Supporting Information for

HMPA-H_2O mediated oxygenative carbocyclization of 2-alkynylphenyl-substituted *p*-quinone methides to indenones

Shaheen Fatma, Feroz Ahmad, Yogesh A. Pankhade, Pavit K. Ranga, and Ramasamy Vijaya Anand*

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

E–mail: rvijayan@iisermohali.ac.in

Table of Contents

Experimental Section

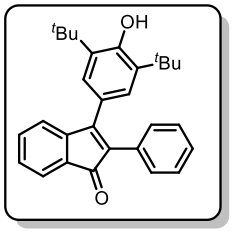
1. *General Information*. All reactions were carried out in an oven dried round bottom flask. All the solvents were distilled before use and stored under nitrogen atmosphere. Most of the reagents and starting materials were purchased from commercial sources and used as such. HMPA (98.5 % purity; contains 1.5 % H_2O) used was purchased from BLD pharma. All the 2-alkynated *p*-Quinone Methides were prepared by following a literature procedure.[1] Melting points were recorded on SMP20 melting point apparatus and are uncorrected. ^{1}H, ^{13}C and ^{19}F spectra were recorded in $CDCl_3$ (400, 100 and 376 MHz respectively) on Bruker FT–NMR spectrometer. Chemical shift (δ) values are reported in parts per million relative to TMS and the coupling constants (J) are reported in Hz. High resolution mass spectra were recorded on Waters Q–TOF Premier–HAB213 spectrometer. FT-IR spectra were recorded on a Perkin-Elmer FTIR spectrometer. Thin layer chromatography was performed on Merck silica gel 60 F_{254} TLC pellets and visualized by UV irradiation and $KMnO_4$ stain. Column chromatography was carried out through silica gel (100–200 mesh) using EtOAc/hexane as an eluent.

General procedure for the synthesis of indenone derivatives (2a-u and 3a-f):

HMPA [(98.5 % purity with 1.5% water), 1 mL] was added to a round bottom flask containing 2-alkynylphenyl-substituted *p*-quinone methide (50 mg) and the reaction mixture was stirred at 140 °C in a preheated oil bath for 8 h. The reaction mixture was then diluted with water (5 mL) and extracted with ether (10 mL x 2). The combined organic layer was dried over anhydrous sodium sulphate, filtered and concentrated under reduced pressure. The residue was then purified through a silica gel column chromatography, using hexane/EtOAc mixture as an eluent to get the pure indenone product.

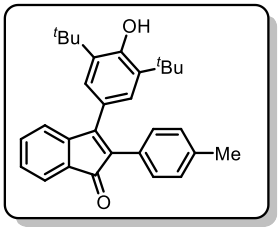
2. *Characterisation of products (2a to 2u)*

3-(3,5-di-*tert*-butyl-4-hydroxyphenyl)-2-phenyl-1*H*-inden-1-one (2a).



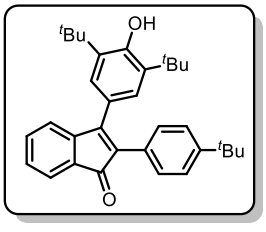
The reaction was performed at 0.12 mmol scale of **1a**; red solid (40 mg, 78% yield); m. p. = 220–222 °C; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.59 (d, J = 7.1 Hz, 1H), 7.41 (td, J = 7.4, 1.2 Hz, 1H), 7.33 – 7.29 (m, 3H), 7.28 – 7.25 (m, 4H), 7.24 (s, 2H), 5.47 (s, 1H), 1.34 (s, 18H); ^{13}C{^{1}H} NMR (100 MHz, $CDCl_3$) δ 196.7, 156.6, 155.3, 145.1, 136.0, 133.2, 131.8, 131.7, 131.6, 130.2, 128.9, 128.1, 127.5, 126.4, 123.3, 122.8, 121.5, 34.4, 30.2; FT-IR (thin film, neat): 3629, 2957, 2924, 1700, 1601, 1256, 1238, 769, 699 cm^{-1};HRMS (ESI): *m/z* calcd for $C_{29}H_{31}O_2$ $[M+H]^+$: 411.2324; found : 411.2328.

3-(3,5-di-*tert*-butyl-4-hydroxyphenyl)-2-(*p*-tolyl)-1*H*-inden-1-one (2b).



The reaction was performed at 0.12 mmol scale of **1b**; red solid (28 mg, 55% yield); m. p. = 200–202 °C; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.55 (d, J = 7.0 Hz 1H), 7.39 – 7.35 (m, 1H), 7.28 – 7.26 (m, 2H), 7.22 (s, 2H), 7.13 (d, J = 8.2 Hz, 2H), 7.07 (d, J = 8.0 Hz, 2H), 5.43 (s, 1H), 2.31 (s, 3H), 1.32 (s, 18H); ^{13}C{^{1}H} NMR (100 MHz, $CDCl_3$) δ 197.0, 155.9, 155.2, 145.3, 137.3, 135.9, 133.2, 131.7, 131.6, 130.0, 128.8, 128.75, 128.74, 126.4, 123.4, 122.8, 121.4, 34.4, 30.3, 21.4; FT-IR (thin film, neat): 3624, 2959, 2923, 1700, 1259, 1239, 751; HRMS (ESI): *m/z* calcd for $C_{30}H_{33}O_2$ $[M+H]^+$: 425.2481; found : 425.2484.

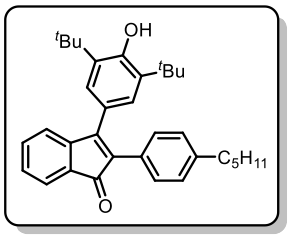
2-(4-(*tert*-butyl)phenyl)-3-(3,5-di-*tert*-butyl-4-hydroxyphenyl)-1H-inden-1-one (2c).



The reaction was performed at 0.11 mmol scale of **1c**; red solid (32 mg, 63% yield); m. p. = 223–225 °C; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.57 (d, J = 7.0 Hz, 1H), 7.41 – 7.37 (m, 1H), 7.32 – 7.26 (m, 4H), 7.21 (s, 2H),

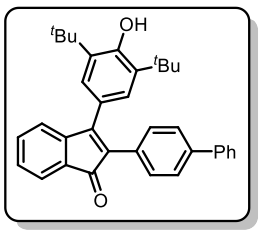
7.15 (d, *J* = 8.3 Hz, 2H), 5.44 (s, 1H), 1.32 (s, 18H), 1.30 (s, 9H); $^{13}C\{^{1}H\}$ NMR (100 MHz, $CDCl_3$) δ 196.9, 156.3, 155.2, 150.4, 145.1, 135.8, 133.1, 131.9, 131.8, 129.8, 128.9, 128.8, 126.6, 125.2, 123.3, 122.8, 121.4, 34.7, 34.4, 31.4, 30.2; FT-IR (thin film, neat): 2958, 2923, 1734, 1611, 1259, 816; HRMS (ESI): *m/z* calcd for $C_{33}H_{39}O_2$ $[M+H]^+$: 467.2950; found : 467.2973.

3-(3,5-di-*tert*-butyl-4-hydroxyphenyl)-2-(4-pentylphenyl)-1*H*-inden-1-one (2d).



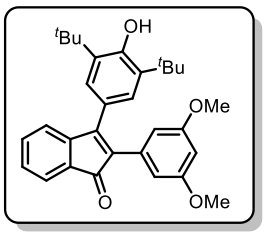
The reaction was performed at 0.11 mmol scale of **1d**; red solid (30 mg, 59% yield); m. p. = 170–172 °C; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.57 (d, *J* = 6.9 Hz, 1H), 7.41 – 7.37 (m, 1H), 7.31 – 7.26 (m, 2H) 7.24 (s, 2H), 7.15 (d, *J* = 8.1 Hz, 2H), 7.10 (d, *J* = 8.1 Hz, 2H), 5.45 (s, 1H), 2.58 (t, *J* = 7.6 Hz, 2H), 1.62 – 1.55 (m, 2H), 1.34 (s, 18H), 1.32 – 1.28 (m, 4H), 0.89 (t, *J* = 7.0 Hz, 3H); $^{13}C\{^{1}H\}$ NMR (100 MHz, $CDCl_3$) δ 197.0, 156.0, 155.2, 145.2, 142.4, 135.9, 133.1, 131.8, 131.7, 130.0, 129.0, 128.7, 128.3, 126.4, 123.4, 122.8, 121.4, 35.9, 34.4, 31.5, 31.3, 30.3, 22.7, 14.2; FT-IR (thin film, neat): 3628, 2957, 2928, 1784, 1259, 1084, 801; HRMS (ESI): *m/z* calcd for $C_{34}H_{41}O_2$ $[M+H]^+$: 481.3107; found : 481.3125.

2-([1,1'-biphenyl]-4-yl)-3-(3,5-di-*tert*-butyl-4-hydroxyphenyl)-1*H*-inden-1-one (2e).



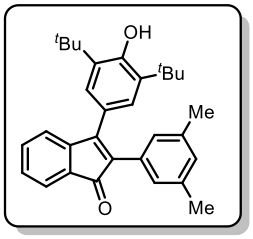
The reaction was performed at 0.11 mmol scale of **1e**; red solid (35 mg, 69% yield); m. p. = 221–223 °C; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.61 – 7.52 (m, 5H), 7.46 – 7.40 (m, 3H), 7.36 – 7.31 (m, 5H), 7.28 (s, 2H), 5.49 (s, 1H), 1.35 (s, 18H); $^{13}C\{^{1}H\}$ NMR (100 MHz, $CDCl_3$) δ, 196.8, 156.7, 155.4, 145.1, 141.2, 140.2, 136.0, 133.3, 131.7, 131.2, 130.9, 130.6, 129.0, 128.9, 127.4, 127.2, 126.9, 126.5, 123.3, 122.9, 121.6, 34.5, 30.3; FT-IR (thin film, neat): 3626, 2960, 2924, 1702, 1259, 1030, 799; HRMS (ESI): *m/z* calcd for $C_{35}H_{35}O_2$ $[M+H]^+$: 487.2637; found : 487.2651.

3-(3,5-di-*tert*-butyl-4-hydroxyphenyl)-2-(3,5-dimethoxyphenyl)-1H-inden-1-one (2f).



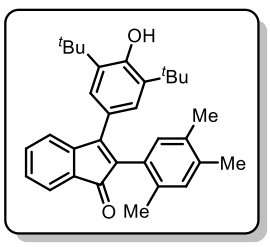
The reaction was performed at 0.11 mmol scale of **1f**; dark red solid (44 mg, 86% yield); m. p. = 187–189 °C; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.59 (d, J = 6.4 Hz, 1H), 7.44 – 7.40 (m, 1H), 7.32 – 7.30 (m, 2H), 7.27 (s, 2H), 6.43 (s, 2H), 6.39 (s, 1H), 5.50 (s, 1H), 3.67 (s, 6H), 1.38 (s, 18H); ^{13}C{^{1}H} NMR (100 MHz, $CDCl_3$) δ 196.4, 160.4, 157.1, 155.3, 145.0, 136.1, 133.5, 133.2, 131.6, 131.5, 129.0, 126.3, 123.4, 122.8, 121.6, 108.0, 100.5, 55.3, 34.5, 30.3; FT-IR (thin film, neat): 3624, 2958, 1703, 1594, 1360, 1155, 750; HRMS (ESI): *m/z* calcd for $C_{31}H_{35}O_4$ $[M+H]^+$: 471.2535; found : 471.2520.

3-(3,5-di-*tert*-butyl-4-hydroxyphenyl)-2-(3,5-dimethylphenyl)-1H-inden-1-one (2g).



The reaction was performed at 0.12 mmol scale of **1g**; red solid (42 mg, 83% yield); m. p. = 155–157 °C; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.57 (d, J = 7.0 Hz, 1H), 7.40 (t, J = 7.4 Hz, 1H), 7.30 (t, J = 6.9 Hz, 2H), 7.26 (s, 2H), 6.89 (s, 1H), 6.86 (s, 2H), 5.46 (s, 1H), 2.24 (s, 6H), 1.35 (s, 18H); ^{13}C{^{1}H} NMR (100 MHz, $CDCl_3$) δ 198.7, 158.0, 157.0, 147.0, 139.2, 137.7, 134.9, 133.8, 133.5, 133.3, 131.1, 130.6, 129.7, 128.2, 125.3, 124.6, 123.3, 36.3, 32.1, 23.2; FT-IR (thin film, neat): 3632, 2960, 2920, 1728, 1608, 1259, 802; HRMS (ESI): *m/z* calcd for $C_{31}H_{35}O_2$ $[M+H]^+$: 439.2637; found : 439.2676.

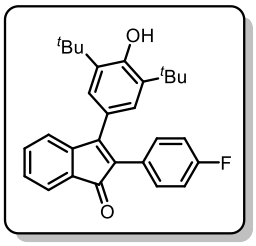
3-(3,5-di-*tert*-butyl-4-hydroxyphenyl)-2-(2,4,5-trimethylphenyl)-1H-inden-1-one (2h).



The reaction was performed at 0.11 mmol scale of **1h**; red solid (20 mg, 40% yield); m. p. = 161–163 °C; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.58 (d, J = 7.0 Hz, 1H), 7.40 (d, J = 6.4 Hz, 2H), 7.31 – 7.27 (m, 1H), 7.21 (s, 2H), 6.93 (s, 1H), 6.86 (s, 1H), 5.43 (s, 1H), 2.21 (s, 3H), 2.17 (s, 3H),

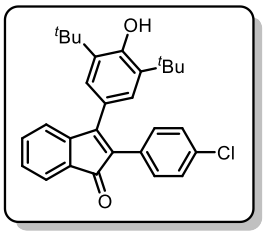
1.88 (s, 3H), 1.30 (s, 18H); $^{13}C\{^{1}H\}$ NMR (100 MHz, $CDCl_3$) δ, 197.0, 156.7, 155.2, 145.0, 136.2, 135.8, 134.5, 133.7, 133.4, 132.9, 132.1, 131.6, 131.5, 129.2, 128.7, 126.1, 123.9, 122.8, 121.5, 34.4, 30.2, 19.6, 19.5, 19.3; FT-IR (thin film, neat): 3624, 2957, 1700, 1456, 1267, 866, 750; HRMS (ESI): *m/z* calcd for $C_{32}H_{37}O_2$ $[M+H]^+$: 453.2794; found : 453.2796.

3-(3,5-di-*tert*-butyl-4-hydroxyphenyl)-2-(4-fluorophenyl)-1*H*-inden-1-one (2i).



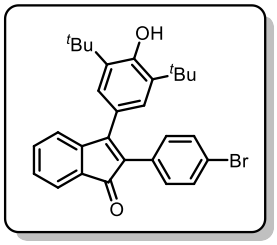
The reaction was performed at 0.12 mmol scale of **1i**; red solid (36 mg, 70% yield); m. p. = 206–208 °C; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.57 (d, J = 7.4 Hz, 1H), 7.40 (t, J = 7.8 Hz, 1H), 7.31 – 7.28 (m, 2H), 7.26 – 7.24 (m, 2H), 7.22 (s, 2H), 7.00 (t, J = 8.8 Hz, 2H), 5.48 (s, 1H), 1.35 (s, 18H); $^{13}C\{^{1}H\}$ NMR (100 MHz, $CDCl_3$) δ 196.7, 162.3 (d, $^{1}J_{C-F}$ = 245.8 Hz), 156.6, 155.4, 145.0, 136.1, 133.3, 132.0 (d, $^{3}J_{C-F}$ = 7.8 Hz), 131.5, 130.4, 129.0, 127.8 (d, $^{4}J_{C-F}$ = 3.3 Hz), 126.3, 123.1, 122.9, 121.6, 115.2 (d, $^{2}J_{C-F}$ = 21.3 Hz), 34.5, 30.3; ^{19}F NMR (376 MHz, $CDCl_3$) δ -114.1; FT-IR (thin film, neat): 3628, 2960, 2924, 1696, 1496, 1234, 840; HRMS (ESI): *m/z* calcd for $C_{29}H_{30}FO_2$ $[M+H]^+$: 429.2230; found : 429.2247.

2-(4-chlorophenyl)-3-(3,5-di-*tert*-butyl-4-hydroxyphenyl)-1H-inden-1-one (2j).



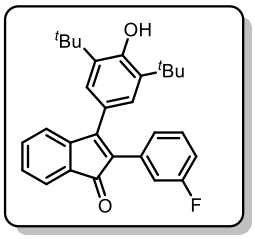
The reaction was performed at 0.11 mmol scale of **1j**; red solid (34 mg, 67% yield); m. p. = 212–214 °C; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.59 – 7.57 (m, 1H), 7.43 – 7.39 (m, 1H), 7.32 – 7.25 (m, 4H), 7.22 – 7.20 (m, 4H), 5.50 (s, 1H), 1.36 (s, 18H); $^{13}C\{^{1}H\}$ NMR (100 MHz, $CDCl_3$) δ 196.4, 157.1, 155.5, 144.9, 136.2, 133.4, 133.3, 131.53, 131.51, 130.3, 130.2, 129.1, 128.3, 126.3, 123.0, 122.9, 121.7, 34.5, 30.3; FT-IR (thin film, neat): 3627, 2923, 1703, 1490, 1257, 1092, 730; HRMS (ESI): *m/z* calcd for $C_{29}H_{30}ClO_2$ $[M+H]^+$: 445.1934; found : 445.1926.

2-(4-bromophenyl)-3-(3,5-di-*tert*-butyl-4-hydroxyphenyl)-1H-inden-1-one (2k).



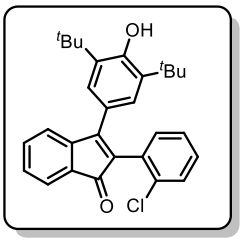
The reaction was performed at 0.11 mmol scale of **1k**; red solid (33 mg, 65% yield); m. p. = 214–216 °C; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.59 – 7.57 (m, 1H), 7.43 – 7.39 (m, 3H), 7.32 – 7.29 (m, 2H), 7.22 (s, 2H), 7.15 (d, J = 8.5 Hz, 2H), 5.51 (s, 1H), 1.36 (s, 18H); ^{13}C{^{1}H} NMR (100 MHz, $CDCl_3$) δ 196.3, 157.1, 155.5, 144.9, 136.2, 133.3, 131.8, 131.5, 131.3, 130.8, 130.2, 129.1, 126.3, 123.0, 122.9, 121.71, 121.67, 34.5, 30.3; FT-IR (thin film, neat): 3634, 2921, 1700, 1456, 1238, 765, 751; HRMS (ESI): *m/z* calcd for $C_{29}H_{30}BrO_2$ $[M+H]^+$: 489.1429; found : 489.1422.

3-(3,5-di-*tert*-butyl-4-hydroxyphenyl)-2-(3-fluorophenyl)-1H-inden-1-one (2l).



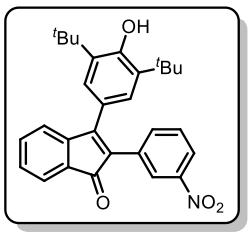
The reaction was performed at 0.12 mmol scale of **1l**; red solid (38 mg, 74% yield); m. p. = 142–144 °C; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.59 (d, J = 7.1 Hz, 1H), 7.41 (t, J = 7.8 Hz, 1H), 7.33 – 7.28 (m, 3H), 7.24 (s, 2H), 7.06 (d, J = 7.7 Hz, 1H), 6.99-6.93 (m, 2H), 5.50 (s, 1H), 1.35 (s, 18H), ^{13}C{^{1}H} NMR (100 MHz, $CDCl_3$) δ 196.1, 162.6 (d, $^{1}J_{C\text{-}F}$ = 243.5 Hz), 157.5, 155.6, 144.8, 136.2, 134.0 (d, $^{3}J_{C\text{-}F}$ = 8.0 Hz), 133.3, 131.5, 130.2 (d, $^{5}J_{C\text{-}F}$ = 2.2 Hz), 129.6 (d, $^{3}J_{C\text{-}F}$ = 8.6 Hz), 129.2, 126.3, 126.0 (d, $^{4}J_{C\text{-}F}$ = 2.6 Hz), 123.0, 122.9, 121.8, 117.0 (d, $^{2}J_{C\text{-}F}$ = 22.0 Hz), 114.4 (d, $^{2}J_{C\text{-}F}$ = 21.0 Hz), 34.5, 30.3; ^{19}F NMR (376 MHz, $CDCl_3$) δ -113.7; FT-IR (thin film, neat): 3626, 2957, 2922, 1699, 1497, 1237, 805; HRMS (ESI): *m/z* calcd for $C_{29}H_{30}FO_2$ $[M+H]^+$: 429.2230; found : 429.2247.

2-(2-chlorophenyl)-3-(3,5-di-*tert*-butyl-4-hydroxyphenyl)-1H-inden-1-one (2m).



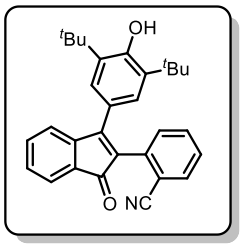
The reaction was performed at 0.11 mmol scale of **1m**; red solid (32 mg, 63% yield); m. p. = 205–207 °C; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.61 (d, J = 7.0 Hz, 1H), 7.45 – 7.41 (m, 3H), 7.33 (td, J = 6.8, 2.0 Hz, 1H), 7.28 – 7.20 (m, 4H), 7.11 (dd, J = 7.3, 5.6 Hz, 1H), 5.47 (s, 1H), 1.32 (s, 18H); ^{13}C{^{1}H} NMR (100 MHz, $CDCl_3$) δ 195.4, 158.3, 155.5, 144.5, 135.9, 134.9, 133.1, 132.3, 132.1, 132.0, 131.2, 129.7, 129.2, 129.1, 126.8, 126.1, 123.4, 123.0, 122.0, 34.4, 30.2; FT-IR (thin film, neat): 3628, 2960, 2918, 1684, 1260, 1047, 750; HRMS (ESI): *m/z* calcd for $C_{29}H_{30}ClO_2$ $[M+H]^+$: 445.1934; found : 445.1937.

3-(3,5-di-*tert*-butyl-4-hydroxyphenyl)-2-(3-nitrophenyl)-1H-inden-1-one (2n).



The reaction was performed at 0.11 mmol scale of **1n**; red solid (44 mg, 87% yield); m. p. = 186–188 °C; ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.16 – 8.15 (m, 1H), 8.11 – 8.09 (m, 1H), 7.65 – 7.61 (m, 2H), 7.48 – 7.43 (m, 2H), 7.37 – 7.32 (m, 2H), 7.22 (s, 2H), 5.55 (s, 1H), 1.34 (s, 18H); ^{13}C{^{1}H} NMR (100 MHz, $CDCl_3$) δ 195.6, 158.8, 155.9, 148.2, 144.5, 136.7, 136.3, 133.8, 133.5, 131.3, 129.6, 129.0, 128.8, 126.1, 125.1, 123.2, 122.5, 122.2, 122.1, 34.5, 30.2; FT-IR (thin film, neat): 3634, 2963, 1703, 1261, 1090, 1041, 799; HRMS (ESI): *m/z* calcd for $C_{29}H_{30}NO_4$ $[M+H]^+$: 456.2175; found : 456.2177.

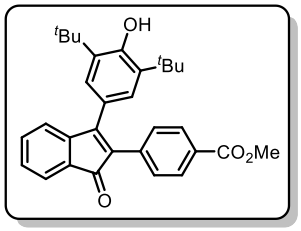
2-(3-(3,5-di-*tert*-butyl-4-hydroxyphenyl)-1-oxo-1H-inden-2-yl)benzonitrile (2o).



The reaction was performed at 0.11 mmol scale of **1o**; red solid (30 mg, 59% yield); m. p. = 194–196 °C; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.63 (d, J = 7.3 Hz, 2H), 7.58 (td, J = 7.7, 6.6 Hz, 1H), 7.47 – 7.33 (m, 5H), 7.17 (s, 2H), 5.52 (s, 1H), 1.31 (s, 18H); ^{13}C{^{1}H} NMR (100 MHz, $CDCl_3$) δ 194.8, 160.2, 155.9, 144.2, 136.8, 136.2, 133.3, 133.2, 132.5, 131.8, 131.7, 129.7, 129.1, 128.0, 126.6, 123.4, 122.7, 122.3, 118.0, 113.8, 34.4, 30.2; FT-IR (thin film, neat): 3631, 2959, 1704,

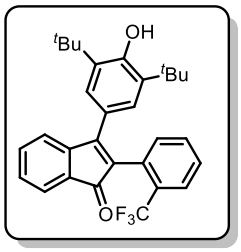
1352, 1274, 1077, 764; HRMS (ESI): *m/z* calcd for $C_{30}H_{30}NO_2$ $[M+H]^+$: 436.2277; found : 436.2267.

Methyl 4-(3-(3,5-di-*tert*-butyl-4-hydroxyphenyl)-1-oxo-1H-inden-2-yl) benzoate (2p).



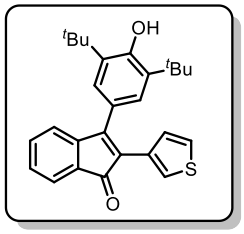
The reaction was performed at 0.11 mmol scale of **1p**; red solid (39 mg, 77% yield); m. p. = 235–237 °C; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.97 – 7.95 (m, 2H), 7.60 – 7.58 (m, 1H), 7.44 – 7.40 (m, 1H), 7.36-7.31 (m, 4H), 7.22 (s, 2H), 5.51 (s, 1H), 3.91 (s, 3H), 1.34 (s, 18H); ^{13}C{^{1}H} NMR (100 MHz, $CDCl_3$) δ, 196.1, 167.1, 158.1, 155.7, 144.8, 136.9, 136.3, 133.4, 131.6, 130.3, 130.2, 129.33, 129.30, 128.7, 126.3, 123.0, 122.9, 121.9, 52.2, 34.5, 30.3; FT-IR (thin film, neat): 3593, 2962, 1733, 1611, 1276, 1031, 800; HRMS (ESI): *m/z* calcd for $C_{31}H_{33}O_4$ $[M+H]^+$: 469.2379; found : 469.2388.

3-(3,5-di-*tert*-butyl-4-hydroxyphenyl)-2-(2-(trifluoromethyl)phenyl)-1H-inden-1-one (2q).



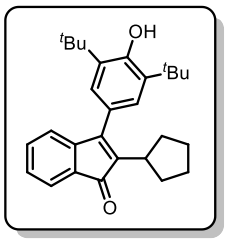
The reaction was performed at 0.11 mmol scale of **1q**; red solid (26 mg, 50% yield); m. p. = 209–211 °C; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.73 (d, J = 7.6 Hz 1H), 7.61 (d, J = 7.0 Hz 1H), 7.52 – 7.40 (m, 4H), 7.33 (td, J_1 = 7.1, J_2 = 1.6 Hz, 1H), 7.19 (s, 2H), 7.16 (d, J = 7.4 Hz 1H), 5.45 (s, 1H), 1.29 (s, 18H); ^{13}C{^{1}H} NMR (100 MHz, $CDCl_3$) δ 195.6, 157.7, 155.5, 144.7, 135.9, 133.1, 132.5, 132.1 (q, $^5J_{C\text{-}F}$ = 2.2 Hz), 131.9, 131.8, 131.5, 130.5 (q, $^2J_{C\text{-}F}$ = 29.8 Hz), 129.1, 128.1, 126.80 (q, $^3J_{C\text{-}F}$ = 4.9 Hz), 126.4, 124.1 (q, $^1J_{C\text{-}F}$ = 272.3 Hz), 123.1, 123.0, 122.2, 34.4, 30.2: ^{19}F NMR (376 MHz, $CDCl_3$) δ -60.0; FT-IR (thin film, neat): 3628, 2964, 1696, 1256, 1041, 764; HRMS (ESI): *m/z* calcd for $C_{30}H_{30}F_3O_2$ $[M+H]^+$: 479.2198; found : 479.2193.

3-(3,5-di-*tert*-butyl-4-hydroxyphenyl)-2-(thiophen-3-yl)-1H-inden-1-one (2r).



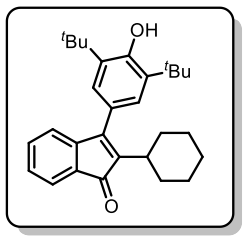
The reaction was performed at 0.12 mmol scale of **1r**; red solid (31 mg, 60% yield); m. p. = 208–210 °C; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.67 – 7.66 (m, 1H), 7.54 (d, J = 7.0 Hz, 1H), 7.36 (t, J = 7.6 Hz, 1H), 7.28 (s, 2H), 7.26 (s, 1H), 7.20 – 7.15 (m, 2H), 6.86 (d, J = 5.0 Hz, 1H), 5.49 (s, 1H), 1.40 (s, 18H); ^{13}C{^{1}H} NMR (100 MHz, $CDCl_3$) δ 196.9, 155.3, 155.1, 145.7, 136.2, 133.4, 131.7, 131.5, 128.8, 128.2, 126.7, 125.9, 125.8, 124.3, 123.7, 122.8, 121.4, 34.5, 30.4; FT-IR (thin film, neat): 2963, 2932, 1705, 1275, 1267, 750; HRMS (ESI): *m/z* calcd for $C_{27}H_{29}O_2S$ $[M+H]^+$: 417.1888; found : 417.1873.

2-cyclopentyl-3-(3,5-di-*tert*-butyl-4-hydroxyphenyl)-1H-inden-1-one (2s).



The reaction was performed at 0.12 mmol scale of **1s**; red solid (27 mg, 52% yield); m. p. = 195–197 °C; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.41 (d, J = 6.8 Hz, 1H), 7.30 – 7.26 (m, 3H), 7.19 – 7.15 (m, 1H), 7.02 (d, J = 7.2 Hz, 1H), 5.46 (s, 1H), 2.97 – 2.88 (m, 1H), 2.02 – 1.85 (m, 4H), 1.80 – 1.73 (m, 2H), 1.59 – 1.54 (m, 2H), 1.49 (s, 18H); ^{13}C{^{1}H} NMR (100 MHz, $CDCl_3$) δ 198.4, 156.3, 154.8, 145.6, 136.3, 136.1, 133.0, 131.9, 128.1, 125.3, 124.0, 122.0, 120.5, 36.7, 34.6, 32.3, 30.4, 26.7; FT-IR (thin film, neat):3626, 2963, 1699, 1260, 1038, 800, 752; HRMS (ESI): *m/z* calcd for $C_{28}H_{35}O_2$ $[M+H]^+$: 403.2637; found : 403.2624.

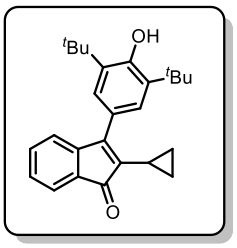
2-cyclohexyl-3-(3,5-di-*tert*-butyl-4-hydroxyphenyl)-1*H*-inden-1-one (2t).



The reaction was performed at 0.12 mmol scale of **1t**; orange solid (20 mg, 39% yield); m. p. = 197–199 °C; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.41 (d, J = 6.9 Hz, 1H), 7.30 – 7.26 (m, 3H), 7.17 (t, J = 7.4 Hz, 1H), 7.03 (d, J = 7.2 Hz, 1H), 5.46 (s, 1H), 2.59 – 2.53 (m, 1H), 2.02 – 1.92 (m, 2H), 1.68

– 1.62 (m, 2H), 1.49 (s, 18H), 1.29 – 1.18 (m, 6H); $^{13}C\{^{1}H\}$ NMR (100 MHz, $CDCl_3$) δ 198.6, 155.7, 154.8, 145.6, 137.7, 136.0, 132.9, 131.7, 128.1, 125.3, 124.0, 122.0, 120.7, 36.4, 34.6, 31.2, 30.4, 26.9, 26.0; FT-IR (thin film, neat): 3640, 2956, 2924, 1702, 1461, 765, 750; HRMS (ESI): *m/z* calcd for $C_{29}H_{37}O_2$ $[M+H]^+$: 417.2794; found : 417.2787.

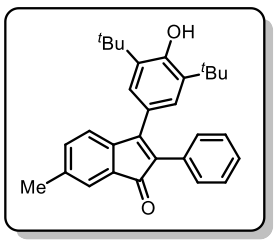
2-cyclopropyl-3-(3,5-di-*tert*-butyl-4-hydroxyphenyl)-1*H*-inden-1-one (2u).



The reaction was performed at 0.13 mmol scale of **1u**; orange solid (21 mg, 40% yield); m. p. = 192–194 °C; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.42 (s, 2H), 7.37 (d, J = 7.0 Hz, 1H), 7.30 – 7.26 (m, 1H), 7.1 (t, J = 7.4 Hz, 1H), 7.0 (d, J = 7.2 Hz, 1H), 5.46 (s, 1H), 1.76 – 1.69 (m, 1H), 1.49 (s, 18H), 0.89-0.77 (m, 4H); $^{13}C\{^{1}H\}$ NMR (100 MHz, $CDCl_3$) δ 197.9, 156.3, 154.8, 145.5, 136.0, 133.1, 133.0, 131.6, 127.9, 125.6, 123.9, 122.11, 122.10, 34.6, 30.5, 8.7, 7.4; FT-IR (thin film, neat): 3546, 2956, 2914, 1693, 1374, 1109, 724; HRMS (ESI): *m/z* calcd for $C_{26}H_{31}O_2$ $[M+H]^+$: 375.2324; found : 375.2329.

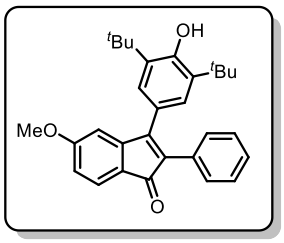
3. *Characterisation of products 3a to 3f*

3-(3,5-di-*tert*-butyl-4-hydroxyphenyl)-6-methyl-2-phenyl-1H-inden-1-one (3a).



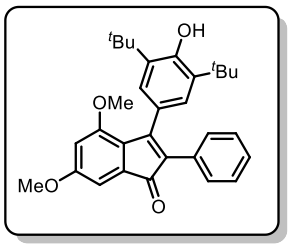
The reaction was performed at 0.12 mmol scale of **1v**; red solid (31 mg, 61% yield); m. p. = 180–182 °C; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.43 (s, 1H), 7.30 – 7.25 (m, 7H), 7.21 (s, 2H), 5.47 (s, 1H), 2.41 (s, 3H), 1.35 (s, 18H); $^{13}C\{^{1}H\}$ NMR (100 MHz, $CDCl_3$) δ 197.0, 156.8, 155.3, 142.2, 139.2, 135.9, 133.1, 132.02, 132.00, 131.1, 130.2, 128.1, 127.4, 126.4, 124.0, 123.4, 121.4, 34.4, 30.2, 21.5; FT-IR (thin film, neat): 3628, 2958, 2923, 1701, 1348, 794, 695; HRMS (ESI): *m/z* calcd for $C_{30}H_{33}O_2$ $[M+H]^+$: 425.2481; found : 425.2495.

3-(3,5-di-*tert*-butyl-4-hydroxyphenyl)-5-methoxy-2-phenyl-1*H*-inden-1-one (3b).



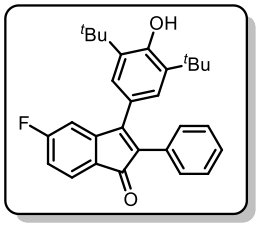
The reaction was performed at 0.11 mmol scale of **1w**; dark red solid (27 mg, 53% yield); m. p. = 198–200 °C; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.53 (d, J = 8.0 Hz, 1H), 7.30 – 7.23 (m, 5H), 7.20 (s, 2H), 6.88 (d, J = 1.9 Hz, 1H), 6.68 (dd, J_1 = 8.0 Hz, J_2 = 1.9 Hz, 1H), 5.44 (s, 1H), 3.85 (s, 3H), 1.33 (s, 18H); ^{13}C{^{1}H} NMR (100 MHz, $CDCl_3$) δ 195.4, 164.2, 155.1, 154.3, 147.7, 136.0, 133.0, 131.9, 130.2, 128.1, 127.5, 126.4, 124.6, 124.3, 123.2, 110.6, 110.5, 55.8, 34.4, 30.3; FT-IR (thin film, neat): 3626, 2958, 1775, 1705, 1597, 1236, 749; HRMS (ESI): *m/z* calcd for $C_{30}H_{33}O_3$ $[M+H]^+$: 441.2430; found : 441.2438.

3-(3,5-di-*tert*-butyl-4-hydroxyphenyl)-4,6-dimethoxy-2-phenyl-1H-inden-1-one (3c).



The reaction was performed at 0.11 mmol scale of **1x**; dark red solid (28 mg, 55% yield); m. p. = 190–192 °C; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.24 – 7.19 (m, 4H), 7.18 – 7.14 (m, 1H),7.08 – 7.06 (m, 2H), 6.89 (d, J = 2.2 Hz, 1H), 6.48 (d, J = 2.1 Hz, 1H), 5.35 (s, 1H), 3.87 (s, 3H), 3.69 (s, 3H), 1.30 (s, 18H); ^{13}C{^{1}H} NMR (100 MHz, $CDCl_3$) δ 196.1, 162.8, 160.2, 154.9, 154.8, 135.4, 134.4, 132.4, 130.7, 130.3, 127.9, 127.4, 126.8, 124.3, 121.8, 103.7, 102.5, 56.0, 55.6, 34.3, 30.3; FT-IR (thin film, neat): 3626, 2959, 1700, 1600, 1260, 1031, 799; HRMS (ESI): *m/z* calcd for $C_{31}H_{35}O_4$ $[M+H]^+$: 471.2535; found : 471.2531. HRMS (ESI): *m/z* calcd for $C_{31}H_{35}O_4$ $[M+H]^+$: 471.2535; found : 471.2531.

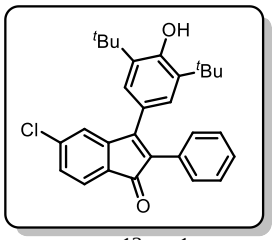
3-(3,5-di-*tert*-butyl-4-hydroxyphenyl)-5-fluoro-2-phenyl-1H-inden-1-one (3d).



The reaction was performed at 0.12 mmol scale of **1y**; red solid (18 mg, 35% yield); m. p. = 203–205 °C; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.56 (dd, J = 7.9, 5.2 Hz, 1H), 7.32 – 7.24 (m, 5H), 7.20 (s, 2H), 7.01 (dd, J = 8.7,

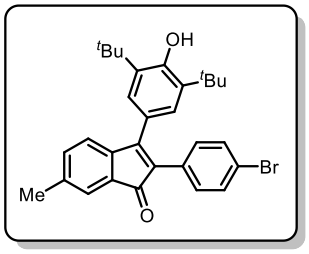
2.0 Hz, 1H), 6.96 – 6.91 (m, 1H), 5.48 (s, 1H), 1.34 (s, 18H); $^{13}C\{^{1}H\}$ NMR (100 MHz, $CDCl_3$) δ 195.0, 166.2 (d, $^{1}J_{C\text{-}F}$ = 251.6 Hz), 155.4, 154.4 (d, $^{5}J_{C\text{-}F}$ = 2.3 Hz), 148.4 (d, $^{3}J_{C\text{-}F}$ = 9.2 Hz), 136.1, 132.8, 131.4, 130.1, 128.2, 127.8, 127.4 (d, $^{4}J_{C\text{-}F}$ = 3.0 Hz), 126.2, 124.5 (d, $^{3}J_{C\text{-}F}$ = 9.7 Hz), 122.8, 114.3 (d, $^{2}J_{C\text{-}F}$ = 22.9 Hz), 110.5 (d, $^{2}J_{C\text{-}F}$ = 24.8 Hz), 34.4, 30.2; ^{19}F NMR (376 MHz, $CDCl_3$) δ -104.6; FT-IR (thin film, neat): 3627, 2963, 1711, 1260, 1031, 866, 799; HRMS (ESI): *m/z* calcd for $C_{29}H_{30}FO_2$ $[M+H]^+$: 429.2230; found : 429.2238.

5-chloro-3-(3,5-di-*tert*-butyl-4-hydroxyphenyl)-2-phenyl-1*H*-inden-1-one (3e).



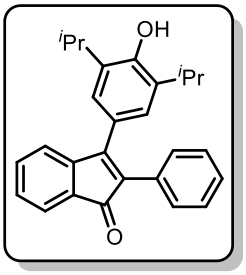
The reaction was performed at 0.11 mmol scale of **1z**; red solid (31 mg, 60% yield); m. p. = 172–174 °C; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.51 (d, J = 7.3 Hz, 1H), 7.29 – 7.24 (m, 7H), 7.21 (s, 2H), 5.50 (s, 1H), 1.34 (s, 18H); $^{13}C\{^{1}H\}$ NMR (100 MHz, $CDCl_3$) δ 195.2, 155.5, 155.3, 147.1, 139.3, 136.2, 132.6, 131.4, 130.2, 129.8, 128.4, 128.2, 127.8, 126.3, 123.7, 122.8, 122.4, 34.5, 30.2; FT-IR (thin film, neat):3629, 2959, 1701, 1603, 1260, 1081, 750; HRMS (ESI): *m/z* calcd for $C_{29}H_{30}ClO_2$ $[M+H]^+$:445.1934; found : 445.1931.

2-(4-bromophenyl)-3-(3,5-di-*tert*-butyl-4-hydroxyphenyl)-6-methyl-1H-inden-1-one (3f).



The reaction was performed at 0.102 mmol scale of **1aa**; red solid (28 mg, 54% yield); m. p. = 225–227 °C; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.42 (s, 1H), 7.40 (s, 2H), 7.21 (s, 2H), 7.18 (d, J = 2.4 Hz, 2H), 7.15 (s, 1H), 7.13 (s, 1H), 5.49 (s, 1H), 2.38 (s, 3H), 1.35 (s, 18H); $^{13}C\{^{1}H\}$ NMR (100 MHz, $CDCl_3$) δ 196.6, 157.4, 155.5, 142.0, 139.5, 136.1, 133.2, 131.9, 131.8, 131.3, 131.0, 129.7, 126.3, 124.1, 123.2, 121.6, 121.5, 34.5, 30.3, 21.5; FT-IR (thin film, neat): 3627, 2957, 1698, 1345, 1238, 1010, 819 ; HRMS (ESI): *m/z* calcd for $C_{30}H_{32}BrO_2$ $[M+H]^+$: 503.1586; found : 503.1589.

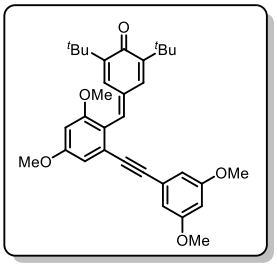
3-(4-hydroxy-3,5-diisopropylphenyl)-2-phenyl-1H-inden-1-one (3g).



The reaction was performed at 0.136 mmol scale of **1ab**; red solid (42 mg, 80% yield); m. p. = 192–194 °C; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.58 (d, J = 6.7 Hz, 1H), 7.41– 7.38 (m, 1H), 7.30 – 7.26 (m, 7H), 7.10 (s, 2H), 5.12 (s, 1H), 3.15 – 3.08 (m, 2H), 1.14 (d, J = 6.6 Hz, 12H). ^{13}C{^{1}H} NMR (100 MHz, $CDCl_3$) δ 196.8, 156.4, 151.3, 145.2, 133.9, 133.3, 131.7, 131.5, 130.1, 128.9, 128.2 (2C), 127.5, 124.8, 124.5, 122.9, 121.5, 27.0, 22.7; FT-IR (thin film, neat): 3627, 2957, 1698, 1345, 1238, 1010, 819; HRMS (ESI): *m/z* calcd for $C_{27}H_{27}O_2$ $[M+H]^+$: 383.2011; found : 383.2023.

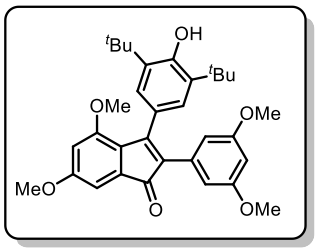
4. *Characterisation of products 6 & 7*

2,6-di-*tert*-butyl-4-(2-((3,5-dimethoxyphenyl)-ethynyl)-4,6-dimethoxybenzylidene)-cyclohexa-2,5-dien-1-ol (6).



The reaction was performed at 0.46 mmol scale of **4**; dark purple solid (162 mg, 68% yield); m. p. = 158–160 °C; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.29 (d, J = 2.2 Hz, 1H), 7.20 (s, 1H), 7.12 (d, J = 2.2 Hz, 1H), 6.77 (d, J = 2.3 Hz, 1H), 6.51 (d, J = 2.3 Hz, 1H), 6.41 – 6.38 (m, 3H), 3.89 (s, 3H), 3.84 (s, 3H), 3.70 (s, 6H), 1.33 (s, 9H) 1.14 (s, 9H); ^{13}C{^{1}H} NMR (100 MHz, $CDCl_3$) δ 187.0, 161.1, 160.6, 159.0, 147.13, 147.10, 137.9, 135.2, 132.9, 130.6, 124.7, 124.0, 120.3, 109.2, 108.4, 102.6, 99.7, 93.5, 88.4, 55.9, 55.7, 55.5, 35.3, 35.1, 29.7, 29.5; FT-IR (thin film, neat): 3626, 2956, 2152, 1690, 1594, 1310, 1142, 795; HRMS (ESI): *m/z* calcd for $C_{33}H_{39}O_5$ $[M+H]^+$: 515.2797; found 515.2783.

3-(3,5-di-*tert*-butyl-4-hydroxyphenyl)-2-(3,5-dimethoxyphenyl)-4,6-dimethoxy-1*H*-inden-1-one (7).



The reaction was performed at 0.097 mmol scale of **6**; dark purple solid (27 mg, 53% yield); m. p. = 211–213 °C; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.20 (s, 2H), 6.88 (d, J = 2.1 Hz, 1H), 6.47 (d, J = 2.1 Hz, 1H), 6.29 (t, J = 2.3 Hz, 1H), 6.22 (d, J = 2.3 Hz, 2H), 5.36 (s, 1H), 3.87 (s, 3H), 3.69 (s, 3H), 3.58 (s, 6H), 1.32 (s, 18H); ^{13}C{^{1}H} NMR (100 MHz, $CDCl_3$) δ 195.7, 162.9, 160.7, 160.2, 154.9, 154.8, 135.2, 134.6, 133.9, 130.5, 127.1, 124.8, 121.7, 107.9, 103.6, 102.5, 100.1, 56.1, 55.6, 55.2, 34.3, 30.4; FT-IR (thin film, neat): 3626, 2957, 1697, 1598, 1312, 1152, 803; HRMS (ESI): *m/z* calcd for $C_{33}H_{39}O_6$ $[M+H]^+$: 531.2747; found : 531.2753.

5. Procedure for gram scale synthesis of 2a.

Commercially available HMPA (5 mL) was added to a RB flask containing 2-alkynylphenyl-substituted *p*-QM **1a** (1.00 g, 2.54 mmol) and the reaction mixture was stirred at 140 °C for 8 h. The reaction mixture was then diluted with water (10 mL) and extracted with ether (15 mL x 3). The combined organic layer was dried over anhydrous sodium sulphate, filtered and concentrated under reduced pressure. The residue was then purified through a silica gel column to get **2a** as a red solid (645 mg, 62% yield).

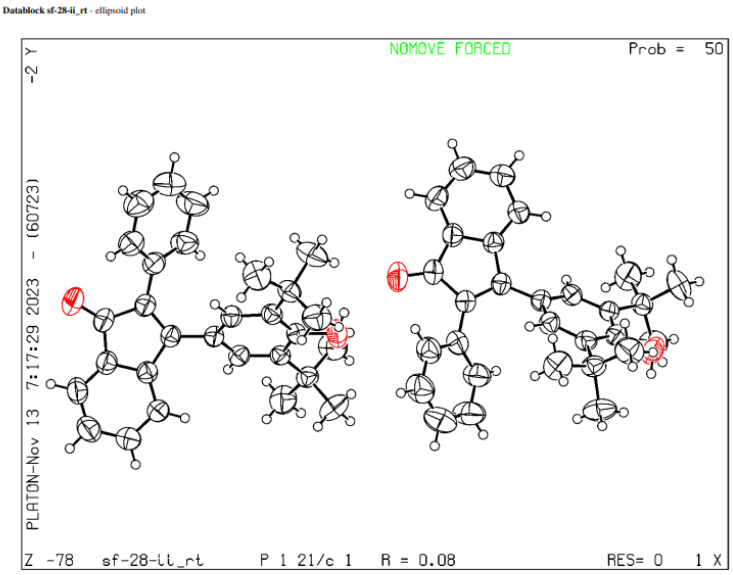
6. References:

(1) A. S. Jadhav, Y. A. Pankhade and R. V. Anand, *J. Org. Chem.*, **2018**, *83*, 8596 – 8606.

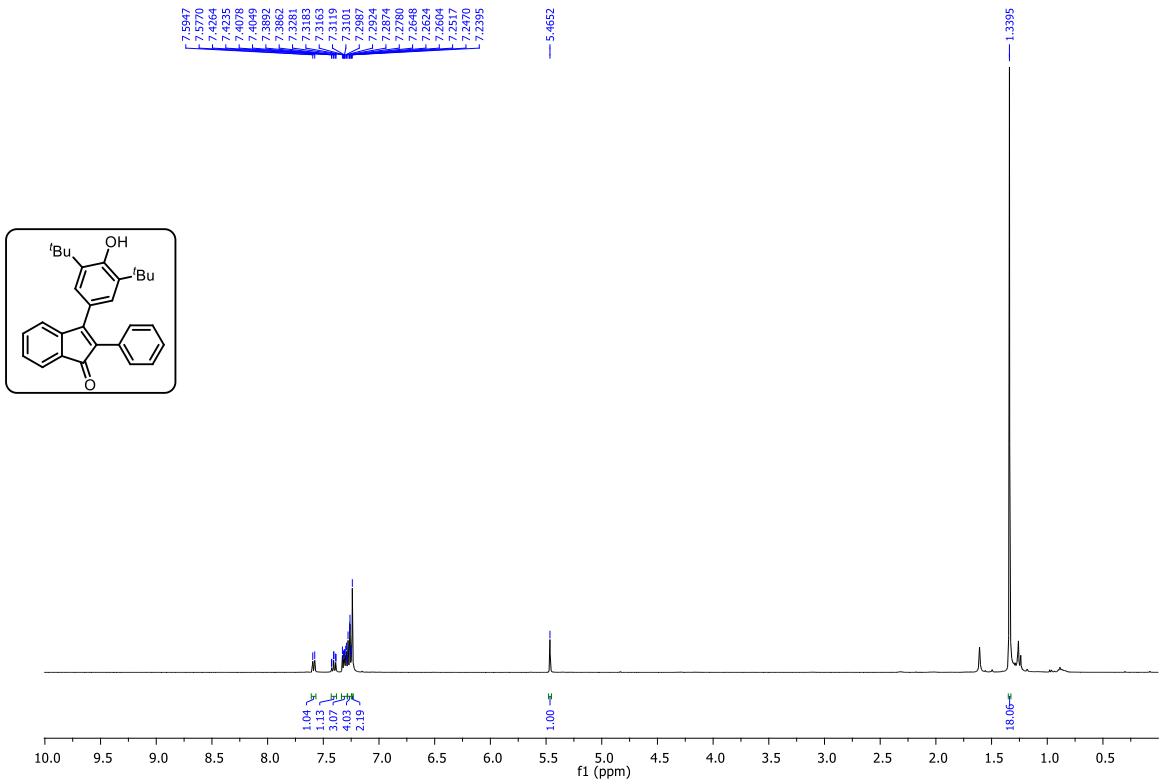
X-ray crystallographic analysis for compound 2a:

Table 2. Crystal data and structure refinement for compound 2a (CCDC 2307508)

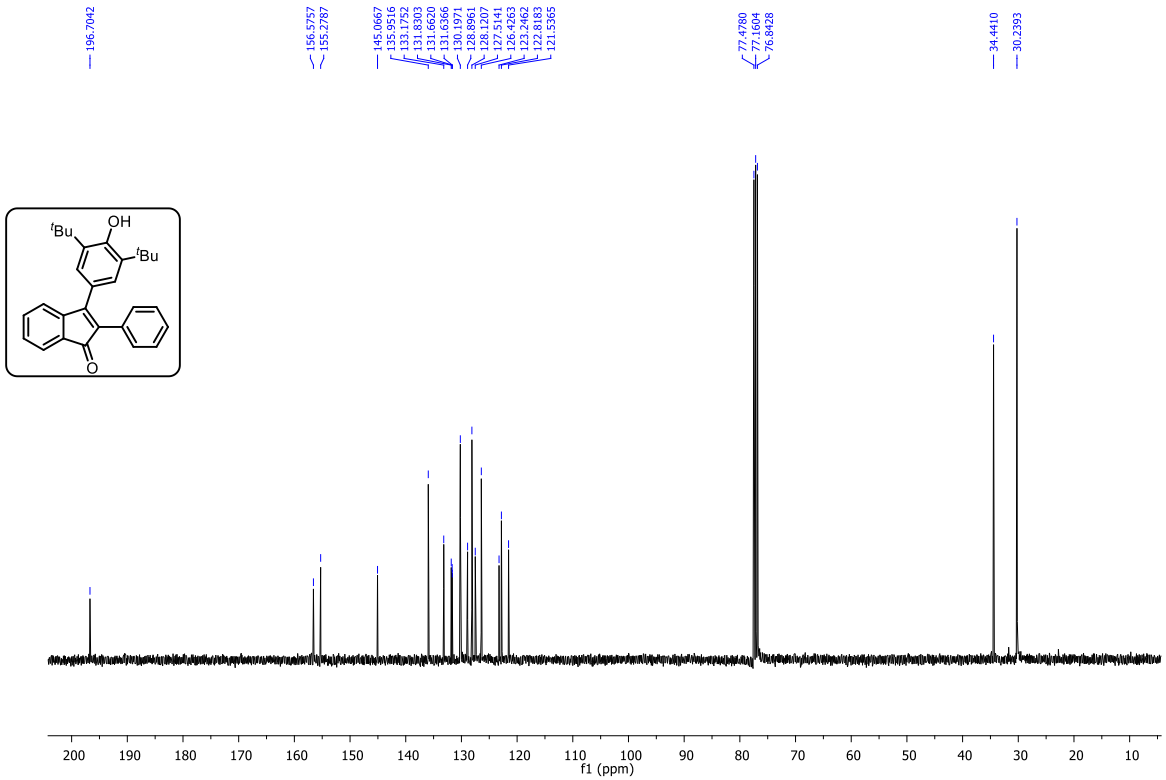
Complex	**SF-28-II**
Empirical formula	$C_{58}H_{60}O_4$
Formula Weight	821.06
Crystal system	Monoclinic
Space group	$P2_1/c$
T[K]	298k
a[Å]	11.6424(5)
b[Å]	21.0313(8)
c[Å]	19.3533(15)
α [°]	90.00
β [°]	90.006(4)
γ [°]	90.00
V [Å^3]	4738.8(5)
Z	4
D(calcd.) [g·cm^{-3}]	1.151
μ(Mo-K$_\alpha$) [mm^{-1}]	0.070
Reflections collected	44402
Independent reflections	15523
Data/restraints/parameters	15523/0/573
$R1$, $wR_2[I>2\sigma(I)]$[a]	0.0835, 0.2014
$R1$, wR_2 (all data)[a]	0.1724, 0.2625
GOF	1.103
CCDC	2307508



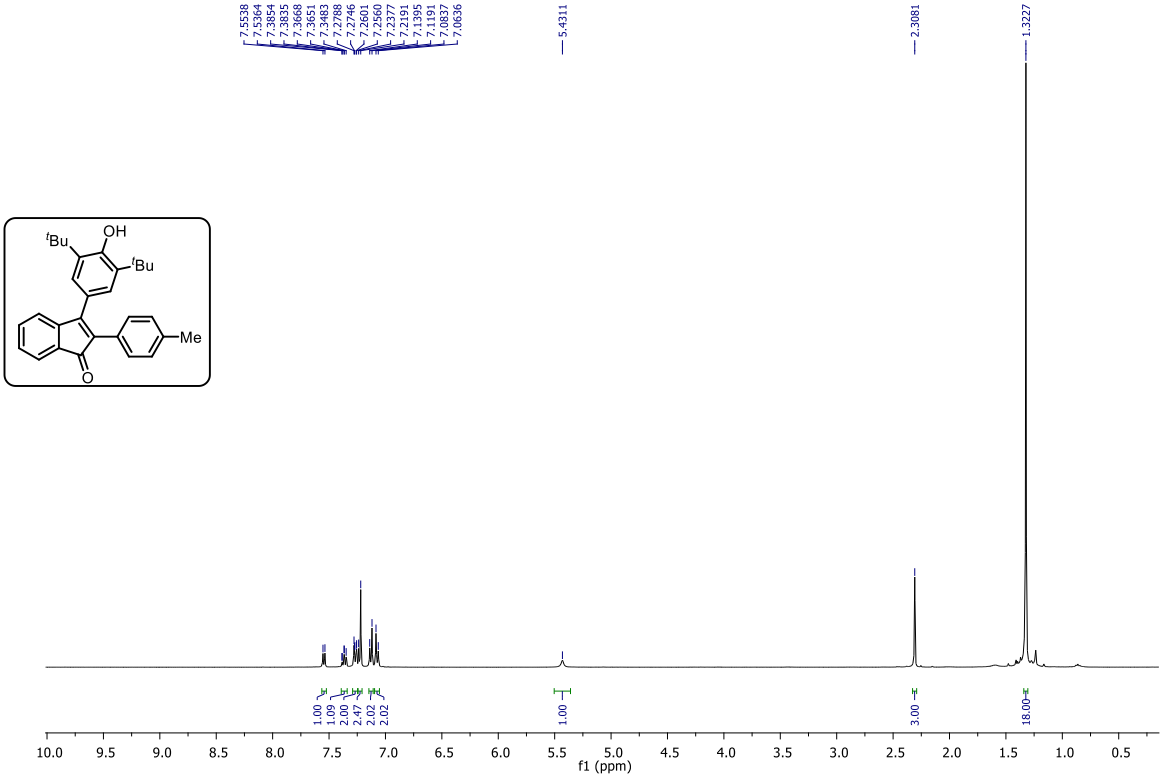
^{1}H NMR (400 MHz, $CDCl_3$) spectrum of **2a**



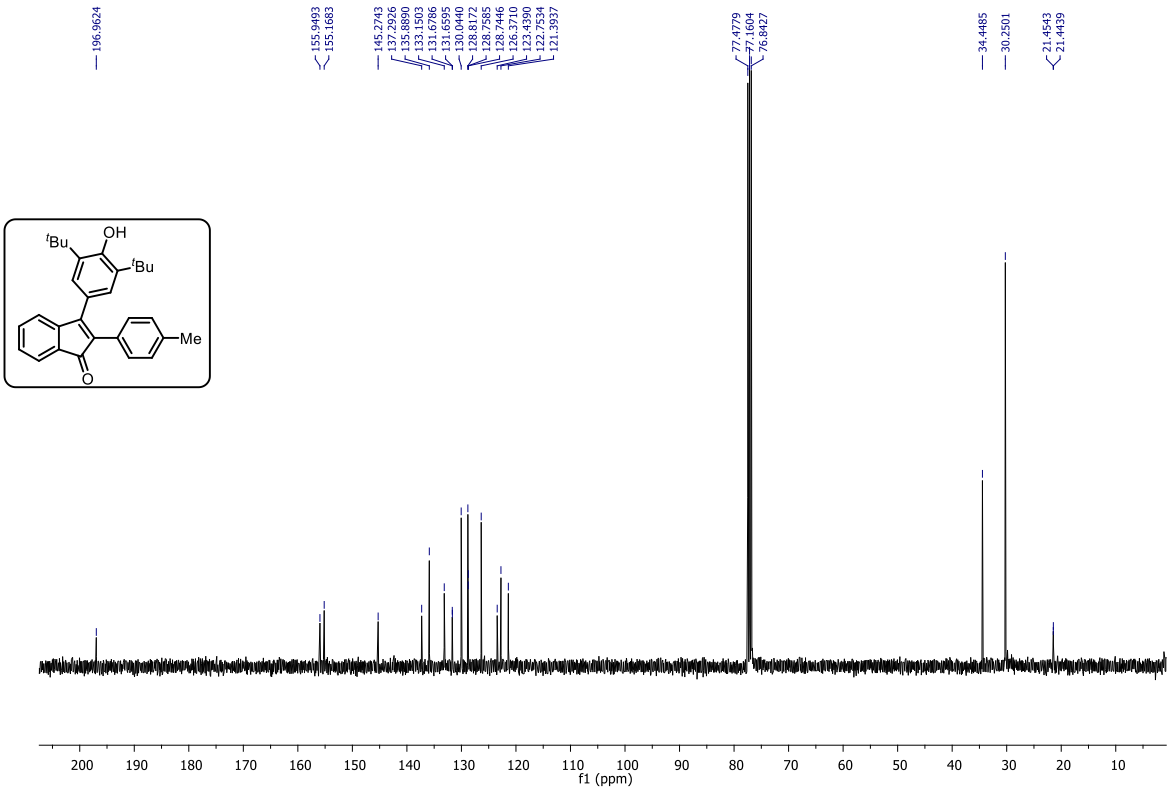
^{13}C{1H} NMR (100 MHz, $CDCl_3$) spectrum of **2a**



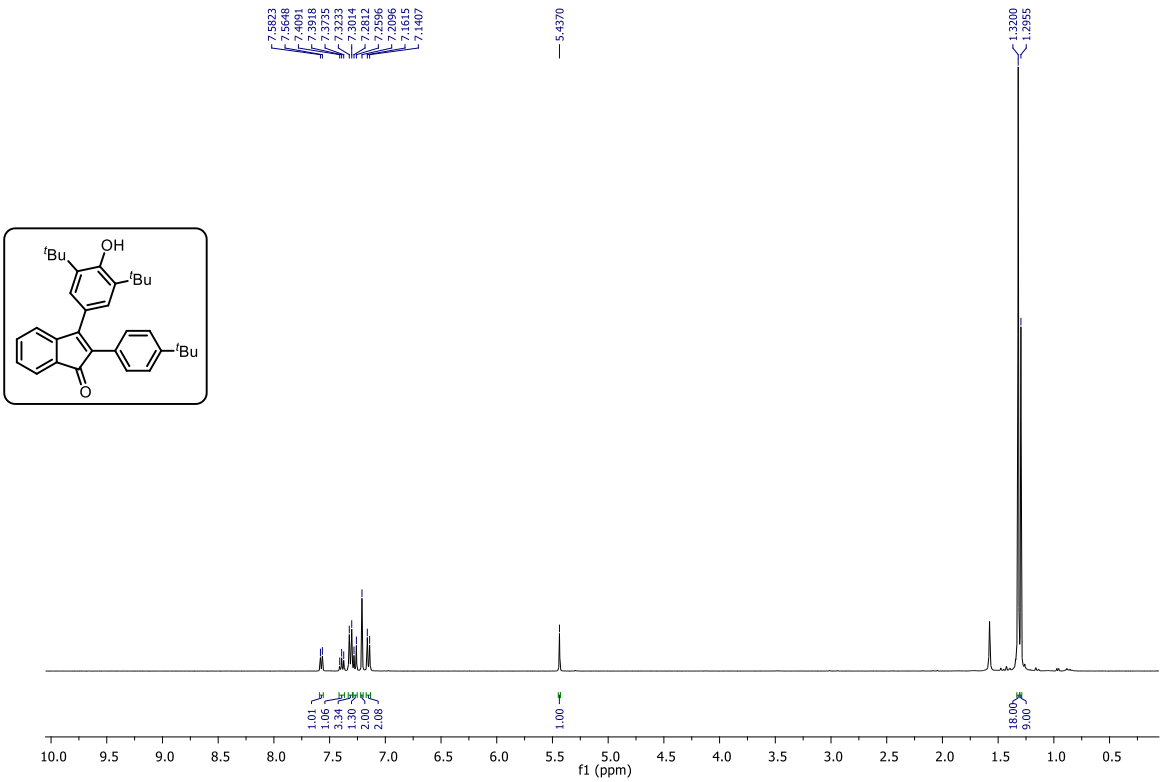
^{1}H NMR (400 MHz, $CDCl_3$) spectrum of **2b**



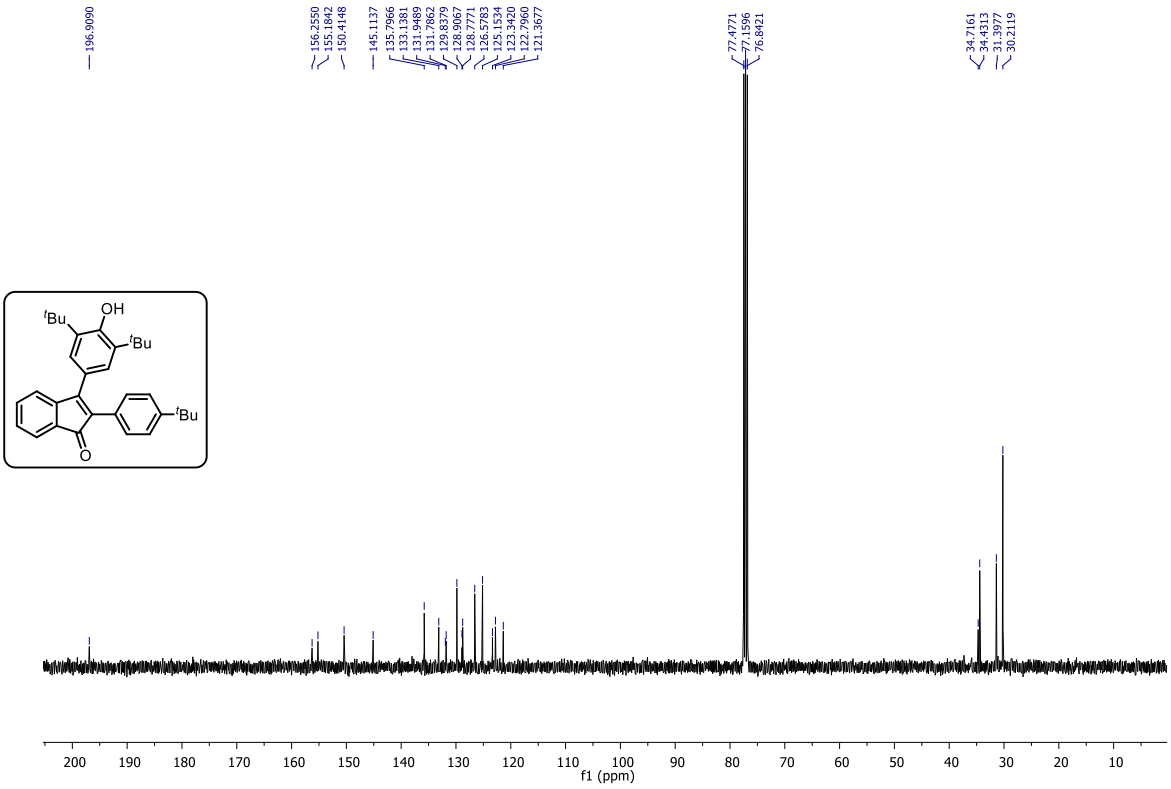
^{13}C{1H} NMR (100 MHz, $CDCl_3$) spectrum of **2b**



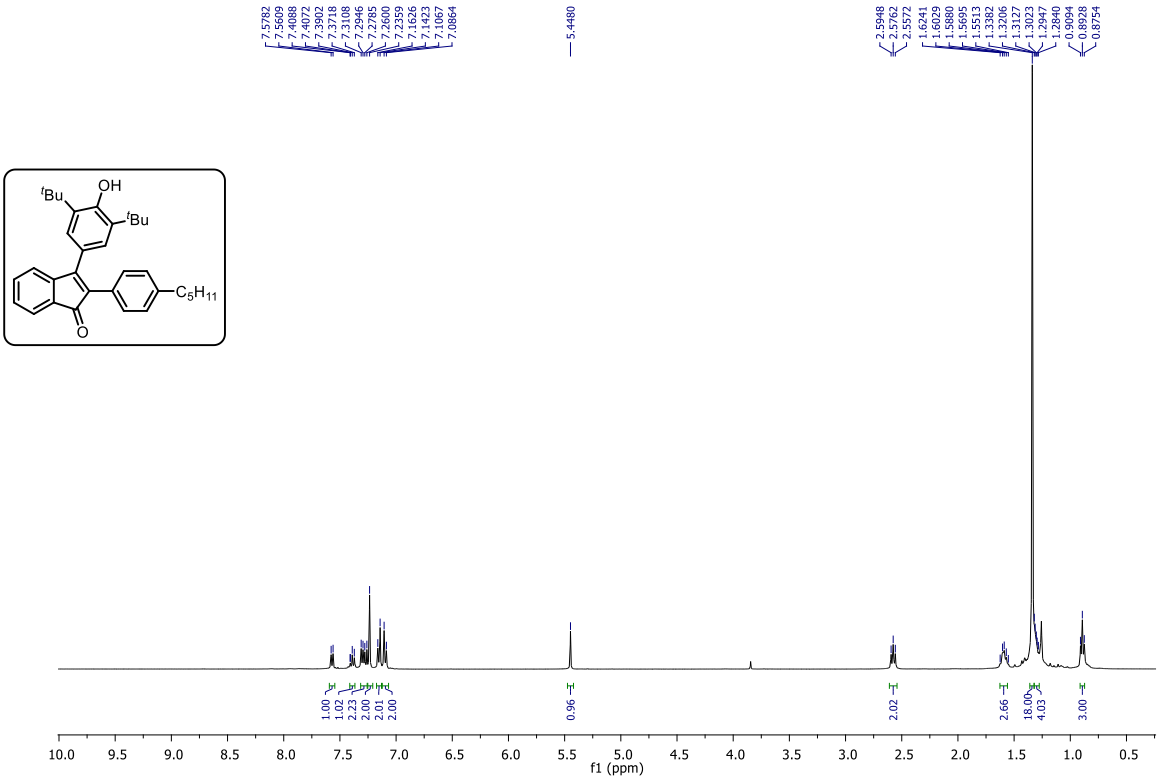
^{1}H NMR (400 MHz, $CDCl_3$) spectrum of **2c**



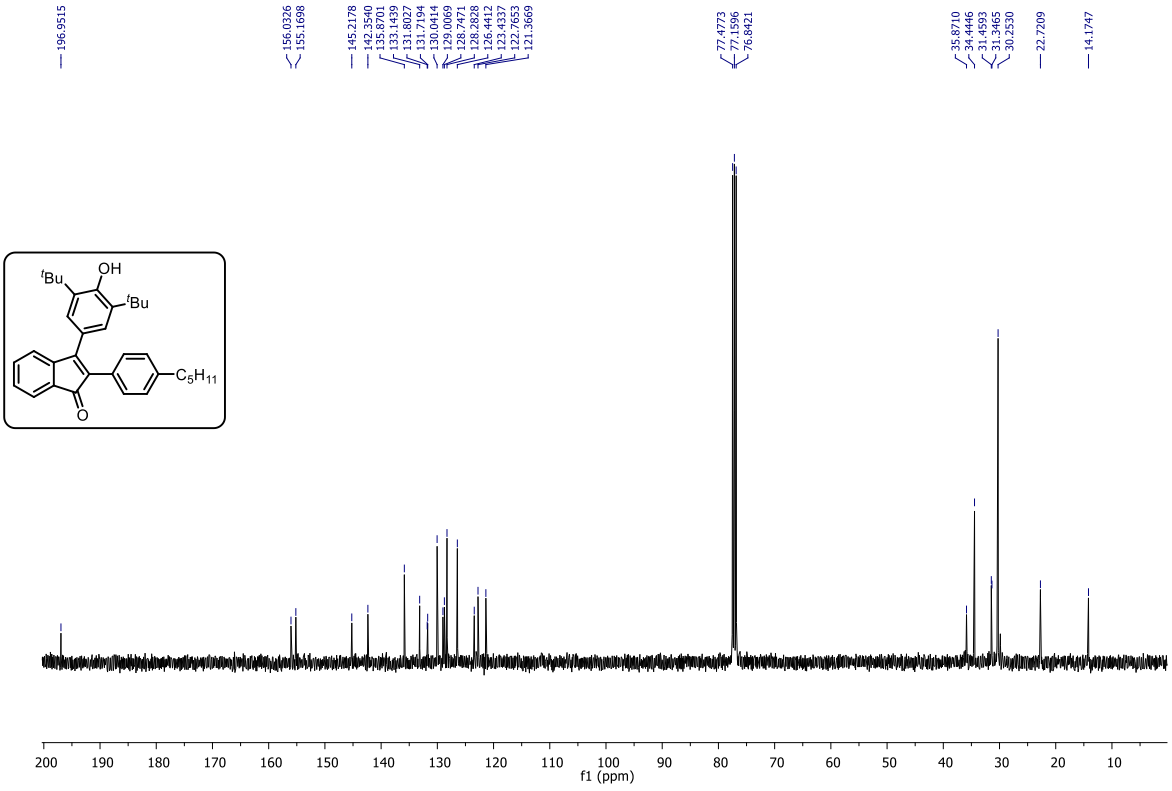
^{13}C{1H} NMR (100 MHz, $CDCl_3$) spectrum of **2c**



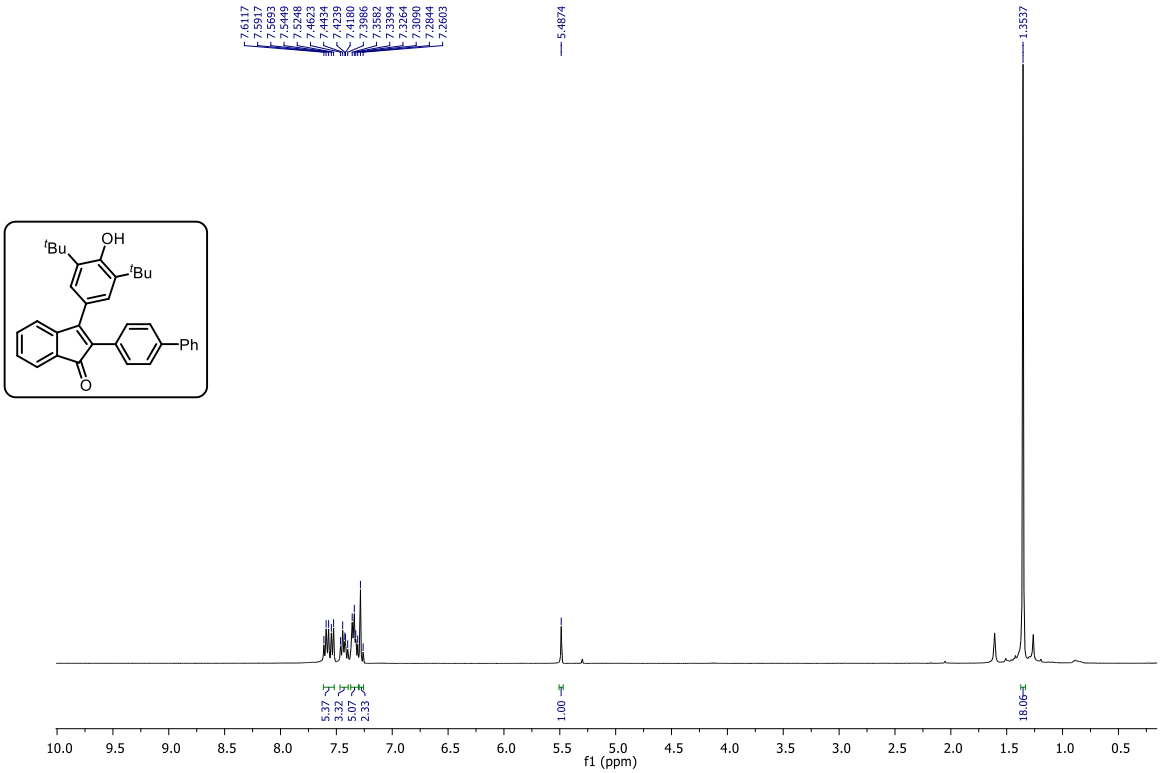
^{1}H NMR (400 MHz, $CDCl_3$) spectrum of **2d**



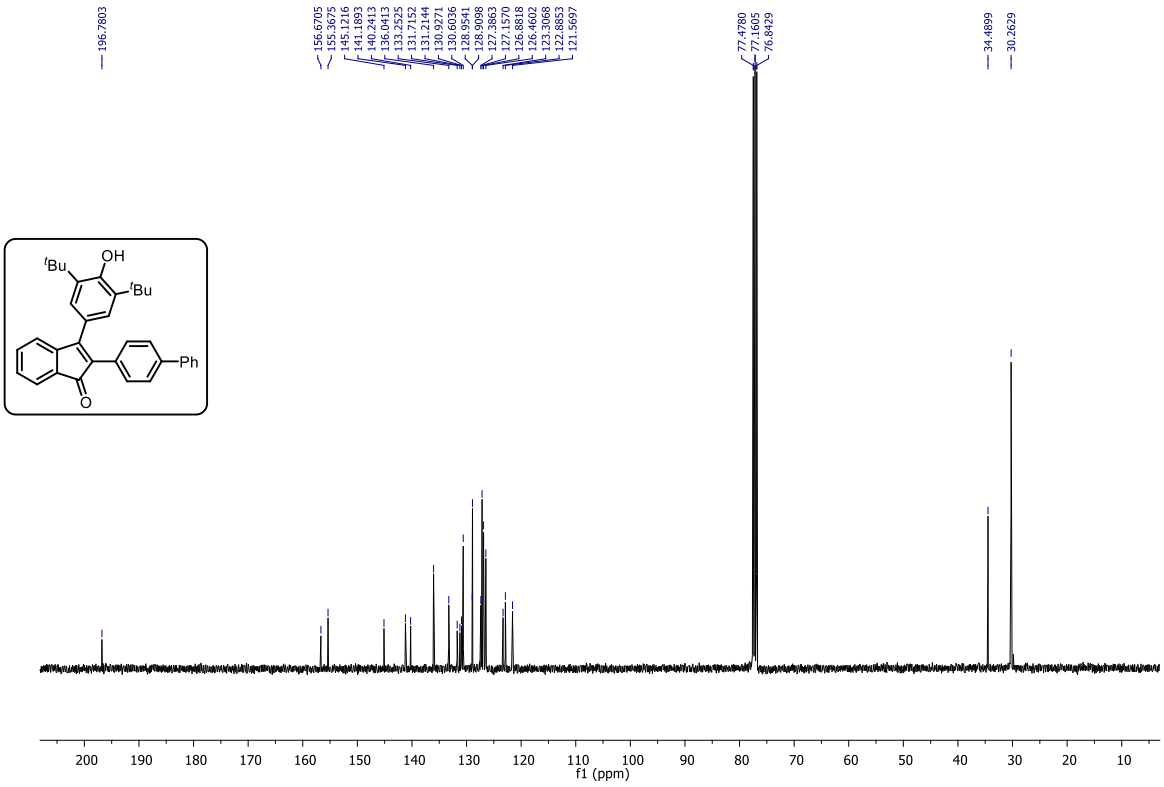
^{13}C{1H} NMR (100 MHz, $CDCl_3$) spectrum of **2d**



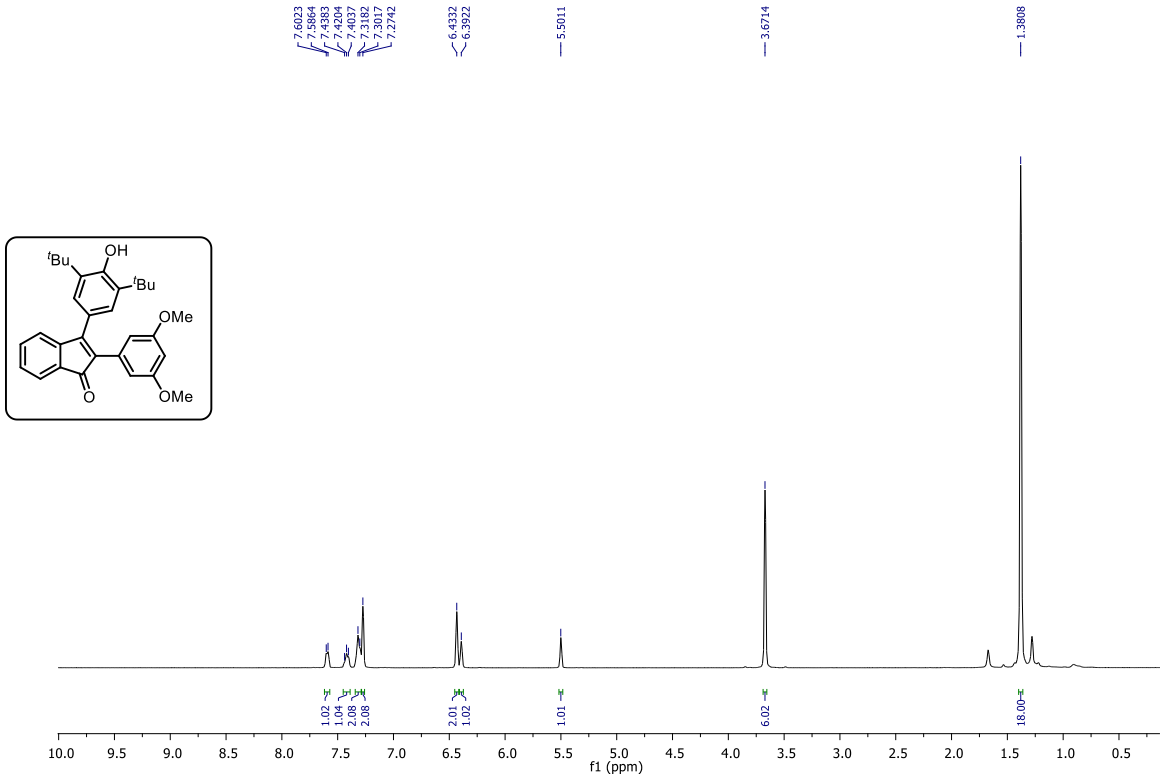
^{1}H NMR (400 MHz, $CDCl_3$) spectrum of **2e**



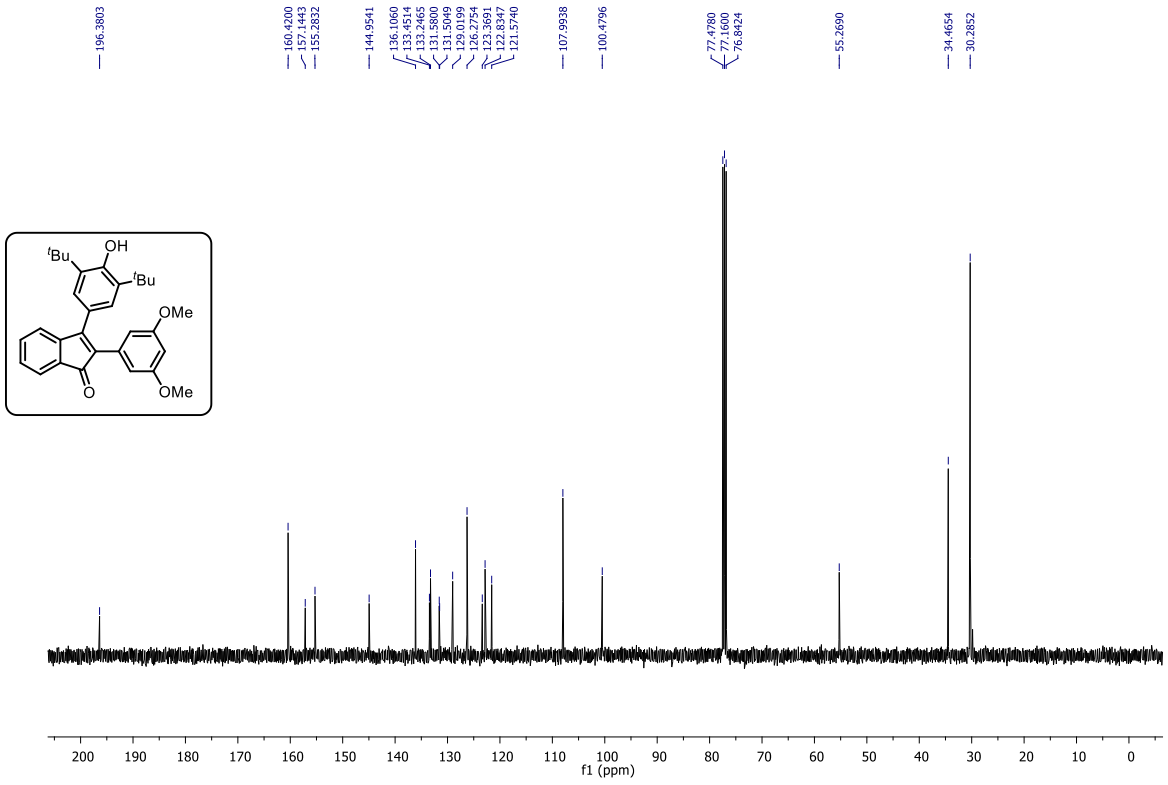
^{13}C{1H} NMR (100 MHz, $CDCl_3$) spectrum of **2e**



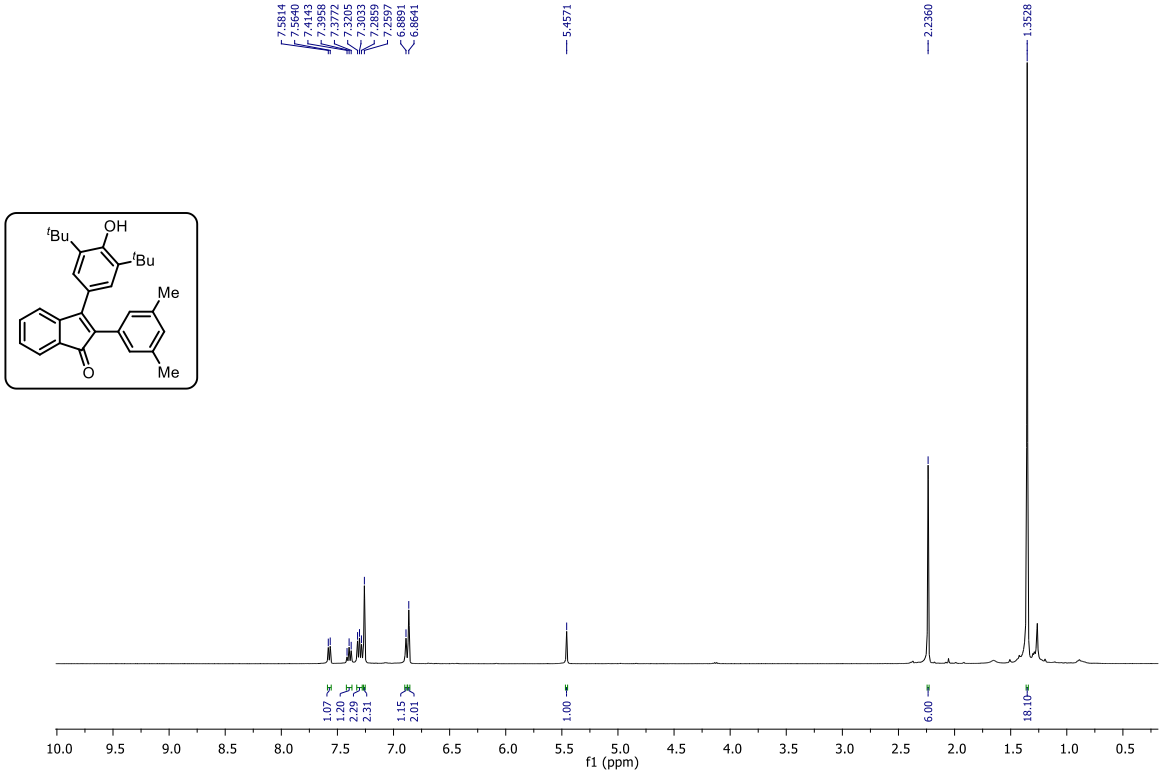
^{1}H NMR (400 MHz, $CDCl_3$) spectrum of **2f**



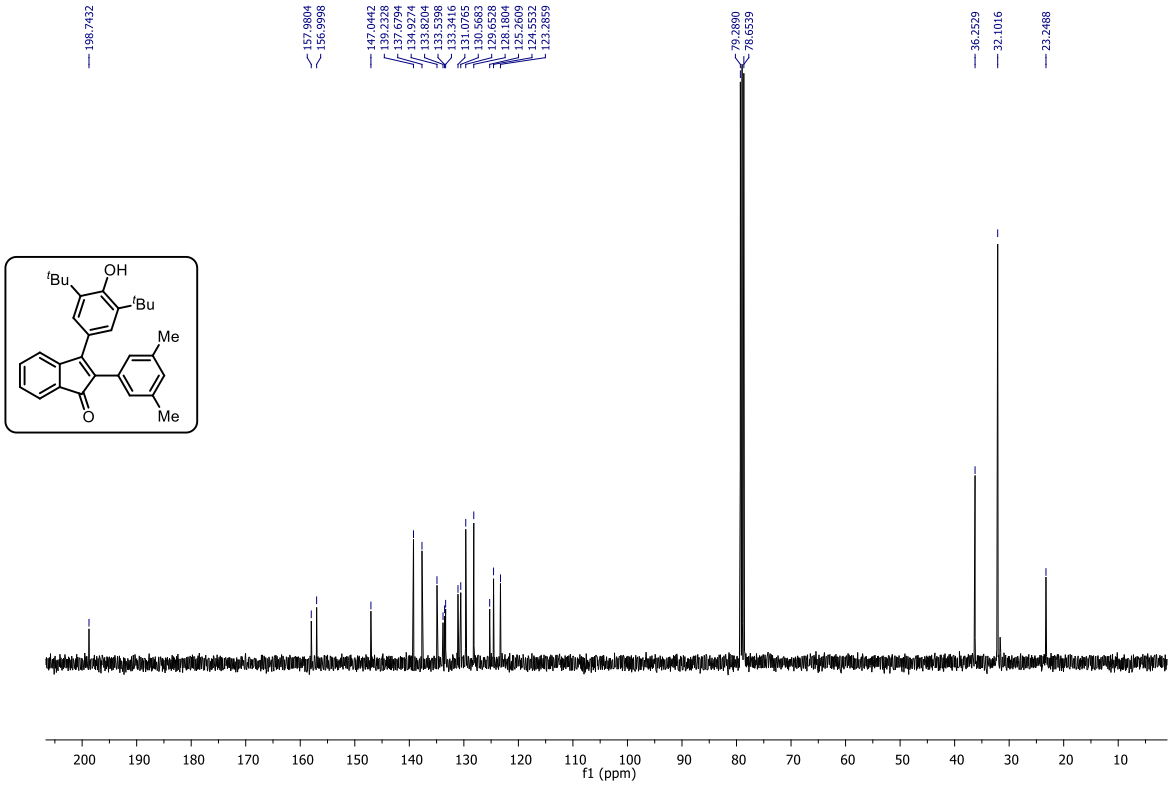
^{13}C{1H} NMR (100 MHz, $CDCl_3$) spectrum of **2f**



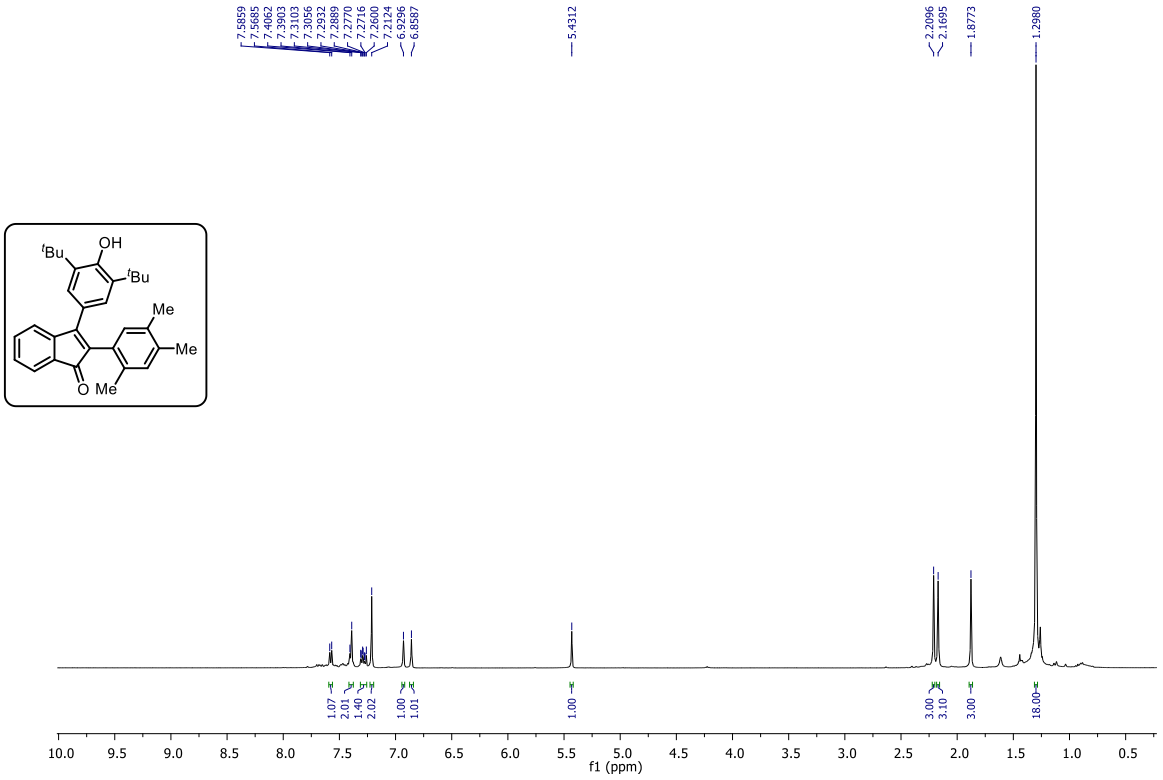
^{1}H NMR (400 MHz, $CDCl_3$) spectrum of **2g**



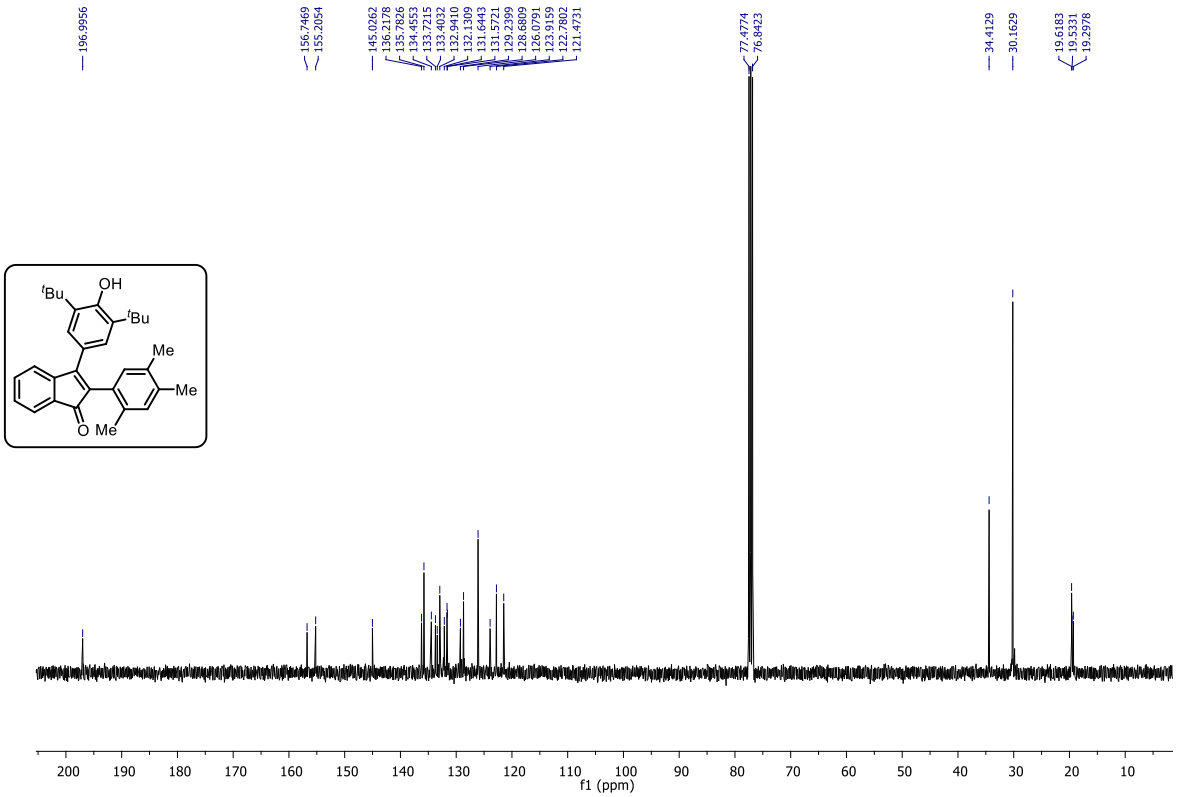
^{13}C{1H} NMR (100 MHz, $CDCl_3$) spectrum of **2g**



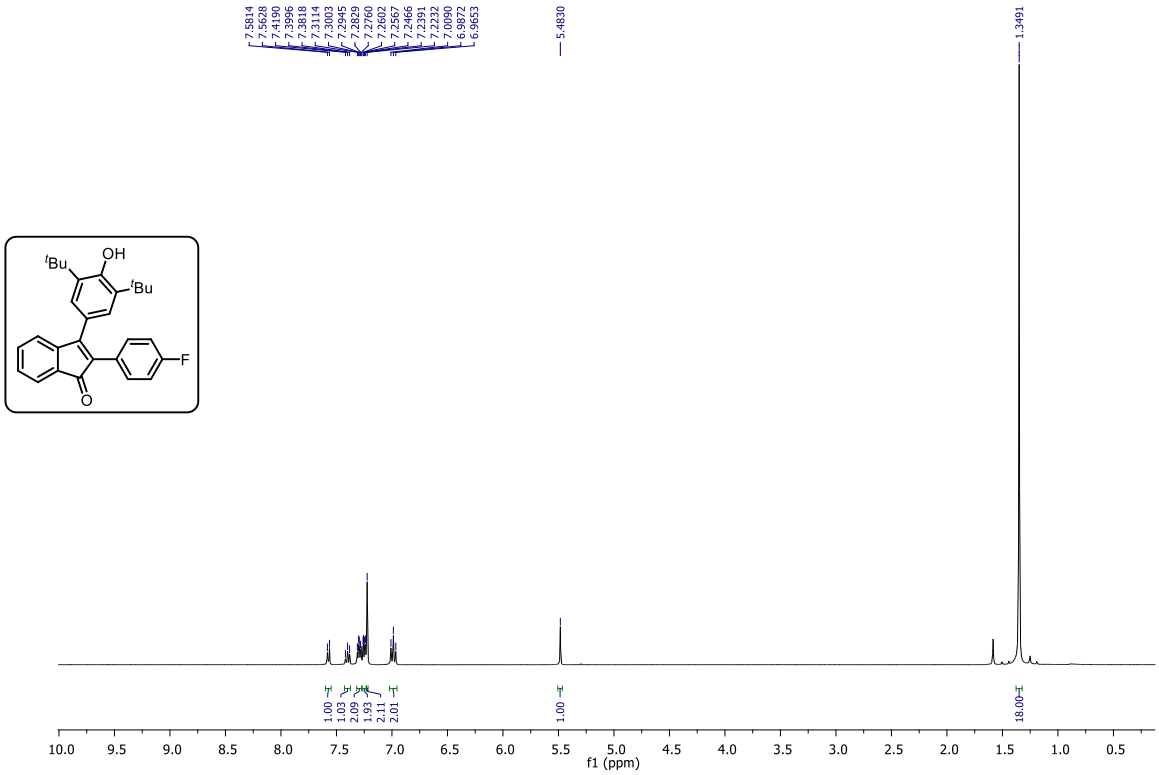
^{1}H NMR (400 MHz, $CDCl_3$) spectrum of **2h**



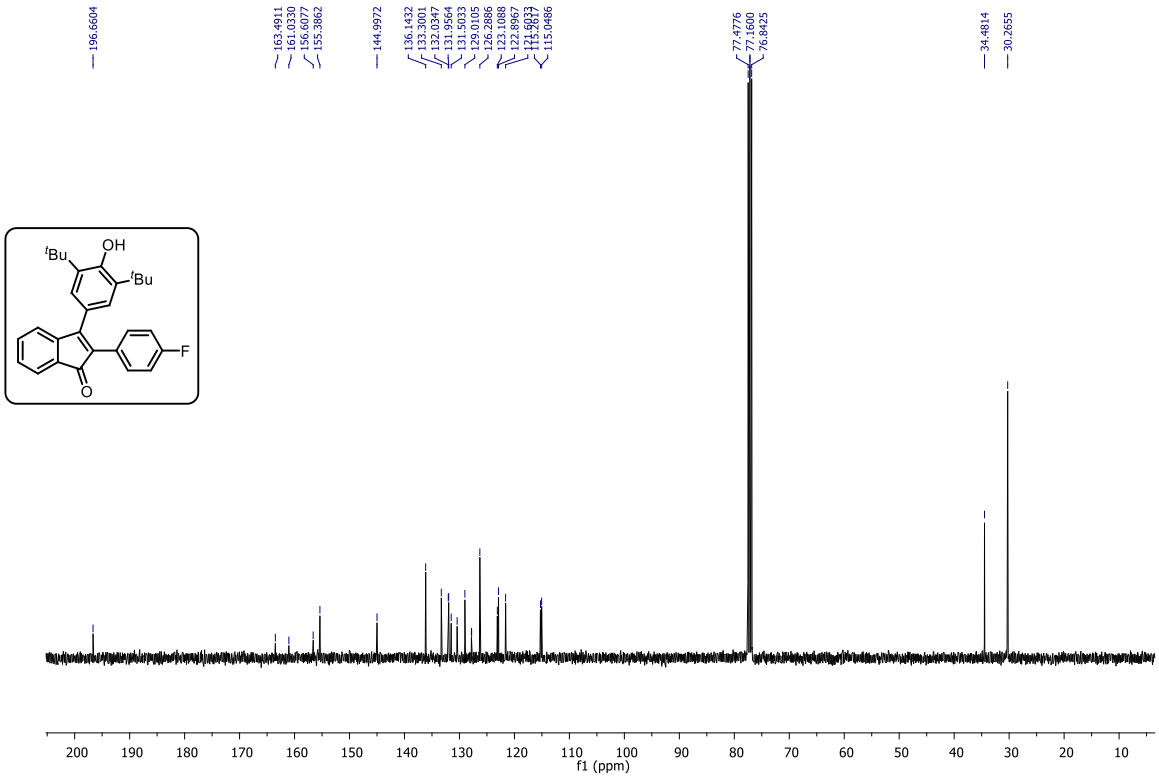
^{13}C{1H} NMR (100 MHz, $CDCl_3$) spectrum of **2h**



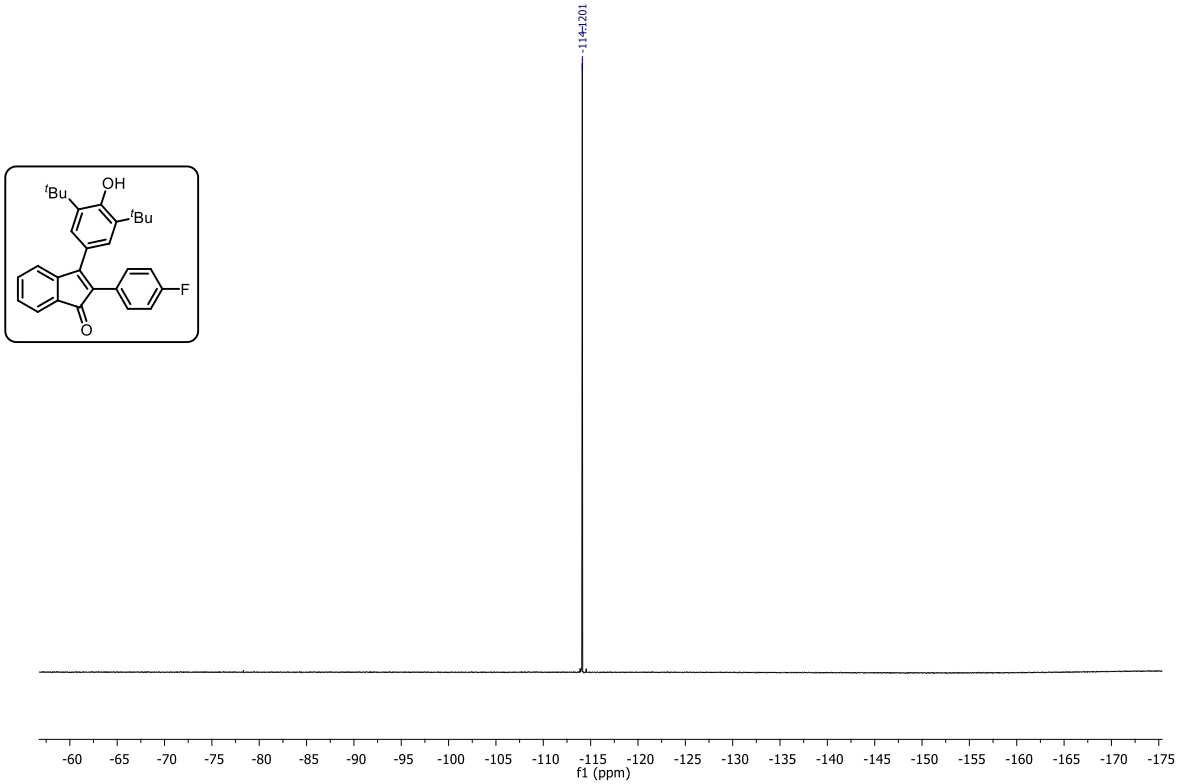
^{1}H NMR (400 MHz, $CDCl_3$) spectrum of **2i**



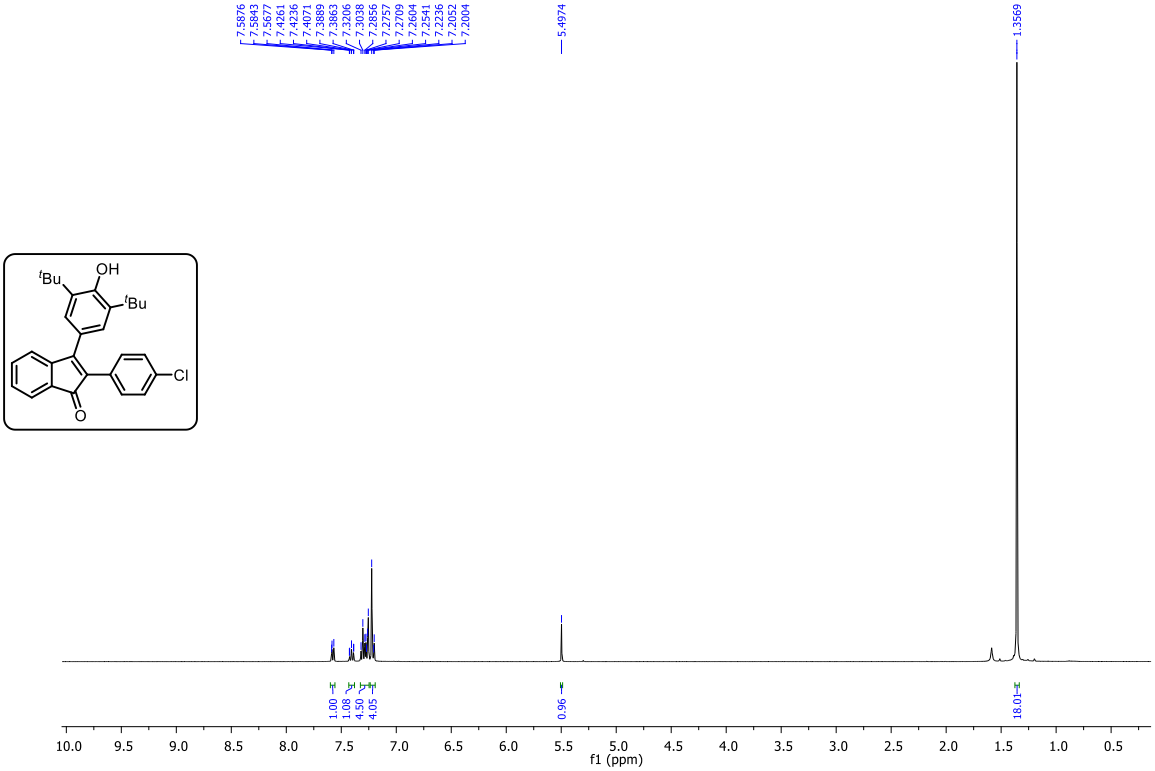
^{13}C{1H} NMR (100 MHz, $CDCl_3$) spectrum of **2i**



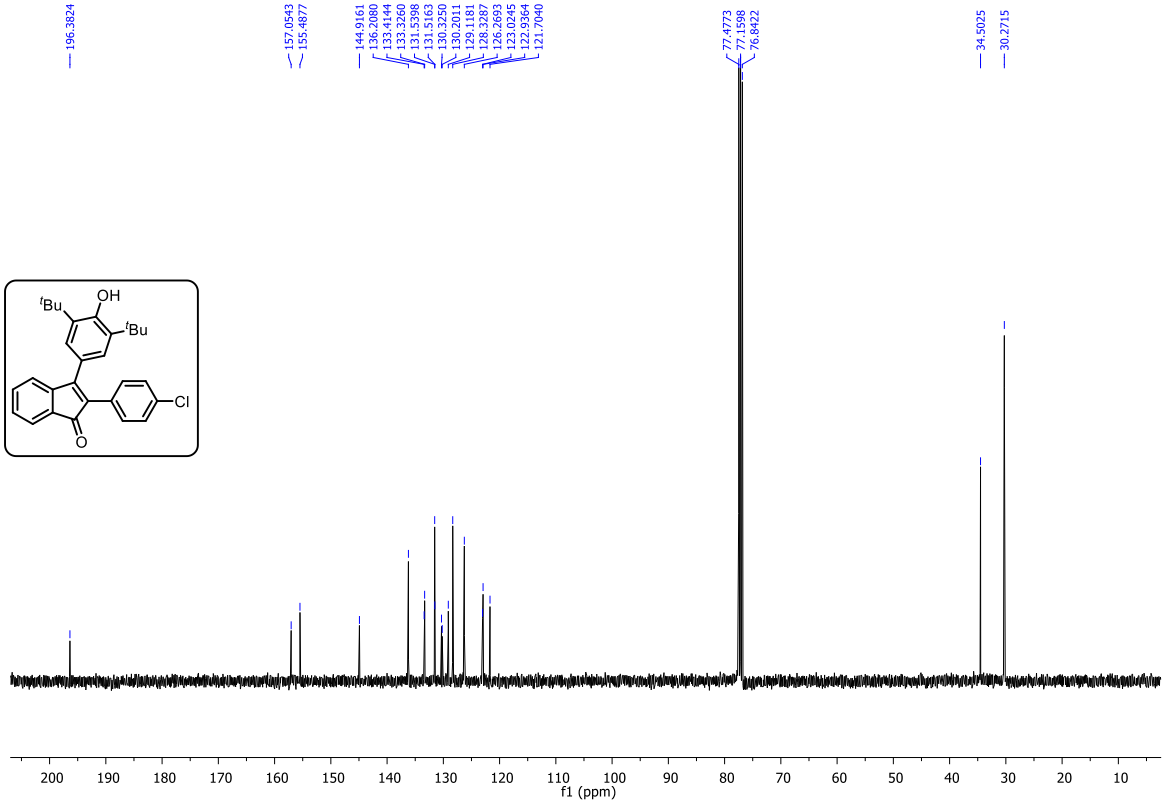
$^{19}F\{^{1}H\}$ NMR (376 MHz, $CDCl_3$) spectrum of **2i**



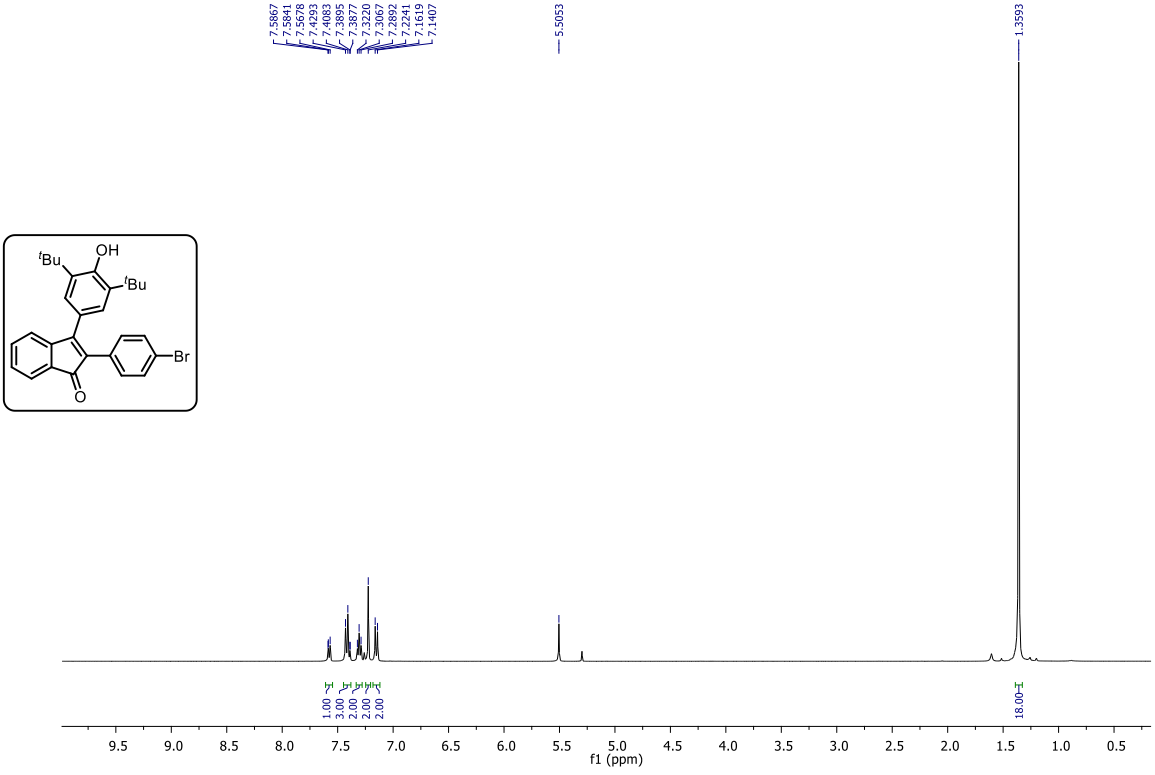
^{1}H NMR (400 MHz, $CDCl_3$) spectrum of **2j**



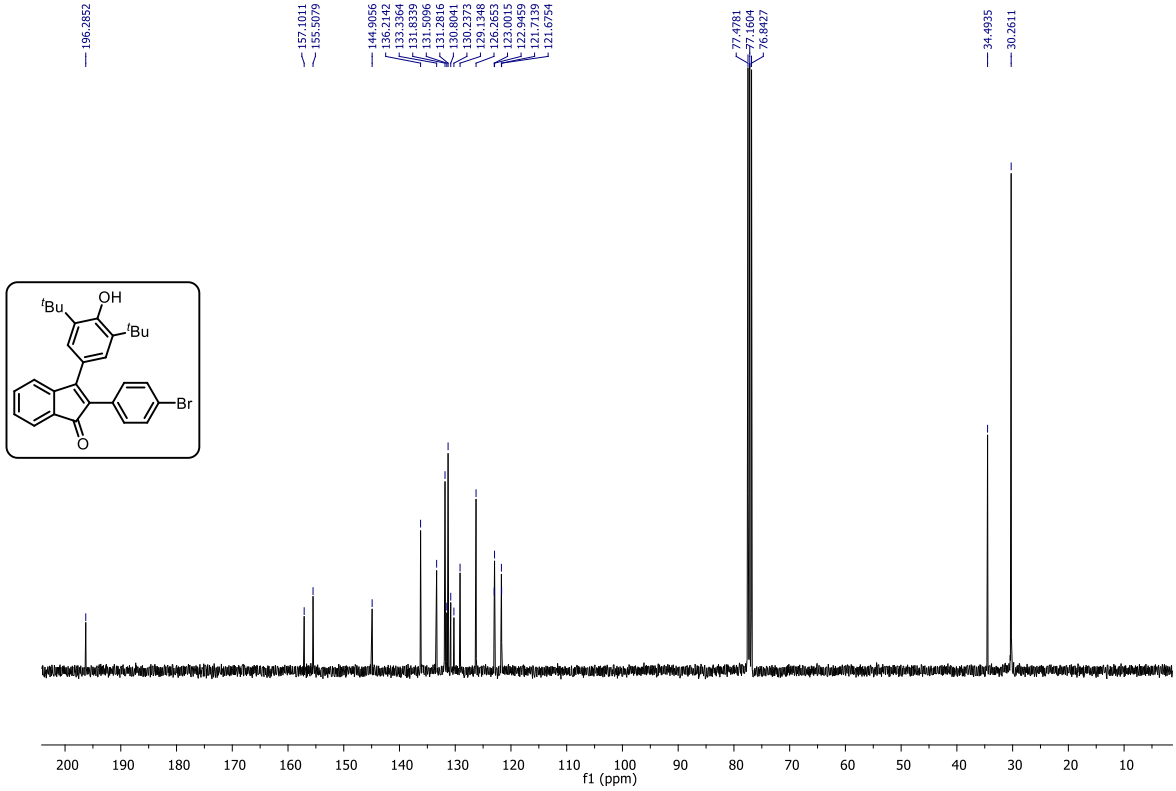
$^{13}C\{1H\}$ NMR (100 MHz, $CDCl_3$) spectrum of **2j**



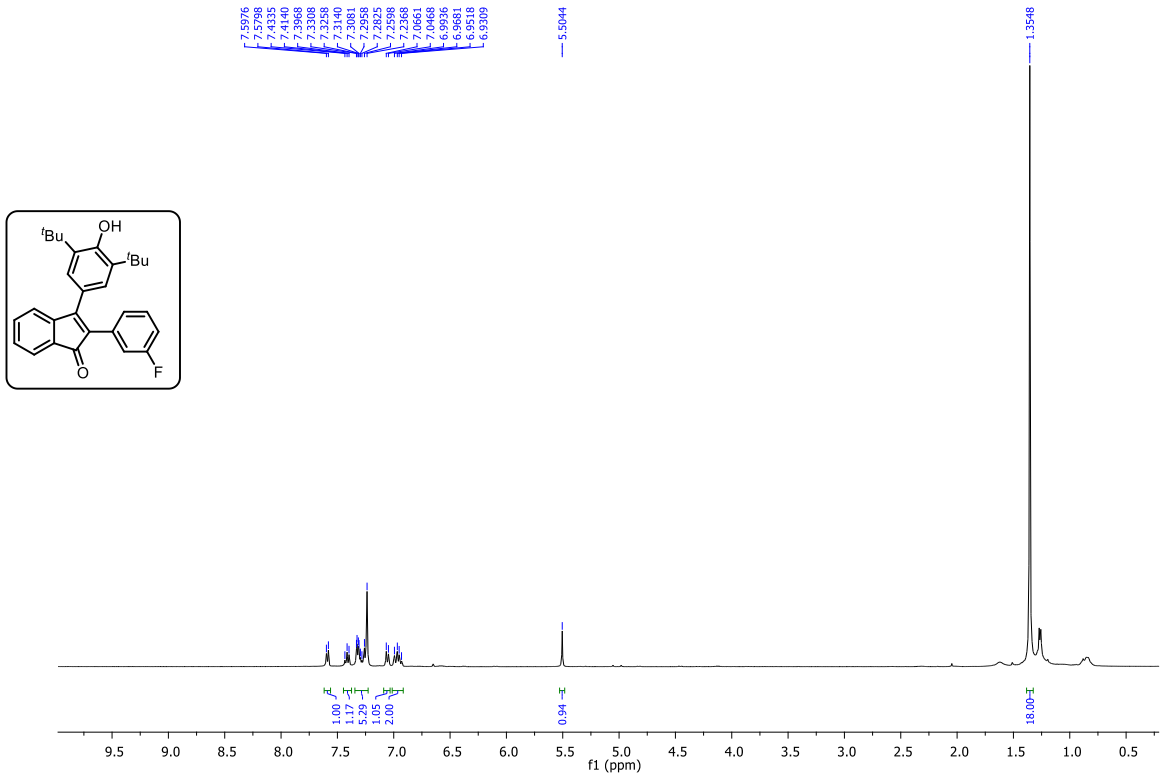
^{1}H NMR (400 MHz, $CDCl_3$) spectrum of **2k**



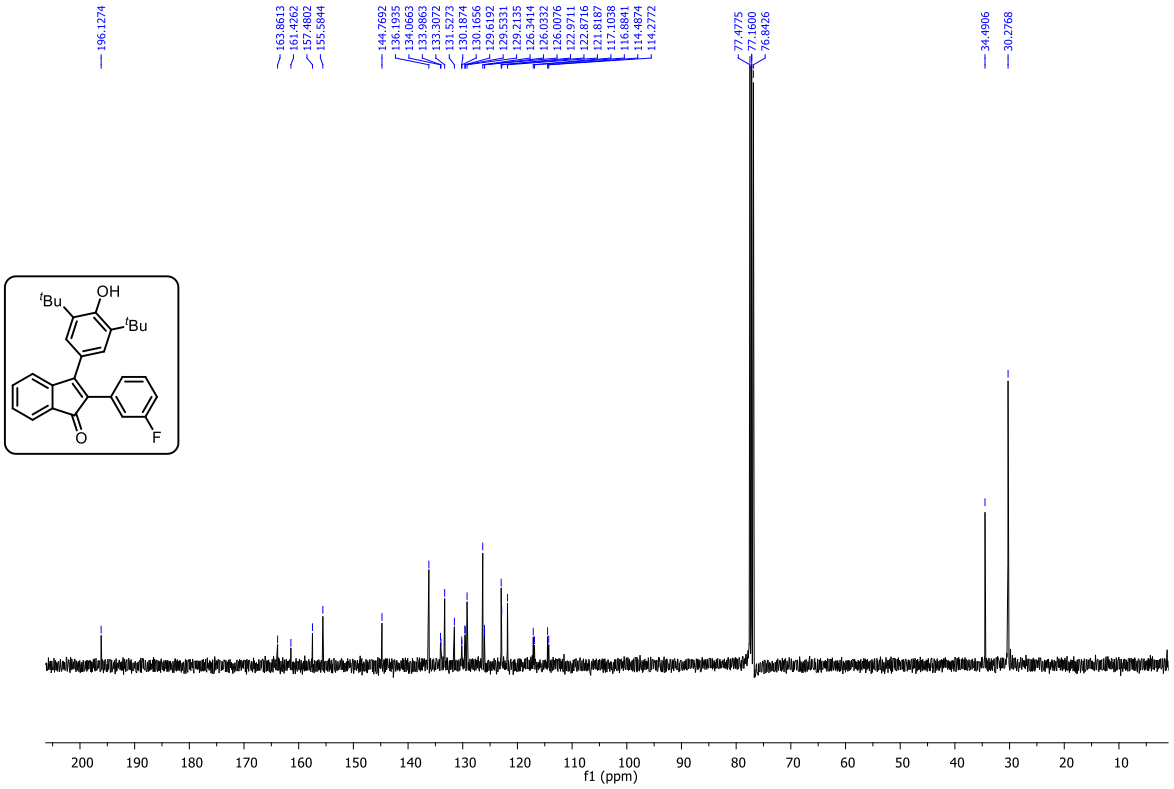
$^{13}C\{1H\}$ NMR (100 MHz, $CDCl_3$) spectrum of **2k**



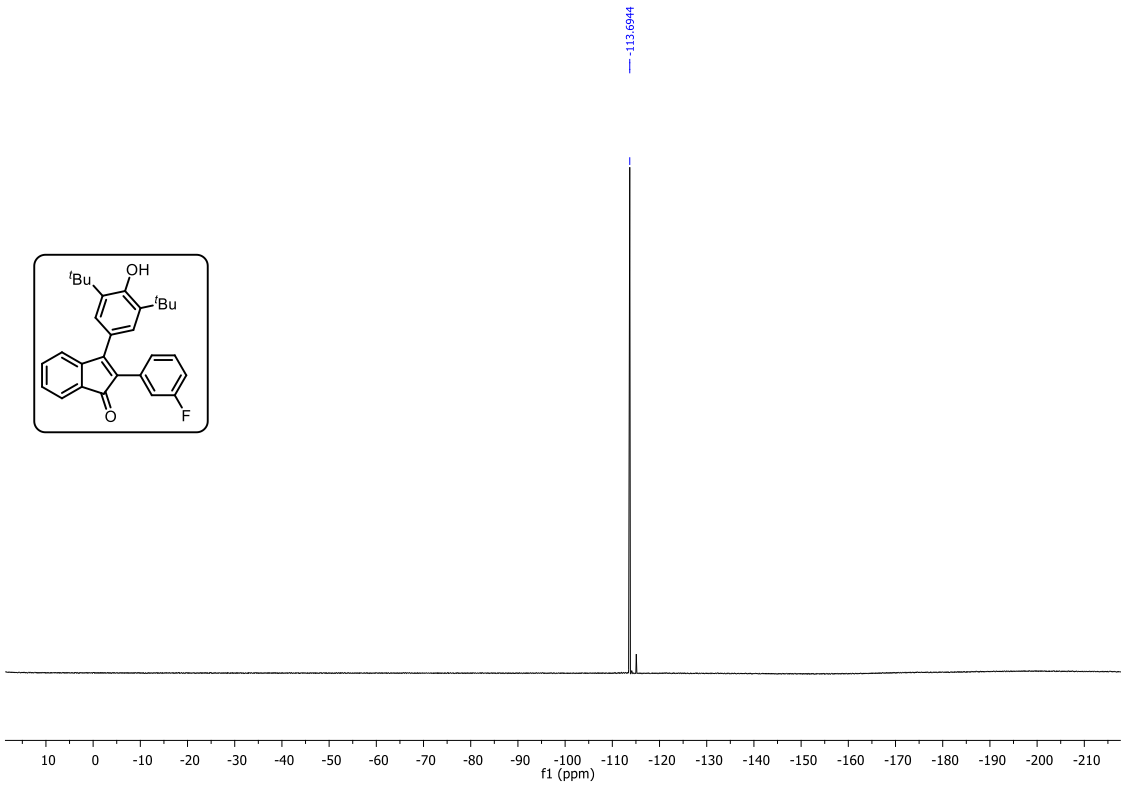
^{1}H NMR (400 MHz, $CDCl_3$) spectrum of **2l**



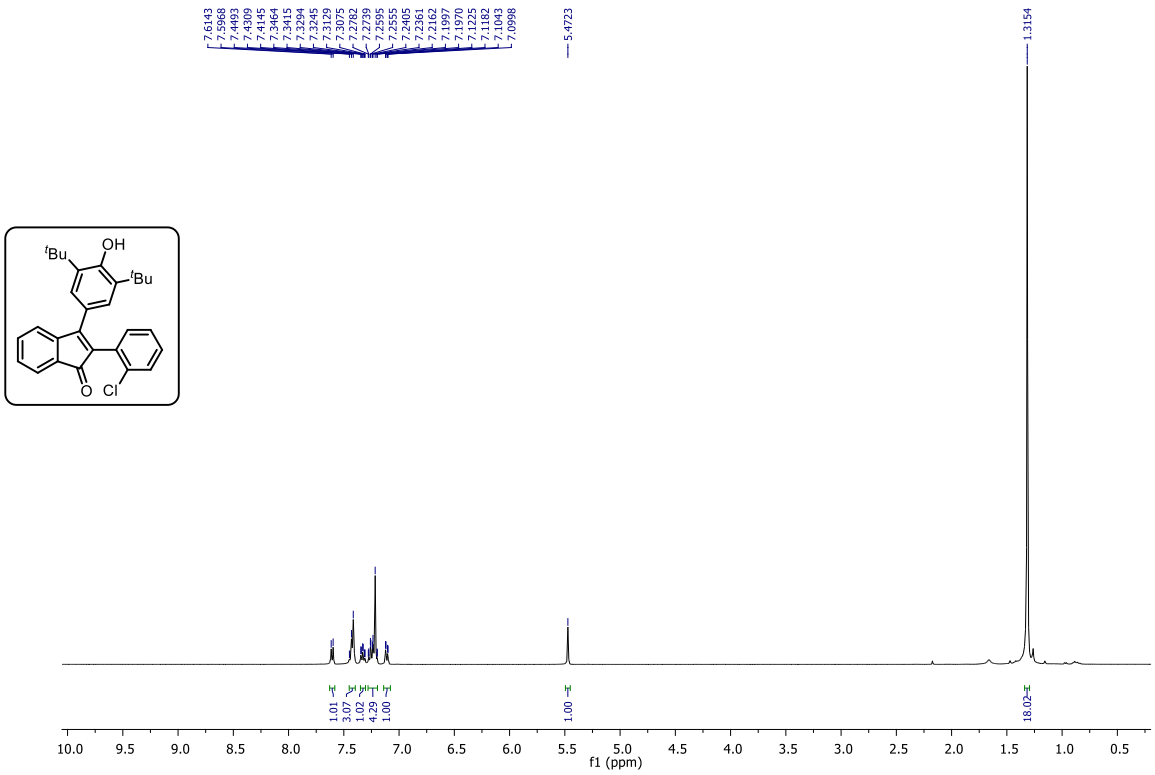
$^{13}C\{1H\}$ NMR (100 MHz, $CDCl_3$) spectrum of **2l**



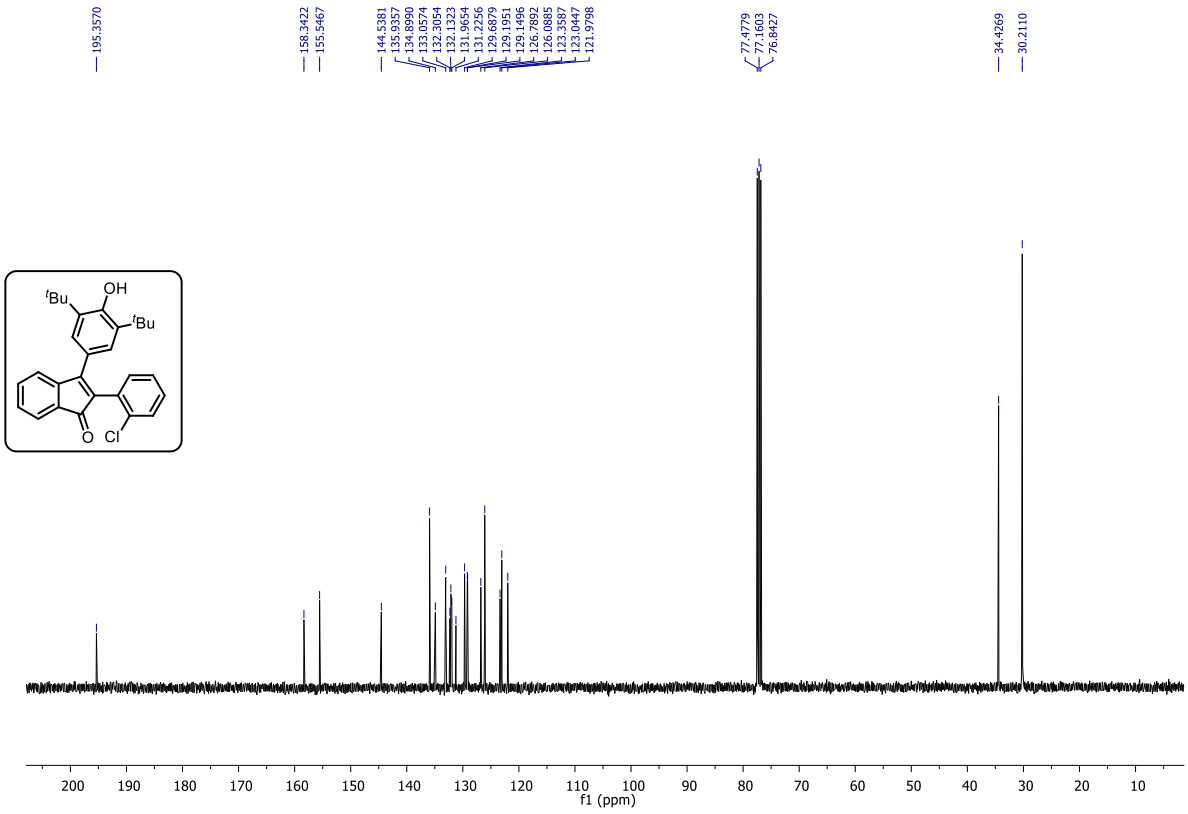
$^{19}F\{^{1}H\}$ NMR (376 MHz, $CDCl_3$) spectrum of **2l**



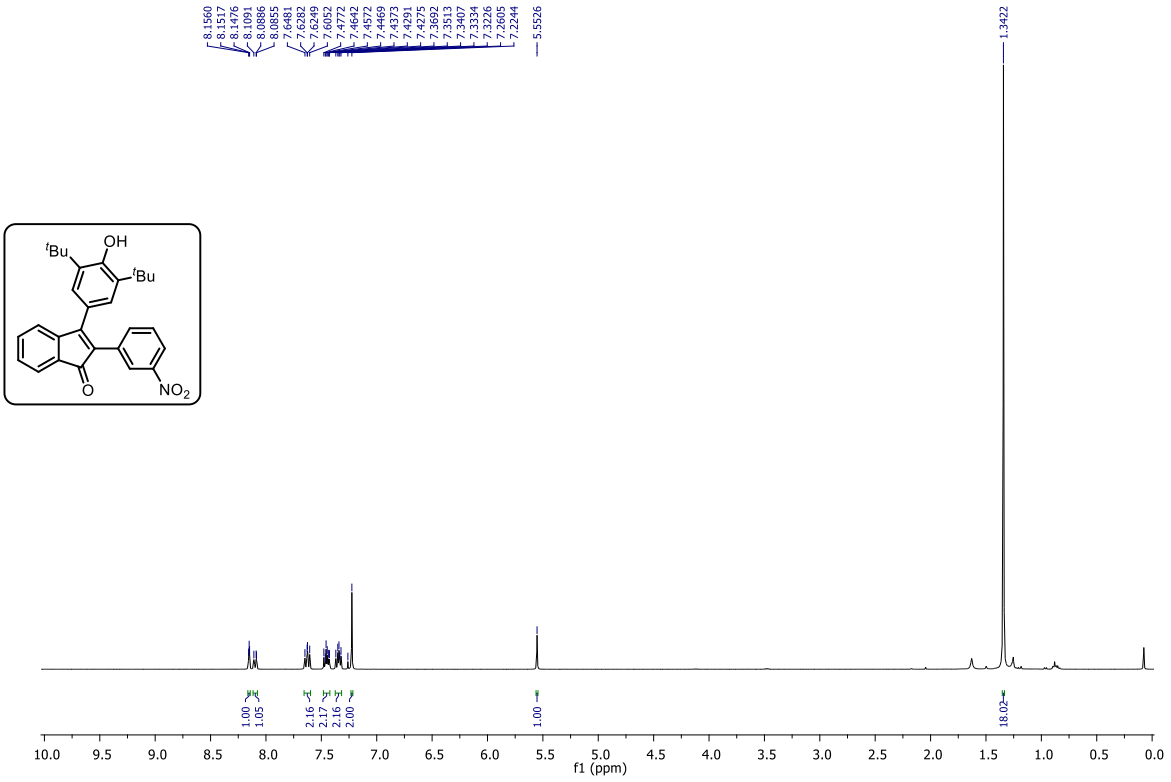
^{1}H NMR (400 MHz, $CDCl_3$) spectrum of **2m**



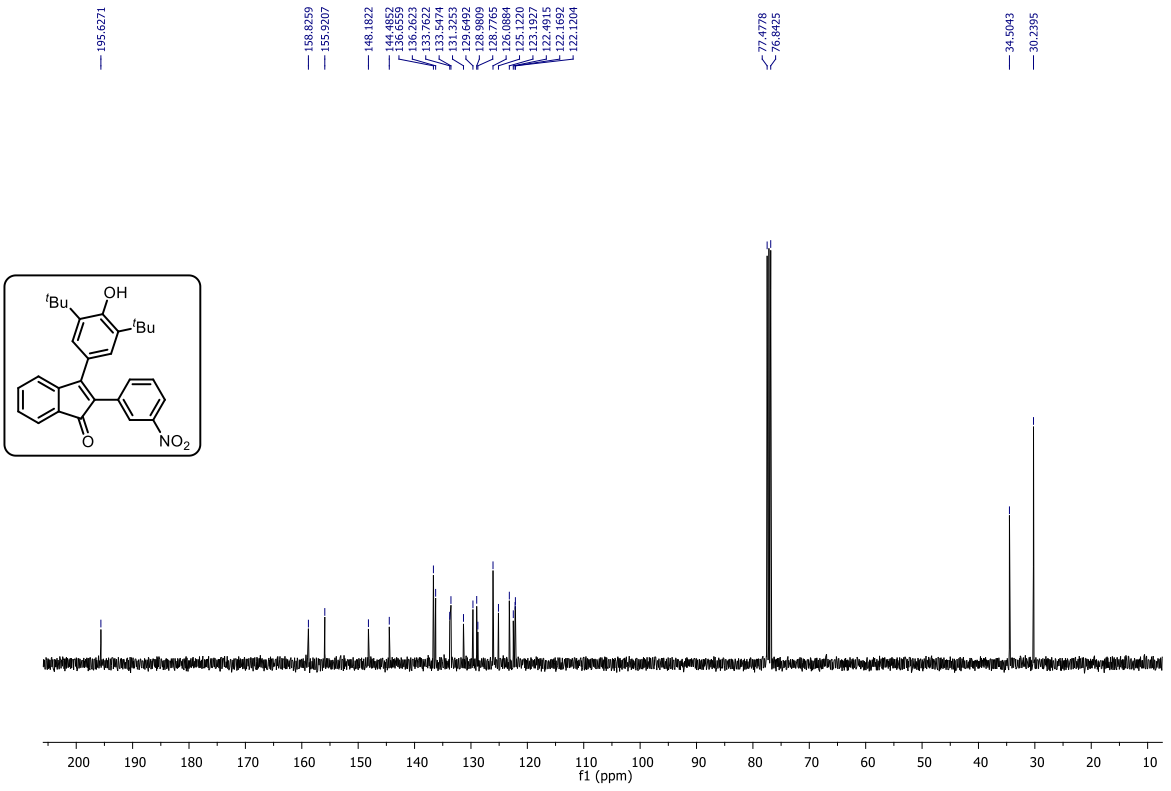
^{13}C{1H} NMR (100 MHz, $CDCl_3$) spectrum of **2m**



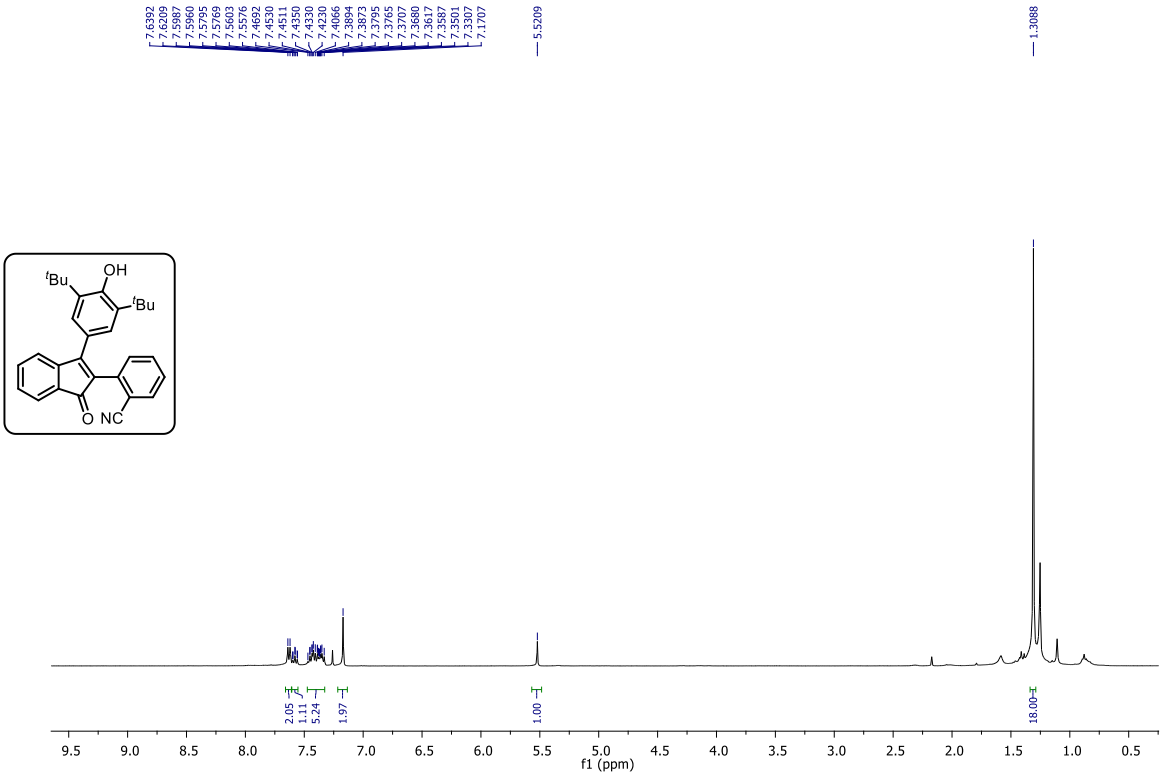
^{1}H NMR (400 MHz, $CDCl_3$) spectrum of **2n**



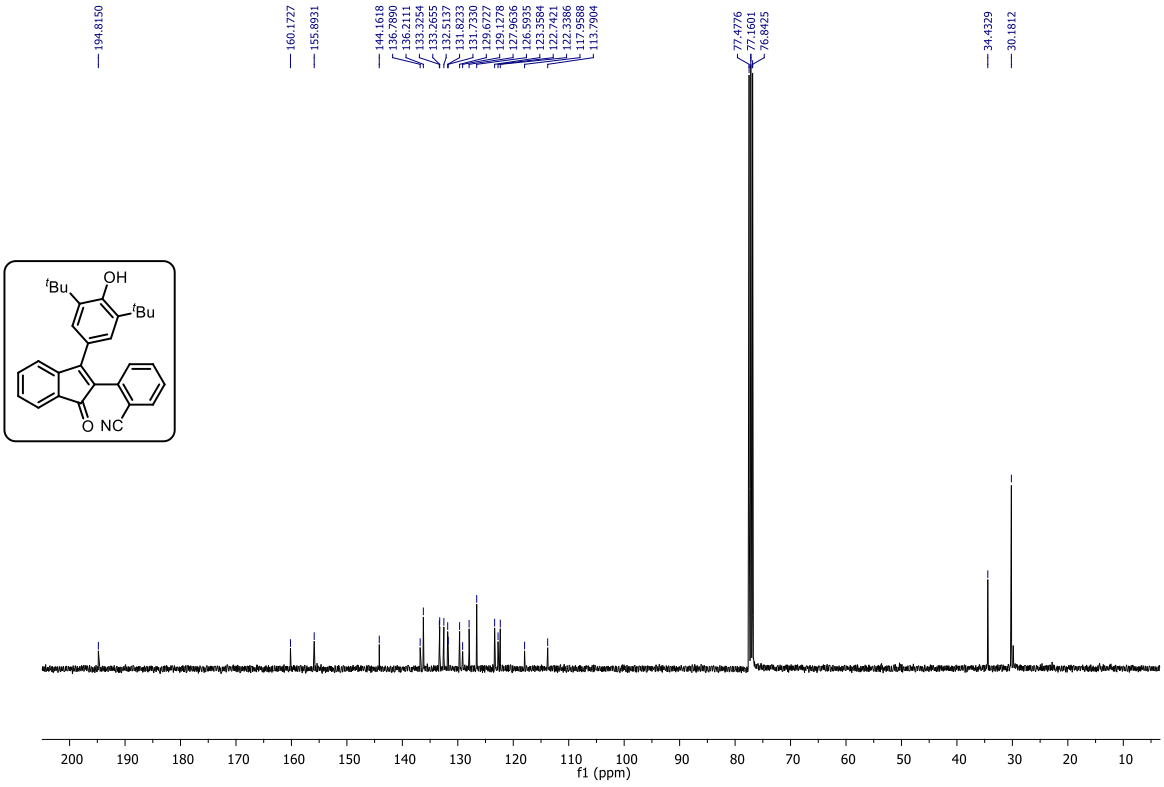
^{13}C{1H} NMR (100 MHz, $CDCl_3$) spectrum of **2n**



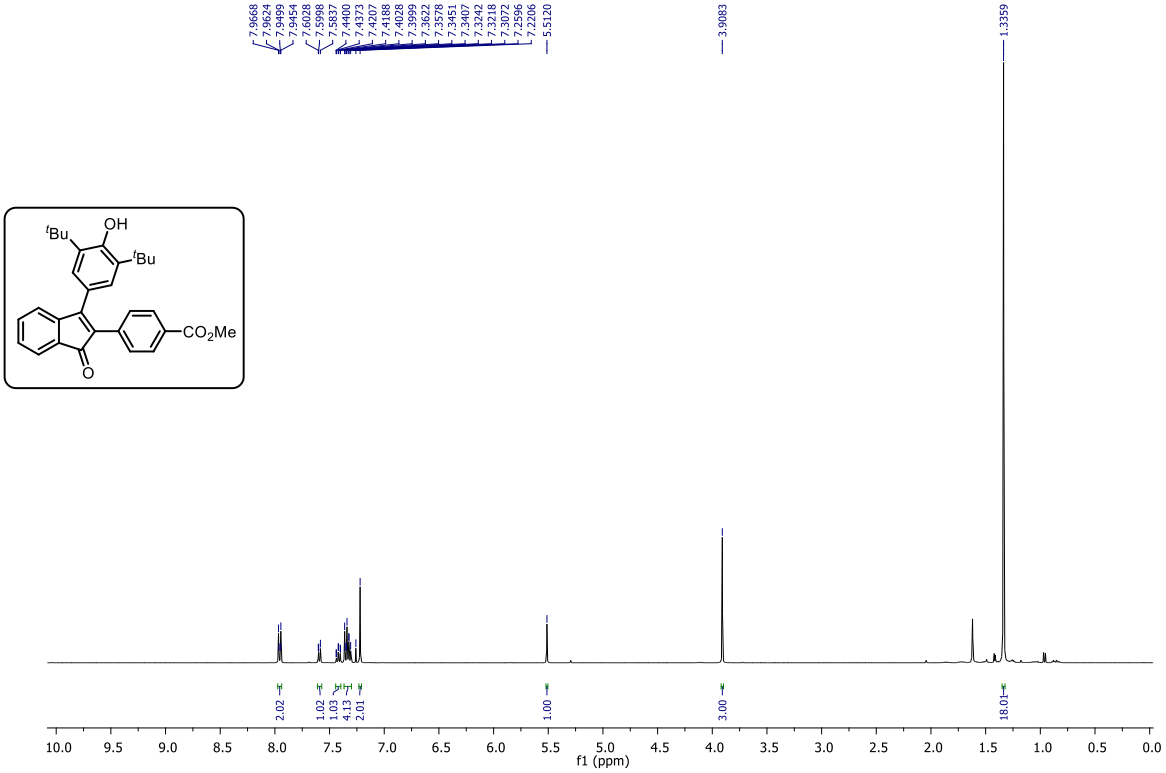
^{1}H NMR (400 MHz, $CDCl_3$) spectrum of **2o**



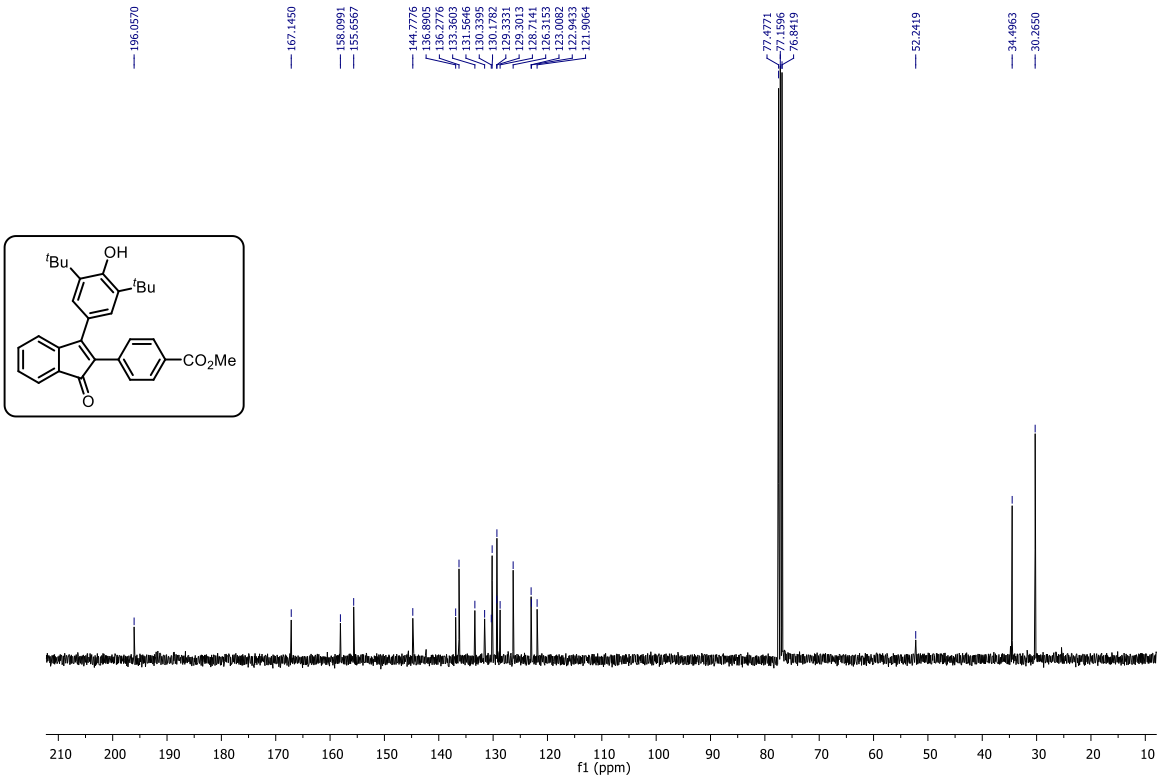
^{13}C{1H} NMR (100 MHz, $CDCl_3$) spectrum of **2o**



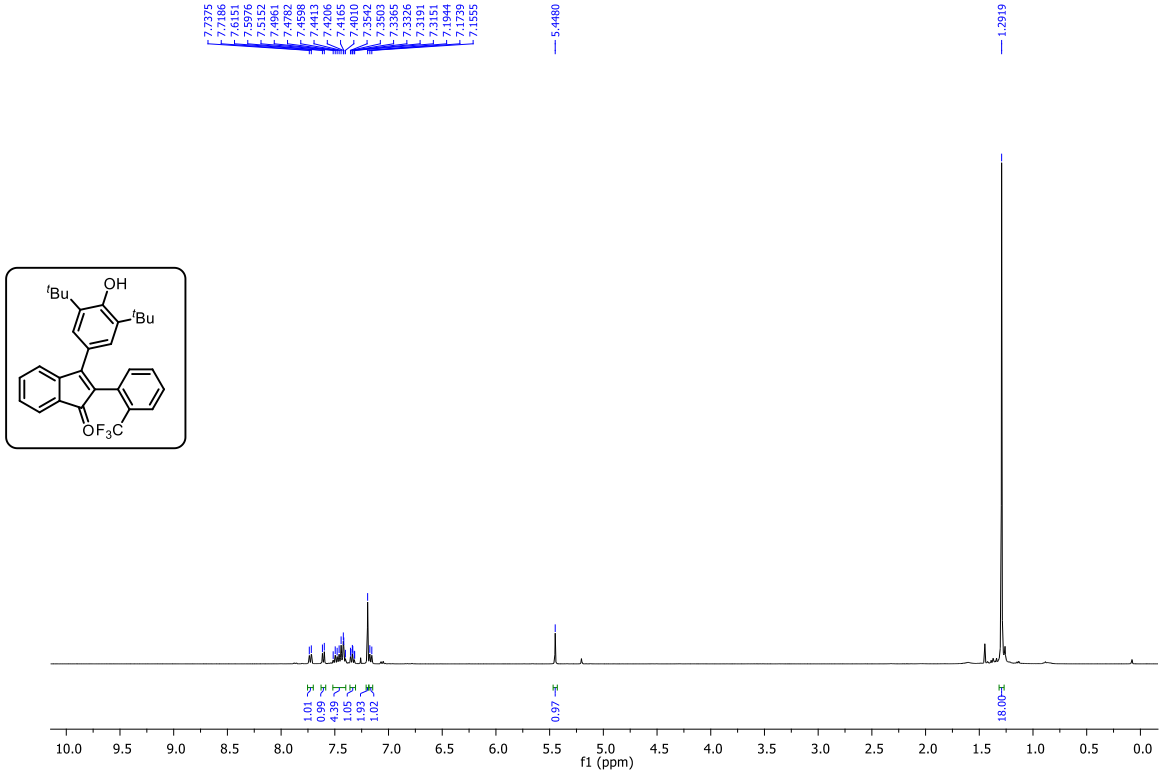
^{1}H NMR (400 MHz, $CDCl_3$) spectrum of **2p**



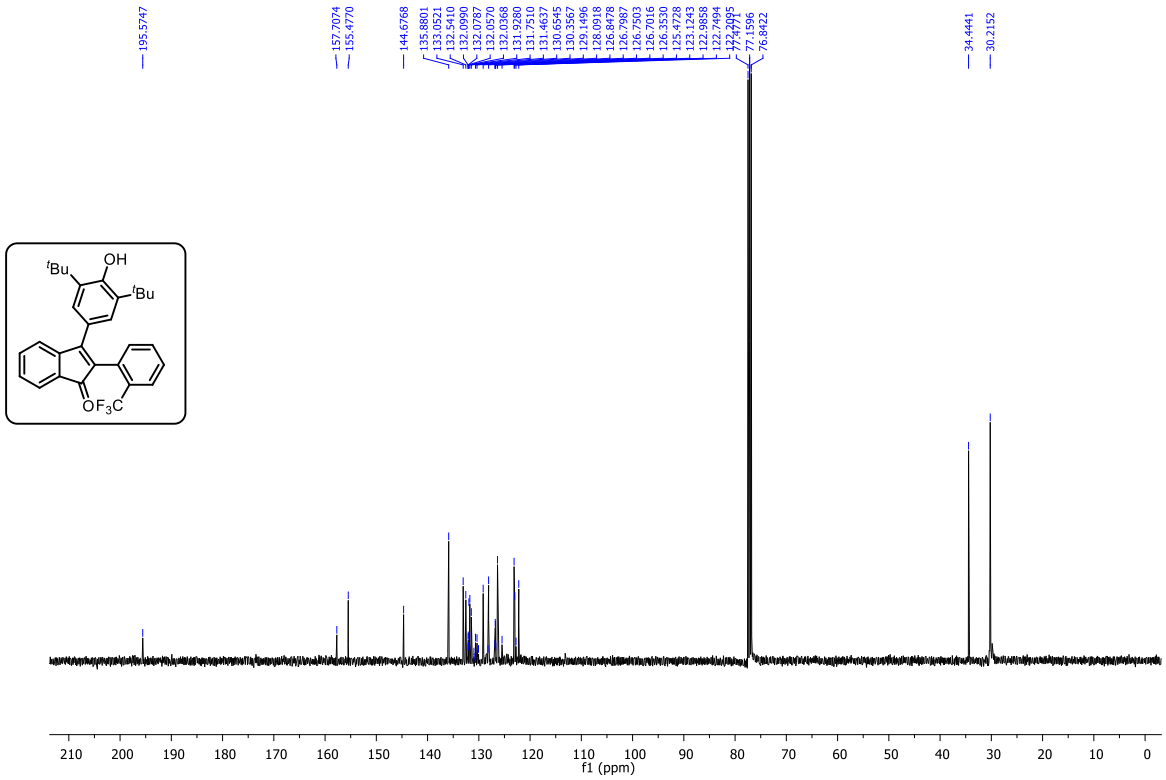
^{13}C{1H} NMR (100 MHz, $CDCl_3$) spectrum of **2p**



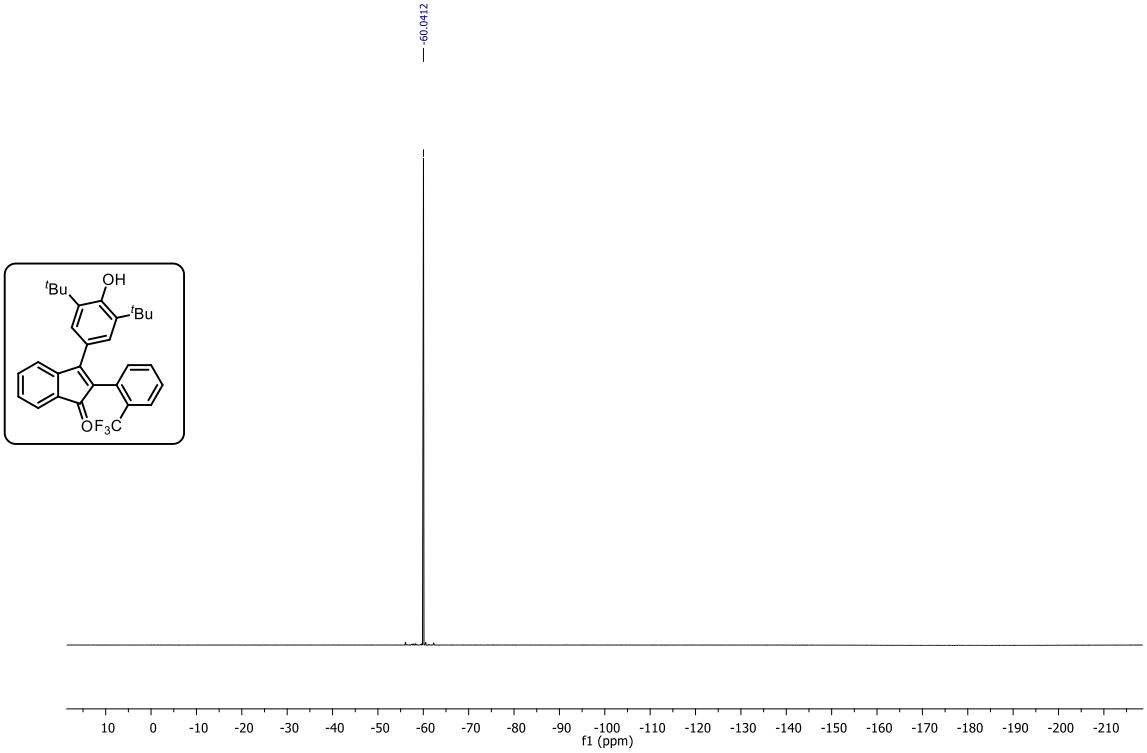
^{1}H NMR (400 MHz, $CDCl_3$) spectrum of **2q**



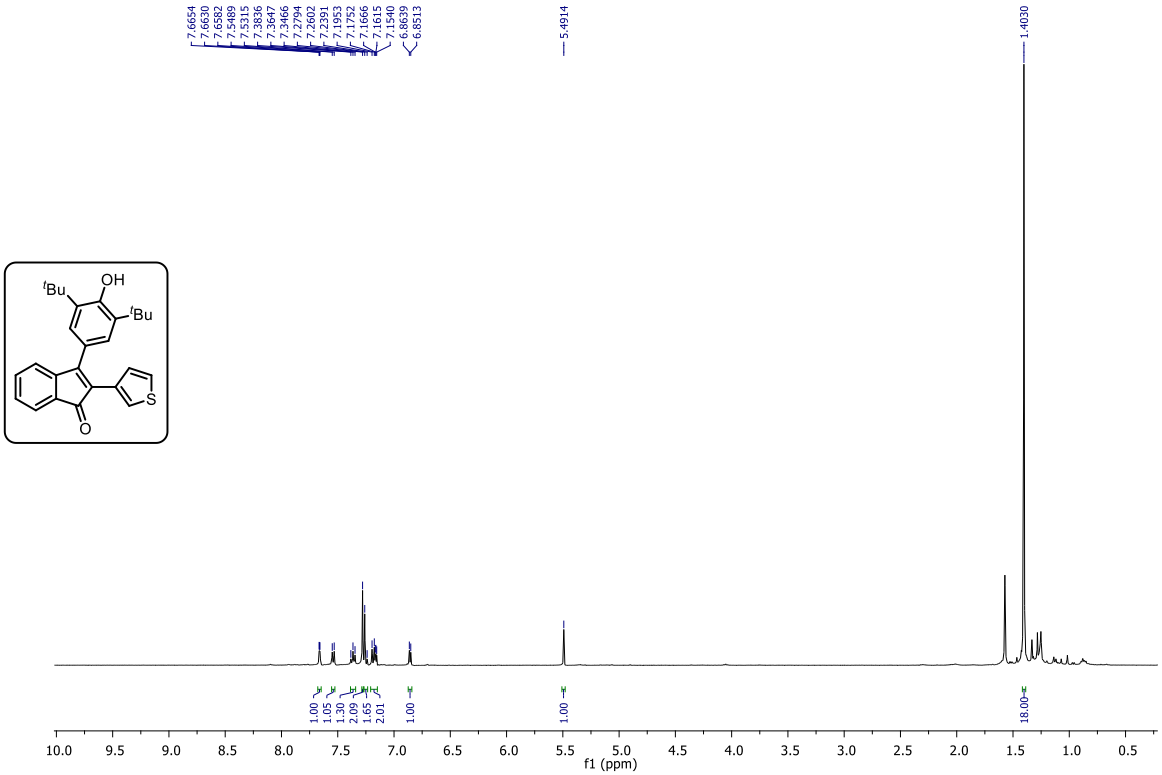
^{13}C{1H} NMR (100 MHz, $CDCl_3$) spectrum of **2q**



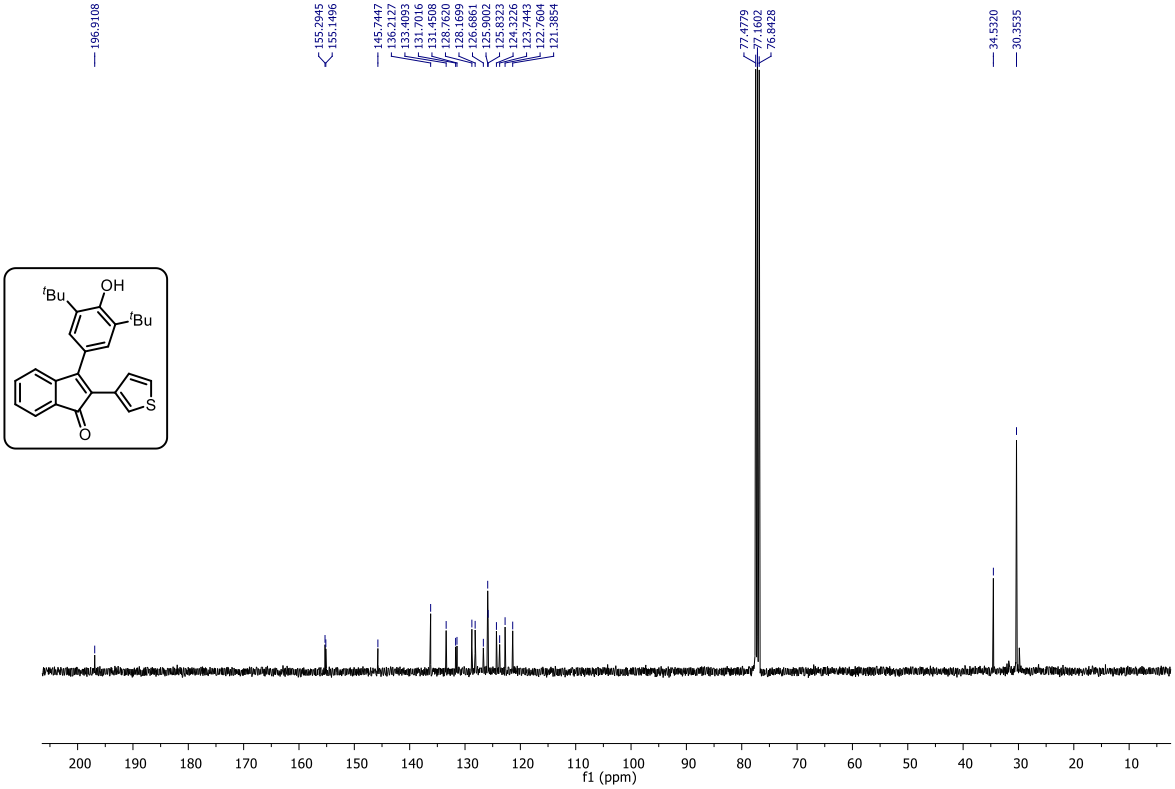
$^{19}F\{^{1}H\}$ NMR (376 MHz, $CDCl_3$) spectrum of **2q**



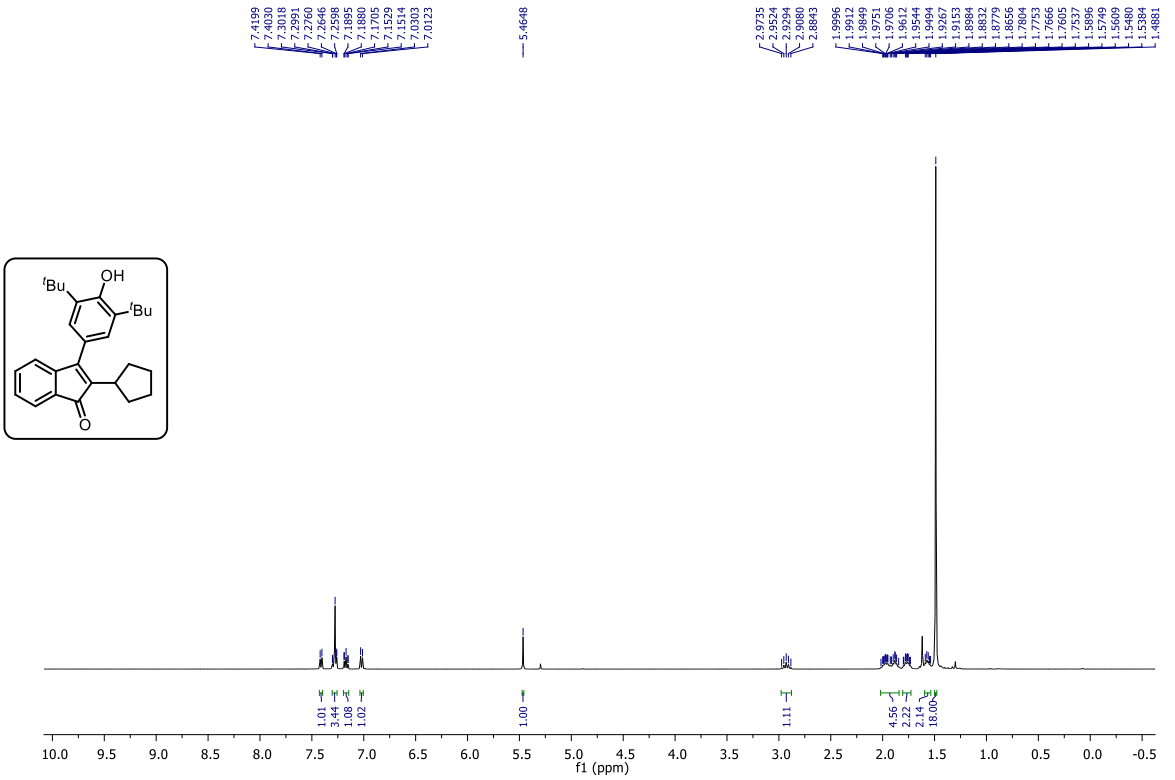
^{1}H NMR (400 MHz, $CDCl_3$) spectrum of **2r**



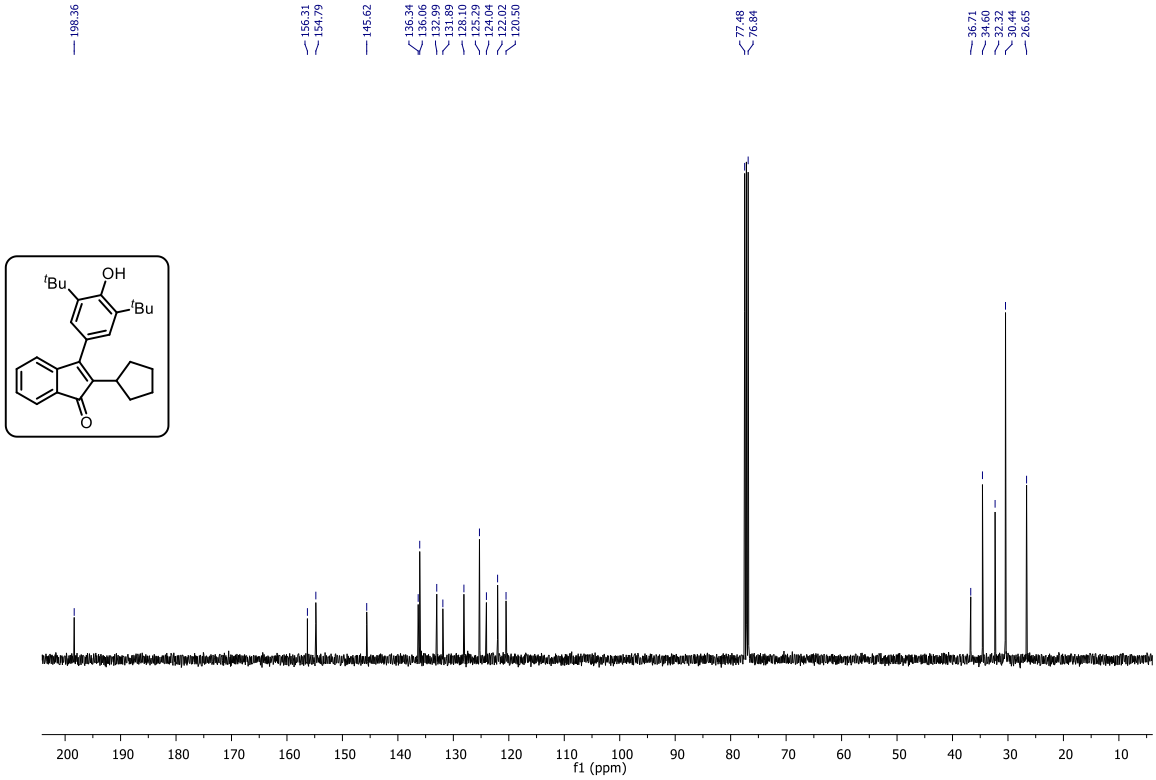
$^{13}C\{1H\}$ NMR (100 MHz, $CDCl_3$) spectrum of **2r**



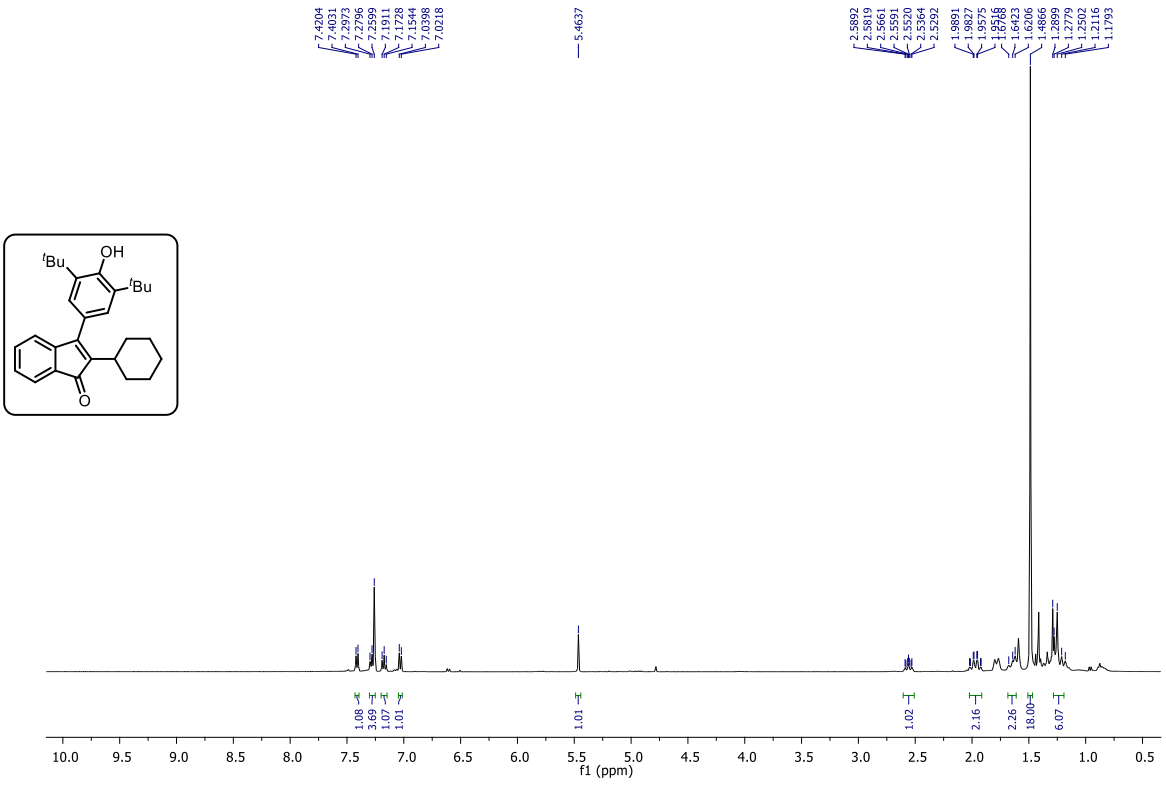
^{1}H NMR (400 MHz, $CDCl_3$) spectrum of **2s**



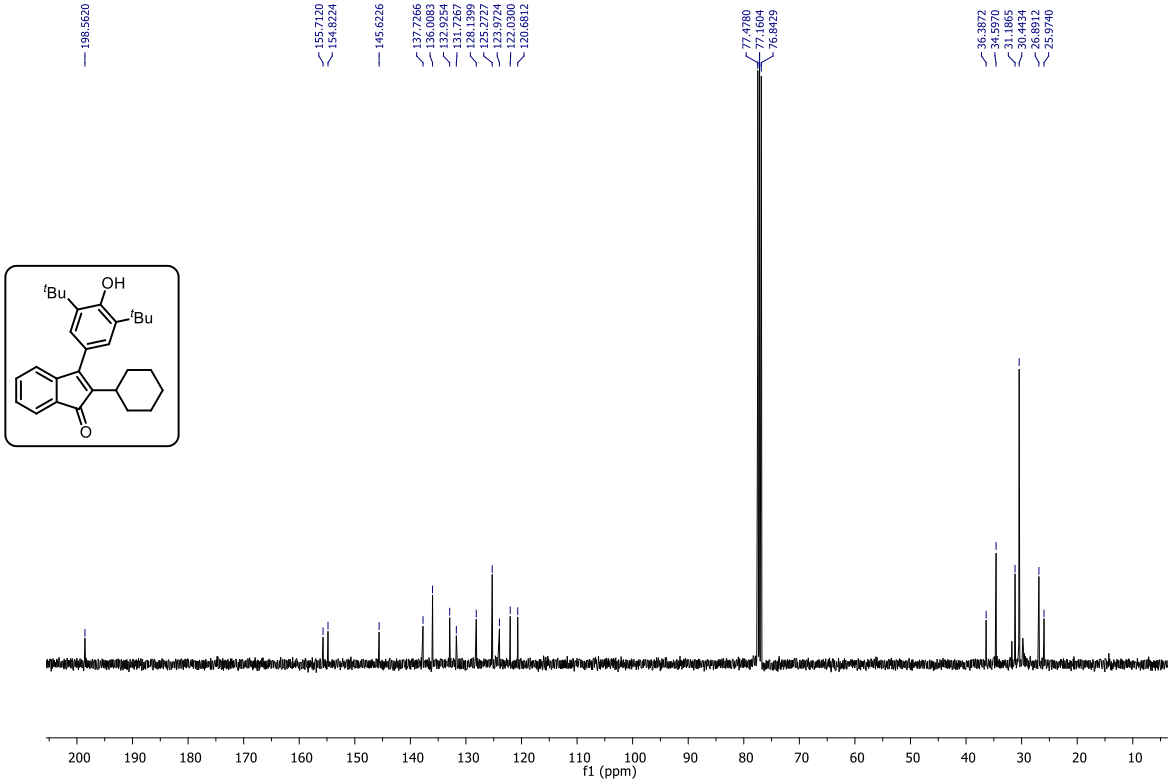
$^{13}C\{1H\}$ NMR (100 MHz, $CDCl_3$) spectrum of **2s**



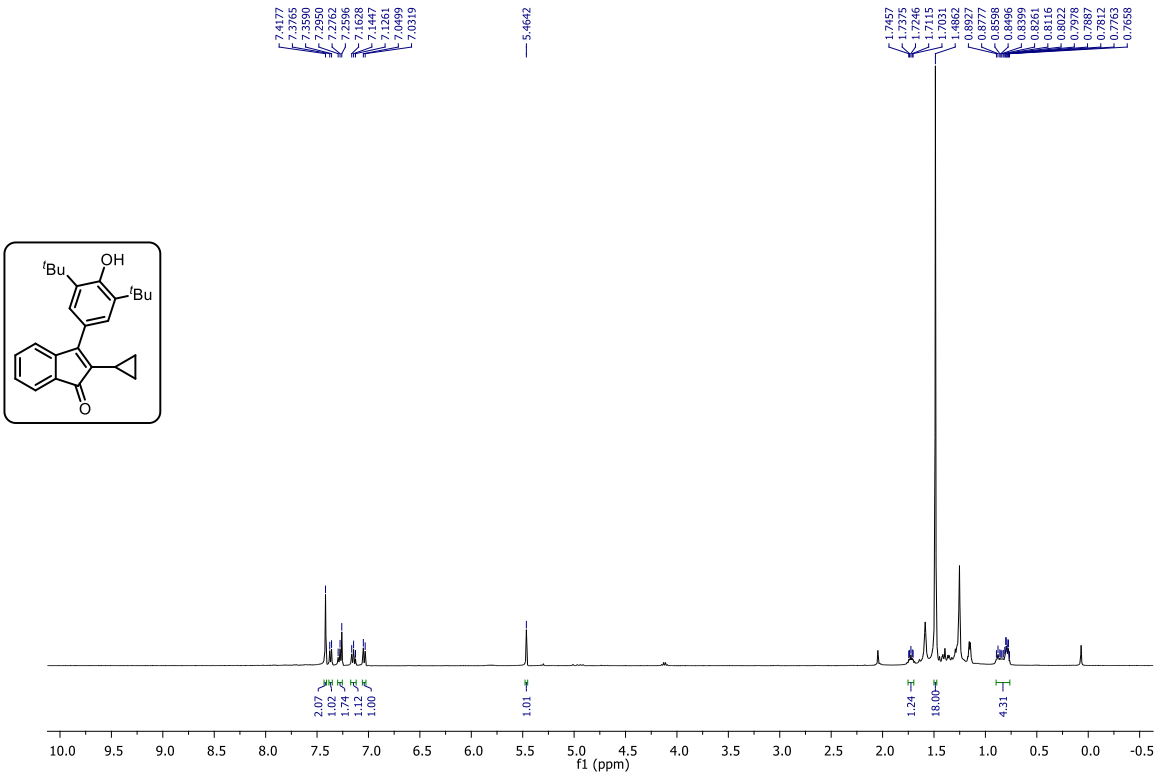
^{1}H NMR (400 MHz, $CDCl_3$) spectrum of **2t**



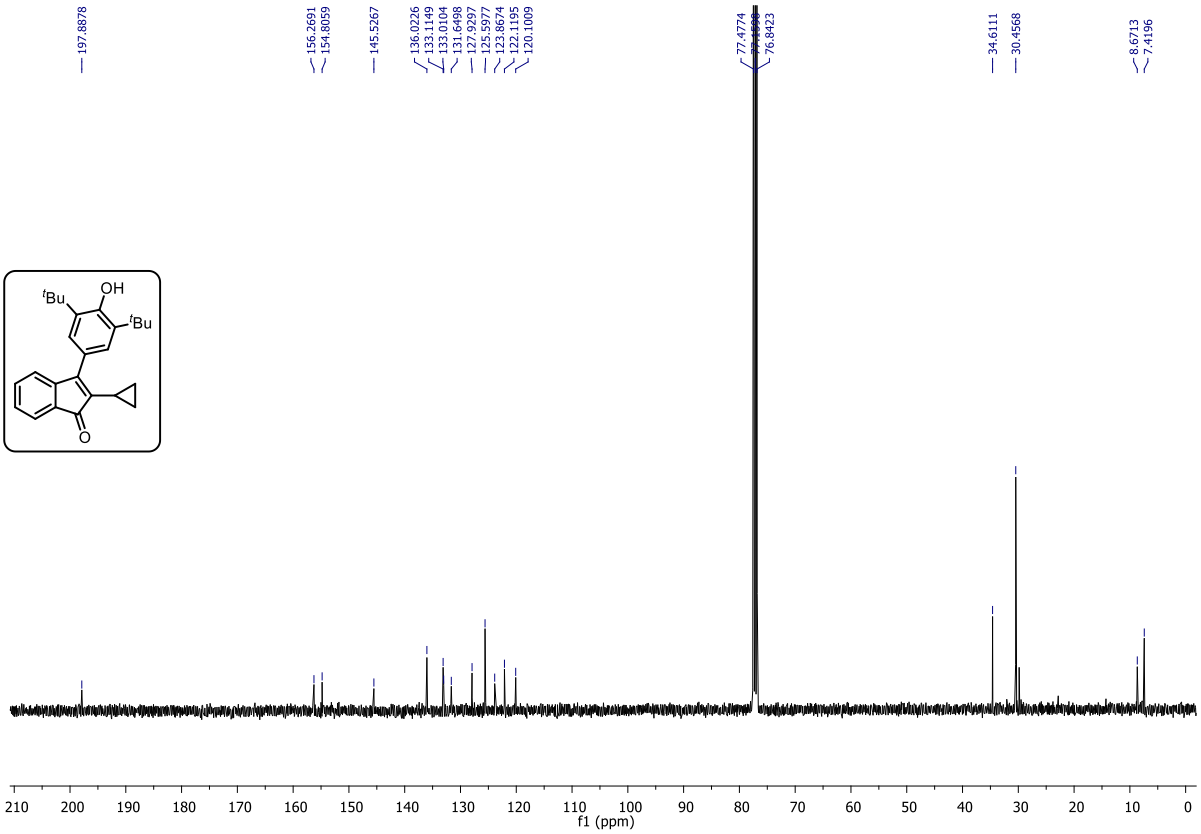
$^{13}C\{1H\}$ NMR (100 MHz, $CDCl_3$) spectrum of **2t**



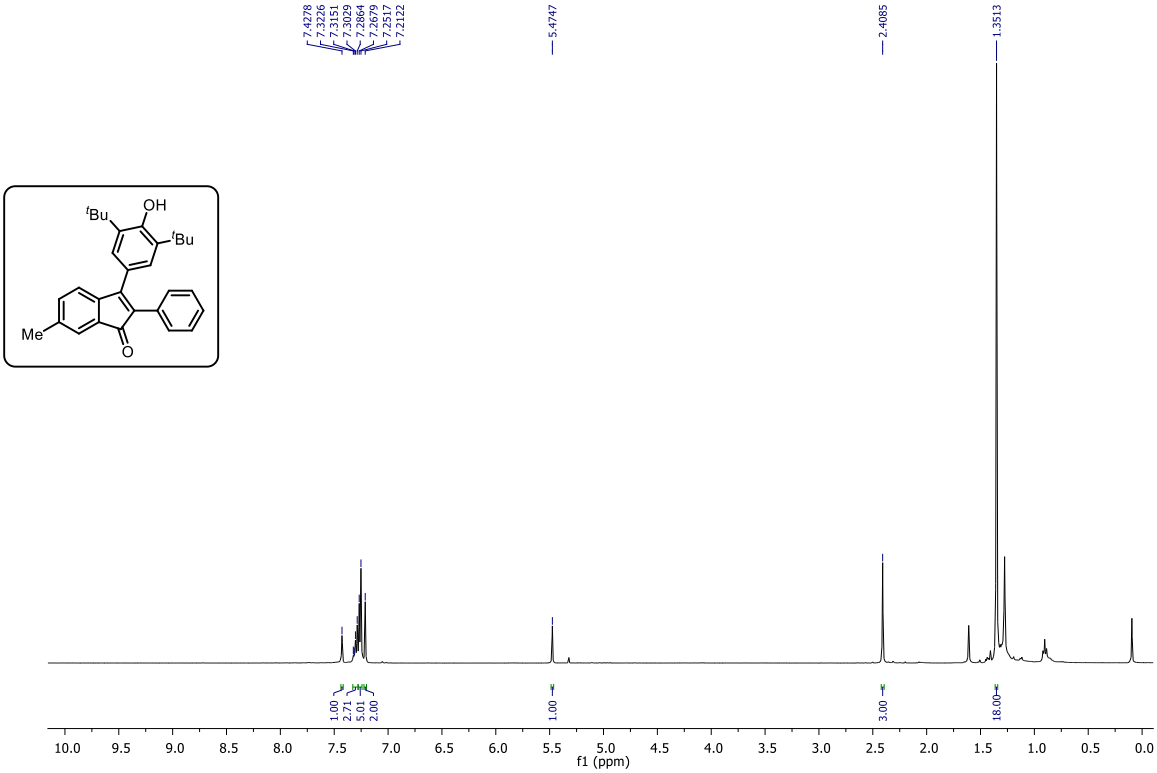
^{1}H NMR (400 MHz, $CDCl_3$) spectrum of **2u**



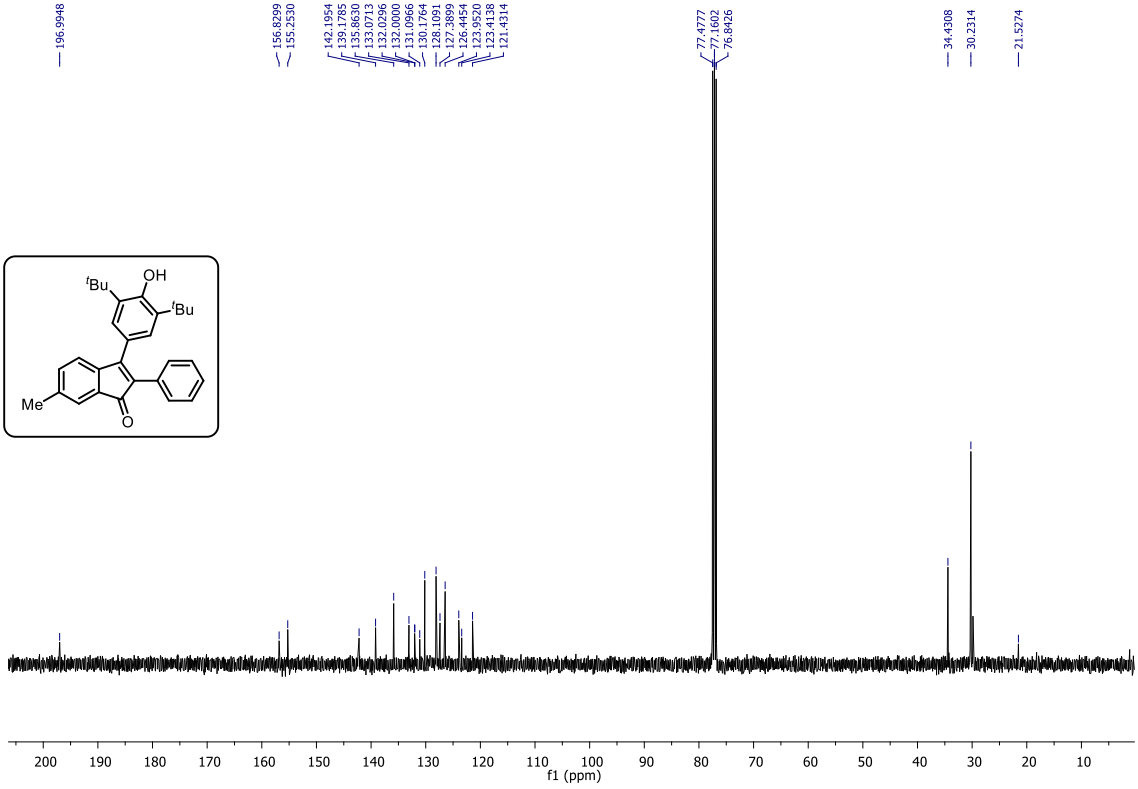
$^{13}C\{1H\}$ NMR (100 MHz, $CDCl_3$) spectrum of **2u**



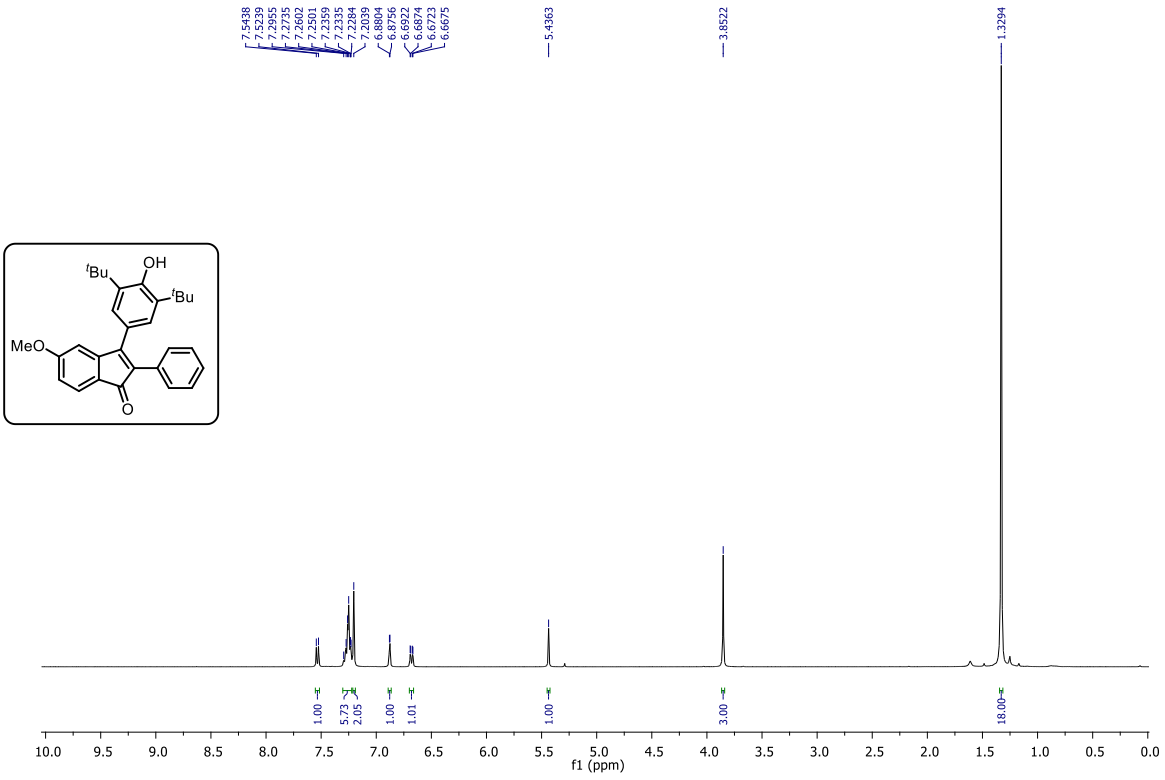
^{1}H NMR (400 MHz, $CDCl_3$) spectrum of **3a**



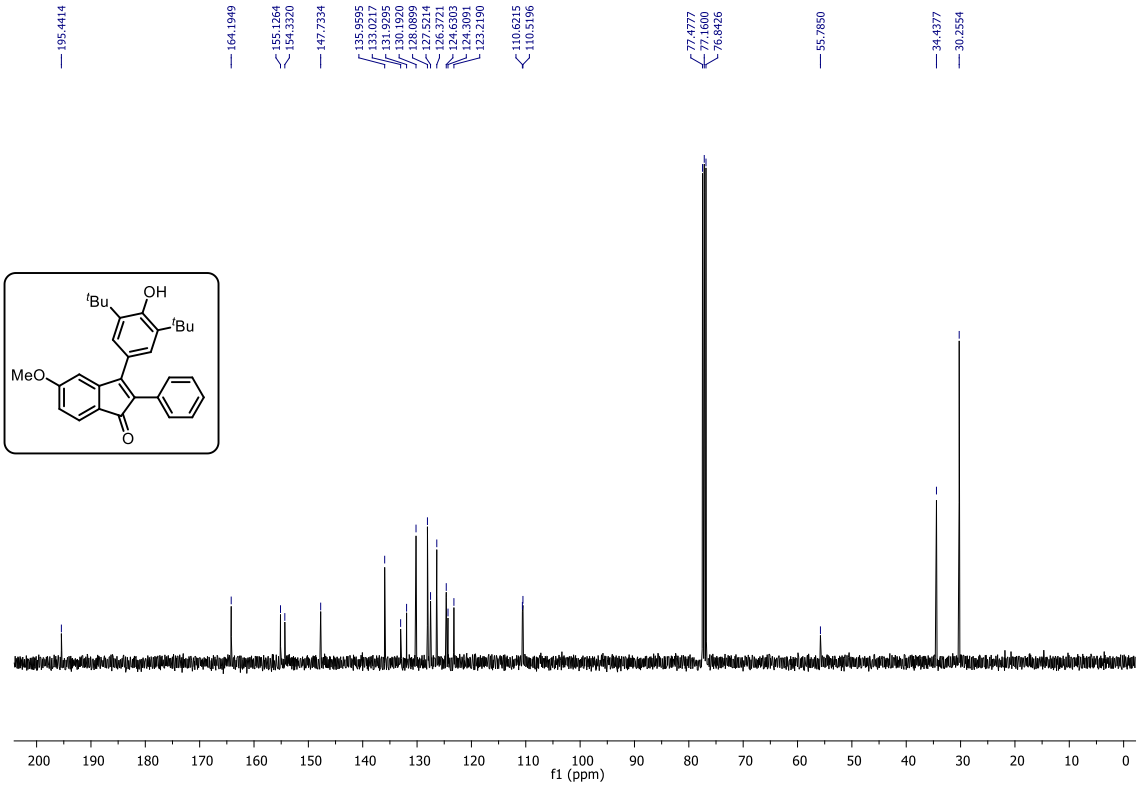
$^{13}C\{1H\}$ NMR (100 MHz, $CDCl_3$) spectrum of **3a**



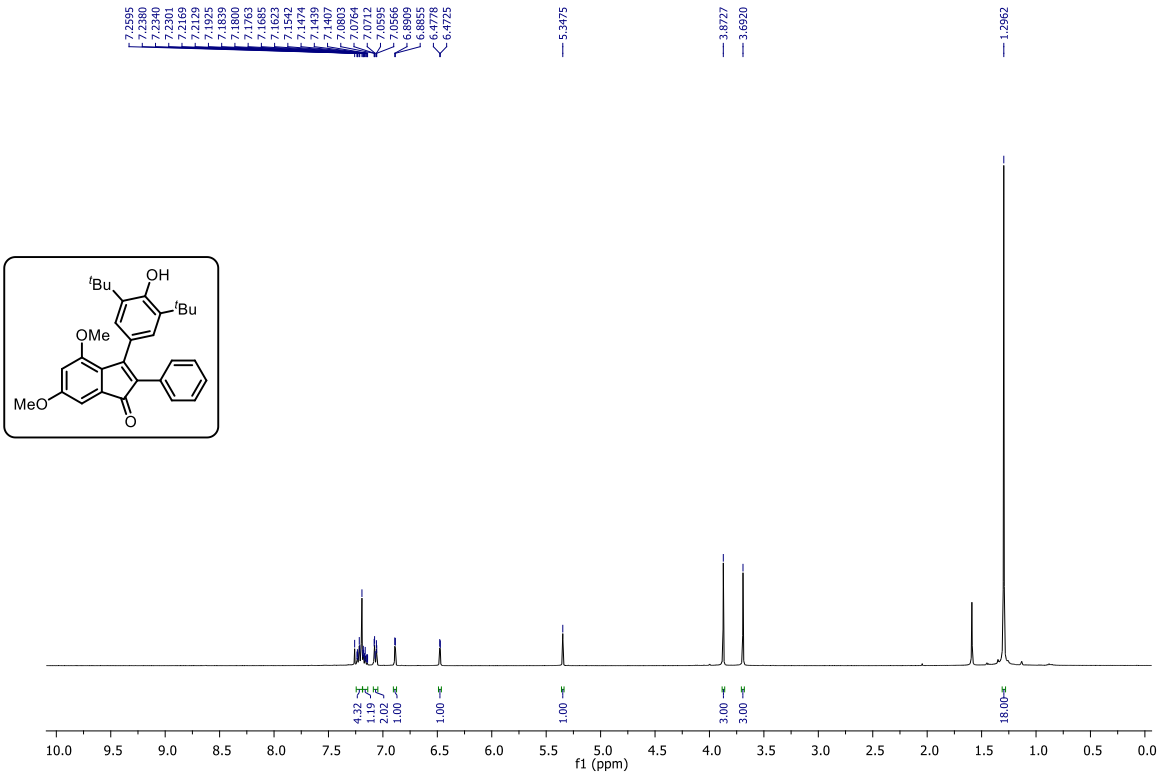
^{1}H NMR (400 MHz, $CDCl_3$) spectrum of **3b**



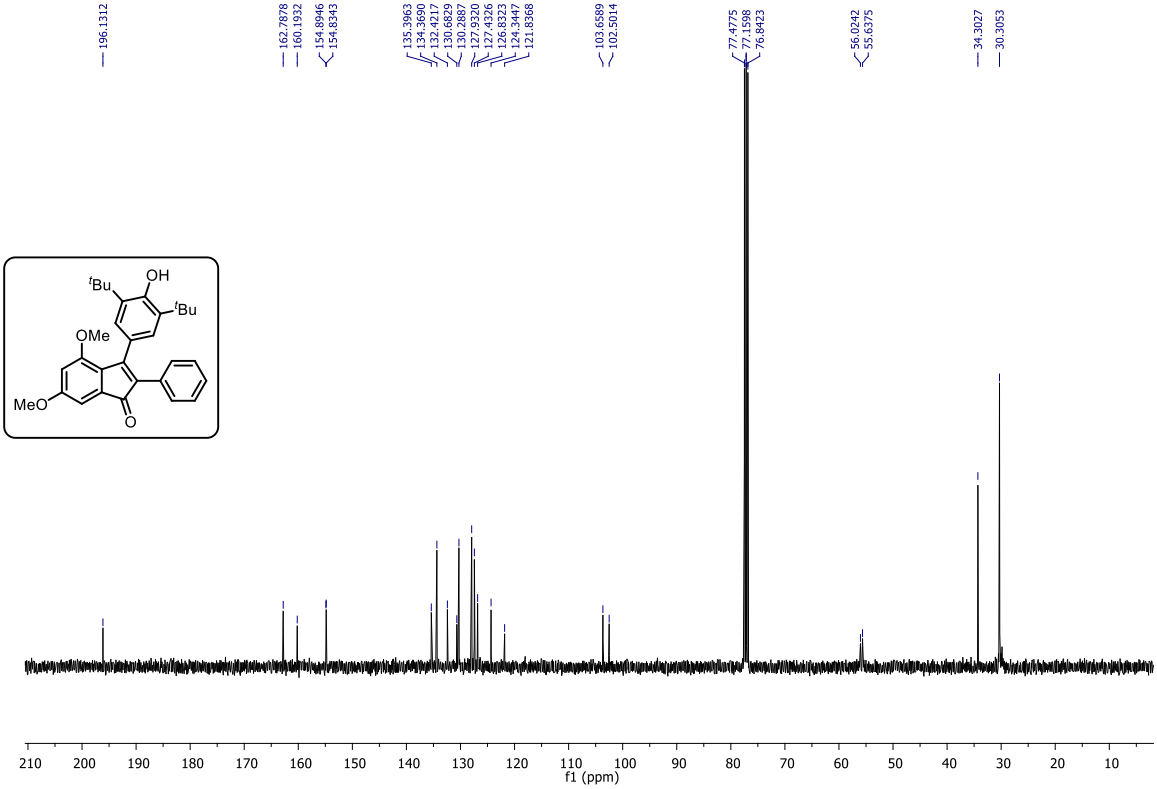
$^{13}C\{1H\}$ NMR (100 MHz, $CDCl_3$) spectrum of **3b**



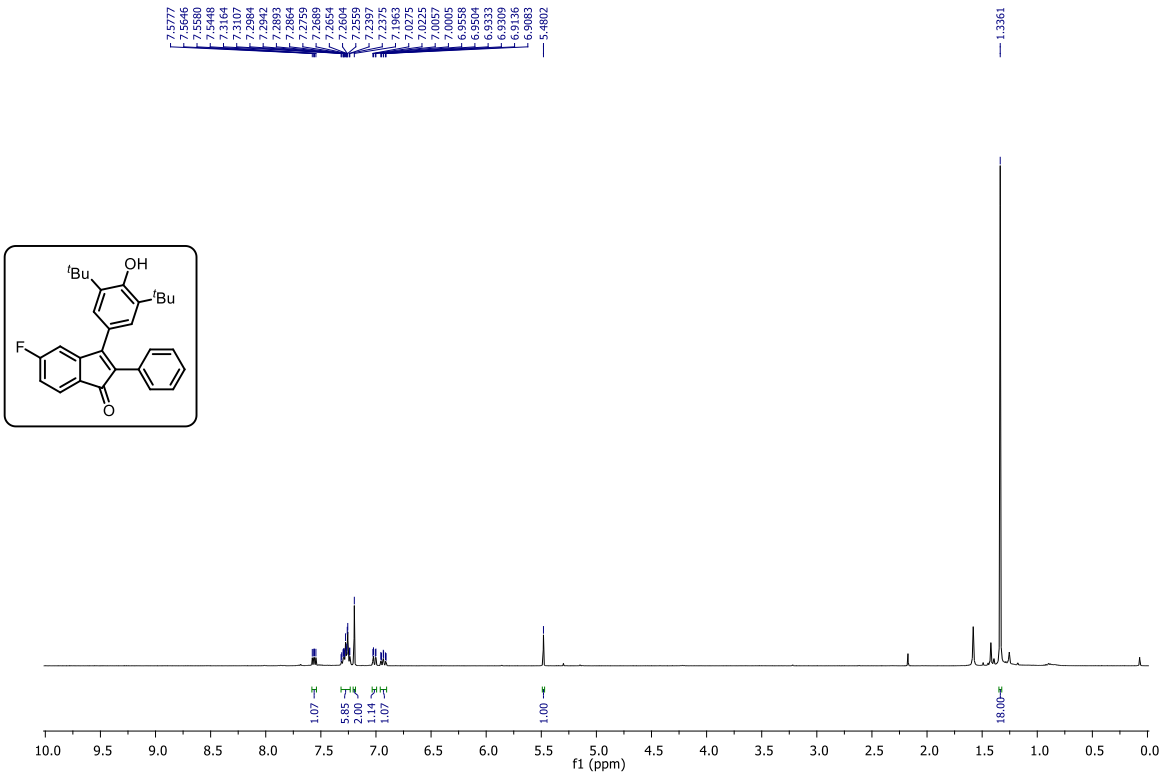
^{1}H NMR (400 MHz, $CDCl_3$) spectrum of **3c**



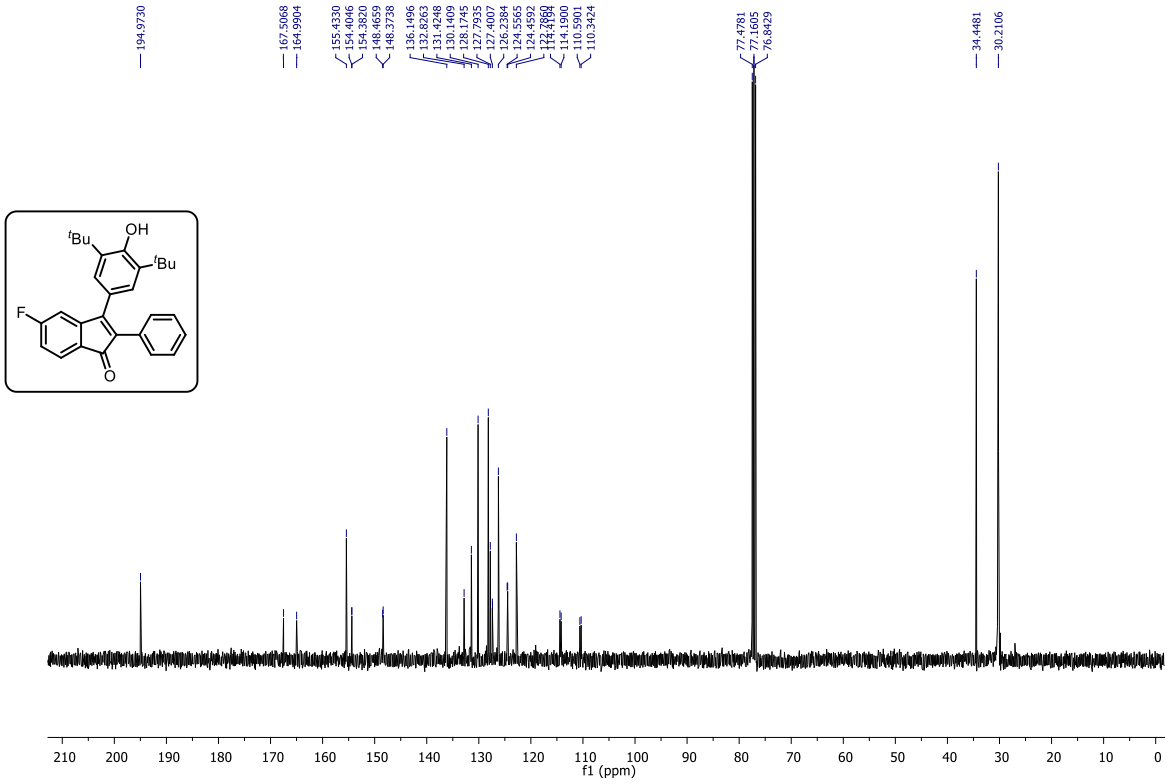
$^{13}C\{1H\}$ NMR (100 MHz, $CDCl_3$) spectrum of **3c**



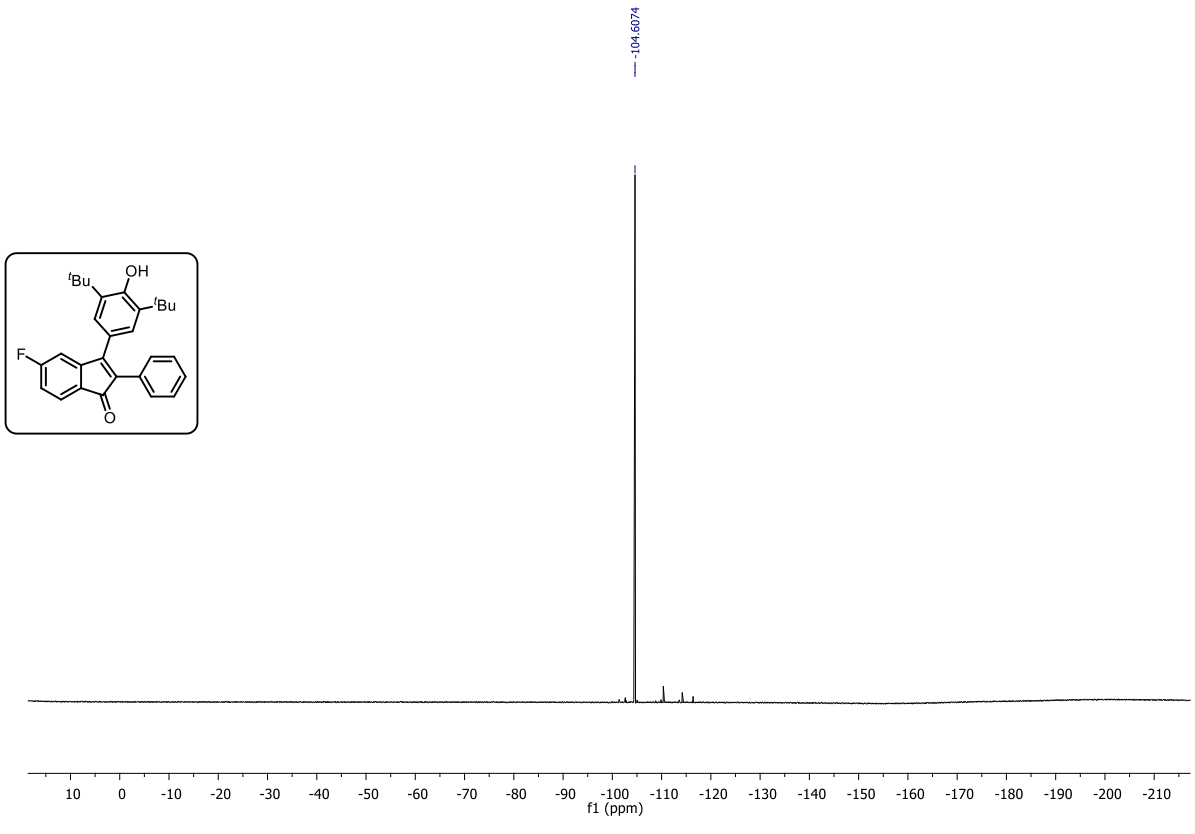
^{1}H NMR (400 MHz, $CDCl_3$) spectrum of **3d**



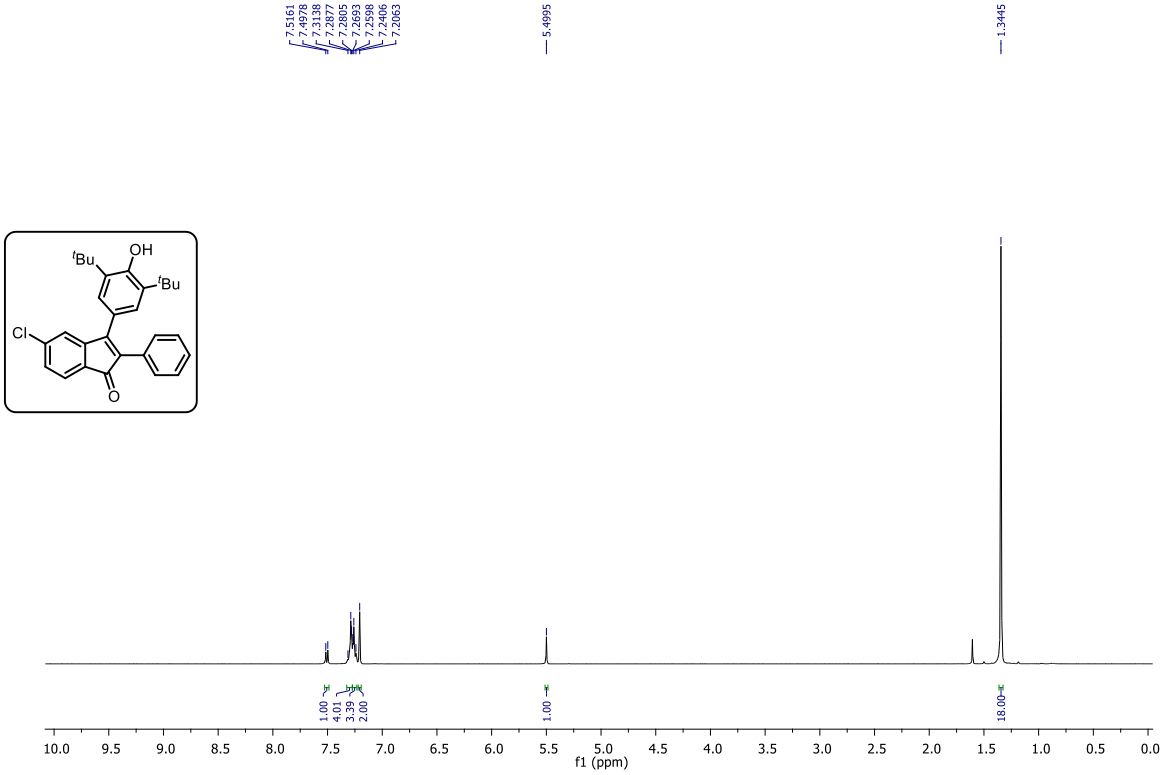
$^{13}C\{1H\}$ NMR (100 MHz, $CDCl_3$) spectrum of **3d**



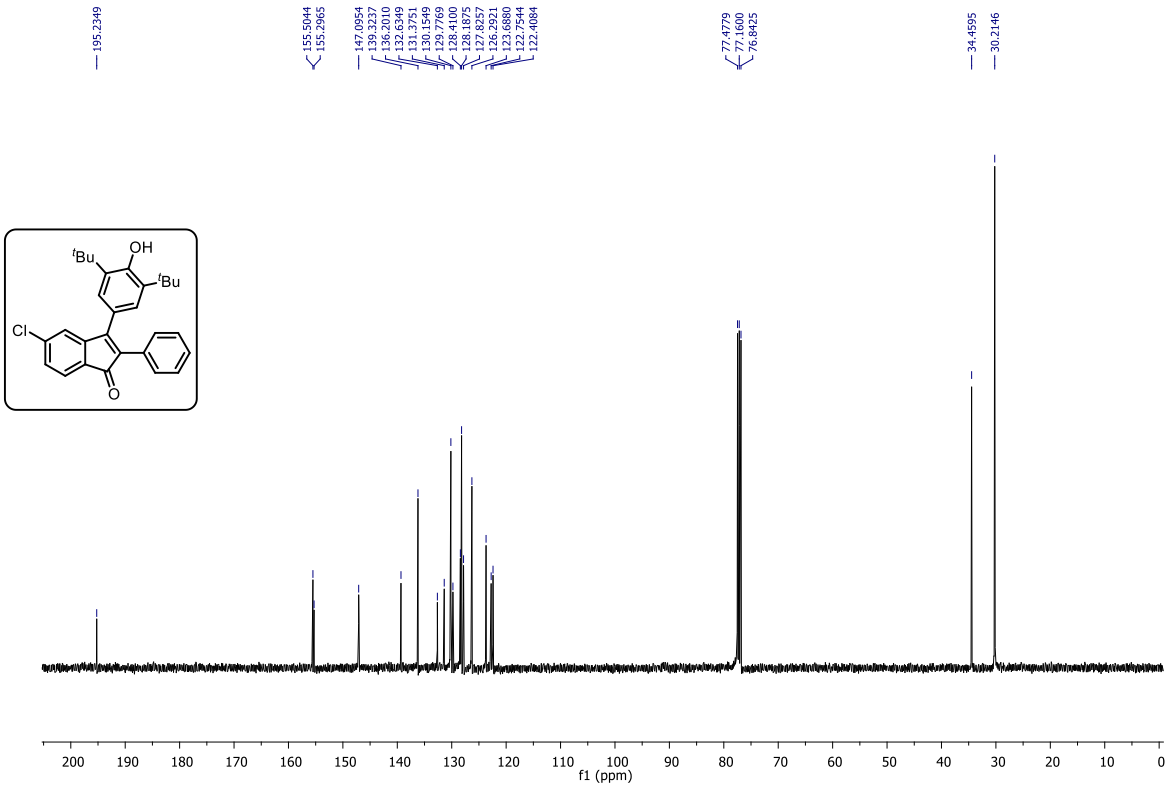
$^{19}F\{^1H\}$ NMR (376 MHz, $CDCl_3$) spectrum of **3d**



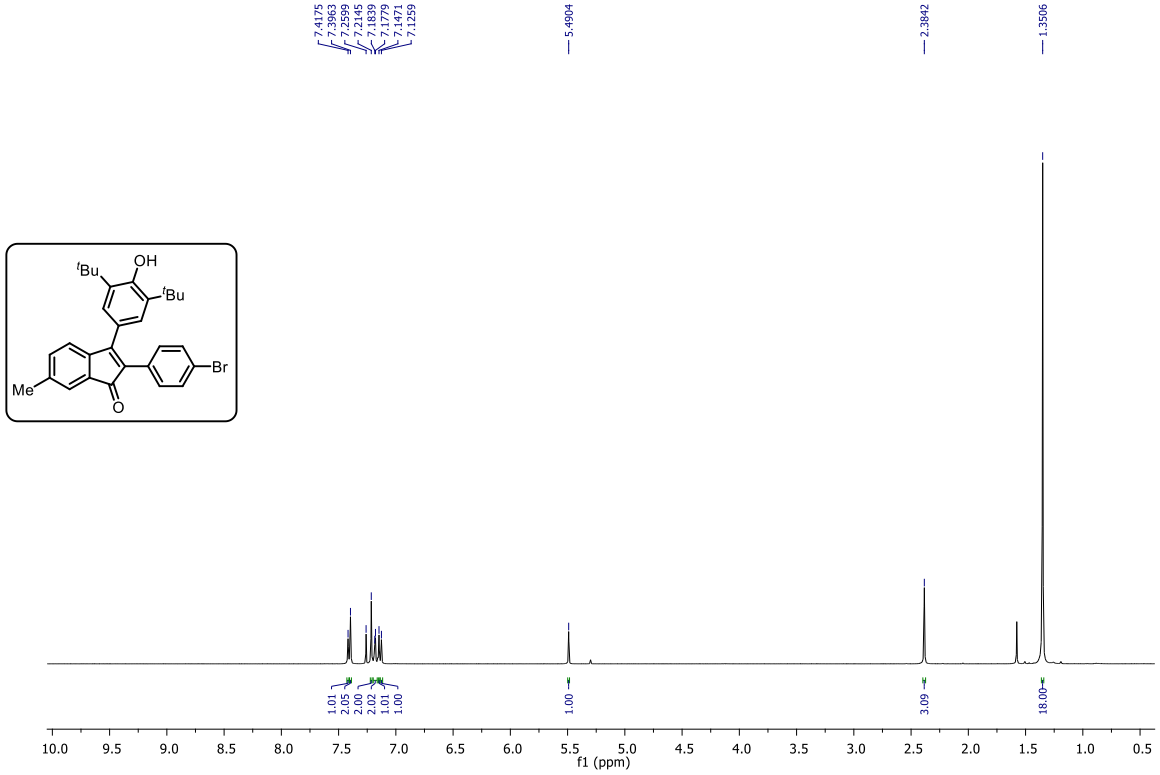
^{1}H NMR (400 MHz, $CDCl_3$) spectrum of **3e**



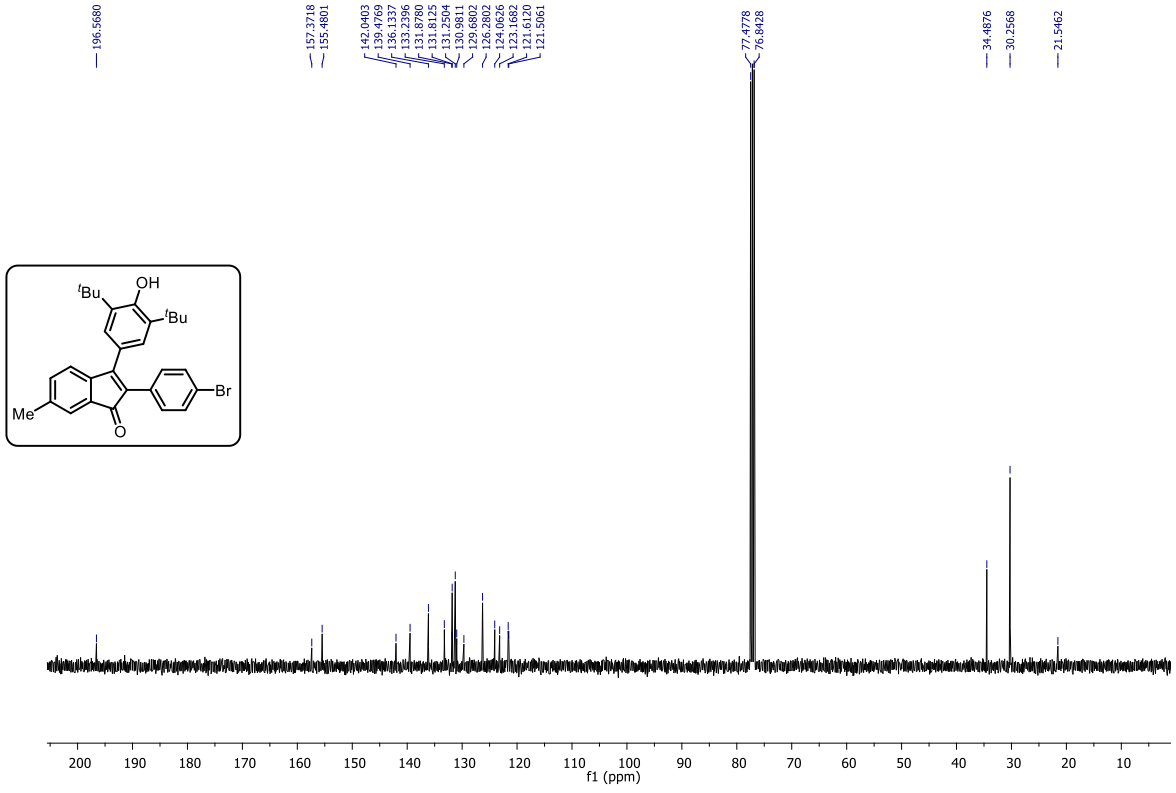
^{13}C{1H} NMR (100 MHz, $CDCl_3$) spectrum of **3e**



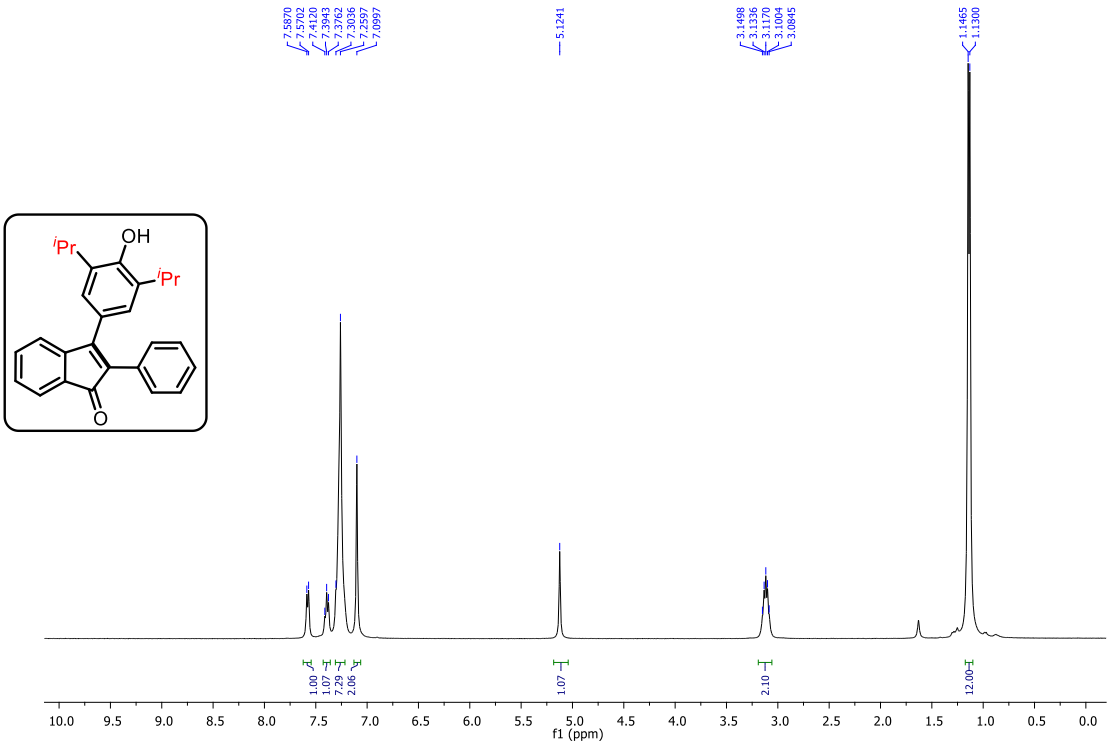
^{1}H NMR (400 MHz, $CDCl_3$) spectrum of **3f**



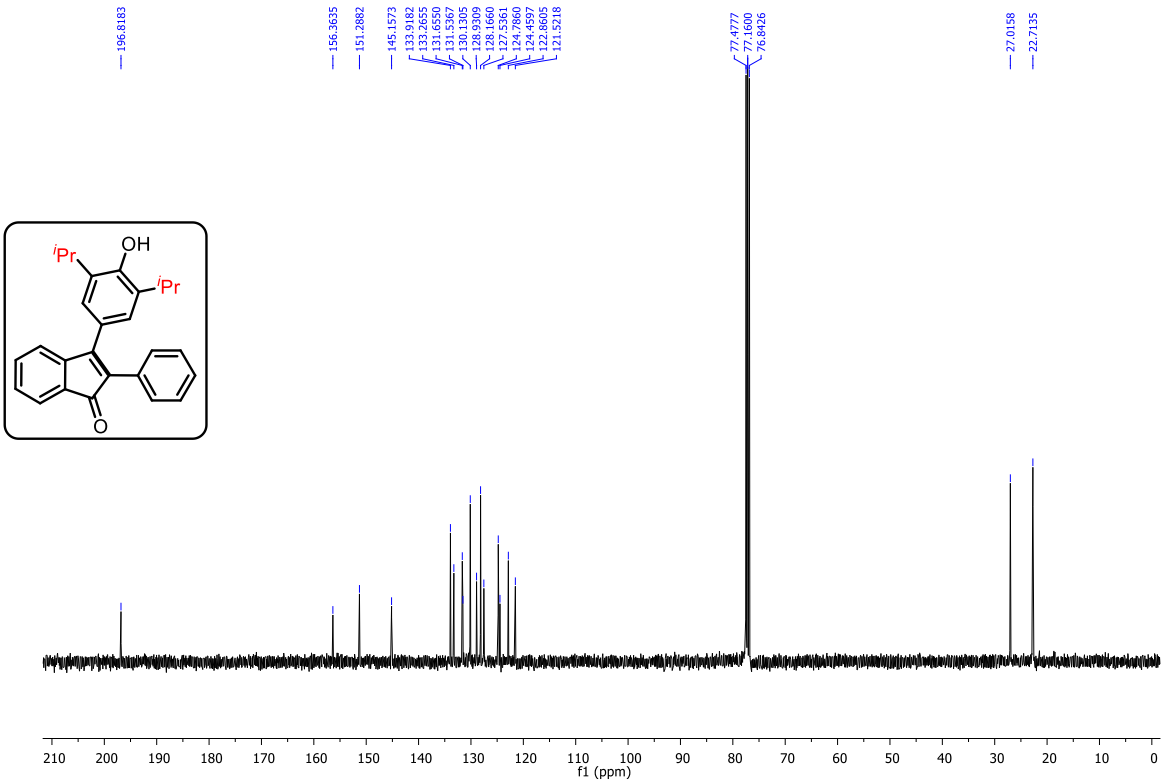
^{13}C{1H} NMR (100 MHz, $CDCl_3$) spectrum of **3f**



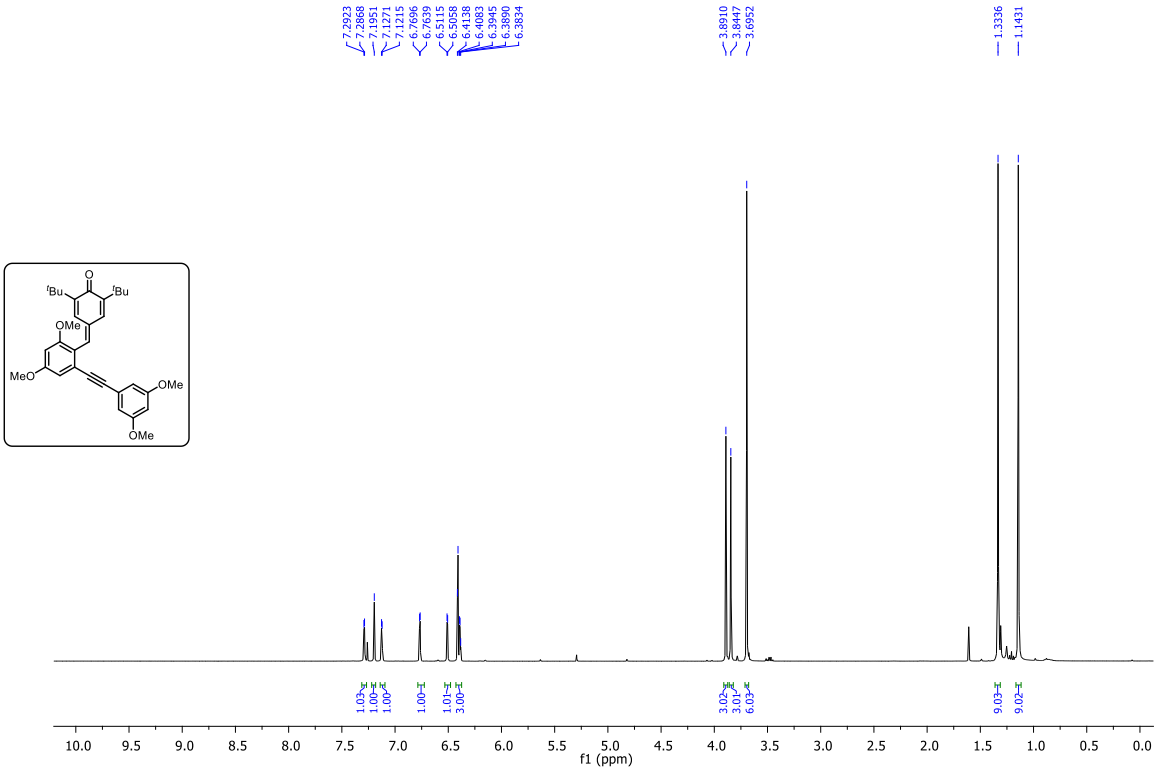
^{1}H NMR (400 MHz, $CDCl_3$) spectrum of **3g**



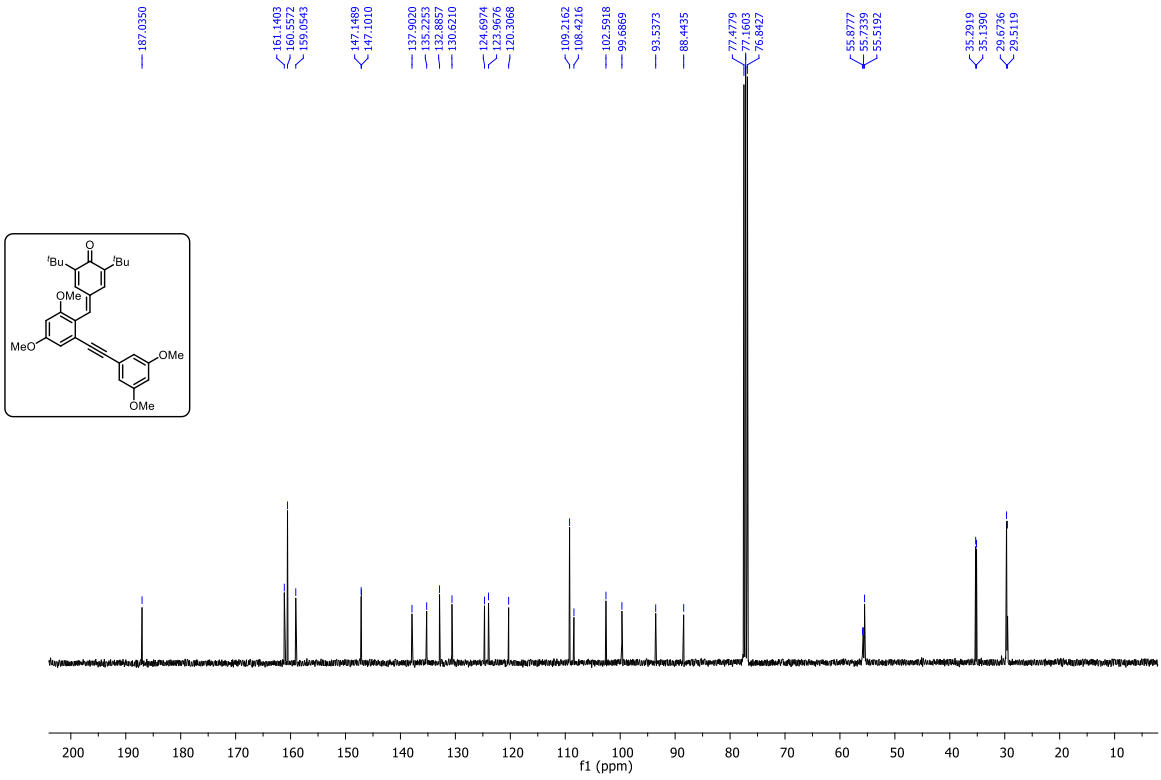
^{13}C{^{1}H} NMR (100 MHz, $CDCl_3$) spectrum of **3g**



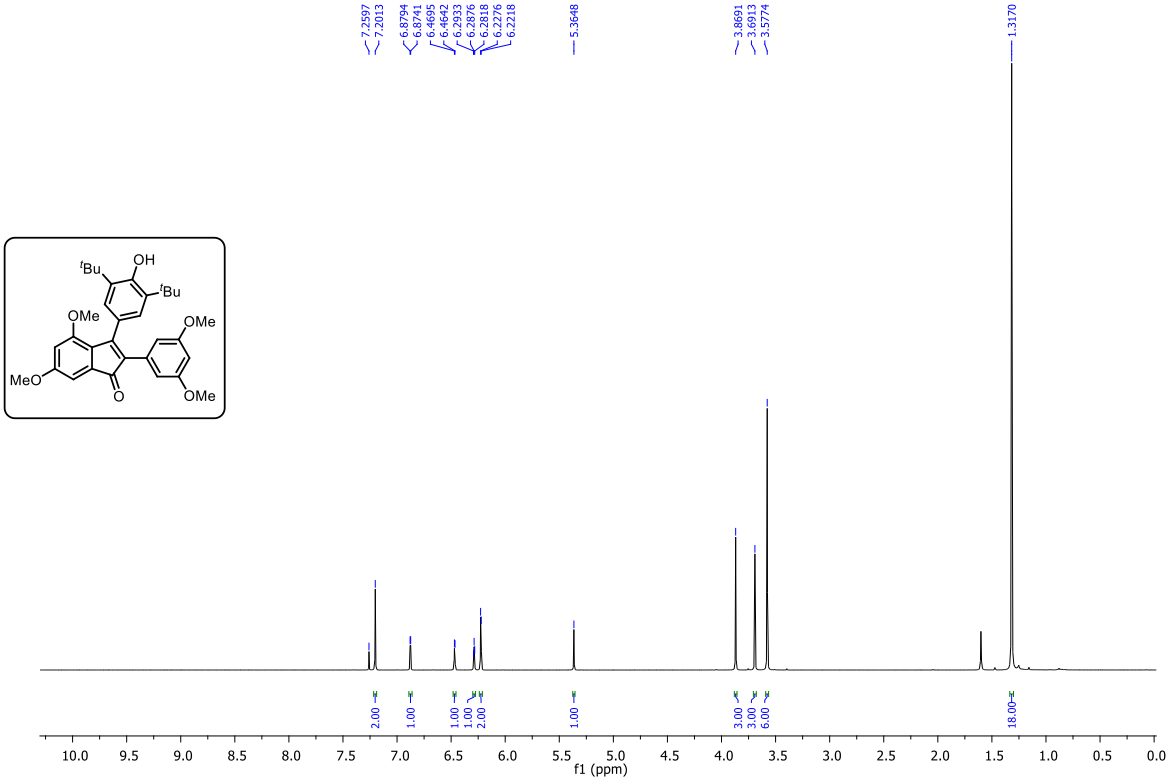
^{1}H NMR (400 MHz, $CDCl_3$) spectrum of **6**



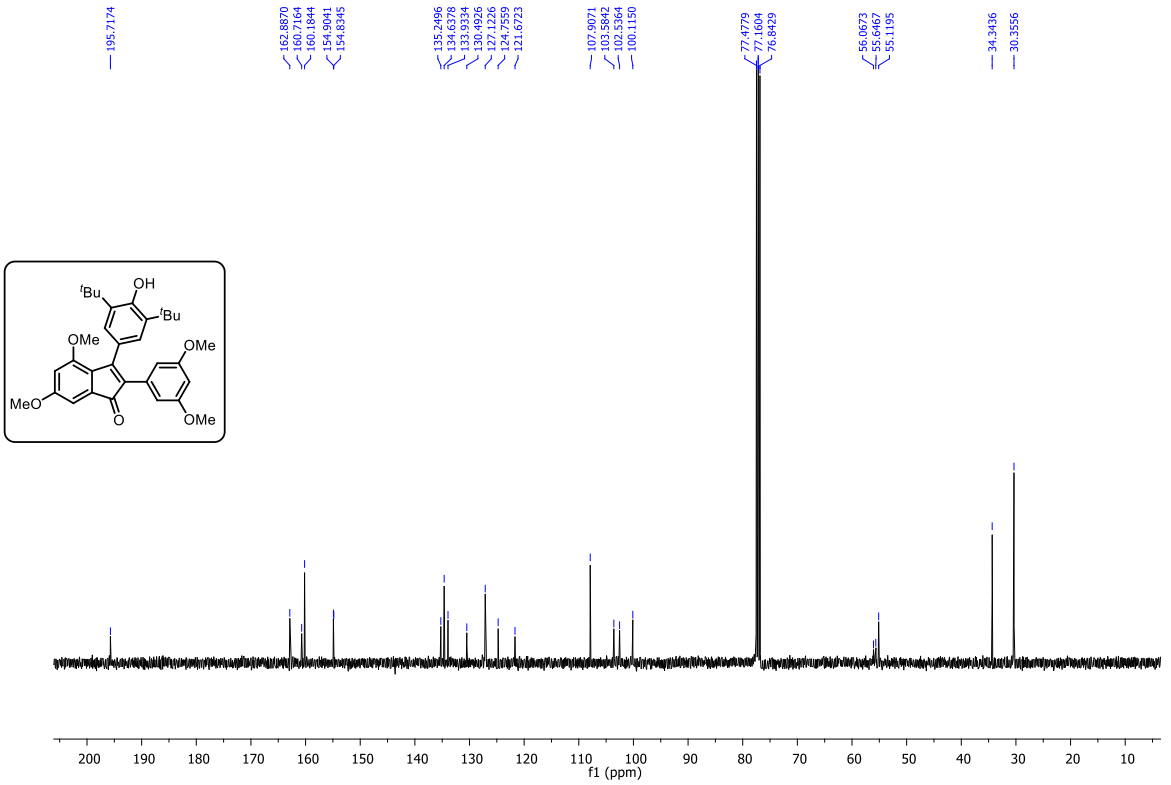
^{13}C{1H} NMR (100 MHz, $CDCl_3$) spectrum of **6**



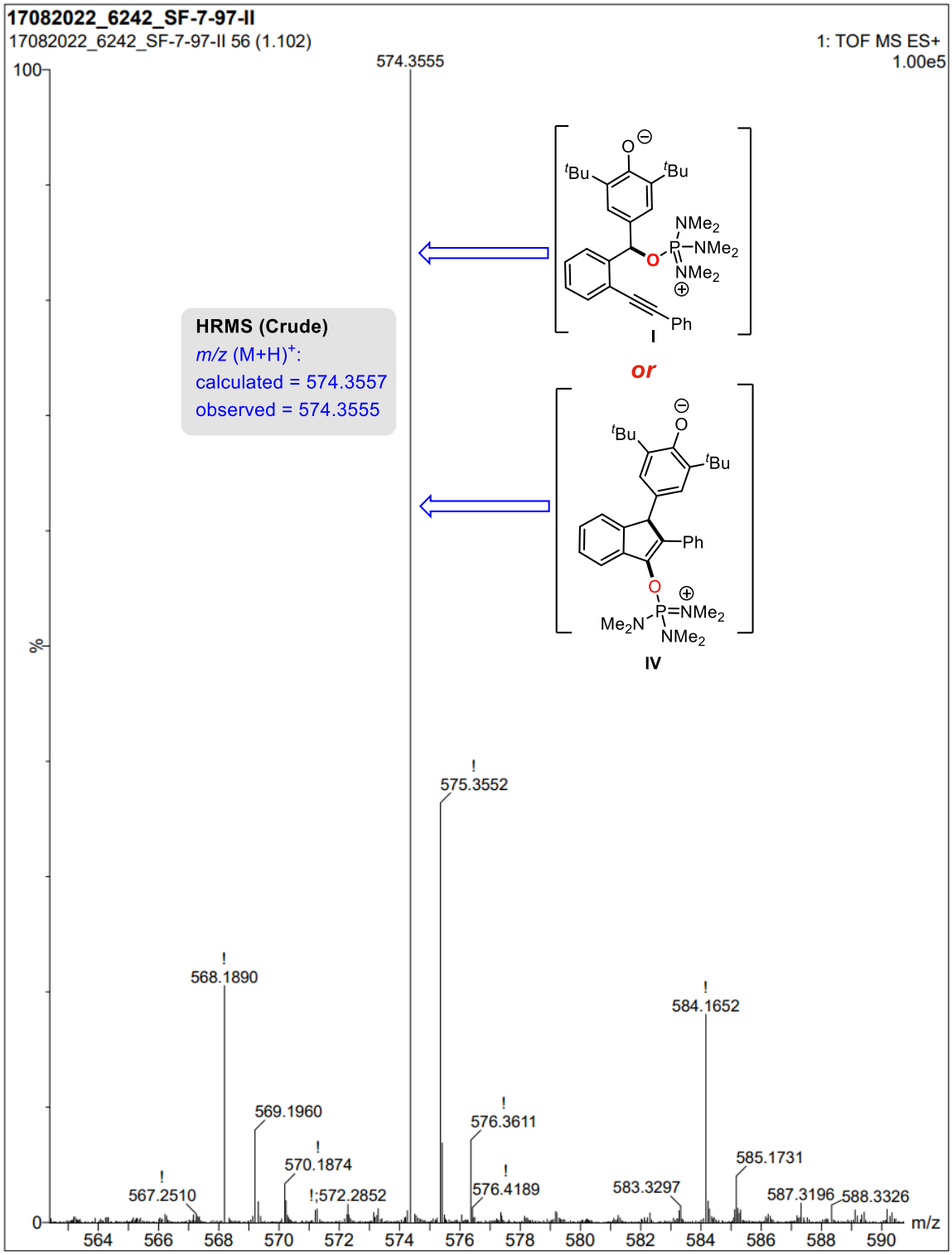
^{1}H NMR (400 MHz, $CDCl_3$) spectrum of **7**



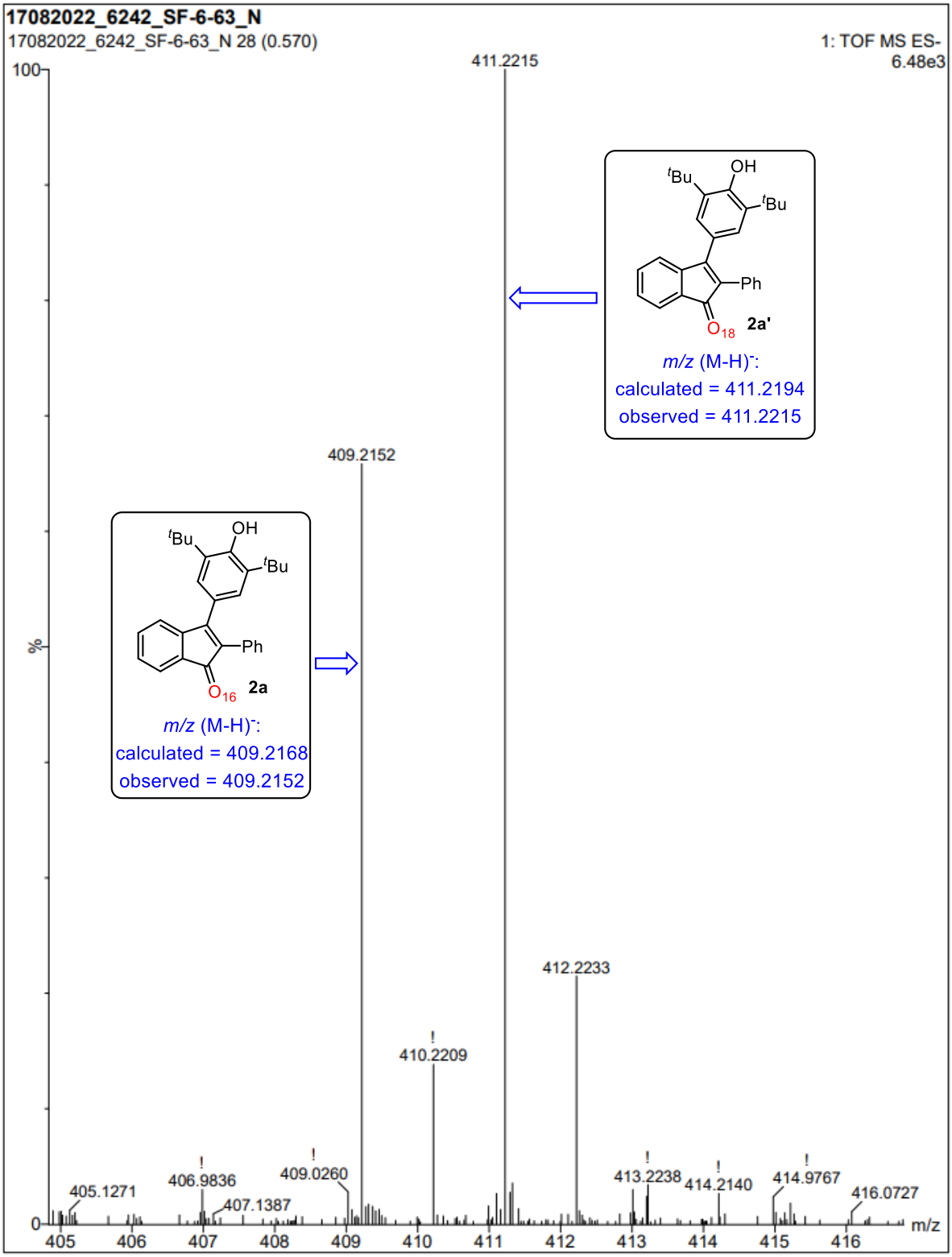
^{13}C{1H} NMR (100 MHz, $CDCl_3$) spectrum of **7**



11. HRMS analysis of crude reaction mixture: (indicating the presence of Intermediate I or IV)



12. HRMS analysis of the reaction of 1a with ^{18}O-labeled water: (H_2O^{18})



13. HRMS data for 2a