

**DMSO-Promoted Direct δ -Selective Arylation of *p*-Quinone
Methides to Generate Fuchsones under Metal-free Conditions
by Employing *p*-QMs themselves or Substituted Phenols as Aryl
Sources**

Kunpeng Wang,^{+,a} Jingping Li,^{+,a} Haoxiang Zhang,^a Yan Chen,^a Mengfan Li,^a Junju
Xu,^{*,b} Benren Liao,^{*,c} and Weiyin Yi ^{*,a}

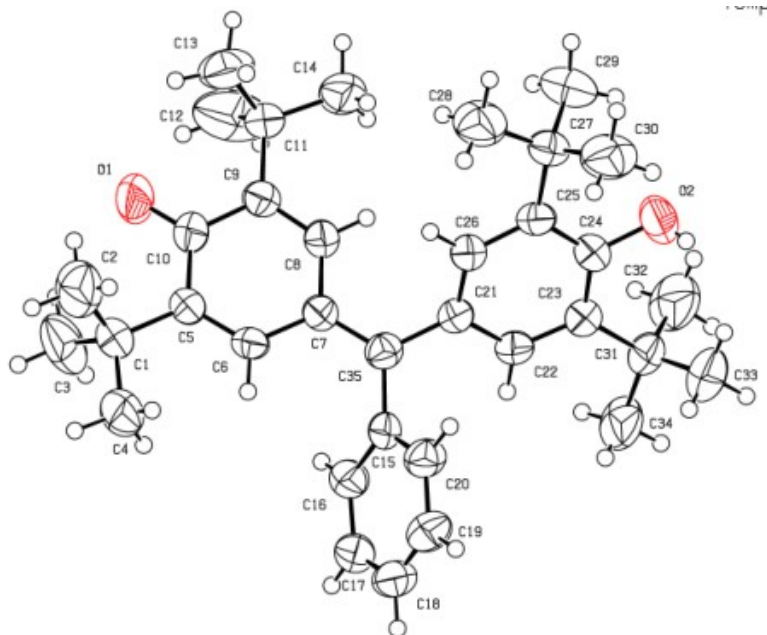
Supporting information

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1. X-Ray Data

Crystal structure of the compound **2a**. Thermal ellipsoids are shown at 40% probability level.



key bond length(Å)
C(7)-C(35) 1.385(6)
C(15)-C(35) 1.488(6)
C(21)-C(35)
1.477(6)
C(10)-O(1) 1.232(5)
C(24)-O(2) 1.371(5)

2a: CCDC: 2141501

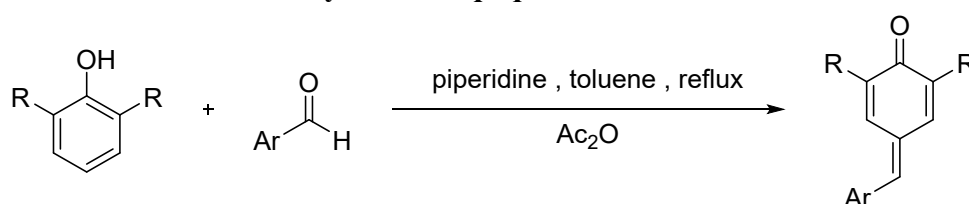
| Identification code | 1_a | |
|-----------------------------------|--|-------------------|
| Empirical formula | C ₃₅ H ₄₆ O ₂ | |
| Formula weight | 498.72 | |
| Temperature | 296(2) K | |
| Wavelength | 0.71073 Å | |
| Crystal system | Triclinic | |
| Space group | P-1 | |
| Unit cell dimensions | a = 10.448(9) Å | α = 111.204(17)°. |
| | b = 11.226(9) Å | β = 98.515(18)°. |
| | c = 14.378(12) Å | γ = 95.224(19)°. |
| Volume | 1536(2) Å ³ | |
| Z | 2 | |
| Density (calculated) | 1.078 Mg/m ³ | |
| Absorption coefficient | 0.065 mm ⁻¹ | |
| F(000) | 544 | |
| Crystal size | 0.200 x 0.200 x 0.200 mm ³ | |
| Theta range for data collection | 2.575 to 25.000°. | |
| Index ranges | -12 ≤ h ≤ 12, -13 ≤ k ≤ 13, -17 ≤ l ≤ 17 | |
| Reflections collected | 31939 | |
| Independent reflections | 5398 [R(int) = 0.1473] | |
| Completeness to theta = 25.000° | 99.6 % | |
| Absorption correction | Semi-empirical from equivalents | |
| Refinement method | Full-matrix least-squares on F ² | |
| Data / restraints / parameters | 5398 / 0 / 346 | |
| Goodness-of-fit on F ² | 1.035 | |
| Final R indices [I > 2σ(I)] | R1 = 0.0965, wR2 = 0.2324 | |
| R indices (all data) | R1 = 0.2475, wR2 = 0.2933 | |
| Extinction coefficient | n/a | |
| Largest diff. peak and hole | 0.266 and -0.236 e.Å ⁻³ | |

2. Experimental Section

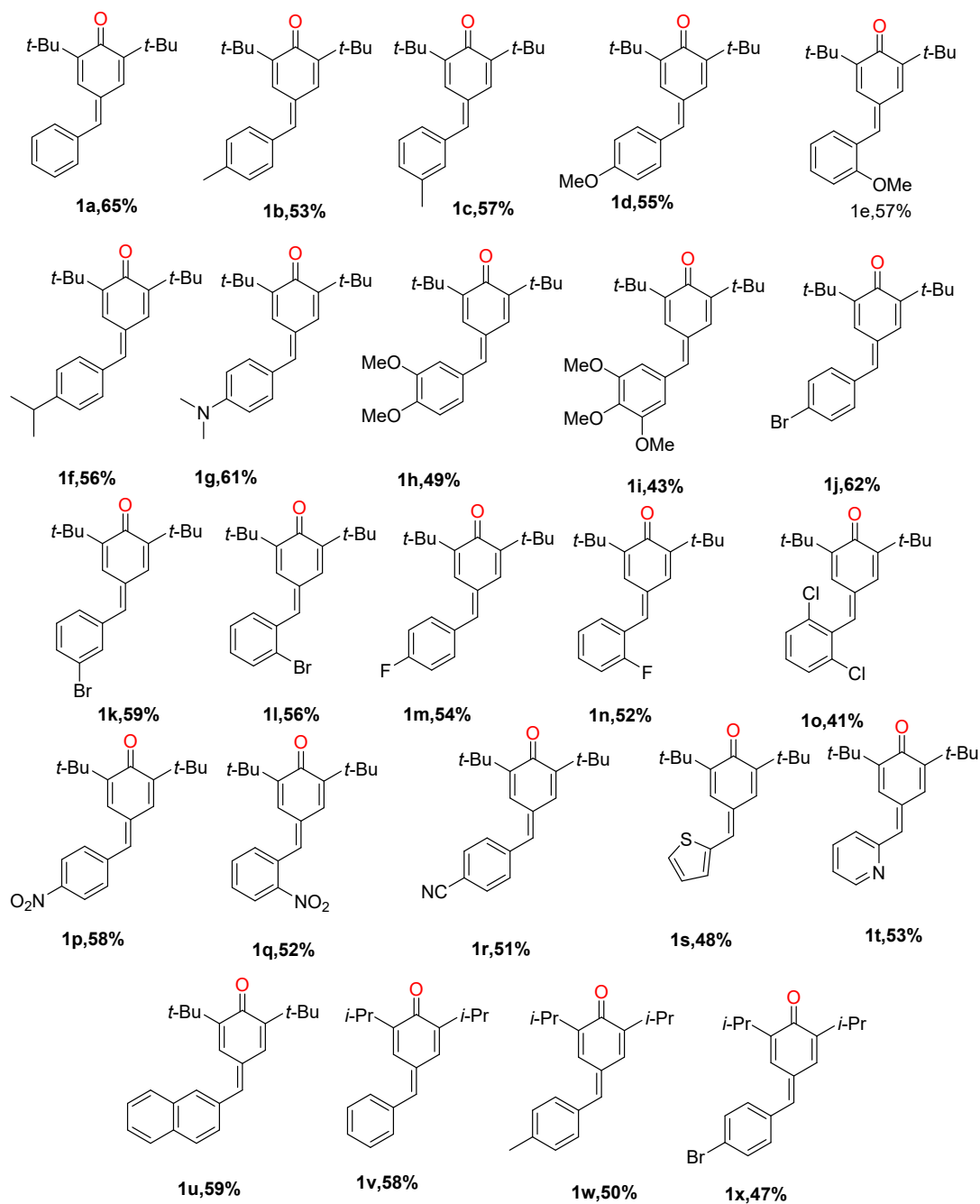
General Information

All reagents and all solvents were purchased from commercial suppliers, and were used without further purification. The progress of reactions was monitored by TLC. For chromatographic purifications, 200-300 mesh silica gel was used. ^1H (400 MHz) and ^{13}C (101 MHz) NMR spectra were recorded with tetramethylsilane as an internal standard. HRMS measurements were carried out using the ESI ionization technique with an FT-ICR analyzer. Data are reported as follows: chemical shift, multiplicity (s = singlet, d = doublet, t = triplet, q = quartet, m = multiplet), coupling constants (Hz) and integration. CCDC (for **2a**) contains the supplementary crystallographic data for this paper. These data can be obtained free of charge from The Cambridge Crystallographic Data Centre.

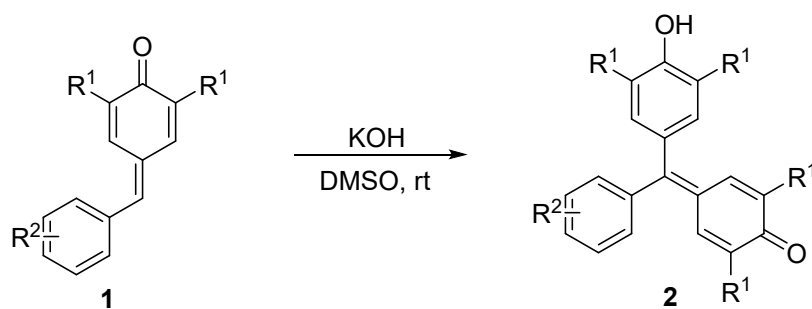
General Procedure for the Synthesis of *p*-quinone methide **1a-1x**.



In a Dean-Stark apparatus, a solution of phenols (25.0 mmol) and the corresponding aldehydes (25.0 mmol) in toluene (100 mL) was heated to reflux. Piperidine (50.0 mmol, 4.94 mL) was dropwise added within 1 h. The reaction mixture was continued to reflux for 12 h. After cooling just below the boiling point of the reaction mixture, acetic anhydride (50.0 mmol, 2.55g) was added and stirring was continued for 15 min. Then the reaction mixture was poured on ice-water (500 mL) and extracted with CH₂Cl₂ (4 x 200 mL). The combined organic phases were dried over anhydrous Na₂SO₄, and the solvent of the filtrate was removed under reduced pressure. The crude products were purified by flash column chromatography and further recrystallized from n-hexane, affording the desired *p*-QMs **1a-1x**.^[1]



General Procedure for the Synthesis of 2a-2x



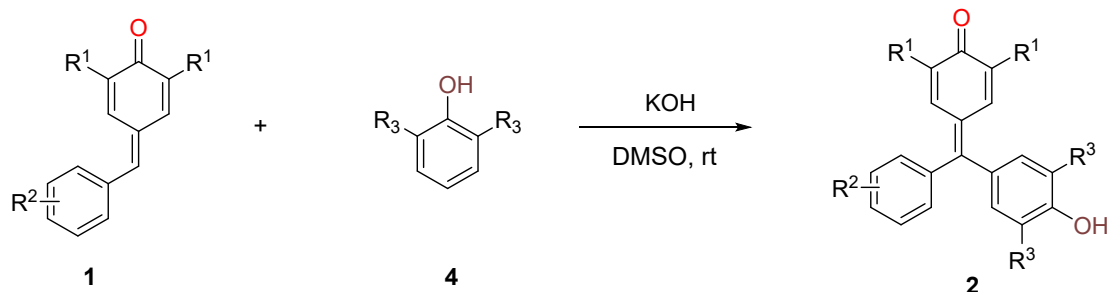
Unless otherwise noted, A dried 10 mL round flask was charged with DMSO

(2.0 ml), *p*-quinone methide (1.0 mmol), and KOH (1.0 mmol), and the mixture is stirred at room temperature until the reaction is complete. After the completion of reaction as was indicated by TLC monitoring. Dilute the mixed species with water and ethyl acetate and continue stirring for 30 minutes, separation. Then the mixture was extracted with EtOAc, and dried over anhydrous Na₂SO₄. The solvent of the filtrate was removed under the reduced pressure. The crude product was purified by flash column chromatography on silica gel to give the desired product **2a-2x**. **1g** reacted for 12 hours at room temperature, and then for 12 hours at 65 °C to afford **2g**.

Gram scale synthesis method of **2a** and **2i**

A dried 50 mL round flask was charged with DMSO (10 ml), *p*-quinone methide (5 mmol, 1.47 g), and KOH (5 mmol), and the mixture was stirred at room temperature until the reaction is complete. After the completion of reaction as was indicated by TLC monitoring. Dilute the mixed species with water and ethyl acetate and continue stirring for 30 minutes, separation. Then the mixture was extracted with EtOAc, and dried over anhydrous Na₂SO₄. The solvent of the filtrate was removed under the reduced pressure. The crude product was purified by flash column chromatography on silica gel to give the desired product **2a** (0.997g, 80%). Similar result was obtained when *p*-QM **1i** (1.92 g) was used and the desired **2i** was furnished in 62% yield (0.913g).

General Procedure for the Synthesis of **2a-2ar**



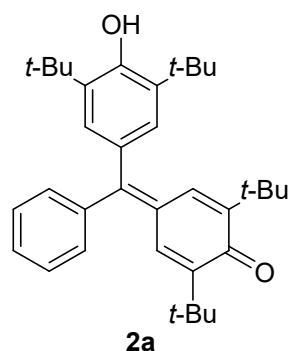
Unless otherwise noted, A dried 10 mL round flask was charged with DMSO (2.0 ml), *p*-quinone methide (1.0 mmol), phenol (1.0 mmol) and KOH (1.0 mmol), and the mixture is stirred at room temperature until the reaction is complete. After the completion of reaction as was indicated by TLC monitoring. Dilute the mixed species with water and ethyl acetate and continue stirring for 30 minutes, separation. Then the mixture was extracted with EtOAc, and dried over anhydrous Na₂SO₄. The solvent of the filtrate was removed under the reduced pressure. The crude product was purified by flash column chromatography on silica gel to give the desired product **2a-2ar**.

Reference

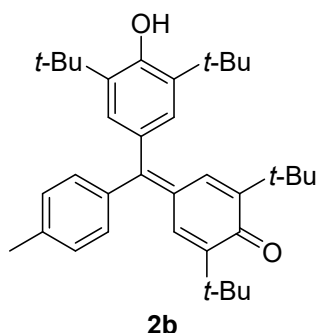
- 1 (a) D. Wang, Z. F. Song, W. J. Wang and T. Xu, *Org. Lett.*, 2019, **21**, 3963–3967; (b) M. L. Ke and Q. L. Song, *Adv. Synth. Catal.*, 2017, **359**, 384–389; (c) K. G. Ghosh, P. Chandu, S. Mondal and D. Sureshkumar, *Tetrahedron*, 2019, **75**, 4471–4478; (d)

W. D. Chu, L. F. Zhang, X. Bao, X. H. Zhao, C. Zeng, J. Y. Du, G. B. Zhang, F. X. Wang, X. Y. Ma and C. A. Fan, *Angew. Chem. Int. Ed.*, 2013, **52**, 9229–9233.

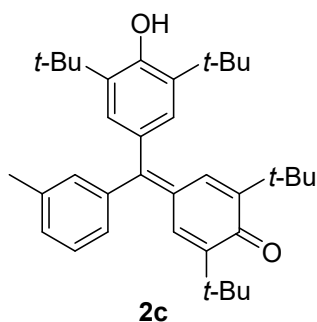
3. Characterization data for all products.



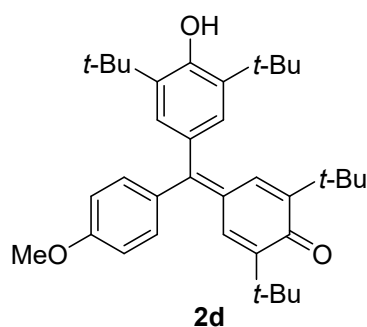
2,6-di-tert-butyl-4-((3,5-di-tert-butyl-4-hydroxyphenyl)(phenyl)methylene)cyclohexa-2,5-dien-1-one (2a) 92%(one step), 59.8% (two steps)(**path-a**); 88%(one step), 57.2% (two steps) (**path-b**): orange solid. m.p.:222.6-228.0 °C. ¹H NMR (400 MHz, CDCl₃) δ 7.50 – 7.40 (m, 3H), 7.35 – 7.26 (m, 3H), 7.16 (d, *J* = 2.4 Hz, 1H), 7.07 (s, 2H), 5.56 (s, 1H), 1.44 (s, 18H), 1.33 (s, 9H), 1.27 (s, 9H). ¹³C NMR (101 MHz, CDCl₃) δ 186.17, 158.39, 155.54, 146.73, 146.55, 141.22, 135.24, 132.76, 132.69, 132.36, 131.95, 130.15, 129.20, 128.74, 127.80, 120.89, 35.36, 35.27, 34.44, 30.34, 29.75, 29.57, 29.45. HRMS: calcd. for C₃₅H₄₆O₂ [M+H]⁺ 499.3570; found 499.3571.



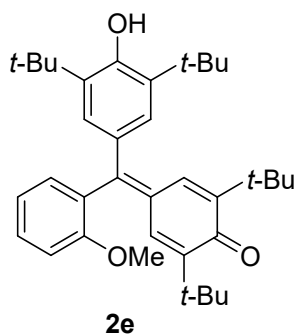
2,6-di-tert-butyl-4-((3,5-di-tert-butyl-4-hydroxyphenyl)(p-tolyl)methylene)cyclohexa-2,5-dien-1-one(2b) 75%(one step), 39.8%(two steps) (**path-a**); 77%(one step), 40.8%(two steps)(**path-b**): orange solid. m.p.:263.6-282.2 °C. ¹H NMR (400 MHz, CDCl₃) δ 7.24 (d, *J* = 2.5 Hz, 1H), 7.18 (q, *J* = 8.2 Hz, 5H), 7.03 (s, 2H), 5.51 (s, 1H), 2.43 (s, 3H), 1.47 – 1.18 (m, 37H). ¹³C NMR (101 MHz, CDCl₃) δ 186.09, 158.77, 155.49, 146.40, 146.31, 139.44, 138.19, 135.15, 132.89, 132.81, 132.53, 132.06, 130.20, 128.52, 128.49, 35.28, 35.22, 34.39, 30.33, 29.71, 29.59. HRMS: calcd. for C₃₆H₄₈O₂ [M+H]⁺ 513.3727; found 513.3722.



2,6-di-tert-butyl-4-((3,5-di-tert-butyl-4-hydroxyphenyl)(m-tolyl)methylene)cyclohexa-2,5-dien-1-one(2c) 85%(one step), 48.5%(two steps) (**path-a**); 87%(one step), 50%(two steps) (**path-b**): orange solid. m.p.:265.7-285.4 °C. ¹H NMR (400 MHz, CDCl₃) δ 7.30 – 7.20 (m, 3H), 7.19 – 6.99 (m, 5H), 5.54 (s, 1H), 2.38 (s, 3H), 1.41 (s, 18H), 1.33 – 1.21 (m, 18H). ¹³C NMR (101 MHz, CDCl₃) δ 186.18, 158.83, 146.61, 146.31, 141.07, 137.31, 135.18, 133.12, 132.88, 131.93, 130.21, 130.04, 129.67, 128.75, 128.69, 127.66, 35.23, 34.46, 30.34, 29.77, 29.61. HRMS: calcd. for C₃₆H₄₈O₂ [M+H]⁺ 513.3727; found 513.3722.

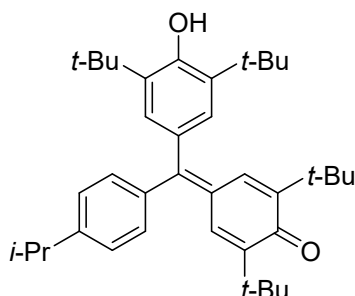


2,6-di-tert-butyl-4-((3,5-di-tert-butyl-4-hydroxyphenyl)(4-methoxyphenyl)methylene)cyclohexa-2,5-dien-1-one(2d) 81%(one step), 44.6%(two steps) (**path-a**); 79%(one step), 43.5%(two steps) (**path-b**): orange solid. m.p.:277.1-290.1 °C. ¹H NMR (400 MHz, CDCl₃) δ 7.21 (t, *J* = 8.4 Hz, 4H), 7.03 (s, 2H), 6.93 (d, *J* = 8.7 Hz, 2H), 5.54 (s, 1H), 3.88 (s, 3H), 1.41 (s, 18H), 1.27 (d, *J* = 8.0 Hz, 18H). ¹³C NMR (101 MHz, CDCl₃) δ 186.03, 160.72, 158.78, 155.67, 146.18, 135.19, 134.41, 133.48, 133.10, 132.96, 132.09, 130.42, 128.16, 113.26, 55.40, 35.32, 35.28, 34.44, 30.38, 29.76, 29.65. HRMS: calcd. for C₃₆H₄₈O₃ [M+H]⁺ 529.3676; found 529.3676.



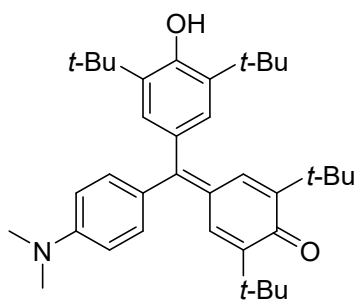
2,6-di-tert-butyl-4-((3,5-di-tert-butyl-4-hydroxyphenyl)(2-methoxyphenyl)methylene)cyclohexa-2,5-dien-1-one(2e) 49%(one step), 27.9%(two steps) (**path-a**); 57%(one step), 27.9%(two steps) (**path-b**): orange solid. m.p.:277.1-290.1 °C. ¹H NMR (400 MHz, CDCl₃) δ 7.21 (t, *J* = 8.4 Hz, 4H), 7.03 (s, 2H), 6.93 (d, *J* = 8.7 Hz, 2H), 5.54 (s, 1H), 3.88 (s, 3H), 1.41 (s, 18H), 1.27 (d, *J* = 8.0 Hz, 18H). ¹³C NMR (101 MHz, CDCl₃) δ 186.03, 160.72, 158.78, 155.67, 146.18, 135.19, 134.41, 133.48, 133.10, 132.96, 132.09, 130.42, 128.16, 113.26, 55.40, 35.32, 35.28, 34.44, 30.38, 29.76, 29.65. HRMS: calcd. for C₃₆H₄₈O₃ [M+H]⁺ 529.3676; found 529.3676.

p), 32.5%(two steps) (**path-b**): orange solid. m.p.:284.3-300.9 °C. ¹H NMR (400 MHz, CDCl₃) δ 7.21 (t, *J* = 8.4 Hz, 4H), 7.03 (s, 2H), 6.93 (d, *J* = 8.7 Hz, 2H), 5.54 (s, 1H), 3.88 (s, 3H), 1.41 (s, 18H), 1.27 (d, *J* = 8.0 Hz, 18H). ¹³C NMR (101 MHz, CDCl₃) δ 186.03, 160.72, 158.78, 155.67, 146.18, 135.19, 134.41, 133.48, 133.10, 132.96, 132.09, 130.42, 128.16, 113.26, 55.40, 35.32, 35.28, 34.44, 30.38, 29.76, 29.65. HRMS: calcd. for C₃₆H₄₈O₃ [M+H]⁺ 529.3676; found 529.3676.



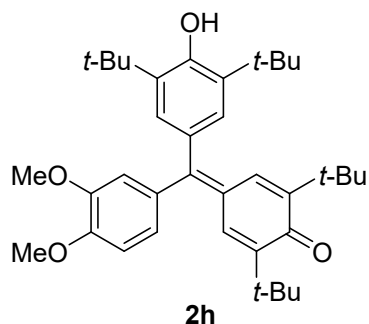
2f

2,6-di-tert-butyl-4-((3,5-di-tert-butyl-4-hydroxyphenyl)(4-isopropylphenyl)methylene)cyclohexa-2,5-dien-1-one(2f) 70%(one step), 39.2%(two steps) (**path-a**); 74%(one step), 41.4%(two steps) (**path-b**): orange solid. m.p.:240.6-252.1 °C. ¹H NMR (400 MHz, CDCl₃) δ 7.21 (t, *J* = 8.4 Hz, 4H), 7.03 (s, 2H), 6.93 (d, *J* = 8.7 Hz, 2H), 5.54 (s, 1H), 3.88 (s, 3H), 1.41 (s, 18H), 1.27 (d, *J* = 8.0 Hz, 18H). ¹³C NMR (101 MHz, CDCl₃) δ 186.03, 160.72, 158.78, 155.67, 146.18, 135.19, 134.41, 133.48, 133.10, 132.96, 132.09, 130.42, 128.16, 113.26, 55.40, 35.32, 35.28, 34.44, 30.38, 29.76, 29.65. HRMS: calcd. for C₃₈H₅₂O₂ [M+H]⁺ 541.4040; found 541.4039.

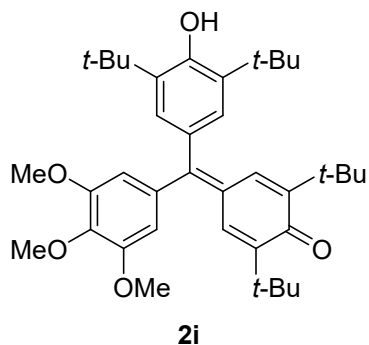


2g

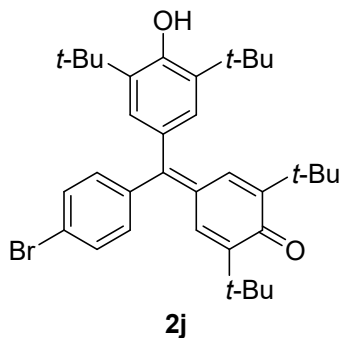
2,6-di-tert-butyl-4-((3,5-di-tert-butyl-4-hydroxyphenyl)(4-(dimethylamino)phenyl)methylene)cyclohexa-2,5-dien-1-one(2g) 50%(one step), 30.5%(**path-a**); 61%(two steps) (one step), 37.2%(two steps) (**path-b**): orange solid. m.p.:251.4-270.0 °C. ¹H NMR (400 MHz, CDCl₃) δ 7.48 – 7.02 (m, 6H), 6.73 (d, *J* = 8.7 Hz, 2H), 5.56 (s, 1H), 3.11 (s, 6H), 1.35 (d, *J* = 38.4 Hz, 36H). ¹³C NMR (101 MHz, CDCl₃) δ 185.09, 160.64, 155.59, 151.33, 145.35, 135.07, 133.44, 130.68, 128.20, 110.82, 77.00, 40.23, 40.22, 34.98, 34.51, 30.30, 29.96. HRMS: calcd. for C₃₈H₅₂O₂ [M+H]⁺ 541.4040; found 541.4039.



2,6-di-tert-butyl-4-((3,5-di-tert-butyl-4-hydroxyphenyl)(3,4-dimethoxyphenyl)methylene)cyclohexa-2,5-dien-1-one(2h) 72%(one step), 35.3%(two steps) (**path-a**); 72%(one step), 35.3%(two steps) (**path-b**): orange solid. m.p.:260.6-268.0 °C. ¹H NMR (400 MHz, CDCl₃) δ 7.22 (d, J = 3.4 Hz, 2H), 7.06 (s, 2H), 6.95 – 6.79 (m, 3H), 5.54 (s, 1H), 3.98 (s, 3H), 3.84 (s, 3H), 1.42 (s, 18H), 1.28 (d, J = 7.2 Hz, 18H). ¹³C NMR (101 MHz, CDCl₃) δ 186.03, 160.72, 158.78, 155.67, 146.18, 135.19, 134.41, 133.48, 133.10, 132.96, 132.09, 130.42, 128.16, 113.26, 55.40, 35.32, 35.28, 34.44, 30.38, 29.76, 29.65. HRMS: calcd. for C₃₇H₅₀O₄ [M+H]⁺ 559.3782; found 559.3776.

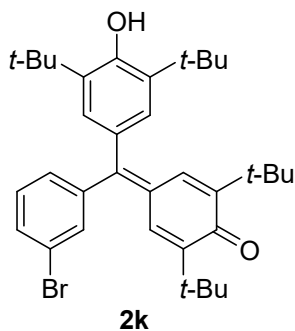


2,6-di-tert-butyl-4-((3,5-di-tert-butyl-4-hydroxyphenyl)(3,4,5-trimethoxyphenyl)methylene)cyclohexa-2,5-dien-1-one(2i) 73%(one step), 31.4% (two steps) (**path-a**); 78%(one step), 33.5%(two steps) (**path-b**): orange solid. m.p.:280.5-296.5 °C. ¹H NMR (400 MHz, CDCl₃) δ 7.23 (s, 2H), 7.07 (s, 2H), 6.50 (s, 2H), 5.56 (s, 1H), 3.97 (s, 3H), 3.81 (s, 6H), 1.43 (s, 18H), 1.28 (d, J = 8.1 Hz, 18H). ¹³C NMR (101 MHz, CDCl₃) δ 186.14, 158.21, 155.70, 152.41, 146.56, 146.33, 139.20, 136.46, 135.22, 132.94, 132.65, 131.46, 130.35, 128.65, 110.40, 61.09, 56.34, 35.30, 35.24, 34.42, 30.35, 29.69. HRMS: calcd. for C₃₈H₅₂O₅ [M+H]⁺ 589.3887; found 589.3882.

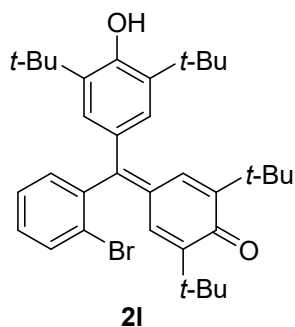


4-((4-bromophenyl)(3,5-di-tert-butyl-4-hydroxyphenyl)methylene)-2,6-di-tert-butylcyclohexa-2,5-dien-1-one(2j)

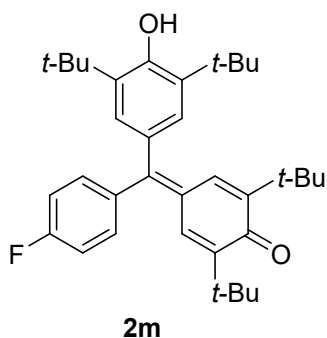
yclohexa-2,5-dien-1-one(2j) 86%(one step), 53.3%(two steps) (**path-a**); 91%(one step), 56.4%(two steps) (**path-b**): orange solid. m.p.:264.4-272.2 °C. ¹H NMR (400 MHz, CDCl₃) δ 7.59 – 7.49 (m, 2H), 7.23 (d, J = 2.6 Hz, 1H), 7.20 – 7.13 (m, 2H), 7.08 (d, J = 2.5 Hz, 1H), 7.01 (s, 2H), 5.55 (s, 1H), 1.42 (s, 18H), 1.27 (d, J = 13.8 Hz, 18H). ¹³C NMR (101 MHz, CDCl₃) δ 186.10, 156.55, 155.72, 146.97, 140.12, 135.44, 133.92, 132.69, 132.11, 131.50, 131.14, 130.13, 129.05, 123.80, 35.35, 34.47, 30.36, 29.75, 29.64. HRMS: calcd. for C₃₅H₄₅BrO₂ [M+H]⁺ 579.2657; found 579.2651.



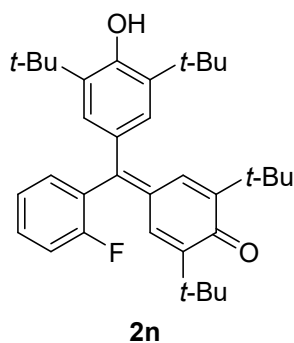
4-((3-bromophenyl)(3,5-di-tert-butyl-4-hydroxyphenyl)methylene)-2,6-di-tert-butylcyclohexa-2,5-dien-1-one(2k) 76%(one step), 44.8%(two steps) (**path-a**); 74%(one step), 43.7%(two steps) (**path-b**): orange solid. m.p.:268.5-273.6 °C. ¹H NMR (400 MHz, CDCl₃) δ 7.59 – 7.51 (m, 1H), 7.45 (t, J = 1.7 Hz, 1H), 7.29 – 7.20 (m, 3H), 7.12 – 7.00 (m, 3H), 5.55 (s, 1H), 1.49 – 1.20 (m, 36H). ¹³C NMR (101 MHz, CDCl₃) δ 186.16, 155.91, 155.76, 147.20, 147.05, 143.29, 135.86, 135.49, 134.99, 132.55, 132.08, 131.49, 131.31, 130.93, 130.56, 130.36, 130.08, 129.86, 129.38, 126.13, 124.48, 122.04, 35.43, 35.35, 34.49, 30.38, 29.78, 29.60. HRMS: calcd. for C₃₅H₄₅BrO₂ [M+H]⁺ 579.2657; found 579.2651.



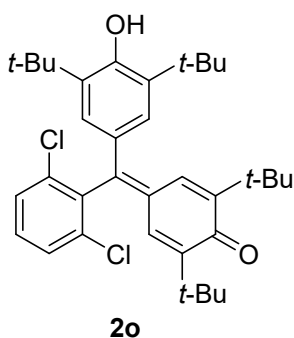
4-((2-bromophenyl)(3,5-di-tert-butyl-4-hydroxyphenyl)methylene)-2,6-di-tert-butylcyclohexa-2,5-dien-1-one(2l) 71%(one step), 39.8%(two steps) (**path-a**); 70%(one step), 30.2%(two steps) (**path-b**): orange solid. m.p.:270.5-277.0 °C. ¹H NMR (400 MHz, CD₃OD) δ 7.67 (d, J = 8.0 Hz, 1H), 7.53 – 7.17 (m, 4H), 7.08 (s, 2H), 6.76 (s, 1H), δ 3.33 (s, 1H), 1.56 – 1.04 (m, 36H). ¹³C NMR (101 MHz, CD₃OD) δ 186.77, 156.28, 155.63, 147.33, 146.70, 141.74, 136.19, 132.91, 132.35, 132.14, 131.99, 129.80, 129.75, 129.06, 128.94, 126.94, 123.77, 35.24, 34.90, 34.34, 29.88, 29.43, 29.10. HRMS: calcd. for C₃₅H₄₅BrO₂ [M+H]⁺ 579.2657; found 579.2651.



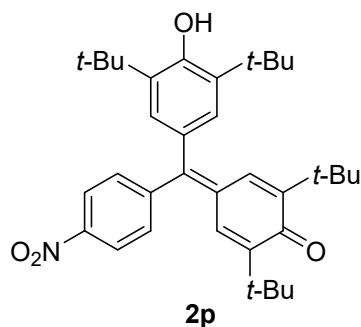
2,6-di-tert-butyl-4-((3,5-di-tert-butyl-4-hydroxyphenyl)(4-fluorophenyl)methylene)cyclohexa-2,5-dien-1-one(2m) 87%(one step), 47.0%(two steps) (**path-a**); 89%(one step), 48.1%(two steps) (**path-b**): orange solid. m.p.:260.7-264.2 °C. ¹H NMR (400 MHz, CDCl₃) δ 7.29 – 7.21 (m, 3H), 7.15 – 7.05 (m, 3H), 7.02 (s, 2H), 5.54 (s, 1H), 1.41 (s, 18H), 1.27 (d, J = 16.3 Hz, 18H). ¹³C NMR (101 MHz, CDCl₃) δ 186.07, 164.51, 162.03, 156.78, 155.62, 146.82, 146.77, 137.26, 137.23, 135.37, 134.22, 134.14, 132.61, 132.23, 131.75, 130.05, 128.82, 115.08, 114.87, 35.31, 35.24, 34.40, 30.29, 29.68, 29.53. ¹⁹F NMR (376 MHz, CDCl₃) δ -111.44. HRMS: calcd. for C₃₅H₄₅FO₂ [M+H]⁺ 517.3476; found 517.3477.



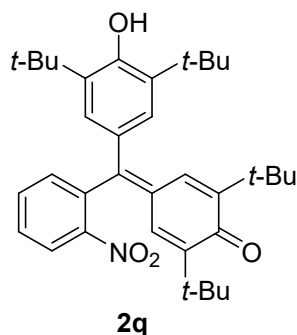
2,6-di-tert-butyl-4-((3,5-di-tert-butyl-4-hydroxyphenyl)(2-fluorophenyl)methylene)cyclohexa-2,5-dien-1-one(2n) 71%(one step), 36.9%(two steps) (**path-a**); 75%(one step), 39.0%(two steps) (**path-b**): orange solid. m.p.:279.7-281.1 °C. ¹H NMR (400 MHz, CDCl₃) δ 7.43 – 7.33 (m, 2H), 7.23 – 7.11 (m, 3H), 7.06 (s, 2H), 6.93 (t, J = 2.4 Hz, 1H), 5.50 (s, 1H), 1.41 (s, 18H), 1.26 (d, J = 35.4 Hz, 18H). ¹³C NMR (101 MHz, CDCl₃) δ 186.43, 163.46, 159.86, 156.27, 151.68, 148.87, 148.36, 135.45, 133.15, 131.88, 131.72, 131.04, 130.97, 130.89, 129.83, 128.98, 128.83, 128.68, 123.86, 123.83, 115.95, 115.73, 35.26, 33.76, 30.78, 29.78, 28.05. ¹⁹F NMR (376 MHz, CDCl₃) δ -112.02. HRMS: calcd. for C₃₅H₄₅FO₂ [M+H]⁺ 517.3476; found 517.3477.



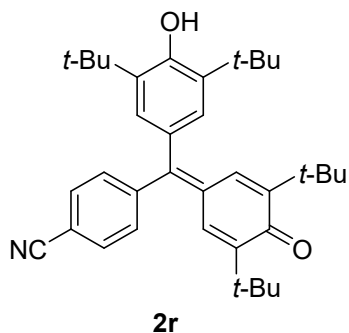
2,6-di-tert-butyl-4-((3,5-di-tert-butyl-4-hydroxyphenyl)(2,6-dichlorophenyl)methylene)cyclohexa-2,5-dien-1-one(2o) 40%(one step), 16.4% (two steps) (**path-a**); 82%(one step), 33.6%(two steps) (**path-b**): orange solid. m.p.:256.7-264.1^oC. ¹H NMR (400 MHz, CDCl₃) δ 7.54 (s, 1H), 7.40 – 7.32 (m, 2H), 7.21 (d, *J* = 8.2 Hz, 1H), 7.06 (s, 2 H), 6.74 (s, 1H), 5.53 (s, 1H), 1.44 (s, 18H), 1.33 (s, 9H), 1.23 (s, 9H). ¹³C NMR (101 MHz, CDCl₃) δ 186.45, 155.39, 151.68, 147.85, 147.47, 138.53, 135.61, 134.89, 134.87, 133.10, 131.29, 131.22, 129.99, 129.79, 129.76, 128.81, 126.91, 35.49, 35.22, 34.45, 30.30, 29.75, 29.51. HRMS: calcd. for C₃₅H₄₄Cl₂O₂ [M+H]⁺ 567.2791; found 567.2787.



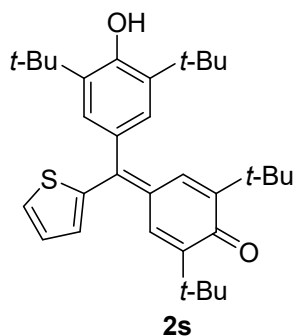
2,6-di-tert-butyl-4-((3,5-di-tert-butyl-4-hydroxyphenyl)(4-nitrophenyl)methylene)cyclohexa-2,5-dien-1-one(2p) 80%(one step), 46.4%(two steps) (**path-a**); 74%(one step), 42.9%(two steps) (**path-b**): orange solid. m.p.:239.6-251.7 ^oC. ¹H NMR (400 MHz, CDCl₃) δ 8.28 (d, *J* = 8.4 Hz, 2H), 7.47 (d, *J* = 8.4 Hz, 2H), 7.25 (d, *J* = 2.5 Hz, 1H), 6.97 (d, *J* = 4.3 Hz, 3H), 5.59 (s, 1H), 1.41 (s, 18H), 1.28 (s, 9H), 1.22 (s, 9H). ¹³C NMR (101 MHz, CDCl₃) δ 186.13, 155.84, 154.11, 148.05, 147.85, 147.81, 147.76, 135.74, 132.93, 132.20, 131.28, 130.93, 130.20, 129.86, 123.11, 35.47, 35.39, 34.49, 30.29, 29.71, 29.54. HRMS: calcd. for C₃₅H₄₅NO₄ [M+H]⁺ 544.3421; found 544.3422.



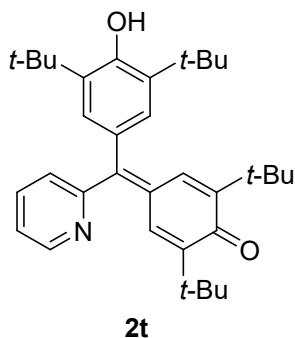
2,6-di-tert-butyl-4-((3,5-di-tert-butyl-4-hydroxyphenyl)(2-nitrophenyl)methylene)cyclohexa-2,5-dien-1-one(2q) 69%(one step), 35.9%(two steps) (**path-a**); 88%(one step), 45.8%(two steps) (**path-b**): orange solid. m.p.:241.3-254.7 ^oC. ¹H NMR (400 MHz, CDCl₃) δ 7.45 – 7.33 (m, 2H), 7.24 – 7.09 (m, 3H), 7.06 (s, 2H), 6.93 (t, *J* = 2.5 Hz, 1H), 5.50 (s, 1H), 1.41 (s, 18H), 1.26 (d, *J* = 35.3 Hz, 18H). ¹³C NMR (101 MHz, CDCl₃) δ 186.45, 161.32, 158.84, 155.42, 150.41, 147.25, 147.04, 135.46, 133.17, 131.88, 131.73, 131.05, 130.98, 130.90, 129.84, 128.99, 128.83, 128.69, 123.87, 123.84, 115.96, 115.74, 35.44, 35.21, 34.45, 30.32, 29.77, 29.52. HRMS: calcd. for C₃₅H₄₅NO₄ [M+H]⁺ 544.3421; found 544.3422.



2,6-di-tert-butyl-4-((3,5-di-tert-butyl-4-hydroxyphenyl)(4-isocyanophenyl)methylene)cyclohexa-2,5-dien-1-one(2r) 62%(one step), 31.6%(two steps) (**path-a**); 57% (one step), 29.1%(two steps) (**path-b**): orange solid. m.p.:293.9-301.1^oC. ¹H NMR (400 MHz, CDCl₃) δ 7.77 – 7.67 (m, 2H), 7.45 – 7.33 (m, 2H), 7.29 – 7.23 (m, 1H), 7.00 – 6.87 (m, 3H), 5.56 (s, 1H), 1.41 (s, 18H), 1.25 (d, J = 21.6 Hz, 18H). ¹³C NMR (101 MHz, CDCl₃) δ 186.06, 155.70, 154.52, 147.73, 147.62, 146.04, 135.67, 132.60, 132.12, 131.57, 131.28, 130.95, 129.86, 129.78, 118.61, 112.45, 35.40, 35.32, 34.42, 30.25, 29.65, 29.48. HRMS: calcd. for C₃₆H₄₅NO₂ [M+H]⁺ 524.3523; found 524.3525.

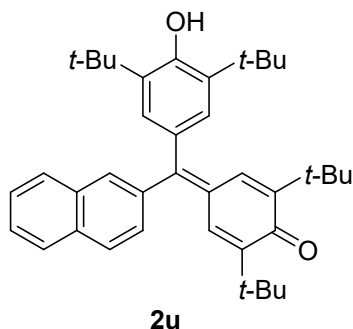


2,6-di-tert-butyl-4-((3,5-di-tert-butyl-4-hydroxyphenyl)(thiophen-2-yl)methylene)cyclohexa-2,5-dien-1-one(2s) 53%(one step), 25.4%(two steps) (**path-a**); 72%(one step), 34.6%(two steps) (**path-b**): orange solid. m.p.:233.9-242.0 ^oC. ¹H NMR (400 MHz, CDCl₃) δ 7.60 (d, J = 5.0 Hz, 2H), 7.22 (d, J = 2.8 Hz, 1H), 7.18 – 7.08 (m, 4H), 5.55 (s, 1H). ¹³C NMR (101 MHz, CDCl₃) δ 186.15, 155.84, 149.86, 146.93, 146.45, 144.16, 135.15, 133.57, 132.78, 131.99, 131.76, 131.07, 130.14, 128.92, 127.55, 35.44, 35.36, 34.47, 30.38, 29.71. HRMS: calcd. for C₃₃H₄₄O₂S [M+H]⁺ 505.3135; found 53136.

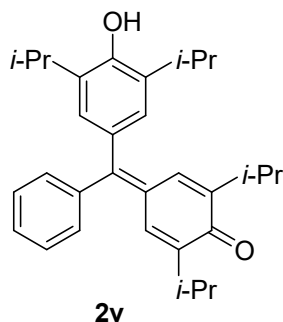


2,6-di-tert-butyl-4-((3,5-di-tert-butyl-4-hydroxyphenyl)(pyridin-2-yl)methylene)cyclohexa-2,5-dien-1-one(2t) 66%(one step), 35.0%(two steps) (**path-a**); 72%(one step), 3

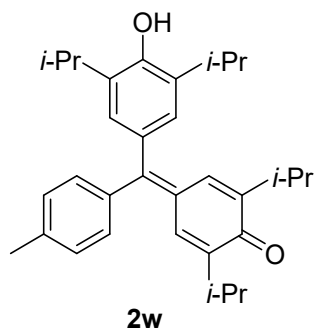
8.2%(two steps) (**path-b**): orange solid. m.p.:220.6-230.7 °C. ¹H NMR (400 MHz, CDCl₃) δ 8.82 – 8.72 (m, 1H), 7.75 (td, J = 7.7, 1.7 Hz, 1H), 7.36 – 7.23 (m, 3H), 7.12 – 7.00 (m, 3H), 5.52 (s, 1H), 1.40 (s, 18H), 1.25 (d, J = 21.2 Hz, 18H). ¹³C NMR (101 MHz, CDCl₃) δ 186.31, 159.55, 155.45, 154.39, 149.50, 147.62, 147.11, 135.78, 135.43, 132.49, 131.96, 130.72, 130.06, 129.59, 127.52, 122.93, 35.38, 35.24, 34.39, 30.25, 29.68, 29.46. HRMS: calcd. for C₃₅H₄₅NO₂ [M+H]⁺ 500.3523; found 500.3522.



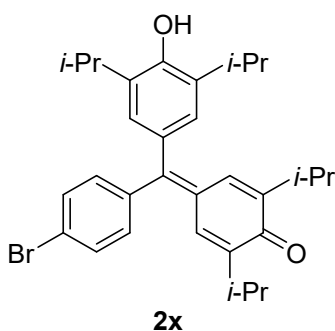
2,6-di-tert-butyl-4-((3,5-di-tert-butyl-4-hydroxyphenyl)(naphthalen-2-yl)methylene)cyclohexa-2,5-dien-1-one(2u) 83%(one step), 49.0%(two steps) (**path-a**); 85%(one step), 50.2%(two steps) (**path-b**): orange solid. m.p.:292.1.6-300.8 °C. ¹H NMR (400 MHz, CDCl₃) δ 7.92 – 7.79 (m, 4H), 7.55 (tt, J = 6.9, 5.3 Hz, 2H), 7.39 – 7.28 (m, 2H), 7.28 – 7.18 (m, 1H), 7.08 (s, 2H), 5.54 (s, 1H), 1.40 (s, 18H), 1.27 (d, J = 38.0 Hz, 18 H). ¹³C NMR (101 MHz, CDCl₃) δ 186.19, 158.38, 155.70, 146.78, 138.53, 135.36, 133.59, 132.97, 132.88, 131.90, 130.35, 129.72, 129.30, 128.64, 127.85, 127.39, 127.20, 126.68, 35.44, 35.33, 34.49, 31.99, 30.40, 29.82, 29.67, 29.14. HRMS: calcd. for C₃₉H₄₈O₂ [M+H]⁺ 549.3727; found 549.3721.



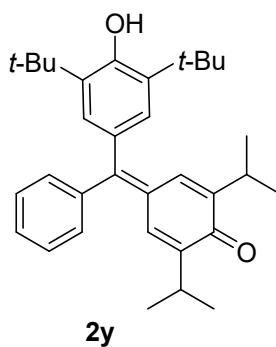
4-((4-hydroxy-3,5-diisopropylphenyl)(phenyl)methylene)-2,6-diisopropylcyclohexa-2,5-dien-1-one(2v) 30%(one step), 17.4%(two steps) (**path-a**); 85%(one step), 49.3%(two steps) (**path-b**): orange solid. m.p.:210.4-213.8 °C. ¹H NMR (400 MHz, CDCl₃) δ 7.48 – 7.42 (m, 2H), 7.42 (d, J = 2.2 Hz, 1H), 7.24 (dd, J = 7.8, 2.2 Hz, 2H), 7.06 (s, 1H), 6.92 (s, 2H), 5.33 (s, 1H), 3.30 – 3.11 (m, 4H), 1.23 (d, J = 6.8 Hz, 12H), 1.10 (d, J = 6.9 Hz, 6H), 1.05 (d, J = 6.9 Hz, 6H). ¹³C NMR (101 MHz, CDCl₃) δ 186.19, 158.38, 155.70, 146.78, 138.53, 135.36, 133.59, 132.97, 132.88, 131.90, 130.35, 129.72, 129.30, 128.64, 127.85, 127.39, 127.20, 126.68, 35.44, 35.33, 34.49, 31.99, 30.40, 29.82, 29.67, 29.14. HRMS: calcd. for C₃₁H₃₈O₂ [M+H]⁺ 443.2945; found 443.2950.



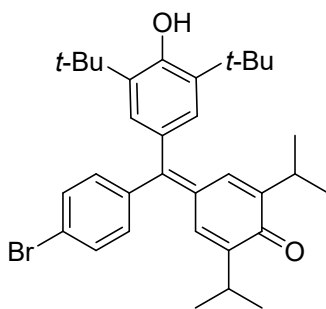
4-((4-hydroxy-3,5-diisopropylphenyl)(p-tolyl)methylene)-2,6-diisopropylcyclohexa-2,5-dien-1-one(2w) 34%(one step), 17.0%(two steps) (**path-a**); 65%(one step), 32.5%(two steps) (**path-b**): orange solid. m.p.:230.6-237.7 °C. ¹H NMR (400 MHz, CDCl₃) δ 6.97 (d, J = 7.8 Hz, 2H), 6.90 (d, J = 8.1 Hz, 2H), 6.72 (s, 4H), 5.24 (s, 1H), 3.02 (p, J = 6.8 Hz, 4H), 2.22 (s, 3H), 1.09 (d, J = 7.0 Hz, 24H). ¹³C NMR (101 MHz, CDCl₃) δ 141.59, 135.43, 134.04, 131.80, 128.00, 127.65, 123.44, 26.20, 21.78, 21.68, 19.98. HRMS: calcd. for C₃₁H₄₀O₂ [M+H]⁺ 457.3101; found 457.3108.



4-((4-bromophenyl)(4-hydroxy-3,5-diisopropylphenyl)methylene)-2,6-diisopropylcyclohexa-2,5-dien-1-one(2x) 31%(one step), 14.6%(two steps) (**path-a**); 60%(one step), 28.2%(two steps) (**path-b**): orange solid. m.p.:243.5-251.1 °C. ¹H NMR (400 MHz, CDCl₃) δ 7.58 – 7.47 (m, 1H), 7.33 – 7.24 (m, 2H), 6.94 – 6.85 (m, 2H), 6.68 (s, 3H), 5.23 (s, 1H), 3.12 – 2.93 (m, 4H), 1.23 – 1.03 (m, 24H). ¹³C NMR (101 MHz, CDCl₃) δ 183.86, 153.50, 147.20, 143.80, 138.91, 136.24, 134.56, 132.29, 130.38, 130.36, 130.02, 129.99, 128.46, 127.83, 125.67, 123.35, 118.60, 26.19, 26.16, 21.76, 21.68. HRM S: calcd. for C₃₁H₃₇BrO₂ [M+H]⁺ 523.2031; found 523.2028.

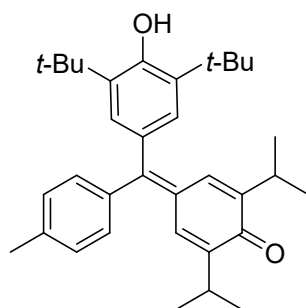


4-((3,5-di-tert-butyl-4-hydroxyphenyl)(phenyl)methylene)-2,6-diisopropylcyclohexa-2,5-dien-1-one(2y) 90%(one step), 58.5%(two steps): orange solid. m.p.:244.3-251.2 °C. ¹H NMR (400 MHz, CDCl₃) δ 7.35 – 7.28 (m, 3H), 7.22 (d, J = 2.6 Hz, 1H), 7.19 – 7.14 (m, 2H), 7.06 (d, J = 2.6 Hz, 1H), 6.84 (s, 2H), 5.30 (s, 1H), 3.11 (p, J = 6.9 Hz, 2H), 1.22 – 1.11 (m, 30H). ¹³C NMR (101 MHz, CDCl₃) δ 186.21, 158.13, 151.71, 146.84, 146.17, 141.25, 133.31, 132.96, 132.68, 132.33, 129.23, 128.77, 128.60, 127.76, 35.30, 30.37, 29.72, 29.54, 27.13, 22.76. HRMS: calcd. for C₃₃H₄₂O₂ [M+H]⁺ 471.3257; found 471.3252.



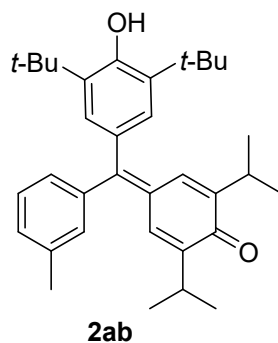
2z

4-((4-bromophenyl)(3,5-di-tert-butyl-4-hydroxyphenyl)methylene)-2,6-diisopropylcyclohexa-2,5-dien-1-one(2z) 86%(one step), 53.3%(two steps): orange solid. m.p.:249.8-253.3 °C. ¹H NMR (400 MHz, CDCl₃) δ 7.59 – 7.49 (m, 2H), 7.25 (d, J = 2.6 Hz, 1H), 7.13 (d, J = 8.5 Hz, 2H), 7.09 (d, J = 2.6 Hz, 1H), 6.90 (s, 2H), 5.28 (s, 1H), 3.18 (h, J = 6.9 Hz, 2H), 1.25 (dd, J = 12.5, 8.3 Hz, 30H). ¹³C NMR (101 MHz, CDCl₃) δ 186.16, 156.11, 151.77, 147.12, 140.14, 133.82, 133.41, 132.52, 132.03, 131.04, 129.11, 128.53, 125.88, 124.42, 123.77, 35.28, 30.34, 29.68, 29.56, 27.16, 22.74. HRMS: calcd. for C₃₃H₄₁BrO₂ [M+H]⁺ 548.2290; found 548.2291.

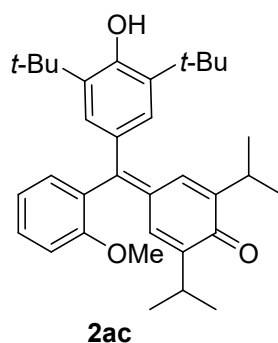


2aa

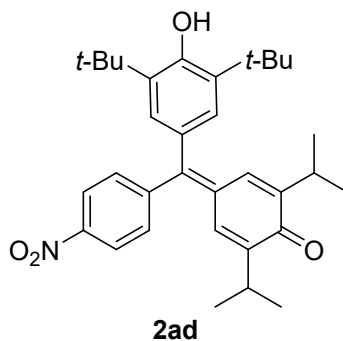
4-((3,5-di-tert-butyl-4-hydroxyphenyl)(p-tolyl)methylene)-2,6-diisopropylcyclohexa-2,5-dien-1-one(2aa) 70%(one step), 37.1%(two steps): orange solid. m.p.:222.1-223.0 °C. ¹H NMR (400 MHz, CDCl₃) δ 7.19 – 7.12 (m, 2H), 7.11 (s, 2H), 7.06 (d, J = 7.9 Hz, 2H), 6.84 (s, 2H), 3.10 (p, J = 6.9 Hz, 2H), 2.36 (s, 3H), 1.19 (d, J = 9.3 Hz, 18H), 1.15 (d, J = 6.8 Hz, 12H). ¹³C NMR (101 MHz, CDCl₃) δ 185.09, 157.40, 150.53, 145.47, 145.31, 138.48, 137.18, 134.12, 132.06, 131.77, 131.48, 129.53, 128.02, 127.65, 127.47, 124.90, 123.45, 34.21, 34.17, 28.64, 28.52, 26.10, 21.69. HRMS: calcd. for C₃₄H₄₄O₃ [M+H]⁺ 485.3414; found 485.3410.



4-((3,5-di-tert-butyl-4-hydroxyphenyl)(m-tolyl)methylene)-2,6-diisopropylcyclohexa-2,5-dien-1-one(2ab) 60%(one step), 34.2%(two steps): orange solid. m.p.:226.6-230.1 °C. ¹H NMR (400 MHz, CDCl₃) δ 7.21 – 7.17 (m, 3H), 7.14 (d, J = 8.2 Hz, 2H), 7.07 – 6.98 (m, 1H), 6.92 (s, 2H), 5.29 (s, 1H), 3.24 – 3.12 (m, 2H), 2.43 (s, 3H), 1.25 (dd, J = 17.8, 8.3 Hz, 30H). ¹³C NMR (101 MHz, CDCl₃) δ 186.17, 158.52, 151.66, 146.55, 146.43, 142.81, 139.55, 138.26, 135.22, 133.12, 132.80, 132.55, 128.72, 128.56, 125.97, 124.52, 35.25, 34.36, 30.38, 29.72, 29.60, 27.26, 27.16, 22.77. HRMS: calcd. for C₃₄H₄₄O₂[M+H]⁺ 485.3414; found 485.3410.

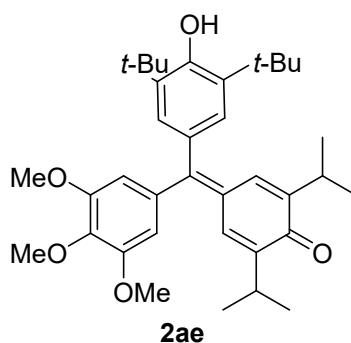


4-((3,5-di-tert-butyl-4-hydroxyphenyl)(3-methoxyphenyl)methylene)-2,6-diisopropylcyclohexa-2,5-dien-1-one(2ac) 70%(one step), 39.9%(two steps): orange solid. m.p.: 227.6-235.4 °C. ¹H NMR (400 MHz, CDCl₃) δ 7.42 – 7.37 (m, 2H), 7.11 (dd, J = 7.5, 1.8 Hz, 1H), 7.03 – 6.99 (m, 1H), 6.98 – 6.93 (m, 4H), 5.05 (s, 1H), 3.60 (s, 3H), 3.15 (p, J = 6.9 Hz, 2H), 1.28 (d, J = 1.8 Hz, 9H), 1.24 – 1.15 (m, 21H). ¹³C NMR (101 MHz, CDCl₃) δ 186.42, 157.48, 154.01, 150.95, 146.88, 146.39, 133.04, 132.89, 132.61, 132.48, 131.70, 130.37, 130.27, 129.15, 127.16, 120.35, 111.59, 35.31, 35.08, 29.70, 29.50, 27.17, 22.73. HRMS: calcd. for C₃₄H₄₄O₃ [M+H]⁺ 501.3363; found 501.3367.

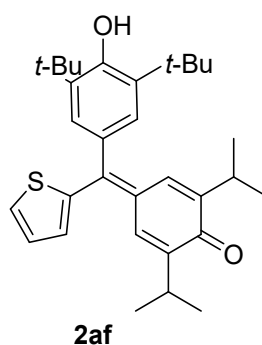


4-((3,5-di-tert-butyl-4-hydroxyphenyl)(4-nitrophenyl)methylene)-2,6-diisopropylcyclohexa-2,5-dien-1-one(2ad)

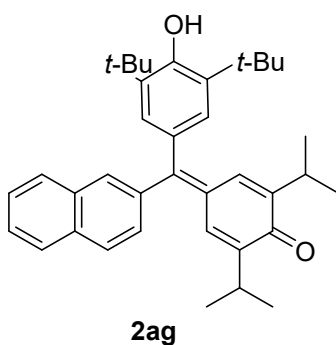
ohexa-2,5-dien-1-one(2ad) 70%(one step),40.6%(two steps): orange solid. m.p.:241.4-260.9 °C. ¹H NMR (400 MHz, CDCl₃) δ 7.38 – 7.31 (m, 1H), 7.29 (d, J = 2.6 Hz, 1H), 7.18 (s, 1H), 7.15 – 7.03 (m, 3H), 6.87 (s, 2H), 5.07 (s, 1H), 3.07 (dq, J = 13.6, 6.8 Hz, 2H), 1.23 – 1.08 (m, 30H). ¹³C NMR (101 MHz, CDCl₃) δ 185.72, 157.81, 150.38, 148.92, 146.32, 146.04, 134.23, 132.27, 132.08, 131.05, 130.76, 130.47, 129.90, 129.81, 128.80, 127.64, 126.36, 124.83, 123.33, 122.65, 114.89, 114.67, 34.30, 34.10, 29.28, 29.20, 28.64, 28.39, 26.11, 21.62. HRMS: calcd. for C₃₃H₄₁NO₄[M+H]⁺ 515.3036; found 515.3039.



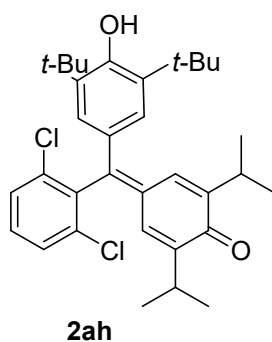
4-((3,5-di-tert-butyl-4-hydroxyphenyl)(3,4,5-trimethoxyphenyl)methylene)-2,6-diisopropylcyclohexa-2,5-dien-1-one(2ae) 42%(one step), 18.1%(two steps): orange solid. m.p.:247.6-267.0 °C. ¹H NMR (400 MHz, CDCl₃) δ 7.26 – 7.23 (m, 2H), 6.96 (s, 2H), 6.49 (s, 2H), 3.97 (s, 3H), 3.80 (s, 6H), 3.20 (p, J = 6.9 Hz, 2H), 1.28 (d, J = 4.8 Hz, 18H), 1.25 (d, J = 6.8 Hz, 12H). ¹³C NMR (101 MHz, CDCl₃) δ 185.72,136.51, 135.31, 133.20, 132.84, 132.70, 132.53, 128.90, 125.83, 124.37, 110.71, 110.33, 106.72, 106.55, 35.28, 34.37, 30.36, 30.13, 29.70, 27.18, 27.13, 22.79, 22.36. HRMS: calcd. for C₃₆H₄₈O₅ [M+H]⁺ 561.3574; found 561.3574.



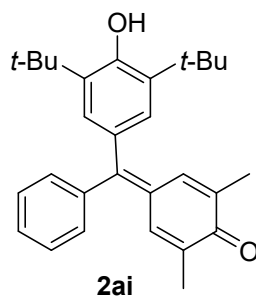
4-((3,5-di-tert-butyl-4-hydroxyphenyl)(thiophen-2-yl)methylene)-2,6-diisopropylcyclohexa-2,5-dien-1-one(2af) 87%(one step), 41.8%(two steps): orange solid. m.p.:212.1-220.0 °C. ¹H NMR (400 MHz, CDCl₃) δ 7.89 – 7.69 (m, 3H), 7.51 – 7.40 (m, 2H), 7.20 – 7.11 (m, 1H), 6.89 (d, J = 8.0 Hz, 2H), 5.20 (s, 1H), 3.07 (dp, J = 25.0, 6.9 Hz, 2H), 1.34 – 1.19 (m, 12H), 1.17 – 1.07 (m, 18H). ¹³C NMR (101 MHz, CDCl₃) δ 186.19, 157.83, 151.70, 146.84, 138.56, 135.36, 133.24, 132.83, 132.66, 129.63, 129.30, 128.76, 128.57, 127.93, 127.77, 127.31, 127.16, 126.63, 126.10, 125.67, 125.24, 124.65, 35.35, 35.28, 34.43, 30.38, 30.33, 29.75, 29.60, 27.29, 27.20, 22.77, 22.39, 22.18. HRMS: calcd. for C₃₁H₄₀O₂S [M+H]⁺ 477.2821; found 477.2820.



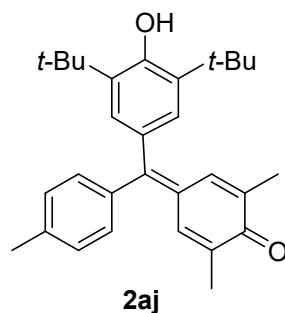
4-((3,5-di-tert-butyl-4-hydroxyphenyl)(naphthalen-2-yl)methylene)-2,6-diisopropylcyclohexa-2,5-dien-1-one(2ag) 68%(one step), 40.1%(two steps): orange solid. m.p.: 90.4-301.7 °C. ¹H NMR (400 MHz, CDCl₃) δ 7.92 – 7.78 (m, 4H), 7.61 – 7.51 (m, 2 H), 7.31 (dd, *J* = 8.5, 1.7 Hz, 1H), 7.28 – 7.23 (m, 2H), 6.98 (s, 2H), 5.29 (s, 1H), 3.18 (p, *J* = 6.9 Hz, 2H), 1.32 – 1.18 (m, 30H). ¹³C NMR (101 MHz, CDCl₃) δ 157.89, 138.55, 133.53, 132.70, 132.64, 129.60, 128.56, 127.75, 127.49, 127.29, 127.13, 126.61, 53.44, 35.22, 29.71, 27.16, 27.10, 22.70. HRMS: calcd. for C₃₇H₄₄O₂ [M+H]⁺ 521.3414; found 521.3418.



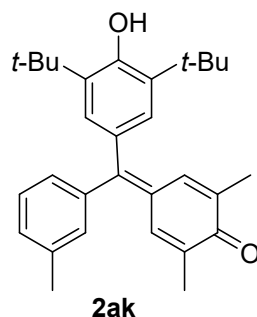
4-((3,5-di-tert-butyl-4-hydroxyphenyl)(2,6-dichlorophenyl)methylene)-2,6-diisopropylcyclohexa-2,5-dien-1-one(2ah) 53%(one step), 21.7%(two steps): orange solid. m.p.: 253.3-260.1 °C. ¹H NMR (400 MHz, CDCl₃) δ 7.42 (d, *J* = 2.1 Hz, 1H), 7.30 (s, 1H), 7.24 (dd, *J* = 8.2, 2.1 Hz, 1H), 7.10 (d, *J* = 8.3 Hz, 1H), 6.84 (s, 2H), 6.69 – 6.60 (m, 1 H), 5.13 (s, 1H), 3.08 (p, *J* = 6.8 Hz, 2H), 1.29 – 1.06 (m, 30H). ¹³C NMR (101 MHz, CDCl₃) δ 185.35, 150.41, 146.91, 146.47, 137.43, 133.91, 132.52, 132.34, 132.11, 130.11, 129.95, 128.80, 128.76, 126.33, 125.74, 123.51, 34.34, 34.12, 30.41, 28.67, 28.46, 26.14, 21.79, 21.62. HRMS: calcd. for C₃₃H₄₀O₂Cl [M+H]⁺ 539.2478; found 539.2475.



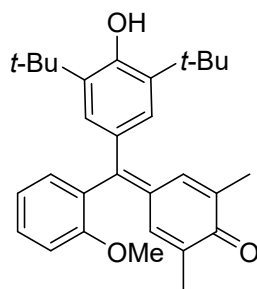
4-((3,5-di-tert-butyl-4-hydroxyphenyl)(phenyl)methylene)-2,6-dimethylcyclohexa-2,5-dien-1-one(2ai) 70%(one step), 45.5%(two steps): orange solid. m.p.:210.4-212.9 °C. ¹H NMR (400 MHz, CDCl₃) δ 7.44 – 7.38 (m, 3H), 7.27 – 7.22 (m, 3H), 7.10 (d, J = 2.7 Hz, 1H), 6.88 (s, 2H), 4.98 (d, J = 4.4 Hz, 1H), 2.25 (s, 6H), 1.25 (d, J = 17.7 Hz, 18H). ¹³C NMR (101 MHz, CDCl₃) δ 186.09, 156.76, 153.63, 146.79, 141.08, 133.09, 132.74, 132.56, 132.36, 132.14, 129.16, 129.00, 127.87, 122.11, 35.23, 29.59, 29.51, 15.82. HRMS: calcd. for C₂₉H₃₄O₂ [M+H]⁺ 415.2631; found 415.2631.



4-((3,5-di-tert-butyl-4-hydroxyphenyl)(p-tolyl)methylene)-2,6-dimethylcyclohexa-2,5-dien-1-one(2aj) 73%(one step), 38.7%(two steps): orange solid. m.p.:215.0-220.6 °C. ¹H NMR (400 MHz, CDCl₃) δ 7.21 – 6.62 (m, 8H), 5.01 (d, J = 25.1 Hz, 1H), 2.38 – 2.06 (m, 9H), 1.35 – 1.09 (m, 18H). ¹³C NMR (101 MHz, CDCl₃) δ 186.10, 157.54, 142.43, 139.53, 138.17, 136.65, 135.22, 134.70, 133.21, 132.89, 132.81, 132.60, 132.36, 129.47, 129.14, 128.78, 128.66, 125.95, 122.68, 122.54, 35.25, 34.37, 30.38, 29.58, 21.50, 21.06, 16.06, 15.85. HRMS: calcd. for C₃₀H₃₆O₂ [M+H]⁺ 429.2788; found 429.2790.

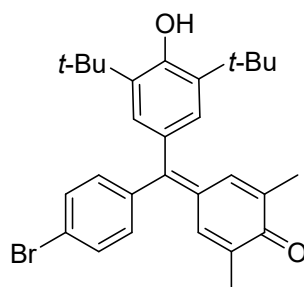


4-((3,5-di-tert-butyl-4-hydroxyphenyl)(m-tolyl)methylene)-2,6-dimethylcyclohexa-2,5-dien-1-one(2ak) 81%(one step), 46.2%(two steps): orange solid. m.p.:239.3-244.0 °C. ¹H NMR (400 MHz, CDCl₃) δ 7.19 (dd, J = 9.6, 7.2 Hz, 3H), 7.05 (d, J = 2.3 Hz, 1H), 6.92 – 6.87 (m, 1H), 6.84 (s, 1H), 6.81 (s, 2H), 6.65 (s, 1H), 2.18 (s, 6H), 2.10 (s, 3H), 1.17 (d, J = 14.1 Hz, 18H). ¹³C NMR (101 MHz, CDCl₃) δ 186.34, 157.36, 153.13, 153.08, 146.69, 146.48, 132.51, 132.49, 132.28, 131.88, 131.75, 130.32, 129.99, 129.40, 122.46, 120.29, 111.49, 55.72, 53.46, 35.29, 35.07, 30.39, 30.31, 29.59, 29.49, 15.85. HRMS: calcd. for C₃₀H₃₆O₂ [M+H]⁺ 429.2788; found 429.2790.



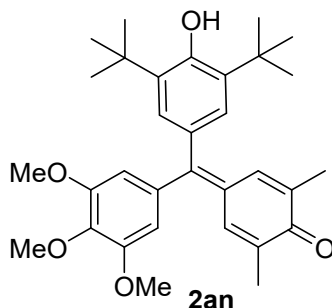
2al

4-((3,5-di-tert-butyl-4-hydroxyphenyl)(2-methoxyphenyl)methylene)-2,6-dimethylcyclohexa-2,5-dien-1-one(2al) 66%(one step), 37.6%(two steps): orange solid. m.p.:241.8-248.3 °C. ¹H NMR (400 MHz, CDCl₃) δ 7.43 – 7.37 (m, 2H), 7.09 (dd, J = 7.5, 1.9 Hz, 1H), 7.03 – 6.94 (m, 2H), 6.92 – 6.86 (m, 3H), 4.90 (s, 1H), 3.65 (s, 3H), 2.24 (s, 6H), 1.27 (s, 9H), 1.18 (s, 9H). ¹³C NMR (101 MHz, CDCl₃) δ 186.34, 157.36, 153.08, 146.69, 146.48, 132.51, 132.29, 131.88, 131.75, 130.32, 129.99, 129.40, 122.46, 120.29, 111.49, 35.29, 35.07, 29.59, 29.49, 15.85. HRMS: calcd. for C₃₀H₃₆O₃ [M+H]⁺ 445.2737; found 445.2732.



2am

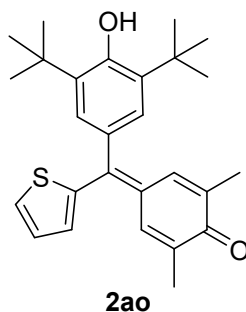
4-((4-bromophenyl)(3,5-di-tert-butyl-4-hydroxyphenyl)methylene)-2,6-dimethylcyclohexa-2,5-dien-1-one(2am) 67%(one step), 41.5%(two steps): orange solid. m.p.:275.2-279.4 °C. ¹H NMR (400 MHz, CDCl₃) δ 7.57 – 7.52 (m, 2H), 7.25 (d, J = 2.7 Hz, 1H), 7.15 – 7.09 (m, 2H), 7.06 (d, J = 2.6 Hz, 1H), 6.85 (s, 2H), 5.03 (s, 1H), 2.25 (s, 6H), 1.26 (s, 9H), 1.24 (s, 9H). ¹³C NMR (101 MHz, CDCl₃) δ 186.06, 155.15, 153.79, 147.21, 147.04, 139.99, 133.66, 133.07, 132.41, 132.29, 131.76, 131.20, 129.22, 123.71, 122.82, 35.29, 29.54, 21.10, 15.83, 14.23. HRMS: calcd. for C₂₉H₃₃BrO₂ [M+H]⁺ 495.1717; found 495.1713.



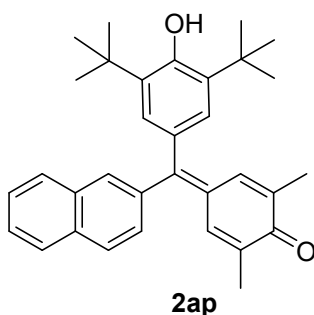
2an

4-((3,5-di-tert-butyl-4-hydroxyphenyl)(3,4,5-trimethoxyphenyl)methylene)-2,6-dimethylcyclohexa-2,5-dien-1-one(2an) 90%(one step), 38.7%(two steps): orange solid. m.p.:249.8-261.1 °C. ¹H NMR (400 MHz, CDCl₃) δ 7.25 (d, J = 2.7 Hz, 1H), 7.19 (d, J = 2.5 Hz, 1H), 6.91 (s, 2H), 6.47 (s, 2H), 5.20 (d, J = 7.6 Hz, 1H), 3.96 (s, 3H), 3.80 (s,

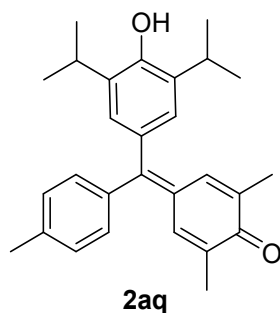
6H), 2.28 (s, 6H), 1.26 (d, J = 4.6 Hz, 18H). ^{13}C NMR (101 MHz, CDCl_3) δ 191.20, 186.10, 157.12, 153.87, 153.66, 152.49, 146.59, 143.62, 139.00, 136.41, 133.25, 132.77, 132.40, 132.33, 131.70, 128.82, 109.89, 106.74, 35.25, 29.67, 15.87. HRMS: calcd. for $\text{C}_{32}\text{H}_{40}\text{O}_5[\text{M}+\text{H}]^+$ 505.2948; found 505.2944.



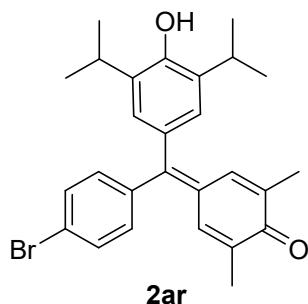
4-((3,5-di-tert-butyl-4-hydroxyphenyl)(thiophen-2-yl)methylene)-2,6-dimethylcyclohexa-2,5-dien-1-one(2ao) 75%(one step), 36%(two steps): orange solid. m.p.:258.6-263.9 $^{\circ}\text{C}$. ^1H NMR (400 MHz, CDCl_3) δ 7.60 (dd, J = 4.9, 1.3 Hz, 2H), 7.32 – 6.89 (m, 5 H), 5.16 (d, J = 52.2 Hz, 1H), 2.24 (d, J = 29.5 Hz, 6H), 1.37 – 1.18 (m, 18H). ^{13}C NMR (101 MHz, CDCl_3) δ 148.72, 144.05, 133.28, 133.02, 132.50, 130.98, 129.17, 127.60, 125.36, 60.51, 35.30, 30.35, 29.62, 16.10, 15.92, 14.23. HRMS: calcd. for $\text{C}_{37}\text{H}_{42}\text{O}_2\text{S}[\text{M}+\text{H}]^+$ 421.2195; found 421.2194.



4-((3,5-di-tert-butyl-4-hydroxyphenyl)(naphthalen-2-yl)methylene)-2,6-dimethylcyclohexa-2,5-dien-1-one(2ap) 84%(one step), 49.6%(two steps): orange solid. m.p.:254.0-255.0 $^{\circ}\text{C}$. ^1H NMR (400 MHz, CDCl_3) δ 7.94 – 7.69 (m, 4H), 7.61 – 7.46 (m, 2H), 7.35 – 7.15 (m, 3H), 6.94 (d, J = 24.3 Hz, 2H), 5.08 (d, J = 7.4 Hz, 1H), 2.21 (d, J = 28.4 Hz, 6H), 1.34 – 1.16 (m, 18H). ^{13}C NMR (101 MHz, CDCl_3) δ 186.09, 156.97, 147.01, 146.83, 135.39, 133.25, 132.64, 132.50, 129.49, 129.34, 128.61, 127.76, 127.49, 127.17, 126.67, 126.07, 125.75, 125.32, 122.76, 60.49, 56.28, 34.39, 29.63, 16.06, 15.85, 14.24. HRMS: calcd. for $\text{C}_{33}\text{H}_{36}\text{O}_2[\text{M}+\text{H}]^+$ 465.1423; found 465.1423.



4-((4-hydroxy-3,5-diisopropylphenyl)(p-tolyl)methylene)-2,6-dimethylcyclohexa-2,5-dien-1-one (2aq) 70%(one step), 35%(two steps): orange solid. m.p.:200.1-219.0 °C. ¹H NMR (400 MHz, CDCl₃) δ 7.23 (s, 1H), 7.21 (s, 1H), 7.14 (d, *J* = 8.1 Hz, 2H), 7.06 (s, 2H), 6.97 (s, 2H), 3.20 (p, *J* = 6.9 Hz, 2H), 2.44 (s, 3H), 2.19 (s, 6H), 1.12 (s, 6H), 1.11 (s, 6H). ¹³C NMR (101 MHz, CDCl₃) δ 158.61, 139.88, 138.01, 136.53, 134.46, 132.63, 128.87, 128.80, 128.68, 127.41, 127.23, 122.85, 122.68, 27.38, 26.79, 22.72, 22.30, 21.49, 16.12.

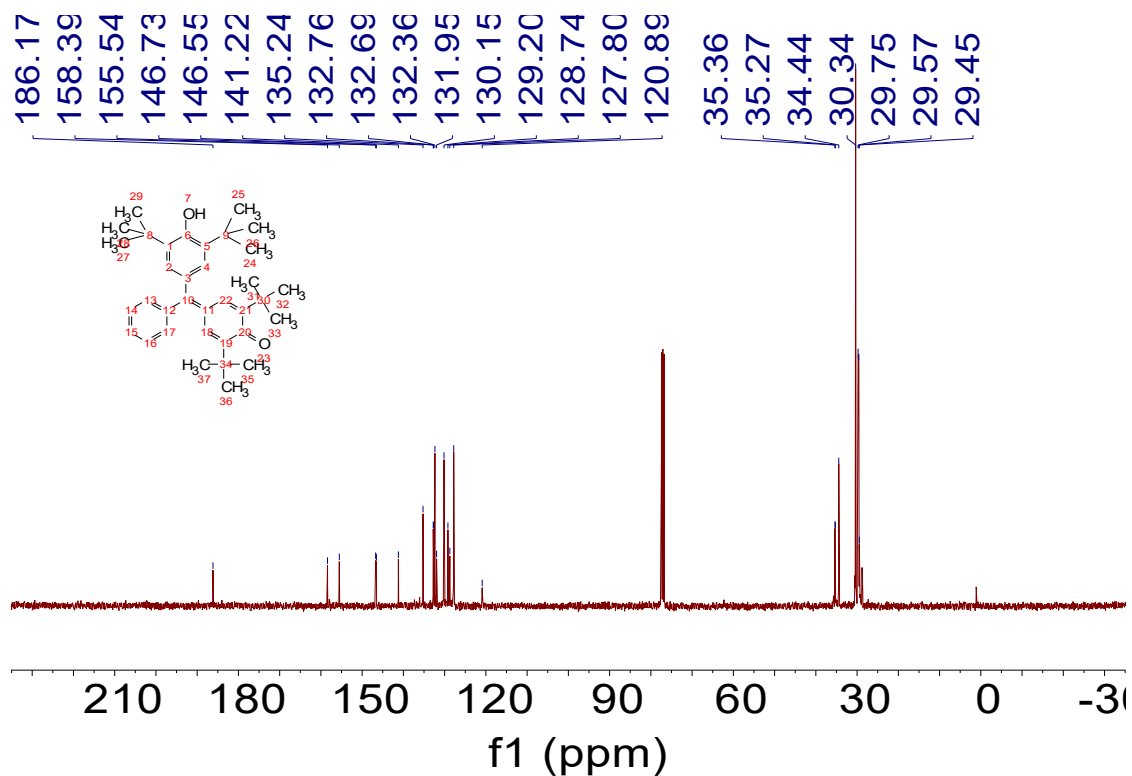
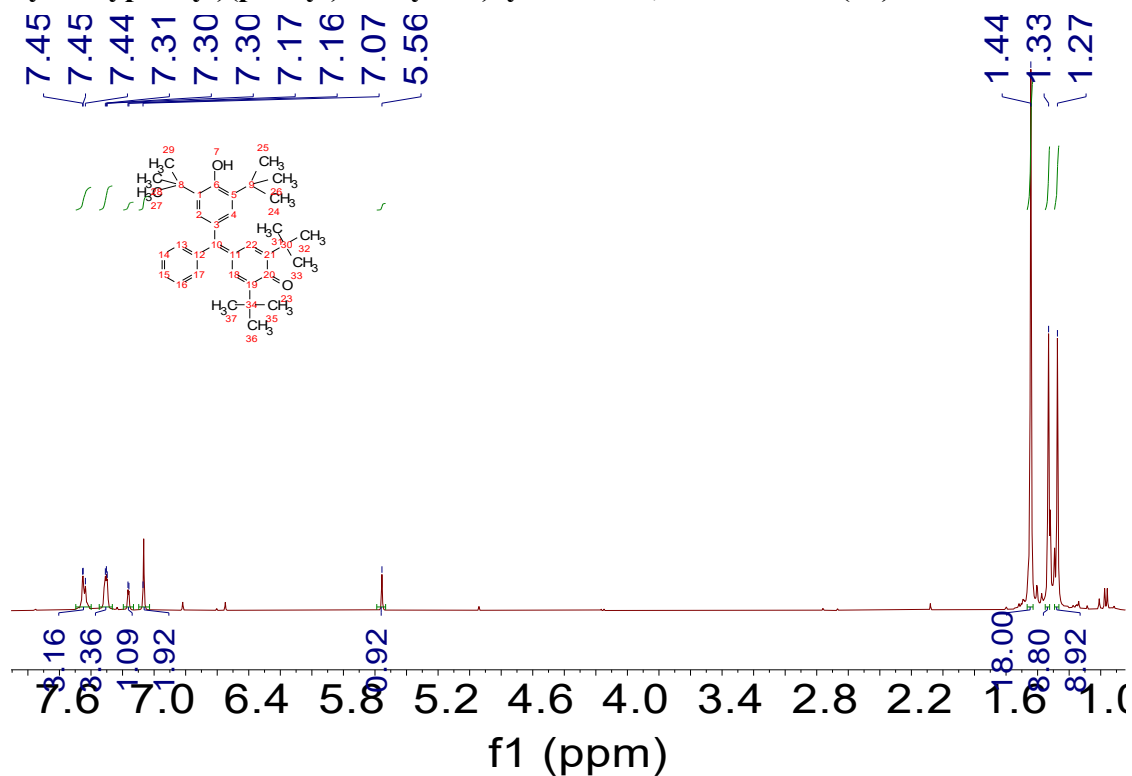


4-((4-bromophenyl)(4-hydroxy-3,5-diisopropylphenyl)methylene)-2,6-dimethylcyclohexa-2,5-dien-1-one(2ar) 60%(one step), 28.2%(two steps): orange solid. m.p.:252.6-260.0 °C. ¹H NMR (400 MHz, CDCl₃) δ 7.55 – 7.43 (m, 1H), 7.32 – 7.00 (m, 3H), 6.94 – 6.75 (m, 2H), 6.68 (s, 1H), 6.60 (s, 1H), 5.21 (d, *J* = 8.0 Hz, 1H), 4.05 (q, *J* = 7.2 Hz, 1H), 3.03 (p, *J* = 6.9 Hz, 1H), 2.14 – 1.92 (m, 6H), 1.24 – 1.04 (m, 12H). ¹³C NMR (101 MHz, CDCl₃) δ 171.31, 154.20, 150.59, 148.45, 144.42, 135.37, 133.42, 131.07, 129.51, 124.43, 122.78, 26.80, 22.72, 22.10, 21.10, 15.88, 14.23. HRMS: calcd. For C₂₇H₂₉BrO₂[M+H]⁺465.1423; found465.1423.

4. ¹H and ¹³C NMR spectra of the products

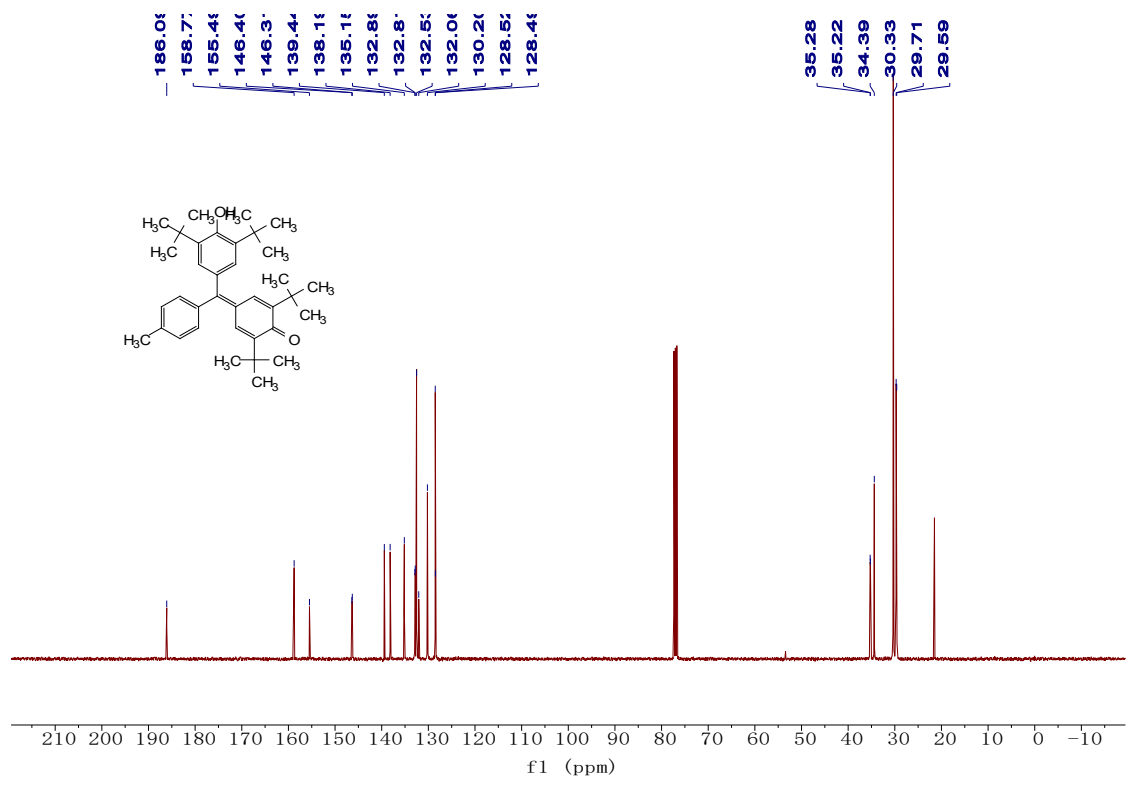
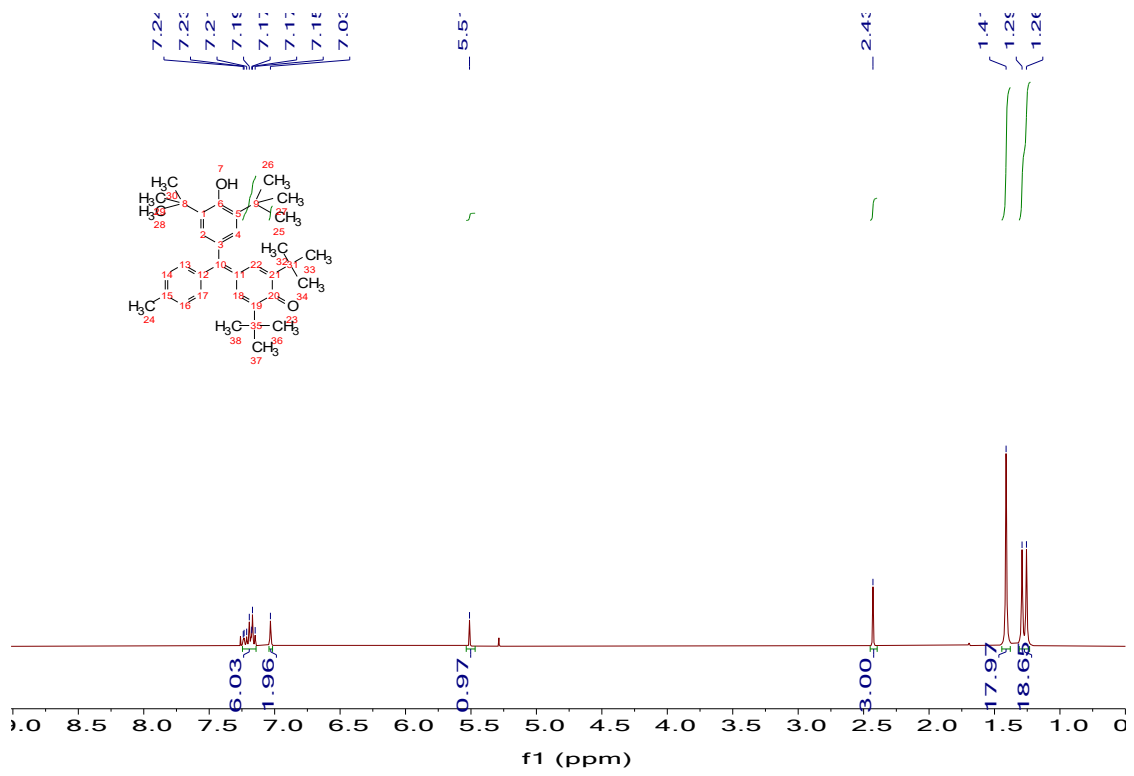
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hydroxyphenyl)(phenyl)methylene)cyclohexa-2,5-dien-1-one (2a)

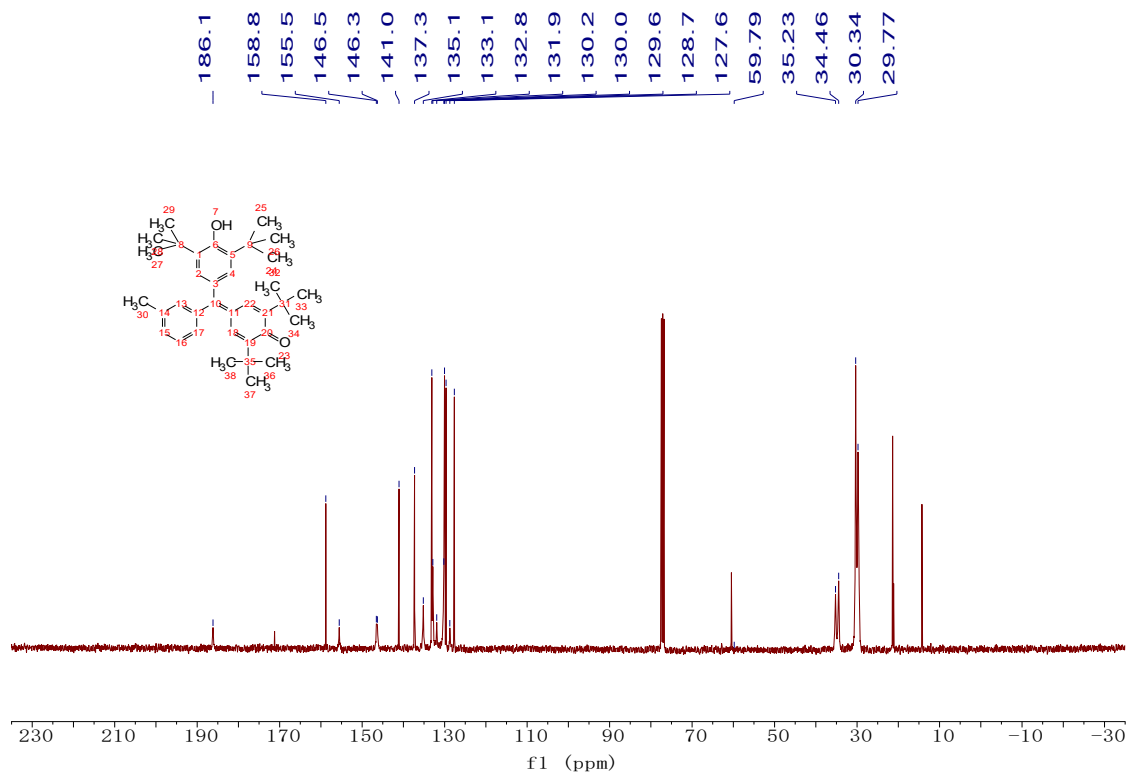
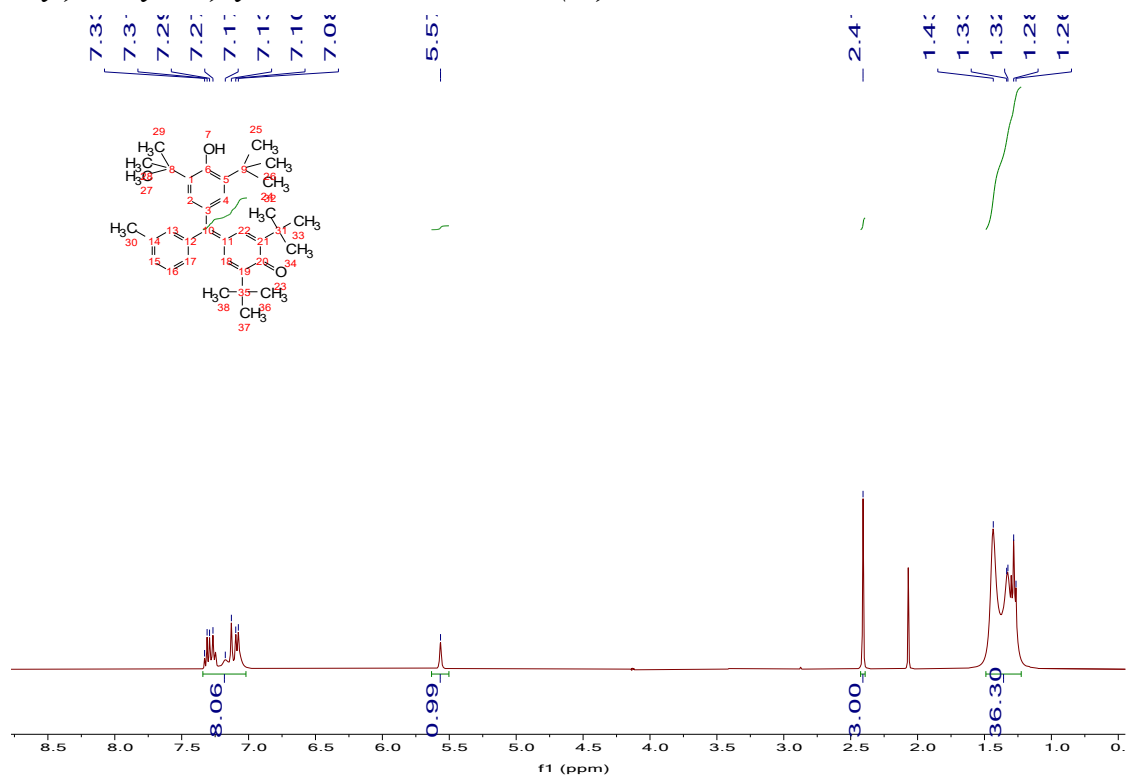


2,6-di-tert-butyl-4-((3,5-di-tert-butyl-4-hydroxyphenyl)(p-

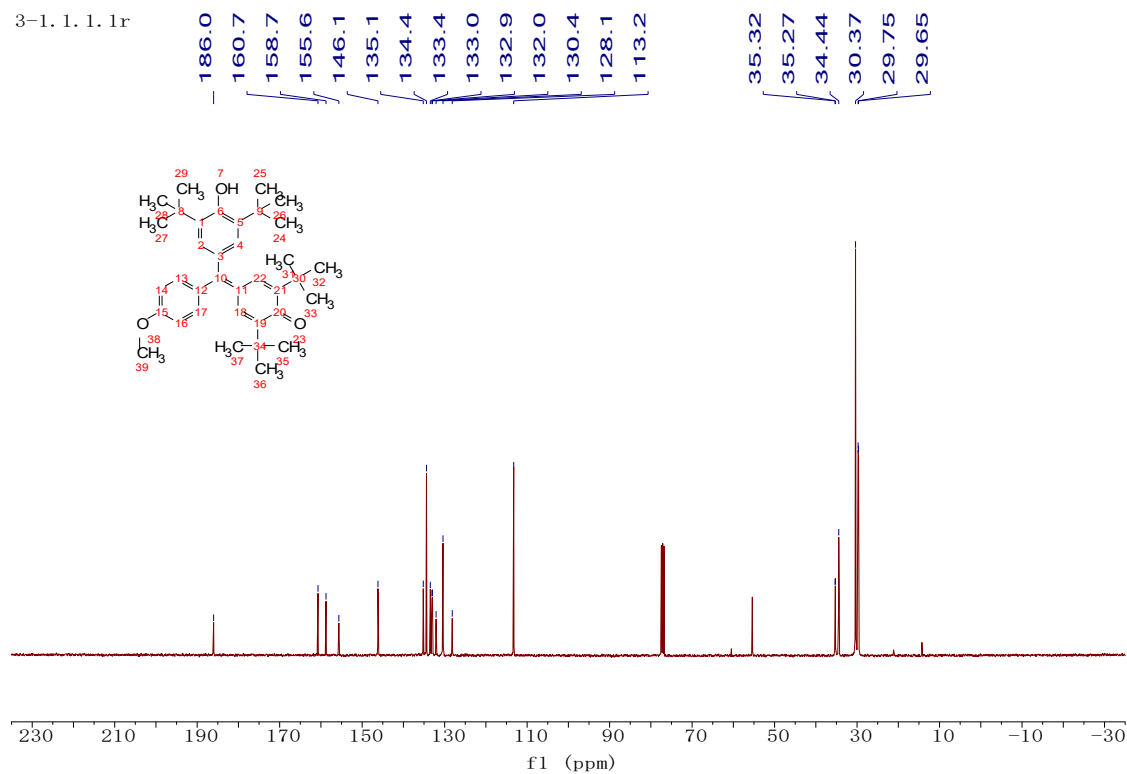
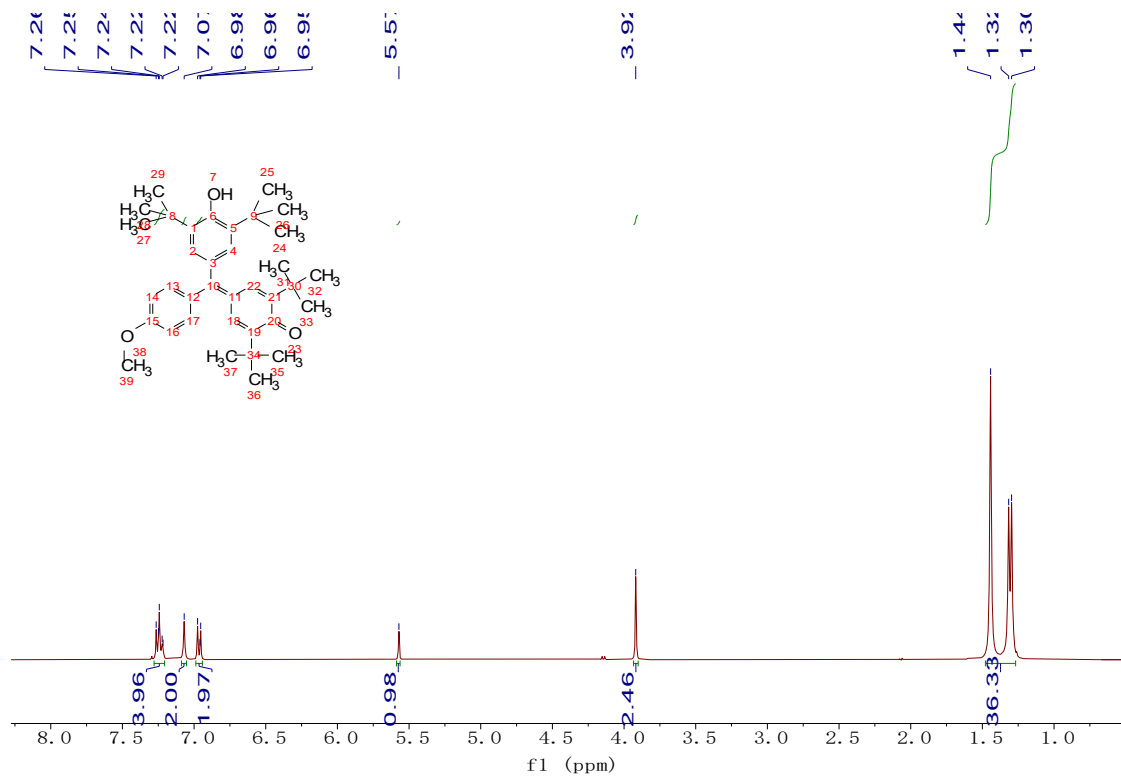
tolyl)methylene)cyclohexa-2,5-dien-1-one(2b)



2,6-di-tert-butyl-4-((3,5-di-tert-butyl-4-hydroxyphenyl)(m-tolyl)methylene)cyclohexa-2,5-dien-1-one(2c)

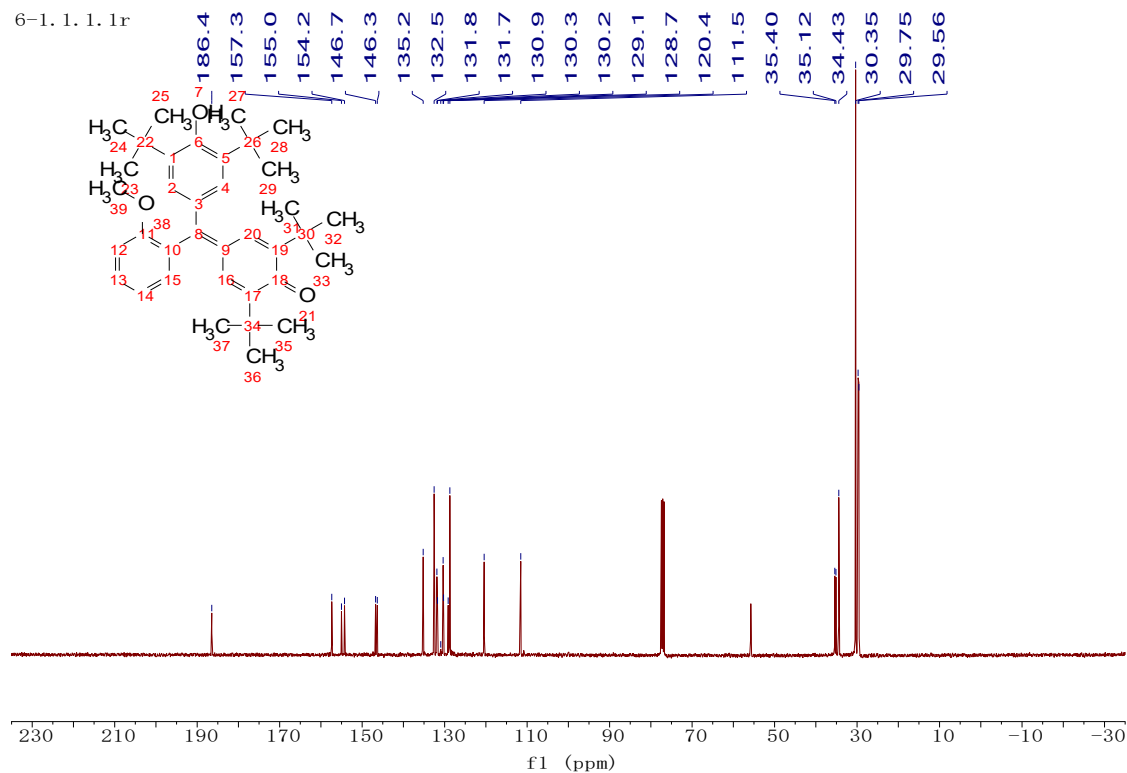
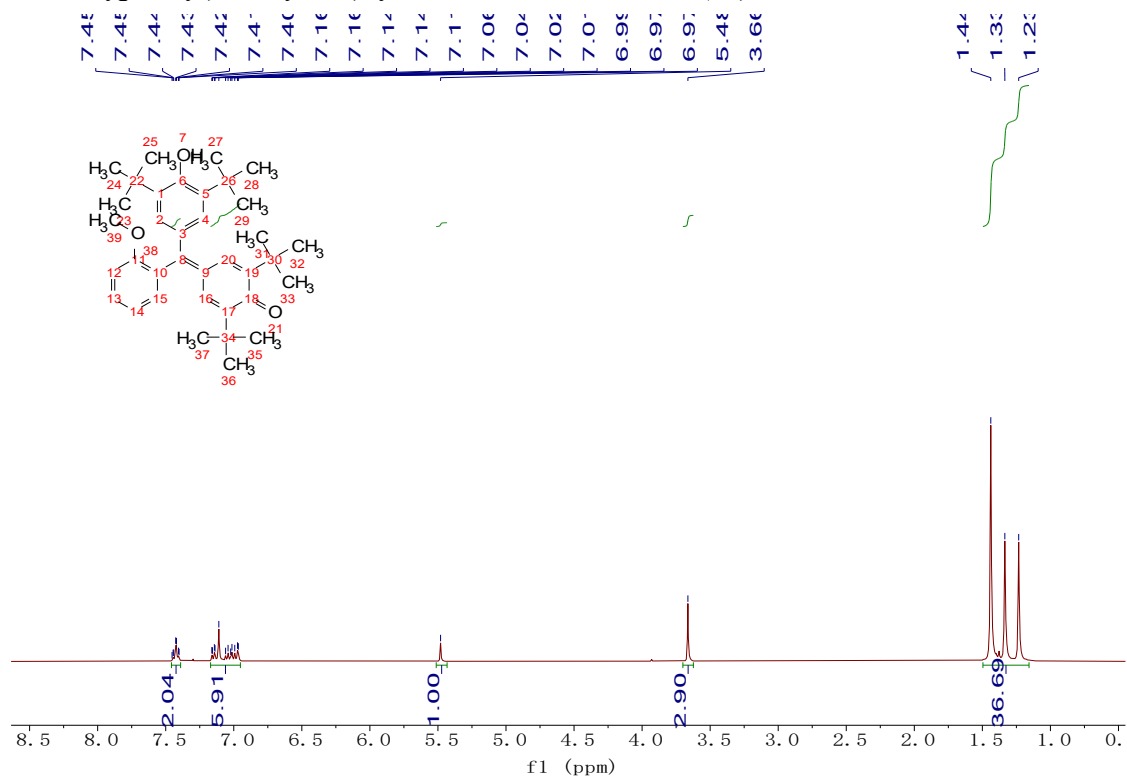


2,6-di-tert-butyl-4-((3,5-di-tert-butyl-4-hydroxyphenyl)(4-methoxyphenyl)methylene)cyclohexa-2,5-dien-1-one(2d)

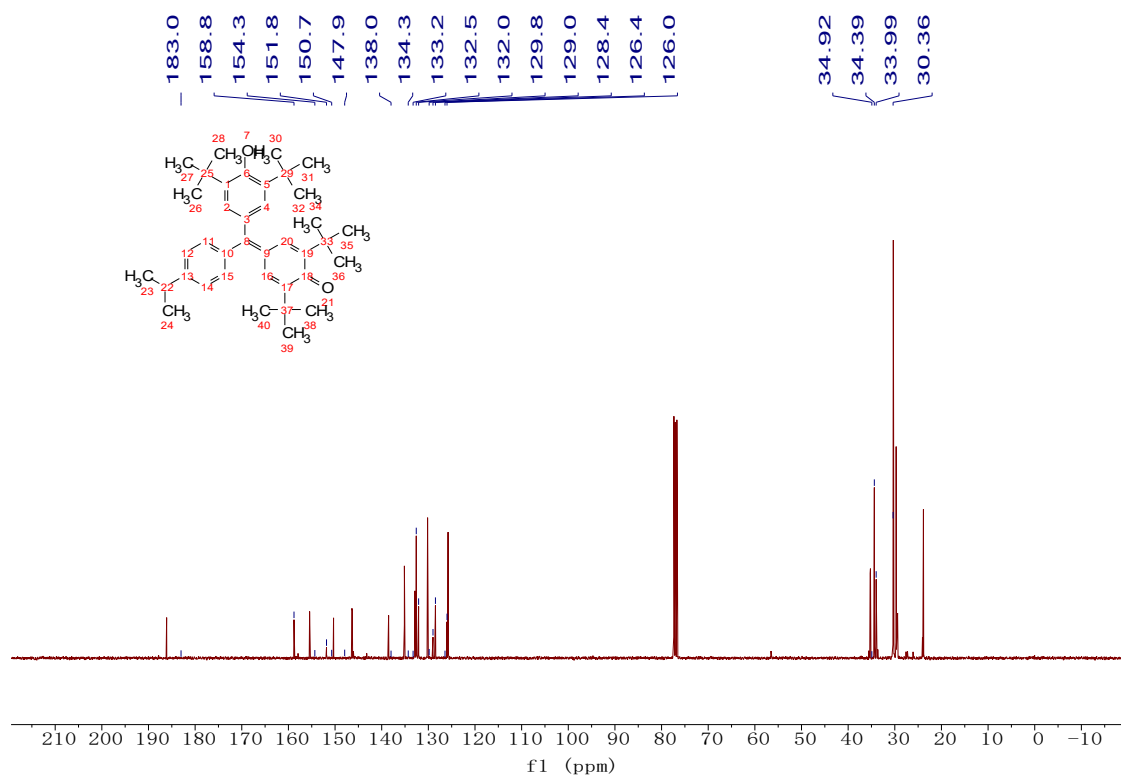
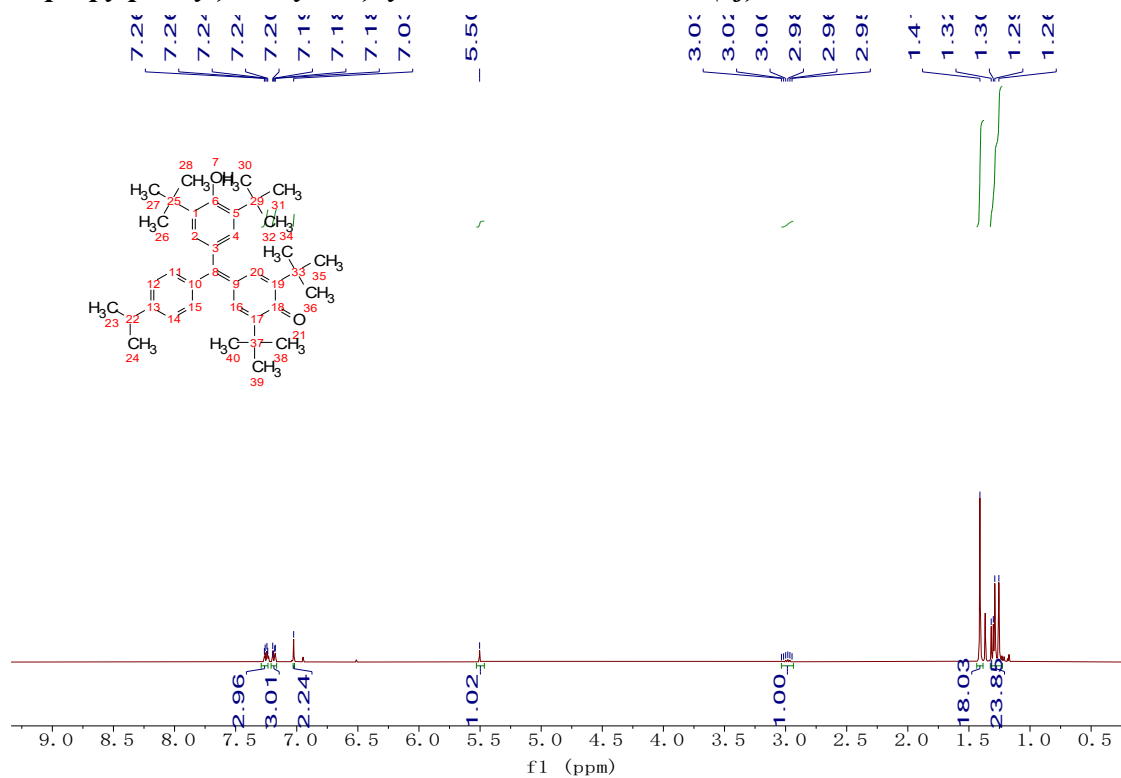


2,6-di-tert-butyl-4-((3,5-di-tert-butyl-4-hydroxyphenyl)(2-

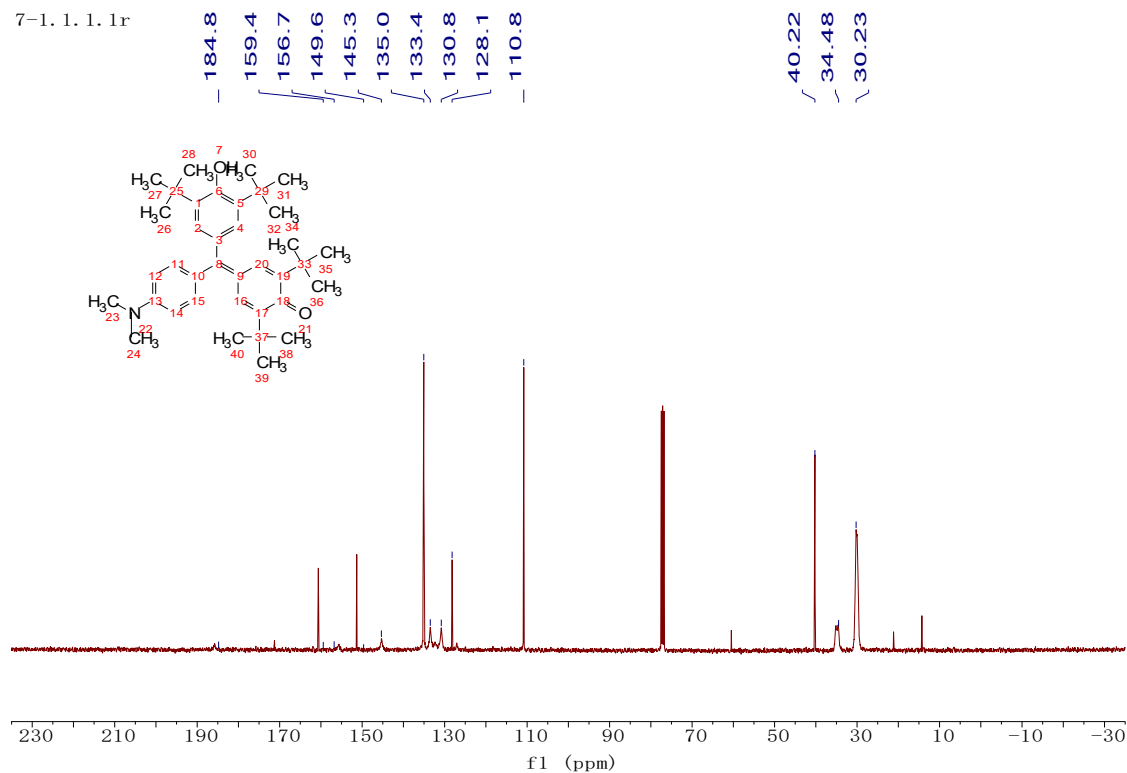
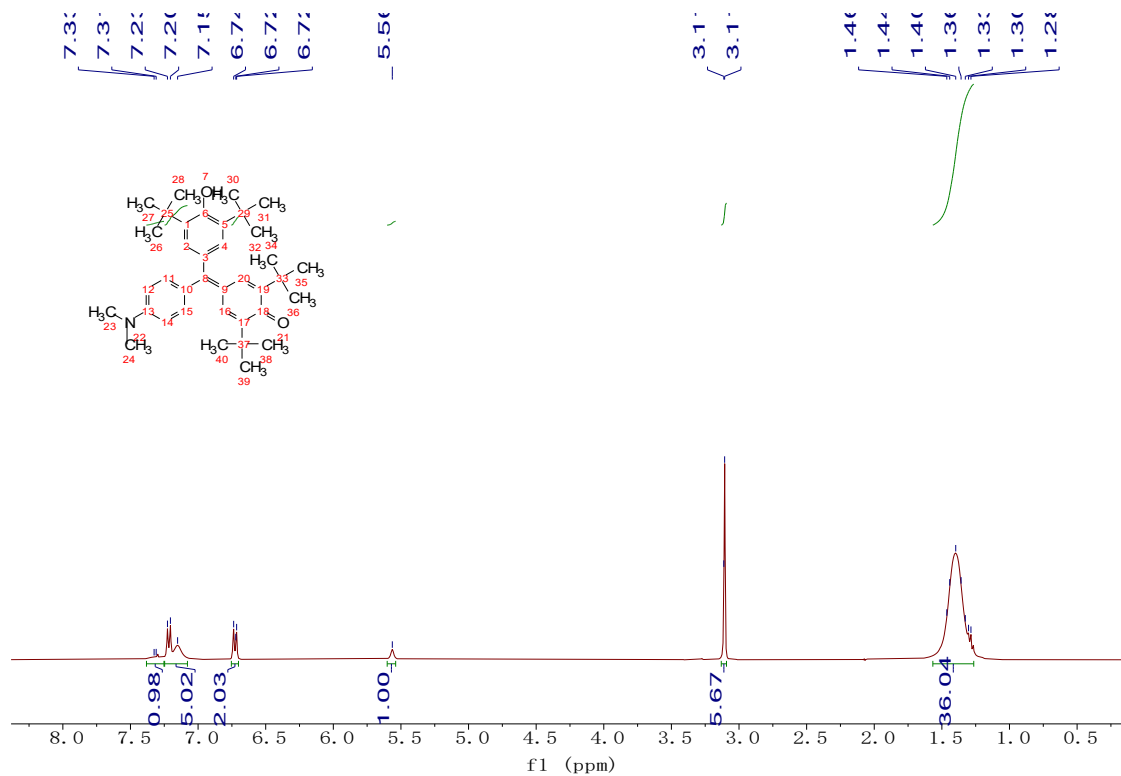
methoxyphenyl)methylene)cyclohexa-2,5-dien-1-one(2e)



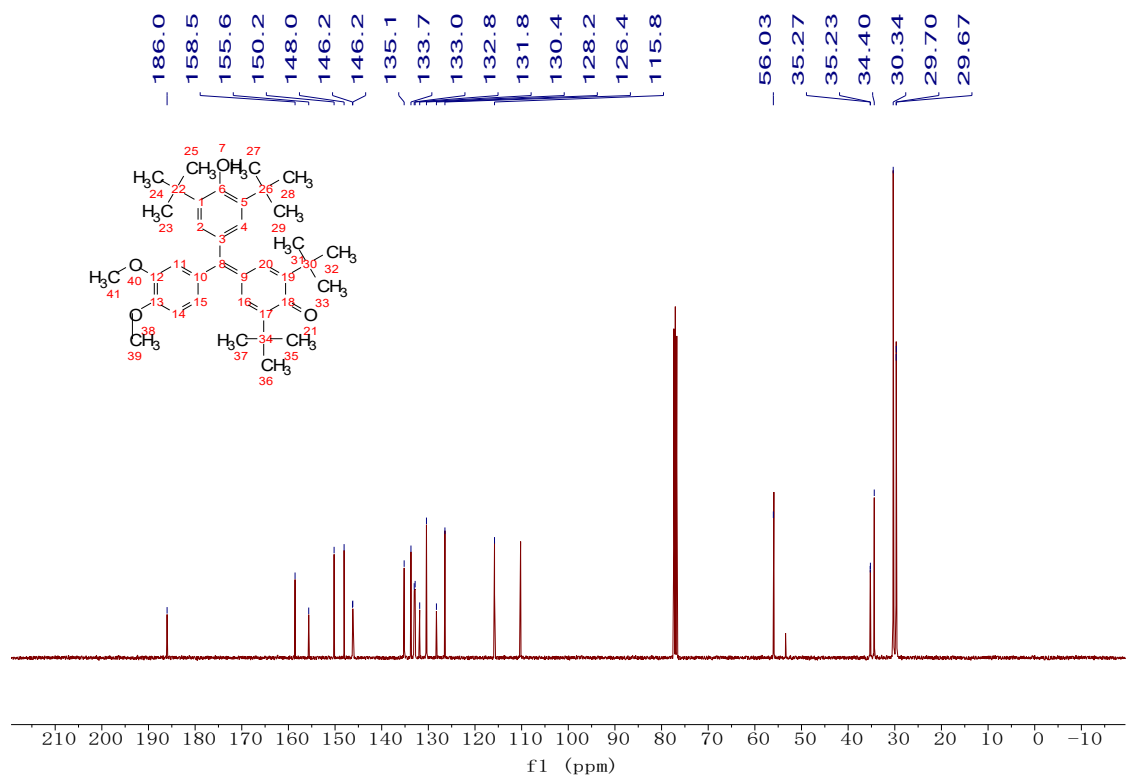
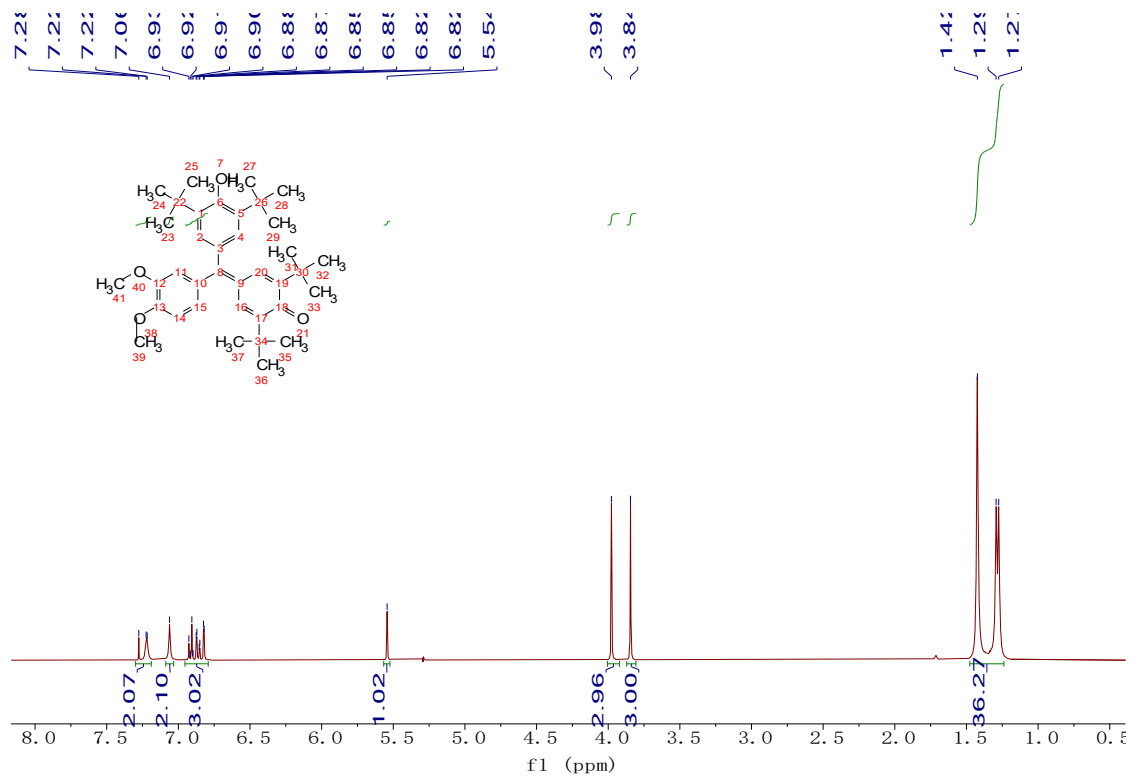
2,6-di-tert-butyl-4-((3,5-di-tert-butyl-4-hydroxyphenyl)(4-isopropylphenyl)methylene)cyclohexa-2,5-dien-1-one(2f)



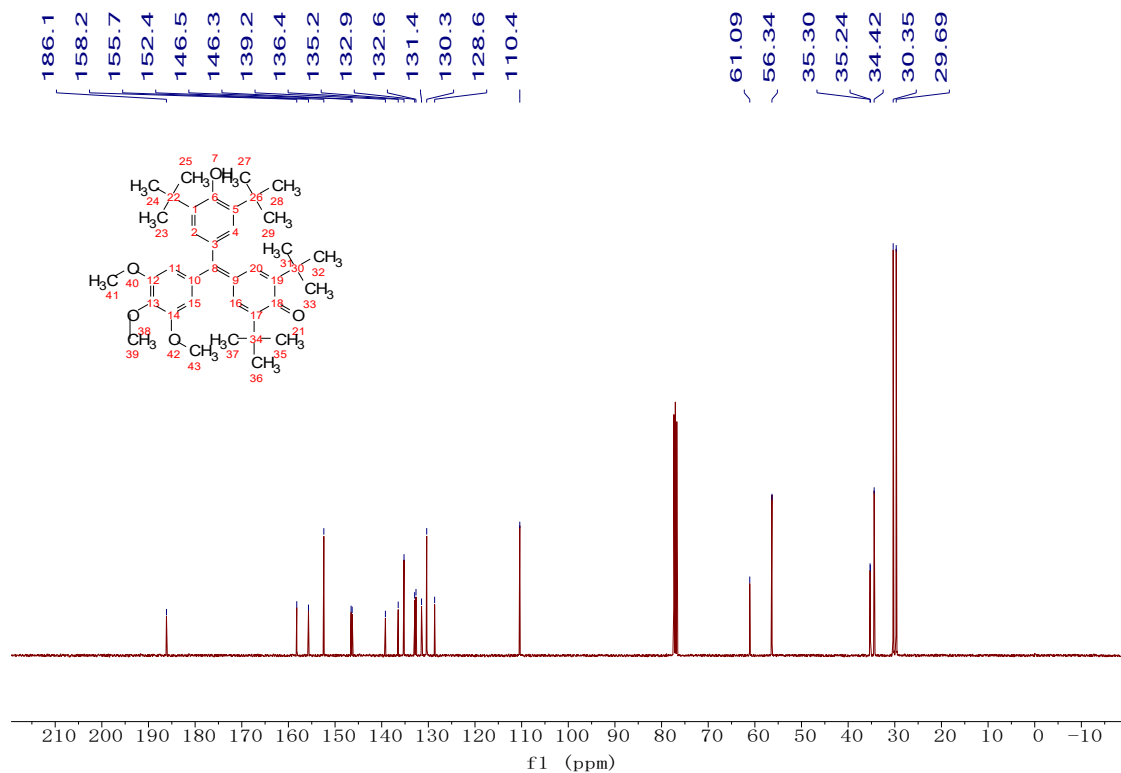
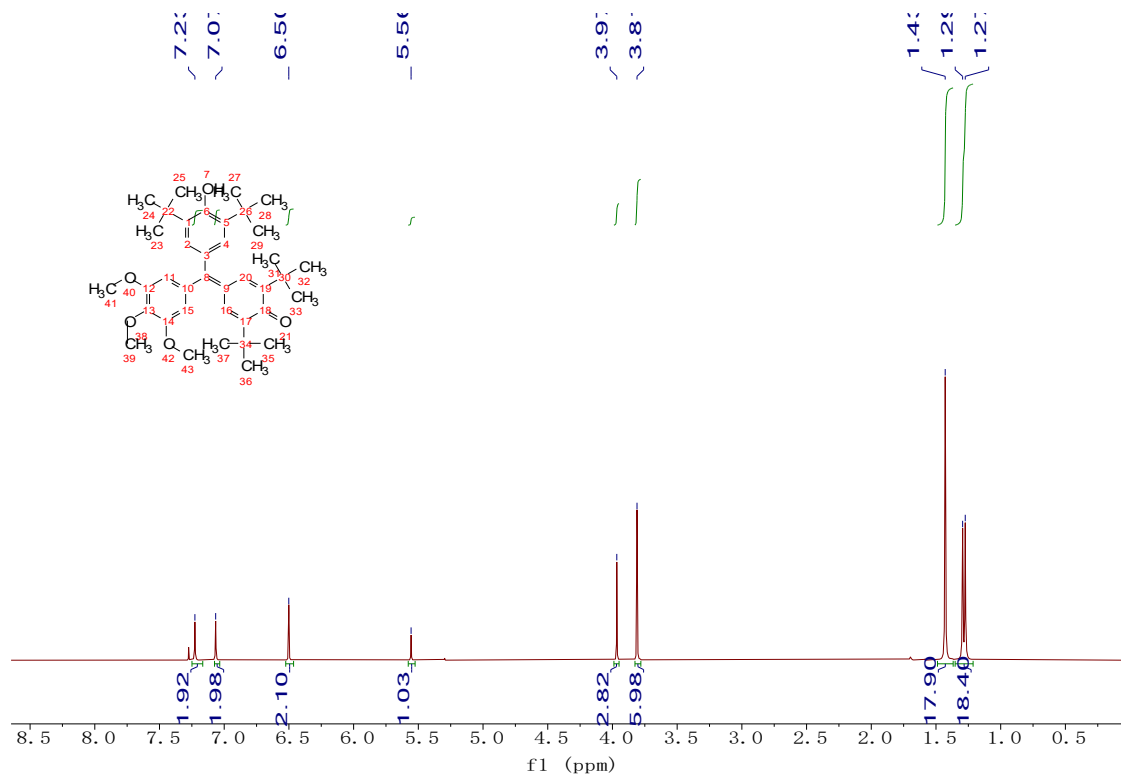
2,6-di-tert-butyl-4-((3,5-di-tert-butyl-4-hydroxyphenyl)(4-(dimethylamino)phenyl)methylene)cyclohexa-2,5-dien-1-one(2g)



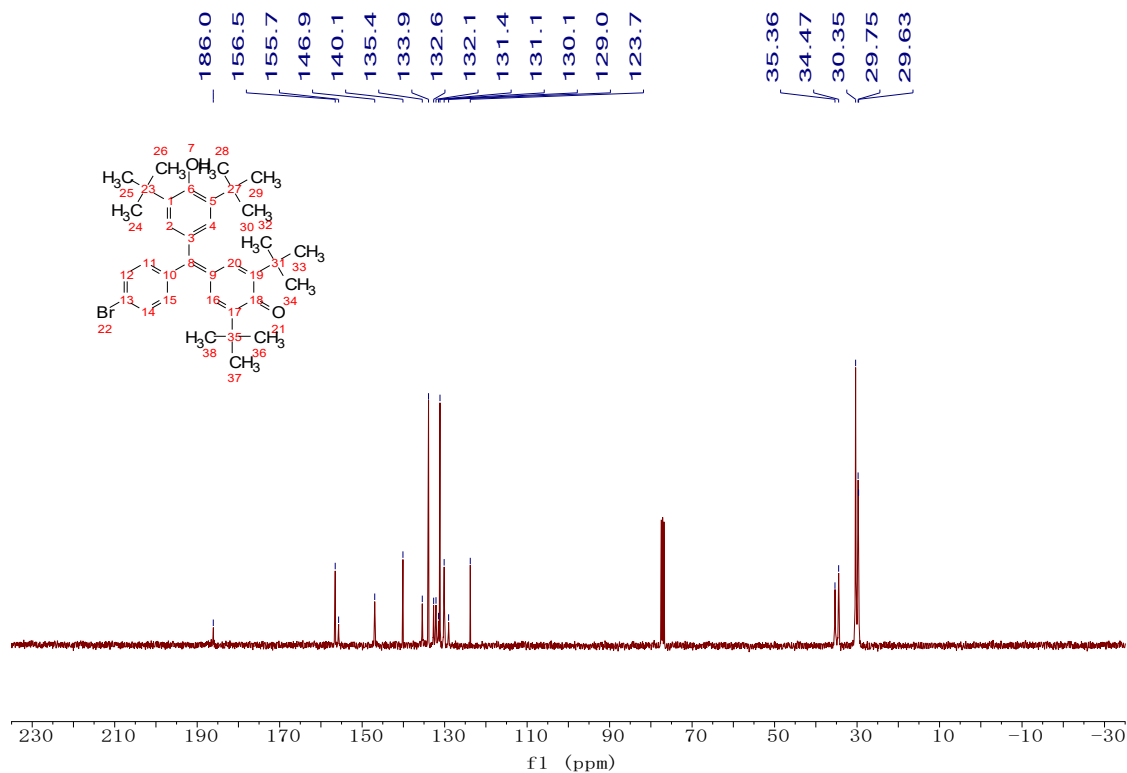
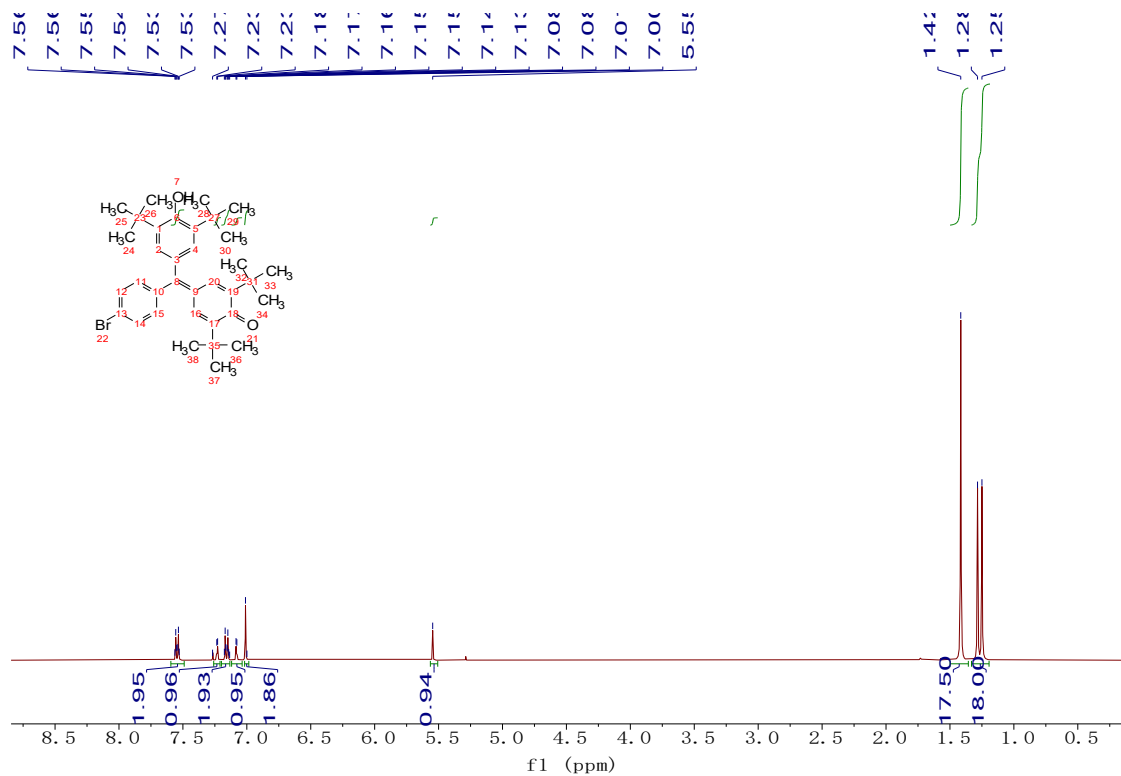
2,6-di-tert-butyl-4-((3,5-di-tert-butyl-4-hydroxyphenyl)(3,4-dimethoxyphenyl)methylene)cyclohexa-2,5-dien-1-one(2h)



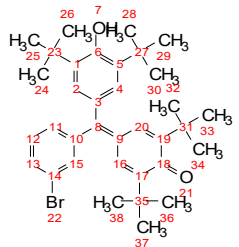
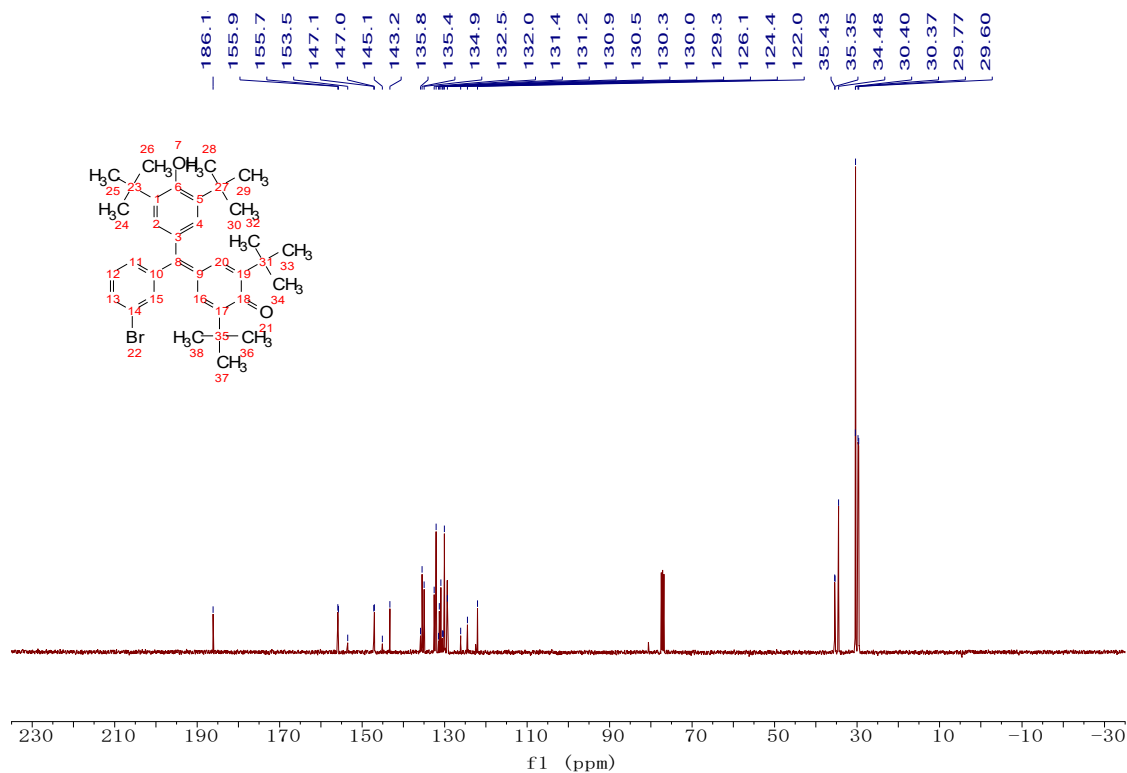
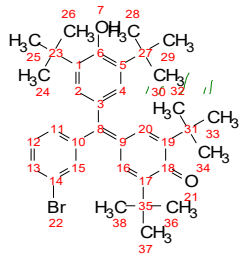
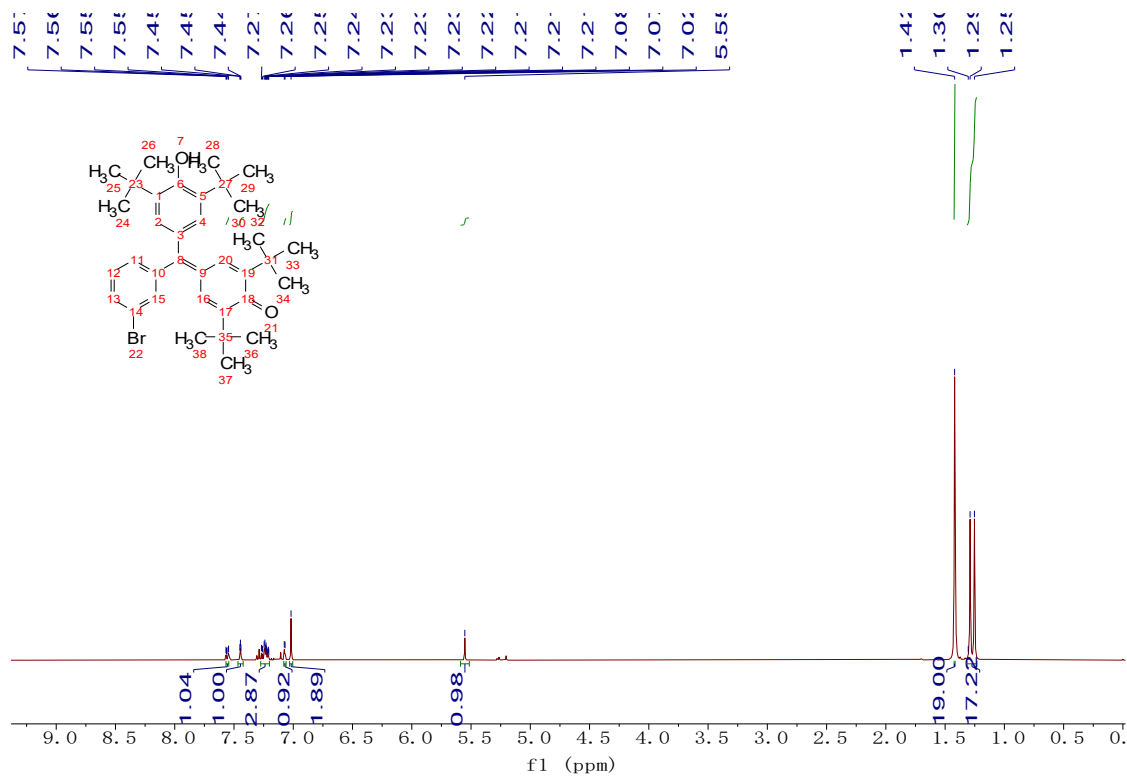
2,6-di-tert-butyl-4-((3,5-di-tert-butyl-4-hydroxyphenyl)(3,4,5-trimethoxyphenyl)methylene)cyclohexa-2,5-dien-1-one(2i)



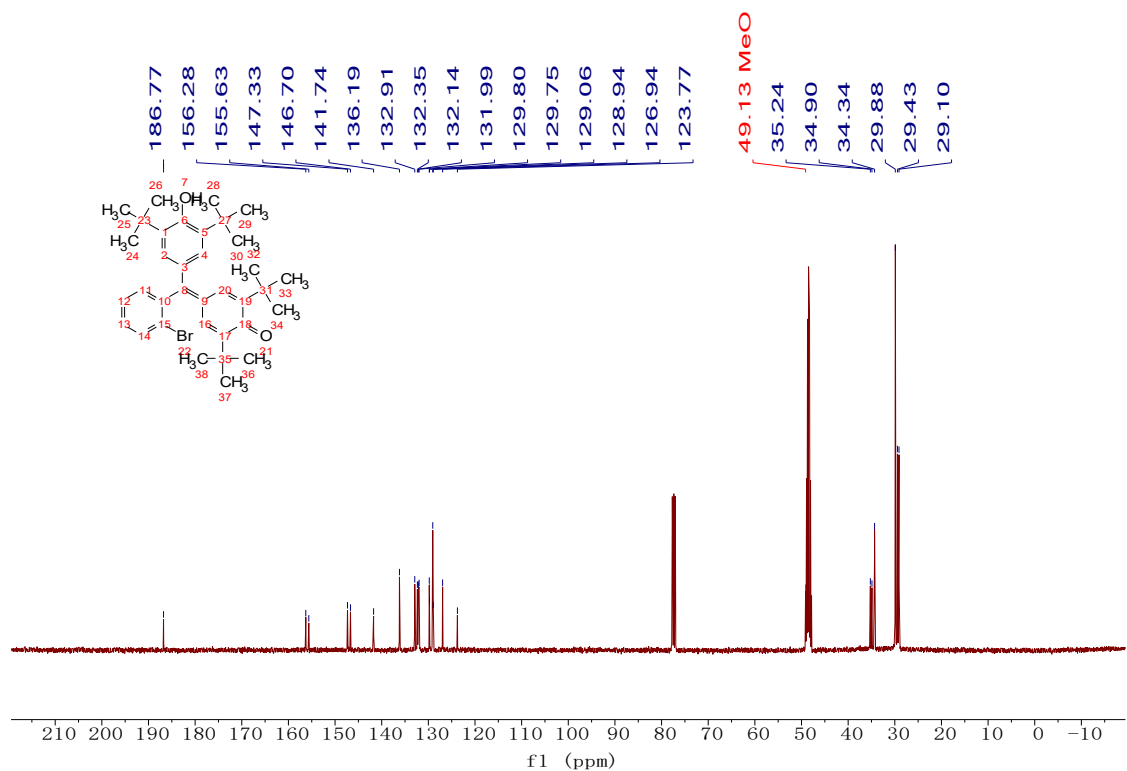
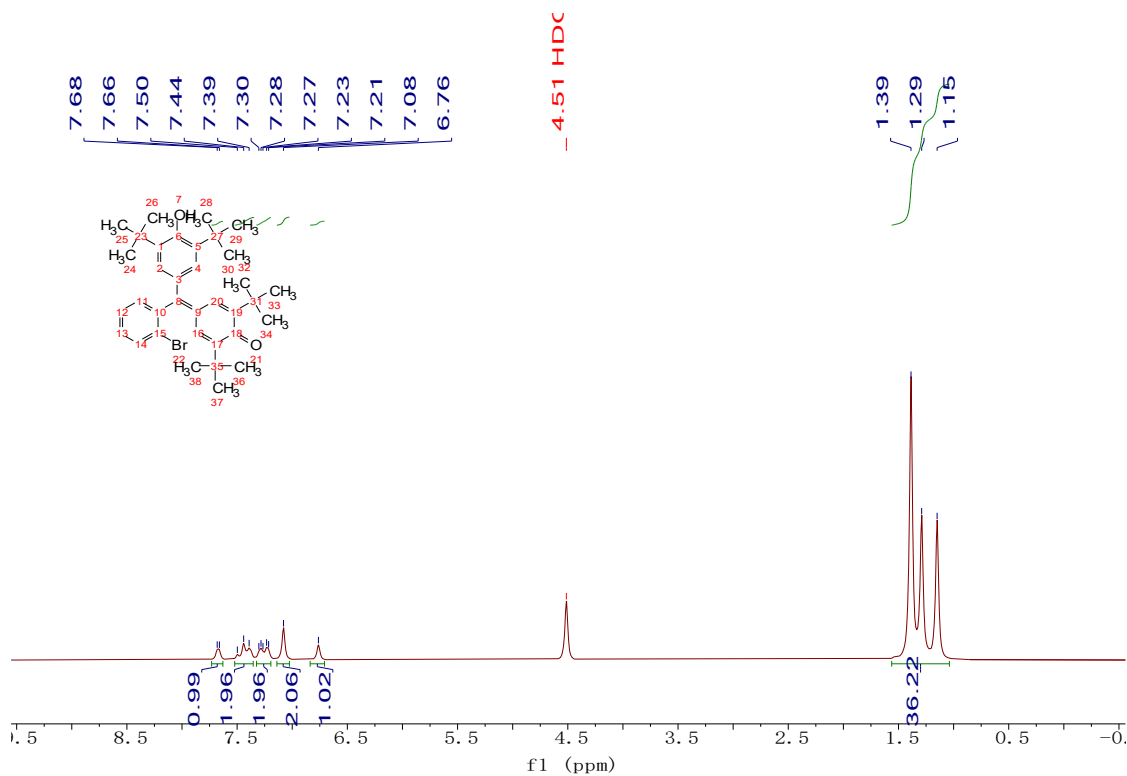
4-((4-bromophenyl)(3,5-di-tert-butyl-4-hydroxyphenyl)methylene)-2,6-di-tert-butylcyclohexa-2,5-dien-1-one(2j)

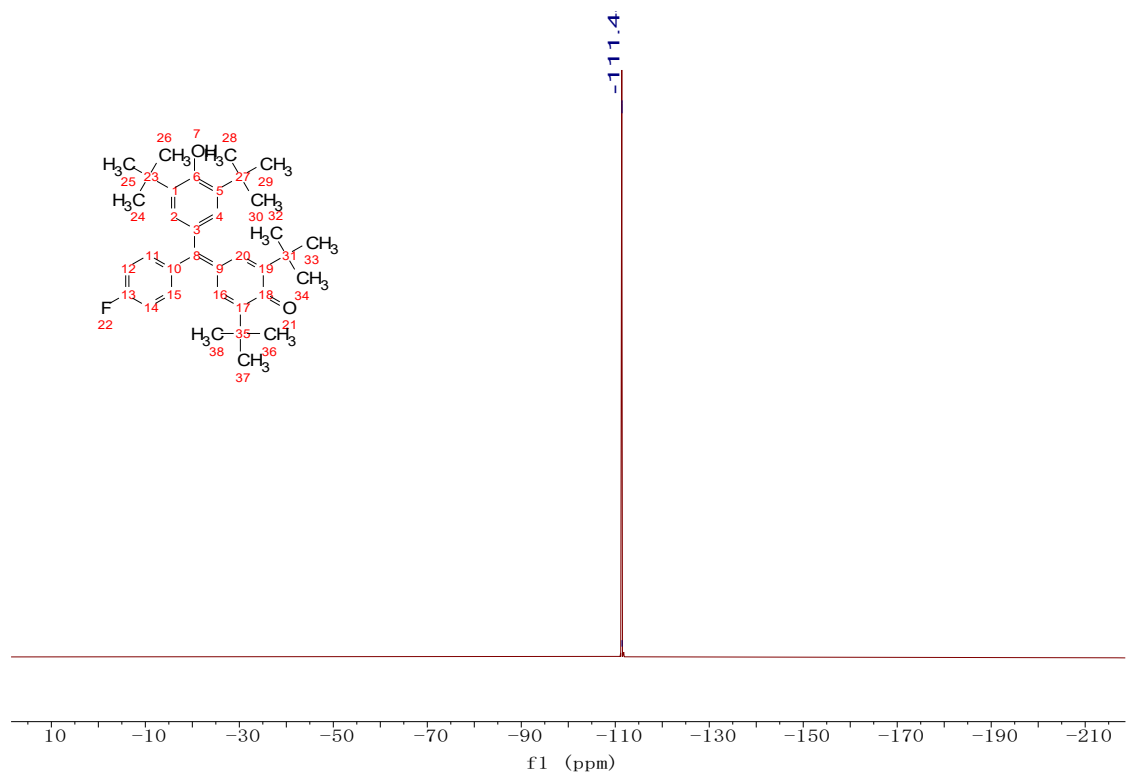


4-((3-bromophenyl)(3,5-di-tert-butyl-4-hydroxyphenyl)methylene)-2,6-di-tert-butylcyclohexa-2,5-dien-1-one(2k)

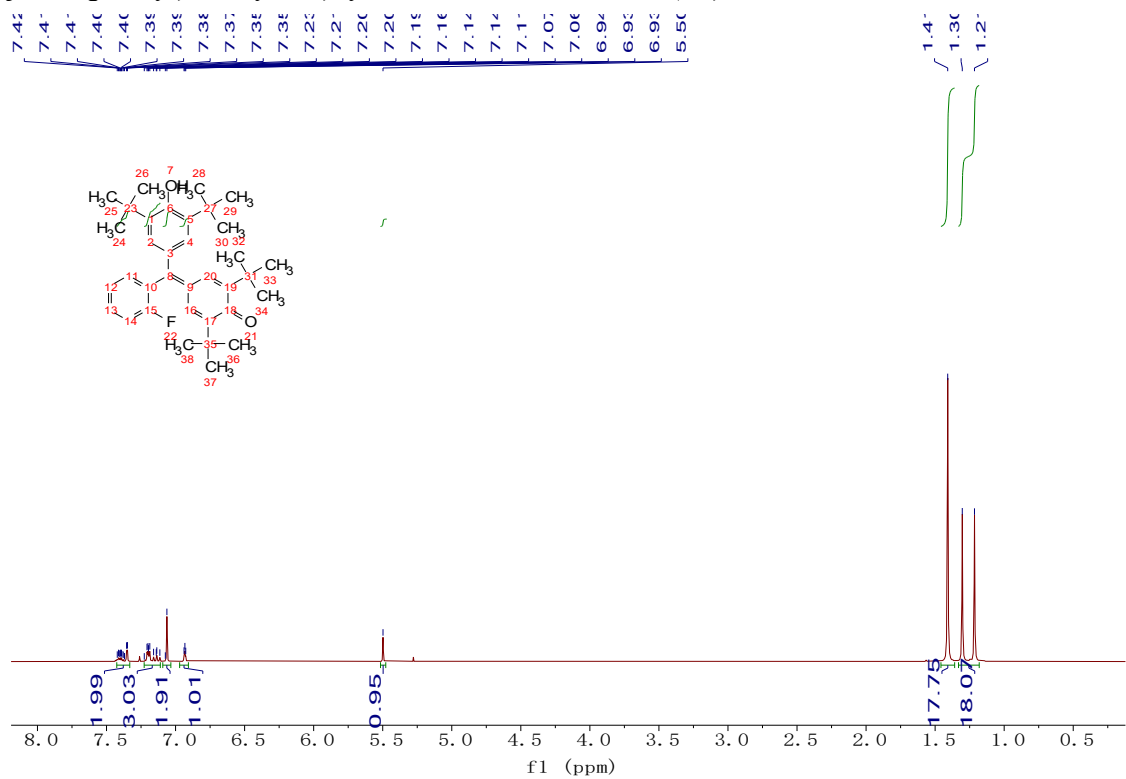


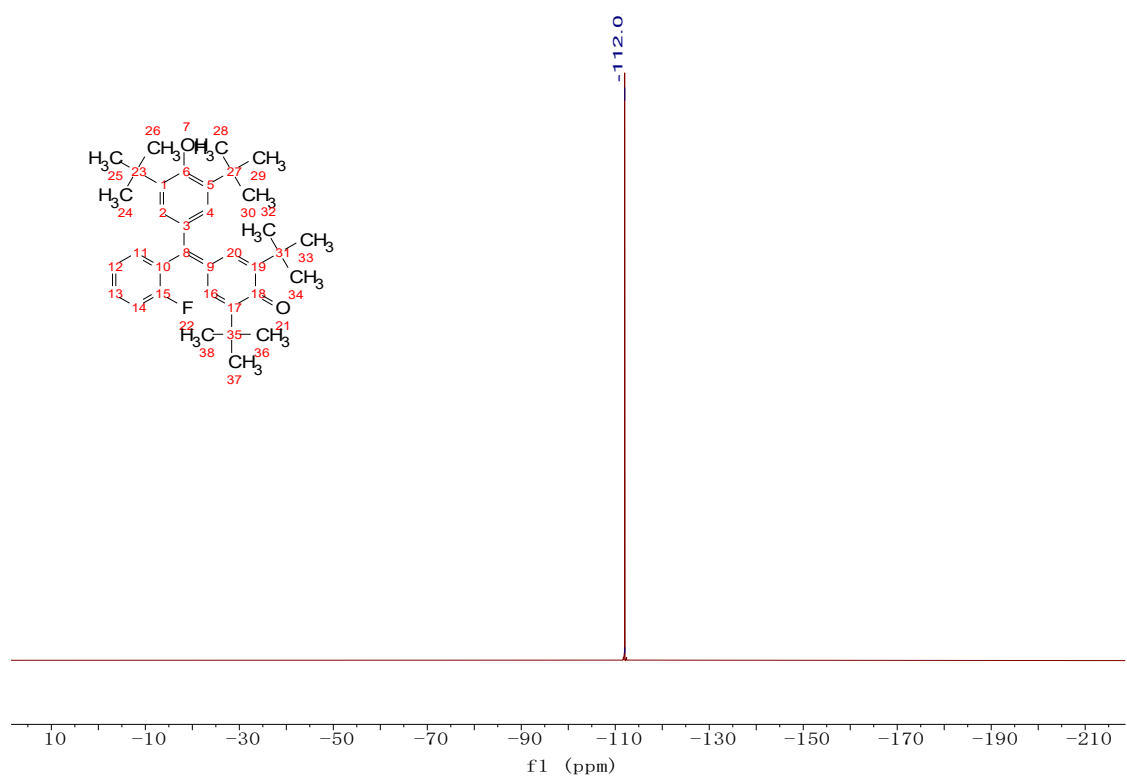
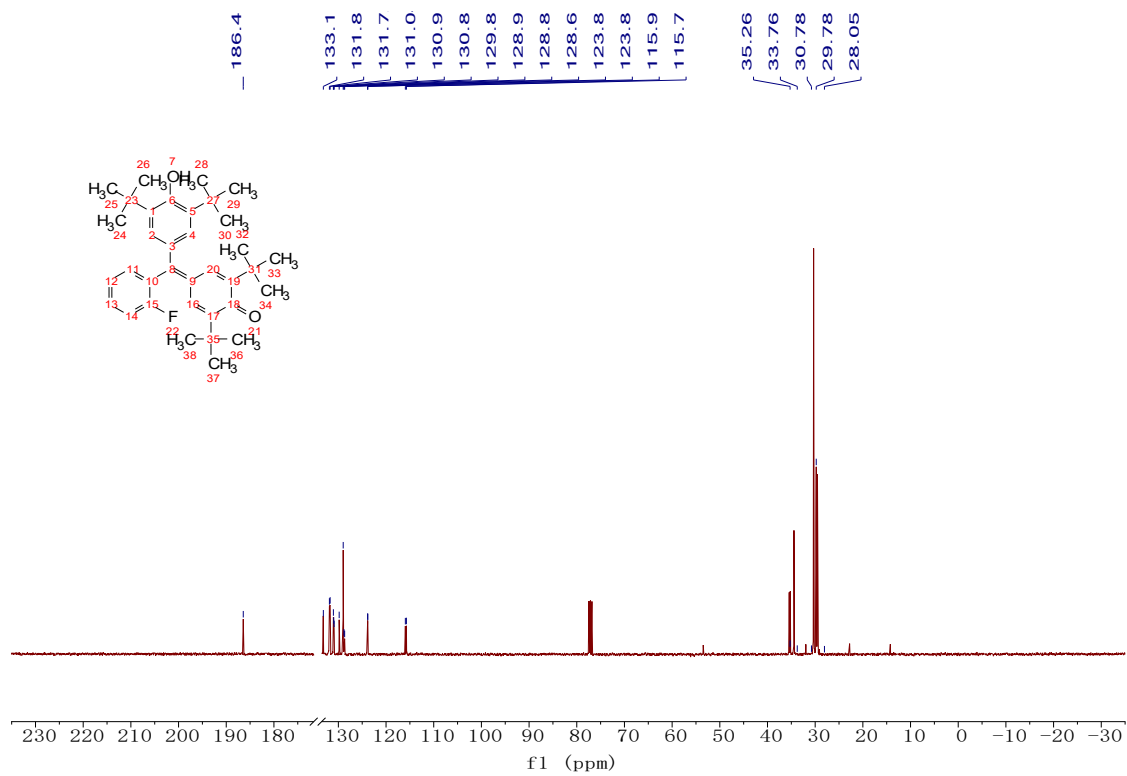
4-((2-bromophenyl)(3,5-di-tert-butyl-4-hydroxyphenyl)methylene)-2,6-di-tert-butylcyclohexa-2,5-dien-1-one(2l)



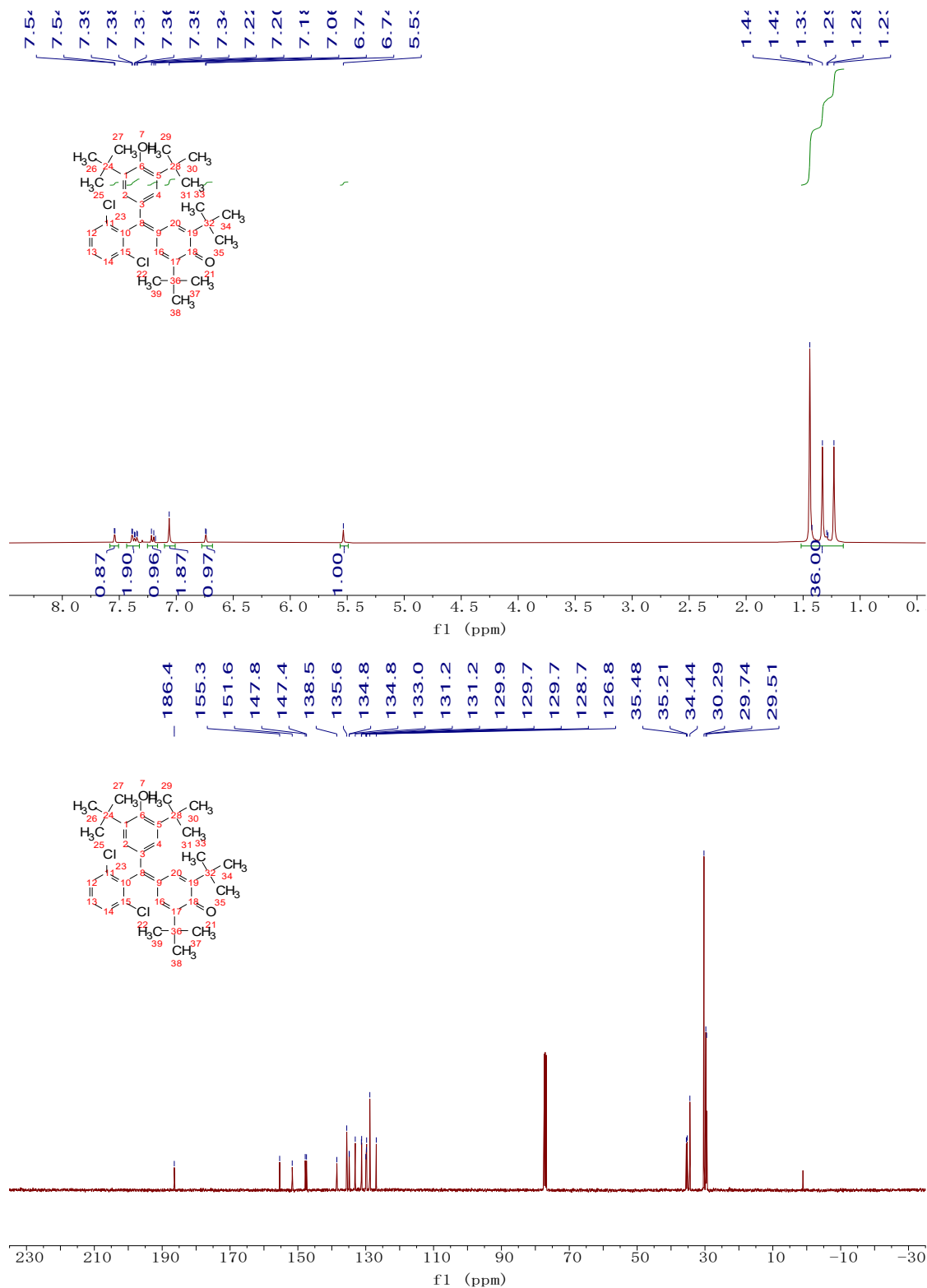


2,6-di-tert-butyl-4-((3,5-di-tert-butyl-4-hydroxyphenyl)(2-fluorophenyl)methylene)cyclohexa-2,5-dien-1-one(2n)

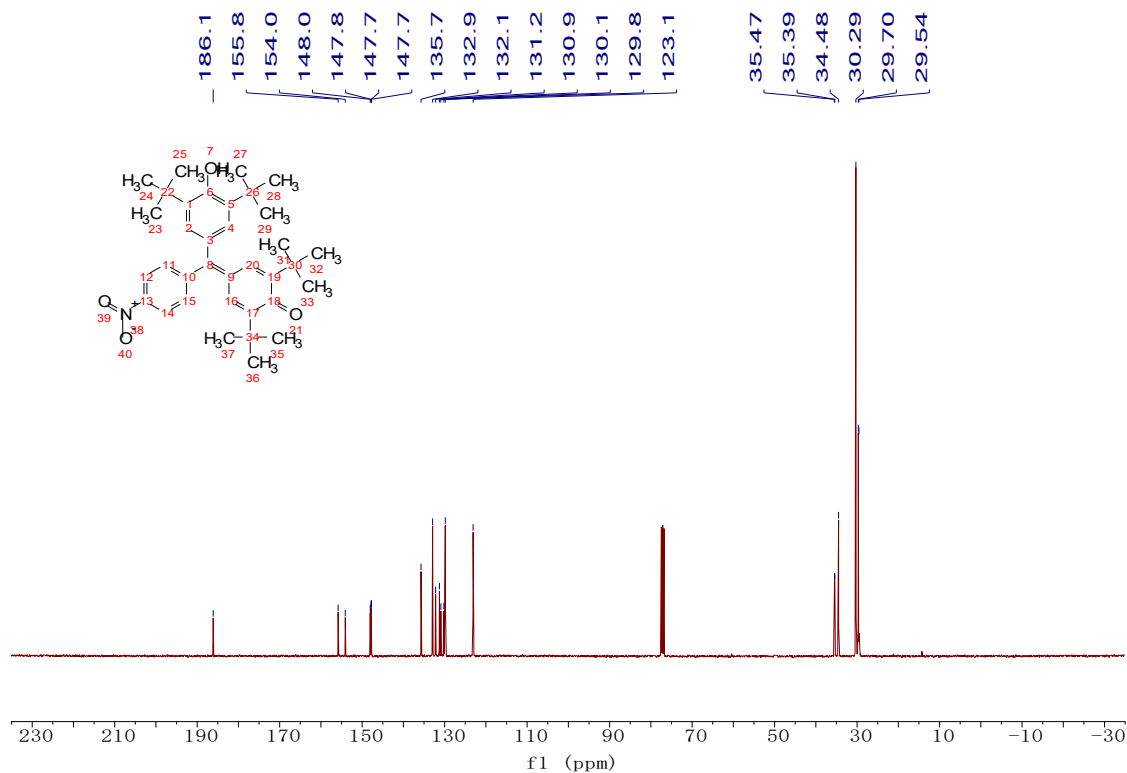
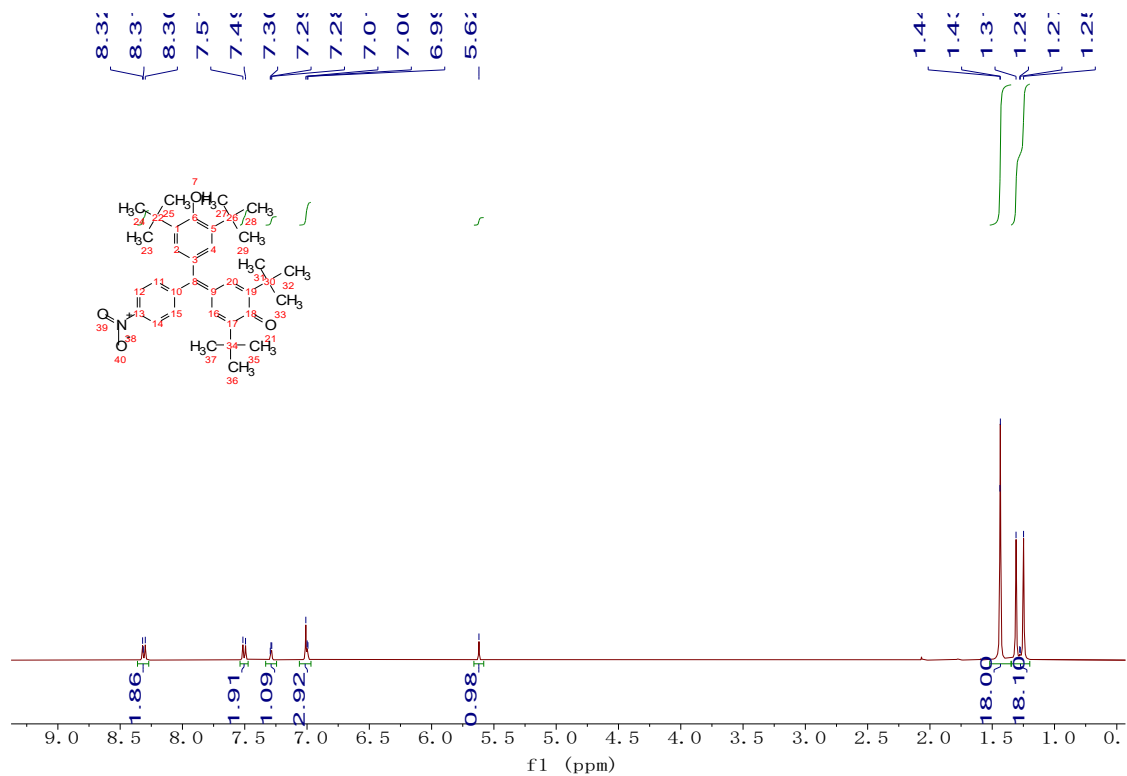




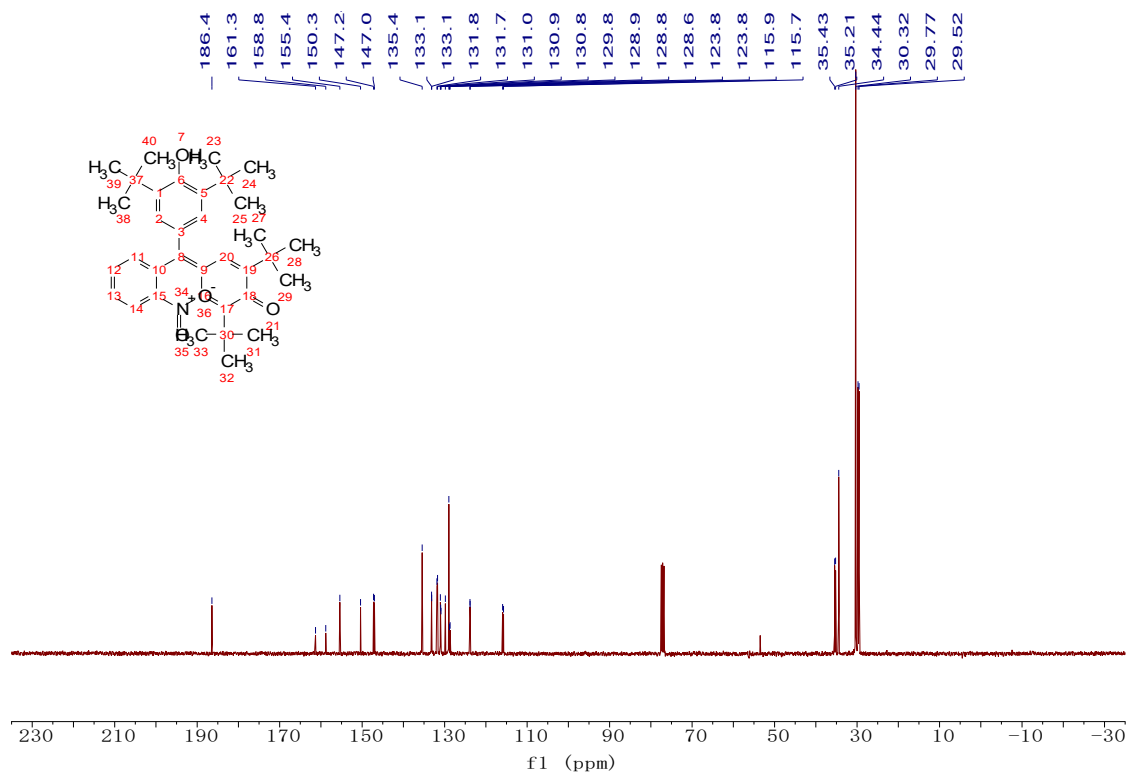
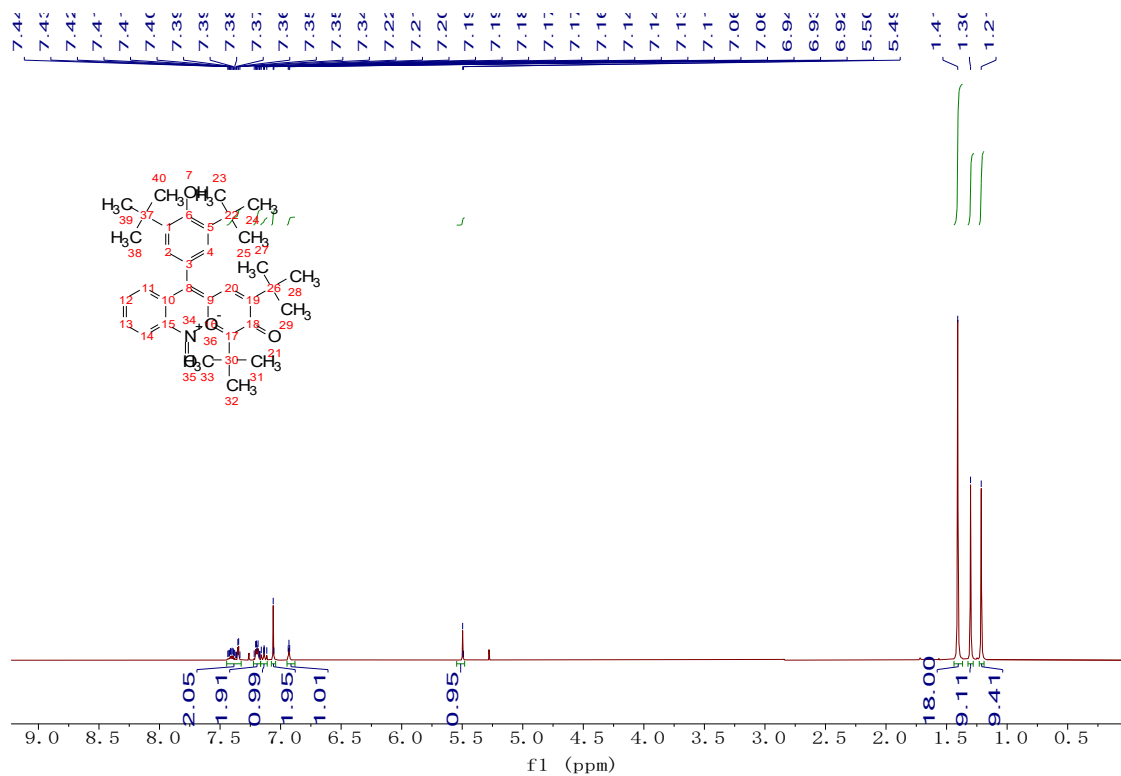
2,6-di-tert-butyl-4-((3,5-di-tert-butyl-4-hydroxyphenyl)(2,6-dichlorophenyl)methylene)cyclohexa-2,5-dien-1-one(2o)



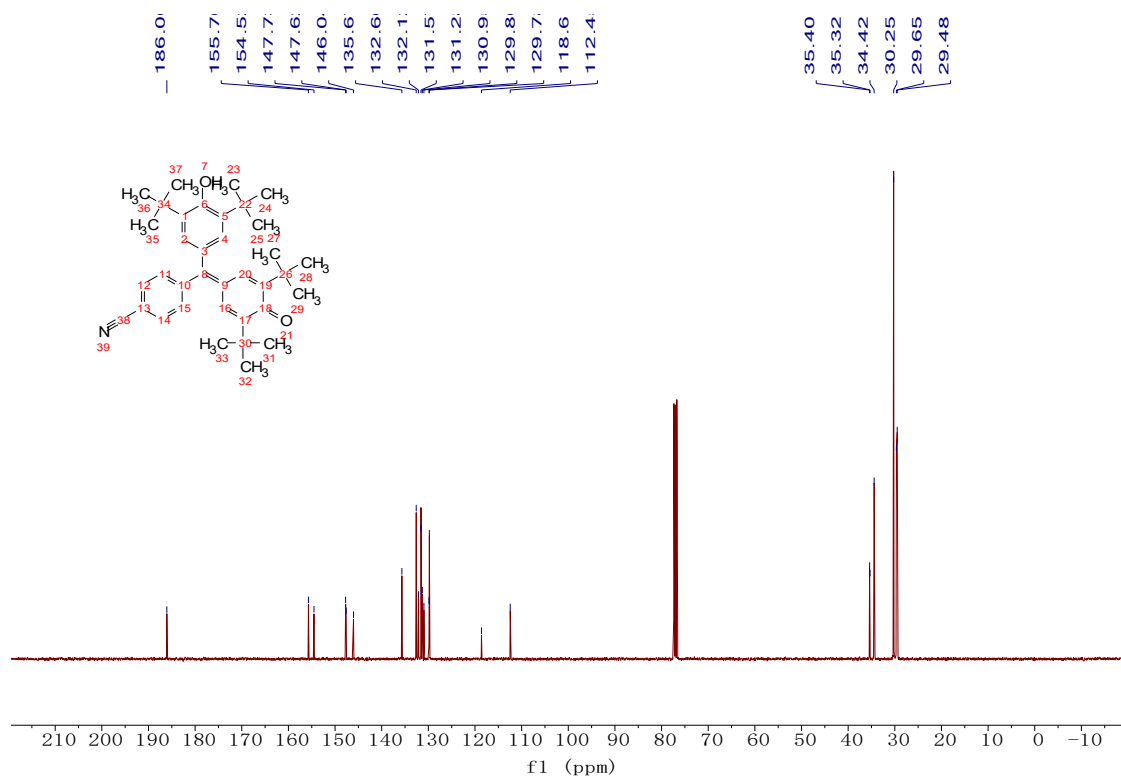
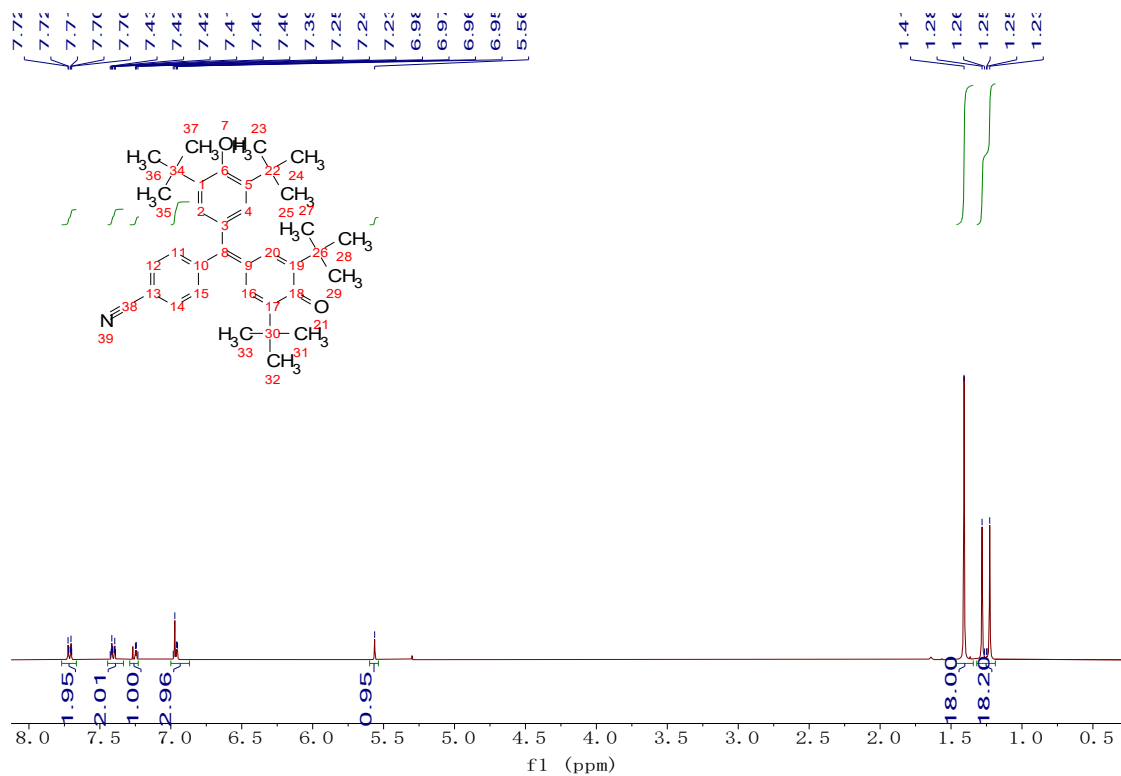
2,6-di-tert-butyl-4-((3,5-di-tert-butyl-4-hydroxyphenyl)(4-nitrophenyl)methylene)cyclohexa-2,5-dien-1-one(2p)



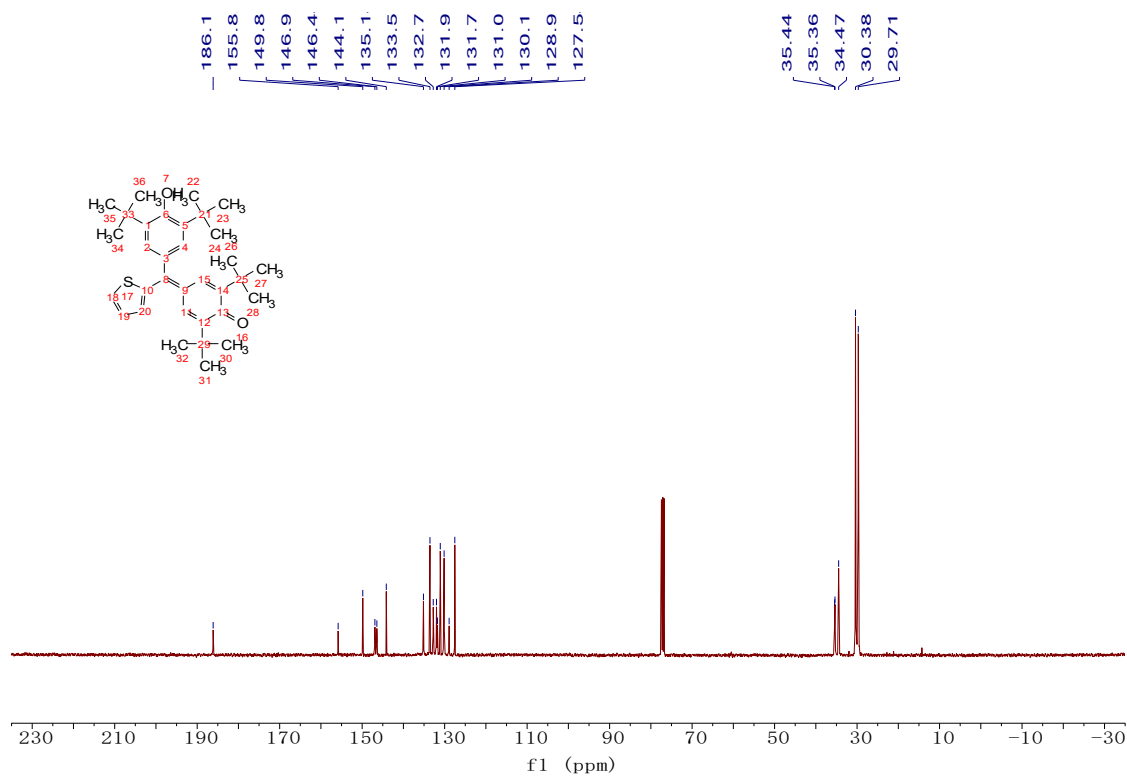
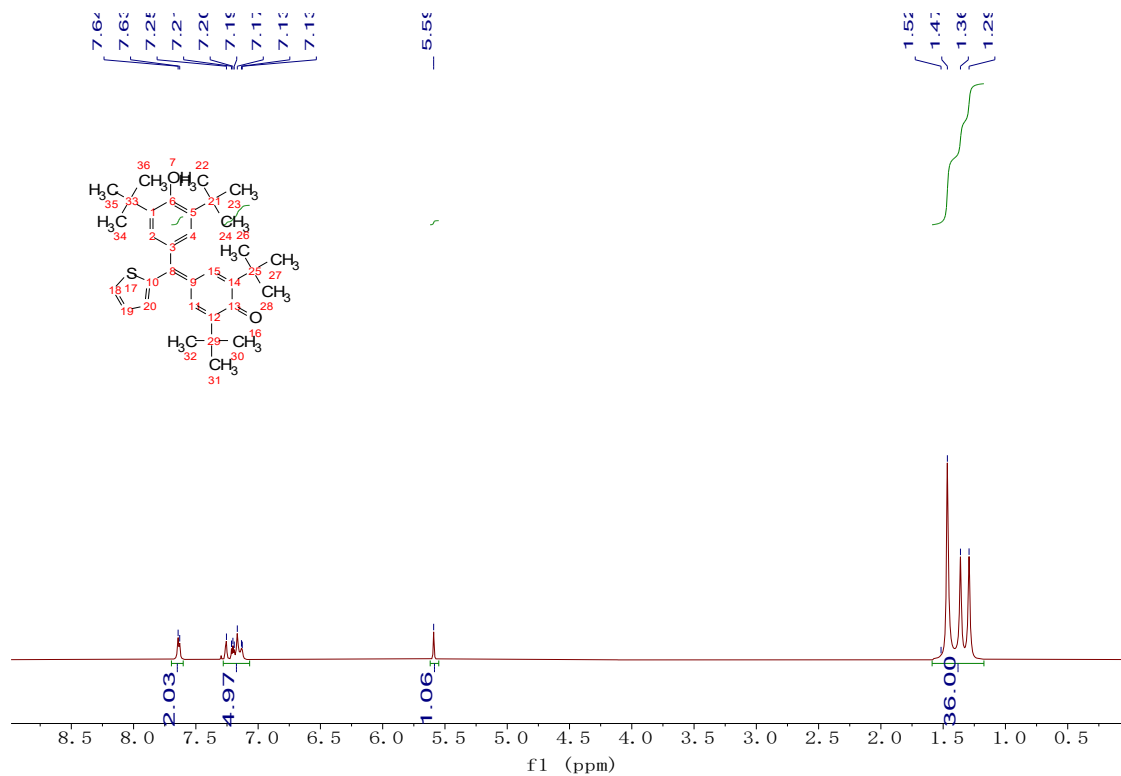
2,6-di-tert-butyl-4-((3,5-di-tert-butyl-4-hydroxyphenyl)(2-nitrophenyl)methylene)cyclohexa-2,5-dien-1-one(2q)



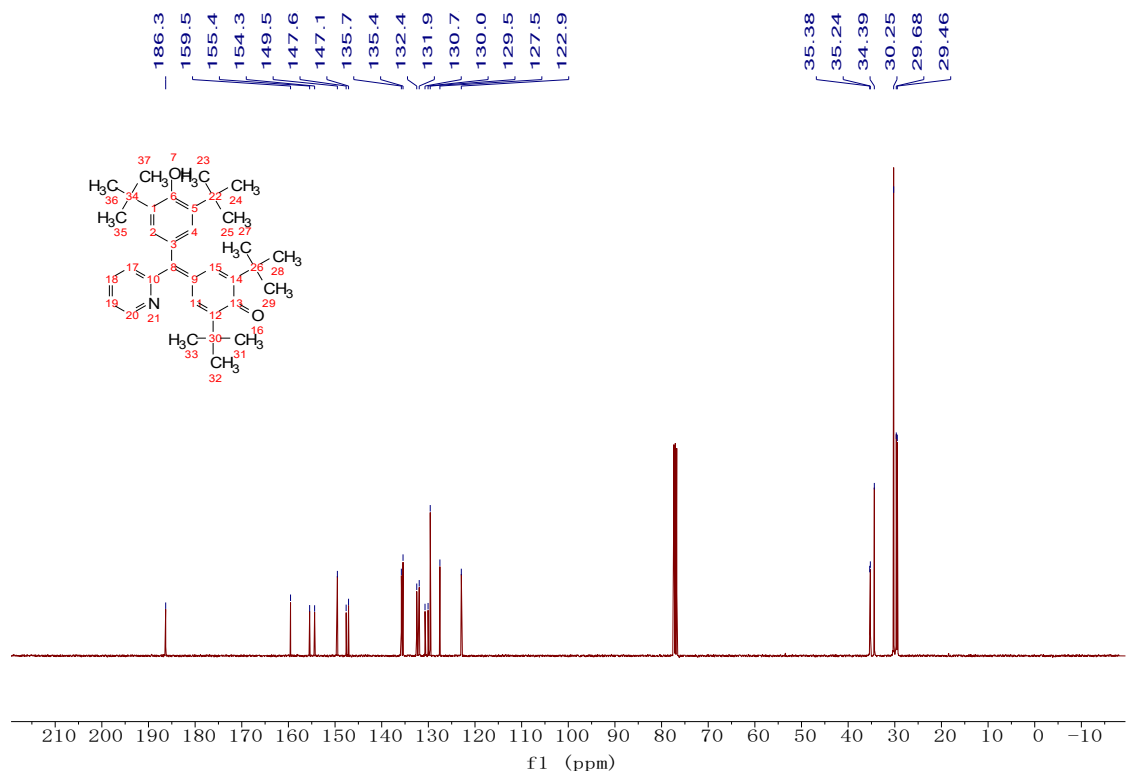
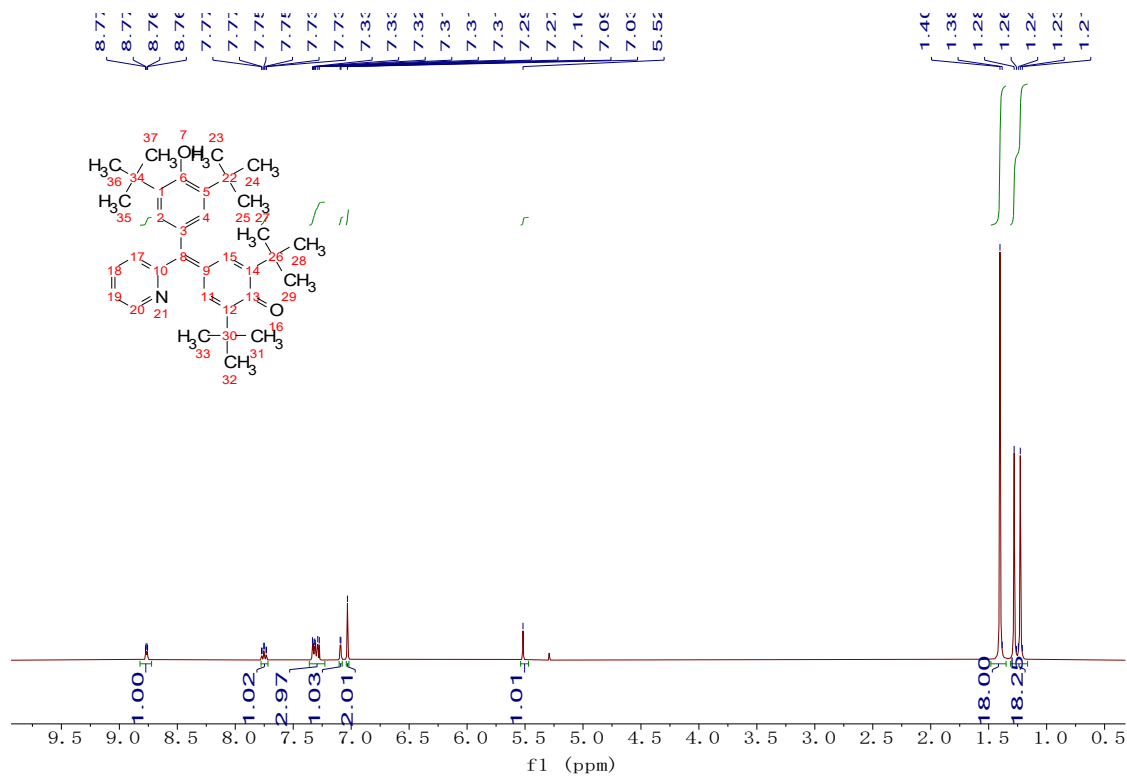
2,6-di-tert-butyl-4-((3,5-di-tert-butyl-4-hydroxyphenyl)(4-isocyanophenyl)methylene)cyclohexa-2,5-dien-1-one(2r)



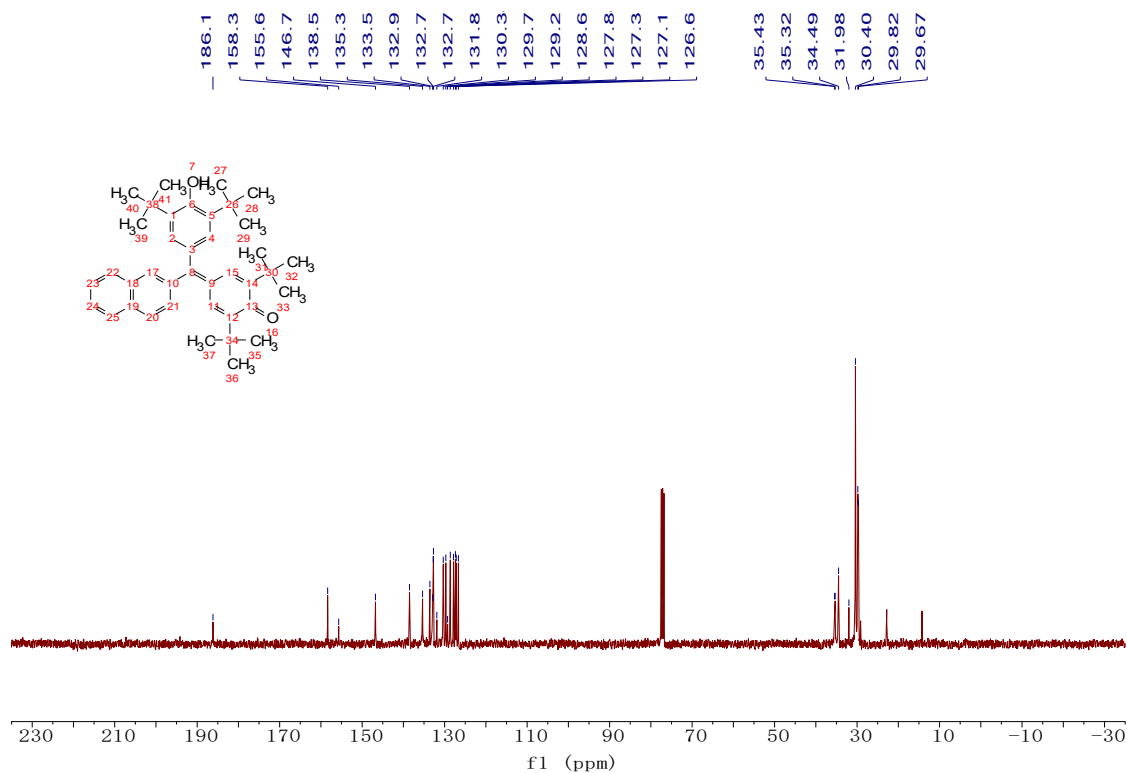
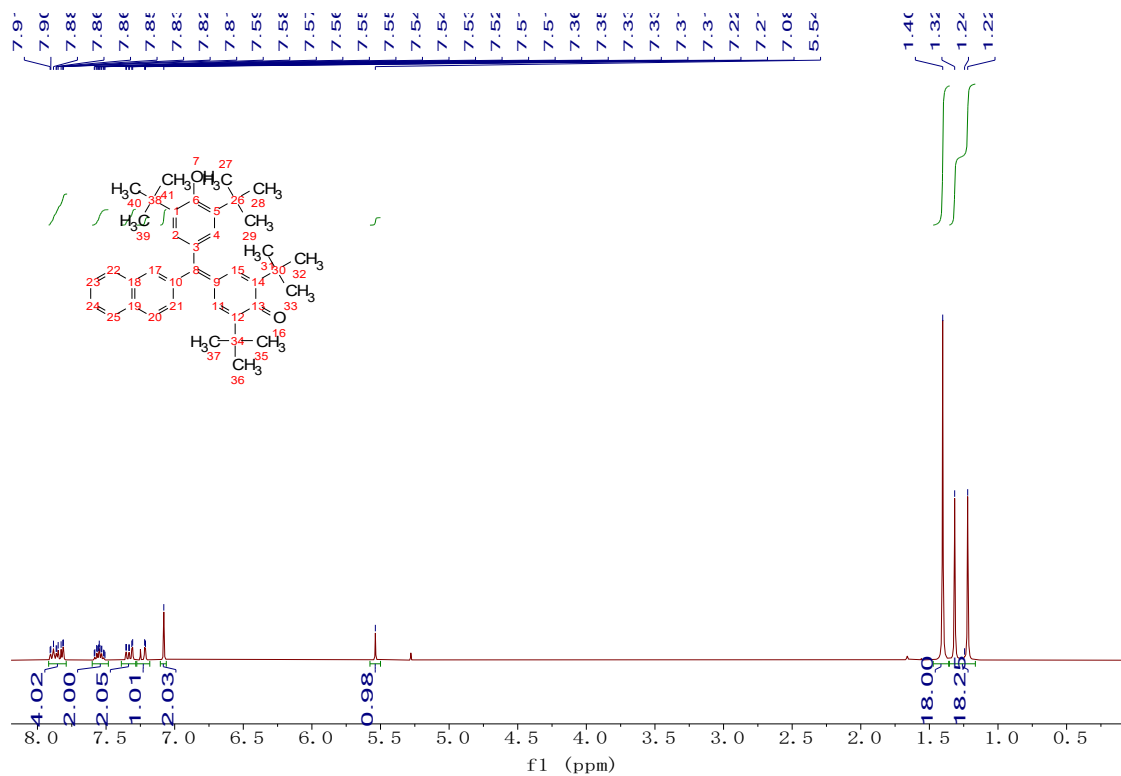
2,6-di-tert-butyl-4-((3,5-di-tert-butyl-4-hydroxyphenyl)(thiophen-2-yl)methylene)cyclohexa-2,5-dien-1-one(2s)



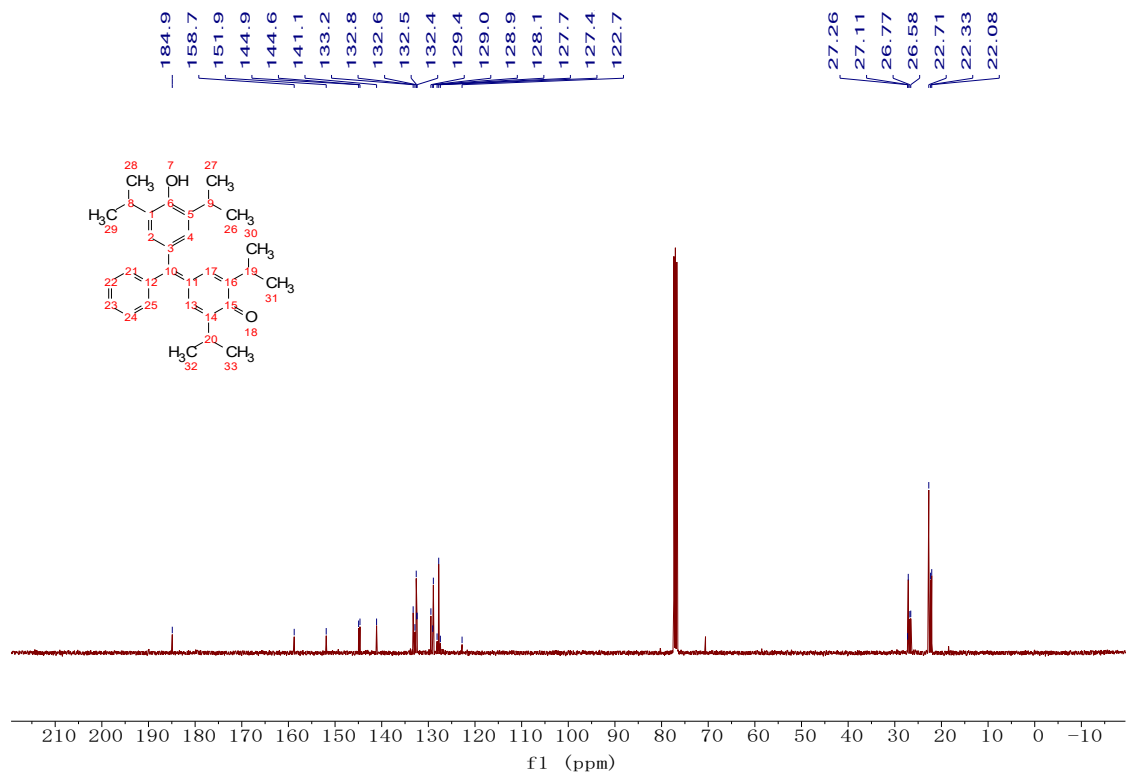
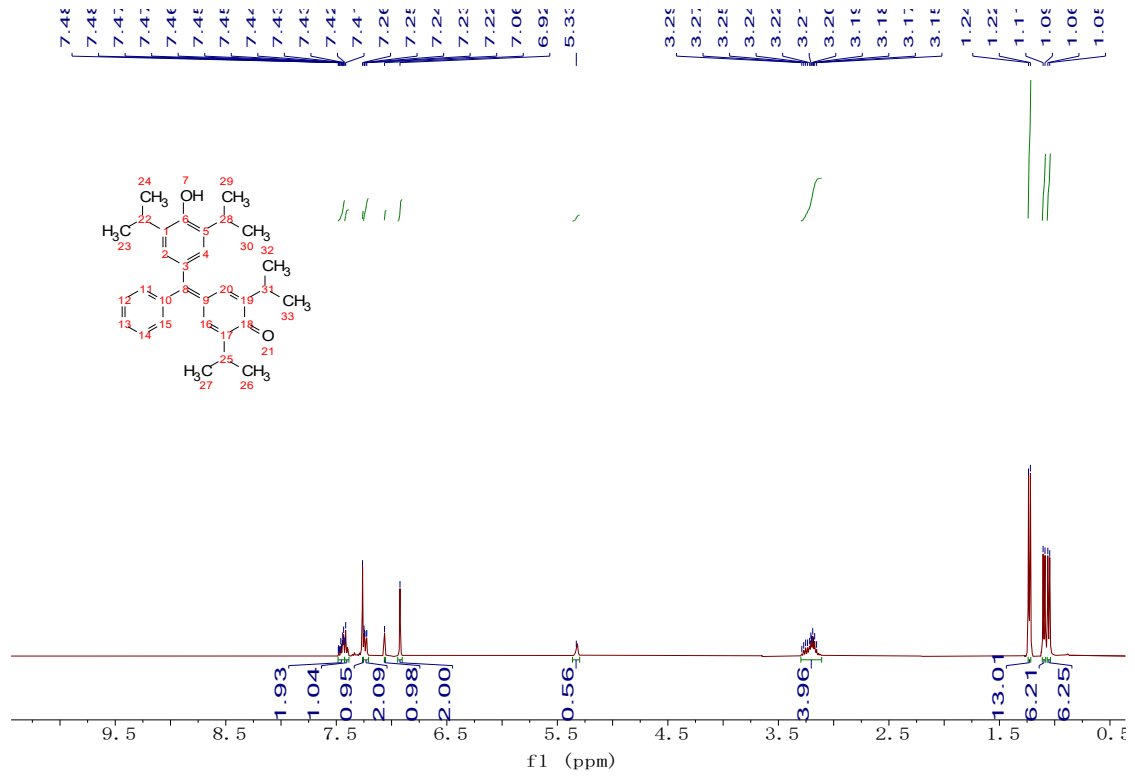
2,6-di-tert-butyl-4-((3,5-di-tert-butyl-4-hydroxyphenyl)(pyridin-2-yl)methylene)cyclohexa-2,5-dien-1-oen(2t)



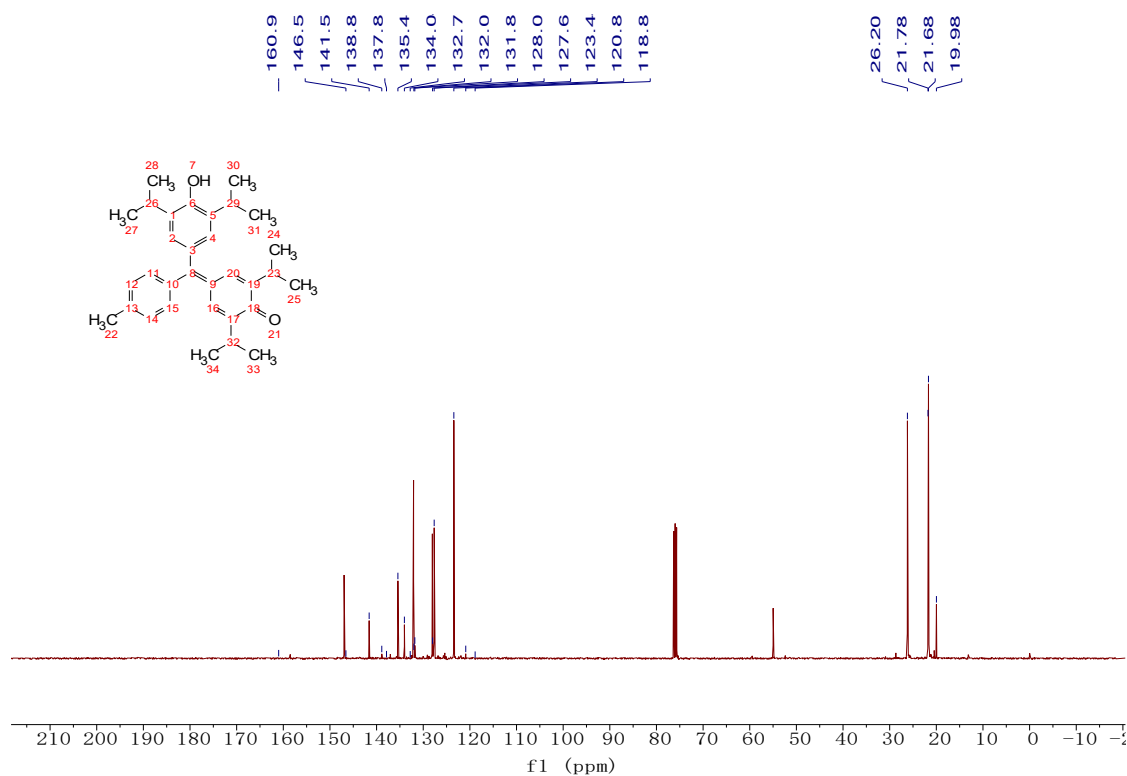
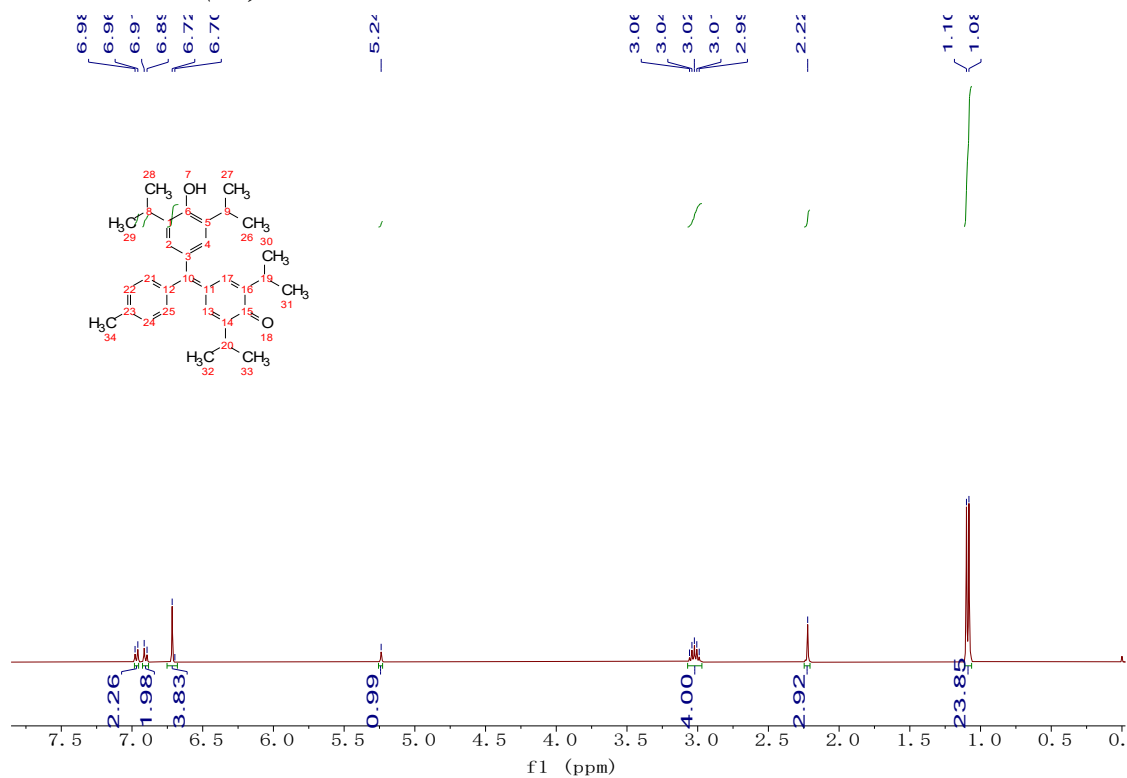
2,6-di-tert-butyl-4-((3,5-di-tert-butyl-4-hydroxyphenyl)(naphthalen-2-yl)methylene)cyclohexa-2,5-dien-1-one(2u)



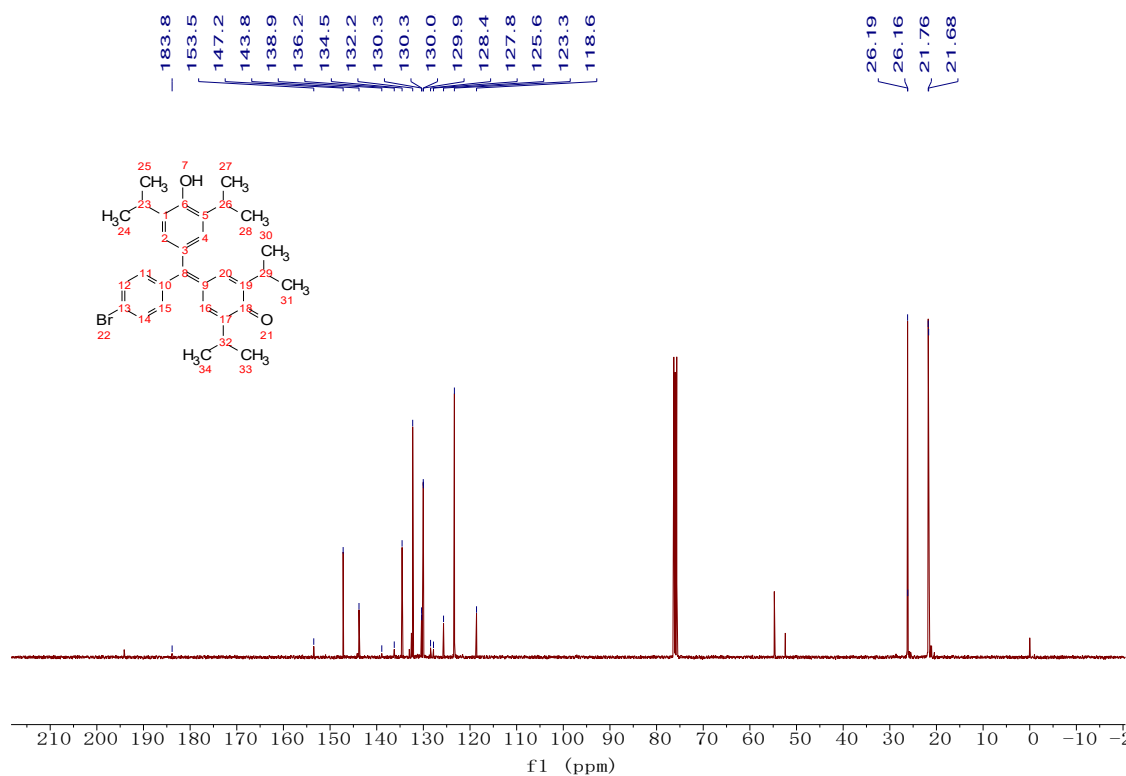
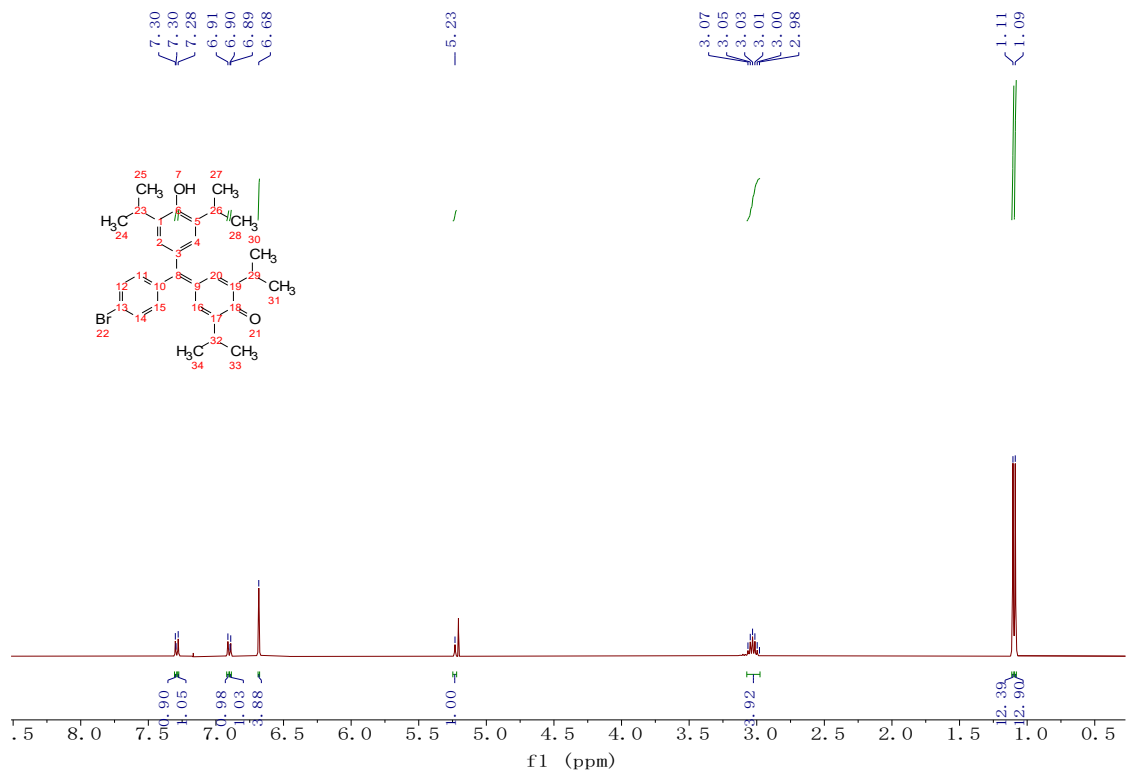
4-((4-hydroxy-3,5-diisopropylphenyl)methylene)-2,6-diisopropylcyclohexa-2,5-dien-1-one(2v)



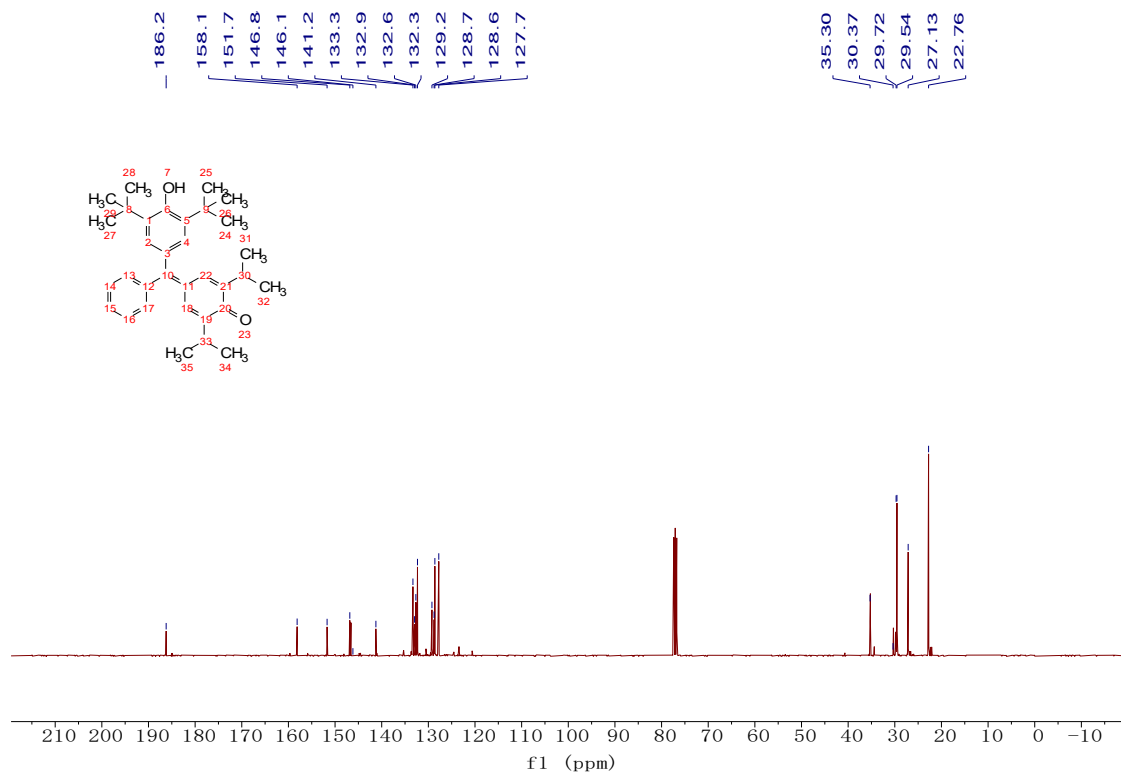
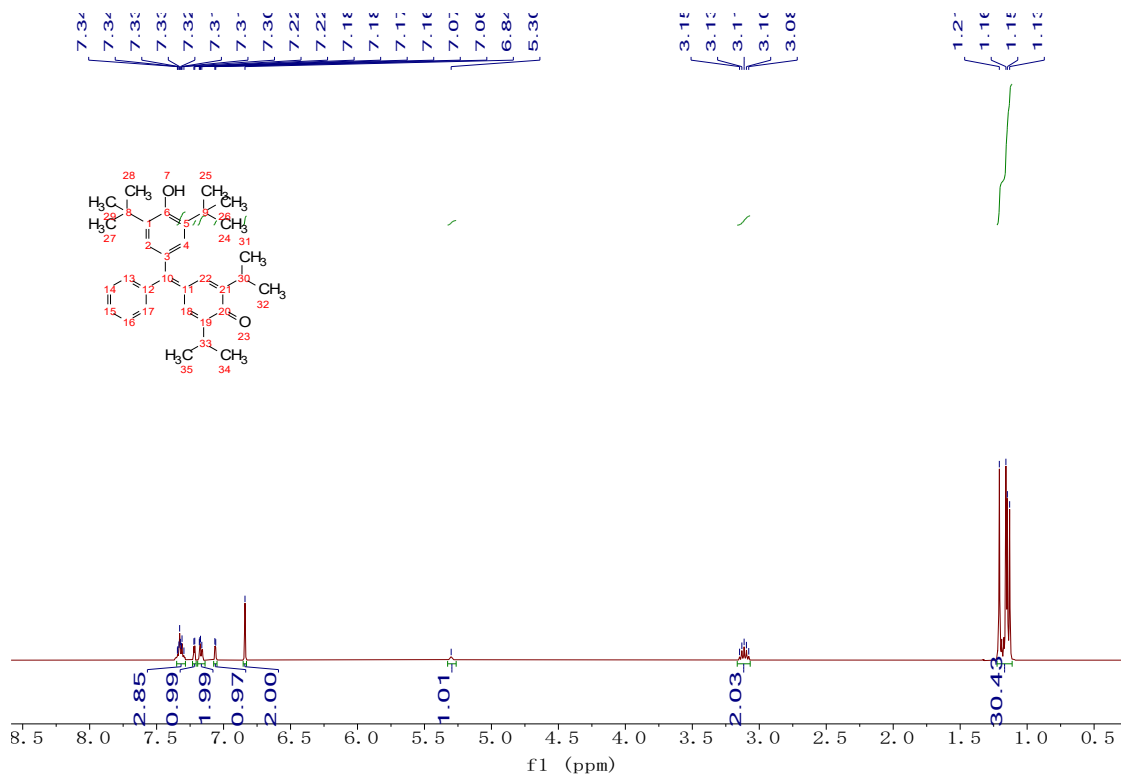
4-((4-hydroxy-3,5-diisopropylphenyl)(p-tolyl)methylene)-2,6-diisopropylcyclohexa-2,5-dien-1-one(2w)



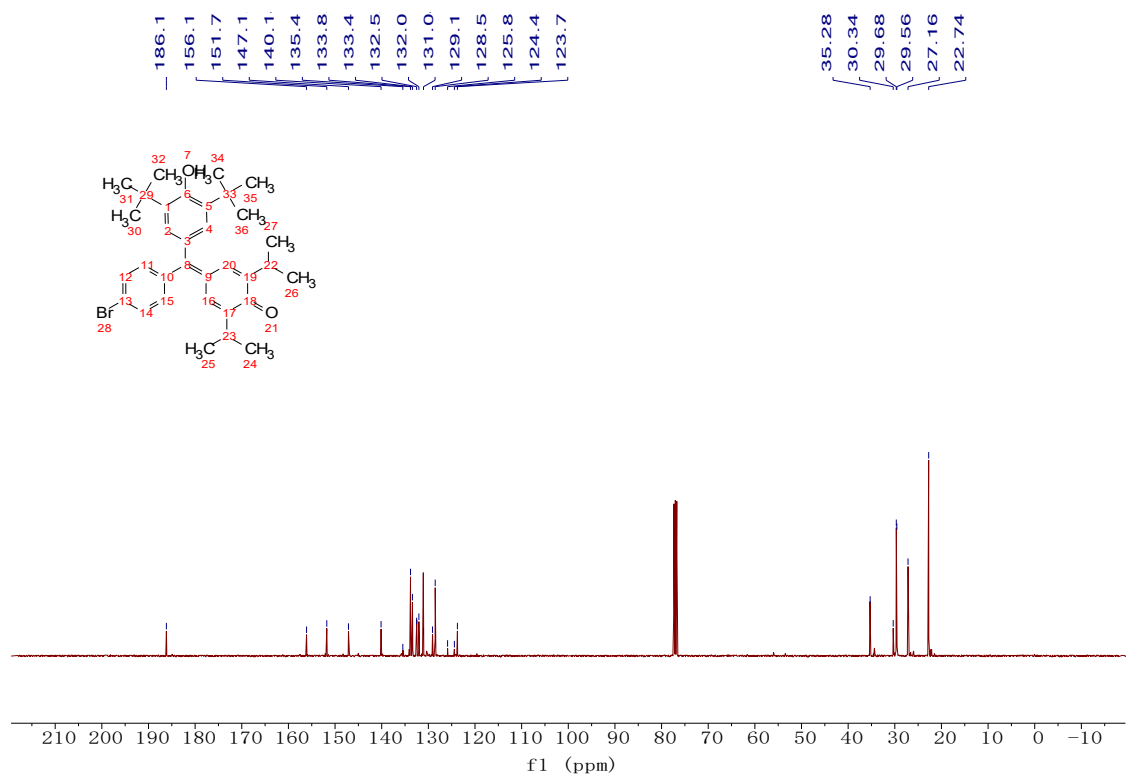
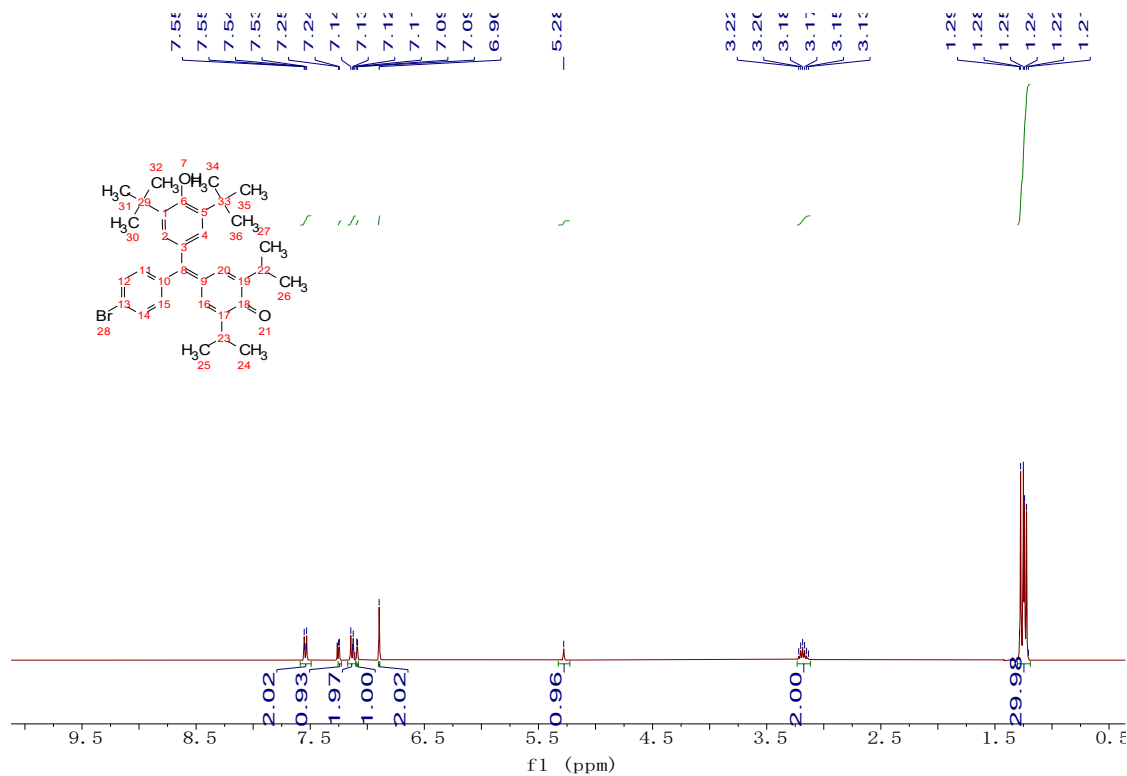
4-((4-bromophenyl)(4-hydroxy-3,5-diisopropylphenyl)methylene)-2,6-diisopropylcyclohexa-2,5-dien-1-one(2x)



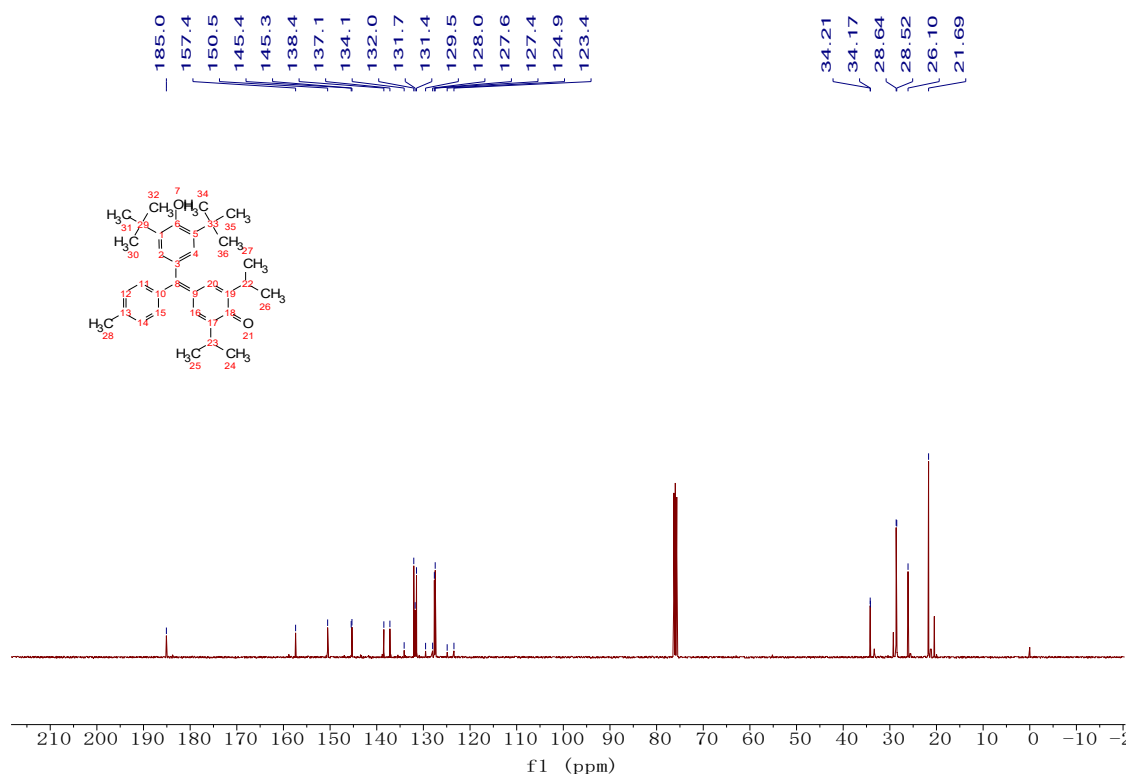
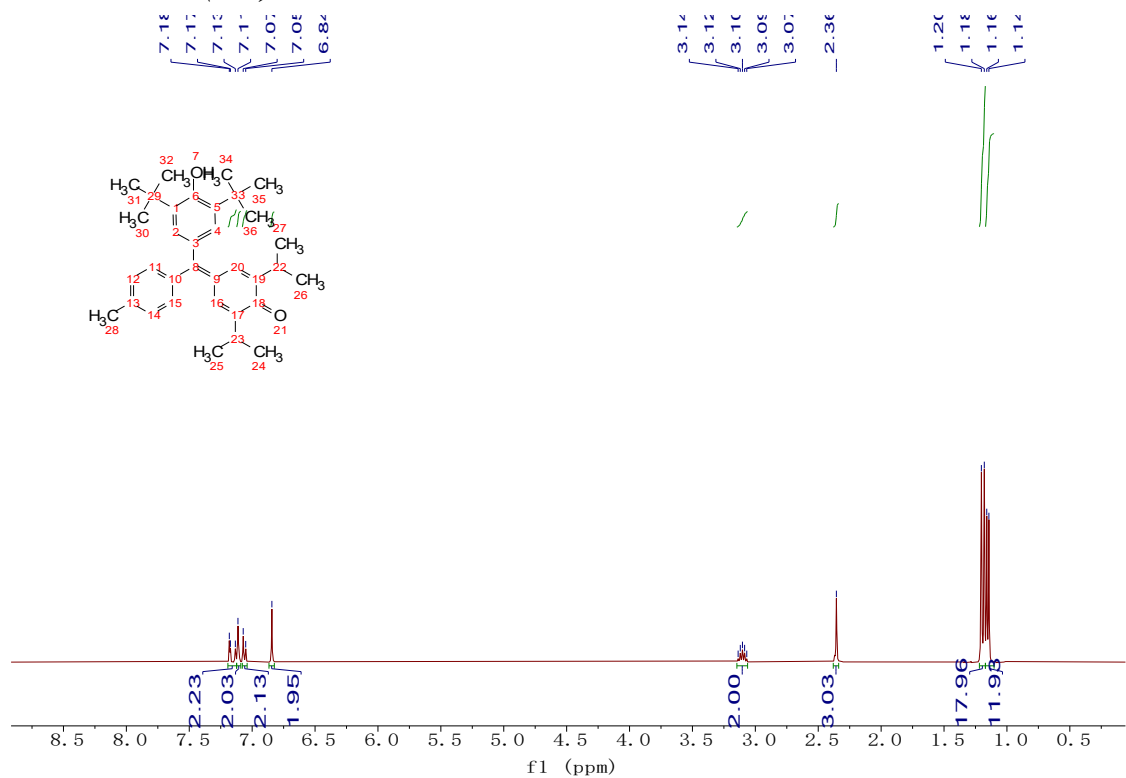
4-((3,5-di-tert-butyl-4-hydroxyphenyl)(phenyl)methylene)-2,6-diisopropylcyclohexa-2,5-dien-1-one(2y)



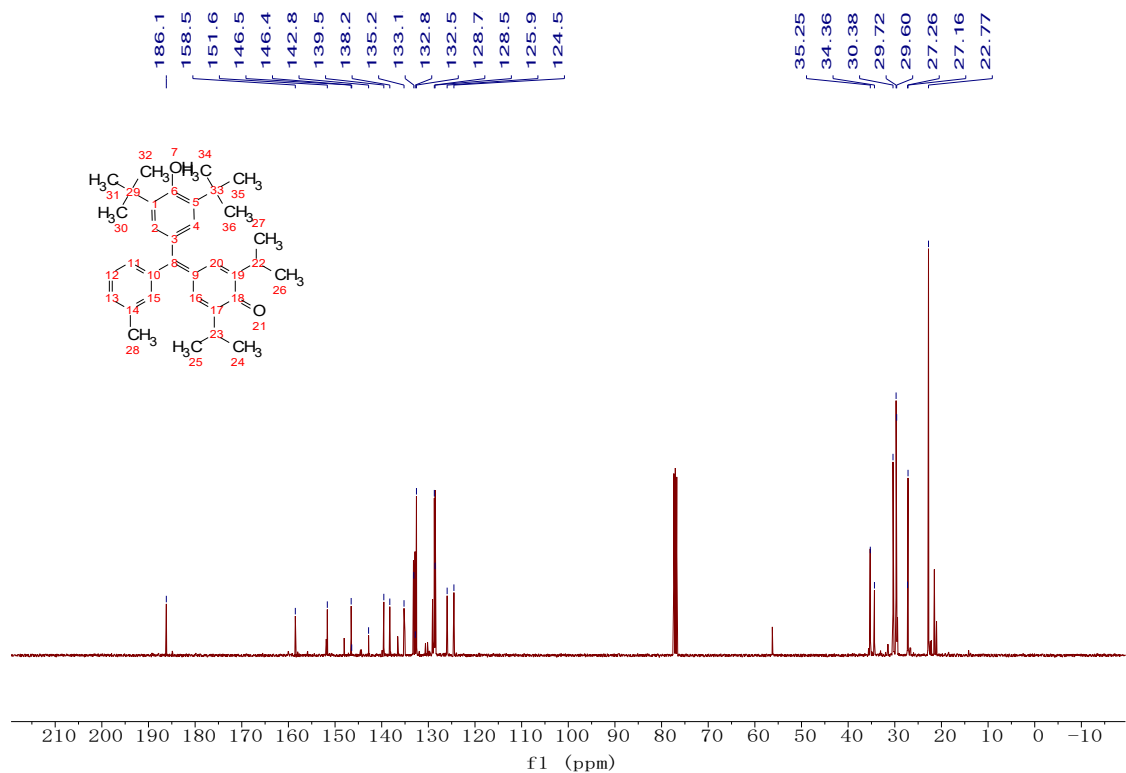
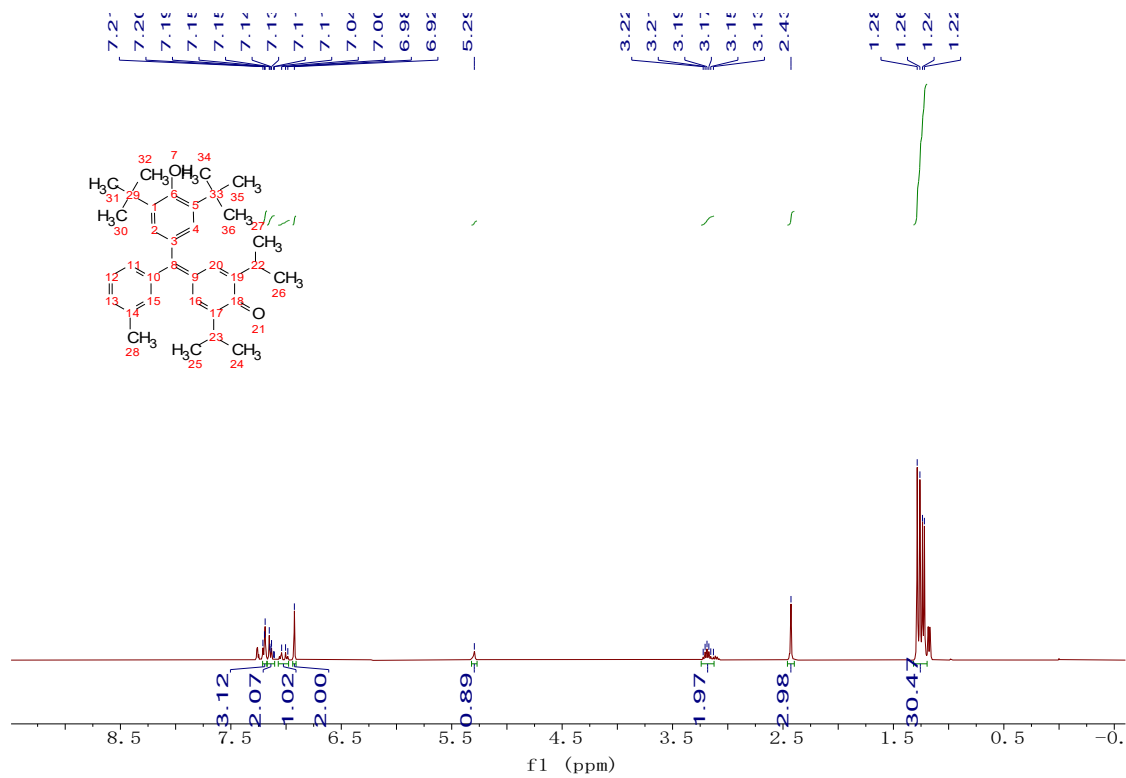
4-((4-bromophenyl)(3,5-di-tert-butyl-4-hydroxyphenyl)methylene)-2,6-diisopropylcyclohexa-2,5-dien-1-one(2z)



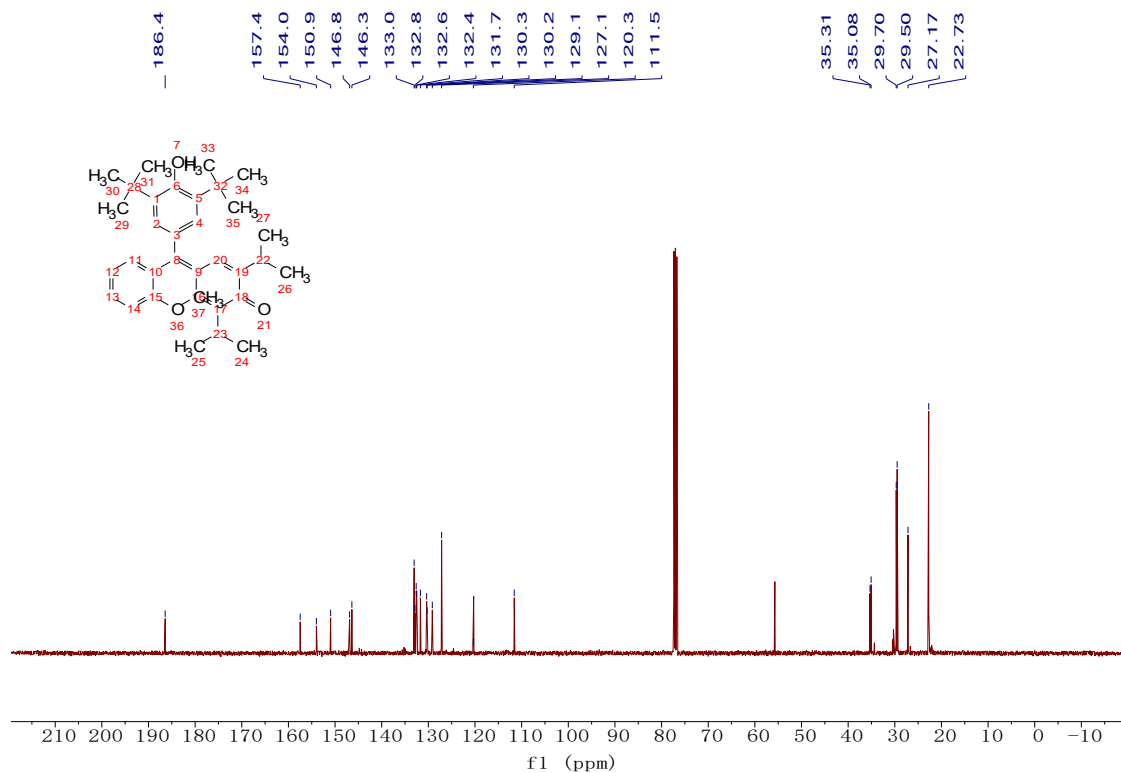
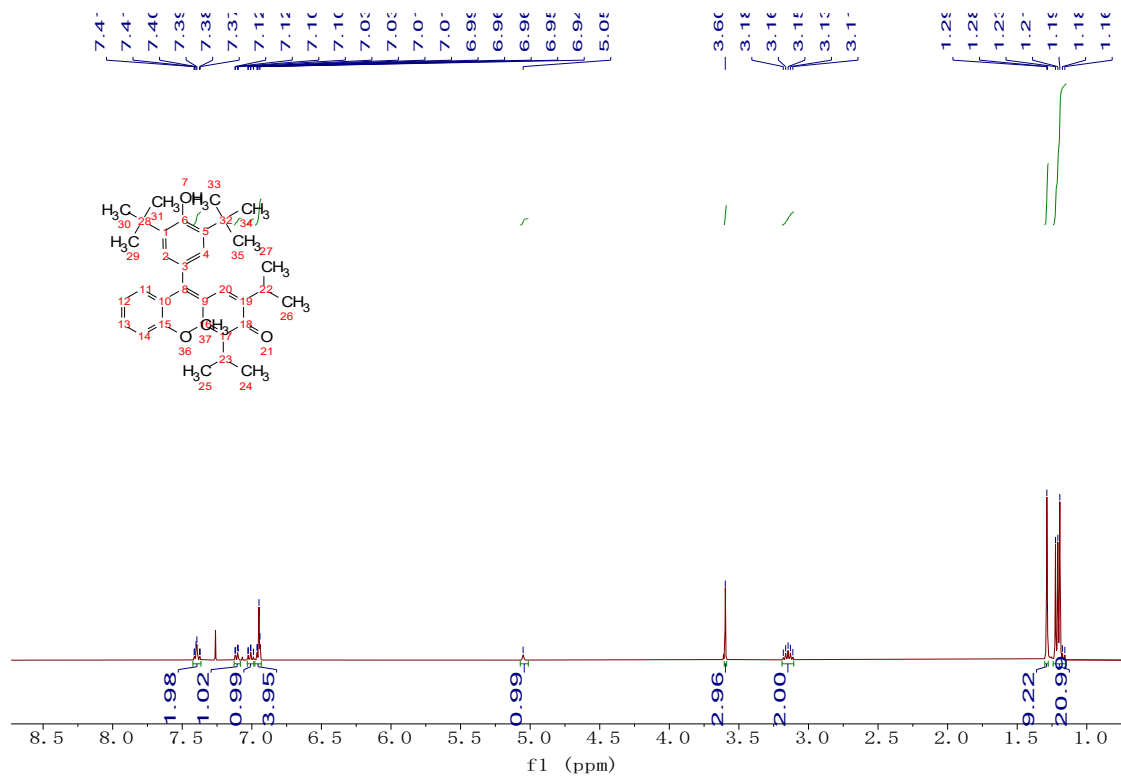
4-((3,5-di-tert-butyl-4-hydroxyphenyl)(p-tolyl)methylene)-2,6-diisopropylcyclohexa-2,5-dien-1-one(2aa)



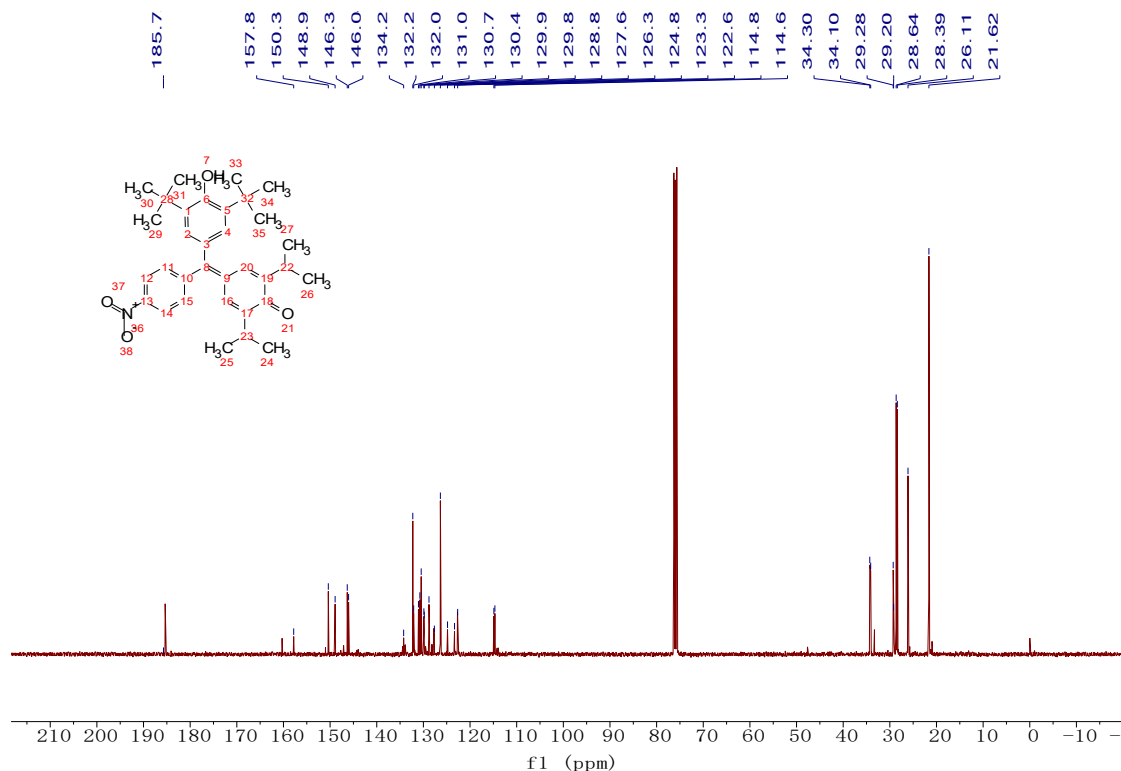
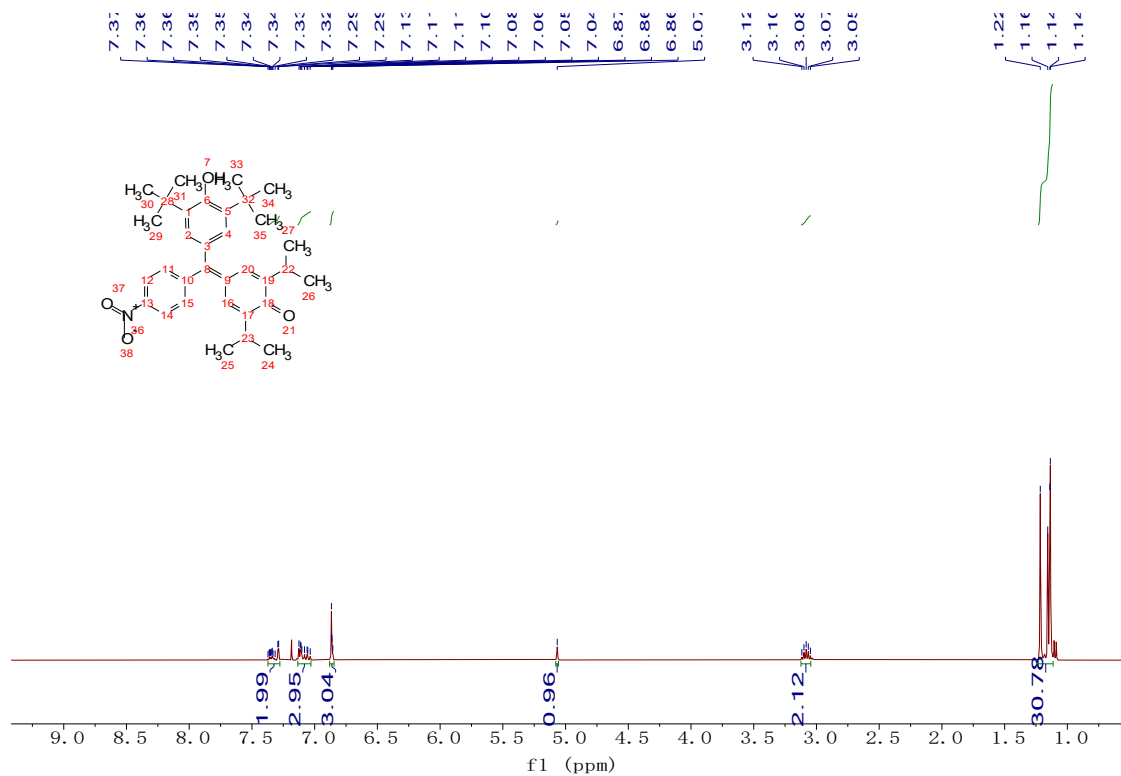
4-((3,5-di-tert-butyl-4-hydroxyphenyl)(m-tolyl)methylene)-2,6-diisopropylcyclohexa-2,5-dien-1-one(2ab)



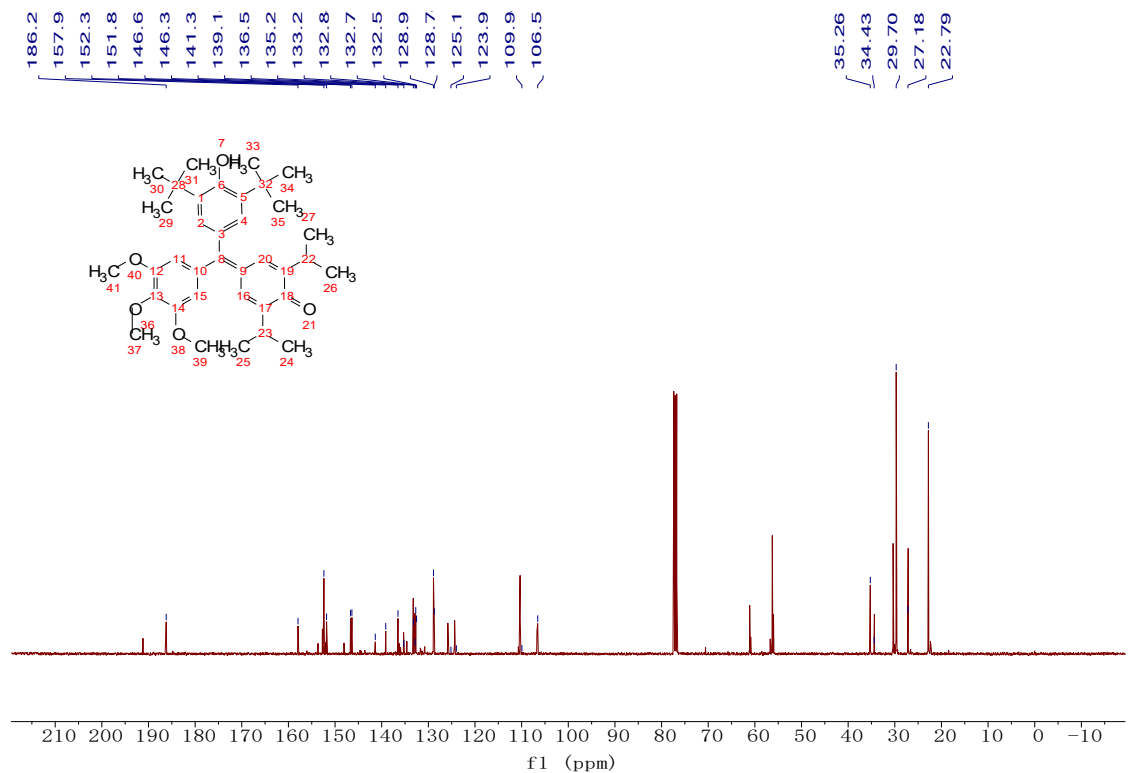
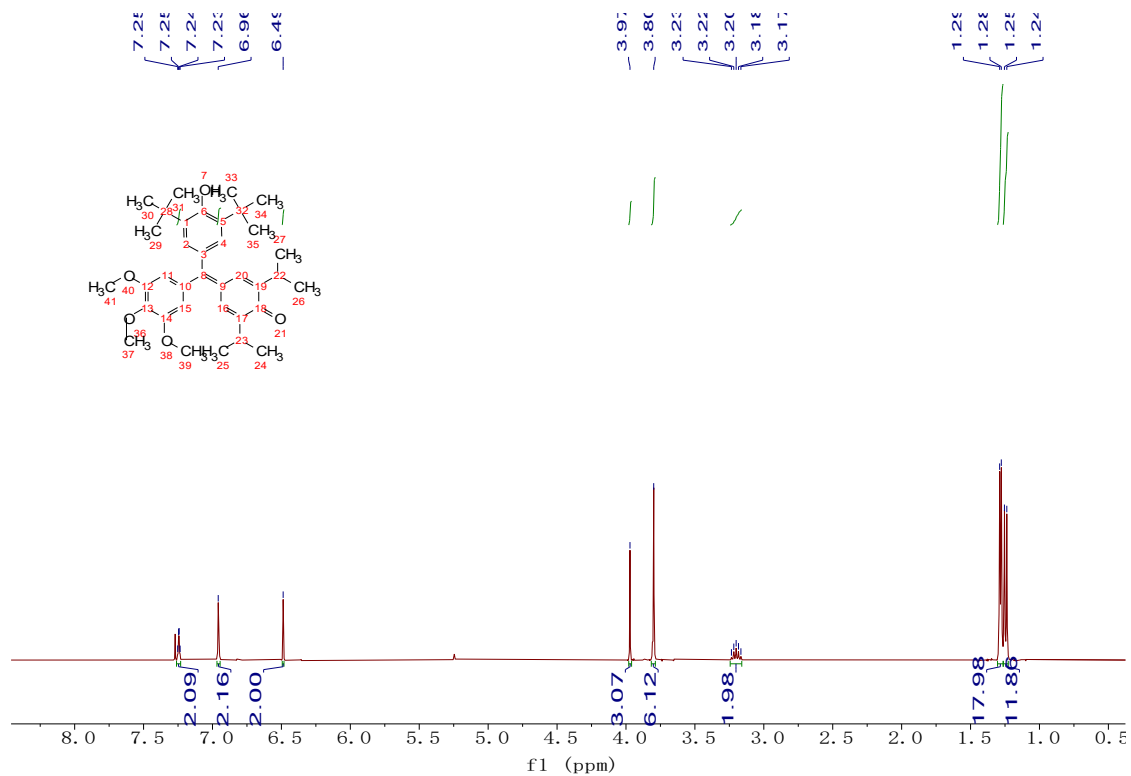
4-((3,5-di-tert-butyl-4-hydroxyphenyl)(3-methoxyphenyl)methylene)-2,6-diisopropylcyclohexa-2,5-dien-1-one(2ac)



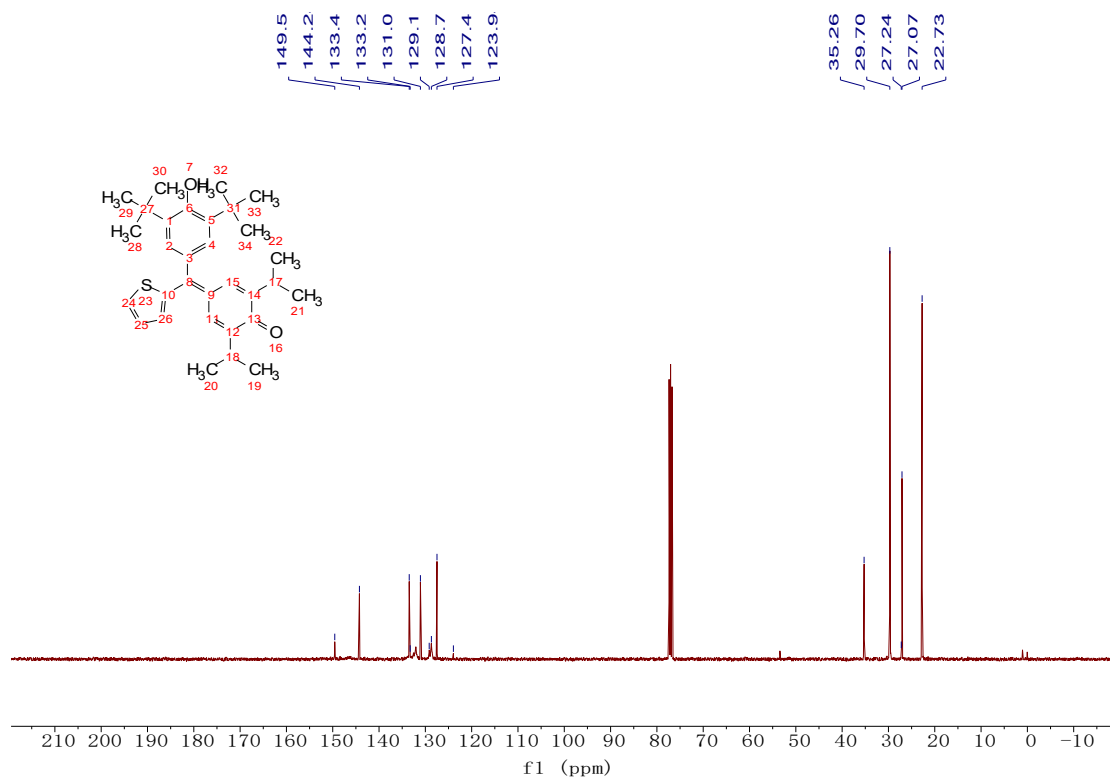
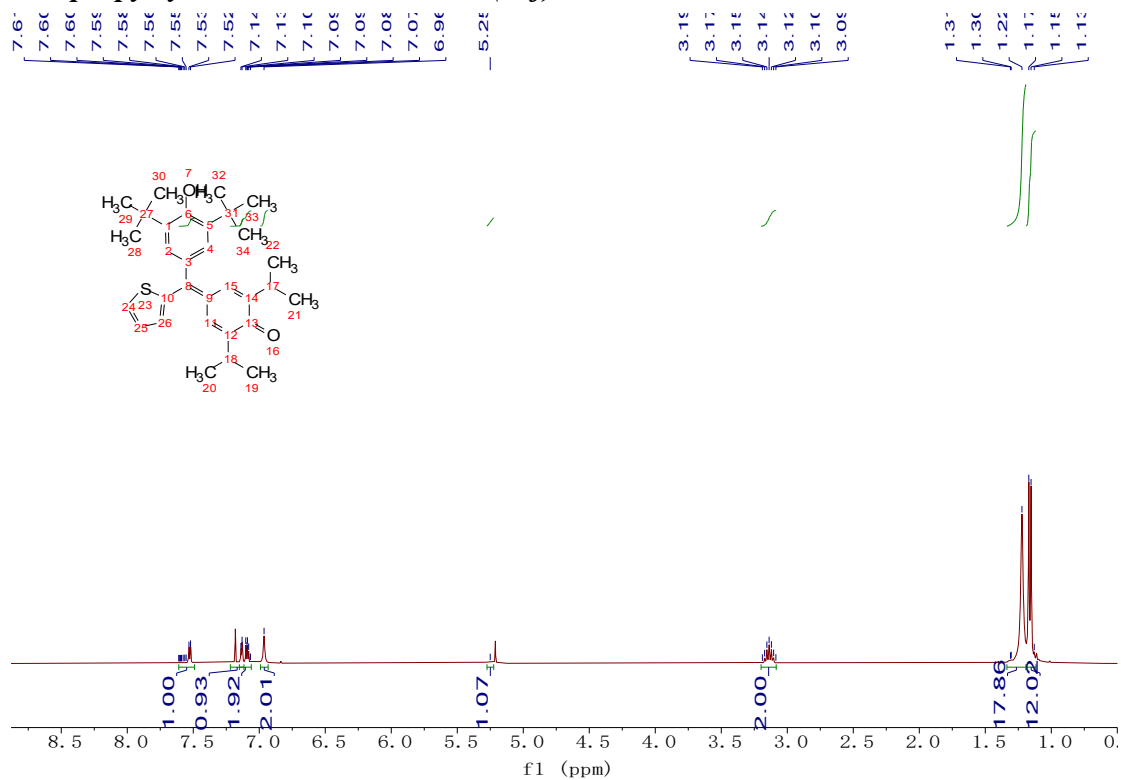
4-((3,5-di-tert-butyl-4-hydroxyphenyl)(4-nitrophenyl)methylene)-2,6-diisopropylcyclohexa-2,5-dien-1-one(2ad)



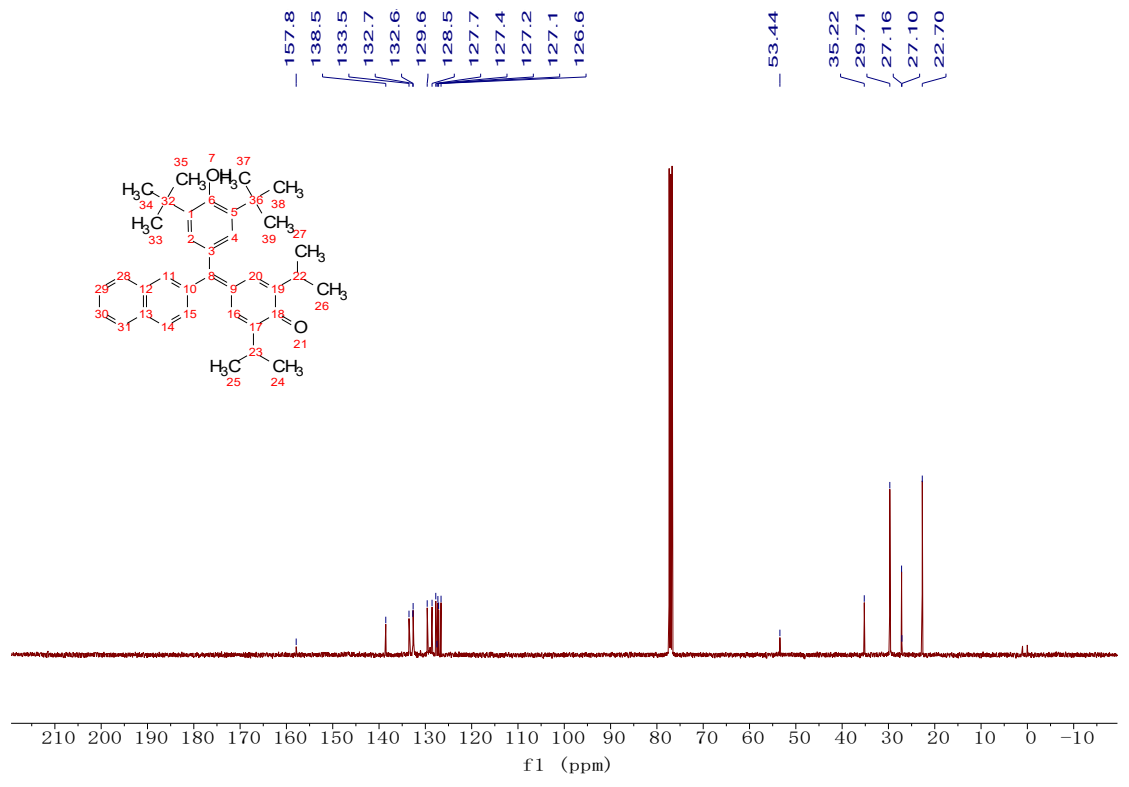
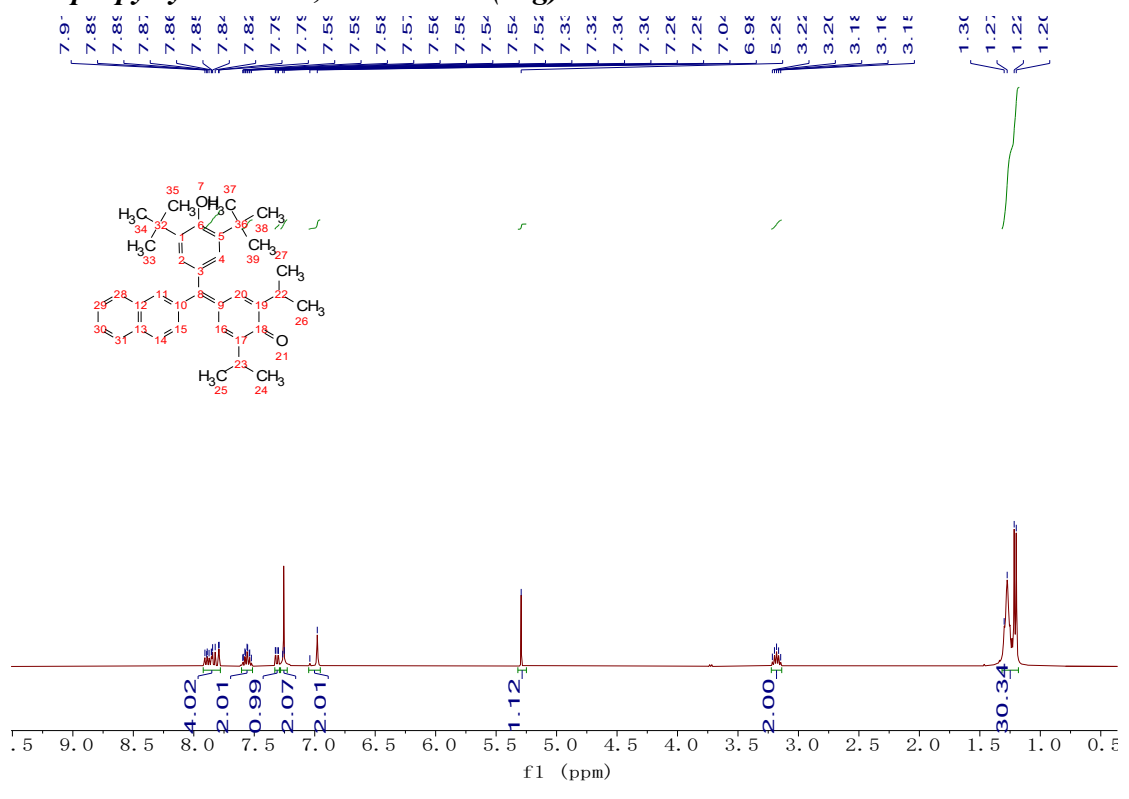
4-((3,5-di-tert-butyl-4-hydroxyphenyl)(3,4,5-trimethoxyphenyl)methylene)-2,6-diisopropylcyclohexa-2,5-dien-1-one(2ae)



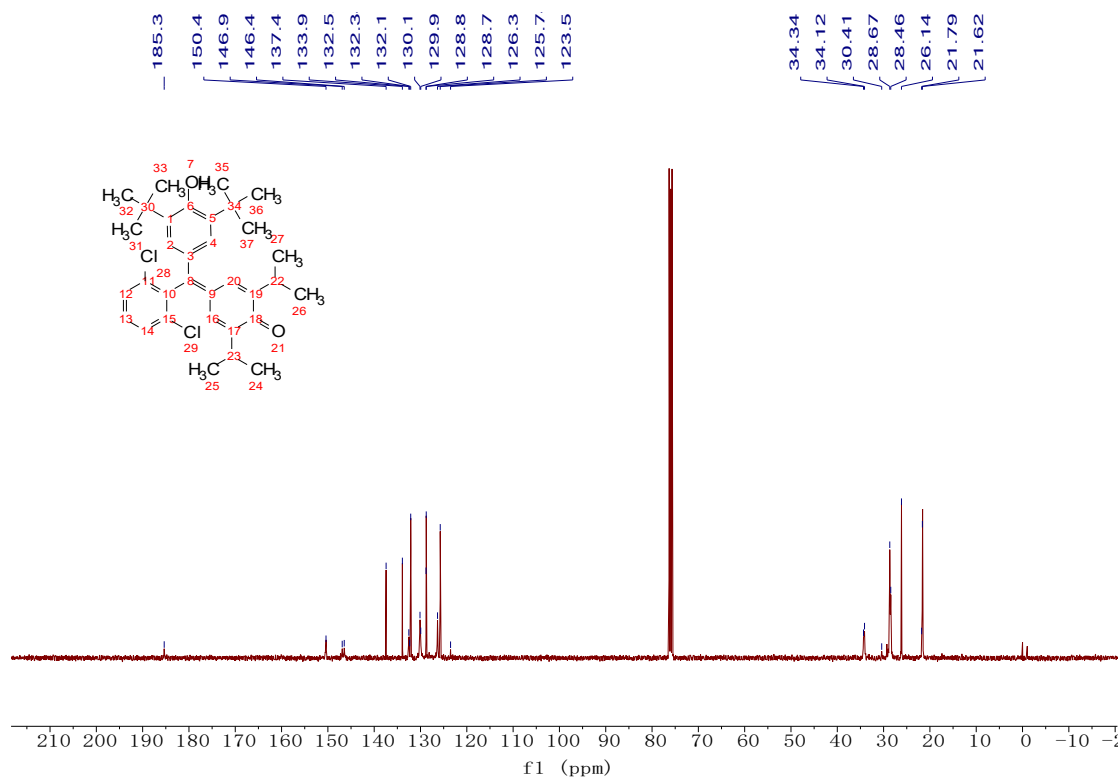
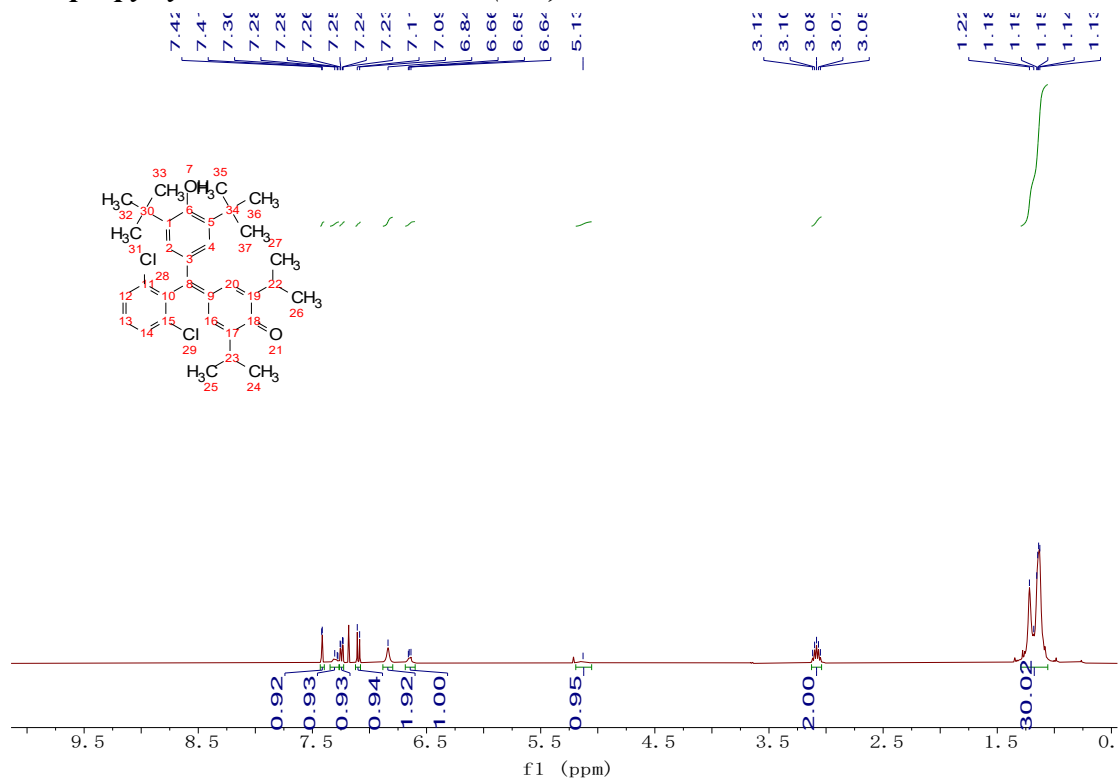
4-((3,5-di-tert-butyl-4-hydroxyphenyl)(thiophen-2-yl)methylene)-2,6-diisopropylcyclohexa-2,5-dien-1-one(2af)



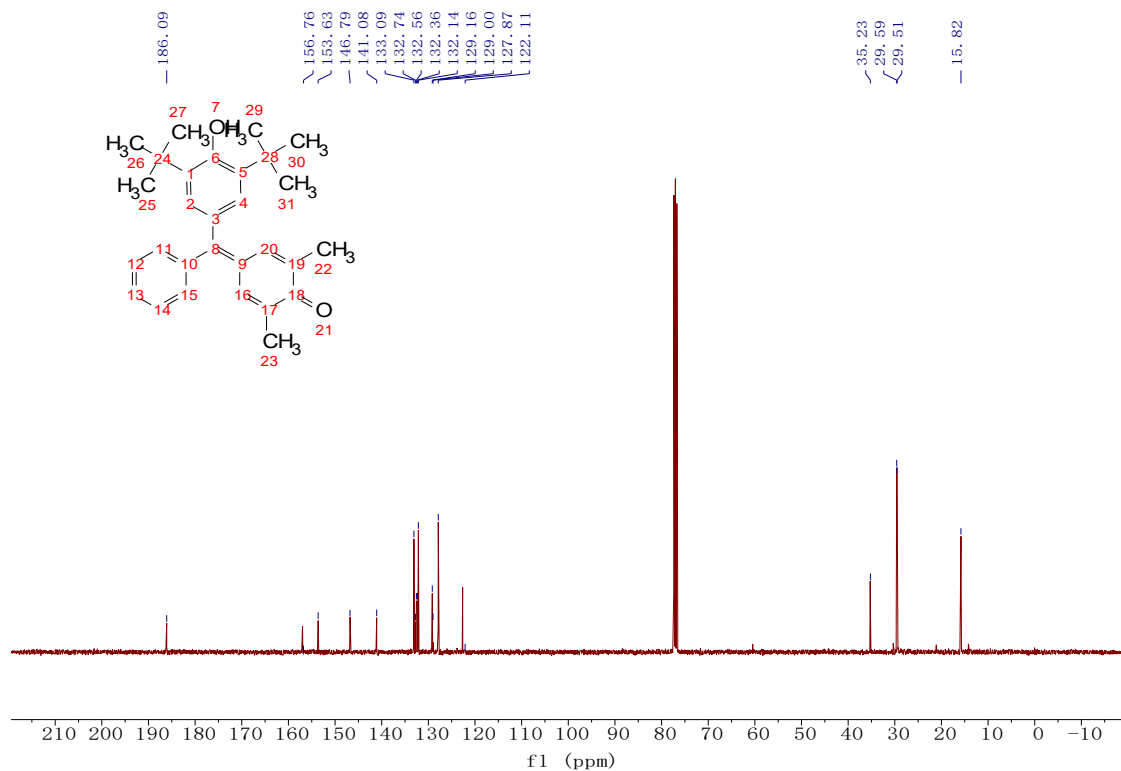
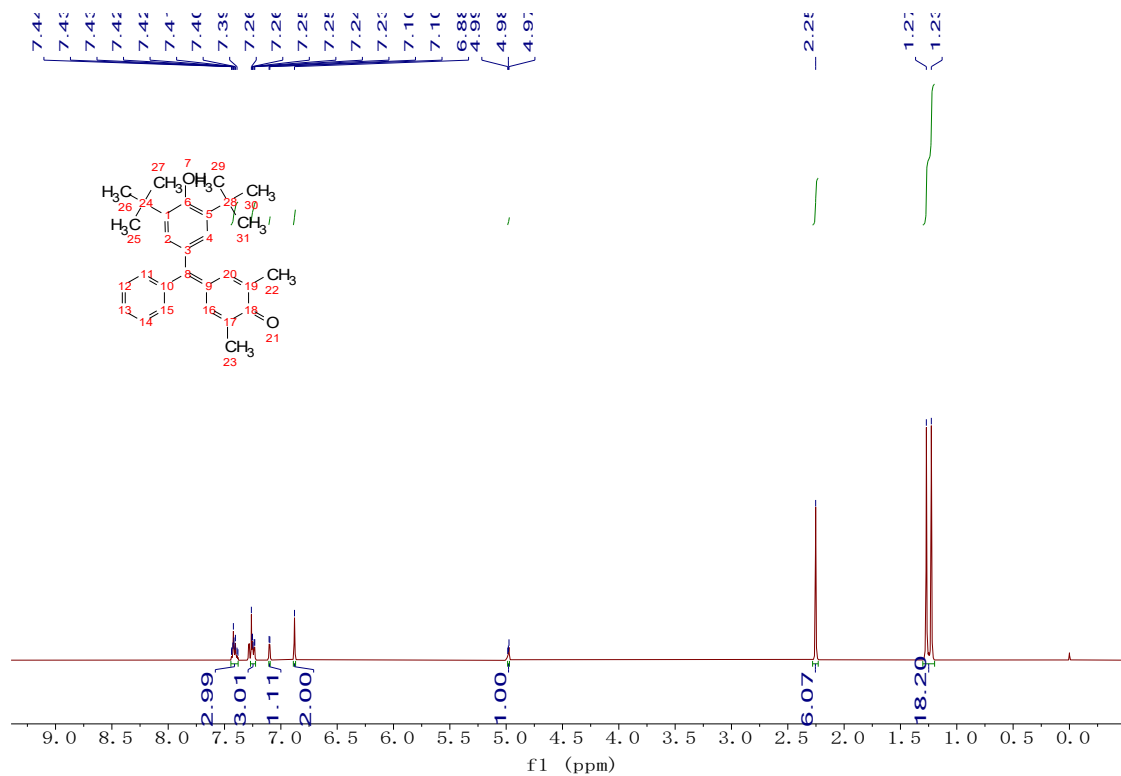
4-((3,5-di-tert-butyl-4-hydroxyphenyl)(naphthalen-2-yl)methylene)-2,6-diisopropylcyclohexa-2,5-dien-1-one(2ag)



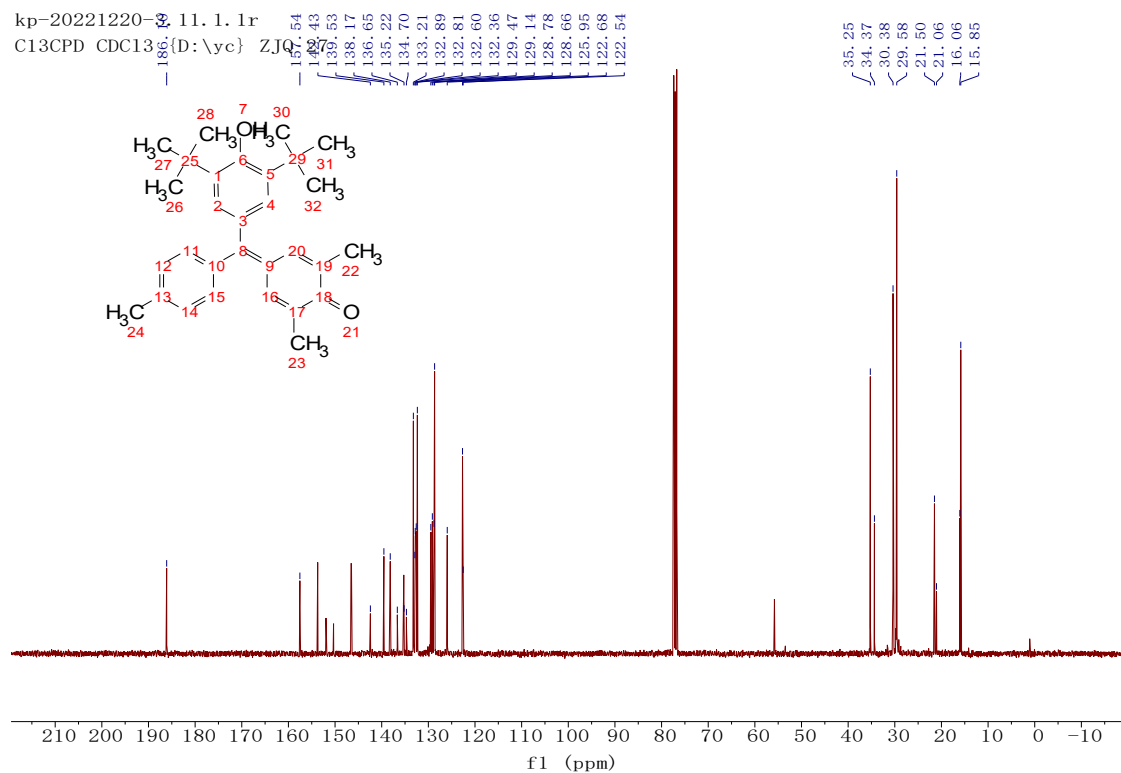
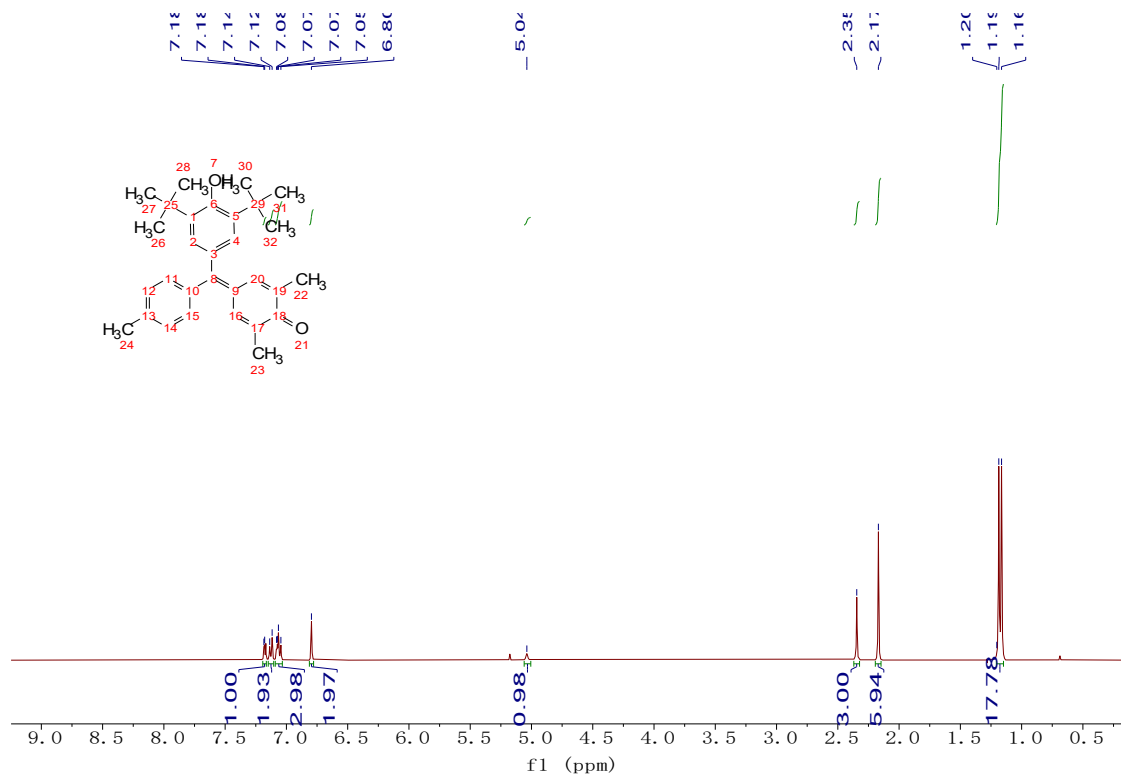
4-((3,5-di-tert-butyl-4-hydroxyphenyl)(2,6-dichlorophenyl)methylene)-2,6-diisopropylcyclohexa-2,5-dien-1-one(2ah)



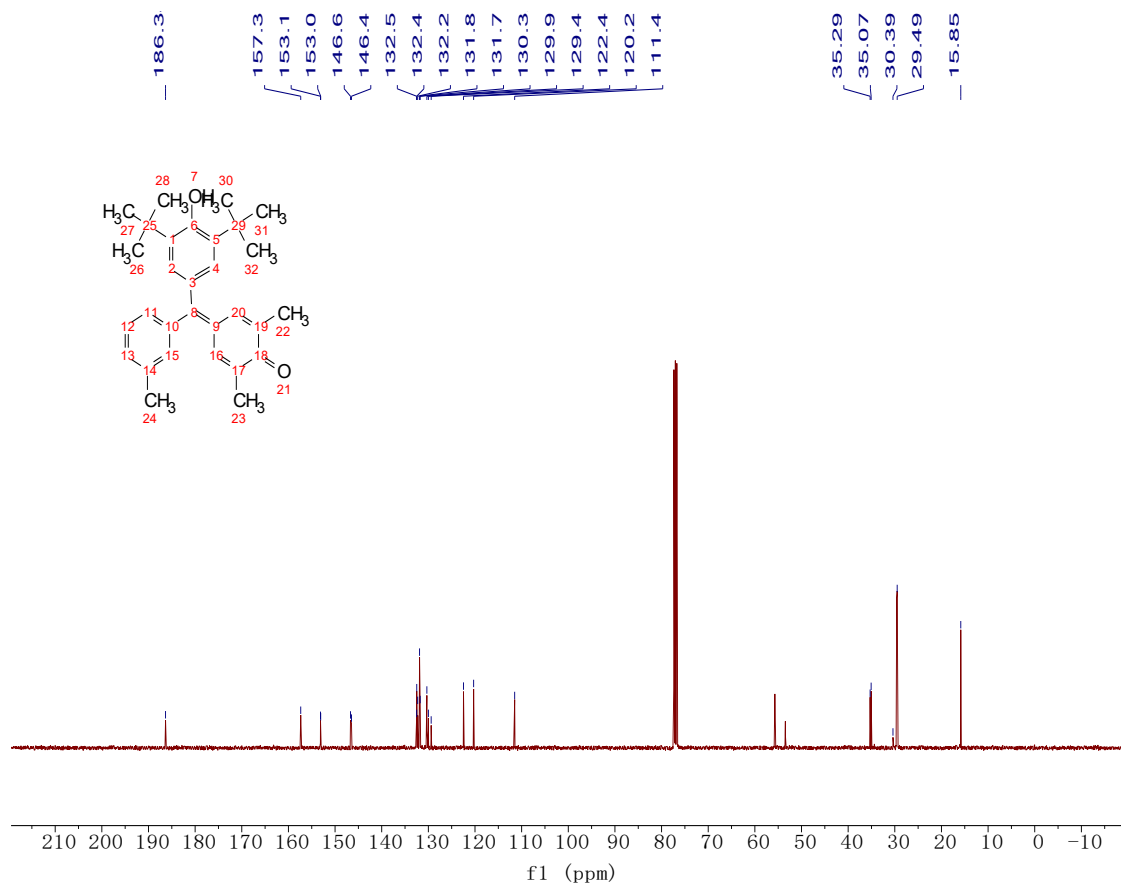
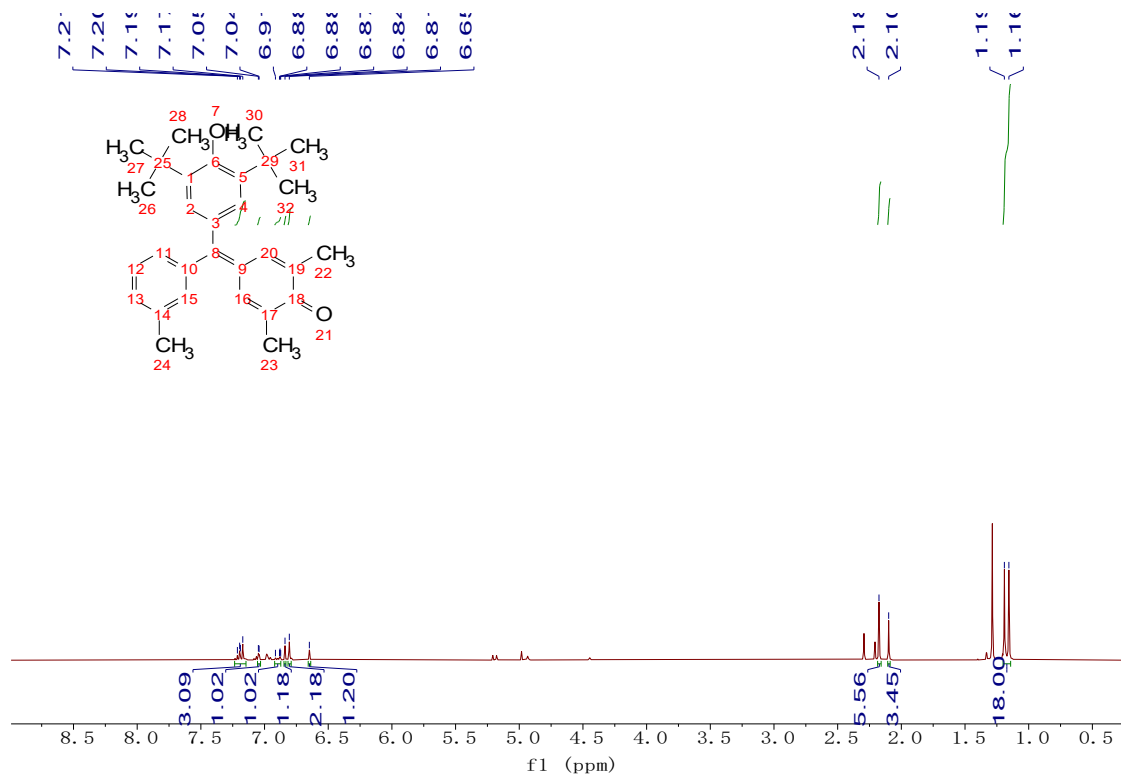
4-((3,5-di-tert-butyl-4-hydroxyphenyl)(phenyl)methylene)-2,6-dimethylcyclohexa-2,5-dien-1-one(2ai)



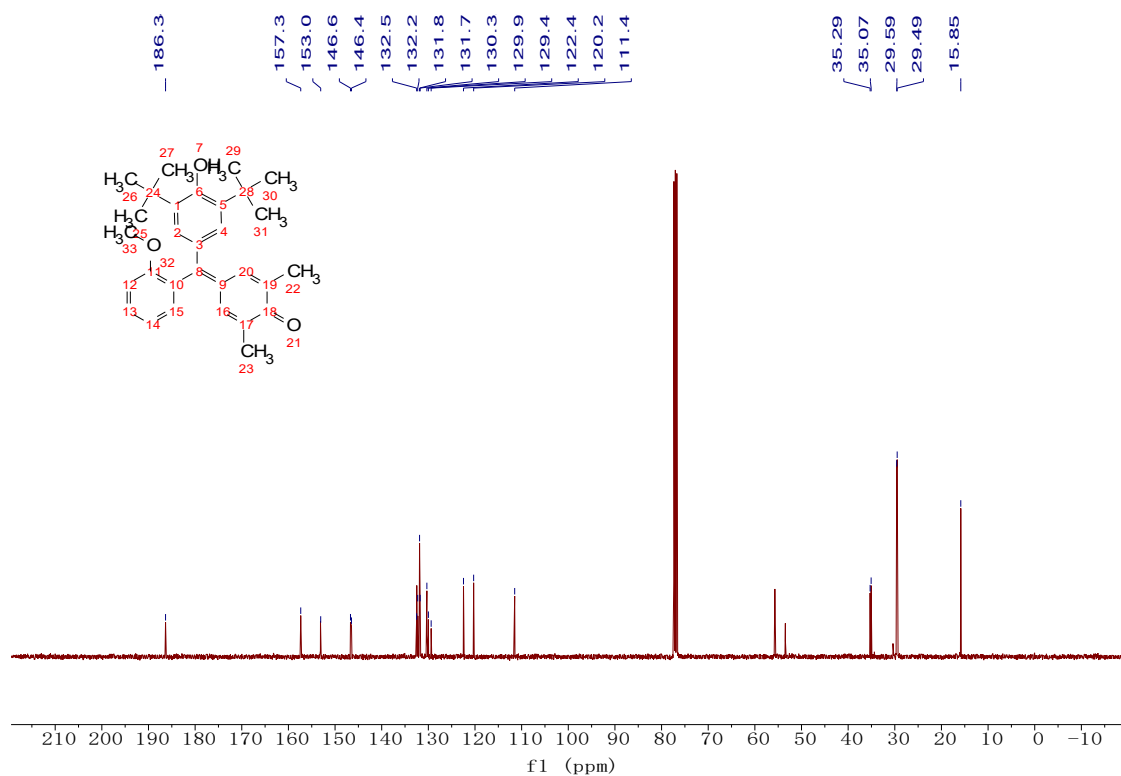
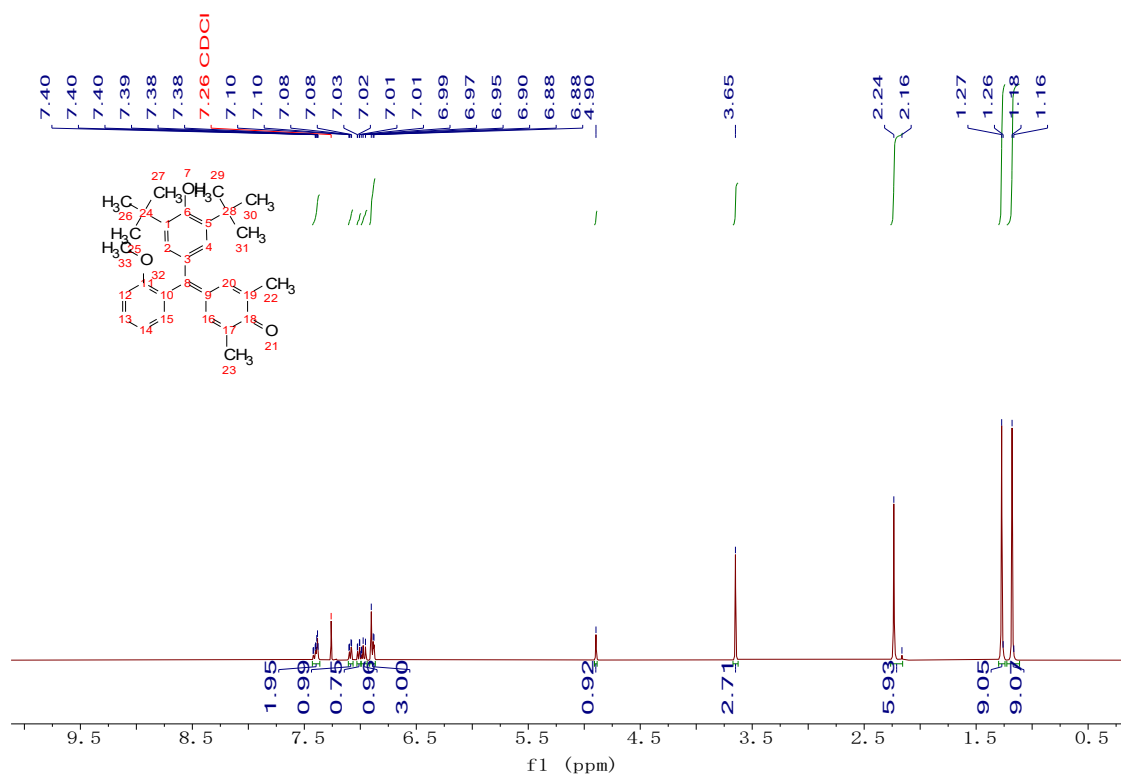
4-((3,5-di-tert-butyl-4-hydroxyphenyl)(p-tolyl)methylene)-2,6-dimethylcyclohexa-2,5-dien-1-one(2aj)



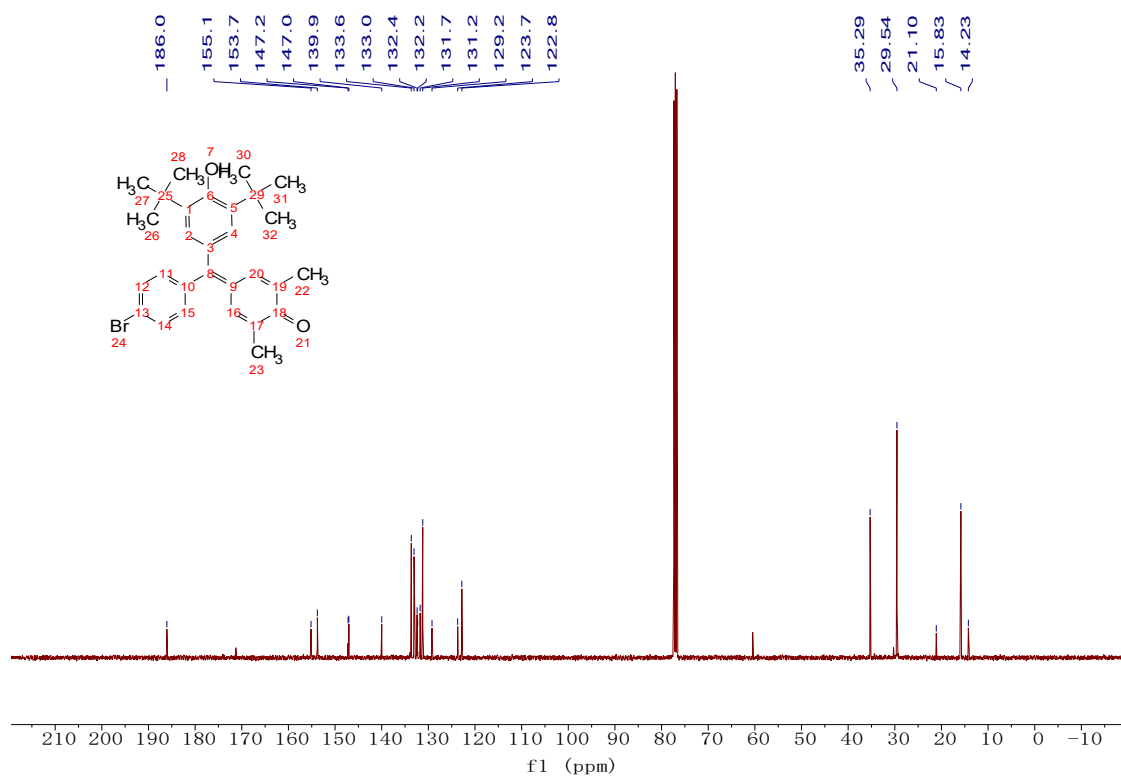
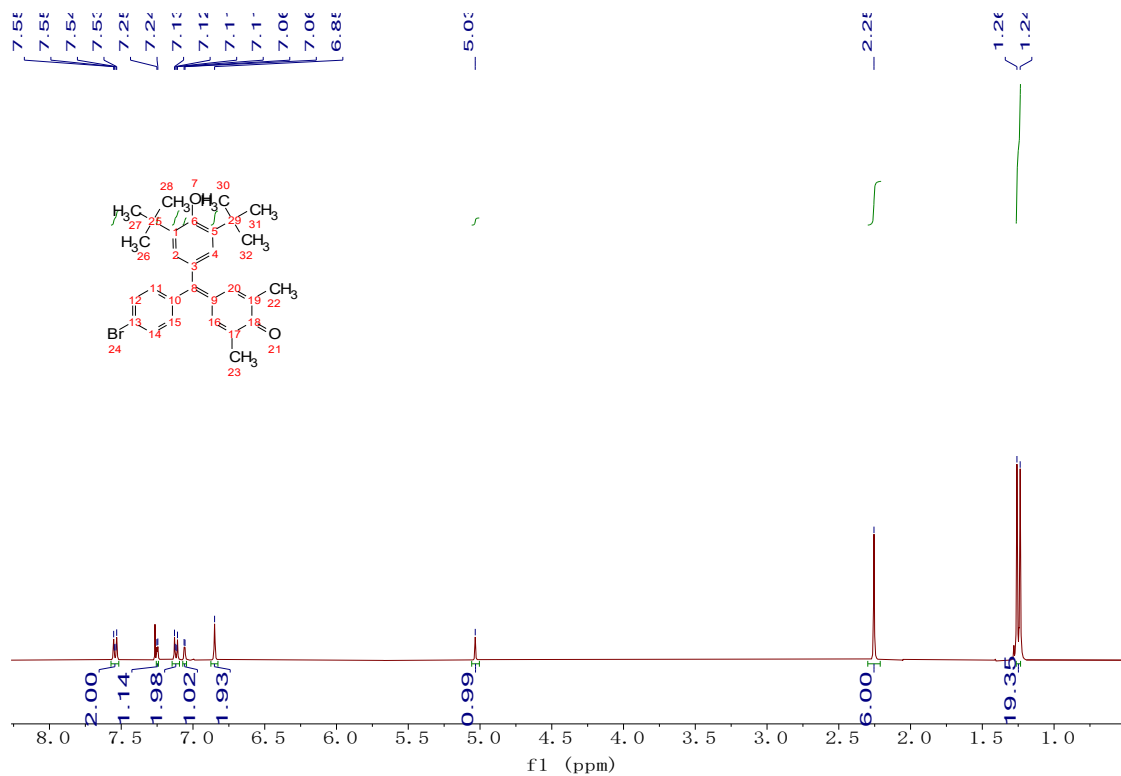
4-((3,5-di-tert-butyl-4-hydroxyphenyl)(m-tolyl)methylene)-2,6-dimethylcyclohexa-2,5-dien-1-one(2ak)



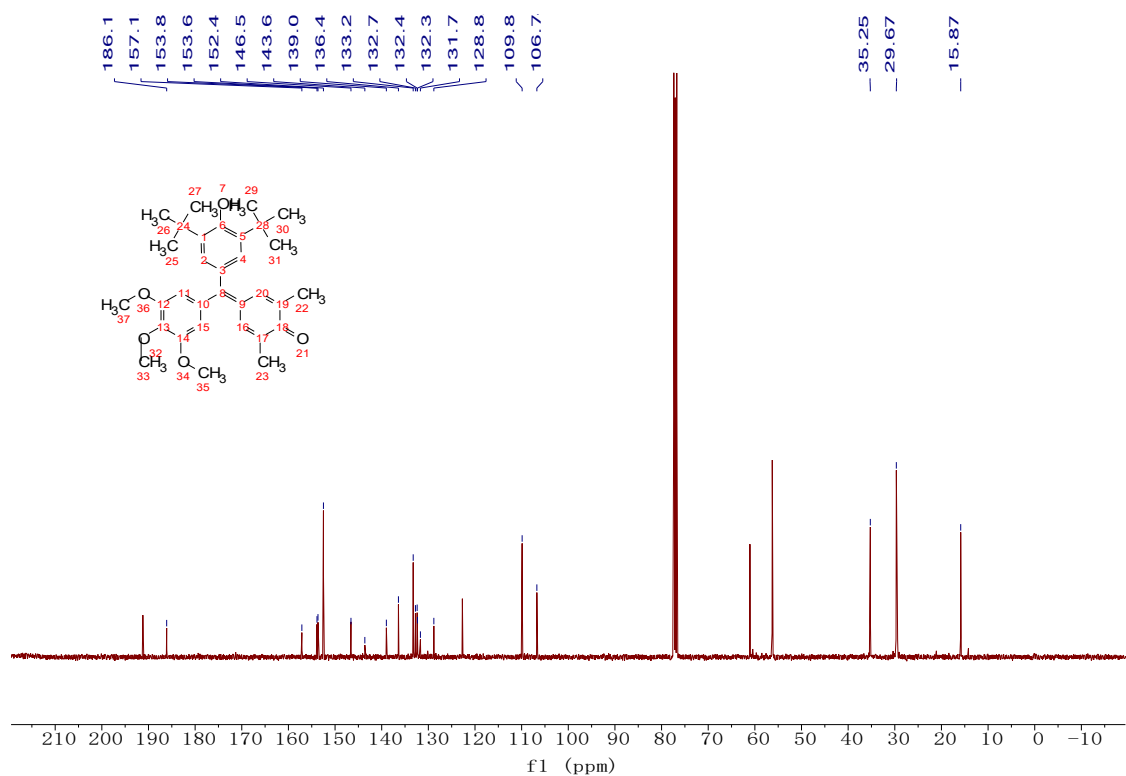
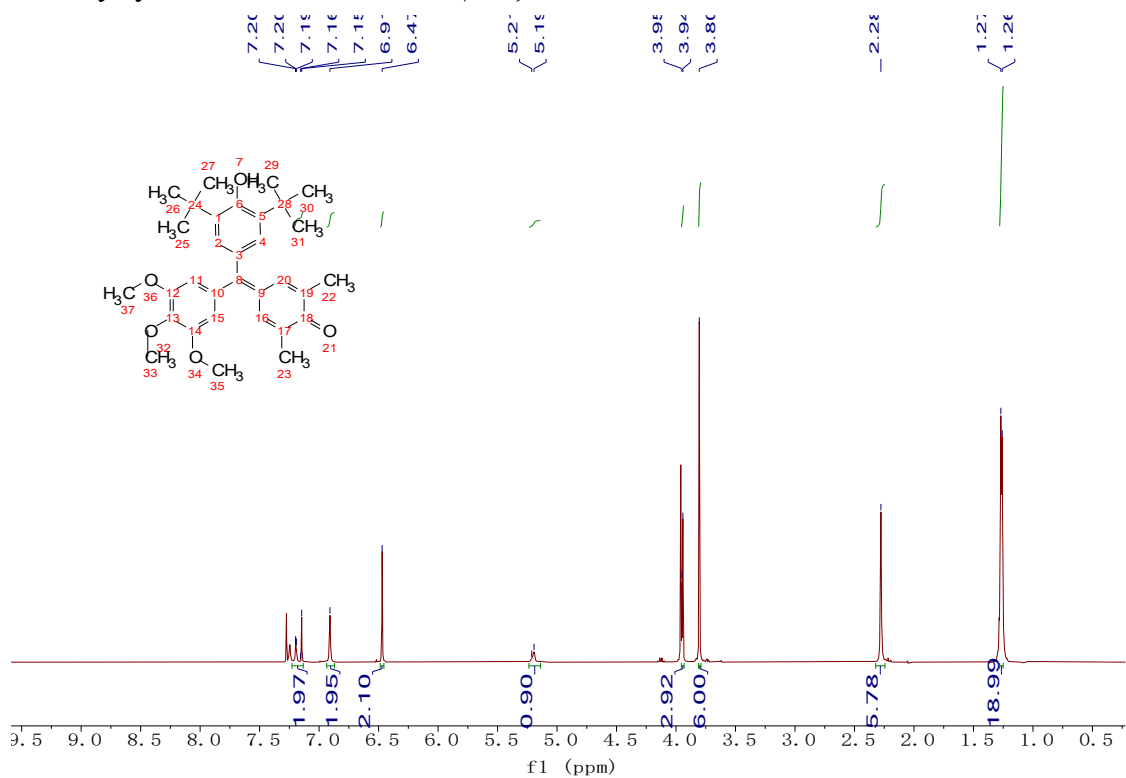
4-((3,5-di-tert-butyl-4-hydroxyphenyl)(2-methoxyphenyl)methylene)-2,6-dimethylcyclohexa-2,5-dien-1-one(2a)



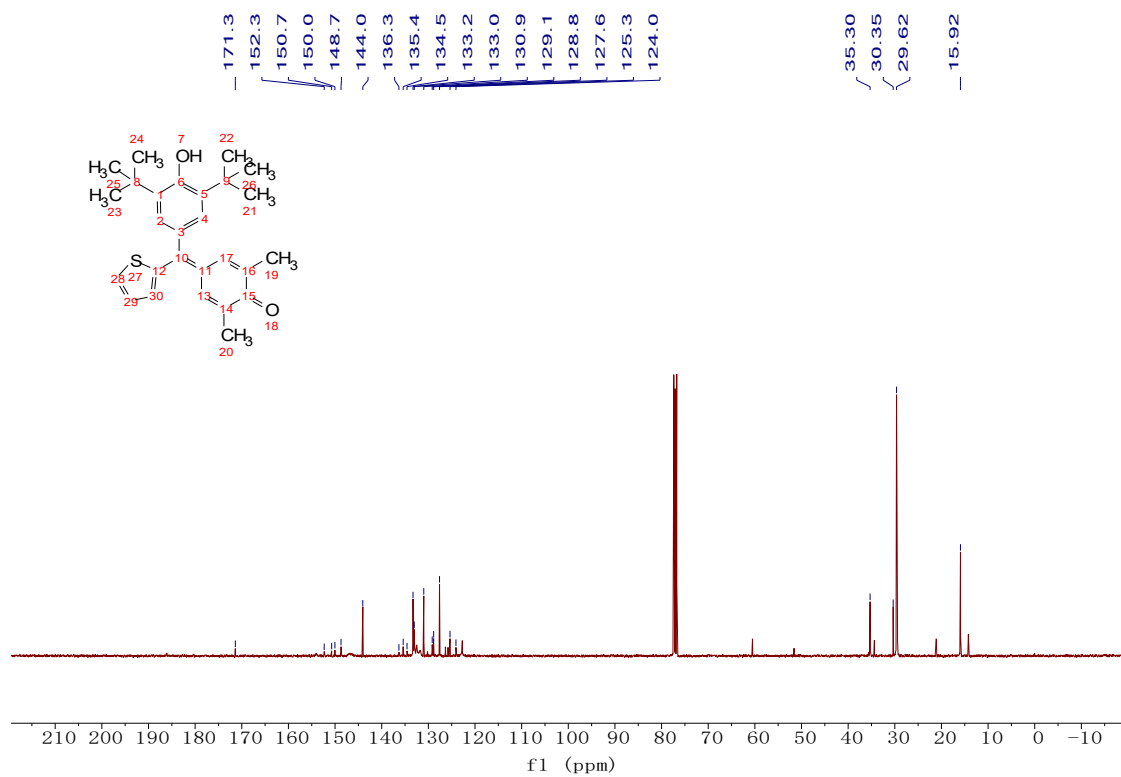
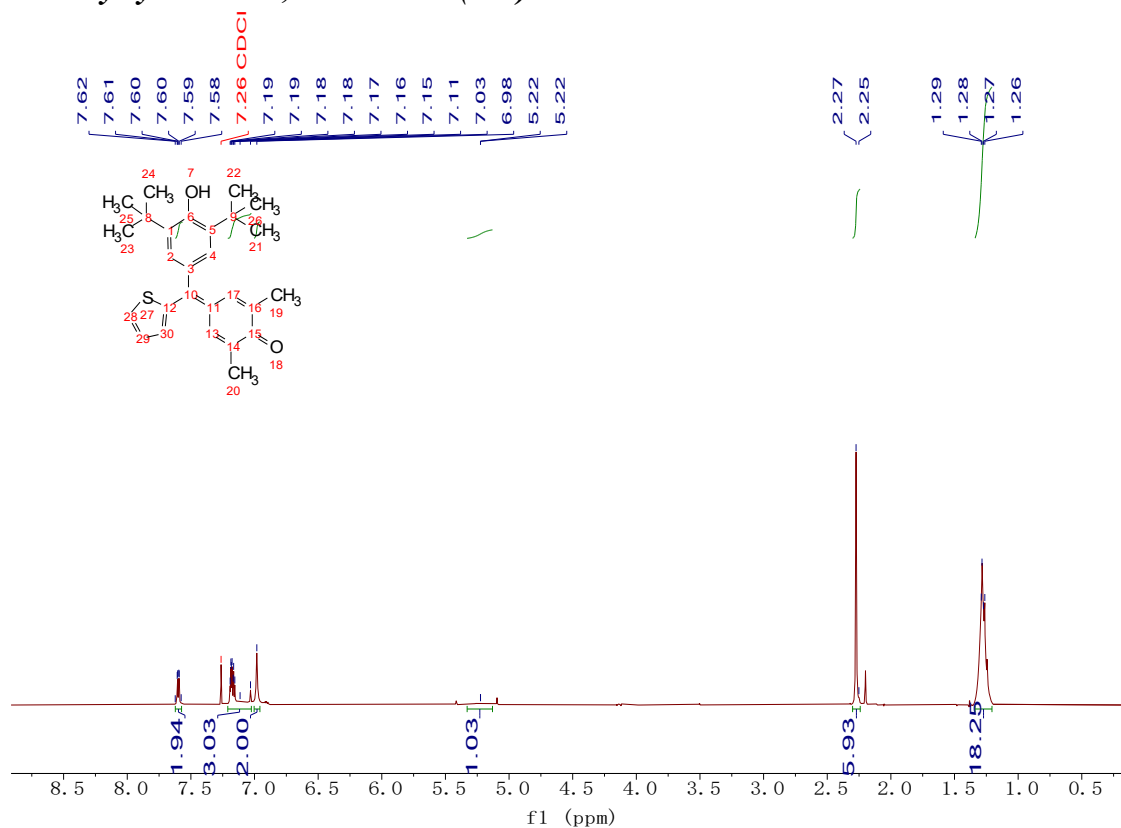
4-((4-bromophenyl)(3,5-di-tert-butyl-4-hydroxyphenyl)methylene)-2,6-dimethylcyclohexa-2,5-dien-1-one(2am)



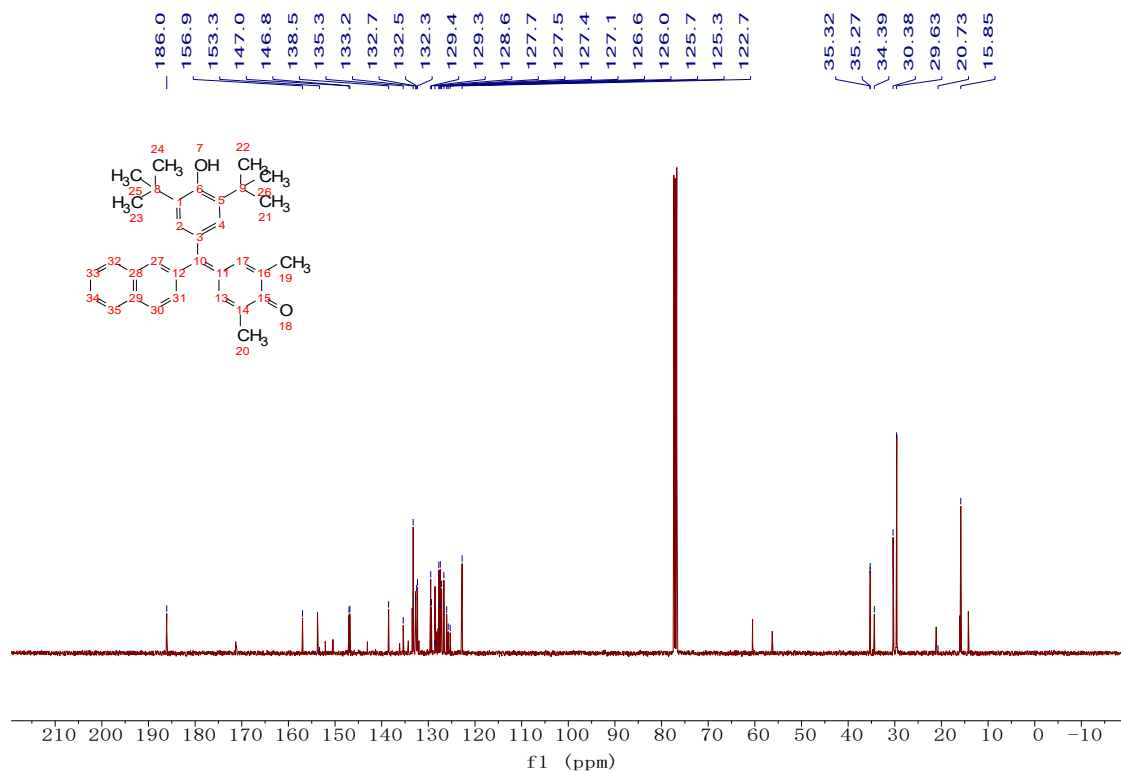
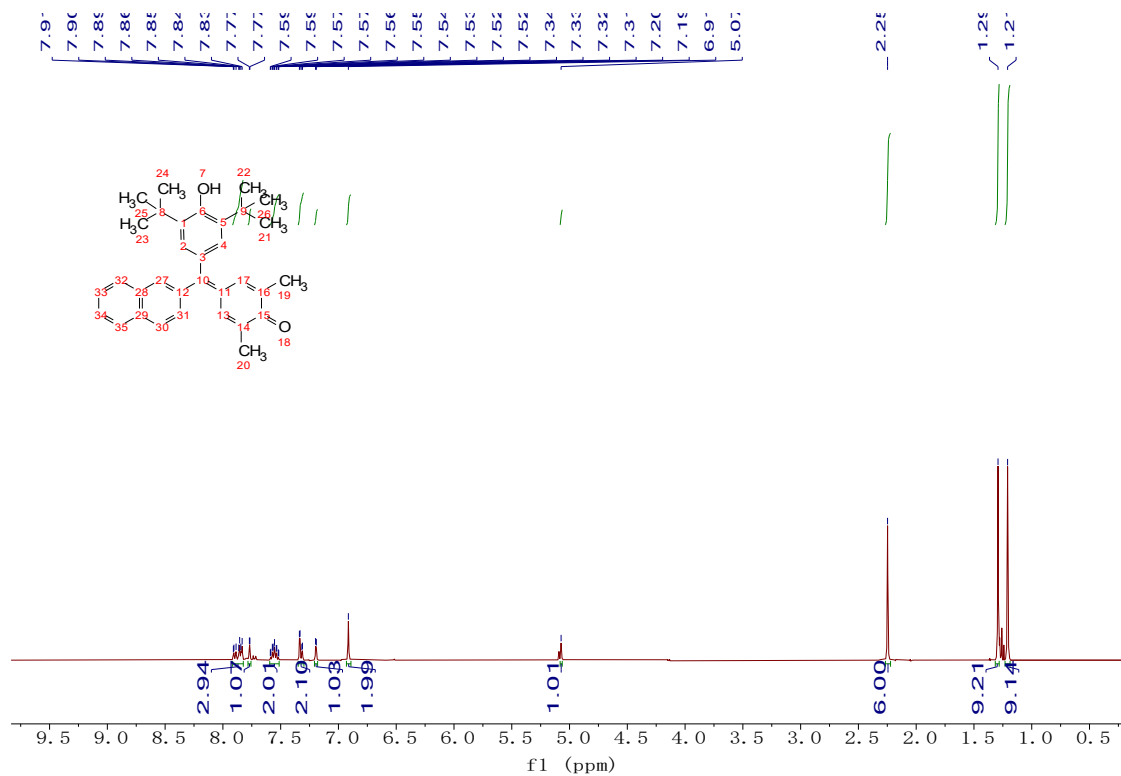
4-((3,5-di-tert-butyl-4-hydroxyphenyl)methylene)-2,6-dimethylcyclohexa-2,5-dien-1-one(2an)



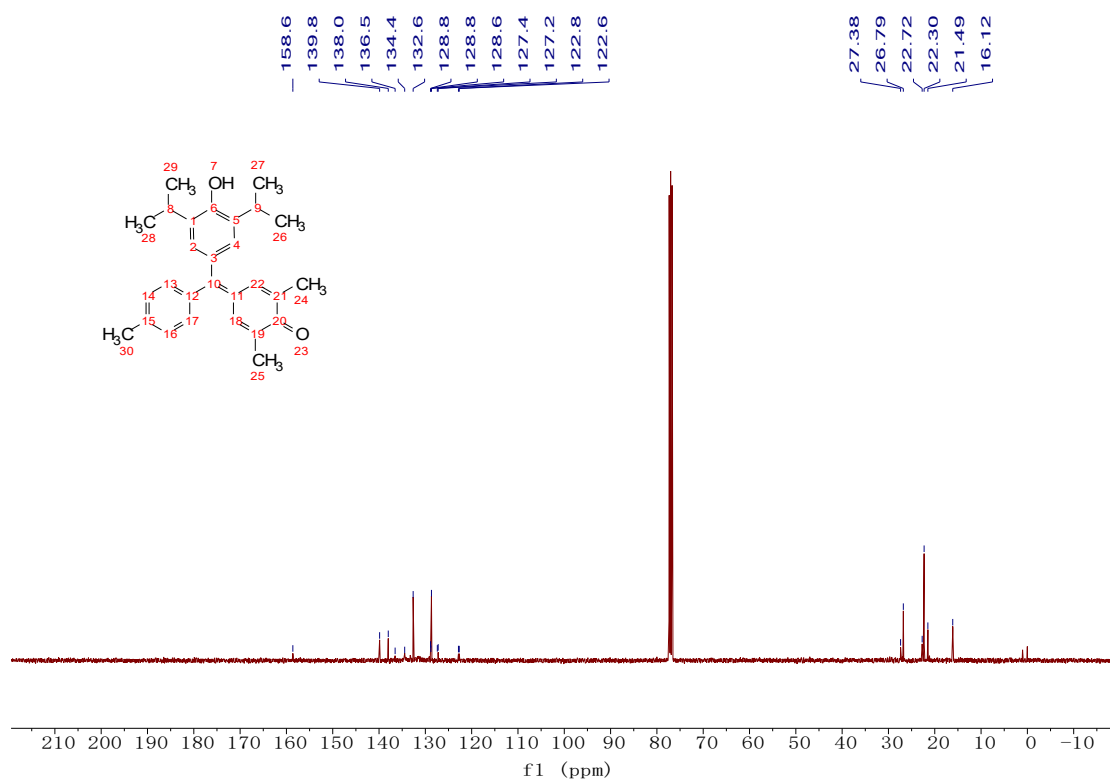
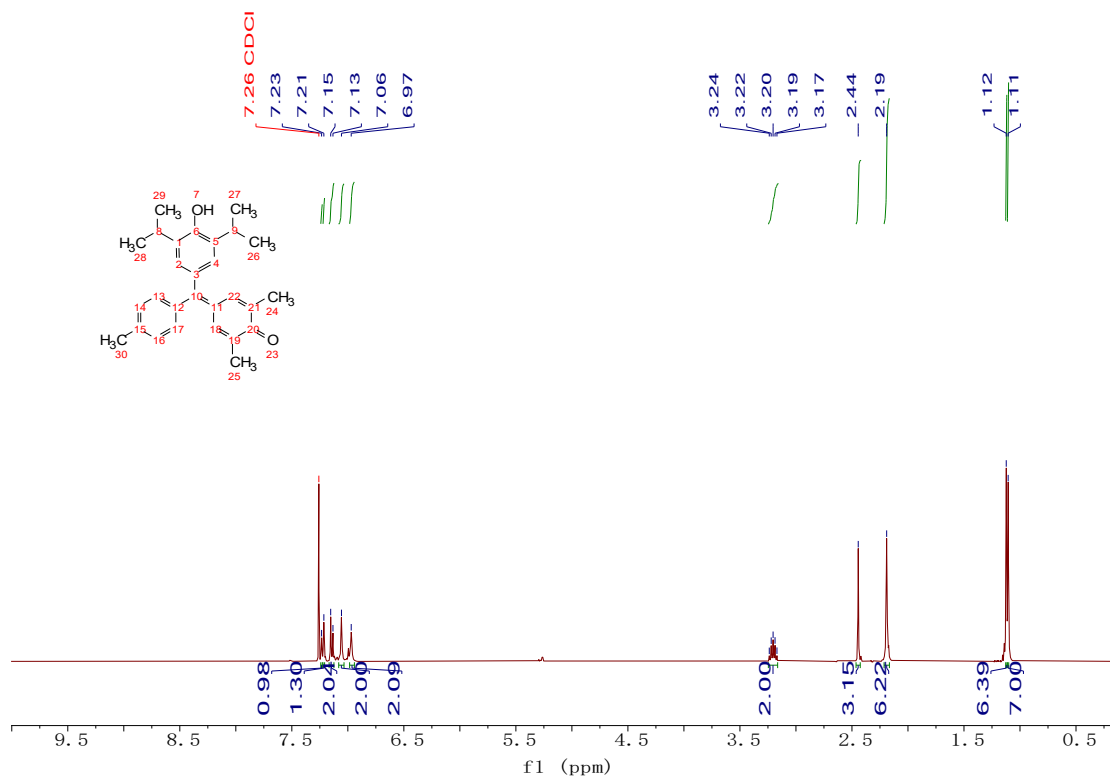
4-((3,5-di-tert-butyl-4-hydroxyphenyl)(thiophen-2-yl)methylene)-2,6-dimethylcyclohexa-2,5-dien-1-one(2ao)



4-((3,5-di-tert-butyl-4-hydroxyphenyl)(naphthalen-2-yl)methylene)-2,6-dimethylcyclohexa-2,5-dien-1-one(2ap)



4-((4-hydroxy-3,5-diisopropylphenyl)(p-tolyl)methylene)-2,6-dimethylcyclohexa-2,5-dien-1-one (2aq)



4-((4-bromophenyl)(4-hydroxy-3,5-diisopropylphenyl)methylene)-2,6-dimethylcyclohexa-2,5-dien-1-one(2ar)

