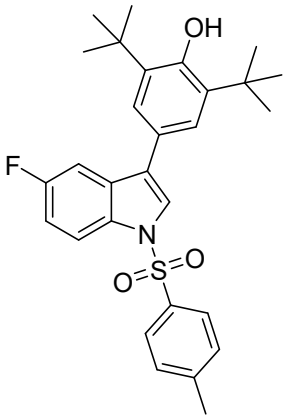
2,6-di-tert-butyl-4-(1-tosyl-1H-indol-3-yl)phenol carboxylate (6a); Red brown solid, 65 mg, 63% yield, R_f = 0.7, column chromatography on silica gel (*n*-Hexane/EtOAc 90:10), mp 222−224°C; **^{1}H NMR (400 MHz, $CDCl_3$)**: δ 8.05 (d, *J* = 8.2 Hz, 1H), 7.79 (d, *J* = 8.4 Hz, 2H), 7.74 (d, *J* = 7.8 Hz, 1H), 7.63 (s, 1H), 7.41 (s, 2H), 7.38 – 7.32 (m, 1H), 7.31 – 7.26 (m, 1H), 7.21 (d, *J* = 8.1 Hz, 2H), 5.31 (s, 1H), 2.33 (s, 3H), 1.49 (s, 18H); **^{13}C {^{1}H} NMR (101 MHz, $CDCl_3$):** δ 153.7, 145.0, 136.6, 135.7, 135.4, 130.0, 129.9, 127.1, 125.0, 124.8, 124.2, 123.6, 122.3, 120.7, 114.1, 34.6, 30.5, 21.7 ; **HRMS (ESI)** calcd for: $C_{29}H_{34}NO_3S$: $[M + H]^+$, 476.2254 found: 476.2251.



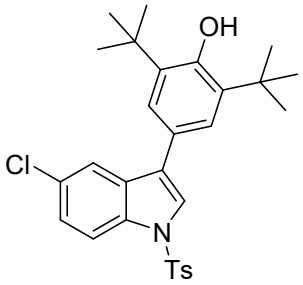
2,6-di-tert-butyl-4-(5-methyl-1-tosyl-1H-indol-3-yl)phenol (6b); Red brown solid, 63 mg, 61% yield, R_f = 0.7, column chromatography on silica gel (*n*-Hexane/EtOAc 90:10), mp 214−216°C; **^{1}H NMR (400 MHz, CDCl$_3$)**: δ 7.92 (d, *J* = 8.5 Hz, 1H), 7.77 (d, *J* = 8.3 Hz, 2H), 7.57 (s, 1H), 7.51 (s, 1H), 7.39 (s, 2H), 7.21 (s, 1H), 7.19 (s, 1H), 7.17 (d, *J* = 9.1 Hz, 1H), 5.30 (s, 1H), 2.42 (s, 3H), 2.32 (s, 3H), 1.49 (s, 18H); **^{13}C {^{1}H} NMR (101 MHz, CDCl$_3$):** 153.7, 144.9, 136.6, 135.4, 134.0, 133.2, 130.2, 130.0, 127.0, 126.2, 124.9, 124.3, 122.5, 120.6, 113.7, 34.6, 30.5, 21.7; **HRMS (ESI)** calcd for: $C_{30}H_{36}NO_3S$: $[M + H]^+$, 490.2410 found: 490.2414.



2,6-di-tert-butyl-4-(5-methoxy-1-tosyl-1H-indol-3-yl)phenol (6c); Brown solid, 70 mg, 68% yield, R_f = 0.7, column chromatography on silica gel (*n*-Hexane/EtOAc 90:10), mp 222−224°C; **^{1}H NMR (400 MHz, CDCl$_3$)**: δ 7.94 (d, *J* = 9.0 Hz, 1H), 7.76 (d, *J* = 8.2 Hz, 2H), 7.59 (s, 1H), 7.40 (s, 2H), 7.23 – 7.15 (m, 3H), 6.96 (dd, *J* = 9.0, 2.0 Hz, 1H), 5.31 (s, 1H), 3.80 (s, 3H), 2.32 (s, 3H), 1.49 (s, 18H).; **^{13}C {^{1}H} NMR (101 MHz, CDCl$_3$):** δ 156.8, 153.7, 144.9, 136.7, 135.4, 130.8, 130.4, 130.0, 127.0, 125.0, 124.7, 124.3, 123.1, 115.0, 113.9, 103.1, 55.7, 34.6, 30.5, 21.9; **HRMS (ESI)** calcd for: $C_{30}H_{36}NO_4S$: $[M + H]^+$, 506.2360 found: 506.2367.

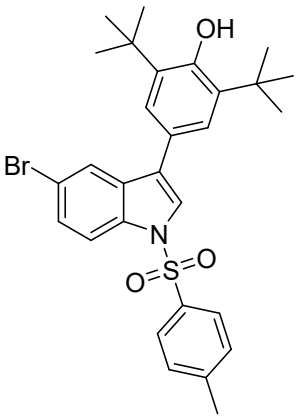


2,6-di-tert-butyl-4-(5-fluoro-1-tosyl-1H-indol-3-yl)phenol (6d); Pale yellow solid, 70 mg, 68% yield, R_f = 0.7, column chromatography on silica gel (*n*-Hexane/EtOAc 90:10), mp 212−214°C; **^{1}H NMR (400 MHz, CDCl$_3$)**: δ 7.99 (dd, *J* = 9.0, 4.4 Hz, 1H), 7.77 (d, *J* = 8.2 Hz, 2H), 7.65 (s, 1H), 7.40 – 7.32 (m, 3H), 7.22 (d, *J* = 8.1 Hz, 2H), 7.07 (td, *J* = 8.9, 2.2 Hz, 1H), 5.32 (s, 1H), 2.34 (s, 3H), 1.49 (s, 18H); **^{13}C {^{1}H}NMR (101 MHz, CDCl$_3$):** δ 160.0 (d, *J* = 240.1 Hz), 153.9, 145.2, 136.8, 135.2, 132.0, 131.0 (d, *J* = 9.6 Hz), 130.1, 127.0, 125.0 (d, *J* = 4.1 Hz), 124.6, 123.9, 123.8, 115.1 (d, *J* = 9.3 Hz), 112.9 (d, *J* = 25.6 Hz), 106.4 (d, *J* = 24.6 Hz), 34.6, 30.5, 21.7; **^{19}F{^{1}H} NMR (377 MHz, CDCl$_3$):** δ -119.22 (s); **HRMS (ESI)** calcd for: $C_{29}H_{32}FNO_3S$: $[M + H]^+$, 494.2160 found: 494.2148.

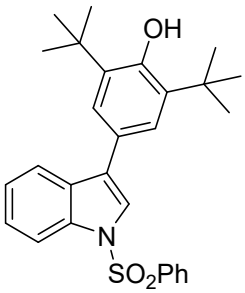


2,6-di-tert-butyl-4-(5-chloro-1-tosyl-1H-indol-3-yl)phenol (6e); Red brown solid, 68 mg, 66% yield, R_f = 0.7, column chromatography on silica gel (*n*-Hexane/EtOAc 90:10), mp 198−200°C; **^{1}H NMR (400 MHz, CDCl$_3$)**: δ 7.97 (d, *J* = 8.8 Hz, 1H), 7.77 (d, *J* = 8.2 Hz, 2H), 7.67 (d, *J* = 1.4 Hz, 1H), 7.62 (s, 1H), 7.34 (s, 2H), 7.30 (dd, *J* = 8.8, 1.5 Hz, 1H), 7.26 – 7.21 (m, 2H), 5.33 (s, 1H), 2.34 (s, 3H), 1.49 (s, 18H).; **^{13}C {^{1}H}NMR (101 MHz, CDCl$_3$):** δ 153.9, 145.3, 136.8, 135.2, 134.0, 131.2, 130.1, 129.6, 127.0, 125.1, 124.8, 124.6,

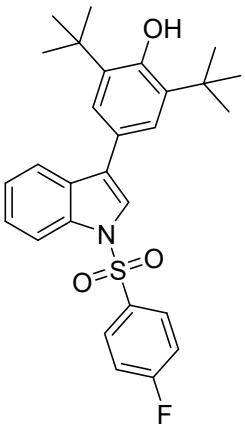
123.6, 120.5, 115.1, 34.6, 30.5, 21.7; **HRMS (ESI)** calcd for: $C_{29}H_{33}ClNO_3S$: $[M + H]^+$, 510.1864 found: 510.1858.



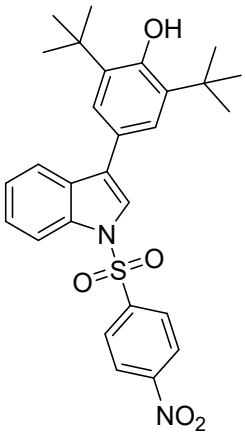
4-(5-bromo-1-tosyl-1H-indol-3-yl)-2,6-di-tert-butylphenol (6f); Red brown solid, 59 mg, 58% yield, R_f = 0.7, column chromatography on silica gel (*n*-Hexane/EtOAc 90:10), mp 196−198°C; **^{1}H NMR (400 MHz, $CDCl_3$)**: δ 7.92 (d, *J* = 8.8 Hz, 1H), 7.83 (s, 1H), 7.77 (d, *J* = 8.3 Hz, 2H), 7.60 (s, 1H), 7.44 (d, *J* = 8.8 Hz, 1H), 7.33 (s, 2H), 7.23 (d, *J* = 8.0 Hz, 2H), 5.33 (s, 1H), 2.34 (s, 3H), 1.49 (s, 18H); **^{13}C {^{1}H}NMR (101 MHz, $CDCl_3$):** 153.9, 145.4, 136.8, 135.1, 134.4, 131.7, 130.1, 127.7, 127.0, 124.8, 124.6, 123.6, 123.4, 117.3, 115.5, 34.6, 30.5, 21.7; **HRMS (ESI)** calcd for: $C_{29}H_{33}BrNO_3S$: $[M + H]^+$, 554.1359 found: 554.1371.



2,6-di-tert-butyl-4-(1-(phenylsulfonyl)-1H-indol-3-yl)phenol (6g); Pale yellow solid, 65 mg, 63% yield, R_f = 0.7, column chromatography on silica gel (*n*-Hexane/EtOAc 90:10), mp 196−198°C; **^{1}H NMR (400 MHz, $CDCl_3$)**: δ 8.07 (d, *J* = 8.2 Hz, 1H), 7.91 (d, *J* = 7.5 Hz, 2H), 7.74 (d, *J* = 7.7 Hz, 1H), 7.63 (s, 1H), 7.52 (t, *J* = 7.4 Hz, 1H), 7.47 – 7.39 (m, 4H), 7.36 (t, *J* = 7.5 Hz, 1H), 7.29 (t, *J* = 7.3 Hz, 1H), 5.30 (s, 1H), 1.49 (s, 18H).; **^{13}C {^{1}H}NMR (101 MHz, $CDCl_3$):** δ 153.8, 138.4, 136.7, 135.8, 133.9, 130.0, 129.4, 127.0, 125.2, 125.0, 124.8, 124.2, 123.7, 122.2, 120.7, 114.1, 34.6, 30.5; **HRMS (ESI)** calcd for: $C_{28}H_{32}NO_3S$: $[M + H]^+$, 462.2097 found: 462.2124.



2,6-di-tert-butyl-4-(1-((4-fluorophenyl)sulfonyl)-1H-indol-3-yl)phenol (6h); Pale yellow solid, 68 mg, 66% yield, R_f = 0.7, column chromatography on silica gel (*n*-Hexane/EtOAc 90:10), mp 178−180°C; **^{1}H NMR (400 MHz, $CDCl_3$)**: δ 8.04 (d, *J* = 8.2 Hz, 1H), 7.98 – 7.85 (m, 2H), 7.75 (d, *J* = 7.7 Hz, 1H), 7.60 (s, 1H), 7.40 (s, 2H), 7.38 – 7.23 (m, 2H), 7.09 (t, *J* = 8.5 Hz, 2H), 5.32 (s, 1H), 1.49 (s, 18H); **^{13}C {^{1}H}NMR (101 MHz, $CDCl_3$):** δ 165.8 (d, *J* = 257.0 Hz), 153.8, 136.7, 135.7, 134.3 (d, *J* = 3.2 Hz), 130.1, 129.9 (d, *J* = 9.7 Hz), 125.6, 125.1, 124.8, 124.0, 123.9, 122.1, 120.9, 116.8 (d, *J* = 22.8 Hz), 114.0, 34.6, 30.5; **^{19}F{^{1}H} NMR (377 MHz, $CDCl_3$):** δ -102.81 (s); **HRMS (ESI)** calcd for: $C_{28}H_{31}FNO_3S$: $[M + H]^+$, 480.2003 found: 480.1983.



2,6-di-tert-butyl-4-(1-((4-nitrophenyl)sulfonyl)-1H-indol-3-yl)phenol (6i); Red brown solid, 33 mg, 32% yield, R_f = 0.7, column chromatography on silica gel (*n*-Hexane/EtOAc 90:10), mp 196−198°C; **^{1}H NMR (400 MHz, $CDCl_3$)**: δ 8.26 (d, *J* = 8.6 Hz, 2H), 8.06 (t, *J* = 8.4 Hz, 3H), 7.74 (d, *J* = 7.7 Hz, 1H), 7.58 (s, 1H), 7.39 (s, 2H), 7.33 (t, *J* = 7.4 Hz, 1H), 7.26 (s, 1H), 5.34 (s, 1H), 1.49 (s, 18H); **^{13}C {^{1}H}NMR (101 MHz, $CDCl_3$):** δ 154.1, 150.8, 143.4, 136.8, 135.7, 130.3, 128.3, 126.7, 125.5, 124.8, 124.7, 124.5, 123.6, 121.7, 121.2, 114.0, 34.6, 30.5; **HRMS (ESI)** calcd for: $C_{28}H_{31}N_2O_5S$: $[M + H]^+$, 507.1948 found: 507.1952.

7. Experimental procedure for gram-scale synthesis of 6a:

To an oven-dried 100 mL round bottom flask was added *ortho*-tosylaminophenyl-subsituted *p*-QM (2.6 mmol, 1.0 equiv.), bromonitromethane (2.2 mmol, 1.2 equiv.), and K_2CO_3 (5.4 mmol, 2.5 equiv.) in anhydrous acetone (10.0 mL), and the resulting solution was stirred at room temperature for 12 h. After completion of the reaction, the mixture was diluted with water (50 mL) and extracted with EtOAc (3×50 mL). The organic layer was collected and dried over anhydrous Na_2SO_4. The combined organic layer was concentrated under reduced pressure. The resultant crude material was purified by column chromatography on silica gel using *n*-hexane/EtOAc as an eluent. (*n*-hexane/EtOAc 90:10) (0.62 g, 60% yield).

8. Experimental procedure for the attempted synthesis of 9:

To an oven-dried 50 mL round bottom flask was added *para*-hydroxyphenyl-subsituted *p*-QM (0.32 mmol, 1.0 equiv.), bromonitromethane (0.39 mmol, 1.2 equiv.), and K_2CO_3 (0.81 mmol, 2.5 equiv.) in anhydrous MeCN (1.5 mL), and the resulting solution was stirred at room temperature until *para*-hydroxyphenyl-subsituted *p*-QM was completely consumed (based on TLC analysis). After completion of the reaction, the mixture was diluted with water (10 mL) and extracted with EtOAc (3×10 mL). The organic layer was collected and dried over anhydrous Na_2SO_4. The combined organic layer was concentrated under reduced pressure. The resultant crude material was directly used for HRMS analysis.

9. Experimental procedure for the synthesis of 10:

To an oven-dried 50 mL round bottom flask was added *p*-QM (0.32 mmol, 1.0 equiv.), bromonitromethane (0.39 mmol, 1.2 equiv.), and K_2CO_3 (0.81 mmol, 2.5 equiv.) in anhydrous MeCN (1.5 mL), and the resulting solution was stirred at room temperature until *p*-QM was consumed (based on TLC analysis). After completion of the reaction, the resultant crude material was directly used for HRMS analysis (unstable on column chromatography on silica gel).

10. Experimental procedure for the synthesis of 4a using 3a:

To an oven-dried 50 mL round bottom flask was added dihydrobenzofuran derivative **3a** (0.27 mmol, 1.0 equiv.), DDQ (0.54 mmol, 2.0 equiv.) in anhydrous MeCN (1.5 mL) was stirred at room temperature. After the consumption of **3a** (based on TLC analysis), the residue was filtered through a pad of celite, and the filtrate was then concentrated under reduced pressure. The residue was purified by column chromatography on silica gel using *n*-hexane/EtOAc as an eluent. (**4a**, 78 mg, 86% yield).

11. Experimental procedure for the attempted synthesis of 12:

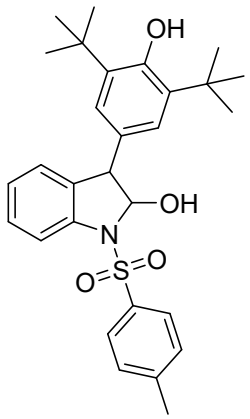
To an oven-dried 50 mL round bottom flask was added *ortho*-tosylaminophenyl acrylate (0.29 mmol, 1.0 equiv), bromonitromethane (0.44 mmol, 1.2 equiv.), and K_2CO_3 (0.72 mmol, 2.5 equiv.) in anhydrous MeCN (1.5 mL), and the resulting solution was stirred at room temperature. After 48 h starting remains as it is (based on TLC analysis).

12. Experimental procedure for the attempted synthesis of 6a using a precursor of 5a:

To an oven-dried 50 mL round bottom flask was added precursor of 5a (0.22 mmol, 1.0 equiv), bromonitromethane (0.26 mmol, 1.2 equiv.), MnO_2 (1.08 mmol, 5.0 equiv.) and K_2CO_3 (0.54 mmol, 2.5 equiv.) in anhydrous MeCN (1.5 mL), and the resulting solution was stirred at room temperature until precursor of 5a was completely consumed (based on TLC analysis). After completion of the reaction, the residue was filtered through a pad of celite, and the filtrate was then concentrated under reduced pressure. The combined organic layer was concentrated under reduced pressure. The resultant crude material was purified by column chromatography on silica gel using *n*-hexane/EtOAc as an eluent.

13. Experimental procedure for synthesis of 6a and 6a':

To an oven-dried 100 mL round bottom flask was added *ortho*-tosylaminophenyl-subsituted *p*-QM (2.6 mmol, 1.0 equiv.), bromonitromethane (2.2 mmol, 1.2 equiv.), and K_2CO_3 (5.4 mmol, 2.5 equiv.) in anhydrous acetone (10.0 mL), and the resulting solution was stirred at room temperature for 1 h. Then, it was quenched with H_2O (5 mL) and extracted with EtOAc (3×10 mL). The organic layer was collected and dried over anhydrous Na_2SO_4. The combined organic layer was concentrated under reduced pressure. The resultant crude material was purified by column chromatography on silica gel using *n*-hexane/EtOAc as an eluent. (*n*-hexane/EtOAc 90:10) (**6a**, 18 mg, 18% yield, **6a'**, 45 mg, 42% yield).



3-(3,5-di-tert-butyl-4-hydroxyphenyl)-1-tosylindolin-2-ol (6a'); White solid, 45 mg, 42% yield, 12:1 dr, R_f = 0.5, flash chromatography on silica gel (*n*-Hexane/EtOAc 90:10), mp 152−154°C; **^{1}H NMR (400 MHz, $CDCl_3$)**: δ 7.73 (d, *J* = 8.3 Hz, 2H), 7.57 (d, *J* = 8.1 Hz, 1H), 7.26 (t, *J* = 3.7 Hz, 1H), 7.21 (d, *J* = 8.1 Hz, 2H), 6.98 (dt, *J* = 12.0, 5.3 Hz, 2H), 6.57 (s, 2H), 5.59 (t, 1H), 5.10 (s, 1H), 4.24 (d, *J* = 3.6 Hz, 1H), 3.75 (d, *J* = 2.0 Hz, 1H), 2.36 (s, 3H), 1.27 (s,

18H); **^{13}C {^{1}H}NMR (101 MHz, $CDCl_3$):** δ 153.0, 144.4, 140.1, 136.1, 134.9, 132.0, 131.5, 129.9, 128.4, 127.2, 126.2, 124.5, 123.9, 113.3, 94.4, 55.2, 34.2, 30.1, 21.6; **HRMS (ESI)** calcd for: $C_{29}H_{35}NNaO_4S$: $[M + H]^+$, 516.2179 found: 516.2189.

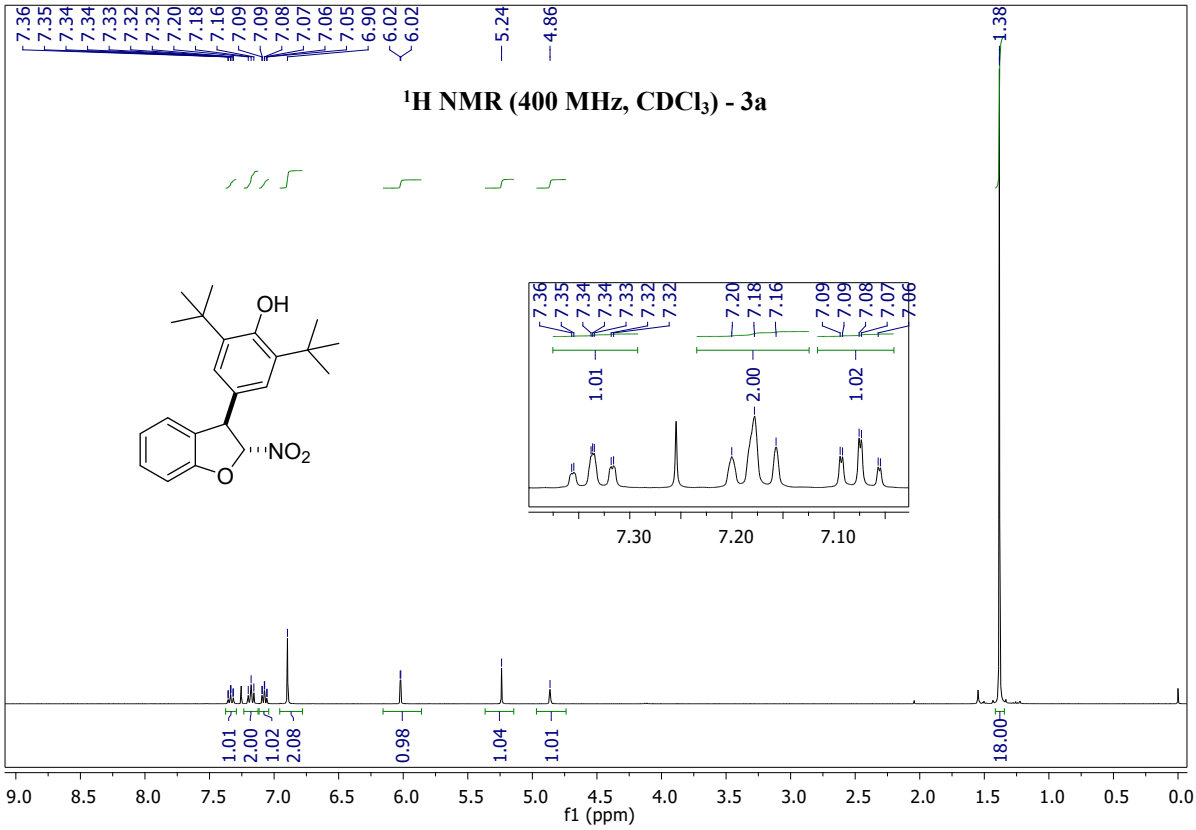
References:

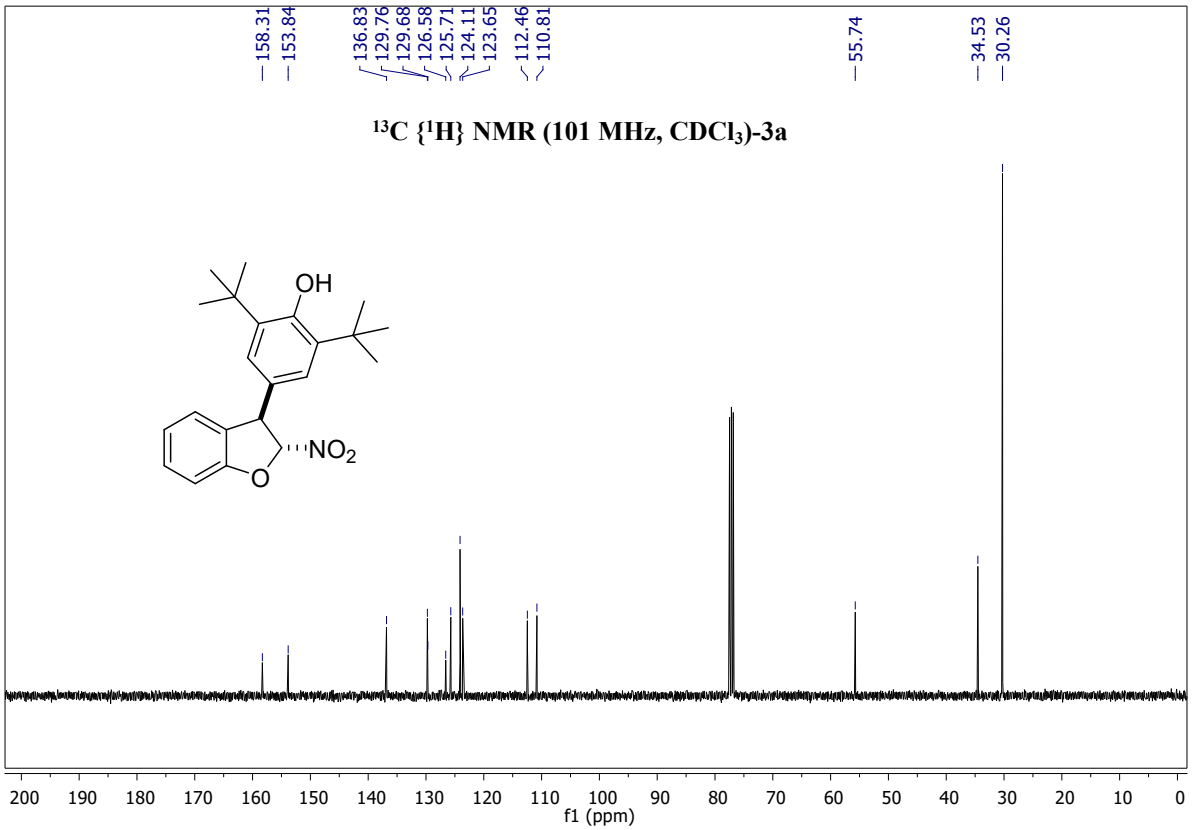
1 K. Zhao, Y. Zhi, T. Shu, A. Valkonen, K. Rissanen and D. Enders, *Angew. Chemie Int. Ed.*, 2016, **55**, 12104–12108.

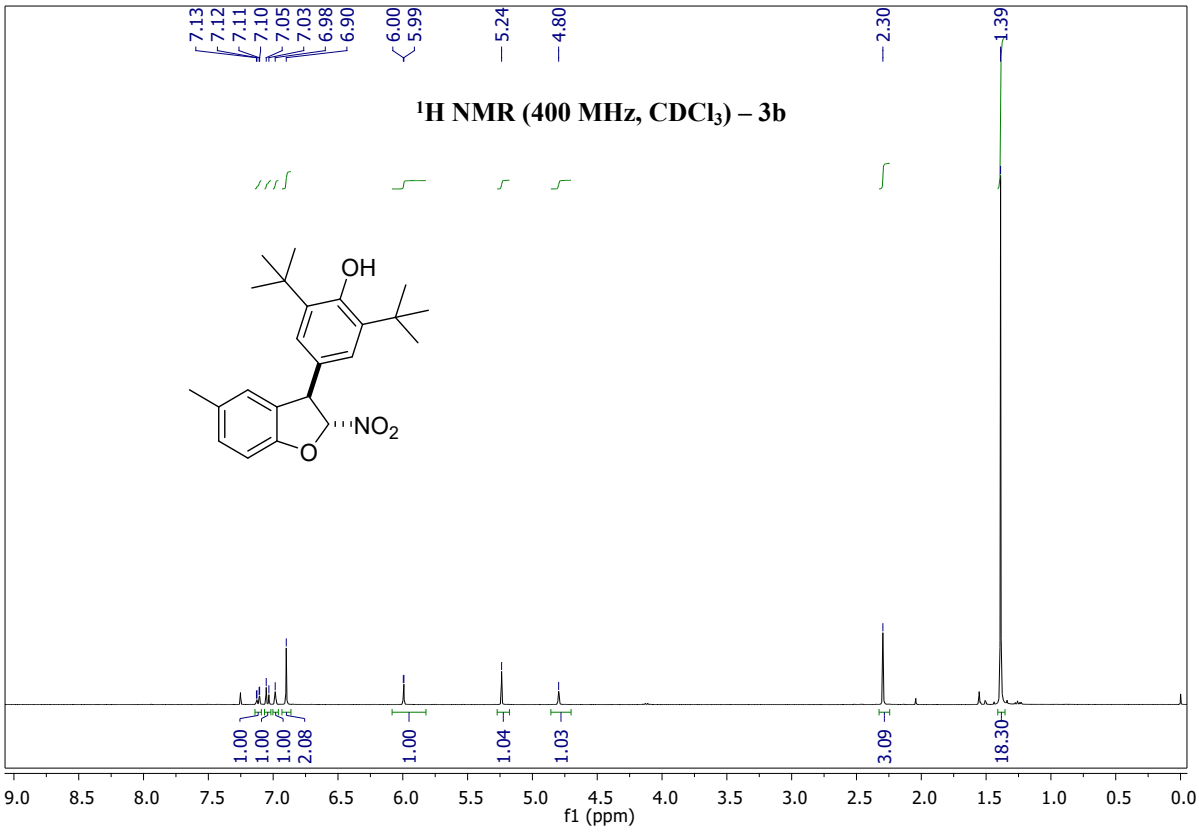
2 F. Luo, H. Dong, W. Ren and Y. Wang, *Org. Lett.*, 2022, **24**, 7727–7731.

3 V. Pitchumani, M. Breugst and D. W. Lupton, *Org. Lett.*, 2021, **23**, 9413–9418.

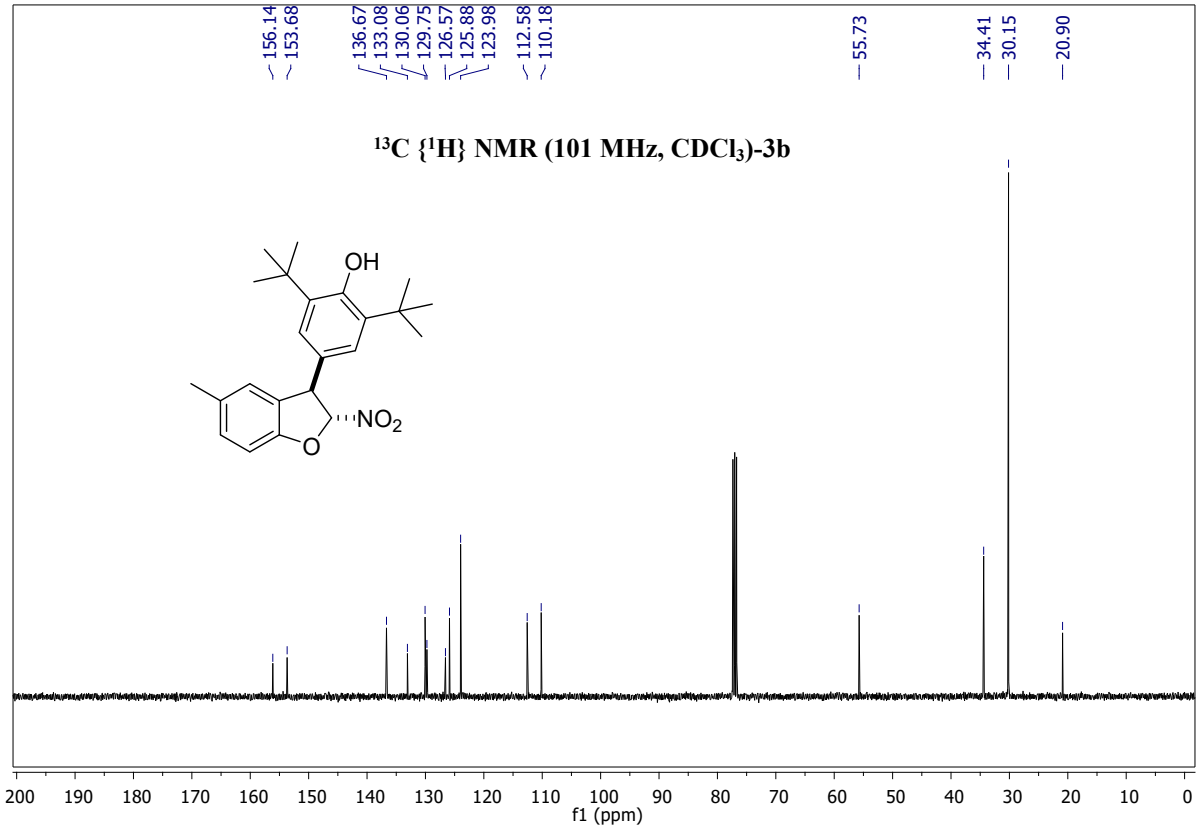
8. ^{1}H NMR, ^{13}C NMR and ^{19}F Spectra of products



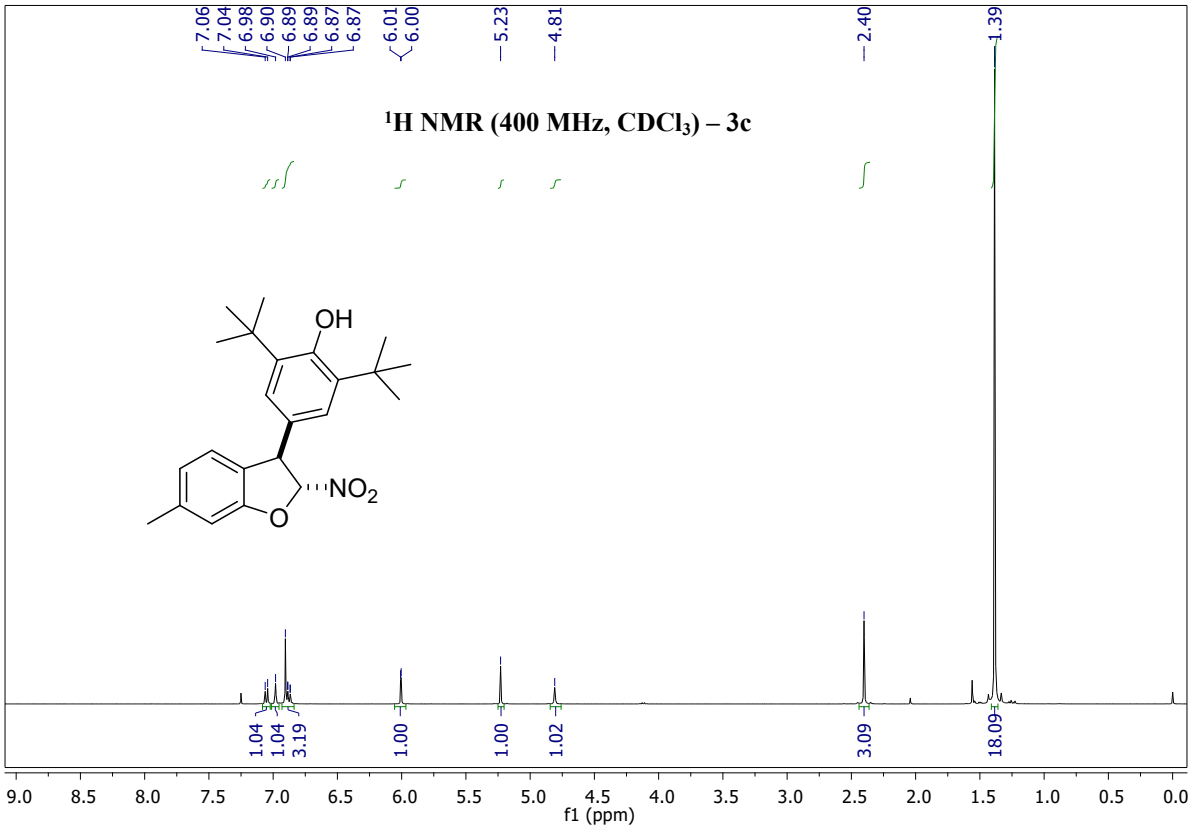


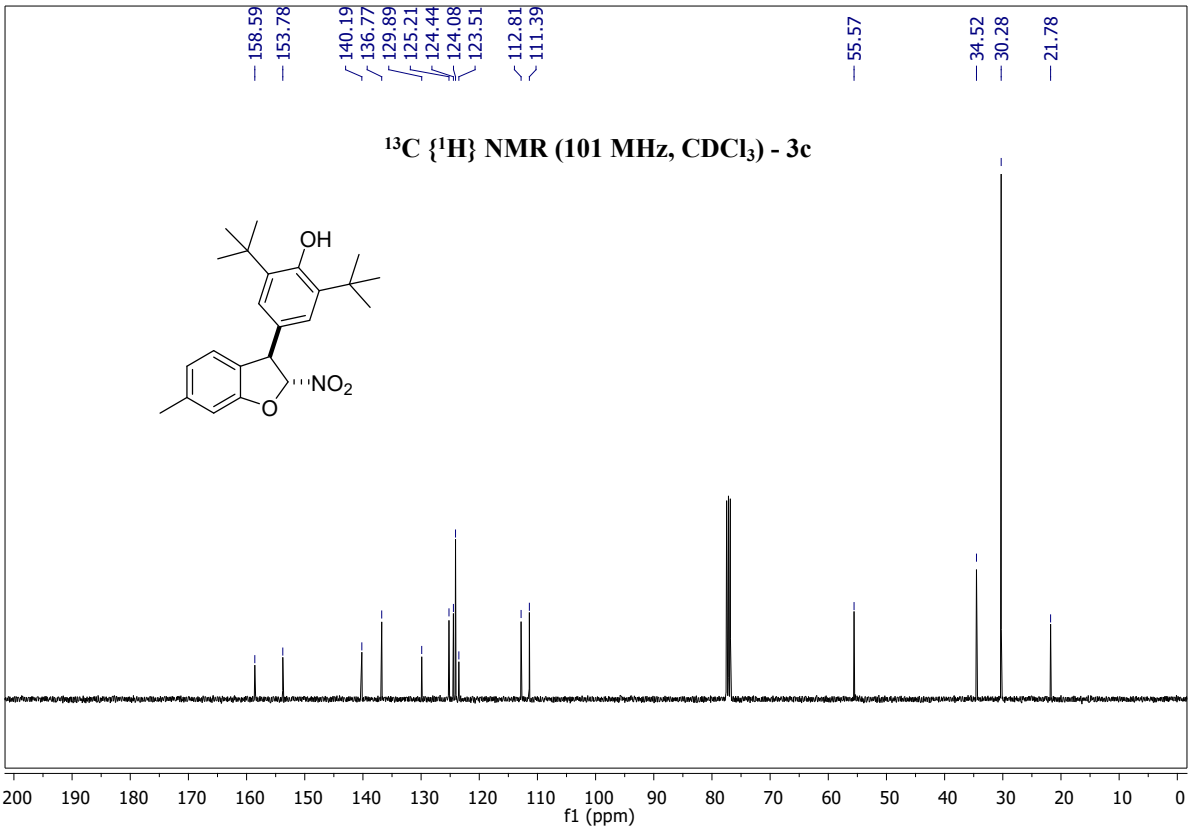


^{1}H NMR (400 MHz, $CDCl_3$) – 3b

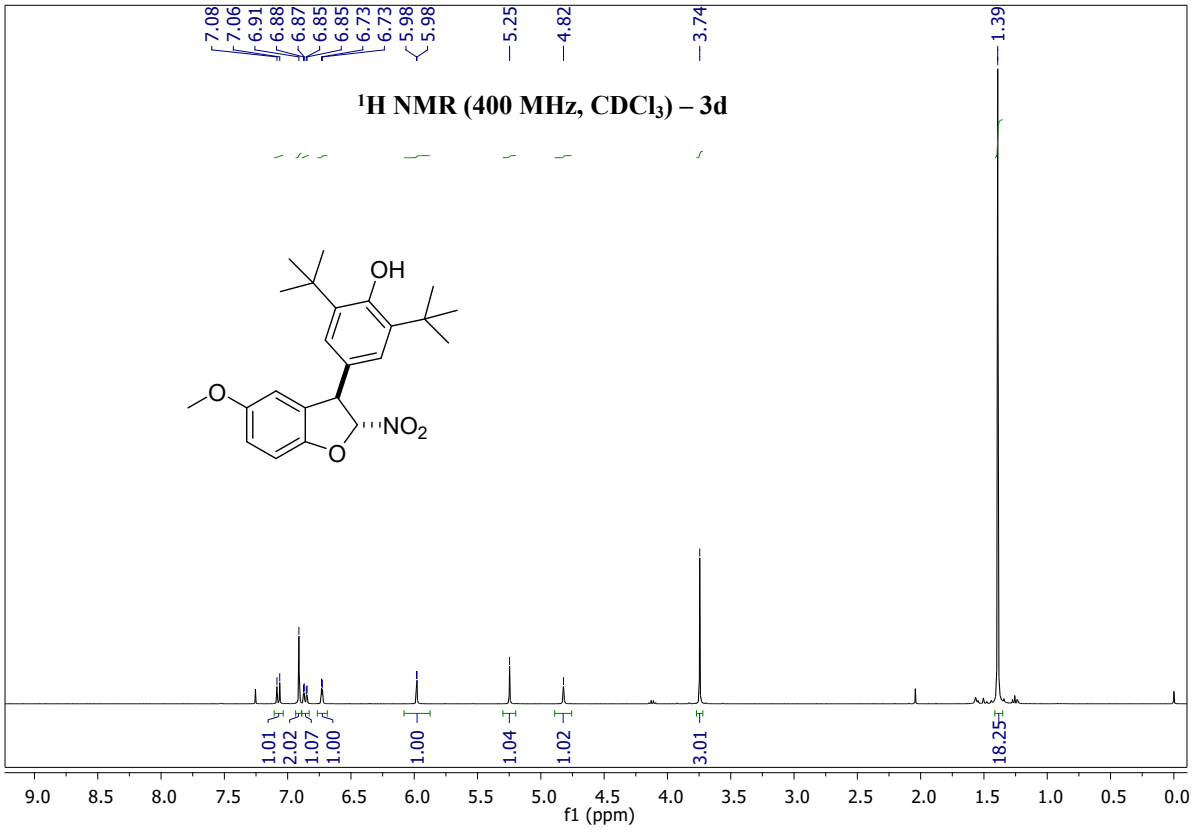


^{13}C {^{1}H} NMR (101 MHz, $CDCl_3$)-3b

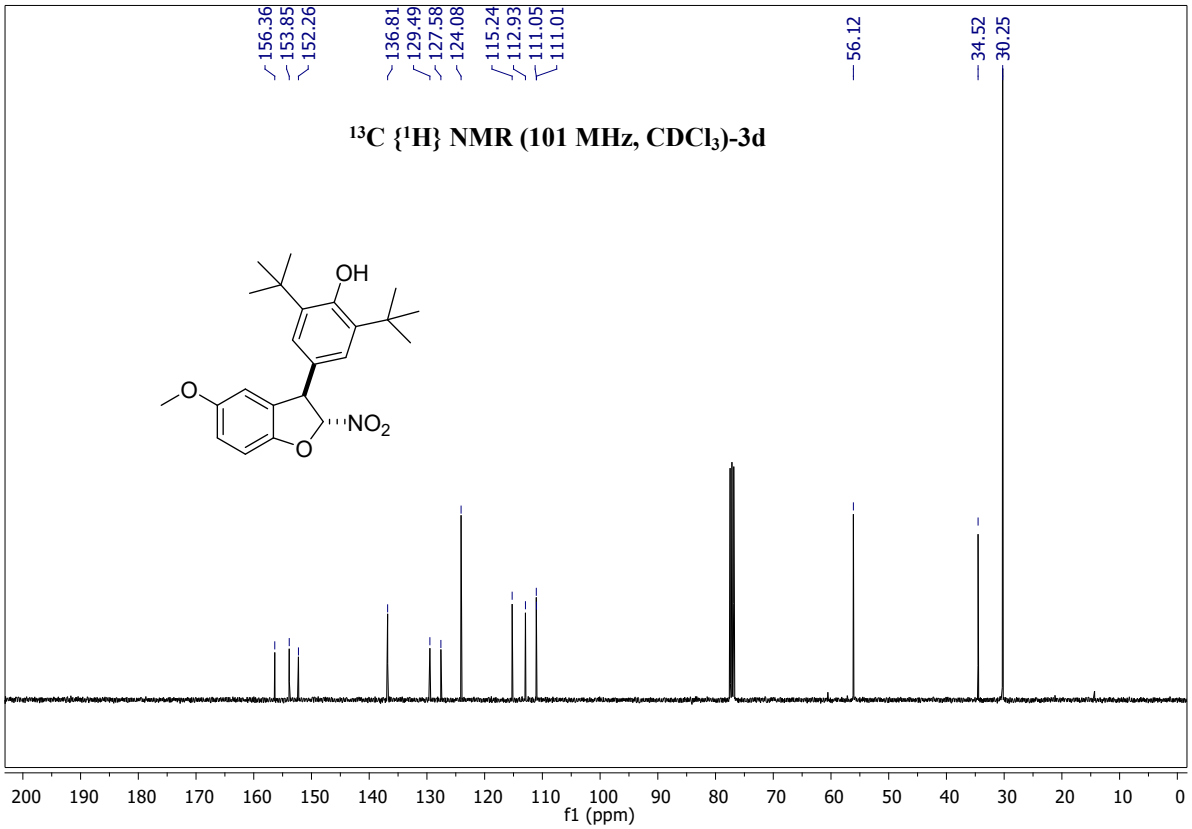

7.06
7.04
6.98
6.90
6.89
6.89
6.87
6.87
6.01
6.00
5.23
4.81
2.40
1.39
1H NMR (400 MHz, CDCl3) – 3c
OH
NO2
O
1.04
1.04
3.19
1.00
1.00
1.02
3.09
18.09
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
f1 (ppm)



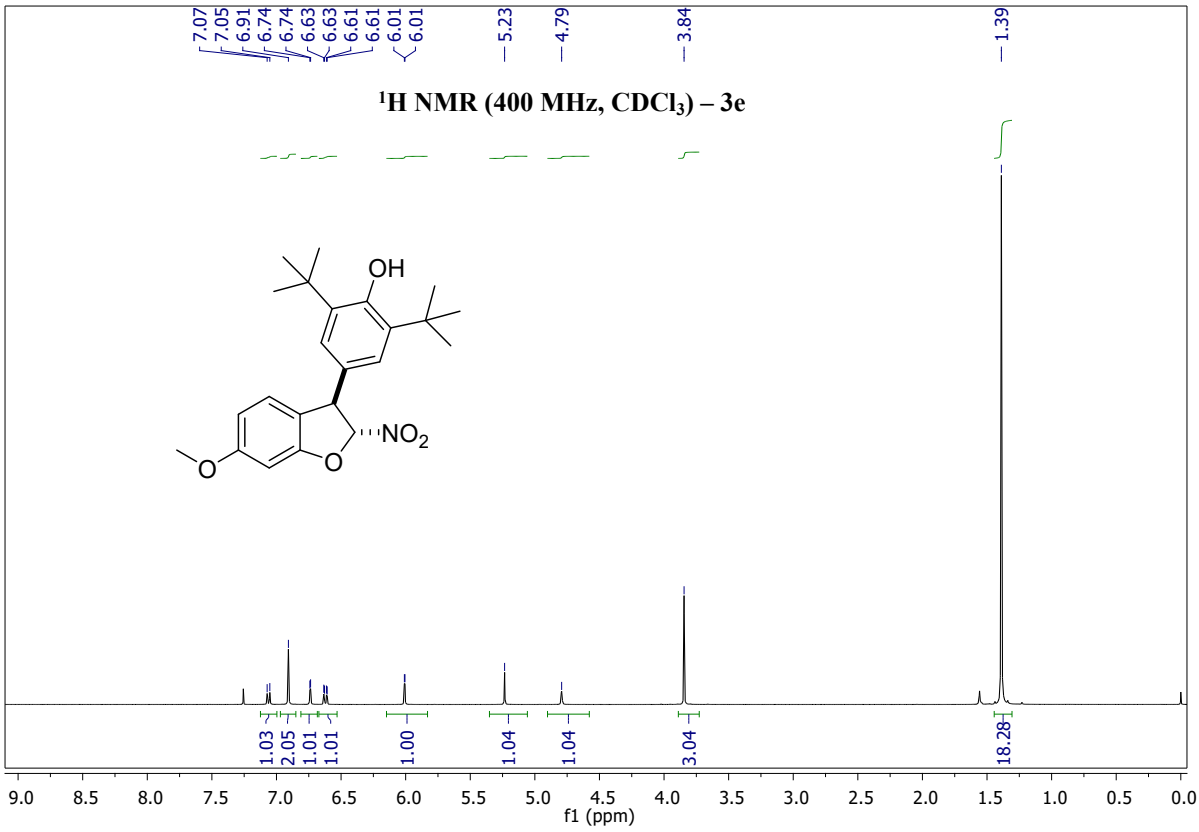
^{13}C {^{1}H} NMR (101 MHz, $CDCl_3$) - 3c



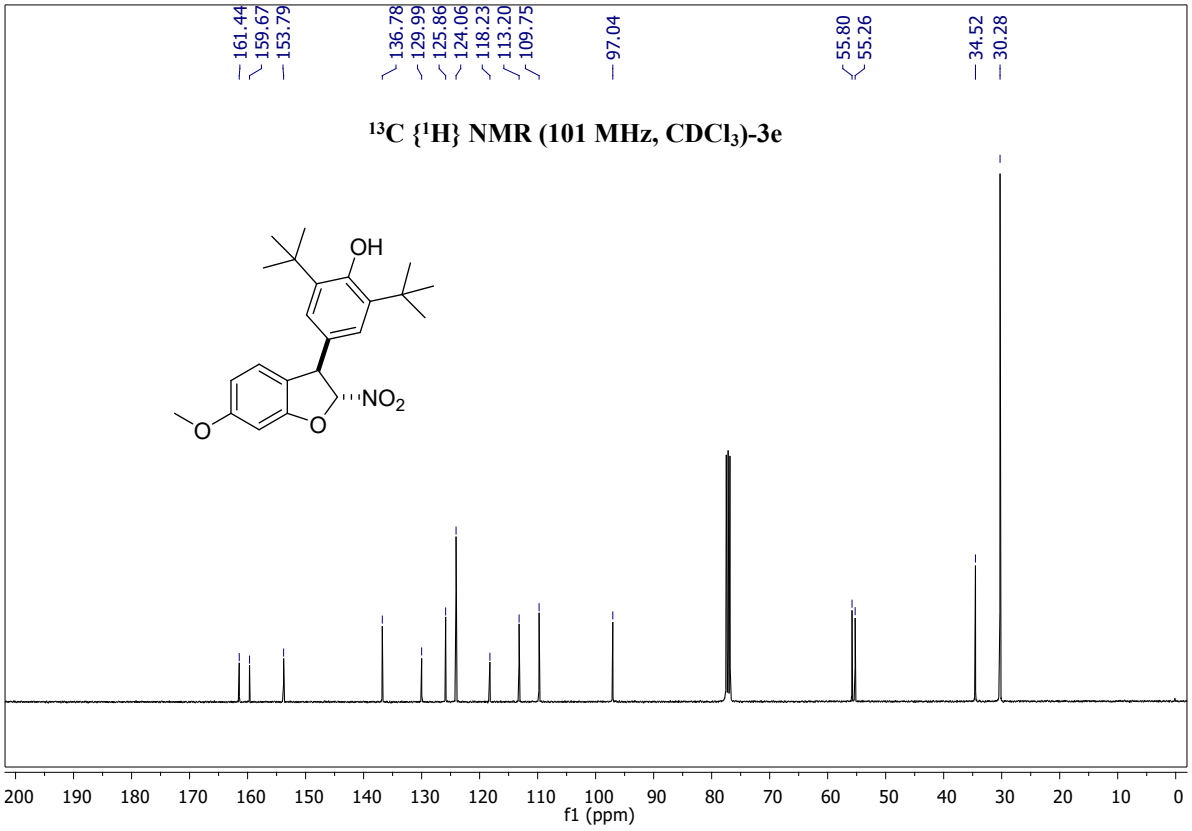
^{1}H NMR (400 MHz, $CDCl_3$) – 3d



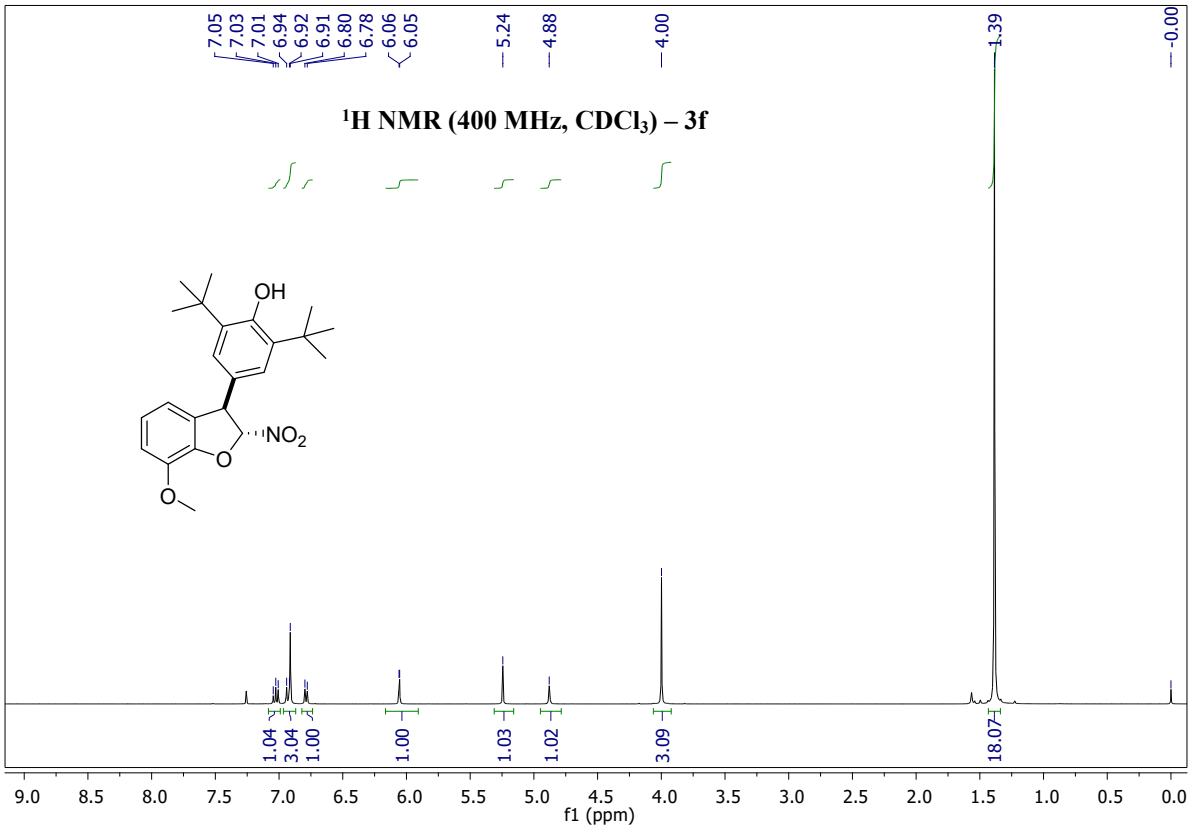
^{13}C {^{1}H} NMR (101 MHz, $CDCl_3$)-3d



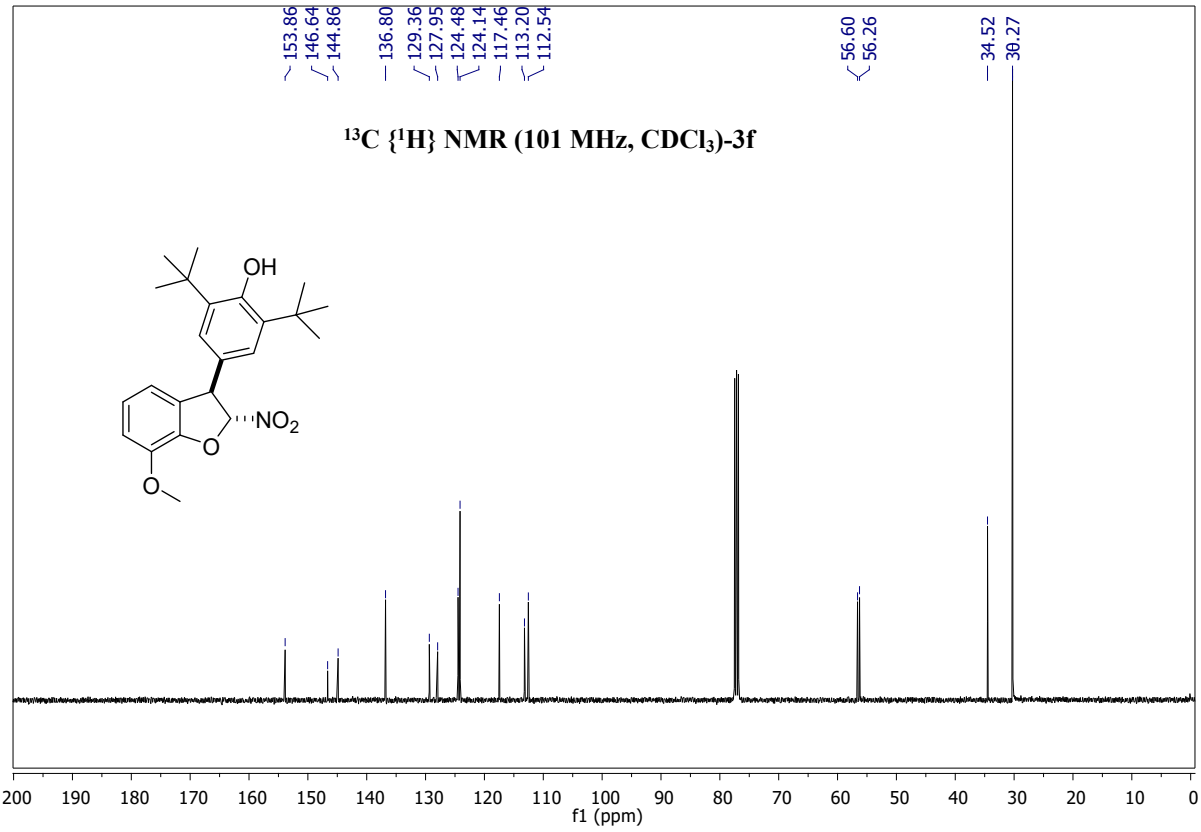
^{1}H NMR (400 MHz, $CDCl_3$) – 3e



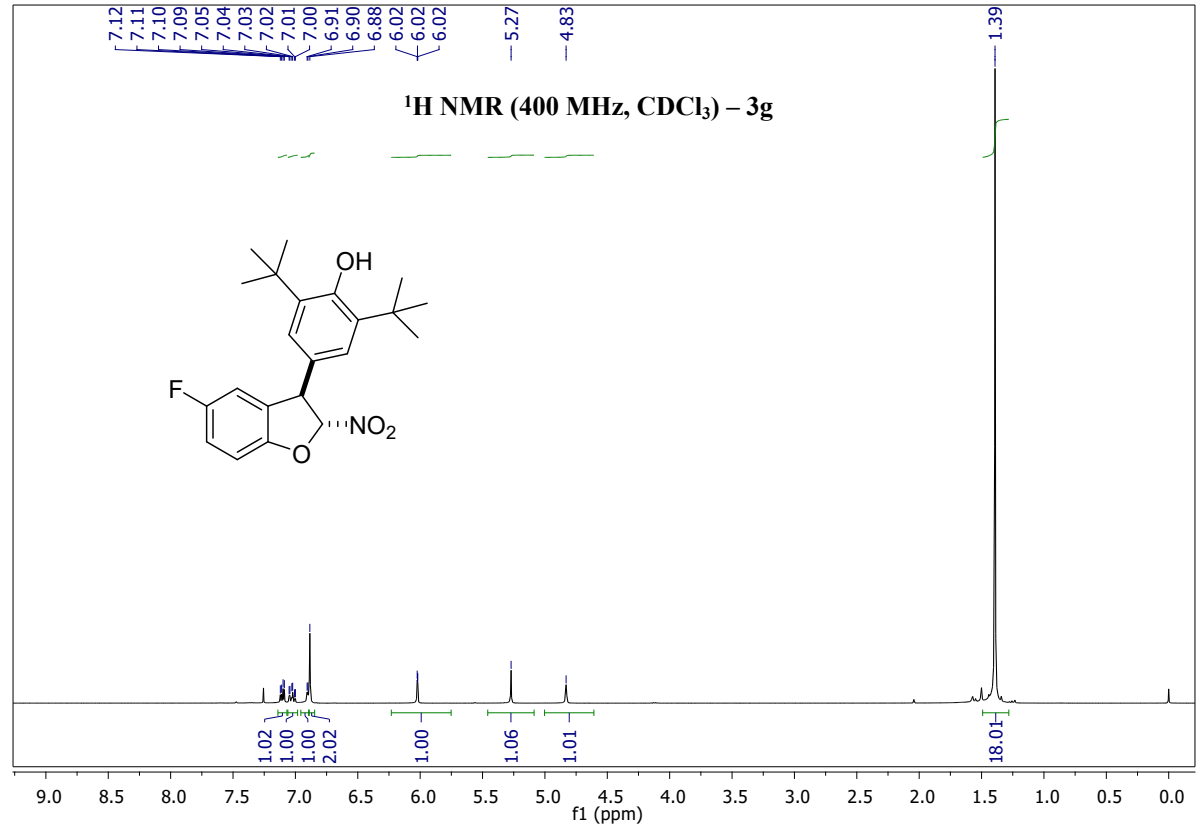
^{13}C {^{1}H} NMR (101 MHz, $CDCl_3$)-3e



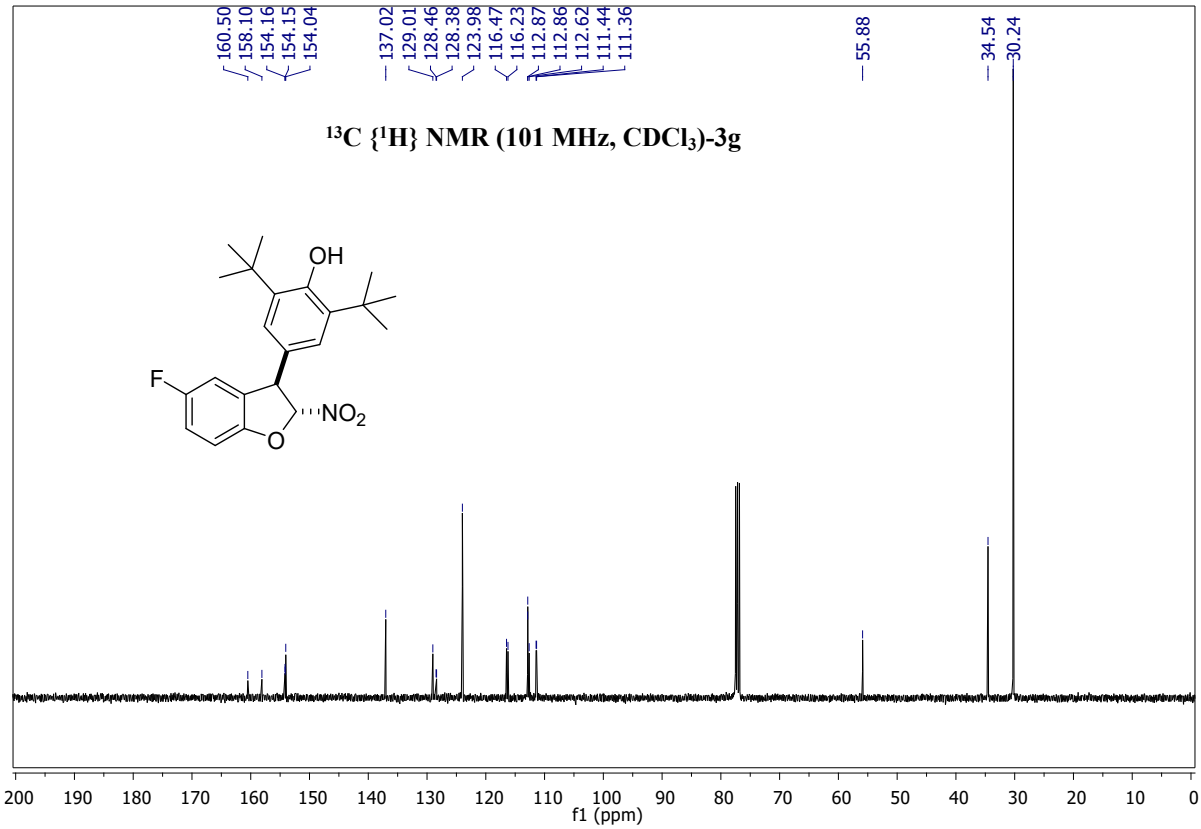
^{1}H NMR (400 MHz, $CDCl_3$) – 3f



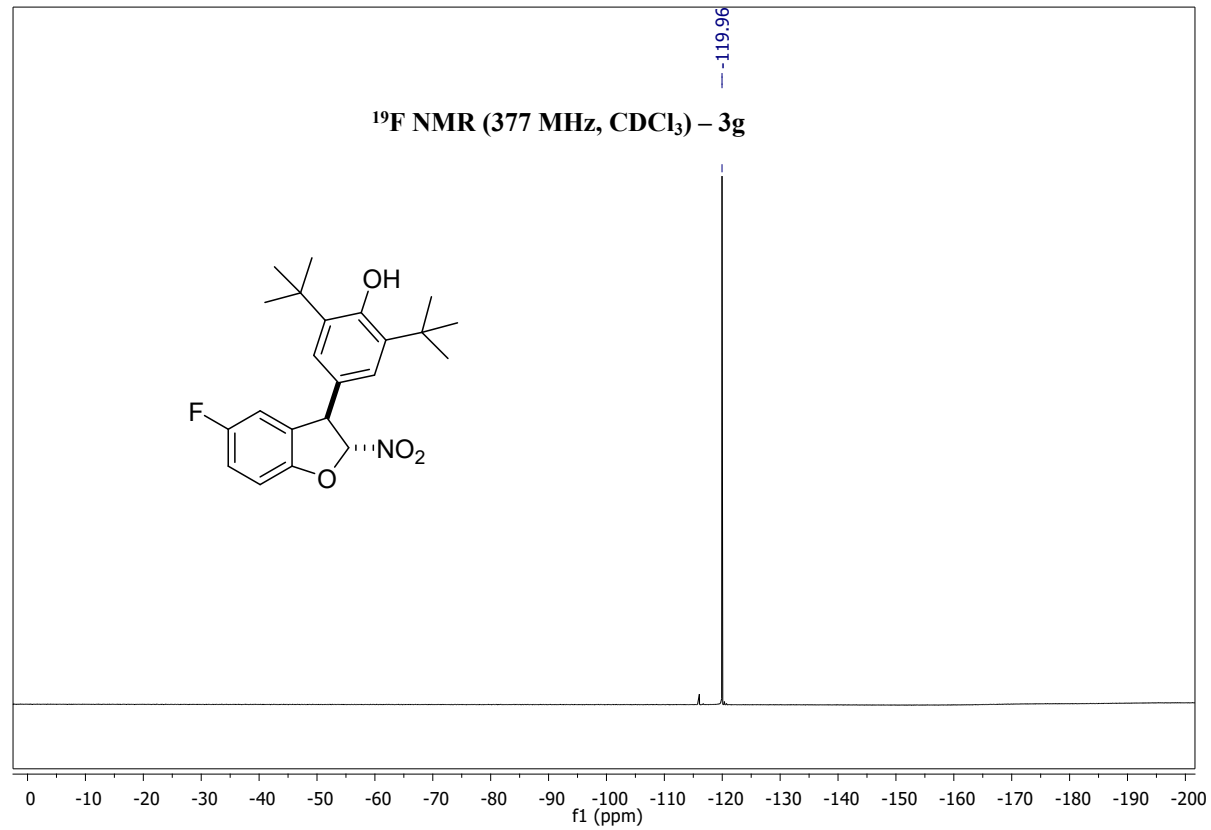
^{13}C {^{1}H} NMR (101 MHz, $CDCl_3$)-3f



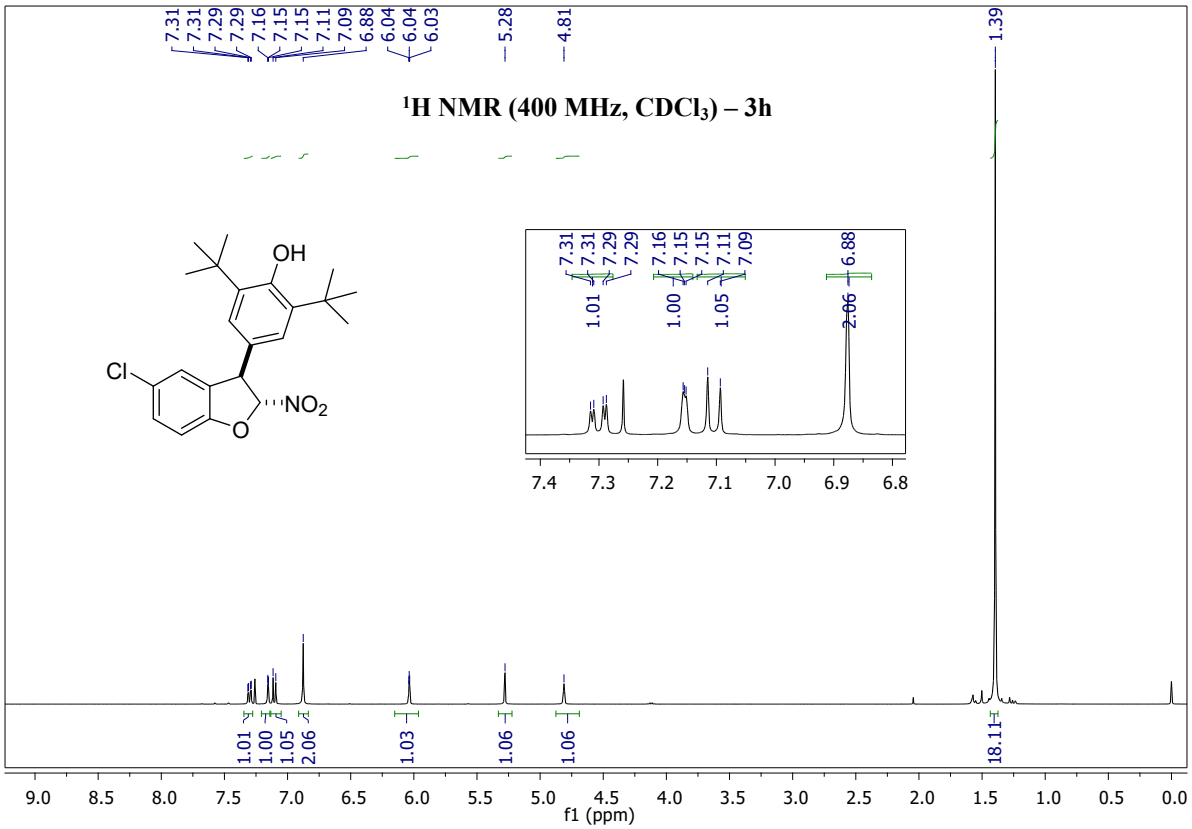
^{1}H NMR (400 MHz, $CDCl_3$) – 3g



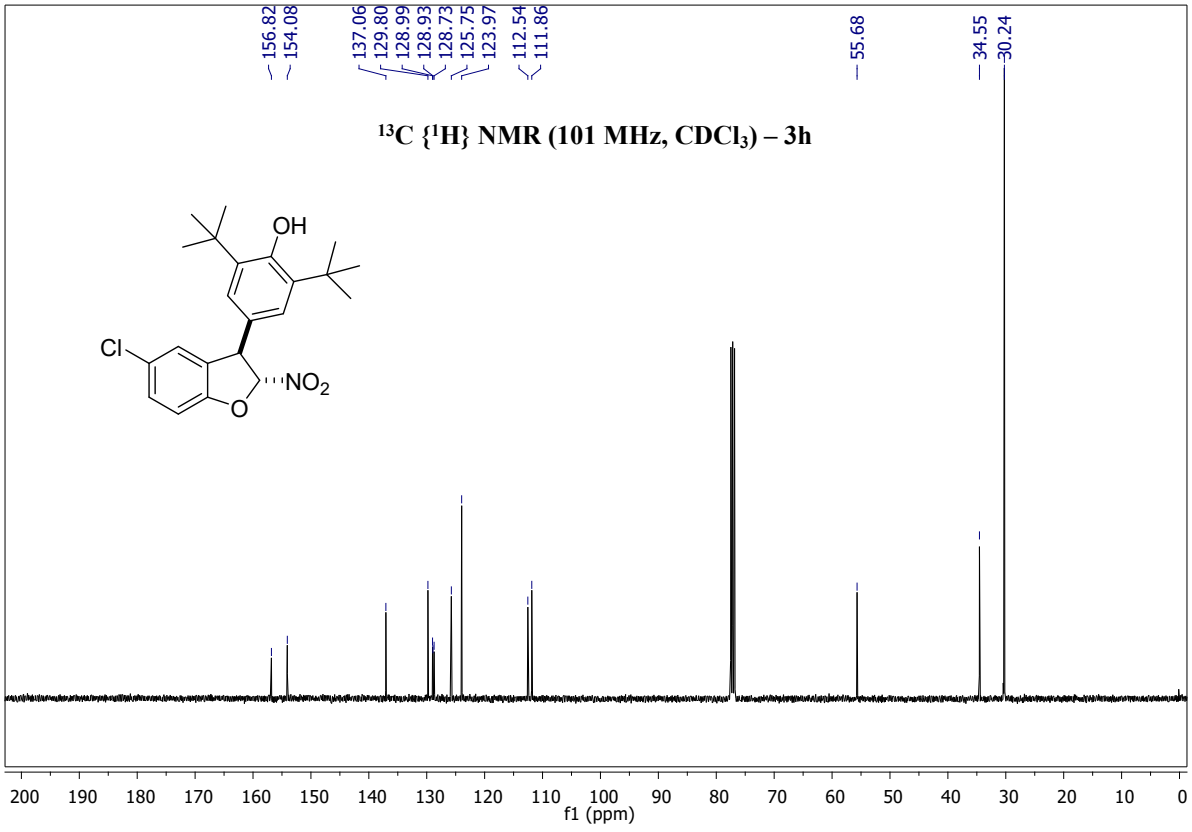
^{13}C {^{1}H} NMR (101 MHz, $CDCl_3$)-3g



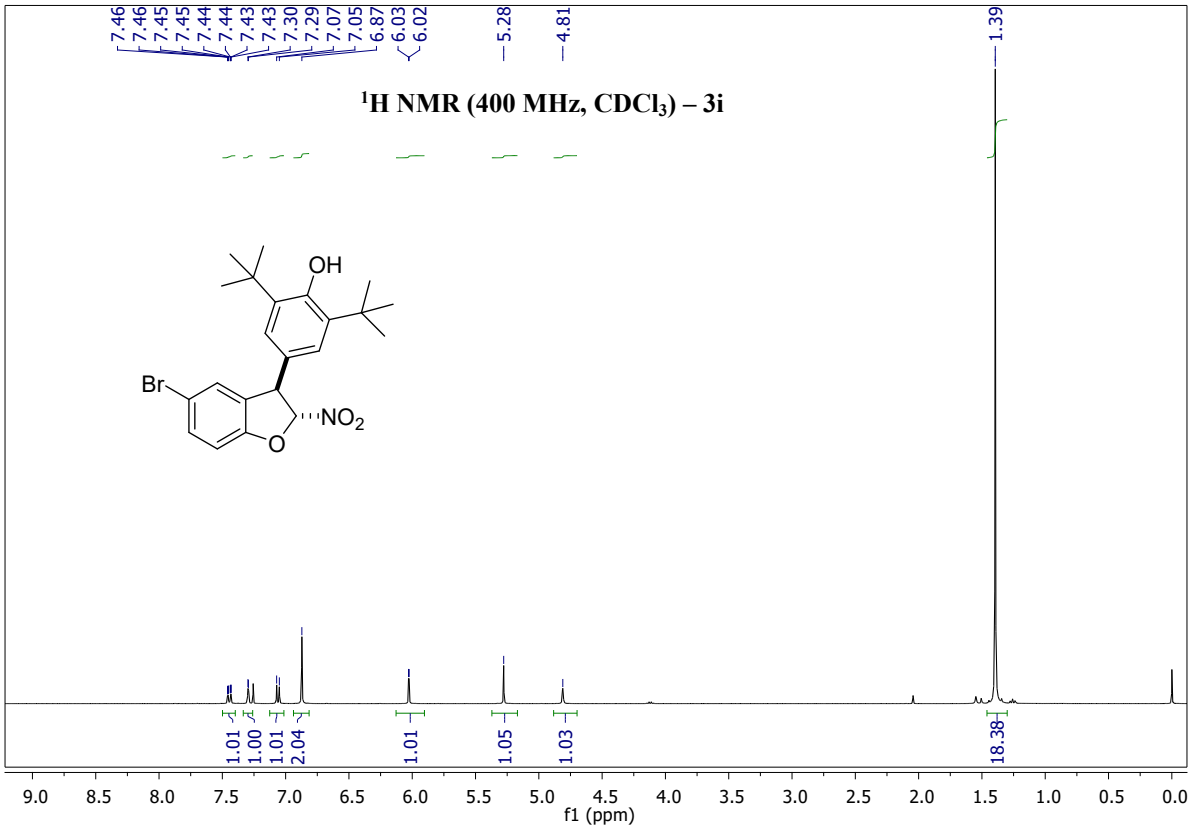
^{19}F NMR (377 MHz, $CDCl_3$) – 3g

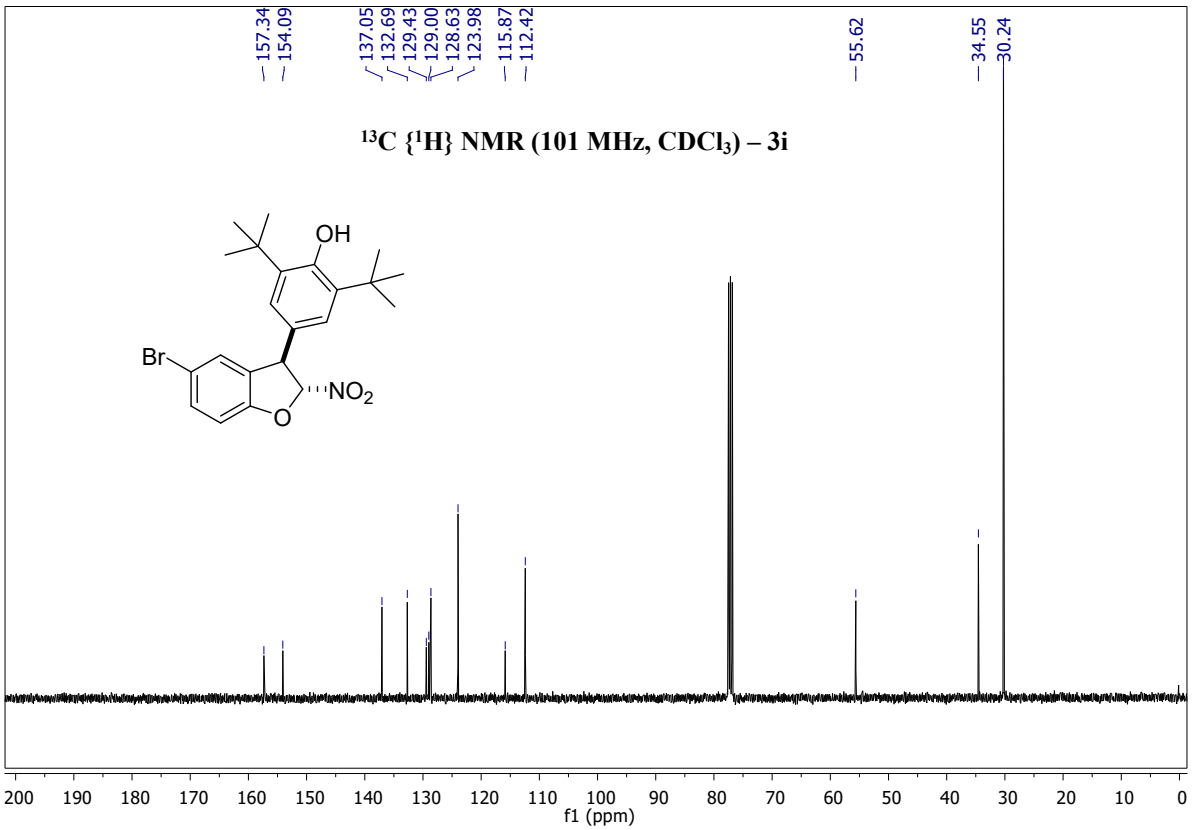


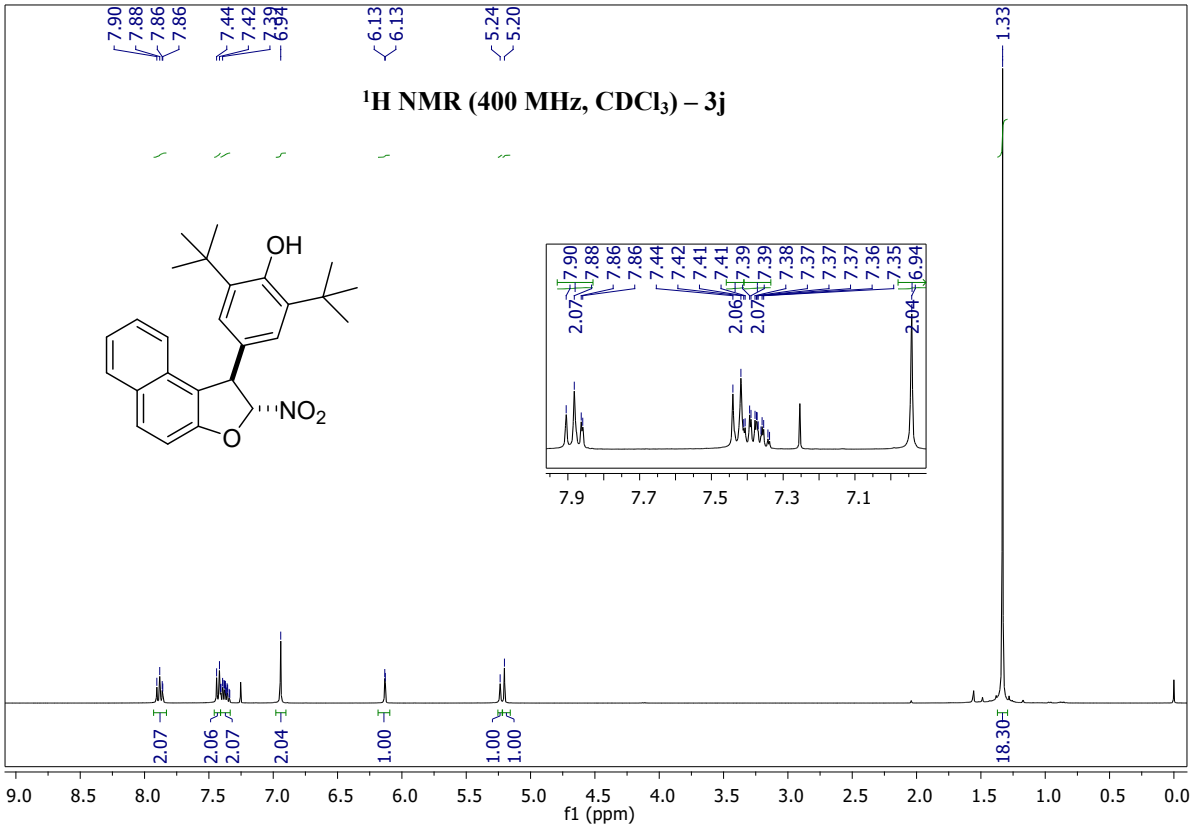
^{1}H NMR (400 MHz, $CDCl_3$) – 3h

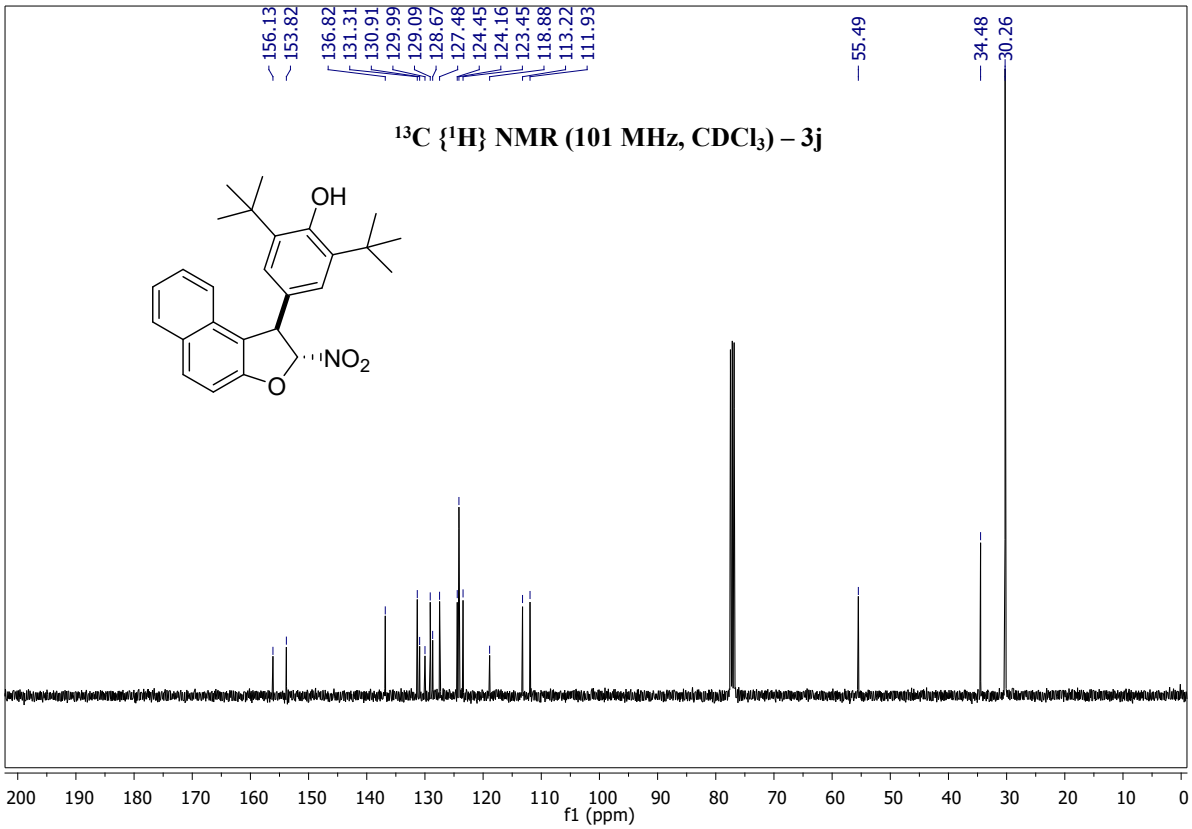


^{13}C {^{1}H} NMR (101 MHz, $CDCl_3$) – 3h

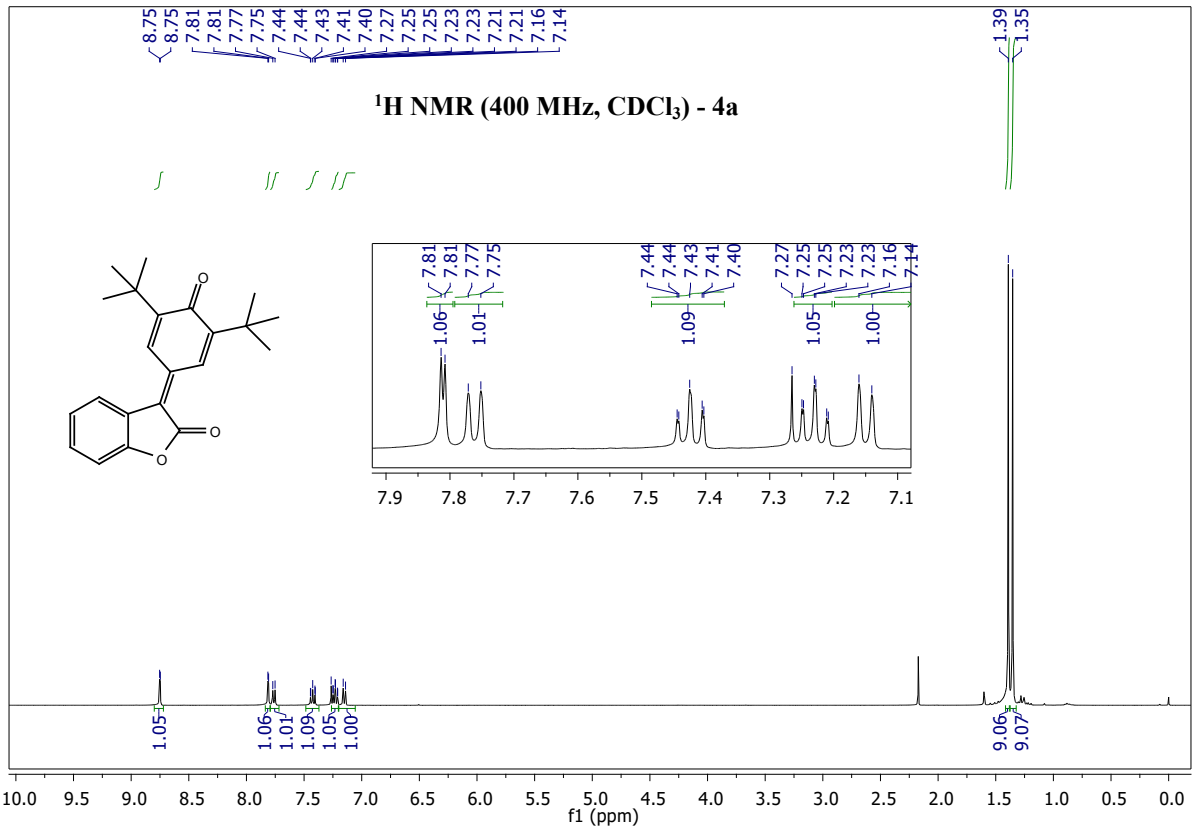

7.46
7.46
7.45
7.45
7.44
7.44
7.43
7.43
7.30
7.29
7.07
7.05
6.87
6.03
6.02
5.28
4.81
1.39
1H NMR (400 MHz, CDCl3) – 3i
OH
Br
NO2
O
1.01
1.00
1.01
2.04
1.01
1.05
1.03
18.38
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
f1 (ppm)


157.34
154.09
137.05
132.69
129.43
129.00
128.63
123.98
115.87
112.42
55.62
34.55
30.24
13C {1H} NMR (101 MHz, CDCl3) – 3i
OH
Br
NO2
O
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
f1 (ppm)

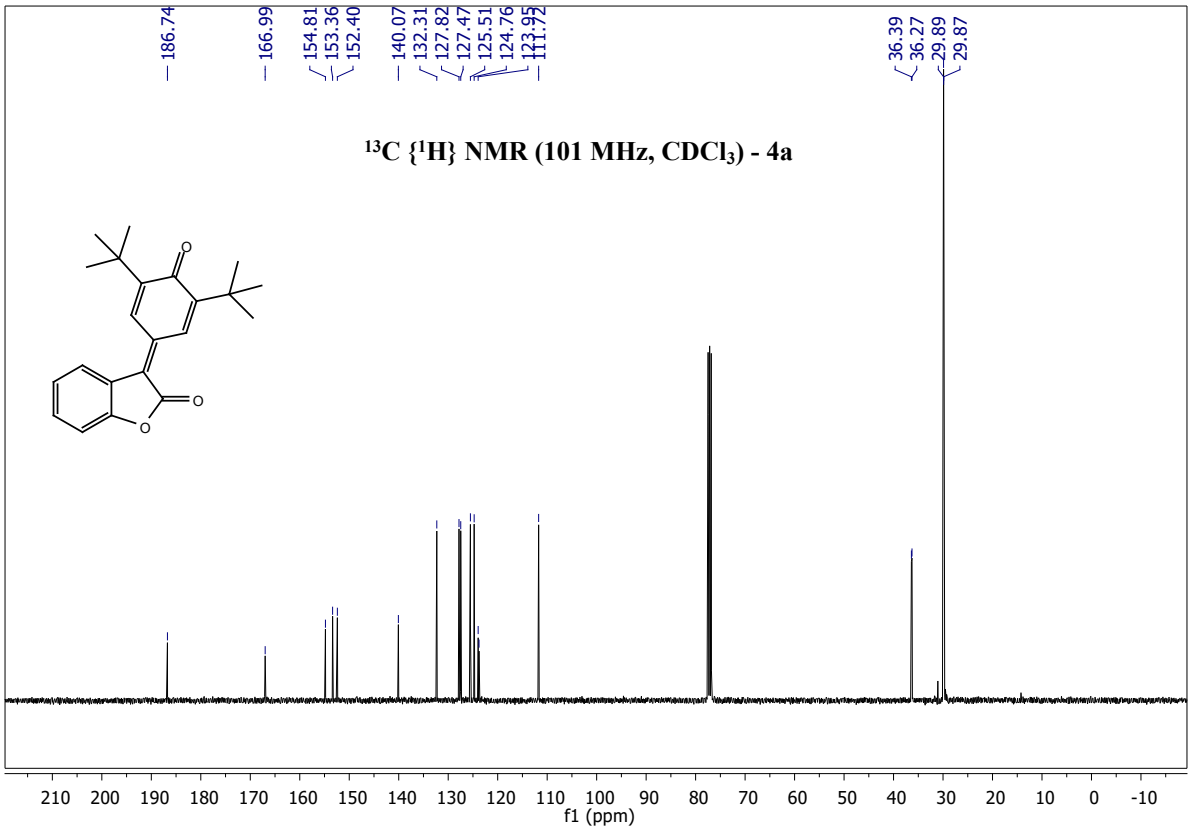

^{1}H NMR (400 MHz, $CDCl_3$) – 3j
OH
NO_2
O
7.90
7.88
7.86
7.86
7.44
7.42
7.39
6.94
6.13
6.13
5.24
5.20
1.33
2.07
2.06
2.07
2.04
1.00
1.00
1.00
18.30
f1 (ppm)



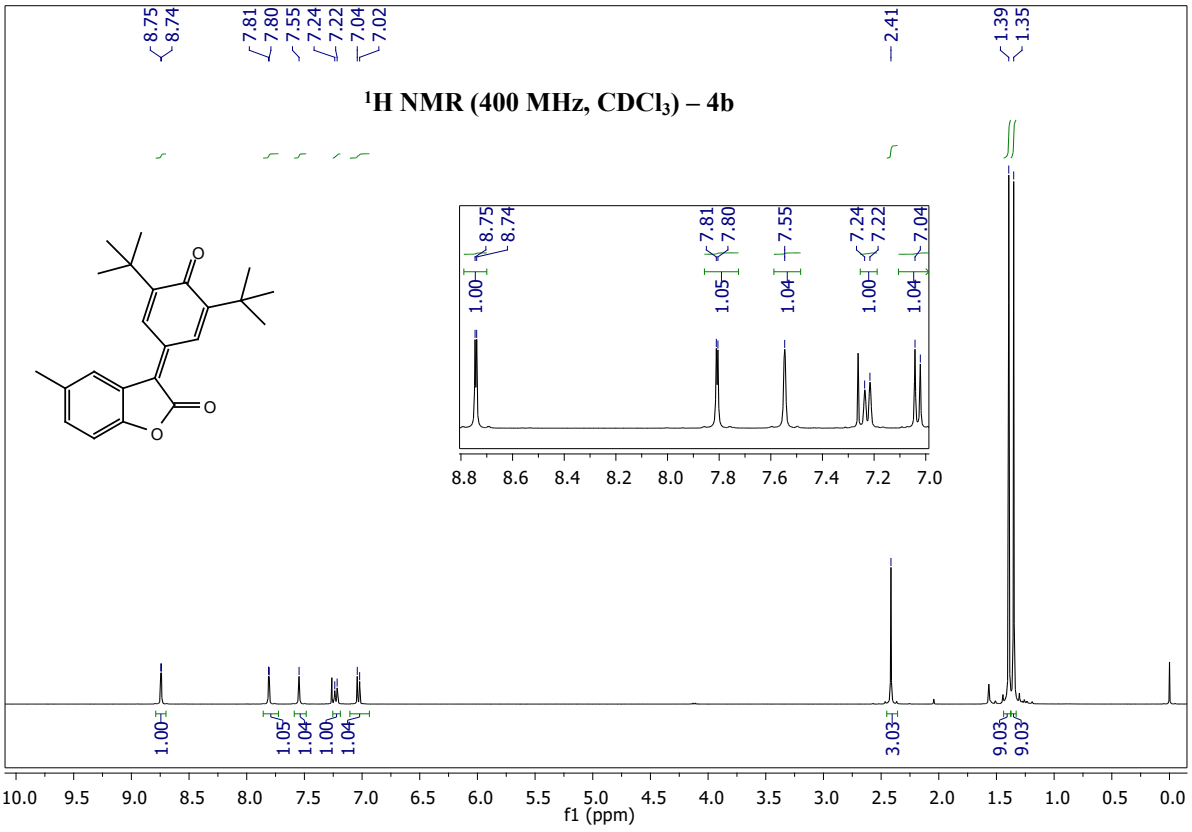
^{13}C {^{1}H} NMR (101 MHz, $CDCl_3$) – 3j



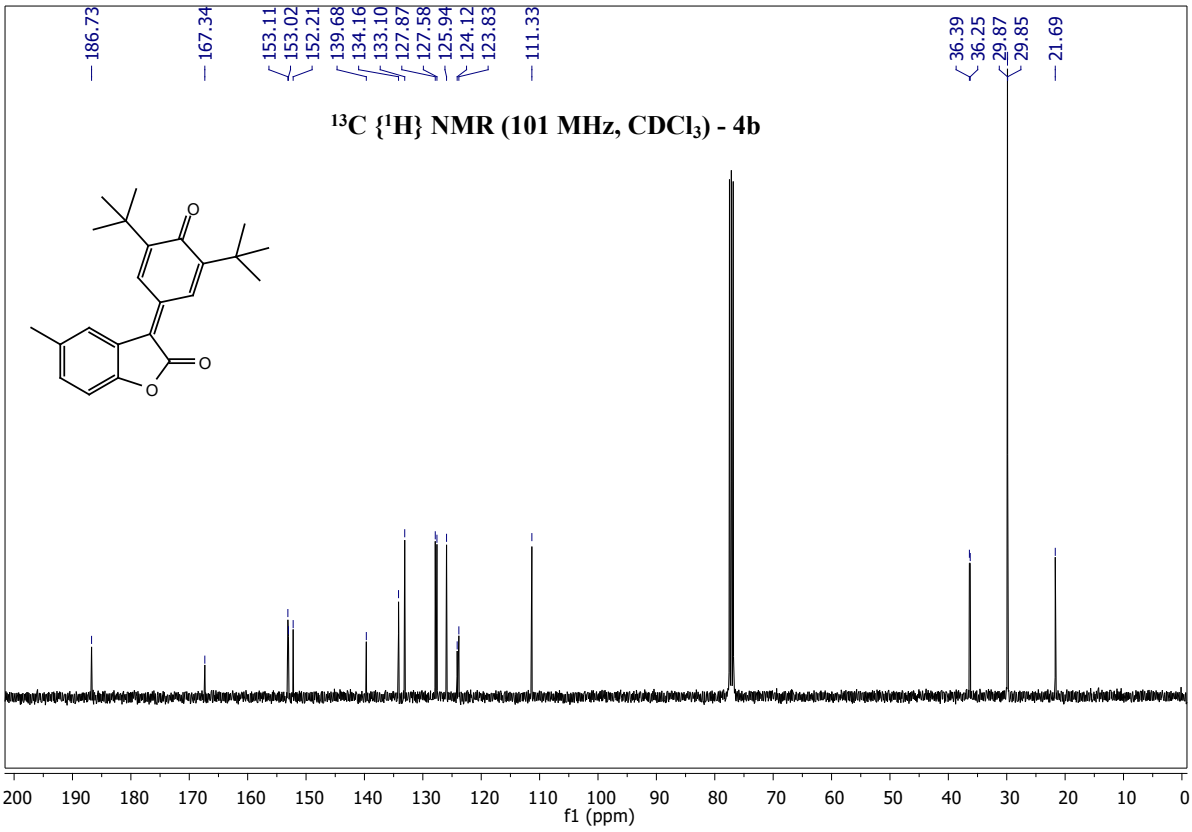
^{1}H NMR (400 MHz, $CDCl_3$) - 4a



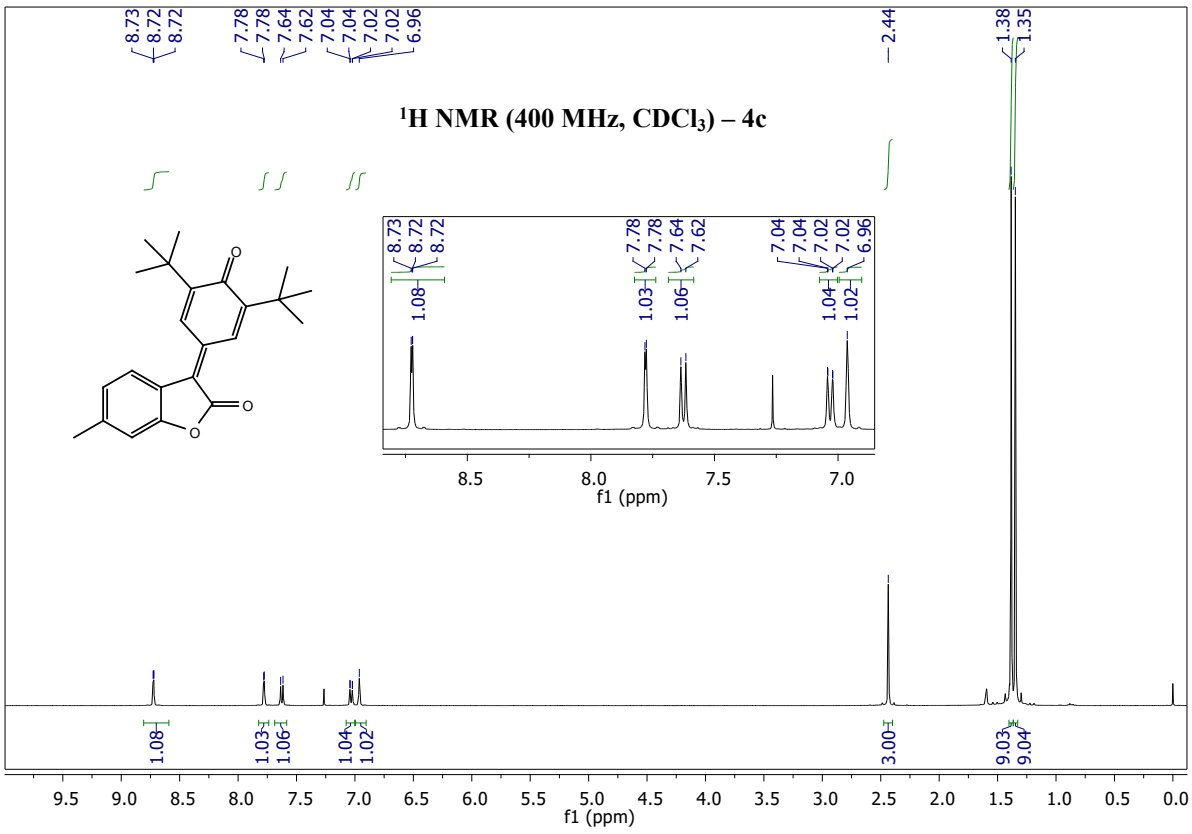
^{13}C {^{1}H} NMR (101 MHz, $CDCl_3$) - 4a



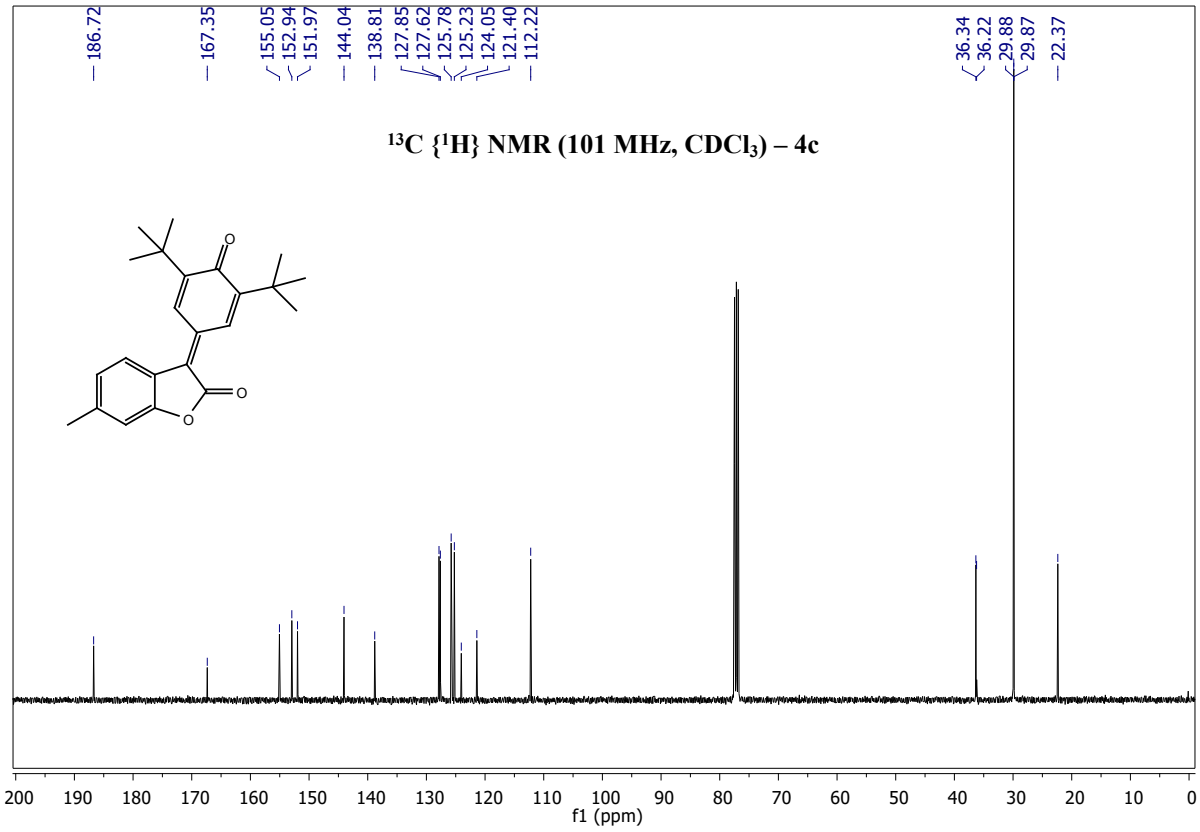
^{1}H NMR (400 MHz, $CDCl_3$) – 4b



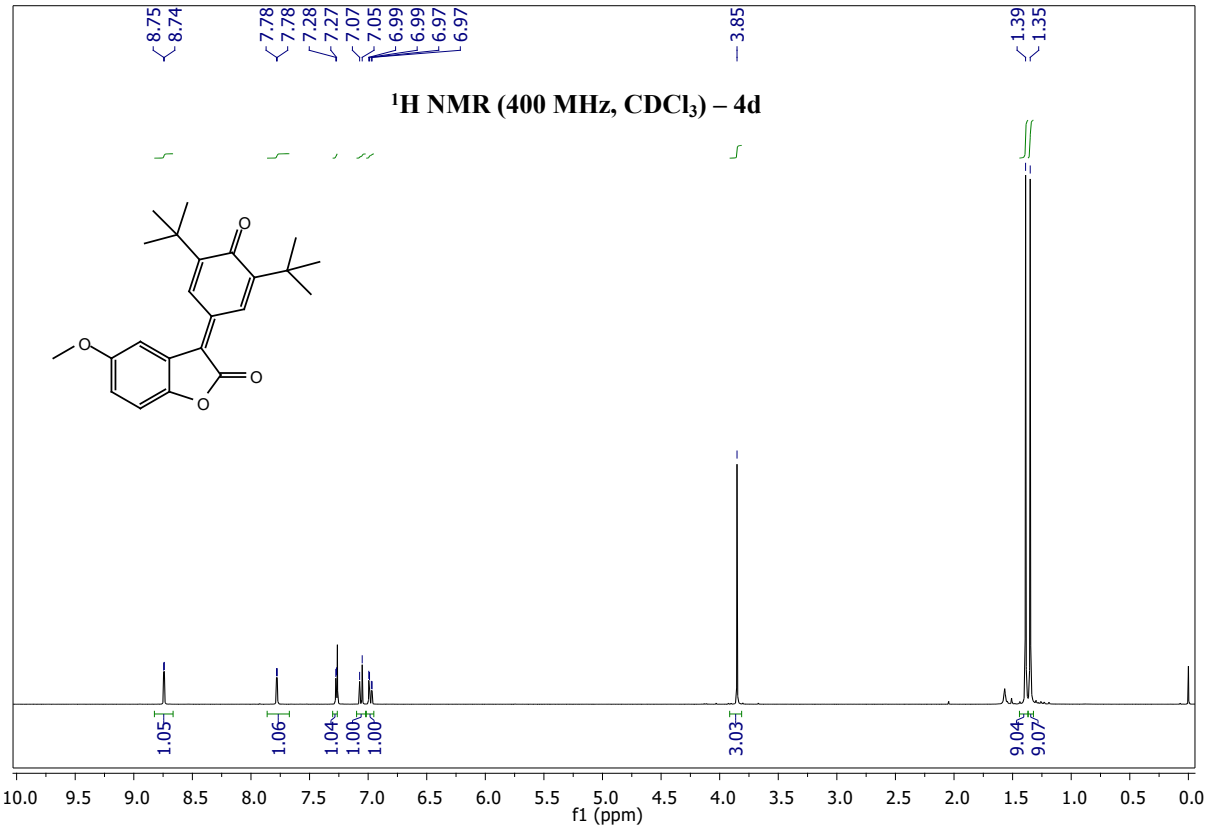
^{13}C {^{1}H} NMR (101 MHz, $CDCl_3$) - 4b



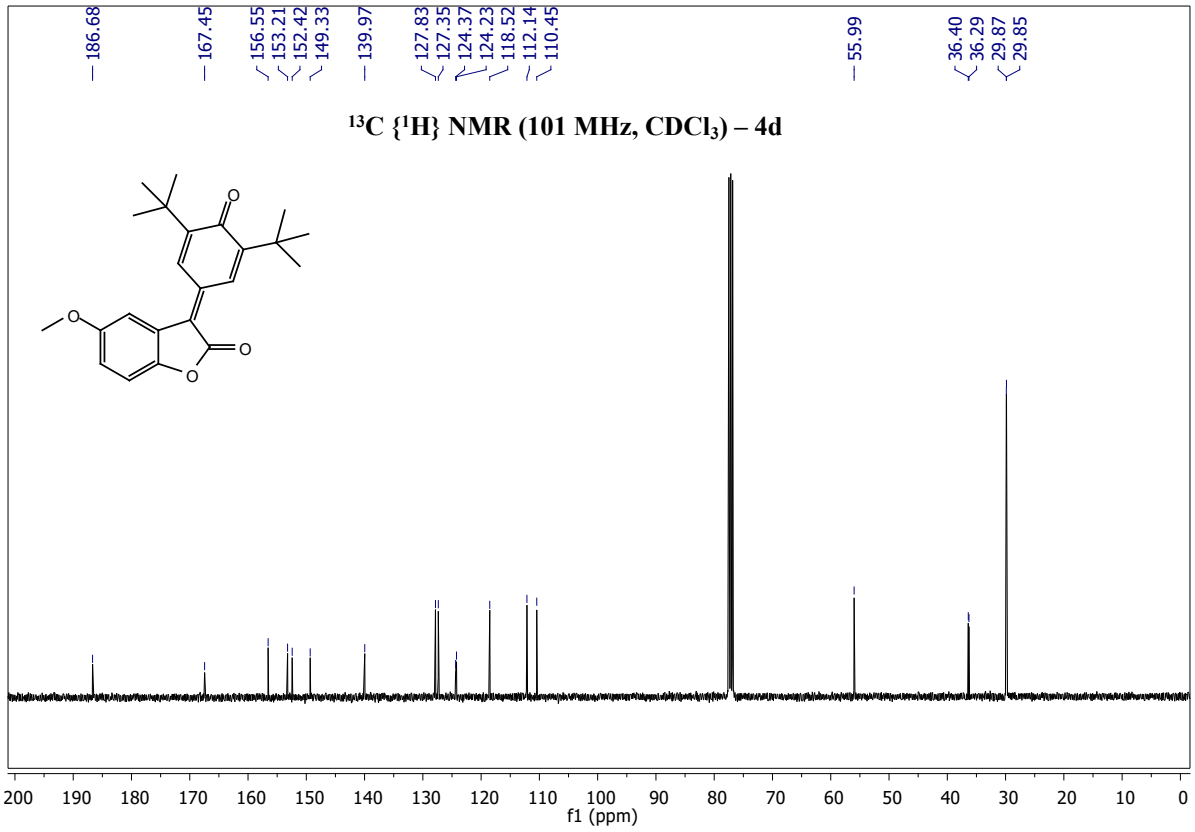
^{1}H NMR (400 MHz, $CDCl_3$) – 4c



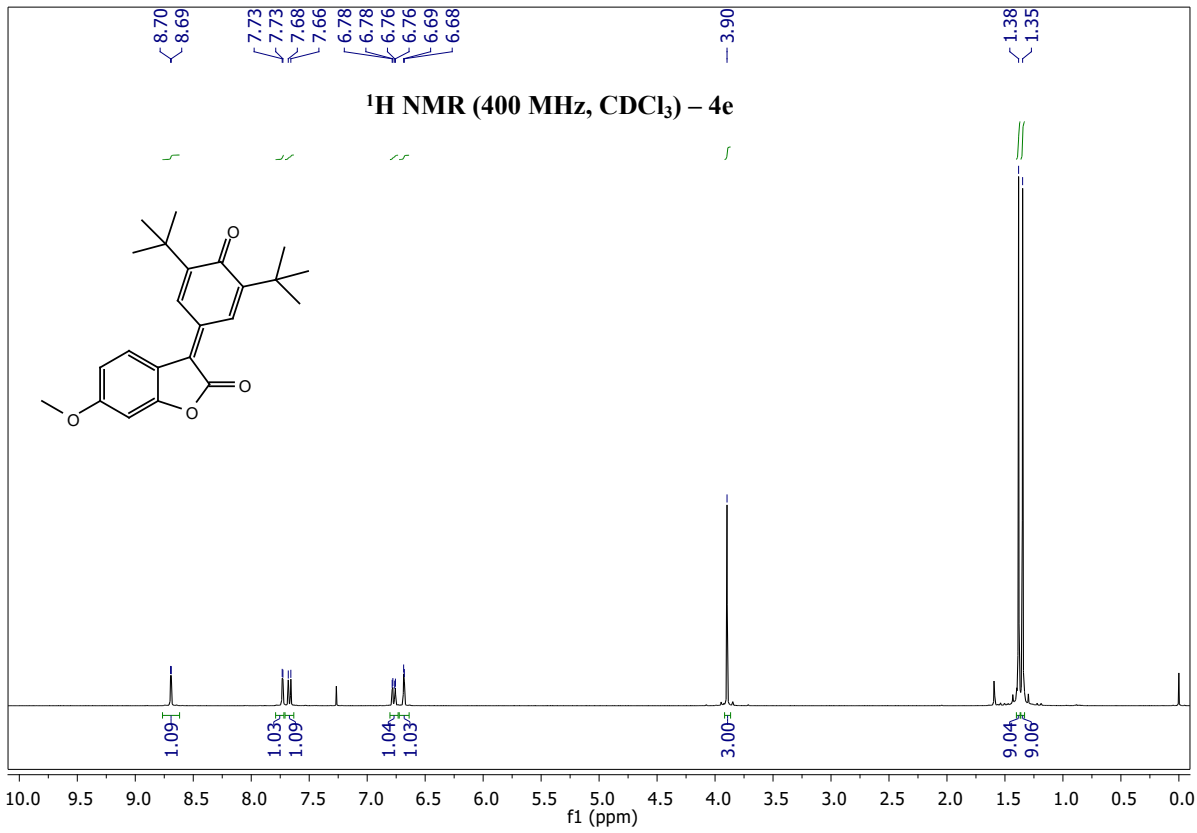
^{13}C {^{1}H} NMR (101 MHz, $CDCl_3$) – 4c



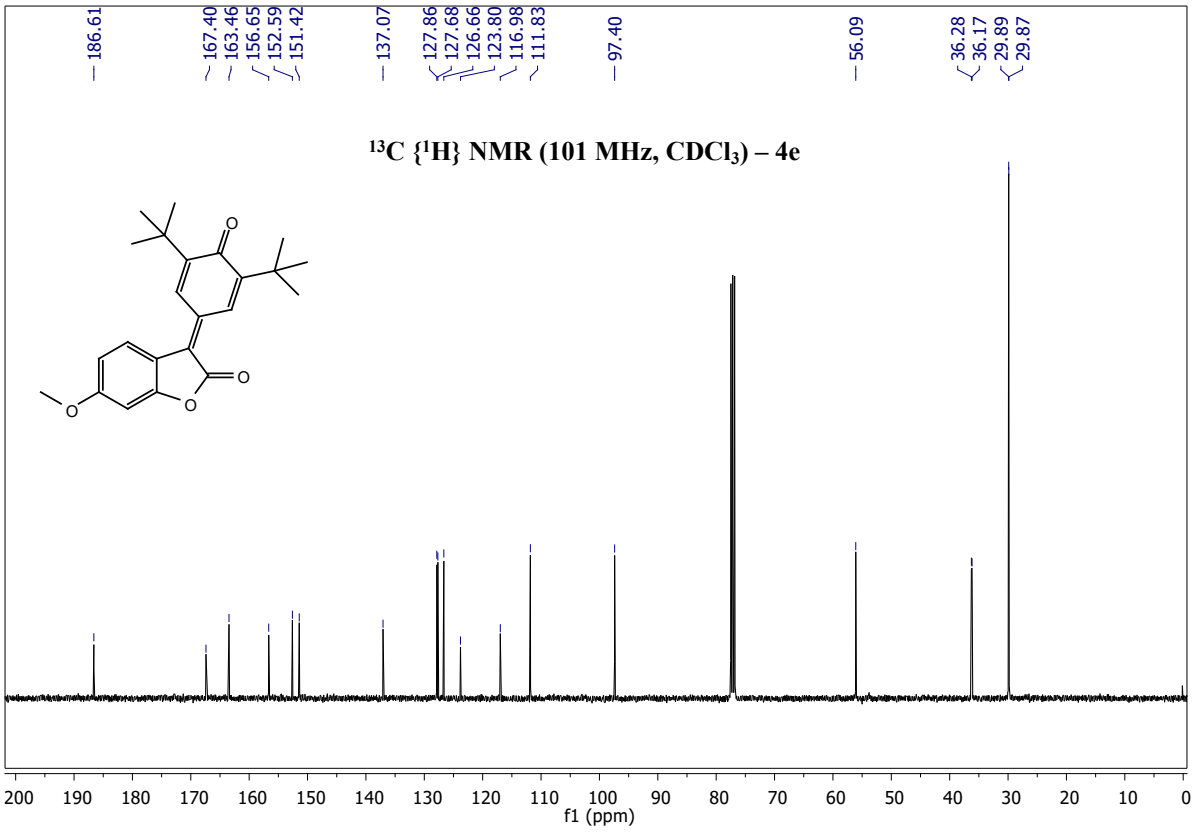
^{1}H NMR (400 MHz, $CDCl_3$) – 4d



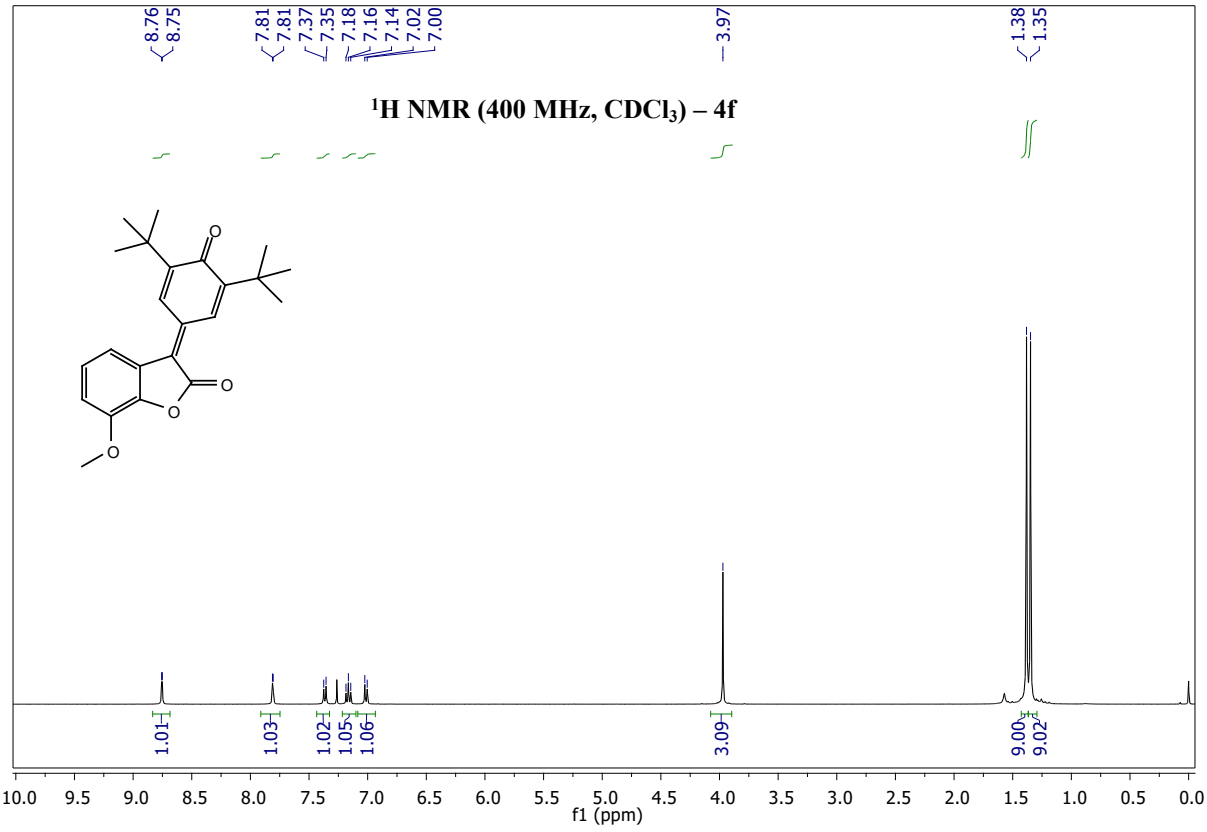
^{13}C {^{1}H} NMR (101 MHz, $CDCl_3$) – 4d



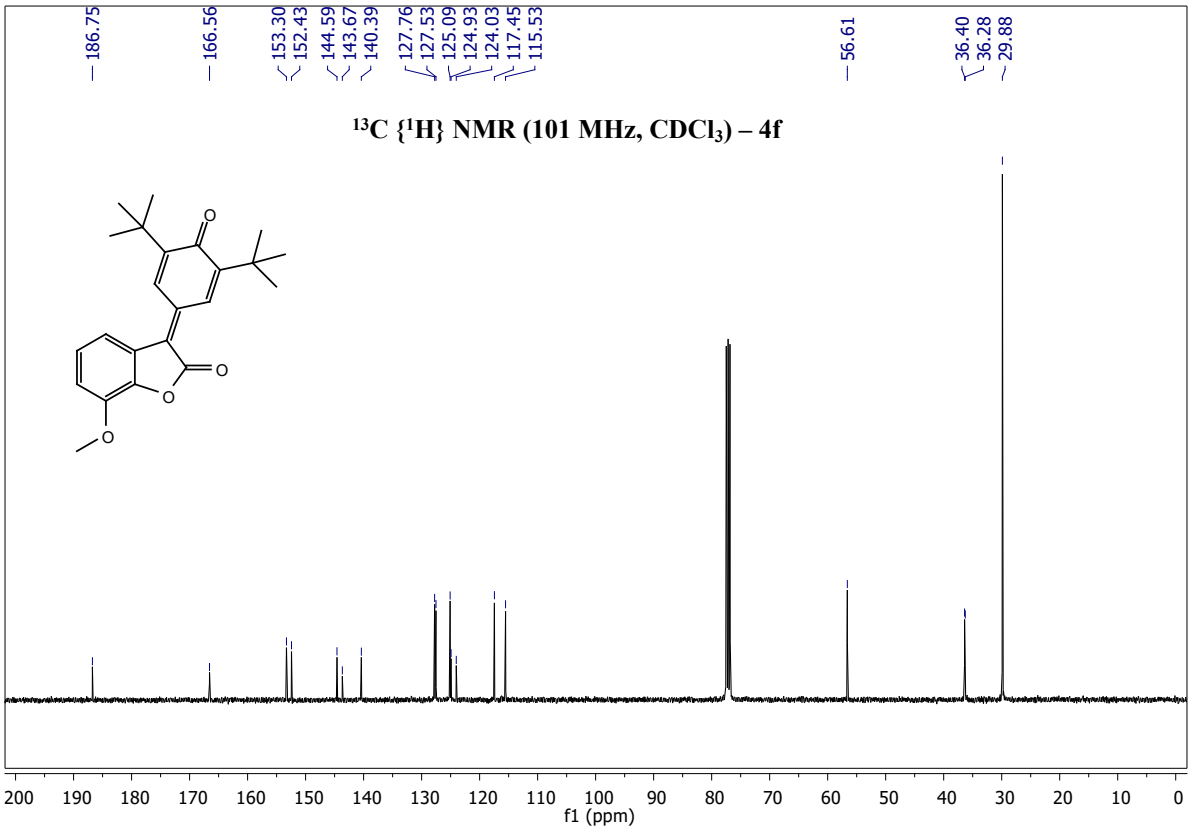
^{1}H NMR (400 MHz, $CDCl_3$) – 4e



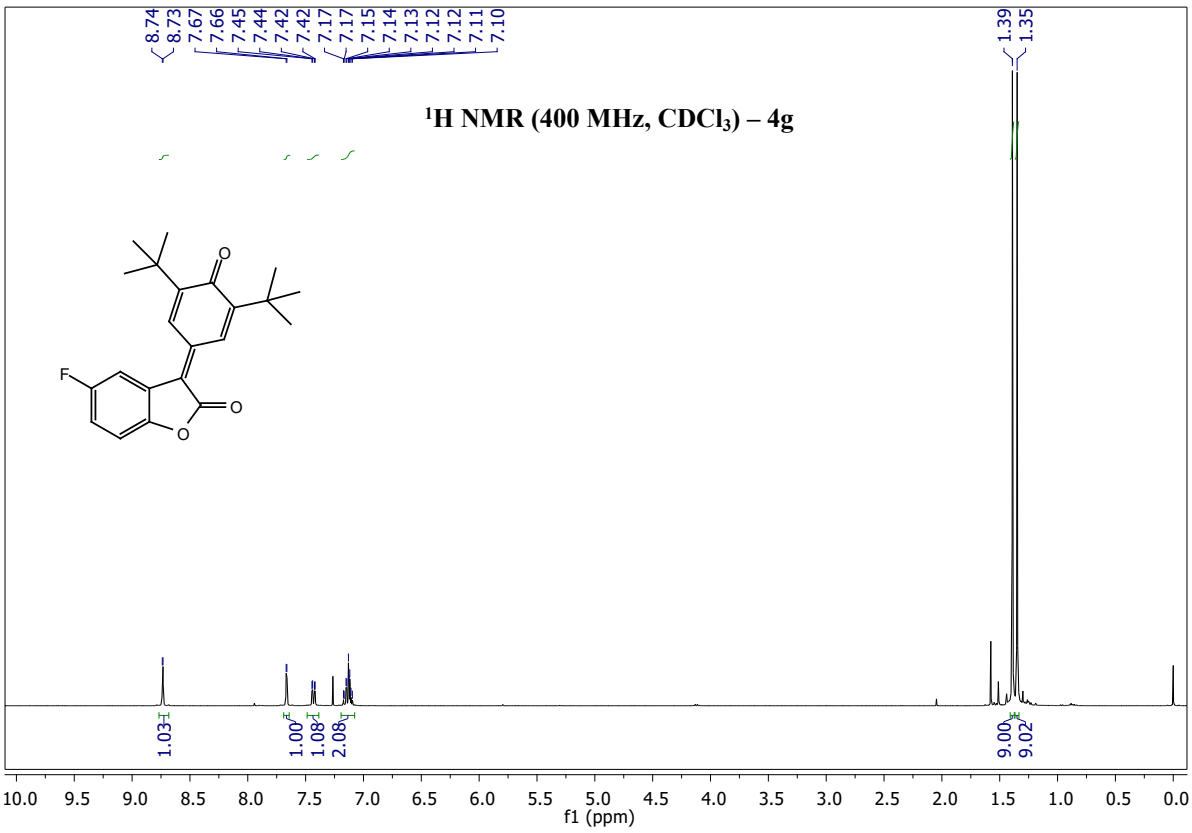
^{13}C {^{1}H} NMR (101 MHz, $CDCl_3$) – 4e



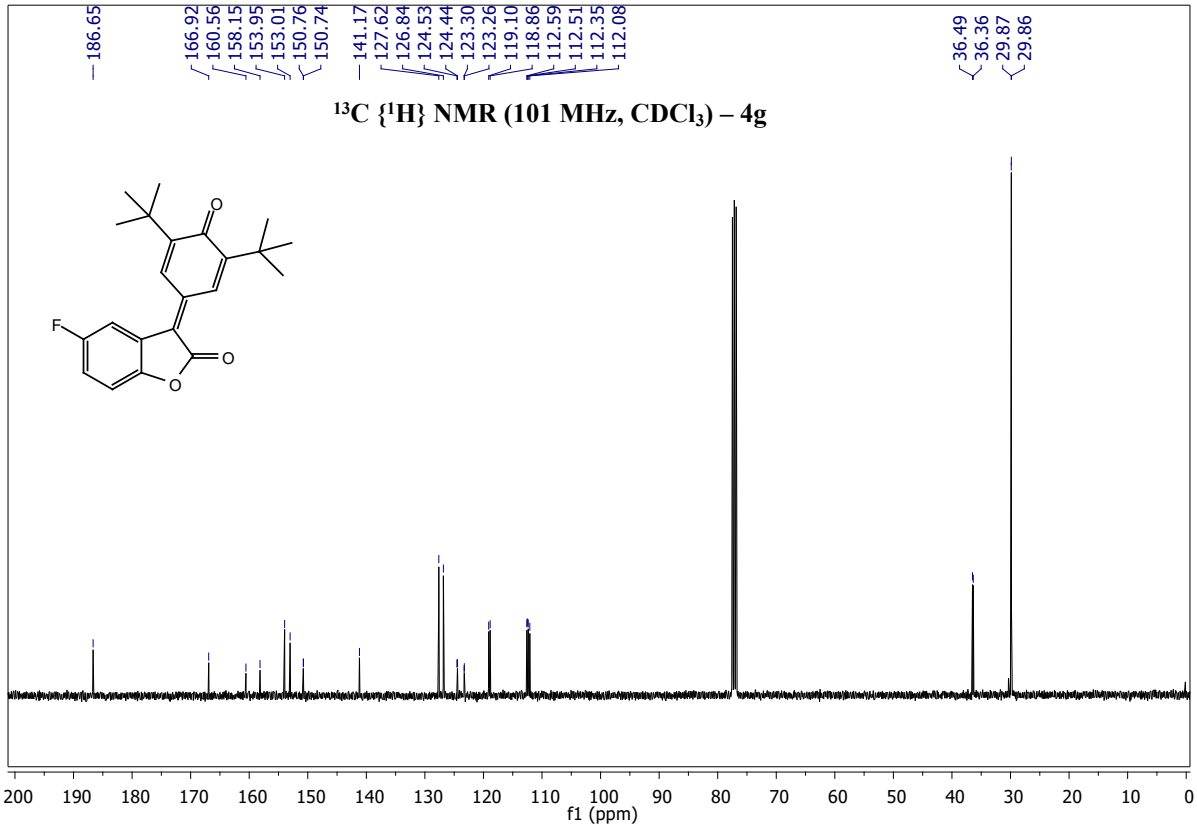
^{1}H NMR (400 MHz, $CDCl_3$) – 4f



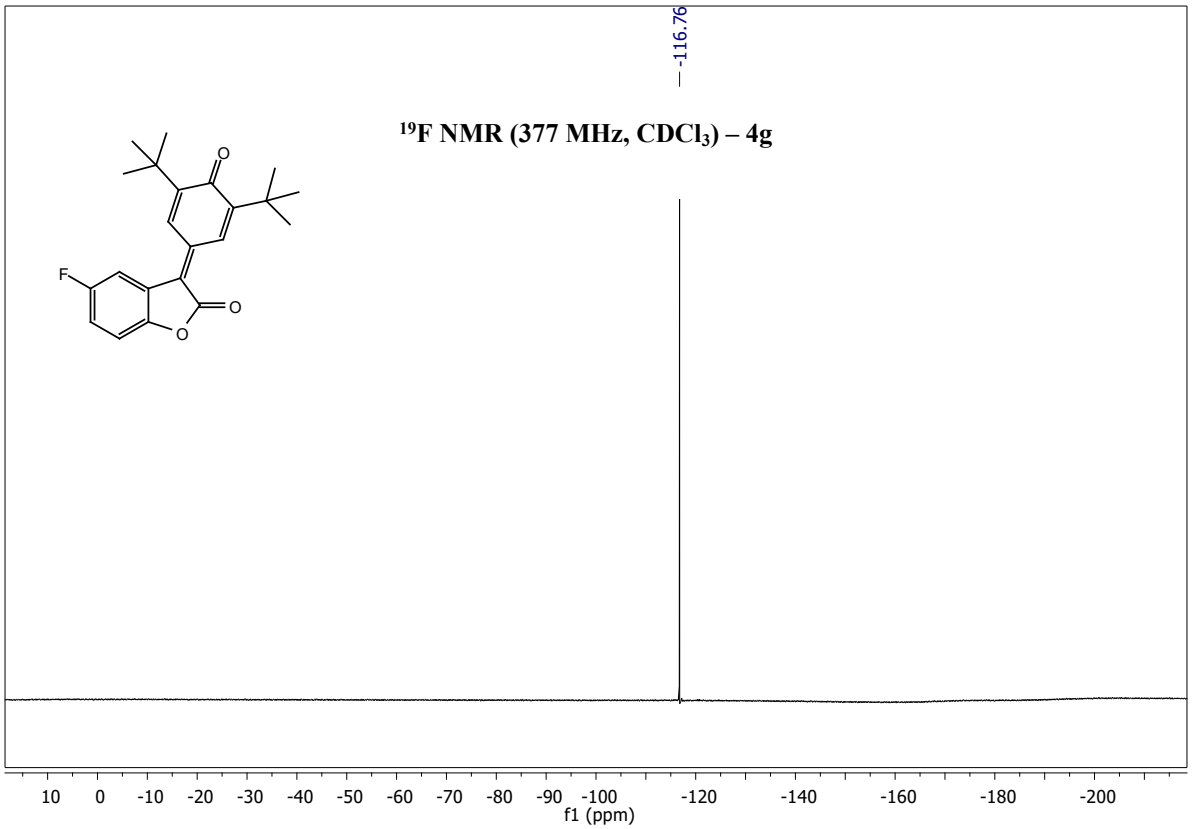
^{13}C {^{1}H} NMR (101 MHz, $CDCl_3$) – 4f



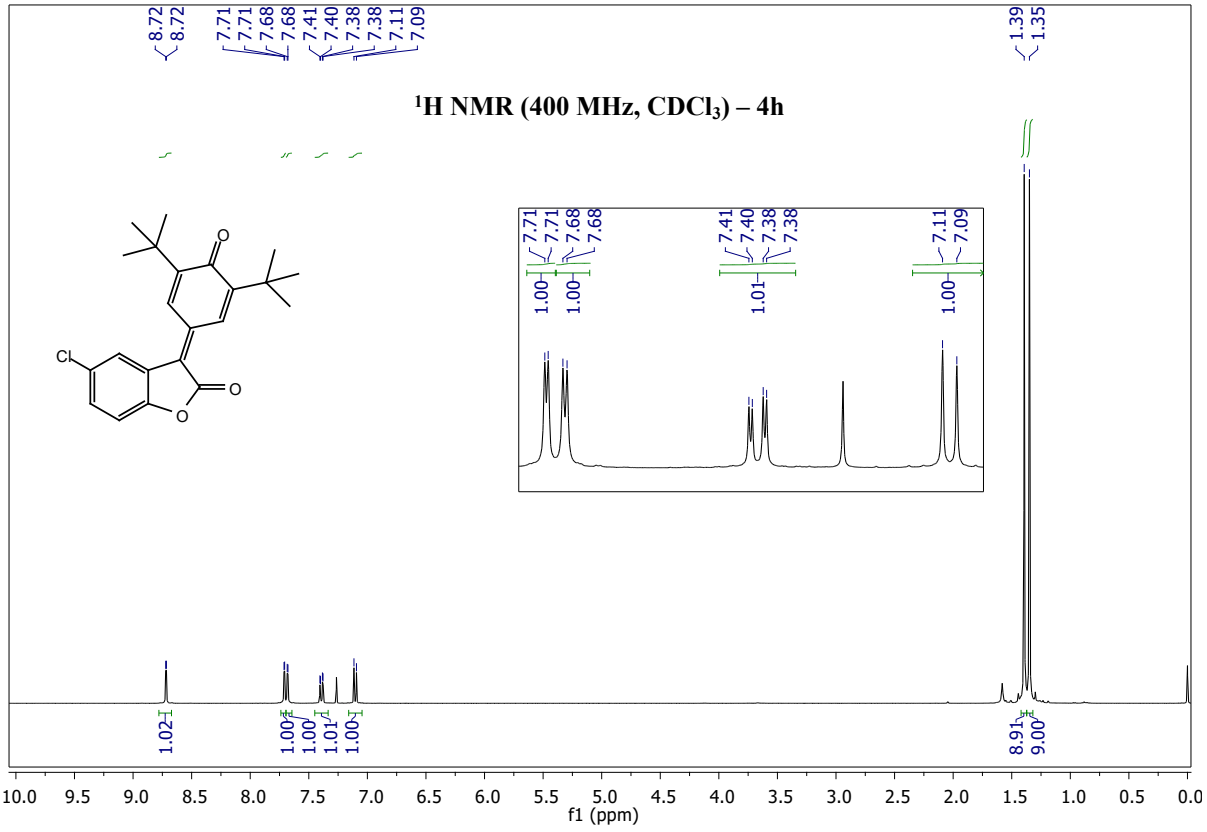
^{1}H NMR (400 MHz, $CDCl_3$) – 4g



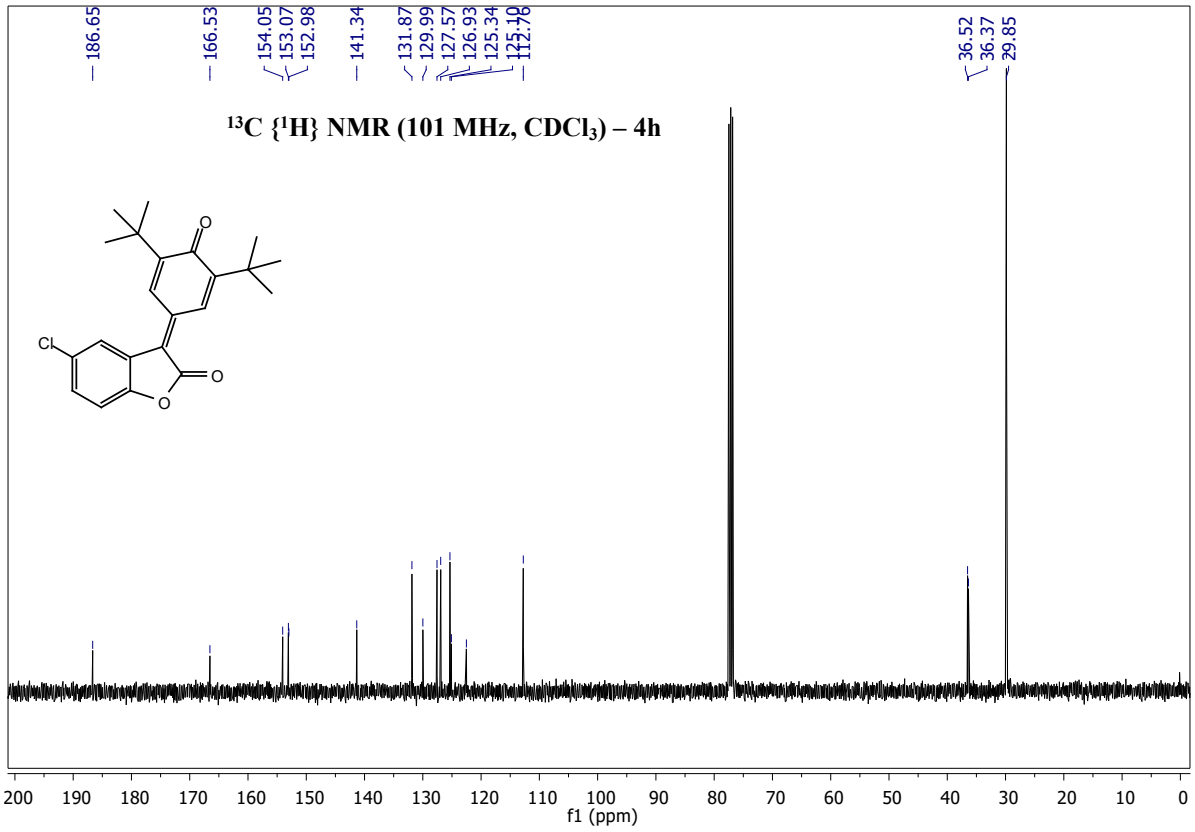
^{13}C {^{1}H} NMR (101 MHz, $CDCl_3$) – 4g

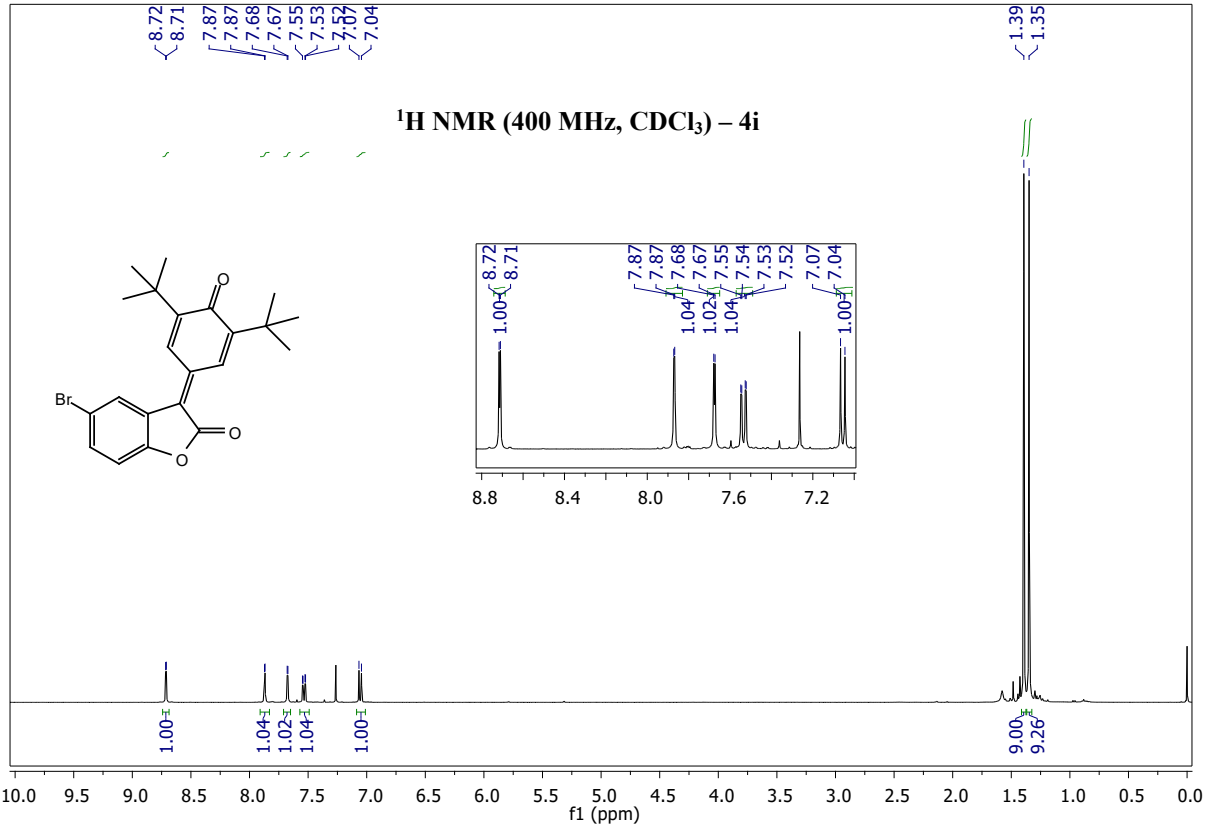


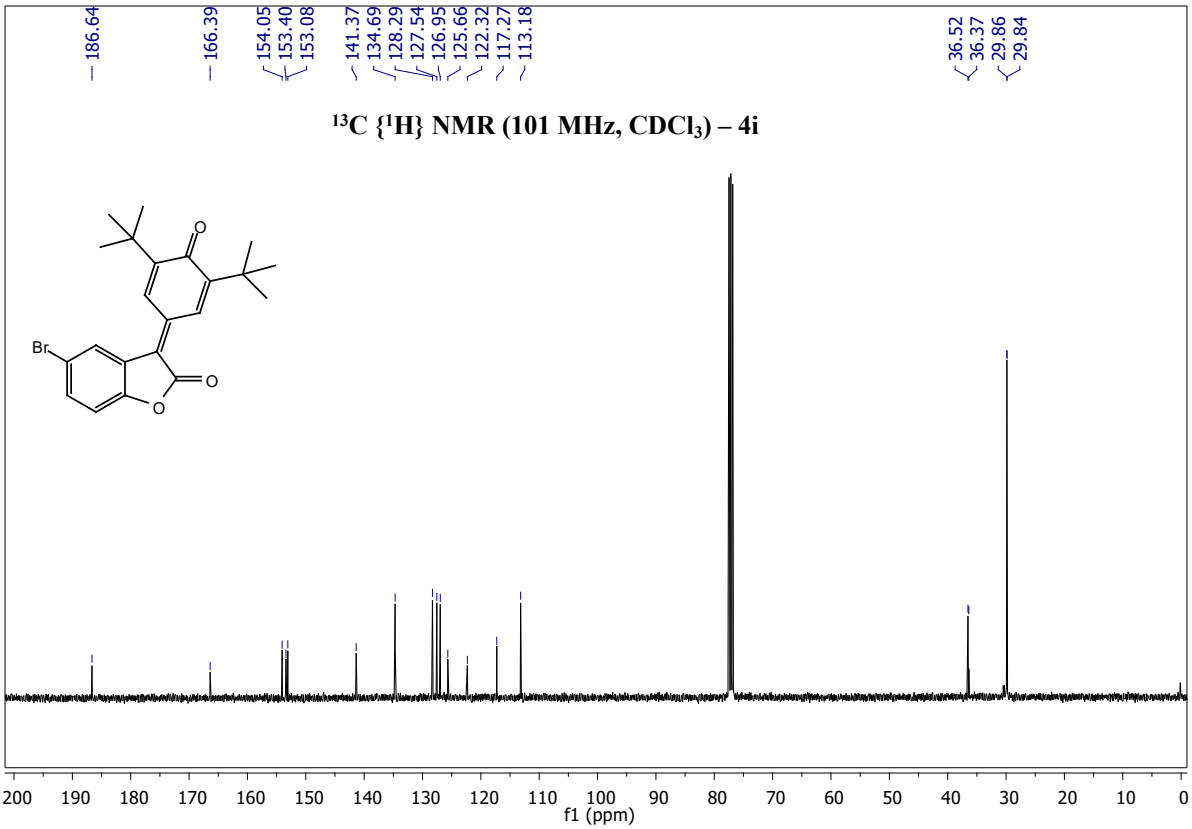
^{19}F NMR (377 MHz, $CDCl_3$) – 4g



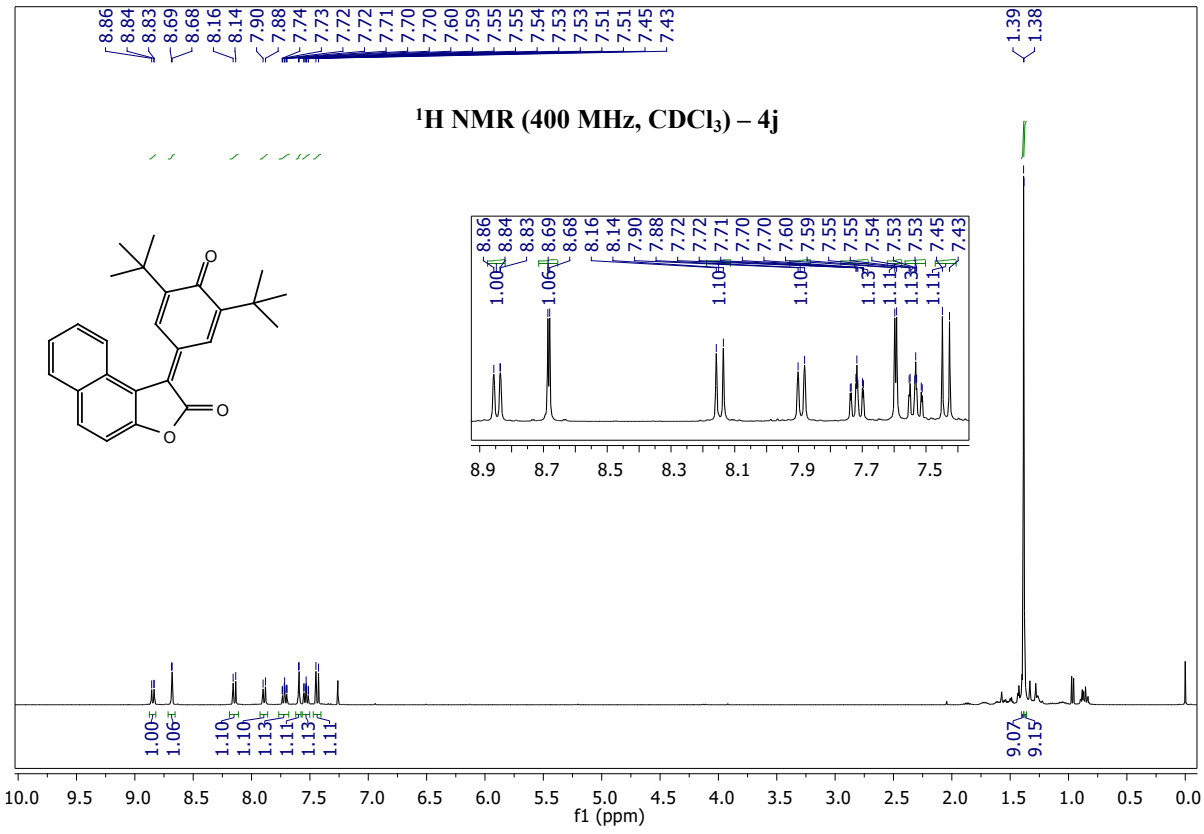
^{1}H NMR (400 MHz, $CDCl_3$) – 4h


186.65
166.53
154.05
153.07
152.98
141.34
131.87
129.99
127.57
126.93
125.34
125.10
112.76
36.52
36.37
29.85
^{13}C {^{1}H} NMR (101 MHz, CDCl$_3$) – 4h
Cl
O
O
O
200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0
f1 (ppm)

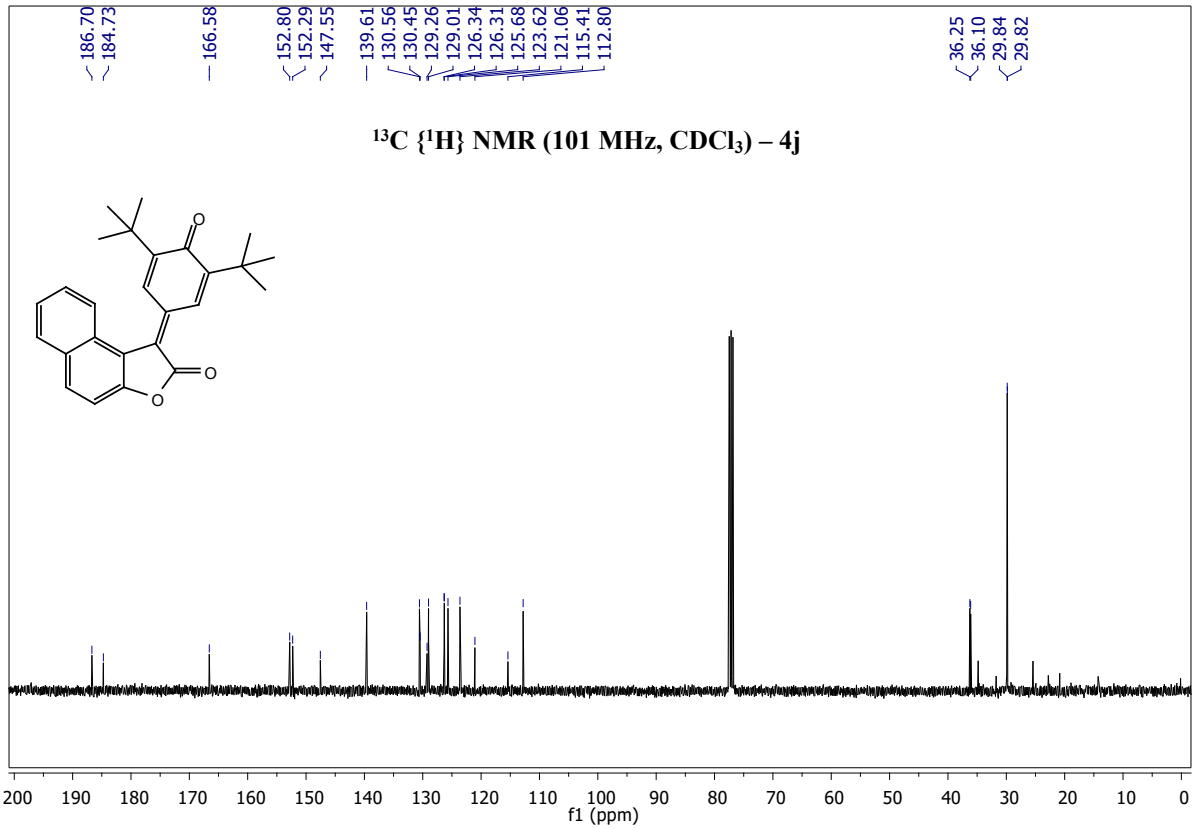

8.72
8.71
7.87
7.87
7.68
7.67
7.55
7.53
7.52
7.07
7.04
1.39
1.35
^{1}H NMR (400 MHz, CDCl$_3$) – 4i
Br
O
O
O
1.00
1.04
1.02
1.04
1.00
9.00
9.26
8.8 8.4 8.0 7.6 7.2
10.0 9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0
f1 (ppm)



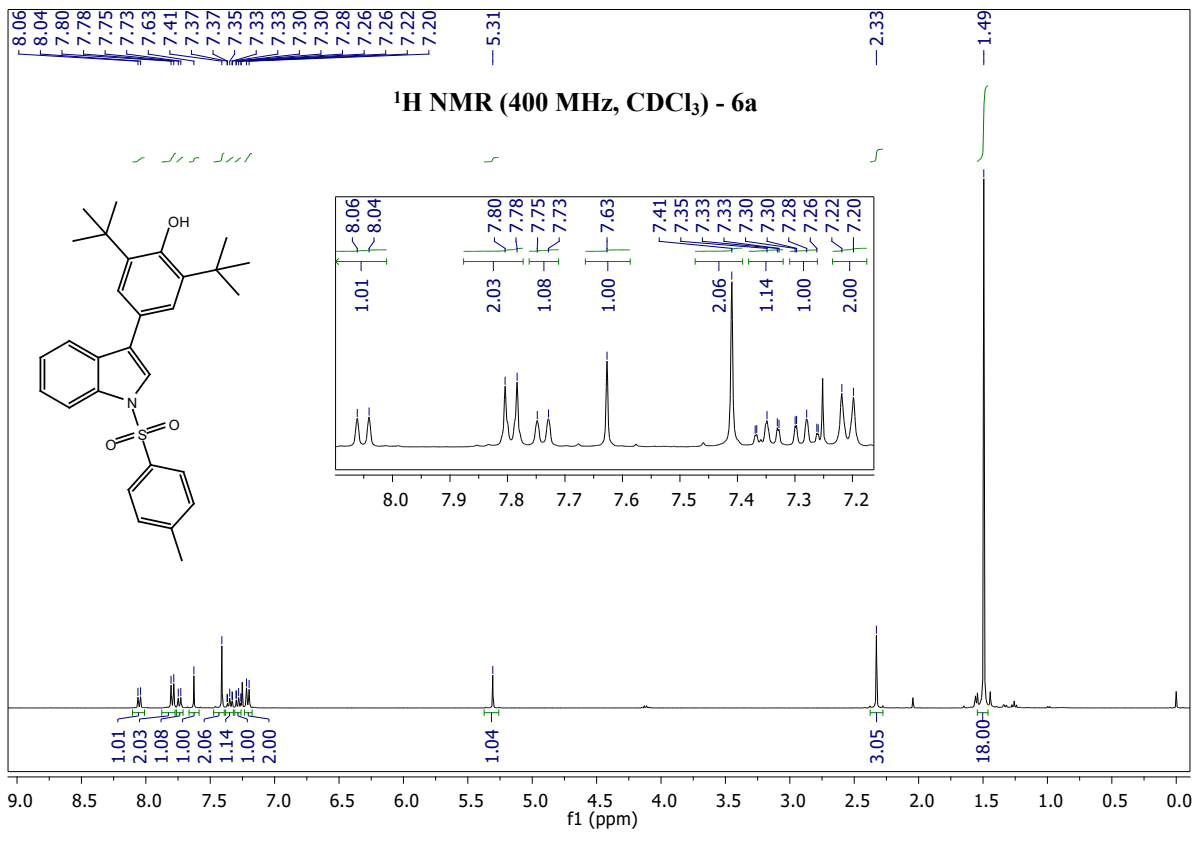
^{13}C {^{1}H} NMR (101 MHz, $CDCl_3$) – 4i



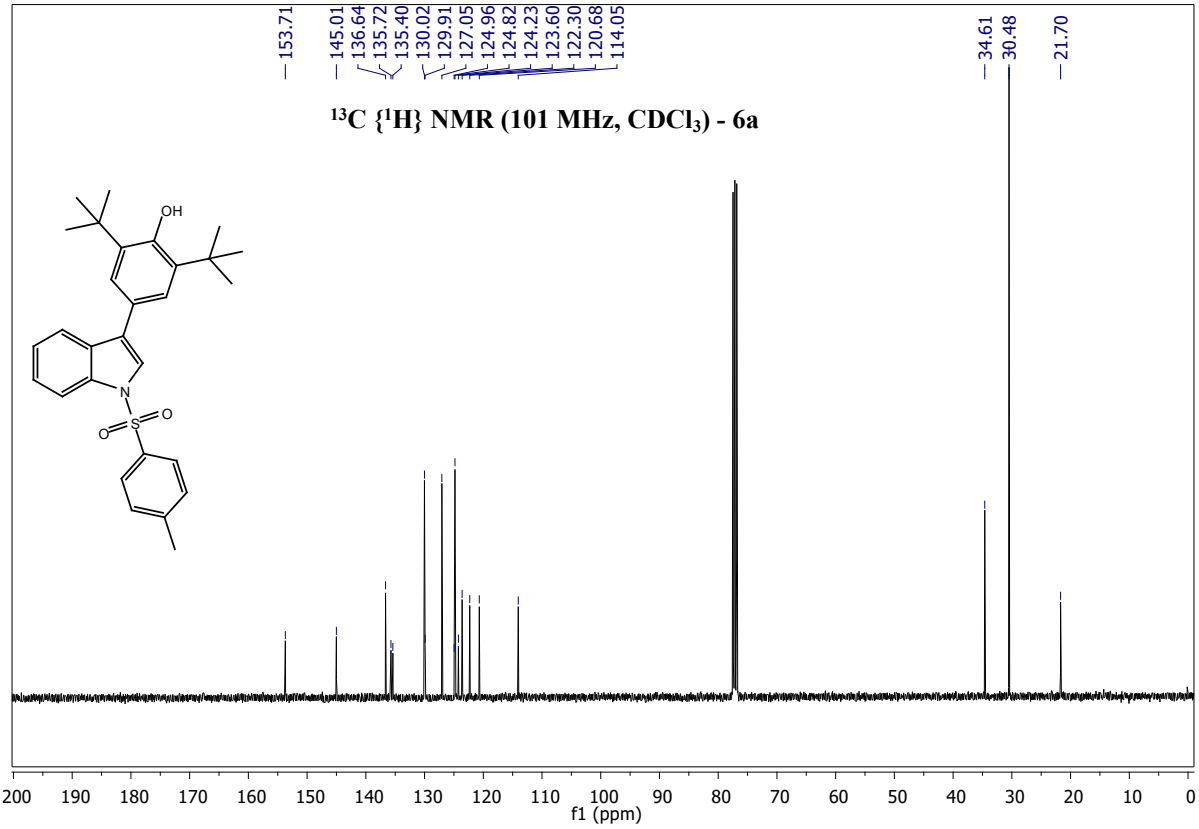
^{1}H NMR (400 MHz, $CDCl_3$) – 4j



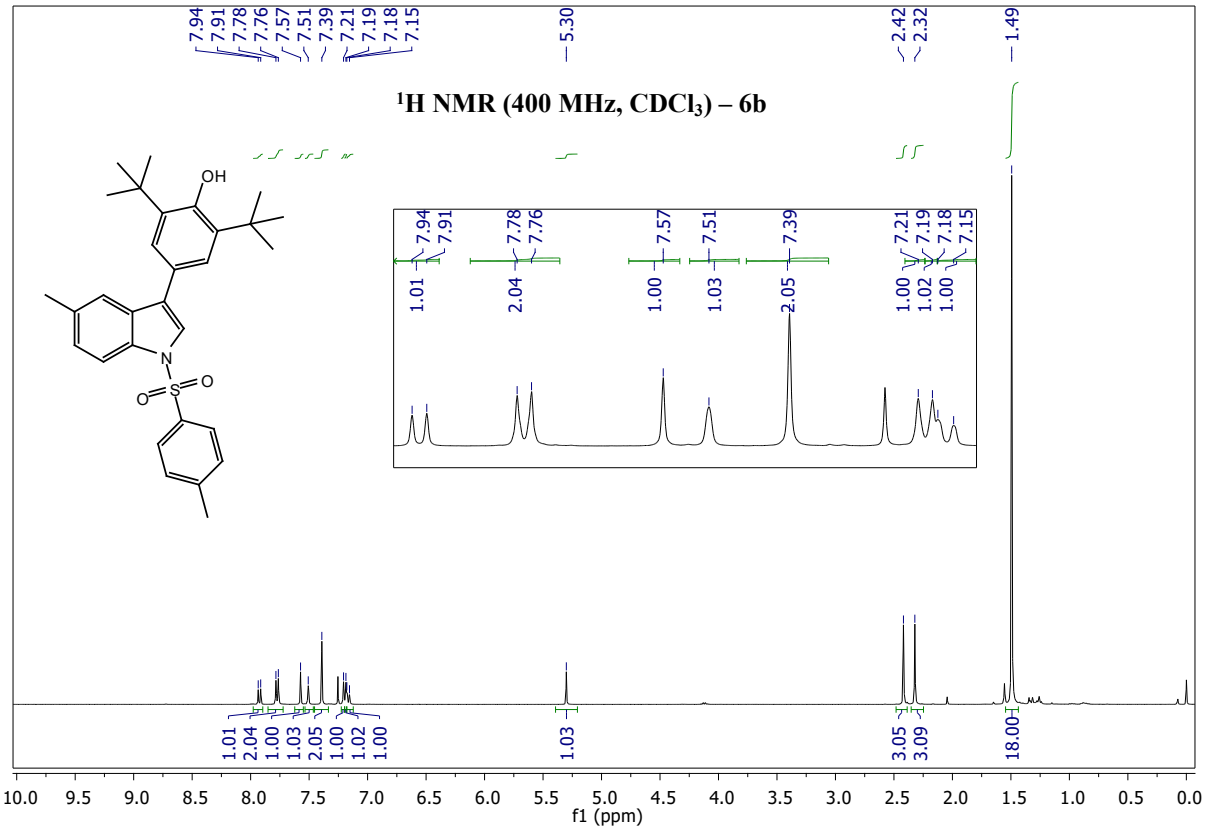
^{13}C {^{1}H} NMR (101 MHz, $CDCl_3$) – 4j

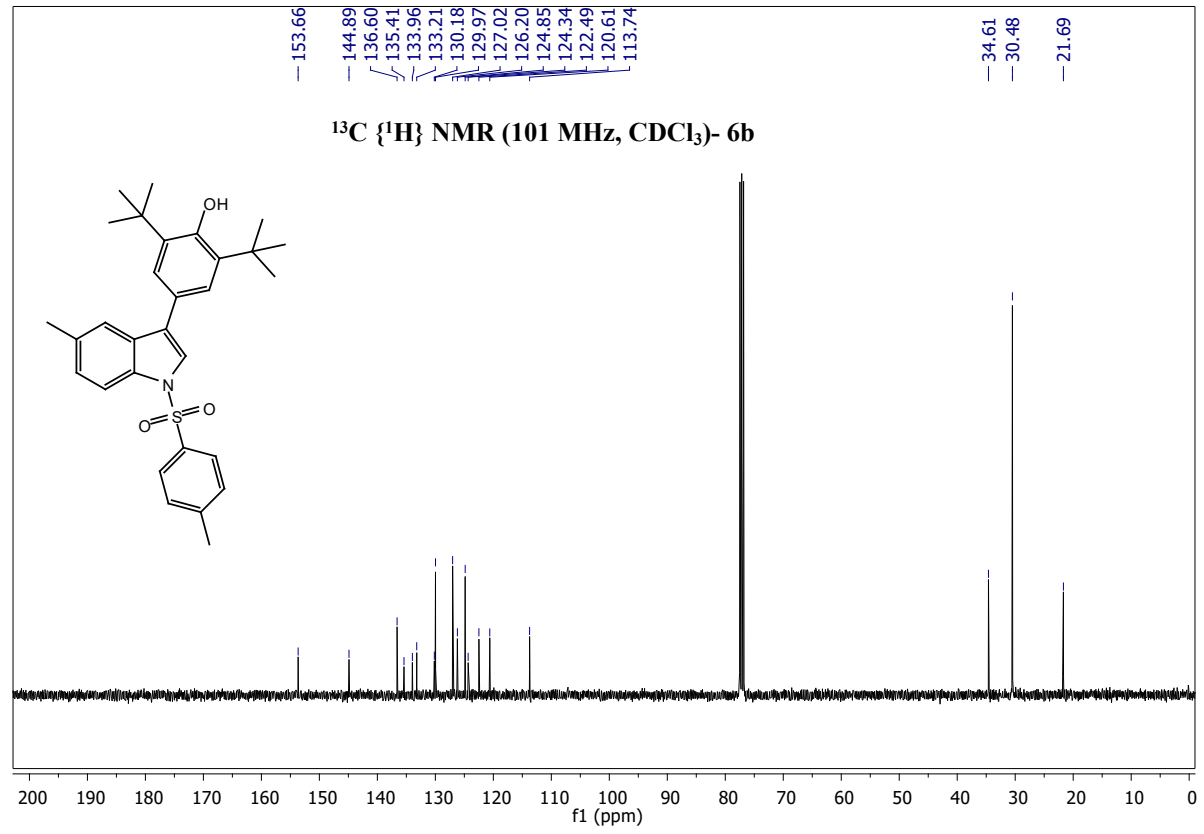


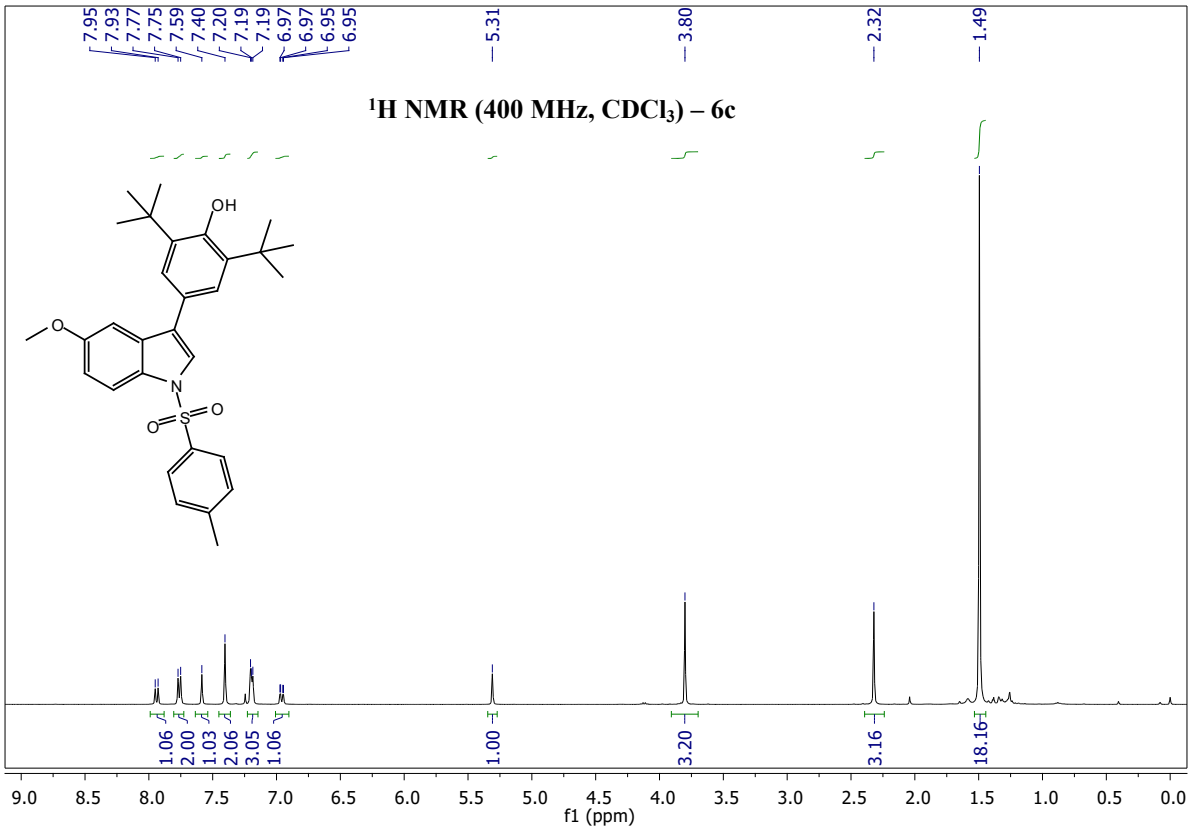
^{1}H NMR (400 MHz, $CDCl_3$) - 6a



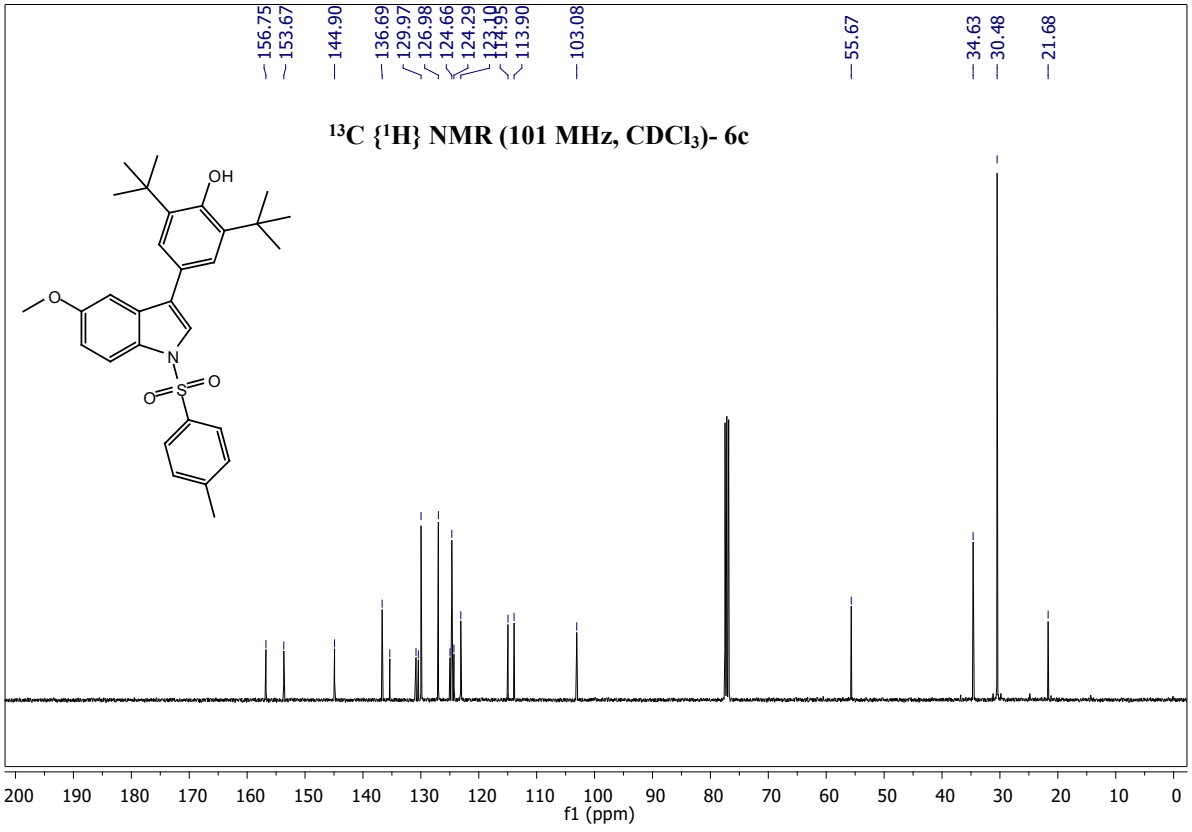
^{13}C {^{1}H} NMR (101 MHz, $CDCl_3$) - 6a


7.94
7.91
7.78
7.76
7.57
7.51
7.39
7.21
7.19
7.18
7.15
5.30
2.42
2.32
1.49
1H NMR (400 MHz, CDCl3) – 6b
OH
N
O
S
O
O
1.01
2.04
1.00
1.03
2.05
1.00
1.02
1.00
1.03
3.05
3.09
18.00
f1 (ppm)

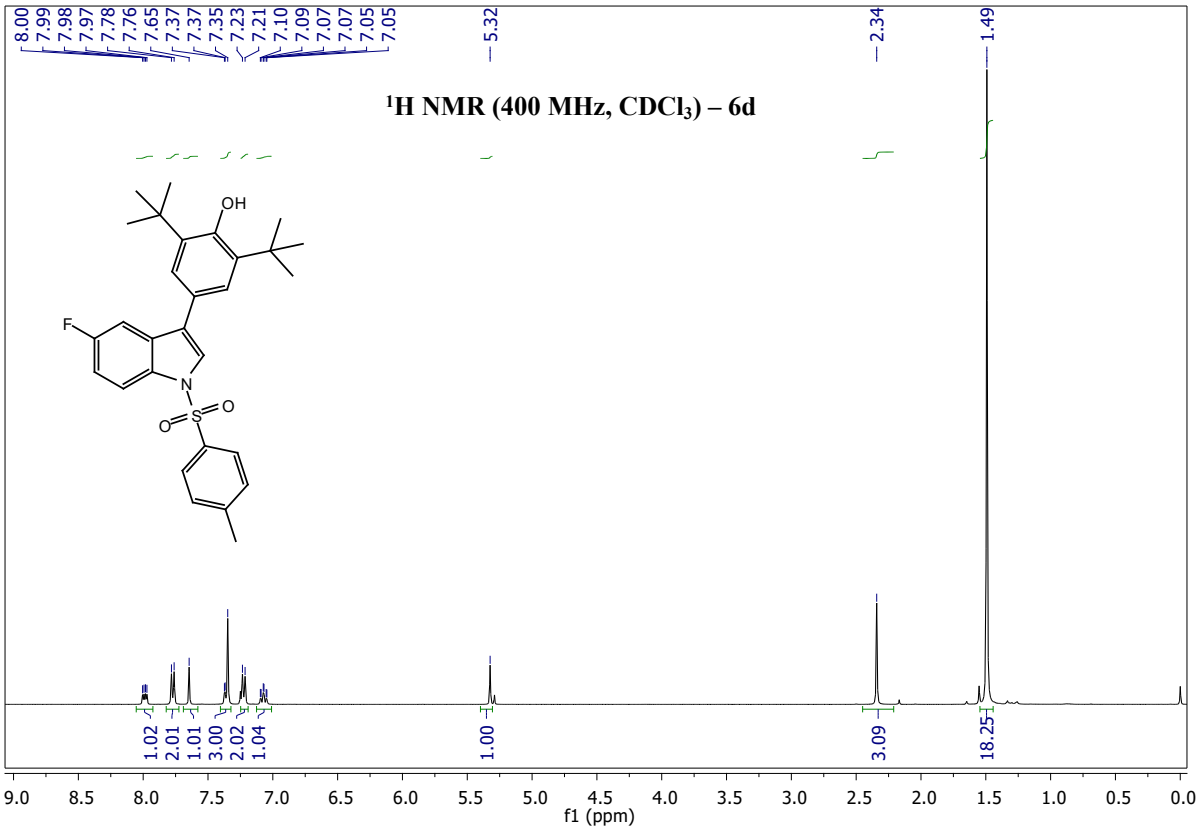

153.66
144.89
136.60
135.41
133.96
133.21
130.18
129.97
127.02
126.20
124.85
124.34
122.49
120.61
113.74
34.61
30.48
21.69
13C {1H} NMR (101 MHz, CDCl3)- 6b
OH
N
O
S
O
O
f1 (ppm)



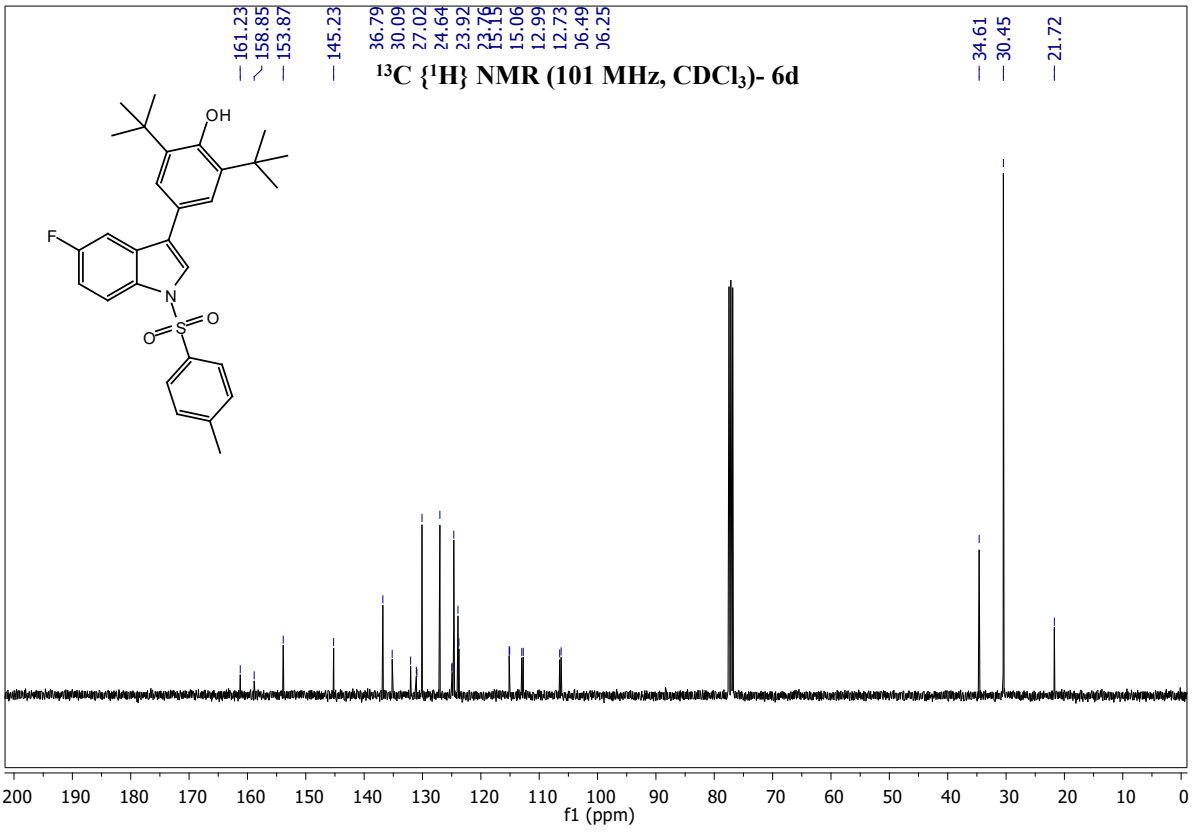
^{1}H NMR (400 MHz, $CDCl_3$) – 6c



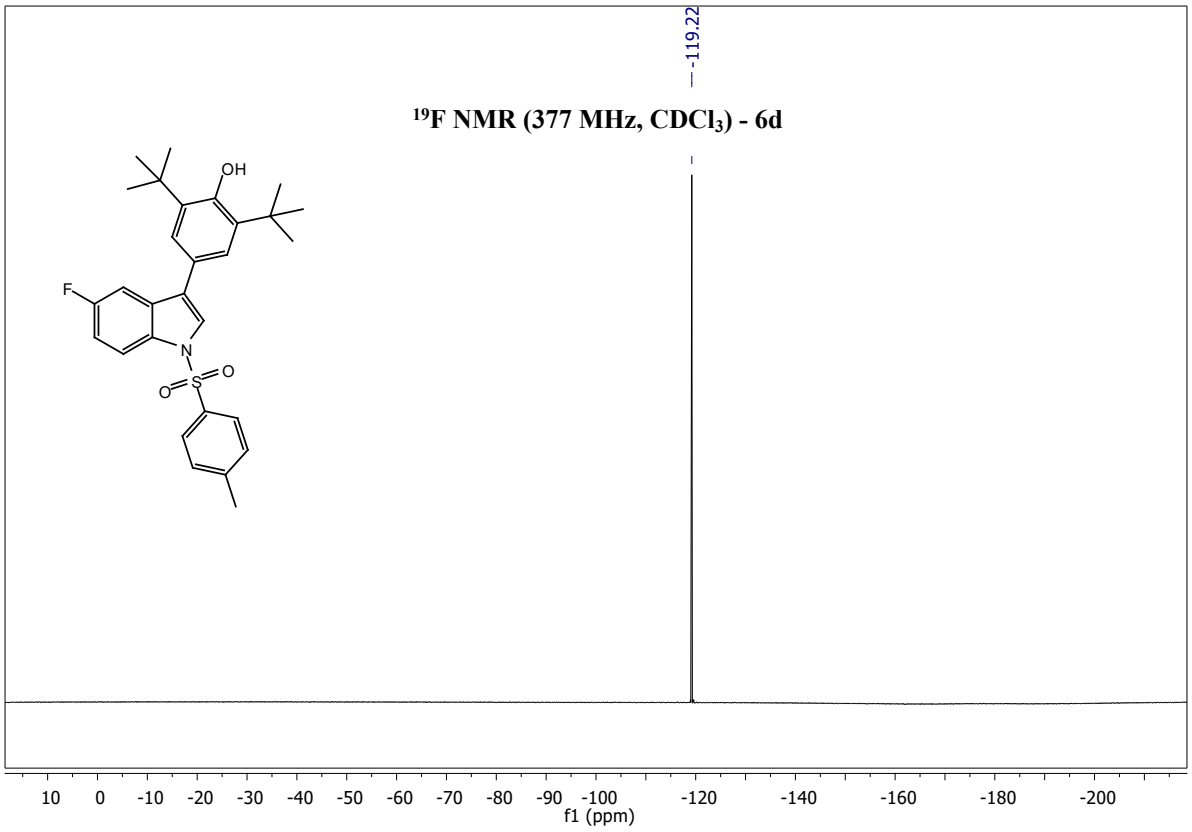
^{13}C {^{1}H} NMR (101 MHz, $CDCl_3$)- 6c



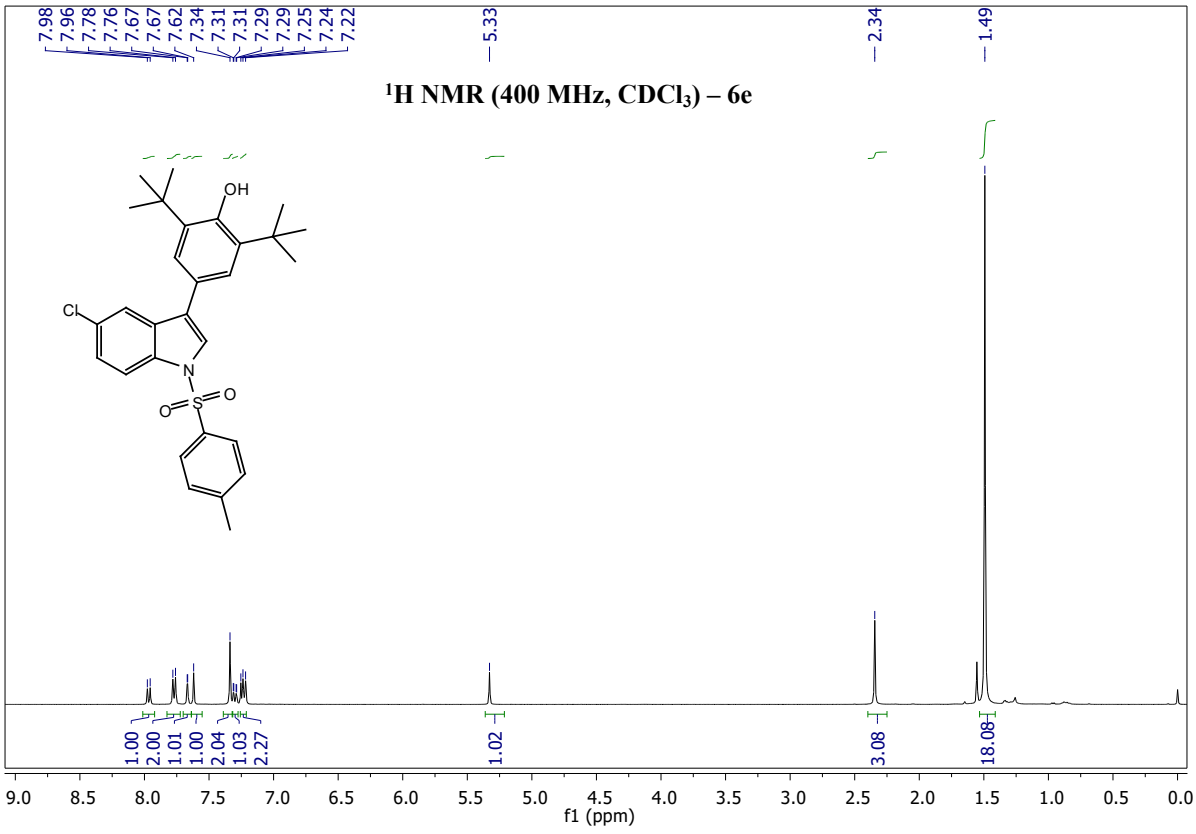
^{1}H NMR (400 MHz, $CDCl_3$) – 6d



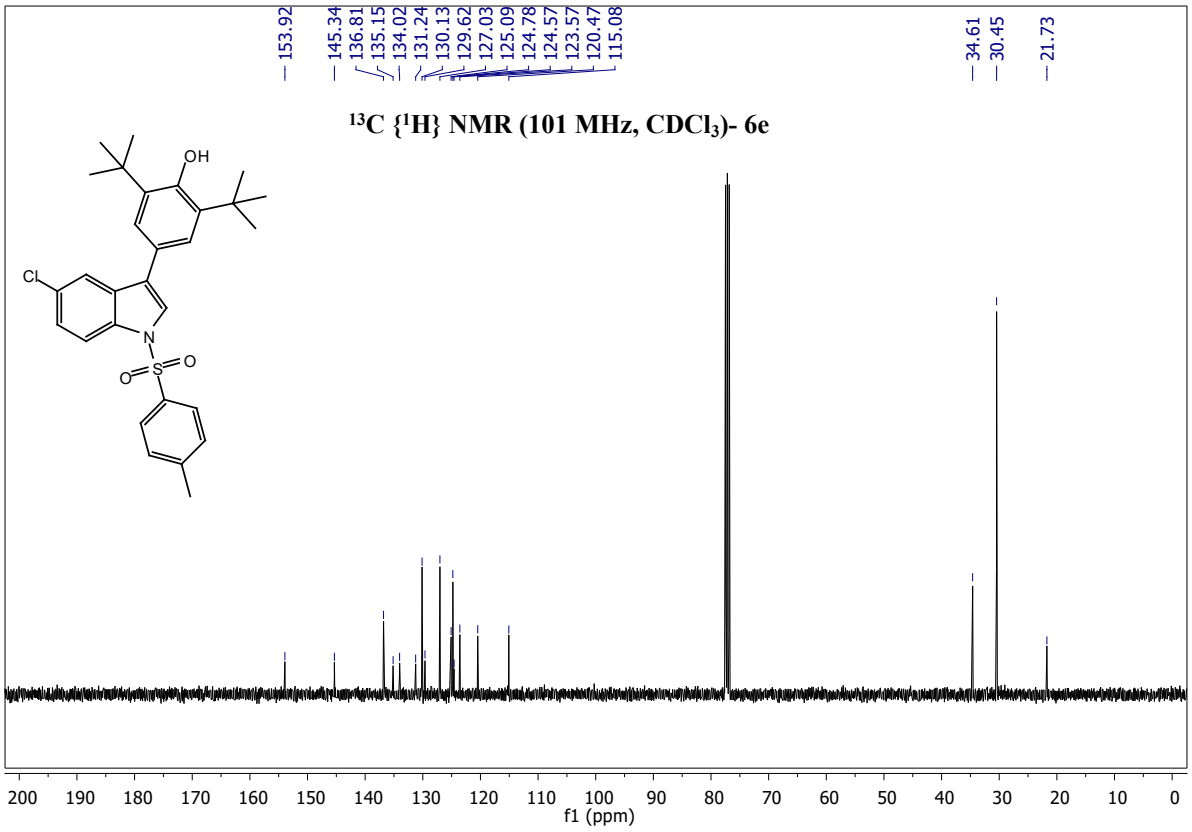
^{13}C {^{1}H} NMR (101 MHz, $CDCl_3$)- 6d



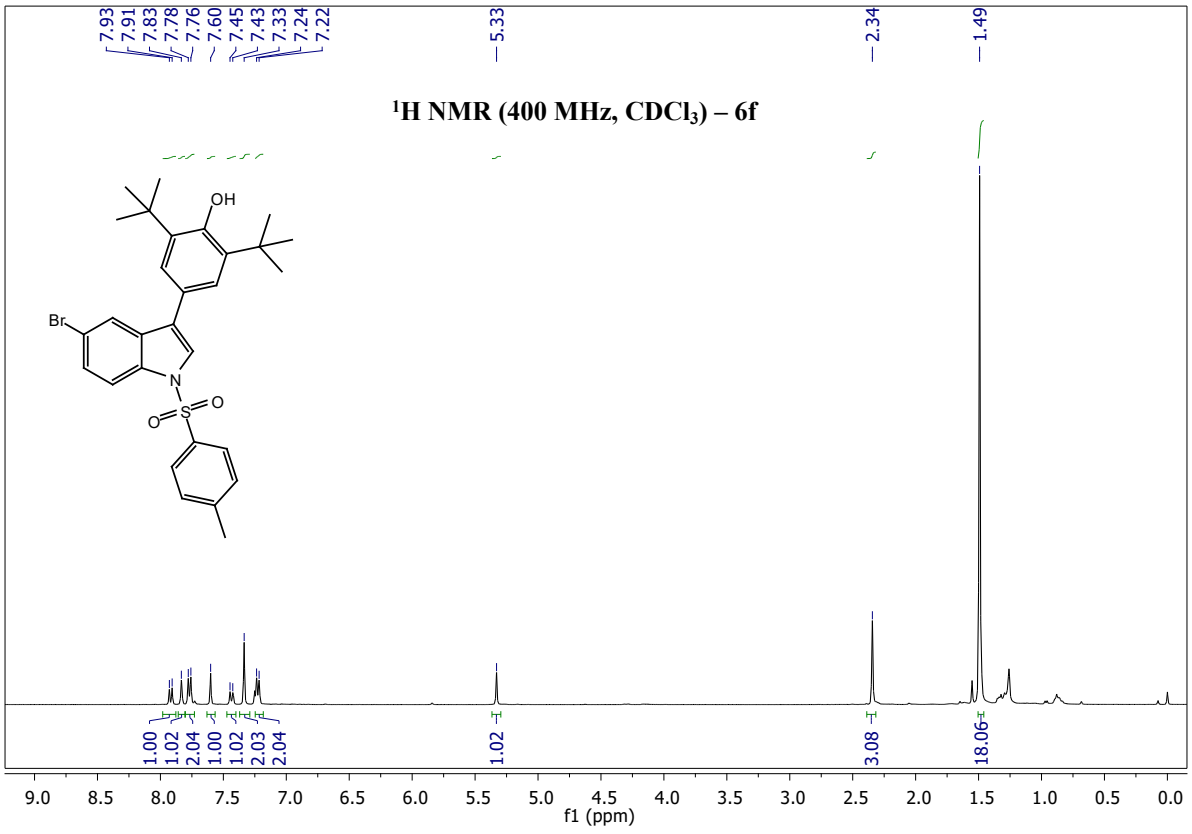
^{19}F NMR (377 MHz, $CDCl_3$) - 6d



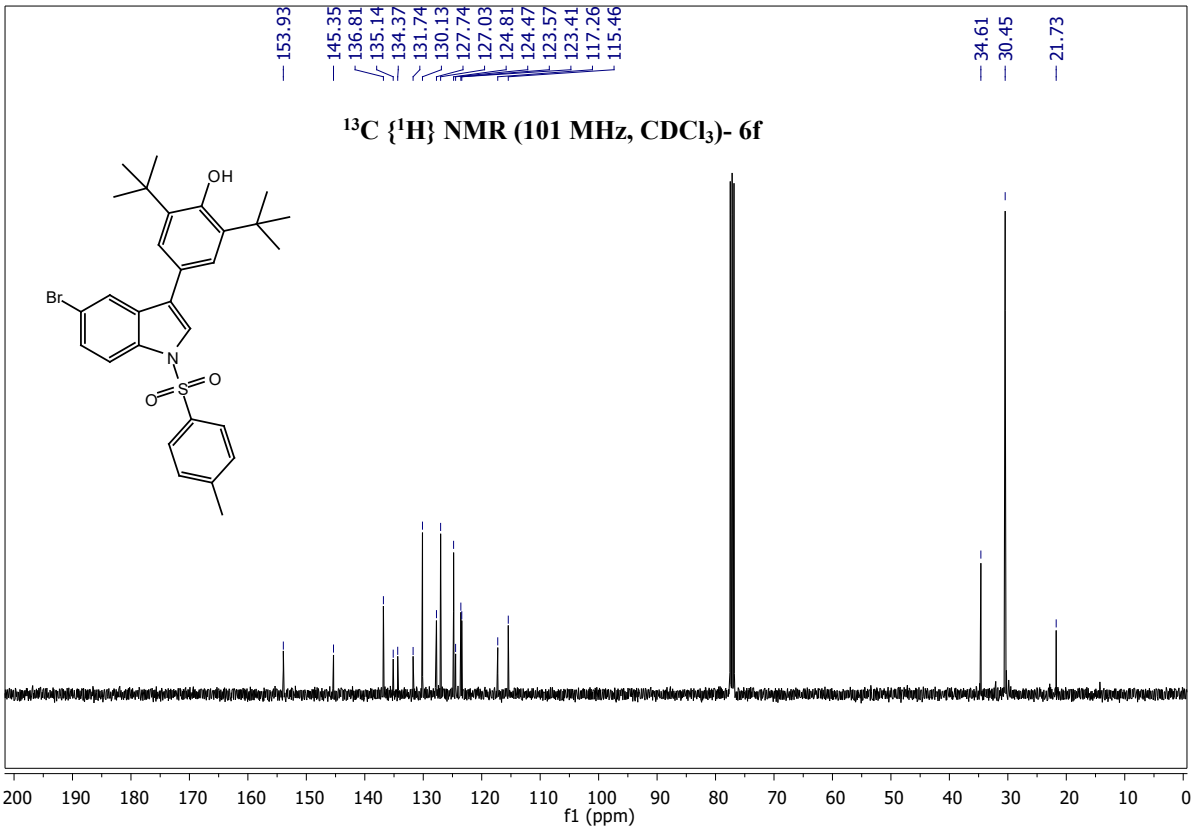
^{1}H NMR (400 MHz, $CDCl_3$) – 6e



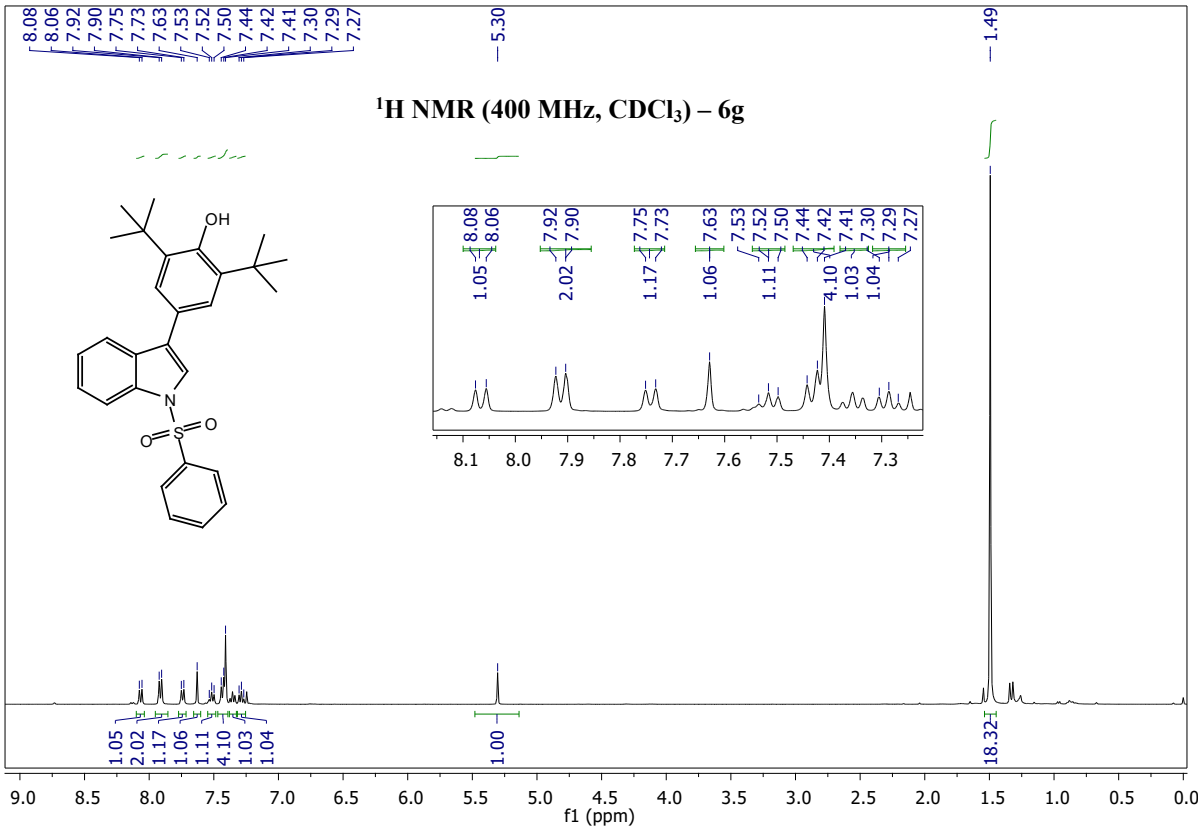
^{13}C {^{1}H} NMR (101 MHz, $CDCl_3$)- 6e



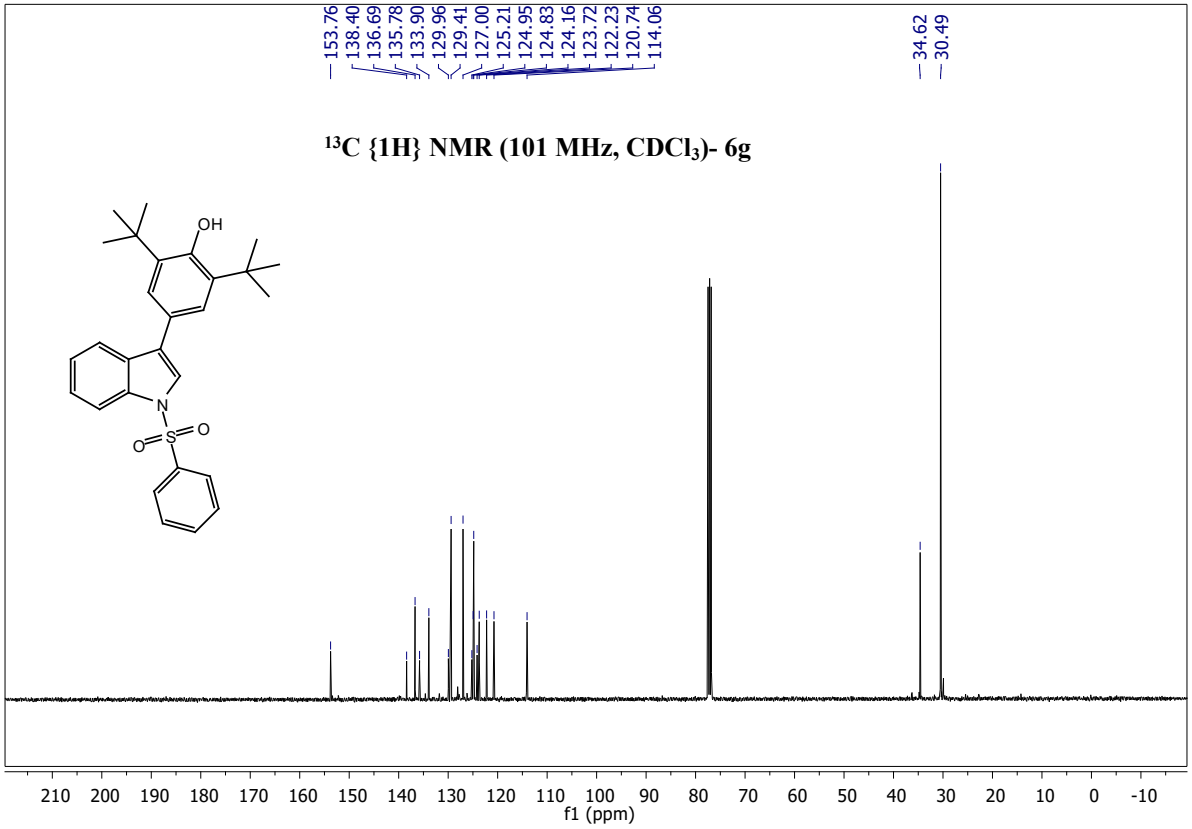
^{1}H NMR (400 MHz, $CDCl_3$) – 6f



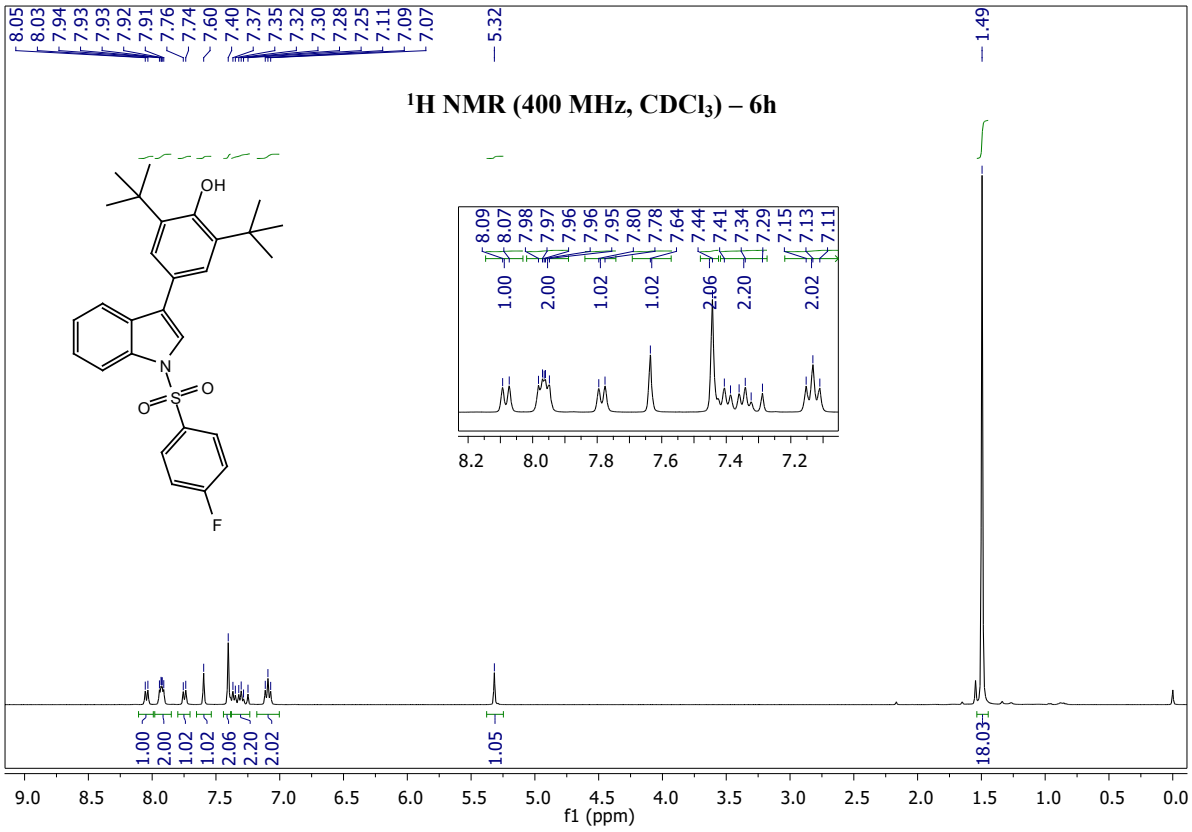
^{13}C {^{1}H} NMR (101 MHz, $CDCl_3$)- 6f



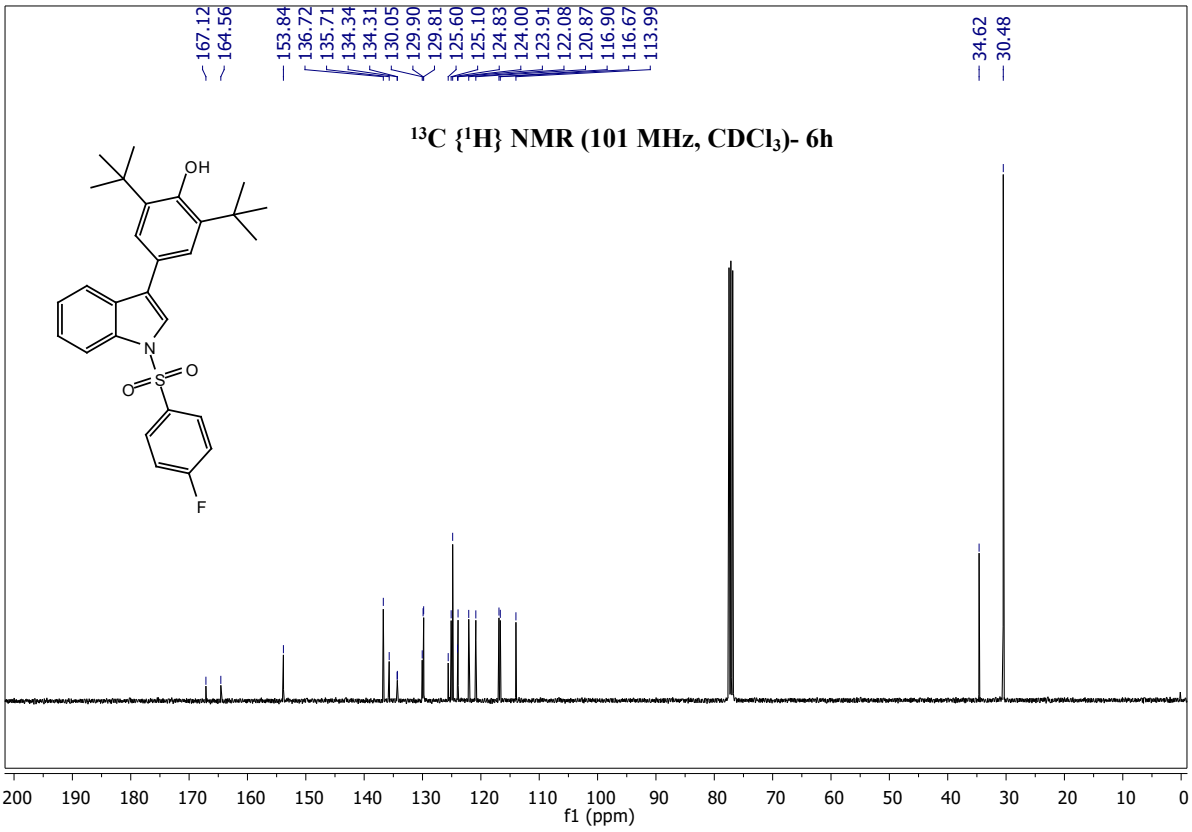
^{1}H NMR (400 MHz, $CDCl_3$) – 6g



^{13}C {1H} NMR (101 MHz, $CDCl_3$)- 6g

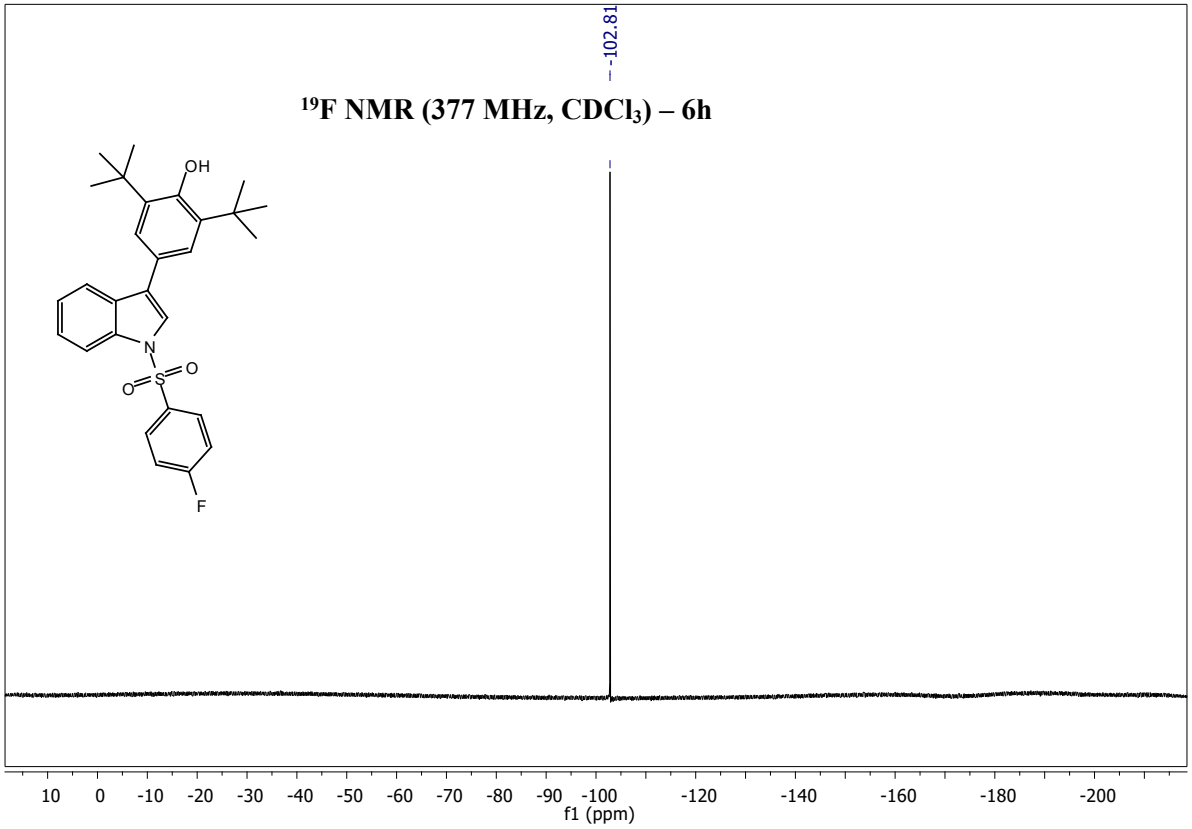


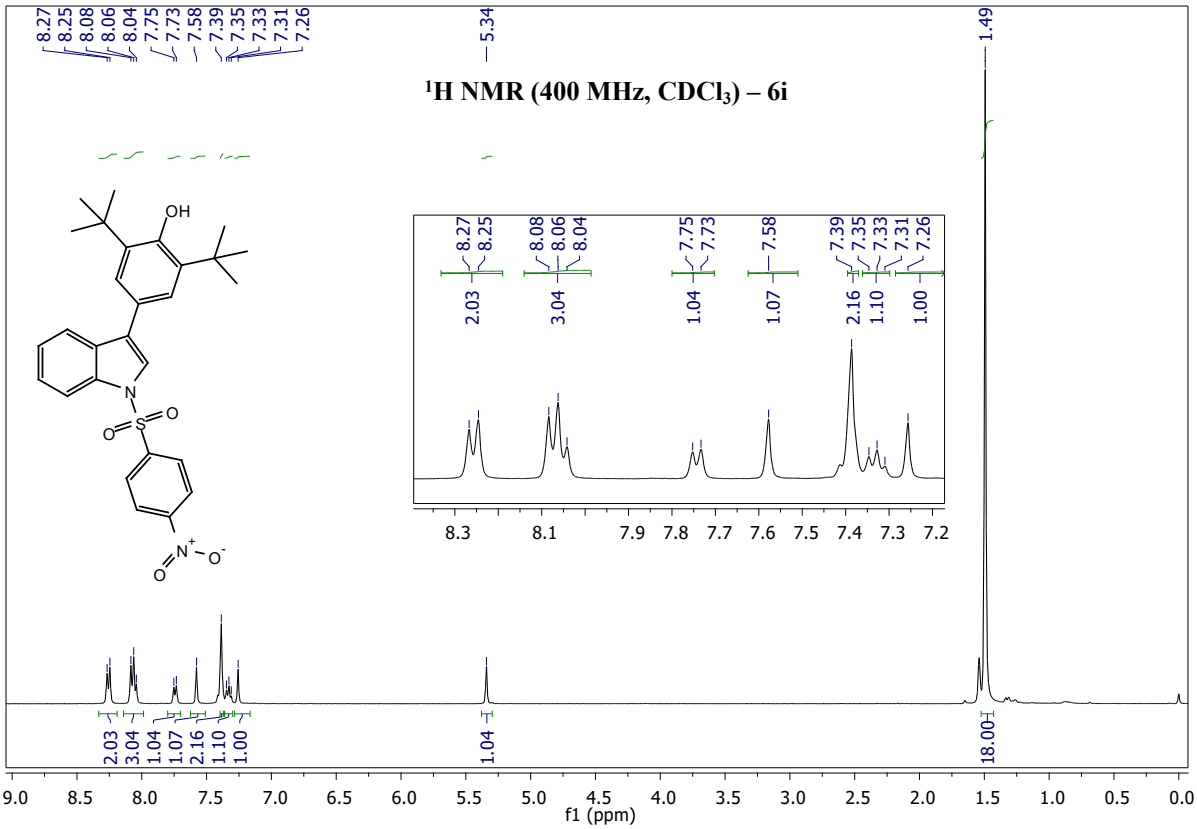
^{1}H NMR (400 MHz, $CDCl_3$) – 6h



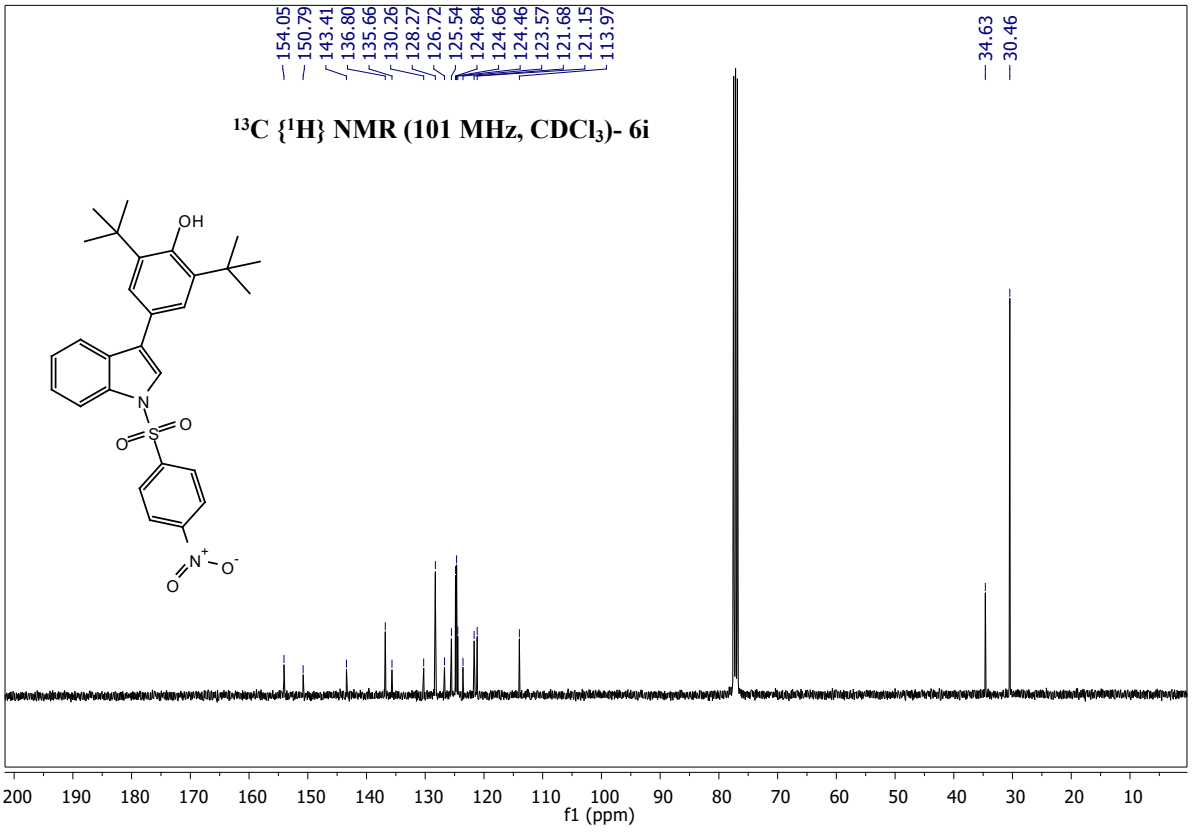
^{13}C {^{1}H} NMR (101 MHz, $CDCl_3$)- 6h

^{19}F NMR (377 MHz, $CDCl_3$) – 6h

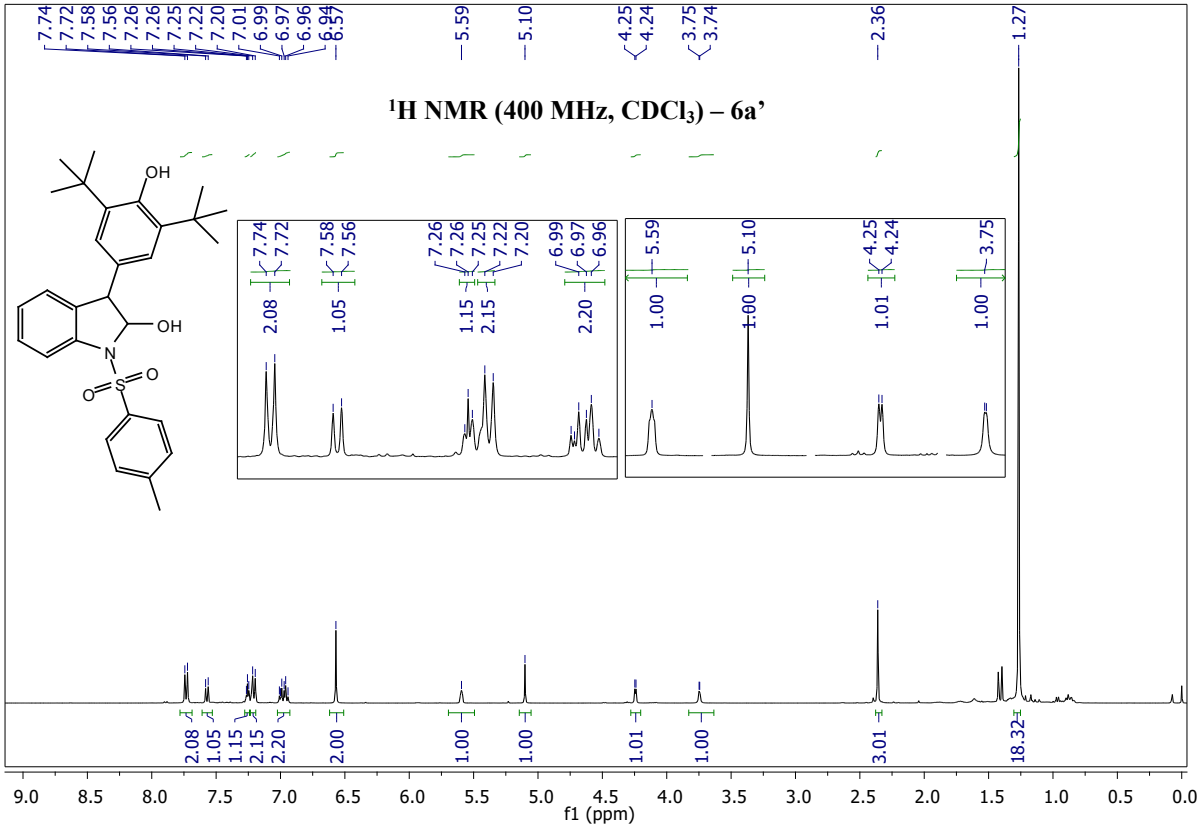


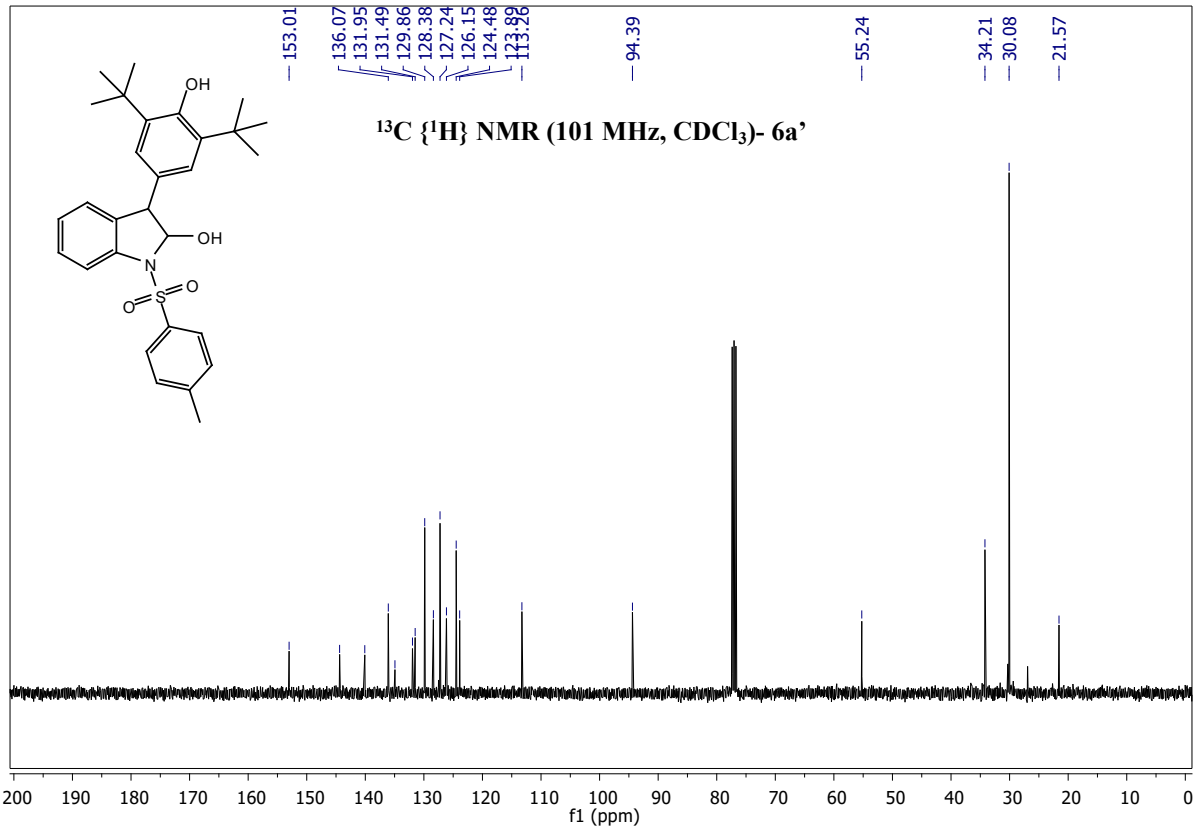


^{1}H NMR (400 MHz, $CDCl_3$) – 6i



^{13}C {^{1}H} NMR (101 MHz, $CDCl_3$)- 6i


7.74
7.72
7.58
7.56
7.26
7.26
7.25
7.22
7.20
7.01
6.99
6.97
6.96
6.94
6.57
5.59
5.10
4.25
4.24
3.75
3.74
2.36
1.27
¹H NMR (400 MHz, CDCl₃) – 6a'
OH
OH
N
S
O
O
2.08
1.05
1.15
2.15
2.20
2.00
1.00
1.00
1.01
1.00
3.01
18.32
f1 (ppm)



^{13}C {^{1}H} NMR (101 MHz, $CDCl_3$)- 6a'