Electronic Supplementary Material (ESI) for Organic & Biomolecular Chemistry.

–Electronic Supporting Information –

Catalyst-free 1,6-conjugate addition of indoles and 4-hydroxycoumarins to *para*-quinone methides: synthesis of unsymmetrical triarylmethanes

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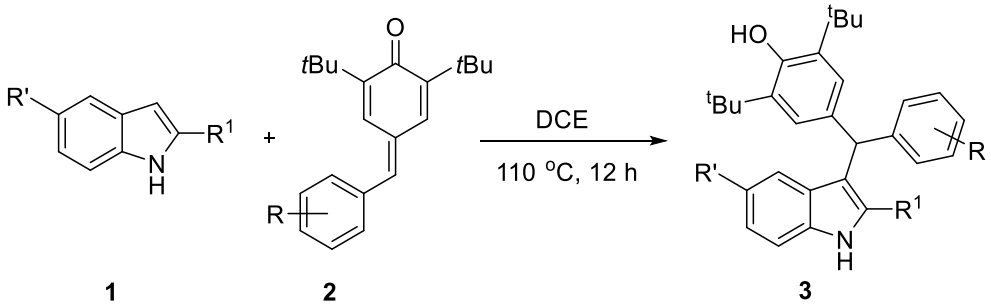
General information

All product mixtures were analysed by thin layer chromatography using aluminium foil backed silica TLC plates. UV-active compounds were detected with a UV lamp (λ = 254 nm). For flash column chromatography, silica gel (230-400 mesh particle size) was used as stationary phase. ^{1}H and ^{13}C NMR spectra were recorded either on a Bruker 300 MHz in deuterated chloroform at 25 °C. Chemical shifts (δ) are reported in ppm, and spin-spin coupling constants (*J*) are given in Hz, while multiplicities are abbreviated by br s (broad singlet), s (singlet), d (doublet), t (triplet), q (quartet) m (multiplet) and dd (doublet of doublet). High resolution mass spectra (HRMS) were recorded on Xevo G2S QTof (ESI) instrument.

All solvents were dried according to known methods and distilled prior to use.[1] All *p*-quinonemethides **2a-n**[2] were synthesized according to literature procedures. The $[Cp^*CoI_2CO]$[3] was prepared according to the literature protocols. All other reagents were purchased from Sigma-Aldrich, Alfa Aesar, Avra, Spectrochem, SRL Pvt. Ltd., India and used without further purification.

General procedure for the synthesis of indole based triarylmethanes



1 **2** **3**

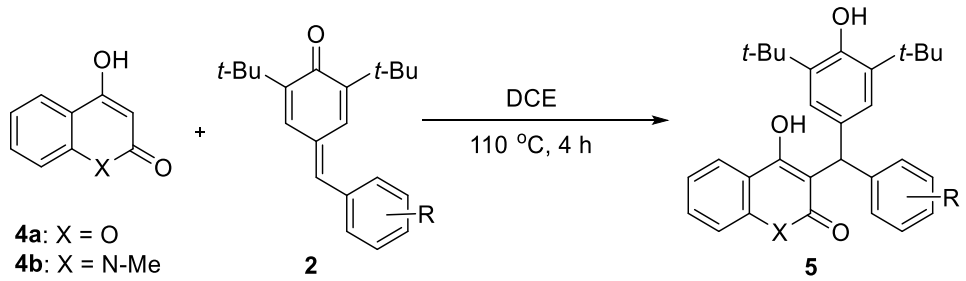
Round bottom (25 mL) flask fixed with refluxing condenser, contain a mixture of indole **1a** (0.51mmol) and 4-benzylidene-2,6-di-tert-butylcyclohexa-2,5-dien-1-one **2a** (0.51mmol) in DCE (4 mL). The reaction mixture was allowed to reflux at 110 °C for 12 h. After completion of reaction (monitor by TLC), solvent was reduced under vacuum. The residue was carefully washed with *n*-hexane to afford the desired pure product **3** (or) crude product was purified by a silica gel column chromatography using hexane–EtOAc as eluent to give pure product.

(or)

A Sealed tube (10 mL) containing indole **1a** (0.51 mmol) and 4-benzylidene-2,6-di-tert-butylcyclohexa-2,5-dien-1-one **2a** (0.51 mmol), then, 1,2-DCE (2.5 mL), were added to the system via a syringe and the reaction mixture was allowed to stir at 110 °C for 12 h. After completion of reaction (monitor by TLC), solvent was reduced under vacuum. The residue was carefully washed with *n*-hexane to afford the desired pure product **3** (or) crude product was purified by a silica gel column chromatography using hexane–EtOAc as eluent to give pure product.

Similar experimental procedure was applied for the reaction of indole **1b-f** with substituted *p*-QMs **2b-n**.

General procedure for the synthesis of 4-hydroxycoumarin based triarylmethanes:



Round bottom flask (25 mL) contain a mixture of 4-hydroxy coumarin **4a** (0.37 mmol) and 4-benzylidene-2,6-di-*tert*-butylcyclohexa-2,5-dien-1-one **2a** (0.37mmol) in DCE (4 mL). The reaction mixture was allowed to reflux at 110 °C for 4h. After completion of reaction (monitor by TLC), solvent was reduced under vacuum. The residue was carefully washed with *n*-hexane to afford the desired pure product **4**.

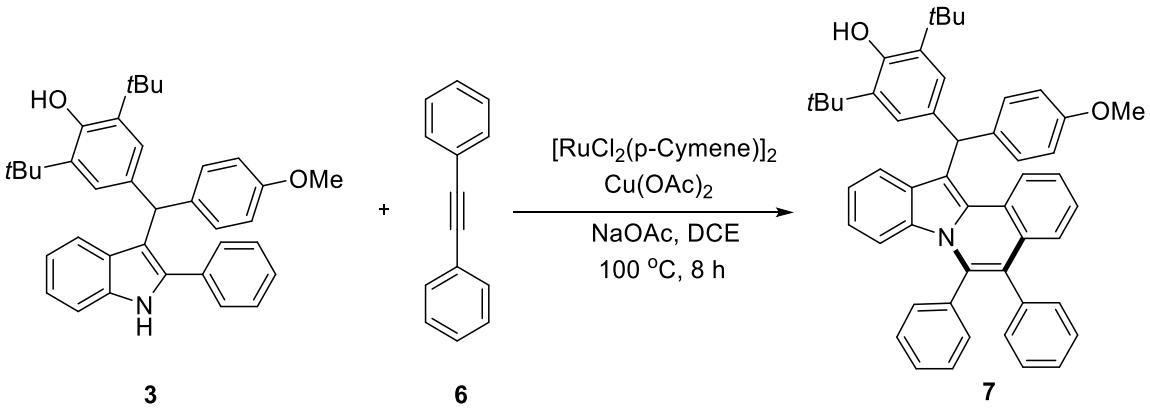
(or)

A Sealed tube (10 mL) containing 4-hydroxycoumarin **1a** (0.37 mmol) and 4-benzylidene-2,6-di-tert-butylcyclohexa-2,5-dien-1-one **2a** (0.37 mmol), then, 1,2-DCE (2 mL), were added to the system via a syringe and the reaction mixture was allowed to stir at 110 °C for 4 h. After completion of reaction (monitor by TLC), solvent was reduced under vacuum. The residue was carefully washed with *n*-hexane to afford the desired pure product **4**.

Similar experimental procedure was applied for the reaction of 4-hydroxy coumarin **4b** with substituted *p*-QMs **2b-n**.

Metal-catalyzed annulations of triarylmethanes with alkyne:

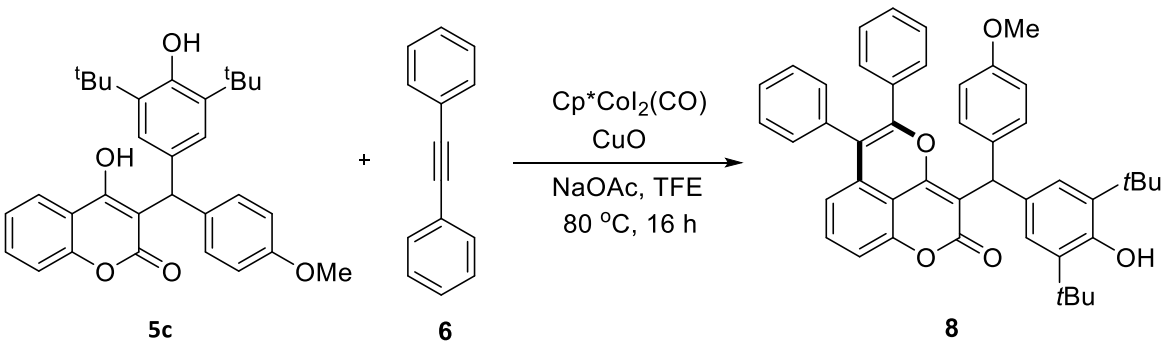
General procedure for the Synthesis of 2,6-di-*tert*-butyl-4-((5,6-diphenylindolo[2,1-*a*]isoquinolin-12-yl)(4-methoxyphenyl)methyl)phenol



3 **6** **7**

A screw-cap sealed tube (10 mL) containing 2,6-Di-*tert*-butyl-4-((4-methoxyphenyl)(2-phenyl-1*H*-indol-3-yl)methyl)phenol **3q** (30 mg, 0.057 mmol), diphenylacetylene **6** (0.069 mmol), $[RuCl_2(p\text{-cymene})]_2$(2.5 mol %), $Cu(OAc)_2$ (2.0 eqiuv) and NaOAc (1.0 eqiuv). Then, 1,2-DCE (1.5 mL), were added to the system via a syringe and the reaction mixture was allowed to stir at 100 °C for 8 h. When the reaction was completed (monitor by TLC), the mixture was cooled and diluted with CH_2Cl_2 (10 mL). The mixture was filtered through a celite pad and the celite pad was washed with dichloromethane (3 x 20 mL). The combined filtrate was concentrated and the residue was purified by a silica gel column chromatography using hexane–EtOAc as eluent to give pure product 7.

General procedure for the Synthesis of 3-((3,5-di-*tert*-butyl-4-hydroxyphenyl)(4-methoxyphenyl)methyl)-5,6-diphenyl-2*H*-pyrano[2,3,4-*de*]chromen-2-one

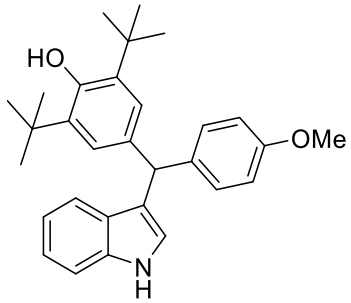


5c **6** **8**

A screw-cap sealed tube (10 mL) containing 3-((3,5-di-*tert*-butyl-4-hydroxyphenyl)(4-methoxyphenyl)methyl)-4-hydroxy-2*H*-chromen-2-one **5c** (30 mg, 0.057 mmol), diphenylacetylene**6** (0.069 mmol), [Cp*CoI_2CO] (5mol %), CuO(2.0 eqiuv) and NaOAc (1.0 eqiuv). Then, 1,2-DCE (1.5 mL) were added to the system via a syringe and the reaction mixture was allowed to stir at 100 °C for 16 h. When the reaction was completed (monitor by TLC), the mixture was cooled and diluted with CH_2Cl_2 (10 mL). The mixture was filtered through a celite pad and the celite pad was washed with dichloromethane (3 x 20 mL). The combined filtrate was concentrated and the residue was purified by a silica gel column chromatography using hexane–EtOAc as eluent to give pure product **8**.

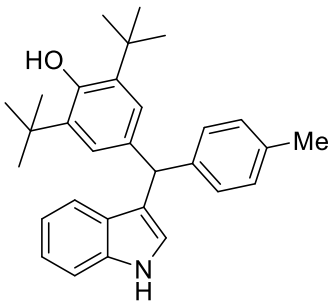
Spectroscopic Data:

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



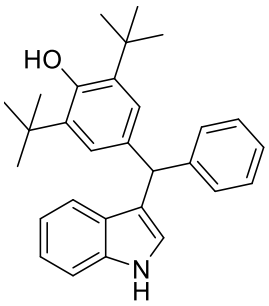
Red solid, Mp (232-234 °C), Yield: 84% (190 mg); **^{1}H NMR (300 MHz, $CDCl_3$):**δ 7.89 (s, 1H), 7.30 (d, *J* = 8.1 Hz, 1H), 7.22 (d, *J* = 7.2 Hz, 1H), 7.14 (d, *J* = 8.1 Hz, 3H), 7.03 (s, 2H), 6.96 (t, *J* = 7.5 Hz, 1H), 6.79 (d, *J* = 8.1 Hz, 2H), 5.50 (s, 1H), 5.04 (s, 1H), 3.76 (s, 3H), 1.35 (s, 18H) ppm. **^{13}C NMR (75 MHz, $CDCl_3$):**δ 157.7, 151.9, 136.8, 136.7, 135.3, 134.7, 129.8, 127.1, 125.4, 123.7, 121.8, 121.2, 120.1, 119.1, 113.4, 110.8, 55.2, 47.9, 34.3, 30.3 ppm. **HRMS(*m/z*):**$[C_{30}H_{35}NO_2+H]^+$Calcd 442.2746, Found 442.2767.

4-((1*H*-indol-3-yl)(*p*-tolyl)methyl-2,6-di-*tert*-butylphenol (3b)



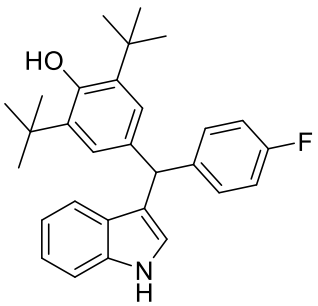
Brown solid, Mp (146-148 °C), Yield: 86% (188 mg); **^{1}H NMR (300 MHz, $CDCl_3$):**δ 7.88 (s, 1H), 7.31 (d, *J* = 8.1 Hz, 1H), 7.22 (d, *J* = 7.5 Hz, 1H), 7.15– 7.11 (m, 3H), 7.06 (s, 2H), 7.04 (s, 2H), 6.95 (t, *J* = 7.8 Hz, 1H), 6.58 (d, *J* = 1.2 Hz, 1H), 5.51 (s, 1H), 5.03 (s, 1H), 2.30 (s, 1H), 1.35 (s, 18H) ppm. **^{13}C NMR (75 MHz, $CDCl_3$):**δ 151.9, 141.7, 136.7, 135.3, 135.2, 134.7, 128.8, 128.7, 127.2, 125.5, 123.7, 121.8, 121.0, 120.1, 119.1, 110.9, 48.4, 34.3, 30.4, 21.0 ppm. **HRMS (*m/z*):** $[C_{30}H_{35}NO+H]^+$Calcd 426.2797, Found 426.2782.

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



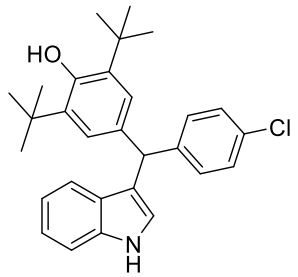
Brown solid, Mp (144-146 °C), Yield: 83% (175 mg); **^{1}H NMR (300 MHz, $CDCl_3$):** δ 7.89 (s, 1H), 7.31 (d, *J* = 8.1 Hz, 1H), 7.23 (s, 4H), 7.20 – 7.11 (m, 3H), 7.03 (s, 2H), 6.96 (t, *J* = 7.5 Hz, 1H), 5.55 (s, 1H), 5.04 (s, 1H), 1.35 (s, 18H) ppm. **^{13}C NMR (75 MHz, $CDCl_3$):** δ 152.0, 144.6, 136.7, 135.4, 134.5, 128.9, 128.1, 127.1, 125.9, 125.5, 123.8, 121.9, 120.8, 120.1, 119.2, 110.9, 48.8, 34.3, 30.4 ppm. **HRMS (*m/z*):** $[C_{29}H_{33}NO+H]^+$Calcd 412.2640, Found 412.2615.

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



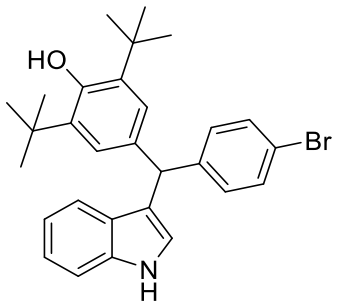
White solid, Mp (158-160 °C), Yield: 80% (176 mg); **^{1}H NMR (300 MHz, $CDCl_3$):**δ 7.76 (s, 1H), 7.22 (d, *J* = 8.1 Hz, 1H), 7.12– 7.02 (m, 4H), 6.92– 6.81 (m, 4H), 6.47 (s, 1H), 5.47 (s, 1H), 4.94 (s, 1H), 1.27 (s, 18H) ppm. **^{13}C NMR (75 MHz, $CDCl_3$):**δ 163.0, 159.7, 152.1, 140.49, 140.44, 136.9, 135.7, 134.4, 130.4, 130.3, 127.1, 125.4, 123.7, 122.0, 120.8, 120.0, 119.3, 114.9, 114.6, 110.9, 48.1, 34.3, 30.4 ppm. **HRMS(*m/z*):**$[C_{29}H_{32}FNO+H]^+$Calcd 430.2546, Found 430.2539.

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



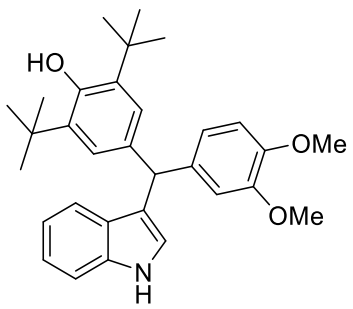
Yellow solid, Mp (160-162 °C), Yield: 82% (189 mg); **^{1}H NMR (300 MHz, $CDCl_3$):**δ 7.94 (s, 1H), 7.33 (d, *J* = 8.1 Hz, 1H), 7.24– 7.12 (m, 6H), 7.00 (s, 2H), 6.96 (d, *J* = 7.5 Hz, 1H), 6.57 (s, 1H), 5.52 (s, 1H), 5.07 (s, 1H), 1.35 (s, 18H) ppm. **^{13}C NMR (75 MHz, $CDCl_3$):**δ 152.1, 143.2, 136.7, 135.5, 133.9, 131.6, 130.3, 128.2, 126.9, 125.4, 123.9, 122.0, 120.3, 119.9, 119.3, 111.0, 48.2, 34.3, 30.3 ppm. **HRMS(*m/z*):**$[C_{29}H_{32}ClNO+H]^+$Calcd 446.2251, Found 446.2259.

2,6-di-*tert*-butyl-4-((4-bromophenyl)(1*H*-indol-3-yl)methyl)phenol (3f)



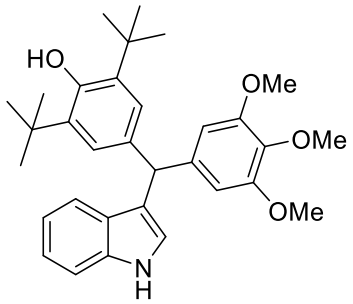
Brown solid, Mp (154-156 °C), Yield: 80% (201 mg); **^{1}H NMR (300 MHz, $CDCl_3$):**δ 7.93 (s, 1H), 7.38– 7.31 (m, 3H), 7.17 (t, *J* = 7.9 Hz, 1H), 7.10 (d, *J* = 8.4 Hz, 2H), 7.00 (s, 2H), 6.96 (d, *J* = 7.5 Hz, 1H), 6.57 (s, 1H), 5.50 (s, 1H), 5.07 (s, 1H), 1.35 (s, 18H) ppm. **^{13}C NMR (75 MHz, $CDCl_3$):**δ 152.1, 143.7, 136.7, 135.6, 133.8, 131.2, 130.7, 126.9, 124.4, 123.9, 122.1, 120.2, 119.9, 119.7, 119.3, 111.0, 48.2, 34.3, 30.4 ppm. **HRMS(*m/z*):**$[C_{29}H_{32}BrNO+H]^+$Calcd 490.1746, Found 490.1751.

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



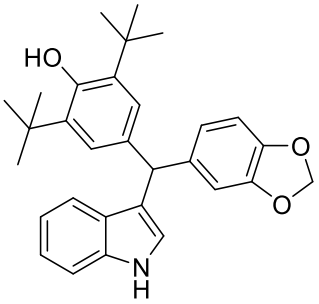
Brown solid, Mp (162-164 °C), Yield: 80% (194 mg); **^{1}H NMR (300 MHz, $CDCl_3$):**δ 7.95 (s, 1H), 7.32 (d, *J* = 8.1 Hz, 1H), 7.23 (d, *J* = 4.8 Hz, 1H), 7.13 (t, *J* = 7.8 Hz, 1H), 7.05 (s, 2H), 6.97 (t, *J* = 8.1 Hz, 1H), 6.81 (s, 1H), 6.75 (s, 2H), 6.58 (s, 1H), 5.50 (s, 1H), 5.05 (s,1H), 3.84 (s, 3H), 3.75 (s, 3H), 1.36 (s, 18H) ppm. **^{13}C NMR (75 MHz, $CDCl_3$):**δ 152.0, 148.6, 147.1, 137.3, 136.7, 135.4, 134.5, 127.1, 125.4, 123.7, 121.9, 121.1, 120.9, 120.1, 119.1, 112.5, 110.9, 110.8, 55.84, 55.81, 48.4, 43.4, 34.3, 30.4 ppm. **HRMS(*m/z*):**$[C_{31}H_{37}NO_3+H]^+$Calcd 472.2852, Found 472.2841.

4-((1*H*-indol-3-yl)(3,4,5-trimethoxyphenyl)methyl)-2,6-di-*tert*-butylphenol (3h)



Brown solid, Mp (208-210 °C), Yield: 86% (221 mg); **^{1}H NMR (300 MHz, $CDCl_3$):**δ 7.99 (s, 1H), 7.33 (d, *J* = 8.1 Hz, 1H), 7.27 (d, *J* = 8.1 Hz, 1H), 7.14 (t, *J* = 7.8 Hz, 1H), 7.08 (s, 2H), 6.61 (d, *J* = 1.5 Hz, 1H), 6.49 (s, 2H), 5.47 (s, 1H), 5.07 (s, 1H), 3.82 (s, 3H), 3.72 (s, 6H), 1.37 (s, 18H) ppm. **^{13}C NMR (75 MHz, $CDCl_3$):**δ 152.2, 152.1, 140.4, 136.7, 136.2, 135.4, 134.1, 127.1, 125.3, 123.6, 121.9, 120.8, 120.0, 119.2, 110.9, 106.2, 60.8, 56.0, 49.1, 34.3, 30.4 ppm. **DEPT 135 NMR(75 MHz, $CDCl_3$):** 125.3, 123.6, 121.9, 120.0, 119.2, 110.8, 106.7, 60.7, 56.1, 49.0, 30.4 ppm. **HRMS(*m/z*):**$[C_{32}H_{39}NO_4+H]^+$Calcd 502.2957, Found 502.2968.

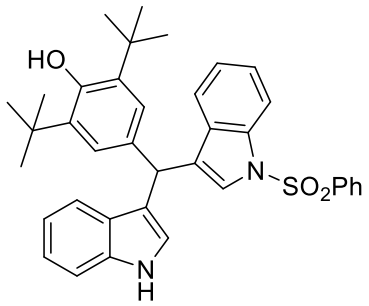
4-(Benzo[*d*][1,3]dioxol-5-yl(1*H*-indol-3-yl)methyl)-2,6-di-*tert*-butylphenol (3i)



Yellow solid, Mp (108-110 °C), Yield: 85% (199 mg); **^{1}H NMR (300 MHz, $CDCl_3$):**δ 7.92 (s, 1H), 7.33 (d, *J* = 8.1 Hz, 1H), 7.24 (t, *J* = 3.9 Hz, 1H), 7.14 (t, *J* = 7.5 Hz, 1H), 7.03 (s, 2H), 6.99 (t, *J* = 7.8 Hz, 1H), 6.73 (d, *J* = 0.6 Hz, 2H), 6.70 (s, 1H), 6.59 (d, *J* = 1.5 Hz, 1H), 5.89 (d, *J* = 4.5 Hz,

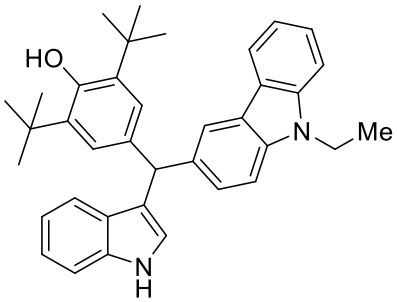
2H), 5.47 (s, 1H), 5.05 (s, 1H), 1.36 (s, 18H) ppm.**^{13}C NMR (75 MHz, $CDCl_3$):**δ 152.0, 147.4, 145.6, 138.8, 136.7, 135.4, 134.5, 127.0, 125.3, 123.7, 121.9, 121.8, 120.8, 120.0, 119.2, 110.9, 109.5, 107.8, 100.7, 48.4, 34.3, 30.3 ppm. **HRMS(*m/z*):**[$C_{30}H_{33}NO_3$+H]$^+$Calcd 456.2539, Found 456.2527.

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



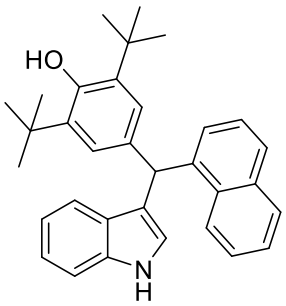
White solid, Mp (180-182 °C), Yield: 80% (242 mg); %. **^{1}H NMR (300 MHz, $CDCl_3$):** δ 7.99 (d, *J* = 8.4 Hz, 1H), 7.95 (s, 1H) 7.73 (d, *J* = 8.1 Hz, 2H), 7.52 (t, *J* = 7.3 Hz, 1H), 7.41 – 7.35 (m, 3H), 7.27 – 7.14 (m, 4H), 7.11 – 7.02 (m, 4H), 6.96 (t, *J* = 7.3 Hz, 1H), 6.60 (d, *J* = 0.9 Hz, 1H), 5.62 (s, 1H), 5.07 (s, 1H), 1.33 (s, 18H) ppm. **^{13}C NMR (75 MHz, $CDCl_3$):** δ 152.3, 138.1, 136.7, 135.8, 135.6, 133.5, 132.3, 130.8, 129.1, 127.6, 126.8, 126.6, 125.1, 125.0, 124.5, 123.4, 123.0, 122.0, 120.6, 119.6, 119.2, 118.8, 113.7, 111.1, 39.9, 34.3, 30.3ppm. **HRMS(*m/z*):**[$C_{37}H_{38}N_2O_3S$+H]$^+$Calcd 591.2681, Found 591.2675.

2,6-Di-*tert*-butyl-4-((9-ethyl-9*H*-carbazol-3-yl)(1*H*-indol-3-yl)methyl)phenol (3k)



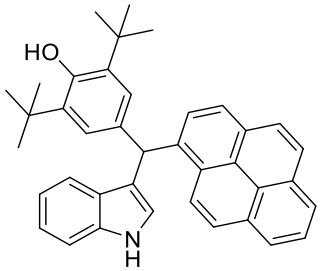
Orange solid, Mp (224-226 °C), Yield: 81% (220 mg); **^{1}H NMR (300 MHz, $CDCl_3$):**δ7.90 (d, *J* = 6.9 Hz, 2H), 7.80 (s, 1H), 7.35 – 7.16 (m, 5H), 7.09 – 7.01 (m, 4H), 6.80 (t, *J* = 7.35, 1H), 6.55 (s, 1H), 5.68 (s, 1H), 4.98 (s, 1H), 4.25 (q, *J* = 7.2 Hz, 2H) 1.34 (t, *J* = 7.2 Hz, 3H), 1.28 (s, 18H) ppm. **^{13}C NMR (75 MHz, $CDCl_3$):**δ151.9, 140.3, 138.8, 136.9, 135.5, 135.3, 127.4, 127.1, 125.6, 125.2, 123.8, 123.2, 122.9, 121.8, 121.8, 120.5, 120.4, 120.3, 119.1, 118.4, 110.8, 108.3, 108.0, 48.9, 37.5, 34.3, 30.4, 13.7 ppm. **HRMS(*m/z*):**[$C_{37}H_{40}N_2O$+H]$^+$Calcd 529.3219, Found 529.3225.

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



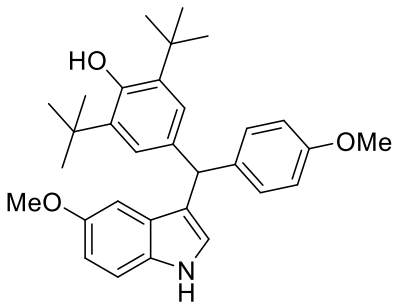
Red solid, Mp (209-210 °C), Yield: 86% (204 mg); **^{1}H NMR (300 MHz, $CDCl_3$):**δ 8.17 (d, *J* = 7.5 Hz, 1H), 7.84 (d, *J* = 6.3 Hz, 2H), 7.70 (d, *J* = 8.1 Hz, 1H), 7.45– 7.40 (m, 2H), 7.31 (d, *J* = 7.5 Hz, 2H), 7.22 (d, *J* = 7.8 Hz, 1H), 7.16– 7.12 (m, 2H), 7.05 (s, 2H), 6.95 (t, *J* = 7.5 Hz, 1H), 6.46 (s, 1H), 6.32 (s, 1H), 5.03 (s, 1H), 1.32 (s, 18H) ppm. **^{13}C NMR (75 MHz, $CDCl_3$):**δ 152.0, 140.5, 136.7, 135.4, 133.9, 133.7, 132.0, 128.6, 127.1, 126.8, 126.6, 125.8, 125.4, 125.2, 124.5, 124.4, 121.9, 120.8, 119.9, 119.2, 110.9, 44.5, 34.3, 30.4 ppm. **HRMS(*m/z*):**$[C_{33}H_{35}NO+H]^+$Calcd 462.2797, Found 462.2801.

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



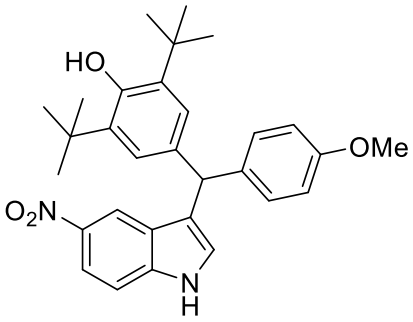
Yellow solid, Mp (255-257 °C), Yield: 83% (228 mg); **^{1}H NMR (300 MHz, $CDCl_3$):**δ 8.38 (d, *J* = 9.3 Hz, 1H), 8.05 (t, *J* = 6.1 Hz, 2H), 7.95 – 7.90 (m, 4H), 7.86 (d, *J* = 7.5 Hz, 1H), 7.78 (s,1H), 7.66 (d, *J* = 8.1 Hz, 1H), 7.25 (d, *J* = 8.1 Hz, 1H), 7.15 (s, 1H), 7.09 – 7.02 (m, 4H), 6.80 (t, *J* = 7.6 Hz, 1H), 6.56 (s, 1H), 6.42 (s, 1H), 4.94 (s, 1H) ppm. **^{13}C NMR (75 MHz, $CDCl_3$):**δ 152.1, 138.7, 136.9, 135.7, 134.1, 131.5, 130.9, 129.9, 128.9, 127.6, 127.3, 127.2, 127.1, 126.7, 125.9, 125.7, 125.2,125.1, 124.8, 124.7, 124.7, 124.6, 123.9, 122.0, 121.2, 120.1, 119.3, 110.9, 45.0, 34.3, 30.4 ppm. **HRMS(*m/z*):**$[C_{39}H_{37}NO+H]^+$Calcd 536.2953, Found 536.2946.

2,6-Di-*tert*-butyl-4-((5-methoxy-1*H*-indol-3-yl)(4-methoxyphenyl)methyl)phenol (3n)



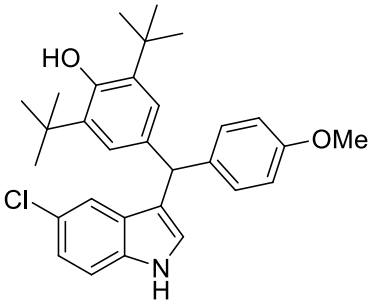
Pale yellow solid, Mp (143-144 ^{o}C), Yield: 86% (166mg); **^{1}H NMR (300 MHz, $CDCl_3$):**δ 7.81 (s, 1H), 7.18 – 7.14 (m, 3H), 7.04 (s, 2H), 6.82 (s, 1H), 6.81 – 6.76 (m, 2H), 6.60 – 6.55 (m, 2H), 3.76 (s, 1H), 3.64 (s, 1H), 1.35 (s, 18H) ppm. **^{13}C NMR (75 MHz, $CDCl_3$)**: δ 157.7, 153.6, 151.9, 136.8, 135.4, 134.7, 131.9, 129.8, 127.5, 125.4, 124.4, 120.9, 113.5, 111.9, 111.5, 102.1, 55.7, 55.2, 48.1, 34.3, 30.4 ppm. **HRMS (*m/z*):**$[C_{31}H_{37}NO_3+H]^+$Calcd 472.2852, Found 472.2857.

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



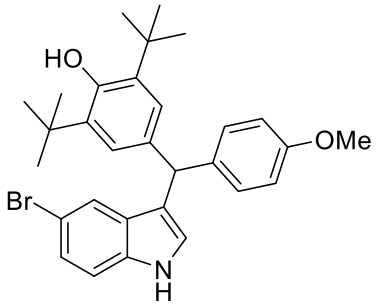
Yellow solid, Mp (130-132 ^{o}C), Yield: 84% (152 mg); **^{1}H NMR (300 MHz, $CDCl_3$):**δ 8.35 (s, 1H), 8.18 (d, *J* = 1.8 Hz, 1H), 8.06 (dd, J_1= 9.0 Hz, J_2 = 9.0 Hz, 1H), 7.36 (d, *J* = 9.0 Hz, 1H), 7.13 (d, *J* = 8.7 Hz, 1H), 7.01 (s, 2H), 6.82 (d, *J* = 8.4 Hz, 2H), 6.78 (s, 1H), 5.54 (s, 1H), 5.09 (s, 1H), 3.79 (s, 3H), 1.35 (s, 18H) ppm. **^{13}C NMR (75 MHz, $CDCl_3$):**δ 158.0, 152.2, 141.5, 139.6, 135.9, 135.7, 133.8, 129.6, 126.56, 126.52, 125.3, 123.8, 117.7, 117.4, 113.7, 110.9, 55.2, 47.6, 34.3, 30.3 ppm. **HRMS (*m/z*):** $[C_{30}H_{34}N_2O_4+H]^+$Calcd 487.2597, Found 487.2583.

2,6-di-*tert*-butyl-4-((5-chloro-1*H*-indol-3-yl)(4-methoxyphenyl)methyl)phenol (3p)



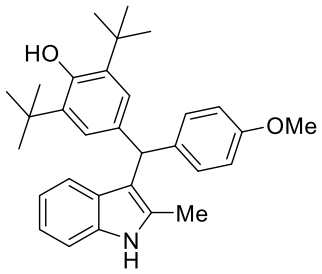
Pale yellow solid, Mp (166-168 °C), Yield: 85% (161 mg); **^{1}H NMR (300 MHz, $CDCl_3$):** δ 7.93 (s, m, 1H), 7.26 – 7.10 (m, 5H), 7.04 (s, 2H), 6.84 (d, *J* = 7.8 Hz, 2H), 6.65 (s, 1H), 5.48 (s, 1H), 5.06 (s, 1H), 3.81 (s, 3H), 1.40 (s, 18H) ppm. **^{13}C NMR (75 MHz, $CDCl_3$)**: δ 158.0, 152.1, 136.6, 135.7, 135.2, 134.4, 129.7, 128.3, 125.4, 125.0, 122.2, 121.1, 119.6, 113.7, 111.9, 55.2, 47.9, 34.3, 30.4 ppm. **HRMS(*m/z*):**[$C_{30}H_{34}ClNO_2$+Na]$^+$Calcd 498. 2176, Found 498.2169.

4-((5-bromo-1*H*-indol-3-yl)(4-methoxyphenyl)methyl)-2,6-di-*tert*-butylphenol (3q)



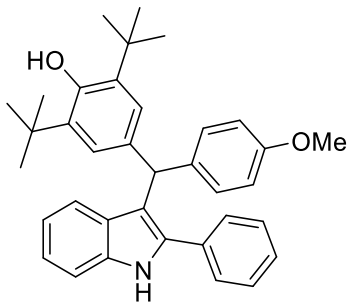
Yellow solid, Mp (174-176 °C), Yield: 83% (132 mg); **^{1}H NMR (300 MHz, $CDCl_3$):**δ 7.93 (s, 1H), 7.37 (s, 1H), 7.27-7.14 (m, 4H), 7.04 (s, 2H), 6.85 (d, *J* = 8.7 Hz, 2H), 6.63 (s, 1H), 5.48 (s, 1H), 5.07 (s, 1H), 3.81 (s, 3H), 1.40 (s, 18H) ppm. **^{13}C NMR (75 MHz, $CDCl_3$)**: δ 158.0, 152.1, 136.6, 135.7, 135.4, 134.4, 129.7, 129.0, 125.4, 124.87, 124.82, 122.7, 121.0, 113.7, 112.5, 112.3, 55.2, 47.8, 34.3, 30.4 ppm. **HRMS(*m/z*):**[$C_{30}H_{34}BrNO_2$+H]$^+$Calcd 519.1773, Found 519.1781.

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



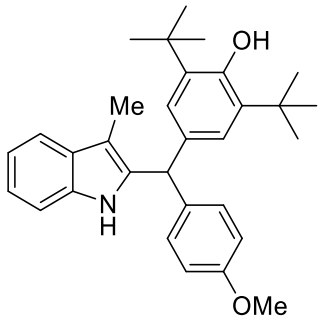
Red solid, Mp (162-164 °C), Yield: 90% (188 mg); **^{1}H NMR (300 MHz, $CDCl_3$):**δ 7.72 (s, 1H), 7.24 (d, *J* = 10.5 Hz, 1H), 7.10 – 7.01 (m, 6H), 6.89 (t, *J* = 7.5 Hz, 1H), 6.77 (d, *J* = 7.8 Hz, 2H), 5.58 (s, 1H), 5.04 (s, 1H), 3.76 (s, 3H), 2.15 (s, 3H), 1.33 (s, 18H) ppm. **^{13}C NMR (75 MHz, $CDCl_3$):**δ 157.5, 151.8, 137.0, 135.3, 135.2, 134.4, 131.5, 129.9, 128.5, 125.8, 120.5, 119.7, 118.9, 115.1, 113.3, 109.9, 55.2, 46.7, 34.3, 30.3, 12.5 ppm. **HRMS (*m/z*):**[$C_{31}H_{37}NO_2$+H]$^+$Calcd 456.2903, Found 456.2911.

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



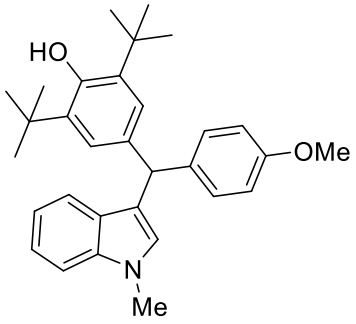
Brown solid, Mp (177-178 ^{o}C), Yield: 79% (128 mg); **^{1}H NMR (300 MHz, CDCl$_3$):**δ 8.05 (s, 1H), 7.49 – 7.32 (m, 6H), 7.15 – 7.09 (m, 4H), 7.05 (s, 2H), 6.90 (t, *J* = 6.9 Hz, 1H), 6.75 (d, *J* = 8.7 Hz, 1H), 5.66 (s, 1H), 5.01 (s, 1H), 3.76 (s, 3H), 1.30 (s, 18H) ppm. **^{1}H NMR (300 MHz, CDCl$_3$):**δ 157.5, 151.8, 137.1, 136.2, 135.36, 135.33, 134.6, 133.3, 129.9, 128.8, 128.5, 128.3, 127.7, 125.9, 121.8, 121.7, 119.3, 116.4, 113.3,110.6, 55.2, 46.8, 34.3, 30.3 ppm. **DEPT 135 NMR (75 MHz, CDCl$_3$):** 130.0, 128.8, 128.5, 127.7, 125.9, 121.85, 121.82, 119.3, 113.4, 110.6, 55.2, 47.0, 30.4 ppm. **HRMS (*m/z*):** $[C_{36}H_{39}NO_2+H]^+$Calcd 518.3059, Found 518.3051.

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



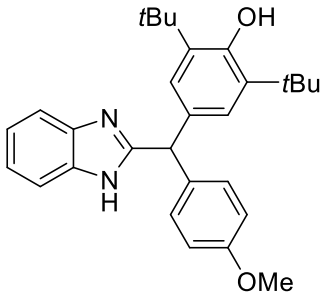
Red solid, Mp (158-160 ^{o}C), Yield: 68% (142 mg); **^{1}H NMR (300 MHz, CDCl$_3$):**δ 7.53 – 7.47 (m, 4H), 7.23 – 7.20 (m, 1H), 7.10 – 7.06 (m, 4H), 7.04 (d, *J* = 8.7 Hz, 2H), 2.13 (s, 1H), 1.36 (s, 18H) ppm. **^{13}C NMR (75 MHz, CDCl$_3$):**δ 158.1, 152.5, 136.5, 135.9, 135.0, 134.9, 132.6, 129.8, 129.7, 125.5, 121.0, 119.0, 118.2, 113.7, 110.5, 107.7, 55.2, 47.8, 34.3, 30.3, 8.7 ppm. **HRMS(*m/z*):**$[C_{31}H_{37}NO_2+H]^+$Calcd 456.2903, Found 456.2911.

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



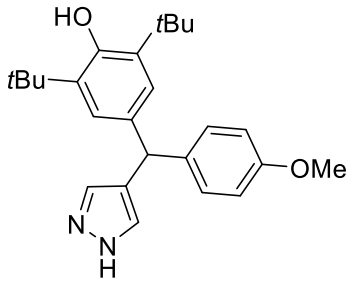
Yellow solid, Mp (88-90°C), Yield: 52% (109 mg); **^{1}H NMR (300 MHz, $CDCl_3$):**δ 7.36 – 7.21 (m, 5H), 7.12 (s, 2H), 7.02 (t, J = 7.3 Hz, 1H), 6.87 (d, J = 8.4 Hz, 2H), 6.51 (s, 1H), 5.57 (s, 1H), 5.07 (s, 1H), 3.83 (s, 3H), 3.75 (s, 3H), 1.44 (s, 18H) ppm. **^{13}C NMR (75 MHz, $CDCl_3$):** δ 157.9, 151.9, 137.6, 137.3, 135.5, 135.0, 129.8, 128.3, 127.7, 125.5, 121.4, 120.3, 119.6, 118.6, 113.5, 108.9, 55.2, 48.1, 34.3, 32.5, 30.4 ppm. **HRMS(*m/z*):**$[C_{31}H_{37}NO_2+H]^+$Calcd 456.2903, Found 456.2907.

4-((1*H*-benzo[d]imidazol-2-yl)(4-methoxyphenyl)methyl)-2,6-di-*tert*-butylphenol (3w)



White solid, Mp (155-157 °C), Yield: 81% (182 mg); **^{1}H NMR (300 MHz, $CDCl_3$):**δ 7.83 (d, *J* = 7.5 Hz, 1H), 7.64 (s, 1H), 7.28 – 7.18 (m, 3H), 7.05 (d, *J* = 8.7 Hz, 2H), 6.99 (s, 2H), 6.89 (d, *J* = 8.4 Hz, 2H), 6.64 (s, 1H), 5.31 (s, 1H), 3.82 (s, 3H), 1.38 (s, 18H) ppm. **^{13}C NMR (75 MHz, $CDCl_3$):** δ 159.4, 153.8, 136.7, 131.1, 128.8, 125.2, 122.2, 122.0, 114.2, 111.1, 63.7, 55.2, 34.4, 30.2 ppm. **HRMS(*m/z*):**$[C_{29}H_{34}N_2O_2+H]^+$Calcd 443.2699, Found 443.2700.

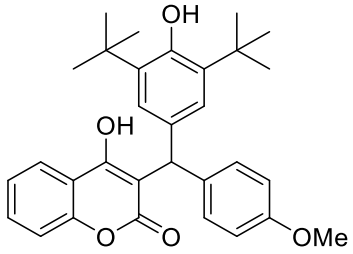
2,6-di-*tert*-butyl-4-((4-methoxyphenyl)(1*H*-pyrazol-4-yl)methyl)phenol (3x)



Pale yellow solid, Mp (110-112 °C), Yield: 78% (270 mg); **^{1}H NMR (300 MHz, $CDCl_3$):** δ 7.60 (s, 1H), 7.26 (s, 1H), 7.05 (d, *J* = 8.4 Hz, 2H), 6.89 – 6.86 (m, 4H), 6.66 (s, 1H), 6.27 (s, 1H), 5.19

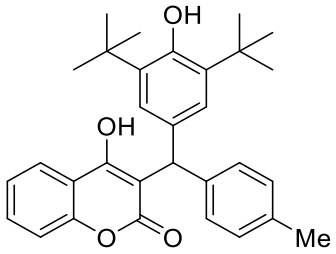
(s, 1H), 3.81 (s, 3H), 1.38 (s, 18H) ppm. **^{13}C NMR (75 MHz, $CDCl_3$):** δ 159.2, 153.4, 136.0, 132.6, 130.4, 129.4, 124.8, 113.9, 105.1, 69.3, 55.2, 34.3, 30.2 ppm. **HRMS(*m/z*):**$[C_{25}H_{32}N_2O_2+H]^+$Calcd 393.2542, Found 393.2537.

3-((3,5-Di-*tert*-butyl-4-hydroxyphenyl)(4-methoxyphenyl)methyl)-4-hydroxy-2*H*-chromen-2-one (5a)



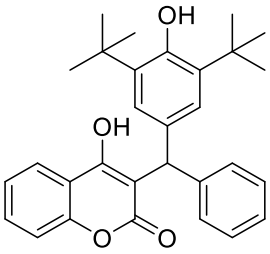
White solid, Mp (185-187 ^oC), Yield: 94% (170 mg); **^{1}H NMR (300 MHz, $CDCl_3$)**: δ 7.64 (d, *J* = 7.8 Hz,1H*),* 7.55 – 7.49 (m, 1H),7.31 (d, *J* = 8.1 Hz, 1H)*,* 7.25 (t, *J* = 7.6 Hz, 1H), 7.1 (d, *J* = 8.4 Hz, 2H), 7.04 (s, 2H), 6.89 (d, *J* = 8.7 Hz, 1H), 6.51 (s, 1H), 5.78 (s, 1H), 5.25 (s, 1H), 3.80 (s, 3H), 1.36 (s, 18H) ppm. **^{13}C NMR (75 MHz, $CDCl_3$):** δ 163.3, 160.5, 158.8, 153.3, 152.7, 137.1, 132.3, 131.8, 130.5, 129.7, 125.3, 123.8, 123.0, 116.4, 116.1, 114.4, 108.3, 55.3, 46.5, 34.4, 30.1 ppm. **DEPT 135 NMR (75 MHz, $CDCl_3$):** 131.8, 129.7, 125.3, 123.8, 123.1, 116.4, 114.4, 55.2, 46.5, 30.2 ppm. **HRMS (*m/z*):**$[C_{31}H_{34}O_5+H]^+$Calcd 487.2484, Found 487.2491.

3-((3,5-Di-*tert*-butyl-4-hydroxyphenyl)(*p*-tolyl)methyl)-4-hydroxy-2*H*-chromen-2-one (5b)



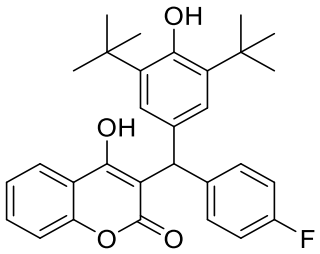
White solid, Mp (198-200^oC), Yield: 91% (159 mg); **^{1}H NMR (300 MHz, $CDCl_3$)**: δ 7.75 (d, J = 7.8 Hz, 1H), 7.54 (t, J = 7.6 Hz, 1H), 7.32 (d, J = 8.4 Hz, 1H), 7.29 – 7.24 (m, 4H), 7.18 (s, 2H), 7.08 (s, 2H), 6.49 (s, 1H), 5.83 (s, 1H), 5.24 (s, 1H), 2.36 (s, 3H), 1.39 (s, 3H) ppm. **^{13}C NMR (75 MHz, $CDCl_3$):** δ 160.5, 153.3, 152.8, 137.6, 137.2, 137.0, 131.7, 130.5, 129.8, 128.6, 125.4, 123.7, 123.1, 116.4, 116.2, 108.4, 47.1, 34.5, 30.2, 21.0 ppm. **HRMS (*m/z*):**$[C_{31}H_{34}O_4+H]^+$Calcd 471.2535, Found 471.2547.

3-((3,5-Di-*tert*-butyl-4-hydroxyphenyl)(phenyl)methyl)-4-hydroxy-2*H*-chromen-2-one (5c)



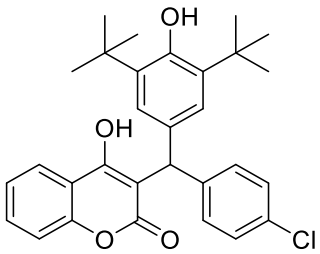
White solid, Mp (190-192 °C), Yield: 92% (156 mg); **^{1}H NMR (300 MHz, $CDCl_3$)**: δ 7.76 (J_1 = 7.8 Hz, J_2 = 8.1 Hz, 1H), 7.57 – 7.52 (m, 1H), 7.40 – 7.28 (m, 7H), 7.06 (s, 2H), 6.49 (s, 1H), 5.87 (s, 1H), 5.26 (s, 1H), 1.38 (s, 18H) ppm. **^{13}C NMR (75 MHz, $CDCl_3$):** δ 163.4, 160.8, 153.4, 152.8, 140.6, 137.4, 130.4, 129.0, 128.7, 127.3, 125.4, 123.8, 123.1, 116.4, 116.2, 108.1, 47.5, 34.5, 30.2 ppm. **HRMS (*m/z*):**$[C_{30}H_{32}O_4+H]^+$Calcd457.2379, Found 457.2368.

3-((3,5-Di-*tert*-butyl-4-hydroxyphenyl)(4-fluorophenyl)methyl)-4-hydroxy-2*H*-chromen-2-one (5d)



Yellow solid, Mp (222-224°C), Yield: 92% (162 mg); **^{1}H NMR (300 MHz, $CDCl_3$)**: δ 7.77 (d, *J* = 8.1 Hz, 1H), 7.56 (t, *J* = 7.6 Hz, 1H), 7.35 – 7.25 (m, 4H), 7.09 – 7.03 (m, 4H), 6.51 (s, 1H), 5.85 (s, 1H), 5.31 (s, 1H), 1.39 (s, 18H) ppm. **^{13}C NMR (75 MHz, $CDCl_3$):** δ 163.6, 163.1, 160.7, 153.6, 152.8, 137.6, 136.1, 131.9, 130.4, 125.3, 123.8, 123.1, 116.4, 116.1, 115.9, 107.8, 46.8, 34.5, 30.1 ppm. **HRMS(*m/z*):**$[C_{30}H_{31}FO_4+H]^+$Calcd475.2285, Found 475.2286.

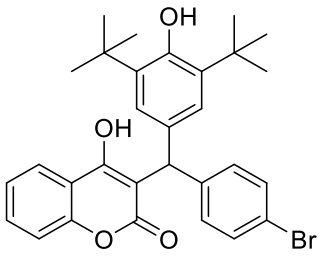
3-((4-Chlorophenyl)(3,5-di-tert-butyl-4-hydroxyphenyl)methyl)-4-hydroxy-2H-chromen-2-one (5e)



Yellow solid, Mp (200-202 °C), Yield: 90% (164 mg); **^{1}H NMR (300 MHz, $CDCl_3$)**: δ 7.78 (d, *J* = 9.0 Hz, 1H), 7.57 (d, *J* = 7.8 Hz, 1H), 7.36 – 7.24 (m, 6H), 7.05 (2H), 6.51 (s, 1H), 5.83 (s, 1H), 5.31 (s, 1H), 1.39 (s, 3H) ppm. **^{13}C NMR (75 MHz, $CDCl_3$):** δ 163.0, 160.7, 153.7, 152.8, 139.1,

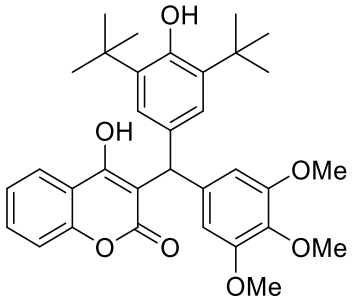
137.7, 133.1, 132.0, 130.1, 130.0, 129.0, 125.3, 123.8, 123.1, 116.4, 116.1, 107.6, 47.0, 34.5, 30.2 ppm. **HRMS(*m/z*):**[$C_{30}H_{31}ClO_4$+H]$^+$Calcd 491.1989, Found 491.1982.

3-((4-Bromophenyl)(3,5-di-*tert*-butyl-4-hydroxyphenyl)methyl)-4-hydroxy-2*H*-chromen-2-one (5f)



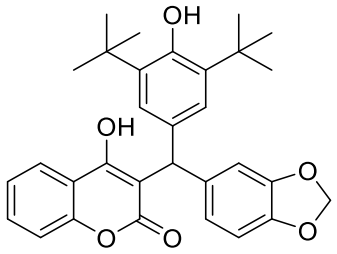
Yellow solid, Mp (178-180 ^{o}C), Yield: 95% (188 mg); **^{1}H NMR (300 MHz, $CDCl_3$)**: δ 7.76 (dd, J_1 =7.8 Hz, J_2 = 8.1 Hz,1H),7.58 – 7.48 (m, 3H), 7.35 – 7.18 (m, 4H), 7.05 (s, 1H), 6.49 (s, 1H),5.81 (s, 1H), 5.31 (s, 1H), 1.39 (s, 18H) ppm. **^{13}C NMR (75 MHz, $CDCl_3$):** δ 163.0, 160.8, 153.6, 152.7, 139.5, 137.7, 131.9, 130.4, 129.9, 125.3, 123.8, 123.1, 121.1, 116.4, 116.0, 107.4, 47.0, 34.5, 30.1 ppm. **HRMS(*m/z*):**[$C_{30}H_{31}BrO_4$+H]$^+$Calcd 535.1484, Found 535.1487.

3-((3,5-Di-*tert*-butyl-4-hydroxyphenyl)(3,4,5-trimethoxyphenyl)methyl)-4-hydroxy-2*H*-chromen-2-one (5g)



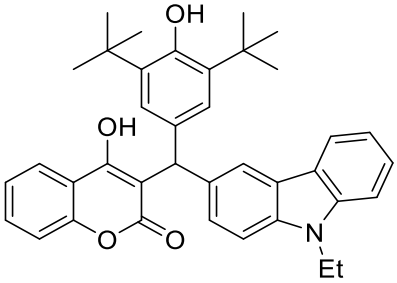
Yellow solid, Mp (163-165 ^{o}C), Yield: 96% (194 mg); **^{1}H NMR (300 MHz, $CDCl_3$)**: δ 7.67 (dd, J_1 = 7.8 Hz, J_2 = 7.8 Hz, 1H), 7.42 – 7.42 (m, 1H), 7.26 – 7.15 (m, 3H), 7.00 (s, 2H), 6.46 (s, 1H), 6.41 (s, 2H), 5.69 (s, 1H), 5.15 (s, 1H), 3,76 (s, 3H), 3.67 (s, 6H), 1.30 (s, 18H) ppm. **^{13}C NMR (75 MHz, $CDCl_3$):** δ 163.3, 160.6, 153.9, 153.4, 152.8, 137.9, 137.2, 136.4, 131.9, 130.1, 125.3, 123.8, 123.1, 116.1, 108.2, 106.4, 60.8, 56.3, 47.5, 345, 30.2 ppm. **HRMS (*m/z*):**[$C_{33}H_{38}O_7$+H]$^+$Calcd547.2696, Found 547.2701.

3-(Benzo[*d*][1,3]dioxol-5-yl(3,5-di-*tert*-butyl-4-hydroxyphenyl)methyl)-4-hydroxy-2*H*-chromen-2-one (5h)



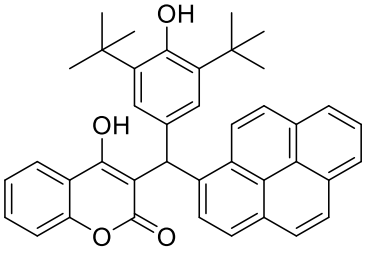
Yellow solid, Mp (148-150 ^{o}C), Yield: 90% (167 mg); **^{1}H NMR (300 MHz, $CDCl_3$)**: δ 7.65 (d, *J* = 7.8 Hz, 1H), 7.43 (t, *J = 7.8* Hz*,* 1H*),* 7.24 – 7.13 (m, 2H), 6.98 (s, 2H), 6.71 – 6.62 (m, 3H), 6.46 (m, 1H), 5.86 (s, 1H), 5.67 (s, 1H), 5.16 (s, 1H), 1.29 (s,18H) ppm. **^{13}C NMR (75 MHz, $CDCl_3$):** δ 163.2, 160.6, 153.4, 152.8, 148.4, 146.9, 137.3, 134.6, 131.8, 130.4, 125.3, 123.8, 123.1, 121.6, 116.4, 116.1, 109.3, 108.5, 101.1, 47.1, 34.5, 30.2 ppm. **HRMS(*m/z*):**$[C_{31}H_{32}O_6+H]^+$Calcd 501.2277, Found 501.2269.

3-((3,5-Di-*tert*-butyl-4-hydroxyphenyl)(9-ethyl-9*H*-carbazol-3-yl)methyl)-4-hydroxy-2*H*-chromen-2-one (5i)



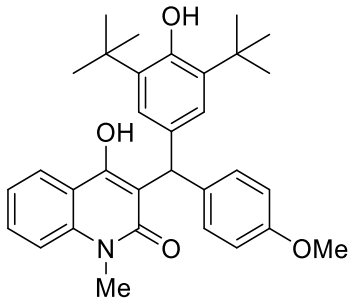
Red solid, Mp (168-170 ^{o}C), Yield: 85% (180 mg); **^{1}H NMR (300 MHz, $CDCl_3$)**: δ 8.04 – 7.99 (m, 2H), 7.77 (d, *J* = 8.1 Hz, 1H), 7.57 – 7.42 (m, 5H), 7.35 (S, 2H), 7.30 – 7.18 (m, 3H), 6.09 (s, 1H), 5.26 (s, 1H), 1.41 (s, 18H), 1.37 (t, *J* = 2.5 Hz, 3H) ppm. **^{13}C NMR (75 MHz, $CDCl_3$):** δ 163.3, 160.5, 153.2, 152.8, 140.5, 139.3, 137.1, 131.6, 131.05, 131.01, 126.4, 125.9, 125.5, 123.7, 123.6, 123.1, 122.8, 120.5, 120.4, 118.9, 116.3, 109.1, 108.5, 47.4, 37.6, 34.5, 30.3, 13.7 ppm. **HRMS(*m/z*):**$[C_{38}H_{39}NO_7+H]^+$Calcd 574.2957, Found 574.2961.

3-((3,5-Di-*tert*-butyl-4-hydroxyphenyl)(8,10-dihydropyren-1-yl)methyl)-4-hydroxy-2*H*-chromen-2-one (5j)



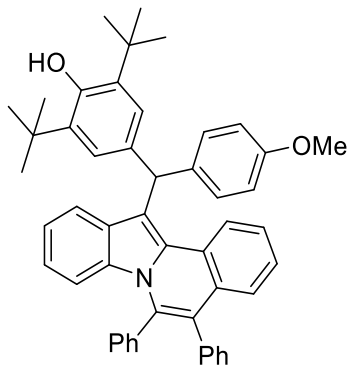
White solid, Mp (160-162 °C), Yield: 88% (190 mg); **^{1}H NMR (300 MHz, $CDCl_3$)**: δ 8.30 (d, *J* = 9.3 Hz, 1H), 8.22 – 8.02 (m, 6H), 7.80 (d, *J* = 7.8 Hz), 7.70 (d, *J = 7.*8 Hz, 1H), 7.70 (d, *J* = 7.8 Hz, 1H), 7.55 (t, *J* = 7.8 Hz, 1H), 7.37 (d, *J* = 8.1Hz,1H),7.28 (s, 2H), 7.23 (d, *J = 7.8* Hz,2H*)*, 7.15 (s, 1H), 6.87 (s, 1H), 5.26 (s, 1H), 1.35 (s, 18H) ppm. **^{13}C NMR (75 MHz, $CDCl_3$):** δ 163.4, 161.6, 153.5, 137.4, 134.6, 131.9, 130.2, 129.8, 128.4, 127.3, 126.2, 125.4, 123.9, 123.3, 123.1, 116.5, 116.1, 108.1, 44.9, 34.5, 30.2 ppm. **HRMS(*m/z*):**$[C_{40}H_{36}O_4+H]^+$Calcd 581.2692, Found 581.2698.

3-((3,5-Di-*tert*-butyl-4-hydroxyphenyl)(4-methoxyphenyl)methyl)-4-hydroxy-1-methylquinolin-2(1*H*)-one (5k)



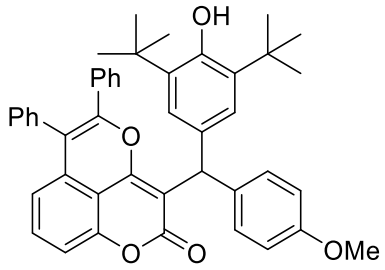
White solid, Mp (202-204 °C), Yield: 86% (148 mg); **^{1}H NMR (300 MHz, $CDCl_3$)**: δ 7.90 (d, *J* = 7.8 Hz, 1H), 7.56 (t, *J* = 7.2 Hz, 1H), 7.33 (d, *J* = 8.4 Hz, 1H), 7.23 – 7.18 (m, 3H), 7.05 (s, 2H), 6.86 (d, *J* = 8.7 Hz, 2H), 6.19 (s, 1H), 5.21 (s, 1H), 3.78 (s, 3H), 3.71 (s, 3H), 1.34 (s, 18H) ppm. **^{13}C NMR (75 MHz, $CDCl_3$):** δ 163.3, 158.5, 157.1, 153.0, 139.0, 136.8, 133.5, 131.5, 130.6, 129.9, 125.4, 123.4, 121.5, 116.3, 114.3, 114.0, 113.7, 55.2, 46.4, 34.4, 30.2 ppm. **HRMS** (*m/z*): $[C_{32}H_{37}NO_4+H]^+$Calcd 501.2879, Found 501.2885.

2,6-Di-*tert*-butyl-4-((5,6-diphenylindolo[2,1-*a*]isoquinolin-12-yl)(4-methoxyphenyl)methyl)phenol (7)



White solid, Mp (236-238^{o}C), Yield: 80% (32 mg); **^{1}H NMR (300 MHz, $CDCl_3$)**: δ 8.51 (d, *J* = 7.8 Hz, 1H), 7.40 – 7.35 (m, 6H), 7.30 – 7.15 (m, 11H), 7.09 (d, *J* = 8.1 Hz, 1H), 6.95 – 6.84 (m, 3H), 6.73 (t, *J* = 7.8 Hz, 1H), 6.53 (s, 1H), 6.06 (d, *J* = 8.7 Hz, 1H), 5.08 (s, 1H), 3.81 (s, 3H), 1.37 (s, 18H) ppm. **^{13}C NMR (75 MHz, $CDCl_3$):** δ 158.0, 152.1, 137.2, 136.8, 136.2, 136.0, 135.8, 134.0, 132.2, 132.0, 131.9, 131.8, 131.7, 131.03, 131.01, 130.3, 130.0, 128.5,3, 128.51, 128.4, 127.9, 127.8, 126.6, 126.4, 126.3, 126.2, 125.8, 125.5, 121.3, 121.1, 120.6, 120.0, 114.3, 113.9, 113.7, 55.2, 48.2, 34.4, 30.4 ppm. **HRMS** (*m/z*): $[C_{50}H_{48}NO_4+H]^+$Calcd 694.3685, Found 694.3661.

3-((3,5-Di-tert-butyl-4-hydroxyphenyl)(4-methoxyphenyl)methyl)-5,6-diphenyl-2*H*-pyrano[2,3,4-*de*]chromen-2-one (8)



White solid, Mp (202-204 ^{o}C), Yield: 75% (31 mg); **^{1}H NMR (300 MHz, $CDCl_3$)**: δ 7.44 – 7.34 (m, 4H), 7.31 – 7.25 (m, 5H), 7.19 – 7.14 (m, 2H), 7.03 (t, *J* = 7.6 Hz, 2H), 6.85 (d, *J* = 8.7 Hz, 2H), 6.76 – 6.70 (m, 3H), 5.83 (s, 1H), 5.08 (s, 1H), 3.83 (s, 3H), 1.31 (s, 18H) ppm. **^{13}C NMR (75 MHz, $CDCl_3$):** δ 163.1, 158.1, 157.9, 152.5, 152.4, 150.0, 135.8, 134.9, 134.0, 132.6, 132.5, 132.2, 131.7, 131.6, 130.9, 129.3, 129.1, 128.9, 128.3, 128.1, 127.7, 125.9, 117.9, 116.7, 114.7, 113.7, 110.6, 106.6, 55.3, 45.6, 34.3, 30.3 ppm. **HRMS** (*m/z*): $[C_{45}H_{43}O_5+H]^+$Calcd 663.3110, Found 663.3112.

References

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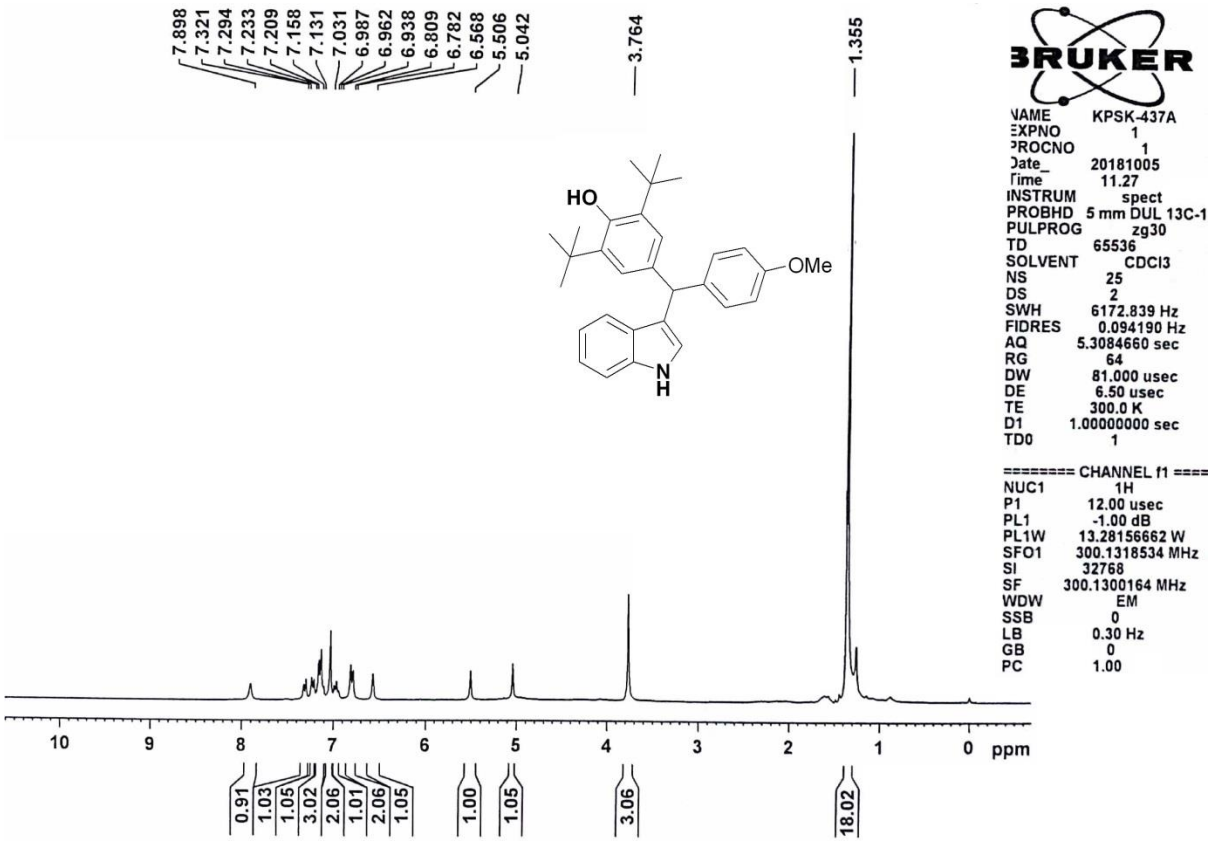
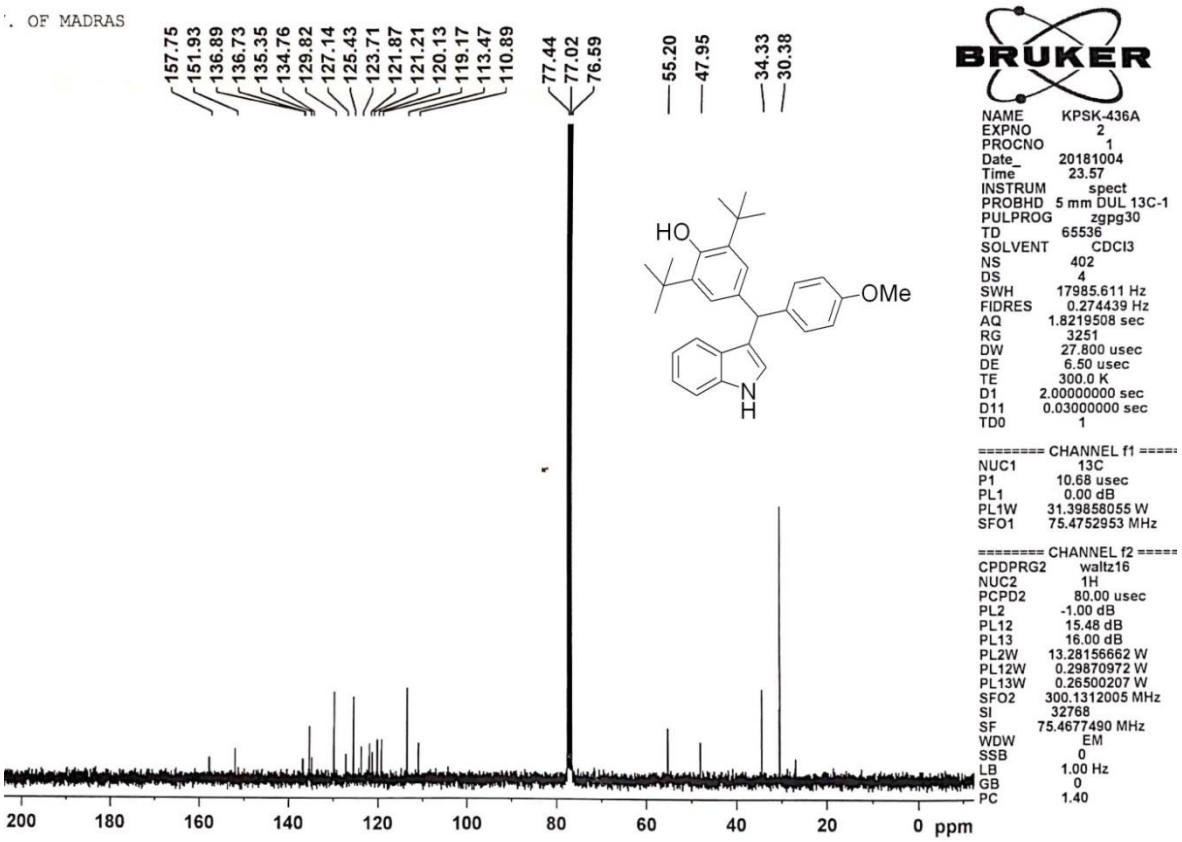
2. (a) L. Roiser, M. Waser, *Org. Lett*, 2017, **19**, 2338. (b) C. Jarava-Barrera, A. Parra, A. Lopez, F. Cruz-Acosta, D. Collado-Sanz, D. J. Cardenas and M. Tortosa, *ACS Catal.*, 2016, **6**, 442. (c) W.-D. Chu, L.-F. Zhang, X. Bao, X.-Y. Zhao, C. Zeng, J.-Y. Du, G.-B. Zhang, F. Z. Wang, Z.-Y. Ma, C.-A. Fan, *Angew. Chem. Int. Ed.*, 2013, **52**, 9229.

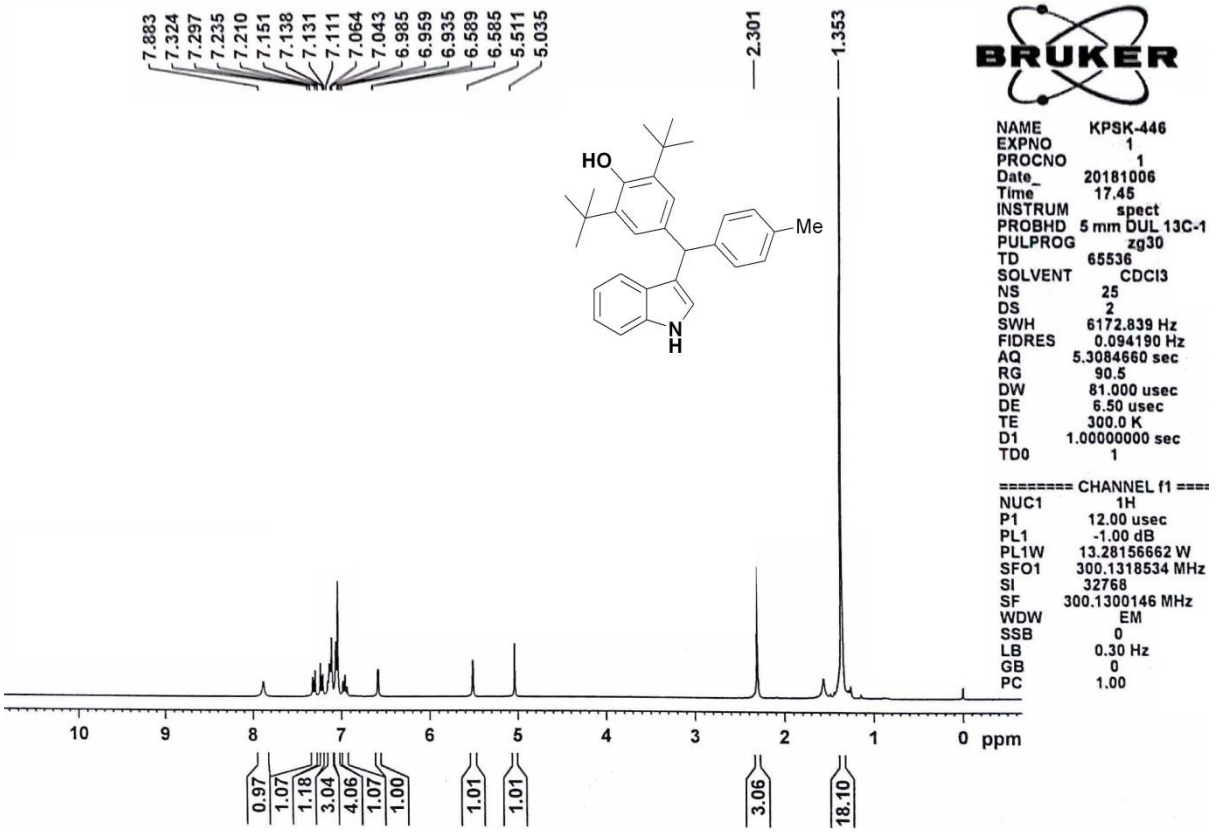
3. (a) T. Yoshino, H. Ikemoto, S. Matsunaga, M. Kanai, *Angew. Chem. Int. Ed.* 2013, **52**, 2207. (b) W. Li, L.-H. Weng, G.-X. Jin, *Inorg. Chem. Commun.* 2004, **7**, 1174.

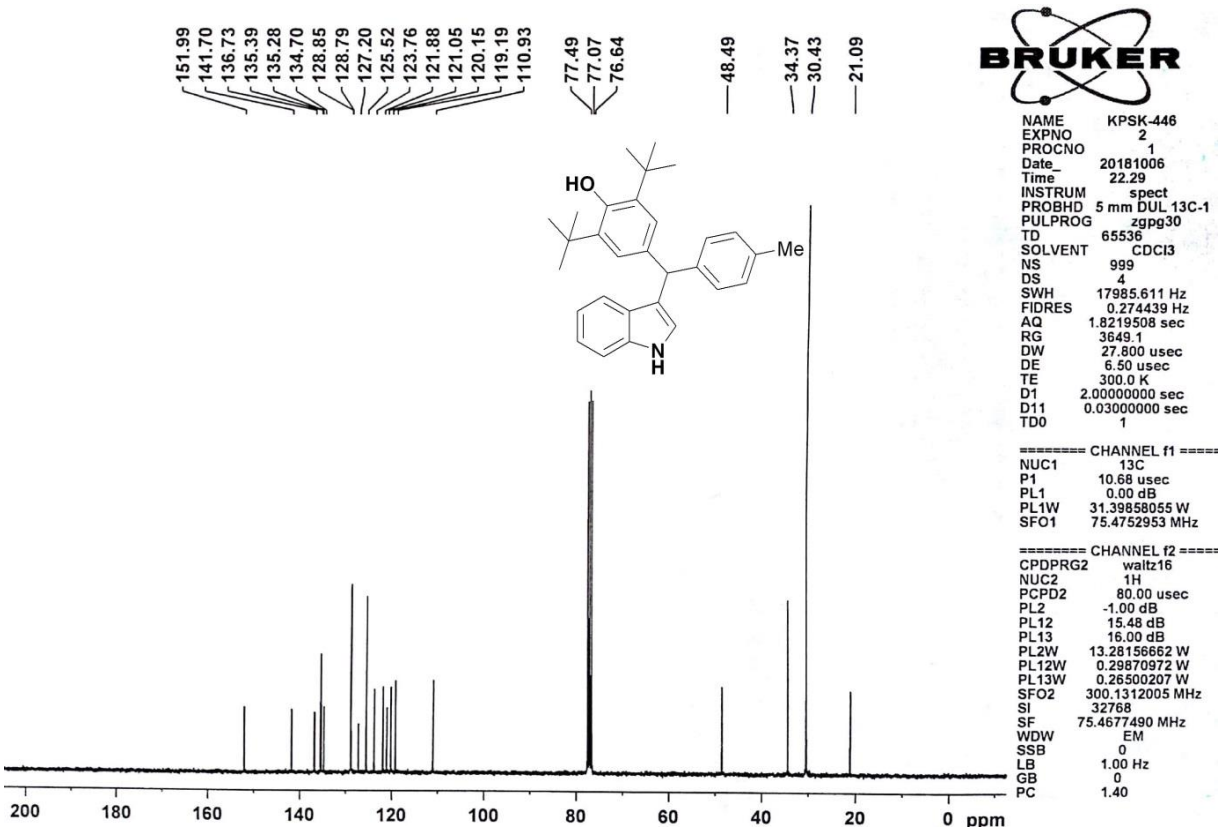
^{1}H and ^{13}C NMR for compound **3a**



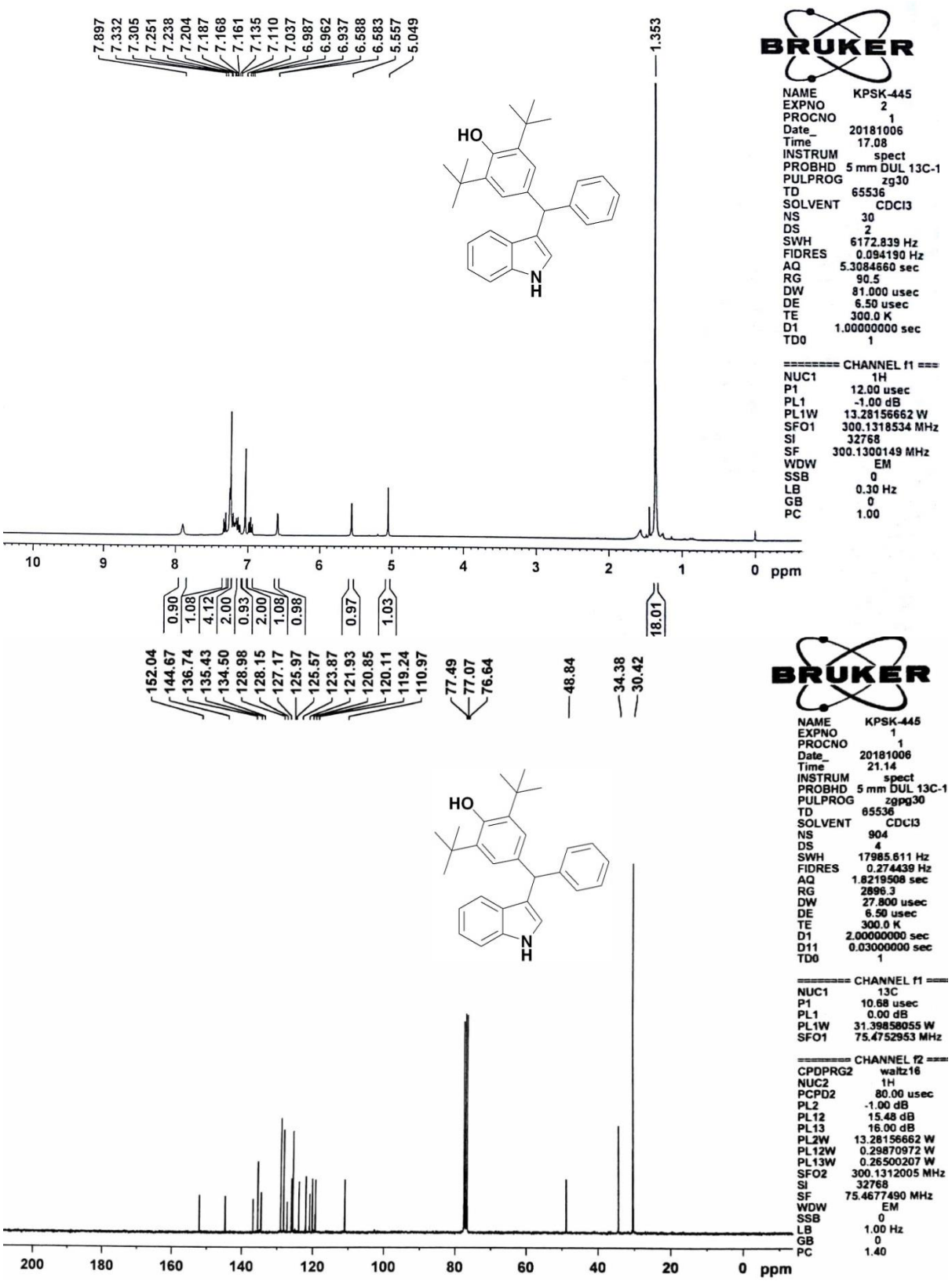


^{1}H and ^{13}C NMR for compound **3b**

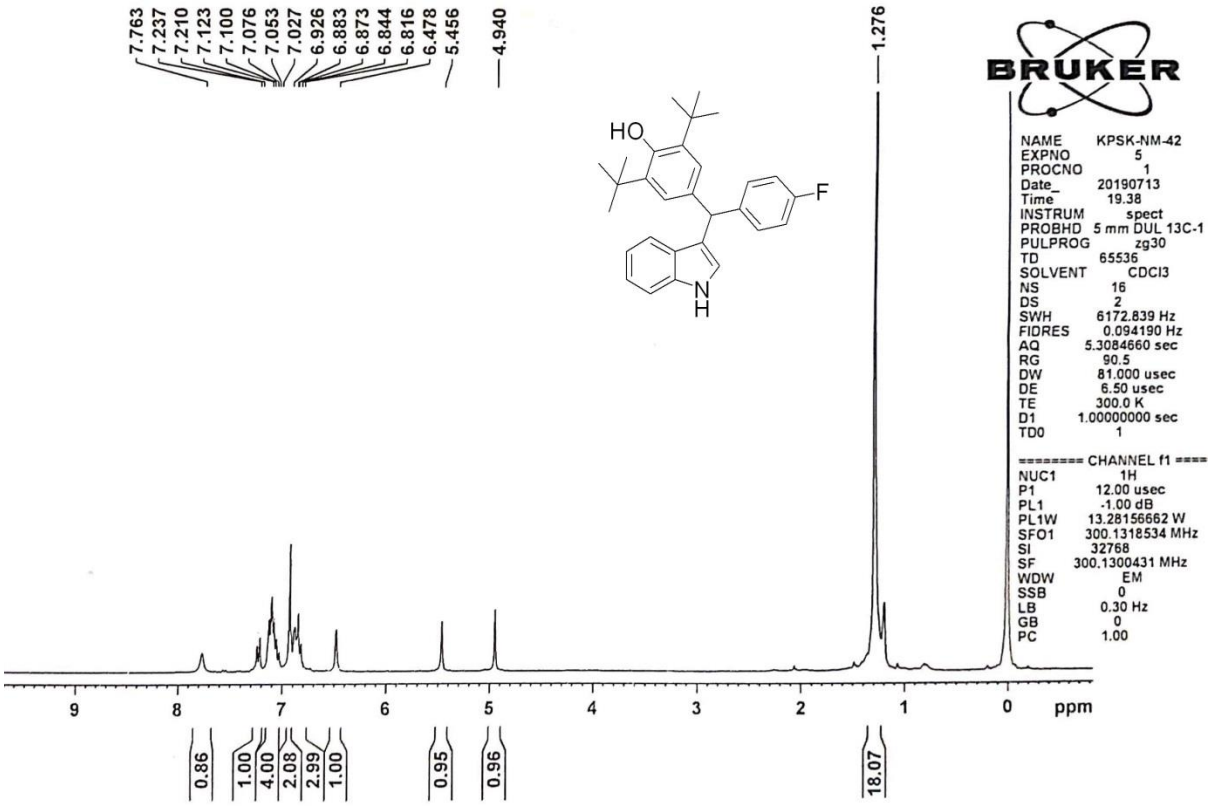


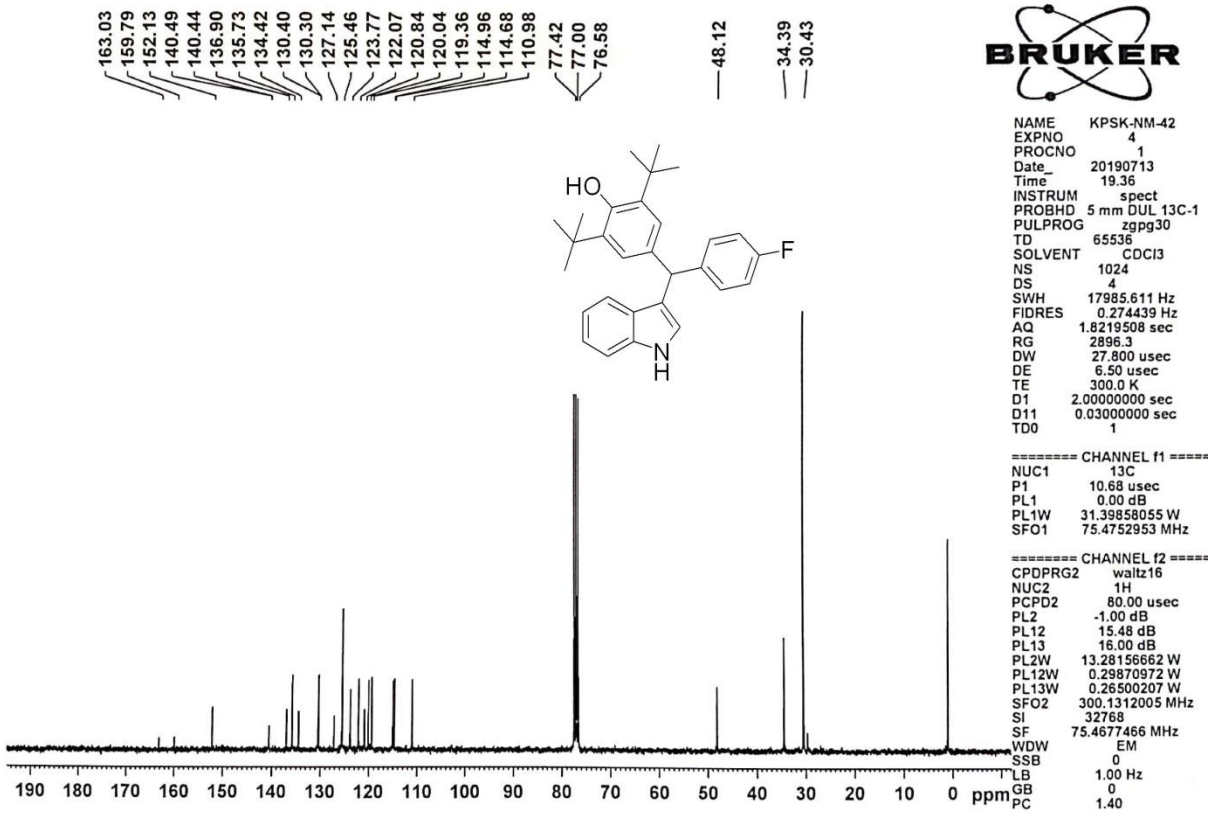


^{1}H and ^{13}C NMR for compound **3c**

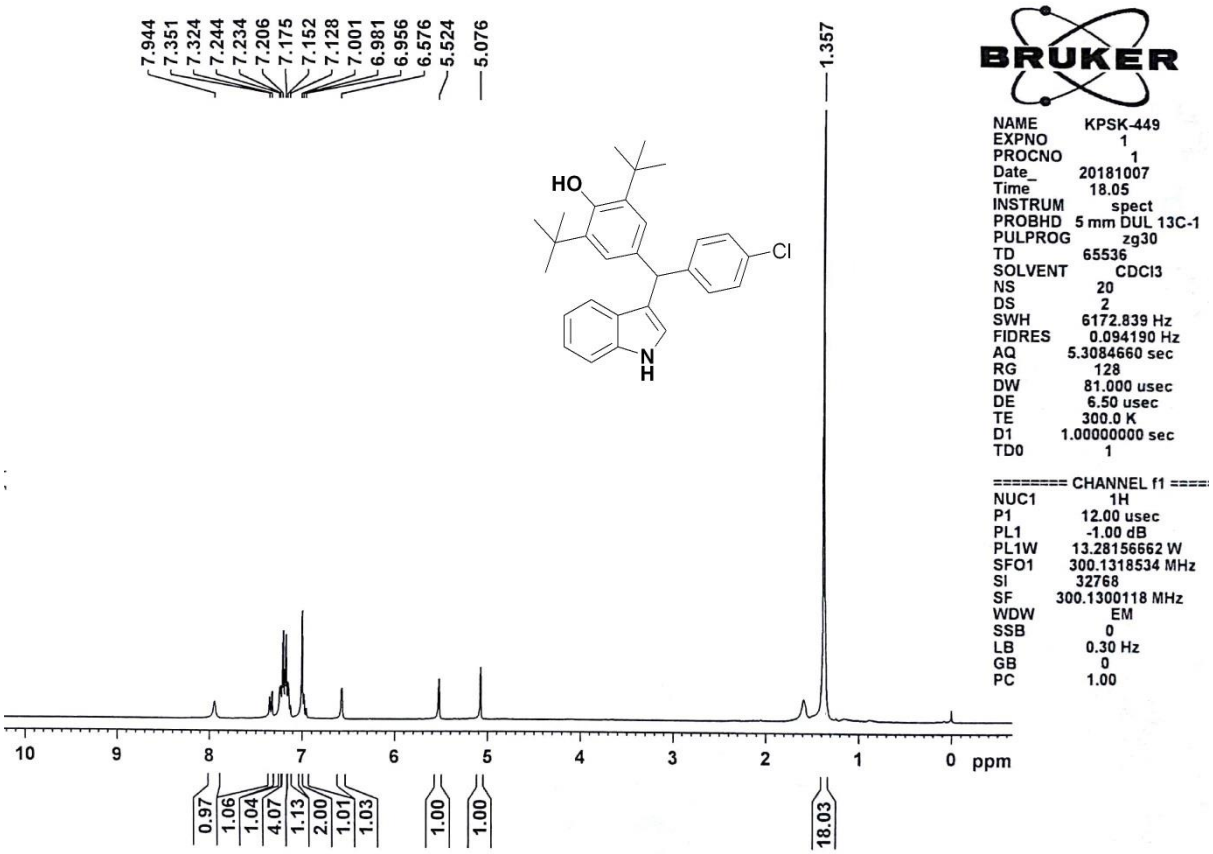


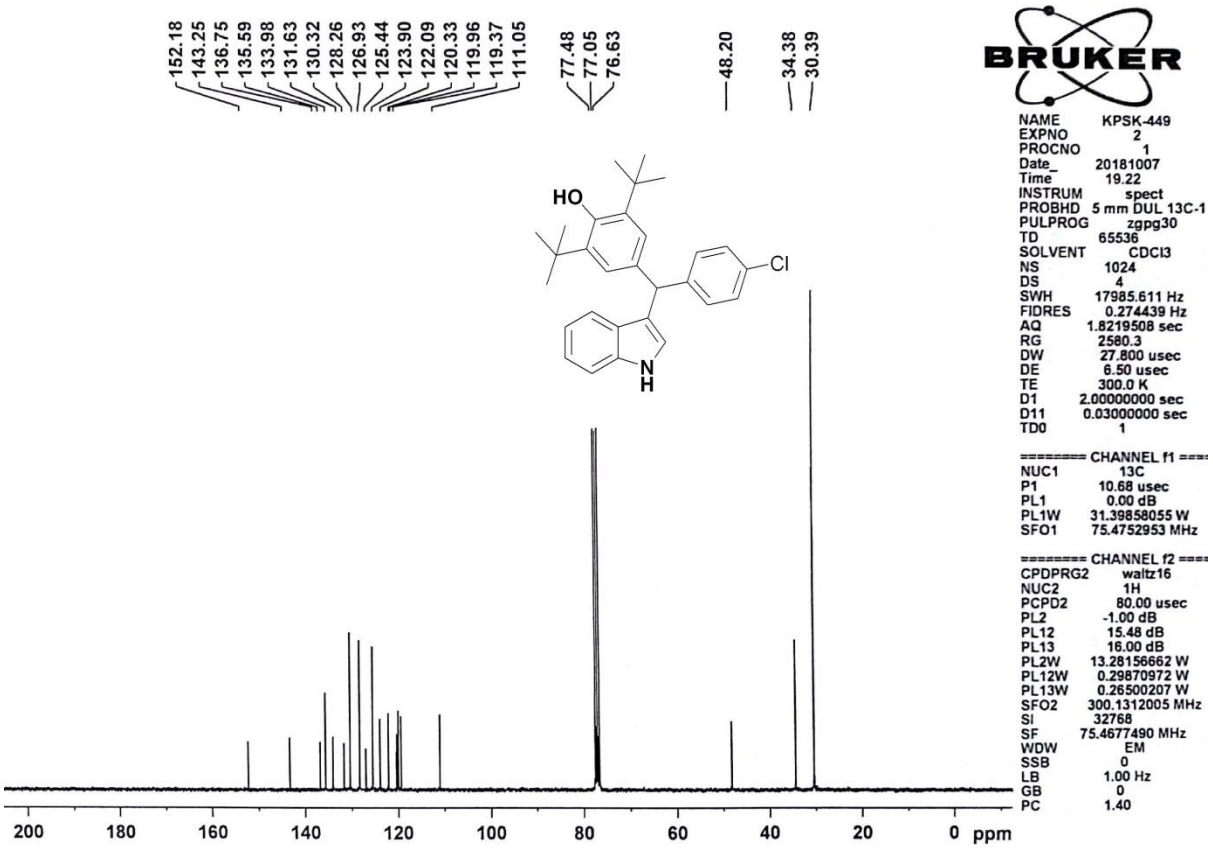
^{1}H and ^{13}C NMR for compound **3d**



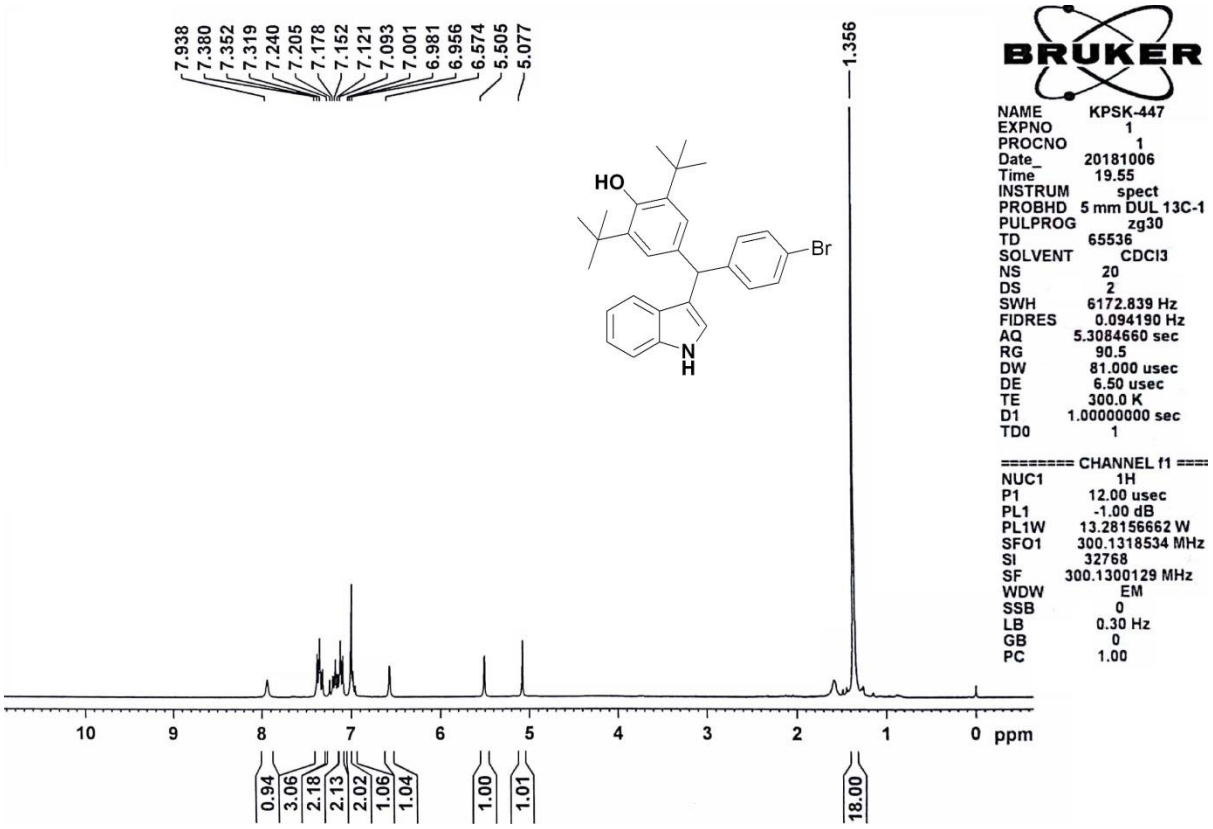


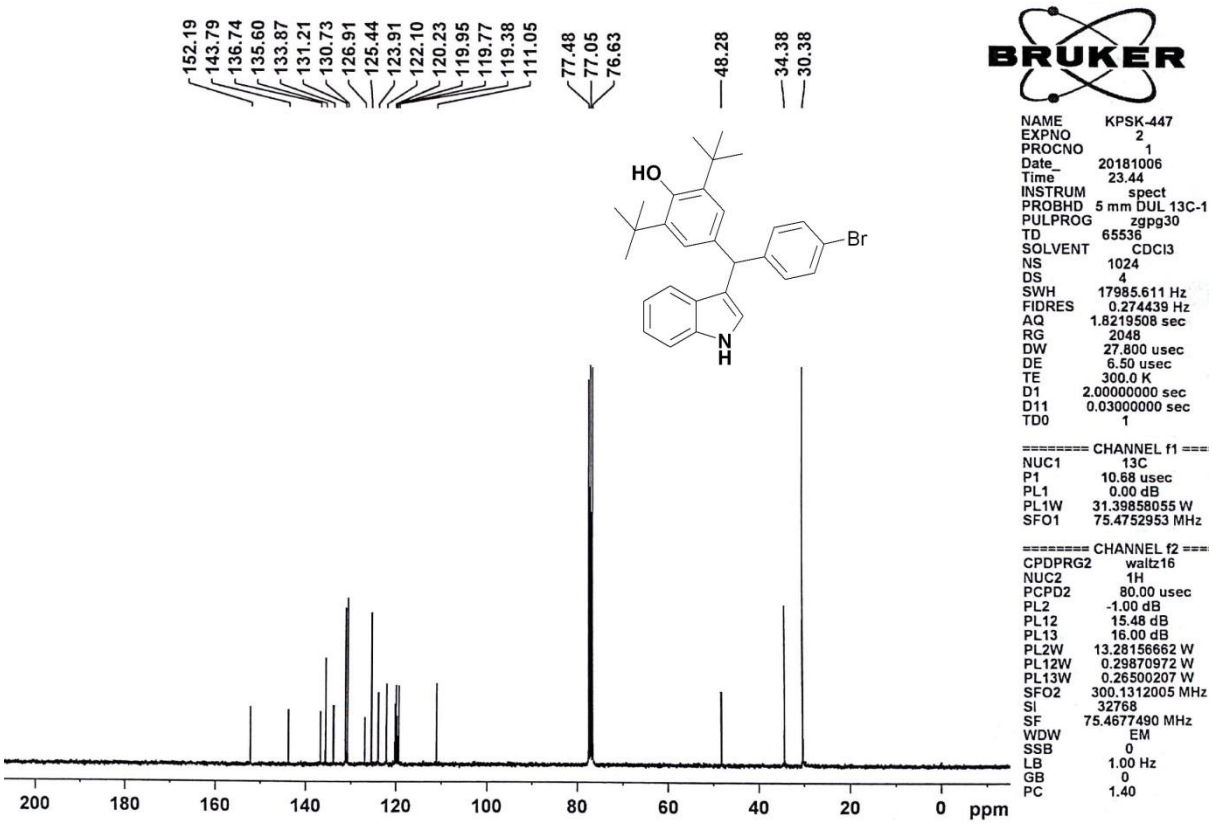
^{1}H and ^{13}C NMR for compound **3e**



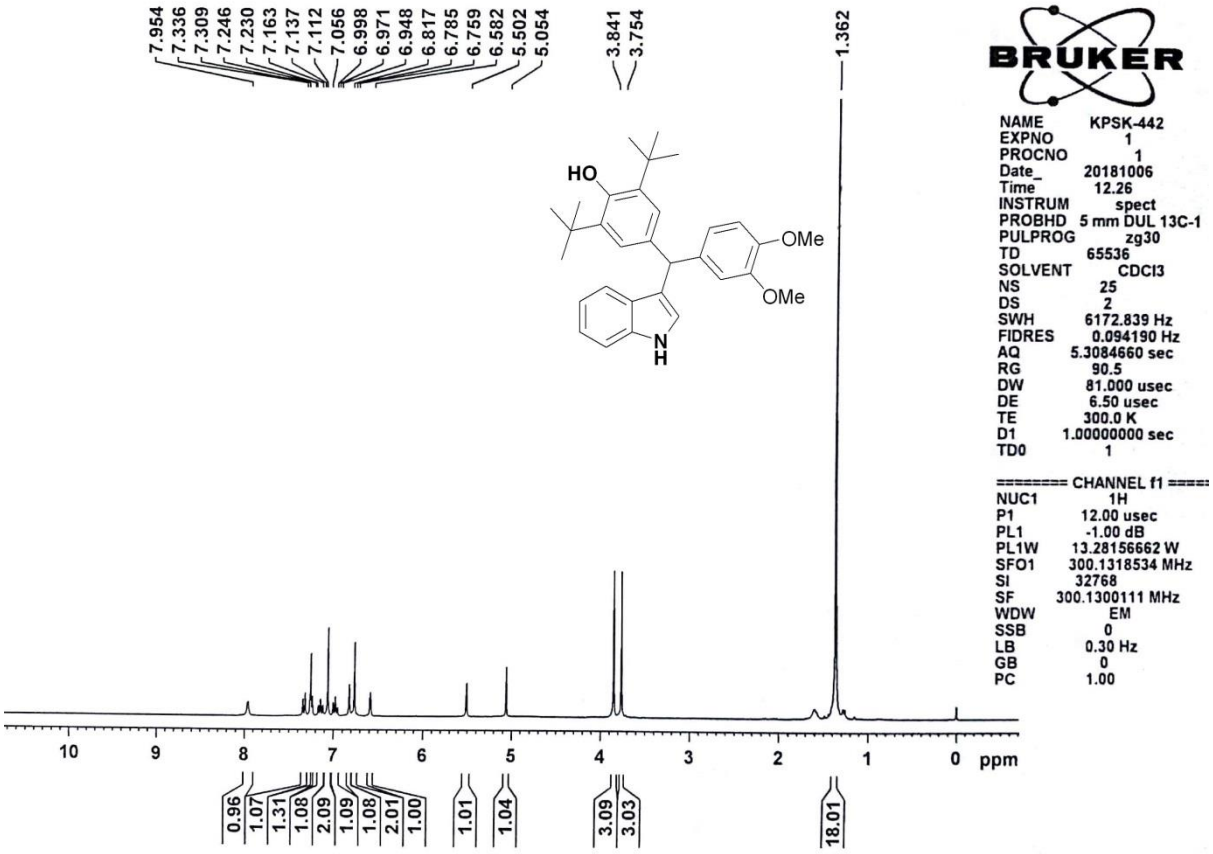


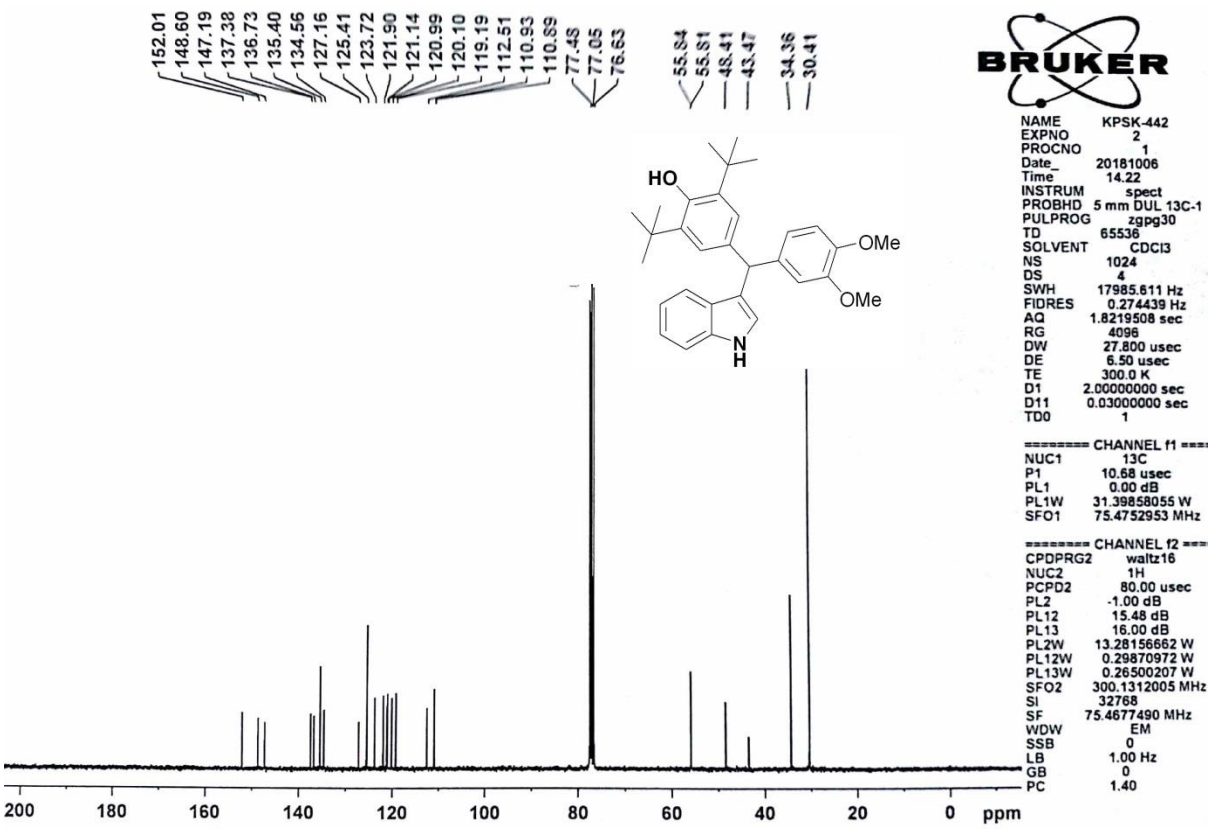
^{1}H and ^{13}C NMR for compound **3f**



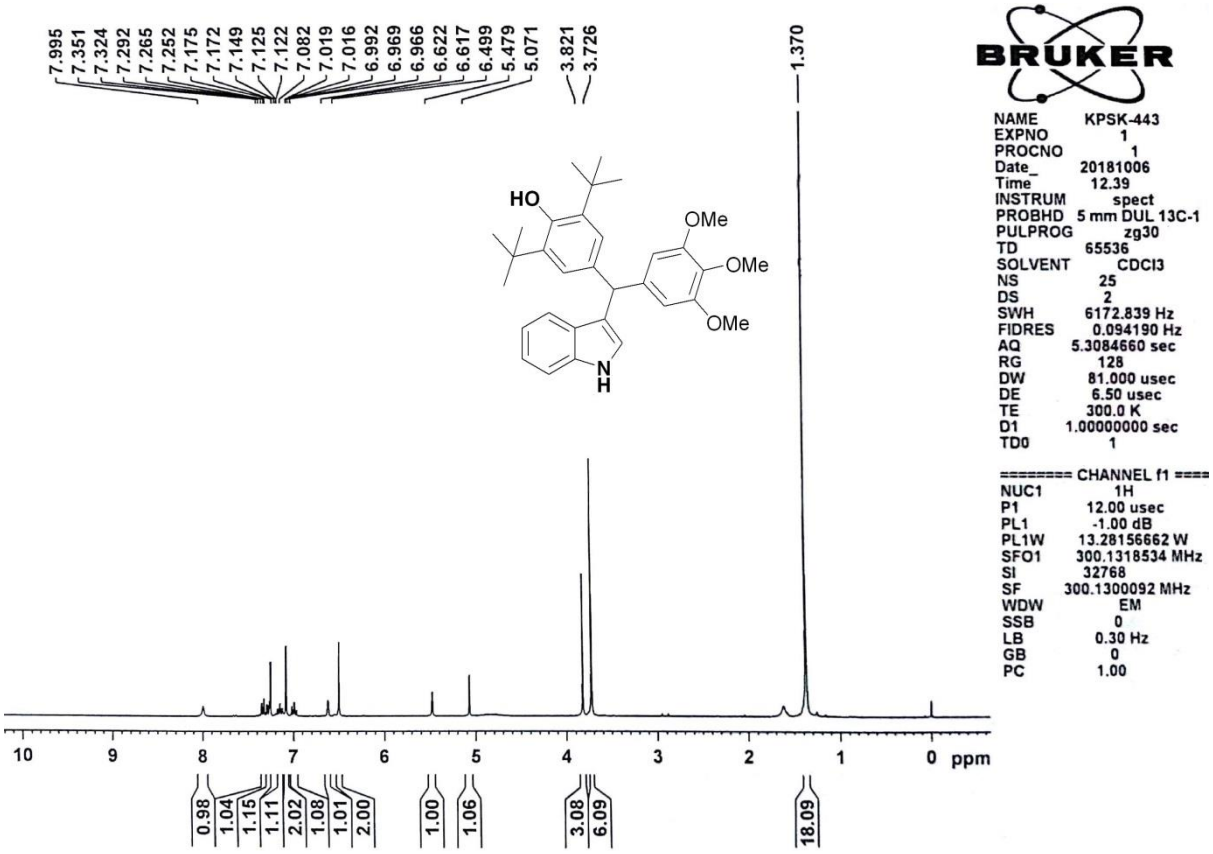


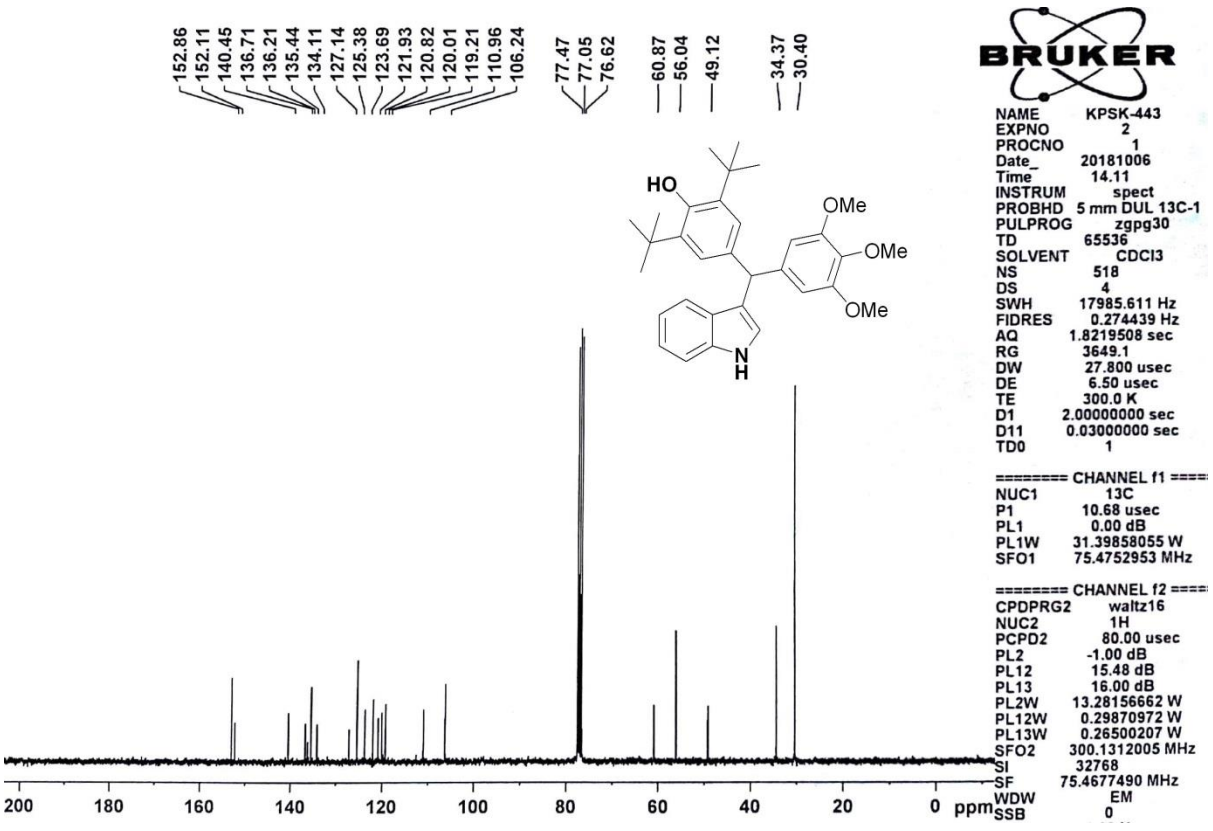
^{1}H and ^{13}C NMR for compound **3g**



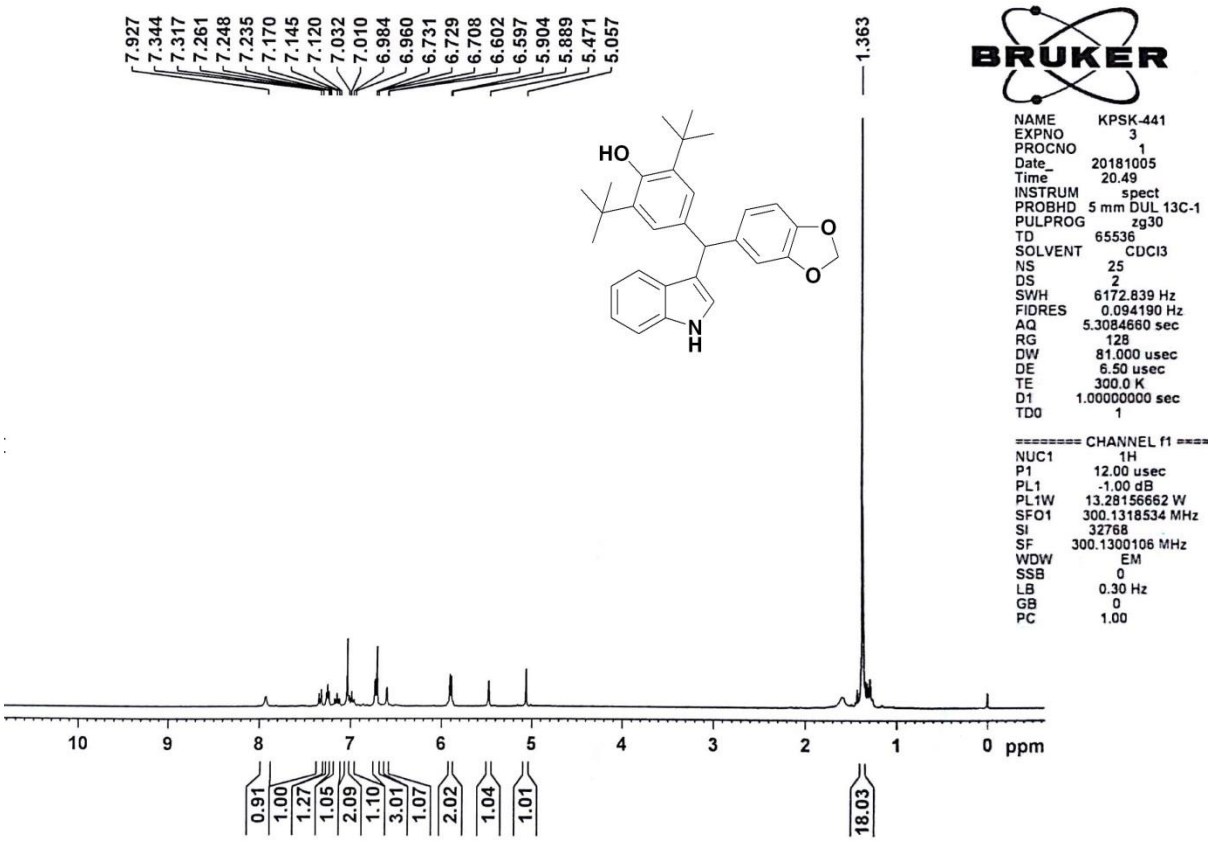


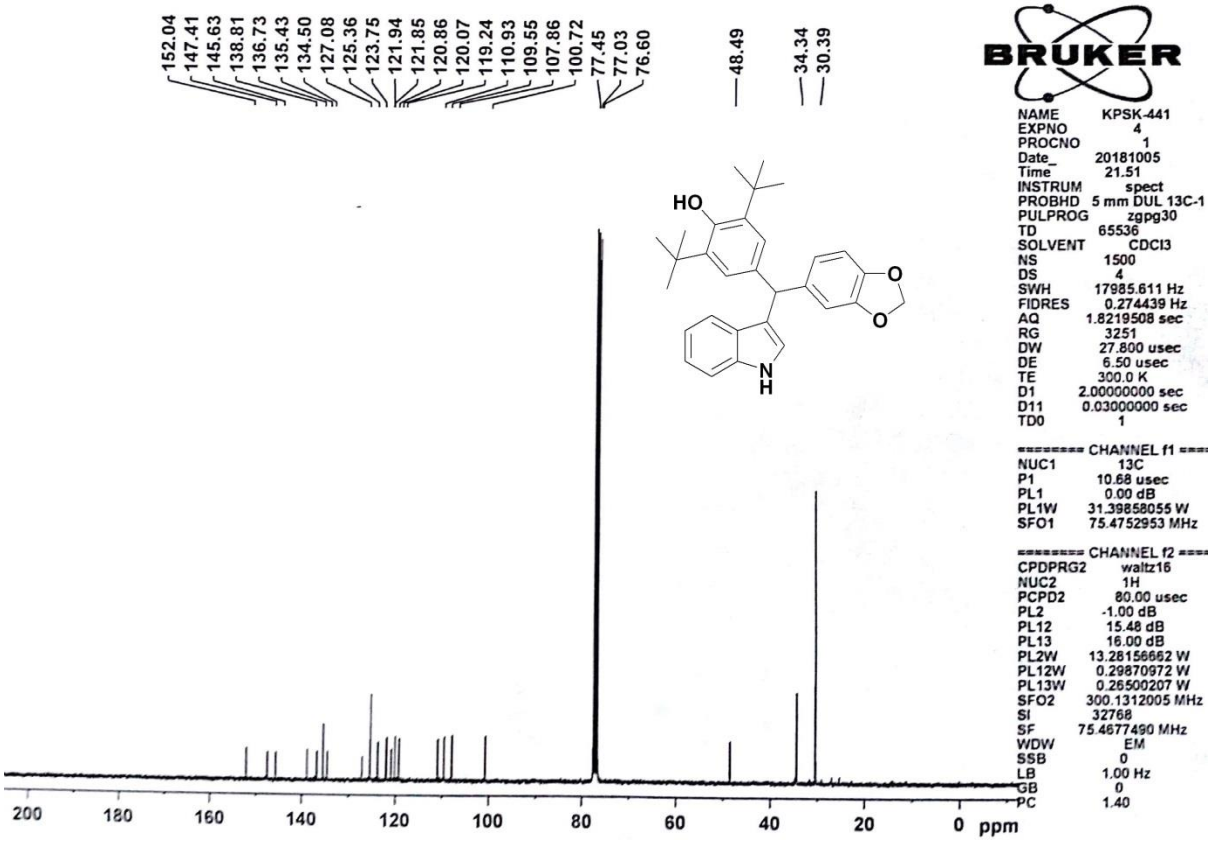
^{1}H and ^{13}C NMR for compound **3h**



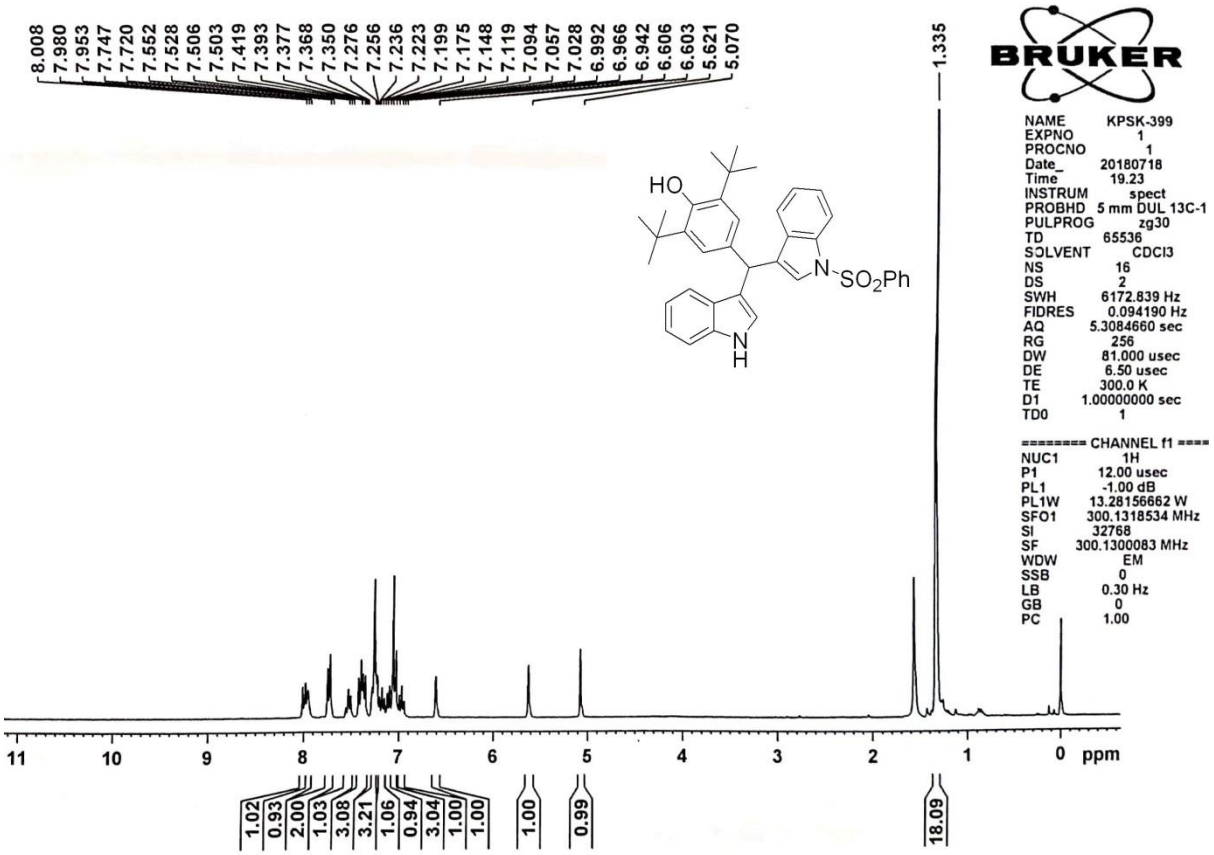


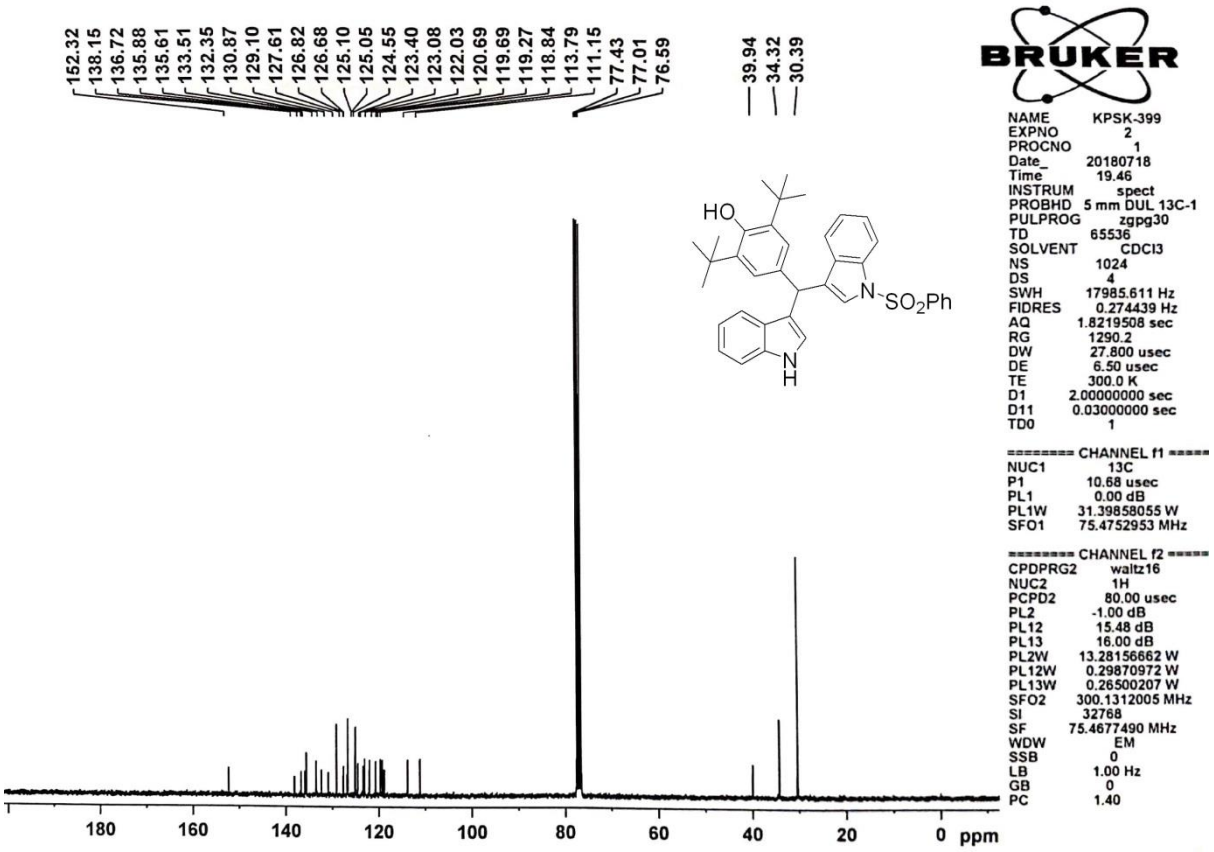
^{1}H and ^{13}C NMR for compound **3i**



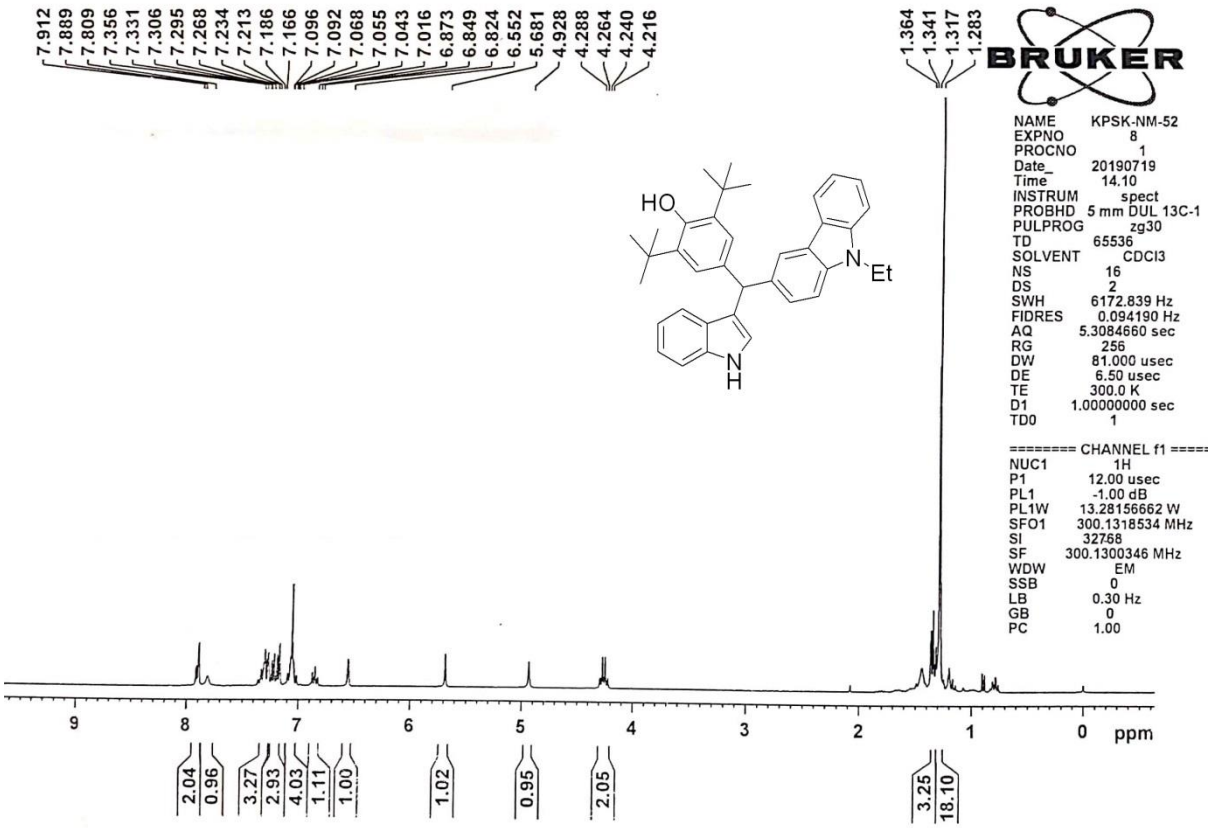


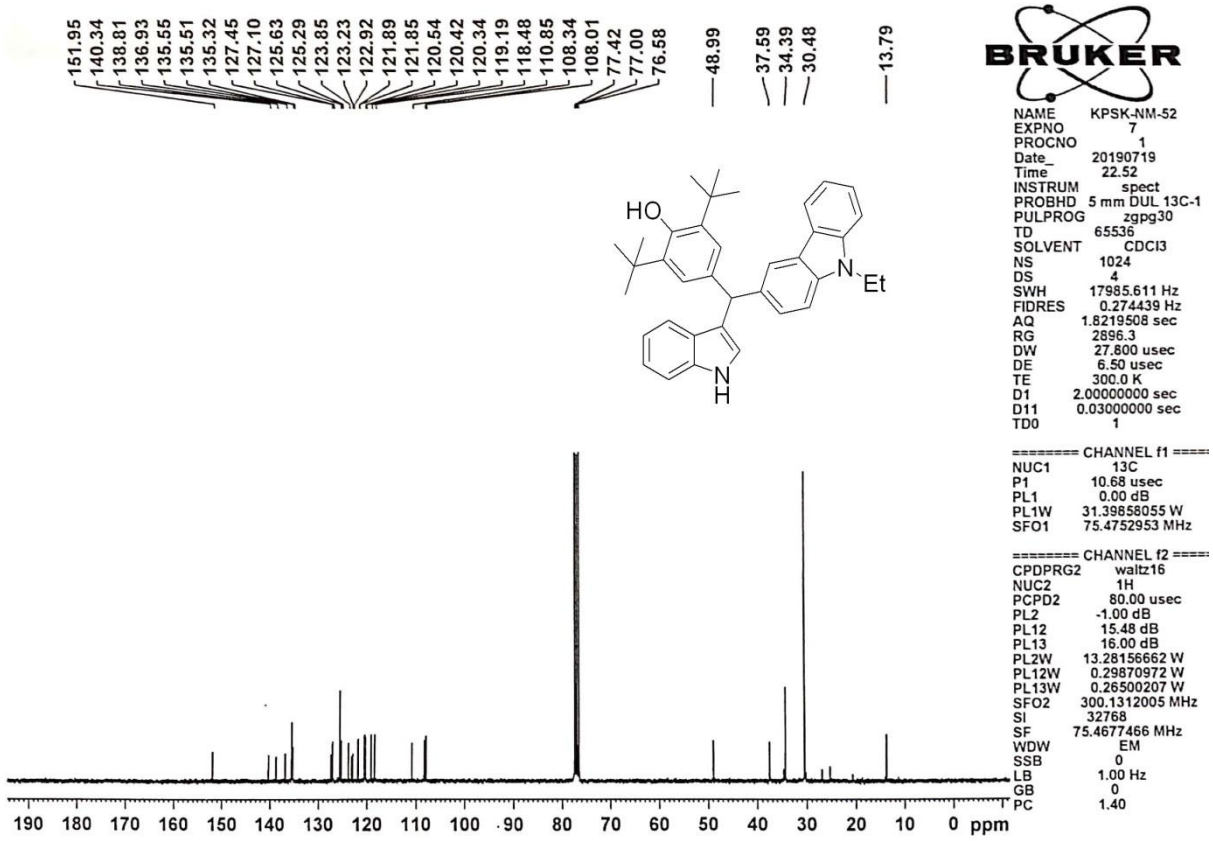
^{1}H and ^{13}C NMR for compound **3j**



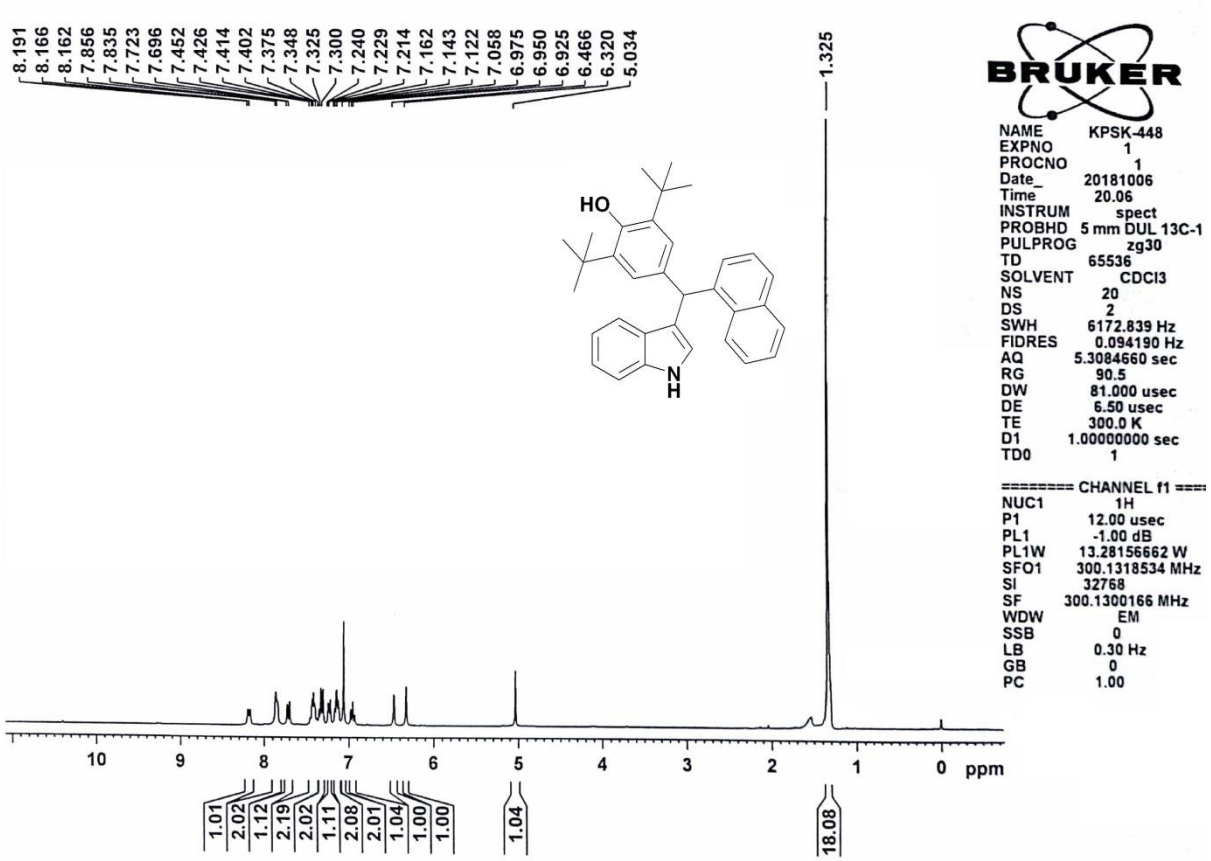


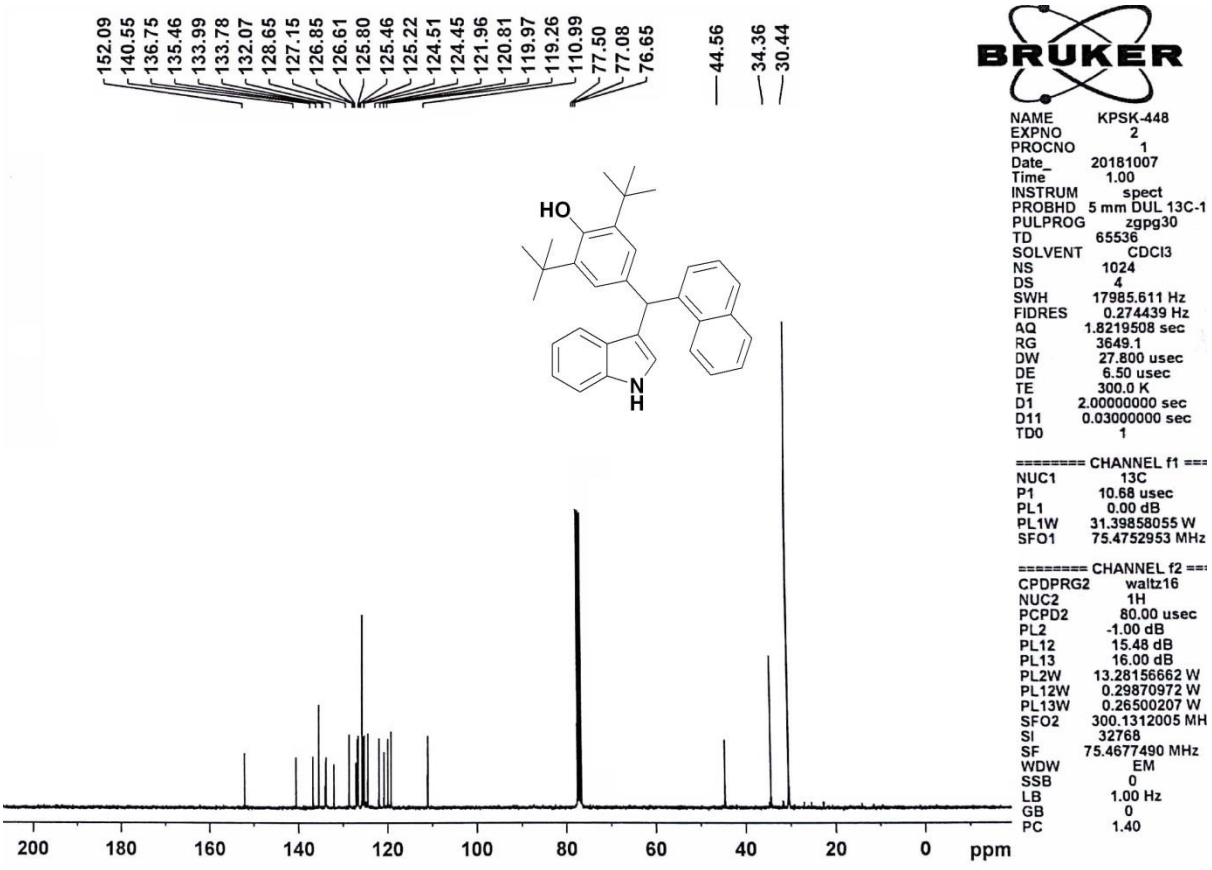
^{1}H and ^{13}C NMR for compound **3k**



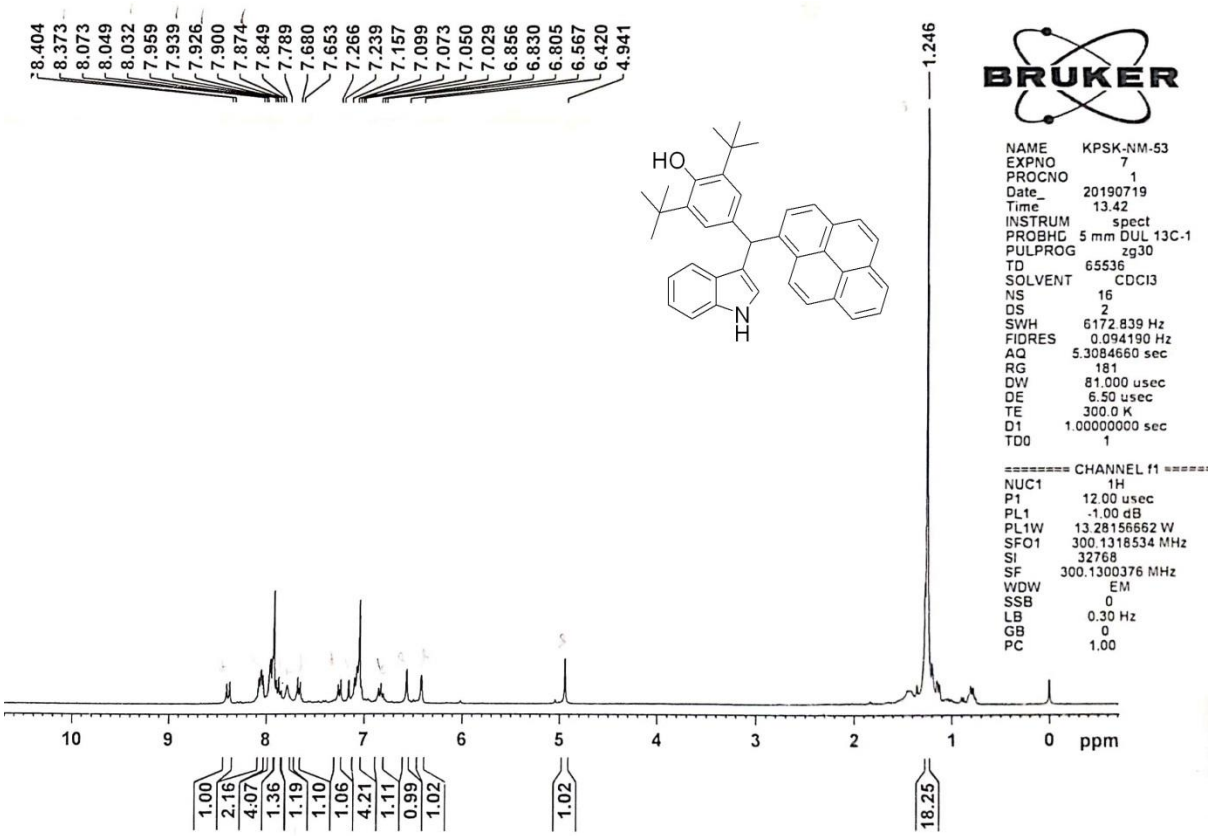


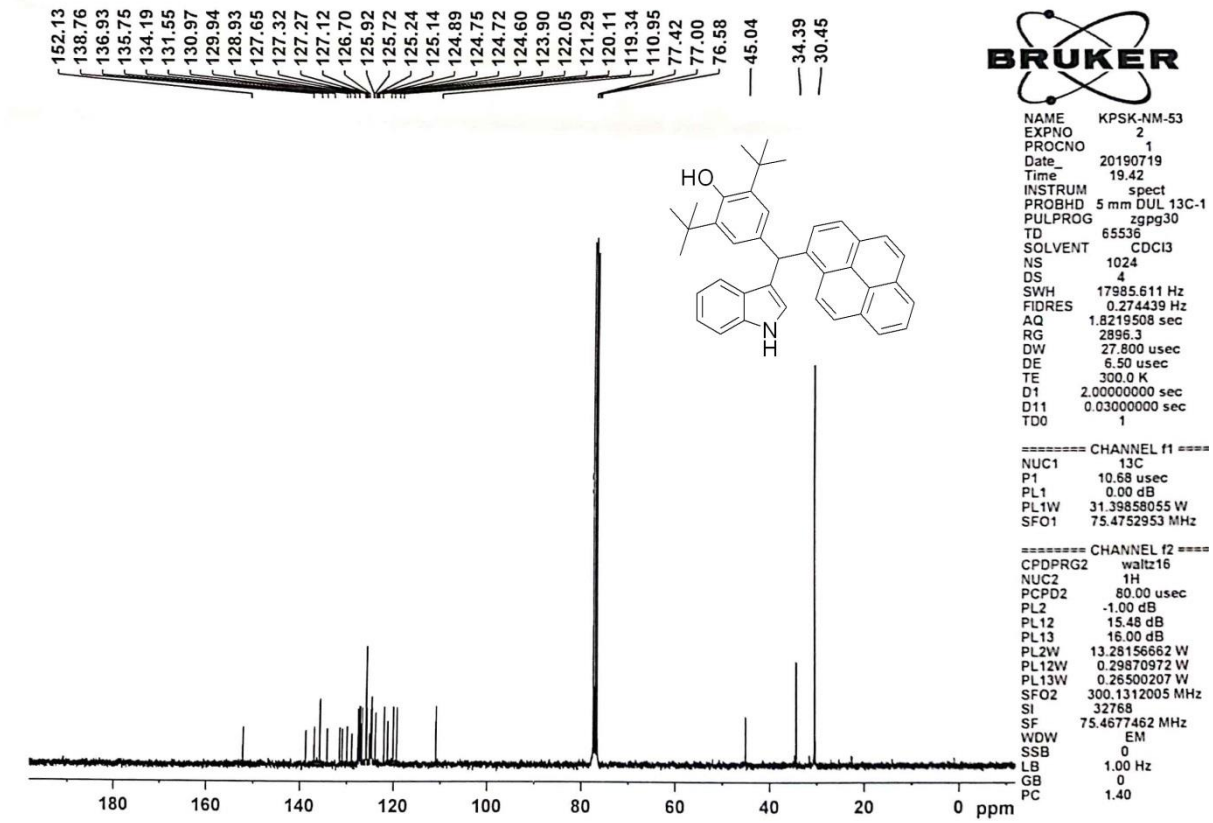
^{1}H and ^{13}C NMR for compound **3l**



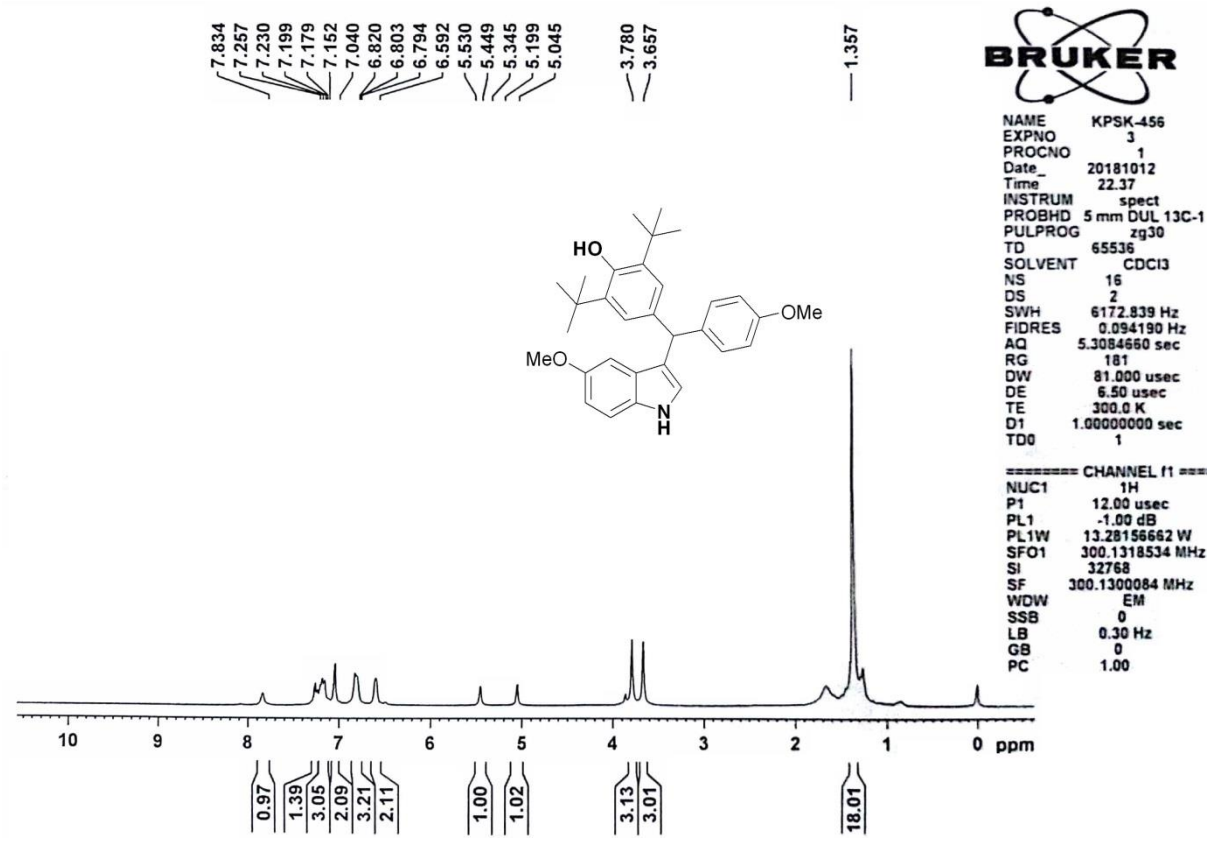


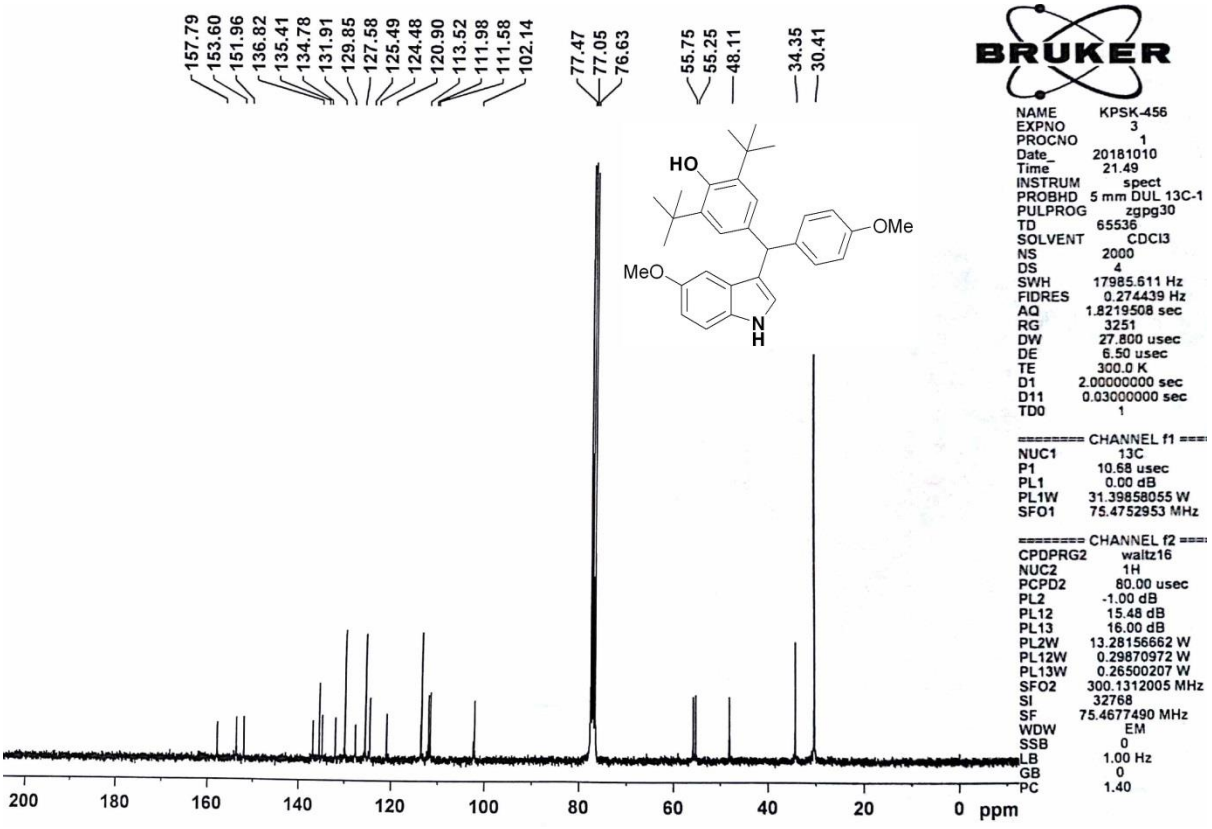
^{1}H and ^{13}C NMR for compound **3m**



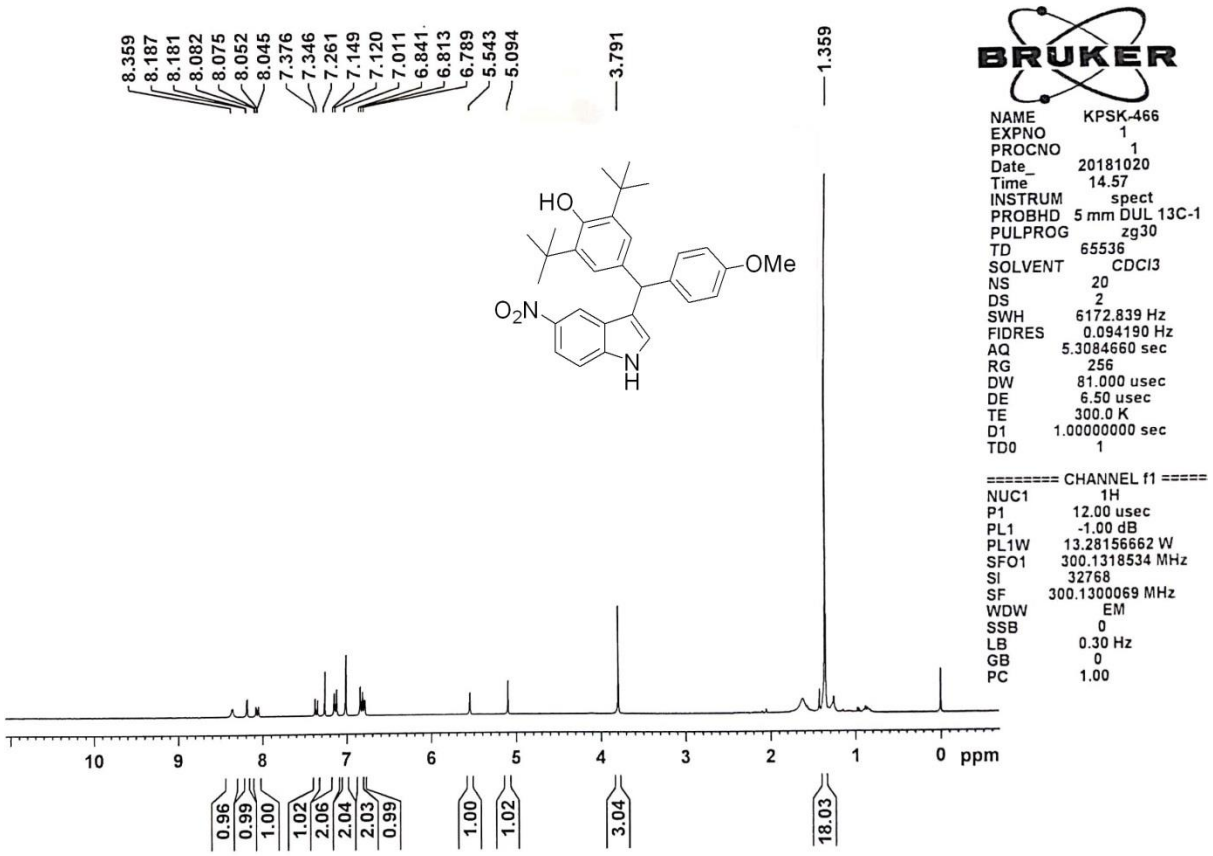


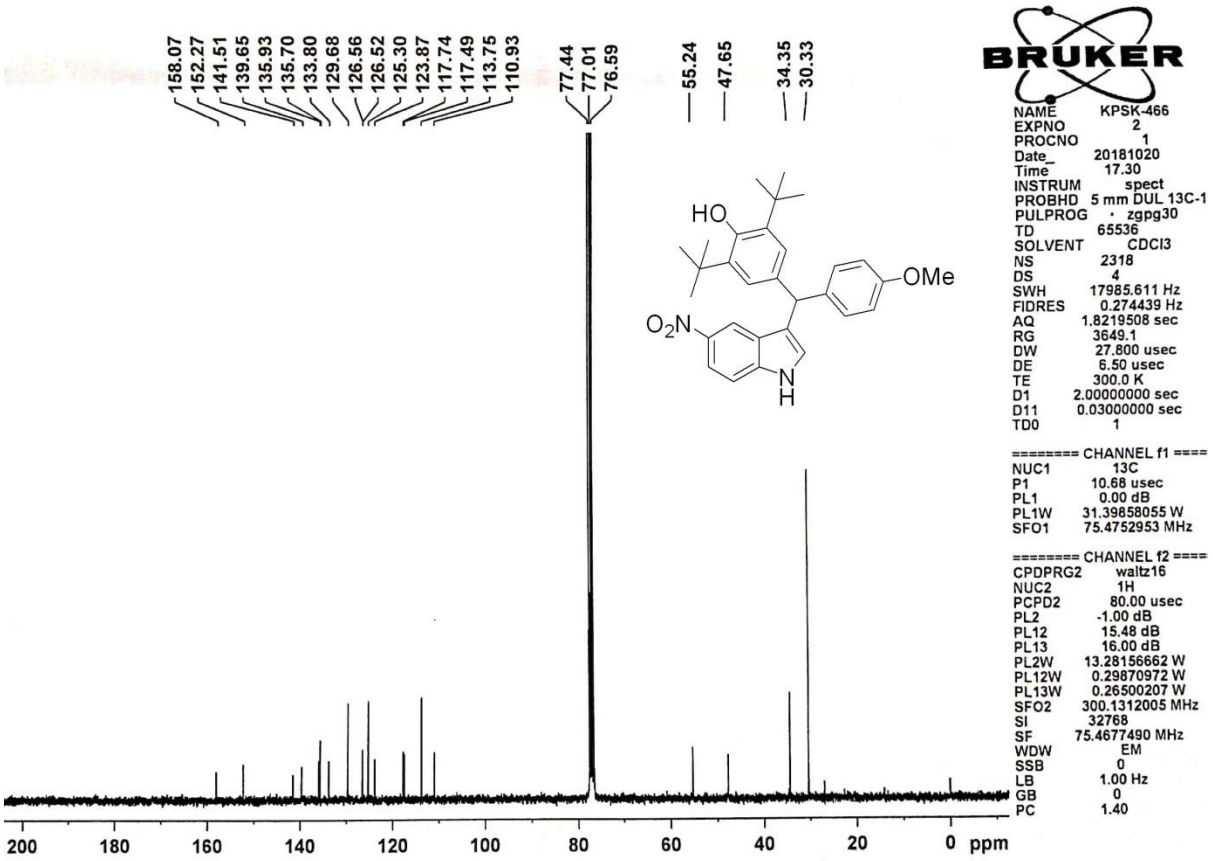
^{1}H and ^{13}C NMR for compound **3n**



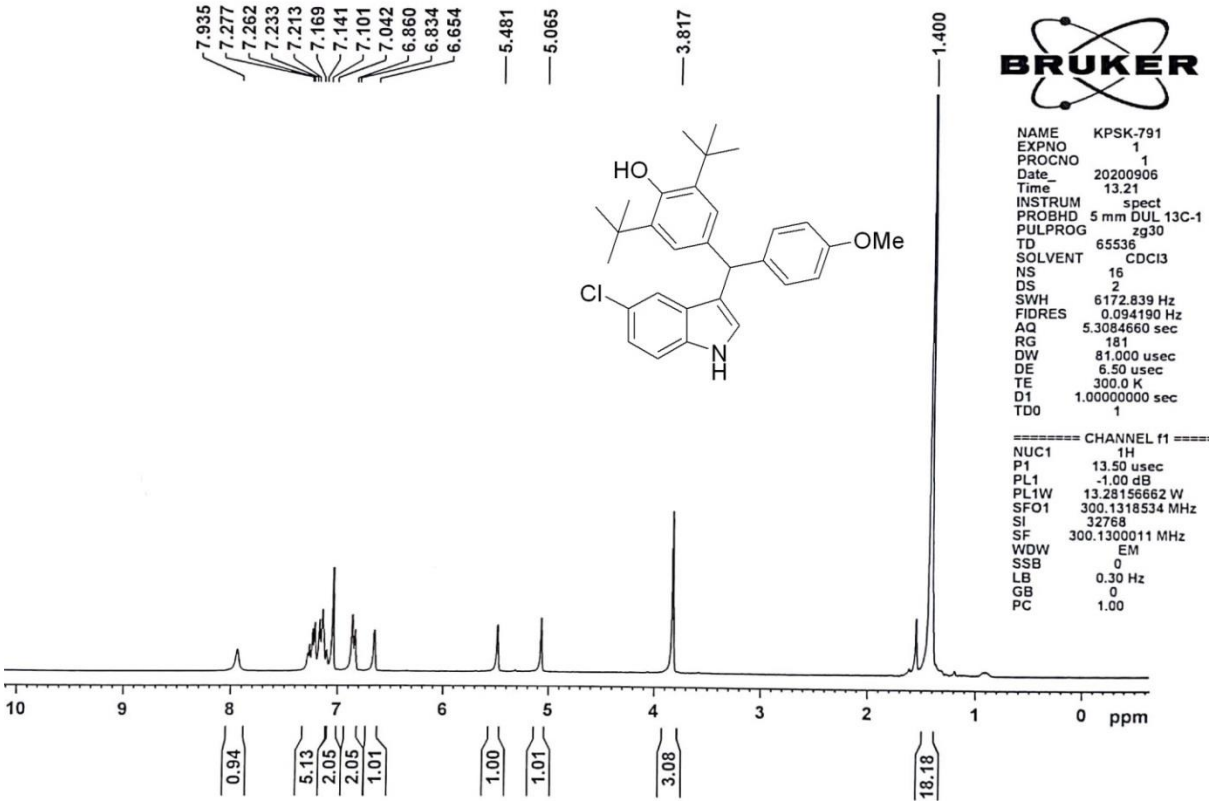


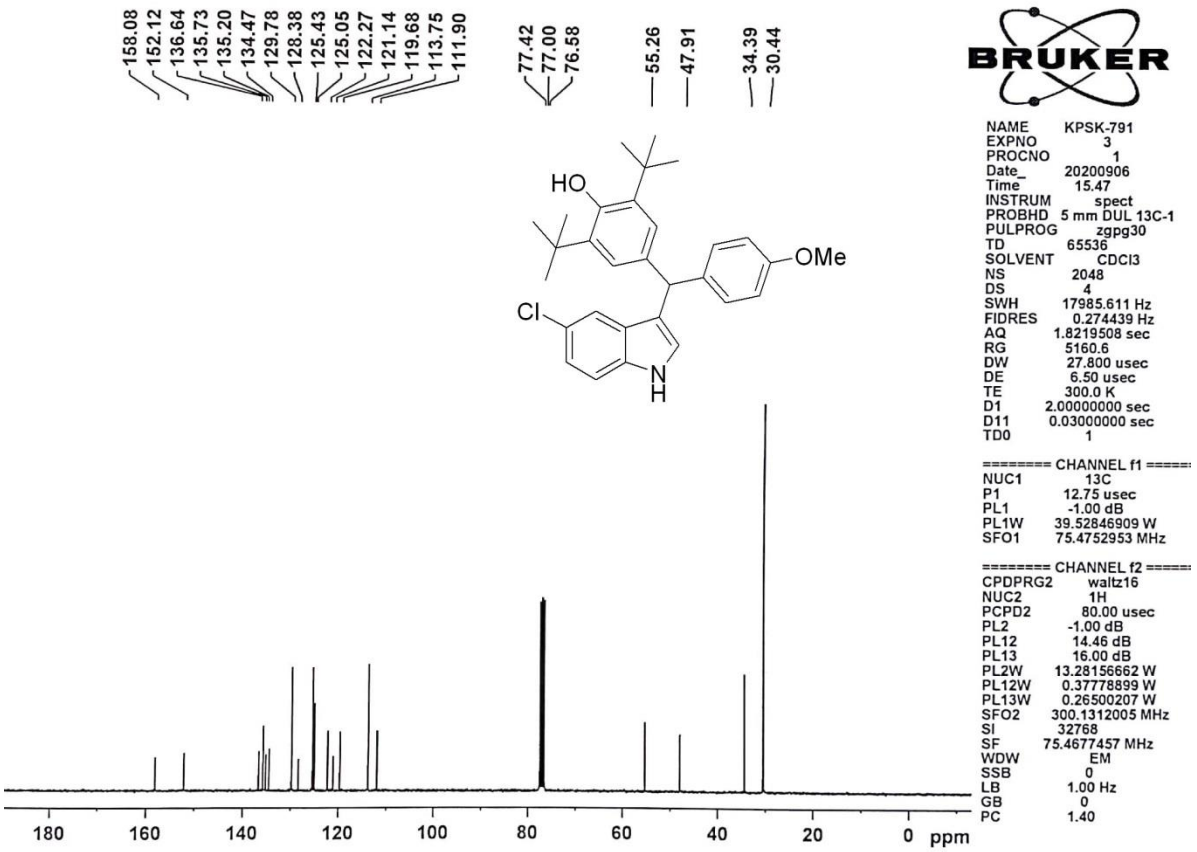
^{1}H and ^{13}C NMR for compound **3o**



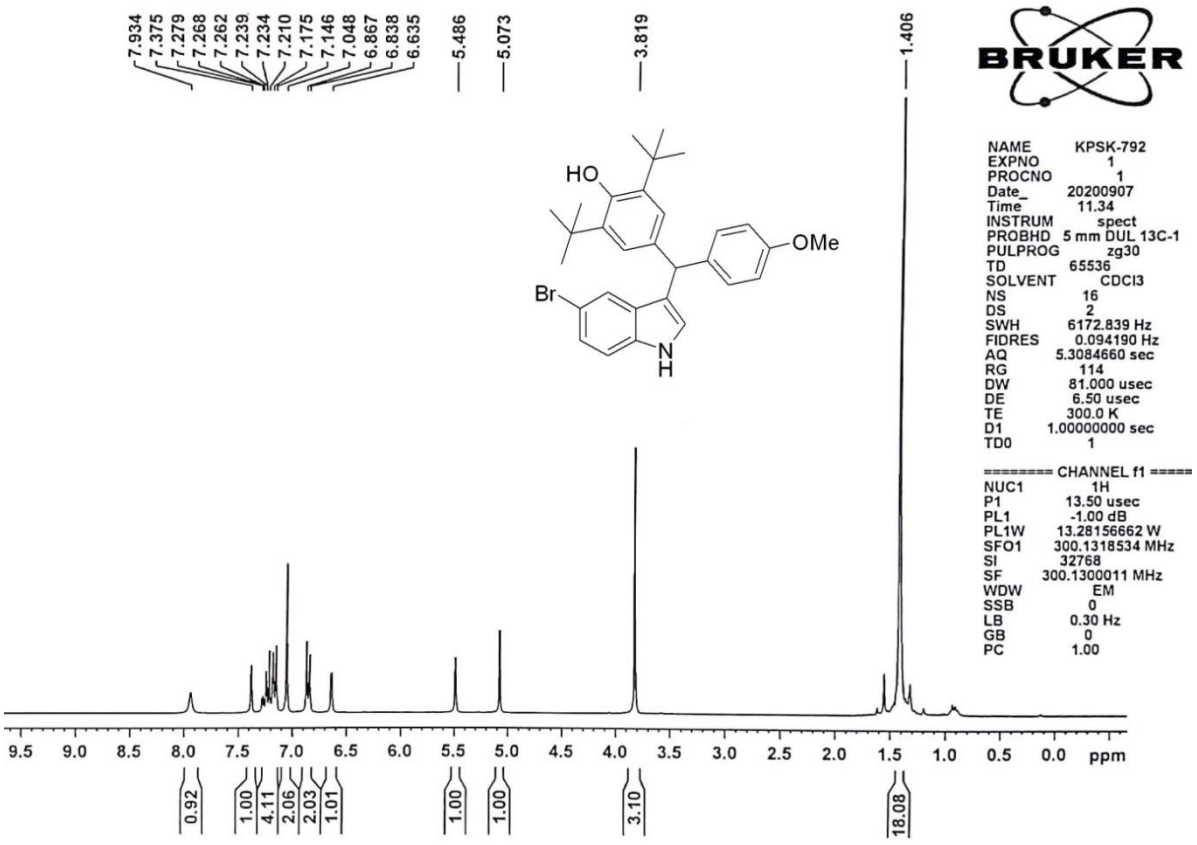


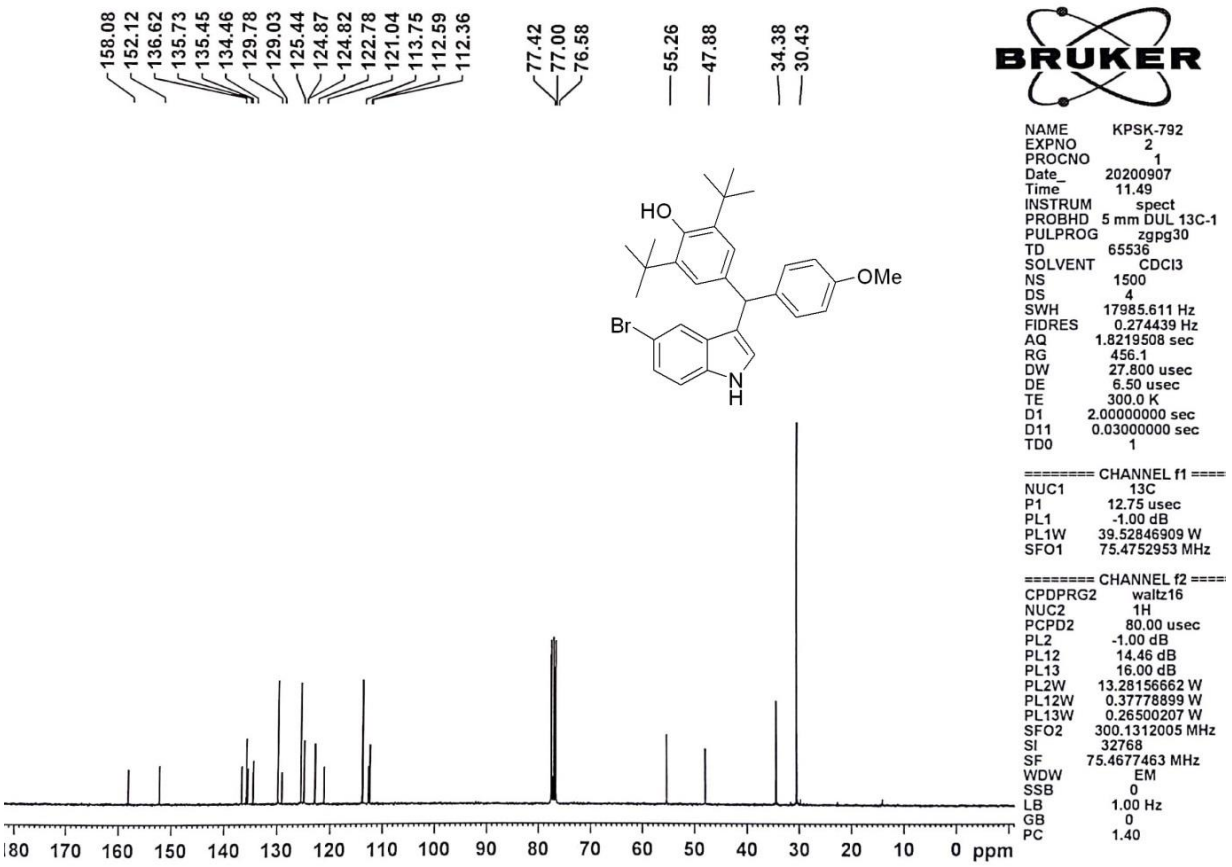
^{1}H and ^{13}C NMR for compound **3p**



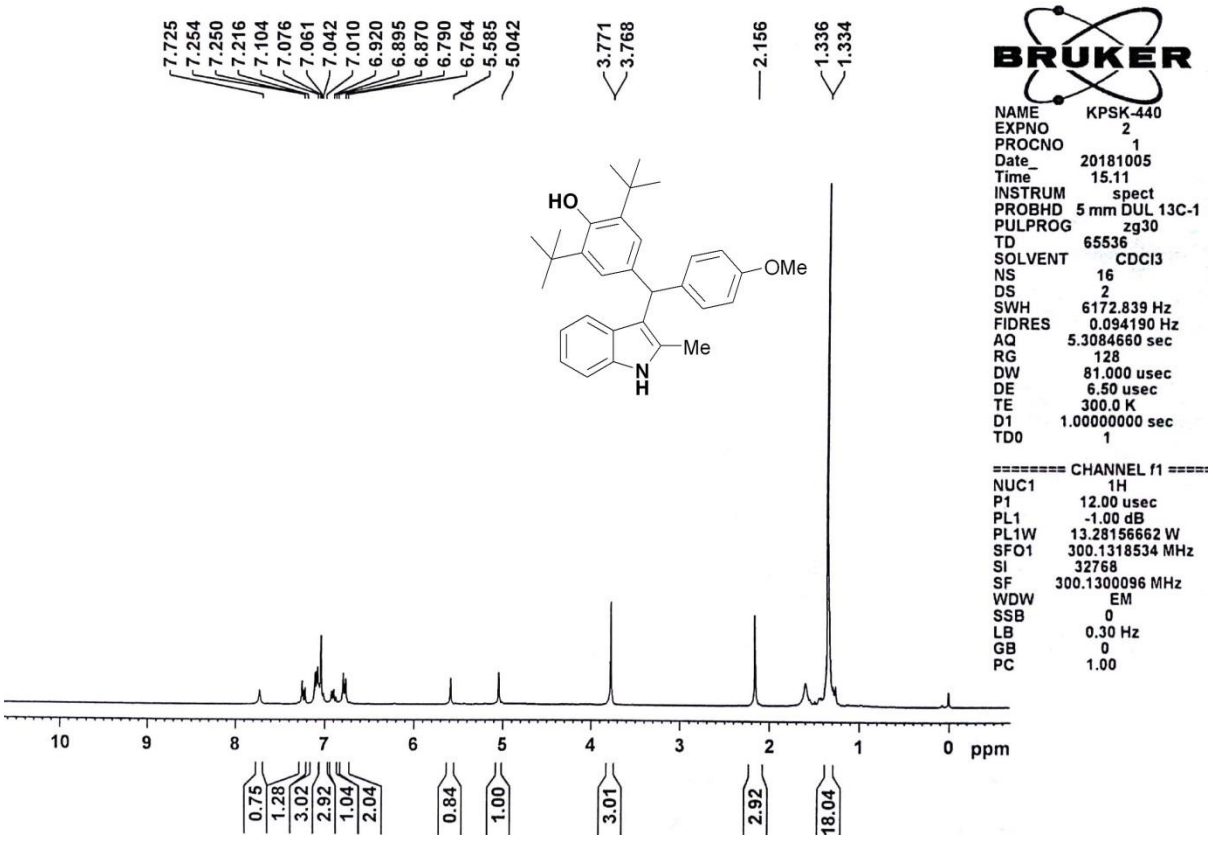


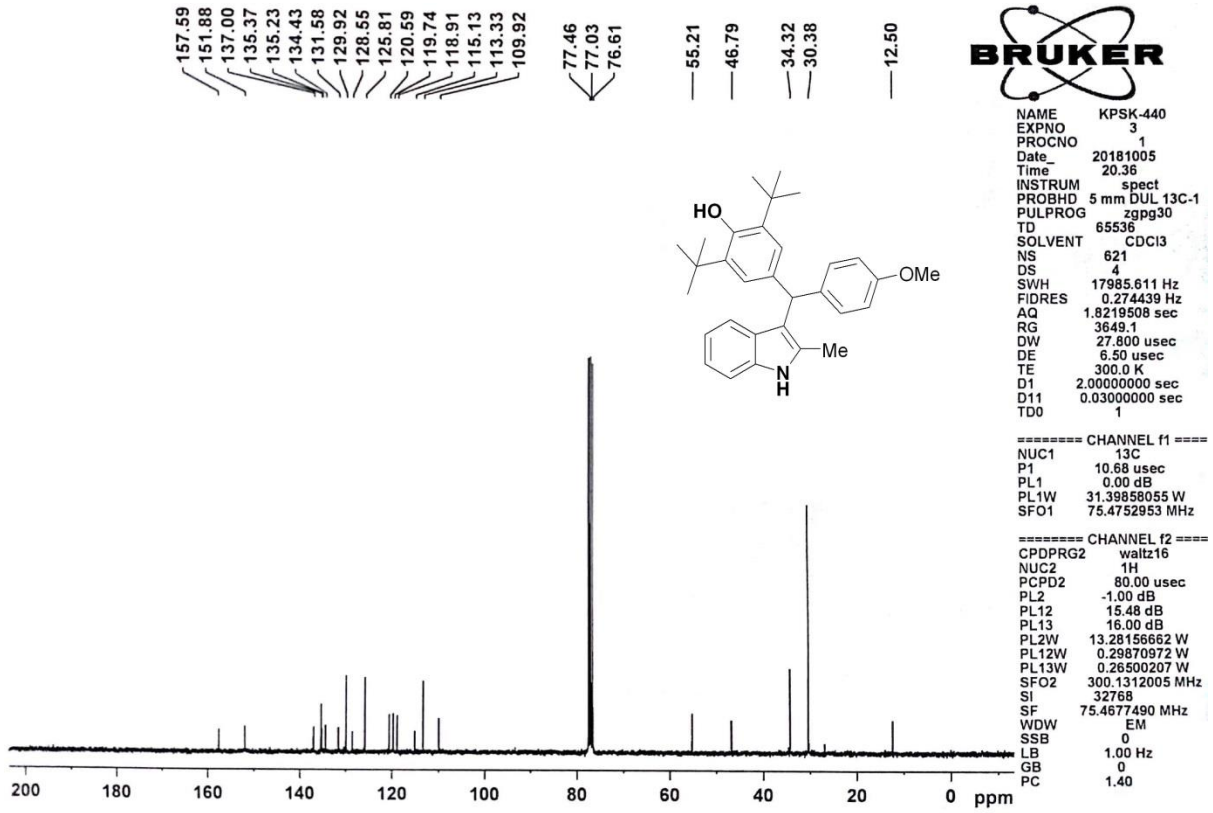
^{1}H and ^{13}C NMR for compound **3q**



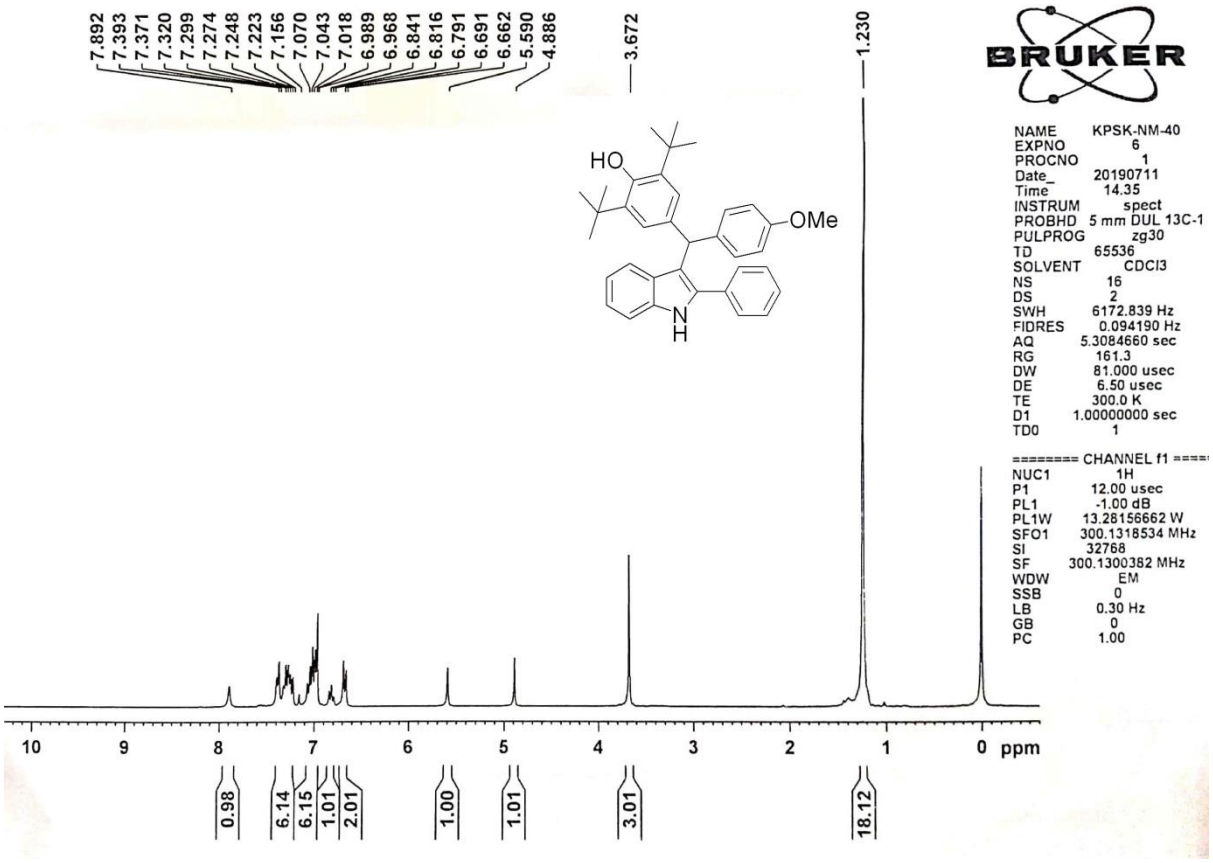


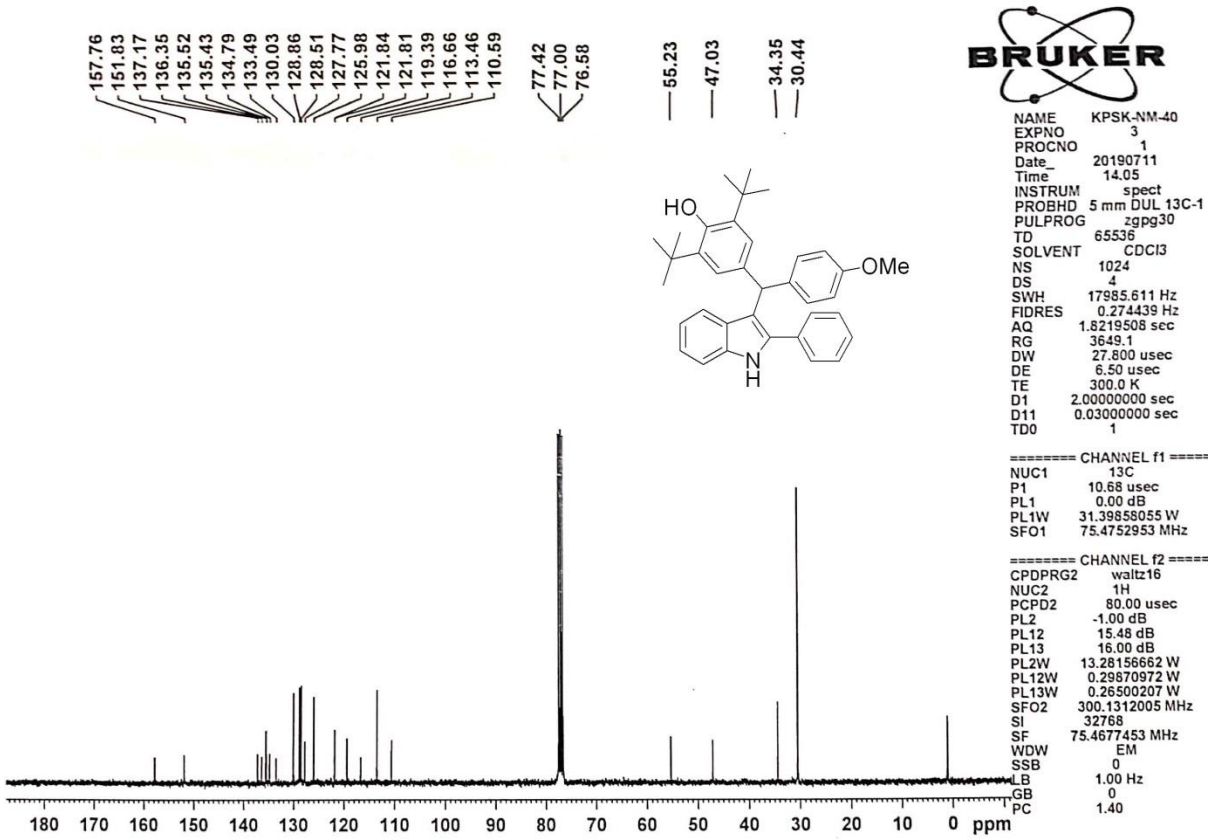
^{1}H and ^{13}C NMR for compound **3r**



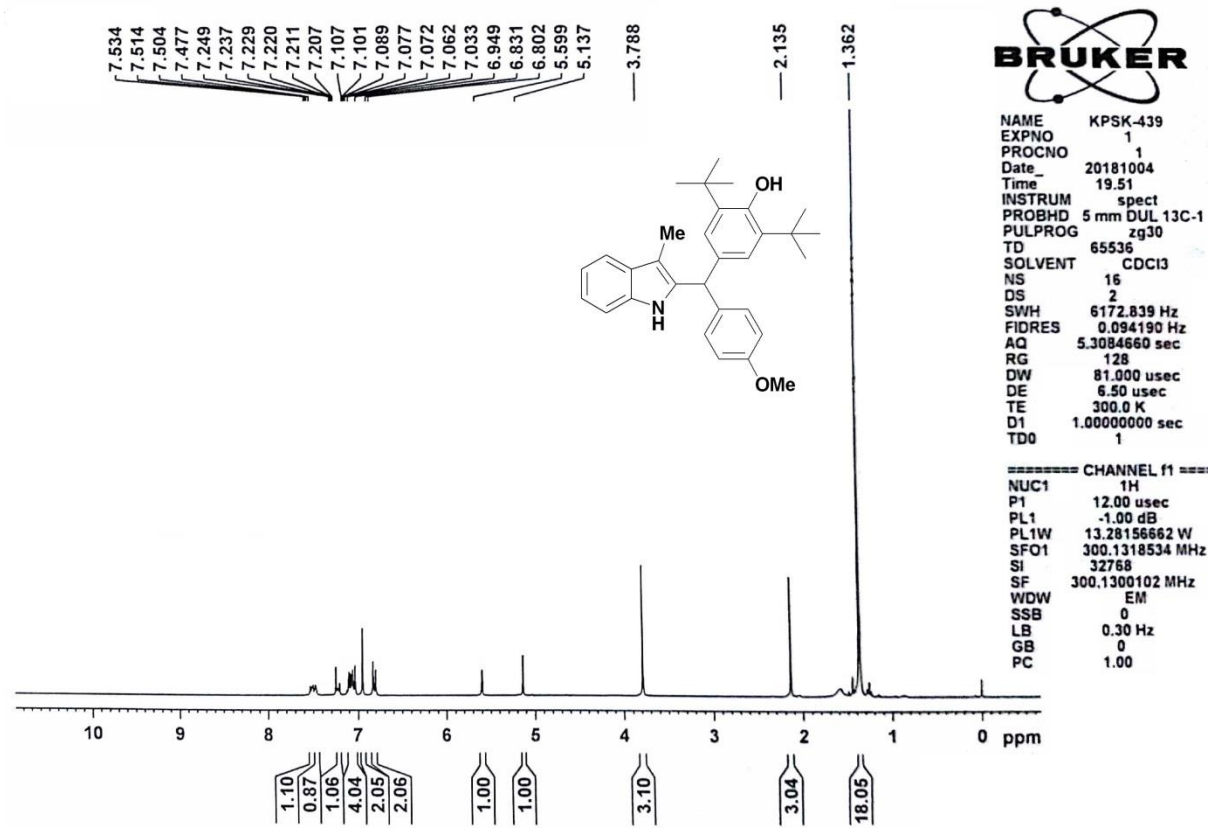


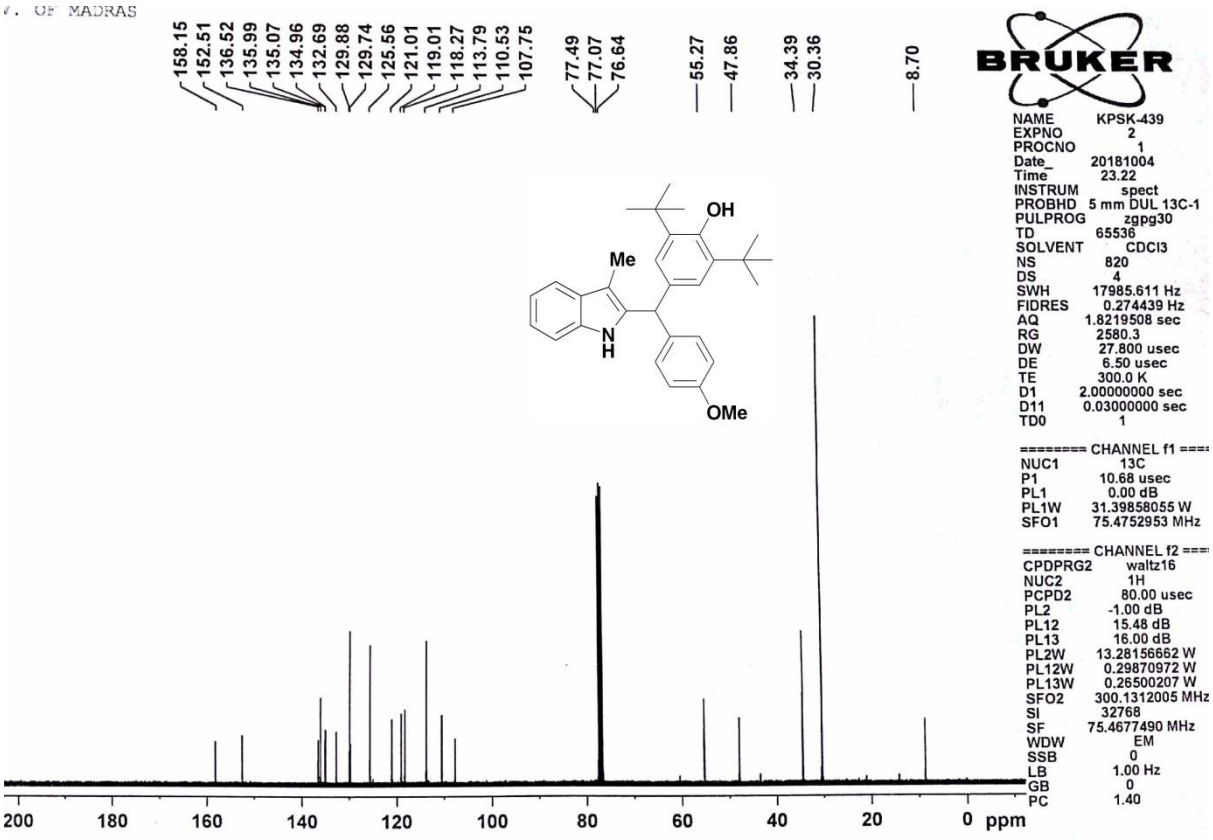
^{1}H and ^{13}C NMR for compound **3s**



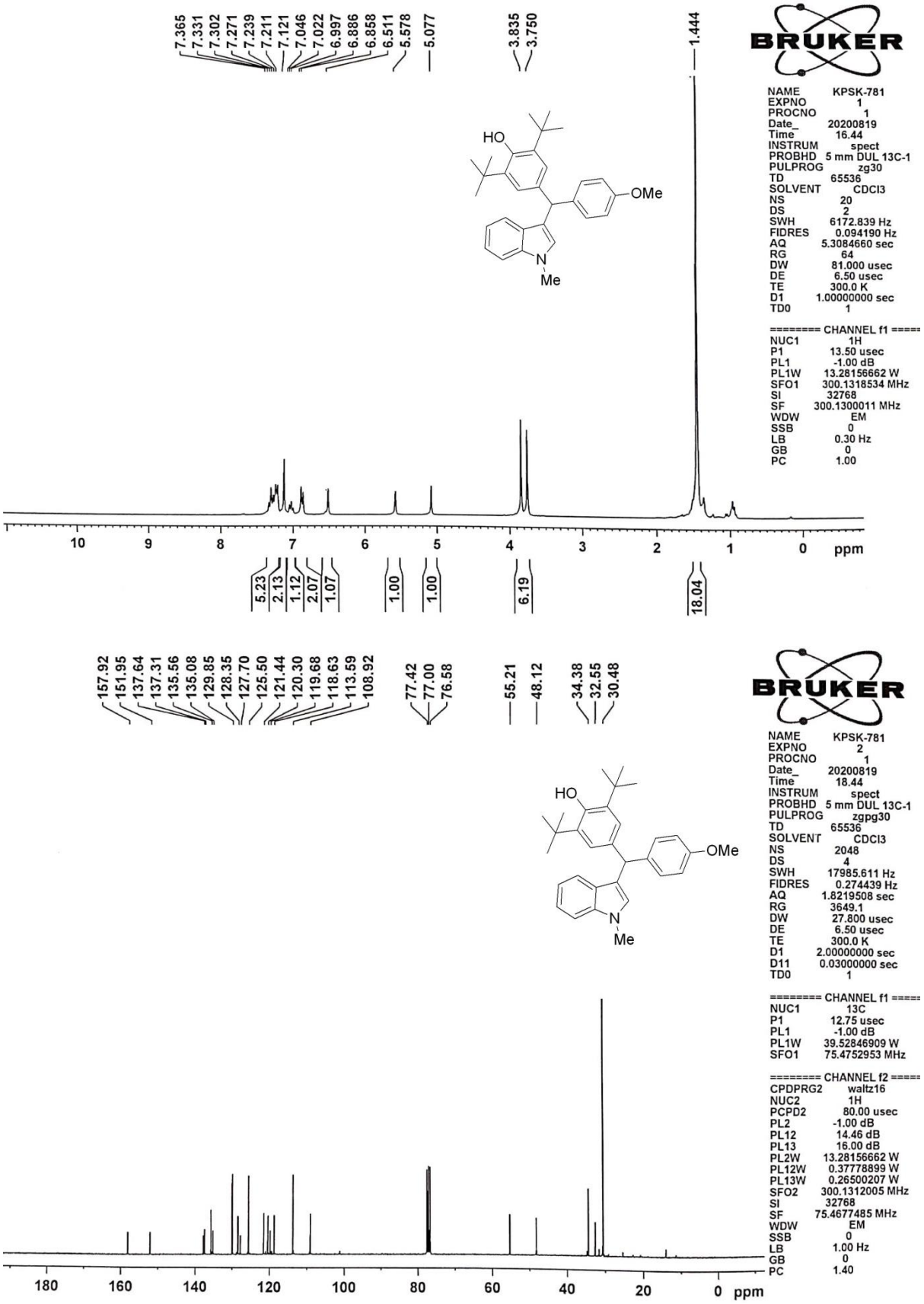


^{1}H and ^{13}C NMR for compound **3u**

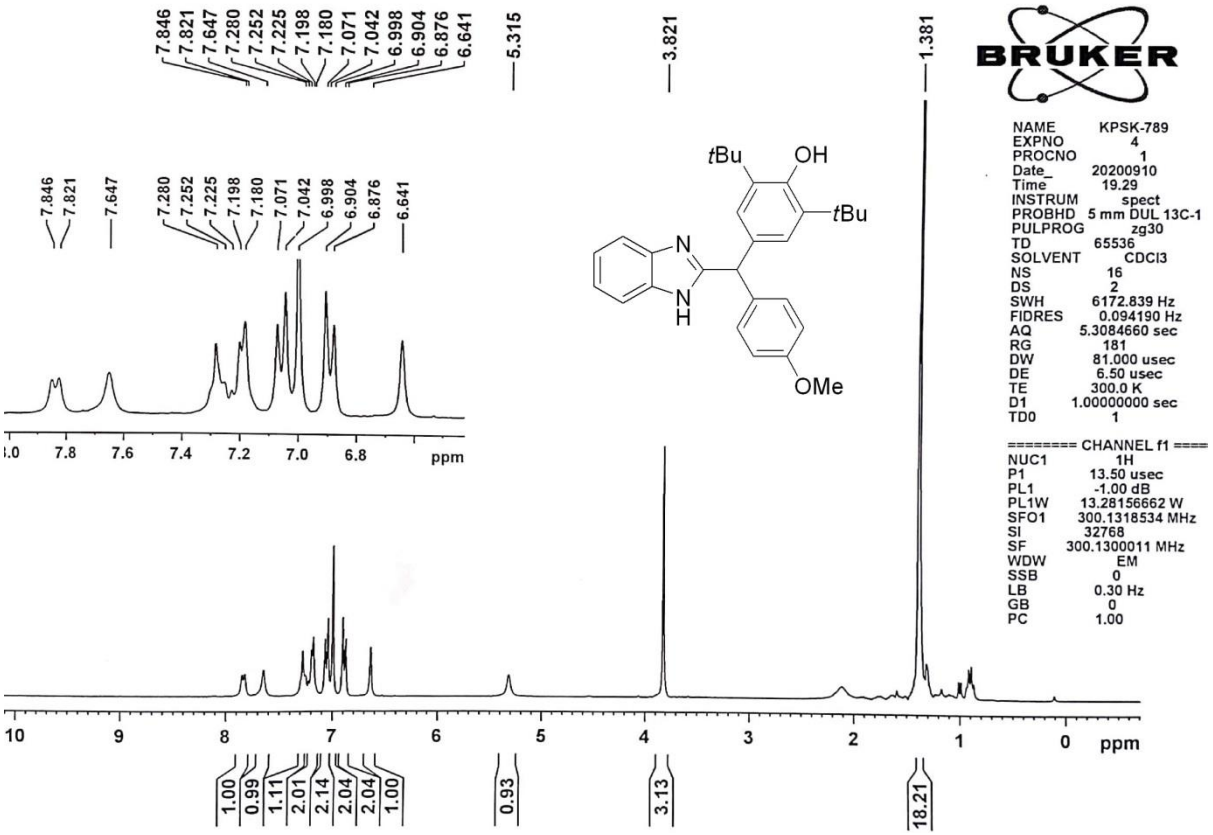


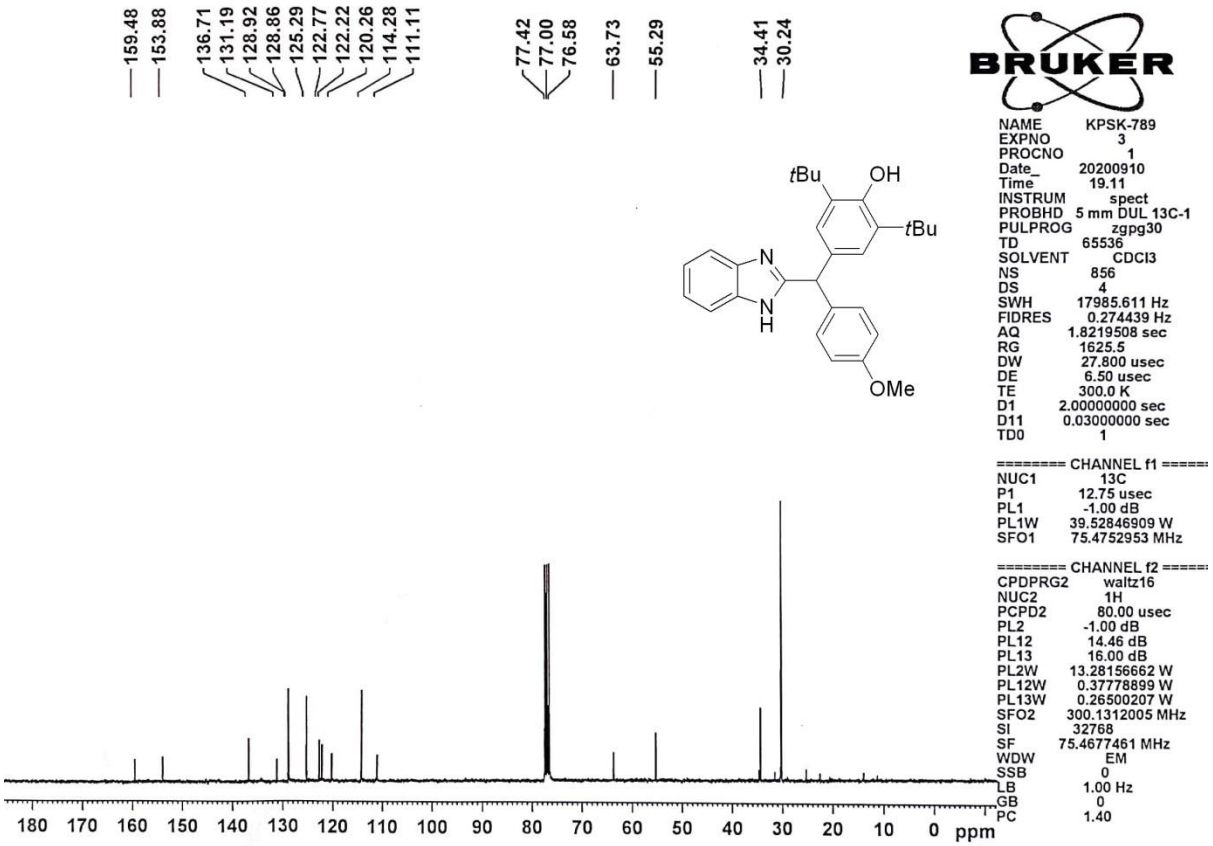


^{1}H and ^{13}C NMR for compound **3v**

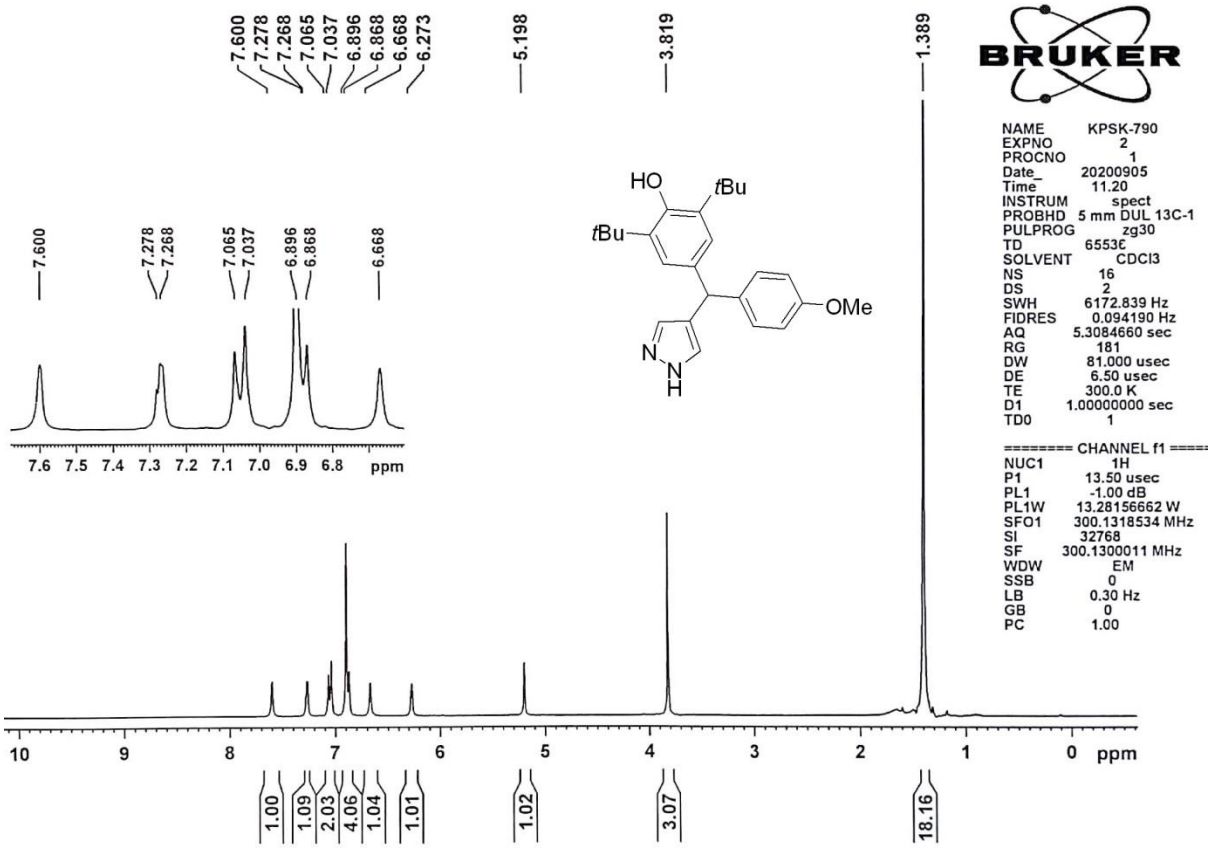


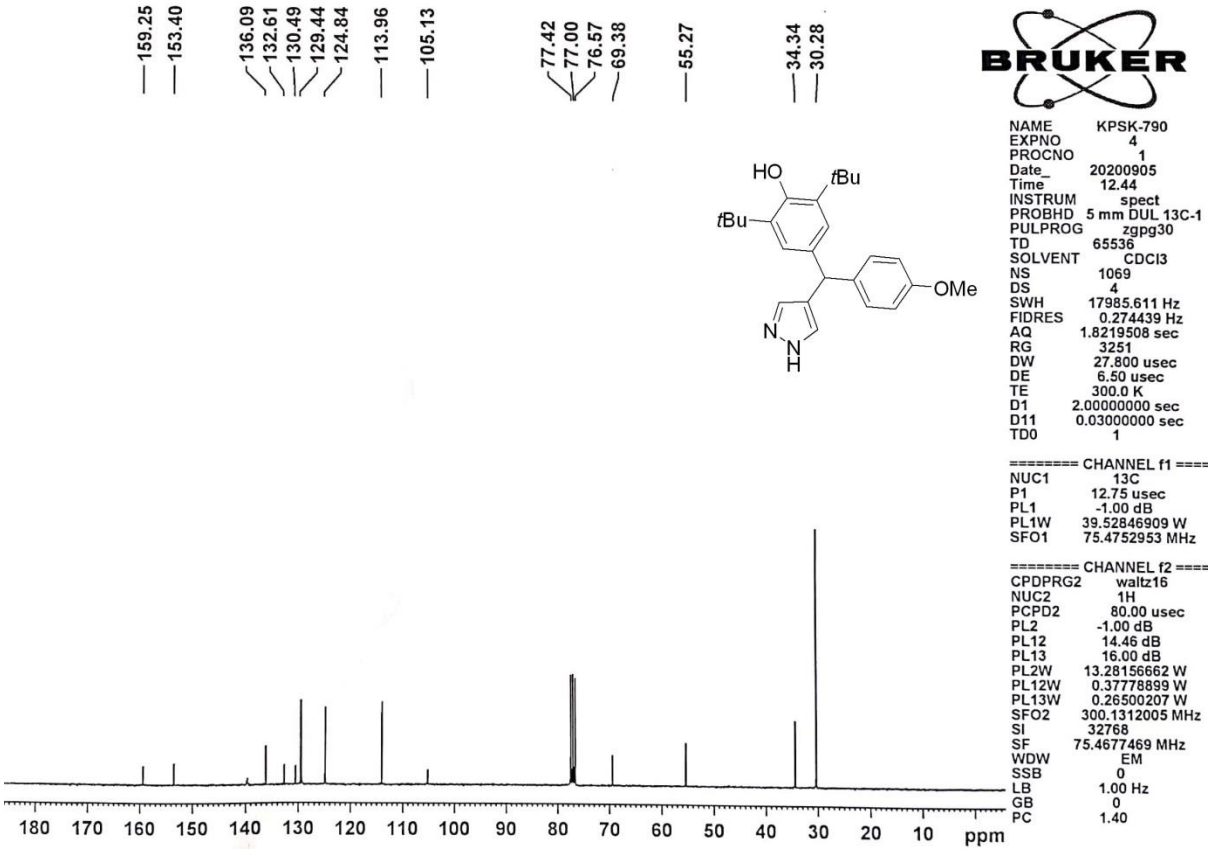
^{1}H and ^{13}C NMR for compound **3w**



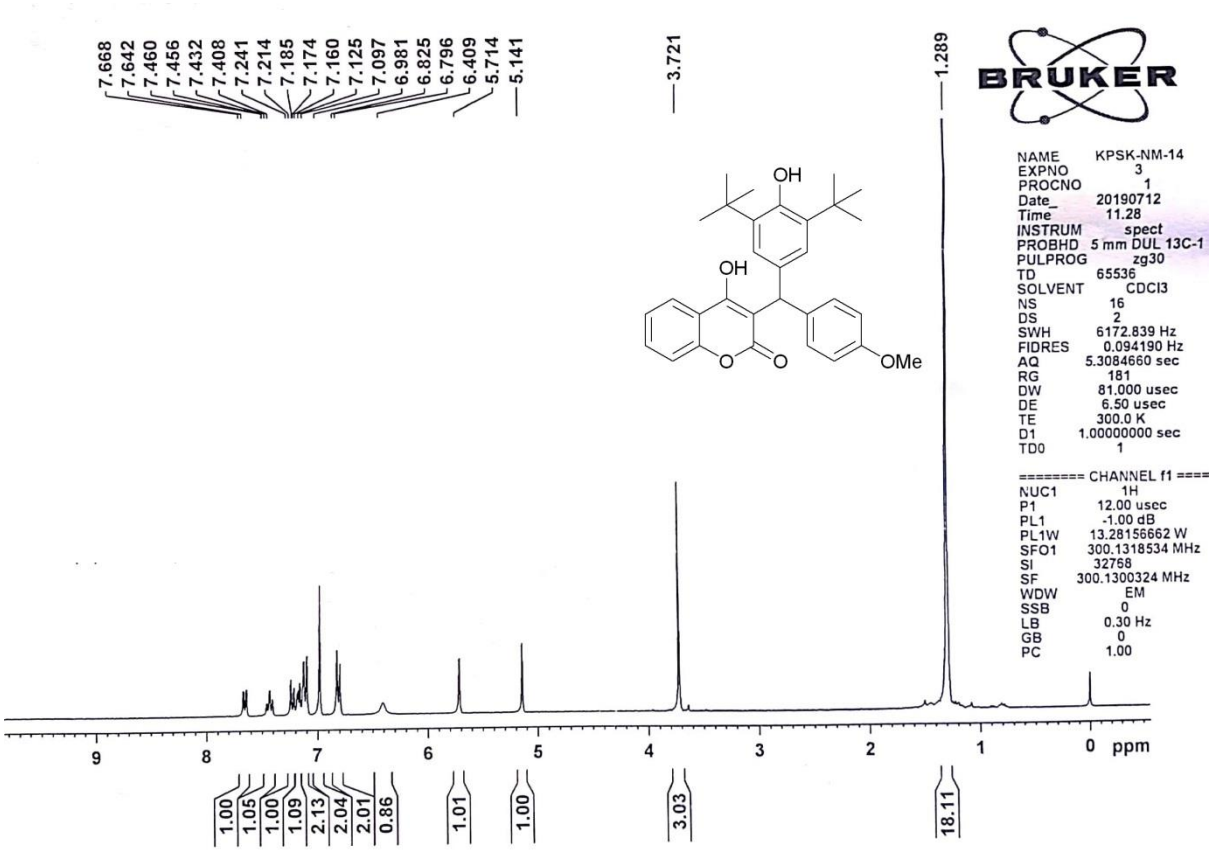


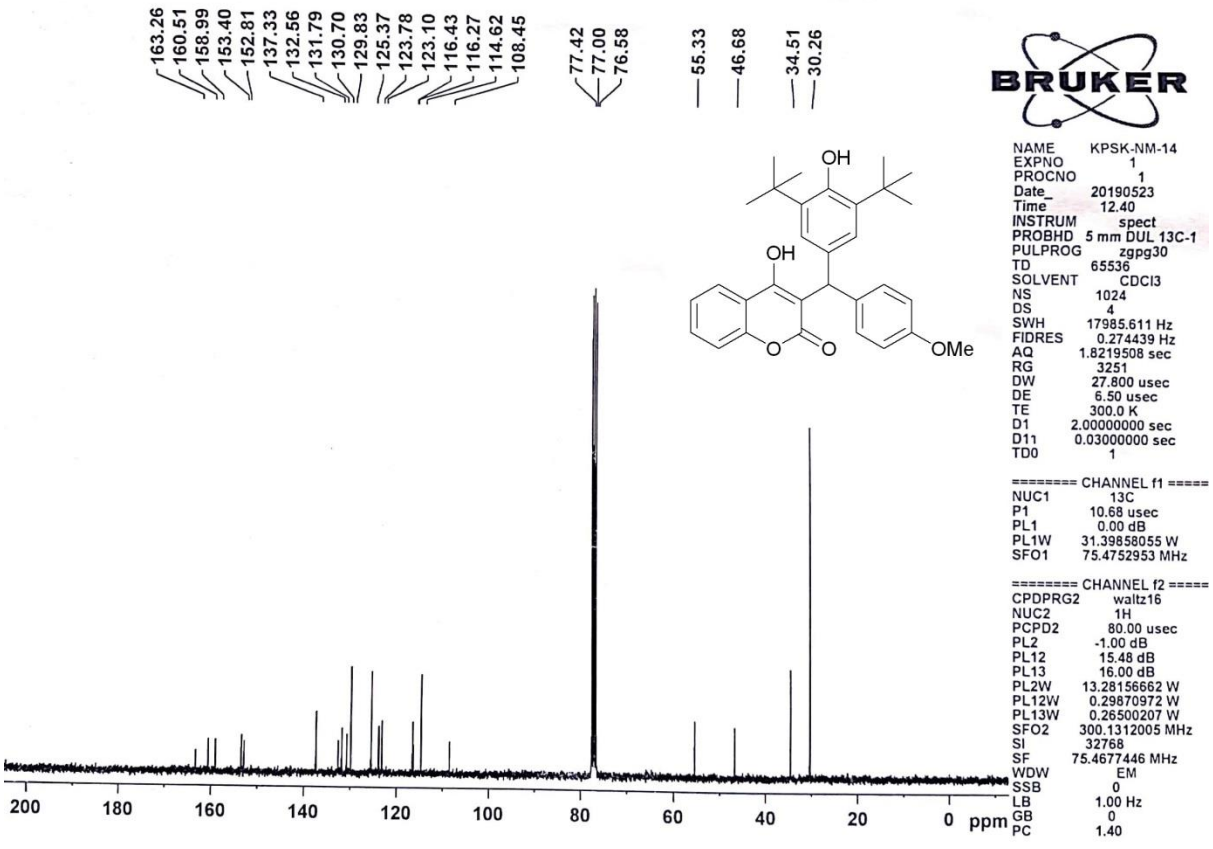
^{1}H and ^{13}C NMR for compound **3x**



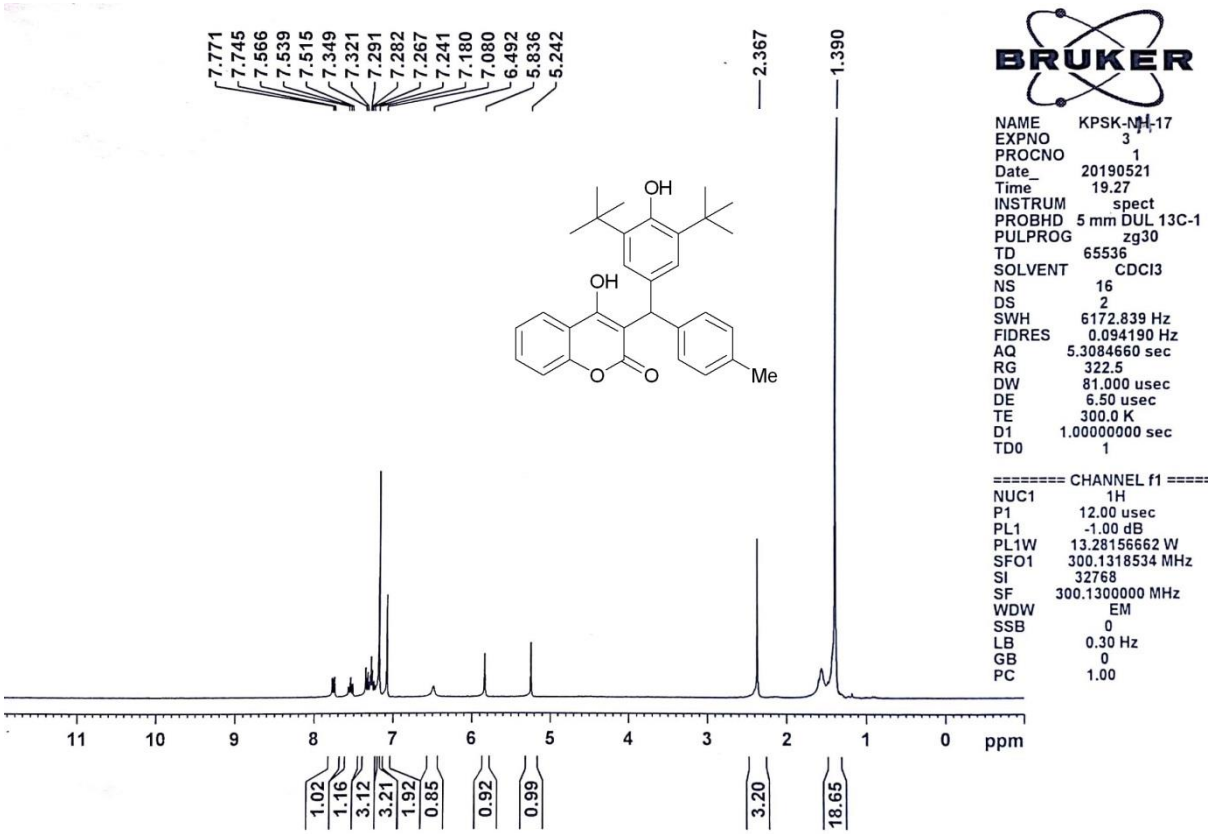


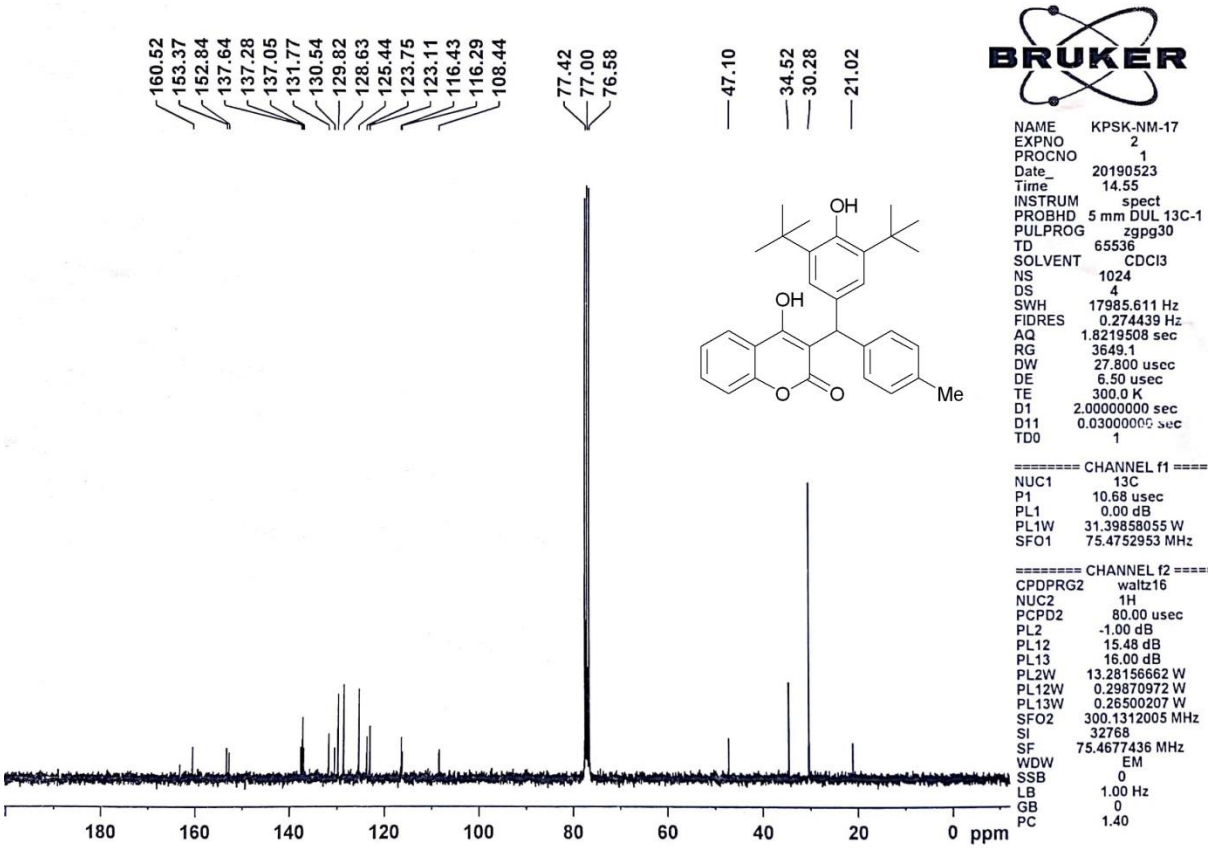
^{1}H and ^{13}C NMR for compound **5a**



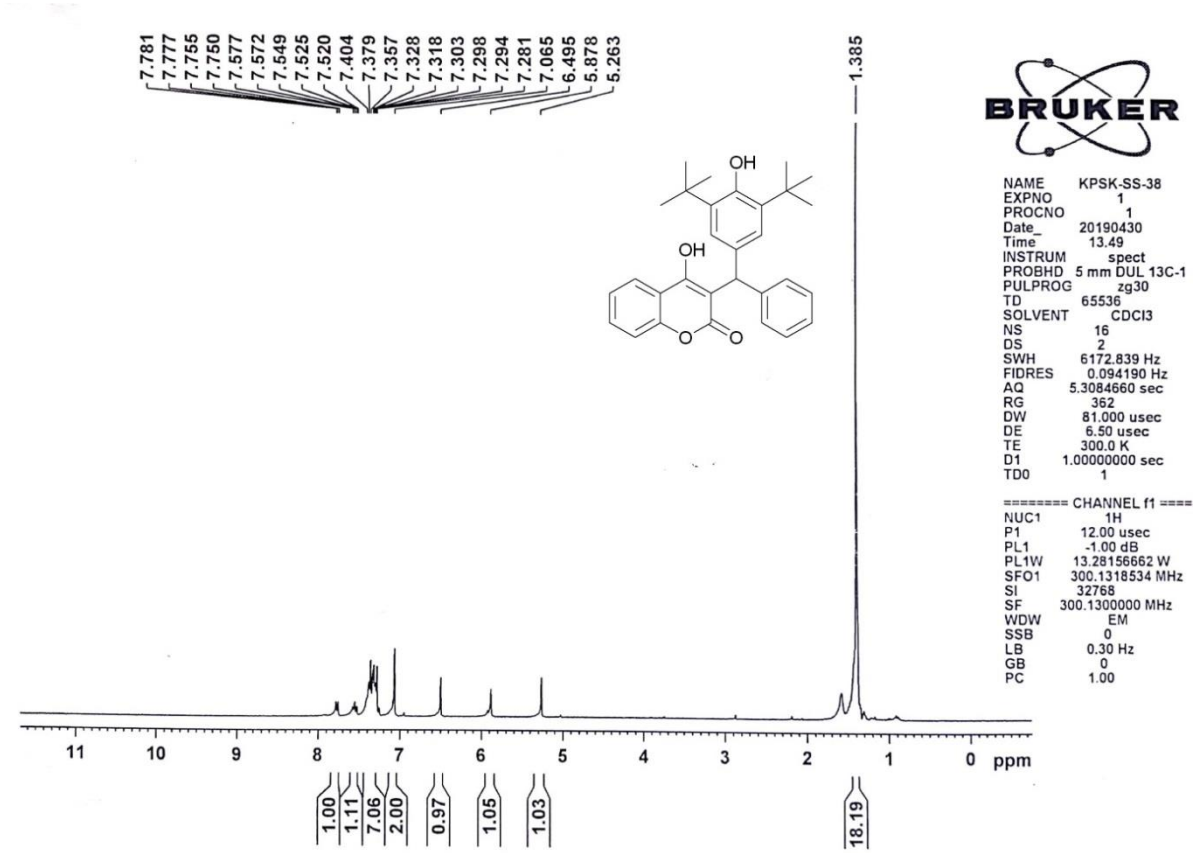


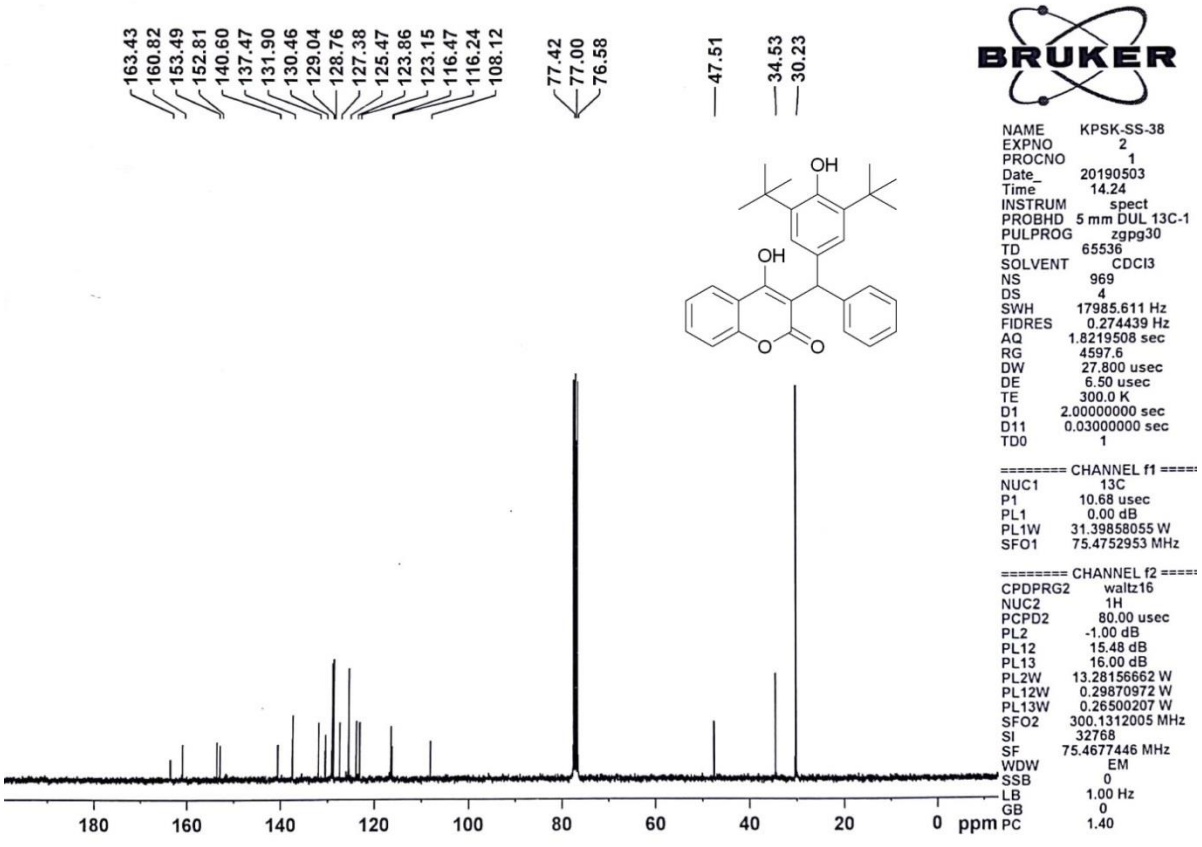
^{1}H and ^{13}C NMR for compound **5b**



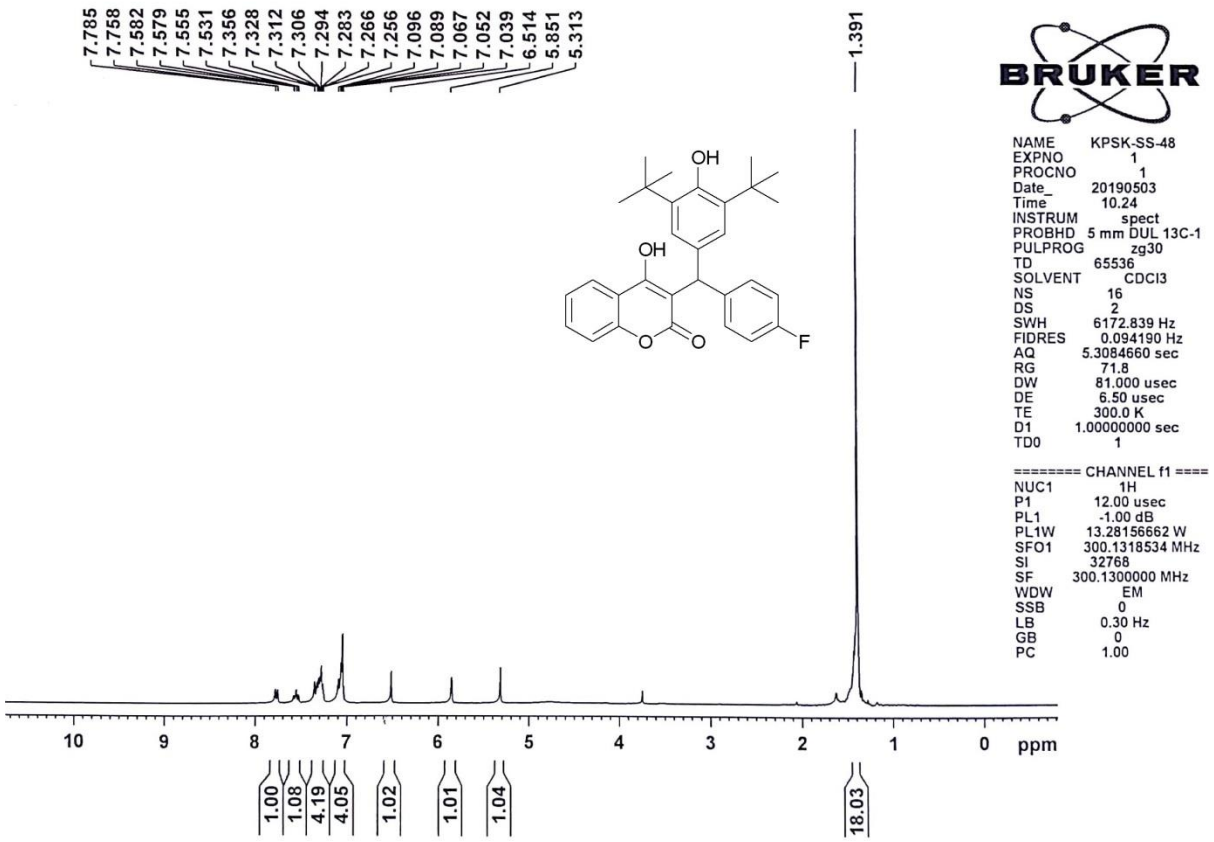


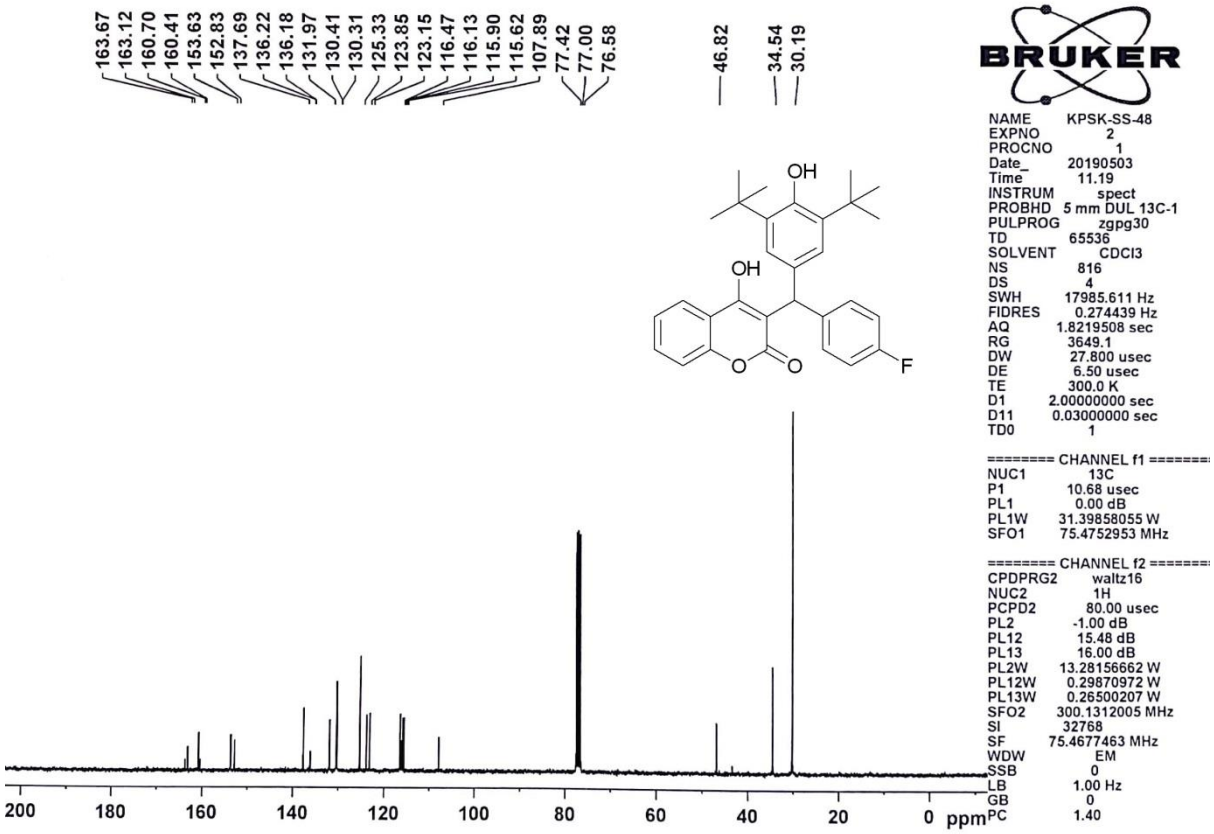
^{1}H and ^{13}C NMR for compound **5c**



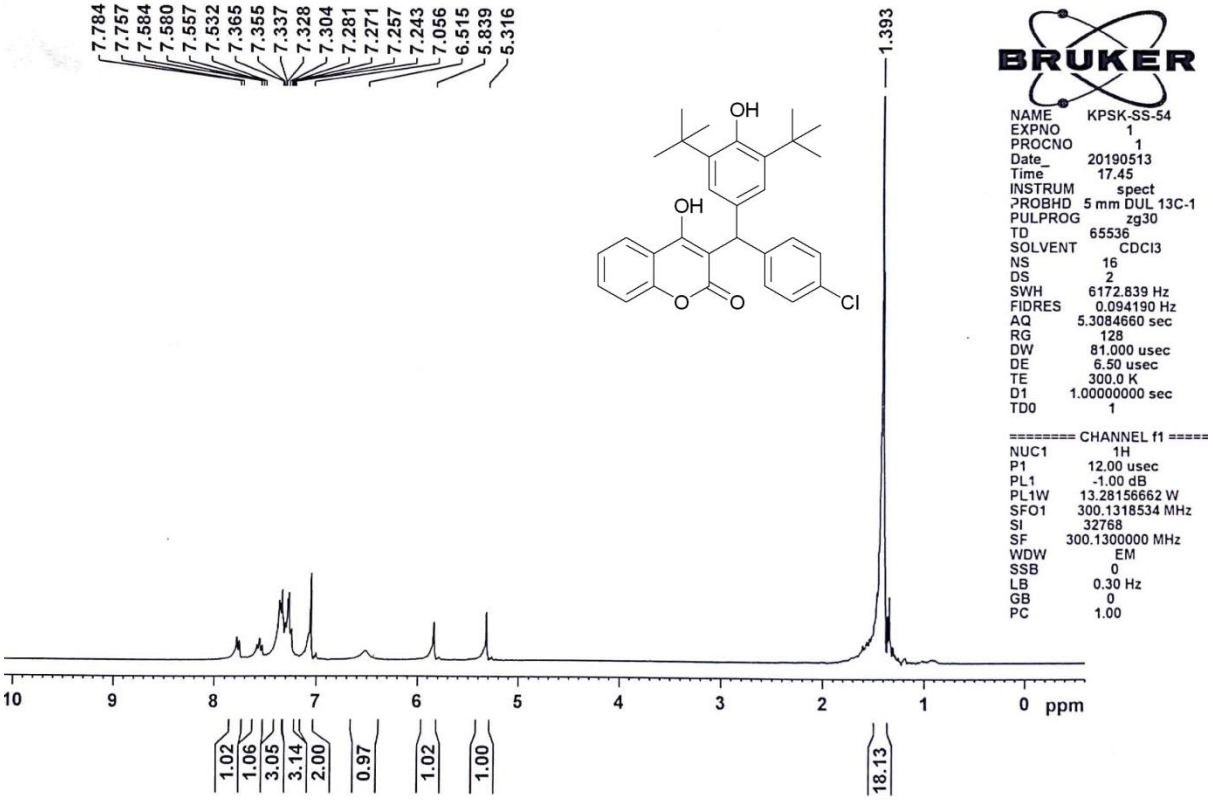


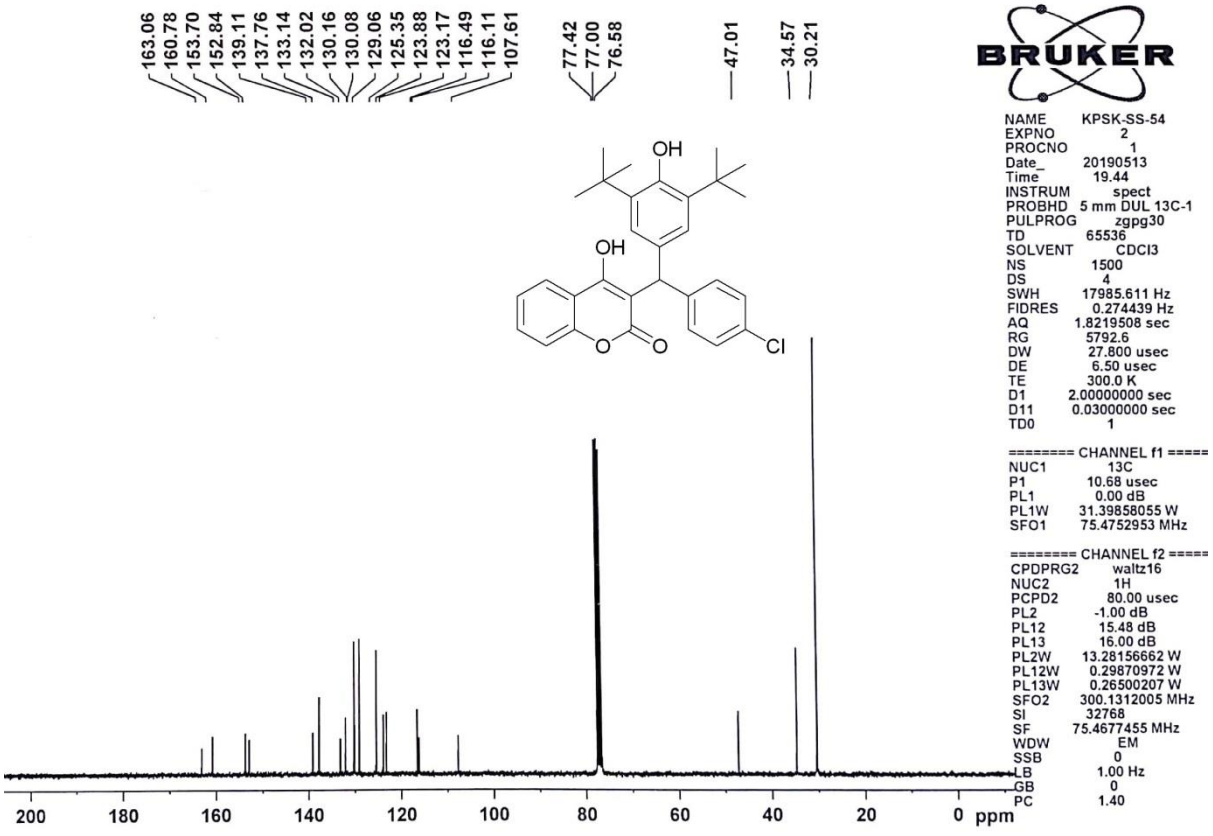
^{1}H and ^{13}C NMR for compound **5d**



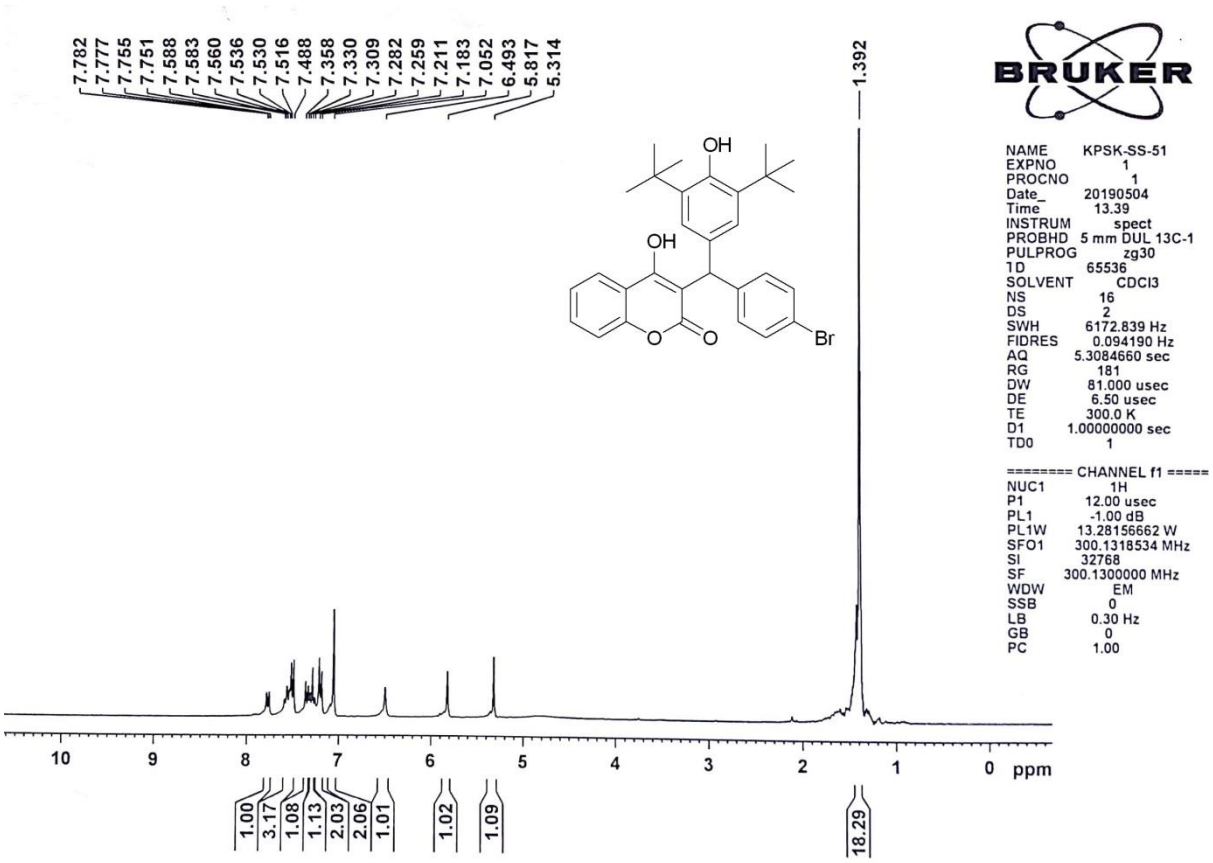


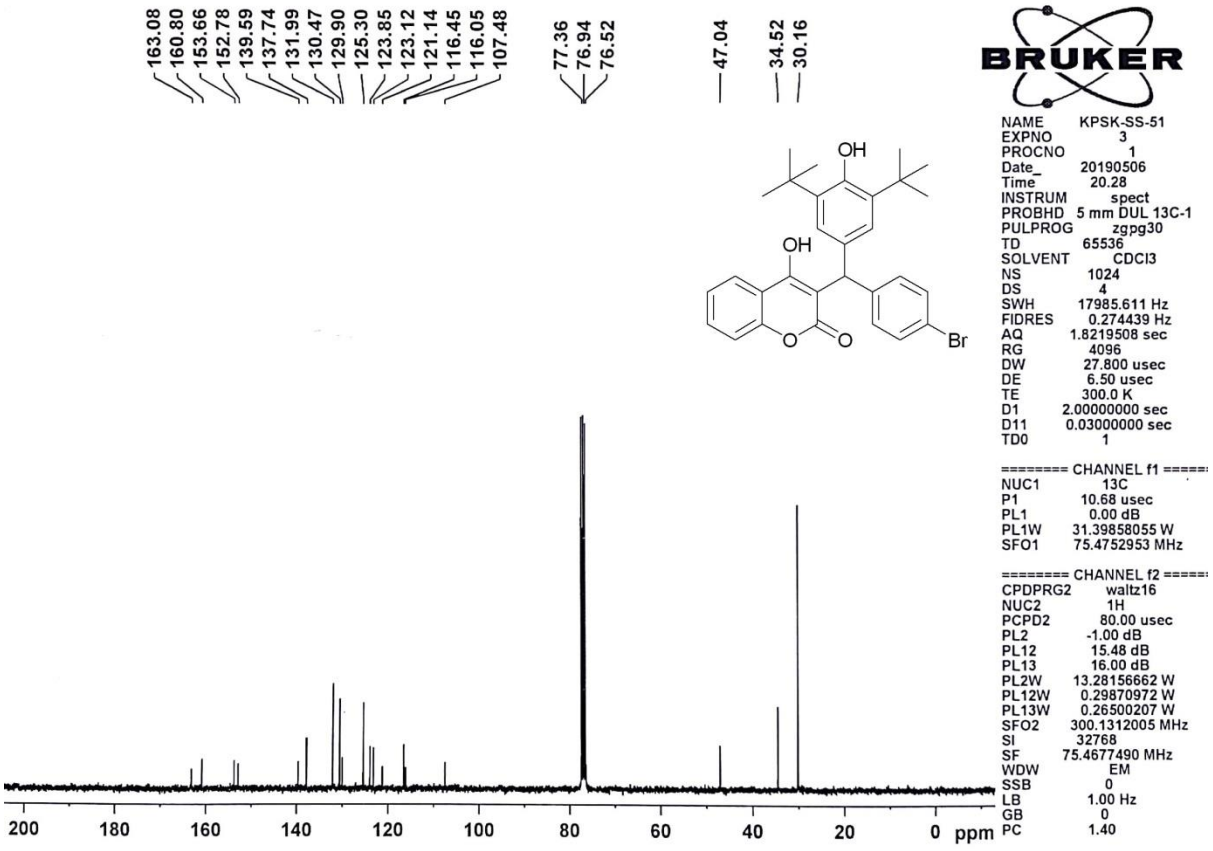
^{1}H and ^{13}C NMR for compound **5e**



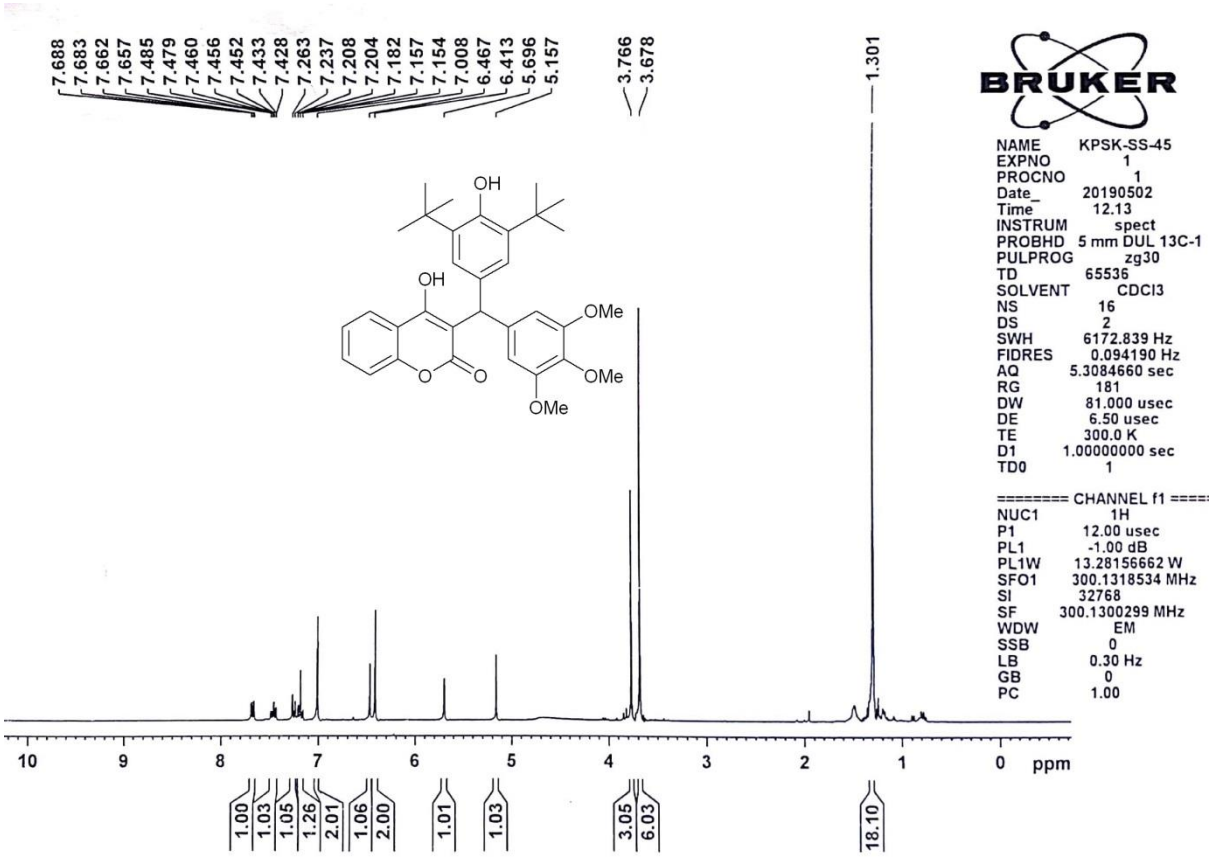


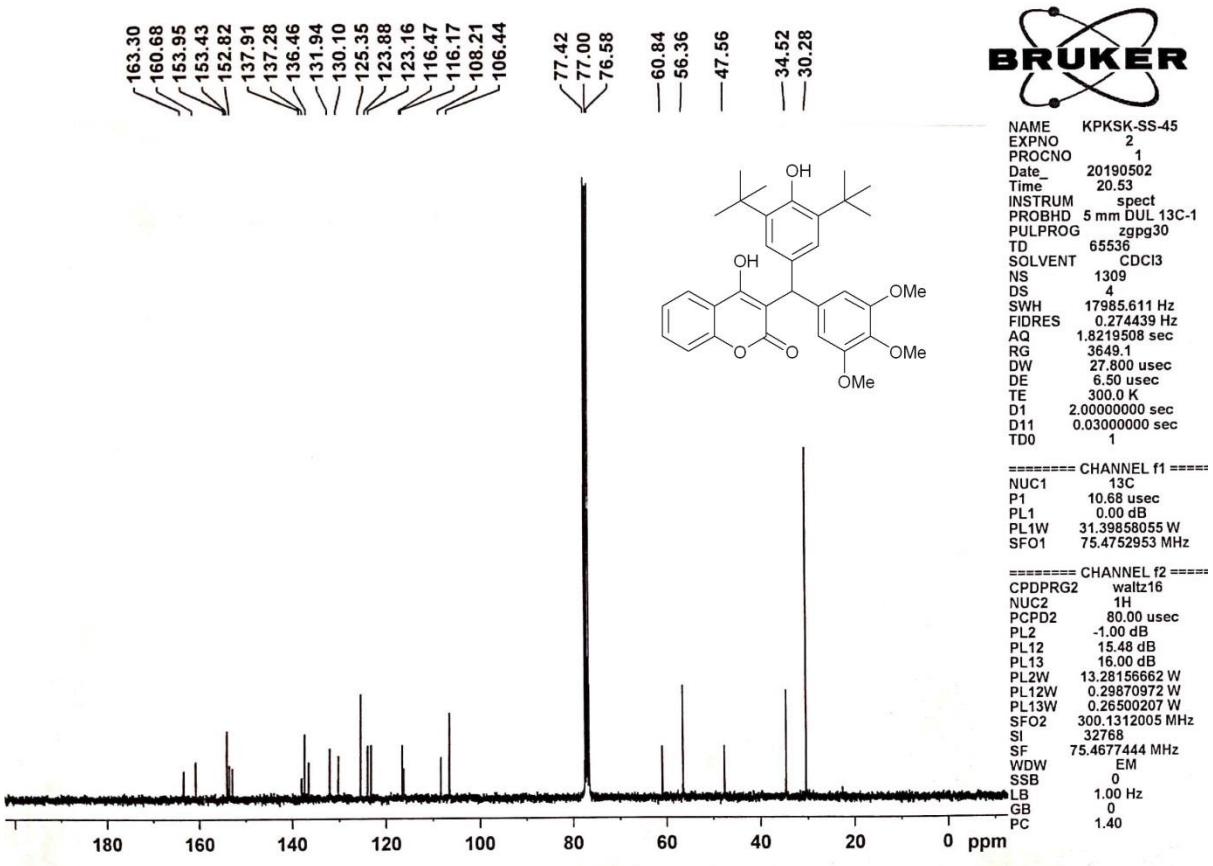
^{1}H and ^{13}C NMR for compound **5f**



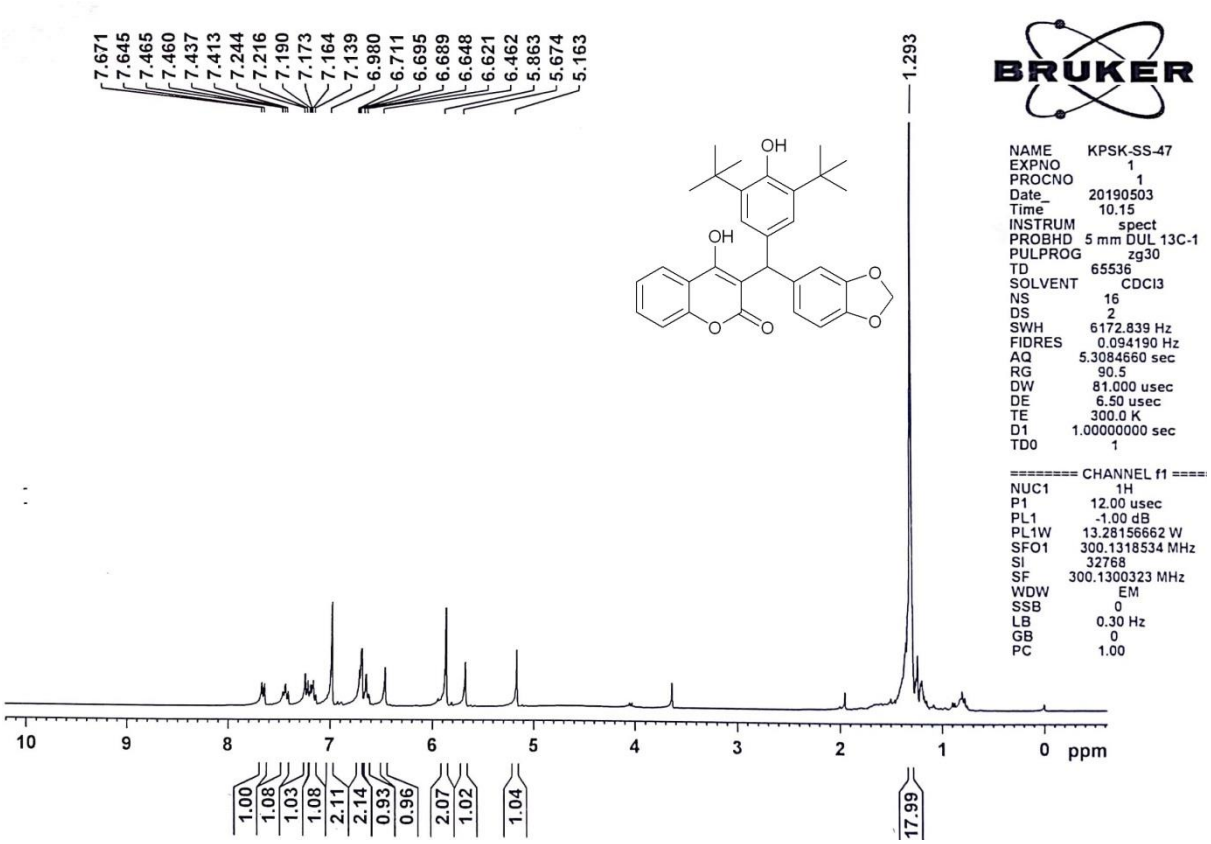


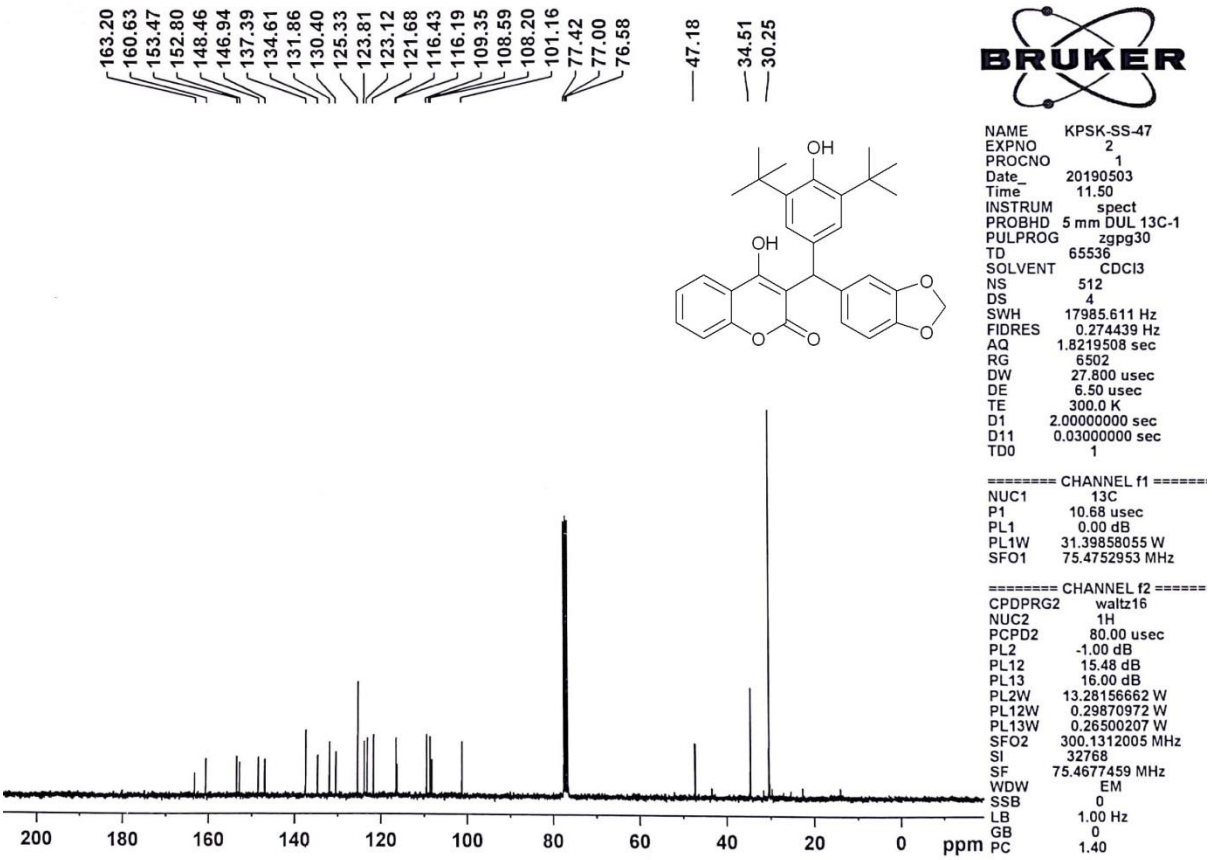
^{1}H and ^{13}C NMR for compound **5g**



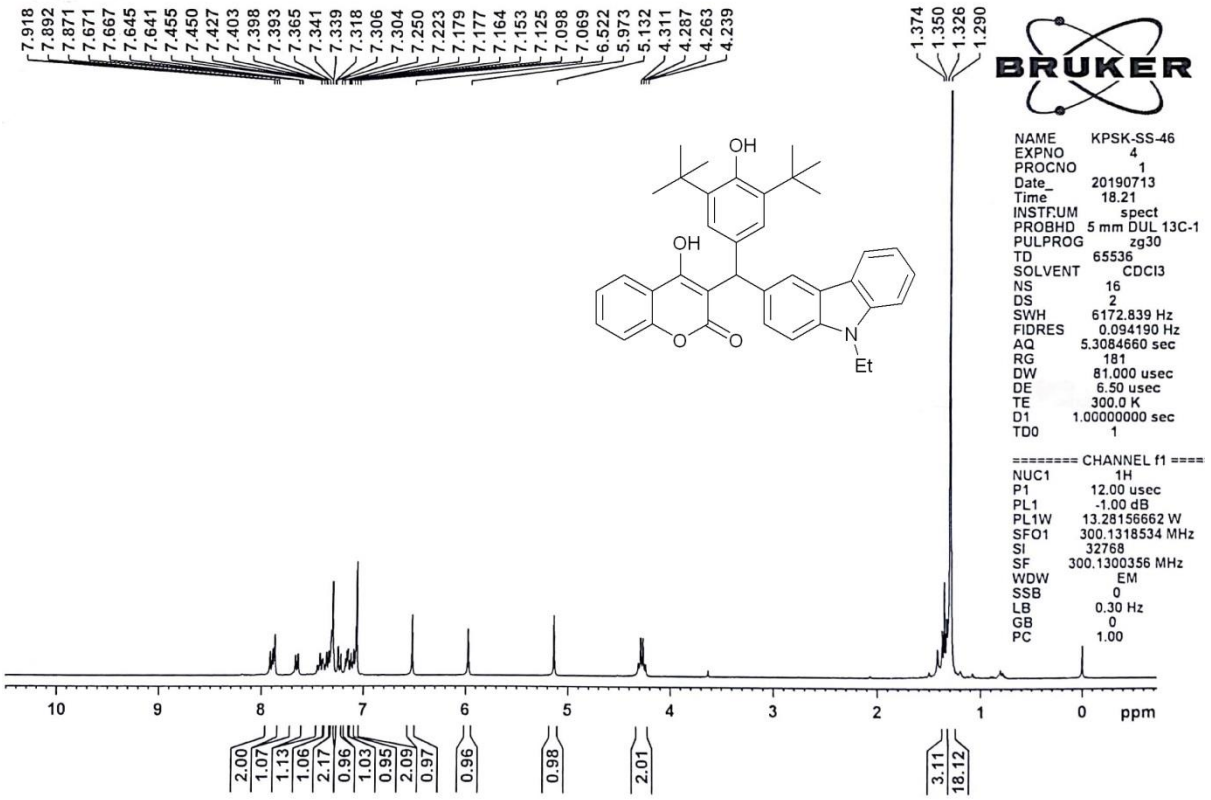


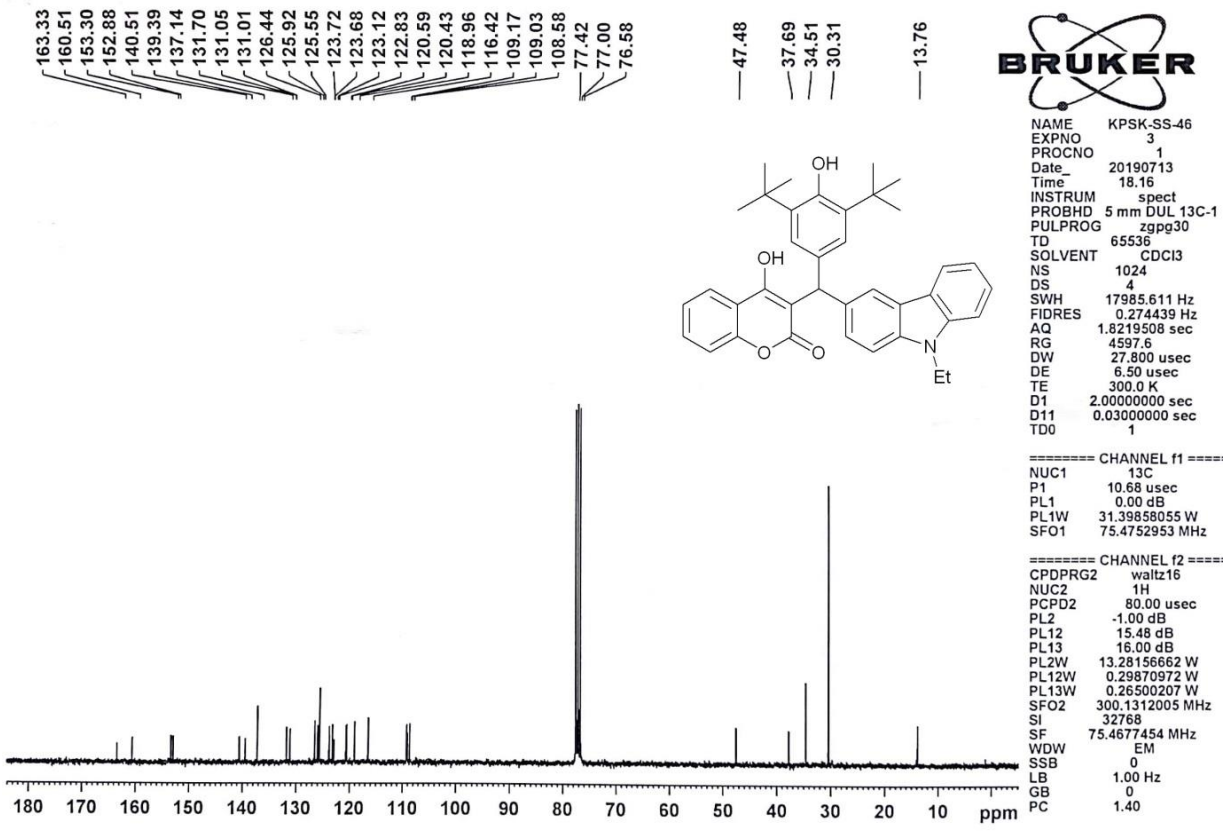
^{1}H and ^{13}C NMR for compound **5h**



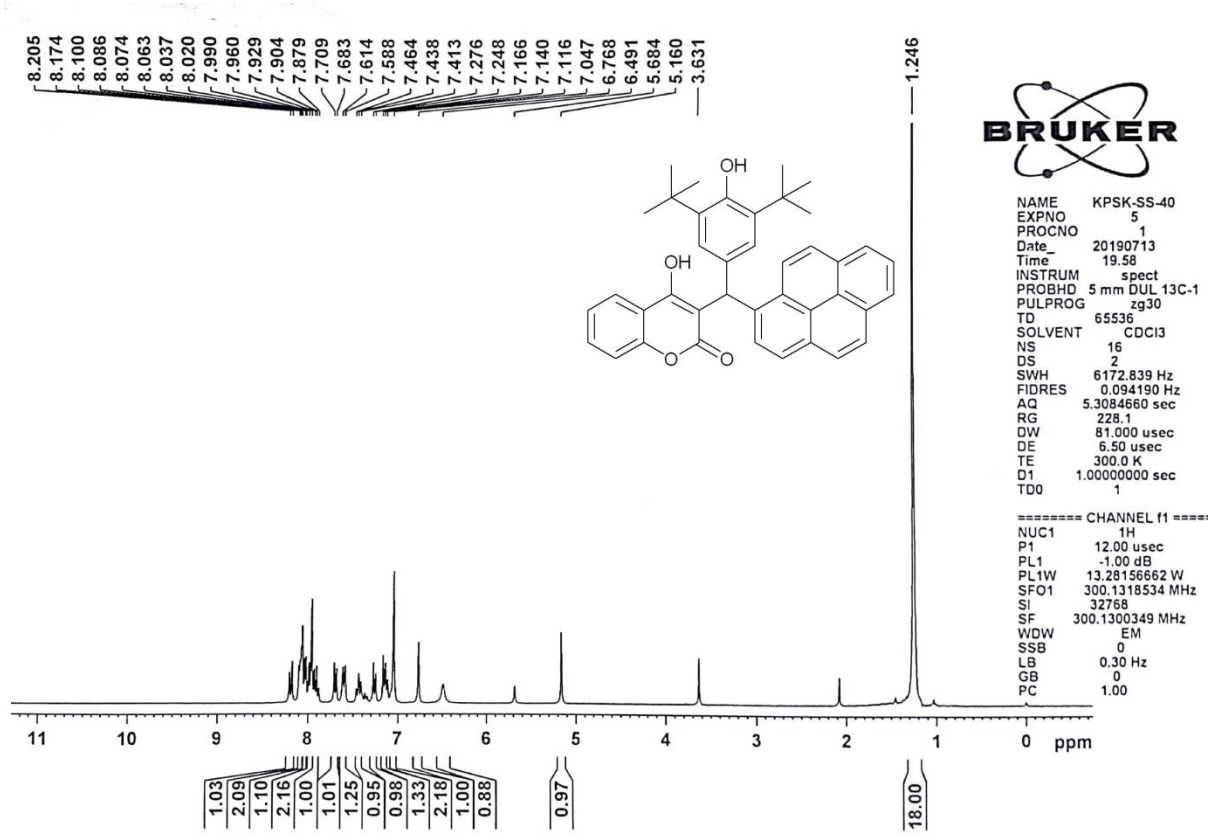


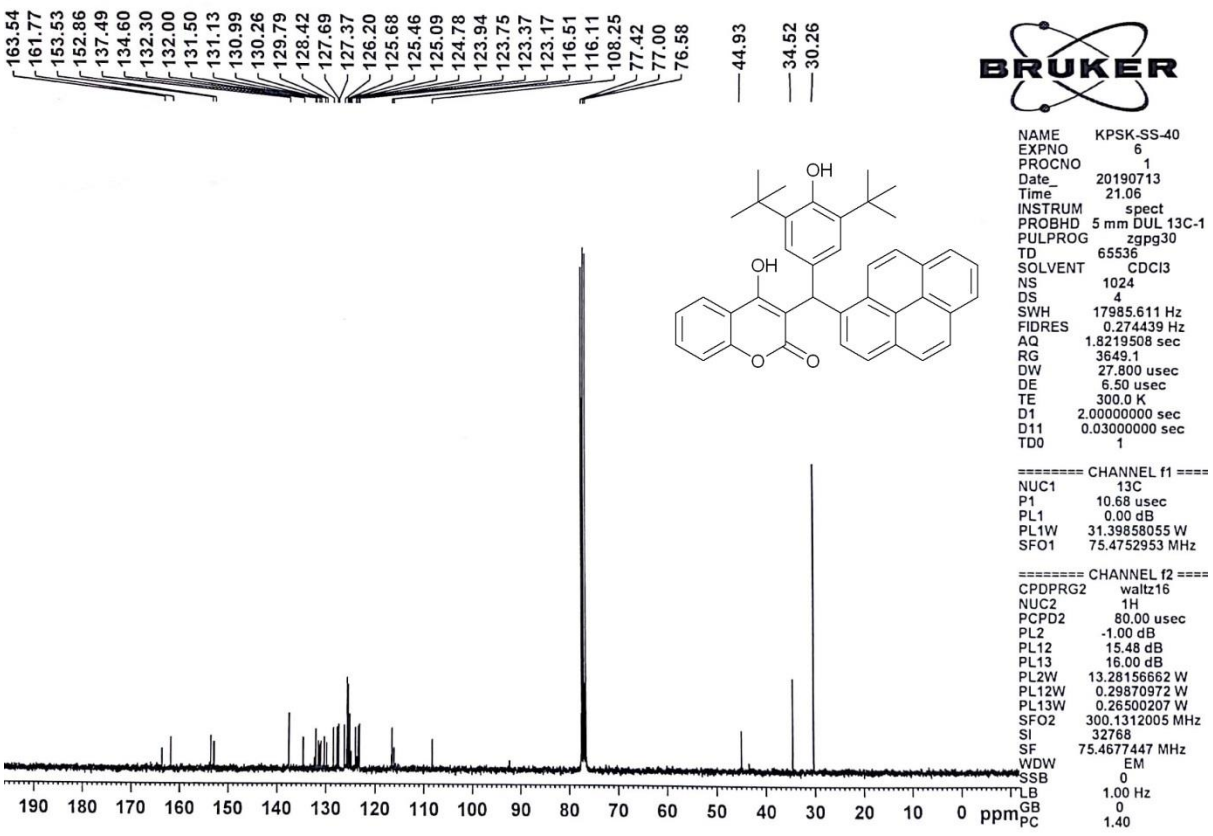
^{1}H and ^{13}C NMR for compound **5i**



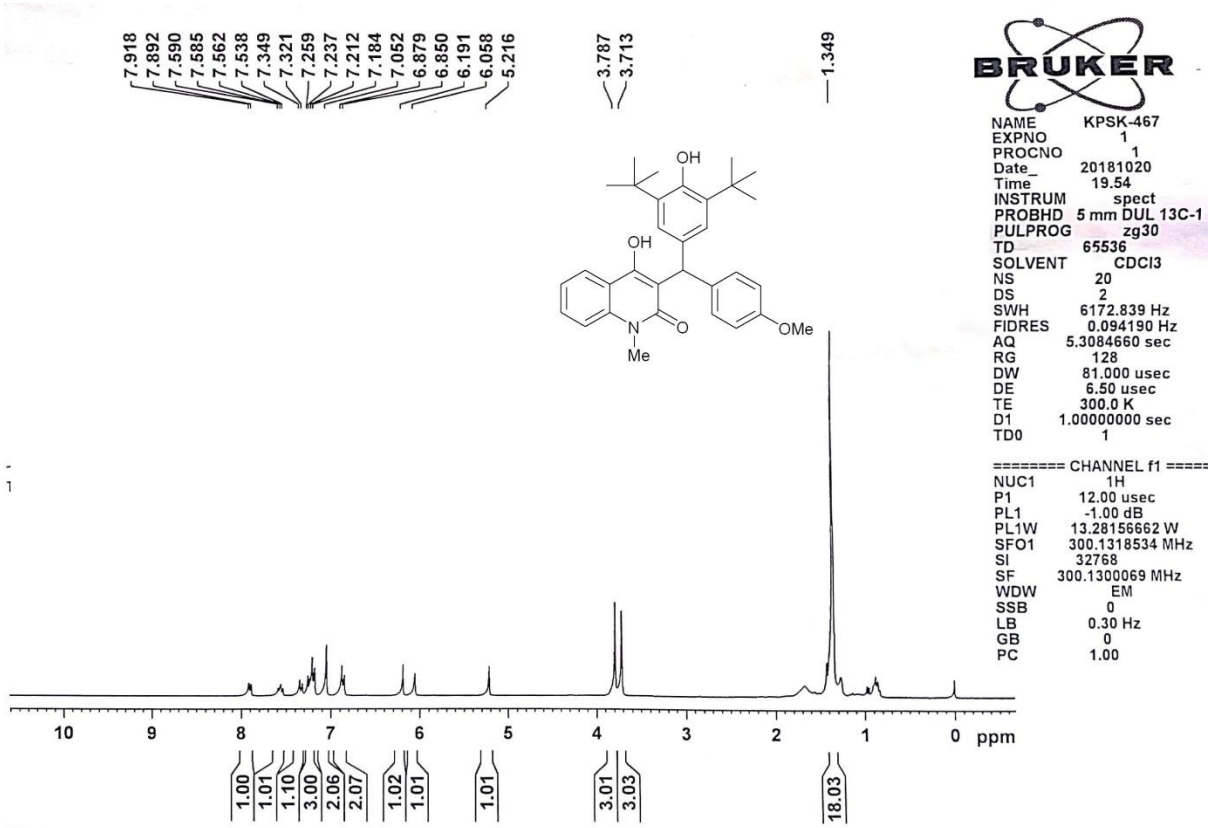


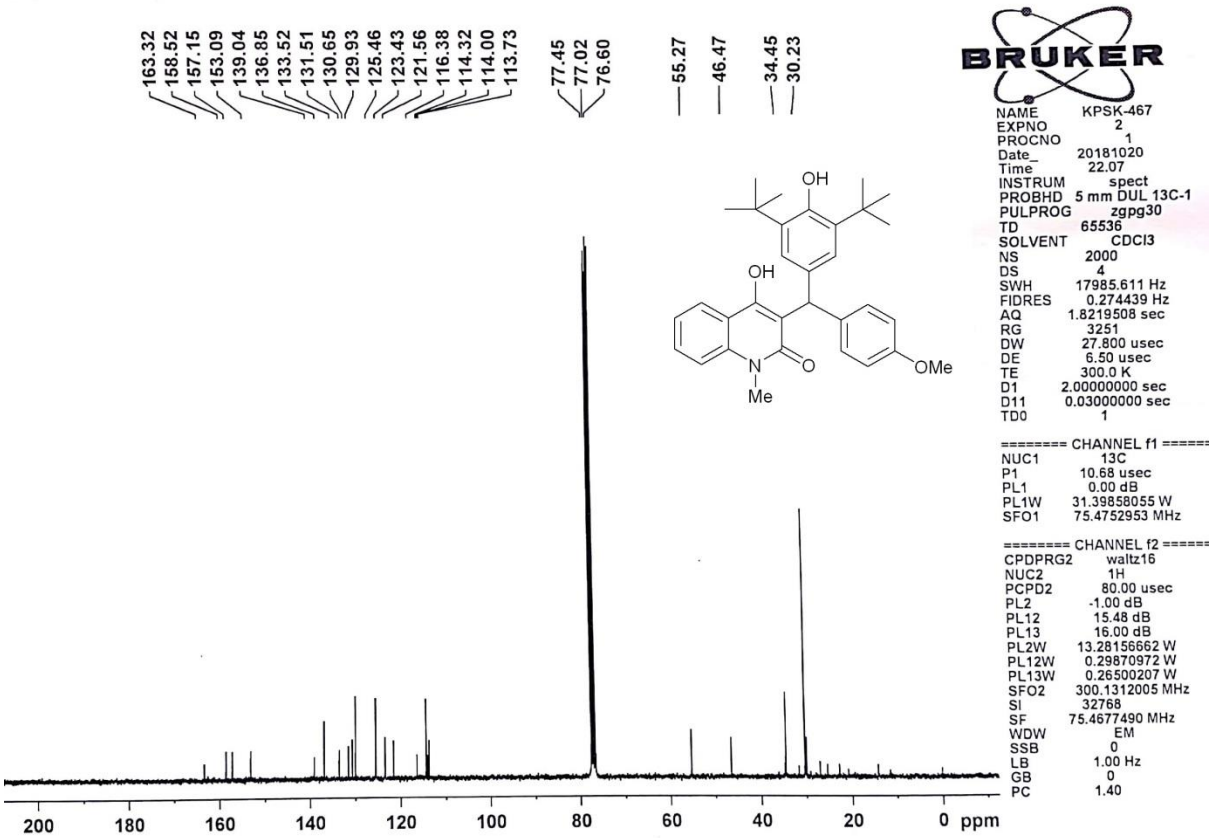
^{1}H and ^{13}C NMR for compound **5j**



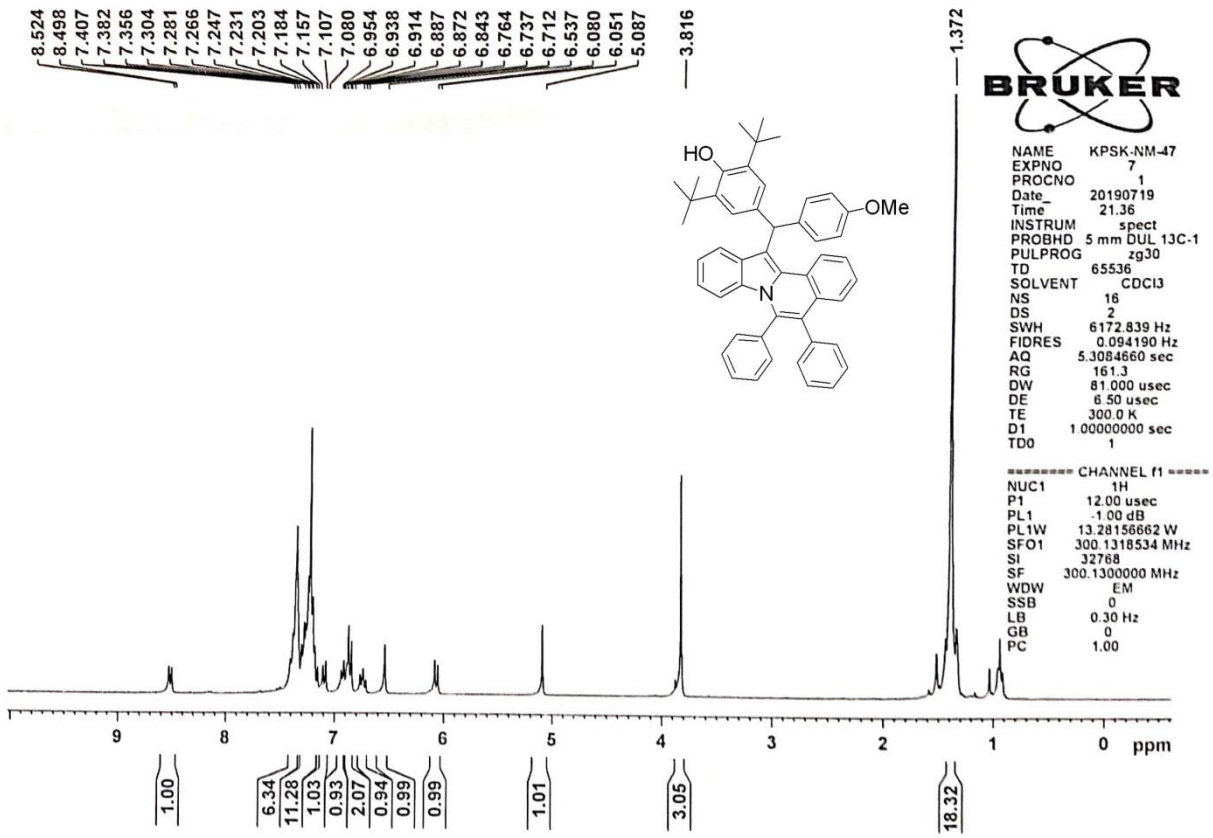


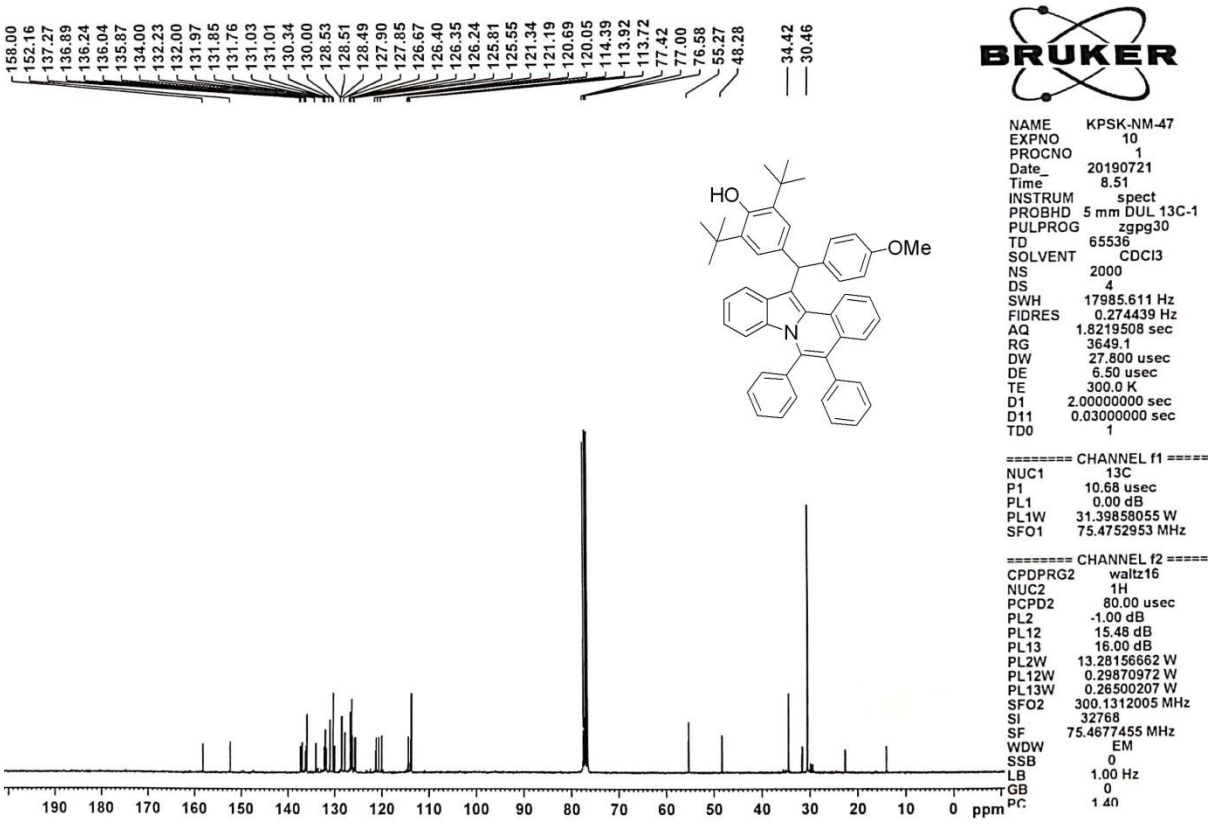
^{1}H and ^{13}C NMR for compound **5k**



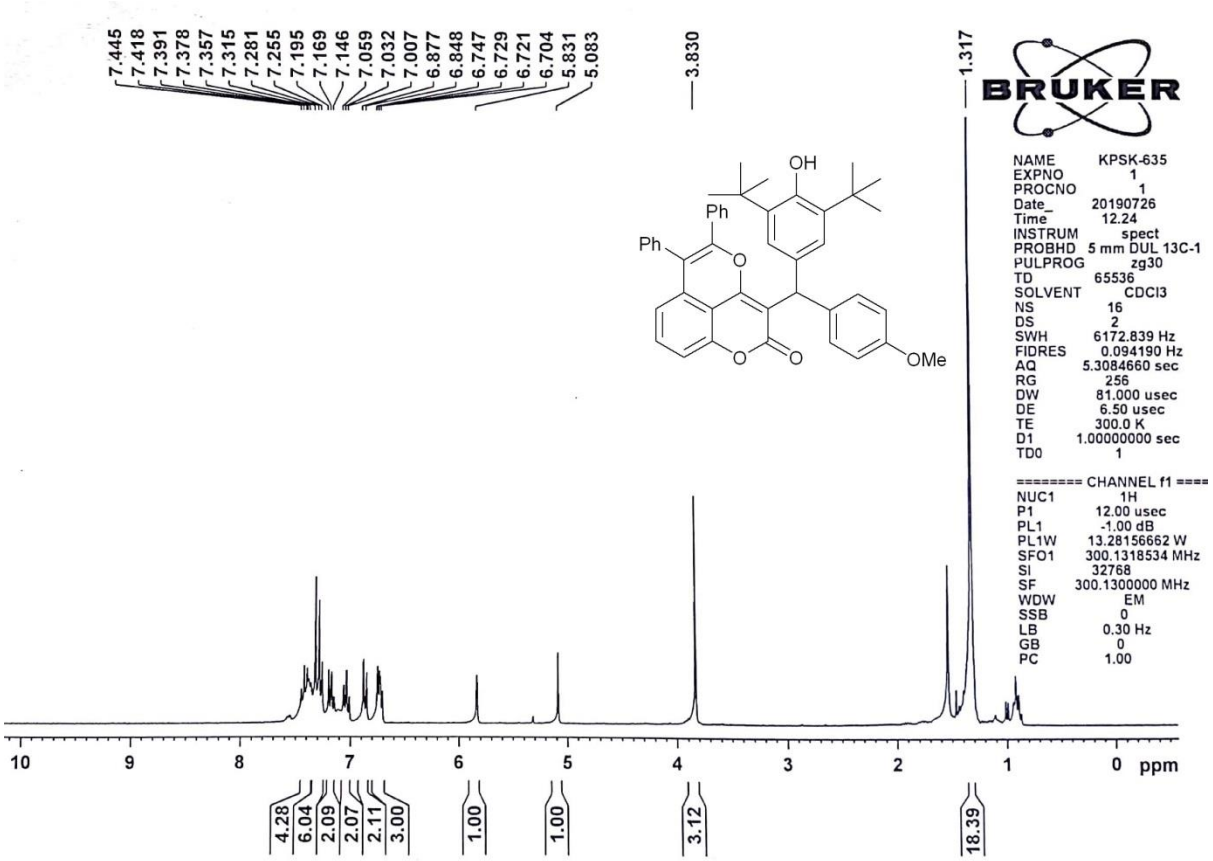


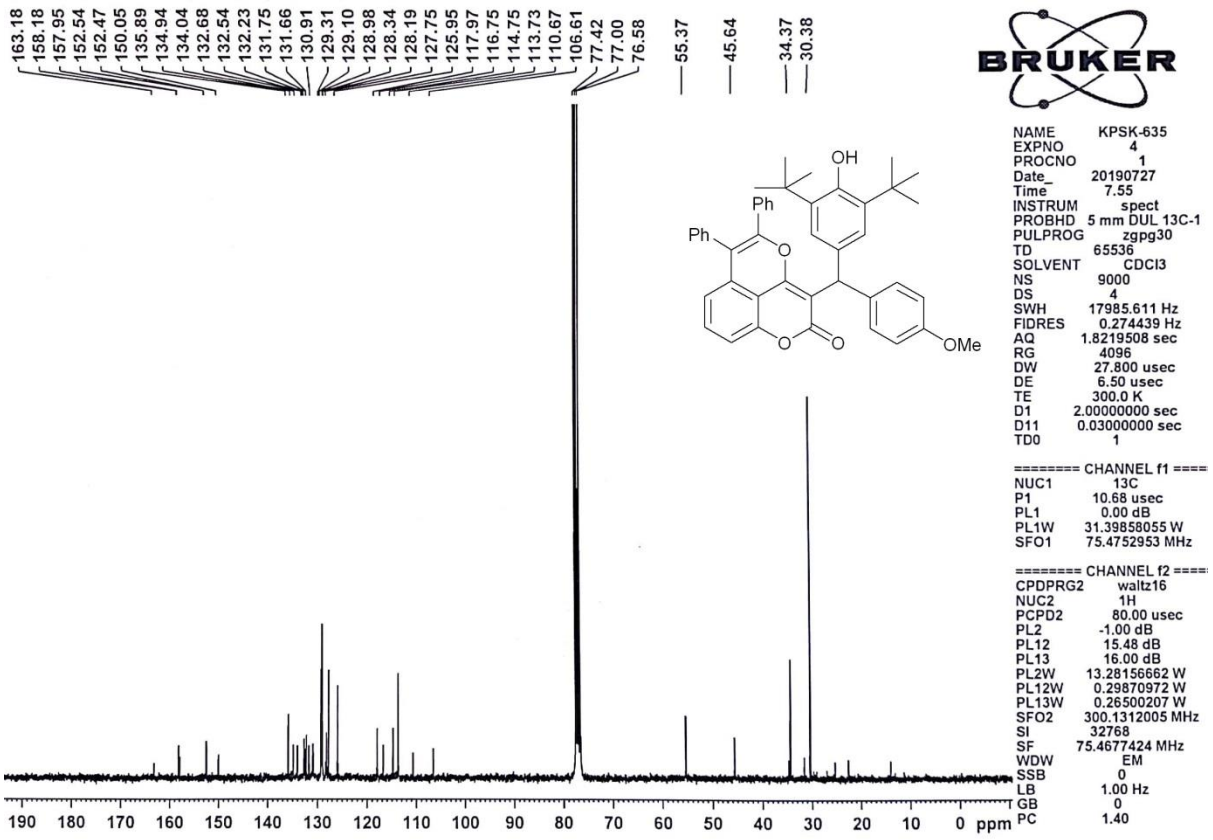
^{1}H and ^{13}C NMR for compound **7**





^{1}H and ^{13}C NMR for compound **8**





X-ray single crystal of compound **3j.**

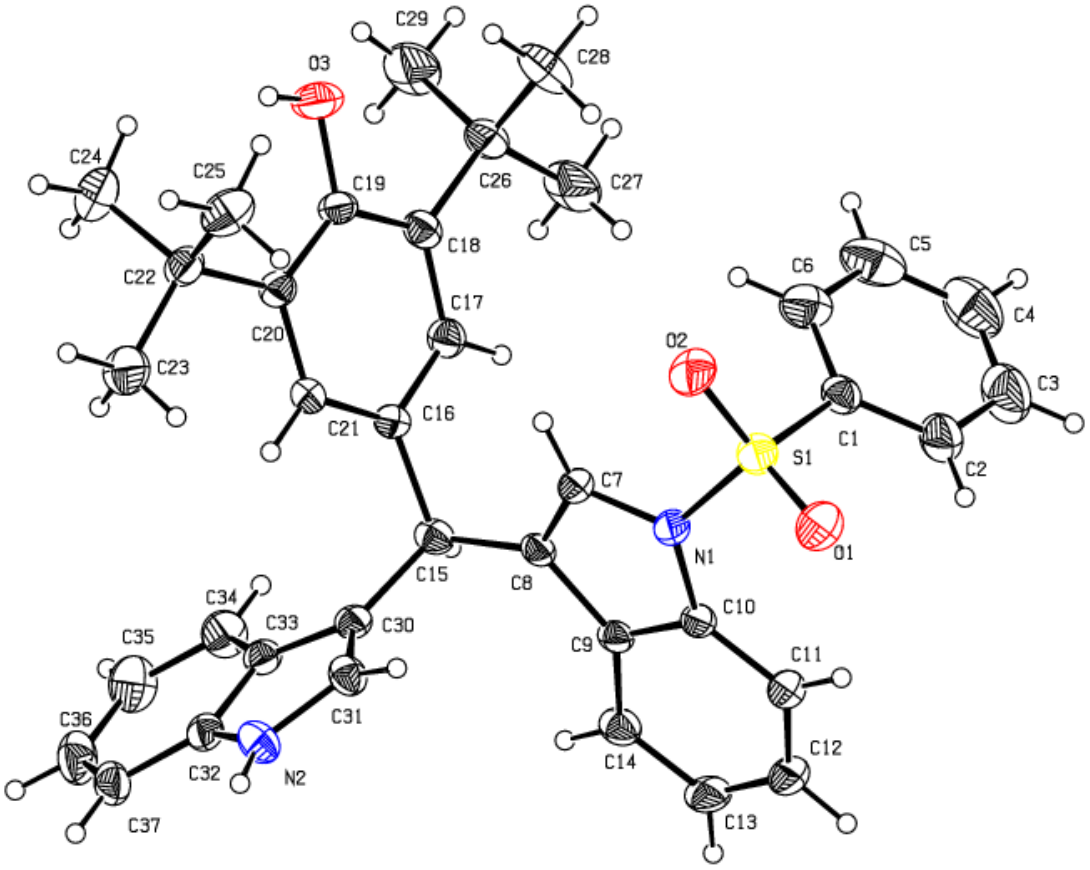


Table 1. Crystal data and structure refinement for **3j**.

Identification code	KPSK-399
CCDC number	2015484
Empirical formula	C37 H38 N2 O3 S
Formula weight	590.75
Temperature	296(2) K
Wavelength	0.71073 A
Crystal system, space group	Monoclinic, P 21/n
Unit cell dimensions	a = 12.3228(14) A alpha = 90 deg. b = 13.5824(12) A beta = 104.136(3) deg. c = 19.942(2) A gamma = 90 deg.
Volume	3236.7(6) A^3
Z, Calculated density	4, 1.212 Mg/m^3
Absorption coefficient	0.138 mm^-1
F(000)	1256
Crystal size	0.20 x 0.20 x 0.15 mm
Theta range for data collection	2.106 to 25.526 deg.
Limiting indices	-14<=h<=14, -16<=k<=16, -24<=l<=24
Reflections collected / unique	33724 / 6033 [R(int) = 0.0802]
Completeness to theta = 25.242	100.0 %
Absorption correction	Semi-empirical from equivalents
Max. and min. transmission	0.95 and 0.90
Refinement method	Full-matrix least-squares on F^2
Data / restraints / parameters	6033 / 0 / 394
Goodness-of-fit on F^2	1.016
Final R indices [I>2sigma(I)]	R1 = 0.0516, wR2 = 0.0994

R indices (all data)	R1 = 0.1282, wR2 = 0.1294
Extinction coefficient	n/a
Largest diff. peak and hole	0.195 and -0.304 e.A^-3

Table 2. Atomic coordinates (x 10^4) and equivalent isotropicdisplacement parameters (A^2 x 10^3) for 399.U(eq) is defined as one third of the trace of the orthogonalizedU_{ij} tensor.

	x	y	z	U(eq)
C(1)	3718(2)	4109(2)	297(1)	43(1)
C(2)	3927(3)	3966(2)	-340(2)	62(1)
C(3)	3569(4)	4647(3)	-857(2)	84(1)
C(4)	3017(4)	5456(3)	-742(2)	93(1)
C(5)	2802(3)	5623(2)	-105(2)	85(1)
C(6)	3153(3)	4938(2)	422(2)	68(1)
C(7)	2207(2)	2878(2)	1305(1)	39(1)
C(8)	1217(2)	2437(2)	1058(1)	34(1)
C(9)	1330(2)	1859(2)	468(1)	36(1)
C(10)	2416(2)	1976(2)	390(1)	37(1)
C(11)	2793(3)	1528(2)	-138(1)	47(1)
C(12)	2034(3)	948(2)	-586(1)	53(1)
C(13)	949(3)	811(2)	-523(1)	53(1)
C(14)	585(3)	1248(2)	6(1)	43(1)
C(15)	198(2)	2500(2)	1345(1)	37(1)
C(16)	287(2)	3389(2)	1824(1)	35(1)
C(17)	190(2)	4324(2)	1541(1)	40(1)
C(18)	405(2)	5173(2)	1942(1)	40(1)
C(19)	725(2)	5037(2)	2664(1)	38(1)
C(20)	791(2)	4111(2)	2977(1)	37(1)
C(21)	572(2)	3299(2)	2533(1)	36(1)
C(22)	1123(3)	3957(2)	3766(1)	45(1)
C(23)	1021(3)	2873(2)	3961(2)	68(1)
C(24)	358(3)	4533(2)	4133(2)	66(1)
C(25)	2349(3)	4264(2)	4059(2)	65(1)
C(26)	307(3)	6203(2)	1603(2)	50(1)
C(27)	-68(3)	6126(2)	814(2)	82(1)
C(28)	1442(3)	6722(2)	1783(2)	78(1)
C(29)	-568(3)	6831(2)	1835(2)	82(1)
C(30)	-4(2)	1543(2)	1680(1)	35(1)
C(31)	774(2)	852(2)	1962(1)	41(1)
C(32)	-830(2)	319(2)	2167(1)	38(1)
C(33)	-1042(2)	1216(2)	1804(1)	37(1)
C(34)	-2129(3)	1580(2)	1641(2)	56(1)
C(35)	-2958(3)	1066(3)	1837(2)	67(1)
C(36)	-2723(3)	179(3)	2198(2)	62(1)
C(37)	-1675(3)	-208(2)	2362(1)	48(1)
N(1)	2990(2)	2594(1)	933(1)	39(1)
N(2)	281(2)	111(2)	2255(1)	46(1)
O(1)	4898(2)	2571(1)	742(1)	58(1)
O(2)	4414(2)	3696(1)	1601(1)	59(1)
O(3)	988(2)	5875(1)	3060(1)	63(1)
S(1)	4133(1)	3224(1)	941(1)	44(1)

Table 3. Bond lengths [A] and angles [deg] for 3j.

C(1)-C(2)	1.371(4)
C(1)-C(6)	1.378(4)
C(1)-S(1)	1.743(3)
C(2)-C(3)	1.374(4)
C(2)-H(2)	0.9300
C(3)-C(4)	1.341(5)
C(3)-H(3)	0.9300
C(4)-C(5)	1.377(5)
C(4)-H(4)	0.9300
C(5)-C(6)	1.393(5)
C(5)-H(5)	0.9300
C(6)-H(6)	0.9300
C(7)-C(8)	1.339(3)
C(7)-N(1)	1.408(3)
C(7)-H(7)	0.9300
C(8)-C(9)	1.449(3)
C(8)-C(15)	1.504(3)
C(9)-C(10)	1.394(4)
C(9)-C(14)	1.403(3)
C(10)-C(11)	1.389(3)
C(10)-N(1)	1.416(3)
C(11)-C(12)	1.373(4)
C(11)-H(11)	0.9300
C(12)-C(13)	1.385(4)
C(12)-H(12)	0.9300
C(13)-C(14)	1.378(4)
C(13)-H(13)	0.9300
C(14)-H(14)	0.9300
C(15)-C(30)	1.510(3)
C(15)-C(16)	1.525(3)
C(15)-H(15)	0.9800
C(16)-C(21)	1.378(3)
C(16)-C(17)	1.383(3)
C(17)-C(18)	1.392(3)
C(17)-H(17)	0.9300
C(18)-C(19)	1.410(4)
C(18)-C(26)	1.545(3)
C(19)-O(3)	1.378(3)
C(19)-C(20)	1.398(3)
C(20)-C(21)	1.398(3)
C(20)-C(22)	1.540(4)
C(21)-H(21)	0.9300
C(22)-C(23)	1.536(4)
C(22)-C(25)	1.538(4)
C(22)-C(24)	1.540(4)
C(23)-H(23A)	0.9600
C(23)-H(23B)	0.9600
C(23)-H(23C)	0.9600
C(24)-H(24A)	0.9600
C(24)-H(24B)	0.9600
C(24)-H(24C)	0.9600
C(25)-H(25A)	0.9600
C(25)-H(25B)	0.9600
C(25)-H(25C)	0.9600
C(26)-C(28)	1.528(4)
C(26)-C(27)	1.531(4)
C(26)-C(29)	1.534(4)
C(27)-H(27A)	0.9600
C(27)-H(27B)	0.9600
C(27)-H(27C)	0.9600
C(28)-H(28A)	0.9600
C(28)-H(28B)	0.9600
C(28)-H(28C)	0.9600
C(29)-H(29A)	0.9600

C(29)-H(29B)	0.9600
C(29)-H(29C)	0.9600
C(30)-C(31)	1.362(4)
C(30)-C(33)	1.431(4)
C(31)-N(2)	1.377(3)
C(31)-H(31)	0.9300
C(32)-N(2)	1.366(3)
C(32)-C(37)	1.395(4)
C(32)-C(33)	1.409(3)
C(33)-C(34)	1.390(4)
C(34)-C(35)	1.371(4)
C(34)-H(34)	0.9300
C(35)-C(36)	1.397(4)
C(35)-H(35)	0.9300
C(36)-C(37)	1.358(4)
C(36)-H(36)	0.9300
C(37)-H(37)	0.9300
N(1)-S(1)	1.645(2)
N(2)-H(2A)	0.8600
O(1)-S(1)	1.4201(19)
O(2)-S(1)	1.4289(18)
O(3)-H(3A)	0.8200

C(2)-C(1)-C(6)	120.1(3)
C(2)-C(1)-S(1)	119.8(2)
C(6)-C(1)-S(1)	120.0(2)
C(1)-C(2)-C(3)	120.0(3)
C(1)-C(2)-H(2)	120.0
C(3)-C(2)-H(2)	120.0
C(4)-C(3)-C(2)	120.5(4)
C(4)-C(3)-H(3)	119.8
C(2)-C(3)-H(3)	119.8
C(3)-C(4)-C(5)	120.8(4)
C(3)-C(4)-H(4)	119.6
C(5)-C(4)-H(4)	119.6
C(4)-C(5)-C(6)	119.5(4)
C(4)-C(5)-H(5)	120.3
C(6)-C(5)-H(5)	120.3
C(1)-C(6)-C(5)	119.1(3)
C(1)-C(6)-H(6)	120.5
C(5)-C(6)-H(6)	120.5
C(8)-C(7)-N(1)	111.3(2)
C(8)-C(7)-H(7)	124.3
N(1)-C(7)-H(7)	124.3
C(7)-C(8)-C(9)	106.4(2)
C(7)-C(8)-C(15)	127.1(2)
C(9)-C(8)-C(15)	126.5(2)
C(10)-C(9)-C(14)	119.1(2)
C(10)-C(9)-C(8)	108.3(2)
C(14)-C(9)-C(8)	132.6(3)
C(11)-C(10)-C(9)	122.8(2)
C(11)-C(10)-N(1)	130.0(3)
C(9)-C(10)-N(1)	107.2(2)
C(12)-C(11)-C(10)	116.4(3)
C(12)-C(11)-H(11)	121.8
C(10)-C(11)-H(11)	121.8
C(11)-C(12)-C(13)	122.4(3)
C(11)-C(12)-H(12)	118.8
C(13)-C(12)-H(12)	118.8
C(14)-C(13)-C(12)	120.9(3)
C(14)-C(13)-H(13)	119.6
C(12)-C(13)-H(13)	119.6
C(13)-C(14)-C(9)	118.4(3)
C(13)-C(14)-H(14)	120.8
C(9)-C(14)-H(14)	120.8
C(8)-C(15)-C(30)	111.3(2)
C(8)-C(15)-C(16)	110.1(2)
C(30)-C(15)-C(16)	113.5(2)

C(8)-C(15)-H(15)	107.2
C(30)-C(15)-H(15)	107.2
C(16)-C(15)-H(15)	107.2
C(21)-C(16)-C(17)	118.4(2)
C(21)-C(16)-C(15)	122.3(2)
C(17)-C(16)-C(15)	119.1(2)
C(16)-C(17)-C(18)	122.9(2)
C(16)-C(17)-H(17)	118.6
C(18)-C(17)-H(17)	118.6
C(17)-C(18)-C(19)	116.4(2)
C(17)-C(18)-C(26)	121.1(2)
C(19)-C(18)-C(26)	122.5(2)
O(3)-C(19)-C(20)	120.5(2)
O(3)-C(19)-C(18)	116.5(2)
C(20)-C(19)-C(18)	123.1(2)
C(21)-C(20)-C(19)	116.5(2)
C(21)-C(20)-C(22)	120.1(2)
C(19)-C(20)-C(22)	123.4(2)
C(16)-C(21)-C(20)	122.8(2)
C(16)-C(21)-H(21)	118.6
C(20)-C(21)-H(21)	118.6
C(23)-C(22)-C(25)	107.2(2)
C(23)-C(22)-C(20)	111.8(2)
C(25)-C(22)-C(20)	110.0(2)
C(23)-C(22)-C(24)	105.6(2)
C(25)-C(22)-C(24)	109.9(2)
C(20)-C(22)-C(24)	112.1(2)
C(22)-C(23)-H(23A)	109.5
C(22)-C(23)-H(23B)	109.5
H(23A)-C(23)-H(23B)	109.5
C(22)-C(23)-H(23C)	109.5
H(23A)-C(23)-H(23C)	109.5
H(23B)-C(23)-H(23C)	109.5
C(22)-C(24)-H(24A)	109.5
C(22)-C(24)-H(24B)	109.5
H(24A)-C(24)-H(24B)	109.5
C(22)-C(24)-H(24C)	109.5
H(24A)-C(24)-H(24C)	109.5
H(24B)-C(24)-H(24C)	109.5
C(22)-C(25)-H(25A)	109.5
C(22)-C(25)-H(25B)	109.5
H(25A)-C(25)-H(25B)	109.5
C(22)-C(25)-H(25C)	109.5
H(25A)-C(25)-H(25C)	109.5
H(25B)-C(25)-H(25C)	109.5
C(28)-C(26)-C(27)	107.6(3)
C(28)-C(26)-C(29)	110.1(3)
C(27)-C(26)-C(29)	106.9(3)
C(28)-C(26)-C(18)	110.2(2)
C(27)-C(26)-C(18)	111.1(2)
C(29)-C(26)-C(18)	110.9(2)
C(26)-C(27)-H(27A)	109.5
C(26)-C(27)-H(27B)	109.5
H(27A)-C(27)-H(27B)	109.5
C(26)-C(27)-H(27C)	109.5
H(27A)-C(27)-H(27C)	109.5
H(27B)-C(27)-H(27C)	109.5
C(26)-C(28)-H(28A)	109.5
C(26)-C(28)-H(28B)	109.5
H(28A)-C(28)-H(28B)	109.5
C(26)-C(28)-H(28C)	109.5
H(28A)-C(28)-H(28C)	109.5
H(28B)-C(28)-H(28C)	109.5
C(26)-C(29)-H(29A)	109.5
C(26)-C(29)-H(29B)	109.5
H(29A)-C(29)-H(29B)	109.5
C(26)-C(29)-H(29C)	109.5
H(29A)-C(29)-H(29C)	109.5

H(29B)-C(29)-H(29C)	109.5
C(31)-C(30)-C(33)	106.4(2)
C(31)-C(30)-C(15)	126.9(3)
C(33)-C(30)-C(15)	126.6(2)
C(30)-C(31)-N(2)	109.8(3)
C(30)-C(31)-H(31)	125.1
N(2)-C(31)-H(31)	125.1
N(2)-C(32)-C(37)	130.7(3)
N(2)-C(32)-C(33)	107.3(2)
C(37)-C(32)-C(33)	122.0(3)
C(34)-C(33)-C(32)	118.4(3)
C(34)-C(33)-C(30)	134.4(2)
C(32)-C(33)-C(30)	107.3(2)
C(35)-C(34)-C(33)	119.7(3)
C(35)-C(34)-H(34)	120.2
C(33)-C(34)-H(34)	120.2
C(34)-C(35)-C(36)	120.7(3)
C(34)-C(35)-H(35)	119.7
C(36)-C(35)-H(35)	119.7
C(37)-C(36)-C(35)	121.6(3)
C(37)-C(36)-H(36)	119.2
C(35)-C(36)-H(36)	119.2
C(36)-C(37)-C(32)	117.7(3)
C(36)-C(37)-H(37)	121.2
C(32)-C(37)-H(37)	121.2
C(7)-N(1)-C(10)	106.7(2)
C(7)-N(1)-S(1)	123.29(17)
C(10)-N(1)-S(1)	125.59(17)
C(32)-N(2)-C(31)	109.1(2)
C(32)-N(2)-H(2A)	125.4
C(31)-N(2)-H(2A)	125.4
C(19)-O(3)-H(3A)	109.5
O(1)-S(1)-O(2)	120.70(13)
O(1)-S(1)-N(1)	107.31(11)
O(2)-S(1)-N(1)	104.83(11)
O(1)-S(1)-C(1)	108.68(13)
O(2)-S(1)-C(1)	109.34(12)
N(1)-S(1)-C(1)	104.80(12)

Symmetry transformations used to generate equivalent atoms: