Supporting Information for

Visible-light-mediated radical reactions of indoles with *para*-quinone methides using Eosin Y as an organophotoredox catalyst

Rekha, Sonam Sharma and Ramasamy Vijaya Anand*

Indian Institute of Science Education and Research (IISER) Mohali, Sector 81, S. A. S. Nagar, Manauli (PO). Punjab – 140306, India

E–mail: rvijayan@iisermohali.ac.in

Table of Contents

1. Fluorescence quenching studies and Stern-Volmer plots

The Stern-Volmer fluorescence quenching experiments were carried out with 1.65 μM eosin Y solution in MeCN at room temperature. The solutions were excited at 490 nm and fluorescence emission was measured from 500 nm to 700 nm.

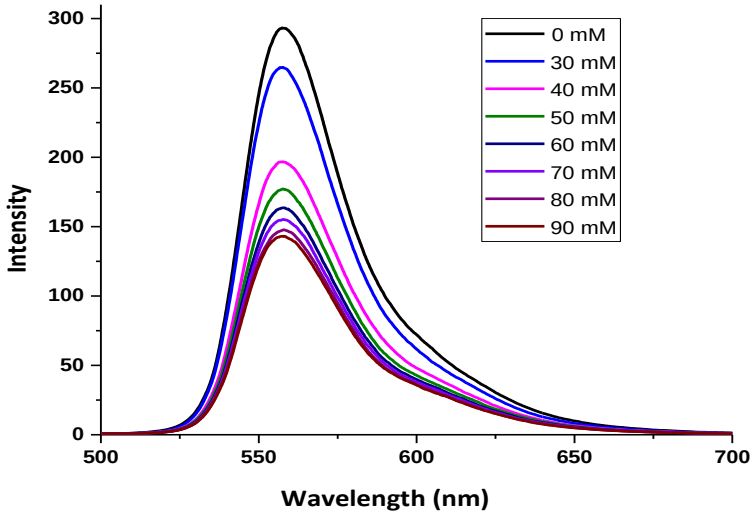


Figure S1. Eosin Y emission quenching by adding variable amounts of indole **1a**

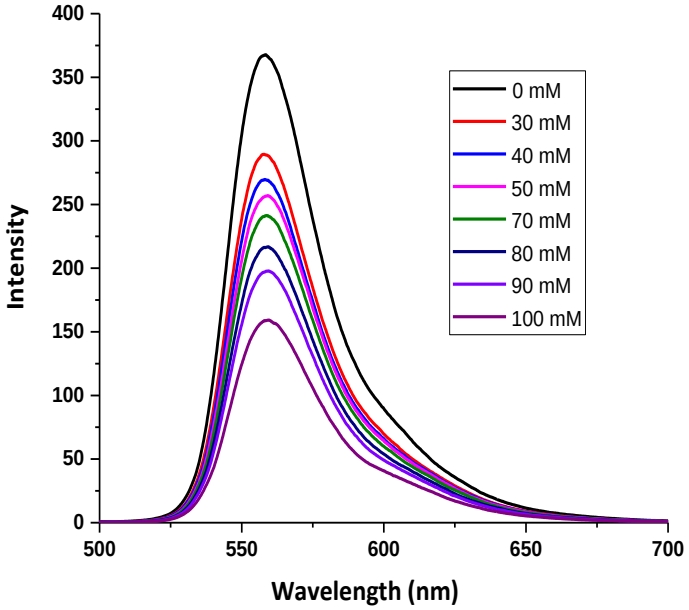


Figure S2. Eosin Y emission quenching by adding variable amounts of *p*-QM **2a**

These fluorescence quenching studies revealed that excited eosin Y get quenched effectively by indole **1a** as well as *p*-QM **2a**.

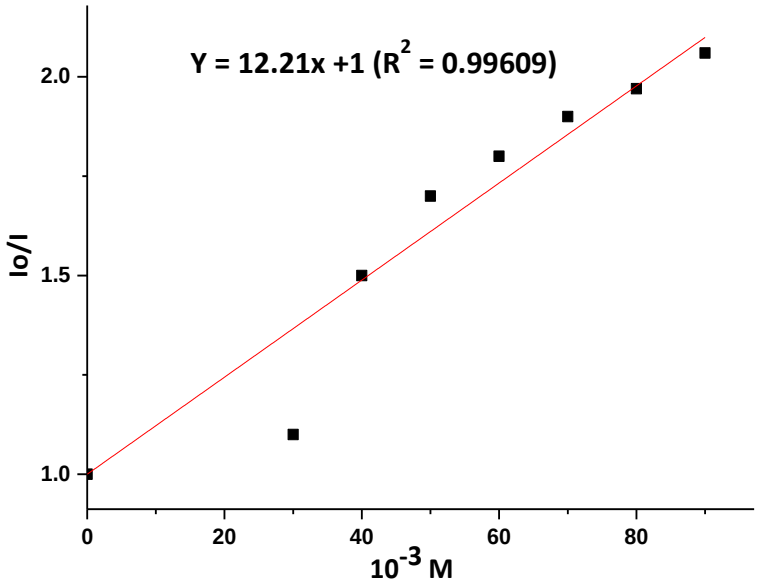


Figure S3. Stern-Volmer plot for fluorescence quenching of eosin Y by **1a**

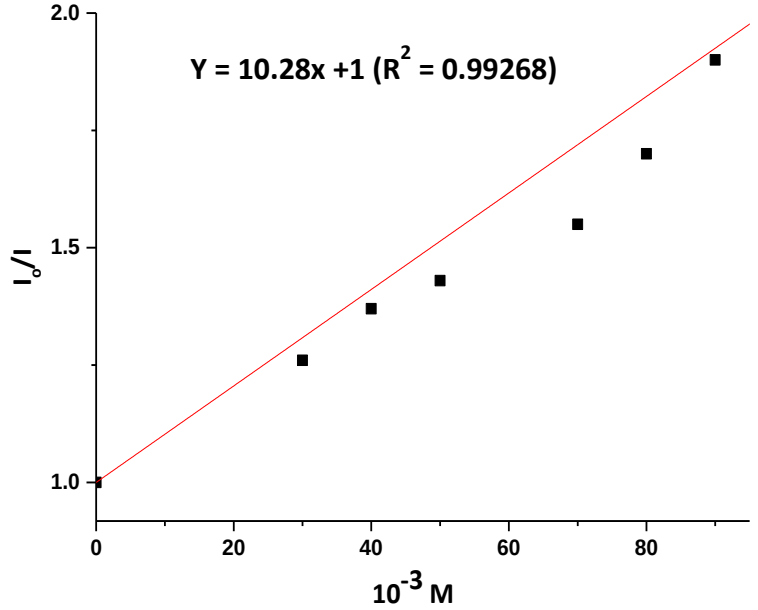


Figure S4. Stern-Volmer plot for fluorescence quenching of eosin Y by **2a**

Fluorescence intensities were plotted against variable concentration of quenchers using Stern-Volmer equation (eq. 1)

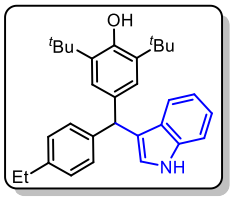
$$\frac{I_0}{I} = 1 + K[Q] = 1 + k_q \tau [Q] \quad \text{(eq. 1)}$$

Where, I_0 = fluorescence intensity of eosin Y in absence of quencher, I = fluorescence intensity of eosin Y in prescence of quencher, *K* = Stern-Volmer constant which is a product of quenching rate constant (*kq*) and average radiative lifetime (τ) of eosin Y.

Using Stern-Volmer equation, quenching rate constant (*kq*) was calculated using both quenchers; indole **1a** and *p*-QM **2a**. *kq* was found 50.9×10^7 $M^{-1}s^{-1}$ with eosin Y and **1a**; and 42.8×10^7 $M^{-1}s^{-1}$ [1] with eosin Y and **2a.**

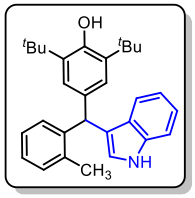
2. *Characterisation of products 3b-3u*

2,6-Di-*tert*-butyl-4-((4-ethylphenyl)(1*H*-indol-3-yl)methyl)phenol (3b)[1]



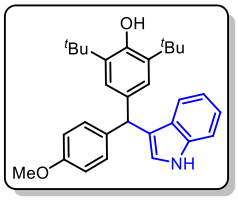
The reaction was performed at 0.171 mmol scale of **1a**; R_f = 0.5 (5% EtOAc in hexane); white solid (72.3mg, 97% yield in MeCN and 72.5mg, 97% yield in H_2O); ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.90 (s, 1H), 7.34 (d, *J* = 8.1 Hz, 1H), 7.28 – 7.26 (m, 1H), 7.20 – 7.08 (m, 7H), 7.00 (t, *J* = 7.5 Hz, 1H), 6.63 (s, 1H), 5.60 (s, 1H), 5.07 (s, 1H), 2.64 (q, *J* = 7.6 Hz, 2H), 1.39 (s, 18H), 1.24 (t, *J* = 7.6 Hz, 3H); ^{13}C{^{1}H} NMR (100 MHz, $CDCl_3$) δ 152.1, 142.0, 141.8, 136.8, 135.4, 134.8, 128.9, 127.7, 127.3, 125.6, 123.8, 122.0, 121.2, 120.3, 119.3, 111.0, 48.6, 34.5, 30.5, 28.6, 15.7; FT-IR (thin film, neat): 3639, 3421, 2962, 1511, 1456, 1233, 741 cm^{-1}.

4-((1*H*-Indol-3-yl)(*o*-tolyl)methyl)-2,6-di-*tert*-butylphenol (3c)



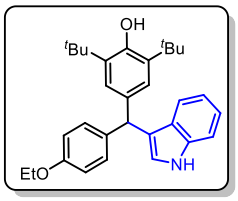
The reaction was performed at 0.171 mmol scale of **1a**; R_f = 0.4 (5% EtOAc in hexane); pale yellow solid (no reaction in MeCN and 46.7mg, 63% yield in H_2O); m. p. = 155–157 ºC; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.89 (br s, 1H), 7.34 (d, J = 8.1 Hz, 1H), 7.22 – 7.16 (m, 3H), 7.14 – 7.10 (m, 1H), 7.07 (td, J = 7.8, 1.2 Hz, 1H), 7.03 – 6.97 (m, 4H), 6.53 – 6.52 (m, 1H), 5.71 (s, 1H), 5.06 (s, 1H), 2.37 (s, 3H), 1.37 (s, 18H); ^{13}C{^{1}H} NMR (100 MHz, $CDCl_3$) δ 152.0, 142.9, 136.8, 136.3, 135.4, 133.5, 130.2, 128.8, 127.3, 126.0, 125.84, 125.81, 124.2, 122.0, 120.8, 120.0, 119.3, 111.0, 45.1, 34.4, 30.5, 20.0; FT-IR (thin film, neat): 3639, 3421, 2958, 1457, 1435, 741 cm^{-1}; HRMS (ESI): *m/z* calcd for $C_{30}H_{34}NO$ $[M–H]^–$: 424.2640; found : 424.2658.

4-((1*H*-Indol-3-yl)(4-methoxyphenyl)methyl)-2,6-di-*tert*-butylphenol (3d)



The reaction was performed at 0.171 mmol scale of **1a**; R_f = 0.2 (5% EtOAc in hexane); orange solid (52.3mg, 71% yield in MeCN and 50.0mg, 68% yield in H_2O); ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.92 (br s, 1H), 7.34 (d, J = 8.1 Hz, 1H), 7.24 (d, J = 8.0 Hz, 1H), 7.17 – 7.13 (m, 3H), 7.01 (s, 2H), 6.98 (t, J = 7.4 Hz, 1H), 6.81 (d, J = 8.4 Hz, 2H), 6.59 (s, 1H), 5.52 (s, 1H), 5.06 (s, 1H), 3.79 (s, 3H), 1.37 (s, 18H); ^{13}C{^{1}H} NMR (100 MHz, $CDCl_3$) δ 157.8, 152.1, 137.0, 136.8, 135.4, 134.9, 130.0, 127.2, 125.6, 123.9, 122.0, 121.3, 120.2, 119.3, 113.6, 111.0, 55.3, 48.1, 34.5, 30.5; FT-IR (thin film, neat): 3638, 3417, 2957, 1610, 1509, 1263, 741 cm^{-1}; HRMS (ESI): *m/z* calcd for $C_{30}H_{34}NO_2$ $[M–H]^–$: 440.2590; found : 440.2610.

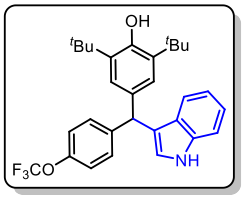
2,6-Di-*tert*-butyl-4-((4-ethoxyphenyl)(1*H*-indol-3-yl)methyl)phenol (3e)[1]



The reaction was performed at 0.171 mmol scale of **1a**; R_f = 0.2 (5% EtOAc in hexane); brown solid (71.4mg, 92% yield in MeCN and 68.7mg, 89% yield in H_2O); ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.90 (br s, 1H), 7.33 (d, J = 8.1 Hz,

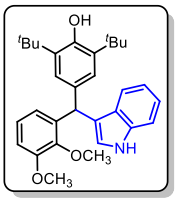
1H), 7.25 (d, *J* = 7.6 Hz, 1H), 7.17 – 7.15 (m, 3H), 7.06 (s, 2H), 6.99 (t, *J* = 7.5 Hz, 1H), 6.54 (d, *J* = 8.2 Hz, 2H), 6.59 (s, 1H), 5.53 (s, 1H), 5.07 (s, 1H), 4.01 (q, *J* = 7.0 Hz, 2H), 1.43 – 1.38 (m, 21H); $^{13}C\{^{1}H\}$ NMR (100 MHz, $CDCl_3$) δ 157.2, 152.0, 136.84, 136.81, 135.4, 134.9, 129.9, 127.2, 125.6, 123.9, 122.0, 121.3, 120.3, 119.3, 114.2, 111.0, 64.4, 48.1, 34.5, 30.5, 15.1; FT-IR (thin film, neat): 3638, 3418, 2959, 1610, 1508, 1435, 1236, 741 cm^{-1}.

4-((1*H*-Indol-3-yl)(4-(trifluoromethoxyphenyl)methyl)-2,6-di-*tert*-butylphenol (3f)[1]



The reaction was performed at 0.171 mmol scale of **1a**; R_f = 0.2 (5% EtOAc in hexane); white solid (82.3mg, 98% yield in MeCN and 69.1mg, 82% yield in H_2O); ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.95 (br s, 1H), 7.37 (d, *J* = 8.1 Hz, 1H), 7.30 – 7.24 (m, 3H), 7.20 (t, *J* = 7.8 Hz, 1H), 7.14 (d, *J* = 8.2 Hz, 2H), 7.04 – 7.01 (m, 3H), 6.62 (s, 1H), 5.61 (s, 1H), 5.13 (s, 1H), 1.40 (s, 18H); $^{13}C\{^{1}H\}$ NMR (100 MHz, $CDCl_3$) δ 152.3, 147.6 (q, $^{3}J_{C-F}$ = 1.7 Hz), 143.5, 136.8, 135.7, 134.0, 130.3, 127.0, 125.6, 124.0, 122.2, 120.7, 120.67 (q, $^{1}J_{C-F}$ = 255.0 Hz), 120.4, 120.0, 119.5, 111.2, 48.2, 34.5, 30.4; $^{19}F\{^{1}H\}$ NMR (376 MHz, $CDCl_3$) δ –57.78; FT-IR (thin film, neat): 3640, 3417, 2960, 1505, 1435, 1262, 1164, 742 cm^{-1}.

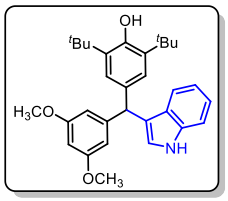
2,6-Di-*tert*-butyl-4-((2,3-dimethoxyphenyl)(1*H*-indol-3-yl)methyl)phenol (3g)[1]



The reaction was performed at 0.171 mmol scale of **1a**; R_f = 0.1 (5% EtOAc in hexane); colorless gummy solid (75.3mg, 94% yield in MeCN and 64.8mg, 81% yield in H_2O); ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.96 (br s, 1H), 7.32 (d, *J* = 8.1 Hz, 1H), 7.28 (d, *J* = 8.0 Hz, 1H), 7.14 (td, *J* = 8.0, 0.8 Hz, 1H), 7.10 (s, 2H), 6.98 (td, *J* = 7.8, 0.6 Hz, 1H), 6.92 (t, *J* = 8.0 Hz, 1H), 6.79 (dd, *J* = 6.8, 1.3 Hz, 1H), 6.72 (dd, *J* = 6.5, 1.3 Hz, 1H), 6.65 – 6.64 (m, 1H), 6.02 (s, 1H), 5.05 (s, 1H), 3.87 (s, 3H), 3.60 (s, 3H), 1.38 (s, 18H); $^{13}C\{^{1}H\}$ NMR (100 MHz, $CDCl_3$) δ 152.7, 152.0, 146.8, 139.0, 136.8, 135.3, 134.5, 127.2, 125.7, 124.1, 123.6,

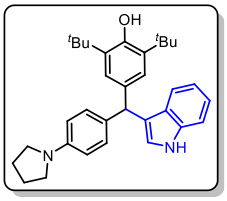
121.91, 121.89, 120.6, 120.2, 119.2, 111.0, 110.2, 60.5, 55.8, 41.6, 34.4, 30.5; FT-IR (thin film, neat): 3638, 3414, 2961, 1584, 1477, 1262, 1090, 1073, 1012, 802, 741 cm^{-1}.

2,6-Di-*tert*-butyl-4-((3,5-dimethoxyphenyl)(1*H*-indol-3-yl)methyl)phenol (3h)



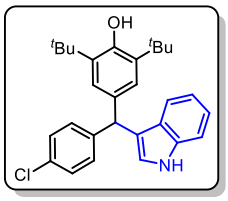
The reaction was performed at 0.171 mmol scale of **1a**; R_f = 0.1 (5% EtOAc in hexane); off white solid (71.9mg, 90% yield in MeCN and 58.5mg, 73% yield in H_2O); m.p = 106 – 108 ºC; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.94 (br s, 1H), 7.34 – 7.32 (m, 1H), 7.29 (d, *J* = 8.0 Hz, 1H), 7.15 (td, *J* = 7.1, 1.0 Hz, 1H), 7.09 (s, 2H), 6.99 (td, *J* = 8.0, 0.9 Hz, 1H), 6.64 (dd, *J* = 2.3, 0.9 Hz, 1H), 6.46 (d, *J* = 2.2 Hz, 2H), 6.32 (t, *J* = 2.3 Hz, 1H), 5.49 (s, 1H), 5.07 (s, 1H), 3.72 (s, 6H), 1.38 (s, 18H); ^{13}C{^{1}H} NMR (100 MHz, $CDCl_3$) δ 160.6, 152.2, 147.4, 136.8, 135.4, 134.1, 127.3, 125.3, 123.8, 122.0, 120.6, 120.1, 119.3, 111.0, 107.5, 98.0, 55.3, 49.2, 34.4, 30.5; FT-IR (thin film, neat): 3635, 3418, 2958, 1595, 1457, 1432,1203, 1156, 741 cm^{-1}; HRMS (ESI): *m/z* calcd for $C_{31}H_{36}NO_3$ $[M–H]^-$: 470.2695; found : 470.2690.

4-((1*H*-Indol-3-yl)(4-(pyrrolidin-1-yl)phenyl)methyl)-2,6-di-*tert*-butylphenol (3i)



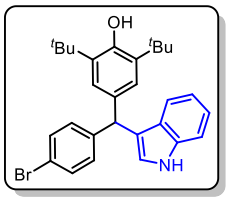
The reaction was performed at 0.171 mmol scale of **1a**; R_f = 0.2 (5% EtOAc in hexane); red solid (71.8mg, 88% yield in MeCN and 57.4mg, 80% yield in H_2O); m. p. = 192 – 194 ºC; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.88 (br s, 1H), 7.32 (d, *J* = 8.0 Hz, 1H), 7.23 (s, 1H), 7.15 – 7.08 (m, 5H), 6.97 (t, *J* = 7.5 Hz, 1H), 6.61 (s, 1H), 6.50 (d, *J* = 7.8 Hz, 2H) , 5.47 (s, 1H), 5.02 (s, 1H), 3.26 (br s, 4H), 1.98 (br s, 4H), 1.37 (s, 18H); ^{13}C{^{1}H} NMR (100 MHz, $CDCl_3$) δ 151.8, 146.3, 136.8, 135.4, 135.2, 131.8, 129.6, 127.4, 125.5, 123.7, 121.83, 121.76, 120.4, 119.1, 111.5, 110.9, 48.0, 47.8, 34.4, 30.5, 25.5; FT-IR (thin film, neat): 3639, 3417, 2958, 1613, 1594, 1519, 1433, 1358, 1185, 740 cm^{-1}; HRMS (ESI): *m/z* calcd for $C_{35}H_{41}N_2O$ $[M+H]^+$: 481.3219; found : 481.3223.

2,6-Di-*tert*-butyl-4-((4-chlorophenyl)(1*H*-indol-3-yl)methyl)phenol (3j)[1]



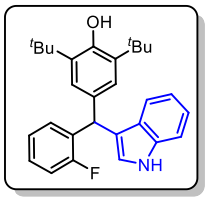
The reaction was performed at 0.171 mmol scale of **1a**; R_f = 0.3 (5% EtOAc in hexane); white solid (69.3mg, 91% yield in MeCN and 66.4mg, 87% yield in H_2O); ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.94 (br s, 1H), 7.36 (d, J = 8.12 Hz, 1H), 7.26 – 7.16 (m, 6H), 7.03 – 6.99 (m, 3H), 6.60 (s, 1H), 5.56 (s, 1H), 5.11 (s, 1H), 1.39 (s, 18H); ^{13}C{^{1}H} NMR (100 MHz, $CDCl_3$) δ 152.3, 143.3, 136.8, 135.6, 134.1, 131.7, 130.4, 128.4, 127.0, 125.5, 124.0, 122.2, 120.4, 120.1, 119.5, 111.1, 48.3, 34.5, 30.5; FT-IR (thin film, neat): 3637, 3417, 2959, 1489, 1456, 1435, 1234, 1091, 1023, 741 cm^{-1}.

2,6-Di-*tert*-butyl-4-((4-bromophenyl)(1*H*-indol-3-yl)methyl)phenol (3k)[1]



The reaction was performed at 0.171 mmol scale of **1a**; R_f = 0.3 (5% EtOAc in hexane); white solid (74.7mg, 90% yield in MeCN and 74.5mg, 90% yield in H_2O); ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.94 (br s, 1H), 7.39 – 7.34 (m, 3H), 7.22 – 6.12 (m, 4H), 7.02 – 6.98 (m, 3H), 6.59 (s, 1H), 5.52 (s, 1H), 5.09 (s, 1H), 1.38 (s, 18H); ^{13}C{^{1}H} NMR (100 MHz, $CDCl_3$) δ 152.3, 143.9, 136.8, 135.7, 134.0, 131.3, 130.8, 127.0, 125.5, 124.0, 122.2, 120.3, 120.1, 120.0, 119.5, 111.1, 48.4, 34.5, 30.5; FT-IR (thin film, neat): 3636, 3417, 2959, 1468, 1434, 1219, 1011, 741 cm^{-1}.

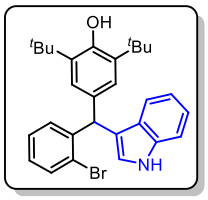
2,6-Di-*tert*-butyl-4-((2-fluorophenyl)(1*H*-indol-3-yl)methyl)phenol (3l)[1]



The reaction was performed at 0.171 mmol scale of **1a**; R_f = 0.2 (5% EtOAc in hexane); white solid (69.6mg, 95% yield in MeCN and 53.2mg, 73% yield in H_2O); ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.92 (br s, 1H), 7.35 (d, J = 8.1 Hz, 1H), 7.26 (d, J = 7.9 Hz, 1H), 7.22 – 6.98 (m, 9H), 6.63 (d, J = 1.2 Hz, 1H), 5.92 (s, 1H), 5.10 (s, 1H), 1.39 (s, 18H); ^{13}C{^{1}H} NMR (100 MHz, $CDCl_3$) δ 160.8 (d, $^1J_{C–F}$ = 244.5 Hz), 152.3, 136.8, 135.5, 133.1, 131.7 (d, $^2J_{C–F}$ = 14.1 Hz), 130.5 (d, $^4J_{C–F}$ = 4.1 Hz), 127.8 (d, $^3J_{C–F}$ = 8.1 Hz) 127.0, 125.5,

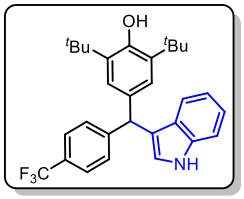
124.1, 123.6 (d, $^{5}J_{C–F}$ = 3.5 Hz), 122.1, 119.9, 119.7, 119.4, 115.3 (d, $^{6}J_{C–F}$ = 22.2 Hz), 111.1, 41.1 (d, $^{5}J_{C–F}$ = 3.4 Hz), 34.5, 30.5; $^{19}F\{^{1}H\}$ NMR (376 MHz, $CDCl_3$) δ –117.8; FT-IR (thin film, neat): 3635, 3437, 2958, 1486, 1456, 1435, 1225, 1094, 757, 742 cm^{-1}.

2,6-Di-*tert*-butyl-4-((2-bromophenyl)(1*H*-indol-3-yl)methyl)phenol (3m)[1]



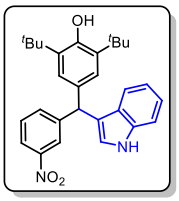
The reaction was performed at 0.171 mmol scale of **1a**; R_f = 0.2 (5% EtOAc in hexane); white solid (no reaction in MeCN and 54.6mg, 65% yield in H_2O); ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.94 (br s, 1H), 7.59 (d, *J* = 7.8 Hz, 1H), 7.35 (d, *J* = 8.1 Hz, 1H), 7.21 – 7.14 (m, 4H), 7.07 – 7.03 (m, 3H), 7.01 – 6.97 (m, 1H), 6.61 – 6.60 (m, 1H), 5.97 (s, 1H), 5.07 (s, 1H), 1.37 (s, 18H); $^{13}C\{^{1}H\}$ NMR (100 MHz, $CDCl_3$) δ 152.2, 143.8, 136.8, 135.4, 133.0, 132.5, 130.7, 127.8, 127.3, 127.1, 125.9, 125.2, 124.2, 122.2, 120.2, 120.1, 119.5, 111.1, 47.9, 34.5, 30.5; FT-IR (thin film, neat): 3637, 3419, 2958, 1457, 1234, 805 cm^{-1}.

4-((1*H*-Indol-3-yl)(4-(trifluoromethyl)phenyl)methyl)-2,6-di-*tert*-butylphenol (3n)[1]



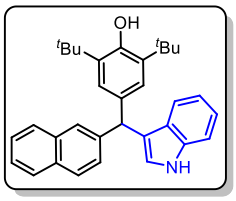
The reaction was performed at 0.171 mmol scale of **1a**; R_f = 0.2 (5% EtOAc in hexane); white solid (74.9mg, 92% yield in MeCN and 69.6mg, 85% yield in H_2O); ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.97 (br s, 1H), 7.54 (d, *J* = 8.0 Hz, 2H), 7.39 – 7.36 (m, 3H), 7.21 – 7.17 (m, 2H), 705 – 7.00 (m, 3H), 6.62 (s, 1H), 5.64 (s, 1H), 5.13 (s, 1H), 1.39 (s, 18H); $^{13}C\{^{1}H\}$ NMR (100 MHz, $CDCl_3$) δ 152.4, 148.9, 136.8, 135.8, 133.6, 129.3, 128.3 (q, $^{2}J_{C–F}$ = 31.8 Hz), 126.9, 125.6, 125.2 (q, $^{3}J_{C–F}$ = 3.8 Hz), 124.6 (q, $^{1}J_{C–F}$ = 270.3 Hz), 124.1, 122.3, 119.98, 119.97, 119.6, 111.2, 48.8, 34.5, 30.5; $^{19}F\{^{1}H\}$ NMR (376 MHz, $CDCl_3$) δ –62.1; FT-IR (thin film, neat): 3640, 3417, 2960, 1617, 1457, 1435, 1326, 1235, 1163, 1068, 742 cm^{-1}.

4-((1*H*-Indol-3-yl)(3-nitrophenyl)methyl)-2,6-di-*tert*-butylphenol (3o)[1]



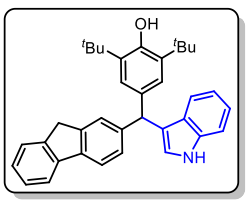
The reaction was performed at 0.171 mmol scale of **1a**; R_f = 0.2 (5% EtOAc in hexane); yellow solid (70.0mg, 90% yield in MeCN and 55.9mg, 72% yield in H_2O); ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.17 (br s, 1H), 8.09 – 8.05 (m, 2H), 7.60 (d, J = 7.7 Hz, 1H), 7.43 (t, J = 8.0 Hz, 1H), 7.38 (d, J = 8.2 Hz, 1H), 7.21 – 7.17 (m, 2H), 7.04 – 7.00 (m, 3H), 6.65 (d, J = 1.8 Hz, 1H), 5.69 (s, 1H), 5.16 (s, 1H), 1.39 (s, 18H); ^{13}C{^{1}H} NMR (100 MHz, $CDCl_3$) δ 152.6, 148.5, 147.1, 136.9, 136.0, 135.2, 133.1, 129.1, 126.7, 125.5, 124.2, 123.9, 122.4, 121.4, 119.7, 119.4, 111.4, 48.6, 34.5, 30.4; FT-IR (thin film, neat): 3636, 3418, 2958, 1609, 1508, 1456, 1434, 1234, 1174, 740 cm^{-1}.

4-((1*H*-Indol-3-yl)(naphthalen-2-yl)methyl)-2,6-di-*tert*-butylphenol (3p)[1]



The reaction was performed at 0.171 mmol scale of **1a**; R_f = 0.2 (5% EtOAc in hexane); white solid (no reaction in MeCN and 22.3mg, 28% yield in H_2O); ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.2 (d, J = 7.7 Hz, 1H), 7.90 – 7.85 (m, 2H), 7.72 (d, J = 8.2 Hz, 1H), 7.47 – 7.40 (m, 2H), 7.36 – 7.32 (m, 2H), 7.24 (d, J = 7.9 Hz, 1H), 7.18 – 7.14 (m, 2H), 7.02 (s, 2H), 6.98 – 6.95 (m, 1H), 6.49 (d, J = 1.5 Hz, 1H), 6.33 (s, 1H), 5.04 (s, 1H), 1.33 (s, 18H); ^{13}C{^{1}H} NMR (100 MHz, $CDCl_3$) δ 152.2, 140.6, 136.8, 135.5, 134.1, 133.8, 132.1, 128.7, 127.2, 126.9, 126.7, 125.88, 125.87, 125.5, 125.3, 124.6, 124.5, 122.1, 121.0, 120.1, 119.3, 111.1, 44.6, 34.4, 30.5; FT-IR (thin film, neat): 3626, 3422, 2958, 1434, 1233, 1156, 1105 745 cm^{-1}.

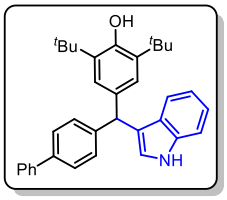
4-((9*H*-Fluoren-2-yl)(1*H*-indol-3-yl) methyl)-2,6-di-*tert*-butylphenol (3q)



The reaction was performed at 0.171 mmol scale of **1a**; R_f = 0.2 (5% EtOAc in hexane); orange solid (no reaction in MeCN and 48.4mg, 57% yield in H_2O); m. p. = 152–154 ^{o}C; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.92 (br s, 1H), 7.79 (d, J = 7.5 Hz, 1H), 7.72 (d, J = 7.8 Hz, 1H), 7.54 (d, J = 7.4 Hz, 1H), 7.49 (s, 1H), 7.41 –

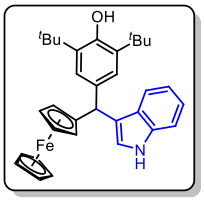
7.35 (m, 2H), 7.33 – 7.28 (m, 3H), 7.20 – 7.15 (m, 3H), 7.01 (t, *J* = 7.5 Hz, 1H), 6.648 – 6.645 (m, 1H), 5.69 (s, 1H), 5.12 (s, 1H), 3.87 (d, *J* = 0.8 Hz, 2H), 1.42 (s, 18H); $^{13}C\{^{1}H\}$ NMR (100 MHz, $CDCl_3$) δ 152.1, 143.6, 143.5, 143.4, 142.0, 139.7, 136.8, 135.5, 134.8, 127.8, 127.3, 126.8, 126.3, 125.70, 125.68, 125.1, 124.0, 122.0, 121.1, 120.3, 119.8, 119.6, 119.4, 111.1, 49.1, 37.1, 34.5, 30.5; FT-IR (thin film, neat): 3635, 3418, 2958, 1456, 1434, 1233, 1154, 766, 740 cm^{-1}; HRMS (ESI): *m/z* calcd for $C_{36}H_{36}NO$ $[M–H]^-$: 498.2797; found : 498.2808.

4-([1,1'-Biphenyl]-4-yl(1*H*-indol-3-yl) methyl)-2,6-di-*tert*-butylphenol (3r)[1]



The reaction was performed at 0.171 mmol scale of **1a**; R_f = 0.2 (5% EtOAc in hexane); pale orange solid (81.0mg, 98% yield in MeCN and 77.8mg, 94% yield in H_2O); ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.94 (br s, 1H), 7.61 (d, *J* = 7.6 Hz, 2H), 7.53 (d, *J* = 8.1 Hz, 2H), 7.43 (t, *J* = 7.5 Hz, 2H), 7.37 – 7.29 (m, 5H), 7.18 (t, *J* = 7.4 Hz, 1H), 7.11 (s, 2H), 7.02 (t, *J* = 7.4 Hz, 1H), 6.67 (s, 1H), 5.63 (s, 1H), 5.10 (s, 1H), 1.40 (s, 18H); $^{13}C\{^{1}H\}$ NMR (100 MHz, $CDCl_3$) δ 152.2, 144.0, 141.2, 138.7, 136.8, 135.5, 134.5, 129.4, 128.8, 127.2, 127.1, 126.9, 125.7, 124.0, 122.1, 120.8, 120.2, 119.4, 111.1, 48.6, 34.5, 30.5; FT-IR (thin film, neat): 3636, 3421, 2958, 1487, 1434, 1234, 763, 740, 699 cm^{-1}.

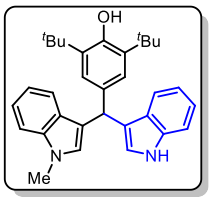
4-((1*H*-Indol-3-yl)(ferrocene-2-yl)methyl)-2,6-di-*tert*-butylphenol (3s)[1]



The reaction was performed at 0.171 mmol scale of **1a**; R_f = 0.3 (5% EtOAc in hexane); white solid (68.0mg, 77% yield in MeCN and 50.3mg, 57% yield in H_2O); ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.84 (br s, 1H), 7.36 (d, *J* = 7.9 Hz, 1H), 7.28 – 7.23 (m, 1H), 7.18 (s, 2H), 7.10 (t, *J* = 7.2 Hz, 1H), 6.97 (t, *J* = 7.5 Hz, 1H), 6.81 (s, 1H), 5.18 (s, 1H), 5.02 (s, 1H), 4.15 (m, 1H), 4.09 – 4.08 (m, 2H), 3.94 (s, 6H), 1.40 (s, 18H); $^{13}C\{^{1}H\}$ NMR (100 MHz, $CDCl_3$) δ 152.0, 136.5, 135.2 , 127.0, 125.3, 122.3, 122.1, 121.8, 120.0, 119.1,

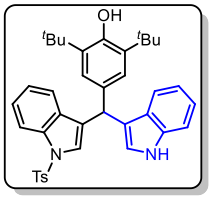
111.0, 94.0, 69.0, 68.9, 68.7, 68.4, 67.3, 67.2, 43.52, 43.51, 35.7, 34.5, 30.6; FT-IR (thin film, neat): 3638, 3416, 2957, 1656, 1456, 1434, 1233, 818, 740 cm^{-1}.

4-((1*H*-Indol-3-yl)(1-methyl-1*H*-indol-3-yl)methyl)-2,6-di-*tert*-butylphenol (3t)



The reaction was performed at 0.171 mmol scale of **1a**; R_f = 0.2 (10% EtOAc in hexane); orange solid (61.8 mg, 78% yield in MeCN and 57.1 mg, 72% yield in H_2O); m. p. = 138-140 ^oC; ^1H NMR (400 MHz, $CDCl_3$) δ 7.85 (br s, 1H), 7.43 (dd, *J* = 7.9, 3.9 Hz, 2H), 7.33 (d, *J* = 8.1 Hz, 1H), 7.29 (d, *J* = 8.2 Hz, 1H), 7.21 – 7.20 (m, 3H), 7.18 – 7.15 (m, 1H), 7.03 – 6.98 (m, 2H), 6.71 (d, *J* = 1.5 Hz, 1H), 6.58 (s, 1H), 5.80 (s, 1H), 5.05 (s, 1H), 3.69 (s, 3H), 1.39 (s, 18H); $^{13}C\{^1H\}$ NMR (100 MHz, $CDCl_3$) δ 151.99, 137.50, 136.73, 135.34, 134.69, 128.04, 127.72, 127.33, 125.31, 123.39, 121.73, 121.33, 120.72, 120.29, 120.18, 119.08, 119.04, 118.52, 111.01, 109.07, 40.28, 34.43, 32.74, 32.72, 30.54; FT-IR (thin film, neat): 3405, 2954, 2925, 1463, 1435, 1364, 728 cm^{-1}; HRMS (ESI): *m/z* calcd for $C_{32}H_{35}N_2O$ $[M–H]^–$: 463.2749; found : 463.2731.

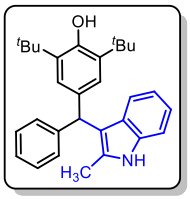
4-((1*H*-Indol-3-yl)(1-tosyl-1*H*-indol-3-yl)methyl)-2,6-di-*tert*-butylphenol (3u)



The reaction was performed at 0.171 mmol scale of **1a**; R_f = 0.3 (5% EtOAc in hexane); white solid (71.2mg, 69% yield in MeCN and 64.9mg, 63% yield in H_2O); ^1H NMR (400 MHz, $CDCl_3$) δ 8.01 (d, *J* = 8.2 Hz, 1H), 7.98 (br s, 1H), 7.64 (d, *J* = 8.2 Hz, 2H), 7.37 (d, *J* = 8.1 Hz, 1H), 7.29 – 7.25 (m, 3H), 7.20 – 7.17 (m, 3H), 7.11 (d, *J* = 7.5 Hz, 1H), 7.08 (s, 2H), 7.05 (s, 1H), 6.99 (t, *J* = 7.6 Hz, 1H), 6.63 (d, *J* = 1.9 Hz, 1H), 5.65 (s, 1H), 5.10 (s, 1H), 2.37 (s, 3H), 1.36 (s, 18H); $^{13}C\{^1H\}$ NMR (100 MHz, $CDCl_3$) δ 152.4, 144.7, 136.8, 136.0, 135.6, 135.2, 132.5, 131.0, 129.9, 127.5, 126.91, 126.85, 125.23, 125.18, 124.6, 123.6, 123.1, 122.1, 120.8, 119.8, 119.3, 118.9, 113.9, 111.3, 40.0, 34.4, 30.5, 21.71, 21.69; FT-IR (thin film, neat): 3625, 3426, 2970, 2954, 1738, 1435, 1370, 1217, 980, 743 cm^{-1}; HRMS (ESI): *m/z* calcd for $C_{38}H_{39}N_2O_3S$ $[M–H]^–$: 603.2681; found : 603.2676.

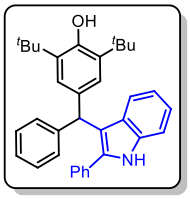
3. *Characterisation of product 4a-4k*

2,6-Di-*tert*-butyl-4-((2-methyl-1*H*-indol-3-yl)(phenyl)methyl)phenol (4a)



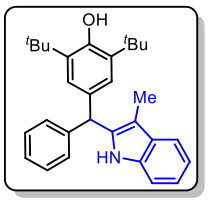
The reaction was performed at 0.151 mmol scale of **1b**; R_f = 0.2 (5% EtOAc in hexane); yellow solid (58.4 mg, 90% yield in MeCN and 62.9 mg, 97% yield in H_2O); m. p. = 182–184 °C; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.69 (br s, 1H), 7.28 – 7.17 (m, 6H), 7.12 (d, J = 8.0 Hz, 1H), 7.08 – 7.05 (m, 3H), 6.93 (t, J = 7.7 Hz, 1H), 5.68 (s, 1H), 5.09 (s, 1H), 2.17 (s, 3H), 1.37 (s, 18H); ^{13}C{^{1}H} NMR (100 MHz, $CDCl_3$) δ 152.04, 144.9, 135.5, 135.3, 134.2, 131.8, 129.1, 128.6, 128.1, 126.0, 125.8, 120.7, 119.8, 119.0, 115.0, 110.1, 47.7, 34.4, 30.5, 12.62, 12.61; FT-IR (thin film, neat): 3639, 3406, 2958, 1599, 1460, 1434, 1233, 1154, 743, 701, 600 cm^{-1}; HRMS (ESI): *m/z* calcd for $C_{30}H_{34}NO$ $[M–H]^–$: 424.2640; found : 424.2646.

2,6-Di-*tert*-butyl-4-(phenyl(2-phenyl-1*H*-indol-3-yl)methyl)phenol (4b)



The reaction was performed at 0.103 mmol scale of **1c**; R_f = 0.2 (5% EtOAc in hexane); white solid (44.4 mg, 88% yield in MeCN and 44.4 mg, 88% yield in H_2O); m. p. = 165–167 °C; ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.06 (br s, 1H), 7.52 – 7.50 (m, 2H), 7.45 – 7.35 (m, 4H), 7.26 – 7.10 (m, 9H), 6.95 – 6.91 (m, 1H), 5.76 (s, 1H), 5.06 (s, 1H), 1.34 (s, 18H); ^{13}C{^{1}H} NMR (100 MHz, $CDCl_3$) δ 152.0, 145.1, 136.3, 135.6, 135.4, 134.4, 133.4, 129.1, 128.9, 128.7, 128.4, 128.1, 127.9, 126.2, 125.8, 121.9, 121.8, 119.5, 116.3, 110.8, 47.8, 34.4, 30.5; FT-IR (thin film, neat): 3639, 3405, 2957, 1739, 1435, 1365, 1232, 1154, 742, 700 cm^{-1}; HRMS (ESI): *m/z* calcd for $C_{35}H_{36}NO$ $[M–H]^–$: 486.2797; found : 486.2789.

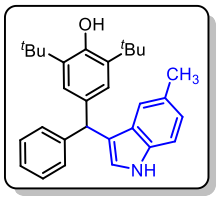
2,6-Di-*tert*-butyl-4-((3-methyl-1*H*-indol-2-yl)(phenyl)methyl)phenol (4c)



The reaction was performed at 0.152 mmol scale of **1d**; R_f = 0.3 (5% EtOAc in hexane); yellow solid (48.6 mg, 75% yield in MeCN and 55.0 mg, 84% yield in H_2O); m. p. = 160–162 °C; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.55 – 7.47 (m, 2H), 7.32 – 7.28 (m, 2H), 7.26 – 7.21 (m, 2H), 7.16 – 7.08 (m, 4H), 6.97 (s, 2H), 5.67 (s, 1H), 5.16 (s,

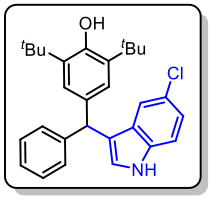
1H), 2.16 (s, 3H), 1.38 (s, 18H); $^{13}C\{^{1}H\}$ NMR (100 MHz, $CDCl_3$) δ 152.7, 142.9, 136.3, 136.1, 135.2, 132.4, 129.8, 129.0, 128.5, 126.6, 125.8, 121.2, 119.1, 118.4, 110.6, 108.0, 48.7, 34.5, 30.4, 8.82, 8.81; FT-IR (thin film, neat): 3638, 3459, 2958, 1611, 1435, 1236, 740, 701 cm^{-1}; HRMS (ESI): *m/z* calcd for $C_{30}H_{34}NO$ $[M–H]^-$: 424.2640; found : 424.2650.

2,6-Di-*tert*-butyl-4-((5-methyl-1*H*-indol-3-yl)(phenyl)methyl)phenol (4d)



The reaction was performed at 0.158 mmol scale of **1e**; R_f = 0.3 (5% EtOAc in hexane); White solid (41.0 mg, 88% yield in MeCN and 38.9 mg, 84% yield in H_2O); m. p. = 190–192 ºC; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.82 (br s, 1H), 7.29 – 7.26 (m, 4H), 7.24 – 7.17 (m, 2H), 7.05 (s, 3H), 6.99 (d, *J* = 8.3 Hz, 1H), 6.58 (d, *J* = 1.6 Hz, 1H), 5.56 (s, 1H), 5.07 (s, 1H), 2.34 (s, 3H),1.38 (s, 18H); $^{13}C\{^{1}H\}$ NMR (100 MHz, $CDCl_3$) δ 152.1, 144.8, 135.4, 135.1, 134.8, 129.1, 128.5, 128.2, 127.5, 126.0, 125.7, 124.1, 123.6, 120.4, 119.7, 110.7, 48.8, 34.5, 30.5, 21.6; FT-IR (thin film, neat): 3639, 3417, 2958, 1434, 1232, 1155, 795, 701 cm^{-1}; HRMS (ESI): *m/z* calcd for $C_{30}H_{34}NO$ $[M–H]^-$: 424.2640; found : 424.2651.

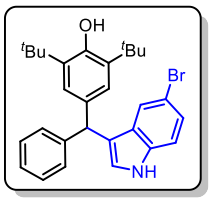
2,6-Di-*tert*-butyl-4-((5-chloro-1*H*-indol-3-yl)(phenyl)methyl)phenol (4e)



The reaction was performed at 0.131 mmol scale of **1f**; R_f = 0.2 (5% EtOAc in hexane); White solid (52.0 mg, 88% yield in MeCN and 49.0 mg, 83% yield in H_2O); m. p. = 177–179 ºC; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.94 (br s, 1H), 7.31 – 7.29 (m, 1H), 7.27 – 7.26 (m, 1H), 7.25 – 7.19 (m, 5H), 7.10 (dd, *J* = 8.6, 1.9 Hz, 1H), 7.03 (s, 2H), 6.64 (d, *J* = 1.6 Hz, 1H), 5.52 (s, 1H), 5.09 (s, 1H), 1.38 (s, 18H); $^{13}C\{^{1}H\}$ NMR (100 MHz, $CDCl_3$) δ 152.3, 144.3, 135.1, 135.4, 134.1, 129.0, 128.4, 128.3, 126.3, 125.6, 125.3, 125.0, 122.4, 120.7, 119.6, 112.1, 48.7, 34.5, 30.5; FT-IR (thin film, neat): 3635, 3424, 2958, 1463, 1435, 1234,

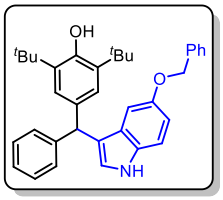
1154, 1077, 794, 702 cm^{-1}; HRMS (ESI): *m/z* calcd for $C_{29}H_{31}ClNO$ $[M–H]^-$: 444.2094; found : 444.2095.

4-((5-Bromo-1*H*-indol-3-yl)(phenyl)methyl)-2,6-di-*tert*-butylphenol (4f)



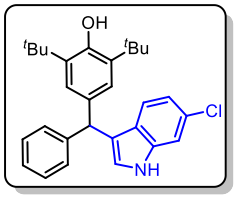
The reaction was performed at 0.102 mmol scale of **1g**; R_f = 0.1 (5% EtOAc in hexane); White solid (48.3 mg, 97% yield in MeCN and 41.9 mg, 84% yield in H_2O); m. p. = 191–193 ºC; $^1H\{^1H\}$ NMR (400 MHz, $CDCl_3$) δ 7.95 (br s, 1H), 7.354 – 7.35 (m, 1H), 7.31 – 7.28 (m, 1H), 7.27 – 7.26 (m, 1H), 7.25 – 7.19 (m, 5H), 7.02 (s, 2H), 6.63 (dd, *J* = 2.4, 0.9 Hz, 1H), 5.51 (s, 1H), 5.09 (s, 1H), 1.38 (s, 18H); ^{13}C NMR (1F00 MHz, $CDCl_3$) δ 152.3, 144.3, 135.6, 135.4, 134.1, 128.96, 128.95, 128.4, 126.3, 125.6, 125.1, 124.9, 122.7, 120.6, 112.6, 112.5, 48.7, 34.5, 30.5; FT-IR (thin film, neat): 3635, 3423, 2959, 1493, 1435, 1234, 1155, 739, 702 cm^{-1}; HRMS (ESI): *m/z* calcd for $C_{29}H_{31}BrNO$ $[M–H]^-$: 488.1589; found : 488.1578.

4-((5-(Benzyloxy-1*H*-indol-3-yl)(phenyl)methyl)-2,6-di-*tert*-butylphenol (4g)



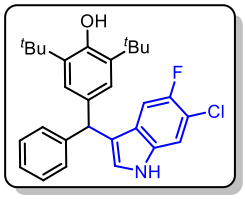
The reaction was performed at 0.090 mmol scale of **1h**; R_f = 0.1 (5% EtOAc in hexane); Yellow solid (44.9 mg, 97% yield in MeCN and 39.4 mg, 85% yield in H_2O); m. p. = 143–145 ºC; ^1H NMR (400 MHz, $CDCl_3$) δ 7.82 (br s, 1H), 7.39 – 7.34 (m, 4H), 7.32 – 7.26 (m, 5H), 7.24 – 7.18 (m, 2H), 7.07 (s, 2H), 6.89 (dd, *J* = 8.8, 2.2 Hz, 1H), 6.71 (d, *J* = 1.5 Hz, 1H), 5.60 (d, *J* = 1.5 Hz, 1H), 5.51 (s, 1H), 5.08 (s, 1H), 4.88 (s, 2H), 1.38 (s, 18H); $^{13}C\{^1H\}$ NMR (100 MHz, $CDCl_3$) δ 152.9, 152.1, 144.6, 137.7, 135.5, 134.5, 132.1, 129.0, 128.6, 128.3, 127.84, 127.79, 127.6, 126.1, 125.7, 124.7, 120.7, 112.8, 111.7, 103.6, 70.8, 49.0, 34.5, 30.5; FT-IR (thin film, neat): 3635, 3422, 2958, 1481, 1453, 1435, 1265, 1186, 737, 700 cm^{-1}; HRMS (ESI): *m/z* calcd for $C_{36}H_{38}NO_2$ $[M–H]^-$: 516.2903; found : 5162897.

2,6-Di-*tert*-butyl-4-((6-chloro-1*H*-indol-3-yl)(phenyl)methyl)phenol (4h)



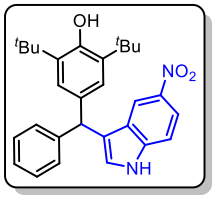
The reaction was performed at 0.132 mmol scale of **1i**; R_f = 0.3 (5% EtOAc in hexane); brown solid (51.3 mg, 87% yield in MeCN and 48.2 mg, 82% yield in H_2O); m. p. = 132–134 ºC; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.92 (br s, 1H), 7.32 (d, J = 1.4 Hz, 1H), 7.30 – 7.26 (m, 2H), 7.24 – 7.18 (m, 3H), 7.09 (d, J = 8.5 Hz, 1H), 7.03 (s, 2H), 6.95 (dd, J = 8.5, 1.5 Hz, 1H), 6.59 (d, J = 1.3 Hz, 1H), 5.53 (s, 1H), 5.09 (s, 1H), 1.37 (s, 18H); ^{13}C{^{1}H} NMR (100 MHz, $CDCl_3$) δ 152.2, 144.4, 137.2, 135.6, 134.2, 129.0, 128.3, 127.9, 126.2, 125.8, 125.6, 124.6, 121.1, 120.1, 111.0, 48.8, 34.5, 30.5; FT-IR (thin film, neat): 3636, 3420, 2959, 1600, 1452, 1234, 1154, 807, 739, 703 cm^{-1}; HRMS (ESI): *m/z* calcd for $C_{29}H_{31}ClNO$ $[M–H]^–$: 444.2094; found : 444.2099.

2,6-Di-*tert*-butyl-4-((6-chloro-5-fluoro-1*H*-indol-3-yl)(phenyl)methyl)phenol (4i)



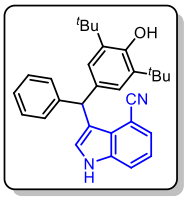
The reaction was performed at 0.118 mmol scale of **1j**; R_f = 0.1 (5% EtOAc in hexane); Yellow solid (46.7 mg, 85% yield in MeCN and 49.3mg, 90% yield in H_2O); m. p. = 148–150 ºC; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.90 (br s, 1H), 7.34 (d, J = 6.1 Hz, 1H), 7.30 – 7.27 (m, 2H), 7.23 – 7.19 (m, 3H), 7.02 (s, 2H), 6.89 (d, J = 9.9 Hz, 1H), 6.65 (d, J = 1.6 Hz, 1H), 5.46 (s, 1H), 5.10 (s, 1H), 1.37 (s, 18H); ^{13}C{^{1}H} NMR (100 MHz, $CDCl_3$) δ 152.7 (d, $J_{C\text{-}F}$ = 236.2 Hz), 152.3, 144.1, 135.7, 133.8, 133.0, 128.9, 128.4, 126.4, 126.17 (d, $J_{C\text{-}F}$ = 8.5 Hz), 126.1, 125.5 (2C), 121.3 (d, $J_{C\text{-}F}$ = 4.6 Hz), 115.7 (d, $J_{C\text{-}F}$ = 21.4 Hz), 112.2, 106.3 (d, $J_{C\text{-}F}$ = 23.6 Hz), 48.8, 34.5, 30.5; ^{19}F{^{1}H} NMR (376 MHz, $CDCl_3$) δ –126.91; FT-IR (thin film, neat): 3638, 3410, 2959, 1473, 1456, 1435, 1316, 1235, 702 cm^{-1}; HRMS (ESI): *m/z* calcd for $C_{29}H_{30}ClFNO$ $[M–H]^–$: 462.2000; found : 462.2010.

2,6-Di-*tert*-butyl-4-((5-nitro-1*H*-indol-3-yl)(phenyl)methyl)phenol (4j)



The reaction was performed at 0.123 mmol scale of **1k**; R_f = 0.2 (10% EtOAc in hexane); Yellow solid (53.4mg, 95% yield in MeCN and 46.0mg, 82% yield in H_2O); m. p. = 198–200 ºC; ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.40 (s, 1H), 8.19 (d, *J* = 2.0 Hz, 1H), 8.07 (dd, *J* = 9.0, 2.2 Hz, 1H), 7.36 (d, *J* = 9.0 Hz, 1H), 7.31 – 7.28 (m, 2H), 7.26 – 7.20 (m, 3H), 7.03 (s, 2H), 6.81 (d, *J* = 1.2 Hz, 1H), 5.60 (s, 1H), 5.12 (s, 1H), 1.37 (s, 18H); ^{13}C{^{1}H} NMR (100 MHz, $CDCl_3$) δ 152.4, 143.8, 141.5, 139.8, 135.9, 133.6, 128.9, 128.5, 126.8, 126.7, 126.6, 125.5, 123.5, 117.9, 117.6, 111.1, 48.6, 34.5, 30.4; FT-IR (thin film, neat): 3634, 3400, 2959, 1519, 1470, 1434, 1333, 739, 702 cm^{-1}; HRMS (ESI): *m/z* calcd for $C_{29}H_{31}N_2O_3$ [M–H]$^-$: 455.2335; found : 455.2349.

3-((3,5-Di-*tert*-butyl-4-hydroxyphenyl)(phenyl)methyl)-1*H*-indole-4-carbonitrile (4k)

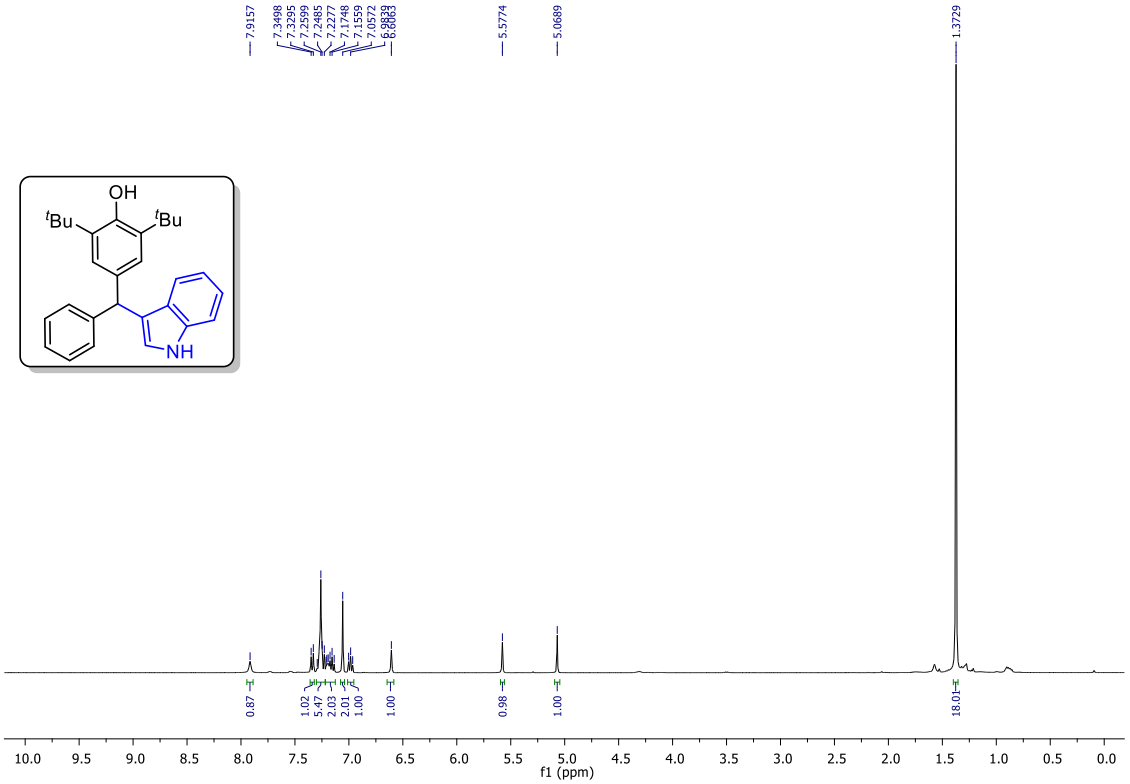


The reaction was performed at 0.140 mmol scale of **1l**; R_f = 0.2 (10% EtOAc in hexane); Brownish white solid (58.3mg, 95% yield in MeCN and 50.3mg, 82% yield in H_2O); m. p. = 194–196 ºC; ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.53 (br s, 1H), 7.56 (d, *J* = 8.2 Hz, 1H), 7.39 (d, *J* = 7.3 Hz, 1H), 7.28 – 7.26 (m, 1H), 7.24 – 7.22 (m, 3H), 7.20 – 7.15 (m, 2H), 7.05 (s, 2H), 6.80 (d, *J* = 2.2 Hz, 1H), 6.16 (s, 1H), 5.10 (s, 1H), 1.38 (s, 18H); ^{13}C{^{1}H} NMR (100 MHz, $CDCl_3$) δ 152.2, 144.5, 136.9, 135.5, 134.5, 129.2, 128.2, 127.4, 126.7, 126.3, 126.2, 125.9, 121.5, 120.8, 119.4, 116.3, 102.4, 47.4, 34.4, 30.4; FT-IR (thin film, neat): 3635, 3400, 3333, 2959, 2217, 1600, 1434, 1348, 1234, 1155, 1121, 1045, 740, 702 cm^{-1}; HRMS (ESI): *m/z* calcd for $C_{30}H_{32}N_2NaO$ [M+Na]$^+$: 459.2412; found : 459.2424.

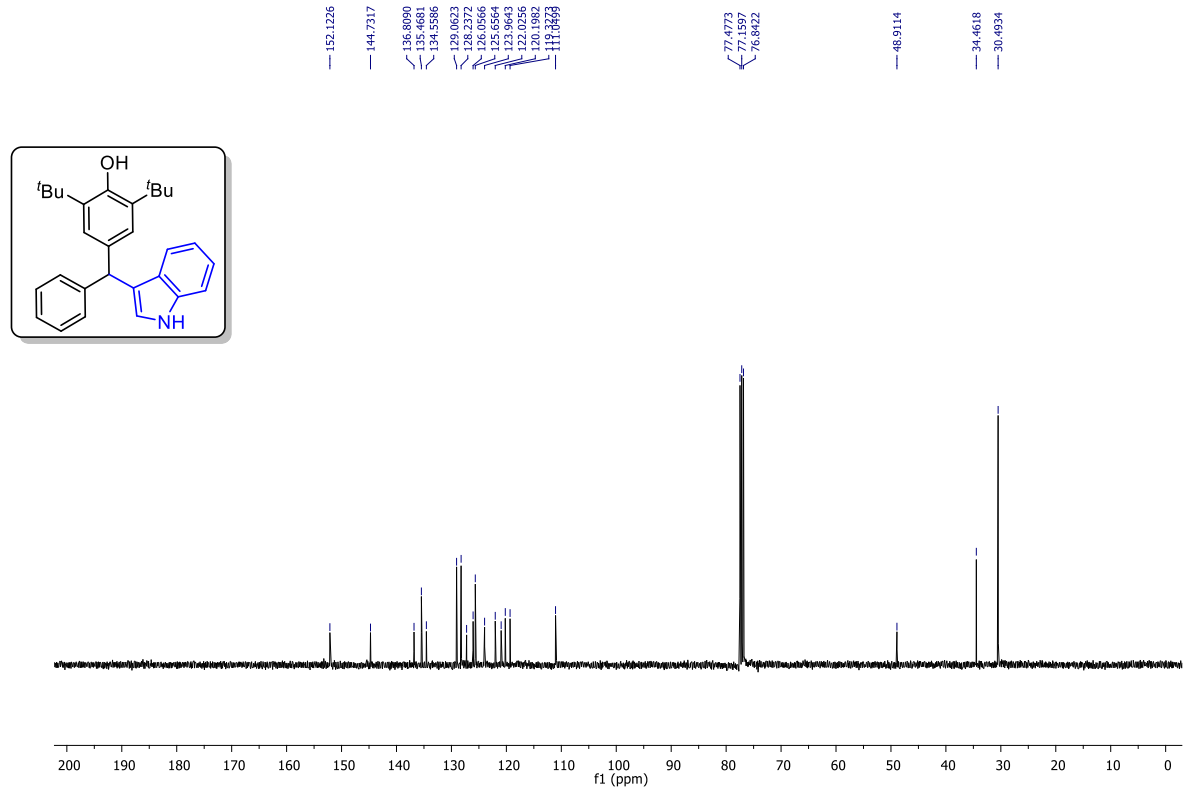
4. References:

(1) P. K. Ranga, F. Ahmad, P. Nager, P. S. Rana and R. V. Anand, *J. Org. Chem.*, 2021, **86**, 4994.

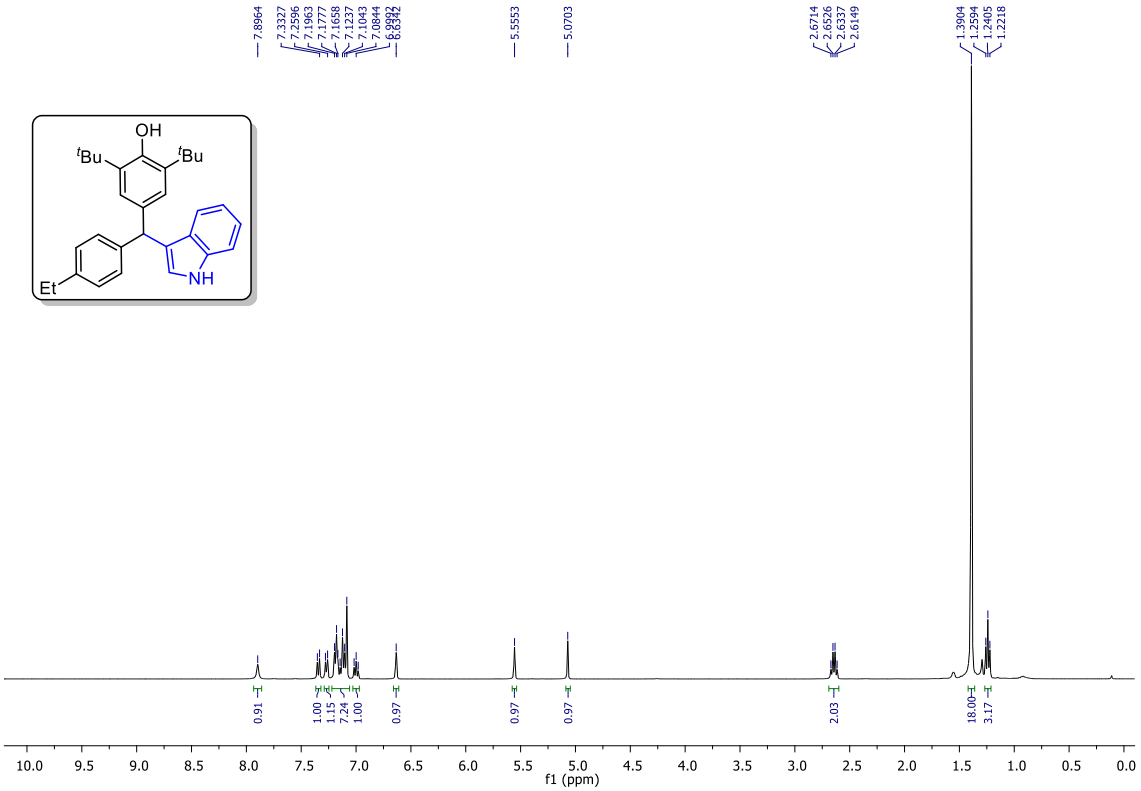
^{1}H NMR (400 MHz, $CDCl_3$) spectrum of **3a**



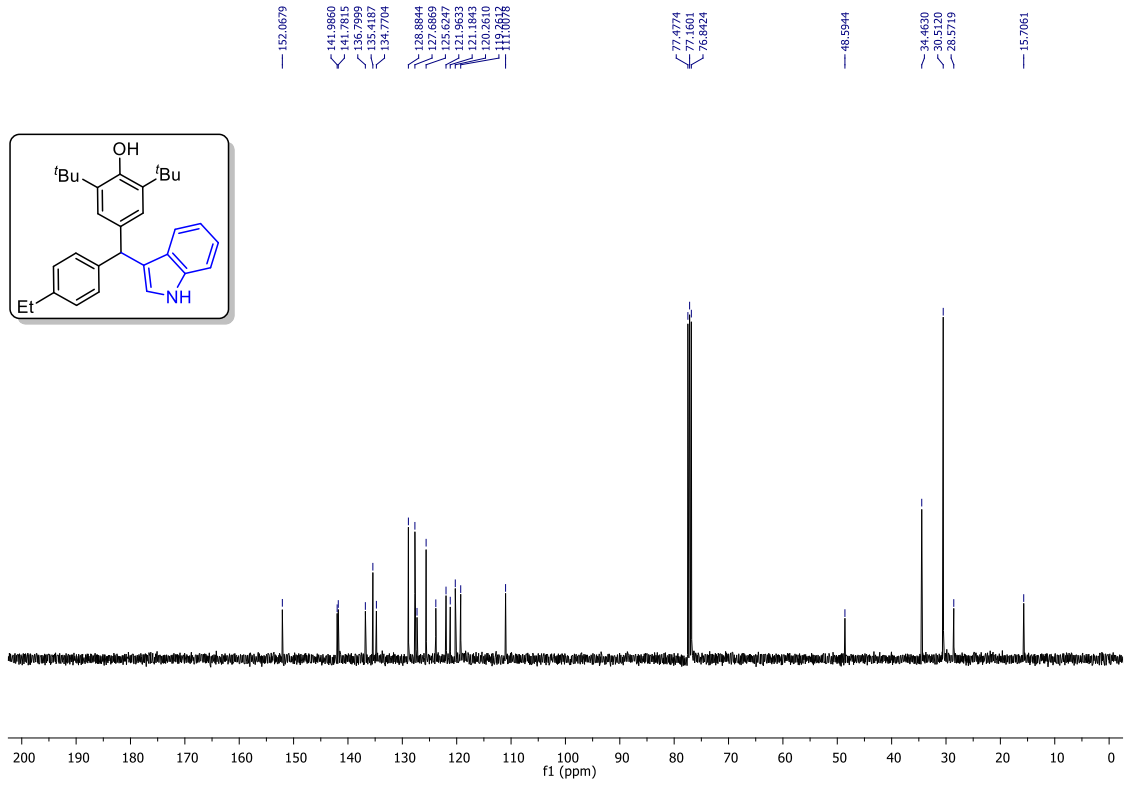
$^{13}C\{^{1}H\}$ NMR (100 MHz, $CDCl_3$) spectrum of **3a**



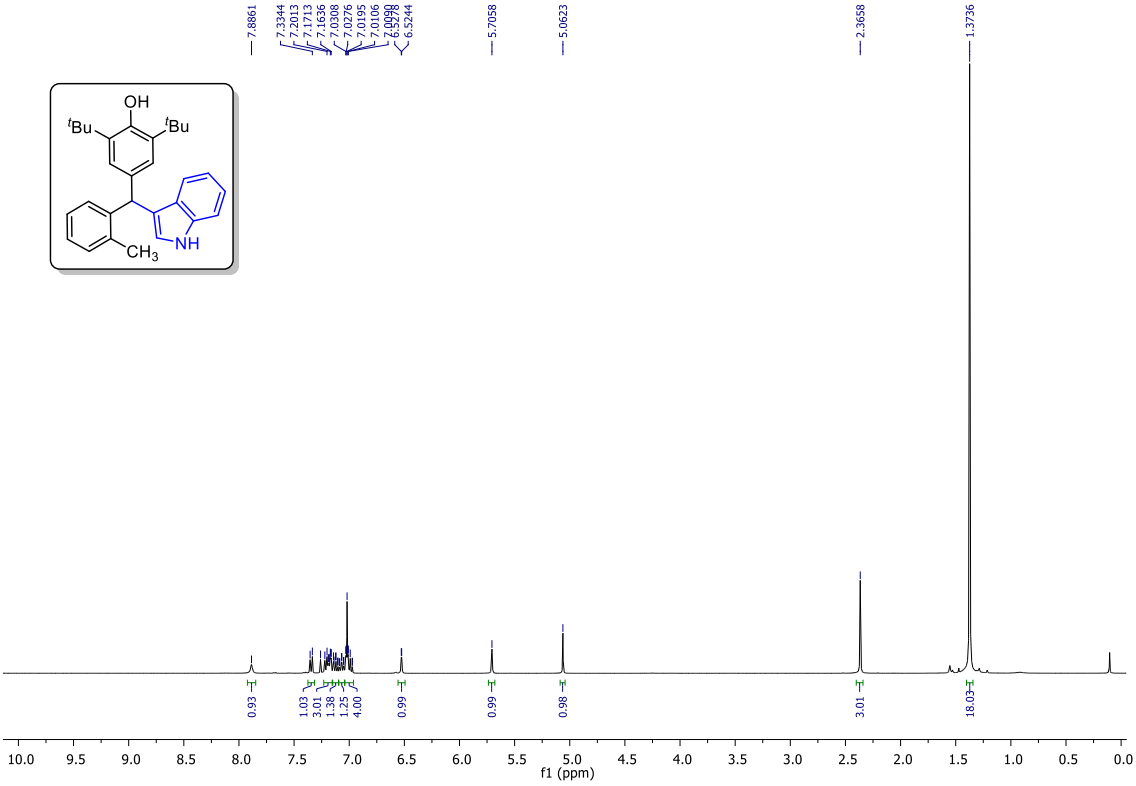
^{1}H NMR (400 MHz, $CDCl_3$) spectrum of **3b**



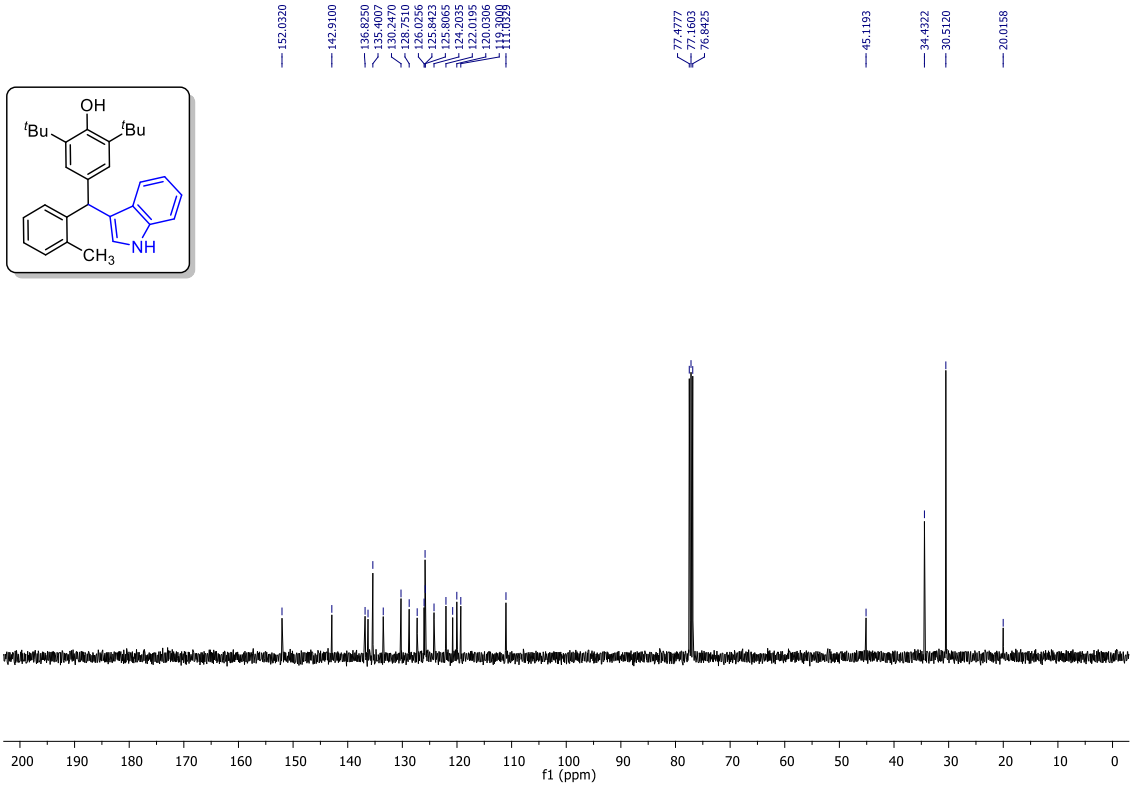
^{13}C{^{1}H} NMR (100 MHz, $CDCl_3$) spectrum of **3b**



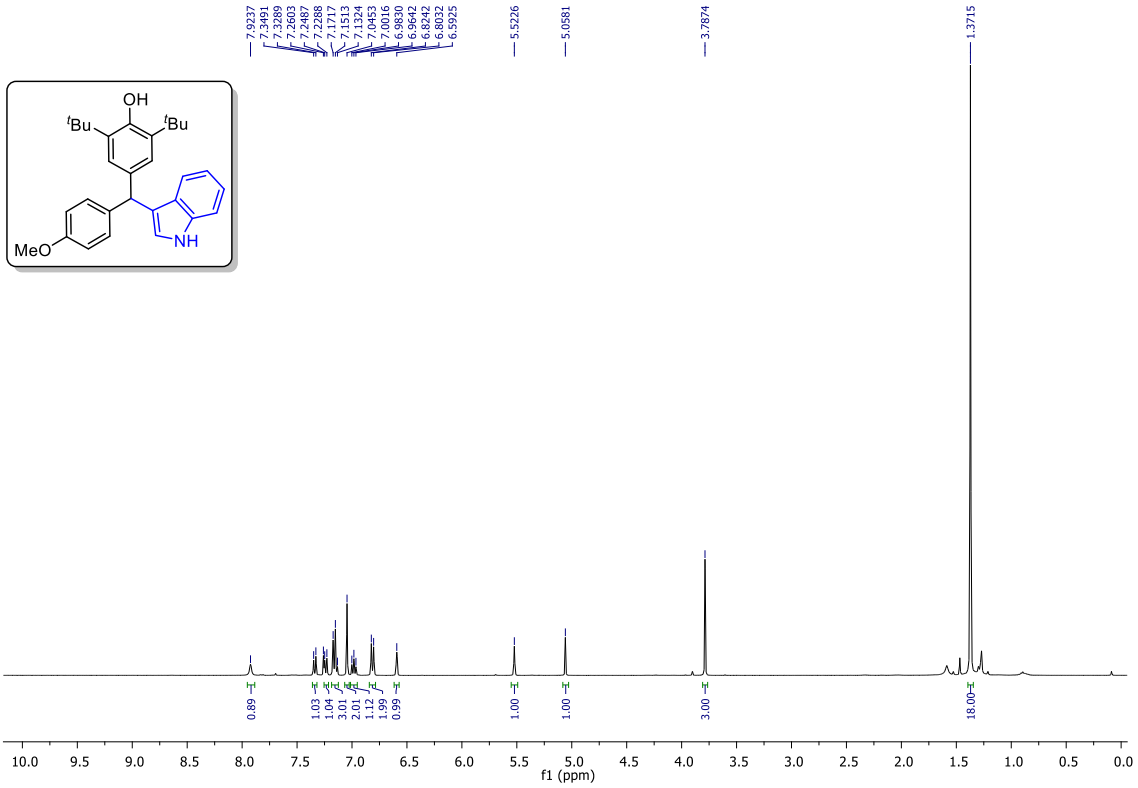
^{1}H NMR (400 MHz, $CDCl_3$) spectrum of **3c**



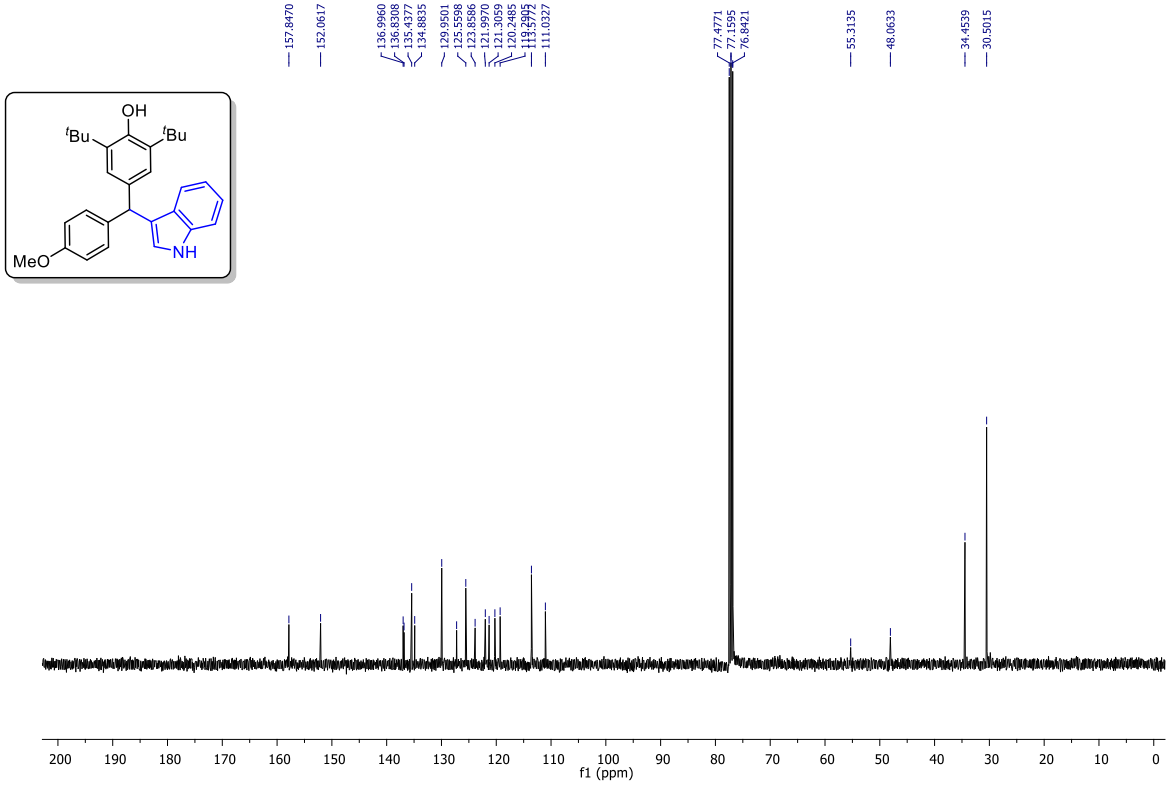
^{13}C{^{1}H} NMR (100 MHz, $CDCl_3$) spectrum of **3c**



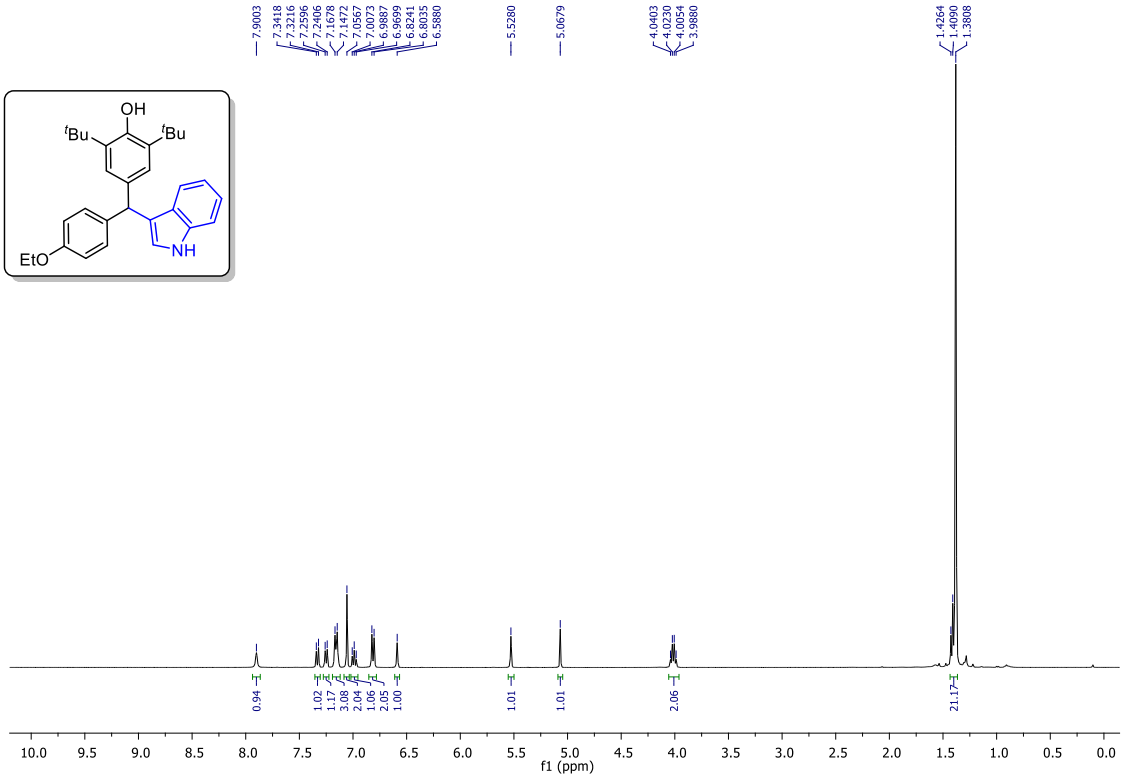
^{1}H NMR (400 MHz, $CDCl_3$) spectrum of **3d**



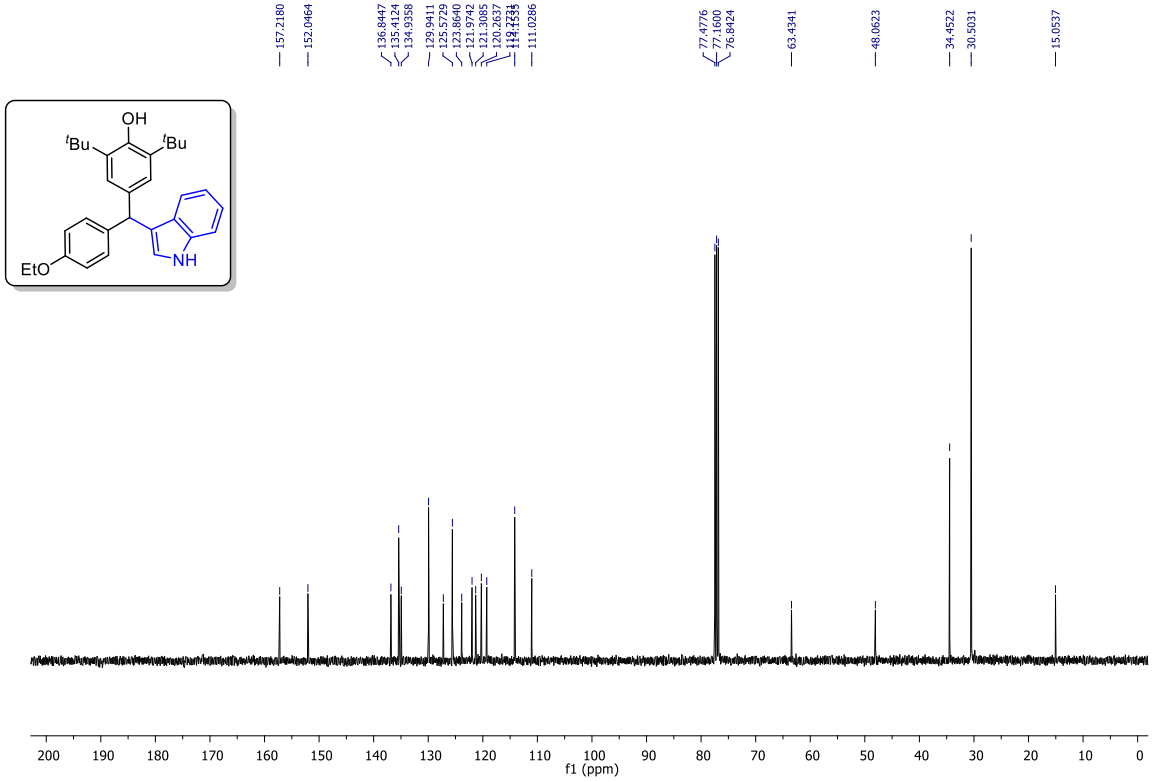
$^{13}C\{^{1}H\}$ NMR (100 MHz, $CDCl_3$) spectrum of **3d**



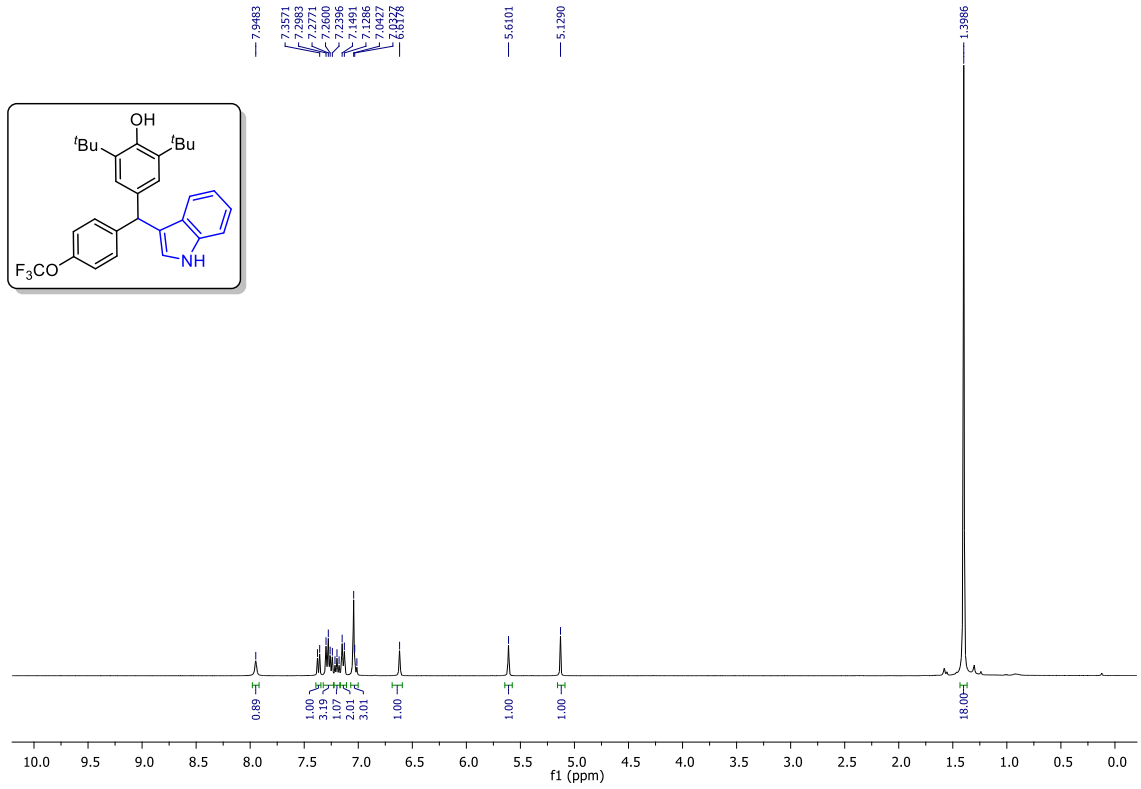
^{1}H NMR (400 MHz, $CDCl_3$) spectrum of **3e**



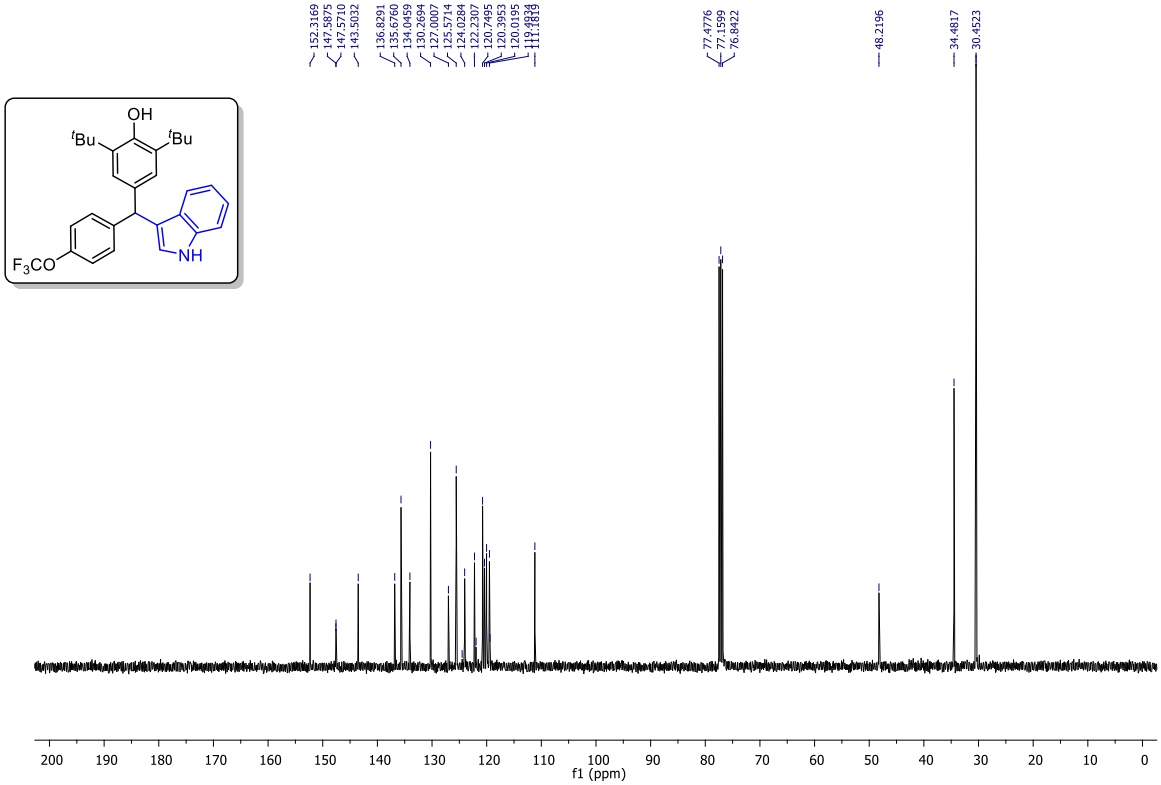
^{13}C{^{1}H} NMR (100 MHz, $CDCl_3$) spectrum of **3e**



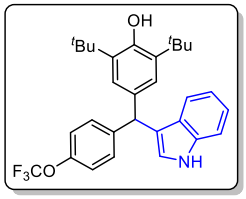
^{1}H NMR (400 MHz, $CDCl_3$) spectrum of **3f**



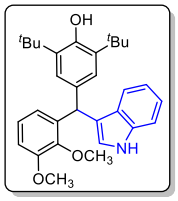
^{13}C{^{1}H} NMR (100 MHz, $CDCl_3$) spectrum of **3f**



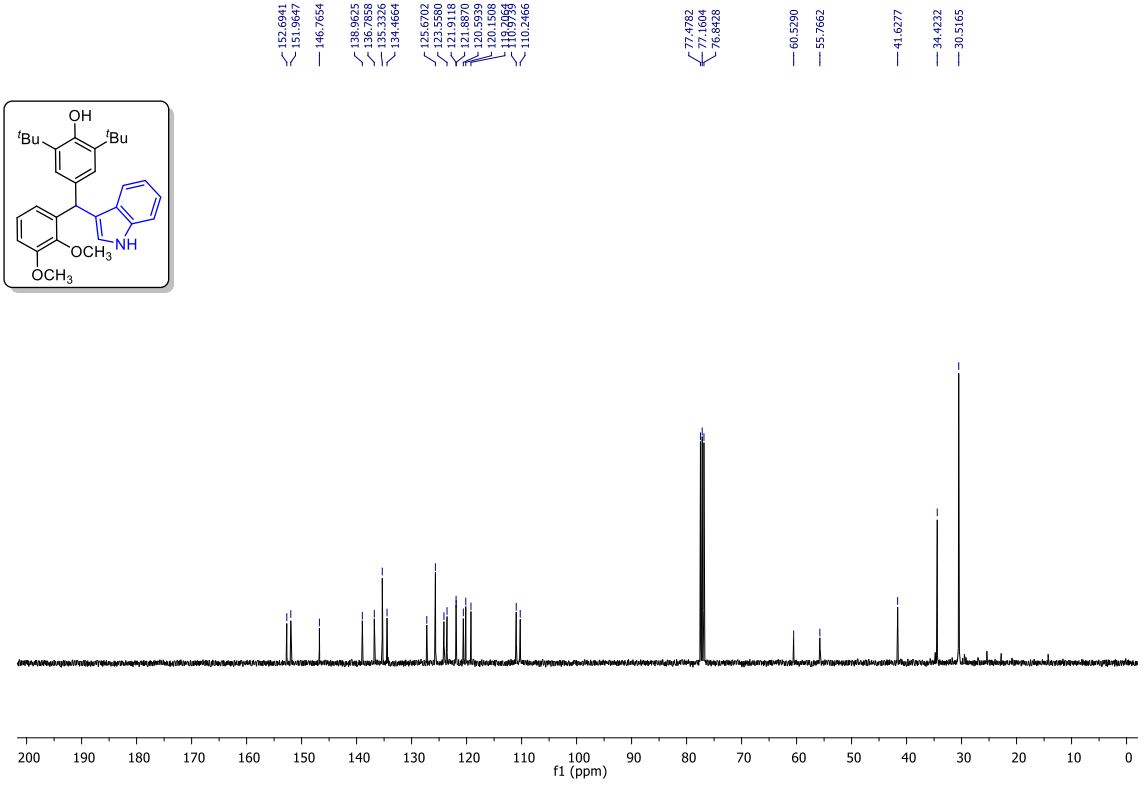
$^{19}F\{^{1}H\}$ NMR (376 MHz, $CDCl_3$) spectrum of **3f**



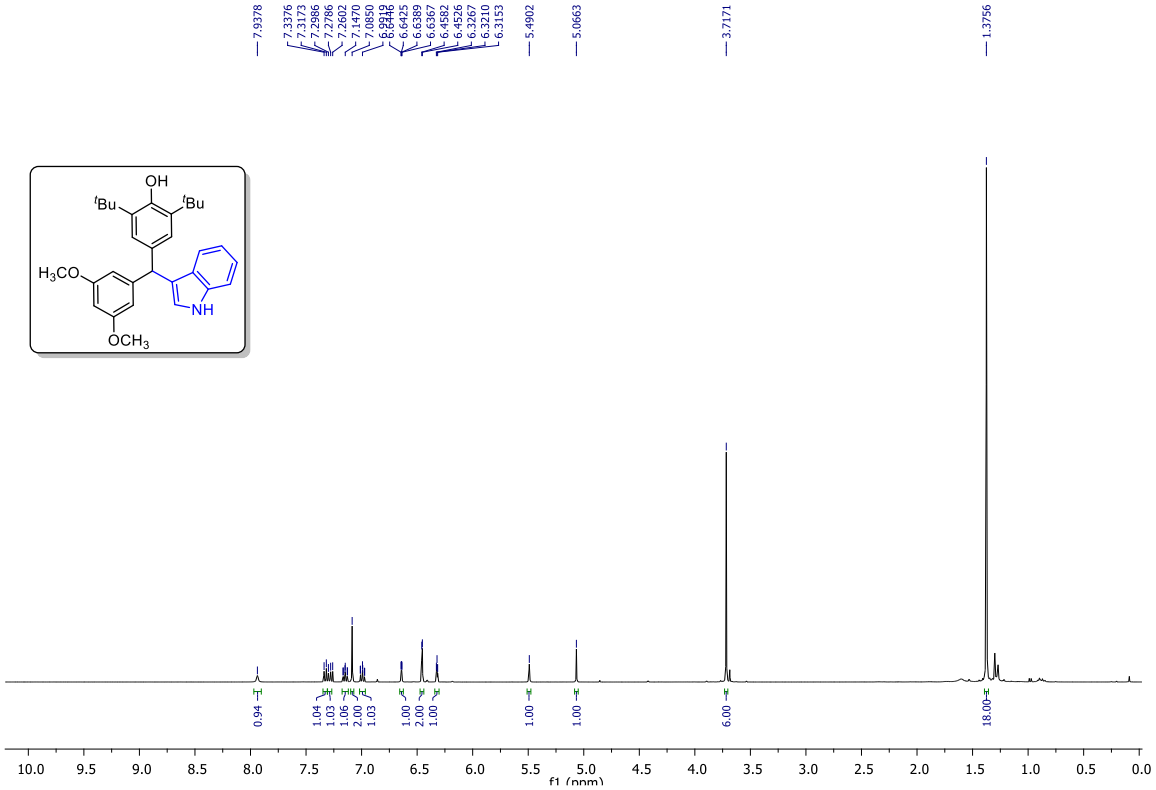
^{1}H NMR (400 MHz, $CDCl_3$) spectrum of **3g**



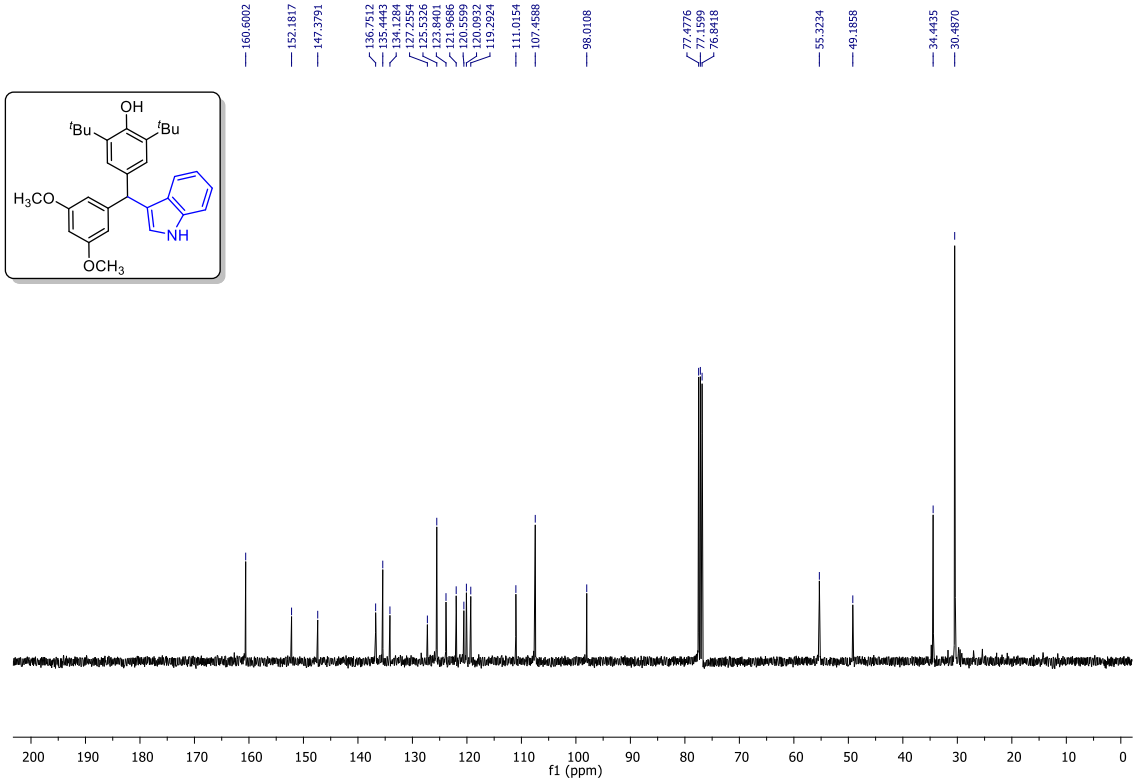
$^{13}C\{^{1}H\}$ NMR (100 MHz, $CDCl_3$) spectrum of **3g**



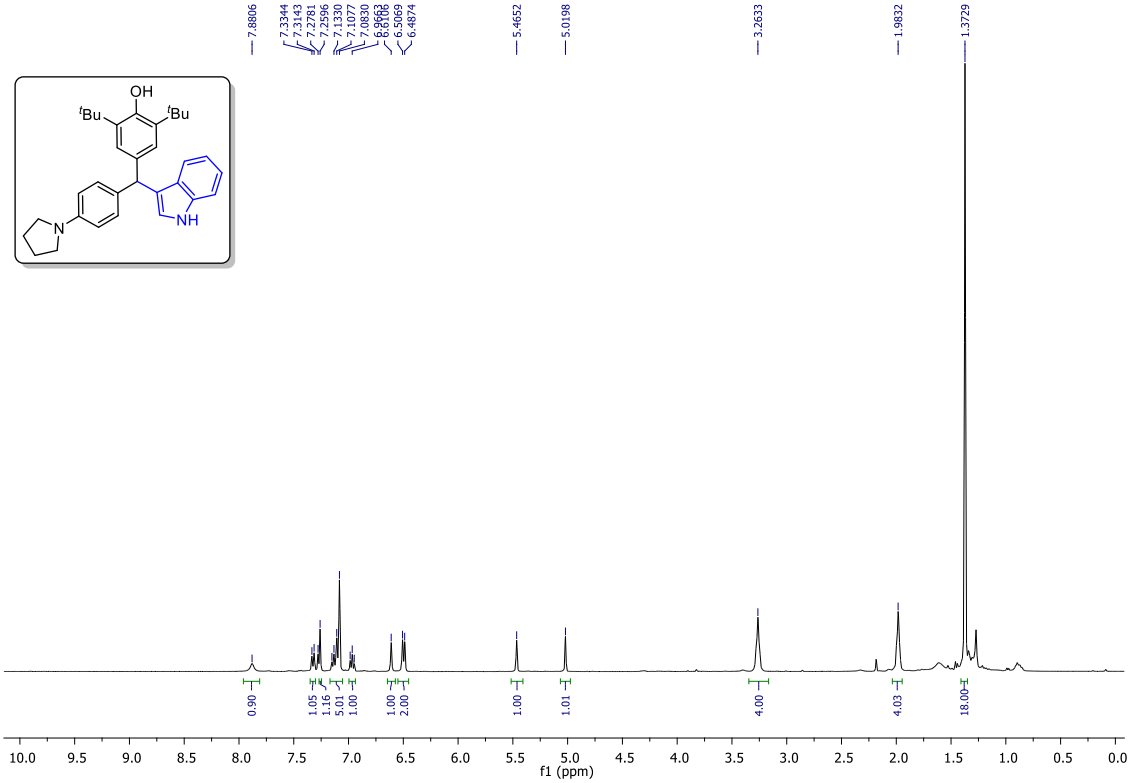
^{1}H NMR (400 MHz, $CDCl_3$) spectrum of **3h**



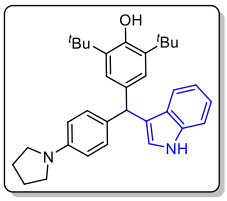
$^{13}C\{^{1}H\}$ NMR (100 MHz, $CDCl_3$) spectrum of **3h**



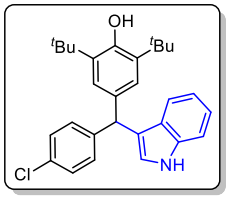
^{1}H NMR (400 MHz, $CDCl_3$) spectrum of **3i**

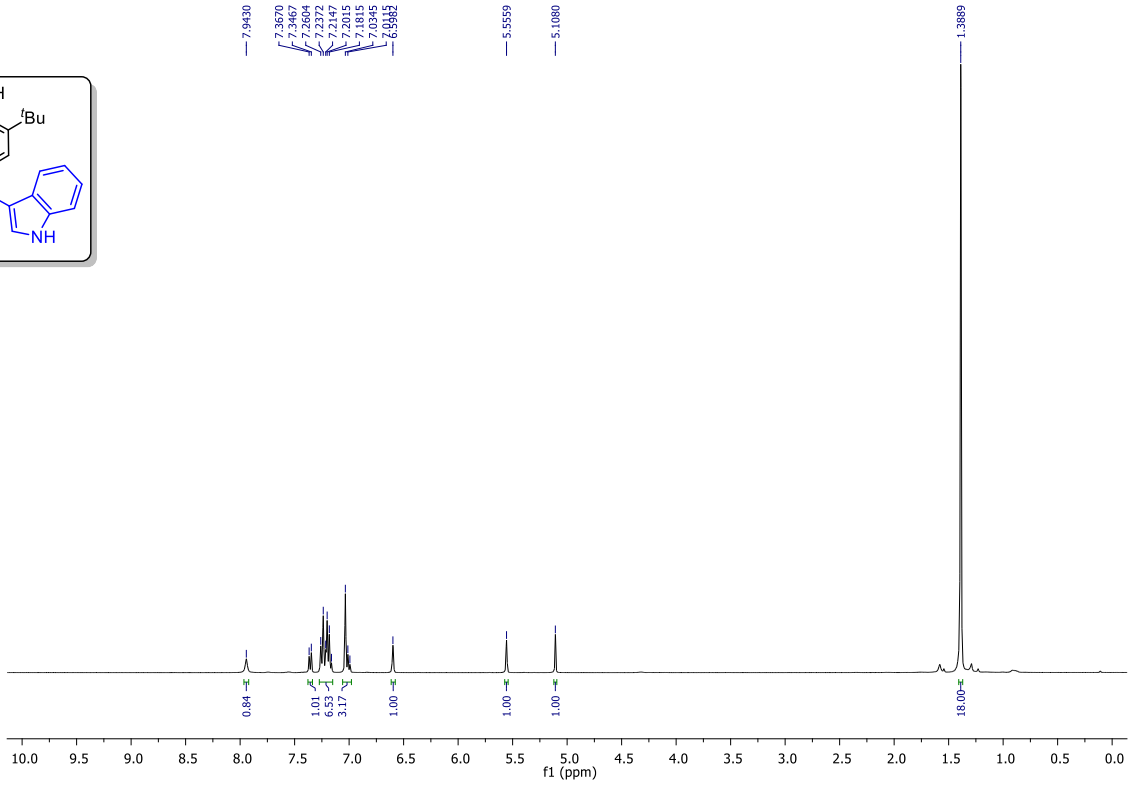


$^{13}C\{^{1}H\}$ NMR (100 MHz, $CDCl_3$) spectrum of **3j**

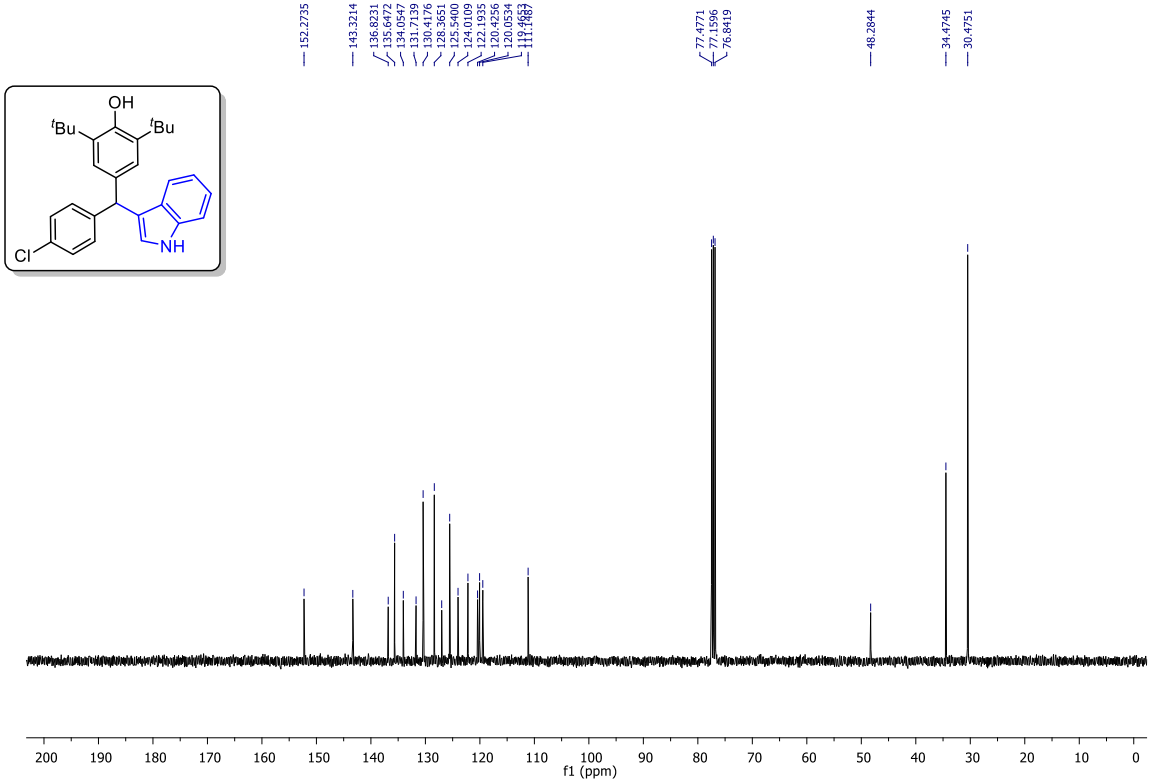


^{1}H NMR (400 MHz, $CDCl_3$) spectrum of **3j**

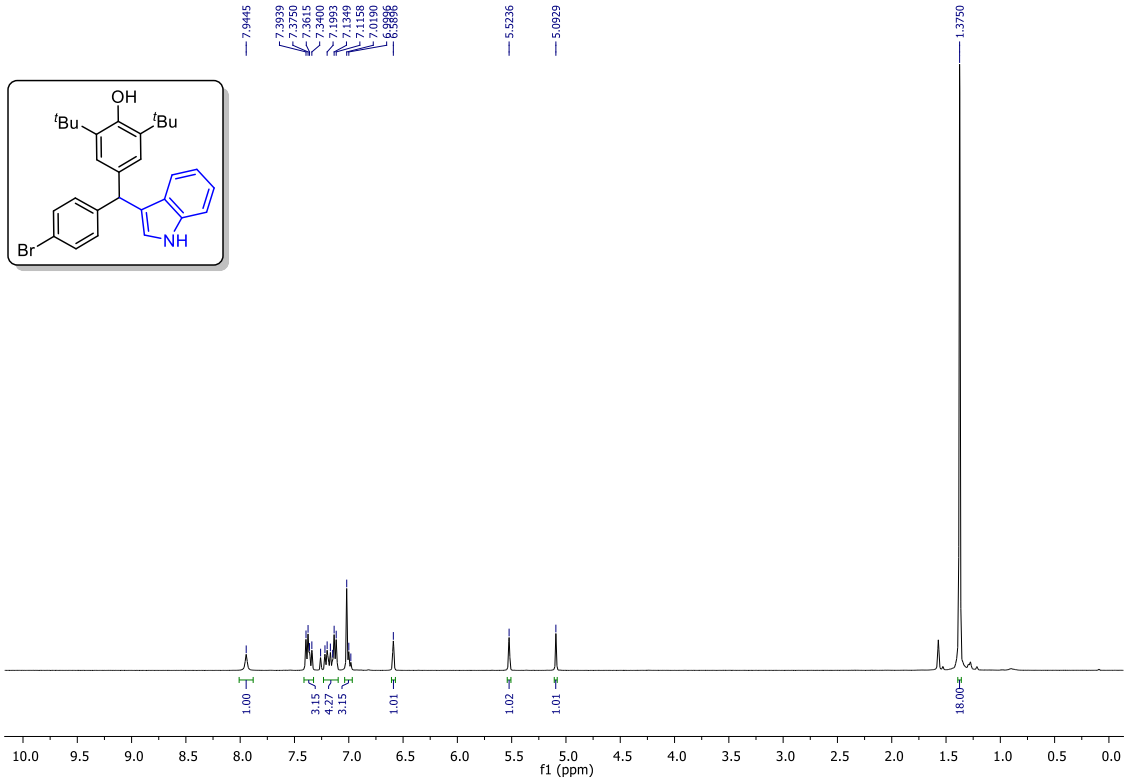




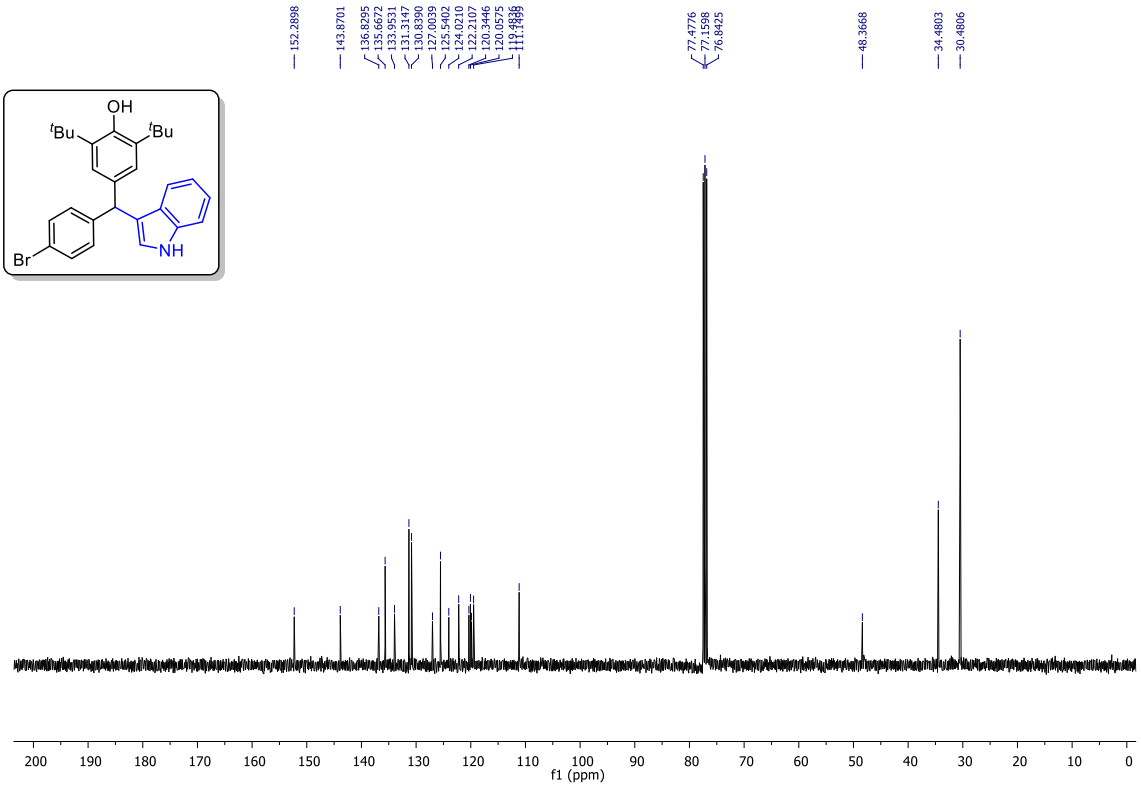
$^{13}C\{^{1}H\}$ NMR (100 MHz, $CDCl_3$) spectrum of **3j**



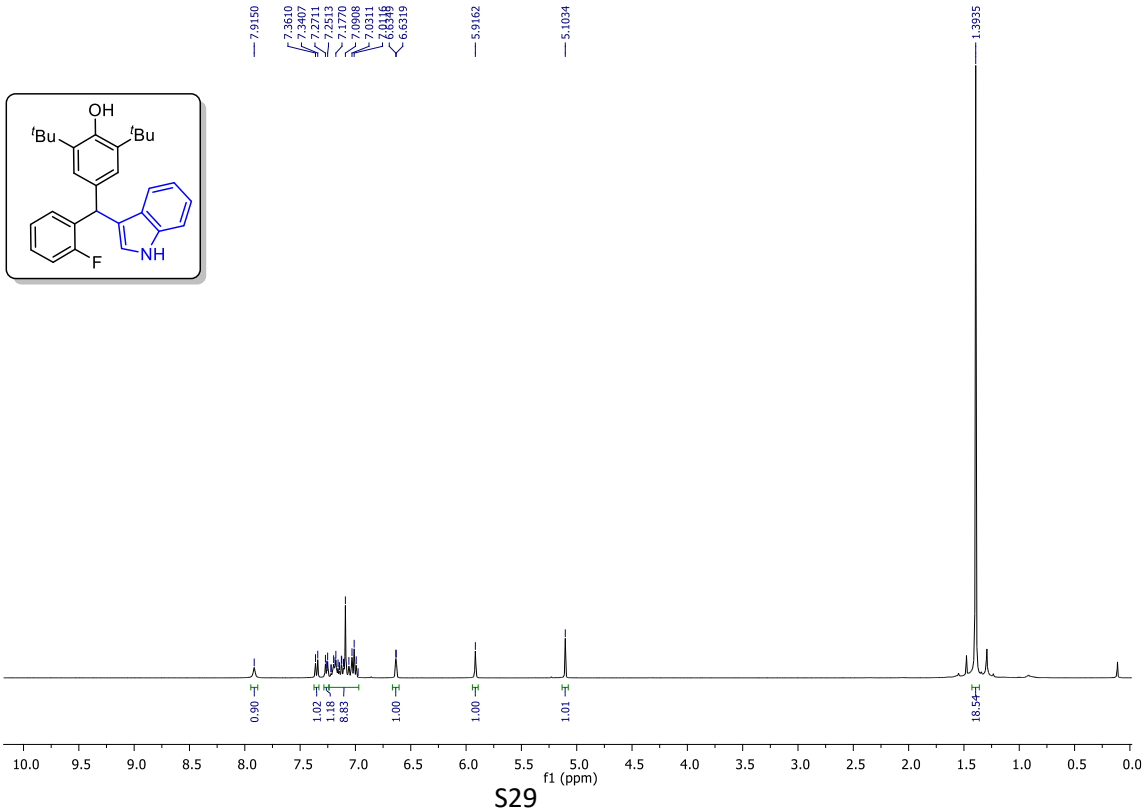
^{1}H NMR (400 MHz, $CDCl_3$) spectrum of **3k**



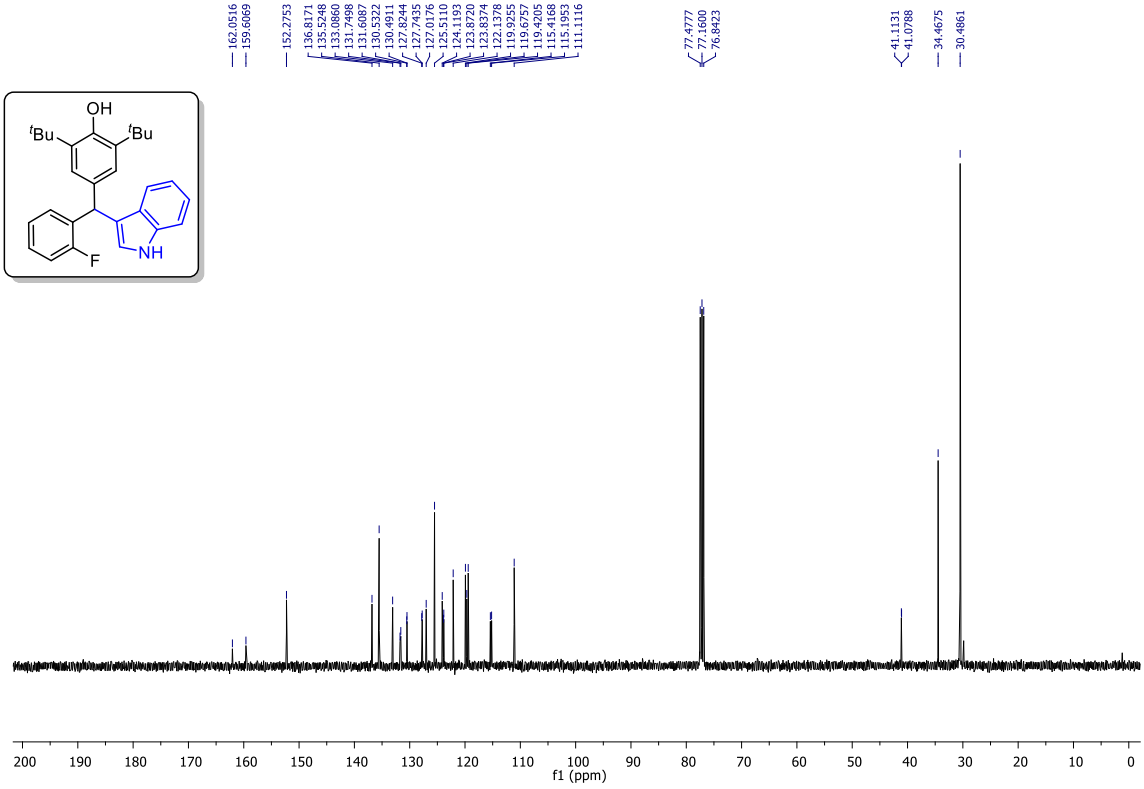
$^{13}C\{^{1}H\}$ NMR (100 MHz, $CDCl_3$) spectrum of **3k**



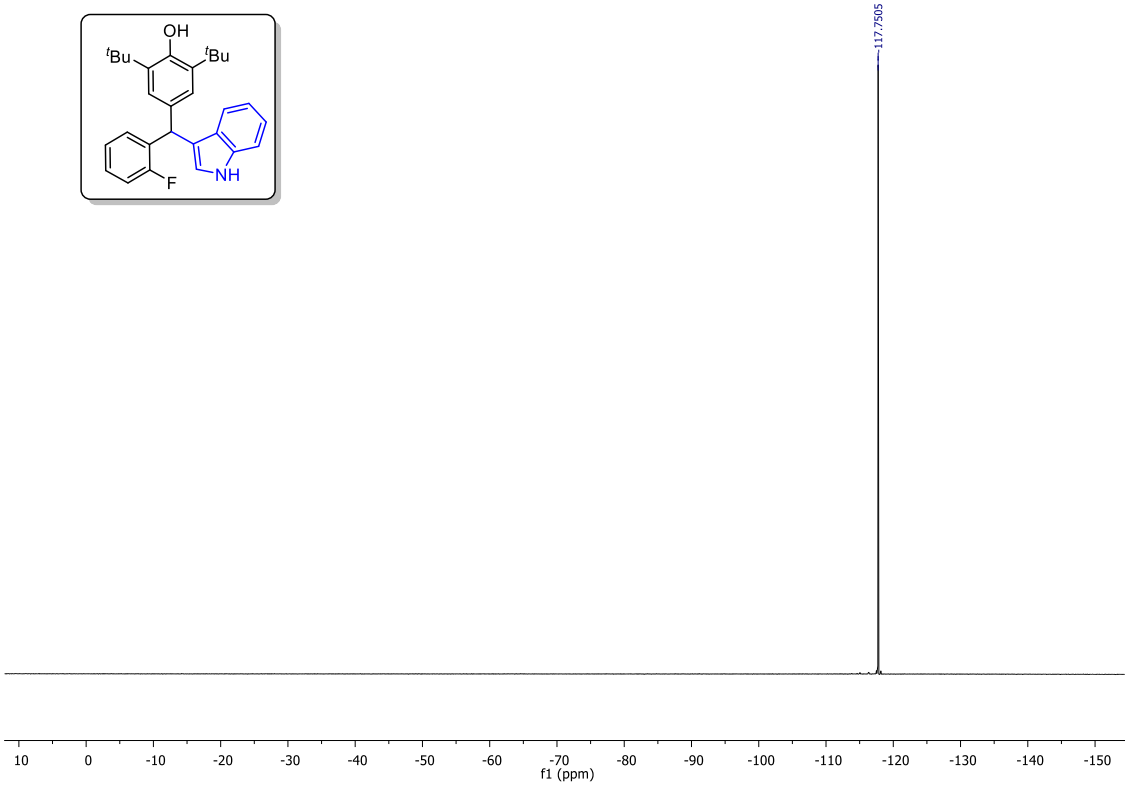
^{1}H NMR (400 MHz, $CDCl_3$) spectrum of **3l**



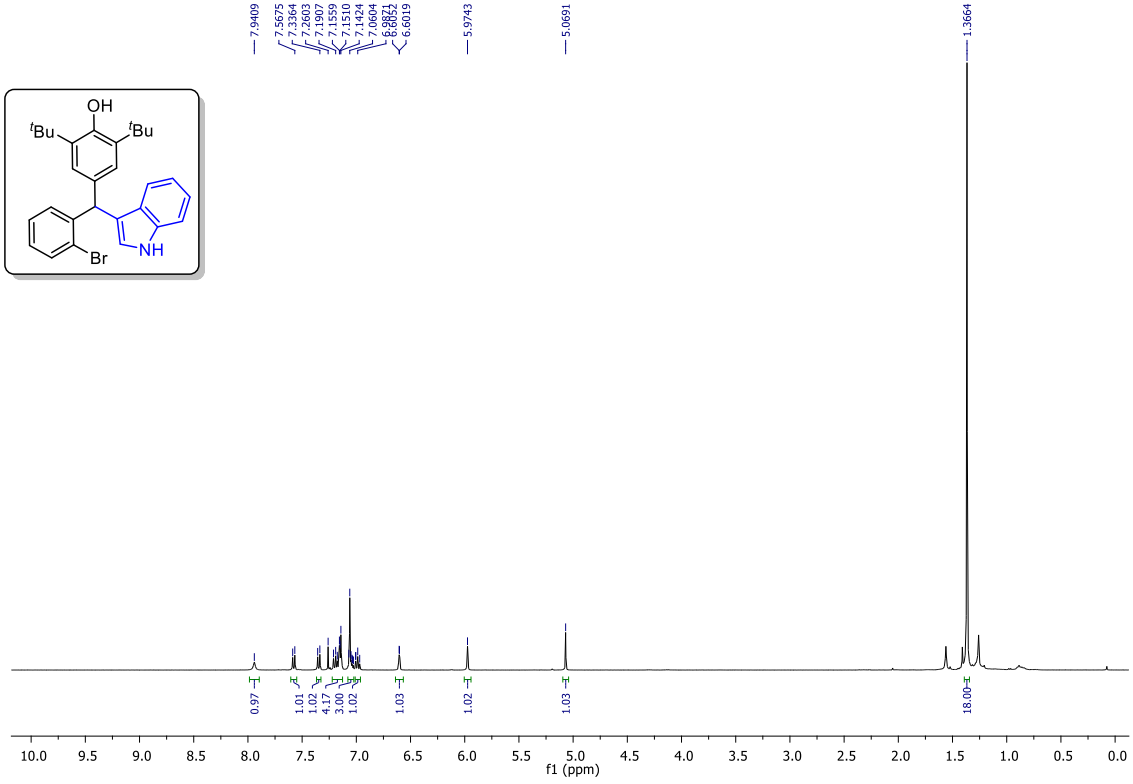
$^{13}C\{^{1}H\}$ NMR (100 MHz, $CDCl_3$) spectrum of **3l**



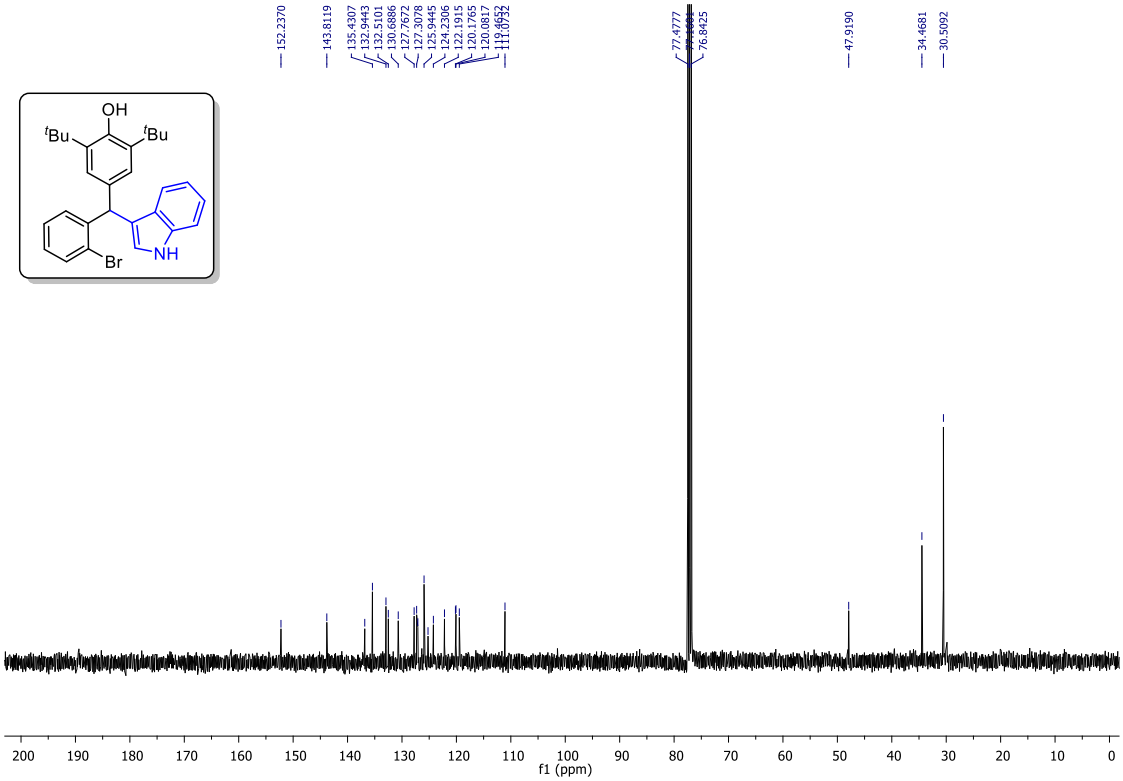
$^{19}F\{^{1}H\}$ NMR (376 MHz, $CDCl_3$) spectrum of **3l**



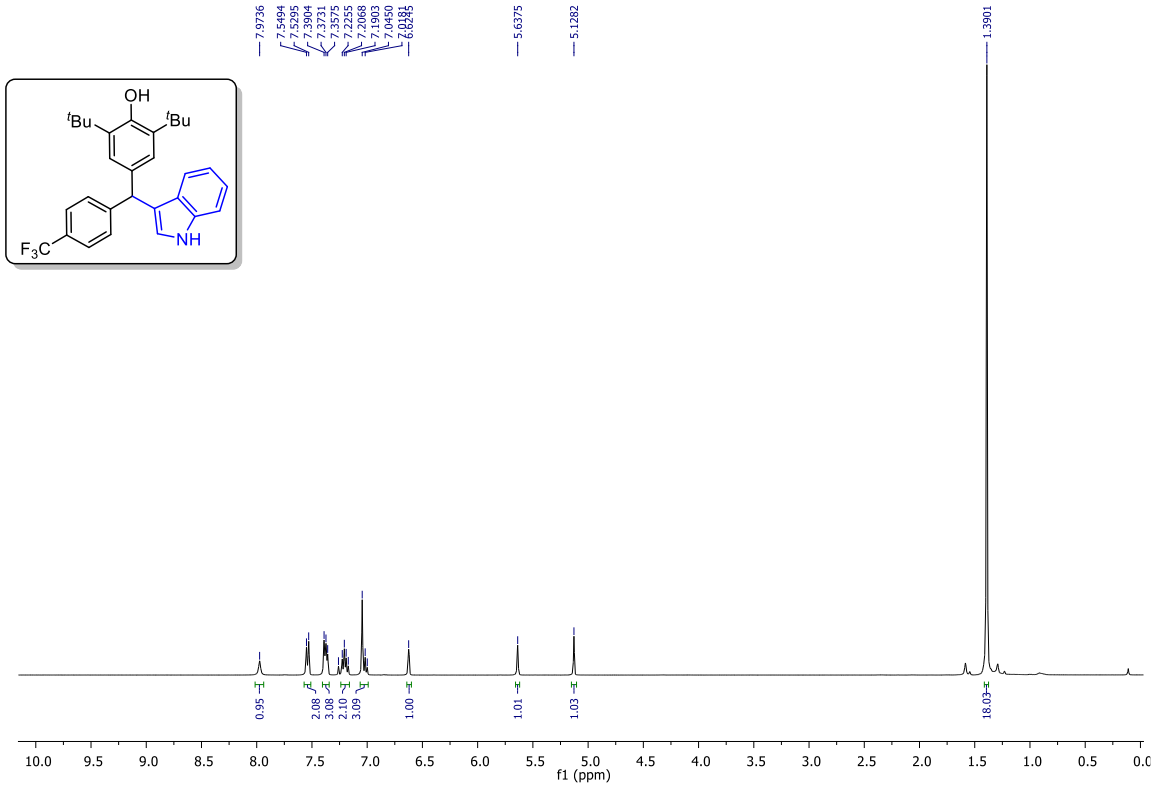
^{1}H NMR (400 MHz, $CDCl_3$) spectrum of **3m**



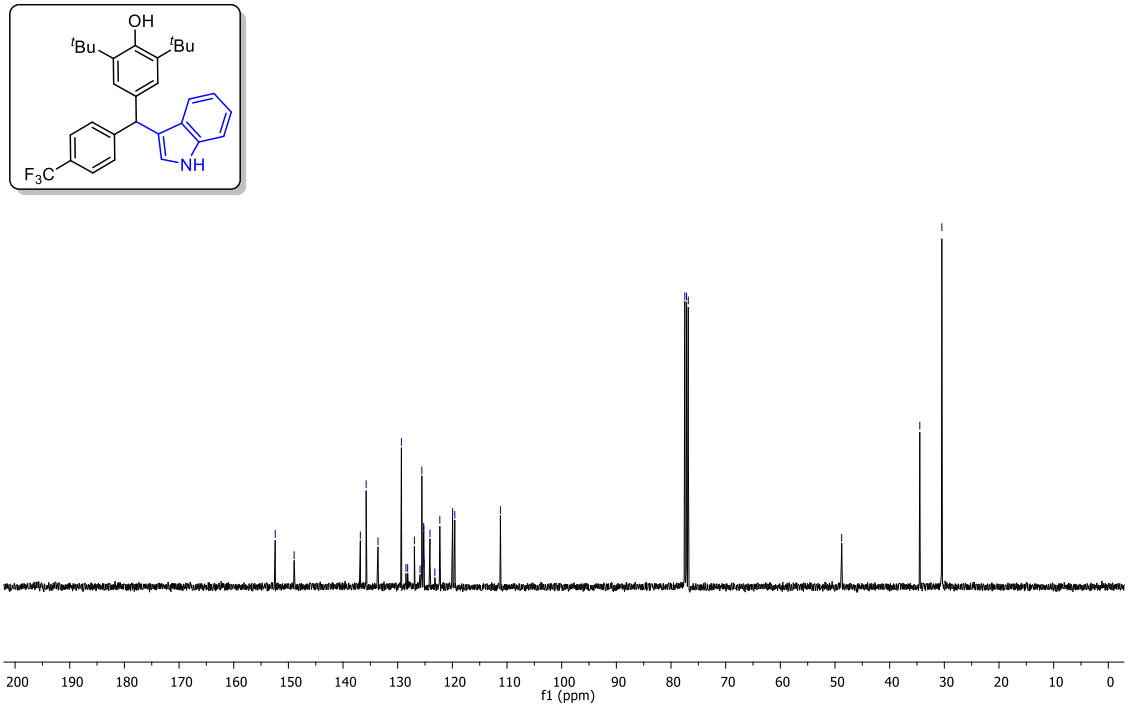
^{13}C{^{1}H} NMR (100 MHz, $CDCl_3$) spectrum of **3m**



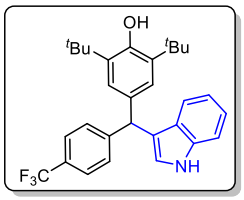
^{1}H NMR (400 MHz, $CDCl_3$) spectrum of **3n**



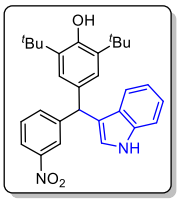
^{13}C{^{1}H} NMR (100 MHz, $CDCl_3$) spectrum of **3n**



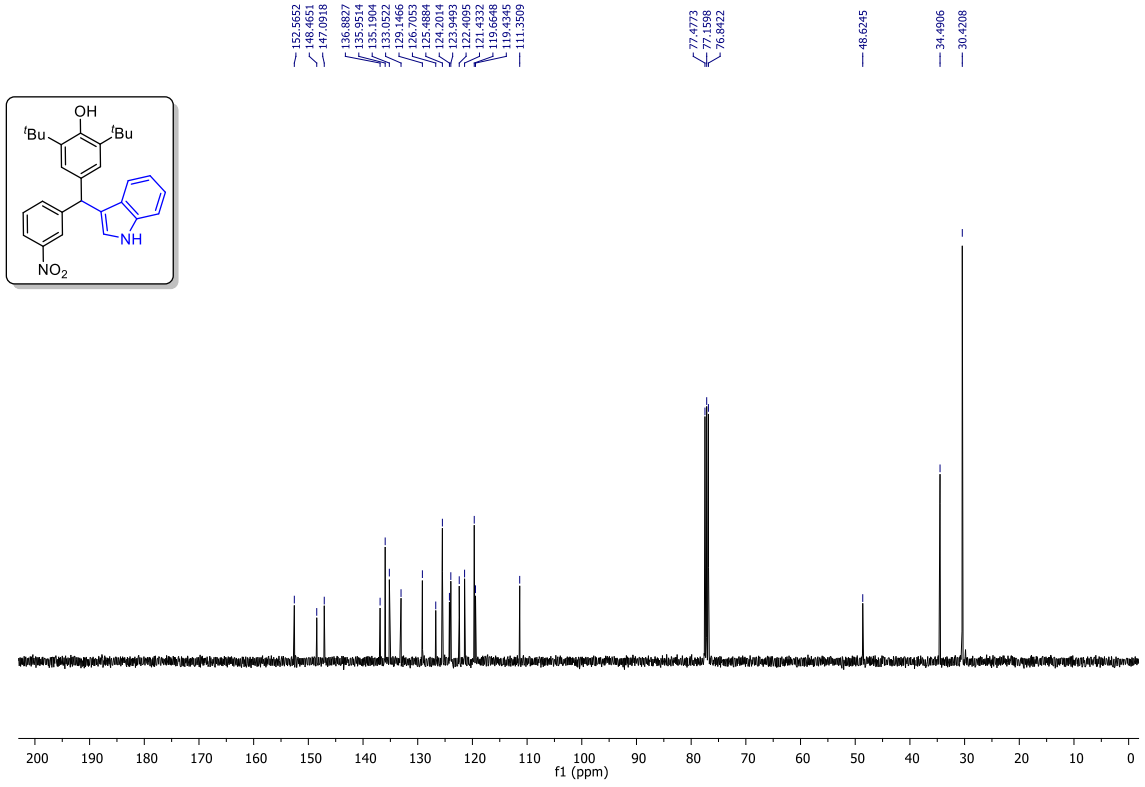
$^{19}F\{^{1}H\}$ NMR (376 MHz, $CDCl_3$) spectrum of **3n**



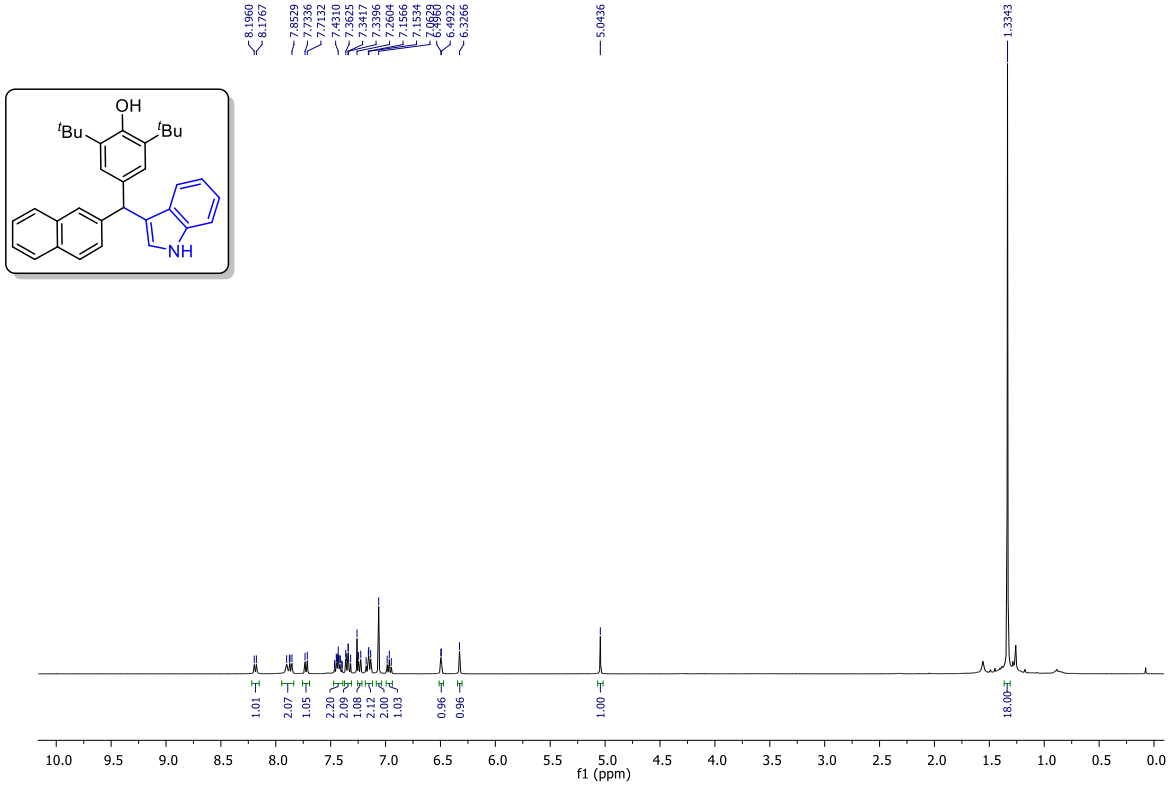
^{1}H NMR (400 MHz, $CDCl_3$) spectrum of **3o**



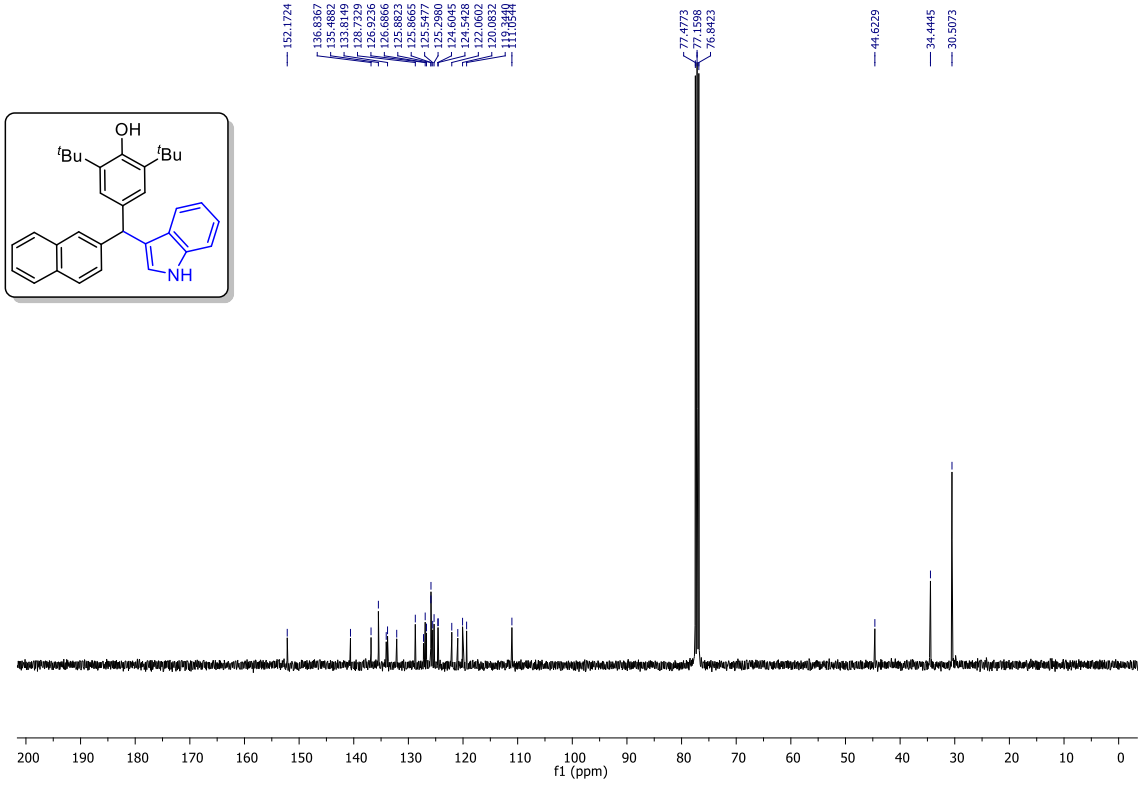
$^{13}C\{^{1}H\}$ NMR (100 MHz, $CDCl_3$) spectrum of **3o**



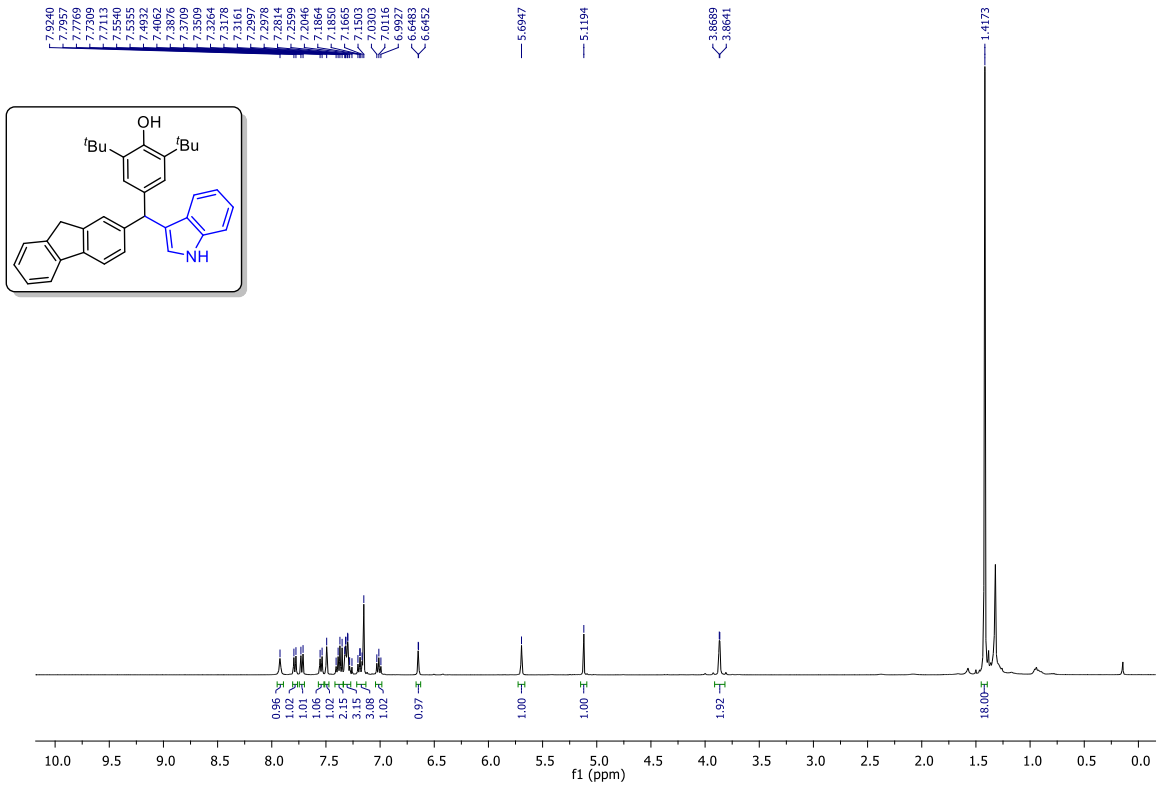
^{1}H NMR (400 MHz, $CDCl_3$) spectrum of **3p**



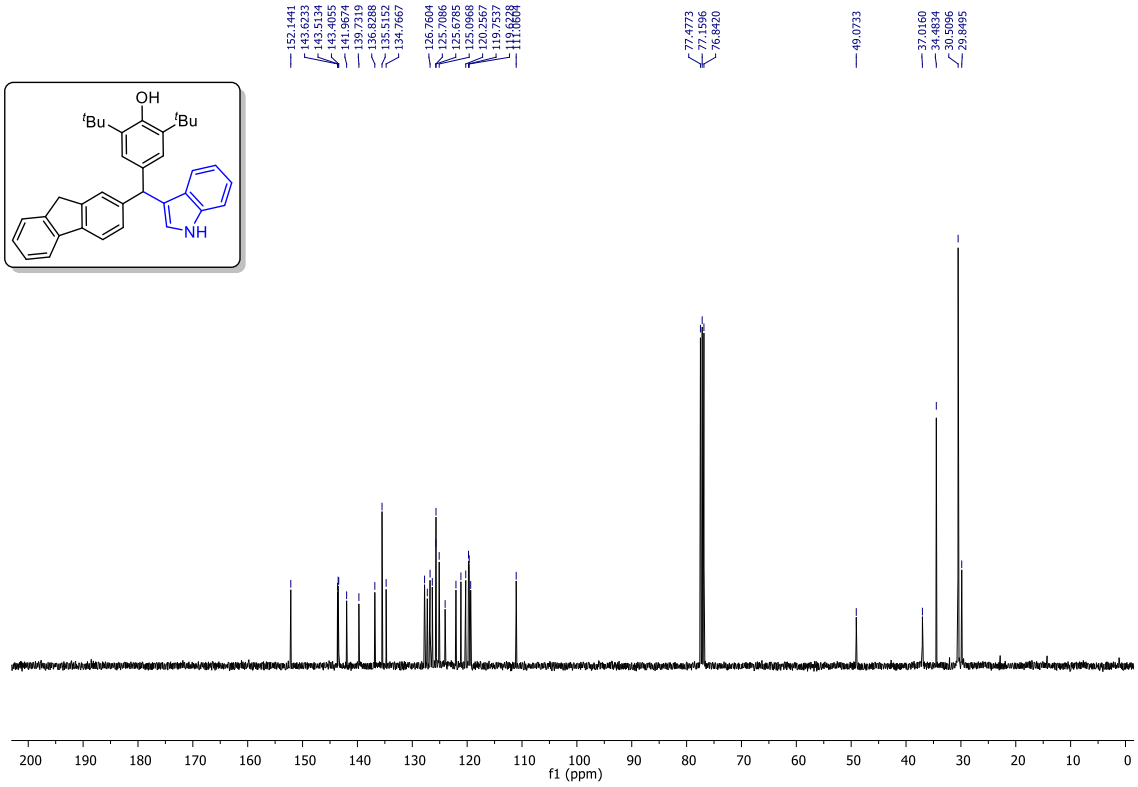
$^{13}C\{^{1}H\}$ NMR (100 MHz, $CDCl_3$) spectrum of **3p**



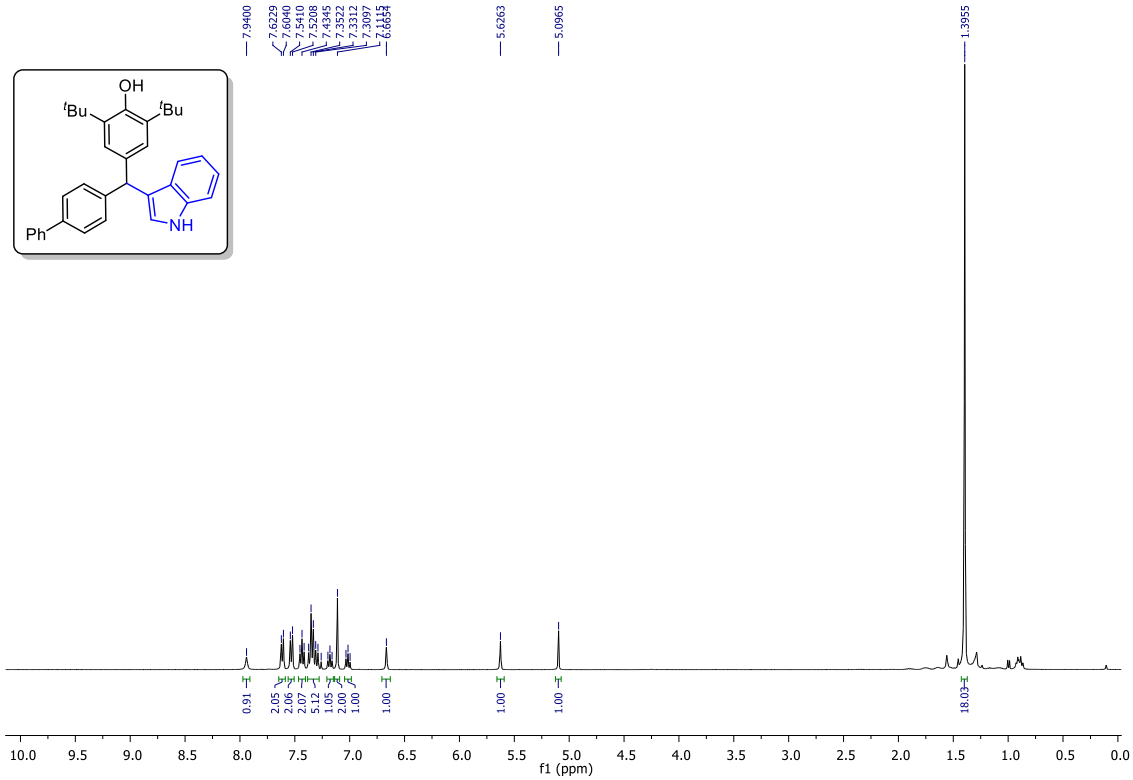
^{1}H NMR (400 MHz, $CDCl_3$) spectrum of **3q**



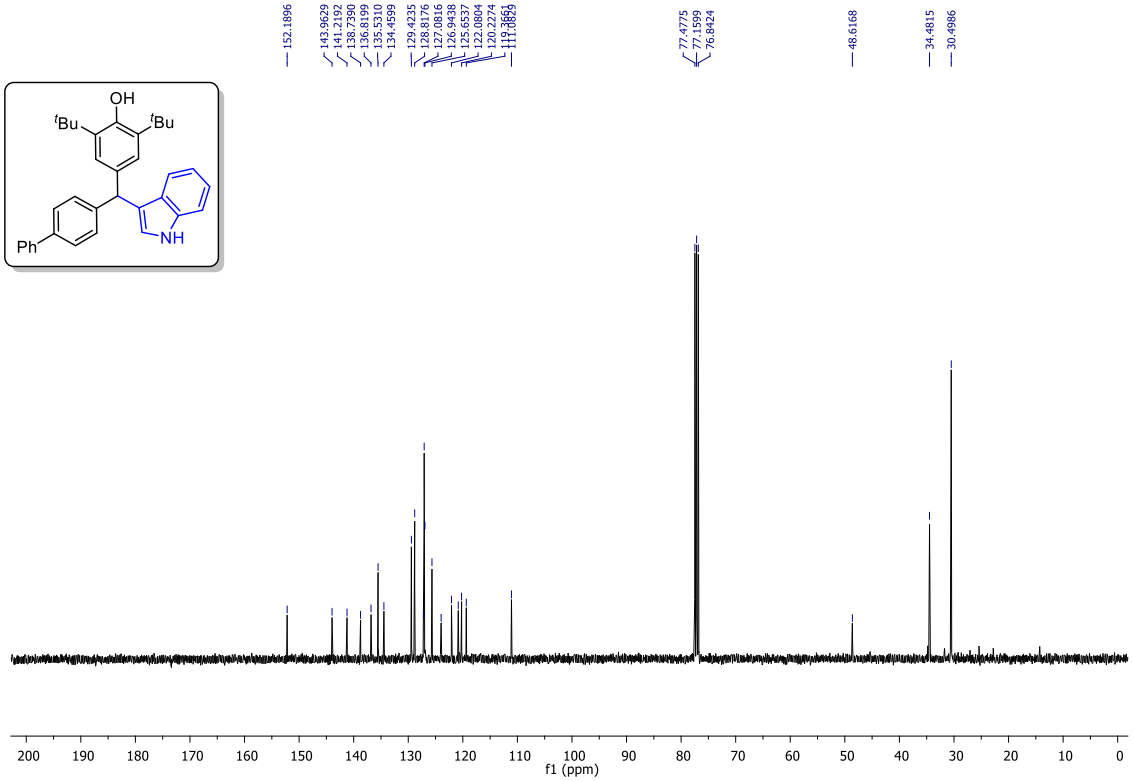
$^{13}C\{^{1}H\}$ NMR (100 MHz, $CDCl_3$) spectrum of **3q**



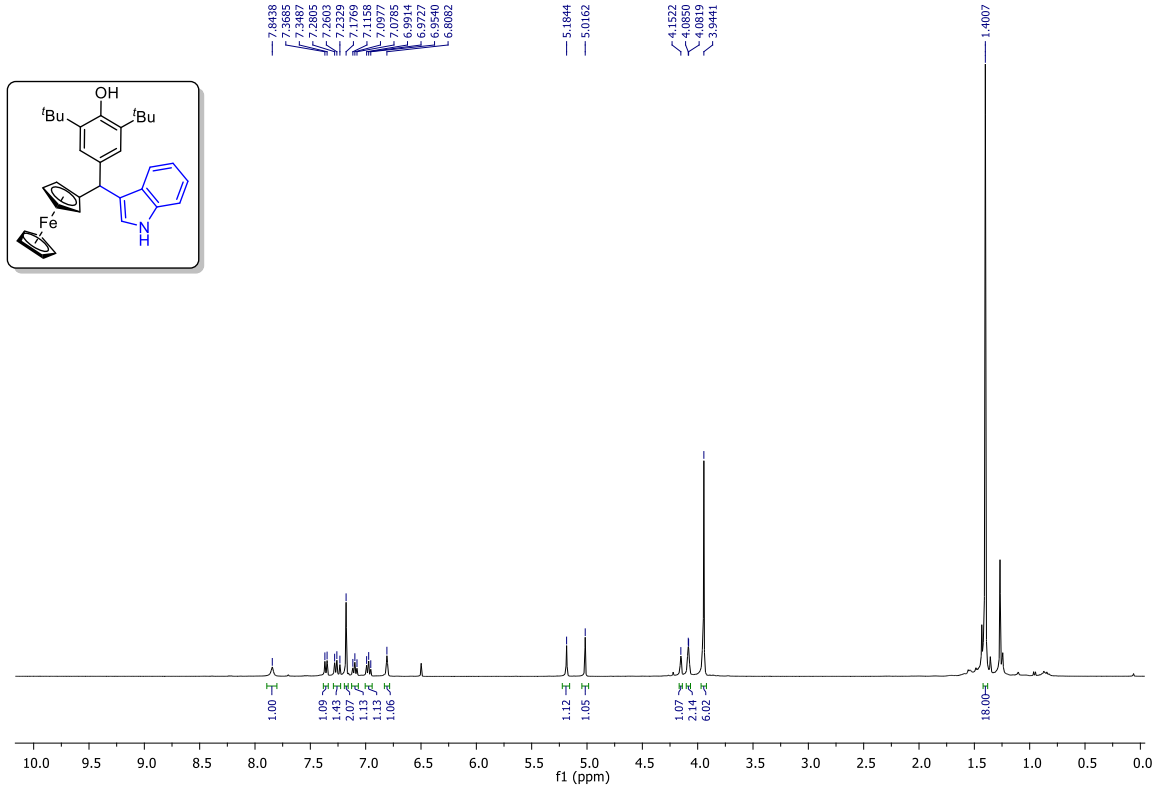
^{1}H NMR (400 MHz, $CDCl_3$) spectrum of **3r**



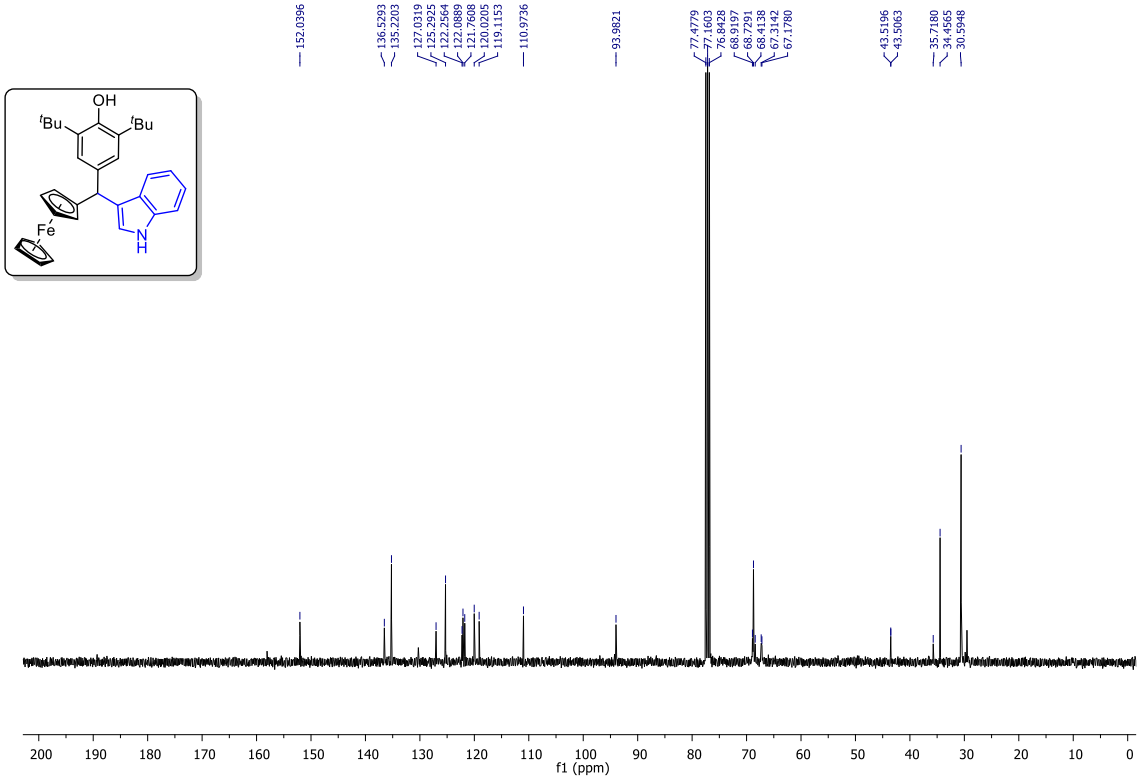
$^{13}C\{^{1}H\}$ NMR (100 MHz, $CDCl_3$) spectrum of **3r**



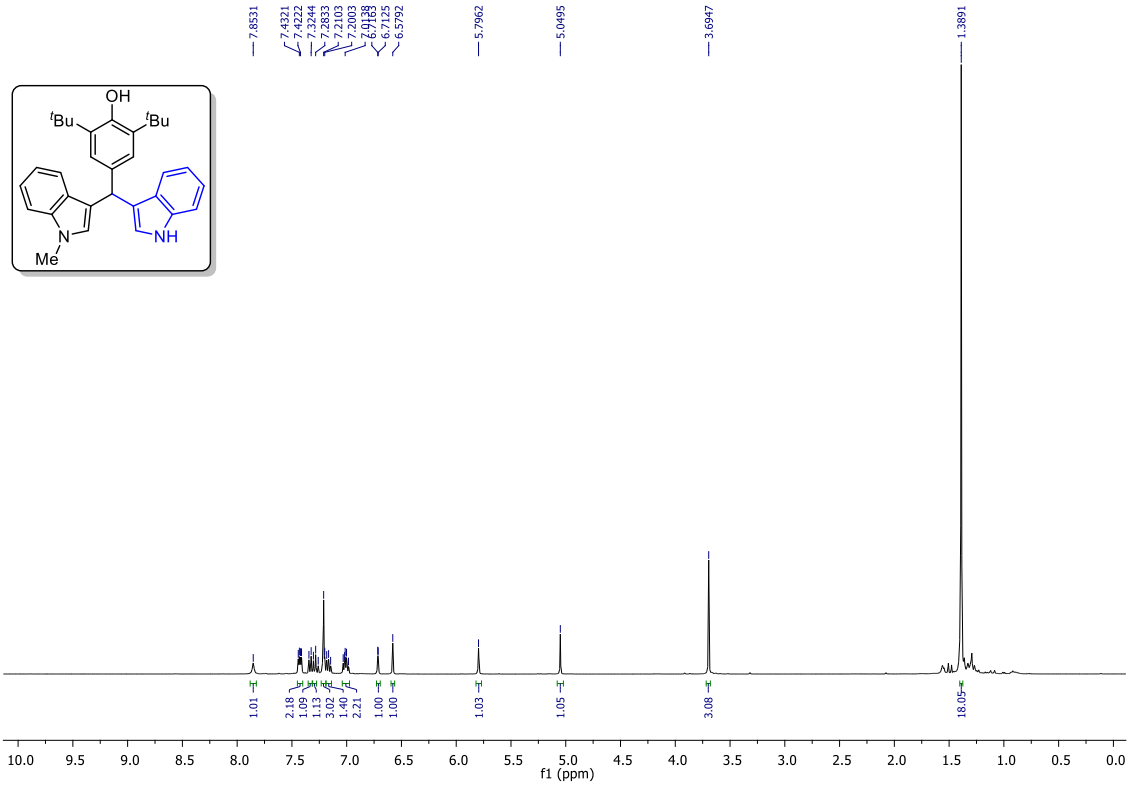
^{1}H NMR (400 MHz, $CDCl_3$) spectrum of **3s**



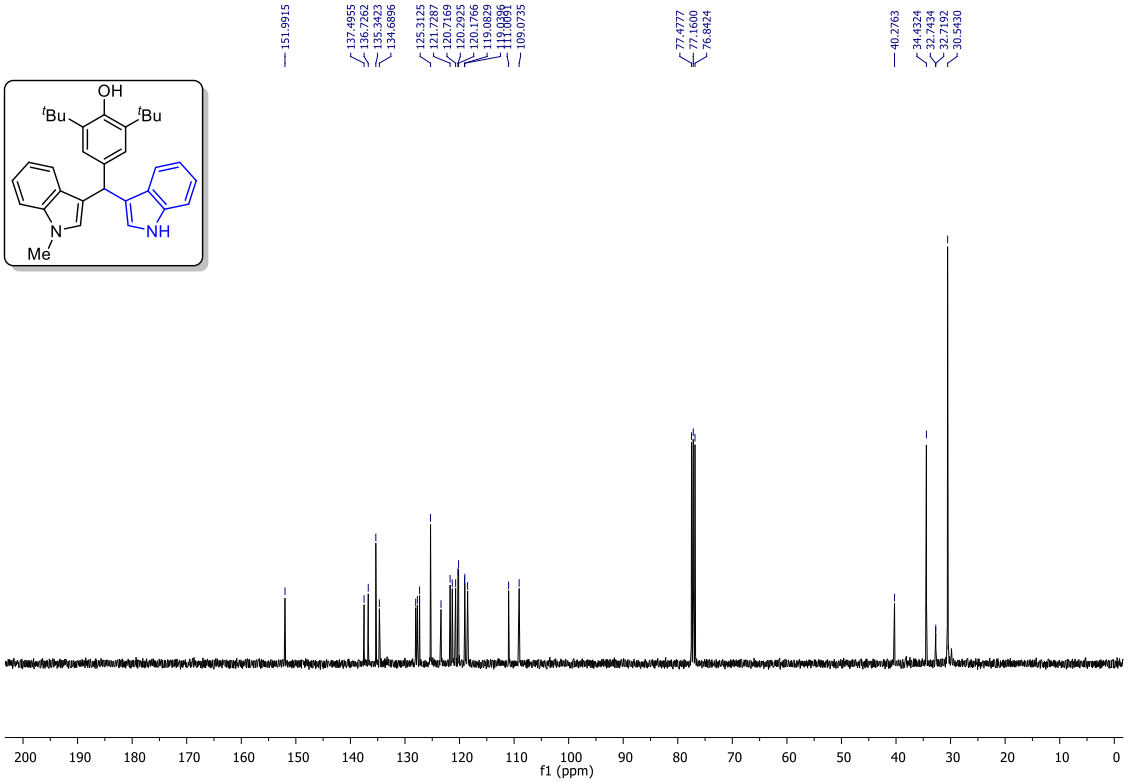
$^{13}C\{^{1}H\}$ NMR (100 MHz, $CDCl_3$) spectrum of **3s**



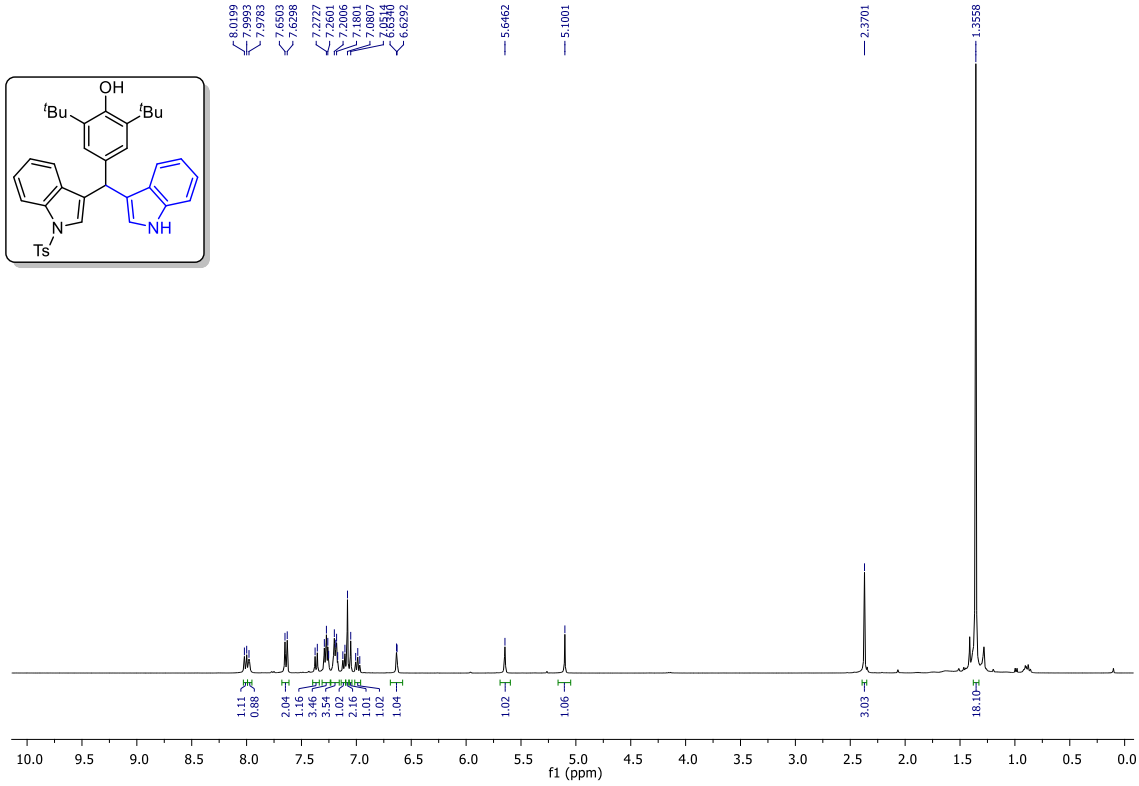
^{1}H NMR (400 MHz, $CDCl_3$) spectrum of **3t**



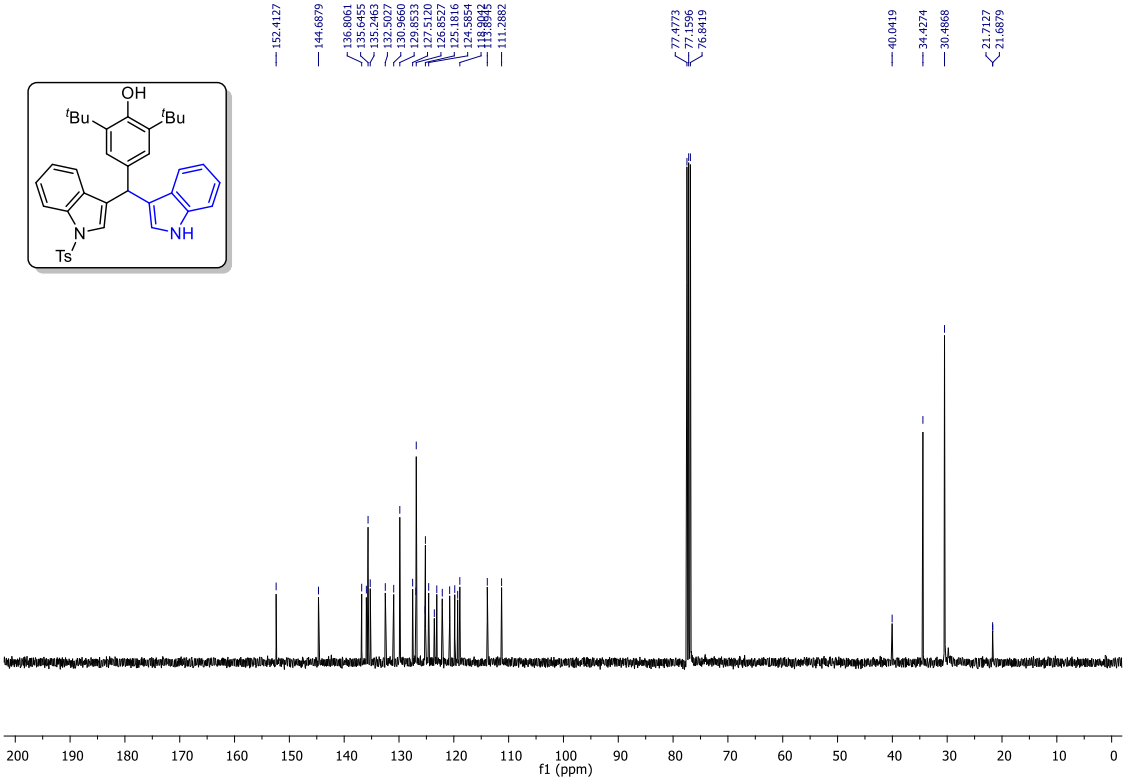
$^{13}C\{^{1}H\}$ NMR (100 MHz, $CDCl_3$) spectrum of **3t**



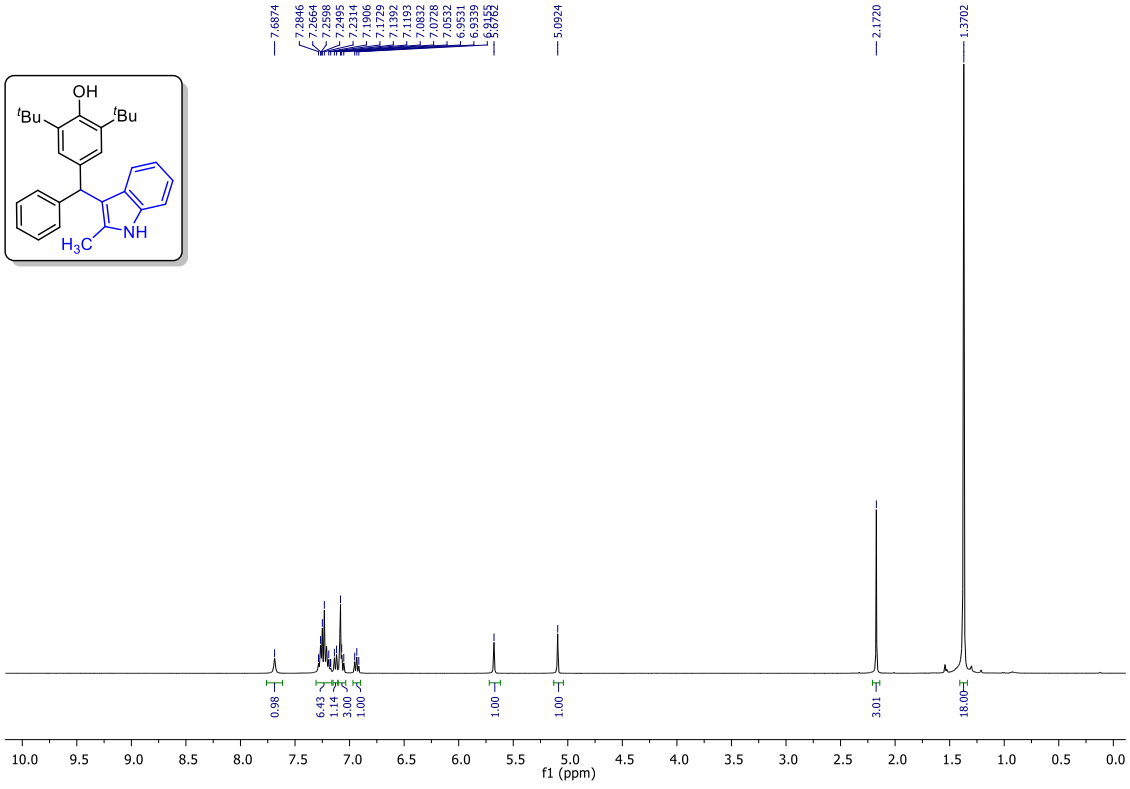
^{1}H NMR (400 MHz, $CDCl_3$) spectrum of **3u**



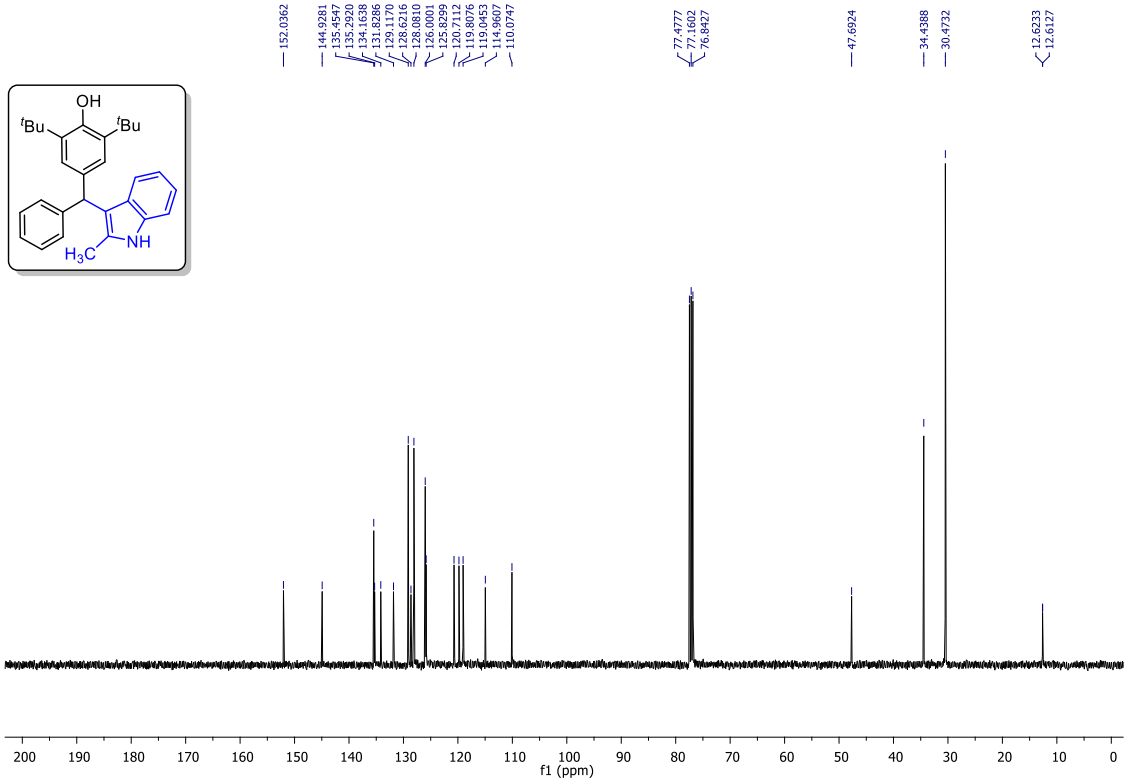
$^{13}C\{^{1}H\}$ NMR (100 MHz, $CDCl_3$) spectrum of **3u**



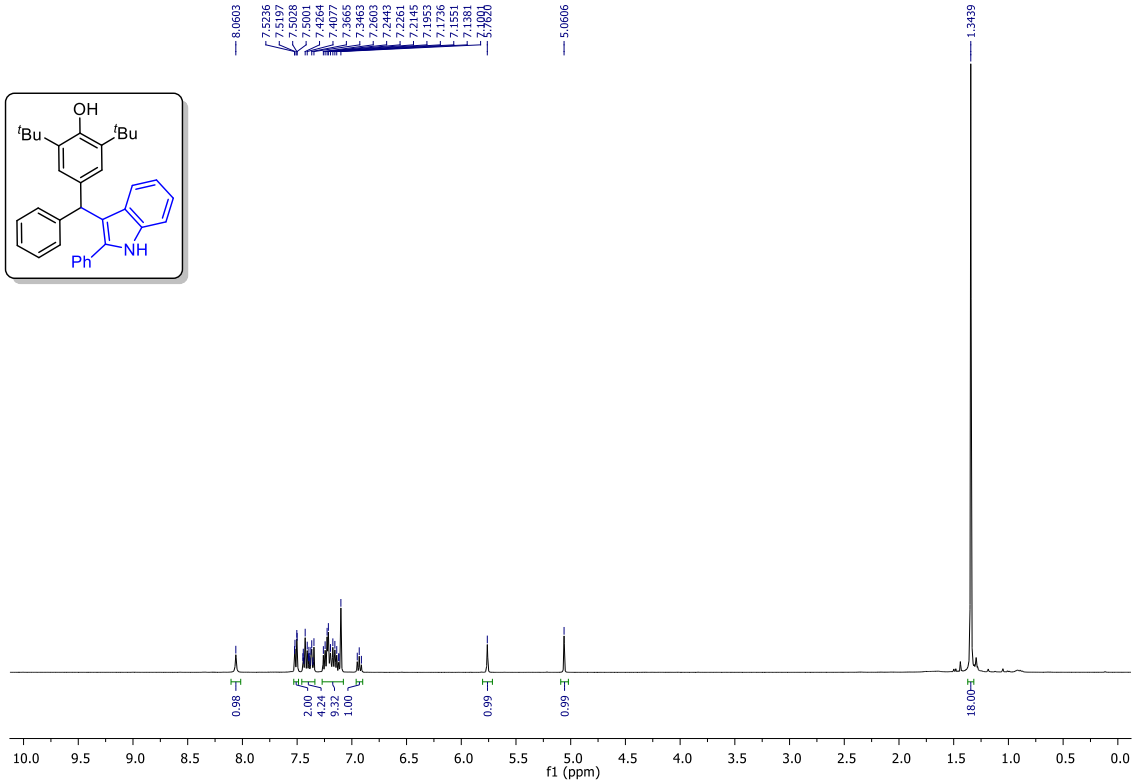
^{1}H NMR (400 MHz, $CDCl_3$) spectrum of **4a**



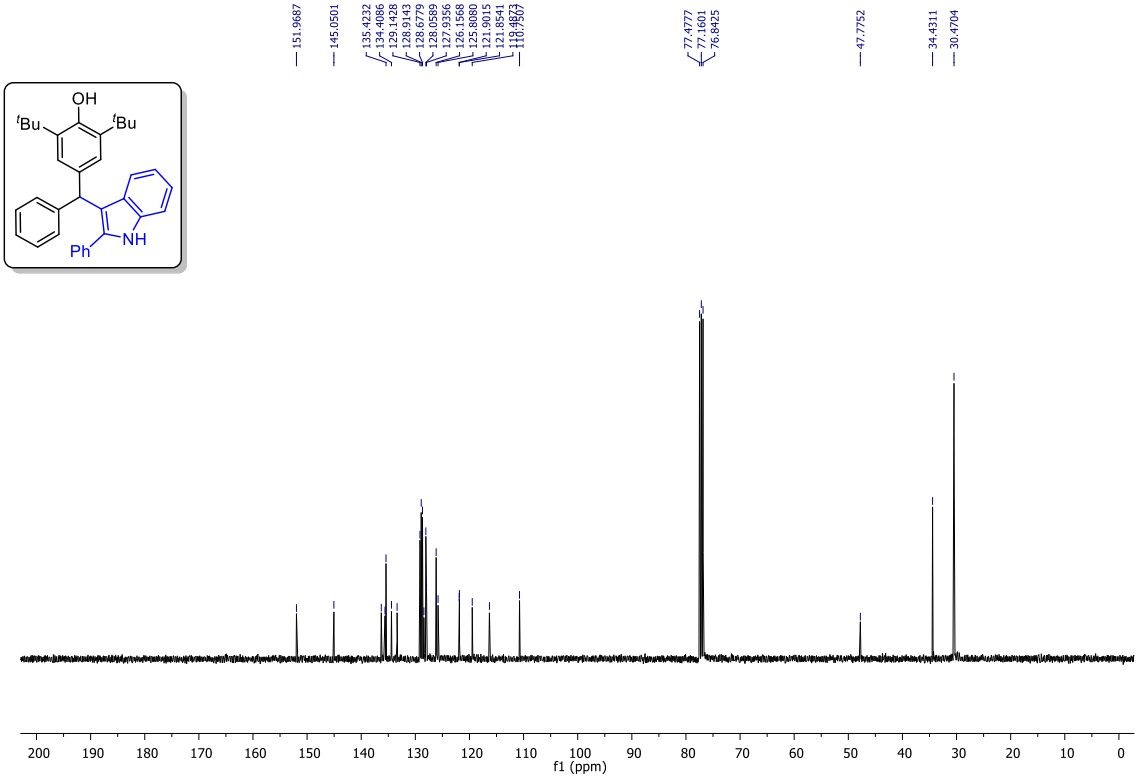
$^{13}C\{^{1}H\}$ NMR (100 MHz, $CDCl_3$) spectrum of **4a**



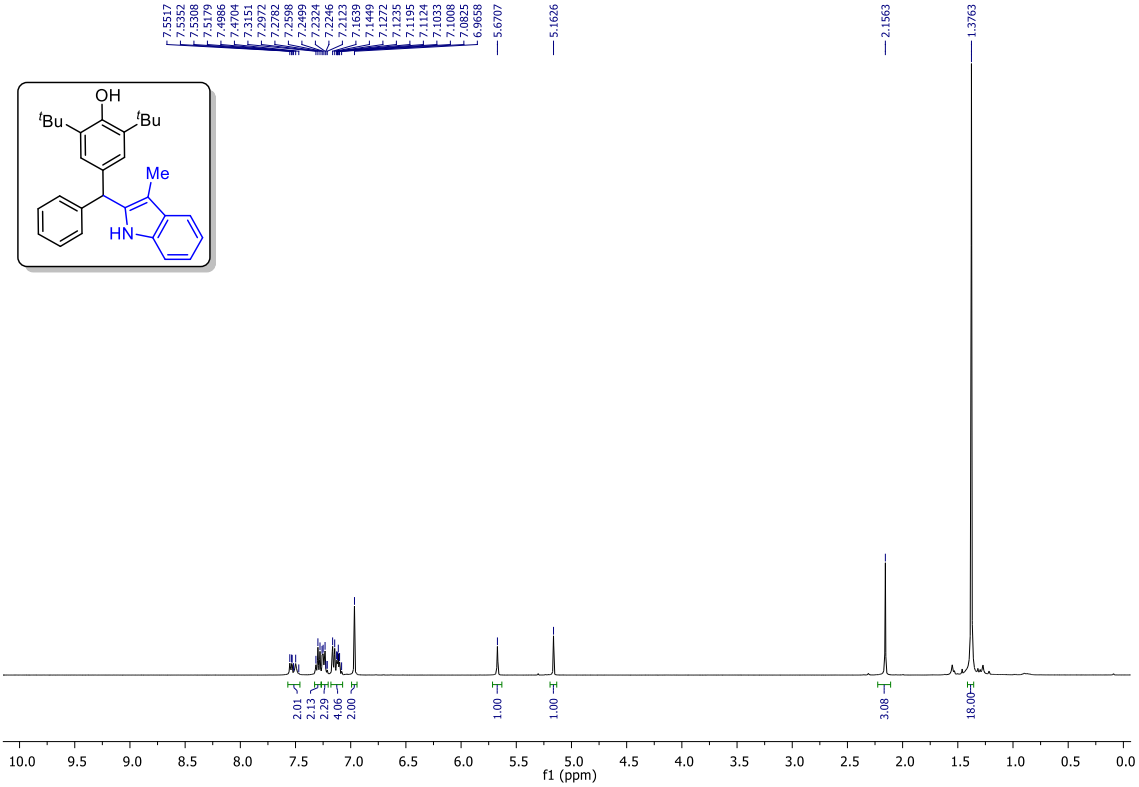
^{1}H NMR (400 MHz, $CDCl_3$) spectrum of **4b**



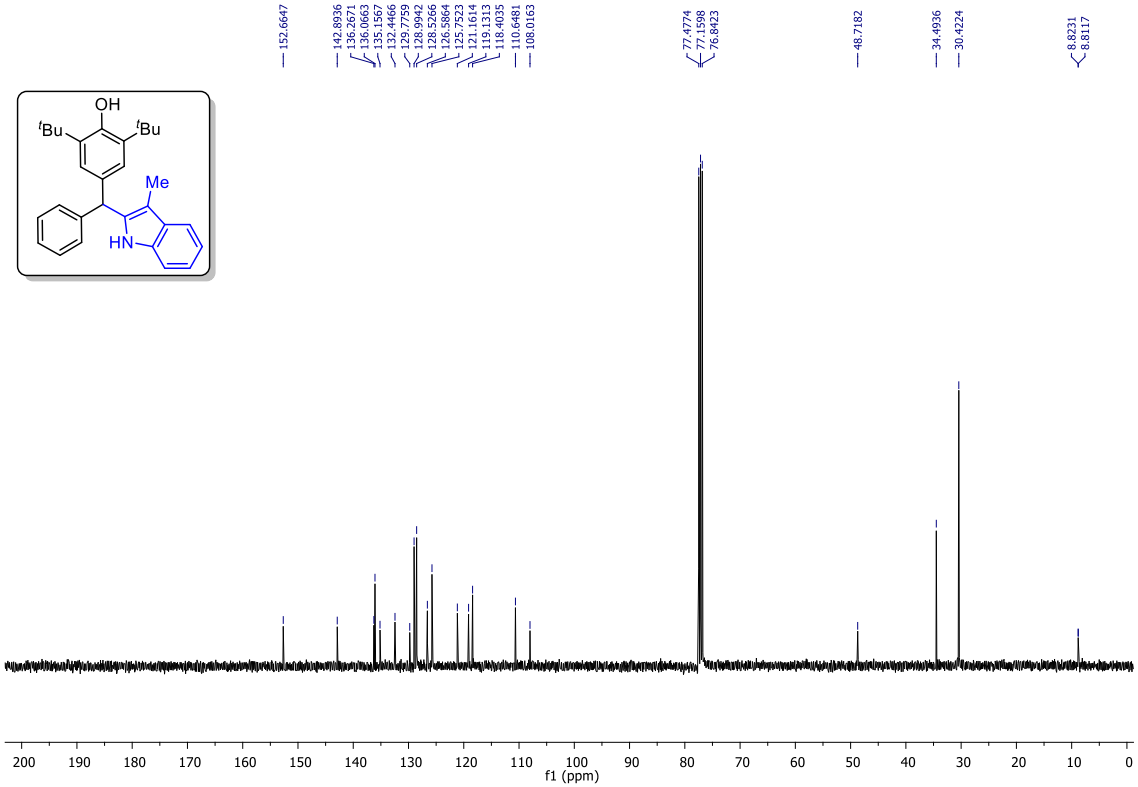
$^{13}C\{^{1}H\}$ NMR (100 MHz, $CDCl_3$) spectrum of **4b**



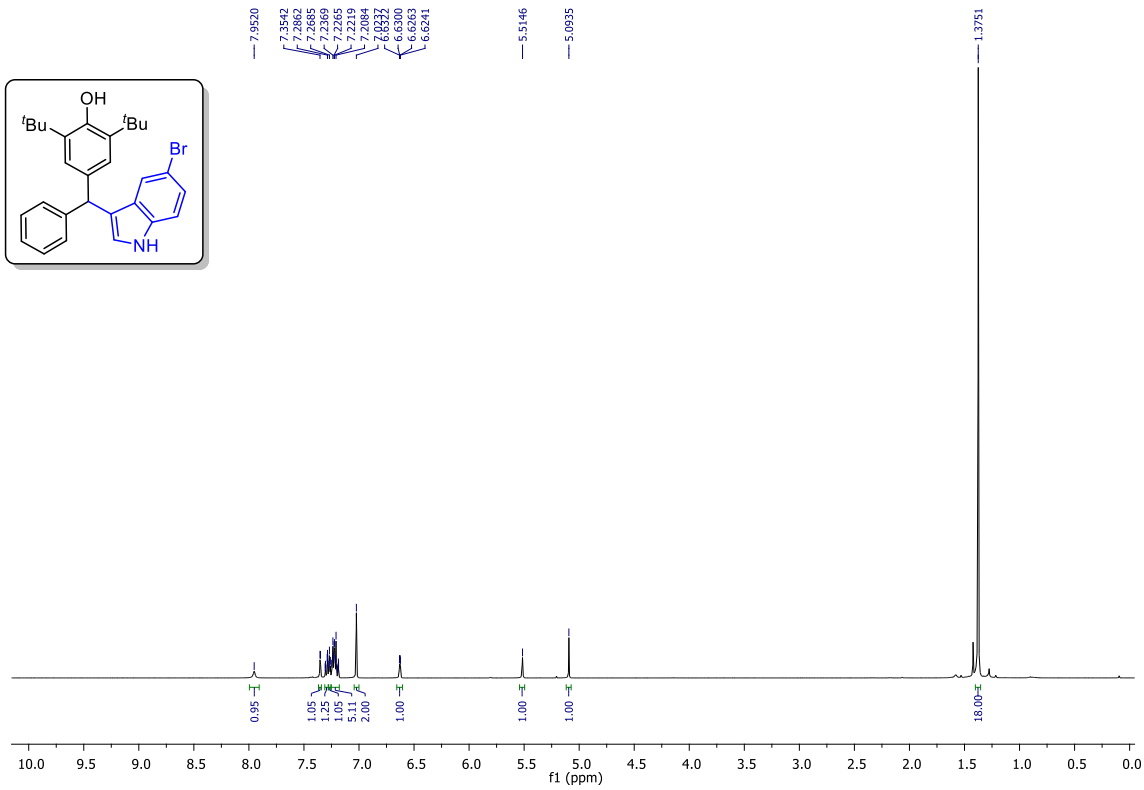
^{1}H NMR (400 MHz, $CDCl_3$) spectrum of **4c**



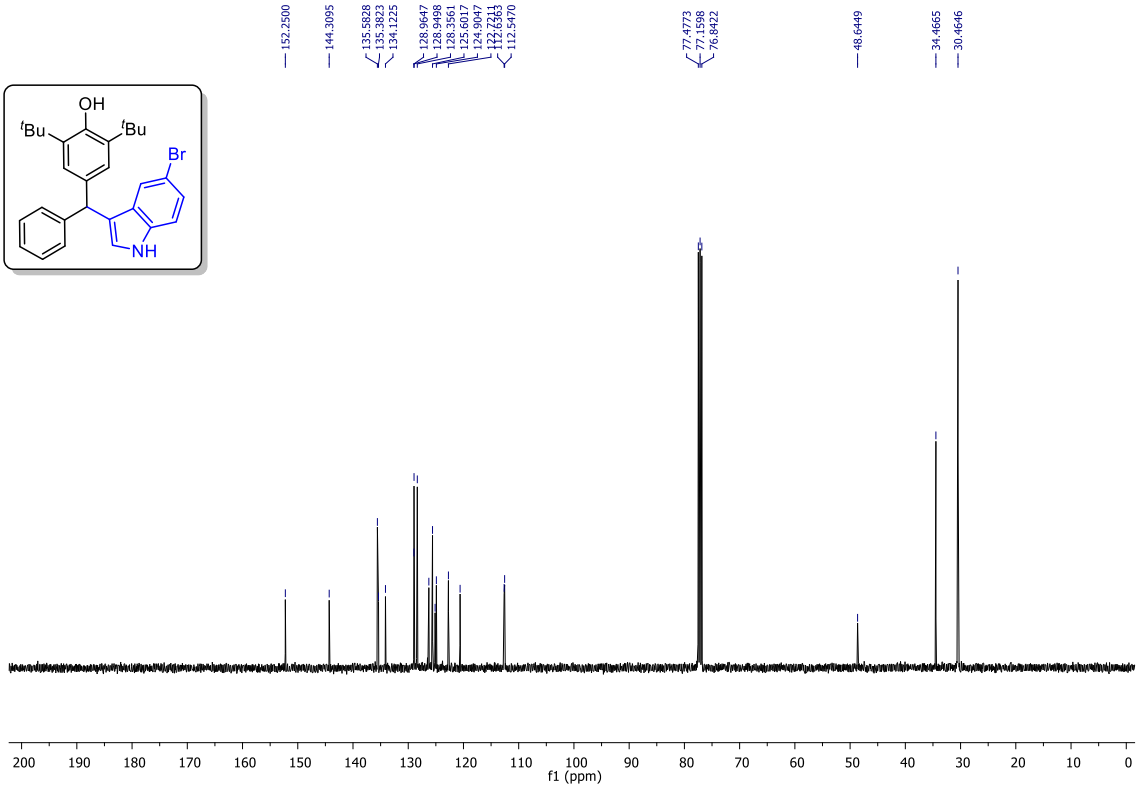
$^{13}C\{^{1}H\}$ NMR (100 MHz, $CDCl_3$) spectrum of **4c**



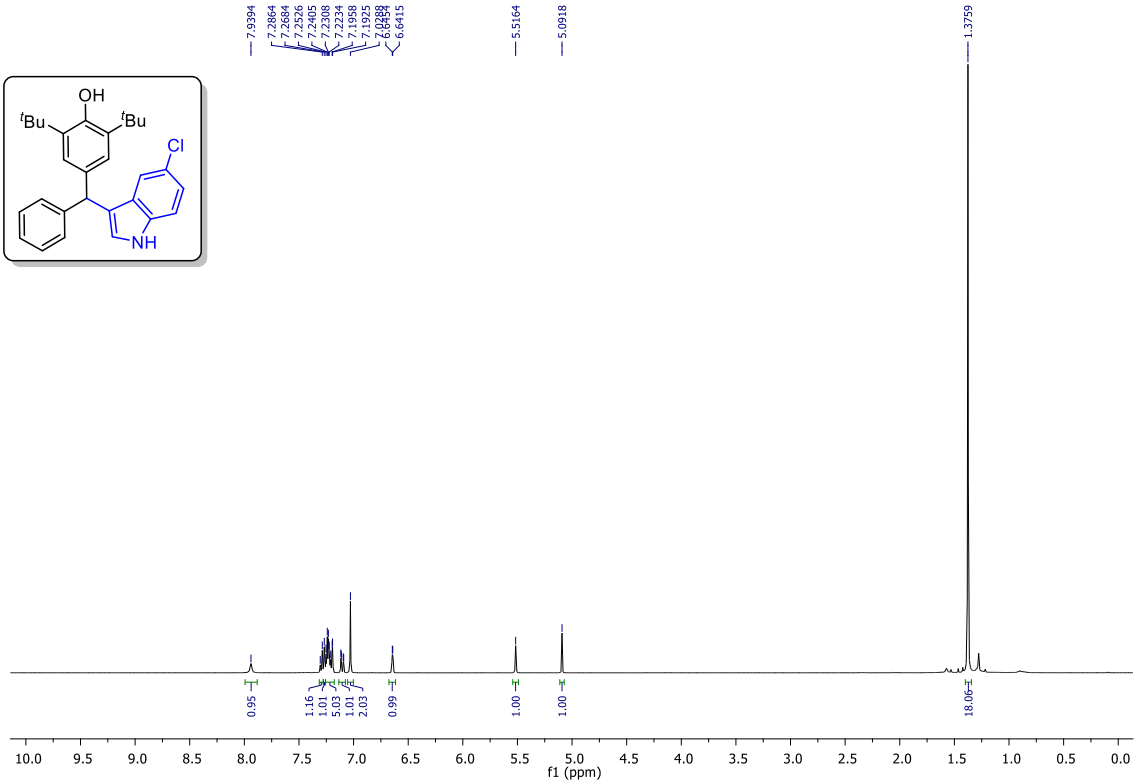
^{1}H NMR (400 MHz, $CDCl_3$) spectrum of **4f**



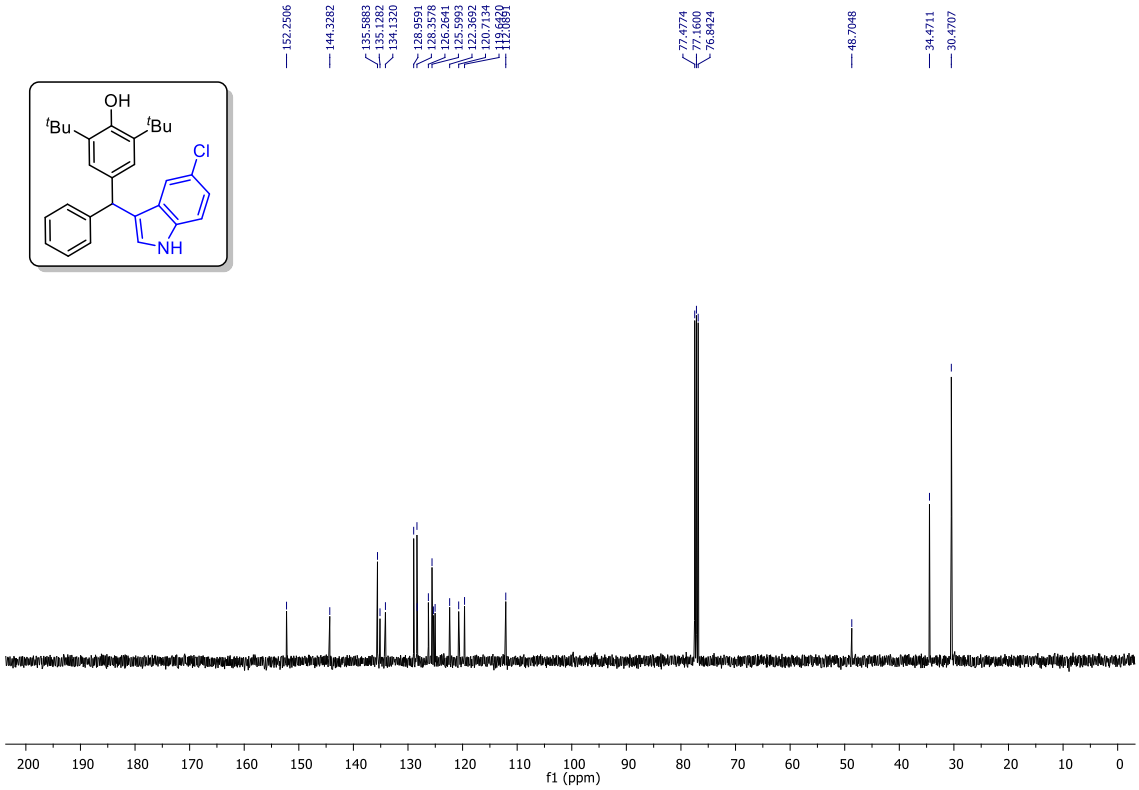
$^{13}C\{^{1}H\}$ NMR (100 MHz, $CDCl_3$) spectrum of **4f**



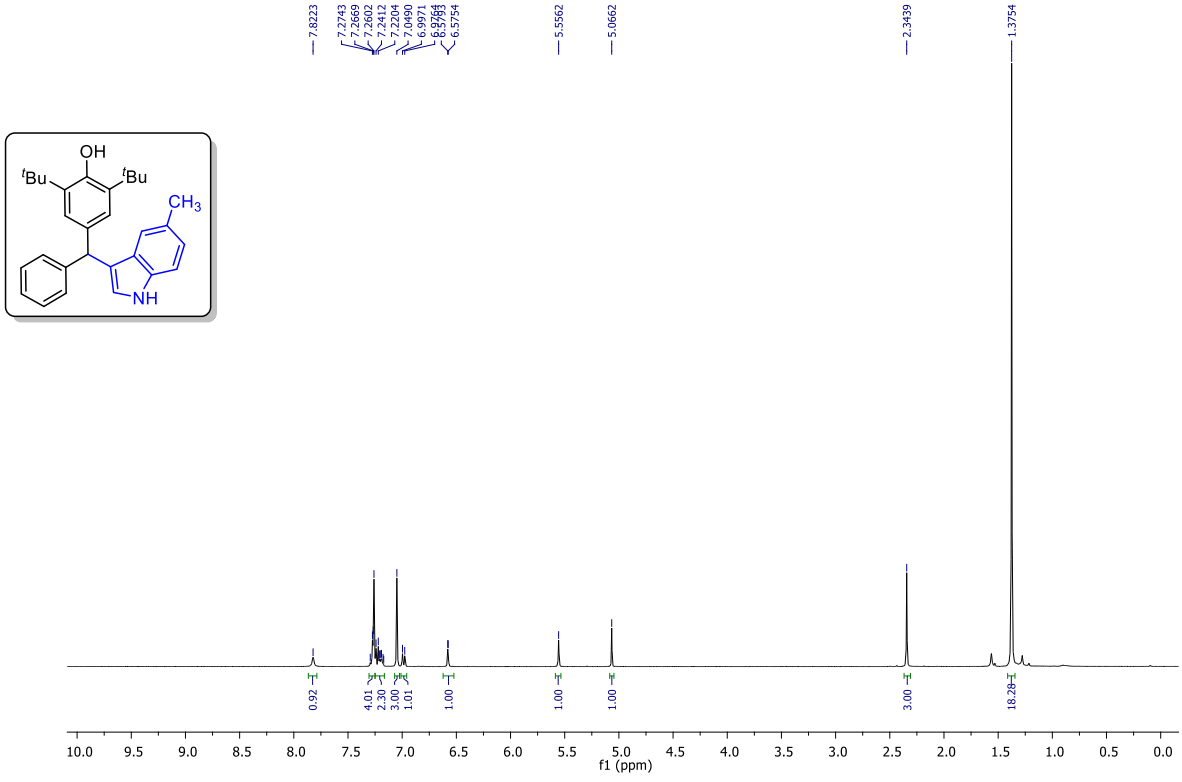
^{1}H NMR (400 MHz, $CDCl_3$) spectrum of **4e**



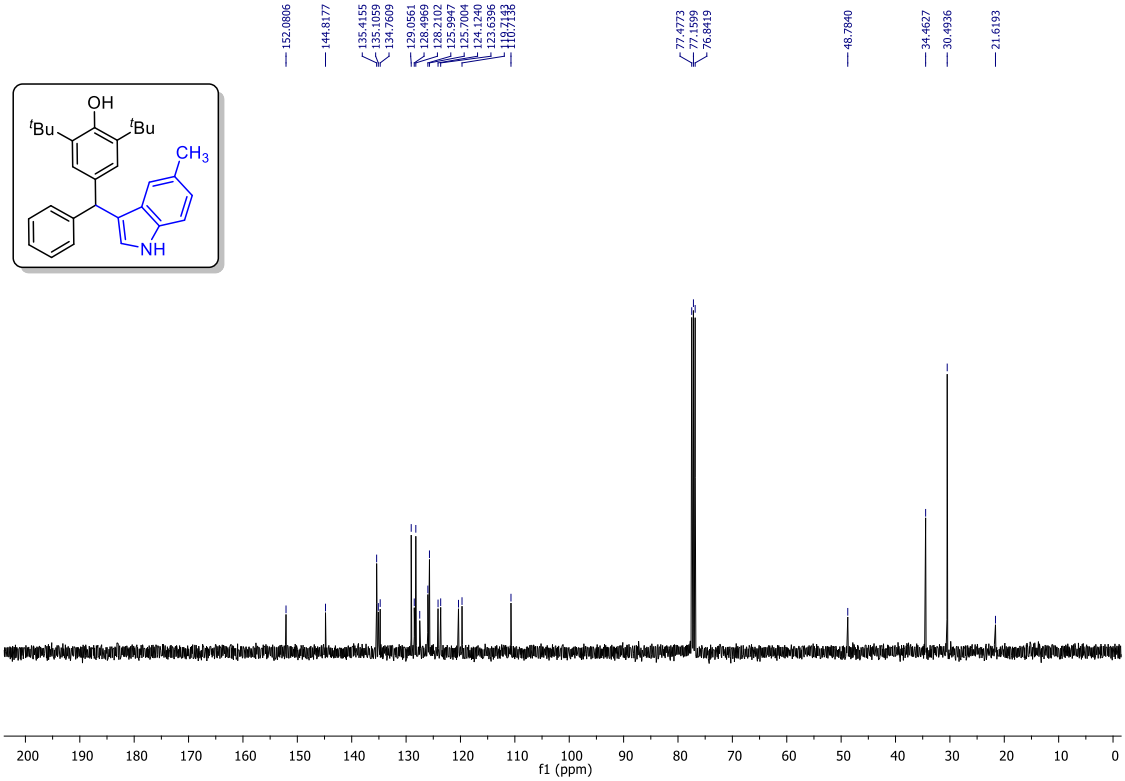
$^{13}C\{^{1}H\}$ NMR (100 MHz, $CDCl_3$) spectrum of **4e**



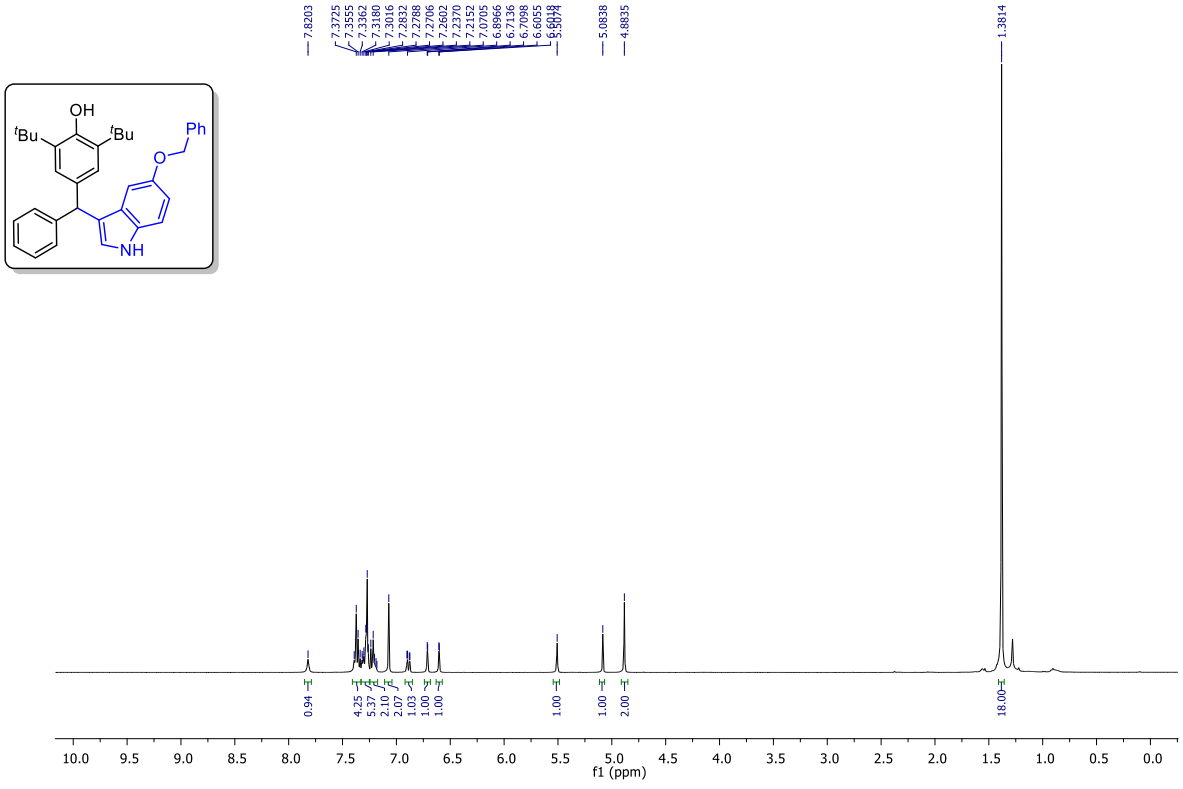
^{1}H NMR (400 MHz, $CDCl_3$) spectrum of **4d**



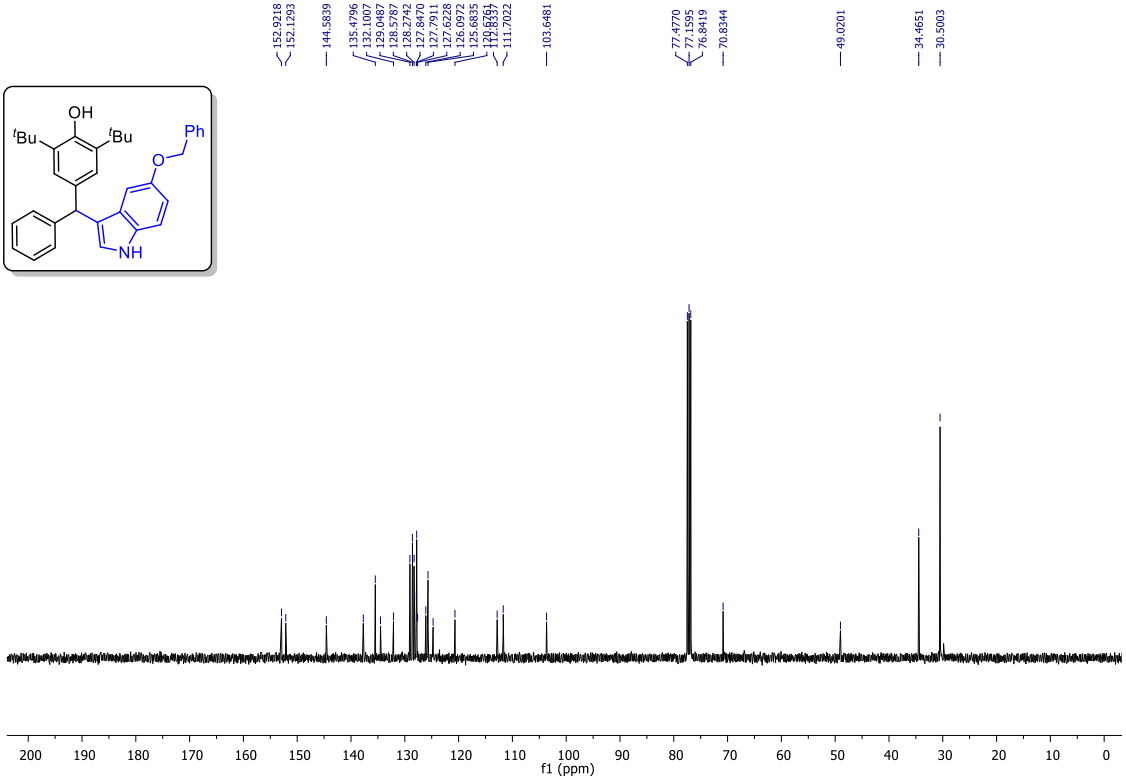
$^{13}C\{^{1}H\}$ NMR (100 MHz, $CDCl_3$) spectrum of **4d**



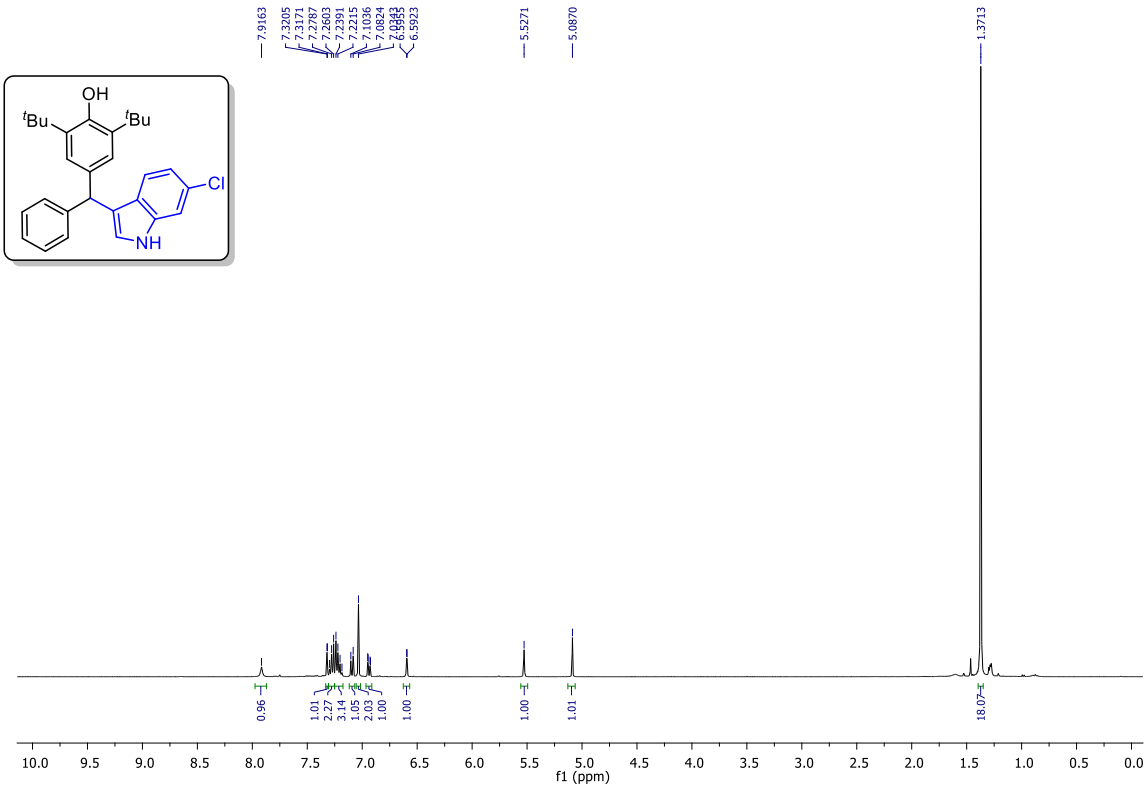
^{1}H NMR (400 MHz, $CDCl_3$) spectrum of **4g**



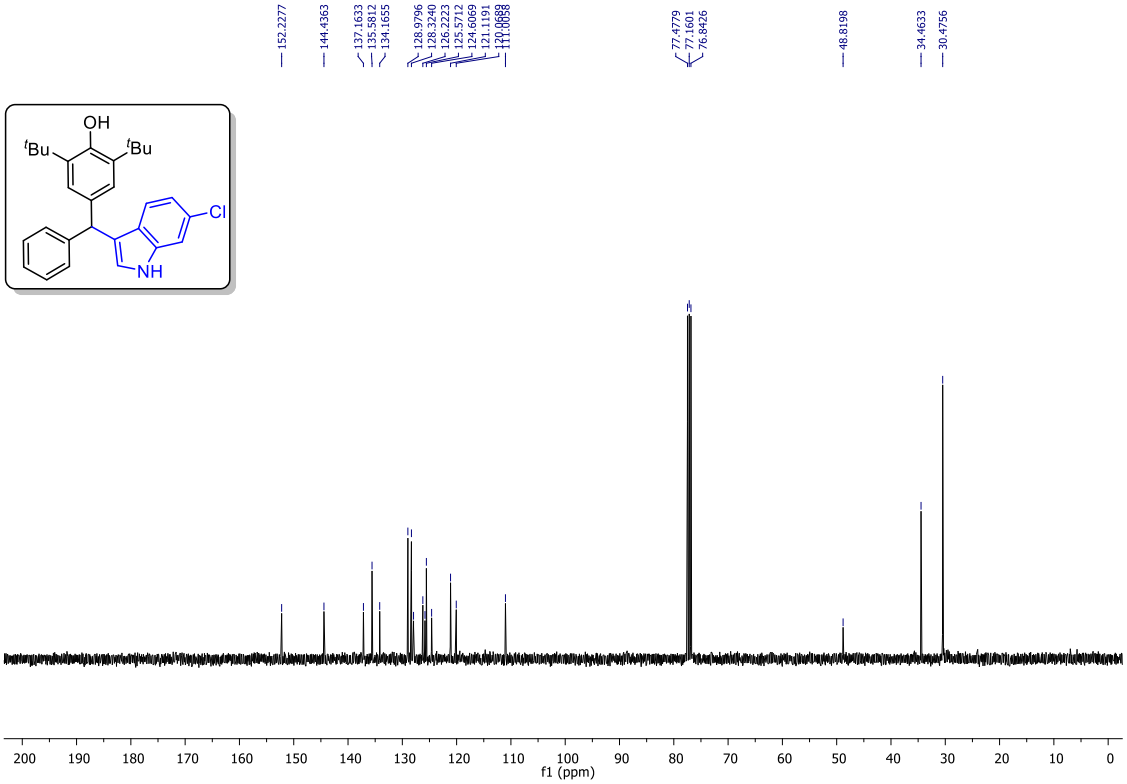
$^{13}C\{^{1}H\}$ NMR (100 MHz, $CDCl_3$) spectrum of **4g**



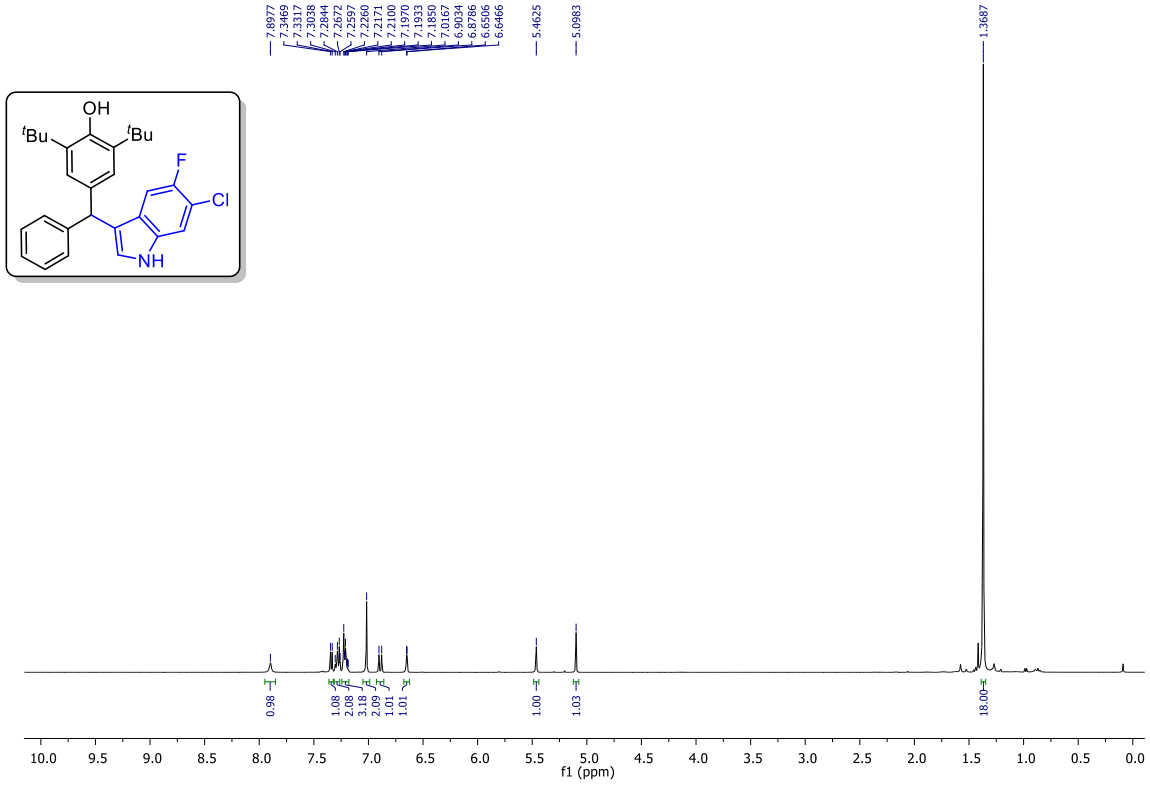
^{1}H NMR (400 MHz, $CDCl_3$) spectrum of **4h**



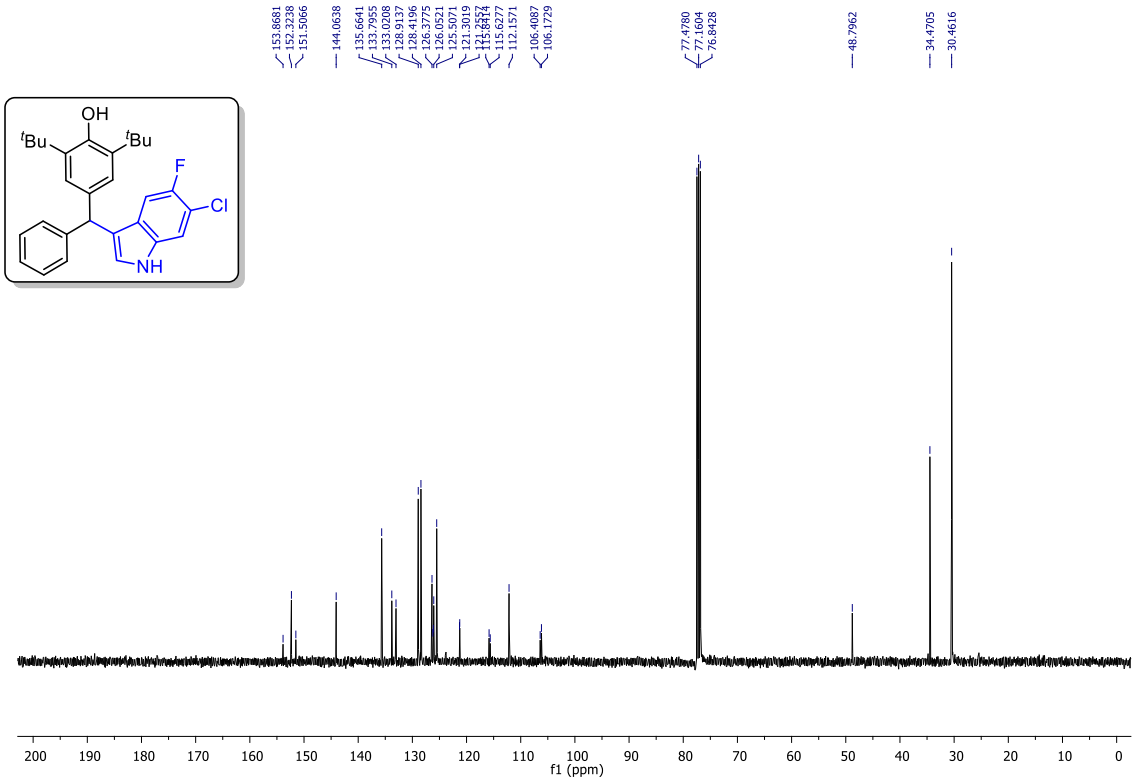
$^{13}C\{^{1}H\}$ NMR (100 MHz, $CDCl_3$) spectrum of **4h**



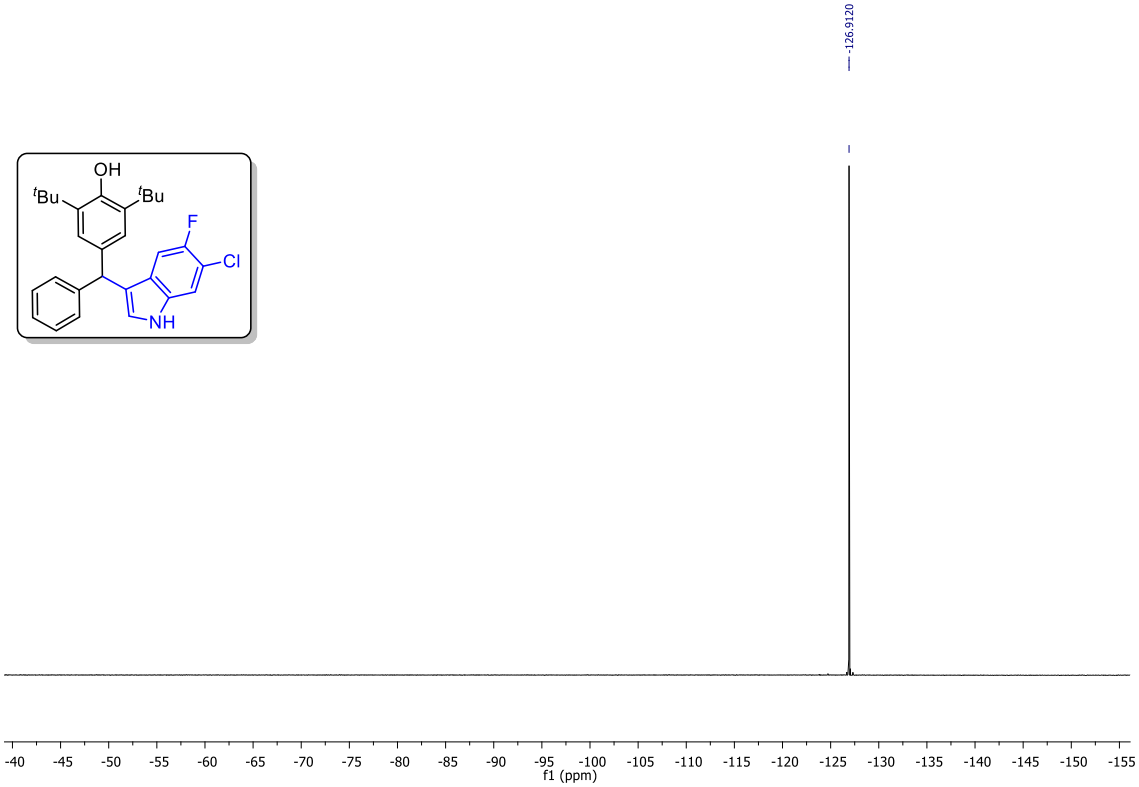
^{1}H NMR (400 MHz, $CDCl_3$) spectrum of **4i**



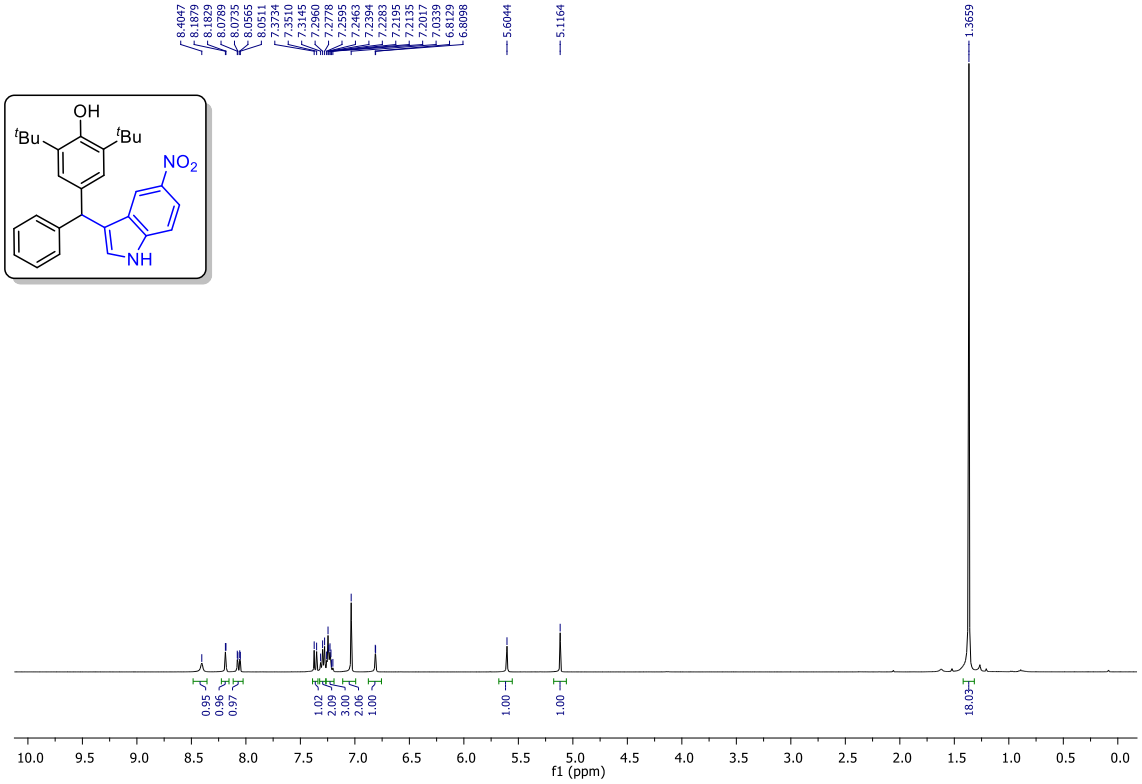
$^{13}C\{^{1}H\}$ NMR (100 MHz, $CDCl_3$) spectrum of **4i**



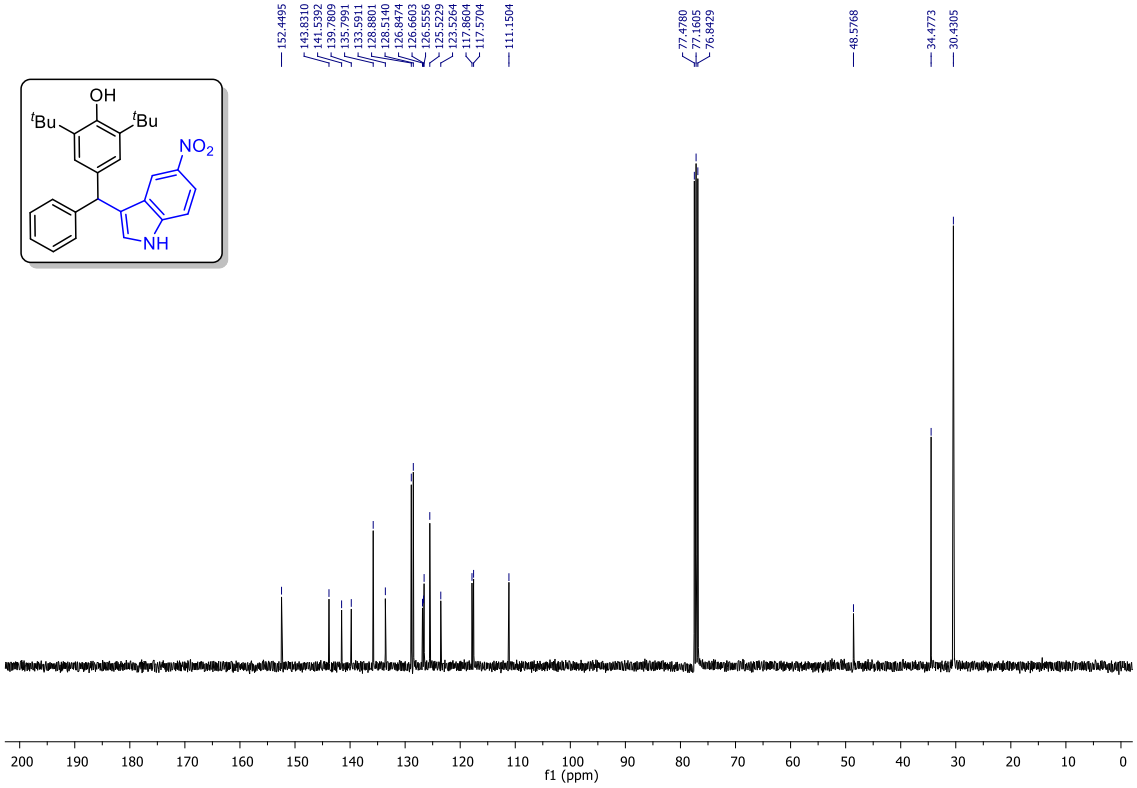
$^{19}F\{^{1}H\}$ NMR (376 MHz, $CDCl_3$) spectrum of **4i**



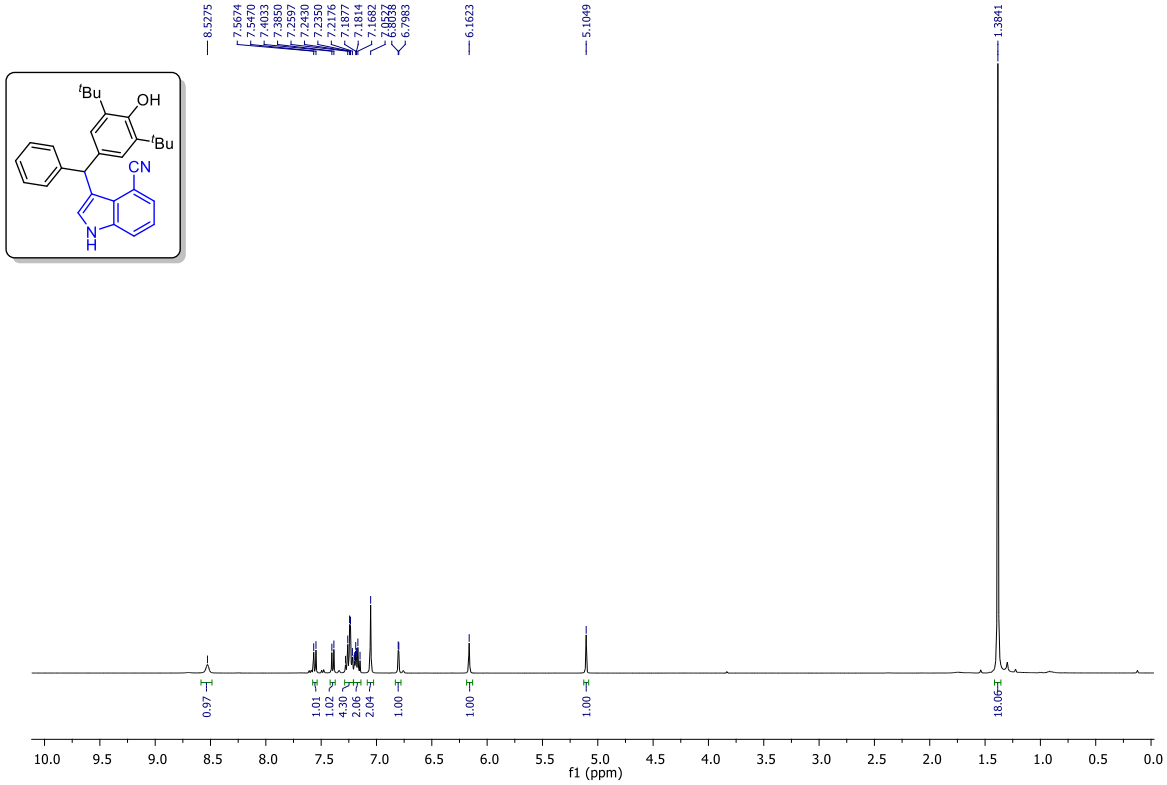
^{1}H NMR (400 MHz, $CDCl_3$) spectrum of **4j**



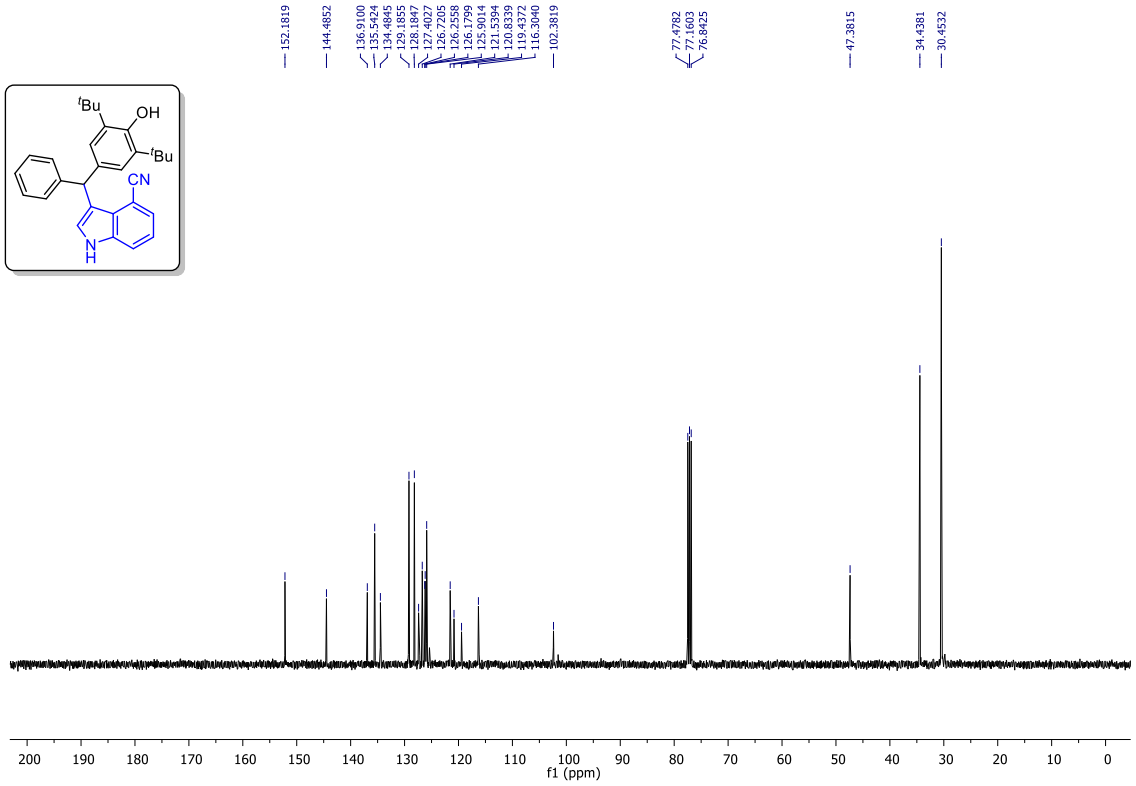
^{13}C{^{1}H} NMR (100 MHz, $CDCl_3$) spectrum of **4j**



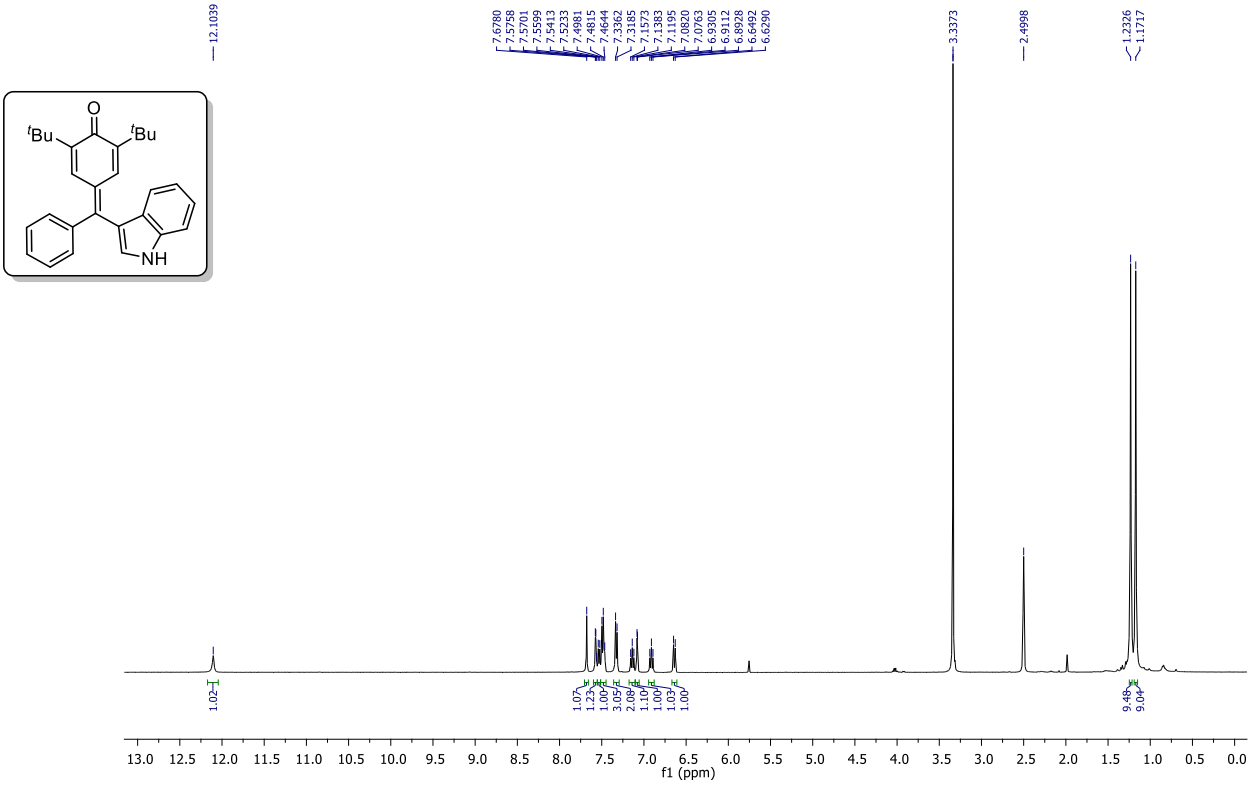
^{1}H NMR (400 MHz, $CDCl_3$) spectrum of **4k**



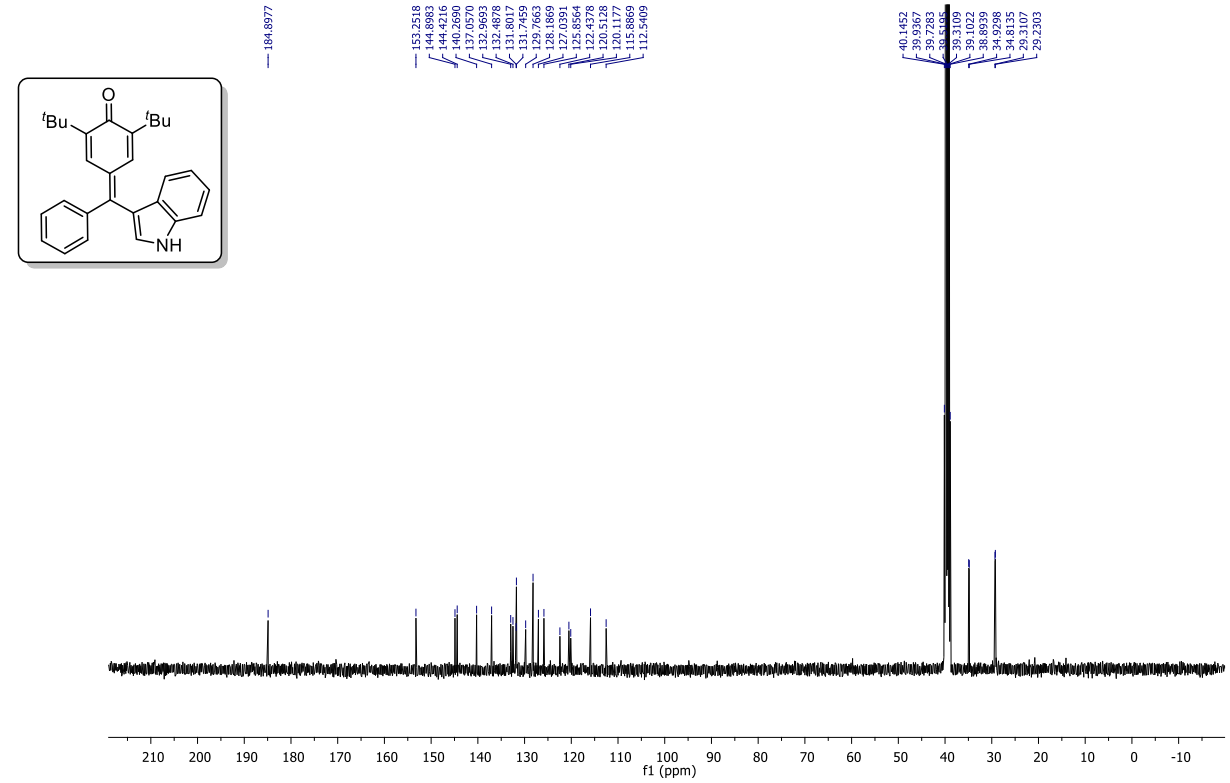
^{13}C{^{1}H} NMR (100 MHz, $CDCl_3$) spectrum of **4k**



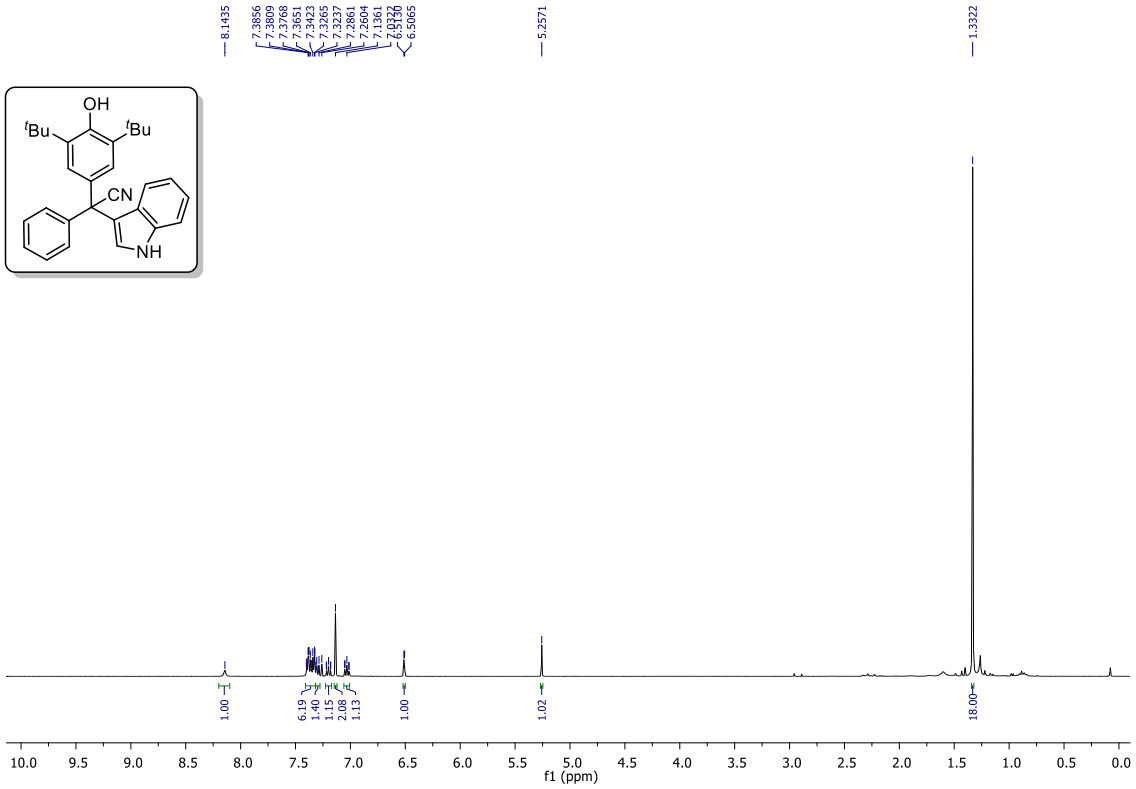
^{1}H NMR (400 MHz, $(CD_3)_2SO$) spectrum of **6**



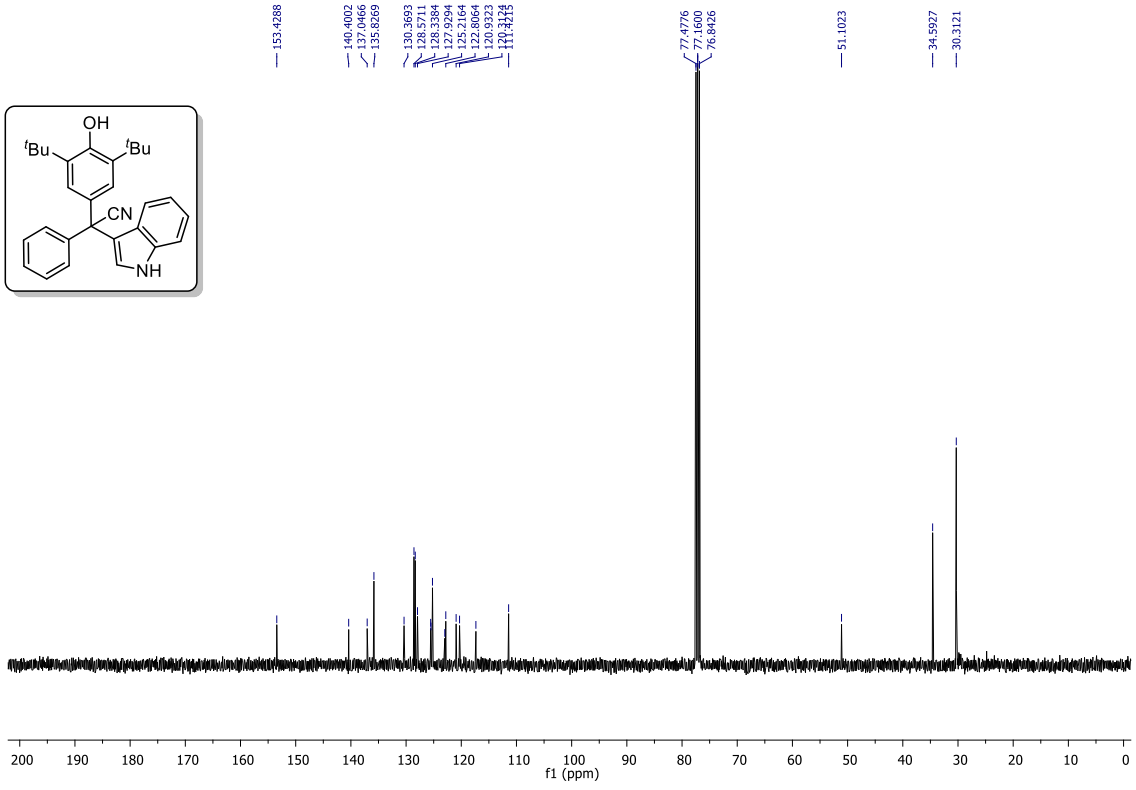
^{13}C {^{1}H} NMR (100 MHz, $(CD_3)_2SO$) spectrum of **6**



^{1}H NMR (400 MHz, $CDCl_3$) spectrum of **8**



^{13}C{^{1}H} NMR (100 MHz, $CDCl_3$) spectrum of **8**



ESI-MS of adduct 5