

Supporting information for

Acid-catalysed intramolecular Friedel-Craft annulation of hetero-atom-functionalized *para*-quinone methides: Access to *O*-, *S*- and *N*-based heterocycles

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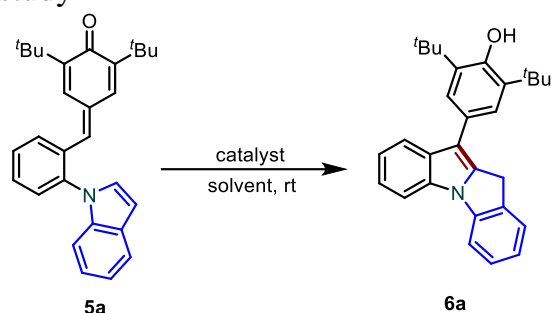
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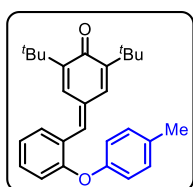
Table 5. Optimization study^a

Entry	Acid	Solvent	Time [min]	Yield [%] ^b
1	TfOH	CH ₂ Cl ₂	30	86
2	TfOH	CH ₃ CN	30	82
3	TfOH	Acetone	45	80
4	TfOH	PhMe	30	90
5	TfOH	THF	120	trace
6	TfOH	DMF	720	nr
7	TfOH	1,4-dioxane	120	50

^aAll reactions were carried out using **5a** (0.098 mmol) in 1.5 mL of PhMe. Yields reported are isolated yields

2. Characterization of **1b** to **1u**:

2,6-di-tert-butyl-4-(2-(p-tolyl)oxy)benzylidene)cyclohexa-2,5-dien-1-one (1b): Yellow solid



(1.12 g, 53% yield); m. p. = 120 – 122 °C; R_f = 0.5 (5% EtOAc in hexane);

¹H NMR (400 MHz, CDCl₃) 7.52 (d, J = 2.3 Hz, 1H), 7.49 (dd, J = 7.6 1.0 Hz, 1H), 7.45 (s, 1H), 7.33–7.29 (m, 1H), 7.18 – 7.14 (m, 3H), 7.05 (d, J =

2.3 Hz, 1H), 6.96 – 6.92 (m, 2H), 6.87 (dd, J = 8.2, 0.8 Hz, 1H), 2.35 (s, 3H), 1.33 (s, 9H) 1.32

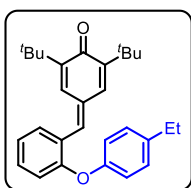
(s, 9H); ¹³C{¹H} NMR (100 MHz, CDCl₃) δ 186.8, 157.0, 154.2, 149.3, 147.7, 138.0, 135.4,

133.7, 132.3, 132.1, 130.8, 130.6, 128.2, 127.0, 122.9, 119.4, 117.8, 35.6, 35.1, 29.7, 29.6,

20.9, 20.88; FT-IR (thin film, neat): 2954, 1613, 1575, 1475, 1301, 797 cm⁻¹; HRMS (ESI):

m/z calcd for C₂₈H₃₁O₂ [M-H]⁻ : 399.2324; found : 399.2327.

2,6-di-*tert*-butyl-4-(2-(4-ethylphenoxy)benzylidene)cyclohexa-2,5-dien-1-one (1c): Yellow



solid (1.20 g, 59% yield); m. p. = 140–142 °C; R_f = 0.5 (5% EtOAc in hexane);

^1H NMR (400 MHz, CDCl_3) 7.52 (d, J = 2.3 Hz, 1H), 7.48 (dd, J = 7.5, 0.7

Hz, 1H), 7.44 (s, 1H), 7.34–7.29 (m, 1H), 7.20–7.14 (m, 3H), 7.04 (d, J =

2.3 Hz, 1H), 6.98–6.94 (m, 2H), 6.90–6.88 (m, 1H), 2.65 (q, J = 7.6 Hz, 2H), 1.32 (s, 9H),

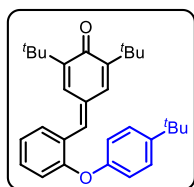
1.31 (s, 9H), 1.25 (t, J = 7.6 Hz, 3H); $^{13}\text{C}\{^1\text{H}\}$ NMR (100 MHz, CDCl_3) δ 186.8, 157.0, 154.4,

149.3, 147.7, 140.1, 138.0, 135.4, 132.3, 132.1, 130.8, 129.4, 128.2, 127.1, 122.9, 119.4, 117.9,

35.6, 35.1, 29.7, 29.6, 28.3, 15.9; FT-IR (thin film, neat): 2956, 1613, 1451, 1359, 1236, 742

cm^{-1} ; HRMS (ESI): m/z calcd for $\text{C}_{29}\text{H}_{35}\text{O}_2$ $[\text{M}+\text{H}]^+$: 415.2637; found : 415.2633.

2,6-di-*tert*-butyl-4-(2-(4-(*tert*-butyl)phenoxy)benzylidene)cyclohexa-2,5-dien-1-one (1d):



Yellow solid (0.35 g, 39% yield); m. p. = 137–138 °C; R_f = 0.5 (5% EtOAc

in hexane); ^1H NMR (400 MHz, CDCl_3) δ 7.52 (d, J = 2.2 Hz, 1H), 7.49 (d,

J = 7.6 Hz, 1H), 7.43 (s, 1H), 7.39–7.36 (m, 2H), 7.34–7.30 (m, 1H), 7.16

(t, J = 7.5 Hz, 1H), 7.03 (d, J = 2.3 Hz, 1H), 6.98–6.95 (m, 2H), 6.92 (d, J = 8.2 Hz, 1H), 1.33

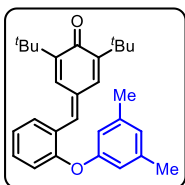
(s, 9H), 1.32 (s, 9H), 1.31 (s, 9H); $^{13}\text{C}\{^1\text{H}\}$ NMR (100 MHz, CDCl_3) δ 186.8, 156.8, 154.2,

149.3, 147.7, 147.0, 138.0, 135.4, 132.3, 132.1, 130.8, 128.2, 127.2, 126.9, 123.0, 118.9, 118.1,

35.6, 35.1, 34.5, 31.6, 29.7, 29.6; FT-IR (thin film, neat): 2957, 1613, 1474, 1390, 1301, 755

cm^{-1} ; HRMS (ESI): m/z calcd for $\text{C}_{31}\text{H}_{39}\text{O}_2$ $[\text{M}+\text{H}]^+$: 443.2950; found : 443.2946.

2,6-di-*tert*-butyl-4-(2-(3,5-dimethylphenoxy)benzylidene)cyclohexa-2,5-dien-1-one (1e):



Yellow solid (0.70 g, 32% yield); m. p. = 123–125 °C; R_f = 0.5 (5% EtOAc

in hexane); ^1H NMR (400 MHz, CDCl_3) δ 7.51 (d, J = 2.3 Hz, 1H), 7.48 (dd,

J = 7.7, 1.2 Hz, 1H), 7.44 (s, 1H), 7.33–7.28 (m, 1H), 7.16–7.09 (m, 2H),

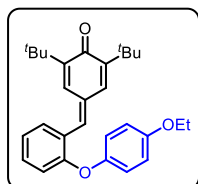
7.04 (d, J = 2.3 Hz, 1H), 6.87 (dd, J = 8.3, 0.9 Hz, 1H), 6.84 (d, J = 2.4 Hz, 1H), 6.77 (dd, J =

8.2, 2.6 Hz, 1H), 2.25–2.24 (m, 6H), 1.32 (s, 9H), 1.31 (s, 9H); $^{13}\text{C}\{^1\text{H}\}$ NMR (100 MHz,

CDCl_3) δ 186.8, 157.0, 154.4, 149.3, 147.7, 138.6, 138.1, 135.4, 132.4, 132.3, 132.0, 130.9,

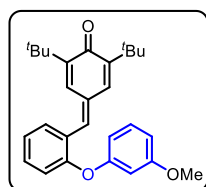
130.7, 128.3, 127.0, 122.8, 120.7, 117.8, 116.7, 35.6, 35.1, 29.7, 29.6, 20.1, 19.2; FT-IR (thin film, neat): 2921, 1740, 1616, 1457, 1251, 742 cm^{-1} ; HRMS (ESI): m/z calcd for $\text{C}_{29}\text{H}_{35}\text{O}_2$ $[\text{M}+\text{H}]^+$: 415.2637; found :415.2622.

2,6-di-*tert*-butyl-4-(2-(4-ethoxyphenoxy)benzylidene)cyclohexa-2,5-dien-1-one (1f):



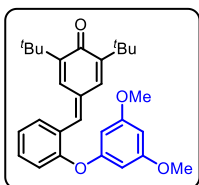
Yellow solid (0.95 g, 60% yield); m. p. = 140–142 °C R_f = 0.4 (5% EtOAc in hexane); ^1H NMR (400 MHz, CDCl_3) δ 7.52 (d, J = 2.2 Hz, 1H), 7.48 – 7.46 (m, 2H), 7.31 – 7.27 (m, 1H), 7.14 – 7.10 (m, 1H), 7.06 (d, J = 2.3 Hz, 1H), 7.00 – 6.96 (m, 2H), 6.92 – 6.88 (m, 2H), 6.80 (dd, J = 8.2, 0.7 Hz, 1H), 4.03 (q, J = 7.0 Hz, 2H), 1.43 (t, J = 7.0 Hz, 3H), 1.32 (s, 9H), 1.31 (s, 9H); $^{13}\text{C}\{^1\text{H}\}$ NMR (100 MHz, CDCl_3) δ 186.8, 157.7, 155.8, 149.5, 149.3, 147.7, 138.1, 135.4, 132.2, 132.1, 130.7, 128.3, 126.4, 122.5, 121.2, 116.8, 115.7, 64.0, 35.6, 35.2, 29.7, 29.6, 15.0; FT-IR (thin film, neat): 2923, 1614, 1503, 1360, 1228, 753 cm^{-1} ; HRMS (ESI): m/z calcd for $\text{C}_{29}\text{H}_{33}\text{O}_2$ $[\text{M}-\text{H}]^-$: 429.2430; found : 429.2433.

2,6-di-*tert*-butyl-4-(2-(3-methoxyphenoxy)benzylidene)cyclohexa-2,5-dien-1-one (1g):



yellow solid (1.00 g, 24% yield); m. p. = 127– 129 °C; R_f = 0.4 (5% EtOAc in hexane); ^1H NMR (400 MHz, CDCl_3) δ 7.51 – 7.48 (m, 2H), 7.39 (s, 1H), 7.35 (td, J = 7.9, 1.5 Hz, 1H), 7.27 – 7.23 (m, 1H), 7.20 (t, J = 7.4 Hz, 1H), 7.03 (d, J = 2.3 Hz, 1H), 6.96 (dd, J = 8.2, 0.8 Hz, 1H), 6.71 – 6.68 (m, 1H), 6.61 – 6.58 (m, 2H), 3.78 (s, 3H), 1.32 (s, 9H), 1.31 (s, 9H); $^{13}\text{C}\{^1\text{H}\}$ NMR (100 MHz, CDCl_3) δ 186.8, 161.2, 158.0, 156.1, 149.4, 147.7, 137.7, 135.3, 132.5, 132.1, 130.8, 130.5, 128.2, 127.5, 123.5, 118.9, 111.2, 109.5, 105.2, 55.54, 55.5, 35.6, 35.1, 29.7, 29.6; FT-IR (thin film, neat): 2923, 1693, 1483, 1273, 1153, 754 cm^{-1} ; HRMS (ESI): m/z calcd for $\text{C}_{28}\text{H}_{33}\text{O}_3$ $[\text{M}+\text{H}]^+$ 417.2430; found : 417.2430.

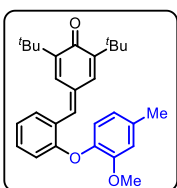
2,6-di-tert-butyl-4-(2(3,5-dimethoxyphenoxy)benzylidene)cyclohexa-2,5-dien-1-one (1h):



Yellow solid (0.26 g, 32% yield); m. p. = 132–134 °C; R_f = 0.3 (5% EtOAc in hexane); ^1H NMR (400 MHz, CDCl_3) δ 7.59 (d, J = 2.2 Hz, 1H), 7.36 – 7.32 (m, 2H), 7.29 (s, 1H), 7.12 – 7.07 (m, 2H), 6.98 – 6.96 (m, 3H), 6.57 (s, 1H), 3.93 (s, 3H), 3.81 (s, 3H), 1.33 (s, 9H), 1.30 (s, 9H); $^{13}\text{C}\{^1\text{H}\}$ NMR (100 MHz, CDCl_3) δ 186.5, 158.0, 151.5, 150.0, 149.1, 147.4, 145.7, 137.4, 135.6, 131.1, 130.1, 128.0, 123.2, 120.1, 117.6, 113.5, 104.4, 56.4, 56.32, 56.3, 35.6, 35.1, 29.8, 29.6; FT-IR (thin film, neat): 2956, 1456, 1229, 1143, 1091, 756 cm^{-1} ; HRMS (ESI): m/z calcd for $\text{C}_{29}\text{H}_{35}\text{O}_4$ $[\text{M}+\text{H}]^+$: 447.2535; found : 447.2536.

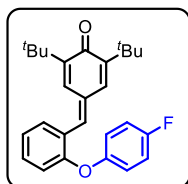
2,6-di-tert-butyl-4-(2-(2-methoxy-4-methylphenoxy)benzylidene)cyclohexa-2,5-dien-1-

one (1i): yellow solid (1.80 g, 62% yield); m. p. = 137–139 °C; R_f = 0.4 (5% EtOAc in hexane);



^1H NMR (400 MHz, CDCl_3) δ 7.57 (s, 1H), 7.54 (d, J = 2.3 Hz, 1H), 7.45 (dd, J = 7.6, 1.1 Hz, 1H), 7.27 – 7.23 (m, 1H), 7.11 – 7.07 (m, 2H), 6.90 (d, J = 8.0 Hz, 1H), 6.83 (d, J = 1.6 Hz, 1H), 6.77 – 6.74 (m, 1H), 6.69 (dd, J = 8.3 0.9 Hz, 1H), 3.79 (s, 3H), 2.37 (s, 3H), 1.32 (s, 9H), 1.31 (s, 9H); $^{13}\text{C}\{^1\text{H}\}$ NMR (100 MHz, CDCl_3) δ 186.9, 157.7, 151.3, 149.1, 147.5, 142.0, 138.5, 135.8, 135.6, 132.0, 131.9, 130.6, 128.5, 125.8, 122.1, 121.8, 121.7, 115.7, 113.9, 56.0, 55.99, 35.6, 35.1, 29.7, 29.6, 21.54, 21.5; FT-IR (thin film, neat): 2955, 1612, 1473, 1359, 1266, 747 cm^{-1} ; HRMS (ESI): m/z calcd for $\text{C}_{29}\text{H}_{35}\text{O}_3$ $[\text{M}+\text{H}]^+$: 431.2586; found : 431.2586.

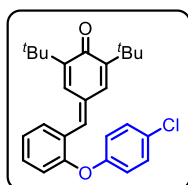
2,6-di-tert-butyl-4-(2-(4-fluorophenoxy)benzylidene)cyclohexa-2,5-dien-1-one (1j):



Yellow solid (0.85 g, 33% yield); m. p. = 146–148 °C; R_f = 0.5 (5% EtOAc in hexane); ^1H NMR (400 MHz, CDCl_3) δ 7.50 – 7.48 (m, 2H), 7.41 (s, 1H), 7.35 – 7.31 (m, 1H), 7.20 – 7.16 (m, 1H), 7.08 – 6.98 (m, 5H), 6.85 (d, J = 8.2 Hz, 1H), 1.32 (s, 9H), 1.31 (s, 9H); $^{13}\text{C}\{^1\text{H}\}$ NMR (100 MHz, CDCl_3) δ 186.8, 159.2 (d, $J_{\text{C-F}}$ = 241.2 Hz), 156.7, 152.4 (d, $J_{\text{C-F}}$ = 10.2 Hz), 149.4, 147.8, 137.5, 136.2, 132.5, 132.2,

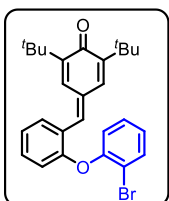
130.8, 128.1, 127.0, 123.2, 120.9 (d, $J_{C-F} = 8.2$ Hz), 117.6, 116.7 (d, $J_{C-F} = 23.2$ Hz), 35.6, 35.2, 29.7, 29.6; $^{19}\text{F}\{^1\text{H}\}$ NMR (376 MHz, CDCl_3) δ -119.04; FT-IR (thin film, neat): 2955, 1695, 1618, 1450, 1265, 757 cm^{-1} ; HRMS (ESI): m/z calcd for $\text{C}_{27}\text{H}_{30}\text{FO}_2$ $[\text{M}+\text{H}]^+$: 405.2230; found : 405.2243.

2,6-di-*tert*-butyl-4-(2-(4-chlorophenoxy)benzylidene)cyclohexa-2,5-dien-1-one (Ik):



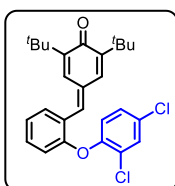
Yellow solid (0.28 g, 52% yield); m. p. = 131–133 °C; $R_f = 0.5$ (5% EtOAc in hexane); ^1H NMR (400 MHz, CDCl_3) δ 7.50 – 7.47 (m, 2H), 7.37 – 7.29 (m, 4H), 7.23 – 7.19 (m, 1H), 7.01 (d, $J = 2.3$ Hz, 1H), 6.97 – 6.93 (m, 2H), 6.91 (dd, $J = 8.0, 0.6$ Hz, 1H), 1.31 (s, 9H), 1.30 (s, 9H); $^{13}\text{C}\{^1\text{H}\}$ NMR (100 MHz, CDCl_3) δ 186.8, 155.9, 155.4, 149.5, 147.9, 137.2, 135.2, 132.6, 132.3, 130.9, 130.1, 129.0, 128.0, 127.5, 123.8, 120.4, 118.6, 35.6, 35.2, 29.7, 29.6; FT-IR (thin film, neat): 2955, 1692, 1612, 1479, 1234, 757 cm^{-1} ; HRMS (ESI): m/z calcd for $\text{C}_{27}\text{H}_{28}\text{ClO}_2$ $[\text{M}-\text{H}]^-$: 419.1778; found : 419.1763.

4-(2-(2-bromophenoxy)benzylidene)-2,6-di-*tert*-butylcyclohexa-2,5-dien-1-one (Il):



Yellow solid (0.76 g, 43% yield); m. p. = 122–124 °C; $R_f = 0.5$ (5% EtOAc in hexane); ^1H NMR (400 MHz, CDCl_3) δ 7.66 (d, $J = 7.9$ Hz, 1H), 7.51 – 7.48 (m, 3H), 7.33 – 7.28 (m, 2H), 7.19 (t, $J = 7.5$ Hz, 1H), 7.09 – 7.05 (m, 2H), 7.01 (d, $J = 8.1$ Hz, 1H), 6.75 (d, $J = 8.2$ Hz, 1H), 1.33 (s, 9H), 1.31 (s, 9H); $^{13}\text{C}\{^1\text{H}\}$ NMR (100 MHz, CDCl_3) δ 186.8, 156.1, 153.1, 149.4, 147.8, 137.5, 135.3, 134.2, 132.5, 132.2, 130.8, 129.0, 128.1, 126.8, 125.9, 123.4, 121.5, 117.1, 115.4, 35.6, 35.2, 29.7, 29.6; FT-IR (thin film, neat): 2921, 1616, 1464, 1360, 1237, 750 cm^{-1} ; HRMS (ESI): m/z calcd for $\text{C}_{27}\text{H}_{28}\text{BrO}_2$ $[\text{M}-\text{H}]^-$: 463.1273; found : 463.1268.

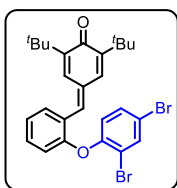
2,6-di-*tert*-butyl-4-(2-(2,4-dichlorophenoxy)benzylidene)cyclohexa-2,5-dien-1-one (Im):



Yellow solid (2.50 g, 58% yield); m. p. = 160–162 °C; $R_f = 0.5$ (5% EtOAc in hexane); ^1H NMR (400 MHz, CDCl_3) δ 7.50 – 7.47 (m, 3H), 7.41 (s, 1H), 7.33 (td, $J = 7.8, 1.6$ Hz, 1H), 7.24 – 7.19 (m, 2H), 7.04 (d, $J = 2.3$ Hz, 1H), 6.94 (d,

$J = 8.7$ Hz, 1H), 6.75 (dd, $J = 8.2, 0.8$ Hz, 1H), 1.32 (s, 9H), 1.30 (s, 9H); $^{13}\text{C}\{^1\text{H}\}$ NMR (100 MHz, CDCl_3) δ 186.8, 155.7, 150.8, 149.5, 147.9, 136.9, 135.2, 132.7, 132.3, 130.82, 130.8, 130.1, 128.4, 128.0, 127.0, 126.8, 123.7, 122.2, 117.0, 35.6, 35.2, 29.7, 29.6; FT-IR (thin film, neat): 2955, 1774, 1470, 1253, 1100, 744 cm^{-1} ; HRMS (ESI): m/z calcd for $\text{C}_{27}\text{H}_{27}\text{Cl}_2\text{O}_2$ [$\text{M}-\text{H}$] $^-$: 453.1388; found : 453.1366.

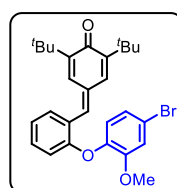
2,6-di-*tert*-butyl-4-(2-(2,4-dibromophenoxy)benzylidene)cyclohexa-2,5-dien-1-one (1n):



Yellow solid (1.55 g, 56% yield); m. p. = 145–147 °C; $R_f = 0.5$ (5% EtOAc in hexane) ^1H NMR (400 MHz, CDCl_3) δ 7.80 (d, $J = 2.3$ Hz, 1H), 7.51 – 7.49 (m, 1H), 7.47 (d, $J = 2.2$ Hz, 1H), 7.41 – 7.39 (m, 2H), 7.34 (td, $J = 7.8, 1.5$ Hz, 1H), 7.22 (t, $J = 7.5$ Hz, 1H), 7.04 (d, $J = 2.3$ Hz, 1H), 6.85 (d, $J = 8.7$ Hz, 1H), 6.78 – 6.76 (m, 1H), 1.32 (s, 9H), 1.30 (s, 9H); $^{13}\text{C}\{^1\text{H}\}$ NMR (100 MHz, CDCl_3) δ 186.8, 155.5, 152.7, 149.5, 148.0, 136.9, 136.4, 135.2, 132.7, 132.4, 132.0, 130.8, 128.0, 127.0, 123.9, 122.2, 117.4 (2C), 116.1, 35.6, 35.2, 29.7, 29.6; FT-IR (thin film, neat): 2921, 1616, 1462, 1360, 1238, 755 cm^{-1} ; HRMS (ESI): m/z calcd for $\text{C}_{27}\text{H}_{27}\text{Br}_2\text{O}_2$ [$\text{M}-\text{H}$] $^-$: 541.0378; found : 541.0381.

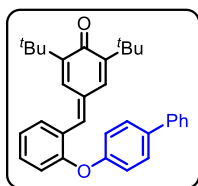
4-(2-(4-bromo-2-methoxyphenoxy)benzylidene)-2,6-di-*tert*-butylcyclohexa-2,5-dien-1-

one (1o): Yellow solid (1.20 g, 43% yield); m. p. = 139–141 °C; $R_f = 0.4$ (5% EtOAc in



hexane); ^1H NMR (400 MHz, CDCl_3) δ 7.50 (d, $J = 2.2$ Hz, 1H), 7.48 – 7.45 (m, 2H), 7.30 – 7.26 (m, 1H), 7.15 – 7.12 (m, 2H), 7.09 – 7.06 (m, 2H), 6.87 (d, $J = 8.5$ Hz, 1H), 6.71 (dd, $J = 8.2, 0.7$ Hz, 1H), 3.80 (s 3H), 1.32 (s, 9H), 1.31 (s, 9H); $^{13}\text{C}\{^1\text{H}\}$ NMR (100 MHz, CDCl_3) δ 186.8, 156.8, 152.2, 149.3, 147.7, 143.9, 137.8, 135.4, 132.3, 132.1, 130.7, 128.3, 126.2, 124.2, 122.9, 122.8, 117.9, 116.5, 116.1, 56.32, 56.3, 35.6, 35.2; FT-IR (thin film, neat): 2955, 1612, 1452, 1359, 1230, 751 cm^{-1} ; HRMS (ESI): m/z calcd for $\text{C}_{28}\text{H}_{32}\text{BrO}_3$ [$\text{M}+\text{H}$] $^+$: 495.1535; found : 495.1522.

4-(2-([1,1'-biphenyl]-4-yloxy)benzylidene)-2,6-di-*tert*-butylcyclohexa-2,5-dien-1-one (1p):



Yellow solid (0.80 g, 45% yield); m. p. = 183–185 °C; R_f = 0.5 (5% EtOAc in hexane); $^1\text{H NMR}$ (400 MHz, CDCl_3) δ 7.61 – 7.56 (m, 4H), 7.52 – 7.51

(m, 2H), 7.46 – 7.43 (m, 3H), 7.39 – 7.33 (m, 2H), 7.21 (t, J = 7.3 Hz, 1H),

7.12 – 7.08 (m, 2H), 7.04 (d, J = 2.3 Hz, 1H), 7.00 (dd, J = 8.2, 0.8 Hz, 1H), 1.32 (s, 18H);

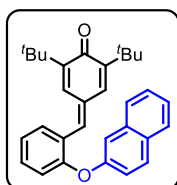
$^{13}\text{C}\{^1\text{H}\}$ NMR (100 MHz, CDCl_3) δ 186.8, 156.33, 156.3, 149.4, 147.8, 140.4, 137.7, 137.0,

135.3, 132.5, 132.2, 130.9, 129.0, 128.7, 128.1, 127.5, 127.3, 127.1, 123.5, 119.4, 118.7, 35.6,

35.2, 29.7, 29.6; FT-IR (thin film, neat): FT-IR (thin film, neat): 2955, 1614, 1459, 1360, 1228,

755 cm^{-1} ; HRMS (ESI): m/z calcd for $\text{C}_{33}\text{H}_{35}\text{O}_2$ $[\text{M}+\text{H}]^+$: 463.2637; found : 463.2654.

2,6-di-*tert*-butyl-4-(2-(naphthalen-2-yloxy)benzylidene)cyclohexa-2,5-dien-1-one (1q):



Yellow solid (1.55 g, 57% yield); m. p. = 127–129 °C; R_f = 0.4 (5% EtOAc in hexane); $^1\text{H NMR}$ (400 MHz, CDCl_3) δ 7.89 – 7.85 (m, 2H), 7.73 (d, J = 8.0

Hz, 1H), 7.59 – 7.57 (m, 2H), 7.51 – 7.43 (m, 3H), 7.40 – 7.36 (m, 2H), 7.32 –

7.22 (m, 2H), 7.06 (d, J = 8.0 Hz, 1H), 7.02 – 7.00 (m, 1H), 1.37 (s, 9H), 1.35 (s, 9H); $^{13}\text{C}\{^1\text{H}\}$

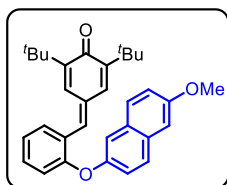
NMR (100 MHz, CDCl_3) δ 186.8, 156.2, 154.5, 143.4, 147.6, 137.7, 135.3, 134.4, 132.5, 132.2,

130.9, 130.5, 130.3, 128.1, 127.9, 127.6, 127.3, 126.8, 125.1, 123.6, 119.9, 118.9, 114.6, 35.6,

35.1, 29.7, 29.6; FT-IR (thin film, neat): 2954, 1614, 1493, 1360, 1261, 752 cm^{-1} ; HRMS (ESI):

m/z calcd for $\text{C}_{31}\text{H}_{33}\text{O}_2$ $[\text{M}+\text{H}]^+$: 437.2481; found : 437.2471.

2,6-di-*tert*-butyl-4-(2-((6-methoxynaphthalen-2-yl)oxy)benzylidene)cyclohexa-2,5-dien-1-



one (1r): yellow solid (1.00 g, 89% yield); m. p. = 98–100 °C; R_f = 0.3 (5%

EtOAc in hexane); $^1\text{H NMR}$ (400 MHz, CDCl_3) δ 7.76 (d, J = 8.9 Hz, 1H),

7.63 (d, J = 9.1 Hz, 1H), 7.56 – 7.53 (m, 2H), 7.49 (s, 1H), 7.38 – 7.32 (m,

2H), 7.26 – 7.14 (m, 4H), 7.05 (s, 1H), 6.94 (d, J = 8.2 Hz, 1H), 3.92 (s, 3H), 1.34 (s, 9H), 1.33

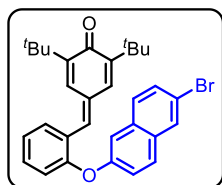
(s, 9H); $^{13}\text{C}\{^1\text{H}\}$ NMR (100 MHz, CDCl_3) δ 186.8, 157.3, 156.8, 152.6, 149.3, 147.7, 137.9,

135.3, 132.4, 132.2, 131.6, 130.8, 129.6, 128.9, 128.7, 128.2, 127.2, 123.2, 120.5, 119.7, 118.2,

115.4, 106.0, 55.5, 55.4, 35.6, 35.1, 29.7, 29.6; FT-IR (thin film, neat): 2954, 1609, 1576, 1473, 1231, 739 cm^{-1} ; HRMS (ESI): m/z calcd for $\text{C}_{32}\text{H}_{35}\text{O}_3$ $[\text{M}+\text{H}]^+$: 467.2586; found : 467.2567.

4-(2-((6-bromonaphthalen-2-yl)oxy)benzylidene)-2,6-di-*tert*-butylcyclohexa-2,5-dien-1-

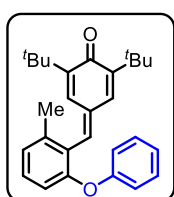
one (1s): Yellow solid (0.95 g, 65% yield); m. p. = 127–129 °C; R_f = 0.4 (5% EtOAc in hexane);



^1H NMR (400 MHz, CDCl_3) δ 7.97 (d, J = 1.4 Hz, 1H), 7.75 – 7.68 (m, 1H), 7.56 – 7.48 (m, 4H), 7.37 – 7.33 (m, 2H), 7.28 – 7.23 (m, 3H), 6.98 – 6.96 (m, 2H), 1.29 (s, 9H), 1.27 (s, 9H); $^{13}\text{C}\{^1\text{H}\}$ NMR (100 MHz, CDCl_3)

δ 186.8, 155.8, 155.1, 149.5, 147.9, 137.3, 135.2, 132.9, 132.7, 132.3, 131.4, 130.9, 130.2, 130.0, 129.4, 128.9, 128.1, 127.8, 124.0, 120.9, 119.2, 118.8, 114.2, 35.6, 35.2, 29.7, 29.6; FT-IR (thin film, neat): 2954, 1614, 1493, 1360, 1261, 752 cm^{-1} ; HRMS (ESI): m/z calcd for $\text{C}_{31}\text{H}_{30}\text{BrO}_2$ $[\text{M}-\text{H}]^-$: 513.1429; found : 513.1442.

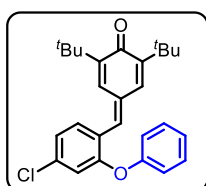
2,6-di-*tert*-butyl-4-(2-methyl-6-phenoxybenzylidene)cyclohexa-2,5-dien-1-one (1t):



Yellow solid (0.21 g, 25% yield); m. p. = 116–118 °C; R_f = 0.4 (5% EtOAc in hexane); ^1H NMR (400 MHz, CDCl_3) δ 7.30 – 7.22 (m, 3H), 7.07 – 7.04 (m, 2H), 7.01 – 6.96 (m, 3H), 6.89 – 6.87 (m, 2H), 6.83 (d, J = 8.2 Hz, 1H), 2.30 (s, 3H), 1.31 (d, J = 1.0 Hz, 9H), 1.26 (d, J = 1.2 Hz, 9H); $^{13}\text{C}\{^1\text{H}\}$ NMR (100 MHz, CDCl_3)

δ 186.9, 157.1, 154.7, 148.5, 147.5, 139.0, 137.5, 134.4, 134.0, 129.8, 129.6, 129.3, 126.9, 125.6, 123.3, 118.5, 116.6, 35.3, 35.1, 29.7, 29.6, 20.75, 20.7; FT-IR (thin film, neat): 2955, 1615, 1455, 1359, 1245, 742 cm^{-1} ; HRMS (ESI): m/z calcd for $\text{C}_{28}\text{H}_{33}\text{O}_2$ $[\text{M}+\text{H}]^+$: 401.2481; found : 401.2464.

2,6-di-*tert*-butyl-4-(4-chloro-2-phenoxybenzylidene)cyclohexa-2,5-dien-1-one (1u):

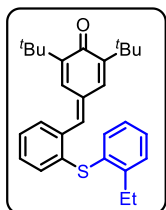


Yellow solid (0.36 g, 45% yield); m. p. = 140–142 °C; R_f = 0.4 (5% EtOAc in hexane); ^1H NMR (400 MHz, CDCl_3) δ 7.44 – 7.39 (m, 4H), 7.34 (s, 1H), 7.21 (t, J = 7.4 Hz, 1H), 7.15 (dd, J = 8.4, 1.9 Hz, 1H), 7.07 – 7.02 (m, 3H), 6.85 (d, J = 2.0 Hz, 1H), 1.32 (s, 9H), 1.31 (s, 9H); $^{13}\text{C}\{^1\text{H}\}$ NMR (100 MHz, CDCl_3) δ 186.8,

157.2, 155.8, 149.7, 148.0, 136.3, 136.2, 135.1, 132.7, 130.3, 127.7, 125.5, 124.8, 123.3, 119.8, 118.04, 118.0, 35.6, 35.2, 29.7, 29.6; FT-IR (thin film, neat): 2955, 1614, 1567, 1473, 1234, 918, 742 cm^{-1} ; HRMS (ESI): m/z calcd for $\text{C}_{27}\text{H}_{30}\text{ClO}_2$ $[\text{M}+\text{H}]^+$: 421.1934; found : 421.1947.

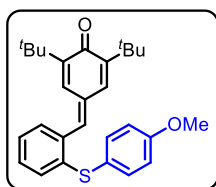
3. Characterization of 3b to 3j:

2,6-di-*tert*-butyl-4-(2-((2-ethylphenyl)thio)benzylidene)cyclohexa-2,5-dien-1-one (3b):



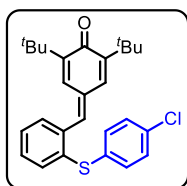
Yellow solid (0.15 g, 33% yield); m. p. = 143–145 °C; R_f = 0.5 (5% EtOAc in hexane); ^1H NMR (400 MHz, CDCl_3) δ 7.45 (s, 1H), 7.40 – 7.37 (m, 1H), 7.34 – 7.335 (m, 1H), 7.32 – 7.30 (m, 2H), 7.29 – 7.23 (m, 3H), 7.17 – 7.13 (m, 1H), 7.08 – 7.05 (m, 2H), 2.82 (q, J = 7.6 Hz, 2H), 1.36 (s, 9H), 1.30 (s, 9H), 1.24 (t, J = 7.6 Hz, 3H); $^{13}\text{C}\{^1\text{H}\}$ NMR (100 MHz, CDCl_3) δ 186.6, 149.2, 147.9, 146.3, 140.1, 138.6, 135.3, 134.8, 134.2, 132.5, 132.2, 131.6, 130.0, 129.6, 129.3, 128.8, 128.2, 127.1, 126.1, 35.5, 35.1, 27.3, 15.15, 15.14; FT-IR (thin film, neat): 2954, 1613, 1563, 1359, 1254, 746 cm^{-1} ; HRMS (ESI): m/z calcd for $\text{C}_{29}\text{H}_{35}\text{OS}$ $[\text{M}+\text{H}]^+$: 431.2409; found : 431.2406.

2,6-di-*tert*-butyl-4-(2((4-methoxyphenyl)thio)benzylidene)cyclohexa-2,5-dien-1-one (3c):



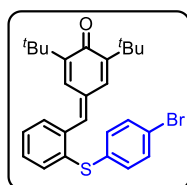
Yellow solid (2.00 g, 80% yield); m. p. = 165–167 °C; R_f = 0.3 (5% EtOAc in hexane); ^1H NMR (400 MHz, CDCl_3) δ 7.43 (s, 1H), 7.42 – 7.38 (m, 2H), 7.34 – 7.30 (m, 2H), 7.25 – 7.20 (m, 2H), 7.07 (d, J = 2.2 Hz, 1H), 7.05 – 7.01 (m, 1H), 6.92 – 6.88 (m, 2H), 3.81 (s, 3H), 1.34 (s, 9H), 1.27 (s, 9H); $^{13}\text{C}\{^1\text{H}\}$ NMR (100 MHz, CDCl_3) δ 186.7, 160.3, 149.3, 147.9, 140.3, 140.0, 135.9, 134.9, 134.2, 132.6, 131.5, 129.5, 128.6, 128.3, 125.6, 123.3, 115.3, 55.5, 55.48, 35.5, 35.2, 29.6; FT-IR (thin film, neat): 2955, 1614, 1493, 1250, 1059, 742 cm^{-1} ; HRMS (ESI): m/z calcd for $\text{C}_{28}\text{H}_{33}\text{O}_2\text{S}$ $[\text{M}+\text{H}]^+$: 433.2201; found : 433.2214.

2,6-di-*tert*-butyl-4-(2-((4-chlorophenyl)thio)benzylidene)cyclohexa-2,5-dien-1-one (3d):



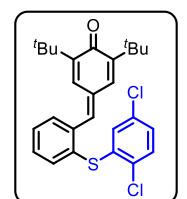
Yellow solid (0.20 g, 45% yield); m. p. = 122–124 °C; R_f = 0.5 (5% EtOAc in hexane); ^1H NMR (400 MHz, CDCl_3) δ 7.40 – 7.34 (m, 3H), 7.33 – 7.29 (m, 2H), 7.27 – 7.21 (m, 5H), 6.99 (s, 1H), 1.32 (s, 9H), 1.26 (s, 9H); $^{13}\text{C}\{^1\text{H}\}$ NMR (100 MHz, CDCl_3) δ 186.6, 149.5, 148.2, 139.9, 136.7, 136.69, 134.7, 133.8, 133.6, 132.8, 132.7, 132.0, 131.9, 129.8, 129.7, 128.0, 127.4, 35.5, 35.2, 29.7; FT-IR (thin film, neat): 2955, 1615, 1475, 1360, 1091, 753 cm^{-1} ; HRMS (ESI): m/z calcd for $\text{C}_{30}\text{H}_{31}\text{Br}_2\text{O}_3$ $[\text{M}+\text{H}]^+$: 437.1706; found : 437.1705.

4-(2-((4-bromophenyl)thio)benzylidene)-2,6-di-*tert*-butylcyclohexa-2,5-dien-1-one (3e):



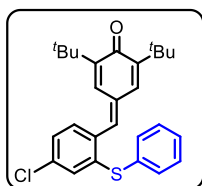
Yellow solid (1.00 g, 41% yield); m. p. = 125–127 °C; R_f = 0.5 (5% EtOAc in hexane); ^1H NMR (400 MHz, CDCl_3) δ 7.40 – 7.38 (m, 3H), 7.37 – 7.32 (m, 4H), 7.23 (d, J = 2.2 Hz, 1H), 7.15 (d, J = 8.4 Hz, 2H), 6.98 (d, J = 2.2 Hz, 1H), 1.32 (s, 9H), 1.26 (s, 9H); $^{13}\text{C}\{^1\text{H}\}$ NMR (100 MHz, CDCl_3) δ 186.6, 149.5, 148.1, 139.9, 136.8, 136.4, 134.7, 134.4, 132.7 (2C), 132.6, 132.2, 131.9, 129.8, 127.9, 127.5, 121.6, 35.5, 35.2, 29.6; FT-IR (thin film, neat): 2955, 1613, 1468, 1359, 1254, 753 cm^{-1} ; HRMS (ESI): m/z calcd for $\text{C}_{27}\text{H}_{30}\text{BrOS}$ $[\text{M}+\text{H}]^+$: 481.1201; found : 481.1229.

2,6-di-*tert*-butyl-(2((2,5-dichlorophenyl)thio)benzylidene)cyclohexa-2,5-dien-1-one (3f):



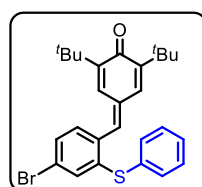
Yellow solid (0.15 g, 25% yield); m. p. = 121–122 °C; R_f = 0.5 (5% EtOAc in hexane); ^1H NMR (400 MHz, CDCl_3) 7.55 – 7.53 (m, 1H), 7.51 – 7.47 (m, 1H), 7.45 – 7.39 (m, 2H), 7.31 (s, 1H), 7.21 (d, J = 8.5 Hz, 1H), 7.18 (d, J = 2.0 Hz, 1H), 7.09 (dd, J = 8.5 2.4 Hz, 1H), 6.95 (d, J = 2.2 Hz, 1H), 6.76 (d, J = 2.4 Hz, 1H), 1.30 (s, 9H), 1.25 (s, 9H); $^{13}\text{C}\{^1\text{H}\}$ NMR (100 MHz, CDCl_3) δ 186.5, 149.6, 148.1, 139.7, 139.0, 137.7, 135.0, 134.4, 133.2, 132.9, 132.89, 132.8, 132.3, 131.6, 130.6, 130.1, 129.4, 129.2, 127.5, 35.5, 35.1, 29.6, 29.5; FT-IR (thin film, neat): 2921, 1616, 1458, 1360, 1091, 744 cm^{-1} ; HRMS (ESI): m/z calcd for $\text{C}_{30}\text{H}_{31}\text{Cl}_2\text{O}_3$ $[\text{M}-\text{H}]^-$: 469.1160; found : 469.1173.

2,6-di-*tert*-butyl-4-(4-chloro-2-(phenylthio)benzylidene)cyclohexa-2,5-dien-1-one (3g):



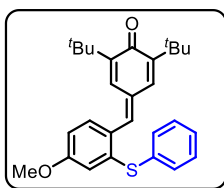
Yellow solid (0.25 g, 28% yield); m. p. = 110–112 °C; R_f = 0.4 (5% EtOAc in hexane); ^1H NMR (400 MHz, CDCl_3) δ 7.42 – 7.34 (m, 5H), 7.32 (s, 1H), 7.30 – 7.26 (m, 2H), 7.24 – 7.22 (m, 1H), 7.12 (d, J = 1.8 Hz, 1H) 7.04 (d, J = 2.2 Hz, 1H), 1.33 (s, 9H), 1.27 (s, 9H); $^{13}\text{C}\{^1\text{H}\}$ NMR (100 MHz, CDCl_3) δ 186.6, 149.7, 148.2, 140.4, 138.4, 135.6, 134.6, 133.7, 133.04, 133.0, 132.8, 132.5, 129.9, 129.7, 128.7, 127.7, 126.7, 35.6, 35.2, 29.6; FT-IR (thin film, neat): 2954, 1613, 1477, 1359, 1254, 739 cm^{-1} ; HRMS (ESI): m/z calcd for $\text{C}_{27}\text{H}_{30}\text{ClOS}$ $[\text{M}+\text{H}]^+$: 437.1706; found : 437.1725.

4-(4-bromo-2-(phenylthio)benzylidene)-2,6-di-*tert*-butylcyclohexa-2,5-dien-1-one (3h):



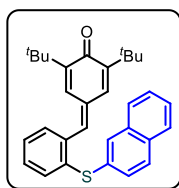
yellow solid (0.19 g 28% yield); m. p. = 108–110 °C; R_f = 0.4 (5% EtOAc in hexane); ^1H NMR (400 MHz, CDCl_3) δ 7.46 – 7.33 (m, 6H), 7.32 – 7.29 (m, 2H), 7.26 – 7.21 (m, 2H), 7.01 (d, J = 1.8 Hz, 1H), 1.32 (s, 9H), 1.27 (s, 9H); $^{13}\text{C}\{^1\text{H}\}$ NMR (100 MHz, CDCl_3) δ 186.6, 149.7, 148.3, 140.4, 138.5, 134.6, 134.3, 134.2, 133.0, 132.9, 132.8, 132.7, 129.9, 129.7, 128.6, 127.7, 123.8, 35.6, 35.2, 29.64, 29.6; FT-IR (thin film, neat): 2921, 1740, 1617, 1458, 1375, 740 cm^{-1} ; HRMS (ESI): m/z calcd for $\text{C}_{27}\text{H}_{30}\text{BrOS}$ $[\text{M}+\text{H}]^+$: 481.1201; found : 481.1213.

2,6-di-*tert*-butyl-4-(4-methoxy-2-(phenylthio)benzylidene)cyclohexa-2,5-dien-1-one (3i):



Yellow solid (0.30 g, 34% yield); m. p. = 171–173 °C; R_f = 0.3 (5% EtOAc in hexane); ^1H NMR (400 MHz, CDCl_3) δ 7.41 (s, 1H), 7.39 – 7.26 (m, 7H), 7.02 (d, J = 2.2 Hz, 1H) 6.86 (dd, J = 8.6, 2.5 Hz, 1H), 6.75 (d, J = 2.5 Hz, 1H) 3.74 (s, 3H), 1.33 (s, 9H), 1.28 (s, 9H); $^{13}\text{C}\{^1\text{H}\}$ NMR (100 MHz, CDCl_3) δ 186.7, 160.7, 149.0, 147.5, 140.1, 139.7, 135.1, 134.0, 133.1, 132.3, 131.7, 129.6, 128.6, 128.3, 128.1, 116.4, 112.7, 55.53, 55.5, 35.5, 35.1, 29.7, 29.6; FT-IR (thin film, neat): 2954, 1610, 1589, 1359, 1252, 743 cm^{-1} ; HRMS (ESI): m/z calcd for $\text{C}_{28}\text{H}_{33}\text{O}_2\text{S}$ $[\text{M}+\text{H}]^+$: 433.2201; found : 433.2208.

2,6-di-*tert*-butyl-4-(2-(naphthalen-2-ylthio)benzylidene)cyclohexa-2,5-dien-1-one (3j):

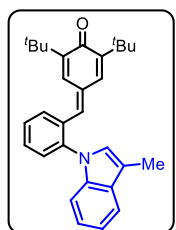


Yellow solid (0.27 g, 32% yield); m. p. = 132–133 °C; R_f = 0.4 (5% EtOAc in hexane); ^1H NMR (400 MHz, CDCl_3) δ 7.82 (d, J = 1.2 Hz, 1H), 7.80 – 7.78 (m, 1H), 7.76 (d, J = 8.6 Hz, 1H), 7.73 – 7.71 (m, 1H), 7.50 – 7.45 (m, 2H), 7.44 (s, 1H), 7.41 – 7.35 (m, 3H), 7.33 – 7.28 (m, 2H), 7.27 – 7.26 (m, 1H), 6.98 (d, J = 2.3 Hz, 1H), 1.29 (s, 9H), 1.26 (s, 9H); $^{13}\text{C}\{^1\text{H}\}$ NMR (100 MHz, CDCl_3) δ 186.7, 149.4, 148.0, 140.2, 137.4, 136.5, 134.6, 133.9, 132.6, 132.5, 132.0, 131.8 (2C), 130.8, 129.7, 129.3, 129.0, 128.1, 127.9, 127.5, 127.1, 126.9, 126.7, 35.5, 35.1, 29.64, 29.60; FT-IR (thin film, neat): 2921, 1740, 1617, 1459, 1376, 743 cm^{-1} ; HRMS (ESI): m/z calcd for $\text{C}_{31}\text{H}_{33}\text{OS}$ $[\text{M}+\text{H}]^+$: 453.2252; found : 453.2259.

4. Characterization of 5b to 5e

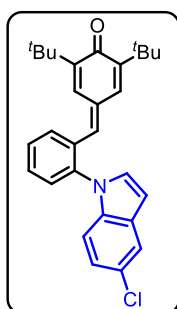
2,6-di-*tert*-butyl-4-(2-(3-methyl-1H-indol-1-yl)benzylidene)cyclohexa-2,5-dien-1-one

(5b): Yellow solid (0.30 g, 52% yield); m. p. = 179–181 °C; R_f = 0.5 (5% EtOAc in hexane);



^1H NMR (400 MHz, CDCl_3) δ 7.68 – 7.65 (m, 1H), 7.63 – 7.62 (m, 1H), 7.57 (d, J = 2.1 Hz, 1H), 7.55 – 7.47 (m, 3H), 7.21 – 7.20 (m, 3H), 6.98 (s, 1H), 6.80 – 6.79 (m, 2H), 2.40 (s, 3H), 1.35 (s, 9H), 1.27 (s, 9H); $^{13}\text{C}\{^1\text{H}\}$ NMR (100 MHz, CDCl_3) δ 186.7, 149.8, 147.9, 139.7, 138.7, 137.4, 134.9, 132.8, 132.68, 132.66, 130.1, 129.5, 127.8, 127.5, 127.4, 127.3, 122.7, 120.1, 119.2, 113.1, 110.7, 35.7, 35.2, 29.7, 29.6, 9.79, 9.76; FT-IR (thin film, neat): 2922, 1738, 1616, 1458, 1360, 741 cm^{-1} ; HRMS (ESI): m/z calcd for $\text{C}_{30}\text{H}_{34}\text{NO}$ $[\text{M}+\text{H}]^+$: 424.2640; found : 424.2620.

2,6-di-*tert*-butyl-4-(2-(5-chloro-1H-indol-1-yl)benzylidene)cyclohexa-2,5-dien-1-one (5c):

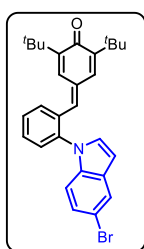


Yellow solid (0.066 g, 41.3% yield); m. p. = 132–134 °C; R_f = 0.4 (5% EtOAc in hexane); ^1H NMR (400 MHz, $\text{DMSO}-d_6$) δ 7.84 (d, J = 1.6 Hz, 1H), 7.69 – 7.62 (m, 3H), 7.61 – 7.57 (m, 1H), 7.49 (d, J = 3.2 Hz, 1H), 7.37 (d, J = 1.2 Hz, 1H), 7.24 (dd, J = 8.7, 1.7 Hz, 1H), 7.11 – 7.09 (m, 1H), 6.95 (brs, 2H),

6.67 (d, $J = 3.2$ Hz, 1H), 1.20 (s, 9H), 1.17 (s, 9H); $^{13}\text{C}\{^1\text{H}\}$ NMR (100 MHz, DMSO- d_6) δ 185.9, 148.2, 146.7, 139.6, 137.9, 135.2, 134.8, 132.5, 132.2, 132.1, 131.8, 130.6, 130.4, 128.2, 127.8, 127.7, 124.8, 123.1, 112.8, 112.4, 103.0, 35.0, 34.7, 29.24, 29.2; FT-IR (thin film, neat FT-IR (thin film, neat): 2925, 1740, 1607, 1459, 1362, 750 cm^{-1} ; HRMS (ESI): m/z calcd for $\text{C}_{29}\text{H}_{31}\text{ClNO}$ $[\text{M}+\text{H}]^+$: 444.2094; found : 444.2079.

4-(2-(5-bromo-1H-indol-1-yl)benzylidene)-2,6-di-*tert*-butylcyclohexa-2,5-dien-1-one

(5d): Yellow solid (0.134 g, 47% yield); m. p. = 134–136 °C; $R_f = 0.4$ (5% EtOAc in hexane);

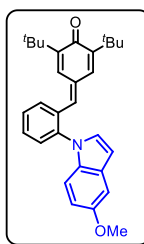


^1H NMR (400 M DMSO- d_6) δ 7.68 – 7.62 (m, 4H), 7.60 – 7.58 (m, 1H), 7.48 (d, $J = 3.2$ Hz, 1H), 7.34 (d, $J = 1.8$ Hz, 1H), 7.12 – 7.09 (m, 1H), 7.08 (s, 1H), 6.96 (s, 1H), 6.94 (d, $J = 2.0$ Hz, 1H), 7.34 (dd, $J = 3.2, 0.6$ Hz, 1H), 1.19 (s, 9H), 1.16 (s, 9H); $^{13}\text{C}\{^1\text{H}\}$ NMR (100 MHz, DMSO- d_6) δ 185.9, 148.4, 146.8, 139.8, 137.7,

136.7, 134.7, 132.4, 132.3, 132.2, 131.3, 130.7, 128.3, 127.72, 127.7, 127.3, 127.1, 122.3, 120.6, 110.2, 103.6, 35.0, 34.7, 29.2, 29.1; FT-IR (thin film, neat FT-IR (thin film, neat): 2955, 1615 1483, 1458, 1360, 742 cm^{-1} ; HRMS (ESI): m/z calcd for $\text{C}_{29}\text{H}_{31}\text{BrNO}$ $[\text{M}+\text{H}]^+$: 488.1589; found : 488.1617.

2,6-di-*tert*-butyl-4-(2-(5-methoxy-1H-indol-1-yl)benzylidene)cyclohexa-2,5-dien-1-one

(5e): Yellow solid (0.15 g, 55.9% yield); m. p. = 143–145 °C; $R_f = 0.3$ (5% EtOAc in hexane);

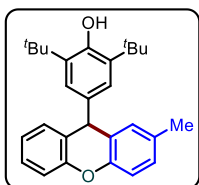


^1H NMR (400 MHz, CDCl_3) δ 7.62 (d, $J = 7.1$ Hz, 1H), 7.54 – 7.52 (m, 3H), 7.51 – 7.48 (m, 1H), 7.17 – 7.15 (m, 3H), 6.87 (dd, $J = 9.0, 2.4$ Hz, 1H), 6.79 (d, $J = 2.2$ Hz, 1H), 6.73 (s, 1H), 6.63 (d, $J = 3.1$ Hz, 1H), 3.89 (s, 3H), 1.33 (s, 9H), 1.27 (s, 9H); $^{13}\text{C}\{^1\text{H}\}$ NMR (100 MHz, CDCl_3) δ 186.7, 154.9, 149.8, 148.0,

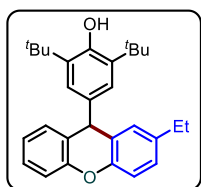
139.5, 138.5, 134.8, 132.9, 132.7, 132.6, 132.3, 130.6, 130.1, 129.5, 127.7, 127.6, 127.4, 112.9, 111.6, 103.5, 102.7, 56.0, 55.98, 35.6, 35.2, 29.7, 29.6; FT-IR (thin film, neat FT-IR (thin film, neat): 2954, 1614, 1578, 1483, 1256, 740 cm^{-1} ; HRMS (ESI): m/z calcd for $\text{C}_{30}\text{H}_{34}\text{NO}_2$ $[\text{M}+\text{H}]^+$: 440.2590; found : 440.2575.

5. Characterization of products 2b to 2u

2,6-di-*tert*-butyl-4-(3-methyl-9H-xanthen-9-yl)phenol (2b): The reaction was performed at

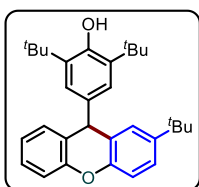


0.125 mmol scale of **1b**; pale yellow solid (48.5 mg, 97% yield); $R_f = 0.4$ (5% EtOAc in hexane); $^1\text{H NMR}$ (400 MHz, CDCl_3) δ 7.22 – 7.18 (m, 1H), 7.15 – 7.12 (m, 2H), 7.06 – 7.04 (m, 1H), 7.02 – 7.00 (m, 2H), 6.97 – 6.95 (m, 3H), 5.11 (s, 1H), 5.07 (s, 1H), 2.27 (s, 3H), 1.38 (s, 18H); ^{13}C $\{^1\text{H}\}$ NMR (100 MHz, CDCl_3) δ 152.5, 151.8, 149.6, 137.3, 135.9, 132.5, 129.9, 129.6, 128.4, 127.6, 125.7, 125.1, 124.7, 123.1, 116.5, 116.2, 44.8, 44.77, 34.4, 30.4, 21.91, 21.9; FT-IR (thin film, neat): 2956, 1599, 1480, 1454, 1313, 751 cm^{-1} ; HRMS (ESI): m/z calcd for $\text{C}_{28}\text{H}_{31}\text{O}_2$ $[\text{M}-\text{H}]^-$: 399.2324 found : 399.2339.



2,6-di-*tert*-butyl-4-(3-ethyl-9H-xanthen-9-yl)phenol (2c): The reaction was performed at 0.121 mmol scale of **1c**; pale yellow solid (48.0 mg, 96% yield); $R_f = 0.4$ (5% EtOAc in hexane); $^1\text{H NMR}$ (400 MHz, CDCl_3) δ 7.21 – 7.17 (m, 1H), 7.14 – 7.10 (m, 2H), 7.06 – 7.03 (m, 2H), 7.01 – 6.99 (m, 1H), 6.97 – 6.96 (m, 1H), 6.94 (s, 2H), 5.19 (s, 1H), 5.05 (s, 1H), 2.56 (q, $J = 7.6$ Hz, 2H), 1.36 (s, 18H), 1.17 (t, $J = 7.6$ Hz, 3H); ^{13}C $\{^1\text{H}\}$ NMR (100 MHz, CDCl_3) δ 152.4, 151.9, 149.8, 139.1, 136.9, 135.8, 129.6, 128.7, 127.6, 127.2, 125.7, 125.3, 124.8, 123.1, 116.5, 116.3, 44.7, 34.4, 30.4, 28.3, 16.0; FT-IR (thin film, neat): 2958, 1630, 1478, 1456, 1235, 754 cm^{-1} ; HRMS (ESI): m/z calcd for $\text{C}_{29}\text{H}_{33}\text{O}_2$ $[\text{M}-\text{H}]^-$: 413.2481; found : 413.2487.

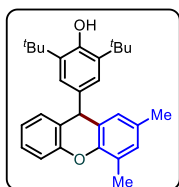
2,6-di-*tert*-butyl-4-(3-(*tert*-butyl)-9H-xanthen-9-yl)phenol (2d): The reaction was



performed at 0.110 mmol scale of **1d**; yellow gummy solid (42.0 mg, 84% yield); $R_f = 0.4$ (5% EtOAc in hexane); $^1\text{H NMR}$ (400 MHz, CDCl_3) δ 7.26 – 7.18 (m, 4H), 7.14 – 7.12 (m, 1H), 7.08 – 7.06 (m, 1H), 7.04 – 7.00 (m, 1H), 6.94 (s, 2H), 5.18 (s, 1H), 5.06 (s, 1H), 1.37 (s, 18H), 1.28 (s, 9H); ^{13}C $\{^1\text{H}\}$ NMR (100 MHz, CDCl_3) δ 152.4, 152.2, 149.7, 145.9, 136.3, 135.8, 129.6, 127.7, 126.2, 125.6, 125.0,

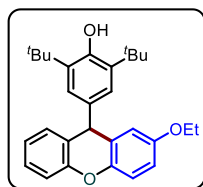
124.9, 124.7, 123.1, 116.5, 115.9, 44.63, 44.6, 34.6, 34.44, 34.4, 31.6, 30.4; FT-IR (thin film, neat): 2958, 1598, 1481, 1433, 1251, 753 cm^{-1} ; HRMS (ESI): m/z calcd for $\text{C}_{31}\text{H}_{37}\text{O}_2$ $[\text{M}-\text{H}]^-$: 441.2794; found : 441.2803.

2,6-di-*tert*-butyl-4-(2,4-dimethyl-9H-xanthen-9-yl)phenol (2e): The reaction was performed



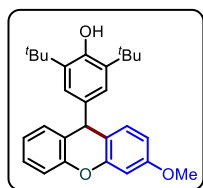
at 0.096 mmol scale of **1e**; white solid (41.0 mg, 80% yield); $R_f = 0.4$ (5% EtOAc in hexane); ^1H NMR (400 MHz, CDCl_3) δ 7.22 – 7.16 (m, 1H), 7.13 – 7.11 (m, 2H), 7.01 – 6.99 (m, 1H), 6.97 (s, 2H), 6.94 (s, 1H), 6.89 (s, 1H), 5.10 (s, 1H), 5.06 (s, 1H), 2.25 (s, 3H), 2.18 (s, 3H), 1.39 (s, 18H); ^{13}C $\{^1\text{H}\}$ NMR (100 MHz, CDCl_3) δ 152.4, 151.8, 149.5, 137.5, 136.1, 135.8, 131.3, 130.2, 129.7, 127.5, 125.8, 124.8, 123.0, 122.5, 117.3, 116.5, 44.4, 44.39, 34.4, 30.4, 19.74, 19.7, 19.2; FT-IR (thin film, neat): 2957, 1482, 1403, 1232, 753 cm^{-1} ; HRMS (APCI): m/z calcd for $\text{C}_{29}\text{H}_{33}\text{O}_2$ $[\text{M}-\text{H}]^-$: 413.2481; found : 413.2494.

2,6-di-*tert*-butyl-4-(2-ethoxy-9H-xanthen-9-yl)phenol (2f): The reaction was performed at



0.116 mmol scale of **1f**; white solid (49.1 mg, 98% yield); $R_f = 0.3$ (5% EtOAc in hexane); ^1H NMR (400 MHz, CDCl_3) δ 7.19 (t, $J = 7.6$ Hz, 1H), 7.10 (d, $J = 7.9$ Hz, 2H), 7.05 (d, $J = 8.8$ Hz, 1H), 7.00 – 6.96 (m, 1H), 6.95 (s, 2H), 6.76 (dd, $J = 8.8, 2.8$ Hz, 1H), 6.64 (d, $J = 2.6$ Hz, 1H), 5.10 (s, 1H), 5.05 (s, 1H), 3.95 (q, $J = 7.0$ Hz, 2H), 1.37 (s, 21H); ^{13}C $\{^1\text{H}\}$ NMR (100 MHz, CDCl_3) δ 154.7, 152.5, 151.9, 145.8, 136.8, 136.0, 129.6, 127.6, 126.3, 125.2, 124.8, 123.0, 117.1, 116.4, 114.9, 114.1, 64.0, 45.1, 45.0, 34.4, 30.4, 15.0; FT-IR (thin film, neat): 2959, 1478, 1434, 1252, 1223, 750 cm^{-1} ; HRMS (ESI): m/z calcd for $\text{C}_{29}\text{H}_{33}\text{O}_3$ $[\text{M}-\text{H}]^-$: 429.2430; found : 429.2441.

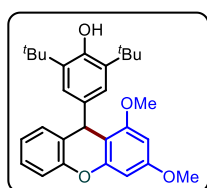
2,6-di-*tert*-butyl-4-(3-methoxy-9H-xanthen-9-yl)phenol (2g): The reaction was performed at



0.120 mmol scale of **1g**; yellow gummy solid (36.5 mg, 71% yield); $R_f = 0.3$ (5% EtOAc in hexane); ^1H NMR (400 MHz, CDCl_3) δ 7.22 – 7.18 (m, 1H), 7.12 – 7.10 (m, 2H), 7.07 (d, $J = 8.9$ Hz, 1H), 7.01 – 6.97 (m, 1H), 6.95 (s,

2H), 6.78 (dd, $J = 8.9, 3.0$ Hz, 1H), 6.65 (d, $J = 2.9$ Hz, 1H), 5.11 (s, 1H), 5.06 (s, 1H), 3.74 (s, 3H), 1.37 (s, 18H); ^{13}C $\{^1\text{H}\}$ NMR (100 MHz, CDCl_3) δ 155.4, 152.5, 151.9, 145.8, 136.7, 135.9, 129.6, 127.7, 126.4, 125.1, 124.8, 123.0, 117.2, 116.4, 114.1, 113.4, 55.8, 55.7, 45.1, 34.4, 30.4; FT-IR (thin film, neat): 2959, 1624, 1481, 1433, 1238, 753 cm^{-1} ; HRMS (ESI): m/z calcd for $\text{C}_{28}\text{H}_{31}\text{O}_3$ $[\text{M}-\text{H}]^-$: 415.2273; found : 415.2294.

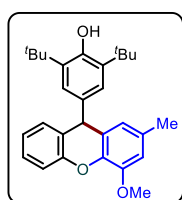
2,6-di-*tert*-butyl-4-(1,3-dimethoxy-9H-xanthen-9-yl)phenol (2h): The reaction was



performed at 0.112 mmol scale of **1h**; white solid (48.0 mg, 96% yield); $R_f = 0.2$ (5% EtOAc in hexane); ^1H NMR (400 MHz, CDCl_3) δ 7.26 – 7.23 (m, 1H), 7.21 – 7.19 (m, 1H), 7.16 – 7.14 (m, 1H), 7.05 (dd, $J = 7.4, 1.2$ Hz,

1H), 7.02 (s, 2H), 6.37 (d, $J = 2.4$ Hz, 1H), 6.21 (d, $J = 2.3$ Hz, 1H), 5.32 (s, 1H), 4.99 (s, 1H), 3.82 (s, 3H), 3.80 (s, 3H), 1.37 (s, 18H); ^{13}C $\{^1\text{H}\}$ NMR (100 MHz, CDCl_3) δ 159.7, 157.9, 153.3, 152.2, 152.0, 137.3, 135.3, 129.7, 127.4, 126.4, 124.3, 123.5, 116.3, 108.1, 94.1, 93.4, 55.70, 55.68, 55.54, 55.52, 38.95, 38.9, 34.4, 30.4; FT-IR (thin film, neat): 2956, 1603, 1454, 1229, 1143, 756 cm^{-1} ; HRMS (ESI): m/z calcd for $\text{C}_{29}\text{H}_{33}\text{O}_4$ $[\text{M}-\text{H}]^-$: 445.2379; found : 445.2382.

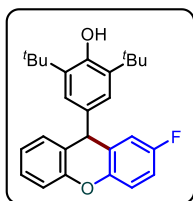
2,6-di-*tert*-butyl-4-(4-methoxy-2-methyl-9H-xanthen-9-yl)phenol (2i): The reaction was



performed at 0.104 mmol scale of **1i**; white solid (38.0 mg, 76% yield); $R_f = 0.3$ (5% EtOAc in hexane); ^1H NMR (400 MHz, CDCl_3) δ 7.27 – 7.25 (m, 1H), 7.22 – 7.18 (m, 1H), 7.13 – 7.11 (m, 1H), 7.02 – 6.98 (m, 1H), 6.96 (s,

2H), 6.63 – 6.57 (m, 2H), 5.10 (s, 1H), 5.06 (s, 1H), 3.95 (s, 3H), 2.27 (s, 3H), 1.37 (s, 18H); ^{13}C $\{^1\text{H}\}$ NMR (100 MHz, CDCl_3) δ 152.4, 151.5, 147.7, 139.0, 137.2, 135.8, 132.4, 129.6, 127.6, 126.0, 125.3, 124.7, 123.3, 121.4, 116.8, 111.0, 56.3, 44.7, 34.4, 30.4, 21.4; FT-IR (thin film, neat): 2959, 1608, 1481, 1241, 1117, 753 cm^{-1} ; HRMS (ESI): m/z calcd for $\text{C}_{29}\text{H}_{33}\text{O}_3$ $[\text{M}-\text{H}]^-$: 429.2430; found : 429.2437.

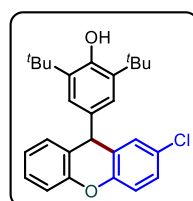
2,6-di-tert-butyl-4-(2-fluoro-9H-xanthen-9-yl)phenol (2j): The reaction was performed at



0.099 mmol scale of **1j**; white gummy solid (20 mg, 50% yield); $R_f = 0.4$ (5% EtOAc in hexane); ^1H NMR (400 MHz, CDCl_3) δ 7.23 – 7.19 (m, 1H), 7.12 – 7.06 (m, 3H), 7.02 – 6.98 (m, 1H), 6.93 – 6.87 (m, 3H), 6.79 (dd, $J = 9.0$,

3.0 Hz, 1H), 5.10 (s, 1H), 5.09 (s, 1H), 1.37 (s, 18H); ^{13}C $\{^1\text{H}\}$ NMR (100 MHz, CDCl_3) δ 158.6 (d, $J_{\text{C-F}} = 238.8$ Hz), 152.7, 151.5, 147.7 (d, $J_{\text{C-F}} = 1.0$ Hz), 136.3, 136.2, 129.6, 127.9, 127.0 (d, $J_{\text{C-F}} = 29.3$ Hz), 124.9, 124.6, 123.4, 117.6 (d, $J_{\text{C-F}} = 8.3$ Hz), 116.5, 115.6 (d, $J_{\text{C-F}} = 23.1$ Hz), 114.6 (d, $J_{\text{C-F}} = 23.7$ Hz), 44.8, 34.5, 30.4; $^{19}\text{F}\{^1\text{H}\}$ NMR (376 MHz, CDCl_3) δ – 120.6; FT-IR (thin film, neat): 2956, 1567, 1450, 1434, 1264, 753 cm^{-1} ; HRMS (ESI): m/z calcd for $\text{C}_{27}\text{H}_{28}\text{FO}_2$ $[\text{M-H}]^-$: 403.2073; found: 403.2072.

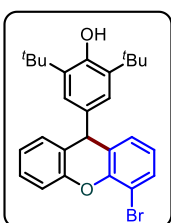
2,6-di-tert-butyl-4-(2-chloro-9H-xanthen-9-yl)phenol (2k): The reaction was performed at



0.107 mmol scale of **1k**; yellow gummy solid (39.5 mg, 79% yield); $R_f = 0.4$ (5% EtOAc in hexane); ^1H NMR (400 MHz, CDCl_3) δ 7.23 – 7.12 (m, 3H), 7.10 – 7.05 (m, 3H), 7.03 – 6.98 (m, 1H), 6.92 (s, 2H), 5.10 (s, 1H), 5.09 (s,

1H), 1.37 (s, 18H); ^{13}C $\{^1\text{H}\}$ NMR (100 MHz, CDCl_3) δ 152.7, 151.2, 150.2, 136.4, 136.1, 129.7, 129.3, 127.9, 127.8, 127.2, 124.9, 124.8, 123.6, 118.9, 117.9, 116.5, 44.6, 34.4, 30.4; FT-IR (thin film, neat): 2956, 1598, 1474, 1434, 1254, 753 cm^{-1} ; HRMS (ESI): m/z calcd for $\text{C}_{27}\text{H}_{28}\text{ClO}_2$ $[\text{M-H}]^-$: 419.1778; found: 419.1784.

4-(1-bromo-9H-xanthen-9-yl)-2,6-di-tert-butylphenol (2l): The reaction was performed at

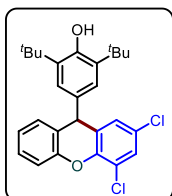


0.115 mmol scale of **1l**; yellow gummy solid (38.0 mg, 76% yield); $R_f = 0.4$ (5% EtOAc in hexane); ^1H NMR (400 MHz, CDCl_3) δ 7.40 (dd, $J = 7.8$, 1.4 Hz, 1H), 7.23 – 7.19 (m, 2H), 7.06 – 6.99 (m, 3H), 6.88 (s, 2H), 6.82 (t, $J = 7.8$ Hz, 1H), 5.11 (s, 1H), 5.05 (s, 1H), 1.32 (s, 18H); ^{13}C $\{^1\text{H}\}$ NMR (100 MHz,

CDCl_3) δ 152.7, 152.6, 151.3, 148.4, 136.1, 136.08, 131.4, 129.5, 128.8, 127.9, 127.5, 125.3,

124.9, 123.9, 116.9, 110.7, 44.9, 44.8, 34.4, 30.4; FT-IR (thin film, neat): 2956, 1474, 1434, 1254, 754 cm^{-1} ; HRMS (ESI): m/z calcd for $\text{C}_{27}\text{H}_{28}\text{BrO}_2$ $[\text{M}-\text{H}]^-$: 463.1273; found: 463.1272.

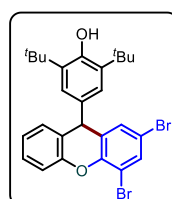
2,6-di-tert-butyl-4-(1,3-dichloro-9H-xanthen-9-yl)phenol (2m): The reaction was



performed at 0.109 mmol scale of **1m**; yellow gummy solid (36.0 mg, 72% yield); $R_f = 0.4$ (5% EtOAc in hexane); ^1H NMR (400 MHz, CDCl_3) δ 7.28 (d, $J = 2.4$ Hz, 1H), 7.25 – 7.23 (m, 2H), 7.08 – 7.02 (m, 2H), 7.00 (dd, $J = 2.4, 0.6$

Hz, 1H), 6.91 (s, 2H), 5.13 (s, 1H), 5.10 (s, 1H), 1.38 (s, 18H); ^{13}C $\{^1\text{H}\}$ NMR (100 MHz, CDCl_3) δ 152.9, 150.8, 146.3, 136.3, 135.7, 129.5, 128.6, 128.2, 128.1, 127.9, 127.6, 124.8, 124.5, 124.2, 122.5, 116.9, 44.76, 44.7, 34.5, 30.4; FT-IR (thin film, neat): 2959, 1595, 1449, 1264, 1183, 752 cm^{-1} ; HRMS (ESI): m/z calcd for $\text{C}_{27}\text{H}_{27}\text{ClO}_2$ $[\text{M}-\text{H}]^-$: 453.1388; found: 453.1393.

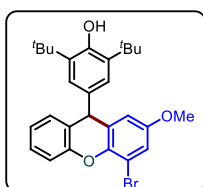
2,6-di-tert-butyl-4-(1,3-dibromo-9H-xanthen-9-yl)phenol (2n): The reaction was performed



at 0.009 mmol scale of **1n**; yellow gummy solid (37.0 mg, 74% yield); $R_f = 0.4$ (5% EtOAc in hexane); ^1H NMR (400 MHz, CDCl_3) δ 7.58 (d, $J = 2.3$ Hz, 1H), 7.24 – 7.23 (m, 2H), 7.18 (dd, $J = 2.3, 0.6$ Hz, 1H), 7.08 – 7.02 (m, 2H), 6.90

(s, 2H), 5.13 (s, 1H), 5.10 (s, 1H), 1.37 (s, 18H); ^{13}C $\{^1\text{H}\}$ NMR (100 MHz, CDCl_3) δ 152.9, 151.0, 147.8, 136.3, 135.6, 133.7, 131.5, 129.5, 129.0, 128.1, 124.8, 124.7, 124.2, 116.9, 115.2, 111.6, 44.83, 44.8, 34.5, 30.4; FT-IR (thin film, neat): 2959, 1558, 1443, 1264, 1158, 753 cm^{-1} ; HRMS (ESI): m/z calcd for $\text{C}_{27}\text{H}_{27}\text{Br}_2\text{O}_2$ $[\text{M}-\text{H}]^-$: 541.0378; found: 541.0378.

4-(2-bromo-4-methoxy-9H-xanthen-9-yl)-2,6-di-tert-butylphenol (2o): The reaction was

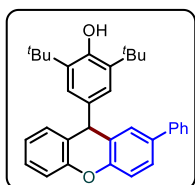


performed at 0.101 mmol scale of **1o**; white solid (37.0 mg, 74% yield); $R_f = 0.3$ (5% EtOAc in hexane); ^1H NMR (400 MHz, CDCl_3) δ 7.26 – 7.19 (m, 2H), 7.09 – 7.07 (m, 1H), 7.03 – 6.99 (m, 1H), 6.92 (s, 3H), 6.88 – 6.87 (m,

1H), 5.09 (s, 1H), 5.08 (s, 1H), 3.94 (s, 3H), 1.37 (s, 18H); ^{13}C $\{^1\text{H}\}$ NMR (100 MHz, CDCl_3) δ 152.7, 150.9, 148.8, 140.3, 136.4, 136.1, 129.6, 127.9 (2C), 124.8, 124.7, 123.9, 123.8, 116.8,

114.8, 113.4, 56.55, 56.5, 44.46, 44.4, 34.4, 30.4; FT-IR (thin film, neat): 2956, 1607, 1481, 1433, 1241, 752 cm^{-1} ; HRMS (ESI): m/z calcd for $\text{C}_{28}\text{H}_{30}\text{BrO}_3$ $[\text{M}-\text{H}]^-$: 493.1378; found : 493.1385.

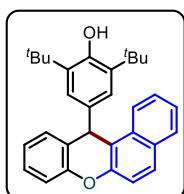
2,6-di-tert-butyl-4-(2-phenyl-9H-xanthen-9-yl)phenol (2p): The reaction was performed at



0.108 mmol scale of **1p**; yellow gummy solid (37.5 mg, 75% yield); $R_f = 0.4$ (5% EtOAc in hexane); ^1H NMR (400 MHz, CDCl_3) δ 7.53 (d, $J = 7.6$ Hz, 2H), 7.47 (dd, $J = 8.4, 2.0$ Hz, 1H), 7.44 – 7.39 (m, 3H), 7.35 – 7.30 (m, 1H),

7.26 – 7.22 (m, 2H), 7.19 – 7.17 (m, 2H), 7.06 (d, $J = 7.5$ Hz, 1H), 7.02 (s, 2H), 5.24 (s, 1H), 5.09 (s, 1H), 1.40 (s, 18H); ^{13}C NMR (100 MHz, CDCl_3) δ 152.6, 151.6, 151.3, 140.9, 136.9, 136.3, 136.0, 129.7, 128.8, 128.3, 127.7, 127.0, 126.9, 126.5, 125.8, 125.5, 124.8, 123.4, 116.9, 116.6, 44.8, 44.77, 34.4, 30.4; FT-IR (thin film, neat): 2958, 1601, 1478, 1434, 1235, 754 cm^{-1} ; HRMS (ESI): m/z calcd for $\text{C}_{29}\text{H}_{33}\text{O}_4$ $[\text{M}-\text{H}]^-$: 461.2481; found : 461.2494.

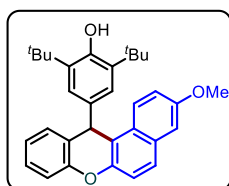
4-(12H-benzo[a]xanthen-12-yl)-2,6-di-tert-butylphenol (2q): The reaction was performed at



0.110 mmol scale of **1q**; pale yellow solid (48.0 mg, 98% yield); $R_f = 0.4$ (5% EtOAc in hexane); ^1H NMR (400 MHz, CDCl_3) δ 8.10 (d, $J = 8.4$ Hz, 1H), 7.84 (d, $J = 8.0$ Hz, 1H), 7.80 (d, $J = 8.9$ Hz, 1H), 7.54 – 7.50 (m, 1H), 7.47 –

7.39 (m, 3H), 7.26 – 7.23 (m, 2H), 7.14 – 7.10 (m, 3H), 5.79 (s, 1H), 5.01 (s, 1H), 1.36 (s, 18H); ^{13}C $\{^1\text{H}\}$ NMR (100 MHz, CDCl_3) δ 152.3, 151.0, 149.8, 136.9, 135.8, 131.9, 130.9, 129.3, 128.7, 128.6, 127.5, 126.6, 126.2, 124.1, 124.0, 123.8, 123.3, 118.1, 117.3, 116.7, 41.74, 41.7, 34.3, 30.3; FT-IR (thin film, neat): 2959, 1582, 1485, 1433, 1245, 738 cm^{-1} ; HRMS (ESI): m/z calcd for $\text{C}_{31}\text{H}_{31}\text{O}_2$ $[\text{M}-\text{H}]^-$: 435.2324; found : 435.2332.

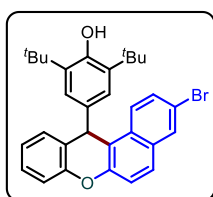
2,6-di-tert-butyl-4-(3-methoxy-12H-benzo[a]xanthen-12-yl)phenol (2r): The reaction was



performed at 0.085 mmol scale of **1r**; pale yellow solid (48.0 mg, 96% yield); $R_f = 0.3$ (5% EtOAc in hexane); ^1H NMR (400 MHz, CDCl_3) δ 7.97 – 7.94 (m, 1H), 7.66 (d, $J = 8.0$ Hz, 1H), 7.39 (d, $J = 8.8$ Hz, 2H),

7.26 – 7.19 (m, 2H), 7.17 – 7.14 (m, 2H), 7.09 – 7.04 (m, 3H), 5.70 (s, 1H), 4.95 (s, 1H), 3.90 (s, 3H), 1.31 (s, 18H); ^{13}C { ^1H } NMR (100 MHz, CDCl_3) δ 156.4, 152.3, 151.2, 148.4, 136.9, 135.8, 132.0, 129.3, 127.44, 127.4, 127.0, 126.2, 124.8, 123.9, 123.6, 118.8, 118.5, 117.7, 116.6, 107.2, 55.43, 55.4, 41.9, 34.3, 30.3; FT-IR (thin film, neat): 2956, 1611, 1514, 1433, 1247, 752 cm^{-1} ; HRMS (ESI): m/z calcd for $\text{C}_{32}\text{H}_{33}\text{O}_3$ [$\text{M}-\text{H}$] $^-$: 465.2430; found : 465.2433.

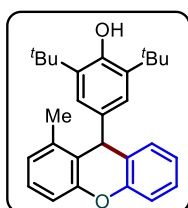
4-(3-bromo-12H-benzo[*a*]xanthen-12-yl)-2,6-di-*tert*-butylphenol (2s): The reaction was



performed at 0.120 mmol scale of **1s**; yellow white solid (42.0 mg, 85% yield); $R_f = 0.4$ (5% EtOAc in hexane); ^1H NMR (400 MHz, CDCl_3) δ 7.94 (d, $J = 2.0$ Hz, 1H), 7.88 (d, $J = 9.0$ Hz, 1H), 7.66 (d, $J = 9.0$ Hz, 1H), 7.52

(dd, $J = 9.0, 2.0$ Hz, 1H), 7.42 (d, $J = 8.9$ Hz, 1H), 7.38 (d, $J = 7.4$ Hz, 1H), 7.26 – 7.13 (m, 2H), 7.11 – 7.07 (m, 1H), 7.01 (s, 2H), 5.67 (s, 1H), 4.98 (s, 1H), 1.31 (s, 18H); ^{13}C { ^1H } NMR (100 MHz, CDCl_3) δ 152.4, 150.7, 149.9, 136.6, 136.0, 132.1, 130.6, 130.5, 129.8, 129.3, 127.8, 127.6, 125.8, 125.1, 124.0, 123.9, 119.3, 117.9, 117.5, 116.7, 41.7, 34.3, 30.3; FT-IR (thin film, neat): 2958, 1627, 1488, 1434, 1249, 753 cm^{-1} ; HRMS (ESI): m/z calcd for $\text{C}_{31}\text{H}_{30}\text{BrO}_2$ [$\text{M}-\text{H}$] $^-$: 513.1429; found : 513.1427.

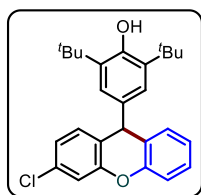
2,6-di-*tert*-butyl-4-(1-methyl-9H-xanthen-9-yl)phenol (2t): The reaction was performed at



0.124 mmol scale of **1t**; pale yellow solid (48.0 mg, 96% yield); m. p. = 88–90 $^\circ\text{C}$; $R_f = 0.4$ (5% EtOAc in hexane); δ 7.31 (dd, $J = 7.6, 1.0$ Hz, 1H), 7.21 – 7.12 (m, 3H), 7.09–7.07 (m, 1H), 7.03 (td, $J = 7.4, 1.2$ Hz, 1H), 6.99 (s, 2H),

6.91 (d, $J = 7.3$ Hz, 1H), 5.14 (s, 1H), 5.01 (s, 1H), 2.28 (s, 3H), 1.36 (s, 18H); ^{13}C { ^1H } NMR (100 MHz, CDCl_3) δ 152.5, 152.3, 151.5, 137.3, 136.2, 135.8, 129.1, 127.5, 127.4, 126.9, 125.1, 124.4, 124.1, 123.3, 116.6, 114.5, 42.83, 42.8, 34.4, 30.4, 19.4; FT-IR (thin film, neat): 2923, 1656, 1462, 1436, 1257, 1155, 749 cm^{-1} ; HRMS (ESI): m/z calcd for $\text{C}_{28}\text{H}_{31}\text{O}_2$ [$\text{M}-\text{H}$] $^-$: 399.2324; found : 399.2325.

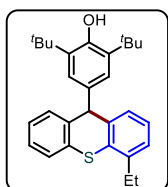
2,6-di-tert-butyl-4-(3-chloro-9H-xanthen-9-yl)phenol (2u): The reaction was performed at



0.118 mmol scale of **1u**; pale yellow solid (46.0 mg, 92 % yield); m. p. = 187–189 °C; $R_f = 0.4$ (5% EtOAc in hexane); $^1\text{H NMR}$ (400 MHz, CDCl_3) δ 7.24 – 7.20 (m, 1H), 7.16 – 7.09 (m, 3H), 7.05 – 7.00 (m, 2H), 6.99 – 6.97 (m, 1H), 6.94 (s, 2H), 5.12 (s, 1H), 5.10 (s, 1H), 1.38 (s, 18H); $^{13}\text{C}\{^1\text{H}\}$ NMR (100 MHz, CDCl_3) δ 152.7, 152.0, 151.1, 136.5, 136.1, 132.7, 130.7, 129.7, 127.9, 125.1, 124.9, 124.2, 123.7, 123.5, 116.8, 116.5, 44.1, 34.4, 30.4; FT-IR (thin film, neat): 2921, 1739, 1457, 1274, 929, 753 cm^{-1} ; HRMS (ESI): m/z calcd for $\text{C}_{27}\text{H}_{28}\text{ClO}_2$ $[\text{M}-\text{H}]^-$: 419.1778; found : 419.1787.

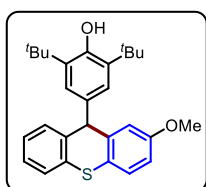
6. Characterization of products 4b to 4j

2,6-di-tert-butyl-4-(4-ethyl-9H-thioxanthen-9-yl)phenol (4b): The reaction was performed



at 0.116 mmol scale of **3b**; yellow gummy solid (32.8 mg, 66% yield); $R_f = 0.4$ (5% EtOAc in hexane); $^1\text{H NMR}$ (400 MHz, CDCl_3) δ 7.45 (dd, $J = 7.4, 1.3$ Hz, 1H), 7.39 (dd, $J = 7.4, 1.4$ Hz, 1H), 7.26 – 7.17 (m, 4H), 7.14 – 7.12 (m, 1H), 6.89 (s, 2H), 5.23 (s, 1H), 5.03 (s, 1H), 2.87 – 2.81 (m, 2H), 1.32 (s, 18H), 1.28 (t, $J = 7.5$ Hz, 3H); $^{13}\text{C}\{^1\text{H}\}$ NMR (100 MHz, CDCl_3) δ 152.4, 141.2, 138.5, 137.8, 135.3, 133.0, 132.2, 131.6, 129.1, 127.3, 127.2, 126.63, 126.6, 126.5, 126.4, 124.9, 53.65, 53.6, 34.4, 30.3, 27.4, 14.7; FT-IR (thin film, neat): 2959, 1588, 1434, 1235, 1120, 739 cm^{-1} ; HRMS (ESI): m/z calcd for $\text{C}_{29}\text{H}_{33}\text{OS}$ $[\text{M}-\text{H}]^-$: 429.2252; found : 429.2260.

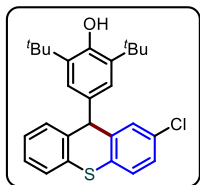
2,6-di-tert-butyl-4-(2-methoxy-9H-thioxanthen-9-yl)phenol (4c): The reaction was



performed at 0.115 mmol scale of **3c**; pale yellow solid (42.0 mg, 84% yield); m. p. = 216–218 °C; $R_f = 0.3$ (5% EtOAc in hexane); $^1\text{H NMR}$ (400 MHz, CDCl_3) δ 7.45 – 7.43 (m, 1H), 7.39 – 7.35 (m, 2H), 7.26 – 7.19 (m, 2H), 6.97 (s, 3H), 6.82 (dd, $J = 8.5, 2.7$ Hz, 1H), 5.18 (s, 1H), 5.09 (s, 1H), 3.81 (s, 3H), 1.36 (s, 18H); $^{13}\text{C}\{^1\text{H}\}$ NMR (100 MHz, CDCl_3) δ 158.8, 152.5, 139.7, 138.0, 135.5, 133.7, 131.2, 129.3, 127.9, 127.0, 126.7, 126.5, 125.0, 124.2, 115.0, 112.9, 55.6, 55.56, 53.7, 53.65, 34.4,

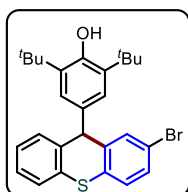
30.3; FT-IR (thin film, neat): 2957, 1598, 1466, 1434, 1236, 739 cm^{-1} ; HRMS (ESI): m/z calcd for $\text{C}_{28}\text{H}_{31}\text{O}_2\text{S}$ $[\text{M}-\text{H}]^-$: 431.2045; found : 431.2054.

2,6-di-*tert*-butyl-4-(2-chloro-9H-thioxanthen-9-yl)phenol (4d): The reaction was performed



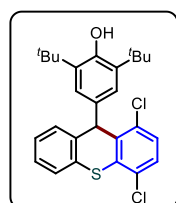
at 0.115 mmol scale of **3d**; white solid (33.0 mg, 66% yield); $R_f = 0.4$ (5% EtOAc in hexane); ^1H NMR (400 MHz, CDCl_3) δ 7.43 (dd, $J = 7.0, 1.4$ Hz, 1H), 7.38 – 7.35 (m, 3H), 7.28 – 7.19 (m, 3H), 6.93 (s, 2H), 5.17 (s, 1H), 5.10 (s, 1H), 1.35 (s, 18H); ^{13}C $\{^1\text{H}\}$ NMR (100 MHz, CDCl_3) δ 152.7, 139.9, 137.4, 135.7, 132.5, 132.3, 131.7, 131.0, 129.5, 129.4, 128.1, 127.0, 126.94, 126.9, 126.8, 124.8, 53.1, 34.4, 30.3; FT-IR (thin film, neat): 2958, 1740, 1432, 1320, 805, 753 cm^{-1} ; HRMS (APCI): m/z calcd for $\text{C}_{27}\text{H}_{28}\text{ClOS}$ $[\text{M}-\text{H}]^-$: 435.1549; found : 435.1542.

4-(2-bromo-9H-thioxanthen-9-yl)-2,6-di-*tert*-butylphenol (4e): The reaction was performed



at 0.103 mmol scale of **3e**; pale yellow solid (36.5 mg, 73% yield); $R_f = 0.4$ (5% EtOAc in hexane); ^1H NMR (400 MHz, CDCl_3) δ 7.52 (d, $J = 1.9$ Hz, 1H), 7.42 – 7.39 (m, 1H), 7.35 – 7.26 (m, 3H), 7.25 – 7.18 (m, 2H), 6.91 (s, 2H), 5.15 (s, 1H), 5.08 (s, 1H), 1.34 (s, 18H); ^{13}C $\{^1\text{H}\}$ NMR (100 MHz, CDCl_3) δ 152.7, 140.1, 137.4, 135.7, 132.4, 132.3, 132.2, 131.0, 129.6, 129.5, 128.3, 127.0, 126.93, 126.9, 124.8, 120.2, 53.0, 52.9, 34.4, 30.3; FT-IR (thin film, neat): 2959, 1462, 1436, 1235, 1156, 751 cm^{-1} ; HRMS (ESI): m/z calcd for $\text{C}_{27}\text{H}_{28}\text{BrOS}$ $[\text{M}-\text{H}]^-$: 479.1044; found : 479.1054.

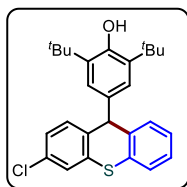
2,6-di-*tert*-butyl-4-(2,5-dichloro-9H-thioxanthen-9-yl)phenol (4f): The reaction was



performed at 0.136 mmol scale of **3f**; white solid (34.0 mg, 74% yield); m. p. = 178–180 $^\circ\text{C}$; $R_f = 0.4$ (5% EtOAc in hexane); ^1H NMR (400 MHz, CDCl_3) δ 7.52 – 7.49 (m, 1H), 7.48 – 7.45 (m, 1H), 7.34 – 7.28 (m, 3H), 7.24 – 7.22 (m, 1H), 6.90 (s, 2H), 5.98 (s, 1H), 5.04 (s, 1H), 1.29 (s, 18H); ^{13}C $\{^1\text{H}\}$ NMR (100 MHz, CDCl_3) δ 152.7, 139.8, 137.4, 135.7, 132.5, 132.3, 131.7, 131.0, 129.5, 129.4, 128.0, 127.0, 126.93,

126.9, 126.8, 124.8, 53.1, 34.4, 30.3; FT-IR (thin film, neat): 2958, 1592, 1459, 1155, 809, 742 cm^{-1} ; HRMS (ESI): m/z calcd for $\text{C}_{27}\text{H}_{27}\text{Cl}_2\text{OS}$ $[\text{M}-\text{H}]^-$: 469.1160; found : 469.1183.

2,6-di-*tert*-butyl-4-(3-chloro-9H-thioxanthen-9-yl)phenol (4g): The reaction was performed



at 0.115 mmol scale of **3g**; yellow gummy solid (29.0 mg, 58% yield); m. p.

= 138–140 °C; R_f = 0.4 (5% EtOAc in hexane); ^1H NMR (400 MHz, CDCl_3)

δ 7.44 – 7.42 (m, 2H), 7.37 – 7.35 (m, 1H), 7.30 – 7.28 (m, 1H), 7.26 – 7.19

(m, 3H), 6.89 (s, 2H), 5.19 (s, 1H), 5.08 (s, 1H), 1.34 (s, 18H); $^{13}\text{C}\{^1\text{H}\}$ NMR (100 MHz,

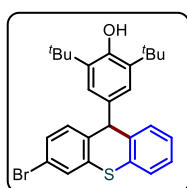
CDCl_3) δ 152.6, 137.7, 136.7, 135.6, 135.0, 132.31, 132.3, 131.1, 130.4, 129.5, 127.0, 126.9

(2C), 126.7, 126.6, 124.8, 52.6, 52.59, 34.4, 30.3; FT-IR (thin film, neat): 2957, 1580, 1464,

1435, 1235, 746 cm^{-1} ; HRMS (ESI): m/z calcd for $\text{C}_{27}\text{H}_{28}\text{ClOS}$ $[\text{M}-\text{H}]^-$: 435.1549; found :

435.1566.

4-(3-bromo-9H-thioxanthen-9-yl)-2,6-di-*tert*-butylphenol (4h): The reaction was



performed at 0.110 mmol scale of **3h**; white solid (35.0 mg, 68% yield); m.

p. = 196–198 °C; R_f = 0.4 (5% EtOAc in hexane); ^1H NMR (400 MHz,

CDCl_3) δ 7.29 (d, J = 2.0 Hz, 1H), 7.23 – 7.19 (m, 1H), 7.11 (dd, J = 8.1, 1.7

Hz, 2H), 7.08 (dd, J = 7.8, 1.6 Hz, 1H), 7.04 – 7.01 (m, 1H), 7.00 – 6.95 (m, 1H), 6.91 (s, 2H),

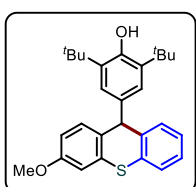
5.08 (s, 2H), 1.36 (s, 18H); $^{13}\text{C}\{^1\text{H}\}$ NMR (100 MHz, CDCl_3) δ 152.7, 152.1, 151.1, 136.4,

136.1, 131.0, 129.7, 127.9, 126.3, 125.0, 124.9, 124.7, 123.7, 120.4, 119.7, 116.5, 44.2, 44.16,

34.4, 30.4; FT-IR (thin film, neat): 2956, 1595, 1475, 1274, 917, 755 cm^{-1} ; HRMS (ESI): m/z

calcd for $\text{C}_{27}\text{H}_{29}\text{BrOS}$ $[\text{M}+\text{H}]^+$: 481.1201; found : 481.1217.

2,6-di-*tert*-butyl-4-(3-methoxy-9H-thioxanthen-9-yl)phenol (4i): The reaction was



performed at 0.114 mmol scale of **3i**; pale yellow solid (36.4 mg, 73% yield);

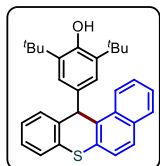
m. p. = 90–92 °C; R_f = 0.3 (5% EtOAc in hexane); ^1H NMR (400 MHz,

CDCl_3) δ 7.44 – 7.42 (m, 1H), 7.39 – 7.37 (m, 1H), 7.28 (d, J = 8.5 Hz, 1H),

7.26 – 7.19 (m, 2H), 7.10 (d, J = 2.6 Hz, 1H), 6.93 (s, 2H), 6.81 (dd, J = 8.4, 2.6 Hz, 1H), 5.19

(s, 1H), 5.06 (s, 1H), 3.82 (s, 3H), 1.35 (s, 18H); $^{13}\text{C}\{^1\text{H}\}$ NMR (100 MHz, CDCl_3) δ 158.2, 152.4, 138.4, 135.4, 134.1, 132.8, 132.1, 130.3, 130.2, 129.4, 128.5, 126.9, 126.6, 124.8, 113.0, 111.6, 55.6, 55.5, 52.34, 52.3, 34.4, 30.3, FT-IR (thin film, neat): 2956, 1600, 1435, 1246, 1056, 739 cm^{-1} ; HRMS (ESI): m/z calcd for $\text{C}_{28}\text{H}_{32}\text{O}_2\text{S}$ $[\text{M}-\text{H}]^-$: 431.2045; found : 435.2049.

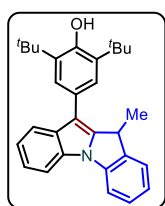
4-(12H-benzo[a]thioxanthen-12-yl)-2,6-di-*tert*-butylphenol (4j): The reaction was



performed at 0.110 mmol scale of **3j**; white solid (35.0 mg, 70% yield); m. p. = 84–86 °C; R_f = 0.4 (5% EtOAc in hexane); ^1H NMR (400 MHz, CDCl_3) δ 8.35 (d, J = 8.6, Hz, 1H), 7.87 – 7.85 (m, 1H), 7.73 (d, J = 8.5 Hz, 1H), 7.60 – 7.56 (m, 1H), 7.52 (d, J = 8.6 Hz, 1H), 7.49 – 7.45 (m, 2H), 7.30 (td, J = 7.4, 1.4 Hz, 1H), 7.26 – 7.22 (m, 2H), 6.90 (s, 2H), 6.24 (s, 1H), 4.97 (s, 1H), 1.24 (s, 18H); $^{13}\text{C}\{^1\text{H}\}$ NMR (100 MHz, CDCl_3) δ 152.4, 137.3, 135.3, 132.8, 132.6, 132.3, 132.2, 131.8, 131.0, 130.0, 129.0, 127.2, 127.0, 126.8, 126.75, 126.7, 125.4, 125.2, 124.4, 122.9, 47.0, 34.3, 30.2; FT-IR (thin film, neat): 2956, 1592, 1435, 1235, 806, 740 cm^{-1} ; HRMS (ESI): m/z calcd for $\text{C}_{31}\text{H}_{32}\text{OS}$ $[\text{M}-\text{H}]^-$: 451.2096; found : 451.2088.

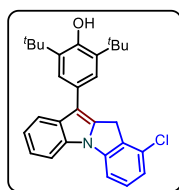
7. Characterization of products 6b to 6e

2,6-di-*tert*-butyl-4-(10-methyl-10H-indolo[1,2-*a*]indol-11-yl)phenol (6b): The reaction was



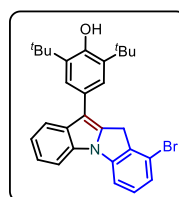
performed at 0.094 mmol scale of **5b**; Greyish gummy solid (37 mg, 92% yield); R_f = 0.4 (5% EtOAc in hexane); ^1H NMR (400 MHz, CDCl_3) δ 7.89 (d, J = 7.9 Hz, 1H), 7.82 (d, J = 8.2 Hz, 1H), 7.62 – 7.60 (m, 1H), 7.56 (s, 2H), 7.44 – 7.32 (m, 3H), 7.27 – 7.23 (m, 1H), 7.14 (td, J = 7.5, 0.6 Hz, 1H), 5.22 (s, 1H), 4.55 (q, J = 7.2 Hz 1H), 1.57 – 1.55 (m, 21H); $^{13}\text{C}\{^1\text{H}\}$ NMR (100 MHz, CDCl_3) δ 152.3, 143.4, 140.6, 139.8, 136.1, 131.9, 130.8, 128.0, 125.6, 124.9, 124.8, 122.6, 122.1, 120.7, 120.3, 112.5, 110.9, 110.5, 36.3, 34.7, 30.6, 17.6; FT-IR (thin film, neat FT-IR (thin film, neat): 3634, 2955, 1603, 1492, 1312, 740 cm^{-1} ; HRMS (ESI): m/z calcd for $\text{C}_{30}\text{H}_{34}\text{NO}$ $[\text{M}+\text{H}]^+$: 424.2640; found : 424.2620.

4-(9-chloro-10H-indolo[1,2-*a*]indol-11-yl)-2,6-di-*tert*-butylphenol (6c): The reaction was



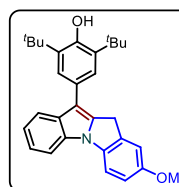
performed at 0.009 mmol scale of **5c**; Greyish gummy solid (36 mg, 90% yield); $R_f = 0.4$ (5% EtOAc in hexane); $^1\text{H NMR}$ (400 MHz, CDCl_3) δ 7.93 (d, $J = 7.9$ Hz, 1H), 7.76 (d, $J = 8.0$ Hz, 1H), 7.59 (d, $J = 1.1$ Hz, 1H), 7.54 (s, 2H), 7.52 – 7.49 (m, 1H), 7.36 – 7.32 (m, 1H), 7.26 (s, 2H), 5.25 (s, 1H), 4.21 (s, 2H), 1.53 (s, 18H); $^{13}\text{C}\{^1\text{H}\}$ NMR (100 MHz, CDCl_3) δ 152.4, 137.7, 136.5, 135.8, 131.5, 131.1, 130.9, 129.2, 125.9, 124.4, 122.2, 122.19, 121.2, 120.5, 115.0, 112.5, 111.6, 110.9, 34.7, 30.6, 29.6; FT-IR (thin film, neat FT-IR (thin film, neat): 3674, 2926, 1743, 1493, 1378, 767 cm^{-1} ; HRMS (ESI): m/z calcd for $\text{C}_{29}\text{H}_{31}\text{ClNO}$ $[\text{M}+\text{H}]^+$: 444.2094; found : 444.2076.

2,6-di-*tert*-butyl-4-(9-bromo-10H-indolo[1,2-*a*]indol-11-yl)phenol (6d): The reaction was



performed at 0.081 mmol scale of **5d**; Greyish gummy solid (38 mg, 95% yield); $R_f = 0.4$ (5% EtOAc in hexane); $^1\text{H NMR}$ (400 MHz, CDCl_3) δ 7.94 (d, $J = 7.8$ Hz, 1H), 7.76 (d, $J = 8.0$ Hz, 1H), 7.59 – 7.58 (m, 1H), 7.55 (s, 2H), 7.38 – 7.34 (m, 2H), 7.31 – 7.26 (m, 1H), 7.09 (dd, $J = 7.9, 1.8$ Hz, 1H), 5.26 (s, 1H), 4.15 (s, 2H), 1.55 (s, 18H); $^{13}\text{C}\{^1\text{H}\}$ NMR (100 MHz, CDCl_3) δ 152.4, 142.4, 138.3, 136.4, 133.7, 132.0, 131.6, 131.1, 126.6, 125.8, 124.4, 122.3 (2C), 121.3, 120.4, 112.6, 111.1, 111.0, 34.7, 30.6, 29.3; 3640, 2924, 1599, 1493, 1305, 736 cm^{-1} ; HRMS (ESI): m/z calcd for $\text{C}_{29}\text{H}_{31}\text{BrNO}$ $[\text{M}+\text{H}]^+$: 488.1589; found : 488.1613.

2,6-di-*tert*-butyl-4-(7-methoxy-10H-indolo[1,2-*a*]indol-11-yl)phenol (6e): The reaction was

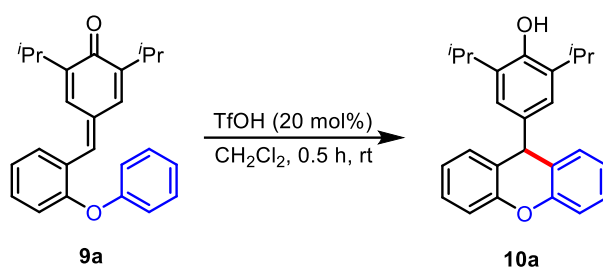


performed at 0.091 mmol scale of **5e**; Greyish gummy solid (30 mg, 75% yield); $R_f = 0.3$ (5% EtOAc in hexane); $^1\text{H NMR}$ (400 MHz, CDCl_3) δ 7.96 (d, $J = 7.9$ Hz, 1H), 7.77 (d, $J = 8.0$ Hz, 1H), 7.58 (s, 2H), 7.52 (d, $J = 8.5$ Hz, 1H), 7.35 – 7.31 (m, 1H), 7.27 – 7.23 (m, 1H), 7.09 (d, $J = 2.4$ Hz, 1H), 6.93 (dd, $J = 8.5, 2.5$ Hz, 1H), 5.24 (s, 1H), 4.20 (s, 2H), 3.86 (s, 3H), 1.55 (s, 18H); $^{13}\text{C}\{^1\text{H}\}$ NMR (100 MHz, CDCl_3) δ 155.9, 152.1, 138.3, 136.4, 135.5, 135.1, 131.0, 130.9, 126.4, 124.3, 121.8, 120.5,

120.3, 113.1, 112.3, 111.7, 110.64, 110.6, 56.0, 55.96, 34.7, 30.6, 30.1; FT-IR (thin film, neat) FT-IR (thin film, neat): 3644, 2922, 1599, 1498, 1247, 737 cm^{-1} ; HRMS (ESI): m/z calcd for $\text{C}_{30}\text{H}_{34}\text{NO}_2$ $[\text{M}+\text{H}]^+$: 440.2590; found : 440.2575.

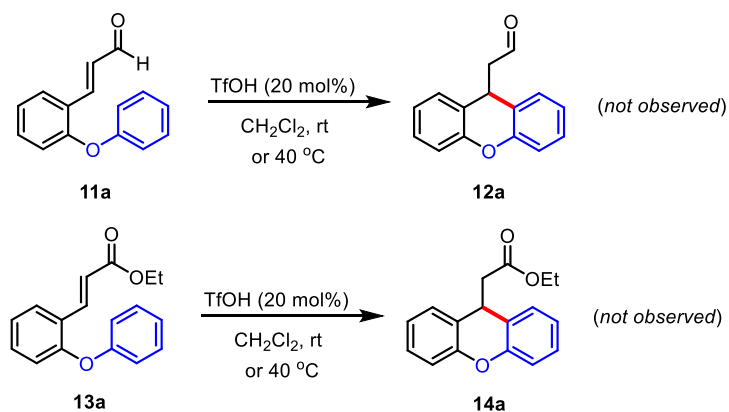
8. Unsuccessful attempts

A reaction has been tried with a *p*-QM having isopropyl groups in the 2- and 6-positions of *p*-QM. In this case, we found that the reaction was proceeding. However, unfortunately, we were unable to isolate the product purest form. For reference, spectra for both the starting material as well as the product are given at the end of the SI.



Scheme 4. Reaction with *p*-QM having isopropyl groups.

Other electrophiles such as cinnamaldehyde and ethyl-cinnamate were also subjected to react under the standard reaction condition. However, in those cases, we did not observe any product formation under standard reaction condition as well as at elevated temperature.

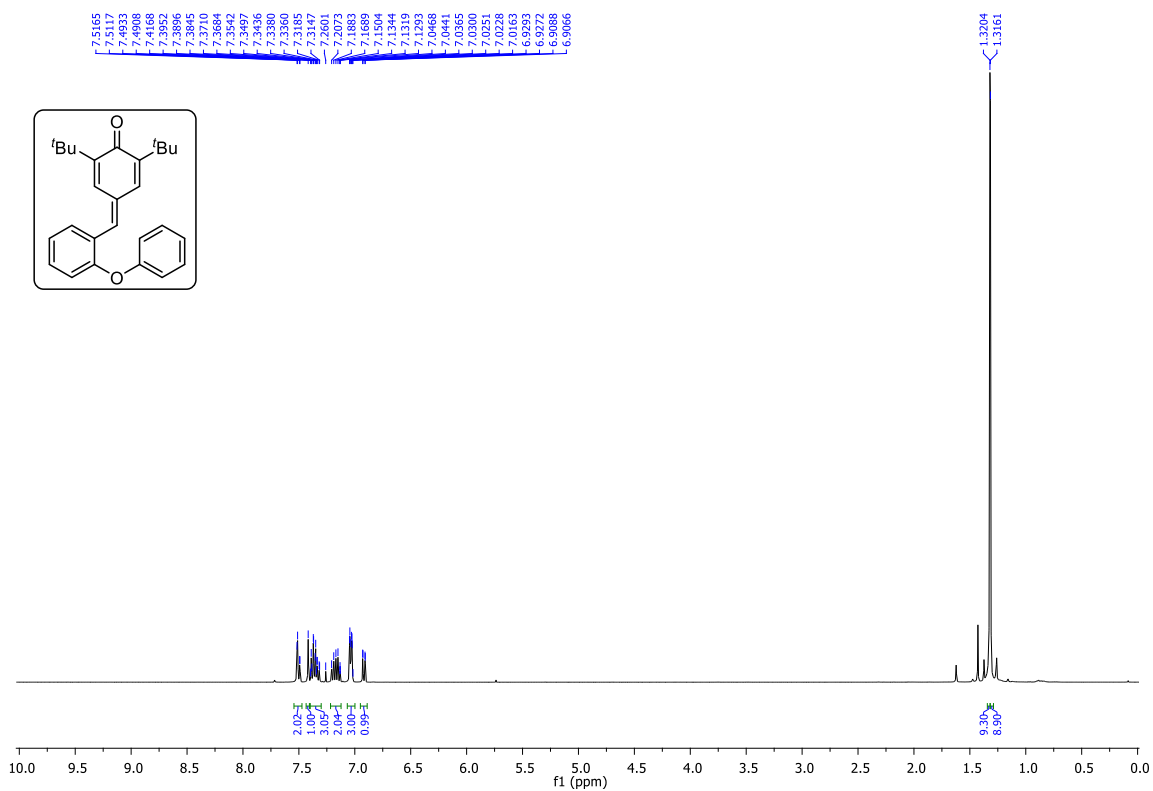


Scheme 5. Reaction with other Electrophiles

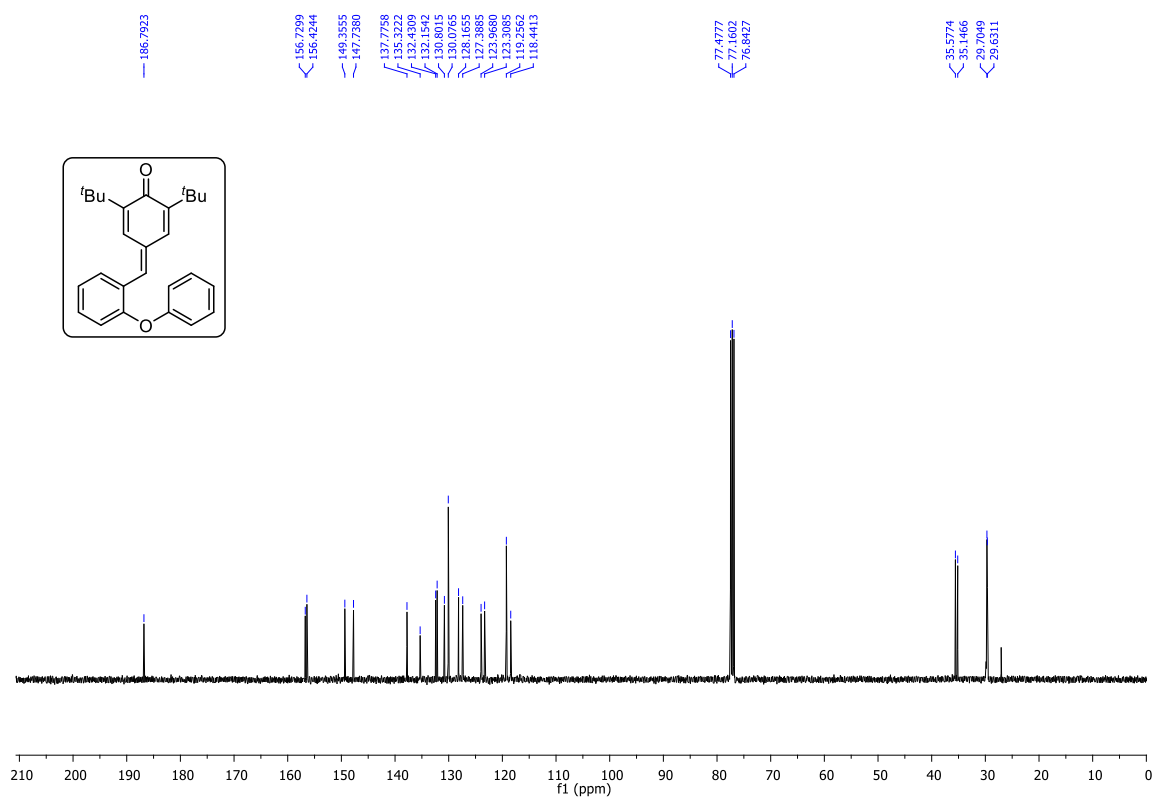
9. References:

- (a) W. -D. Chu, L. -F. Zhang, X. Bao, X. -H. Zhao, C. Zeng, J. -Y. Du, G. -B. Zhang, F. -X. Wang, X. -Y. Ma, and C. -A. Fan, *Angew. Chem. Int. Ed.*, 2013, **52**, 9229. (b) V. Reddy and R. V. Anand, *Org. Lett.* 2015., **17**, 3390.

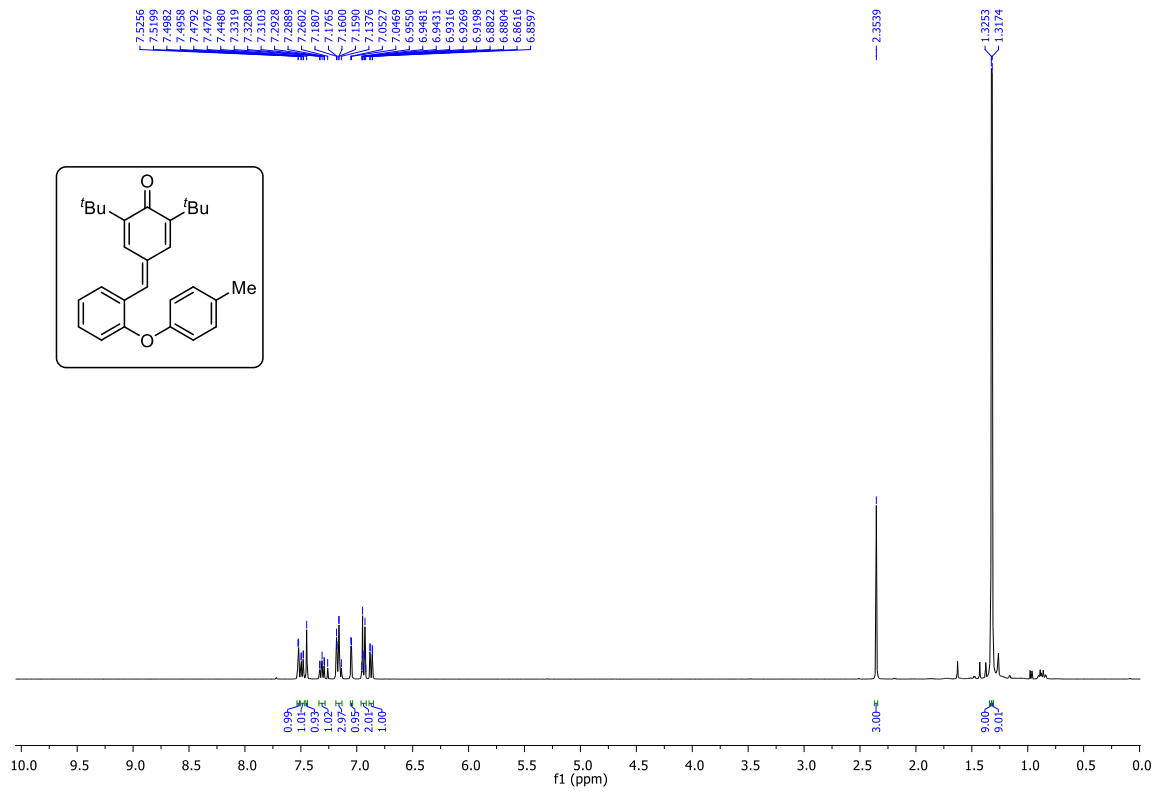
¹H NMR (400 MHz, CDCl₃) spectrum of **1a**



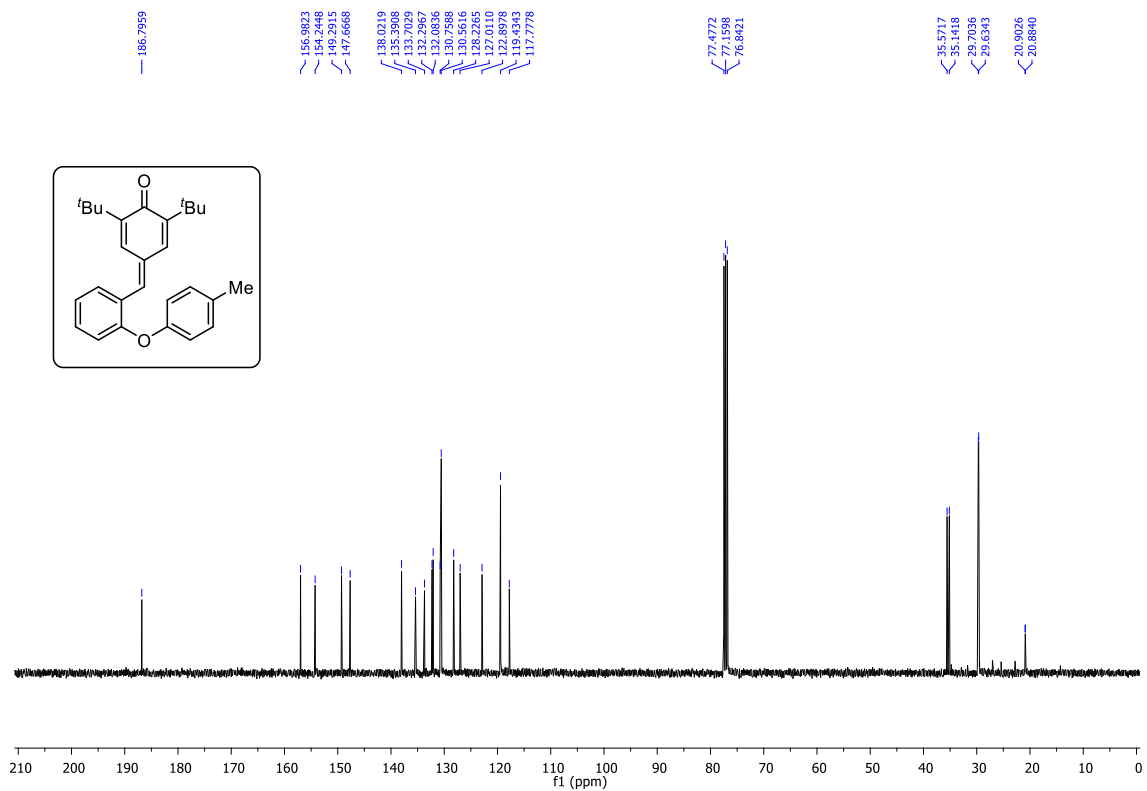
¹³C NMR (100 MHz, CDCl₃) spectrum of **1a**



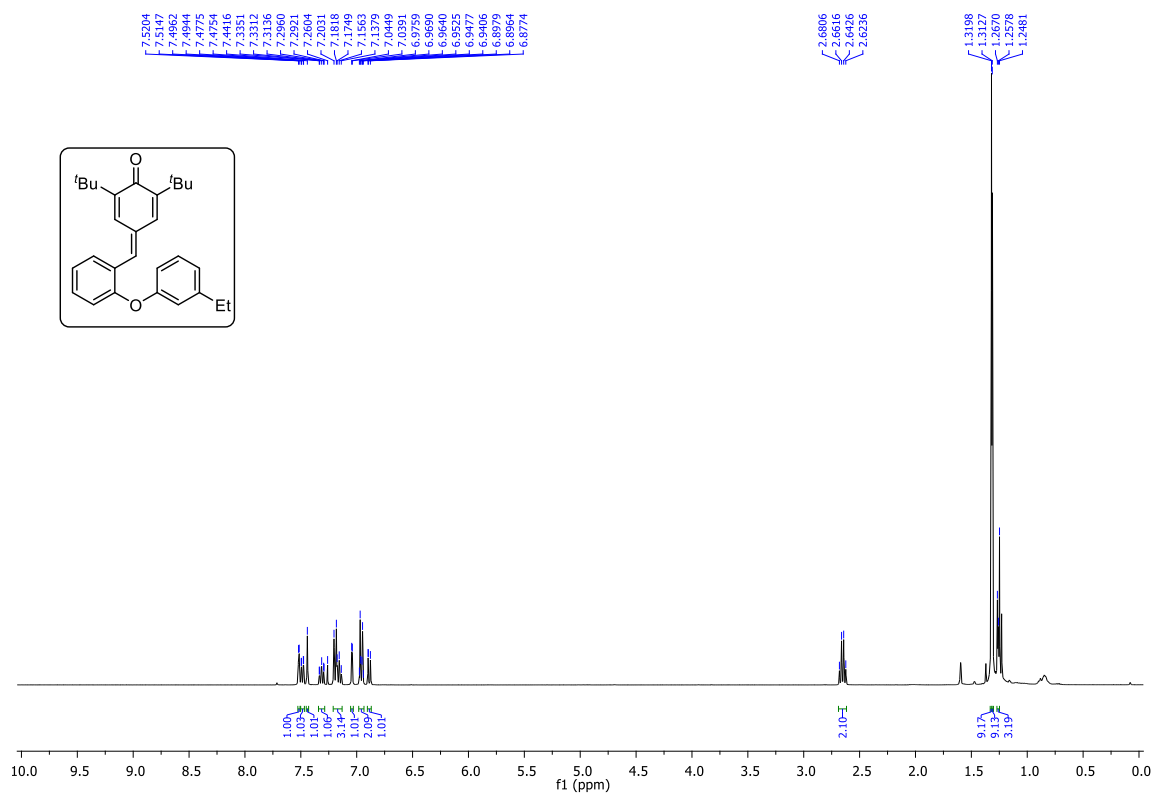
¹H NMR (400 MHz, CDCl₃) spectrum of **1b**



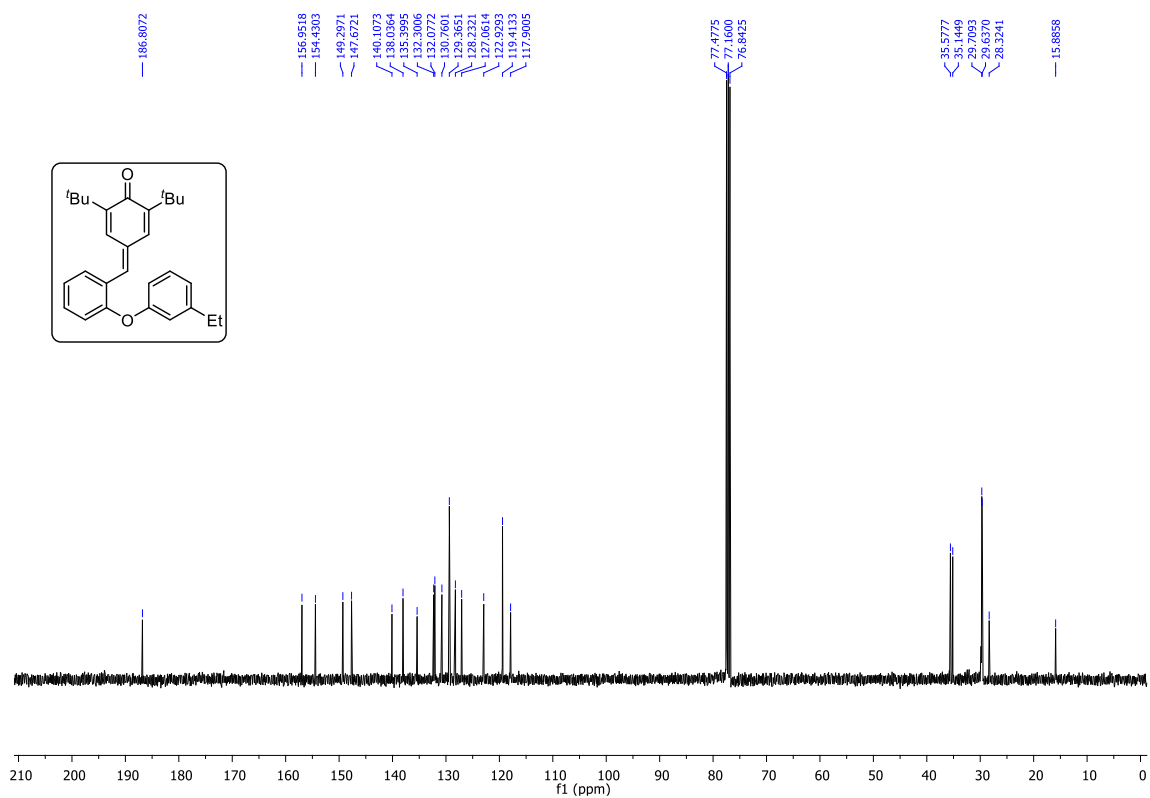
¹³C NMR (100 MHz, CDCl₃) spectrum of **1b**



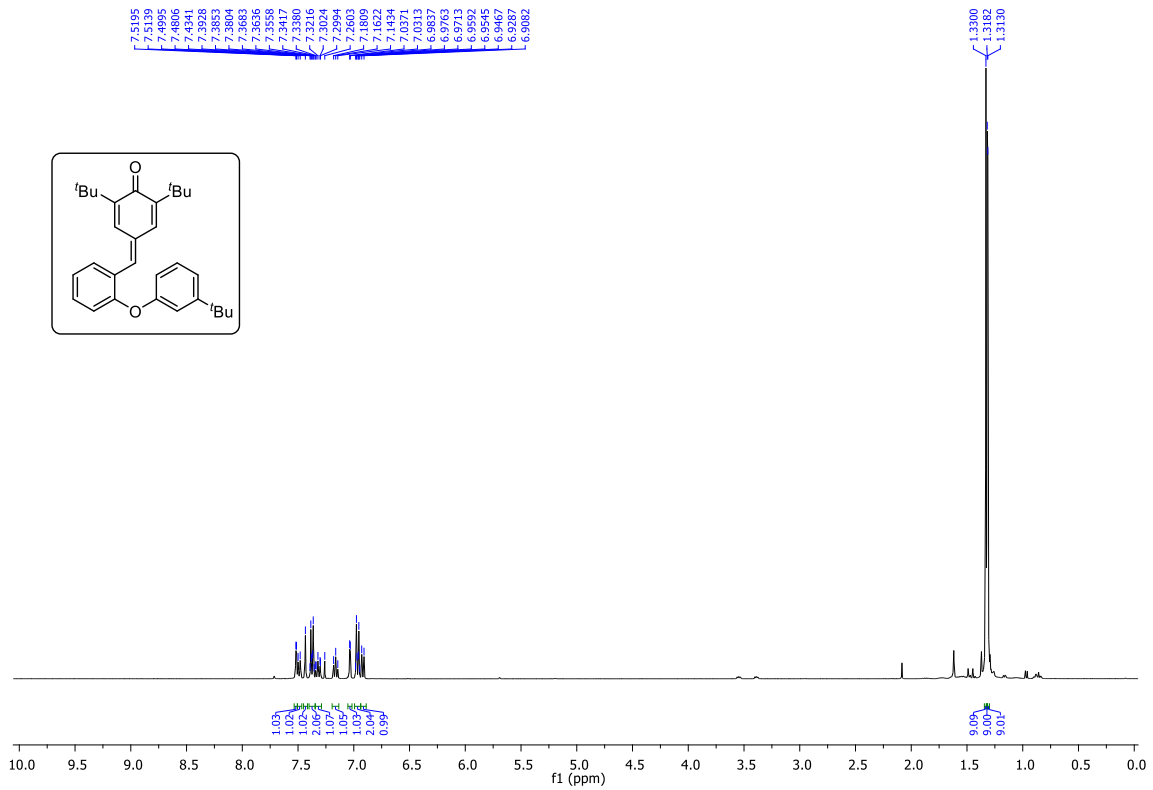
¹H NMR (400 MHz, CDCl₃) spectrum of **1c**



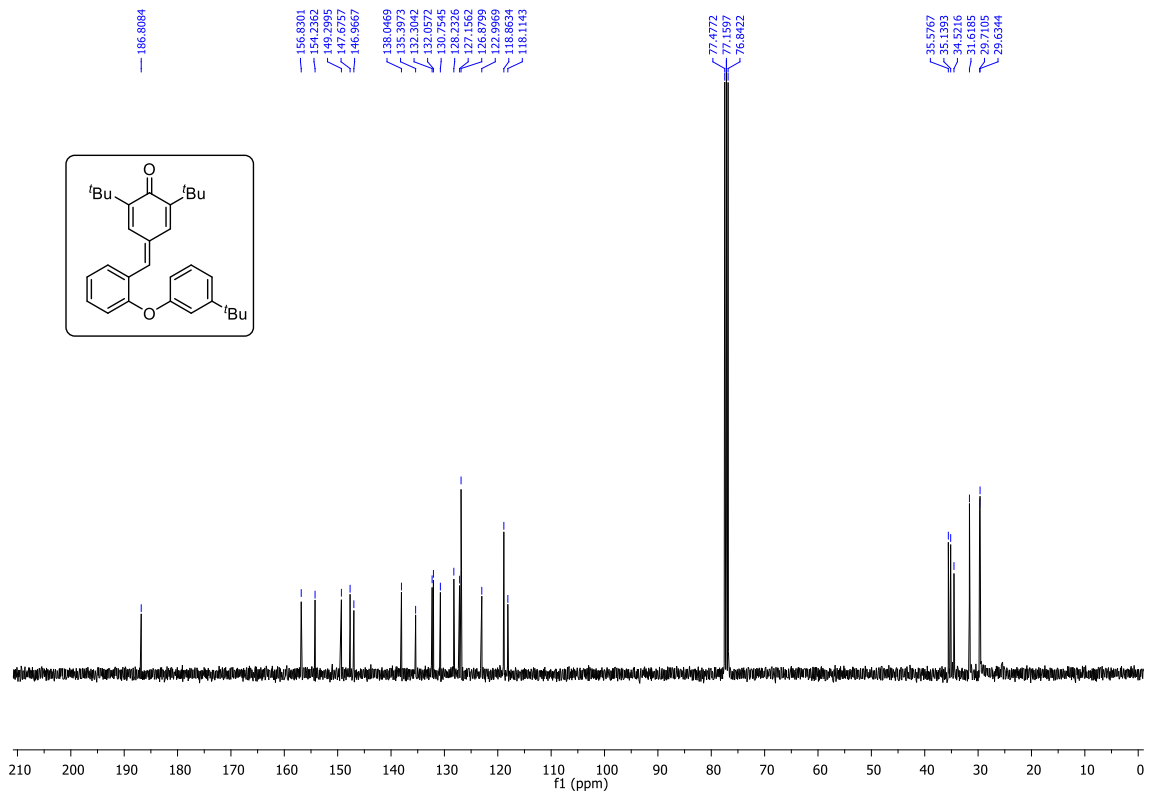
¹³C NMR (100 MHz, CDCl₃) spectrum of **1c**



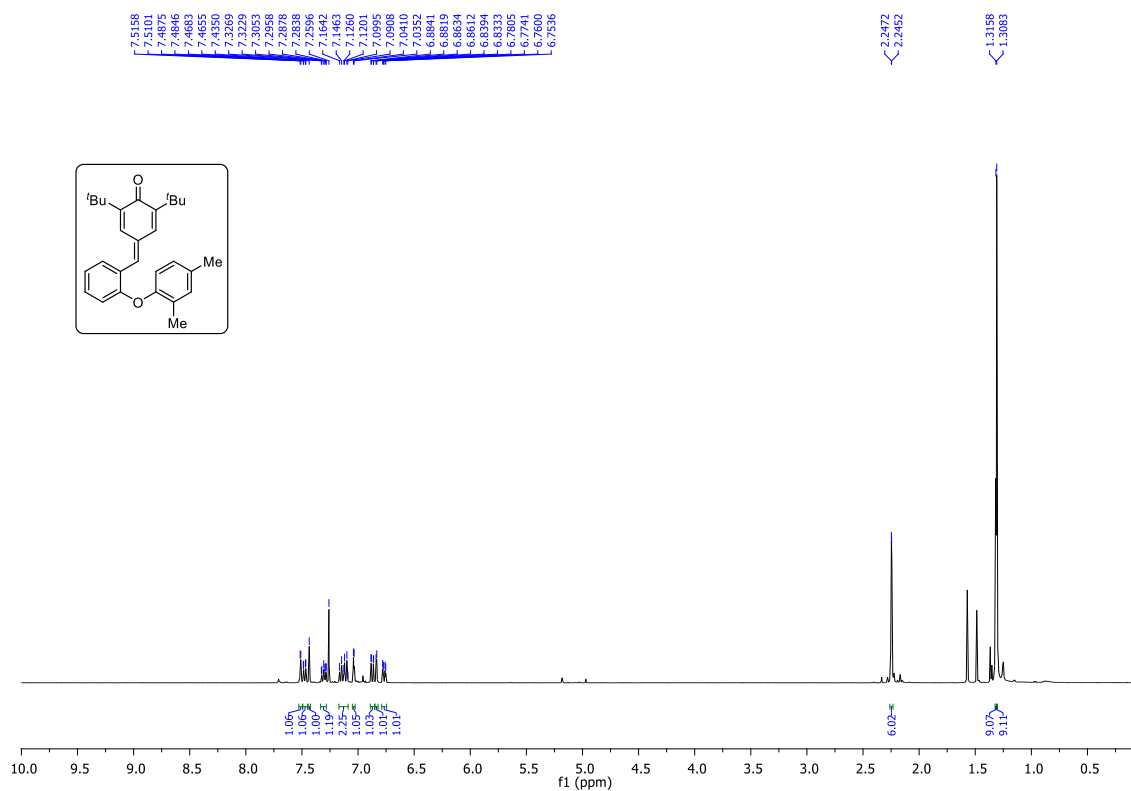
¹H NMR (400 MHz, CDCl₃) spectrum of **1d**



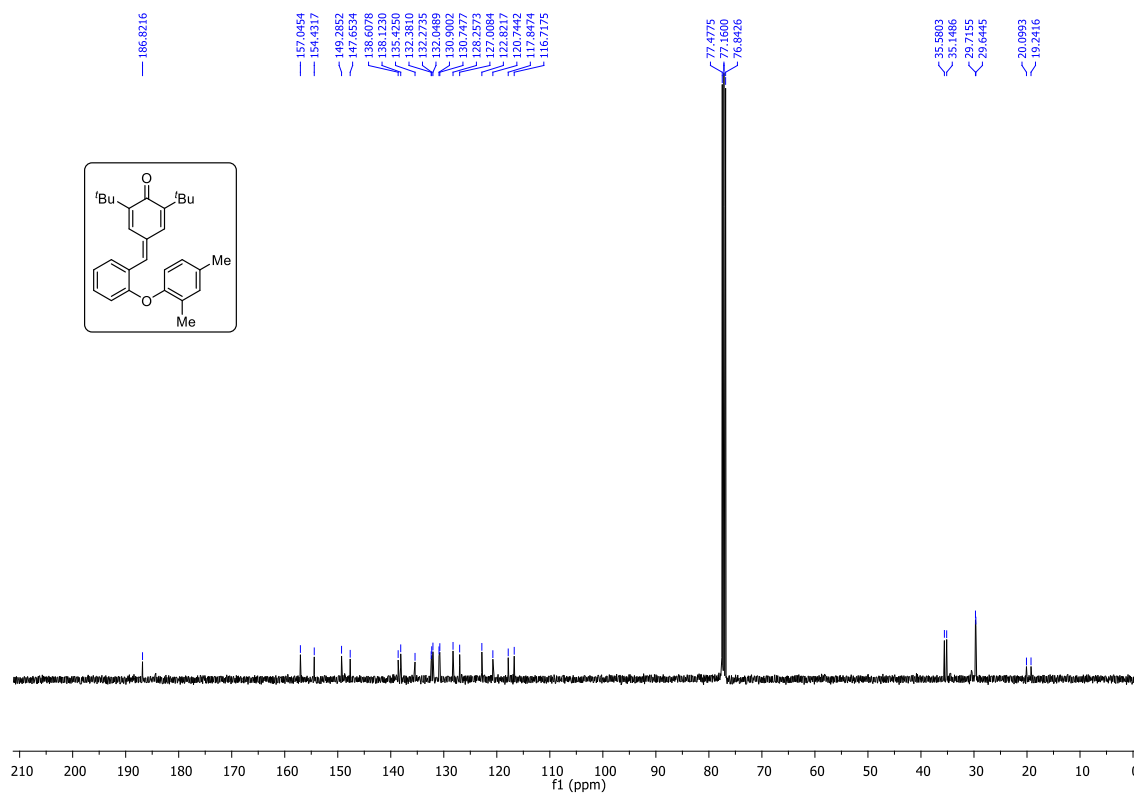
¹³C NMR (100 MHz, CDCl₃) spectrum of **1d**



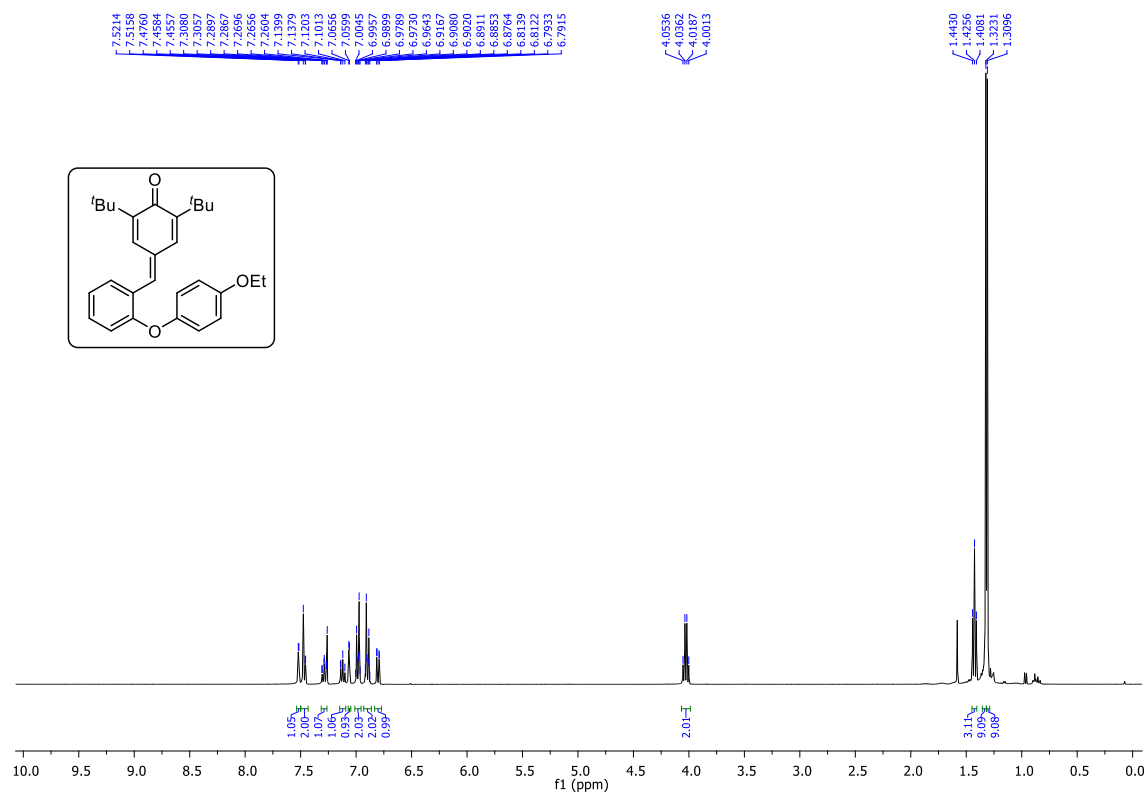
¹H NMR (400 MHz, CDCl₃) spectrum of **1e**



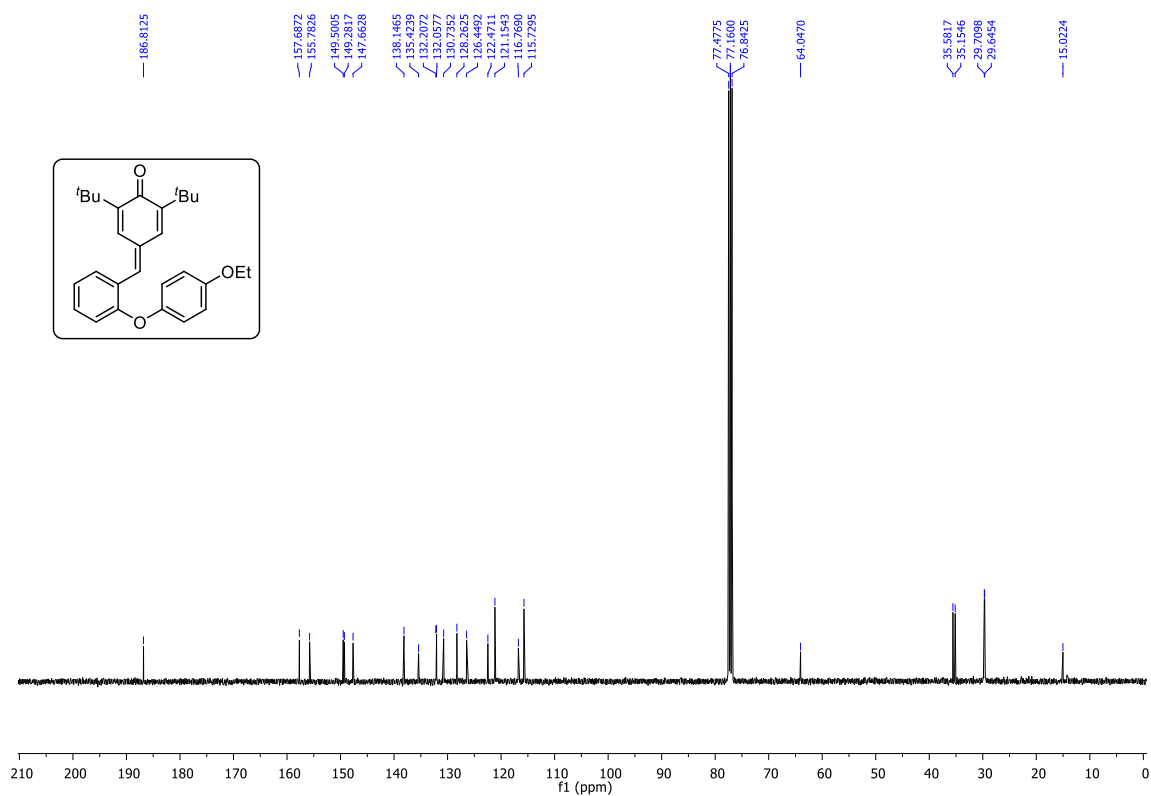
¹³C NMR (100 MHz, CDCl₃) spectrum of **1e**



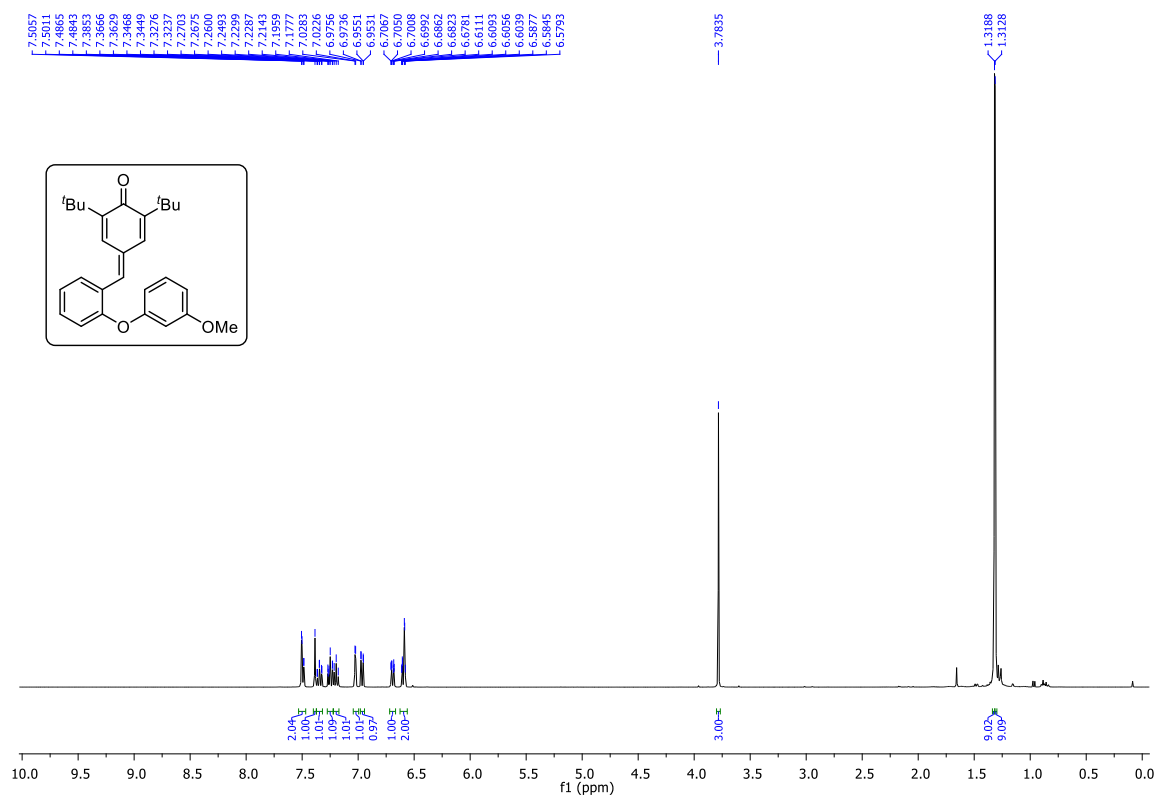
¹H NMR (400 MHz, CDCl₃) spectrum of **1f**



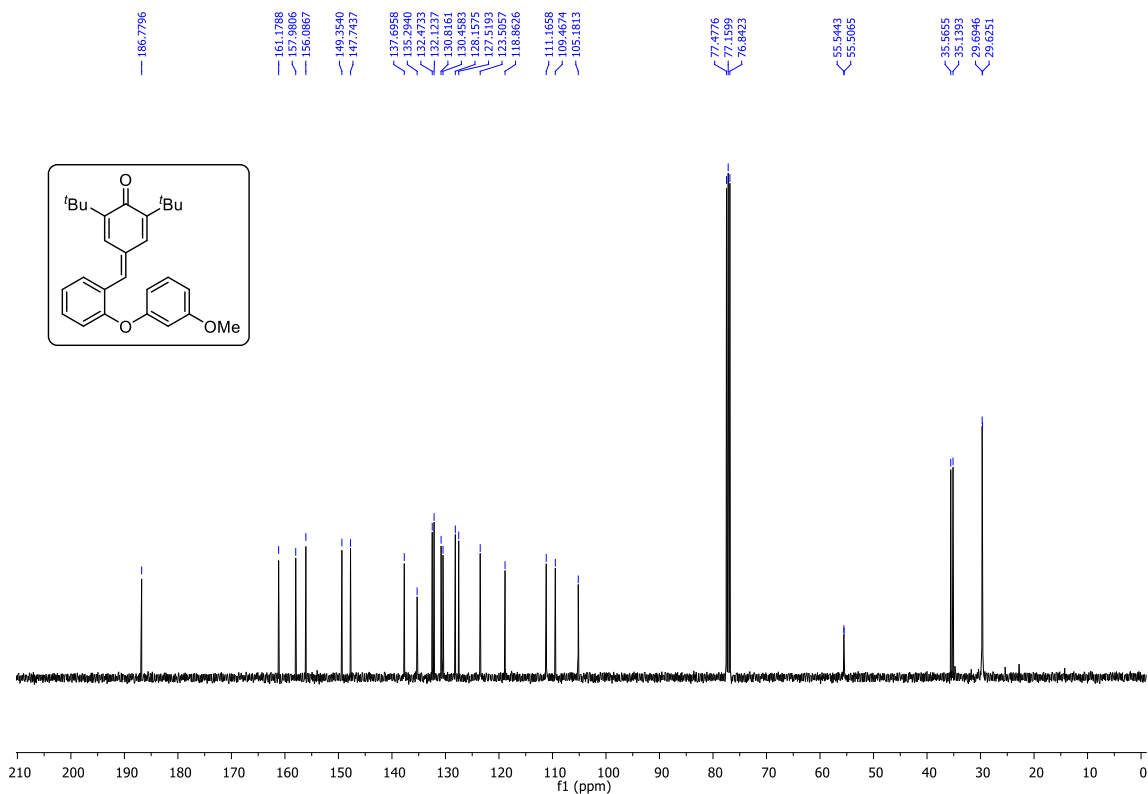
¹³C NMR (100 MHz, CDCl₃) spectrum of **1f**



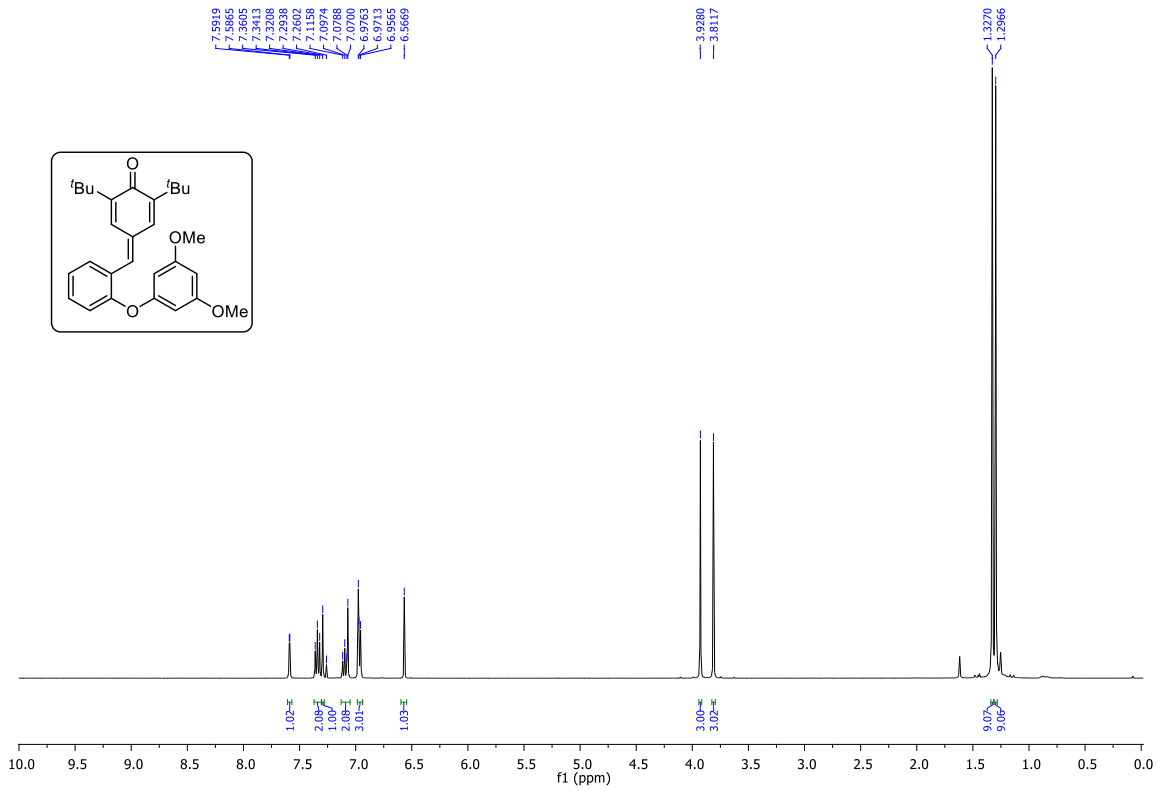
¹H NMR (400 MHz, CDCl₃) spectrum of **1g**



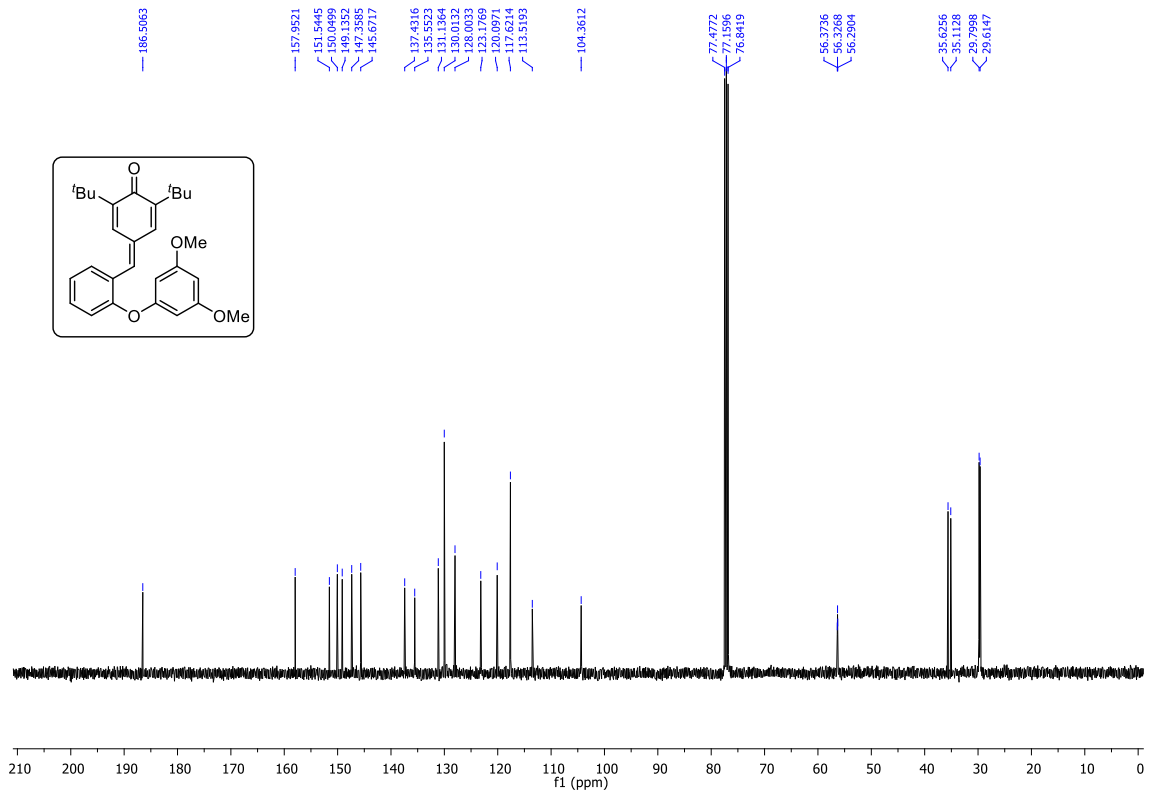
¹³C NMR (100 MHz, CDCl₃) spectrum of **1g**



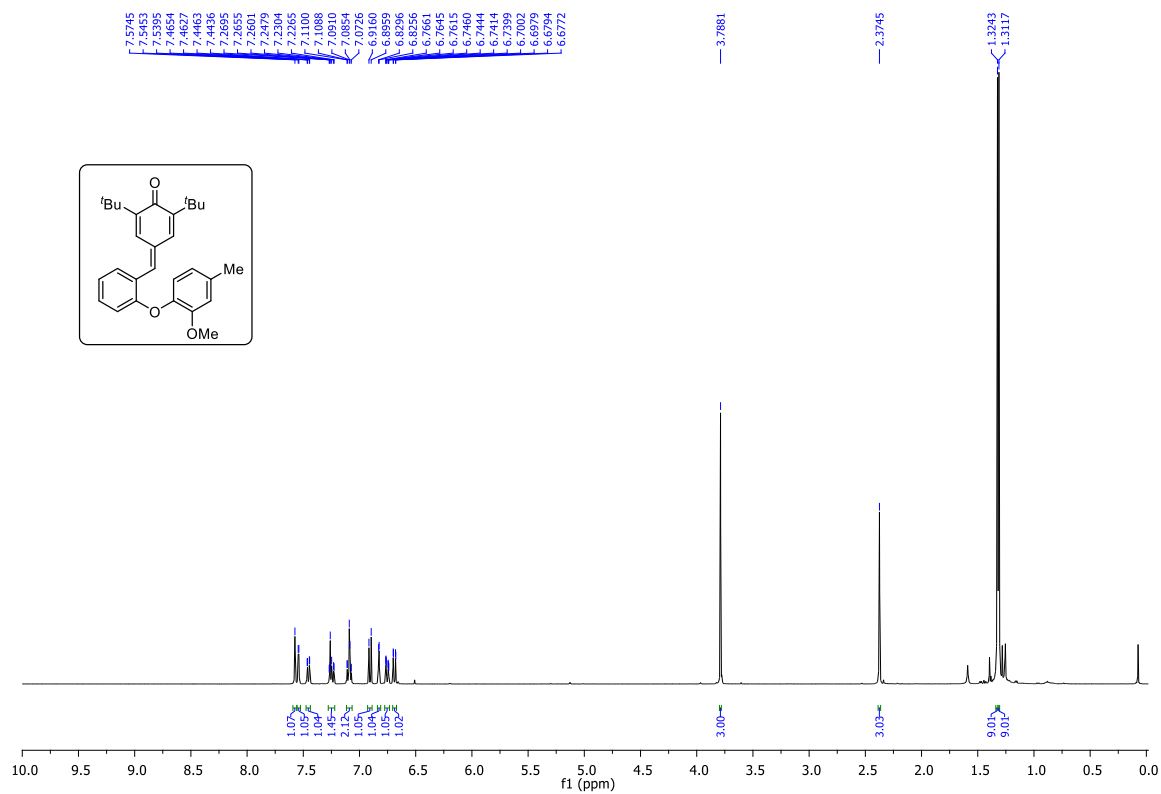
¹H NMR (400 MHz, CDCl₃) spectrum of **1h**



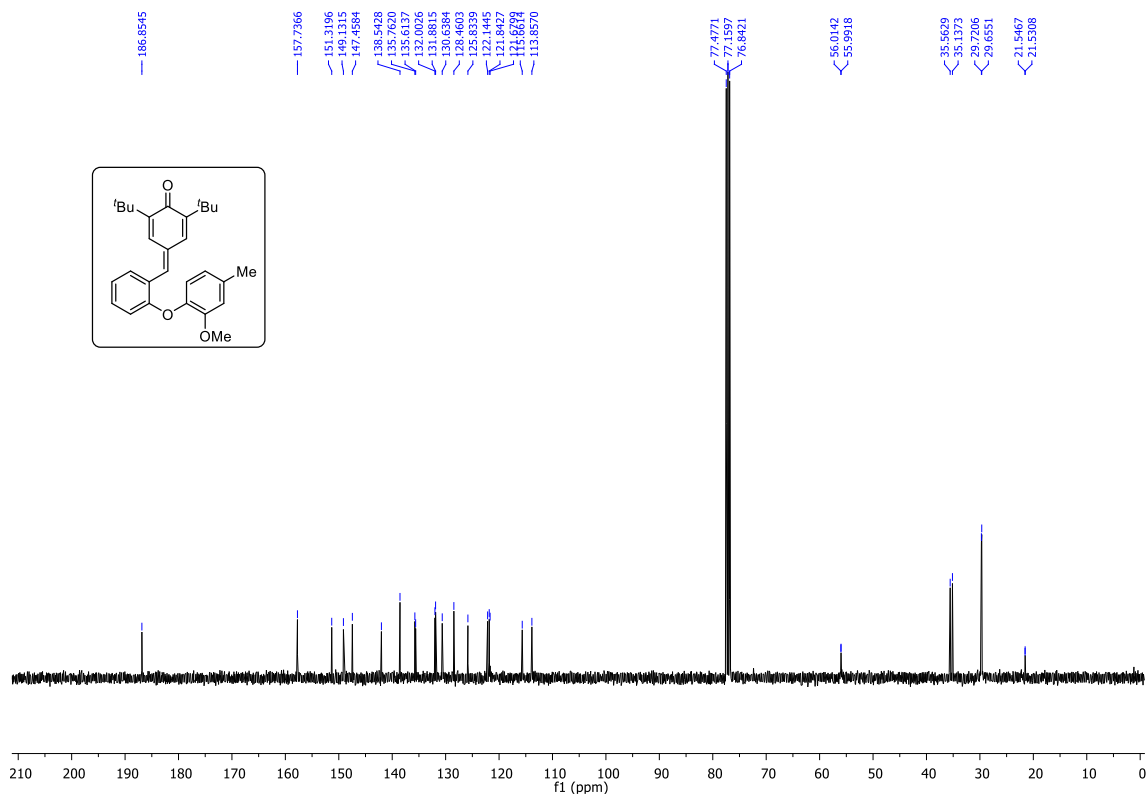
¹³C NMR (100 MHz, CDCl₃) spectrum of **1h**



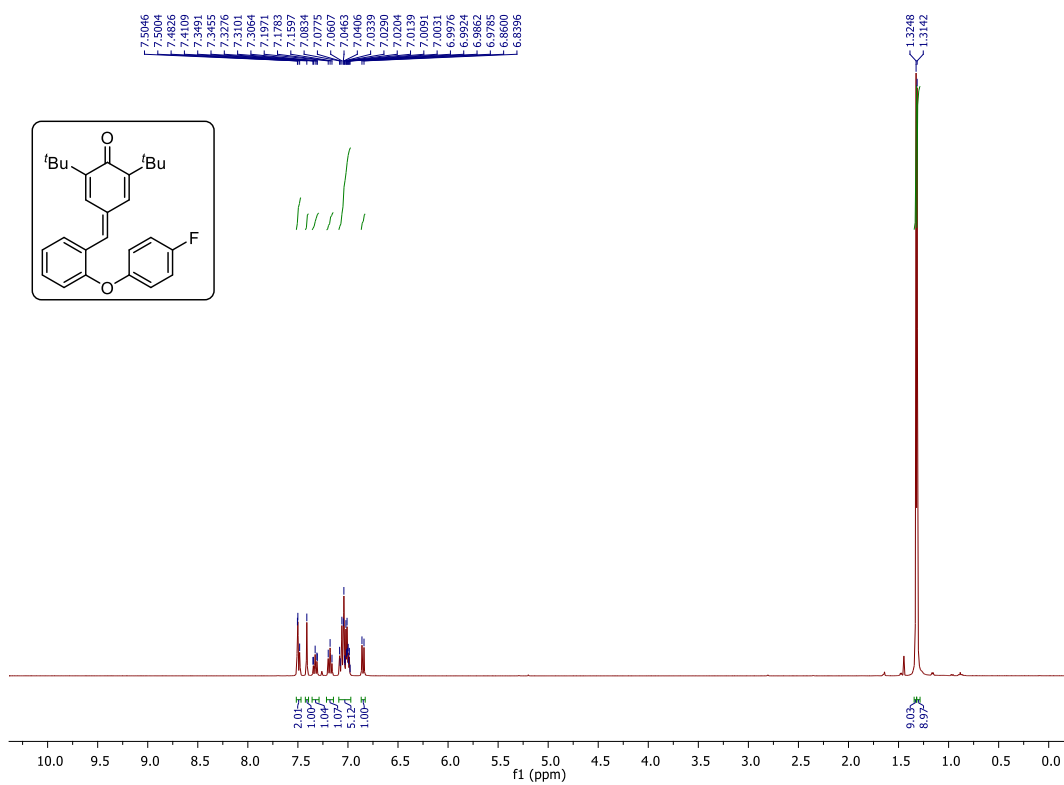
¹H NMR (400 MHz, CDCl₃) spectrum of **1i**



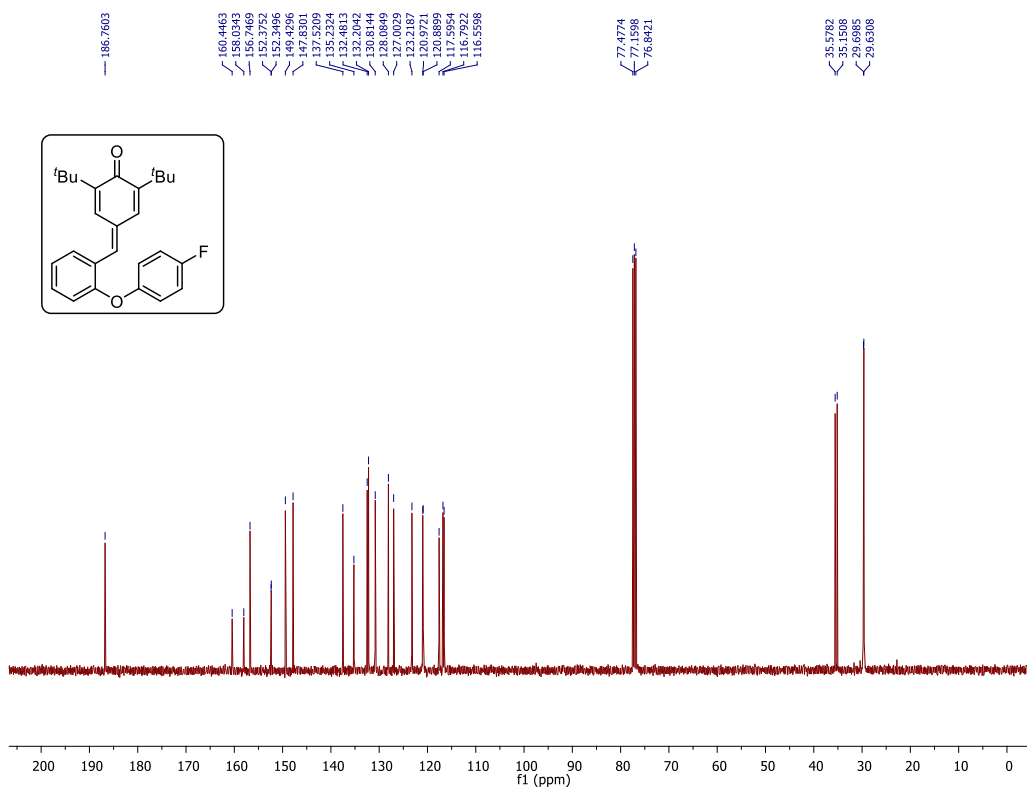
¹³C NMR (100 MHz, CDCl₃) spectrum of **1i**



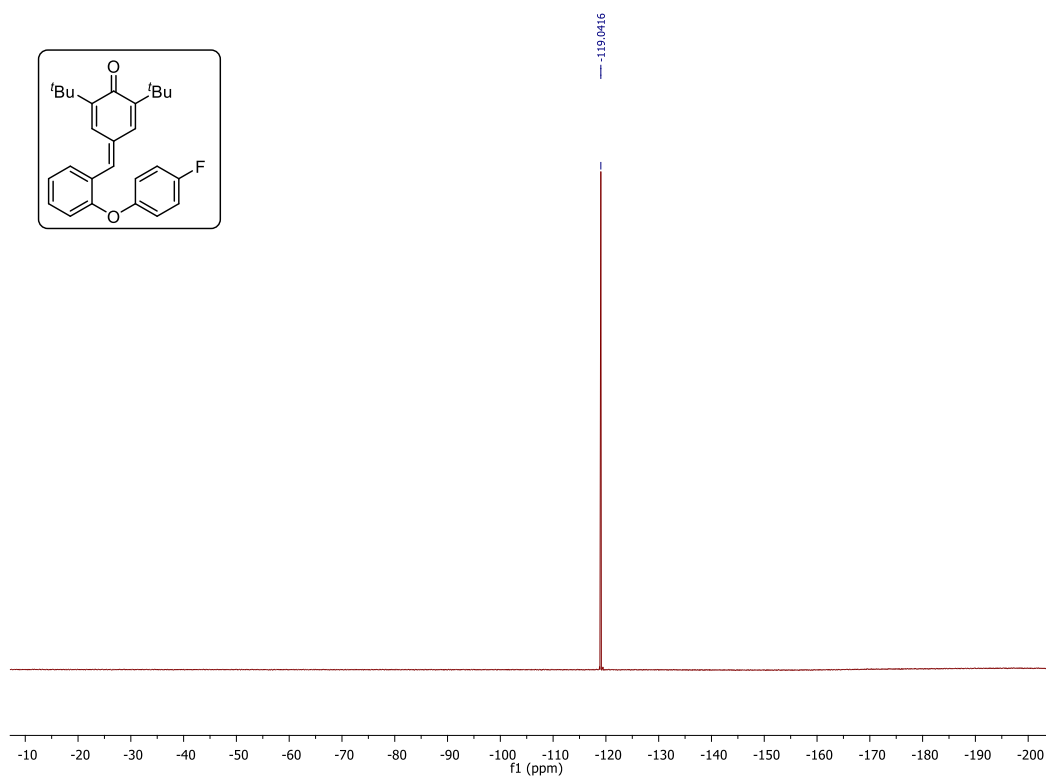
¹H NMR (400 MHz, CDCl₃) spectrum of **1j**



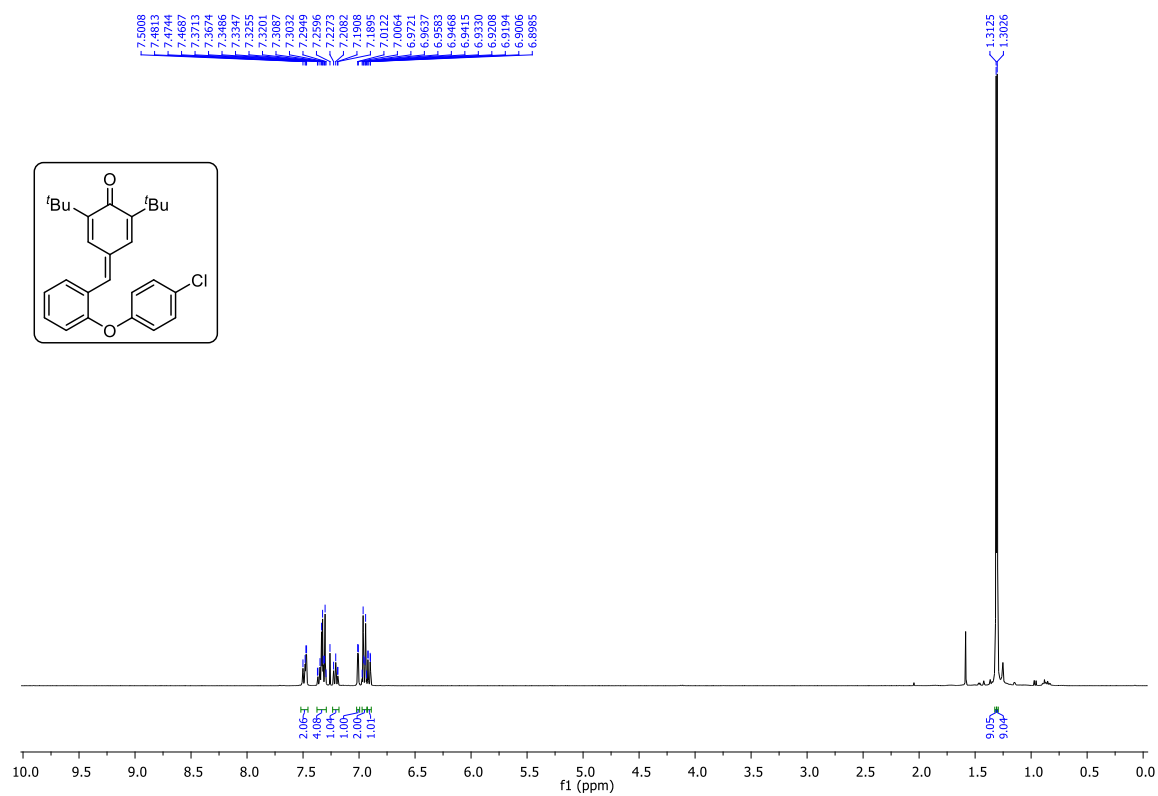
¹³C NMR (100 MHz, CDCl₃) spectrum of **1j**



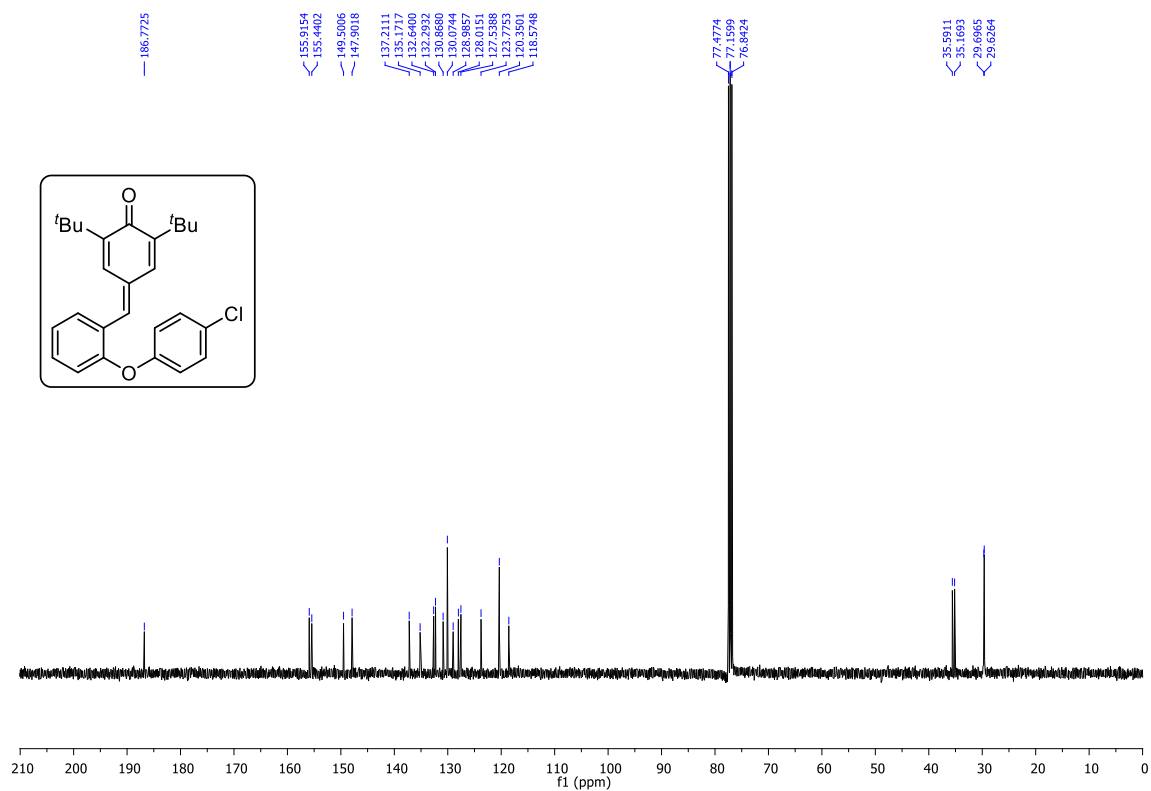
^{19}F $\{^1\text{H}\}$ NMR (376 MHz, CDCl_3) Spectrum of **1j**



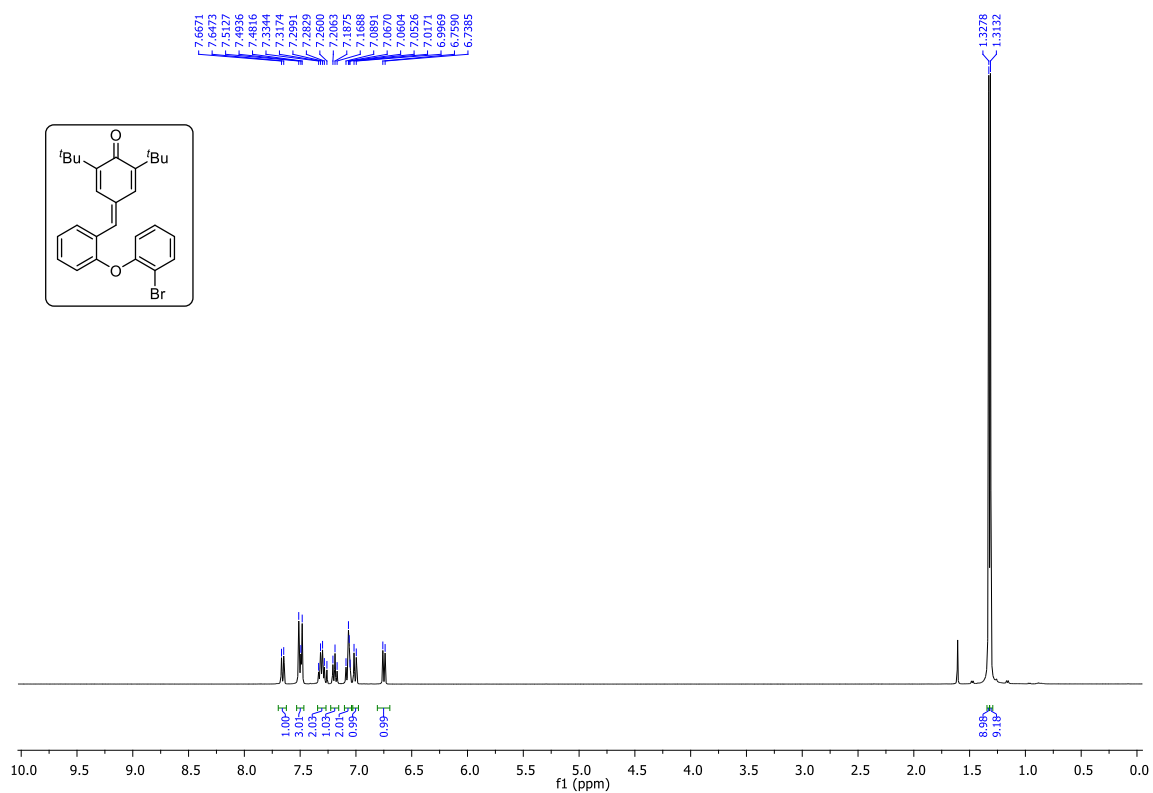
^1H NMR (400 MHz, CDCl_3) spectrum of **1k**



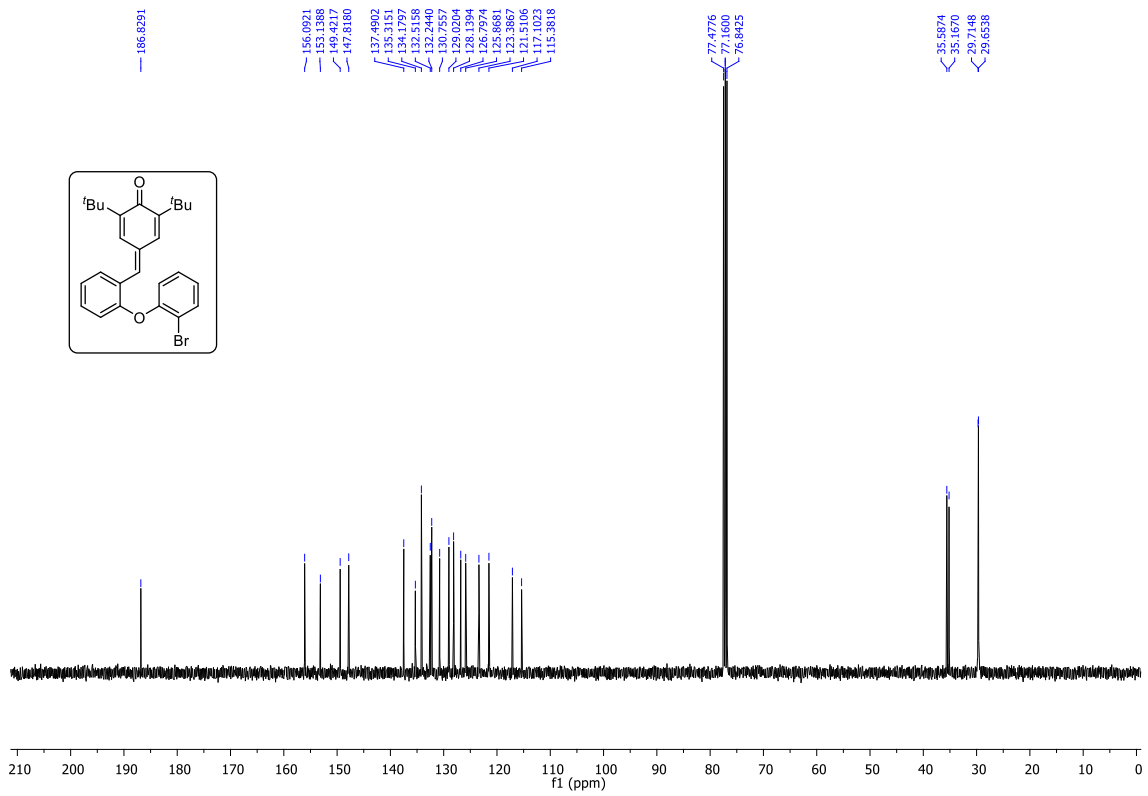
¹³C NMR (100 MHz, CDCl₃) spectrum of **1k**



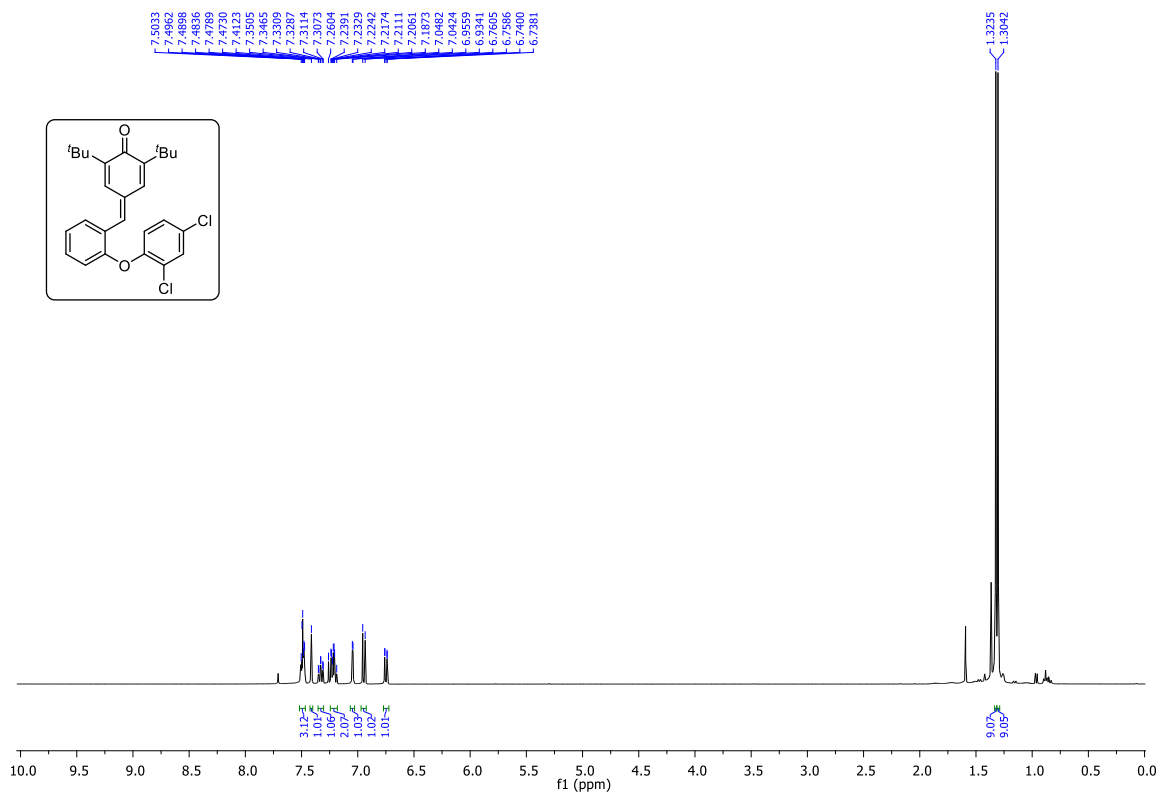
¹H NMR (400 MHz, CDCl₃) spectrum of **1l**



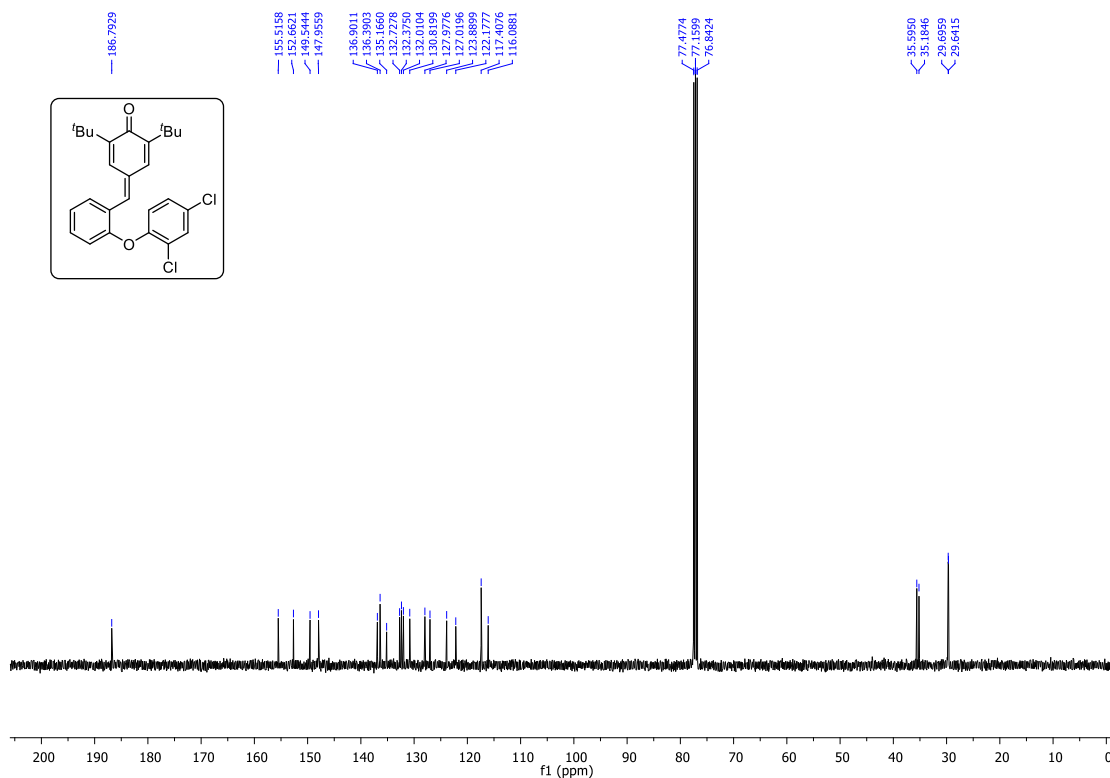
^{13}C NMR (100 MHz, CDCl_3) spectrum of **1l**



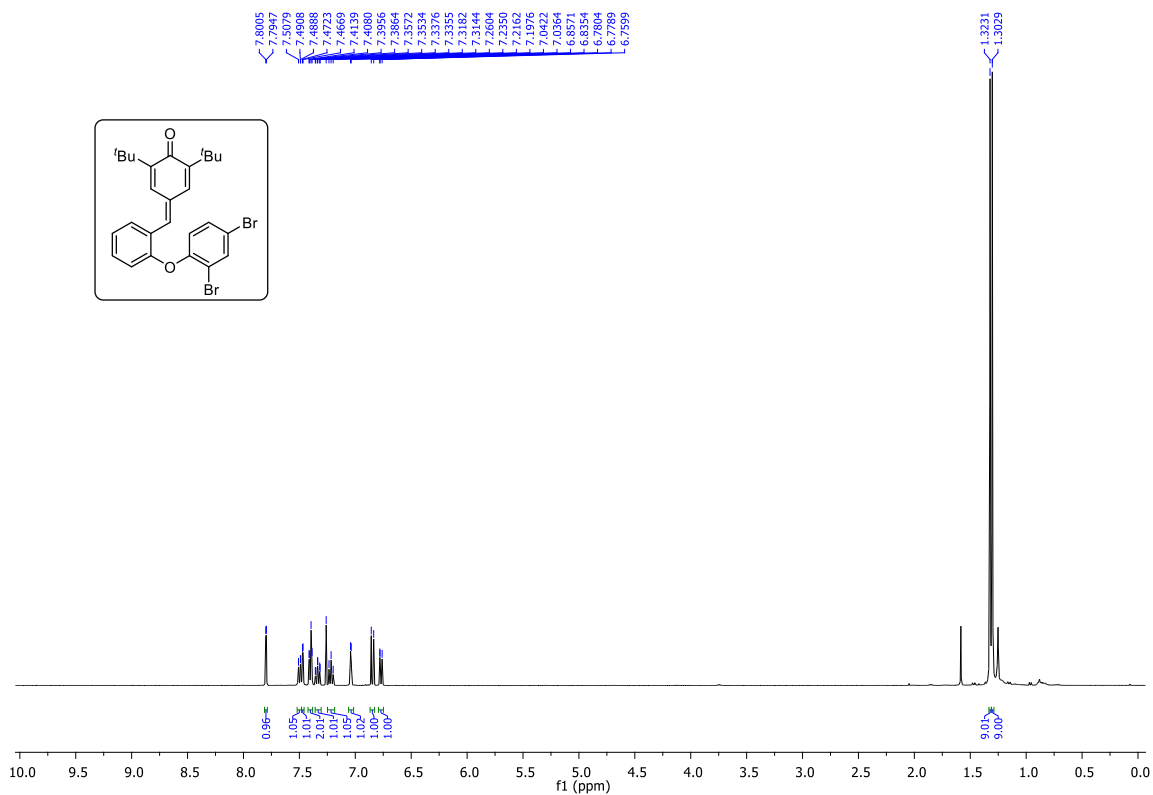
^1H NMR (400 MHz, CDCl_3) spectrum of **1m**



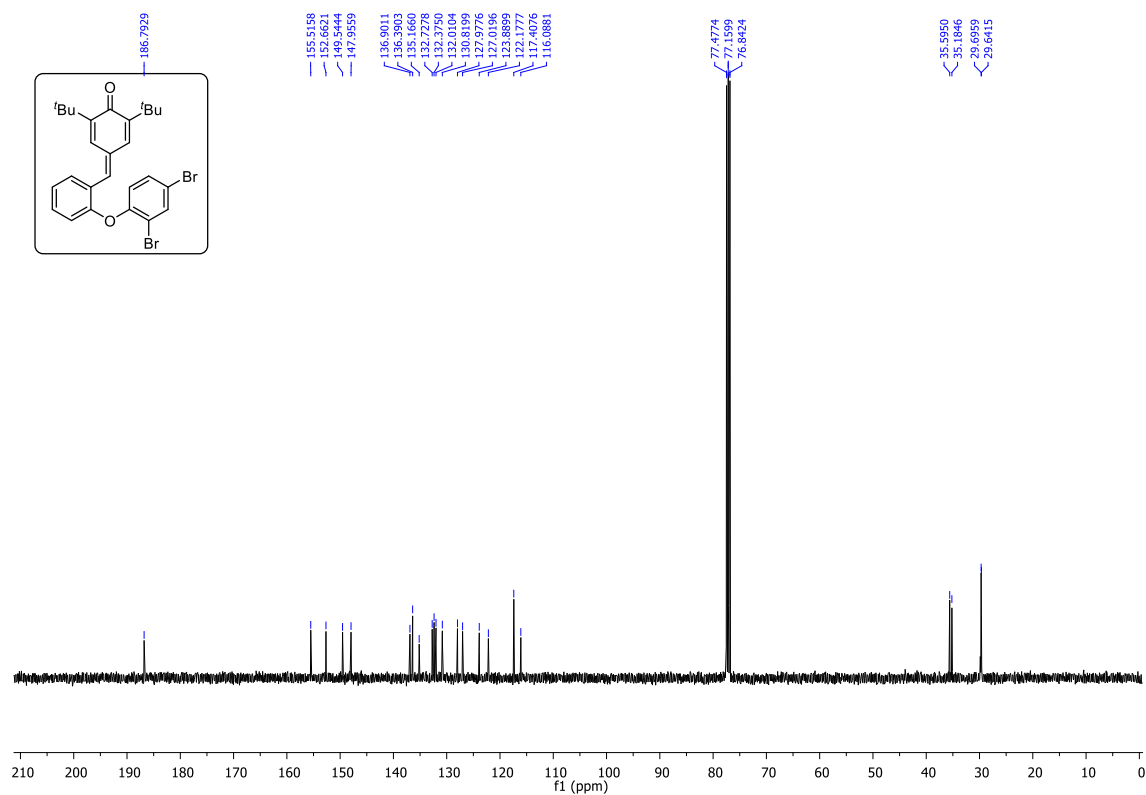
^{13}C NMR (100 MHz, CDCl_3) spectrum of **1m**



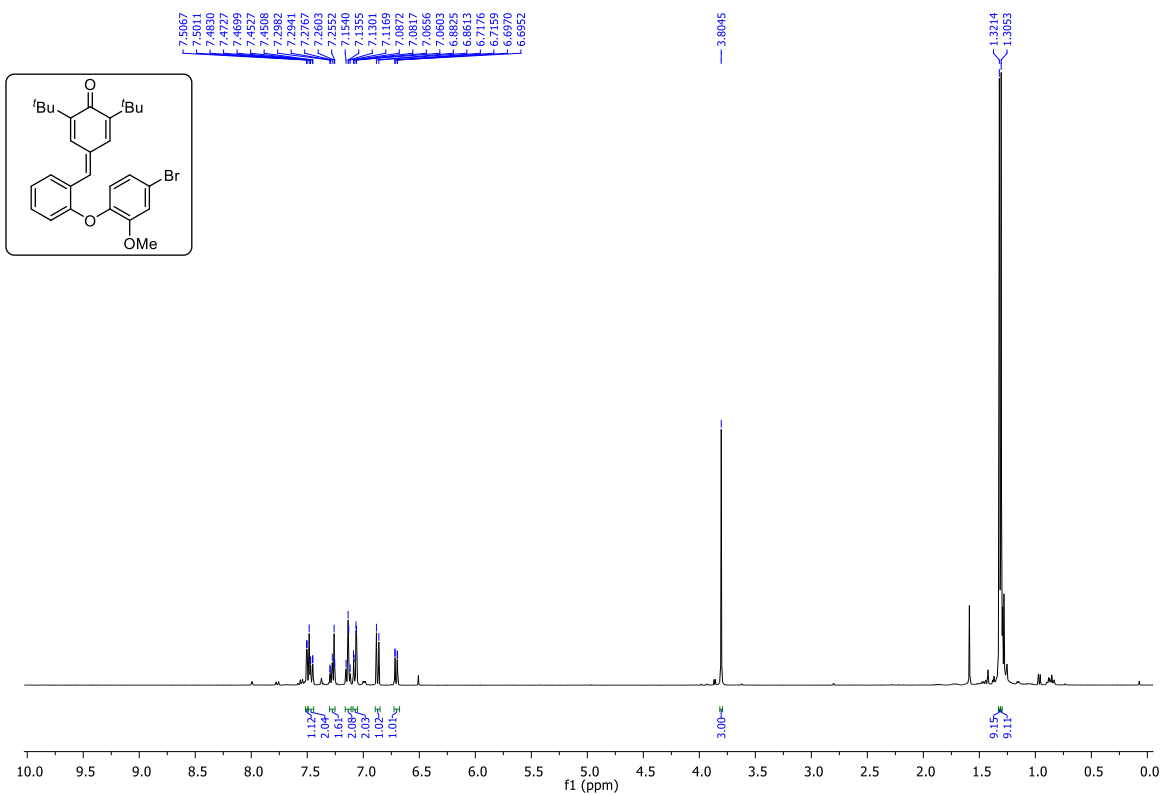
^1H NMR (400 MHz, CDCl_3) spectrum of **1n**



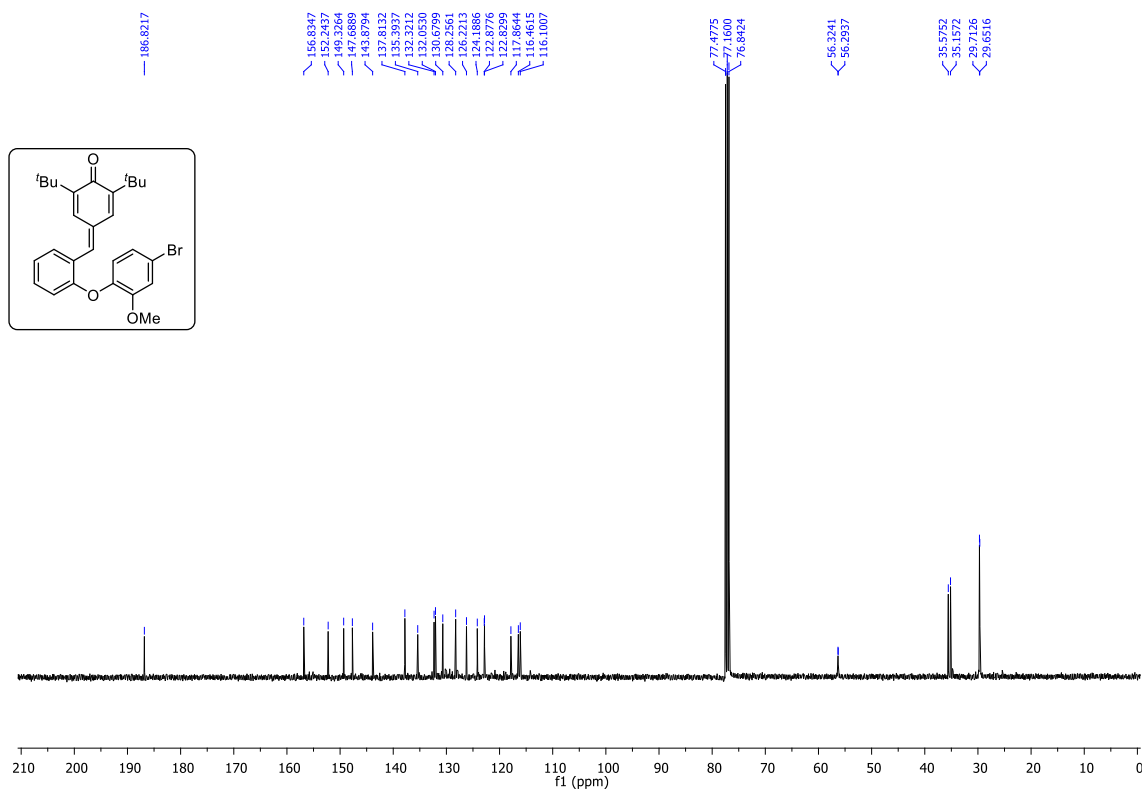
^{13}C NMR (100 MHz, CDCl_3) spectrum of **1n**



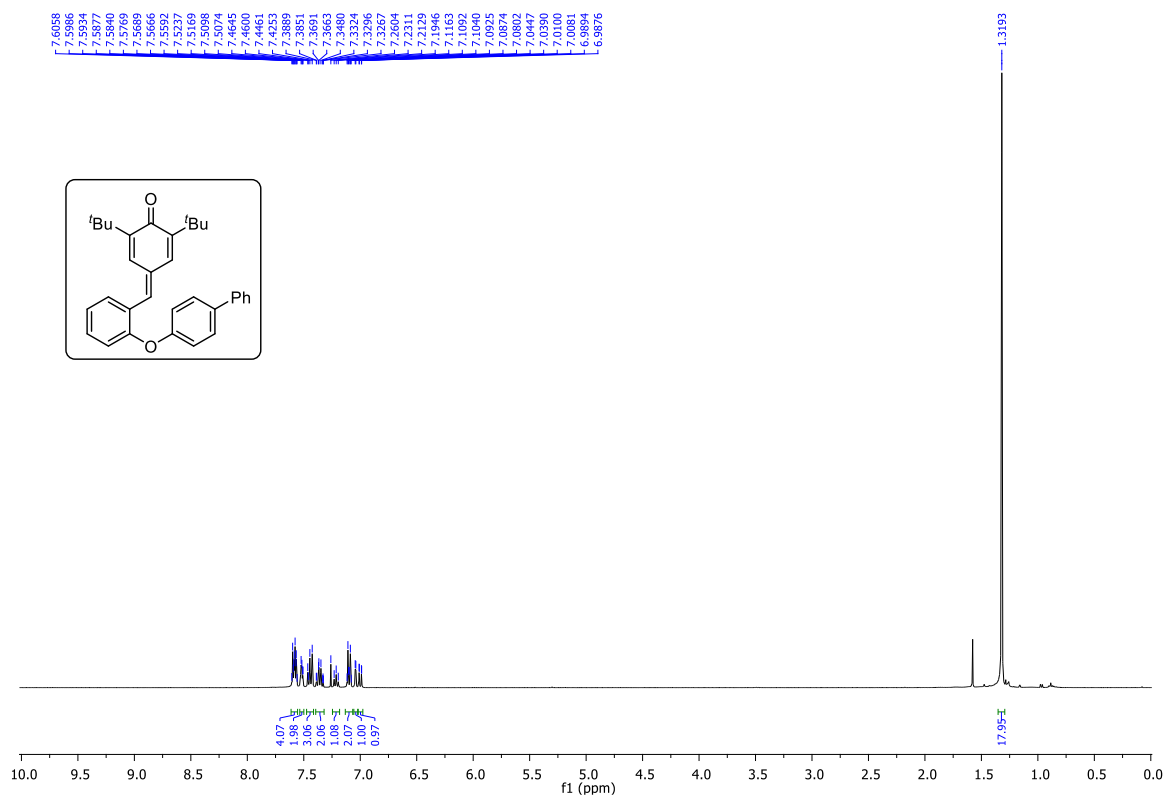
^1H NMR (400 MHz, CDCl_3) spectrum of **1o**



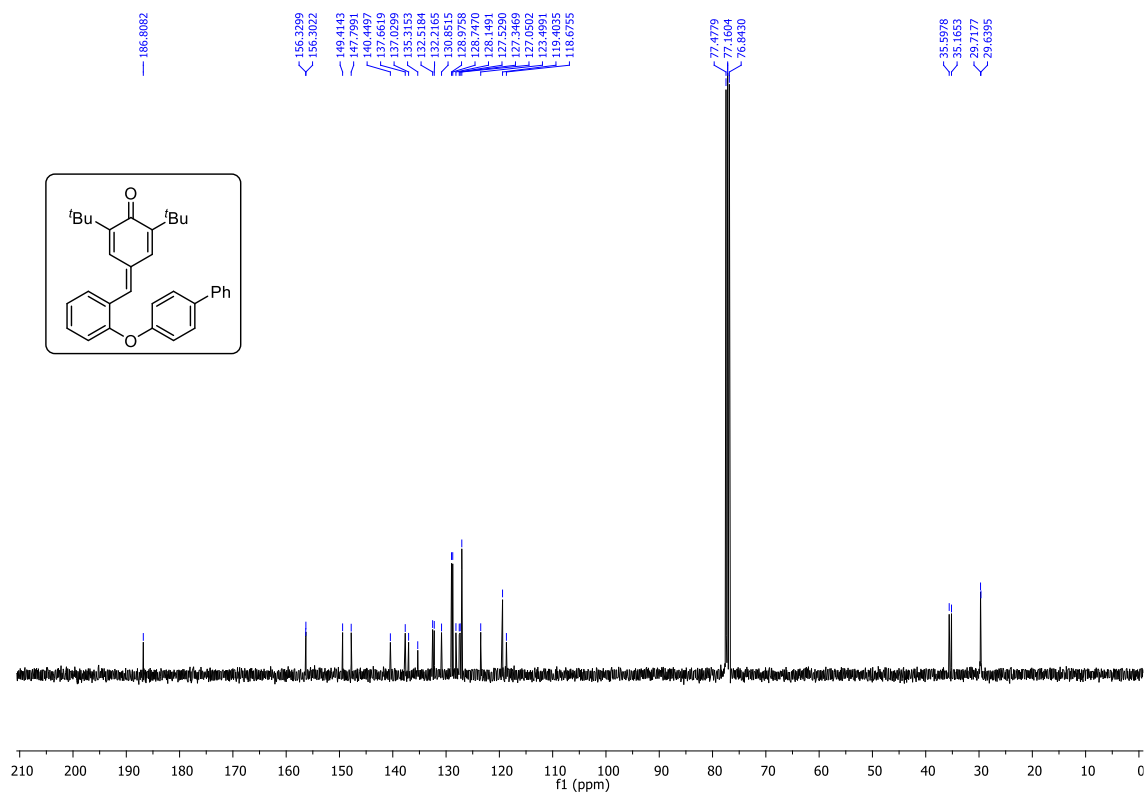
^{13}C NMR (100 MHz, CDCl_3) spectrum of **1o**



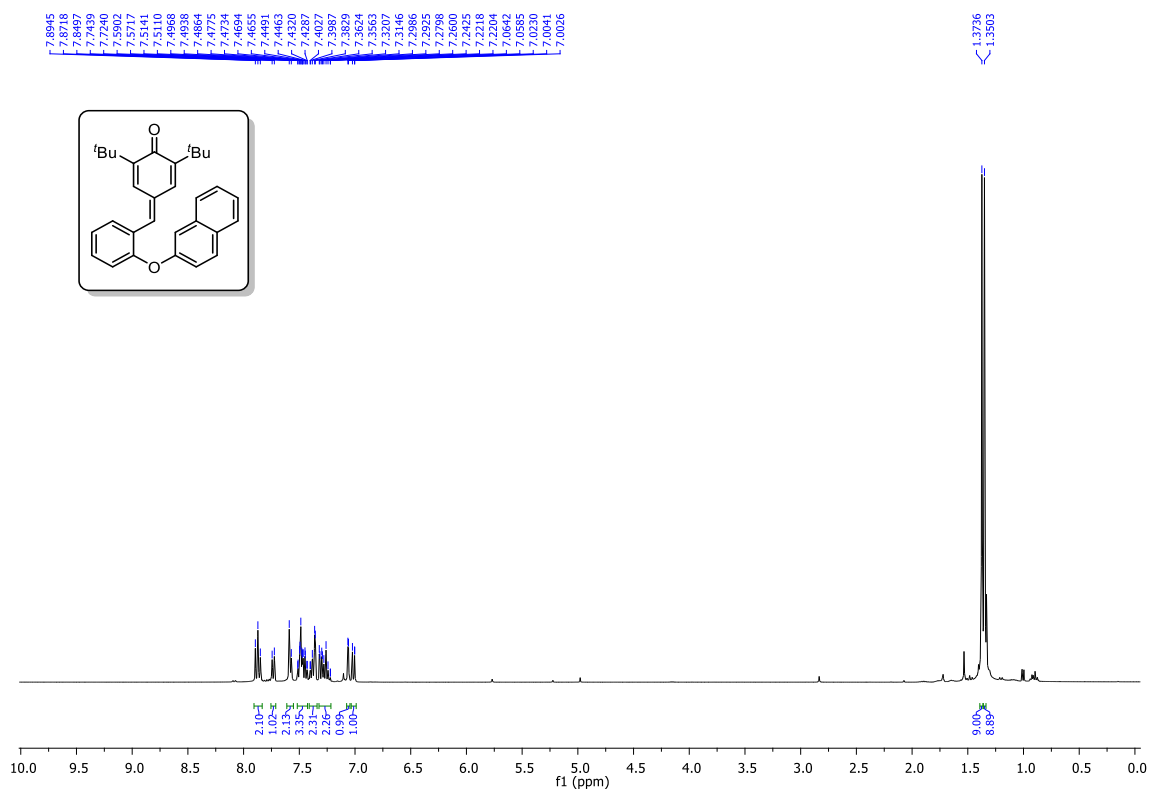
^1H NMR (400 MHz, CDCl_3) spectrum of **1p**



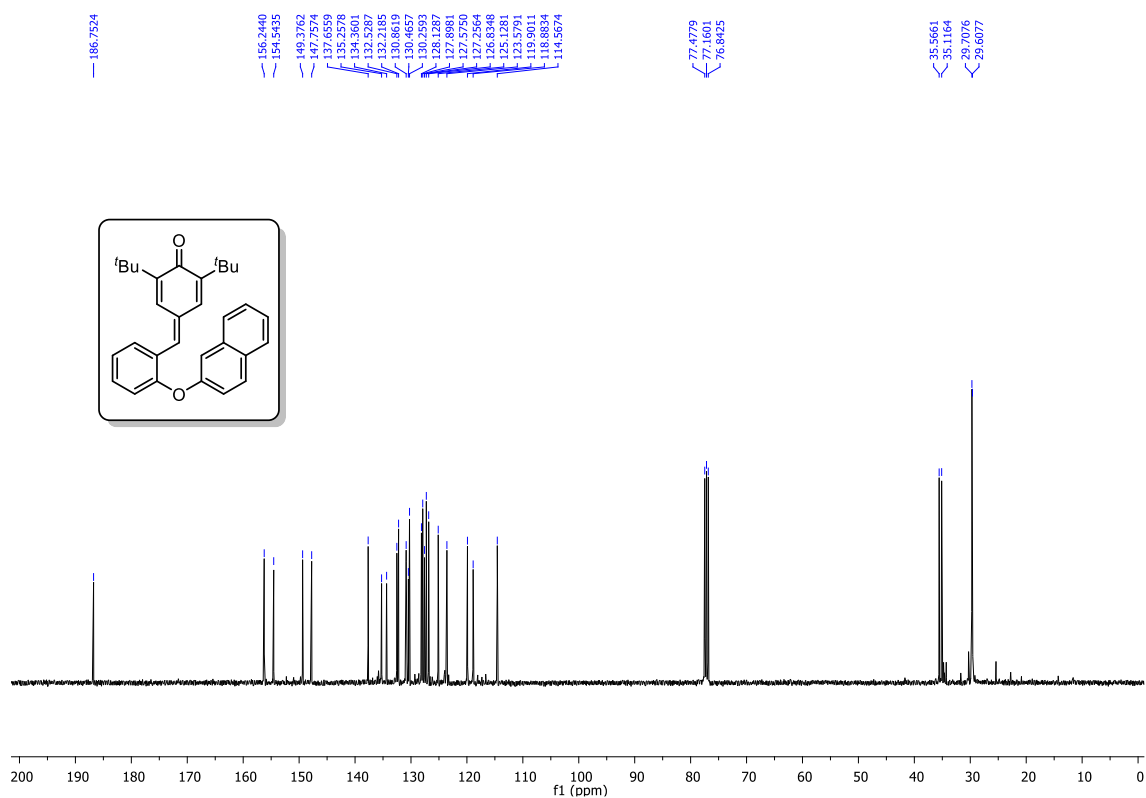
¹³C NMR (100 MHz, CDCl₃) spectrum of **1p**



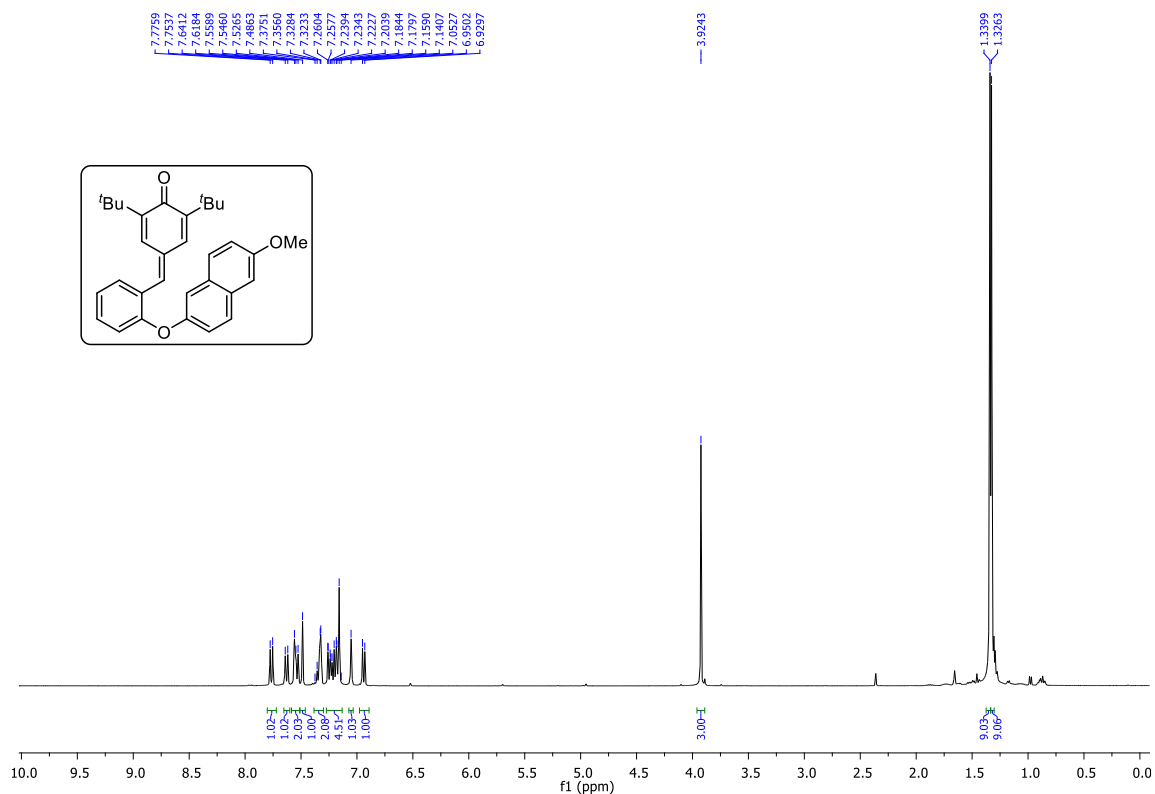
¹H NMR (400 MHz, CDCl₃) spectrum of **1q**



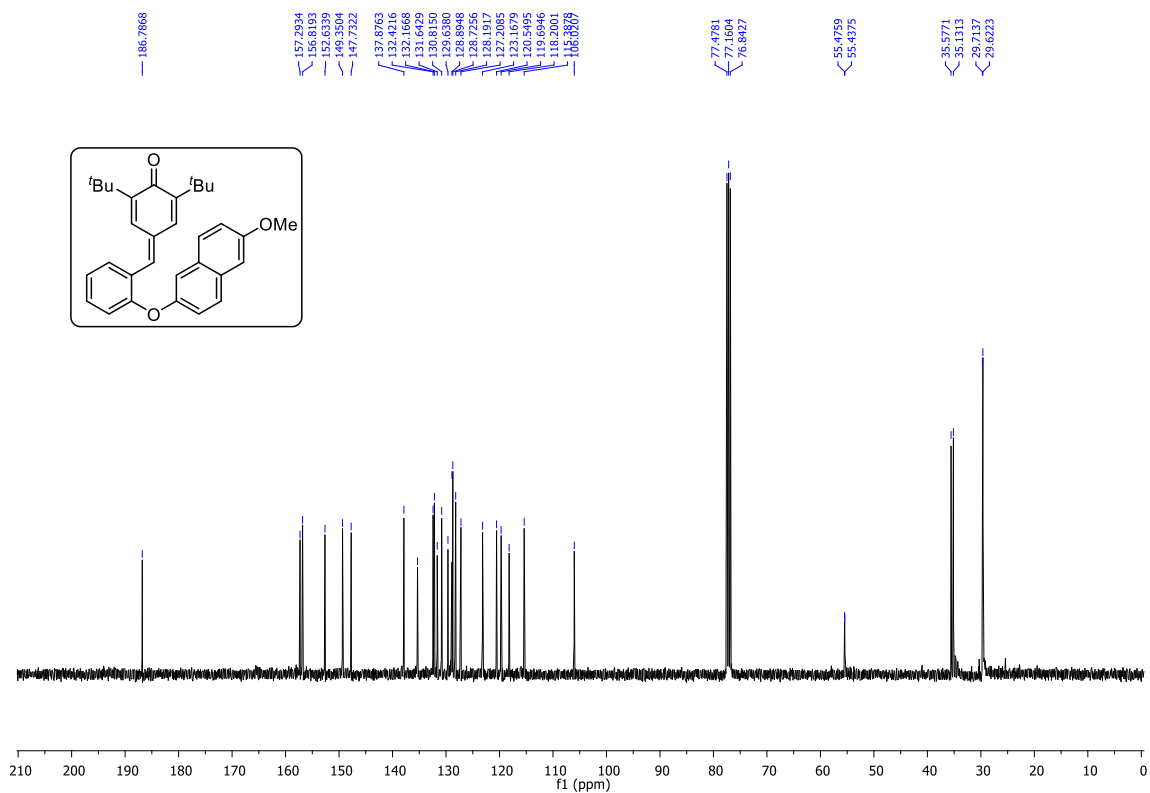
¹³C NMR (100 MHz, CDCl₃) spectrum of **1q**



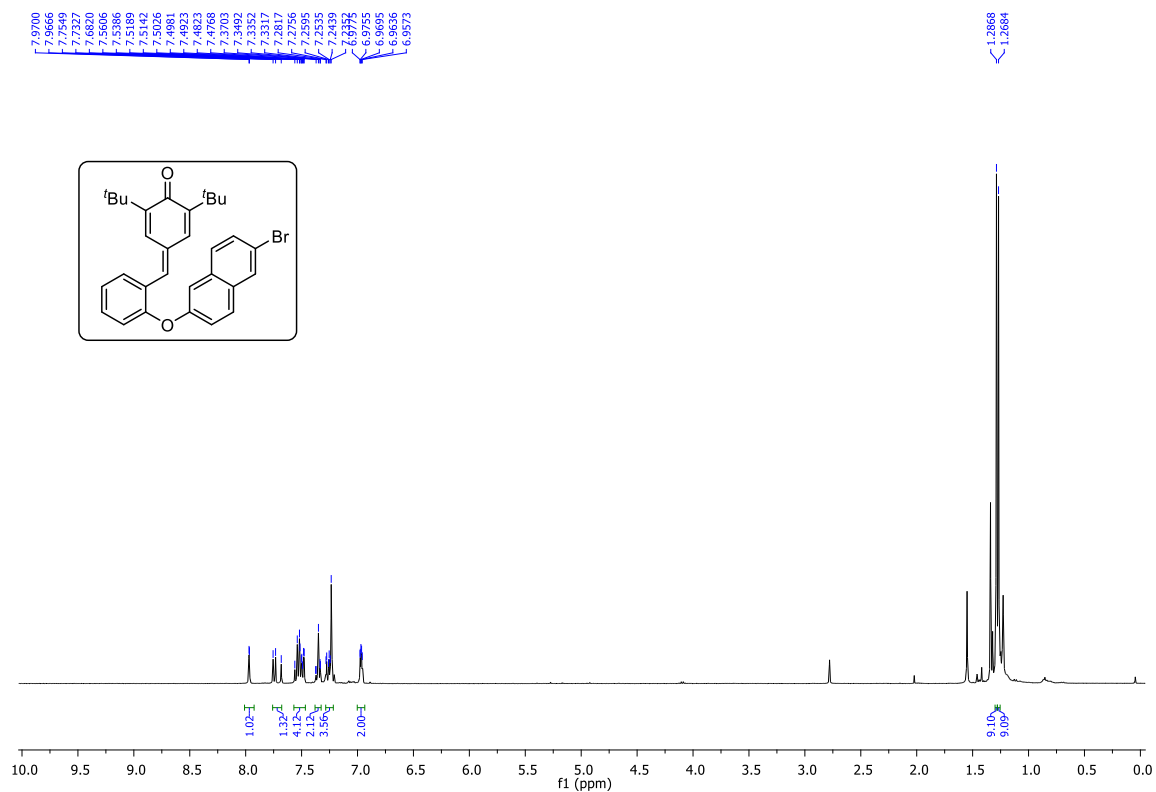
¹H NMR (400 MHz, CDCl₃) spectrum of **1r**



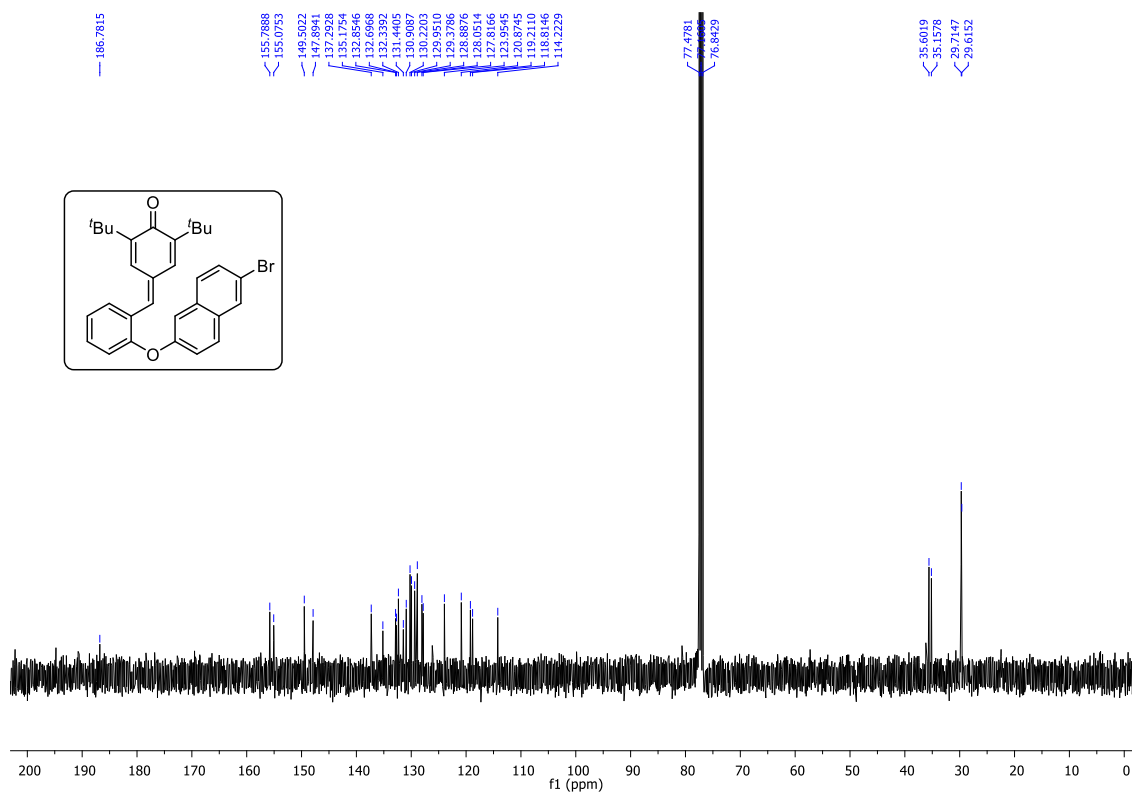
^{13}C NMR (100 MHz, CDCl_3) spectrum of **1r**



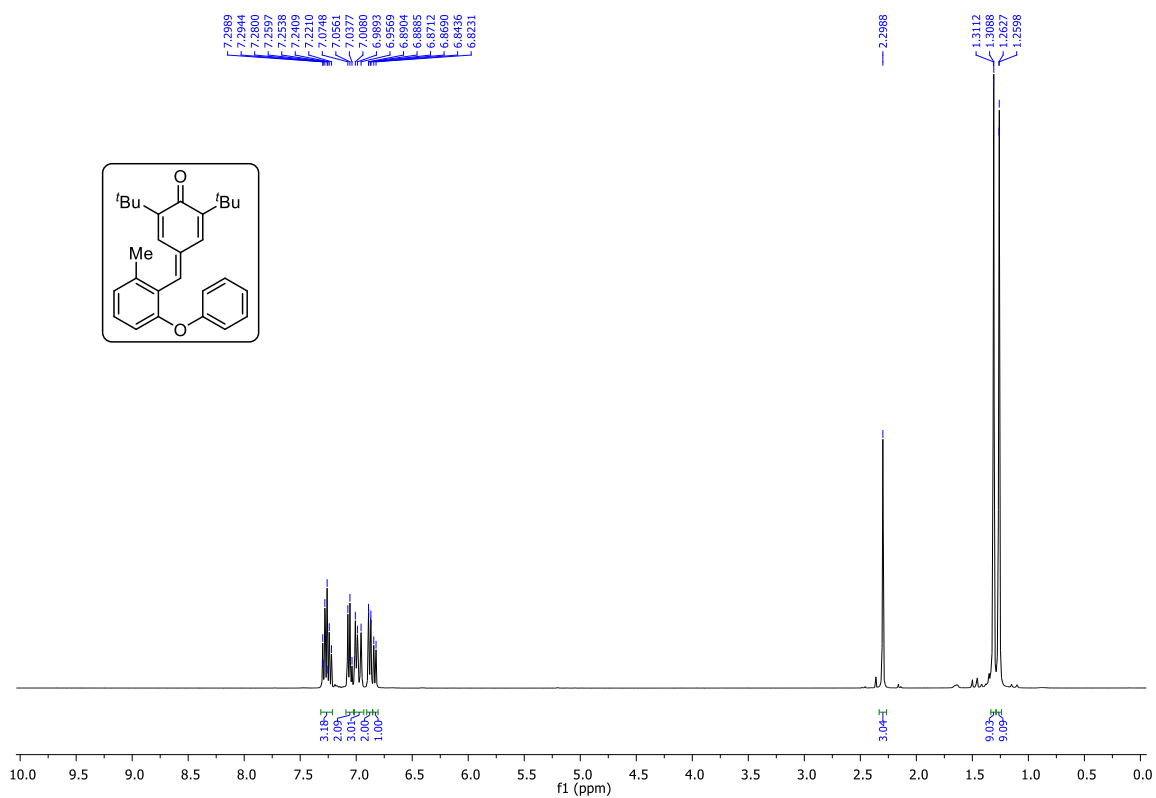
^1H NMR (400 MHz, CDCl_3) spectrum of **1s**



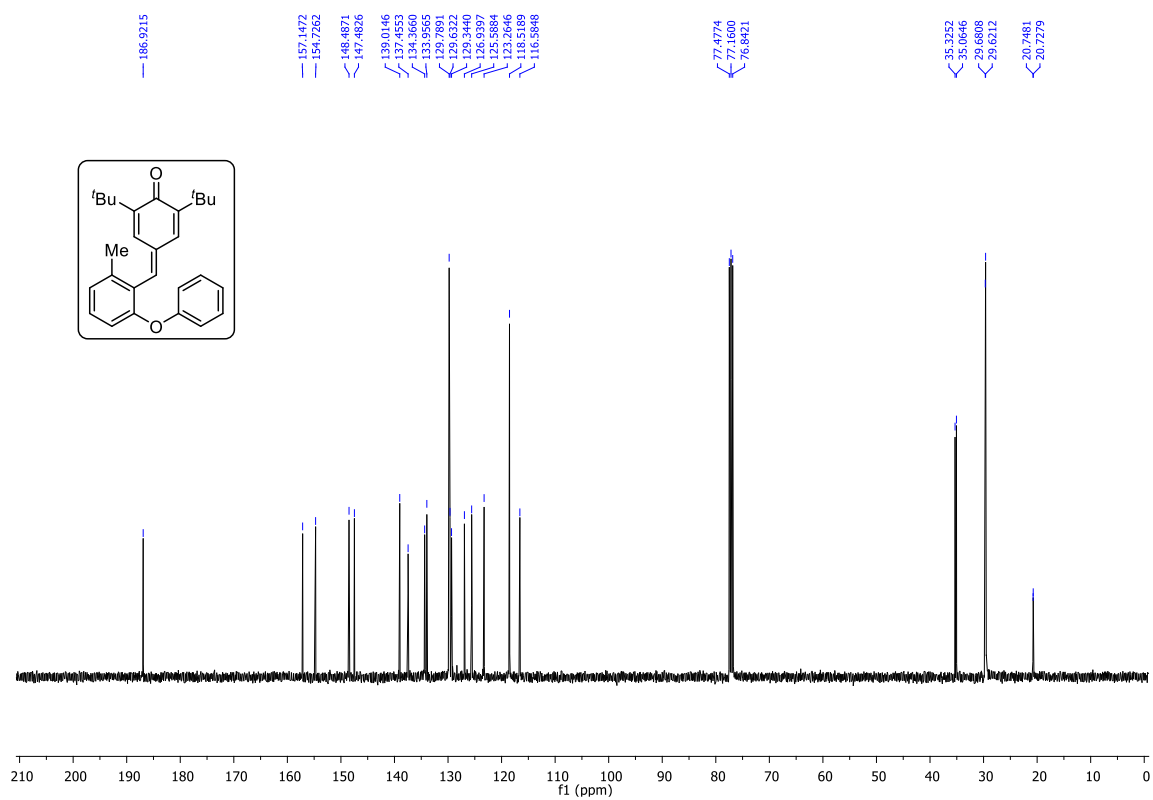
¹³C NMR (100 MHz, CDCl₃) spectrum of **1s**



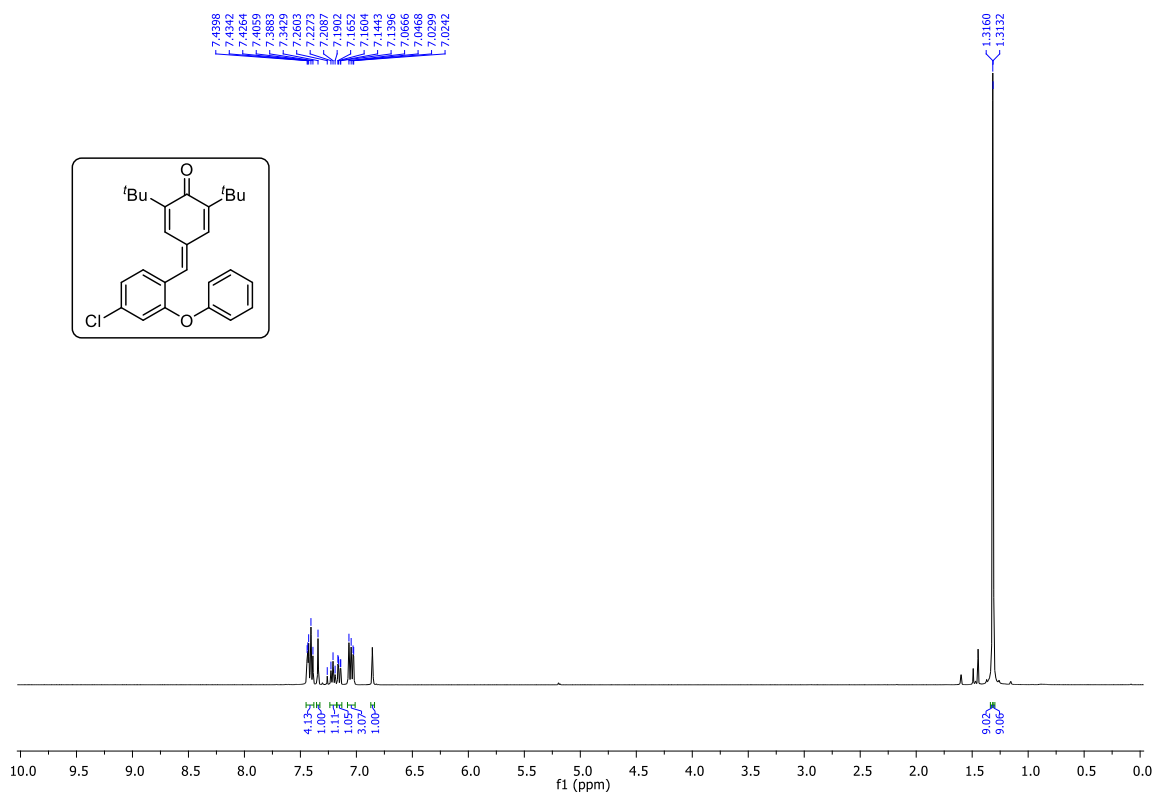
¹H NMR (400 MHz, CDCl₃) spectrum of **1t**



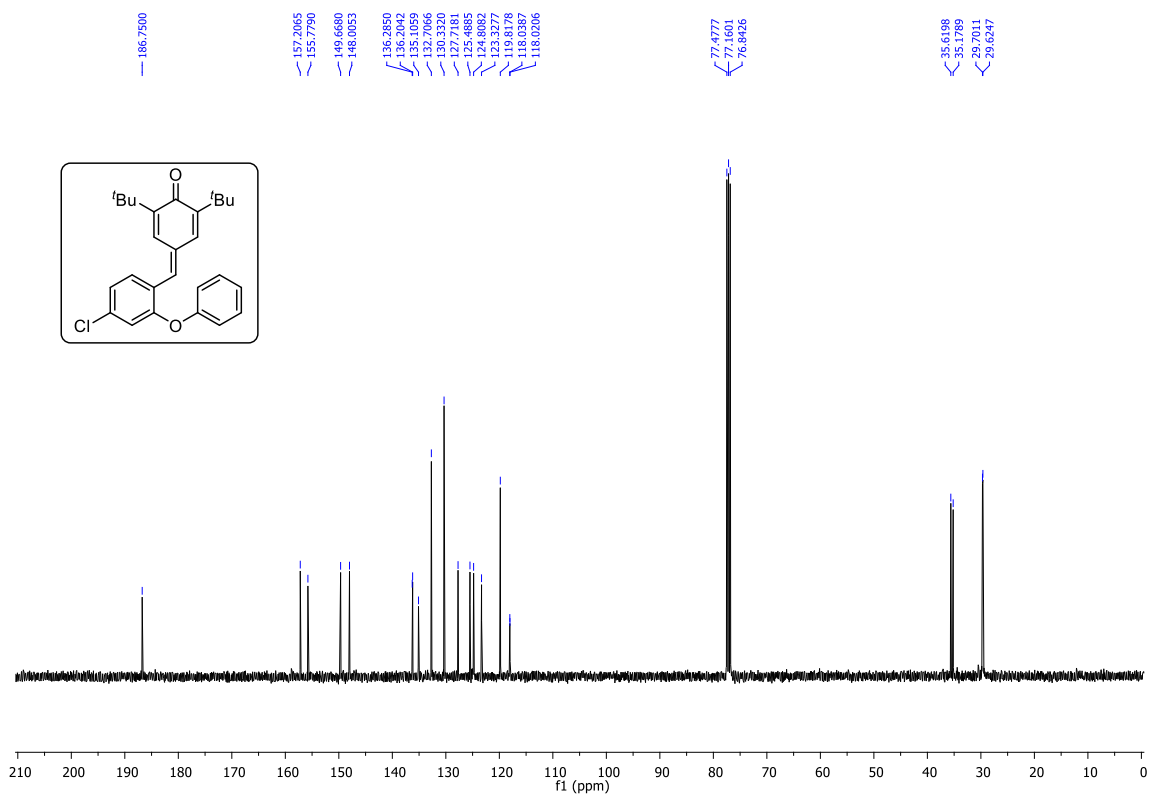
^{13}C NMR (100 MHz, CDCl_3) spectrum of **1t**



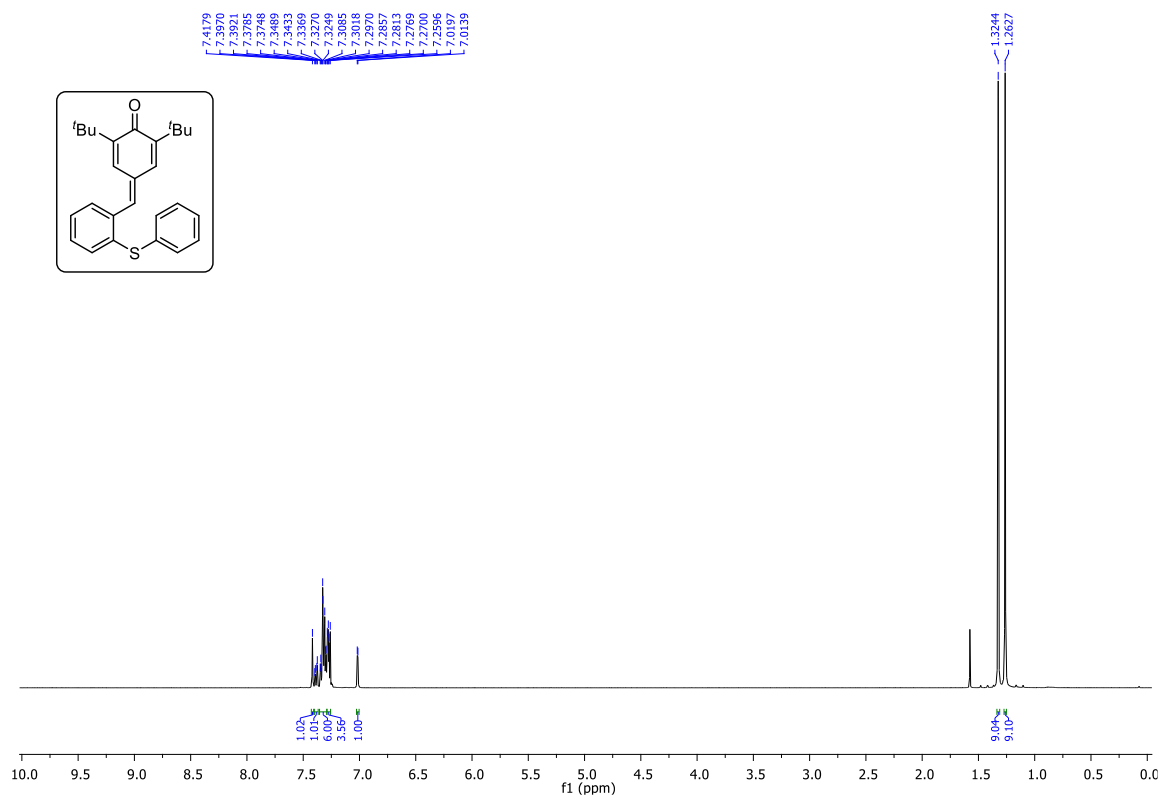
^1H NMR (400 MHz, CDCl_3) spectrum of **1u**



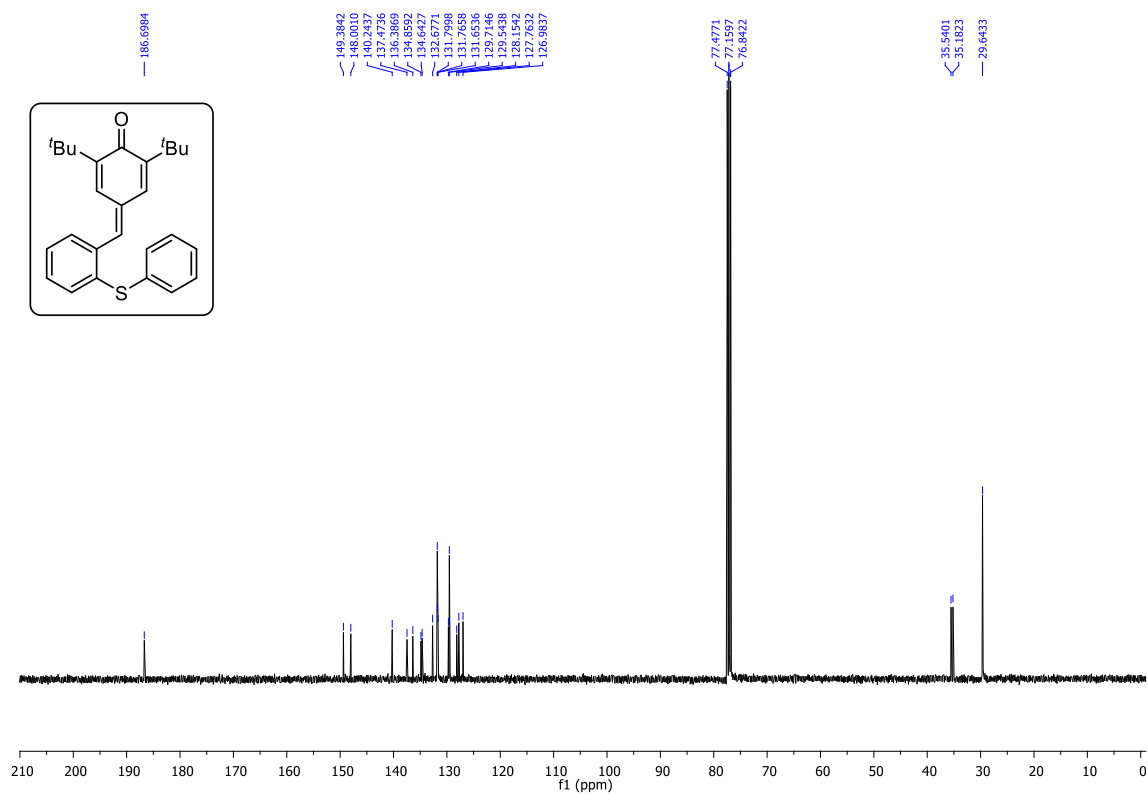
^{13}C NMR (100 MHz, CDCl_3) spectrum of **1u**



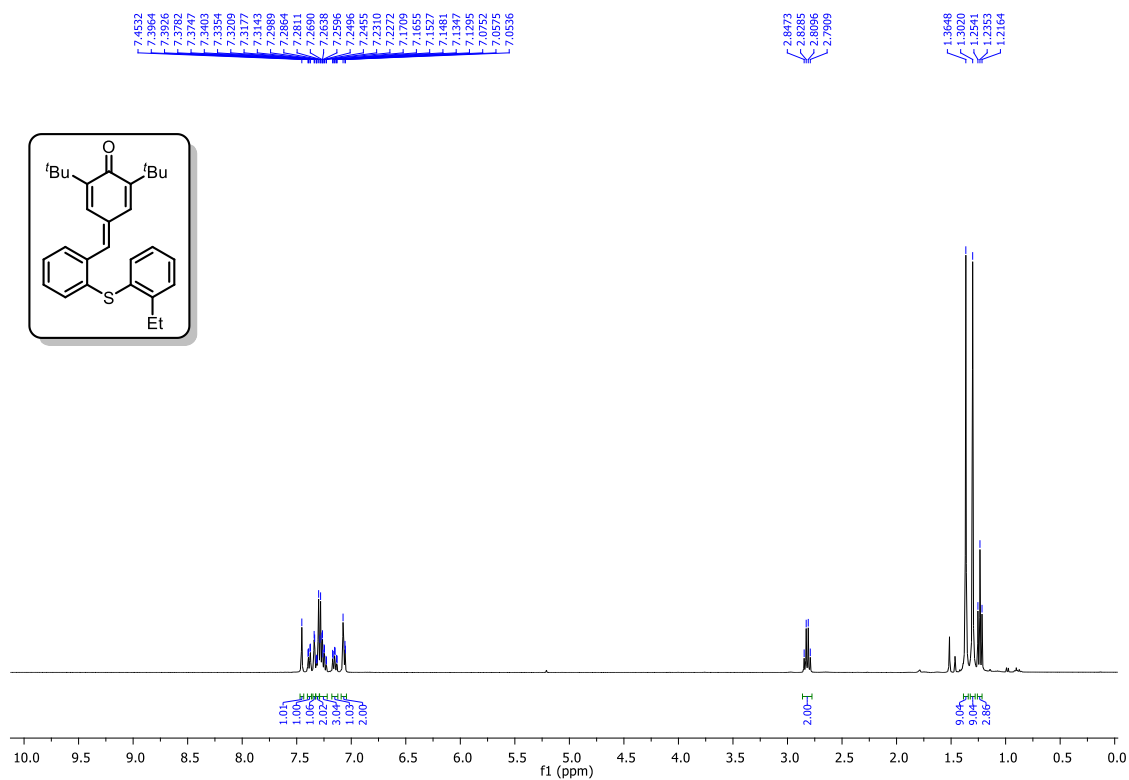
^1H NMR (400 MHz, CDCl_3) spectrum of **3a**



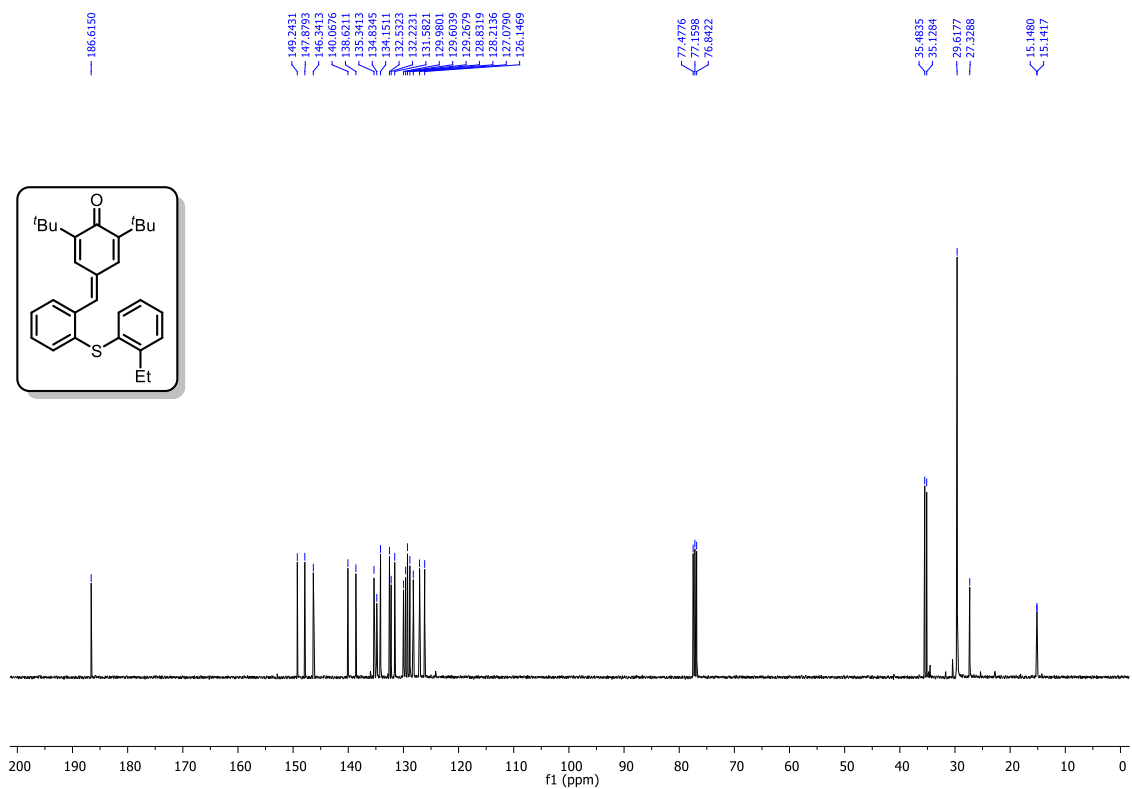
¹³C NMR (100 MHz, CDCl₃) spectrum of **3a**



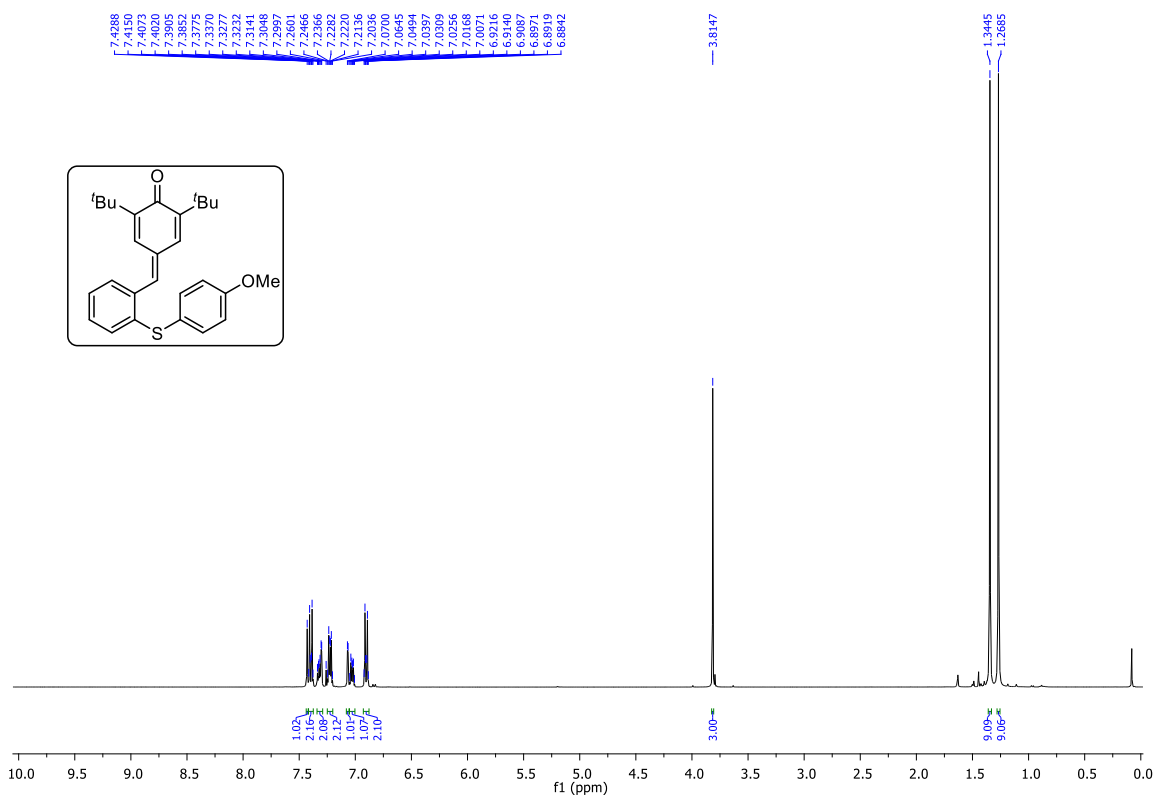
¹H NMR (400 MHz, CDCl₃) spectrum of **3b**



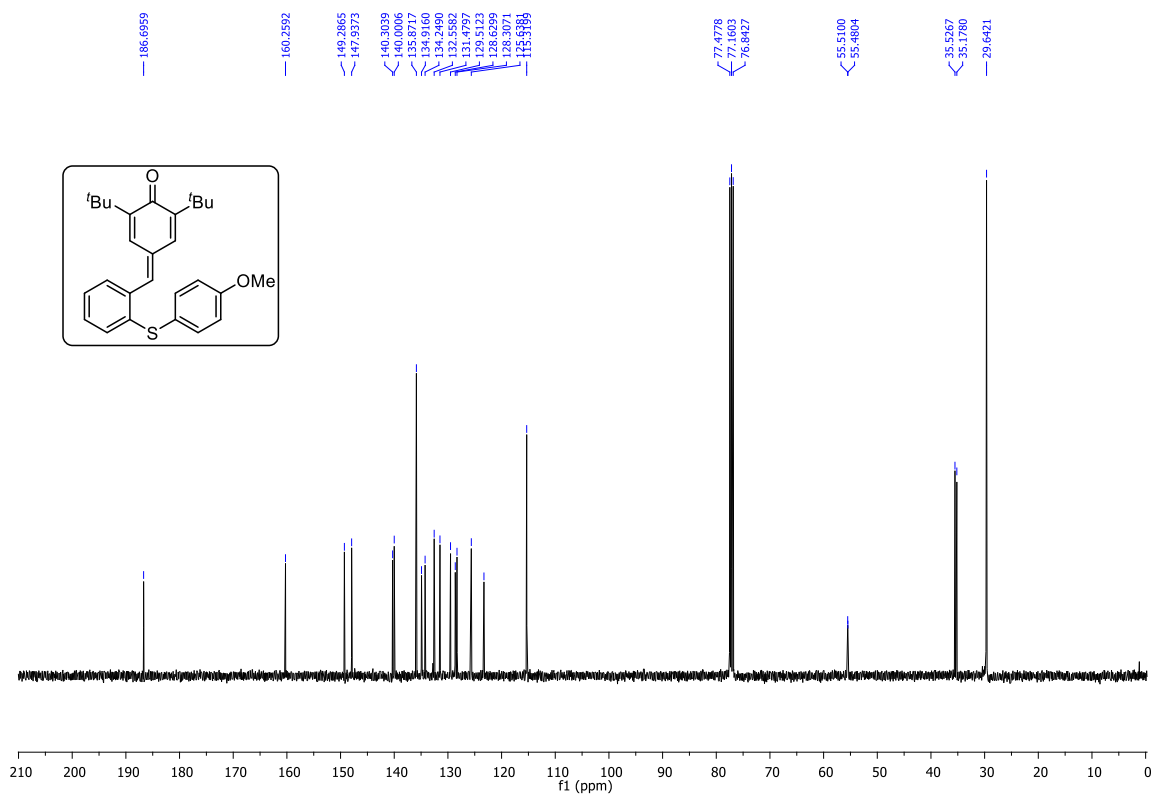
¹³C NMR (100 MHz, CDCl₃) spectrum of **3b**



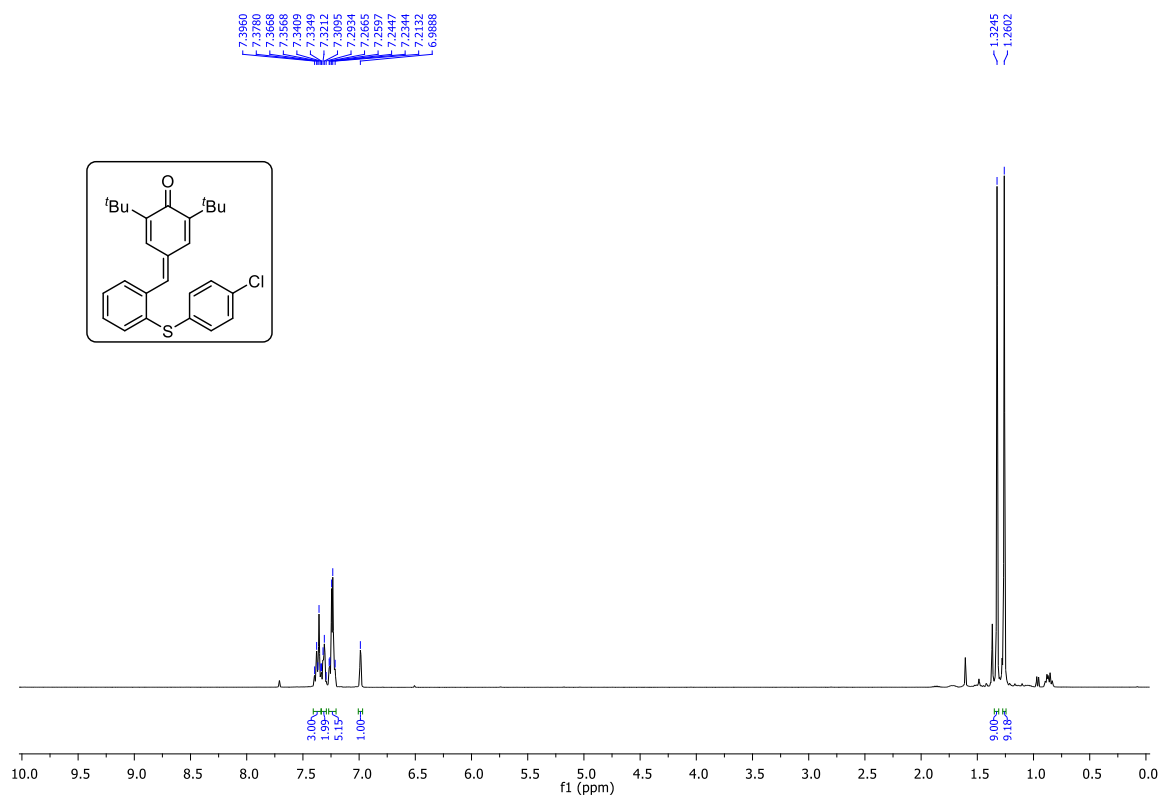
¹H NMR (400 MHz, CDCl₃) spectrum of **3c**



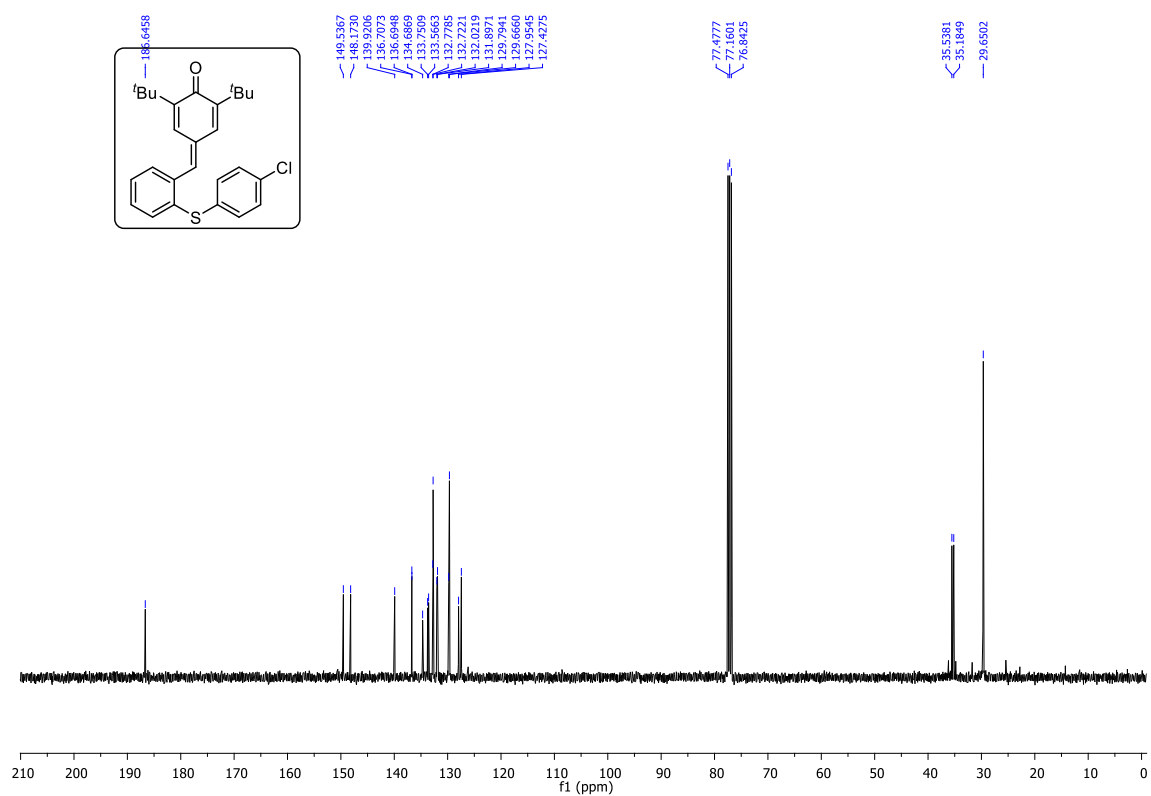
^{13}C NMR (100 MHz, CDCl_3) spectrum of **3c**



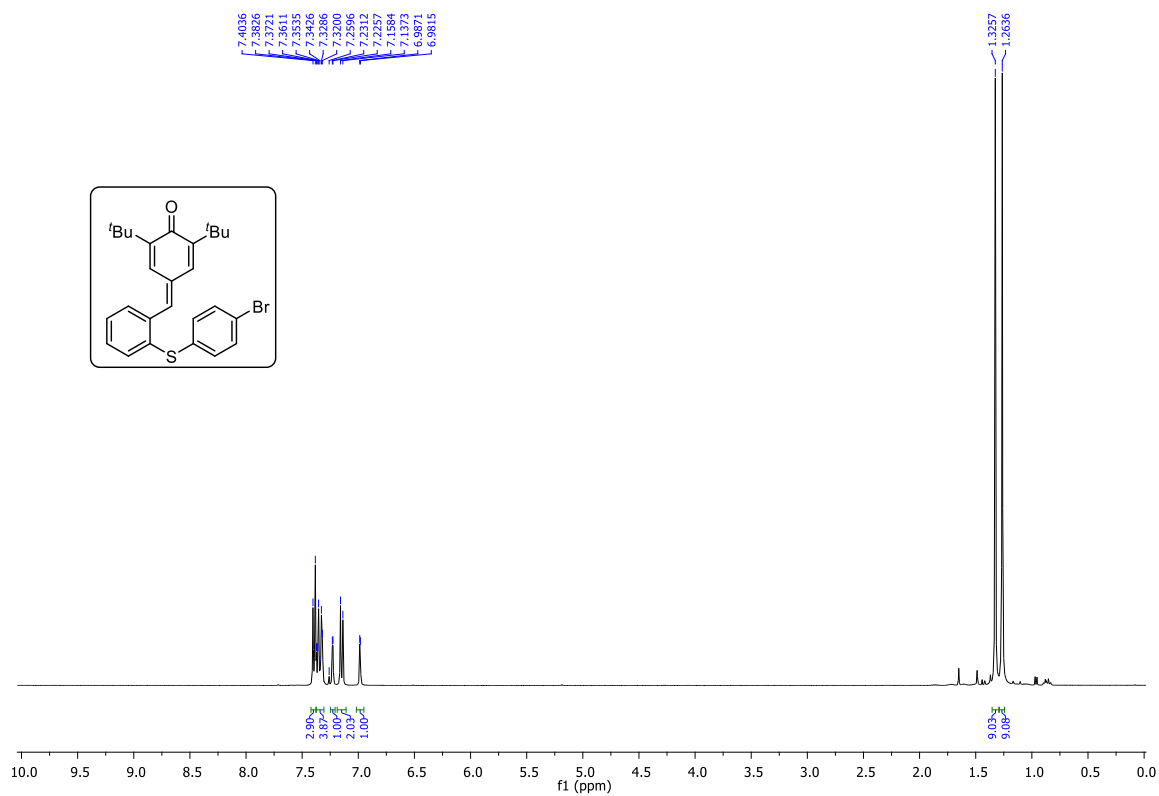
^1H NMR (400 MHz, CDCl_3) spectrum of **3d**



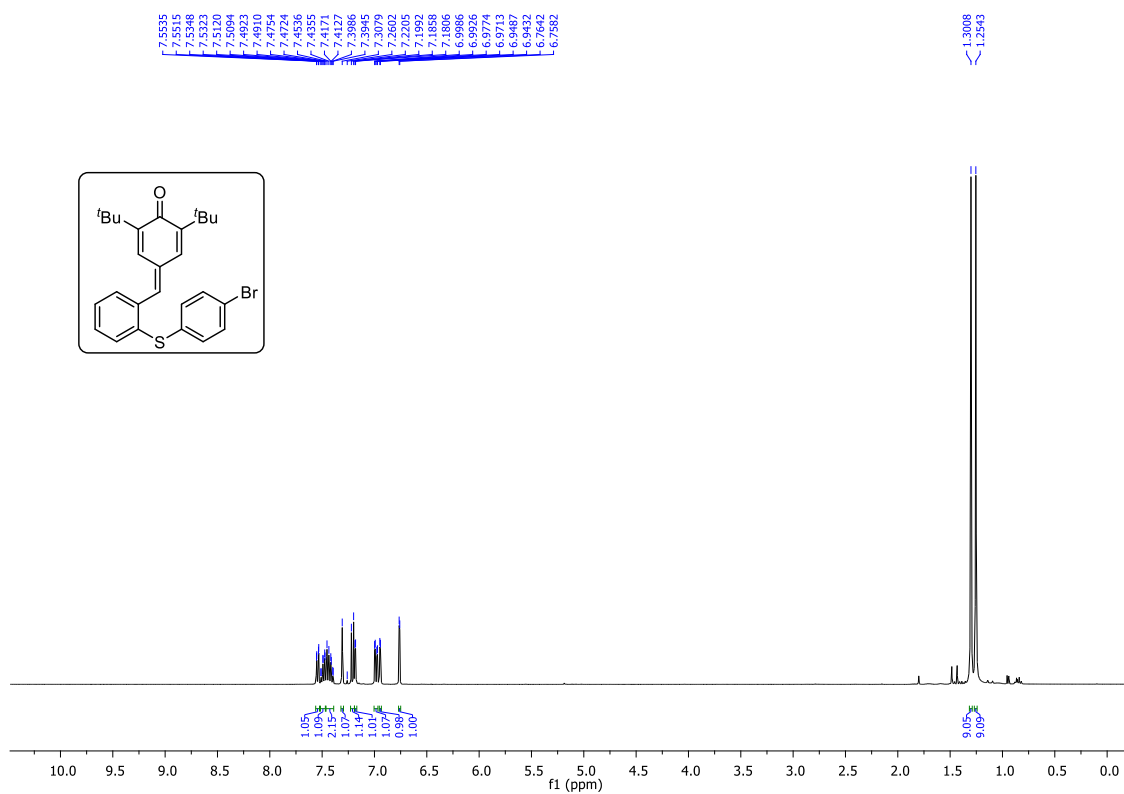
^{13}C NMR (100 MHz, CDCl_3) spectrum of **3d**



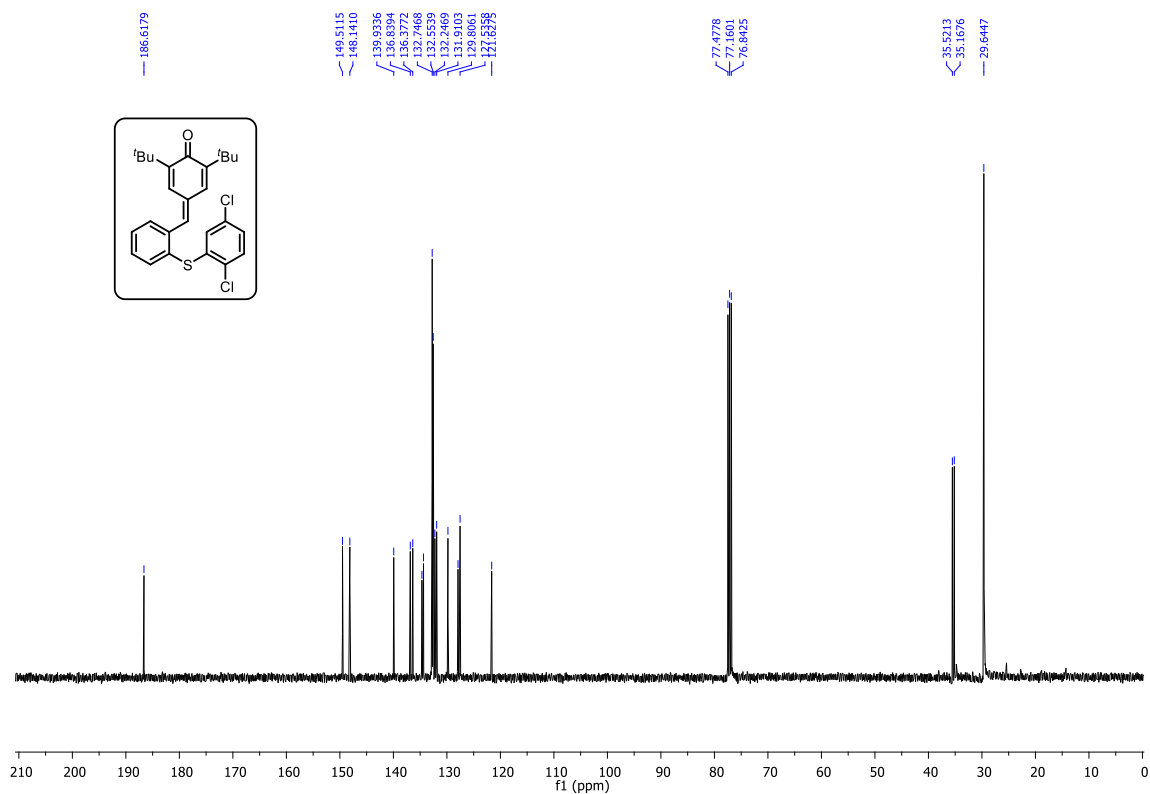
^1H NMR (400 MHz, CDCl_3) spectrum of **3e**



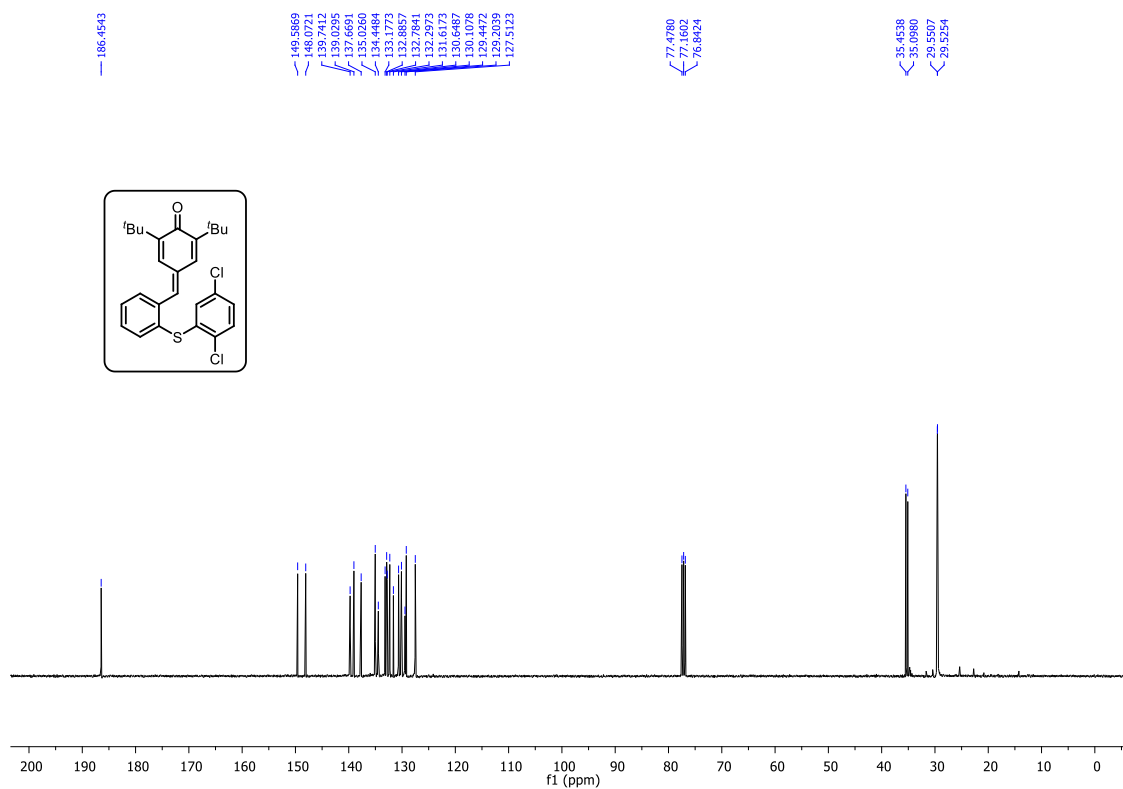
¹³C NMR (100 MHz, CDCl₃) spectrum of **3e**



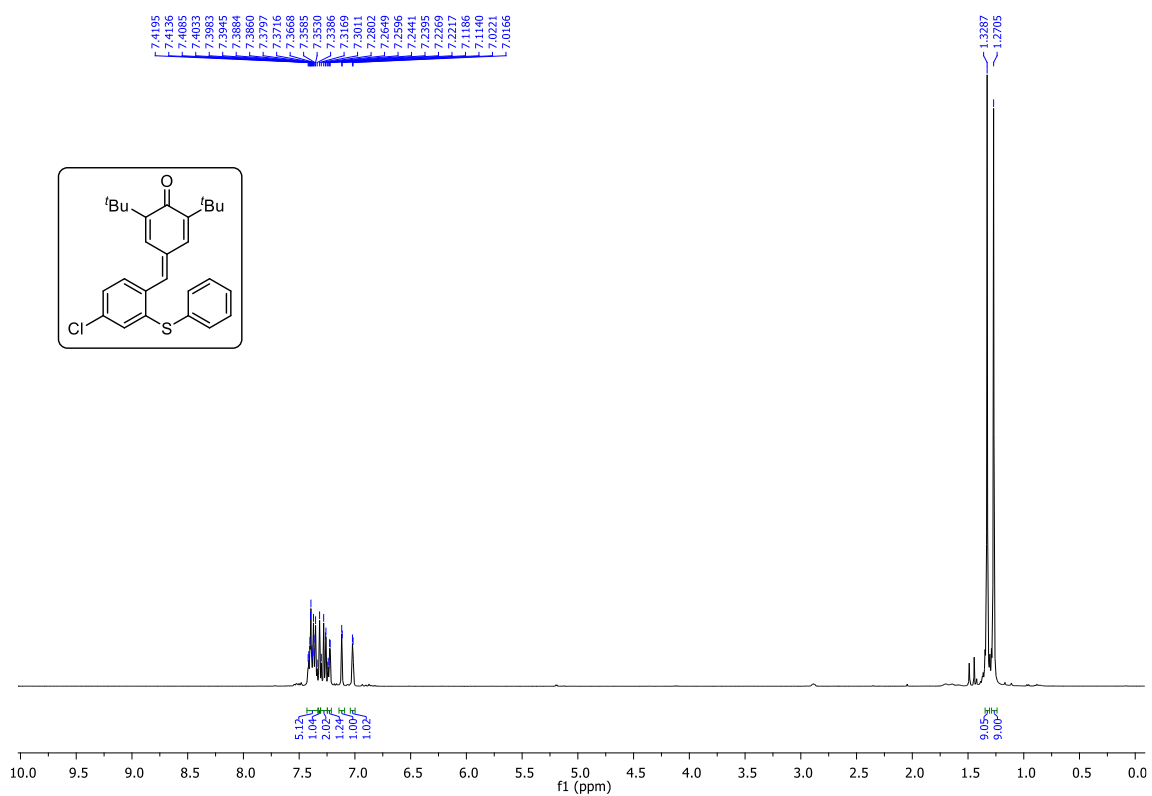
¹H NMR (400 MHz, CDCl₃) spectrum of **3f**



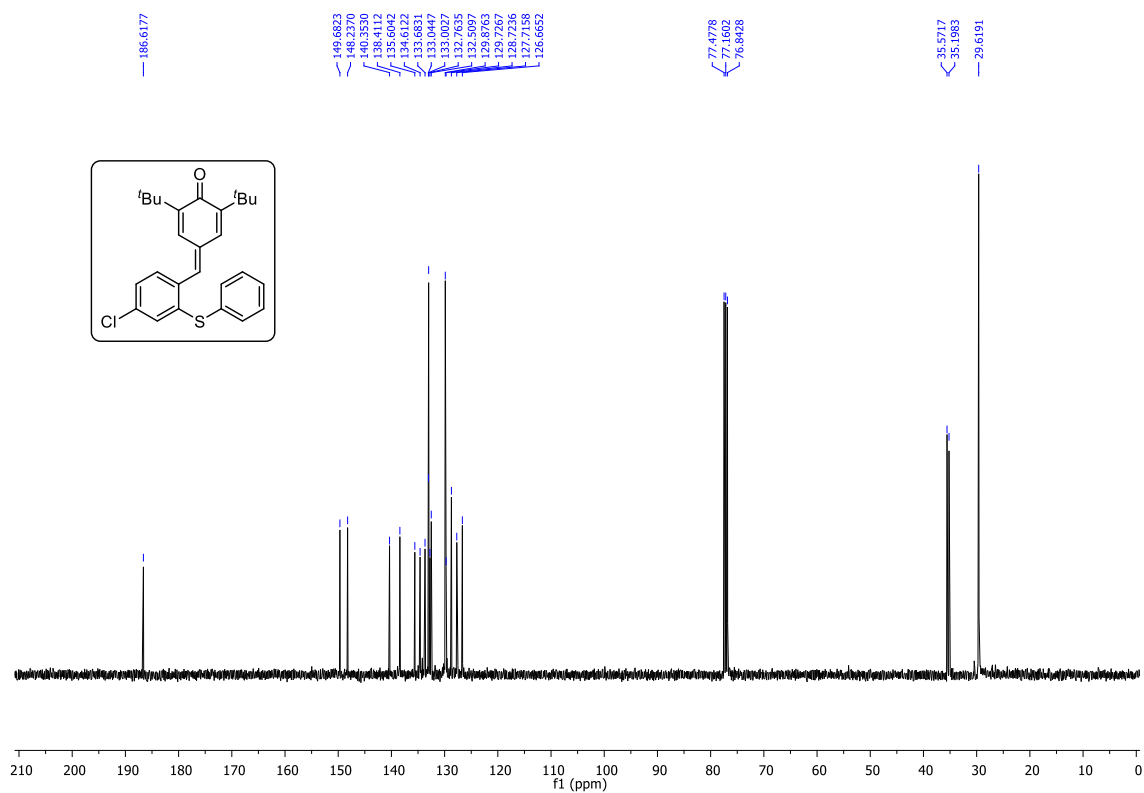
¹³C NMR (100 MHz, CDCl₃) spectrum of **3f**



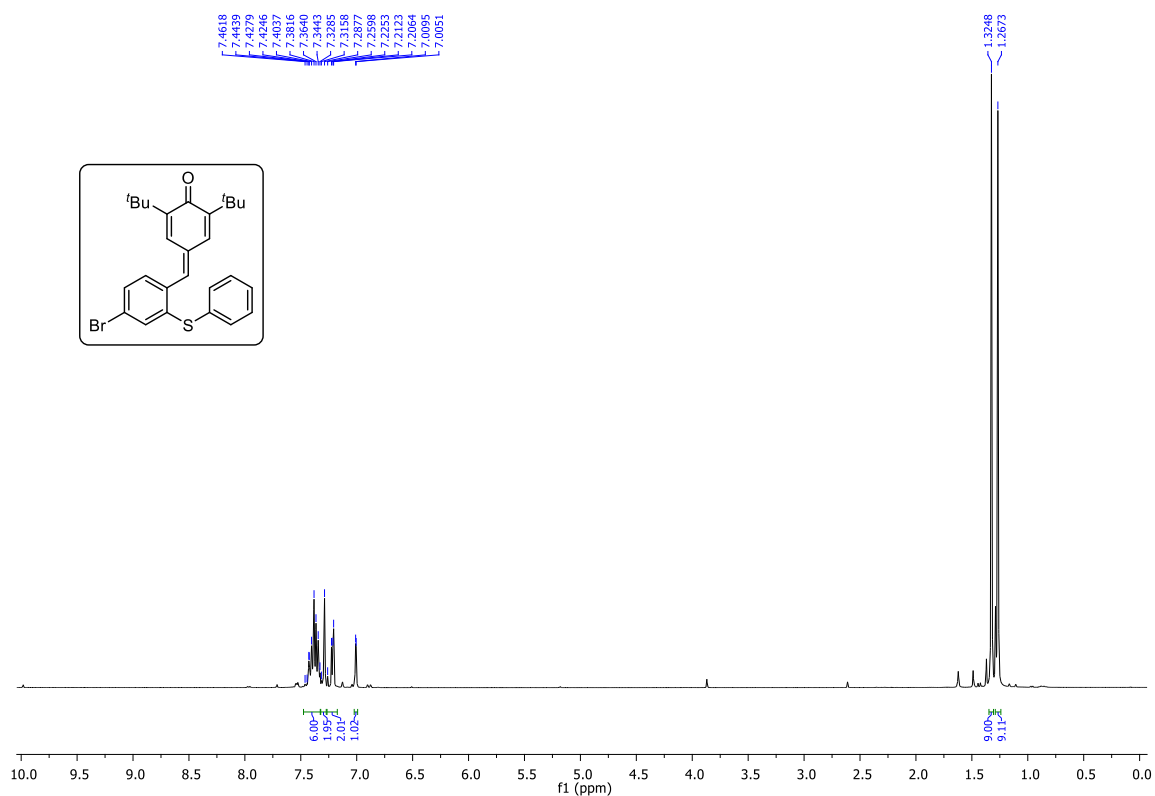
¹H NMR (400 MHz, CDCl₃) spectrum of **3g**



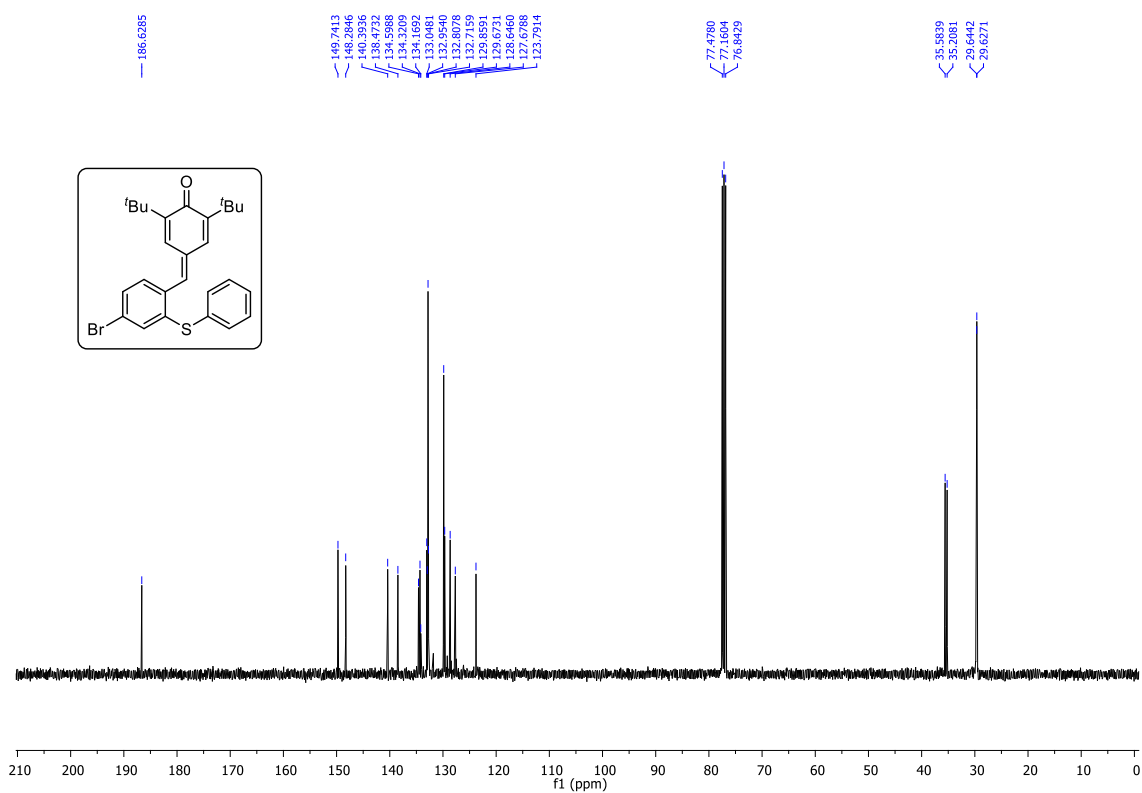
^{13}C NMR (100 MHz, CDCl_3) spectrum of **3g**



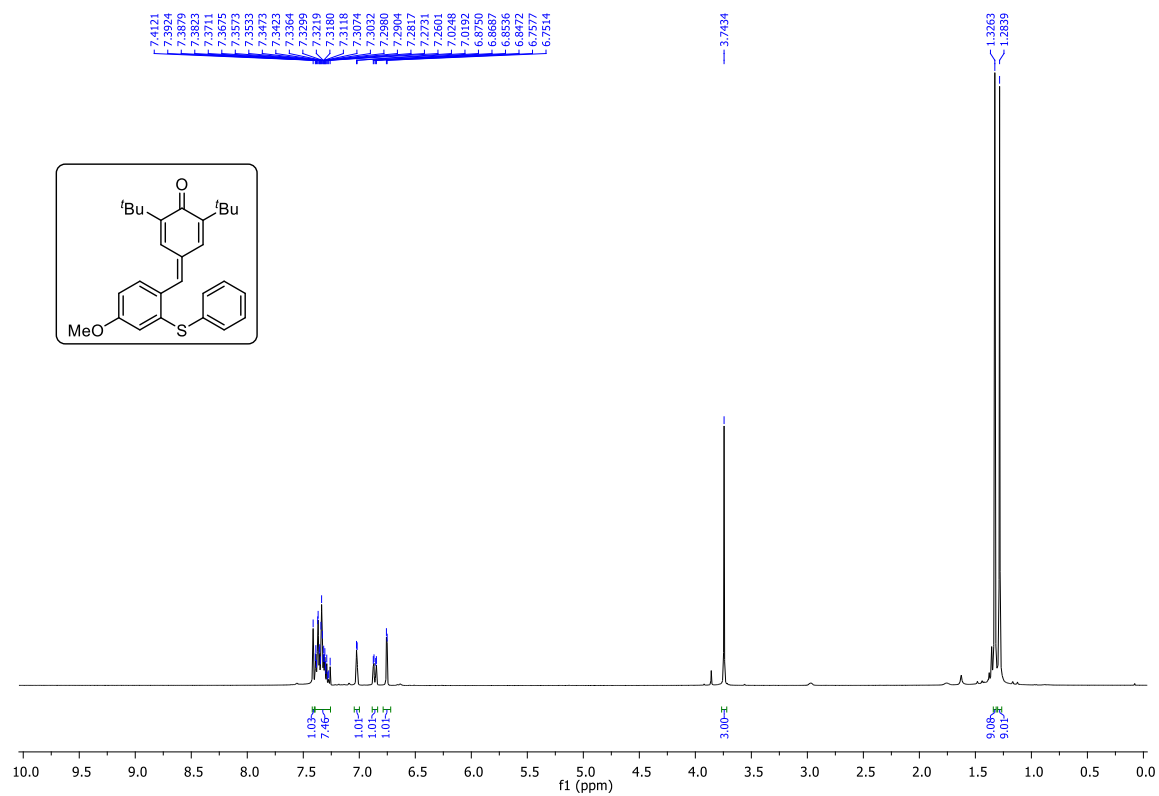
^1H NMR (400 MHz, CDCl_3) spectrum of **3h**



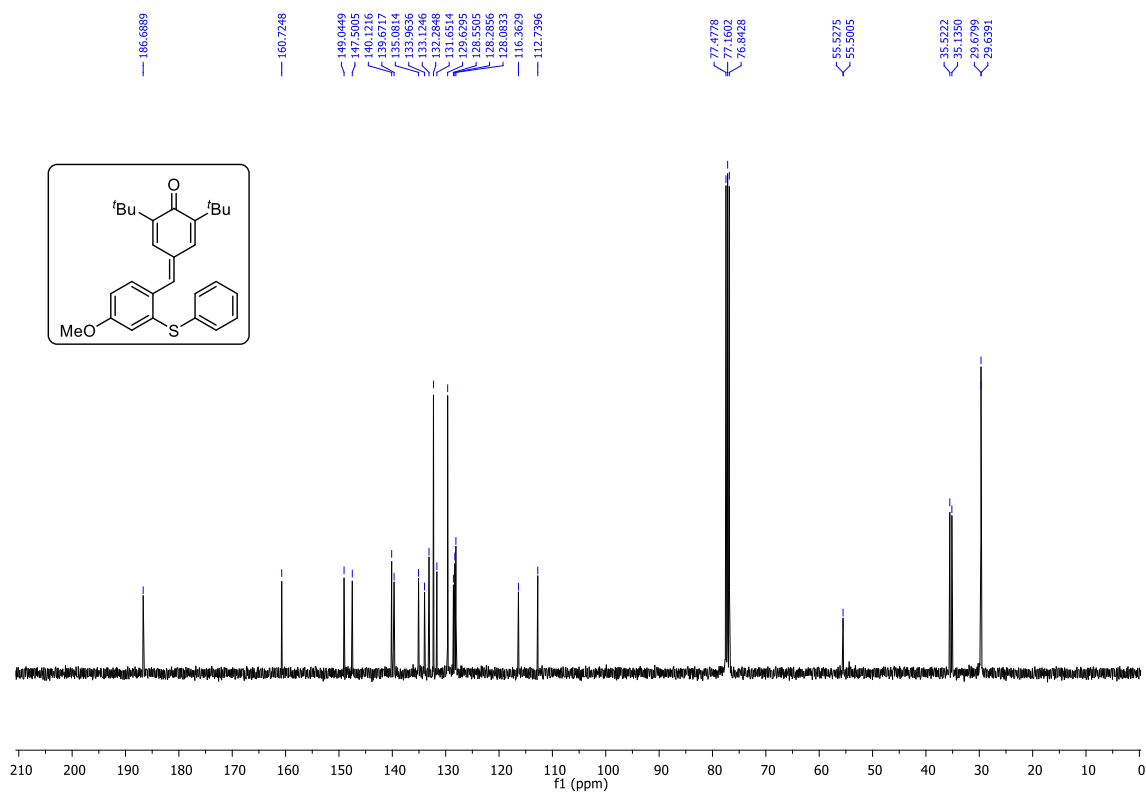
¹³C NMR (100 MHz, CDCl₃) spectrum of **3h**



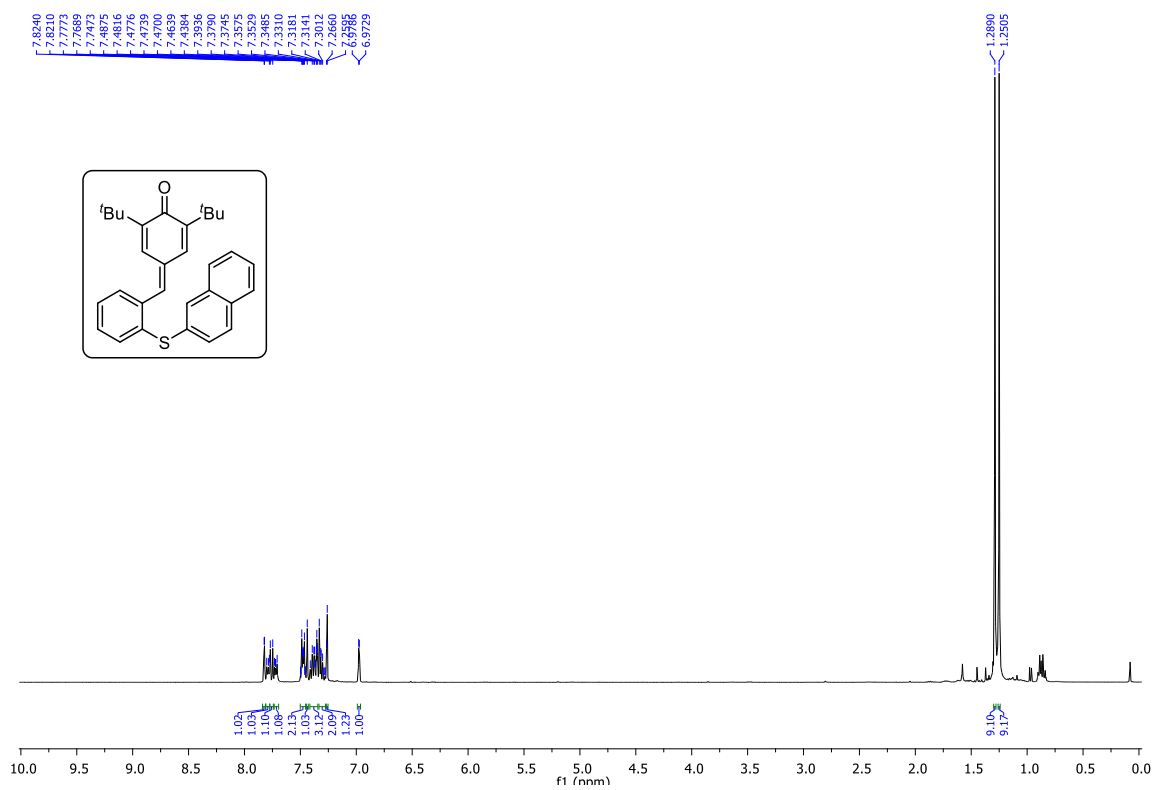
¹H NMR (400 MHz, CDCl₃) spectrum of **3i**



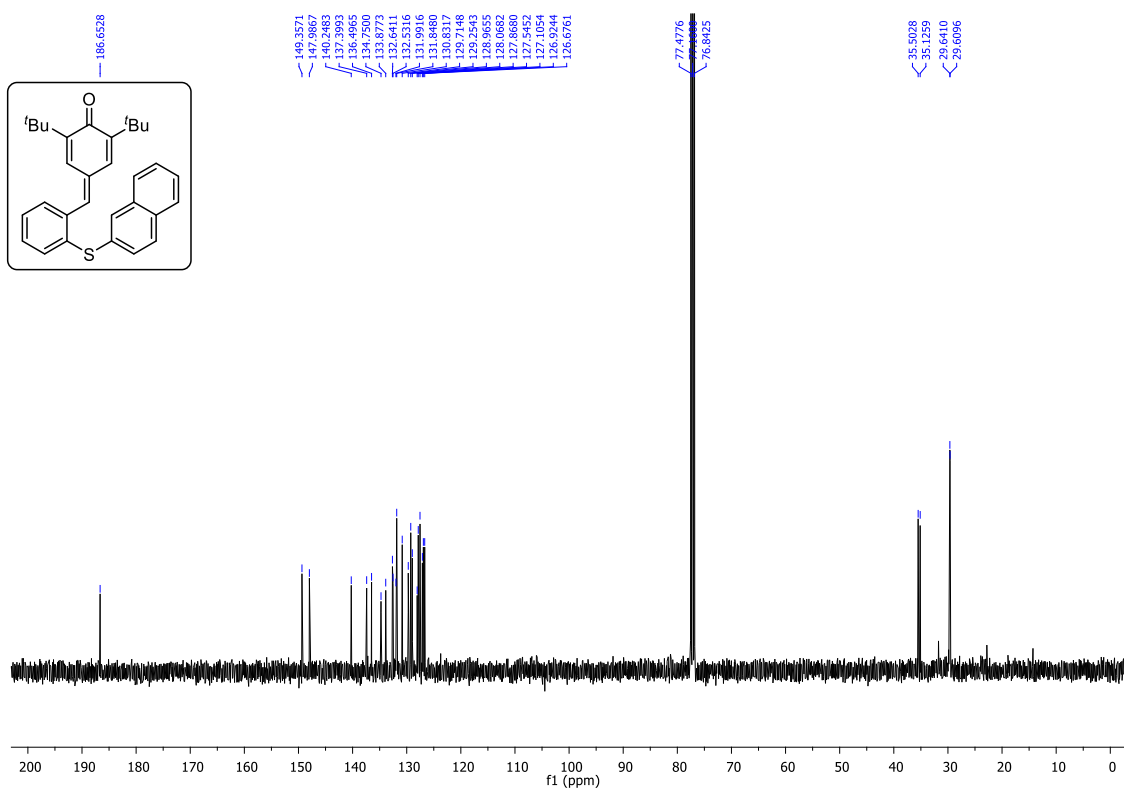
^{13}C NMR (100 MHz, CDCl_3) spectrum of **3i**



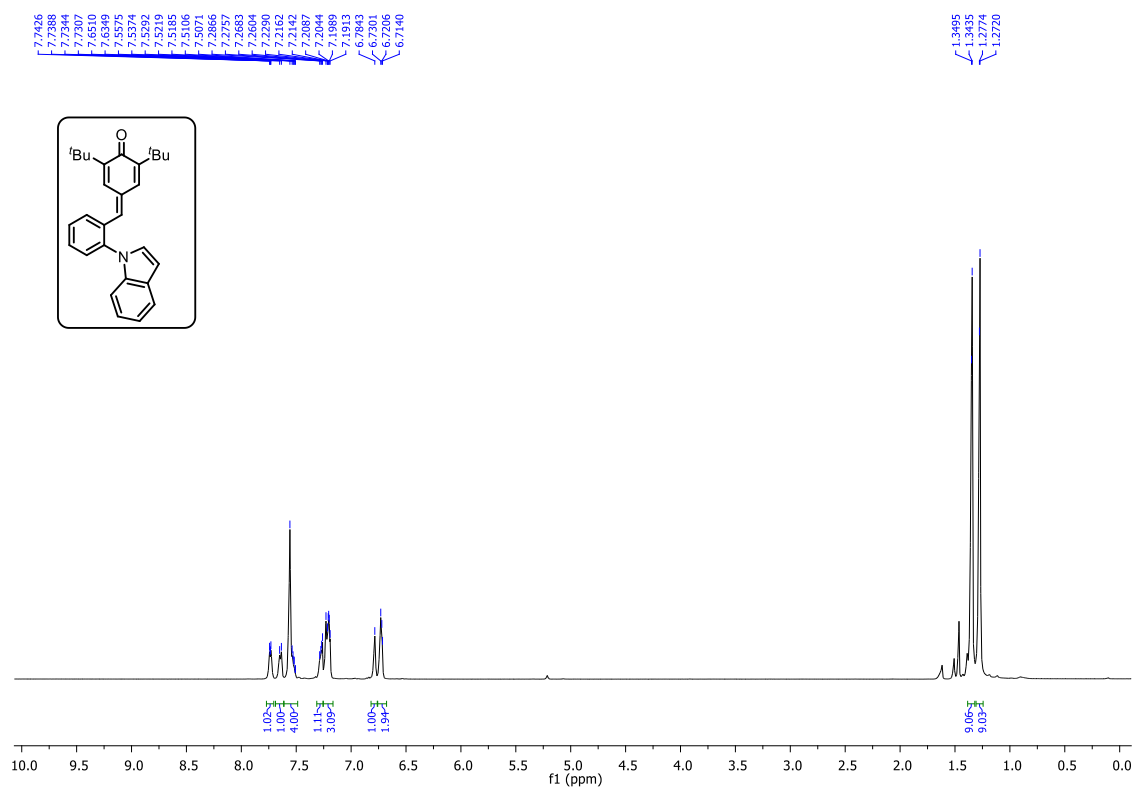
^1H NMR (400 MHz, CDCl_3) spectrum of **3j**



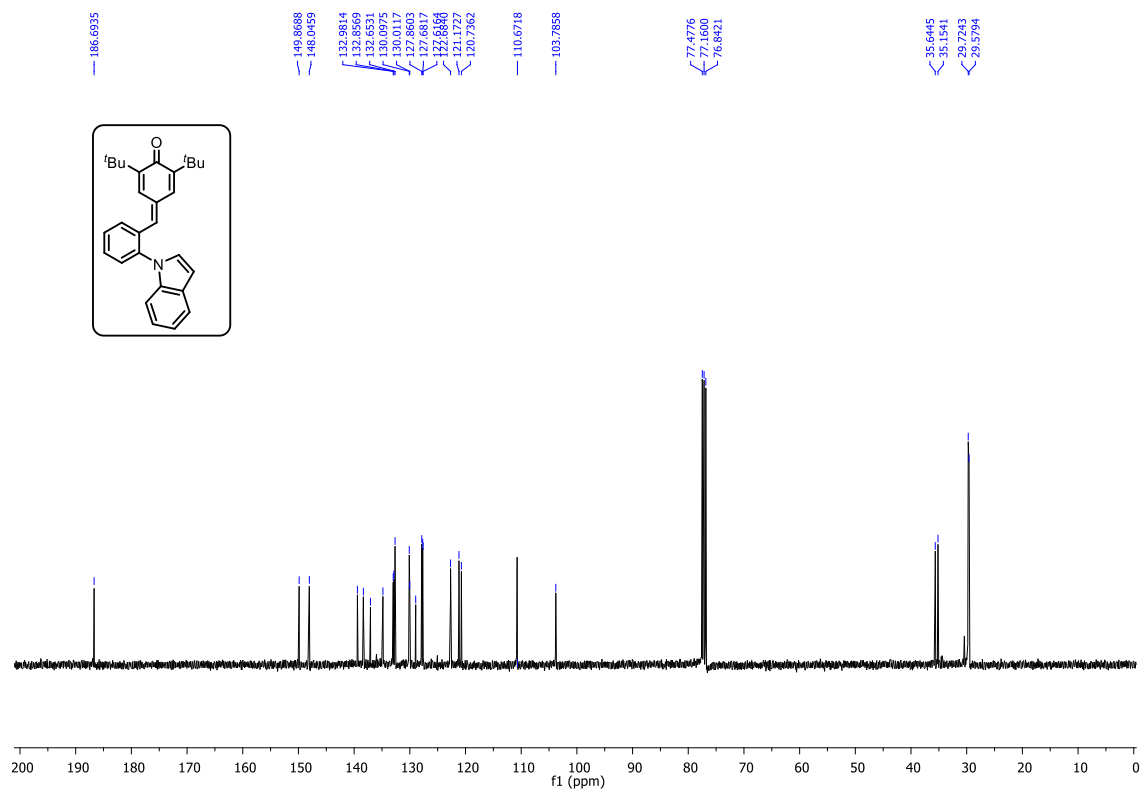
^{13}C NMR (100 MHz, CDCl_3) spectrum of **3j**



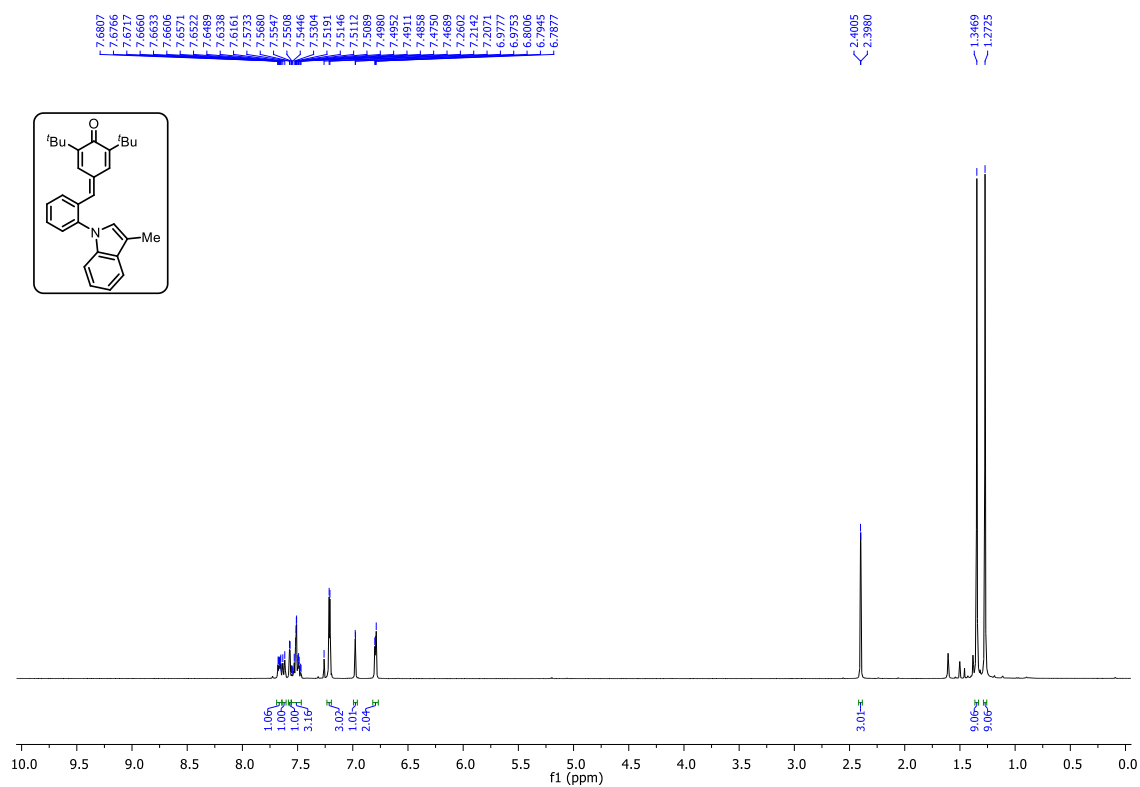
^1H NMR (400 MHz, CDCl_3) spectrum of **5a**



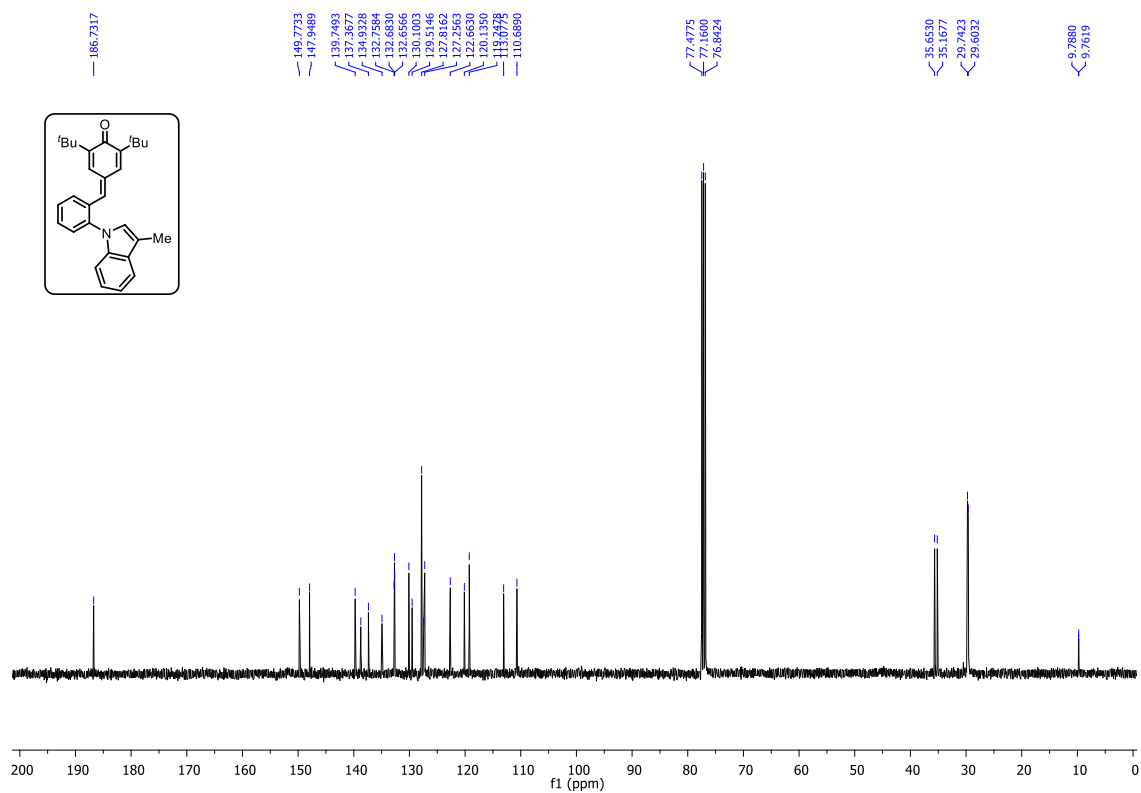
¹³C NMR (100 MHz, CDCl₃) spectrum of 5a



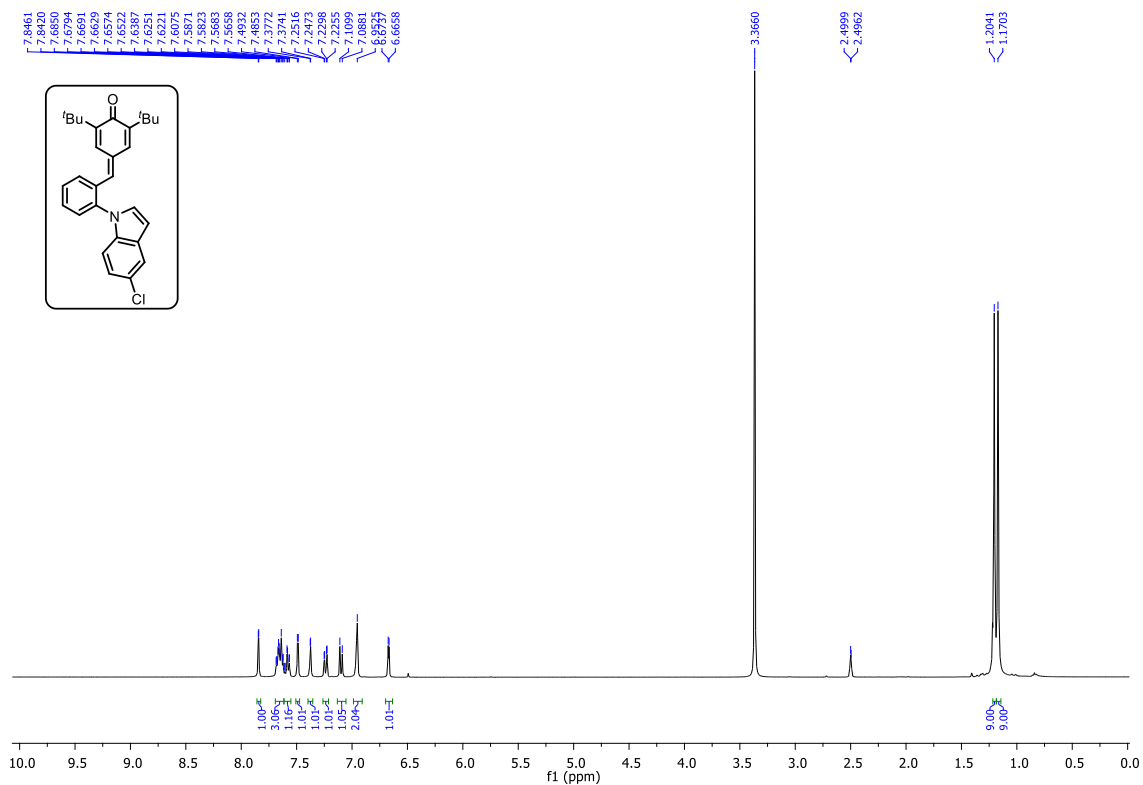
¹H NMR (400 MHz, CDCl₃) spectrum of 5b



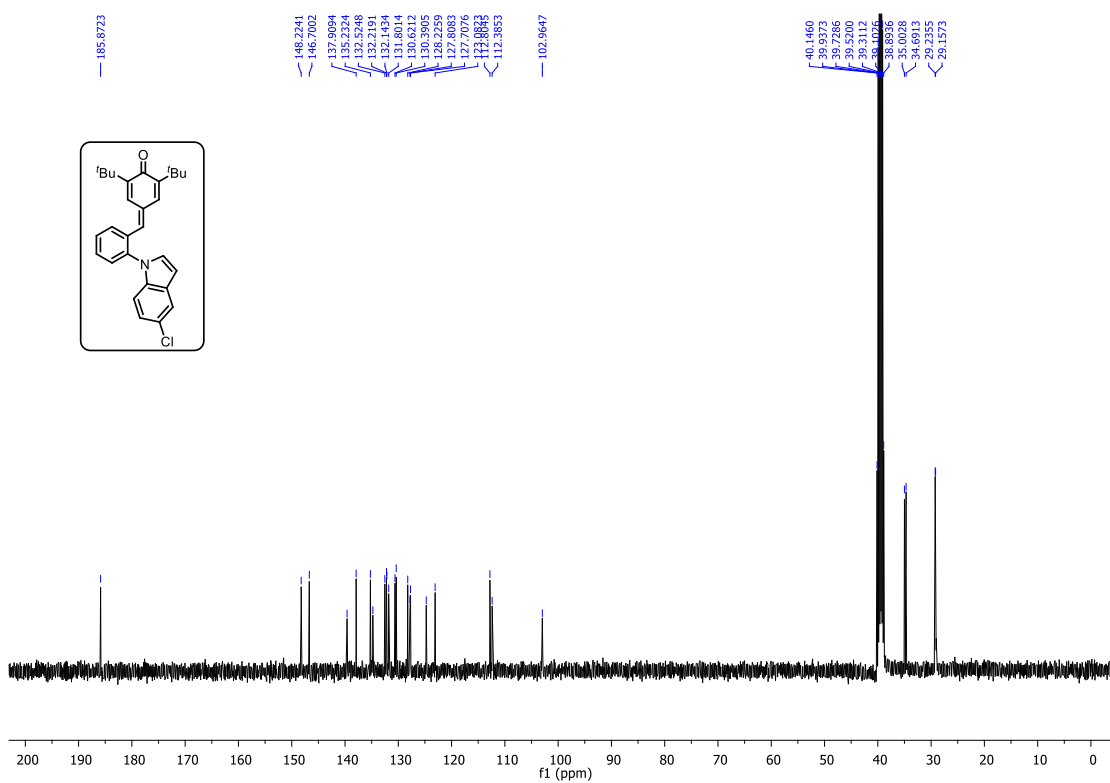
^{13}C NMR (100 MHz, CDCl_3) spectrum of **5b**



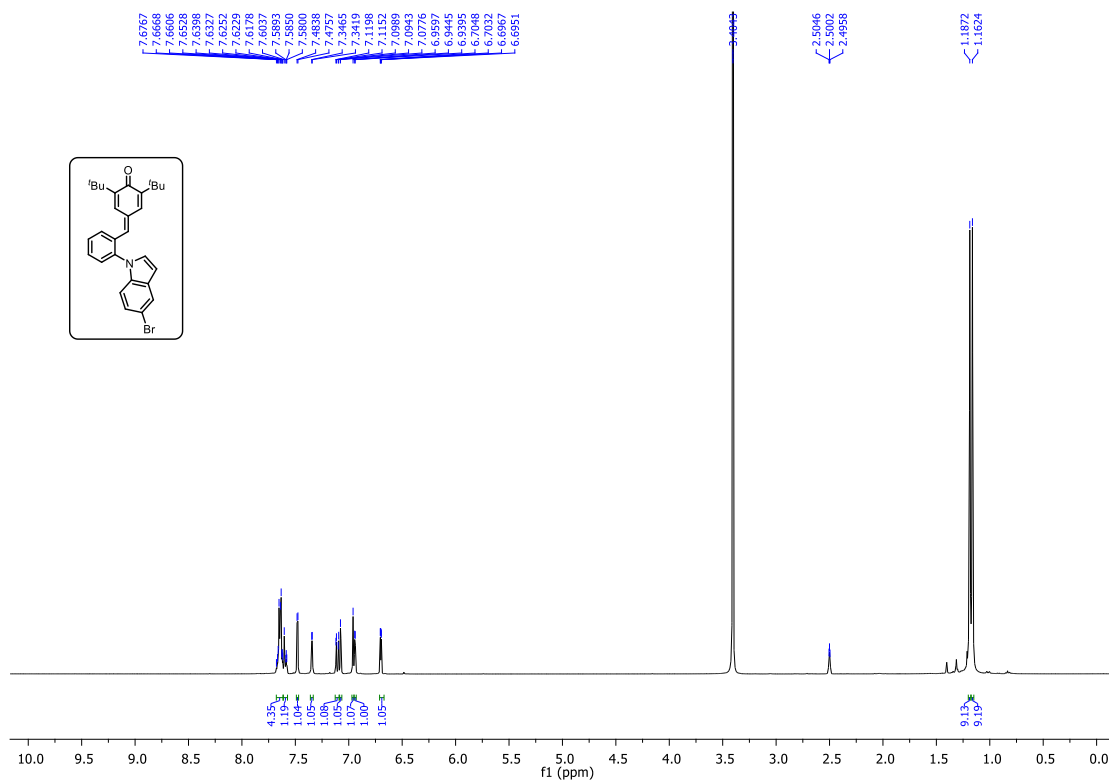
^1H NMR (400 MHz, $\text{DMSO}-d_6$) spectrum of **5c**



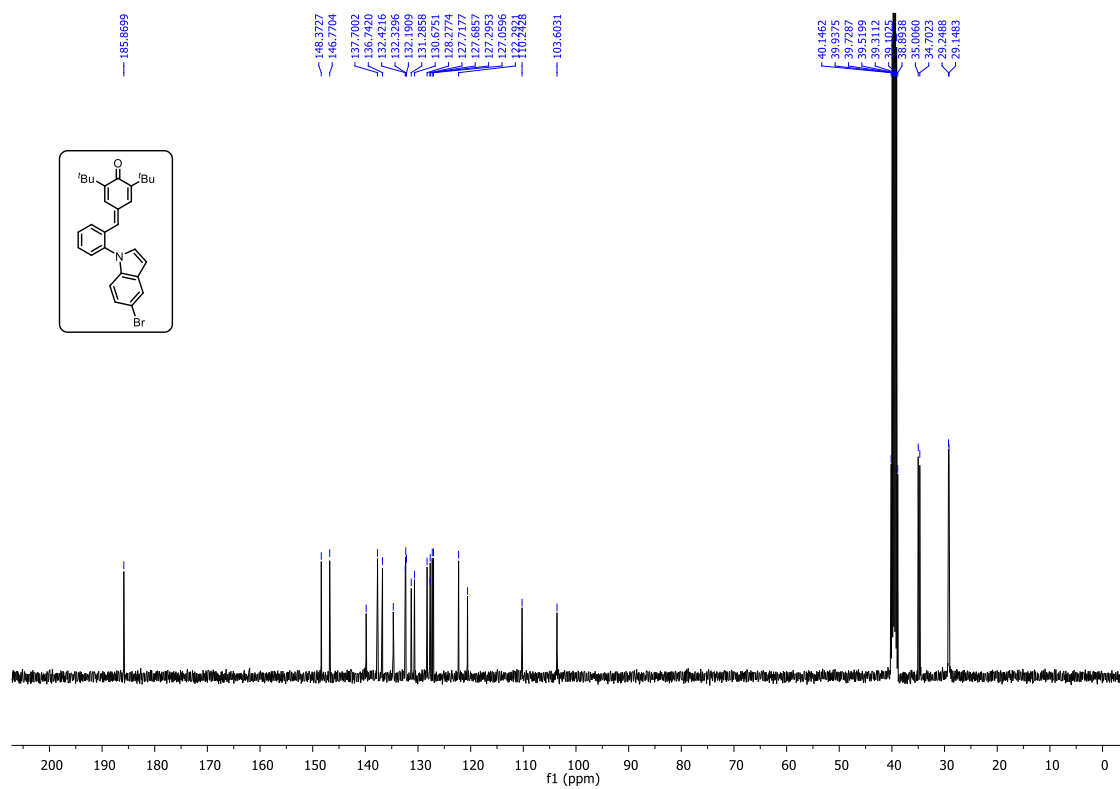
^{13}C NMR (100 MHz, $\text{DMSO-}d_6$) spectrum of **5c**



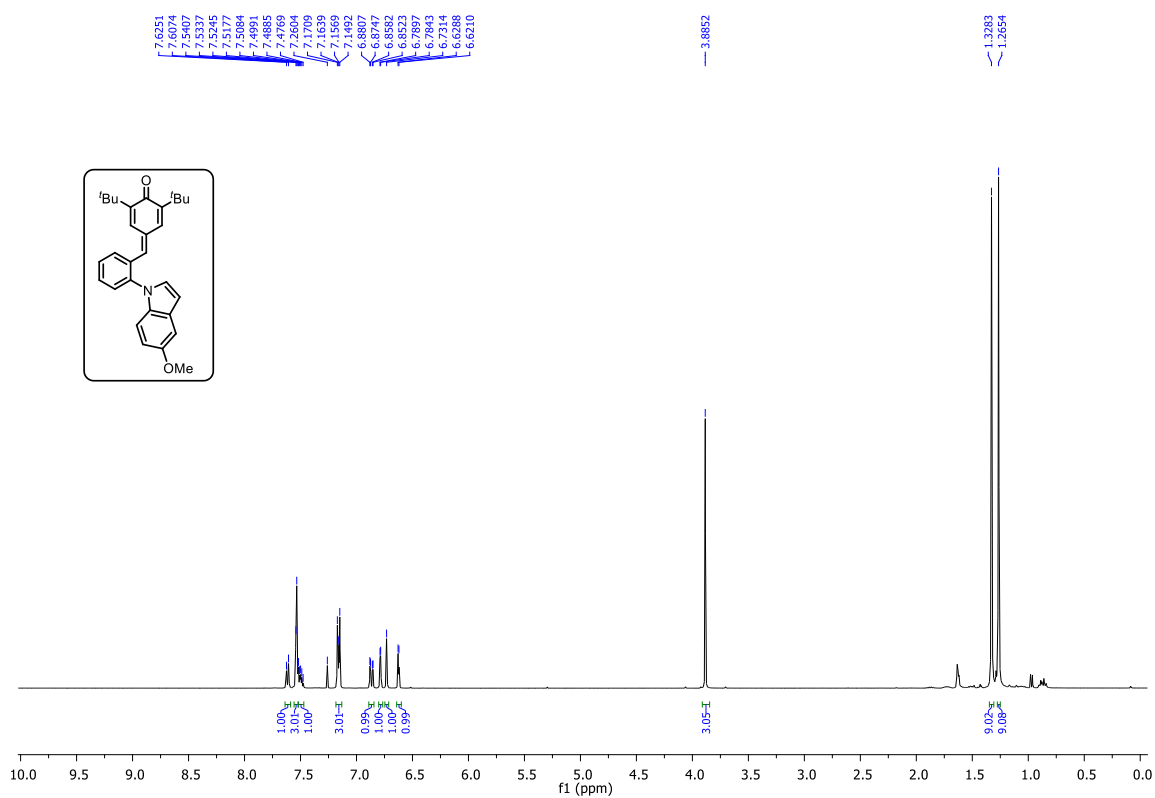
^1H NMR (400 MHz, $\text{DMSO-}d_6$) spectrum of **5d**



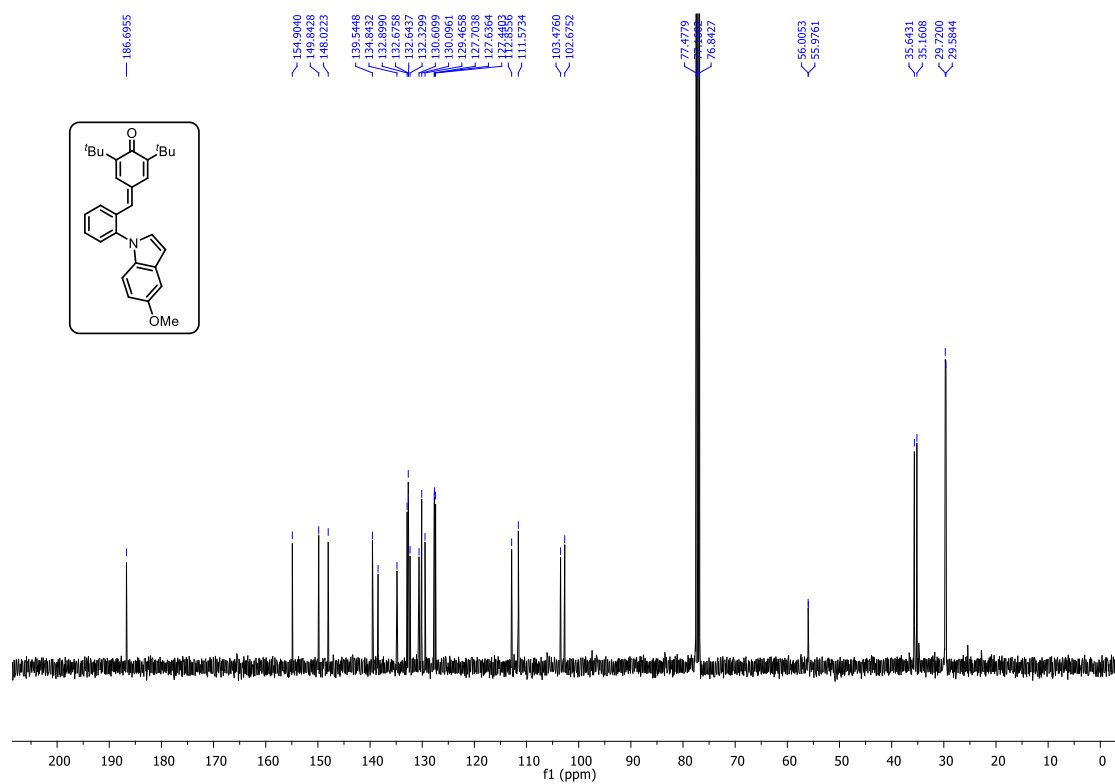
^{13}C NMR (100 MHz, $\text{DMSO-}d_6$) spectrum of **5d**



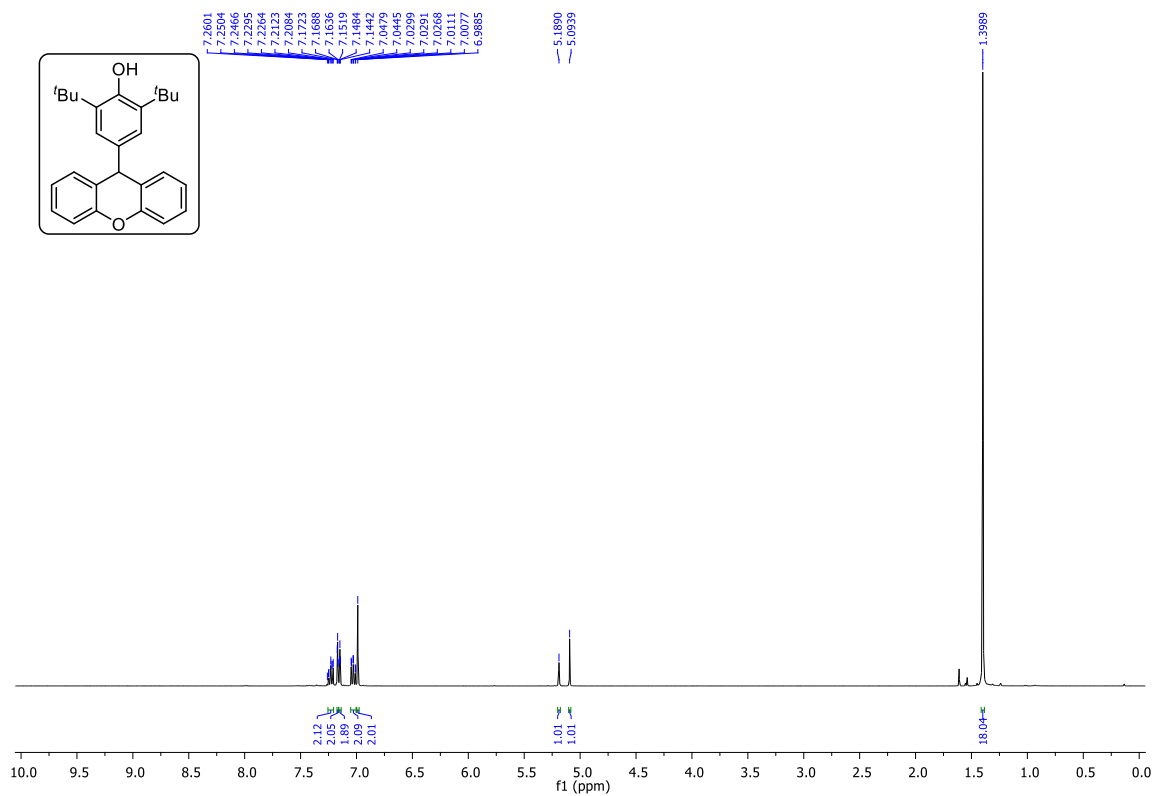
^1H NMR (400 MHz, CDCl_3) spectrum of **5e**



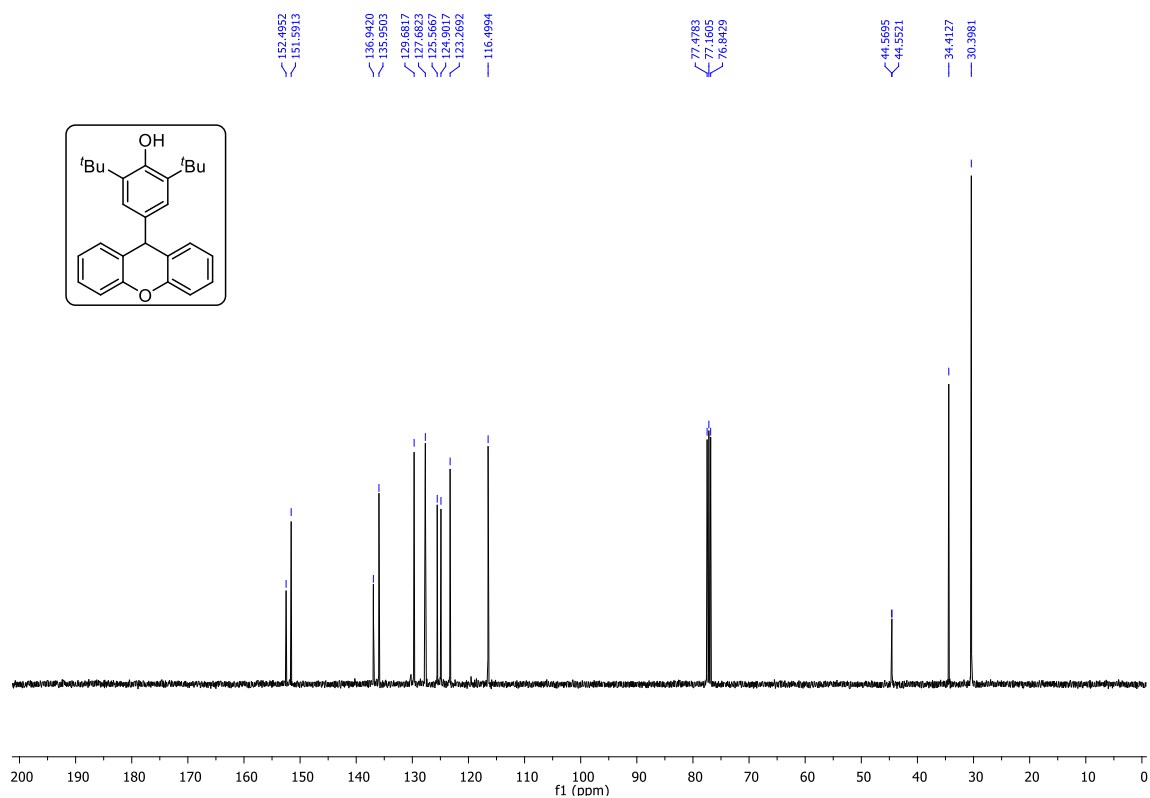
^{13}C NMR (100 MHz, CDCl_3) spectrum of **5e**



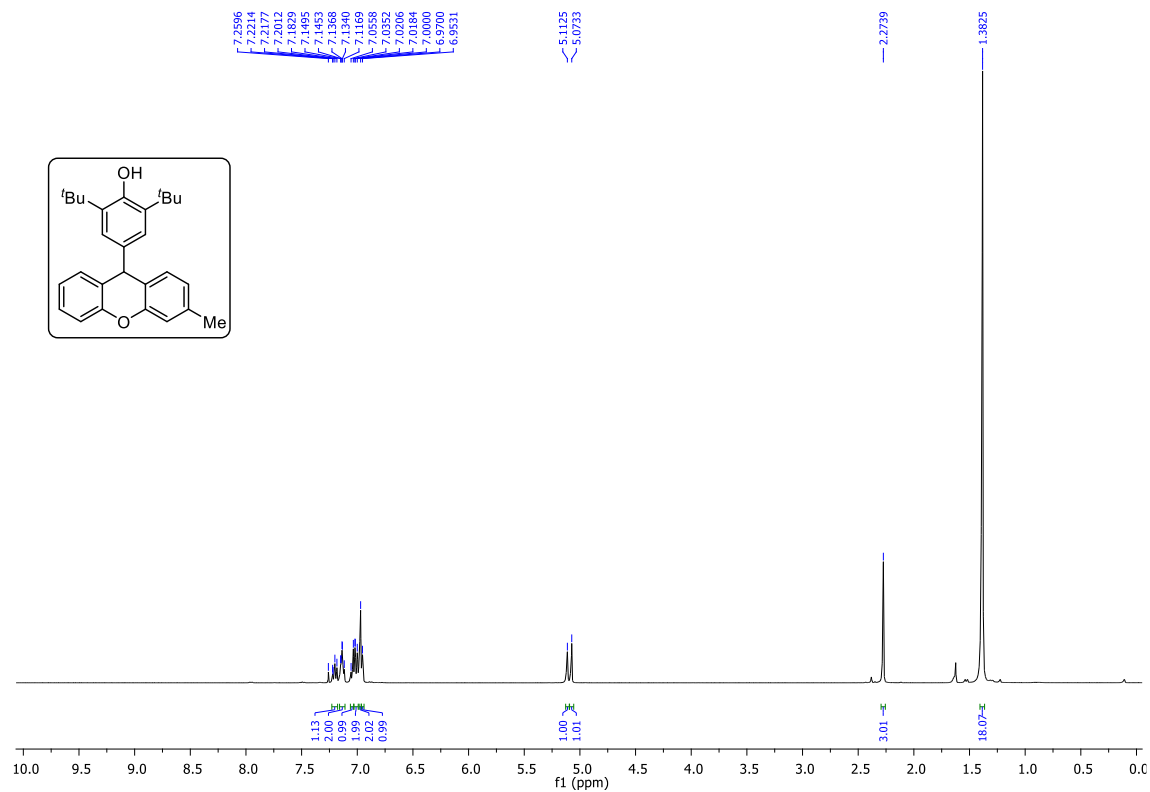
^1H NMR (400 MHz, CDCl_3) spectrum of **2a**



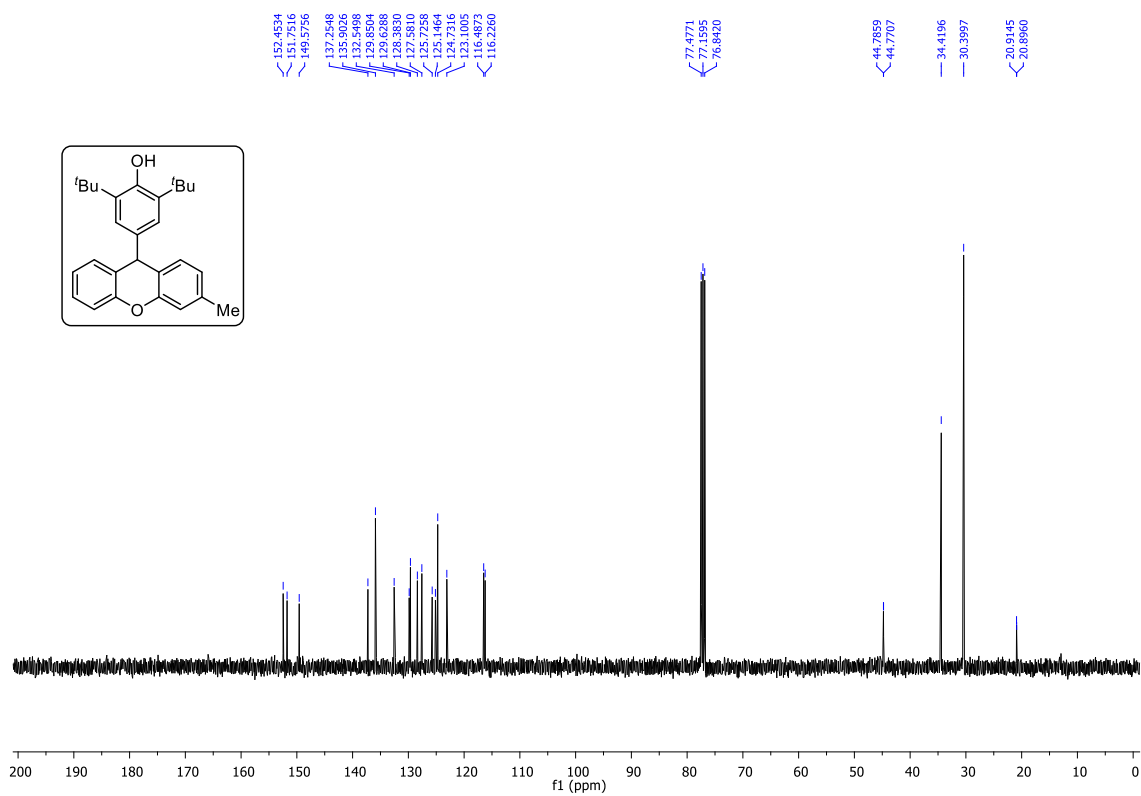
^{13}C $\{^1\text{H}\}$ NMR (100 MHz, CDCl_3) spectrum of **2a**



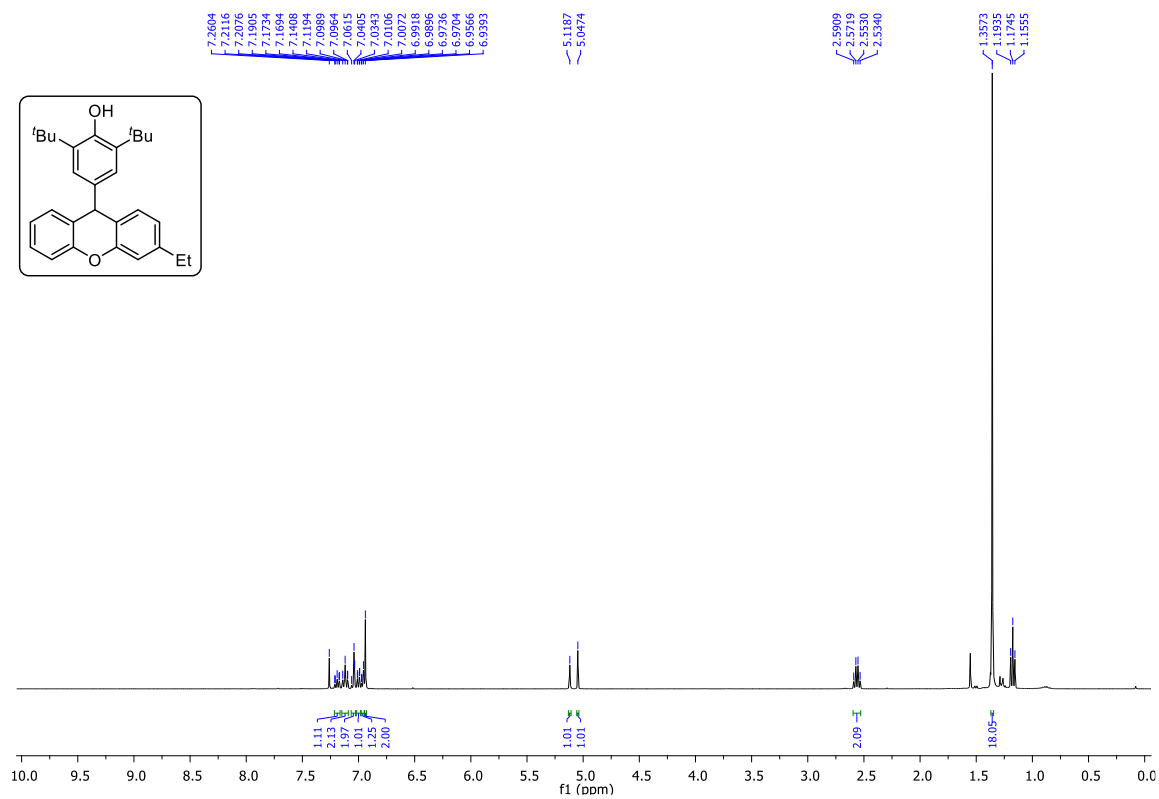
^1H NMR (400 MHz, CDCl_3) spectrum of **2b**



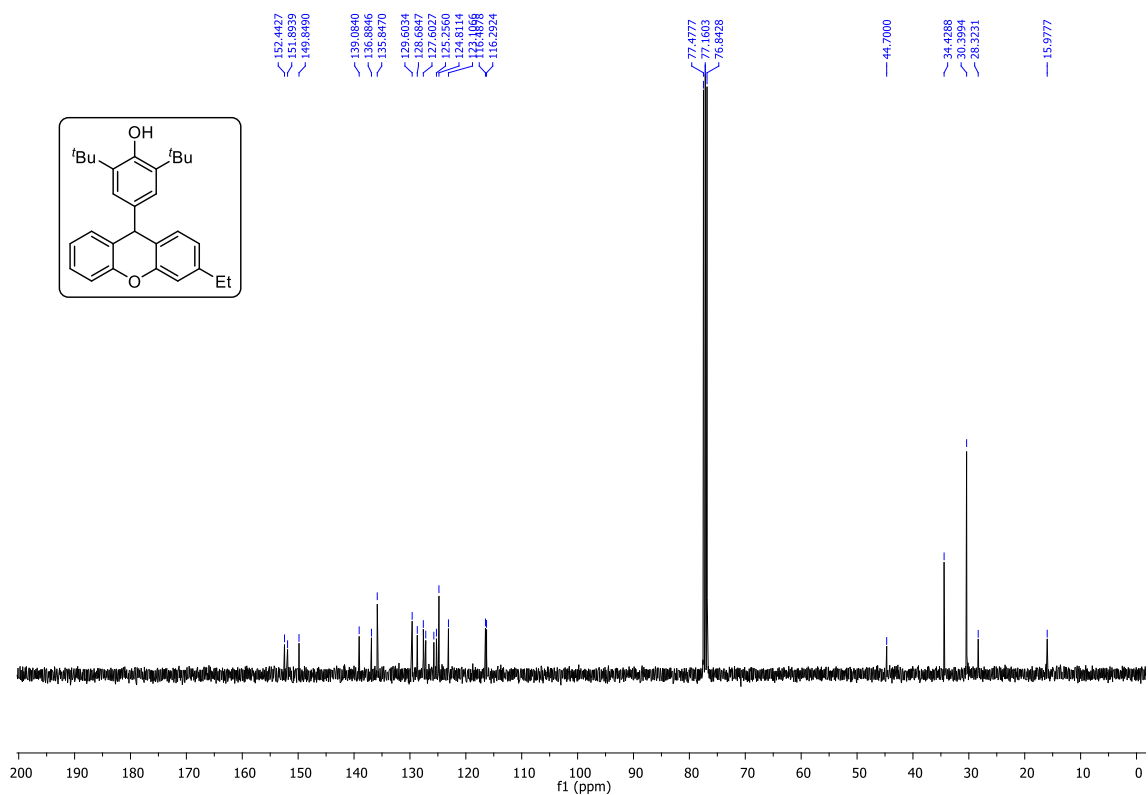
^{13}C $\{^1\text{H}\}$ NMR (100 MHz, CDCl_3) spectrum of **2b**



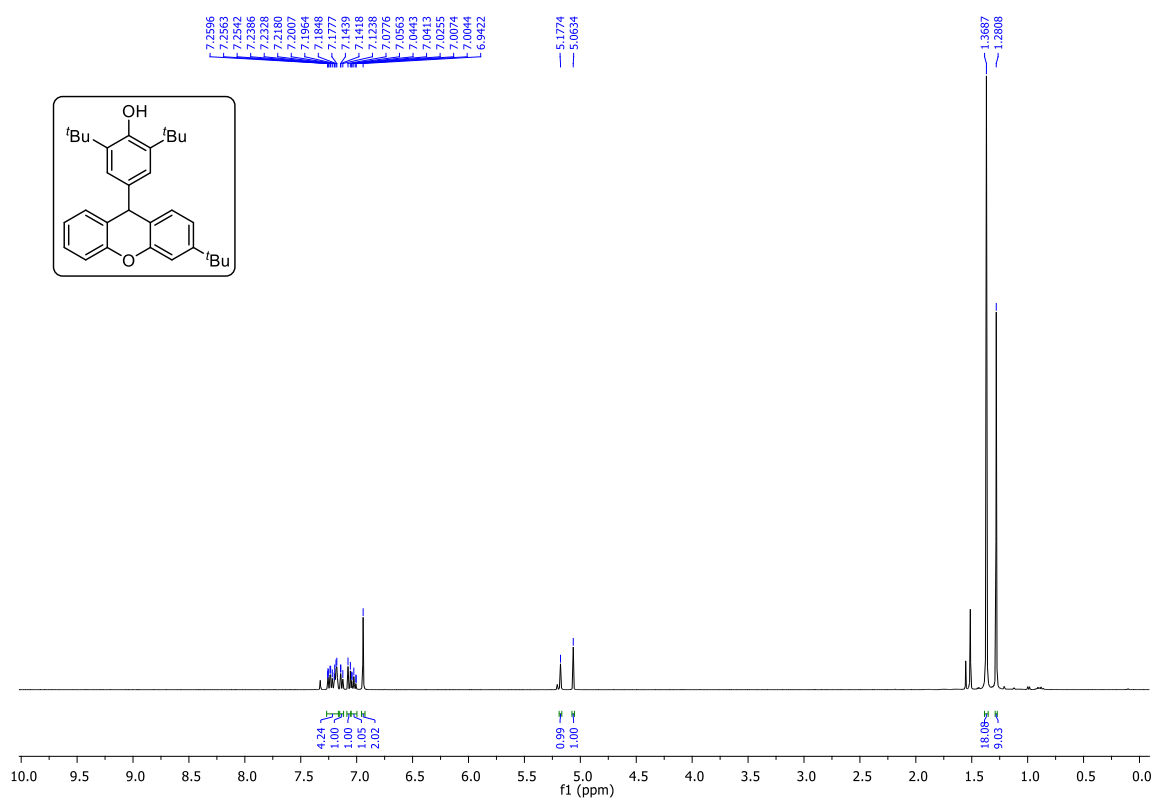
^1H NMR (400 MHz, CDCl_3) spectrum of **2c**



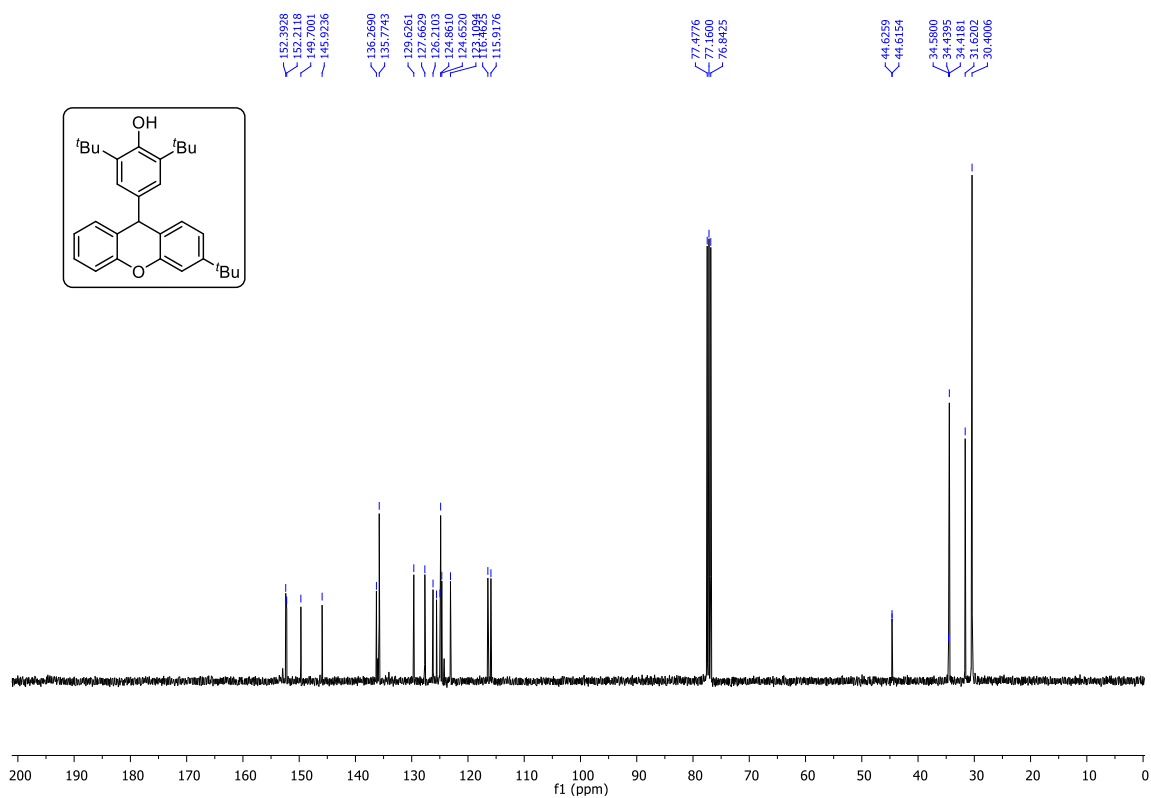
^{13}C $\{^1\text{H}\}$ NMR (100 MHz, CDCl_3) spectrum of **2c**



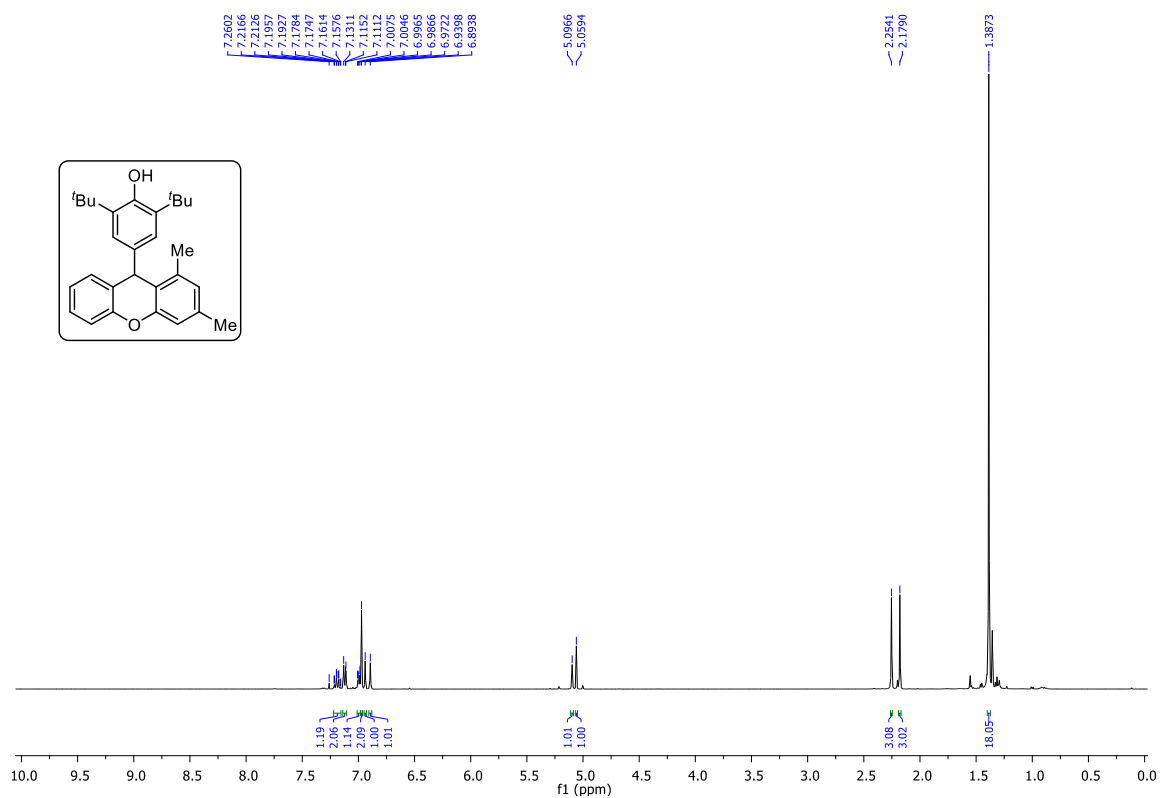
^1H NMR (400 MHz, CDCl_3) spectrum of **2d**



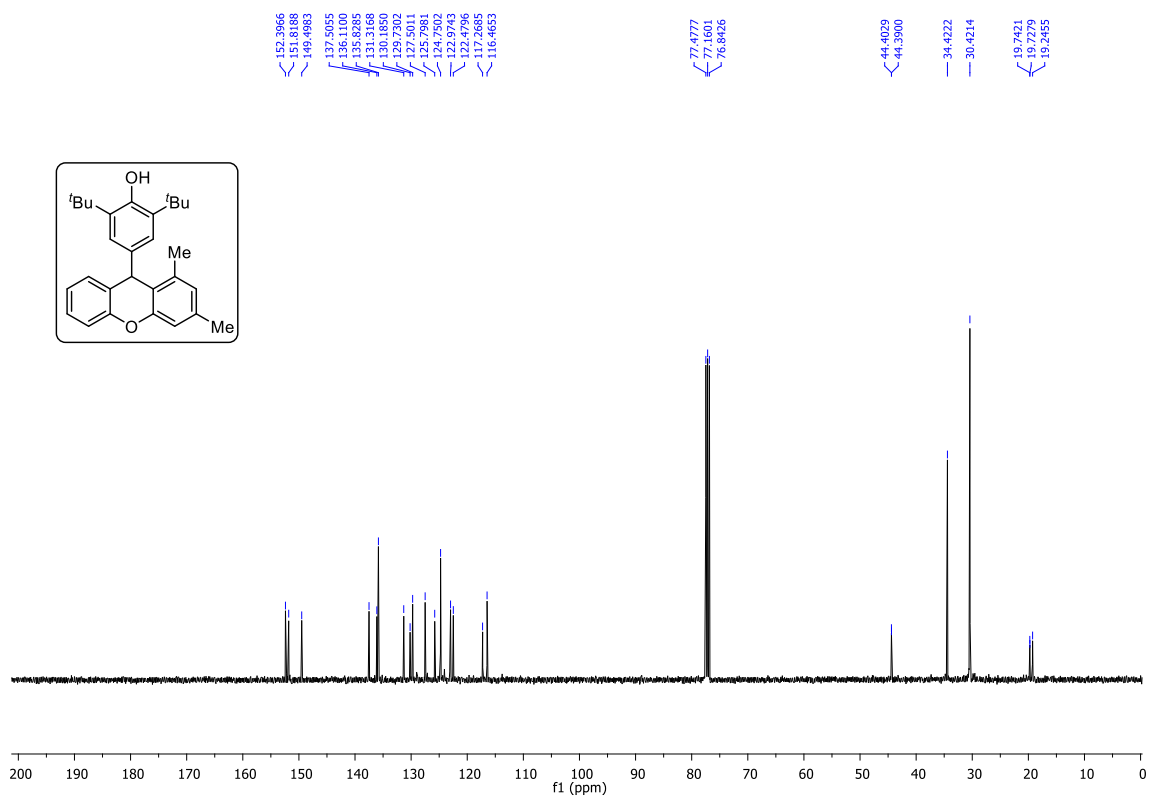
^{13}C $\{^1\text{H}\}$ NMR (100 MHz, CDCl_3) spectrum of **2d**



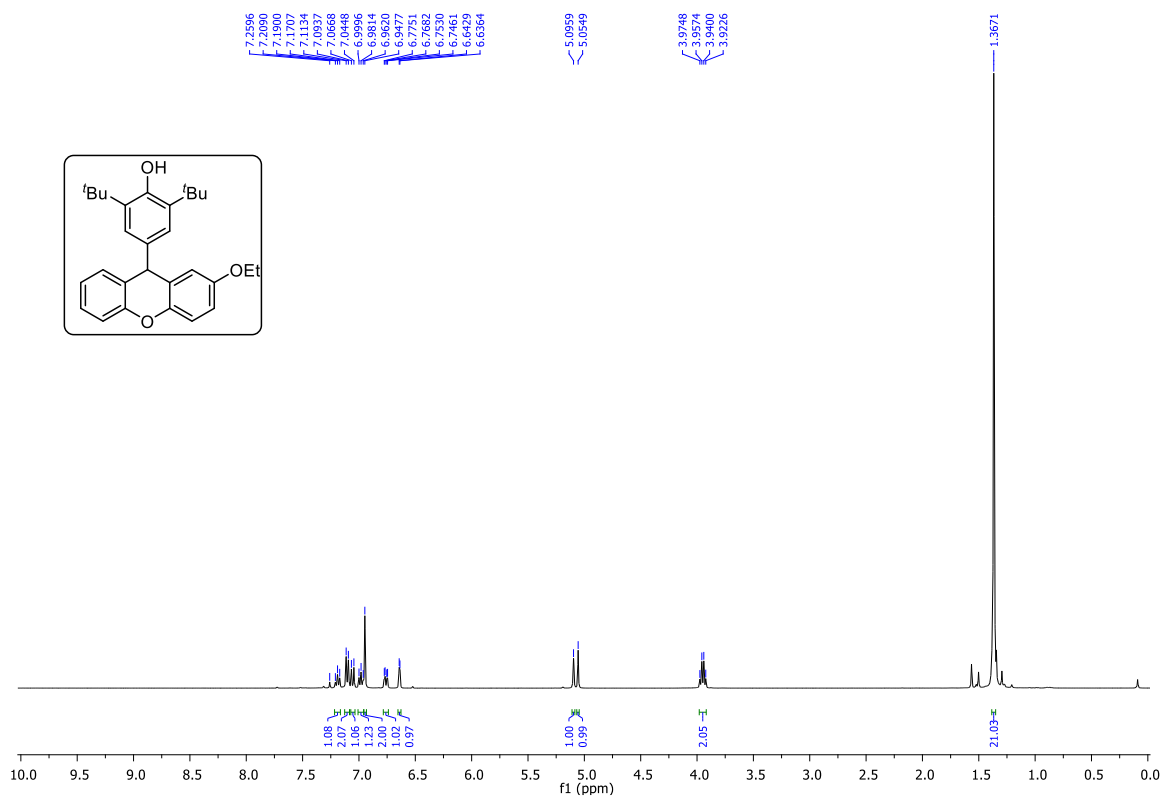
^1H NMR (400 MHz, CDCl_3) spectrum of **2e**



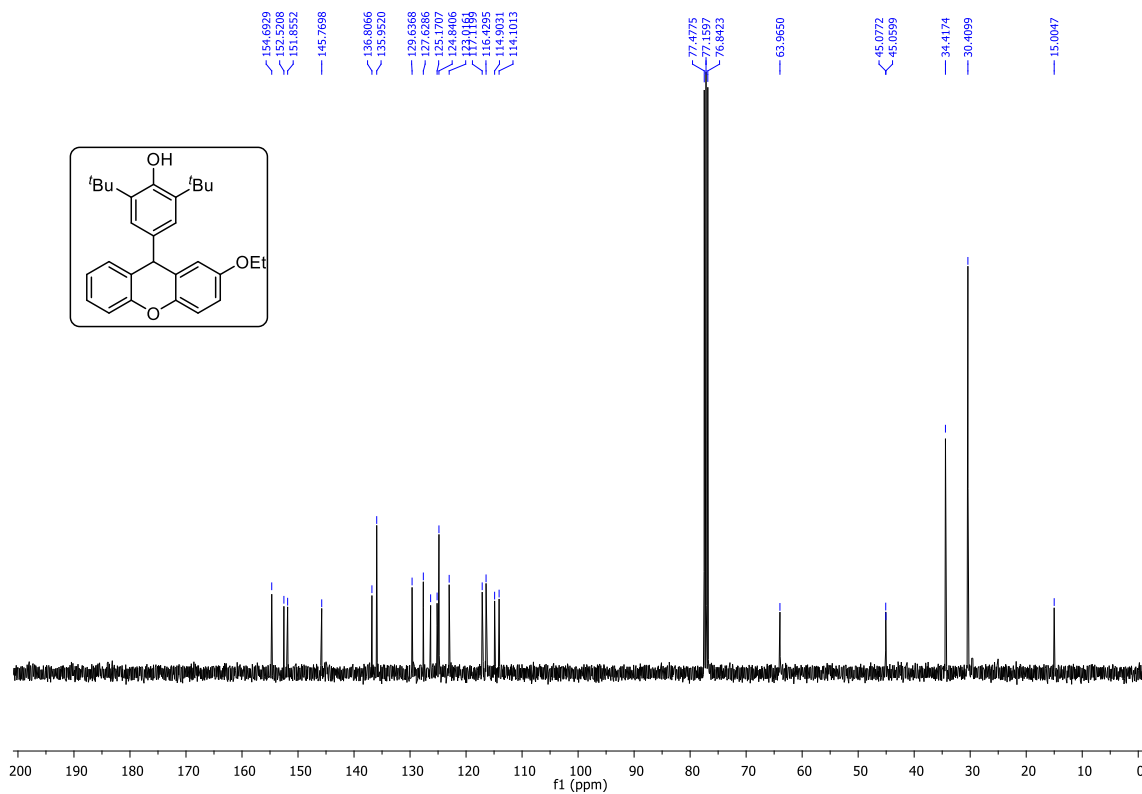
^{13}C $\{^1\text{H}\}$ NMR (100 MHz, CDCl_3) spectrum of **2e**



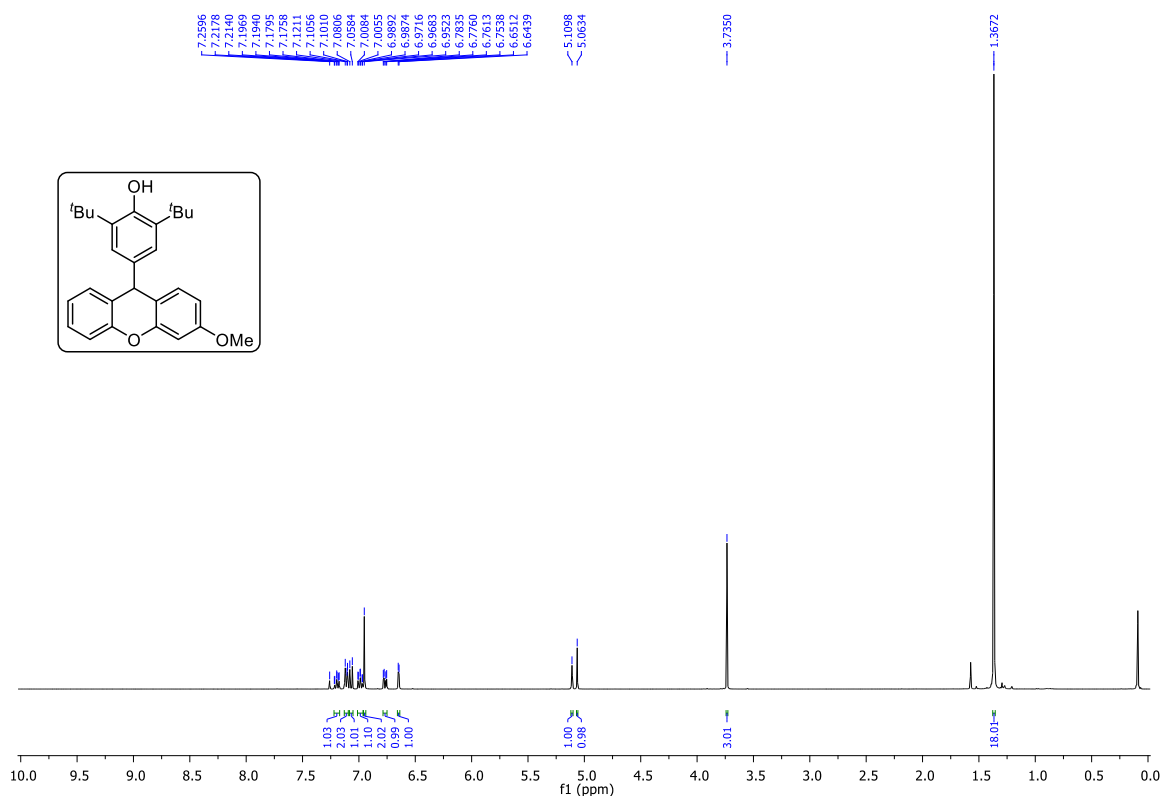
^1H NMR (400 MHz, CDCl_3) spectrum of **2f**



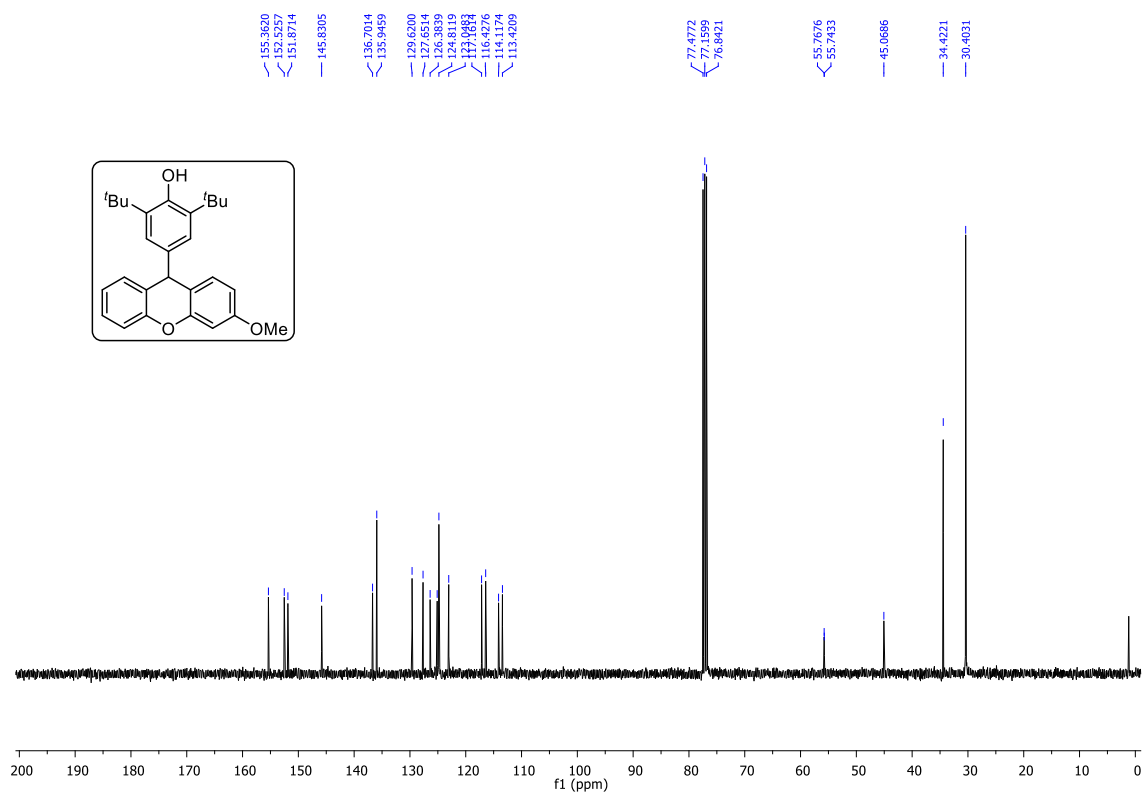
^{13}C $\{^1\text{H}\}$ NMR (100 MHz, CDCl_3) spectrum of **2f**



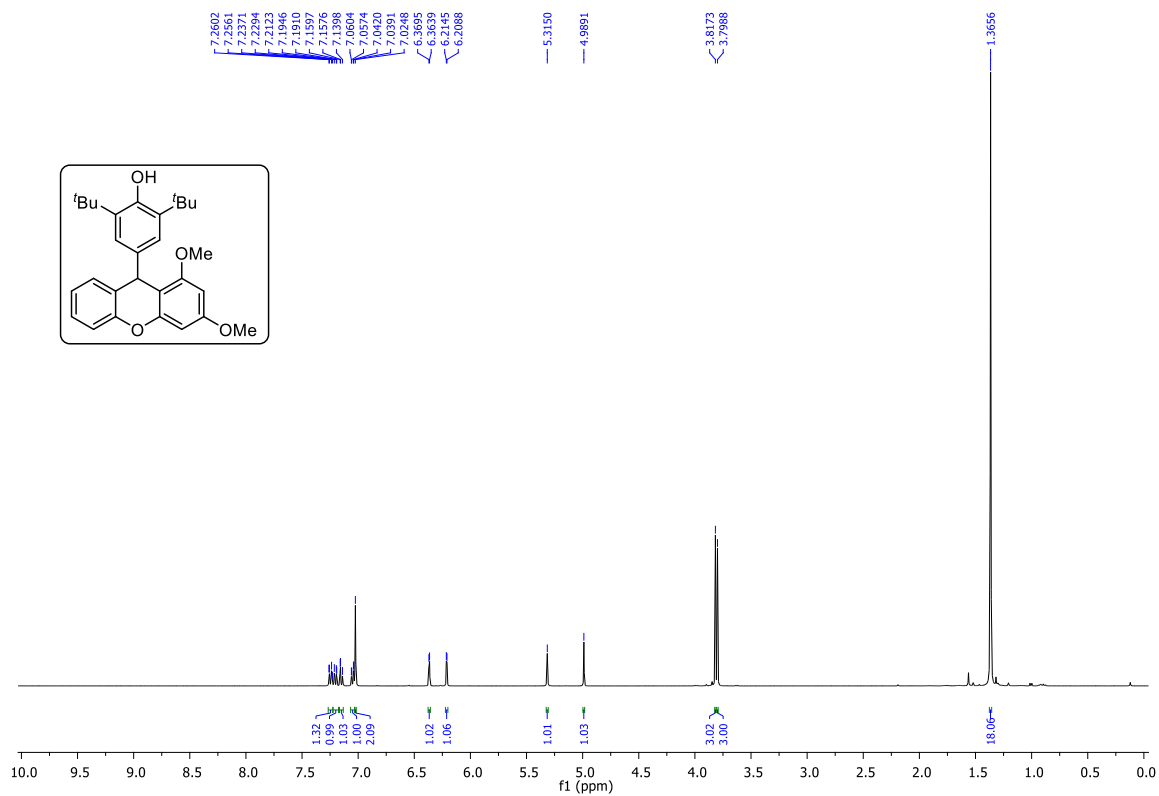
^1H NMR (400 MHz, CDCl_3) spectrum of **2g**



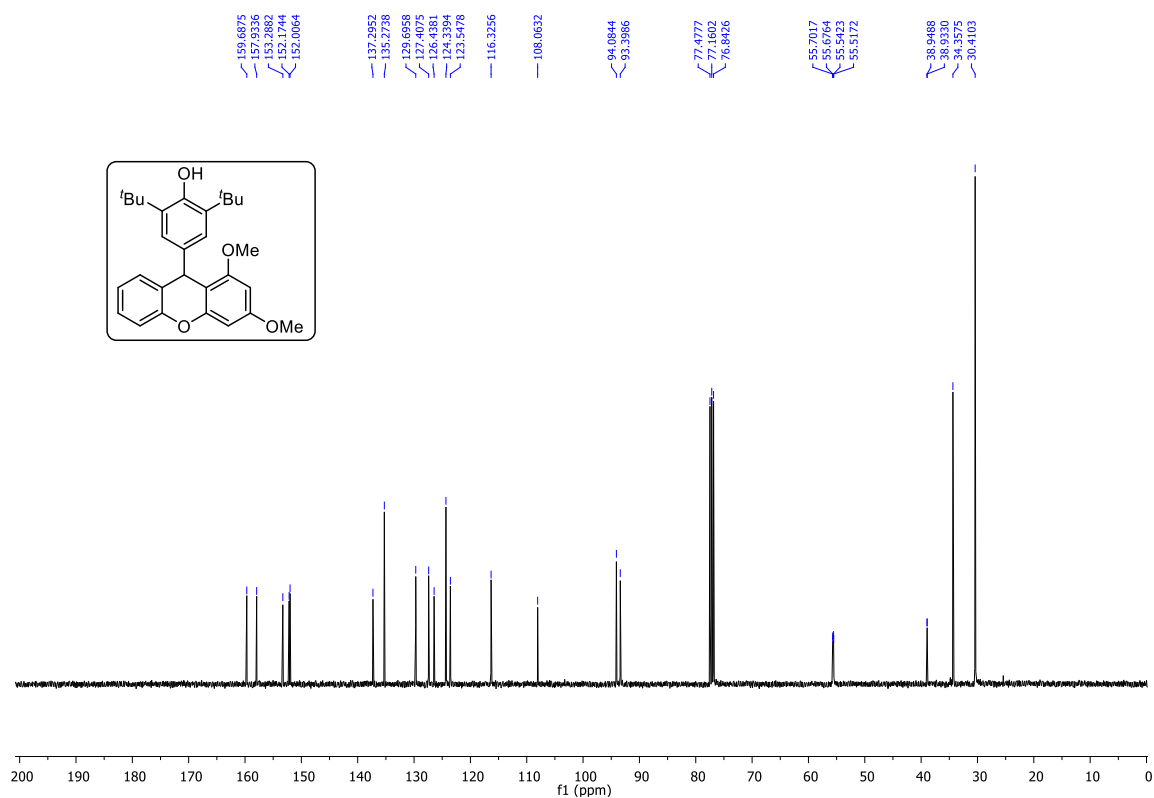
^{13}C $\{^1\text{H}\}$ NMR (100 MHz, CDCl_3) spectrum of **2g**



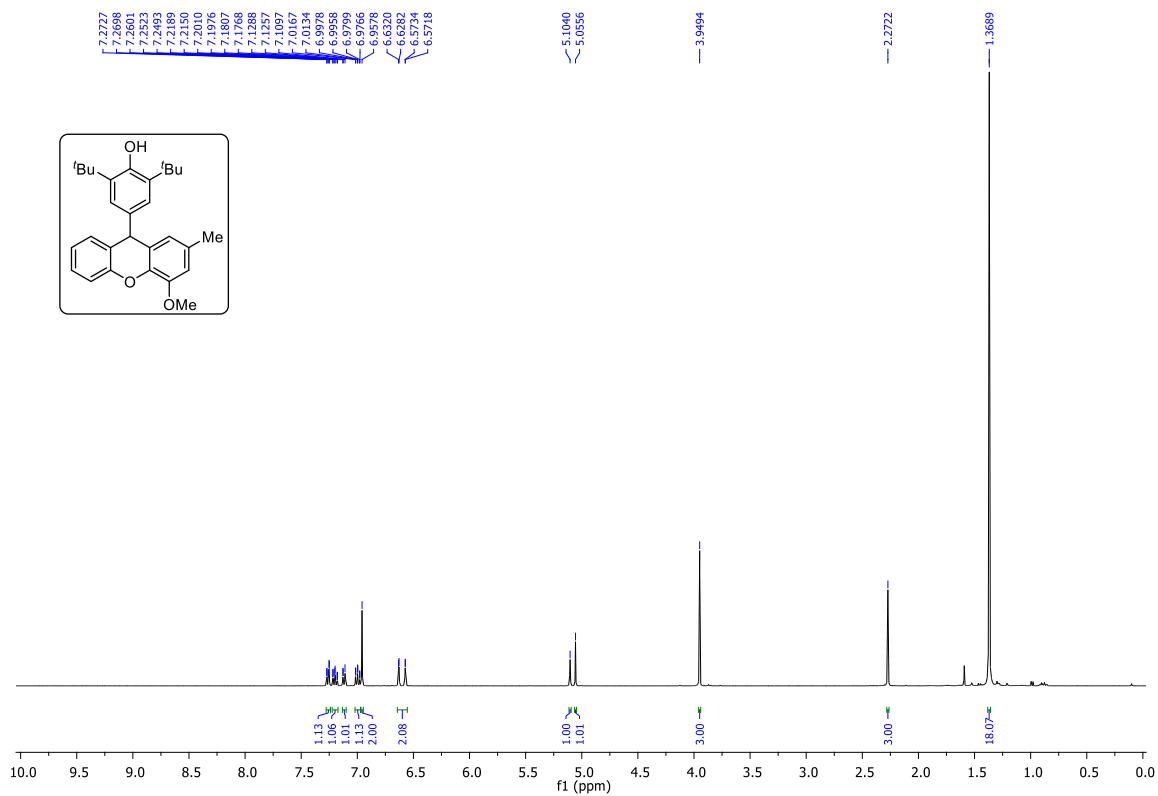
^1H NMR (400 MHz, CDCl_3) spectrum of **2h**



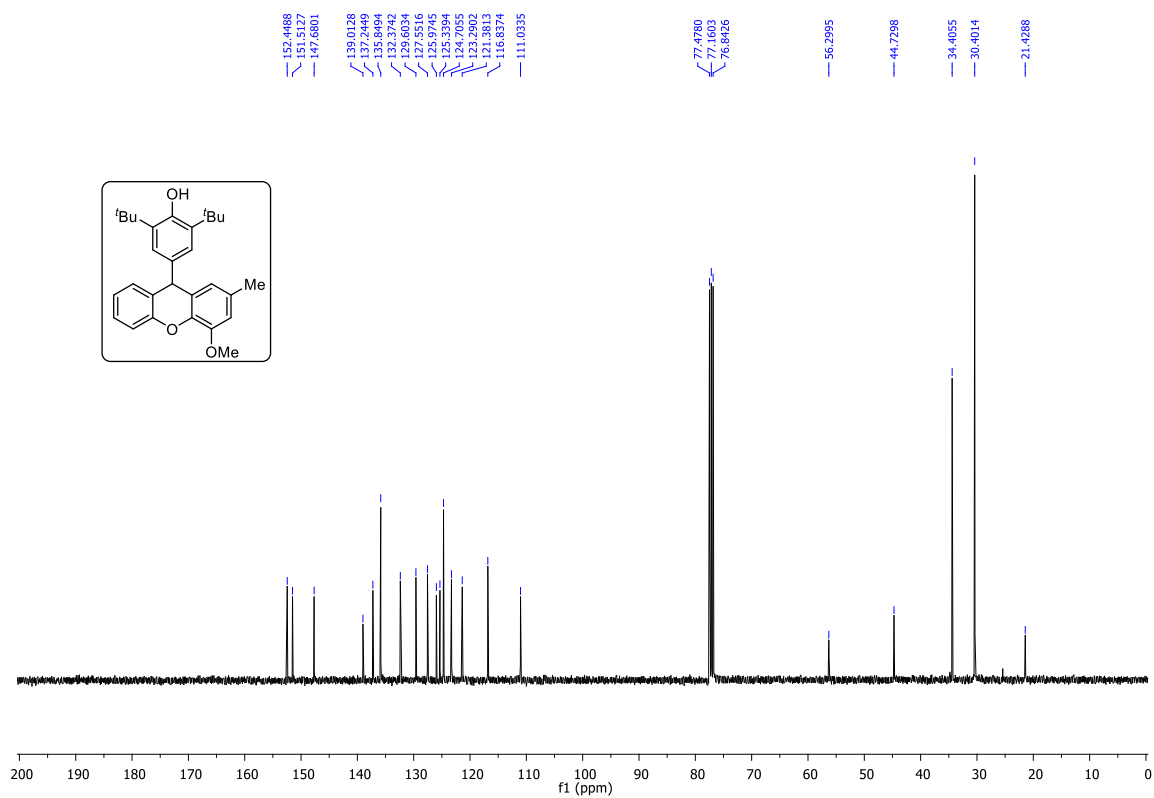
^{13}C $\{^1\text{H}\}$ NMR (100 MHz, CDCl_3) spectrum of **2h**



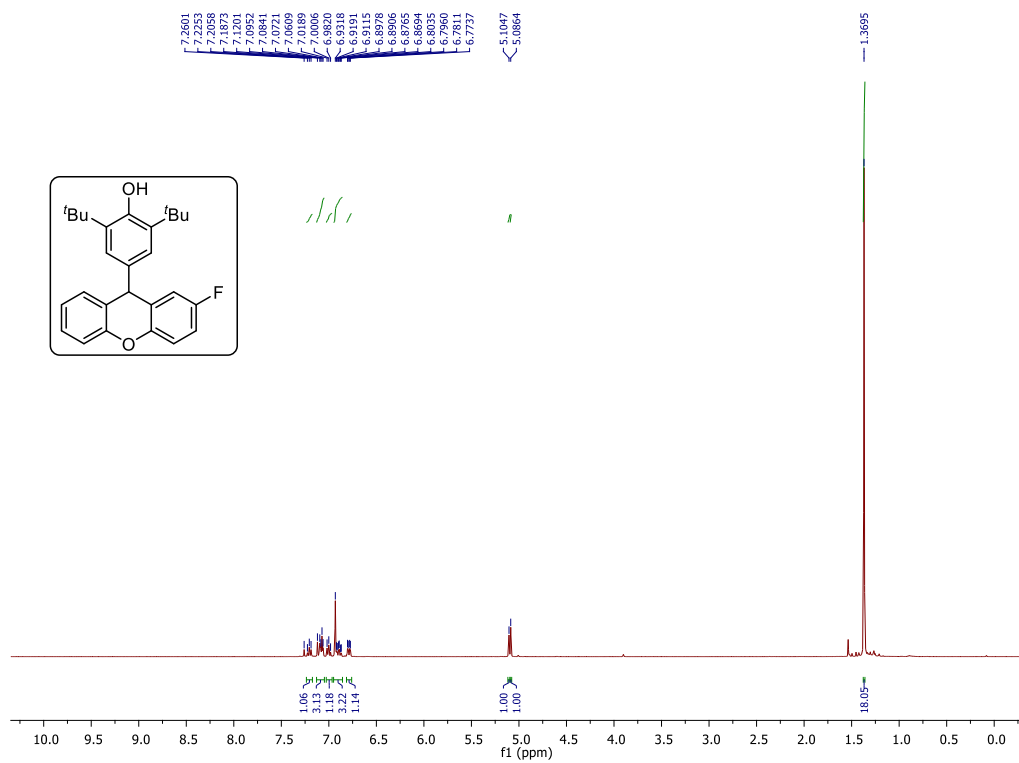
^1H NMR (400 MHz, CDCl_3) spectrum of **2i**



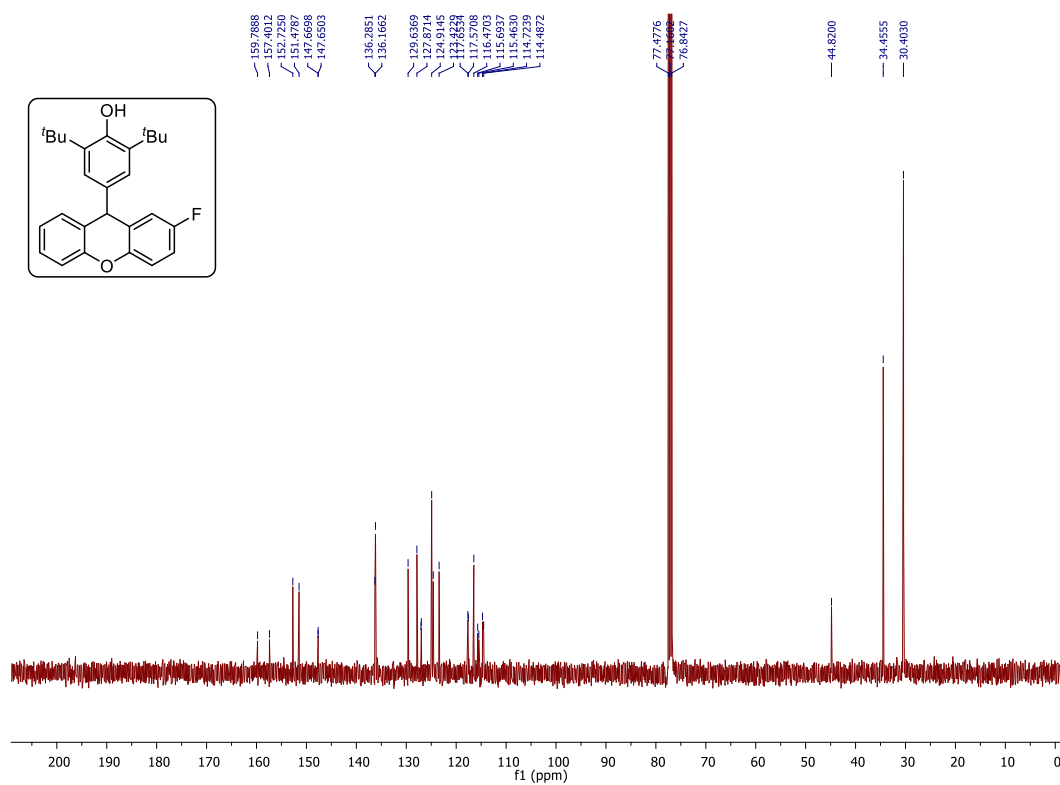
^{13}C $\{^1\text{H}\}$ NMR (100 MHz, CDCl_3) spectrum of **2i**



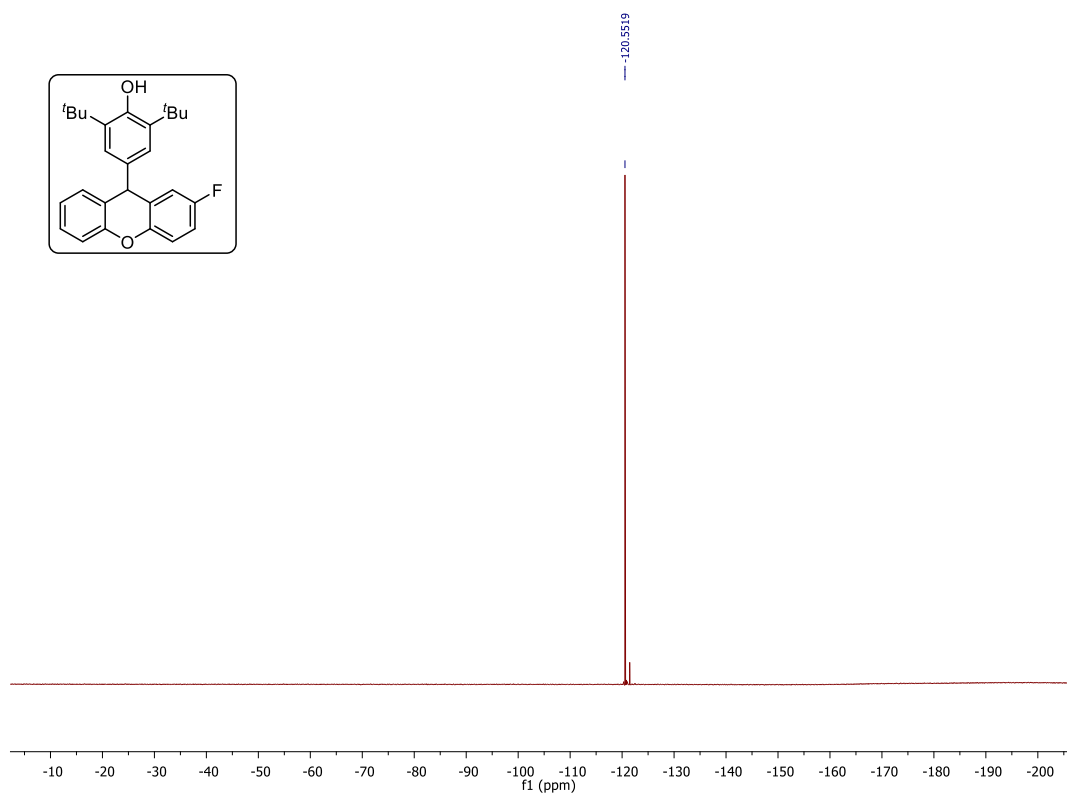
^1H NMR (400 MHz, CDCl_3) spectrum of **2j**



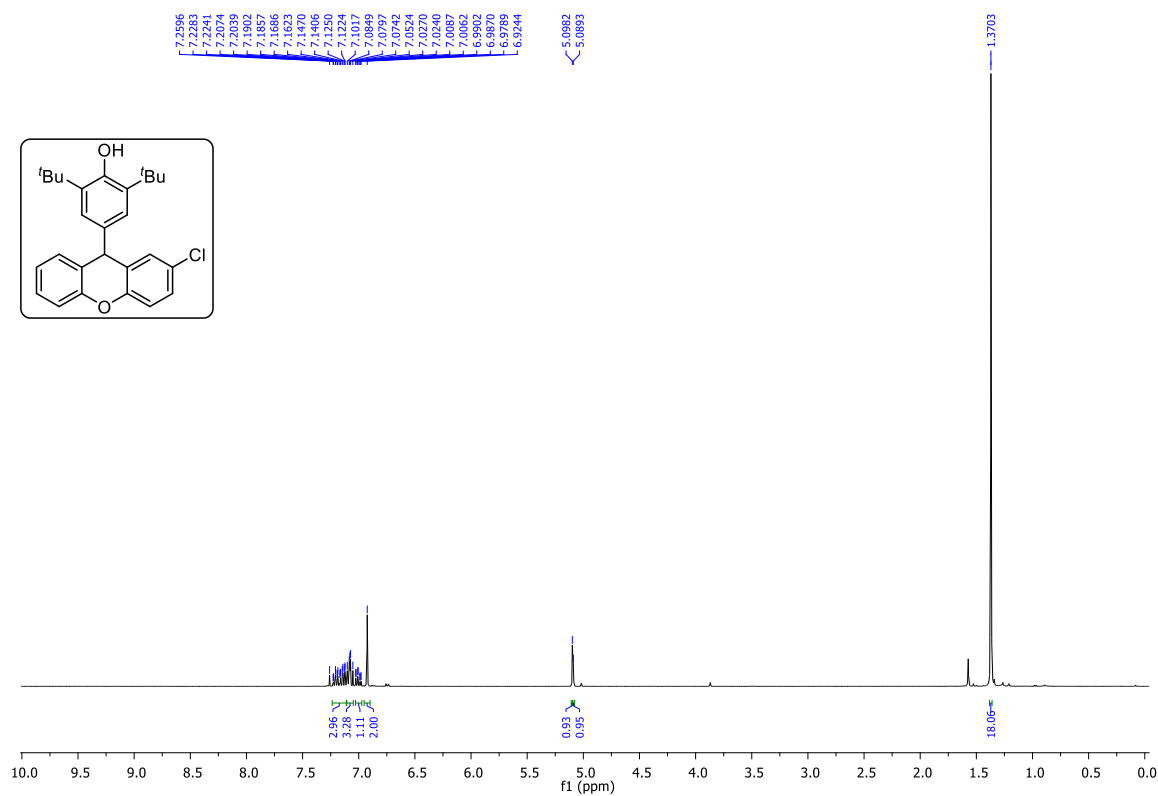
^{13}C { ^1H } NMR (100 MHz, CDCl_3) spectrum of **2j**



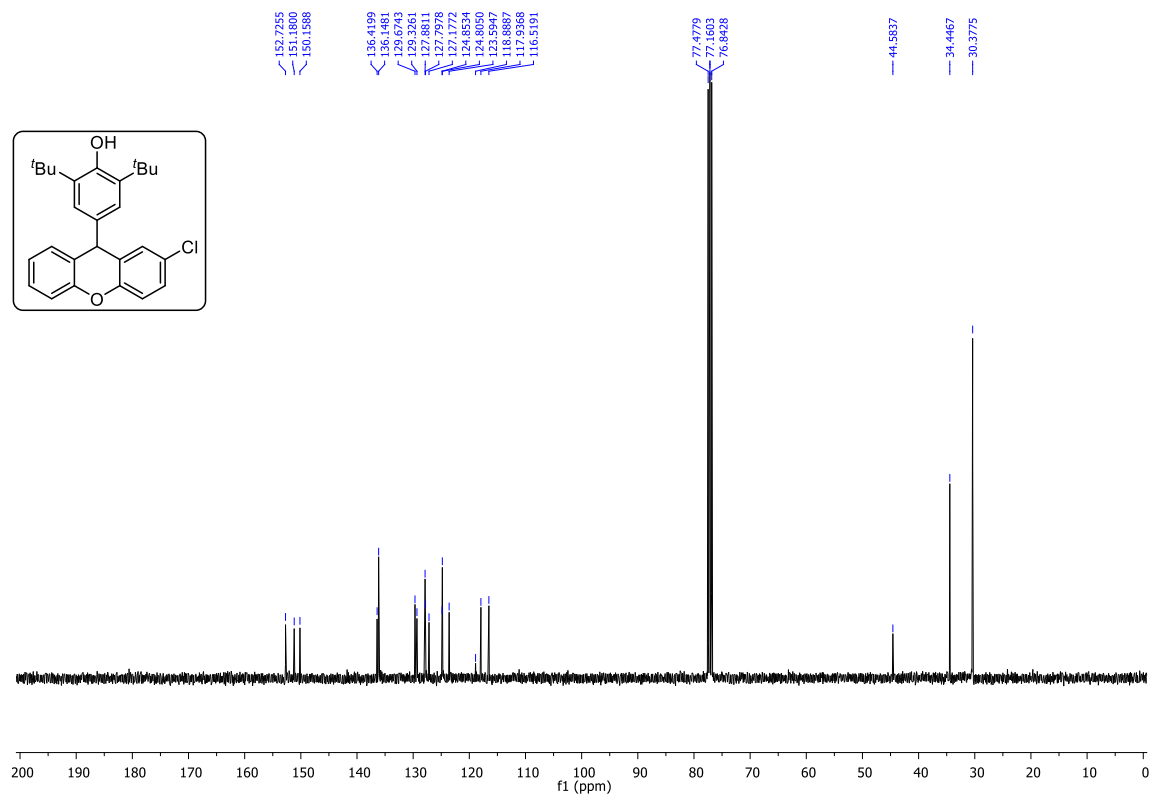
^{19}F { ^1H } NMR (376 MHz, CDCl_3) spectrum of **2j**



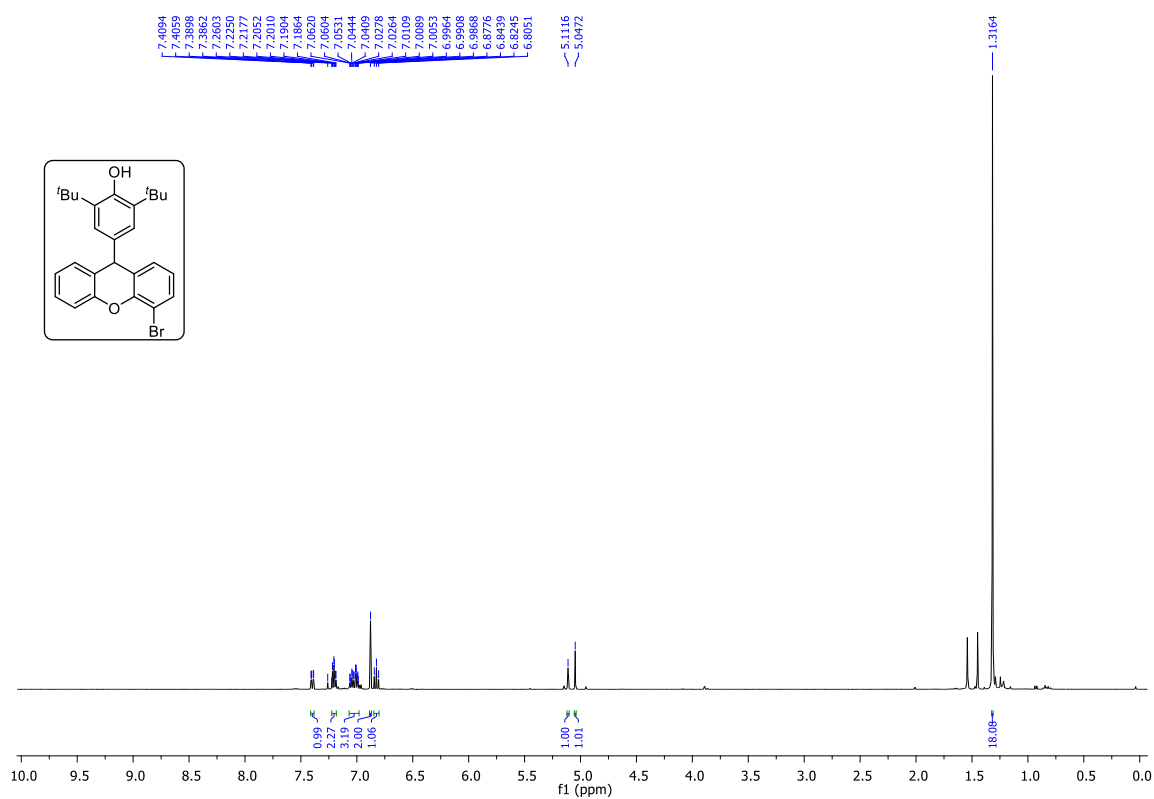
^1H NMR (400 MHz, CDCl_3) spectrum of **2k**



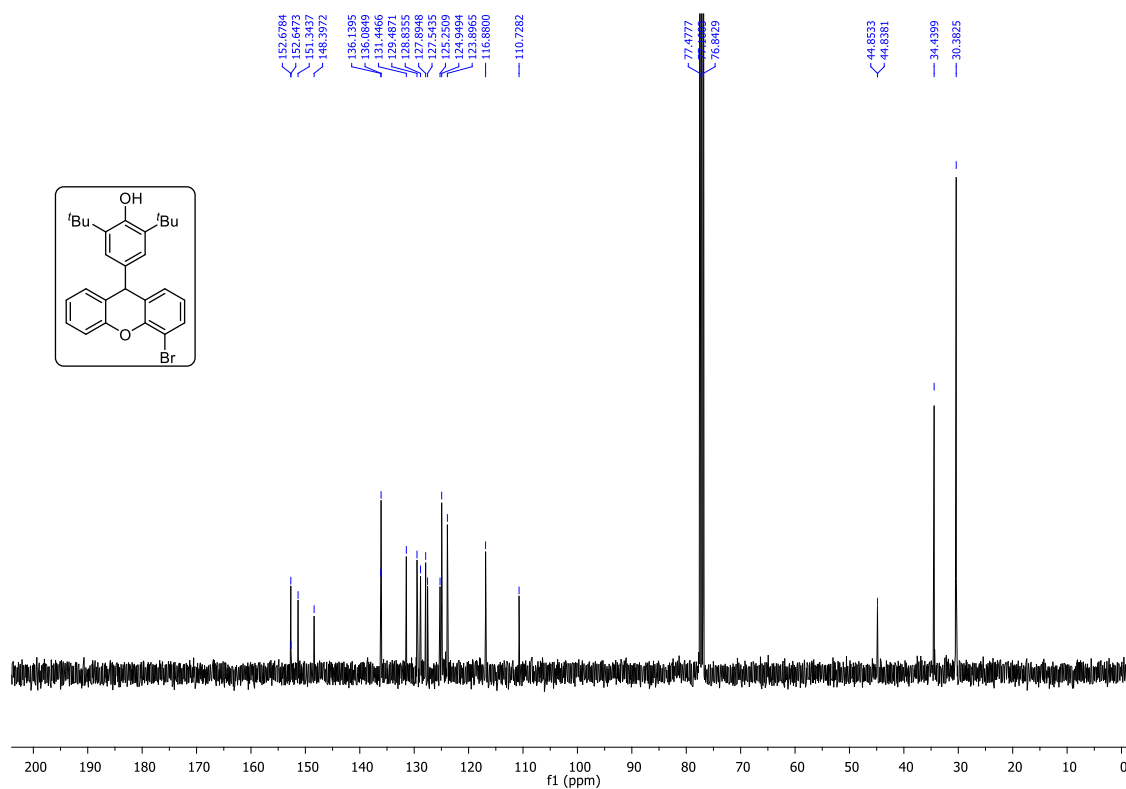
^{13}C $\{^1\text{H}\}$ NMR (100 MHz, CDCl_3) spectrum of **2k**



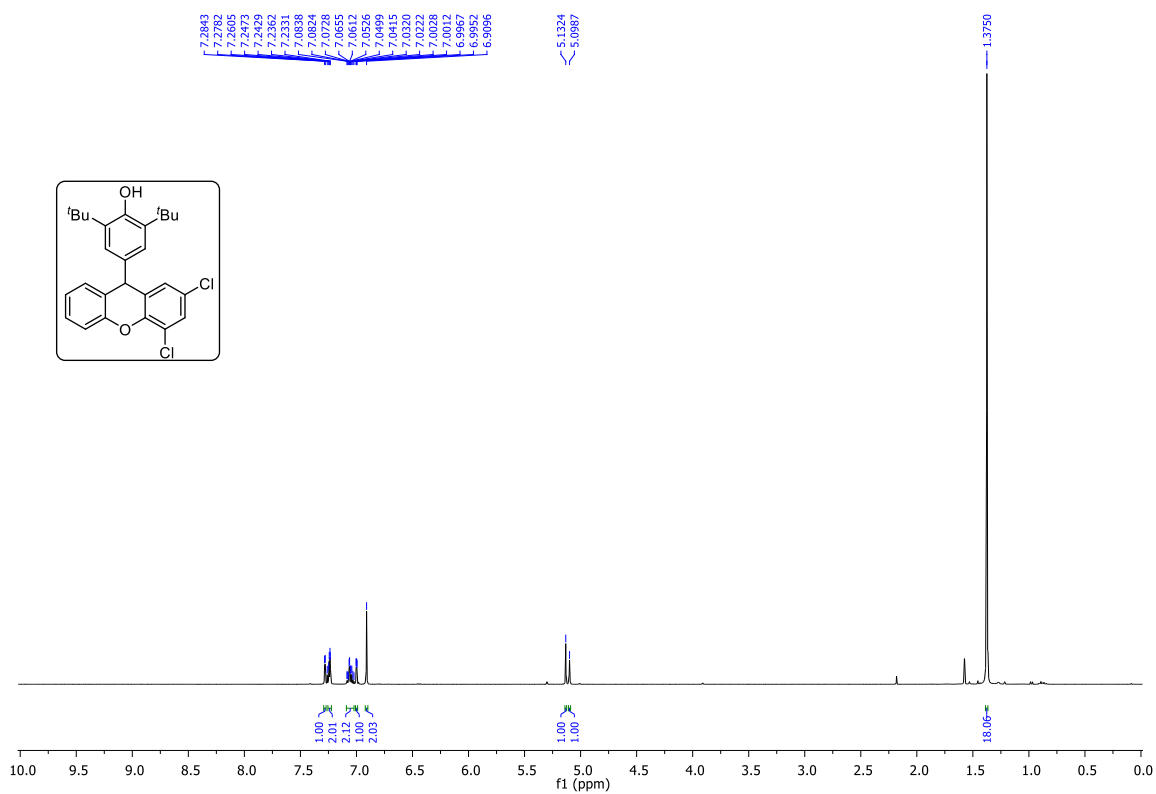
¹H NMR (400 MHz, CDCl₃) spectrum of **21**



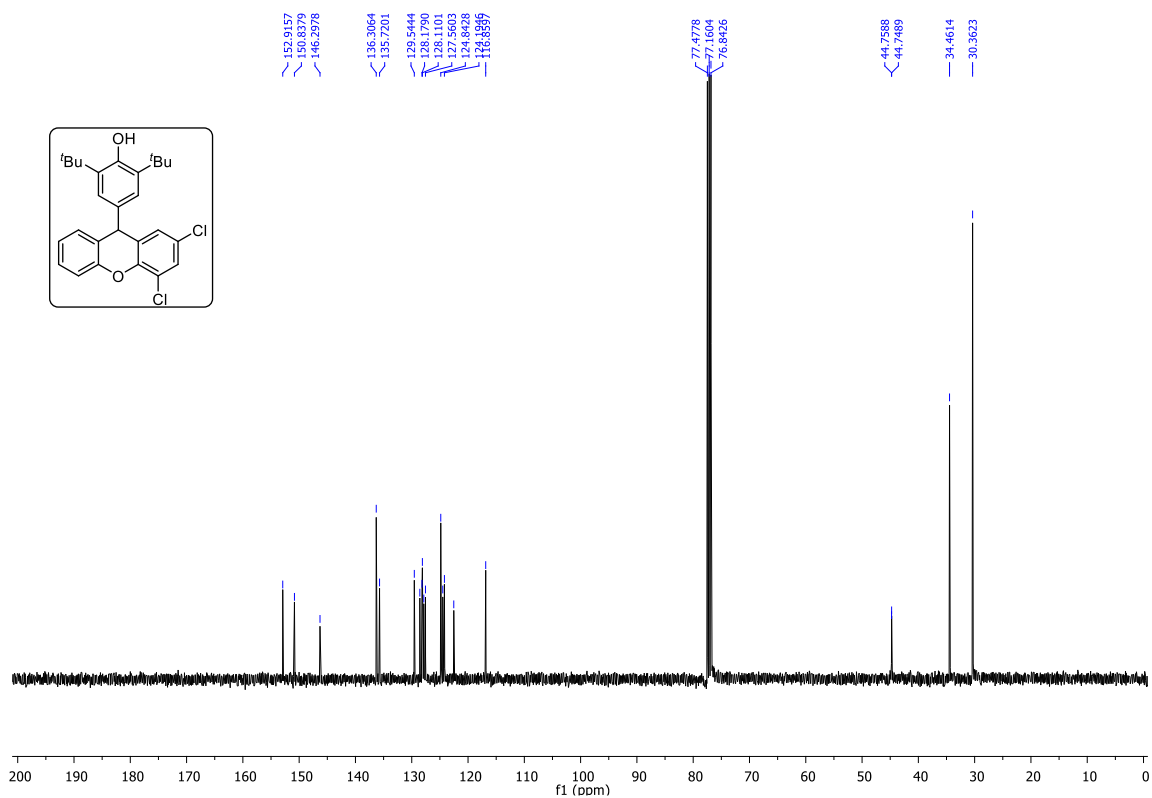
¹³C {¹H} NMR (100 MHz, CDCl₃) spectrum of **21**



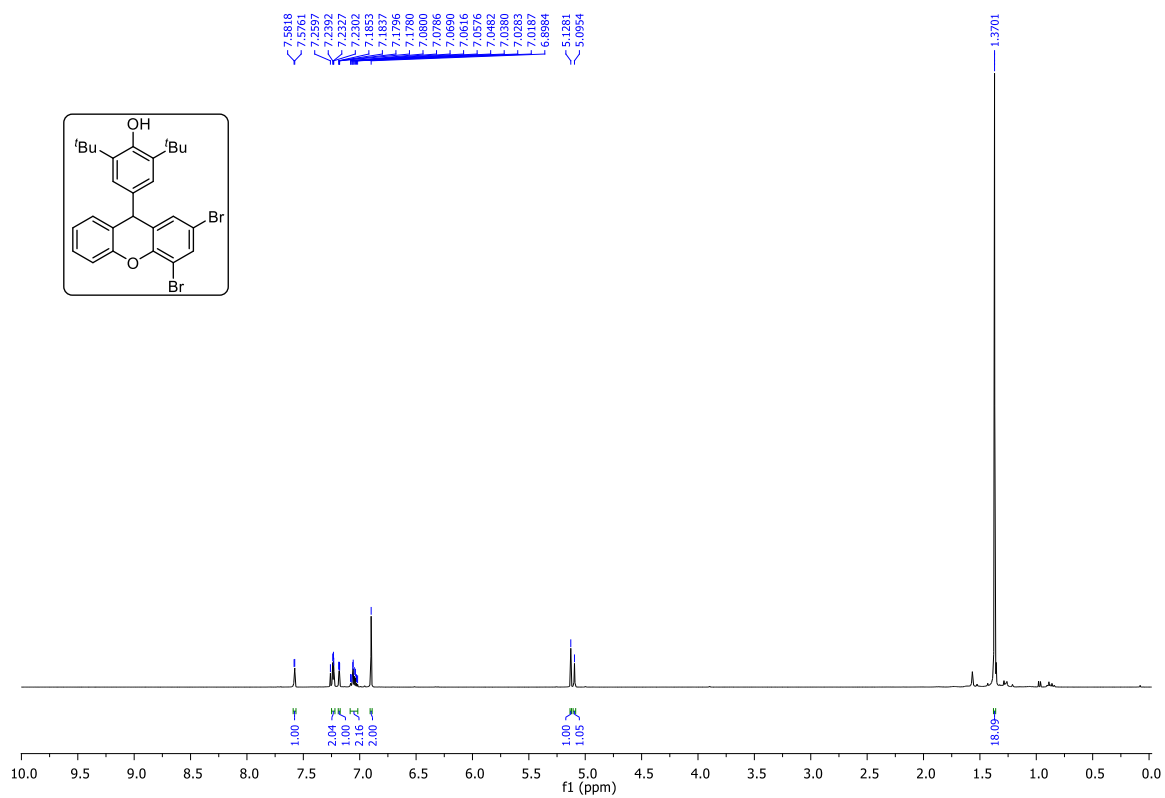
^1H NMR (400 MHz, CDCl_3) spectrum of **2m**



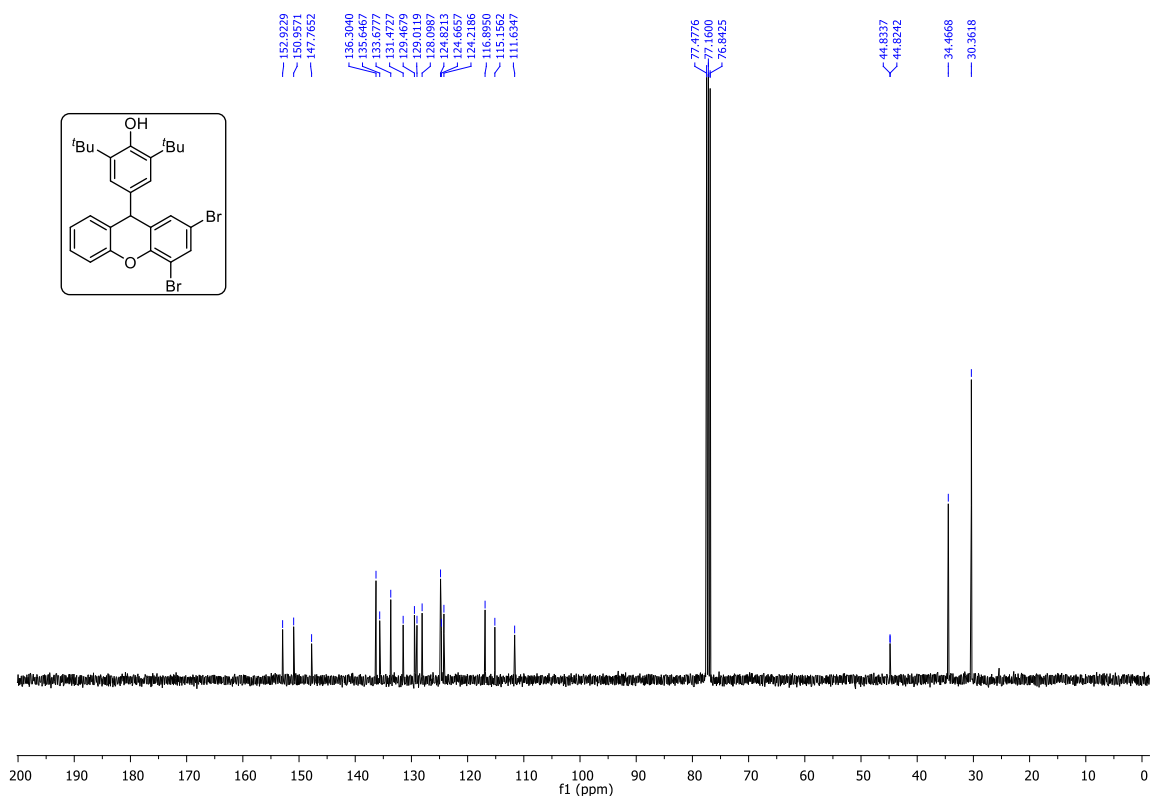
^{13}C { ^1H } NMR (100 MHz, CDCl_3) spectrum of **2m**



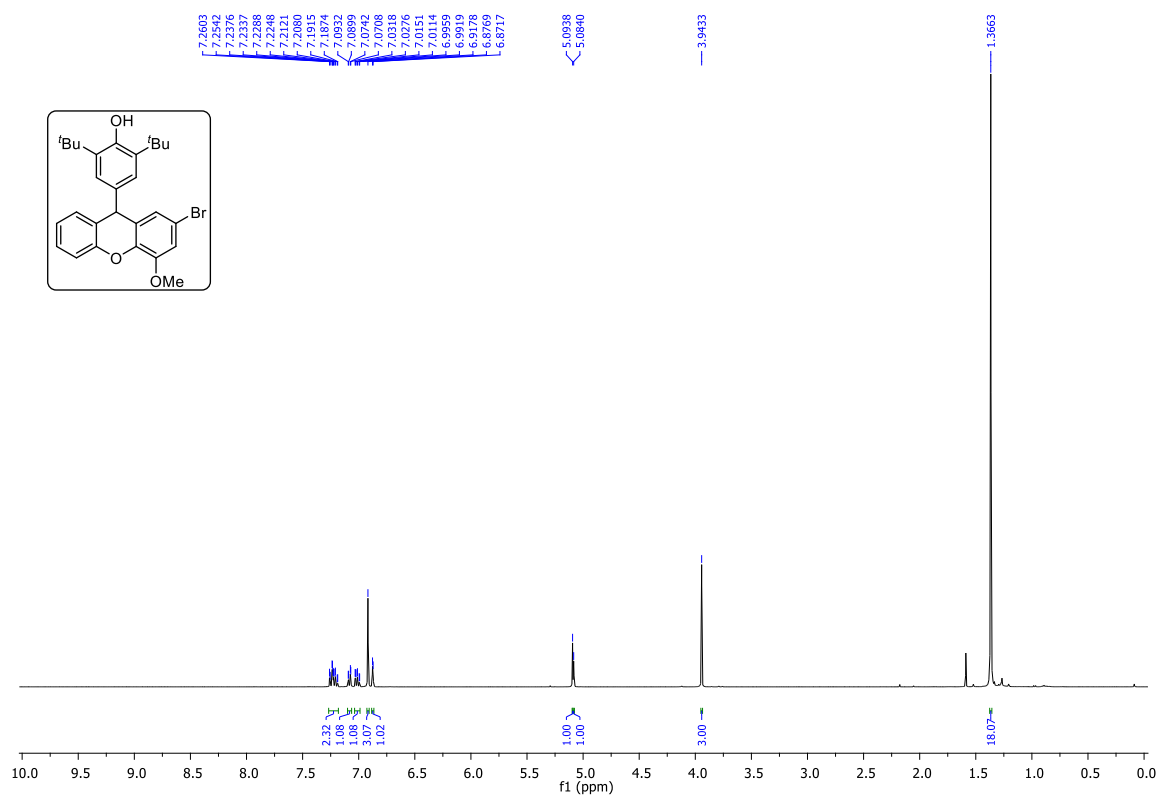
¹H NMR (400 MHz, CDCl₃) spectrum of **2n**



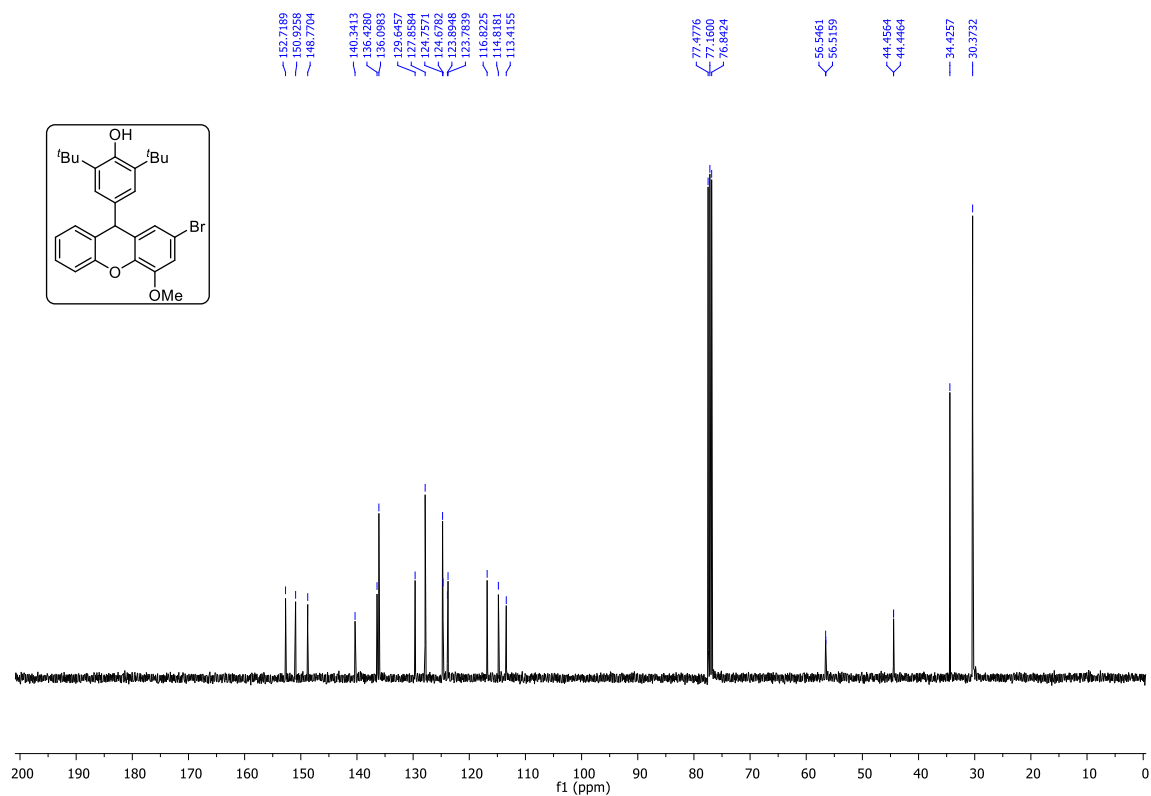
¹³C {¹H} NMR (100 MHz, CDCl₃) spectrum of **2n**



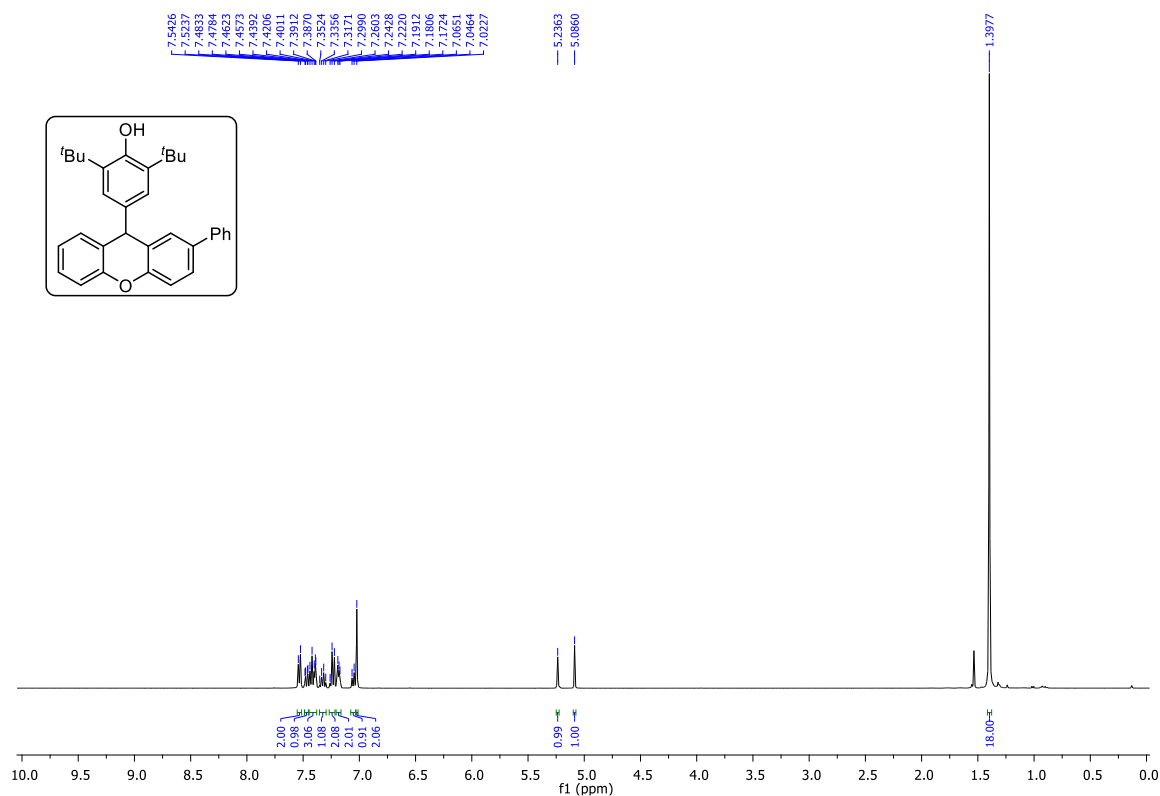
^1H NMR (400 MHz, CDCl_3) spectrum of **2o**



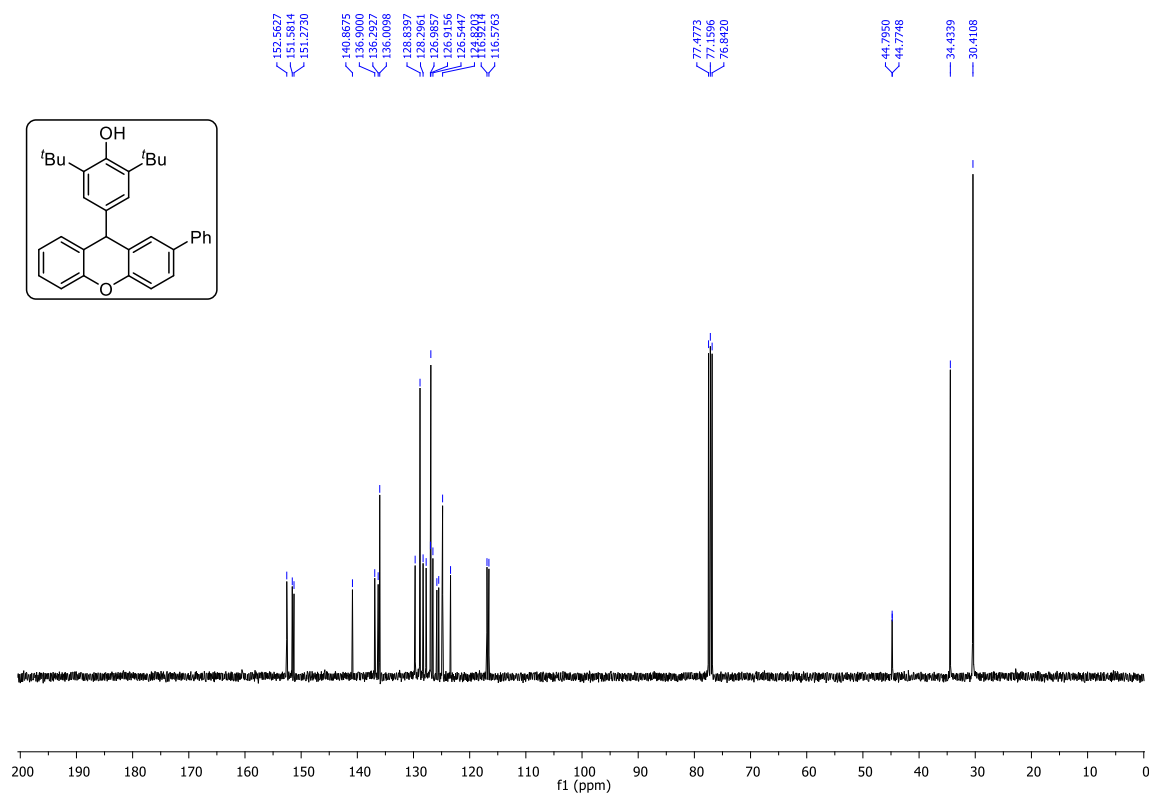
^{13}C $\{^1\text{H}\}$ NMR (100 MHz, CDCl_3) spectrum of **2o**



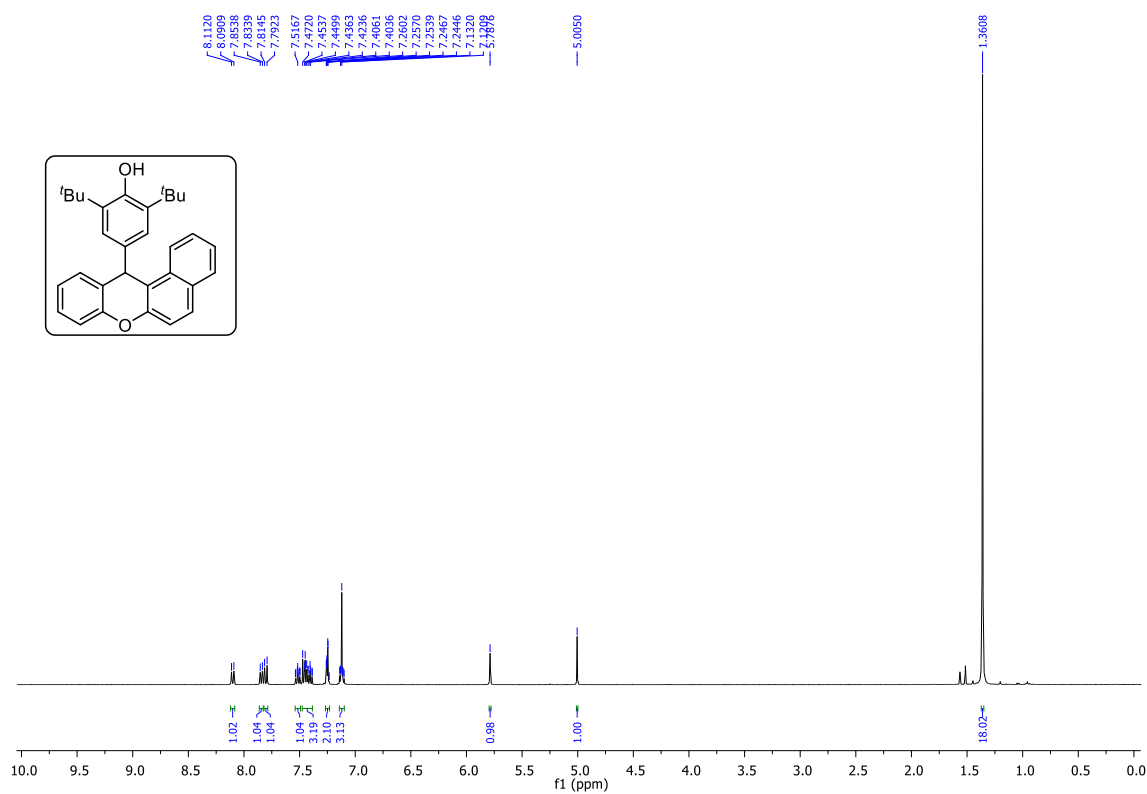
^1H NMR (400 MHz, CDCl_3) spectrum of **2p**



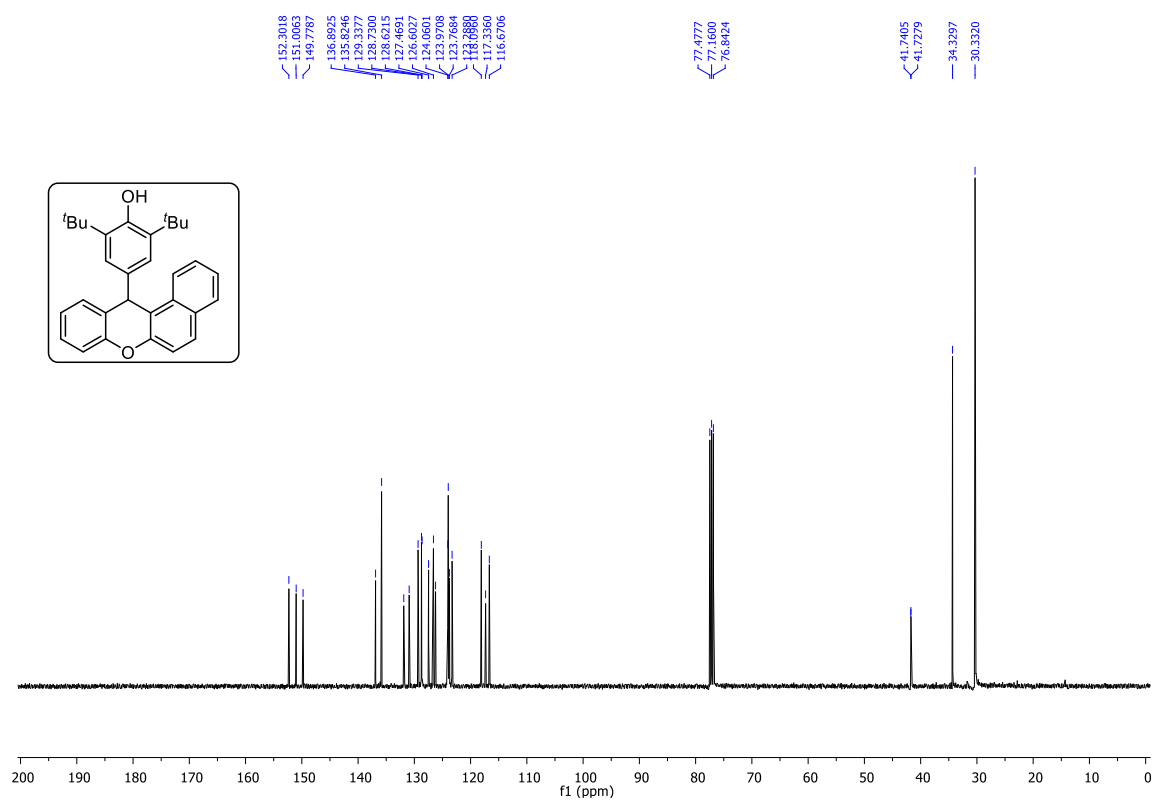
^{13}C $\{^1\text{H}\}$ NMR (100 MHz, CDCl_3) spectrum of **2p**



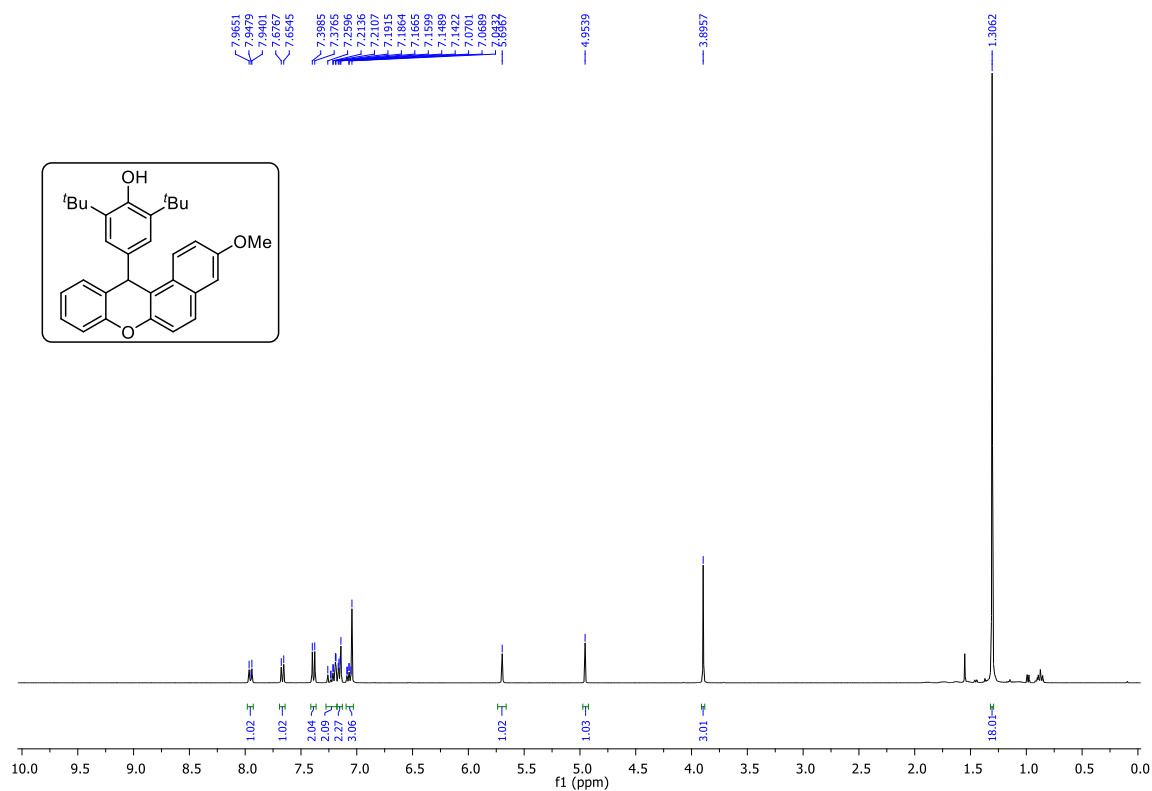
¹H NMR (400 MHz, CDCl₃) spectrum of **2q**



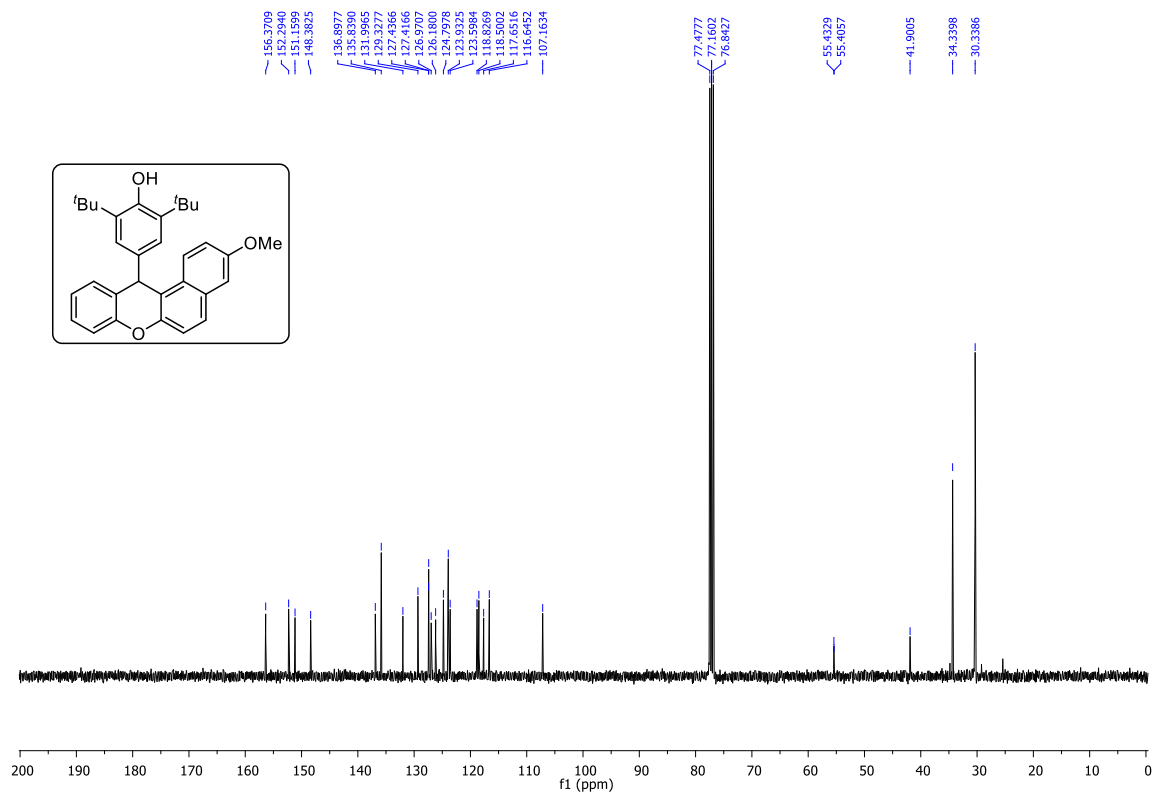
¹³C {¹H} NMR (100 MHz, CDCl₃) spectrum of **2q**



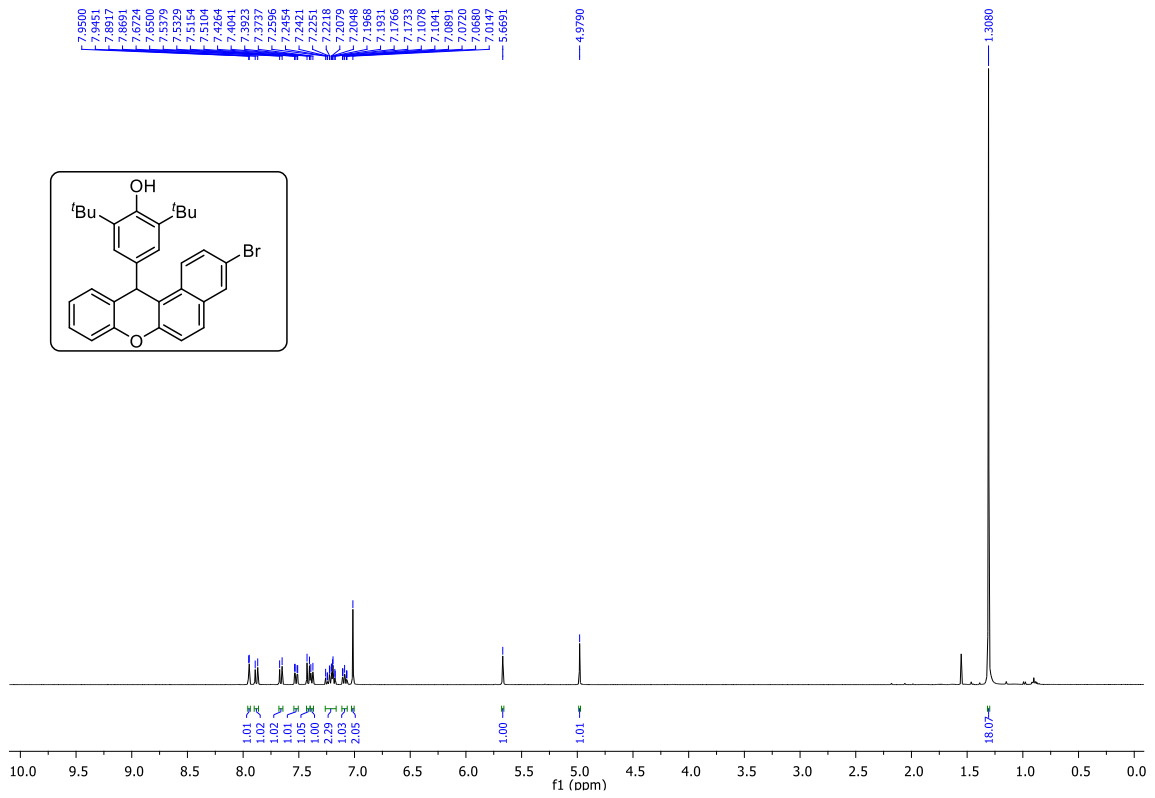
¹H NMR (400 MHz, CDCl₃) spectrum of **2r**



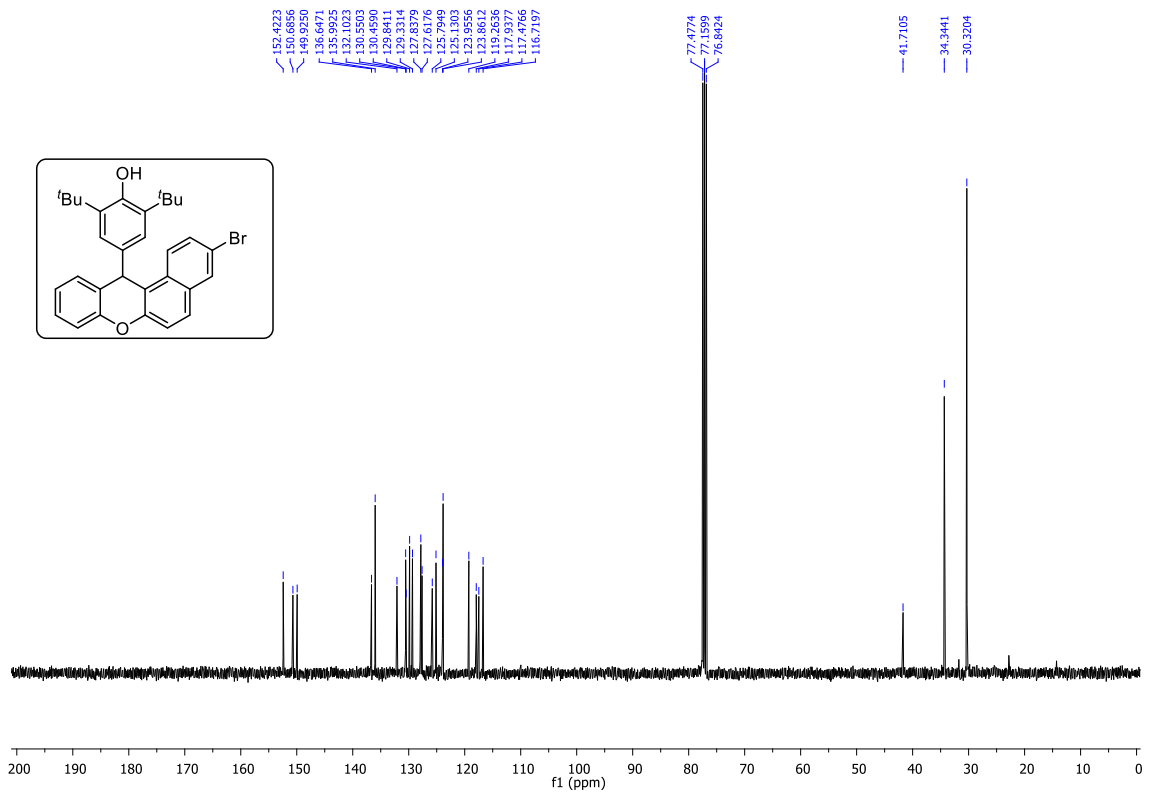
¹³C {¹H} NMR (100 MHz, CDCl₃) spectrum of **2r**



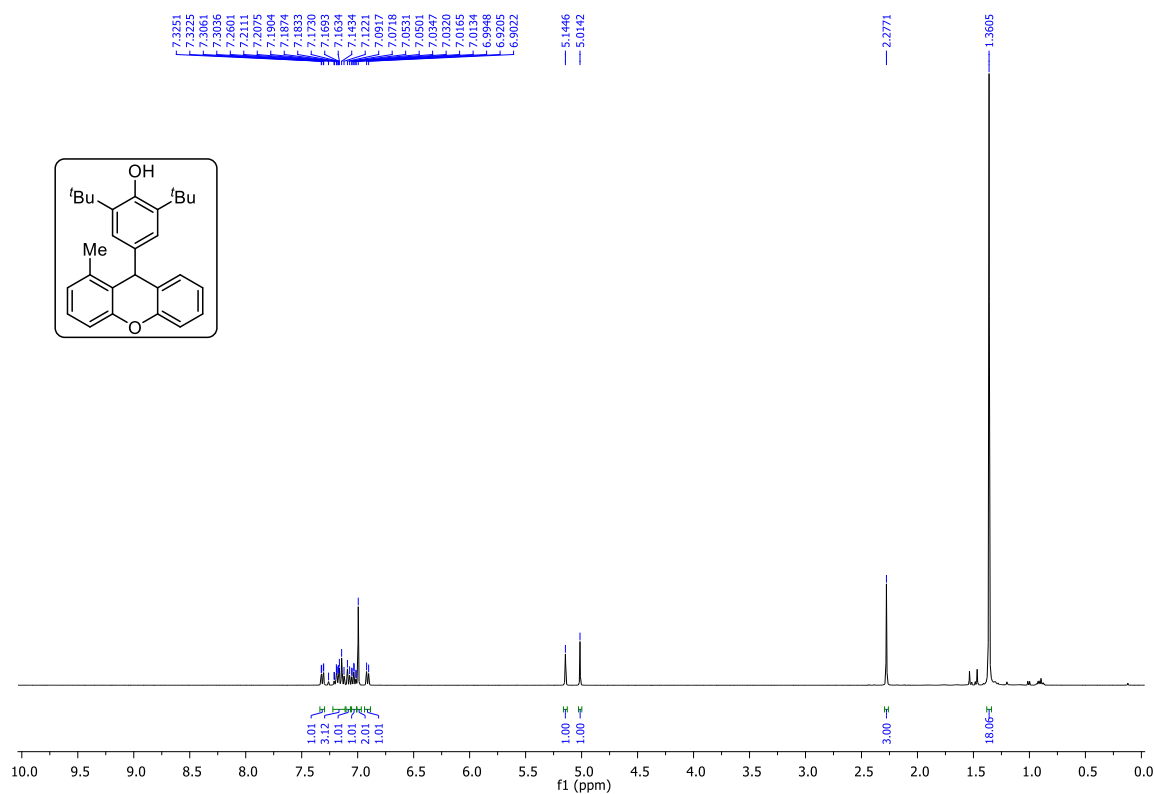
¹H NMR (400 MHz, CDCl₃) spectrum of **2s**



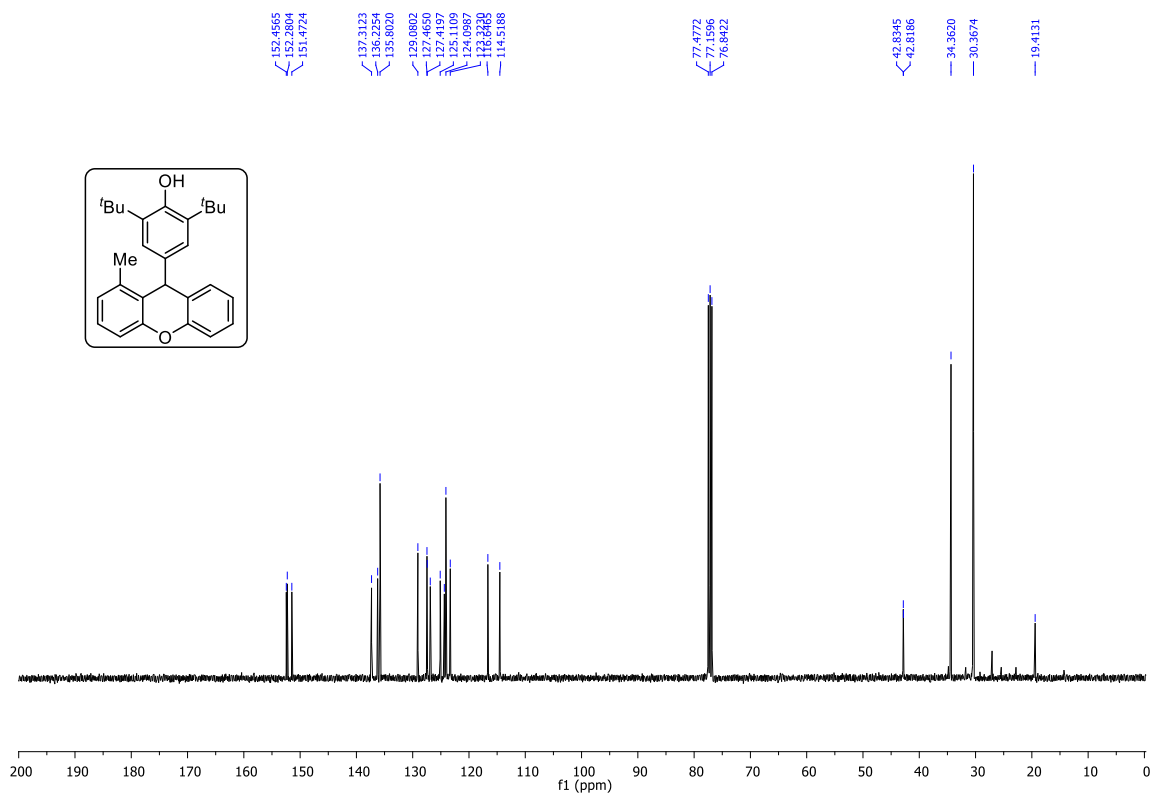
¹³C {¹H} NMR (100 MHz, CDCl₃) spectrum of **2s**



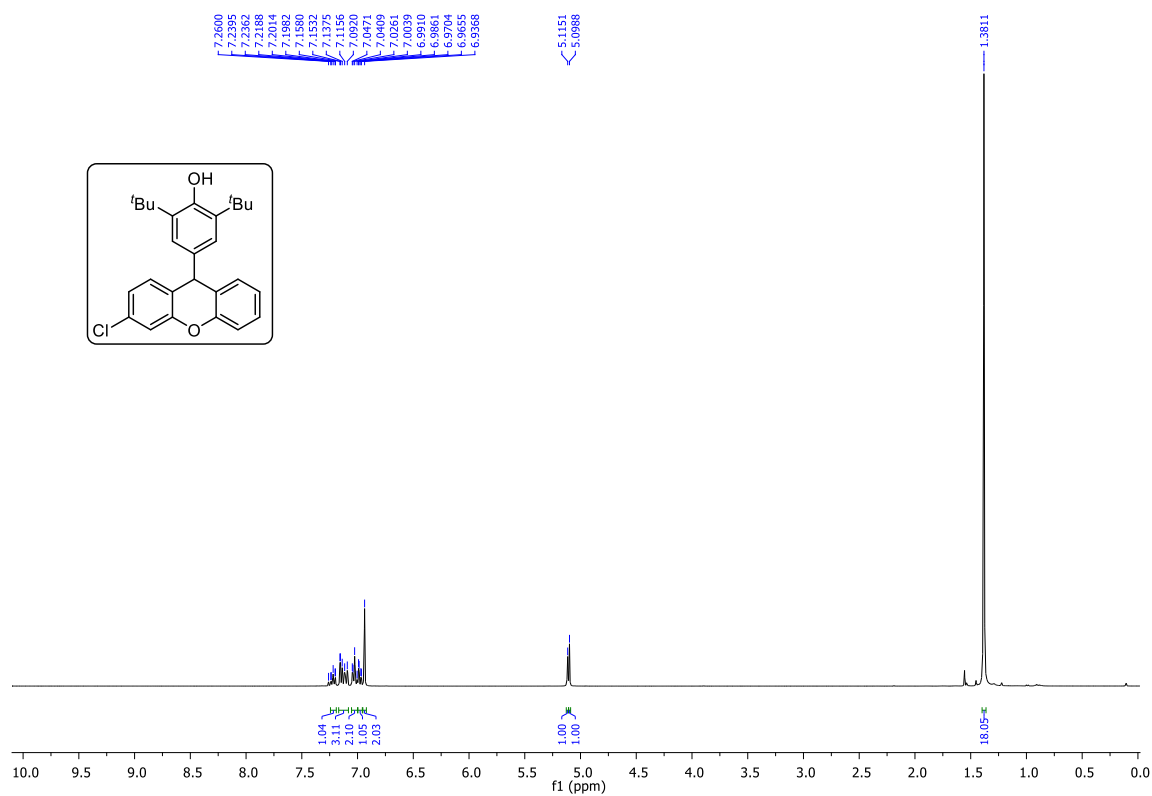
¹H NMR (400 MHz, CDCl₃) spectrum of **2t**



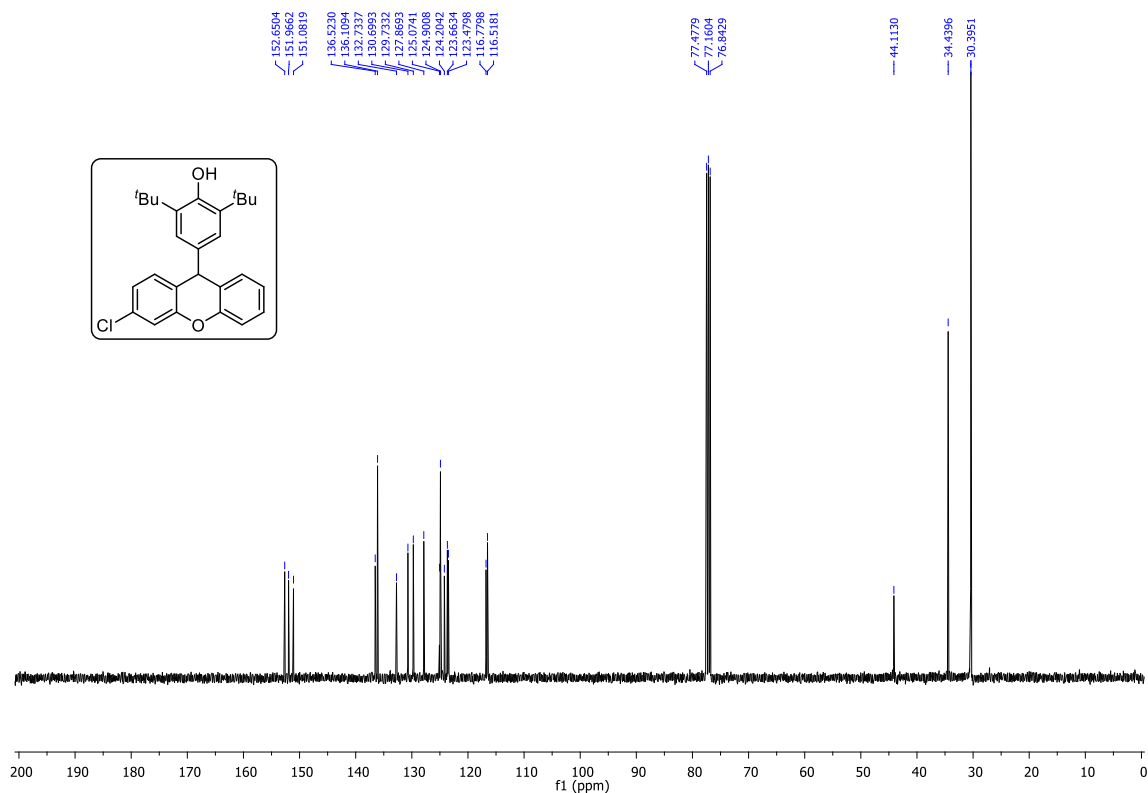
¹³C {¹H} NMR (100 MHz, CDCl₃) spectrum of **2t**



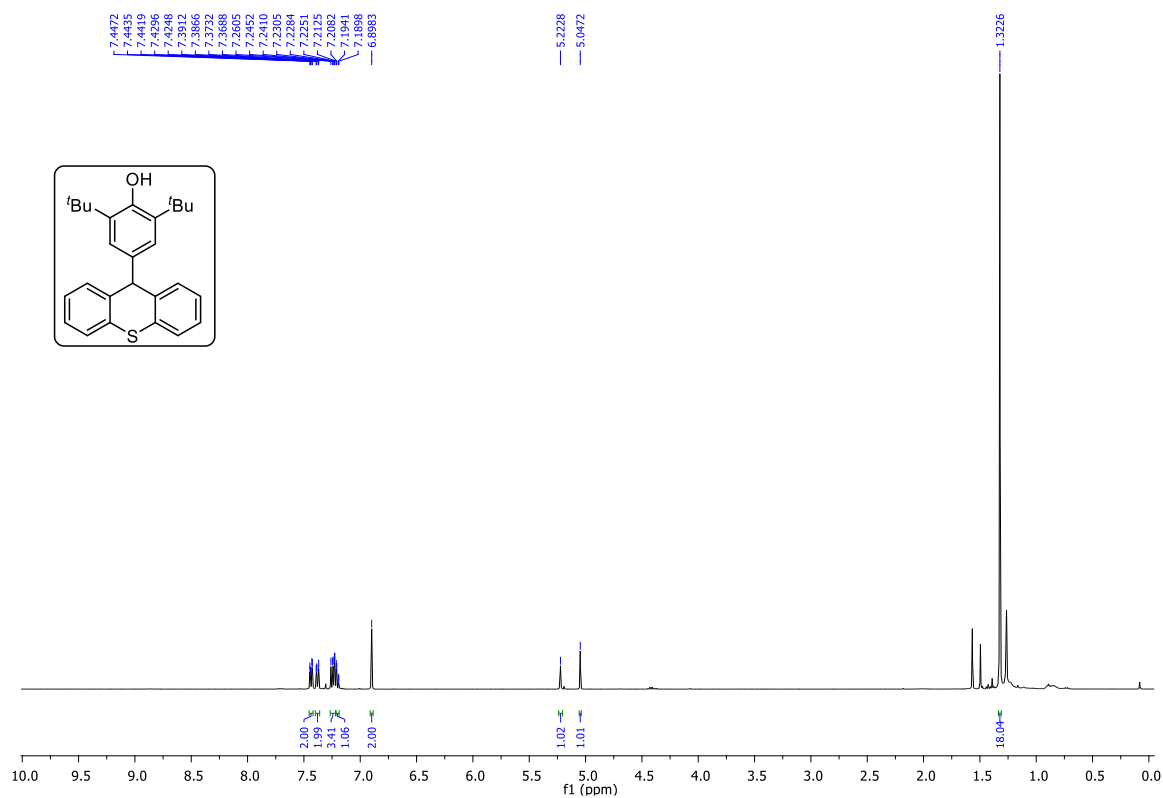
^1H NMR (400 MHz, CDCl_3) spectrum of **2u**



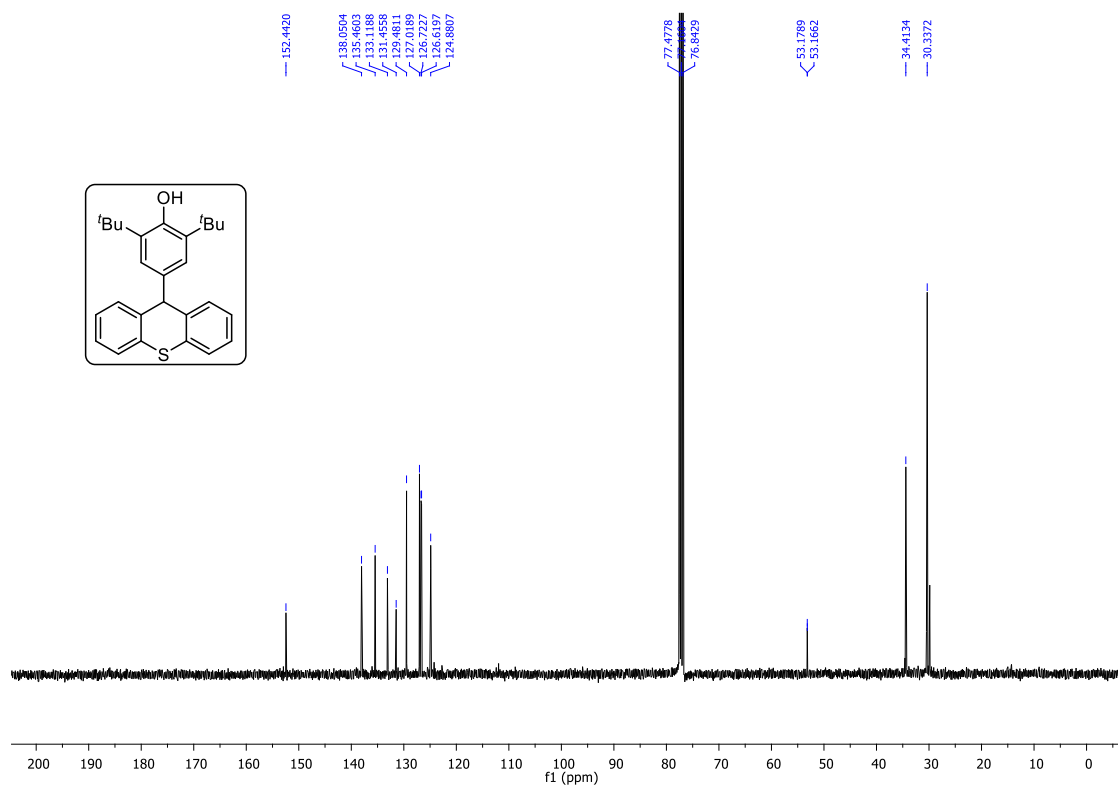
^{13}C { ^1H } NMR (100 MHz, CDCl_3) spectrum of **2u**



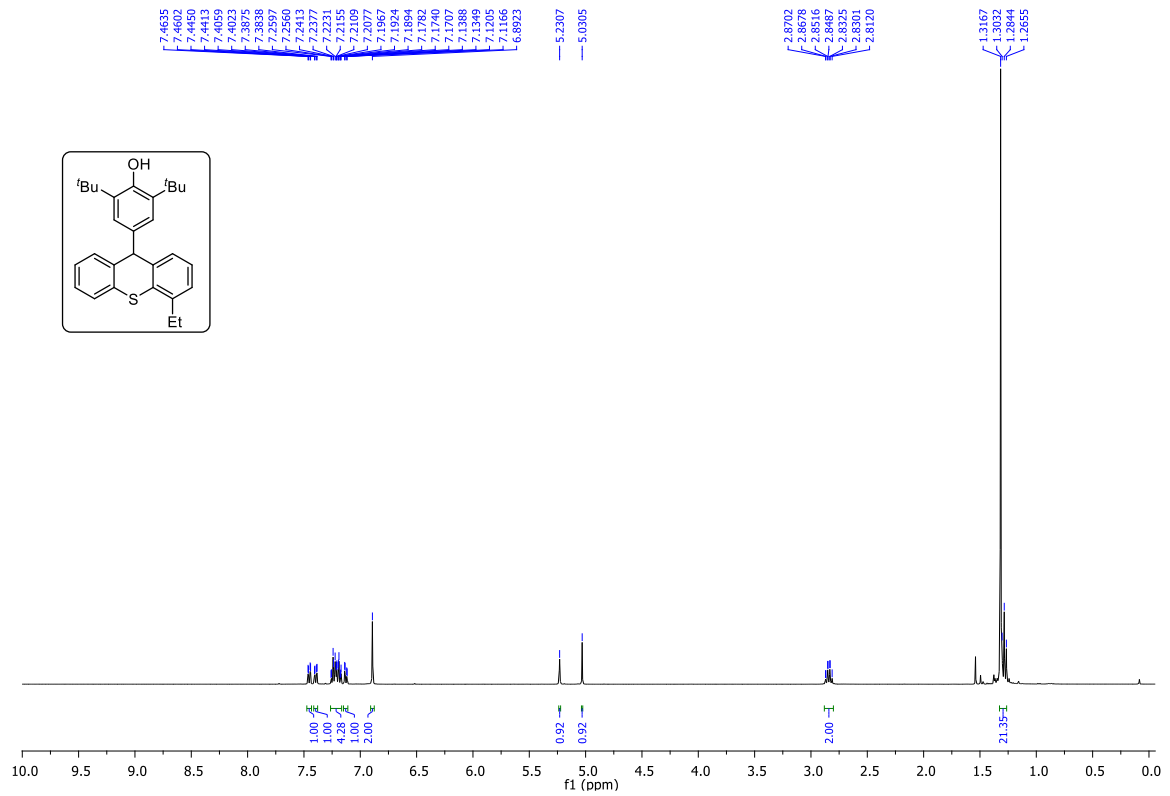
¹H NMR (400 MHz, CDCl₃) spectrum of **4a**



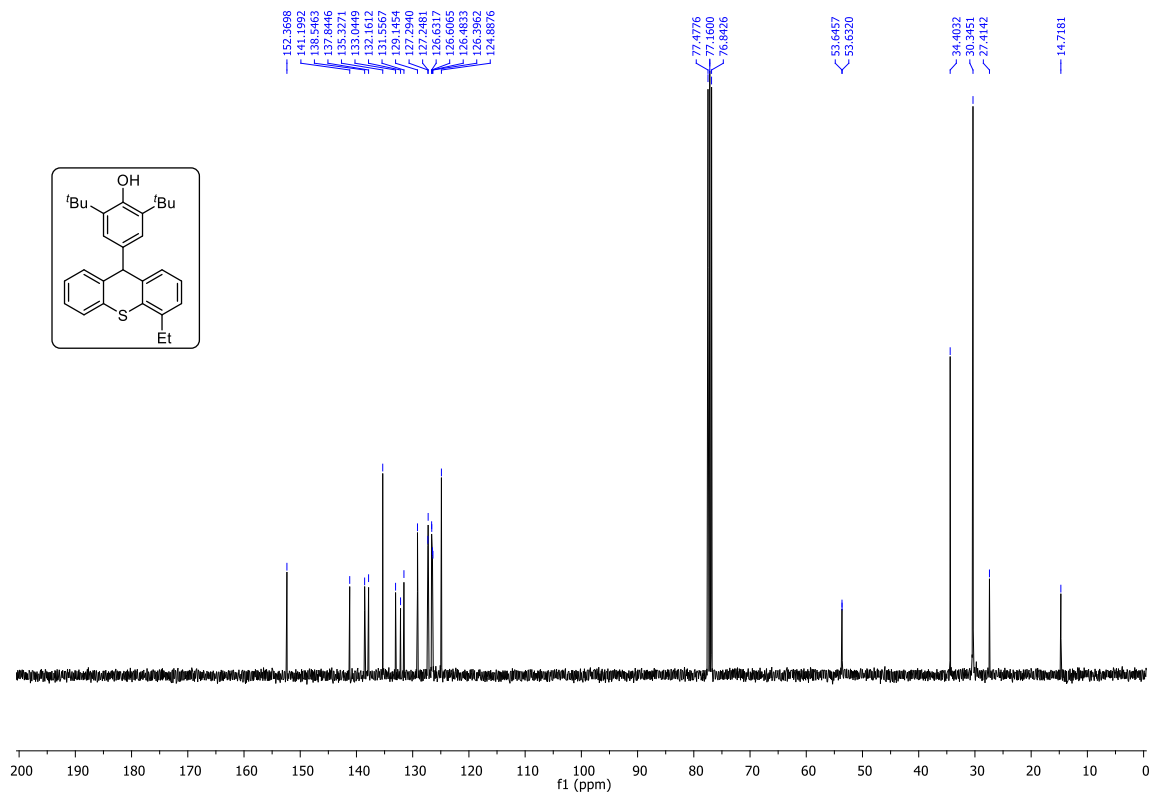
¹³C {¹H} NMR (100 MHz, CDCl₃) spectrum of **4a**



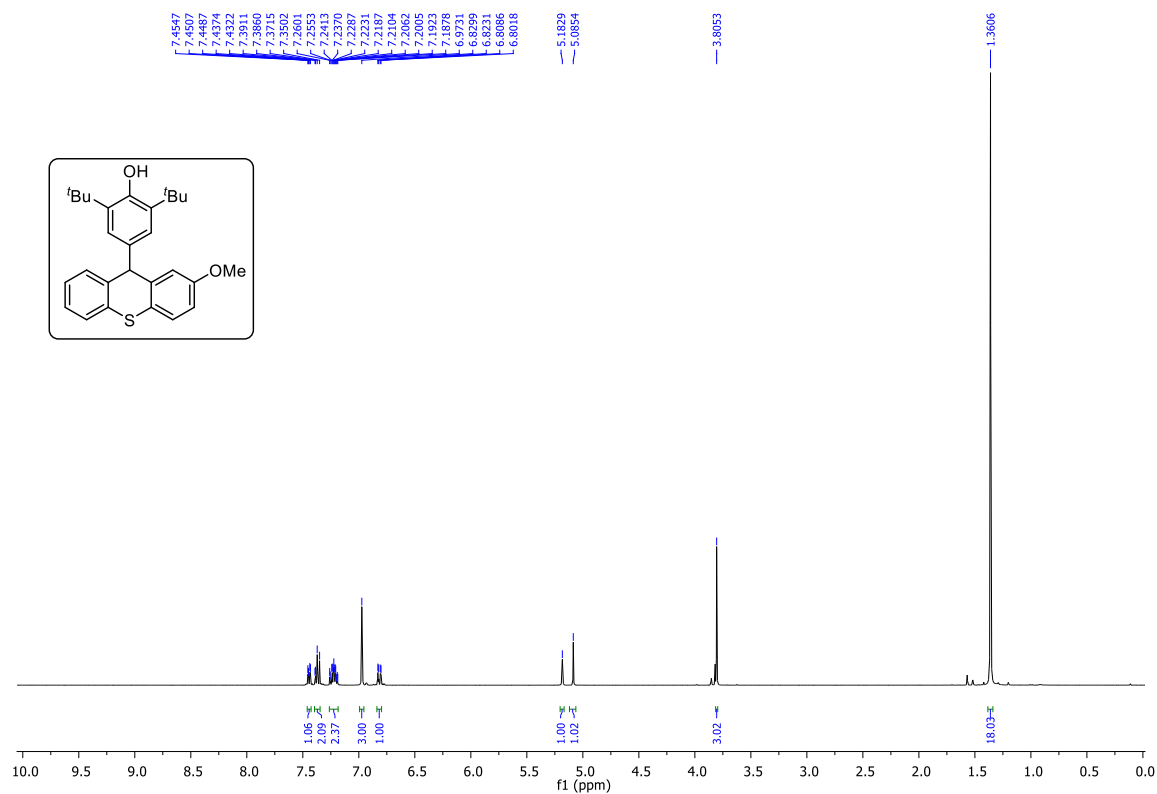
^1H NMR (400 MHz, CDCl_3) spectrum of **4b**



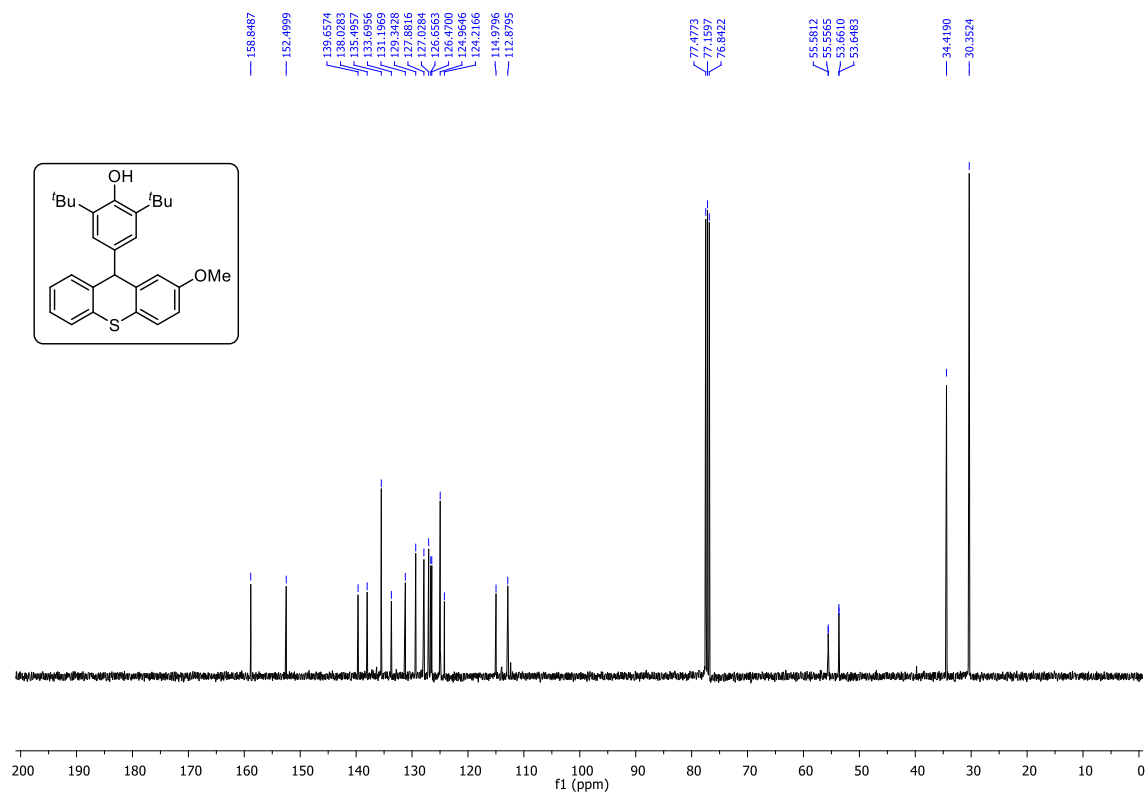
^{13}C $\{^1\text{H}\}$ NMR (100 MHz, CDCl_3) spectrum of **4b**



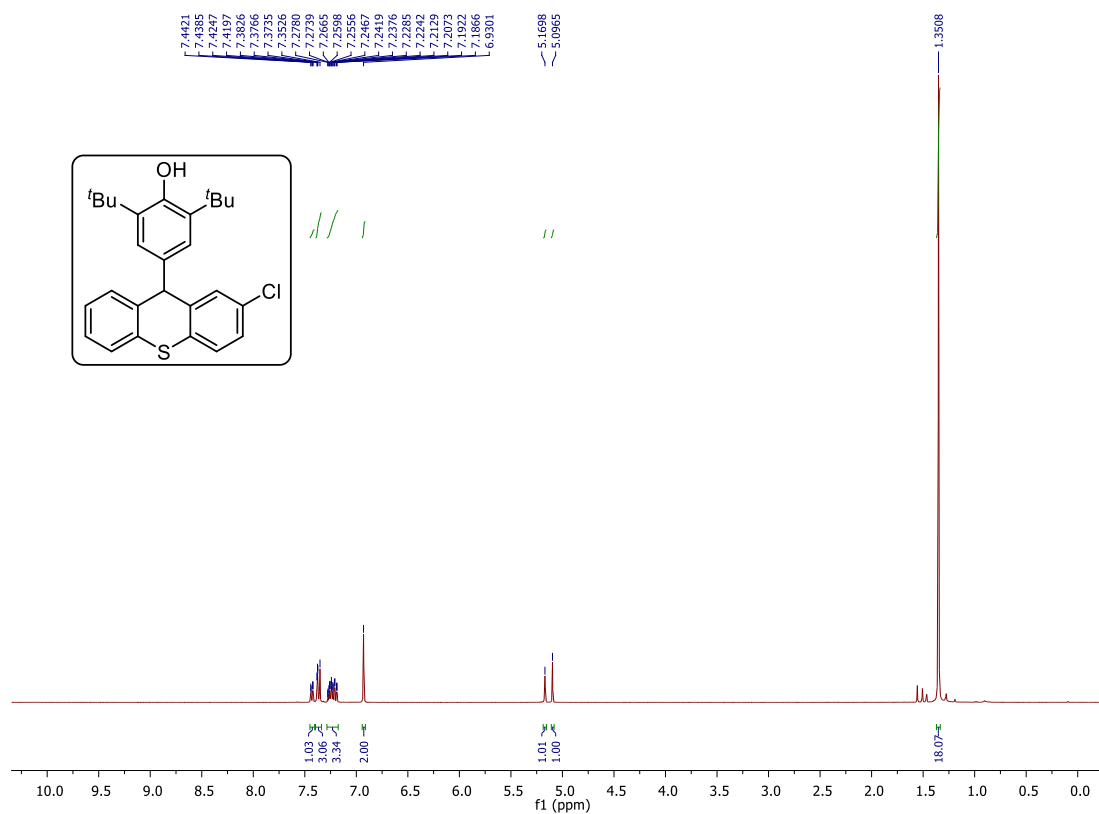
^1H NMR (400 MHz, CDCl_3) spectrum of **4c**



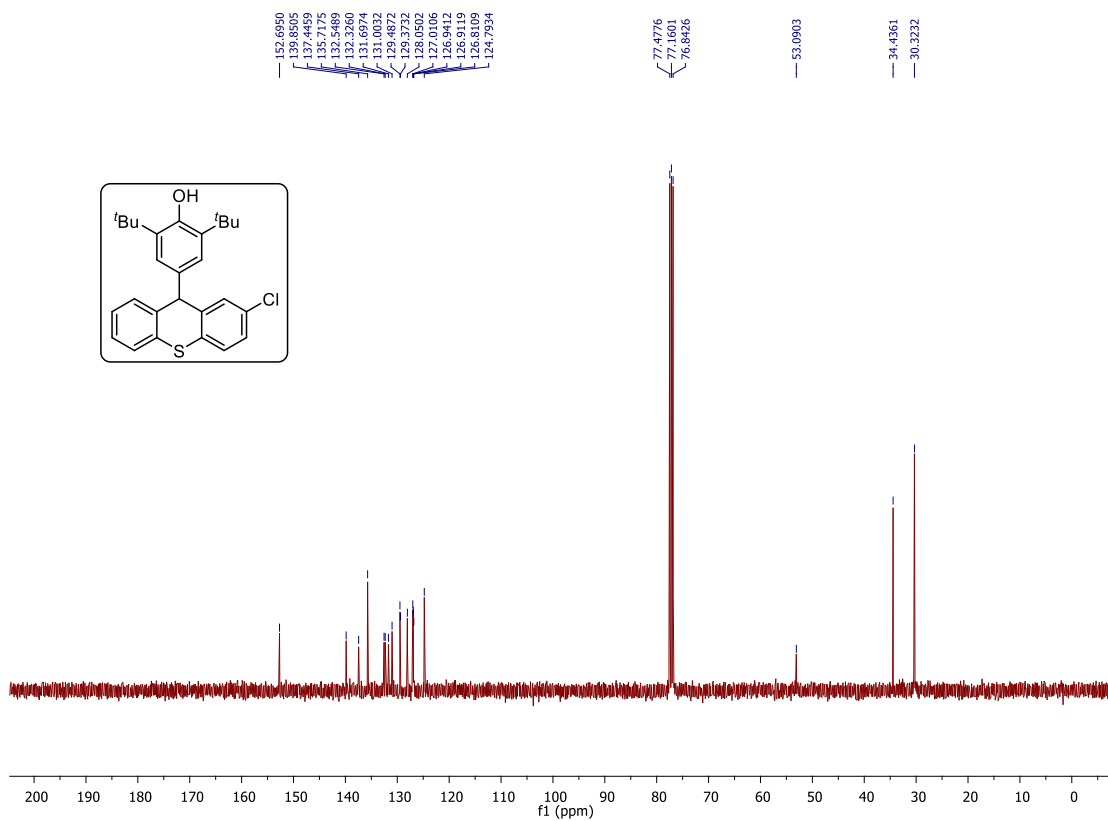
^{13}C $\{^1\text{H}\}$ NMR (100 MHz, CDCl_3) spectrum of **4c**



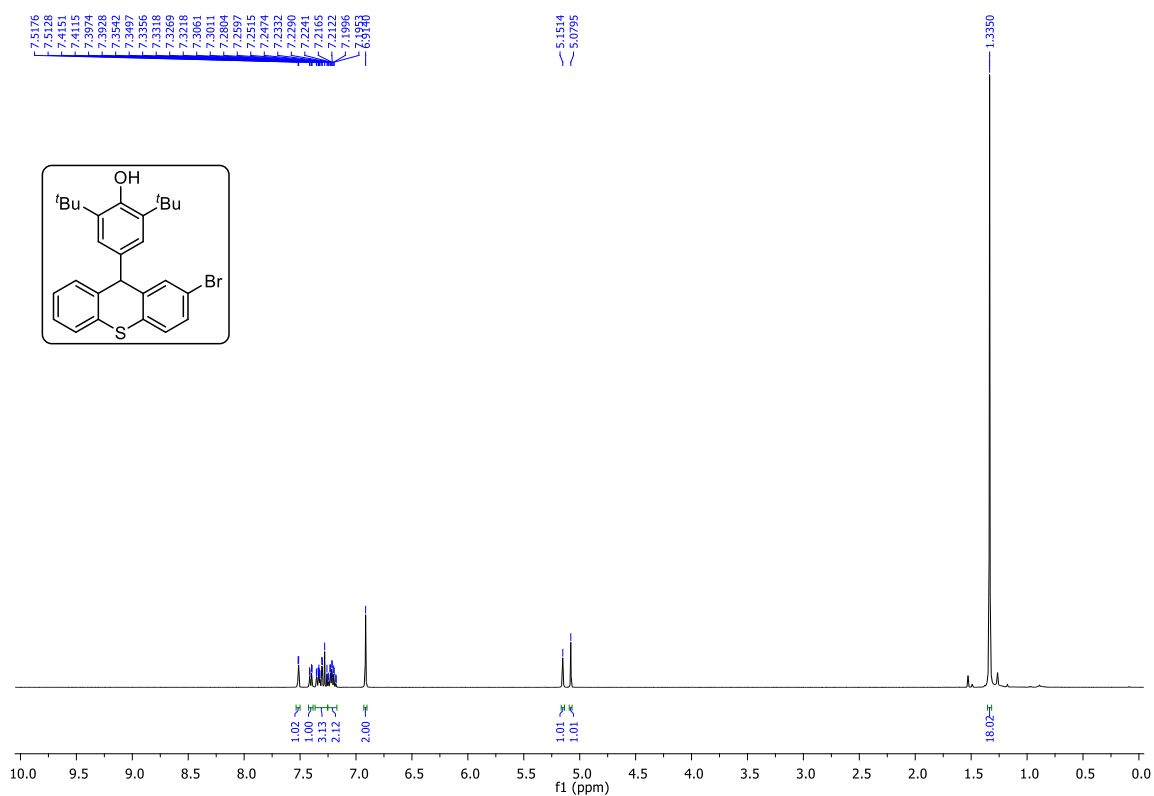
^1H NMR (400 MHz, CDCl_3) spectrum of **4d**



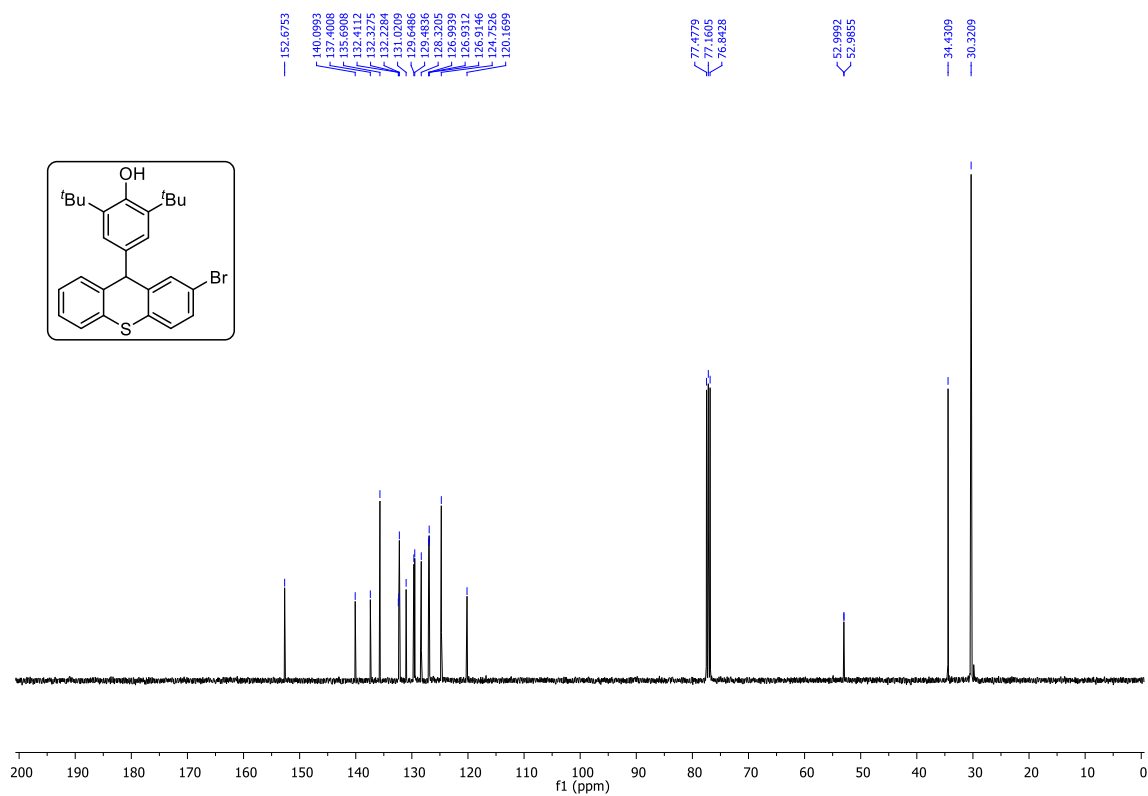
^{13}C { ^1H } NMR (100 MHz, CDCl_3) spectrum of **4d**



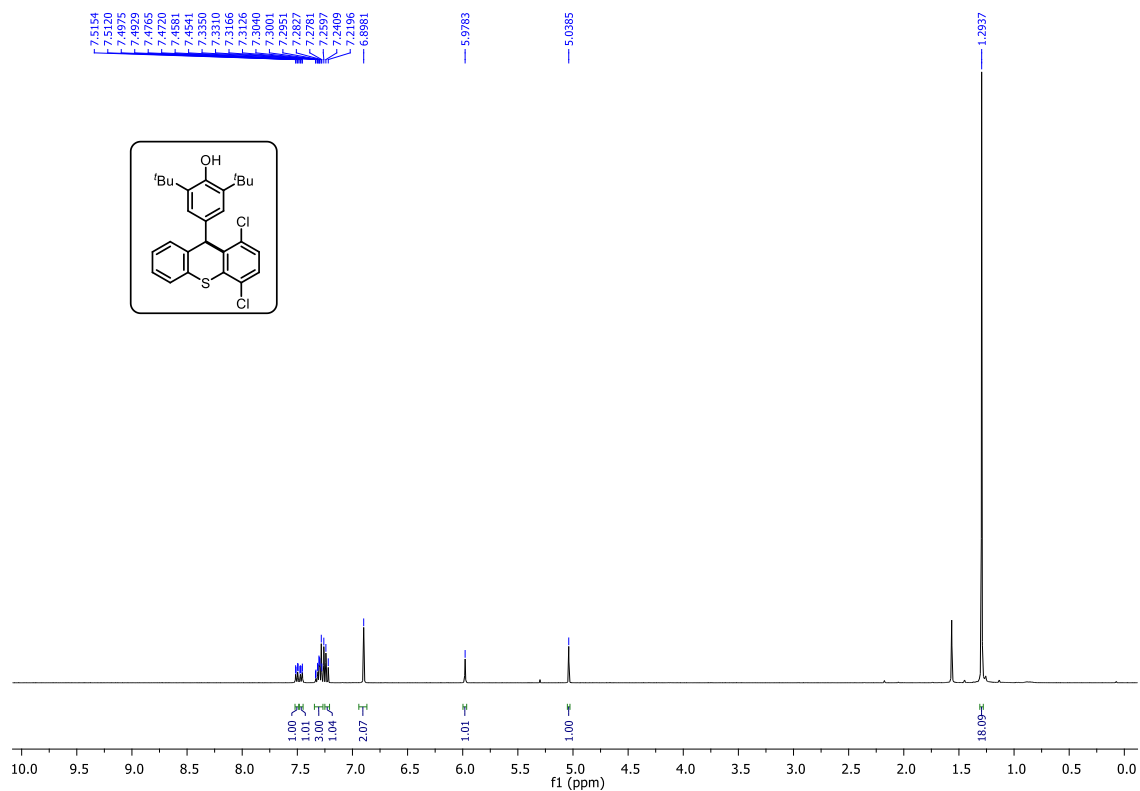
¹H NMR (400 MHz, CDCl₃) spectrum of **4e**



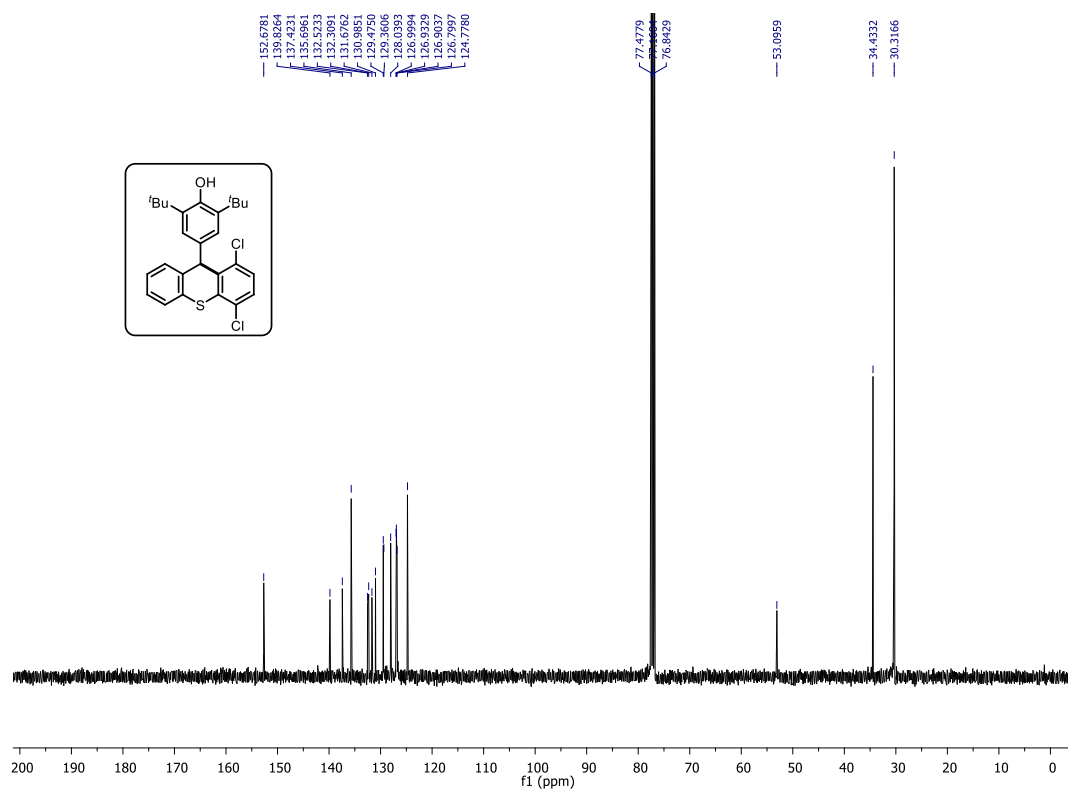
¹³C {¹H} NMR (100 MHz, CDCl₃) spectrum of **4e**



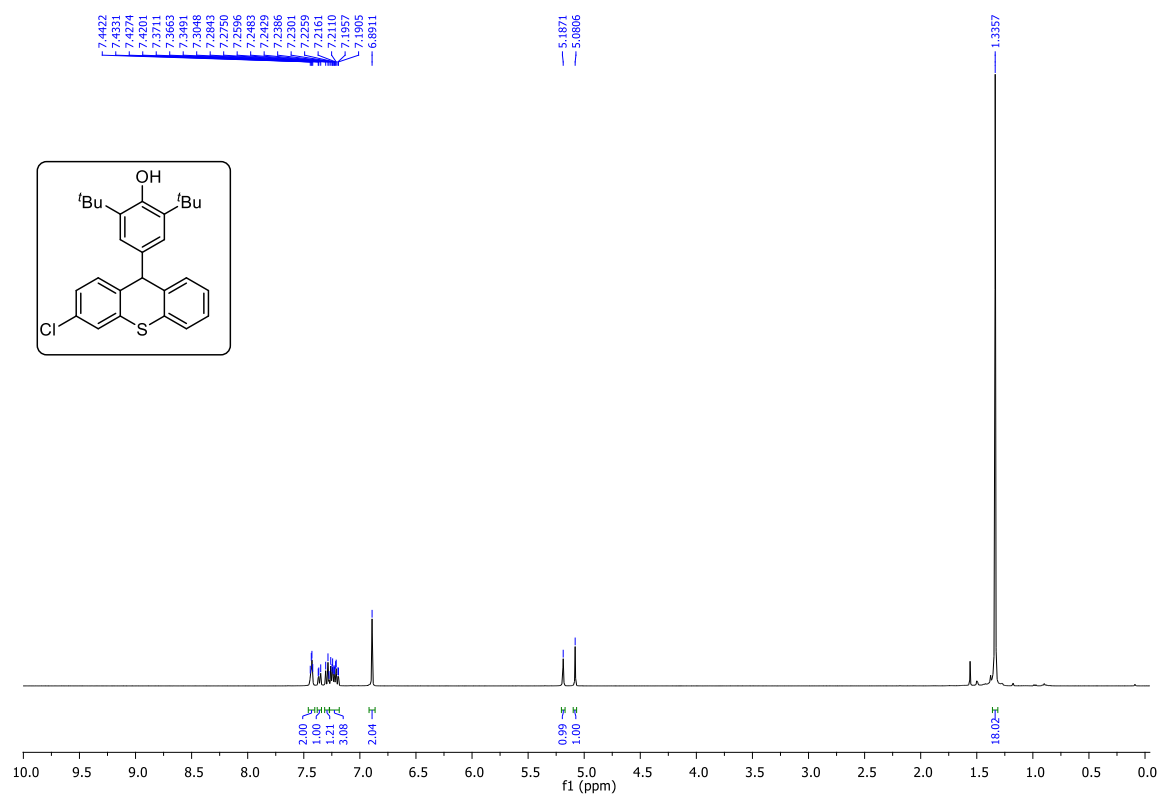
¹H NMR (400 MHz, CDCl₃) spectrum of **4f**



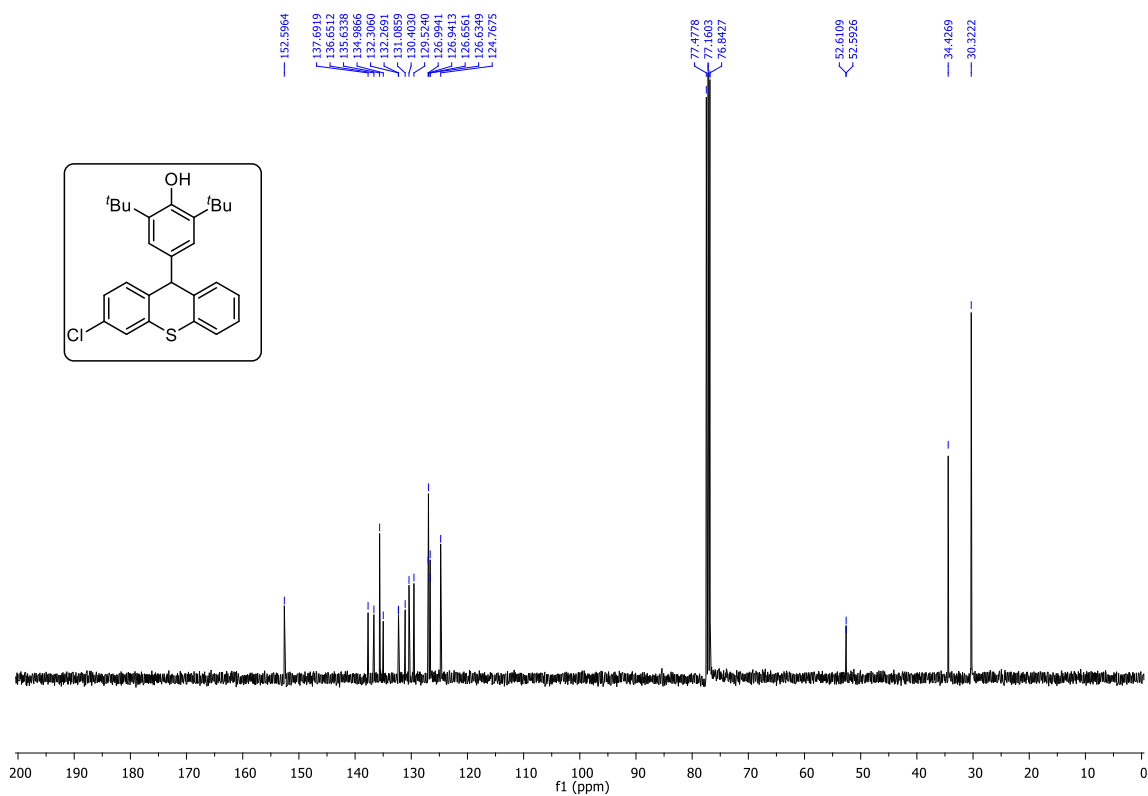
¹³C {¹H} NMR (100 MHz, CDCl₃) spectrum of **4f**



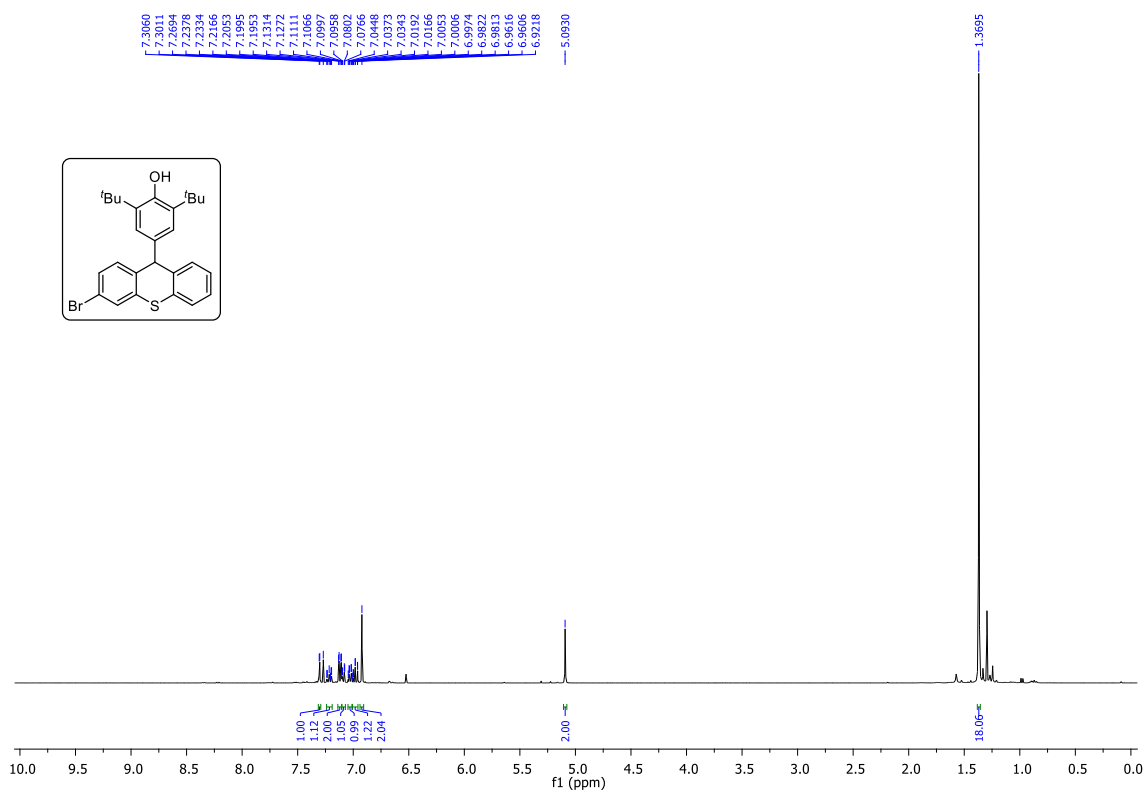
¹H NMR (400 MHz, CDCl₃) spectrum of **4g**



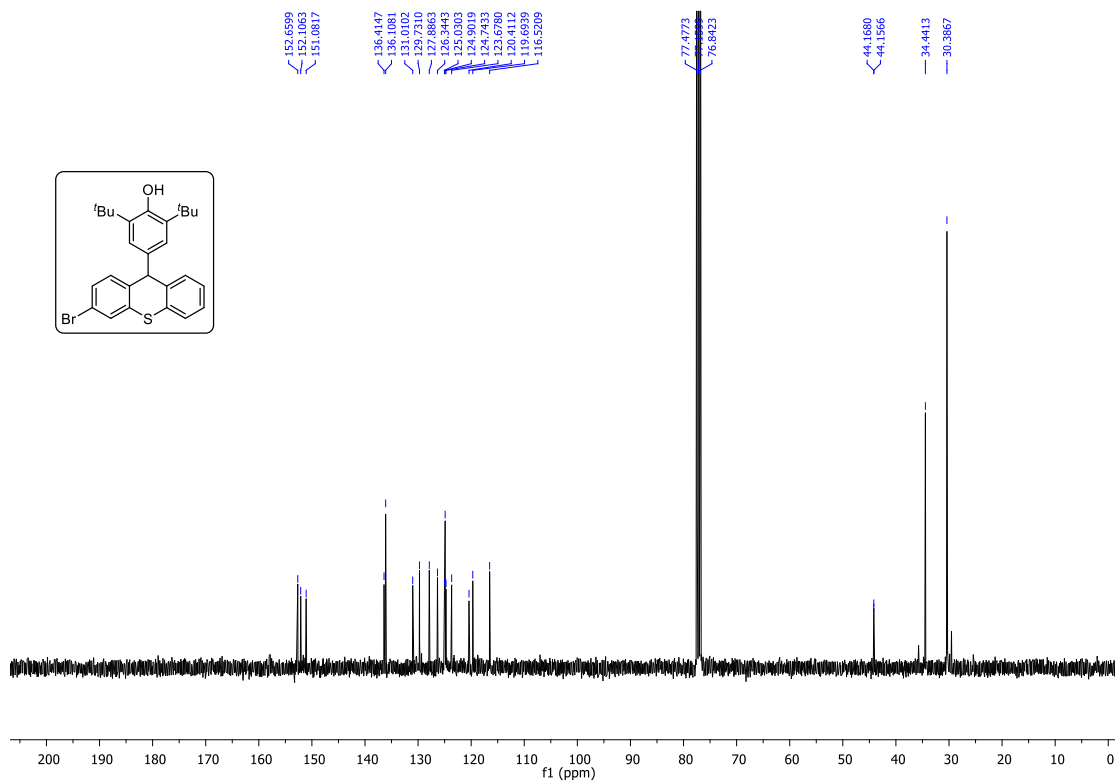
¹³C {¹H} NMR (100 MHz, CDCl₃) spectrum of **4g**



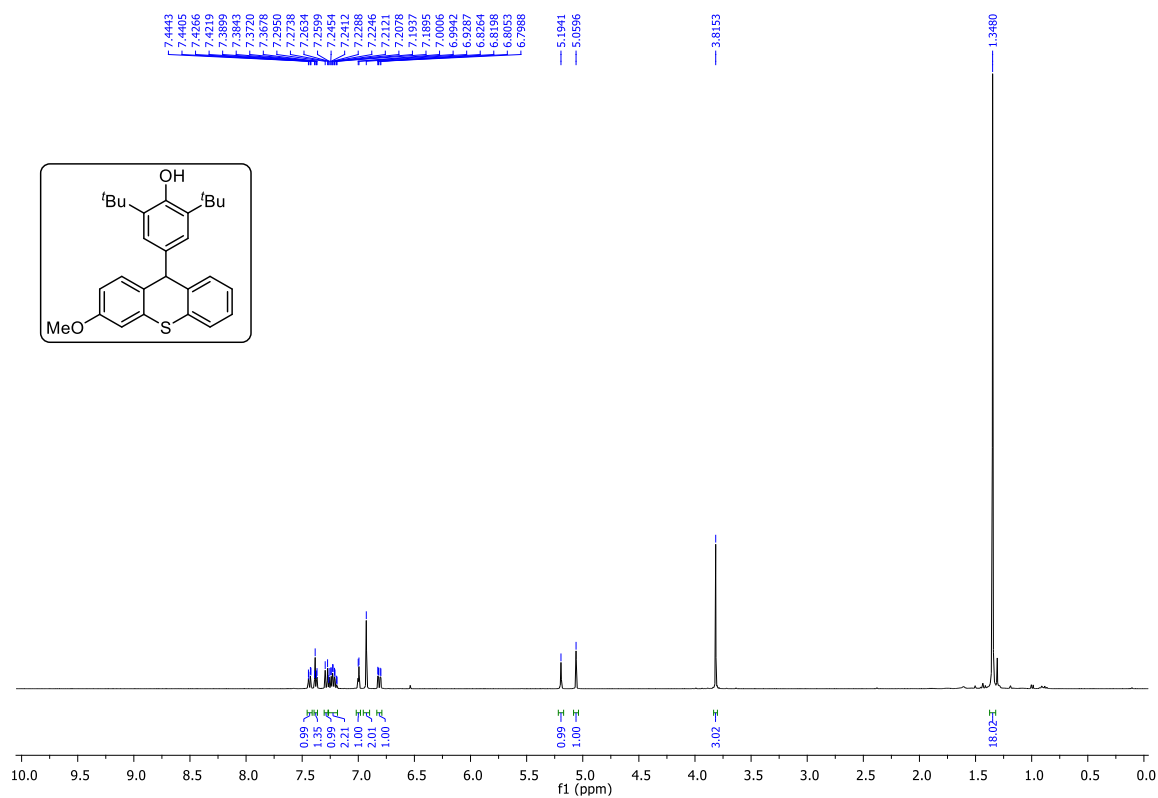
¹H NMR (400 MHz, CDCl₃) spectrum of **4h**



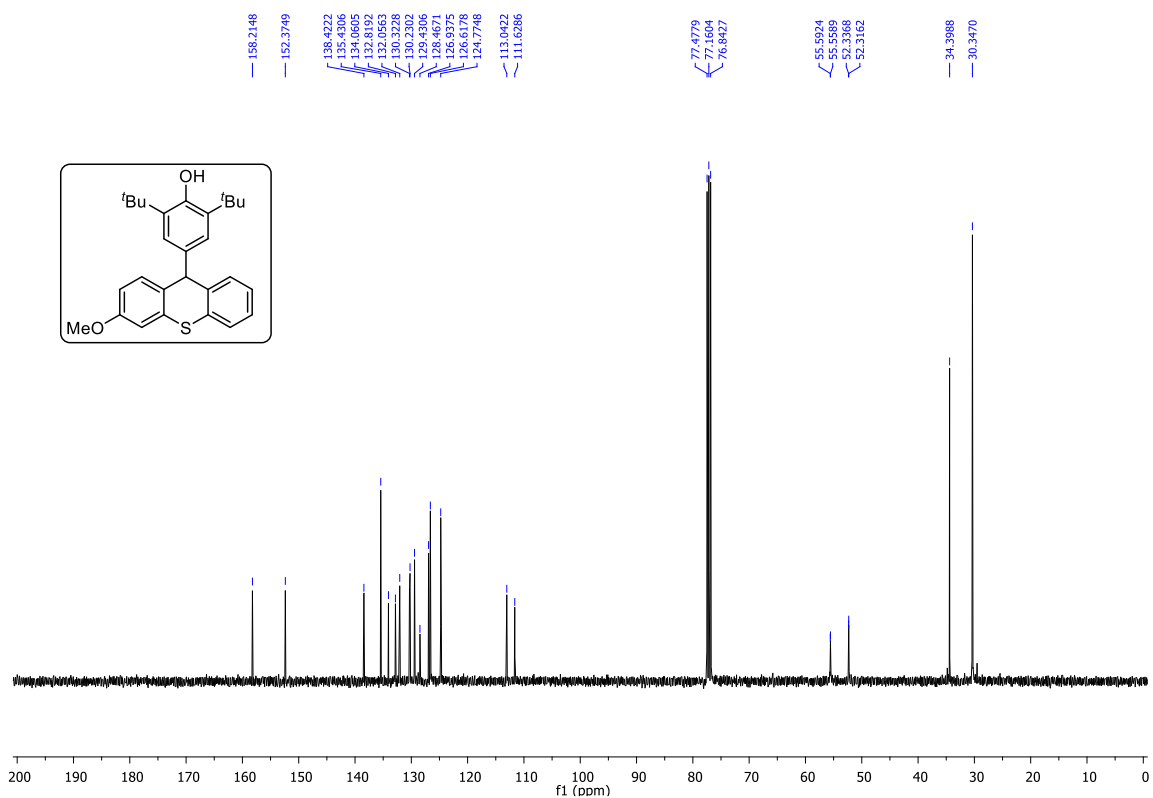
¹³C {¹H} NMR (100 MHz, CDCl₃) spectrum of **4h**



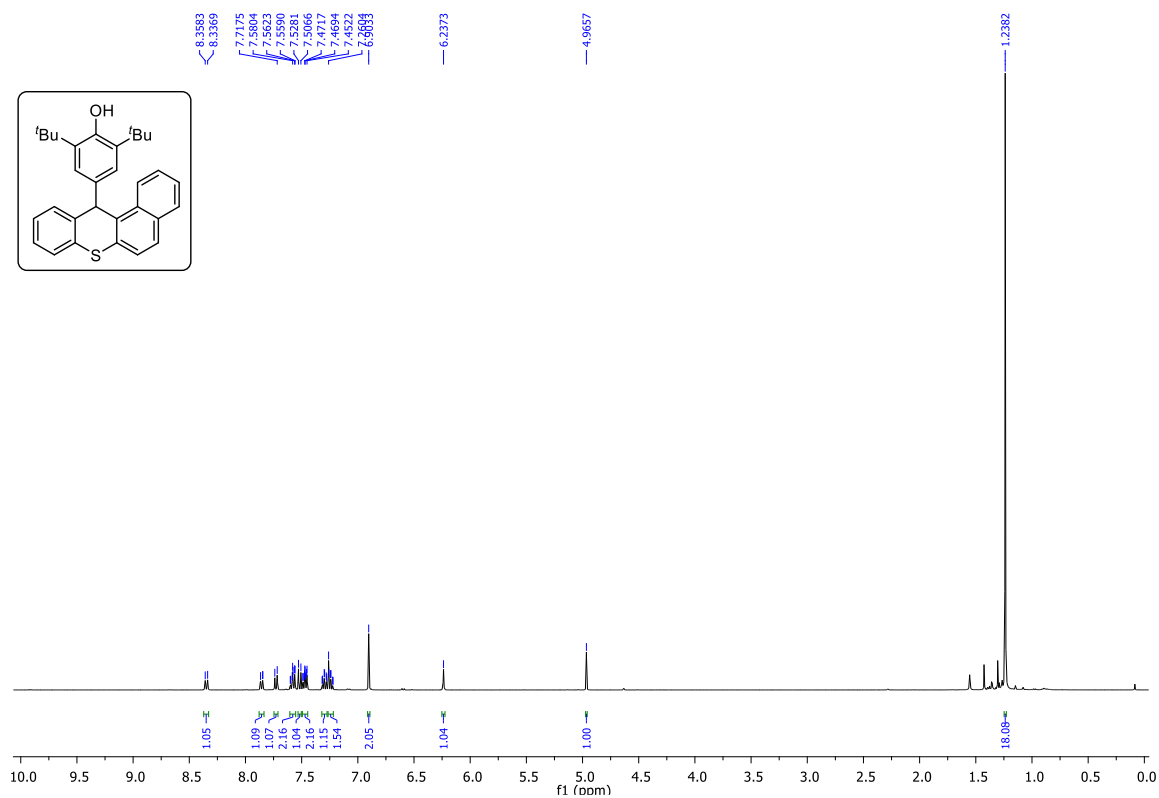
¹H NMR (400 MHz, CDCl₃) spectrum of **4i**



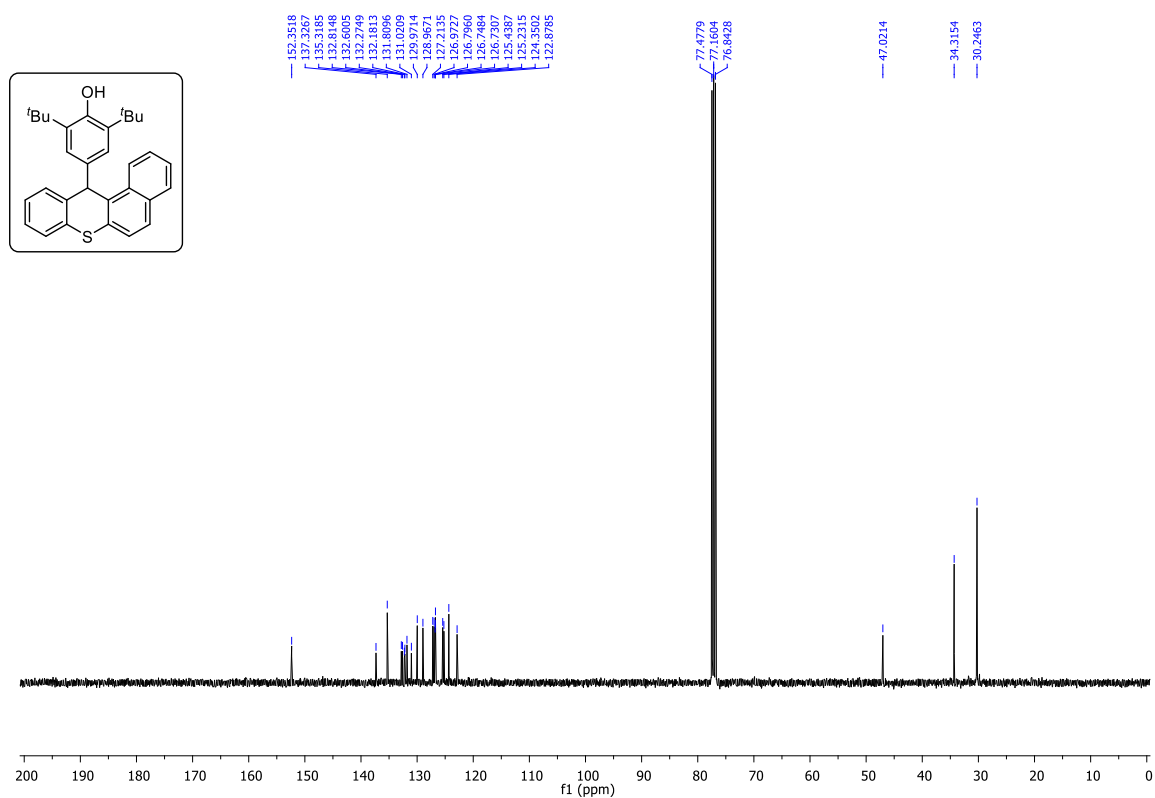
¹³C {¹H} NMR (100 MHz, CDCl₃) spectrum of **4i**



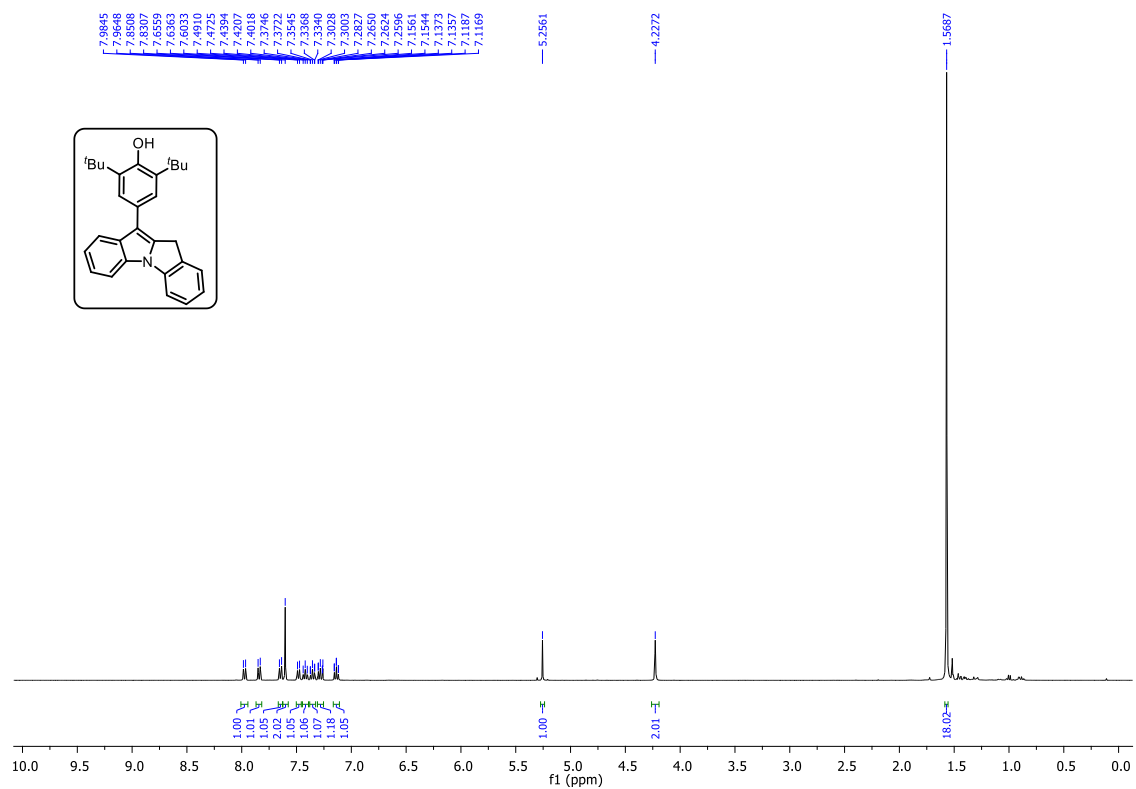
¹H NMR (400 MHz, CDCl₃) spectrum of **4j**



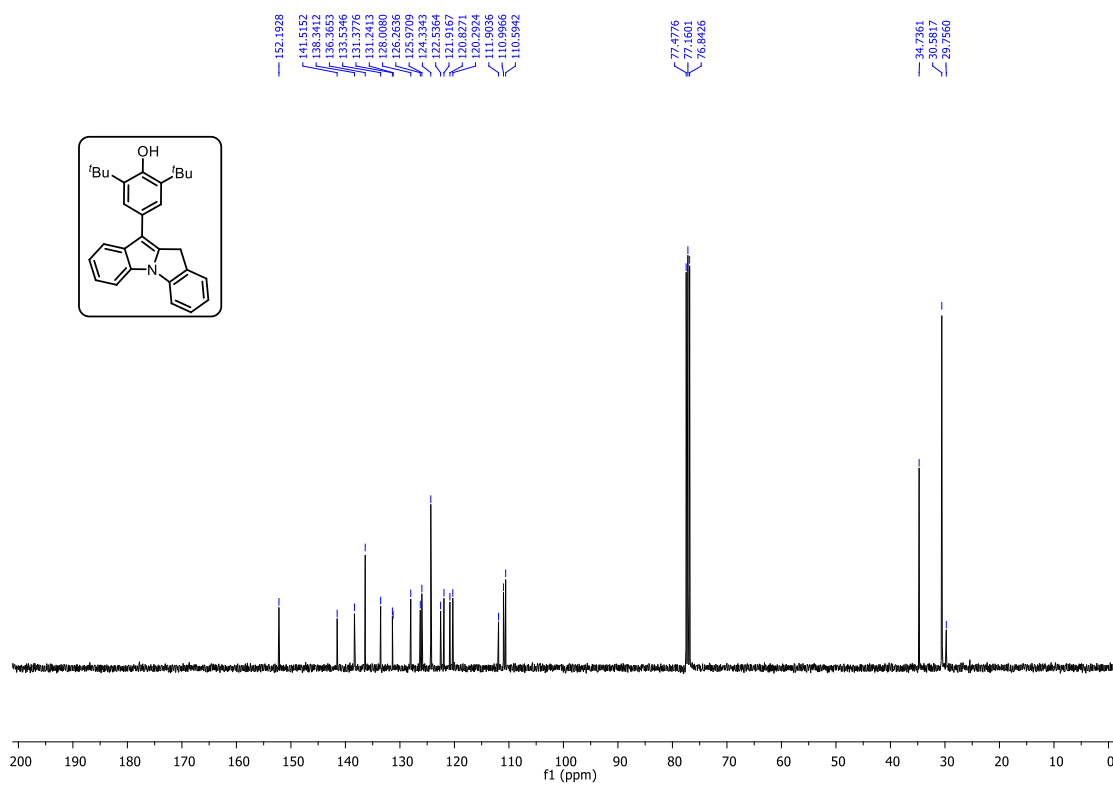
¹³C {¹H} NMR (100 MHz, CDCl₃) spectrum of **4j**



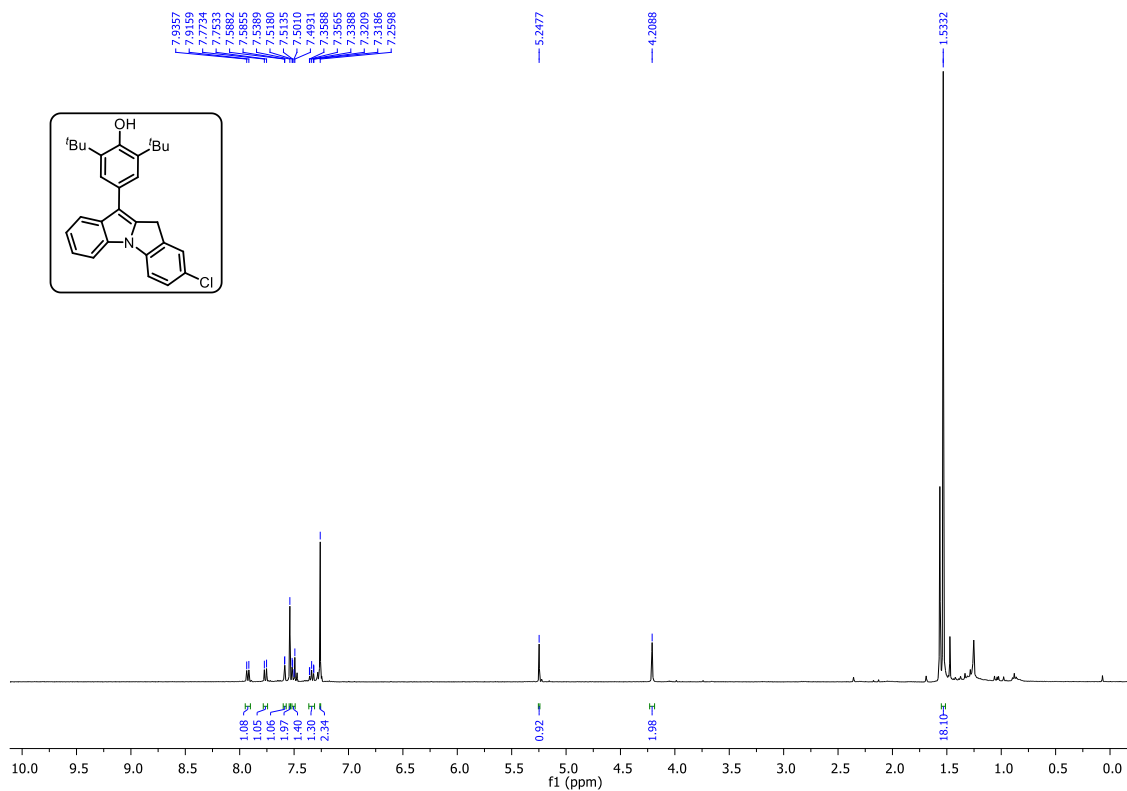
¹H NMR (400 MHz, CDCl₃) spectrum of **6a**



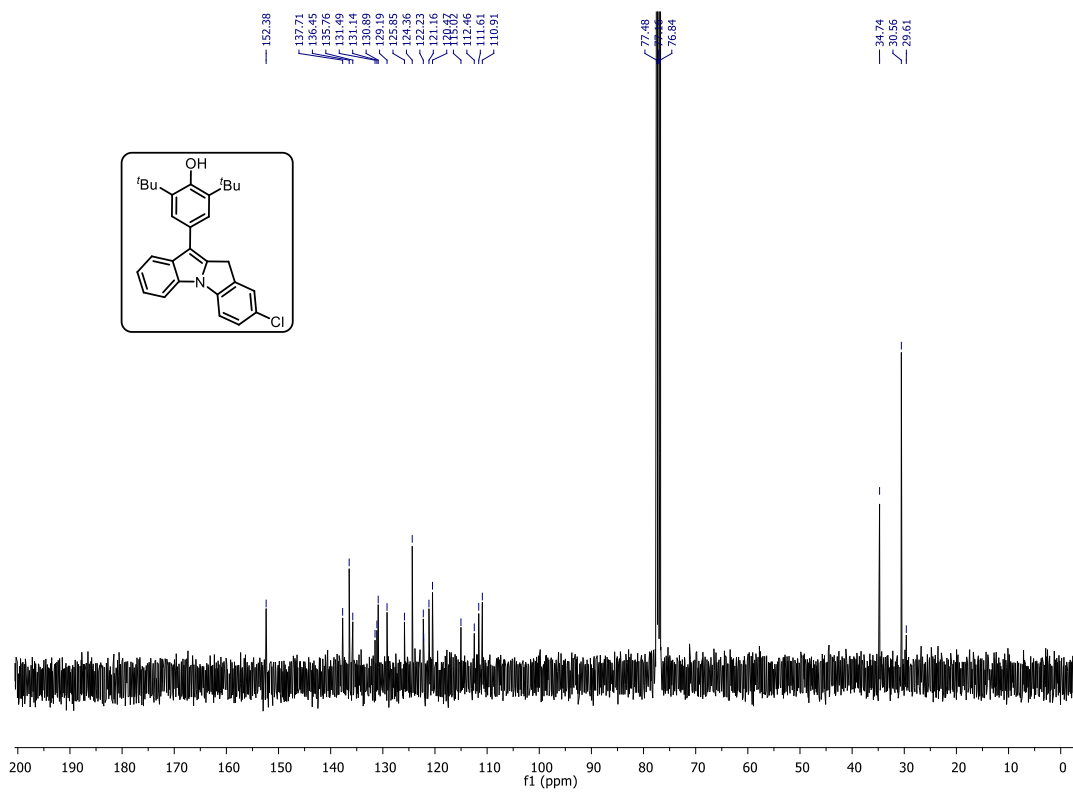
¹³C NMR (100 MHz, CDCl₃) spectrum of **6a**



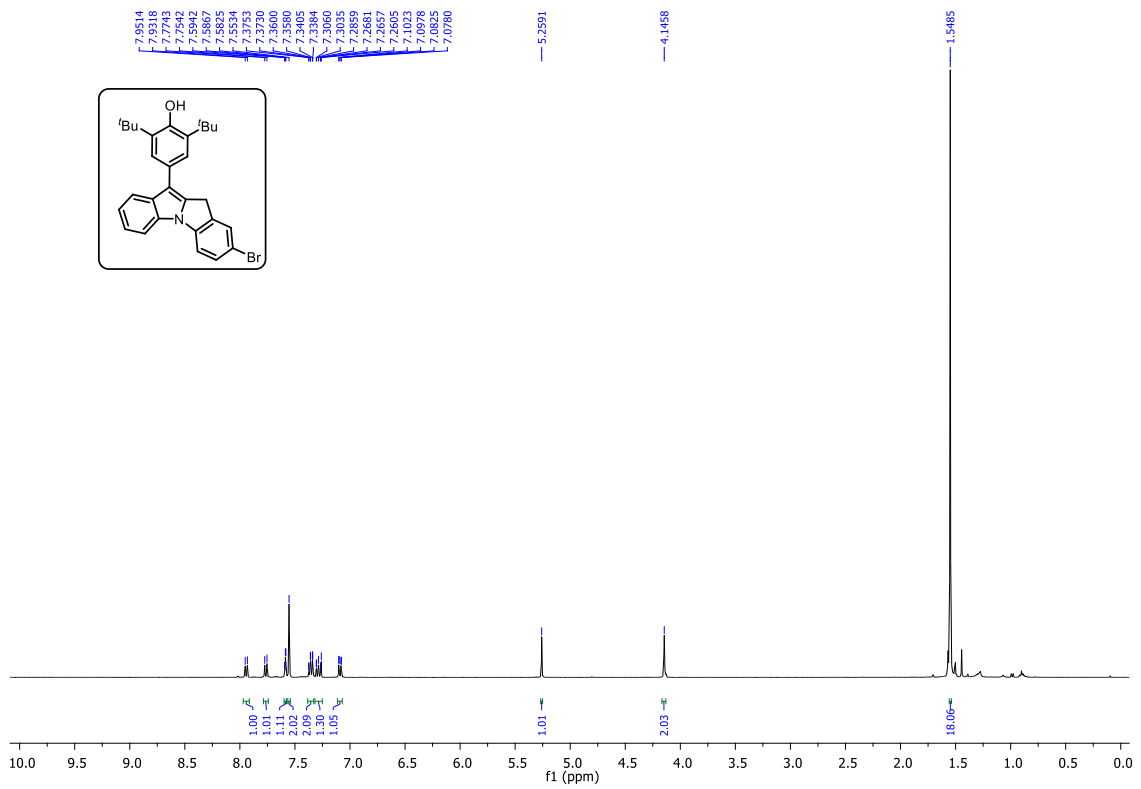
¹H NMR (400 MHz, CDCl₃) spectrum of **6c**



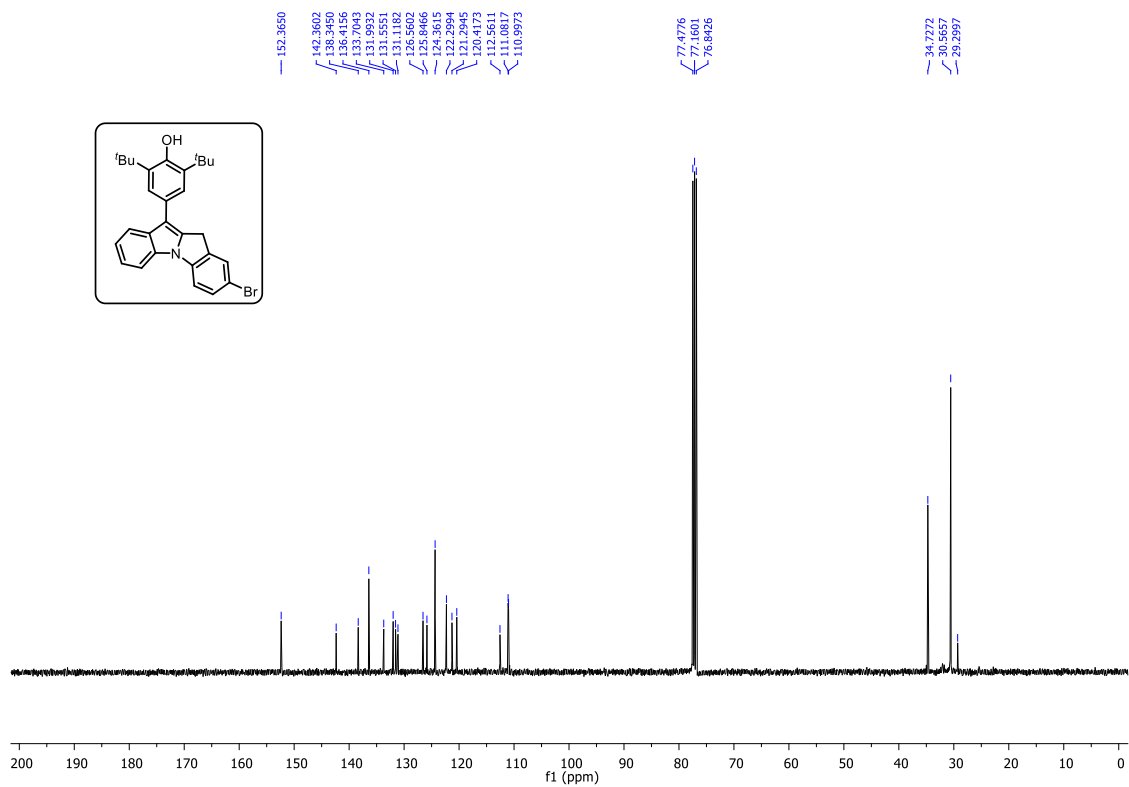
¹³C NMR (100 MHz, CDCl₃) spectrum of **6c**



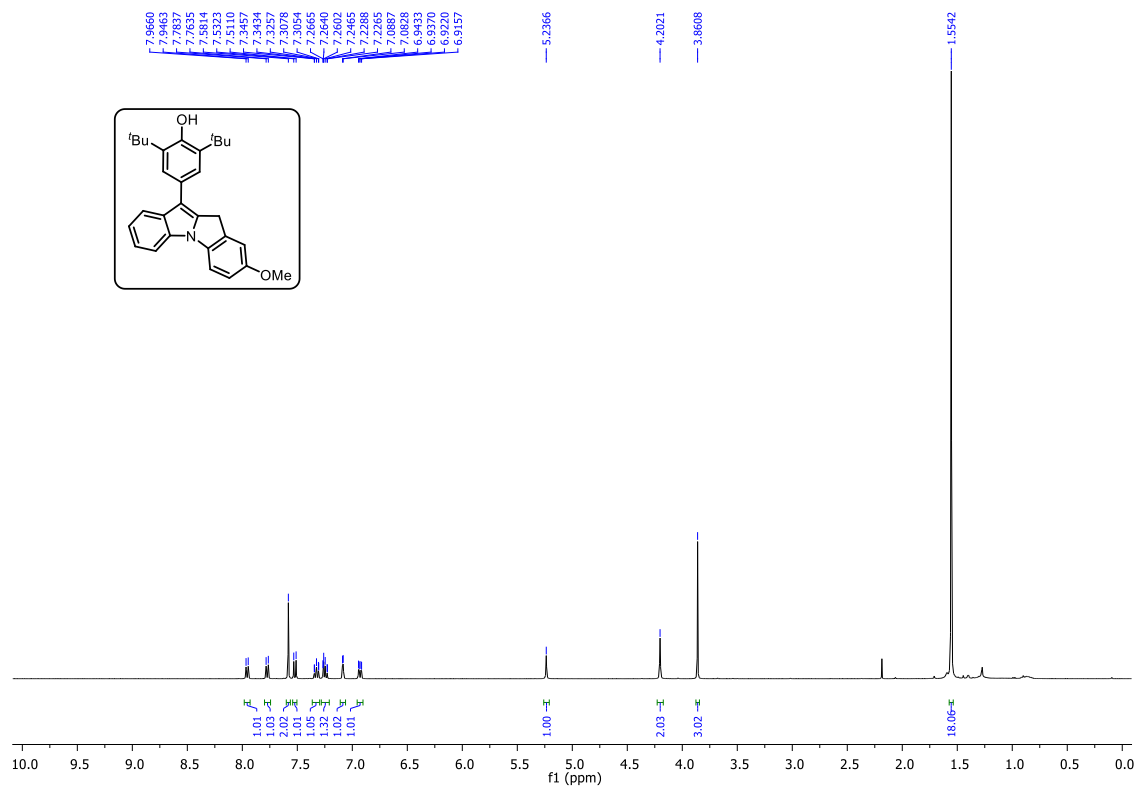
¹H NMR (400 MHz, CDCl₃) spectrum of **6d**



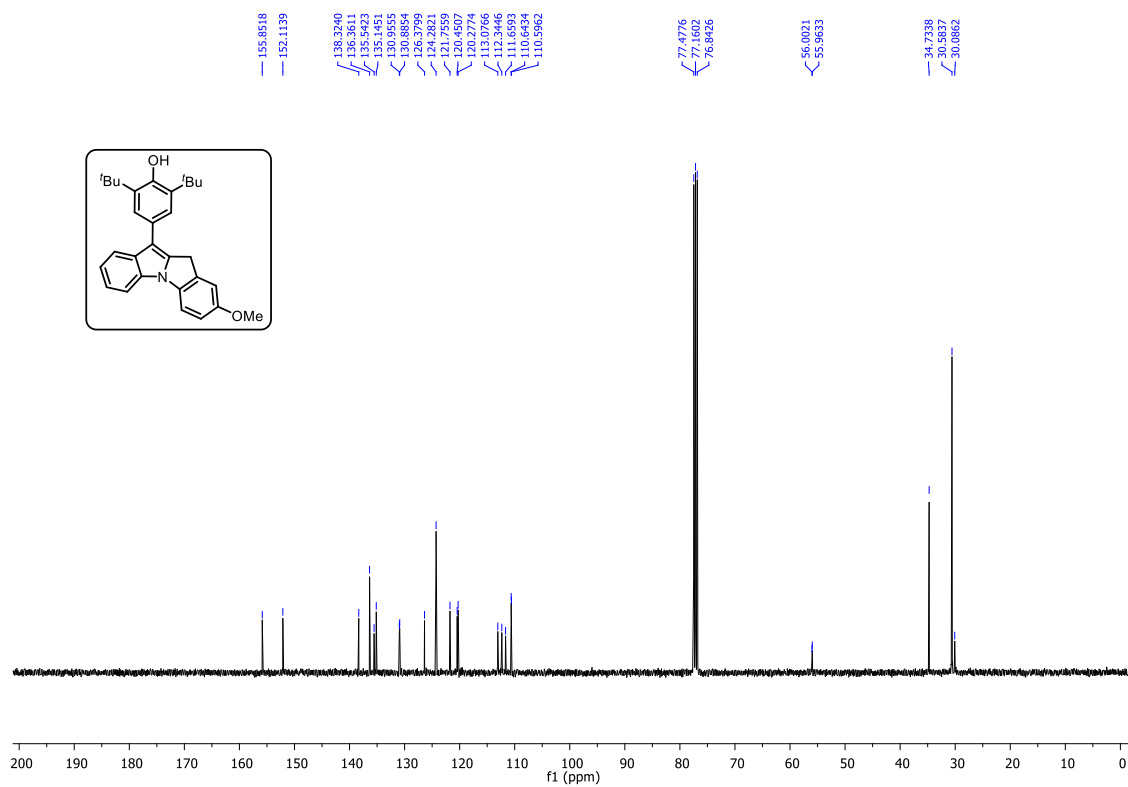
¹³C NMR (100 MHz, CDCl₃) spectrum of **6d**



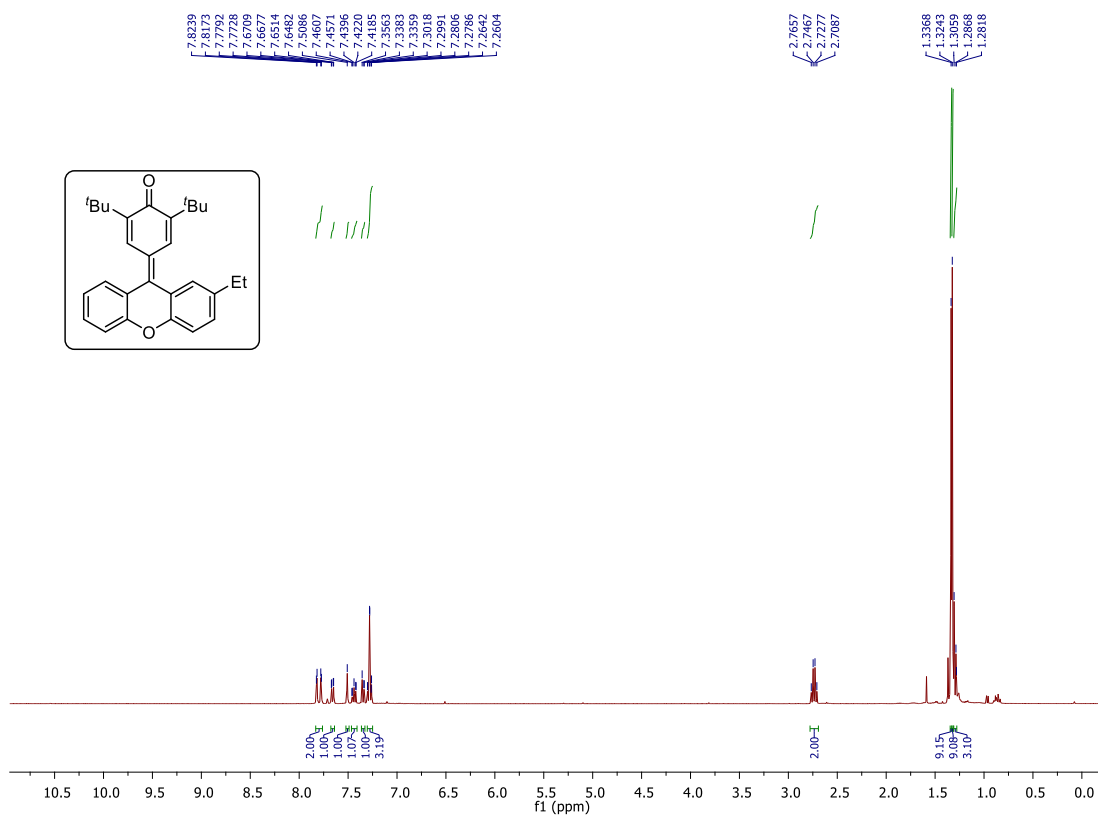
¹H NMR (400 MHz, CDCl₃) spectrum of **6e**



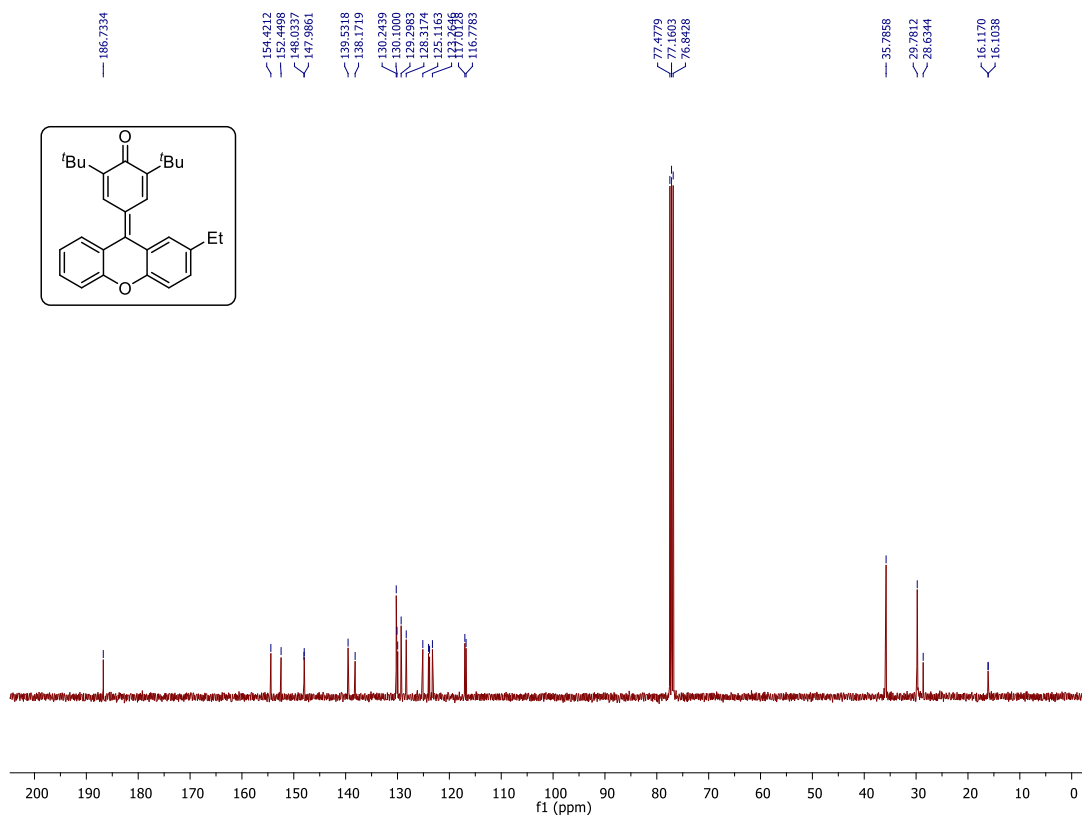
¹³C NMR (100 MHz, CDCl₃) spectrum of **6e**



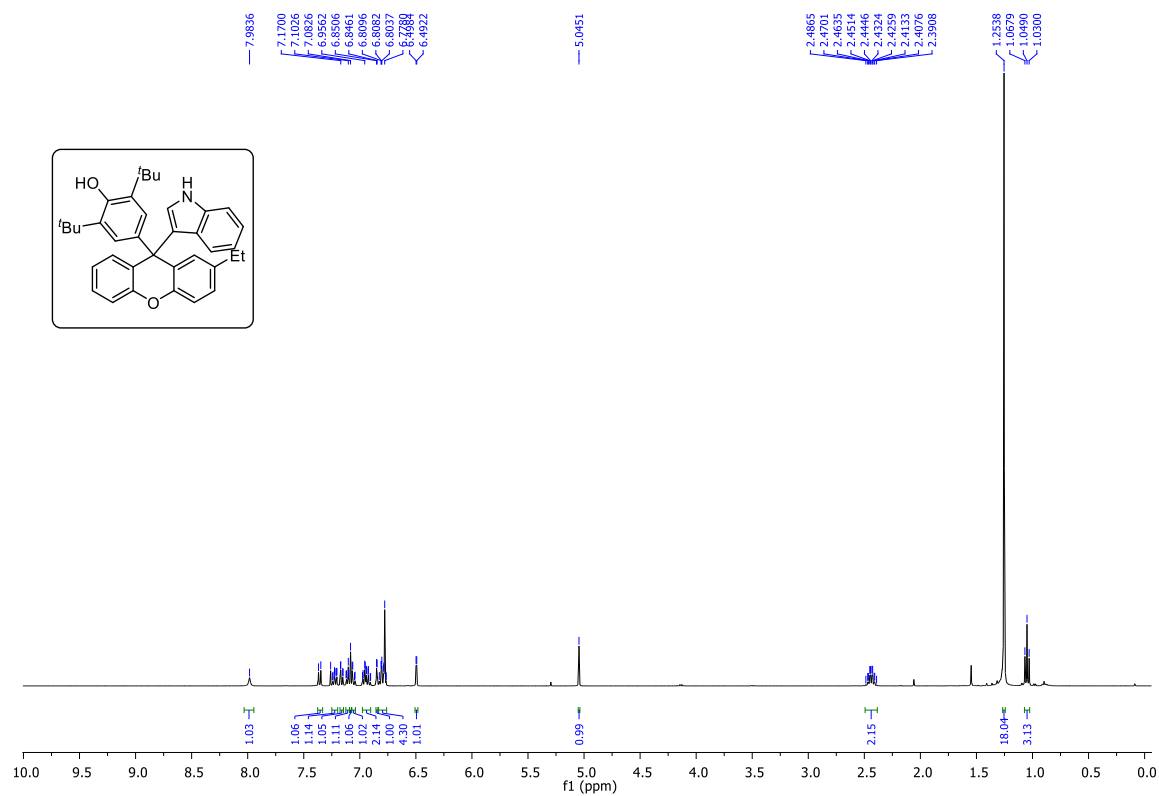
¹H NMR (400 MHz, CDCl₃) spectrum of **7a**



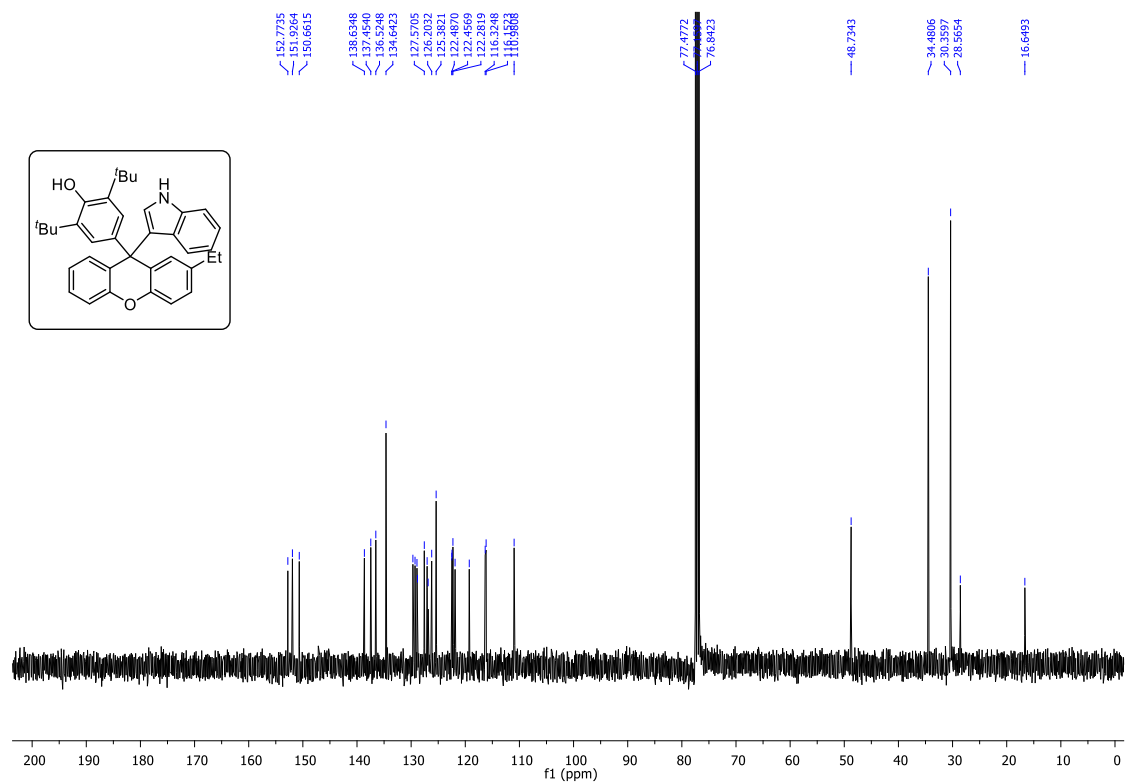
¹³C {¹H} NMR (100 MHz, CDCl₃) spectrum of **7a**



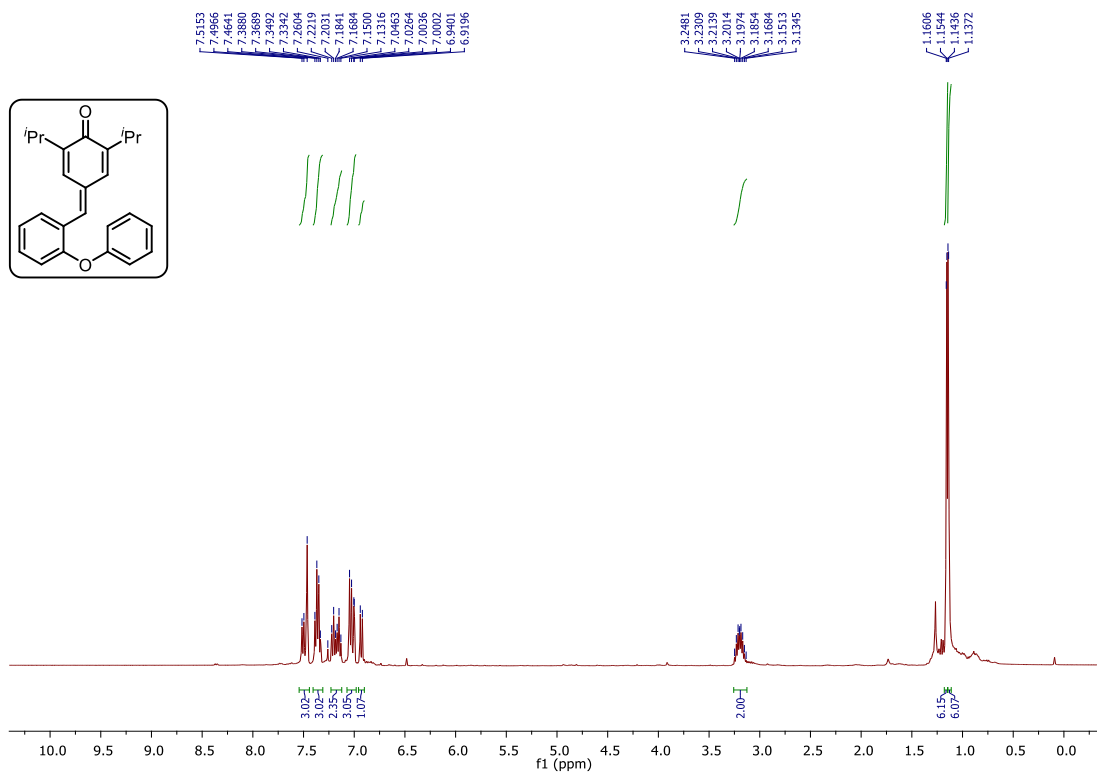
^1H NMR (400 MHz, CDCl_3) spectrum of **8a**



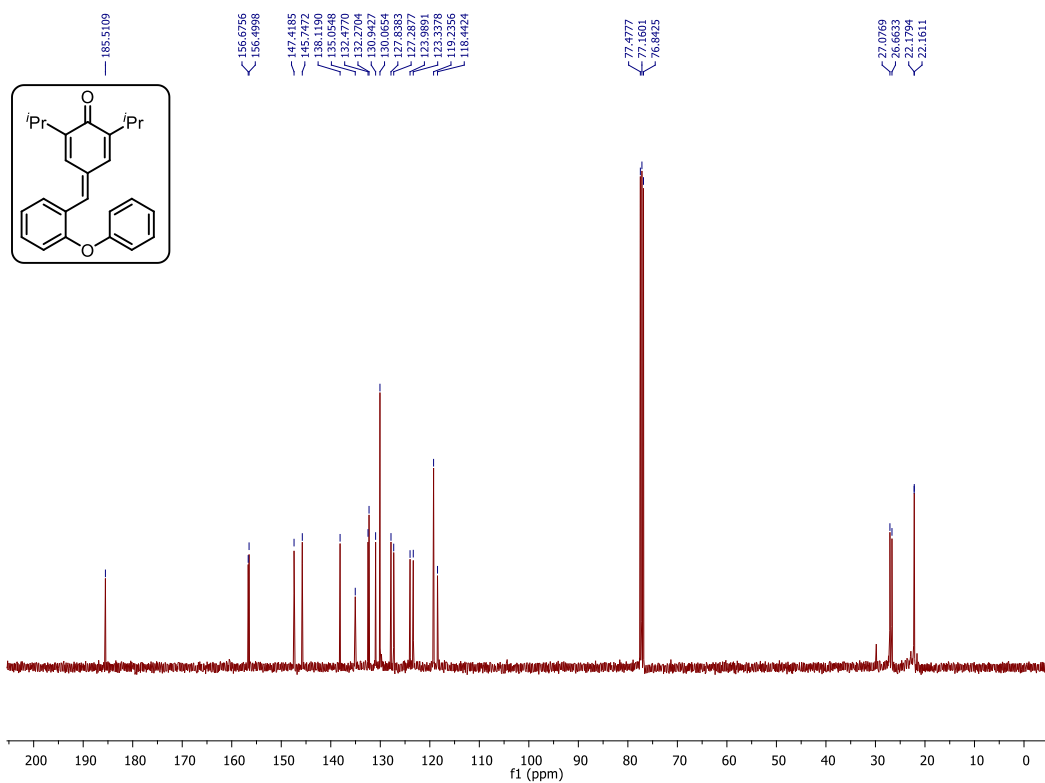
^{13}C $\{^1\text{H}\}$ NMR (100 MHz, CDCl_3) spectrum of **8a**



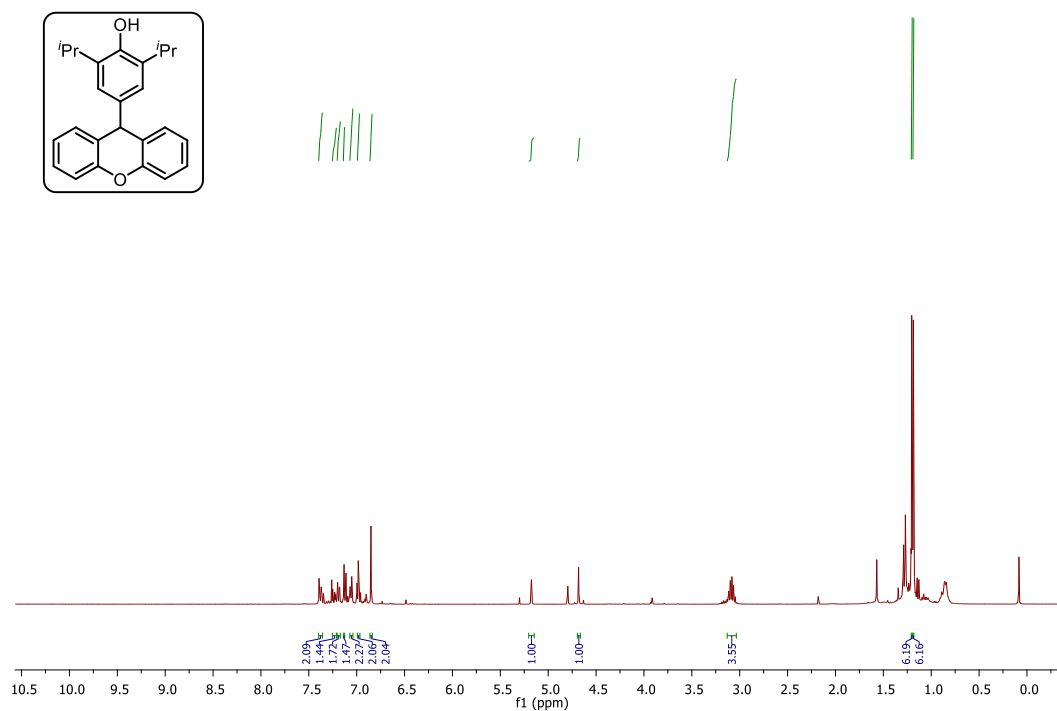
¹H NMR (400 MHz, CDCl₃) spectrum of **9a**



¹³C {¹H} NMR (100 MHz, CDCl₃) spectrum of **9a**



^1H NMR (400 MHz, CDCl_3) spectrum of **10a**



^{13}C $\{^1\text{H}\}$ NMR (100 MHz, CDCl_3) spectrum of **10a**

