Supporting Information

Synthesis of Indol-3-yl-benzofurans and Carbazoles via $Cu(OTf)_2$ Catalyzed [3+2] and [4+2] Cycloaddition

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General Information: All the reactions were performed using pre-dried glassware and screw-cap vials. All the solvents and reagents were obtained from Merck, Sigma-Aldrich and Avra and used without further drying or fresh distillation unless otherwise mentioned. The indoles and indole carbaldehydes were obtained from commercial sources and used without further purification. All the corresponding acrylates, protected and unprotected, are synthesized following the procedures given on the next page. Reactions were monitored by thin layer chromatography (TLC) on Merck pre-coated silica gel 60 F_{254} aluminium sheets with detection under UV light at 254 nm and an ethanolic solution of anisaldehyde is used as stain. Products were purified by column chromatography carried out on Avra silica gel (100-200 mesh or 230−400 mesh) packing using ethyl acetate and hexane as a solvent medium. The reported yields of isolated compounds are estimated to be >95% pure as determined by ^{1}H NMR and ^{13}C NMR. NMR spectra were recorded on Bruker High Performance Digital FT-NMR (Model: AVANCE III HD, Ascend TM WB, 500 MHz Equipment control: Topspin 3.2 Features (Standard operating procedure) and Bruker ALPHA (Eco-ATR) spectrometer and calibrated using deuterated solvents ^{1}H NMR [δH = 7.26 ($CDCl_3$) and δH = 2.50 (DMSO-d_6)] and ^{13}C deuterated solvent for ^{13}C {1H} NMR [δC = 77.00 ($CDCl_3$) and δC = 39.52 ± 0.06 (DMSO-d_6)] as a solvent and TMS as an internal reference at 298 K. The following abbreviations were used to explain the multiplicities: s = singlet, d = doublet, t = triplet, q = quartet, h = heptet, dd = doublet of doublet, ddd = doublet of a doublet of a doublet, dt = doublet of a triplet, m = multiplet, br = broad, ap = apparent.

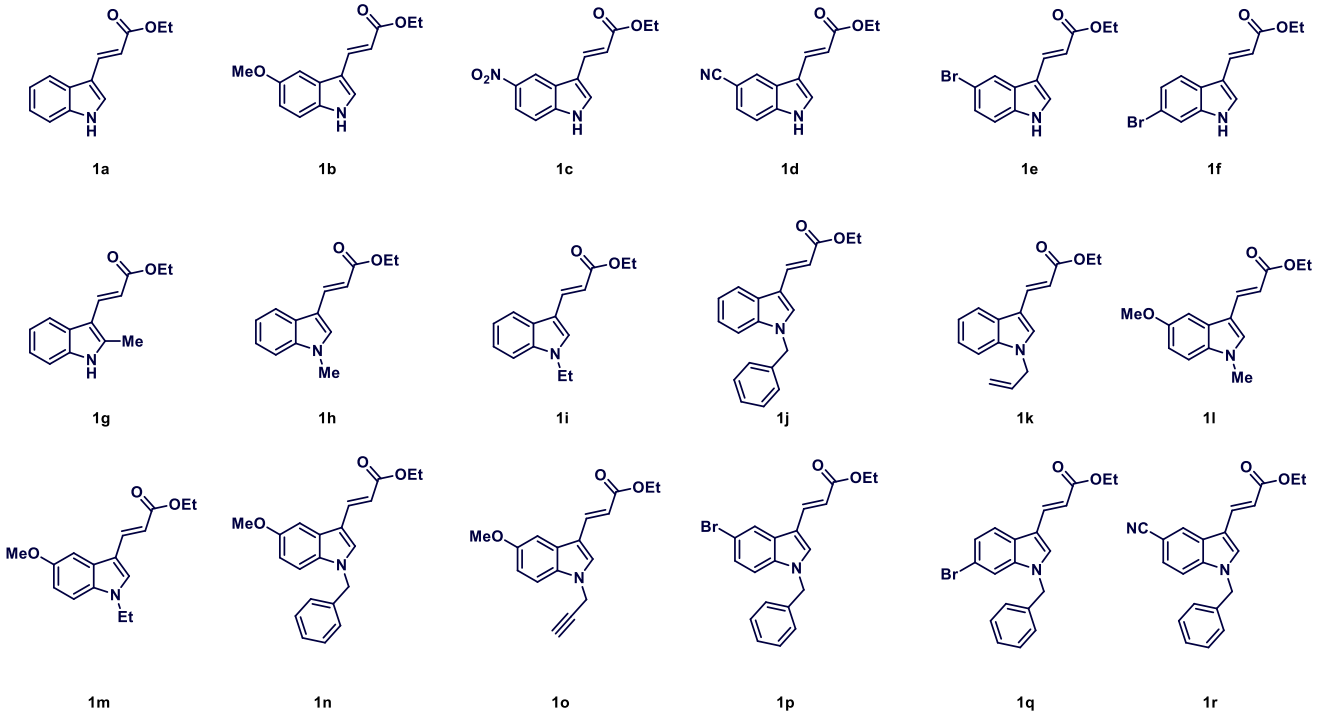
Single Crystal X-Ray diffraction data was recorded with Bruker Smart Apex Single Crystal-XRD at 100 K. ^{1}H and ^{13}C NMR spectra were recorded on a Bruker High-Performance Digital 500 MHz FT-NMR, in $CDCl_3$ solvent and tetramethylsilane was used as a reference for the chemical shift. FTIR spectra were recorded on a Bruker Vertex, 70V PMA50 spectrometer using MeOH or $CHCl_3$ as solvent /KBr Pellet. Elemental analysis was carried out on a model- UNICUBE, Elementar Analysensysteme GmbH, Germany. The HRMS data were collected using a 6545 LC/Q-TOF HRMS. Melting point was recorded on a SHIVAKI SI-6002. Melting points of all the synthesized compounds were determined in open capillary tube.

General procedure

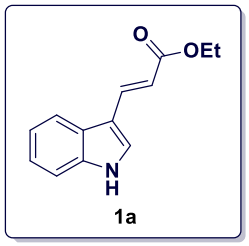
A- Synthesis and characterization of indole acrylates (standard Wittig protocol):

To the magnetically stirred solution of indole-carbaldehyde (1equivalent) in anhydrous CH_2Cl_2, $PPh_3CHCOOEt$ (1.5 equivalent) was added. The reaction was continued for 6h-18h and monitored by TLC, after completion of reaction solvent was evaporated and purification of the residue on silica gel column using EtOAc: hexane (1.5:8.5) as eluent gave the corresponding ester.

Synthesis and characterization of starting materials:



Synthesis of ethyl (E)-3-(1H-indol-3-yl)acrylate (1a)

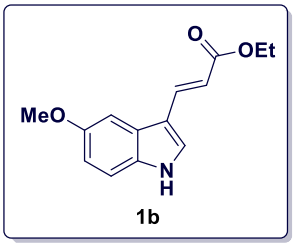


1a

The compound was prepared according to general procedure-A, using 1H-indole-3-carbaldehyde (0.2 g, 1.37 mmol, 1 eq.) and $PPh_3CHCOOEt$ (0.71 g, 2.06 mmol, 1.5 eq), in 4 mL DCM to afford ethyl E-3-(1H-indol-3-yl)acrylate. After 8 h, purification by column chromatography (15% ethyl acetate in hexane) gave **1a** as a white solid (0.25g, 87%); Rf (EtOAc/ hexane 1:3) = 0.5.

mp: 176-178 ºC; **FT-IR** (neat): ν_{max}/cm^{-1}: 3270, 1685, 1578, 1479, 1230, 760; **^{1}H NMR** (500 MHz, $CDCl_3$); δ 8.63 (s, 1H), 7.84 (dd, J = 12.1, 3.8 Hz, 2H), 7.36 (d, J = 2.6 Hz, 1H), 7.34 – 7.30 (m, 1H), 7.22 – 7.15 (m, 2H), 6.39 (d, J = 16.0 Hz, 1H), 4.20 (q, J = 7.1 Hz, 2H), 1.28 (t, J = 7.1 Hz, 3H). **^{13}C{^{1}H} NMR** (126 MHz, $CDCl_3$); δ 168.4, 138.3, 137.1, 128.9, 125.3, 123.3, 121.5, 120.5, 113.5, 113.4, 111.8, 60.1, 14.4; **HRMS-ESI (**m/z): Calcd for $C_{13}H_{13}NO_2$ $[M + H]^+$ 216.1019; found 216.1019.

Synthesis of ethyl (E)-3-(5-methoxy-1H-indol-3-yl)acrylate (1b)

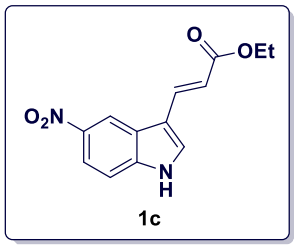


1b

The compound was prepared according to general procedure-A, using 5-methoxy-1H-indole-3-carbaldehyde (0.2 g, 1.14 mmol, 1eq.) and $PPh_3CHCOOEt$ (0.59g, 1.71 mmol, 1.5 eq), in 4 mL DCM to afford ethyl E-3-(5-methoxy-1H-indol-3-yl)acrylate. After 12 h, purification by column chromatography (18% ethyl acetate in hexane) gave **1b** as a creamy white solid (0.24g, 84%); Rf (EtOAc/ hexane 1:2) = 0.5.

mp: 182-184 ºC; **FT-IR** (neat): ν_{max}/cm^{-1}: 3257, 2374, 1680, 1612, 1570, 1430, 1230, 770; **^{1}H NMR** (500 MHz, $CDCl_3$); δ 8.94 (s, 1H), 7.94 (d, J = 16.0 Hz, 1H), 7.46 (d, J = 2.8 Hz, 1H), 7.34 (d, J = 2.2 Hz, 1H), 7.32 (d, J = 8.8 Hz, 1H), 6.94 (dd, J = 8.8, 2.3 Hz, 1H), 6.41 (d, J = 16.0 Hz, 1H), 4.32 (q, J = 7.1 Hz, 2H), 3.90 (s, 3H), 1.39 (t, J = 7.1 Hz, 3H). **^{13}C{^{1}H} NMR** (126 MHz, $CDCl_3$)**;** δ 168.6, 155.4, 138.5, 132.1, 129.4, 125.9, 113.2, 113.2, 112.6, 112.4, 102.5, 60.2, 56.0, 14.4. **HRMS-ESI (**m/z): Calcd for $C_{14}H_{15}NO_3$ $[M + H]^+$ 246.1125; found 246.1128.

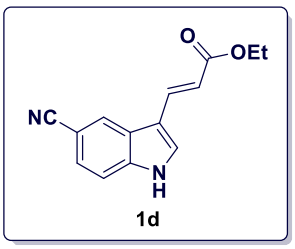
Synthesis of ethyl (E)-3-(5-nitro-1H-indol-3-yl)acrylate (1c)



The compound was prepared according to general procedure-A, using 5-nitro-1H-indole-3-carbaldehyde (0.2 g, 1.05 mmol, 1 eq.) and $PPh_3CHCOOEt$ (0.54 g, 1.57 mmol, 1.5 eq), in 4 mL DCM to afford ethyl E-3-(5-nitro-1H-indol-3-yl)acrylate. After 8 h, purification by column chromatography (30% ethyl acetate in hexane) gave **1c** as a yellow solid (0.22g, 89%); Rf (EtOAc/ hexane 2:3) = 0.5.

mp: 190-192 °C; **FT-IR** (neat): ν_{max}/cm^{-1}: 3390, 2962, 1720, 1640, 1570, 1474, 1230, 770; **^{1}H NMR** (500 MHz, $CDCl_3$ + DMSO-d_6); δ 11.18 (s, 1H), 8.78 (d, J = 2.0 Hz, 1H), 8.10 (dd, J = 9.0, 2.1 Hz, 1H), 7.86 (d, J = 16.1 Hz, 1H), 7.60 (s, 1H), 7.46 (d, J = 9.0 Hz, 1H), 6.45 (d, J = 16.1 Hz, 1H), 4.26 (q, J = 7.1 Hz, 2H), 1.35 (t, J = 7.1 Hz, 3H). **^{13}C{^{1}H} NMR** (126 MHz, $CDCl_3$ + DMSO-d_6); δ 166.8, 141.4, 139.6, 135.7 130.7, 123.7, 117.2, 116.1, 113.7, 113.7, 111.2, 59.3, 13.4. **HRMS-ESI (**m/z): Calcd for $C_{13}H_{12}N_2O_4$ $[M + H]^+$ 261.0870; found 261.0879.

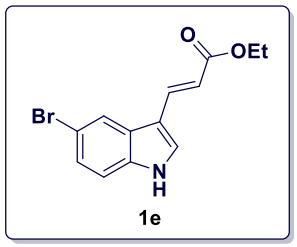
Synthesis of ethyl (E)-3-(5-cyano-1H-indol-3-yl)acrylate (1d)



The compound was prepared according to general procedure-A, using 3-formyl-1H-indole-5-carbonitrile (0.2 g, 1.17 mmol, 1 eq.) and $PPh_3CHCOOEt$ (0.61 g, 1.76 mmol, 1.5 eq), in 4 mL DCM to afford ethyl E-3-(5-cyano-1H-indol-3-yl)acrylate. After 9 h, purification by column chromatography (35% ethyl acetate in hexane) gave **1d** as a pale greenish solid (0.25g, 89%); Rf (EtOAc/ hexane 2:3) = 0.5.

mp: 160-162 °C; **FT-IR** (neat): ν_{max}/cm^{-1}: 3494, 2962, 2376, 1720, 1512, 1232, 770, 688; **^{1}H NMR** (500 MHz, $CDCl_3$ + DMSO-d_6); δ 11.23 (s, 1H), 8.15 (s, 1H), 7.81 (d, J = 16.1 Hz, 1H), 7.54 (d, J = 1.8 Hz, 1H), 7.45 (d, J = 8.4 Hz, 1H), 7.39 (d, J = 8.4 Hz, 1H), 6.34 (d, J = 16.0 Hz, 1H), 4.21 (q, J = 7.1 Hz, 2H), 1.30 (t, J = 7.1 Hz, 3H). **^{13}C{^{1}H} NMR** (126 MHz, $CDCl_3$ + DMSO-d_6); δ 166.8, 138.3, 136.1, 130.1, 124.4(X2C), 124.1, 119.4, 113.2, 112.2, 112.1, 102.8, 59.2, 13.4. **HRMS-ESI (**m/z): Calcd for $C_{14}H_{12}N_2O_2$ $[M + H]^+$ 241.0972; found 241 .0970

Synthesis of ethyl (E)-3-(5-bromo-1H-indol-3-yl)acrylate (1e)

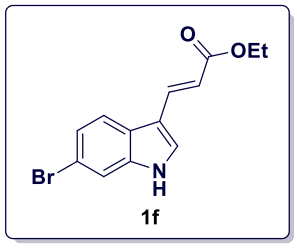


1e

The compound was prepared according to general procedure-A, using 5-bromo-1H-indole-3-carbaldehyde (0.2 g, 0.089 mmol, 1 eq.) and $PPh_3CHCOOEt$ (0.46 g, 1.33 mmol, 1.5 eq), in 4 mL DCM to afford ethyl E-3-(5-bromo-1H-indol-3-yl)acrylate. After 12 h, purification by column chromatography (25% ethyl acetate in hexane) gave **1e** as a creamy white solid (0.22g, 84%); Rf (EtOAc/ hexane 2:3) = 0.5.

mp: 120-122 °C; **FT-IR** (neat): ν_{max}/cm^{-1}: 3450, 2977, 2374, 1720, 1619, 1240, 757; **^{1}H NMR** (500 MHz, $CDCl_3$); δ 8.73 (s, 1H), 8.06 (d, J = 1.6 Hz, 1H), 7.87 (d, J = 16.0 Hz, 1H), 7.48 (d, J = 2.5 Hz, 1H), 7.39 (d, J = 1.8 Hz, 1H), 7.37 (d, J = 1.8 Hz, 1H), 6.43 (d, J = 16.0 Hz, 1H), 4.31 (q, J = 7.1 Hz, 2H), 1.39 (t, J = 7.1 Hz, 3H). **^{13}C{^{1}H} NMR** (126 MHz, $CDCl_3$); δ 168.1, 137.4, 135.6, 129.4, 126.9, 126.2, 123.1, 114.9, 114.1, 113.2, 113.1, 60.3, 14.4. **HRMS-ESI (**m/z): Calcd for $C_{13}H_{12}BrNO_2$ $[M + H]^+$ 294.0124; found 294.0122.

Synthesis of ethyl (E)-3-(6-bromo-1H-indol-3-yl)acrylate (1f)

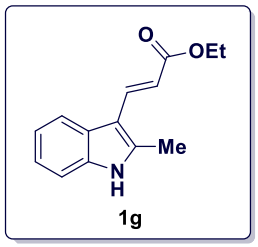


1f

The compound was prepared according to general procedure-A, using 6-bromo-1H-indole-3-carbaldehyde (0.2 g, 0.089 mmol, 1 eq.) and $PPh_3CHCOOEt$ (0.46 g, 1.33 mmol, 1.5 eq), in 4 mL DCM to afford ethyl E-3-(6-bromo-1H-indol-3-yl)acrylate. After 12 h, purification by column chromatography (25-30% ethyl acetate in hexane) gave **1f** as a creamy white solid (0.23g, 87%); Rf (EtOAc/ hexane 2:3) = 0.5.

mp: 135-137 °C; **FT-IR** (neat): ν_{max}/cm^{-1}: 3230, 2945, 2275, 1715, 1680, 1250, 752; **^{1}H** NMR (500 MHz, $CDCl_3$); δ 8.90 (s, 1H), 7.78 (d, J = 16.0 Hz, 1H), 7.67 (d, J = 8.5 Hz, 1H), 7.47 (d, J = 1.3 Hz, 1H), 7.34 (d, J = 2.5 Hz, 1H), 7.25 (dd, J = 8.5, 1.5 Hz, 1H), 6.33 (d, J = 16.0 Hz, 1H), 4.20 (q, J = 7.1 Hz, 2H), 1.28 (t, J = 7.1 Hz, 3H). **^{13}C{^{1}H} NMR** (126 MHz, $CDCl_3$); δ 168.2, 137.9, 137.7, 129.2, 124.6, 124.2, 121.5, 116.7, 114.8, 113.9, 113.5, 60.3, 14.4. **HRMS-ESI (**m/z): Calcd for $C_{13}H_{12}BrNO_2$ $[M + H]^+$ 294.0124; found 294.0125.

Synthesis of ethyl (E)-3-(2-methyl-1H-indol-3-yl)acrylate (1g)



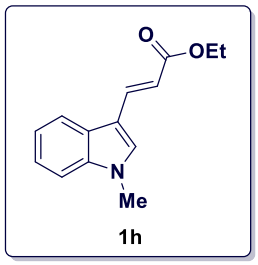
The compound was prepared according to general procedure-A, using 2-methyl-1H-indole-3-carbaldehyde (0.2 g, 1.22 mmol, 1 eq.) and $PPh_3CHCOOEt$ (0.65 g, 1.89 mmol, 1.5 eq), in 4 mL DCM to afford ethyl E-3-(2-methyl-1H-indol-3-yl)acrylate. After 12 h, purification by column chromatography (15% ethyl acetate in hexane) gave **1g** as a pale brown solid (0.23g, 87%); Rf (EtOAc/ hexane 1:3) = 0.5.

mp: 128-130 °C; **FT-IR** (neat): ν_{max}/cm^{-1}: 3367, 2928, 2366, 2372, 1699, 1250; **^{1}H NMR** (500 MHz, $CDCl_3$); δ 8.57 (s, 1H), 7.99 (d, J = 15.9 Hz, 1H), 7.88 (d, J = 5.0 Hz, 1H), 7.36 – 7.33 (m, 1H), 7.25 – 7.21 (m, 2H), 6.47 (d, J = 15.9 Hz, 1H), 4.32 (q, J = 7.1 Hz, 2H), 2.55 (s, 3H), 1.40 (t, J = 7.1 Hz, 3H). **^{13}C{^{1}H} NMR** (126 MHz, $CDCl_3$); δ 168.8, 140.1, 137.6, 135.7, 126.3, 122.4, 121.4, 120.0, 112.0, 110.9, 109.6, 60.1, 14.51, 12.3. **HRMS-ESI** (m/z): Calcd for $C_{14}H_{15}NO_2$ $[M + H]^+$ 230.1176; found 230.1175.

B- Synthesis and characterization of protected indole acrylates :

To the magnetically stirred solution of indole-ester (1equiv) in anhydrous ACN, slowly add NaH (1.5 equivalent) at 0°C followed by addition of second reacting partner (alkyl, aryl, allyl, benzyl, propargyl halides, 1.2 equivalents). The reaction was continued to stirred at room temperature for 3-4h and monitored by TLC, after completion of reaction solvent was evaporated and purification of the residue on silica gel column using EtOAc (15-40%) as eluent gave the corresponding protected ester.

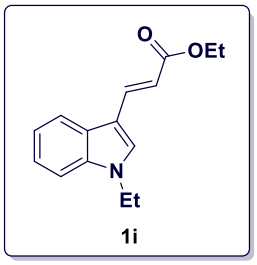
Synthesis of ethyl (E)-3-(1-methyl-1H-indol-3-yl)acrylate (1h)



The compound was prepared according to general procedure-B, using ethyl (E)-3-(1H-indol-3-yl)acrylate **1a** (0.1 g, 0.464 mmol, 1 eq.), NaH (0.022 g, 0.92 mmol, 2 eq.) at 0ºC and MeI (0.079 g, 0.55 mmol, 1.2 eq.) room temperature in 2 mL ACN affording ethyl (E)-3-(1-methyl-1H-indol-3-yl)acrylate. After 3 h, purification by column chromatography (13% ethyl acetate in hexane) gave **1h** as a white solid (0.104g, 98%); Rf (EtOAc/ hexane 1:3) = 0.5.

mp: 156-158 ºC; **FT-IR** (neat): ν_{max}/cm^{-1}: 3365, 3033, 2374, 1684, 1230, 1166, 765; **^{1}H NMR** (500 MHz, $CDCl_3$); δ 7.95 (d, J = 7.9 Hz, 1H), 7.92 (d, J = 16.0 Hz, 1H), 7.37 (d, J = 7.9 Hz, 1H), 7.35 – 7.32 (m, 2H), 7.31 – 7.26 (m, 1H), 6.45 (d, J = 15.9 Hz, 1H), 4.30 (q, J = 7.1 Hz, 2H), 3.81 (s, 3H), 1.38 (t, J = 7.5, 6.7 Hz, 3H). **^{13}C{^{1}H} NMR** (126 MHz, $CDCl_3$); δ 168.3, 138.0, 137.9, 133.1, 126.0, 122.9, 121.2, 120.6, 112.6, 112.1, 109.9, 60.0, 33.1, 14.5. **HRMS-ESI (**m/z): Calcd for $C_{14}H_{15}NO_2$ $[M + H]^+$ 230.1176; found 230.1175.

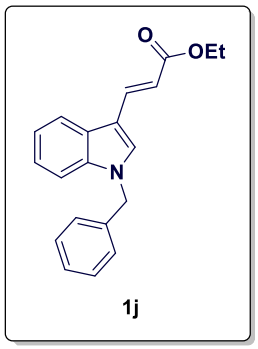
Synthesis of ethyl (E)-3-(1-ethyl-1H-indol-3-yl)acrylate (1i)



The compound was prepared according to general procedure-B, using ethyl (E)-3-(1H-indol-3-yl)acrylate **1a** (0.1 g, 0.464 mmol, 1 eq.), NaH (0.022 g, 0.92 mmol, 2 eq.) at 0ºC and EtI (0.087 g, 0.55 mmol, 1.2 eq.) room temperature in 2 mL ACN affording ethyl (E)-3-(1-ethyl-1H-indol-3-yl)acrylate. After 2.5 h, purification by column chromatography (15% ethyl acetate in hexane) gave **1i** as a white solid (0.109g, 97%); Rf (EtOAc/ hexane 1:3) = 0.5.

Mp: 146-148 ºC; **FT-IR** (neat): ν_{max}/cm^{-1}: 3230, 2370, 1716, 1669, 1583, 1232, 763; **^{1}H NMR** (500 MHz, $CDCl_3$); δ 7.98 – 7.94 (m, 1H), 7.93 (s, 1H), 7.41 (s, 1H), 7.39 (d, J = 8.3 Hz, 1H), 7.35 – 7.31 (m, 1H), 7.30 – 7.26 (m, 1H), 6.46 (d, J = 15.9 Hz, 1H), 4.31 (q, J = 7.1 Hz, 2H), 4.17 (q, J = 7.3 Hz, 2H), 1.50 (t, J = 7.3 Hz, 3H), 1.39 (t, J = 7.1 Hz, 3H). **^{13}C{^{1}H} NMR** (126 MHz, $CDCl_3$); δ 168.3, 138.1, 137.1, 131.4, 126.2, 122.8, 121.2, 120.7, 112.4, 112.1, 110.0, 60.0, 41.3, 15.2, 14.5. **HRMS-ESI (**m/z): Calcd for $C_{15}H_{17}NO_2$ $[M + H]^+$ 244.1332; found 244.1333.

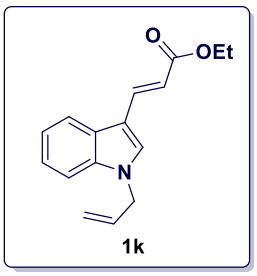
Synthesis of ethyl (E)-3-(1-benzyl-1H-indol-3-yl)acrylate (1j)



The compound was prepared according to general procedure-B, using ethyl (E)-3-(1H-indol-3-yl)acrylate **1a** (0.1 g, 0.464 mmol, 1 eq.), NaH (0.022 g, 0.92 mmol, 2 eq.) at 0°C and benzylchloride (0.07 g, 0.92 mmol, 1.2 eq.) room temperature in 2 mL ACN affording ethyl (E)-3-(1-benzyl-1H-indol-3-yl)acrylate. After 3 h, purification by column chromatography (12% ethyl acetate in hexane) gave **1j** as a white solid (0.109g, 97%); Rf (EtOAc/ hexane 1:2) = 0.5.

mp: 136-138 °C; **FT-IR** (neat): ν_{max}/cm^{-1}: 3368, 3023, 2374, 1706, 1230, 1154, 763; **^{1}H NMR** (500 MHz, $CDCl_3$); δ 7.98 – 7.95 (m, 1H), 7.92 (d, J = 16.0 Hz, 1H), 7.43 (s, 1H), 7.36 – 7.34 (m, 2H), 7.32 (s, 1H), 7.29 (d, J = 1.8 Hz, 2H), 7.28 – 7.26 (m, 1H), 7.21 – 7.14 (m, 2H), 6.46 (d, J = 16.0 Hz, 1H), 5.35 (s, 2H), 4.29 (q, J = 7.1 Hz, 2H), 1.37 (t, J = 7.1 Hz, 3H). **^{13}C{^{1}H} NMR** (126 MHz, $CDCl_3$); δ 168.2, 137.8, 137.6, 136.1, 132.3, 128.9, 128.0, 126.9, 126.3, 123.1, 121.4, 120.7, 113.12, 112.7, 110.4, 60.0, 50.4, 14.4. **HRMS-ESI (**m/z): Calcd for $C_{20}H_{19}NO_2$ [M] 305.1416; found 305.1569.

Synthesis of ethyl (E)-3-(1-allyl-1H-indol-3-yl)acrylate (1k)

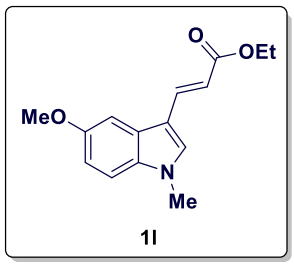


The compound was prepared according to general procedure-B, using ethyl (E)-3-(1H-indol-3-yl)acrylate **1a** (0.1 g, 0.464 mmol, 1 eq.), NaH (0.022 g, 0.92 mmol, 2 eq.) at 0°C and allyl bromide (0.067 g, 0.55 mmol, 1.2 eq.) room temperature in 2 mL ACN affording ethyl (E)-3-(1-allyl-1H-indol-3-yl)acrylate. After 2.5 h, purification by column chromatography (10% ethyl acetate in hexane) gave **1k** as a white solid (0.107 g, 91%); Rf (EtOAc/ hexane 1:3) = 0.5.

mp: 145-147°C; **FT-IR** (neat): ν_{max}/cm^{-1}: 3270, 2978, 2970, 1665, 1630, 1517, 1479, 1230, 760; **^{1}H NMR** (500 MHz, $CDCl_3$); δ 7.98 – 7.90 (m, 2H), 7.42 (s, 1H), 7.38 (d, J = 7.9 Hz, 1H), 7.35 – 7.31 (m, 1H), 7.31 – 7.26 (m, 1H), 6.46 (d, J = 15.9 Hz, 1H), 6.07 – 5.97 (m, 1H), 5.29 (d, J = 10.2 Hz, 1H), 5.18 (d, J = 17.1 Hz, 1H), 4.76 (d, J = 5.3 Hz, 2H), 4.30 (q, J = 7.1 Hz, 2H), 1.38 (t, J =

7.1 Hz, 3H). **$^{13}C\{^{1}H\}$ NMR** (126 MHz, $CDCl_3$); δ 168.3, 137.9, 137.4, 132.4, 132.0, 126.2, 122.9, 121.3, 120.7, 118.2, 112.9, 112.5, 110.3, 60.0, 49.0, 14.4. **HRMS-ESI (**m/z): Calcd for $C_{16}H_{17}NO_2$ $[M+Na]^+$ 279.1230; found 279.1294.

3.5 Synthesis of ethyl (E)-3-(5-methoxy-1-methyl-1H-indol-3-yl)acrylate (1l)

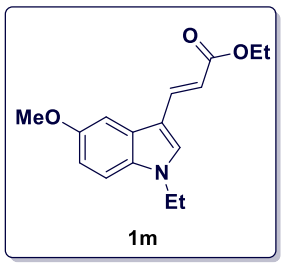


1l

The compound was prepared according to general procedure-B, using ethyl (E)-3-(5-methoxy-1H-indol-3-yl)acrylate **1b** (0.1 g, 0.407 mmol, 1 eq.), NaH (0.019 g, 0.815 mmol, 2 eq.) at 0°C and MeI (0.069 g, 0.48 mmol, 1.2 eq.) room temperature in 2 mL ACN affording ethyl (E)-3-(5-methoxy-1-methyl-1H-indol-3-yl)acrylate. After 2.5 h, purification by column chromatography (15% ethyl acetate in hexane) gave **1l** as a white solid (0.098 g, 93%); Rf (EtOAc/ hexane 1:2) = 0.5.

mp: 177-179 °C; **FT-IR** (neat): ν_{max}/cm^{-1}: 3256, 2924, 1686, 1620, 1485, 1366, 1274, 757; **^{1}H NMR** (500 MHz, $CDCl_3$); δ 7.90 (d, J = 15.9 Hz, 1H), 7.35 (s, 1H), 7.32 (s, 1H), 7.25 (d, J = 8.9 Hz, 1H), 6.98 (dd, J = 8.9, 2.2 Hz, 1H), 6.34 (d, J = 15.9 Hz, 1H), 4.30 (q, J = 7.1 Hz, 2H), 3.93 (s, 3H), 3.79 (s, 3H), 1.38 (t, J = 7.1 Hz, 3H). **$^{13}C\{^{1}H\}$ NMR** (126 MHz, $CDCl_3$); δ 168.4, 155.4, 138.0, 133.2, 133.2, 126.6, 112.8, 111.8, 111.6, 110.7, 102.6, 60.0, 56.0, 33.3, 14.5. **HRMS-ESI (**m/z): Calcd for $C_{15}H_{17}NO_3$ $[M + H]^+$ 260.1281; found 260.1284.

Synthesis of ethyl (E)-3-(1-ethyl-5-methoxy-1H-indol-3-yl)acrylate (1m)



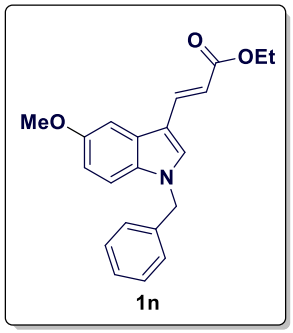
1m

The compound was prepared according to general procedure-B, using ethyl (E)-3-(5-methoxy-1H-indol-3-yl)acrylate **1b** (0.1 g, 0.407 mmol, 1 eq.), NaH (0.019 g, 0.815 mmol, 2 eq.) at 0°C and ethyl iodide (0.076 g, 0.48 mmol, 1.2 eq.) room temperature in 2 mL ACN affording ethyl (E)-3-(1-ethyl-5-methoxy-1H-indol-3-yl)acrylate. After 3.5 h, purification by column chromatography (15% ethyl acetate in hexane) gave **1m** as a creamy white solid (0.104 g, 94%); Rf (EtOAc/ hexane 1:2) = 0.5.

mp: 165-167 °C; **FT-IR** (neat): ν_{max}/cm^{-1}: 3260, 2941, 1689, 1622, 1452, 1358, 1260, 757; **^{1}H NMR** (500 MHz, $CDCl_3$); δ 7.92 (d, J = 15.9 Hz, 1H), 7.39 (s, 1H), 7.35 (s, 1H), 7.27 (d, J = 8.9

Hz, 1H), 6.97 (d, J = 7.4 Hz, 1H), 6.35 (d, J = 15.9 Hz, 1H), 4.30 (q, J = 7.0 Hz, 2H), 4.15 (q, J = 7.2 Hz, 2H), 3.93 (s, 3H), 1.50 (t, J = 7.2 Hz, 3H), 1.38 (t, J = 7.1 Hz, 3H). **^{13}C{^{1}H} NMR** (126 MHz, $CDCl_3$); δ 168.4, 155.4, 138.1, 132.2, 131.5, 126.8, 112.8, 111.7, 111.7, 110.7, 102.7, 60.0, 56.0, 41.5, 15.2, 14.5. **HRMS-ESI (**m/z): Calcd for $C_{16}H_{19}NO_3$ $[M + H]^+$ 274.1438; found 274.1444.

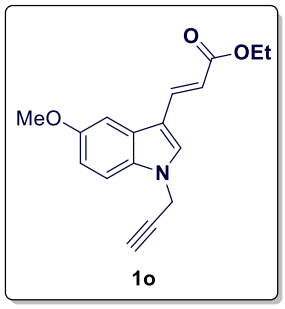
Synthesis of ethyl (E)-3-(1-benzyl-5-methoxy-1H-indol-3-yl)acrylate (1n)



The compound was prepared according to general procedure-B, using ethyl (E)-3-(5-methoxy-1H-indol-3-yl)acrylate **1b** (0.1 g, 0.407 mmol, 1 eq.), NaH (0.019 g, 0.815 mmol, 2 eq.) at 0^{o}C and benzyl chloride (0.062 g, 0.48 mmol, 1.2 eq.) room temperature in 2 mL ACN affording ethyl (E)-3-(1-benzyl-5-methoxy-1H-indol-3-yl)acrylate. After 3 h, purification by column chromatography (18% ethyl acetate in hexane) gave **1n** as a creamy white solid (0.121 g, 89%), Rf (EtOAc/ hexane 1:2) = 0.5.

mp: 165-167 ^{o}C; **FT-IR** (neat): ν_{max}/cm^{-1}: 3521, 3033, 2374, 1706, 1558, 1230, 756; **^{1}H NMR** (500 MHz, $CDCl_3$); δ 7.80 (d, J = 16.0 Hz, 1H), 7.28 (s, 1H), 7.26 – 7.22 (m, 2H), 7.22 – 7.16 (m, 2H), 7.09 (d, J = 8.9 Hz, 1H), 7.06 – 6.99 (m, 2H), 6.80 (dd, J = 8.9, 2.3 Hz, 1H), 6.25 (d, J = 16.0 Hz, 1H), 5.17 (s, 2H), 4.18 (q, J = 7.1 Hz, 2H), 3.80 (s, 3H), 1.26 (t, J = 7.1 Hz, 3H). **^{13}C{^{1}H} NMR** (126 MHz, $CDCl_3$); δ 168.3, 155.5, 138.0, 136.2, 132.6, 132.6, 128.9, 128.0, 126.9, 126.9, 113.0, 112.3, 112.2, 111.3, 102.6, 60.0, 55.9, 50.6, 14.5. **HRMS-ESI (**m/z): Calcd for $C_{21}H_{21}NO_3$ $[M + H]^+$ 336.1594; found 336.1588.

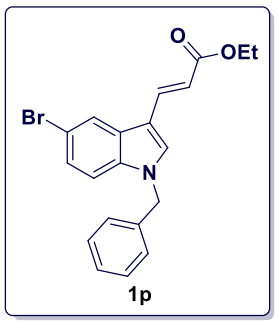
Synthesis of ethyl (E)-3-(5-methoxy-1-(prop-2-yn-1-yl)-1H-indol-3-yl)acrylate (1o)



The compound was prepared according to general procedure-B, using ethyl (E)-3-(5-methoxy-1H-indol-3-yl)acrylate **1b** (0.1 g, 0.407 mmol, 1 eq.), NaH (0.019 g, 0.815 mmol, 2 eq.) at 0ºC and propargyl bromide (0.058 g, 0.48 mmol, 1.2 eq.) room temperature in 2 mL ACN affording ethyl (E)-3-(5-methoxy-1-(prop-2-yn-1-yl)-1H-indol-3-yl)acrylate. After 2 h, purification by column chromatography (20 % ethyl acetate in hexane) gave **1o** as a light brownish solid (0.099 g, 86%), Rf (EtOAc/ hexane 1:2) = 0.5.

mp: 150-152 ºC; **FT-IR** (neat): ν_{max}/cm^{-1}: 3530, 2370, 1702, 1558, 1220, 749; **^{1}H NMR** (500 MHz, $CDCl_3$); δ 7.90 (d, J = 16.0 Hz, 1H), 7.52 (s, 1H), 7.36 – 7.34 (m, 1H), 7.31 (d, J = 21.0 Hz, 1H), 7.00 (dd, J = 8.8, 1.9 Hz, 1H), 6.37 (d, J = 16.0 Hz, 1H), 4.87 (d, J = 2.2 Hz, 2H), 4.30 (q, J = 7.1 Hz, 2H), 3.93 (s, 3H), 2.50 (s, 1H), 1.38 (t, J = 7.1 Hz, 3H). **^{13}C{^{1}H} NMR** (126 MHz, $CDCl_3$); δ 168.2, 155.7, 137.7, 132.0, 131.4, 127.1, 113.1, 112.8, 112.5, 110.7, 102.8, 76.6, 74.6, 60.1, 56.0, 36.3, 14.4. **HRMS-ESI (**m/z): Calcd for $C_{17}H_{17}NO_3$ $[M + H]^+$ 284.1281; found 284.1236.

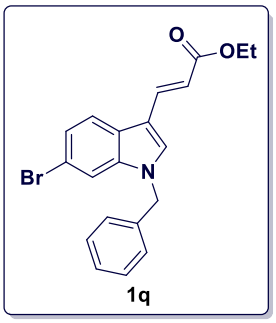
Synthesis of ethyl (E)-3-(1-benzyl-5-bromo-1H-indol-3-yl)acrylate (1p)



The compound was prepared according to general procedure-B, using ethyl (E)-3-(5-bromo-1H-indol-3-yl)acrylate **1e** (0.1 g, 0.339 mmol, 1 eq.), NaH (0.016 g, 0.67 mmol, 2 eq.) at 0ºC and benzyl chloride (0.052 g, 0.40 mmol, 1.2 eq.) room temperature in 2 mL ACN affording ethyl (E)-3-(1-benzyl-5-bromo-1H-indol-3-yl)acrylate. After 4 h, purification by column chromatography (35% ethyl acetate in hexane) gave **1p** as a creamy white solid (0.113 g, 87%), Rf (EtOAc/ hexane 2:1) = 0.5.

mp: 145-147 ºC; **FT-IR** (neat): ν_{max}/cm^{-1}: 3260, 2984, 2370, 1702, 1628, 1558, 1391, 1220,1037, 749; **^{1}H NMR** (500 MHz, $CDCl_3$); δ 7.96 (d, J = 1.7 Hz, 1H), 7.74 (d, J = 16.0 Hz, 1H), 7.30 (s, 1H), 7.27 – 7.24 (m, 1H), 7.22 (d, J = 6.3 Hz, 2H), 7.22 – 7.19 (m, 1H), 7.07 (d, J = 8.7 Hz, 1H), 7.04 – 6.98 (m, 2H), 6.29 (d, J = 16.0 Hz, 1H), 5.20 (s, 2H), 4.19 (q, J = 7.1 Hz, 2H), 1.27 (t, J = 7.1 Hz, 3H). **^{13}C{^{1}H} NMR** (126 MHz, $CDCl_3$); δ 166.9, 136.0, 135.1, 134.6, 132.0, 128.0, 127.2, 126.7, 125.8, 124.9, 122.2, 113.9, 112.6, 111.0, 110.8, 59.1, 49.5, 13.4. **HRMS-ESI (**m/z): Calcd for $C_{20}H_{18}BrNO_2$ $[M + H]^+$ 384.0594; found 384.0597.

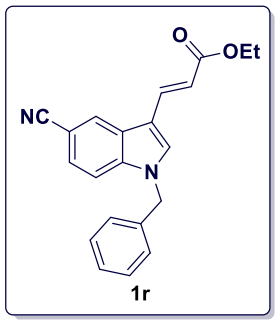
Synthesis of ethyl (E)-3-(1-benzyl-6-bromo-1H-indol-3-yl)acrylate (1q)



The compound was prepared according to general procedure-B, using ethyl (E)-3-(6-bromo-1H-indol-3-yl)acrylate **1f** (0.1 g, 0.339 mmol, 1 eq.), NaH (0.016 g, 0.67 mmol, 2 eq.) at 0°C and benzyl chloride (0.052 g, 0.40 mmol, 1.2 eq.) room temperature in 2 mL ACN affording ethyl (E)-3-(1-benzyl-6-bromo-1H-indol-3-yl)acrylate. After 4.5 h, purification by column chromatography (40% ethyl acetate in hexane) gave **1f** as a creamy white solid (0.113 g, 87%), Rf (EtOAc/ hexane 1:2) = 0.5.

mp: 143-152 °C; **FT-IR** (neat): ν_{max}/cm^{-1}: 3150, 2955, 1700, 1605, 1345, 1276, 1150, 1045, 760; **^{1}H NMR** (500 MHz, $CDCl_3$); δ 7.76 (d, J = 16.0 Hz, 1H), 7.69 (d, J = 8.5 Hz, 1H), 7.39 (s, 1H), 7.31 – 7.20 (m, 5H), 7.04 (d, J = 7.5 Hz, 2H), 6.30 (d, J = 16.0 Hz, 1H), 5.18 (s, 2H), 4.18 (q, J = 7.1 Hz, 2H), 1.26 (t, J = 7.1 Hz, 3H). **^{13}C{^{1}H} NMR** (126 MHz, $CDCl_3$); δ 166.9, 137.3, 136.1, 134.5, 131.4, 128.0, 127.2, 125.9, 124.0, 123.6, 120.8, 115.7, 112.8, 112.4, 111.7, 59.1, 49.4, 13.4. **HRMS-ESI (**m/z): Calcd for $C_{20}H_{18}BrNO_2$ $[M + H]^+$ 384.0594; found 384.0597.

Synthesis of ethyl (E)-3-(1-benzyl-5-cyano-1H-indol-3-yl)acrylate (1r)

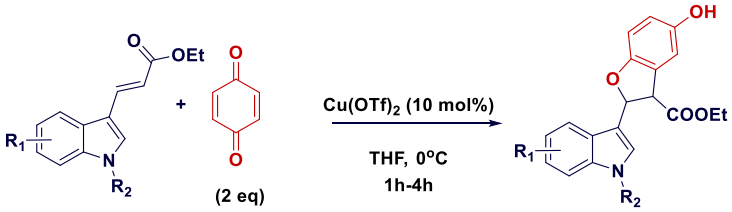


The compound was prepared according to general procedure-B, using ethyl (E)-3-(5-cyano-1H-indol-3-yl)acrylate **1d** (0.1 g, 0.416 mmol, 1 eq.), NaH (0.019g, 0.83 mmol, 2 eq.) at 0°C and benzyl chloride (0.064 g, 0.41 mmol, 1.2 eq.) room temperature in 2 mL ACN affording ethyl (E)-3-(1-benzyl-5-cyano-1H-indol-3-yl)acrylate. After 4.5 h, purification by column chromatography (35% ethyl acetate in hexane) gave **1r** as a creamy white solid (0.108 g, 79%), Rf (EtOAc/ hexane 3:2) = 0.5.

mp: 160-162 °C; **FT-IR** (neat): ν_{max}/cm^{-1}: 3495, 3125, 2966, 1720, 1605, 1514, 1276, 1045, 760; **^{1}H NMR** (500 MHz, $CDCl_3$); δ 8.24 (s, 1H), 7.85 (d, J = 16.1 Hz, 1H), 7.53 (s, 1H), 7.48 (d, J = 8.5 Hz, 1H), 7.39 (d, J = 8.6 Hz, 1H), 7.38 (d, J = 6.0 Hz, 1H), 7.37 – 7.33 (m, 2H), 7.15 (d, J = 6.3 Hz, 2H), 6.42 (d, J = 16.1 Hz, 1H), 5.37 (s, 2H), 4.30 (q, J = 7.1 Hz, 2H), 1.37 (t, J = 7.1 Hz, 3H). **^{13}C{^{1}H} NMR** (126 MHz, $CDCl_3$); δ 167.5, 139.0, 136.0, 135.2, 133.6, 129.2, 128.5, 126.9,

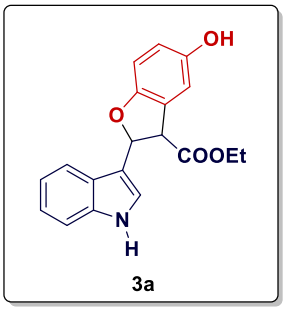
126.1, 125.9, 125.8, 120.0, 115.2, 113.2, 111.4, 104.6, 60.3, 50.7, 14.4. **HRMS-ESI (**m/z): Calcd for $C_{21}H_{18}N_2O_2$ $[M + H]^+$ 331.1441; found 331.1442.

C- Synthesis and characterization of 1H-indol-3-yl-2,3-dihydrobenzofuran (scheme 1):



A Screw-cap vial was charged with indole ester (1 equiv) with subsequent addition of benzoquinone (2.0 equiv) in THF, and then the reaction mixture was stirred at 0°C for 5 min. further a catalytic quantity of $Cu(OTf)_2$ (10 mol%) was added. Then reaction mixture was continued to stir at 0°C till the completion of reaction (monitored by TLC). After completion reaction was quenched by adding water, further the organic layer was then washed with brine and dried over Na_2SO_4. Finally, reaction mixture was concentrated under vacuum and crude residue was purified by column chromatography (10-50% ethyl acetate in hexane) to obtain the corresponding product.

Synthesis of 5-hydroxy-2-(1H-indol-3-yl)-2,3-dihydrobenzofuran-3-carboxylate (3a)



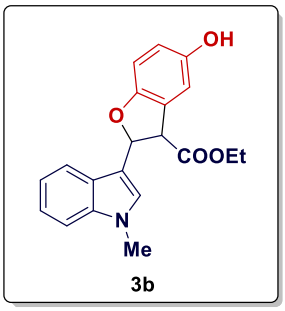
3a

The compound was prepared according to general procedure-(C), using ethyl (E)-3-(1H-indol-3-yl)acrylate (0.05 g, 0.23 mmol, 1 eq.) **1a** and benzoquinone (0.05 g, 0.46 mmol, 2 eq.) **2** under catalytic quantity of $Cu(OTf)_2$ (0.007 g, 0.02 mmol, 10 mol%) at 0°C affording ethyl 5-hydroxy-2-(1H-indol-3-yl)-2,3-dihydrobenzofuran-3-carboxylate. After 1 h, purification by column chromatography (20% ethyl acetate in hexane) gave **3a** as a brown oily liquid (0.05 g, 88%), R_f (EtOAc/ hexane 1:2) = 0.5.

FT-IR (neat): ν_{max}/cm^{-1}: 3611, 2350, 2321, 1724, 1699, 1544, 1220, 1180, 759, 710; **^{1}H NMR** (500 MHz, $CDCl_3$); δ 8.10 (s, 1H), 7.39 (d, J = 7.6 Hz, 1H), 7.30 (d, J = 7.9 Hz, 1H), 7.17 (d, J = 18.0 Hz, 1H), 7.15 – 6.99 (m, 2H), 6.86 (s, 1H), 6.66 (s, 2H), 6.29 (d, J = 7.7 Hz, 1H), 4.66 (s,

1H), 4.49 (d, J = 7.7 Hz, 1H), 4.19 (q, 2H), 1.24 (t, J = 6.8 Hz, 3H). **^{13}C{^{1}H} NMR** (126 MHz, $CDCl_3$); δ 171.0, 153.5, 149.7, 136.8, 125.4, 125.2, 122.9, 122.7, 120.2, 119.5, 116.2, 115.3, 112.2, 111.5, 110.0, 81.1, 61.6, 54.0, 14.2. **HRMS-ESI** (m/z): Calcd for $C_{19}H_{17}NO_4$ $[M + H]^+$ 324.22; found 324.1230.

Synthesis of ethyl 5-hydroxy-2-(1-methyl-1H-indol-3-yl)-2,3-dihydrobenzofuran-3-carboxylate (3b)

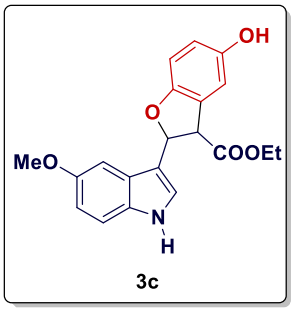


3b

The compound was prepared according to general procedure-(C), using ethyl (E)-3-(1-methyl-1H-indol-3-yl)acrylate (0.05 g, 0.21 mmol, 1 eq.) **1h** and benzoquinone (0.04 g, 0.43 mmol, 2 eq.) **2** under catalytic quantity of $Cu(OTf)_2$ (0.007 g, 0.02 mmol, 10 mol%) at 0^{o}C affording ethyl 5-hydroxy-2-(1-methyl-1H-indol-3-yl)-2,3-dihydrobenzofuran-3-carboxylate. After 1.5 h, purification by column chromatography (18% ethyl acetate in hexane) gave **3b** as a brown oily liquid (0.05 g, 78%), R_f (EtOAc/ hexane 1:2) = 0.5.

FT-IR (neat): ν_{max}/cm^{-1}: 3615, 2364, 2321, 1745, 1687, 1524, 1238, 1195, 769, 714; **^{1}H NMR** (500 MHz, $CDCl_3$); δ 7.45 (d, J = 7.3 Hz, 1H), 7.30 (d, J = 8.2 Hz, 1H), 7.25 – 7.20 (m, 1H), 7.14 (d, J = 2.0 Hz, 1H), 7.08 – 7.03 (m, 1H), 6.91 (s, 1H), 6.72 – 6.63 (m, 2H), 6.33 (dd, J = 8.0, 2.1 Hz, 1H), 5.10 (s, 1H), 4.54 (d, J = 8.0 Hz, 1H), 4.23 (q, J = 4.4, 2.7 Hz, 2H), 3.73 (s, 3H), 1.29 (t, J = 7.1 Hz, 3H). **^{13}C{^{1}H} NMR** (126 MHz, $CDCl_3$); δ 171.2, 153.5, 149.8, 137.7, 127.6, 125.8, 125.5, 122.3, 119.8, 119.6, 116.3, 113.6, 112.2, 110.1, 109.7, 81.1, 61.7, 54.2, 32.8, 14.3. **HRMS-ESI** (m/z): Calcd for $C_{20}H_{19}NO_4$ $[M + H]^+$ 338.1387; found 338.1394.

Synthesis of ethyl 5-hydroxy-2-(5-methoxy-1H-indol-3-yl)-2,3-dihydrobenzofuran-3-carboxylate (3c)

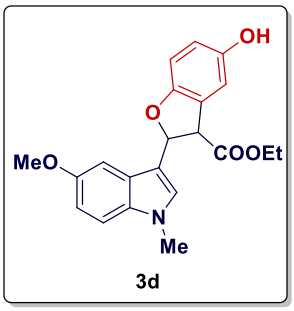


3c

The compound was prepared according to general procedure-(C), ethyl (E)-3-(5-methoxy-1H-indol-3-yl)acrylate (0.05 g, 0.20 mmol, 1 eq.) **1b** and benzoquinone (0.04 g, 0.40 mmol, 2 eq.) **2** under catalytic quantity of $Cu(OTf)_2$ (0.007 g, 0.02 mmol, 10 mol%) at 0°C affording ethyl 5-hydroxy-2-(5-methoxy-1H-indol-3-yl)-2,3-dihydrobenzofuran-3-carboxylate. After 1.5 h, purification by column chromatography (20% ethyl acetate in hexane) gave **3c** as a brown oily liquid (0.064 g, 93%), R_f (EtOAc/ hexane 2:3) = 0.5.

FT-IR (neat): ν_{max}/cm^{-1}: 3612, 2348, 2310, 1720, 1684, 1520, 1210, 1150, 789, 774; **^{1}H NMR** (500 MHz, $CDCl_3$); δ 8.20 (s, 1H), 7.19 (dd, J = 8.7, 1.9 Hz, 1H), 7.15 (d, J = 2.4 Hz, 1H), 6.90 (s, 1H), 6.86 – 6.80 (m, 2H), 6.68 (d, J = 0.8 Hz, 2H), 6.30 (d, J = 7.5 Hz, 1H), 4.49 (d, J = 7.4 Hz, 1H), 4.22 (q, J = 7.1, 4.5 Hz, 2H), 3.69 (s, 3H), 1.27 (t, J = 7.1 Hz, 3H). **^{13}C{^{1}H} NMR** (126 MHz, $CDCl_3$); δ 171.3, 154.3, 153.4, 150.0, 132.0, 125.7, 125.5, 123.7, 116.3, 115.0, 112.7, 112.3, 112.2, 110.1, 101.5, 81.2, 61.8, 55.8, 53.9, 14.3. **HRMS-ESI** (m/z): Calcd for $C_{20}H_{19}NO_5$ $[M + H]^+$ 354.1336; found 354.1347.

Synthesis of ethyl 5-hydroxy-2-(5-methoxy-1-methyl-1H-indol-3-yl)-2,3-dihydrobenzofuran-3-carboxylate (3d)



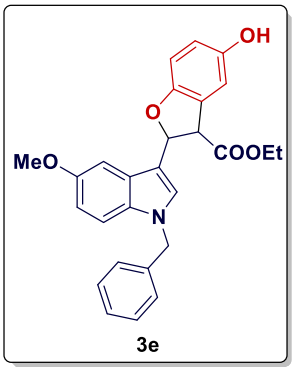
3d

The compound was prepared according to general procedure-(C), using ethyl (E)-3-(5-methoxy-1-methyl-1H-indol-3-yl)acrylate (0.04 g, 0.15 mmol, 1 eq.) **1l** and benzoquinone (0.03 g, 0.30 mmol, 2 eq.) **2** under catalytic quantity of $Cu(OTf)_2$ (0.005 g, 0.01 mmol, 10 mol%) at 0°C affording ethyl 5-hydroxy-2-(5-methoxy-1-methyl-1H-indol-3-yl)-2,3-dihydrobenzofuran-3-carboxylate. After 1.5 h, purification by column chromatography (18% ethyl acetate in hexane) gave **3d** as a reddish oily liquid (0.039 g, 87%), R_f (EtOAc/ hexane 2:3) = 0.5.

FT-IR (neat): ν_{max}/cm^{-1}:, 3558, 2362, 1652, 1529, 1234, 1033, 771, 751; **^{1}H NMR** (500 MHz, $CDCl_3$); δ 7.17 (d, J = 8.2 Hz, 1H), 7.10 (s, 1H), 6.91 (d, J = 0.9 Hz, 1H), 6.87 (d, J = 8.3 Hz, 2H), 6.72 – 6.65 (m, 2H), 6.29 (d, J = 7.5 Hz, 1H), δ 5.05 (s, 1H), 4.49 (d, J = 7.6 Hz, 1H), 4.22 (q, J = 11.5, 7.2 Hz, 2H), 3.71 (s, 3H), 3.70 (s, 3H), 1.29 (t, J = 7.1 Hz, 3H). **^{13}C{^{1}H} NMR** (126 MHz,

$CDCl_3$); δ 171.2, 154.2, 153.5, 149.9, 133.0, 128.0, 126.1, 125.5, 116.3, 113.2, 112.4, 112.1, 110.5, 110.1, 101.6, 81.1, 61.7, 55.8, 54.0, 33.0, 14.3. **HRMS-ESI (**m/z): Calcd for $C_{21}H_{21}NO_5$ $[M + H]^+$ 368.1492; found 368.1505.

Synthesis of ethyl 5-hydroxy-2-(5-methoxy-1-methyl-1H-indol-3-yl)-2,3-dihydrobenzofuran-3-carboxylate (3e)

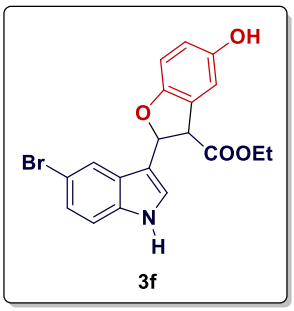


3e

The compound was prepared according to general procedure-(C), using ethyl (E)-3-(1-benzyl-5-methoxy-1H-indol-3-yl)acrylate (0.05 g, 0.14 mmol, 1 eq.) **1n** and benzoquinone (0.03 g, 0.29 mmol, 2 eq.) **2** under catalytic quantity of $Cu(OTf)_2$ (0.005 g, 0.01 mmol, 10 mol%) at 0°C affording ethyl 2-(1-benzyl-5-methoxy-1H-indol-3-yl)-5-hydroxy-2,3-dihydrobenzofuran-3-carboxylate. After 2 h, purification by column chromatography (25% ethyl acetate in hexane) gave **3e** as a brown oily liquid (0.06 g, 92%), R_f (EtOAc/ hexane 2:3) = 0.5.

FT-IR (neat): ν_{max}/cm^{-1}:, 3617, 2940, 2364, 2321, 1699, 1524, 1238, 1187, 767, 751; **^{1}H NMR** (500 MHz, $CDCl_3$); δ 7.31 – 7.21 (m, 3H), 7.17 (d, J = 3.8 Hz, 1H), 7.15 – 7.06 (m, 3H), 6.91 (s, 1H), 6.87 (s, 1H), 6.83 – 6.78 (m, 1H), 6.74 – 6.66 (m, 2H), 6.30 (d, J = 7.6 Hz, 1H), 5.21 (s, 2H), 4.93 (s, 1H), 4.51 (d, J = 4.3 Hz, 1H), 4.23 (q, J = 7.1, 4.7 Hz, 2H), 3.69 (s, 3H), 1.28 (t, J = 7.1 Hz, 3H). **^{13}C{^{1}H} NMR** (126 MHz, $CDCl_3$); δ 171.1, 154.3, 153.5, 149.8, 137.1, 132.6, 128.8, 127.8, 127.4, 126.9, 126.4, 125.5, 116.3, 113.9, 112.5, 112.1, 111.0, 110.1, 101.7, 81.2, 61.7, 55.8, 54.0, 50.4, 14.3. **HRMS-ESI (**m/z): Calcd for $C_{27}H_{25}NO_5$ $[M + H]^+$ 444.1805; found 444.1815.

Synthesis of ethyl 2-(5-bromo-1H-indol-3-yl)-5-hydroxy-2,3-dihydrobenzofuran-3-carboxylate (3f)



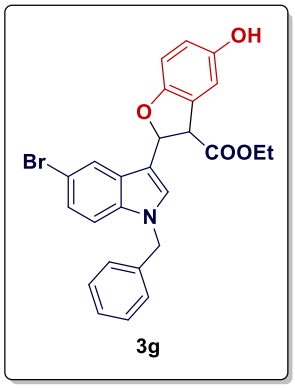
3f

The compound was prepared according to general procedure-(C), using ethyl (E)-3-(5-bromo-1H-indol-3-yl)acrylate (0.04 g, 0.13 mmol, 1 eq.) **1e** and benzoquinone (0.29 g, 0.27 mmol, 2 eq.) **2** under catalytic quantity of $Cu(OTf)_2$ (0.004 g, 0.01 mmol, 10 mol%) at 0°C affording ethyl 2-(5-bromo-1H-indol-3-yl)-5-hydroxy-2,3-dihydrobenzofuran-3-carboxylate **3f**. After 1.5 h, purification by column chromatography

(28% ethyl acetate in hexane) gave **3f** as a golden-brown oil (0.037 g, 70%), R_f (EtOAc/ hexane 2:1) = 0.5.

FT-IR (neat): ν_{max}/cm^{-1}: 3681, 2366, 1732, 1489, 1193, 771, 714; **^{1}H NMR** (500 MHz, $CDCl_3$); δ 8.30 (s, 1H), 7.61 (d, J = 1.8 Hz, 1H), 7.26 (dd, J = 8.6, 1.8 Hz, 1H), 7.22 – 7.18 (m, 2H), 6.91 – 6.89 (m, 1H), 6.71 (d, J = 0.8 Hz, 2H), 6.26 (d, J = 8.2 Hz, 1H), 4.46 (d, J = 8.3 Hz, 1H), 4.25 (q, J = 7.1, 5.0 Hz, 2H), 1.30 (t, J = 7.1 Hz, 3H). **^{13}C{^{1}H} NMR** (126 MHz, $CDCl_3$); δ 171.1, 153.2, 150.0, 135.4, 127.0, 125.6, 125.2, 124.1, 122.1, 116.4, 114.8, 113.5, 113.0, 112.3, 110.2, 80.9, 61.9, 54.0, 14.3. **HRMS-ESI (**m/z): Calcd for $C_{19}H_{16}BrNO_4$ $[M + H]^+$ 402.0335; found 402.0343.

Synthesis of ethyl 2-(1-benzyl-5-bromo-1H-indol-3-yl)-5-hydroxy-2,3-dihydrobenzofuran-3-carboxylate (3g)

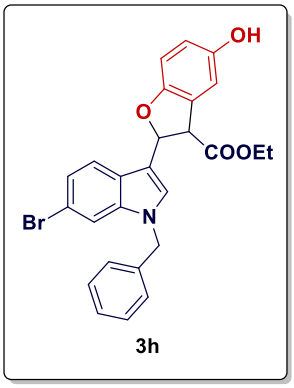


3g

The compound was prepared according to general procedure-(C), using ethyl (E)-3-(1-benzyl-5-bromo-1H-indol-3-yl)acrylate (0.05 g, 0.13 mmol, 1 eq.) **1p** and benzoquinone (0.028 g, 0.26 mmol, 2 eq.) **2** under catalytic quantity of $Cu(OTf)_2$ (0.004 g, 0.03 mmol, 10 mol%) at 0ºC affording ethyl 2-(1-benzyl-5-bromo-1H-indol-3-yl)-5-hydroxy-2,3-dihydrobenzofuran-3-carboxylate. After 2 h, purification by column chromatography (30% ethyl acetate in hexane) gave **3g** as a brown oily liquid (0.053 g, 84%), R_f (EtOAc/ hexane 1:3) = 0.5.

FT-IR (neat): ν_{max}/cm^{-1}:, 3688, 2950, 2333, 1654, 1542, 1245, 1184, 789, 745; **^{1}H NMR** (500 MHz, $CDCl_3$); δ 7.64 (d, J = 1.8 Hz, 1H), 7.32 – 7.23 (m, 5H), 7.21 (s, 1H), 7.11 (d, J = 8.8 Hz, 1H), 7.08 (d, J = 5.7 Hz, 2H), 6.93 – 6.91 (m, 1H), 6.71 (d, J = 2.5 Hz, 2H), 6.28 (d, J = 8.5 Hz, 1H), 5.22 (s, 2H), 4.49 (d, J = 8.3 Hz, 1H), 4.25 (q, J = 7.1, 5.1 Hz, 2H), 1.30 (t, J = 7.1 Hz, 3H). **^{13}C{^{1}H} NMR** (126 MHz, $CDCl_3$); 171.0, 153.2, 150.1, 136.5, 135.9, 128.0, 128.0, 127.8, 126.9, 125.4, 125.2, 122.3, 116.4, 116.2, 113.9, 113.5, 112.3, 111.7, 110.2, 80.8, 61.9, 54.2, 50.4, 14.3. **HRMS-ESI (**m/z): Calcd for $C_{26}H_{22}BrNO_4$ $[M + H]^+$ 492.0805; found 492.0816.

Synthesis of ethyl 2-(1-benzyl-6-bromo-1H-indol-3-yl)-5-hydroxy-2,3-dihydrobenzofuran-3-carboxylate (3h)

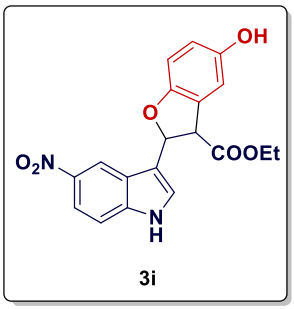


3h

The compound was prepared according to general procedure-(C), using ethyl (E)-3-(1-benzyl-6-bromo-1H-indol-3-yl)acrylate (0.04 g, 0.10 mmol, 1 eq.) **1q** and benzoquinone (0.022 g, 0.20 mmol, 2 eq.) **2** under catalytic quantity of $Cu(OTf)_2$ (0.003 g, 0.010 mmol, 10 mol%) at 0°C affording ethyl 2-(1-benzyl-6-bromo-1H-indol-3-yl)-5-hydroxy-2,3-dihydrobenzofuran-3-carboxylate. After 1.5 h, purification by column chromatography (30% ethyl acetate in hexane) gave **3h** as a brown oily liquid (0.045 g, 88%), R_f (EtOAc/ hexane 2:1) = 0.5.

FT-IR (neat): ν_{max}/cm^{-1}: 3655, 2988, 2354, 1652, 1520, 1245, 1178, 745, 713; **^{1}H NMR** (500 MHz, $CDCl_3$); 7.42 (s, 1H), 7.32 (d, J = 8.7 Hz, 2H), 7.29 – 7.24 (m, 2H), 7.18 (s, 1H), 7.17 – 7.14 (m, 1H), 7.09 (d, J = 6.3 Hz, 2H), 6.92 (s, 1H), 6.69 (d, J = 13.2 Hz, 2H), 6.29 (d, J = 8.0 Hz, 1H), 5.20 (s, 2H), 4.47 (d, J = 8.0 Hz, 1H), 4.24 (q, J = 7.0 Hz, 2H), 1.29 (t, J = 7.1 Hz, 3H). **^{13}C{^{1}H} NMR** (126 MHz, $CDCl_3$); δ 171.1, 153.2, 150.1, 138.1, 136.4, 129.0, 128.0, 127.5, 126.9, 125.2, 124.9, 123.4, 121.1, 116.4, 116.2, 114.7, 113.1, 112.2, 110.1, 80.8, 61.9, 54.2, 50.2, 14.3. **HRMS-ESI** (m/z): Calcd for $C_{26}H_{22}BrNO_4$ $[M + H]^+$ 492.0805; found 492.0803.

Synthesis of ethyl 5-hydroxy-2-(5-nitro-1H-indol-3-yl)-2,3-dihydrobenzofuran-3-carboxylate (3i)



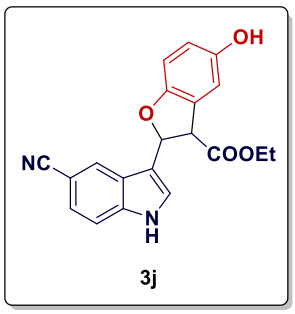
3i

The compound was prepared according to general procedure-(C), using ethyl (E)-3-(5-nitro-1H-indol-3-yl)acrylate (0.04 g, 0.15 mmol, 1 eq.) **1c** and benzoquinone (0.032 g, 0.30 mmol, 2 eq.) **2** under catalytic quantity of $Cu(OTf)_2$ (0.005 g, 0.015 mmol, 10 mol%) at 0°C affording ethyl 5-hydroxy-2-(5-nitro-1H-indol-3-yl)-2,3-dihydrobenzofuran-3-carboxylate **3i**. After 3 h, purification by column chromatography (40% ethyl acetate in hexane) gave **3i** as a yellow oily liquid (0.04 g, 75%), R_f (EtOAc/ hexane 3:1) = 0.5.

FT-IR (neat): ν_{max}/cm^{-1}:, 3645, 2378, 2320, 1745, 1699, 1524, 1213, 774; **^{1}H NMR** (500 MHz, $CDCl_3$ +DMSO-d_6); δ 11.94 (s, 1H), 9.06 (s, 1H), 8.37 (d, J = 2.2 Hz, 1H), 8.03 (dd, J = 9.0, 2.2 Hz, 1H), 7.81 (d, J = 2.4 Hz, 1H), 7.59 (d, J = 9.0 Hz, 1H), 6.85 (d, J = 1.5 Hz, 1H), 6.74 – 6.62 (m, 2H), 6.26 (d, J = 7.7 Hz, 1H), 4.62 (d, J = 7.7 Hz, 1H), 4.22 (q, J = 11.8, 7.1 Hz, 2H), 1.26 (t,

J = 7.1 Hz, 3H). **^{13}C{^{1}H} NMR** (126 MHz, $CDCl_3$+DMSO-d_6); δ 171.0, 152.0, 151.8, 141.1, 140.3, 128.3, 125.5, 125.1, 117.5, 116.8, 116.4, 116.2, 112.8, 112.3, 110.1, 80.1, 61.7, 53.7, 14.5. **HRMS-ESI (**m/z): Calcd for $C_{19}H_{16}N_2O_6$ $[M + H]^+$ 369.1081; found 369.1077.

Synthesis of ethyl 2-(5-cyano-1H-indol-3-yl)-5-hydroxy-2,3-dihydrobenzofuran-3-carboxylate (3j)

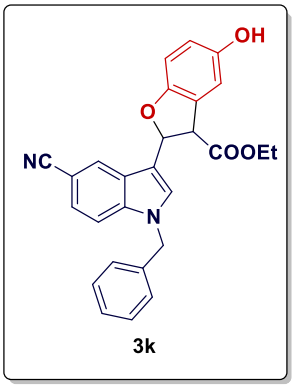


3j

The compound was prepared according to general procedure-(C), using ethyl (E)-3-(5-cyano-1H-indol-3-yl)acrylate (0.04 g, 0.16 mmol, 1 eq.) **1d** and benzoquinone (0.036 g, 0.32 mmol, 2 eq.) **2** under catalytic quantity of $Cu(OTf)_2$ (0.005 g, 0.016 mmol, 10 mol%) at 0^{o}C affording ethyl 2-(5-cyano-1H-indol-3-yl)-5-hydroxy-2,3-dihydrobenzofuran-3-carboxylate. After 2 h, purification by column chromatography (40% ethyl acetate in hexane) gave **3j** as a brown oily liquid (0.05 g, 90%), R_f (EtOAc/ hexane 3:1) = 0.5.

FT-IR (neat): ν_{max}/cm^{-1}:, 3612, 2354, 2310, 1720, 1652, 1520, 1220, 774; **^{1}H NMR** (500 MHz, $CDCl_3$ +DMSO-d_6); δ 11.23 (s, 1H), 7.72 (s, 1H), 7.47 – 7.37 (m, 2H), 7.36 – 7.26 (m, 1H), 6.85 (s, 1H), 6.72 – 6.53 (m, 2H), 6.20 (d, J = 4.5 Hz, 1H), 4.38 (d, J = 4.4 Hz, 1H), 4.19 (dd, J = 7.0, 3.0 Hz, 2H), 1.26 (t, J = 8.3, 5.2 Hz, 3H). **^{13}C{^{1}H} NMR** (126 MHz, $CDCl_3$ +DMSO-d_6); δ 169.85, 151.0, 150.8, 138.0, 124.8, 124.2, 123.9, 123.7, 123.6, 119.8, 115.2, 114.3, 112.1, 111.1, 108.7, 101.1, 79.4, 60.5, 53.2, 13.3. **HRMS-ESI (**m/z): Calcd for $C_{20}H_{16}N_2O_4$ $[M + H]^+$ 349.1183; found 349.1180.

Synthesis of ethyl 2-(1-benzyl-5-cyano-1H-indol-3-yl)-5-hydroxy-2,3-dihydrobenzofuran-3-carboxylate (3k)

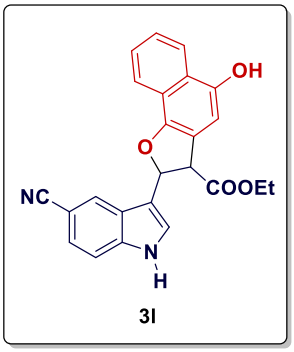


3k

The compound was prepared according to general procedure-(C), using ethyl (E)-3-(1-benzyl-5-cyano-1H-indol-3-yl)acrylate (0.04 g, 0.12 mmol, 1 eq.) **1r** and benzoquinone (0.027 g, 0.24 mmol, 2 eq.) **2** under catalytic quantity of $Cu(OTf)_2$ (0.004 g, 0.016 mmol, 10 mol%) at 0°C affording ethyl 2-(1-benzyl-5-cyano-1H-indol-3-yl)-5-hydroxy-2,3-dihydrobenzofuran-3-carboxylate. After 2 h, purification by column chromatography (40% ethyl acetate in hexane) gave **3k** as a brown oily liquid (0.04 g, 88%), R_f (EtOAc/ hexane 3:1) = 0.5.

FT-IR (neat): ν_{max}/cm^{-1}:, 3655, 2320, 2300, 1722, 1655, 1520, 1220, 1123, 774, 716; **^{1}H NMR** (500 MHz, $CDCl_3$); δ 7.88 (d, J = 0.9 Hz, 1H), 7.38 (dd, J = 8.6, 1.4 Hz, 1H), 7.34 – 7.31 (m, J = 6.2 Hz, 2H), 7.31 – 7.29 (m, 1H), 7.29 – 7.27 (m, 2H), 7.12 – 7.07 (m, J = 7.4, 1.9 Hz, 2H), 6.96 – 6.93 (m, 1H), 6.74 – 6.72 (m, 2H), 6.30 (d, J = 8.5 Hz, 1H), 5.27 (s, 2H), 4.45 (d, J = 8.3 Hz, 1H), 4.25 (q, 2H), 1.30 (t, J = 7.1 Hz, 3H). **^{13}C{^{1}H} NMR** (126 MHz, $CDCl_3$); δ 170.8, 152.9, 150.5, 138.8, 135.9, 129.1, 129.0, 128.3, 126.9, 125.9, 125.6, 125.4, 124.8, 120.5, 116.5, 115.6, 112.4, 111.1, 110.2, 103.0, 80.3, 62.0, 54.4, 50.5, 14.3. **HRMS-ESI** (m/z): Calcd for $C_{27}H_{22}N_2O_4$ $[M + H]^+$ 439.1652; found 439.1659.

Synthesis of ethyl 2-(5-cyano-1H-indol-3-yl)-5-hydroxy-2,3-dihydronaphtho[1,2-b]furan-3-carboxylate (3l)



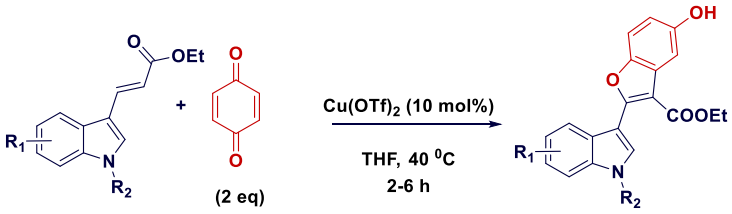
3l

The compound was prepared according to general procedure-(C), using ethyl (E)-3-(5-cyano-1H-indol-3-yl)acrylate (0.04 g, 0.16 mmol, 1 eq.) **1d** and 1,4-Naphthoquinone (0.052 g, 0.33 mmol, 2 eq.) under catalytic quantity of $Cu(OTf)_2$ (0.005 g, 0.016 mmol, 10 mol%) at 0°C affording ethyl 2-(5-cyano-1H-indol-3-yl)-5-hydroxy-2,3-dihydronaphtho[1,2-b]furan-3-carboxylate. After 2 h, purification by column chromatography (40% ethyl acetate in hexane) gave **3l** as a brown oily liquid (0.055 g, 87%), R_f (EtOAc/ hexane 3:1) = 0.5.

FT-IR (neat): ν_{max}/cm^{-1}:, 3661, 3617, 2364, 2321, 1745, 1699, 1524, 1191, 769, 689; **^{1}H NMR** (500 MHz, $CDCl_3$); δ 8.84 (s, 1H), 8.22 – 8.15 (m, 1H), 7.98 – 7.93 (m, 1H), 7.90 (s, 1H), 7.51 – 7.44 (m, 2H), 7.40 (s, 3H), 6.97 (s, 1H), 6.53 (d, J = 7.8 Hz, 1H), 4.61 (d, J = 7.8 Hz, 1H), 4.28 (q,

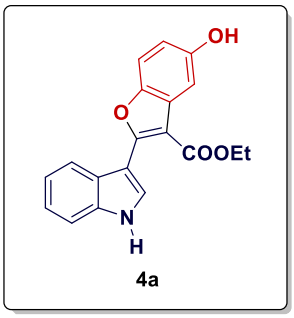
J = 9.3, 7.3 Hz, 2H), 1.32 (t, 3H). **^{13}C{^{1}H} NMR** (126 MHz, $CDCl_3$); δ 170.4, 147.6, 145.3, 137.5, 125.3, 124.8, 124.4, 124.4, 124.2, 124.0, 121.3, 120.6, 119.8, 119.5, 115.4, 114.8, 111.5, 104.1, 101.9, 79.5, 60.9, 54.2, 28.6, 13.2. **HRMS-ESI (**m/z): Calcd for $C_{24}H_{18}N_2O_4$ $[M + Na]^+$ 421.1164; found 421.1155.

D- Synthesis and characterization of 1H-indol-3-yl-benzofuran (scheme 2):



To the magnetically stirred solution of indole ester (1.0 equiv) in THF, 2 equivalents of benzoquinone were added at room temperature, under catalytic quantity of $Cu(OTf)_2$. Then the reaction mixture is allowed to stir at 40 °C till completion of reaction (monitored by TLC). After completion reaction was quenched by adding water, further the organic layer was then washed with brine and dried over Na_2SO_4. Finally, reaction mixture was concentrated under vacuum and crude residue was purified by column chromatography (10-50% ethyl acetate in hexane) to obtain the corresponding product. (note: compounds formed are insoluble in CDCl3 and not completely miscible in DMSO-d6, 0.5-0.6 mL of solvent is used to obtaine the respective NMR spectra.

Synthesis of ethyl 5-hydroxy-2-(1H-indol-3-yl)benzofuran-3-carboxylate (4a)



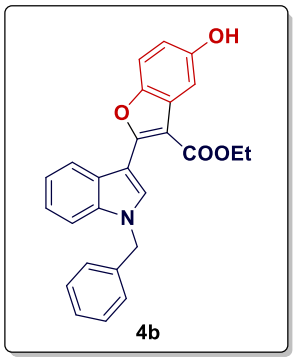
4a

The compound was prepared according to general procedure-(D) using ethyl (E)-3-(1H-indol-3-yl)acrylate (0.03 g, 0.14 mmol, 1 eq.) **1a** and benzoquinone (0.03 g, 0.29 mmol, 2 eq.) **2** under catalytic quantity of $Cu(OTf)_2$ (0.004 g, 0.014 mmol, 10 mol%) at 40 °C to furnish ethyl 5-hydroxy-2-(1H-indol-3-yl)benzofuran-3-carboxylate. After 2 h, purification by column chromatography (15% ethyl acetate in hexane) **4a** obtained as a light brown oily liquid (0.030 g, 69%), R_f (EtOAc/ hexane 1:3) = 0.5.

FT-IR (neat): ν_{max}/cm^{-1}:, 3617, 2315, 1687, 1524, 1238, 1191, 759, 714; **^{1}H NMR** (500 MHz, DMSO-d_6); δ 11.98 (s, 1H), 9.34 (s, 1H), 8.86 (d, J = 2.5 Hz, 1H), 8.26 (d, J = 7.6 Hz, 1H), 7.54 (t, J = 8.9 Hz, 2H), 7.37 (d, J = 1.9 Hz, 1H), 7.30 – 7.19 (m, 2H), 6.77 (dd, J = 8.6, 2.0 Hz, 1H),

4.39 (q, J = 7.0 Hz, 2H), 1.41 (t, J = 7.1 Hz, 3H). **^{13}C {^{1}H} NMR** (126 MHz, DMSO-d_6); δ 163.4, 159.7, 153.7, 146.0, 135.4, 130.8, 126.9, 124.8, 122.0, 120.8, 120.5, 112.0, 111.8, 110.5, 106.0, 104.2, 103.2, 59.4, 13.7.; **HRMS** (ESI)**:** m/z: $[M+H]^+$ Calcd for $C_{19}H_{15}NO_4$ 322.1074; found 322.1072.

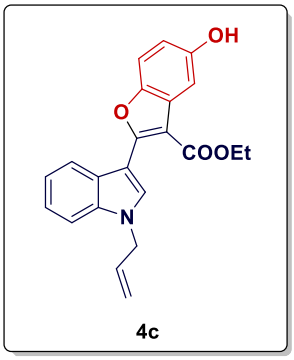
Synthesis of ethyl 2-(1-benzyl-1H-indol-3-yl)-5-hydroxybenzofuran-3-carboxylate (4b)



The compound was prepared according to general procedure-(D) using ethyl (E)-3-(1-benzyl-1H-indol-3-yl)acrylate (0.03 g, 0.09 mmol, 1 eq.) **1j** and benzoquinone (0.021 g, 0.19 mmol, 2 eq.) **2** under catalytic quantity of $Cu(OTf)_2$ (0.0032 g, 0.009 mmol, 10 mol%) at 40 °C to furnish ethyl 2-(1-benzyl-1H-indol-3-yl)-5-hydroxybenzofuran-3-carboxylate. After 1.5 h, purification by column chromatography (18% ethyl acetate in hexane) obtained as a brown oily liquid **4b** (0.03 g, 85%), R_f (EtOAc/ hexane 1:3) = 0.5.

FT-IR (neat): ν_{max}/cm^{-1}:, 3654, 2310, 1680, 1542, 1210, 1190, 1047, 759, 723; **^{1}H NMR** (500 MHz, DMSO-d_6); δ 9.37 (s, 1H), 8.96 (s, 1H), 8.30 (dd, J = 12.0, 7.0 Hz, 1H), 7.63 – 7.60 (m, 1H), 7.54 (d, J = 8.7 Hz, 1H), 7.39 (d, J = 2.3 Hz, 1H), 7.37 – 7.32 (m, 2H), 7.31 – 7.25 (m, 5H), 6.79 (dd, J = 8.7, 2.4 Hz, 1H), 5.61 (s, 2H), 4.38 (q, J = 7.1 Hz, 2H), 1.38 (t, J = 7.1 Hz, 3H). **^{13}C {^{1}H} NMR** (126 MHz, DMSO-d_6); δ 164.3, 159.9, 154.7, 147.1, 137.7, 136.3, 134.7, 129.1, 128.1, 127.8, 127.6, 126.5, 123.2, 122.2, 121.9, 113.1, 111.6, 107.0, 105.0, 104.6, 79.6, 60.5, 50.1, 14.7. **HRMS** (ESI)**:** m/z: $[M+H]^+$ Calcd for $C_{26}H_{21}NO_4$ 412.1543; found 412.1543.

Synthesis of ethyl 2-(1-allyl-1H-indol-3-yl)-5-hydroxybenzofuran-3-carboxylate (4c)

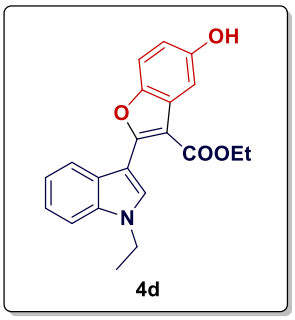


4c

The compound was prepared according to general procedure-(D) using ethyl (E)-3-(1-allyl-1H-indol-3-yl)acrylate (0.03 g, 0.11 mmol, 1 eq.) **1k** and benzoquinone (0.025 g, 0.23 mmol, 2 eq.) **2** under catalytic quantity of $Cu(OTf)_2$ (0.0032 g, 0.011 mmol, 10 mol%) at 40 °C to furnish ethyl 2-(1-allyl-1H-indol-3-yl)-5-hydroxybenzofuran-3-carboxylate **4c**. After 2.5 h, purification by column chromatography (20% ethyl acetate in hexane) obtained as a brown oily liquid (0.027 g, 75%), R_f (EtOAc/ hexane 1:3) = 0.5.

FT-IR (neat): ν_{max}/cm^{-1}:, 3625, 2340, 1650, 1620, 1510, 1241, 1122, 789, 724; **^{1}H NMR** (500 MHz, DMSO-d_6); δ 8.85 (s, 1H), 8.45 – 8.38 (m, 1H), 7.48 (d, J = 2.6 Hz, 1H), 7.40 (d, J = 8.7 Hz, 1H), 7.39 – 7.36 (m, 1H), 7.32 – 7.29 (m, 2H), 6.81 (dd, J = 8.7, 2.6 Hz, 1H), 6.08 – 5.95 (m, 1H), 5.25 (dd, J = 10.3, 1.2 Hz, 1H), 5.16 (dd, J = 17.1, 1.1 Hz, 1H), 4.82 – 4.78 (m, 2H), 4.43 (q, J = 7.1 Hz, 2H), 1.46 (t, J = 7.1 Hz, 3H). **^{13}C {^{1}H} NMR** (126 MHz, DMSO-d_6); δ 165.2, 161.2, 152.5, 148.1, 136.2, 134.3, 132.5, 128.2, 126.9, 122.9, 122.6, 121.6, 118.1, 112.2, 111.1, 110.3, 107.5, 105.6, 104.6, 60.4, 49.5, 14.5. **HRMS** (ESI)**:** m/z: $[M+H]^+$ Calcd for $C_{22}H_{19}NO_4$ 362.1387; found 362.1385.

Synthesis of ethyl 2-(1-ethyl-1H-indol-3-yl)-5-hydroxybenzofuran-3-carboxylate (4d)



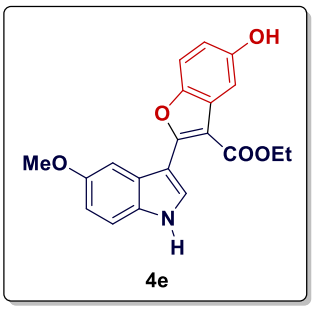
4d

The compound was prepared according to general procedure-(D) using ethyl (E)-3-(1-ethyl-1H-indol-3-yl)acrylate (0.03 g, 0.12 mmol, 1 eq.) **1i** and benzoquinone (0.026 g, 0.24 mmol, 2 eq.) **2** under catalytic quantity of $Cu(OTf)_2$ (0.0043 g, 0.012 mmol, 10 mol%) at 40 °C to furnish ethyl 2-(1-ethyl-1H-indol-3-yl)-5-hydroxybenzofuran-3-carboxylate **4d**. After 1.5 h, purification by column chromatography (20% ethyl acetate in hexane) obtained as a brown oily liquid (0.029 g, 70%), R_f (EtOAc/ hexane 1:3) = 0.5.

FT-IR (neat): ν_{max}/cm^{-1}:, 3640, 2320, 1644, 1625, 1522, 1224, 1120, 778, 724; **^{1}H NMR** (500 MHz, DMSO-d_6); δ 9.36 (s, 1H), 8.89 (s, 1H), 8.29 (d, J = 7.8 Hz, 1H), 7.64 (d, J = 8.0 Hz, 1H), 7.53 (d, J = 8.7 Hz, 1H), 7.39 (d, J = 2.5 Hz, 1H), 7.34 – 7.25 (m, 2H), 6.78 (dd, J = 8.7, 2.5 Hz, 1H), 4.47 – 4.25 (m, 4H), 1.53 – 1.35 (m, 6H). **^{13}C {^{1}H} NMR** (126 MHz, DMSO-d_6); δ 164.4, 160.2, 154.7, 147.0, 135.9, 133.8, 127.8, 126.4, 123.0, 122.2, 121.8, 113.0, 111.5, 111.1, 107.0,

104.5, 104.2, 60.4, 41.5, 15.6, 14.7. **HRMS** (ESI)**:** m/z: $[M+H]^+$ Calcd for $C_{21}H_{19}NO_4$ 350.1387; found 350.1383.

Synthesis of ethyl 5-hydroxy-2-(5-methoxy-1H-indol-3-yl)benzofuran-3-carboxylate (4e)

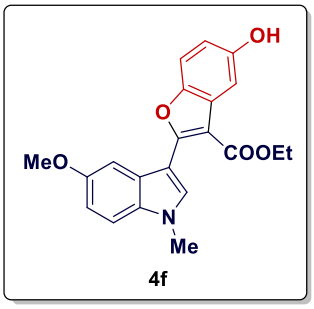


4e

The compound was prepared according to general procedure-(D) using ethyl (E)-3-(5-methoxy-1H-indol-3-yl)acrylate (0.04 g, 0.16 mmol, 1 eq.) **1b** and benzoquinone (0.035 g, 0.32 mmol, 2 eq.) **2** under catalytic quantity of $Cu(OTf)_2$ (0.005 g, 0.016 mmol, 10 mol%) at 40 °C to furnish ethyl 5-hydroxy-2-(5-methoxy-1H-indol-3-yl)benzofuran-3-carboxylate **4e**. After 1.5 h, purification by column chromatography (20% ethyl acetate in hexane) obtained as a brown oily liquid (0.033 g, 71%), R_f (EtOAc/ hexane 2:3) = 0.5.

FT-IR (neat): ν_{max}/cm^{-1}:, 3654, 2320, 1690, 1500, 1222, 1185, 795, 725; **^{1}H NMR** (500 MHz, DMSO-d_6); δ 11.86 (s, 1H), 9.33 (s, 1H), 8.80 (d, J = 3.0 Hz, 1H), 7.73 (s, 1H), 7.54 (d, J = 8.7 Hz, 1H), 7.45 (d, J = 8.8 Hz, 1H), 7.37 (d, J = 2.4 Hz, 1H), 6.92 (dd, J = 8.7, 2.4 Hz, 1H), 6.76 (dd, J = 8.7, 2.4 Hz, 1H), 4.38 (q, J = 7.0 Hz, 2H), 3.86 (s, 3H), 1.41 (t, J = 7.1 Hz, 3H). **^{13}C {^{1}H} NMR** (126 MHz, DMSO-d_6); δ 163.4, 159.8, 154.2, 153.7, 145.9, 131.2, 130.4, 126.9, 125.5, 112.4, 111.8, 111.6, 110.5, 106.0, 104.0, 103.1, 102.9, 59.4, 54.9, 13.7. **HRMS** (ESI)**:** m/z: $[M+H]^+$ Calcd for $C_{20}H_{17}NO_5$ 352.1178; found 352.1179.

Synthesis of ethyl 5-hydroxy-2-(5-methoxy-1-methyl-1H-indol-3-yl)benzofuran-3-carboxylate (4f)



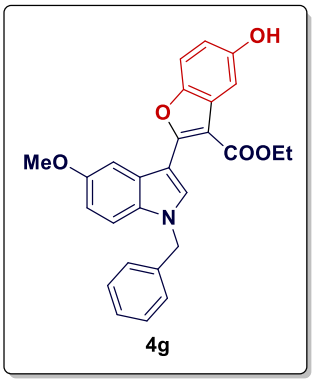
4f

The compound was prepared according to general procedure-(D) using ethyl (E)-3-(5-methoxy-1-methyl-1H-indol-3-yl)acrylate (0.035 g, 0.13 mmol, 1 eq.) **1l** and benzoquinone (0.029 g, 0.26 mmol, 2 eq.) **2** under catalytic quantity of $Cu(OTf)_2$ (0.004 g, 0.013 mmol, 10 mol%) at 40 °C to furnish ethyl 5-hydroxy-2-(5-methoxy-1-methyl-1H-indol-3-yl)benzofuran-3-carboxylate **4f**. After 1.5 h, purification by column chromatography (20% ethyl acetate in hexane) obtained as a brown oily liquid (0.035 g, 79%), R_f (EtOAc/ hexane 2:3) = 0.5.

FT-IR (neat): ν_{max}/cm^{-1}:, 3658, 2320, 1650, 1502, 1272, 1187, 798, 725; **^{1}H NMR** (500 MHz, DMSO-d_6); δ 9.35 (s, 1H), 8.77 (s, 1H), 7.74 (d, J = 2.3 Hz, 1H), 7.54 (d, J = 8.7 Hz, 1H), 7.48 (d,

J = 8.9 Hz, 1H), 7.37 (d, J = 2.4 Hz, 1H), 6.97 (dd, J = 8.8, 2.2 Hz, 1H), 6.77 (dd, J = 8.7, 2.5 Hz, 1H), 4.39 (q, J = 7.1 Hz, 2H), 3.89 (s, 3H), 3.87 (s, 3H), 1.42 (t, J = 7.1 Hz, 3H). **^{13}C {^{1}H} NMR** (126 MHz, DMSO-d_6); 164.4, 160.4, 155.5, 154.7, 146.9, 135.7, 132.1, 127.8, 126.9, 112.8, 112.4, 111.8, 111.5, 107.0, 104.4, 103.9, 103.7, 60.4, 55.9, 33.8, 14.7. **HRMS** (ESI)**:** m/z: $[M+H]^+$ Calcd for $C_{21}H_{19}NO_5$ 366.1336; found 366.1331.

Synthesis of ethyl 2-(1-benzyl-5-methoxy-1H-indol-3-yl)-5-hydroxybenzofuran-3-carboxylate (4g)

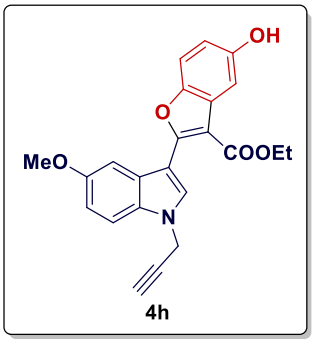


4g

The compound was prepared according to general procedure-(D) using ethyl (E)-3-(1-benzyl-5-methoxy-1H-indol-3-yl)acrylate (0.035 g, 0.13 mmol, 1 eq.) **1n** and benzoquinone (0.029 g, 0.26 mmol, 2 eq.) **2** under catalytic quantity of $Cu(OTf)_2$ (0.004 g, 0.013 mmol, 10 mol%) at 40 °C to furnish ethyl 2-(1-benzyl-5-methoxy-1H-indol-3-yl)-5-hydroxybenzofuran-3-carboxylate **4g**. After 1.5 h, purification by column chromatography (20% ethyl acetate in hexane) obtained as a brown oily liquid (0.040 g, 87%), R_f (EtOAc/ hexane 2:3) = 0.5.

FT-IR (neat): ν_{max}/cm^{-1}:, 3655, 2320, 1690, 1540, 1210, 1150, 1182, 1044, 759, 724; **^{1}H NMR** (500 MHz, DMSO-d_6); δ 8.82 (s, 1H), 7.82 (s, 1H), 7.42 (s, 1H), 7.28 (d, J = 8.6 Hz, 1H), 7.18 (t, J = 9.6 Hz, 3H), 7.08 (d, J = 8.6 Hz, 3H), 6.78 (dd, J = 20.2, 8.6 Hz, 2H), 6.63 (s, 1H), 5.27 (s, 2H), 4.31 (d, J = 7.0 Hz, 2H), 3.83 (s, 3H), 1.35 (t, J = 6.9 Hz, 3H). **^{13}C {^{1}H} NMR** (126 MHz, DMSO-d_6); 165.1, 160.8, 155.4, 153.4, 149.8, 147.6, 136.5, 134.9, 131.4, 128.8, 128.0, 127.8, 127.6, 126.7, 116.1, 111.0, 110.7, 107.5, 105.4, 105.0, 104.6, 60.2, 55.9, 51.0, 14.4. **HRMS** (ESI)**:** m/z: $[M+H]^+$ Calcd for $C_{27}H_{23}NO_5$ 442.1649; found 442.1645.

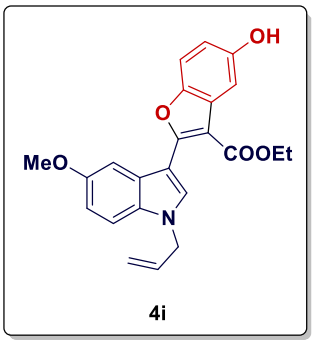
Synthesis of ethyl 5-hydroxy-2-(5-methoxy-1-(prop-2-yn-1-yl)-1H-indol-3-yl)benzofuran-3-carboxylate (4h)



The compound was prepared according to general procedure-(D) using ethyl (E)-3-(5-methoxy-1-(prop-2-yn-1-yl)-1H-indol-3-yl)acrylate (0.04 g, 0.14 mmol, 1 eq.) **1o** and benzoquinone (0.035 g, 0.26 mmol, 2 eq.) **2** under catalytic quantity of $Cu(OTf)_2$ (0.004 g, 0.013 mmol, 10 mol%) at 40 °C to furnish ethyl 5-hydroxy-2-(5-methoxy-1-(prop-2-yn-1-yl)-1H-indol-3-yl)benzofuran-3-carboxylate **4h**. After 1.5 h, purification by column chromatography (25% ethyl acetate in hexane) obtained as a brown oily liquid (0.030 g, 55%), R_f (EtOAc/ hexane 2:3) = 0.5.

FT-IR (neat): ν_{max}/cm^{-1}:, 3610, 2665, 2305, 1650, 1502, 1272, 1190, 803, 723; **^{1}H NMR** (500 MHz, DMSO-d_6); δ 9.36 (s, 1H), 8.89 (s, 1H), 7.75 (s, 1H), 7.65 – 7.53 (m, 2H), 7.38 (s, 1H), 7.02 (d, J = 8.9 Hz, 1H), 6.78 (d, J = 8.7 Hz, 1H), 5.26 (s, 2H), 4.40 (q, J = 7.0 Hz, 2H), 3.88 (s, 3H), 3.55 (s, 1H), 1.43 (t, J = 7.0 Hz, 3H). **^{13}C {^{1}H} NMR** (126 MHz, DMSO-d_6); δ 164.3, 159.9, 155.7, 154.7, 147.0, 134.2, 131.1, 127.7, 127.1, 113.1, 112.7, 112.1, 111.6, 107.0, 104.8, 104.6, 104.4, 78.9, 76.9, 60.5, 55.9, 36.4, 14.7. **HRMS** (ESI)**:** m/z: $[M+H]^+$ Calcd for $C_{23}H_{19}NO_5$ 390.1336; found 390.1331.

Synthesis of ethyl 2-(1-allyl-5-methoxy-1H-indol-3-yl)-5-hydroxybenzofuran-3-carboxylate (4i)

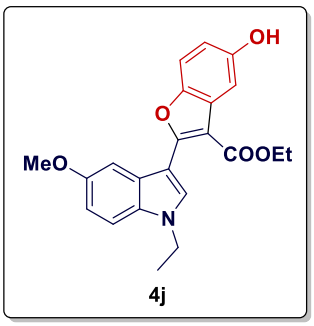


The compound was prepared according to general procedure-5(D) using ethyl (E)-3-(1-allyl-5-methoxy-1H-indol-3-yl)acrylate (0.03 g, 0.10 mmol, 1 eq.) **1o** and benzoquinone (0.022 g, 0.21 mmol, 2 eq.) **2** under catalytic quantity of $Cu(OTf)_2$ (0.003 g, 0.013 mmol, 10 mol%) at 40 °C to furnish ethyl 2-(1-allyl-5-methoxy-1H-indol-3-yl)-5-hydroxybenzofuran-3-carboxylate **4i**. After 1.5 h, purification by column chromatography (25% ethyl acetate in hexane) obtained as a brown oily liquid (0.029 g, 71%), R_f (EtOAc/ hexane 2:3) = 0.5.

FT-IR (neat): ν_{max}/cm^{-1}:, 3633, 2620, 2334, 1620, 1510, 1270, 1180, 845, 789; **^{1}H NMR** (500 MHz, DMSO-d_6); δ 9.36 (s, 1H), 8.80 (s, 1H), 7.75 (s, 1H), 7.53 (dd, J = 24.4, 8.6 Hz, 2H), 7.38 (s, 1H), 6.97 (d, J = 8.6 Hz, 1H), 6.78 (d, J = 8.4 Hz, 1H), 6.18 – 5.88 (m, 1H), 5.20 (dd, J = 41.6, 13.5 Hz, 2H), 4.96 (s, 2H), 4.39 (d, J = 6.8 Hz, 2H), 3.87 (s, 3H), 1.42 (t, J = 6.6 Hz, 3H). **^{13}C {^{1}H} NMR** (126 MHz, DMSO-d_6); δ 164.4, 160.2, 155.5, 154.7, 146.9, 134.7, 134.1, 131.4, 127.8,

127.0, 118.0, 112.9, 112.6, 112.2, 111.6, 107.0, 104.5, 104.4, 104.0, 60.4, 55.9, 49.2, 14.7. **HRMS** (ESI)**:** m/z: $[M+H]^+$ Calcd for $C_{23}H_{21}NO_5$ 392.1492; found 392.1486.

Synthesis of ethyl 2-(1-ethyl-5-methoxy-1H-indol-3-yl)-5-hydroxybenzofuran-3-carboxylate (4j)

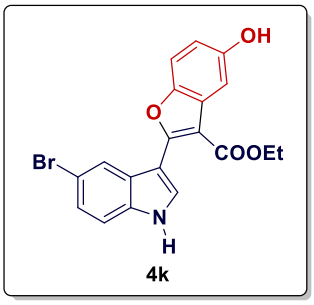


4j

The compound was prepared according to general procedure-(D) using ethyl (E)-3-(1-ethyl-5-methoxy-1H-indol-3-yl)acrylate (0.03 g, 0.10 mmol, 1 eq.) **1m** and benzoquinone (0.022 g, 0.21 mmol, 2 eq.) **2** under catalytic quantity of $Cu(OTf)_2$ (0.004 g, 0.012 mmol, 10 mol%) at 40 °C to furnish ethyl 2-(1-ethyl-5-methoxy-1H-indol-3-yl)-5-hydroxybenzofuran-3-carboxylate **4j**. After 1.5 h, purification by column chromatography (25% ethyl acetate in hexane) obtained as a brown oily liquid (0.028 g, 72%), R_f (EtOAc/ hexane 2:3) = 0.5.

FT-IR (neat): ν_{max}/cm^{-1}:, 3615, 2611, 2320, 1641, 1501, 1250, 1160, 855, 795; **^{1}H NMR** (500 MHz, DMSO-d_6); δ 9.35 (s, 1H), 8.83 (s, 1H), 7.74 (d, J = 2.3 Hz, 1H), 7.54 (dd, J = 8.8, 2.7 Hz, 2H), 7.37 (d, J = 2.4 Hz, 1H), 6.96 (dd, J = 8.9, 2.4 Hz, 1H), 6.76 (dd, J = 8.7, 2.5 Hz, 1H), 4.39 (q, J = 7.1 Hz, 2H), 4.31 (q, J = 7.2 Hz, 2H), 3.86 (s, 3H), 1.42 (q, J = 7.3 Hz, 6H). **^{13}C {^{1}H} NMR** (126 MHz, DMSO-d_6); δ 164.4, 160.4, 155.5, 154.7, 146.9, 134.1, 131.1, 127.9, 127.1, 112.8, 112.4, 111.9, 111.5, 107.0, 104.5, 104.1, 103.8, 60.4, 55.9, 41.7, 15.7, 14.7. **HRMS** (ESI)**:** m/z: $[M+H]^+$ Calcd for $C_{22}H_{21}NO_5$ 380.1492; found 380.1488.

Synthesis of ethyl 2-(5-bromo-1H-indol-3-yl)-5-hydroxybenzofuran-3-carboxylate (4k)



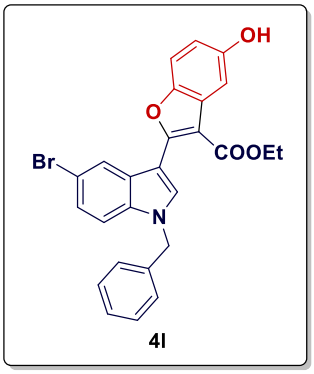
4k

The compound was prepared according to general procedure-(D) using ethyl (E)-3-(5-bromo-1H-indol-3-yl)acrylate (0.03 g, 0.10 mmol, 1 eq.) **1e** and benzoquinone (0.022 g, 0.21 mmol, 2 eq.) **2** under catalytic quantity of $Cu(OTf)_2$ (0.003 g, 0.013 mmol, 10 mol%) at 40 °C to furnish ethyl 2-(5-bromo-1H-indol-3-yl)-5-hydroxybenzofuran-3-carboxylate **4k**. After 1.5 h, purification by column chromatography (25% ethyl acetate in hexane) obtained as a brown oily liquid (0.024 g, 64%), R_f (EtOAc/ hexane 2:1) = 0.5.

FT-IR (neat): ν_{max}/cm^{-1}:, 3640, 2623, 2310, 1620, 1520, 1230, 1136, 890, 789; **^{1}H NMR** (500 MHz, DMSO-d_6); δ 12.17 (s, 1H), 9.37 (s, 1H), 8.86 (s, 1H), 8.34 (s, 1H), 7.55 (dd, J = 23.7, 8.4

Hz, 2H), 7.38 (d, J = 11.7 Hz, 2H), 6.78 (d, J = 8.6 Hz, 1H), 4.39 (q, 2H), 1.41 (t, J = 6.4 Hz, 3H). **^{13}C {^{1}H} NMR** (126 MHz, DMSO-d_6); δ 164.3, 159.7, 154.8, 147.0, 135.2, 132.9, 127.7, 127.4, 125.6, 123.7, 114.8, 114.2, 113.2, 111.7, 107.0, 104.9, 104.8, 60.5, 14.7. **HRMS** (ESI)**:** m/z: $[M+H]^+$ Calcd for $C_{19}H_{14}BrNO_4$ 400.0179; found 400.0174.

Synthesis of ethyl 2-(1-benzyl-5-bromo-1H-indol-3-yl)-5-hydroxybenzofuran-3-carboxylate (4l)

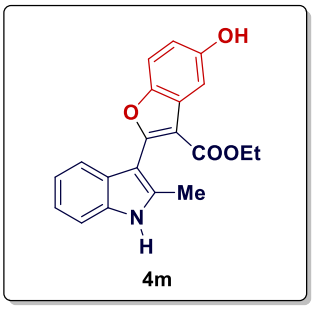


4l

The compound was prepared according to general procedure-(D) using ethyl (E)-3-(1-benzyl-5-bromo-1H-indol-3-yl)acrylate (0.03 g, 0.08 mmol, 1 eq.) **1p** and benzoquinone (0.017 g, 0.14 mmol, 2 eq.) 2 under catalytic quantity of $Cu(OTf)_2$ (0.004 g, 0.013 mmol, 10 mol%) at 40 °C to furnish ethyl 2-(1-benzyl-5-bromo-1H-indol-3-yl)-5-hydroxybenzofuran-3-carboxylate **4l**. After 1.5 h, purification by column chromatography (25% ethyl acetate in hexane) obtained as a brown oily liquid (0.027 g, 78%), R_f (EtOAc/ hexane 2:1) = 0.5.

FT-IR (neat): ν_{max}/cm^{-1}:, 3650, 2611, 2312, 1678, 1654, 1520, 1250, 1178, 877, 752; **^{1}H NMR** (500 MHz, DMSO-d_6); δ 9.39 (s, 1H), 8.95 (s, 1H), 8.36 (d, J = 1.8 Hz, 1H), 7.62 – 7.55 (m, 8.8 Hz, 2H), 7.41 (dd, J = 8.7, 1.8 Hz, 1H), 7.39 (d, J = 2.4 Hz, 1H), 7.37 – 7.26 (m, 5H), 6.80 (dd, J = 8.8, 2.5 Hz, 1H), 5.61 (s, 2H), 4.37 (q, J = 7.1 Hz, 2H), 1.37 (t, J = 7.1 Hz, 3H). **^{13}C {^{1}H} NMR** (126 MHz, DMSO-d_6); δ 164.2, 158.9, 154.8, 147.1, 137.4, 135.7, 135.1, 129.2, 128.2, 128.0, 127.6, 127.5, 125.8, 124.1, 114.7, 113.7, 113.4, 111.8, 107.0, 105.2, 104.6, 60.6, 50.2, 14.6. **HRMS** (ESI)**:** m/z: $[M+H]^+$ Calcd for $C_{26}H_{20}BrNO_4$ 490.0648; found 490.0642.

Synthesis of ethyl 5-hydroxy-2-(2-methyl-1H-indol-3-yl)benzofuran-3-carboxylate (4m)



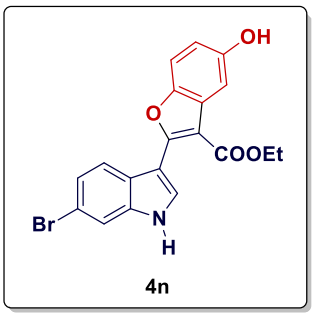
4m

The compound was prepared according to general procedure-5(D) using ethyl (E)-3-(2-methyl-1H-indol-3-yl)acrylate (0.03 g, 0.13 mmol, 1 eq.) **1g** and benzoquinone (0.029 g, 0.26 mmol, 2 eq.) 2 under catalytic quantity of $Cu(OTf)_2$ (0.005 g, 0.013 mmol, 10 mol%) at 40 °C to furnish ethyl 5-hydroxy-2-(2-methyl-1H-indol-3-yl)benzofuran-3-carboxylate **4m**. After 1.5 h, purification by column chromatography

(25% ethyl acetate in hexane) obtained as a brown oily liquid (0.029 g, 73%), R_f (EtOAc/ hexane 1:3) = 0.5.

FT-IR (neat): ν_{max}/cm^{-1}:, 3565, 2603, 2210, 1522, 1501, 1220, 1122, 854, 774; **^{1}H NMR** (500 MHz, DMSO-d_6); δ 11.71 (s, 1H), 9.41 (s, 1H), 7.51 – 7.46 (m, 2H), 7.45 – 7.41 (m, 2H), 7.18 (t, J = 7.3 Hz, 1H), 7.11 (t, J = 7.4 Hz, 1H), 6.84 (dd, J = 8.7, 2.5 Hz, 1H), 4.28 (q, J = 7.1 Hz, 2H), 2.46 (s, 3H), 1.24 (t, J = 7.1 Hz, 3H). **^{13}C {^{1}H} NMR** (126 MHz, DMSO-d_6); δ 163.7, 159.2, 154.6, 147.9, 139.2, 135.5, 127.9, 127.4, 121.7, 120.4, 119.4, 116.1, 113.5, 111.7, 108.0, 106.6, 102.8, 60.2, 14.5, 13.7. **HRMS** (ESI)**:** m/z: $[M+H]^+$ Calcd for $C_{20}H_{17}NO_4$ 336.1230; found 336.1226.

Synthesis of ethyl 2-(5-bromo-1H-indol-3-yl)-5-hydroxybenzofuran-3-carboxylate (4n)

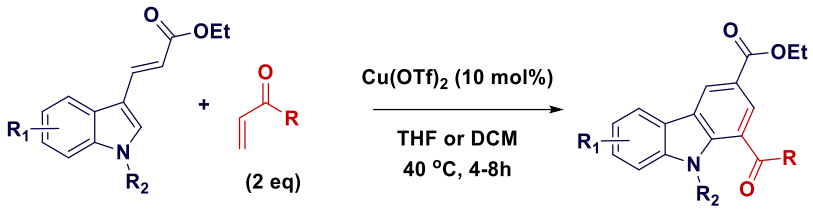


4n

The compound was prepared according to general procedure-(D), using ethyl (E)-3-(6-bromo-1H-indol-3-yl)acrylate (0.03 g, 0.10 mmol, 1 eq.) **1f** and benzoquinone (0.022 g, 0.21 mmol, 2 eq.) **2** under catalytic quantity of $Cu(OTf)_2$ (0.003 g, 0.013 mmol, 10 mol%) at 40 °C to furnish ethyl 2-(6-bromo-1H-indol-3-yl)-5-hydroxybenzofuran-3-carboxylate **4n**. After 1.5 h, purification by column chromatography (25% ethyl acetate in hexane) obtained as a brown oily liquid (0.017 g, 42%), R_f (EtOAc/ hexane 3:2) = 0.5.

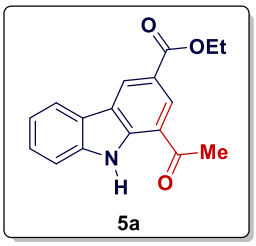
FT-IR (neat): ν_{max}/cm^{-1}:, 3654, 2345, 1650, 1524, 1233, 1110, 789, 754; **^{1}H NMR** (500 MHz, DMSO-d_6); δ 12.10 (s, 1H), 9.38 (s, 1H), 8.85 (s, 1H), 8.19 (d, J = 8.6 Hz, 1H), 7.76 (s, 1H), 7.53 (d, J = 8.7 Hz, 1H), 7.37 (d, J = 7.4 Hz, 2H), 6.79 (d, J = 8.6 Hz, 1H), 4.39 (q, J = 7.0 Hz, 2H), 1.41 (t, J = 7.0 Hz, 3H). **^{13}C {^{1}H} NMR** (126 MHz, DMSO-d_6); δ 164.3, 159.8, 154.7, 147.0, 137.3, 132.5, 127.7, 124.8, 124.3, 123.5, 115.6, 115.4, 113.2, 111.6, 107.0, 105.4, 104.8, 60.5, 14.7. **HRMS** (ESI)**:** m/z: $[M+H]^+$ Calcd for $C_{19}H_{14}BrNO_4$ 400.0179; found 400.0175.

E- Synthesis and characterization of carbazoles (scheme 3):



To the magnetically stirred solution of indole ester (1.0 equiv) in THF, 2 equivalents of vinyl ketone derivatives were added at room temperature, under catalytic quantity of $Cu(OTf)_2$. Then the reaction mixture is allowed to stir at 40 °C till completion of reaction (monitored by TLC). After completion reaction was quenched by adding water, further the organic layer was then washed with brine and dried over Na_2SO_4. Finally, reaction mixture was concentrated under vacuum and crude residue was purified by column chromatography (10-50% ethyl acetate in hexane) to obtain the corresponding product.

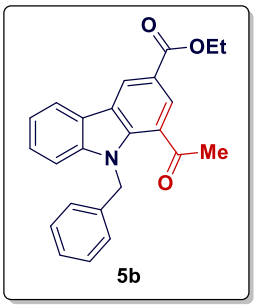
Synthesis of ethyl 1-acetyl-9H-carbazole-3-carboxylate (5a)



The compound was prepared according to general procedure-(E) using ethyl (E)-3-(1H-indol-3-yl)acrylate (0.03 g, 0.14 mmol, 1 eq.) **1a** and methyl vinyl ketone (0.03 g, 0.29 mmol, 2 eq.) **5** under catalytic quantity of $Cu(OTf)_2$ (0.004 g, 0.014 mmol, 10 mol%) at 40 °C to furnish ethyl 5-hydroxy-2-(1H-indol-3-yl)benzofuran-3-carboxylate. After 4 h, purification by column chromatography (15% ethyl acetate in hexane) obtained as a white solid (0.029 g, 80%), R_f (EtOAc/ hexane 1:3) = 0.5.

mp: 111−113 °C, **FT-IR** (neat): ν_{max}/cm^{-1}: 3416, 2854, 2364, 2319, 1654, 1524, 1061, 1003, 831, 775; **^{1}H NMR** (500 MHz, $CDCl_3$); δ 10.71 (s, 1H), 8.93 (s, 1H), 8.66 (s, 1H), 8.12 (d, J = 7.8 Hz, 1H), 7.56 – 7.51 (m, 1H), 7.50 – 7.46 (m, 1H), 7.37 – 7.28 (m, 1H), 4.46 (q, 2H), 2.78 (s, 3H), 1.46 (t, J = 7.1 Hz, 3H).**^{13}C {^{1}H} NMR** (126 MHz, $CDCl_3$); δ 200.2, 166.7, 141.5, 140.5, 129.7, 127.4, 127.3, 125.0, 122.3, 121.1, 120.7 (X 2C), 118.7, 111.7, 61.2, 26.8, 14.5. **HRMS** (ESI)**:** m/z: $[M+H]^+$ Calcd for $C_{17}H_{15}NO_3$ 282.1125; found 282.1124.

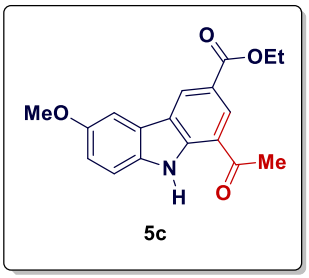
Synthesis of ethyl 1-acetyl-9-benzyl-9H-carbazole-3-carboxylate (5b)



The compound was prepared according to general procedure-(E) using ethyl (E)-3-(1-benzyl-1H-indol-3-yl)acrylate (0.04 g, 0.13 mmol, 1 eq.) **1j** and methyl vinyl ketone (0.023 g, 0.32 mmol, 2 eq.) **5** under catalytic quantity of $Cu(OTf)_2$ (0.006 g, 0.02 mmol, 10 mol%) at 40 °C to furnish ethyl 1-acetyl-9-benzyl-9H-carbazole-3-carboxylate **5b**. After 2.5 h, purification by column chromatography (20% ethyl acetate in hexane) obtained as a white solid (0.036 g, 75%), R_f (EtOAc/ hexane 1:3) = 0.4.

mp: 125−127 °C, **FT-IR** (neat): ν_{max}/cm^{-1}: 3422, 2977, 2368, 2323, 1745, 1701, 1522, 1138, 1045, 956, 851; 635; **^{1}H NMR** (500 MHz, $CDCl_3$); δ 8.98 (s, 1H), 8.30 (s, 1H), 8.25 (d, J = 7.8 Hz, 1H), 7.58 (d, J = 3.4 Hz, 2H), 7.45 – 7.38 (m, 1H), 7.22 – 7.14 (m, 3H), 6.81 – 6.72 (m, 2H), 5.70 (s, 2H), 4.48 (q, J = 7.1 Hz, 2H), 2.26 (s, 3H), 1.48 (t, J = 7.1 Hz, 3H). **^{13}C {^{1}H} NMR** (126 MHz, $CDCl_3$); δ 200.5, 166.5, 143.0, 138.5, 136.3, 128.6, 127.4, 127.3, 127.3, 126.7, 125.8, 125.5, 125.1, 122.5, 121.0, 120.5 (X 2C), 109.9, 61.0, 48.4, 28.9, 14.5. **HRMS** (ESI)**:** m/z: $[M+H]^+$ Calcd for $C_{24}H_{21}NO_3$ 372.1594; found 372.1594.

Synthesis of ethyl 1-acetyl-6-methoxy-9H-carbazole-3-carboxylate (5c)

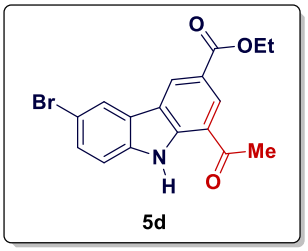


The compound was prepared according to general procedure-(E) using ethyl (E)-3-(5-methoxy-1H-indol-3-yl)acrylateacrylate (0.04 g, 0.20 mmol, 1 eq.) **1b** and methyl vinyl ketone (0.028 g, 0.407 mmol, 2 eq.) **5** under catalytic quantity of $Cu(OTf)_2$ (0.008 g, 0.02 mmol, 10 mol%) at 40 °C to furnish ethyl 1-acetyl-6-methoxy-9H-carbazole-3-carboxylate **5c**. After 2.5 h, purification by column chromatography (20% ethyl acetate in hexane) obtained as a golden yellow solid (0.035 g, 69%), R_f (EtOAc/ hexane 2:3) = 0.5.

mp: 118−120 °C, **FT-IR** (neat): ν_{max}/cm^{-1}: 3412, 2860, 2354, 2317, 1749, 1652, 1008, 854, 779; **^{1}H NMR** (500 MHz, $CDCl_3$); δ 10.53 (s, 1H), 8.81 (s, 1H), 8.57 (s, 1H), 7.50 (s, 1H), 7.35 (d, J = 8.8 Hz, 1H), 7.06 (dd, J = 8.8, 2.4 Hz, 1H), 4.40 (q, J = 7.1 Hz, 2H), 3.86 (s, 3H), 2.71 (s, 3H),

1.41 (t, J = 7.1 Hz, 3H). **^{13}C {^{1}H} NMR** (126 MHz, $CDCl_3$); δ 200.0, 166.6, 154.9, 141.8, 135.1, 129.6, 127.3, 124.9, 122.8, 120.1, 118.6, 116.5, 112.4, 103.2, 61.1, 55.9, 26.7, 14.5. **HRMS** (ESI)**:** m/z: $[M+H]^+$ Calcd for $C_{17}H_{18}NO_4$ 312.1230; found 312.1209.

Synthesis of ethyl 1-acetyl-6-bromo-9H-carbazole-3-carboxylate (5d)

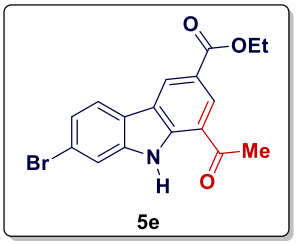


5d

The compound was prepared according to general procedure-(E) using ethyl (E)-3-(5-bromo-1H-indol-3-yl)acrylate (0.03 g, 0.10 mmol, 1 eq.) **1e** and methyl vinyl ketone (0.014 g, 0.204 mmol, 2 eq.) **5** under catalytic quantity of $Cu(OTf)_2$ (0.004 g, 0.01 mmol, 10 mol%) at 40 °C to furnish ethyl 1-acetyl-6-bromo-9H-carbazole-3-carboxylate **5d**. After 2.5 h, purification by column chromatography (20% ethyl acetate in hexane) obtained as a pale yellow solid (0.023 g, 66%), R_f (EtOAc/ hexane 2:3) = 0.4.

mp: 130−132 °C, **FT-IR** (neat): ν_{max}/cm^{-1}: 3449, 2975, 2362, 2319, 1701, 1524, 1345, 1047, 798; **^{1}H NMR** (500 MHz, $CDCl_3$); δ 10.68 (s, 1H), 8.84 (s, 1H), 8.63 (d, J = 1.2 Hz, 1H), 8.18 (d, J = 1.3 Hz, 1H), 7.52 (dd, J = 8.6, 1.8 Hz, 1H), 7.36 (d, J = 8.6 Hz, 1H), 4.41 (q, J = 7.1 Hz, 2H), 2.74 (s, 3H), 1.42 (t, J = 7.1 Hz, 3H). **^{13}C {^{1}H} NMR** (126 MHz, $CDCl_3$); δ 200.1, 166.3, 141.6, 139.0, 130.2, 130.0, 127.6, 124.0, 123.9, 123.5, 121.2, 118.9, 113.9, 113.1, 61.2, 26.8, 14.5. **HRMS** (ESI)**:** m/z: $[M+H]^+$ Calcd for $C_{17}H_{14}BrNO_3$ 360.0230; found 360.0223.

Synthesis of ethyl 1-acetyl-7-bromo-9H-carbazole-3-carboxylate (5e)



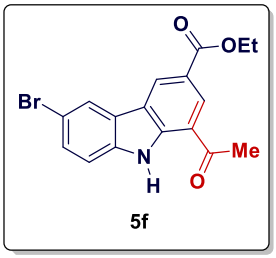
5e

The compound was prepared according to general procedure-(E) using ethyl (E)-3-(6-bromo-1H-indol-3-yl)acrylate (0.03 g, 0.10 mmol, 1 eq.) **1f** and methyl vinyl ketone (0.014 g, 0.204 mmol, 2 eq.) **5** under catalytic quantity of $Cu(OTf)_2$ (0.004 g, 0.01 mmol, 10 mol%) at 40 °C to furnish ethyl 1-acetyl-7-bromo-9H-carbazole-3-carboxylate **5e**. After 2.5 h, purification by column chromatography (20% ethyl acetate in hexane) obtained as a yellow solid (0.024 g, 69%). R_f (EtOAc/ hexane 2:3) = 0.3.

mp: 135−137 °C, **FT-IR** (neat): ν_{max}/cm^{-1}: 3389, 2988, 2267, 2317, 1720, 1547, 1104, 770; **NMR** (500 MHz, $CDCl_3$); δ 10.73 (s, 1H), 8.92 (s, 1H), 8.70 (s, 1H), 7.98 (d, J = 8.3 Hz, 1H), 7.71 (s,

1H), 7.46 (dd, J = 8.3, 1.1 Hz, 1H), 4.51 (q, J = 7.1 Hz, 2H), 2.82 (s, 3H), 1.51 (t, J = 7.1 Hz, 3H). **^{13}C {^{1}H} NMR** (126 MHz, $CDCl_3$); δ 200.1, 166.4, 141.4, 141.2, 129.8, 127.3, 124.3, 124.3, 121.8, 121.3, 121.1, 120.7, 118.9, 114.7, 61.2, 26.8, 14.5. **HRMS** (ESI)**:** m/z: $[M+H]^+$ Calcd for $C_{17}H_{14}BrNO_3$ 360.0230; found 360.0220.

Synthesis of ethyl 1-acetyl-9-benzyl-7-bromo-9H-carbazole-3-carboxylate (5f)

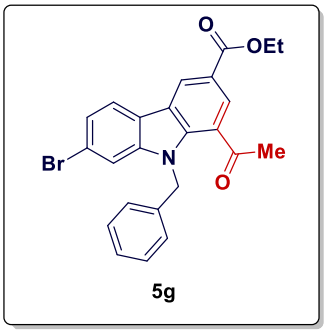


5f

The compound was prepared according to general procedure-(E) using ethyl (E)-3-(1-benzyl-5-bromo-1H-indol-3-yl)acrylate (0.04 g, 0.10 mmol, 1 eq.) **1p** and methyl vinyl ketone (0.014 g, 0.207 mmol, 2 eq.) **5** under catalytic quantity of $Cu(OTf)_2$ (0.004 g, 0.01 mmol, 10 mol%) at 40 °C to furnish ethyl 1-acetyl-9-benzyl-7-bromo-9H-carbazole-3-carboxylate **5f**. After 2.5 h, purification by column chromatography (20% ethyl acetate in hexane) obtained as a creamy white solid (0.035 g, 72%), R_f (EtOAc/ hexane 2:3) = 0.4.

mp: 140−142 °C, **FT-IR** (neat): ν_{max}/cm^{-1}: 3452, 2988, 2854, 2362, 1745, 1701, 1522, 1339,1148, 1047, 998, 683; **^{1}H NMR** (500 MHz, $CDCl_3$); δ 8.82 (s, 1H), 8.23 (d, J = 19.0 Hz, 2H), 7.55 (dd, J = 8.7, 1.7 Hz, 1H), 7.34 (d, J = 8.7 Hz, 1H), 7.13 – 7.05 (m, 3H), 6.68 – 6.60 (m, 2H), 5.55 (s, 2H), 4.37 (q, J = 7.1 Hz, 2H), 2.16 (s, 3H), 1.38 (t, J = 7.1 Hz, 3H). **^{13}C {^{1}H} NMR** (126 MHz, $CDCl_3$); δ 200.3, 166.2, 141.6, 138.7, 135.9, 130.0, 128.7, 128.0, 127.5, 126.6, 125.8, 125.3, 124.7, 124.2, 123.2, 121.0, 113.9, 111.4, 61.2, 48.6, 28.9, 14.5. **HRMS** (ESI)**:** m/z: $[M+H]^+$ Calcd for $C_{24}H_{20}BrNO_3$ 450.0699; found 450.0693.

Synthesis of ethyl 1-acetyl-9-benzyl-7-bromo-9H-carbazole-3-carboxylate (5g)



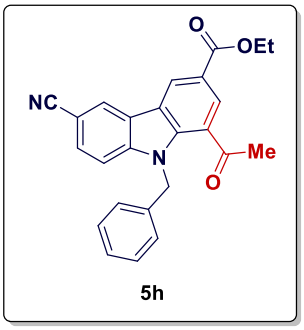
5g

The compound was prepared according to general procedure-5(D) using ethyl (E)-3-(1-benzyl-6-bromo-1H-indol-3-yl)acrylate (0.04 g, 0.10 mmol, 1 eq.) **1q** and methyl vinyl ketone (0.014 g, 0.207 mmol, 2 eq.) **5** under catalytic quantity of $Cu(OTf)_2$ (0.004 g, 0.01 mmol, 10 mol%) at 40 °C to furnish ethyl 1-acetyl-9-benzyl-7-bromo-9H-carbazole-3-carboxylate **5g**. After 2.5 h, purification by column chromatography (20% ethyl acetate in hexane) obtained as a creamy white solid (0.036 g, 74%), R_f (EtOAc/ hexane 2:3) = 0.4.

mp: 145−147 °C, **FT-IR** (neat): ν_{max}/cm^{-1}: 3485, 2970, 2754, 2250, 1720, 1532, 1236, 1099, 759; **^{1}H NMR** (500 MHz, $CDCl_3$); δ 8.93 (s, 1H), 8.30 (s, 1H), 8.09 (d, J = 8.3 Hz, 1H), 7.73 (s, 1H), 7.51 (d, J = 8.3 Hz, 1H), 7.24 – 7.14 (m, 3H), 6.78 – 6.70 (m, 2H), 5.63 (s, 2H), 4.47 (q, J = 7.1 Hz, 2H), 2.23 (s, 3H), 1.47 (t, J = 7.1 Hz, 3H). **^{13}C {^{1}H} NMR** (126 MHz, $CDCl_3$); δ 200.3, 166.3, 143.8, 138.6, 135.7, 128.7, 127.5, 126.6, 125.9, 125.2, 125.0, 124.3, 121.6, 121.1, 121.0, 116.0, 114.8, 113.1, 61.2, 48.5, 28.9, 14.4. **HRMS** (ESI)**:** m/z: $[M+H]^+$ Calcd for $C_{24}H_{20}BrNO_3$ 450.0699; found 450.0697.

Synthesis of ethyl 1-acetyl-9-benzyl-8-bromo-9H-carbazole-3-carboxylate (5h)

Chemical Formula: $C_{25}H_{20}N_2O_3$

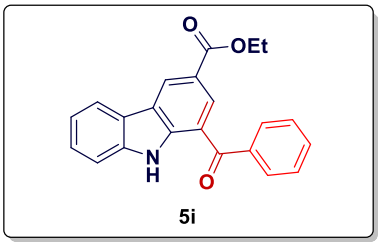


5h

The compound was prepared according to general procedure-(E) using ethyl (E)-3-(1-benzyl-6-cyano-1H-indol-3-yl)acrylate (0.04 g, 0.10 mmol, 1 eq.) **1r** and methyl vinyl ketone (0.014 g, 0.207 mmol, 2 eq.) **5** under catalytic quantity of $Cu(OTf)_2$ (0.004 g, 0.01 mmol, 10 mol%) at 40 °C to furnish ethyl 1-acetyl-9-benzyl-7-cyano-9H-carbazole-3-carboxylate **5h**. After 2.5 h, purification by column chromatography (20% ethyl acetate in hexane) obtained as a light brown solid (0.022 g, 54%), R_f (EtOAc/ hexane 3:1) = 0.5.

mp: 155−157 °C, **FT-IR** (neat): ν_{max}/cm^{-1}: 3459, 3034, 2989, 2450, 1720, 1566, 1365, 1215, 1054, 789; **^{1}H NMR** (500 MHz, $CDCl_3$); δ 8.88 (s, 1H), 8.46 (s, 1H), 8.25 (d, J = 1.5 Hz, 1H), 7.72 (dd, J = 8.6, 1.4 Hz, 1H), 7.54 (d, J = 8.6 Hz, 1H), 7.13 – 7.10 (m, 3H), 6.81 – 6.42 (m, 2H), 5.61 (s, 2H), 4.39 (q, J = 7.1 Hz, 2H), 2.15 (s, 3H), 1.39 (t, J = 7.1 Hz, 3H).**^{13}C {^{1}H} NMR** (126 MHz, $CDCl_3$); δ 199.1, 164.9, 143.6, 138.1, 134.2, 129.3, 127.8, 127.4, 126.7, 125.6 (X2C), 125.3, 124.3, 123.6, 121.7, 121.0, 118.6, 109.7, 103.1, 60.3, 47.7, 27.8, 13.4. **HRMS** (ESI)**:** m/z: $[M+H]^+$ Calcd for $C_{25}H_{20}BrN_2O_3$ 397.1547; found 397.1544.

Synthesis of ethyl 1-benzoyl-9H-carbazole-3-carboxylate (5i)

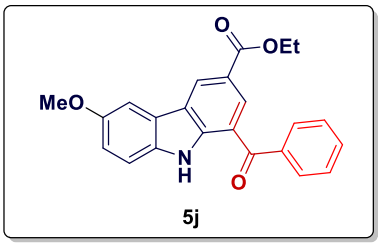


5i

The compound was prepared according to general procedure-(E) using ethyl (E)-3-(1H-indol-3-yl)acrylate (0.03 g, 0.14 mmol, 1 eq.) **1a** and phenyl vinyl ketone (0.037 g, 0.28 mmol, 2 eq.) under catalytic quantity of $Cu(OTf)_2$ (0.006 g, 0.002 mmol, 10 mol%) at 40 °C to furnish ethyl 1-benzoyl-9H-carbazole-3-carboxylate **5i**. After 5 h, purification by column chromatography (5% ethyl acetate in hexane) obtained as a white solid (0.036 g, 74%), R_f (EtOAc/ hexane 1:9) = 0.5.

mp: 140−142 °C, **FT-IR** (neat): ν_{max}/cm^{-1}: 3378, 3033, 2878, 2545, 1725, 1680, 1355, 1210, 1154, 755; **^{1}H NMR** (500 MHz, $CDCl_3$ + DMSO-d_6); δ 10.72 (s, 1H), 9.00 (s, 1H), 8.56 (s, 1H), 8.18 (d, J = 7.8 Hz, 1H), 7.83 (d, J = 8.5 Hz, 2H), 7.64 (t, J = 7.4 Hz, 1H), 7.60 – 7.51 (m, 4H), 7.36 (t, J = 7.4 Hz, 1H), 4.43 (q, J = 7.1 Hz, 2H), 1.43 (t, J = 7.1 Hz, 3H). **^{13}C {^{1}H} NMR** (126 MHz, $CDCl_3$ + DMSO-d_6); δ 197.7, 166.7, 142.7, 140.5, 138.5, 132.4, 132.1, 129.6, 128.6, 127.4, 127.3, 125.2, 122.5, 121.2, 120.8, 120.7, 118.0, 111.8, 61.2, 14.5. **HRMS** (ESI)**:** m/z: $[M+H]^+$ Calcd for $C_{22}H_{17}NO_3$ 344.1281; found 344.1264.

Synthesis of ethyl 1-benzoyl-6-methoxy-9H-carbazole-3-carboxylate (5j)

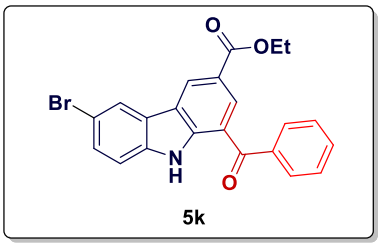


5j

The compound was prepared according to general procedure-(E) using (E)-3-(5-methoxy-1H-indol-3-yl)acrylate (0.04 g, 0.16 mmol, 1 eq.) **1b** and phenyl vinyl ketone (0.043 g, 0.33 mmol, 2 eq.) under catalytic quantity of $Cu(OTf)_2$ (0.006 g, 0.002 mmol, 10 mol%) at 40 °C to furnish ethyl 1-benzoyl-6-methoxy-9H-carbazole-3-carboxylate **(5j)**. After 5 h, purification by column chromatography (5% ethyl acetate in hexane) obtained as a light-yellow solid (0.036 g, 60%), R_f (EtOAc/ hexane 1:9) = 0.5.

mp: 150−152 °C, **FT-IR** (neat): ν_{max}/cm^{-1}: 3375, 3133, 2860, 2555, 1730, 1650, 1320, 1220, 755; **^{1}H NMR** (500 MHz, $CDCl_3$ + DMSO-d_6); δ 10.72 (s, 1H), 8.88 (s, 1H), 8.44 (s, 1H), 7.74 (d, J = 7.2 Hz, 2H), 7.57 (d, J = 2.1 Hz, 2H), 7.51 – 7.42 (m, 3H), 7.08 (d, J = 8.7, 2.2 Hz, 1H), 4.35 (q, J = 7.1 Hz, 2H), 3.88 (s, 3H), 1.35 (t, J = 7.1 Hz, 3H).**^{13}C {^{1}H} NMR** (126 MHz, $CDCl_3$ + DMSO-d_6); δ 197.2, 166.5, 154.9, 142.8, 138.4, 135.2, 132.1, 131.8, 129.3, 128.4, 127.1, 124.9, 122.9, 119.9, 117.9, 116.5, 112.6, 103.1, 60.9, 55.9, 14.4. **HRMS** (ESI)**:** m/z: $[M+H]^+$ Calcd for $C_{23}H_{20}NO_4$ 374.1387; found 374.1371.

Synthesis of ethyl 1-benzoyl-6-bromo-9H-carbazole-3-carboxylate (5k)

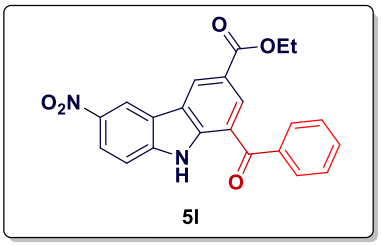


5k

The compound was prepared according to general procedure-(E) using (E)-3-(1-benzyl-5-bromo-1H-indol-3-yl)acrylate (0.04 g, 0.14 mmol, 1 eq.) **1p** and phenyl vinyl ketone (0.036 g, 0.28 mmol, 2 eq.) under catalytic quantity of $Cu(OTf)_2$ (0.005 g, 0.015 mmol, 10 mol%) at 40 °C to furnish ethyl 1-benzoyl-6-bromo-9H-carbazole-3-carboxylate **(5k)**. After 5 h, purification by column chromatography (5% ethyl acetate in hexane) obtained as yellow solid (0.039 g, 67%), R_f (EtOAc/ hexane 1:7) = 0.5.

mp: 155−157 °C, **FT-IR** (neat): ν_{max}/cm^{-1}: 3360, 3033, 2875, 1720, 1650, 1315, 1120, 733; **^{1}H NMR** (500 MHz, DMSO-d_6); δ 12.26 (s, 1H), 9.08 (s, 1H), 8.56 (d, J = 2.0 Hz, 1H), 8.30 (s, 1H), 7.80 (d, J = 7.5 Hz, 2H), 7.75 – 7.67 (m, 2H), 7.64 – 7.55 (m, 3H), 4.33 (q, J = 7.1 Hz, 2H), 1.34 (t, J = 7.1 Hz, 3H).**^{13}C {^{1}H} NMR** (126 MHz, DMSO-d_6); δ 195.3, 165.4, 141.2, 139.8, 137.8, 132.1, 131.3, 129.3, 129.1, 128.4, 127.1, 123.5, 123.2, 119.7, 118.5, 114.5, 112.7, 60.5, 39.5, 14.1. **HRMS** (ESI)**:** m/z: $[M+H]^+$ Calcd for $C_{22}H_{17}BrNO_3$ 422.0387; found 422.0366.

Synthesis of ethyl 1-benzoyl-6-nitro-9H-carbazole-3-carboxylate (5l)



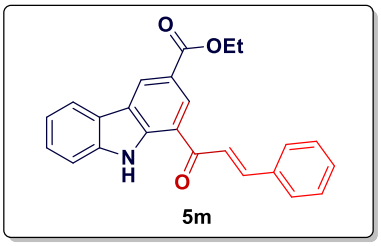
5l

The compound was prepared according to general procedure-(E) using ethyl (E)-3-(5-nitro-1H-indol-3-yl)acrylate (0.04 g, 0.15 mmol, 1 eq.) **1c** and phenyl vinyl ketone (0.04 g, 0.30 mmol, 2 eq.) under catalytic quantity of $Cu(OTf)_2$ (0.006 g, 0.015 mmol, 10 mol%) at 40 °C to furnish ethyl 1-benzoyl-6-nitro-9H-carbazole-3-carboxylate **(5l)**. After 5 h, purification by column chromatography (5% ethyl acetate in hexane) obtained as yellow solid (0.034 g, 57%), R_f (EtOAc/ hexane 1:5) = 0.5.

mp: 160−162 °C, **FT-IR** (neat): ν_{max}/cm^{-1}: 3350, 3152, 2855, 1720, 1610, 1330, 1120, 724; **^{1}H NMR** (500 MHz, DMSO-d_6); δ 12.65 (s, 1H), 9.24 (s, 1H), 8.35 (d, J = 9.0 Hz, 1H), 8.35 (d, J = 9.0 Hz, 1H), 8.29 (s, 1H), 7.87 – 7.80 (m, 3H), 7.73 (d, J = 7.5 Hz, 1H), 7.64 (t, J = 7.5 Hz, 2H), 4.34 (q, J = 7.0 Hz, 2H), 1.34 (t, J = 7.0 Hz, 3H). **^{13}C {^{1}H} NMR** (126 MHz, DMSO-d_6); δ 195.1, 165.3, 144.6, 142.2, 141.3, 137.6, 132.5, 131.7, 129.3, 128.6, 127.8, 124.4, 122.3, 121.5, 120.9,

119.4, 118.1, 112.9, 60.8, 14.2. **HRMS** (ESI)**:** m/z: $[M+H]^+$ Calcd for $C_{22}H_{17}N_2O_5$ 389.1132; found 389.1114.

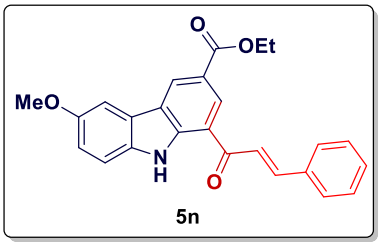
Synthesis of ethyl 1-cinnamoyl-9H-carbazole-3-carboxylate (5m)



The compound was prepared according to general procedure-(E) using ethyl (E)-3-(1H-indol-3-yl)acrylate (0.04 g, 0.18 mmol, 1 eq.) **1a** and (E)-1-phenylpenta-1,4-dien-3-one (0.05 g, 0.36 mmol, 2 eq.) under catalytic quantity of $Cu(OTf)_2$ (0.006 g, 0.01 mmol, 10 mol%) at 40 °C to furnish ethyl 1-cinnamoyl-9H-carbazole-3-carboxylate **(5m)**. After 8 h, purification by column chromatography (5% ethyl acetate in hexane) obtained as white solid (0.050 g, 75%), R_f (EtOAc/ hexane 1:5) = 0.5.

mp: 180−182 °C, **FT-IR** (neat): ν_{max}/cm^{-1}: 3360, 3140, 2840, 1730, 1620, 1320, 1110, 750; **^{1}H NMR** (500 MHz, $CDCl_3$); δ 10.97 (s, 1H), 8.97 (s, 1H), 8.86 (s, 1H), 8.15 (d, J = 7.8 Hz, 1H), 8.02 – 7.83 (m, 2H), 7.79 – 7.68 (m, 2H), 7.57 (d, J = 8.0 Hz, 1H), 7.52 (d, J = 7.4 Hz, 1H), 7.48 – 7.44 (m, 3H), 7.34 (t, J = 7.3 Hz, 1H), 4.37 (q, 2H), 1.51 (t, J = 7.1 Hz, 3H). **^{13}C {^{1}H} NMR** (126 MHz, $CDCl_3$); δ 190.3, 166.8, 144.7, 142.4, 140.5, 134.9, 130.8, 129.1, 128.8, 127.4, 127.4, 125.1, 122.5, (121.1X2C), 120.8, 120.8, (119.3X2C), 111.9, 61.3, 14.6. **HRMS** (ESI)**:** m/z: $[M+H]^+$ Calcd for $C_{24}H_{20}NO_3$ 370.1438; found 370.1422.

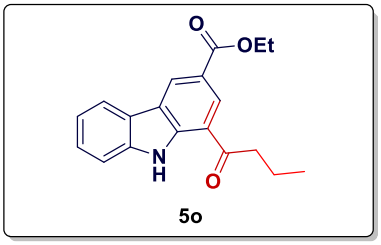
Synthesis of ethyl 1-cinnamoyl-6-methoxy-9H-carbazole-3-carboxylate (5n)



The compound was prepared according to general procedure-(E) using ethyl (E)-3-(5-methoxy-1H-indol-3-yl)acrylate (0.04 g, 0.16 mmol, 1 eq.) **1b** and (E)-1-phenylpenta-1,4-dien-3-one (0.052 g, 0.33 mmol, 2 eq.) under catalytic quantity of $Cu(OTf)_2$ (0.006 g, 0.01 mmol, 10 mol%) at 40 °C to furnish ethyl 1-cinnamoyl-6-methoxy-9H-carbazole-3-carboxylate **(5n)**. After 8 h, purification by column chromatography (5% ethyl acetate in hexane) obtained as white solid (0.046 g, 72%), R_f (EtOAc/ hexane 1:5) = 0.5.

mp: 185−187 °C, **FT-IR** (neat): ν_{max}/cm^{-1}: 3350, 3120, 2850, 1720, 1610, 1310, 1150, 755; **^{1}H NMR** (500 MHz, $CDCl_3$); δ 10.77 (s, 1H), 8.82 (s, 1H), 8.73 (s, 1H), 7.90 – 7.73 (m, 2H), 7.65 (d, J = 6.5 Hz, 2H), 7.51 (s, 1H), 7.42 – 7.33 (m, 4H), 7.06 (d, J = 8.7 Hz, 1H), 4.43 (q, J = 7.1 Hz, 2H), 3.86 (s, 3H), 1.44 (t, J = 7.1 Hz, 3H). **^{13}C {^{1}H} NMR** (126 MHz, $CDCl_3$); δ 190.0, 166.7, 155.0, 144.4, 142.7, 135.1, 134.8, 130.6, 129.0, 128.6, 127.3, 127.2, 124.9, 122.9, 120.7, 120.2, 119.1, 116.5, 112.5, 103.2, 103.2, 61.1, 14.6. **HRMS** (ESI)**:** m/z: $[M+H]^+$ Calcd for $C_{25}H_{22}NO_4$ 400.1543; found 400.1525.

Synthesis of ethyl 1-butyryl-9H-carbazole-3-carboxylate (5o)



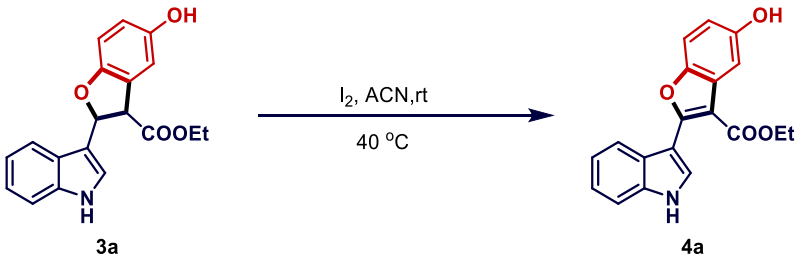
5o

The compound was prepared according to general procedure-(E) using ethyl (E)-3-(1H-indol-3-yl)acrylate (0.03 g, 0.14 mmol, 1 eq.) **1a** and hex-1-en-3-one (0.028 g, 0.28 mmol, 2 eq.) under catalytic quantity of $Cu(OTf)_2$ (0.006 g, 0.01 mmol, 10 mol%) at 40 °C to furnish ethyl 1-butyryl-9H-carbazole-3-carboxylate **(5o)**. After 8 h, purification by column chromatography (2% ethyl acetate in hexane) obtained as creamy white solid (0.02 g, 48%), R_f (EtOAc/ hexane 1:7) = 0.3.

mp: 166−168 °C, **FT-IR** (neat): ν_{max}/cm^{-1}: 3430, 2840, 1720, 1605, 1310, 755; **^{1}H NMR** (500 MHz, $CDCl_3$ +DMSO-d_6); δ 10.82 (s, 1H), 8.97 (s, 1H), 8.73 (s, 1H), 8.15 (d, J = 7.8 Hz, 1H), 7.63 – 7.46 (m, 2H), 7.34 (t, J = 7.3 Hz, 1H), 4.49 (q, J = 7.1 Hz, 2H), 3.18 (q, J = 7.3 Hz, 2H), 1.88 (q, J = 14.7, 7.3 Hz, 2H), 1.49 (t, J = 7.1 Hz, 3H), 1.09 (t, J = 7.4 Hz, 3H). **^{13}C {^{1}H} NMR** (126 MHz, $CDCl_3$ + DMSO-d_6); δ 202.6, 166.8, 141.8, 140.6, 129.0, 127.3, 127.3, 125.1, 122.4, 121.1, 120.8, (118.6X2C), 111.8, 61.2, 40.4, 18.1, 14.6, 14.0. **HRMS** (ESI)**:** m/z: $[M+H]^+$ Calcd for $C_{19}H_{20}NO_3$ 310.1438; found 310.1422.

F- Selected control experiments:

Iodine mediated conversion of 3a to 4a

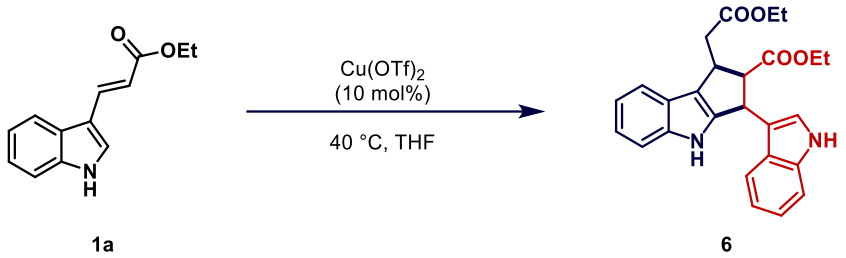


3a 4a

To the magnetically stirred solution of ethyl-5-hydroxy-2-(1H-indol-3-yl)-2,3-dihydrobenzofuran-3-carboxylate **3a** (0.04 g, 0.13 mmol, 1 eq.) in ACN, 10 mol% of iodine was added at room temperature. Then the reaction mixture is allowed to stir at 40 °C till completion of reaction (monitored by TLC). After completion (3h), reaction was quenched by adding water, further the organic layer was then washed with brine and dried over Na_2SO_4. Purification by column chromatography (15% ethyl acetate in hexane) **4a** obtained as a light brown oily liquid (0.030 g, 69%), R_f (EtOAc/ hexane 1:3) = 0.5.

The obtained product was identified by TLC analysis, followed by spectroscopic data: **^{1}H NMR** (500 MHz, DMSO-d_6); δ 11.98 (s, 1H), 9.34 (s, 1H), 8.86 (d, J = 2.5 Hz, 1H), 8.26 (d, J = 7.6 Hz, 1H), 7.54 (t, J = 8.9 Hz, 2H), 7.37 (d, J = 1.9 Hz, 1H), 7.30 – 7.19 (m, 2H), 6.77 (dd, J = 8.6, 2.0 Hz, 1H), 4.39 (q, J = 7.0 Hz, 2H), 1.41 (t, J = 7.1 Hz, 3H). **^{13}C {^{1}H} NMR** (126 MHz, DMSO-d_6); δ 163.4, 159.7, 153.7, 146.0, 135.4, 130.8, 126.9, 124.8, 122.0, 120.8, 120.5, 112.0, 111.8, 110.5, 106.0, 104.2, 103.2, 59.4, 13.7.; **HRMS** (ESI)**:** m/z: $[M+H]^+$ Calcd for $C_{19}H_{15}NO_4$ 322.1074; found 322.1072.

Self-dimerization in absence of electrophilic partner:



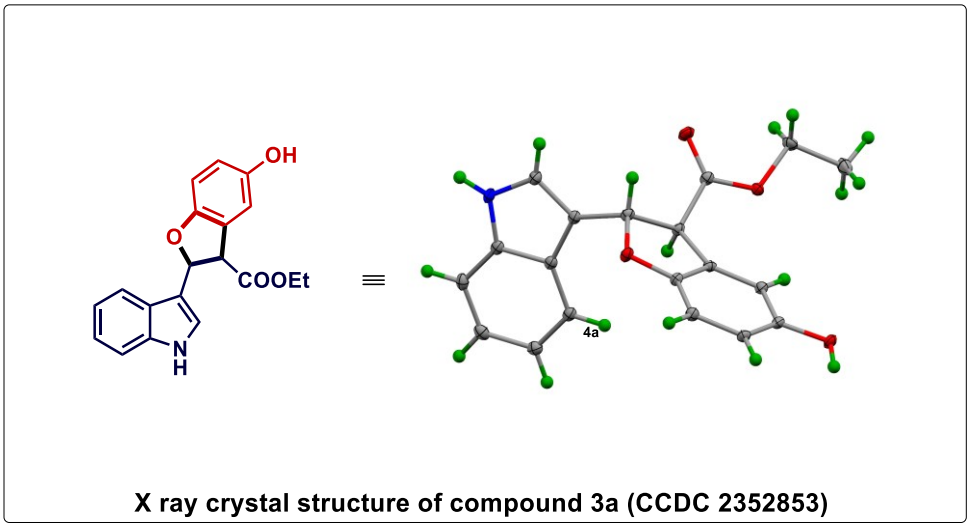
1a 6

To the magnetically stirred solution of indole-3-acrylates **1a** (0.04 g, 0.18 mmol, 1 eq.) in THF, 10 mol% of $Cu(OTf)_2$ (0.006 g, 0.018 mmol) was added at room temperature. Then the reaction mixture is allowed to stir at 40 °C till completion of reaction (monitored by TLC). After completion (6h), reaction was quenched by adding water, further the organic layer was then washed with brine and dried over Na_2SO_4. Purification by column chromatography (15% ethyl acetate in hexane) **6** obtained as a light-yellow oily liquid (0.062 g, 78%), R_f (EtOAc/ hexane 1:3) = 0.5. The obtained product was identified by ^1H, ^{13}C-NMR, DEPT, IR, HRMS data and X-ray analysis.

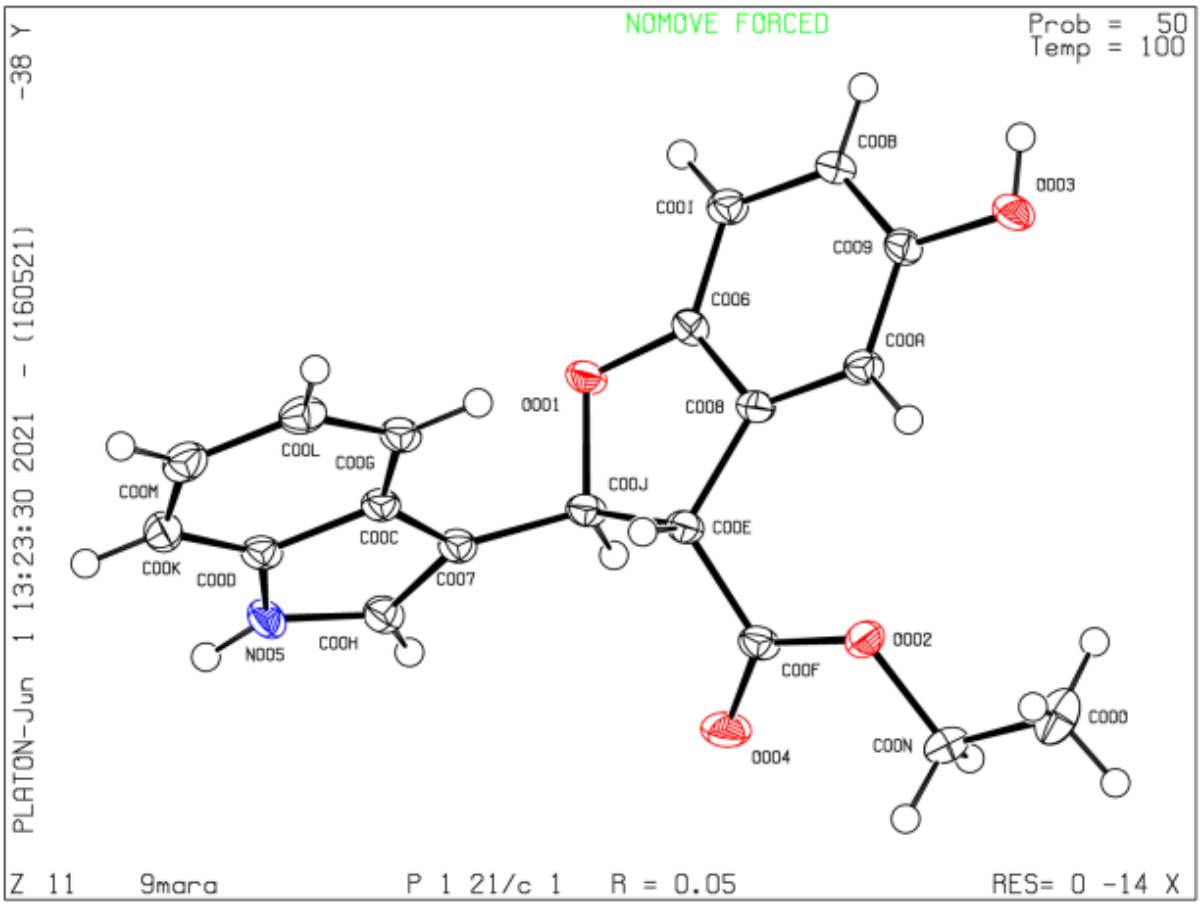
FT-IR (neat): ν_{max}/cm^{-1}: 3327, 3215, 1654, 1547, 1477, 1200, 1140, 760; **^{1}H NMR** (500 MHz, $CDCl_3$ +DMSO-d_6);δ 8.74 (s, 1H), 8.24 (s, 1H), 7.82 (s, 1H), 7.77 – 7.63 (m, 2H), 7.53 – 7.42 (m, 1H), 7.35 (s, 1H), 7.32 – 7.14 (m, 5H), 4.31 – 4.18 (m, 4H), 3.51 (d, J = 15.4 Hz, 1H), 2.54 (t, J = 12.4 Hz, 1H), 1.31 – 1.19 (m, 6H). **^{13}C {^{1}H} NMR** (126 MHz, $CDCl_3$ DMSO-d_6); δ 173.0, 164.7, 144.9, 141.0, 139.6, 135.9, 132.3, 127.8, 127.7, 126.3, 123.7, 122.7, 122.6, 120.7, 120.4, 120.3, 120.0, 112.1, 111.8, 108.5, 60.6, 59.9, 42.2, 36.3, 14.3, 14.2.; **HRMS (ESI) (**m/z): Calcd for $C_{26}H_{24}N_2O_4$ $[M + H]^+$ 431.1965; found 431.1940.

X-ray Crystallographic data:

The crystal was prepared by slow evaporation of the 3a in the solution of ethanol.



X ray crystal structure of compound 3a (CCDC 2352853)



X-ray crystallographic ortep diagram of compound 3a

Table 1: Crystal data and structure refinement for 3a

Emperical formula	C19 H17 N O4
Formula weight	323.33
Crystal color, habit	colorless, block
T / K	100(2)
Crystal system	Monoclinic
Space group	$P2_1/c$ (no. 14)
a/Å	16.790(2)
b/Å	9.1114(12)

c/Å	10.3491(13)
α/°	90.0
β/°	104.207(5)
γ/°	90.0
V/Å^3	1534.8(3)
Z	4
D_c/g cm^{-3}	1.399
μ/mm^{-1}	0.099
Reflections measured	31542
Unique reflections/R_{int}	3814/0.1111
$R(F)$ [$I > 2\sigma(I)$]	2881
$R_1{}^a$, $wR_2{}^b$ [$I > 2\sigma(I)$]	R_1 = 0.0453^a wR_2 = 0.0974^b
$R_1{}^a$, $wR_2{}^b$ (all data)	R_1 = 0.0693^a wR_2 = 0.1111^b
GOF on F^2	1.057

$^a R_1 = \Sigma(||F_o| - |F_c||) / \Sigma(|F_o|)$; $^b wR_2 = \{\Sigma[w(F_o^2 - F_c^2)_2]/\Sigma[w(F_o^2)_2]\}^{1/2}$

checkCIF/PLATON report

Structure factors have been supplied for datablock(s) 9mara

THIS REPORT IS FOR GUIDANCE ONLY. IF USED AS PART OF A REVIEW PROCEDURE FOR PUBLICATION, IT SHOULD NOT REPLACE THE EXPERTISE OF AN EXPERIENCED CRYSTALLOGRAPHIC REFEREE.

No syntax errors found. CIF dictionary Interpreting this report

Datablock: 9mara

Bond precision: C-C = 0.0023 A Wavelength=0.71073

Cell: a=16.790(2) b=9.1114(12) c=10.3491(13)
alpha=90 beta=104.207(5) gamma=90
Temperature: 100 K

	Calculated	Reported
Volume	1534.8(3)	1534.8(3)
Space group	P 21/c	P 1 21/c 1
Hall group	-P 2ybc	-P 2ybc
Moiety formula	C19 H17 N O4	C19 H17 N O4
Sum formula	C19 H17 N O4	C19 H17 N O4
Mr	323.34	323.33
Dx,g cm-3	1.399	1.399
Z	4	4
Mu (mm-1)	0.099	0.099
F000	680.0	680.0
F000'	680.35	
h,k,lmax	22,12,13	22,12,13
Nref	3843	3814
Tmin,Tmax	0.993,0.995	0.607,0.746
Tmin'	0.990	

Correction method= # Reported T Limits: Tmin=0.607 Tmax=0.746
AbsCorr = MULTI-SCAN

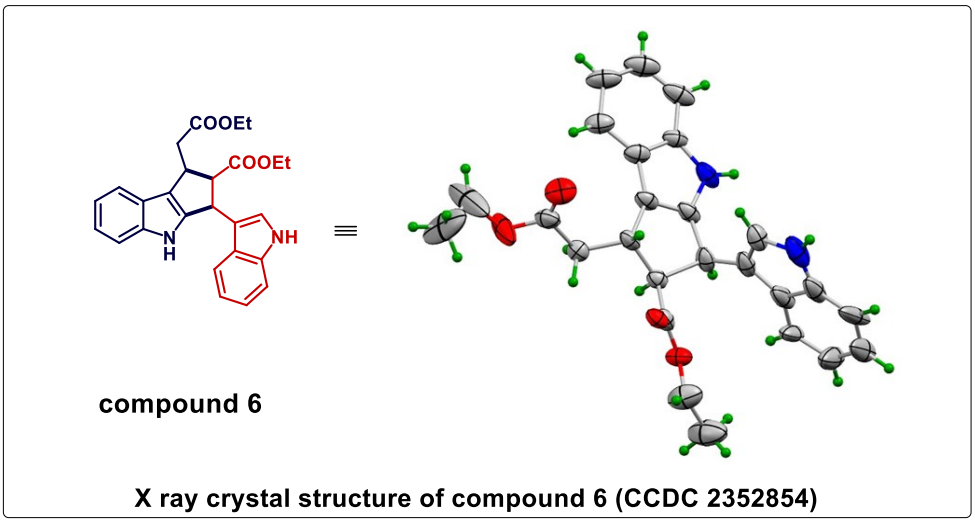
Data completeness= 0.992 Theta(max)= 28.370

R(reflections)= 0.0453(2881) wR2(reflections)= 0.1111(3814)

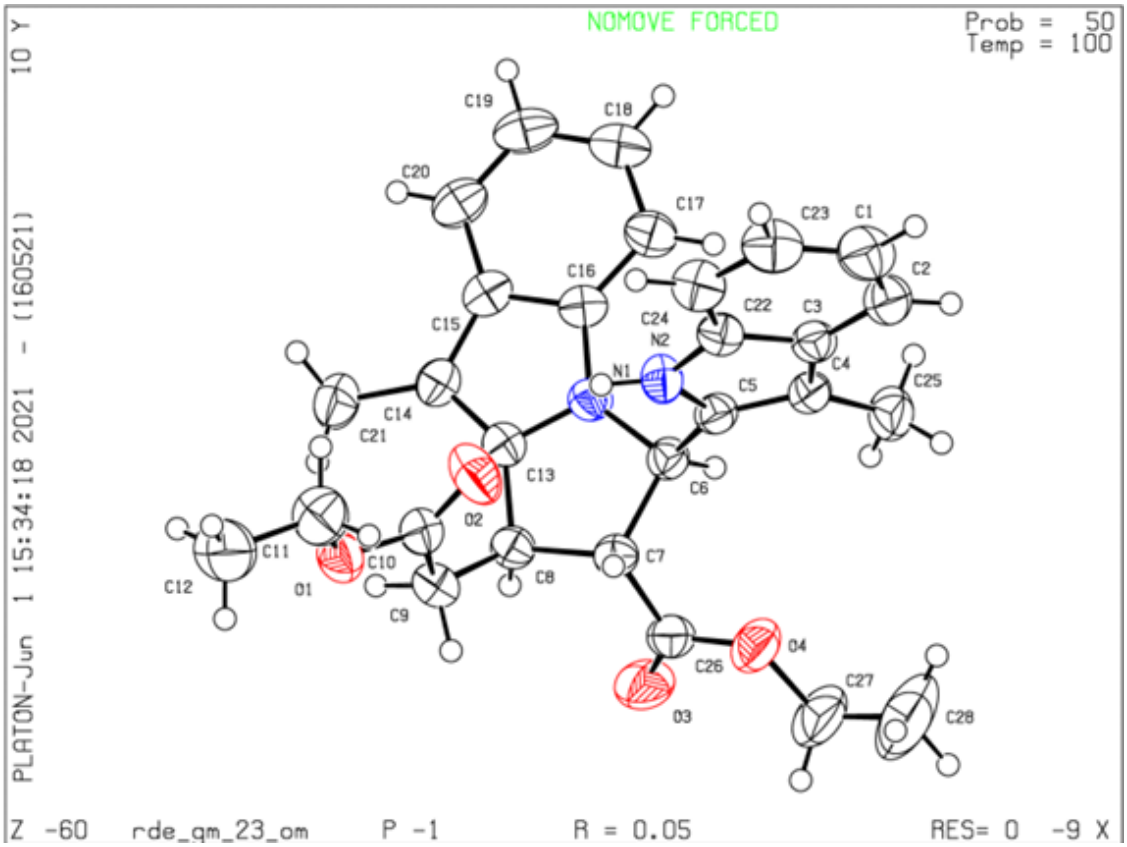
S = 1.057 Npar= 220

The following ALERTS were generated. Each ALERT has the format
test-name_ALERT_alert-type_alert-level.
Click on the hyperlinks for more details of the test.

The crystal was prepared by slow evaporation of the compound 6 in the solution of ethanol.



X ray crystal structure of compound 6 (CCDC 2352854)



X-ray crystallographic ortep diagram of compound 6

checkCIF/PLATON report

Structure factors have been supplied for datablock(s) rde_gm_23_om

THIS REPORT IS FOR GUIDANCE ONLY. IF USED AS PART OF A REVIEW PROCEDURE FOR PUBLICATION, IT SHOULD NOT REPLACE THE EXPERTISE OF AN EXPERIENCED CRYSTALLOGRAPHIC REFEREE.

No syntax errors found. CIF dictionary Interpreting this report

Datablock: rde_gm_23_om

Bond precision: C-C = 0.0030 A Wavelength=0.71073

Cell: a=8.3294(19) b=9.907(2) c=16.337(4)
alpha=75.760(3) beta=78.824(3) gamma=69.309(3)
Temperature: 100 K

	Calculated	Reported
Volume	1213.9(5)	1213.9(5)
Space group	P -1	P -1
Hall group	-P 1	-P 1
Moiety formula	C28 H30 N2 O4	C28 H30 N2 O4
Sum formula	C28 H30 N2 O4	C28 H30 N2 O4
Mr	458.54	458.54
Dx,g cm-3	1.255	1.254
Z	2	2
Mu (mm-1)	0.084	0.084
F000	488.0	488.0
F000'	488.22	
h,k,lmax	10,12,20	10,12,20
Nref	5337	5317
Tmin,Tmax	0.995,0.997	0.660,0.746
Tmin'	0.992	

Correction method= # Reported T Limits: Tmin=0.660 Tmax=0.746
AbsCorr = MULTI-SCAN

Data completeness= 0.996 Theta(max)= 27.055

R(reflections)= 0.0486(3728) wR2(reflections)= 0.1345(5317)

S = 1.032 Npar= 319

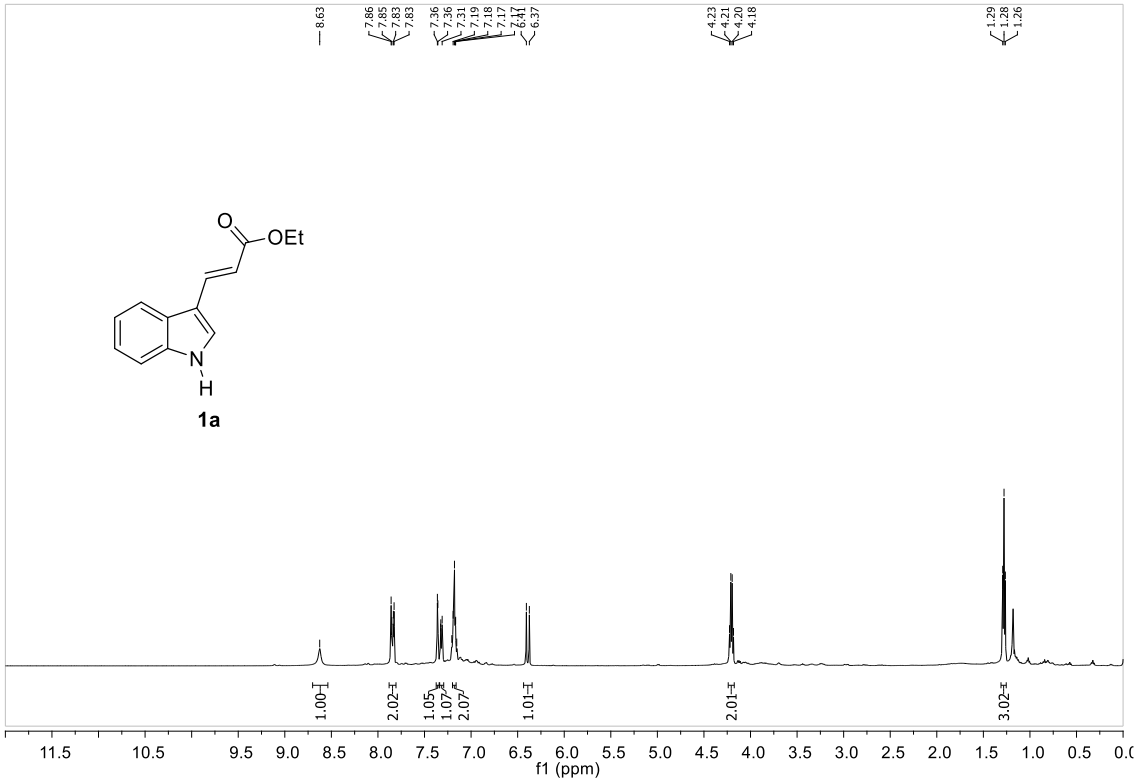
The following ALERTS were generated. Each ALERT has the format
test-name_ALERT_alert-type_alert-level.
Click on the hyperlinks for more details of the test.

Table.2 Crystal data and structure refinement for 6

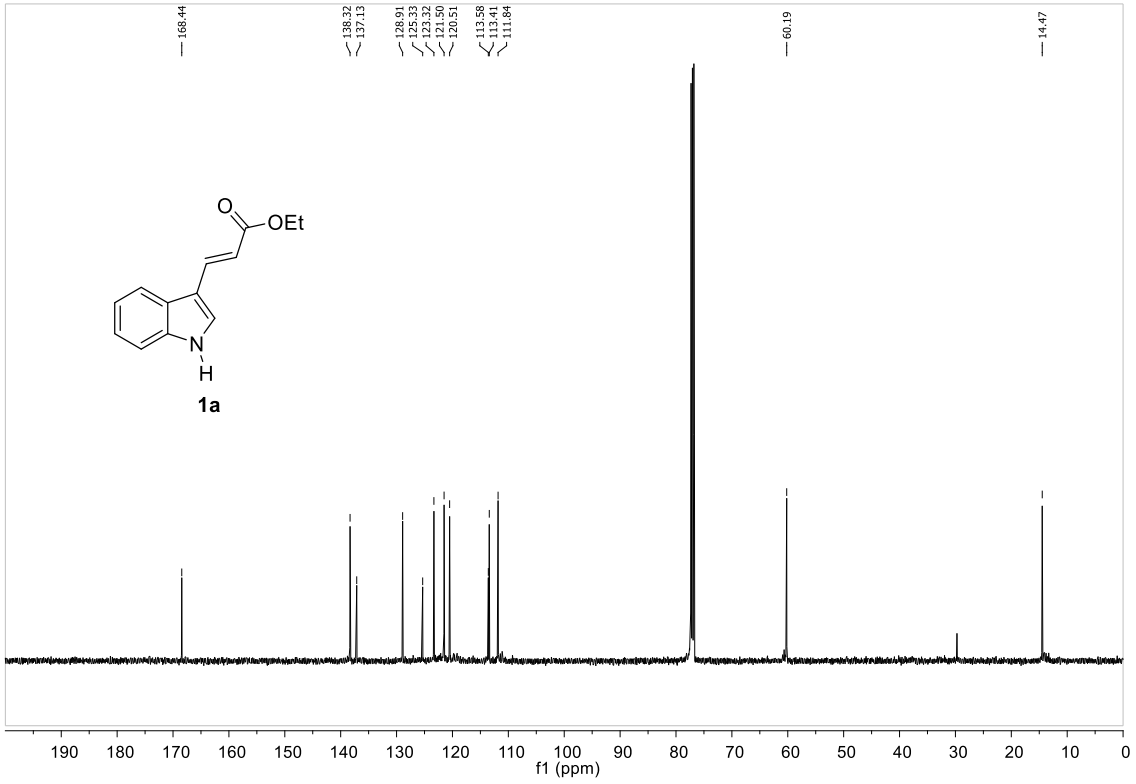
Emperical formula	$C_{26}H_{26}N_2O_4$
Formula weight	430.50
Crystal color, habit	colorless, needle
T / K	100(2)
Crystal system	Monoclinic
Space group	$P2_1/c$ (no. 14)
a/Å	14.203(3)
b/Å	12.372(3)
c/Å	25.592(5)
α/°	90.0
β /°	104.499(6)
γ /°	90.0
V/Å^3	4353.7(15)
Z	8
D_c/g cm^{-3}	1.303
μ/mm^{-1}	0.089
Reflections measured	38332
Unique reflections/R_{int}	10772/0.0790
Final R indexes [I>=2σ (I)]	R_1 = 0.1811, wR_2 = 0.4490
$R_1{}^a$, $wR_2{}^b$ (all data)	R_1 = 0.02916^a wR_2 = 0.5306^b
GOF on F^2	1.590

$^aR_1 = \Sigma(||F_o| - |F_c||) / \Sigma(|F_o|)$; $^bwR_2 = \{\Sigma[w(F_o^2 - F_c^2)_2]/\Sigma[w(F_o^2)_2]\}^{1/2}$

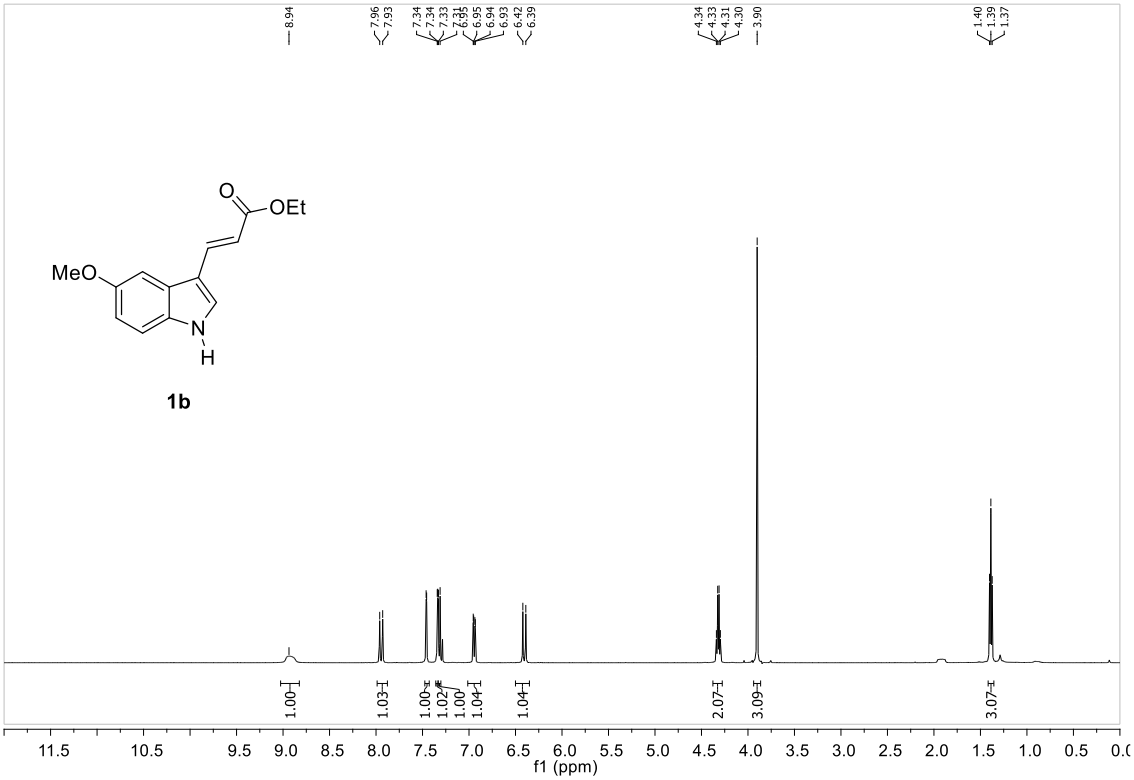
NMR Spectra: **^{1}H NMR** (500 MHz, $CDCl_3$) spectrum of **1a**



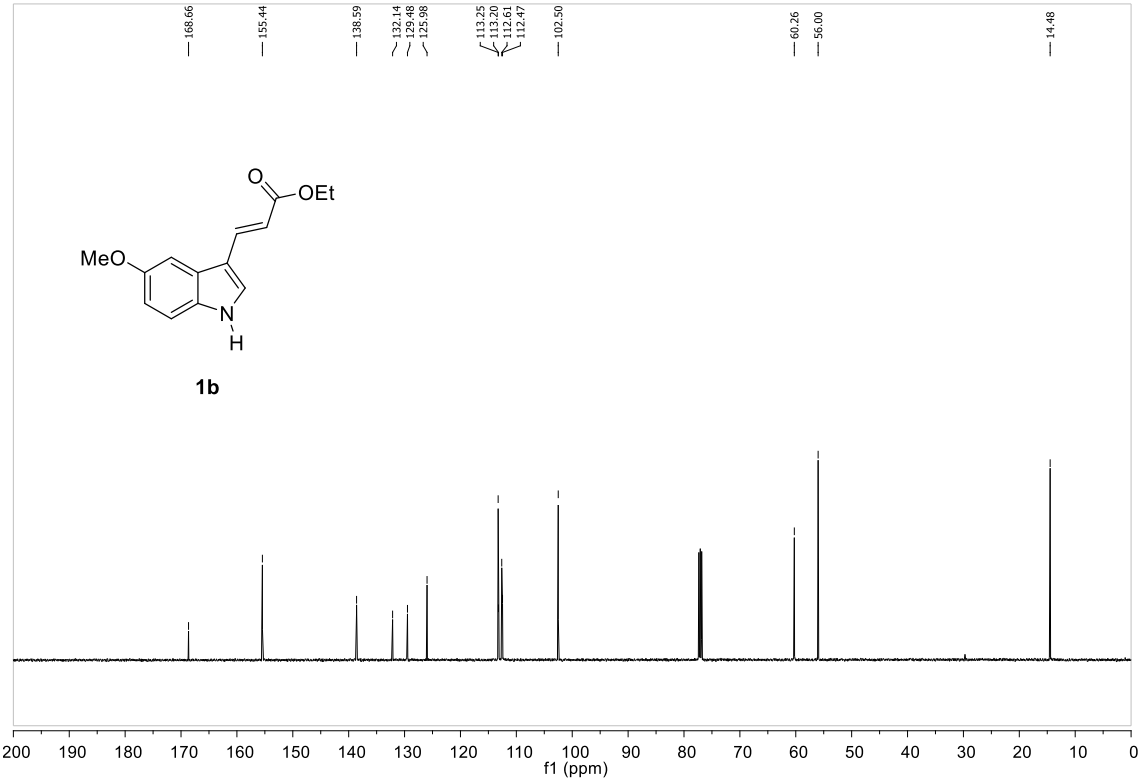
^{13}C {^{1}H} NMR (126 MHz, $CDCl_3$) spectrum of **1a**



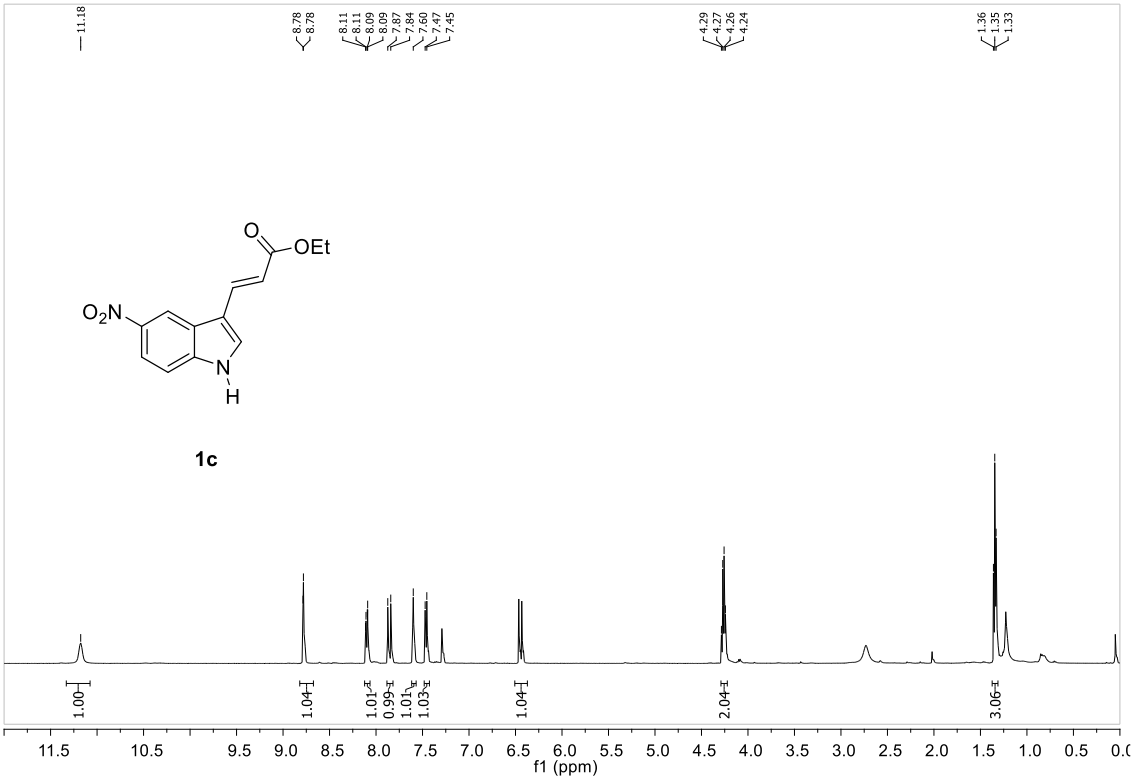
^{1}H NMR (500 MHz, $CDCl_3$) spectrum of **1b**



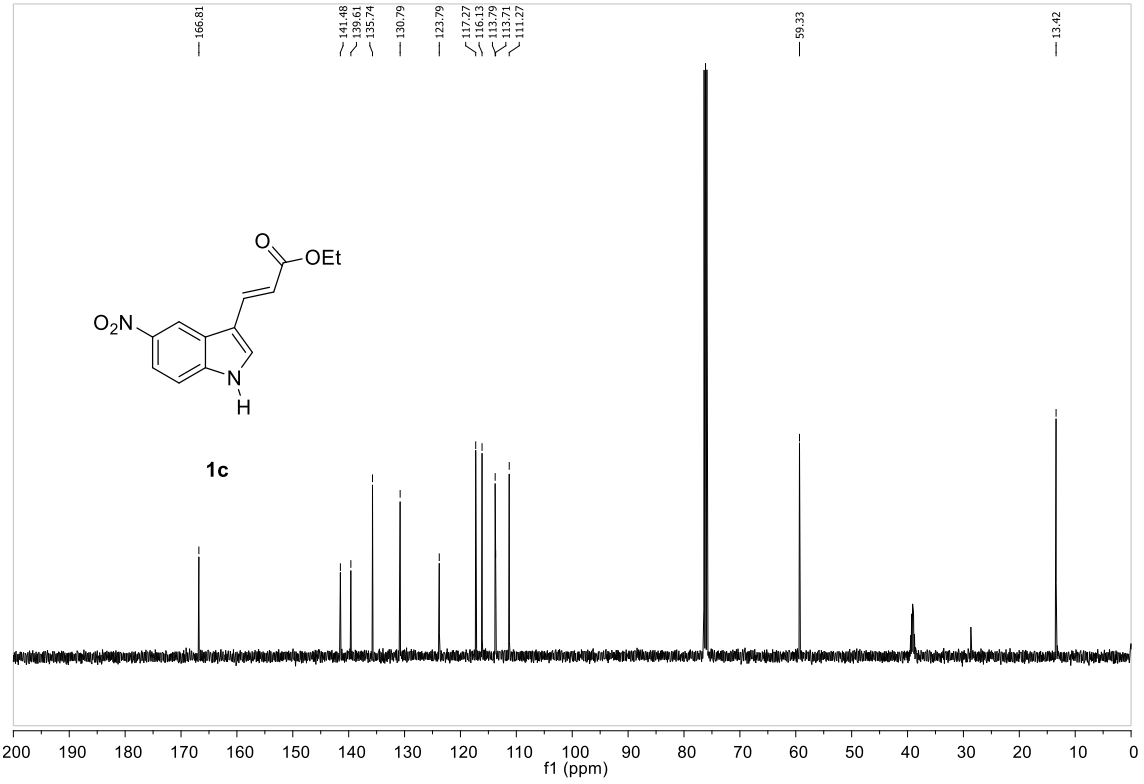
^{13}C {^{1}H} NMR (126 MHz, $CDCl_3$) spectrum of **1b**



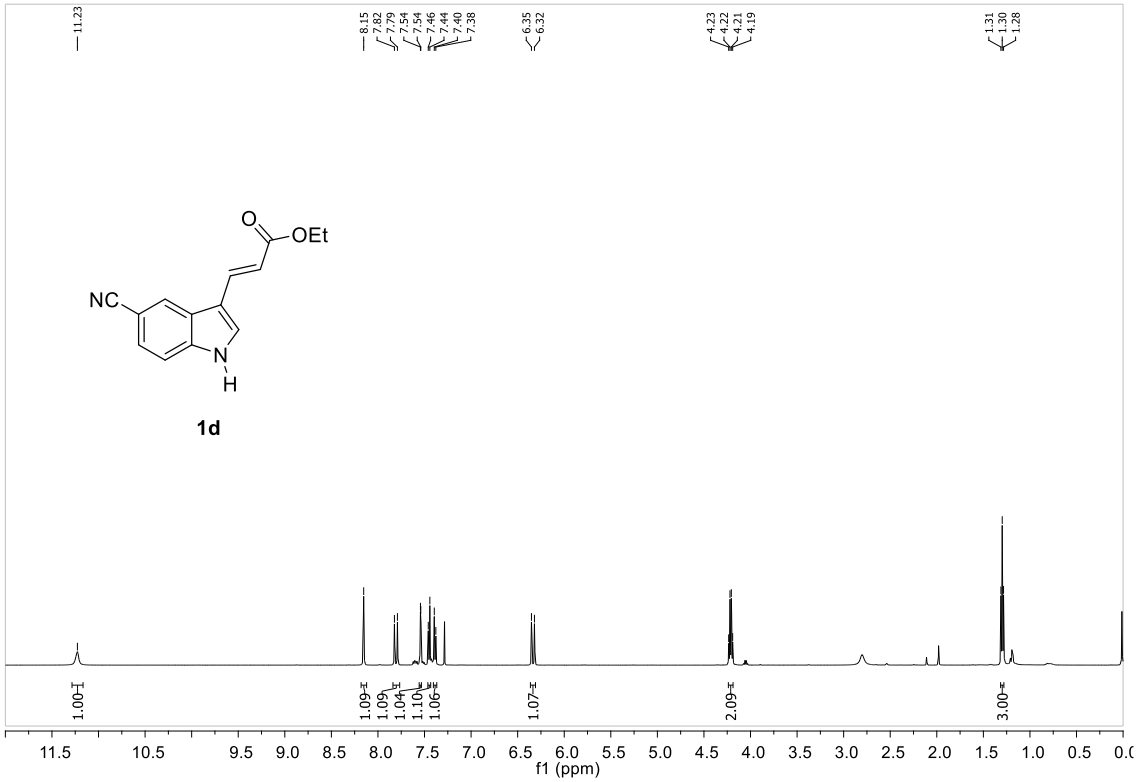
^{1}H NMR (500 MHz, $CDCl_3$) spectrum of **1c**



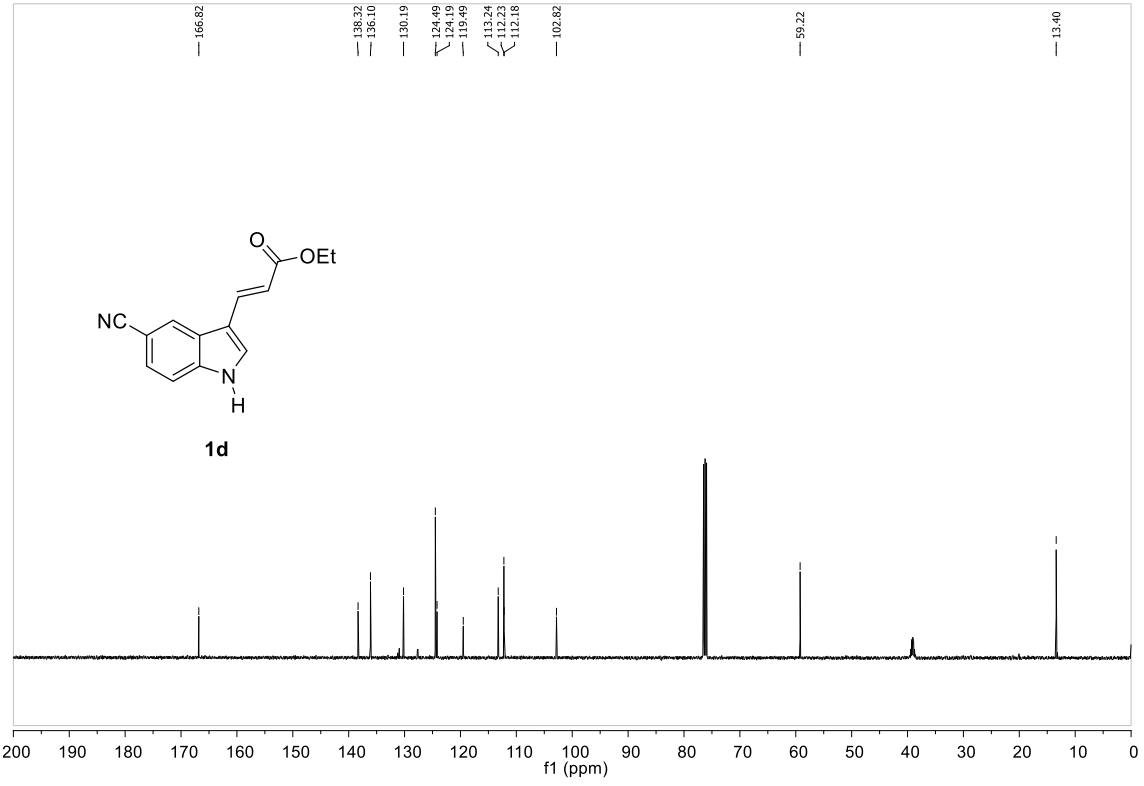
^{13}C {^{1}H} NMR (126 MHz, $CDCl_3$) spectrum of **1c**



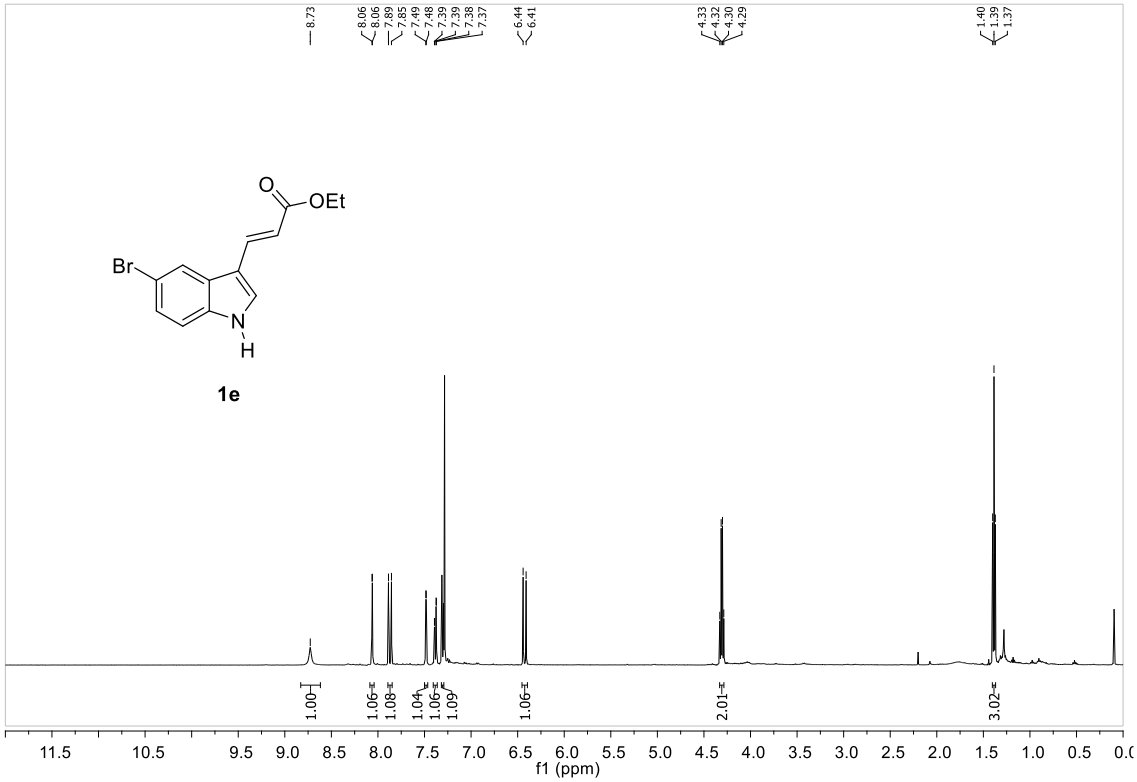
^{1}H NMR (500 MHz, $CDCl_3$) spectrum of **1d**



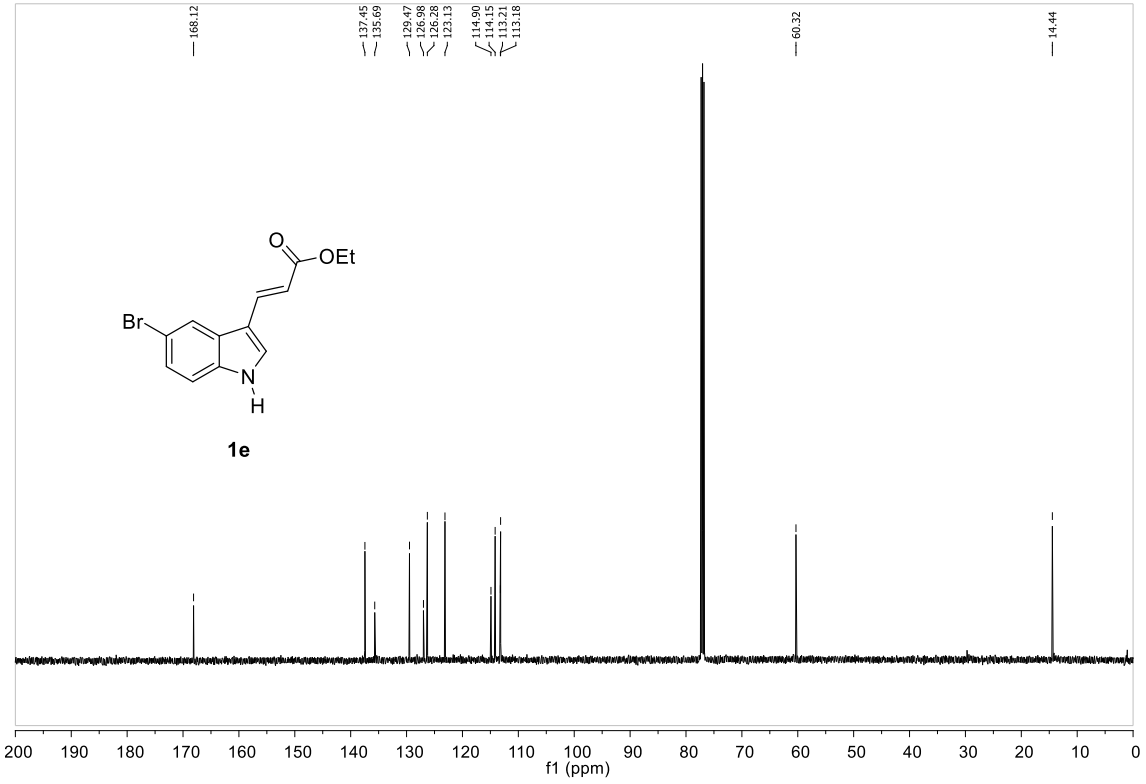
^{13}C {^{1}H} NMR (126 MHz, $CDCl_3$) spectrum of **1d**



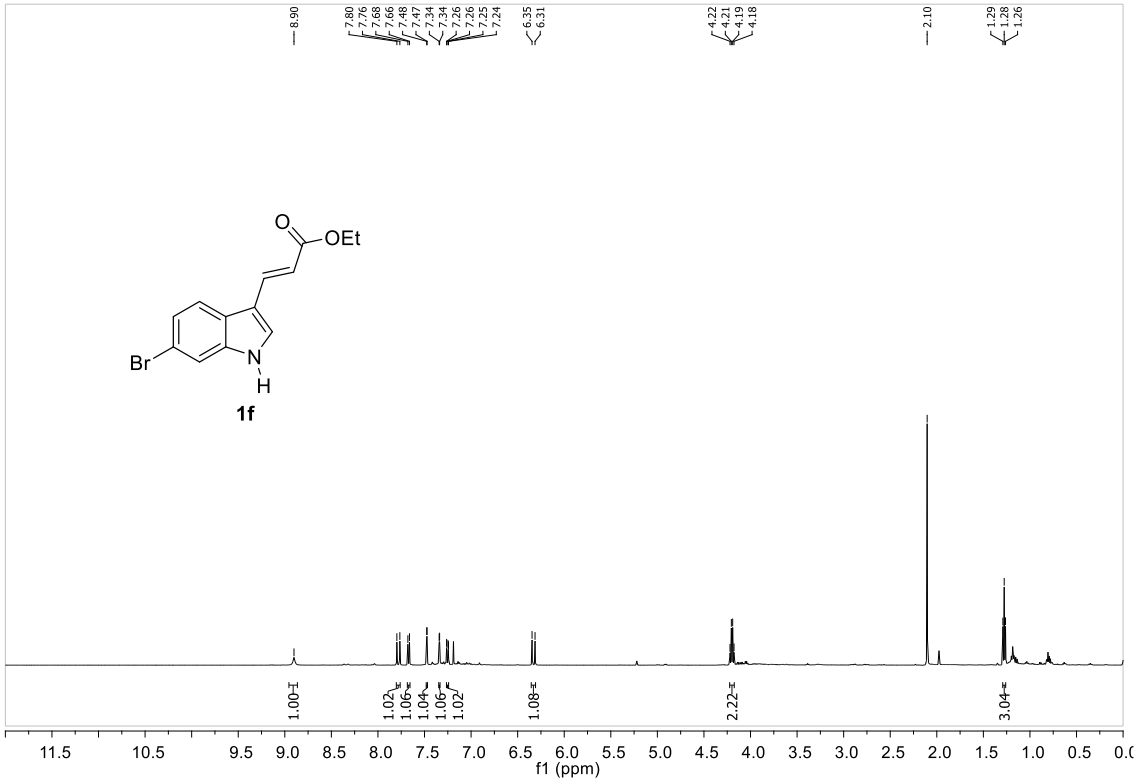
^{1}H NMR (500 MHz, $CDCl_3$) spectrum of **1e**



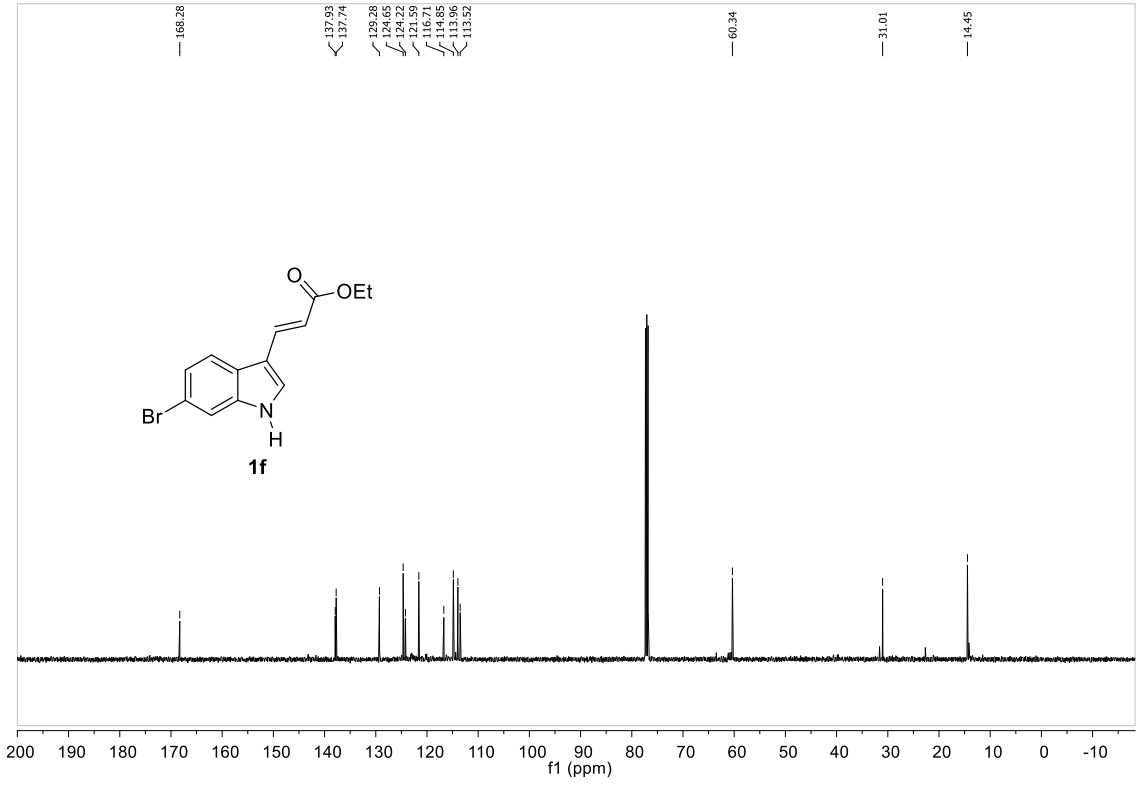
^{13}C {^{1}H} NMR (126 MHz, $CDCl_3$) spectrum of **1e**



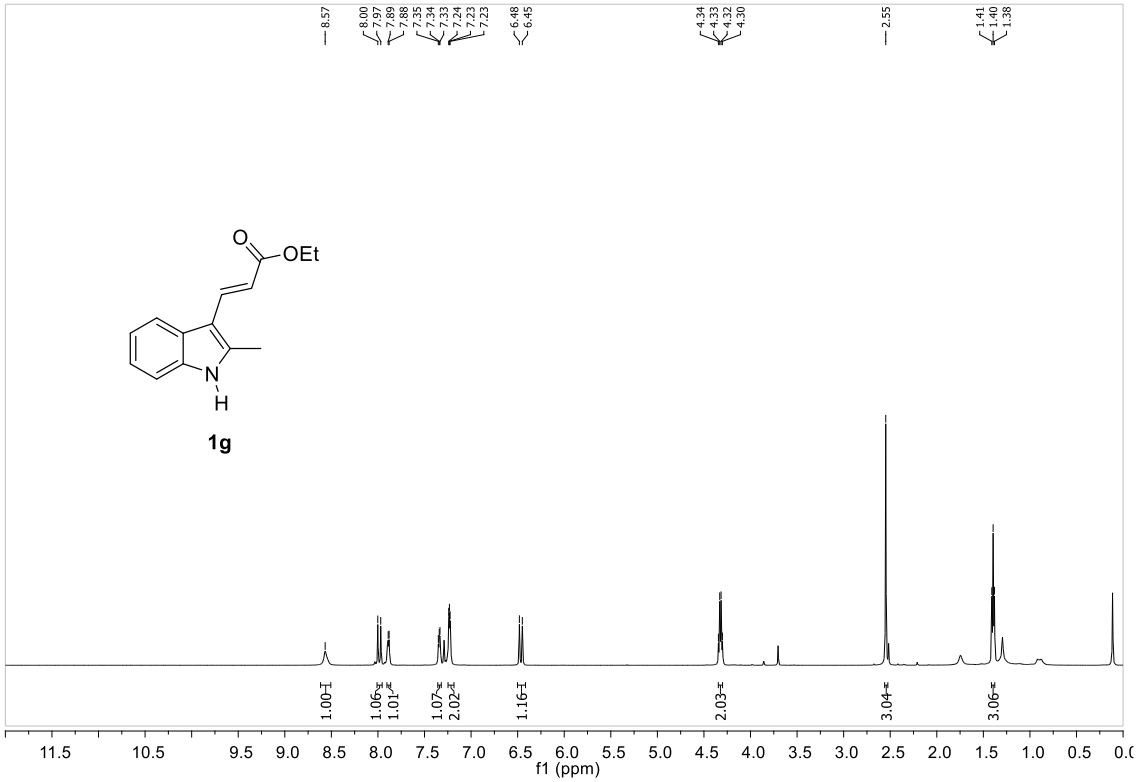
^{1}H NMR (500 MHz, $CDCl_3$) spectrum of **1f**



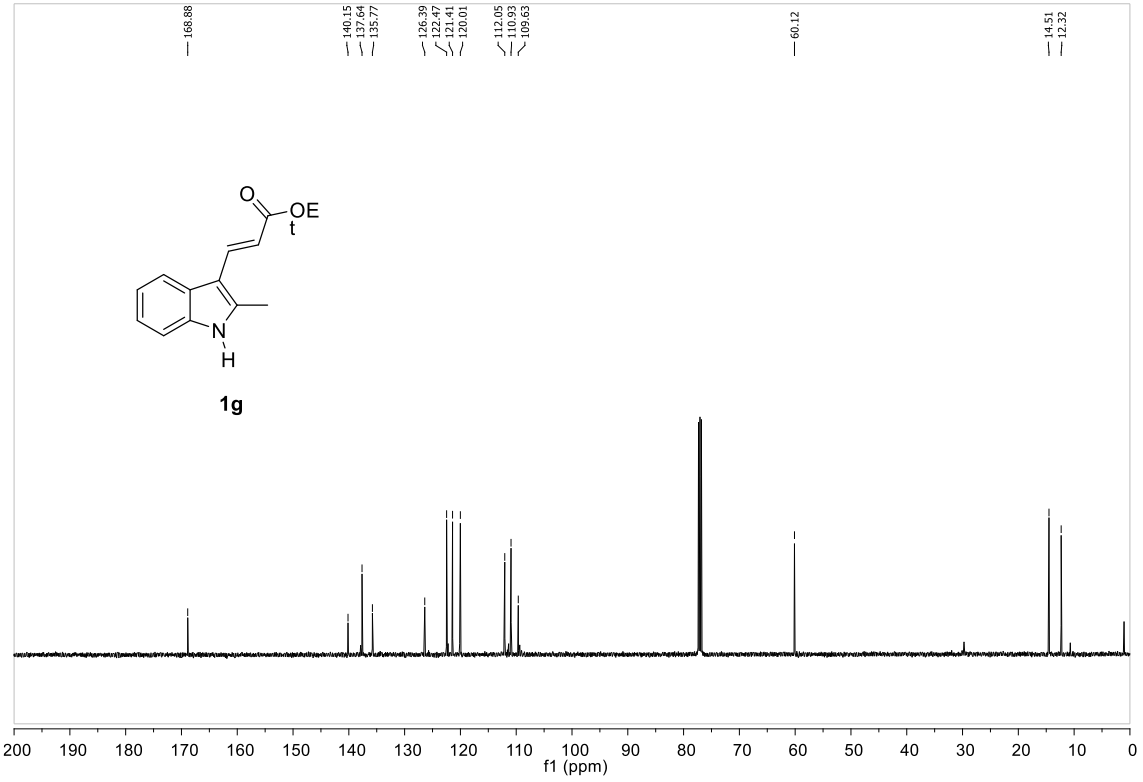
^{13}C {^{1}H} NMR (126 MHz, $CDCl_3$) spectrum of **1f**



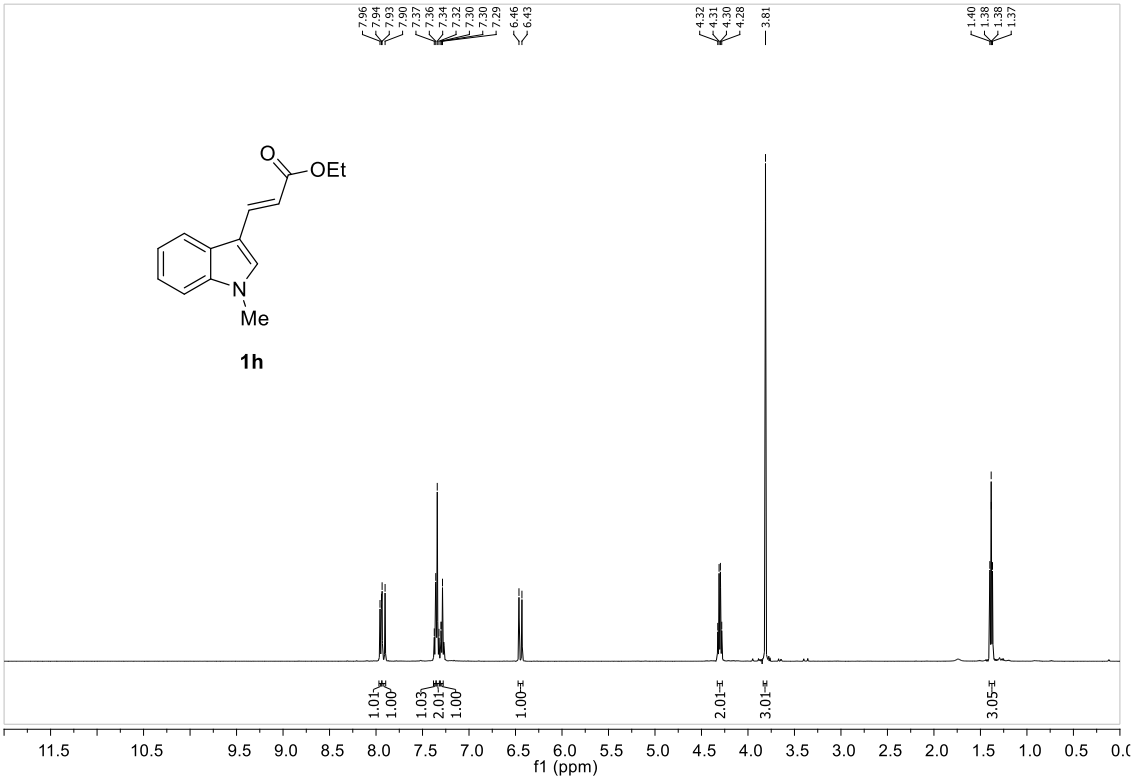
^{1}H NMR (500 MHz, $CDCl_3$) spectrum of **1g**



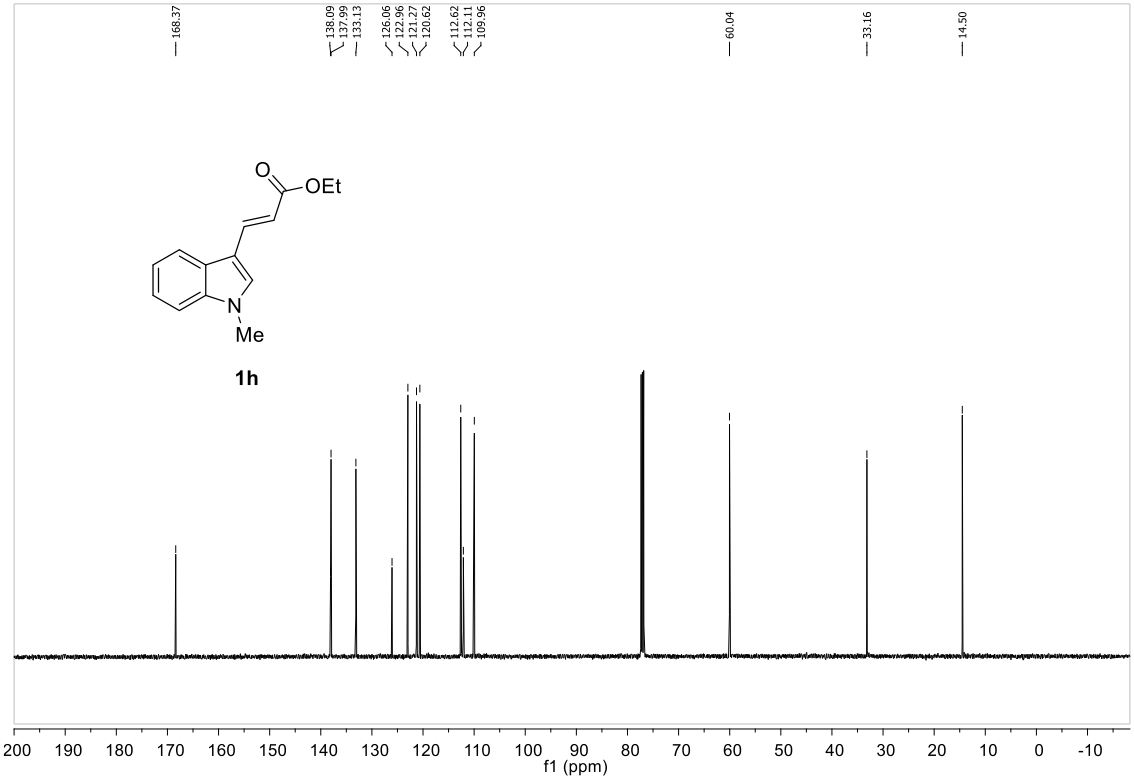
^{13}C {^{1}H} NMR (126 MHz, $CDCl_3$) spectrum of **1g**



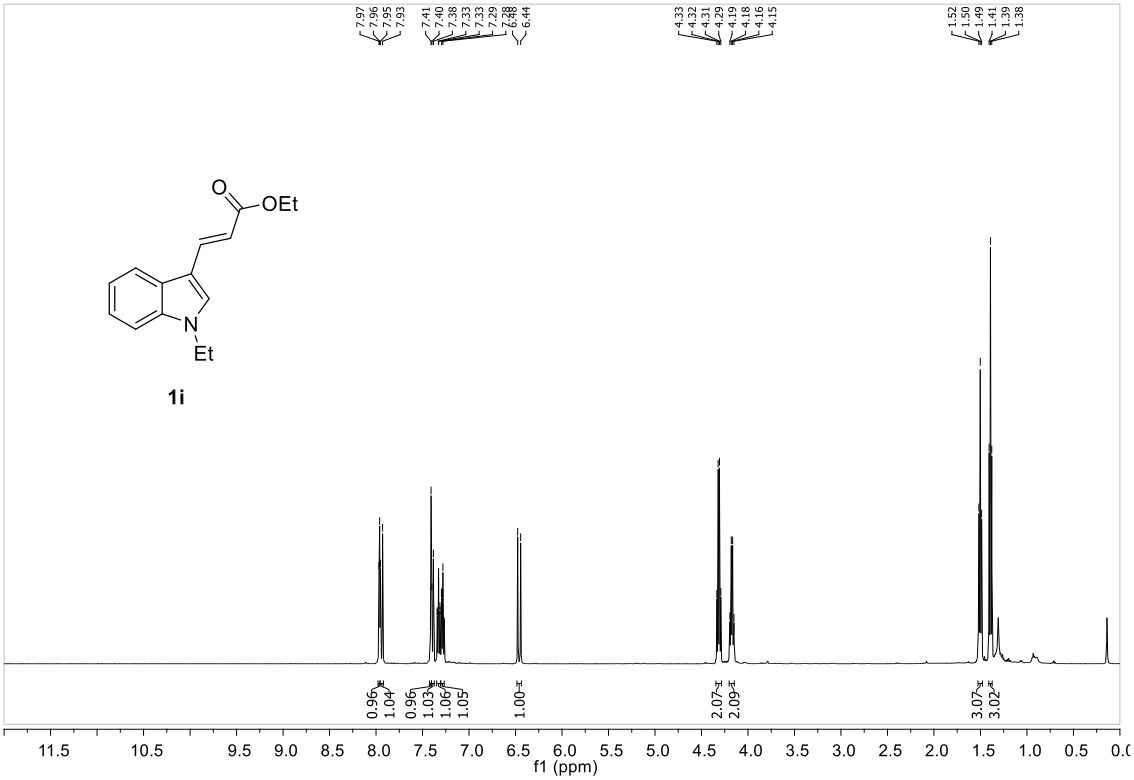
^{1}H NMR (500 MHz, $CDCl_3$) spectrum of **1h**



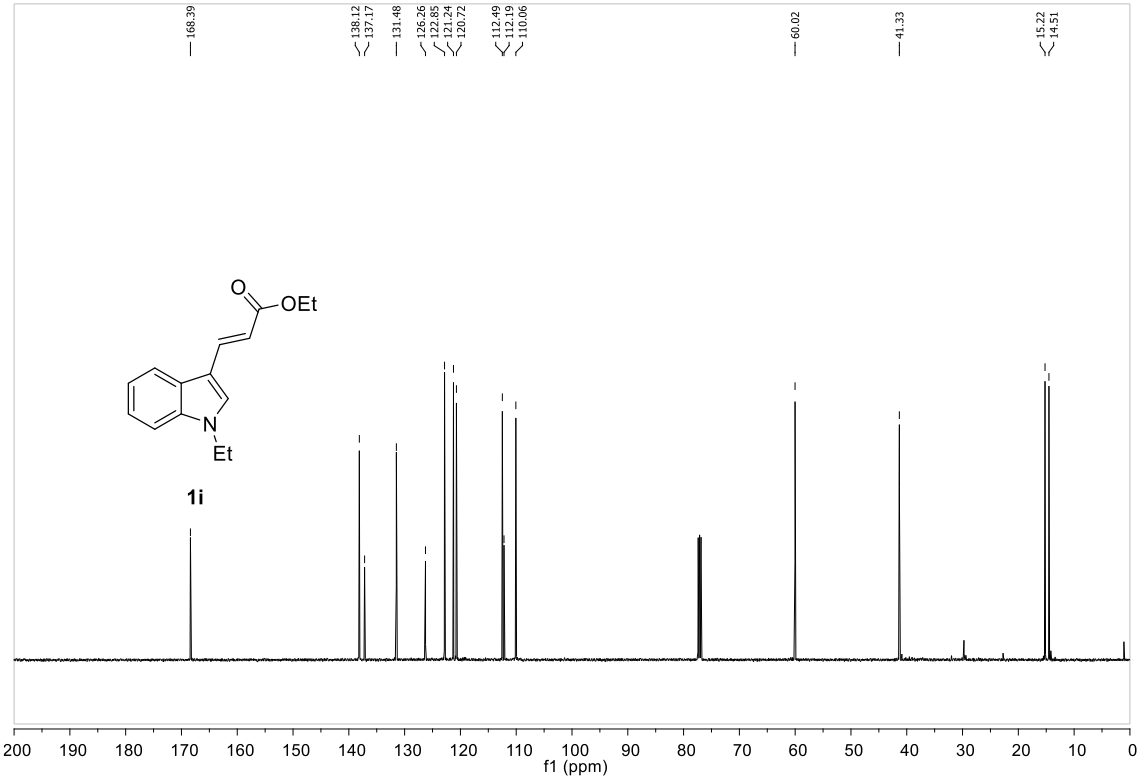
^{13}C {^{1}H} NMR (126 MHz, $CDCl_3$) spectrum of **1h**



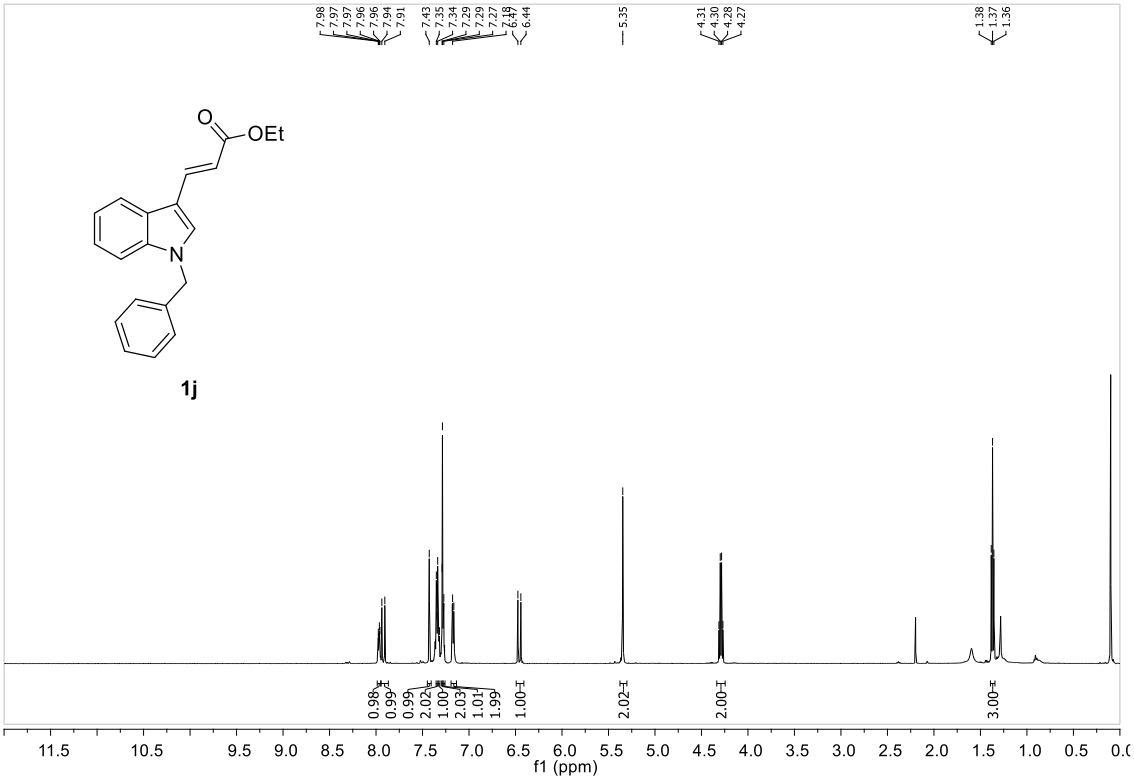
^{1}H NMR (500 MHz, $CDCl_3$) spectrum of **1i**



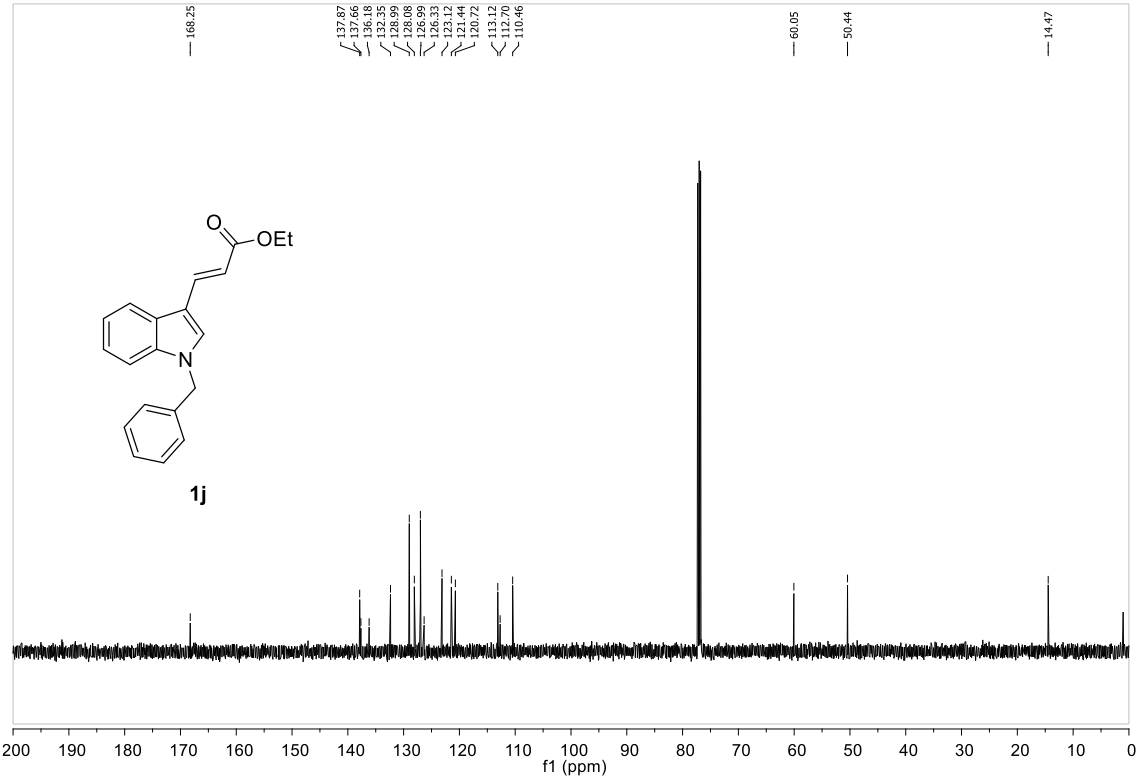
^{13}C {^{1}H} NMR (126 MHz, $CDCl_3$) spectrum of **1i**



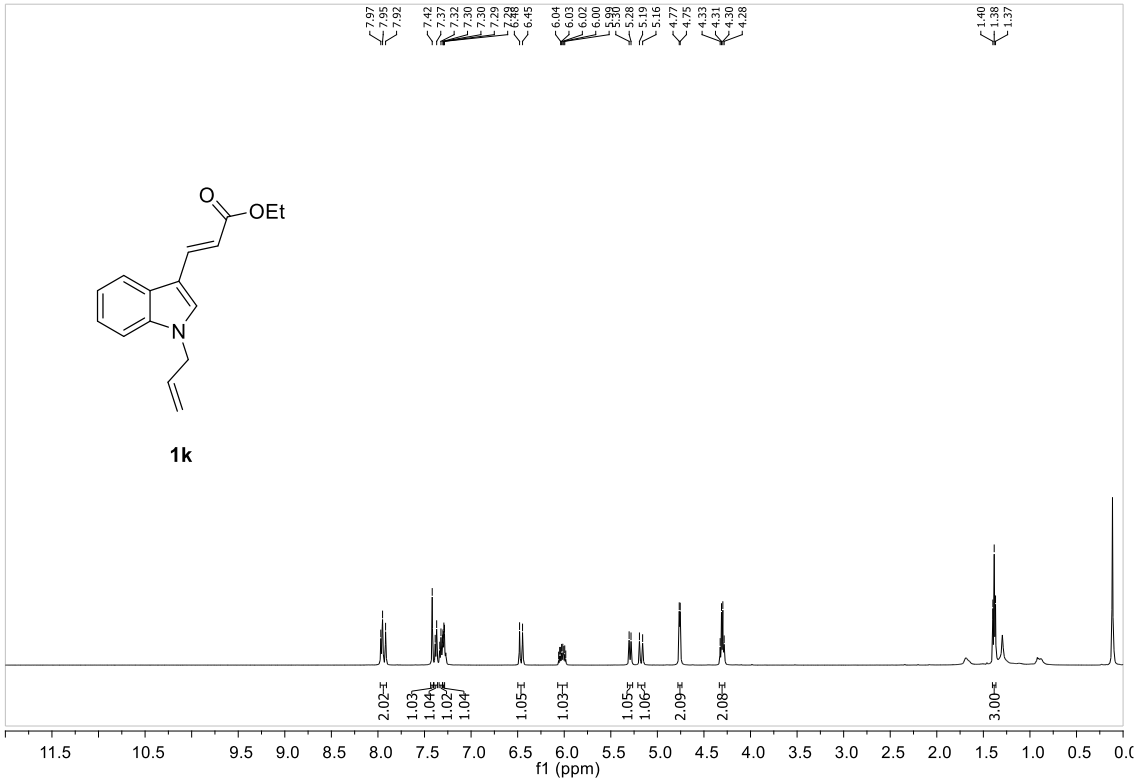
H NMR (500 MHz, $CDCl_3$) spectrum of **1j**



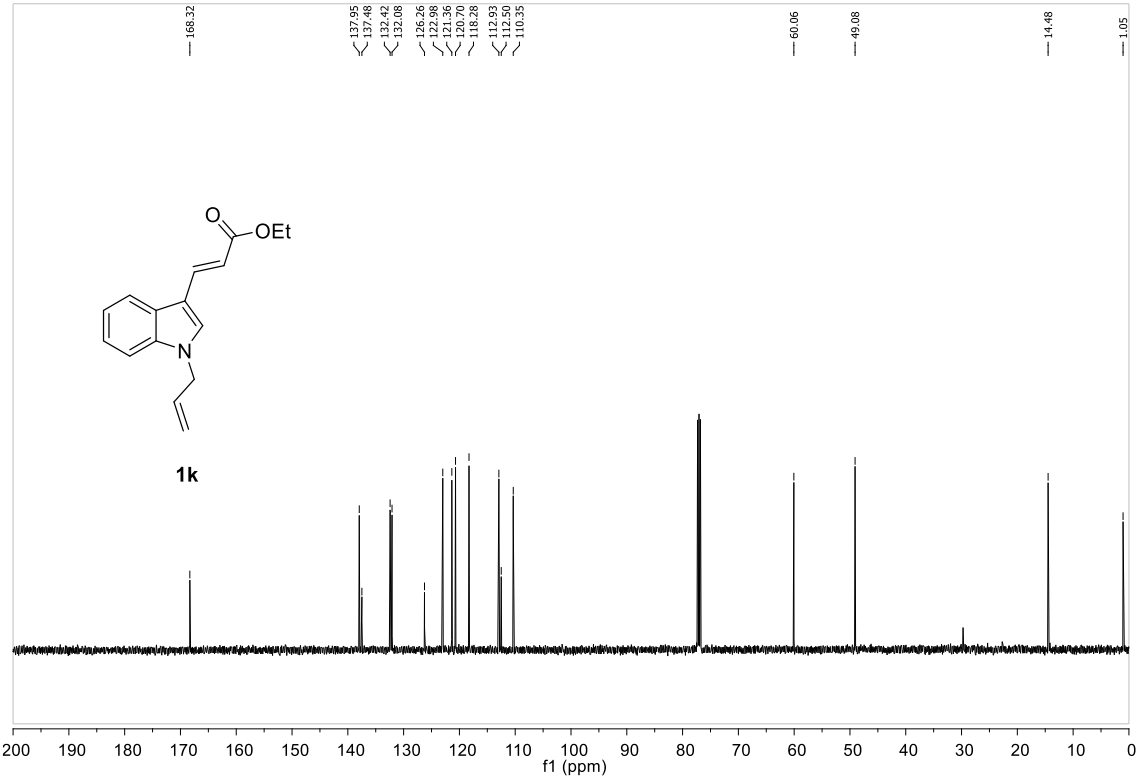
^{13}C {^{1}H} NMR (126 MHz, $CDCl_3$) spectrum of **1j**



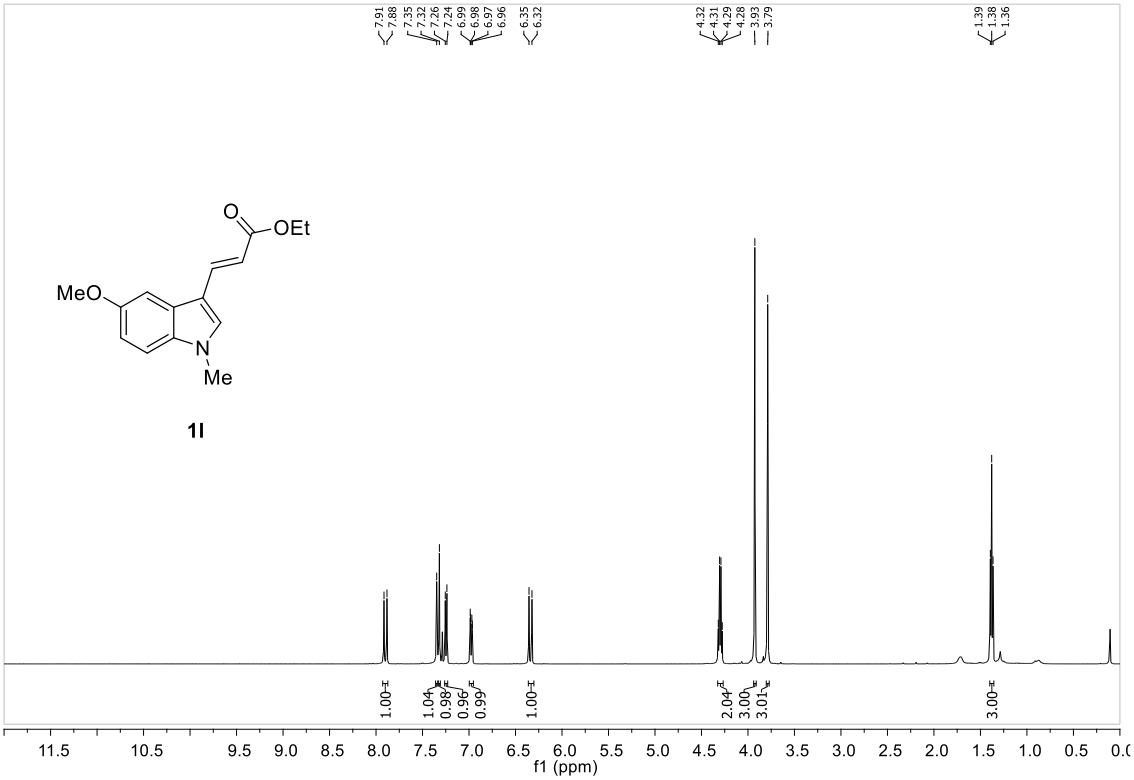
^{1}H NMR (500 MHz, $CDCl_3$) spectrum of **1k**



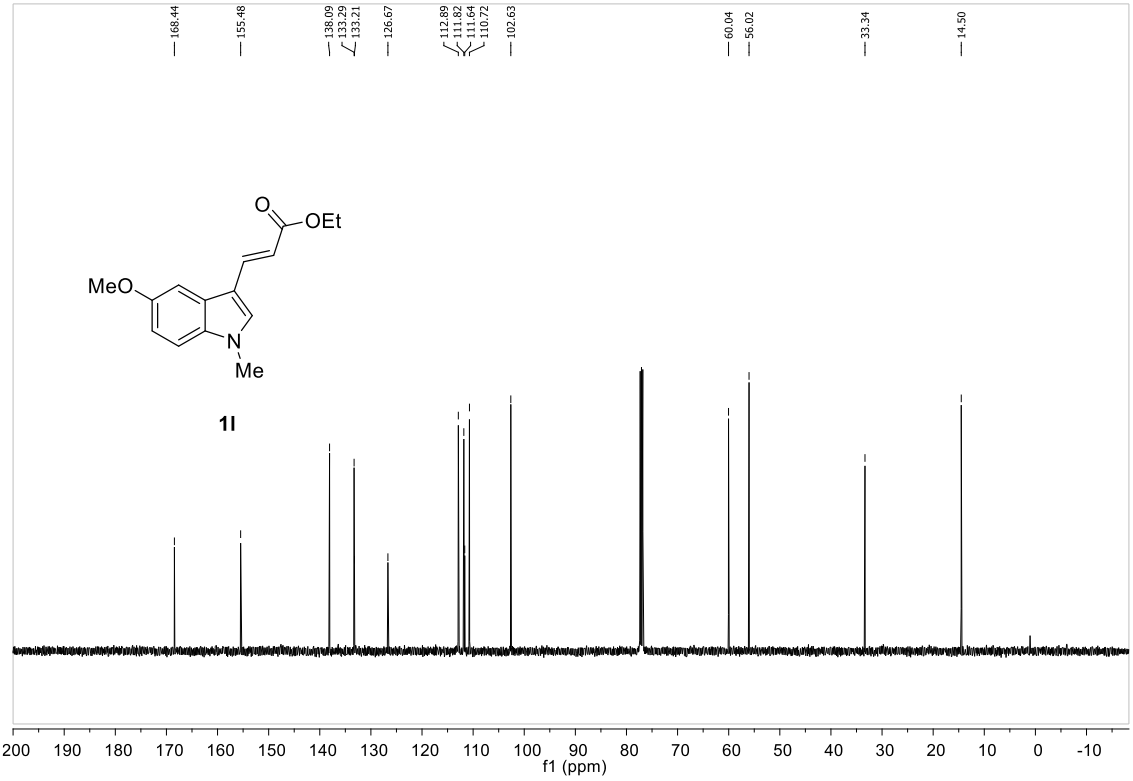
^{13}C {^{1}H} NMR (126 MHz, $CDCl_3$) spectrum of **1k**



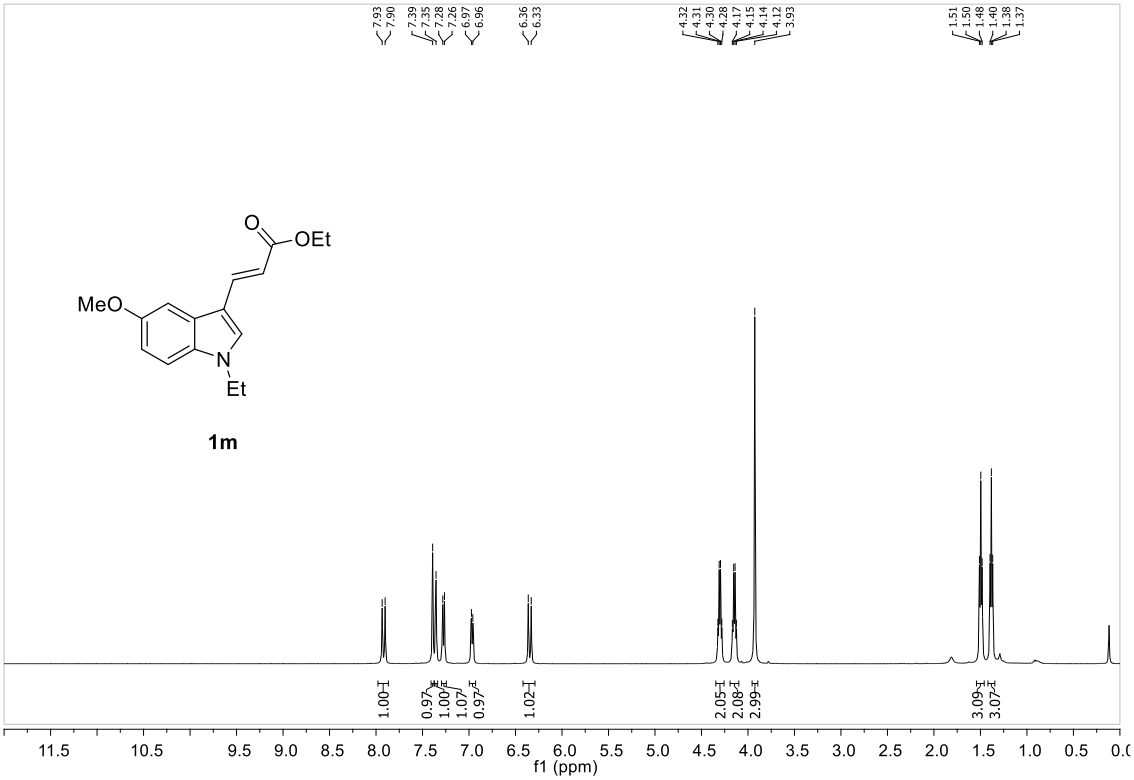
^{1}H NMR (500 MHz, $CDCl_3$) spectrum of **1l**



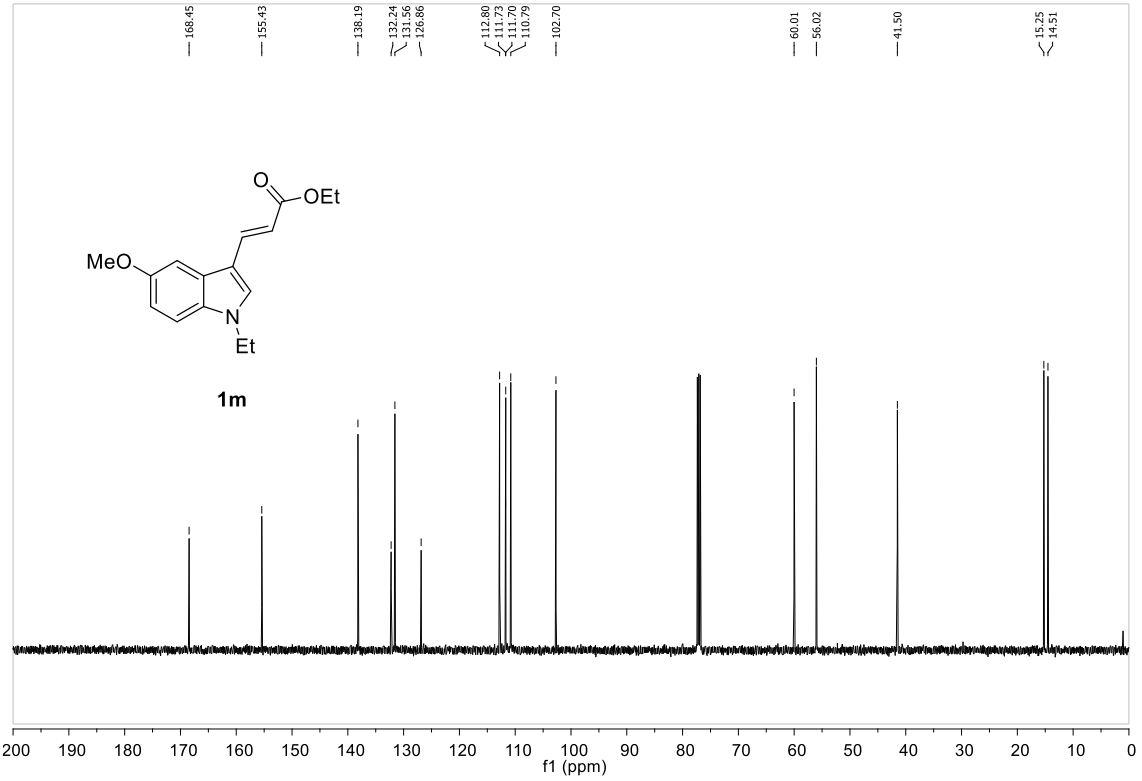
^{13}C {^{1}H} NMR (126 MHz, $CDCl_3$) spectrum of **1l**



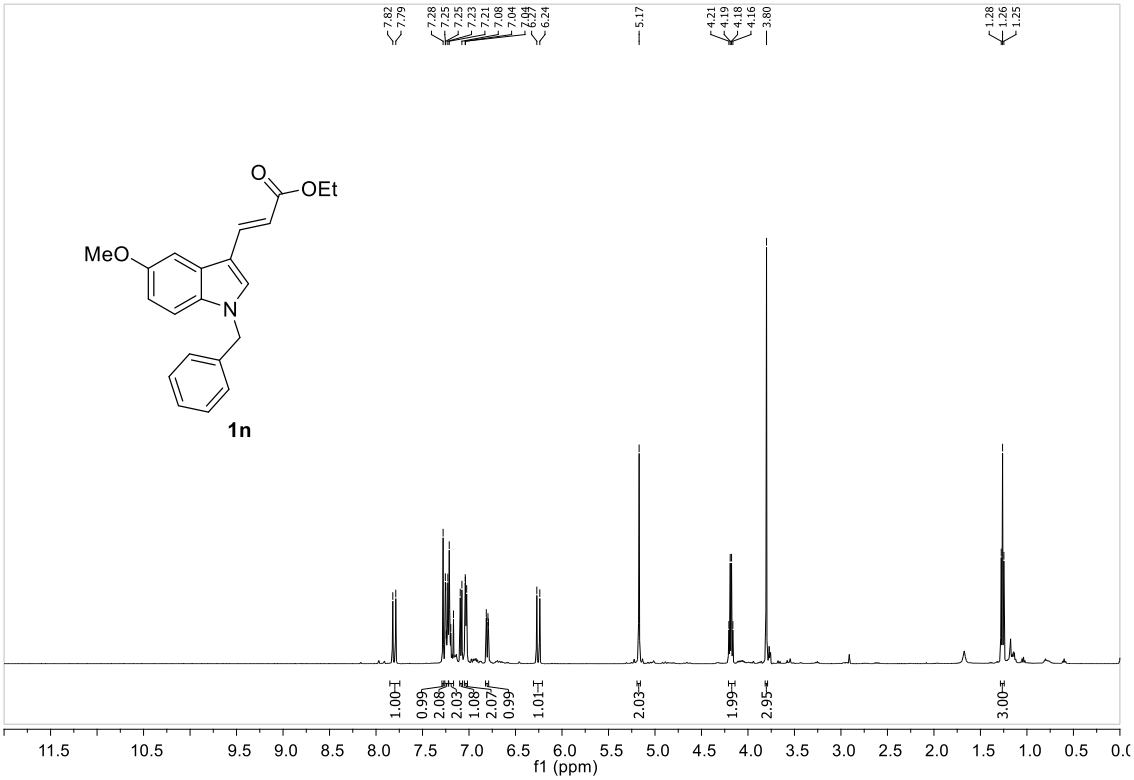
^{1}H NMR (500 MHz, $CDCl_3$) spectrum of **1m**



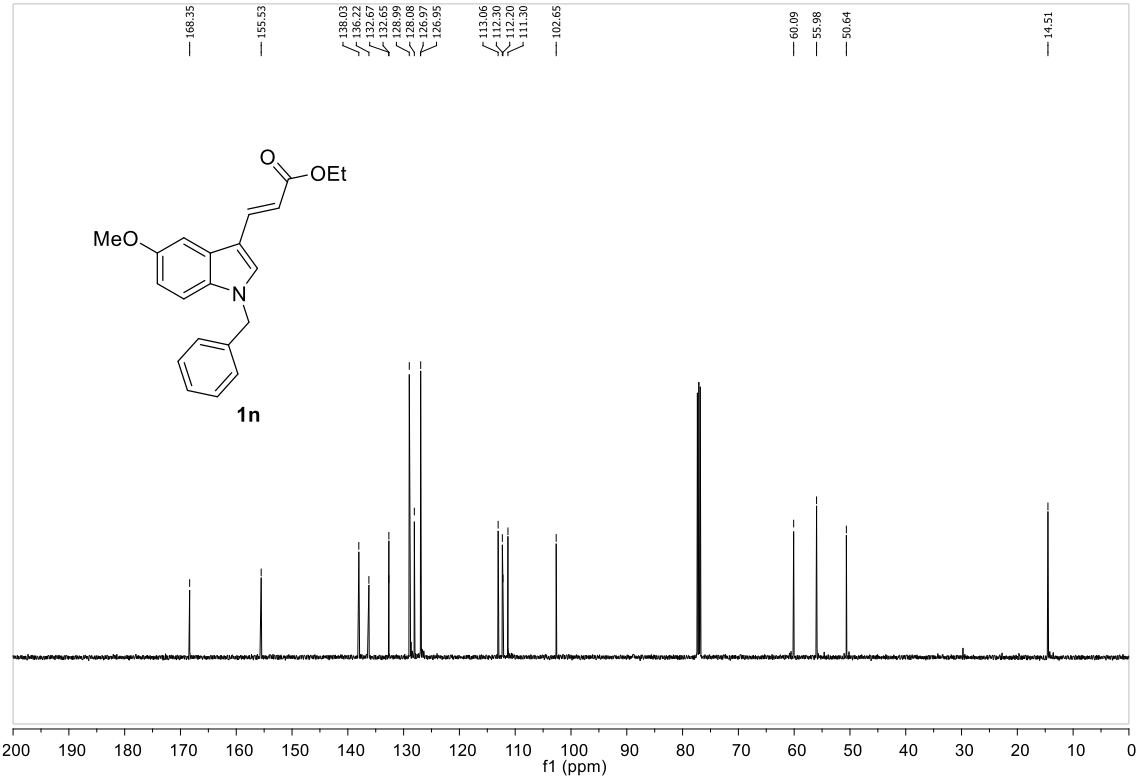
^{13}C {^{1}H} NMR (126 MHz, $CDCl_3$) spectrum of **1m**



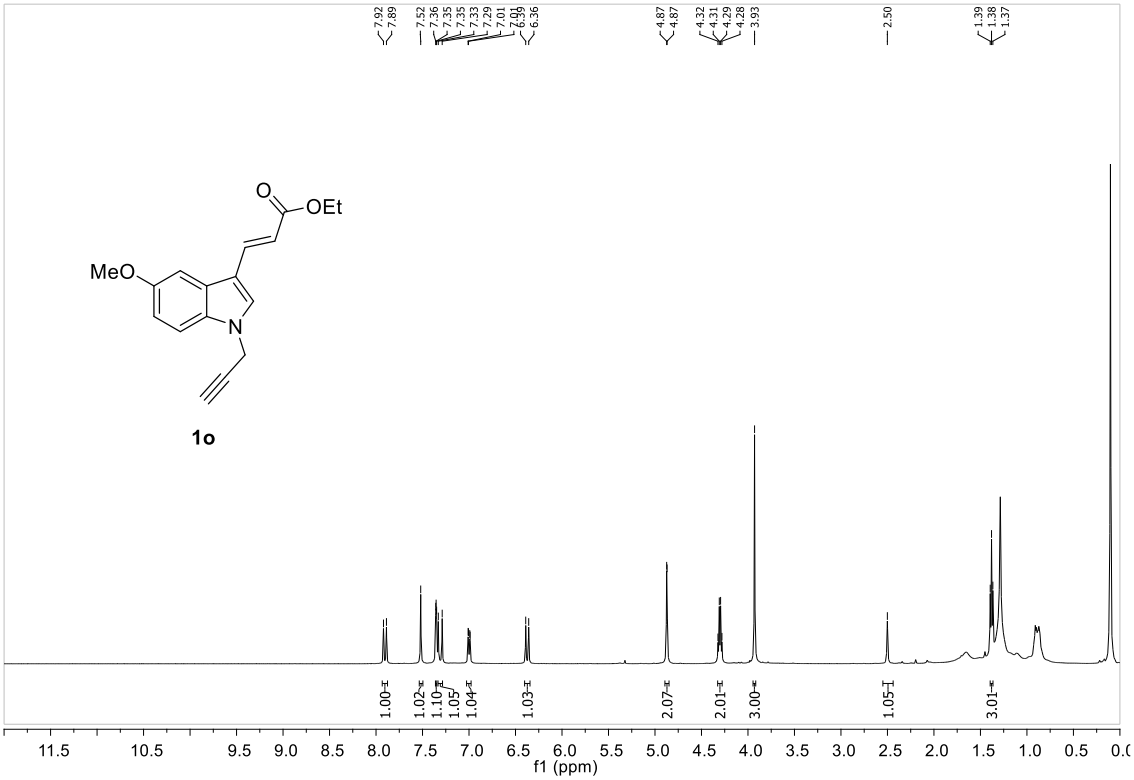
^{1}H NMR (500 MHz, $CDCl_3$) spectrum of **1n**



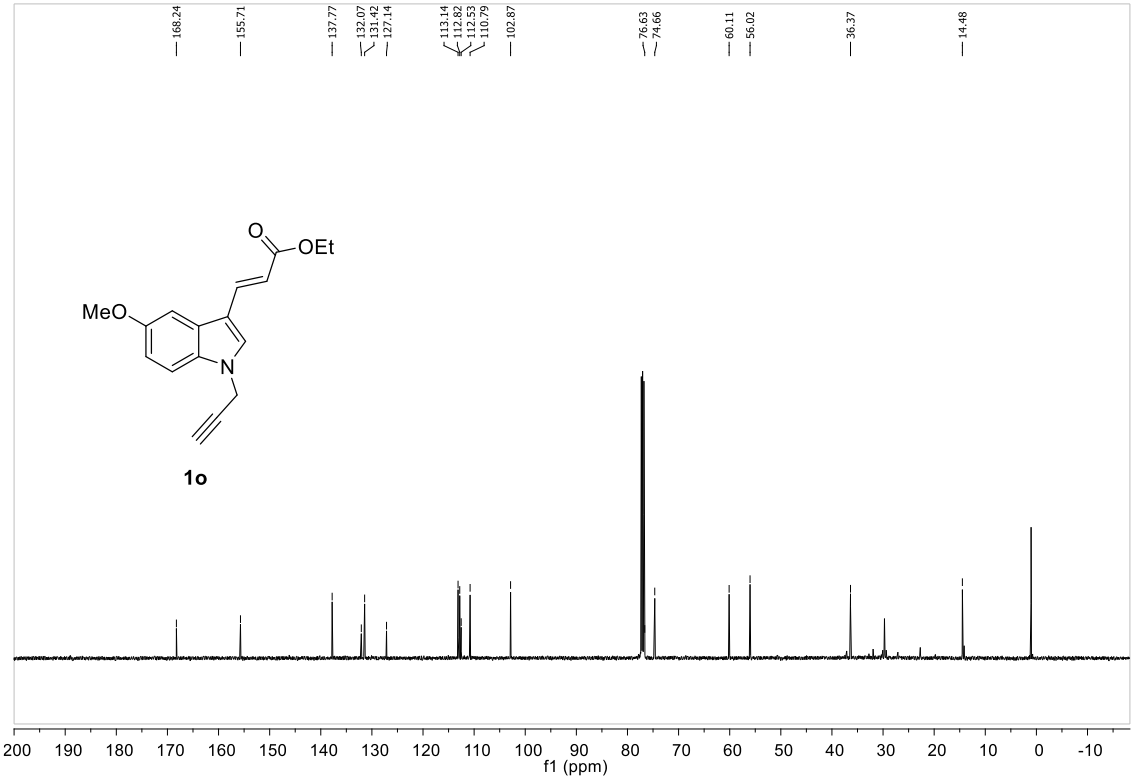
^{13}C {^{1}H} NMR (126 MHz, $CDCl_3$) spectrum of **1n**



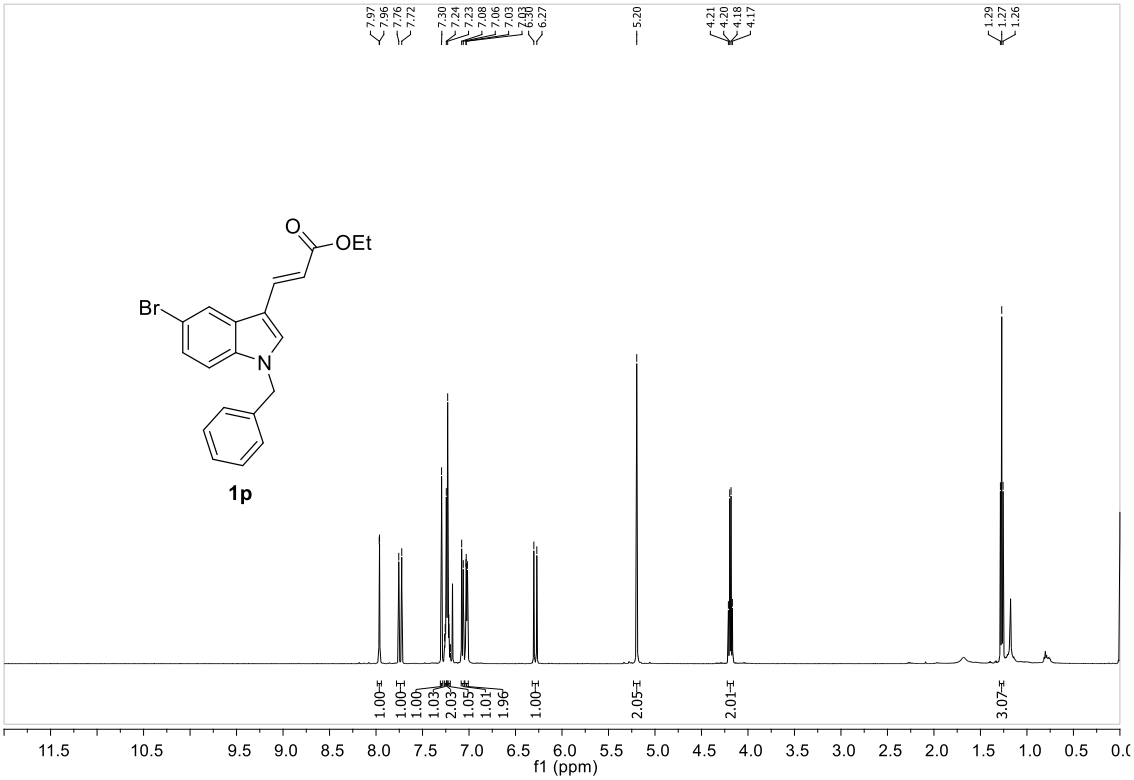
^{1}H NMR (500 MHz, $CDCl_3$) spectrum of **1o**



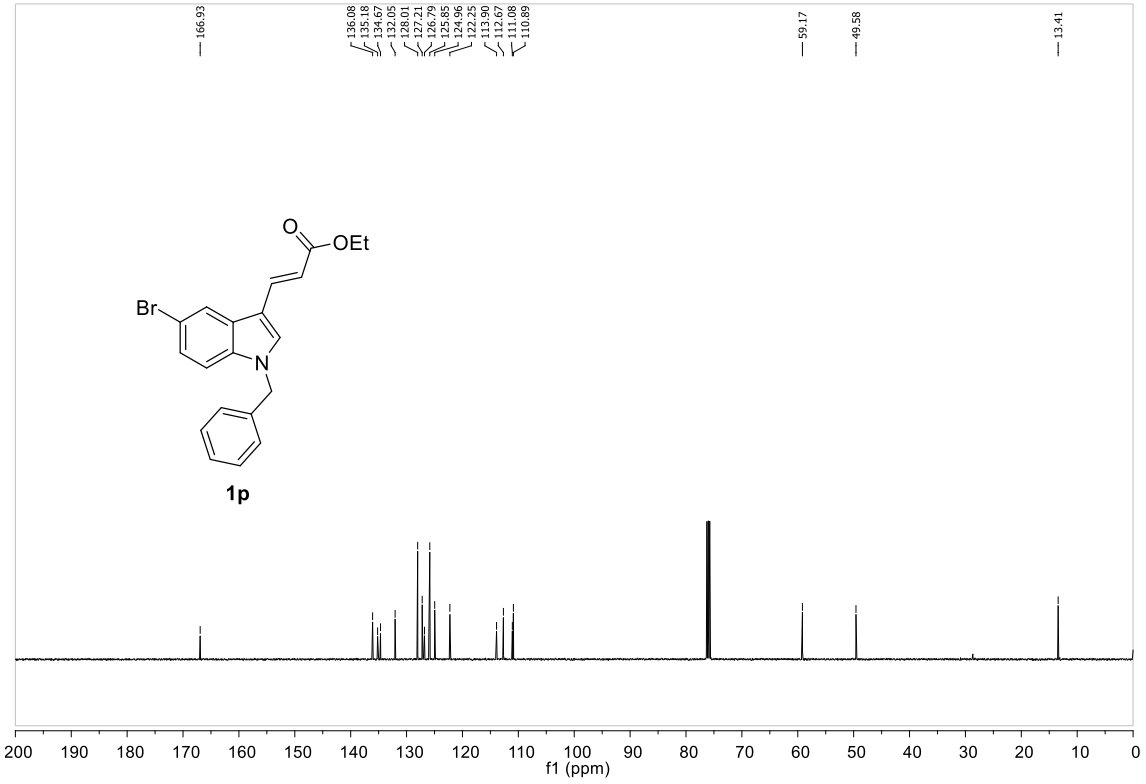
^{13}C {^{1}H} NMR (126 MHz, $CDCl_3$) spectrum of **1o**



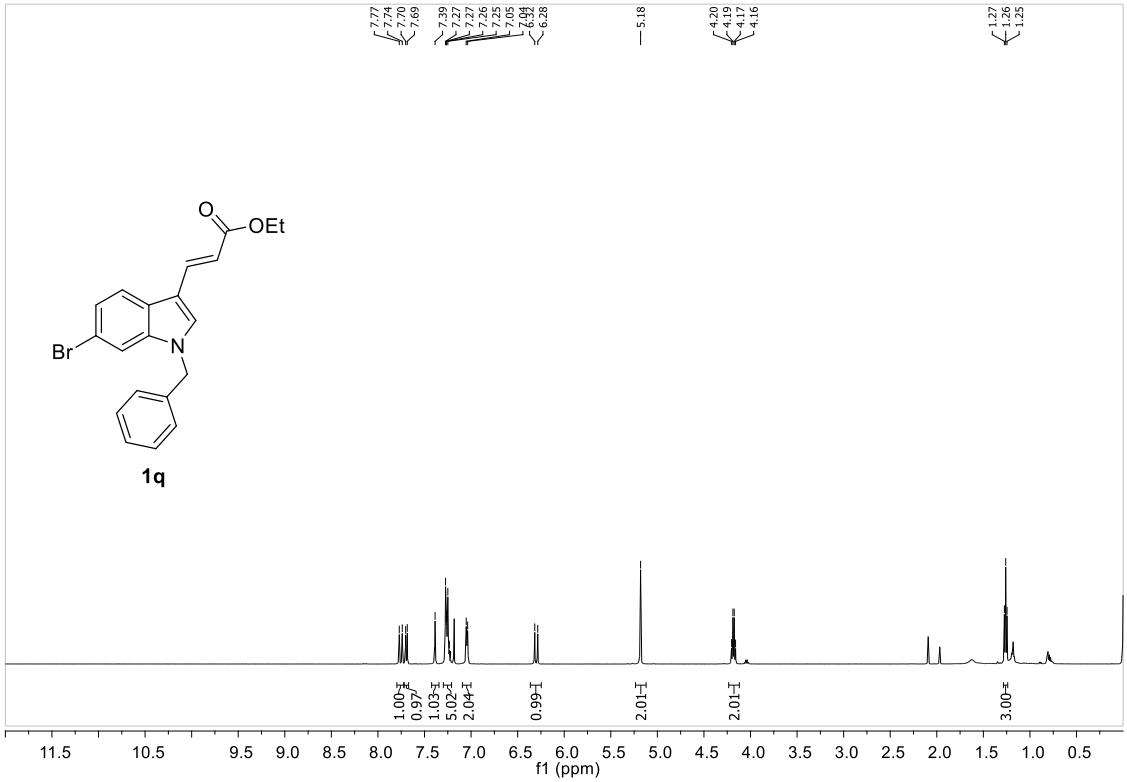
^{1}H NMR (500 MHz, $CDCl_3$) spectrum of **1p**



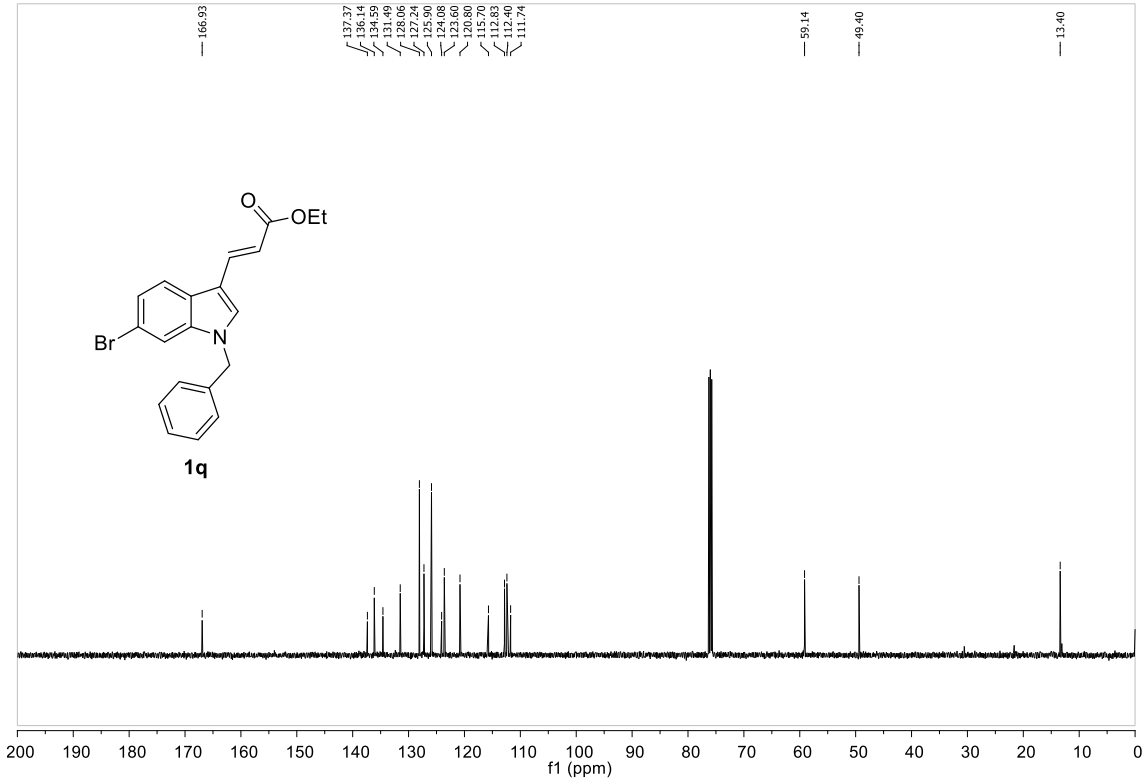
^{13}C {^{1}H} NMR (126 MHz, $CDCl_3$) spectrum of **1p**



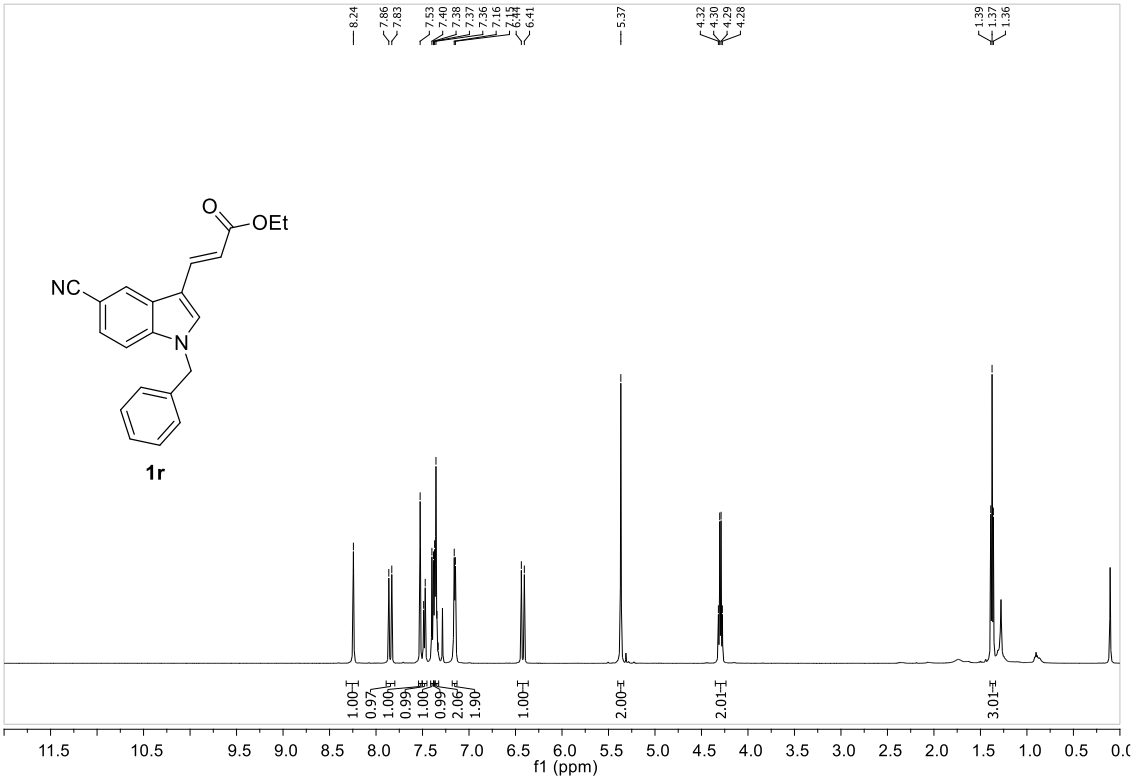
^{1}H NMR (500 MHz, $CDCl_3$) spectrum of **1q**



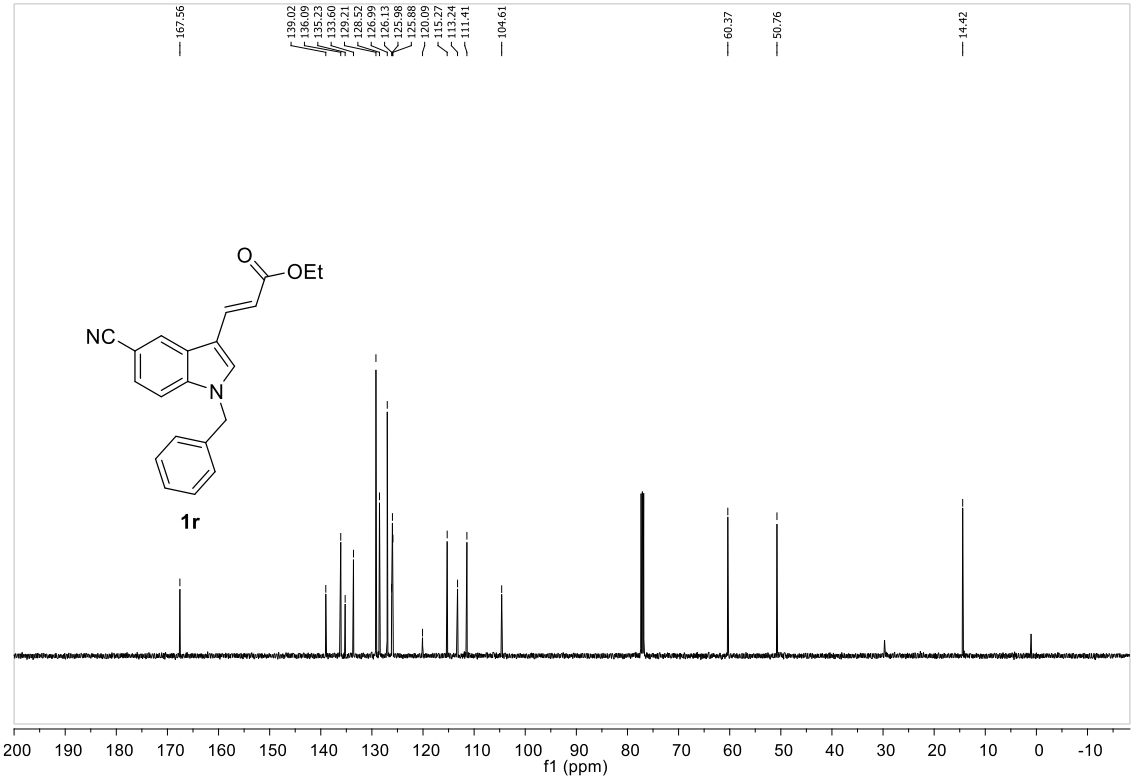
^{13}C {^{1}H} NMR (126 MHz, $CDCl_3$) spectrum of **1q**



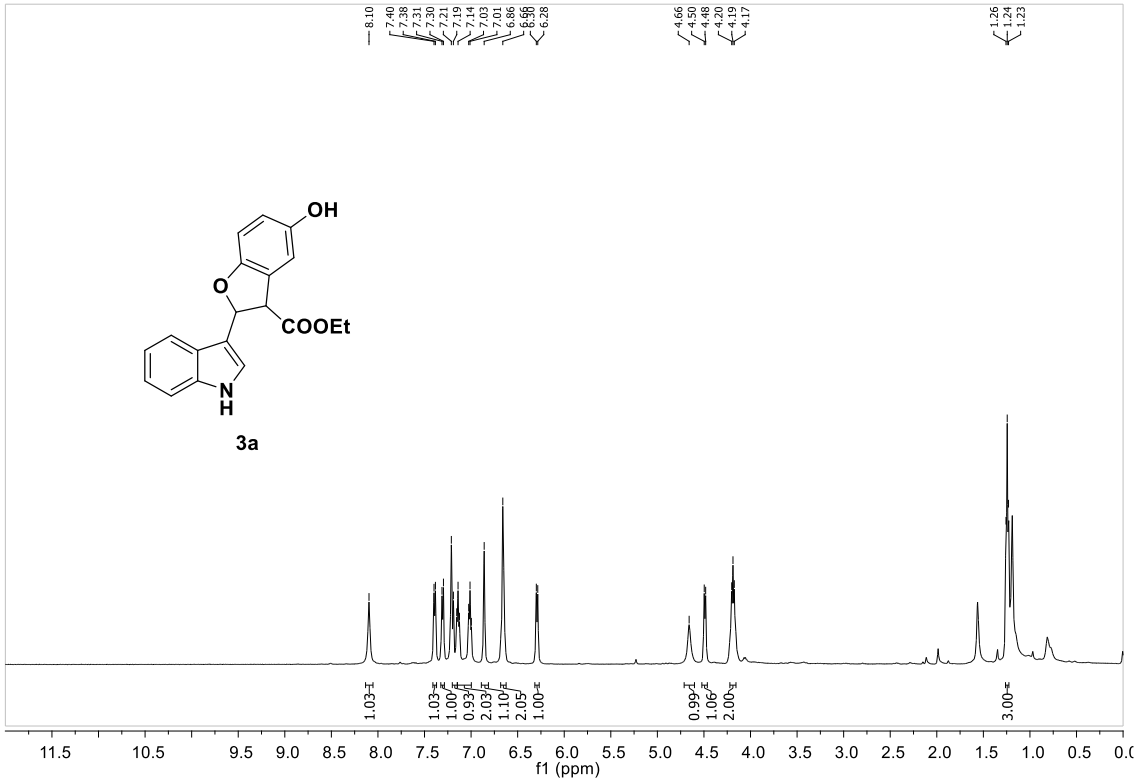
^{1}H NMR (500 MHz, $CDCl_3$) spectrum of **1r**



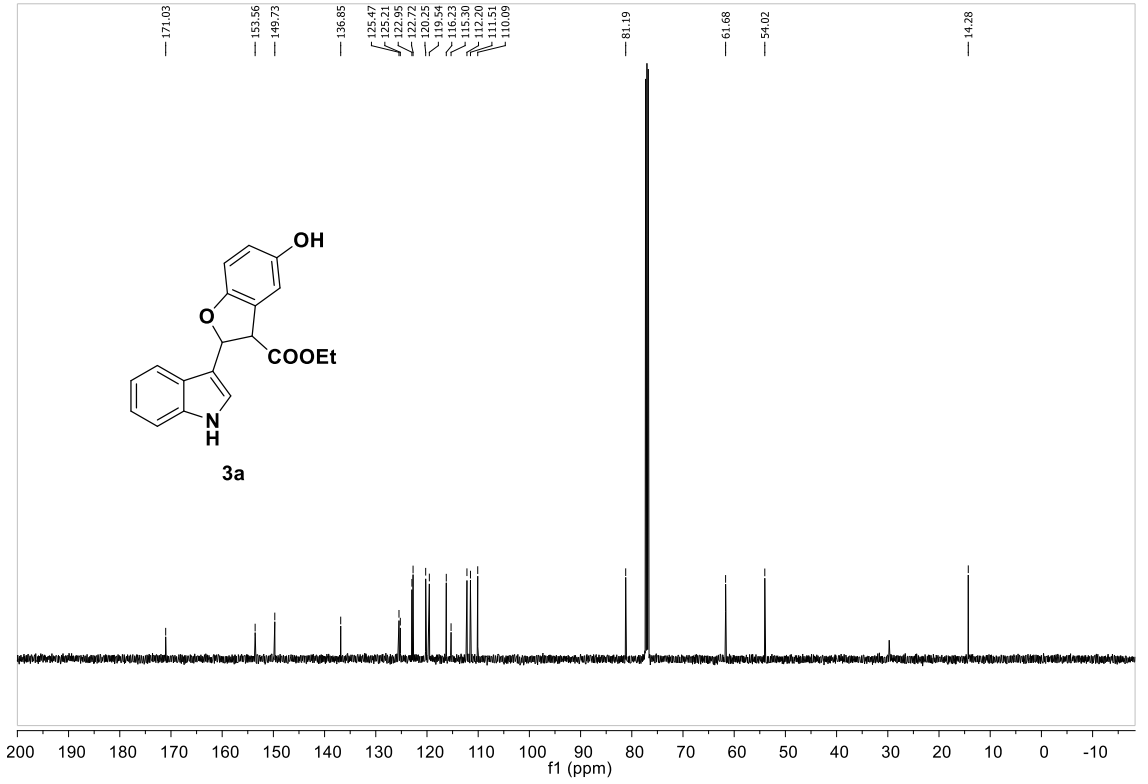
^{13}C{^{1}H} NMR (126 MHz, $CDCl_3$) spectrum of **1r**



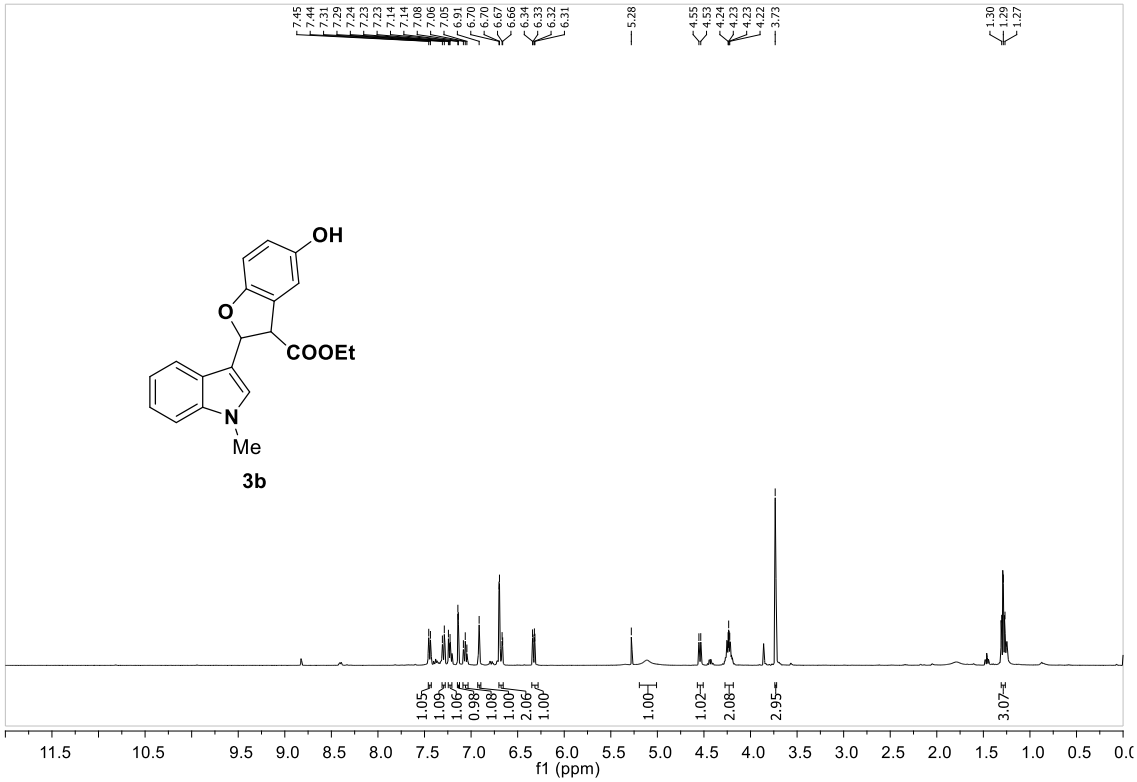
^{1}H NMR (500 MHz, $CDCl_3$) spectrum of **3a**



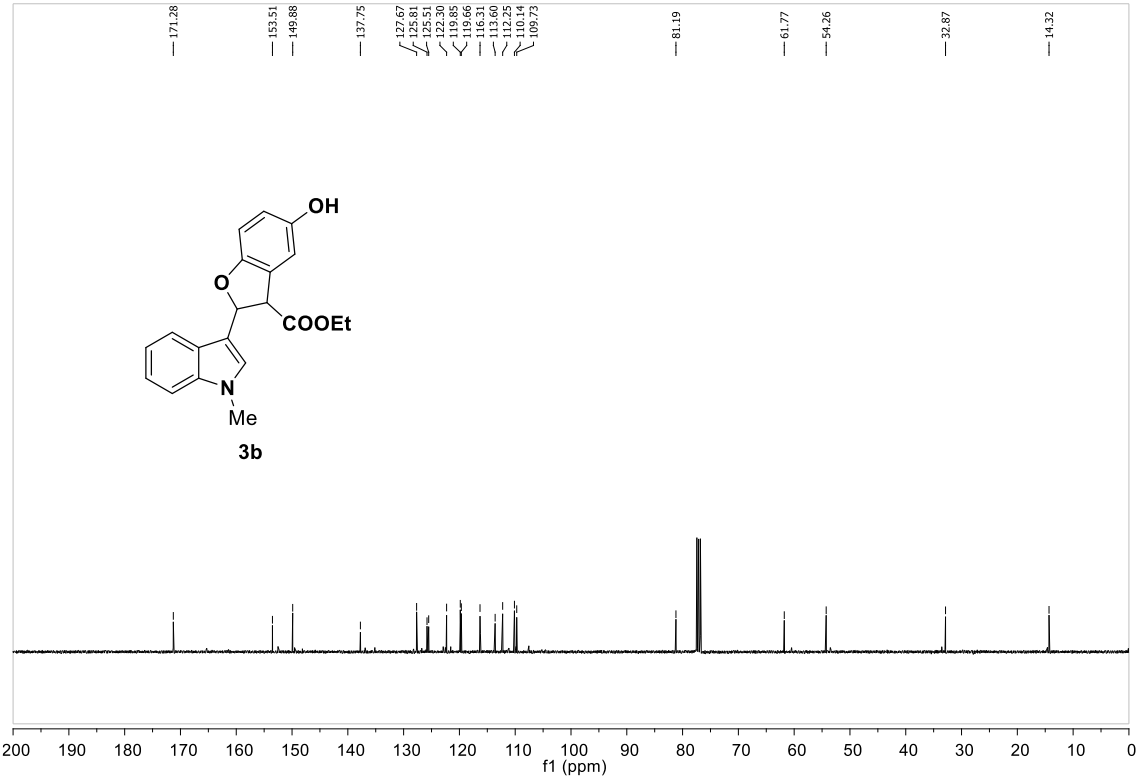
^{13}C {^{1}H} NMR (126 MHz, $CDCl_3$) spectrum of **3a**



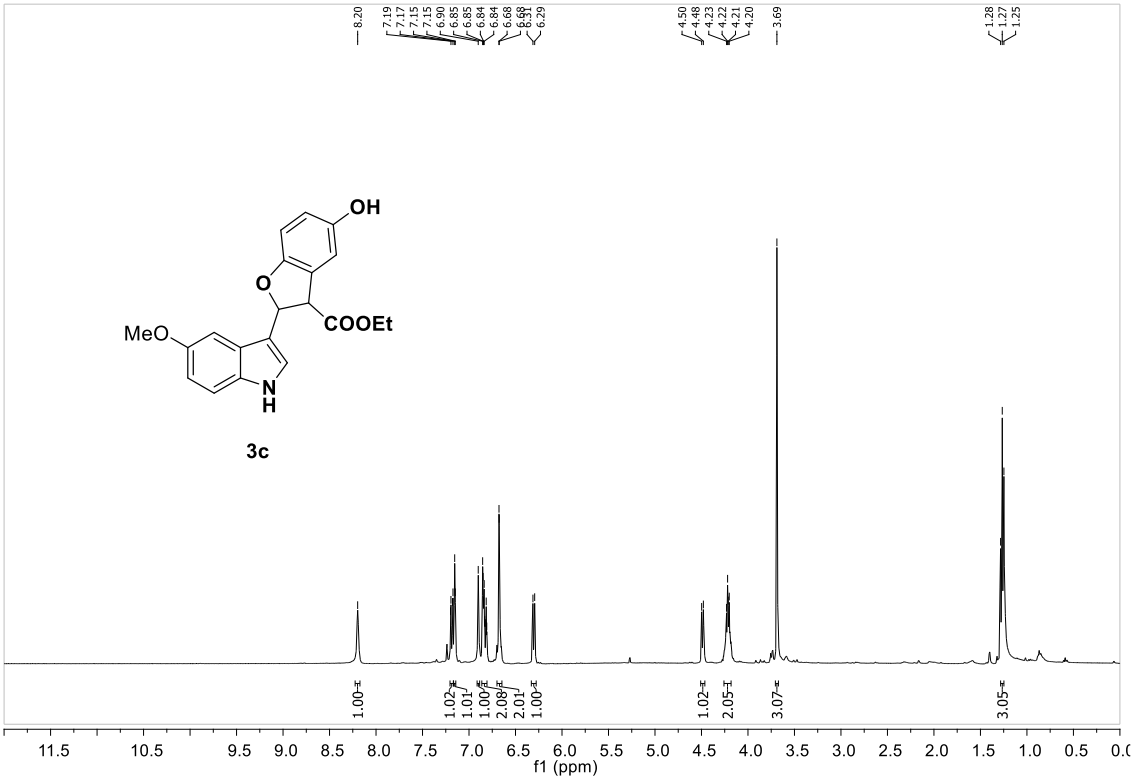
^{1}H NMR (500 MHz, $CDCl_3$) spectrum of **3b**



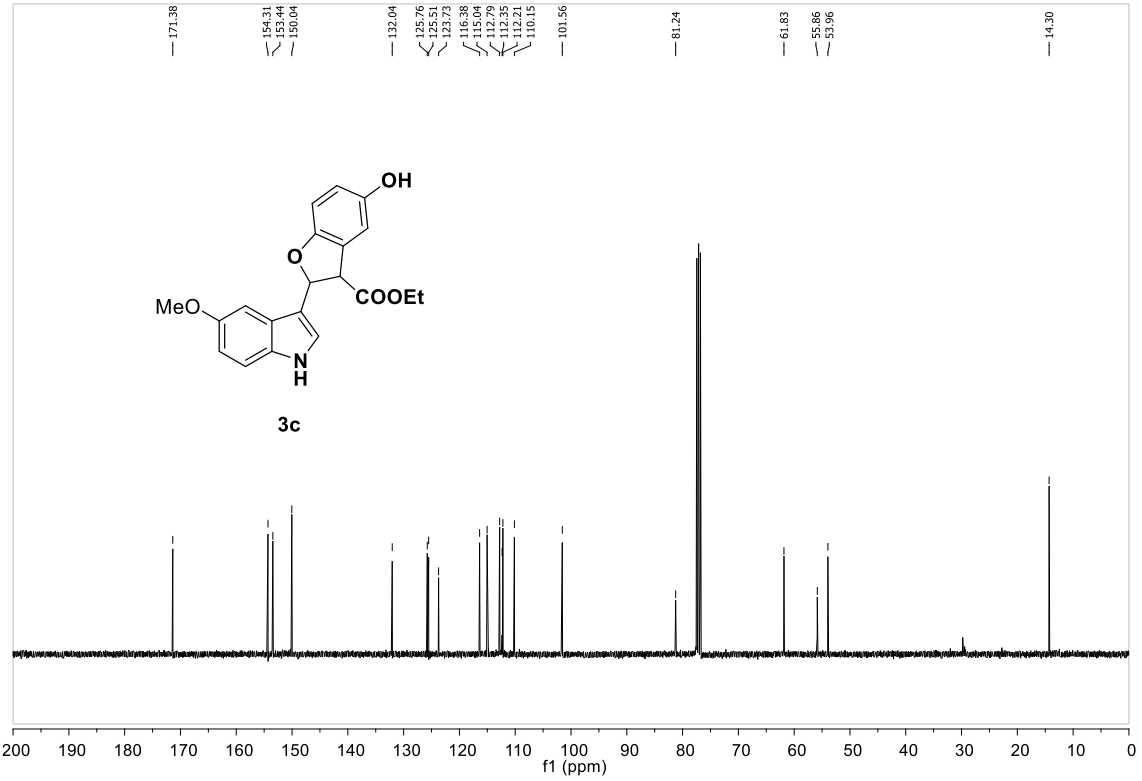
^{13}C{^{1}H} NMR (126 MHz, $CDCl_3$) spectrum of **3b**



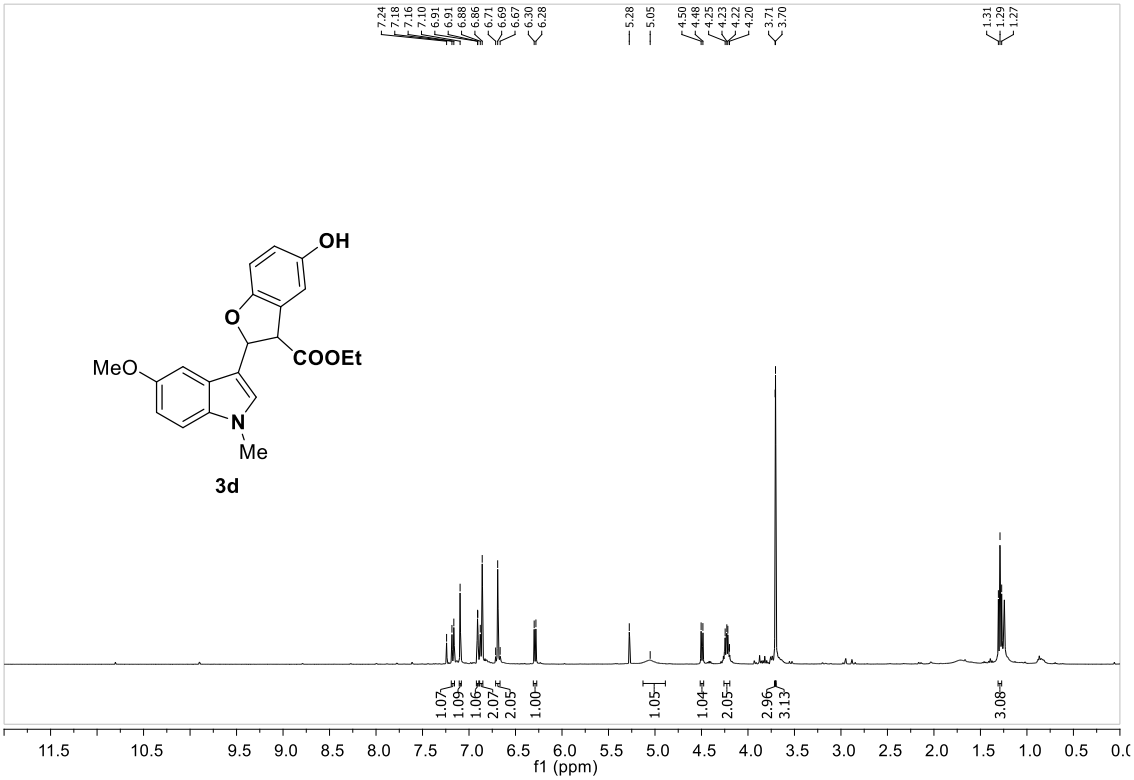
^{1}H NMR (500 MHz, $CDCl_3$) spectrum of **3c**



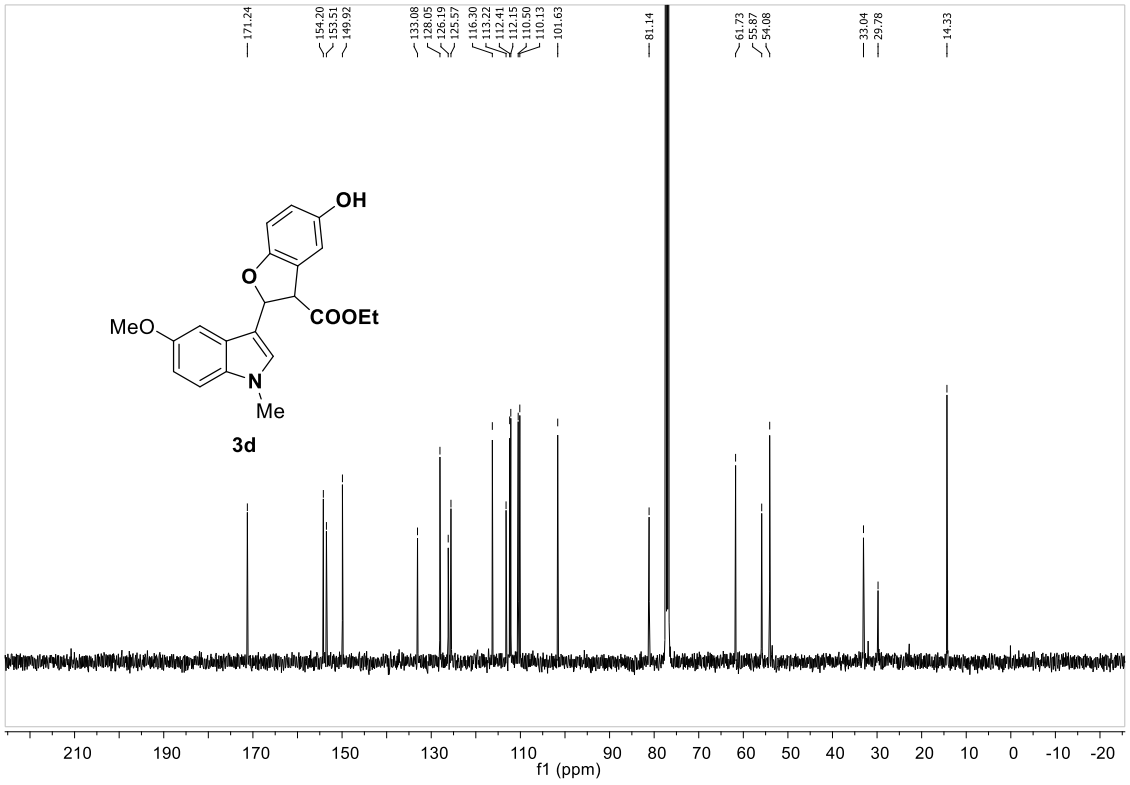
^{13}C {^{1}H} NMR (126 MHz, $CDCl_3$) spectrum of **3c**



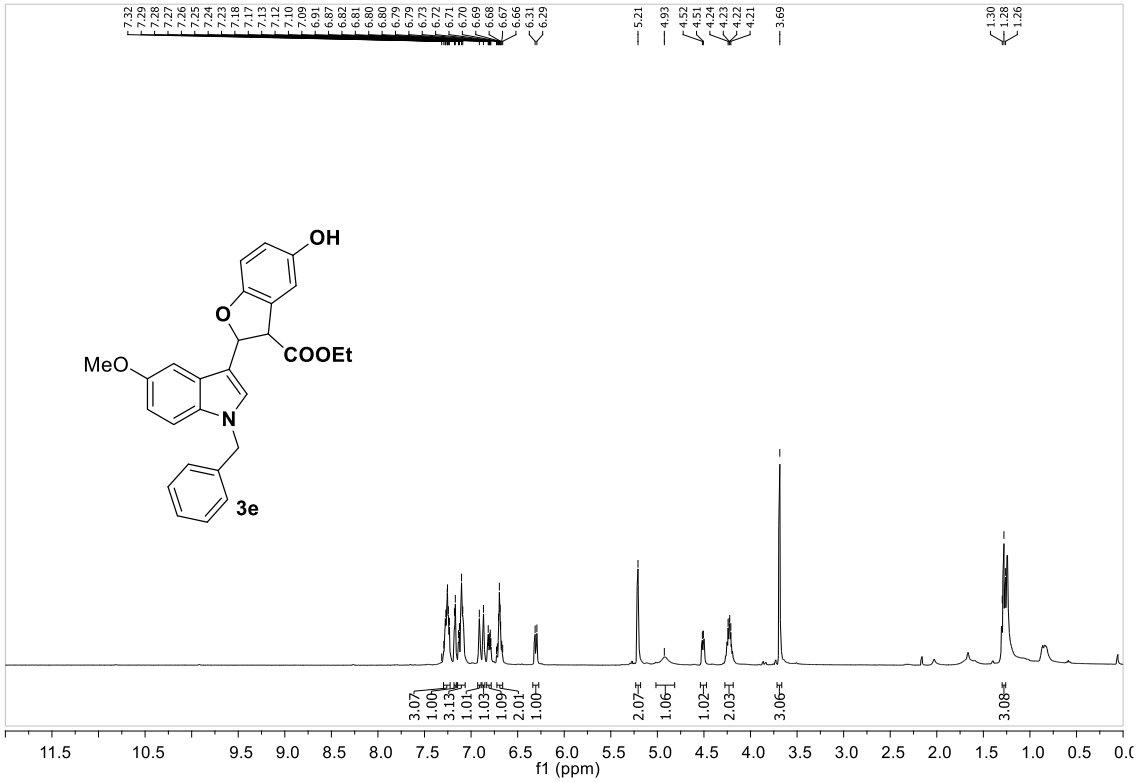
^{1}H NMR (500 MHz, $CDCl_3$) spectrum of **3d**



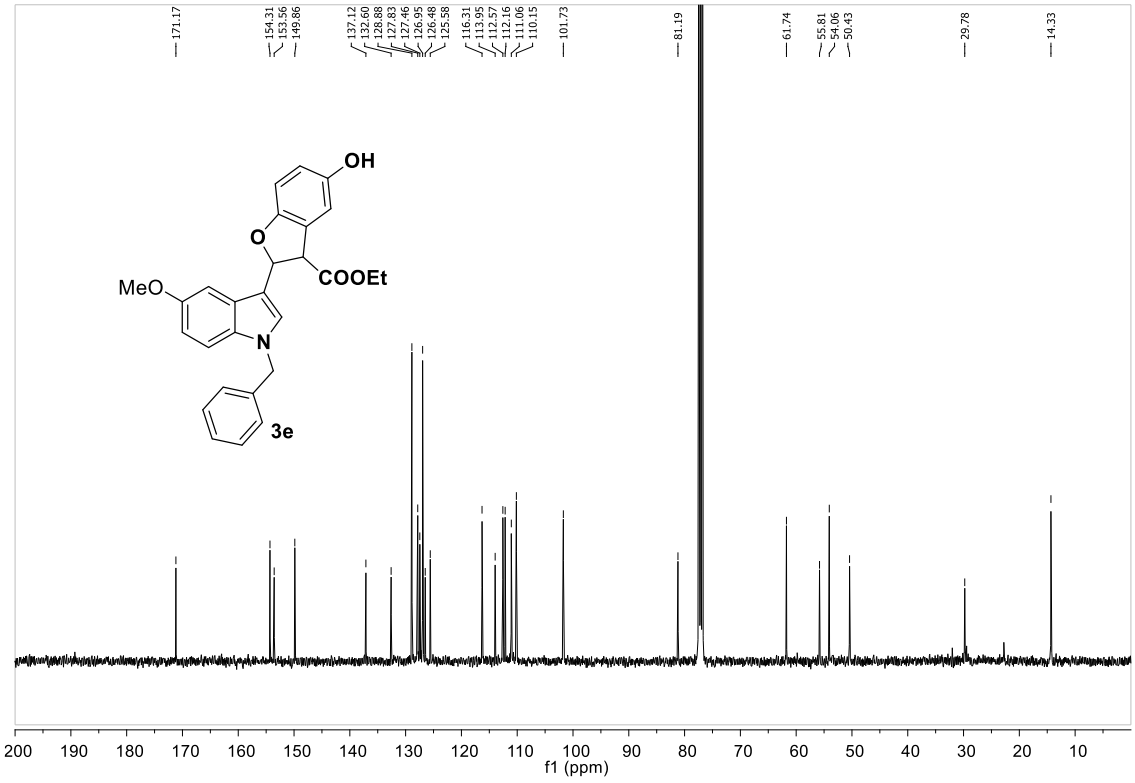
^{13}C {^{1}H} NMR (126 MHz, $CDCl_3$) spectrum of **3d**



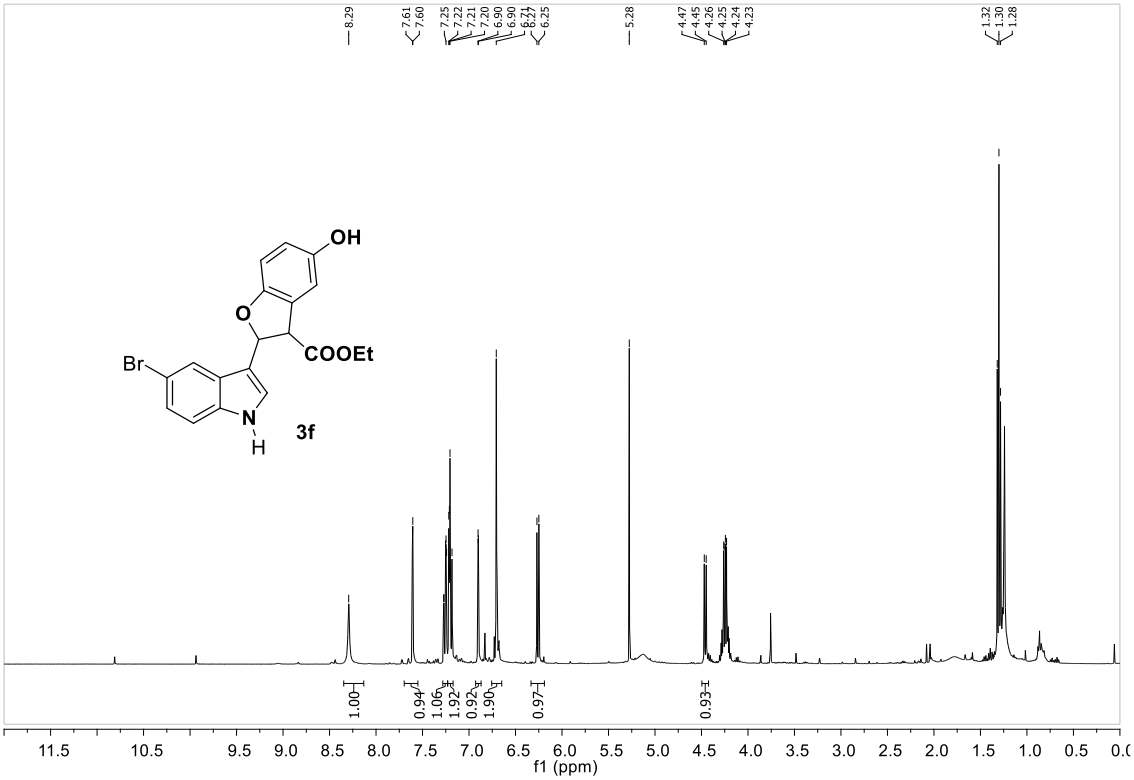
^{1}H NMR (500 MHz, $CDCl_3$) spectrum of **3e**



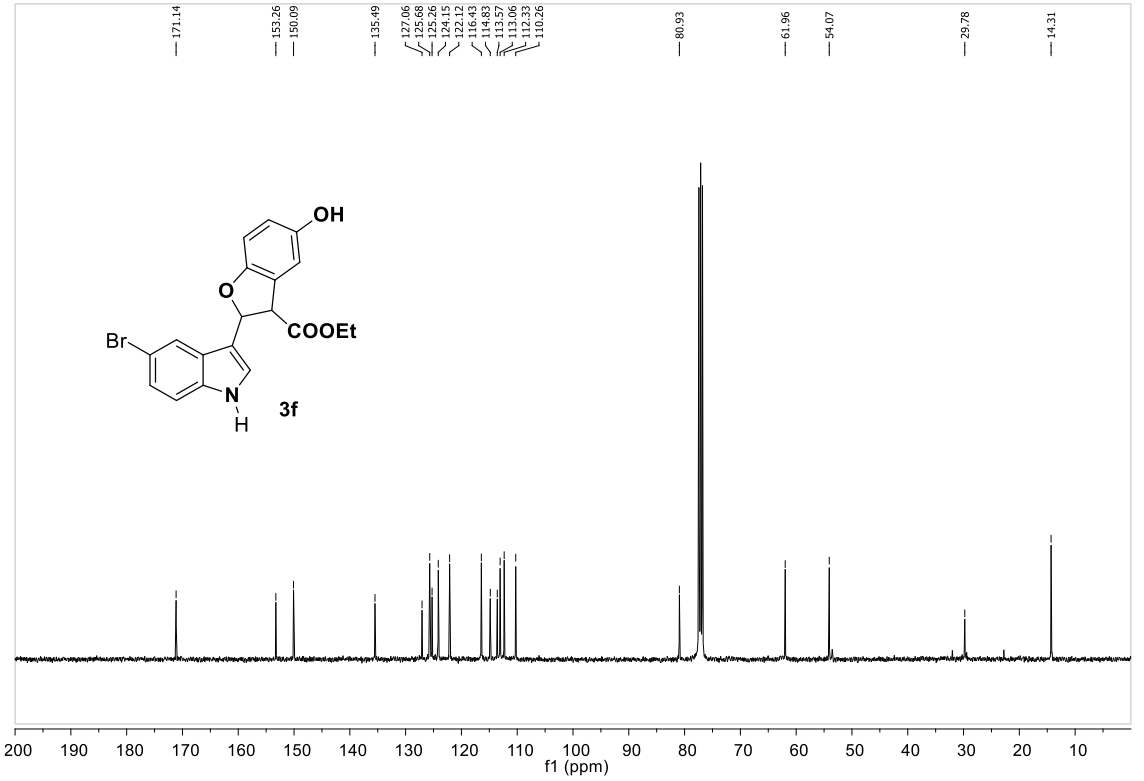
^{13}C {^{1}H} NMR (126 MHz, $CDCl_3$) spectrum of **3e**



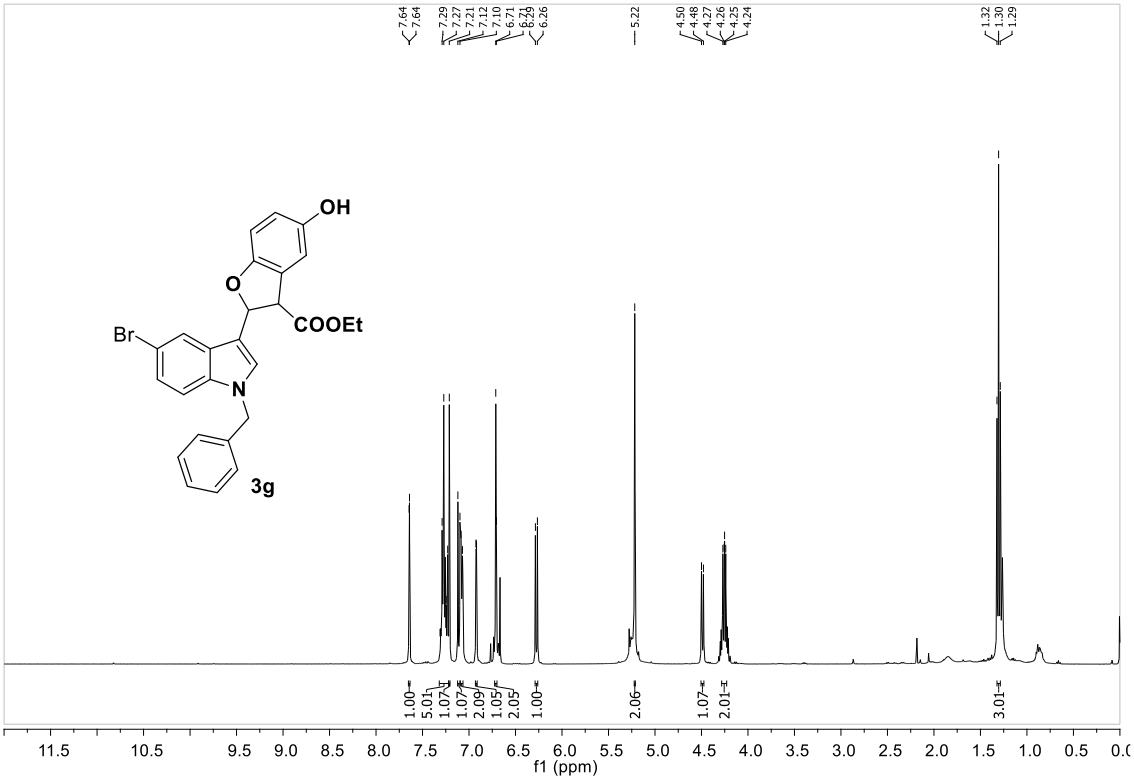
^{1}H NMR (500 MHz, $CDCl_3$) spectrum of **3f**



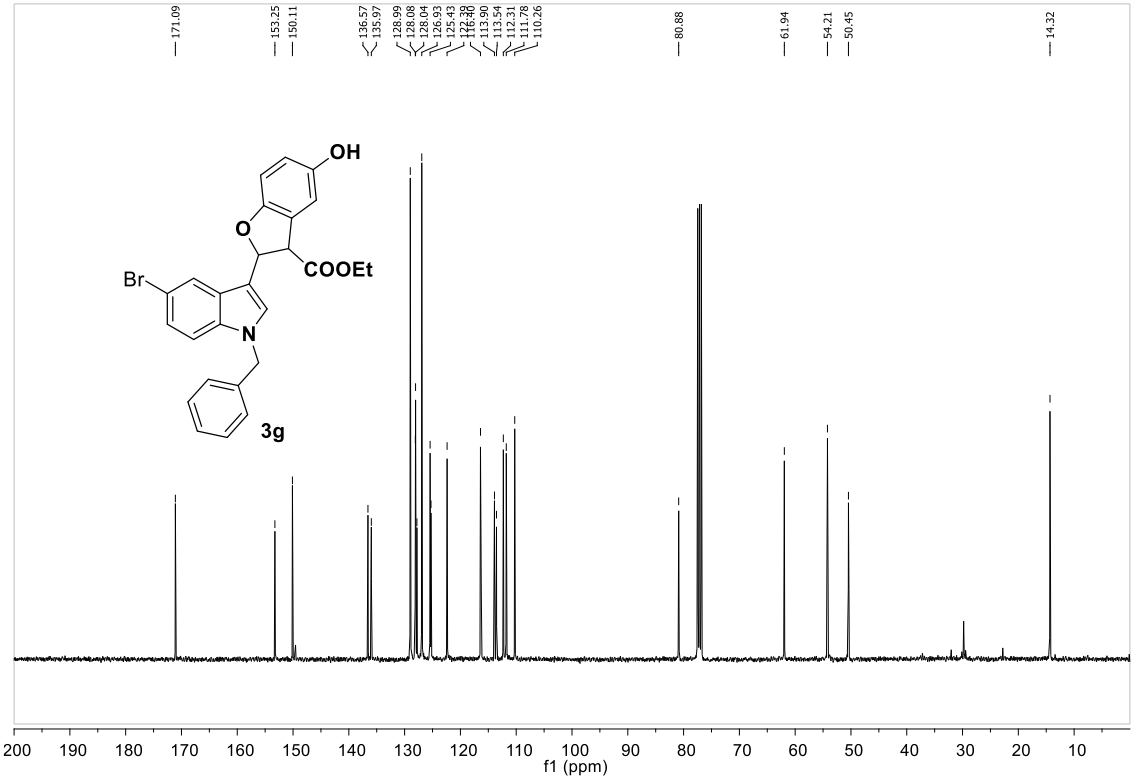
^{13}C {^{1}H} NMR (126 MHz, $CDCl_3$) spectrum of **3f**



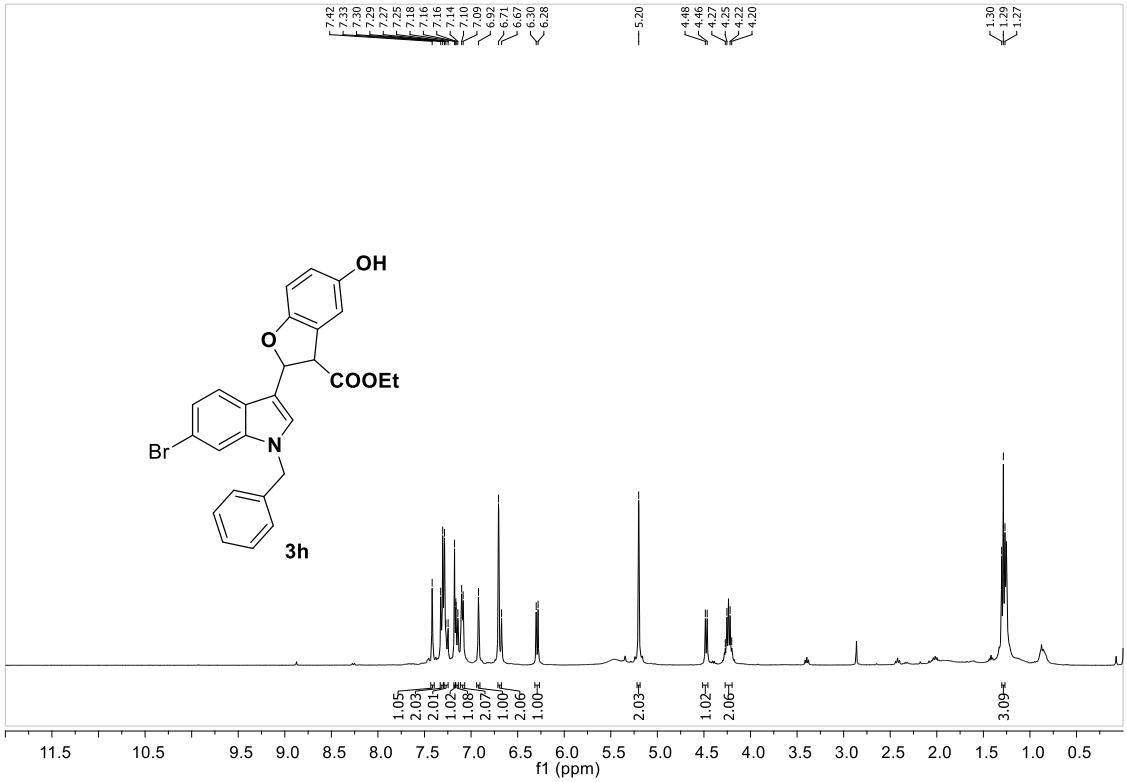
^{1}H NMR (500 MHz, $CDCl_3$) spectrum of **3g**



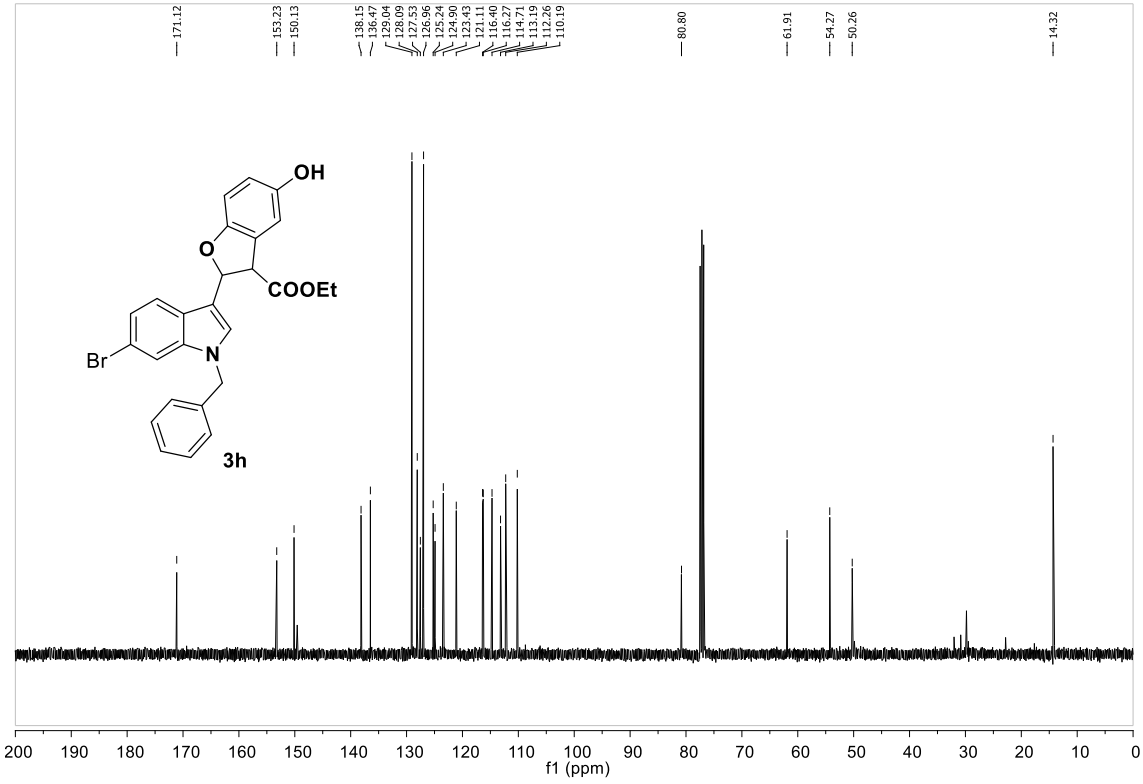
^{13}C {^{1}H} NMR (126 MHz, $CDCl_3$) spectrum of **3g**



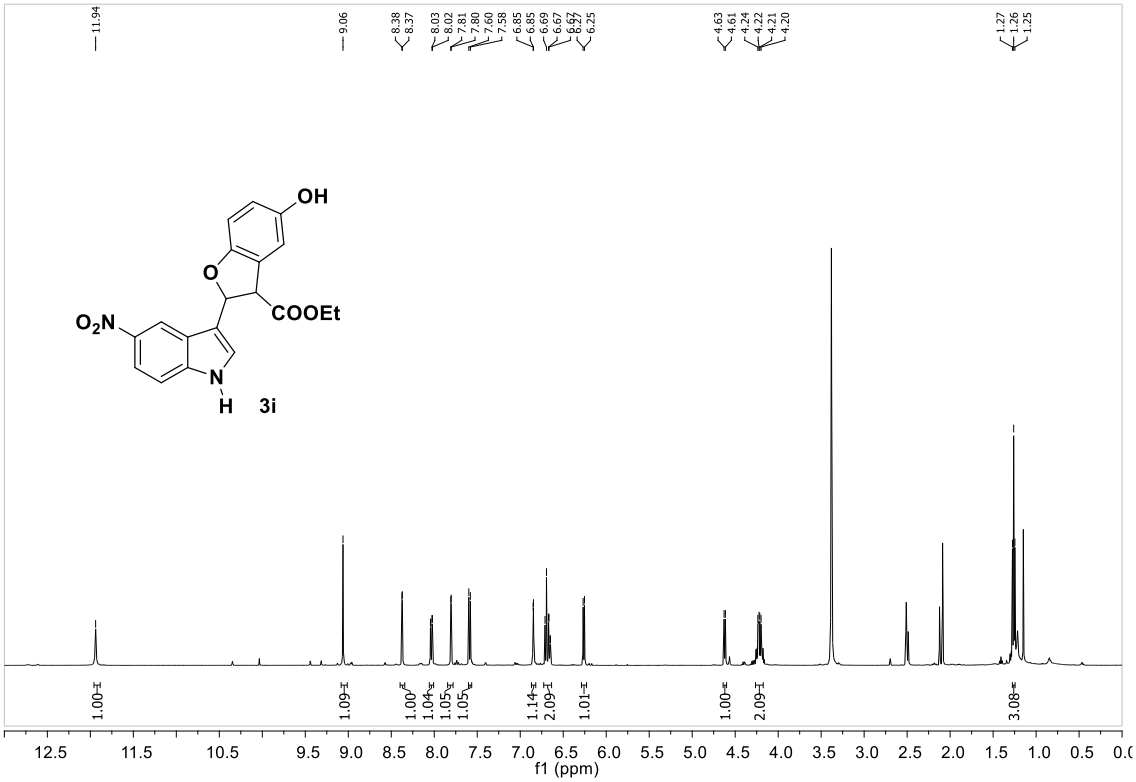
^{1}H NMR (500 MHz, $CDCl_3$) spectrum of **3h**



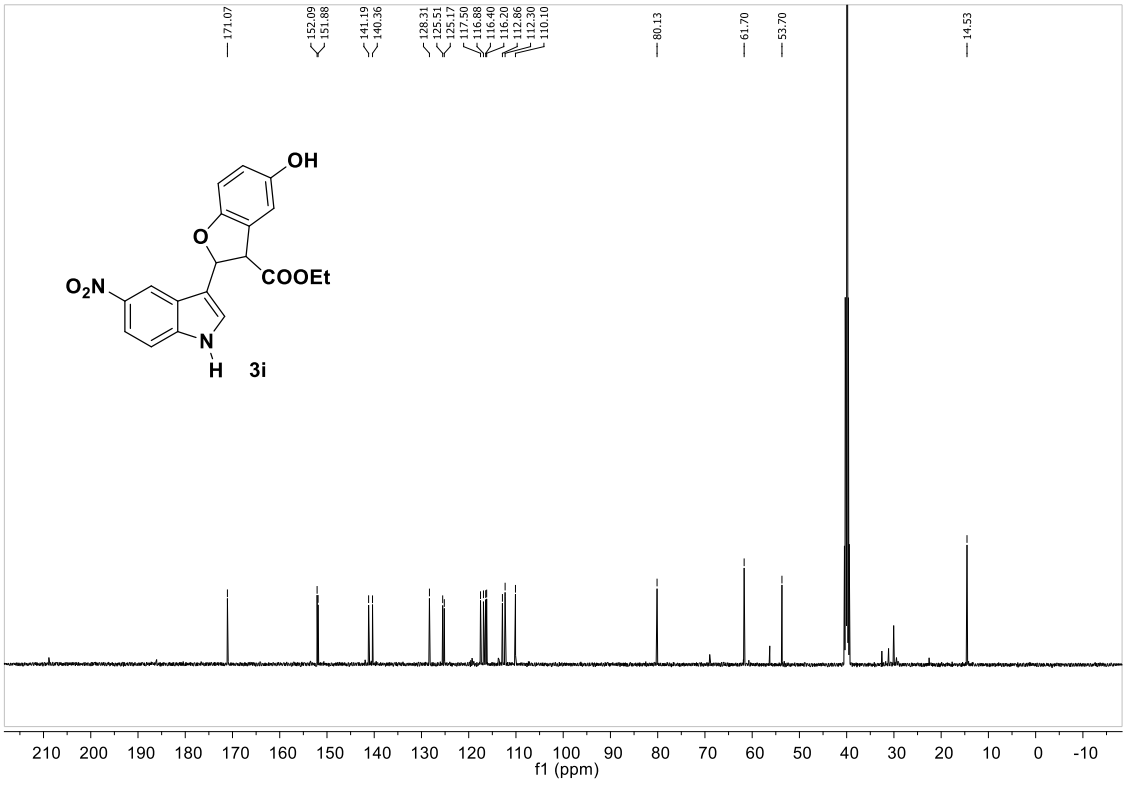
^{13}C {^{1}H} NMR (126 MHz, $CDCl_3$) spectrum of **3h**



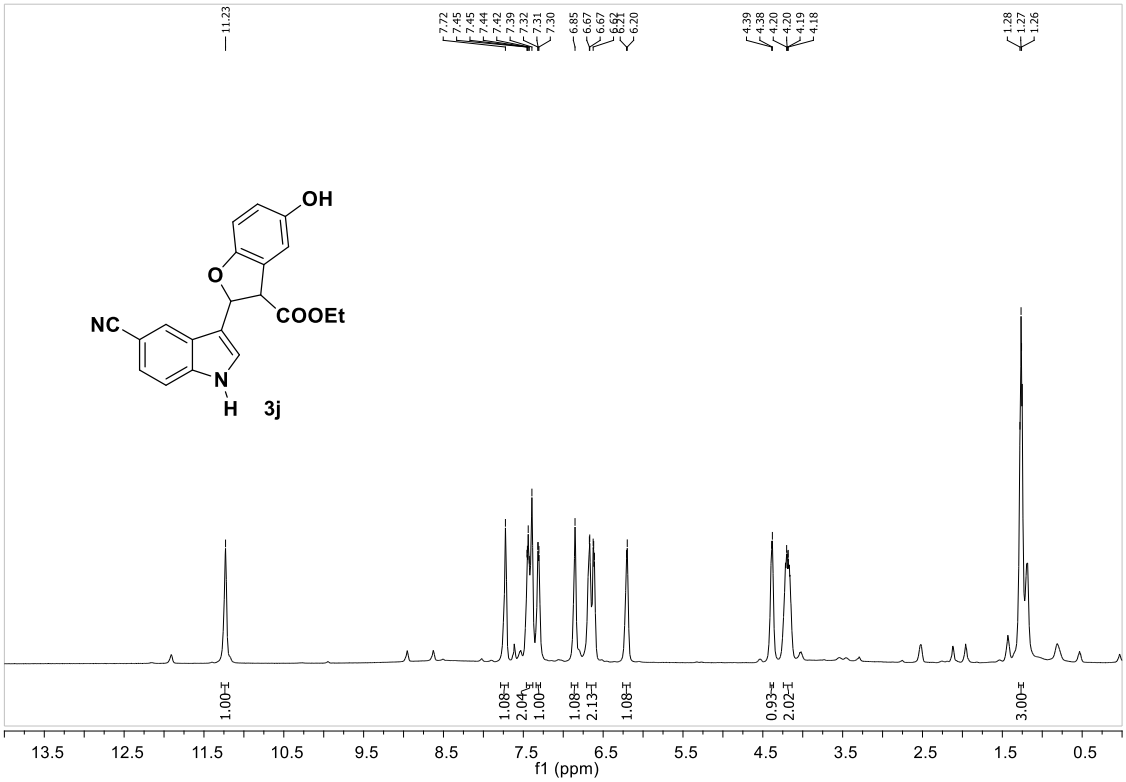
^{1}H NMR (500 MHz, $CDCl_3$) spectrum of **3i**



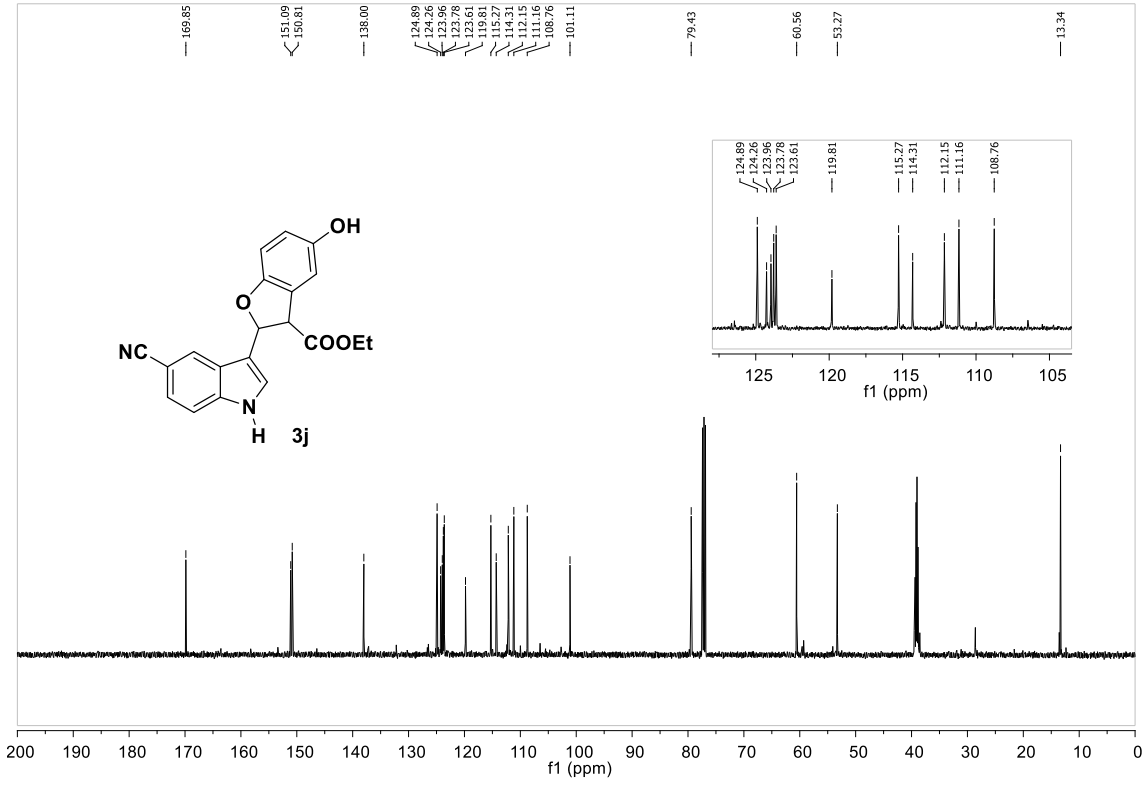
^{13}C {^{1}H} NMR (126 MHz, $CDCl_3$) spectrum of **3i**



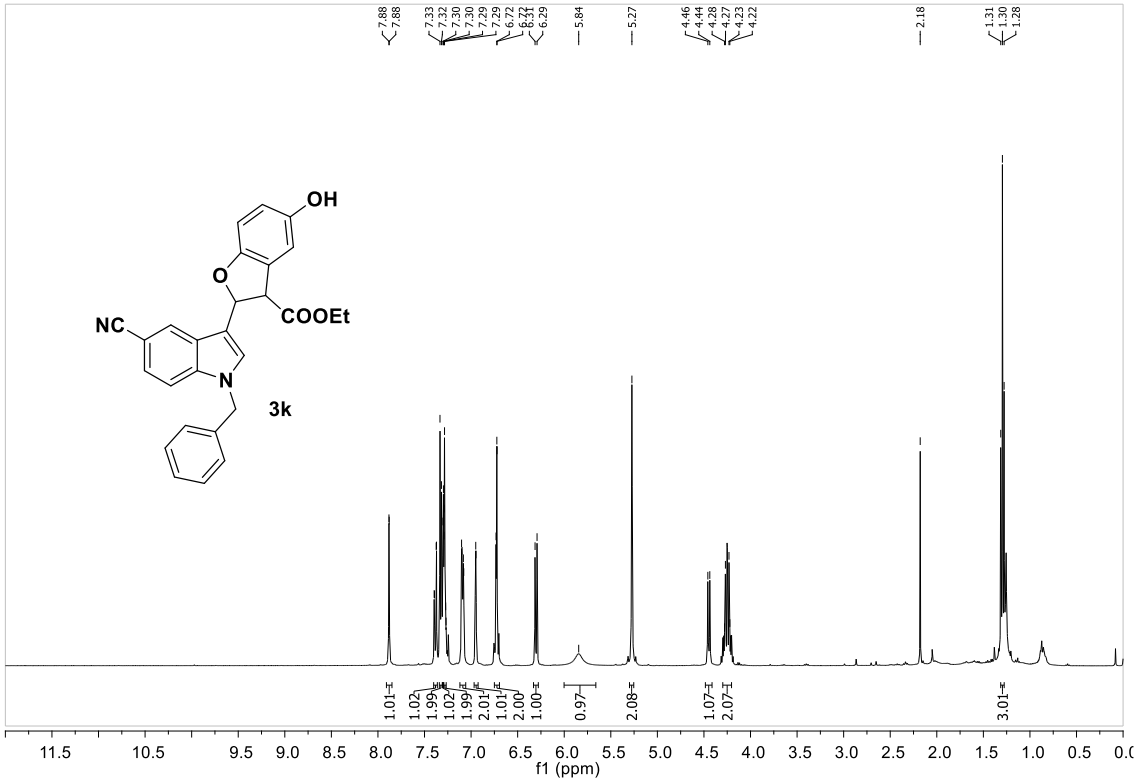
^{1}H NMR (500 MHz, $CDCl_3$) spectrum of **3j**



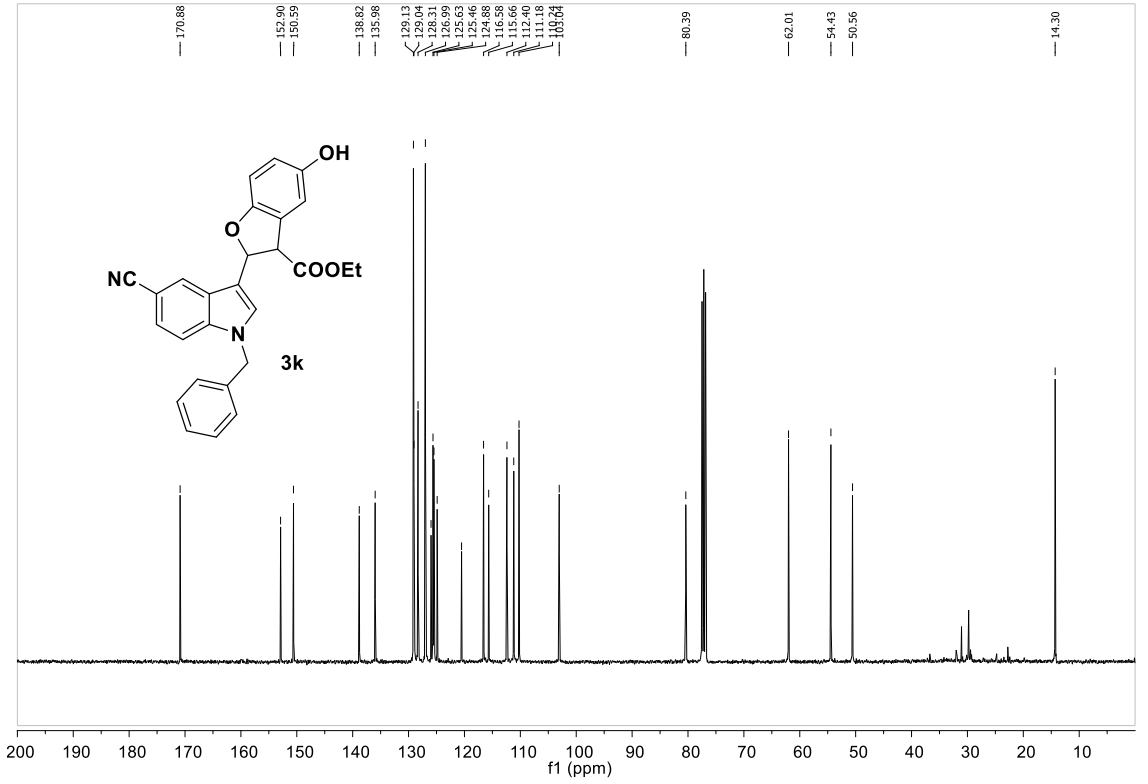
^{13}C {^{1}H} NMR (126 MHz, $CDCl_3$) spectrum of **3j**



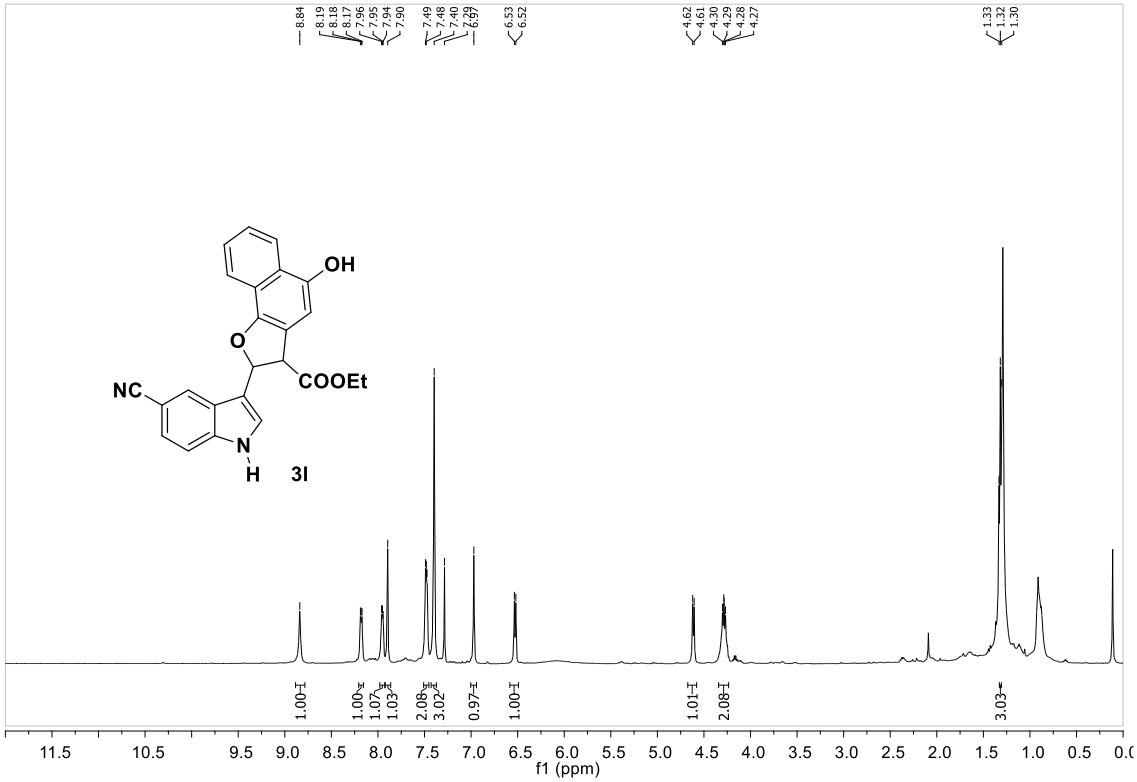
^{1}H NMR (500 MHz, $CDCl_3$) spectrum of **3k**



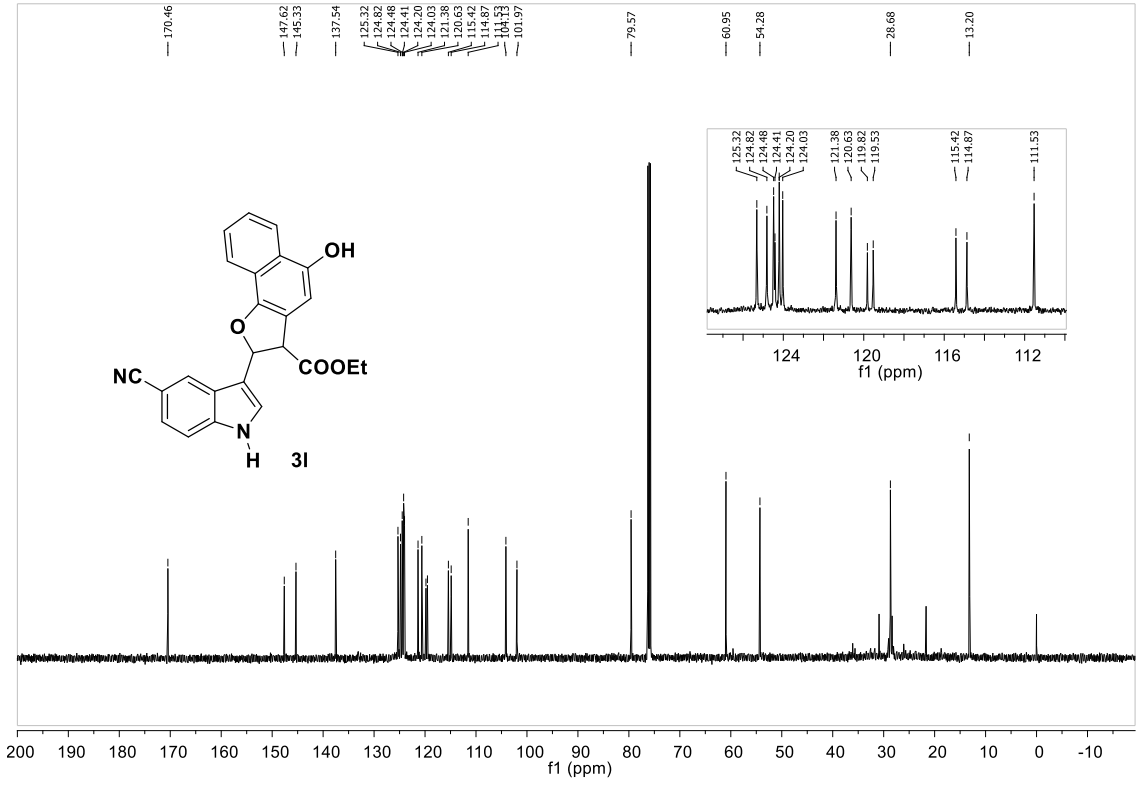
^{13}C {^{1}H} NMR (126 MHz, $CDCl_3$) spectrum of **3k**



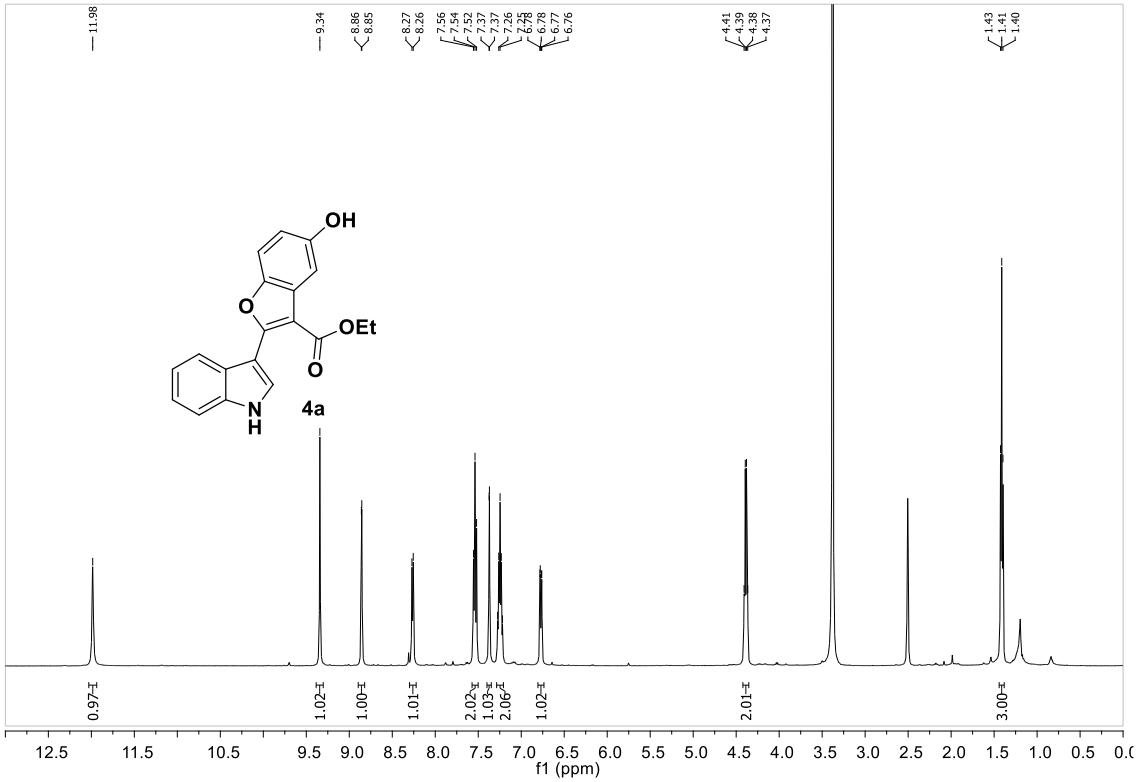
^{1}H NMR (500 MHz, $CDCl_3$) spectrum of **3l**



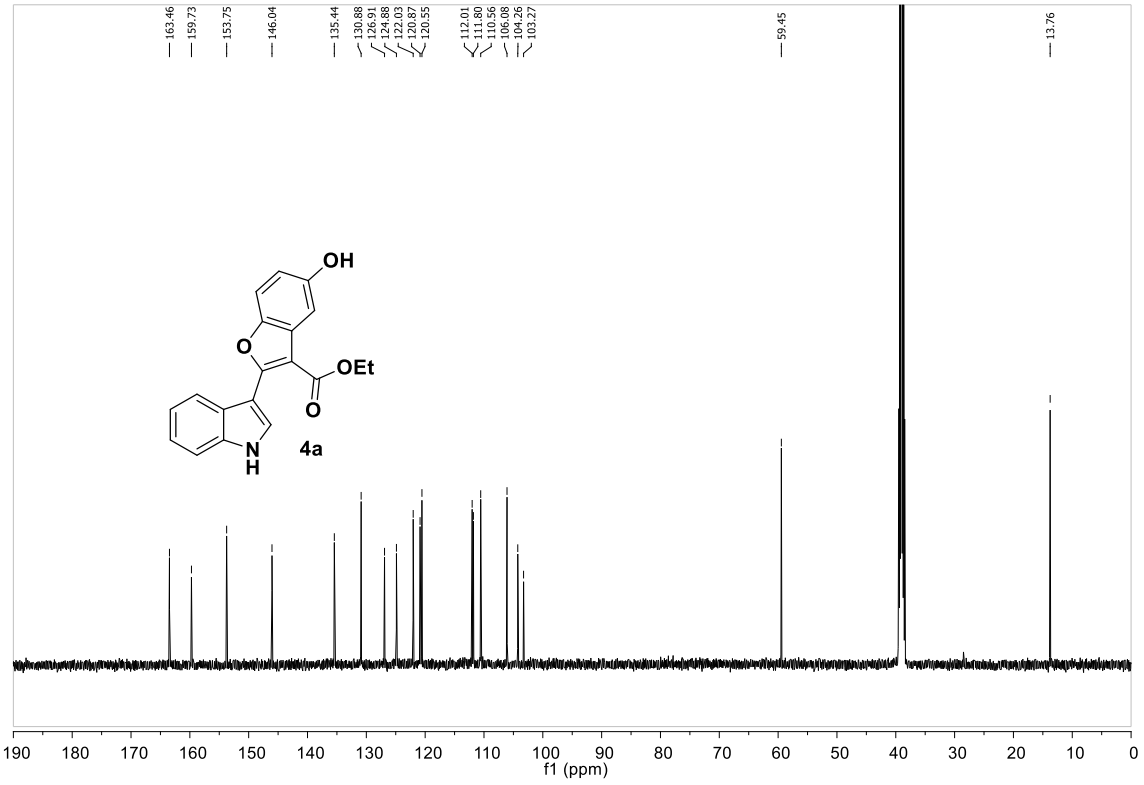
^{13}C {^{1}H} NMR (126 MHz, $CDCl_3$) spectrum of **3l**



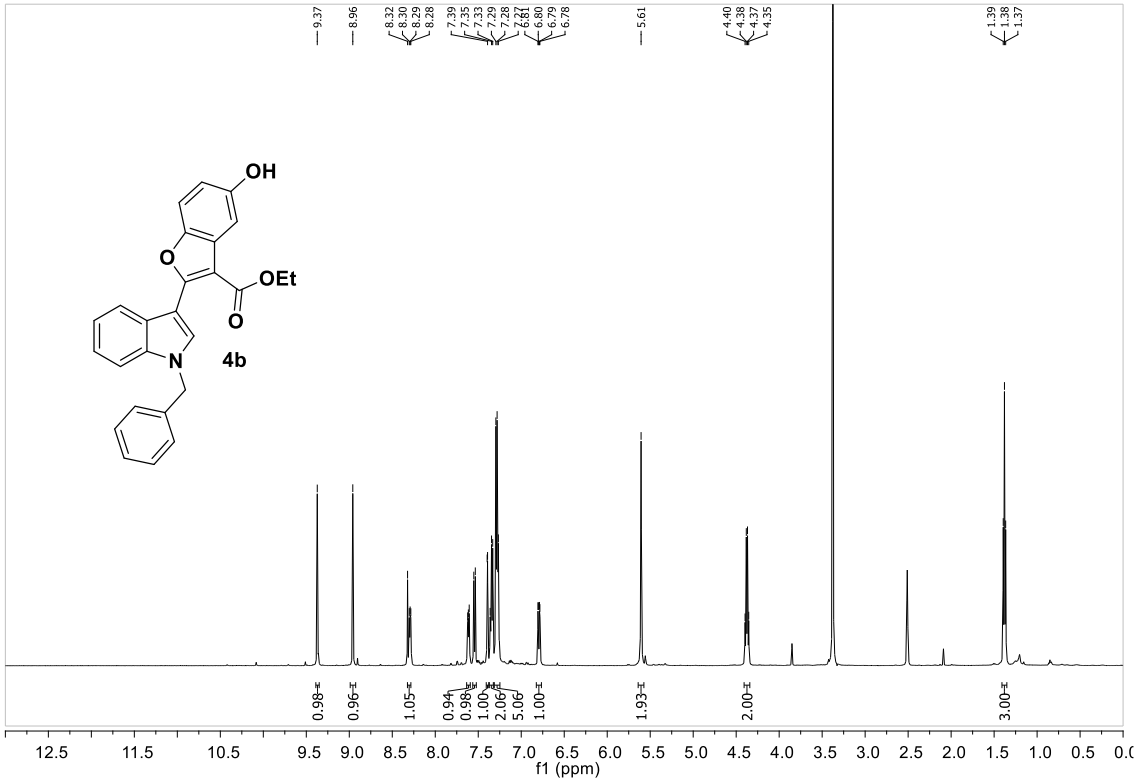
^{1}H NMR (500 MHz, DMSO-d_6) spectrum of **4a**



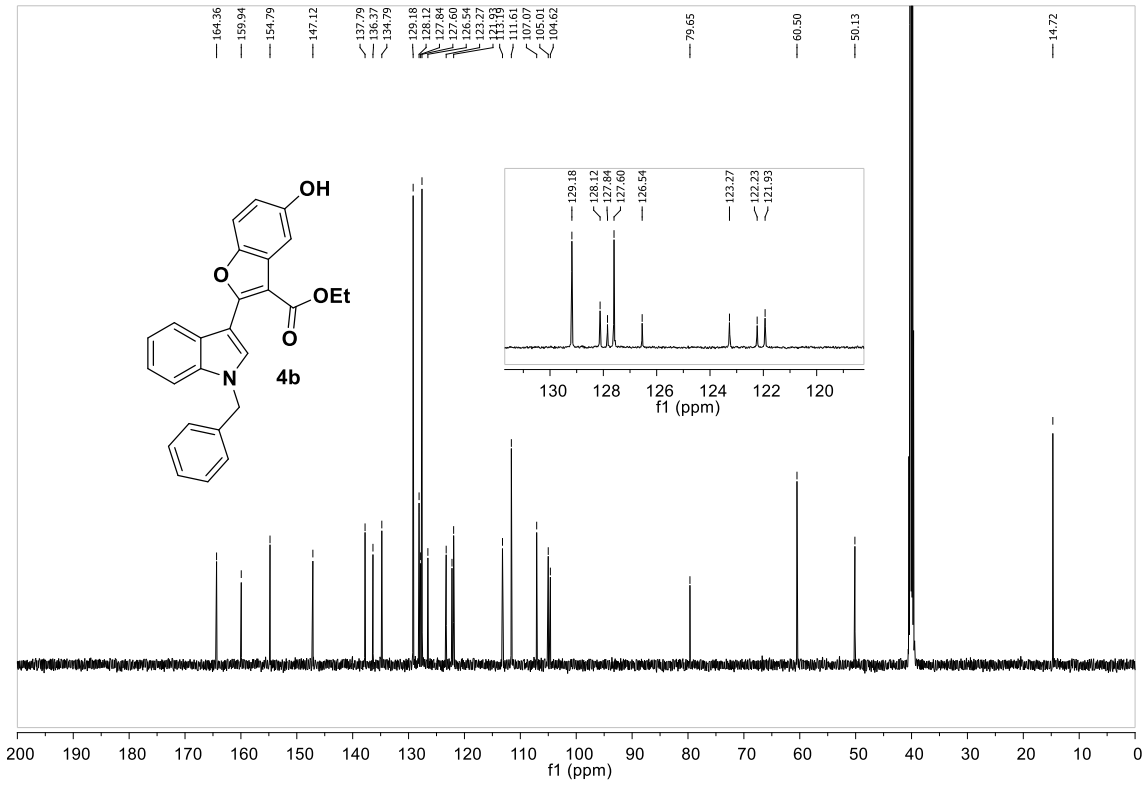
^{13}C NMR (126 MHz, DMSO-d_6) spectrum of **4a**



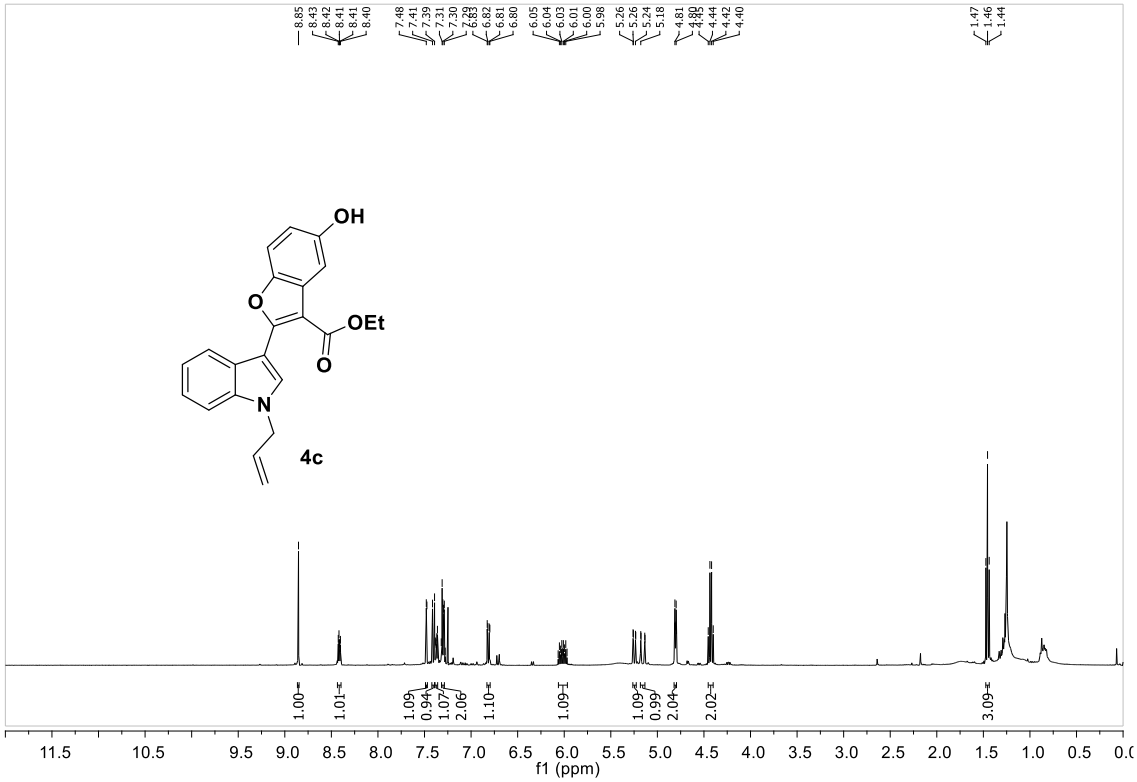
^{1}H NMR (500 MHz, DMSO-d_6) spectrum of **4b**



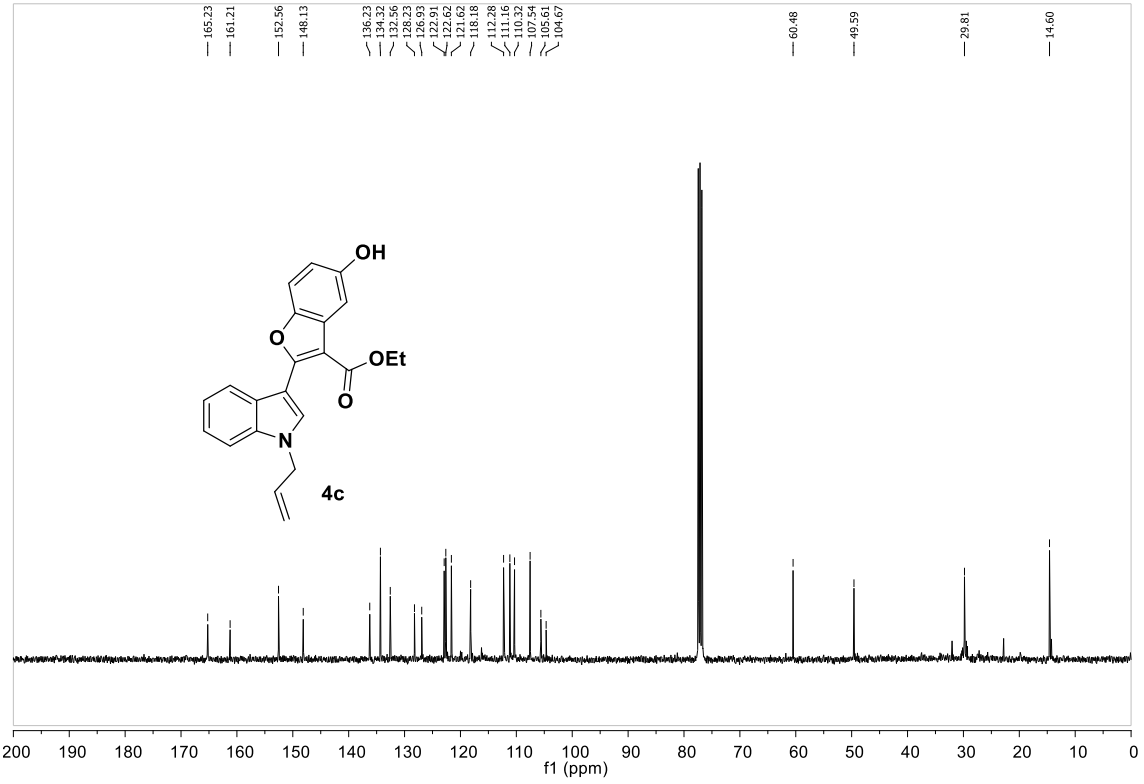
^{13}C NMR (126 MHz, DMSO-d_6) spectrum of **4b**



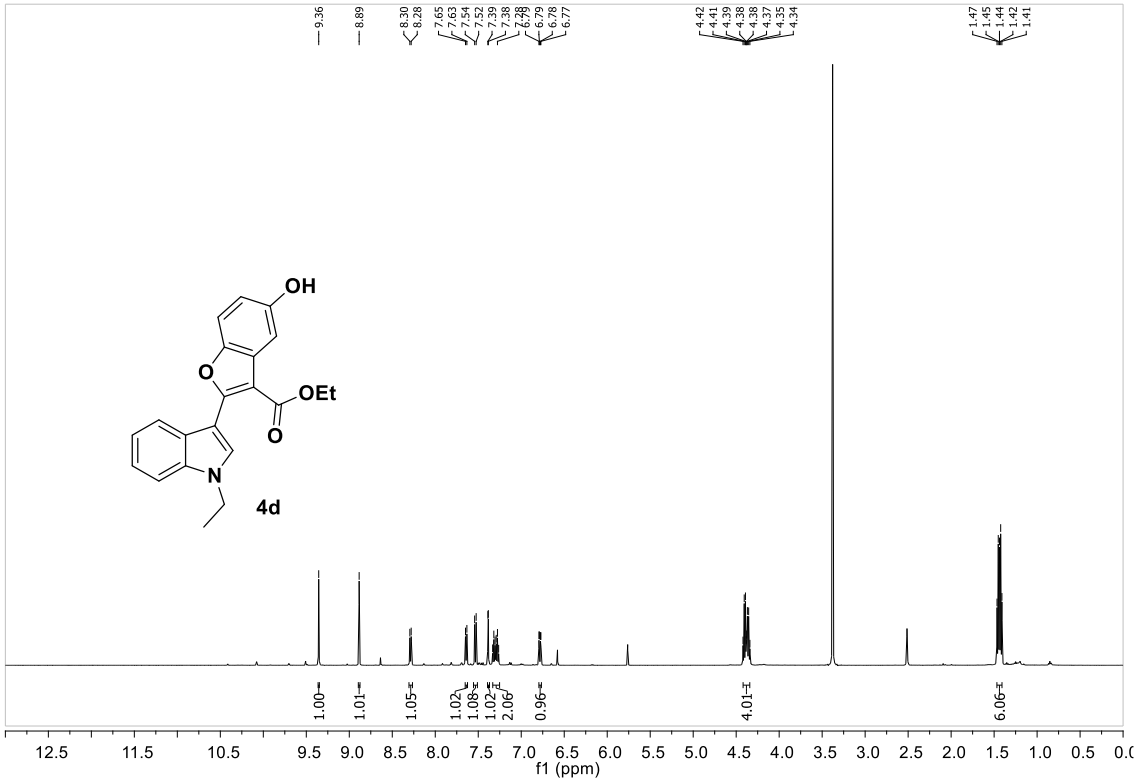
^{1}H NMR (500 MHz, $CDCl_3$) spectrum of **4c**



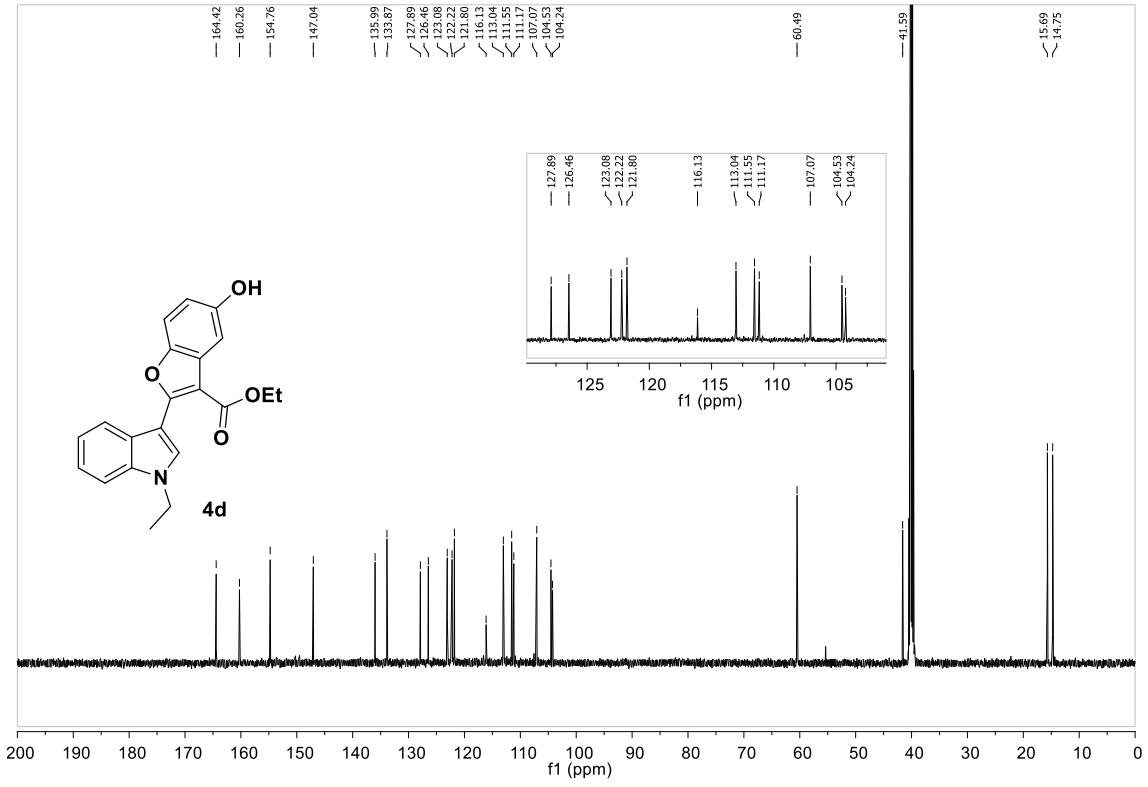
^{13}C NMR (126 MHz, $CDCl_3$) spectrum of **4c**



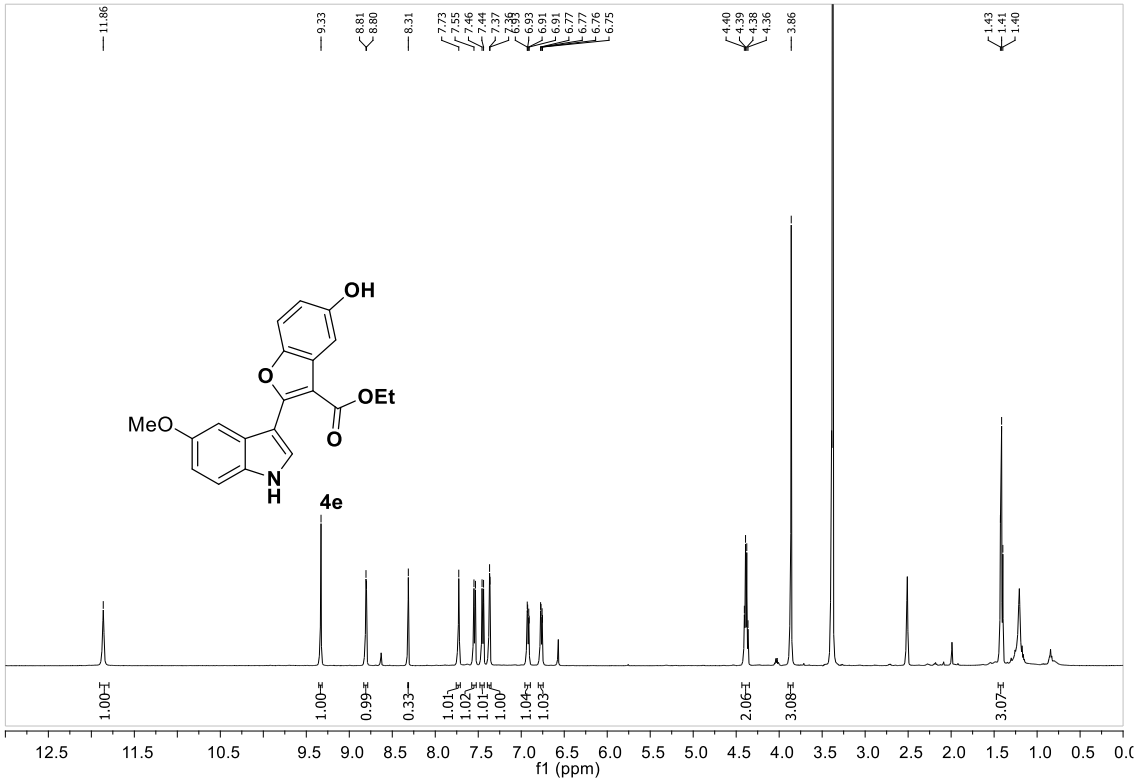
^{1}H NMR (500 MHz, DMSO-d_6) spectrum of **4d**



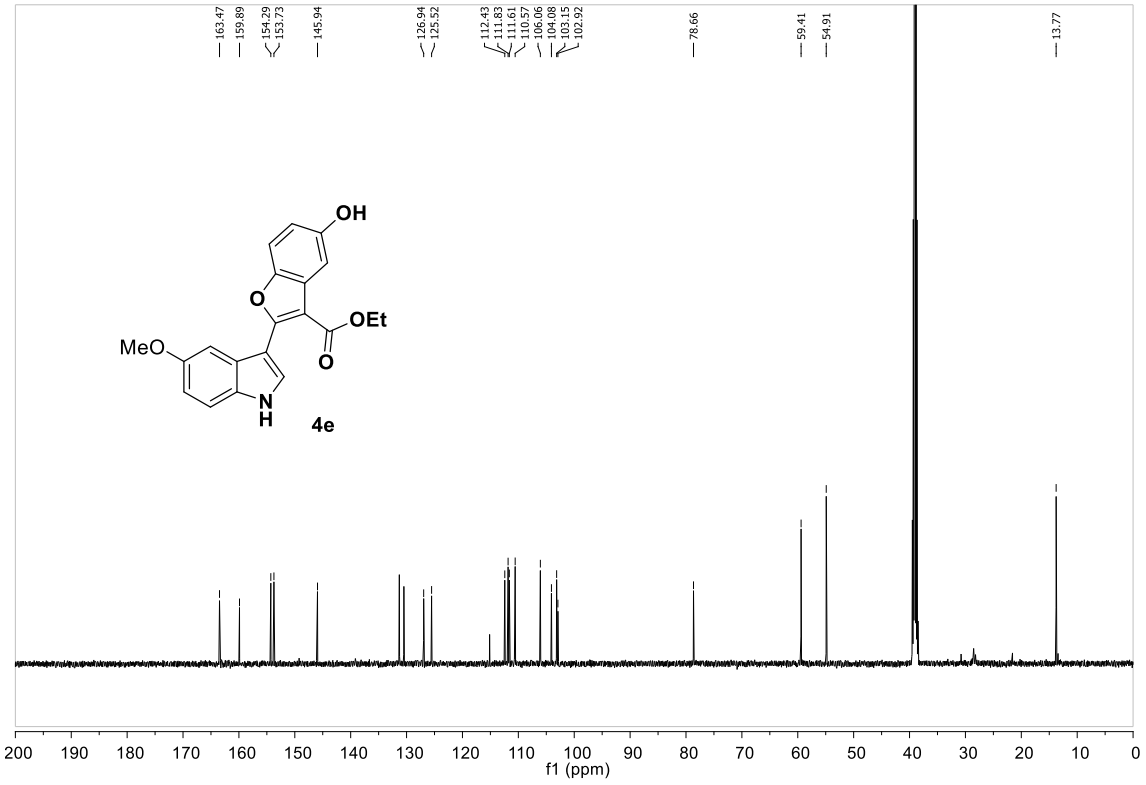
^{13}C NMR (126 MHz, $CDCl_3$) spectrum of **4d**



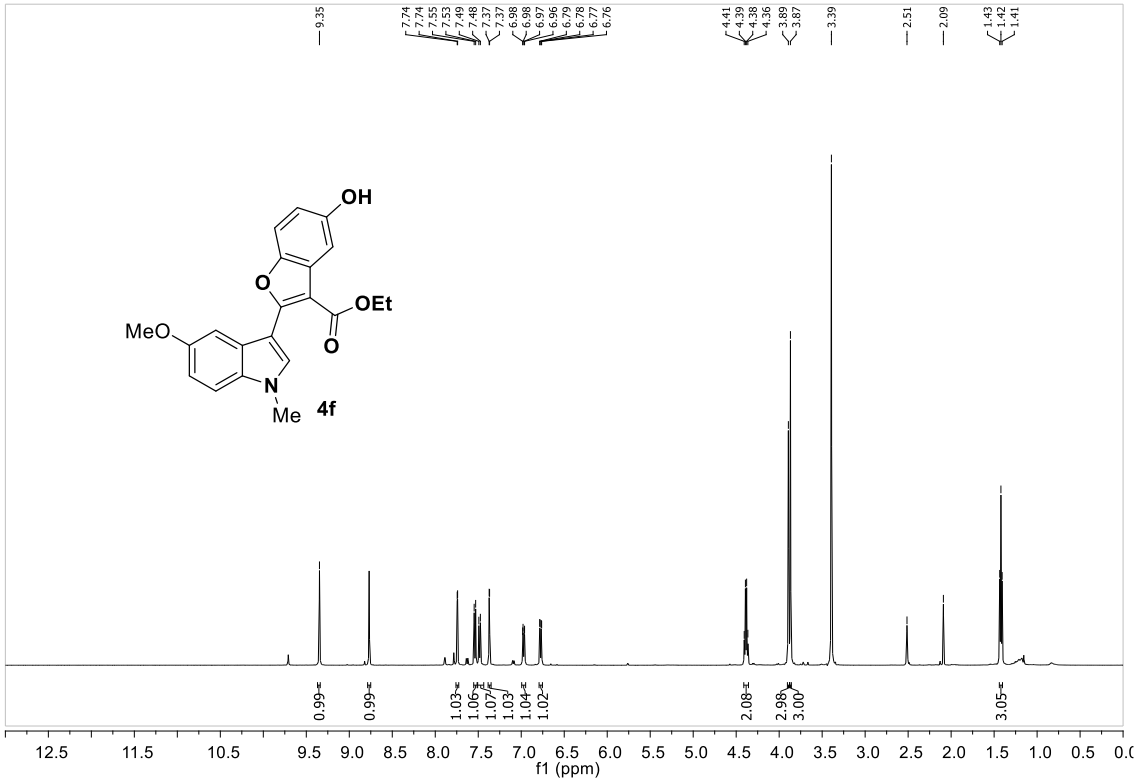
^{1}H NMR (500 MHz, DMSO-d_6) spectrum of **4e**



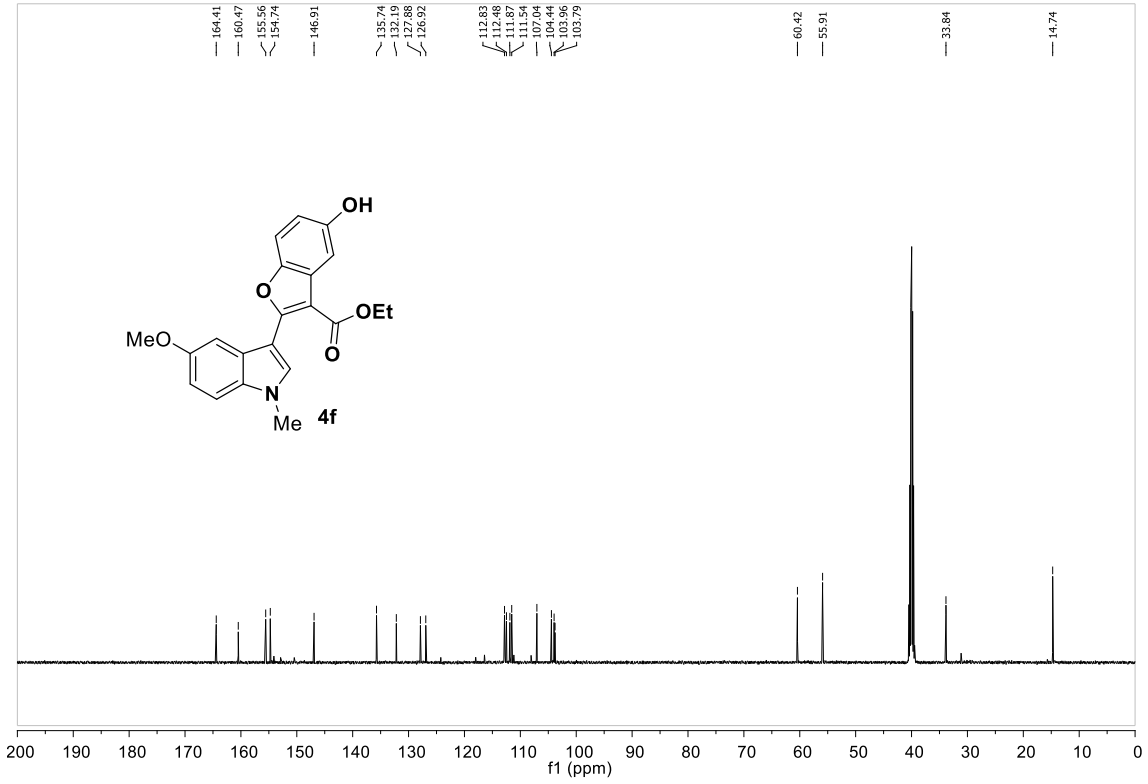
^{13}C NMR (126 MHz, DMSO-d_6) of **4e**



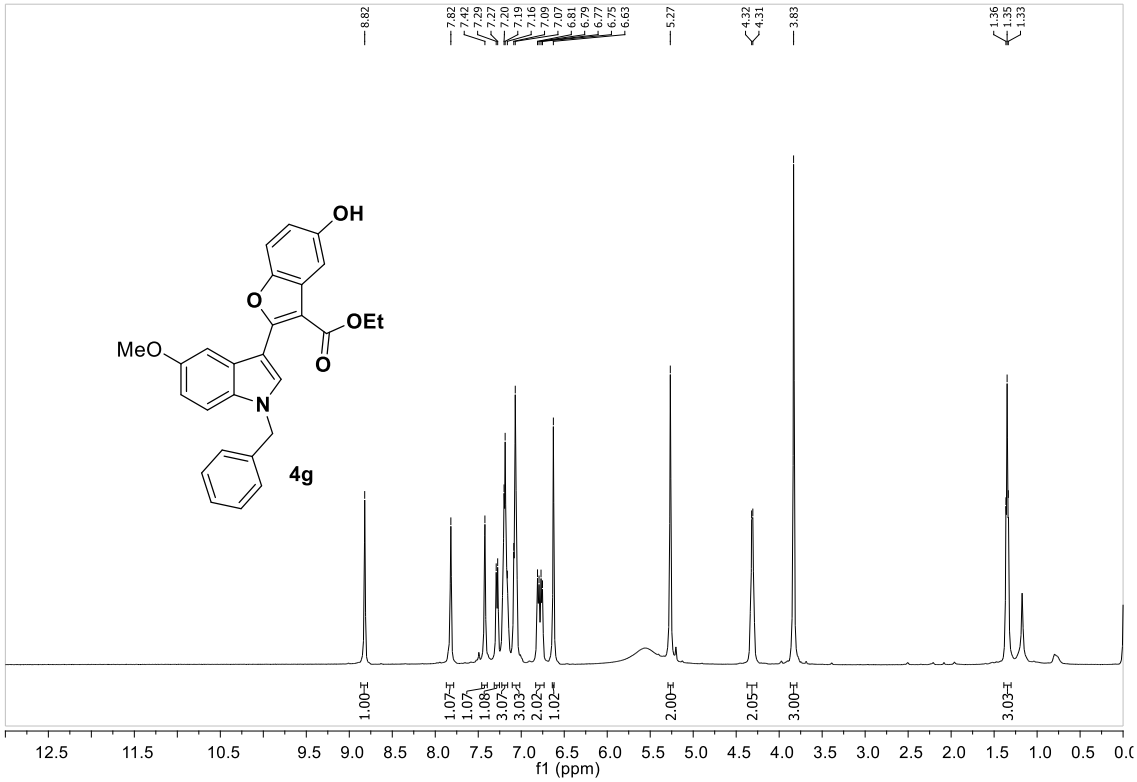
^{1}H NMR (500 MHz, DMSO-d_6) spectrum of **4f**



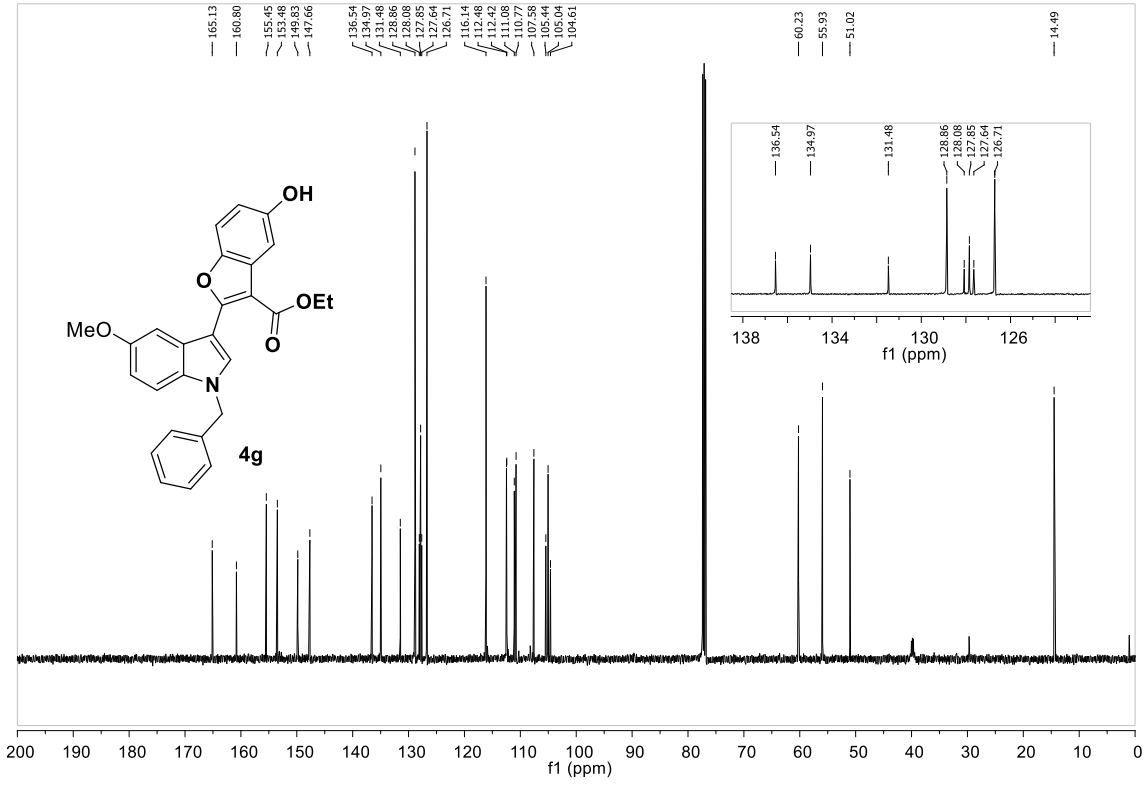
^{13}C NMR (126 MHz, DMSO-d_6) spectrum of **4f**



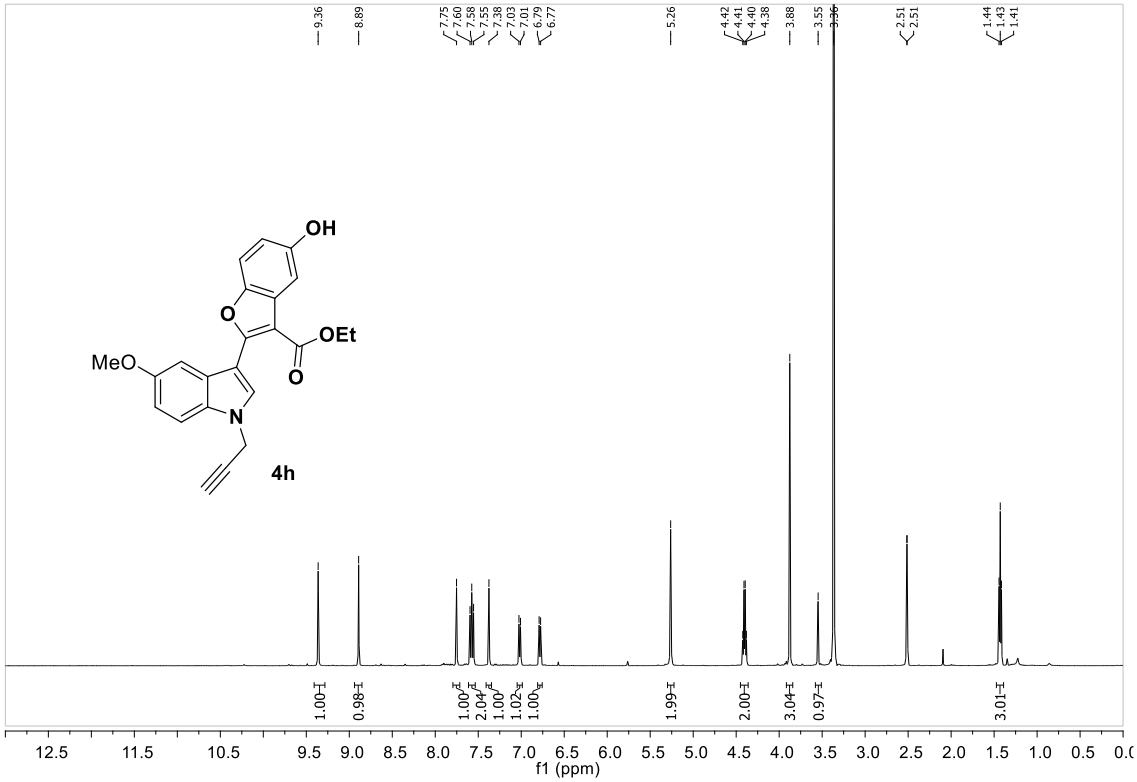
^{1}H NMR (500 MHz, DMSO-d_6) spectrum of **4g**



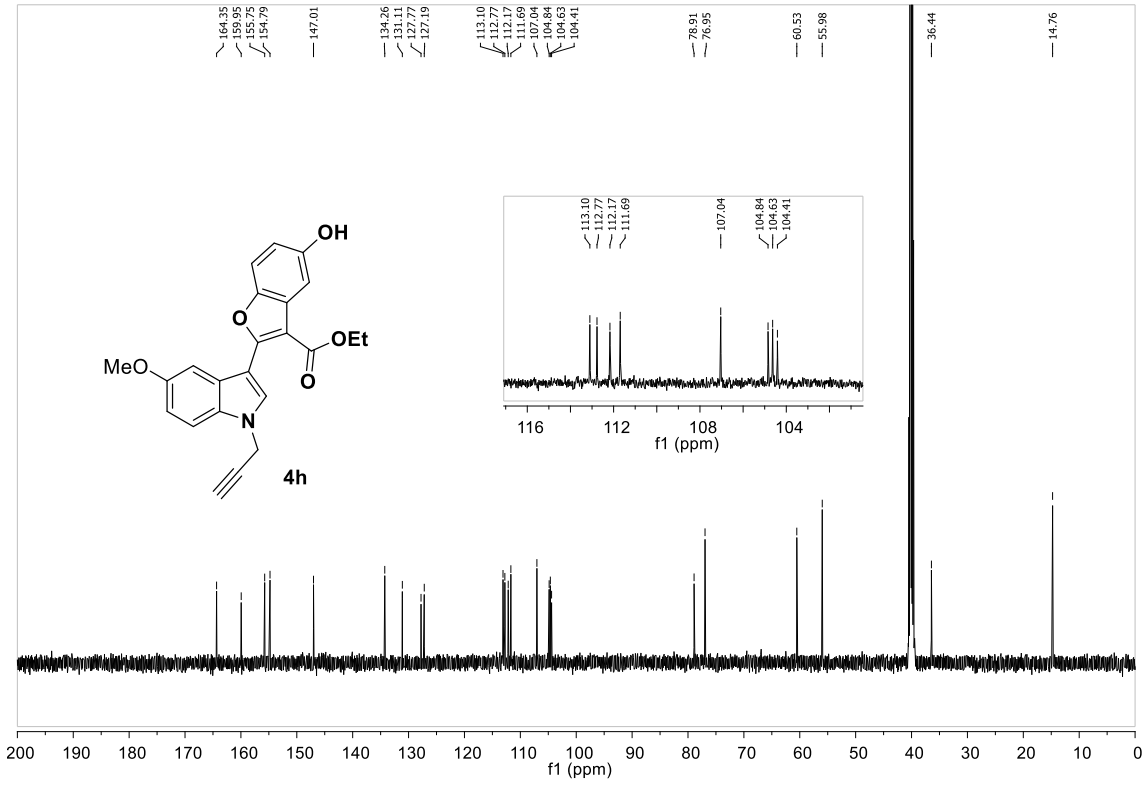
^{13}C NMR (126 MHz, DMSO-d_6) spectrum of **4g**



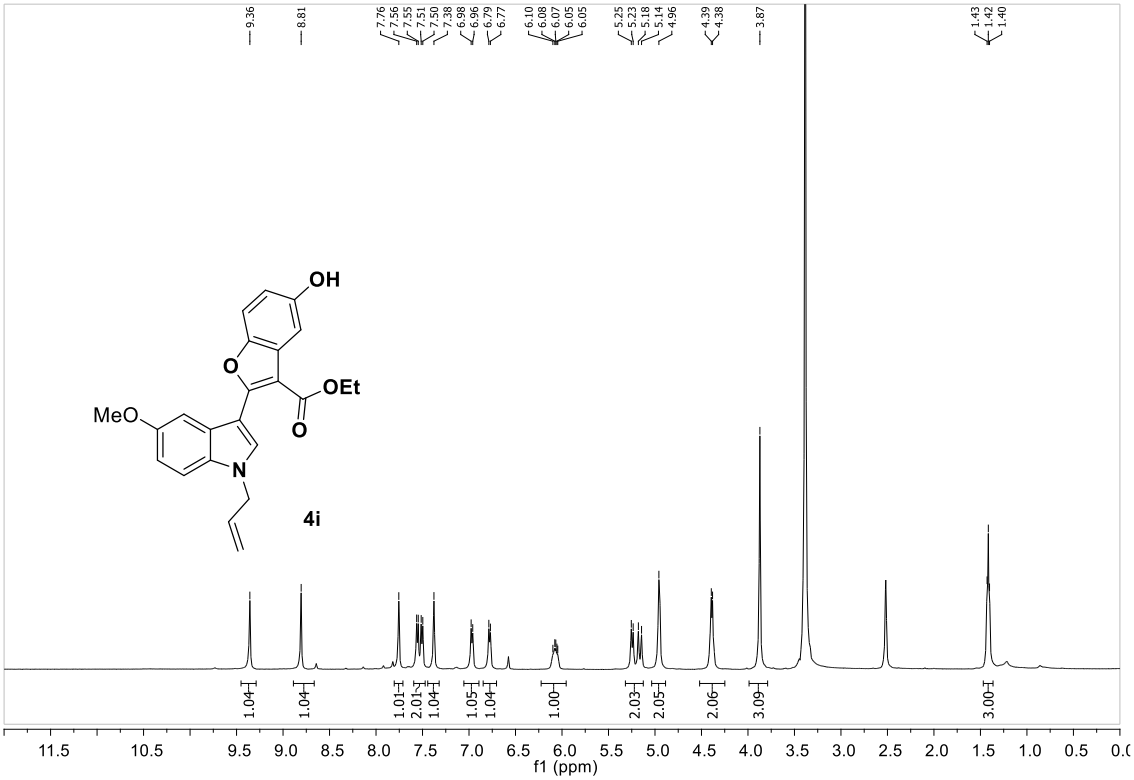
^{1}H NMR (500 MHz, DMSO-d_6) spectrum of **4h**



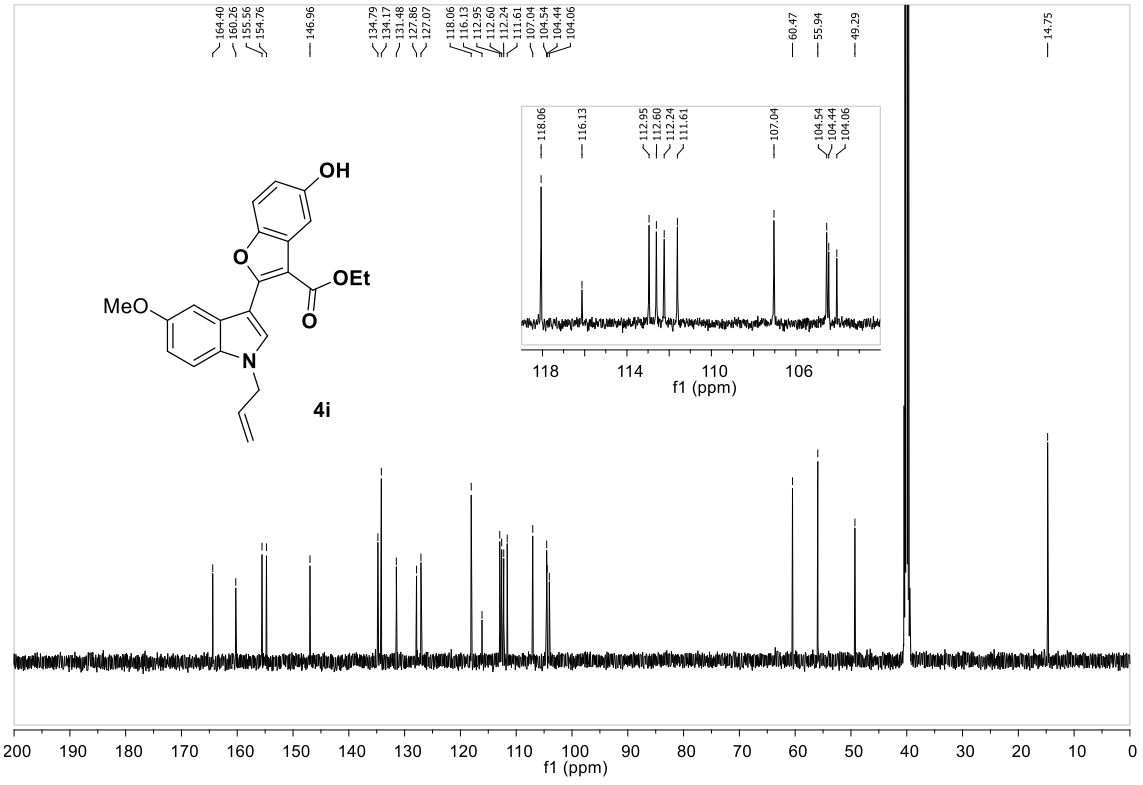
^{13}C NMR (126 MHz, DMSO-d_6) spectrum of **4h**



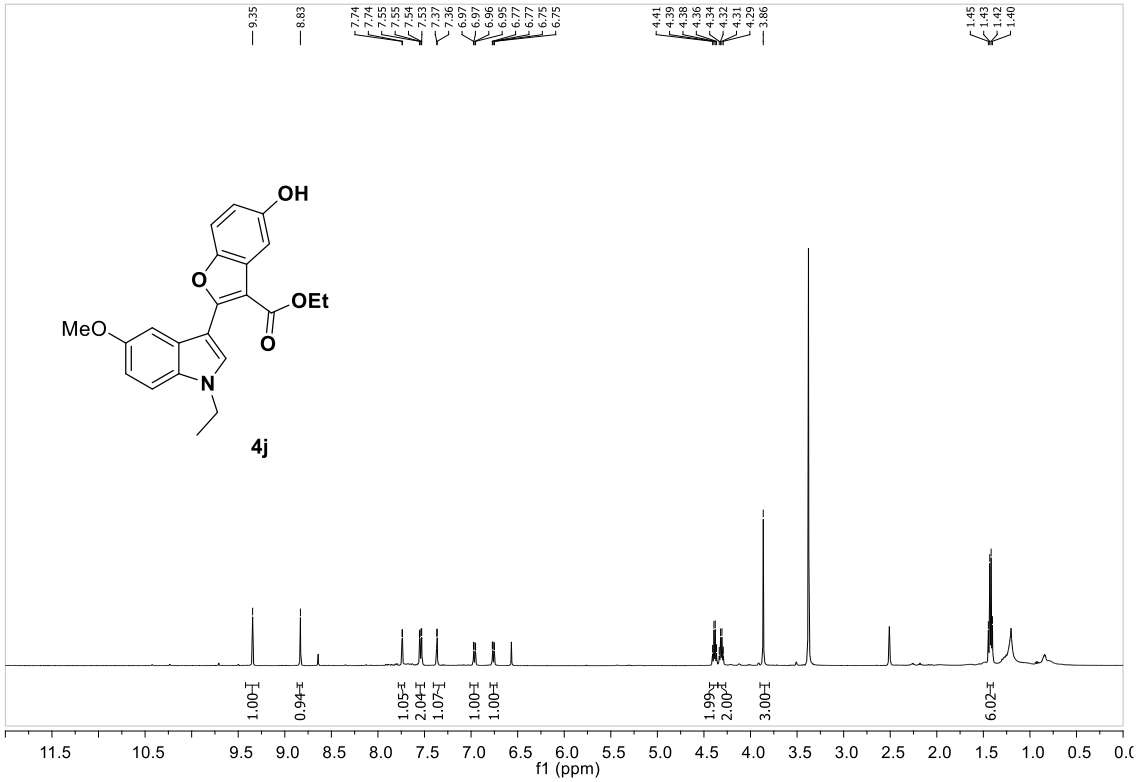
^{1}H NMR (500 MHz, DMSO-d_6) spectrum of **4i**



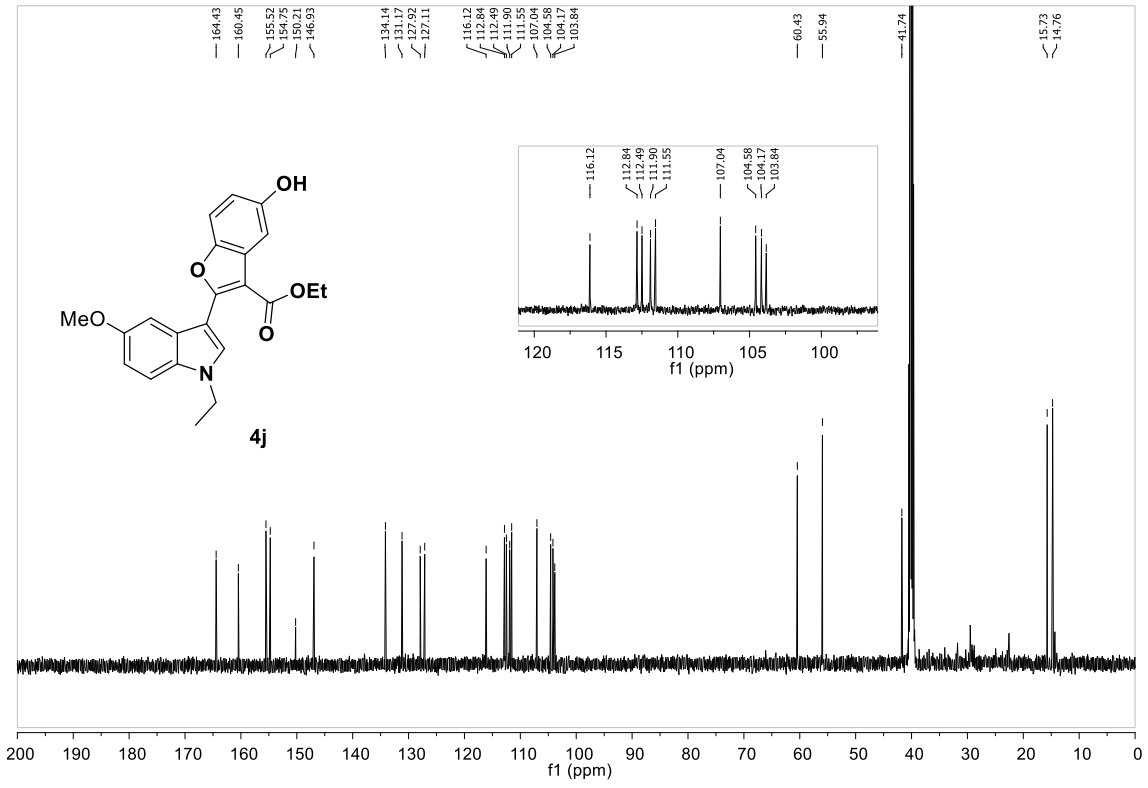
^{13}C NMR (126 MHz, DMSO-d_6) spectrum of **4i**



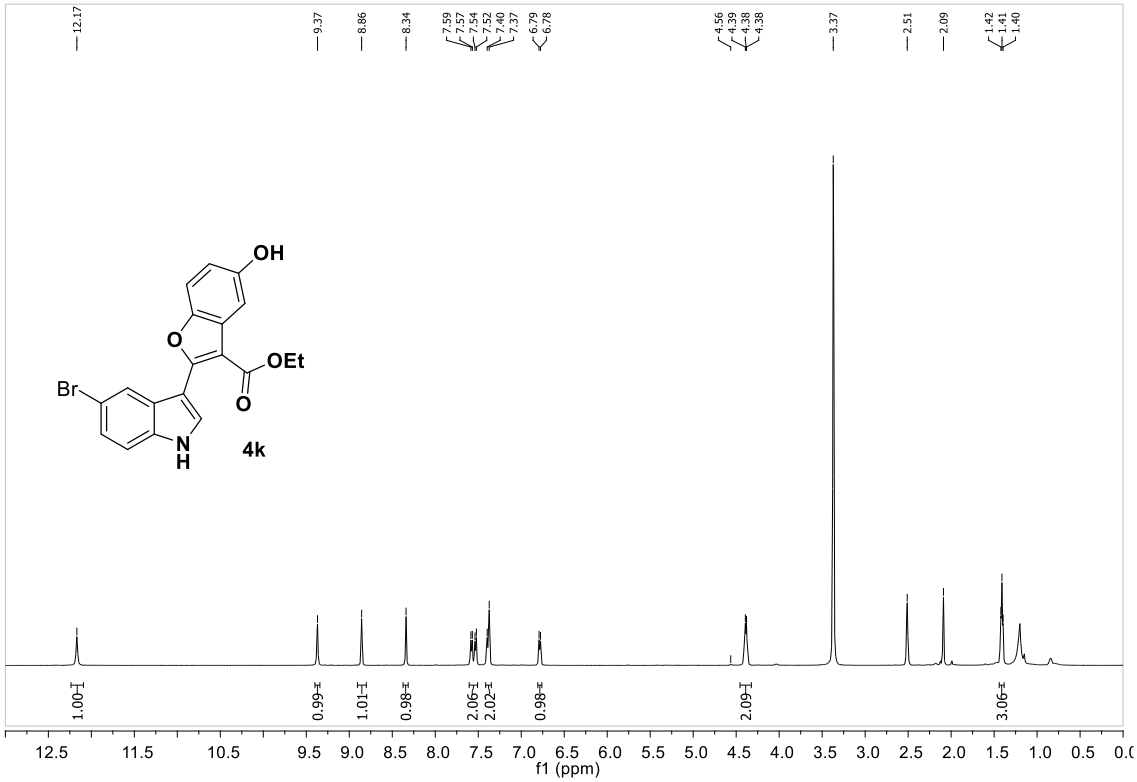
[1]H NMR (500 MHz, DMSO-*d*$_6$) spectrum of **4j**



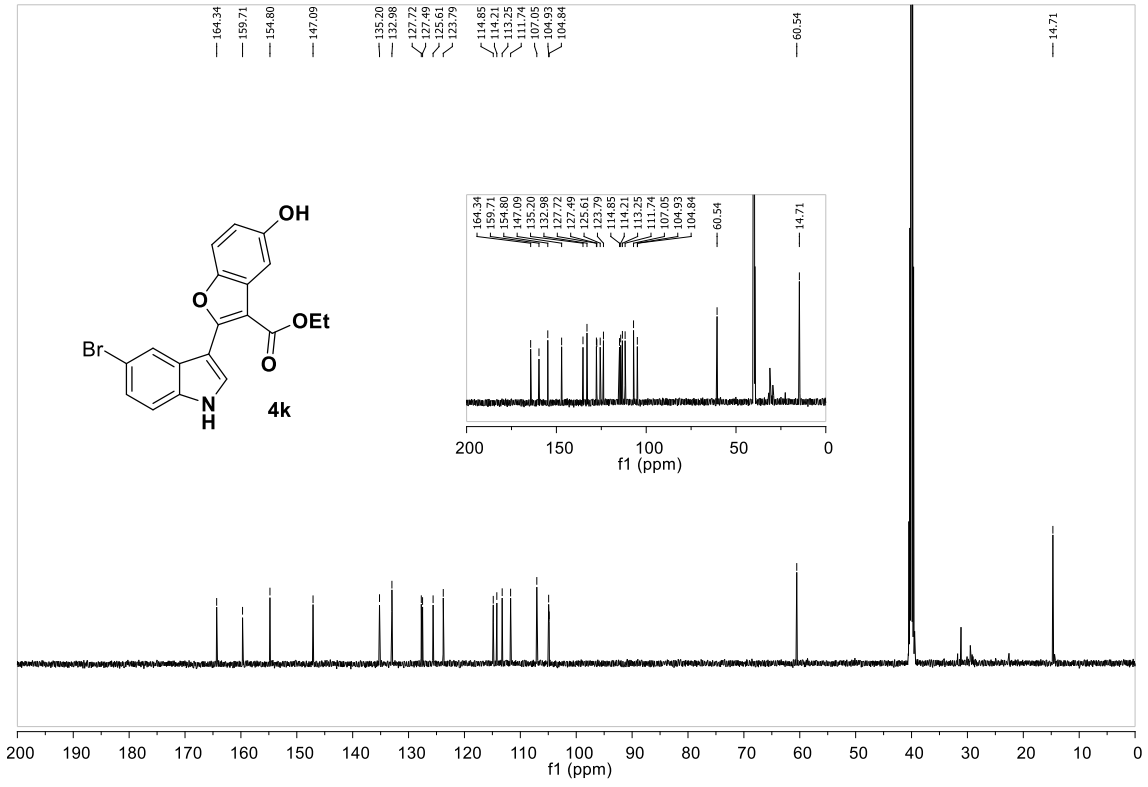
[13]C NMR (126 MHz, DMSO-*d*$_6$) spectrum of **4j**



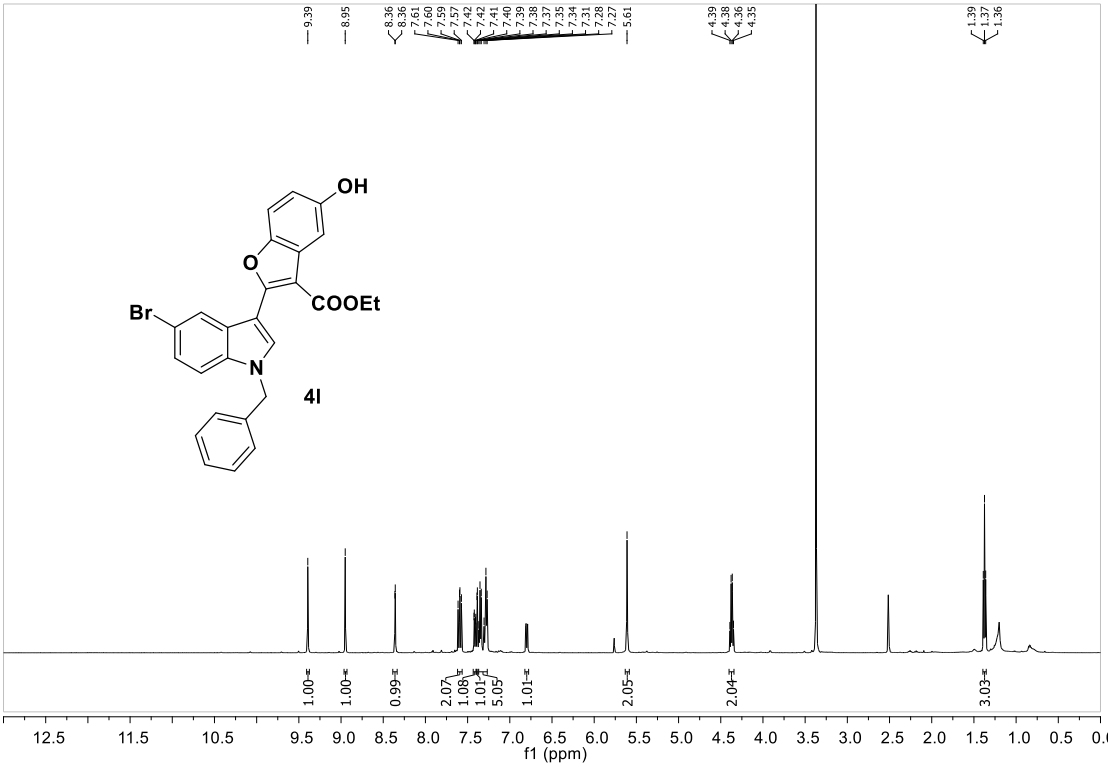
^{1}H NMR (500 MHz, DMSO-d_6) of spectrum **4k**



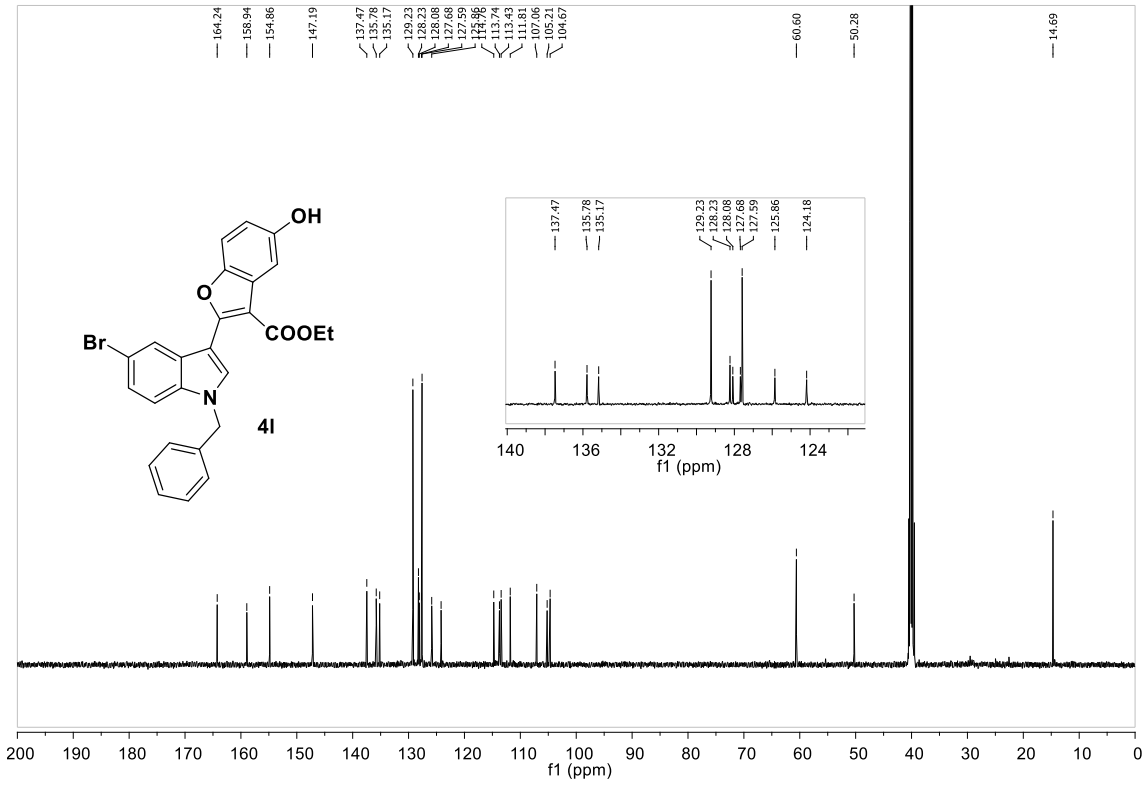
^{13}C NMR (126 MHz, DMSO-d_6) spectrum of **4k**



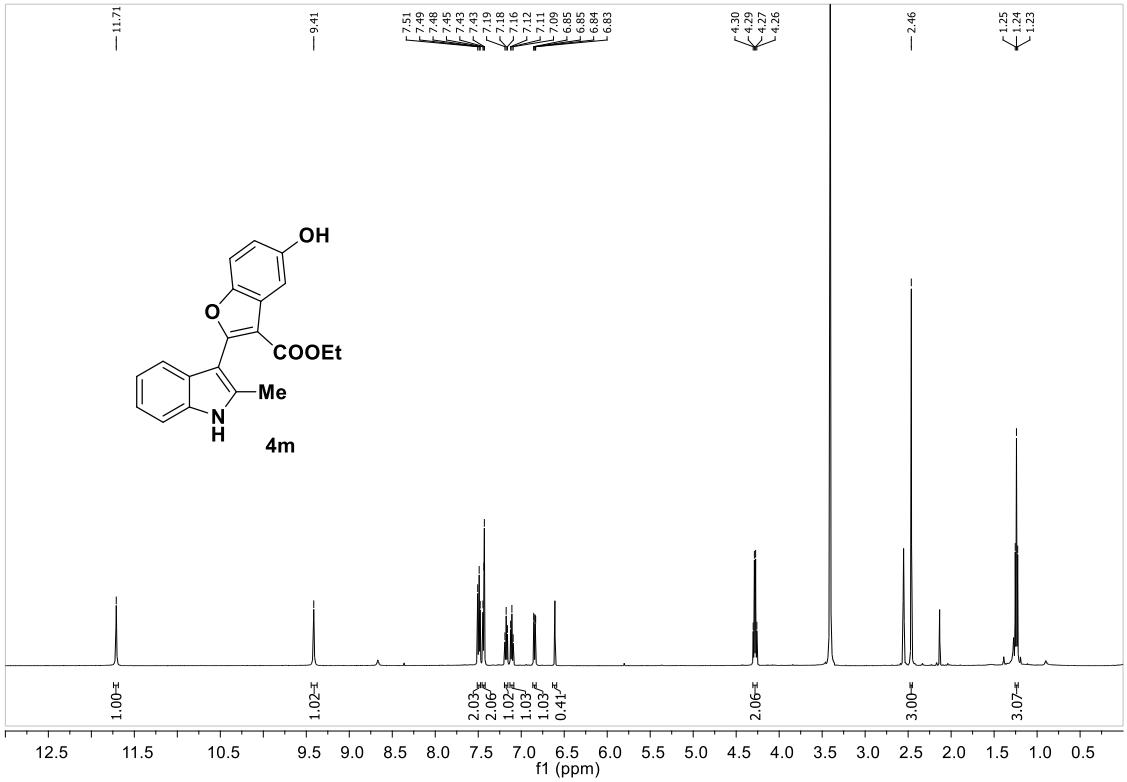
^{1}H NMR (500 MHz, DMSO-d_6) spectrum of **4l**



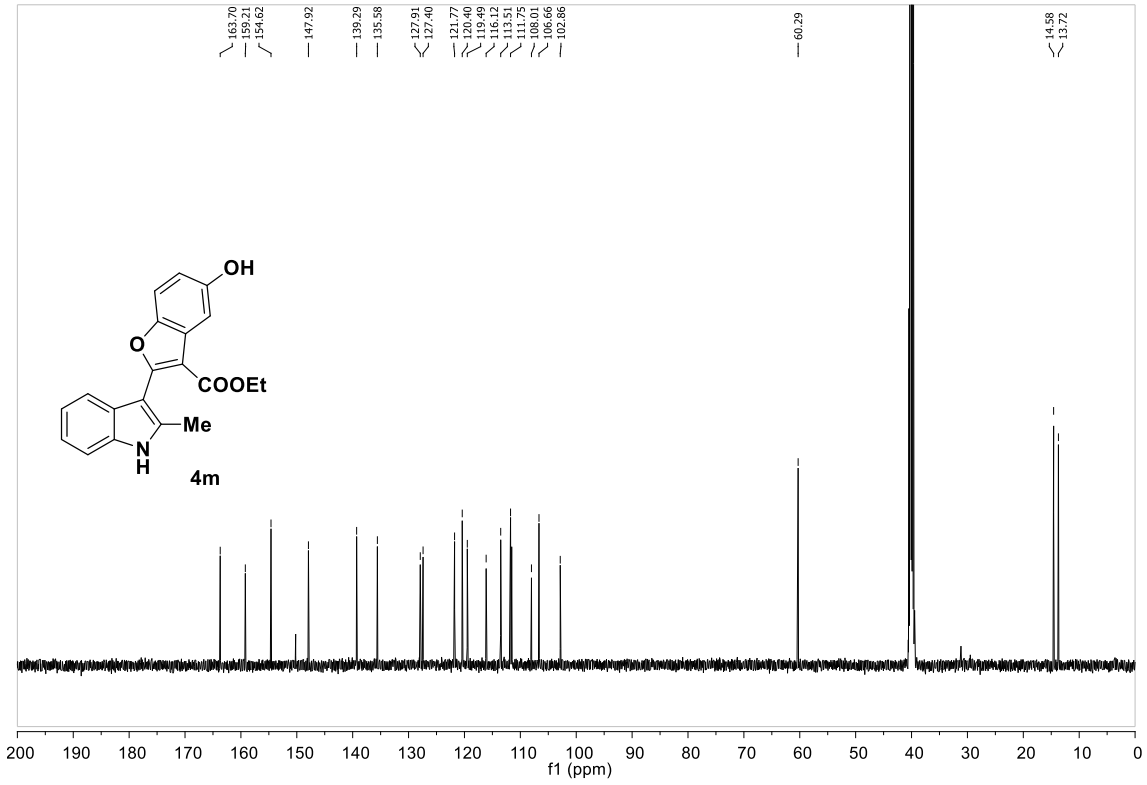
^{13}C NMR (126 MHz, DMSO-d_6) spectrum of **4l**



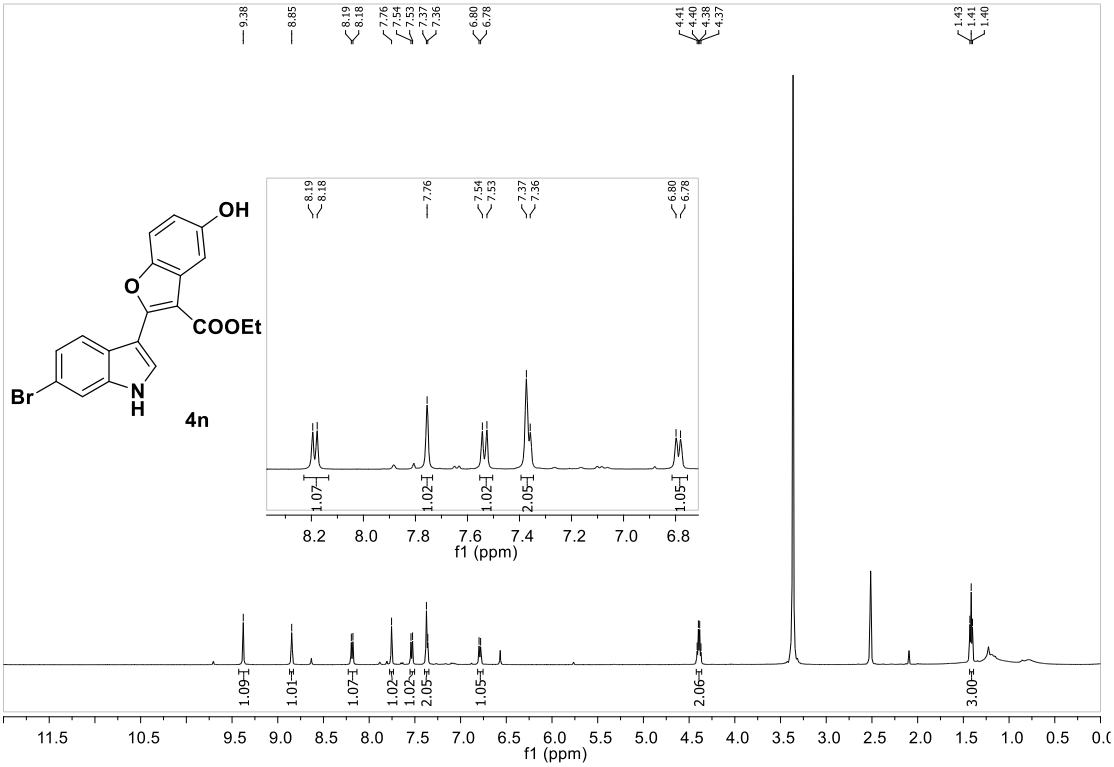
^{1}H NMR (500 MHz, DMSO-d_6) spectrum of **4m**



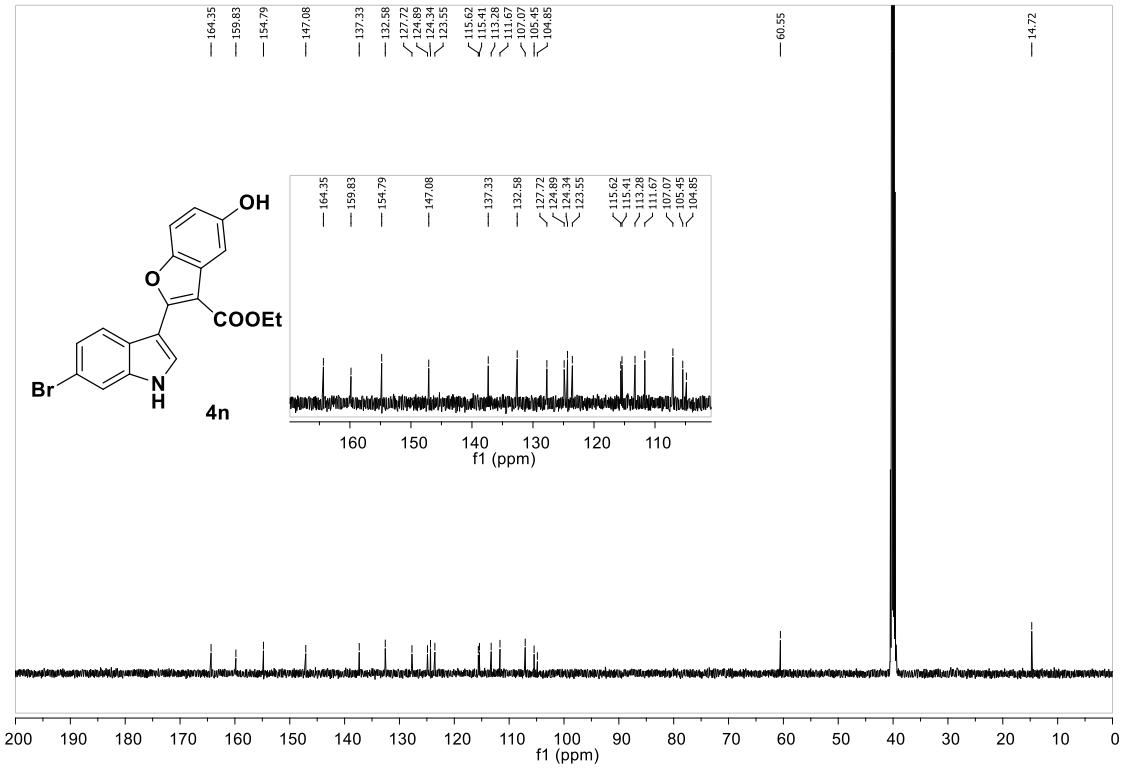
^{13}C NMR (126 MHz, DMSO-d_6) spectrum of **4m**



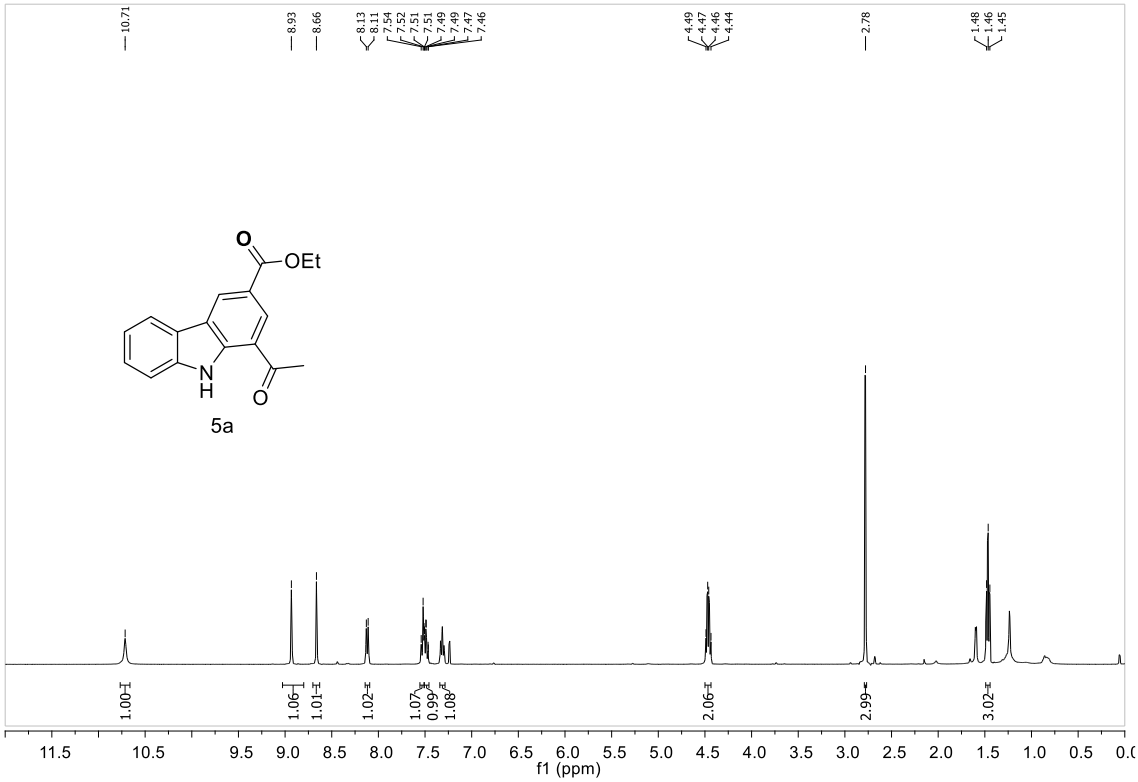
^{1}H NMR (500 MHz, DMSO-d_6) spectrum of **4n**



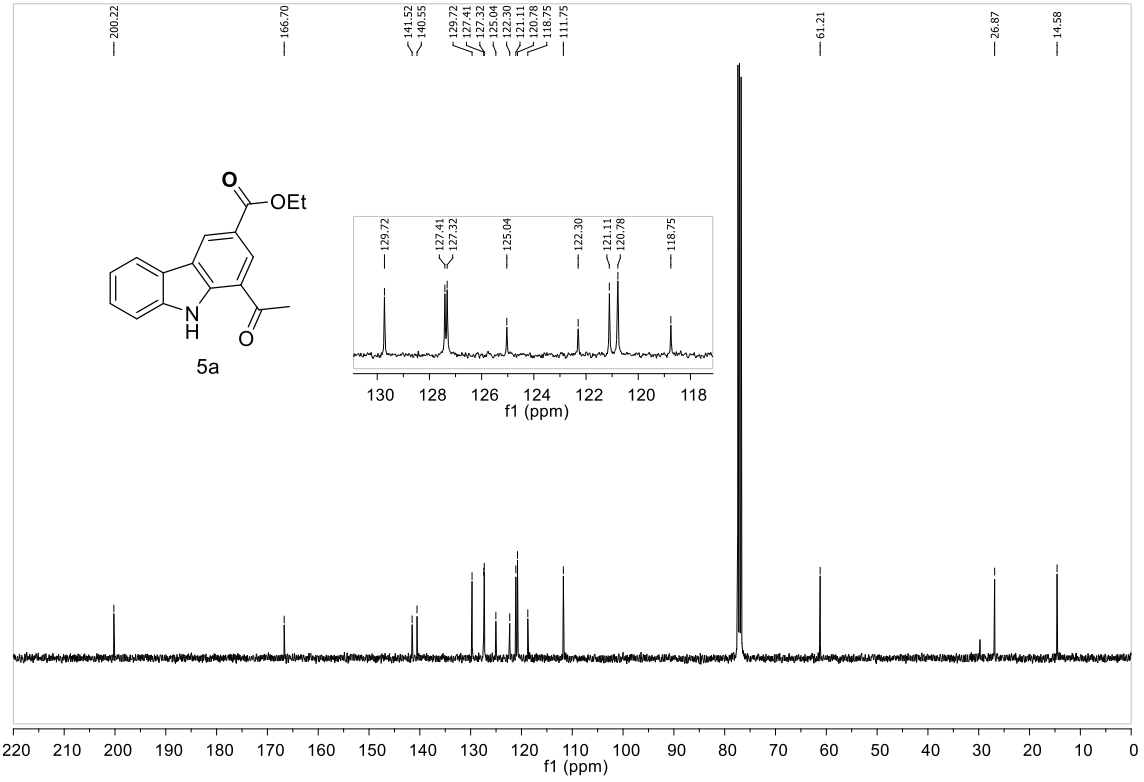
^{13}C NMR (126 MHz, DMSO-d_6) spectrum of **4n**



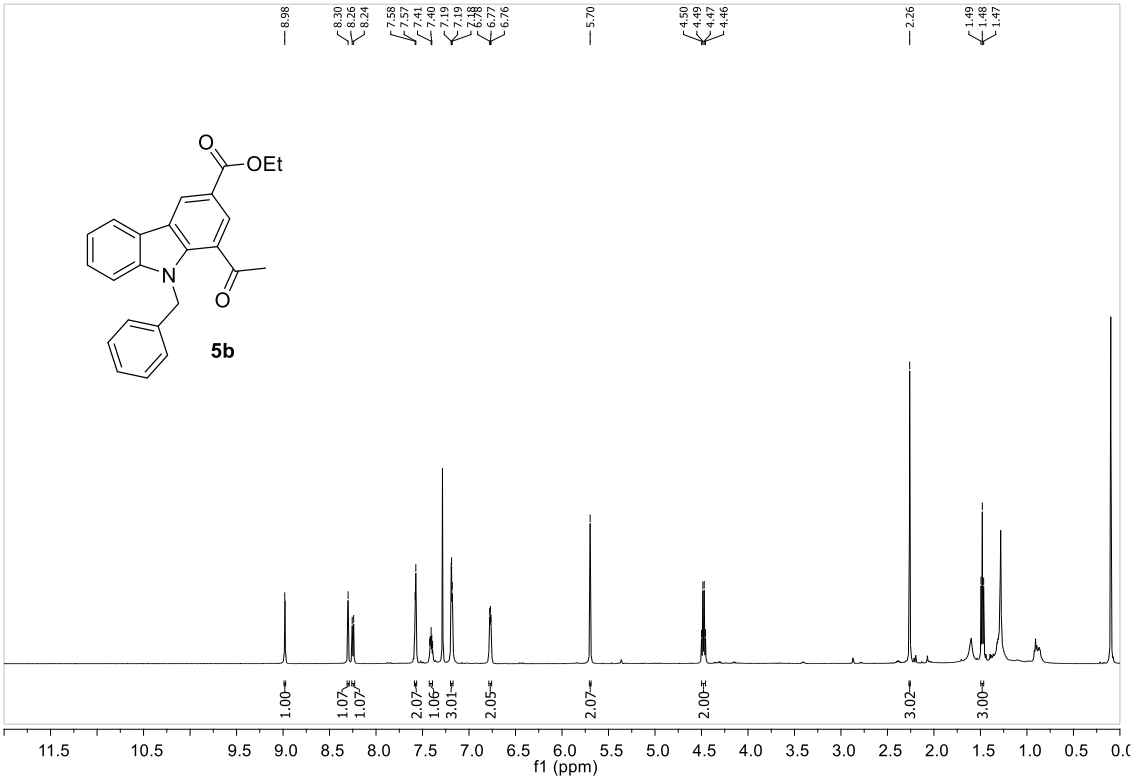
^{1}H NMR (500 MHz, $CDCl_3$) spectrum of **5a**



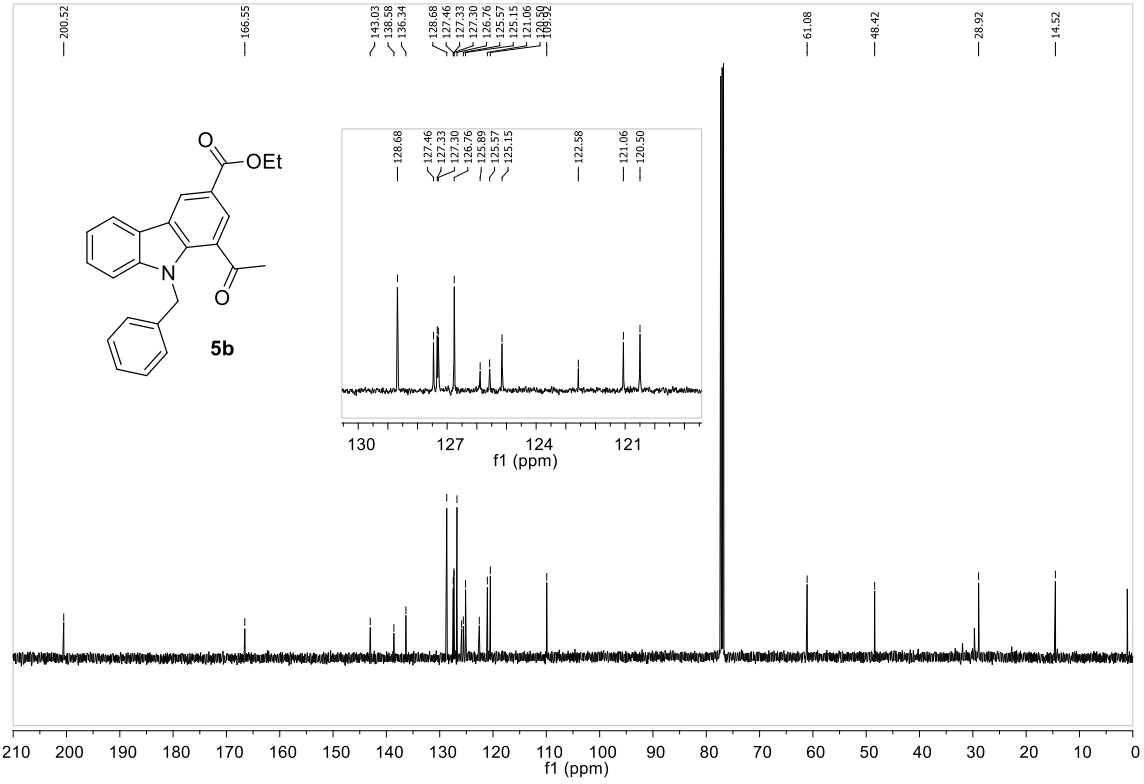
^{13}C{^{1}H} NMR (126 MHz, $CDCl_3$) spectrum of **5a**



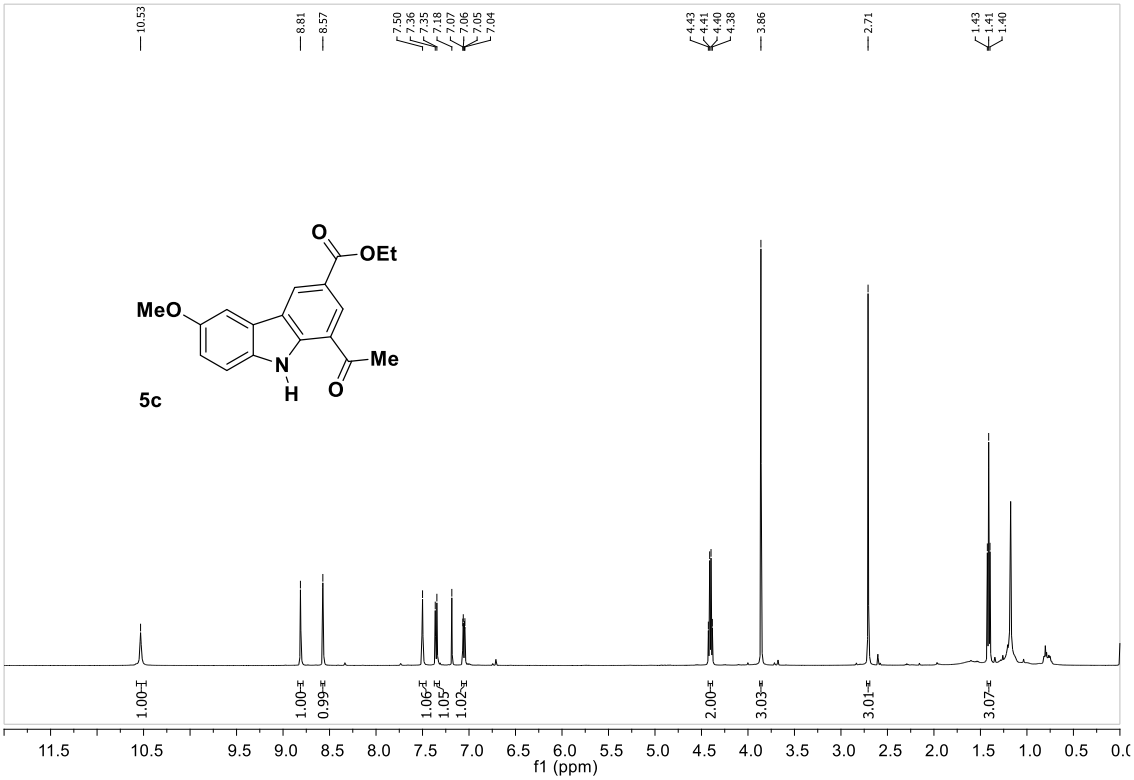
^{1}H NMR (500 MHz, $CDCl_3$) spectrum of **5b**



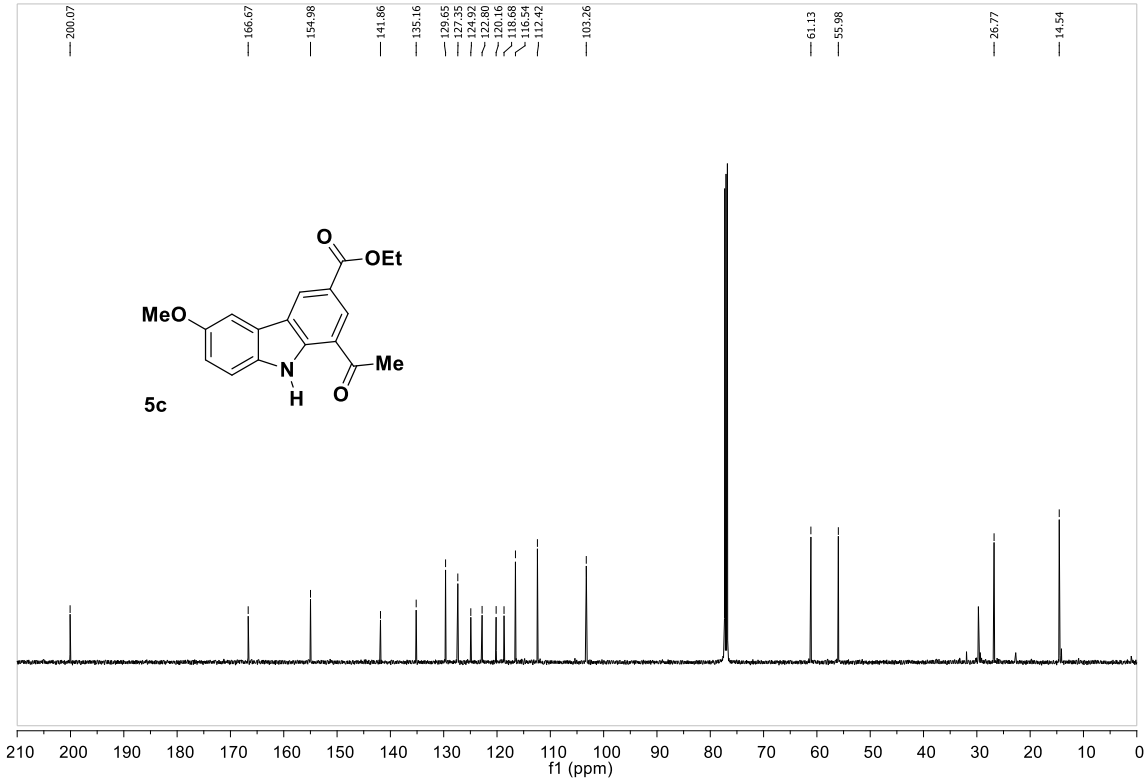
^{13}C{^{1}H} NMR (126 MHz, $CDCl_3$) spectrum of **5b**



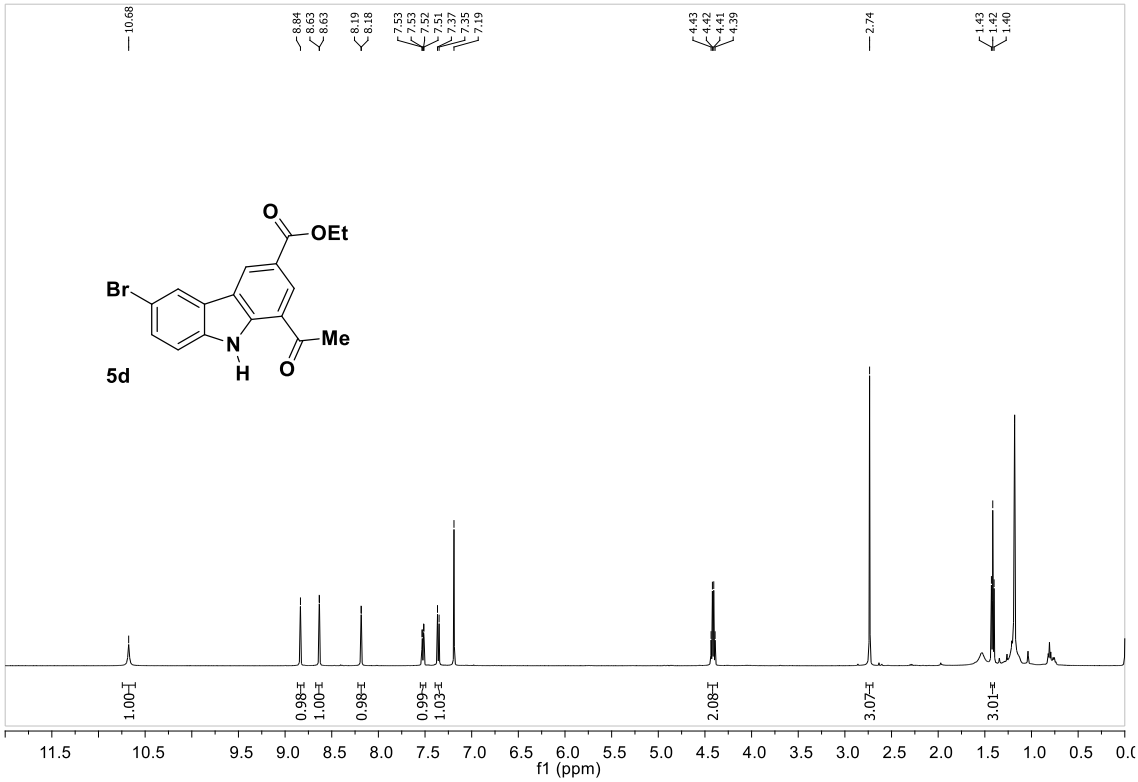
^{1}H NMR (500 MHz, $CDCl_3$) spectrum of **5c**



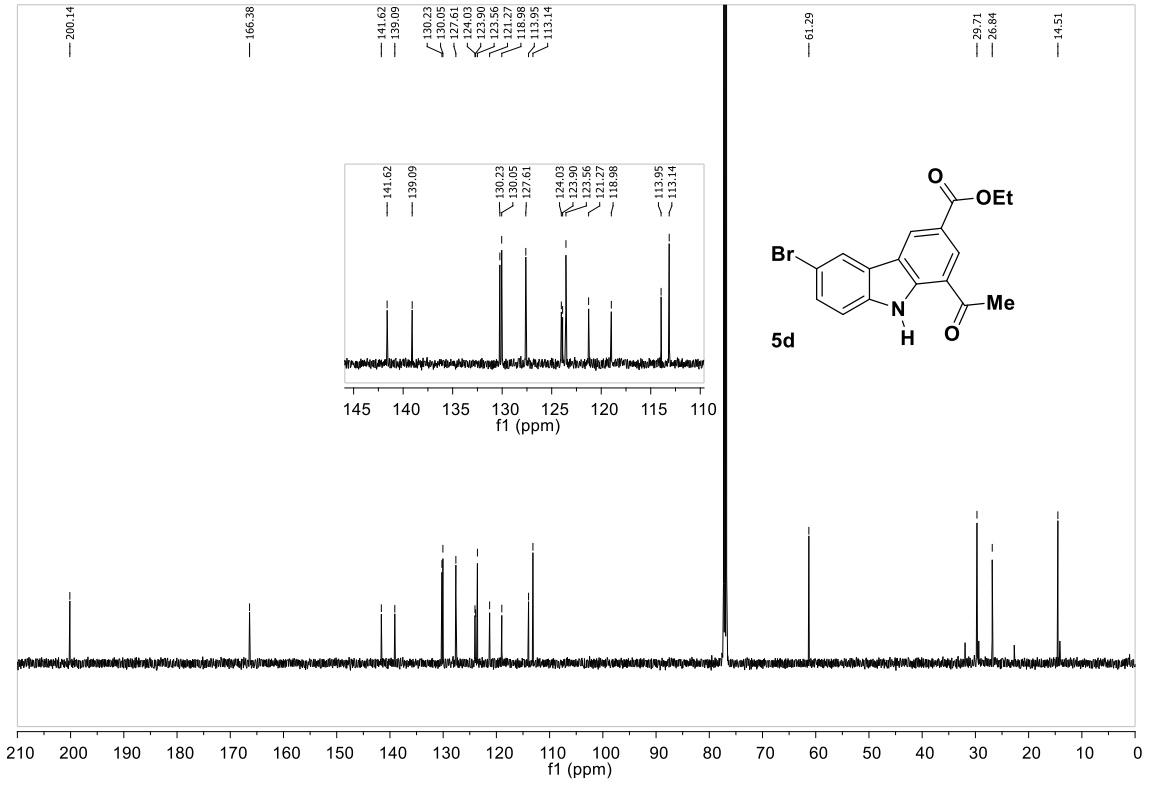
^{13}C{^{1}H} NMR (126 MHz, $CDCl_3$) spectrum of **5c**



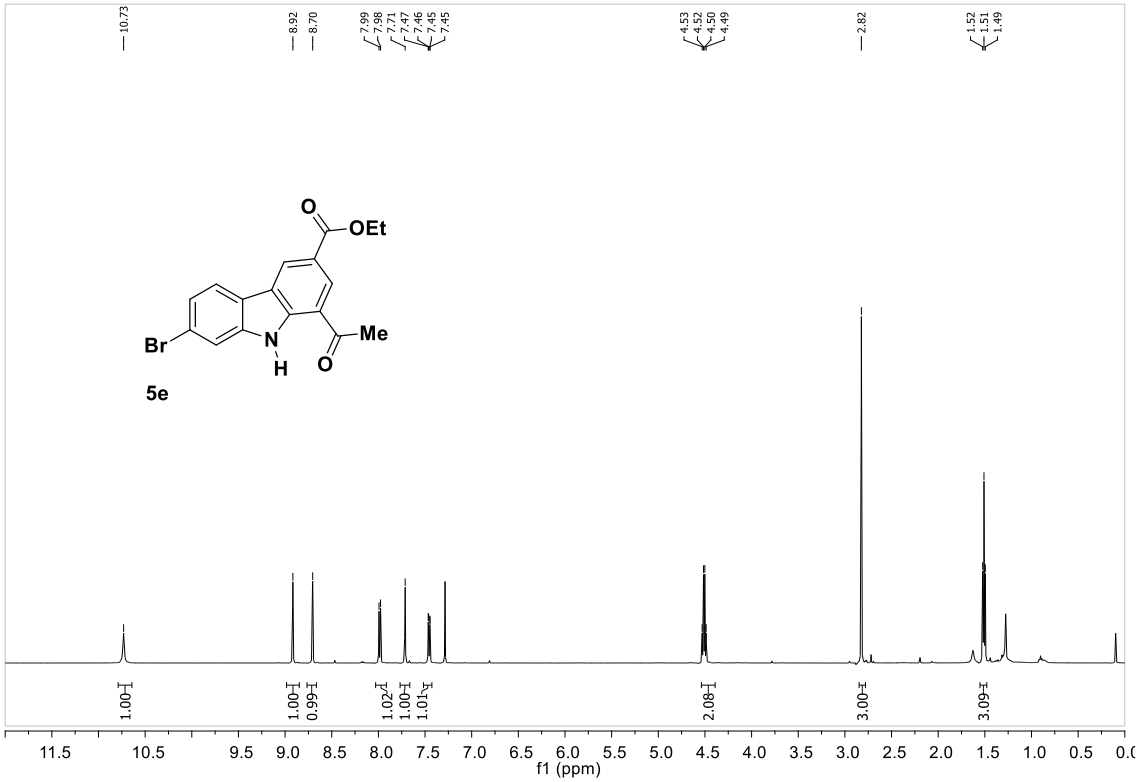
^{1}H NMR (500 MHz, $CDCl_3$) spectrum of **5d**



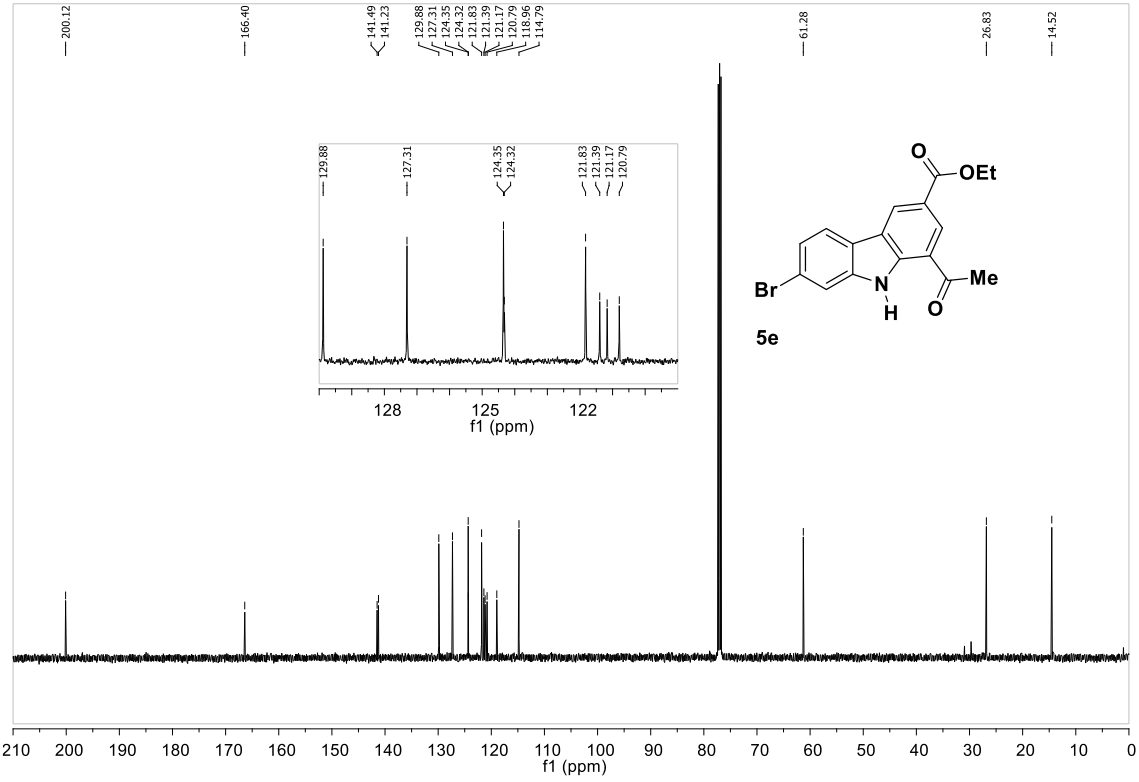
^{13}C{^{1}H} NMR (126 MHz, $CDCl_3$) spectrum of **5d**



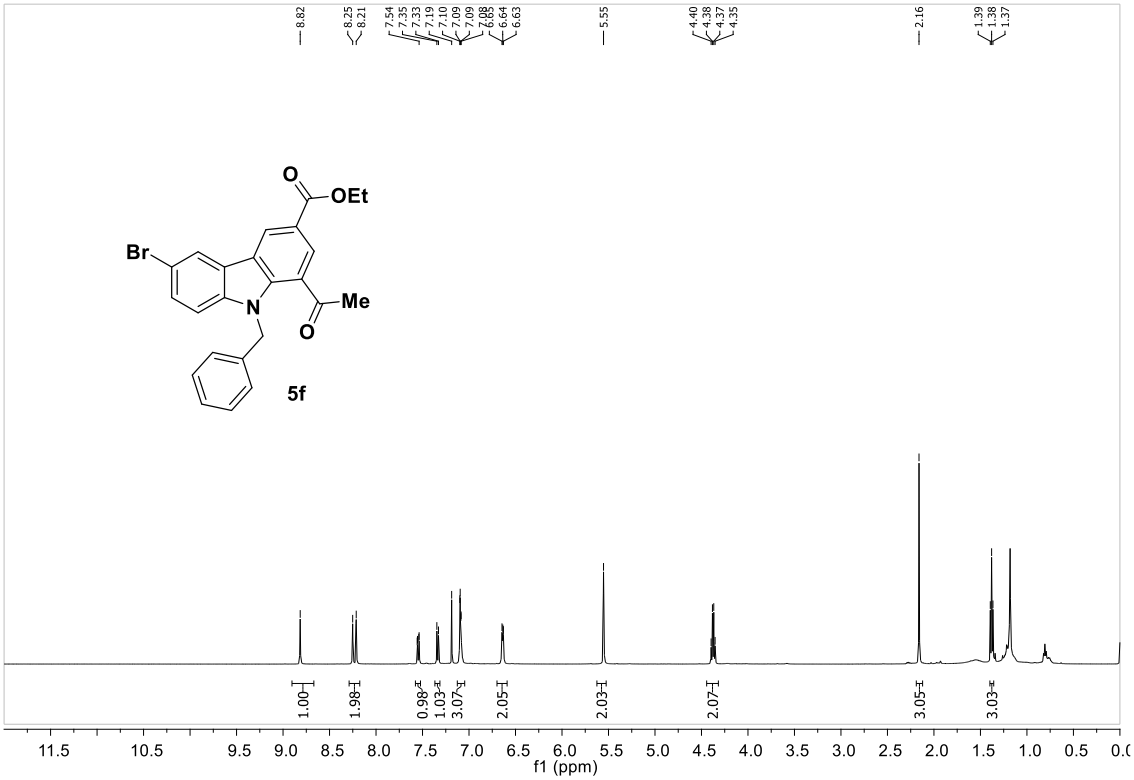
^{1}H NMR (500 MHz, $CDCl_3$) spectrum of **5e**



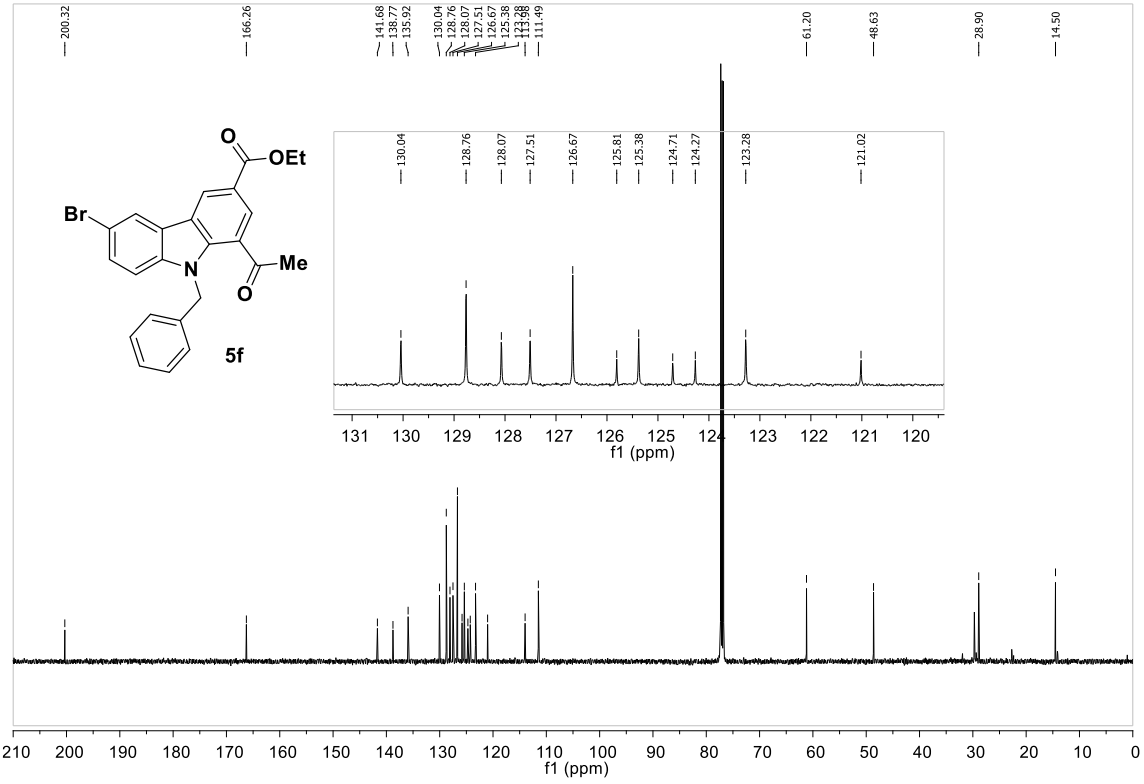
^{13}C{^{1}H} NMR (126 MHz, $CDCl_3$) spectrum of **5e**



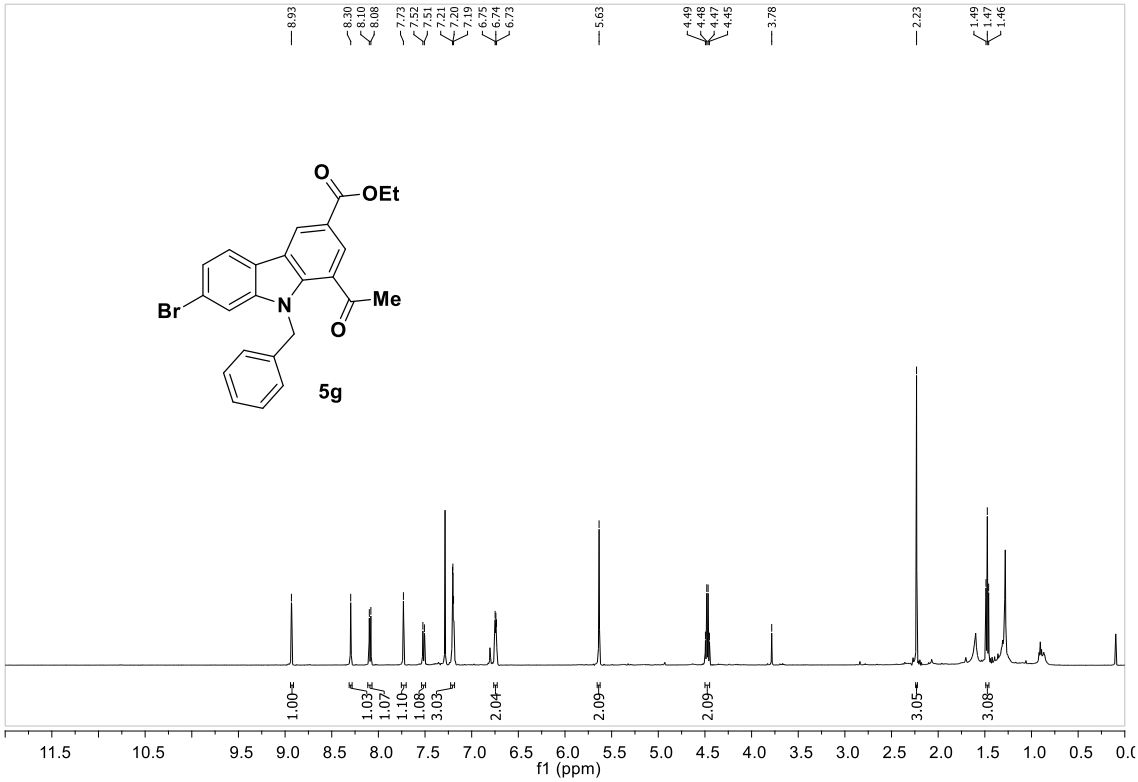
^{1}H NMR (500 MHz, $CDCl_3$) spectrum of **5f**



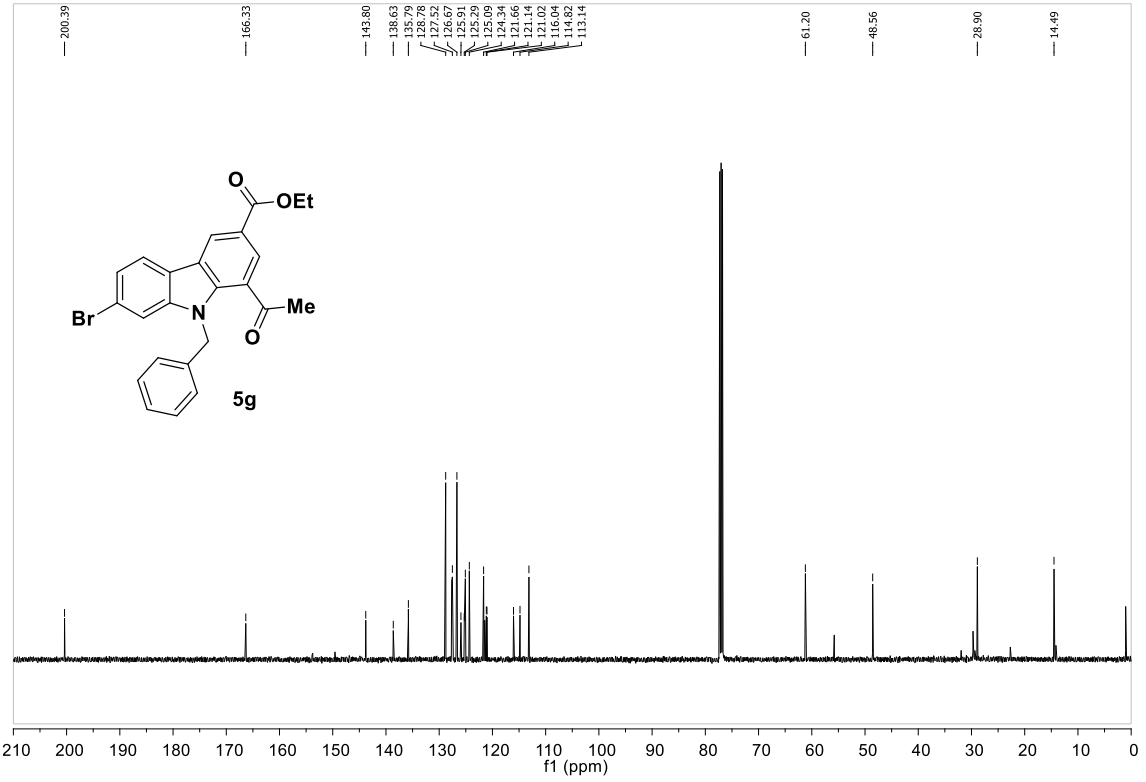
^{13}C{^{1}H} NMR (126 MHz, $CDCl_3$) spectrum of **5f**



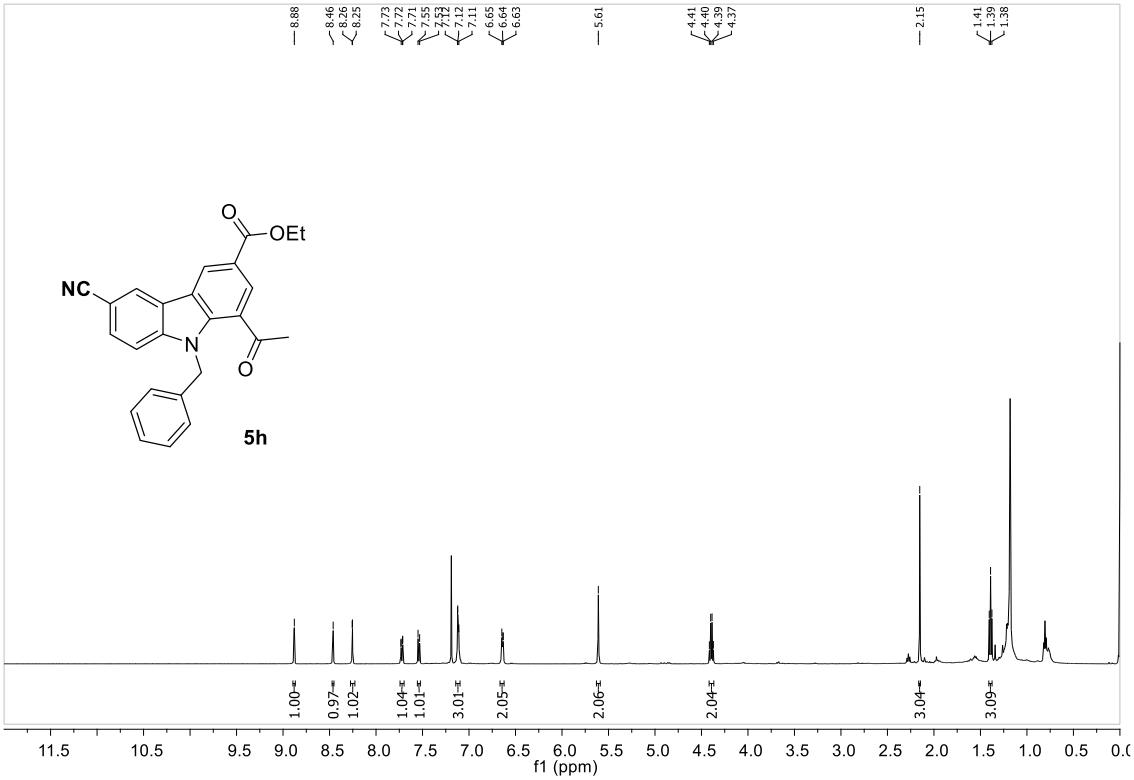
^{1}H NMR (500 MHz, $CDCl_3$) spectrum of **5g**



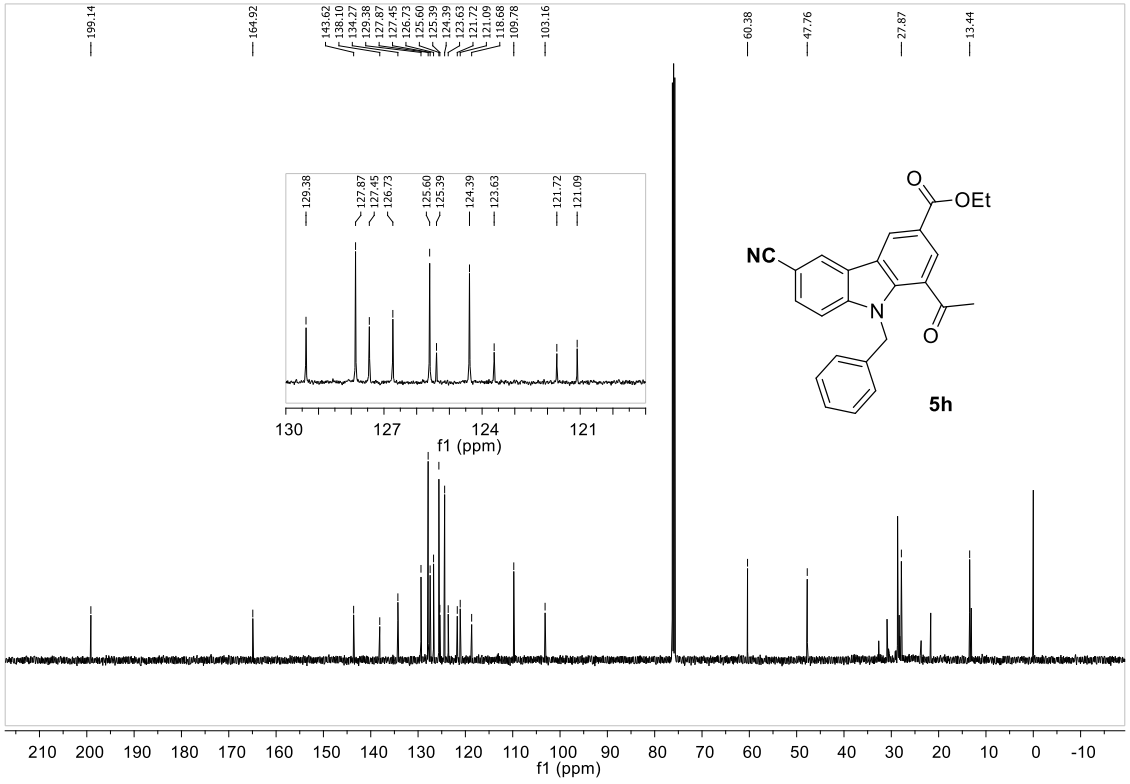
^{13}C{^{1}H} NMR (126 MHz, $CDCl_3$) spectrum of **5g**



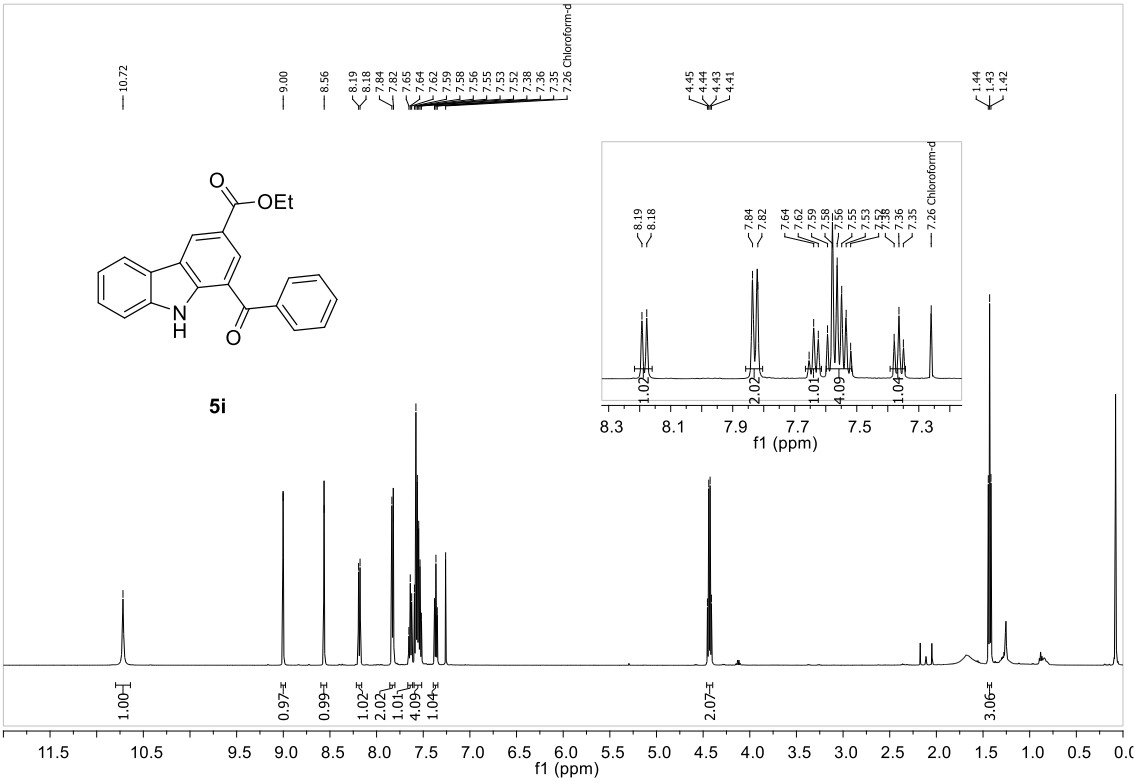
^{1}H NMR (500 MHz, $CDCl_3$) spectrum of **5h**



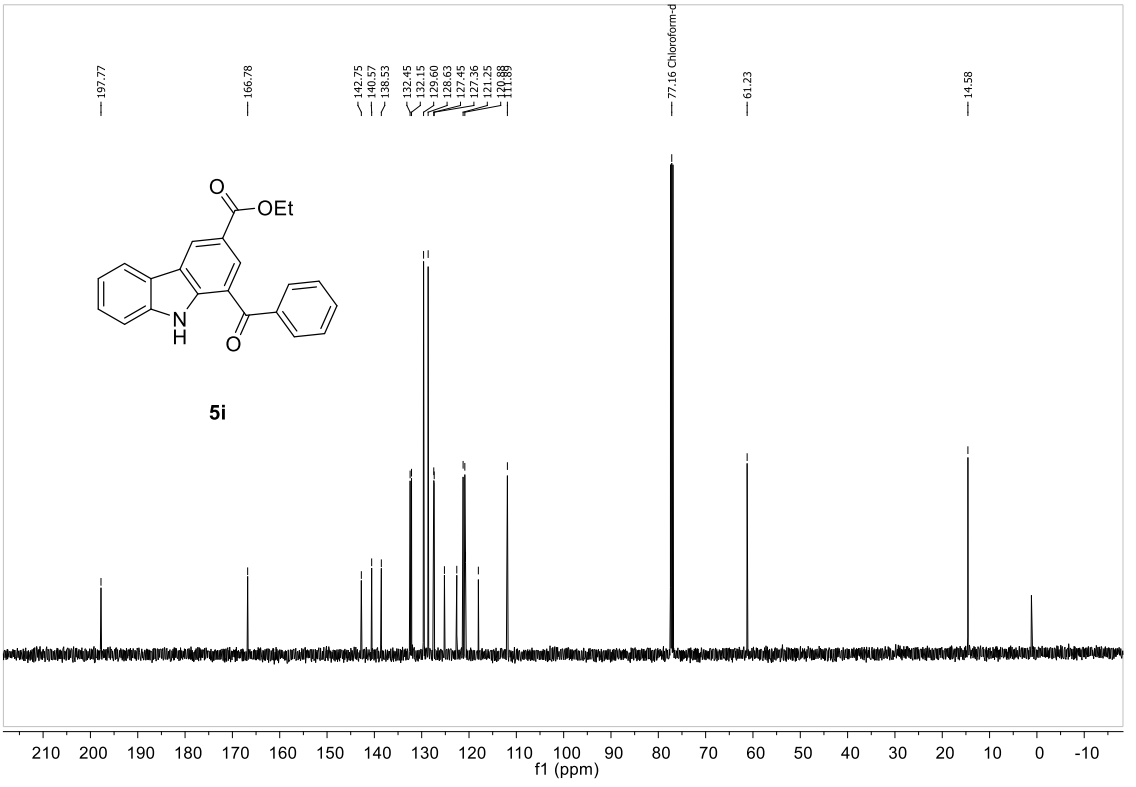
^{13}C{^{1}H} NMR (126 MHz, $CDCl_3$) spectrum of **5h**



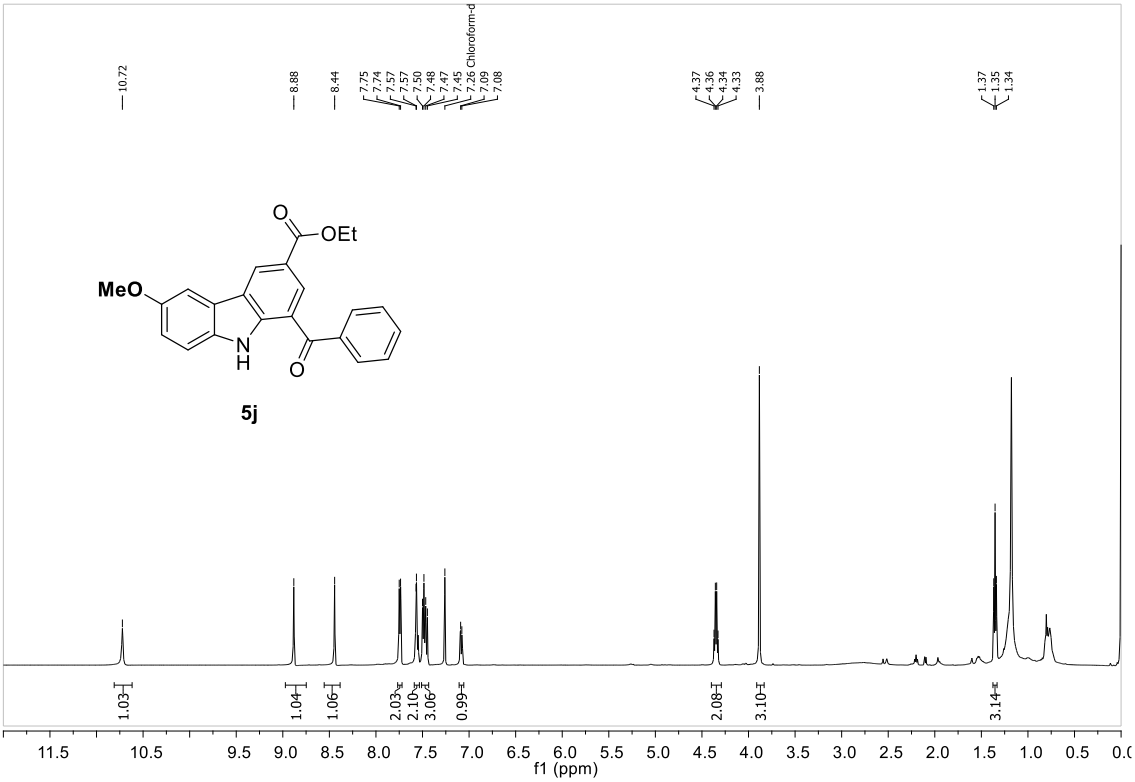
^{1}H NMR (500 MHz, $CDCl_3$) spectrum of **5i**



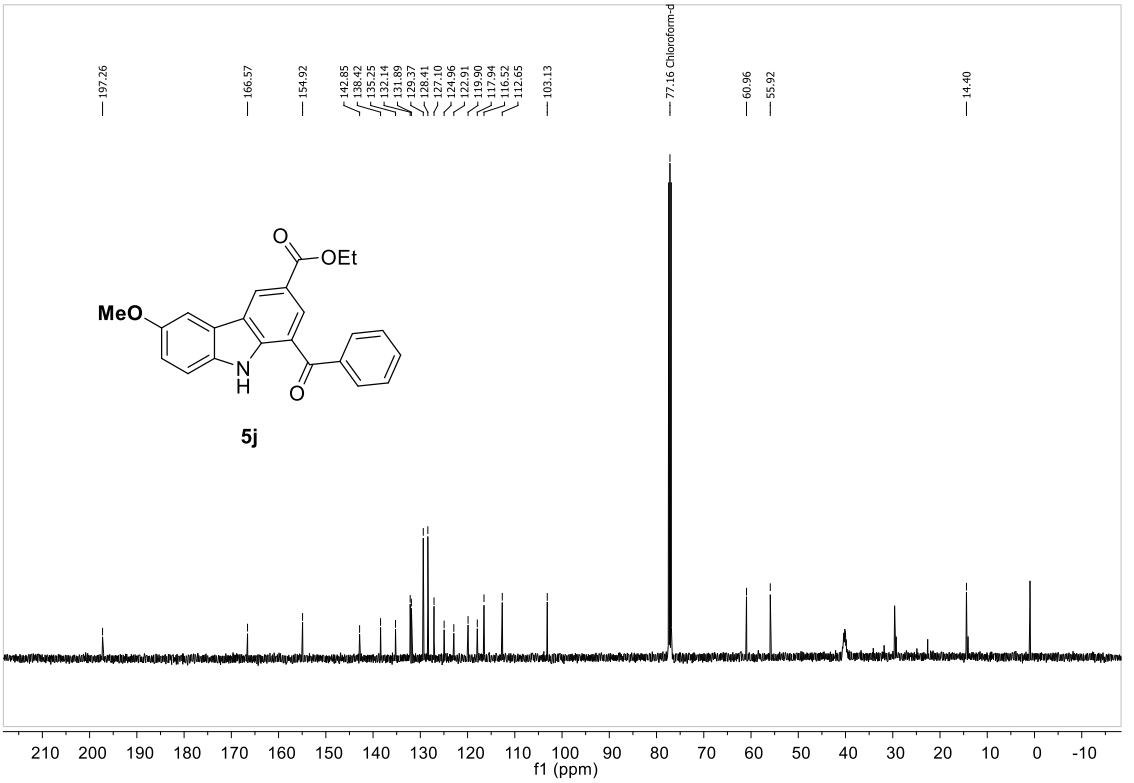
^{13}C{^{1}H} NMR (126 MHz, $CDCl_3$) spectrum of **5i**



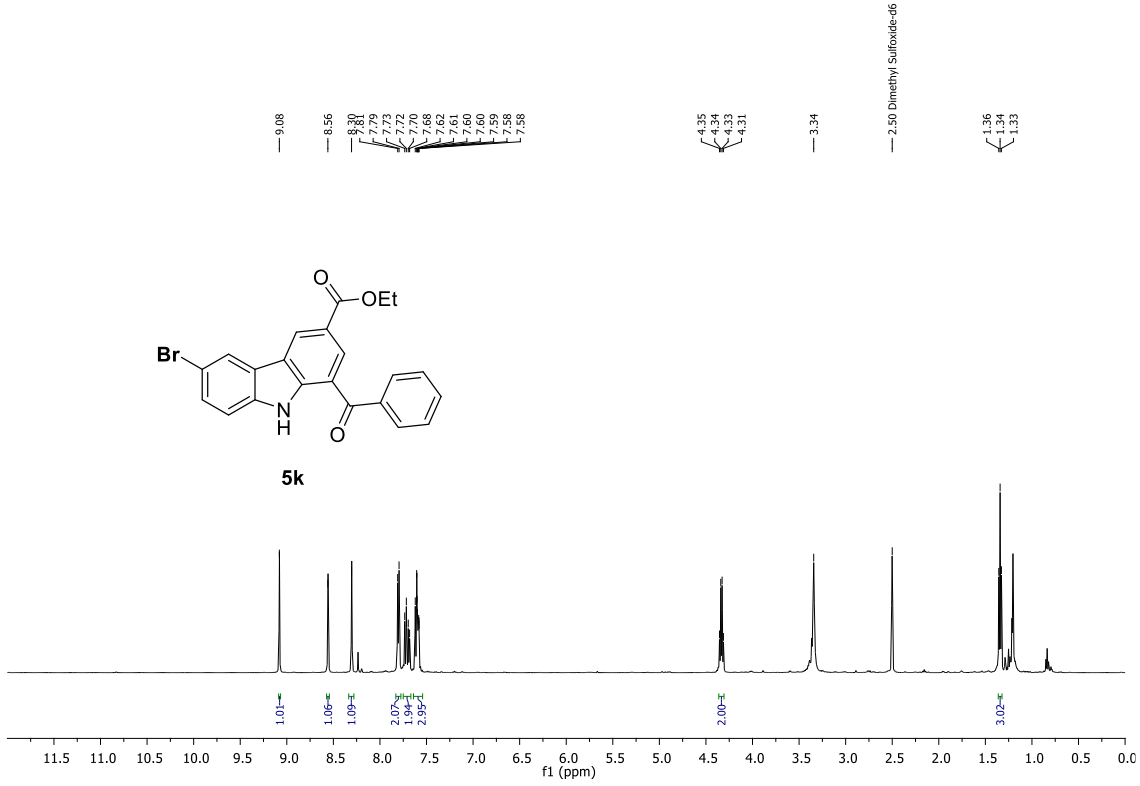
^{1}H NMR (500 MHz, $CDCl_3$ + DMSO-d_6) spectrum of **5j**



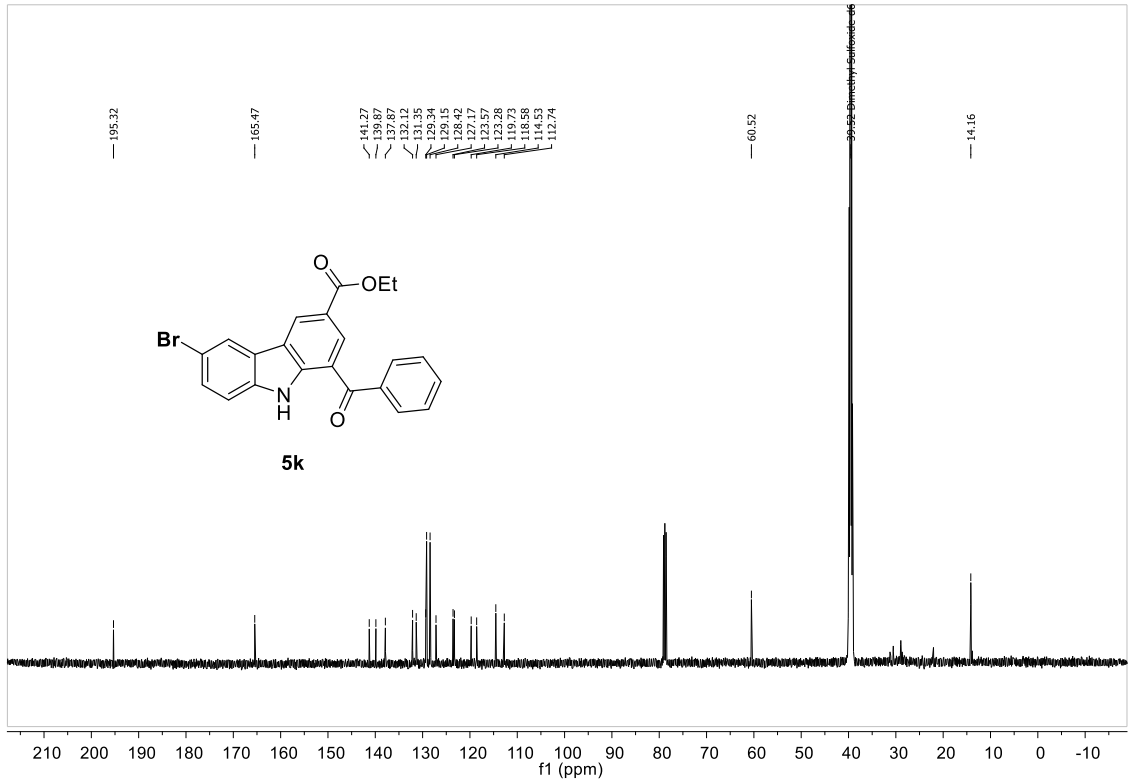
^{13}C{^{1}H} NMR (126 MHz, $CDCl_3$ + DMSO-d_6) spectrum of **5j**



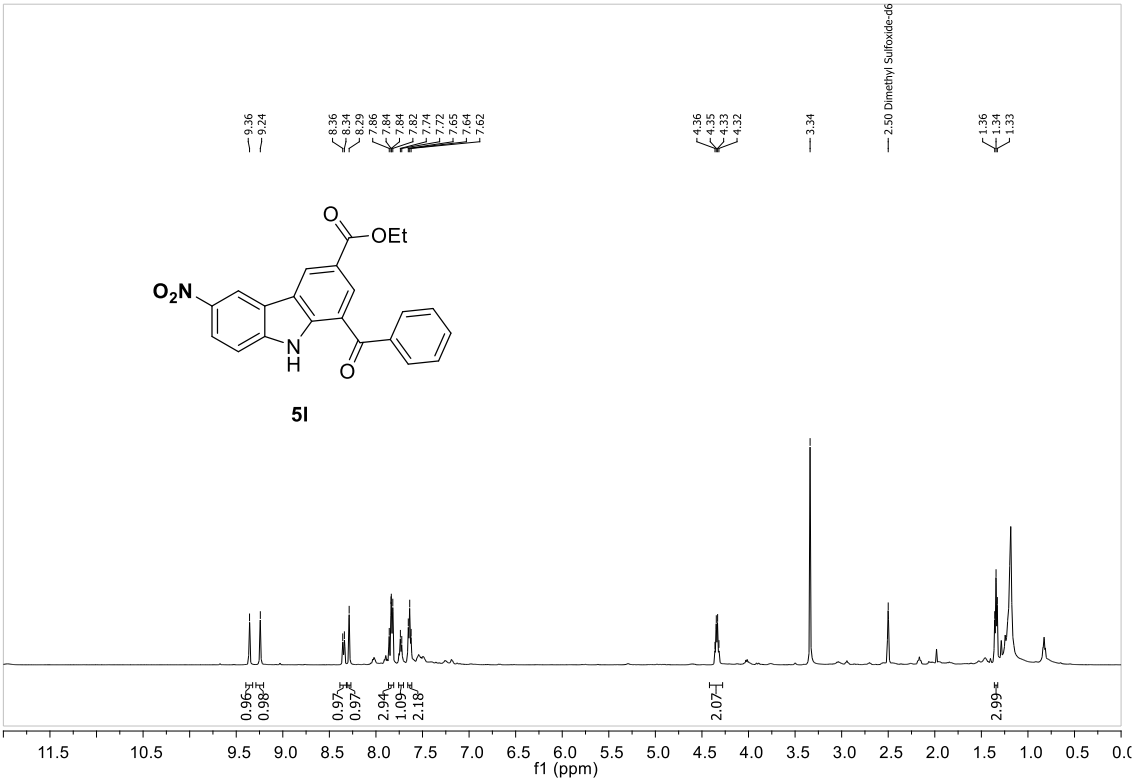
^{1}H NMR (500 MHz, DMSO-d_6) spectrum of **5k**



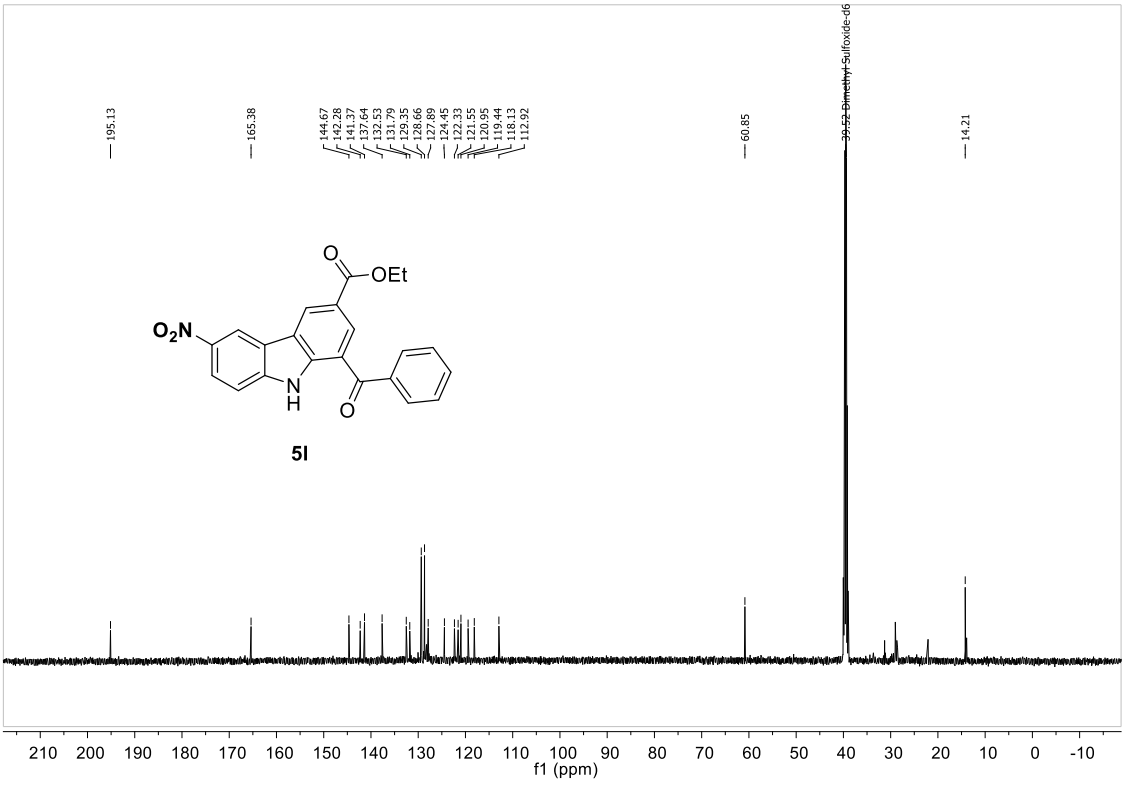
^{13}C{^{1}H} NMR (126 MHz, DMSO-d_6) spectrum of **5k**



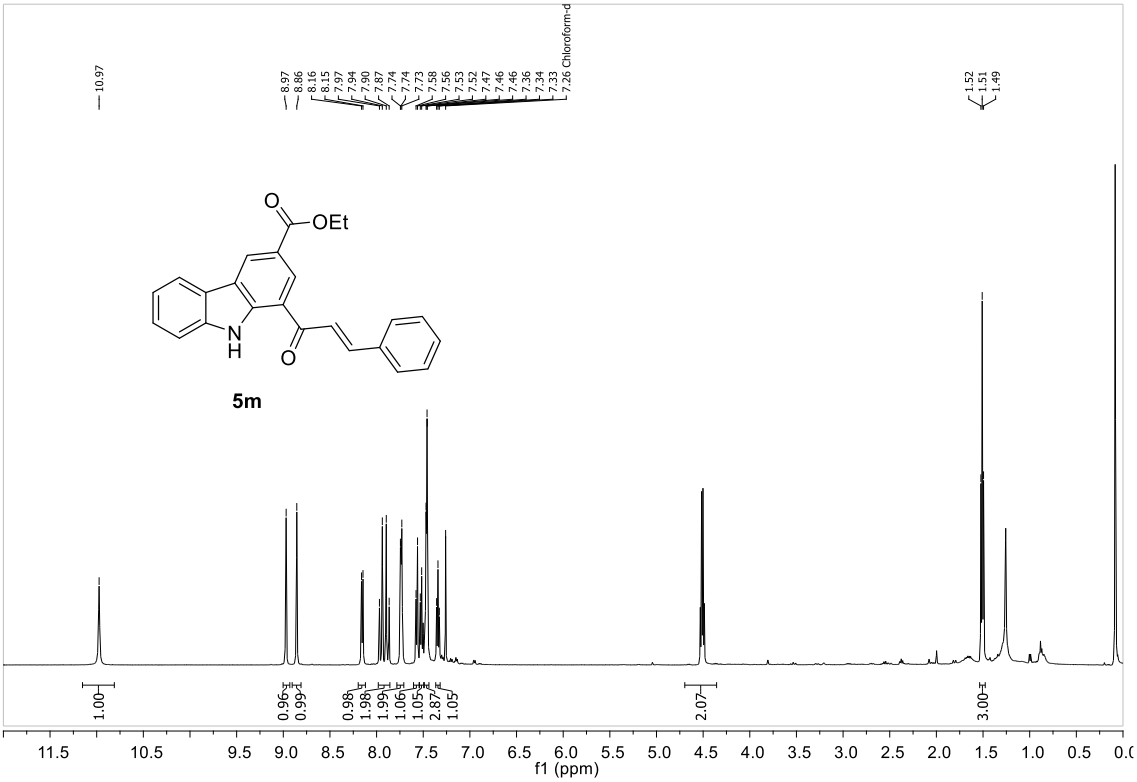
^{1}H NMR (500 MHz, DMSO-d_6) spectrum of **5l**



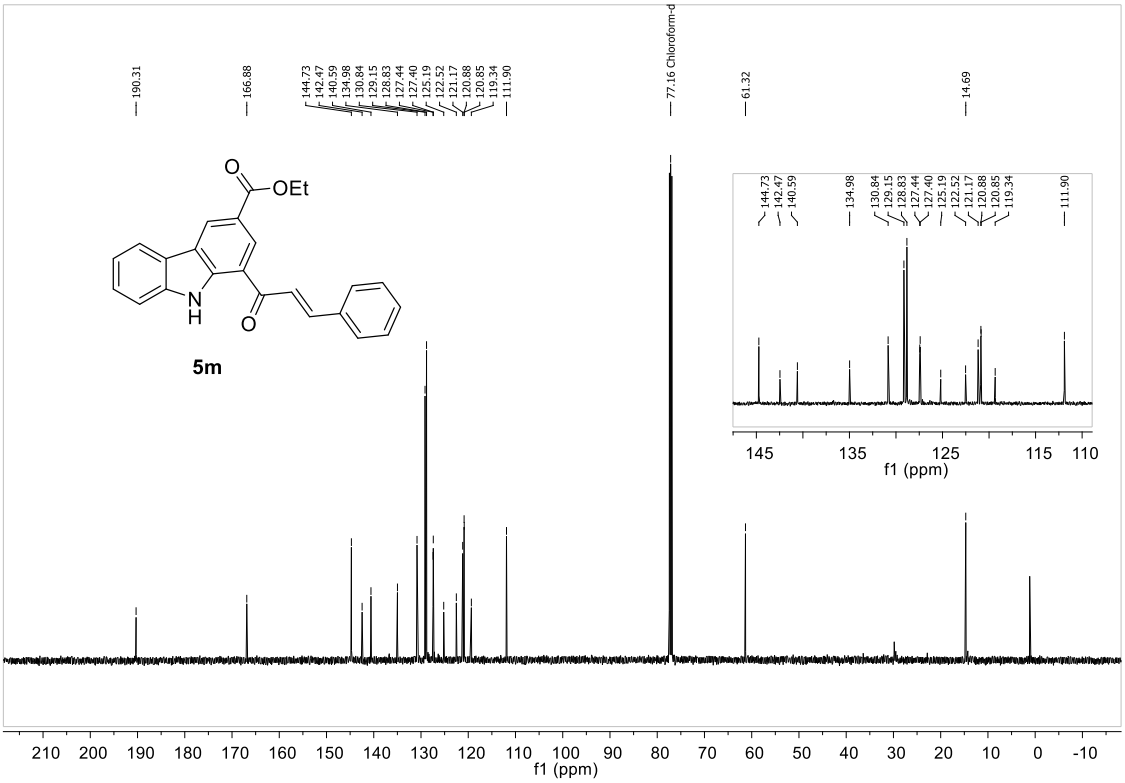
^{13}C{^{1}H} NMR (126 MHz, DMSO-d_6) spectrum of **5l**



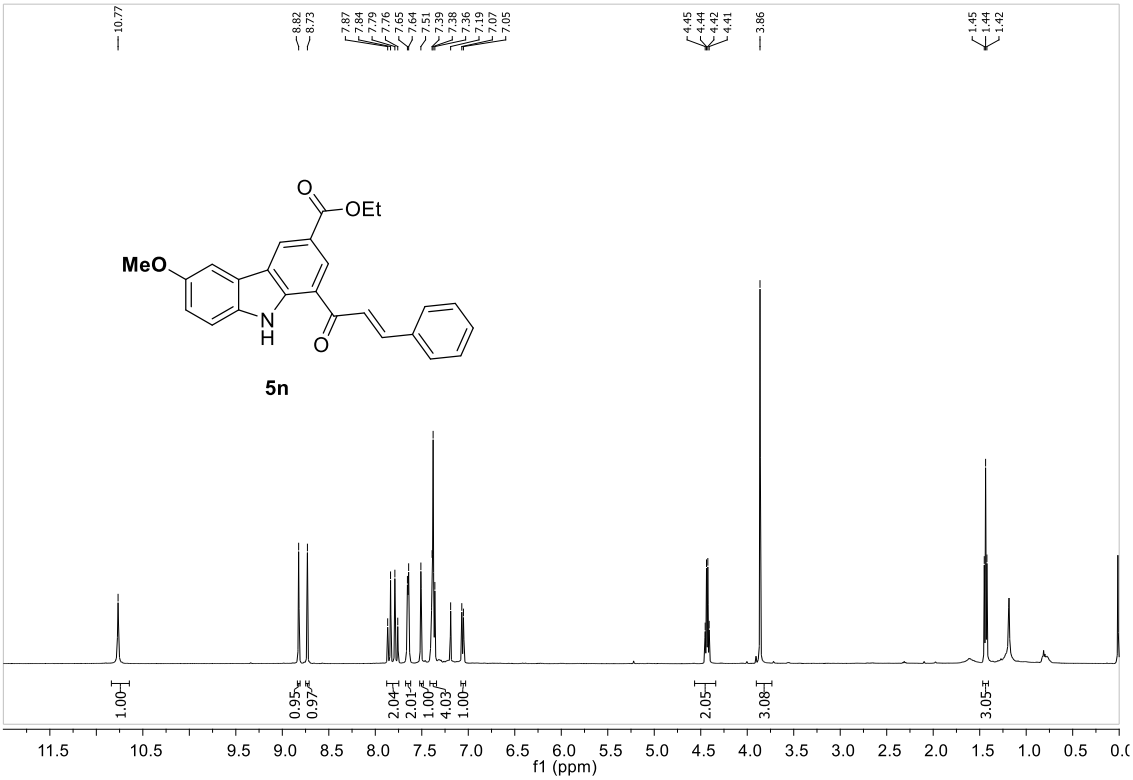
^{1}H NMR (500 MHz, $CDCl_3$) spectrum of **5m**



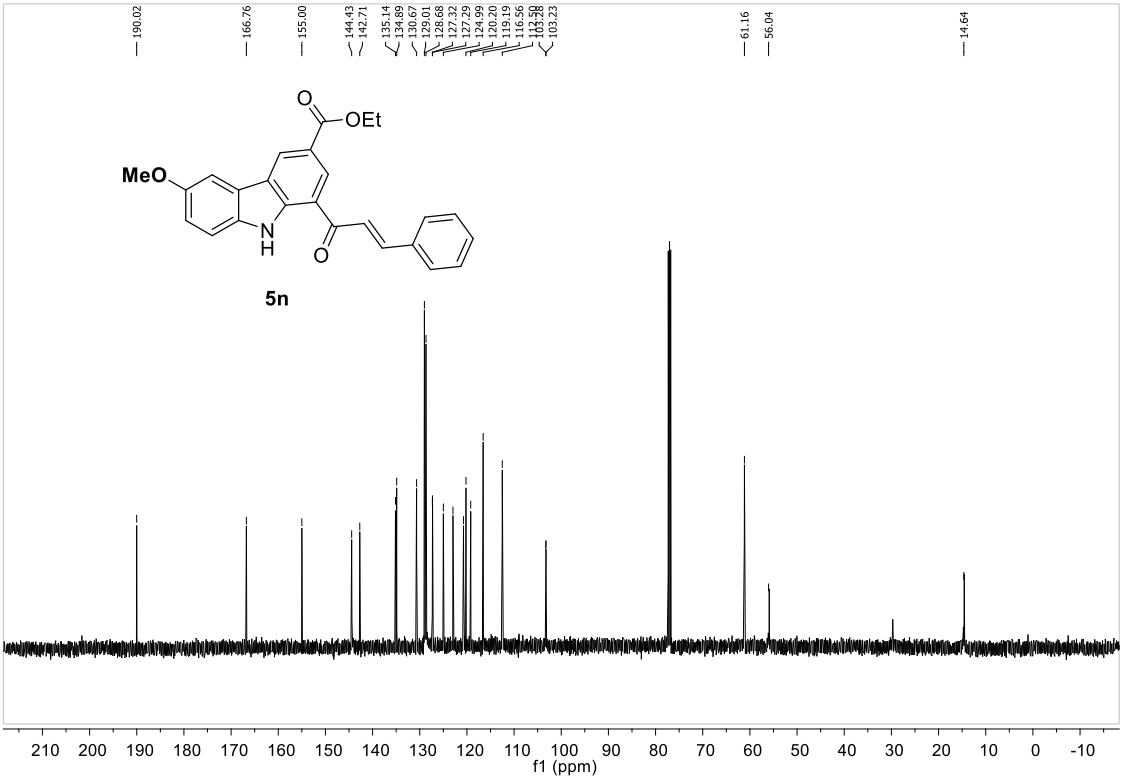
^{13}C{^{1}H} NMR (126 MHz, $CDCl_3$) spectrum of **5m**



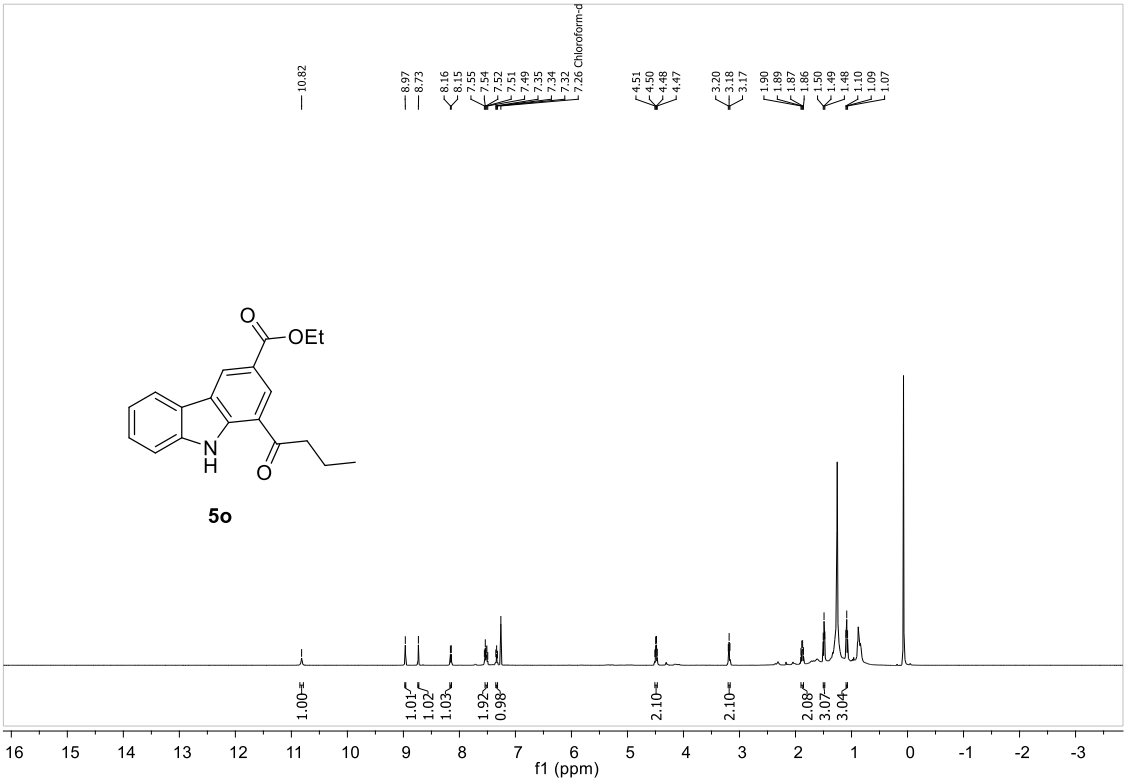
^{1}H NMR (500 MHz, $CDCl_3$) spectrum of **5n**



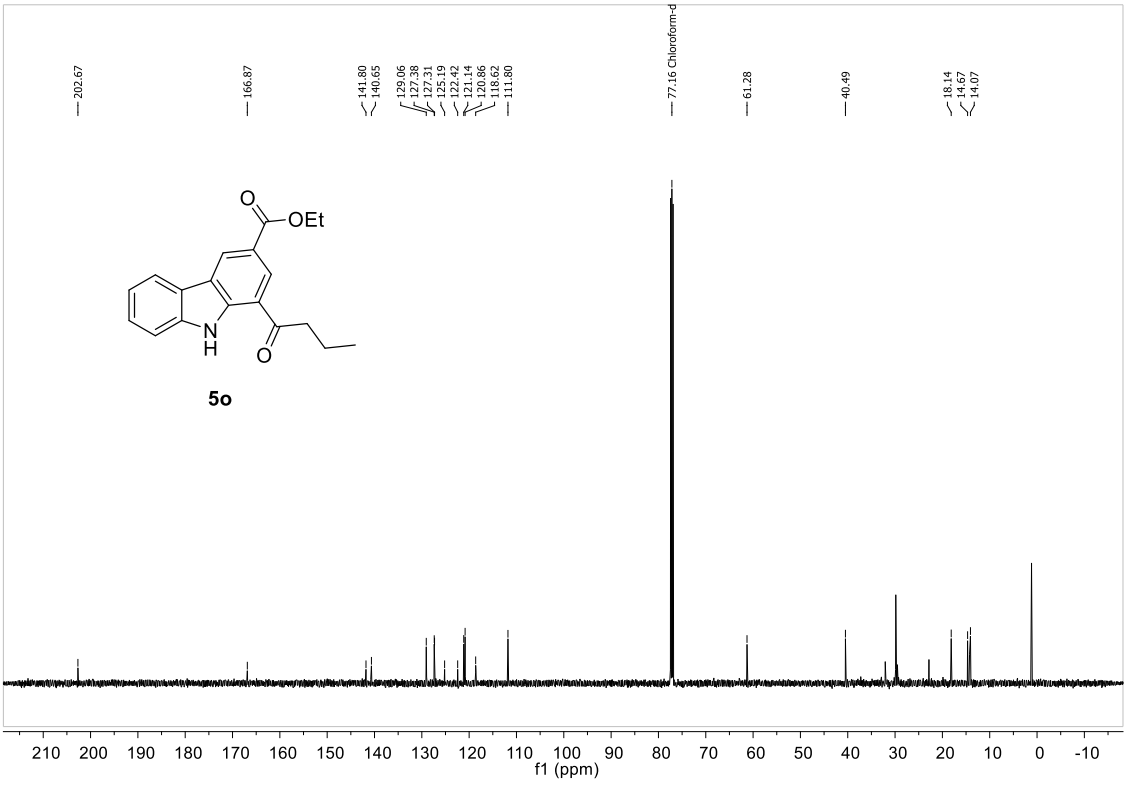
^{13}C{^{1}H} NMR (126 MHz, $CDCl_3$) spectrum of **5m**



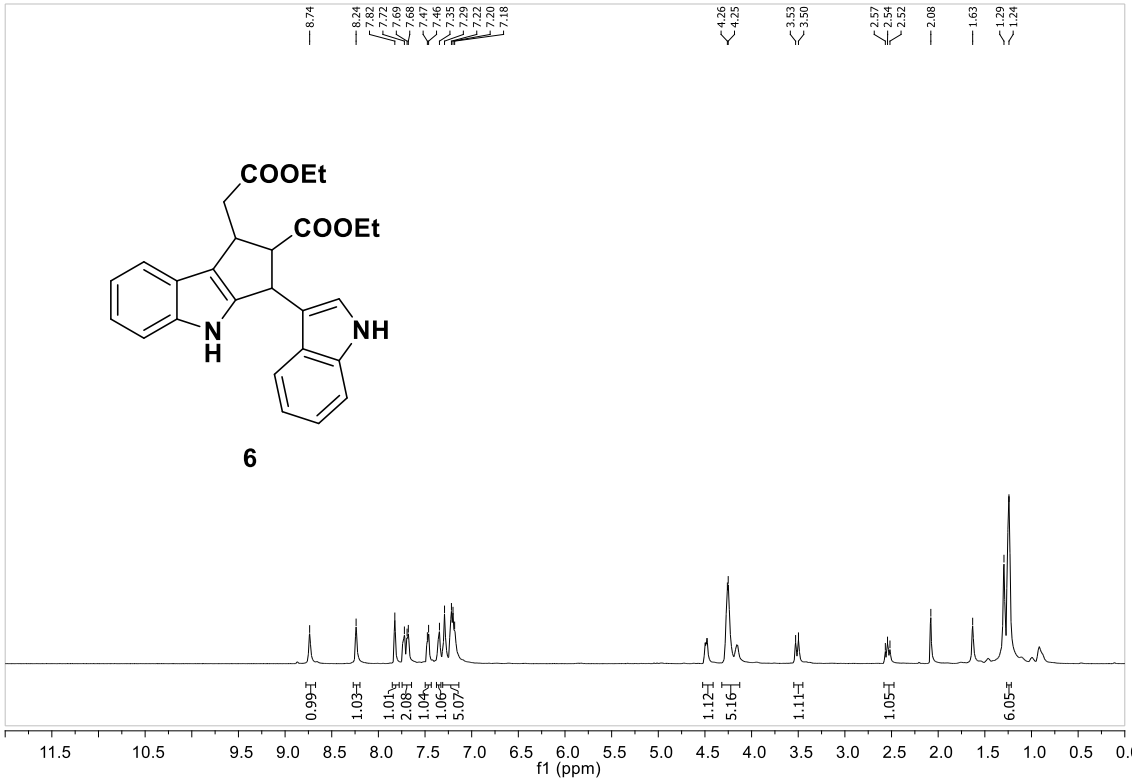
^{1}H NMR (500 MHz, $CDCl_3$ + DMSO-d_6) spectrum of **5o**



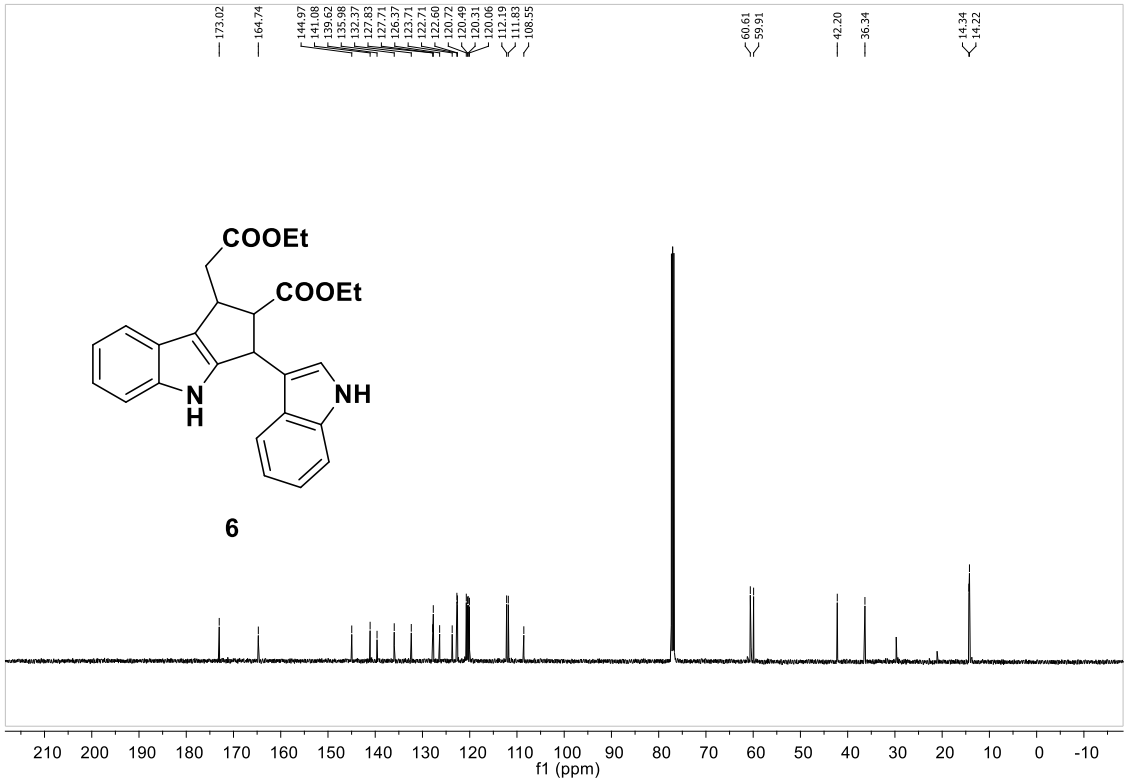
^{13}C{^{1}H} NMR (126 MHz, $CDCl_3$ DMSO-d_6) spectrum of **5o**



^{1}H NMR (500 MHz, $CDCl_3$+ DMSO-d_6) spectrum of **6**



^{13}C{^{1}H} NMR (126 MHz, $CDCl_3$ + DMSO-d_6) spectrum of **6**



DEPT spectrum of **6**