# Supporting Information

## Experimental and spectroscopic evidence of the hidden triplet transition state of quinone methide: A new reactivity paradigm

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## X-Ray Crystallographic Studies of 3aa

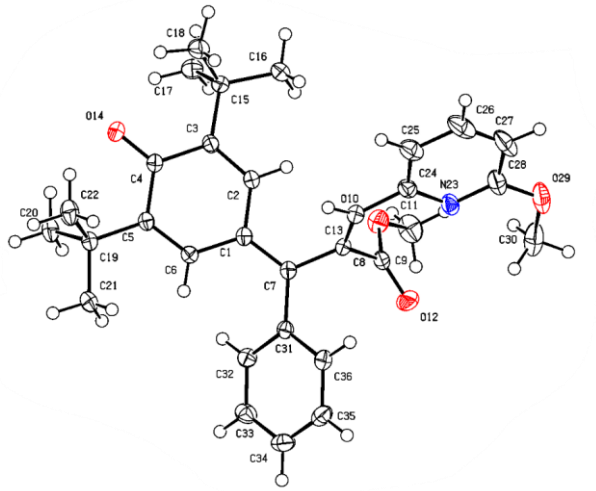



**Figure 1: ORTEP diagram for each molecule of the asymmetric unit of compound 3aa drawn with 50% ellipsoid probability.**

High-quality crystals of **3aa** were procured through $CHCl_2$/*n*-hexane. The compound **3aa** exhibited crystallization within the Monoclinic crystal system, possessing the space group P 21/c. Single-crystal X-ray data were systematically gathered using an Oxford XCalibur CCD diffractometer, employing graphite monochromated Mo Kα radiation. The structural elucidation was accomplished through the implementation of SIR-92, and subsequent refinement ensued via a full matrix least square technique on F2, facilitated by the SHELXL-97 program within the WinGX v 1.80.05 software package. Comprehensive data, encompassing atomic coordinates, bond lengths, bond angles, and thermal parameters for the 6aa compound, have been deposited at the Cambridge Crystallographic Data Centre. The CCDC deposit number associated with 3aa is **2424592**.

**Table S1: Crystallographic data and structure refinement for compounds 3aa**

| | |
|---|---|
| Identification code | **3aa** |
| Empirical formula | $C_{31}\ H_{35}\ NO_4$ |
| Formula weight | 485.60 |
| Temperature | 293 K |
| Wavelength | 0.71073 Å |
| Crystal system | Monoclinic |

| | | |
|---|---|---|
| Space group | P 21/c | |
| Unit cell dimensions | a = 9.2331(3) | α = 90 |
| | b = 14.1143(4) | β = 97.619(3) |
| | c = 20.5532(8) | γ = 90 |
| Volume | 2654.82 $Å^3$ | |
| Z | 4 | |
| Density (calculated) | 1.215 $g/cm^3$ | |
| Absorption coefficient | 0.080 $mm^{-1}$ | |
| F(000) | 1040.0 | |
| Index ranges | h= 10, k = 16, l = 24 | |
| Reflections collected | 0.0383(3781) | |
| Completeness to theta = 26.37 ° | 100% | |
| Final R indices [I>2 sigma(I)][a,b] | R1 = 0.0383, wR2 = 0.1015 | |

[a] $R = \sum(\|Fo\| - |Fc|)/\sum|Fo|$ ; [b] $Rw = \{\sum[w(Fo^2 - Fc^2)^2]/\sum[w(Fo^2)^2]\}^{1/2}$

**X-Ray Crystallographic Studies of 5aa**

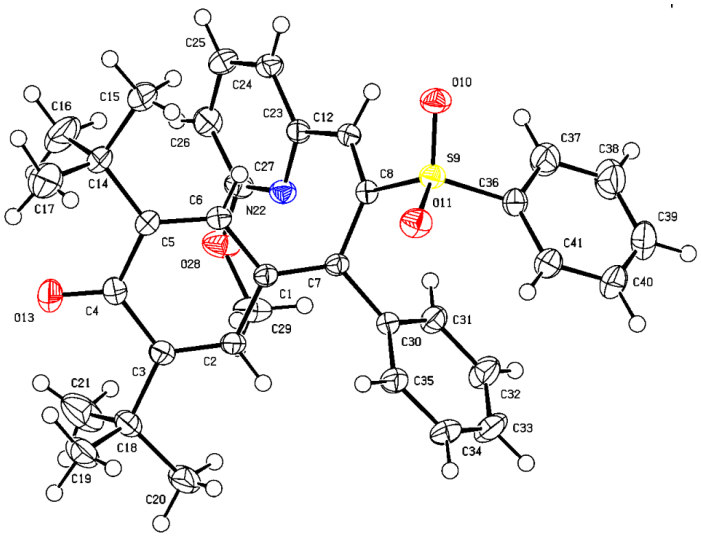



**Figure 2: ORTEP diagram for each molecule of the asymmetric unit of compound 5aa drawn with 50% ellipsoid probability.**

High-quality crystals of compound **5aa** were procured through $CHCl_2$/*n*-hexane. The compound **5aa** exhibited crystallization within the Monoclinic crystal system, possessing the

space group P 21/n. Single-crystal X-ray data were systematically gathered using an Oxford XCalibur CCD diffractometer, employing graphite monochromated Mo Kα radiation. The structural elucidation was accomplished through the implementation of SIR-92, and subsequent refinement ensued via a full matrix least square technique on F2, facilitated by the SHELXL-97 program within the WinGX v 1.80.05 software package. Comprehensive data, encompassing atomic coordinates, bond lengths, bond angles, and thermal parameters for the compound, have been deposited at the Cambridge Crystallographic Data Centre. The CCDC deposit number associated with compound **5aa** is 2394330.

**Table S2: Crystallographic data and structure refinement for compound 5aa**

| | | |
|---|---|---|
| Identification code | **5aa** | |
| Empirical formula | $C_{35}\ H_{37}\ N\ O_4\ S$ | |
| Formula weight | 567.71 | |
| Temperature | 142 K | |
| Wavelength | 0.71073 Å | |
| Crystal system | Monoclinic | |
| Space group | P 21/n | |
| Unit cell dimensions | a =10.4934(3) | α = 90 |
| | b =17.6933(5) | β = 99.353(3) |
| | c =16.8167(5) | γ = 90 |
| Volume | 3080.73(16) $Å^3$ | |
| Z | 4 | |
| Density (calculated) | 1.224 $g/cm^3$ | |
| Absorption coefficient | 0.144 $mm^{-1}$ | |
| F(000) | 1208.0 | |
| Index ranges | h= 13, k = 24, l = 24 | |
| Reflections collected | 0.0531( 6253) | |
| Completeness to theta = 26.37 ° | 80.4 % | |
| Final R indices [I>2 sigma(I)][a,b] | R1 = 0.0531, wR2 = 0.1543 | |

[a] $R = \sum(\|Fo\| - \|Fc\|)/\sum|Fo|$ ; [b] $Rw = \{\sum[w(Fo^2 - Fc^2)^2]/\sum[w(Fo^2)^2]\}^{1/2}$

## X-Ray Crystallographic Studies of 8

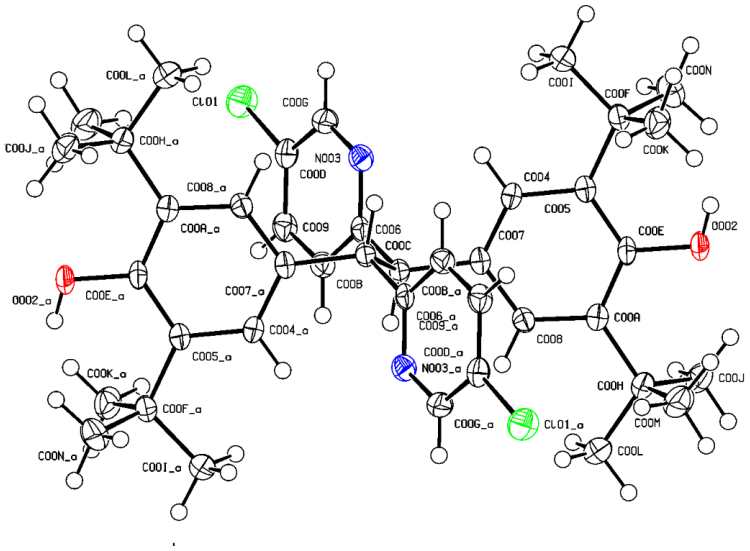



**Figure 3: ORTEP diagram for each molecule of the asymmetric unit of compound 8 drawn with 50% ellipsoid probability.**

High-quality crystals of **8** were procured through $CHCl_3$. The compound **8** exhibited crystallization within the Monoclinic crystal system, possessing the space group P 21/c. Single-crystal X-ray data were systematically gathered using an Oxford XCalibur CCD diffractometer, employing graphite monochromated Mo Kα radiation. The structural elucidation was accomplished through the implementation of SIR-92, and subsequent refinement ensued via a full matrix least square technique on F2, facilitated by the SHELXL-97 program within the WinGX v 1.80.05 software package. Comprehensive data, encompassing atomic coordinates, bond lengths, bond angles, and thermal parameters for the 8 compound, have been deposited at the Cambridge Crystallographic Data Centre. The CCDC deposit number associated with 8 is **2481484**.

**Table S3: Crystallographic data and structure refinement for compounds 8**

| | |
|---|---|
| Identification code | **8** |
| Empirical formula | $C_{20}\ H_{24.75}\ Cl\ N\ O$ |
| Formula weight | 330.61 |
| Temperature | 150 K |
| Wavelength | 0.71073 Å |

| | | |
|---|---|---|
| Crystal system | Monoclinic | |
| Space group | P 21/c | |
| Unit cell dimensions | a = 14.7585(6) | α = 90 |
| | b = 10.9981(4) | β = 112.781(5) |
| | c = 11.9327(6) | γ = 90 |
| Volume | 1785.77(15) $Å^3$ | |
| Z | 4 | |
| Density (calculated) | 1.230 $g/cm^3$ | |
| Absorption coefficient | 0.219 $mm^{-1}$ | |
| F(000) | 707.0 | |
| Index ranges | h= 17, k = 12, l = 14 | |
| Reflections collected | 0.0354( 2703) | |
| Completeness to theta = 26.37 ° | 99.9 % | |
| Final R indices [I>2 sigma(I)][a,b] | R1 = 0.0354, wR2 = 0.095 | |

[a] $R = \sum(\|Fo\| - \|Fc\|)/\sum|Fo|$ ; [b] $Rw = \{\sum[w(Fo^2 - Fc^2)^2]/\sum[w(Fo^2)^2]\}^{1/2}$

**References:**


1. CrysAlisPro, Agilent Technologies, Version 1.171.34.49, 2011.

2. Sheldrick, G. M., *Acta Cryst*. 2008, *A64*, 112.

3. Farrugia, L. J. WinGX Version 1.80.05, An integrated system of Windows Programs for the Solution, Refinement and Analysis of Single Crystal X-Ray Diffraction Data*;* Department of Chemistry, University of Glasgow,1997-2009.

4. (a) Foresman, J. B.; Frisch, A. E. *Exploring Chemistry with Electronic Structure Methods*; Gaussian, Inc.: Pittsburgh, PA. 1995. (b) Hehre, W. J., Radom, L., Schleyer, P. V. R.; Pople, J. A. *Ab Initio Molecular Orbital Theory*; Wiley: New York, 1985.

## General Experimental

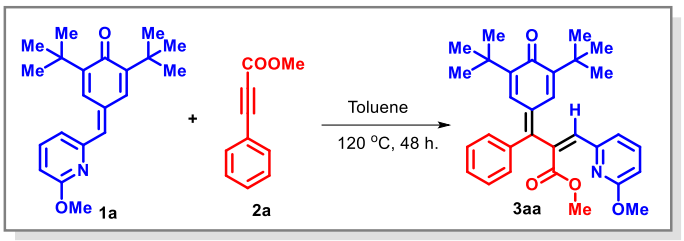
**General Method**. $^{1}H$ NMR (400 MHz) and $^{13}C$ NMR (100 MHz) spectra were recorded on JEOL ECS (400 MHz) instrument using $CDCl_3$/$(CD_3)_2SO$ as solvent. Chemical shifts for protons and carbons are reported in ppm from tetramethylsilane and are referenced to the carbon resonance of the solvent. Data are reported as singlet (s), doublet (d), triplet (t), quartet (q), double doublet (dd), multiplet (m), and coupling constants are reported in Hertz and integration. High resolution mass spectra (HRMS) were recorded on an Agilent 6500 series B5125 mass spectrometer (ESI-TOF). Crystal structure analysis was accomplished on single needles X-ray diffractometer. TLC analysis was performed on commercially prepared 60 $F_{254}$ silica gel plates. All purchased chemicals were used as received. All melting points are uncorrected. Starting materials **1** was synthesised according to the reported literature procedure[1] and **2** was purchased from Sigma-Aldrich Chemical Co. and were used without further purification unless otherwise stated.

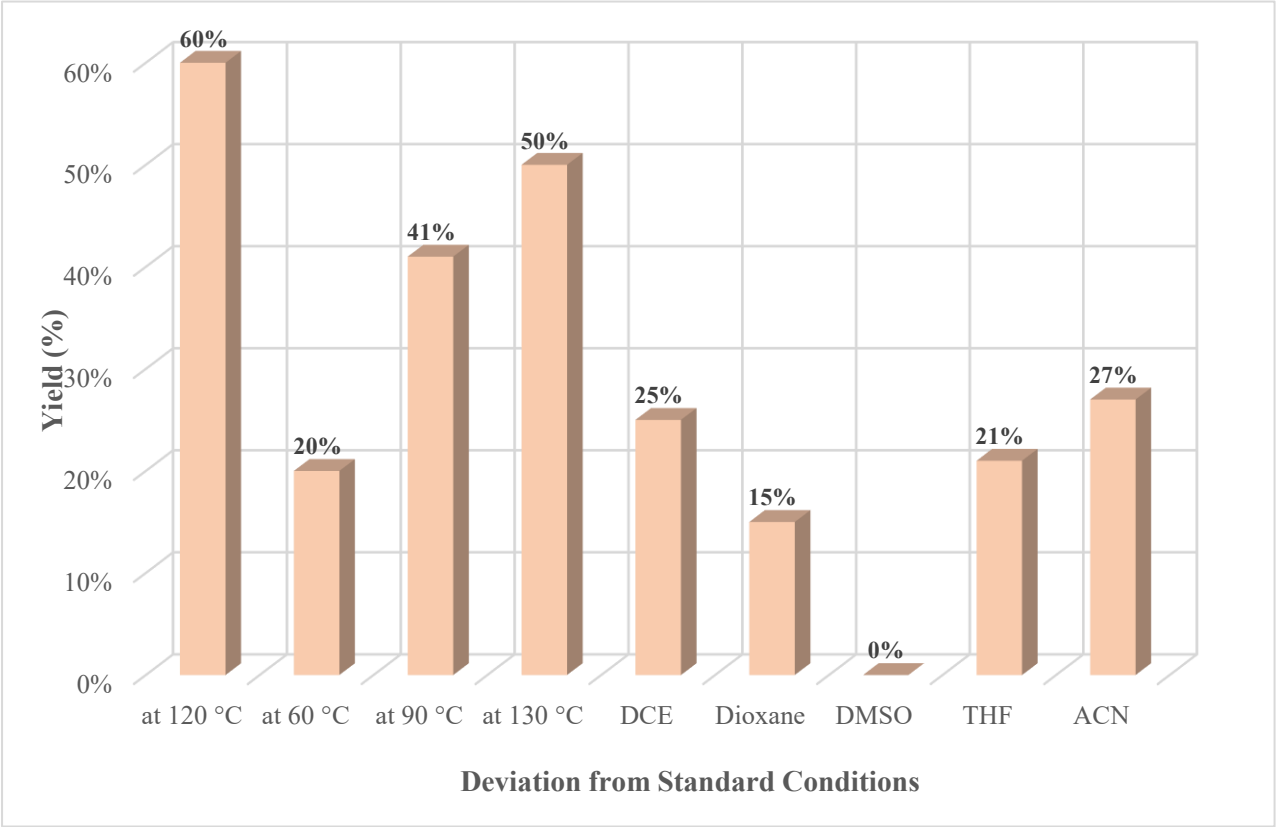
## References:


1. (a) Chu, W.; Zhang, L.; Bao, X.; Zhao, X.; Zeng, C.; Du, J.; Zhang, G.; Wang, F.; Ma, X.; Fan, C. *Angew. Chem. Int. Ed.* **2013**, *52*, 9229-9233. (b) Yuan, Z.; Fang, X.; Li, X.; Wu, J.; Yao, H.; Lin, A. *J. Org.Chem.* **2015**, *80*, 11123−11130. (c) Xiong, B.; Si, L.; Liu, Y.; Xu, W.; Jiang, T.; Cao, F.; Tang, K.W.; Wong, W.Y. *Chem. Asian J.* **2022**, *17*, e202200042. (d) Zhang, X. Z.; Du, J. Y.; Deng, Y. H.; Chu, W. D.; Yan, X.; Yu, K. Y.; Fan, C. A. *J. Org. Chem.* **2016**, *81*, 2598-2606. (e) Ali, A.; Jajoria, R.; Harit, H. K.; Singh, R. P. *J. Org. Chem.* **2022**, *87*(8), 5213-5228.


## Table S4. Optimization of Solvent for the synthesis of *Z*-alkenes

To optimize the reaction conditions, we initially selected *p*-quinone methide (**1a**) and electron-deficient alkyne (**2a**) as model substrates. When **1a** (1 equiv) was reacted with **2a** (1.2 equiv) in toluene (4 mL) at 120 °C for 48 hours, the desired product **3a** was obtained in 60% yield (**entry 1**). Lowering the temperature to 60°C drastically reduced the yield to 20%, while increasing the temperature to 90°C improved the yield to 41%.

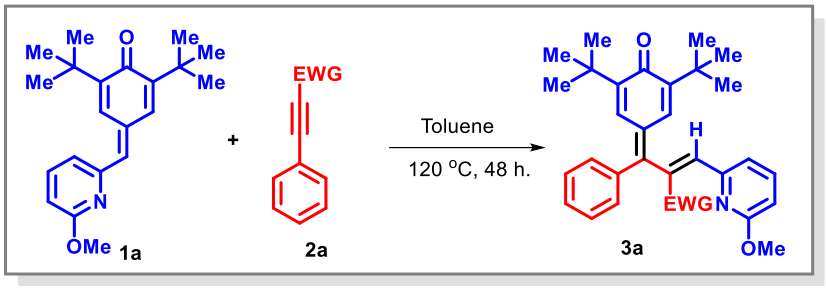



[a]Reaction Conditions: The mixture of **1a** (0.25 mmol), **2a** (.30 mmol) were stirred in toluene (2 mL) at 120°C for 48 h. [b]Isolated yield.

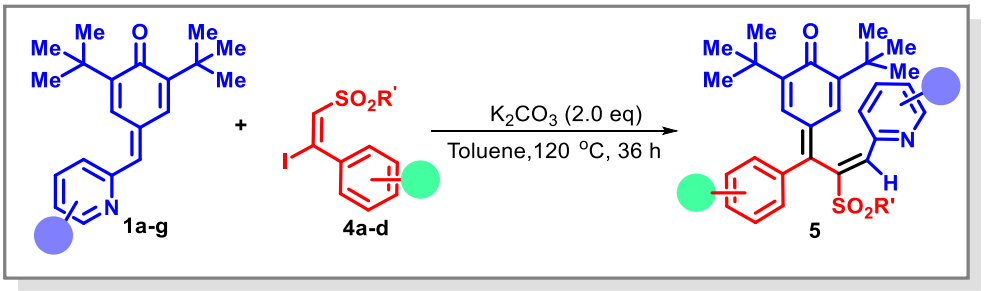
The yield and the reaction time weren't influenced by additional elevated temperatures. Next, we evaluated the effect of different solvents on the reaction efficiency. Among the various screened solvents, DCE afforded **3a** in 25% yield, whereas the use of 1,4-dioxane reduced the yield to 15%. No desired product formation was observed in DMSO. Moreover, THF provided a moderate yield of 21%, while in acetonitrile (ACN), the product **3a** was formed in 27% yield. These findings highlight the critical role of both temperature and solvent in achieving optimal reaction conditions, with toluene at 120°C emerging as the most effective choice, ensuring high yield and excellent stereoselectivity.

**General Procedure for the Synthesis of compounds (3aa-3ak):**



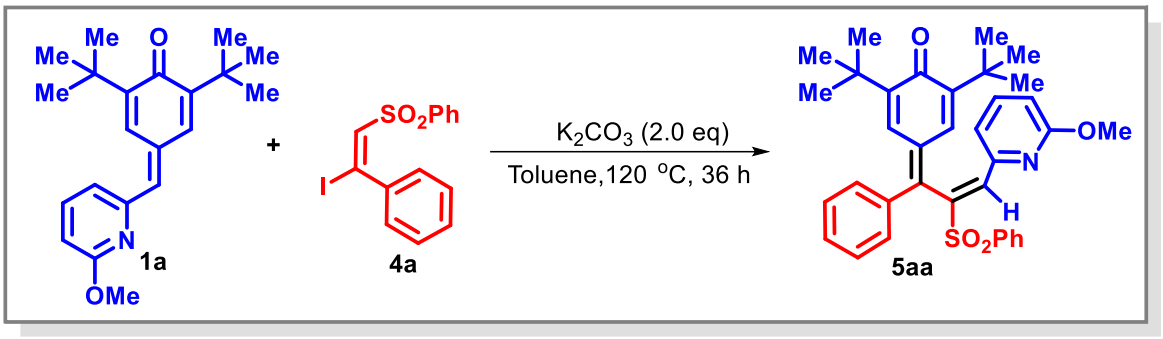

In a 10 mL oven-dried seal tube, *para*-quinone methide **1a** (0.25 mmol) and methyl 3-phenylpropiolate or its derivatives **2a** (0.25 mmol, 1.0 equiv.), in 2.0 mL toluene was taken and stirred at 120 °C temperature for 48 h. Progression of the reaction was monitored by TLC analysis. After the complete consumption of the starting material, the reaction mixture was diluted with water (10 mL) and extracted with ethyl acetate. Then, the organic layer was washed with an aqueous saturated brine solution, dried over $Na_2SO_4$, and concentrated under reduced pressure. The crude material obtained was purified by column chromatography on silica gel (100−200) using hexane: ethyl acetate (98/2) as a mobile phase.

**General Procedure for the Synthesis of compound (5):**



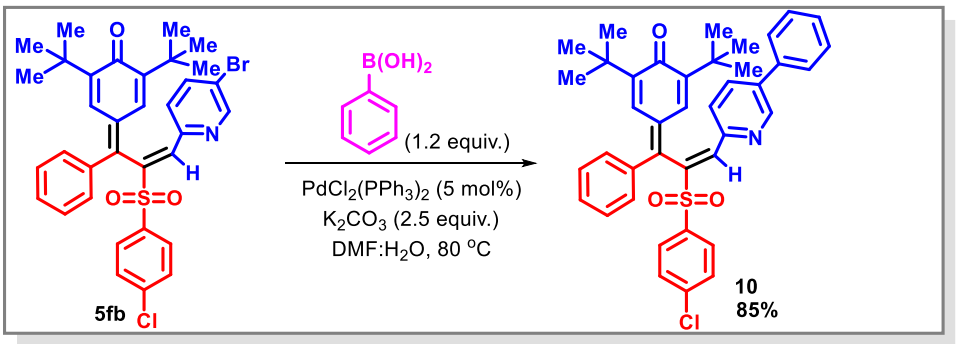

In a 10 mL oven-dried seal tube, *para*-quinone methide **1** (0.25 mmol) and iodo-vinyl sulfones or its derivatives **2** (0.25 mmol, 1.0 equiv.), $K_2CO_3$ (0.50 mmol, 2.0 equiv.), in 2.0 mL toluene was taken and stirred at 120 °C temperature for 36 h. Progression of the reaction was monitored by TLC analysis. After the complete consumption of the starting material, the reaction mixture was diluted with water (10 mL) and extracted with ethyl acetate. Then, the organic layer was washed with an aqueous saturated brine solution, dried over $Na_2SO_4$, and concentrated under reduced pressure. The crude material obtained was purified by column chromatography on silica gel (100−200) using hexane: ethyl acetate (98/2) as a mobile phase.

**General Procedure for the Gram-Scale Synthesis of 5aa:**




In a 10 mL oven-dried seal tube, *para*-quinone methide **1** (10 mmol) and iodo-vinyl sulfones or their derivatives **2** (10 mmol, 1.0 equiv.), $K_2CO_3$ (20 mmol, 2.0 equiv.) in 50.0 mL toluene was taken and stirred at 120 °C for 36 h. Progression of the reaction was monitored by TLC analysis. After the complete consumption of the starting material, the reaction mixture was diluted with water (10 mL) and extracted with ethyl acetate. Then, the organic layer was washed with an aqueous saturated brine solution, dried over $Na_2SO_4$, and concentrated under reduced pressure. The crude material obtained was purified by column chromatography on silica gel (100−200) using hexane: ethyl acetate (98/2) to afford the desired product **5aa** in 72% yield.

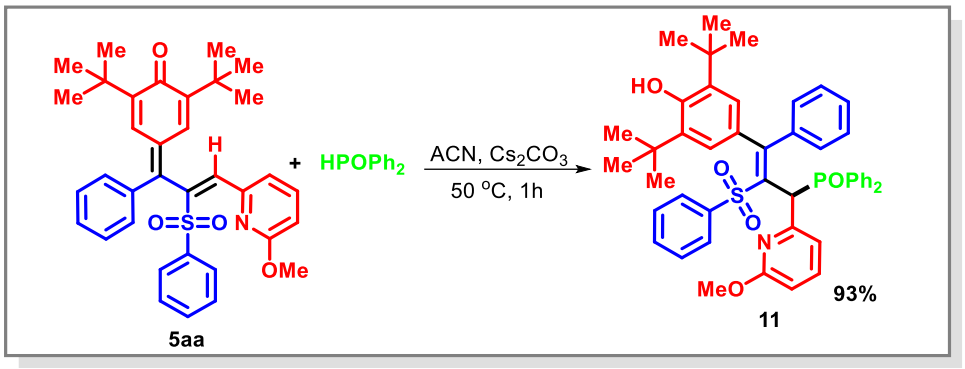
**General Procedure for the synthesis of compound 10:**




In a 10 mL oven-dried round bottom flask, the obtained product **5fb** (0.2 mmol, 1.0 equiv), benzene boronic acid (0.26 mmol, 1.3 equiv.), $Pd(PPh_3)_2Cl_2$ (5 mol %), $K_2CO_3$ (0.4 mmol, 2.0 equiv.) was taken in 3:1 DMF/$H_2O$. The reactants were degassed and filled with $N_2$ for three times. Then the reaction mixture was stirred at 80 °C for 2 h. When the reaction was completed, the reaction mixture was diluted with water (10 mL) and extracted with ethyl acetate. Then organic layer was washed with aqueous saturated brine solution and dried over $Na_2SO_4$ and concentrated under reduced

pressure. The crude material obtained was purified by column chromatography on silica gel (100−200) (hexane: ethyl acetate; 95/5) to afford the desired product **10** in 85% yield.

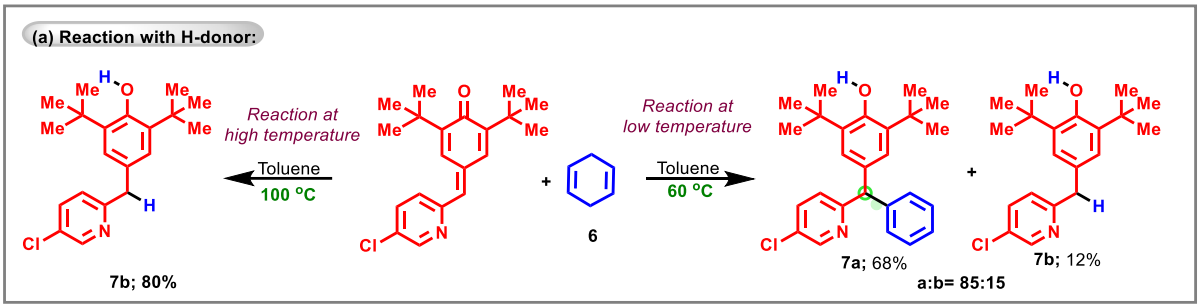
**General Procedure for the synthesis of compound 11:**




In a 10 mL oven-dried round bottom flask, the obtained product **5aa** (0.2 mmol, 1.0 equiv.), diphenyl phosphine oxide (0.26 mmol, 1.3 equiv.), $Cs_2CO_3$ (0.4 mmol, 2.0 equiv.) was taken in 2 mL acetonitrile (ACN). Then the reaction mixture was stirred at 80 °C for 2 h. When the reaction was completed, the reaction mixture was diluted with water (10 mL) and extracted with ethyl acetate. Then organic layer was washed with aqueous saturated brine solution and dried over $Na_2SO_4$ and concentrated under reduced pressure. The crude material obtained was purified by column chromatography on silica gel (100−200) (hexane: ethyl acetate; 95/5) to afford the desired product **11** in 93% yield.

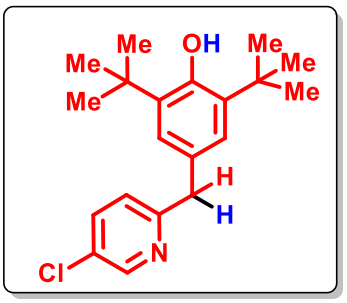
**Mechanistic Investigation Experiments:**

**(I) Reaction with cyclohexadiene (CHD):**



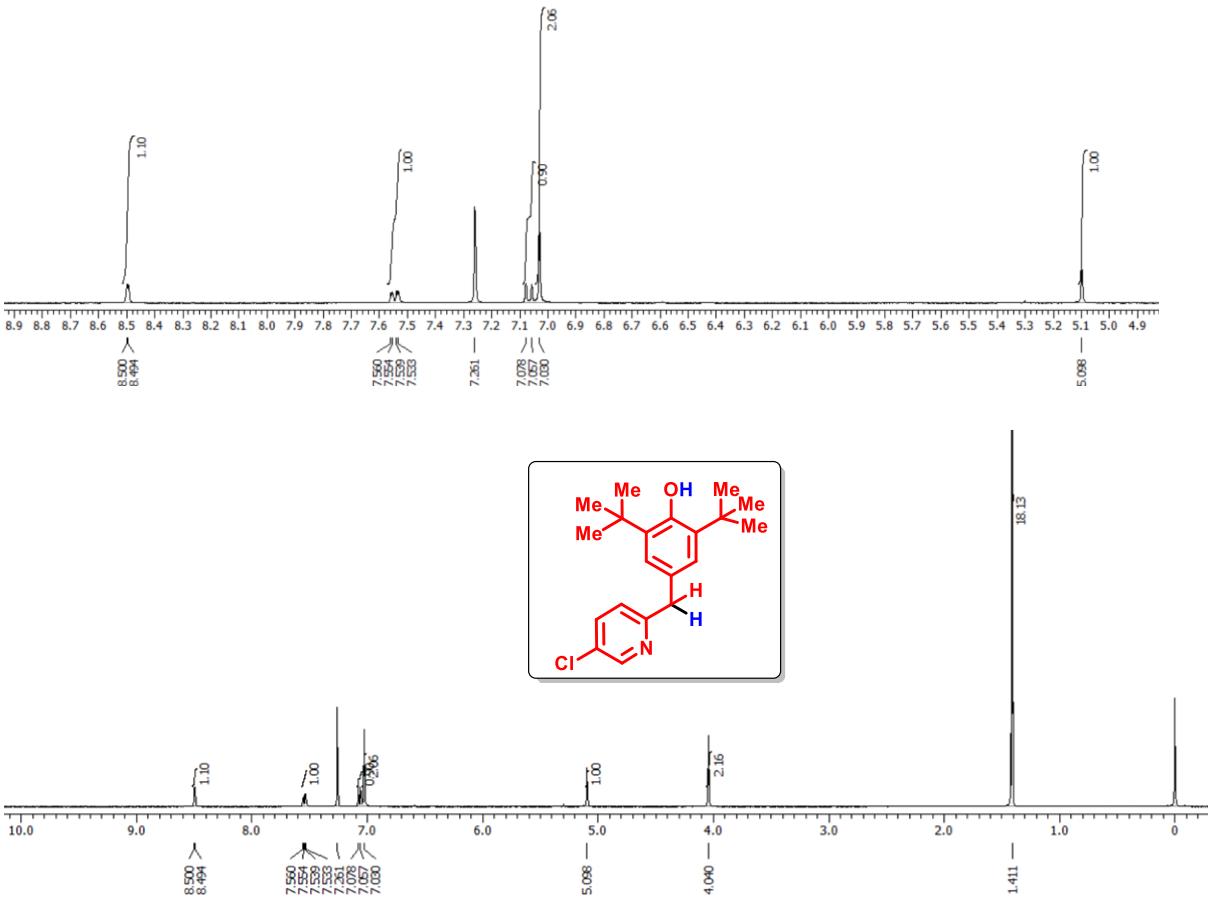

**General Procedure for synthesis of 10:** In a 10 mL oven-dried round bottom flask, *para*-quinone methide **1** (0.1 mmol, 1.0 equiv.), cyclohexadiene (in excess), was taken in 2 mL toluene. Then the reaction mixture was stirred at 100 °C for 12 h. When the reaction was completed, the reaction mixture was diluted with water (10 mL) and extracted with ethyl acetate. Then organic layer was washed with aqueous saturated brine solution and dried over $Na_2SO_4$ and concentrated under

reduced pressure. The crude material obtained was purified by column chromatography on silica gel (100−200) (hexane: ethyl acetate; 95/2) to afford the desired product 7**b** in 80% yield.

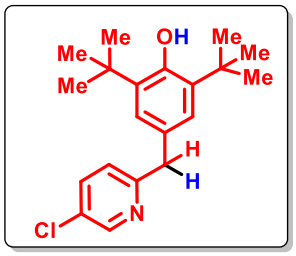


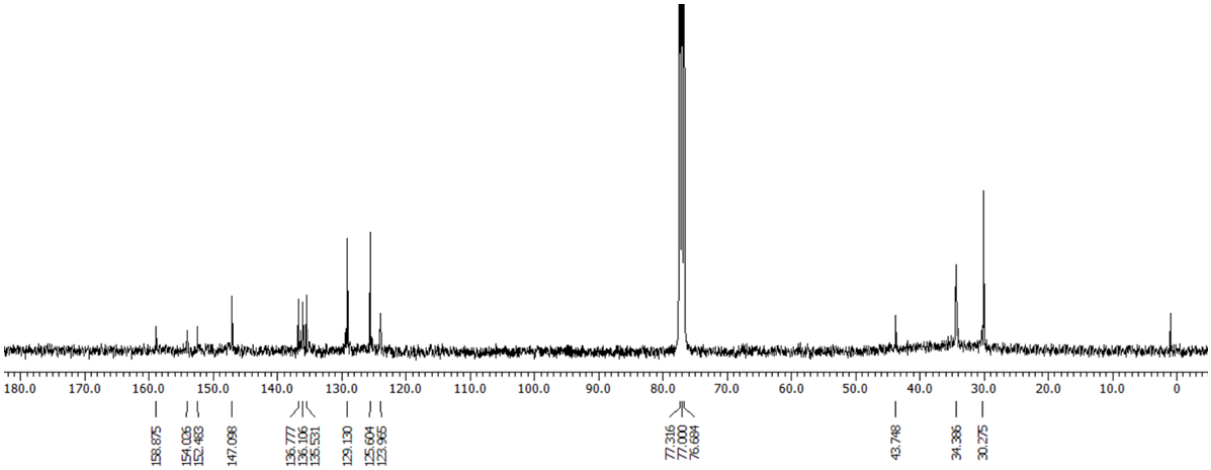

**2,6-di-tert-butyl-4-((5-chloropyridin-2-yl)methyl)phenol (7b).** The crude product was purified by column chromatography (hexane/EtOAc =97/03) to afford **7b** as a white solid (Yield: 90%); $^{1}$H-NMR (400 MHz, $CDCl_3$) $\delta$ 8.50 (d, J = 2.3 Hz, 1H), 7.55 (dd, J = 8.3, 2.4 Hz, 1H), 7.07 (d, J = 8.4 Hz, 1H), 7.03 (s, 2H), 5.10 (s, 1H), 4.04 (s, 2H), 1.41 (s, 18H); $^{13}$C-NMR (100 MHz, $CDCl_3$) δ 158.9, 154.0, 152.5, 147.1, 136.8, 136.1, 135.5, 129.1, 125.6, 124.0, 43.7, 34.4, 30.3; HRMS (ESI) $[M+H]^+$ Calcd for $[C_{20}H_{27}ClNO]$: 332.1781, found: 332.1794.

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

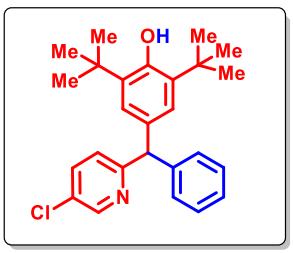


**$^{13}$C NMR (100 MHz, $CDCl_3$) (7b)**



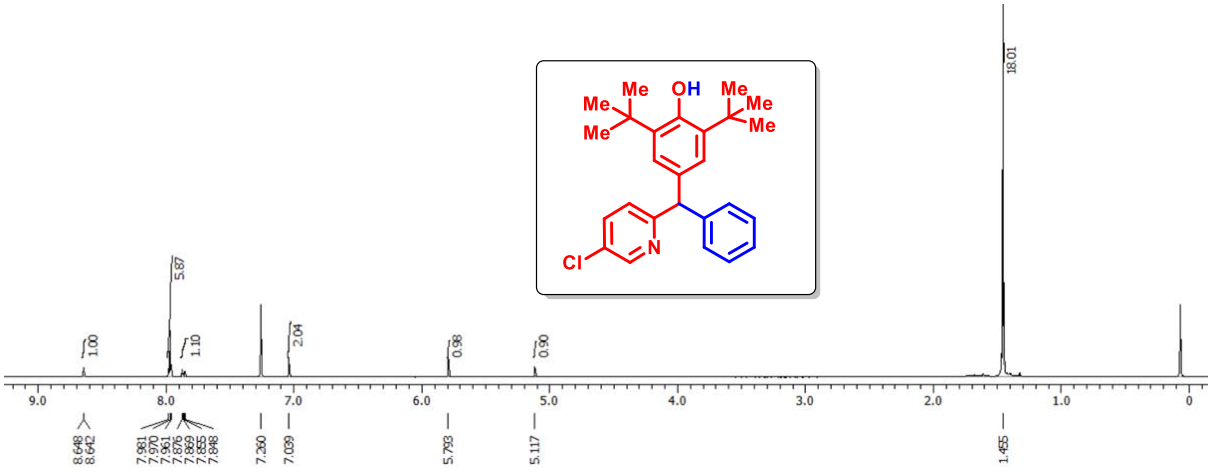

**General Procedure for synthesis of 7a:** In a 10 mL oven-dried round bottom flask, *para*-quinone methide **1** (0.2 mmol, 1.0 equiv), cyclohexadiene (in excess), was taken in 2 mL. toluene. Then the reaction mixture was stirred at 60 °C for 12 h. When the reaction was completed, the reaction mixture was diluted with water (10 mL) and extracted with ethyl acetate. Then organic layer was washed with aqueous saturated brine solution and dried over $Na_2SO_4$ and concentrated under reduced pressure. The crude material obtained was purified by column chromatography on silica gel (100−200) (hexane: ethyl acetate; 95/5) to afford the desired product **7a** in 68% yield.



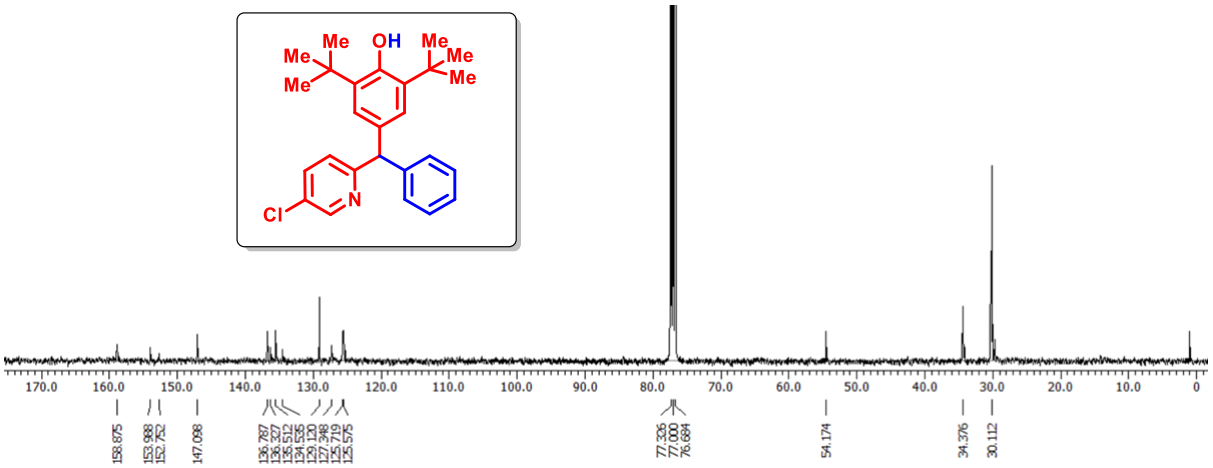

**2,6-di-tert-butyl-4-((5-chloropyridin-2-yl)(phenyl)methyl) phenol (7a).** The crude product was purified by column chromatography (hexane/ EtOAc =95/5) to afford **7a** as a white solid (Yield: 68%); $^1$H-NMR (400 MHz, $CDCl_3$) $\delta$ 8.65 (d, J = 2.1 Hz, 1H), 7.98-7.96 (m, 6H), 7.86 (dd, J = 8.4, 2.5 Hz, 1H), 7.04 (s, 2H), 5.79 (s, 1H), 5.12 (s, 1H), 1.46 (s, 18H);$^{13}$C-NMR (100 MHz, $CDCl_3$) $\delta$ 158.9, 154.0, 152.8, 147.1, 136.8, 136.3, 135.5,

134.5, 129.1, 127.3, 125.7, 125.6, 54.2, 34.4, 30.1; HRMS (ESI) $[M+H]^+$ Calcd for $[C_{26}H_{31}ClNO]$ : 408.2094, found : 408.2084.

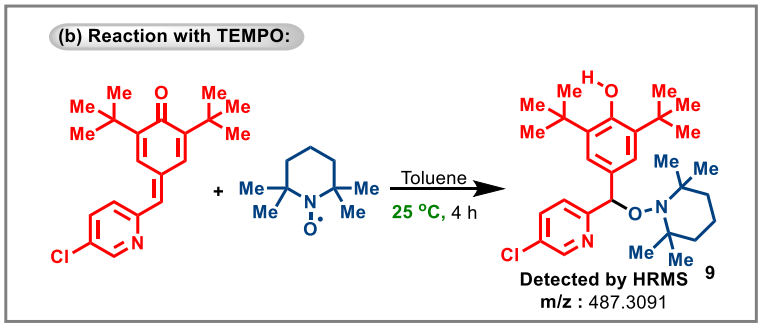
**$^1$H NMR (400 MHz, $CDCl_3$) (7a)**



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



**Reaction with TEMPO:**



In a 10 mL oven-dried round bottom flask, *para*-quinone methide **1** (0.2 mmol, 1.0 equiv.), TEMPO (0.6 mmol, 3.0 equiv.) was taken in 2 mL toluene. Then the reaction mixture was stirred at 25 °C. After the reaction was stirred for 4 h, the plausible adduct involved were detected by HRMS analysis of the reaction mixture.

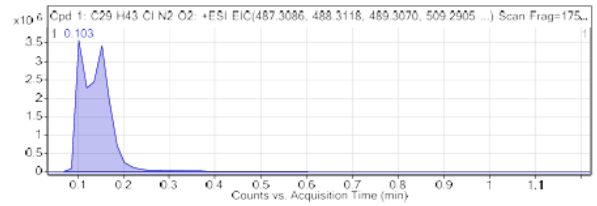
| | | | |
|---|---|---|---|
| **Data File** | TEMPO.d | **Sample Name** | TEMPO |
| **Sample Type** | Sample | **Position** | P1-A5 |
| **Instrument Name** | Instrument 1 | **User Name** | |
| **Acq Method** | MS Scan.m | **Acquired Time** | 30-05-2025 12:50:45 |
| **IRM Calibration Status** | Success | **DA Method** | Default.m |
| **Comment** | | | |

| | | | |
|---|---|---|---|
| **Sample Group** | | **Info.** | 3 |
| **Acquisition SW Version** | 6200 series TOF/6500 series Q-TOF B.05.01 (B5125) | | |

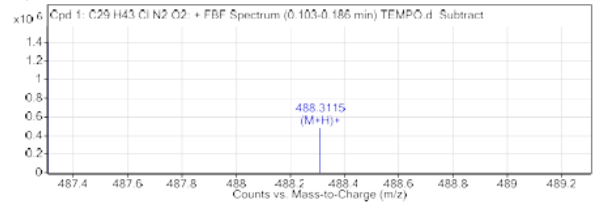
**Compound Table**

| Compound Label | RT | Mass | Abund | Formula | Tgt Mass | Diff (ppm) | MFG Formula | DB Formula |
|---|---|---|---|---|---|---|---|---|
| Cpd 1: C29 H43 Cl N2 O2 | 0.103 | 486.3007 | 1401754 | C29 H43 Cl N2 O2 | 486.3013 | -1.24 | C29 H43 Cl N2 O2 | C29 H43 Cl N2 O2 |

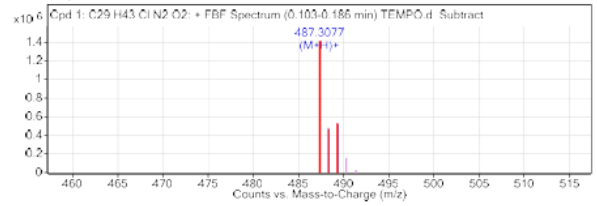
| Compound Label | *m/z* | RT | Algorithm | Mass |
|---|---|---|---|---|
| Cpd 1: C29 H43 Cl N2 O2 | 487.3077 | 0.103 | Find By Formula | 486.3007 |




MS Spectrum

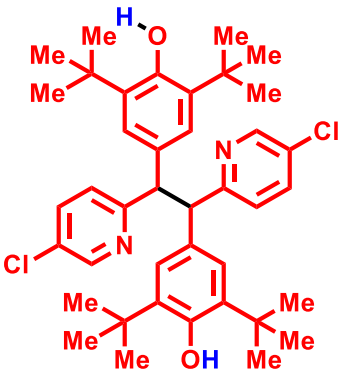



MS Zoomed Spectrum




**MS Spectrum Peak List**

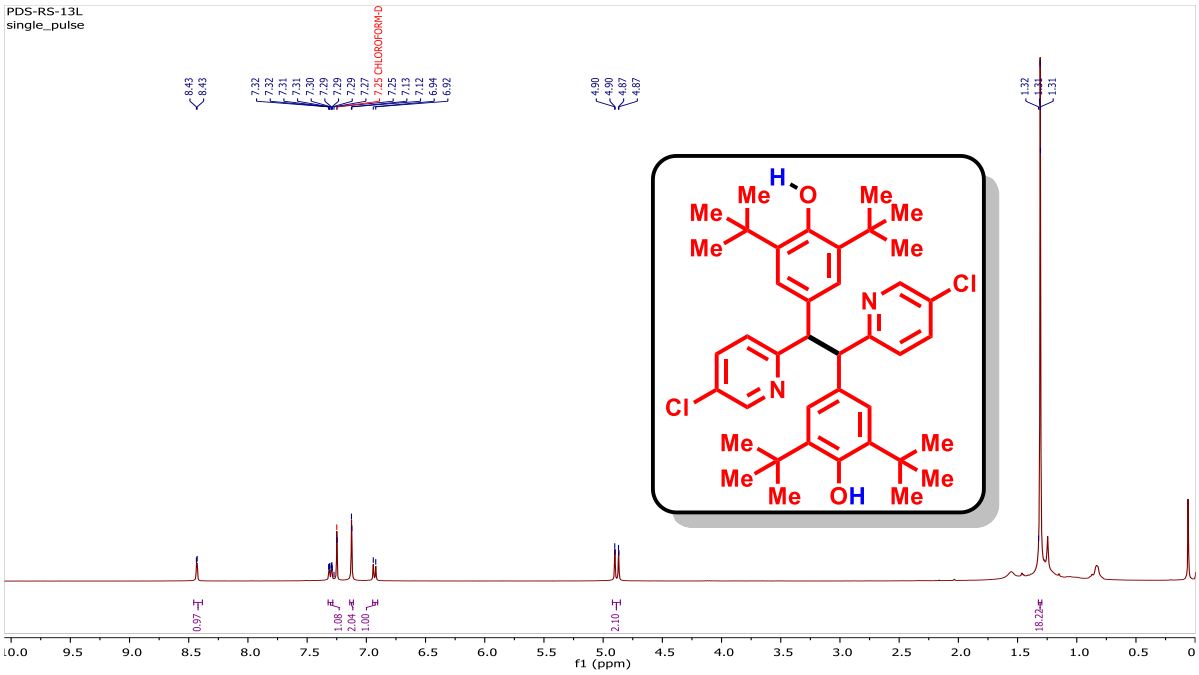
| *m/z* | z | Abund | Formula | Ion |
|---|---|---|---|---|
| 487.3077 | 1 | 1401754 | C29H44ClN2O2 | (M+H)+ |



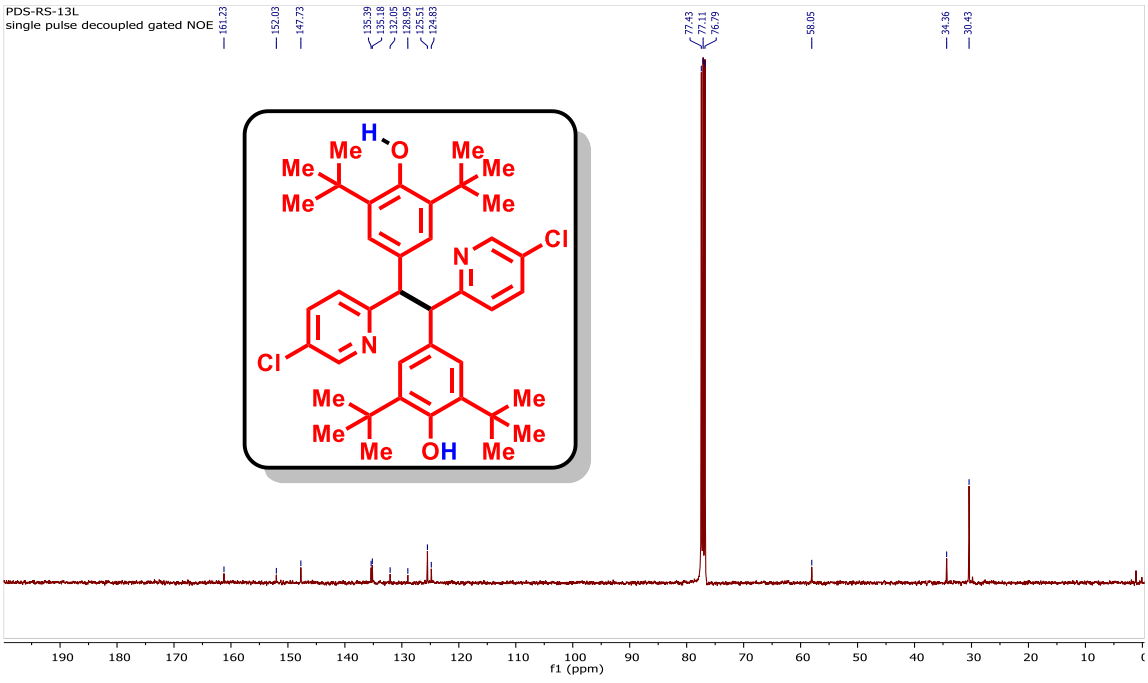

**4,4'-((1R,2R)-1,2-bis(5-chloropyridin-2-yl)ethane-1,2-diyl)bis(2,6-di-tert-butylphenol) (8).** The crude product was purified by column

chromatography (hexane/EtOAc = 96/4) to afford **8** as a white solid (Yield: 40%); $^{1}$H NMR (400 MHz, $CDCl_3$) $\delta$ = 8.432 (d, *J*=2.5, 1H), 7.303 (ddd, *J*=8.3, 2.7, 1.2, 1H), 7.124 (d, *J*=1.2, 2H), 6.931 (d, *J*=8.2, 1H), 4.885 (dd, *J*=12.6, 1.2, 2H), 1.308 (d, *J*=1.3, 18H).; $^{13}$C-NMR (100 MHz, $CDCl_3$) $\delta$ 161.23, 152.03, 147.73, 135.39, 135.18, 132.05, 128.95, 125.51, 124.83, 58.05, 34.36, 30.43.

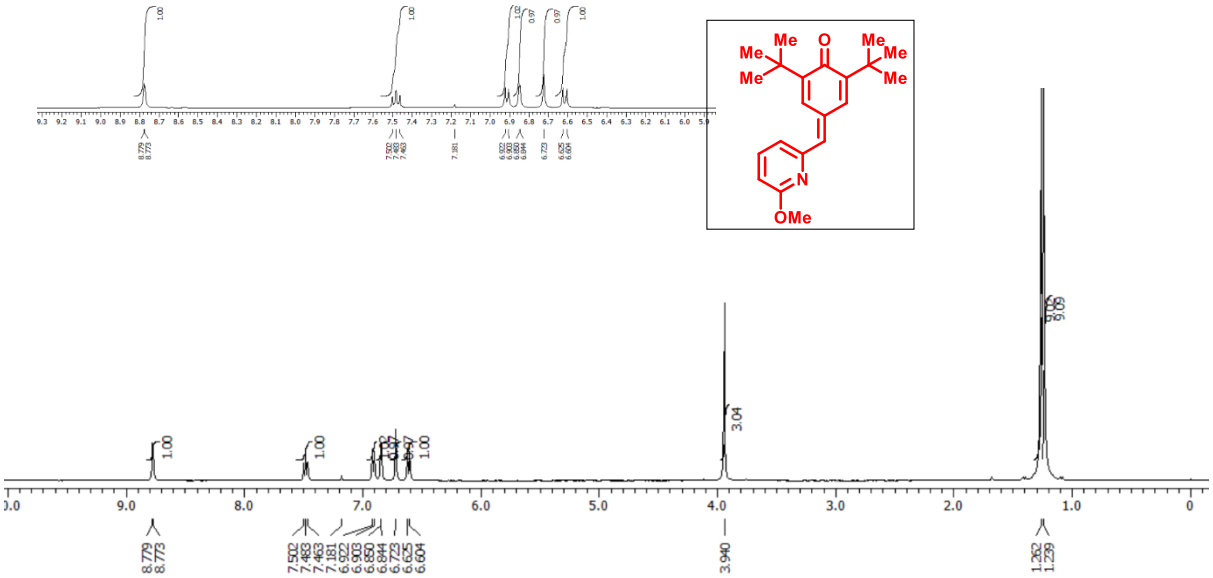
**$^{1}$H NMR (400 MHz, $CDCl_3$) (8)**



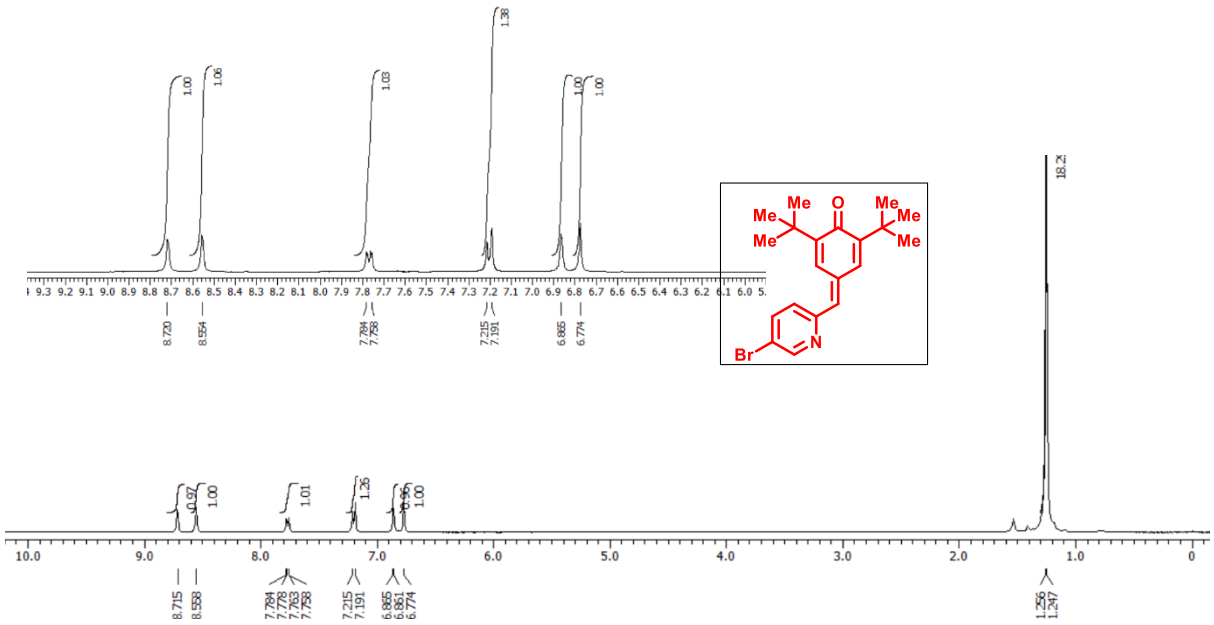

**$^{13}$C NMR (100 MHz, $CDCl_3$) (8)**



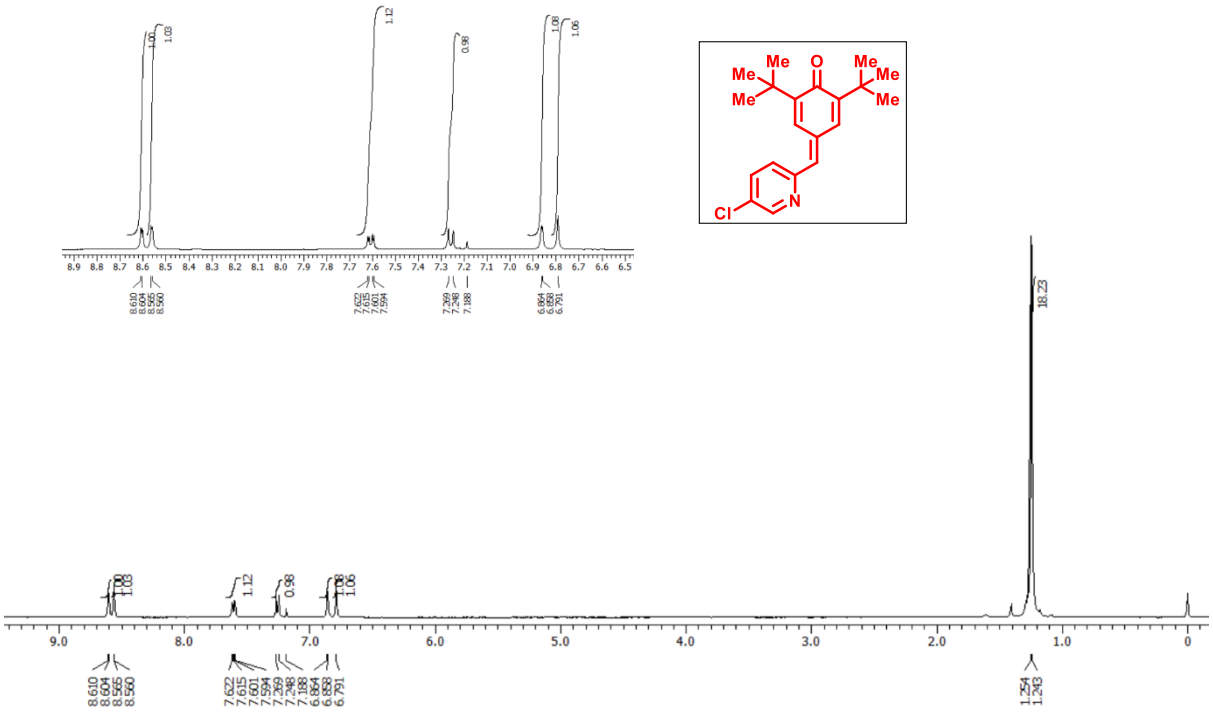
**$^1$H NMR (400 MHz, $CDCl_3$) data of bromo-substituted pyridine *p*-QM to ensure purity of the compound**



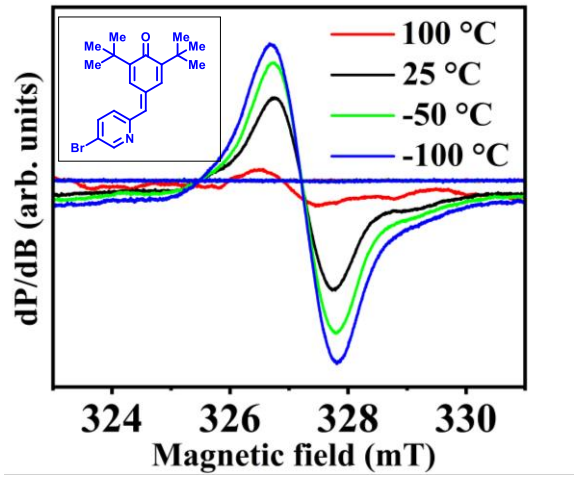
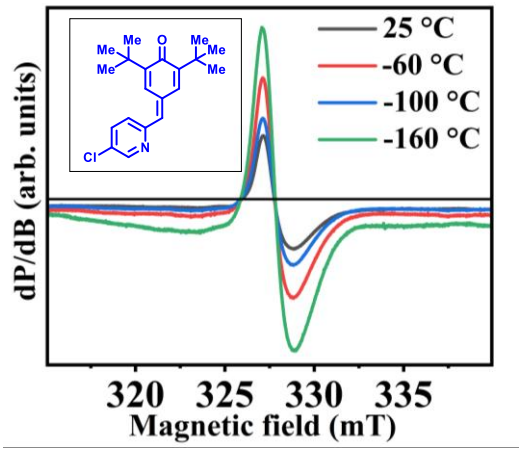

**$^1$H NMR (400 MHz, $CDCl_3$) data of methoxy-substituted pyridine *p*-QM**



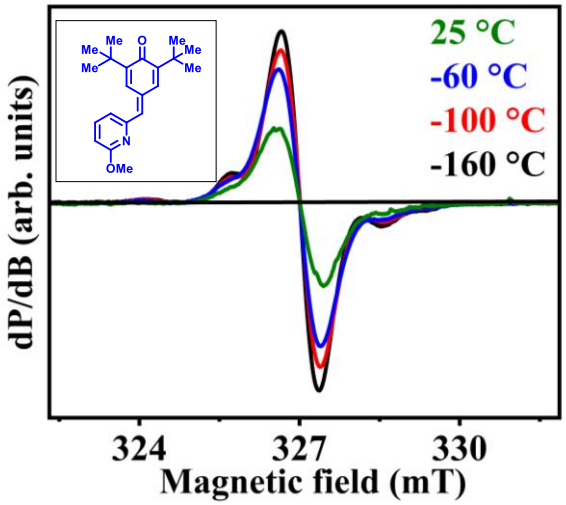
**$^1$H NMR (400 MHz, $CDCl_3$) data of chloro-substituted pyridine *p*-QM**



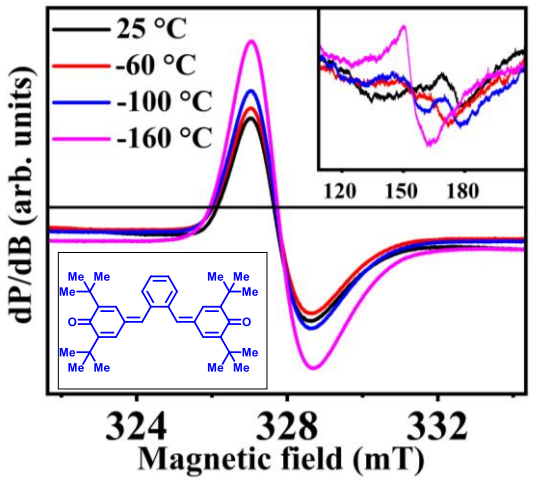

**EPR spectra of various compounds recorded at different temperatures are as follows:**

| (i) Temperature-dependent EPR spectra of bromo-substituted pyridine quinone methide in solid state : | (ii) Temperature-dependent EPR spectra of chloro-substituted pyridine quinone methide in solid state: |
|---|---|
|  |  |

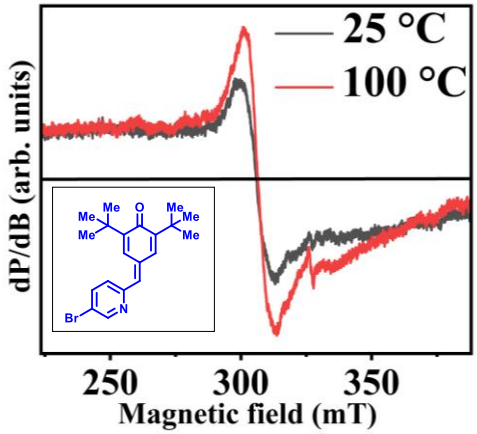
**(iii) Temperature-dependent EPR spectra of methoxy-substituted pyridine quinone methide in solid state:**



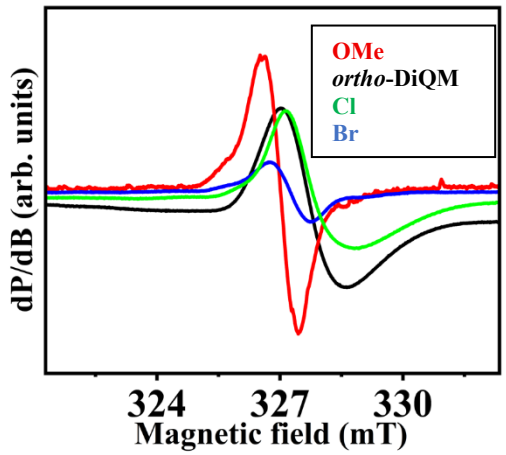

**(iv) Temperature-dependent EPR spectra of ortho di-substituted quinone methide in solid state:**



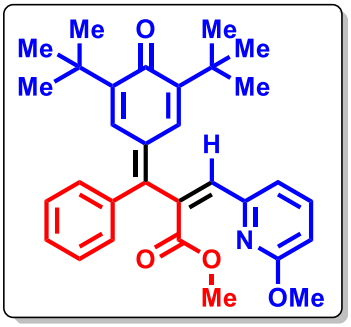

**(v) Temperature-dependent EPR spectra of bromo-substituted pyridine quinone methide in toluene:**



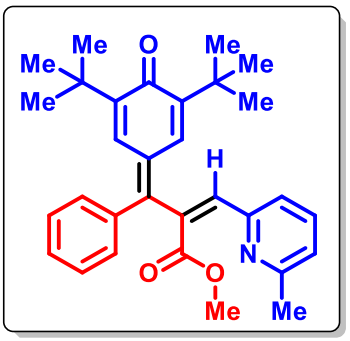

**(vi) Comparison of EPR spectra of different quinone methides at room temperature in solid state:**



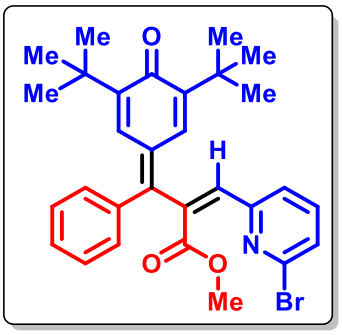
**Characterization data for the products:**



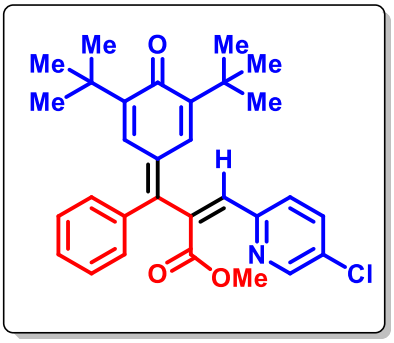

**Methyl (Z)-2-((3,5-di-tert-butyl-4-oxocyclohexa-2,5-dien-1-ylidene)(phenyl)methyl)-3-(6-methoxypyridin-2-yl)acrylate(3aa).** The crude product was purified by column chromatography (hexane/EtOAc = 98/2) to afford **3aa** as a yellow solid (Yield: 60%); m.p = 182-184 °C; $^{1}$H-NMR (400 MHz, $CDCl_3$) $\delta$ 7.59-7.56 (m, 2H), 7.42 (m, 5H), 7.02 (d, J = 2.6 Hz, 1H), 6.90 (d, J = 7.1 Hz, 1H), 6.71 (d, J = 8.2 Hz, 1H), 6.65 (s, 1H), 3.89 (s, 3H), 3.58 (s, 3H), 1.29 (s, 9H), 1.19 (s, 9H); $^{13}$C-NMR (100 MHz, $CDCl_3$) $\delta$ 186.6, 163.5, 151.3, 149.8, 148.0, 147.9, 138.9, 137.8, 137.5, 136.1, 132.3, 131.4, 131.2, 130.6, 129.4, 128.0, 118.6, 112.1, 53.6, 51.9, 35.4, 35.3, 29.7, 29.4**;** HRMS (ESI) $[M+H]^+$ Calcd for $[C_{31}H_{36}NO_4]$: 486.2644, found 486.2653.



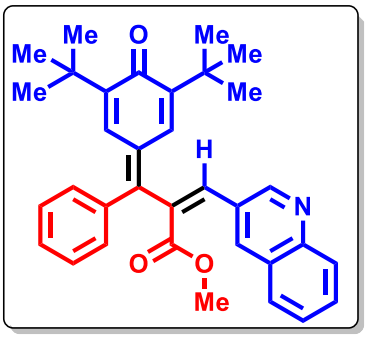

**Methyl (Z)-2-((3,5-di-tert-butyl-4-oxocyclohexa-2,5-dien-1-ylidene)(phenyl)methyl)-3-(6-methylpyridin-2-yl)acrylate (3ba).** The crude product was purified by column chromatography (hexane/EtOAc = 98/2) to afford **3ba** as a yellow sticky compound (Yield: 62%);$^{1}$H NMR (400 MHz, $CDCl_3$) $\delta$ 7.615 – 7.555 (m, 2H), 7.425 (s, 5H), 7.093 (d, J=7.1, 2H), 7.017 (d, J=2.6, 1H), 6.677 (s, 1H), 3.677 (s, 3H), 2.545 (s, 3H), 1.297 (s, 9H), 1.197 (s, 9H).; $^{13}$C-NMR (100 MHz, $CDCl_3$) $\delta$ 185.5, 167.8, 157.2, 146.9, 137.2, 135.7, 131.3, 130.5, 130.3, 129.4, 128.3, 127.0, 122.2, 120.9, 51.1, 34.5, 34.3, 28.6, 28.4, 23.6**;** HRMS (ESI) $[M+H]^+$ Calcd for $[C_{31}H_{36}NO_3]$ : 470.2690, found : 470.2707.



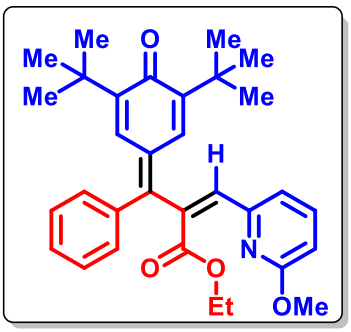

**Methyl (Z)-3-(6-bromopyridin-2-yl)-2-((3,5-di-tert-butyl-4-oxocyclohexa-2,5-dien-1-ylidene)(phenyl)methyl)acrylate (3ca).** The crude product was purified by column chromatography (hexane/EtOAc = 98/2) to afford **3ca** as a yellow sticky solid (Yield: 58%); $^{1}$H NMR (400 MHz, $CDCl_3$) $\delta$ 7.575 – 7.527 (m, 2H), 7.427 (s, 6H), 7.211 (d, *J*=7.5, 1H), 7.006 (d, *J*=2.6, 1H), 6.578 (s, 1H), 3.792 (s, 3H), 1.302 (s, 9H), 1.265 (s, 9H); $^{13}$C NMR (100 MHz, $CDCl_3$) $\delta$ 186.7, 168.4, 153.4, 150.1, 148.4, 141.9, 139.2, 138.9, 138.1, 135.7, 132.8, 131.6, 131.4, 130.3, 129.6, 128.3, 128.0, 123.6, 52.7, 35.7, 35.5, 29.8, 29.6**;** HRMS (ESI) $[M+H]^+$ Calcd for $[C_{30}H_{33}BrNO_3]$: 534.1638, found: 534.1673, 536.1656.



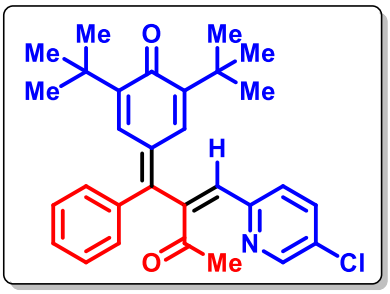

**Methyl (Z)-3-(5-chloropyridin-2-yl)-2-((3,5-di-tert-butyl-4-oxocyclohexa-2,5-dien-1-ylidene)(phenyl)methyl)acrylate (3da)**. The crude product was purified by column chromatography (hexane/EtOAc = 96/4) to afford **3da** as a yellow sticky solid (Yield: 61%); $^{1}$H NMR (400 MHz, $CDCl_3$) $\delta$ 8.542 (d, *J*=2.5, 1H), 7.657 (dd, *J*=8.3, 2.5, 1H), 7.530 (d, *J*=2.7, 1H), 7.405 (d, *J*=1.2, 5H), 7.230 (d, *J*=8.3, 1H), 7.004 (d, *J*=2.6, 1H), 6.666 (s, 1H), 3.638 (s, 3H), 1.269 (s, 9H), 1.179 (s, 9H). $^{13}$C NMR (100 MHz, $CDCl_3$) $\delta$ 186.6, 168.6, 150.8, 150.3, 148.8, 148.4, 148.3, 138.1, 137.9, 136.9, 136.3, 132.6, 131.9, 131.5, 131.3, 130.3, 129.5, 128.3, 125.3, 52.3, 35.6, 35.4, 29.7, 29.5. HRMS (ESI) $[M+H]^+$ Calcd for $[C_{30}H_{33}ClNO_3]$: 490.2143, found: 490.2176.



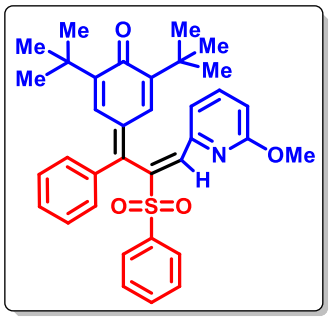

**Methyl (Z/E)-2-((3,5-di-tert-butyl-4-oxocyclohexa-2,5-dien-1-ylidene)(phenyl)methyl)-3-(quinolin-3-yl)acrylate (3ea).** The crude product was purified by column chromatography (hexane/EtOAc = 96/4) to afford **3ea** as a yellow sticky solid (Yield: 55%, mixture of Z:E isomer); $^{1}$H-NMR (400 MHz, $CDCl_3$) $\delta$ 8.99 (d, J = 2.1 Hz, 1H), 8.91 (d, J = 2.2 Hz, 0.4H), 8.27 (d, J = 1.9 Hz, 1H), 8.15 (d, J = 2.2 Hz, 2H), 8.12 (d, J = 8.5 Hz, 1H), 8.01 (d, J = 8.5 Hz, 1H), 7.85 (d, J = 8.1 Hz, 0.4H), 7.79-7.75 (m, 1H), 7.73-7.69 (m, 1H), 7.65 (d, J = 8.1 Hz, 1H), 7.62-7.58 (m, 1H), 7.53 (s, 2H), 7.44 (d, J = 4.3 Hz, 3H), 7.43-7.41 (m, 1H), 7.39-7.36 (m, 3H), 7.12 (dd, J = 4.2, 2.7 Hz, 2H), 7.05 (s, 1H), 6.71 (s, 0.3H), 3.74 (s, 3H), 3.58 (s, 1.5H), 1.28 (s, 4H), 1.24 (s, 9H), 1.22 (s, 4H), 1.05 (s, 9H); $^{13}$C-NMR (100 MHz, $CDCl_3$) $\delta$ 186.2, 167.0, 150.9, 150.2, 149.1, 148.4, 147.7, 146.7, 139.3, 137.5, 136.2, 135.9, 133.3, 132.2, 131.8, 131.4, 131.2, 130.7, 129.9, 129.5, 129.2, 128.4, 127.5, 127.4, 52.9, 52.5, 35.6, 35.3, 29.3, 29.4HRMS (ESI) $[M+H]^+$ Calcd for $[C_{34}H_{36}NO_3]$: 506.2690, found: 506.2731.



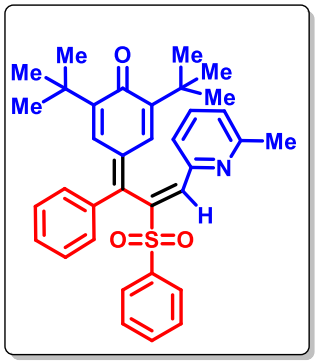

**ethyl (Z)-2-((3,5-di-tert-butyl-4-oxocyclohexa-2,5-dien-1-ylidene)(phenyl)methyl)-3-(6-methoxypyridin-2-yl)acrylate (3ab)**. The crude product was purified by column chromatography (hexane/EtOAc = 97/3) to afford **3ab** as a yellow sticky solid (Yield: 62%) $^{1}$H NMR (400 MHz, $CDCl_3$) $\delta$ 7.640 – 7.546 (m, 2H), 7.424 (s, 5H), 7.051 (d, *J*=2.6, 1H), 6.932 (d, *J*=7.2, 1H), 6.723 (d, *J*=8.3, 1H), 6.678 (s, 1H), 4.051 (q, *J*=7.1, 2H), 3.886 (s, 3H), 1.255 (d, *J*=37.0, 18H), 0.904 (t, *J*=7.1, 3H); $^{13}$C NMR (100 MHz, $CDCl_3$) $\delta$ 186.6, 167.6, 163.4, 151.6, 149.9, 148.0, 147.8, 138.9, 137.6, 137.3, 136.2, 132.3, 131.5, 131.1, 130.8, 129.4, 127.9, 118.5, 111.9, 60.8, 53.5, 35.4, 35.3, 29.6, 29.4, 13.7**;** HRMS (ESI) $[M+H]^+$ Calcd for $[C_{32}H_{38}NO_4]$: 500.2795, found: 500.2823.



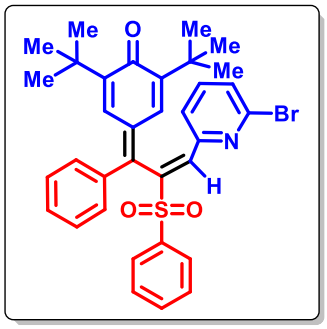

**(Z)-2,6-di-tert-butyl-4-(3-oxo-1-phenyl-2-(pyridin-2-ylmethylene)butylidene)cyclohexa-2,5-dien-1-one (3dc)**. The crude product was purified by column chromatography (hexane/EtOAc = 98/2) to afford **3dc** as a yellow sticky solid (Yield: 68%); $^{1}$H NMR (400 MHz, $CDCl_3$) $\delta$ 8.510 (d, *J*=2.5, 1H), 7.676 (dd, *J*=8.3, 2.5, 1H), 7.533 (d, *J*=2.6, 1H), 7.451 – 7.400 (m, 3H), 7.386 – 7.315 (m, 2H), 7.249 (s, 1H), 7.029 (d, *J*=2.6, 1H), 6.571 (s, 1H), 2.121 (s, 3H), 1.265 (s, 9H), 1.184 (s, 9H); $^{13}$C NMR (100 MHz, $CDCl_3$) $\delta$ 186.5, 150.7, 150.7, 148.5, 148.4, 148.2, 147.2, 136.7, 136.5, 132.4, 132.3, 131.6, 131.2, 130.7, 129.6, 128.3, 125.0, 77.3, 77.0, 76.7, 35.4, 35.4, 31.2, 29.5, 29.4**;** HRMS (ESI) $[M+H]^+$ Calcd for $[C_{30}H_{33}ClNO_2]$: 474.2194, found: 474.2203.



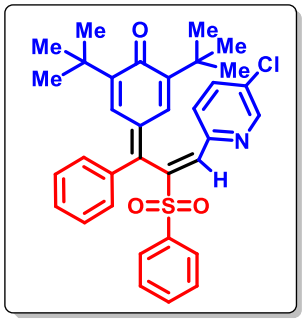

***(E)*-2,6-di-tert-butyl-4-(3-(6-methoxypyridin-2-yl)-1-phenyl-2-(phenylsulfonyl)allylidene)cyclohexa-2,5-dien-1-one (5aa).** The crude product was purified by column chromatography (hexane/EtOAc =83/17) to afford **5aa** as a yellow solid (Yield: 75%); m.p = 175-176 °C .$^{1}$H NMR (400 MHz, $CDCl_3$) $\delta$ 8.042 (s, 1H), 7.621 – 7.536 (m, 3H), 7.417 (t, *J*=7.4, 1H), 7.325 – 7.169 (m, 8H), 7.136 (d, *J*=7.2, 1H), 6.845 (d, *J*=2.6, 1H), 6.658 (d, *J*=8.4, 1H), 3.284 (s, 3H), 1.145 (s, 9H), 1.006 (s, 9H); 13C NMR (100 MHz, $CDCl_3$) $\delta$ 186.3, 163.6, 148.7, 148.3, 148.2, 144.2, 143.7, 139.5, 139.4, 139.1, 136.6, 133.3, 132.4, 131.4, 130.3, 129.8, 129.3, 128.9, 128.4, 128.0, 121.2, 113.6, 53.6, 35.4, 35.1, 29.6, 29.4; HRMS (ESI) $[M+H]^+$ Calcd for $[C_{35}H_{38}NO_4S]$: 568.2522, found: 568.2534.



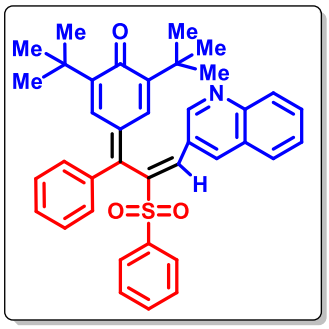

**(*E*)-2,6-di-*tert*-butyl-4-(3-(6-methylpyridin-2-yl)-1-phenyl-2-(phenylsulfonyl)allylidene)cyclohexa-2,5-dien-1-one (5ba).** The crude product was purified by column chromatography (hexane/EtOAc =85/15) to afford **5ba** as a yellow solid (Yield: 74%); m.p = 170-172 °C; $^{1}$H-NMR (400 MHz, $CDCl_3$) $\delta$ 8.17 (s, 1H), 7.61 (d, J = 8.5 Hz, 2H), 7.52-7.43 (m, 2H), 7.34-7.23 (m, 8H + residual $CDCl_3$), 7.20 (d, J = 2.5 Hz, 1H), 7.01 (d, J = 7.8 Hz, 1H), 6.75 (d, J = 2.6 Hz, 1H), 2.26 (s, 3H), 1.17 (s, 9H), 0.98 (s, 9H); $^{13}$C-NMR (100 MHz, $CDCl_3$) $\delta$ 186.1, 158.8, 150.6, 148.5, 148.0, 144.1, 143.5, 140.9, 139.3, 136.6, 136.3, 133.2, 132.8, 131.3, 130.0, 130.0, 129.2, 128.9, 128.3, 128.0, 123.9, 122.5, 35.3, 34.9, 29.5, 29.2, 24.1 HRMS (ESI) $[M+H]^+$ Calcd for $[C_{35}H_{38}NO_3S]$: 552.2572, found: 552.2573.



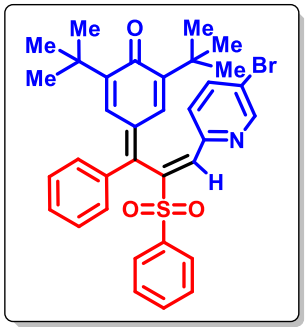

**(*E*)-4-(3-(6-bromopyridin-2-yl)-1-phenyl-2-(phenylsulfonyl)allylidene)-2,6-di-tert-butylcyclohexa-2,5-dien-1-one (5ca).** The crude product was purified by column chromatography (hexane/EtOAc =85/15) to afford **5ca** as a yellow solid (Yield: 63%); m.p = 218-220 °C; $^{1}$H-NMR (400 MHz, $CDCl_3$) $\delta$ 8.11 (s, 1H), 7.61 (d, J = 7.6 Hz, 2H), 7.51-7.46 (m, 2H), 7.41 (d, J = 7.6 Hz, 1H), 7.35-7.26 (m, 8H), 7.20 (d, J = 2.3 Hz, 1H), 6.70 (d, J = 2.3 Hz, 1H), 1.18 (s, 9H), 1.00 (s, 9H); $^{13}$C-NMR (100 MHz, $CDCl_3$) $\delta$ 186.2, 152.2, 148.8, 148.4, 146.4, 142.2, 142.1, 138.9, 138.7, 138.4, 135.9, 133.5, 133.3, 131.2, 130.0, 129.5, 129.4, 129.0, 128.8, 128.4, 128.1, 124.0, 35.3, 35.0, 29.5, 29.3; HRMS (ESI) $[M+H]^+$ Calcd for $[C_{34}H_{35}BrNO_3S]$: 616.1521, found: 616.1544.



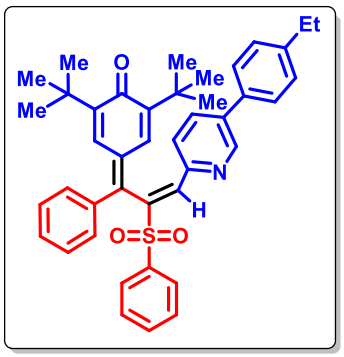

**(E)-2,6-di-tert-butyl-4-(3-(5-chloropyridin-2-yl)-1-phenyl-2-(phenylsulfonyl)allylidene)cyclohexa-2,5-dien-1-one (5da).** The crude product was purified by column chromatography (hexane/EtOAc =85/15) to afford **5da** as a yellow solid (Yield: 70%); m.p = 192-194 °C; $^{1}$H-NMR (400 MHz, $CDCl_3$) $\delta$ 8.45 (d, J = 1.8 Hz, 1H), 8.17 (s, 1H), 7.61-7.58 (m, 3H), 7.47-7.44 (m, 1H), 7.41 (d, J = 8.4 Hz, 1H), 7.33-7.22 (m, 8H + residual $CDCl_3$), 6.77 (d, J = 2.5 Hz, 1H), 1.20 (s, 9H), 1.02 (s, 9H);$^{13}$C-NMR (100 MHz, $CDCl_3$) $\delta$ 186.0, 149.6, 149.2, 148.9, 148.6, 145.3, 142.2, 139.2, 139.0, 136.2, 135.9, 133.4, 132.9, 132.9, 131.3, 129.6, 129.4, 129.0, 128.4, 128.2, 125.5, 35.4, 35.0, 29.5, 29.3, HRMS (ESI) $[M+H]^+$ Calcd for $[C_{34}H_{35}ClNO_3S]$: 572.2026, found: 572.2059.



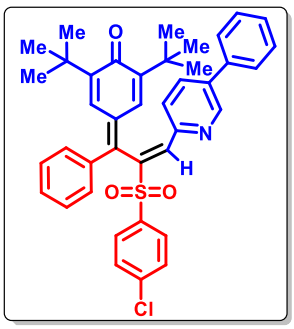

**(E)-2,6-di-tert-butyl-4-(1-phenyl-2-(phenylsulfonyl)-3-(quinolin-3-yl)allylidene)cyclohexa-2,5-dien-1-one (5ea).** The crude product was purified by column chromatography (hexane/EtOAc =75/25) to afford **5ea** as a yellow solid (Yield: 65%); m.p = 224-228 °C; $^{1}$H-NMR (400 MHz, $CDCl_3$) $\delta$ 9.04 (d, J = 1.8 Hz, 1H), 8.32 (s, 1H), 8.25 (d, J = 1.6 Hz, 1H), 8.02 (d, J = 8.5 Hz, 1H), 7.76-7.72 (m, 1H), 7.67-7.62 (m, 4H), 7.54 (t, J = 7.5 Hz, 1H), 7.47 (t, J = 7.4 Hz, 1H), 7.35-7.24 (m, 7H + residual $CDCl_3$), 6.87 (d, J = 2.5 Hz, 1H), 1.21 (s, 9H), 0.94 (s, 9H); $^{13}$C-NMR (100 MHz, $CDCl_3$) $\delta$ 185.9, 150.2, 149.7, 149.5, 148.3, 143.1, 141.4, 139.1, 138.1, 137.8, 135.6, 134.0, 133.5, 131.5, 131.0, 129.8, 129.4, 129.3, 129.0, 128.4, 128.4, 127.7, 127.3, 125.7, 35.5, 35.1, 29.5, 29.2; HRMS (ESI) $[M+H]^+$ Calcd for $[C_{38}H_{38}NO_3S]$: 588.2572, found: 588.2587.



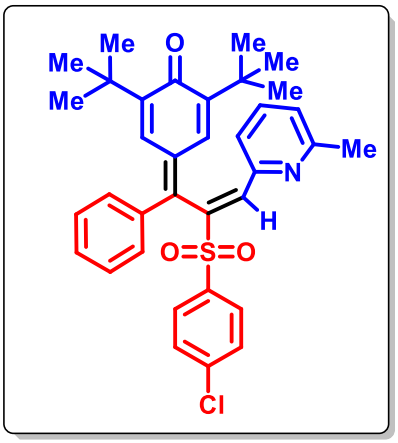

**(*E*)-4-(3-(5-bromopyridin-2-yl)-1-phenyl-2-(phenylsulfonyl)allylidene)-2,6-*di-tert*-butylcyclohexa-2,5-dien-1-one (5fa).** The crude product was purified by column chromatography (hexane/EtOAc =85/15) to afford **5fa** as a yellow solid (Yield: 72%); m.p = 214-216 °C; $^{1}$H-NMR (400 MHz, $CDCl_3$) $\delta$ 8.57 (d, J = 2.0 Hz, 1H), 8.14 (s, 1H), 7.75 (dd, J = 8.4, 2.4 Hz, 1H), 7.60 (d, J = 7.8 Hz, 2H), 7.46 (t, J = 7.4 Hz, 1H), 7.36-7.22 (m, 9H + residual $CDCl_3$), 6.77 (d, J = 2.5 Hz, 1H), 1.20 (s, 9H), 1.02 (s, 9H); $^{13}$C-NMR (100 MHz, $CDCl_3$) $\delta$ 186.1, 151.5, 150.0, 149.0, 148.7, 145.5, 142.2, 139.3, 139.2, 139.0, 135.9, 133.5, 133.0, 131.3, 129.6, 129.5, 129.4, 129.0, 128.5, 128.2, 125.9, 121.9, 35.5, 35.1, 29.6, 29.3; HRMS (ESI) $[M+H]^+$ Calcd for$[C_{34}H_{35}BrNO_3S]$: 616.1521, found: 616.1512.



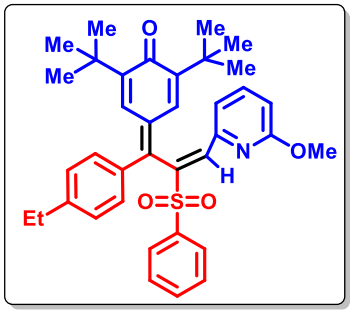

**(*E*)-2,6-di-tert-butyl-4-(3-(5-(4-ethylphenyl)pyridin-2-yl)-1-phenyl-2-(phenylsulfonyl)allylidene)cyclohexa-2,5-dien-1-one (5ga)** The crude product was purified by column chromatography (hexane/EtOAc =85/15) to afford **5ga** as a yellow solid (Yield: 77%); m.p = 196-198 °C; $^{1}$H-NMR (400 MHz, $CDCl_3$) $\delta$ 8.76 (d, J = 1.9 Hz, 1H), 8.26 (s, 1H), 7.77 (dd, J = 8.1, 2.3 Hz, 1H), 7.63-7.58 (m, 3H), 7.52-7.43 (m, 5H), 7.39-7.26 (m, 8H + residual $CDCl_3$), 6.83 (d, J = 2.5 Hz, 1H), 2.68 (q, J = 7.6 Hz, 2H), 1.20 (s, 9H), 0.99 (s, 9H), 0.90-0.87 (m, 3H); $^{13}$C-NMR (100 MHz, $CDCl_3$) $\delta$ 186.1, 149.9, 148.6, 145.2, 144.1, 142.8, 140.8, 134.2, 133.3, 133.0, 131.4, 129.9, 129.5, 129.4, 128.9, 128.8, 128.5, 128.3, 128.2, 127.0, 124.8, 35.4, 35.1, 29.5, 29.3, 28.5, 15.5; HRMS (ESI) $[M+H]^+$ Calcd for $[C_{42}H_{44}NO_3S]$: 642.3042, found: 642.3056.



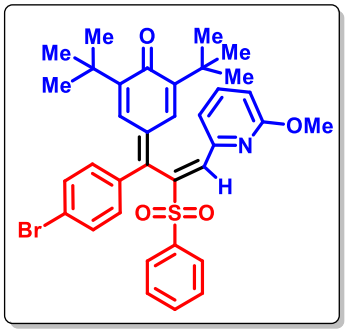

**(*E*)-2,6-di-*tert*-butyl-4-(2-((4-chlorophenyl)sulfonyl)-1-phenyl-3-(5-phenylpyridin-2-yl)allylidene)cyclohexa-2,5-dien-1-one (5hb)** The crude product was purified by column chromatography (hexane/EtOAc =85/15) to afford **5hb** as a yellow solid (Yield: 80%); m.p = 202-204 °C; $^{1}$H-NMR (400 MHz, $CDCl_3$) $\delta$ 8.78 (s, 1H), 8.26 (s, 1H), 7.81 (dd, J = 8.0, 1.8 Hz, 1H), 7.55-7.49 (m, 5H), 7.47-7.40 (m, 3H), 7.34-7.23 (m, 8H + residual $CDCl_3$), 6.90 (d, J = 1.9 Hz, 1H), 1.21 (s, 9H), 1.04 (s, 9H); $^{13}$C-NMR (100 MHz, $CDCl_3$) $\delta$ 186.1, 150.0, 149.0, 148.7, 144.0, 142.2, 140.9, 140.0, 137.9, 137.1, 136.6, 135.9, 134.6, 133.2, 131.3, 129.7, 129.4, 129.3, 129.2, 129.1, 128.7, 128.2, 127.0, 125.0, 35.4, 35.1, 29.5, 29.3; HRMS (ESI) $[M+H]^+$ Calcd for $[C_{40}H_{39}ClNO_3S]$: 648.2339, found: 648.2351.



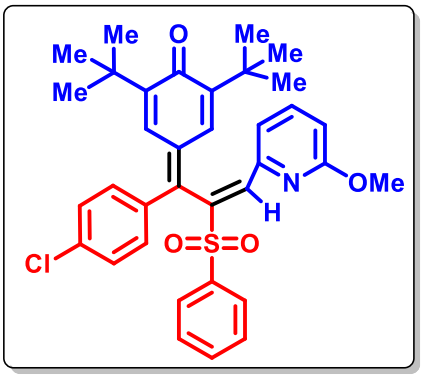

**(E)-2,6-di-tert-butyl-4-(3-(6-methylpyridin-2-yl)-1-phenyl-2-(phenylsulfonyl)allylidene)cyclohexa-2,5-dien-1-one (5bb).** The crude product was purified by column chromatography (hexane/EtOAc = 85/15) to afford **5bb** as a yellow solid (Yield: 78%); m.p. = 199-200 °C; 1H NMR (400 MHz, $CDCl_3$) $\delta$ 8.085 (s, 1H), 7.511 – 7.294 (m, 3H), 7.326 – 7.076 (m, 9H + residual $CDCl_3$), 6.953 (d, $J$ =7.8, 1H), 6.740 (d, $J$ =2.6, 1H), 2.184 (s, 3H), 1.107 (s, 9H), 0.943 (s, 9H); $^{13}$C NMR (100 MHz, $CDCl_3$) $\delta$ 186.2, 158.9, 150.5, 148.7, 148.3, 143.9, 143.0, 141.1, 139.9, 138.0, 136.8, 136.2, 133.1, 131.3, 129.9, 129.9, 129.8, 129.2, 129.2, 128.13, 124.1, 122.7, 35.4, 35.0, 29.5, 29.3, 24.2**;** HRMS (ESI) $[M+H]^+$ Calcd for $[C_{35}H_{38}NO_3S]$: 586.2177, found: 586.2179.



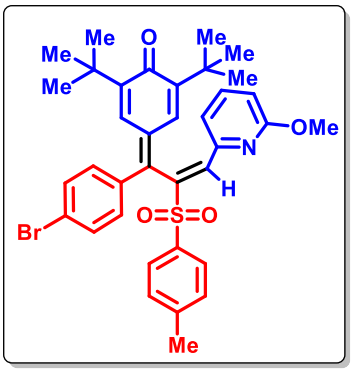

**(E)-2,6-di-tert-butyl-4-(1-(4-ethylphenyl)-3-(6-methoxypyridin-2-yl)-2-(phenylsulfonyl)allylidene)cyclohexa-2,5-dien-1-one(5ab).** The crude product was purified by column chromatography (hexane/EtOAc =82/18) to afford **5ab** as a yellow solid (Yield: 72%); m.p = 212-214 °C; $^{1}$H-NMR (400 MHz, $CDCl_3$) $\delta$ 8.05 (s, 1H), 7.61-7.54 (m, 3H), 7.43-7.39 (m, 1H), 7.29-7.24 (m, 3H + residual $CDCl_3$), 7.19 (d, $J$ = 8.2 Hz, 2H), 7.14 (d, $J$ = 7.0 Hz, 1H), 7.01 (d, $J$ = 8.1 Hz, 2H), 6.90 (d, $J$ = 2.5 Hz, 1H), 6.66 (d, J = 8.0 Hz, 1H), 3.31 (s, 3H), 2.62 (q, $J$ = 7.6 Hz, 2H), 1.24 (t, $J$ = 7.6 Hz, 3H), 1.17 (s, 9H), 1.04 (s, 9H); $^{13}$C-NMR (100 MHz, $CDCl_3$) $\delta$ 186.2, 163.5, 148.7, 148.0, 147.9, 145.5, 144.4, 143.8, 139.5, 139.2, 139.0, 133.6, 133.0, 131.9, 131.4, 130.3, 129.8, 128.8, 128.3, 127.5, 120.9, 113.4, 53.6, 35.3, 35.0, 29.5, 29.3, 28.6, 15.2; HRMS (ESI) $[M+H]^+$ Calcd for $[C_{37}H_{41}NO_4S]$: 596.2835, found: 596.2852.



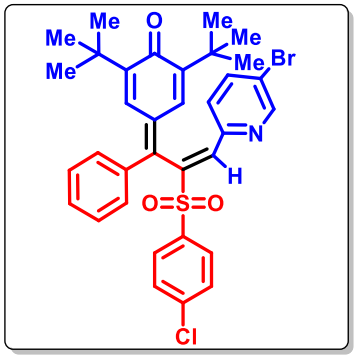

**(*E*)-4-(1-(4-bromophenyl)-3-(6-methoxypyridin-2-yl)-2-(phenylsulfonyl)allylidene)-2,6-di-tert-butylcyclohexa-2,5-dien-1-one (5ac).** The crude product was purified by column chromatography (hexane/EtOAc =82/18) to afford **5ac** as a yellow solid (Yield: 69%); m.p = 234-236 °C; $^{1}$H-NMR (400 MHz, $CDCl_3$) $\delta$ 8.04 (s, 1H), 7.63 (t, $J$ = 7.8 Hz, 1H), 7.48 (d, $J$ = 8.8 Hz, 2H), 7.36 (d, $J$ = 8.3 Hz, 2H), 7.29 (d, $J$ = 8.5 Hz, 3H), 7.18-7.14 (m, 4H), 6.84 (d, $J$ = 2.5 Hz, 1H), 6.70 (d, $J$ = 8.3 Hz, 1H), 3.30 (s, 3H), 1.17 (s, 9H), 1.03 (s, 9H); $^{13}$C-NMR (100 MHz, $CDCl_3$) $\delta$ 186.1, 163.6, 148.9, 148.7, 148.3, 142.9, 141.9, 140.3, 139.9, 139.2, 137.9, 135.4, 132.7, 131.3, 129.6, 129.3, 128.9, 123.9, 121.4, 114.0, 53.6, 35.4, 35.1, 29.5, 29.3; HRMS (ESI) $[M+H]^+$ Calcd for $[C_{35}H_{36}BrNO_4S]$: 680.1237, found: 680.1246.



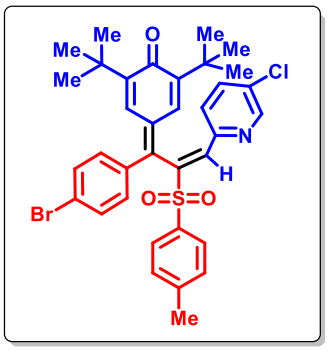

**(E)-2,6-di-tert-butyl-4-(1-(4-chlorophenyl)-3-(6-methoxypyridin-2-yl)-2-(phenylsulfonyl)allylidene)cyclohexa-2,5-dien-1-one (5ad).** The crude product was purified by column chromatography (hexane/EtOAc =82/18) to afford **5ad** as a yellow solid (Yield: 67%); m.p = 216-218 °C; $^{1}$H-NMR (400 MHz, $CDCl_3$) $\delta$ 8.08 (s, 1H), 7.66-7.59 (m, 3H), 7.51 (t, J = 7.5 Hz, 1H), 7.35 (t, J = 7.8 Hz, 2H), 7.28 (s, 2H), 7.21-7.16 (m, 4H), 6.84 (d, J = 2.5 Hz, 1H), 6.70 (d, J = 8.3 Hz, 1H), 3.32 (s, 3H), 1.18 (s, 9H), 1.03 (s, 9H); $^{13}$C-NMR (100 MHz, $CDCl_3$) $\delta$ 186.1, 163.6, 148.7, 148.4, 143.3, 142.4, 139.6, 139.3, 139.1, 135.3, 135.1, 133.3, 132.5, 129.9, 129.0, 128.3, 121.3, 113.7, 53.5, 35.4, 35.1, 29.5, 29.3. HRMS (ESI) $[M+H]^+$ Calcd for $[C_{35}H_{36}ClNO_4S]$: 602.2132, found: 602.2146.



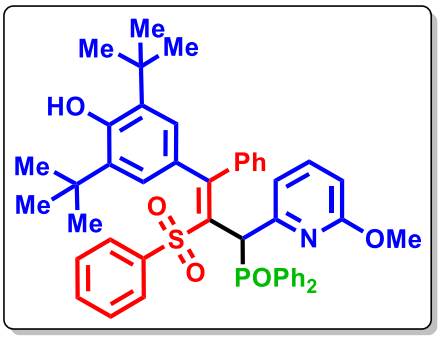

**(*E*)-4-(1-(4-bromophenyl)-3-(6-methoxypyridin-2-yl)-2-tosylallylidene)-2,6-di-tert-butylcyclohexa-2,5-dien-1-one (5ae).** The crude product was purified by column chromatography (hexane/EtOAc =82/18) to afford **5ae** as a yellow solid (Yield: 70%); m.p = 216-218 °C; $^{1}$H-NMR (400 MHz, $CDCl_3$) $\delta$ 8.03 (s, 1H), 7.61 (dd, J = 8.3, 7.3 Hz, 1H), 7.45 (d, J = 8.3 Hz, 2H), 7.34 (d, J = 8.5 Hz, 2H), 7.19-7.11 (m, 6H), 6.81 (d, J = 2.5 Hz, 1H), 6.68 (d, J = 8.5 Hz, 1H), 3.30 (s, 3H), 2.38 (s, 3H), 1.17 (s, 9H), 1.01 (s, 9H); $^{13}$C-NMR (100 MHz, $CDCl_3$) $\delta$ 186.1, 163.6, 148.6, 148.5, 148.4, 144.6, 143.5, 142.7, 139.1, 136.2, 135.7, 132.8, 132.4, 131.1, 130.1, 129.7, 129.1, 128.4, 123.6, 121.2, 113.6, 53.5, 35.4, 35.1, 29.5, 29.3, 21.6. HRMS (ESI) $[M+H]^+$ Calcd for $[C_{36}H_{39}BrNO_4S]$: 660.1778, found: 660.1756.




**(*E*)-4-(3-(5-bromopyridin-2-yl)-2-((4-chlorophenyl)sulfonyl)-1-phenylallylidene)-2,6-di-*tert*-butylcyclohexa-2,5-dien-1-one (5fb).** The crude product was purified by column chromatography (hexane/EtOAc =85/15) to afford **5fb** as a yellow solid (Yield: 76%); m.p = 204-208 °C; $^{1}$H-NMR (400 MHz, $CDCl_3$) $\delta$ 8.57 (d, J = 2.2 Hz, 1H), 8.14 (s, 1H), 7.77 (dd, J = 8.5, 2.3 Hz, 1H), 7.48 (d, J = 8.7 Hz, 2H), 7.37-7.31 (m, 2H), 7.27-7.22 (m, 7H + residual $CDCl_3$), 6.84 (d, J = 2.6 Hz, 1H), 1.21 (s, 9H), 1.06 (s, 9H); $^{13}$C-NMR (100 MHz, $CDCl_3$) $\delta$ 186.0, 151.5, 149.8, 149.2, 148.9, 145.1, 141.7, 140.2, 139.5, 139.3, 137.5, 135.7, 133.1, 131.3, 129.8, 129.5, 129.4, 129.3, 129.2, 128.2, 126.0, 122.1, 35.5, 35.1, 29.5, 29.3; HRMS (ESI) $[M+H]^+$ Calcd for $[C_{34}H_{34}BrClNO_3S]$: 650.1131, found: 650.1147.



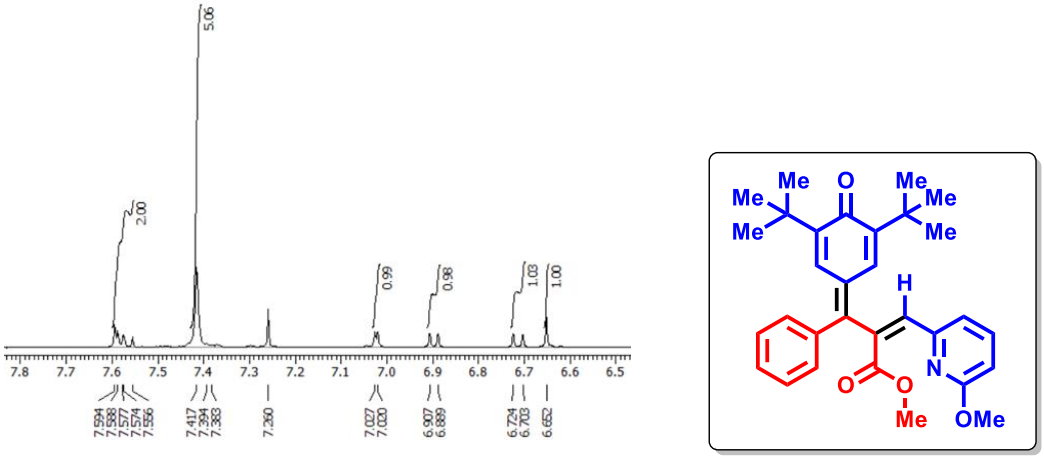

**(E)-4-(1-(4-bromophenyl)-3-(5-chloropyridin-2-yl)-2-tosylallylidene)-2,6-di-tert-butylcyclohexa-2,5-dien-1-one (5dd).** The crude product was purified by column chromatography (hexane/EtOAc = 85/15) to afford **5dd** as a yellow sticky compound (Yield: 68%); m.p = 222-224 °C; $^{1}$H NMR (400 MHz, $CDCl_3$) $\delta$ 8.391 (d, $J$ =2.4 Hz, 1H), 8.104 (d, $J$ =1.2 Hz, 1H), 7.625 – 7.578 (m, 1H), 7.477 – 7.433 (m, 2H), 7.382 – 7.327 (m, 3H), 7.174 – 7.093 (m, 5H), 6.701 (s, 1H), 2.361 (s, 3H), 1.210 – 1.165 (m, 9H), 1.011 – 0.959 (m, 9H); $^{13}$C-NMR (100 MHz, $CDCl_3$) $\delta$ 186.2, 149.5, 149.4, 149.3, 148.7, 145.4, 145.0, 141.3, 138.7, 136.4, 135.9, 135.3, 133.1, 132.9, 131.4, 129.9, 129.7, 129.1, 128.6, 126.1, 124.0, 35.6, 35.2, 29.7, 29.4, 21.7**;** HRMS (ESI) $[M+H]^+$ Calcd for $[C_{35}H_{336}BrClNO_3S]$: 664.1282, found: 664.1283, 666.1316.

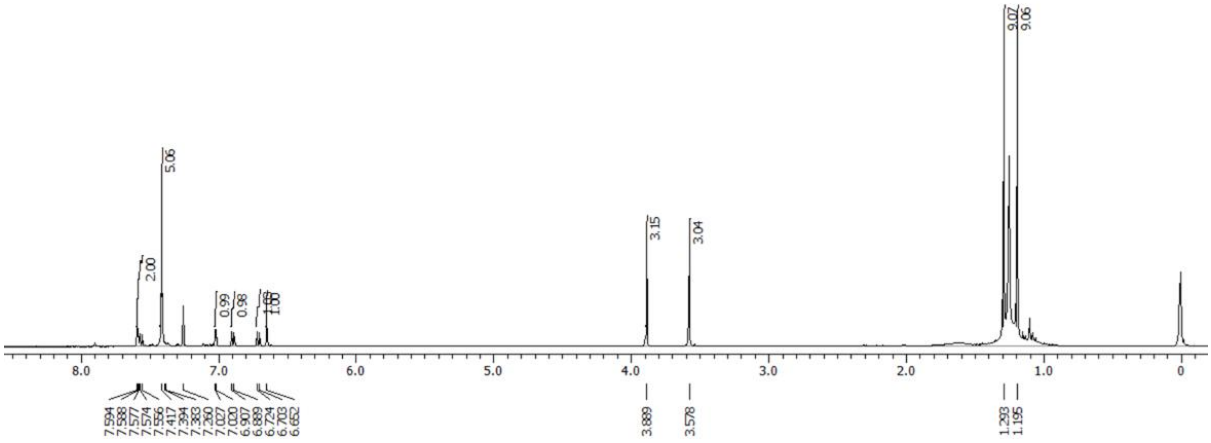



**(Z/E)-(3-(3,5-di-tert-butyl-4-hydroxyphenyl)-1-(6-methoxypyridin-2-yl)-3-phenyl-2-(phenylsulfonyl)allyl)diphenylphosphine oxide (11).** The crude product was purified by column chromatography (hexane/EtOAc = 95/05) to afford **11** as a yellow sticky solid (Yield: 54%, Z: E = 80:20); $^{1}$H-NMR (400 MHz, $CDCl_3$) $\delta$ 7.79-7.68 (m, 5H), 7.57-7.23 (m, 20H), 7.17-7.04 (m, 9H), 6.63-6.57 (m, 2H), 5.95-5.86 (m, 1H), 5.15 (s, 1H), 3.78 (s, 3H), 3.59 (s, 1H), 1.25 (s, 23H); $^{13}$C-NMR (100 MHz, $CDCl_3$) $\delta$ 162.8, 162.8, 154.0, 153.8, 153.2, 153.1, 153.0, 142.6, 141.5, 139.8, 139.6, 139.4, 139.0, 139.0, 138.3, 136.4, 136.1, 134.3, 134.3, 132.4, 132.3, 132.3, 132.1, 132.0, 131.9, 131.8, 131.7, 131.6, 131.1, 129.7, 129.2, 128.3, 128.1, 128.0, 127.9, 127.7, 127.6, 127.5, 127.4, 127.1, 119.6, 109.2, 53.5, 53.2, 34.3, 34.0, 30.0, 29.7; $^{31}$P-NMR (162 MHz, $CDCl_3$) $\delta$ 32.4, 31.8. HRMS (ESI) $[M+H]^+$ Calcd for $[C_{47}H_{49}NO_5PS]$: 770.3064, found: 770.3128.

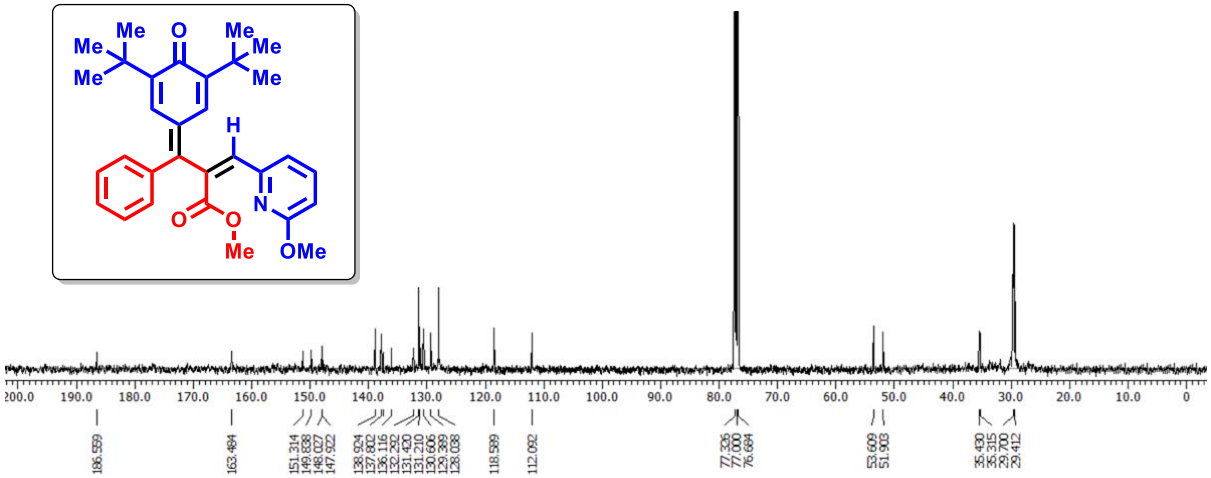
## $^{1}H$ and $^{13}C$ spectra of compounds

### $^{1}H$ NMR (400 MHz, $CDCl_3$)3aa

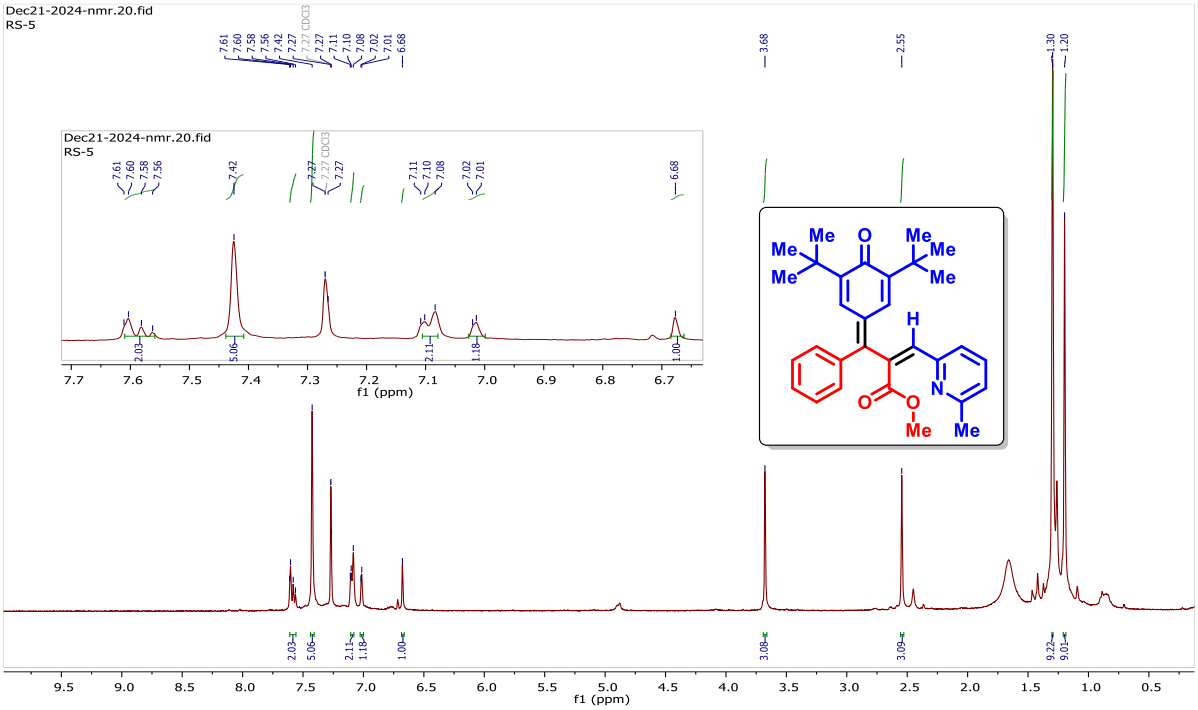


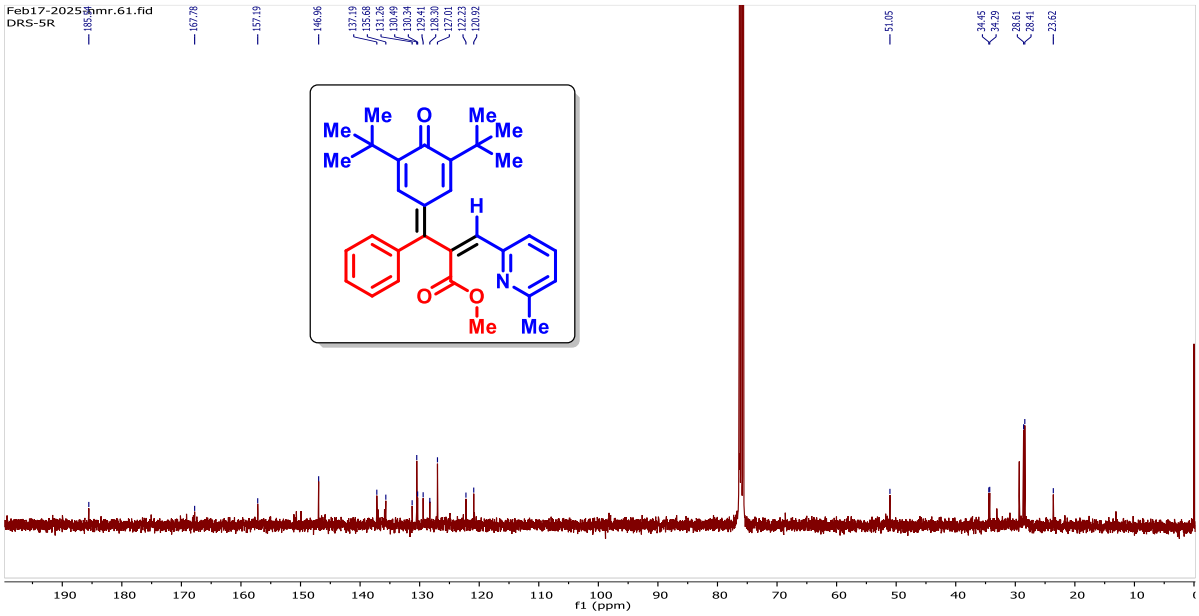
### $^{13}C$ NMR (100 MHz, $CDCl_3$) (3aa)



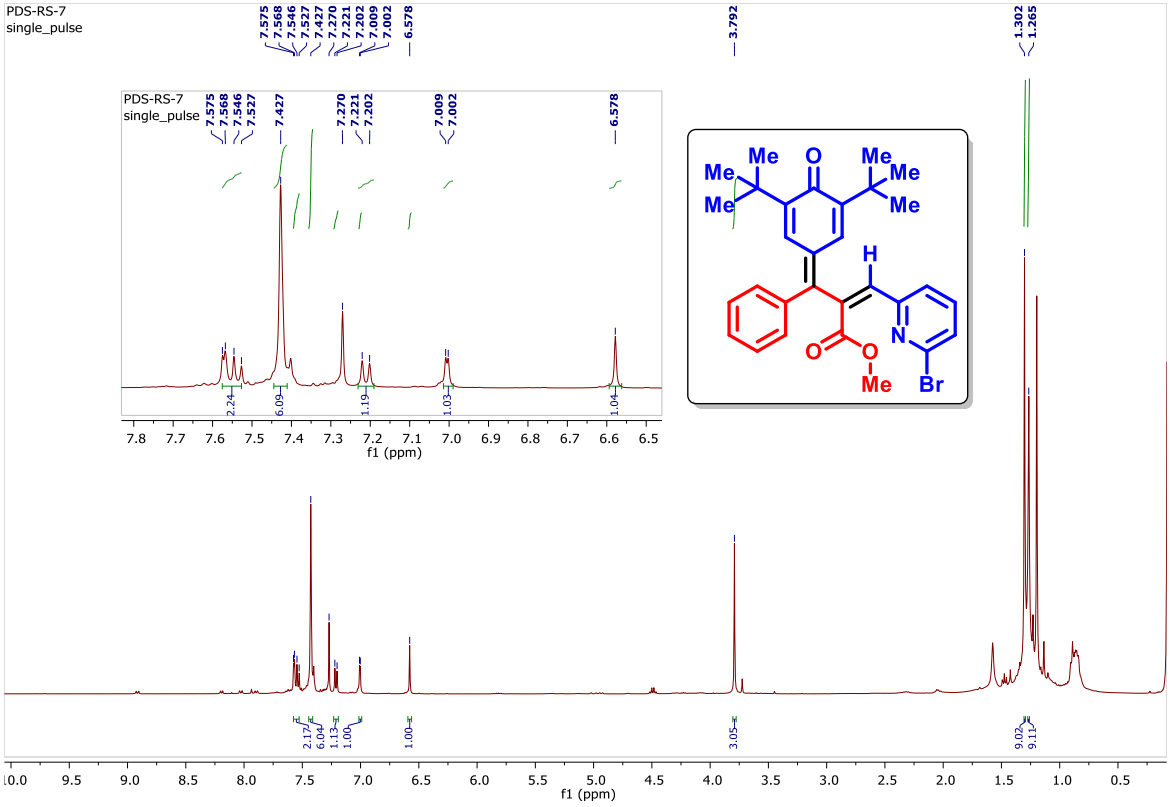
## $^{1}$H NMR (400 MHz, $CDCl_3$) (3ba)



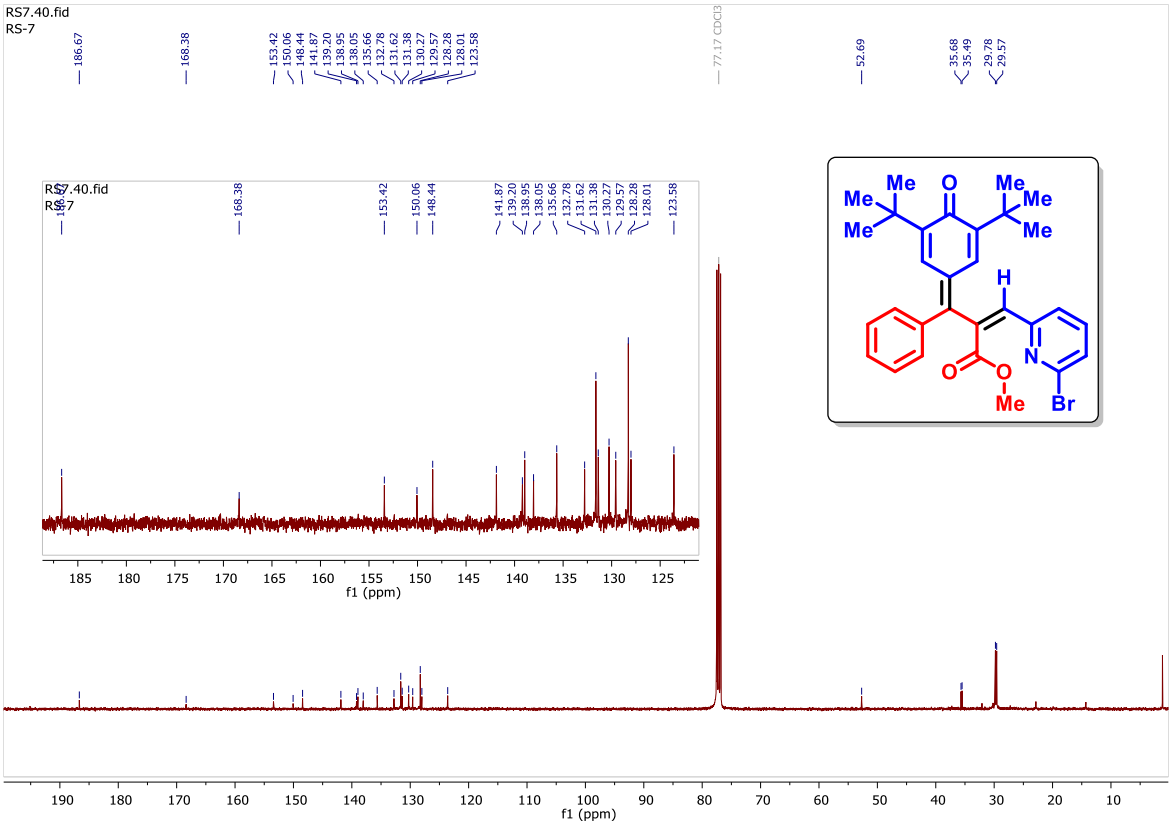

## $^{13}$C NMR (100 MHz, $CDCl_3$) (3ba)



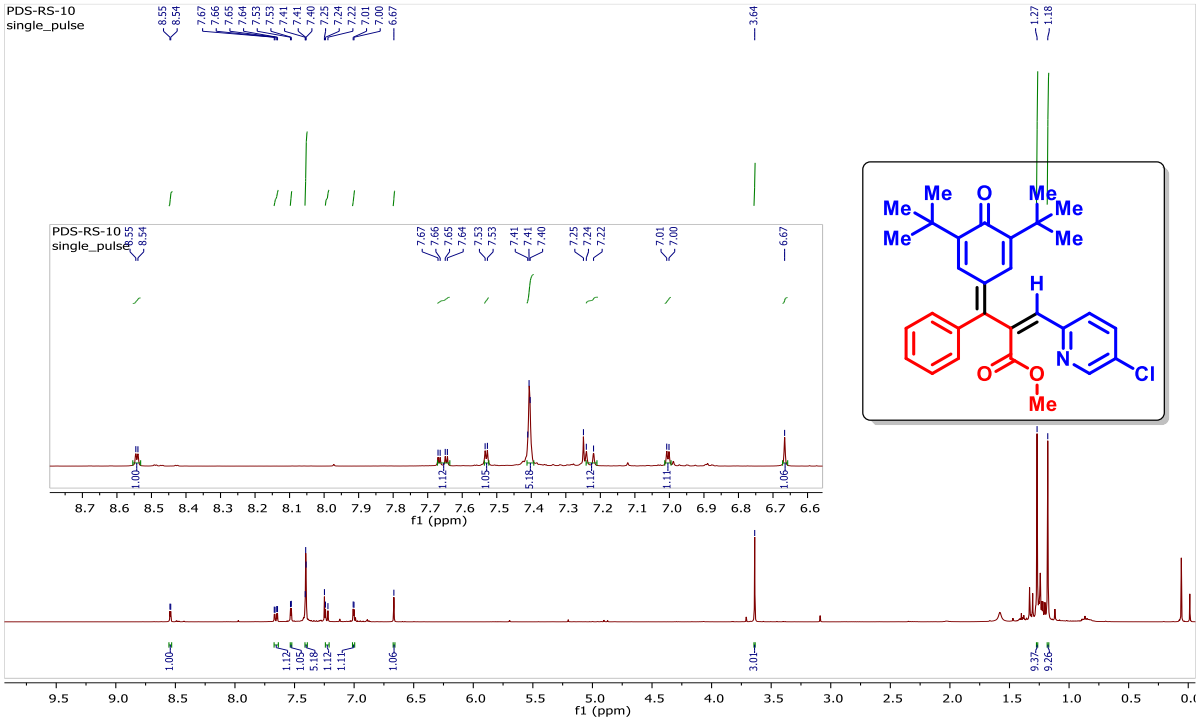
## $^{1}$H NMR (400 MHz, $CDCl_3$) (3ca)



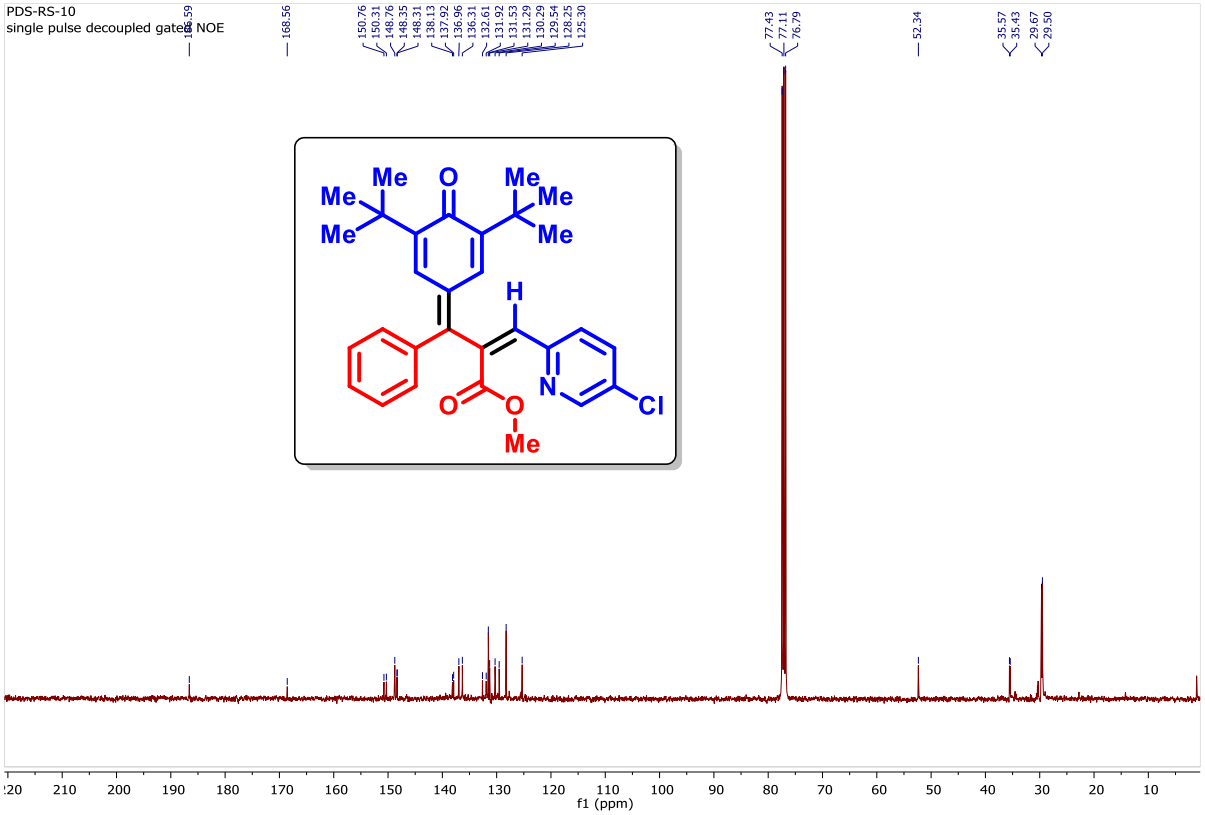

## $^{13}$C NMR (100 MHz, $CDCl_3$) (3ca)



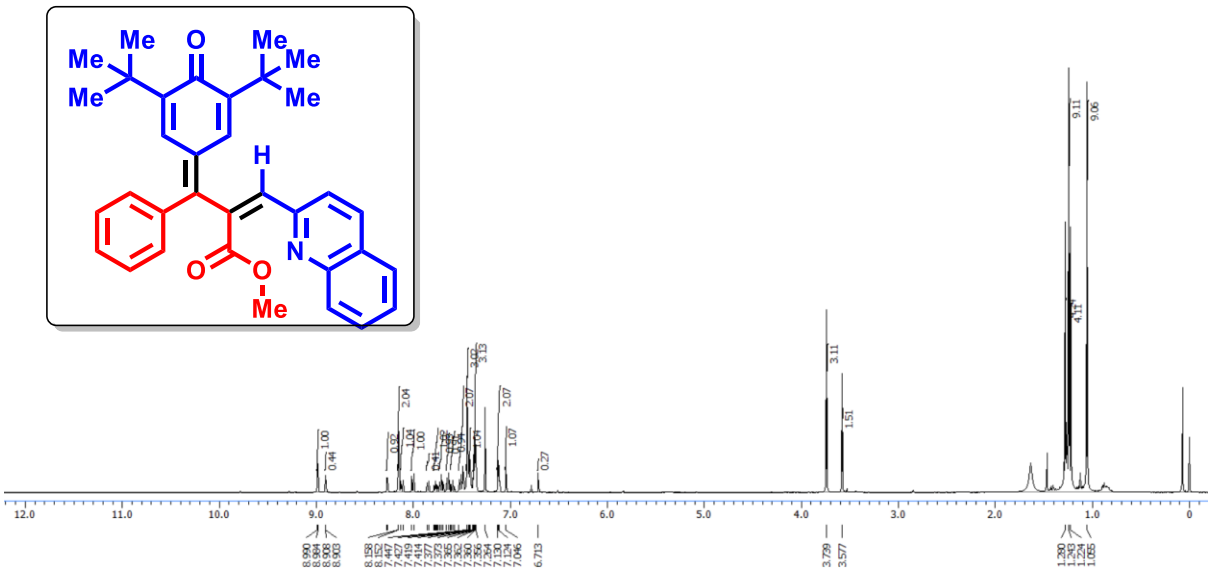
## $^{1}$H NMR (400MHz, $CDCl_3$) (3da)



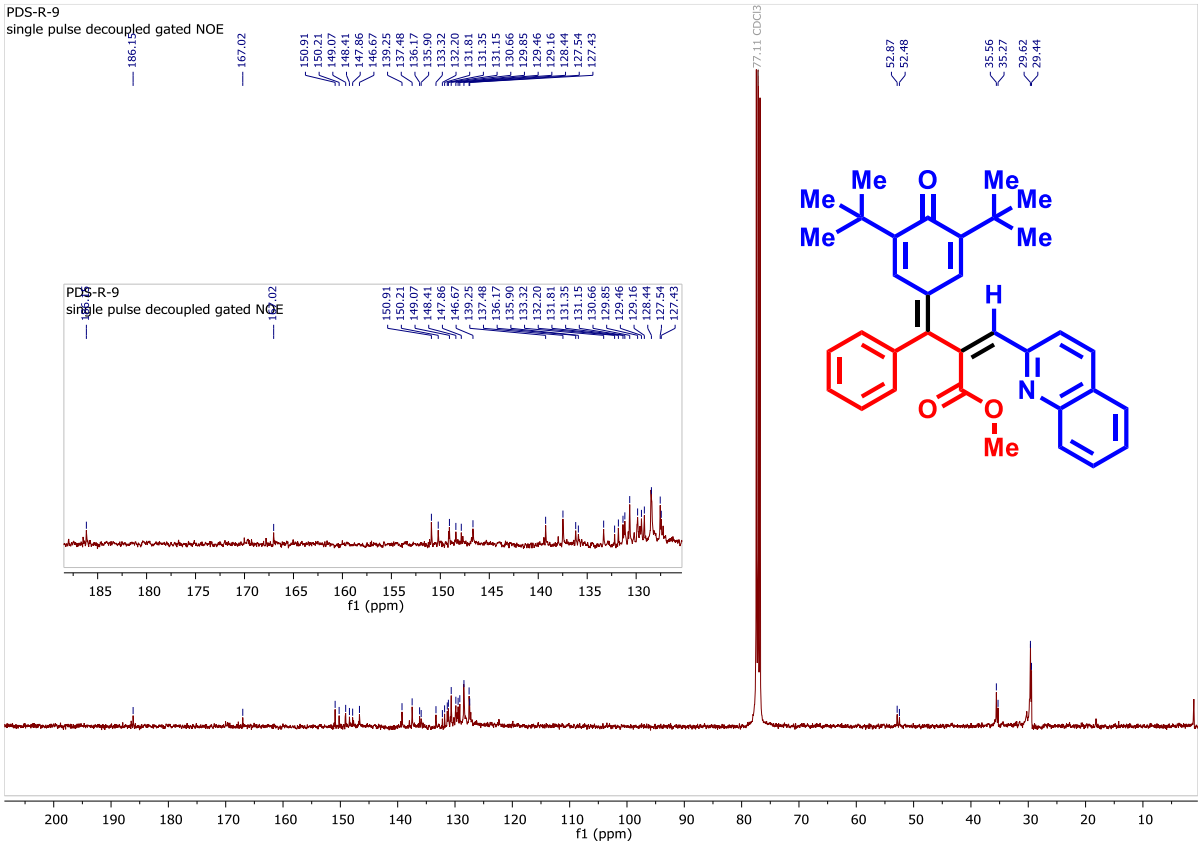

## $^{13}$C NMR (100 MHz, $CDCl_3$) (3da)



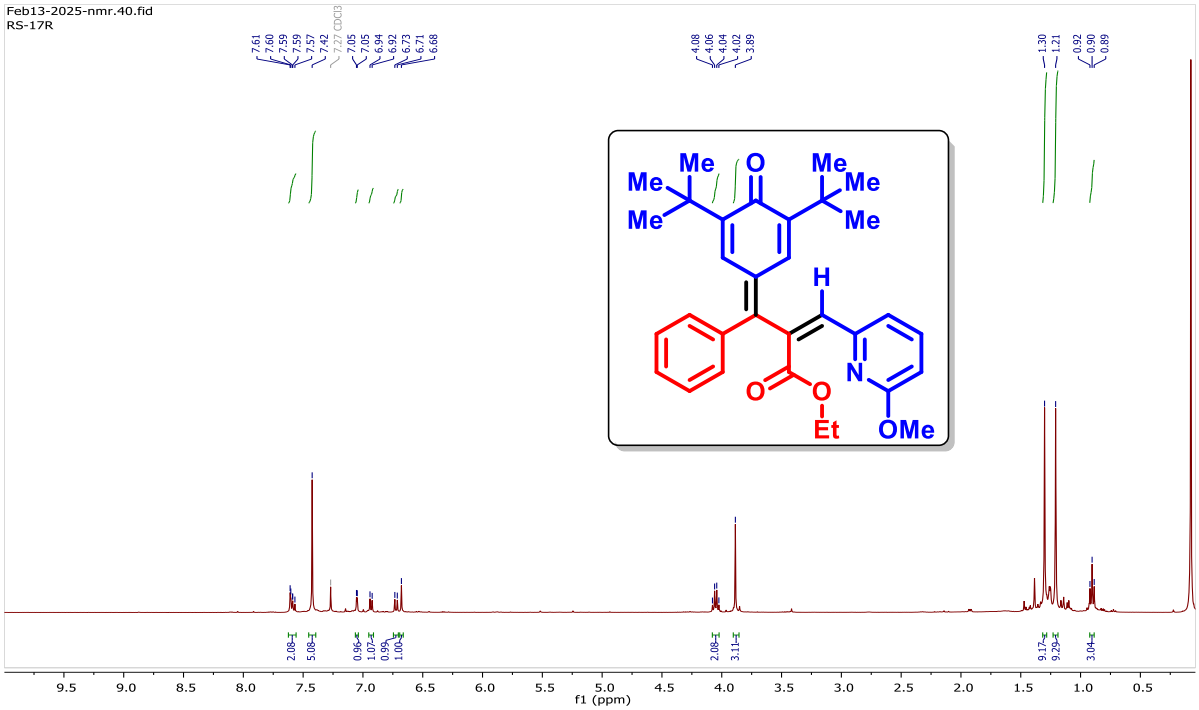
**$^{1}$H NMR (400 MHz, $CDCl_3$) (3ea)**



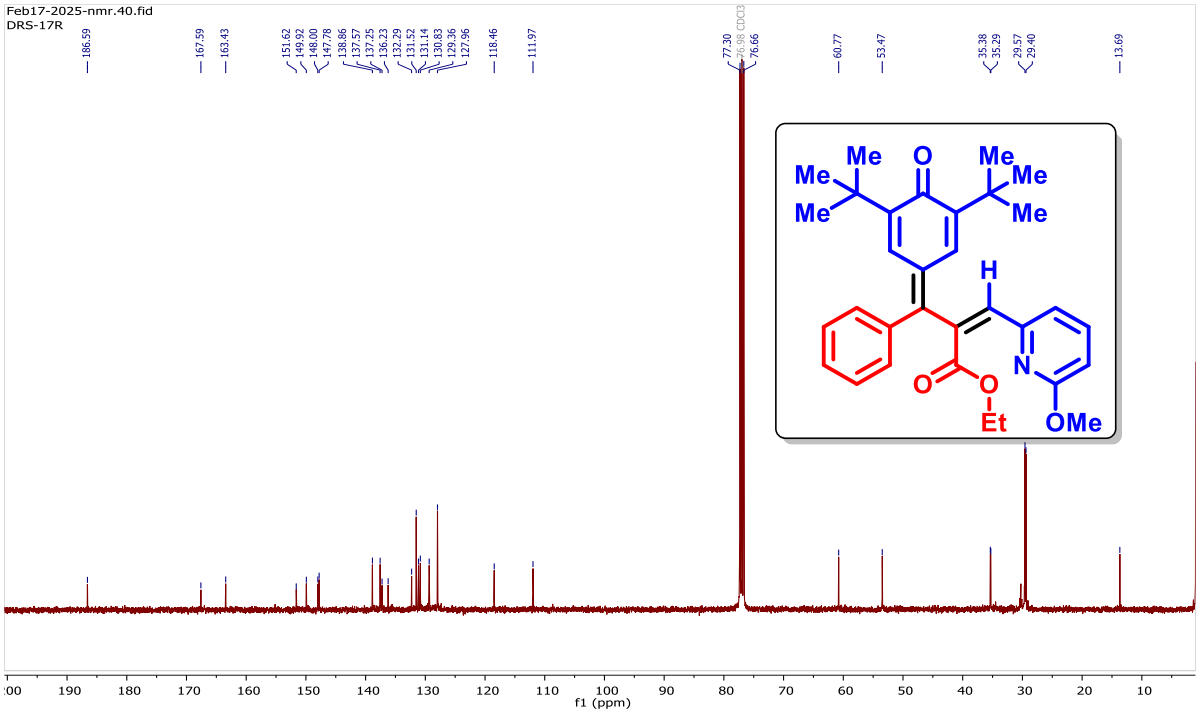
**$^{13}$C NMR (100 MHz, $CDCl_3$) (3ea)**



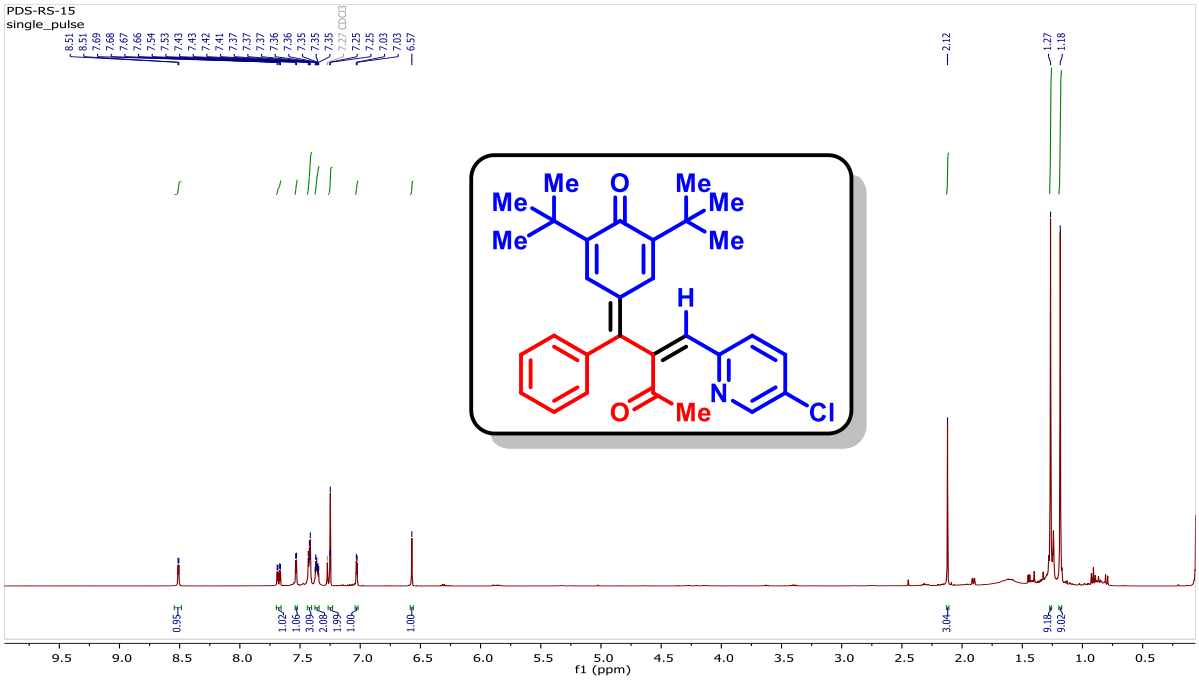
**$^{1}$H NMR (400 MHz, $CDCl_3$) (3ab)**



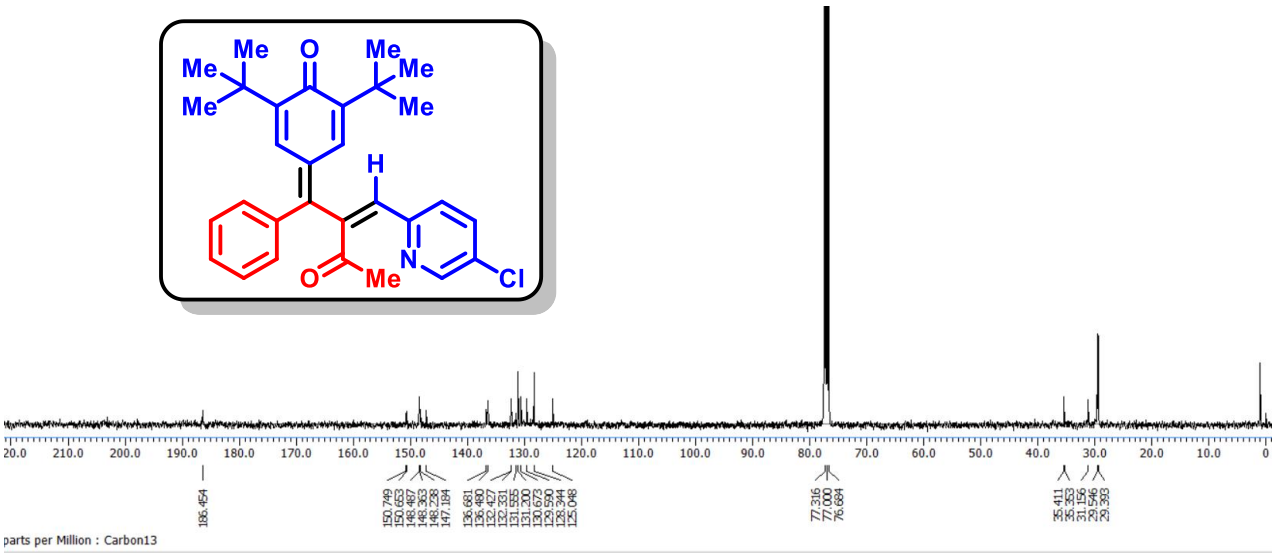

**$^{13}$C NMR (100 MHz, $CDCl_3$) (3ab)**



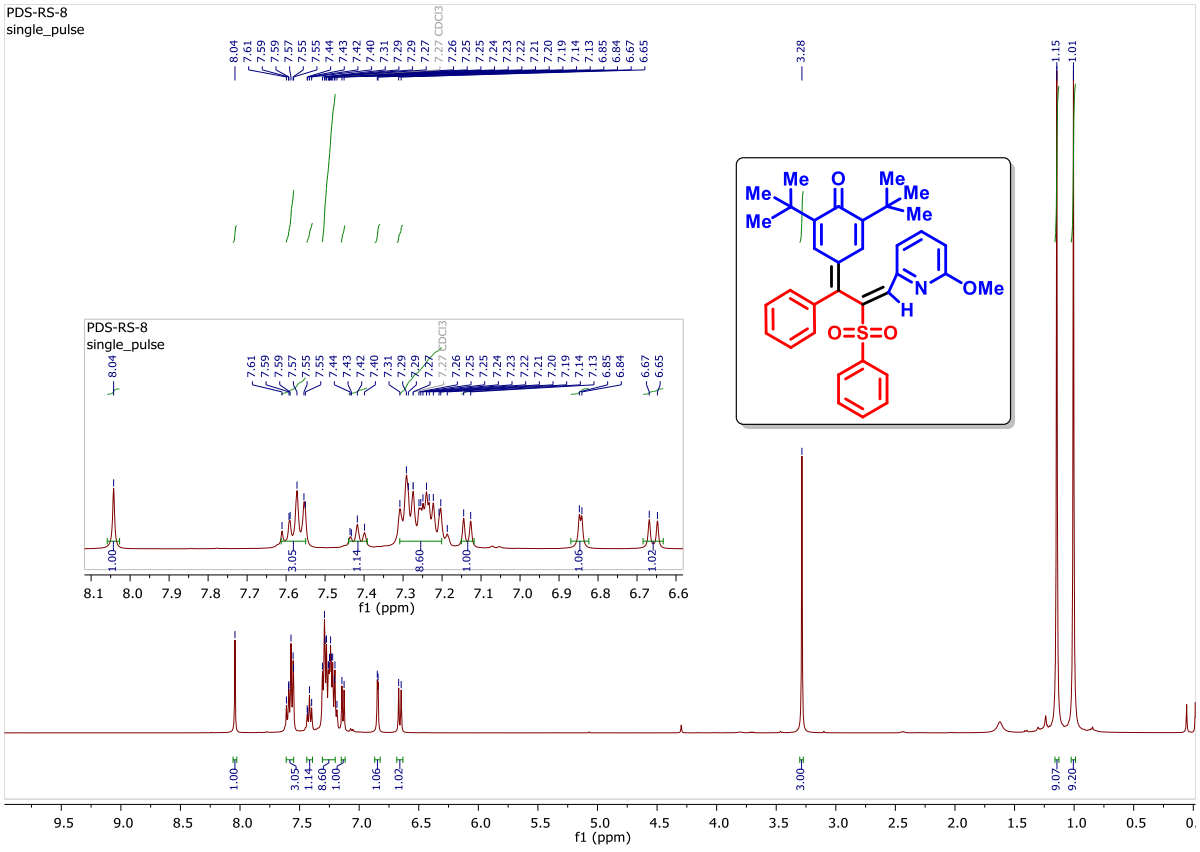

**$^{1}$H NMR (400 MHz, $CDCl_3$) (3dc)**



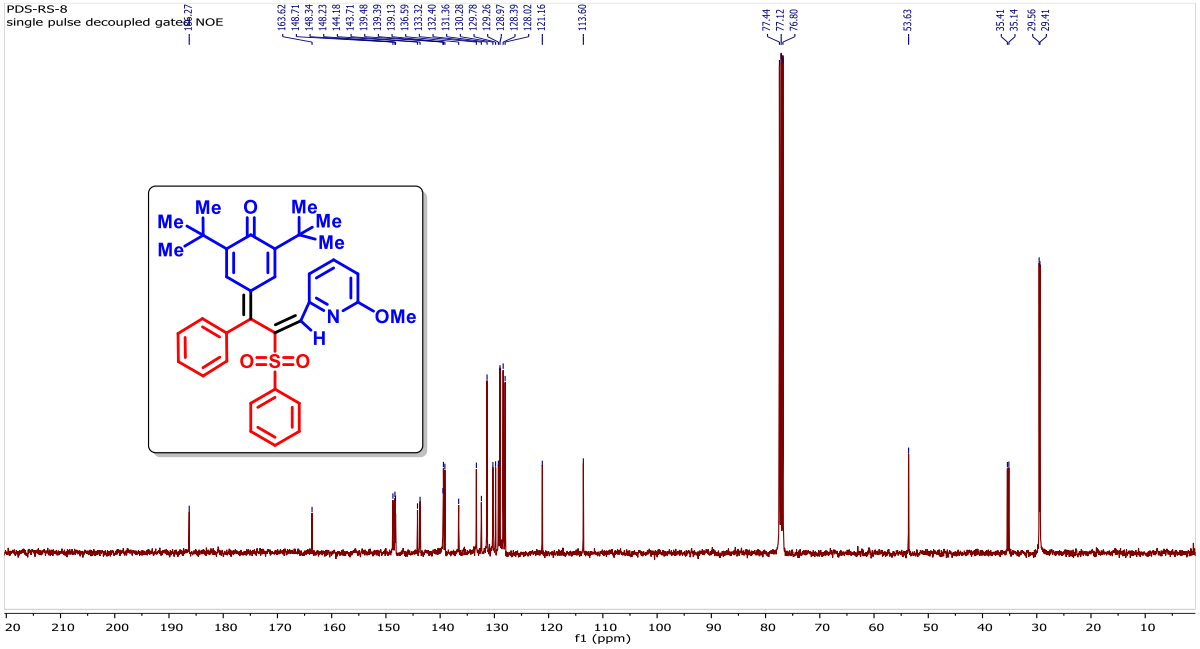

**$^{13}$C NMR (100 MHz, $CDCl_3$) (3dc)**



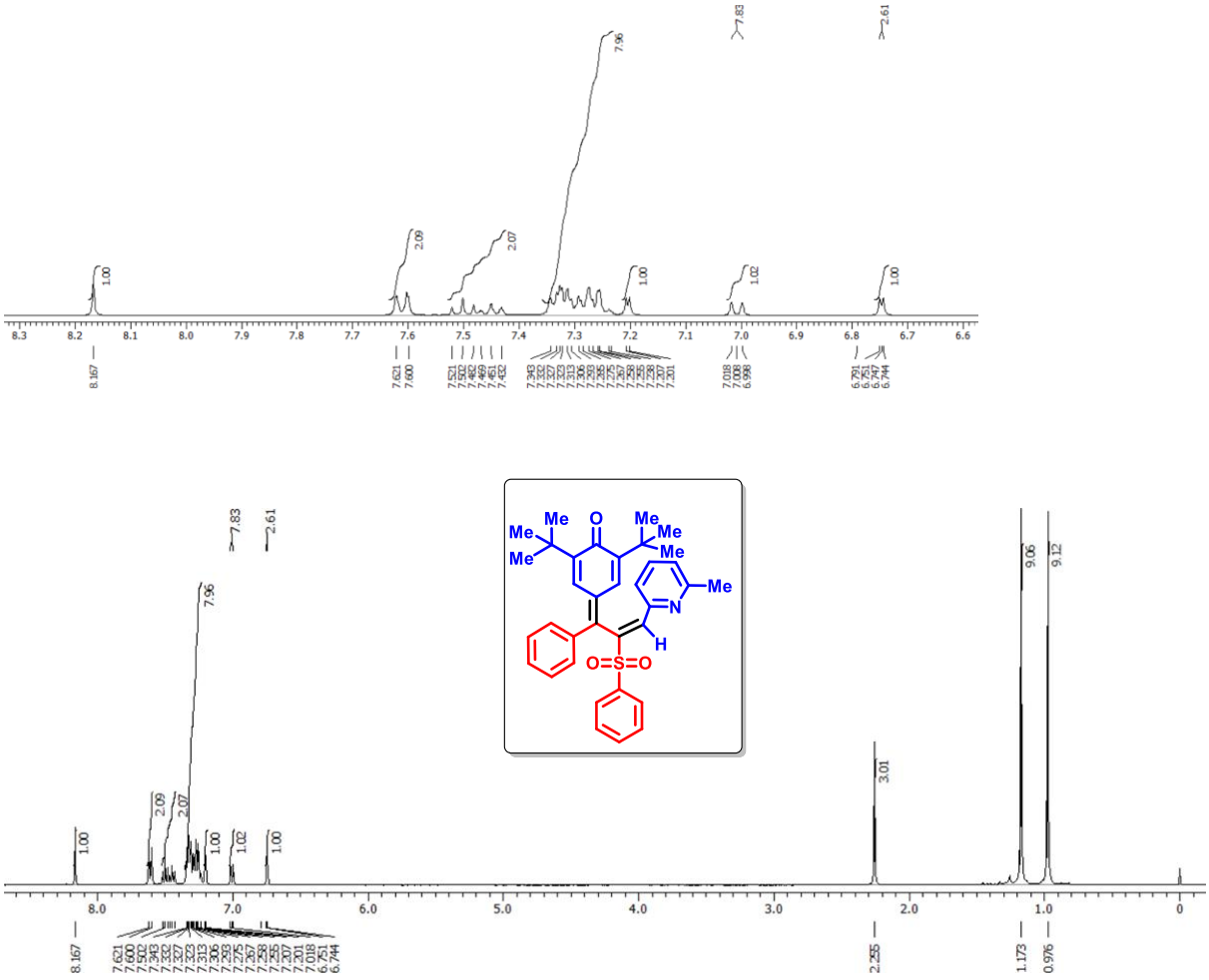

**$^{1}$H NMR (400 MHz, $CDCl_3$) (5aa)**



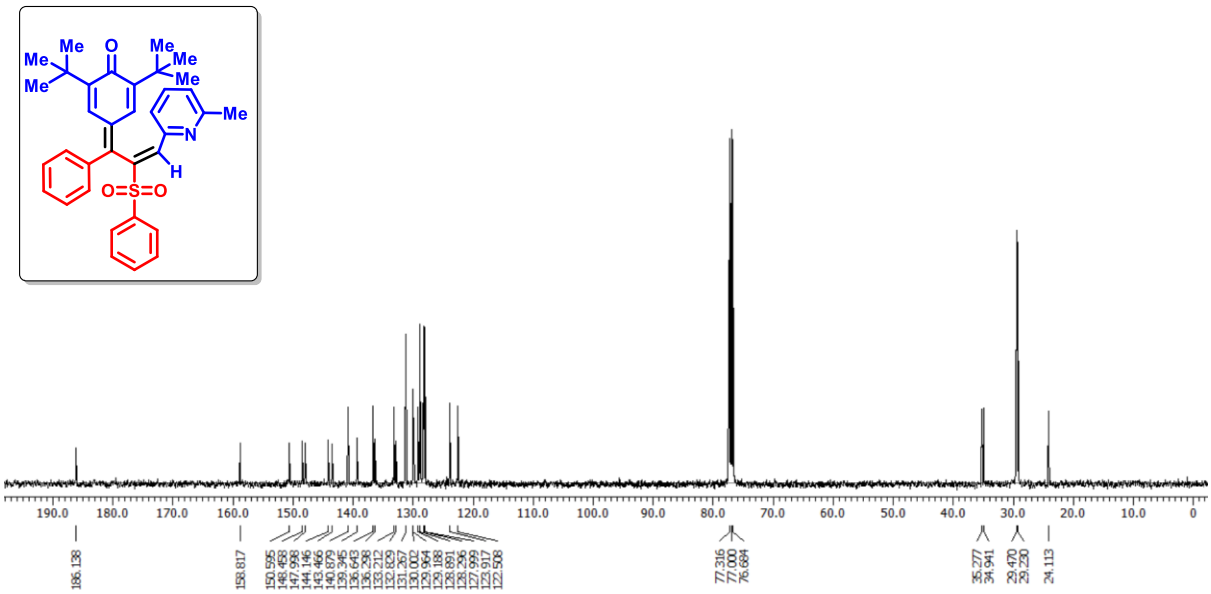

## $^{13}$C-NMR (100 MHz, $CDCl_3$) (5aa)



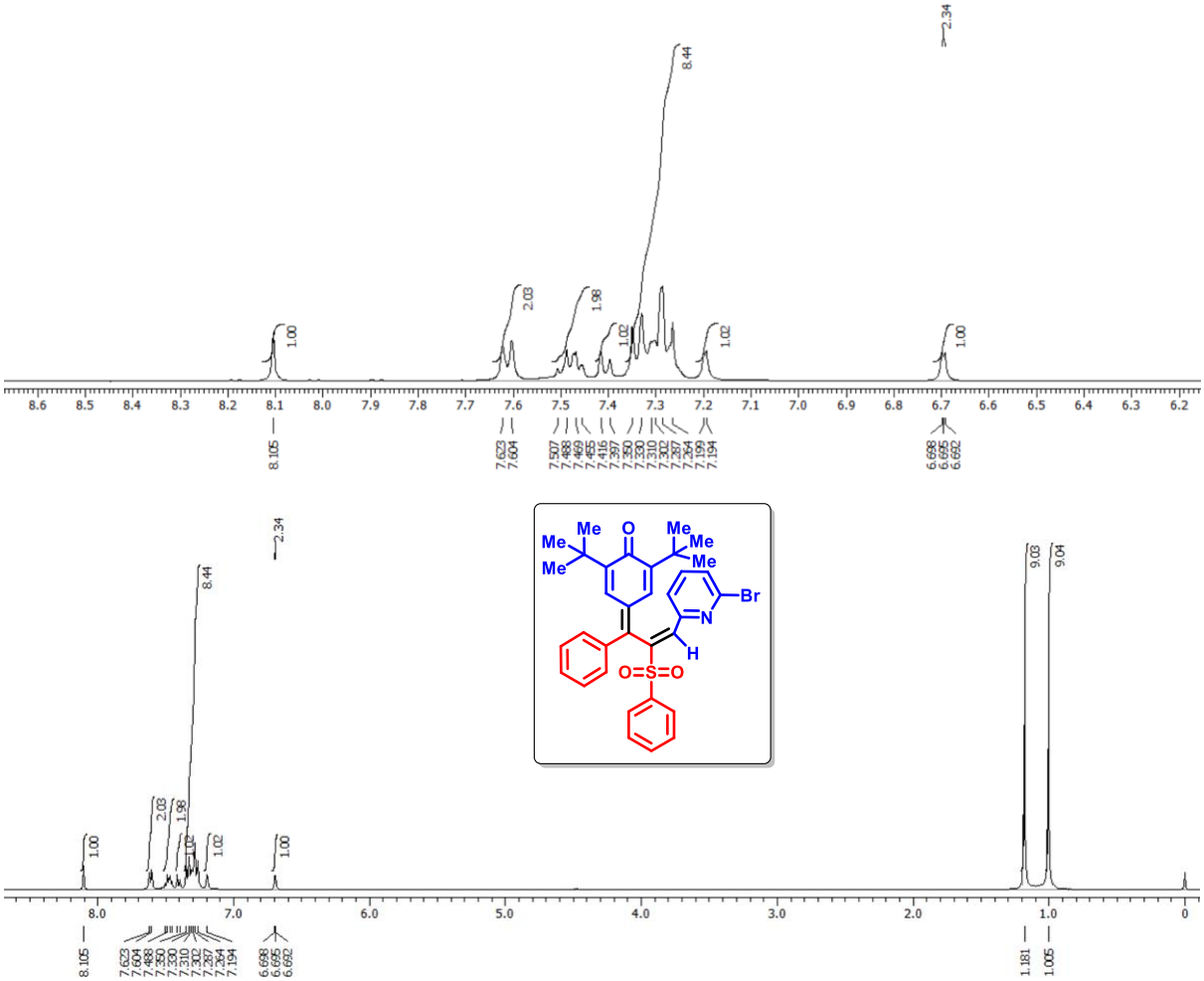
## $^{1}$H NMR (400 MHz, $CDCl_3$) (5ba)



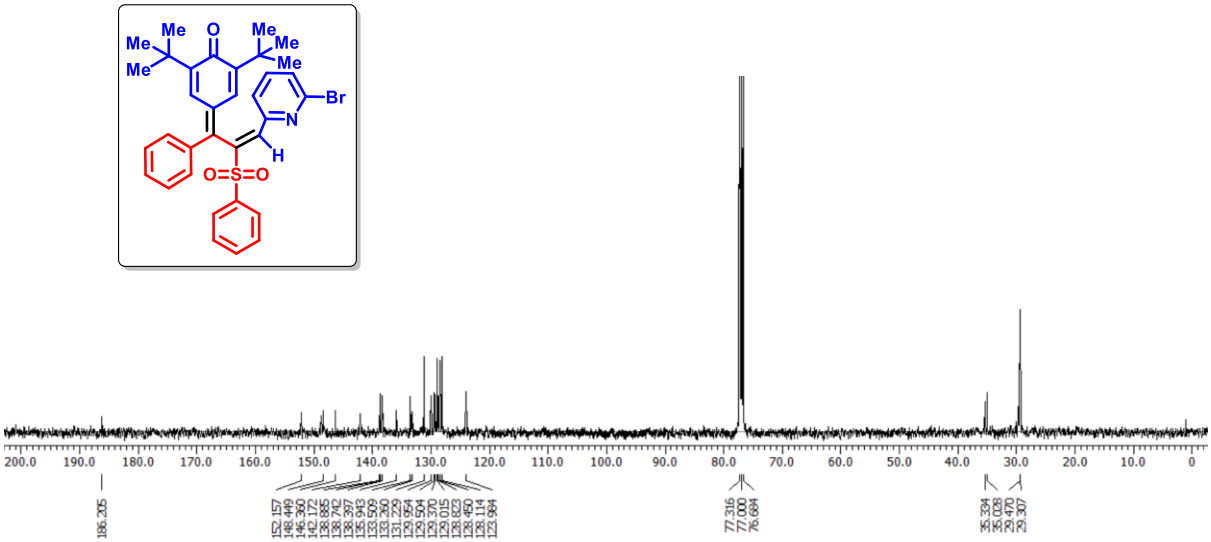

## $^{13}$C {1H} NMR (100 MHz, $CDCl_3$) (5ba)



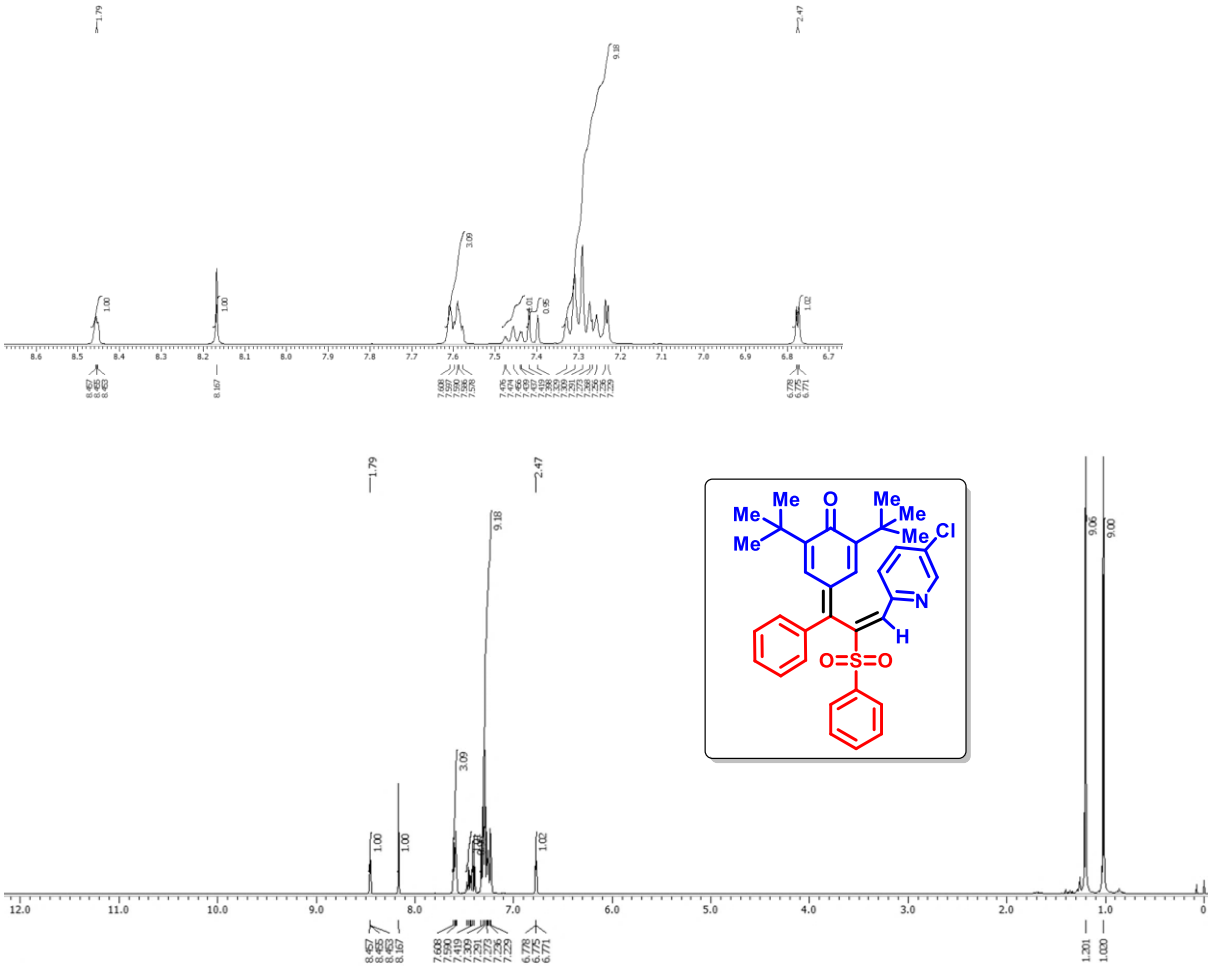
## $^{1}$H NMR (400 MHz, $CDCl_3$) (5ca)



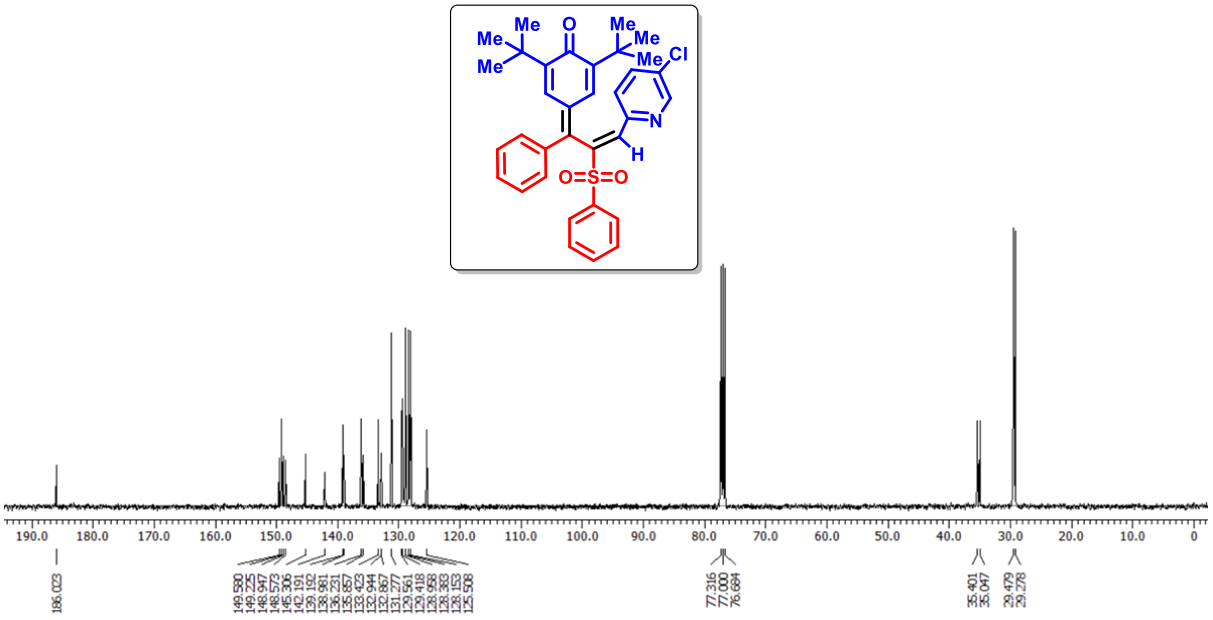

## $^{13}$C {1H} NMR (100 MHz, $CDCl_3$) (5ca)



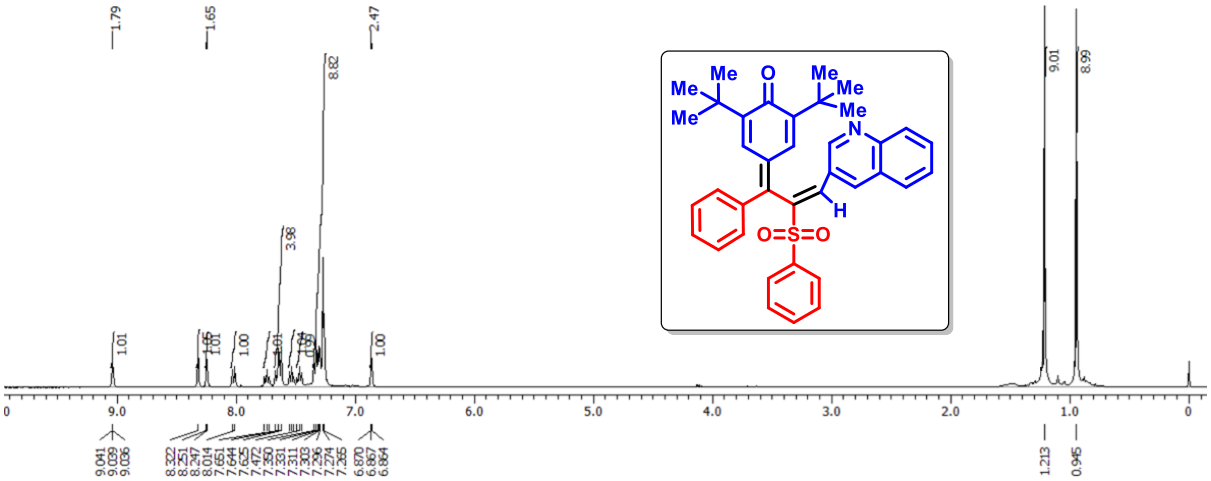
**$^{1}$H NMR (400 MHz, $CDCl_3$) (5da)**



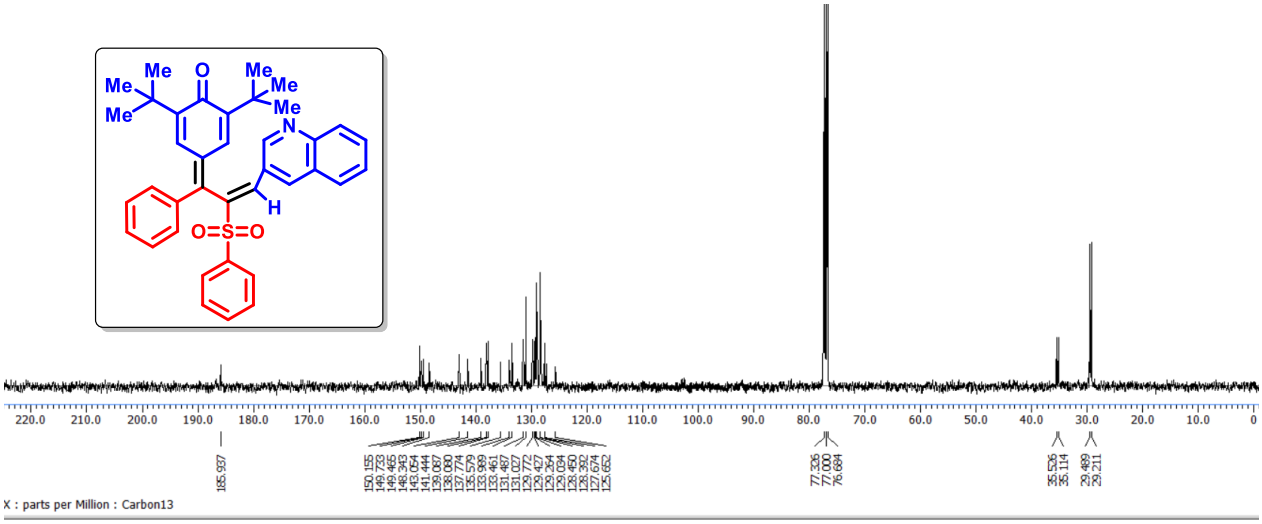

**$^{13}$C {1H} NMR (100 MHz, $CDCl_3$) (5da)**



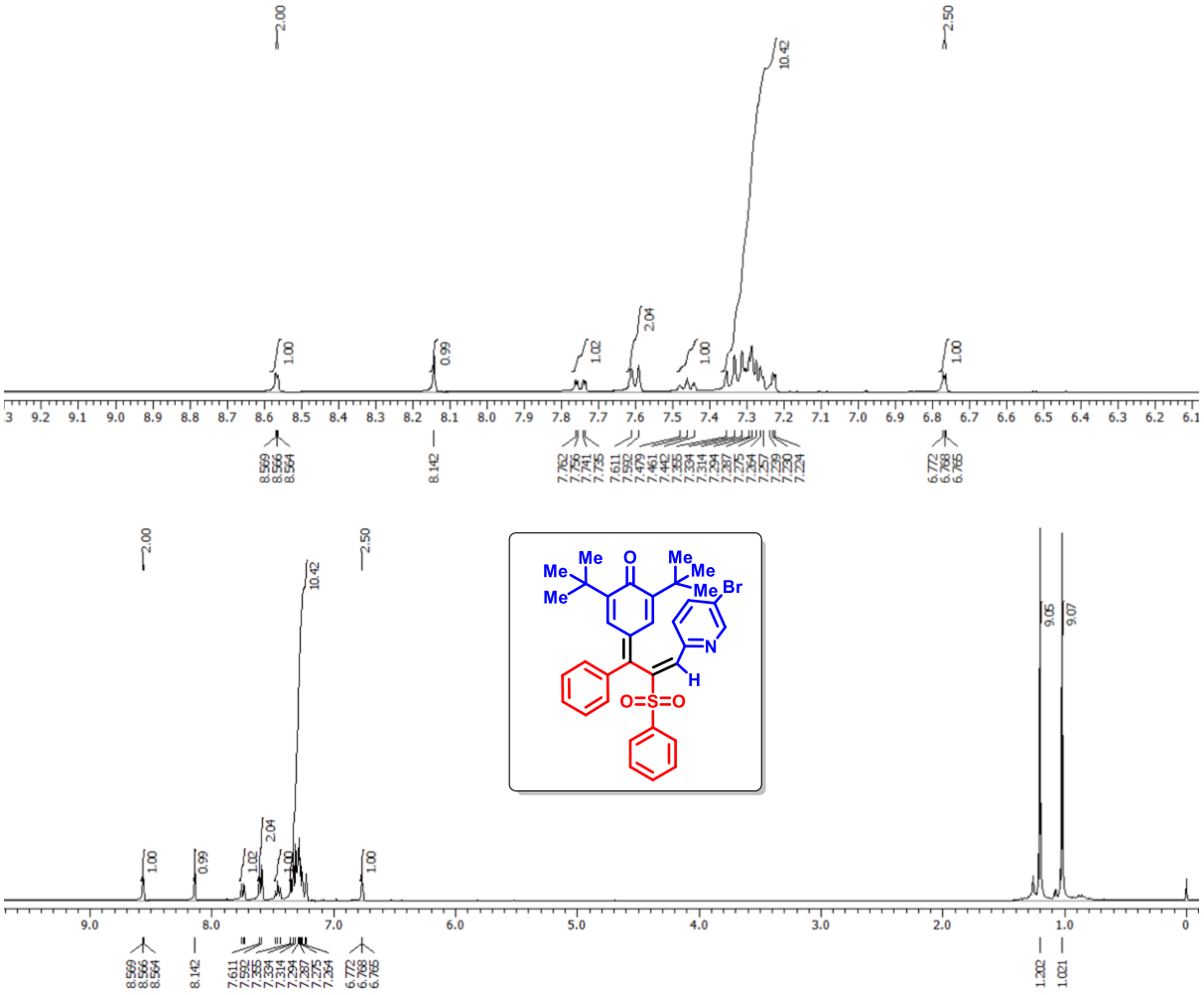
## $^{1}$H NMR (400 MHz, $CDCl_3$) (5ea)



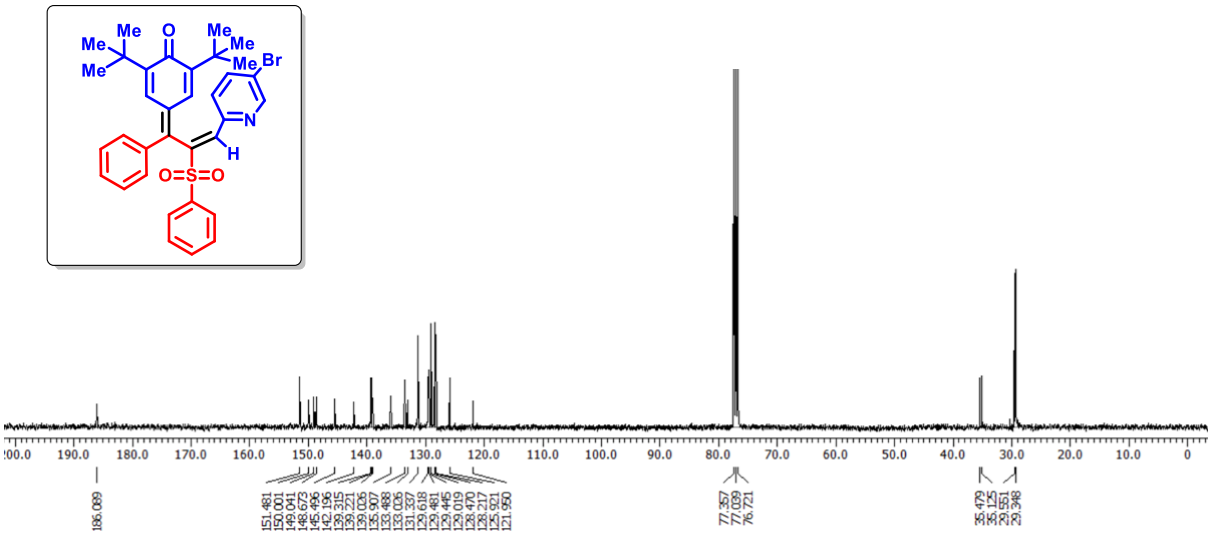

## $^{13}$C {1H} NMR (100 MHz, $CDCl_3$) (5ea)



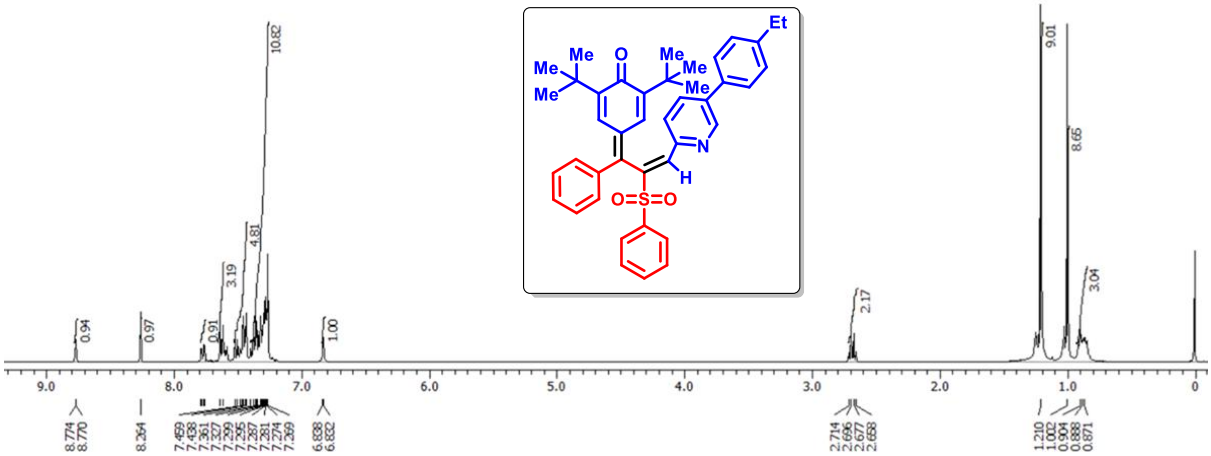
## $^{1}$H NMR (400 MHz, $CDCl_3$) (5fa)



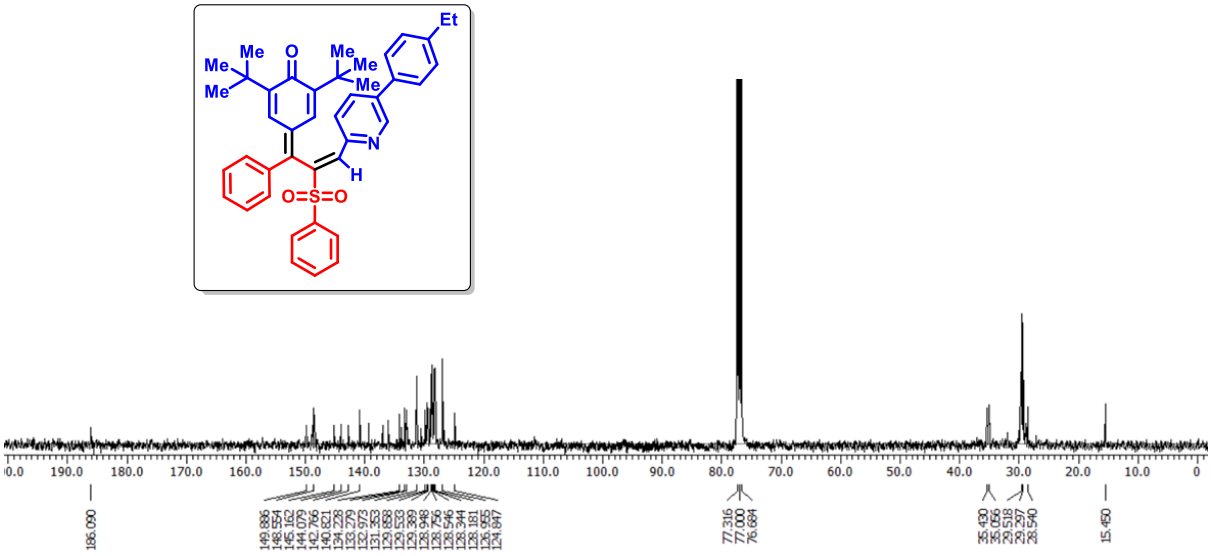

## $^{13}$C {1H} NMR (100 MHz, $CDCl_3$) (5fa)



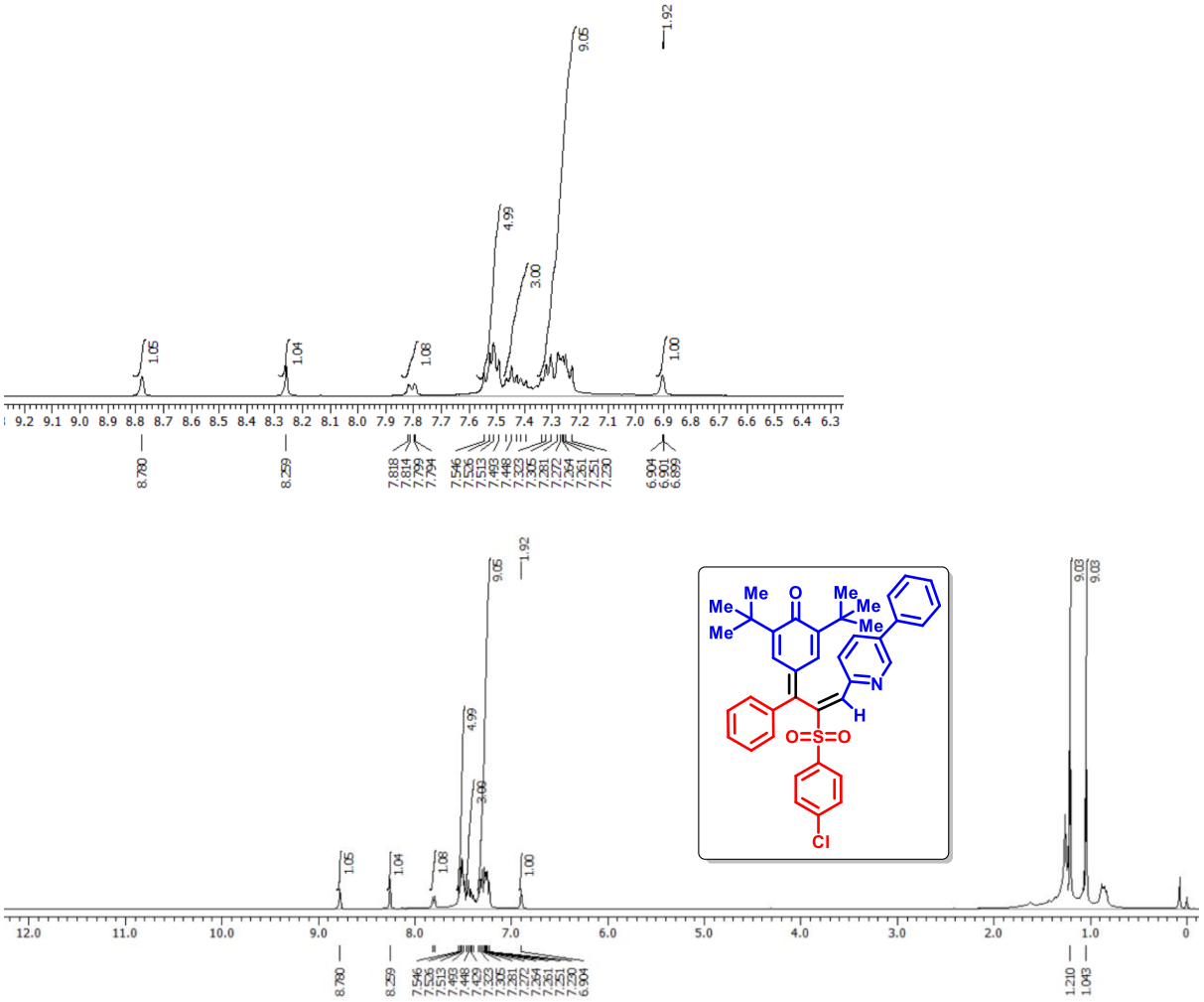
## $^{1}$H NMR (400 MHz, $CDCl_3$) (5ga)



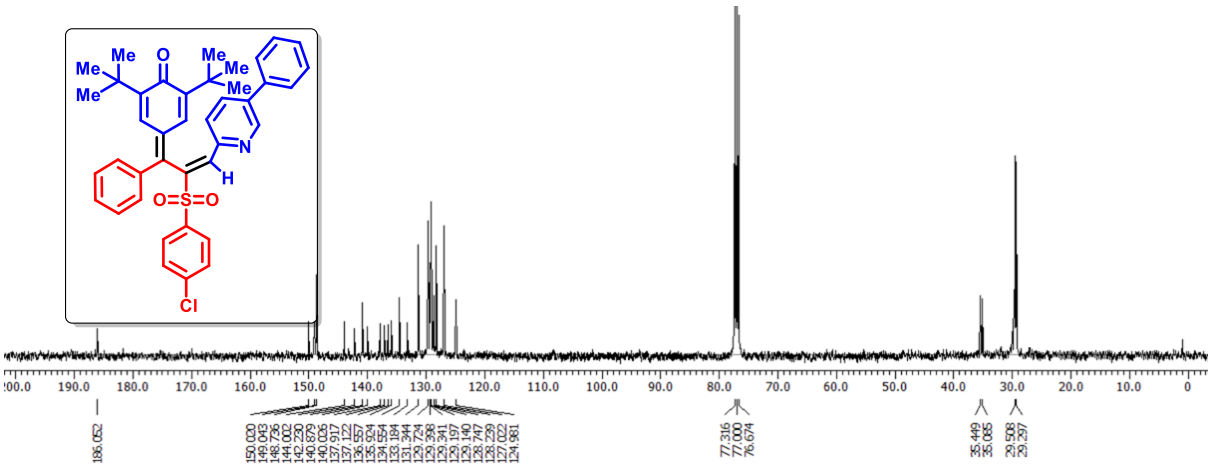

## $^{13}$C {1H} NMR (100 MHz, $CDCl_3$) (5ga)



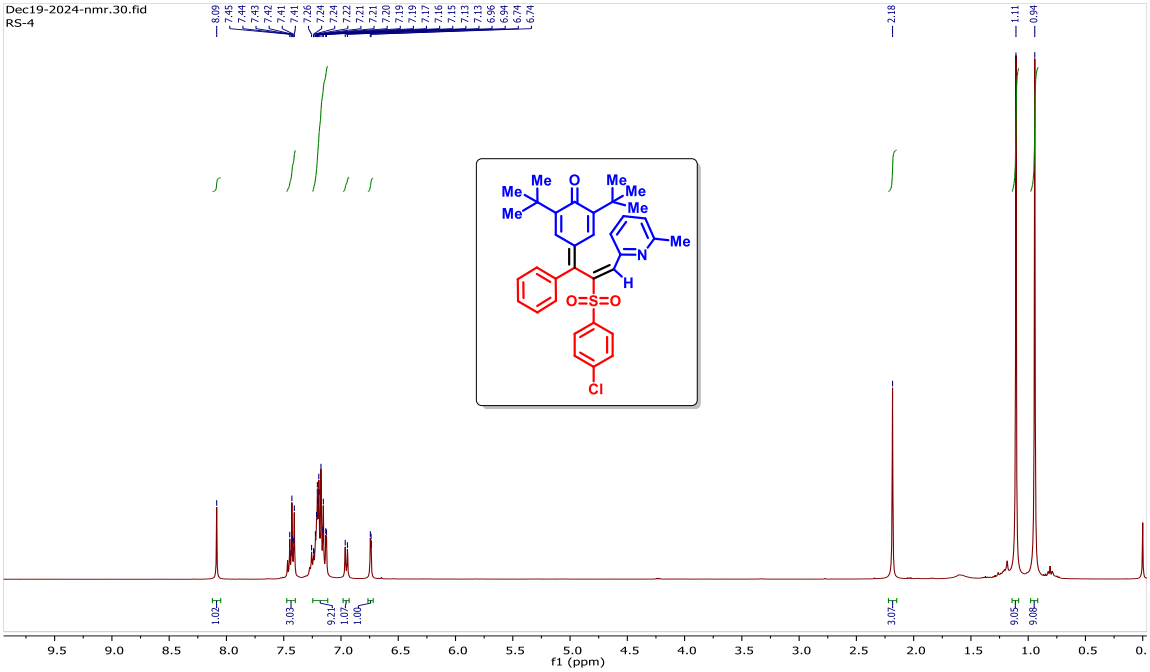
## $^{1}$H NMR (400 MHz, $CDCl_3$) (5hb)



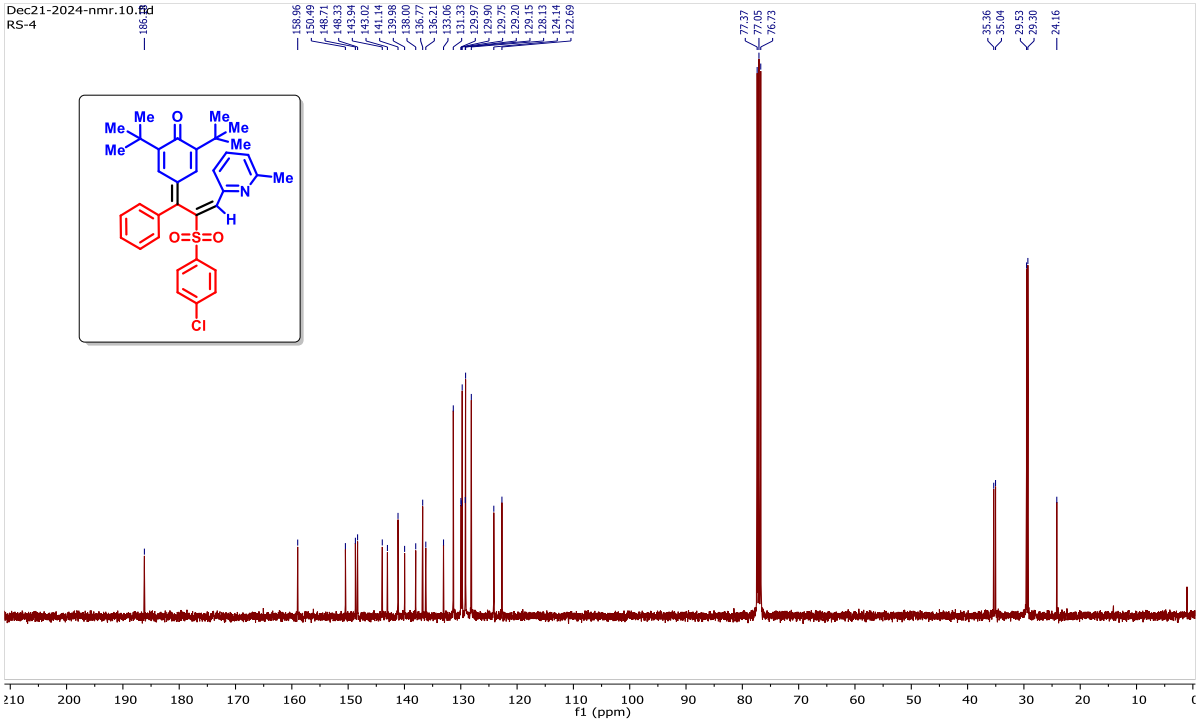

## $^{13}$C {1H} NMR (100 MHz, $CDCl_3$) (5hb)



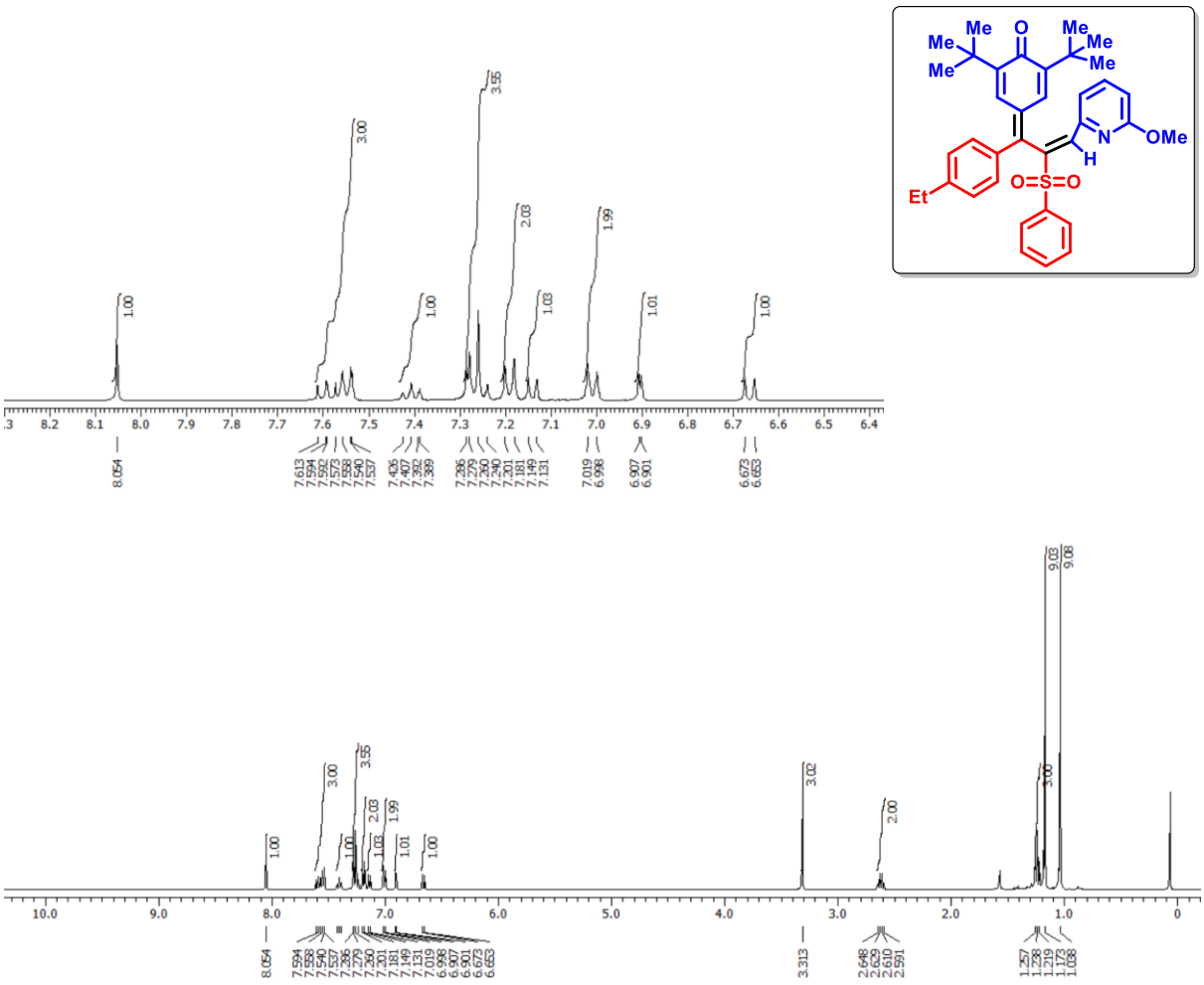
## $^{1}$H NMR (100 MHz, $CDCl_3$) (5bb)



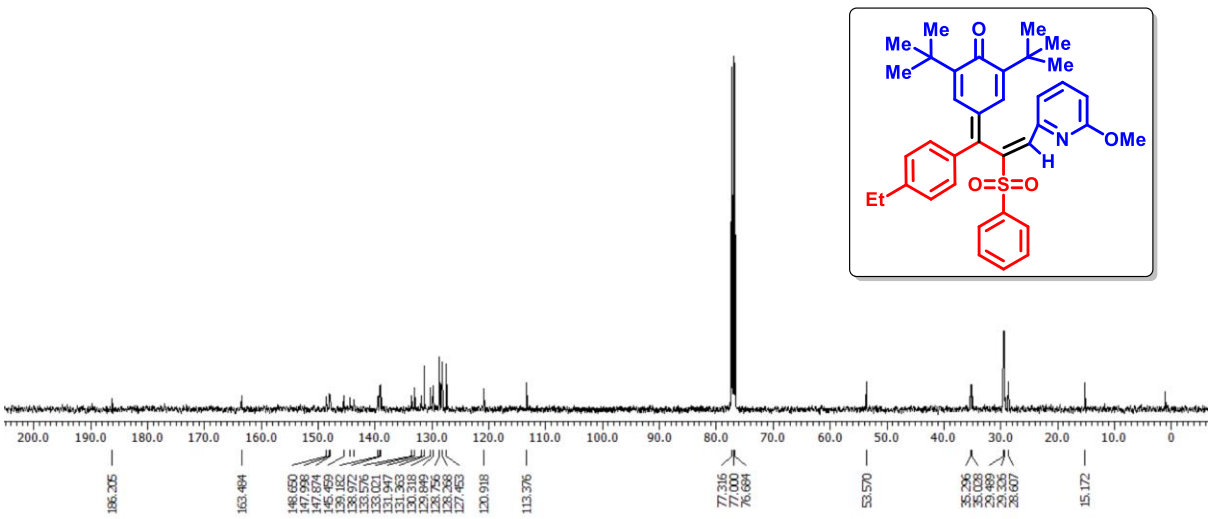

## $^{13}$C-NMR (100 MHz, $CDCl_3$) (5bb)



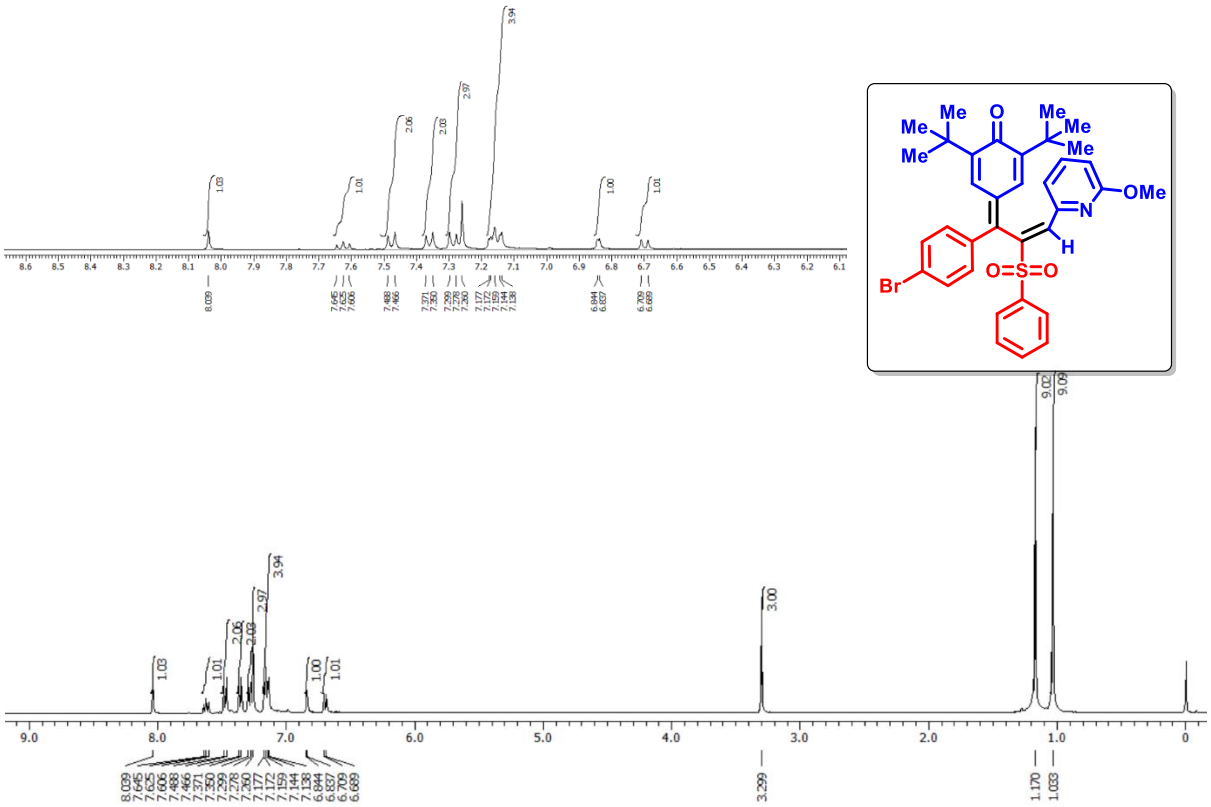
## $^{1}$H NMR (400 MHz, $CDCl_3$) (5ab)



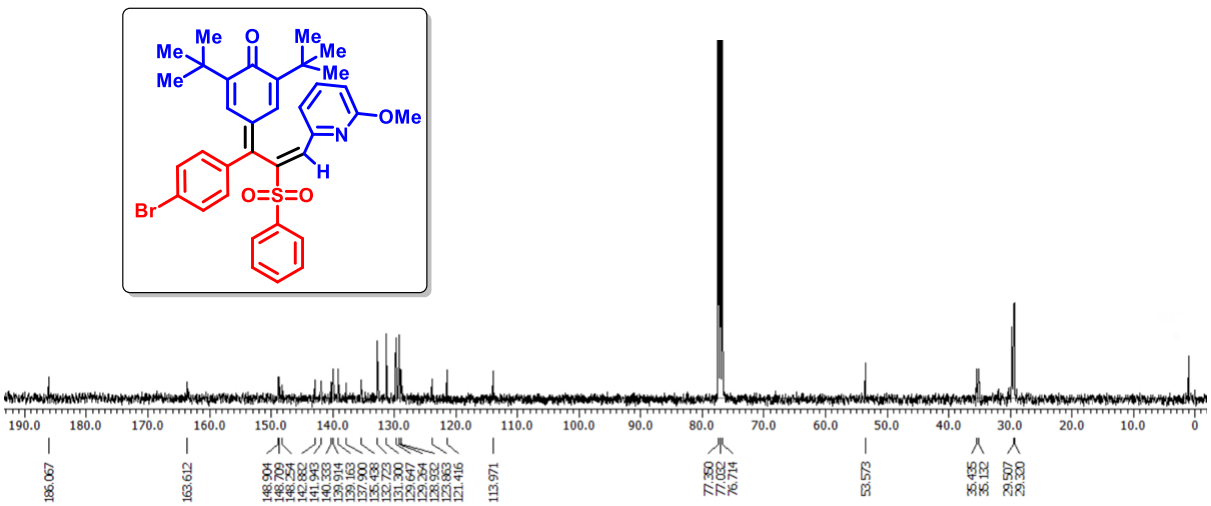

## $^{13}$C {1H} NMR (100 MHz, $CDCl_3$) (5ab)



**$^{1}$H NMR (400 MHz, $CDCl_3$) (5ac)**

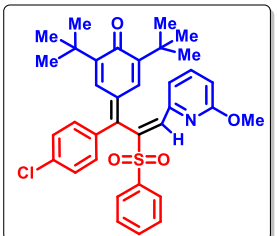


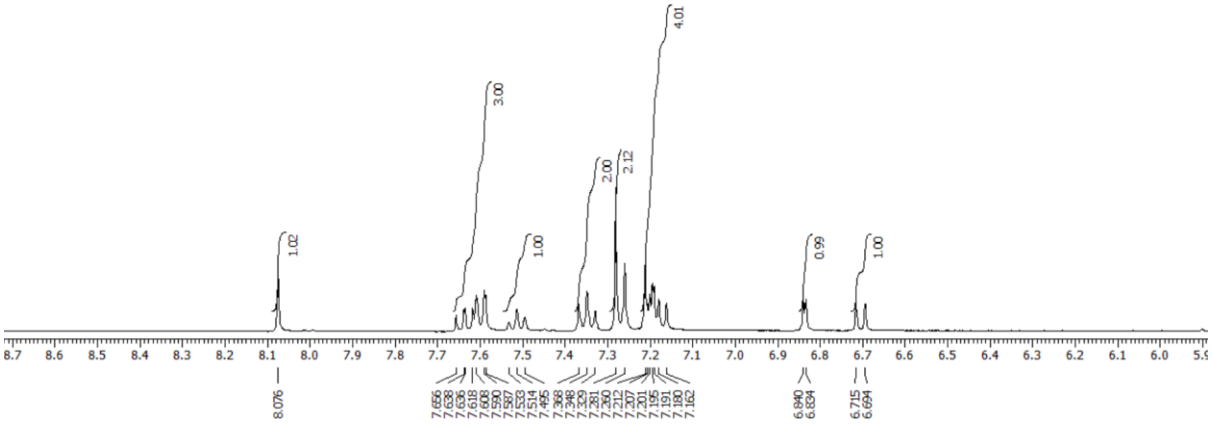

**$^{13}$C {1H} NMR (100 MHz, $CDCl_3$) (5ac)**

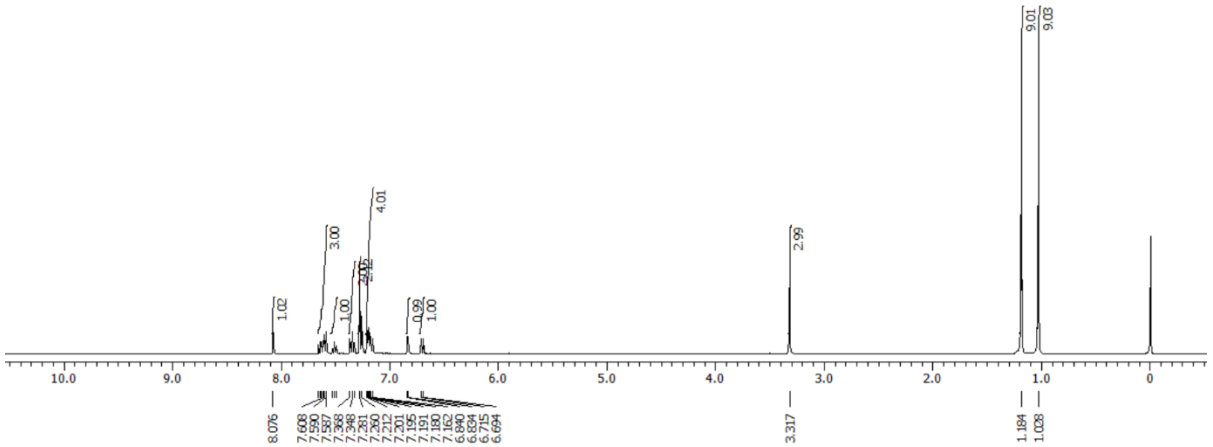



**$^{1}$H NMR (400 MHz, $CDCl_3$) (5ad)**

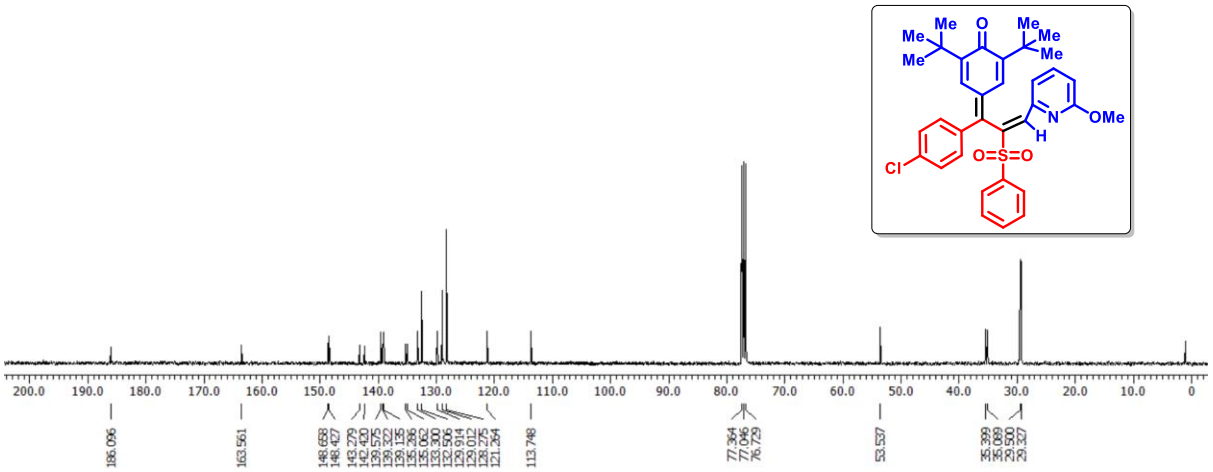




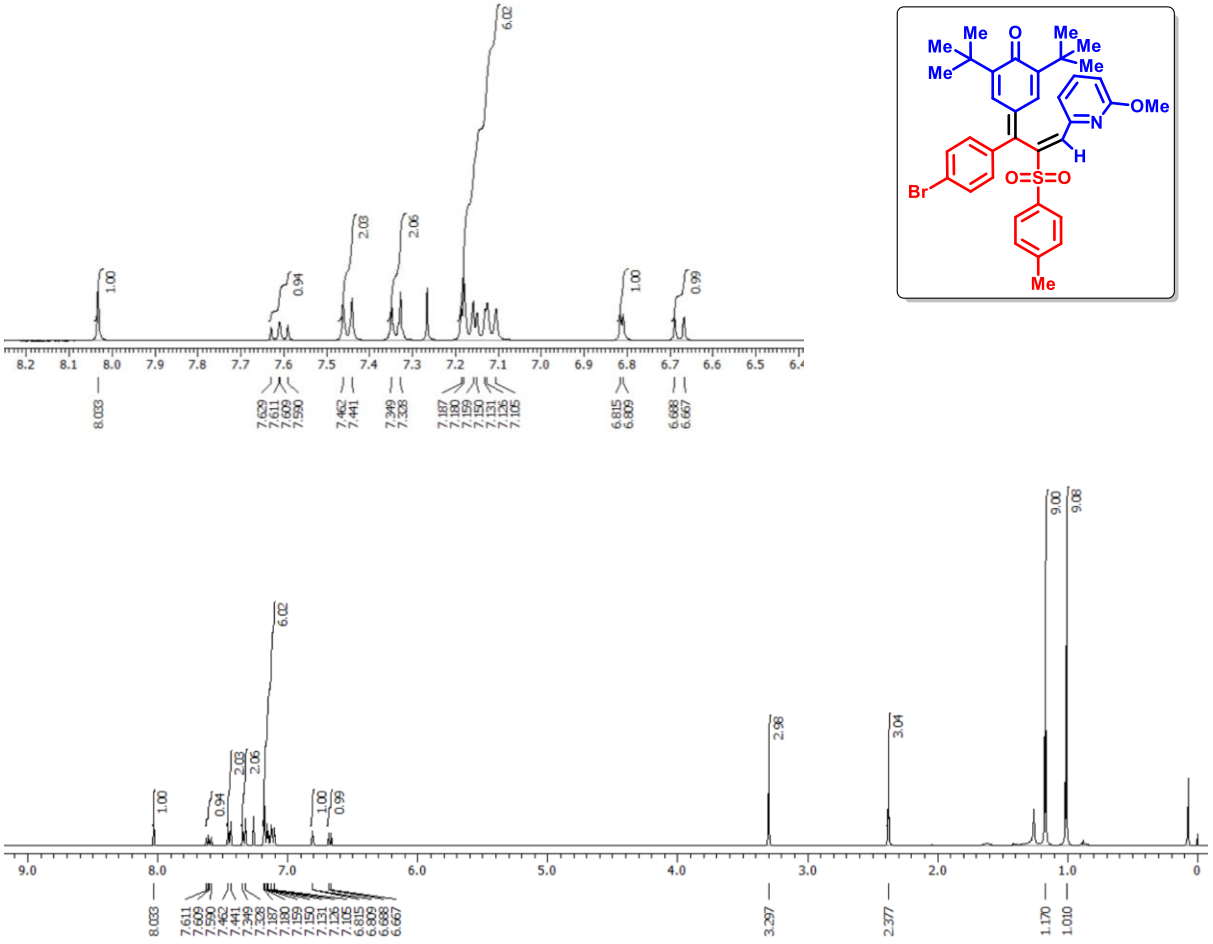




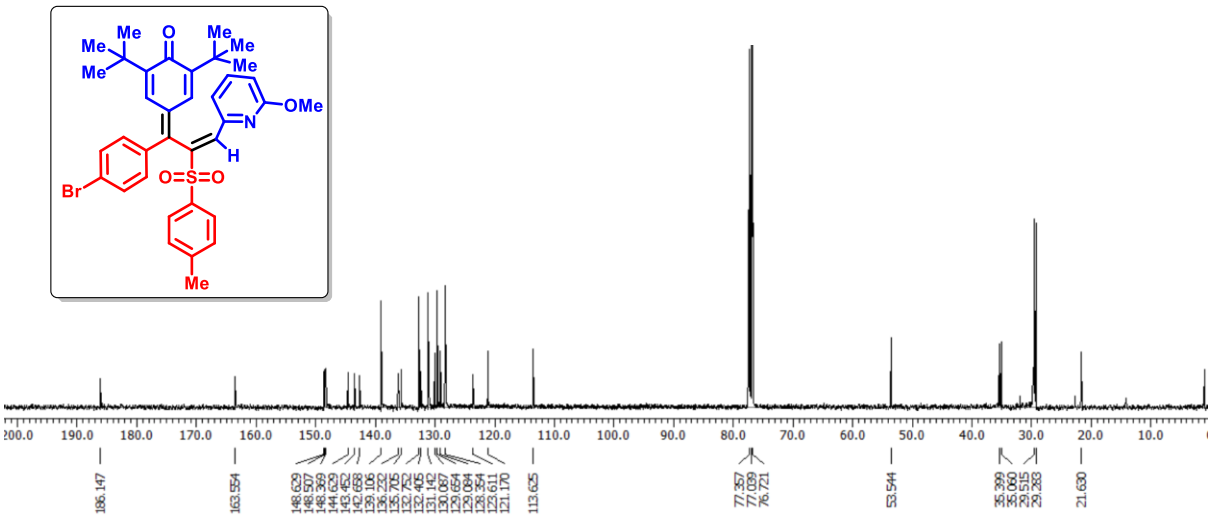
**$^{13}$C {1H} NMR (100 MHz, CDCl$_3$) (5ad)**



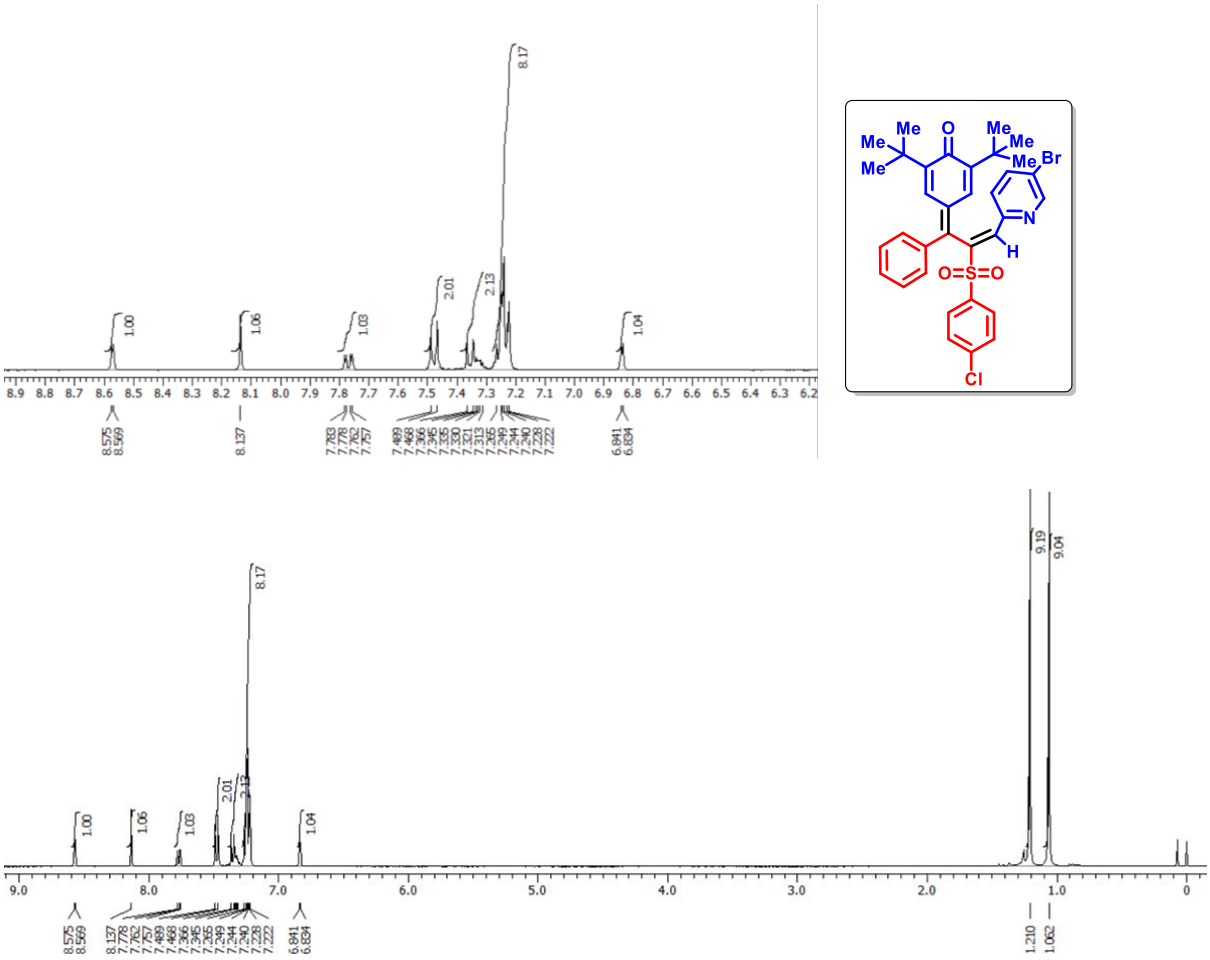
## $^{1}$H NMR (400 MHz, $CDCl_3$) (5ae)



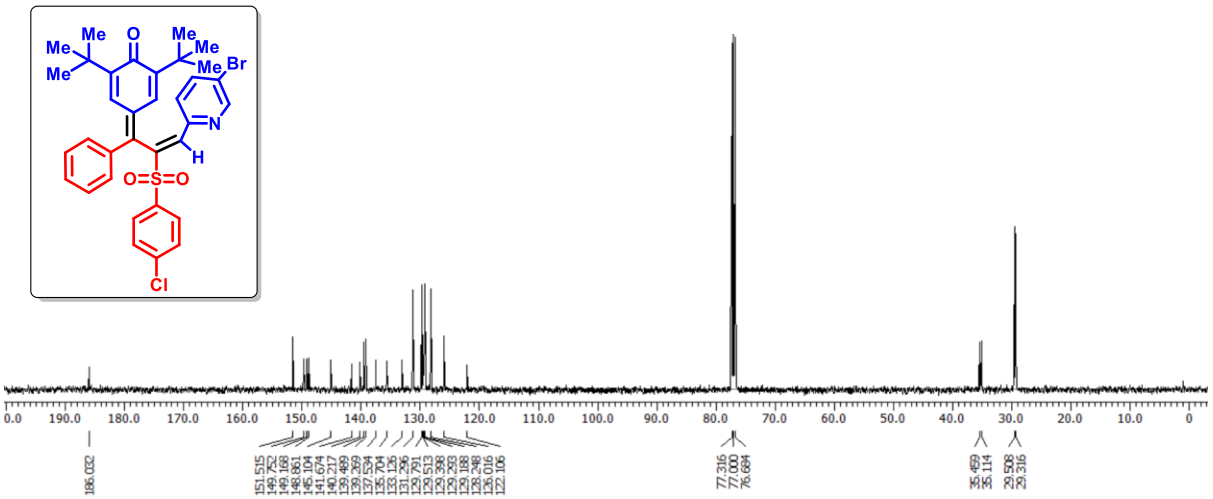

## $^{13}$C {1H} NMR (100 MHz, $CDCl_3$) (5ae)



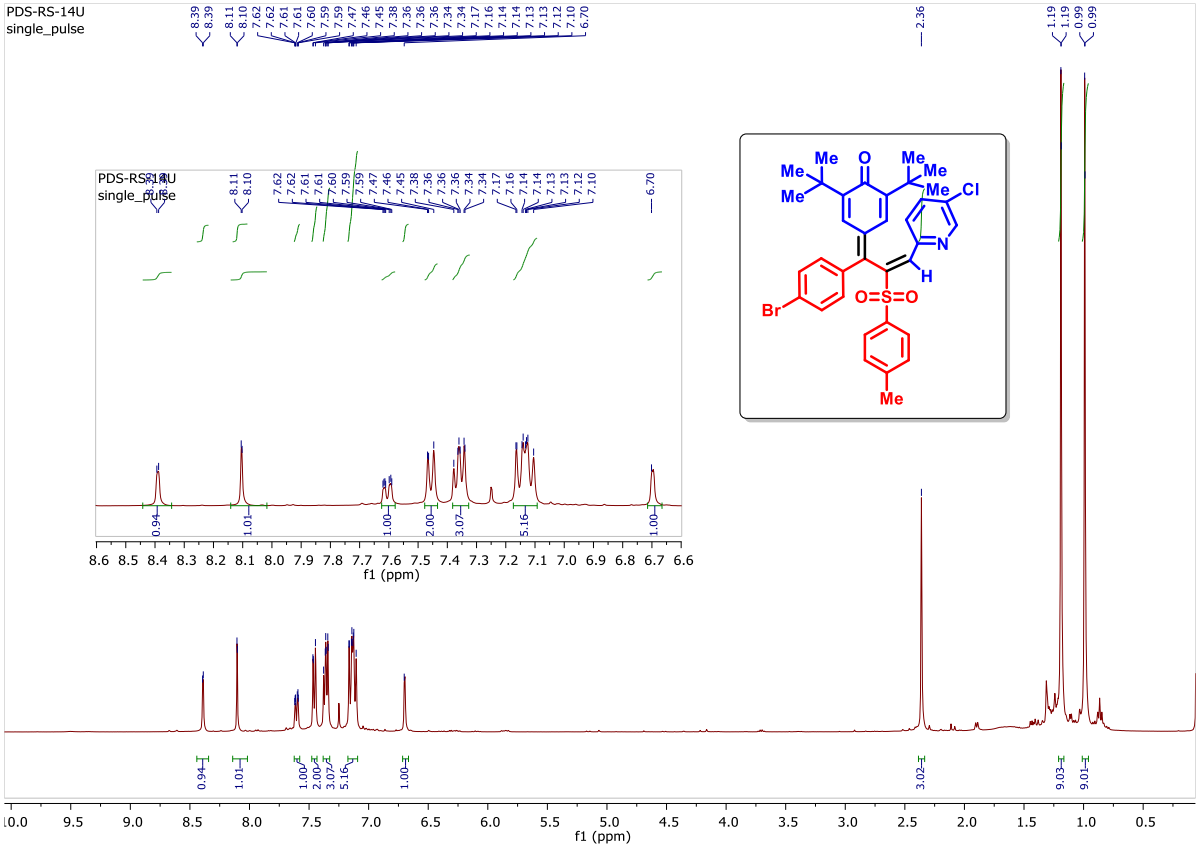
## $^{1}$H NMR (400 MHz, $CDCl_3$) (5fb)



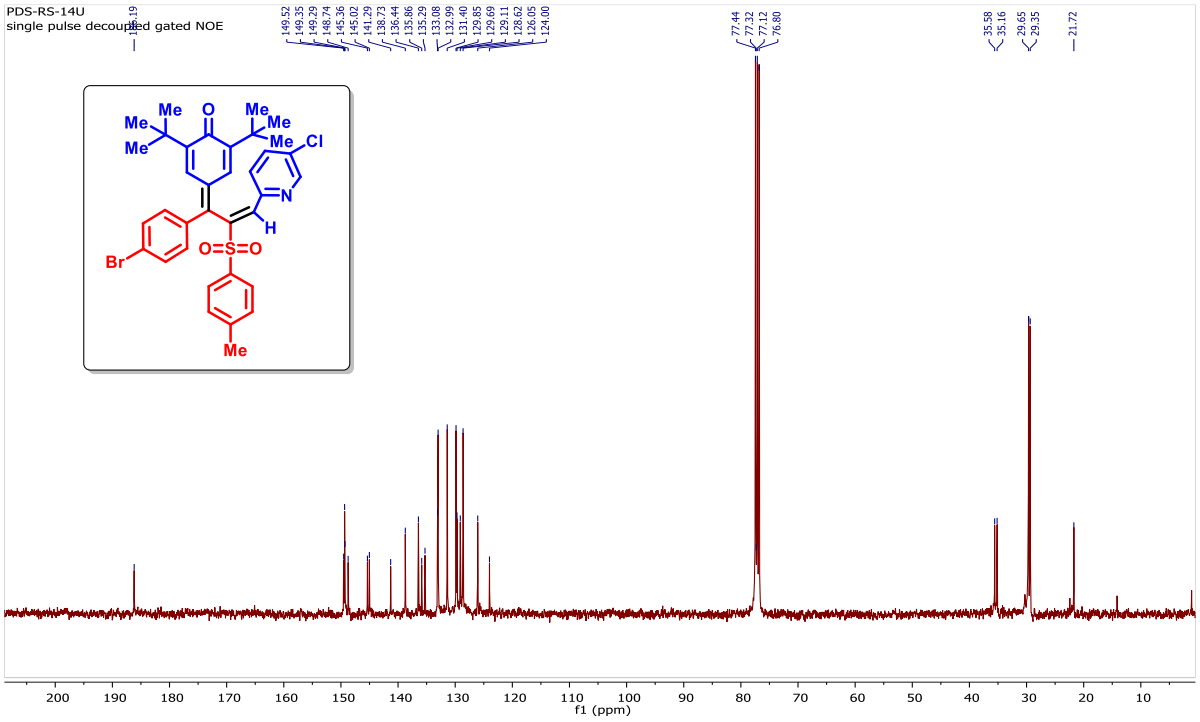

## $^{13}$C {1H} NMR (100 MHz, $CDCl_3$) (5fb)



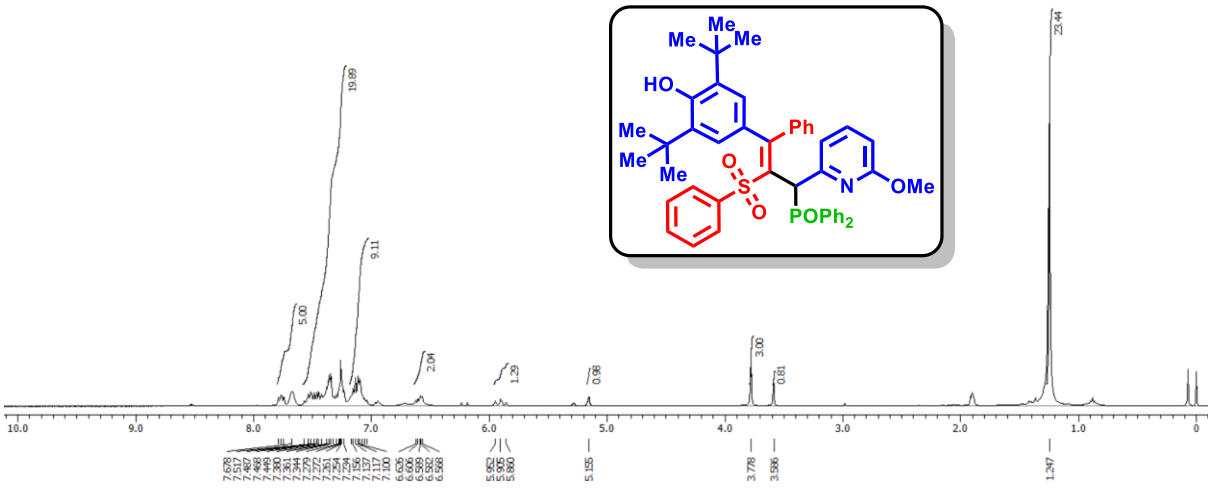
## $^{1}$H NMR (400 MHz, $CDCl_3$), (5dd)



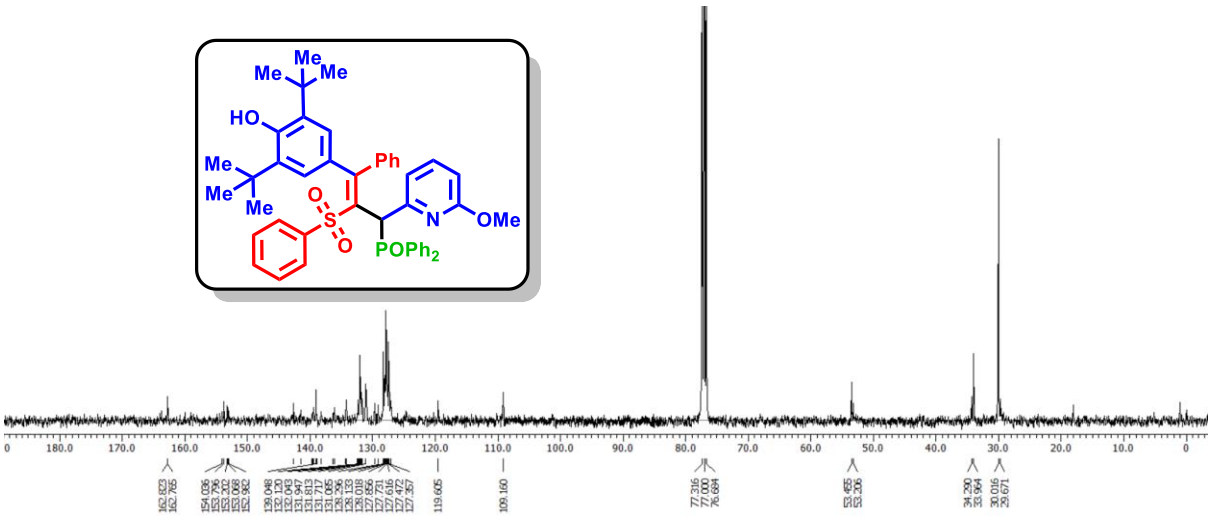

## $^{13}$C NMR (100 MHz, $CDCl_3$), (5dd)



**$^{1}$H NMR (400 MHz, $CDCl_3$) (11)**




**$^{13}$C {1H} NMR (100 MHz, $CDCl_3$) (11)**




**$^{31}$P NMR (162 MHz, $CDCl_3$) (11)**