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Supporting Information

Cu(II)-Catalyzed formal [4+2] cycloaddition between quinone methides (QMs) and electron-poor 3-vinylindoles

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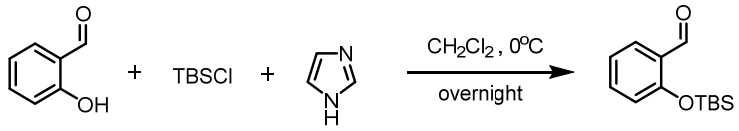
Context

General Information

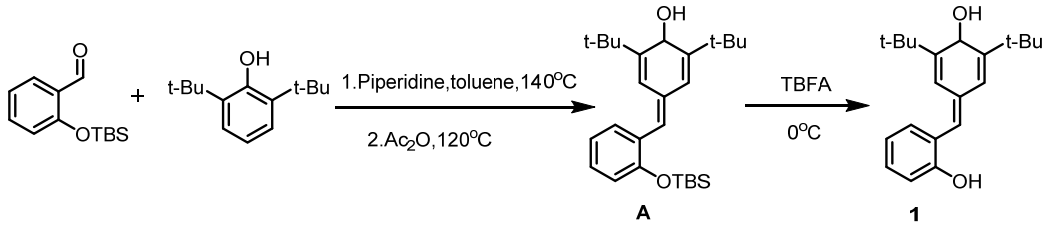
^{1}H NMR (^{13}C NMR) spectra were measured on a Bruker DPX 400 MHz spectrometer in $CDCl_3$ with chemical shift (δ) given in ppm relative to TMS as internal standard [(s = singlet, d = doublet, t = triplet, brs = broad singlet, m = multiplet), coupling constant (Hz)]. High-resolution mass spectra (HRMS) were obtained on an Agilent mass spectrometer using ESI-TOF (electrospray ionization-time of flight). X-Ray crystallographic analysis was performed with a Siemens SMART CCD and a Siemens P4 diffractometer. Column chromatography was generally performed on silica gel (200-300 mesh) and reactions were monitored with thin-layer chromatography (TLC) using 254 nm UV light. The melting points were measured with digital melting point detector.

General Procedure for the Synthesis of Compounds 1

Example for the Synthesis of 1a:



A solution of 2-hydroxybenzaldehyde (10.0 mmol) and 1H-imidazole (20.0 mmol, 1.37 g) in CH_2Cl_2 (40 mL) was placed into a 100mL reaction vial, which was sealed at 0 °C. Then, TBSCl (1.2 equiv, 1.80 g) was added by dropwise slowly. The reaction mixture was stirred overtime. After that, a saturated $NaHCO_3$ solution was added dropwise to quench the reaction. The resulting solution was extracted with acetic ester (3×30 mL). Then the combined organic phases were washed with brine and dried over anhydrous Na_2SO_4, resulting in a white viscous liquid and used directly in the next step without purification.[1]



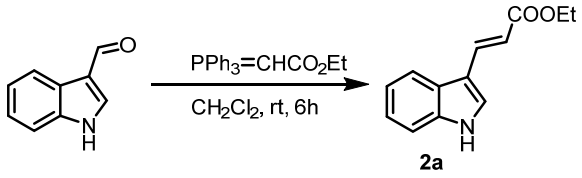
A solution of phenols (2.2 mmol, 453 mg) and aldehydes (2.0 mmol, 472 mg) in toluene (10 mL) was placed in a Dean-Stark apparatus which was heated to reflux. Piperidine (2.0 equiv, 341 mg) was added by dropwise slowly. Then, the temperature was raised to 140°C and stirred for 12 h. After that, the reaction mixture was cooled to 120°C and acetic anhydride (2.0 equiv, 408 mg) was added by dropwise. The stirring was continued for 30 min and the solution was poured on ice-water and extracted with ethyl acetate (3 × 20 mL). The organic phases were combined, washed with brine and dried over anhydrous Na_2SO_4. Then the solvent was evaporated under reduced pressure and the corresponding products **A** (551mg, 65% yield) were obtained after flash column

chromatography.[2]

To a solution of **A** (1 mmol, 424 mg) in THF (10 mL) at 0°C was added tetrabutylammonium fluoride trihydrate (TBAF 1.1 equiv, 1.1 mL). The reaction mixture was stirred for 10 min and a saturated NH_4Cl solution was added by dropwise to quench the reaction. The resulting solution was extracted with ethyl acetate (3 × 20 mL). Then the combined organic phases were washed with brine and dried over anhydrous Na_2SO_4. The solvent was removed to give the crude product which was purified by flash column chromatography to afford the desired compound **1a** (254 mg, 82% yield).

General Procedure for the Synthesis of Compounds 2

Example for the Synthesis of **2a**:

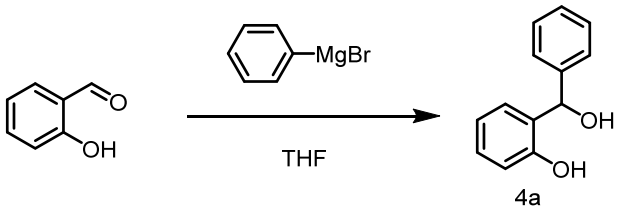


2a

To a solution of aldehyde (1 equiv) in anhydrous CH_2Cl_2 was added dry $Ph_3P{=}CHCO_2Et$ (1.5equiv) and stirred magnetically for 6 h at rt. Solvent was evaporated and residue was purified by flash chromatography over silica gel column.[3]

General Procedure for the Synthesis of Compounds 4

Example for the Synthesis of **4a**:



4a

To a solution of salicylaldehyde (10 mmol, 1 equiv) in THF (50 mL) at 0°C was added a solution of phenylmagnesium bromide in THF (30 mmol, 3 equiv) dropwise. The reaction was then removed from ice and stirred for 2 hours at rt. Upon completion, the reaction was then quenched at 0°C with saturated aqueous NH_4Cl solution. It was then extracted with EtOAc (3 x 25 mL) and the combined organic layers were washed with brine, dried over $MgSO_4$, filtered, and concentrated. Purification by silica gel chromatography yielded the product as an off-white solid.[4]

Reference

1. X.-G. Song, S.-F. Zhu, X.-L. Xie and Q.-L. Zhou, *Angew. Chem. Int. Ed.*, 2013, 52, 2555.

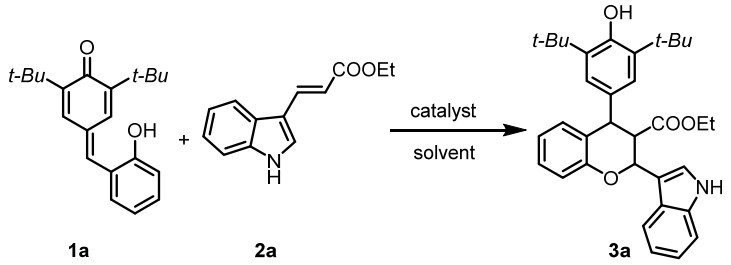
2. K. Zhao, Y. Zhi, T. Shu, A. Valkonen, K. Rissanen and D. Enders, *Angew. Chem. Int. Ed.*, 2016, 55,12104.

3. D. H. Dethe , R. Boda and S. Das, *Chem. Commun.*, 2013, 49, 3260.

4. C. R. Wong, G. Humme, Y. Cai, S. E. Schaus, J. S. Panek, *Org. Lett.*, 2019,21,32.

General Procedure for the Synthesis of Compounds 3

Example for the Synthesis of **3a**:

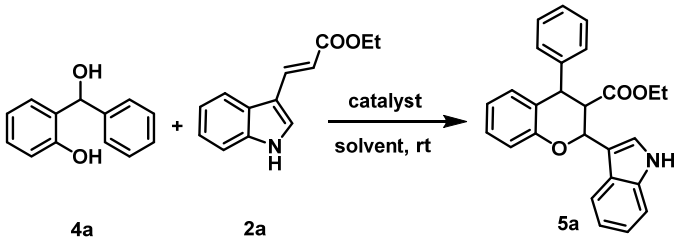


1a **2a** **3a**

To a solution of **1a** (0.2 mmol, 1 equiv) and **2a** (0.2 mmol, 1 equiv) in anhydrous CH_2Cl_2 (2 mL) at the room temperature was added $Cu(OTf)_2$ (0.1 equiv). The reaction was stirred for 12 h and monitored by TLC in 3:1 Hexanes:EtOAc. Upon completion, Purification by silica gel chromatography yielded **3a** as a white solid**.**

General Procedure for the Synthesis of Compounds 5

Example for the Synthesis of **5a**:

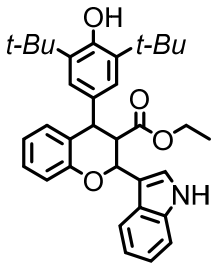


4a **2a** **5a**

To a solution of **4a** (0.50 mmol, 1 equiv) and **2a** (0.60 mmol, 1.2 equiv) in anhydrous CH_2Cl_2 (5 mL) at the room temperature was added $Cu(OTf)_2$ (0.1 equiv). The reaction was stirred for 12 h and monitored by TLC in 3:1 Hexanes:EtOAc. Upon completion, Purification by silica gel chromatography yielded **5a** as a white solid**.**

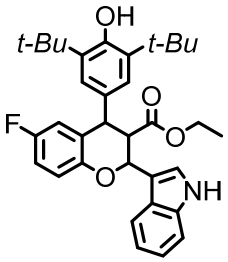
Characterization data

Ethyl 4-(3,5-di-tert-butyl-4-hydroxyphenyl)-2-(1*H*-indol-3-yl)chromane-3-carboxylate (3a).



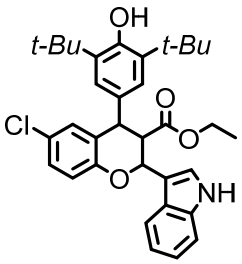
White solid, mp 181 -182°C; ^{1}H NMR (400 MHz, $CDCl_3$; δ, ppm) 8.07 (s, 1H), 7.56 (d, J = 8.0 Hz, 1H), 7.31-7.22 (m, 1H), 7.16-6.74 (m, 9H), 5.60 (d, J = 11.2 Hz, 1H), 5.05 (s, 1H), 4.51-4.40 (m, 1H), 3.67-3.32 (m, 3H), 1.32 (s, 18H), 0.67 (t, J = 7.2 Hz, 3H). ^{13}C NMR (100 MHz, $CDCl_3$; δ, ppm) 170.8, 154.5, 152.8, 136.2, 135.3, 132.7, 130.5, 128.1, 126.1, 125.9, 125.4, 123.5, 123.3, 122.3, 120.7, 119.9, 119.7, 116.7, 111.3, 67.9, 60.0, 50.3, 44.7, 34.3, 30.4, 13.5. IR (KBr, v, cm^{-1}) 3627, 3435, 2954, 1735, 1433, 1240, 1161, 1007, 749. HR-MS (ESI-TOF, m/z) calcd for $C_{34}H_{39}NO_4$ $[M+Na]^+$ 548.2771, found 548.2776.

Ethyl 4-(3,5-di-tert-butyl-4-hydroxyphenyl)-6-fluoro-2-(1*H*-indol-3-yl)chromane-3-carboxylate (3b).



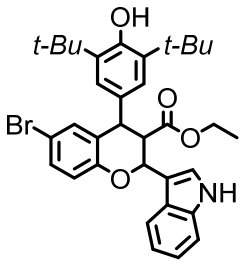
White solid, mp 139-140°C; ^{1}H NMR (400 MHz, $CDCl_3$; δ, ppm) 8.07 (s, 1H), 7.54 (d, J = 7.6 Hz, 1H), 7.34-7.23 (m, 1H), 7.16-6.98 (m, 3H), 6.96-6.66 (m, 5H), 5.58 (d, J = 10.8 Hz, 1H), 5.08 (s, 1H), 4.47-4.39 (m, 1H), 3.64-3.31 (m, 3H), 1.33 (s, 18H), 0.67 (t, J = 7.2 Hz, 3H). ^{13}C NMR (100 MHz, $CDCl_3$; δ, ppm) 170.6, 157.0 (d, J = 236.9 Hz), 153.0, 150.6 (d, J = 1.9 Hz), 136.2, 136.0, 135.5, 132.04, 126.1, 125.8, 124.6, 123.3, 122.3, 119.8 (d, J = 39.8 Hz), 117.7 (d, J = 8.0 Hz), 116.1 (d, J = 22.8 Hz), 115.2 (d, J = 23.4 Hz), 114.8, 113.7, 111.3, 68.1, 60.2, 50.1, 44.7, 34.3, 30.3, 13.4. ^{19}F NMR (376 MHz, $CDCl_3$; δ, ppm): -123.9(s). IR (KBr, v, cm^{-1}) 3623, 3341, 2958, 1720, 1490, 1434, 1233, 1176, 1019, 745. HR-MS (ESI-TOF, m/z) calcd for $C_{34}H_{38}FNO_4$ $[M+Na]^+$ 566.2677, found 566.2682.

Ethyl 6-chloro-4-(3,5-di-tert-butyl-4-hydroxyphenyl)-2-(1*H*-indol-3-yl)chromane-3-carboxylate(3c).



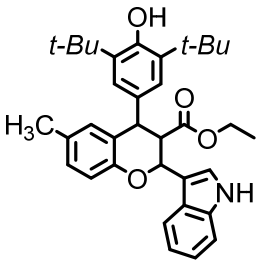
White solid, mp 175–177°C; ^{1}H NMR (400 MHz, $CDCl_3$; δ, ppm) 8.07 (s, 1H), 7.52 (d, J = 8.8 Hz, 1H), 7.31-6.99(m, 6H), 6.89-6.75 (m, 3H), 5.60 (d, J = 11.2 Hz, 1H), 5.09 (s, 1H), 4.48-4.34 (m, 1H), 3.66-3.23 (m, 3H), 1.33 (s, 18H), 0.68 (t, J = 7.2 Hz, 3H). ^{13}C NMR (100 MHz, $CDCl_3$; δ, ppm)170.4, 153.1, 153.0, 136.2, 135.5, 131.8, 129.8, 128.3, 126.0, 125.8, 125.3, 125.3, 123.3, 122.4, 120.0, 119.5, 118.1, 114.7, 111.4, 68.3, 60.2, 49.9, 44.5, 34.3, 30.3, 13.5. IR (KBr, v, cm^{-1}) 3640, 3374, 2959, 1719, 1478, 1435, 1236, 1006, 737. HR-MS (ESI-TOF, m/z) calcd for $C_{34}H_{38}ClNO_4$ $[M+Na]^+$ 582.2382, found 582.2386.

Ethyl 6-bromo-4-(3,5-di-tert-butyl-4-hydroxyphenyl)-2-(1*H*-indol-3-yl)chromane-3-carboxylate (3d).



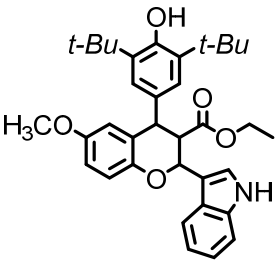
White solid, mp 169–170°C; ^{1}H NMR (400 MHz, $CDCl_3$; δ, ppm) 8.08 (s, 1H), 7.52 (d, J = 7.2 Hz, 1H), 7.31-7.19 (m, 2H), 7.17-6.93 (m, 4H), 6.87-6.73 (m, 3H), 5.60 (d, J = 10.8 Hz, 1H), 5.09 (s, 1H), 4.46-4.39 (m, 1H), 3.62-3.29 (m, 3H), 1.33 (s, 18H), 0.69 (t, J = 7.2 Hz, 3H).^{13}C NMR (100 MHz, $CDCl_3$; δ, ppm) 170.4, 153.7, 153.0, 136.2, 135.6, 132.7, 131.8, 131.2, 126.0, 125.8, 125.7, 123.4, 122.4, 120.0, 119.5, 118.6, 114.6, 112.6, 111.4, 68.3, 60.2, 49.8, 44.5, 34.3, 30.3, 13.5. IR (KBr, v, cm^{-1}) 3631, 3375, 2957, 1719, 1475, 1434, 1225, 1001, 737. HR-MS (ESI-TOF, m/z) calcd for $C_{34}H_{38}BrNO_4$ $[M+Na]^+$ 626.1876, found 626.1884.

Ethyl 4-(3,5-di-tert-butyl-4-hydroxyphenyl)-2-(1*H*-indol-3-yl)-6-methylchromane -3-carboxylate (3e).



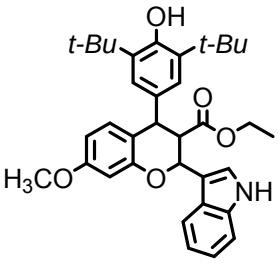
White solid, mp 183-184°C; ^{1}H NMR (400 MHz, $CDCl_3$; δ, ppm) 8.06 (s, 1H), 7.55 (d, J = 7.6 Hz, 1H), 7.28-7.19 (m, 1H), 7.15-6.97 (m, 3H), 6.94-6.60 (m, 5H), 5.58 (d, J = 12.8 Hz, 1H), 5.06 (s, 1H), 4.47-4.40 (m, 1H), 3.69-3.22 (m, 3H), 2.16 (s, 3H), 1.33 (s, 18H), 0.66 (t, J = 7.2 Hz, 3H). ^{13}C NMR (100 MHz, $CDCl_3$; δ, ppm) 170.9, 152.8, 152.3, 136.2, 135.3, 132.8, 130.6, 129.7, 129.0, 126.2, 125.9, 123.3, 123.0, 122.2, 119.8, 119.7, 116.4, 115.1, 111.3, 67.7, 60.1, 50.4, 44.8, 34.3, 30.4, 20.6, 13.5. IR (KBr, v, cm^{-1}) 3631, 3369, 2957, 1711, 1496, 1434, 1225, 1027, 739. HR-MS (ESI-TOF, m/z) calcd for $C_{35}H_{41}NO_4$ $[M+Na]^+$ 562.2928, found 562.2938.

Ethyl 4-(3,5-di-tert-butyl-4-hydroxyphenyl)-2-(1*H*-indol-3-yl)-6-methoxychromane-3-carboxylate (3f).



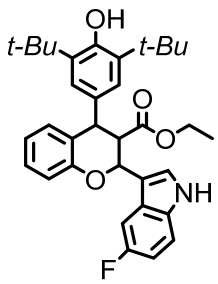
White solid, mp 160-162°C; ^{1}H NMR (400 MHz, $CDCl_3$; δ, ppm) 8.02 (s, 1H), 7.23 (d, J = 2.4 Hz, 1H), 7.20-7.03 (m, 3H), 6.93-6.85 (m, 3H), 6.84-6.72 (m, 3H), 5.51 (d, J = 10.4 Hz, 1H), 5.04 (s, 1H), 3.78 (s, 3H), 4.47 (d, J = 11.2 Hz, 1H), 3.67-3.51 (m, 2H), 3.36 (t, J = 10.4 Hz, 1H), 1.32 (s, 18H), 0.57 (t, J = 7.2 Hz, 3H). ^{13}C NMR (100 MHz, $CDCl_3$; δ, ppm) 172.3, 154.9, 154.3, 152.8, 135.8, 131.8, 131.4, 129.8, 127.7, 126.6, 125.4, 125.3, 123.7, 120.7, 116.7, 113.7, 112.8, 111.9, 101.4, 73.6, 60.1, 55.9, 53.8, 47.5, 34.3, 30.4, 13.7. IR (KBr, v, cm^{-1}) 3615, 3309, 2959, 1716, 1493, 1434, 1233, 1024, 744. HR-MS (ESI-TOF, m/z) calcd for $C_{35}H_{41}NO_5$ $[M+Na]^+$ 578.2877, found 578.2886.

Ethy 4-(3,5-di-tert-butyl-4-hydroxyphenyl)-2-(1*H*-indol-3-yl)-7-methoxychromane-3-carboxylate (3g).



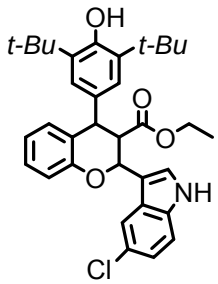
White solid, mp 164–165°C; ^{1}H NMR (400 MHz, $CDCl_3$; *δ*, ppm) 8.10 (s, 1H), 7.72 (d, J = 7.2 Hz, 1H), 7.35-7.23 (m, 2H), 7.17-7.04 (m, 2H), 6.88 (s, 2H), 6.70 (dd, *J* = 8.8, 1.2 Hz, 1H), 6.44 (d, *J* = 2.8 Hz, 1H), 6.37 (dd, *J* = 8.4, 2.4 Hz, 1H), 5.53 (d, *J* = 10.4 Hz, 1H), 5.03 (s, 1H), 4.40 (dd, *J* = 11.2, 1.2 Hz, 1H), 3.69 (s, 3H), 3.63-3.48 (m, 2H), 3.33 (dd, *J* = 12.0, 8.0 Hz, 1H), 1.32 (s, 18H), 0.55 (t, *J* = 6.8 Hz, 3H). ^{13}C NMR (100 MHz, $CDCl_3$; δ, ppm) 172.3, 159.2, 155.6, 152.8, 136.3, 135.7, 131.9, 130.4, 126.0, 125.3, 123.2, 122.5, 120.1, 119.9, 117.4, 113.9, 111.2, 108.0, 100.9, 74.0, 60.1, 55.3, 54.1, 47.1, 34.3, 30.4, 13.6. IR (KBr, ν, cm^{-1}) 3629, 3394, 2957, 1721, 1486, 1435, 1229, 753. HR-MS (ESI-TOF, m/z) calcd for $C_{35}H_{41}NO_5$ $[M+Na]^+$ 578.2877, found 578.2884.

Ethyl 4-(3,5-di-tert-butyl-4-hydroxyphenyl)-2-(5-fluoro-1*H*-indol-3-yl)chromane-3-carboxylate(3h).



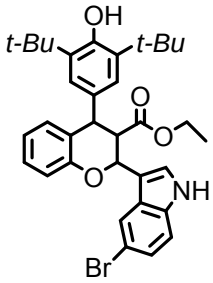
White solid , mp 192–194°C; ^{1}H NMR (400 MHz, $CDCl_3$; *δ*, ppm) 8.17 (s, 1H), 7.36 (dd, *J* = 9.6, 2.4Hz, 1H), 7.24 (s, 1H), 7.21-7.13 (m, 1H), 7.12-7.05 (m, 1H), 6.92-6.73 (m, 6H), 5.47 (d, *J* = 10.4 Hz, 1H), 5.05 (s, 1H), 4.46 (d, *J* = 11.2 Hz, 1H), 3.66-3.50 (m, 2H), 3.32 (t, *J* = 12.0, 1H), 1.32 (s, 18H), 0.58 (t, *J* = 8.0 Hz, 3H). ^{13}C NMR (100 MHz, $CDCl_3$; δ, ppm) 172.3, 158.0 (d, *J* = 233.5 Hz), 153.8 (d, *J* = 184.1 Hz), 135.9, 132.8, 131.6, 129.8, 127.8, 126.4, 126.3, 125.4, 125.2, 124.9, 120.8, 116.7, 114.1 (d, *J* = 4.7 Hz), 111.9 (d, *J* = 9.6 Hz), 111.0 (d, *J* = 26.3 Hz), 104.9 (d, *J* = 23.8 Hz), 73.7, 60.2, 54.0, 47.5, 34.3, 30.4, 13.7. ^{19}F NMR (376 MHz, $CDCl_3$; δ, ppm): -123.8(s). IR (KBr, *v*, cm^{-1}) 3620, 3353, 2961, 1721, 1458, 1435, 1229, 1161,1007, 623. HR-MS (ESI-TOF, m/z) calcd for $C_{34}H_{38}FNO_4$ $[M+Na]^+$ 566.2677, found 566.2683.

Ethyl 2-(5-chloro-1*H*-indol-3-yl)-4-(3,5-di-tert-butyl-4-hydroxyphenyl) chromane-3-carboxylate(3i).



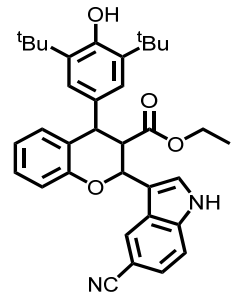
White solid, mp 176-178°C; ^{1}H NMR (400 MHz, $CDCl_3$; *δ*, ppm) 8.14 (s, 1H), 7.51 (d, *J* = 2.0 Hz, 1H), 7.27-7.19 (m, 1H), 7.18-6.91 (m, 4H), 6.93-6.75 (m, 4H), 5.55 (d, *J* = 10.8 Hz, 1H), 5.08 (s, 1H), 4.52-4.45 (m, 1H), 3.68-3.25 (m, 3H), 1.34 (s, 18H), 0.70 (t, *J* = 7.2 Hz, 3H).^{13}C NMR (100 MHz, $CDCl_3$; δ, ppm) δ 170.7, 154.3, 152.9, 135.4, 134.4, 132.7, 130.6, 128.2, 127.2, 125.9, 125.4, 124.7, 122.9, 122.7, 120.9, 119.2, 116.7, 114.9, 112.3, 67.5, 60.2, 50.6, 44.6, 34.3, 30.4, 13.4. IR (KBr, *v*, cm^{-1})3628, 3402, 2956, 1734, 1433, 1229, 1114, 1036, 1006, 799, 754. HR-MS (ESI-TOF, m/z) calcd for $C_{34}H_{38}ClNO_4$ $[M+Na]^+$ 582.2382, found 582.2390.

Ethyl 2-(5-bromo-1*H*-indol-3-yl)-4-(3,5-di-tert-butyl-4 hydroxyphenyl)chromane-3-carboxylate(3j).



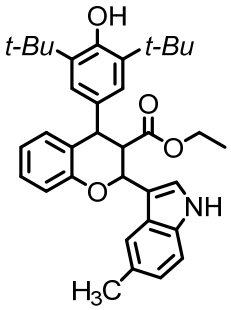
White solid, mp 196-197°C; ^{1}H NMR (400 MHz, $CDCl_3$; δ, ppm) 8.16 (s, 1H), 7.85 (d, *J* = 1.6 Hz, 1H), 7.29-7.20 (m, 2H), 7.18-7.05 (m, 2H), 6.92-6.85 (m, , 3H), 6.84-6.74 (m, 2H), 5.48 (d, *J* = 10.4 Hz, 1H), 5.05 (s, 1H), 4.47 (d, *J* = 11.4 Hz, 1H), 3.68-3.54 (m, 2H), 3.30 (dd, *J* = 12.0, 8.0 Hz, 1H), 1.33 (s, 18H), 0.61 (t, *J* = 7.2 Hz, 3H). ^{13}C NMR (100 MHz, $CDCl_3$; δ, ppm) 172.2, 154.6, 152.9, 135.8, 134.9, 131.6, 129.8, 127.8, 127.7, 125.5, 125.4, 125.2, 124.3, 122.5, 120.9, 116.7, 113.8, 113.5, 112.7, 73.5, 60.3, 54.0, 47.5, 34.3, 30.4, 13.7. IR (KBr, ν, cm^{-1}) 3629, 3400, 2956, 1736, 1432, 1228, 1113, 1037, 797, 752. HR-MS (ESI-TOF, m/z) calcd for $C_{34}H_{38}BrNO_4$ $[M+Na]^+$ 626.1876, found 626.1881.

Ethyl 2-(5-cyano-1H-indol-3-yl)-4-(3,5-di-tert-butyl-4-hydroxyphenyl)chromane-3-carboxylate(3k).



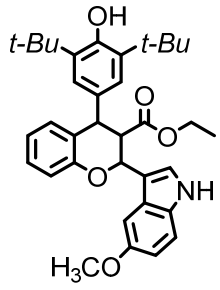
White solid, mp 211 -213°C; ^{1}H NMR (400 MHz, $CDCl_3$; *δ*, ppm) 8.67 (s, 1H), 8.18 (s, 1H), 7.49-7.27 (m, 3H), 7.24-6.76 (m, 6H), 5.59 (d, *J* = 10.4 Hz, 1H), 5.14 (s, 1H), 4.60-4.48 (m, 1H), 3.77-3.29 (m, 3H), 1.40 (s, 18H), 0.66 (t, *J* = 7.2 Hz, 3H). ^{13}C NMR (100 MHz, $CDCl_3$; *δ*, ppm) δ 172.2, 154.4, 153.0, 137.9, 135.9, 131.3, 129.8, 127.9, 125.9, 125.8, 125.5, 125.4, 125.1, 121.1, 120.7, 116.6, 115.0, 112.3, 103.3, 73.5, 34.3, 30.4, 26.9, 13.7. IR (KBr, *v*, cm^{-1}) 3611, 3332, 2924, 2218, 1710, 1471, 1374, 808, 756. HR-MS (ESI-TOF, m/z) calcd for $C_{35}H_{38}N_2O_4$ $[M+Na]^+$ 573.2724, found 573.2736.

Ethyl 4-(3,5-di-tert-butyl-4-hydroxyphenyl)-2-(5-methyl-1*H*-indol-3-yl)chromane-3-carboxylate(3l).



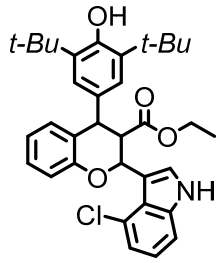
White solid, mp 205–206°C; ^{1}H NMR (400 MHz, $CDCl_3$; δ, ppm) 7.99 (s, 1H), 7.48 (s, 1H), 7.22 (d, *J* = 2.4Hz, 1H), 7.16 (s, 1H), 7.10-7.04 (m, 1H), 6.97-6.93 (m, 1H), 6.91-6.85 (m, 3H), 6.83-6.73 (m, 2H), 5.51 (d, *J* = 10.4 Hz, 1H), 5.03 (s, 1H), 4.47 (d, *J* = 11.6 Hz, 1H), 3.65-3.50 (m, 2H), 3.36 (dd, *J* = 11.6, 10.0 Hz, 1H), 2.38 (s, 3H), 1.32 (s, 18H), 0.57 (t, *J* = 8.0 Hz, 3H).^{13}C NMR (100 MHz, $CDCl_3$; *δ*, ppm) 172.3, 154.9, 152.8, 135.8, 134.6, 131.8, 129.8, 129.3, 127.6, 126.4, 125.5, 125.3, 124.2, 123.2, 120.6, 119.4, 116.7, 113.5, 110.9, 73.7, 60.1, 53.8, 47.6, 34.3, 30.4, 21.6, 13.7. IR (KBr, *v*, cm^{-1}) 3629, 3381, 2955, 1721, 1432, 1230, 1156, 800, 755. HR-MS (ESI-TOF, m/z) calcd for $C_{35}H_{41}NO_4$ $[M+Na]^+$ 562.2928, found 562.2934.

Ethyl 4-(3,5-di-tert-butyl-4-hydroxyphenyl)-2-(5-methoxy-1*H*-indol-3-yl)chromane-3-carboxylate (3m).



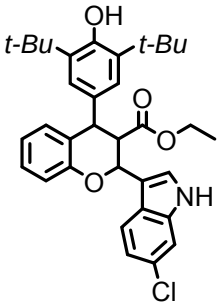
White solid, mp 179-181°C; ^{1}H NMR (400 MHz, $CDCl_3$; δ, ppm) 8.11 (s, 1H), 7.72 (d, J = 7.2 Hz, 1H), 7.29-7.26 (m, 1H), 7.24 (d, J = 2.4 Hz, 1H), 7.16-7.05 (m, 2H), 6.88 (s, 2H), 6.81 (d, J = 8.8 Hz, 1H), 6.68-6.63 (m, 1H), 6.35 (d, J = 4.0 Hz, 1H), 5.47 (d, J = 10.4 Hz, 1H), 5.03 (s, 1H), 4.46 (d, J = 11.6 Hz, 1H), 3.62-3.50 (m, 5H), 3.36 (dd, J = 11.4, 10.3 Hz, 1H), 1.32 (s, 18H), 0.54 (t, J = 7.2 Hz, 3H).^{13}C NMR (100 MHz, $CDCl_3$; δ, ppm) 172.4, 153.5, 152.8, 149.2, 136.3, 135.8, 131.6, 126.1, 125.4, 123.1, 122.5, 120.1, 119.9, 117.3,114.6,114.1,113.6,111.2, 73.8, 60.1, 55.8, 54.1, 47.7, 34.3, 30.4, 30.4,13.6. IR (KBr, v, cm^{-1}) 3614 , 3311, 2959, 1715, 1493, 1434, 1208, 1024, 744. HR-MS (ESI-TOF, m/z) calcd for $C_{35}H_{41}NO_5$ $[M+Na]^+$ 578.2877, found 528.2886.

Ethyl 2-(4-chloro-1*H*-indol-3-yl)-4-(3,5-di-tert-butyl-4-hydroxyphenyl) chromane -3-carboxylate (3n).



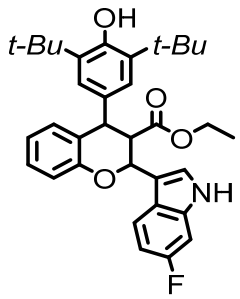
White solid, mp 210-212°C; ^{1}H NMR (400 MHz, $CDCl_3$; δ, ppm) 8.42 (s, 1H), 7.43 (s, 1H), 7.26-7.21 (m, 1H), 7.21-7.06 (m, 3H), 7.04-6.79 (m, 5H), 6.23-5.97 (m, 1H), 5.11 (s, 1H), 4.61-4.49 (m, 1H), 3.98-3.45 (m, 3H), 1.40 (s, 18H), 0.76 (t, J = 6.8 Hz, 3H). ^{13}C NMR (100 MHz, $CDCl_3$; δ, ppm) 172.3, 154.7, 152.8, 135.9, 132.2, 129.8, 127.6, 126.3, 125.4, 123.7, 123.0, 121.7, 120.6, 116.7, 114.1, 110.1, 68.1, 60.3, 53.7, 47.8, 34.3, 30.4, 13.8. IR (KBr, v, cm^{-1}) 3626 , 3432, 2961, 1715, 1486, 1434, 1229, 1179, 1015, 738. HR-MS (ESI-TOF, m/z) calcd for $C_{34}H_{38}ClNO_4$ $[M+Na]^+$ 582.2382, found 582.2395.

Ethyl 2-(6-chloro-1*H*-indol-3-yl)-4-(3,5-di-tert-butyl-4-hydroxyphenyl) chromane-3-carboxylate (3o).



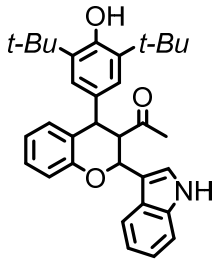
White solid, mp 200-201°C; ^{1}H NMR (400 MHz, $CDCl_3$; δ, ppm) 8.21 (s, 1H), 7.46 (d, J = 8.8 Hz, 1H), 7.25-7.19 (m, 1H), 7.16-6.96 (m, 3H), 6.94-6.74 (m, 5H), 5.50 (d, J = 10.0 Hz, 1H), 5.06 (s, 1H), 4.51-4.46 (m, 1H), 3.66-3.27 (m, 3H), 1.33 (s, 18H), 0.57 (t, J = 7.2 Hz, 3H). ^{13}C NMR (100 MHz, $CDCl_3$; δ, ppm) 172.3, 154.7, 152.9, 136.6, 135.9, 131.6, 129.8, 128.2, 127.8, 125.9, 125.2, 124.1, 123.9, 120.9, 120.8, 120.5, 116.6, 114.1, 111.2, 73.7, 60.3, 47.5, 34.3, 34.3, 30.4, 13.7. IR (KBr, v, cm^{-1}) 3624 , 3415, 2961, 1735, 1486, 1434, 1231, 1114, 1018, 754. HR-MS (ESI-TOF, m/z) calcd for $C_{34}H_{38}ClNO_4$ $[M+Na]^+$ 582.2382, found 582.2386.

Ethyl 4-(3,5-di-tert-butyl-4-hydroxyphenyl)-2-(6-fluoro-1*H*-indol-3-yl) chromane-3-carboxylate (3p).



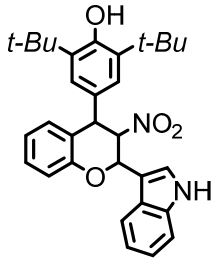
White solid, mp 183-184°C; ^{1}H NMR (400 MHz, $CDCl_3$; δ, ppm) 8.09 (s, 1H), 7.45 (dd, J = 8.8, 5.2 Hz, 1H), 7.23-7.04 (m, 2H), 7.04-6.72 (m, 7H), 5.55 (d, J = 12.0 Hz, 1H), 5.06 (s, 1H), 4.50-4.41 (m, 1H), 3.64-3.27 (m, 3H), 1.32 (s, 18H), 0.68 (t, J = 7.2 Hz, 3H). ^{13}C NMR (100 MHz, $CDCl_3$; δ, ppm) 172.3, 160.3 (d, J = 243.0 Hz), 153.8 (d, J = 192.7 Hz), 136.2 (d, J = 12.4 Hz), 135.9, 131.7, 129.8, 127.7, 125.4, 125.3, 123.4 (d, J = 3.4 Hz), 122.5, 120.8, 120.7, 116.6, 114.2, 109.0 (d, J = 24.4 Hz), 97.5 (d, J = 26.0 Hz), 73.8, 60.2, 54.1, 47.5, 34.3, 30.4, 13.7. ^{19}F NMR (376 MHz, $CDCl_3$; δ, ppm): -120.6(s). IR (KBr, v, cm^{-1}) 3630 , 3411, 2959, 1735, 1486, 1433, 1228, 1142, 1015, 755. HR-MS (ESI-TOF, m/z) calcd for $C_{34}H_{38}FNO_4$ $[M+Na]^+$ 566.2677, found 566.2686.

1-(4-(3,5-Di-tert-butyl-4-hydroxyphenyl)-2-(1*H*-indol-3-yl) chroman-3-yl)ethan-1-one (3q).



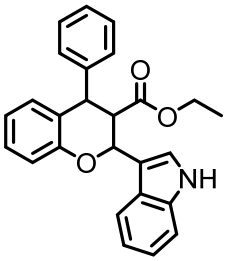
Yellow solid, mp 158-160°C; ^{1}H NMR (400 MHz, $CDCl_3$; δ, ppm) 8.13 (s, 1H), 7.77 (d, J = 8.0 Hz, 1H), 7.32-7.26 (m, 1H), 7.17-7.04 (m, 4H), 6.91-6.84 (m, 3H), 6.83-6.73 (m, 2H), 5.36 (d, J = 12.0 Hz, 1H), 5.06 (s, 1H), 4.40 (d, J = 12.0 Hz, 1H), 3.73 (t, J = 12.0 Hz, 1H), 1.32 (s, 18H), 1.20 (s, 3H). ^{13}C NMR (100 MHz, $CDCl_3$; δ, ppm) 210.7, 154.8, 152.7, 136.6, 136.2, 132.1, 129.7, 127.6, 125.7, 125.5, 125.2, 123.5, 122.6, 120.6, 120.3, 120.1, 116.7, 113.7, 111.5, 74.5, 58.9, 47.3, 34.4, 33.2, 30.4. IR (KBr, v, cm^{-1}) 3600, 3449, 2960, 1707, 1433, 1230, 741. HR-MS (ESI-TOF, m/z) calcd for $C_{33}H_{37}NO_3$ $[M+Na]^+$ 518.2666, found 518.2671.

4-(2-(1*H*-indol-3-yl)-3-nitrochroman-4-yl)-2,6-di-tert butylphenol (3r).



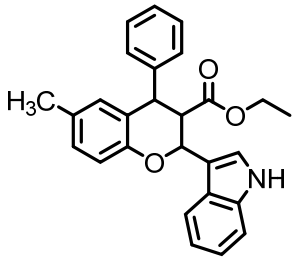
Yellow solid, mp 185 -187°C; ^{1}H NMR (400 MHz, $CDCl_3$; δ, ppm) 8.17 (s, 1H), 7.71 (d, J = 7.8 Hz, 1H), 7.34-7.26 (m, 1H), 7.27-7.04 (m, 5H), 6.94-6.80 (m, 4H), 5.70-5.62 (m, 1H), 5.29 (t, J = 10.4 Hz, 1H), 5.12 (s, 1H), 4.84 (d, J = 10.8 Hz, 1H), 1.32 (s, 18H).^{13}C NMR (100 MHz, $CDCl_3$; δ, ppm) 152.5, 135.3, 128.9, 127.3, 124.9, 124.2, 122.9, 121.9, 120.8, 119.6, 118.4, 115.8, 110.5, 90.2, 73.2, 48.2, 33.3, 29.3. IR (KBr, v, cm^{-1}) 3616, 3431, 2957, 1553, 1434, 1225, 748. HR-MS (ESI-TOF, m/z) calcd for $C_{31}H_{34}N_2O_4$ $[M+Na]^+$ 521.2411, found 521.2418.

Ethyl 2-(1*H*-indol-3-yl)-4-phenylchromane-3-carboxylate(5a).



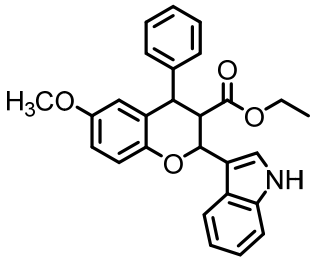
White solid Yield, mp 90-92°C; ^{1}H NMR (400 MHz, $CDCl_3$; δ, ppm) 8.09 (s, 1H), 7.62 (d, J = 8.0 Hz, 1H), 7.28-7.18 (m, 4H), 7.18-6.95 (m, 7H), 6.95-6.72 (m, 2H), 5.63 (d, J = 10.8 Hz, 1H), 4.63-4.54 (m, 1H), 3.79-3.47 (m, 3H), 0.77 (t, J = 7.2 Hz, 3H). ^{13}C NMR (100 MHz, $CDCl_3$; δ, ppm) 170.7, 154.7, 142.0, 136.3, 130.4, 129.5, 128.4, 128.3, 127.2, 125.9, 123.8, 123.0, 122.3, 120.9, 119.9, 119.9, 117.0, 114.4, 111.4, 68.3, 60.3, 49.7, 44.6, 27.0, 13.6. IR (KBr, v, cm^{-1}) 3409, 3058, 3028, 2979, 2931, 1726, 1486, 1454, 1243, 1010, 745. HR-MS (ESI-TOF, m/z) calcd for $C_{26}H_{23}NO_3$ $[M+Na]^+$ 420.1570, found 420.1570.

Ethyl 2-(1*H*-indol-3-yl)-6-methyl-4-phenylchromane-3-carboxylate(5b).



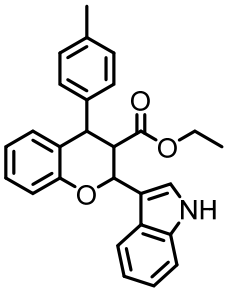
White solid, mp 122-124°C; ^{1}H NMR (400 MHz, $CDCl_3$; δ, ppm) 8.06 (s, 1H), 7.58 (d, J = 8.0 Hz, 1H), 7.28-7.18 (m, 2H), 7.19-6.71 (m, 10H), 5.57 (d, J = 11.2 Hz, 1H), 4.50 (d, J = 6.0 Hz, 1H), 3.75-3.40 (m, 3H), 2.13 (s, 3H), 0.72 (t, J = 7.2 Hz, 3H). ^{13}C NMR (100 MHz, $CDCl_3$; δ, ppm) 170.8, 152.5, 142.1, 136.3, 130.5, 130.1, 129.5, 129.3, 128.7, 128.3, 127.2, 125.9, 123.8, 122.6, 122.2, 119.9, 119.9, 116.7, 114.4, 111.5, 68.2, 60.3, 49.8, 44.7, 20.6, 13.6. IR (KBr, v, cm^{-1}) 3426, 3054, 3028, 2986, 2958, 2903, 1717, 1497, 1454, 1217, 971, 742. HR-MS (ESI-TOF, m/z) calcd for $C_{27}H_{25}NO_3$ $[M+Na]^+$ 434.1727, found 434.1734.

Ethyl 2-(1*H*-indol-3-yl)-6-methoxy-4-phenylchromane-3-carboxylate(5c).



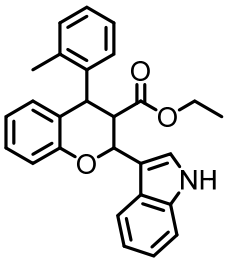
White solid, mp 134-135°C; ^{1}H NMR (400 MHz, $CDCl_3$; δ, ppm) 8.16 (s, 1H), 7.66 (d, J = 8.0 Hz, 1H), 7.32-7.20 (m, 4H), 7.22-6.99 (m, 5H), 6.96-6.70 (m, 2H), 6.54 (d, J = 2.8 Hz, 1H), 5.64 (d, J = 11.2 Hz, 1H), 4.58 (d, J = 6.0 Hz, 1H), 3.78 (dd, J = 11.2, 6.0 Hz, 1H), 3.67 (s, 3H), 3.63-3.49 (m, 2H), 0.79 (t, J = 7.2 Hz, 3H). ^{13}C NMR (100 MHz, $CDCl_3$; δ, ppm) 170.7, 153.7, 148.9, 141.8, 136.3, 129.5, 128.3, 127.3, 125.9, 123.7, 123.4, 122.2, 119.9, 117.7, 115.2, 114.5, 114.2, 111.4, 68.2, 60.2, 55.7, 49.9, 44.9, 13.6. IR (KBr, v, cm^{-1}) 3408, 3062, 3027, 2953, 2833, 1727, 1494, 1455, 1214, 1035, 743. HR-MS (ESI-TOF, m/z) calcd for $C_{27}H_{25}NO_4$ $[M+Na]^+$ 450.1676, found 450.1681.

Ethyl 2-(1*H*-indol-3-yl)-4-(p-tolyl)chromane-3-carboxylate(5d).



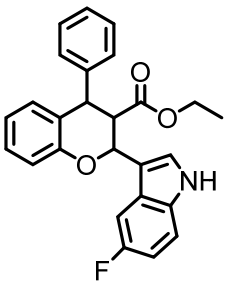
White solid, mp 90-91°C; ^{1}H NMR (400 MHz, $CDCl_3$; δ, ppm) 8.06 (s, 1H), 7.62 (d, J = 7.6 Hz, 1H), 7.25 (d, J = 9.2 Hz, 1H), 7.18-6.87 (m, 10H), 6.87-6.73 (m, 1H), 5.63 (d, J = 11.2 Hz, 1H), 4.53 (d, J = 6.0 Hz, 1H), 3.77-3.42 (m, 3H), 2.26 (s, 3H), 0.80 (t, J = 7.2 Hz, 3H). ^{13}C NMR (100 MHz, $CDCl_3$; δ, ppm) 170.7, 154.6, 138.9, 136.8, 136.3, 130.3, 129.3, 129.0, 128.3, 126.0, 123.7, 123.3, 122.2, 120.8, 120.0, 119.9, 116.9, 114.6, 111.3, 68.3, 60.2, 49.6, 44.2, 21.1, 13.6. IR (KBr, ν, cm^{-1}) 3407, 3056, 2980, 2924, 2869, 1723, 1486, 1455, 1227, 1011, 744. HR-MS (ESI-TOF, m/z) calcd for $C_{27}H_{25}NO_3$ $[M+Na]^+$ 434.1727, found 434.1732.

Ethyl 2-(1*H*-indol-3-yl)-4-(o-tolyl)chromane-3-carboxylate(5e).



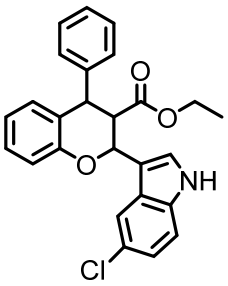
White solid, mp 128-129°C; ^{1}H NMR (400 MHz, $CDCl_3$; δ, ppm) 8.07 (s, 1H), 7.65 (d, J = 8.0 Hz, 1H), 7.29-7.20 (m, 1H), 7.17-7.00 (m, 8H), 6.99-6.73 (m, 3H), 5.76 (d, J = 10.8 Hz, 1H), 4.90 (d, J = 6.0 Hz, 1H), 3.77 (dd, J = 10.8, 6.2 Hz, 1H), 3.61-3.44 (m, 2H), 2.35 (s, 3H), 0.64 (t, J = 7.2 Hz, 3H). ^{13}C NMR (100 MHz, $CDCl_3$; δ, ppm) 171.0, 154.7, 140.7, 136.317, 136.2, 130.7, 130.4, 130.2, 128.1, 126.8, 126.1, 125.9, 124.0, 123.5, 122.4, 120.9, 112.0, 119.9, 117.0, 114.2, 111.4, 68.6, 60.3, 49.4, 38.9, 19.9, 13.4. IR (KBr, ν, cm^{-1}) 3385, 3024, 2978, 2952, 2898, 1720, 1486, 1453, 1228, 1017, 748. HR-MS (ESI-TOF, m/z) calcd for $C_{27}H_{25}NO_3$ $[M+Na]^+$ 434.1727, found 434.1731.

Ethyl 2-(5-fluoro-1*H*-indol-3-yl)-4-phenylchromane-3-carboxylate(5f).



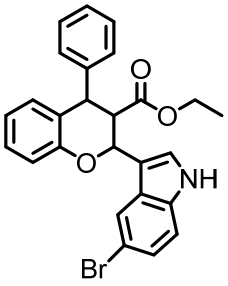
White solid, mp 178-179°C; ^{1}H NMR (400 MHz, $CDCl_3$; δ, ppm) 8.18 (s, 1H), 7.48-7.17 (m, 6H), 7.18-7.10 (m, 3H), 7.06-6.75 (m, 4H), 5.62 (d, J = 11.2 Hz, 1H), 4.63 (d, J = 5.6 Hz, 1H), 3.79-3.45 (m, 3H), 0.83 (t, J = 7.2 Hz, 3H). ^{13}C NMR (100 MHz, $CDCl_3$; δ, ppm) 170.6, 157.90 (d, J = 234.9 Hz), 154.5, 141.9, 132.7, 130.4, 129.5, 128.5, 128.3, 127.3, 126.3 (d, J = 10.2 Hz), 125.4, 122.9, 121.0, 116.9, 114.7 (d, J = 4.7 Hz), 112.0 (d, J = 9.7 Hz), 110.8 (d, J = 26.6 Hz), 104.8 (d, J = 24.0 Hz), 68.0, 60.4, 49.7, 44.6, 13.6. ^{19}F NMR (376 MHz, $CDCl_3$; δ, ppm): -124.0(s). IR (KBr, ν, cm^{-1}) 3430, 3062, 3032, 2981, 2934, 2895, 1715, 1488, 1454, 1242, 1032, 753. HR-MS (ESI-TOF, m/z) calcd for $C_{26}H_{22}FNO_3$ $[M+Na]^+$ 438.1476, found 438.1481.

Ethyl 2-(5-chloro-1*H*-indol-3-yl)-4-phenylchromane-3-carboxylate(5g).



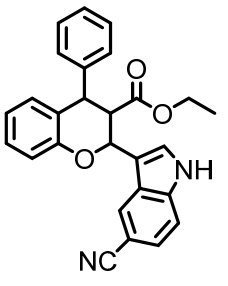
White solid, mp 178-180°C; ^{1}H NMR (400 MHz, $CDCl_3$; δ, ppm) 8.15 (s, 1H), 7.56 (d, J = 2.0 Hz, 1H), 7.27-7.18 (m, 3H), 7.17-7.02 (m, 6H), 6.99-6.69 (m, 3H), 5.54 (d, J = 11.2 Hz, 1H), 4.59-4.53 (m, 1H), 3.71-3.36 (m, 3H), 0.77 (t, J = 6.8 Hz, 3H).^{13}C NMR (100 MHz, $CDCl_3$; δ, ppm) 170.6, 154.4, 141.9, 134.6, 130.5, 129.5, 128.5, 128.3, 127.3, 127.0, 125.7, 125.0, 122.8, 122.7, 121.1, 119.3, 117.0, 114.3, 112.4, 67.8, 60.4, 49.8, 44.5, 13.6. IR (KBr, v, cm^{-1}) 3430, 3061, 3031, 2978, 2931, 2894, 1716, 1490, 1453, 1229, 1110, 752. HR-MS (ESI-TOF, m/z) calcd for $C_{26}H_{22}ClNO_3$ $[M+Na]^+$ 454.1180, found 454.1191.

Ethyl 2-(5-bromo-1*H*-indol-3-yl)-4-phenylchromane-3-carboxylate(5h).



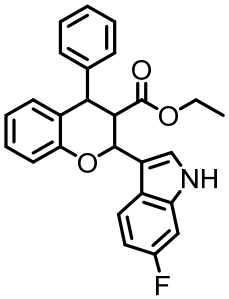
White solid, mp 159-160°C; ^{1}H NMR (400 MHz, $CDCl_3$; δ, ppm) 8.28-8.18 (m, 1H), 7.79 (d, J = 2.0 Hz, 1H), 7.35-7.16 (m, 6H), 7.15-7.07 (m, 3H), 7.06-6.76 (m, 3H), 5.61 (d, J = 11.2 Hz, 1H), 4.66-4.58 (m, 1H), 3.81-3.40 (m, 3H), 0.84 (t, J = 7.2 Hz, 3H). ^{13}C NMR (100 MHz, $CDCl_3$; δ, ppm) 170.6, 154.4, 141.9, 134.9, 130.5, 129.5, 128.5, 128.3, 127.6, 127.3, 125.2, 124.9, 122.8, 122.3, 121.1, 117.0, 114.2, 113.3, 112.9, 67.8, 60.4, 49.8, 44.5, 13.6. IR (KBr, v, cm^{-1}) 3430, 3060, 3028, 2979, 2931, 2895, 1718, 1487, 1453, 1230, 1110, 751. HR-MS (ESI-TOF, m/z) calcd for $C_{26}H_{22}BrNO_3$ $[M+Na]^+$ 498.0675, found 498.0670.

Ethyl 2-(5-cyano-1H-indol-3-yl)-4-phenylchromane-3-carboxylate(5i).



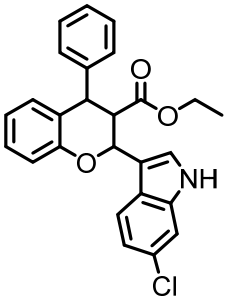
White solid, mp111-112°C; ^{1}H NMR (400 MHz, $CDCl_3$; δ, ppm) 8.67 (s, 1H), 8.05 (s, 1H), 7.47-7.27 (m, 6H), 7.25-7.11 (m, 3H), 7.08-6.78 (m, 3H), 5.66 (d, J = 11.2 Hz, 1H), 4.68-4.61 (m, 1H), 3.79-3.44 (m, 3H), 0.87 (t, J = 7.2 Hz, 3H).^{13}C NMR (100 MHz, $CDCl_3$; δ, ppm) 170.4, 154.2, 141.7, 137.9, 130.5, 129.4, 128.8, 128.9, 127.4, 125.9, 125.7, 125.5, 125.2, 122.7, 121.3, 120.7, 116.9, 115.5, 112.4, 103.1, 67.7, 60.5, 49.9, 44.5, 27.0, 13.7. IR (KBr, v, cm^{-1}) 3339, 3061, 3028, 2976, 2931, 2899, 2221, 1725, 1485, 1472, 1227, 1033, 753, 701. HR-MS (ESI-TOF, m/z) calcd for $C_{27}H_{22}N_2O_3$ $[M+Na]^+$ 445.1523, found 445.1530.

Ethyl 2-(6-fluoro-1*H*-indol-3-yl)-4-phenylchromane-3-carboxylate(5j).



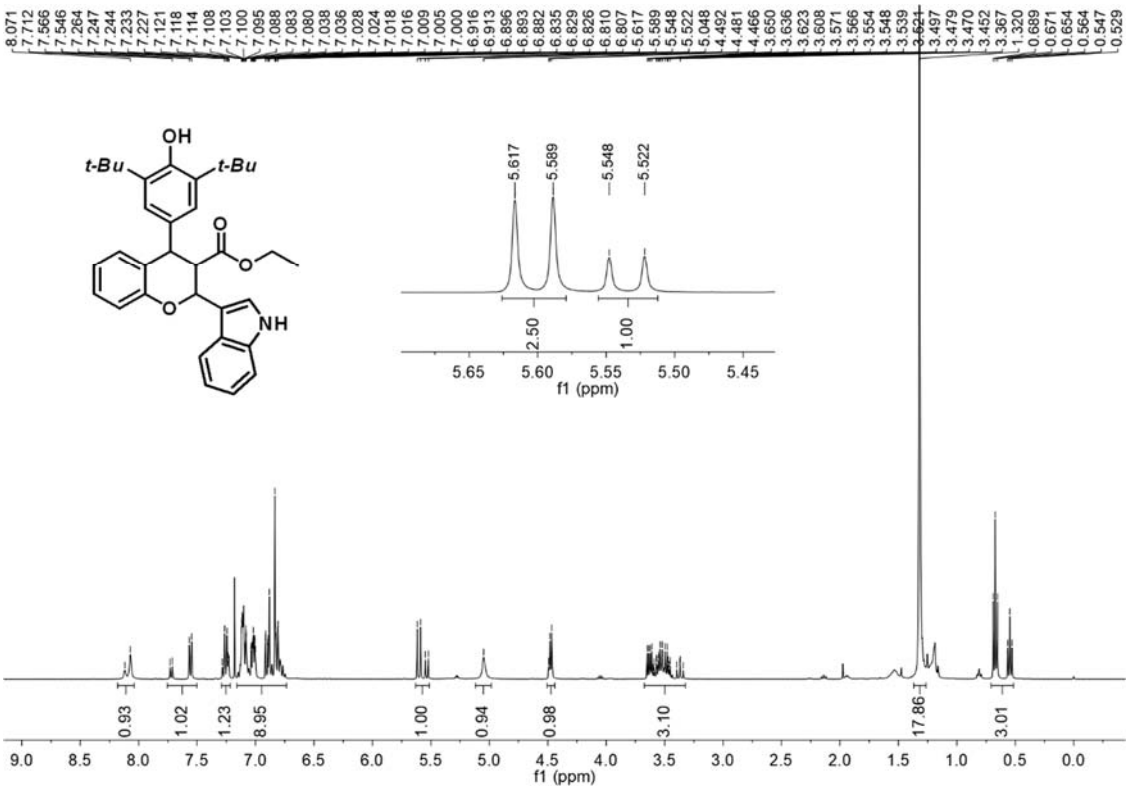
White solid, mp 123-124°C; ^{1}H NMR (400 MHz, $CDCl_3$; δ, ppm) 8.12 (s, 1H), 7.51 (dd, J = 8.8, 5.6 Hz, 1H), 7.31-7.17 (m, 3H), 7.20-7.00 (m, 4H), 7.01-6.70 (m, 5H), 5.58 (d, J = 11.2 Hz, 1H), 4.63-4.38 (m, 1H), 3.76-3.39 (m, 3H), 0.77 (t, J = 7.2 Hz, 3H). ^{13}C NMR (100 MHz, $CDCl_3$; δ, ppm) 170.6, 160.0(d, J = 238.2 Hz), 154.5, 141.9, 136.2 (d, J = 12.3 Hz), 130.4, 129.5, 128.5, 128.3, 127.3, 124.0 (d, J = 3.5 Hz), 123.0, 122.5, 120.60 (d, J = 10.1 Hz), 116.9, 114.6, 108.78 (d, J = 24.2 Hz), 97.7 (d, J = 26.1 Hz), 68.0, 60.3, 49.8, 44.6, 13.6. ^{19}F NMR (376 MHz, $CDCl_3$; δ, ppm): -120.8(s). IR (KBr, v, cm^{-1}) 3339, 3062, 3027, 2994, 2889, 1719, 1487, 1453, 1248, 1018, 756. HR-MS (ESI-TOF, m/z) calcd for $C_{26}H_{22}FNO_3$ $[M+Na]^+$ 438.1476, found 438.1478.

Ethyl 2-(6-chloro-1*H*-indol-3-yl)-4-phenylchromane-3-carboxylate(5k).

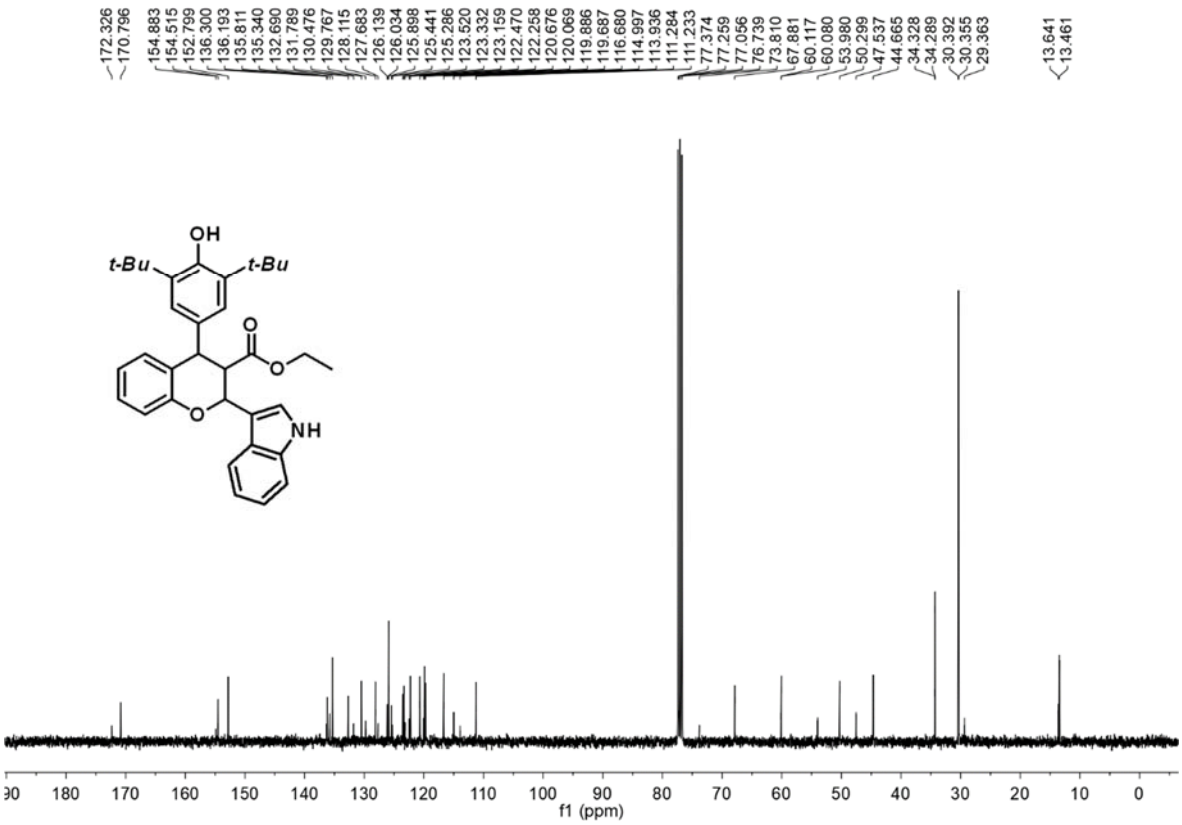


White solid, mp 142-143°C; ^{1}H NMR (400 MHz, $CDCl_3$; δ, ppm) 8.09 (s, 1H), 7.50 (d, J = 8.8 Hz, 1H), 7.28-7.19 (m, 4H), 7.17-7.02 (m, 4H), 7.02-6.70 (m, 4H), 5.57 (d, J = 11.2 Hz, 1H), 4.61-4.48 (m, 1H), 3.72-3.37 (m, 3H), 0.77 (t, J = 7.2 Hz, 3H). ^{13}C NMR (100 MHz, $CDCl_3$; δ, ppm) 170.5, 154.5, 141.8, 136.6 ,130.4, 129.5, 128.7, 128.5, 128.3, 127.3, 124.5, 124.3, 122.9, 121.0, 120.8, 120.7, 116.9, 114.8, 111.3, 67.9, 60.3, 49.8, 44.6, 13.7. IR (KBr, v, cm^{-1}) 3400, 3062, 3027, 2989, 2898, 1715, 1486, 1453, 1244, 1037, 755. HR-MS (ESI-TOF, m/z) calcd for $C_{26}H_{22}ClNO_3$ $[M+Na]^+$ 454.1180, found 454.1182.

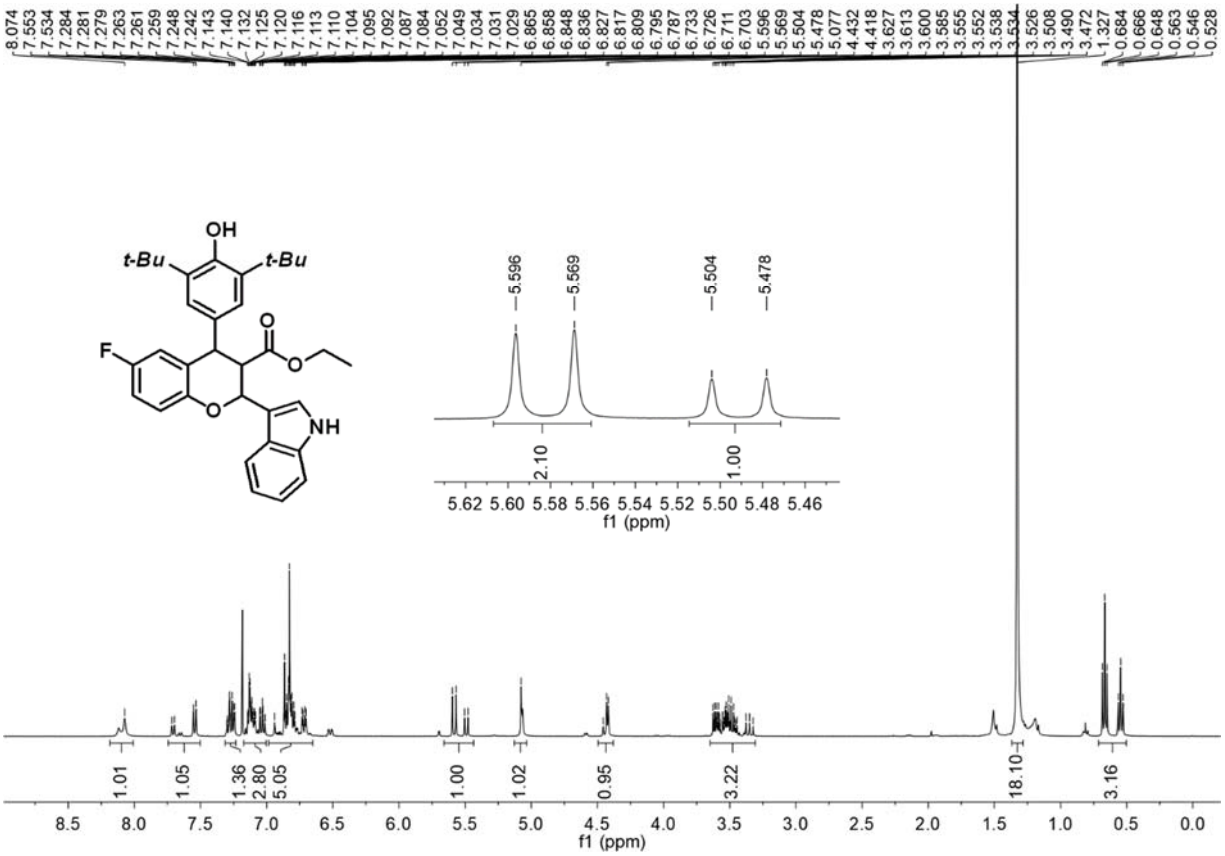
Copies of ^{1}H , ^{13}C NMR and ^{19}F NMR Spectra of Products



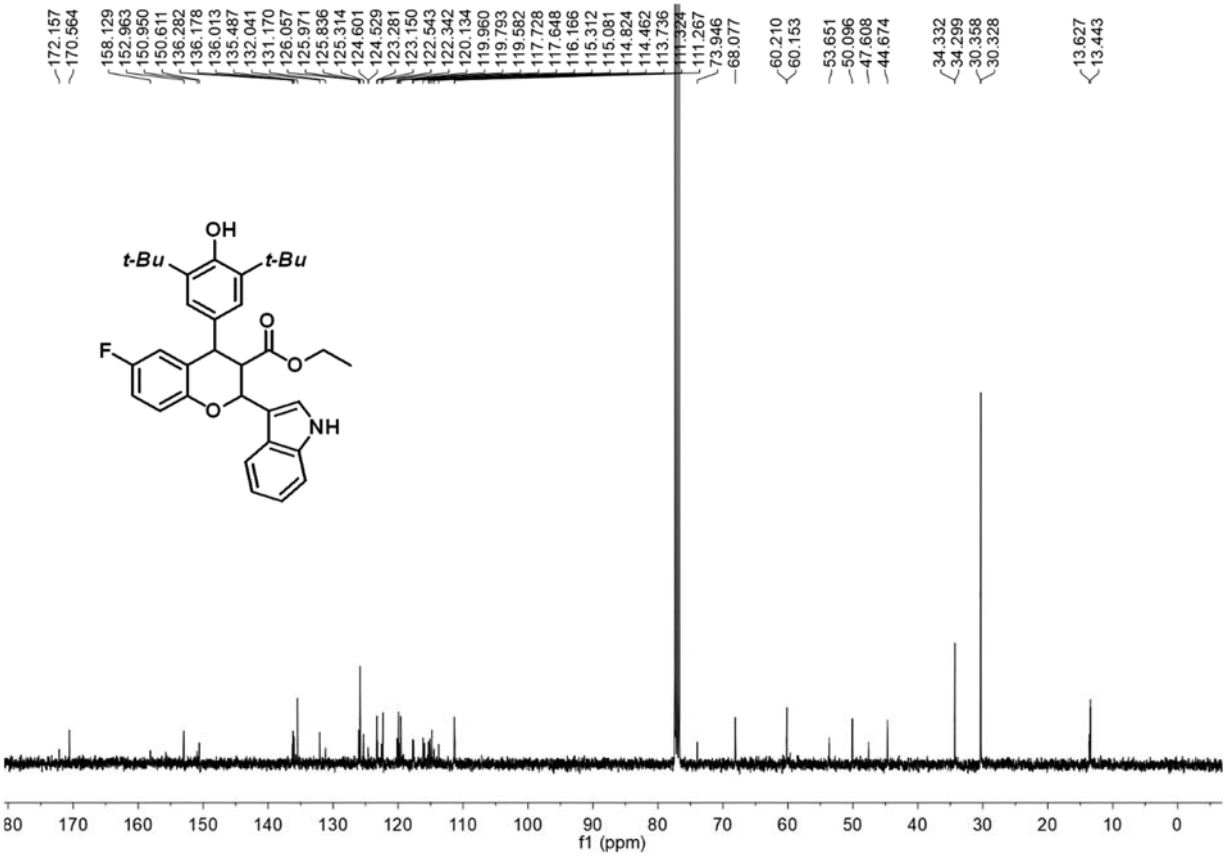
^{1}H NMR Spectrum of Compound **3a**



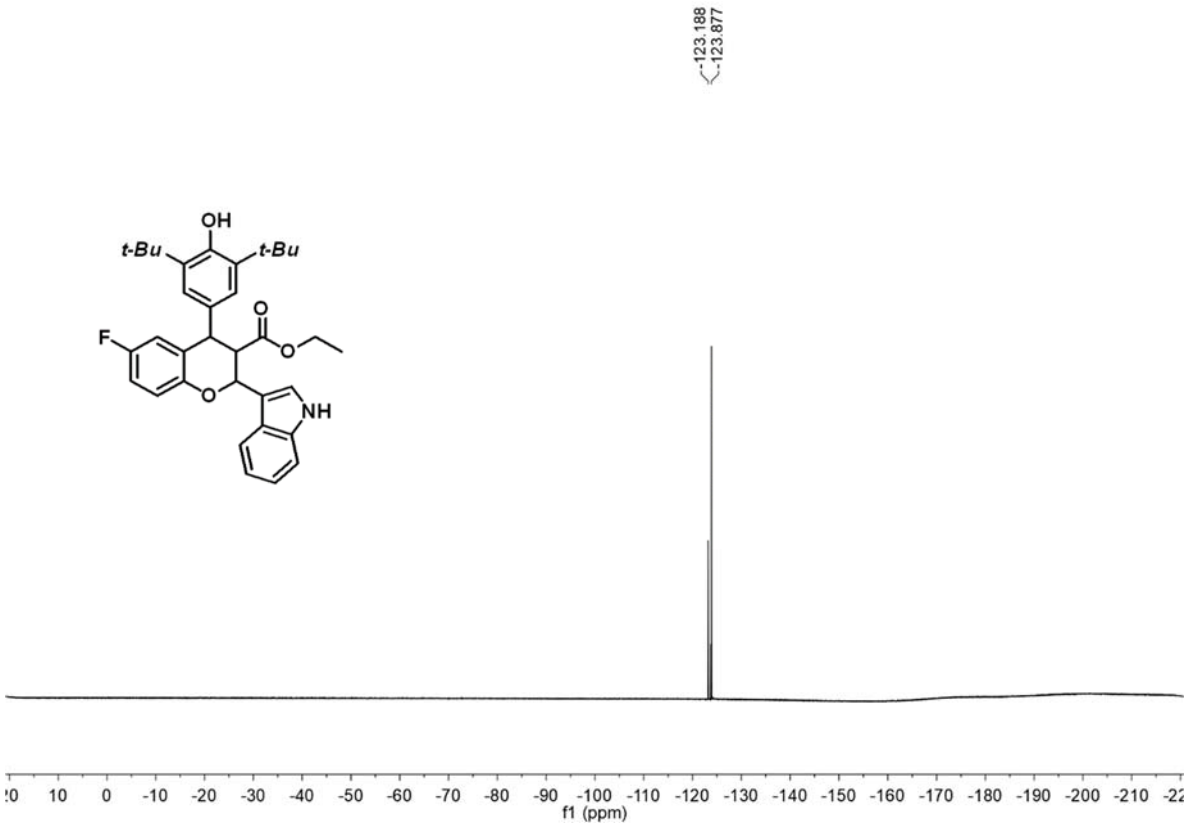
^{13}C NMR Spectrum of Compound **3a**



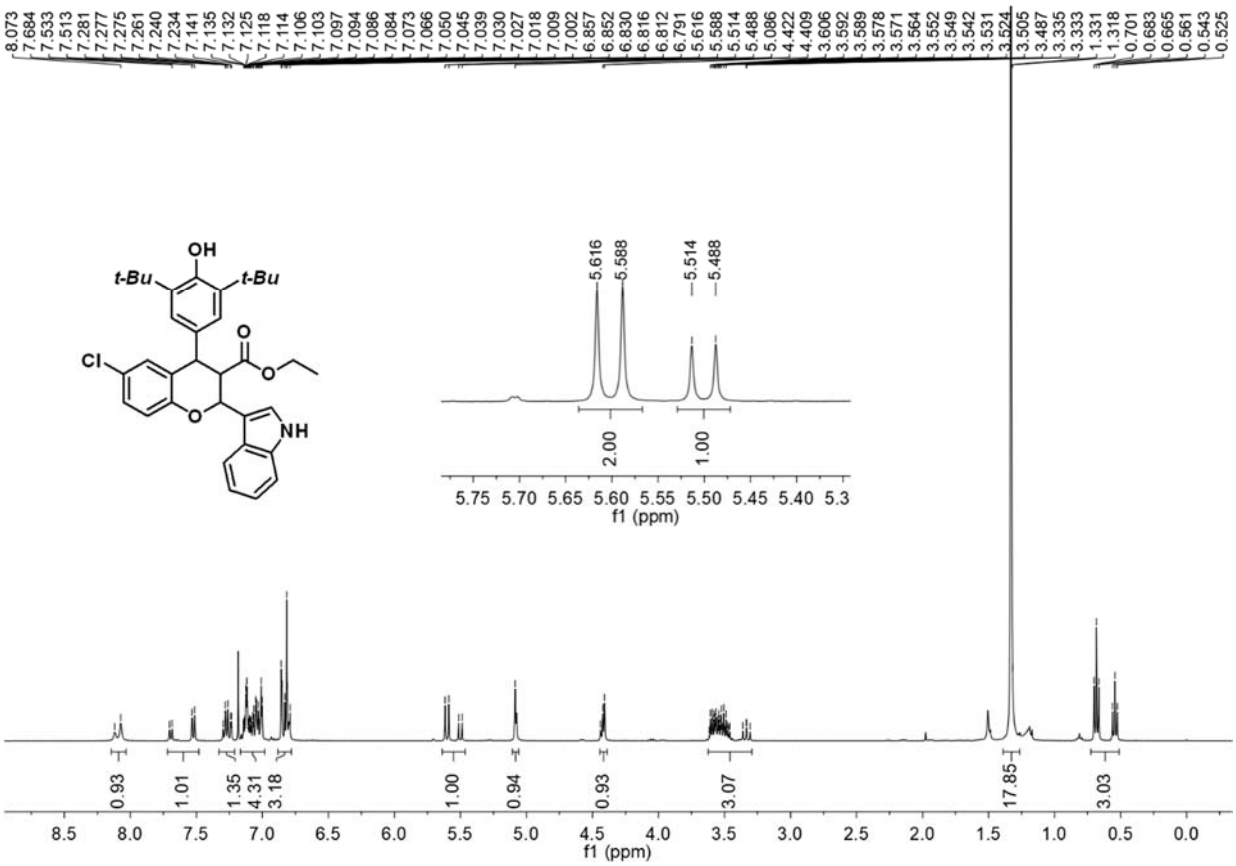
^{1}H NMR Spectrum of Compound **3b**



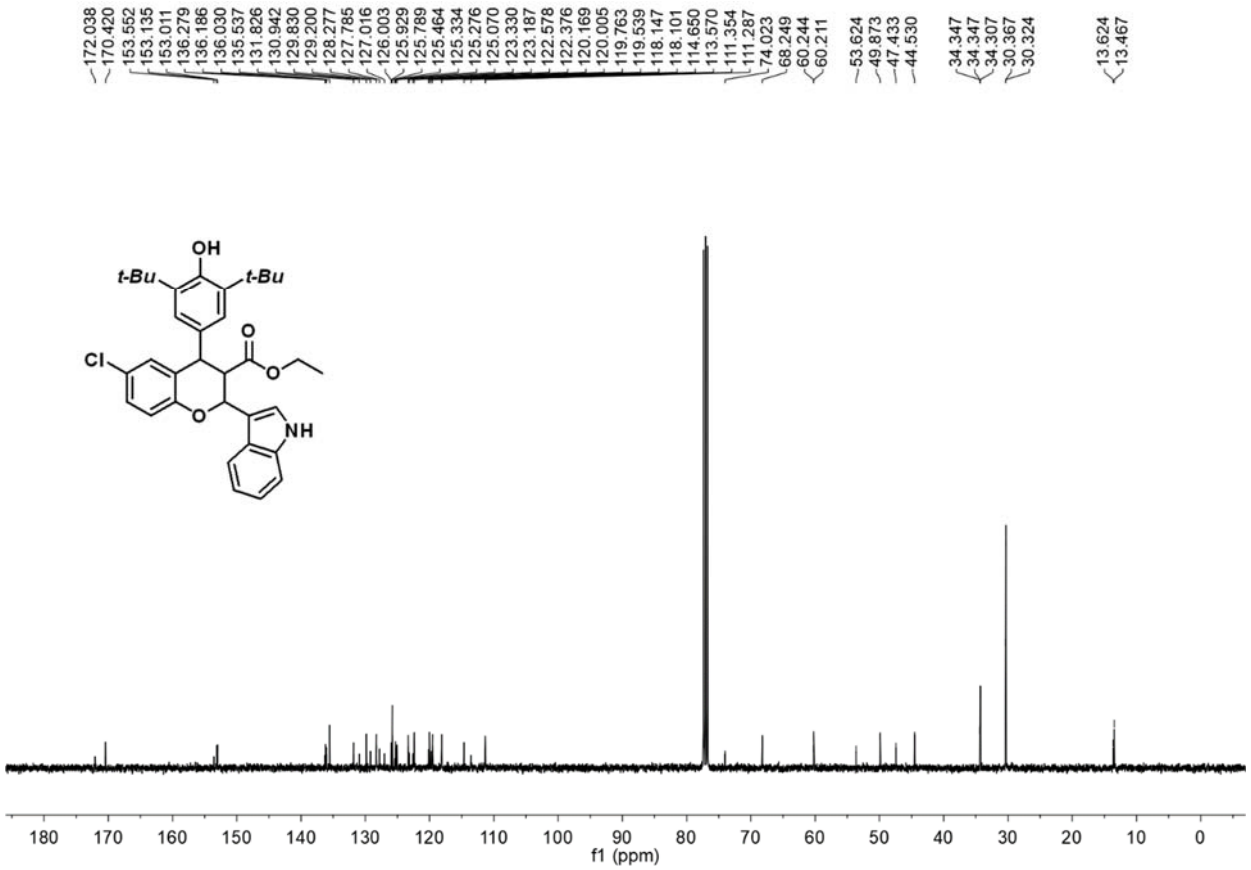
^{13}C NMR Spectrum of Compound **3b**



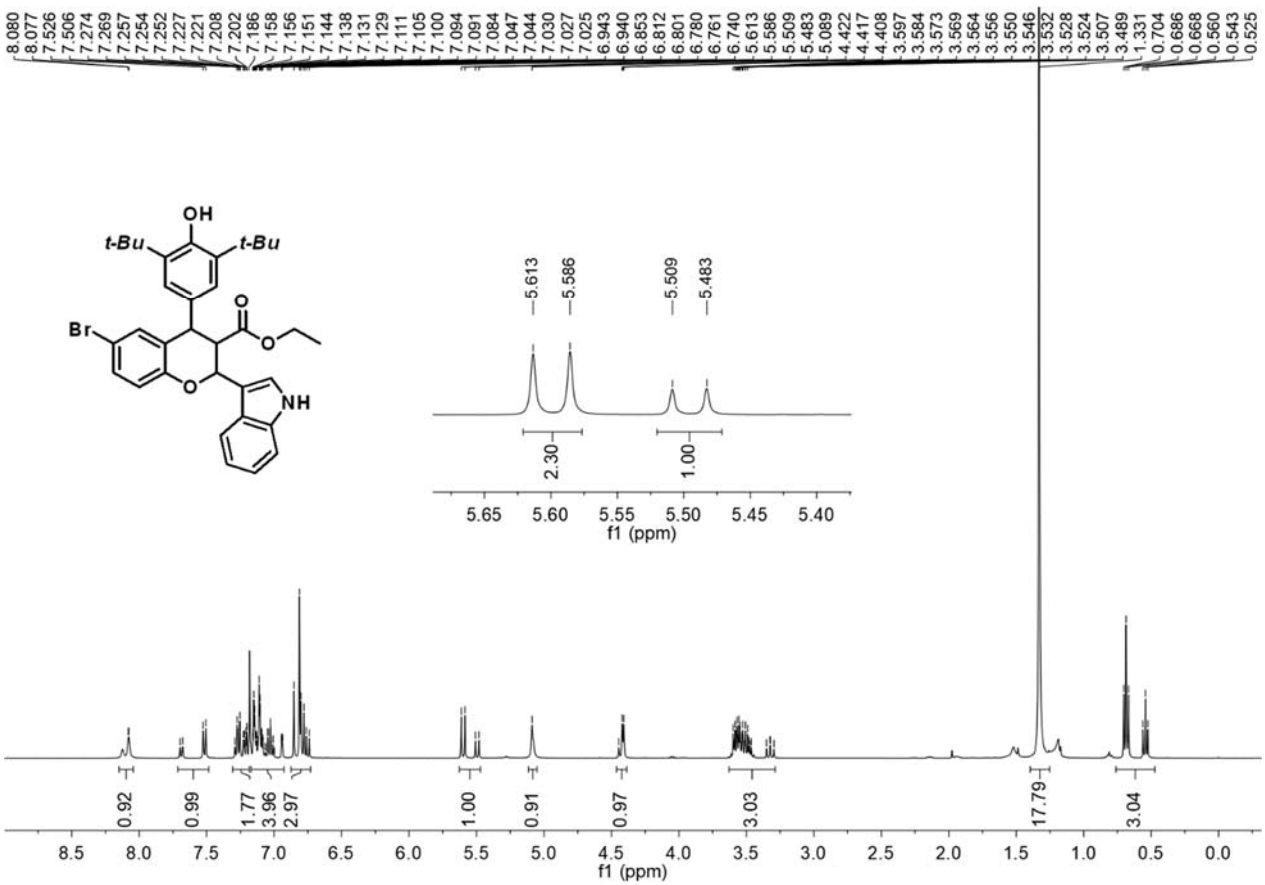
^{19}F NMR Spectrum of Compound **3b**



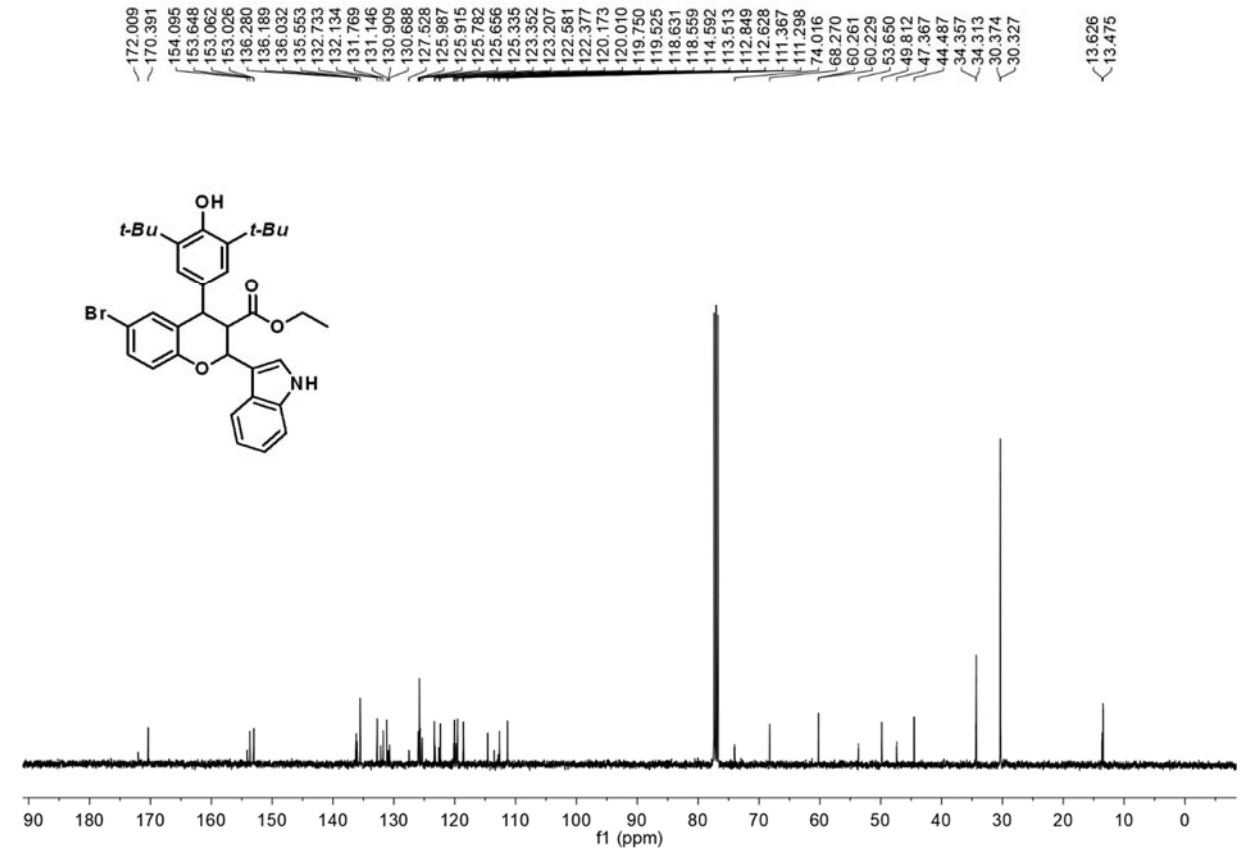
^{1}H NMR Spectrum of Compound **3c**



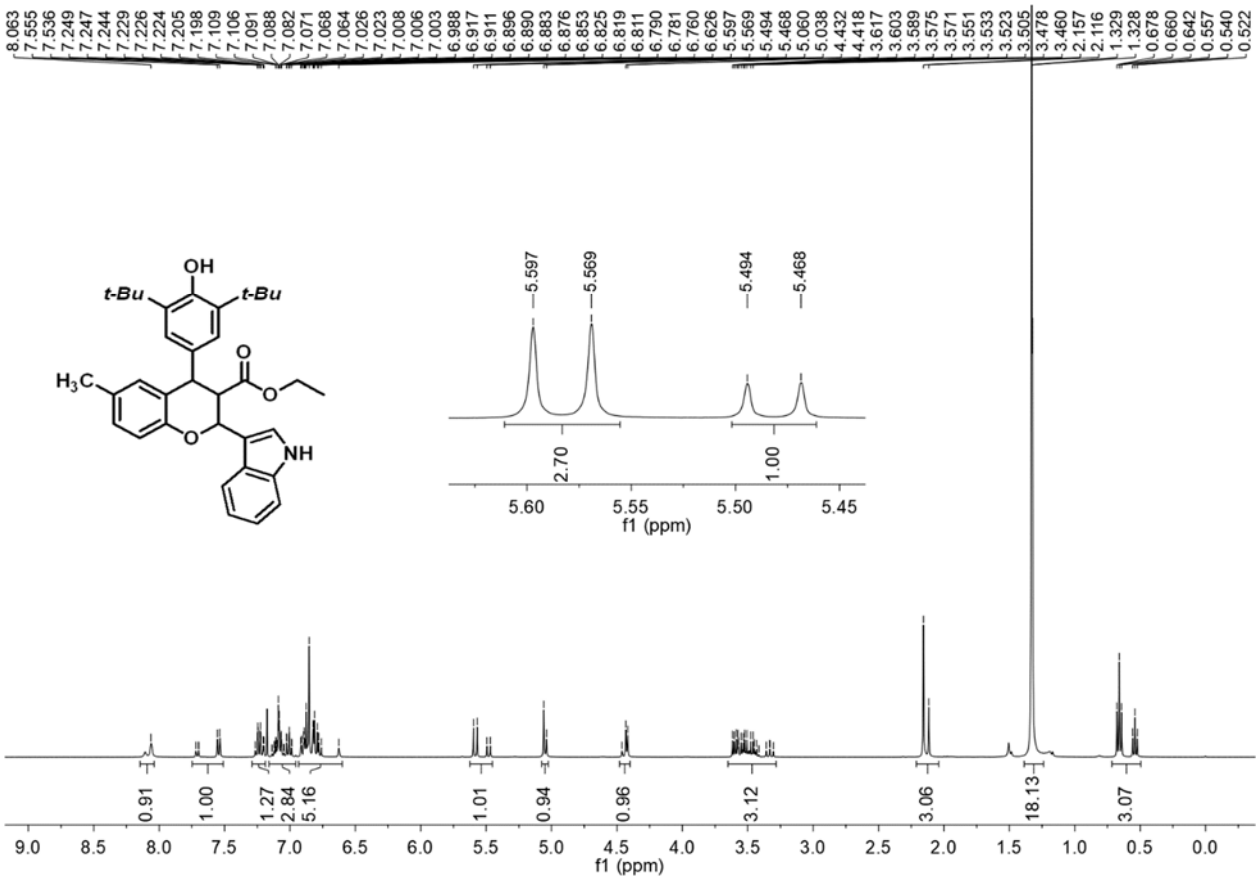
^{13}C NMR Spectrum of Compound **3c**



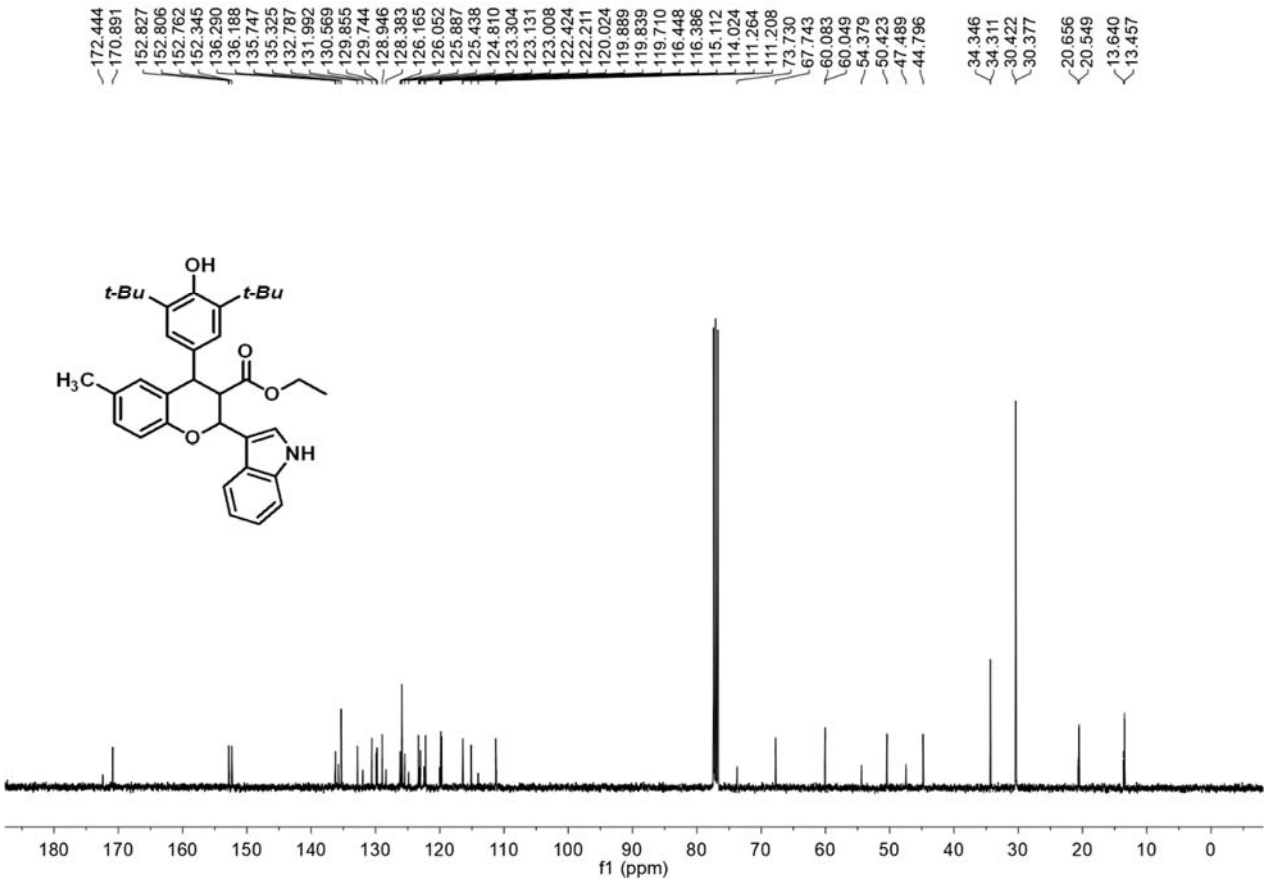
^{1}H NMR Spectrum of Compound **3d**



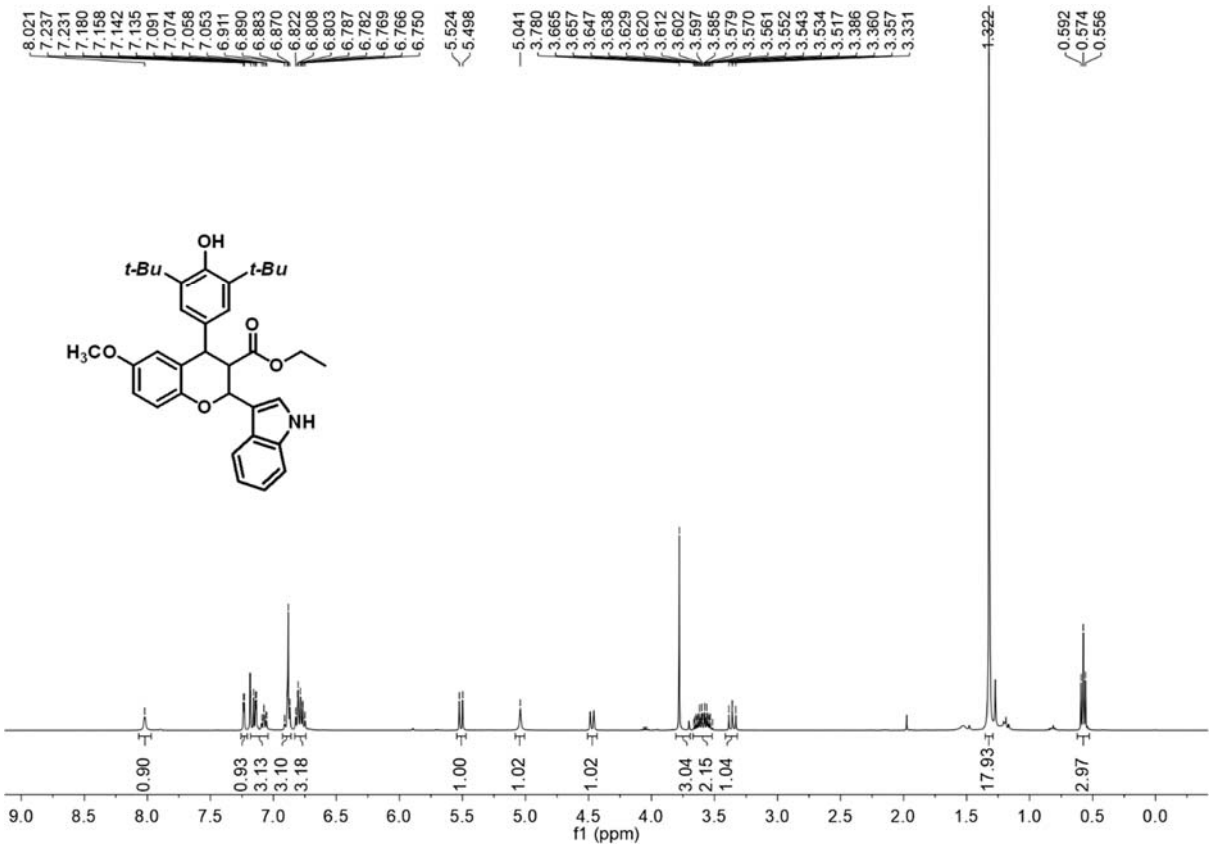
^{13}C NMR Spectrum of Compound **3d**



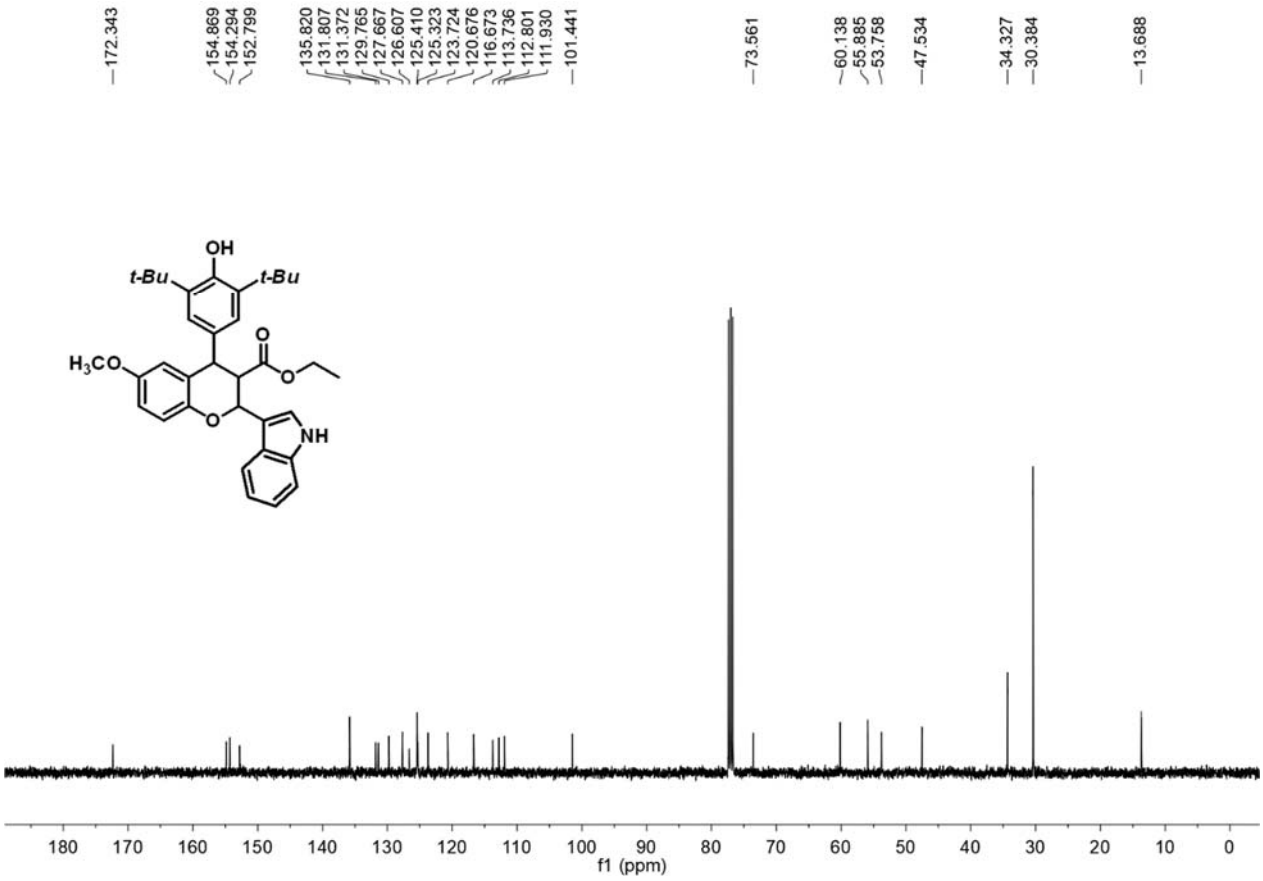
^{1}H NMR Spectrum of Compound **3e**



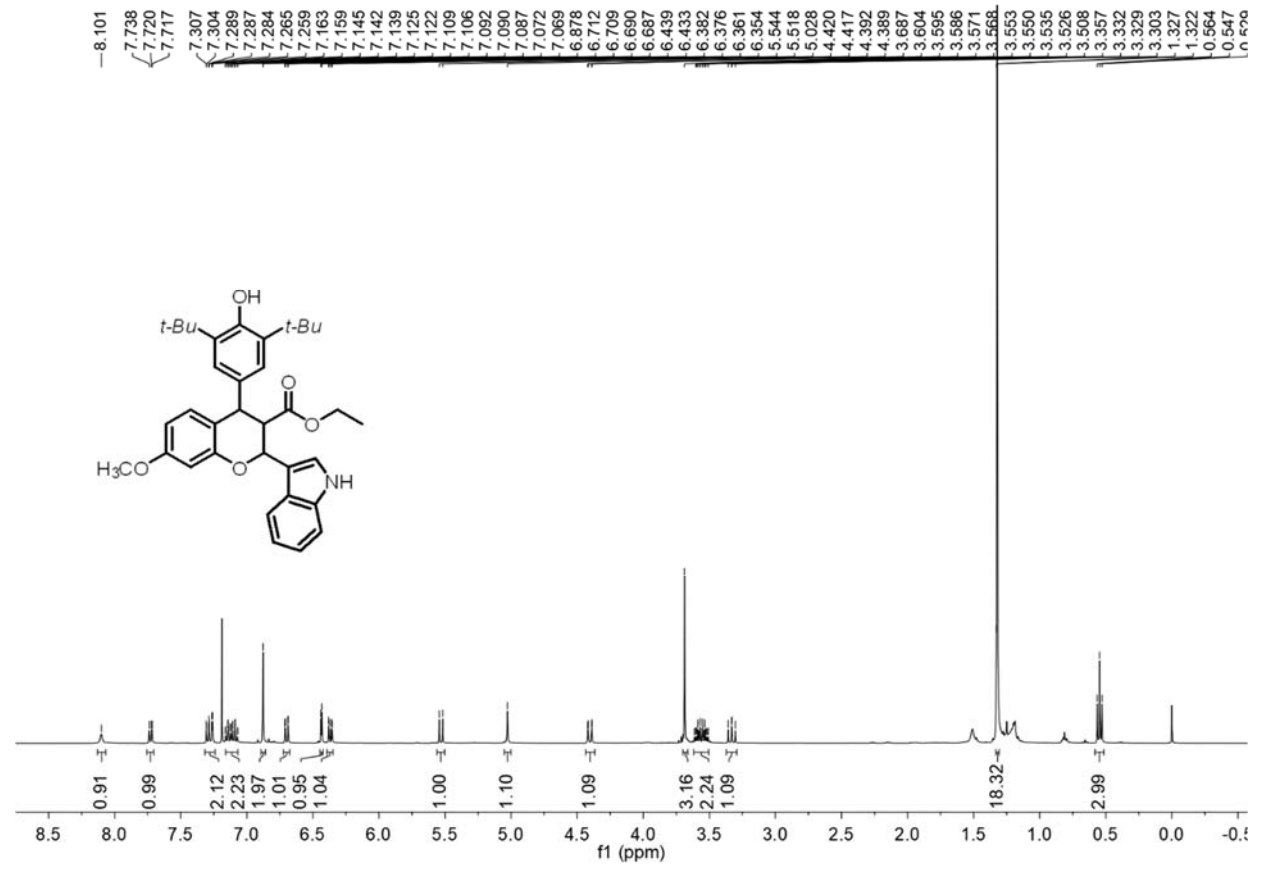
^{13}C NMR Spectrum of Compound **3e**



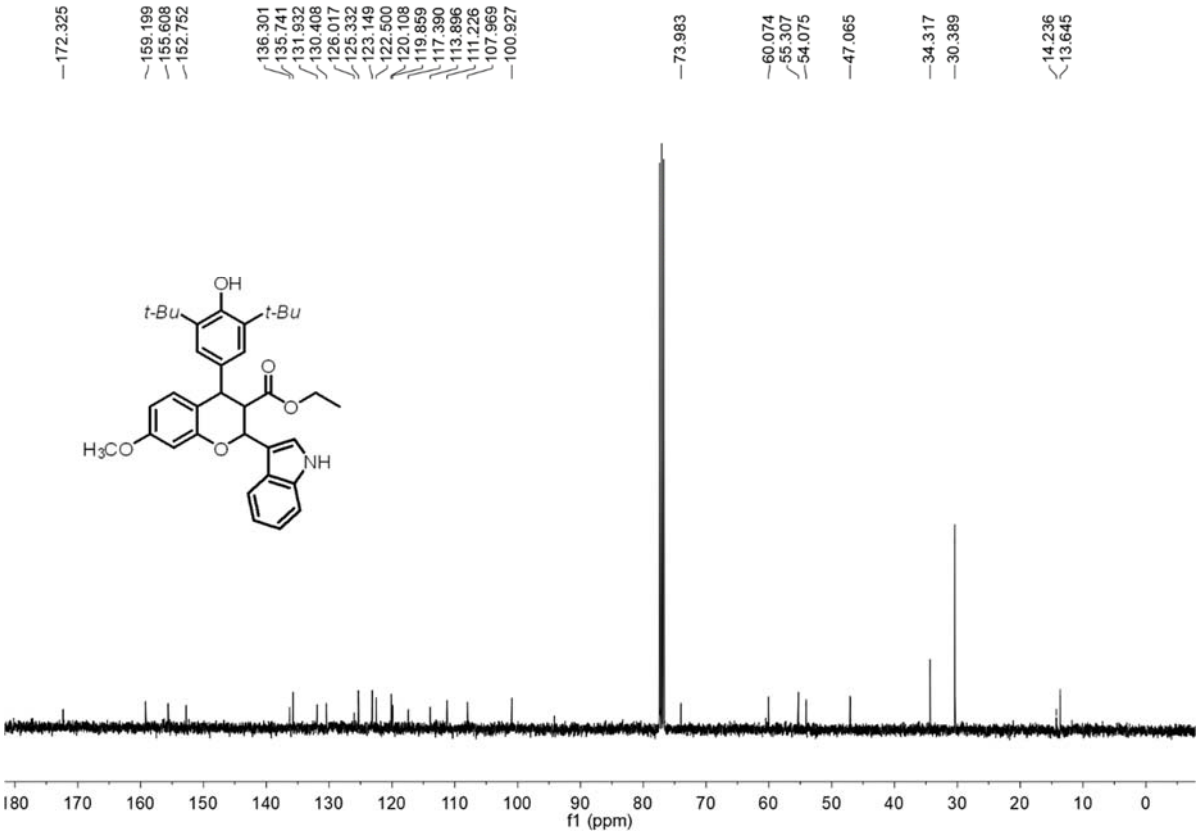
^{1}H NMR Spectrum of Compound **3f**



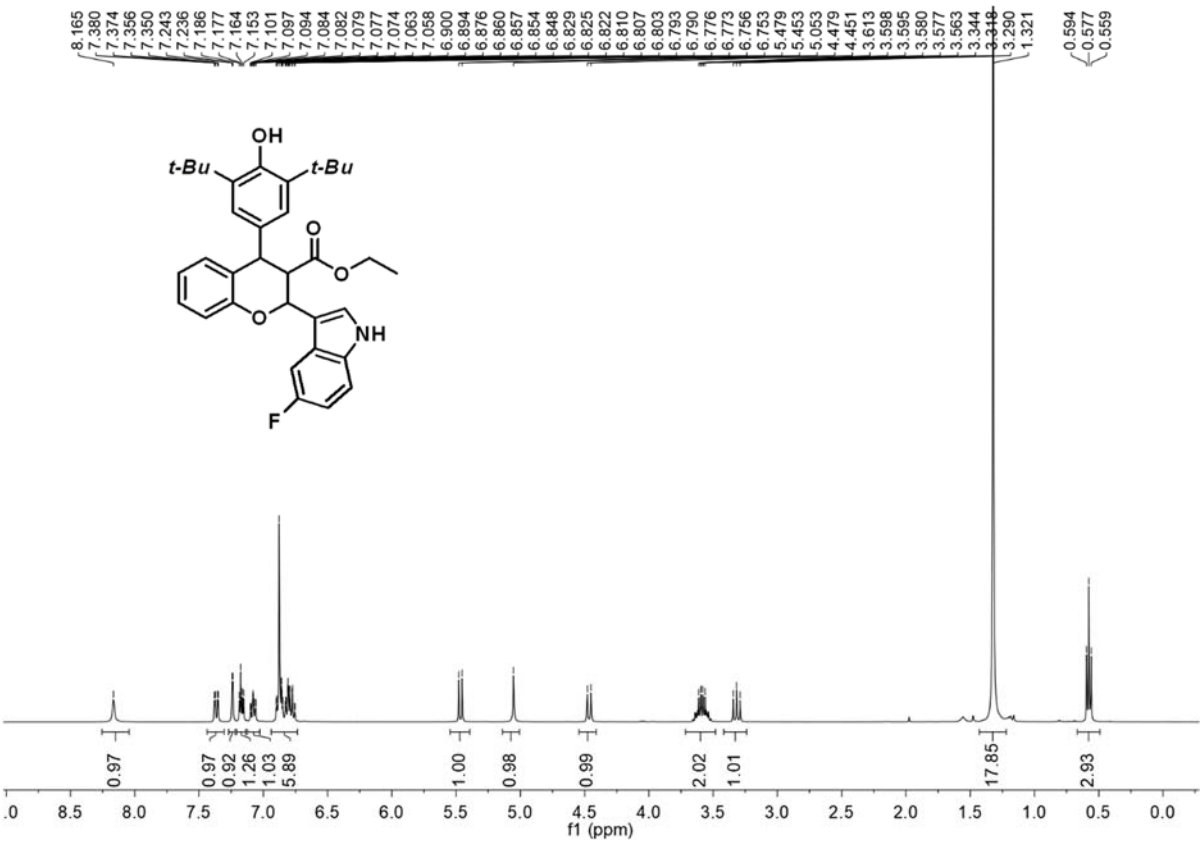
^{13}C NMR Spectrum of Compound **3f**



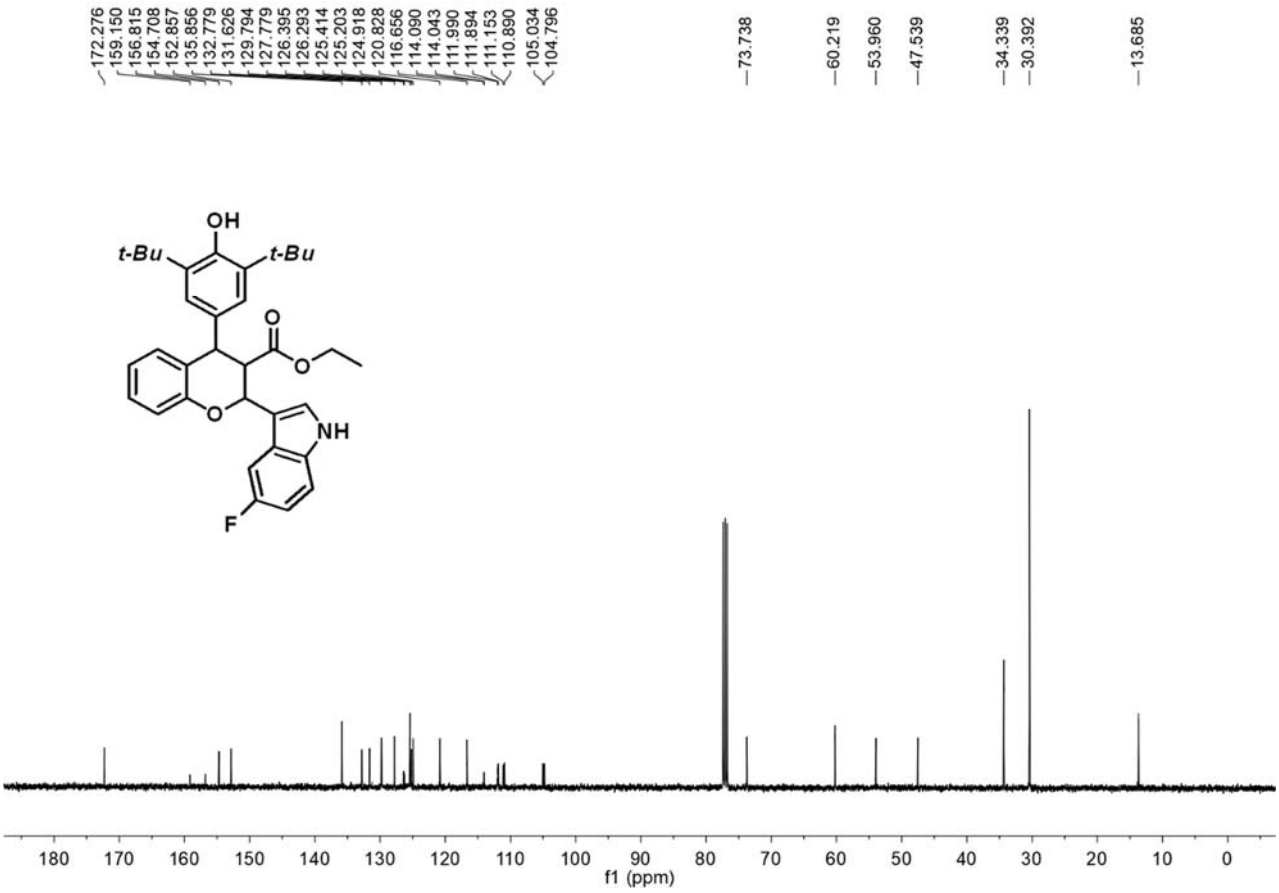
^{1}H NMR Spectrum of Compound **3g**



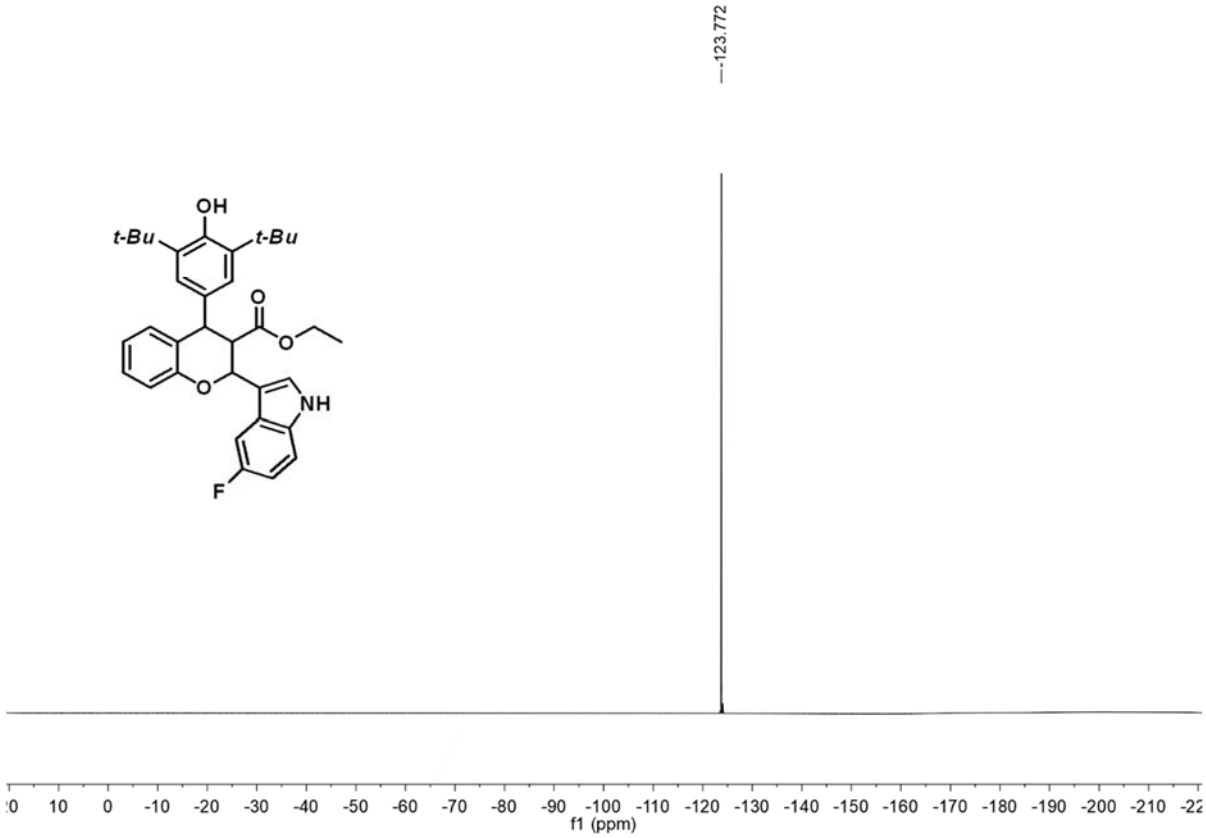
^{13}C NMR Spectrum of Compound **3g**



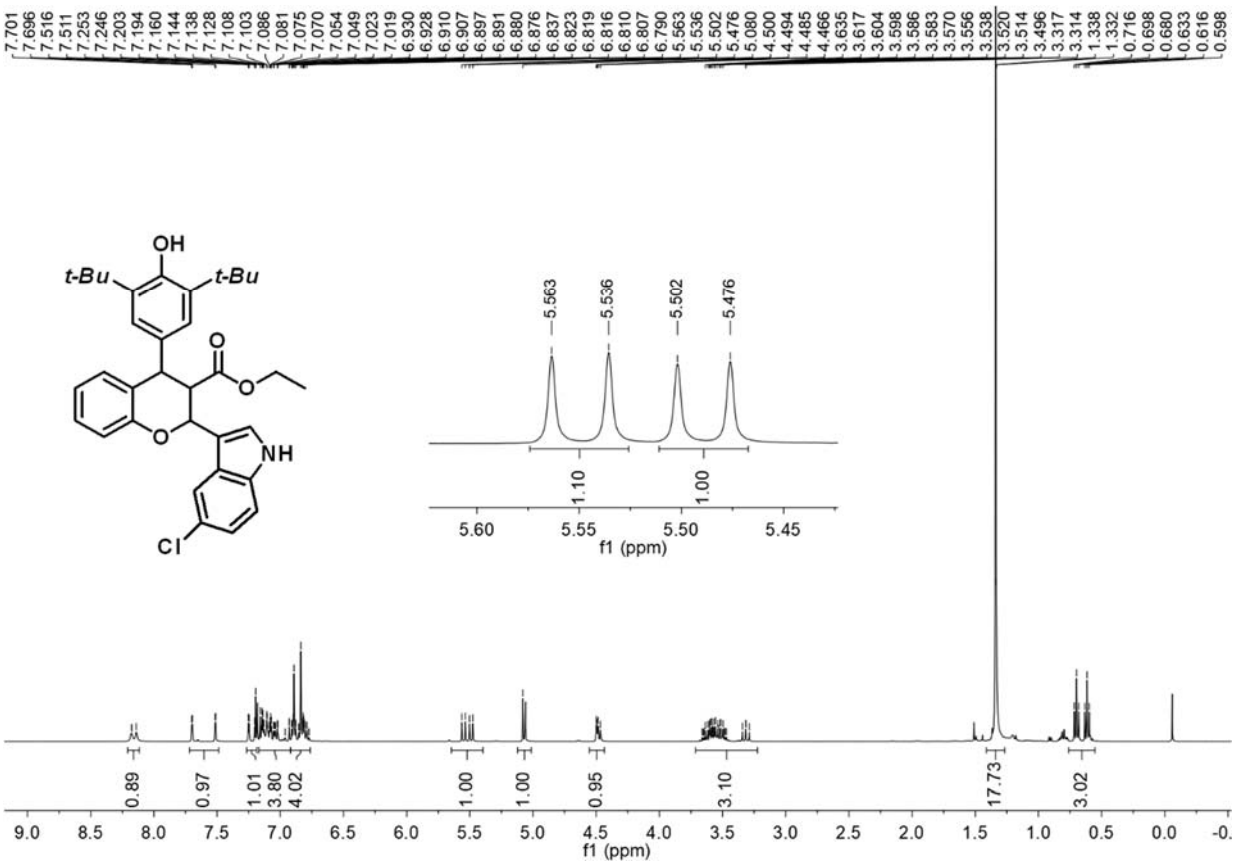
^{1}H NMR Spectrum of Compound **3h**



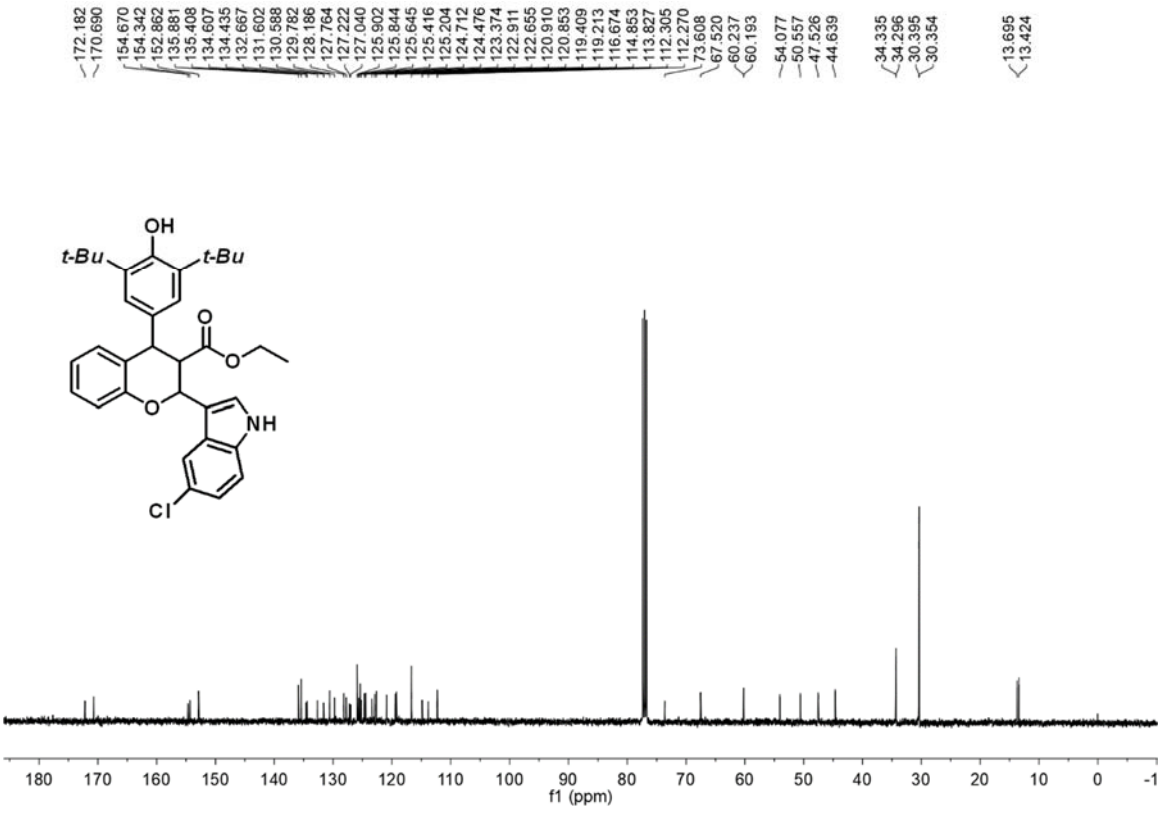
^{13}C NMR Spectrum of Compound **3h**



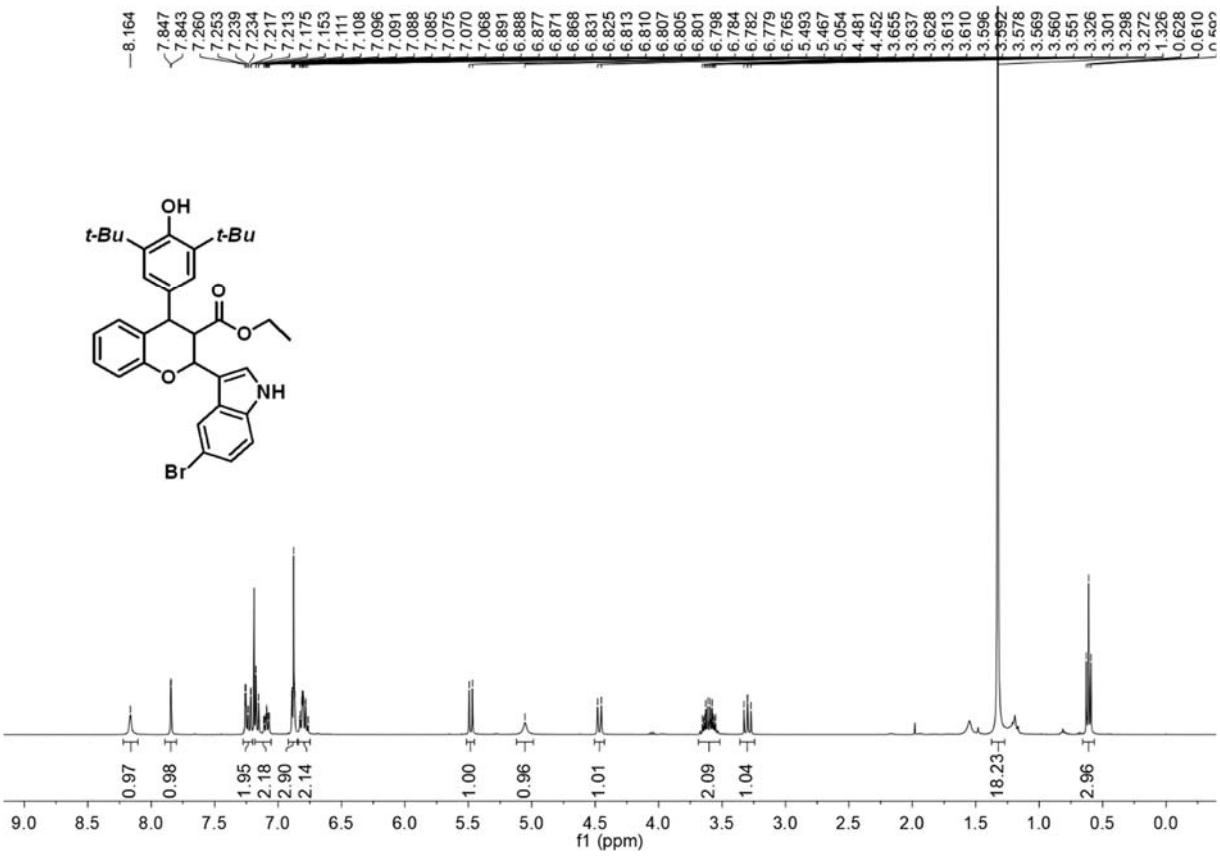
^{19}F NMR Spectrum of Compound **3h**



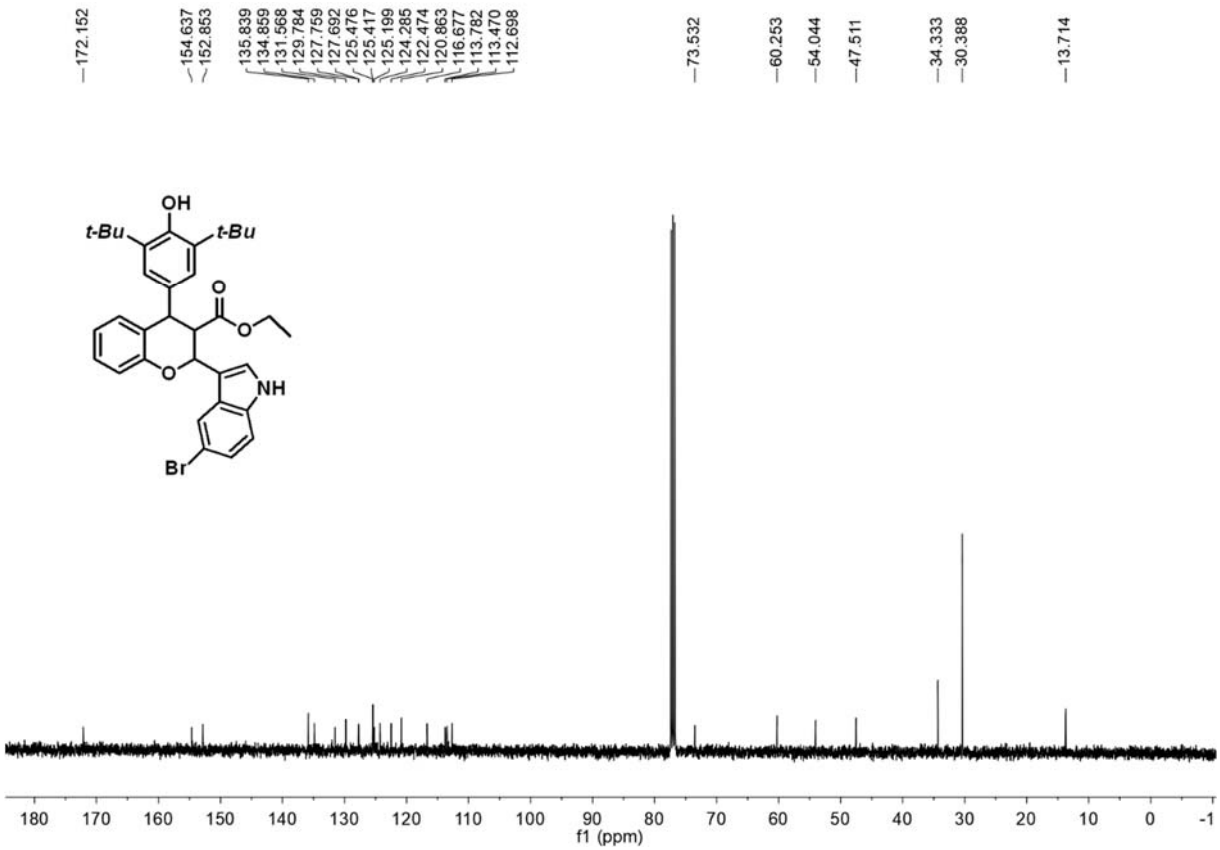
^{1}H NMR Spectrum of Compound **3i**



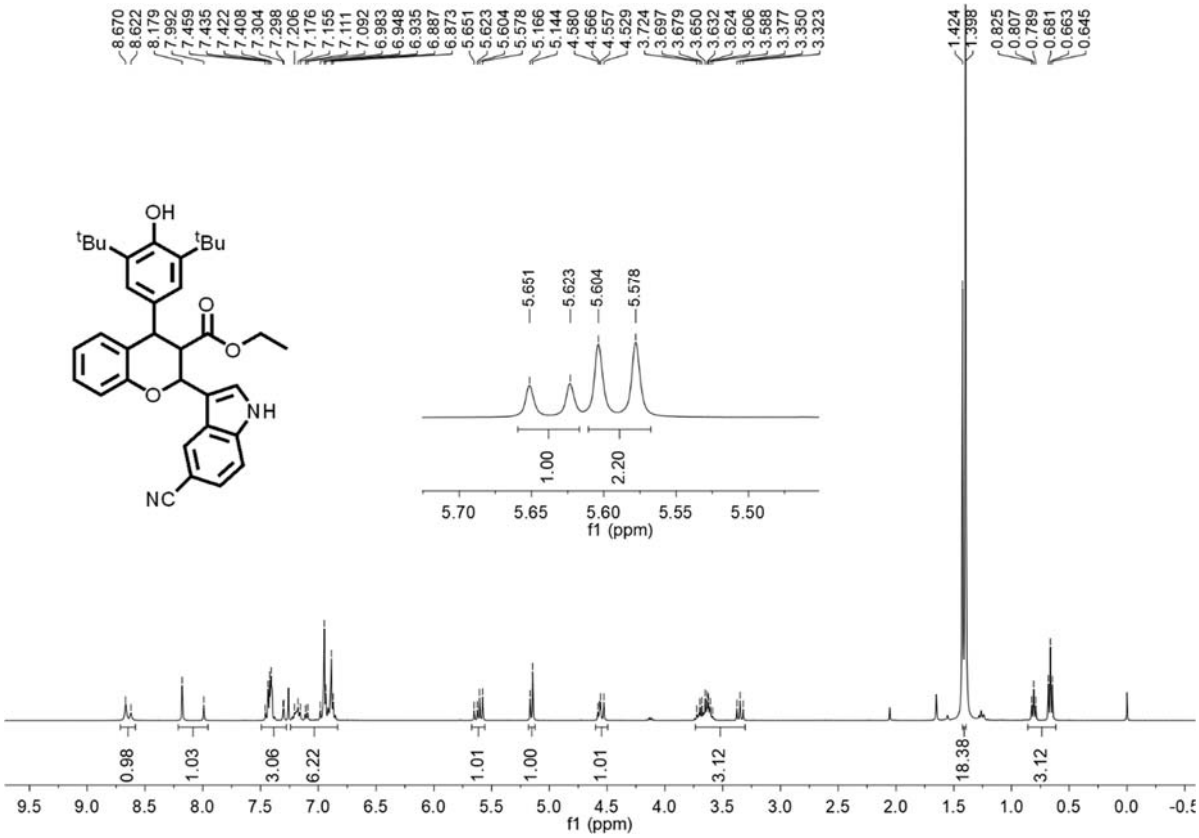
^{13}C NMR Spectrum of Compound **3i**



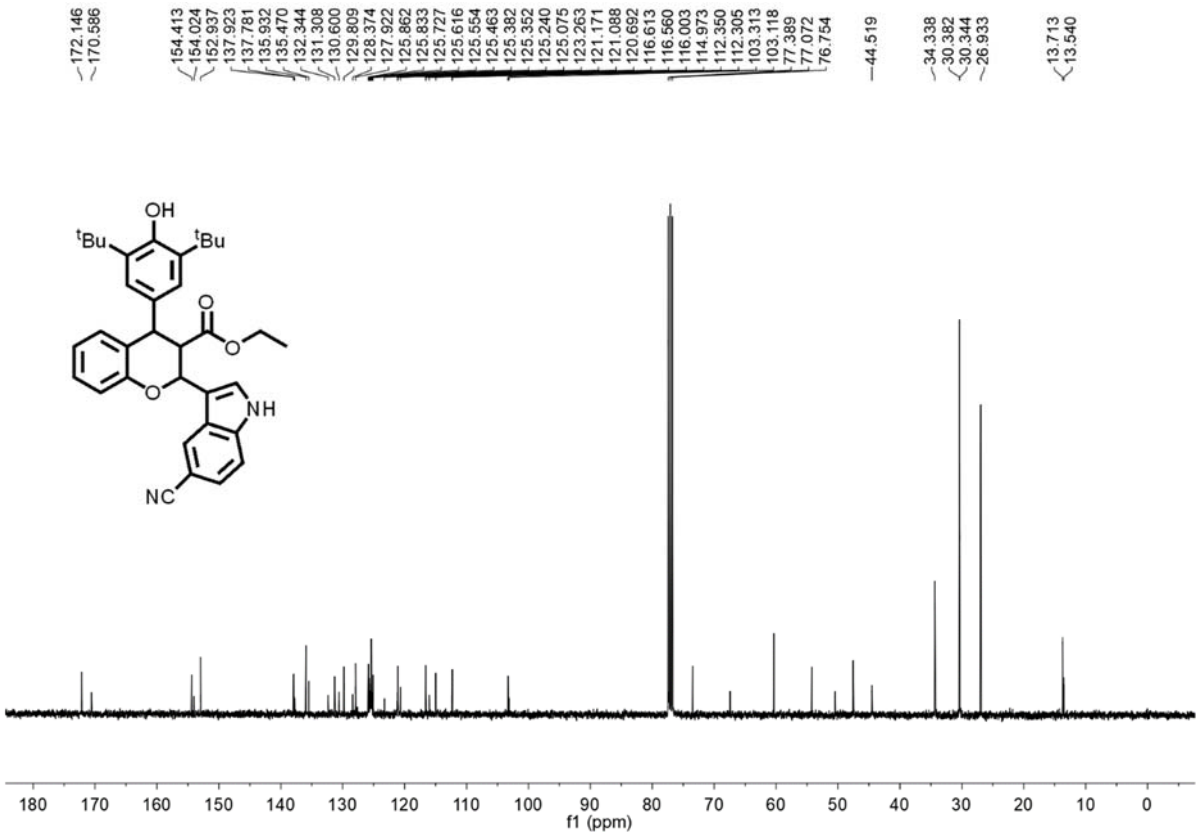
^{1}H NMR Spectrum of Compound **3j**



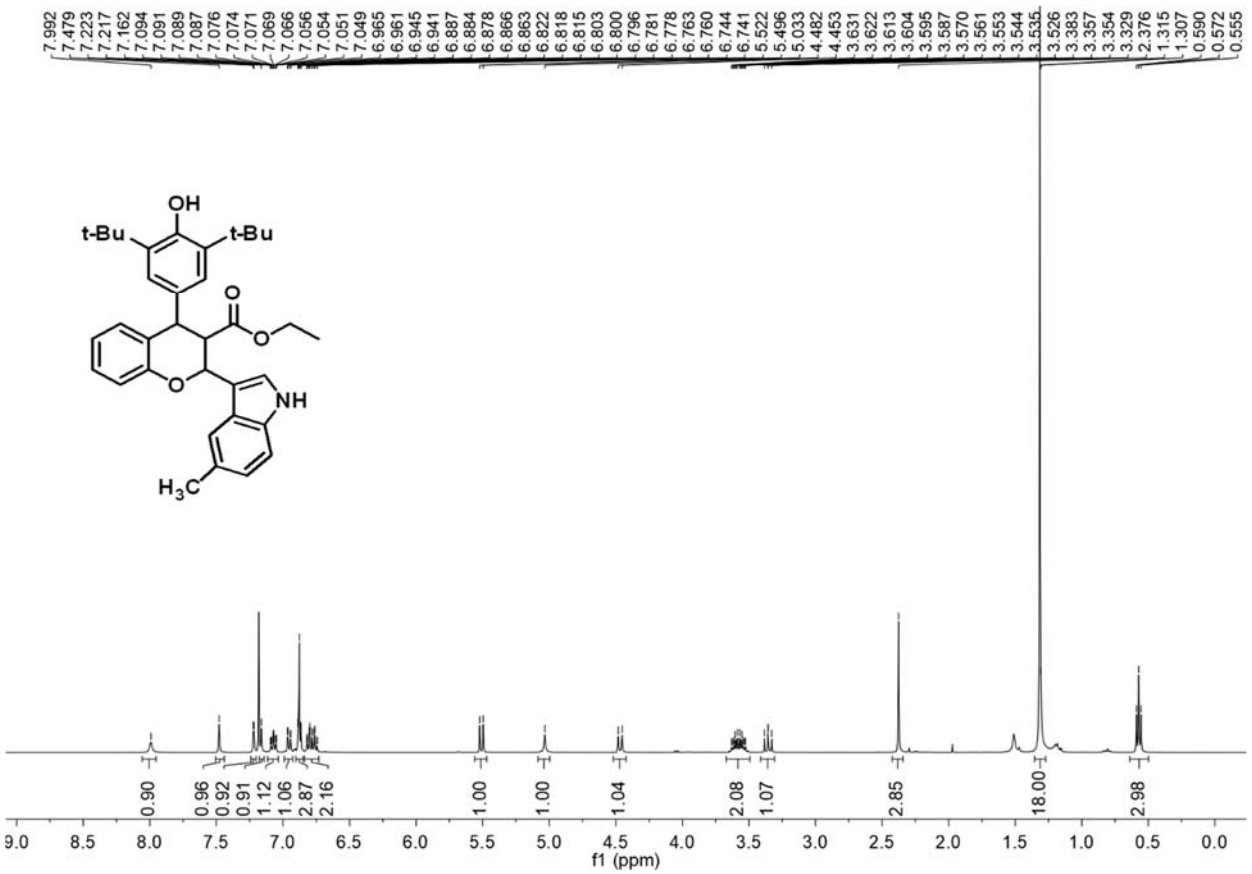
^{13}C NMR Spectrum of Compound **3j**



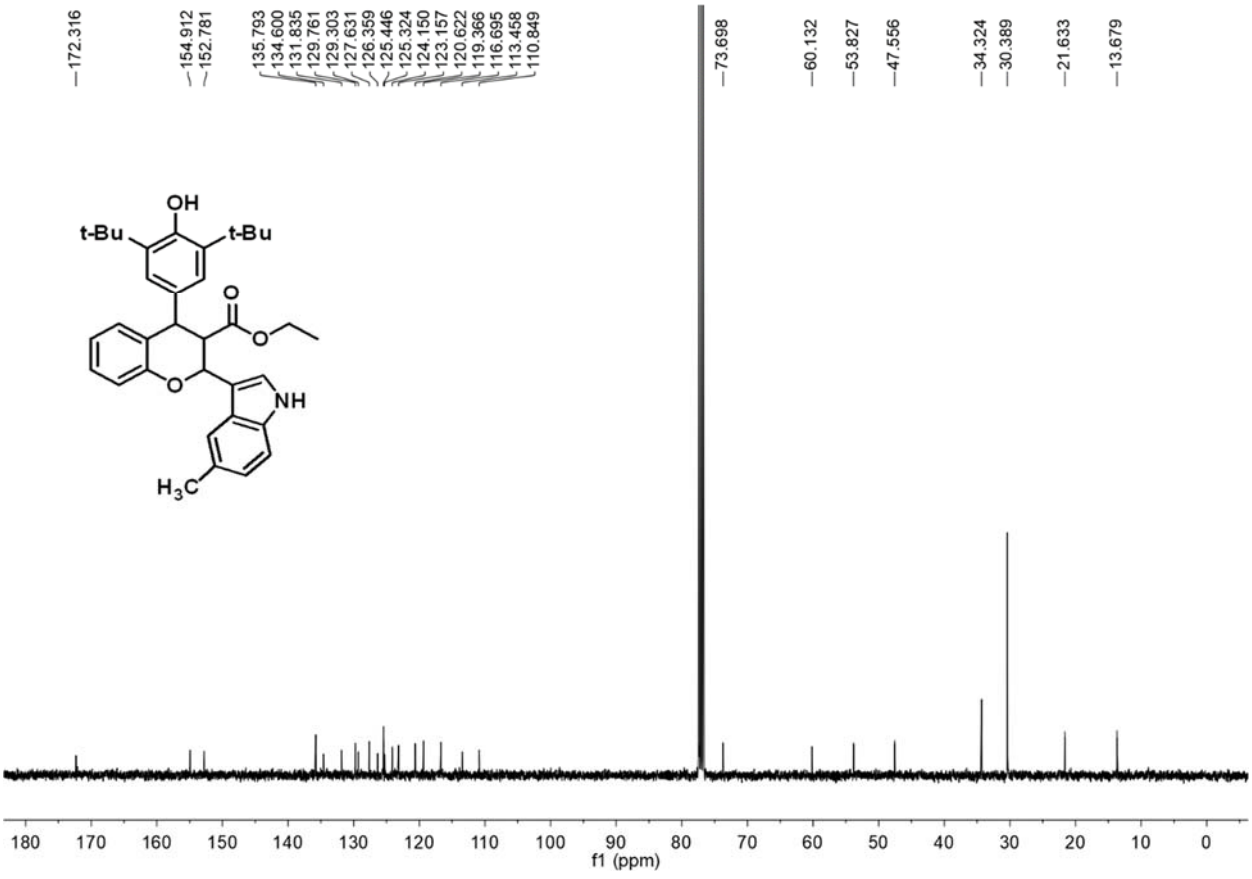
^{1}H NMR Spectrum of Compound **3k**



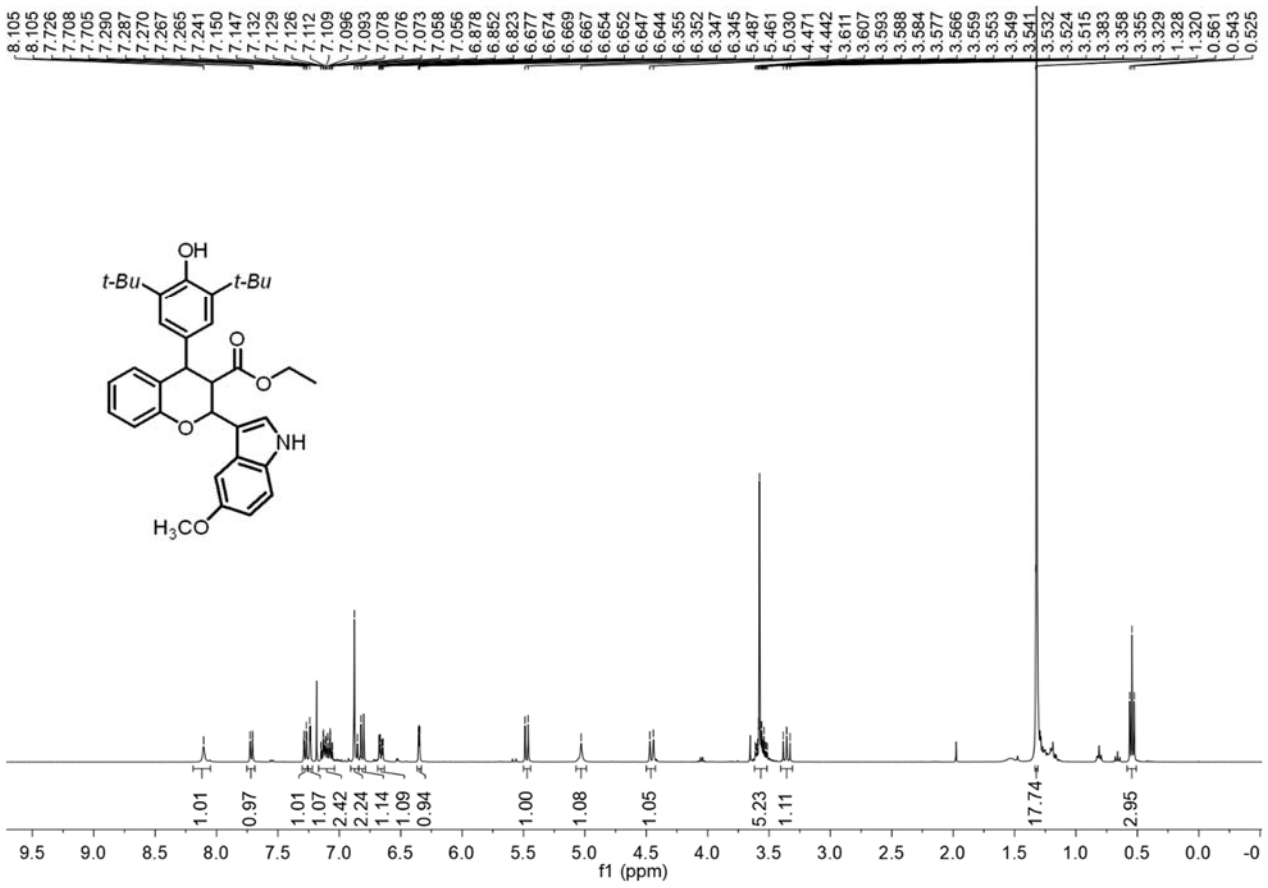
^{13}C NMR Spectrum of Compound **3k**



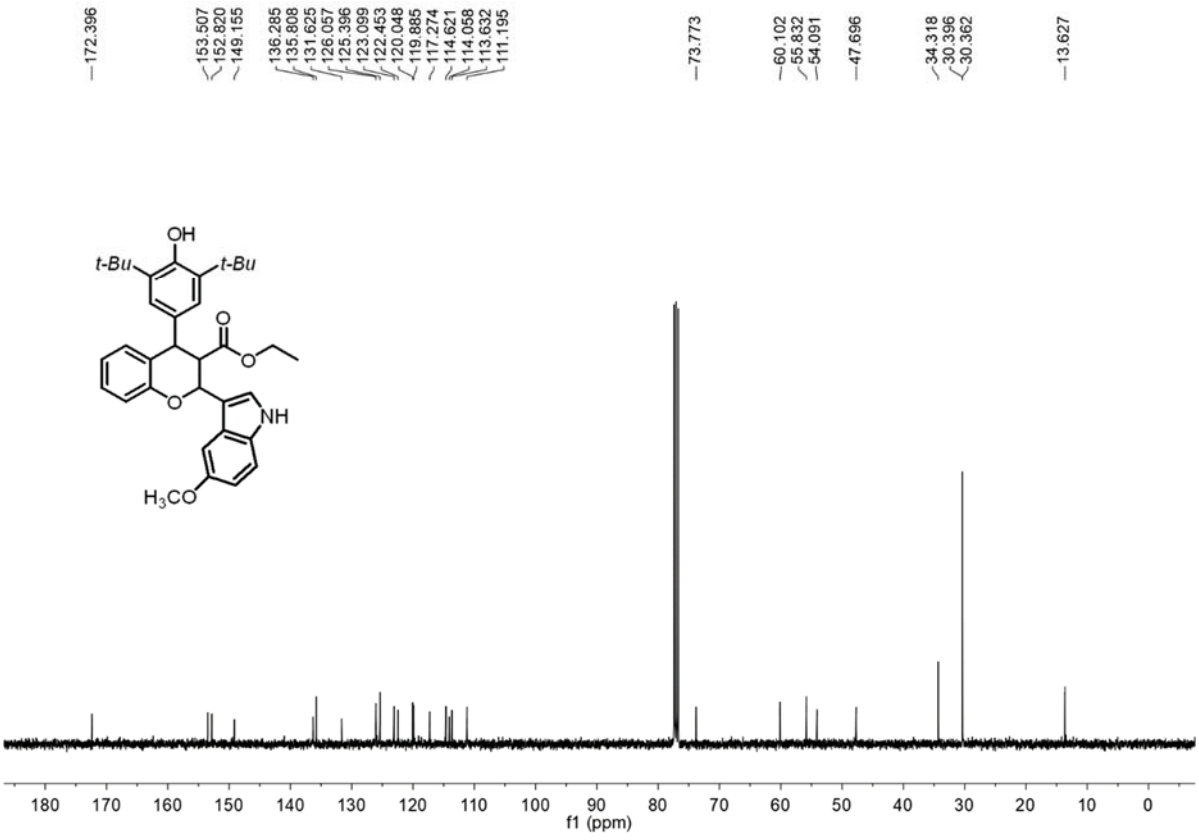
^{1}H NMR Spectrum of Compound **3l**



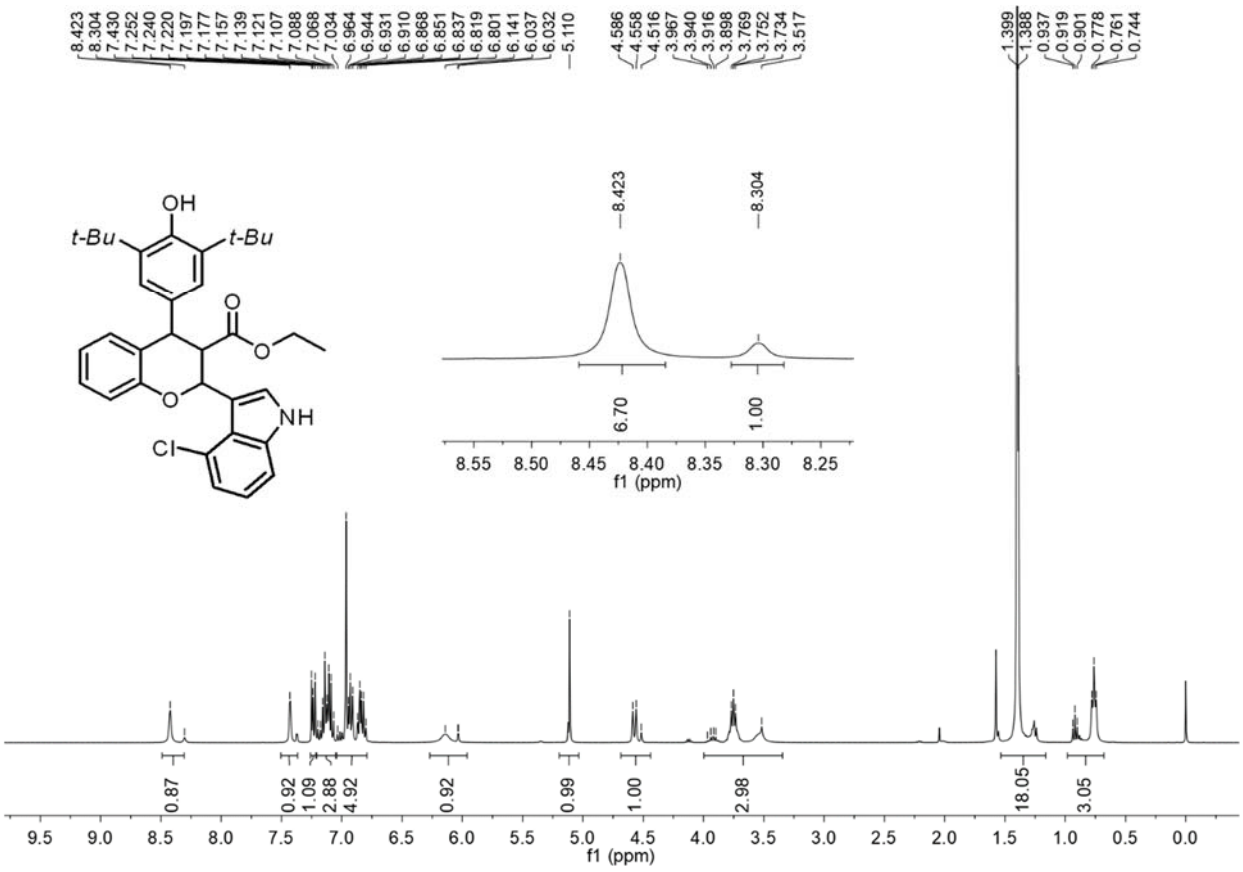
^{13}C NMR Spectrum of Compound **3l**



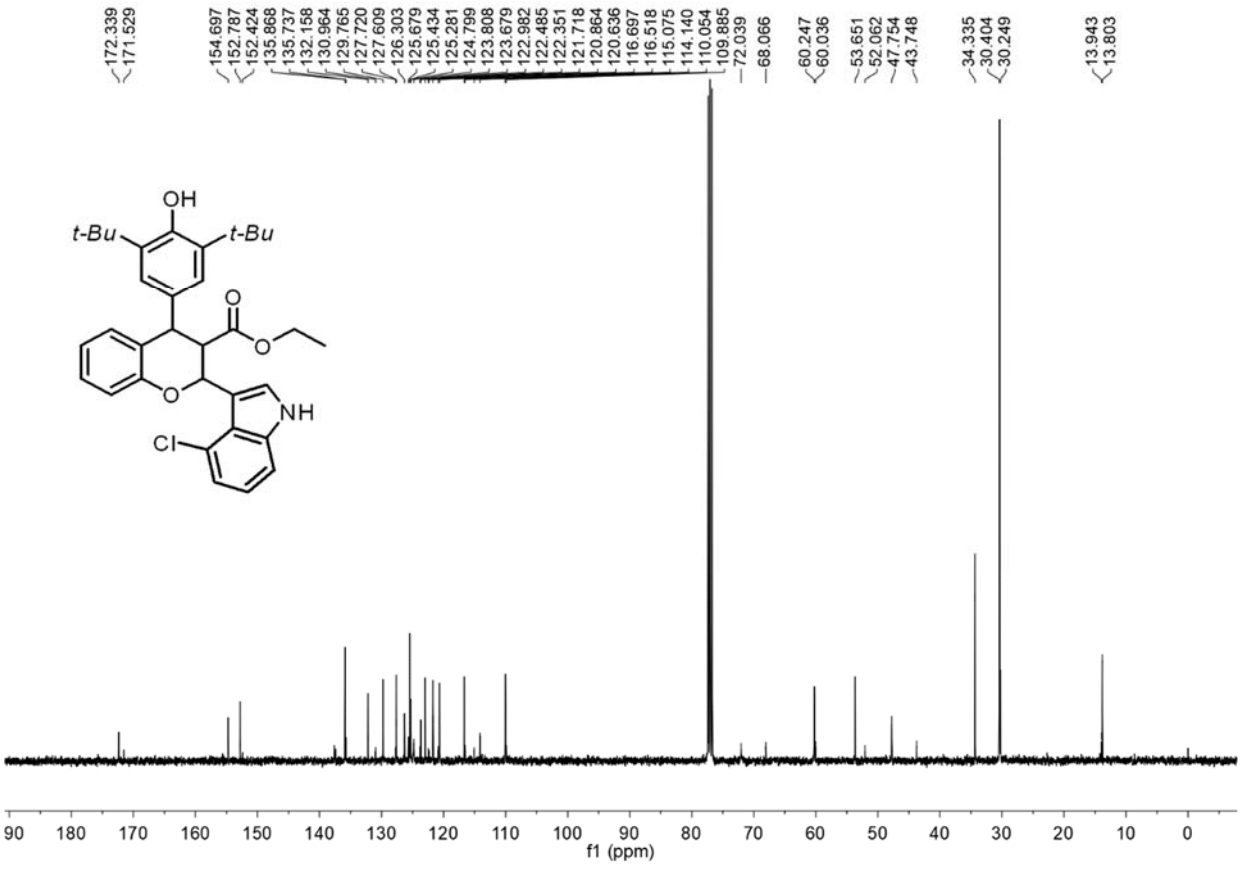
^{1}H NMR Spectrum of Compound **3m**



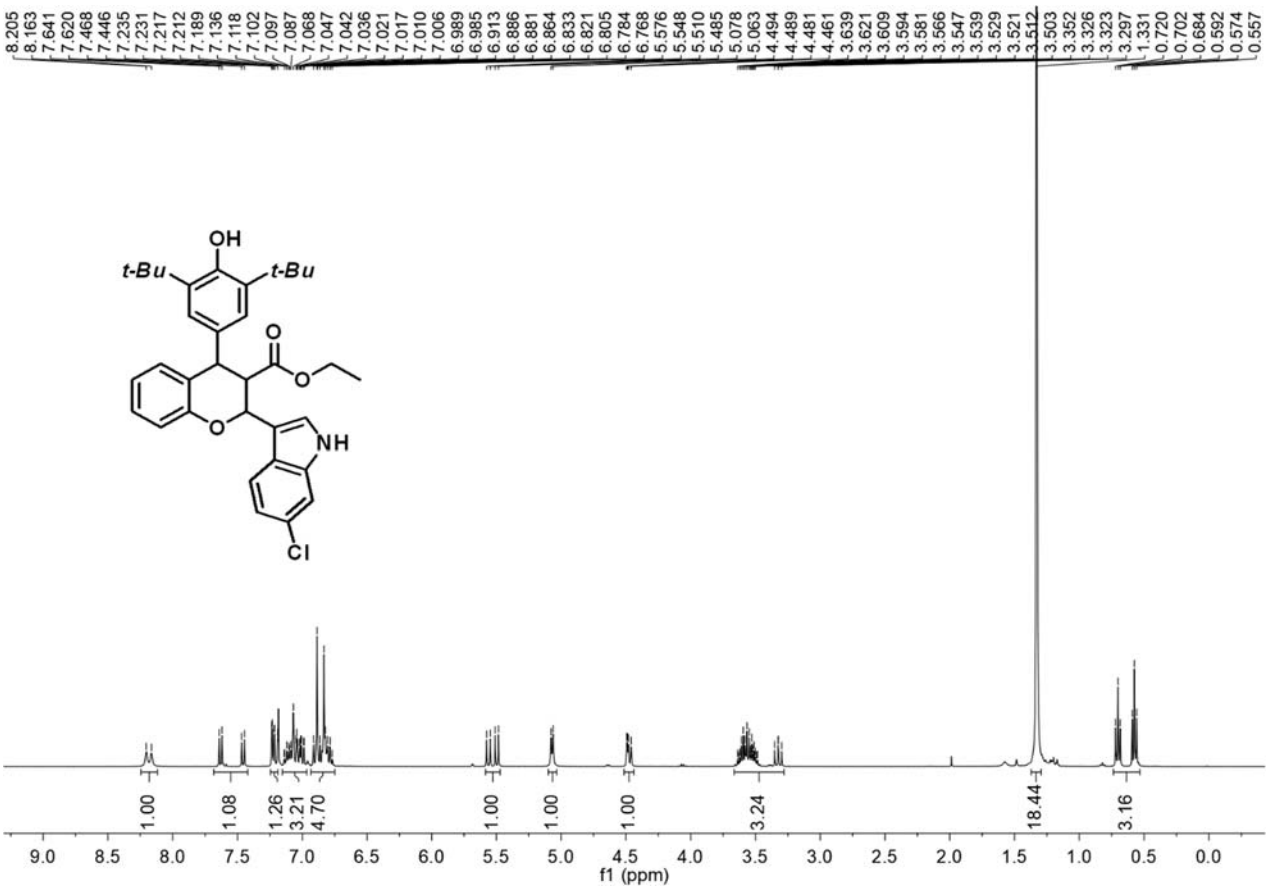
^{13}C NMR Spectrum of Compound **3m**



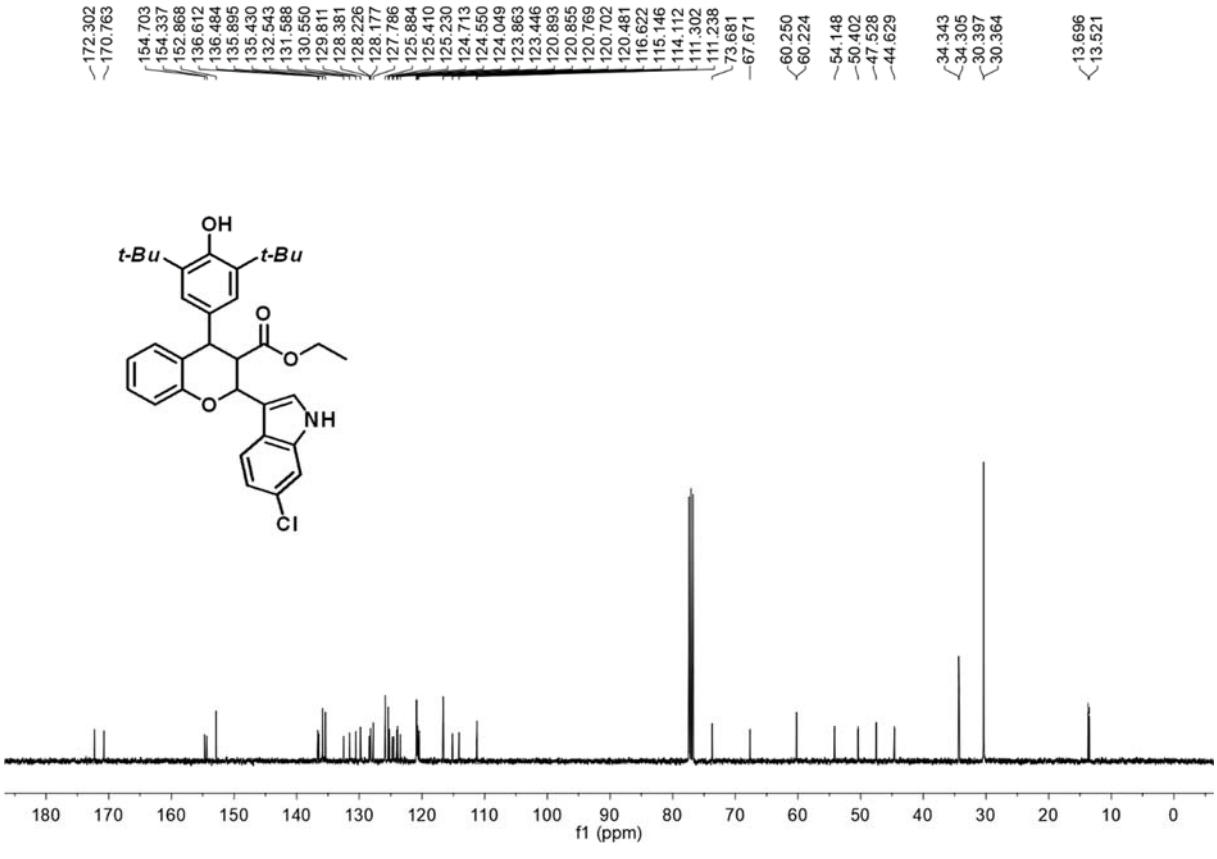
^{1}H NMR Spectrum of Compound **3n**



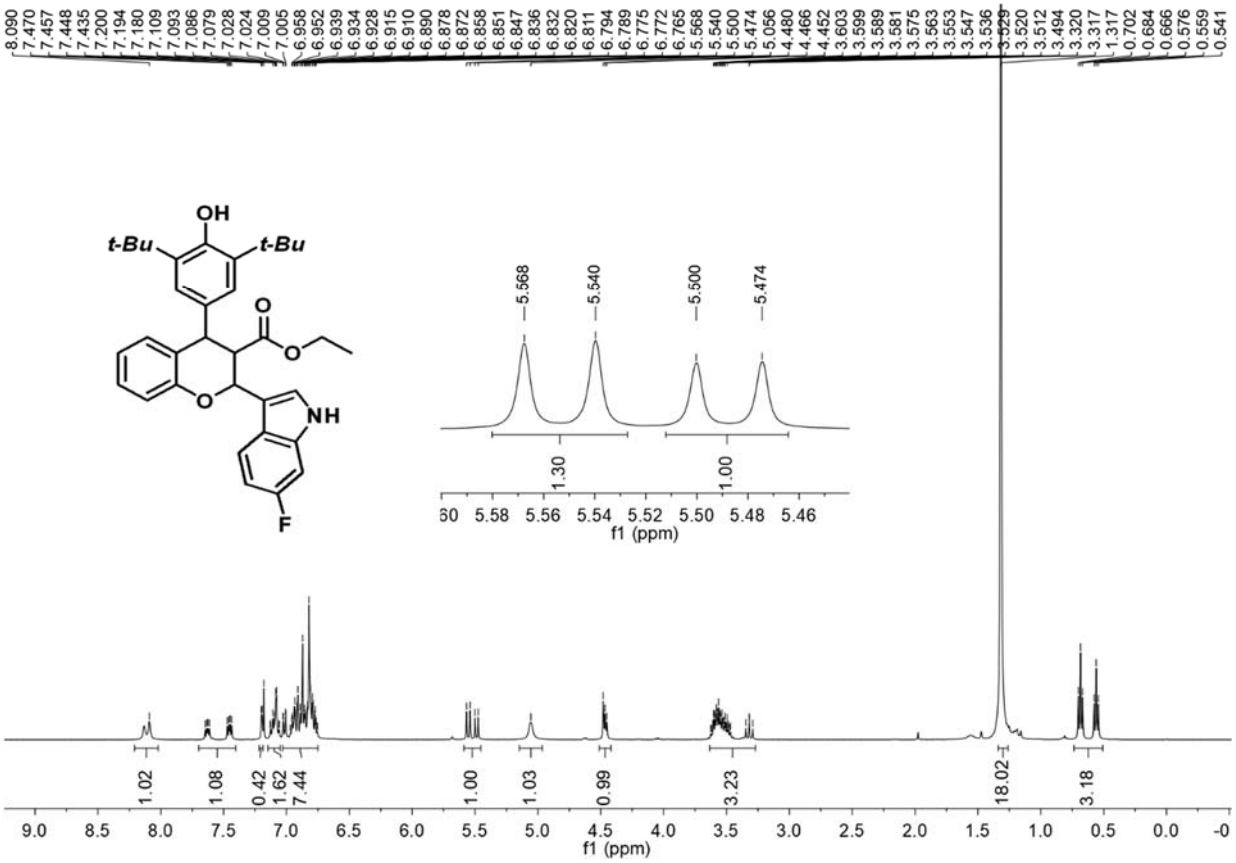
^{13}C NMR Spectrum of Compound **3n**



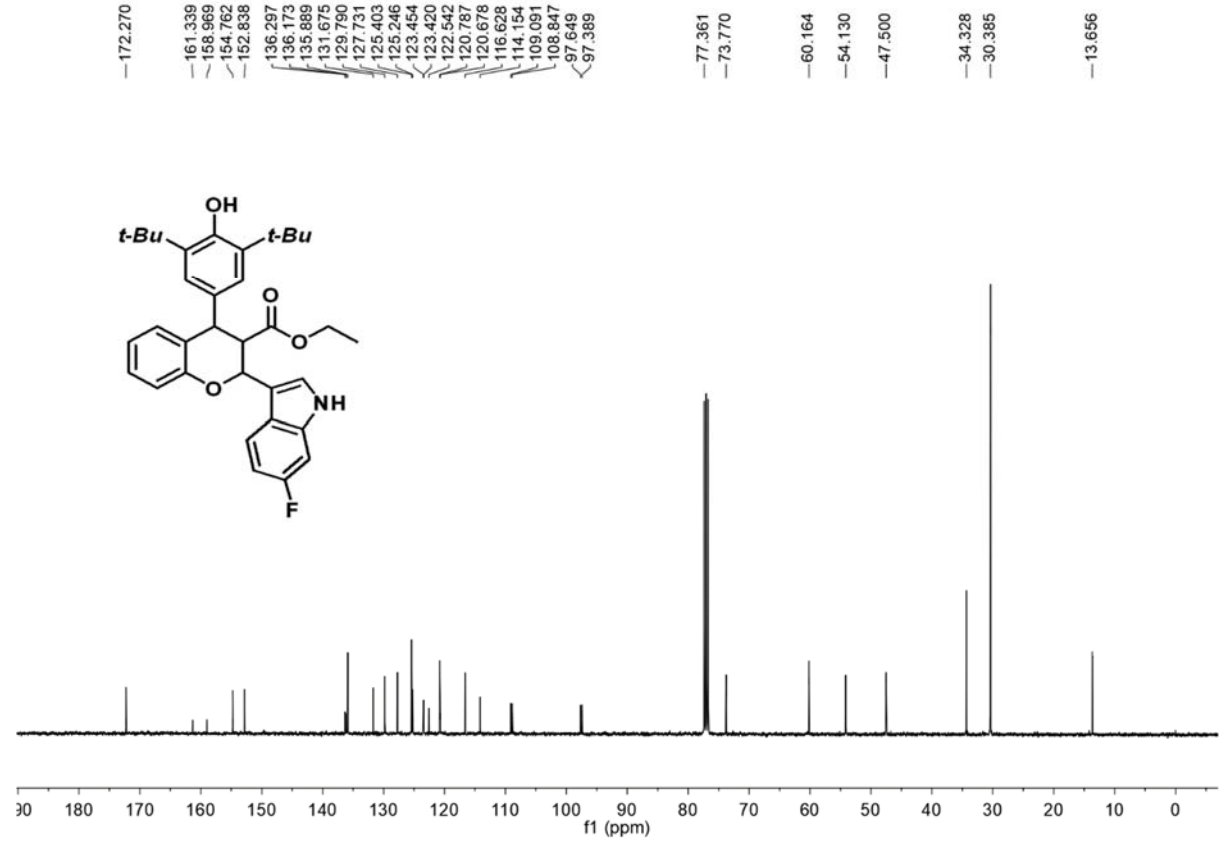
^{1}H NMR Spectrum of Compound **3o**



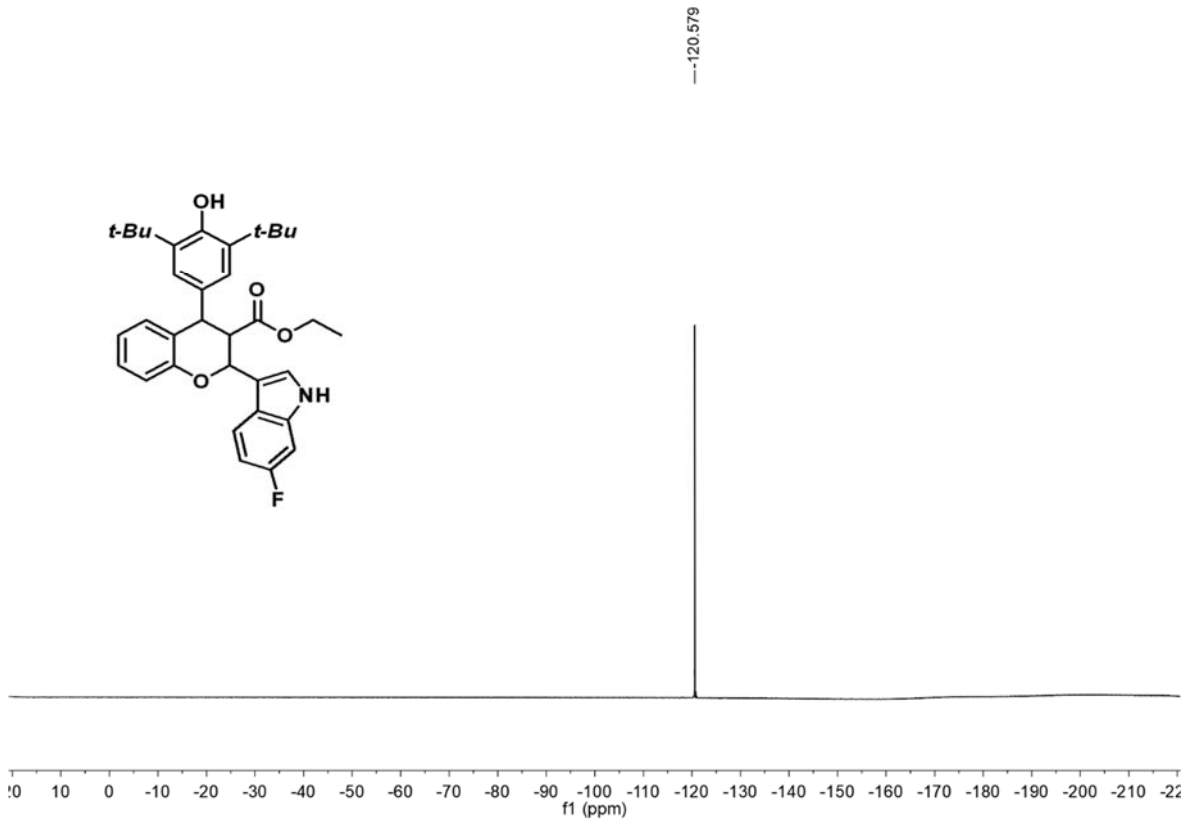
^{13}C NMR Spectrum of Compound **3o**



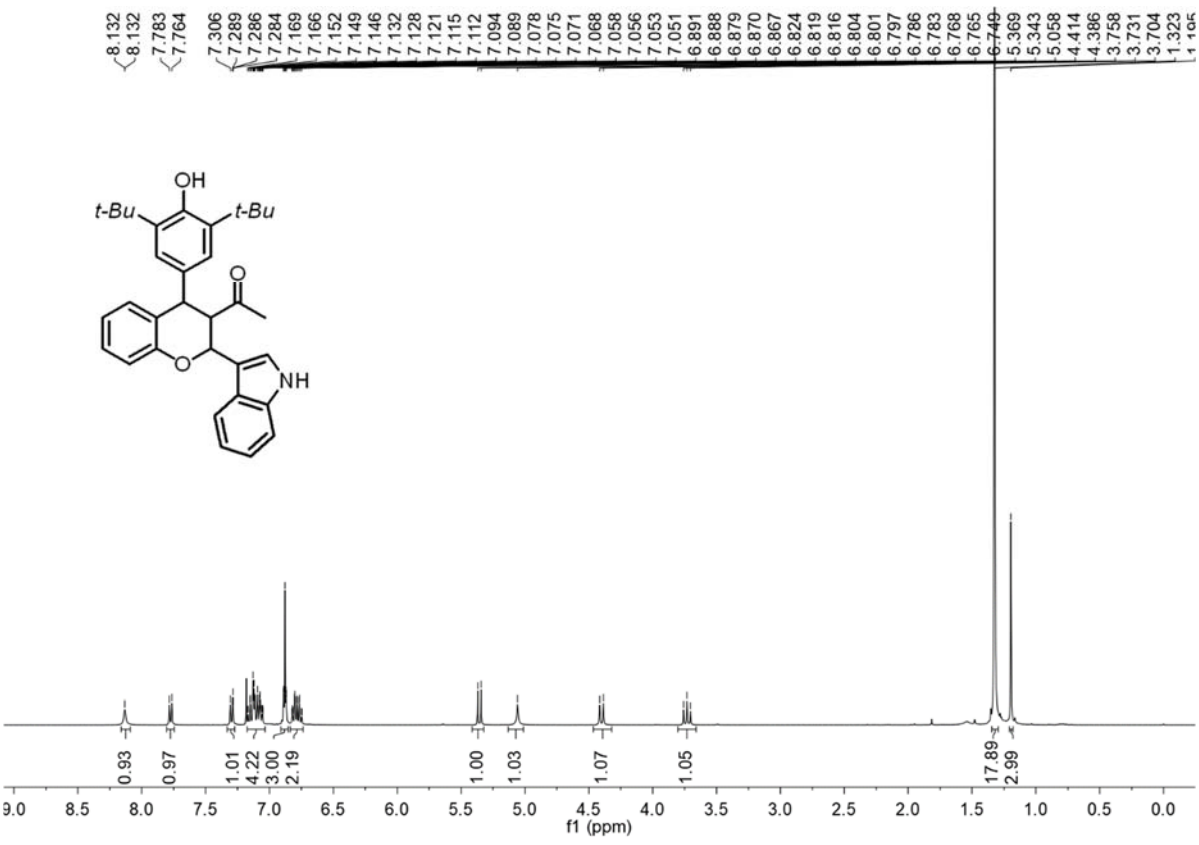
^{1}H NMR Spectrum of Compound **3p**



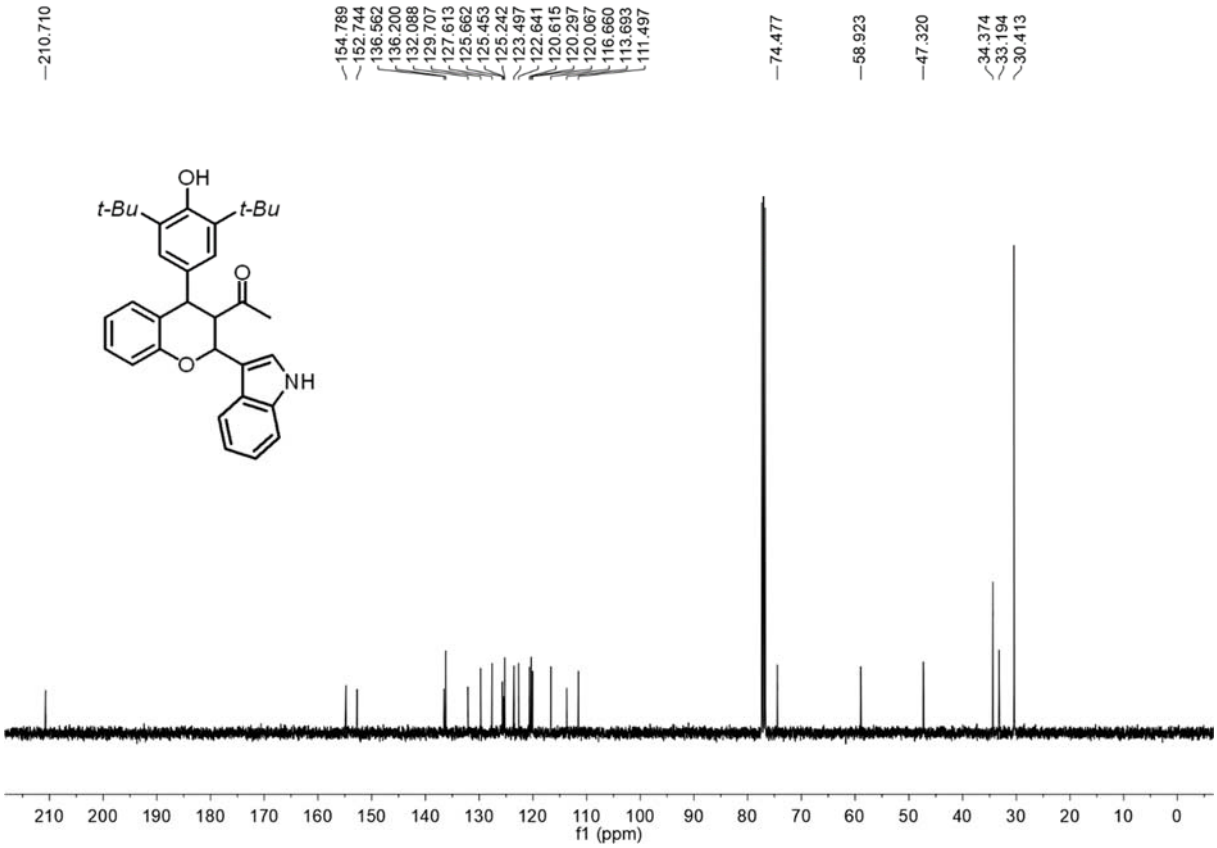
^{13}C NMR Spectrum of Compound **3p**



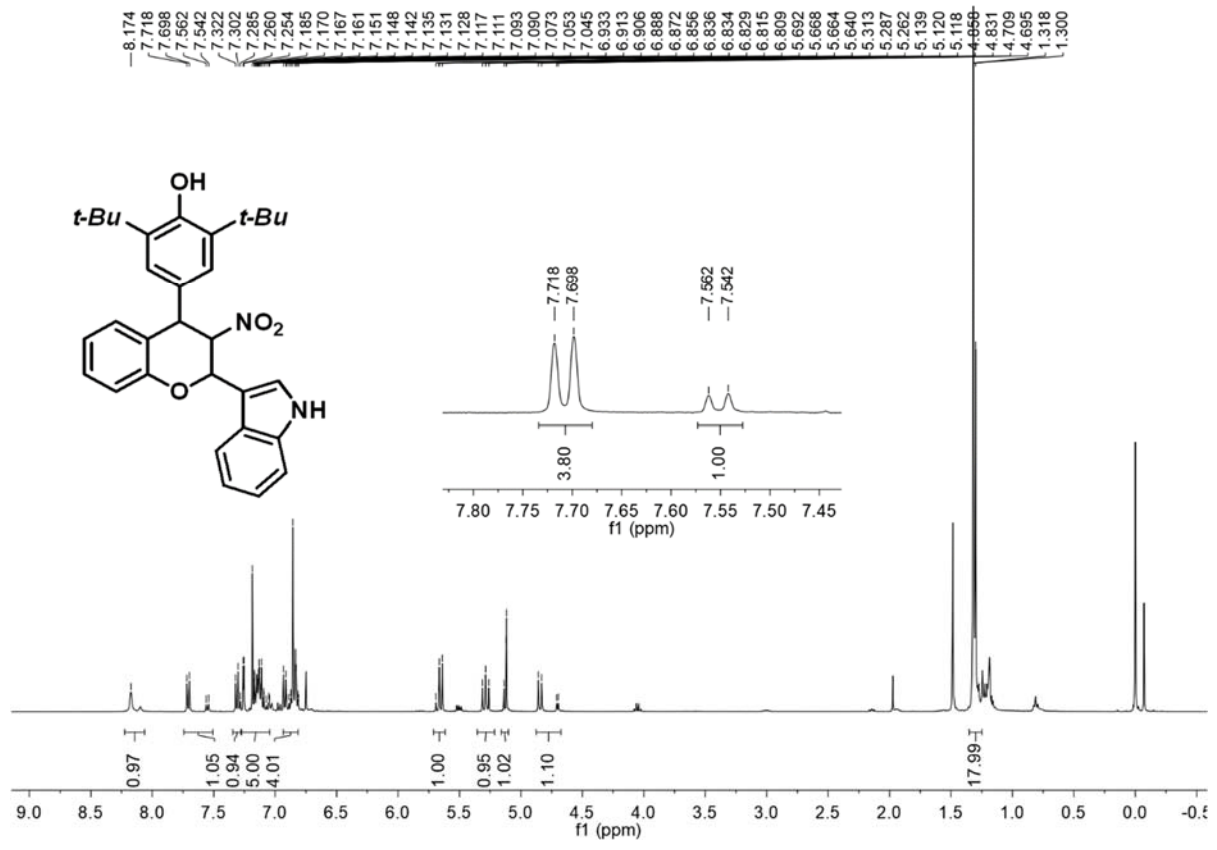
^{19}F NMR Spectrum of Compound **3p**



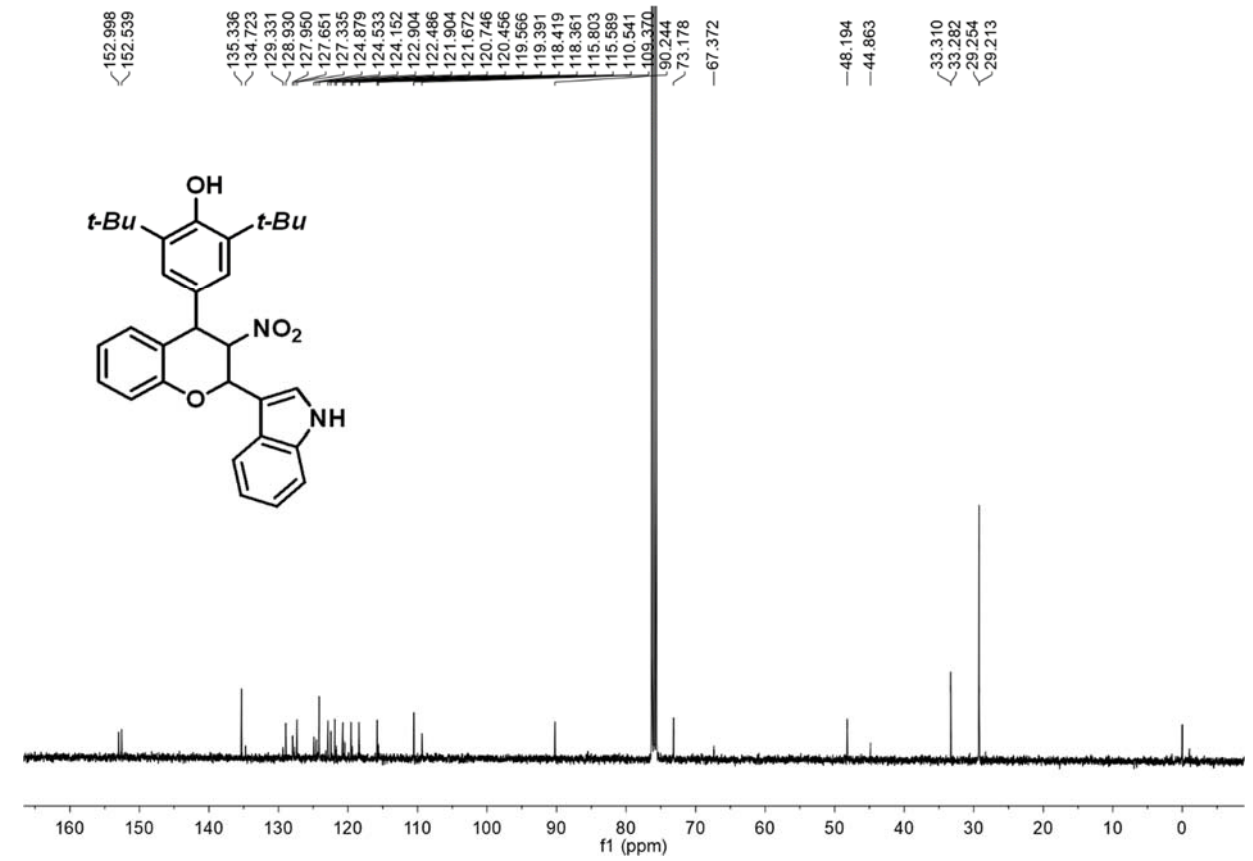
^{1}H NMR Spectrum of Compound **3q**



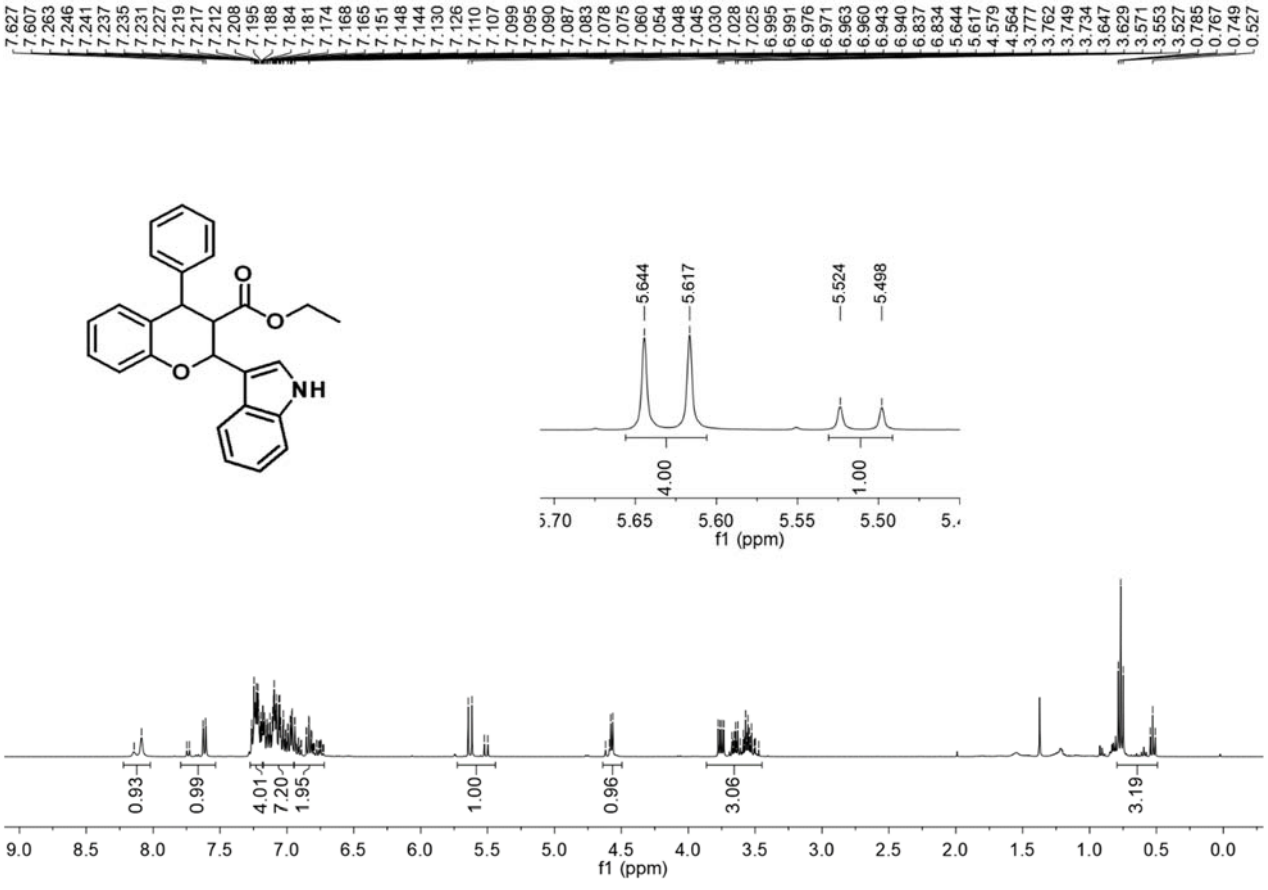
^{13}C NMR Spectrum of Compound **3q**



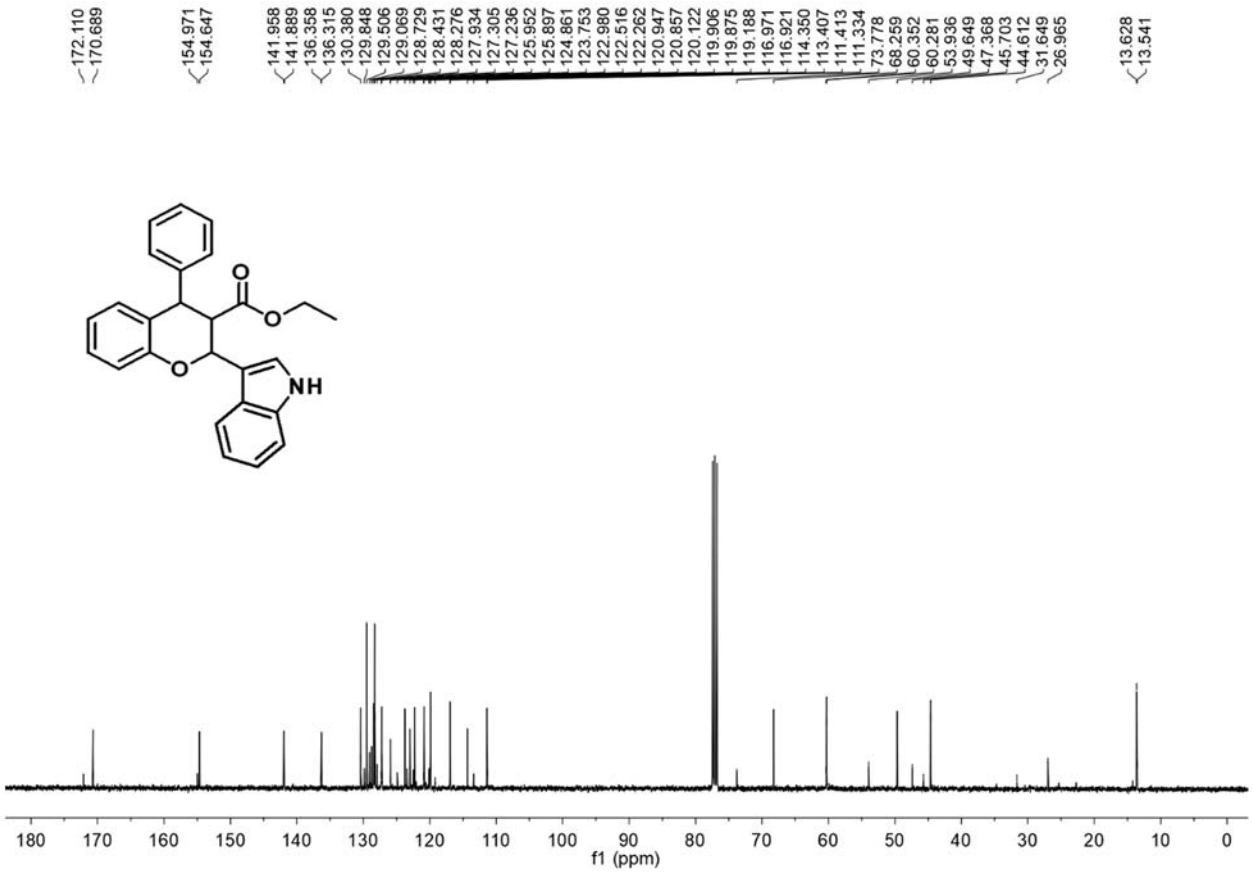
^{1}H NMR Spectrum of Compound **3r**



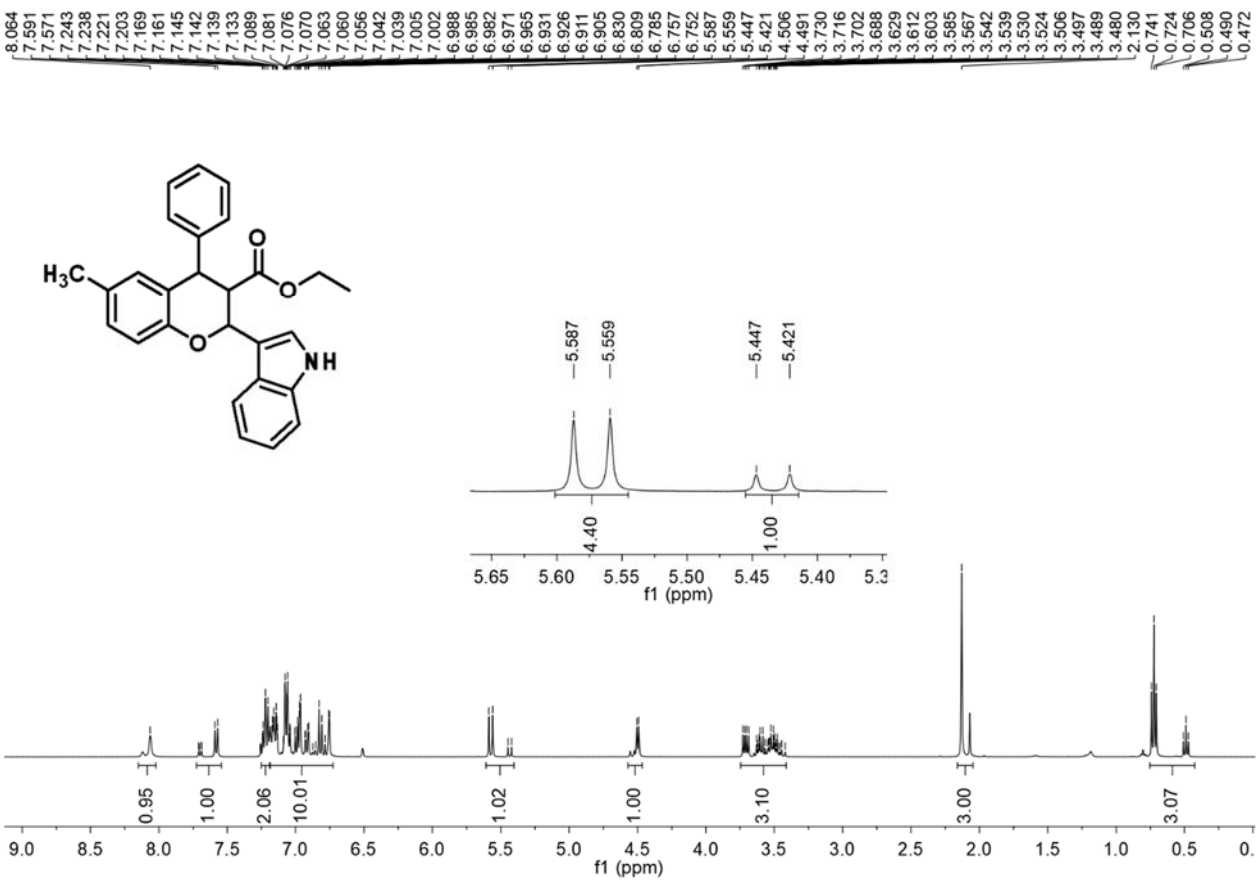
^{13}C NMR Spectrum of Compound **3r**



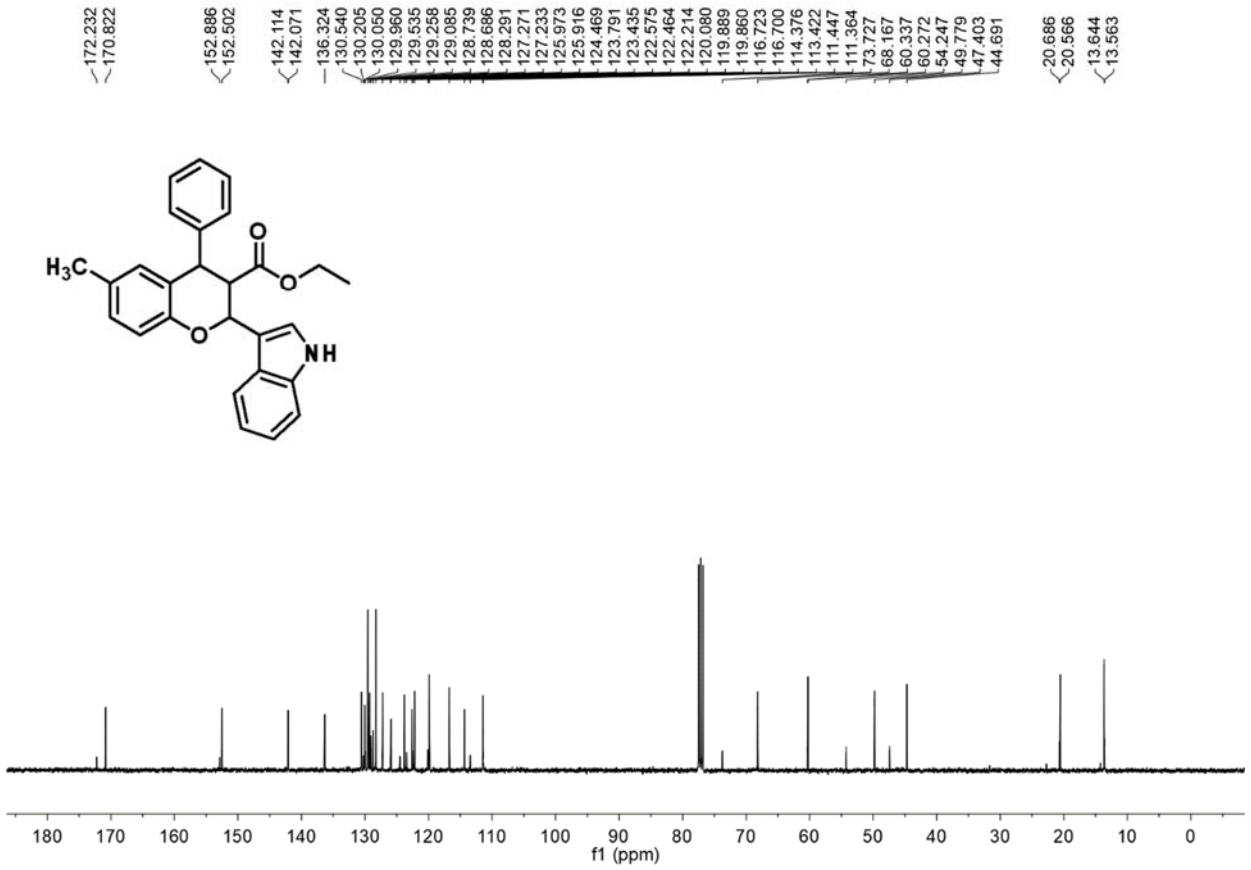
^{1}H NMR Spectrum of Compound **5a**



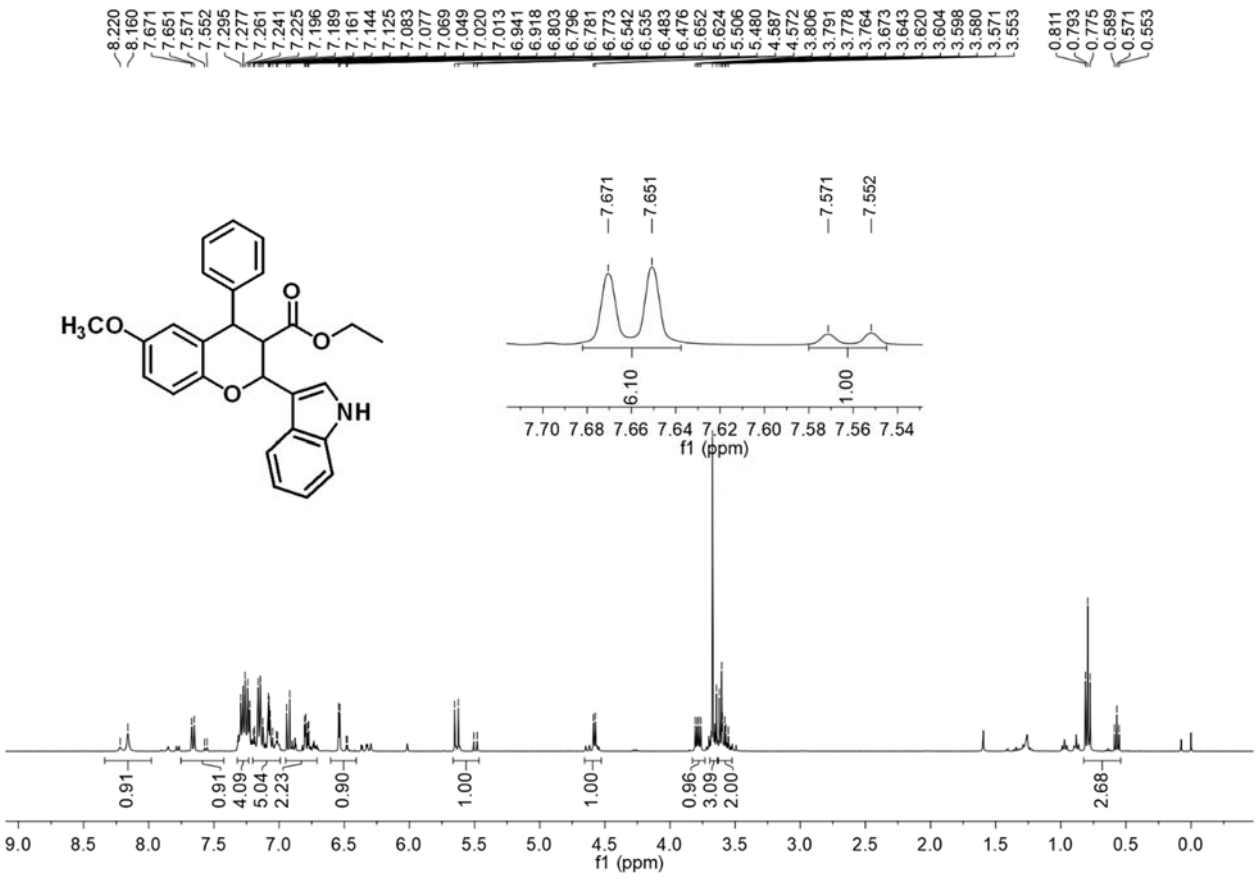
^{13}C NMR Spectrum of Compound **5a**



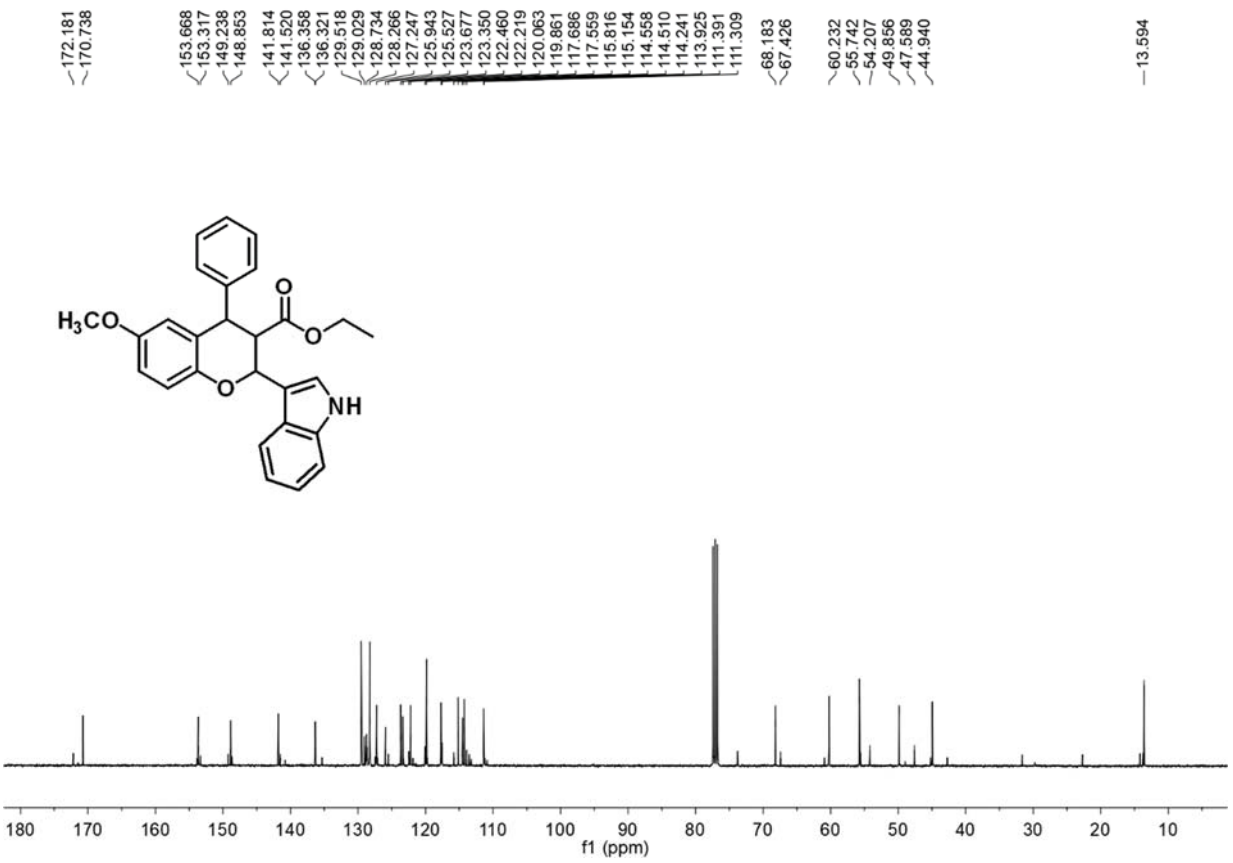
^{1}H NMR Spectrum of Compound **5b**



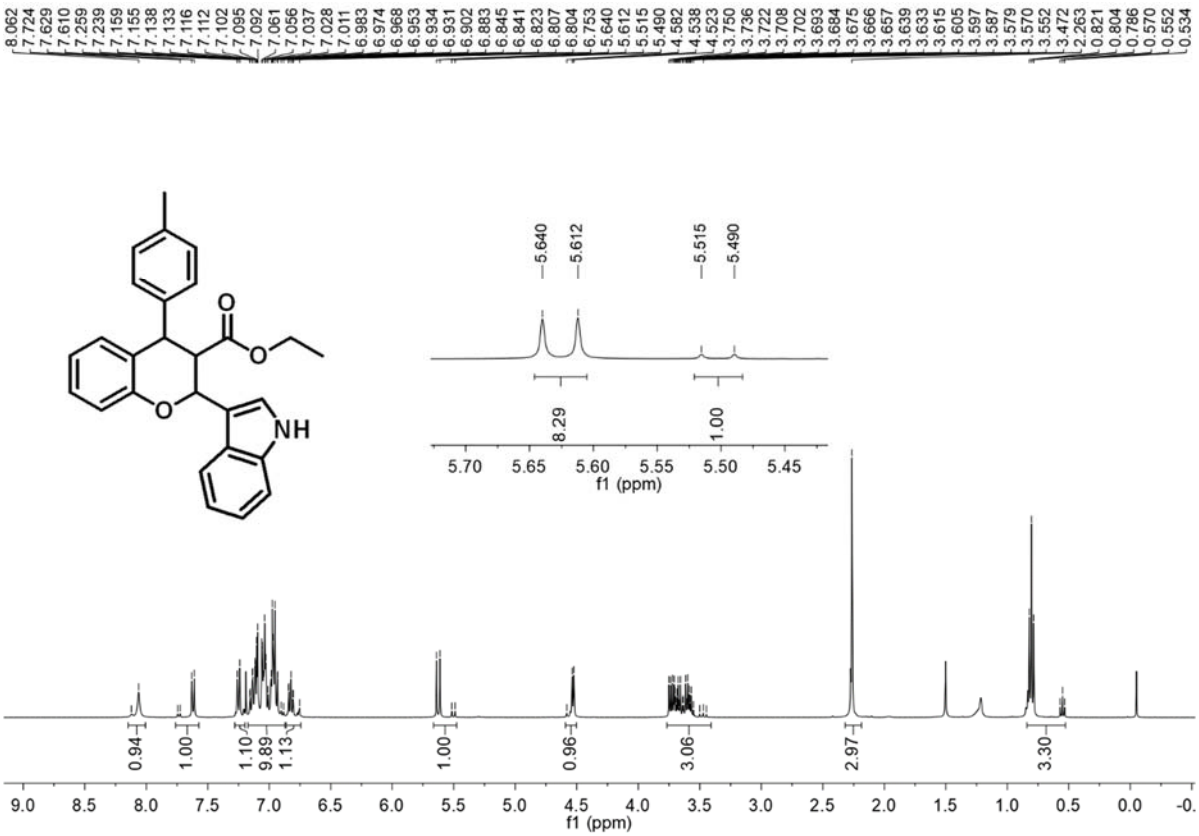
^{13}C NMR Spectrum of Compound **5b**



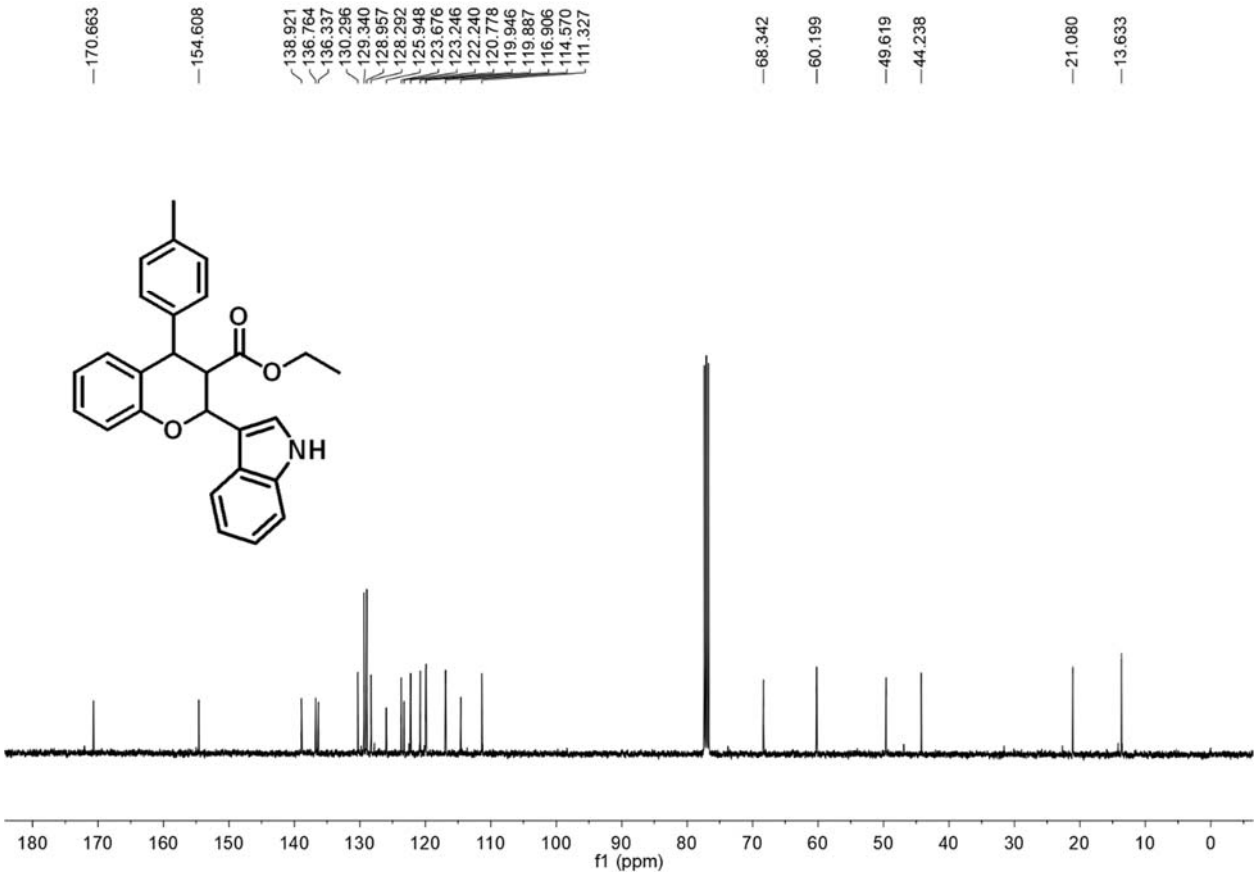
^{1}H NMR Spectrum of Compound **5c**



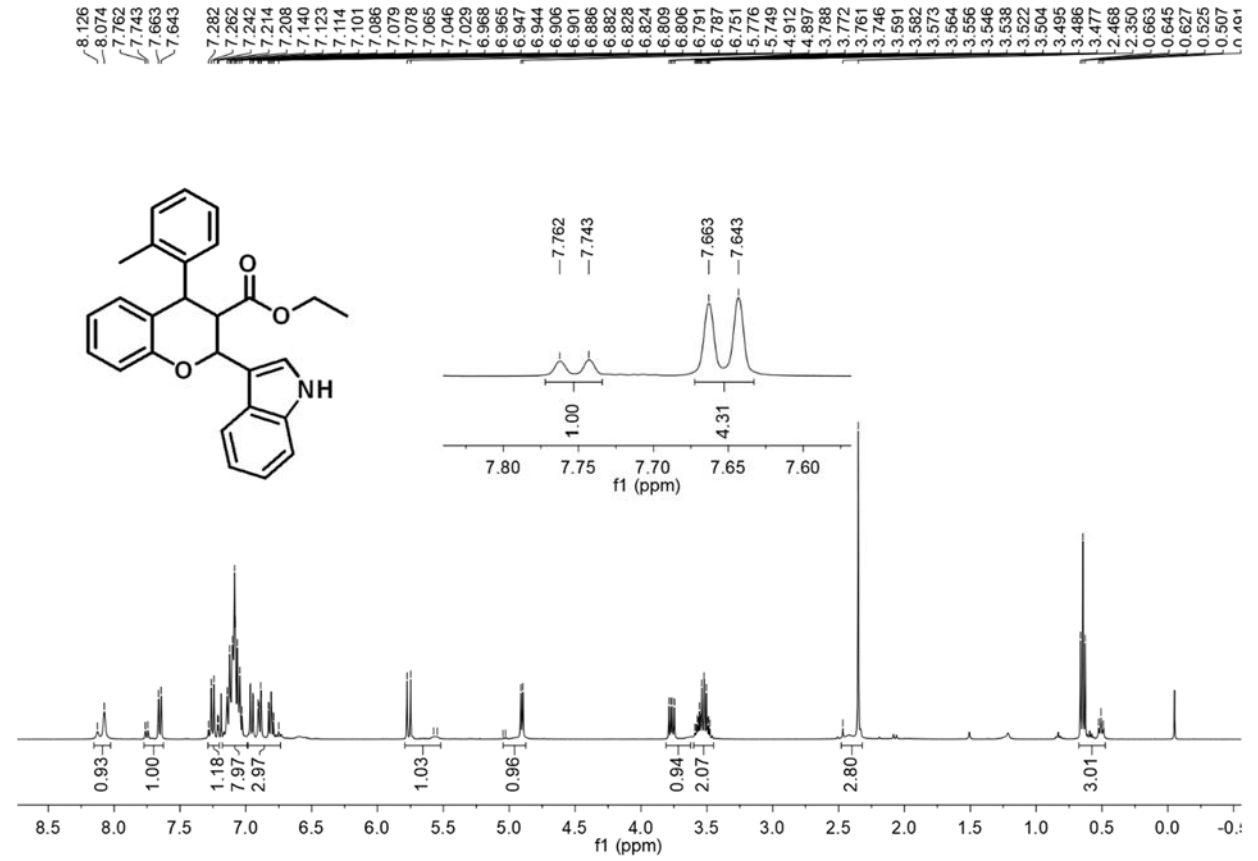
^{13}C NMR Spectrum of Compound **5c**



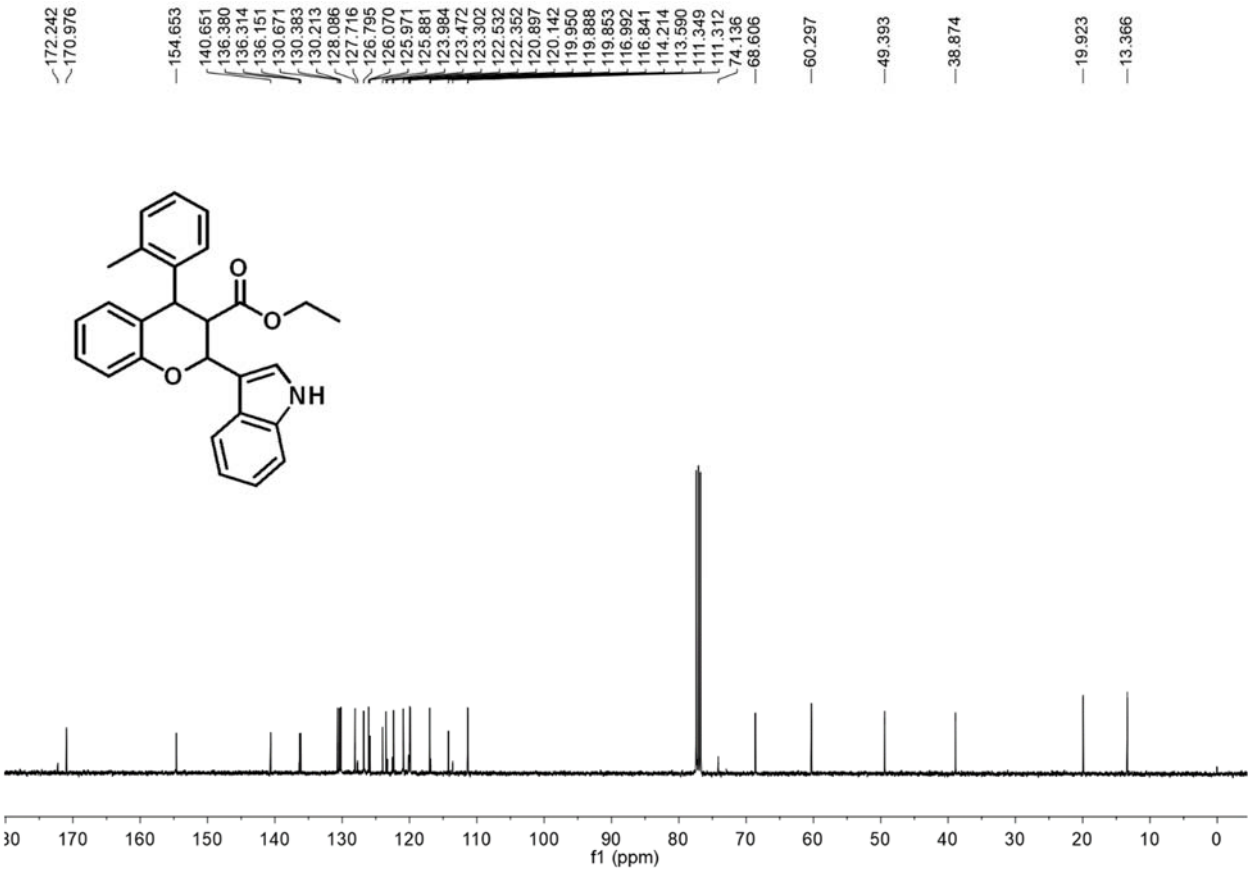
^{1}H NMR Spectrum of Compound **5d**



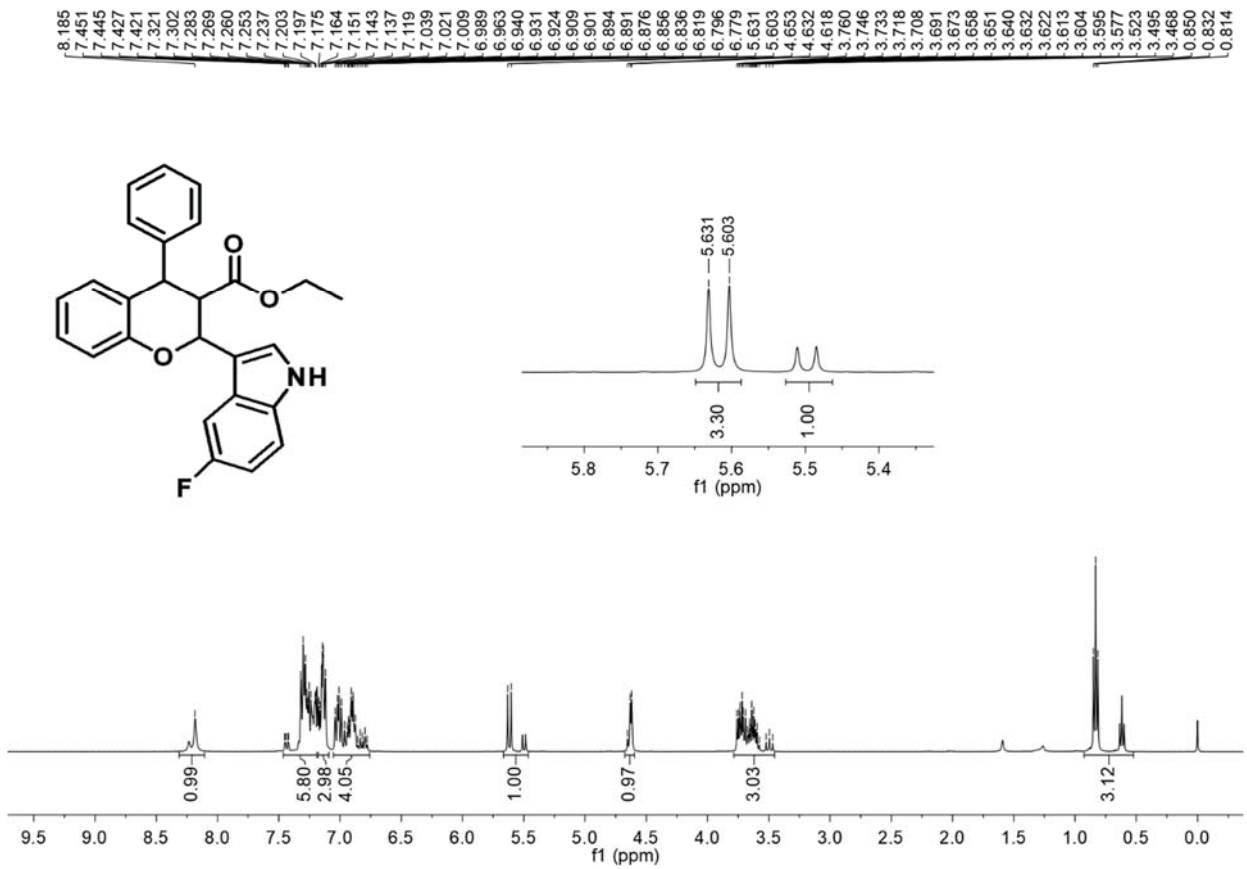
^{13}C NMR Spectrum of Compound **5d**



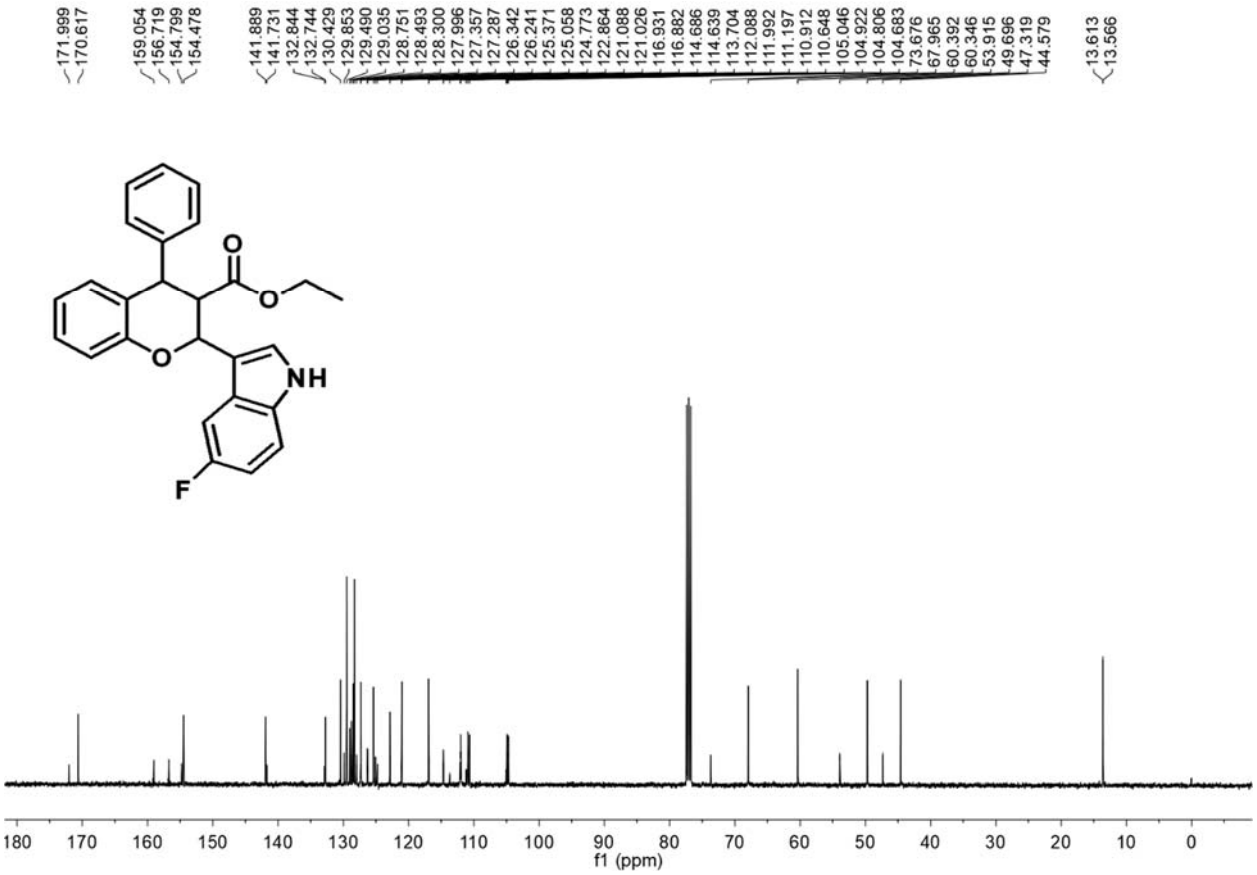
^{1}H NMR Spectrum of Compound **5e**



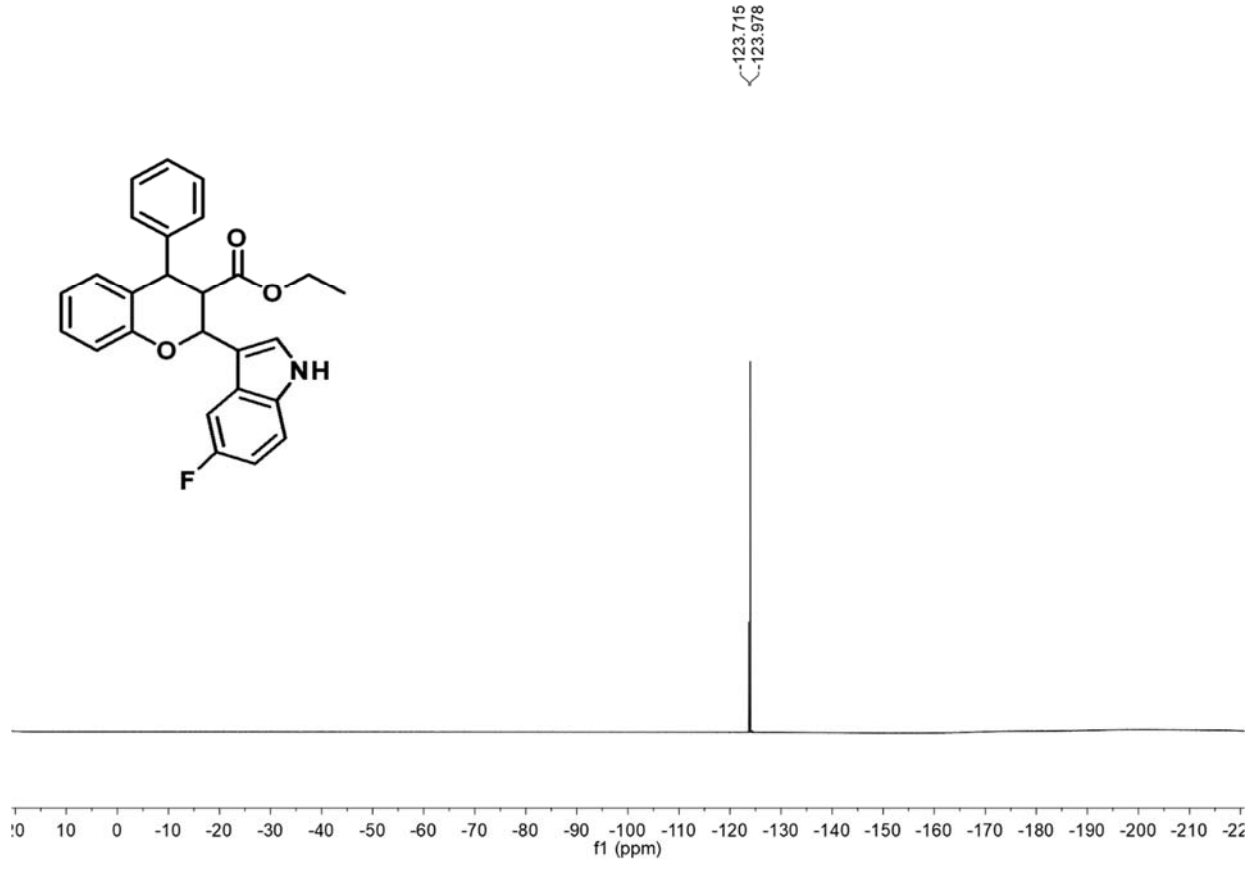
^{13}C NMR Spectrum of Compound **5e**



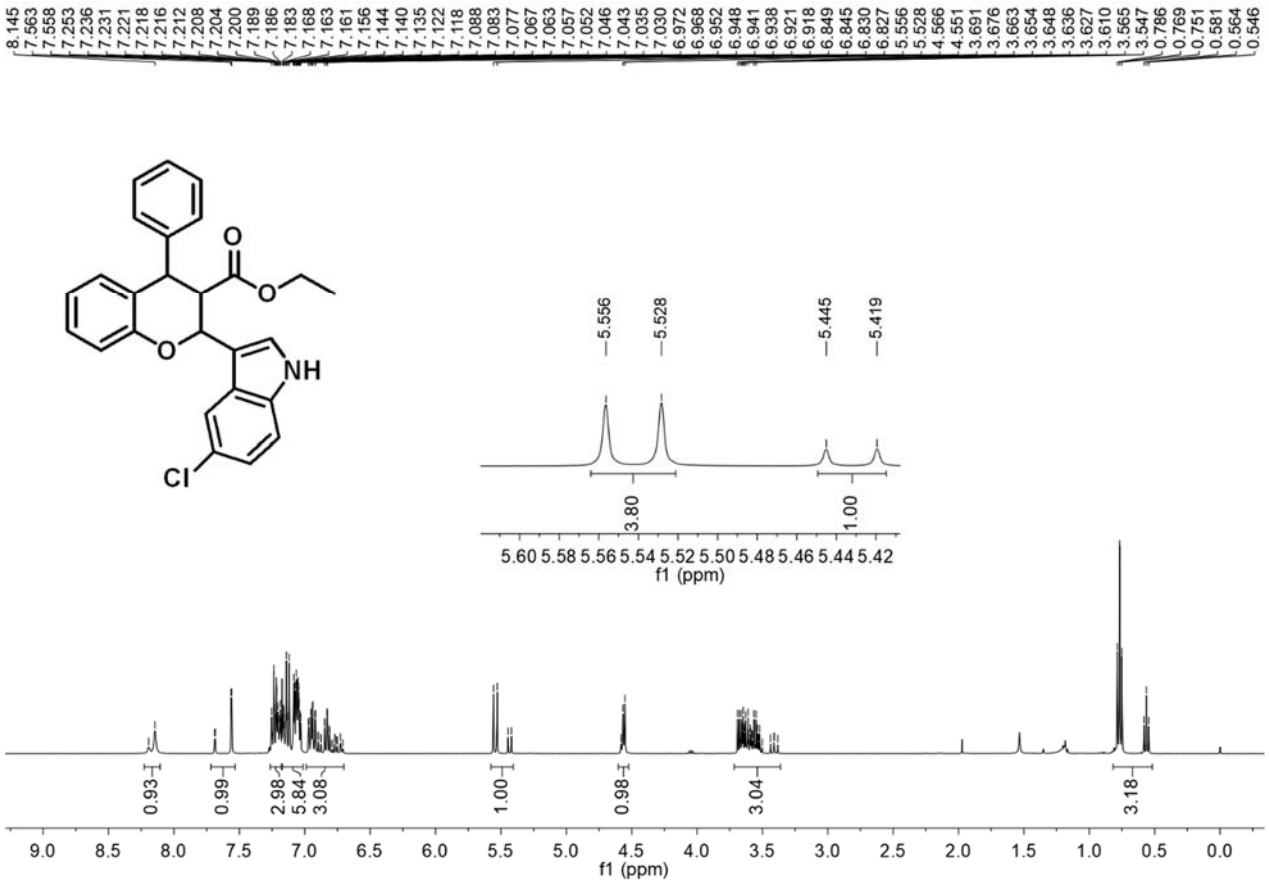
^{1}H NMR Spectrum of Compound **5f**



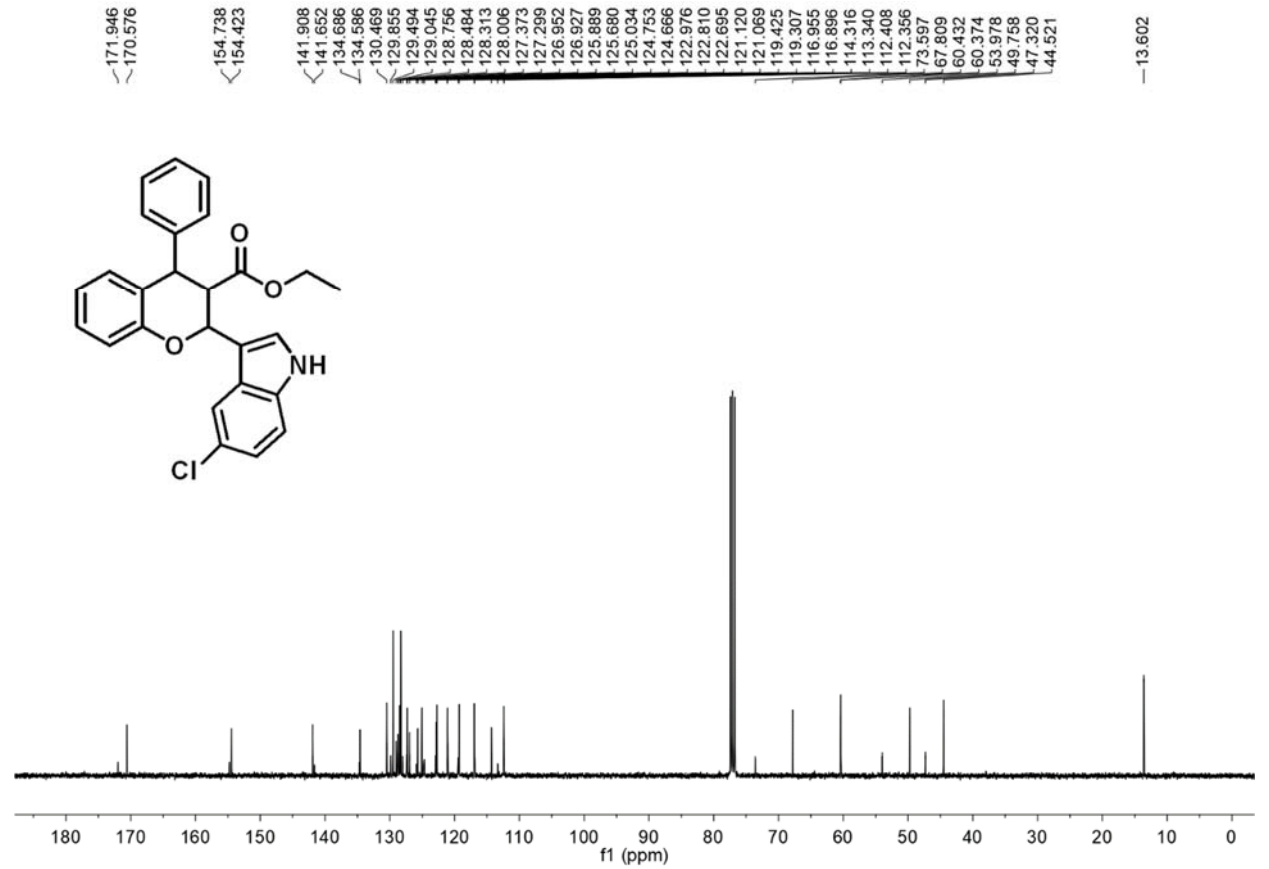
^{13}C NMR Spectrum of Compound **5f**



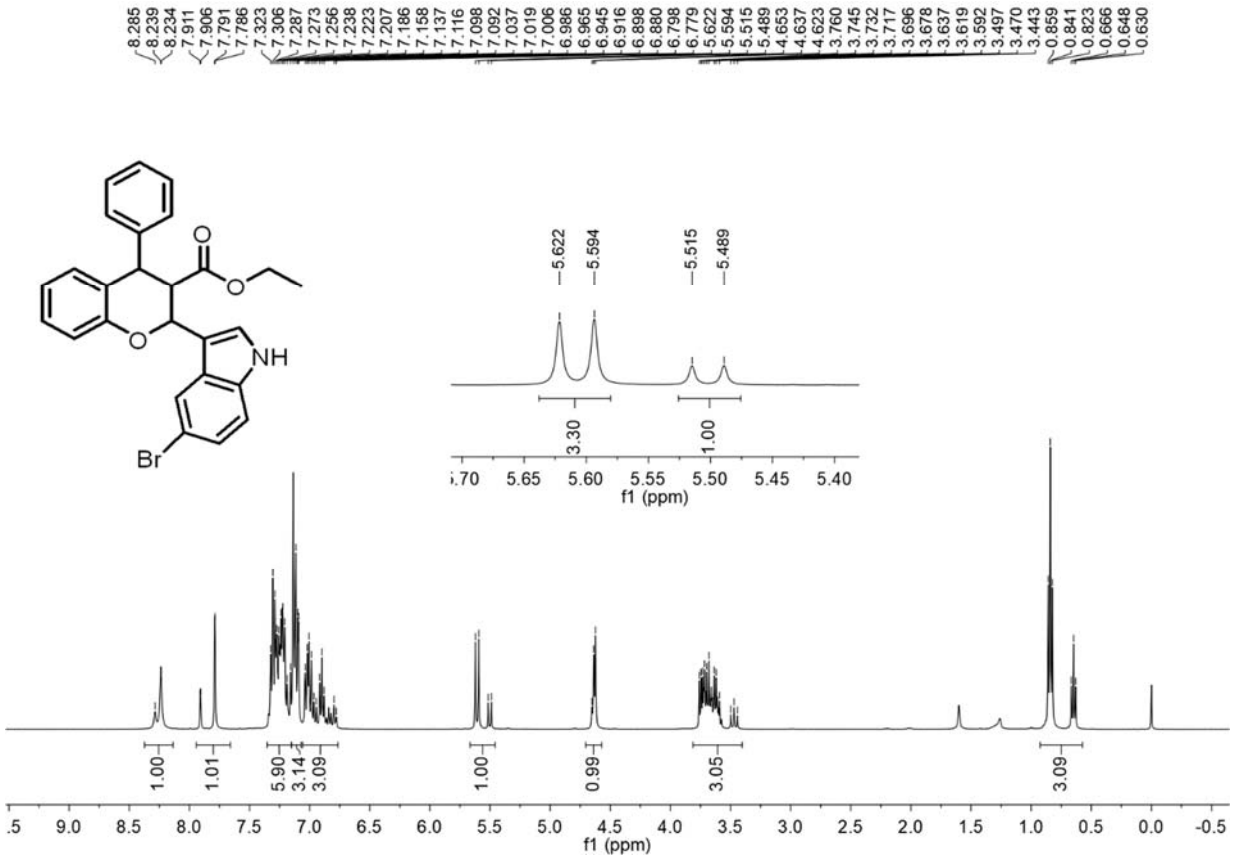
^{19}F NMR Spectrum of Compound **5f**



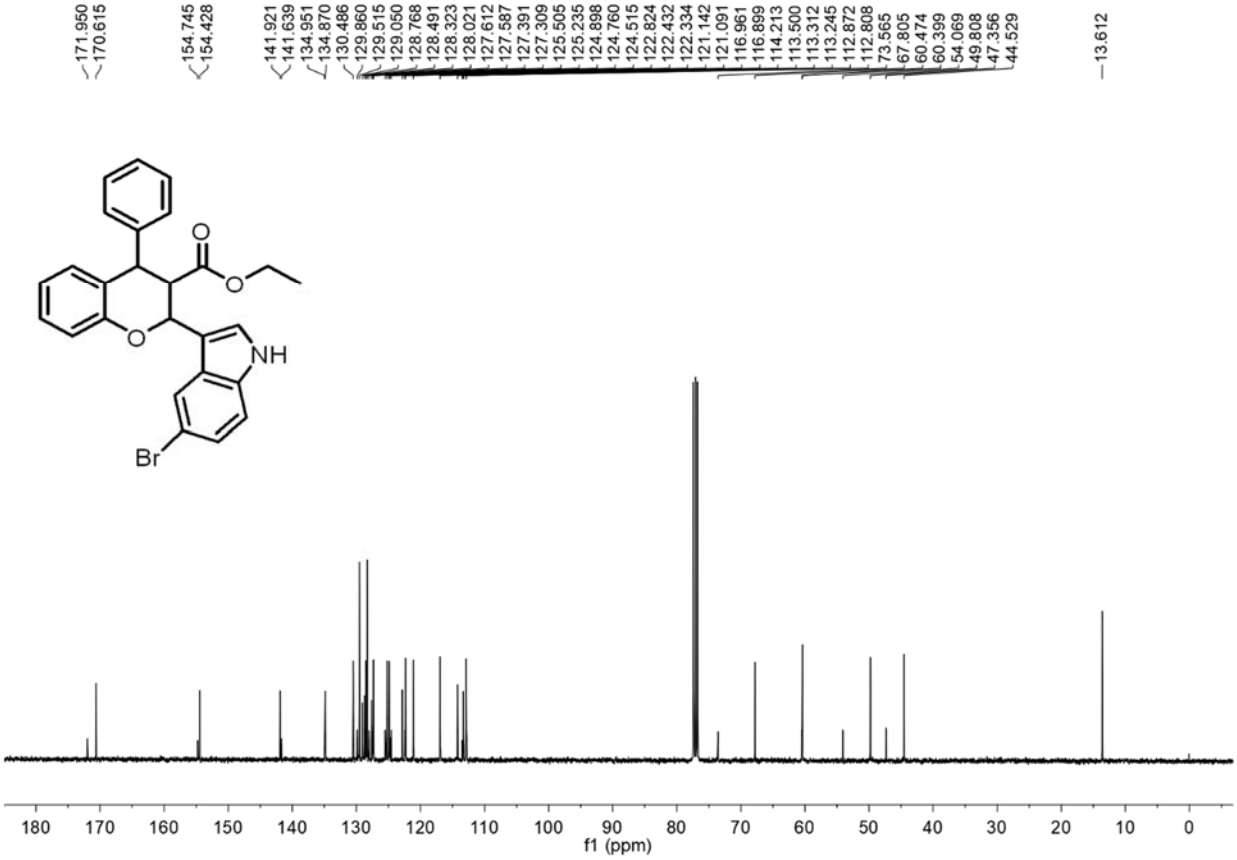
^{1}H NMR Spectrum of Compound **5g**



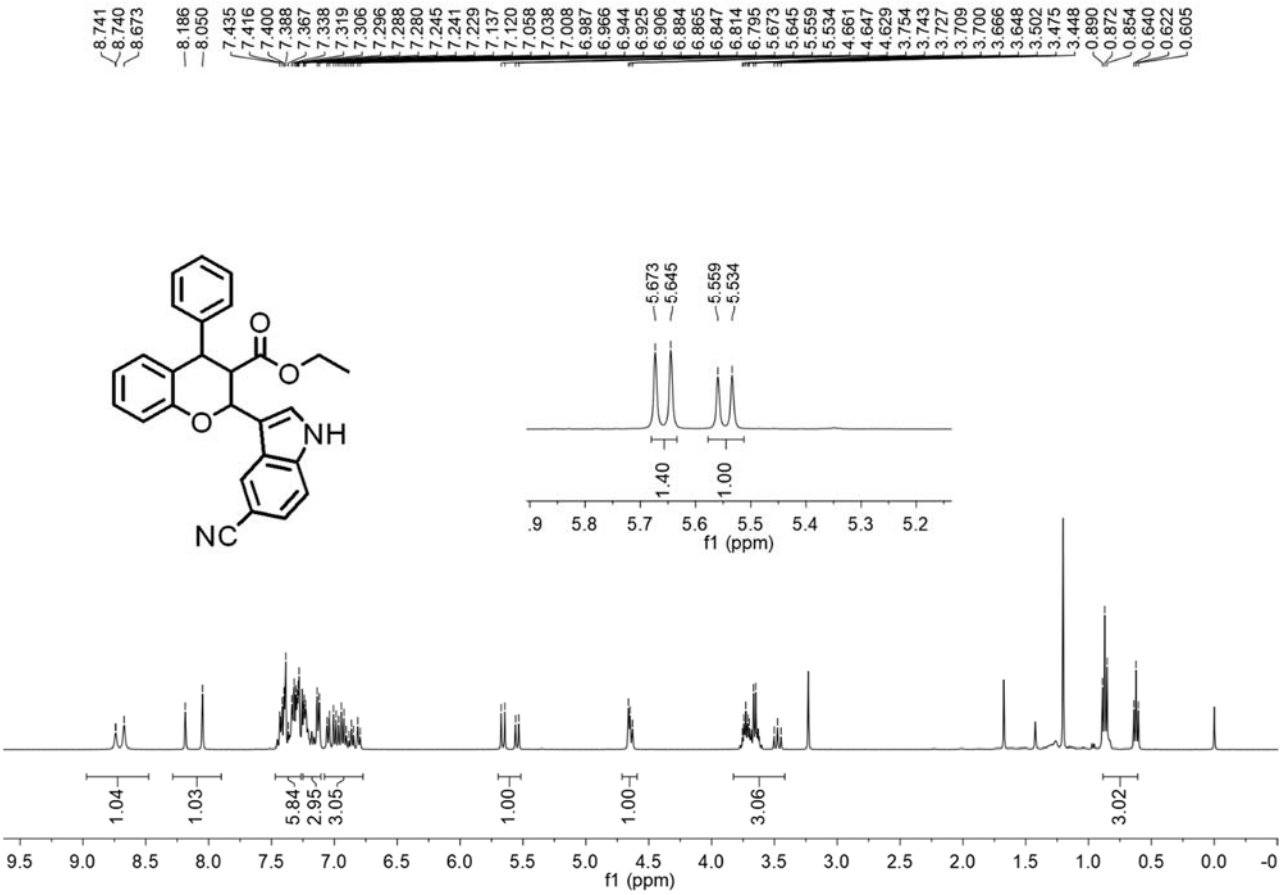
^{13}C NMR Spectrum of Compound **5g**



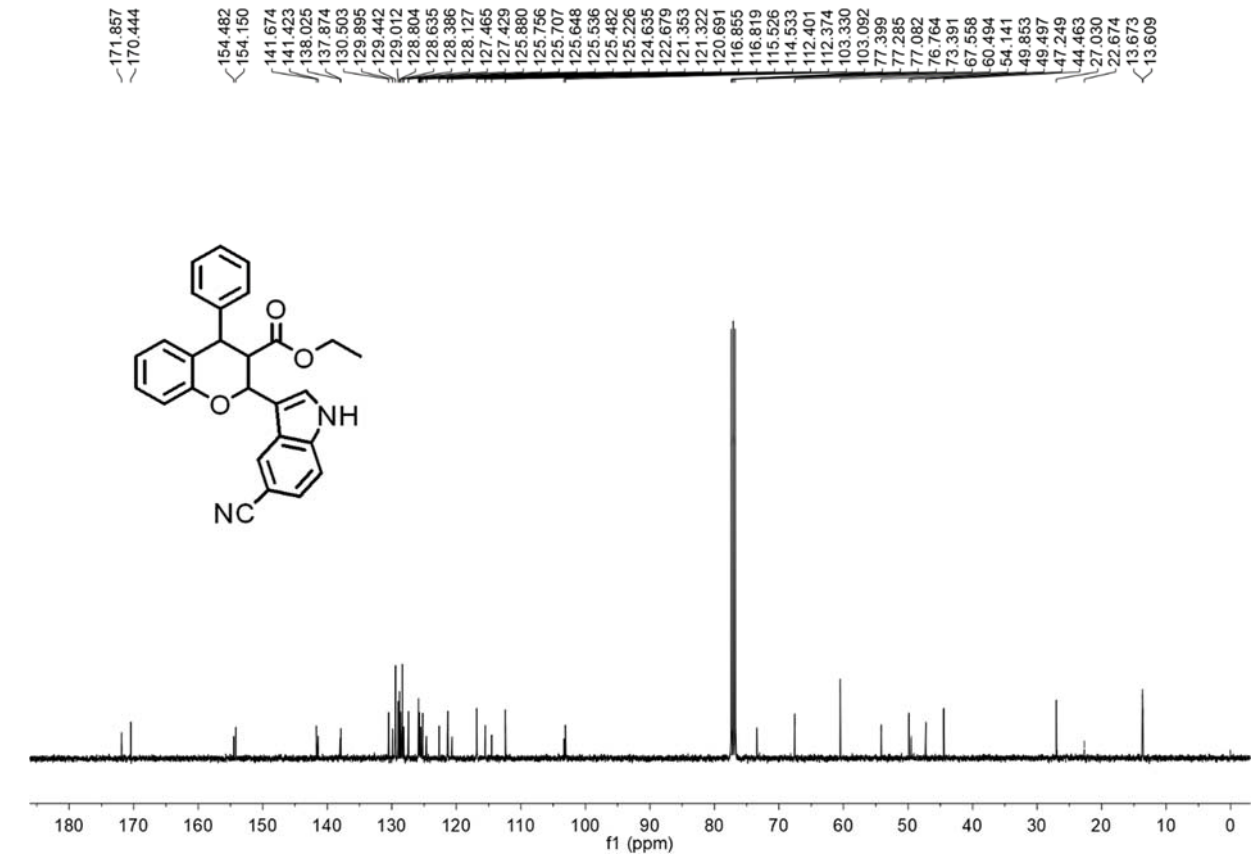
^{1}H NMR Spectrum of Compound **5h**



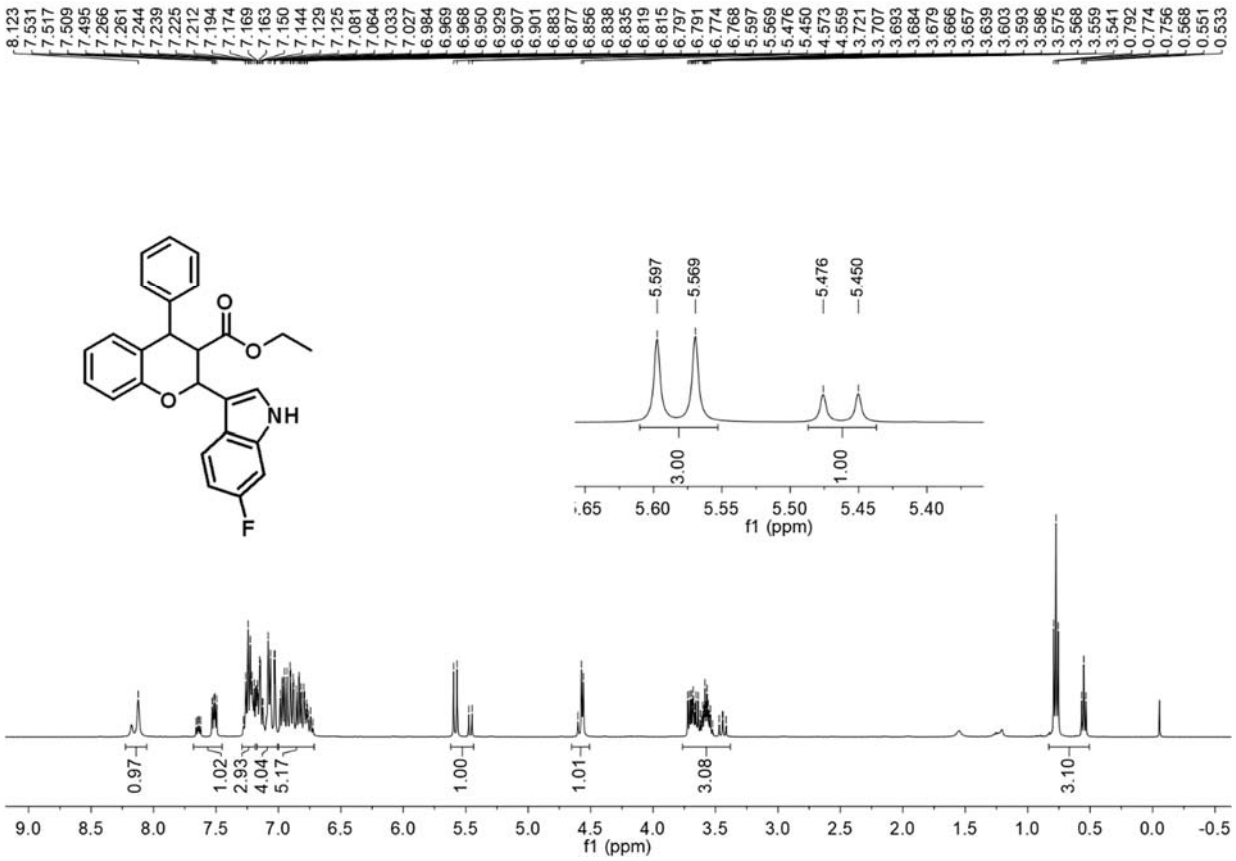
^{13}C NMR Spectrum of Compound **5h**



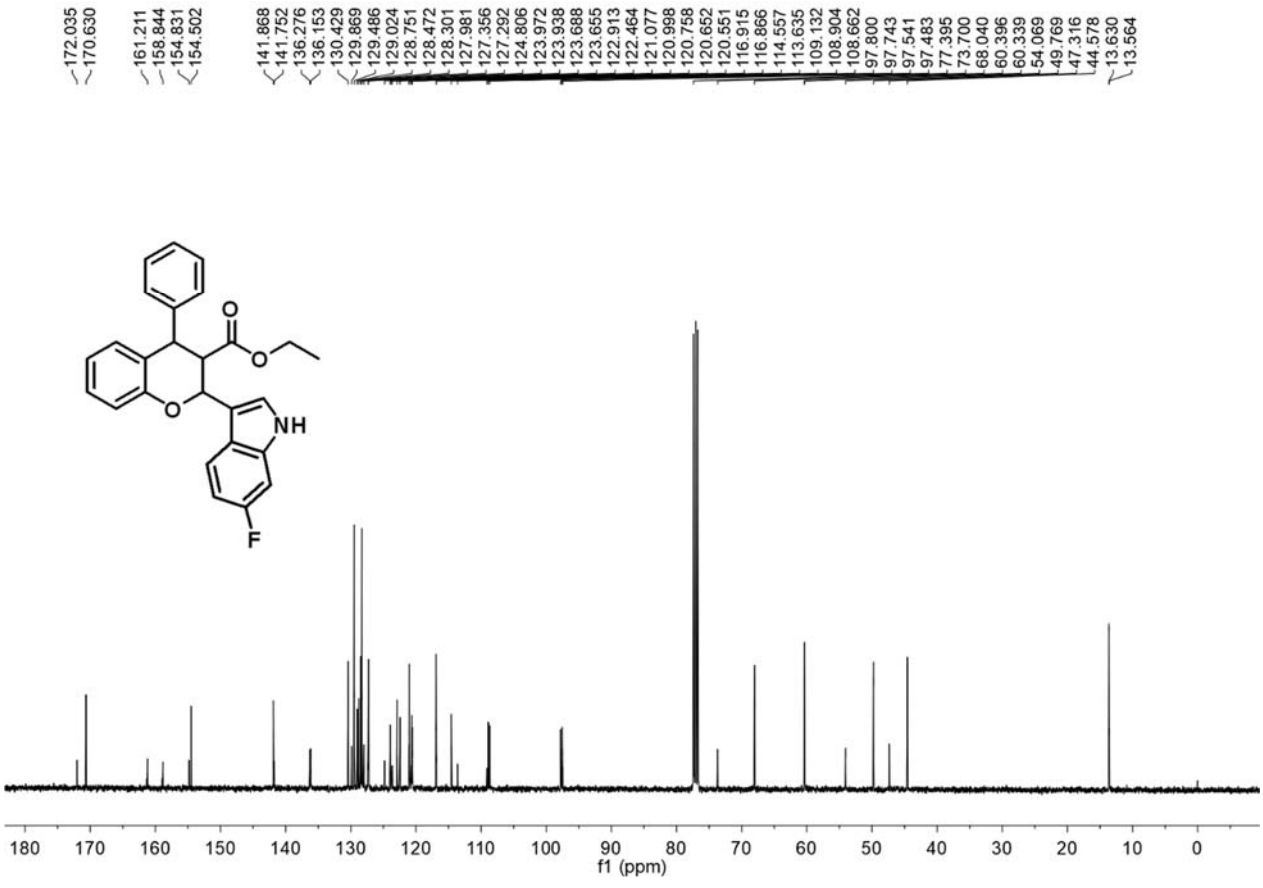
^{1}H NMR Spectrum of Compound **5i**



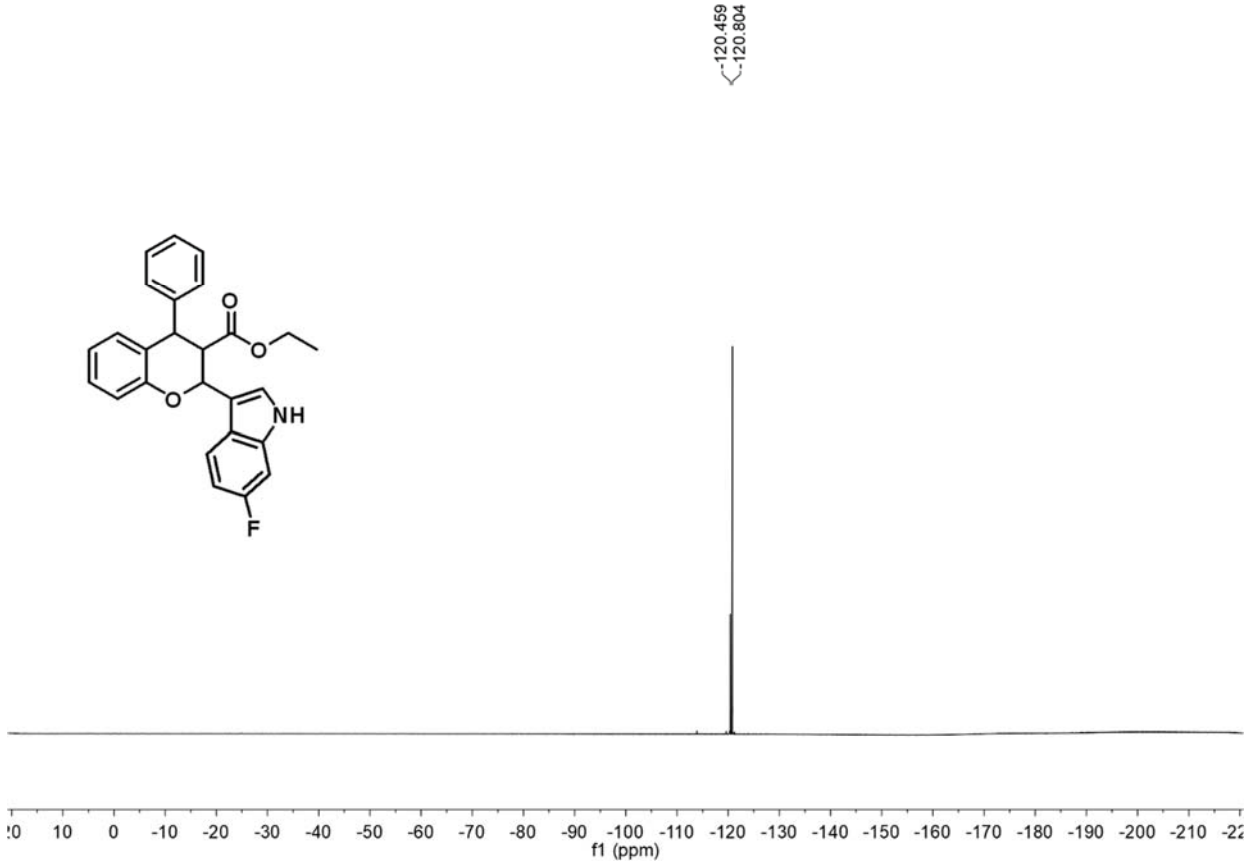
^{13}C NMR Spectrum of Compound **5i**



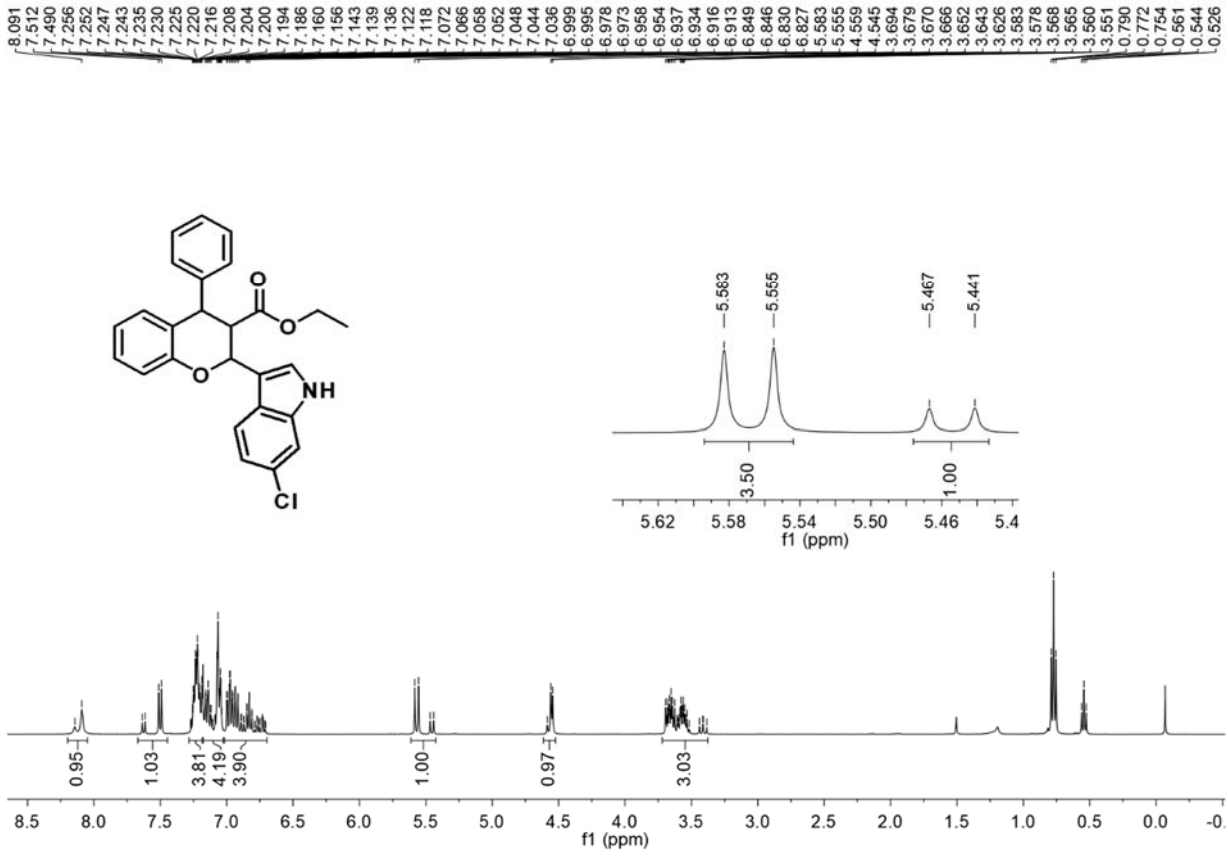
^{1}H NMR Spectrum of Compound **5j**



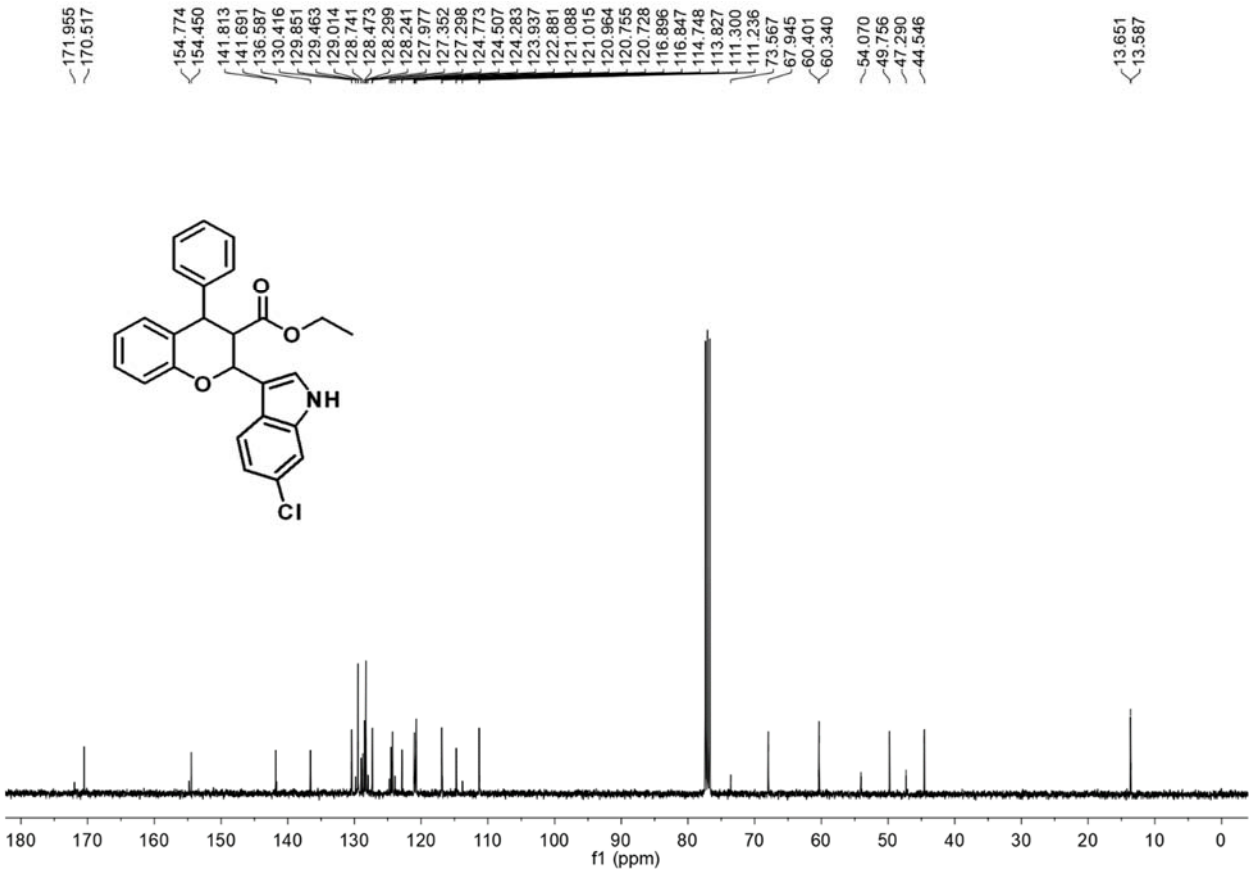
^{13}C NMR Spectrum of Compound **5j**



^{19}F NMR Spectrum of Compound **5j**



^{1}H NMR Spectrum of Compound **5k**



^{13}C NMR Spectrum of Compound **5k**