

Supporting Information

Silver(I)-Catalyzed Novel *ipso*-Cycloaddition and retro-Friedel-Crafts Reaction of *ortho*-Hydroxyphenyl-Substituted *para*-Quinone Methides

Caiqi Zhuo,[†] Ran Song,[†] Zhanxu Liu, Qirui Xiang, Daoshan Yang, Wen Si,^{*} and Jian Lv^{*}

Key Laboratory of Optic-electric Sensing and Analytic Chemistry for Life Science, MOE, College of Chemistry and Molecular Engineering, Qingdao University of Science & Technology, Qingdao 266042, China

**Email: lvjian@iccas.ac.cn (for J. Lv); siwen@qust.edu.cn (for W. Si)*

Table of Contents

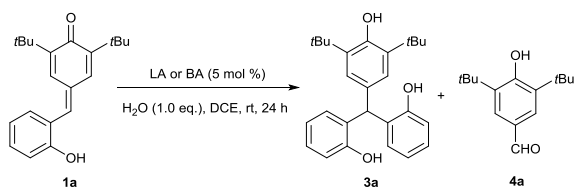
1. General Experiment Information and Materials	S1
2. Investigation of Water effect	S2
3. Experimental Procedures and Characterization Data	S3
4. Control Experiments	S25
5. X-ray crystal Data	S30
6. NMR Spectrum	S34
7. References	S75

1. General Experiment Information and Materials

All commercial reagents were used without further purification unless otherwise noted. Solvents were freshly dried according to *the purification handbook Purification of Laboratory Chemicals* before using. All of *p*-QMs **1**¹ and 4-aryl or 5-aryl salicylic aldehyde² were prepared according to literature procedure. Proton and carbon magnetic resonance spectra (¹H NMR and ¹³C NMR) were recorded on a Bruker Avance 500MHz spectrometer. Tetramethylsilane (TMS) served as the internal standard for ¹H NMR, and CDCl₃ served as the internal standard for ¹³C NMR. ¹H NMR data were reported as follows: chemical shift, multiplicity (s = singlet, d = doublet, t = triplet, m = multiplet, td = triplet of doublet, dt = doublet of triplet, dd = doublet of doublet), coupling constants (Hz), and integration. Infrared Spectroscopy was conducted on Thermo Fisher Nicolet is10. The X-ray single-crystal diffraction was performed on Saturn 724+ instrument. High resolution mass spectra were obtained on an Ultima Global spectrometer with an ESI source.

2. Investigation of water effect

Table S1 Screening of reaction conditions ^a



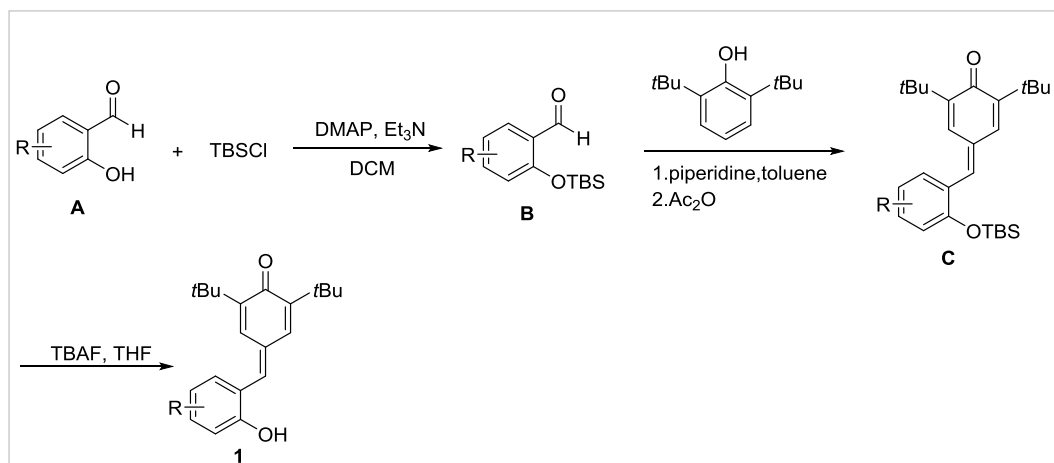
Entry	Acids	Yield (3a , %) ^b
1	InCl ₃	60
2	In(OAc) ₃	nr
3	HfCl ₄	54
4	Sc(OTf) ₃	62
5	AgBF ₄	49
6	AgSbF ₆	25

^a Reaction conditions: **1a** (0.1 mmol) and Lewis acid (5 mol %) in DCE (1.0 mL) at room temperature for 24 h, DCE removing water with CaH₂. ^b Isolated yield. DCE = 1,2-dichloroethane, nr = no reaction.

3. Experimental Procedures and Characterization Data

A) Synthesis of *ortho*-hydroxyphenyl-substituted *para*-quinone methides (*p*-QMs)

1:

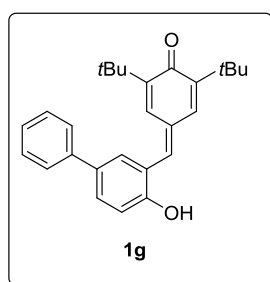


General procedure I: To an oven-dried reaction tube was added 2-hydroxybenzaldehyde **A** (8 mmol, 1.0 equiv) and DMAP (0.4 mmol, 5 mol%) in CH₂Cl₂ (0.2 M, 40 mL), which was sealed at room temperature. Then TBSCl (8.8 mmol, 1.1 equiv) was added by dropwise slowly. The solvent was stirred overnight, and a saturated NaHCO₃ solution was added dropwise to quench the reaction. The resulting solution was extracted with CH₂Cl₂ (3×10 mL). Then the combined organic phases were washed with brine and dried over anhydrous Na₂SO₄, resulting crude product **S2** and used directly in the next step without purification.

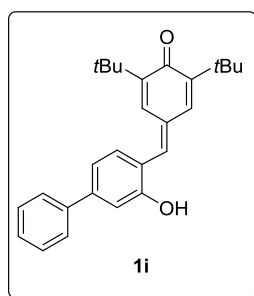
A solution of aldehydes **B** (7.2 mmol, 1.0 equiv) and phenols (7.92mmol, 1.1 equiv) in toluene (0.2 M, 36 mL) was placed in a Dean-Stark apparatus, and the solution was heated to reflux. Piperidine (14.4 mmol, 2.0 equiv) was added dropwise slowly. Then, the solution was stirred at 140 °C for 12 h. Then the reaction mixture was cooled to 120 °C, and acetic anhydride (14.4 mmol, 2.0 equiv) was dropwise added. After stirring for 30 min, the solution was poured on ice-water and extracted with CH₂Cl₂ (3×30 mL). The organic phases were combined, washed with brine and dried over anhydrous Na₂SO₄. Then the solvent was evaporated under reduced pressure and the corresponding products **C** were obtained after flash column chromatography (PE/ethyl acetate = 100/1).

To a solution of **C** (3.96 mmol, 1.0 equiv) in THF (0.2M, 20 mL) at 0 °C was added

tetrabutylammonium fluoride trihydrate (TBAF) (4.36 mmol, 1.1 equiv). The reaction mixture was stirred for 15 minutes and a saturated NH₄Cl solution was added dropwise to quench the reaction. The resulting solution was extracted with ethyl acetate (3×10 mL). Then the combined organic phases were washed with brine and dried over anhydrous Na₂SO₄. The solvent was removed to give the crude product which was purified by flash column chromatography (PE/ethyl acetate = 80/1 to 10/1) to afford the desired compounds **1**.

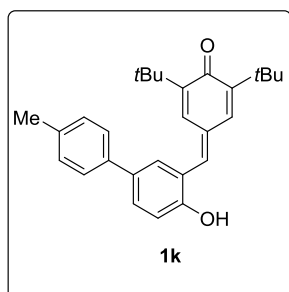


2,6-di-tert-butyl-4-((4-hydroxy-[1,1'-biphenyl]-3-yl)methylene)cyclohexa-2,5-dien-1-one (1g): Prepared according to the general procedure **I** above and obtained as yellow solid (0.93 g, 35% yield for 4 steps), melting point: 159-160 °C; ¹H NMR (500 MHz, DMSO-*d*₆) δ 10.47 (s, 1H), 7.65 – 7.55 (m, 6H), 7.42 (t, *J* = 7.5 Hz, 2H), 7.29 (t, *J* = 7.5 Hz, 1H), 7.25 (d, *J* = 1.0 Hz, 1H), 7.06 (d, *J* = 9.0 Hz, 1H), 1.25 (d, *J* = 20.5 Hz, 18H) ppm; ¹³C NMR (125 MHz, DMSO-*d*₆) δ 185.6, 156.6, 147.6, 146.1, 140.9, 139.4, 135.6, 131.2, 130.1, 129.7, 129.3, 128.90, 128.3, 126.8, 125.9, 122.9, 116.5, 34.9, 34.6, 29.3, 29.2 ppm.

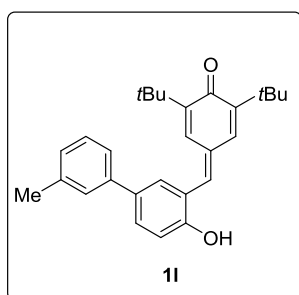


2,6-di-tert-butyl-4-((3-hydroxy-[1,1'-biphenyl]-4-yl)methylene)cyclohexa-2,5-dien-1-one (1i): Prepared according to the general procedure **I** above and obtained as yellow solid (0.98g, 36% yield for 4 steps), melting point: 232-233 °C; ¹H NMR (500 MHz, DMSO-*d*₆) δ 10.41 (s, 1H), 7.66 – 7.63 (m, 3H), 7.54 (s, 1H), 7.50 – 7.47 (m, 3H), 7.40 (t, *J* = 7.5 Hz, 1H), 7.26-7.23 (m, 3H), 1.28 (d, *J* = 13.0 Hz, 18H) ppm; ¹³C

NMR (125 MHz, DMSO-*d*₆) δ 185.7, 157.5, 147.6, 145.9, 143.1, 140.5, 139.2, 135.7, 132.0, 129.8, 129.0, 128.3, 128.0, 126.5, 121.9, 117.9, 113.7, 35.0, 34.7, 29.3, 29.2 ppm.

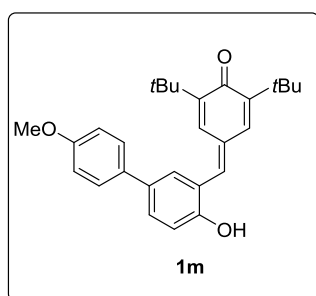


2,6-di-tert-butyl-4-((4-hydroxy-4'-methyl-[1,1'-biphenyl]-3-yl)methylene)cyclohexa-2,5-dien-1-one (1k): Prepared according to the general procedure I above and obtained as yellow solid (1.5 g, 39% yield for 4 steps), melting point: 190-192 °C; ¹H NMR (500 MHz, DMSO-*d*₆) δ 10.36 (s, 1H), 7.64 (s, 1H), 7.59 (d, *J* = 7.5 Hz, 3H), 7.50 (d, *J* = 8.0 Hz, 2H), 7.26 – 7.23 (m, 3H), 7.03 (d, *J* = 8.0 Hz, 1H), 2.31 (s, 3H), 1.26 (d, *J* = 20.0 Hz, 18H) ppm; ¹³C NMR (125 MHz, DMSO-*d*₆) δ 185.7, 156.4, 147.6, 146.1, 140.9, 136.6, 136.1, 135.7, 131.2, 130.1, 129.5, 129.44, 129.0, 128.3, 125.7, 122.8, 116.5, 34.7, 34.7, 29.3, 29.2, 20.5 ppm.

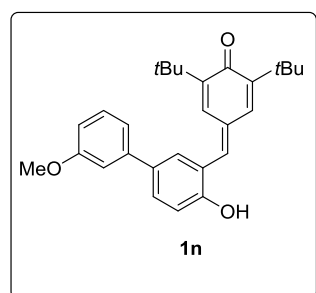


2,6-di-tert-butyl-4-((4-hydroxy-3'-methyl-[1,1'-biphenyl]-3-yl)methylene)cyclohexa-2,5-dien-1-one (1l): Prepared according to the general procedure I above and obtained as yellow solid (1.3 g, 34% yield for 4 steps), melting point: 170-171 °C; ¹H NMR (500 MHz, DMSO-*d*₆) δ 10.43 (s, 1H), 7.65 (s, 1H), 7.61 – 7.59 (m, 3H), 7.43 – 7.39 (m, 2H), 7.31 (t, *J* = 7.5 Hz, 1H), 7.26 (d, *J* = 1.5 Hz, 1H), 7.12 (d, *J* = 7.0 Hz, 1H), 7.04 (d, *J* = 8.5 Hz, 1H), 2.34 (s, 3H), 1.27 (d, *J* = 9.0 Hz, 18H) ppm; ¹³C NMR (125 MHz, DMSO-*d*₆) δ 185.7, 156.6, 147.6, 146.1, 140.8, 139.4, 138.0, 135.7, 131.3,

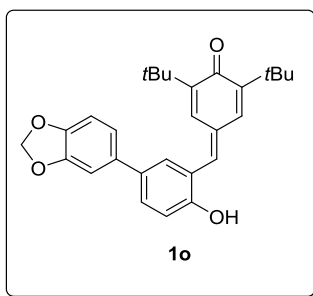
130.0, 129.6, 129.4, 128.8, 128.3, 127.5, 126.7, 122.7, 122.8, 116.4, 35.0, 34.7, 29.3, 29.2, 21.0 ppm.



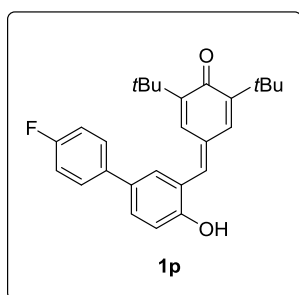
2,6-di-tert-butyl-4-((4-hydroxy-4'-methoxy-[1,1'-biphenyl]-3-yl)methylene)cyclohexa-2,5-dien-1-one (1m): Prepared according to the general procedure **I** above and obtained as yellow solid (1.26 g, 30% yield for 4 steps), melting point: 195-196 °C; ^1H NMR (500 MHz, DMSO- d_6) δ 10.29 (s, 1H), 7.64 (s, 1H), 7.58 – 7.53 (m, 5H), 7.26 (s, 1H), 7.04 – 6.99 (m, 3H), 3.78 (s, 3H), 1.27 (d, $J = 18.1$ Hz, 18H) ppm; ^{13}C NMR (125 MHz, DMSO- d_6) δ 183.8, 156.6, 154.3, 145.8, 144.3, 139.2, 133.9, 130.1, 129.2, 128.2, 127.5, 126.9, 126.5, 125.1, 121.0, 114.6, 112.5, 53.3, 33.2, 32.8, 27.5, 27.4 ppm.



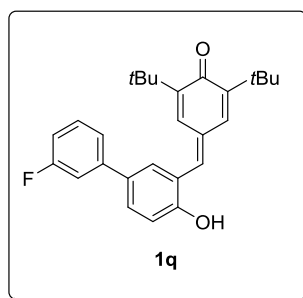
2,6-di-tert-butyl-4-((4-hydroxy-3'-methoxy-[1,1'-biphenyl]-3-yl)methylene)cyclohexa-2,5-dien-1-one (1n): Prepared according to the general procedure **I** above and obtained as yellow solid (1.1 g, 26% yield for 4 steps), melting point: 168-169 °C; ^1H NMR (500 MHz, DMSO- d_6) δ 10.43 (s, 1H), 7.64 – 7.62 (m, 3H), 7.58 (d, $J = 1.0$ Hz, 1H), 7.33 (t, $J = 8.0$ Hz, 1H), 7.26 (s, 1H), 7.17 (d, $J = 7.5$ Hz, 1H), 7.13 (s, 1H), 7.05 (d, $J = 8.5$ Hz, 1H), 6.87 (dd, $J = 8.1, 1.9$ Hz, 1H), 3.80 (s, 3H), 1.27 (d, $J = 17.0$ Hz, 18H) ppm; ^{13}C NMR (125 MHz, DMSO- d_6) δ 185.7, 159.7, 156.8, 147.6, 146.1, 141.0, 140.9, 135.7, 131.1, 130.1, 129.9, 129.8, 129.3, 128.3, 122.8, 118.3, 116.4, 112.7, 111.2, 55.1, 35.0, 34.7, 29.3, 29.2 ppm.



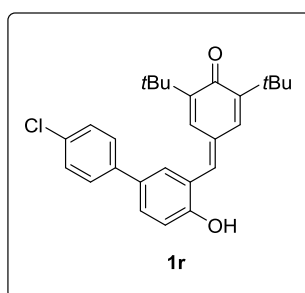
4-(5-(benzo[d][1,3]dioxol-5-yl)-2-hydroxybenzylidene)-2,6-di-tert-butylcyclohexa-2,5-dien-1-one (1o): Prepared according to the general procedure **I** above and obtained as yellow solid (1.64 g, 38% yield for 4 steps), melting point: 175-176 °C; ^1H NMR (500 MHz, $\text{DMSO-}d_6$) δ 10.33 (s, 1H), 7.62 (s, 1H), 7.57 – 7.53 (m, 3H), 7.26 (d, $J = 1.5$ Hz, 1H), 7.16 (d, $J = 1.5$ Hz, 1H), 7.07 (dd, $J = 8.1, 1.6$ Hz, 1H), 7.01 (d, $J = 8.0$ Hz, 1H), 6.96 (d, $J = 8.0$ Hz, 1H), 6.04 (s, 2H), 1.27 (d, $J = 18.0$ Hz, 18H) ppm; ^{13}C NMR (126 MHz, $\text{DMSO-}d_6$) δ 185.6, 156.3, 147.9, 147.6, 146.4, 146.1, 140.9, 135.7, 133.9, 131.1, 130.1, 129.5, 129.0, 128.3, 122.7, 119.3, 116.4, 108.6, 106.5, 101.1, 35.0, 34.7, 29.3, 29.2 ppm.



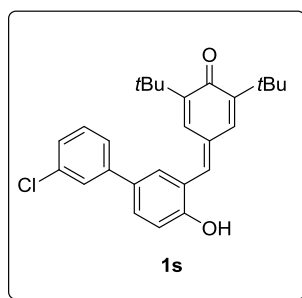
2,6-di-tert-butyl-4-((4'-fluoro-4-hydroxy-[1,1'-biphenyl]-3-yl)methylene)cyclohexa-2,5-dien-1-one (1p): Prepared according to the general procedure **I** above and obtained as yellow solid (1.4 g, 35% yield for 4 steps), melting point: 142-143 °C; ^1H NMR (500 MHz, $\text{DMSO-}d_6$) δ 10.39 (s, 1H), 7.65 – 7.55 (m, 6H), 7.25 (t, $J = 8.0$ Hz, 3H), 7.04 (d, $J = 8.0$ Hz, 1H), 1.26 (d, $J = 24.5$ Hz, 18H) ppm; ^{13}C NMR (125 MHz, $\text{DMSO-}d_6$) δ 185.6, 161.4 (d, $J = 243.7$ Hz), 156.5, 147.6, 146.0, 140.8, 136.0, 135.6, 130.2 (d, $J = 7.8$ Hz), 129.6, 129.3, 128.3, 127.8, 127.7, 122.9, 116.5, 115.7 (d, $J = 21.3$ Hz), 35.0, 34.7, 29.3, 29.2 ppm.



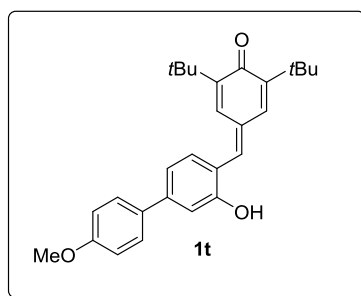
2,6-di-tert-butyl-4-((3'-fluoro-4-hydroxy-[1,1'-biphenyl]-3-yl)methylene)cyclohexa-2,5-dien-1-one (1q): Prepared according to the general procedure I above and obtained as yellow solid (1.52 g, 38% yield for 4 steps), melting point: 200-201 °C; ¹H NMR (500 MHz, DMSO-*d*₆) δ 10.50 (s, 1H), 7.69 – 7.61 (m, 3H), 7.56 (s, 1H), 7.49 – 7.44 (m, 3H), 7.27 (d, *J* = 2.0 Hz, 1H), 7.16 – 7.10 (m, 1H), 7.06 (d, *J* = 8.0 Hz, 1H), 1.27 (d, *J* = 22.0 Hz, 18H) ppm; ¹³C NMR (125 MHz, DMSO-*d*₆) δ 185.7, 162.7 (d, *J* = 243.2 Hz), 157.0, 147.6, 146.2, 142.0 (d, *J* = 7.7 Hz), 140.6, 135.6, 130.8, 130.7, 130.3, 129.7, 129.5, 128.3, 122.9, 121.8 (d, *J* = 2.3 Hz), 116.5, 113.4 (d, *J* = 21.0 Hz), 112.6 (d, *J* = 21.0 Hz), 35.0, 34.7, 29.3, 29.2 ppm.



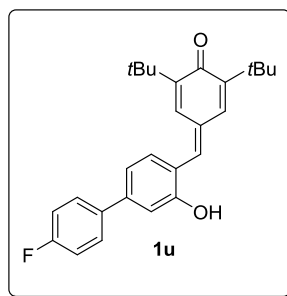
2,6-di-tert-butyl-4-((4'-chloro-4-hydroxy-[1,1'-biphenyl]-3-yl)methylene)cyclohexa-2,5-dien-1-one (1r): Prepared according to the general procedure I above and obtained as yellow solid (1.05 g, 25% yield for 4 steps), melting point: 174-175 °C; ¹H NMR (500 MHz, DMSO-*d*₆) δ 10.48 (s, 1H), 7.64– 7.60 (m, 5H), 7.53 (d, *J* = 1.5 Hz, 1H), 7.47 (d, *J* = 8.5 Hz, 2H), 7.25 (d, *J* = 2.0 Hz, 1H), 7.05 (d, *J* = 8.5 Hz, 1H), 1.25 (d, *J* = 27.0 Hz, 18H) ppm; ¹³C NMR (125 MHz, DMSO-*d*₆) δ 185.6, 156.8, 147.6, 146.2, 140.7, 138.3, 135.6, 131.6, 130.3, 129.8, 129.6, 129.31, 128.8, 128.3, 127.6, 123.0, 116.5, 35.0, 34.7, 29.3, 29.2 ppm.



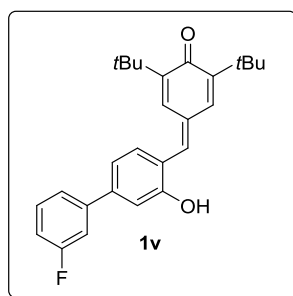
2,6-di-tert-butyl-4-((3'-chloro-4-hydroxy-[1,1'-biphenyl]-3-yl)methylene)cyclohexa-2,5-dien-1-one (1s): Prepared according to the general procedure **I** above and obtained as yellow solid (0.95 g, 22% yield for 4 steps), melting point: 212-213 °C; ¹H NMR (500 MHz, DMSO-*d*₆) δ 10.51 (s, 1H), 7.66– 7.63 (m, 4H), 7.60 – 7.57 (m, 2H), 7.46 (t, *J* = 8.0 Hz, 1H), 7.36 (d, *J* = 7.5 Hz, 1H), 7.27 (d, *J* = 1.5 Hz, 1H), 7.06 (d, *J* = 8.0 Hz, 1H), 1.27 (d, *J* = 15.5 Hz, 18H) ppm; ¹³C NMR (126 MHz, DMSO) δ 186.2, 157.6, 148.1, 146.7, 142.1, 141.0, 136.1, 134.2, 131.2, 130.8, 130.2, 130.1, 130.1, 128.8, 127.1, 126.2, 125.0, 123.5, 117.0, 35.5, 35.2, 29.8, 29.7 ppm.



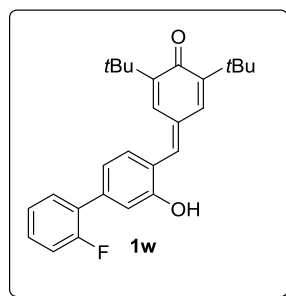
2,6-di-tert-butyl-4-((3-hydroxy-4'-methoxy-[1,1'-biphenyl]-4-yl)methylene)cyclohexa-2,5-dien-1-one (1t): Prepared according to the general procedure **I** above and obtained as yellow solid (1.14 g, 27% yield for 4 steps), melting point: 248-249 °C; ¹H NMR (500 MHz, DMSO-*d*₆) δ 10.36 (s, 1H), 7.66 – 7.58 (m, 3H), 7.55 (s, 1H), 7.46 (d, *J* = 8.0 Hz, 1H), 7.29 – 7.16 (m, 3H), 7.05 (d, *J* = 8.5 Hz, 2H), 3.81 (s, 3H), 1.28 (d, *J* = 11.5 Hz, 18H) ppm; ¹³C NMR (125 MHz, DMSO-*d*₆) δ 186.1, 159.9, 158.0, 148.0, 146.3, 143.4, 141.1, 136.2, 132.4, 131.9, 130.0, 128.8, 128.17, 121.7, 117.9, 115.0, 113.6, 55.7, 35.5, 35.1, 29.8, 29.7 ppm.



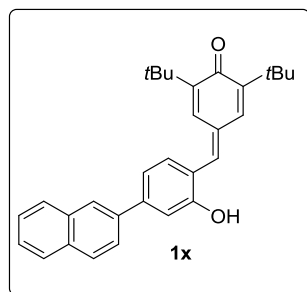
2,6-di-tert-butyl-4-((4'-fluoro-3-hydroxy-[1,1'-biphenyl]-4-yl)methylene)cyclohexa-2,5-dien-1-one (1u): Prepared according to the general procedure I above and obtained as yellow solid (1.48 g, 37% yield for 4 steps), melting point: 247-248 °C; ^1H NMR (500 MHz, $\text{DMSO-}d_6$) δ 10.42 (s, 1H), 7.70 – 7.68 (m, 2H), 7.62 (s, 1H), 7.53 (s, 1H), 7.47 (d, $J = 8.5$ Hz, 1H), 7.32 (t, $J = 8.5$ Hz, 2H), 7.24 – 7.22 (m, 2H), 7.19 (s, 1H), 1.27 (d, $J = 13.5$ Hz, 18H) ppm; ^{13}C NMR (125 MHz, $\text{DMSO-}d_6$) δ 185.8, 162.1 (d, $J = 245.8$ Hz), 157.4, 147.6, 146.0, 142.0, 140.4, 135.7, 132.0, 130.0, 128.6, 128.5, 128.2, 121.9, 117.9, 115.9 (d, $J = 21.5$ Hz), 113.7, 35.0, 34.6, 29.3, 29.2 ppm.



2,6-di-tert-butyl-4-((3'-fluoro-3-hydroxy-[1,1'-biphenyl]-4-yl)methylene)cyclohexa-2,5-dien-1-one (1v): Prepared according to the general procedure I above and obtained as yellow solid (1.37 g, 34% yield for 4 steps), melting point: 243-244 °C; ^1H NMR (500 MHz, $\text{DMSO-}d_6$) δ 7.60 (s, 1H), 7.51 – 7.46 (m, 5H), 7.27 – 7.21 (m, 4H), 1.25 (d, $J = 13.5$ Hz, 18H) ppm; ^{13}C NMR (125 MHz, $\text{DMSO-}d_6$) δ 186.2, 163.1 (d, $J = 244.1$ Hz), 157.9, 148.2, 146.5, 142.3 (d, $J = 7.8$ Hz), 142.1, 140.8, 136.2, 132.5, 131.5 (d, $J = 8.4$ Hz), 130.5, 128.7, 123.1, 123.0, 118.5, 115.2 (d, $J = 21.1$ Hz), 114.4, 113.7 (d, $J = 22.1$ Hz), 35.5, 35.2, 29.8, 29.7 ppm.

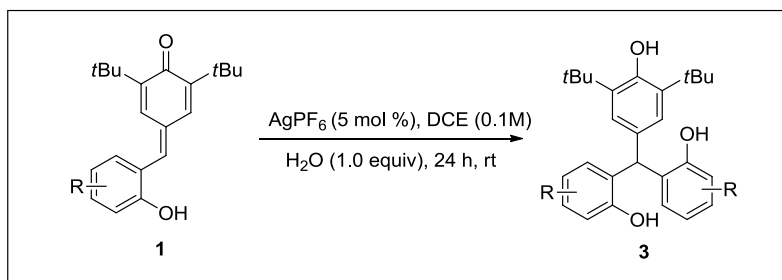


2,6-di-tert-butyl-4-((2'-fluoro-3-hydroxy-[1,1'-biphenyl]-4-yl)methylene)cyclohexa-2,5-dien-1-one (1w): Prepared according to the general procedure **I** above and obtained as yellow solid (1.3 g, 31% yield for 4 steps), melting point: 230-232 °C; ¹H NMR (500 MHz, DMSO-*d*₆) δ 10.42 (s, 1H), 7.62 (s, 1H), 7.57 – 7.54 (m, 2H), 7.49 (d, *J* = 8.0 Hz, 1H), 7.46 – 7.43 (m, 1H), 7.35 – 7.30 (m, 2H), 7.26 (d, *J* = 2.0 Hz, 1H), 7.17 (s, 1H), 7.13 (d, *J* = 8.0 Hz, 1H), 1.27 (d, *J* = 14.5 Hz, 18H) ppm; ¹³C NMR (125 MHz, DMSO-*d*₆) δ 185.7, 159.1 (d, *J* = 247.1 Hz), 156.9, 147.7, 146.1, 140.3, 137.9, 135.7, 131.6, 130.4 (d, *J* = 3.2 Hz), 130.0, 130.0 (d, *J* = 8.4 Hz), 128.2, 127.4 (d, *J* = 12.7 Hz), 125.0 (d, *J* = 3.4 Hz), 122.2, 119.9 (d, *J* = 2.3 Hz), 116.2 (d, *J* = 22.7 Hz), 116.1 (d, *J* = 3.4 Hz), 35.0, 34.7, 29.3, 29.2 ppm.



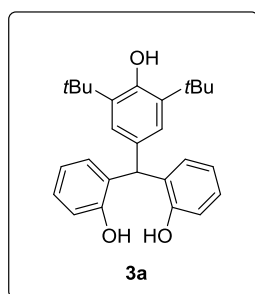
2,6-di-tert-butyl-4-(2-hydroxy-4-(naphthalen-2-yl)benzylidene)cyclohexa-2,5-dien-1-one (1x): Prepared according to the general procedure **I** above and obtained as yellow solid (1.57 g, 36% yield for 4 steps), melting point: 263-265 °C; ¹H NMR (500 MHz, DMSO-*d*₆) δ 10.47 (s, 1H), 8.23 (s, 1H), 8.02 (d, *J* = 8.0 Hz, 2H), 7.95 (d, *J* = 7.3 Hz, 1H), 7.82 (d, *J* = 8.5 Hz, 1H), 7.66 (s, 1H), 7.61 – 7.50 (m, 4H), 7.45 – 7.35 (m, 2H), 7.26 (d, *J* = 0.5 Hz, 1H), 1.28 (d, *J* = 9.5 Hz, 18H) ppm; ¹³C NMR (125 MHz, DMSO-*d*₆) δ 186.2, 158.0, 148.1, 146.5, 143.4, 141.0, 137.1, 136.2, 133.7, 133.0, 132.5, 130.4, 129.1, 128.8, 128.0, 127.0, 126.9, 125.9, 125.2, 122.5, 118.7, 114.5, 35.5, 35.2, 29.8, 29.7 ppm.

B) Synthesis of triarylmethanes (TRAMs)

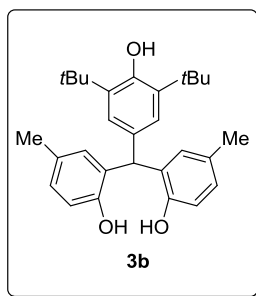


General Procedure II: To an oven-dried reaction tube was added *p*-QMs **1** (0.1 mmol) and AgPF₆ (5 mol %), and DCE (1.0 mL) was added, Then H₂O (0.1 mmol) was added by dropwise slowly. The mixture was stirred for 24 h at room temperature. Purification of mixture by column chromatography on silica gel (PE/EA = 5:1 as eluent) gave the desired product **3**.

Large-scale Reaction: To an oven-dried reaction tube was added *p*-QMs **1a** (1.0 g, 3.2 mmol) and AgPF₆ (5 mol %), and DCE (32 mL) was added, Then H₂O (58 μL, 3.2 mmol) was added by dropwise slowly. The mixture was stirred for 24 h at room temperature. Purification of mixture by column chromatography on silica gel (PE/EA = 5:1 as eluent) gave the desired product **3a** (0.65 g, 90% yield).

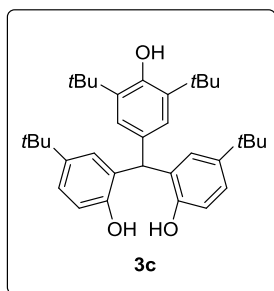


2,2'-((3,5-di-tert-butyl-4-hydroxyphenyl)methylene)diphenol (3a): Prepared according to the general procedure **II** above and obtained as yellow solid (37.2 mg, 92% yield), melting point: 161-162 °C; ¹H NMR (500 MHz, DMSO-*d*₆) δ 9.14 (s, 2H), 6.99-6.96 (m, 2H), 6.77 (s, 2H), 6.74 (d, *J* = 7.5 Hz, 2H), 6.68 (s, 1H), 6.66 (d, *J* = 4.0 Hz, 4H), 5.94 (s, 1H), 1.28 (s, 18H) ppm; ¹³C NMR (125 MHz, DMSO-*d*₆) δ=154.6, 151.5, 138.4, 134.4, 131.0, 129.4, 126.5, 125.2, 118.2, 114.8, 42.2, 34.4, 30.4 ppm; IR (KBr, cm⁻¹): 3633, 2956, 1594, 1484, 1453, 1434, 1277, 1233, 1023, 820, 756; HRMS (ESI) calcd for C₂₇H₃₁O₃⁻ [M-H]⁻: 403.2279, found: 403.2280.



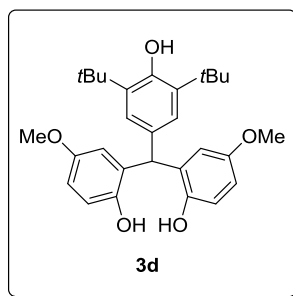
2,2'-((3,5-di-tert-butyl-4-hydroxyphenyl)methylene)bis(4-methylphenol) (3b):

Prepared according to the general procedure **II** above and obtained as colorless oil (42 mg, 97% yield); ^1H NMR (500 MHz, $\text{DMSO-}d_6$) δ 8.87 (s, 2H), 6.80– 6.77 (m, 4H), 6.67 (s, 1H), 6.62 (d, $J = 8.0$ Hz, 2H), 6.53 (s, 2H), 5.87 (s, 1H), 2.08 (s, 6H), 1.29 (s, 18H) ppm; ^{13}C NMR (125 MHz, $\text{DMSO-}d_6$) δ 152.4, 151.5, 138.3, 134.3, 130.8, 129.9, 126.8, 126.2, 125.3, 114.7, 42.2, 34.4, 30.4, 20.5 ppm; IR (KBr, cm^{-1}): 3643, 2956, 2924, 1610, 1506, 1434, 1232, 1034, 814, 769; HRMS (ESI) calcd for $\text{C}_{29}\text{H}_{35}\text{O}_3$ $[\text{M-H}]^-$: 431.2592, found: 431.2590.

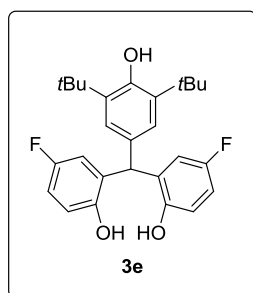


2,2'-((3,5-di-tert-butyl-4-hydroxyphenyl)methylene)bis(4-(tert-butyl)phenol) (3c):

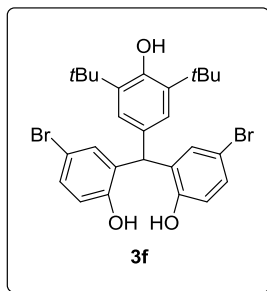
Prepared according to the general procedure **II** above and obtained as yellow solid (40 mg, 78% yield), melting point: 108-109 $^{\circ}\text{C}$, ^1H NMR (500 MHz, $\text{DMSO-}d_6$) δ 8.92 (s, 2H), 6.95 (dd, $J = 8.3, 2.2$ Hz, 2H), 6.87 – 6.86 (m, 4H), 6.68 (s, 1H), 6.64 (d, $J = 8.5$ Hz, 2H), 6.00 (s, 1H), 1.30 (s, 18H), 1.11 (s, 18H) ppm; ^{13}C NMR (125 MHz, $\text{DMSO-}d_6$) δ 152.1, 151.4, 139.8, 138.4, 134.5, 130.1, 126.6, 125.3, 122.6, 114.3, 41.7, 34.4, 33.5, 31.3, 30.4 ppm; IR (KBr, cm^{-1}): 3636, 2956, 2868, 1609, 1508, 1427, 1231, 1202, 824, 765; HRMS (ESI) calcd for $\text{C}_{35}\text{H}_{47}\text{O}_3$ $[\text{M-H}]^-$: 515.3531, found: 515.3523.



2,2'-((3,5-di-tert-butyl-4-hydroxyphenyl)methylene)bis(4-methoxyphenol) (3d): Prepared according to the general procedure **II** above and obtained as colorless oil (20 mg, 43% yield); ^1H NMR (500 MHz, $\text{DMSO-}d_6$) δ 8.74 (s, 2H), 6.81 (s, 2H), 6.74 (s, 1H), 6.66 (d, $J = 8.5$ Hz, 2H), 6.60– 6.58 (m, 2H), 6.24 (s, 2H), 5.84 (s, 1H), 3.54 (s, 6H), 1.30 (s, 18H) ppm; ^{13}C NMR (125 MHz, $\text{DMSO-}d_6$) δ 151.7, 151.7, 148.6, 138.5, 133.8, 132.0, 125.1, 116.0, 115.1, 110.7, 55.1, 42.8, 34.4, 30.4 ppm; IR (KBr, cm^{-1}), 3606, 2958, 1590, 1502, 1431, 1275, 1235, 1148, 1040, 818, 721; HRMS (ESI) calcd for $\text{C}_{29}\text{H}_{35}\text{O}_5$ $[\text{M-H}]^-$: 463.2490, found: 463.2490.

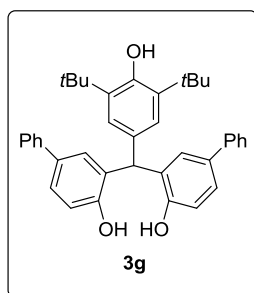


2,2'-((3,5-di-tert-butyl-4-hydroxyphenyl)methylene)bis(4-fluorophenol) (3e): Prepared according to the general procedure **II** above and obtained as colorless oil (27 mg, 63% yield); ^1H NMR (500 MHz, $\text{DMSO-}d_6$) δ 9.30 (s, 2H), 6.87 – 6.82 (m, 3H), 6.76– 6.73 (m, 4H), 6.34 (dd, $J = 9.9, 3.0$ Hz, 2H), 5.84 (s, 1H), 1.29 (s, 18H) ppm; ^{13}C NMR (125 MHz, $\text{DMSO-}d_6$) δ 155.6 (d, $J = 233.7$ Hz), 152.5, 151.4, 139.3, 133.4, 132.7 (d, $J = 5.6$ Hz), 125.5, 116.1 (d, $J = 7.6$ Hz), 115.8 (d, $J = 23.6$ Hz), 113.4 (d, $J = 22.6$ Hz), 43.4, 34.9, 30.9 ppm; IR (KBr, cm^{-1}): 2954, 1555, 1506, 1436, 1258, 1026, 822, 760; HRMS (ESI) calcd for $\text{C}_{27}\text{H}_{29}\text{F}_2\text{O}_3$ $[\text{M-H}]^-$: 439.2090, found: 439.2091.



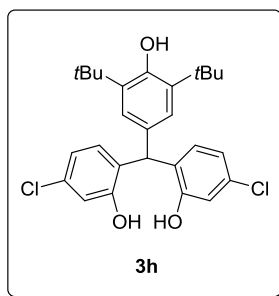
2,2'-((3,5-di-tert-butyl-4-hydroxyphenyl)methylene)bis(4-bromophenol) (3f):

Prepared according to the general procedure **II** above and obtained as colorless oil (18.5 mg, 33% yield); ^1H NMR (500 MHz, $\text{DMSO-}d_6$) δ 9.66 (s, 2H), 7.19 (dd, $J = 8.5, 2.3$ Hz, 2H), 6.84 (s, 1H), 6.77 – 6.73 (m, 4H), 6.70 (d, $J = 2.5$ Hz, 2H), 5.80 (s, 1H), 1.30 (s, 18H) ppm; ^{13}C NMR (125 MHz, $\text{DMSO-}d_6$) δ 154.1, 152.0, 138.9, 133.2, 132.3, 131.3, 129.6, 125.1, 117.1, 109.5, 42.9, 34.4, 30.4 ppm; IR (KBr, cm^{-1}): 3632, 2956, 1597, 1490, 1434, 1232, 816, 769; HRMS (ESI) calcd for $\text{C}_{27}\text{H}_{29}\text{Br}_2\text{O}_3^-[\text{M-H}]^-$: 559.0489, found: 559.0475.



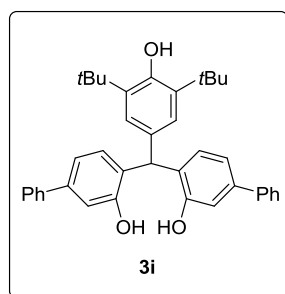
3,3'-((3,5-di-tert-butyl-4-hydroxyphenyl)methylene)bis([1,1'-biphenyl]-4-ol) (3g):

Prepared according to the general procedure **II** above and obtained as colorless oil (53 mg, 96% yield). ^1H NMR (500 MHz, CDCl_3) δ 9.45 (s, 2H), 7.37 – 7.30 (m, 10H), 7.22 – 7.20 (m, 2H), 7.07 (d, $J = 2.0$ Hz, 2H), 6.99 (s, 2H), 6.86 (d, $J = 8.0$ Hz, 2H), 6.78 (s, 1H), 6.01 (s, 1H), 1.33 (s, 18H) ppm; ^{13}C NMR (125 MHz, $\text{DMSO-}d_6$) δ 154.6, 151.8, 140.8, 138.7, 133.5, 131.3, 130.2, 128.8, 127.7, 126.2, 125.6, 125.4, 125.1, 115.5, 42.9, 34.5, 30.4 ppm; IR (KBr, cm^{-1}): 3627, 2957, 1606, 1514, 1486, 1453, 1433, 1278, 1233, 764; HRMS (ESI) calcd for $\text{C}_{39}\text{H}_{39}\text{O}_3^-[\text{M-H}]^-$: 555.2905, found: 555.2897.



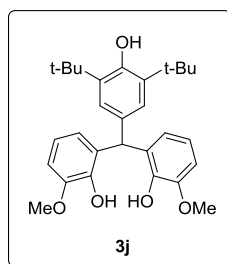
6,6'-((3,5-di-tert-butyl-4-hydroxyphenyl)methylene)bis(3-chlorophenol) (3h):

Prepared according to the general procedure **II** above and obtained as colorless oil (39 mg, 83% yield); $^1\text{H NMR}$ (500 MHz, $\text{DMSO-}d_6$) δ 9.79 (s, 2H), 6.78 – 6.74 (m, 7H), 6.61 (d, $J = 8.5$ Hz, 2H), 5.80 (s, 1H), 1.28 (s, 18H) ppm; $^{13}\text{C NMR}$ (125 MHz, $\text{DMSO-}d_6$) δ 155.6, 151.9, 138.7, 133.1, 130.6, 130.5, 129.9, 125.0, 118.2, 114.6, 41.8, 34.4, 30.4 ppm; IR (KBr, cm^{-1}): 3633, 2957, 1587, 1501, 1414, 1262, 1232, 856, 820; HRMS (ESI) calcd for $\text{C}_{27}\text{H}_{29}\text{Cl}_2\text{O}_3^- [\text{M-H}]^-$: 471.1499, found: 471.1500.



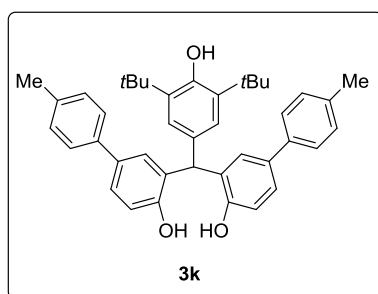
4,4'-((3,5-di-tert-butyl-4-hydroxyphenyl)methylene)bis([1,1'-biphenyl]-3-ol) (3i):

Prepared according to the general procedure **II** above and obtained as colorless oil (42 mg, 42% yield); $^1\text{H NMR}$ (500 MHz, $\text{DMSO-}d_6$) δ 9.40 (s, 2H), 7.56 (d, $J = 8.0$ Hz, 4H), 7.44 (t, $J = 8.0$ Hz, 4H), 7.32 (t, $J = 7.5$ Hz, 2H), 7.04 – 7.01 (m, 4H), 6.88 (s, 2H), 6.82 (d, $J = 8.0$ Hz, 2H), 6.73 (s, 1H), 5.99 (s, 1H), 1.31 (s, 18H) ppm; $^{13}\text{C NMR}$ (125 MHz, $\text{DMSO-}d_6$) δ 155.0, 151.70, 140.3, 138.7, 138.6, 134.0, 130.5, 129.9, 128.8, 127.1, 126.3, 125.2, 116.8, 113.1, 42.2, 34.4, 30.4 ppm; IR (KBr, cm^{-1}): 3629, 2957, 1610, 1568, 1488, 1433, 1232, 821; HRMS (ESI) calcd for $\text{C}_{39}\text{H}_{39}\text{O}_3^- [\text{M-H}]^-$: 555.2905, found: 555.2896.

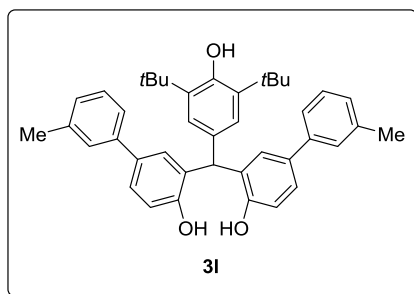


6,6'-((3,5-di-tert-butyl-4-hydroxyphenyl)methylene)bis(2-methoxyphenol) (3j):

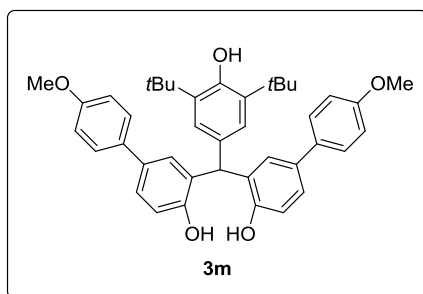
Prepared according to the general procedure **II** above and obtained as yellow solid (22 mg, 47% yield), melting point: 80-82 °C; ¹H NMR (500 MHz, DMSO-*d*₆) δ 8.31 (s, 2H), 6.77 (d, *J* = 8.0 Hz, 4H), 6.69 (s, 1H), 6.63 (t, *J* = 8.0 Hz, 2H), 6.30 (d, *J* = 7.5 Hz, 2H), 6.00 (s, 1H), 3.75 (s, 6H), 1.28 (s, 18H) ppm; ¹³C NMR (125 MHz, DMSO-*d*₆) δ 151.6, 147.0, 143.5, 138.4, 134.4, 131.3, 125.1, 121.5, 117.7, 109.3, 55.7, 42.2, 34.4, 30.4 ppm; IR (KBr, cm⁻¹): 3622, 2957, 1610, 1479, 1434, 1275, 1214, 1025, 770, 749; HRMS (ESI) calcd for C₂₉H₃₅O₅⁻[M-H]⁻: 463.2490, found: 463.2492.



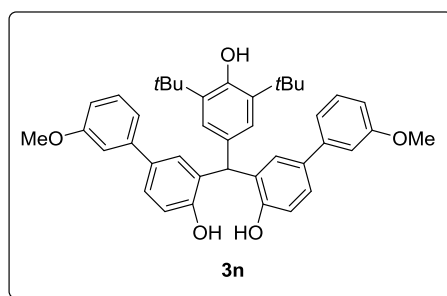
3,3''-((3,5-di-tert-butyl-4-hydroxyphenyl)methylene)bis(4'-methyl-[1,1'-biphenyl]-4-ol) (3k): Prepared according to the general procedure **II** above and obtained as colorless oil (52 mg, 90% yield); ¹H NMR (500 MHz, DMSO-*d*₆) δ 9.39 (s, 2H), 7.28 – 7.23 (m, 6H), 7.14 (d, *J* = 8.0 Hz, 4H), 7.04 (s, 2H), 6.98 (s, 2H), 6.83 (d, *J* = 8.5 Hz, 2H), 6.77 (s, 1H), 6.00 (s, 1H), 2.25 (s, 6H), 1.32 (s, 18H) ppm; ¹³C NMR (125 MHz, DMSO-*d*₆) δ 154.3, 151.8, 138.6, 137.9, 135.4, 133.5, 131.3, 130.2, 129.4, 127.5, 125.5, 125.4, 124.8, 115.4, 42.7, 34.5, 30.4, 20.5 ppm; IR (KBr, cm⁻¹): 3626, 2957, 1606, 1498, 1432, 1231, 1024, 888, 811, 762; HRMS (ESI) calcd for C₄₁H₄₃O₃⁻[M-H]⁻: 583.3218, found: 583.3210.



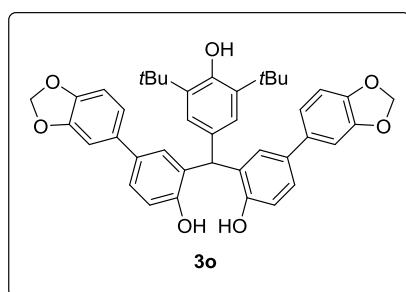
3,3'-(3,5-di-tert-butyl-4-hydroxyphenyl)methylenebis(3'-methyl-[1,1'-biphenyl]-4-ol) (3l): Prepared according to the general procedure **II** above and obtained as colorless oil (32 mg, 56% yield); ^1H NMR (500 MHz, $\text{DMSO-}d_6$) δ 9.48 (s, 2H), 7.30 – 7.29 (m, 2H), 7.23 – 7.16 (m, 6H), 7.10 (s, 2H), 7.02 (d, $J = 7.5$ Hz, 4H), 6.85 (d, $J = 8.0$ Hz, 2H), 6.81 (s, 1H), 6.03 (s, 1H), 2.27 (s, 6H), 1.34 (s, 18H) ppm; ^{13}C NMR (125 MHz, $\text{DMSO-}d_6$) δ 154.5, 151.8, 140.7, 138.7, 137.7, 133.4, 131.2, 130.3, 128.7, 127.8, 126.9, 126.4, 125.4, 125.1, 122.8, 115.4, 42.6, 34.5, 30.4, 21.1 ppm; IR (KBr, cm^{-1}): 2955, 1604, 1511, 1481, 1433, 1232, 1024, 888, 824, 703; HRMS (ESI) calcd for $\text{C}_{41}\text{H}_{43}\text{O}^3\text{[M-H]}^-$: 583.3218, found: 583.3207.



3,3'-(3,5-di-tert-butyl-4-hydroxyphenyl)methylenebis(4'-methoxy-[1,1'-biphenyl]-4-ol) (3m): Prepared according to the general procedure **II** above and obtained as colorless oil (22 mg, 36% yield); ^1H NMR (500 MHz, $\text{DMSO-}d_6$) δ 9.33 (s, 2H), 7.27 (d, $J = 8.5$ Hz, 4H), 7.24 (dd, $J = 8.3, 2.2$ Hz, 2H), 6.99 (d, $J = 2.0$ Hz, 2H), 6.97 (s, 2H), 6.91 (d, $J = 8.5$ Hz, 4H), 6.81 (d, $J = 8.0$ Hz, 2H), 6.77 (s, 1H), 5.98 (s, 1H), 3.73 (s, 6H), 1.32 (s, 18H) ppm; ^{13}C NMR (125 MHz, $\text{DMSO-}d_6$) δ 158.0, 154.0, 151.7, 138.6, 133.6, 133.3, 131.3, 130.0, 127.2, 126.7, 125.4, 124.6, 115.4, 114.3, 55.1, 42.7, 34.5, 30.4 ppm; IR (KBr, cm^{-1}): 3625, 2956, 1607, 1498, 1434, 1245, 1025, 822, 763; HRMS (ESI) calcd for $\text{C}_{41}\text{H}_{43}\text{O}_5^3\text{[M-H]}^-$: 615.3116, found: 615.3105.

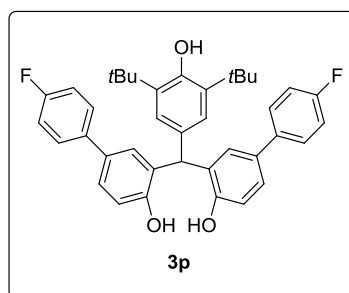


3,3'-((3,5-di-tert-butyl-4-hydroxyphenyl)methylene)bis(3'-methoxy-[1,1'-biphenyl]-4-ol) (3n): Prepared according to the general procedure **II** above and obtained as colorless oil (30 mg, 49% yield); $^1\text{H NMR}$ (500 MHz, $\text{DMSO-}d_6$) δ 9.47 (s, 2H), 7.31 (dd, $J = 8.2, 2.1$ Hz, 2H), 7.25 (t, $J = 8.0$ Hz, 2H), 7.05 (d, $J = 2.0$ Hz, 2H), 6.98 (s, 2H), 6.94 (d, $J = 7.5$ Hz, 2H), 6.86 – 6.83 (m, 4H), 6.80 – 6.78 (m, 3H), 6.01 (s, 1H), 3.72 (s, 6H), 1.32 (s, 18H) ppm; $^{13}\text{C NMR}$ (125 MHz, $\text{DMSO-}d_6$) δ 159.6, 154.7, 151.8, 142.1, 138.7, 133.4, 131.2, 130.0, 129.8, 127.7, 125.4, 125.1, 118.0, 115.4, 111.8, 111.2, 54.8, 42.6, 34.5, 30.4 ppm; IR (KBr, cm^{-1}): 3626, 2956, 1604, 1578, 1481, 1435, 1363, 1278, 1219, 1024, 888, 824, 699; HRMS (ESI) calcd for $\text{C}_{41}\text{H}_{43}\text{O}_5$ [M-H] $^-$: 615.3116, found: 615.3111.

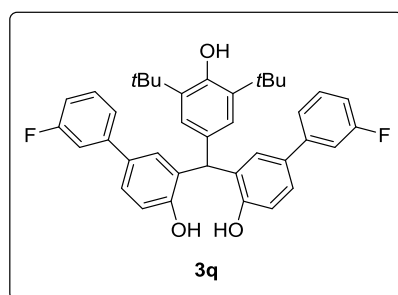


2,2'-((3,5-di-tert-butyl-4-hydroxyphenyl)methylene)bis(4-(benzo[d][1,3]dioxol-5-yl)phenol) (3o): Prepared according to the general procedure **II** above and obtained as colorless oil (29 mg, 45% yield). $^1\text{H NMR}$ (500 MHz, $\text{DMSO-}d_6$) δ 9.46 (s, 2H), 7.23 (dd, $J = 8.3, 1.6$ Hz, 2H), 6.95 (d, $J = 4.0$ Hz, 4H), 6.89 – 6.85 (m, 4H), 6.81 (d, $J = 7.5$ Hz, 5H), 5.97 (d, $J = 2.0$ Hz, 5H), 1.32 (s, 18H) ppm; $^{13}\text{C NMR}$ (125 MHz, $\text{DMSO-}d_6$) δ 154.2, 151.8, 147.8, 145.9, 138.7, 135.2, 133.4, 131.2, 130.0, 127.4, 125.4, 124.9, 118.9, 115.3, 108.6, 106.1, 100.9, 42.8, 34.5, 30.4 ppm; IR (KBr, cm^{-1}):

3623, 2955, 1605, 1482, 1430, 1228, 1026, 859, 809, 763; HRMS (ESI) calcd for $C_{41}H_{39}O_7[M-H]^-$: 643.2701, found: 643.2690.

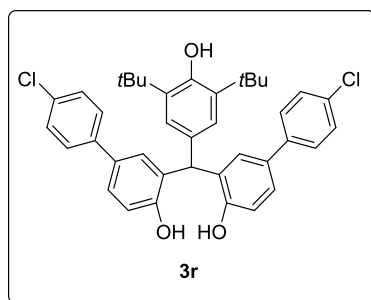


3,3'-((3,5-di-tert-butyl-4-hydroxyphenyl)methylene)bis(4'-fluoro-[1,1'-biphenyl]-4-ol) (3p): Prepared according to the general procedure **II** above and obtained as colorless oil (27 mg, 47% yield); 1H NMR (500 MHz, $DMSO-d_6$) δ 9.46 (s, 2H), 7.37 – 7.34 (m, 4H), 7.29 – 7.27 (m, 2H), 7.18 (t, $J = 8.5$ Hz, 4H), 7.00 (d, $J = 2.0$ Hz, 2H), 6.95 (s, 2H), 6.84 (d, $J = 8.0$ Hz, 2H), 6.78 (s, 1H), 5.98 (s, 1H), 1.31 (s, 18H) ppm; ^{13}C NMR (125 MHz, $DMSO-d_6$) δ 161.1 (d, $J = 243.6$ Hz), 154.6, 151.8, 138.6, 137.3 (d, $J = 3.0$ Hz), 133.4, 131.3, 129.3, 127.6, 127.4 (d, $J = 8.1$ Hz), 125.4, 125.2, 115.6 (d, $J = 21.3$ Hz), 115.5, 42.9, 34.4, 30.4 ppm; IR (KBr, cm^{-1}): 2955, 1605, 1496, 1433, 1225, 1025, 821, 762; HRMS (ESI) calcd for $C_{39}H_{37}F_2O_3[M-H]^-$: 591.2716, found: 591.2708.

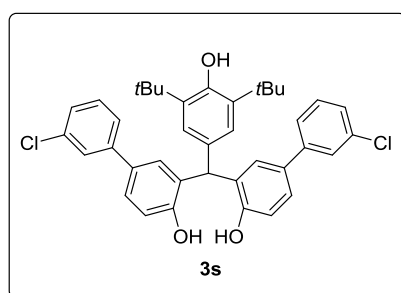


3,3'-((3,5-di-tert-butyl-4-hydroxyphenyl)methylene)bis(3'-fluoro-[1,1'-biphenyl]-4-ol) (3q): Prepared according to the general procedure **II** above and obtained as colorless oil (15.4 mg, 26% yield); 1H NMR (500 MHz, $DMSO-d_6$) δ 9.59 (s, 2H), 7.40 – 7.36 (m, 4H), 7.19 (d, $J = 8.0$ Hz, 2H), 7.13 (d, $J = 10.5$ Hz, 2H), 7.06 – 7.02 (m, 4H), 6.97 (s, 2H), 6.86 (d, $J = 8.5$ Hz, 2H), 6.81 (s, 1H), 5.98 (s, 1H), 1.32 (s, 18H) ppm; ^{13}C NMR (125 MHz, $DMSO-d_6$) δ 164.1, 162.2, 155.7, 152.4, 143.7 (d, $J = 7.3$

Hz), 139.3, 133.7, 131.8, 131.3 (d, $J = 8.2$ Hz), 129.2, 128.1, 125.9, 122.0, 116.0, 113.4 (d, $J = 21.2$ Hz), 112.6 (d, $J = 21.8$ Hz), 43.5, 35.0, 30.9 ppm; IR (KBr, cm^{-1}): 2957, 1608, 1581, 1481, 1435, 1233, 1025, 889, 784, 695; HRMS (ESI) calcd for $\text{C}_{39}\text{H}_{37}\text{F}_2\text{O}_3^-[\text{M-H}]^-$: 591.2716, found: 591.2709.

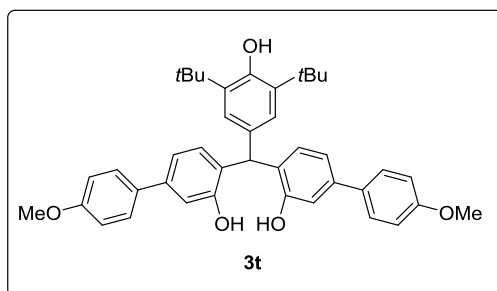


3,3'-((3,5-di-tert-butyl-4-hydroxyphenyl)methylene)bis(4'-chloro-[1,1'-biphenyl]-4-ol) (3r): Prepared according to the general procedure **II** above and obtained as colorless oil (20 mg, 32% yield); ^1H NMR (500 MHz, $\text{DMSO-}d_6$) δ 9.55 (s, 2H), 7.40 (d, $J = 8.5$ Hz, 4H), 7.35 (d, $J = 8.5$ Hz, 4H), 7.32 (dd, $J = 8.2, 2.2$ Hz, 2H), 7.02 (d, $J = 2.5$ Hz, 2H), 6.94 (s, 2H), 6.85 (d, $J = 8.0$ Hz, 2H), 6.79 (s, 1H), 5.98 (s, 1H), 1.31 (s, 18H) ppm; ^{13}C NMR (125 MHz, $\text{DMSO-}d_6$) δ 154.9, 151.8, 139.6, 138.7, 133.3, 131.4, 131.0, 128.9, 128.8, 127.5, 127.3, 125.3, 125.2, 115.6, 42.9, 34.5, 30.4 ppm; IR (KBr, cm^{-1}): 3629, 2957, 1606, 1485, 1432, 1232, 1024, 818, 760; HRMS (ESI) calcd for $\text{C}_{39}\text{H}_{37}\text{Cl}_2\text{O}_3^-[\text{M-H}]^-$: 623.2125, found: 623.2117.

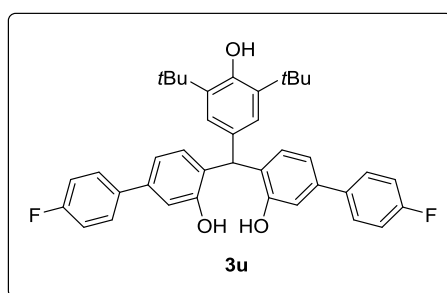


3,3'-((3,5-di-tert-butyl-4-hydroxyphenyl)methylene)bis(3'-chloro-[1,1'-biphenyl]-4-ol) (3s): Prepared according to the general procedure **II** above and obtained as colorless oil (23 mg, 38% yield); ^1H NMR (500 MHz, $\text{DMSO-}d_6$) δ 9.60 (s, 2H), 7.39 – 7.32 (m, 8H), 7.27 (d, $J = 8.0$ Hz, 2H), 7.06 (d, $J = 1.5$ Hz, 2H), 6.98 (s, 2H), 6.86 (d, $J = 8.5$ Hz, 2H), 6.81 (s, 1H), 5.99 (s, 1H), 1.33 (s, 18H) ppm; ^{13}C NMR (125

MHz, DMSO-*d*₆) δ 155.2, 151.9, 142.8, 138.8, 133.6, 133.1, 131.3, 130.7, 128.5, 127.6, 126.0, 125.4, 125.3, 124.2, 115.6, 42.9, 34.5, 30.4 ppm; IR (KBr, cm⁻¹): 3629, 2957, 1595, 1564, 1512, 1434, 1232, 1024, 884, 825, 695; HRMS (ESI) calcd for C₃₉H₃₇Cl₂O₃⁻[M-H]⁻: 623.2125, found: 623.2112.

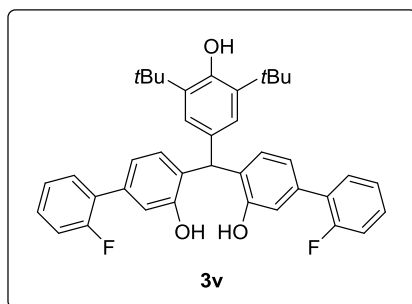


4,4'-((3,5-di-tert-butyl-4-hydroxyphenyl)methylene)bis(4'-methoxy-[1,1'-biphenyl]-3-ol) (3t): Prepared according to the general procedure **II** above and obtained as colorless oil (20 mg, 33% yield); ¹H NMR (500 MHz, DMSO-*d*₆) δ 9.32 (s, 2H), 7.49 (d, *J* = 8.5 Hz, 4H), 7.00 – 6.95 (m, 8H), 6.87 (s, 2H), 6.78 (d, *J* = 8.0 Hz, 2H), 6.73 (s, 1H), 5.95 (s, 1H), 3.78 (s, 6H), 1.31 (s, 18H) ppm; ¹³C NMR (125 MHz, DMSO-*d*₆) δ 159.1, 155.4, 152.2, 139.1, 138.8, 134.7, 133.1, 130.2, 127.8, 125.7, 116.8, 114.8, 113.1, 55.6, 42.6, 34.9, 30.9 ppm; IR (KBr, cm⁻¹): 3634, 2949, 1607, 1501, 1431, 1405, 1231, 1046, 833; HRMS (ESI) calcd for C₄₁H₄₃O₅⁻[M-H]⁻: 615.3116, found: 615.3110.

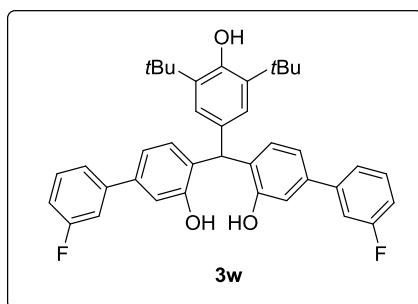


4,4'-((3,5-di-tert-butyl-4-hydroxyphenyl)methylene)bis(4'-fluoro-[1,1'-biphenyl]-3-ol) (3u): Prepared according to the general procedure **II** above and obtained as colorless oil (25mg, 42% yield). ¹H NMR (500 MHz, DMSO-*d*₆) δ 9.45 (s, 2H), 7.60 – 7.57 (m, 4H), 7.25 (t, *J* = 9.0 Hz, 4H), 7.01 – 6.98 (m, 4H), 6.87 (s, 2H), 6.80 (d, *J* = 7.5Hz, 2H), 6.75 (s, 1H), 5.97 (s, 1H), 1.31 (s, 18H) ppm; ¹³C NMR (125 MHz,

DMSO-*d*₆) δ 155.5, 152.2, 139.1, 138.2, 137.2, 134.4, 130.9, 130.4, 128.7 (d, $J = 7.4$ Hz), 125.7, 117.2, 116.1 (d, $J = 21.3$ Hz), 113.5, 42.6, 34.9, 30.9 ppm; IR (KBr, cm^{-1}): 3635, 2959, 1601, 1499, 1432, 1230, 833, 811; HRMS (ESI) calcd for $\text{C}_{39}\text{H}_{37}\text{F}_2\text{O}_3[\text{M-H}]^-$: 591.2716, found: 591.2701.

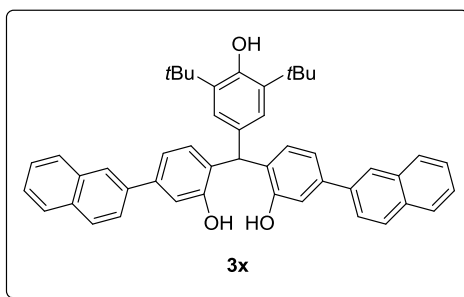


4,4'-((3,5-di-tert-butyl-4-hydroxyphenyl)methylene)bis(2'-fluoro-[1,1'-biphenyl]-3-ol) (3v): Prepared according to the general procedure **II** above and obtained as colorless oil (29mg, 49%); ^1H NMR (500 MHz, DMSO-*d*₆) δ 9.46 (s, 2H), 7.48 – 7.45 (m, 2H), 7.39 – 7.35 (m, 2H), 7.29– 7.25 (m, 4H), 6.98 (s, 2H), 6.92 – 6.87 (m, 4H), 6.83 (d, $J = 8.0$ Hz, 2H), 6.74 (s, 1H), 6.00 (s, 1H), 1.31 (s, 18H) ppm; ^{13}C NMR (125 MHz, DMSO-*d*₆) δ 159.0(d, $J = 244.3$ Hz), 154.5, 151.8, 138.6, 133.5, 130.8, 130.4, 129.5, 129.1 (d, $J = 7.1$ Hz), 128.3, 128.2, 125.3, 124.8, 118.8, 116.1 (d, $J = 22.7$ Hz), 115.3, 42.3, 34.4, 30.4 ppm; IR (KBr, cm^{-1}): 3631, 2957, 1612, 1585, 1485, 1413, 1232, 1025, 812; HRMS (ESI) calcd for $\text{C}_{39}\text{H}_{37}\text{F}_2\text{O}_3[\text{M-H}]^-$: 591.2716, found: 591.2708.



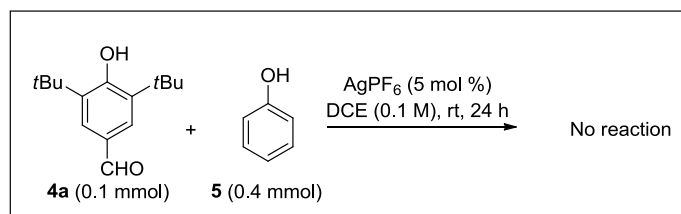
4,4'-((3,5-di-tert-butyl-4-hydroxyphenyl)methylene)bis(3'-fluoro-[1,1'-biphenyl]-3-ol) (3w): Prepared according to the general procedure **II** above and obtained as colorless oil (20mg, 34%); ^1H NMR (500 MHz, DMSO-*d*₆) δ 9.50 (s, 2H), 7.49 – 7.45 (m, 2H), 7.45 – 7.36 (m, 4H), 7.15 (t, $J = 8.0$ Hz, 2H), 7.06 (d, $J = 8.0$ Hz, 4H), 6.87

(s, 2H), 6.82 (d, $J = 8.0$ Hz, 2H), 6.77 (s, 1H), 5.98 (s, 1H), 1.31 (s, 18H) ppm; ^{13}C NMR (125 MHz, $\text{DMSO-}d_6$) δ 163.1 (d, $J = 243.7$ Hz), 155.6, 152.3, 143.2 (d, $J = 7.3$ Hz), 139.2, 137.8, 134.2, 131.6, 131.3 (d, $J = 8.3$ Hz), 130.4, 125.7, 122.9, 117.4, 114.3 (d, $J = 20.9$ Hz), 113.6, 113.4 (d, $J = 22.1$ Hz), 42.8, 34.9, 30.9 ppm; IR (KBr, cm^{-1}): 2958, 1611, 1573, 1483, 1433, 1025, 864, 829; HRMS (ESI) calcd for $\text{C}_{39}\text{H}_{37}\text{F}_2\text{O}_3$ $[\text{M-H}]^-$: 591.2716, found: 591.2709.

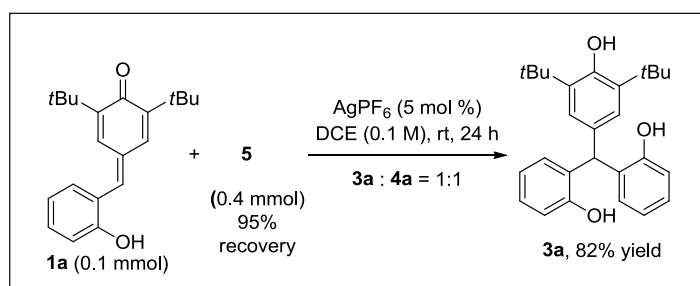


6,6'-((3,5-di-tert-butyl-4-hydroxyphenyl)methylene)bis(3-(naphthalen-2-yl)phenol) (3x): Prepared according to the general procedure **II** above and obtained as colorless oil (45mg, 69% yield); ^1H NMR (500 MHz, $\text{DMSO-}d_6$) δ 9.50 (s, 2H), 8.10 (s, 2H), 7.98 (d, $J = 8.5$ Hz, 4H), 7.92 (d, $J = 7.5$ Hz, 2H), 7.76 (d, $J = 8.5$ Hz, 2H), 7.54 – 7.48 (m, 4H), 7.21 – 7.18 (m, 4H), 6.94 (s, 2H), 6.91 (d, $J = 8.0$ Hz, 2H), 6.78 (s, 1H), 6.05 (s, 1H), 1.34 (s, 18H) ppm; ^{13}C NMR (125 MHz, $\text{DMSO-}d_6$) δ 155.6, 152.3, 139.2, 139.1, 138.2, 134.5, 133.8, 132.6, 131.2, 130.5, 128.9, 128.6, 127.9, 126.8, 126.4, 125.8, 125.5, 125.2, 117.7, 113.9, 42.8, 35.0, 31.0 ppm; IR (KBr, cm^{-1}): 3631, 2922, 1600, 1500, 1433, 1415, 1242, 846, 817; HRMS (ESI) calcd for $\text{C}_{47}\text{H}_{43}\text{O}_3$ $[\text{M-H}]^-$: 655.3218, found: 655.3204.

4. Control Experiments

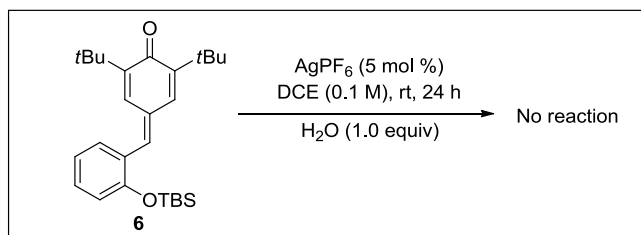


A) Friedel-Crafts reaction of 3,5-di-*tert*-butyl-4-hydroxy benzaldehyde **4a with phenol **5**:** To an oven-dried reaction tube was added 3,5-di-*tert*-butyl-4-hydroxy benzaldehyde **4a** (0.1 mmol), phenol **5** (0.4 mmol) and AgPF_6 (5 mol %), and DCE (1.0 mL) was added. The mixture was stirred for 24 h at room temperature, and no reaction was observed.

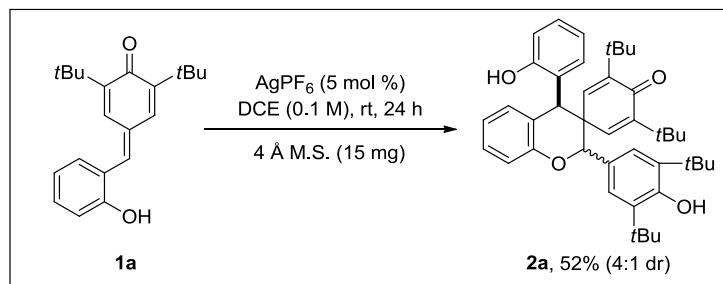


B) 1,6-Michael addition of *ortho*-hydroxyphenyl-substituted *para*-quinone methide **1a with phenol **5**:** To an oven-dried reaction tube was added *ortho*-hydroxyphenyl-substituted *para*-quinone methide **1a** (0.1 mmol), phenol **5** (0.4 mmol) and AgPF_6 (5 mol %), and DCE (1.0 mL) was added. The mixture was stirred for 24 h at room temperature. Purification of mixture by column chromatography on silica gel (PE/EA = 5:1 as eluent) gave the desired product **3a** (33.1 mg, 82% yield) and the recovered phenol **5** (34.6 mg, 95% yield).

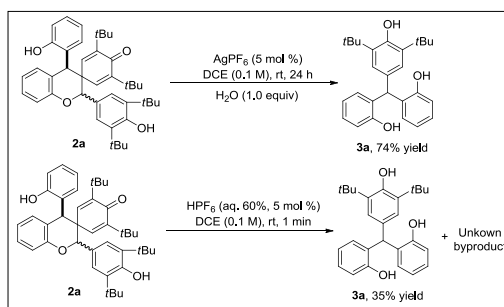
Two observations can exclude the possibility of Michael addition reaction with simple phenol **5**



C) AgPF₆ catalyzed O-TBS protected *ortho*-hydroxyphenyl-substituted *para*-quinone methide **6:** To an oven-dried reaction tube was added **6** (0.1 mmol) and AgPF₆ (5 mol %), and DCE (1.0 mL) was added, Then H₂O (0.1 mmol) was added by dropwise slowly. The mixture was stirred for 24 h at room temperature. No reaction was observed.



D) Synthesis of intermediate 2a: To an oven-dried reaction tube was added *p*-QMs **1a** (0.1 mmol, 1.0 equiv), AgPF₆ (5 mol %), 4 Å M.S. (15 mg) and DCE (1.0 mL). The reaction mixture was then stirred for 24 h at room temperature. Purification of mixture by column chromatography on silica gel (PE/EA = 5:1 as eluent) gave the desired product **2a** (32.0 mg, 52% yield, and 4:1 dr), melting point: 220-222 °C; ¹H NMR (500 MHz, DMSO-*d*₆) δ 9.70 (s, 0.3H), 9.52 (s, 1H), 7.23-7.18 (m, 1.42H), 7.07 (s, 2H), 7.05-6.97 (m, 3H), 6.93-6.80 (m, 7H), 6.75-6.69 (m, 3.2H), 6.60-6.57 (t, *J* = 5 Hz, 0.5H), 6.52-6.45 (m, 2.2H), 5.83 (s, 0.3H), 5.70 (s, 1H), 5.40 (s, 1H), 4.95 (s, 0.3H), 1.34 (s, 23H), 0.98-0.97 (m, 11.6H), 0.92-0.91 (m, 11.8H) ppm; ¹³C NMR (125 MHz, DMSO-*d*₆) δ 185.0, 184.9, 156.1, 154.9, 154.8, 153.9, 153.3, 152.5, 148.9, 148.7, 146.1, 145.0, 142.7, 137.6, 137.5, 136.3, 130.7, 130.1, 129.5, 128.7, 128.2, 127.8, 127.6 (d, *J* = 6.3 Hz), 123.9, 123.7, 123.5, 123.1, 122.6, 120.8, 117.2, 116.4, 116.3, 114.3, 114.2, 83.7, 77.5, 59.7, 47.2, 46.7, 44.3, 34.4, 34.1, 30.2, 28.6, 28.5 ppm; IR (KBr, cm⁻¹): 3638, 2957, 1618, 1582, 1545, 1231, 803, 754; HRMS (ESI) calcd for C₄₂H₅₂O₄Na⁺ [M+Na]⁺: 643.3758, found: 643.3775.



E) Transformation of intermediate 2a: 1) To an oven-dried reaction tube was added **2a** (0.1 mmol, 1.0 equiv), AgPF₆ (5 mol %), H₂O (0.1 mmol, 1.0 equiv) and DCE (1.0 mL). The reaction mixture was then stirred for 24 h at room temperature. Purification of mixture by column chromatography on silica gel (PE/EA = 5:1 as eluent) gave the desired product **3a** (29.9 mg, 74% yield); 2) To an oven-dried reaction tube was added **2a** (0.1 mmol, 1.0 equiv), HPF₆ (aq. 60%, 5 mol %), and DCE (1.0 mL). The reaction mixture was then stirred for 1 min at room temperature. Purification of mixture by column chromatography on silica gel (PE/EA = 5:1 as eluent) gave the desired product **3a** (14.1 mg, 35% yield).

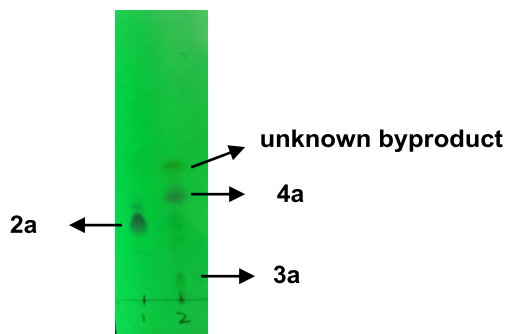
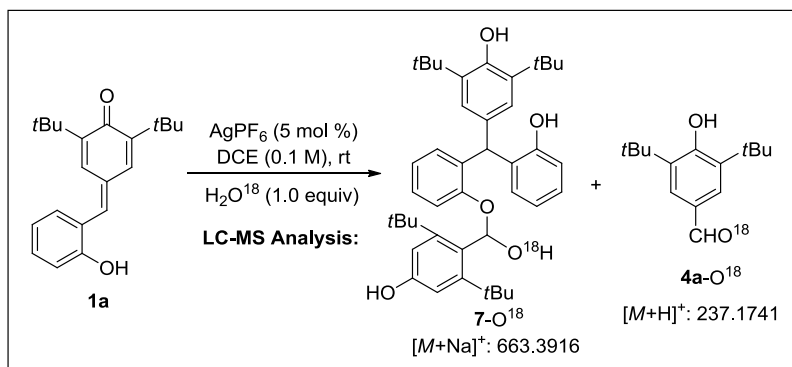
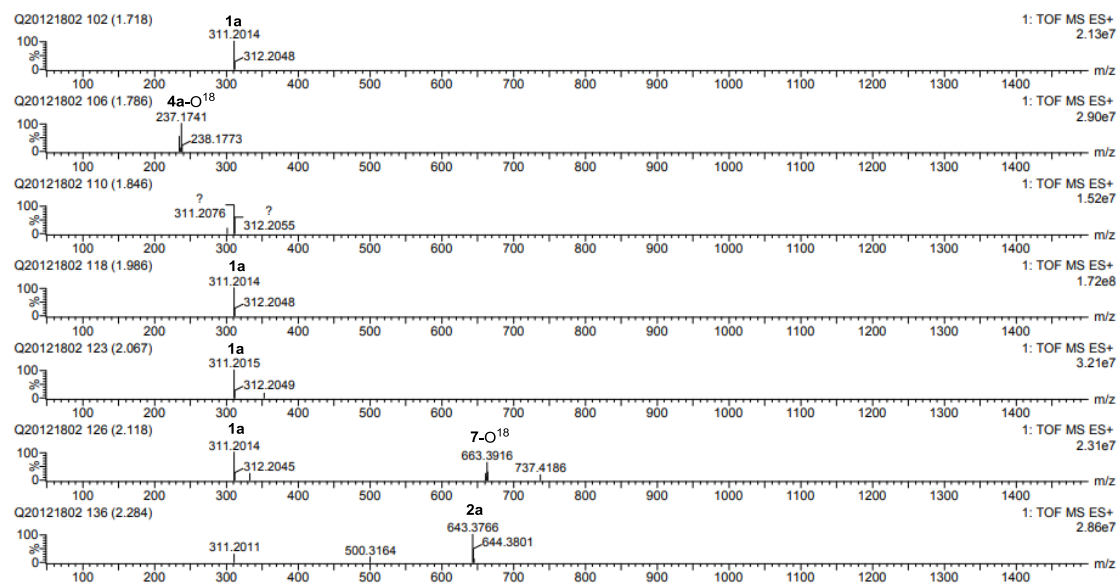


Figure S1 TLC detection in the transformation of intermediate **2a** for 1 min: 1) reaction **E1**; 2) reaction **E2**.



F) The LC-HRMS spectra of the reaction in the presence of H_2O^{18} .



4. X-ray crystal Data

A) X-Ray Structure of product 3a (CCDC 2039963)

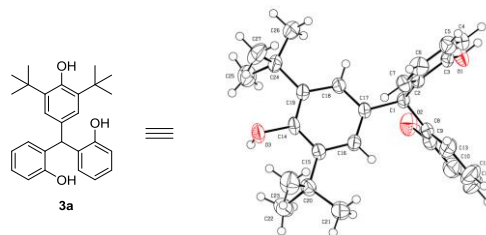


Figure S2 X-Ray Structure of 3a

Table S1 Crystal data and structure refinement for 3a

Empirical formula	C _{13.50} H ₁₆ O _{1.50}
Formula weight	202.26
Temperature	298(2) K
Wavelength	0.71073 Å
Crystal system	Triclinic
Space group	P -1
Unit cell dimensions	a = 10.835(17) Å a = 84.933(17) ° b = 10.925(17) Å b = 64.499(17) ° c = 10.995(17) Å γ = 79.764(19) °
Volume	1156(3) Å ³
Z	4
Density (calculated)	1.162 Mg/m ³
Absorption coefficient	0.074 mm ⁻¹
F(000)	436
Crystal size	0.43 x 0.40 x 0.38 mm ³
Theta range for data collection	2.052 to 25.015 °
Index ranges	-7 ≤ h ≤ 12, -12 ≤ k ≤ 12, -12 ≤ l ≤ 13
Reflections collected	5822
Independent reflections	4006 [R(int) = 0.0382]
Completeness to theta = 25.015 °	98.6 %
Absorption correction	Semi-empirical from equivalents
Max. and min. transmission	0.9724 and 0.9689

Refinement method	Full-matrix least-squares on F ²
Data / restraints / parameters	4006 / 0 / 278
Goodness-of-fit on F ²	1.056
Final R indices [I>2sigma(I)]	R1 = 0.0579, wR2 = 0.1433
R indices (all data)	R1 = 0.0867, wR2 = 0.1576
Extinction coefficient	0.046(5)
Largest diff. peak and hole	0.248 and -0.239 e.Å ⁻³

B) X-Ray Structure of intermediate 2a (CCDC 2085323)

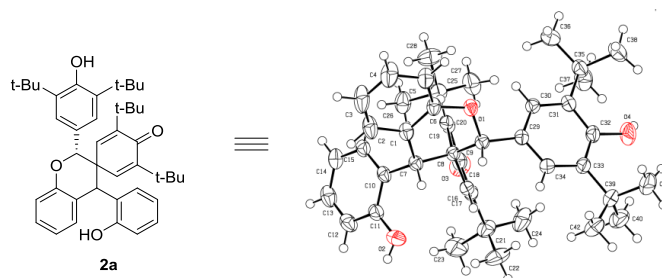


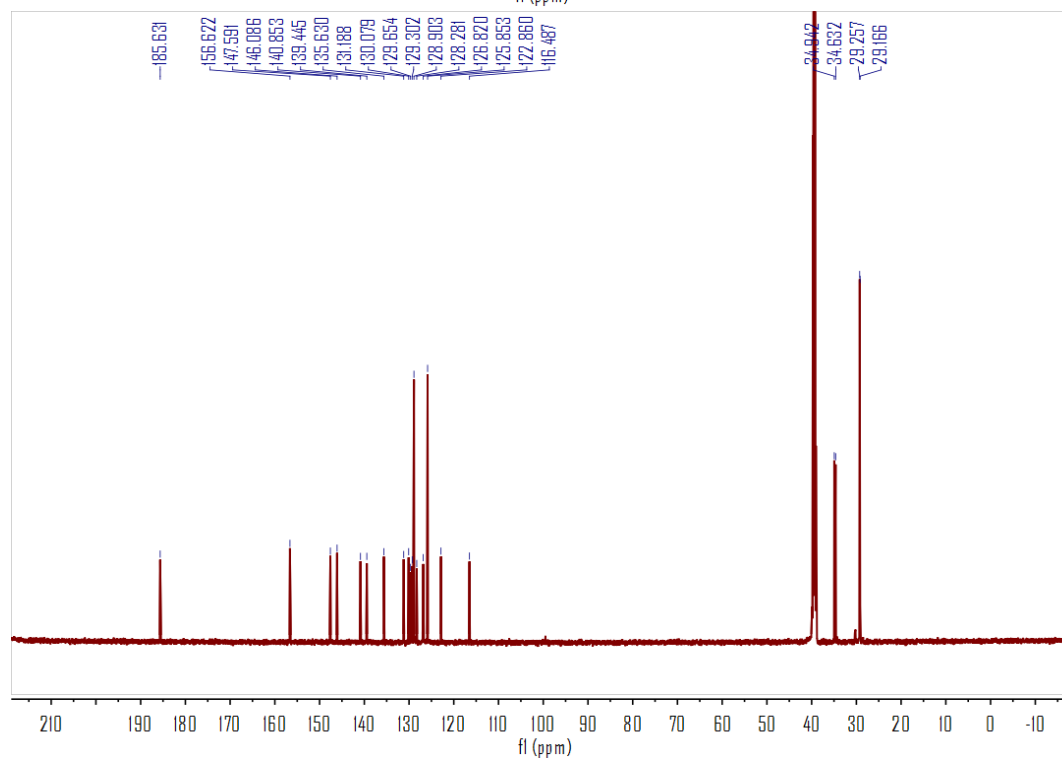
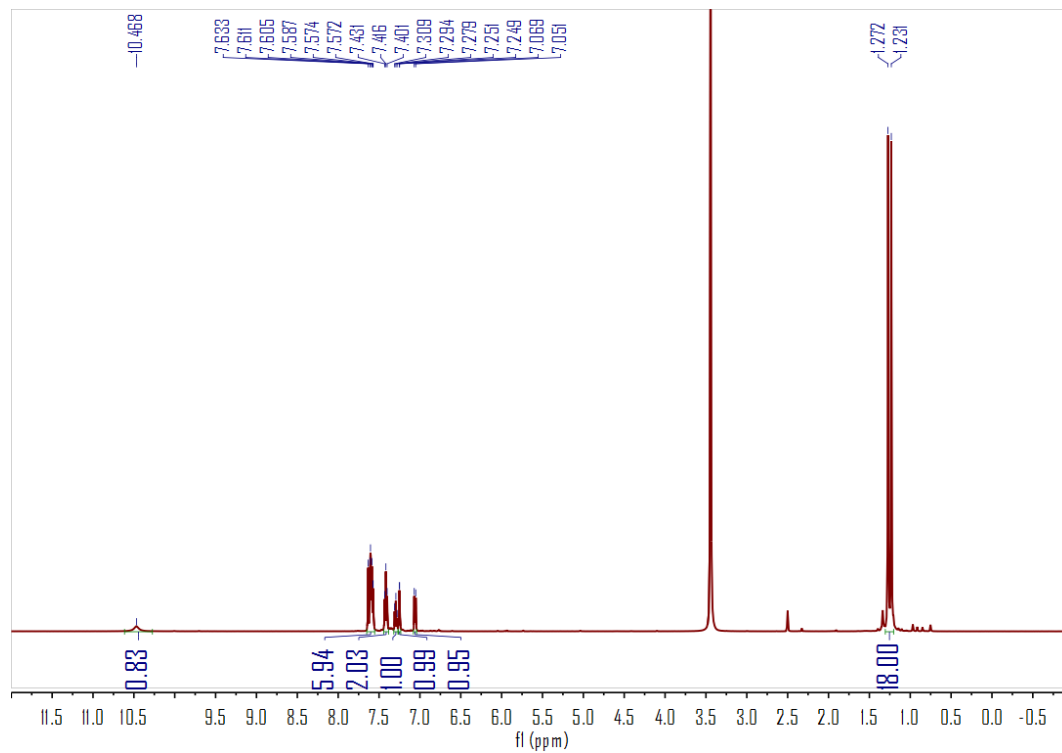
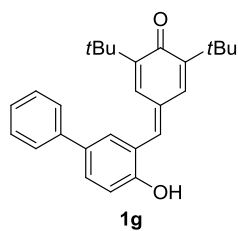
Figure S3 X-Ray Structure of 2a

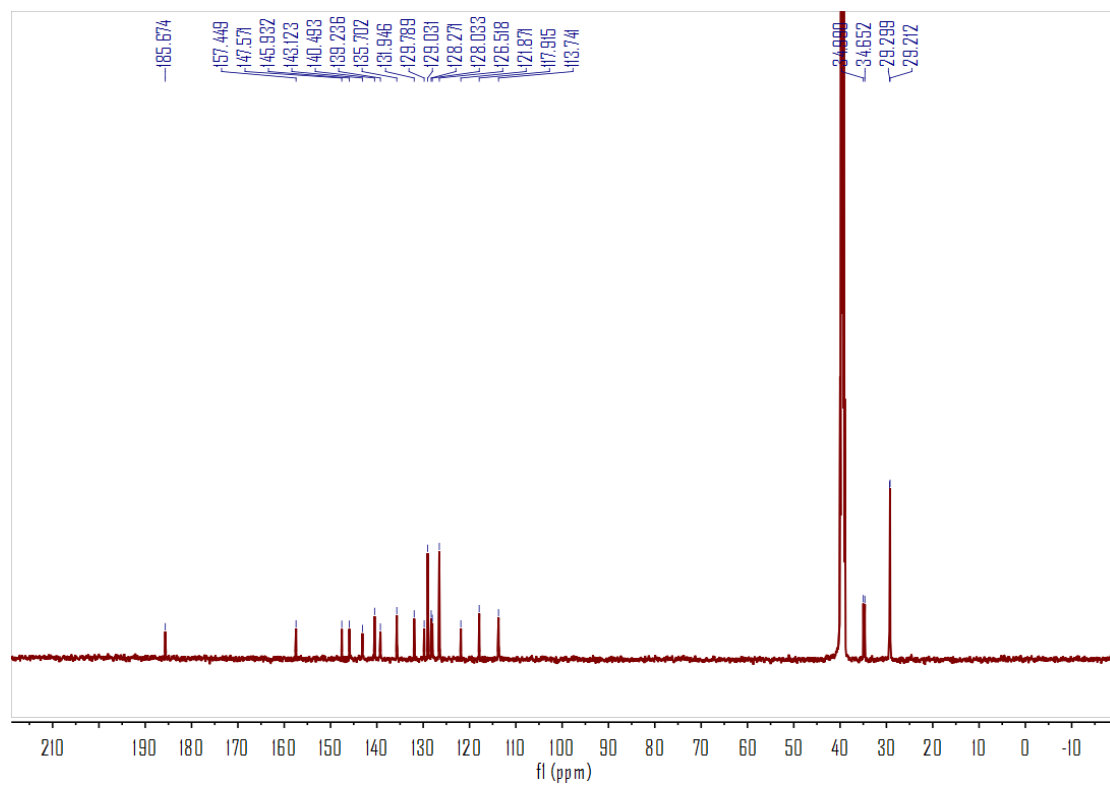
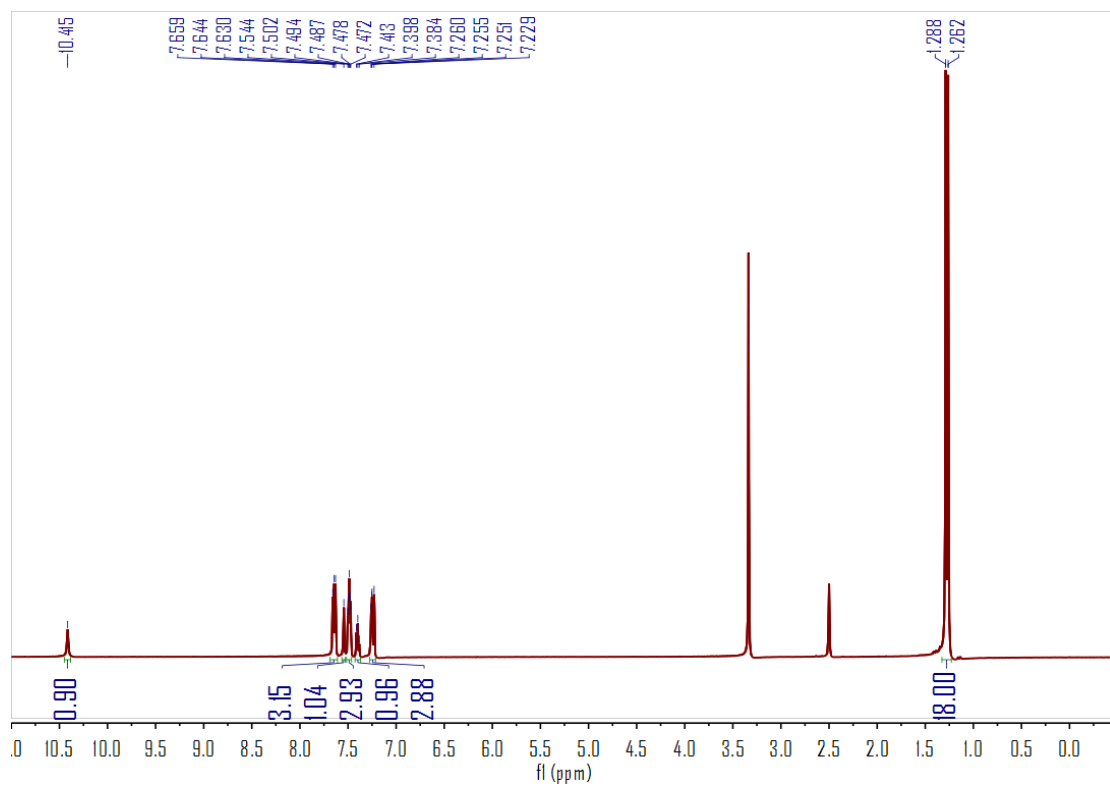
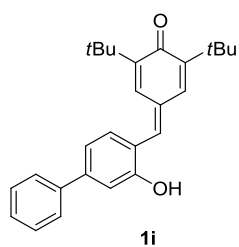
Table S2 Crystal data and structure refinement for 2a

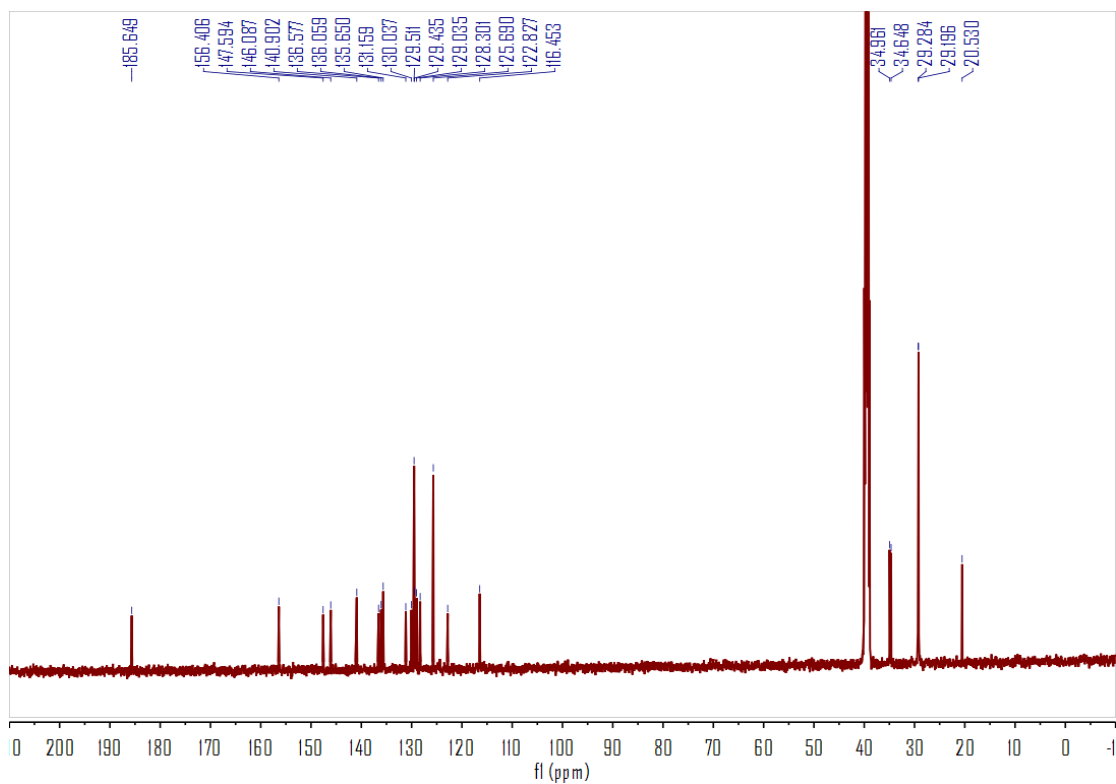
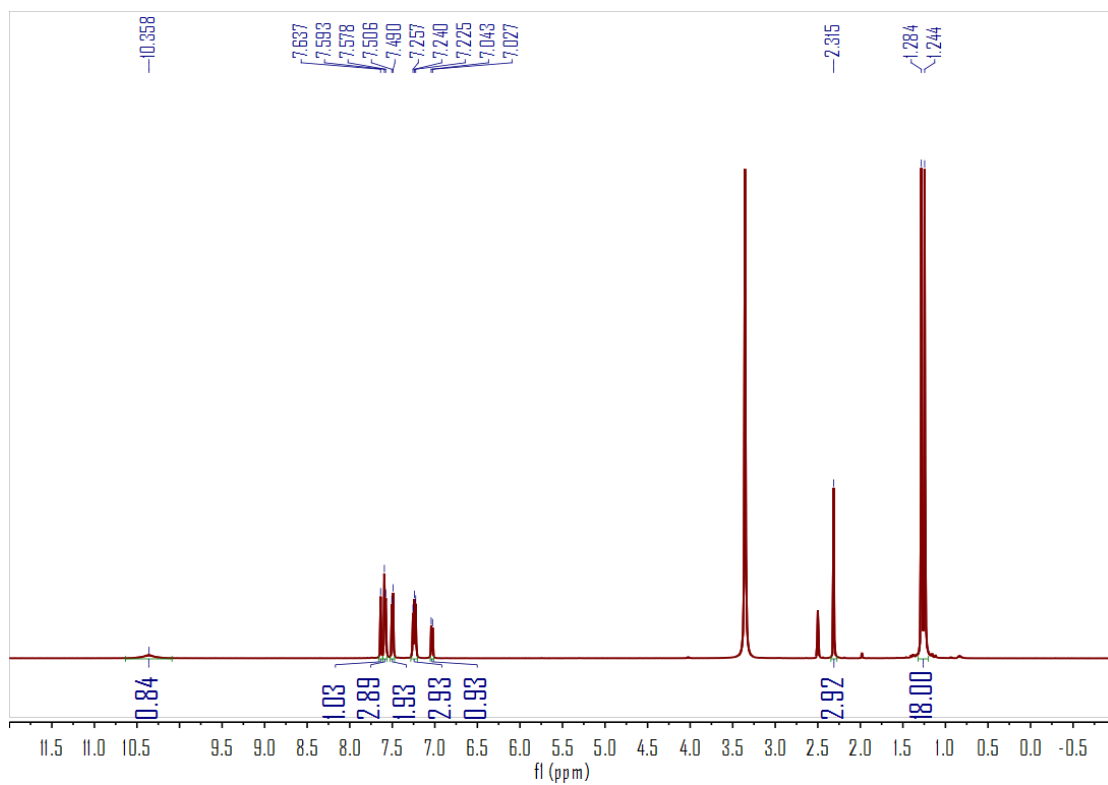
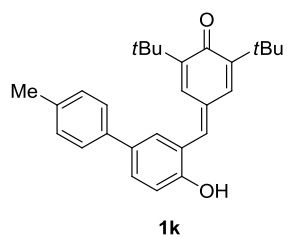
Empirical formula	C ₄₂ H ₅₂ O ₄
Formula weight	620.83
Temperature/K	170.00(10)
Crystal system	monoclinic
Space group	P2 ₁ /n
a/Å	12.5033(6)
b/Å	31.9324(10)
c/Å	12.5127(5)
α /°	90
β /°	108.215(4)
γ /°	90
Volume/Å ³	4745.5(3)
Z	4
$\rho_{\text{calc}}/\text{cm}^3$	0.869
μ/mm^{-1}	0.054
F(000)	1344.0
Crystal size/mm ³	0.28 × 0.23 × 0.17
Radiation	Mo K α (λ = 0.71073)
2 θ range for data collection/°	3.656 to 62.162
Index ranges	-16 ≤ h ≤ 17, -45 ≤ k ≤ 45, -13 ≤ l ≤ 17

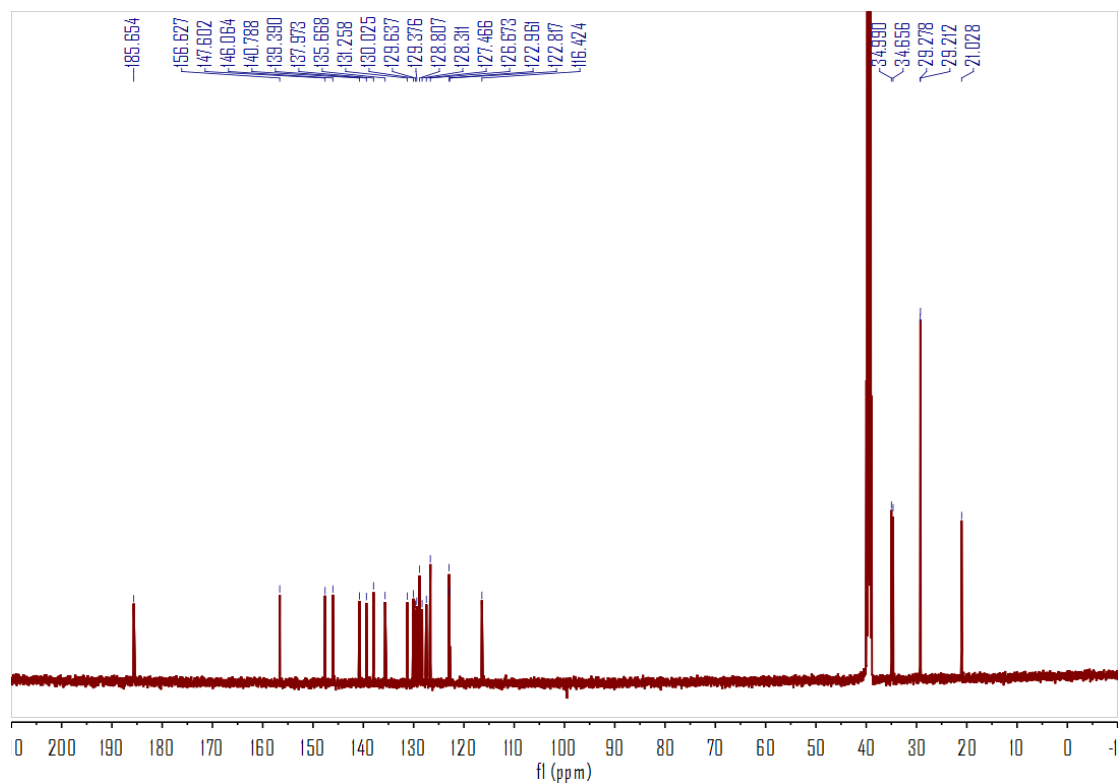
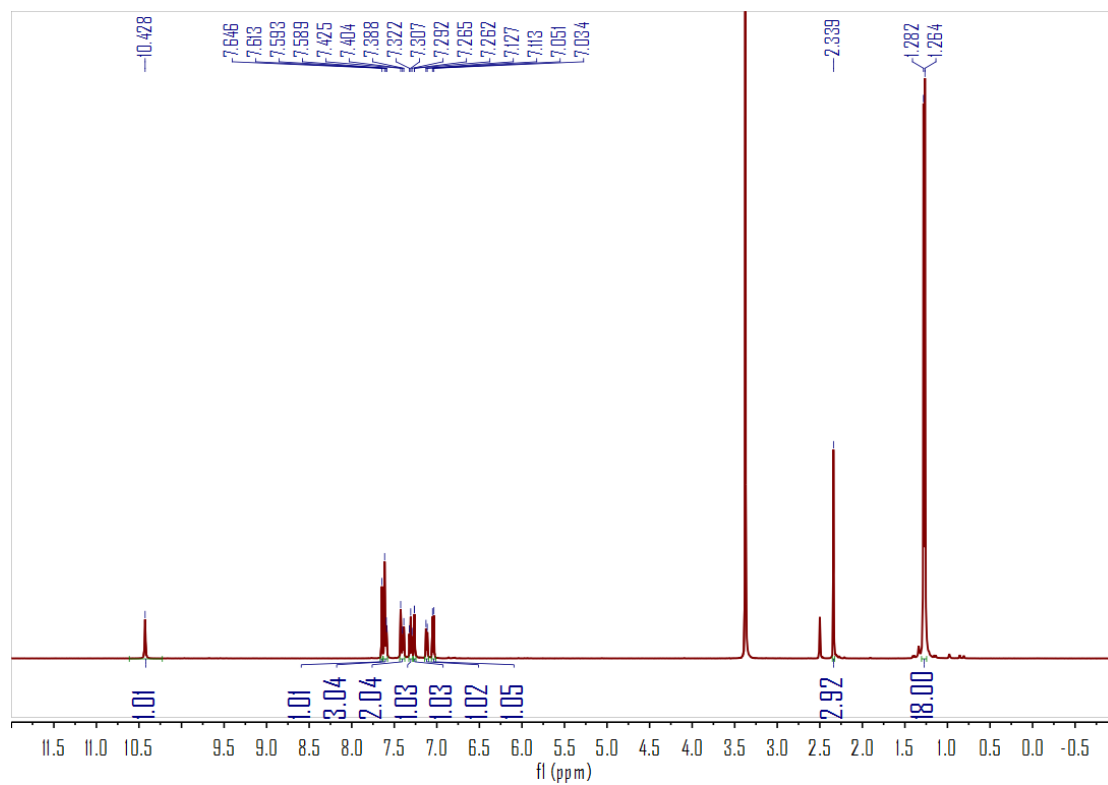
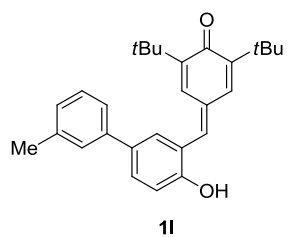
Reflections collected	43438
Independent reflections	12726 [$R_{\text{int}} = 0.0311$, $R_{\text{sigma}} = 0.0414$]
Data/restraints/parameters	12726/1/427
Goodness-of-fit on F^2	1.091
Final R indexes [$I \geq 2\sigma(I)$]	$R_1 = 0.0473$, $wR_2 = 0.1247$
Final R indexes [all data]	$R_1 = 0.0733$, $wR_2 = 0.1334$
Largest diff. peak/hole / $e \text{ \AA}^{-3}$	0.21/-0.29

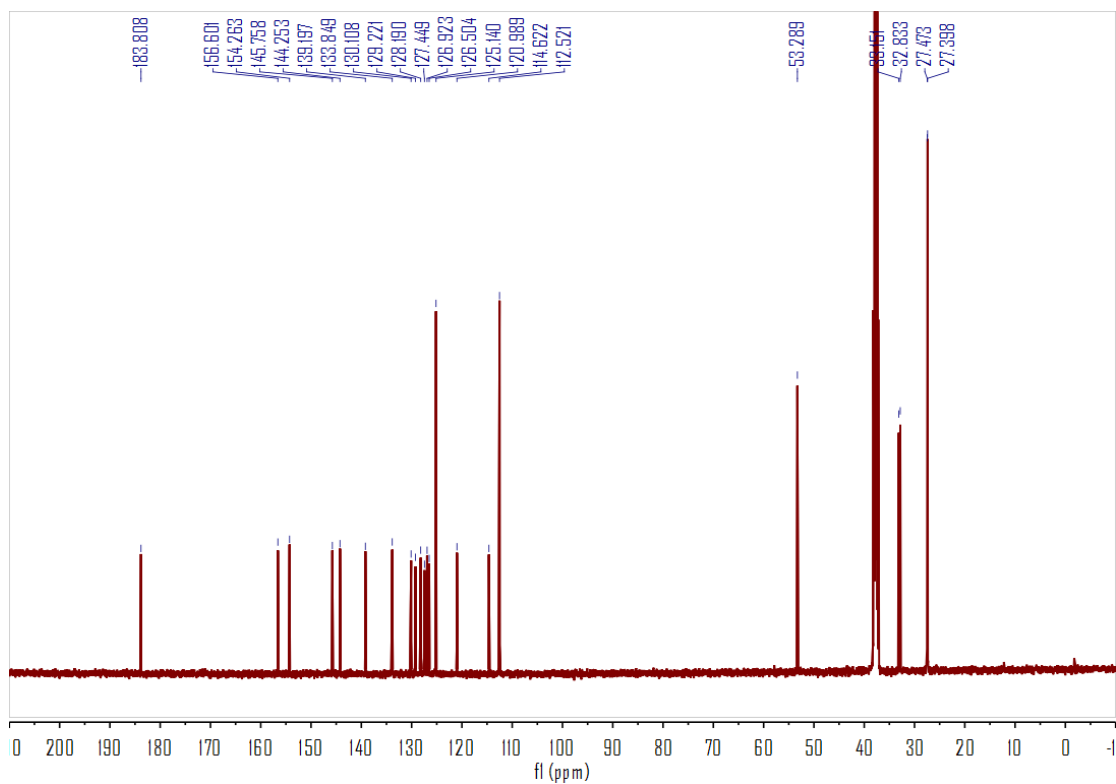
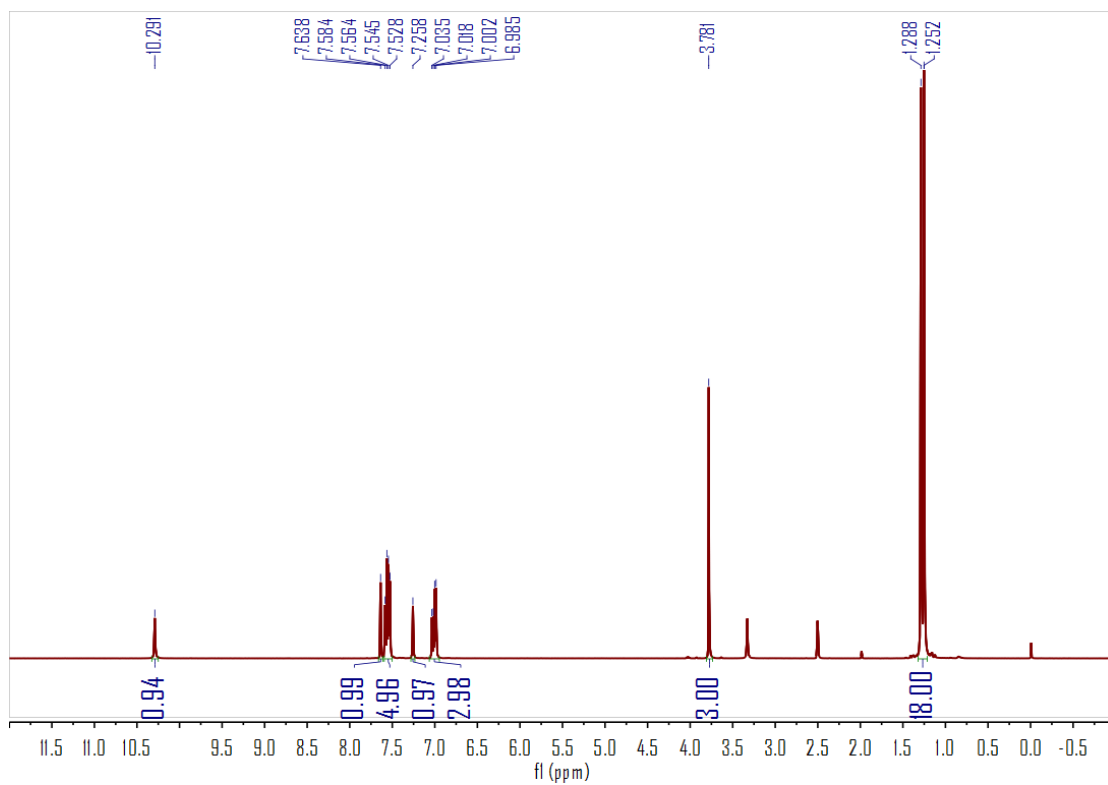
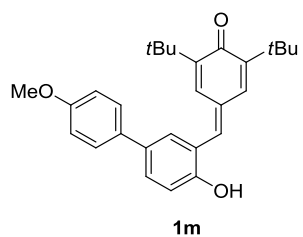
5. NMR Spectrum

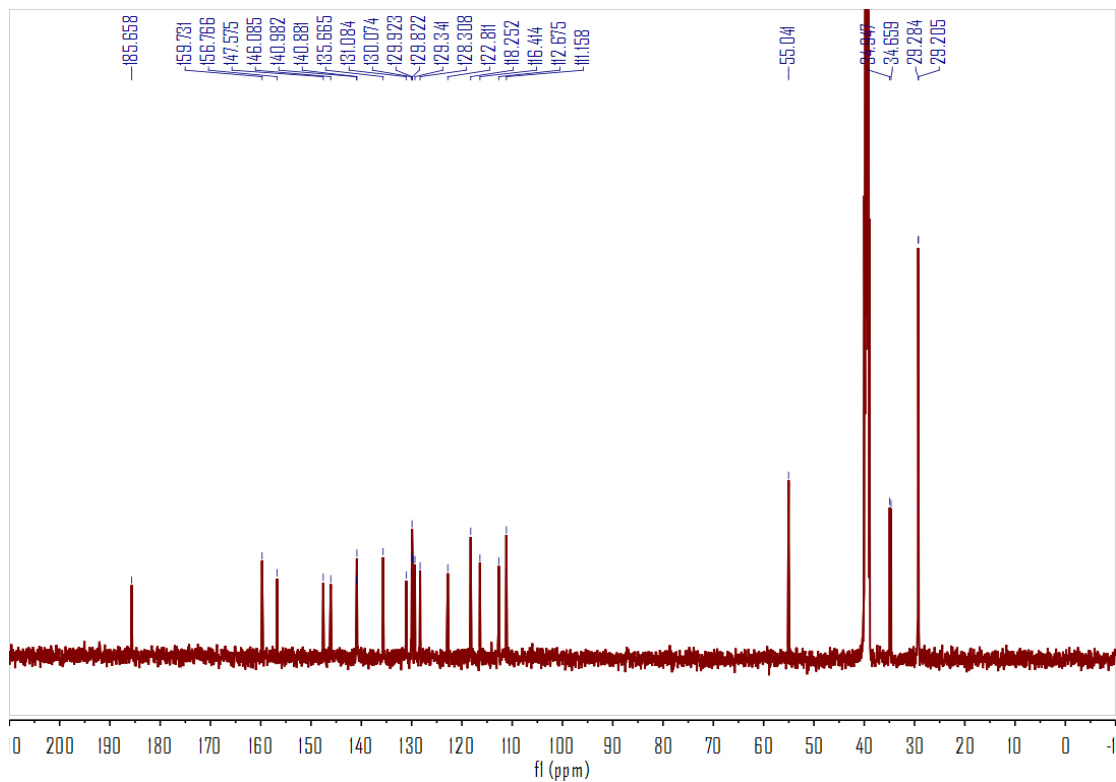
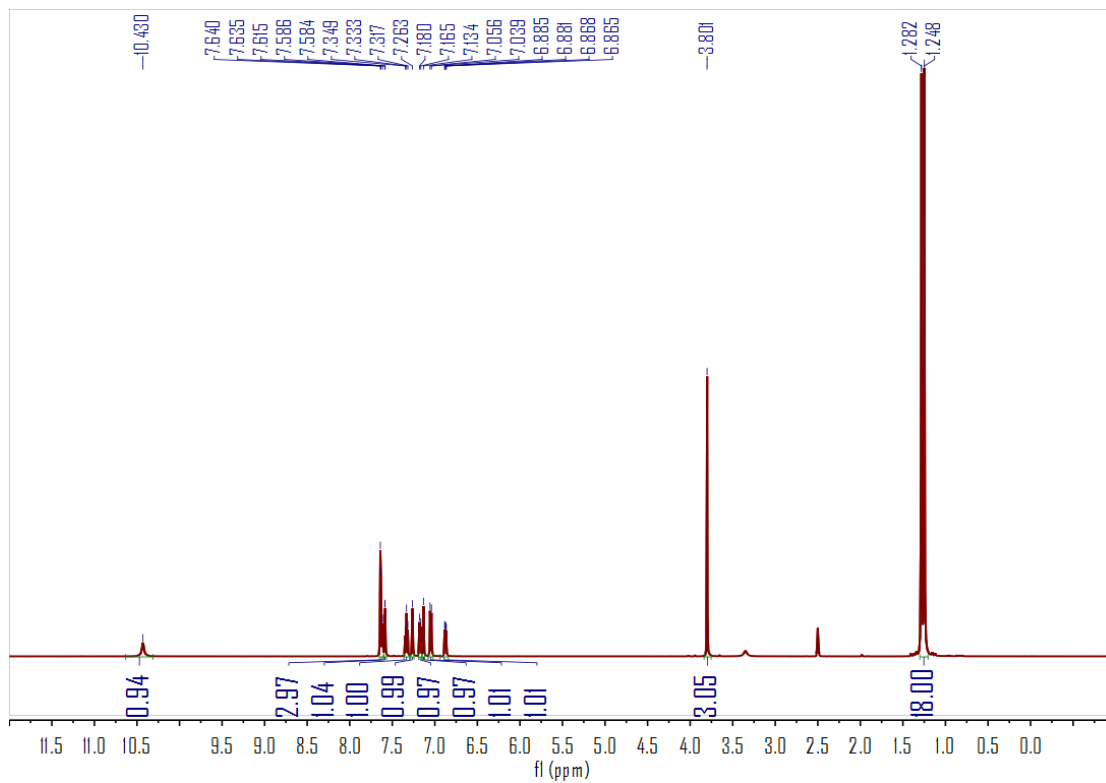
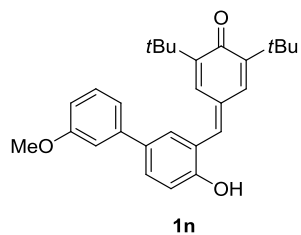


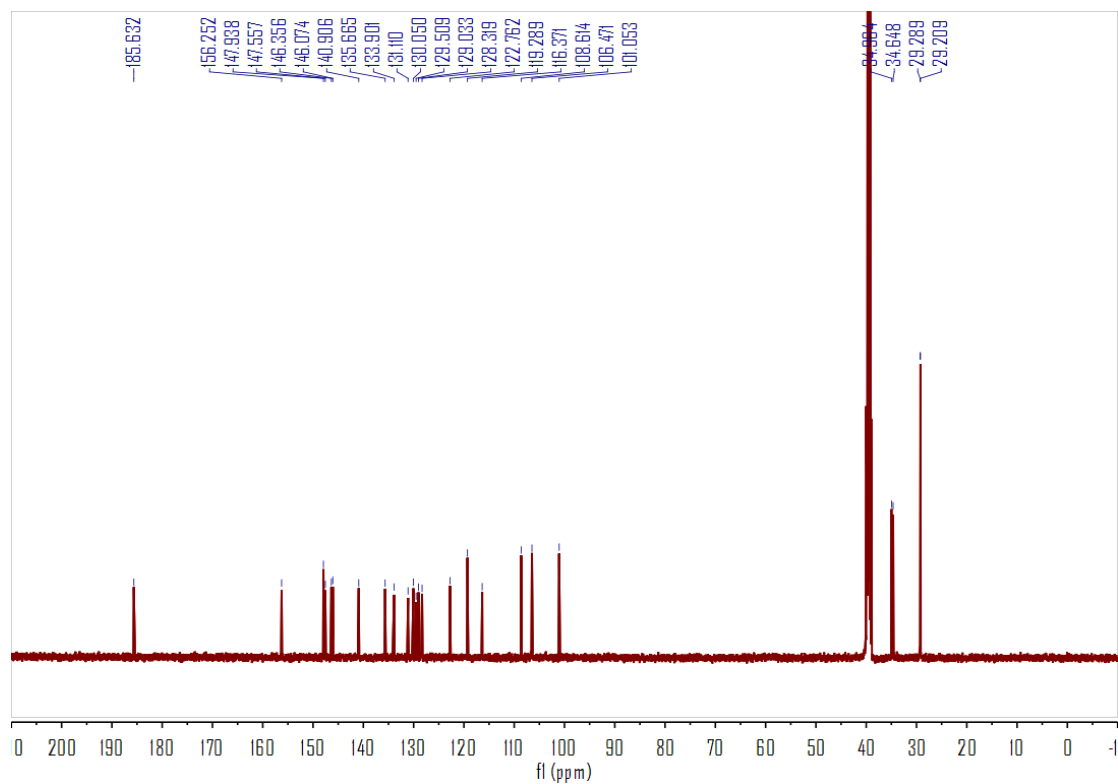
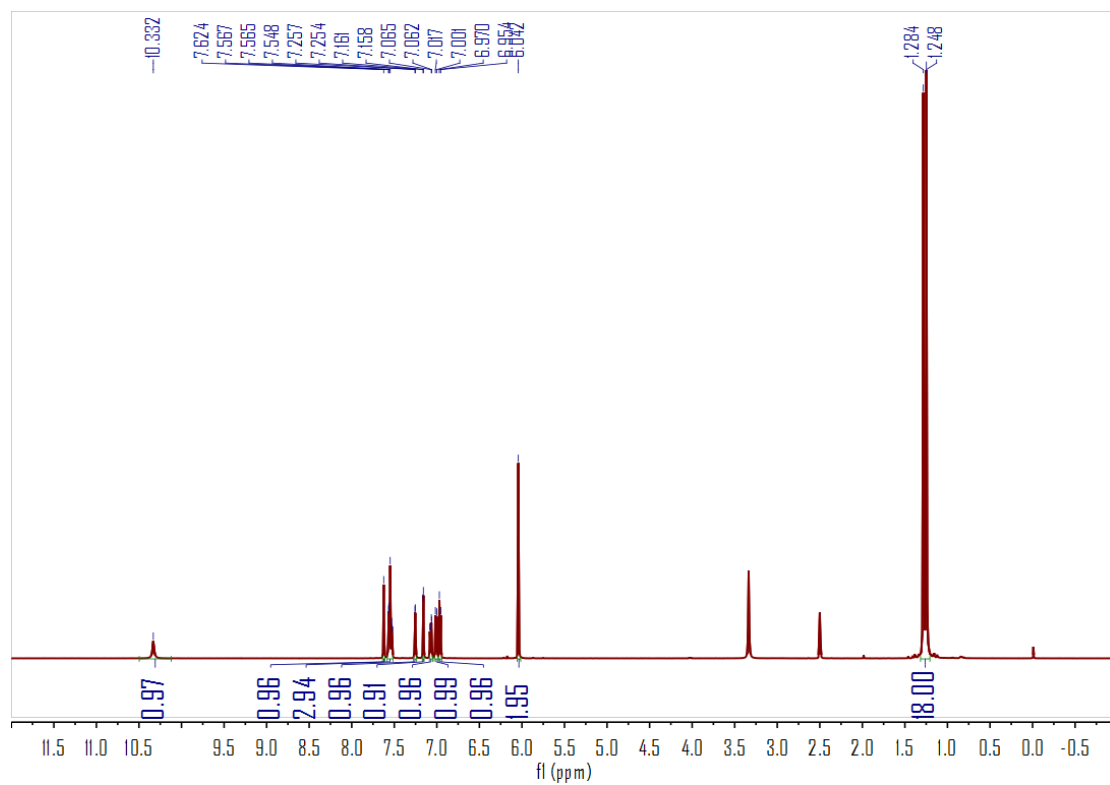
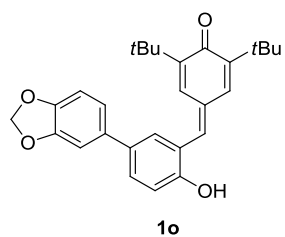


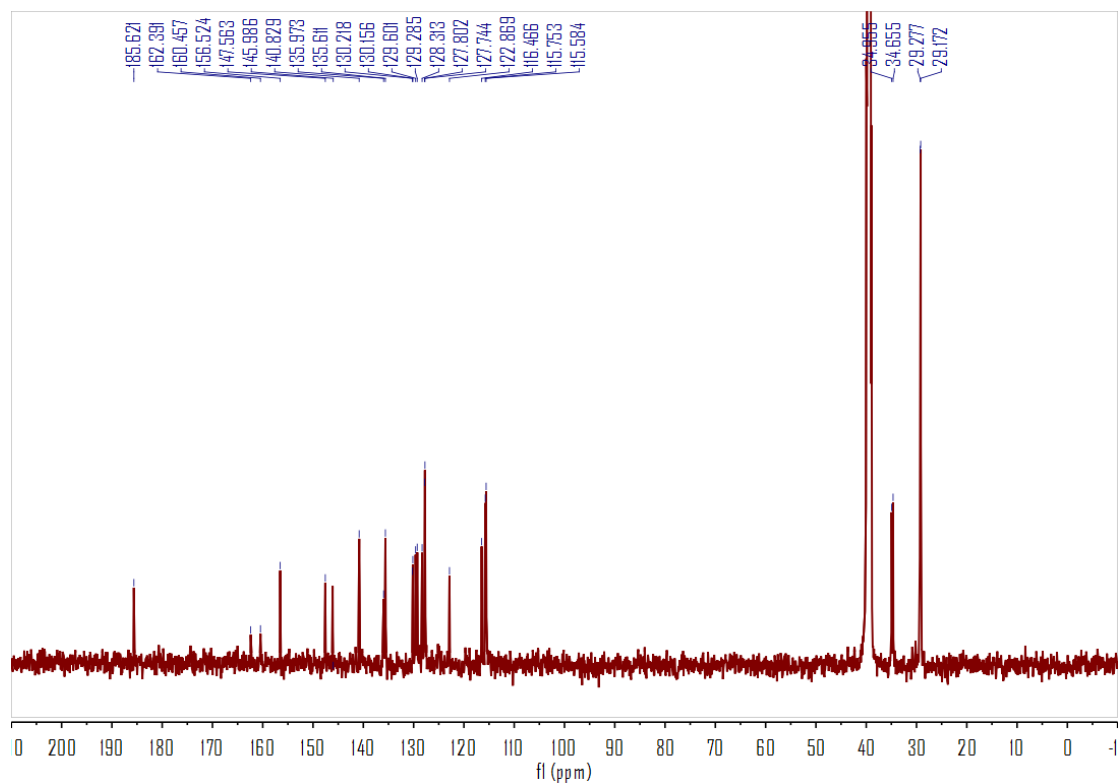
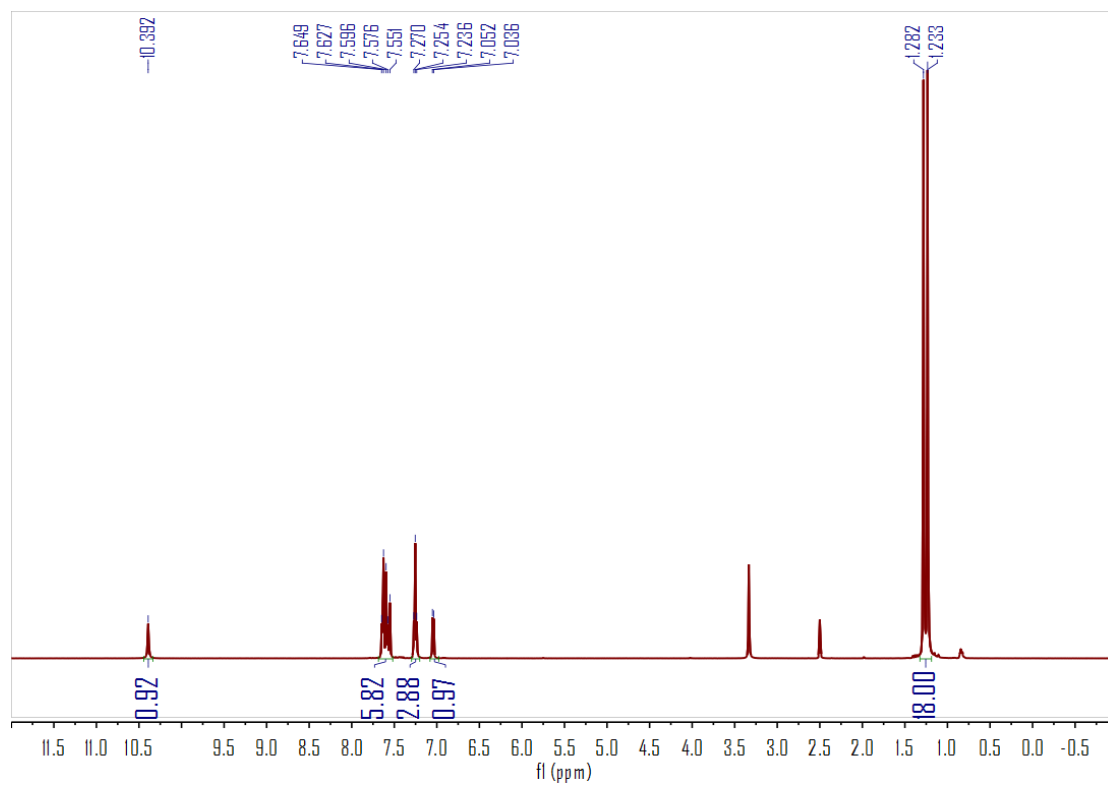
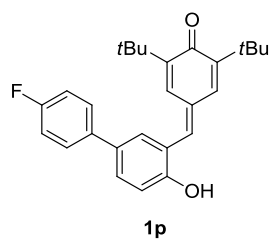


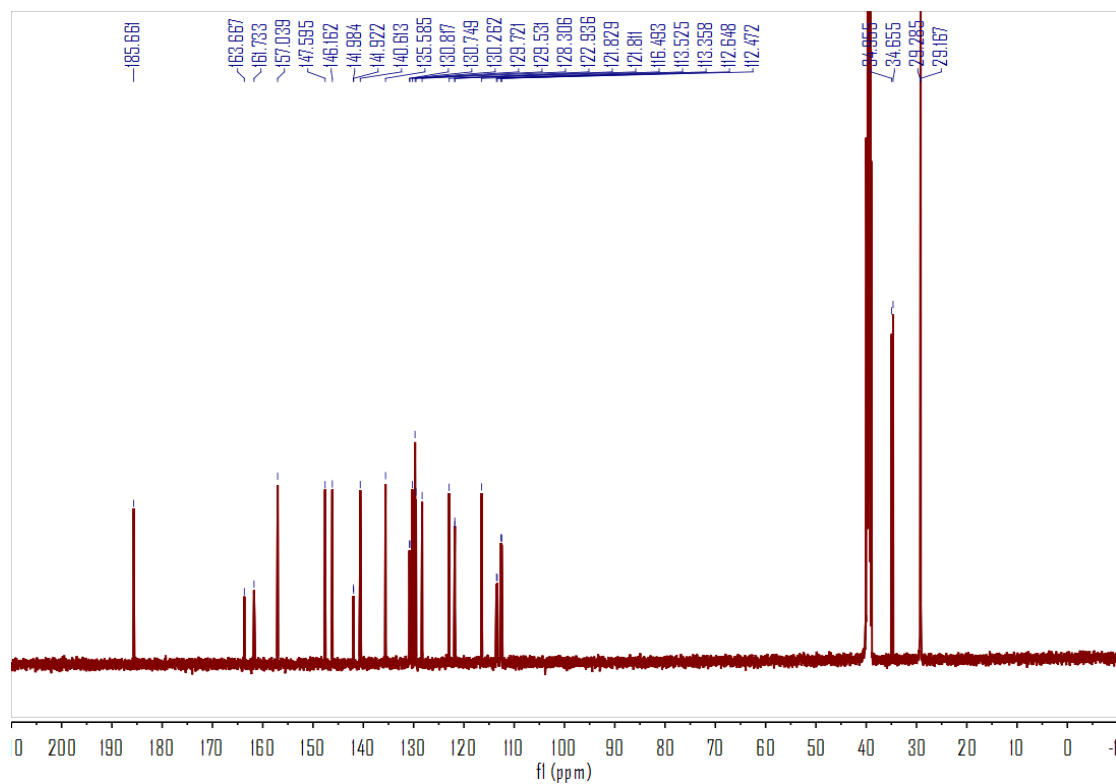
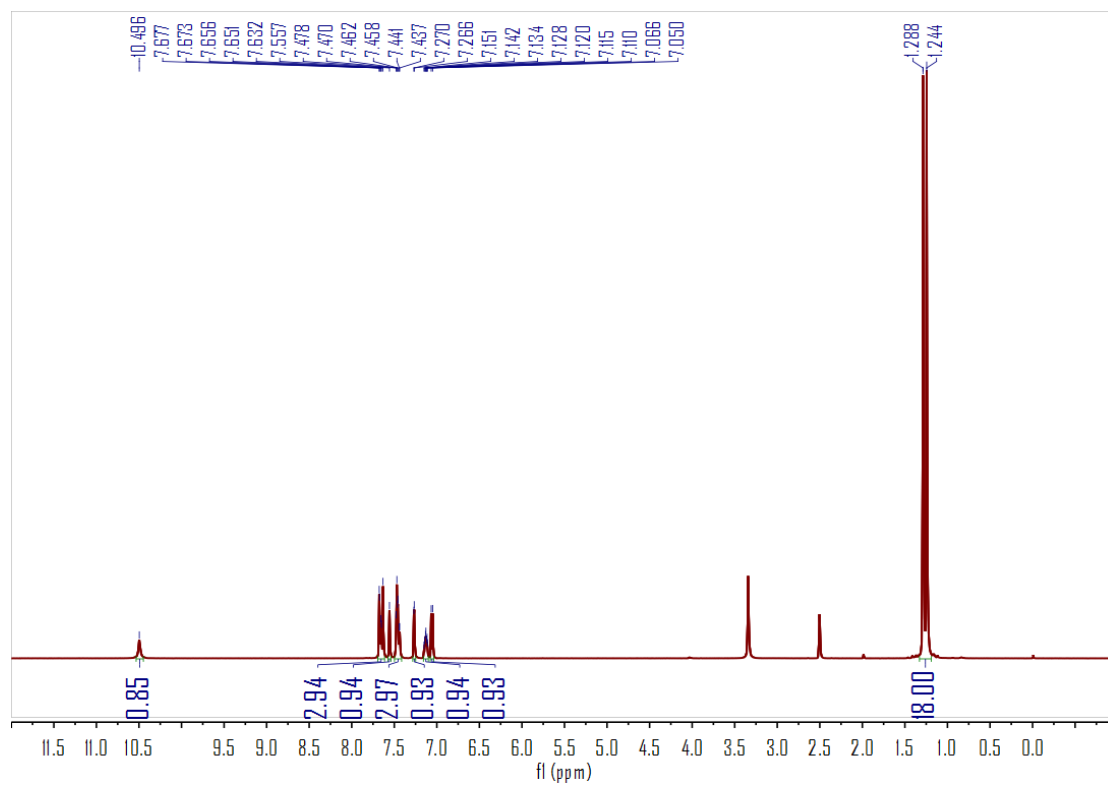
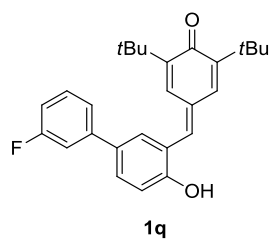


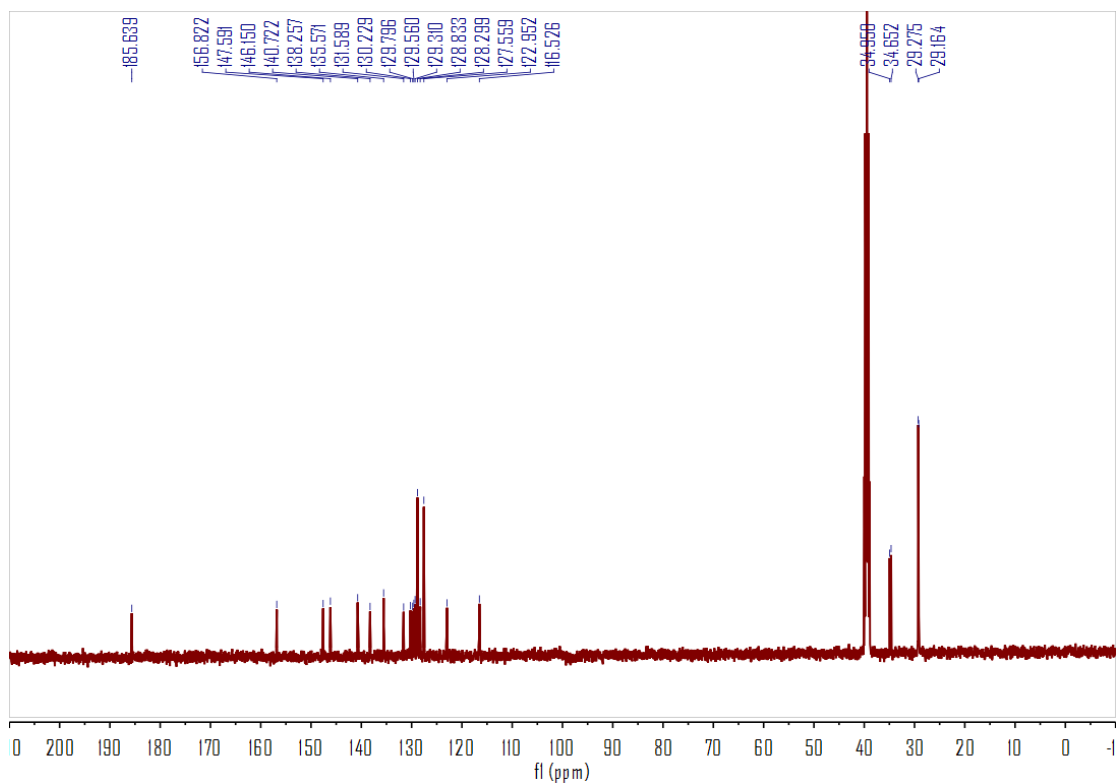
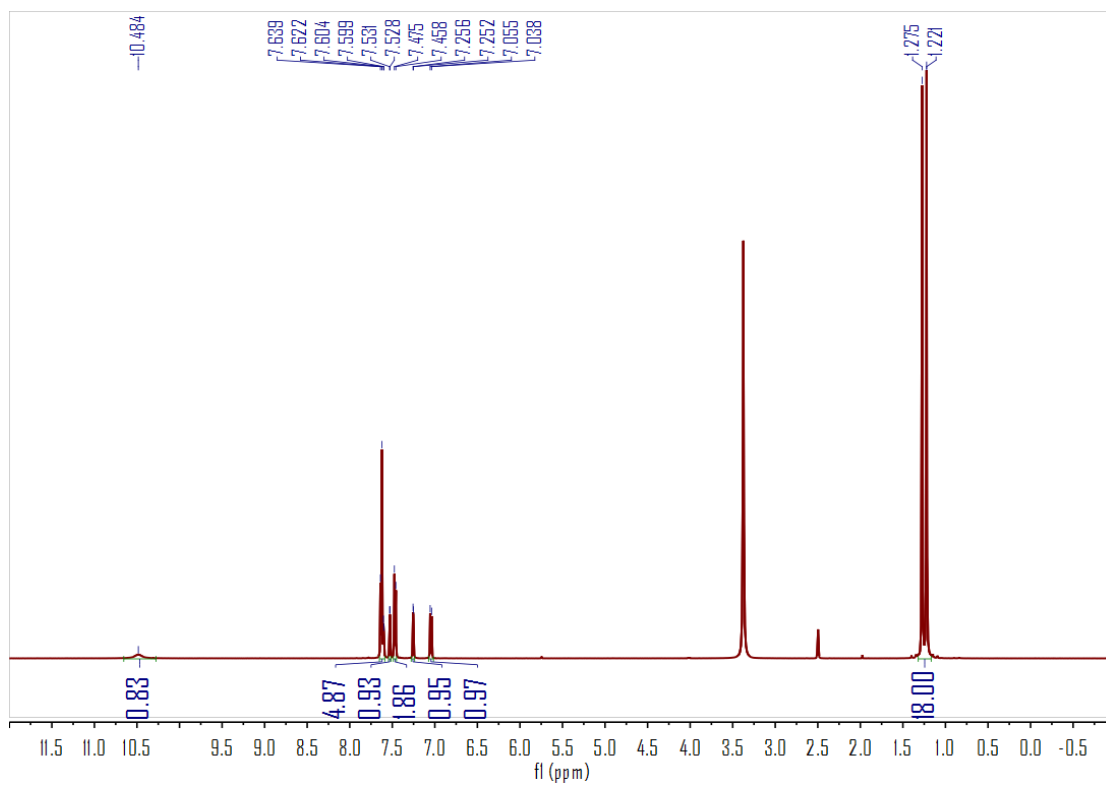
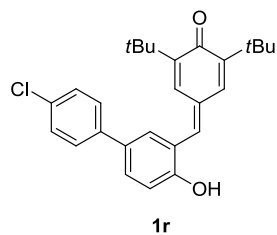


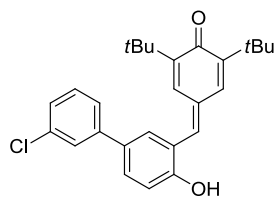




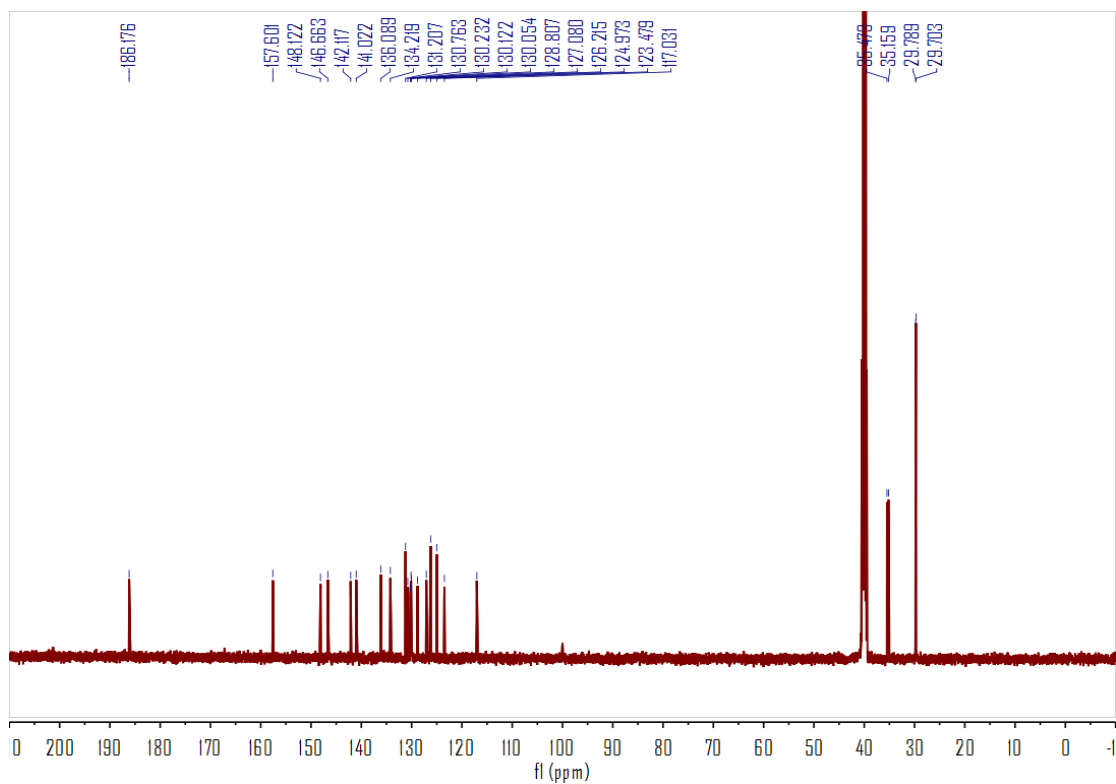
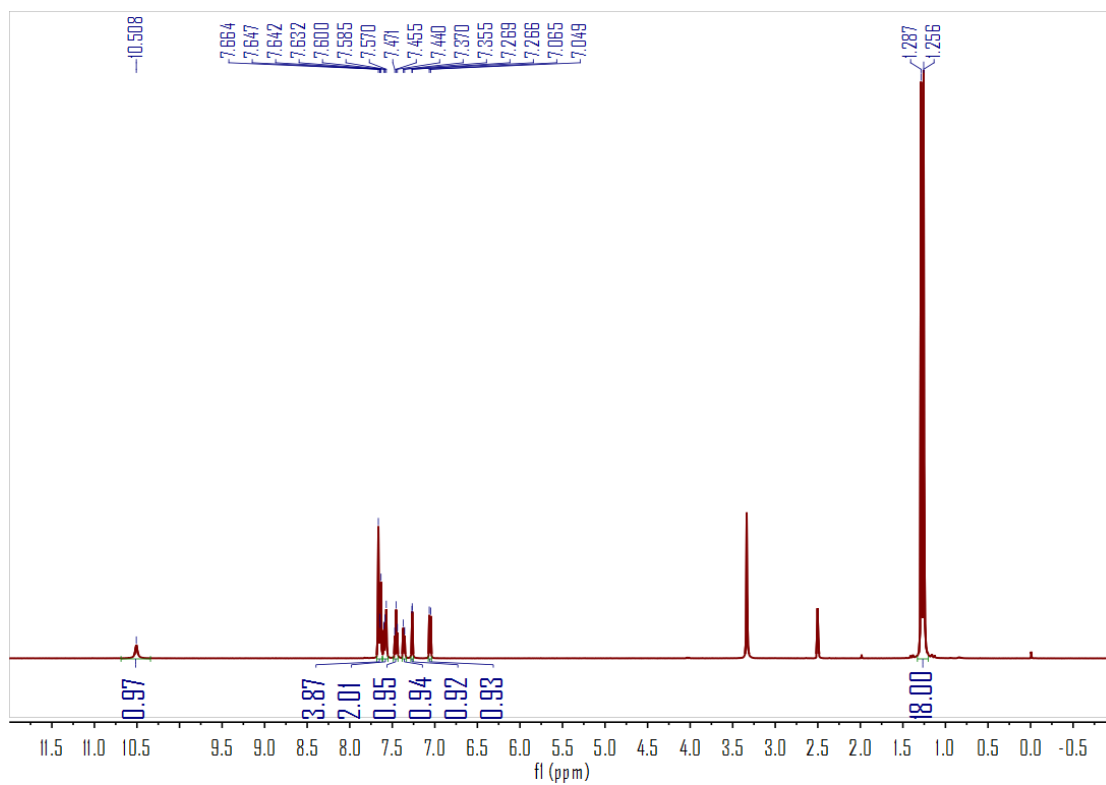


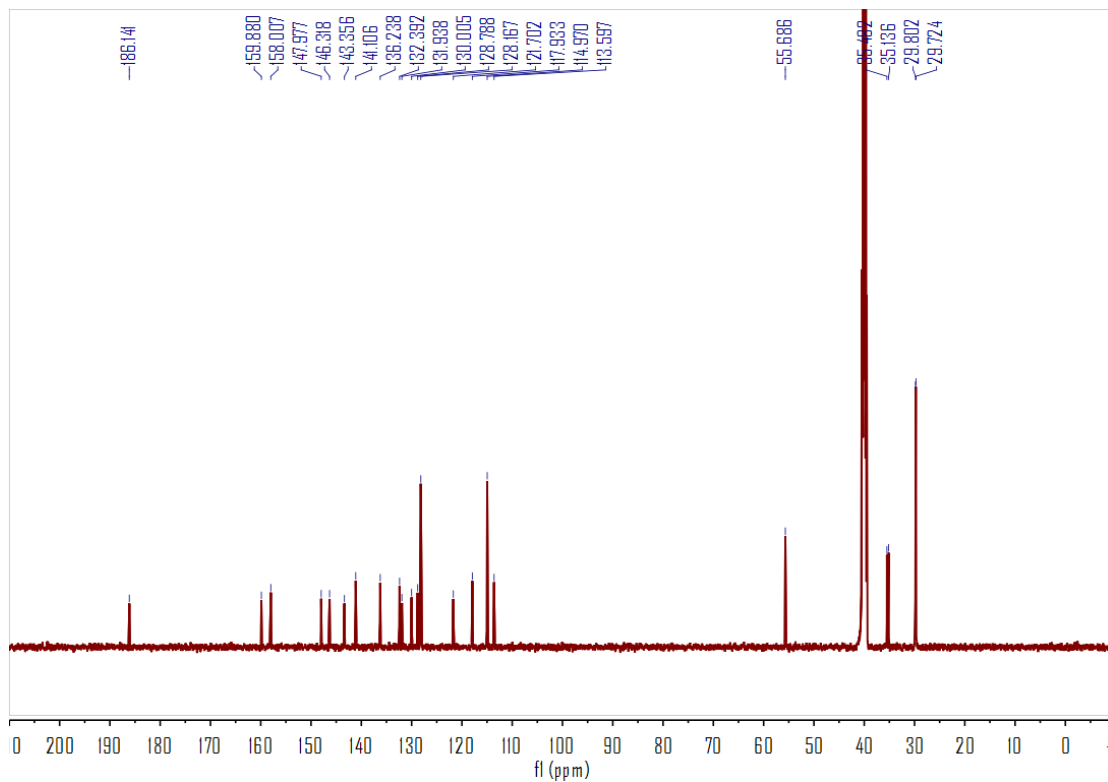
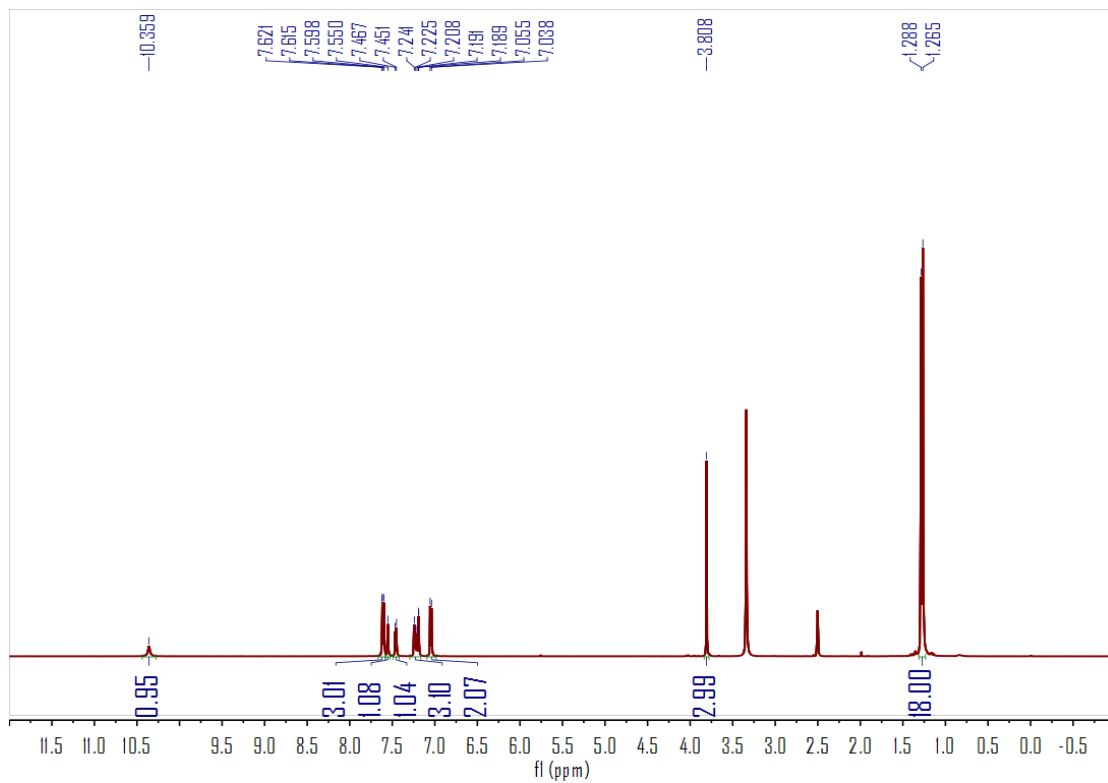
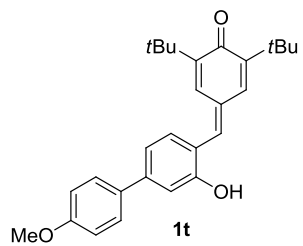


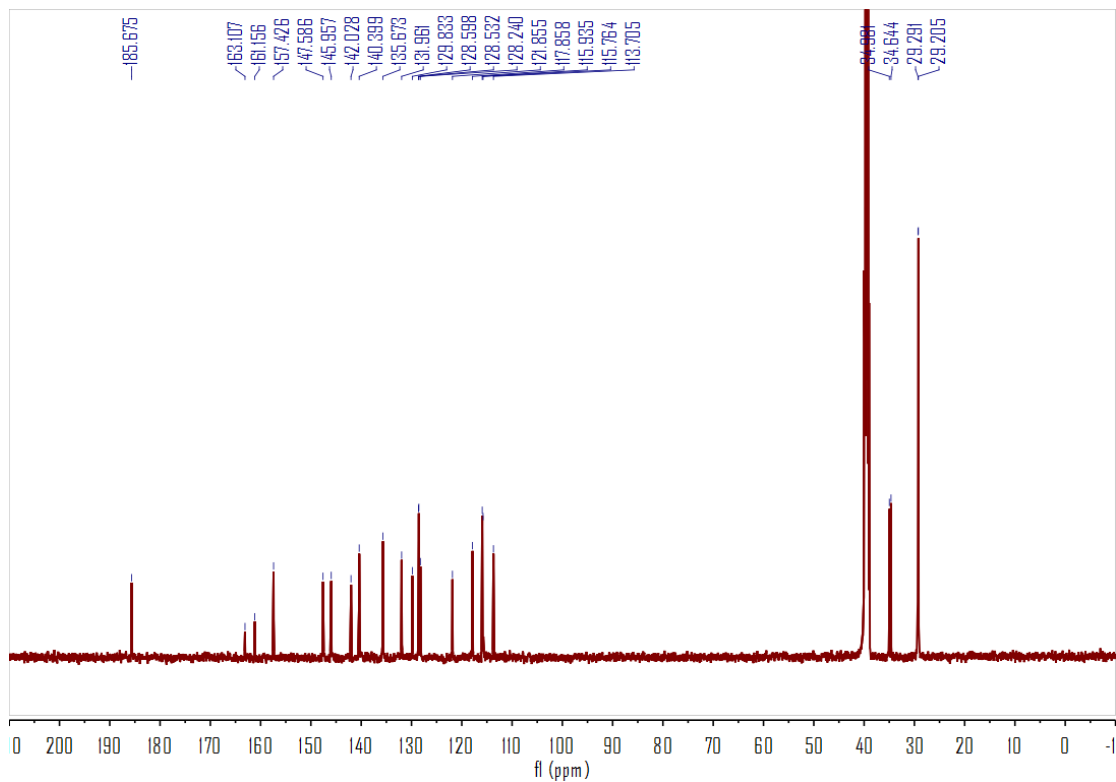
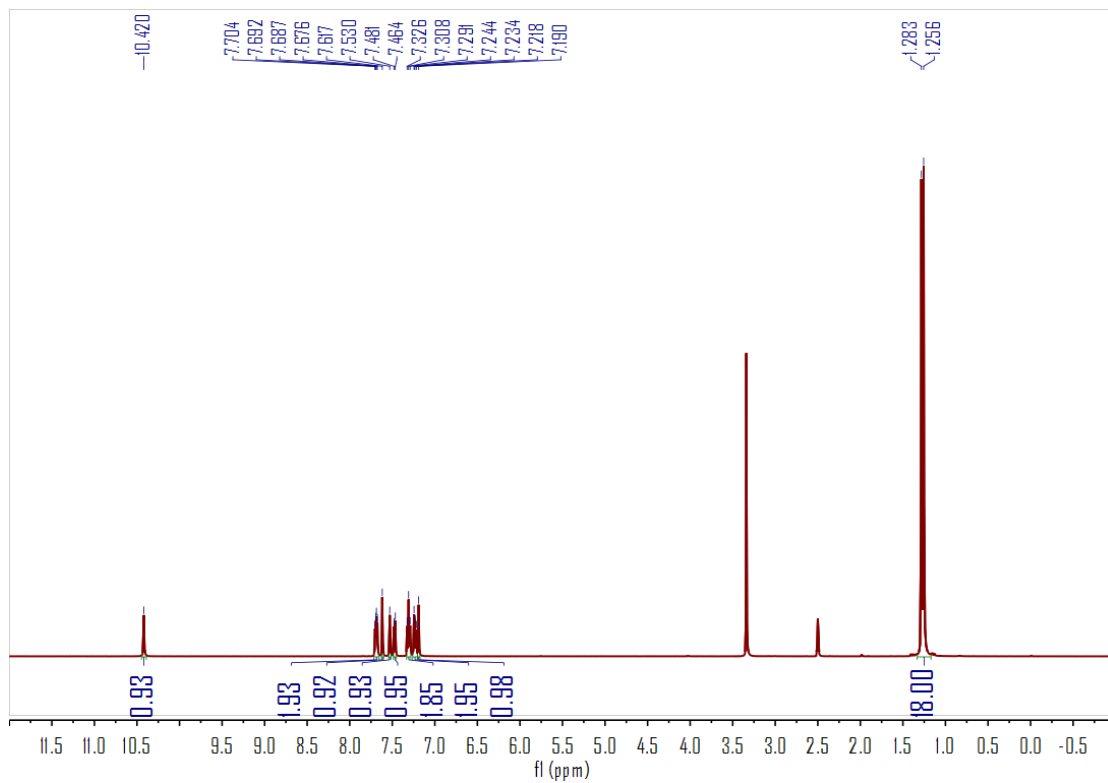
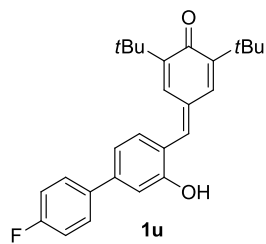


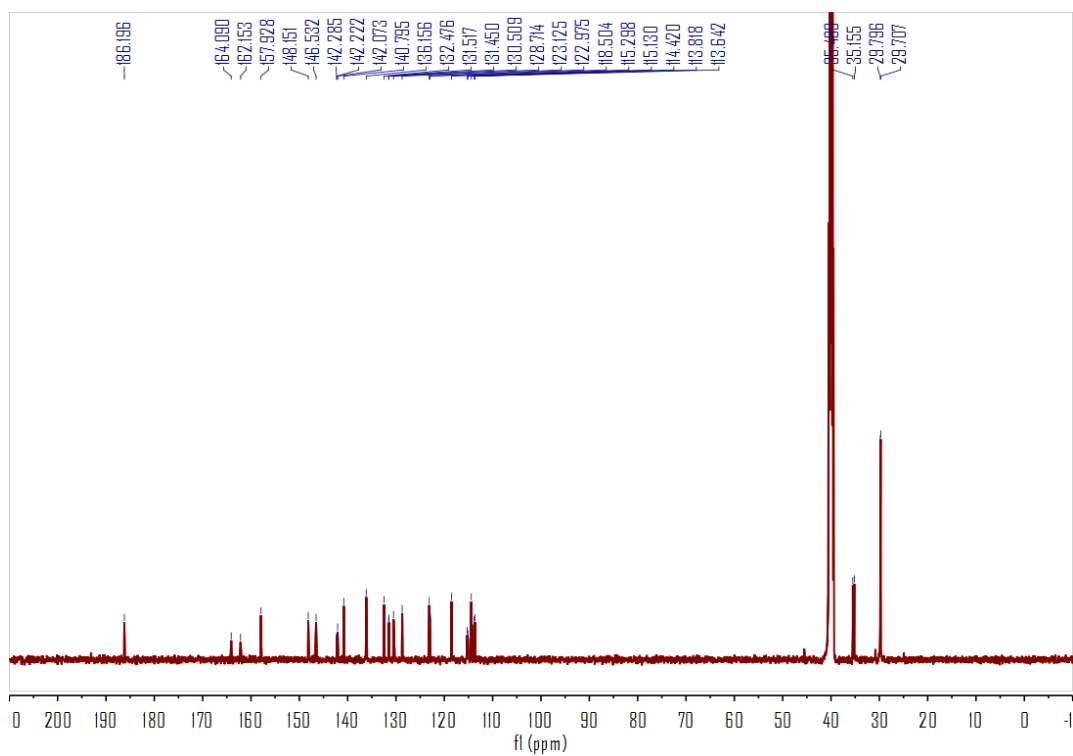
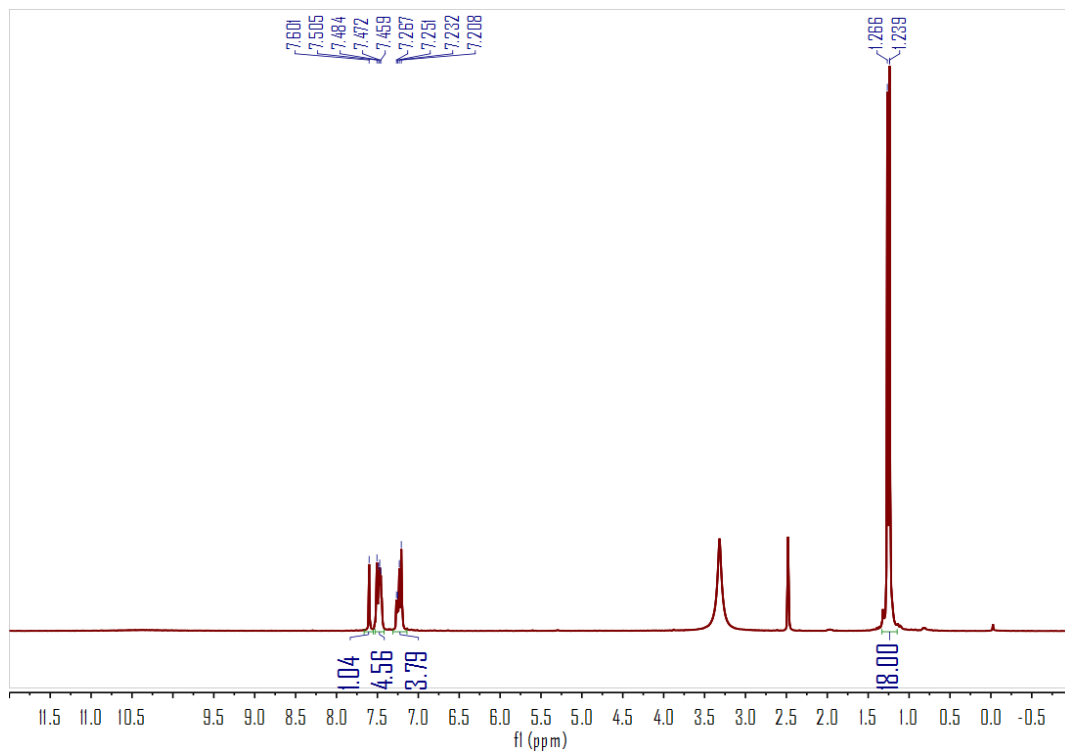
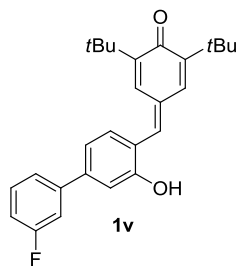


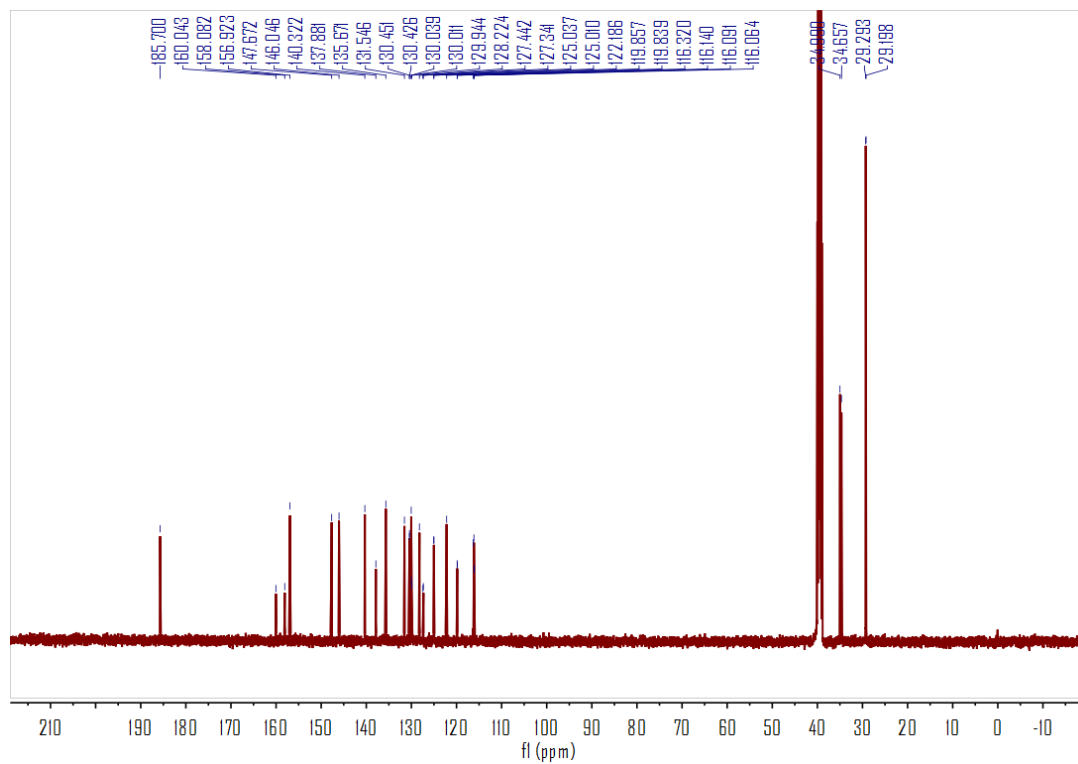
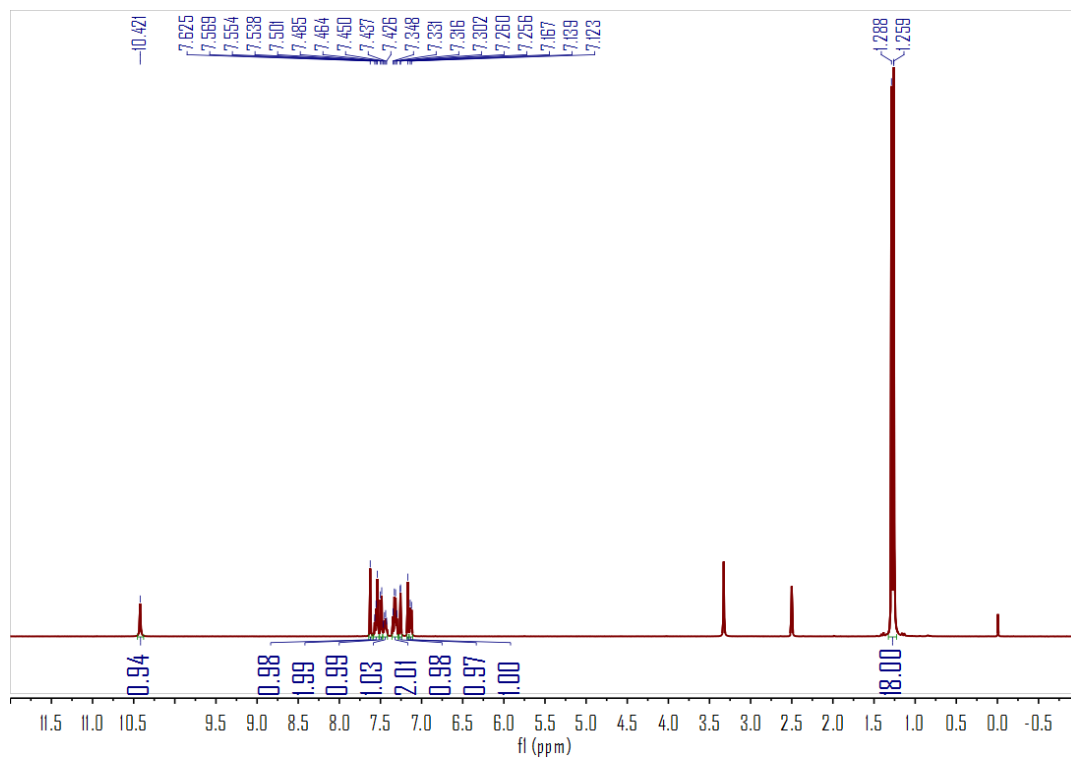
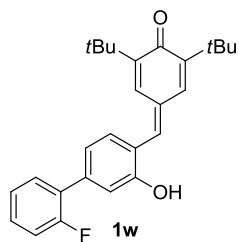
1s

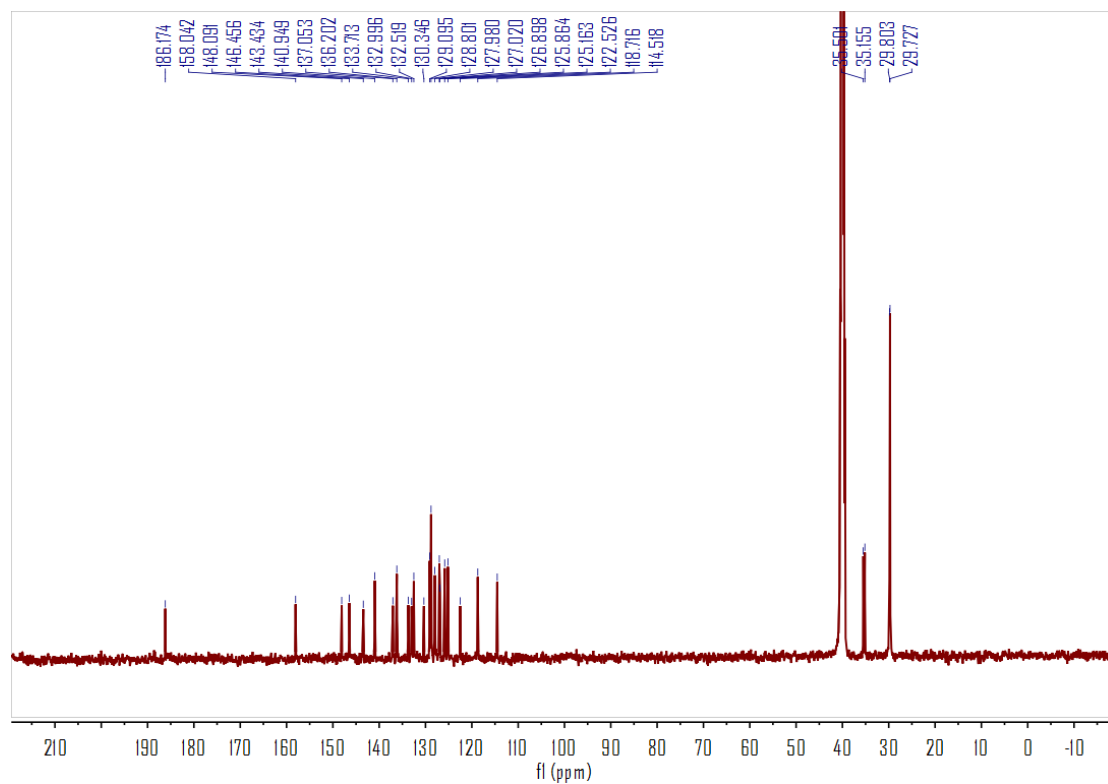
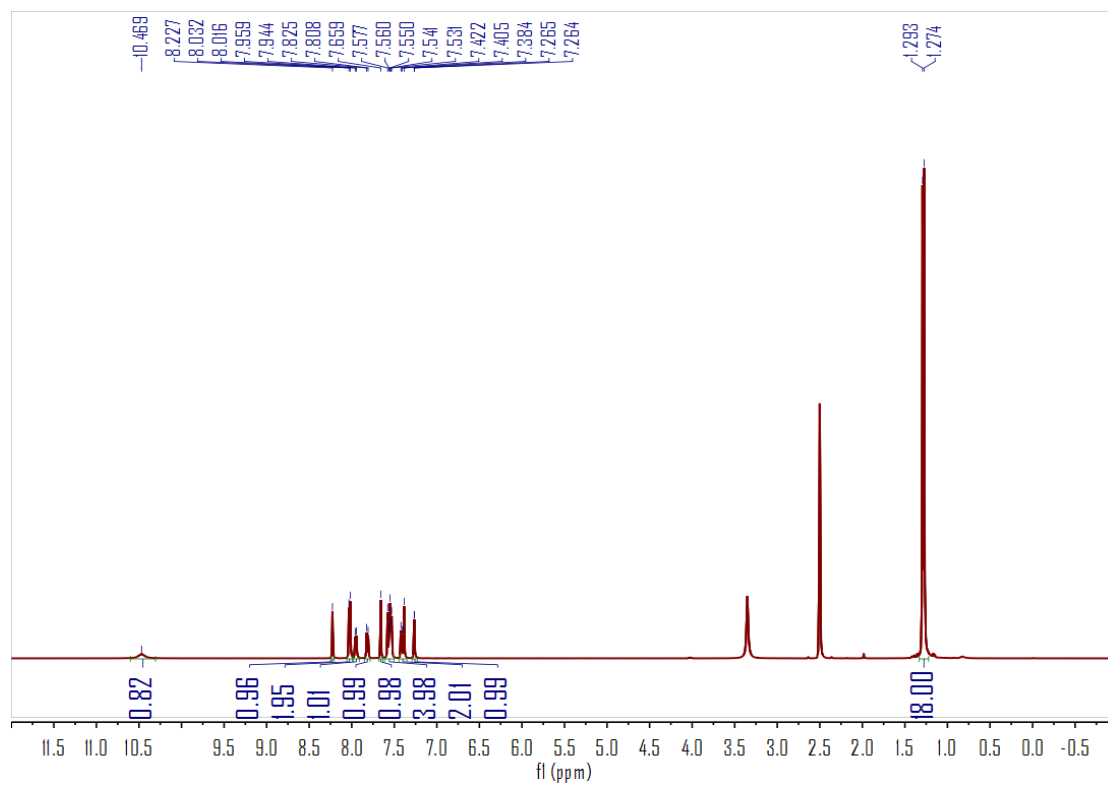
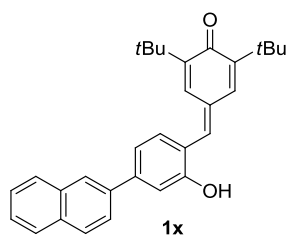


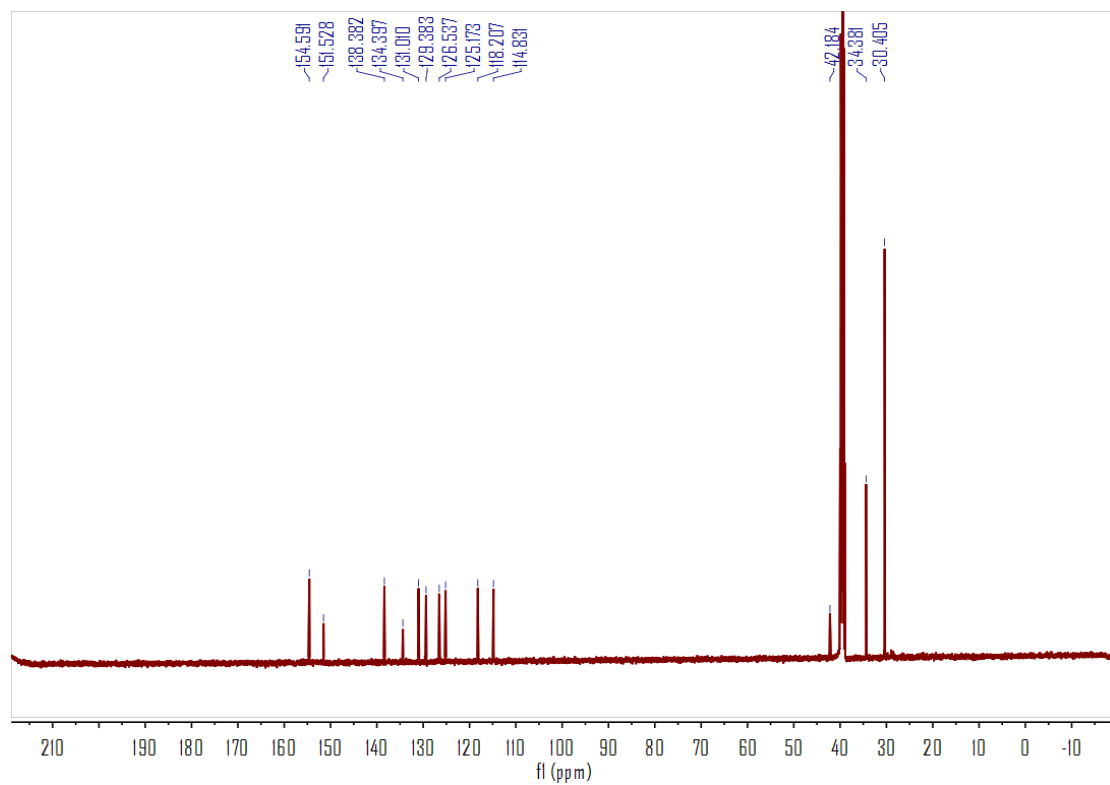
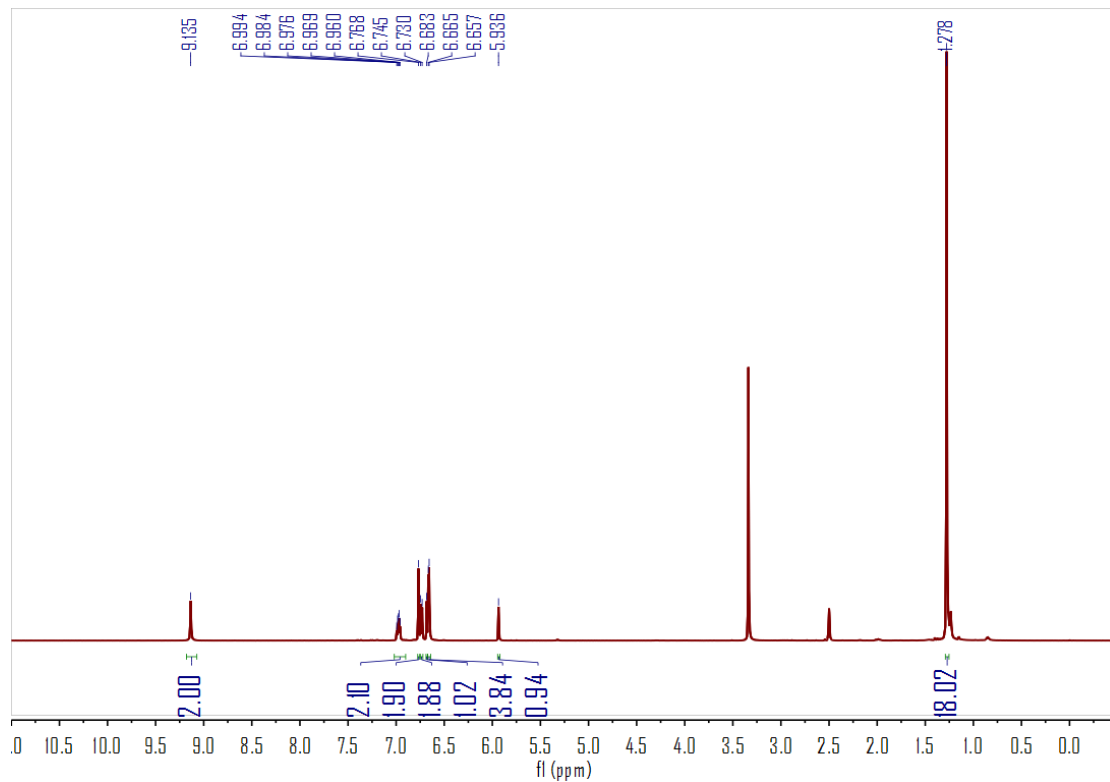
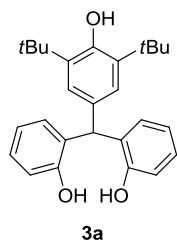


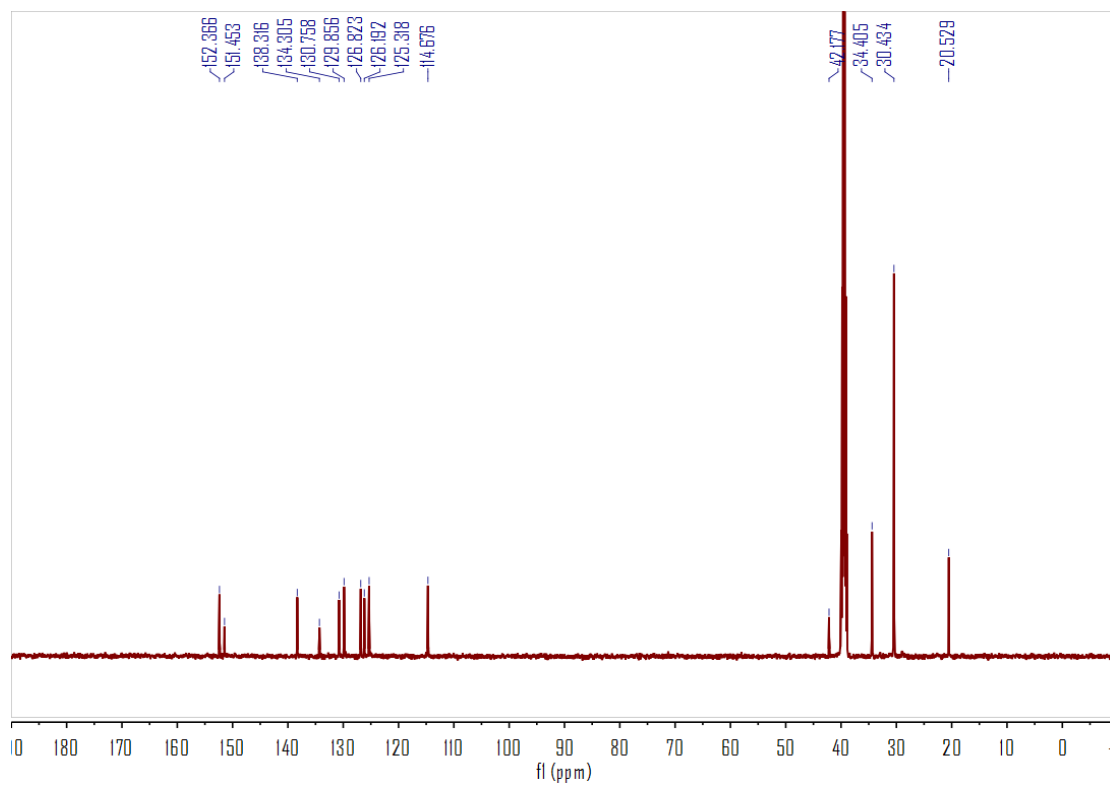
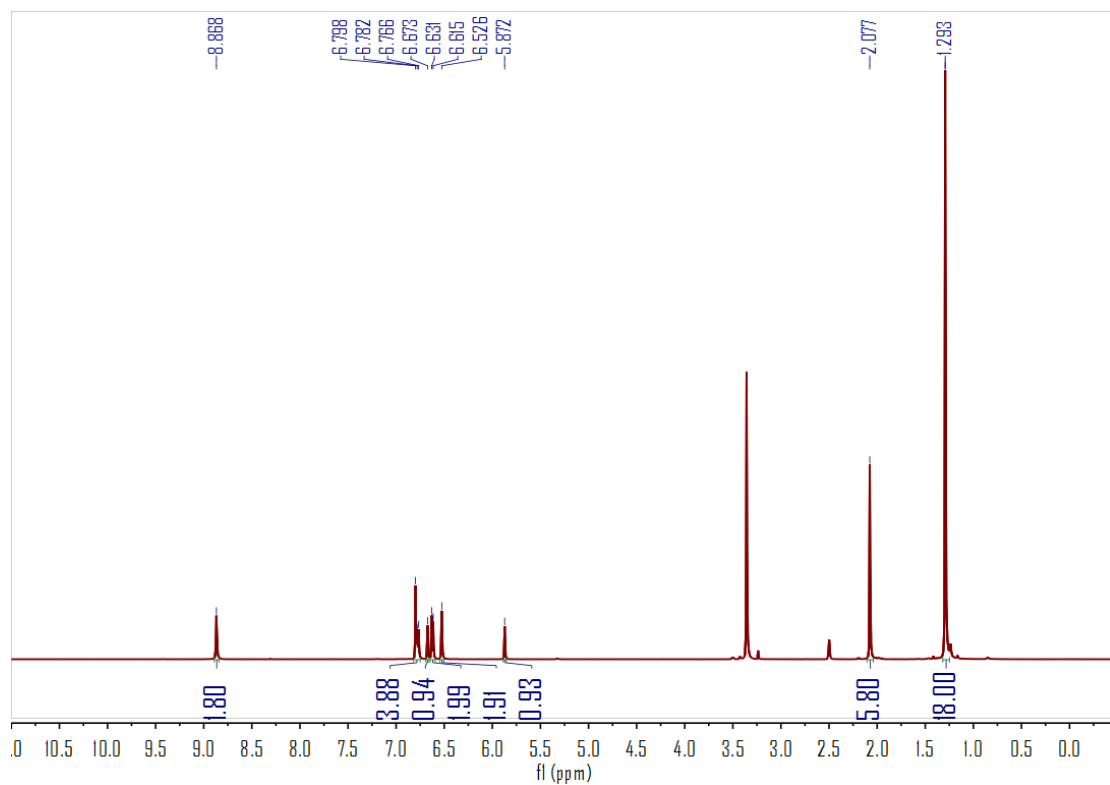
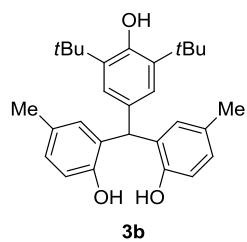


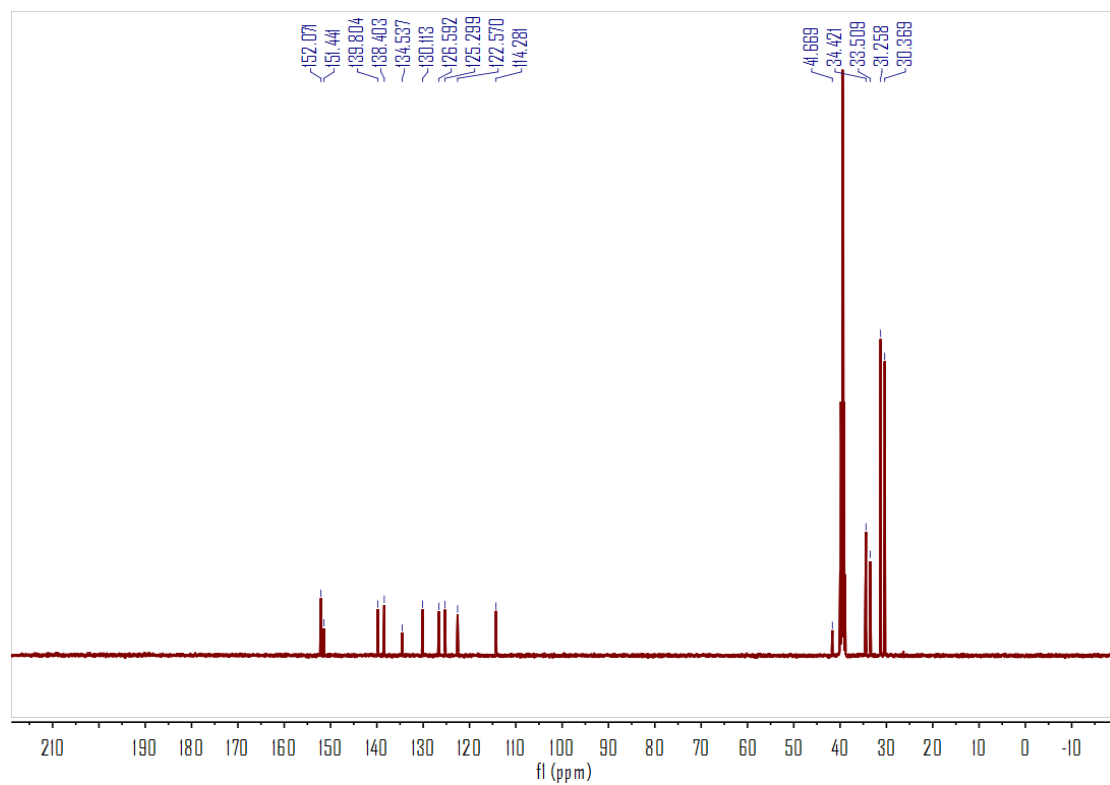
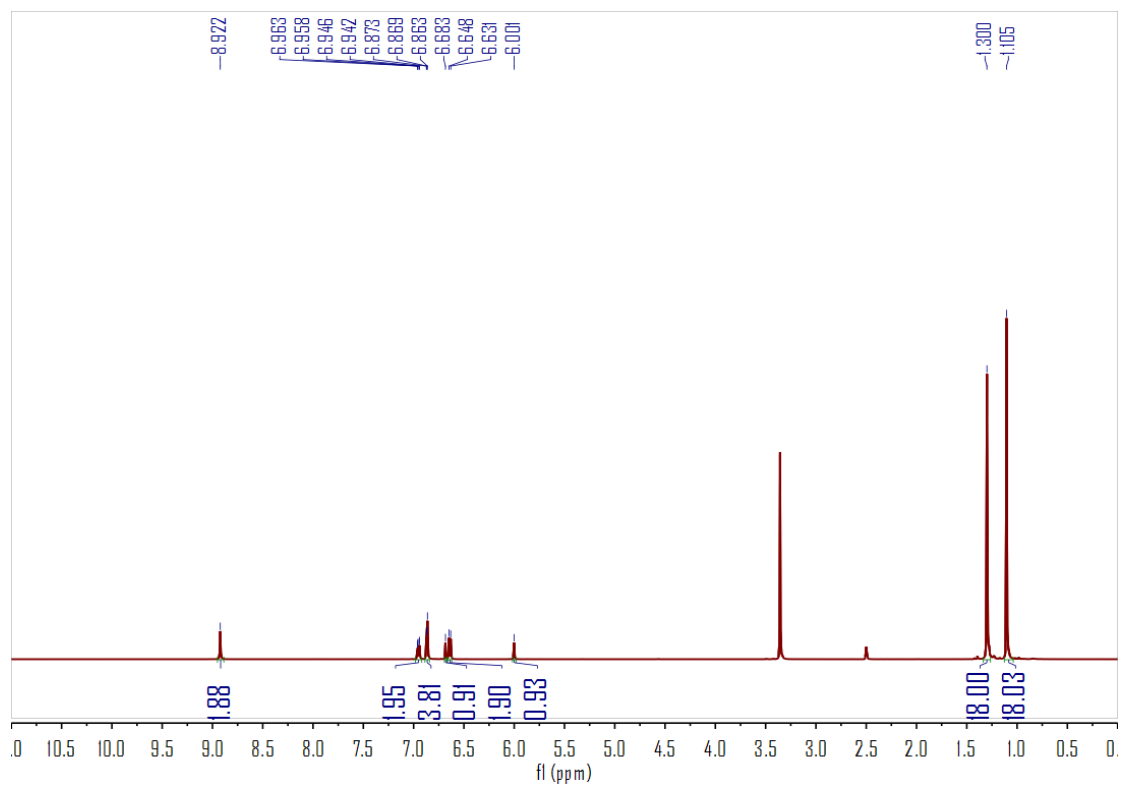
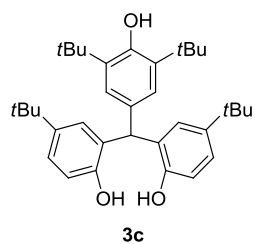


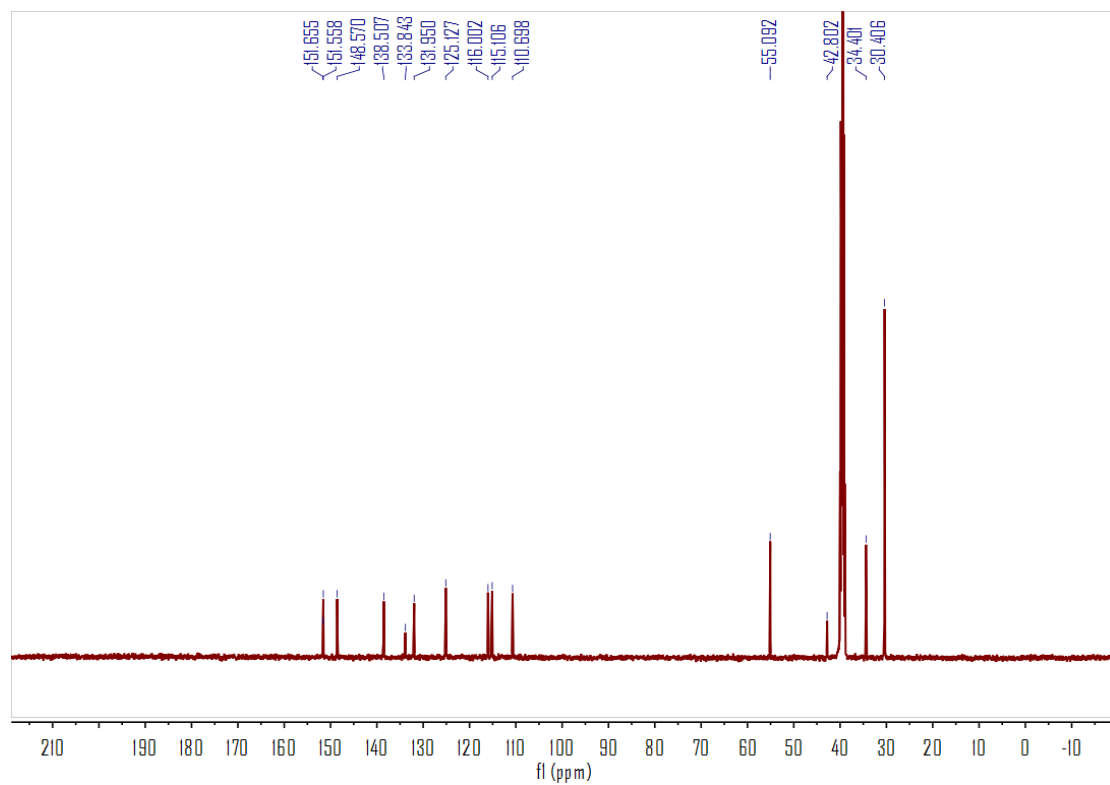
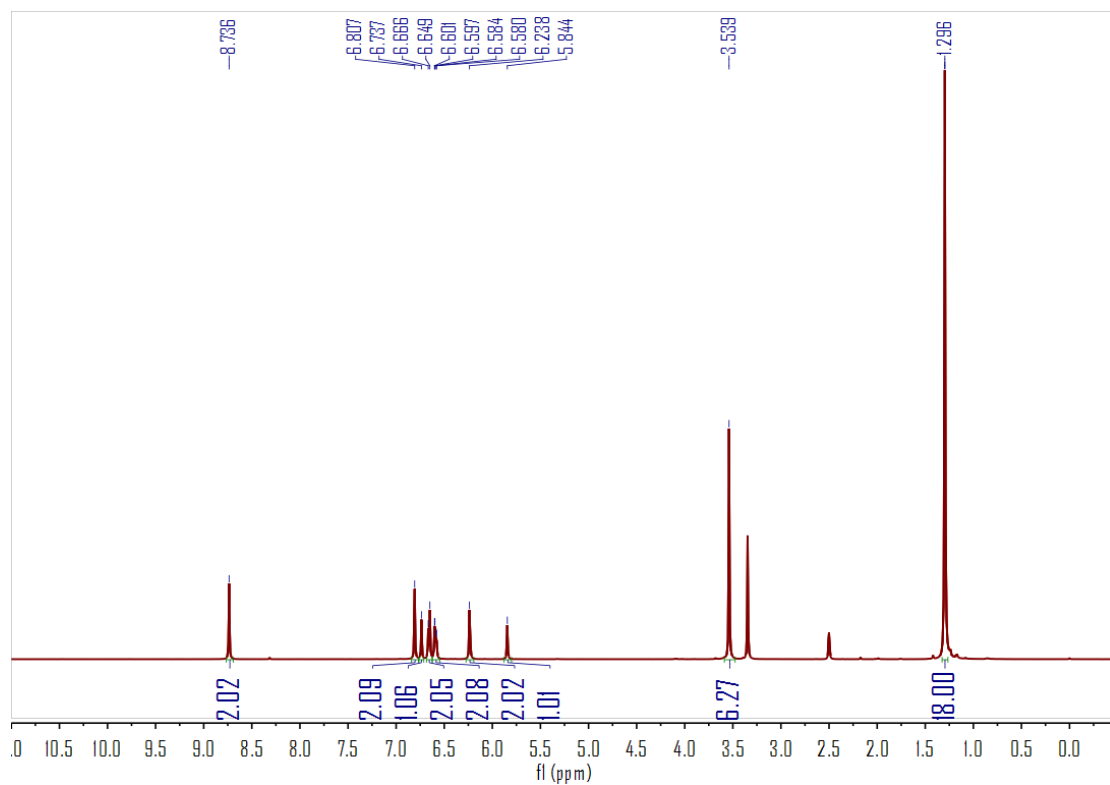
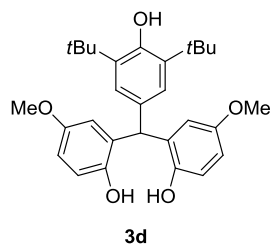


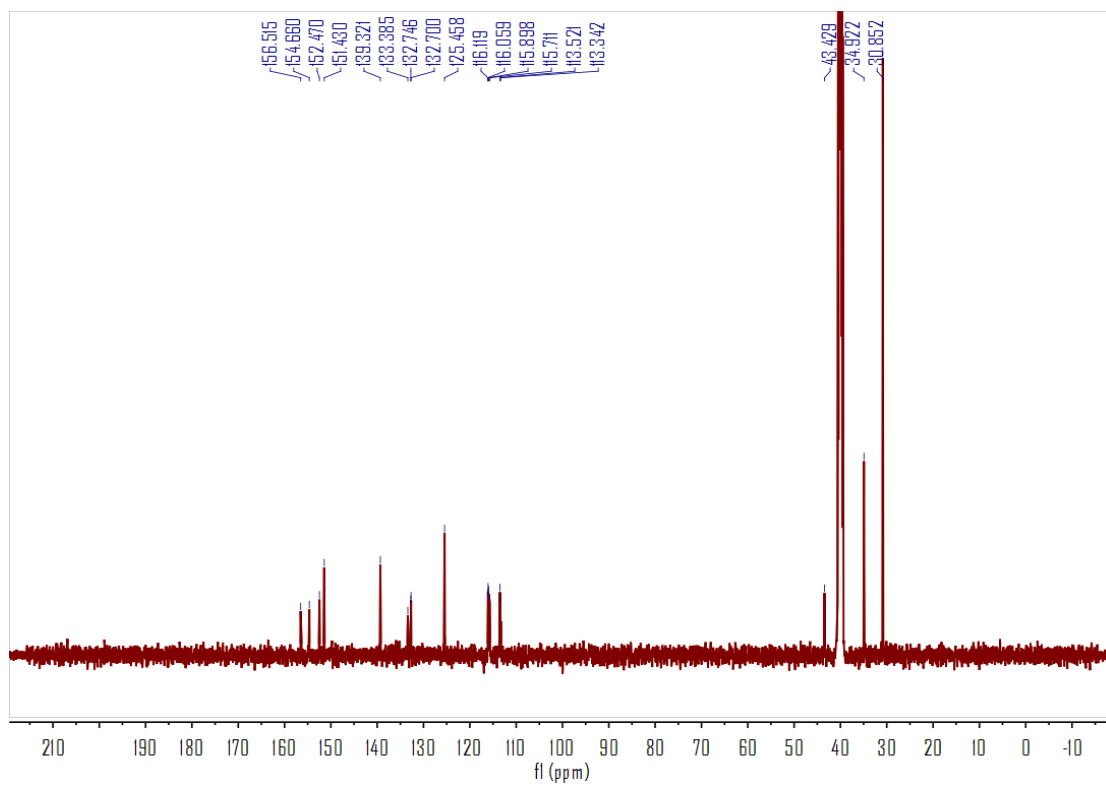
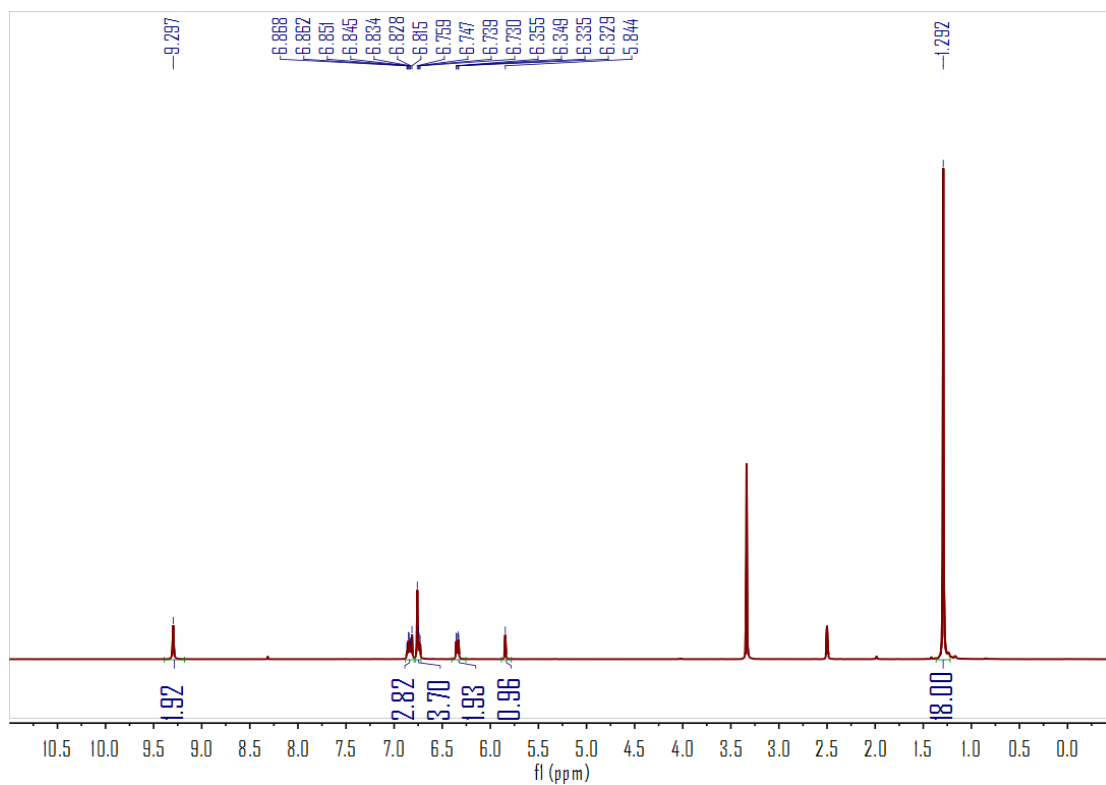
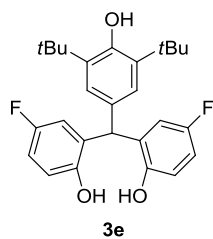


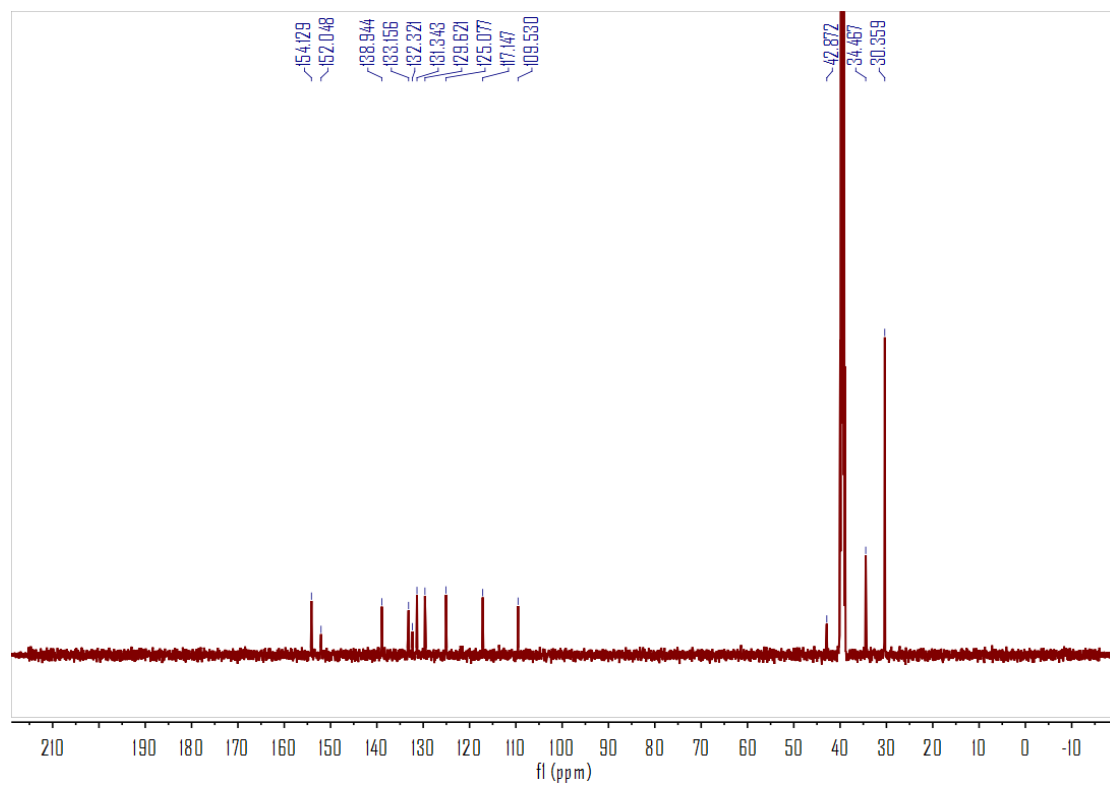
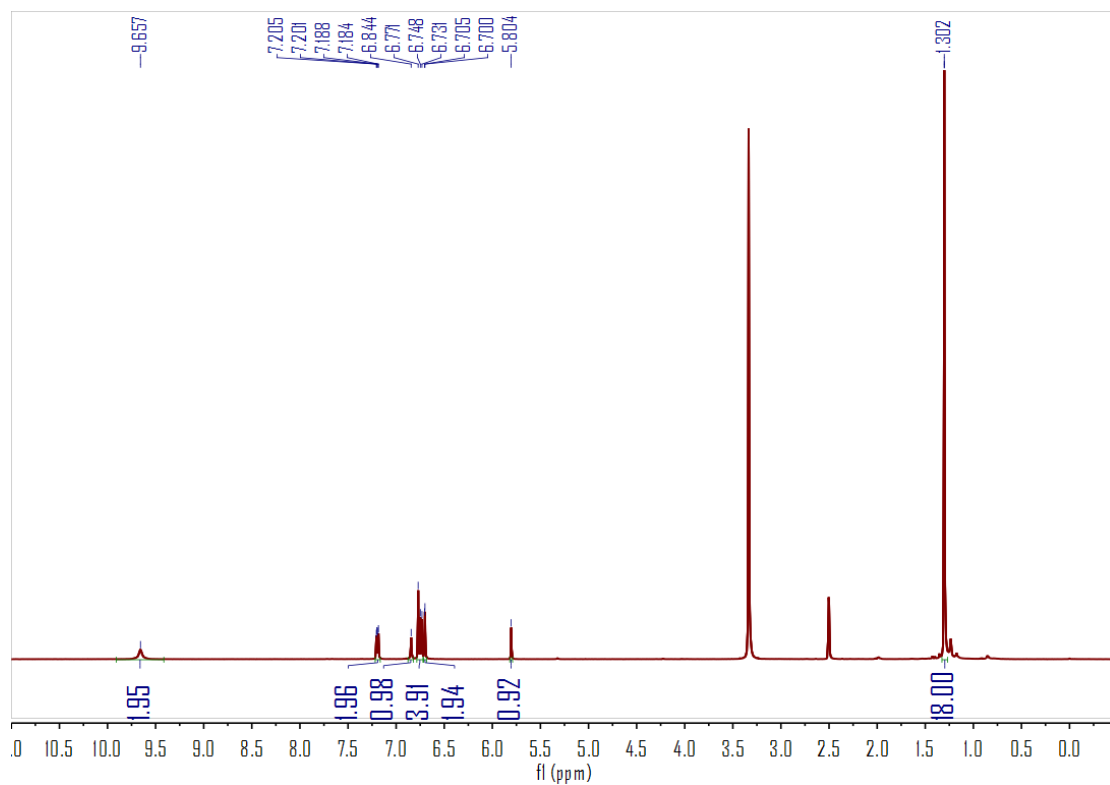
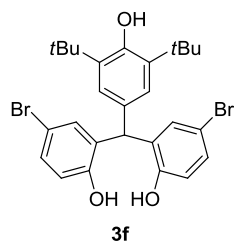


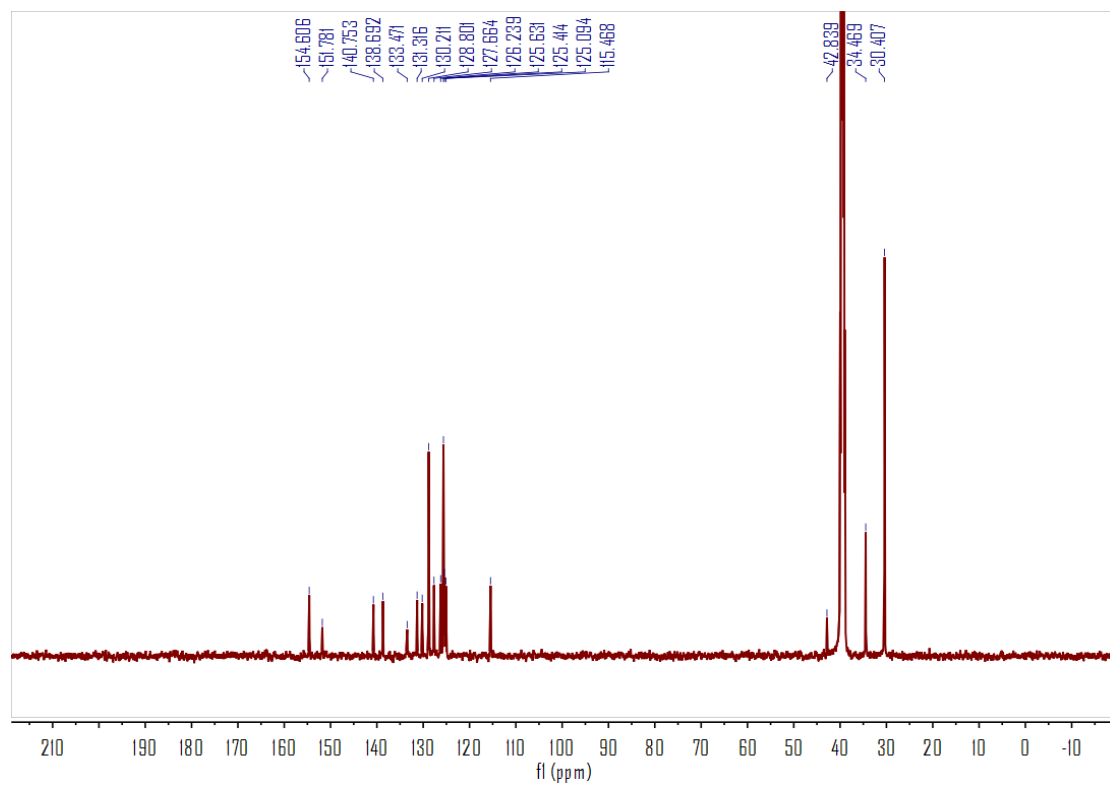
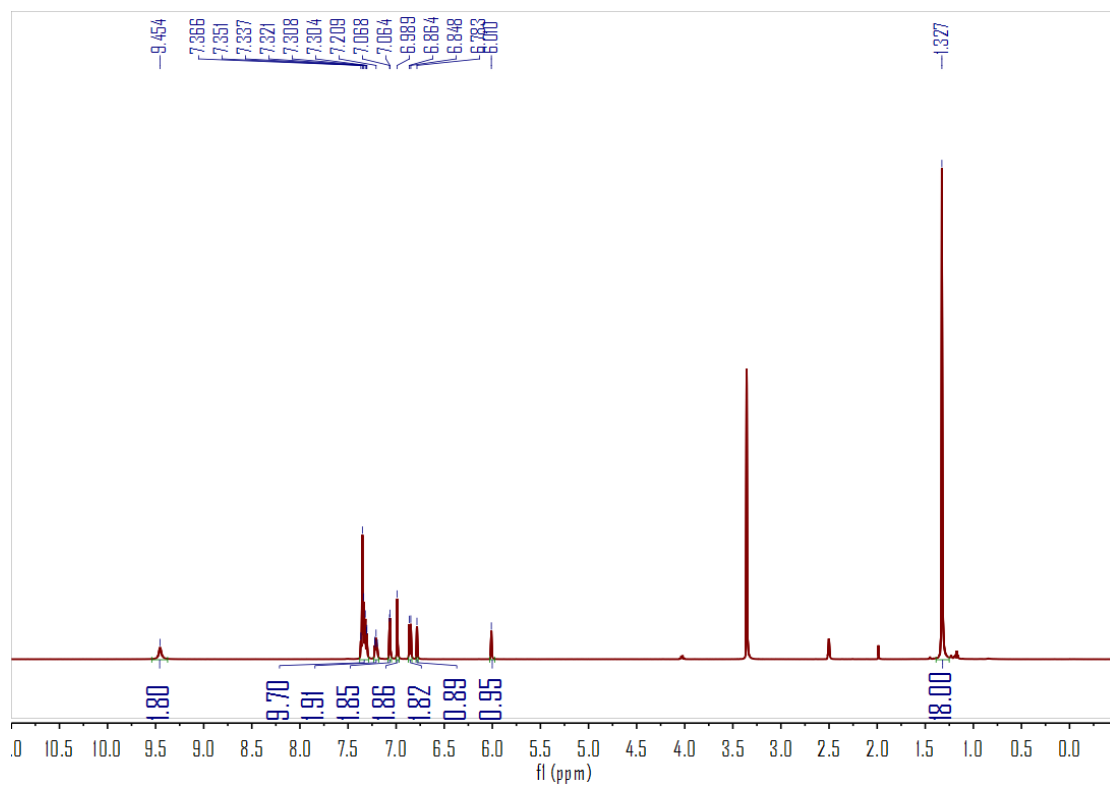
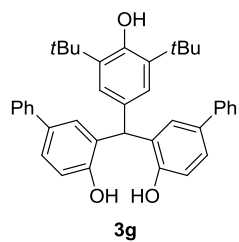


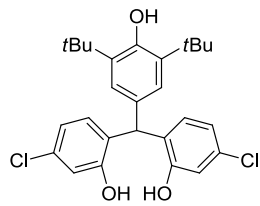




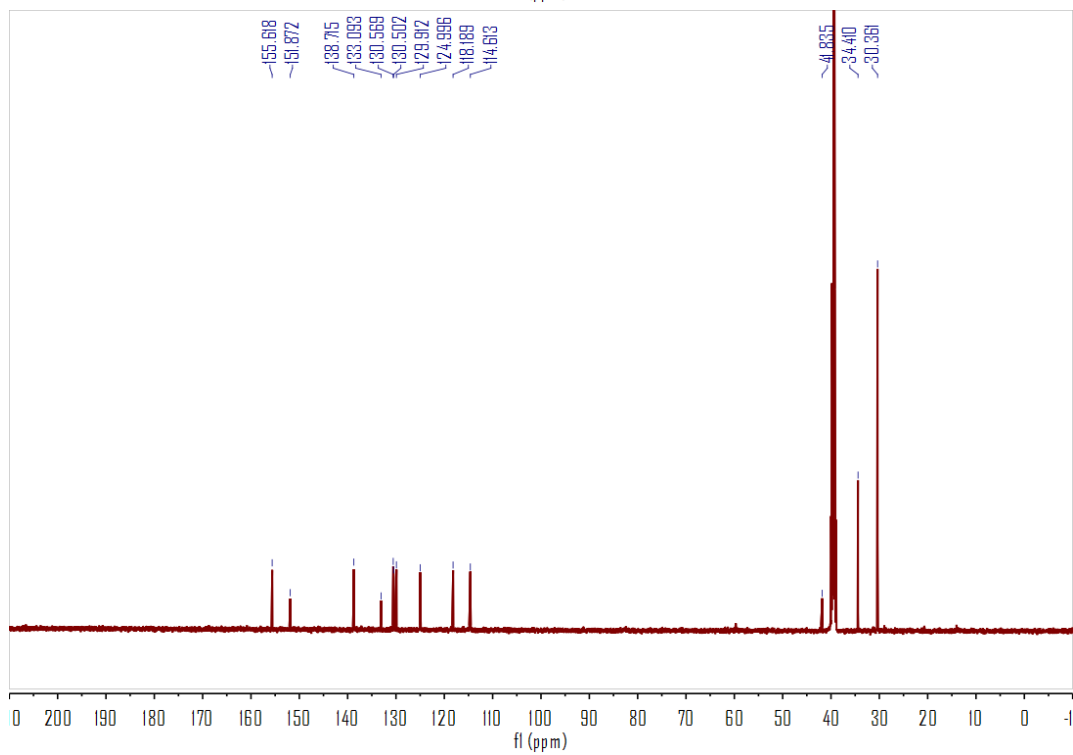
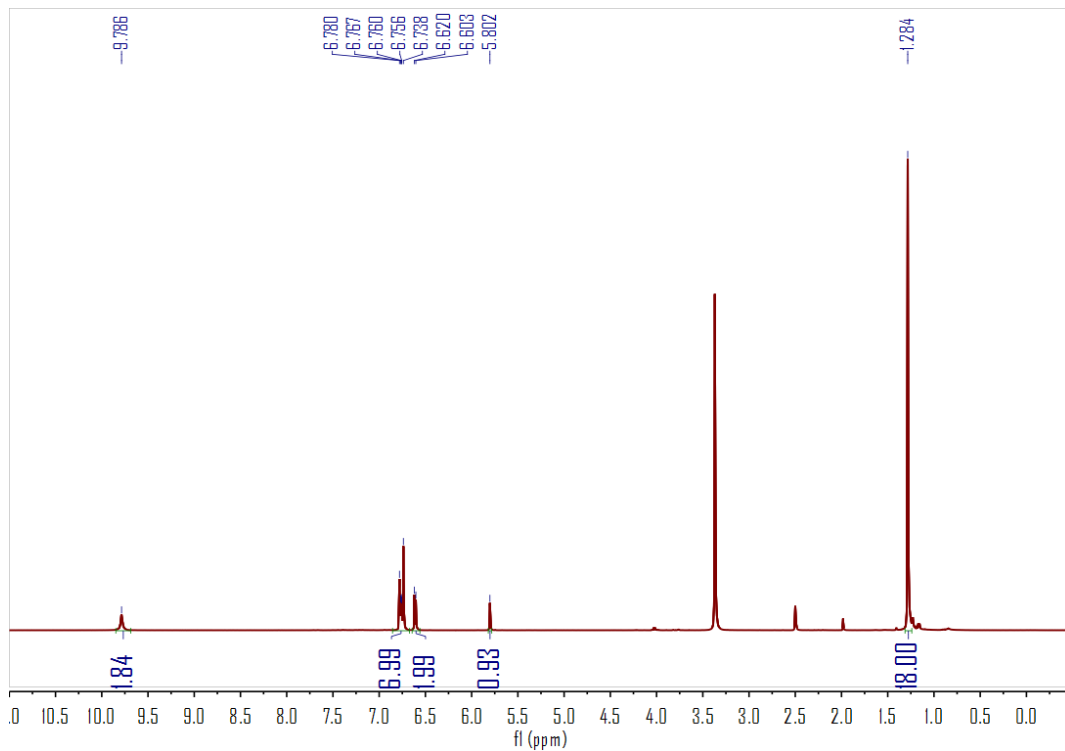


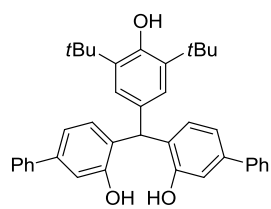




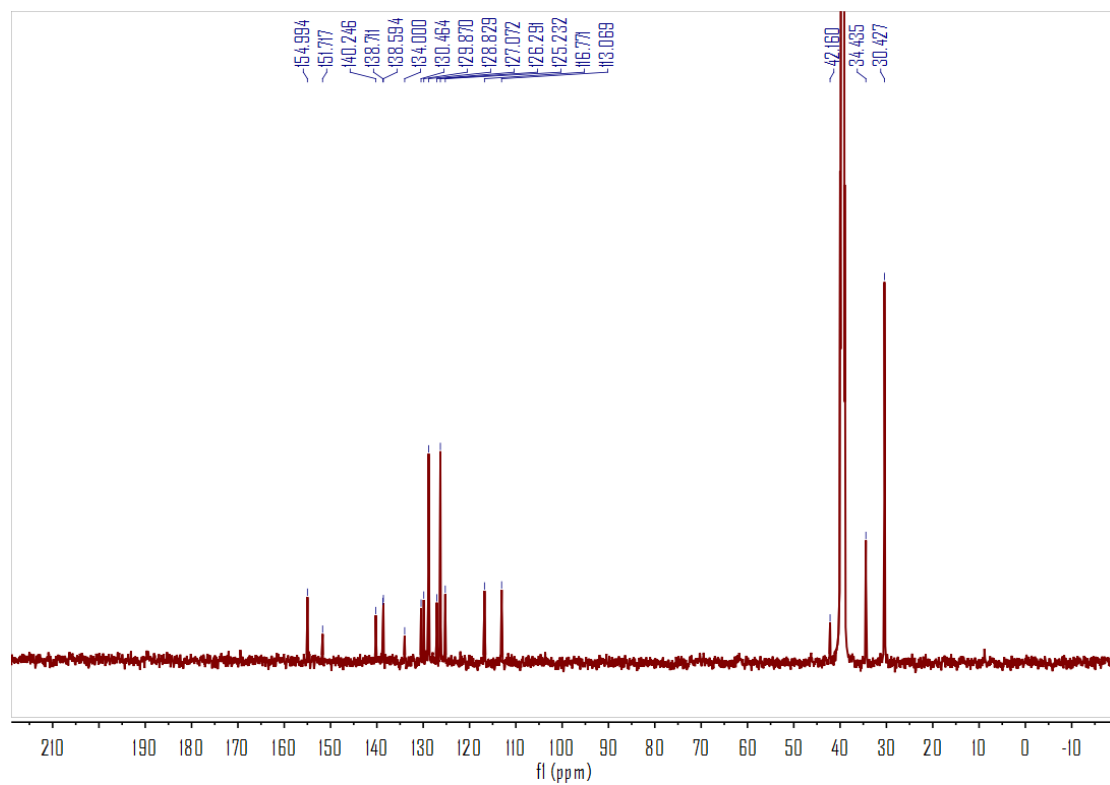
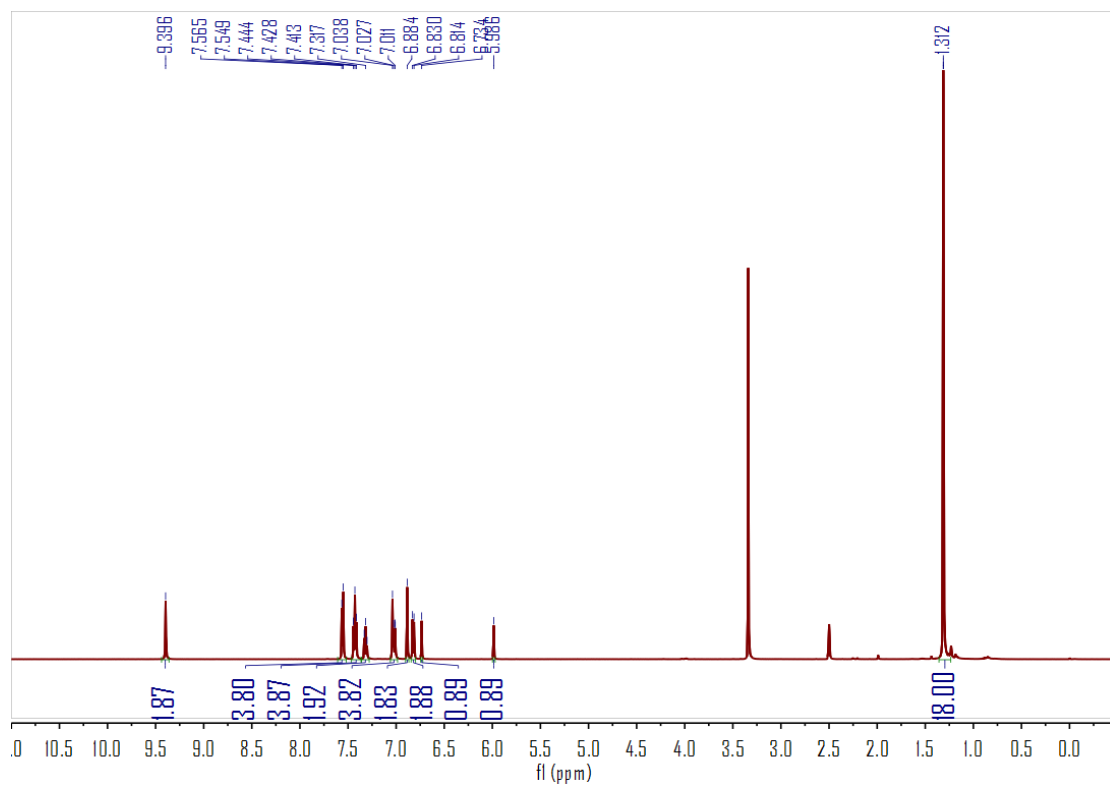


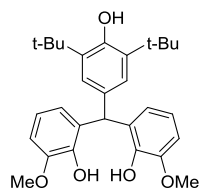
3h



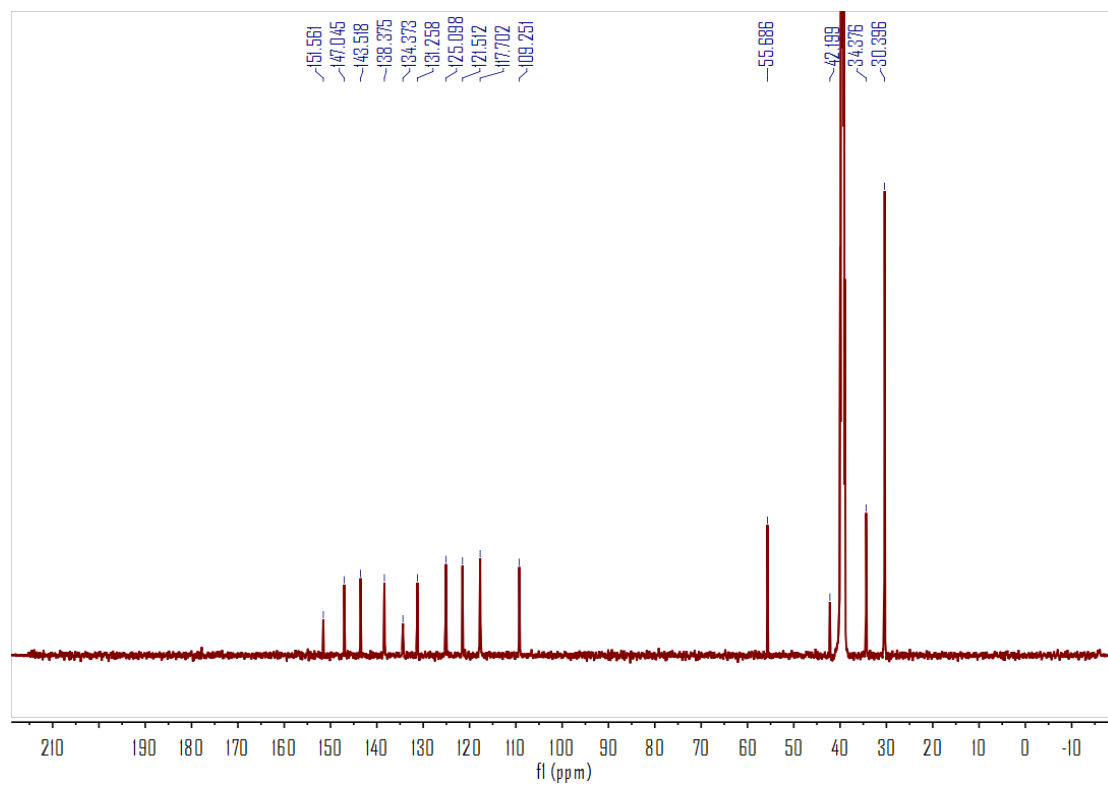
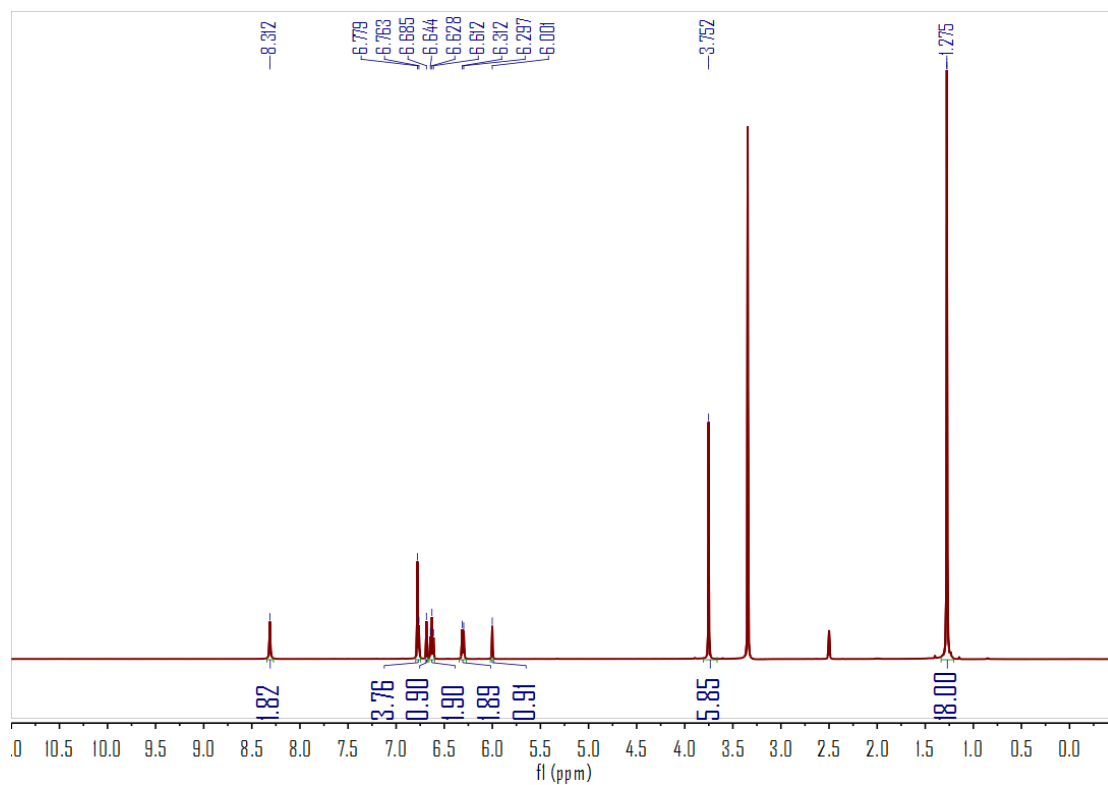


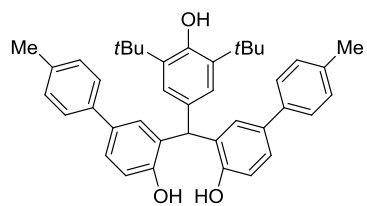
3i



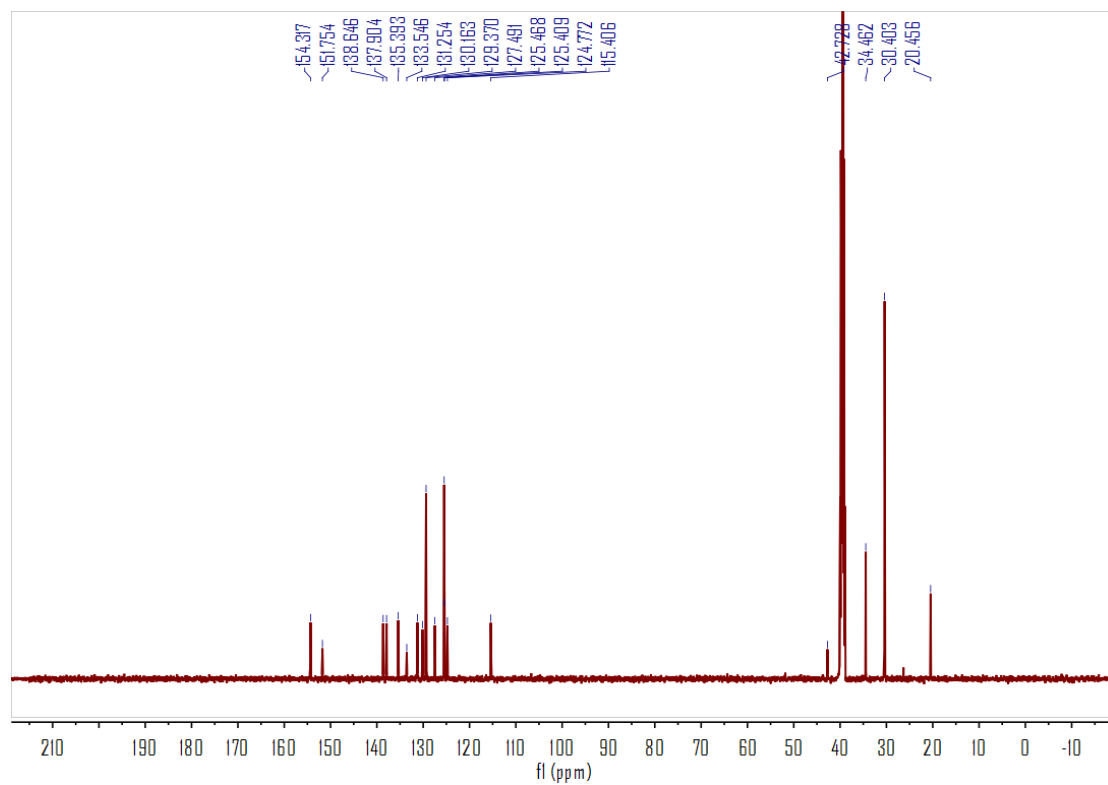
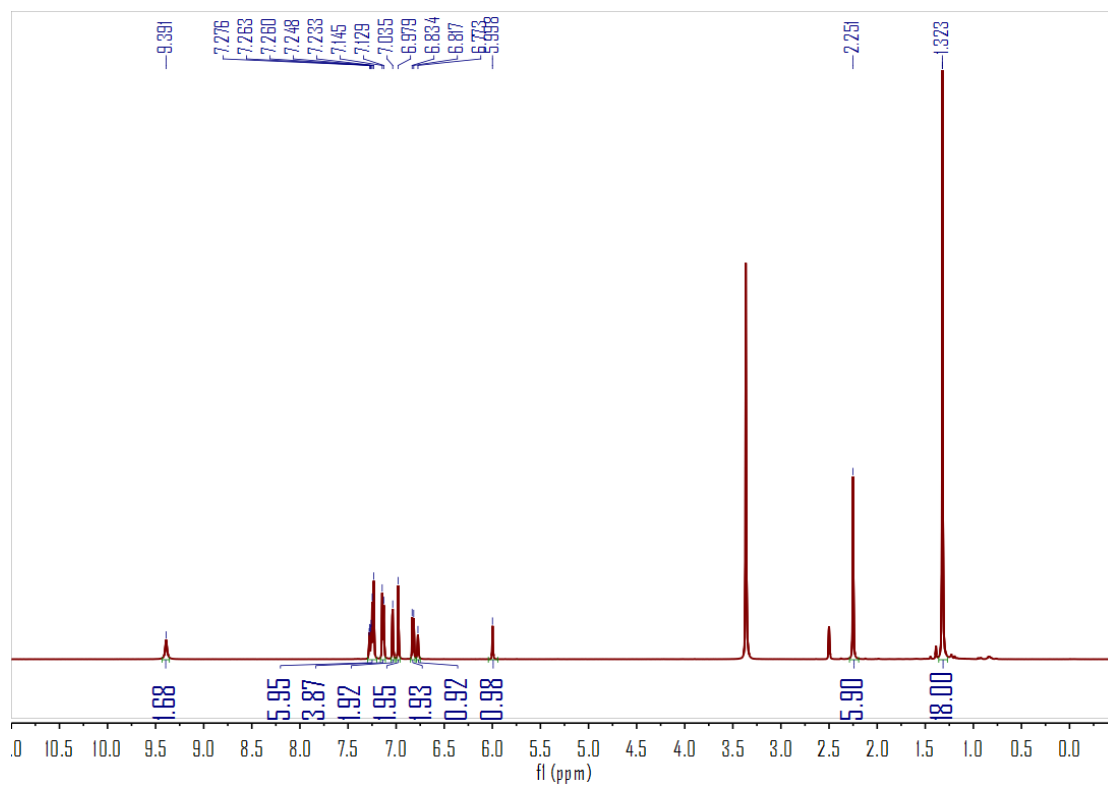


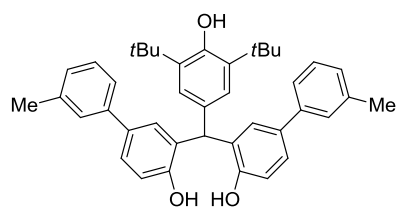
3j



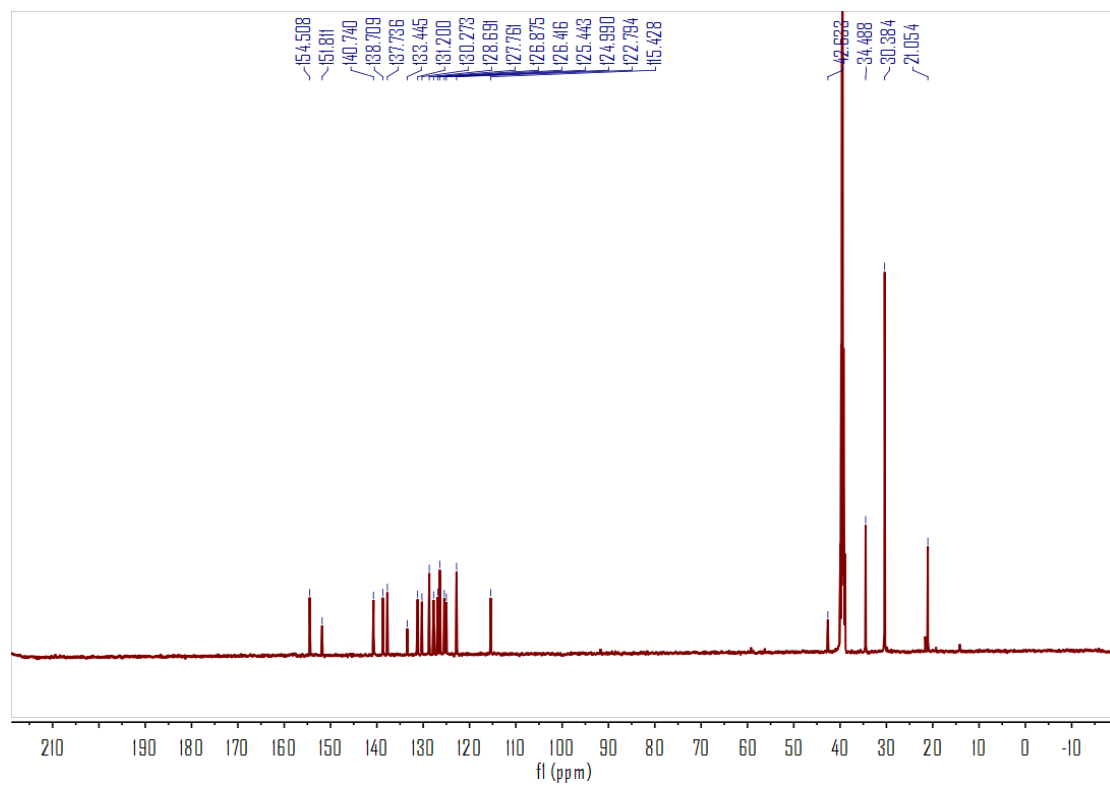
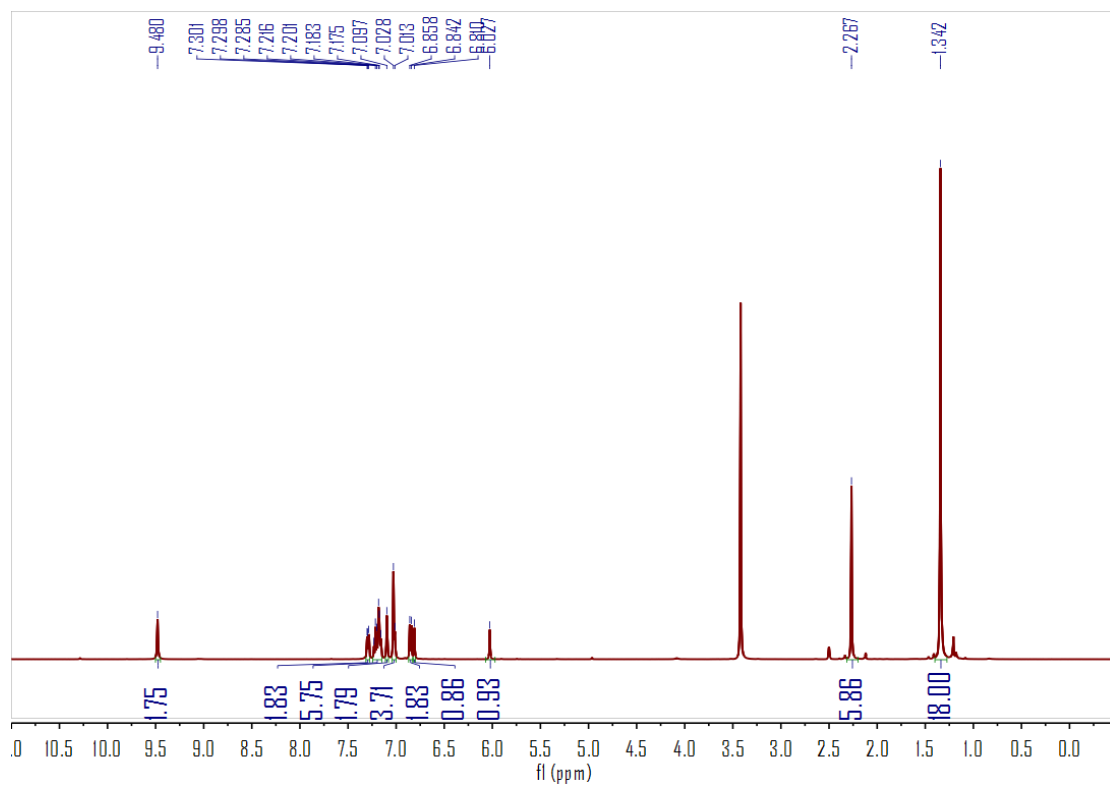


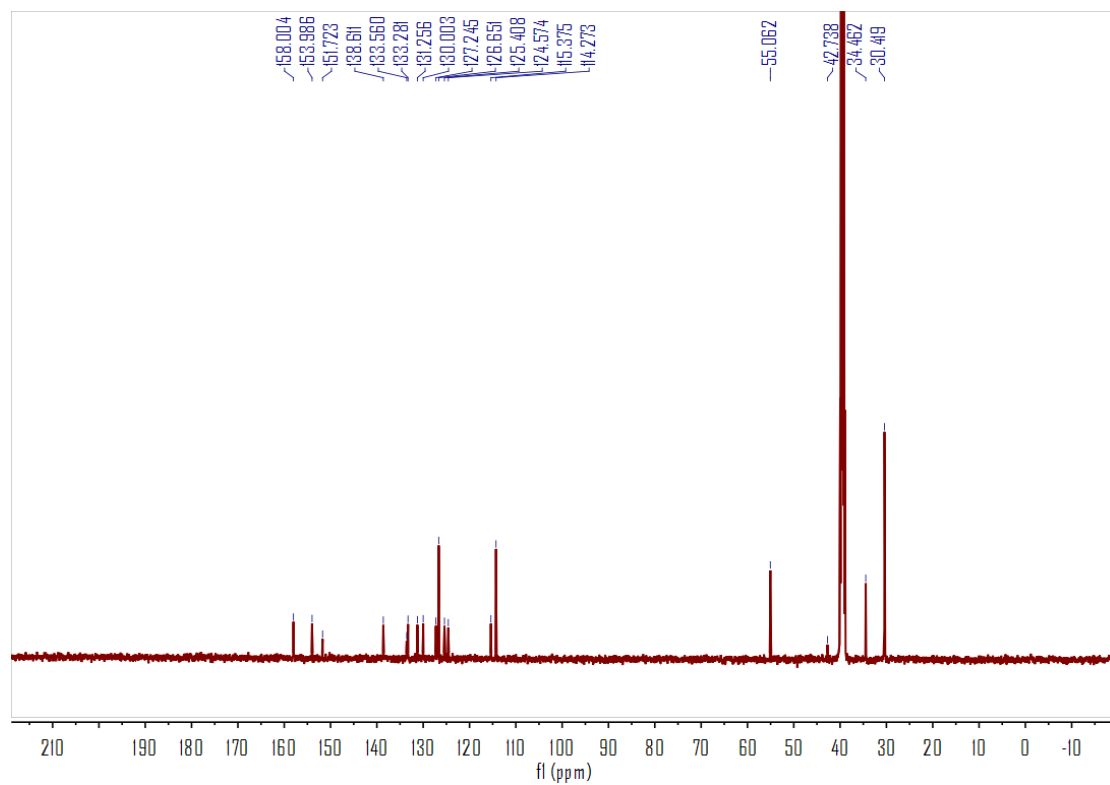
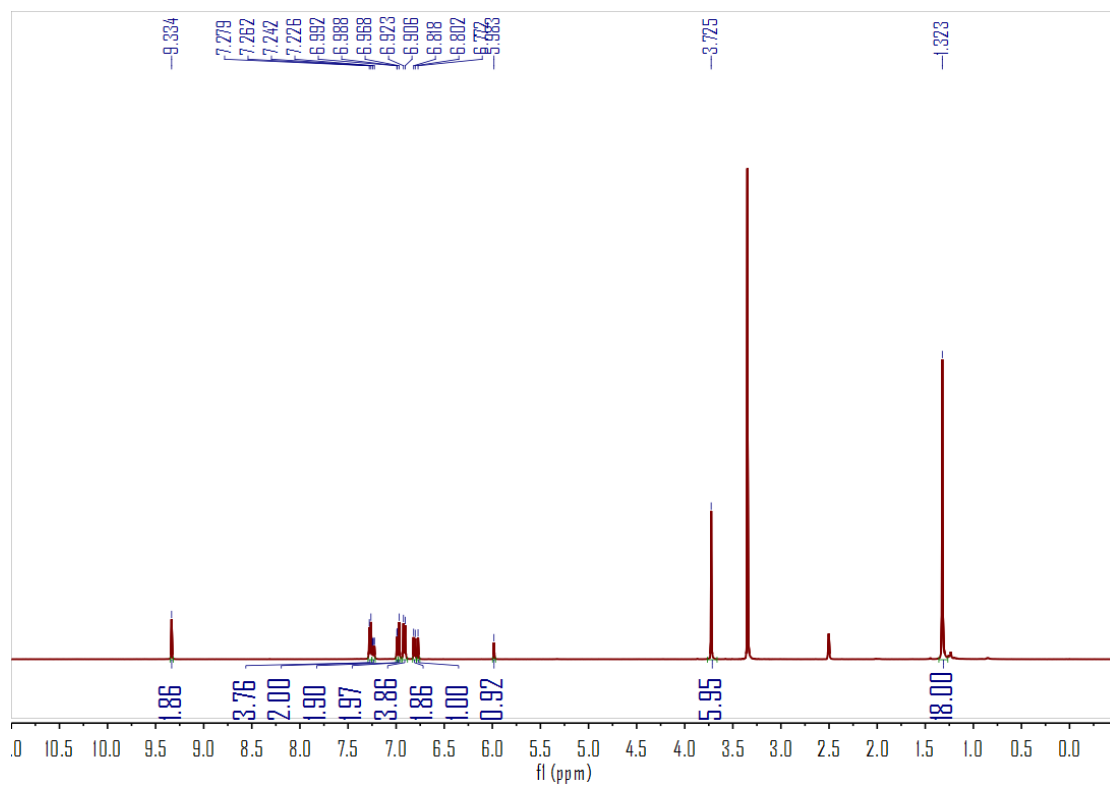
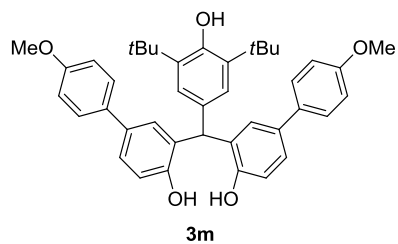
3k

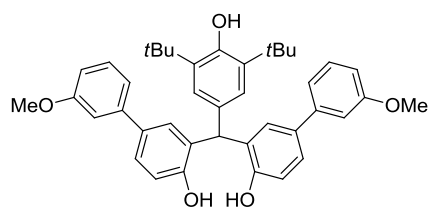




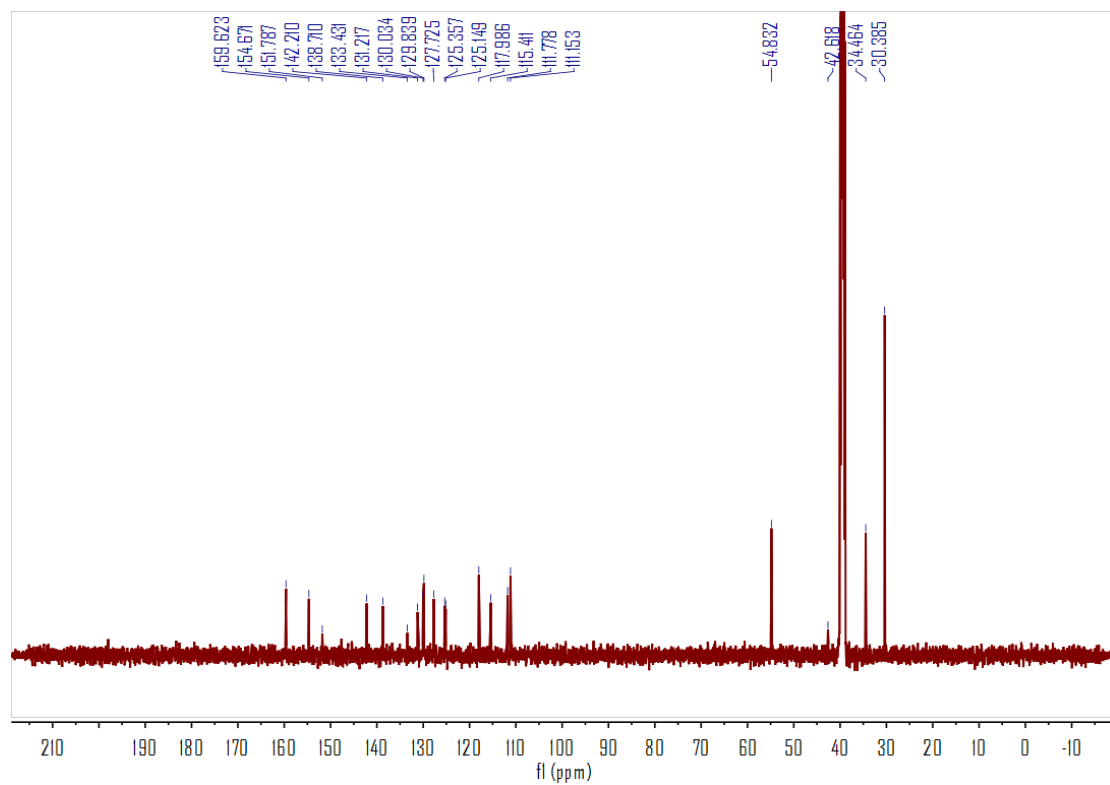
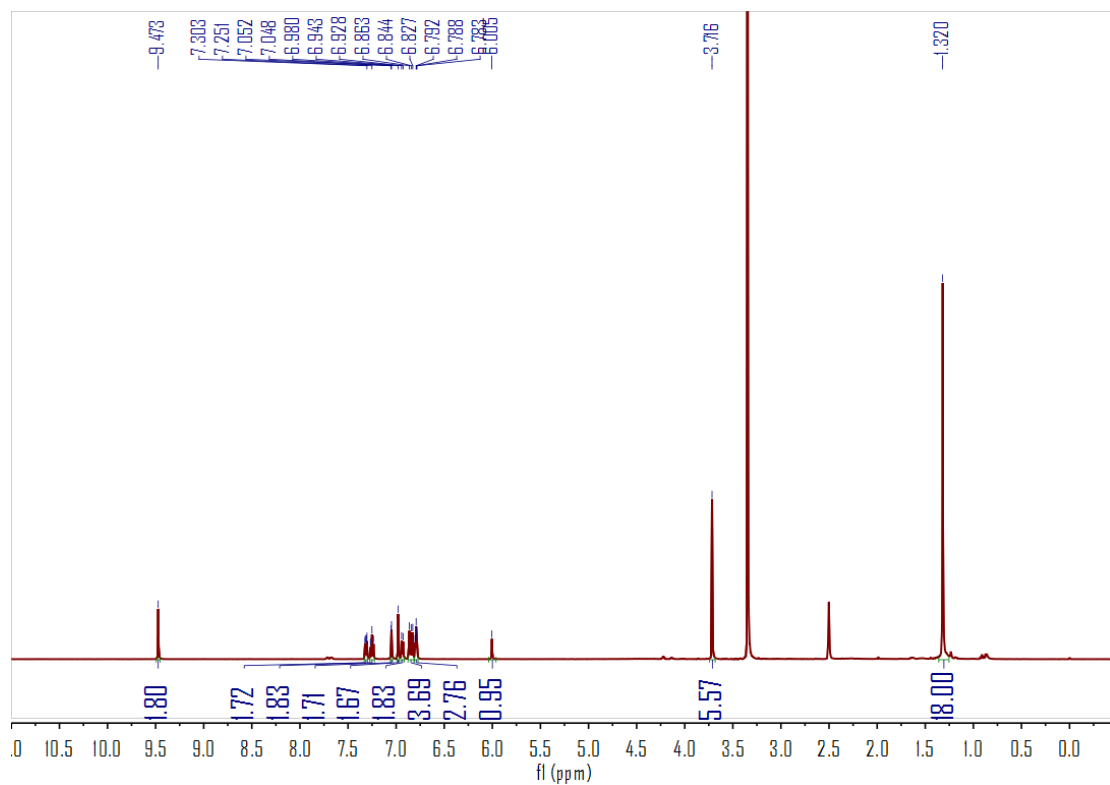
31

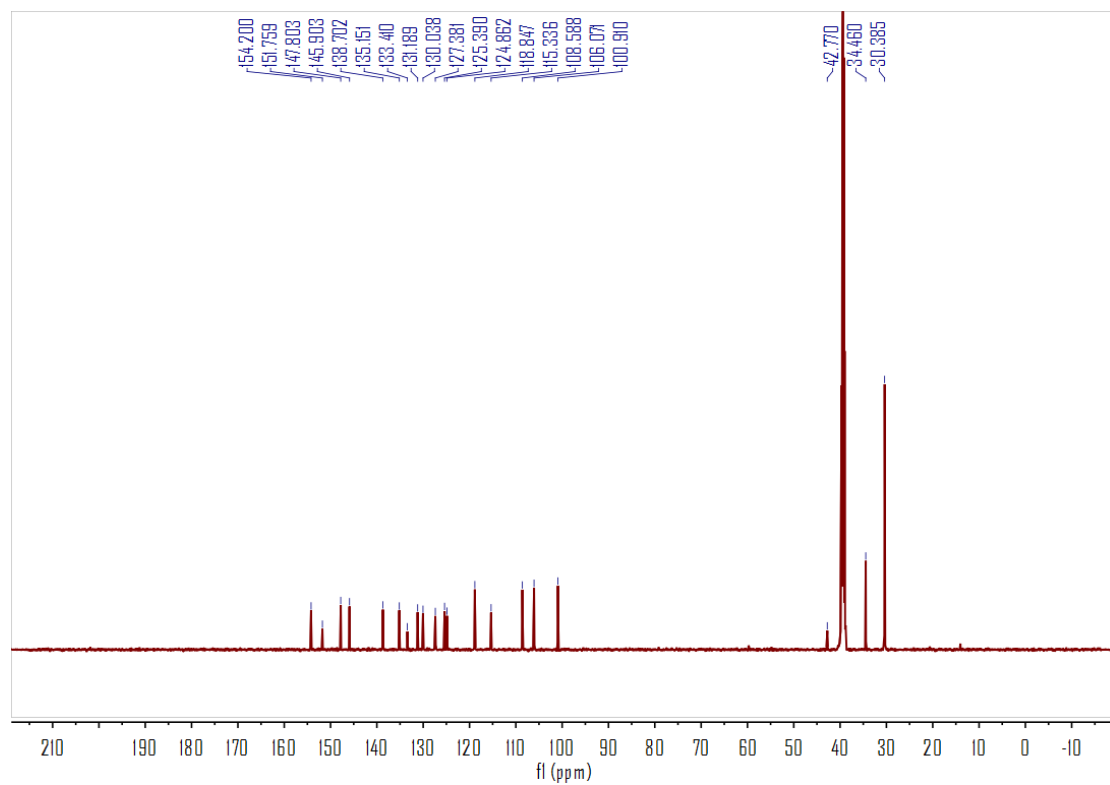
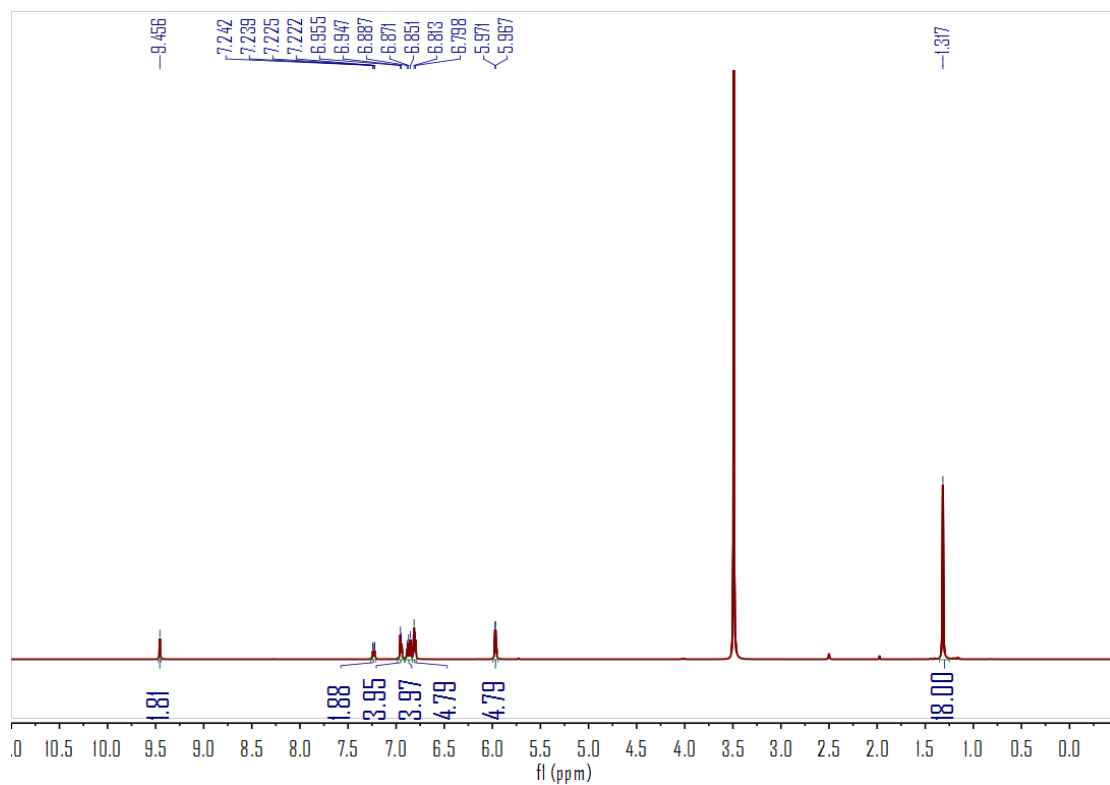
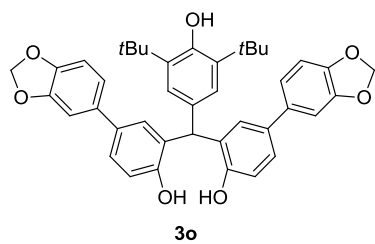


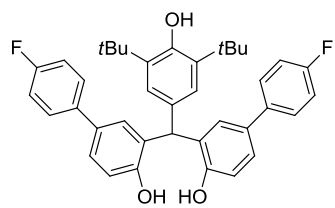




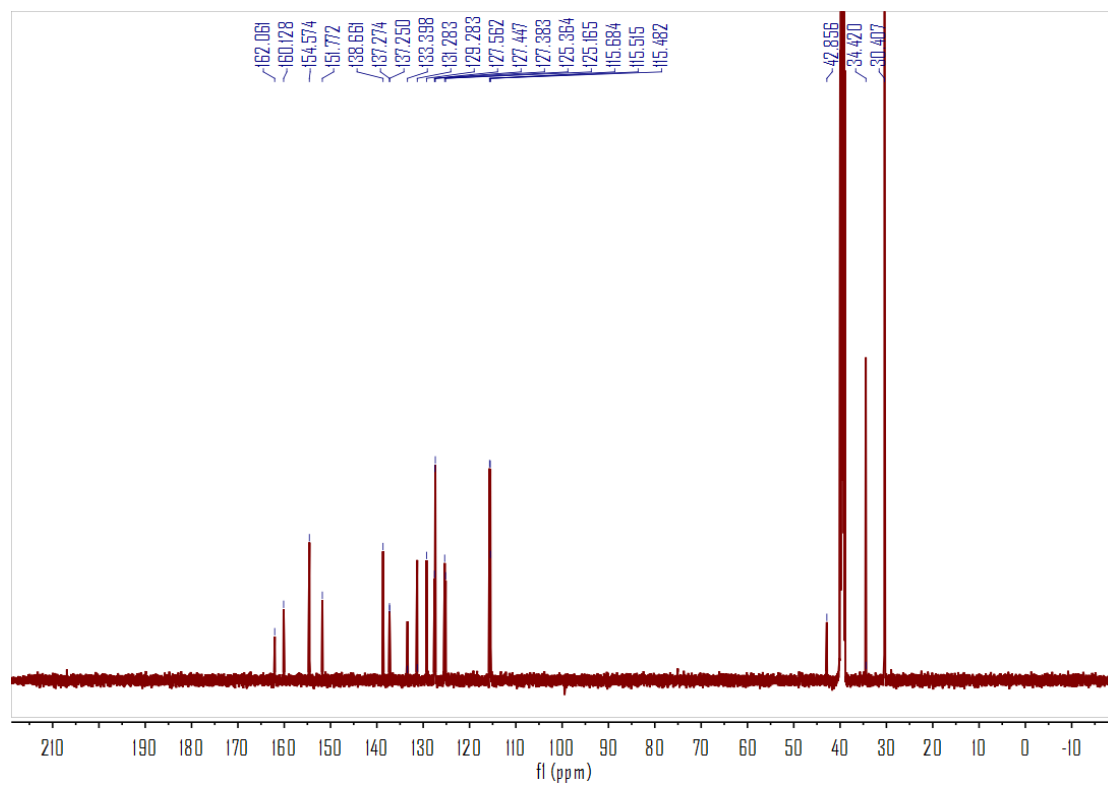
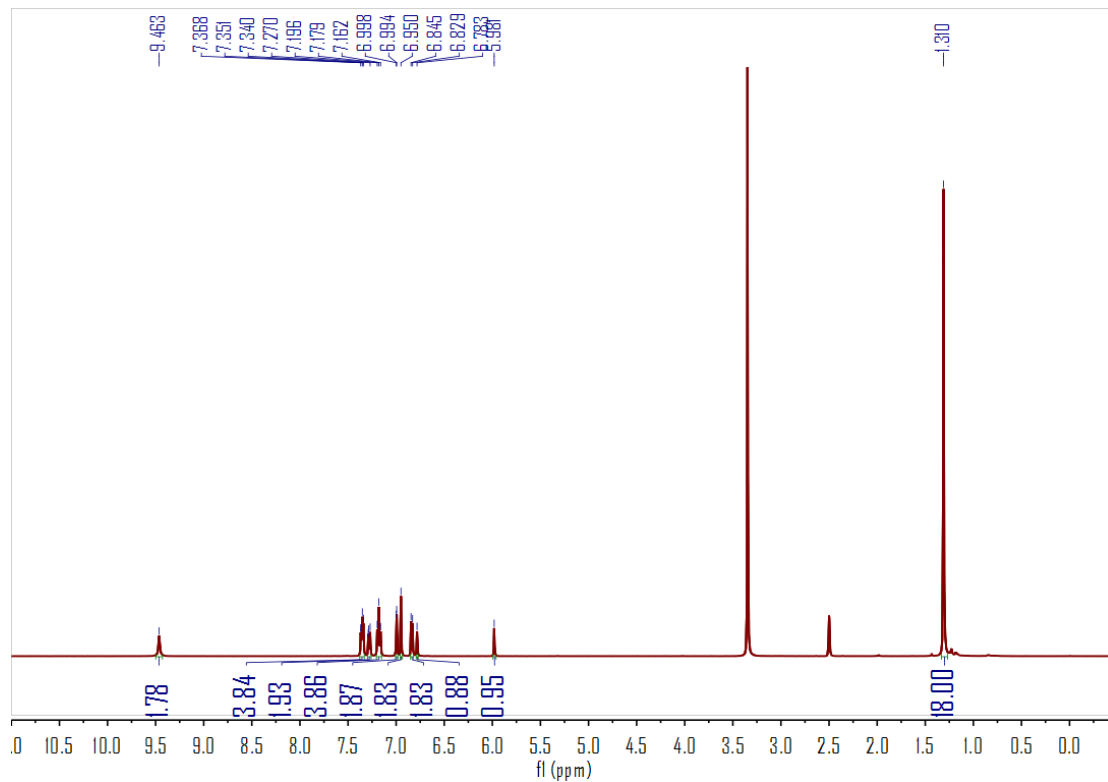
3n

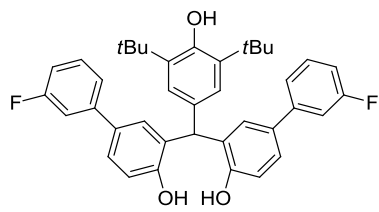




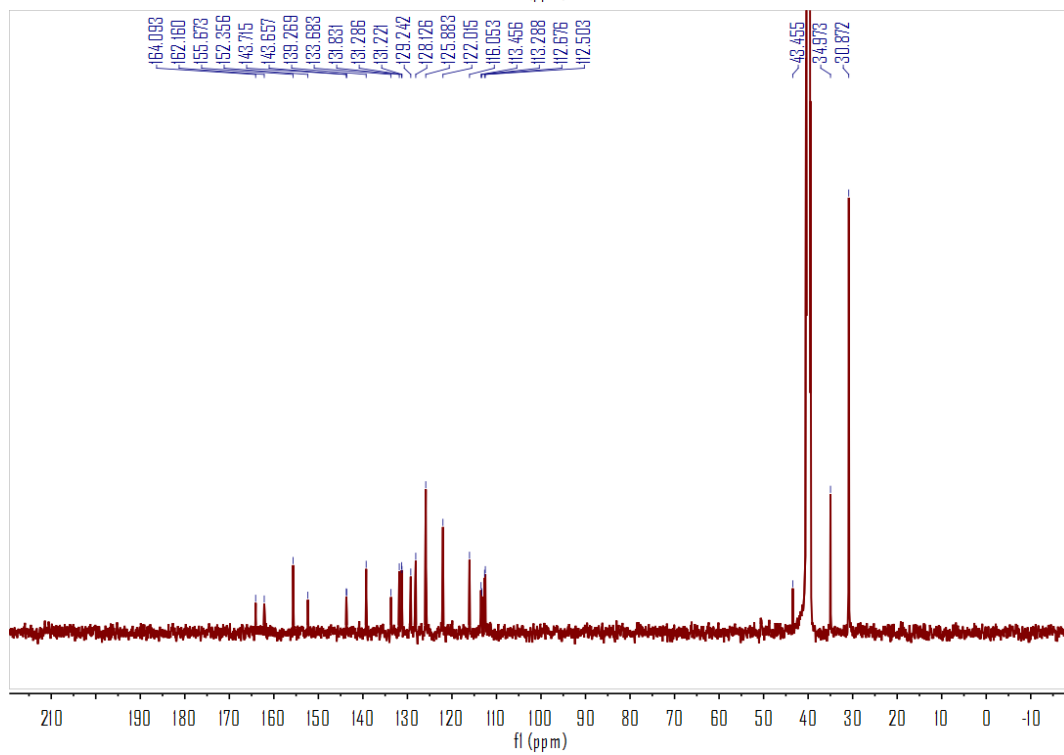
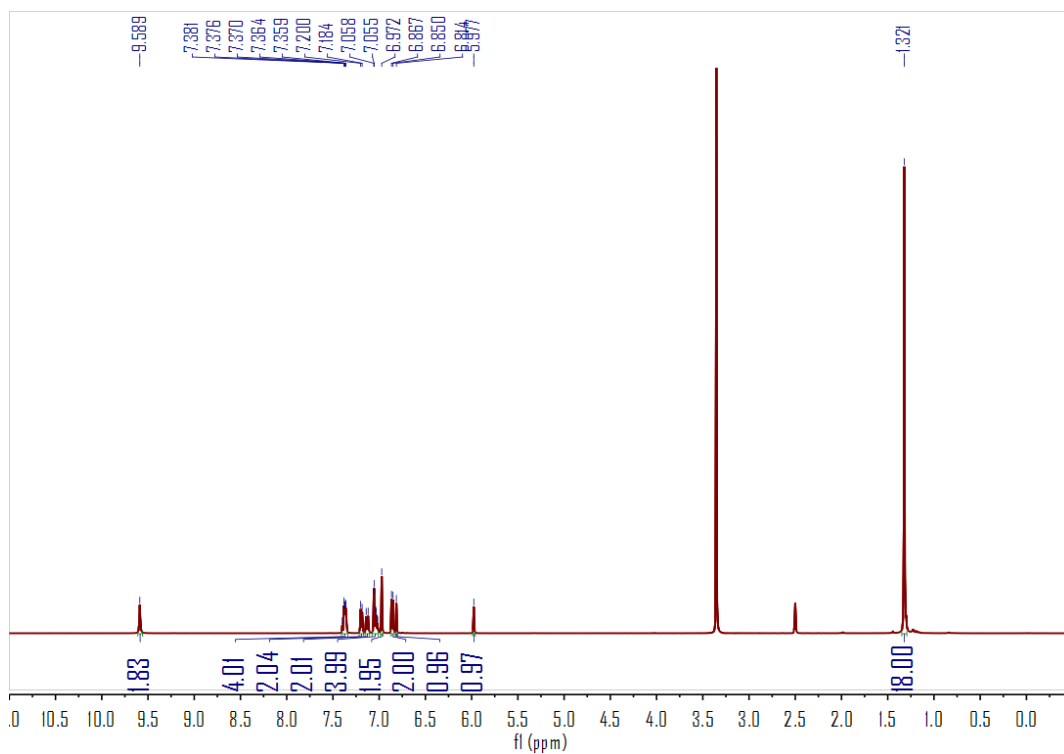


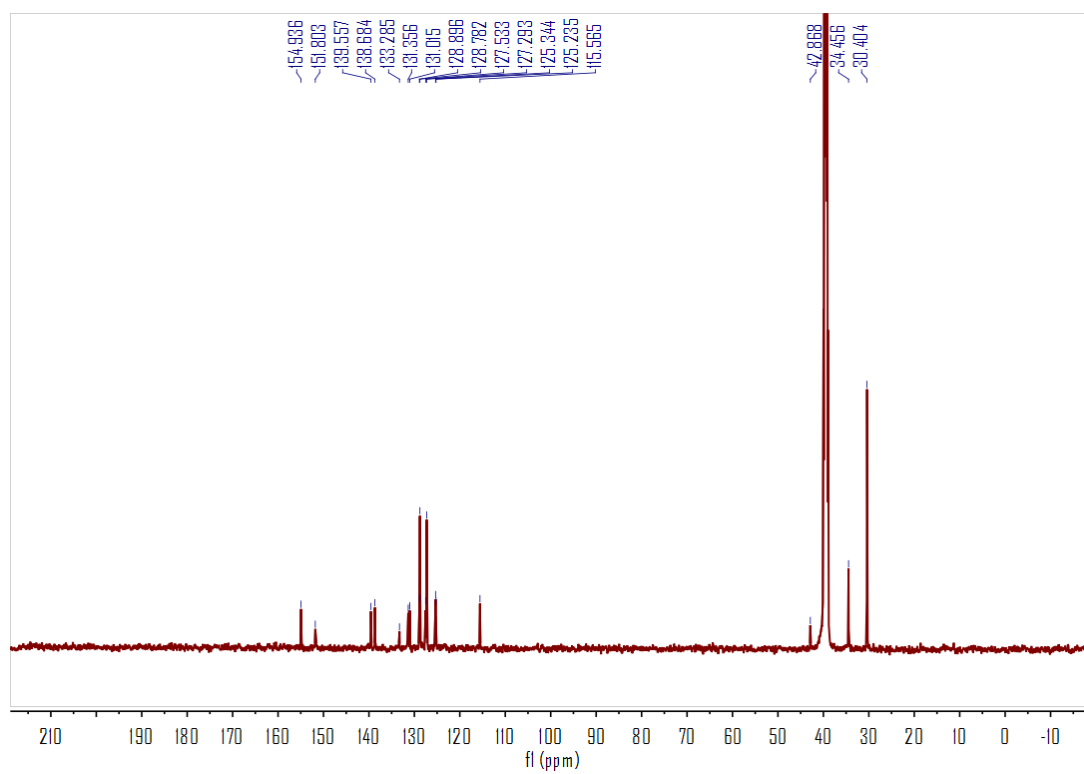
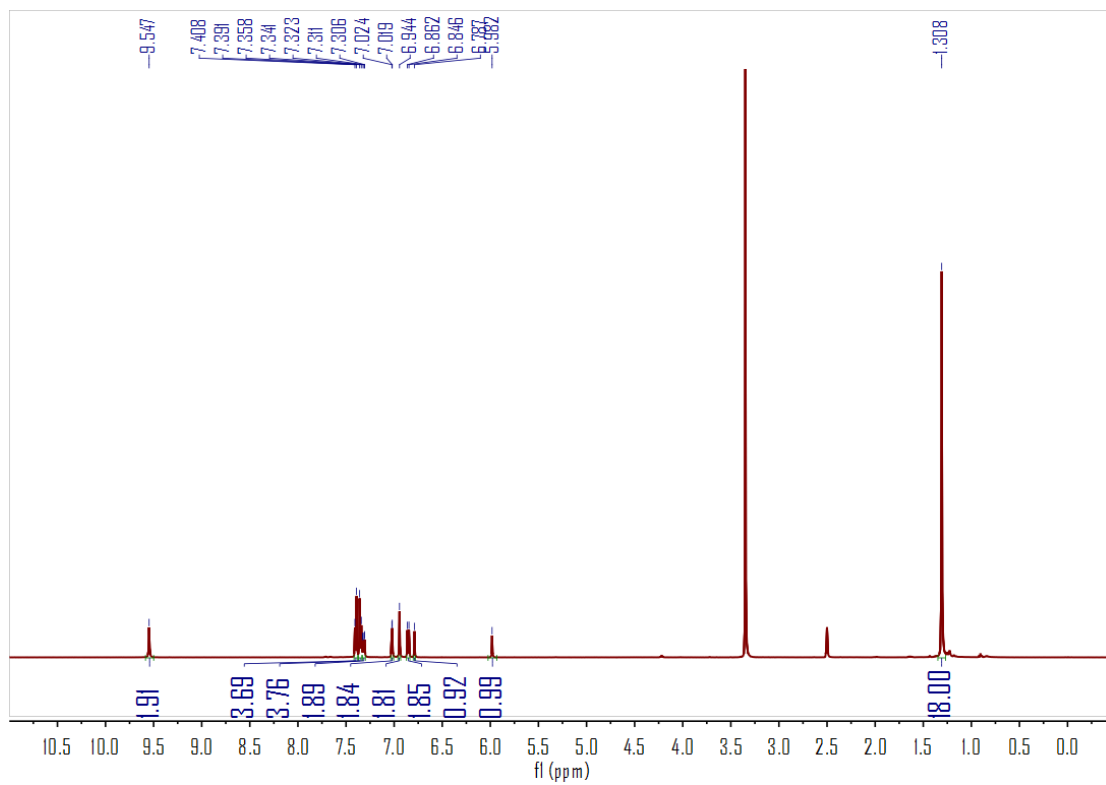
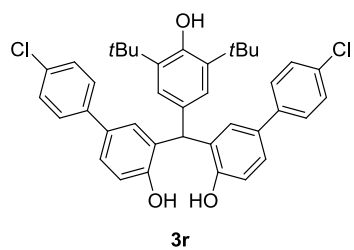
3p

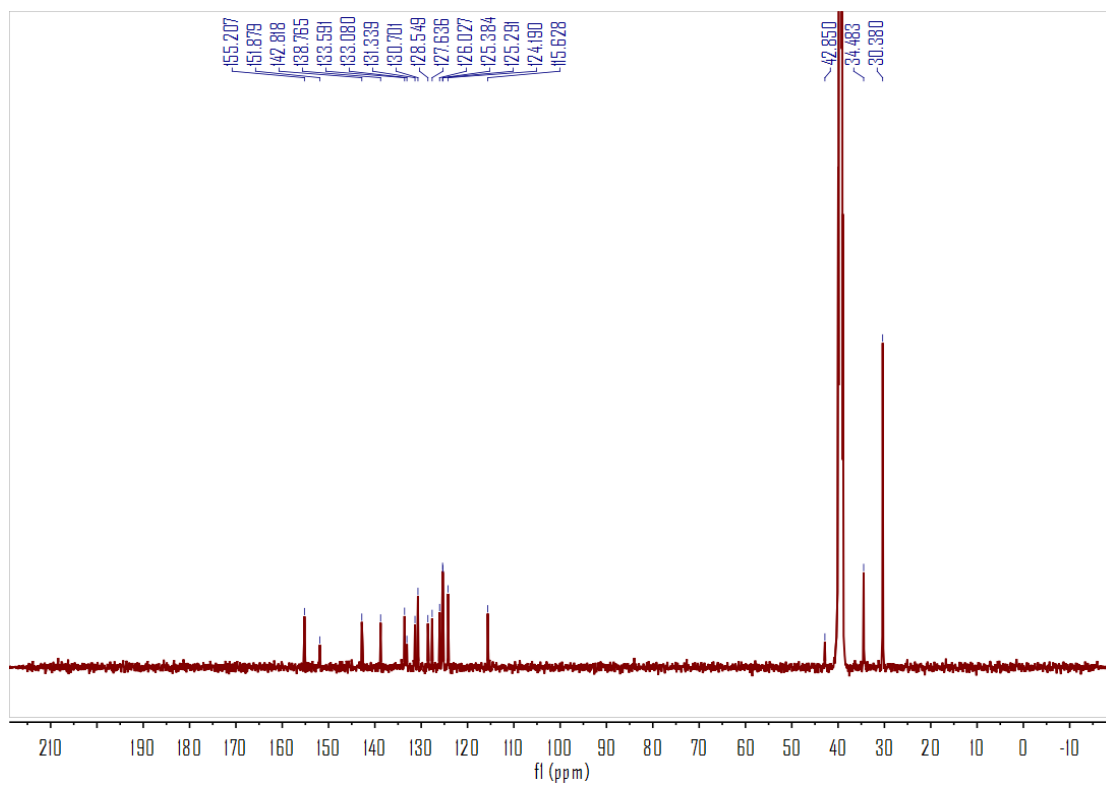
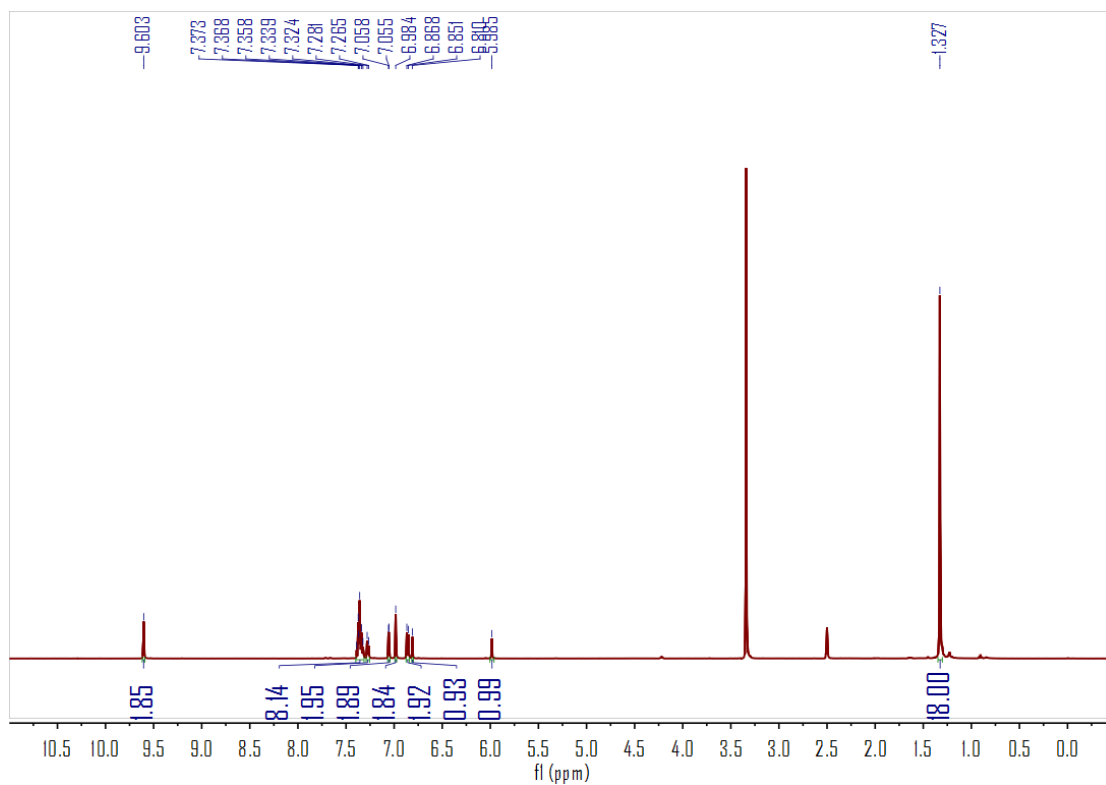
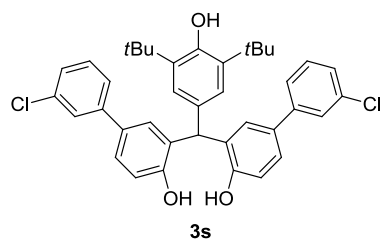


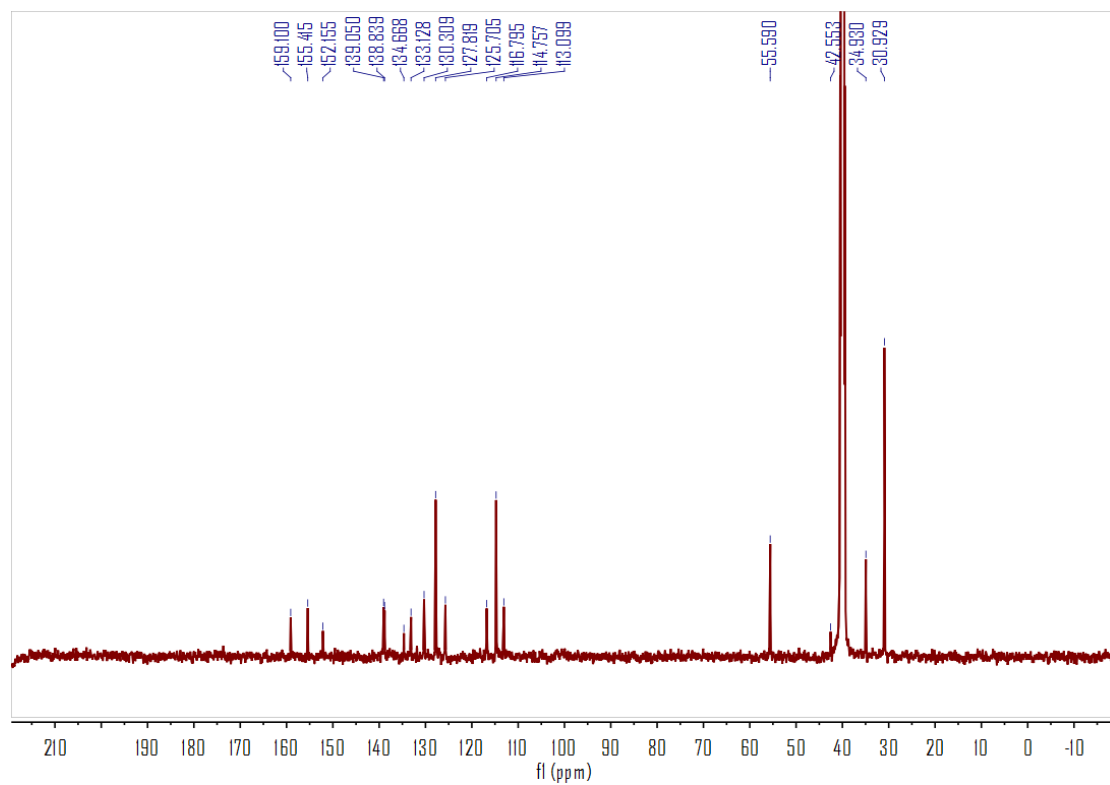
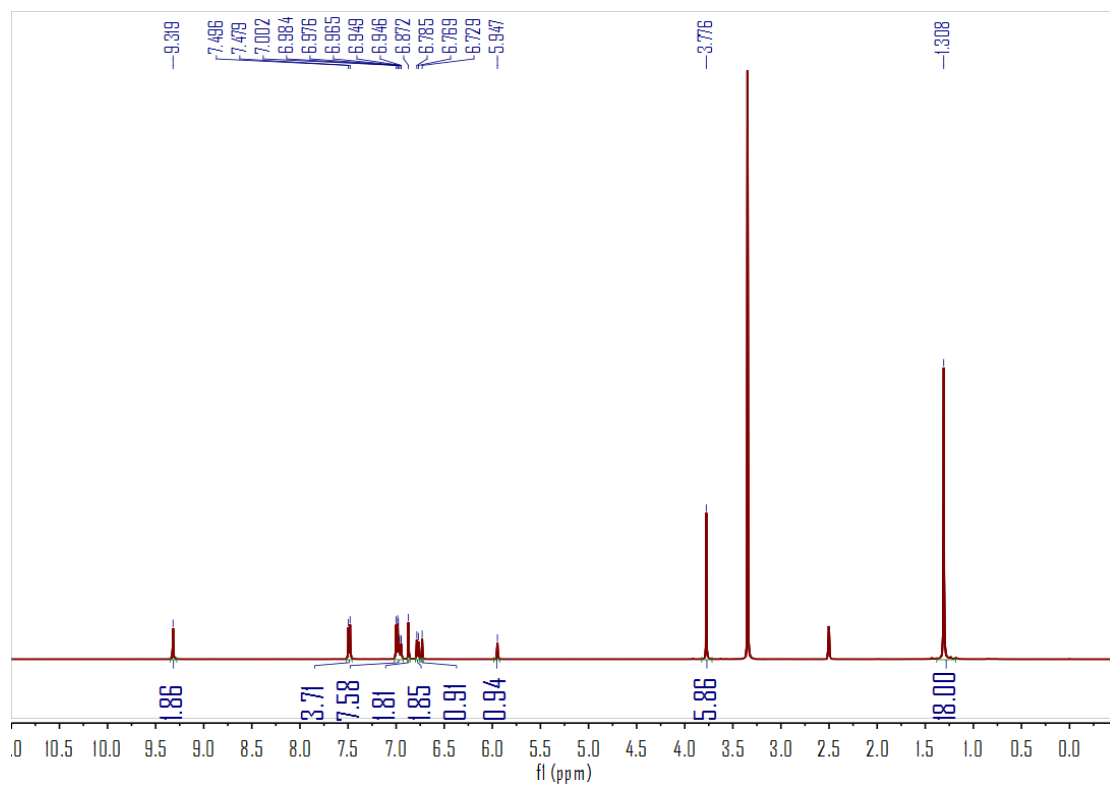
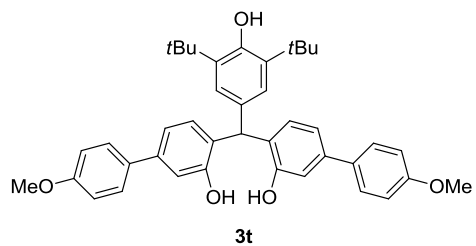


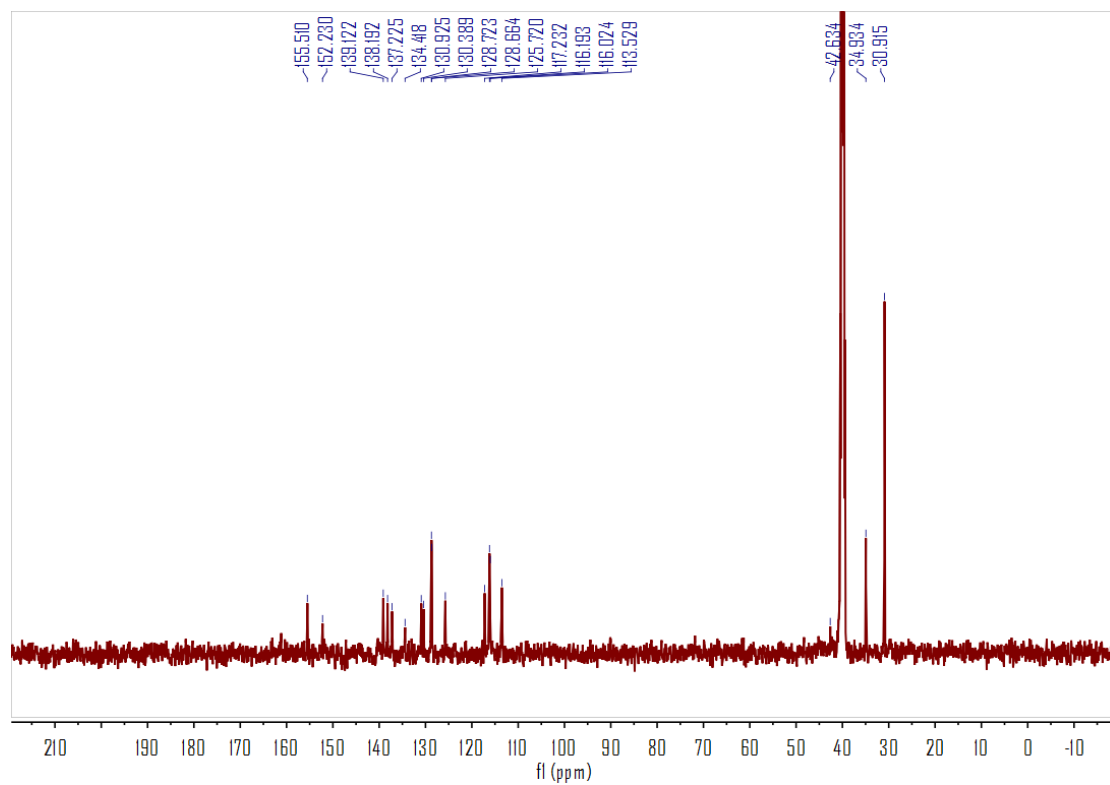
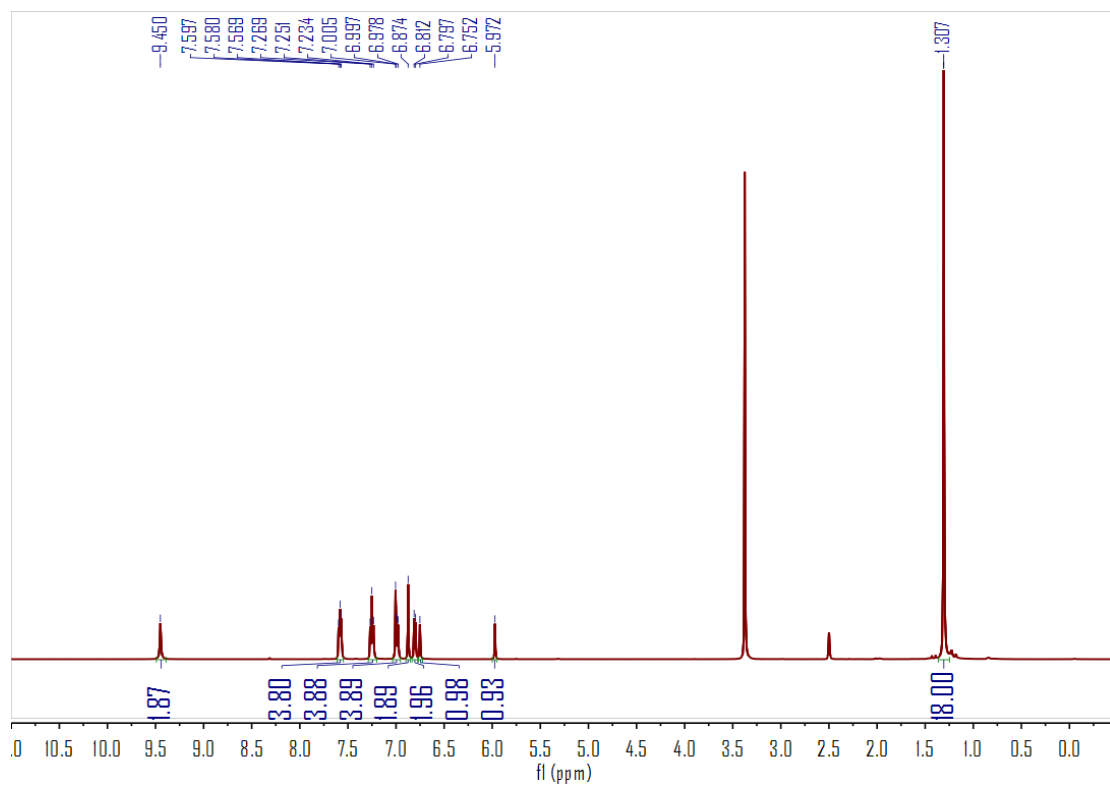
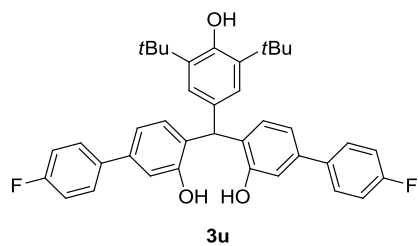
3q

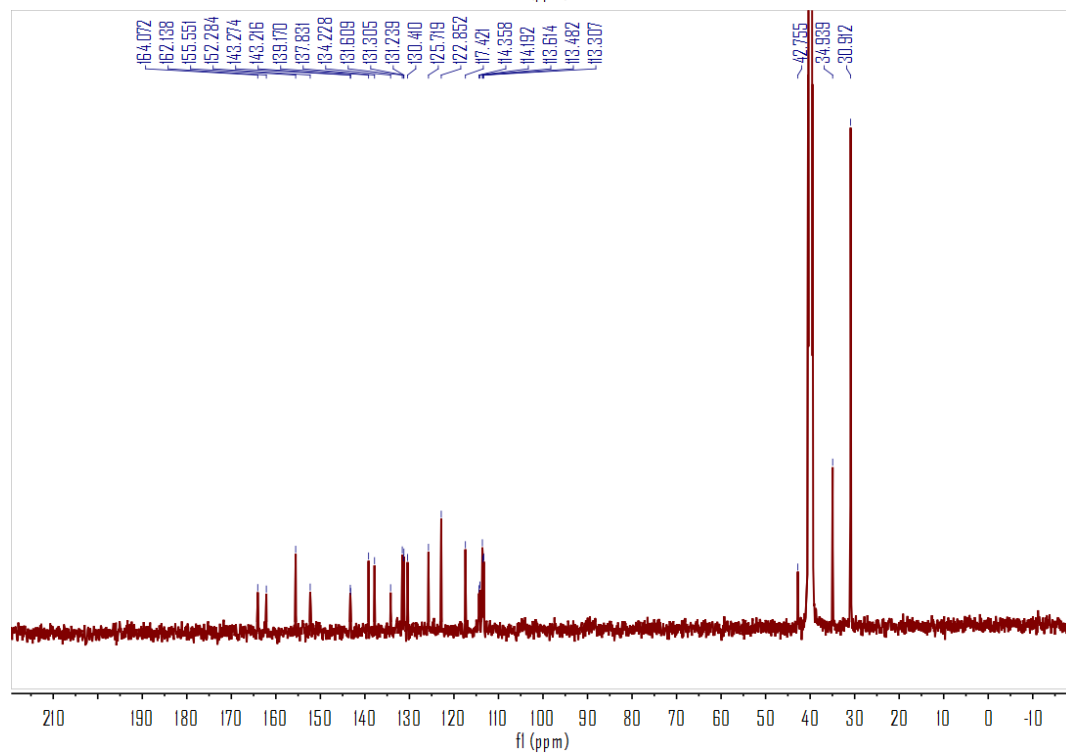
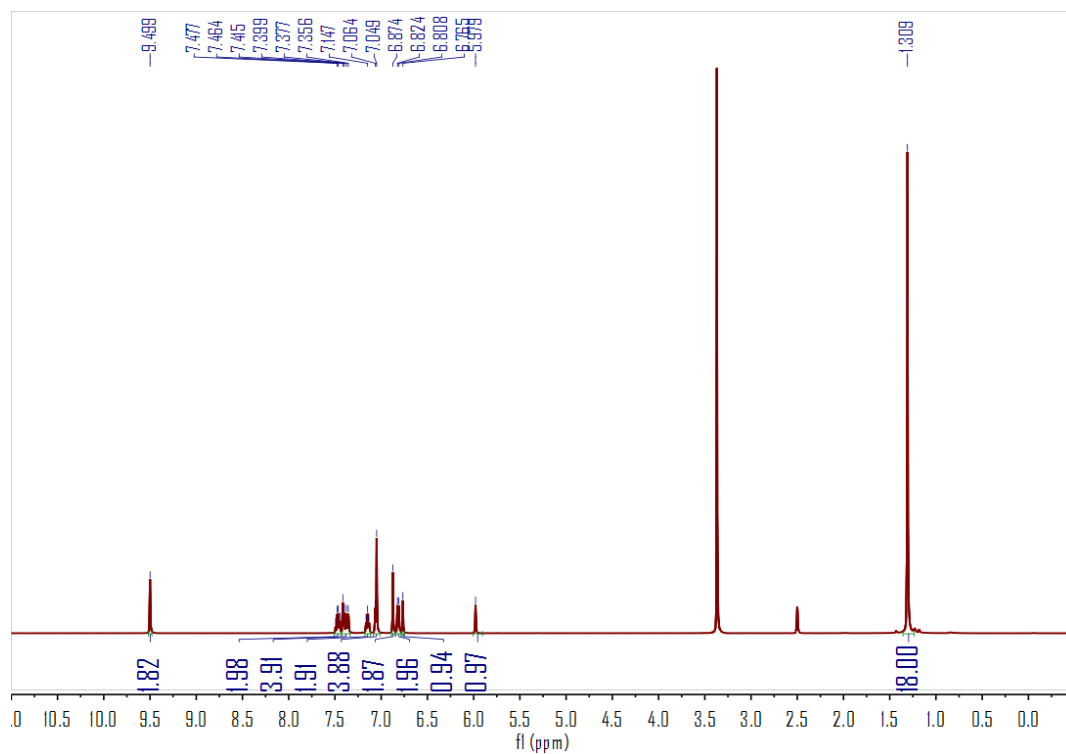
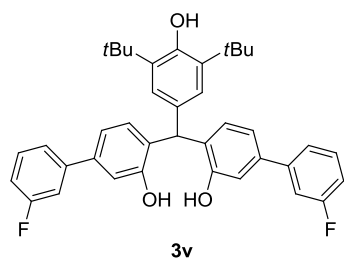


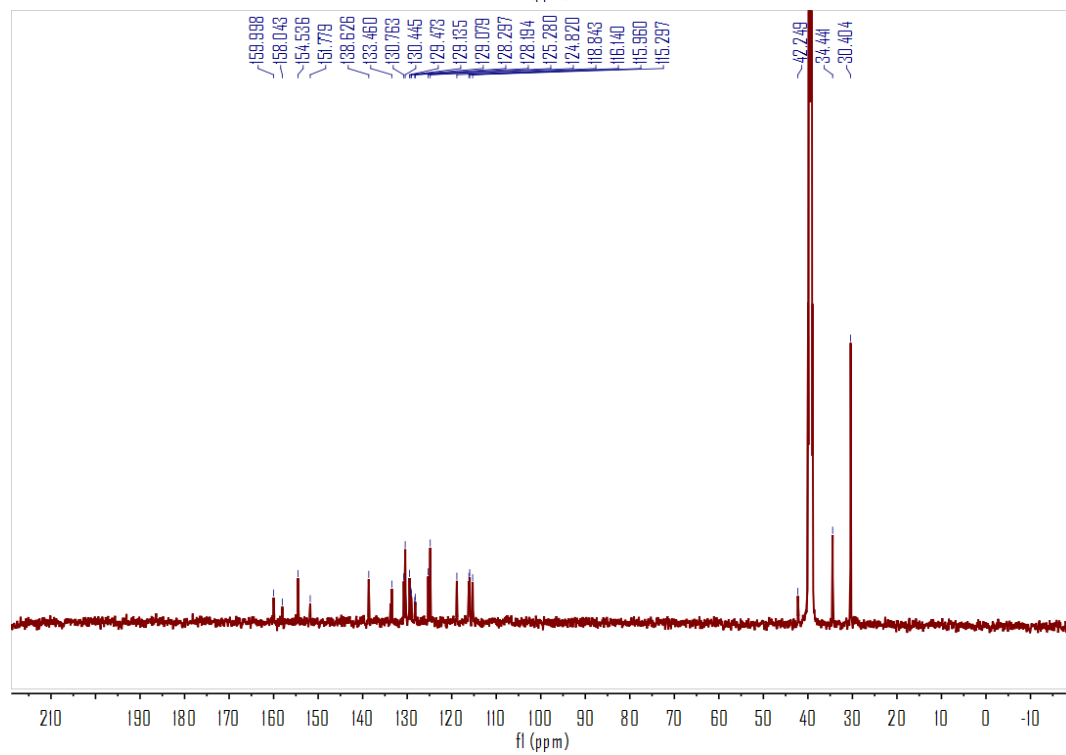
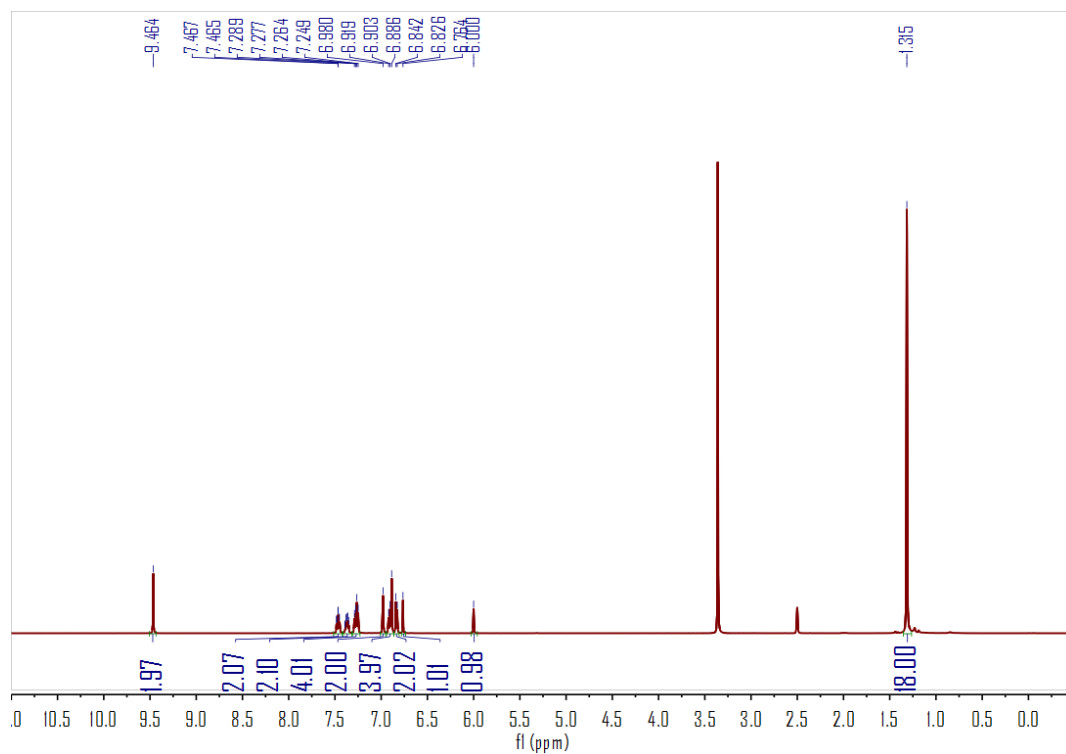
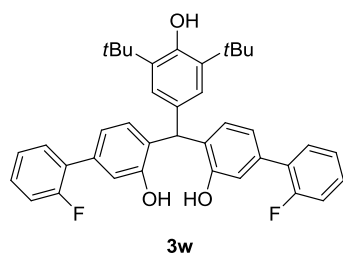


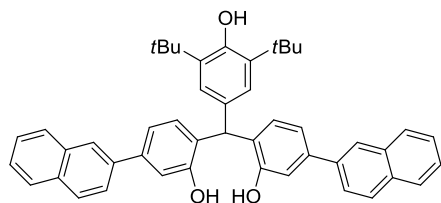




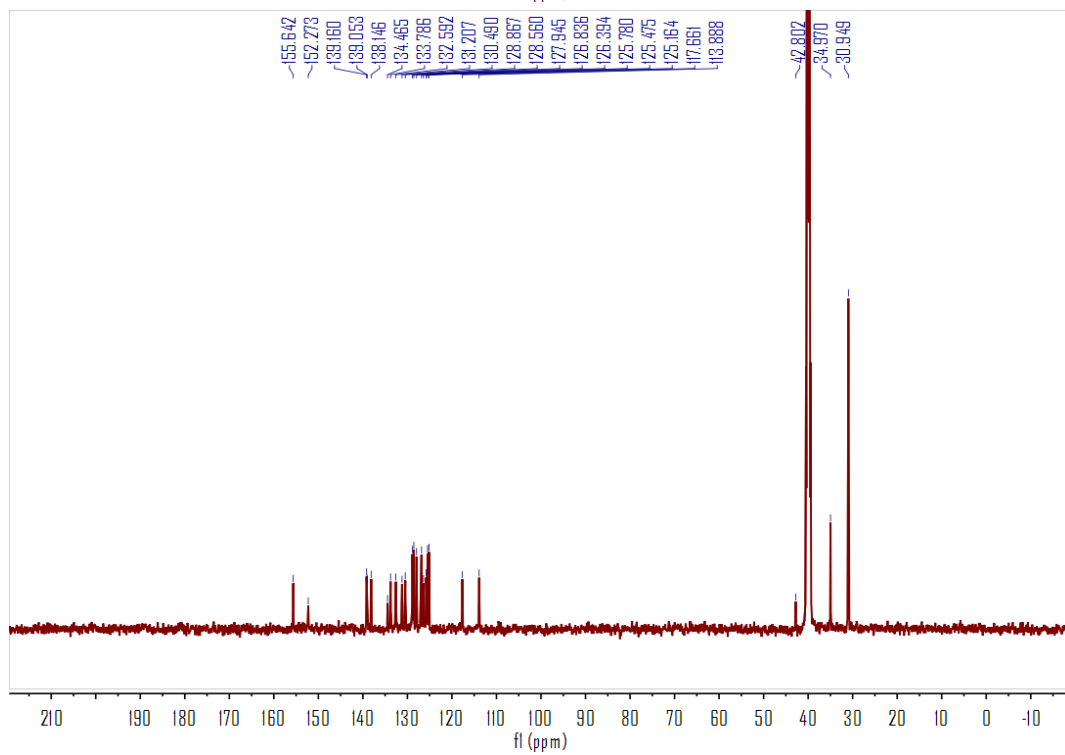
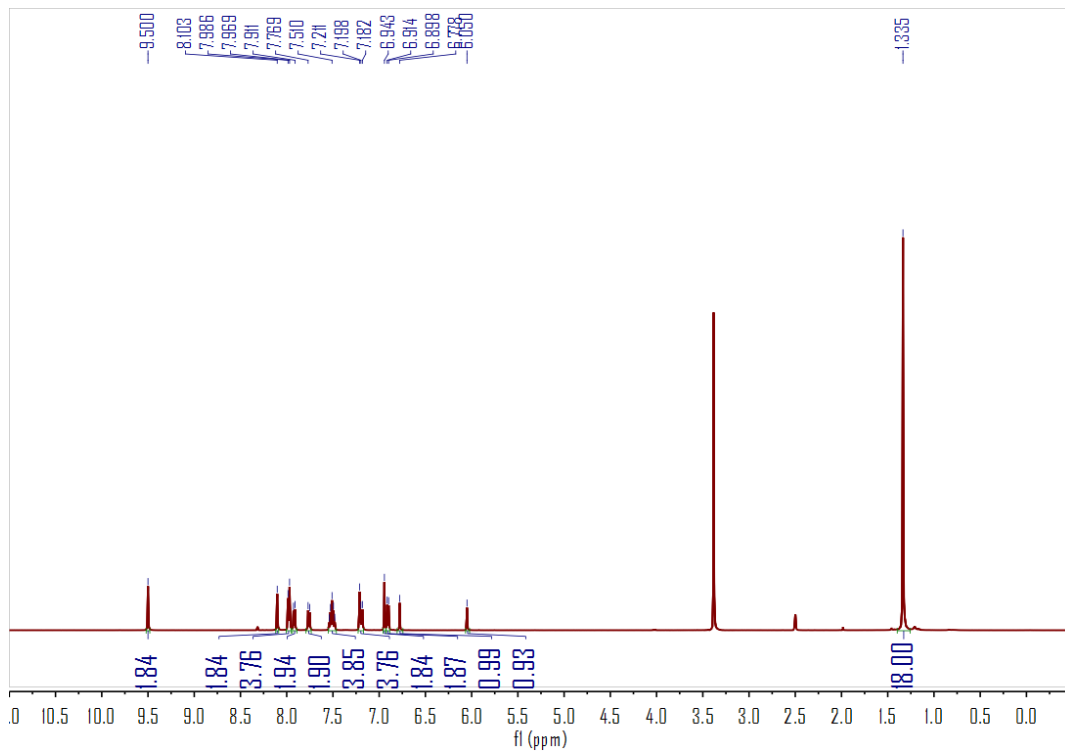


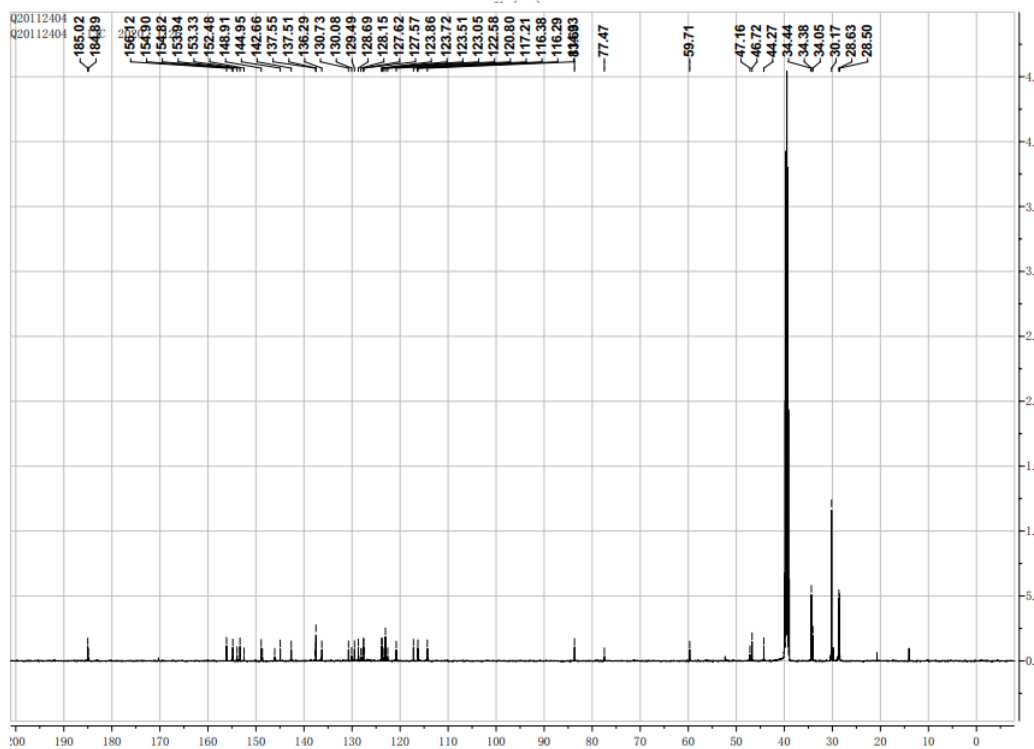
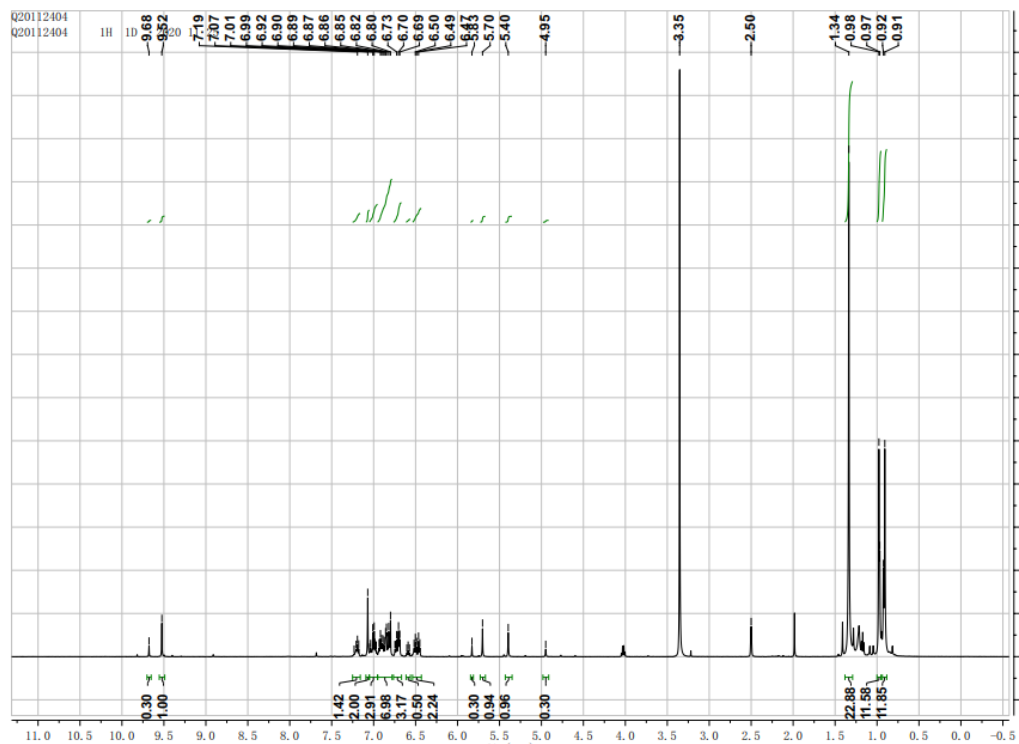
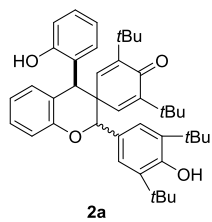






3x





6. References

1. (a) Zhao, K.; Zhi, Y.; Shu, T.; Valkonen, A.; Rissanen, K.; Enders, D. *Angew. Chem. Int. Ed.* **2016**, *55*, 12104-12108. (b) Liu, S.; Lan, X.-C.; Chen, K.; Hao, W.-J.; Li, G.; Tu, S.-J.; Jiang, B. *Org. Lett.* **2017**, *19*, 3831-3834.
2. Sun, P.; Gao, S.; Yang, C.; Guo, S.; Lin, A.; Yao, H.; *Org. Lett.* **2016**, *18*, 6464-6467.