

Supporting Information

Palladium(II)-Catalyzed Substrate-Controlled Diastereoselective Formal (3 + 3) Allylic Annulation of 2- or 3-Substituted 4-Hydroxybut-2-en-1-yl acetates

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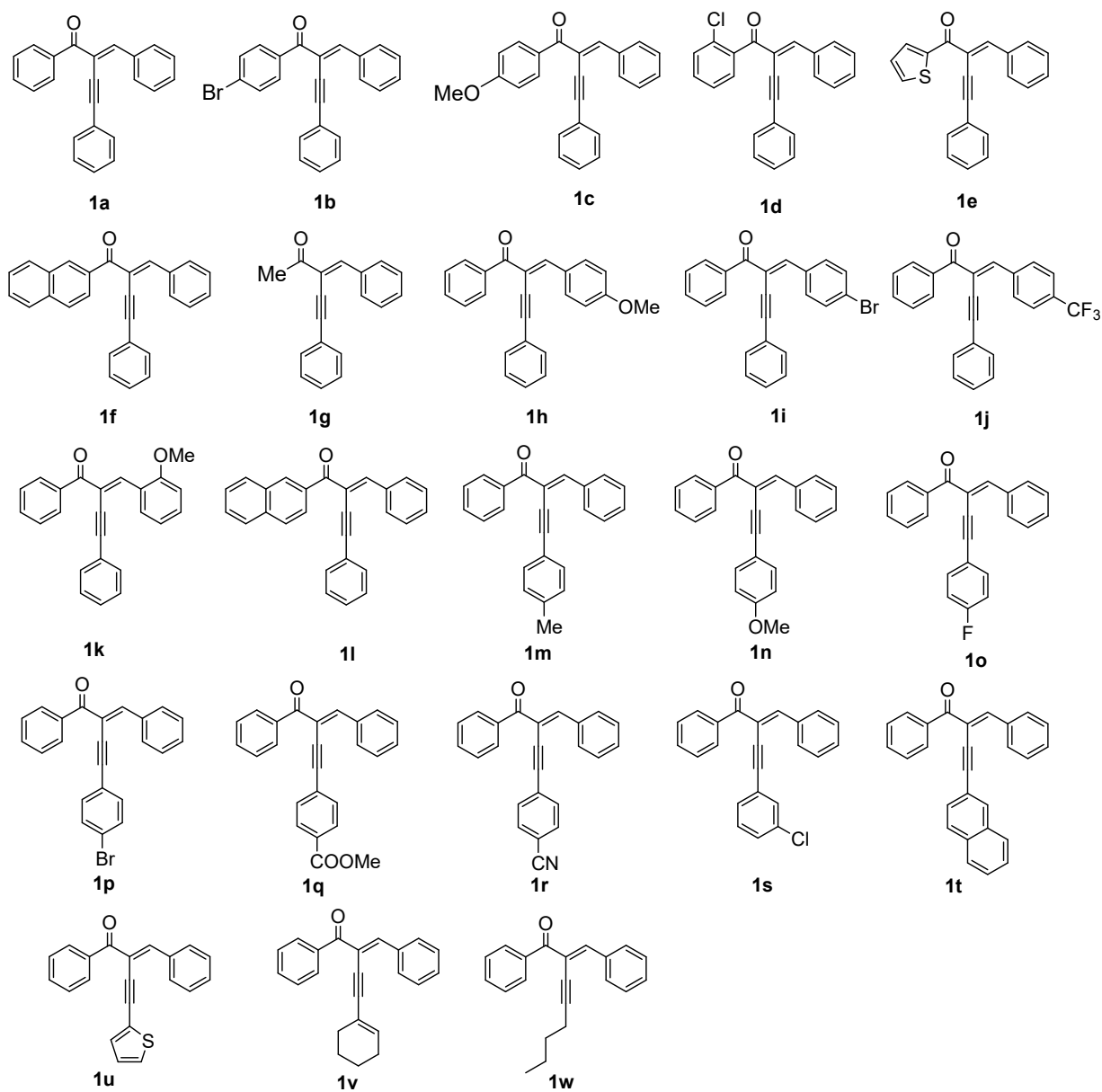
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1. General Information

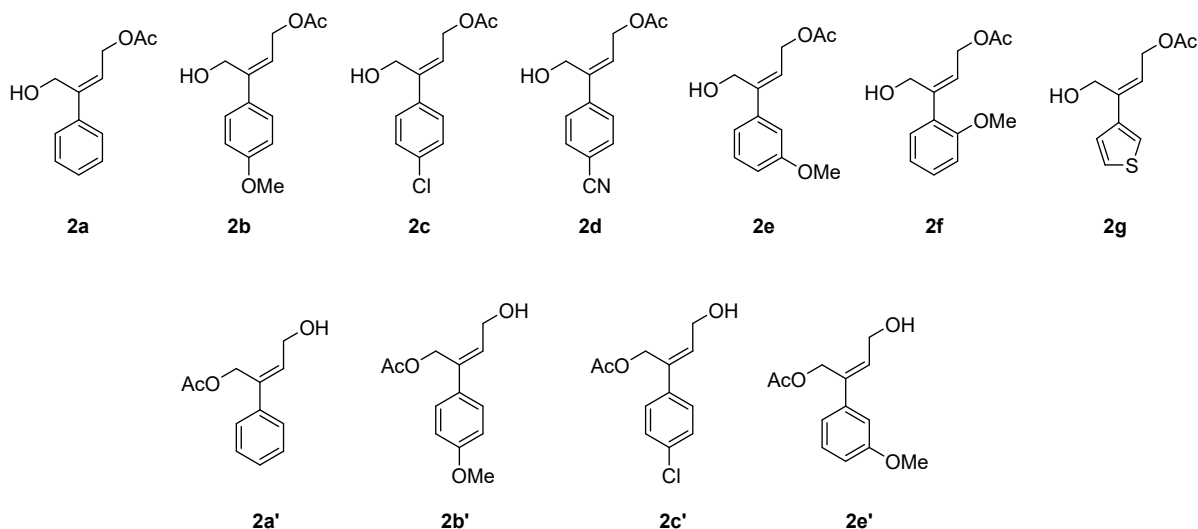
NMR spectra were recorded on a Bruker AM 400 MHz or 600 MHz spectrometer and calibrated using residual undeuterated solvent as an internal reference (CDCl_3 (^1H): $\delta = 7.26$ ppm; CDCl_3 (^{13}C): $\delta = 77.23$ ppm. High-resolution mass analysis was performed using a Thermo Scientific™ Q Exactive™ Hybrid Quadrupole-Orbitrap Mass Spectrometer. Melting points were determined on a Stanford Research Systems OptiMelt apparatus. Crystal measurement was recorded on Bruker D⁸ QUEST. The infrared (IR) spectra were acquired as thin films using a universal ATR sampling accessory on a Bruker Vertex 80 FT-IR spectrometer and the absorption frequencies are reported in cm^{-1} . Flash chromatography separations were carried out using silica gel columns. All new compounds were characterized by ^1H NMR, ^{13}C NMR, HRMS, and IR.

2. Preparation of starting material 1.

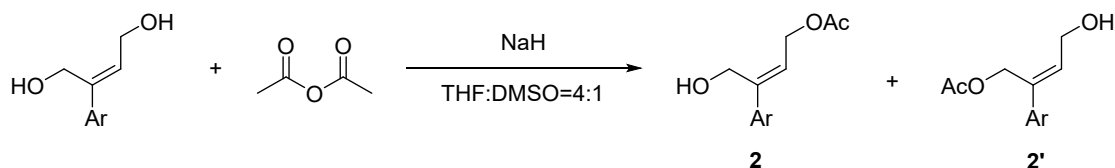


Starting material **1** were prepared by following the literature procedures.¹⁻¹¹

3. preparation of starting material **2** and **2'**.

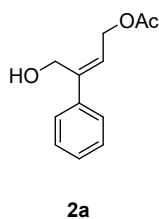


General procedure A for the synthesis of **2** and **2'**



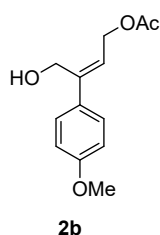
To a solution of NaH (60% in mineral oil, 3.30 mmol 1.10 equiv.) in THF (20 mL) and DMSO (5 mL), was added a solution of substituted (Z)-but-2-ene-1,4-diol¹² (3.0 mmol, 1.00 equiv.) in THF (10 mL), followed by acetic anhydride (3.90 mmol, 1.30 equiv.). The resulting mixture was stirred at 0 °C for 4 h. The completed reaction was quenched with water (10 mL) and extracted with EtOAc (30 mL x 3). The combined organic phases were washed with brine (30 mL), dried (anhydrous Na₂SO₄) and concentrated. The residue was purified by column chromatography (Silica Gel, PE/EtOAc) to afford **2** and **2'**.

(Z)-4-Hydroxy-3-phenylbut-2-en-1-yl acetate (**2a**)



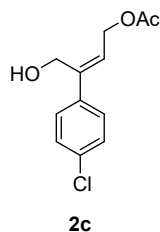
By following general procedure A, (Z)-2-phenylbut-2-ene-1,4-diol (1.31 g, 8.0 mmol) and acetic anhydride (1.06 g, 10.4 mmol) afforded **2a** as a pale yellow oil (0.525 g, 32%). The spectral data were consistent with the literature.¹³ ¹H NMR (600 MHz, CDCl₃) δ 7.40 – 7.37 (m, 2H), 7.27 – 7.18 (m, 3H), 5.91 (t, *J* = 7.2 Hz, 1H), 4.86 (d, *J* = 7.3 Hz, 2H), 4.57 (s, 2H), 2.71 (s, 1H), 2.07 (s, 3H); ¹³C{¹H} NMR (151 MHz, CDCl₃) δ 171.5, 143.8, 140.2, 128.5, 128.0, 126.5, 124.4, 61.3, 60.0, 21.1.

(Z)-4-Hydroxy-3-(4-methoxyphenyl)but-2-en-1-yl acetate (2b)



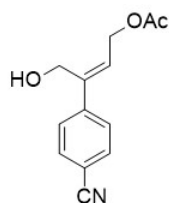
By following general procedure A, (Z)-2-(4-methoxyphenyl)but-2-ene-1,4-diol (0.522 g, 2.69 mmol) and acetic anhydride (0.357 g, 3.49 mmol) afforded **2b** as a pale yellow oil (0.141 g, 22%). The spectral data were consistent with the literature.¹³ ¹H NMR (600 MHz, CDCl₃) δ 7.27 (d, *J* = 8.8 Hz, 2H), 6.72 (d, *J* = 8.8 Hz, 2H), 5.71 (t, *J* = 7.3 Hz, 1H), 4.69 (d, *J* = 7.3 Hz, 2H), 4.40 (s, 2H), 3.65 (s, 3H), 2.59 (s, 1H), 1.92 (s, 3H). ¹³C{¹H} NMR (151 MHz, CDCl₃) δ 171.5, 159.5, 143.2, 132.5, 127.7, 122.7, 114.0, 61.3, 59.8, 55.3, 21.1.

(Z)-3-(4-Chlorophenyl)-4-hydroxybut-2-en-1-yl acetate (2c)



By following general procedure A, (Z)-2-(4-chlorophenyl)but-2-ene-1,4-diol (0.795 g, 4.0 mmol) and acetic anhydride (0.531 g, 5.2 mmol) afforded **2c** as a pale yellow oil (0.278 g, 29%). The spectral data were consistent with the literature.¹³ ¹H NMR (600 MHz, CDCl₃) δ 7.43 (d, *J* = 8.5 Hz, 2H), 7.31 (d, *J* = 8.6 Hz, 2H), 5.90 (t, *J* = 7.3 Hz, 1H), 4.86 (d, *J* = 7.3 Hz, 2H), 4.56 (s, 1H), 2.57 (s, 1H), 2.08 (s, 3H); ¹³C{¹H} NMR (151 MHz, CDCl₃) δ 171.6, 142.9, 138.8, 134.0, 128.8, 127.9, 124.8, 61.2, 60.0, 21.2.

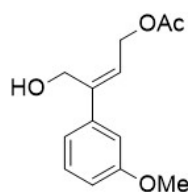
(Z)-3-(4-Cyanophenyl)-4-hydroxybut-2-en-1-yl acetate (2d)



2d

By following general procedure A, (Z)-4-(1,4-dihydroxybut-2-en-2-yl)benzonitrile (0.400 g, 2.11 mmol) and acetic anhydride (0.281 g, 2.75 mmol) afforded **2d** as a pale yellow oil (0.116 g, 24%); $R_f = 0.14$ (PE/EA = 3:1); ^1H NMR (600 MHz, CDCl_3) δ 7.63 – 7.58 (m, 4H), 5.98 (t, $J = 7.2$ Hz, 1H), 4.88 (d, $J = 7.2$ Hz, 2H), 4.57 (s, 2H), 2.81 (s, 1H), 2.08 (s, 3H); $^{13}\text{C}\{^1\text{H}\}$ NMR (151 MHz, CDCl_3) δ 171.6, 145.0, 142.3, 132.4, 127.4, 127.2, 118.9, 111.5, 61.1, 59.7, 21.1; IR (neat): 3419, 1731, 1227, 1080, 827 cm^{-1} ; HRMS(ESI) m/z : $[\text{M}+\text{H}]^+$ calculated for $\text{C}_{13}\text{H}_{14}\text{NO}_3^+$ 232.0968; found 232.0981.

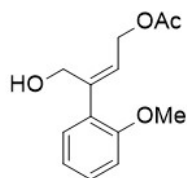
(Z)-4-Hydroxy-3-(3-methoxyphenyl)but-2-en-1-yl acetate (2e)



2e

By following general procedure A, (Z)-2-(3-methoxyphenyl)but-2-ene-1,4-diol (0.713 g, 4.00 mmol) and acetic anhydride (0.531 g, 5.20 mmol) afforded **2e** as a pale yellow oil (0.198 g, 21%). The spectral data were consistent with the literature.¹³ ^1H NMR (600 MHz, CDCl_3) δ 7.23 (m, 1H), 7.03 (d, $J = 7.7$ Hz, 1H), 7.00 (t, $J = 2.2$ Hz, 1H), 6.82 (dd, $J = 8.3, 2.6$ Hz, 1H), 5.89 (t, $J = 7.2$ Hz, 1H), 4.83 (d, $J = 7.2$ Hz, 2H), 4.52 (s, 2H), 3.78 (s, 3H), 2.96 (s, 1H), 2.05 (s, 3H); $^{13}\text{C}\{^1\text{H}\}$ NMR (151 MHz, CDCl_3) δ 171.4, 159.7, 143.5, 141.7, 129.4, 124.5, 118.9, 113.3, 112.2, 61.2, 59.9, 55.2, 21.0.

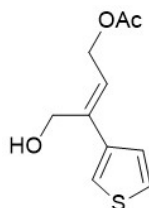
(Z)-4-Hydroxy-3-(2-methoxyphenyl)but-2-en-1-yl acetate (2f)



2f

By following general procedure A, (Z)-2-(2-methoxyphenyl)but-2-ene-1,4-diol (1.07 g, 5.50 mmol) and acetic anhydride (0.730 g, 7.15 mmol) afforded **2f** as a pale yellow oil (0.377 g, 29%): R_f = 0.58 (PE/EA = 3:1); ^1H NMR (400 MHz, CDCl_3) δ 7.16 (m, 1H), 7.09-6.94 (m, 1H), 6.78 (d, J = 8.3 Hz, 1H), 5.63 (t, J = 6.9 Hz, 1H), 4.77 (d, J = 6.9 Hz, 2H), 4.32 (s, 2H), 3.72 (s, 3H), 2.73 (s, 1H), 1.97 (s, 3H); $^{13}\text{C}\{^1\text{H}\}$ NMR (151 MHz, CDCl_3) δ 170.9, 156.2, 143.5, 130.5, 130.1, 128.9, 126.6, 120.8, 110.5, 60.8, 60.6, 55.3, 20.7; IR (neat): 3354, 1511, 1193, 1028, 728 cm^{-1} ; HRMS (ESI) m/z : $[\text{M}+\text{H}]^+$ calculated for $\text{C}_{13}\text{H}_{17}\text{O}_4^+$ 237.1121; found 237.1132.

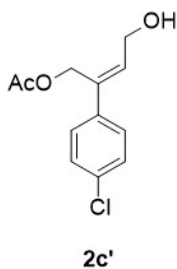
(Z)-4-Hydroxy-3-(thiophen-3-yl)but-2-en-1-yl acetate (2g)



2g

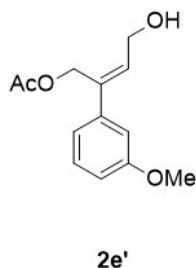
By following general procedure A, (Z)-2-(thiophen-3-yl)but-2-ene-1,4-diol (0.250 g, 1.47 mmol) and acetic anhydride (0.195 g, 1.91 mmol) afforded **2g** (0.074 g, 24%) as a pale yellow oil: R_f = 0.45 (PE/EA = 3:1.); ^1H NMR (600 MHz, CDCl_3) δ 7.44 (m, 1H), 7.30 (m, 1H), 7.27 (d, J = 1.6 Hz, 1H), 6.02 (t, J = 7.5 Hz, 1H), 4.86 (d, J = 7.5 Hz, 2H), 4.57 (s, 2H), 2.53 (s, 1H), 2.08 (s, 3H); $^{13}\text{C}\{^1\text{H}\}$ NMR (151 MHz, CDCl_3) δ 171.6, 141.2, 138.8, 126.1, 125.7, 122.6, 122.0, 61.1, 60.0, 21.2; IR (neat): 3419, 1732, 1511, 1240, 733 cm^{-1} ; HRMS(ESI) m/z : $[\text{M}+\text{H}]^+$ calculated for $\text{C}_{10}\text{H}_{13}\text{SO}_3^+$ 213.0580; found 213.0581.

(Z)-2-(4-Chlorophenyl)-4-hydroxybut-2-en-1-yl acetate (2c')

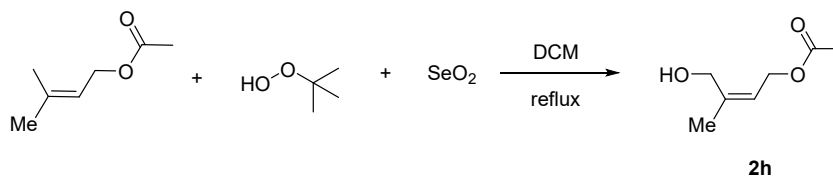


By following general procedure A, (Z)-2-(4-chlorophenyl)but-2-ene-1,4-diol (0.795 g, 4.0 mmol) and acetic anhydride (0.531 g, 5.20 mmol) afforded **2c'** as a pale yellow oil (0.263 g, 27%). The spectral data were consistent with the literature.¹⁴ ¹H NMR (600 MHz, CDCl₃): δ 7.35 (d, *J* = 8.7 Hz, 2H), 7.31 (d, *J* = 8.6 Hz, 2H), 6.18 (t, *J* = 6.9 Hz, 1H), 5.04 (s, 2H), 4.42 (d, *J* = 6.9 Hz, 2H), 2.17 (s, 1H), 2.00 (s, 3H); ¹³C{¹H} NMR (151 MHz, CDCl₃): δ 171.3, 138.1, 135.7, 133.9, 132.8, 128.8, 127.8, 61.0, 59.1, 21.1.

(Z)-4-Hydroxy-2-(3-methoxyphenyl)but-2-en-1-yl acetate (2e')



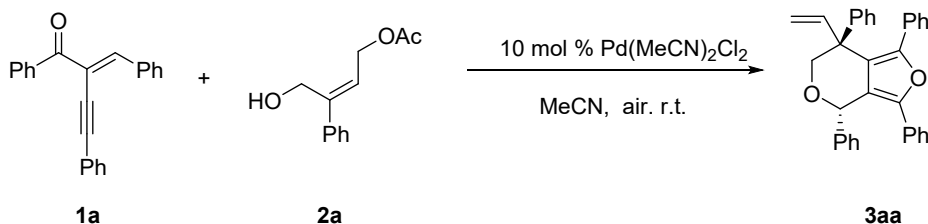
By following general procedure A, (Z)-2-(3-methoxyphenyl)but-2-ene-1,4-diol (0.713 g, 4.00 mmol) and acetic anhydride (0.531 g, 5.20 mmol) afforded **2e'** as an pale yellow oil (0.178 g, 19%): *R*_f = 0.28 (PE/EA = 3:1); ¹H NMR (600 MHz, CDCl₃) δ 7.28 (d, *J* = 8.3 Hz, 1H), 7.02 (d, *J* = 7.7 Hz, 1H), 6.98 (s, 1H), 6.86 (m, 1H), 6.23 (t, *J* = 6.9 Hz, 1H), 5.05 (s, 2H), 4.44 (d, *J* = 6.9 Hz, 2H), 3.83 (s, 3H), 2.59 (s, 1H), 2.02 (s, 3H); ¹³C{¹H} NMR (151 MHz, CDCl₃) δ 171.4, 159.7, 141.2, 136.3, 132.7, 129.5, 118.9, 113.2, 112.3, 61.2, 59.0, 55.3, 21.0. IR (neat): 3402, 1732, 1224, 1023, 720 cm⁻¹; HRMS (ESI) *m/z*: [M+H]⁺ calculated for C₁₃H₁₇O₄⁺ 237.1121; found 237.1109.



To a solution of 3-methylbut-2-en-1-yl acetate (0.513 g, 4.0 mmol, 1.0 equiv.) in DCM (20 mL), 2-hydroperoxy-2-methylpropane (0.735 g, 8.16 mmol, 2.0 equiv.) and SeO₂ (0.133 g, 1.20 mmol, 0.3 equiv.) were added. The resulting mixture was refluxed for 3h. The completed reaction was concentrated. The residue was purified by column chromatography (silica gel, petroleum ether/ethyl acetate = 5:1) to afford product **2h** as a pale yellow oil (0.357 g, 62%). The spectral data were consistent with the literature.¹³ ¹H NMR (600 MHz, CDCl₃) δ 5.53 (t, *J* = 6.2 Hz, 1H), 4.56 (d, *J* = 7.2 Hz, 2H), 3.94 (s, 2H), 2.82 (s, 1H), 1.98 (s, 3H), 1.64 (s, 3H); ¹³C{¹H} NMR (151 MHz, CDCl₃) δ 171.3, 141.0, 118.2, 67.3, 61.0, 20.9, 13.7.

4. Synthesis of 7-vinyl-6,7-dihydro-4H-furo[3,4-c]pyran 3

4.1 Optimization of reaction conditions^a

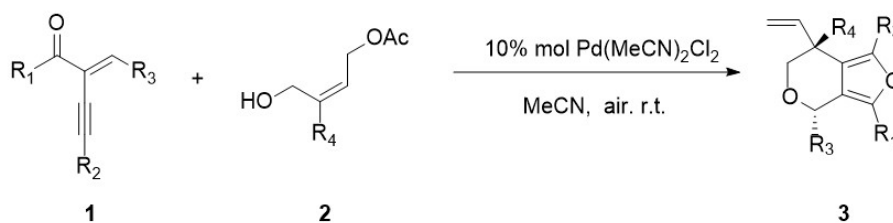


Entry	equiv. of 2a	Pd catalyst	Solvent	Yield ^b
1 ^c	0.80	Pd(MeCN) ₂ Cl ₂	MeCN	42
2 ^c	1.50	Pd(MeCN) ₂ Cl ₂	MeCN	62
3 ^d	1.50	Pd(MeCN) ₂ Cl ₂	MeCN	51
4	1.50	Pd(MeCN) ₂ Cl ₂	MeCN	86
5 ^e	1.50	Pd(MeCN) ₂ Cl ₂	MeCN	80
6	1.50	Pd(MeCN) ₂ Cl ₂	THF	0
7	1.50	Pd(MeCN) ₂ Cl ₂	DCM	9
8	1.50	Pd(MeCN) ₂ Cl ₂	DMF	0
9	1.50	Pd(MeCN) ₂ Cl ₂	DCE	24
10	1.50	Pd(MeCN) ₂ Cl ₂	toluene	0

11	1.50	$\text{Pd}(\text{MeCN})_2\text{Cl}_2$	1,4-dioxane	9
12	1.50	$\text{Pd}(\text{MeCN})_2\text{Cl}_2$	DMSO	0
13	1.50	PdBr_2	MeCN	85
14	1.50	$\text{Pd}(\text{dba})_2$	MeCN	trace
15	1.50	$\text{Pd}(\text{OAc})_2$	MeCN	trace
16	1.50	$\text{Pd}(\text{TFA})_2$	MeCN	N,R
17	1.50	PdCl_2	MeCN	N,R
18	1.50	$\text{Pd}(\text{MeCN})_2\text{Cl}_2/\text{PPh}_3$	MeCN	N,R
19	1.50	$\text{Pd}(\text{MeCN})_2\text{Cl}_2/\text{BINAP}$	MeCN	N,R

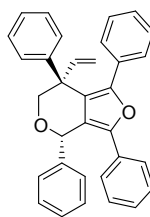
^aReaction conditions: **2a** (0.15 mmol, 1.5 equiv.) and $\text{Pd}(\text{MeCN})_2\text{Cl}_2$ (0.01 mmol, 0.1 equiv.) in MeCN (1.5 mL) were stirred at room temperature. After 30 minutes, a solution of **1a** (0.10 mmol, 1.0 equiv.) in MeCN (0.5 mL) was added. The reaction mixture was stirred at room temperature for 12 h. ^bisolated yield. ^csolution of **1a** in MeCN was added over 6 hours via syringe pump. ^dAll reagents were added at the same time. ^e $\text{Pd}(\text{MeCN})_2\text{Cl}_2$ (5 mol %).

4.2 General procedure B for the synthesis 7-vinyl-6,7-dihydro-4H-furo[3,4-c]pyran **3**



A mixture of **2** (0.15 mmol, 1.50 equiv.) and $\text{Pd}(\text{MeCN})_2\text{Cl}_2$ (0.01 mmol, 0.10 equiv.) in MeCN (1.5 mL) was stirred at room temperature under air for 0.5 h. A solution of **1** (0.10 mmol, 1.0 equiv.) in MeCN (0.50 mL) was added and the mixture was stirred at room temperature for 12 h. The completed reaction was concentrated. The residue was purified by column chromatography (silica gel, petroleum ether/ethyl acetate) to afford product **3**.

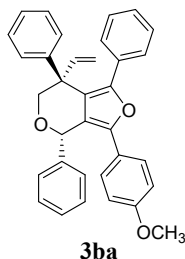
(4S,7S)-1,3,4,7-Tetraphenyl-7-vinyl-6,7-dihydro-4H-furo[3,4-c]pyran (**3aa**)



3aa

The reaction was performed according to general procedure B using **1a** (30.8 mg, 0.1 mmol) and **2a** (30.9 mg, 0.15 mmol) to afford **3aa** as an amorphous white solid (39.0 mg, 85% yield): $R_f = 0.40$ (PE/EtOAc = 30:1); m.p. 144-146 °C; ^1H NMR (400 MHz, CDCl_3) δ 7.46 – 7.37 (m, 8H), 7.33 -7.29 (m, 4H), 7.25 – 7.09 (m, 8H), 6.53 (dd, $J = 17.4, 10.7$ Hz, 1H), 6.20 (s, 1H), 5.36 (d, $J = 10.6$ Hz, 1H), 5.29 (d, $J = 17.4$ Hz, 1H), 3.92 (d, $J = 11.5$ Hz, 1H), 3.81 (d, $J = 11.5$ Hz, 1H); $^{13}\text{C}\{^1\text{H}\}$ NMR (101 MHz, CDCl_3) δ 148.39, 146.38, 143.3, 139.4, 139.2, 130.7, 130.4, 129.2, 128.6, 128.5, 128.4, 127.9, 127.7, 127.3, 127.2, 127.0, 126.9, 125.5, 122.7, 119.78, 117.80, 76.0, 74.0, 47.8 (one carbon missing due to overlap); IR (neat): 3050, 1656, 1550, 985, 702 cm^{-1} ; HRMS (ESI) m/z : $[\text{M}+\text{H}]^+$ calculated for $\text{C}_{33}\text{H}_{27}\text{O}_2^+$ 455.2006; found 455.2001.

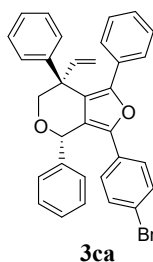
(4S,7S)-3-(4-Methoxyphenyl)-1,4,7-triphenyl-7-vinyl-6,7-dihydro-4H-furo[3,4-c]pyran (3ba)



3ba

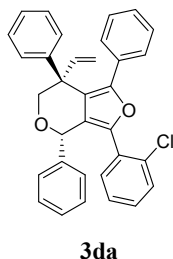
The reaction was performed according to general procedure B using **1b** (33.8 mg, 0.1 mmol) and **2a** (30.9 mg, 0.15 mmol) to give **3ba** as an amorphous white solid (40.7 mg, 84% yield): $R_f = 0.31$ (PE/EtOAc = 30:1); m.p. 165-167 °C; ^1H NMR (400 MHz, CDCl_3) δ 7.67 (s, 1H), 7.48 – 7.37 (m, 6H), 7.32 (m, 5H), 7.27 – 7.12 (m, 6H), 6.73 (d, $J = 8.7$ Hz, 1H), 6.58 (dd, $J = 17.3, 10.6$ Hz, 1H), 6.14 (s, 1H), 5.44 (d, $J = 10.6$ Hz, 1H), 5.34 (d, $J = 17.3$ Hz, 1H), 3.98 (d, $J = 11.5$ Hz, 1H), 3.86 (m, 4H); $^{13}\text{C}\{^1\text{H}\}$ NMR (101 MHz, CDCl_3) δ 154.8, 148.3, 144.9, 142.9, 139.4, 139.1, 130.7, 130.5, 129.2, 128.8, 128.7, 128.5, 127.8, 127.7, 127.3, 126.9, 126.8, 125.8, 124.5, 122.7, 119.4, 118.0, 111.7, 111.5, 76.3, 74.5, 56.3, 48.0; HRMS (ESI) m/z : $[\text{M}+\text{H}]^+$ calculated for $\text{C}_{34}\text{H}_{29}\text{O}_3^+$ 485.2111; found 485.2108.

(4S,7S)-3-(4-Bromophenyl)-1,4,7-triphenyl-7-vinyl-6,7-dihydro-4H-furo[3,4-c] pyran (3ca)



The reaction was performed according to general procedure B using **1c** (38.7 mg, 0.1 mmol) and **2a** (30.9 mg, 0.15 mmol) to give **3ca** as an amorphous white solid (40.6 mg, 76% yield): R_f = 0.56 (PE/EtOAc = 30:1); m.p. 69-71 °C; ^1H NMR (600 MHz, CDCl_3) δ 7.47 – 7.37 (m, 8H), 7.34 – 7.25 (m, 6H), 7.22 – 7.11 (m, 5H), 6.52 (dd, J = 17.4, 10.7 Hz, 1H), 6.18 (s, 1H), 5.36 (d, J = 10.7 Hz, 1H), 5.27 (d, J = 17.4 Hz, 1H), 3.88 (d, J = 11.5 Hz, 1H), 3.82 (d, J = 11.5 Hz, 1H); $^{13}\text{C}\{^1\text{H}\}$ NMR (151 MHz, CDCl_3) δ 148.6, 146.5, 143.2, 139.3, 138.3, 131.8, 130.9, 130.6, 130.2, 128.6, 128.5, 127.9, 127.7, 127.4, 126.98, 126.97, 125.4, 122.7, 122.6, 119.2, 117.8, 75.3, 74.0, 47.8 (one carbon missing due to overlap); IR (neat): 3085, 1594, 1485, 1069, 688 cm^{-1} ; HRMS (ESI) m/z : $[\text{M}+\text{H}]^+$ calculated for $\text{C}_{33}\text{H}_{26}\text{BrO}_2^+$ 533.1111; found 533.1099.

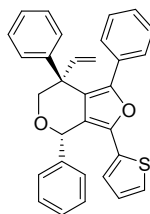
(4S,7S)-3-(2-Chlorophenyl)-1,4,7-triphenyl-7-vinyl-6,7-dihydro-4H-furo[3,4-c]pyran (3da)



The reaction was performed according to general procedure B using **1d** (34.3 mg, 0.1 mmol) and **2a** (30.9 mg, 0.15 mmol) to give **3da** as an amorphous white solid (30.9 mg, 63% yield): R_f = 0.50 (PE/EtOAc = 30:1); m.p. 129-131 °C; ^1H NMR (600 MHz, CDCl_3) δ 7.45 (d, J = 7.7 Hz, 2H), 7.33 (d, J = 7.7 Hz, 2H), 7.28 – 7.21 (m, 3H), 7.22 – 7.15 (m, 3H), 7.11 (m, 1H), 7.09 – 7.00 (m, 8H), 6.67 (dd, J = 17.2, 10.5 Hz, 1H), 5.87 (s, 1H), 5.57 (d, J = 10.5 Hz, 1H), 5.43 (d, J = 17.1 Hz, 1H), 4.15 (d, J = 11.6 Hz, 1H), 3.89 (d, J = 11.6 Hz, 1H); $^{13}\text{C}\{^1\text{H}\}$ NMR (151 MHz, CDCl_3) δ 148.84, 144.83, 142.3, 139.80, 133.82, 131.6, 130.5, 130.2, 129.7, 129.4, 128.7, 128.6, 128.2, 127.9, 127.8, 127.6, 127.1, 127.0, 126.5, 126.1, 123.7, 121.2, 118.2, 77.8, 76.8, 48.5 (one carbon missing due to overlap); IR (neat): 2361, 1489, 1070, 912, 692 cm^{-1} ; HRMS (ESI) m/z :

$[M+H]^+$ calculated for $C_{33}H_{26}ClO_2^+$ 489.1616; found 489.1617.

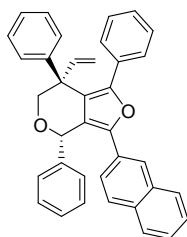
(4S,7S)-1,4,7-Triphenyl-3-(thiophen-2-yl)-7-vinyl-6,7-dihydro-4H-furo[3,4-c]pyran (3ea)



3ea

The reaction was performed according to general procedure B using **1e** (31.4 mg, 0.1 mmol) and **2a** (30.9 mg, 0.15 mmol) to give **3ea** as an amorphous white solid (34.0 mg, 74% yield): R_f = 0.40 (PE/EtOAc = 40:1); 1H NMR (400 MHz, $CDCl_3$) δ 7.46 (d, J = 7.2 Hz, 2H), 7.37 (m, 7H), 7.16 (m, 7H), 6.88 (t, J = 4.3 Hz, 1H), 6.74 (d, 3.7 Hz, 1H), 6.53 (dd, J = 17.4, 10.7 Hz, 1H), 6.05 (s, 1H), 5.39 (d, J = 10.6 Hz, 1H), 5.31 (d, J = 17.2 Hz, 1H), 3.93 (d, J = 11.4 Hz, 1H), 3.81 (d, J = 11.4 Hz, 1H); $^{13}C\{^1H\}$ NMR (101 MHz, $CDCl_3$) δ 148.1, 143.0, 142.9, 139.3, 139.0, 132.9, 130.4, 129.4, 128.8, 128.5, 127.9, 127.7, 127.6, 127.3, 126.93, 126.89, 125.0, 123.9, 122.7, 118.8, 118.0, 75.6, 74.1, 47.8 (one carbon missing due to overlap); IR (neat): 2922, 1486, 1056, 914, 694 cm^{-1} ; HRMS (ESI) m/z : $[M+H]^+$ calculated for $C_{31}H_{25}O_2S^+$, 461.1570; found 461.1565.

(4S,7S)-3-(Naphthalen-2-yl)-1,4,7-triphenyl-7-vinyl-6,7-dihydro-4H-furo[3,4-c]pyran (3fa)

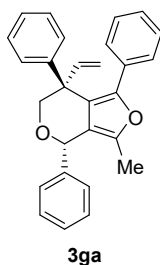


3fa

The reaction was performed according to general procedure B using **1f** (35.8 mg, 0.1 mmol) and **2a** (30.9 mg, 0.15 mmol) to give **3fa** as an amorphous white solid (35.3 mg, 70% yield): R_f = 0.38 (PE/EtOAc = 30:1); m.p. 100-102 $^{\circ}C$; 1H NMR (600 MHz, $CDCl_3$) δ 8.07 (d, J = 9.1 Hz, 1H), 7.73 (m, 2H), 7.69 (d, J = 7.2 Hz, 1H), 7.58 (d, J = 8.3 Hz, 1H), 7.50 (d, J = 7.5 Hz, 2H), 7.44 (m, 4H), 7.35 – 7.24 (m, 7H), 7.19 (m, 4H), 6.57 (dd, J = 17.6, 10.6 Hz, 1H), 6.30 (s, 1H), 5.42 (d, J = 10.9 Hz, 1H), 5.34 (d, J = 17.4 Hz, 1H), 4.00 (d, J = 11.4 Hz, 1H), 3.87 (d, J = 11.6

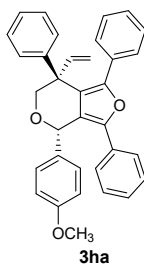
Hz, 1H); $^{13}\text{C}\{^1\text{H}\}$ NMR (151 MHz, CDCl_3) δ 149.1, 145.8, 143.1, 139.5, 139.3, 134.5, 130.8, 130.6, 130.0, 129.2, 128.9, 128.8, 128.6, 128.5, 128.2, 127.9, 127.7, 127.5, 127.3, 127.1, 127.0, 126.8, 124.8, 123.2, 122.7, 121.2, 118.0, 76.4, 74.2, 47.9 (one carbon missing due to overlap); IR (neat): 3100, 1490, 1059, 912, 694 cm^{-1} ; HRMS (ESI) m/z : $[\text{M}+\text{H}]^+$ calculated for $\text{C}_{37}\text{H}_{29}\text{O}_2^+$, 505.2162; found 505.2154.

(4S,7S)-3-Methyl-1,4,7-triphenyl-7-vinyl-6,7-dihydro-4H-furo[3,4-c]pyran (3ga)



The reaction was performed according to general procedure B using **1g** (24.6 mg, 0.1 mmol) and **2a** (30.9 mg, 0.15 mmol) to give **3ga** as a colorless oil (22.1 mg, 56% yield): R_f = 0.50 (PE/EtOAc = 30:1); ^1H NMR (600 MHz, CDCl_3) δ 7.43 (d, J = 6.2 Hz, 2H), 7.41 – 7.32 (m, 5H), 7.25 – 7.18 (m, 4H), 7.13 (t, J = 7.3 Hz, 1H), 7.06 – 6.97 (m, 3H), 6.60 (dd, J = 17.2, 10.5 Hz, 1H), 5.66 (s, 1H), 5.51 (d, J = 10.5 Hz, 1H), 5.34 (d, J = 15.6 Hz, 1H), 4.05 (d, J = 11.6 Hz, 1H), 3.77 (d, J = 11.6 Hz, 1H), 1.84 (s, 3H); $^{13}\text{C}\{^1\text{H}\}$ NMR (151 MHz, CDCl_3) δ 146.9, 145.6, 142.4, 140.7, 140.0, 130.8, 129.0, 128.69, 128.68, 128.4, 127.7, 127.6, 126.9, 126.5, 126.0, 120.8, 119.5, 118.0, 77.2, 76.7, 48.4, 12.7; IR (neat): 3110, 1489, 1060, 915, 694 cm^{-1} ; HRMS (ESI) m/z : $[\text{M}+\text{H}]^+$ calculated for $\text{C}_{28}\text{H}_{25}\text{O}_2^+$; 393.1849; found 393.1845.

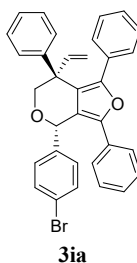
(4S,7S)-4-(4-Methoxyphenyl)-1,3,7-triphenyl-7-vinyl-6,7-dihydro-4H-furo[3,4-c]pyran (3ha)



The reaction was performed according to general procedure B using **1h** (33.8 mg, 0.1 mmol) and **2a** (30.9 mg, 0.15 mmol) to give **3ha** as an amorphous white solid (41.0 mg, 85% yield): R_f

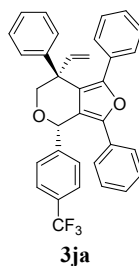
= 0.50 (PE/EtOAc = 30:1); m.p. 73-75 °C; ^1H NMR (600 MHz, CDCl_3) δ 7.41 – 7.31 (m, 6H), 7.29 (d, J = 9.1 Hz, 2H), 7.27 – 7.17 (m, 5H), 7.10 (m, 4H), 6.71 (d, J = 8.9 Hz, 2H), 6.47 (dd, J = 17.4, 10.7 Hz, 1H), 6.10 (s, 1H), 5.30 (d, J = 10.6 Hz, 1H), 5.24 (d, J = 17.5 Hz, 1H), 3.86 (d, J = 11.5 Hz, 1H), 3.75 (d, J = 11.5 Hz, 1H), 3.70 (s, 3H); $^{13}\text{C}\{^1\text{H}\}$ NMR (151 MHz, CDCl_3) δ 158.8, 147.7, 146.5, 143.4, 139.43, 139.36, 130.9, 129.2, 128.58, 128.56, 128.5, 127.8, 127.7, 127.0, 126.9, 126.84, 126.80, 123.4, 122.62, 118.1, 117.7, 113.9, 76.0, 74.0, 55.3, 47.9; IR (neat): 3085, 2400, 1580, 1155, 699 cm^{-1} ; HRMS (ESI) m/z : $[\text{M}+\text{H}]^+$ calculated for $\text{C}_{34}\text{H}_{29}\text{O}_3^+$ 485.2111; found 485.2112.

(4S,7S)-4-(4-Bromophenyl)-1,3,7-triphenyl-7-vinyl-6,7-dihydro-4H-furo[3,4-c]pyran (3ia)



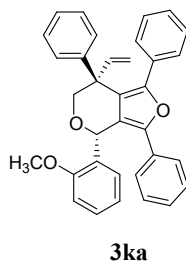
The reaction was performed according to general procedure B using **1i** (38.7 mg, 0.1 mmol) and **2a** (30.9 mg, 0.15 mmol) to give **3ia** as an amorphous white solid (49.1 mg, 92% yield): R_f = 0.18 (PE/EtOAc = 30:1); m.p. 233-235 °C; ^1H NMR (600 MHz, CDCl_3) δ 7.41 – 7.32 (m, 6H), 7.24 (m, 9H), 7.18 (m, 3H), 7.12 (m, 1H), 6.47 (dd, J = 17.4, 10.6 Hz, 1H), 6.14 (s, 1H), 5.35 (d, J = 10.7 Hz, 1H), 5.24 (d, J = 17.4 Hz, 1H), 3.88 (d, J = 11.5 Hz, 1H), 3.77 (d, J = 11.5 Hz, 1H); $^{13}\text{C}\{^1\text{H}\}$ NMR (151 MHz, CDCl_3) δ 147.4, 146.8, 143.0, 139.13, 139.07, 131.0, 130.2, 129.5, 129.2, 128.7, 128.63, 128.61, 128.4, 128.3, 127.6, 127.4, 127.1, 125.6, 123.4, 121.3, 120.1, 118.1, 76.1, 74.3, 47.9; IR (neat): 1592, 1484, 1580, 1274, 912, 691 cm^{-1} ; HRMS (ESI) m/z : $[\text{M}+\text{H}]^+$ calculated for $\text{C}_{33}\text{H}_{26}\text{BrO}_2^+$, 533.1111; found 533.1101.

(4S,7S)-1,3,7-Triphenyl-4-(4-(trifluoromethyl)phenyl)-7-vinyl-6,7-dihydro-4H-furo[3,4-c]pyran (3ja)



The reaction was performed according to general procedure B using **1j** (37.6 mg, 0.1 mmol) and **2a** (30.9 mg, 0.15 mmol) to give **3ja** as a yellow oil (26.5 mg, 51% yield): R_f = 0.63 (PE/EtOAc = 30:1); ^1H NMR (600 MHz, CDCl_3) δ 7.42 (m, 4H), 7.26 (m, 5H), 7.13 (m, 5H), 7.10 – 6.97 (m, 5H), 6.40 (dd, J = 17.5, 10.6 Hz, 1H), 6.12 (s, 1H), 5.25 (d, J = 10.7 Hz, 1H), 5.15 (d, J = 17.4 Hz, 1H), 3.75 (d, J = 11.6 Hz, 1H), 3.71 (d, J = 11.6 Hz, 1H); $^{13}\text{C}\{^1\text{H}\}$ NMR (151 MHz, CDCl_3) δ 148.7, 146.6, 143.1, 143.0, 139.3, 130.7 (q, J = 32.4 Hz), 130.6, 130.2, 129.5, 128.6 (q, J = 2.1 Hz), 127.9, 127.67, 127.49, 127.45, 127.03, 126.97, 125.6 (q, J = 3.5 Hz), 124.1 (q, J = 272.4 Hz), 122.43, 119.0, 117.9, 75.4, 74.3, 47.8; ^{19}F NMR (376 MHz, CDCl_3) δ -62.60; IR (neat): 1574, 1382, 1194, 1067, 691 cm^{-1} ; HRMS (ESI) m/z : $[\text{M}+\text{H}]^+$ calculated for $\text{C}_{34}\text{H}_{26}\text{F}_3\text{O}_2^+$, 523.1879; found 523.1879.

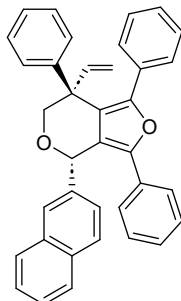
(4S,7S)-4-(2-Methoxyphenyl)-1,3,7-triphenyl-7-vinyl-6,7-dihydro-4H-furo[3,4-c]pyran (3ka)



The reaction was performed according to general procedure B using **1k** (33.8 mg, 0.1 mmol) and **2a** (30.9 mg, 0.15 mmol) to give **3ka** as an amorphous white solid (38.1 mg, 79% yield): R_f = 0.19 (PE/EtOAc = 30:1); m.p. 234-236 $^\circ\text{C}$; ^1H NMR (600 MHz, CDCl_3) δ 7.42-7.39 (m, 6H), 7.30 (d, J = 8.9 Hz, 1H), 7.25 – 7.20 (m, 6H), 7.14 (m, 5H), 6.78 (d, J = 8.8 Hz, 1H), 6.63 (s, 1H), 6.58 (dd, J = 17.3, 10.6 Hz, 1H), 5.48 (d, J = 10.7 Hz, 1H), 5.38 (d, J = 17.3 Hz, 1H), 4.00 (d, J = 11.6 Hz, 1H), 3.95 (s, 3H), 3.84 (d, J = 11.6 Hz, 1H); $^{13}\text{C}\{^1\text{H}\}$ NMR (151 MHz, CDCl_3) δ 157.0, 148.5, 146.2, 142.8, 139.7, 132.8, 132.7, 130.6, 130.4, 129.9, 128.4, 128.3, 127.8, 127.7, 127.24, 127.23, 126.9, 126.9, 125.4, 122.8, 120.0, 118.2, 113.1, 112.6, 74.8, 69.1, 56.2, 48.1; IR

(neat): 1488, 1251, 1066, 909, 690 cm^{-1} ; HRMS (ESI) m/z : $[\text{M}+\text{H}]^+$ calculated for $\text{C}_{34}\text{H}_{29}\text{O}_3^+$, 485.2111; found 485.2112.

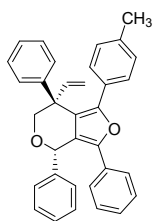
(4S,7S)-4-(Naphthalen-2-yl)-1,3,7-triphenyl-7-vinyl-6,7-dihydro-4H-furo[3,4-c]pyran (3la)



3la (dr = 10:1)

The reaction was performed according to general procedure B using **11** (35.8 mg, 0.1 mmol) and **2a** (30.9 mg, 0.15 mmol) to give **3la** (10:1 inseparable diastereomers) as an amorphous white solid (31.3 mg, 62% yield): R_f = 0.40 (PE/EtOAc = 30:1); For major isomer: ^1H NMR (600 MHz, CDCl_3) δ 7.86 – 7.69 (m, 4H), 7.60 (d, J = 10.3 Hz, 1H), 7.45 (m, 8H), 7.30 (t, J = 7.7 Hz, 2H), 7.19 (m, 6H), 7.09 (m, 1H), 6.52 (dd, J = 17.5, 10.7 Hz, 1H), 6.38 (s, 1H), 5.33 (d, J = 10.7 Hz, 1H), 5.29 (d, J = 17.4 Hz, 1H), 3.93 (d, J = 11.5 Hz, 1H), 3.82 (d, J = 11.4 Hz, 1H); $^{13}\text{C}\{^1\text{H}\}$ NMR (151 MHz, CDCl_3) δ 148.51, 146.54, 143.7, 139.3, 136.6, 133.5, 133.2, 130.8, 130.4, 128.7, 128.6, 128.53, 128.51, 128.46, 127.9, 127.8, 127.7, 127.4, 127.2, 127.1, 126.9, 126.8, 126.4, 126.2, 125.4, 122.8, 119.6, 117.6, 75.8, 73.5, 47.7. For minor isomer: ^1H NMR (600 MHz, CDCl_3) δ 8.32 (s, 1H), 8.21 (m, 2H), 7.71 (s, 1H), 7.58 (s, 1H), 7.42 (m, 8H), 7.31 (m, 2H), 7.15 (m, 6H), 7.12 (s, 1H), 6.59 (dd, J = 17.3, 10.6 Hz, 1H), 6.41 (s, 1H), 5.45 (d, J = 11.2 Hz, 1H), 5.40 (d, J = 17.4 Hz, 1H), 3.97 (d, J = 11.4 Hz, 1H), 3.88 (d, J = 10.8 Hz, 1H); ^{13}C NMR (151 MHz, CDCl_3) δ 148.6, 146.6, 143.7, 139.5, 136.6, 133.5, 133.2, 130.8, 130.2, 129.0, 128.8, 128.5, 128.4, 128.2, 127.9, 127.8, 127.7, 127.4, 127.2, 127.1, 127.0, 126.6, 126.4, 126.2, 125.7, 122.8, 119.3, 117.7, 75.4, 73.6, 48.1; IR (neat): 3054, 2360, 1487, 1056, 687 cm^{-1} ; HRMS (ESI) m/z : $[\text{M}+\text{H}]^+$ calculated for $\text{C}_{37}\text{H}_{29}\text{O}_2^+$, 505.2162; found 505.2156.

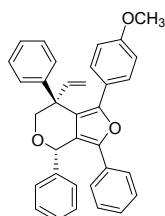
(4S,7S)-3,4,7-Triphenyl-1-(p-tolyl)-7-vinyl-6,7-dihydro-4H-furo[3,4-c]pyran (3ma)



3ma

The reaction was performed according to general procedure B using **1m** (32.2 mg, 0.1 mmol) and **2a** (30.9 mg, 0.15 mmol) to give **3ma** as an amorphous white solid (32.2 mg, 69% yield): R_f = 0.50 (PE/EtOAc = 30:1); m.p. 159-161 °C; ^1H NMR (600 MHz, CDCl_3) δ 7.44 – 7.37 (m, 6H), 7.29 – 7.26 (m, 4H), 7.25 (s, 3H), 7.20 (m, 3H), 7.13 (m, 1H), 6.97 (d, J = 7.8 Hz, 2H), 6.50 (dd, J = 17.5, 10.7 Hz, 1H), 6.19 (s, 1H), 5.32 (d, J = 10.7 Hz, 1H), 5.26 (d, J = 17.4 Hz, 1H), 3.90 (d, J = 11.5 Hz, 1H), 3.79 (d, J = 11.5 Hz, 1H), 2.26 (s, 3H); $^{13}\text{C}\{^1\text{H}\}$ NMR (151 MHz, CDCl_3) δ 148.6, 146.0, 143.7, 139.4, 139.2, 137.2, 130.5, 129.3, 128.64, 128.57, 128.55, 128.5, 128.4, 128.1, 127.7, 127.0, 126.90, 126.85, 125.4, 122.0, 119.7, 117.5, 75.93, 73.8, 47.7, 21.3; IR (neat): 2359, 1500, 1059, 913, 690 cm^{-1} ; HRMS (ESI) m/z : $[\text{M}+\text{H}]^+$ calculated for $\text{C}_{34}\text{H}_{29}\text{O}_2^+$ 469.2162; found 469.2151.

(4S,7S)-1-(4-Methoxyphenyl)-3,4,7-triphenyl-7-vinyl-6,7-dihydro-4H-furo[3,4-c]pyran (3na)

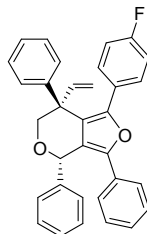


3na

The reaction was performed according to general procedure B using **1n** (33.8 mg, 0.1 mmol) and **2a** (30.9 mg, 0.15 mmol) to give **3na** as an amorphous white solid (32.4 mg, 64% yield): R_f = 0.35 (PE/EtOAc=30:1); m.p. 147-149 °C; ^1H NMR (600 MHz, CDCl_3) δ 7.49 (m, 6H), 7.38 (m, 7H), 7.28 (m, 3H), 7.20 (m, 1H), 6.78 (d, J = 8.8 Hz, 2H), 6.57 (dd, J = 17.5, 11.3 Hz, 1H), 6.27 (s, 1H), 5.41 (d, J = 10.5 Hz, 1H), 5.34 (d, J = 17.4 Hz, 1H), 3.98 (d, J = 11.5 Hz, 1H), 3.87 (d, J = 11.5 Hz, 1H), 3.83 (s, 3H); $^{13}\text{C}\{^1\text{H}\}$ NMR (151 MHz, CDCl_3) δ 158.9, 148.5, 145.8, 143.6, 139.5, 139.3, 130.6, 129.3, 128.58, 128.57, 128.5, 128.44, 128.40, 127.7, 126.93, 126.88,

125.3, 123.8, 121.2, 120.0, 118.5, 113.4, 76.0, 73.9, 54.2, 46.6; IR (neat): 2400, 1503, 1076, 916, 698 cm^{-1} ; HRMS (ESI) m/z : $[M+H]^+$ calculated for $\text{C}_{34}\text{H}_{29}\text{O}_3^+$, 485.2111; found 485.2101.

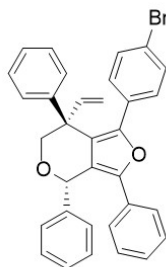
(4S,7S)-1-(4-Fluorophenyl)-3,4,7-triphenyl-7-vinyl-6,7-dihydro-4H-furo[3,4-c]pyran (3oa)



3oa

The reaction was performed according to general procedure B using **1o** (32.6 mg, 0.1 mmol) and **2a** (30.9 mg, 0.15 mmol) to give **3oa** as an amorphous white solid (26.5 mg, 56% yield): R_f = 0.47 (PE/EtOAc = 30:1); m.p. 149-151 $^{\circ}\text{C}$; ^1H NMR (600 MHz, CDCl_3) δ 7.37 – 7.25 (m, 8H), 7.19 (m, 5H), 7.12 (m, 3H), 7.06 (t, J = 7.4 Hz, 1H), 6.77 (d, J = 8.6 Hz, 1H), 6.75 (d, J = 8.7 Hz, 1H), 6.42 (dd, J = 17.4, 10.7 Hz, 1H), 6.10 (s, 1H), 5.30 (d, J = 10.7 Hz, 1H), 5.21 (d, J = 17.3 Hz, 1H), 3.84 (d, J = 11.5 Hz, 1H), 3.73 (d, J = 11.5 Hz, 1H); ^{13}C $\{^1\text{H}\}$ NMR (151 MHz, CDCl_3) δ 161.9 (q, J = 247.9 Hz), 147.5, 146.3, 143.0, 139.3, 139.1, 130.2, 129.1, 128.6 (q, J = 8.0 Hz), 128.48, 128.45, 128.4, 128.3, 127.6, 127.1, 126.9 (q, J = 3.2 Hz), 126.9, 125.4, 122.3, 119.7, 117.8, 114.7 (q, J = 21.6 Hz), 76.0, 74.1, 47.7; ^{19}F NMR (565 MHz, CDCl_3) δ -114.12; IR (neat): 1500, 1243, 1097, 904, 686 cm^{-1} ; HRMS (ESI) m/z : $[M+H]^+$ calculated for $\text{C}_{33}\text{H}_{26}\text{FO}_2^+$, 473.1911; found 473.1913.

(4S,7S)-1-(4-Bromophenyl)-3,4,7-triphenyl-7-vinyl-6,7-dihydro-4H-furo[3,4-c]pyran (3pa)

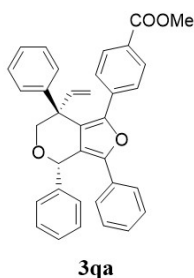


3pa

The reaction was performed according to general procedure B using **1p** (38.7 mg, 0.1 mmol) and **2a** (30.9 mg, 0.15 mmol) to give **3pa** as an amorphous white solid (36.3 mg, 68% yield): R_f = 0.50 (PE/EtOAc = 30:1); m.p. 164-166 $^{\circ}\text{C}$; ^1H NMR (600 MHz, CDCl_3) δ 7.27 – 7.19 (m, 5H), 7.15 – 7.07 (m, 10H), 7.07 – 7.02 (m, 3H), 6.99 (m, 1H), 6.35 (dd, J = 17.4, 10.7 Hz, 1H), 6.02

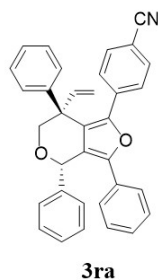
(s, 1H), 5.23 (d, $J = 10.7$ Hz, 1H), 5.12 (d, $J = 17.4$ Hz, 1H), 3.76 (d, $J = 11.5$ Hz, 1H), 3.65 (d, $J = 11.5$ Hz, 1H); $^{13}\text{C}\{^1\text{H}\}$ NMR (151 MHz, CDCl_3) δ 147.3, 146.8, 143.0, 139.13, 139.07, 131.0, 130.2, 129.5, 129.2, 128.7, 128.63, 128.60, 128.4, 128.3, 127.6, 127.4, 127.1, 125.6, 123.4, 121.3, 120.1, 118.1, 76.1, 74.3, 47.9; IR (neat): 2359, 1491, 1073, 909, 689 cm^{-1} ; HRMS (ESI) m/z : $[\text{M}+\text{H}]^+$ calculated for $\text{C}_{33}\text{H}_{26}\text{BrO}_2^+$, 533.1111; found 533.1113.

Methyl 4-((4S,7S)-3,4,7-triphenyl-7-vinyl-6,7-dihydro-4H-furo[3,4-c]pyran-1-yl)benzoate (3qa)



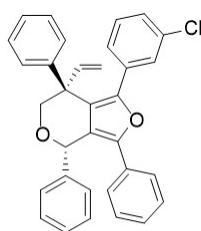
The reaction was performed according to general procedure B using **1q** (36.6 mg, 0.1 mmol) and **2a** (30.9 mg, 0.15 mmol) to give **3qa** as an amorphous white solid (45.6 mg, 89% yield): $R_f = 0.26$ (PE/EtOAc = 30:1); m.p. 161-163 $^{\circ}\text{C}$; ^1H NMR (600 MHz, CDCl_3) δ 7.81 (d, $J = 8.5$ Hz, 2H), 7.46 (d, $J = 8.5$ Hz, 2H), 7.41 (m, 6H), 7.31 – 7.21 (m, 7H), 7.21 – 7.14 (m, 2H), 6.55 (dd, $J = 17.3, 10.7$ Hz, 1H), 6.18 (s, 1H), 5.40 (d, $J = 10.8$ Hz, 1H), 5.30 (d, $J = 17.3$ Hz, 1H), 3.94 (d, $J = 11.6$ Hz, 1H), 3.87 (s, 3H), 3.82 (d, $J = 11.5$ Hz, 1H); $^{13}\text{C}\{^1\text{H}\}$ NMR (151 MHz, CDCl_3) δ 167.0, 147.5, 147.3, 142.9, 139.1, 139.0, 134.6, 130.0, 129.19, 129.17, 128.69, 128.65, 128.6, 128.4, 128.2, 127.6, 127.5, 127.1, 126.4, 125.8, 125.1, 120.4, 118.2, 76.2, 74.5, 52.1, 48.1; IR (neat): 1716, 1274, 1077, 925, 697 cm^{-1} ; HRMS (ESI) m/z : $[\text{M}+\text{H}]^+$ calculated for $\text{C}_{35}\text{H}_{29}\text{O}_4^+$, 513.2060; found 513.2048.

4-((4S,7S)-3,4,7-Triphenyl-7-vinyl-6,7-dihydro-4H-furo[3,4-c]pyran-1-yl)benzonitrile (3ra)



The reaction was performed according to general procedure B using **1r** (33.3 mg, 0.1 mmol) and **2a** (30.9 mg, 0.15 mmol) to give **3ra** as an amorphous white solid (41.8 mg, 87% yield): R_f = 0.23 (PE/EtOAc = 30:1); m.p. 169-171 °C; ^1H NMR (600 MHz, CDCl_3) δ 7.48 (d, J = 8.5 Hz, 2H), 7.39 (m, 8H), 7.27 (m, 5H), 7.25 – 7.15 (m, 4H), 6.56 (dd, J = 17.3, 10.6 Hz, 1H), 6.17 (s, 1H), 5.44 (d, J = 10.7 Hz, 1H), 5.31 (d, J = 17.3 Hz, 1H), 3.95 (d, J = 11.5 Hz, 1H), 3.84 (d, J = 11.5 Hz, 1H); $^{13}\text{C}\{^1\text{H}\}$ NMR (151 MHz, CDCl_3) δ 148.1, 146.39, 142.37, 139.0, 138.9, 134.3, 131.6, 129.8, 129.2, 128.8, 128.73, 128.65, 128.5, 127.9, 127.5, 127.3, 126.7, 126.2, 125.9, 120.7, 119.1, 118.5, 110.0, 76.3, 74.8, 48.3; IR (neat): 2341, 1498, 1088, 929, 685 cm^{-1} ; HRMS (ESI) m/z : $[\text{M}+\text{H}]^+$ calculated for $\text{C}_{34}\text{H}_{26}\text{NO}_2^+$, 480.1958; found 480.1968.

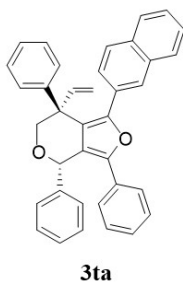
(4S,7S)-1-(3-Chlorophenyl)-3,4,7-triphenyl-7-vinyl-6,7-dihydro-4H-furo[3,4-c]pyran (3sa)



3sa

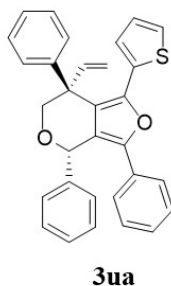
The reaction was performed according to general procedure B using **1s** (34.3 mg, 0.1 mmol) and **2a** (30.9 mg, 0.15 mmol) to give **3sa** as an amorphous white solid (38.6 mg, 79% yield): R_f = 0.45 (PE/EtOAc = 30:1); m.p. 126-128 °C; ^1H NMR (600 MHz, CDCl_3) δ 7.41 – 7.32 (m, 7H), 7.23 (m, 5H), 7.21 – 7.15 (m, 4H), 7.12 (m, 1H), 7.04 (d, J = 7.9 Hz, 1H), 7.00 (t, J = 7.9 Hz, 1H), 6.50 (dd, J = 17.4, 10.6 Hz, 1H), 6.14 (s, 1H), 5.39 (d, J = 10.7 Hz, 1H), 5.27 (d, J = 17.3 Hz, 1H), 3.93 (d, J = 11.5 Hz, 1H), 3.83 (d, J = 11.5 Hz, 1H); $^{13}\text{C}\{^1\text{H}\}$ NMR (151 MHz, CDCl_3) δ 147.04, 146.97, 142.7, 139.2, 139.1, 133.9, 132.2, 130.1, 129.2, 129.0, 128.7, 128.62, 128.58, 128.4, 127.6, 127.5, 127.11, 127.07, 126.8, 125.7, 124.9, 124.1, 120.1, 118.2, 76.3, 74.4, 48.0; IR (neat): 1491, 1141, 1078, 905, 690 cm^{-1} ; HRMS (ESI) m/z : $[\text{M}+\text{H}]^+$ calculated for $\text{C}_{33}\text{H}_{26}\text{ClO}_2^+$, 489.1616; found 489.1614.

(4S,7S)-1-(Naphthalen-2-yl)-3,4,7-triphenyl-7-vinyl-6,7-dihydro-4H-furo[3,4-c]pyran (3ta)



The reaction was performed according to general procedure B using **1t** (35.8 mg, 0.1 mmol) and **2a** (30.9 mg, 0.15 mmol) to give **3ta** as an amorphous white solid (35.4 mg, 70% yield): R_f = 0.5 (PE/EtOAc = 30:1); m.p. 167-169 °C; ^1H NMR (600 MHz, CDCl_3) δ 7.88 (d, J = 9.3 Hz, 1H), 7.82 (d, J = 9.2 Hz, 1H), 7.75 (d, J = 8.2 Hz, 1H), 7.52 (d, J = 7.5 Hz, 2H), 7.49 – 7.46 (m, 2H), 7.41 – 7.35 (m, 4H), 7.32 (m, 3H), 7.20 (m, 3H), 7.14 (m, 3H), 7.08 (m, 2H), 6.34 (s, 1H), 6.11 (dd, J = 17.6, 10.8 Hz, 1H), 5.13 (d, J = 17.6 Hz, 1H), 5.09 (d, J = 10.9 Hz, 1H), 3.96 (d, J = 11.4 Hz, 1H), 3.85 (d, J = 11.4 Hz, 1H); $^{13}\text{C}\{^1\text{H}\}$ NMR (151 MHz, CDCl_3) δ 148.3, 146.7, 144.6, 140.3, 139.2, 133.7, 132.6, 130.6, 129.3, 129.2, 129.0, 128.9, 128.72, 128.6, 128.5, 128.3, 128.0, 127.9, 127.1, 126.54, 126.45, 126.2, 125.9, 125.4, 125.2, 124.7, 118.3, 116.4, 75.5, 71.6, 46.7; IR (neat): 2359, 1489, 1074, 913, 691 cm^{-1} ; HRMS(ESI) m/z : $[\text{M}+\text{H}]^+$ calculated for $\text{C}_{37}\text{H}_{29}\text{O}_2^+$, 505.2162; found 505.2154.

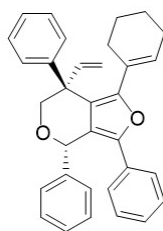
(4S,7S)-3,4,7-Triphenyl-1-(thiophen-2-yl)-7-vinyl-6,7-dihydro-4H-furo[3,4-c]pyran (3ua)



The reaction was performed according to general procedure B using **1u** (31.2 mg, 0.1 mmol) and **2a** (30.9 mg, 0.15 mmol) to give **3ua** as an amorphous yellow oil (30.4 mg, 66% yield): R_f = 0.47 (PE/EtOAc = 30:1); ^1H NMR (600 MHz, CDCl_3) δ 7.41 (d, J = 7.7 Hz, 4H), 7.37 (d, J = 8.2 Hz, 2H), 7.33 – 7.26 (m, 5H), 7.25 – 7.18 (m, 3H), 7.16 – 7.11 (m, 2H), 6.82 – 6.78 (m, 1H), 6.65 (d, J = 2.6 Hz, 1H), 6.51 (dd, J = 17.4, 10.7 Hz, 1H), 6.15 (s, 1H), 5.37 (d, J = 10.7 Hz, 1H), 5.30 (d, J = 18.4 Hz, 1H), 3.97 (d, J = 11.5 Hz, 1H), 3.81 (d, J = 11.6 Hz, 1H); $^{13}\text{C}\{^1\text{H}\}$ NMR (151 MHz, CDCl_3) δ 146.2, 144.6, 142.9, 139.0, 138.7, 133.06, 130.05, 129.3, 128.7, 128.62,

128.58, 128.4, 127.7, 127.3, 127.0, 125.8, 125.6, 125.2, 122.2, 120.0, 117.4, 76.1, 74.0, 47.4 (one carbon missing due to overlap); IR (neat): 2360, 1488, 1066, 930, 712 cm⁻¹; HRMS(ESI) m/z: [M+H]⁺ calculated for C₃₃H₂₅O₂S⁺, 461.1570; found 461.1565.

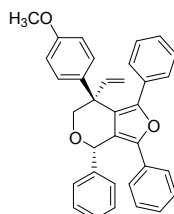
(4S,7S)-1-(Cyclohex-1-en-1-yl)-3,4,7-triphenyl-7-vinyl-6,7-dihydro-4H-furo[3,4-c]pyran (3va)



3va

The reaction was performed according to general procedure B using **1v** (31.2 mg, 0.1 mmol) and **2a** (30.9 mg, 0.15 mmol) to give **3va** as a colorless oil (9.7 mg, 21% yield): *R_f* = 0.57 (PE/EtOAc = 30:1); ¹H NMR (400 MHz, CDCl₃) δ 7.38 (m, 2H), 7.34 – 7.25 (m, 10H), 7.16 (m, 2H), 7.11 – 7.03 (m, 1H), 6.50 (m, 1H), 6.11 (d, *J* = 2.6 Hz, 1H), 5.60 (s, 1H), 5.46 (d, *J* = 13.0 Hz, 1H), 5.27 (d, *J* = 17.2 Hz, 1H), 3.95 – 3.77 (m, 2H), 2.28 (d, *J* = 18.5 Hz, 1H), 2.09 (d, *J* = 17.1 Hz, 1H), 1.88 (s, 1H), 1.66 (d, *J* = 18.3 Hz, 1H), 1.55 (d, *J* = 2.6 Hz, 1H), 1.48 (m, 3H); ¹³C{¹H} NMR (151 MHz, CDCl₃) δ 151.4, 144.8, 143.4, 140.59, 139.7, 130.8, 129.8, 129.2, 128.6, 128.5, 128.2, 128.1, 128.0, 127.8, 126.7, 125.3, 121.5, 119.3, 117.9, 76.6, 74.6, 48.0, 29.9, 26.6, 25.4, 22.6, 21.8; IR (neat): 2920, 2359, 1264, 908, 700 cm⁻¹; HRMS (ESI) m/z: [M+H]⁺ calculated for C₃₃H₃₁O₂⁺, 459.2319; found 459.2324.

(4S,7S)-7-(4-Methoxyphenyl)-1,3,4-triphenyl-7-vinyl-6,7-dihydro-4H-furo[3,4-c]pyran (3ab)

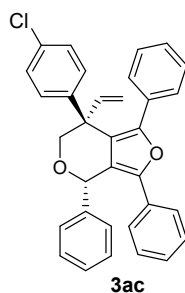


3ab

The reaction was performed according to general procedure B using **1a** (30.8 mg, 0.1 mmol) and **2b** (35.4 mg, 0.15 mmol) to give **3ab** as amorphous white solid (38.6 mg, 80% yield): *R_f* =

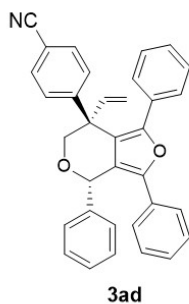
0.28 (PE/EtOAc = 30:1); m.p. 72-74 °C; ^1H NMR (600 MHz, CDCl_3) δ 7.42 (m, 6H), 7.29 (m, 5H), 7.22 (t, J = 7.7 Hz, 2H), 7.17 (m, 4H), 6.81 (d, J = 8.4 Hz, 2H), 6.47 (dd, J = 17.5, 10.7 Hz, 1H), 6.19 (s, 1H), 5.31 (d, J = 10.8 Hz, 1H), 5.25 (d, J = 17.4 Hz, 1H), 3.87 (d, J = 11.5 Hz, 1H), 3.76 (s, 3H), 3.75 (s, 1H); $^{13}\text{C}\{^1\text{H}\}$ NMR (151 MHz, CDCl_3) δ 158.4, 148.4, 146.3, 139.5, 139.2, 135.5, 130.8, 130.4, 129.2, 128.8, 128.58, 128.57, 128.4, 127.9, 127.3, 127.13, 127.06, 125.4, 123.0, 119.75, 117.5, 113.9, 75.9, 73.8, 55.4, 47.1; IR (neat): 3056, 2360, 1247, 913, 690 cm^{-1} ; HRMS (ESI) m/z : $[\text{M}+\text{H}]^+$ calculated for $\text{C}_{34}\text{H}_{29}\text{O}_3^+$, 485.2111; found 485.2101.

(4S,7S)-7-(4-Chlorophenyl)-1,3,4-triphenyl-7-vinyl-6,7-dihydro-4H-furo[3,4-c]pyran (3ac)



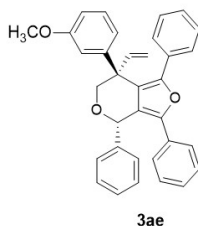
The reaction was performed according to general procedure B using **1a** (30.8 mg, 0.1 mmol) and **2c** (36.1 mg, 0.15 mmol) to give **3ac** as an amorphous white solid (43.5 mg, 89% yield): R_f = 0.32 (PE/EtOAc = 30:1); m.p. 197-199 °C; ^1H NMR (600 MHz, CDCl_3) δ 7.46 – 7.39 (m, 6H), 7.36 (d, J = 8.7 Hz, 2H), 7.32 (m, 3H), 7.28 (d, J = 4.2 Hz, 2H), 7.25 (s, 2H), 7.24 (s, 2H), 7.21 (d, J = 7.1 Hz, 1H), 7.18 (m, 1H), 6.47 (dd, J = 17.3, 10.7 Hz, 1H), 6.22 (s, 1H), 5.36 (d, J = 10.7 Hz, 1H), 5.29 (d, J = 17.5 Hz, 1H), 3.93 (d, J = 11.5 Hz, 1H), 3.78 (d, J = 11.5 Hz, 1H); $^{13}\text{C}\{^1\text{H}\}$ NMR (151 MHz, CDCl_3) δ 147.3, 146.5, 146.2, 139.3, 139.2, 133.7, 130.9, 130.4, 129.2, 128.79, 128.76, 128.69, 128.66, 128.3, 128.1, 127.4, 127.2, 125.6, 125.3, 120.3, 119.8, 117.7, 76.7, 62.7, 38.5; IR (neat): 2353, 1487, 1058, 913, 690 cm^{-1} ; HRMS (ESI) m/z : $[\text{M}+\text{H}]^+$ calculated for $\text{C}_{33}\text{H}_{26}\text{ClO}_2^+$, 489.1616; found 489.1620.

5-((4S,7S)-1,3,4-Triphenyl-7-vinyl-6,7-dihydro-4H-furo[3,4-c]pyran-7-yl)benzonitrile (3ad)



The reaction was performed according to general procedure B using **1a** (30.8 mg, 0.1 mmol) and **2d** (34.7 mg, 0.15 mmol) to give **3ad** as an amorphous white solid (26.8 mg, 56% yield): R_f = 0.09 (PE/EtOAc = 30:1); m.p. 258-260 °C; ^1H NMR (600 MHz, CDCl_3) δ 7.56 (d, J = 8.5 Hz, 2H), 7.52 (d, J = 8.6 Hz, 2H), 7.41 (m, 4H), 7.31 (m, 5H), 7.23 (t, J = 7.7 Hz, 2H), 7.21 – 7.13 (m, 4H), 6.45 (dd, J = 17.4, 10.7 Hz, 1H), 6.21 (s, 1H), 5.40 (d, J = 10.8 Hz, 1H), 5.30 (d, J = 17.4 Hz, 1H), 3.91 (d, J = 11.5 Hz, 1H), 3.74 (d, J = 11.5 Hz, 1H); $^{13}\text{C}\{^1\text{H}\}$ NMR (151 MHz, CDCl_3); δ 149.3, 148.6, 146.9, 138.7, 138.2, 132.3, 130.5, 130.2, 129.2, 128.8, 128.7, 128.63, 128.55, 128.1, 127.8, 127.5, 127.0, 125.5, 121.6, 119.1, 118.9, 118.7, 110.9, 75.9, 73.2, 48.1; IR (neat): 2853, 2224, 1491, 1104, 688 cm^{-1} ; HRMS(ESI) m/z : $[\text{M}+\text{H}]^+$ calculated for $\text{C}_{34}\text{H}_{26}\text{NO}_2^+$, 480.1958; found 480.1954.

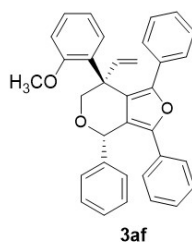
(4S,7S)-7-(3-Methoxyphenyl)-1,3,4-triphenyl-7-vinyl-6,7-dihydro-4H-furo[3,4-c]pyran (3ae)



The reaction was performed according to general procedure B using **1a** (30.8 mg, 0.1 mmol) and **2e** (35.4 mg, 0.15 mmol) to give **3ae** as an amorphous white solid (38.9 mg, 80% yield): R_f = 0.31 (PE/EtOAc = 30:1); m.p. 73-75 °C; ^1H NMR (600MHz, CDCl_3) δ 7.42 (m, 6H), 7.29 (m, 3H), 7.19 (m, 7H), 7.00 (d, J = 7.9 Hz, 1H), 6.95 (s, 1H), 6.74 (d, J = 7.9 Hz, 1H), 6.50 (dd, J = 17.6, 10.7 Hz, 1H), 6.20 (s, 1H), 5.34 (d, J = 10.7 Hz, 1H), 5.28 (d, J = 17.4 Hz, 1H), 3.87 (d, J = 11.5 Hz, 1H), 3.76 (d, J = 11.5 Hz, 1H), 3.72 (s, 3H); $^{13}\text{C}\{^1\text{H}\}$ NMR (151 MHz, CDCl_3) δ 159.8, 148.4, 146.4, 145.1, 139.3, 139.2, 130.8, 130.4, 129.4, 129.2, 128.6, 128.4, 127.9, 127.3, 127.2, 127.0, 125.5, 122.6, 120.2, 119.7, 117.7, 114.3, 111.8, 76.0, 73.8, 55.4, 47.8 (one carbon

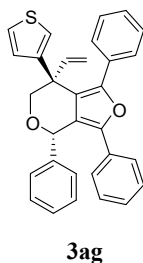
missing due to overlap); IR (neat): 3057, 2359, 1485, 915, 689 cm^{-1} ; HRMS (ESI) m/z : $[\text{M}+\text{H}]^+$ calculated for $\text{C}_{34}\text{H}_{29}\text{O}_3^+$, 485.2111; found 485.2113.

(4S,7S)-7-(2-Methoxyphenyl)-1,3,4-triphenyl-7-vinyl-6,7-dihydro-4H-furo[3,4-c]pyran (3af)



The reaction was performed according to general procedure B using **1a** (30.8 mg, 0.1 mmol) and **2f** (35.4 mg, 0.15 mmol) to give **3af** as an amorphous white solid (34.7 mg, 75% yield): R_f = 0.32 (PE/EtOAc = 30:1); m.p. 178-180 $^{\circ}\text{C}$; ^1H NMR (600 MHz, CDCl_3) δ 7.42 (m, 6H), 7.32 (d, J = 7.8 Hz, 1H), 7.31 – 7.24 (m, 3H), 7.20 (d, J = 7.7 Hz, 2H), 7.14 (m, 5H), 6.87 (t, J = 7.6 Hz, 1H), 6.79 (d, J = 8.2 Hz, 1H), 6.60 (dd, J = 17.4, 10.6 Hz, 1H), 6.14 (s, 1H), 5.30 (d, J = 10.6 Hz, 1H), 5.25 (d, J = 17.4 Hz, 1H), 4.44 (d, J = 11.3 Hz, 1H), 3.76 (d, J = 11.3 Hz, 1H), 3.62 (s, 3H); $^{13}\text{C}\{^1\text{H}\}$ NMR (151 MHz, CDCl_3) δ 157.6, 148.3, 146.1, 140.8, 139.7, 130.9, 130.8, 130.7, 129.9, 129.2, 128.6, 128.54, 128.46, 128.3, 127.6, 127.0, 126.94, 126.91, 125.5, 123.4, 120.7, 119.8, 117.2, 112.5, 76.1, 70.6, 55.5, 47.6; IR (neat): 2359, 1486, 1055, 911, 690 cm^{-1} ; HRMS (ESI) m/z : $[\text{M}+\text{H}]^+$ calculated for $\text{C}_{34}\text{H}_{29}\text{O}_3^+$, 485.2111; found 485.2114.

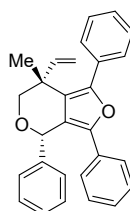
(4S,7R)-1,3,4-Triphenyl-7-(thiophen-3-yl)-7-vinyl-6,7-dihydro-4H-furo[3,4-c]pyran (3ag)



The reaction was performed according to general procedure B using **1a** (30.8 mg, 0.1 mmol) and **2g** (31.8 mg, 0.15 mmol) to give **3ag** as an amorphous white solid (15.2 mg, 33% yield): R_f = 0.09 (PE/EtOAc = 30:1); m.p. 141-143 $^{\circ}\text{C}$; ^1H NMR (600 MHz, CDCl_3) δ 7.48 (d, J = 7.6 Hz, 2H), 7.41 (m, 4H), 7.29 (m, 3H), 7.20 (m, 6H), 7.15 (d, J = 7.7 Hz, 1H), 7.12 (s, 1H), 6.99 (d, J

= 5.0 Hz, 1H), 6.45 (dd, J = 17.2, 10.7 Hz, 1H), 6.18 (s, 1H), 5.36 (d, J = 10.5 Hz, 1H), 5.29 (d, J = 17.3 Hz, 1H), 3.86 (d, J = 11.5 Hz, 1H), 3.82 (d, J = 11.4 Hz, 1H); $^{13}\text{C}\{^1\text{H}\}$ NMR (151 MHz, CDCl_3) δ 148.6, 146.4, 144.2, 139.4, 139.3, 130.7, 130.4, 129.2, 128.6, 128.4, 127.9, 127.3, 127.2, 127.0, 125.8, 125.5, 122.8, 122.4, 119.4, 117.8, 76.1, 73.5, 46.0 (two carbons missing due to overlap); IR (neat): 2355, 1485, 1065, 911, 694 cm^{-1} ; HRMS (ESI) m/z : $[\text{M}+\text{H}]^+$ calculated for $\text{C}_{31}\text{H}_{25}\text{SO}_2^+$, 461.1570; found 461.1580.

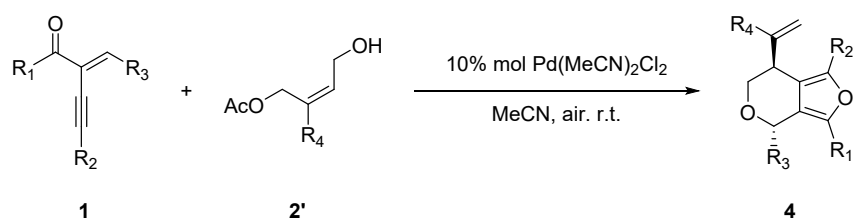
(4S,7R)-7-Methyl-1,3,4-triphenyl-7-vinyl-6,7-dihydro-4H-furo[3,4-c]pyran (3ah)



3ah

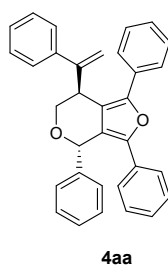
The reaction was performed according to general procedure B using **1a** (30.8 mg, 0.1 mmol) and **2h** (21.6 mg, 0.15 mmol) to give **3ah** as a colorless oil (25.5 mg, 65% yield): R_f = 0.09 (PE/EtOAc = 30:1); ^1H NMR (400 MHz, CDCl_3) δ 7.86 (d, J = 7.6 Hz, 2H), 7.43 (m, 4H), 7.36 (d, J = 7.8 Hz, 2H), 7.33 – 7.27 (m, 4H), 7.21 (t, J = 7.6 Hz, 2H), 7.13 (d, J = 7.2 Hz, 1H), 6.13 – 6.03 (m, 2H), 5.31 (s, 1H), 5.27 (d, J = 7.6 Hz, 1H), 3.61 (d, J = 11.4 Hz, 1H), 3.42 (d, J = 11.4 Hz, 1H), 1.46 (s, 3H); $^{13}\text{C}\{^1\text{H}\}$ NMR (151 MHz, CDCl_3) δ 148.0, 146.0, 143.4, 139.5, 131.6, 130.5, 129.1, 128.6, 128.5, 128.4, 128.2, 127.7, 127.6, 127.0, 125.4, 124.7, 119.0, 115.8, 75.9, 72.9, 38.9, 21.7; IR (neat): 2359, 1486, 1060, 912, 689 cm^{-1} ; HRMS (ESI) m/z : $[\text{M}+\text{H}]^+$ calculated for $\text{C}_{28}\text{H}_{25}\text{O}_2^+$, 393.1849; found 393.1843.

5. General procedure C for Synthesis of 7-vinyl-6,7-dihydro-4H-furo[3,4-c]pyrans 4



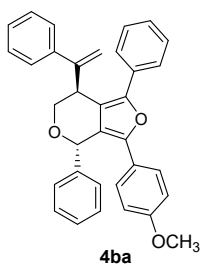
A solution of **2'** (0.15 mmol, 1.50 equiv.) and Pd(MeCN)₂Cl₂ (0.01 mmol, 0.10 equiv.) in MeCN (1.50 mL) was stirred at room temperature under air for 0.5 h. A solution of **1** (0.10 mmol, 1.0 equiv.) in MeCN (0.50 mL) was added. The mixture was stirred at room temperature for 12 h. The completed reaction was concentrated. The residue was purified by column chromatography (silica gel, petroleum ether/ethyl acetate) to afford product **4**.

(4S,7S)-1,3,4-Triphenyl-7-(1-phenylvinyl)-6,7-dihydro-4H-furo[3,4-c]pyran (**4aa**)



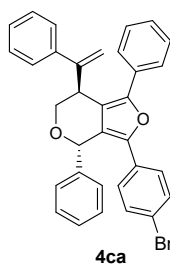
The reaction was performed according to general procedure C using **1a** (30.8 mg, 0.1 mmol) and **2a'** (30.9 mg, 0.15 mmol) to give **4aa** as an amorphous white solid (25.5 mg, 65% yield). *R_f* = 0.09 (PE/EtOAc = 30:1); ¹H NMR (600 MHz, CDCl₃) δ 7.87 (d, *J* = 7.8 Hz, 2H), 7.55 (d, *J* = 7.3 Hz, 2H), 7.52 (d, *J* = 7.7 Hz, 2H), 7.49 – 7.41 (m, 6H), 7.36 (m, 5H), 7.28 (d, *J* = 5.9 Hz, 1H), 7.21 (d, *J* = 7.0 Hz, 1H), 6.07 (s, 1H), 5.57 (s, 1H), 5.34 (s, 1H), 4.37 (t, *J* = 4.1 Hz, 1H), 3.97 (m, 1H), 3.91 (m, 1H); ¹³C{¹H} NMR (151 MHz, CDCl₃) δ 147.6, 147.0, 146.3, 140.9, 139.3, 130.9, 130.4, 129.2, 128.7, 128.62, 128.58, 128.3, 127.8, 127.3, 127.1, 126.7, 125.6, 125.3, 120.5, 120.1, 117.0, 76.7, 66.9, 39.32 (one carbon missing due to overlap); IR (neat): 2360, 1486, 1069, 910, 691 cm⁻¹; HRMS (ESI) *m/z*: [M+H]⁺ calculated for C₃₃H₂₆O₂⁺, 455.2006; found 455.1999.

(4S,7S)-3-(4-Methoxyphenyl)-1,4-diphenyl-7-(1-phenylvinyl)-6,7-dihydro-4H-furo[3,4-c]pyran (**4ba**)



The reaction was performed according to general procedure C using **1b** (33.8 mg, 0.1 mmol) and **2a'** (30.9 mg, 0.15 mmol) to give **4ba** as an amorphous white solid (42.6 mg, 88% yield): R_f = 0.10 (PE/EtOAc = 30:1); m.p. 172-174 °C; ^1H NMR (400 MHz, CDCl_3) δ 7.69 (d, J = 7.2 Hz, 2H), 7.47 (d, J = 2.2 Hz, 1H), 7.45 – 7.40 (m, 2H), 7.39 – 7.34 (m, 3H), 7.34 – 7.20 (m, 9H), 7.10 (m, 1H), 6.61 (d, J = 8.7 Hz, 1H), 5.84 (s, 1H), 5.44 (s, 1H), 5.18 (s, 1H), 4.21 (t, J = 3.8 Hz, 1H), 3.80 (d, J = 3.7 Hz, 2H), 3.76 (s, 3H); $^{13}\text{C}\{^1\text{H}\}$ NMR (101 MHz, CDCl_3) δ 154.8, 147.4, 147.2, 144.9, 140.8, 139.3, 130.8, 130.7, 129.2, 128.84, 128.79, 128.7, 127.9, 127.3, 126.8, 125.9, 125.1, 124.6, 120.1, 120.0, 117.2, 111.6, 111.5, 67.2, 56.3, 39.3. IR (neat): 2920, 2359, 1490, 907, 696 cm^{-1} ; HRMS (ESI) m/z : $[\text{M}+\text{H}]^+$ calculated for $\text{C}_{34}\text{H}_{29}\text{O}_3^+$, 485.2111; found 485.2112.

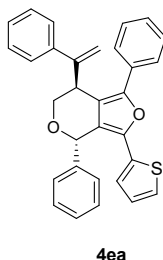
(4S,7S)-3-(4-Bromophenyl)-1,4-diphenyl-7-(1-phenylvinyl)-6,7-dihydro-4H-furo[3,4-c]pyran (4ca)



The reaction was performed according to general procedure C using **1c** (38.7 mg, 0.1 mmol) and **2a'** (30.9 mg, 0.15 mmol) to give **4ca** as an amorphous white solid (38.2 mg, 72% yield): R_f = 0.25 (PE/EtOAc = 30:1); m.p. 85-87 °C; ^1H NMR (400 MHz, CDCl_3) δ 7.80 (d, J = 7.2 Hz, 2H), 7.49 (d, J = 6.6 Hz, 2H), 7.47 - 7.30 (m, 12H), 7.25 (d, J = 7.8 Hz, 2H), 7.19 (m, 1H), 6.01 (s, 1H), 5.50 (s, 1H), 5.24 (s, 1H), 4.34 (t, J = 4.2 Hz, 1H), 3.92 (m, 1H), 3.82 (m, 1H); $^{13}\text{C}\{^1\text{H}\}$ NMR (101 MHz, CDCl_3) δ 147.8, 147.0, 146.4, 140.8, 138.4, 131.8, 130.8, 130.2, 128.8, 128.7, 128.4, 127.9, 127.4, 127.3, 126.8, 125.5, 125.3, 122.7, 119.82, 119.78, 117.1, 75.9, 67.0, 39.3

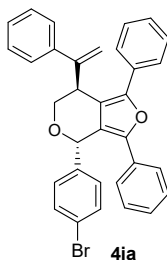
(one carbon missing due to overlap); IR (neat): 1485, 1263, 1069, 927, 689 cm^{-1} ; HRMS(ESI) m/z : $[\text{M}+\text{H}]^+$ calculated for $\text{C}_{33}\text{H}_{26}\text{BrO}_2^+$, 533.1111; found 533.1114.

(4S,7S)-1,4-Diphenyl-7-(1-phenylvinyl)-3-(thiophen-2-yl)-6,7-dihydro-4H-furo[3,4-c]pyran (4ea)



The reaction was performed according to general procedure C using **1e** (31.4 mg, 0.1 mmol) and **2a'** (30.9 mg, 0.15 mmol) to give **4ea** as an amorphous white solid (41.9 mg, 91% yield): R_f = 0.42 (PE/EtOAc = 30:1); m.p. 183-185 $^{\circ}\text{C}$; ^1H NMR (600 MHz, CDCl_3) δ 7.67 (d, J = 7.7 Hz, 2H), 7.40 (d, J = 6.5 Hz, 4H), 7.30 (m, 3H), 7.23 (m, 4H), 7.21 – 7.15 (m, 2H), 7.06 (d, J = 5.1 Hz, 1H), 6.76 (s, 1H), 6.54 (s, 1H), 5.77 (s, 1H), 5.42 (s, 1H), 5.19 (s, 1H), 4.20 (s, 1H), 3.78 (m, 2H); $^{13}\text{C}\{^1\text{H}\}$ NMR (151 MHz, CDCl_3) δ 147.3, 147.1, 142.8, 140.9, 139.4, 133.0, 130.7, 129.4, 128.9, 128.82, 128.77, 128.7, 127.9, 127.5, 127.4, 126.8, 125.3, 125.0, 124.0, 120.1, 119.5, 117.2, 76.4, 67.1, 39.4; IR (neat): 2359, 1490, 1066, 906, 691 cm^{-1} ; HRMS (ESI) m/z : $[\text{M}+\text{H}]^+$ calculated for $\text{C}_{31}\text{H}_{25}\text{SO}_2^+$, 461.1570; found 461.1566.

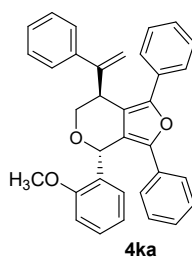
(4S,7S)-4-(4-Bromophenyl)-1,3-diphenyl-7-(1-phenylvinyl)-6,7-dihydro-4H-furo[3,4-c]pyran (4ia)



The reaction was performed according to general procedure C using **1i** (38.7 mg, 0.1 mmol) and **2a'** (30.9 mg, 0.15 mmol) to give **4ia** as an amorphous white solid (39.3mg, 74% yield): R_f = 0.42 (PE/EtOAc = 30:1); ^1H NMR (600 MHz, CDCl_3) δ 7.77 (d, J = 6.7 Hz, 2H), 7.47 (d, J = 9.2 Hz, 2H), 7.44 – 7.34 (m, 6H), 7.34 – 7.27 (m, 7H), 7.20 (d, J = 8.6 Hz, 2H), 5.96 (s, 1H), 5.49 (s, 1H), 5.24 (s, 1H), 4.30 (s, 1H), 3.90 (m, 1H), 3.84 (m, 1H); $^{13}\text{C}\{^1\text{H}\}$ NMR (151 MHz,

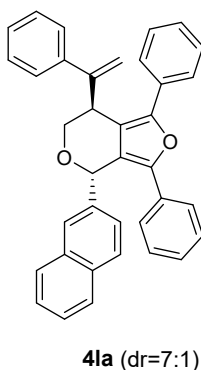
CDCl₃) δ 148.1, 147.2, 145.4, 140.9, 139.2, 131.5, 130.8, 129.3, 129.2, 128.9, 128.8, 128.7, 127.9, 127.5, 127.0, 126.8, 125.4, 121.2, 121.1, 120.3, 117.1, 76.7, 67.0, 39.4 (one carbon missing due to overlap); IR (neat): 1485, 1276, 1066, 907, 691 cm⁻¹; HRMS (ESI) m/z : [M+H]⁺ calculated for C₃₃H₂₆BrO₂⁺, 533.1111; found 533.1117.

(4S,7S)-4-(2-Methoxyphenyl)-1,3-diphenyl-7-(1-phenylvinyl)-6,7-dihydro-4H-furo[3,4-c]pyran (4ka)



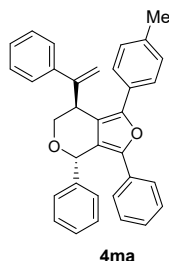
The reaction was performed according to general procedure C using **1k** (33.8 mg, 0.1 mmol) and **2a'** (30.9 mg, 0.15 mmol) to give **4ka** as an amorphous white solid (22.3 mg, 46% yield): R_f = 0.12 (PE/EtOAc = 30:1); ¹H NMR (600 MHz, CDCl₃) δ 7.79 (d, J = 8.1 Hz, 2H), 7.52 (d, J = 5.7 Hz, 2H), 7.38 (m, 6H), 7.35 – 7.31 (m, 2H), 7.31 – 7.27 (m, 3H), 7.22 – 7.17 (m, 2H), 7.13 (m, 1H), 6.76 (d, J = 8.8 Hz, 1H), 6.45 (s, 1H), 5.58 (s, 1H), 5.31 (s, 1H), 4.28 (s, 1H), 3.93 (s, 3H), 3.90 (m, 2H); ¹³C {¹H} NMR (151 MHz, CDCl₃) δ 156.9, 147.7, 147.4, 146.2, 141.0, 132.9, 132.7, 131.0, 130.5, 130.0, 128.8, 128.7, 128.2, 127.9, 127.3, 127.2, 126.9, 125.6, 125.2, 120.6, 120.1, 117.4, 113.2, 112.6, 69.5, 67.4, 56.2, 39.5; IR (neat): 2359, 1480, 1055, 913, 690 cm⁻¹; HRMS (ESI) m/z : [M+H]⁺ calculated for C₃₄H₂₉O₃⁺, 485.2111; found 485.2101.

(4S,7S)-4-(Naphthalen-2-yl)-1,3-diphenyl-7-(1-phenylvinyl)-6,7-dihydro-4H-furo[3,4-c]pyran (4la)



The reaction was performed according to general procedure C using **1l** (35.8 mg, 0.1 mmol) and **2a'** (30.9 mg, 0.15 mmol) to give **4la** (7:1 inseparable diastereomers) as an amorphous white solid (35.8 mg, 71% yield): R_f = 0.35 (PE/EtOAc = 30:1); For major isomer: ^1H NMR (600 MHz, CDCl_3) δ 7.73 (s, 1H), 7.63 (m, 5H), 7.46 (d, J = 8.5 Hz, 1H), 7.37 – 7.26 (m, 8H), 7.23 – 7.10 (m, 4H), 7.01 (t, J = 7.7 Hz, 2H), 6.93 (t, J = 7.6 Hz, 1H), 6.08 (s, 1H), 5.31 (s, 1H), 5.17 (s, 1H), 4.23 (s, 1H), 3.64–3.68 (m, 2H). $^{13}\text{C}\{^1\text{H}\}$ NMR (151 MHz, CDCl_3) δ 148.6, 147.8, 147.3, 141.7, 137.6, 134.3, 134.1, 131.8, 131.2, 129.6, 129.5, 129.42, 129.40, 129.2, 128.6, 128.5, 128.1, 127.9, 127.6, 127.4, 127.1, 126.9, 126.3, 126.2, 121.0, 120.8, 117.8, 77.2, 67.4, 40.4 (one carbon missing due to overlap). For minor isomer: ^1H NMR (600 MHz, CDCl_3) δ 8.25 (s, 1H), 7.63 (m, 5H), 7.47 (m, 1H), 7.41 – 7.35 (m, 8H), 7.26 (m, 4H), 7.04 (m, 2H), 6.96 (m, 1H), 6.14 (s, 1H), 5.44 (s, 1H), 5.27 (s, 1H), 4.27 (s, 1H), 4.03 (m, 1H), 3.77 (m, 1H); $^{13}\text{C}\{^1\text{H}\}$ NMR (151 MHz, CDCl_3) δ 148.6, 148.0, 147.5, 141.7, 139.4, 135.5, 132.6, 131.7, 131.0, 129.8, 129.6, 129.5, 129.4, 129.2, 128.8, 128.7, 128.1, 128.0, 127.6, 127.4, 127.1, 126.9, 126.5, 126.1, 121.0, 120.7, 118.1, 77.6, 67.8, 40.2 (one carbon missing due to overlap). IR (neat): 3054, 2359, 1491, 1057, 689 cm^{-1} ; HRMS (ESI) m/z : $[\text{M}+\text{H}]^+$ calculated for $\text{C}_{37}\text{H}_{29}\text{O}_2^+$ 505.2162; found 505.2156.

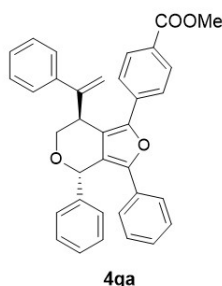
(4S,7S)-3,4-Diphenyl-7-(1-phenylvinyl)-1-(p-tolyl)-6,7-dihydro-4H-furo[3,4-c]pyran (4ma)



The reaction was performed according to general procedure C using **1m** (32.2 mg, 0.1 mmol) and **2a'** (30.9 mg, 0.15 mmol) to give **4ma** as an amorphous white solid (34.0 mg, 73% yield): R_f = 0.38 (PE/EtOAc = 30:1); m.p. 160–162 °C; ^1H NMR (600 MHz, CDCl_3) δ 7.67 (d, J = 8.1 Hz, 2H), 7.47 (d, J = 7.1 Hz, 2H), 7.44 (d, J = 6.6 Hz, 2H), 7.38 – 7.26 (m, 8H), 7.22 – 7.15 (m, 4H), 7.11 (m, 1H), 6.01 (s, 1H), 5.47 (s, 1H), 5.25 (s, 1H), 4.31 (s, 1H), 3.90 (d, J = 11.6 Hz, 1H), 3.81 (d, J = 11.4 Hz, 1H), 2.37 (s, 3H); $^{13}\text{C}\{^1\text{H}\}$ NMR (151 MHz, CDCl_3) δ 147.9, 147.2, 146.0, 141.0, 139.5, 137.2, 130.5, 129.4, 129.3, 128.7, 128.65, 128.63, 128.31, 128.28, 127.8, 127.0, 126.8, 125.6, 125.3, 120.4, 119.3, 117.0, 76.8, 67.0, 39.4, 21.4; IR (neat): 2359,

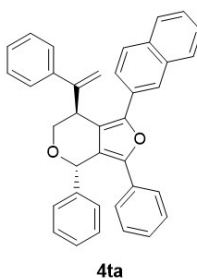
1432, 1055, 913, 691 cm^{-1} ; HRMS (ESI) m/z : $[M+H]^+$ calculated for $\text{C}_{34}\text{H}_{29}\text{O}_2^+$, 469.2162; found 469.2158.

Methyl 4-((4S,7S)-3,4-diphenyl-7-(1-phenylvinyl)-6,7-dihydro-4H-furo[3,4-c]pyran-1-yl)benzoate (4qa)



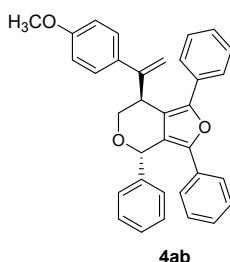
The reaction was performed according to general procedure C using **1q** (36.6 mg, 0.1 mmol) and **2a'** (30.9 mg, 0.15 mmol) to give **4qa** as an amorphous white solid (41.7 mg, 81% yield): R_f = 0.22 (PE/EtOAc = 30:1); m.p. 160-162 $^{\circ}\text{C}$; ^1H NMR (600 MHz, CDCl_3) δ 7.94 (d, J = 8.6 Hz, 2H), 7.71 (d, J = 8.7 Hz, 2H), 7.37 (d, J = 7.1 Hz, 2H), 7.32 (d, J = 6.5 Hz, 2H), 7.27 (d, J = 6.4 Hz, 3H), 7.23 (d, J = 7.2 Hz, 1H), 7.21 – 7.14 (m, 4H), 7.11 (t, J = 7.7 Hz, 2H), 7.05 (m, 1H), 5.92 (s, 1H), 5.38 (s, 1H), 5.13 (s, 1H), 4.24 (s, 1H), 3.84 (s, 1H), 3.82 (m, 3H), 3.73 (m, 1H); $^{13}\text{C}\{^1\text{H}\}$ NMR (151 MHz, CDCl_3) δ 167.0, 147.6, 146.8, 146.7, 140.7, 139.1, 134.9, 130.1, 129.2, 128.8, 128.71, 128.67, 128.4, 128.3, 128.0, 127.6, 126.7, 125.9, 124.8, 122.5, 120.9, 117.0, 76.6, 66.8, 52.2, 39.5 (one carbon missing due to overlap); IR (neat): 1712, 1313, 1070, 892, 697 cm^{-1} ; HRMS (ESI) m/z : $[M+H]^+$ calculated for $\text{C}_{35}\text{H}_{29}\text{O}_4^+$, 513.2060; found 513.2055.

(4S,7S)-1-(Naphthalen-2-yl)-3,4-diphenyl-7-(1-phenylvinyl)-6,7-dihydro-4H-furo[3,4-c]pyran (4ta)



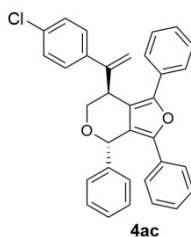
The reaction was performed according to general procedure C using **1t** (35.8 mg, 0.1 mmol) and **2a'** (30.9 mg, 0.15 mmol) to give **4ta** as an amorphous white solid (22.4 mg, 44% yield): R_f = 0.32 (PE/EtOAc = 30:1); m.p. 65-67 °C; ^1H NMR (400 MHz, CDCl_3) δ 8.26-8.22 (m, 1H), 7.96 – 7.83 (m, 2H), 7.70 (d, J = 6.3 Hz, 1H), 7.61 – 7.49 (m, 4H), 7.41 (m, 6H), 7.23 (d, J = 8.0 Hz, 2H), 7.16 (m, 4H), 7.02 (d, J = 5.2 Hz, 2H), 6.25 (s, 1H), 5.10 (s, 2H), 4.40 (t, J = 6.2 Hz, 1H), 3.92 (m, 1H), 3.67 (m, 1H); $^{13}\text{C}\{^1\text{H}\}$ NMR (151 MHz, CDCl_3) δ 148.2, 147.7, 146.9, 141.3, 139.2, 134.0, 131.8, 130.7, 129.3, 129.1, 128.8, 128.7, 128.6, 128.5, 128.1, 127.7, 127.4, 127.0, 126.74, 126.65, 126.2, 126.1, 125.20, 125.17, 122.1, 119.2, 116.6, 75.6, 66.0, 39.9 (one carbon missing due to overlap); IR (neat): 3056, 2356, 1492, 1125, 698 cm^{-1} ; HRMS(ESI) m/z : $[\text{M}+\text{H}]^+$ calculated for $\text{C}_{37}\text{H}_{29}\text{O}_2^+$, 505.2162; found 505.2159.

(4S,7S)-7-(1-(4-Methoxyphenyl)vinyl)-1,3,4-triphenyl-6,7-dihydro-4H-furo[3,4-c]pyran (4ab)



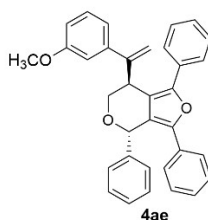
The reaction was performed according to general procedure C using **1a** (30.8 mg, 0.1 mmol) and **2b'** (35.4 mg, 0.15 mmol) to give **4ab** as an amorphous white solid (33.0 mg, 68% yield): R_f = 0.19 (PE/EtOAc = 30:1); m.p. 78-80 °C; ^1H NMR (600 MHz, CDCl_3) δ 7.77 (d, J = 7.1 Hz, 2H), 7.48 – 7.40 (m, 4H), 7.40 – 7.33 (m, 4H), 7.28 (m, 4H), 7.20 (t, J = 8.1 Hz, 2H), 7.13 (d, J = 7.2 Hz, 1H), 6.90 (d, J = 8.7 Hz, 2H), 6.02 (s, 1H), 5.43 (s, 1H), 5.19 (s, 1H), 4.29 (t, J = 4.1 Hz, 1H), 3.90 (m, 1H), 3.84 (s, 3H), 3.81 (m, 1H); $^{13}\text{C}\{^1\text{H}\}$ NMR (151 MHz, CDCl_3) δ 159.4, 147.6, 146.5, 146.4, 139.4, 133.4, 131.0, 130.5, 129.3, 128.7, 128.6, 128.6, 128.3, 127.9, 127.3, 127.1, 125.6, 125.3, 120.5, 120.2, 115.7, 114.0, 76.7, 67.0, 55.5, 39.4; IR (neat): 1511, 1258, 1064, 915, 698 cm^{-1} ; HRMS(ESI) m/z : $[\text{M}+\text{H}]^+$ calculated for $\text{C}_{34}\text{H}_{29}\text{O}_3^+$, 485.2111; found 485.2106.

(4S,7S)-7-(1-(4-Chlorophenyl)vinyl)-1,3,4-triphenyl-6,7-dihydro-4H-furo[3,4-c]pyran (4ac)



The reaction was performed according to general procedure C using **1a** (30.8 mg, 0.1 mmol) and **2c'** (36.1 mg, 0.15 mmol) to give **4ac** as an amorphous white solid (30.3 mg, 62% yield): R_f = 0.40 (PE/EtOAc = 30:1); m.p. 232-234 °C; ^1H NMR (600 MHz, CDCl_3) δ 7.72 (d, J = 7.7 Hz, 2H), 7.36 (m, 8H), 7.31 – 7.26 (m, 4H), 7.24 (m, 2H), 7.18 (m, 2H), 7.11 (d, J = 7.4 Hz, 1H), 6.00 (s, 1H), 5.45 (s, 1H), 5.27 (s, 1H), 4.24 (s, 1H), 3.89 (d, J = 11.5 Hz, 1H), 3.78 (d, J = 7.8 Hz, 1H); $^{13}\text{C}\{^1\text{H}\}$ NMR (151 MHz, CDCl_3) δ 147.7, 146.5, 146.2, 139.3, 139.2, 133.7, 130.9, 130.4, 129.2, 128.79, 128.76, 128.69, 128.66, 128.3, 128.1, 127.4, 127.2, 125.6, 125.3, 120.3, 119.8, 117.7, 76.7, 66.9, 39.5; IR (neat): 2360, 1492, 1067, 906, 689 cm^{-1} ; HRMS (ESI) m/z : $[\text{M}+\text{H}]^+$ calculated for $\text{C}_{33}\text{H}_{26}\text{ClO}_2^+$, 489.1616; found 489.1615.

(4S,7S)-7-(1-(3-Methoxyphenyl)vinyl)-1,3,4-triphenyl-6,7-dihydro-4H-furo[3,4-c]pyran (4ae)

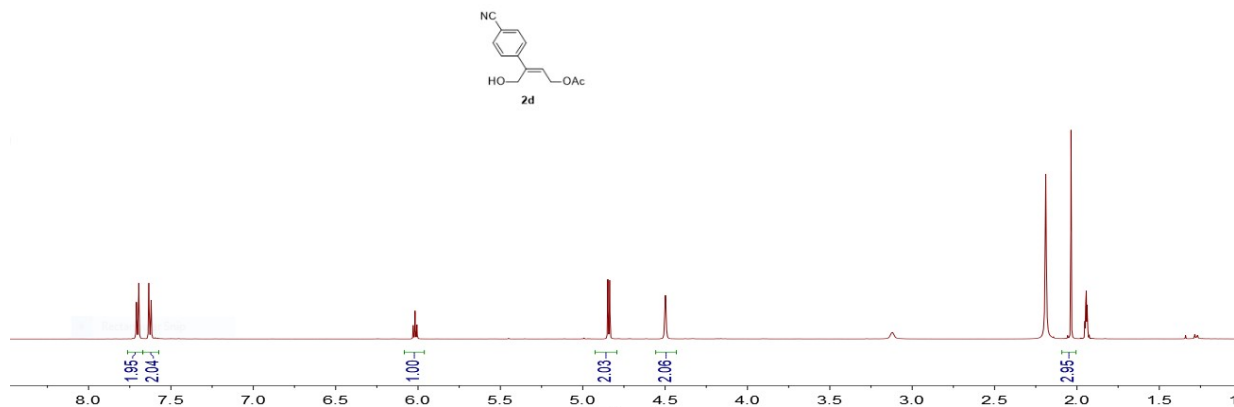


The reaction was performed according to general procedure C using **1a** (30.8 mg, 0.1 mmol) and **2e'** (35.4 mg, 0.15 mmol) to give **4ae** as an amorphous white solid (42.6 mg, 88% yield): R_f = 0.22 (PE/EtOAc = 30:1); m.p. 161-163 °C; ^1H NMR (600 MHz, CDCl_3) δ 7.69 (d, J = 7.2 Hz, 2H), 7.35 (d, J = 6.3 Hz, 2H), 7.31 (t, J = 7.9 Hz, 2H), 7.27 (d, J = 1.4 Hz, 1H), 7.22 – 7.15 (m, 5H), 7.10 (t, J = 7.8 Hz, 2H), 7.03 (t, J = 7.4 Hz, 2H), 6.99 (d, J = 8.4 Hz, 1H), 6.93 – 6.91 (m, 1H), 6.78 (dd, J = 8.7, 2.1 Hz, 1H), 5.93 (s, 1H), 5.40 (s, 1H), 5.17 (s, 1H), 4.21 (t, J = 4.2 Hz, 1H), 3.82 (m, 1H), 3.75 (m, 1H), 3.72 (s, 3H); $^{13}\text{C}\{^1\text{H}\}$ NMR (151 MHz, CDCl_3) δ 159.9, 147.7, 147.1, 146.4, 142.5, 139.4, 131.0, 130.5, 129.6, 129.2, 128.7, 128.62, 128.61, 128.3, 127.3, 127.1, 125.7, 125.4, 120.5, 120.0, 119.2, 117.2, 113.3, 112.8, 76.7, 67.0, 55.4, 39.5; IR (neat):

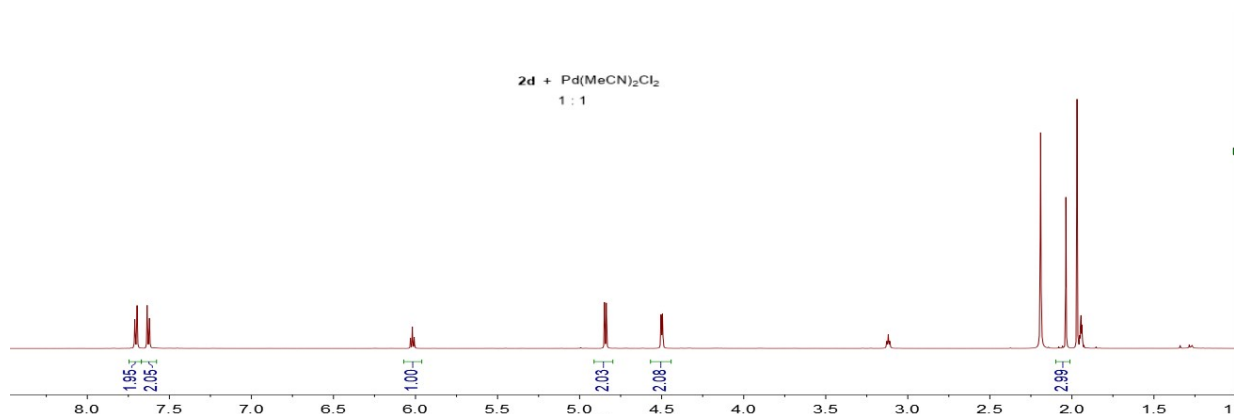
2360, 1596, 1065, 900, 689 cm^{-1} ; HRMS (ESI) m/z : $[\text{M}+\text{H}]^+$ calculated for $\text{C}_{34}\text{H}_{29}\text{O}_3^+$, 485.2111; found 485.2111.

6. Mechanistic study

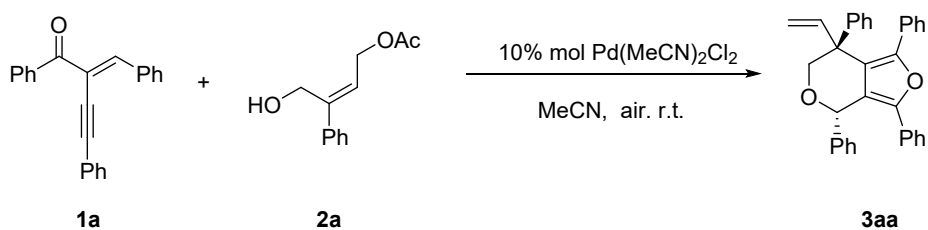
^1H -NMR of **2d** in $\text{D}_3\text{-MeCN}$



^1H -NMR of **2d** and $\text{Pd}(\text{MeCN})_2\text{Cl}_2$ (1:1) in $\text{D}_3\text{-MeCN}$

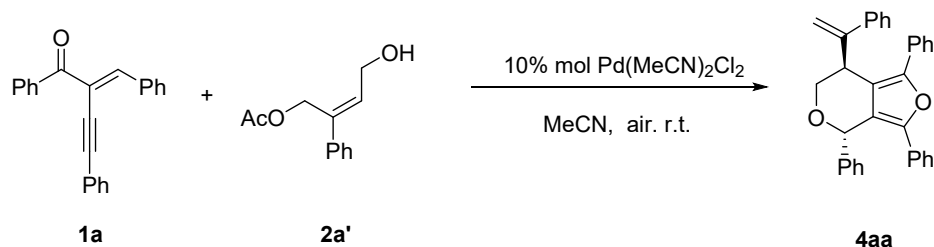


7. Scale-up reactions



To a 100 mL round-bottom flask was added **2a** (309.4 mg, 1.5 mmol, 1.5 equiv.), $\text{Pd}(\text{MeCN})_2\text{Cl}_2$ (25.9 mg, 0.1 mmol, 0.10 equiv.), and MeCN (15.0 mL). The mixture was stirred at room temperature under air for 0.5 h. A solution of **1a** (308.4 mg, 1.0 mmol, 1.0 equiv.) in MeCN (5.0 mL) was added and the resulting mixture was stirred at room temperature under air

for 12 h. The completed reaction was concentrated. The residue was purified by column chromatography (silica gel, PE/EtOAc = 40:1) to afford **3aa** (315.0 mg, 69% yield)



To a 100 mL round-bottom flask was added **2a'** (309.4 mg, 1.5 mmol, 1.5 equiv.), Pd(MeCN)₂Cl₂ (25.9 mg, 0.1 mmol, 0.10 equiv.), and MeCN (15.0 mL). The mixture was stirred at room temperature under air for 0.5 h. A solution of **1a** (308.4 mg, 1.0 mmol, 1.0 equiv.) in MeCN (5.0 mL) was added. The resulting mixture was stirred at room temperature under air for 12 h and the completed reaction was concentrated. The residue was purified by column chromatography (silica gel, PE/EtOAc = 40:1) to afford **4aa** (308 mg, 68%).

8. References

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9. Single Crystal X-ray Structures of 30a.

The single crystal of (4*S*,7*S*)-1-(4-fluorophenyl)-3,4,7-triphenyl-7-vinyl-6,7-dihydro-4*H*-furo[3,4-*c*]pyran (**30a**) suitable for X-ray analysis were obtained by dissolving with petroleum ether at elevated temperatures, cooling to room temperature, and allowing the supersaturated solution to crystallize. Crystal data and structure refinement for **30a** were with thermal ellipsoids at 50% probability.

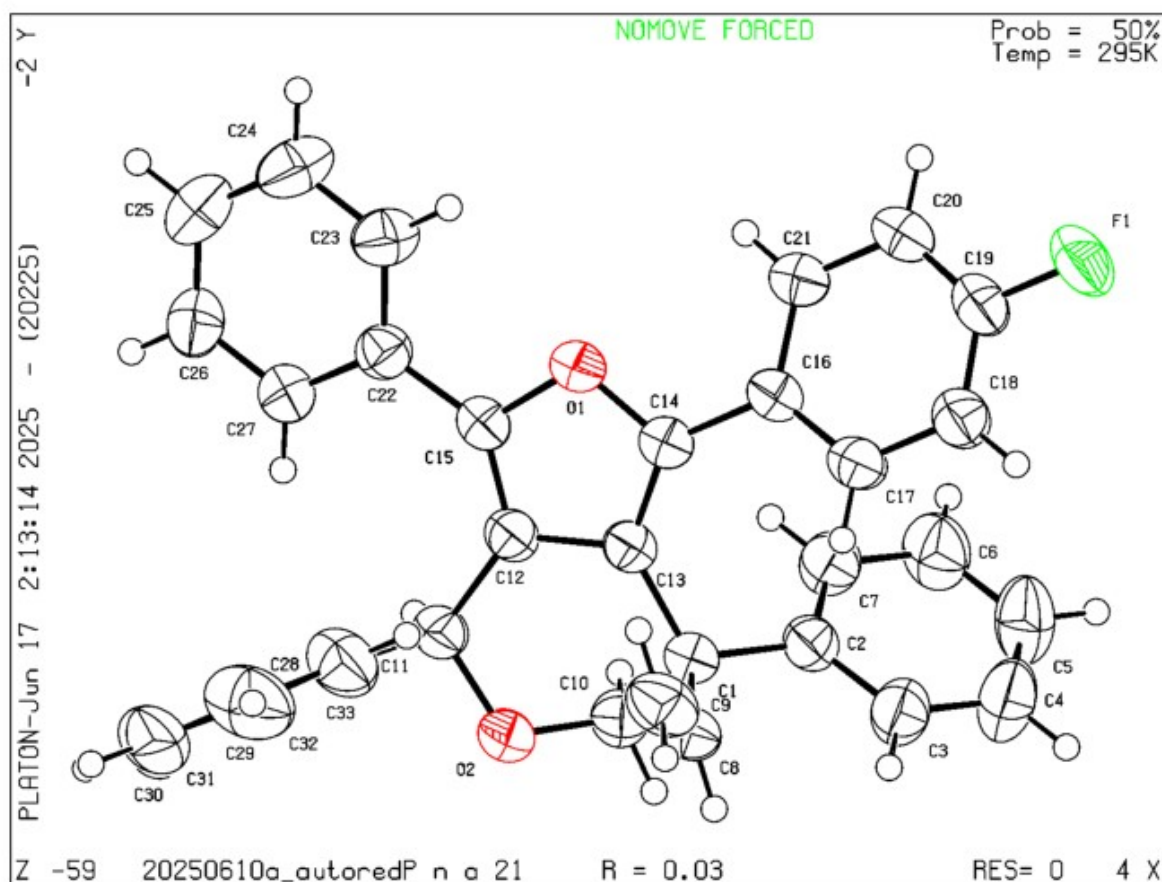


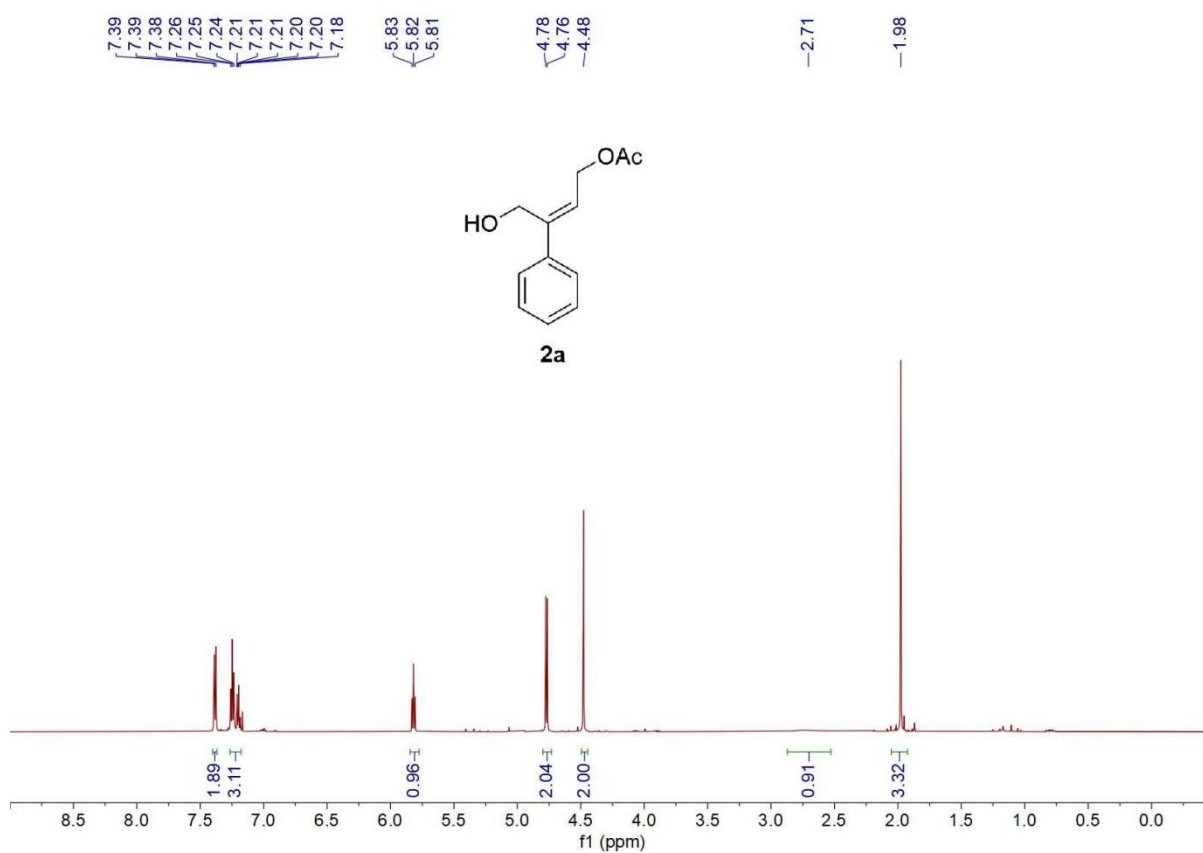
Table 1 Crystal data and structure refinement for **30a**

Identification code	30a
Empirical formula	C ₃₃ H ₂₅ FO ₂
Formula weight	472.53
Temperature/K	295(1)
Crystal system	orthorhombic
Space group	Pna2 ₁
a/Å	10.11190(10)

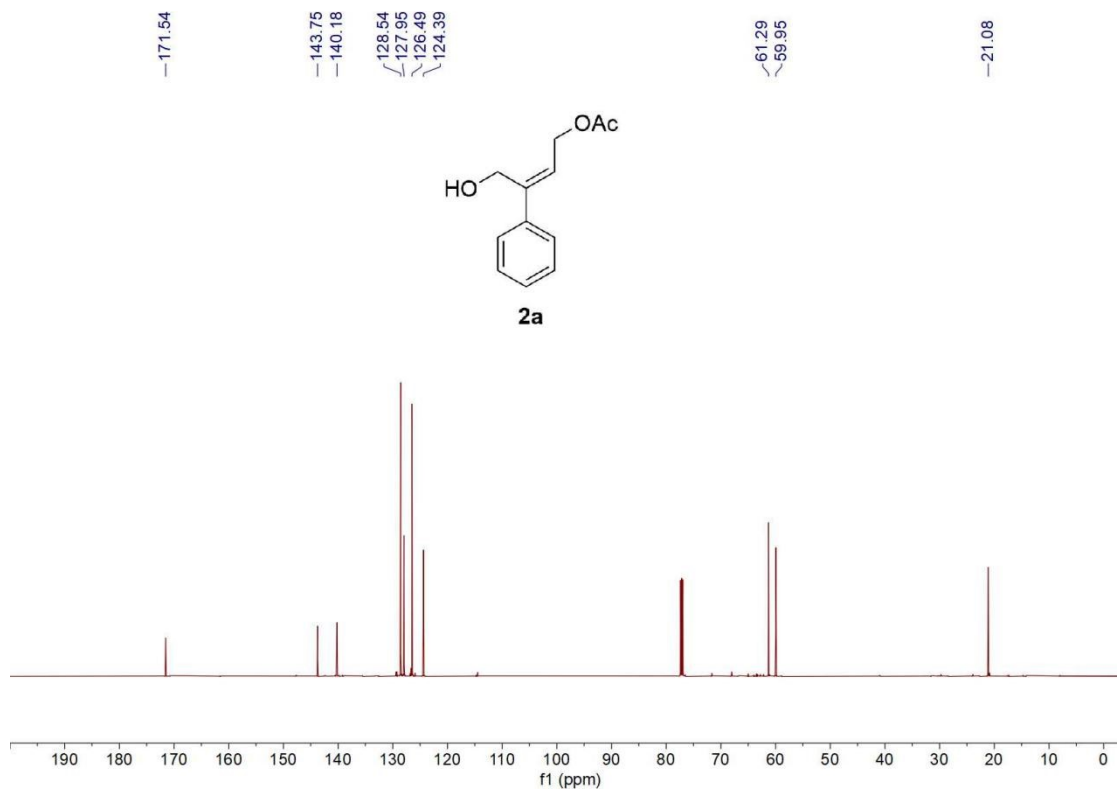
b/Å	22.5003(3)
c/Å	10.8841(2)
α /°	90
β /°	90
γ /°	90
Volume/Å ³	2476.36(6)
Z	4
ρ calcg/cm ³	1.267
μ /mm ⁻¹	0.660
F(000)	992.0
Radiation	Cu K α (λ = 1.54184)
2 Θ range for data collection/°	7.858 to 136.344
Index ranges	-12 $\leq$ h $\leq$ 12, -26 $\leq$ k $\leq$ 26, -12 $\leq$ l $\leq$ 11
Reflections collected	48383
Independent reflections	4254 [R_{int} = 0.0536, R_{sigma} = 0.0185]
Data/restraints/parameters	4254/1/326
Goodness-of-fit on F2	1.084
Final R indexes [$I \geq 2\sigma(I)$]	R_1 = 0.0334, wR_2 = 0.0866
Final R indexes [all data]	R_1 = 0.0342, wR_2 = 0.0880
Largest diff. peak/hole / e Å ⁻³	0.14/-0.13
Flack parameter	0.15(9)

10. ^1H NMR, ^{13}C NMR Spectral Copies.

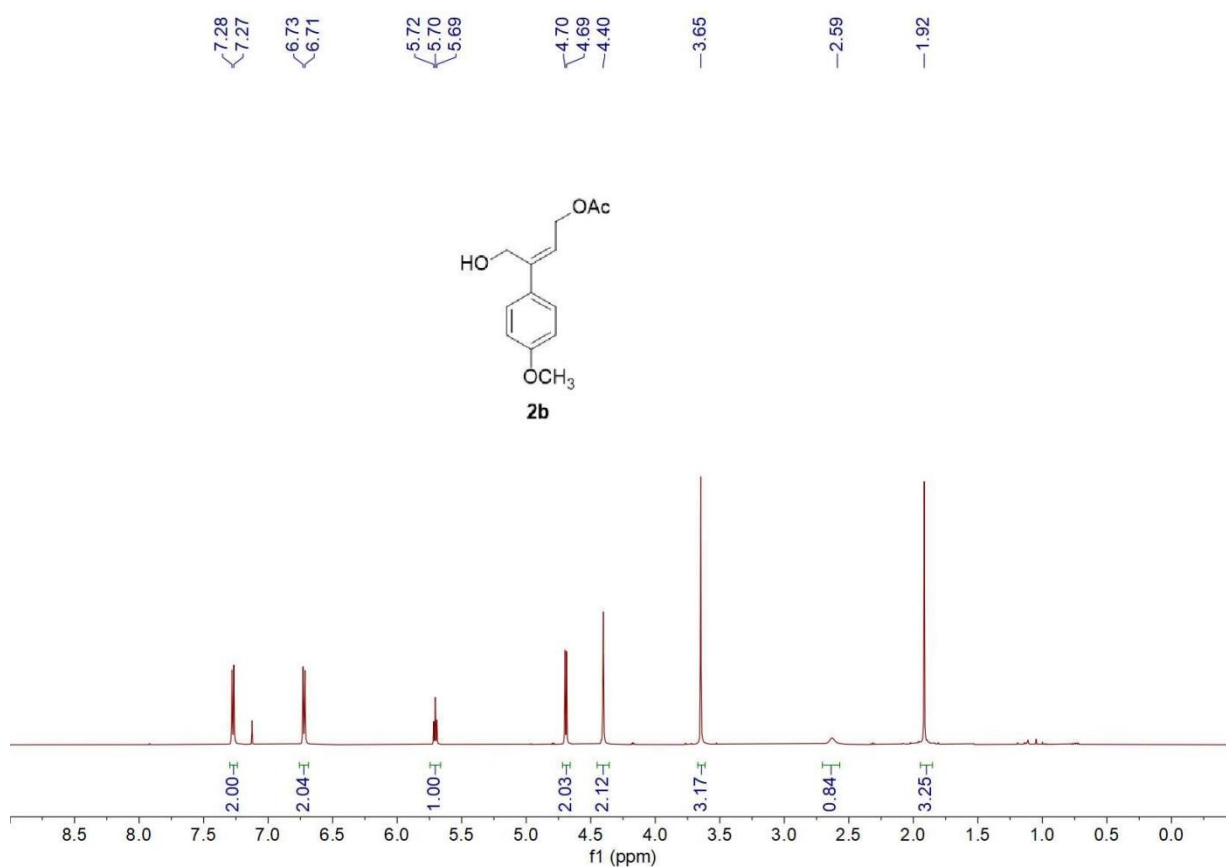
^1H NMR (600 MHz, CDCl_3) for **2a**



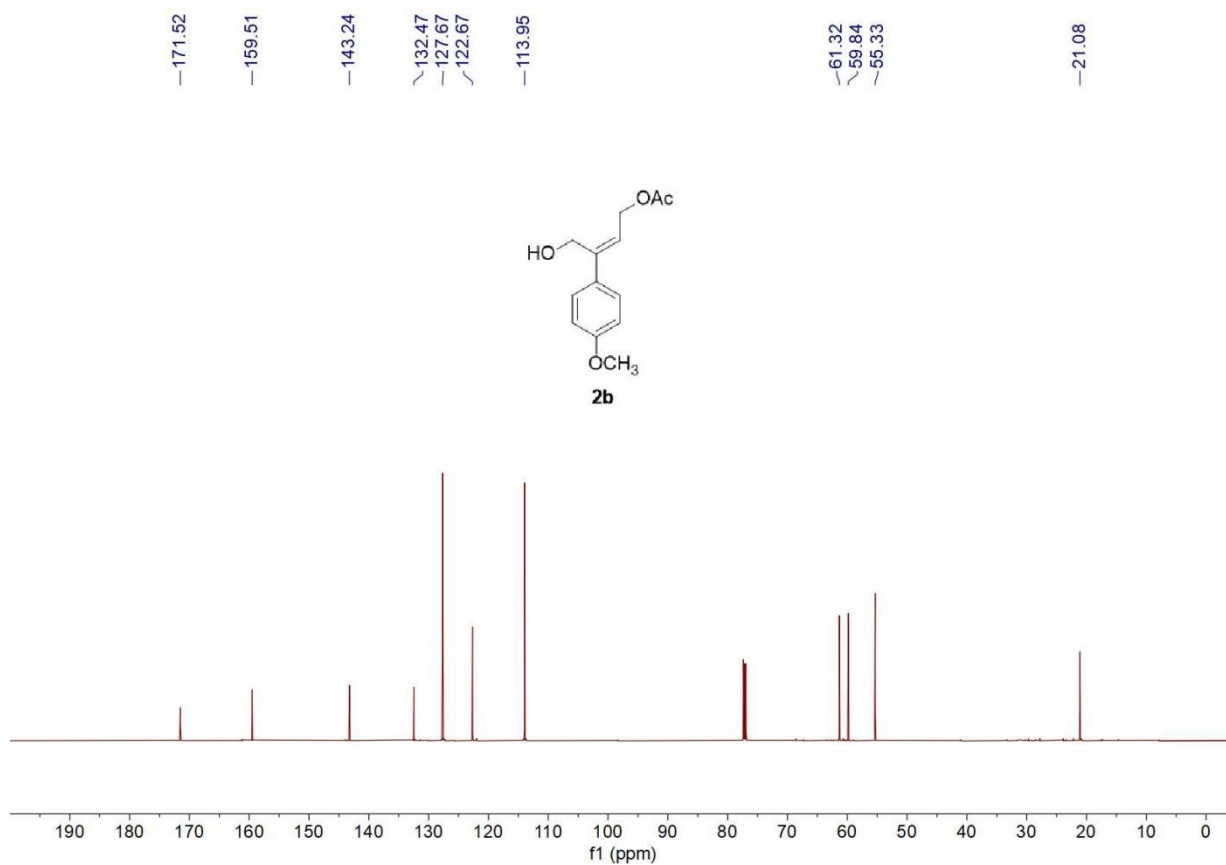
$^{13}\text{C}\{^1\text{H}\}$ NMR (151 MHz, CDCl_3) for **2a**



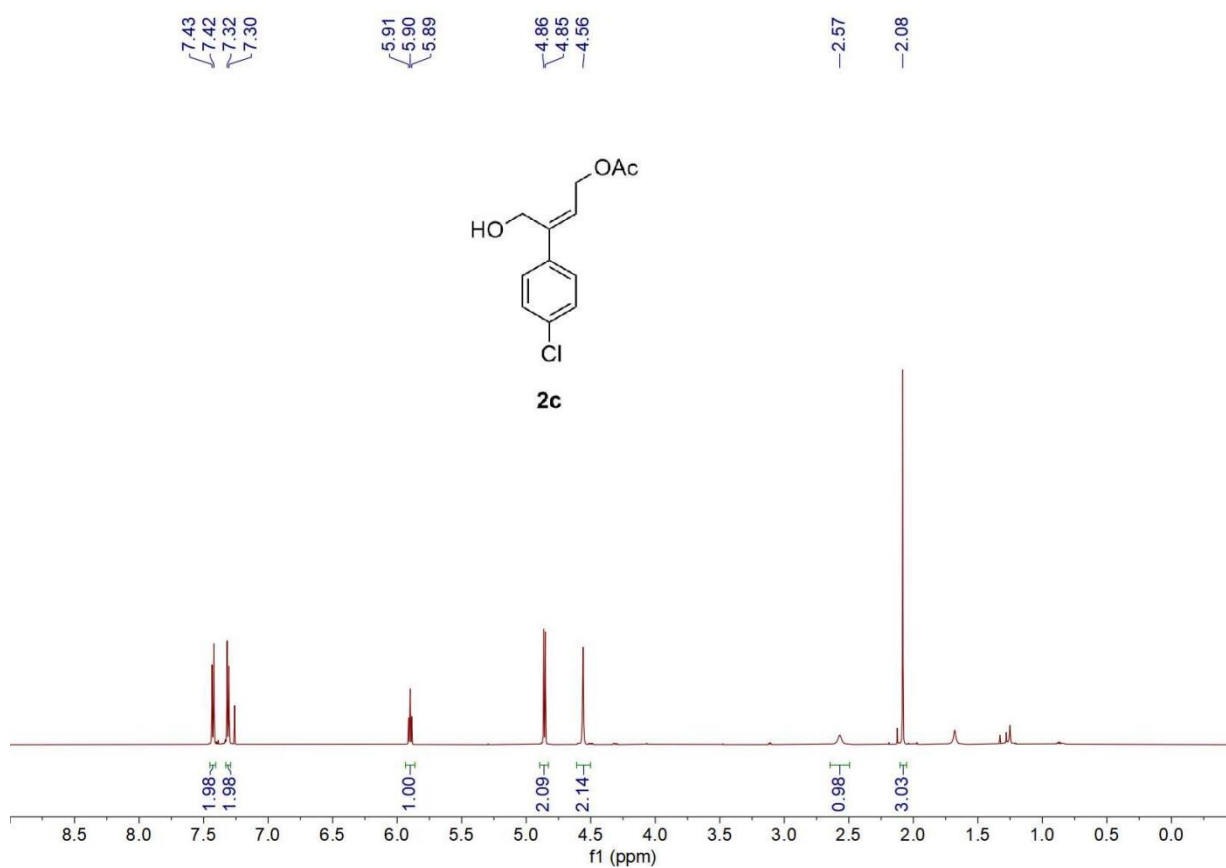
^1H NMR (600MHz, CDCl_3) for **2b**



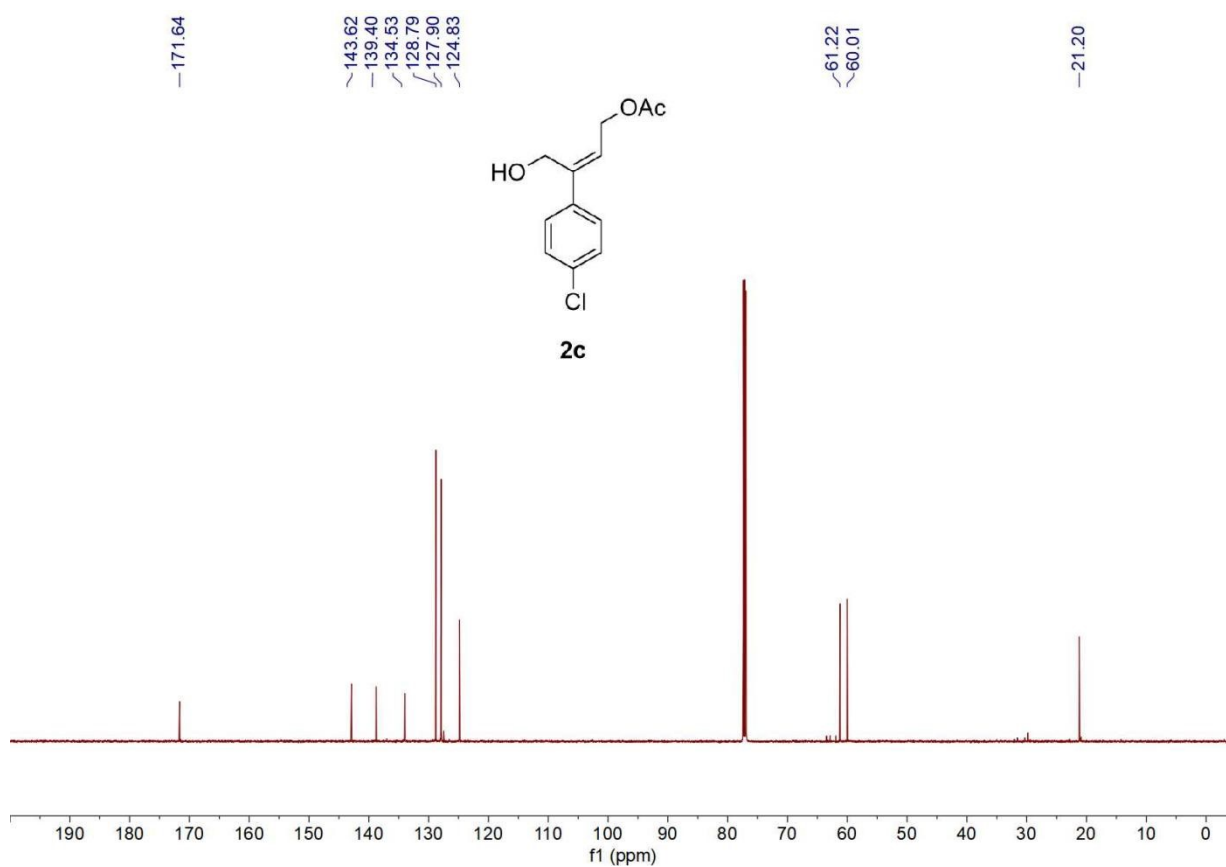
$^{13}\text{C}\{^1\text{H}\}$ NMR (151 MHz, CDCl_3) for **2b**



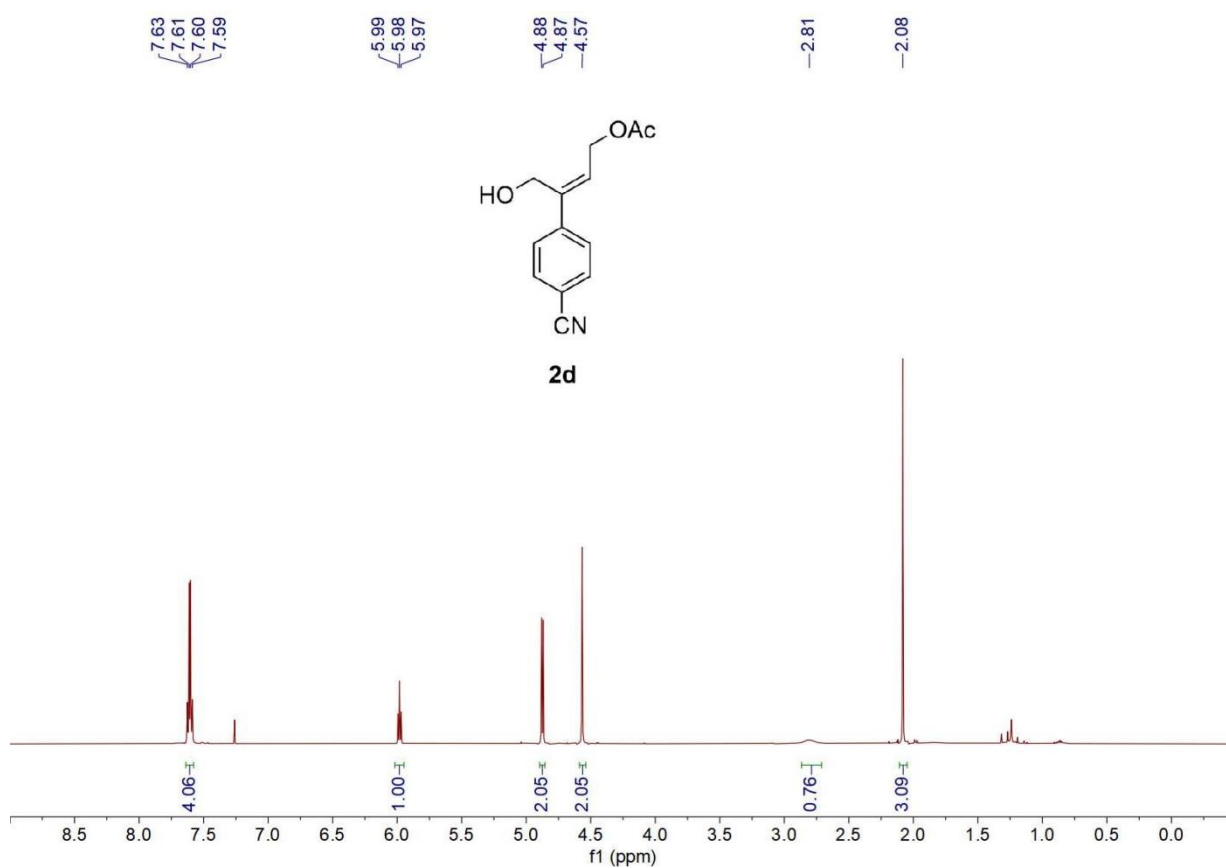
^1H NMR (600 MHz, CDCl_3) for **2c**



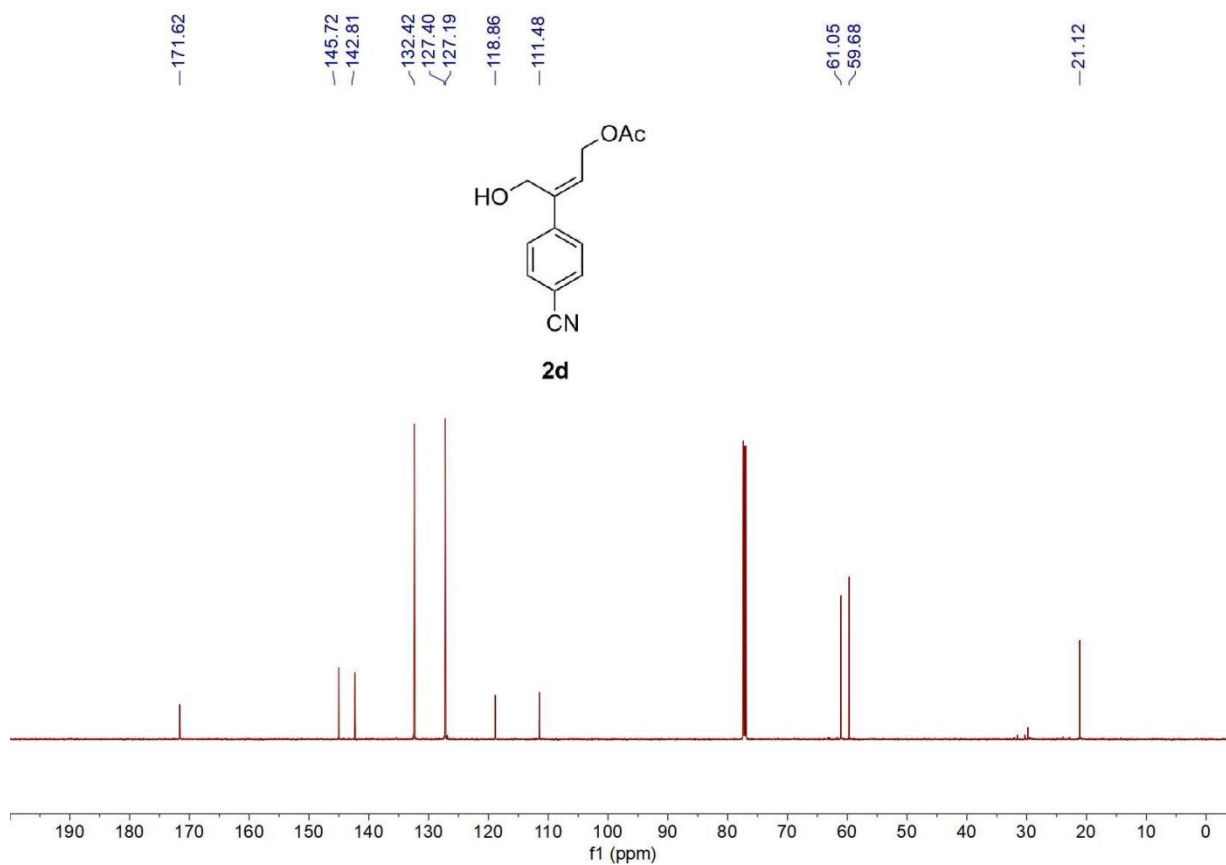
$^{13}\text{C}\{^1\text{H}\}$ NMR (151 MHz, CDCl_3) for **2c**



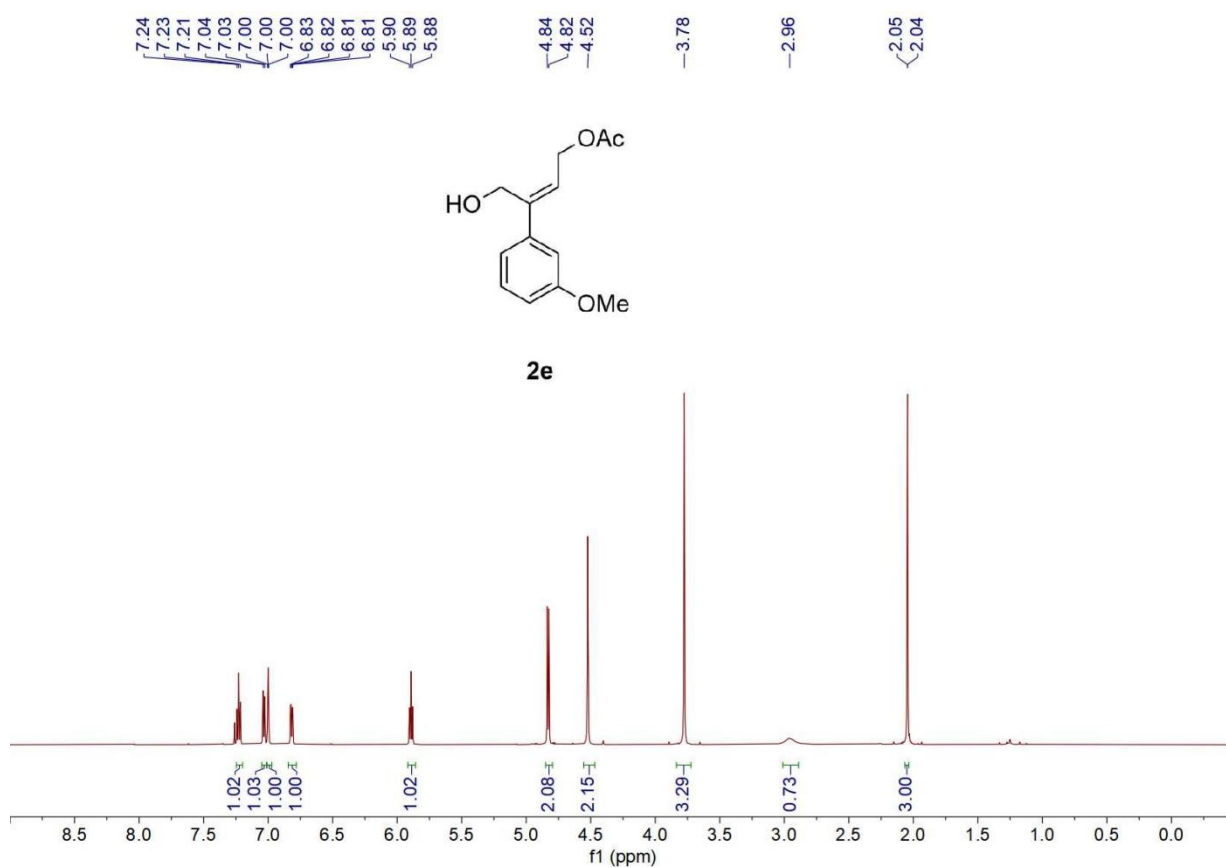
^1H NMR (400 MHz, CDCl_3) for **2d**



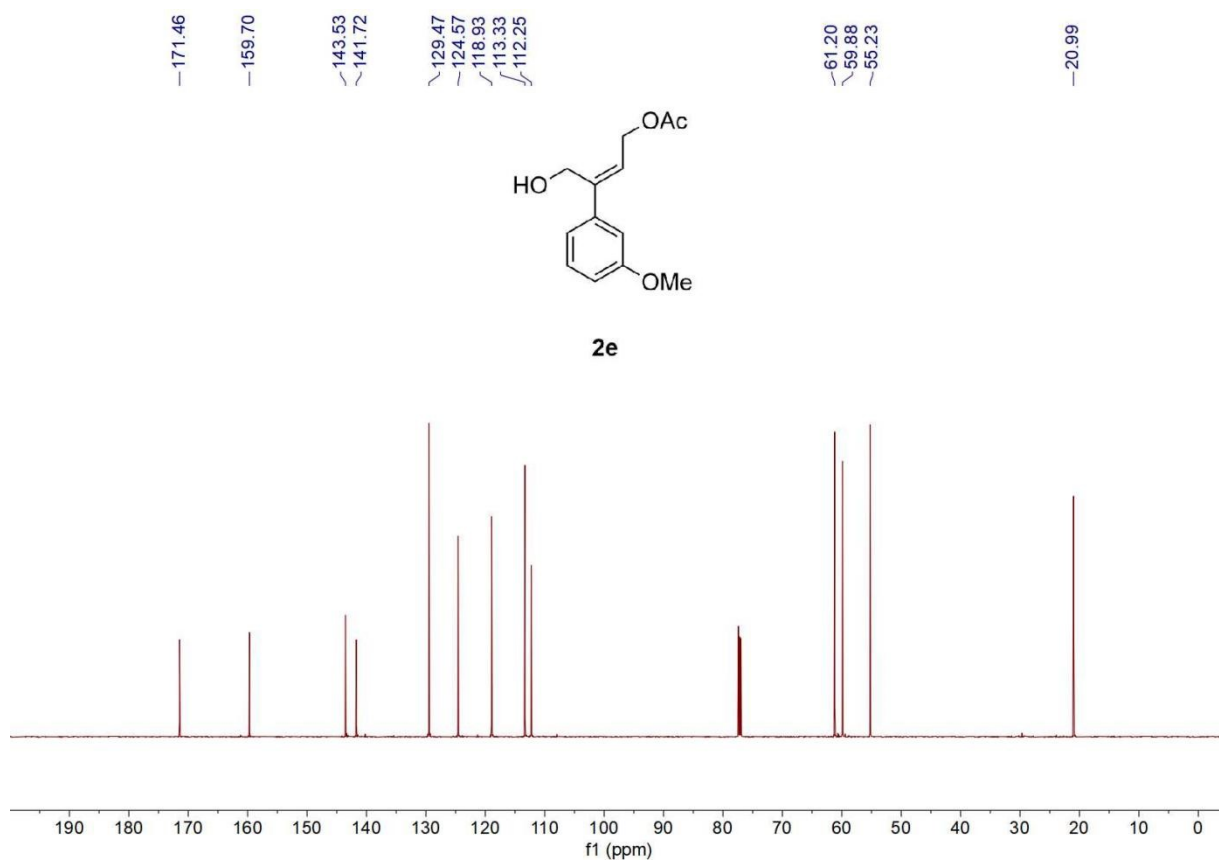
$^{13}\text{C}\{^1\text{H}\}$ NMR (101 MHz, CDCl_3) for **2d**



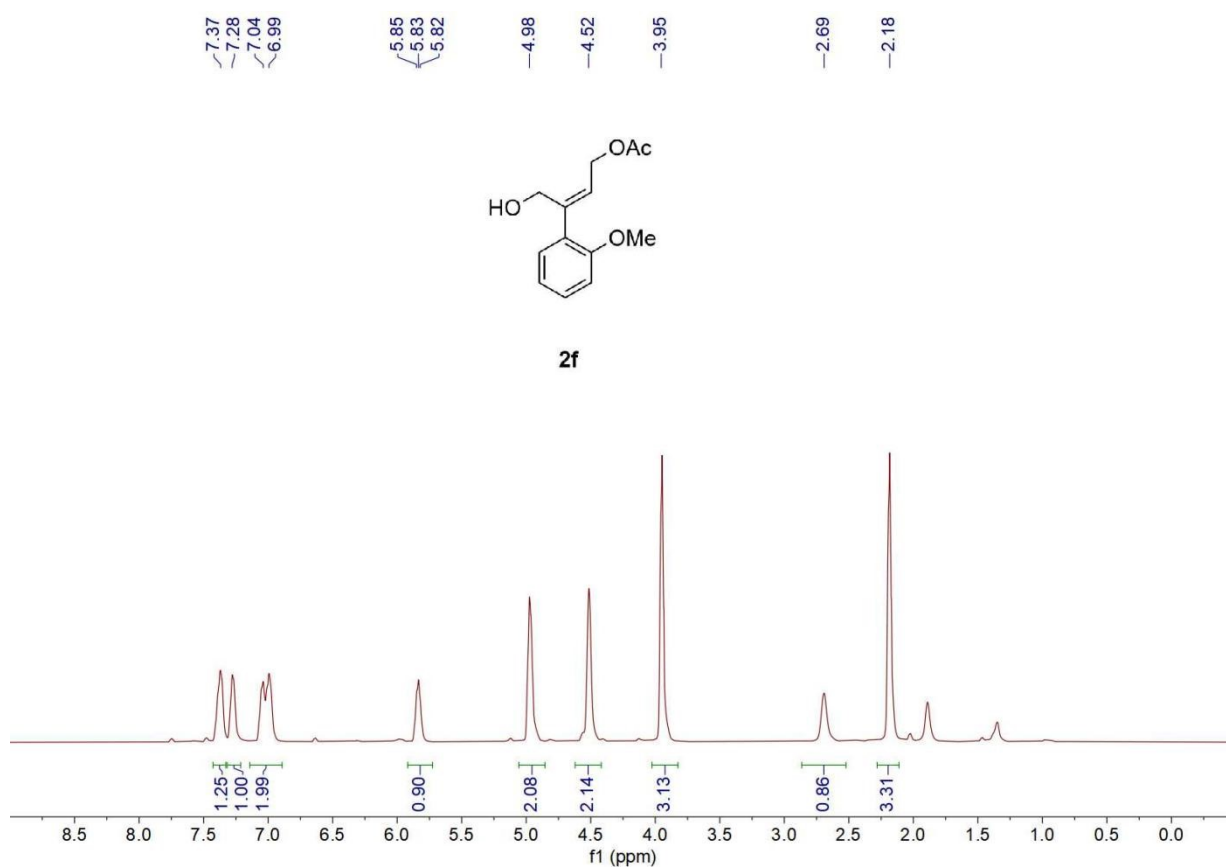
^1H NMR (600 MHz, CDCl_3) for **2e**



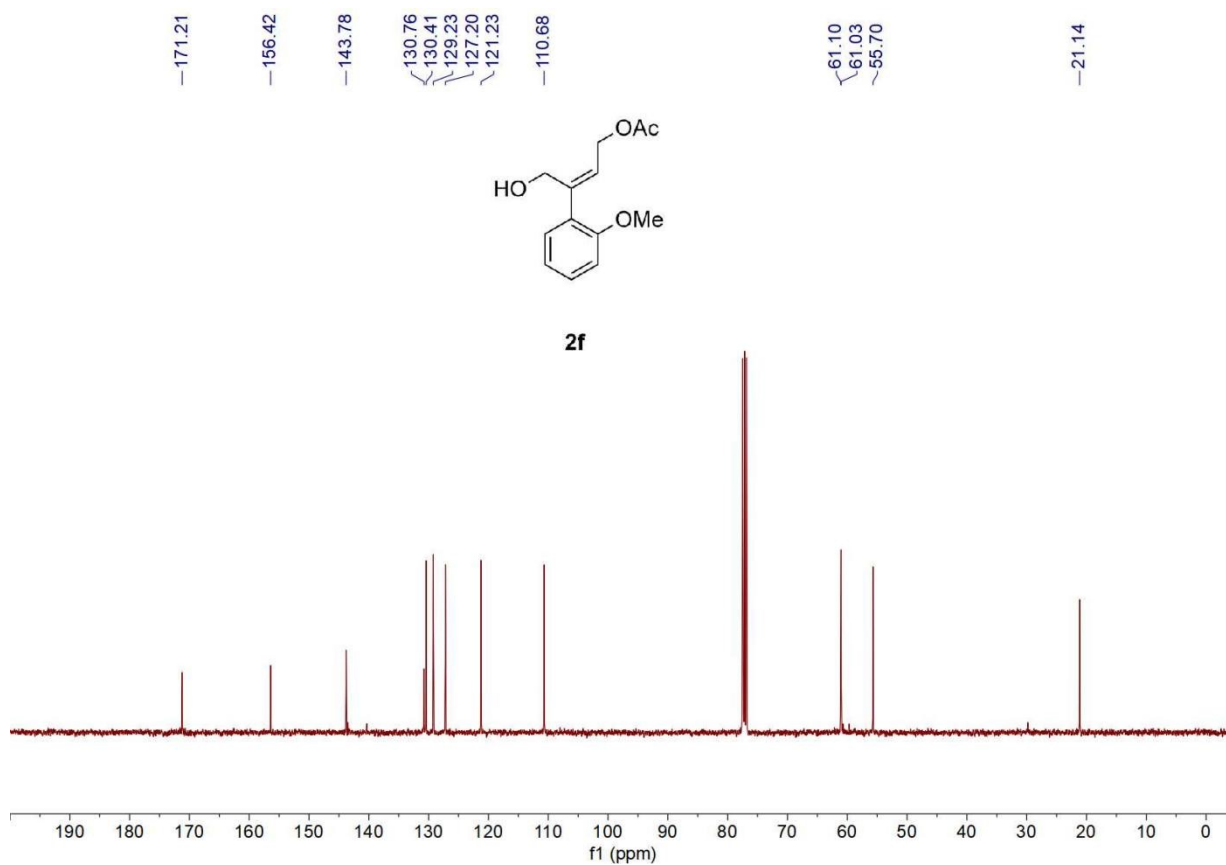
$^{13}\text{C}\{^1\text{H}\}$ NMR (151 MHz, CDCl_3) for **2e**



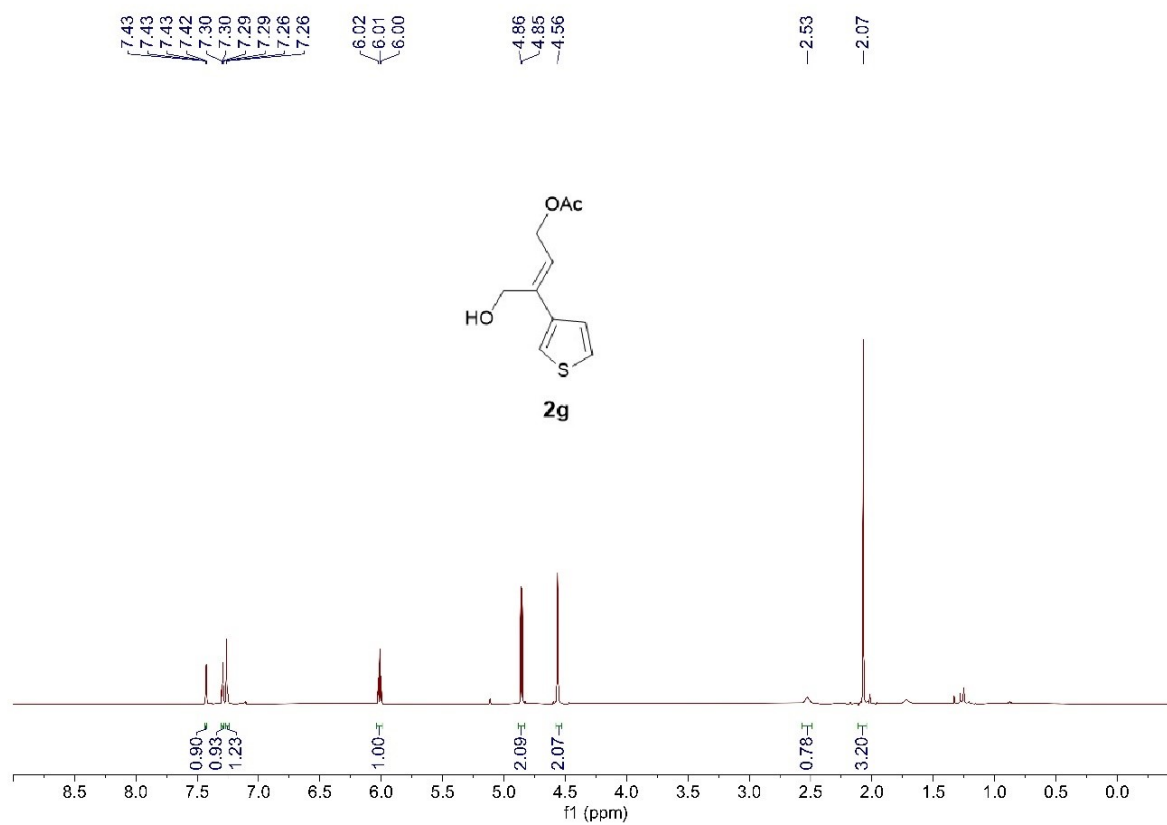
^1H NMR (600 MHz, CDCl_3) for **2f**



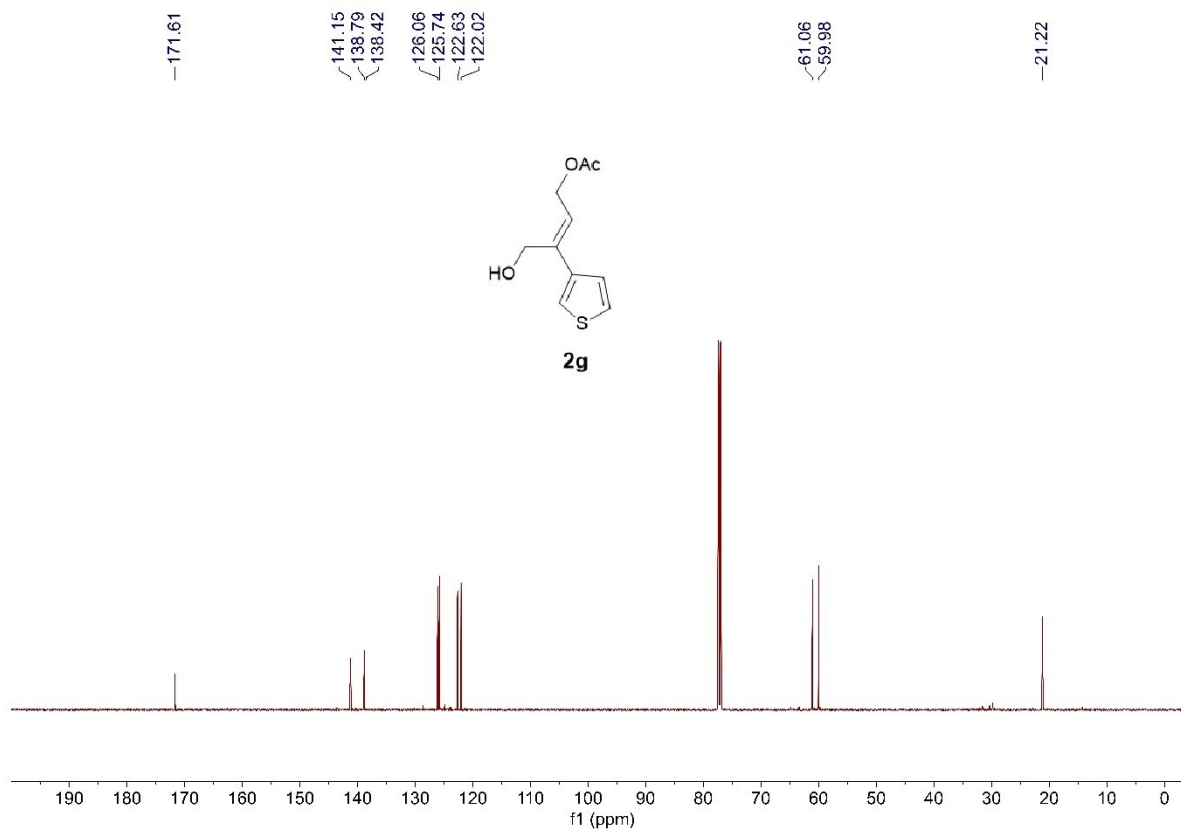
$^{13}\text{C}\{^1\text{H}\}$ NMR (151 MHz, CDCl_3) for **2f**



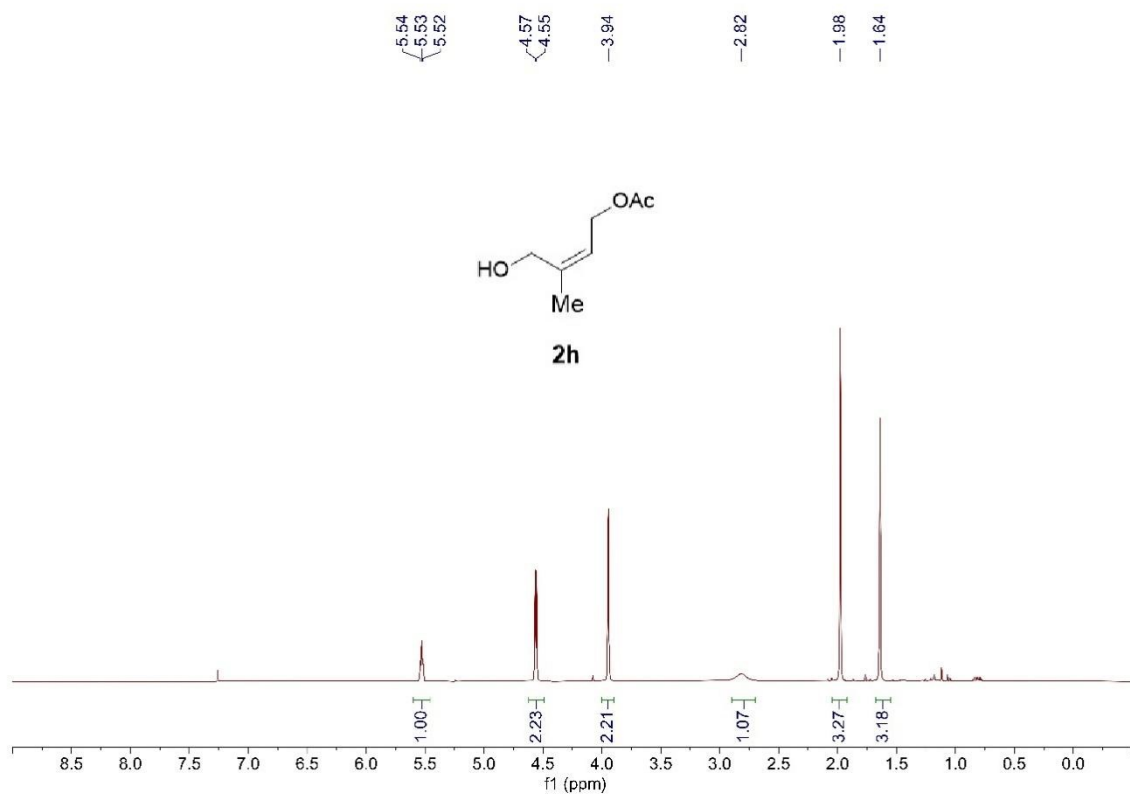
^1H NMR (600 MHz, CDCl_3) for **2g**



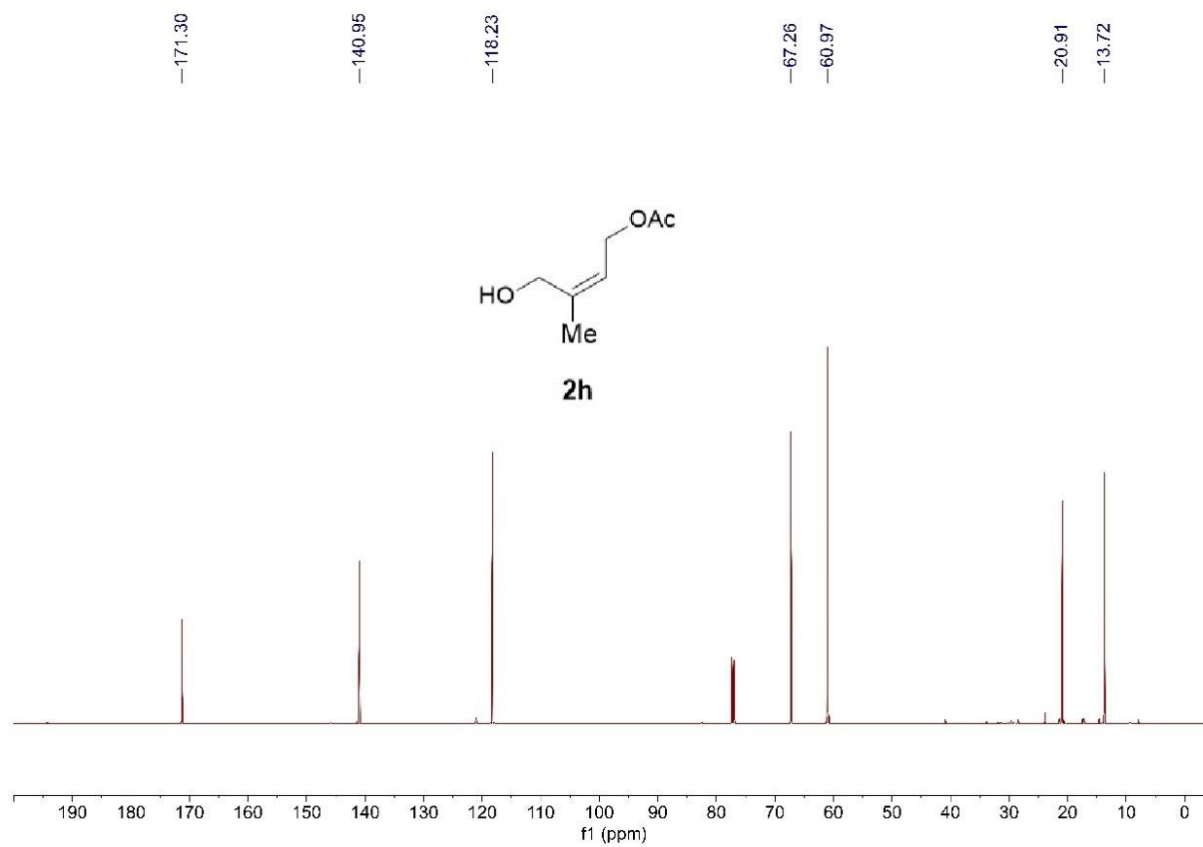
$^{13}\text{C}\{^1\text{H}\}$ NMR (151 MHz, CDCl_3) for **2g**



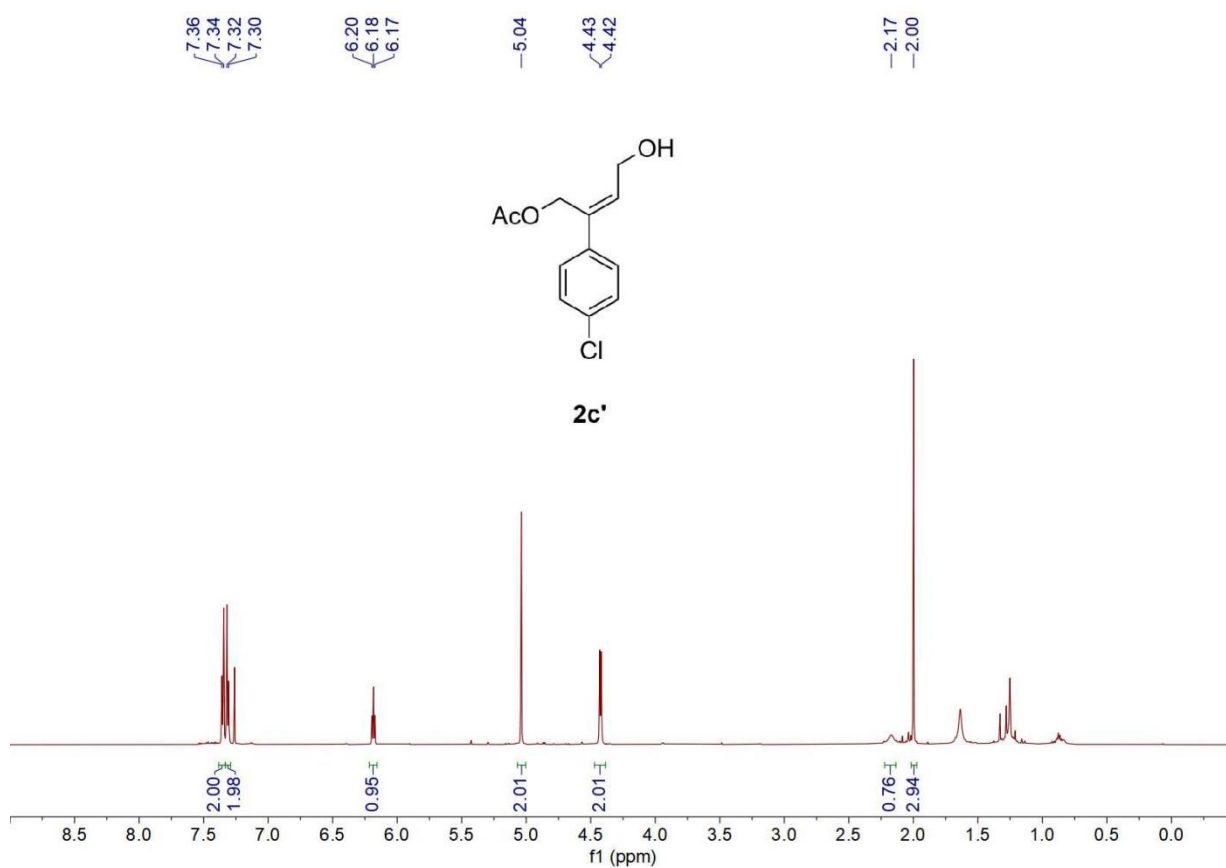
^1H NMR (600 MHz, CDCl_3) for **2h**



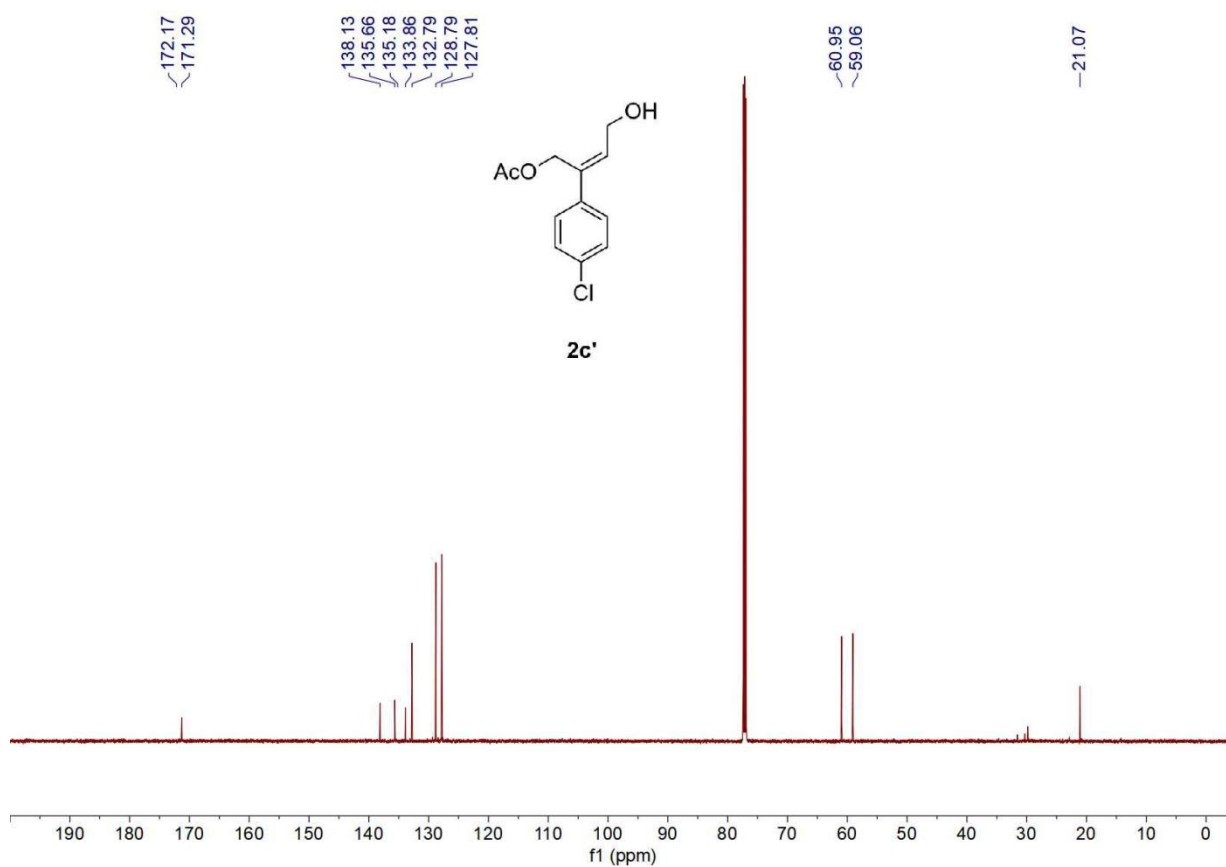
$^{13}\text{C}\{^1\text{H}\}$ NMR (151 MHz, CDCl_3) for **2h**



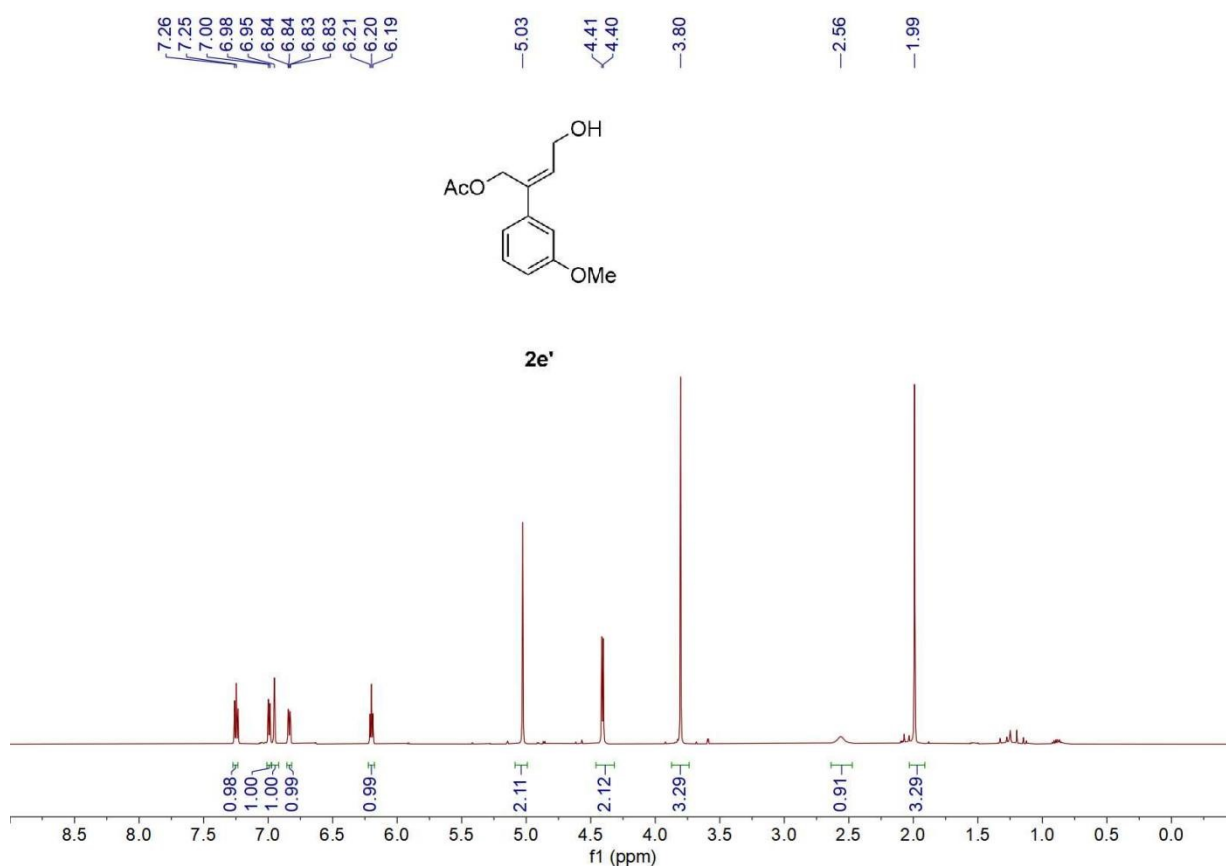
^1H NMR (600 MHz, CDCl_3) for **2c'**



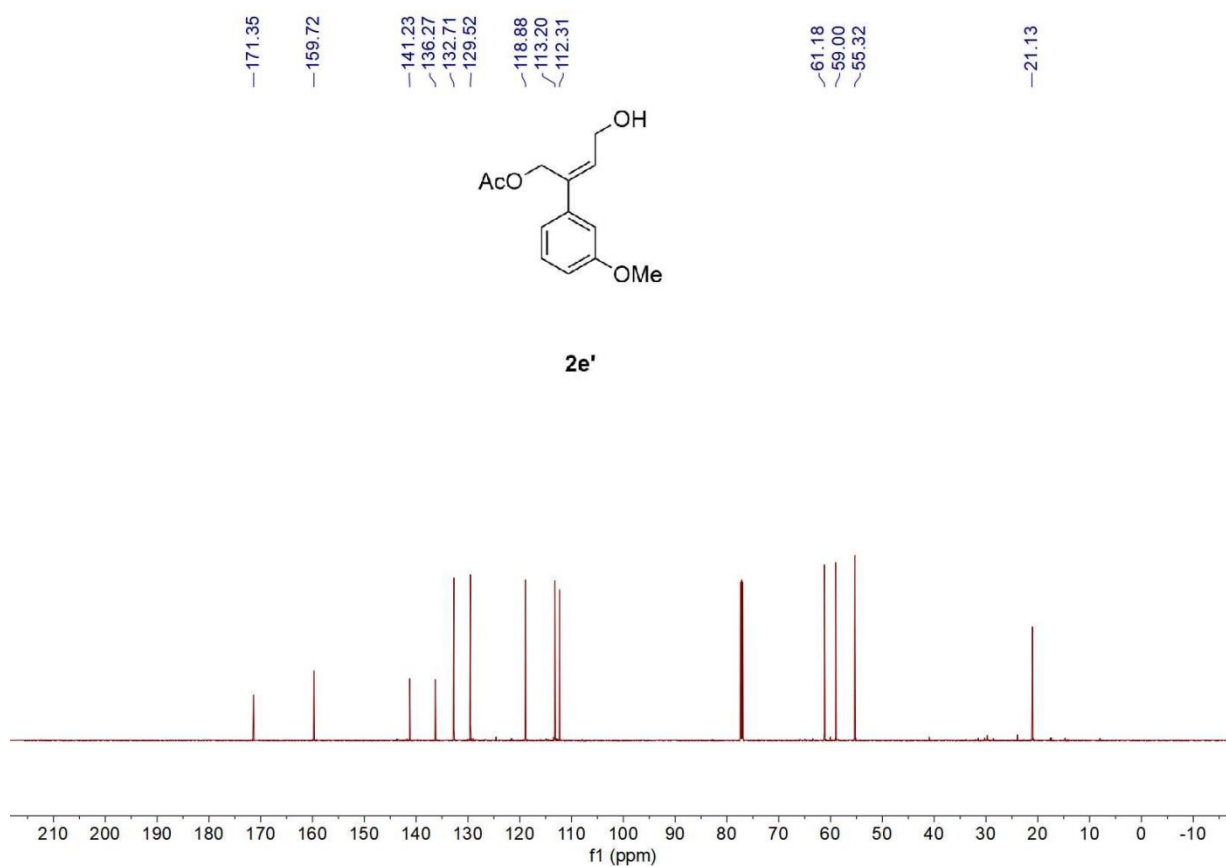
$^{13}\text{C}\{^1\text{H}\}$ NMR (151 MHz, CDCl_3) for **2c'**



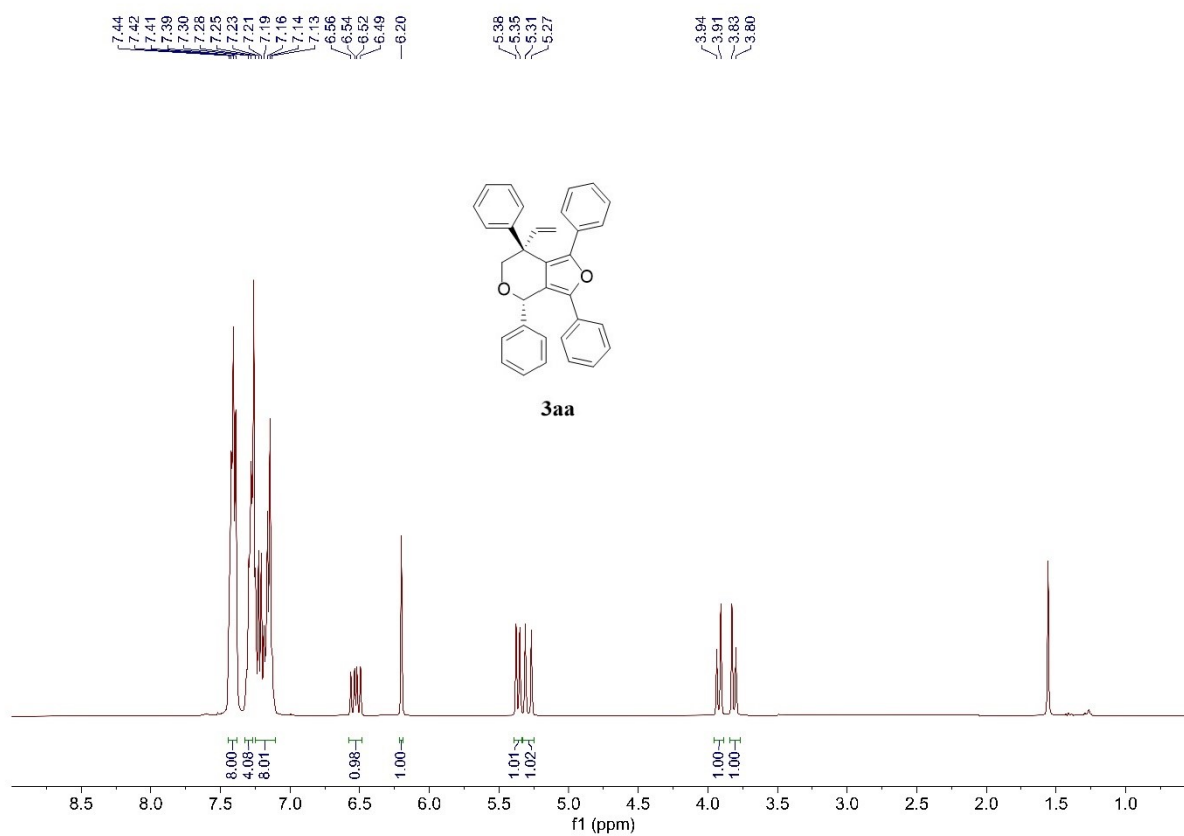
^1H NMR (600 MHz, CDCl_3) for **2e'**



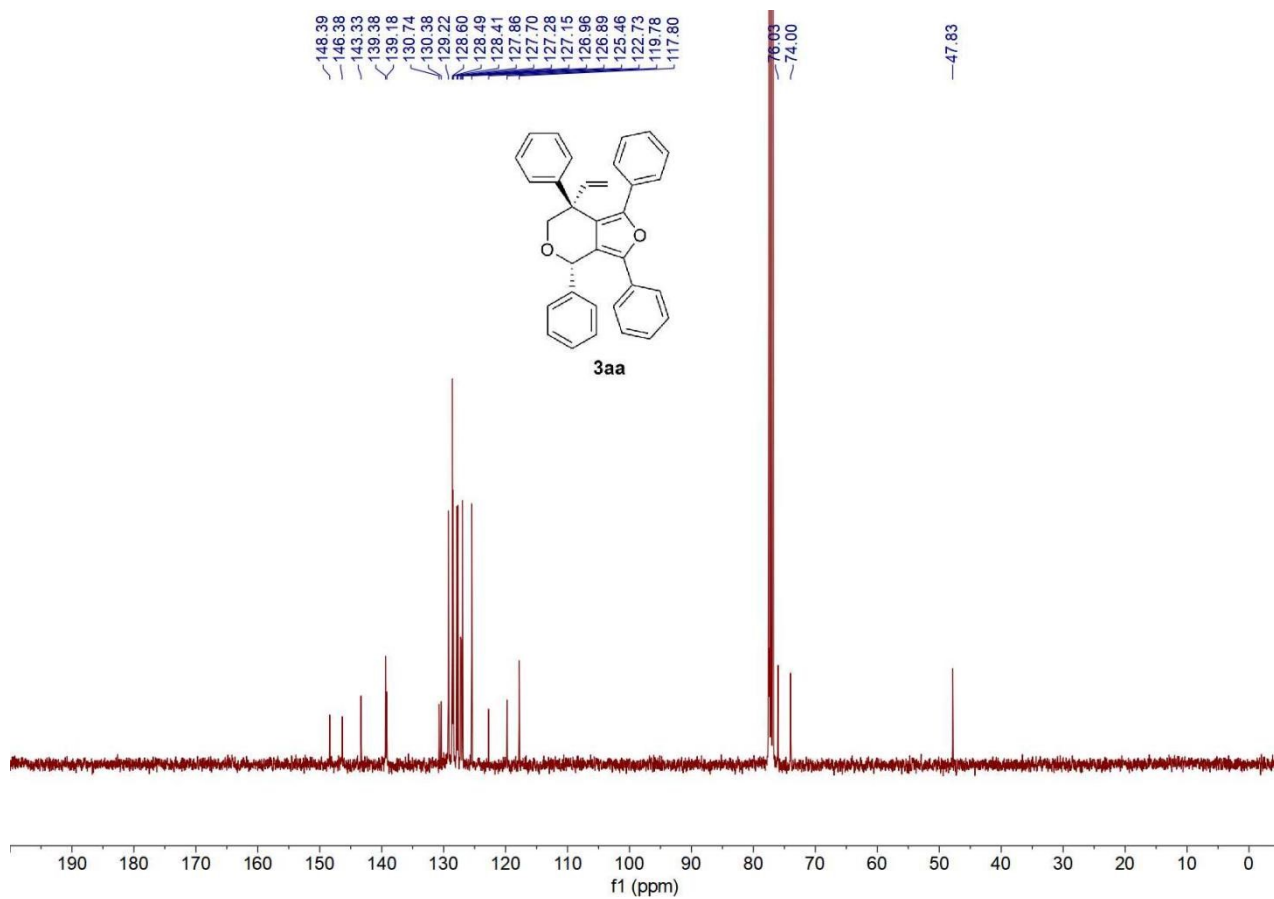
$^{13}\text{C}\{^1\text{H}\}$ NMR (151 MHz, CDCl_3) for **2e'**



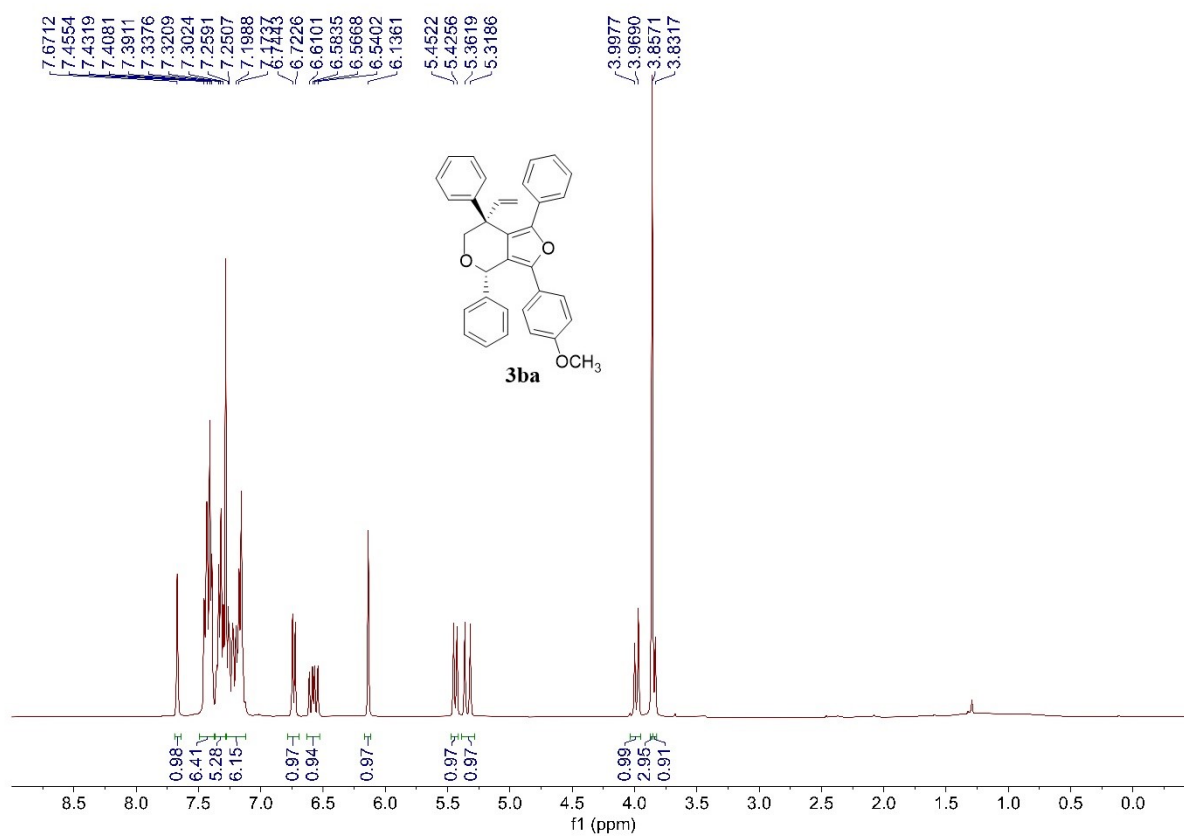
^1H NMR (400 MHz, CDCl_3) for **3aa**



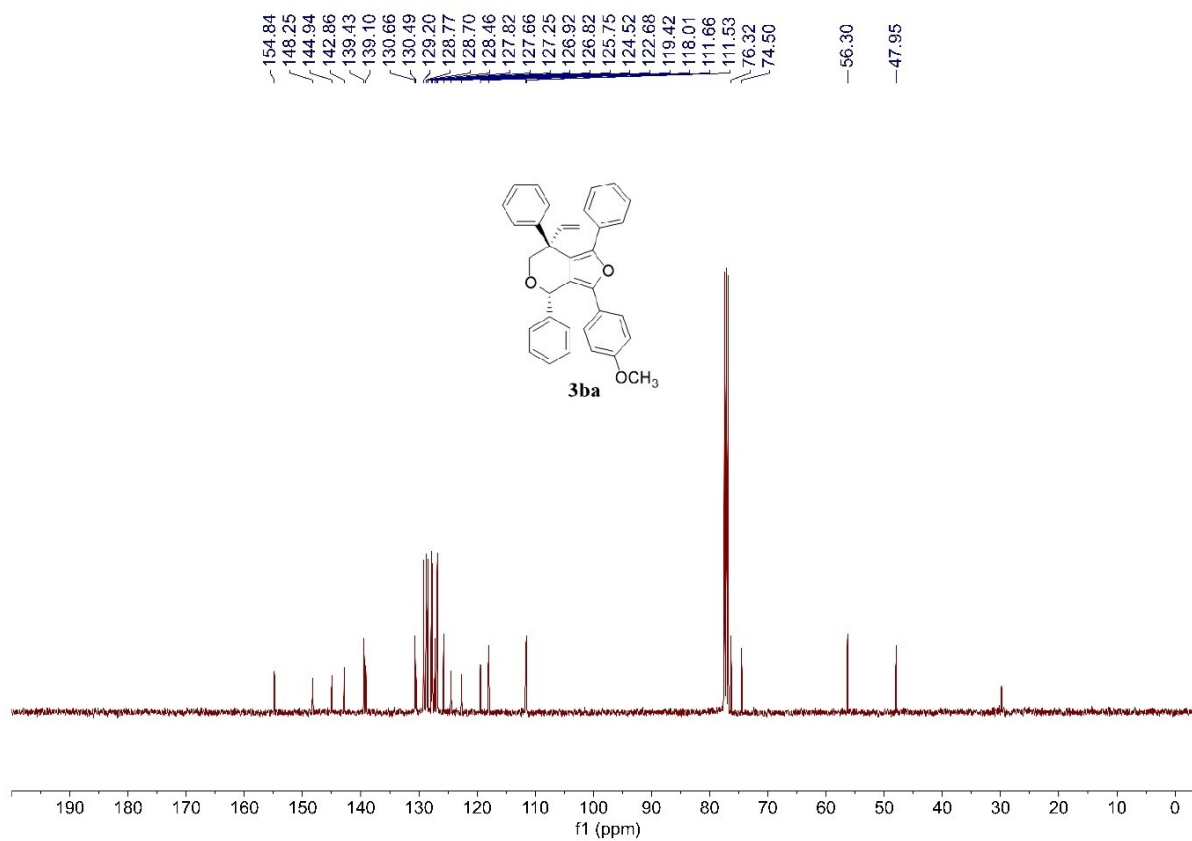
$^{13}\text{C}\{^1\text{H}\}$ NMR (101 MHz, CDCl_3) for **3aa**



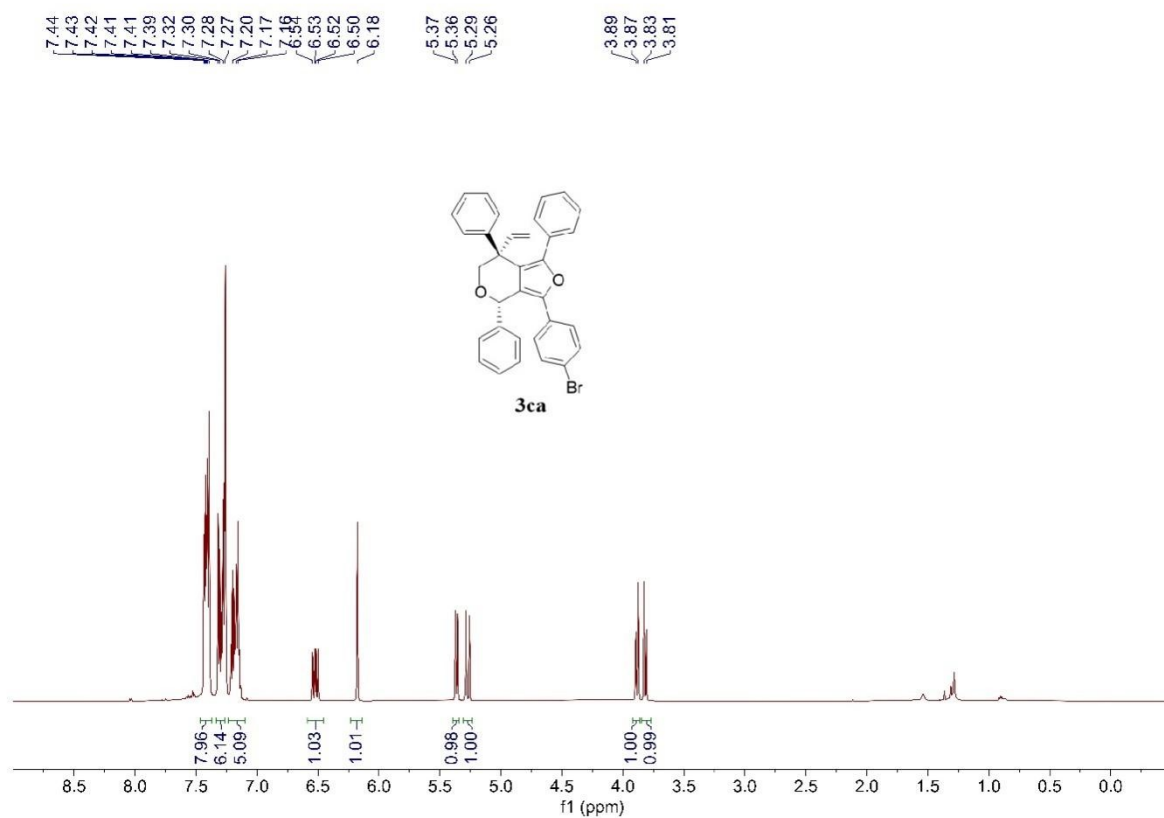
^1H NMR (400 MHz, CDCl_3) for **3ba**



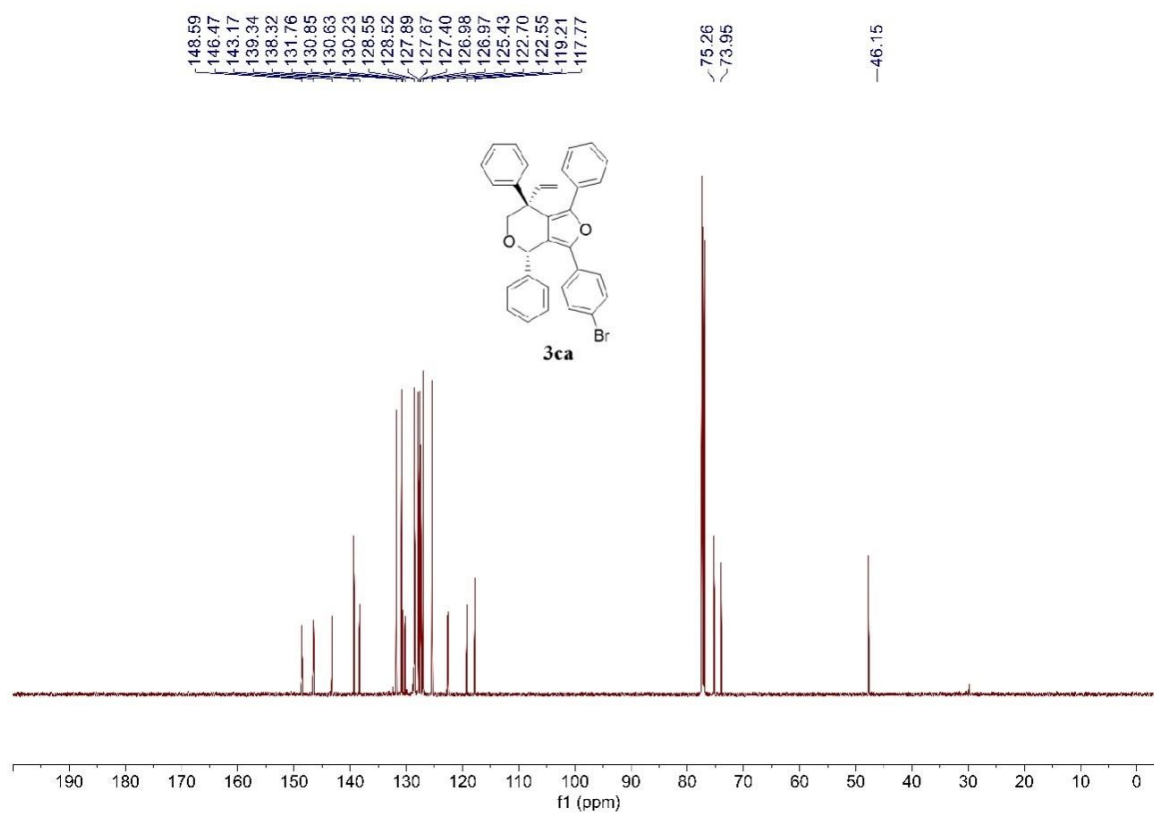
$^{13}\text{C}\{^1\text{H}\}$ NMR (101 MHz, CDCl_3) for **3ba**



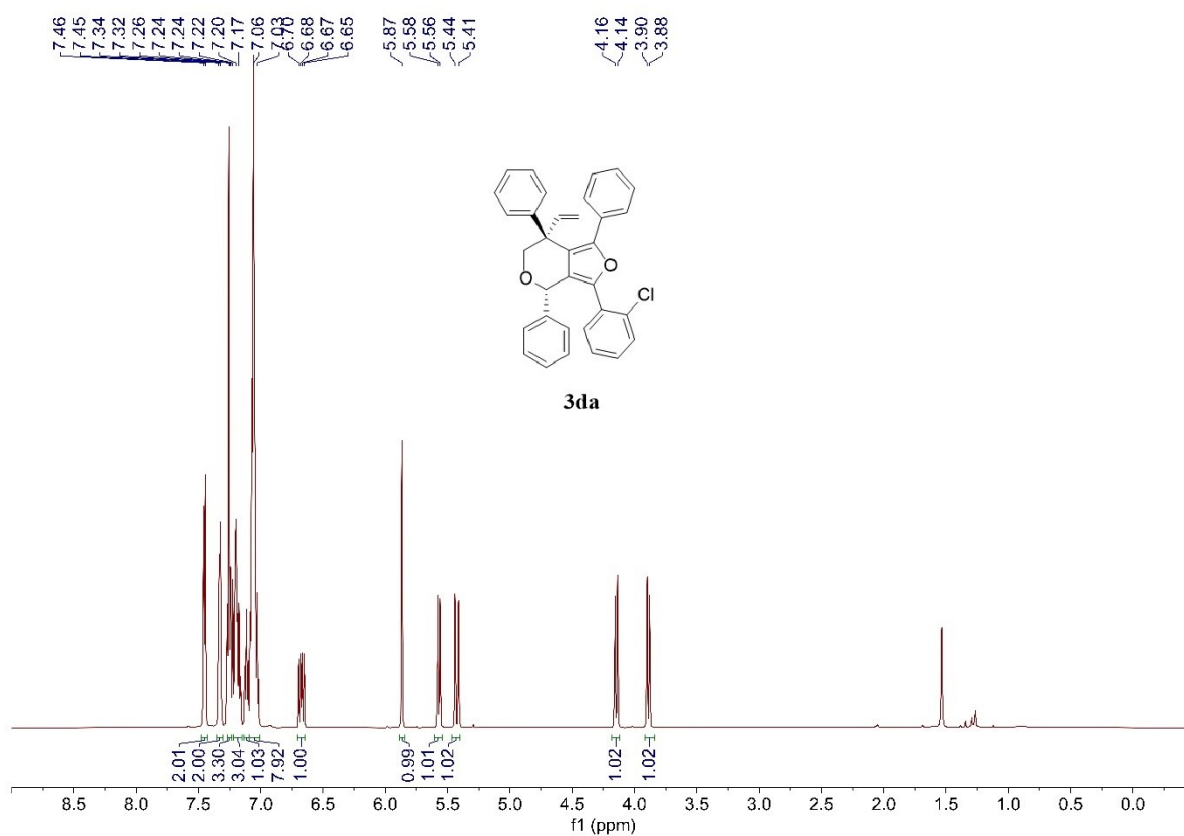
^1H NMR (600 MHz, CDCl_3) for **3ca**



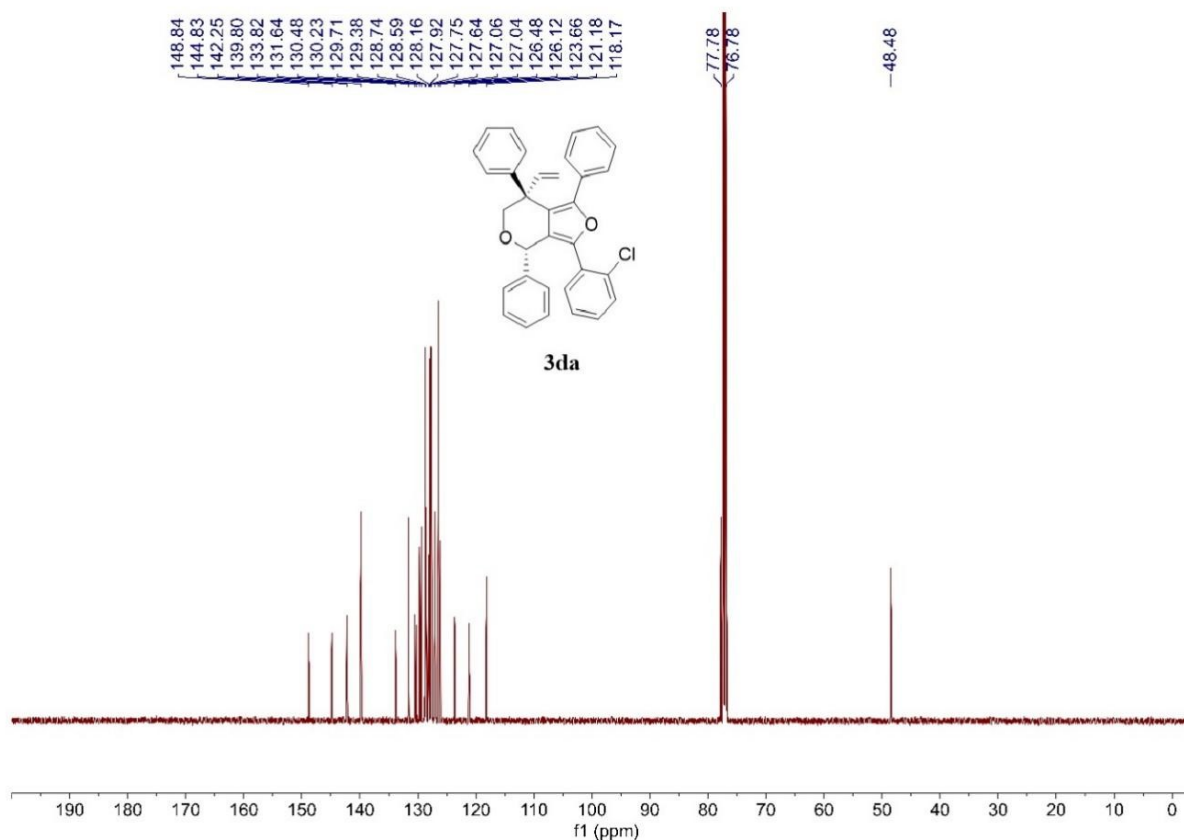
$^{13}\text{C}\{^1\text{H}\}$ NMR (151 MHz, CDCl_3) for **3ca**



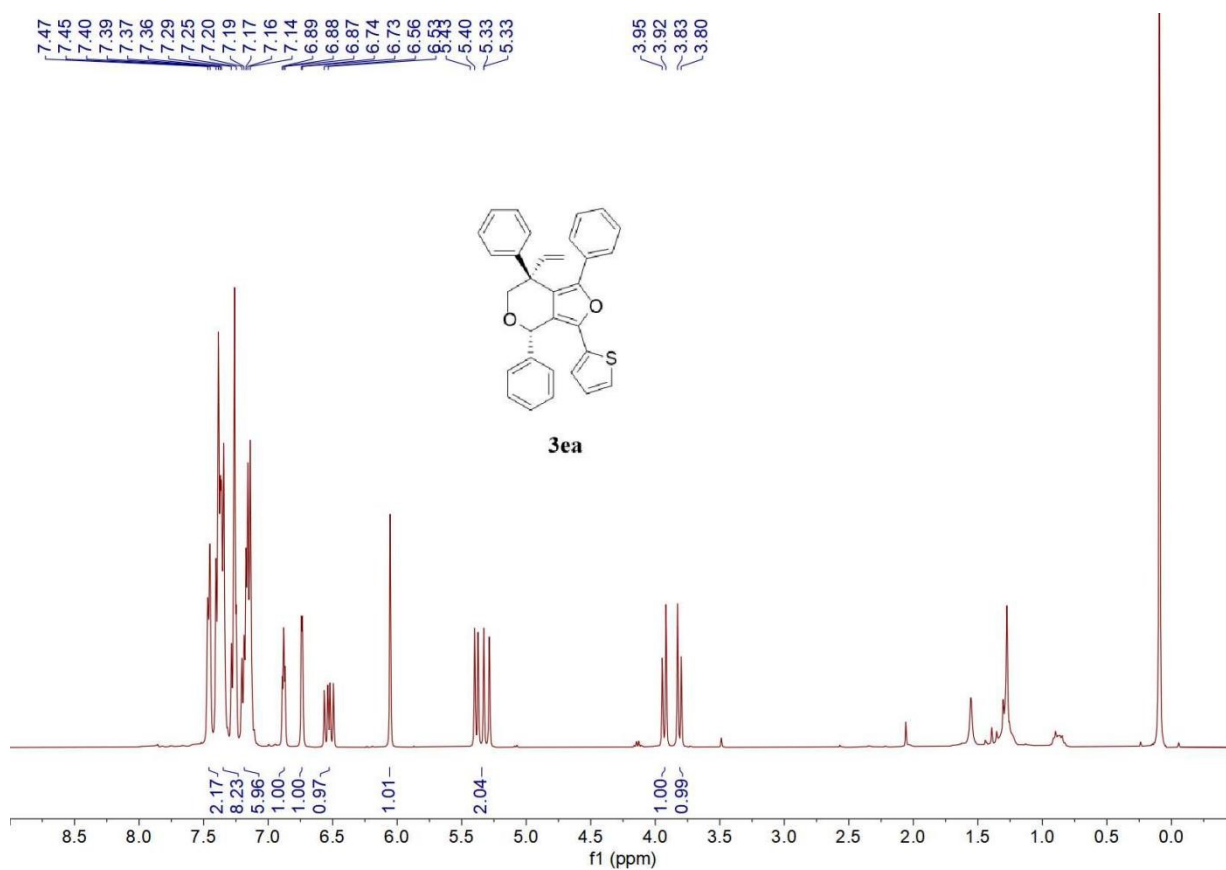
^1H NMR (600 MHz, CDCl_3) for **3da**



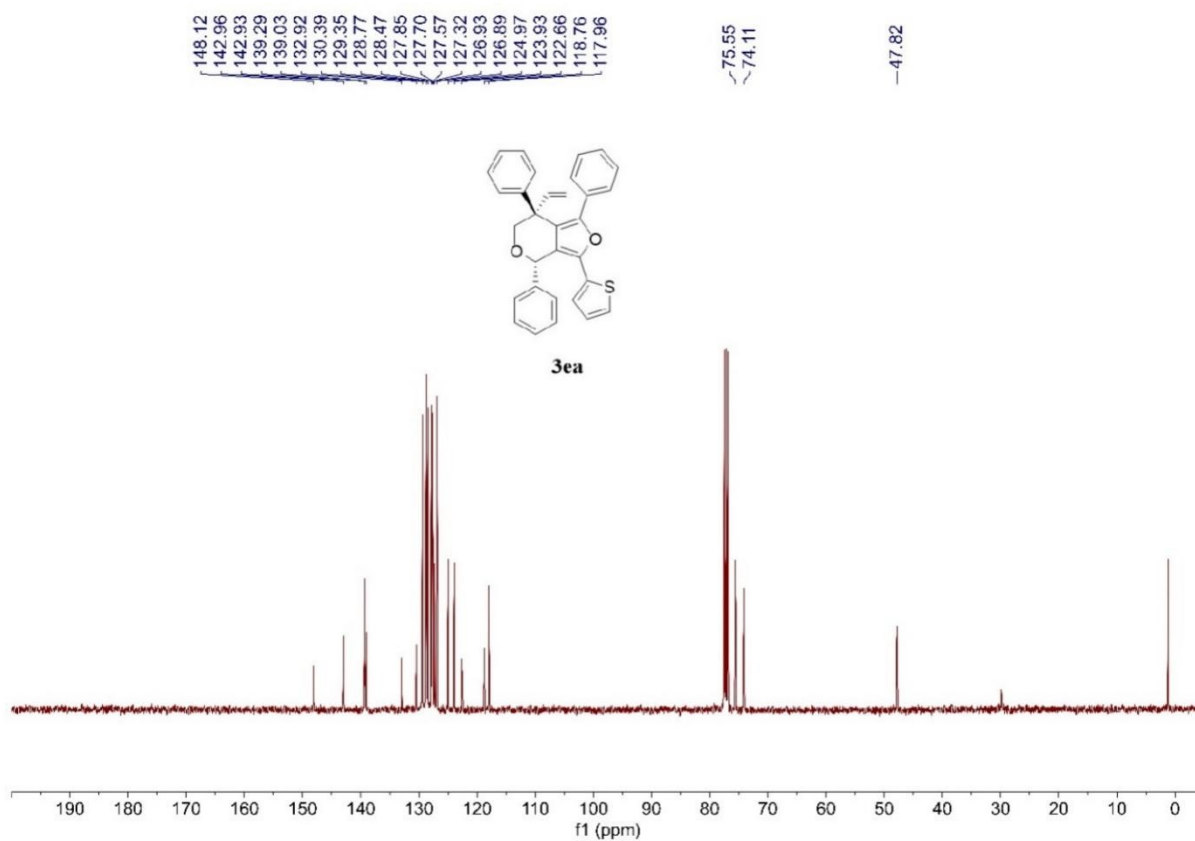
$^{13}\text{C}\{^1\text{H}\}$ NMR (151 MHz, CDCl_3) for **3da**



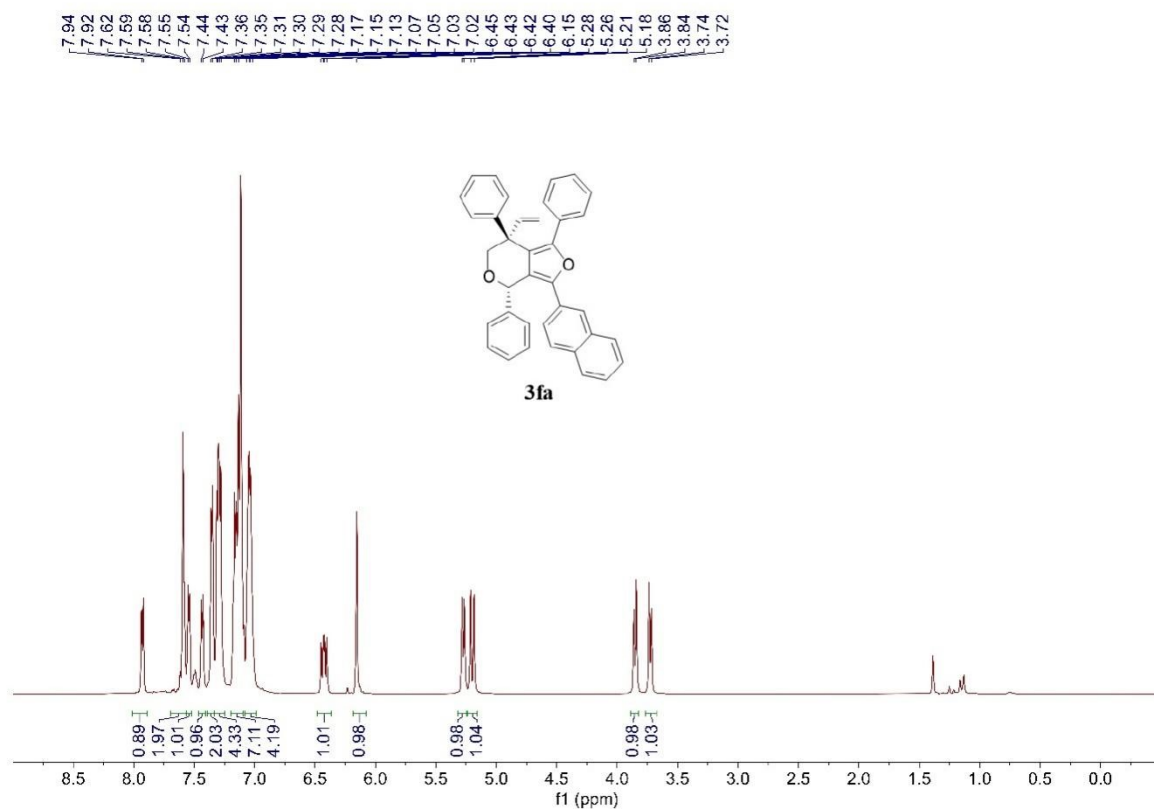
^1H NMR (600 MHz, CDCl_3) for **3ea**



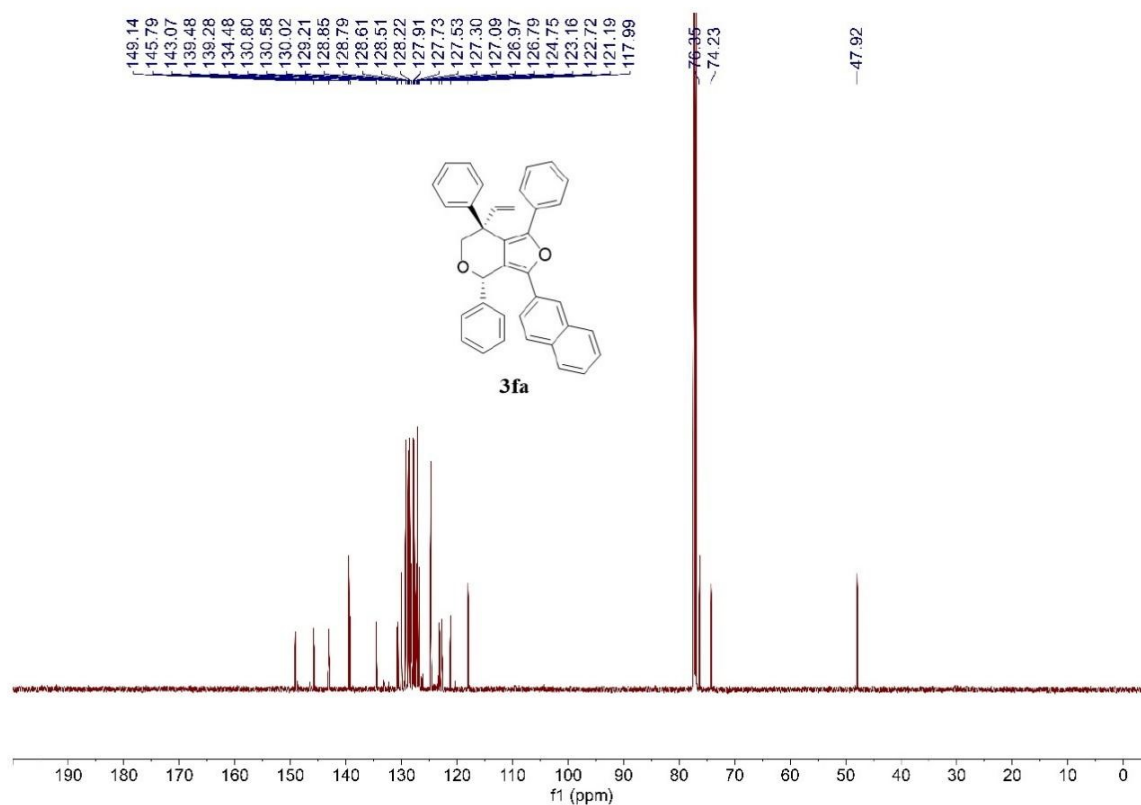
$^{13}\text{C}\{^1\text{H}\}$ NMR (151 MHz, CDCl_3) for **3ea**



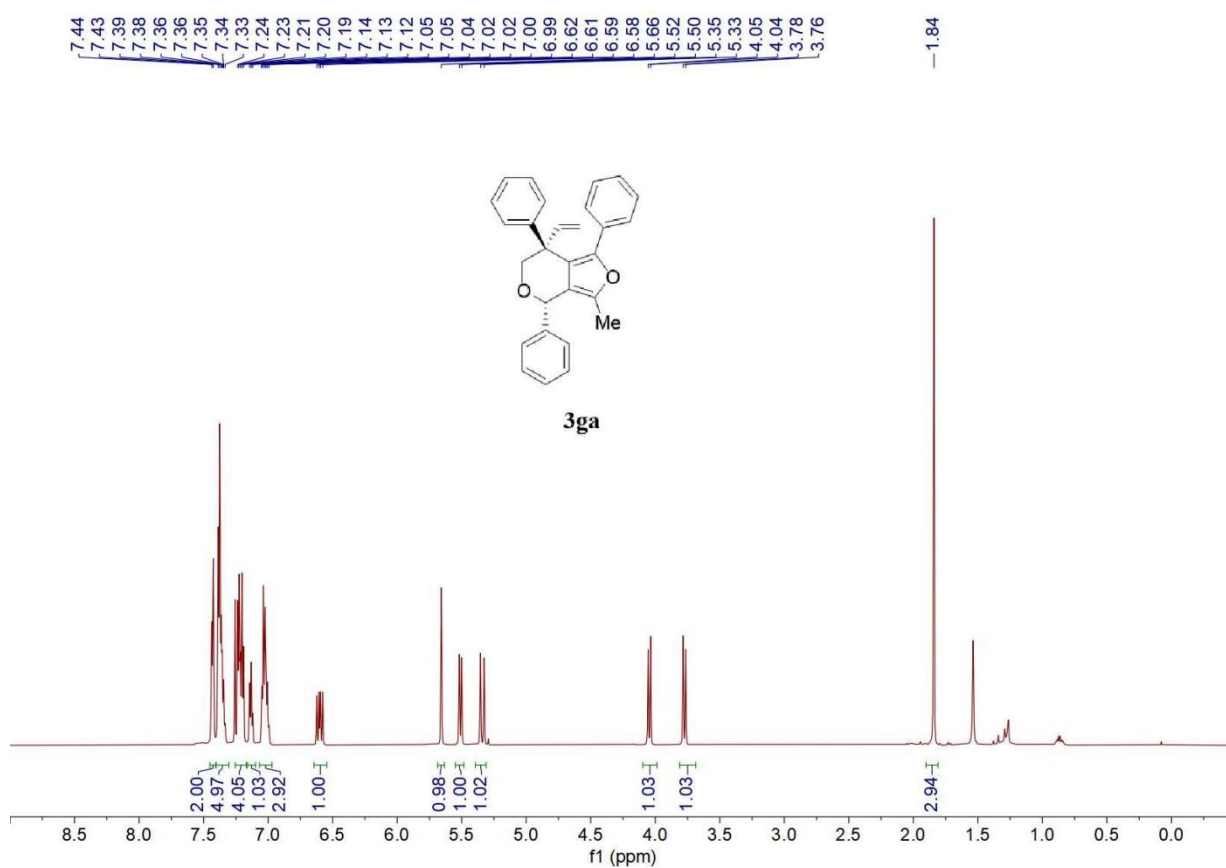
^1H NMR (600 MHz, CDCl_3) for **3fa**



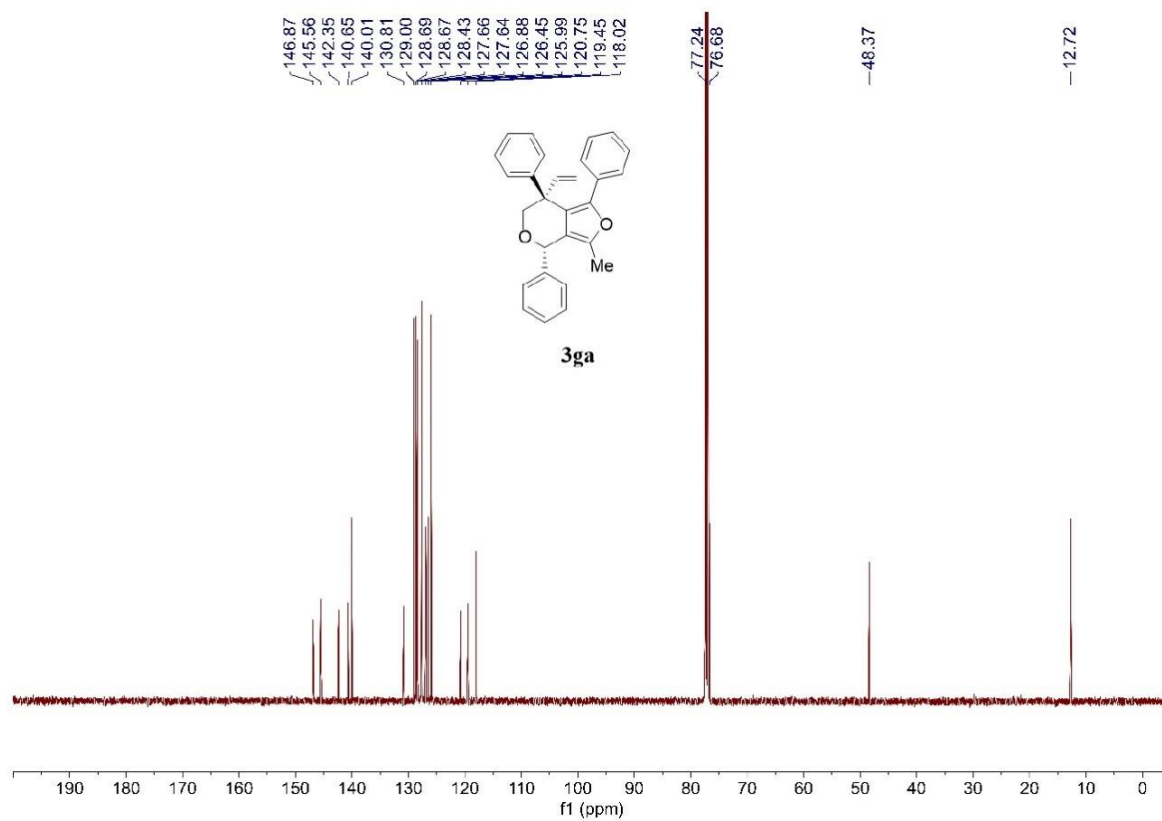
$^{13}\text{C}\{^1\text{H}\}$ NMR (151 MHz, CDCl_3) for **3fa**



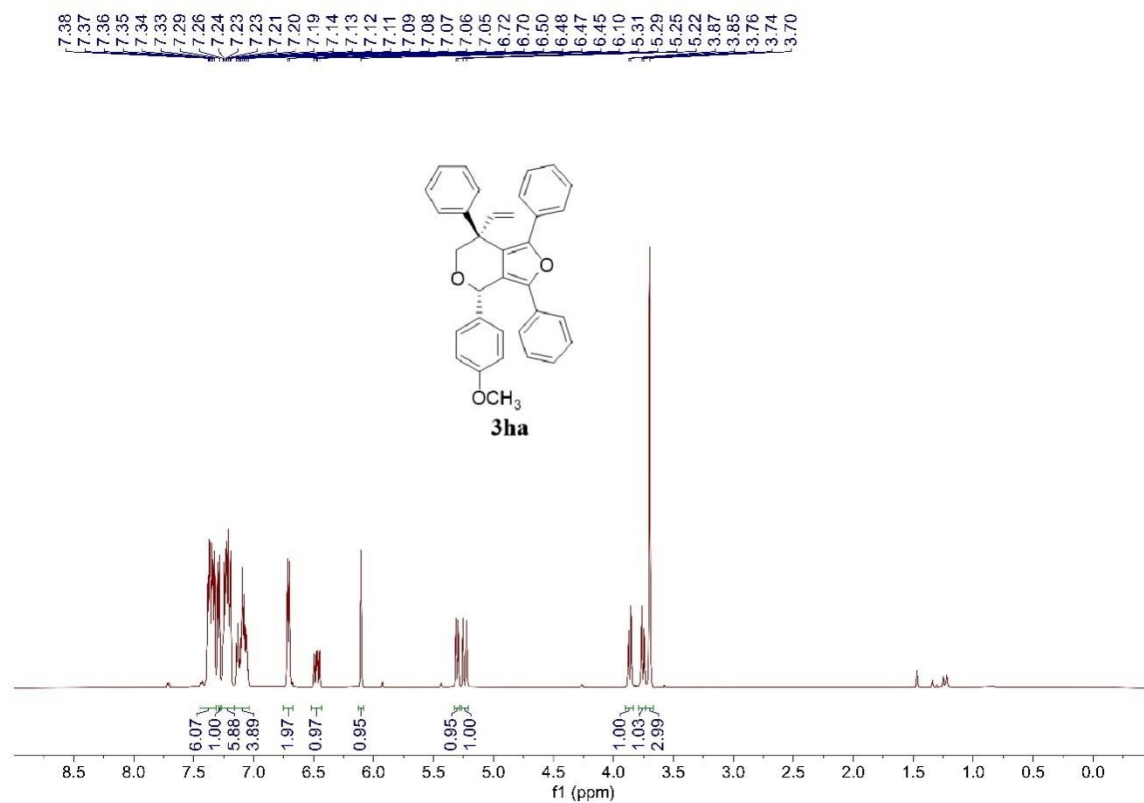
^1H NMR (600 MHz, CDCl_3) for **3ga**



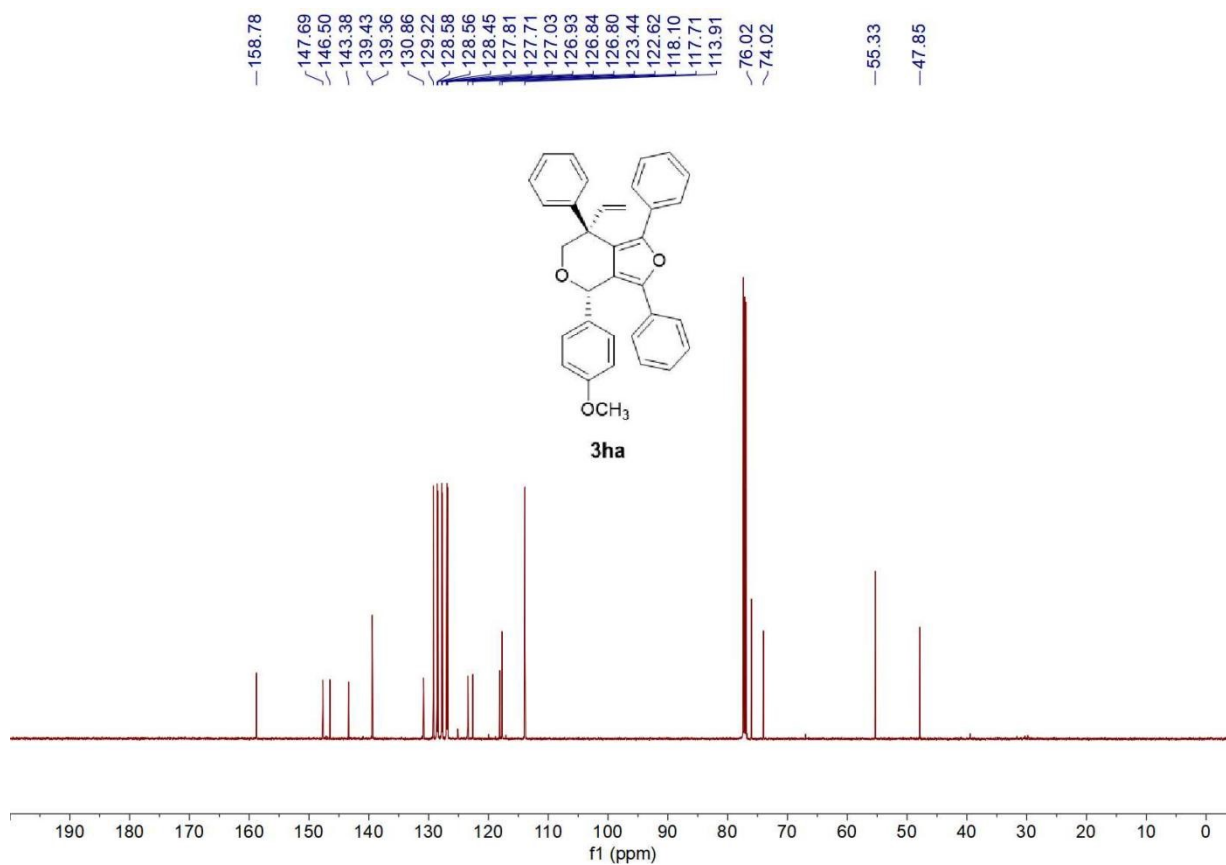
$^{13}\text{C}\{^1\text{H}\}$ NMR (151 MHz, CDCl_3) for **3ga**



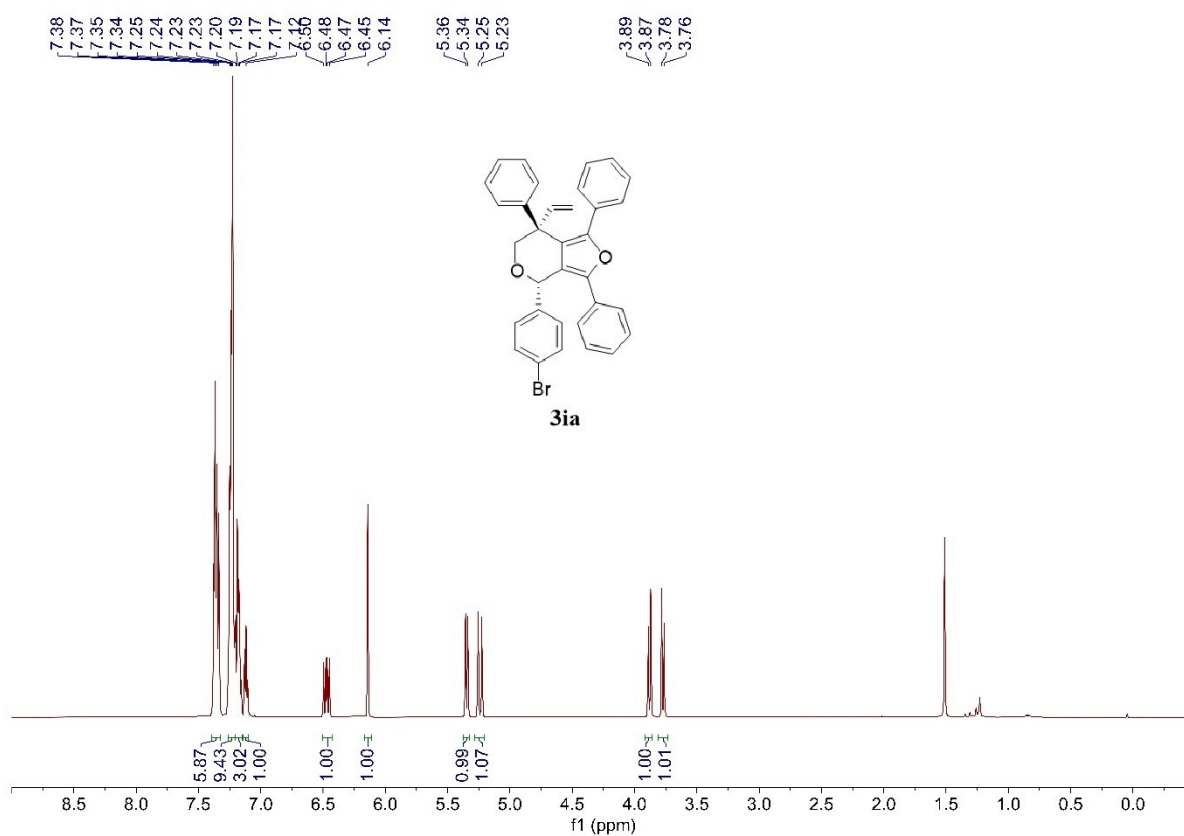
^1H NMR (600 MHz, CDCl_3) for **3ha**



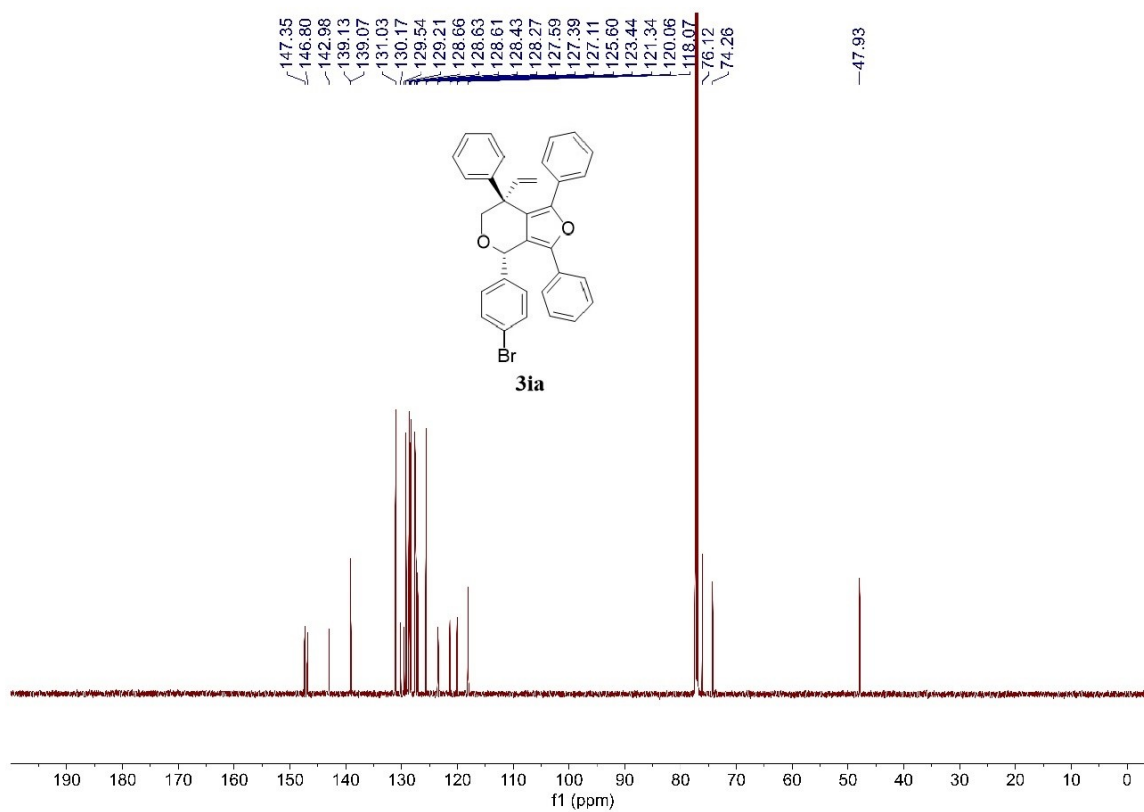
^{13}C $\{^1\text{H}\}$ NMR (151 MHz, CDCl_3) for **3ha**



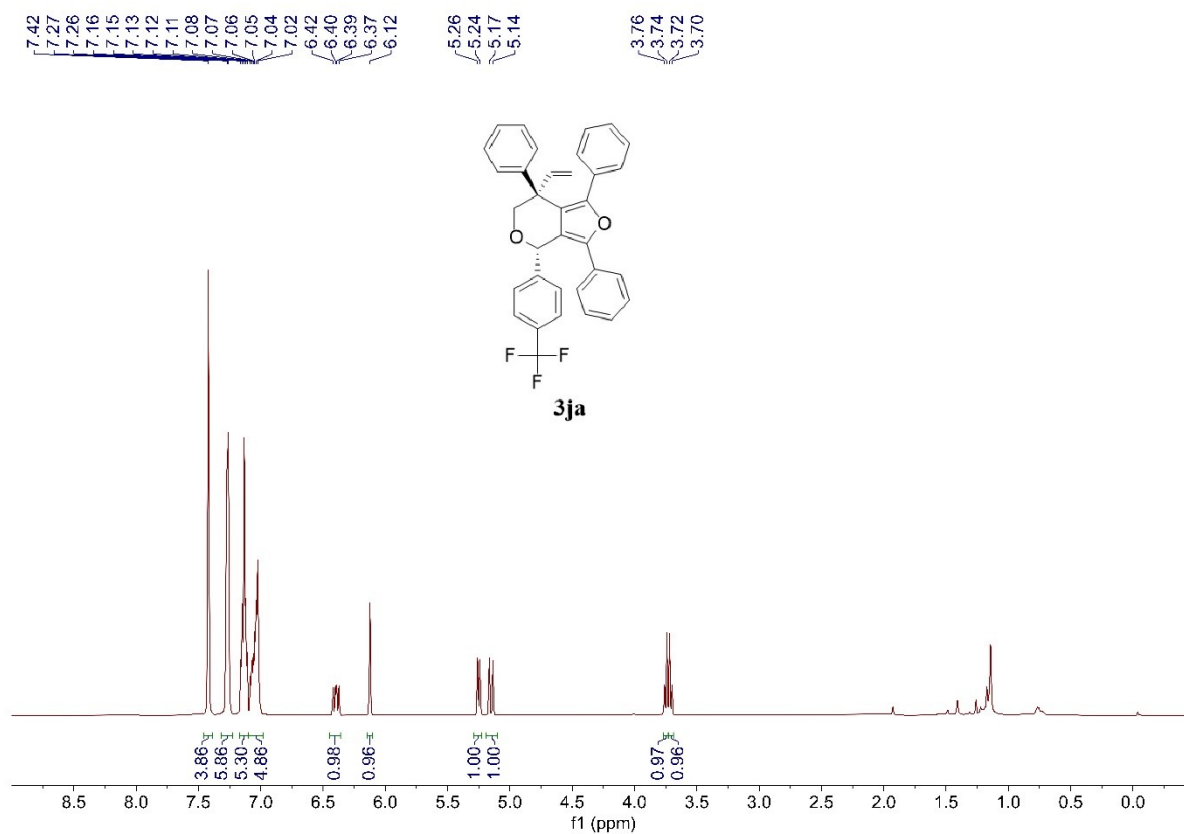
^1H NMR (600 MHz, CDCl_3) for **3ia**



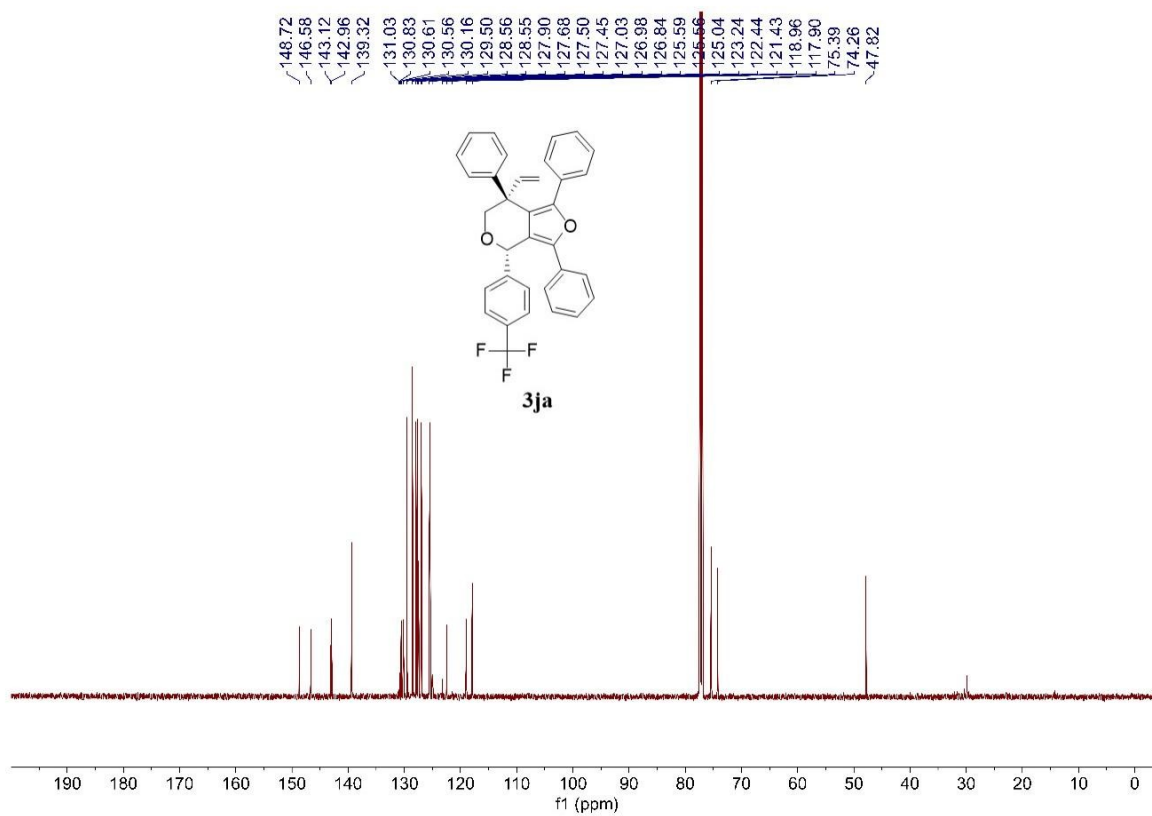
$^{13}\text{C}\{^1\text{H}\}$ NMR (151 MHz, CDCl_3) for **3ia**



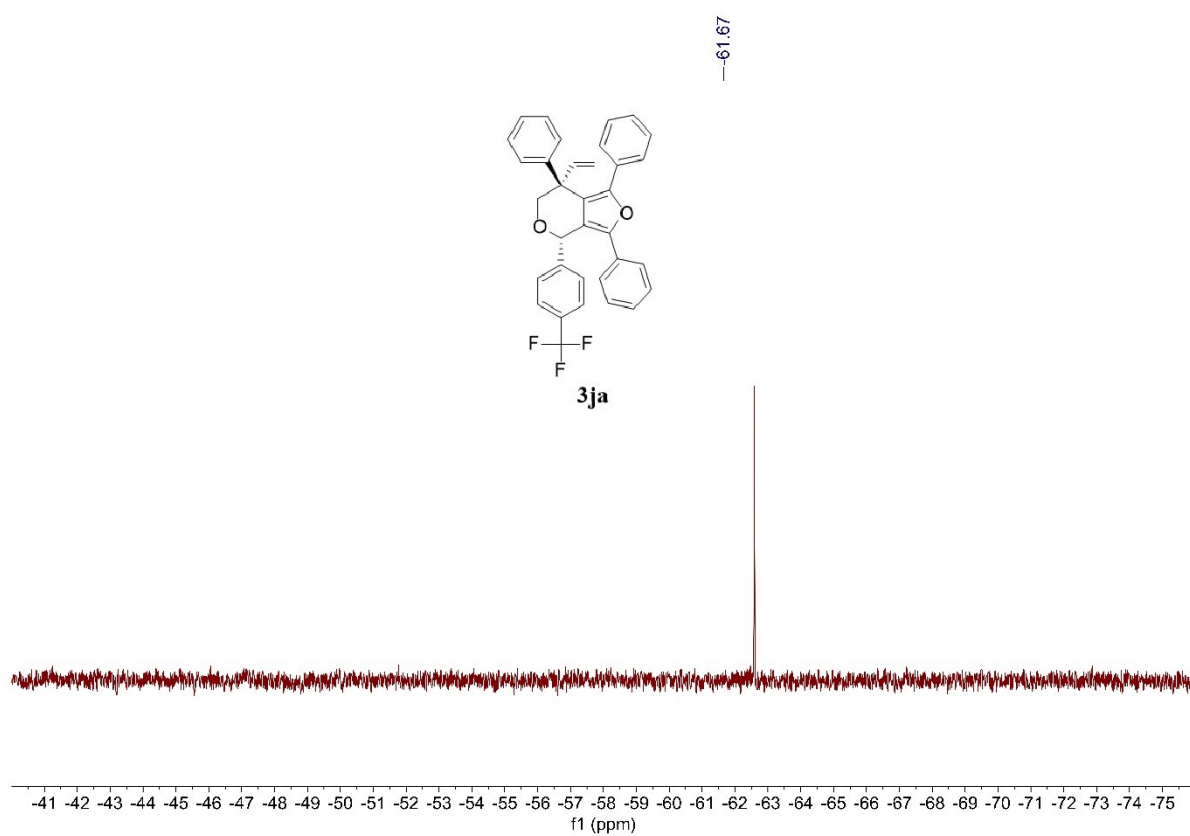
^1H NMR (600 MHz, CDCl_3) for **3ja**



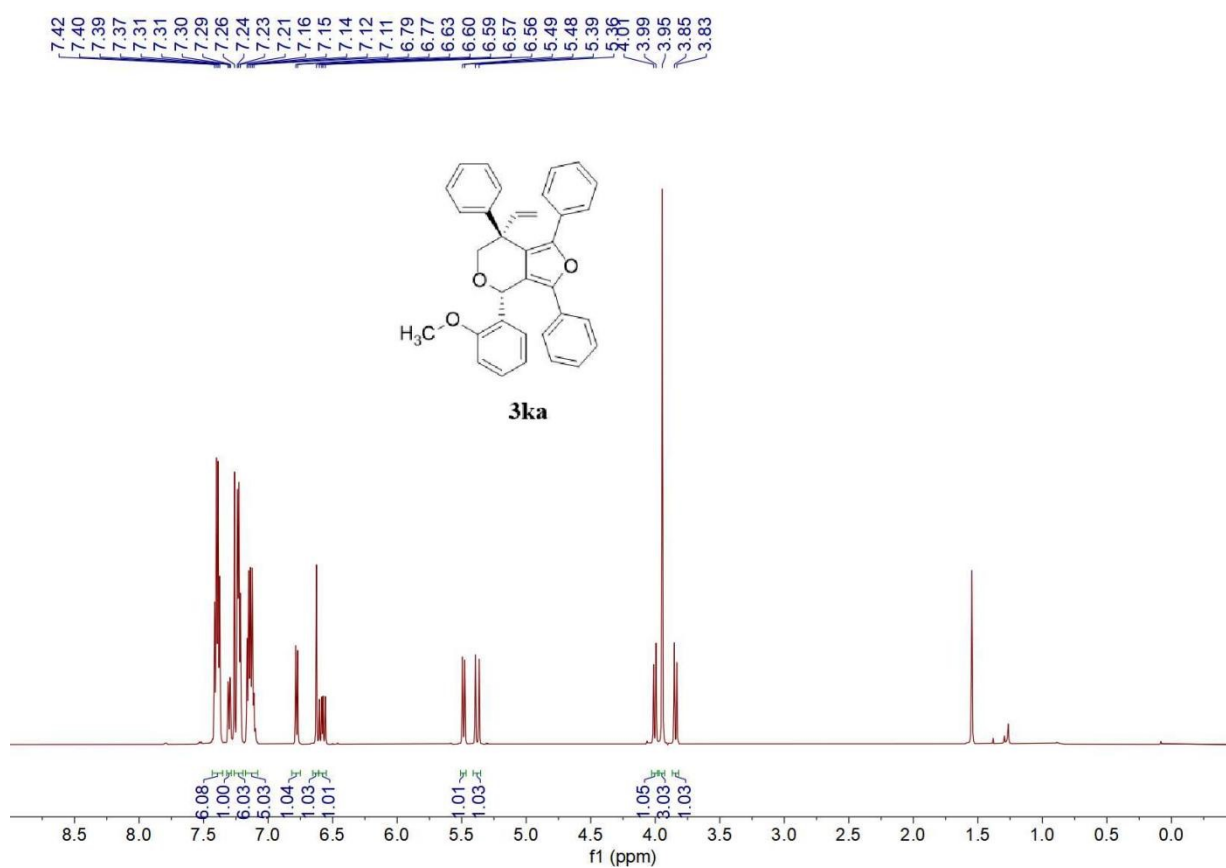
$^{13}\text{C}\{^1\text{H}\}$ NMR (151 MHz, CDCl_3) for **3ja**



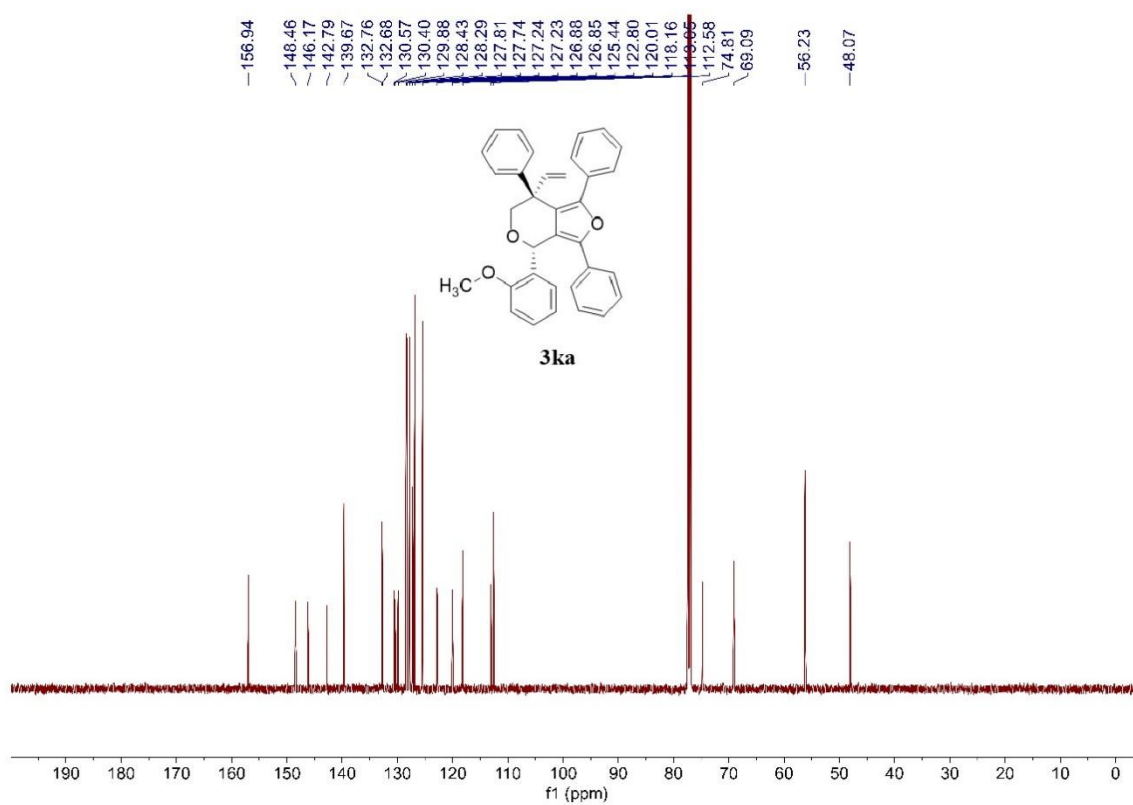
^{19}F NMR (376 MHz, CDCl_3) for **3ja**



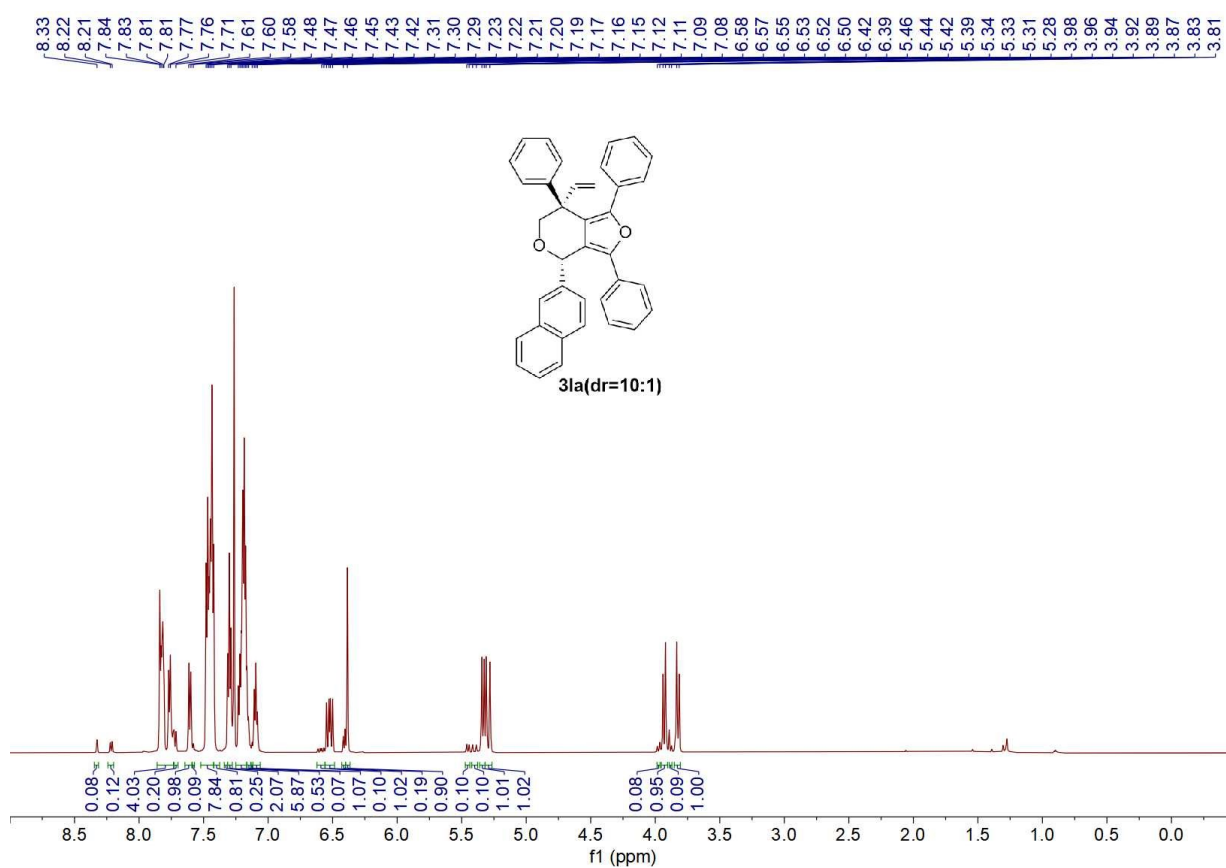
^1H NMR (600 MHz, CDCl_3) for **3ka**



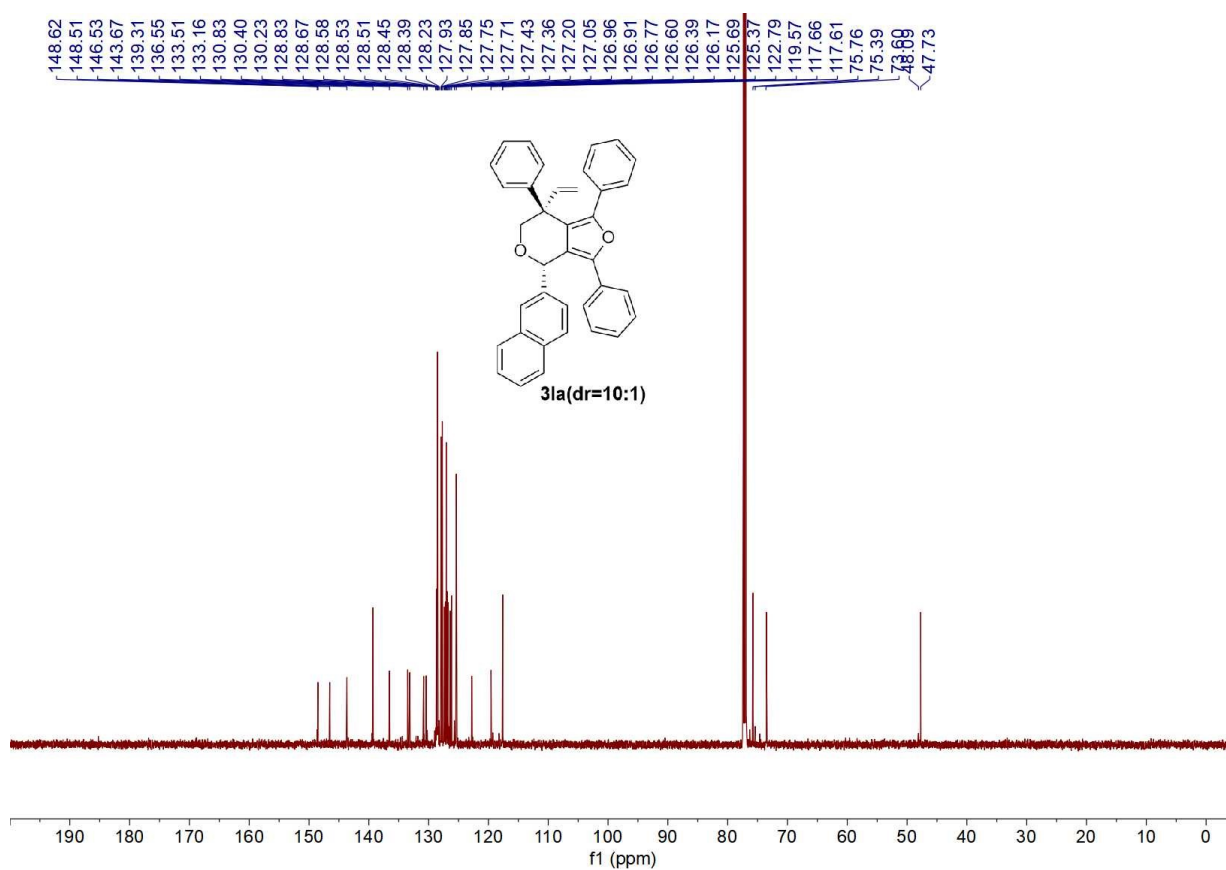
^{13}C $\{^1\text{H}\}$ NMR (151 MHz, CDCl_3) for **3ka**



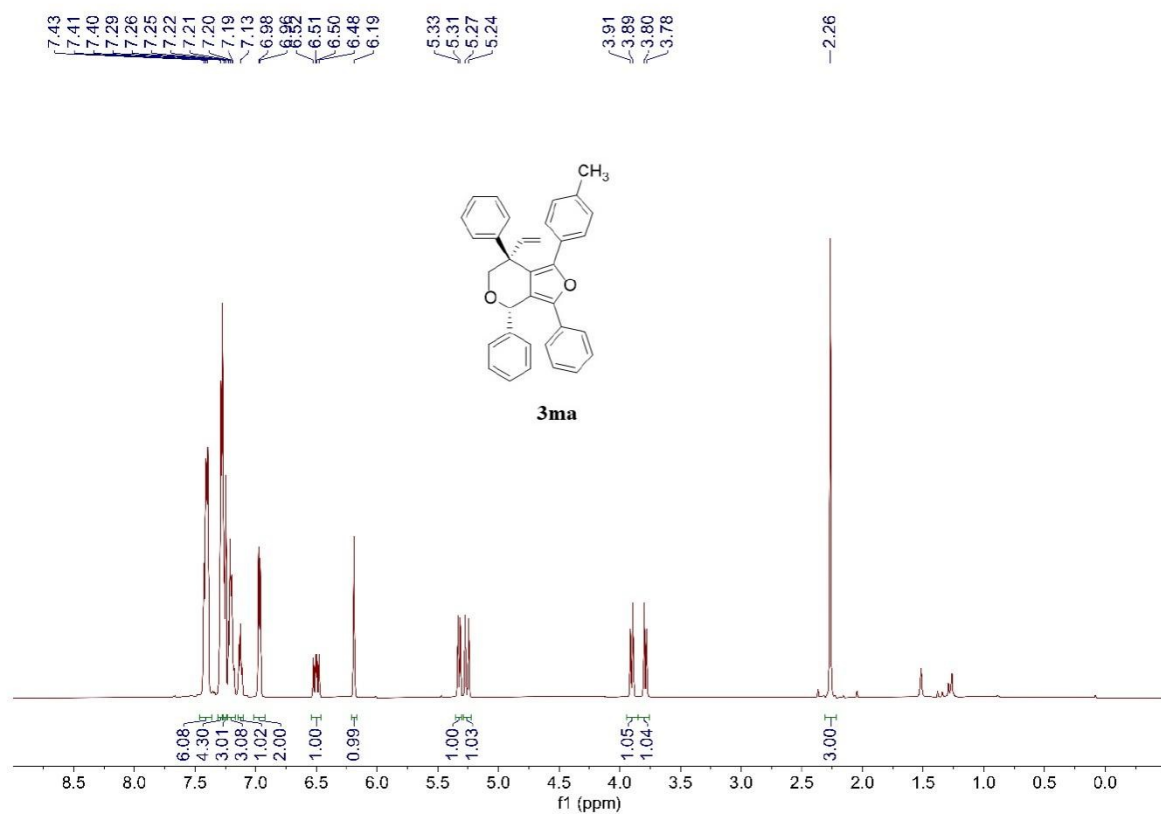
^1H NMR (600 MHz, CDCl_3) for **3la**



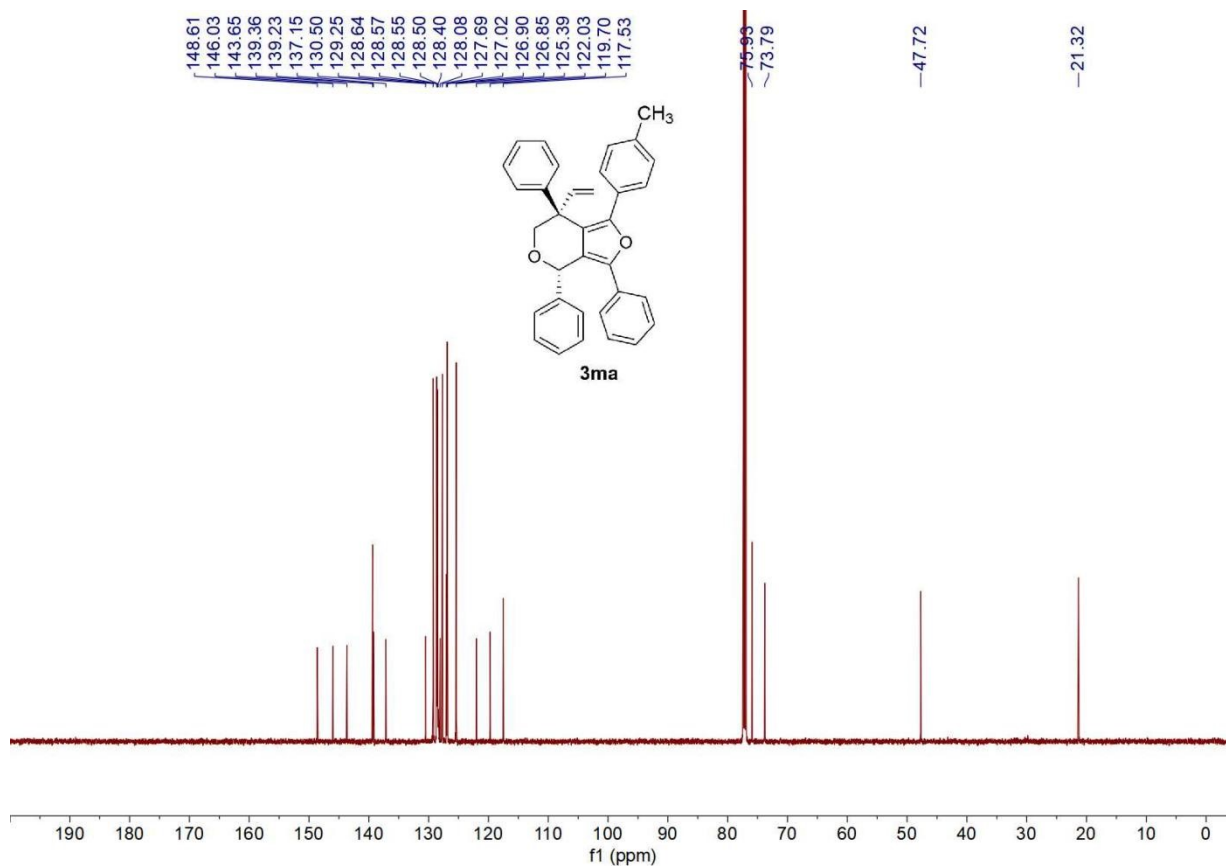
$^{13}\text{C}\{^1\text{H}\}$ NMR (151 MHz, CDCl_3) for **3la**



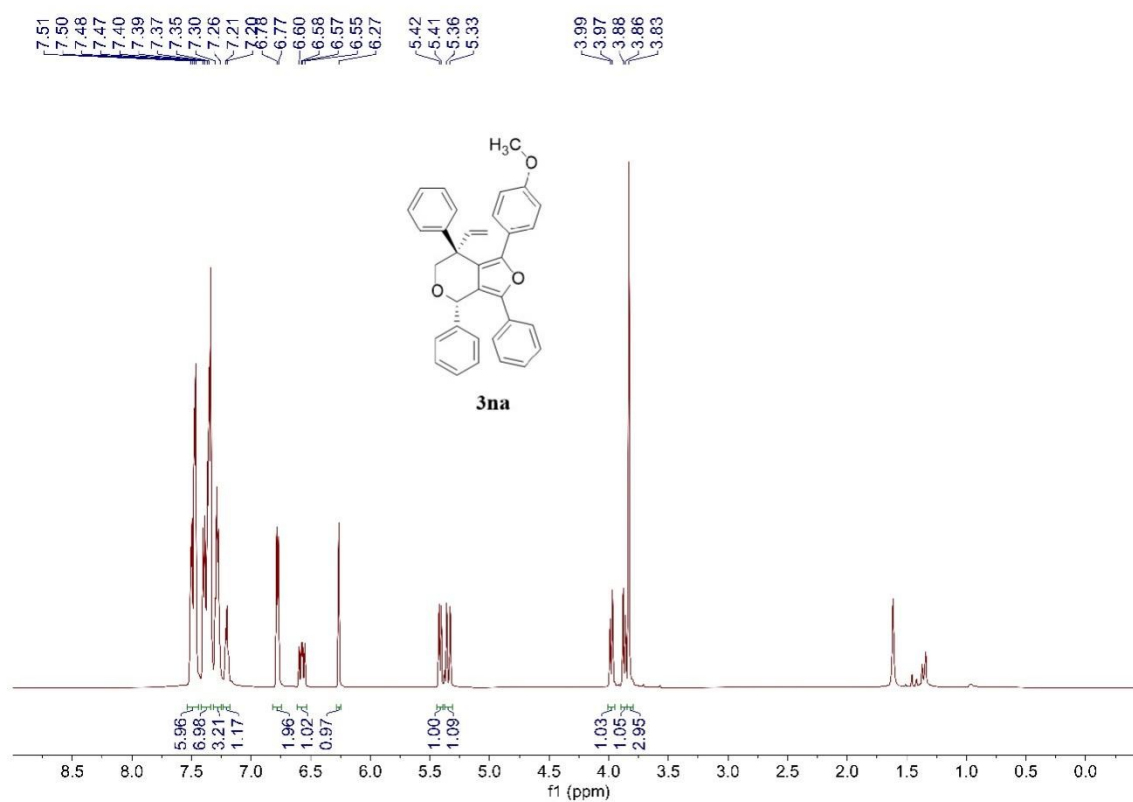
^1H NMR (600 MHz, CDCl_3) for **3ma**



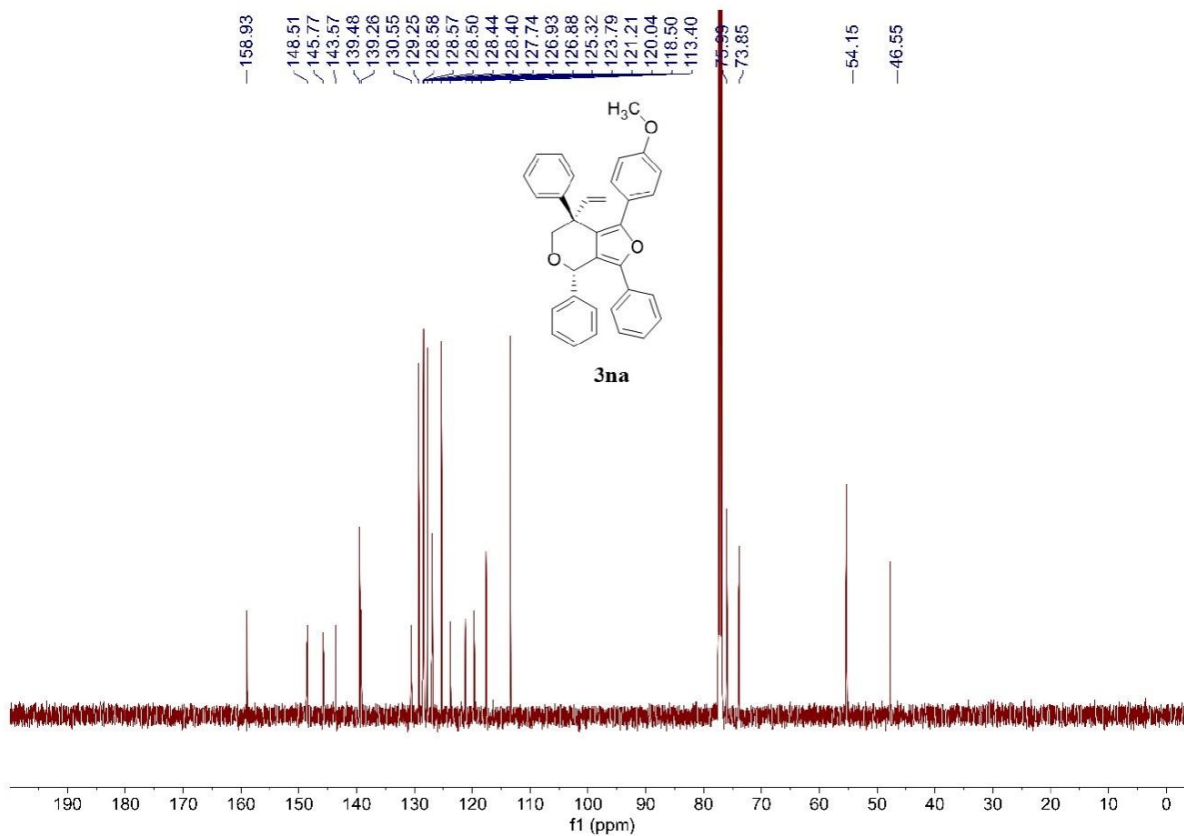
^{13}C $\{^1\text{H}\}$ NMR (151 MHz, CDCl_3) for **3ma**



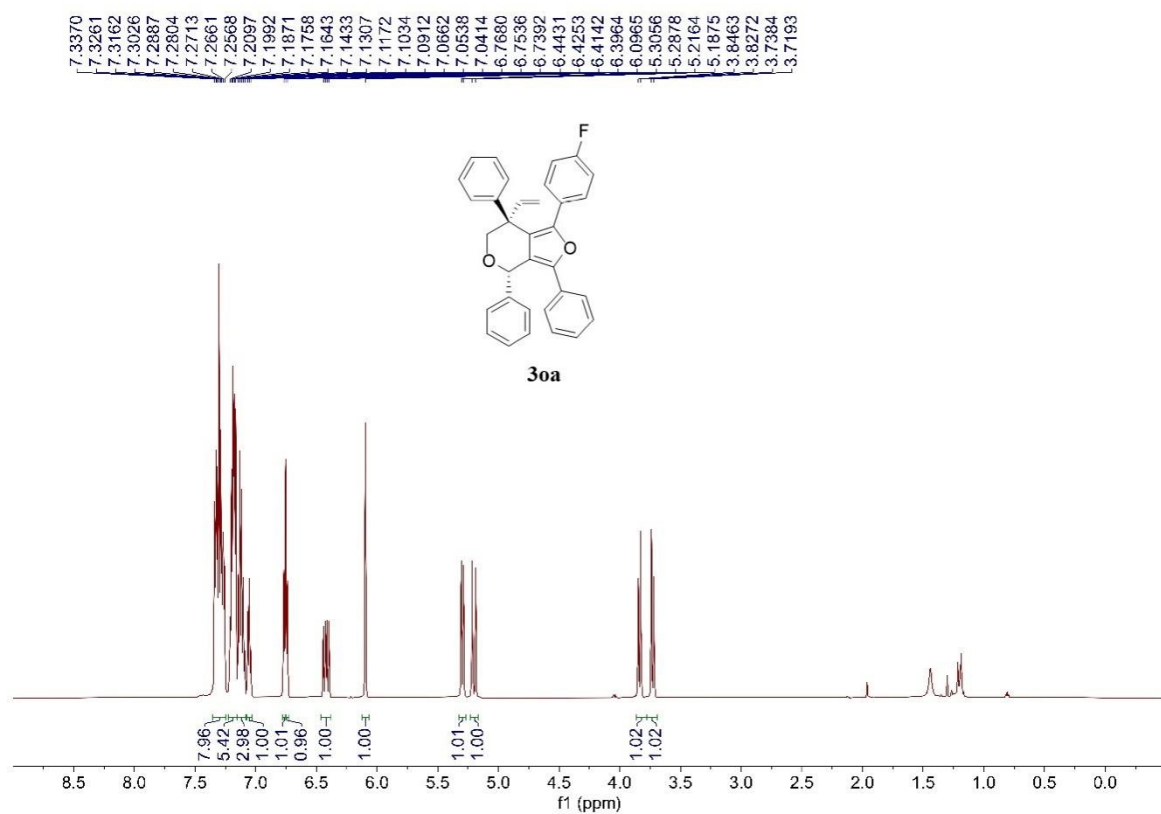
^1H NMR (600 MHz, CDCl_3) for **3na**



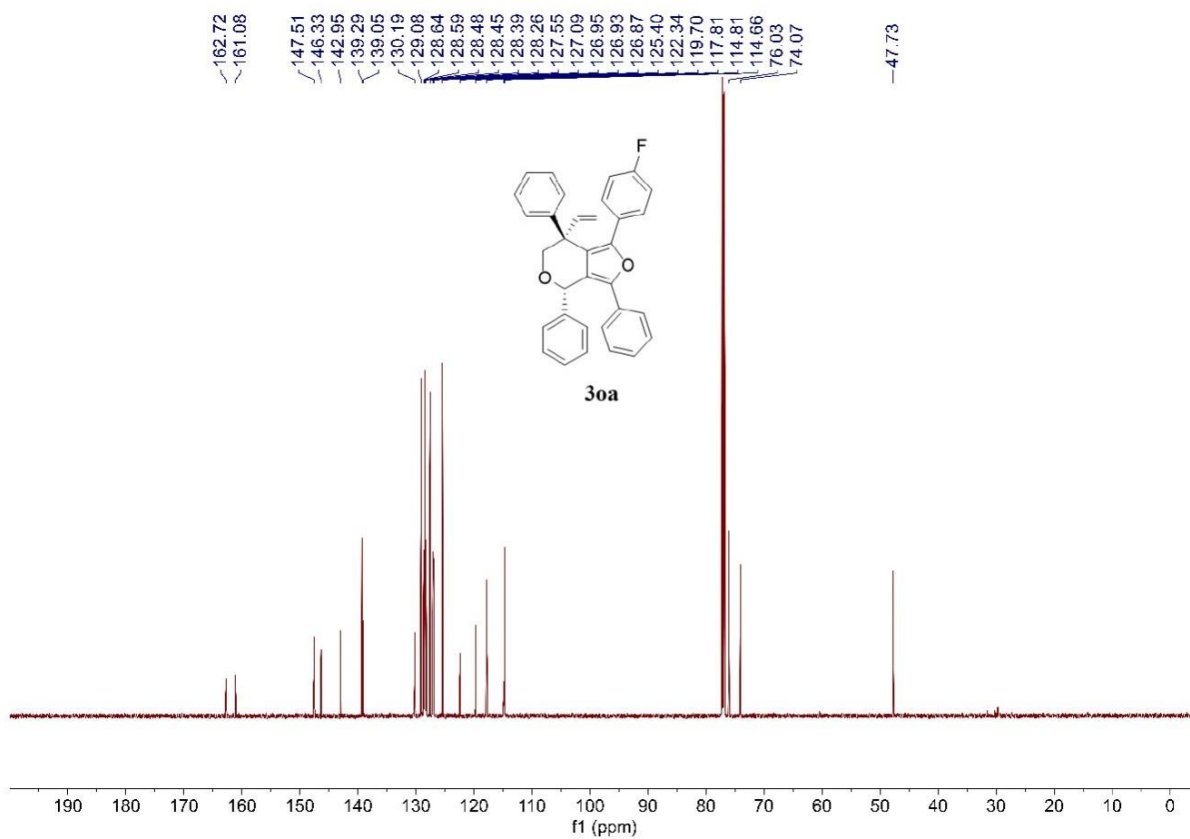
$^{13}\text{C}\{^1\text{H}\}$ NMR (151 MHz, CDCl_3) for **3na**



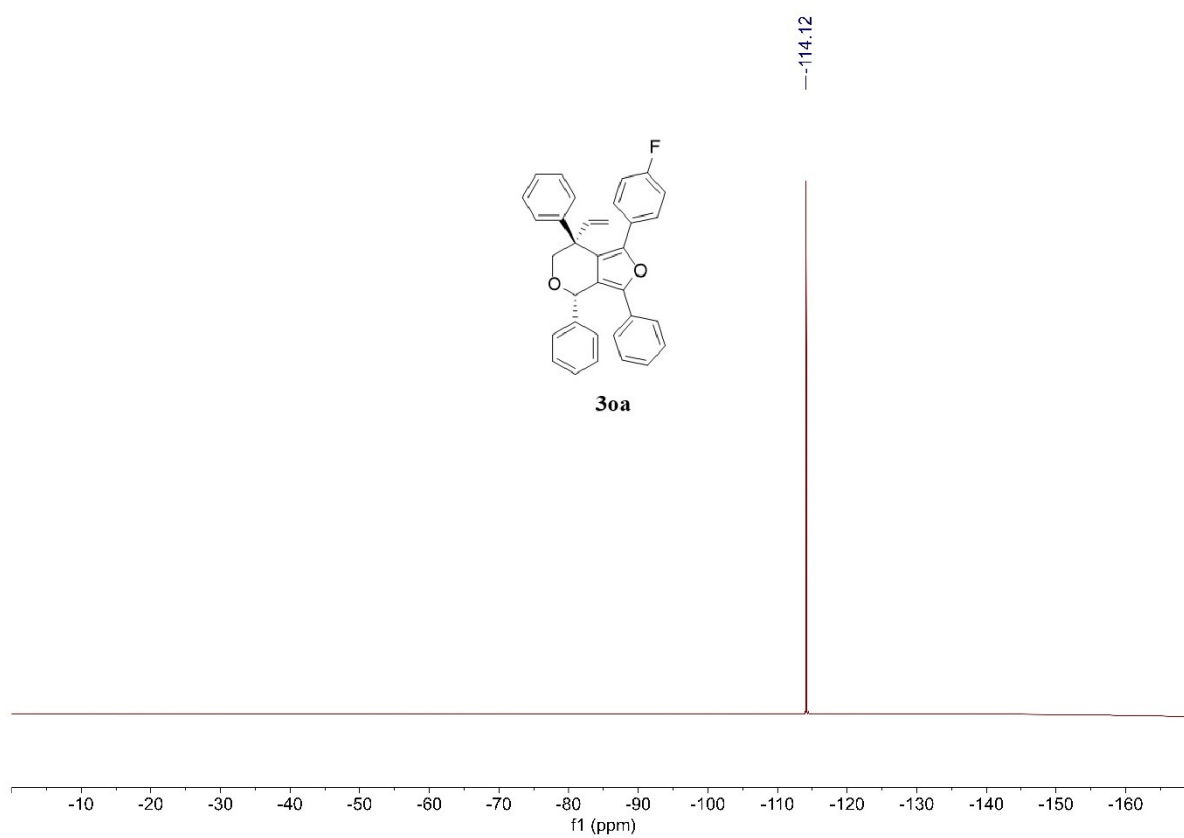
^1H NMR (600 MHz, CDCl_3) for **3oa**



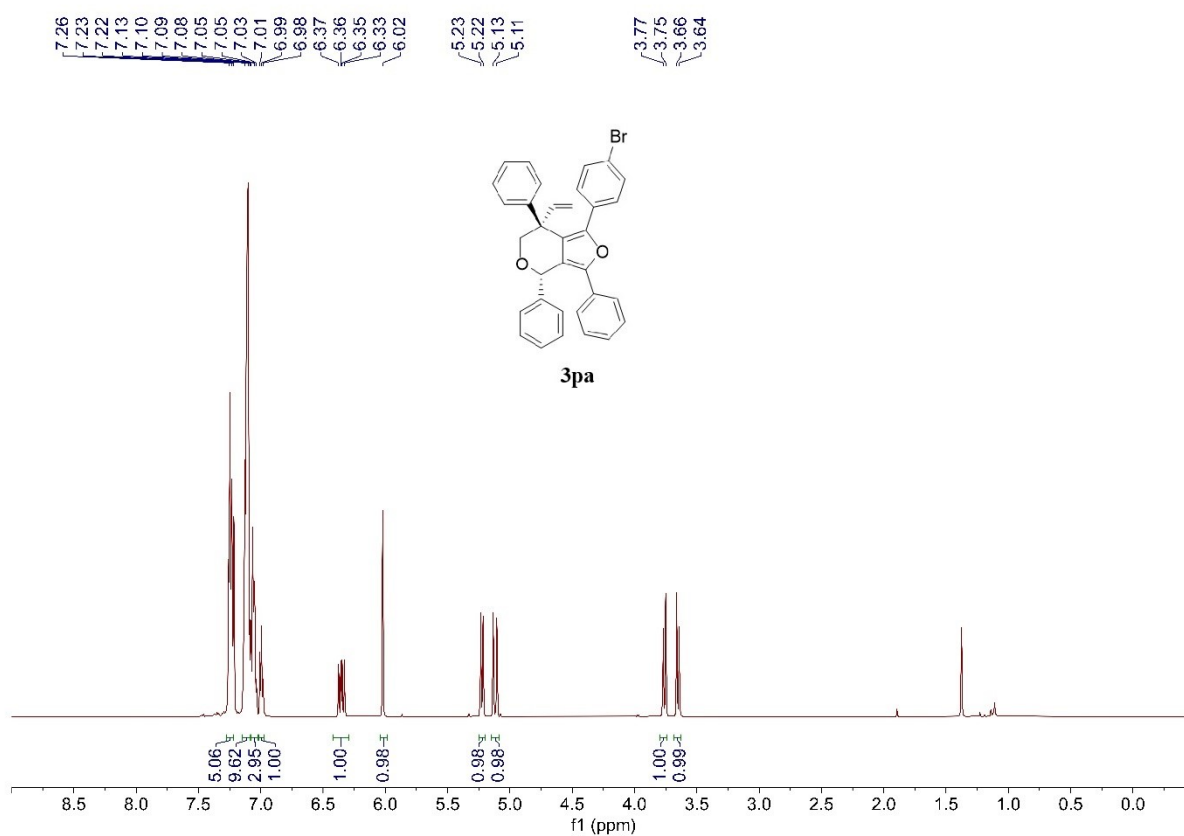
$^{13}\text{C}\{^1\text{H}\}$ NMR (151 MHz, CDCl_3) for **3oa**



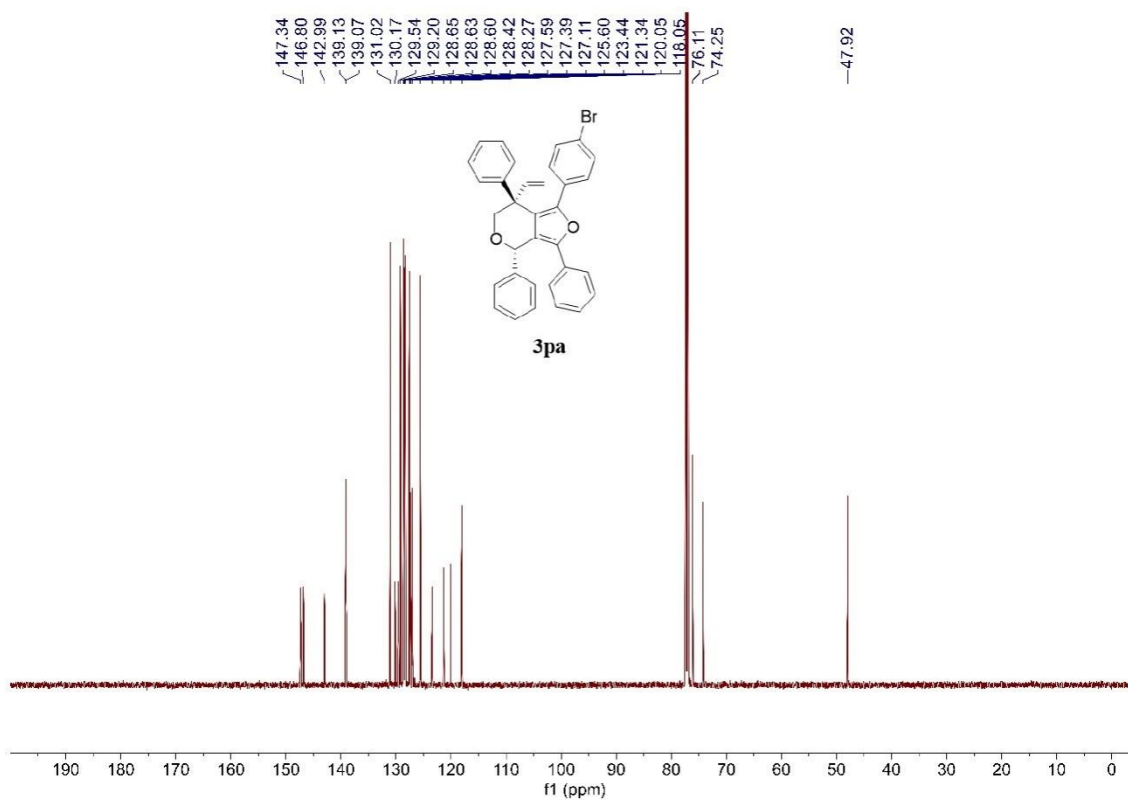
^{19}F NMR (565 MHz, CDCl_3) for **30a**



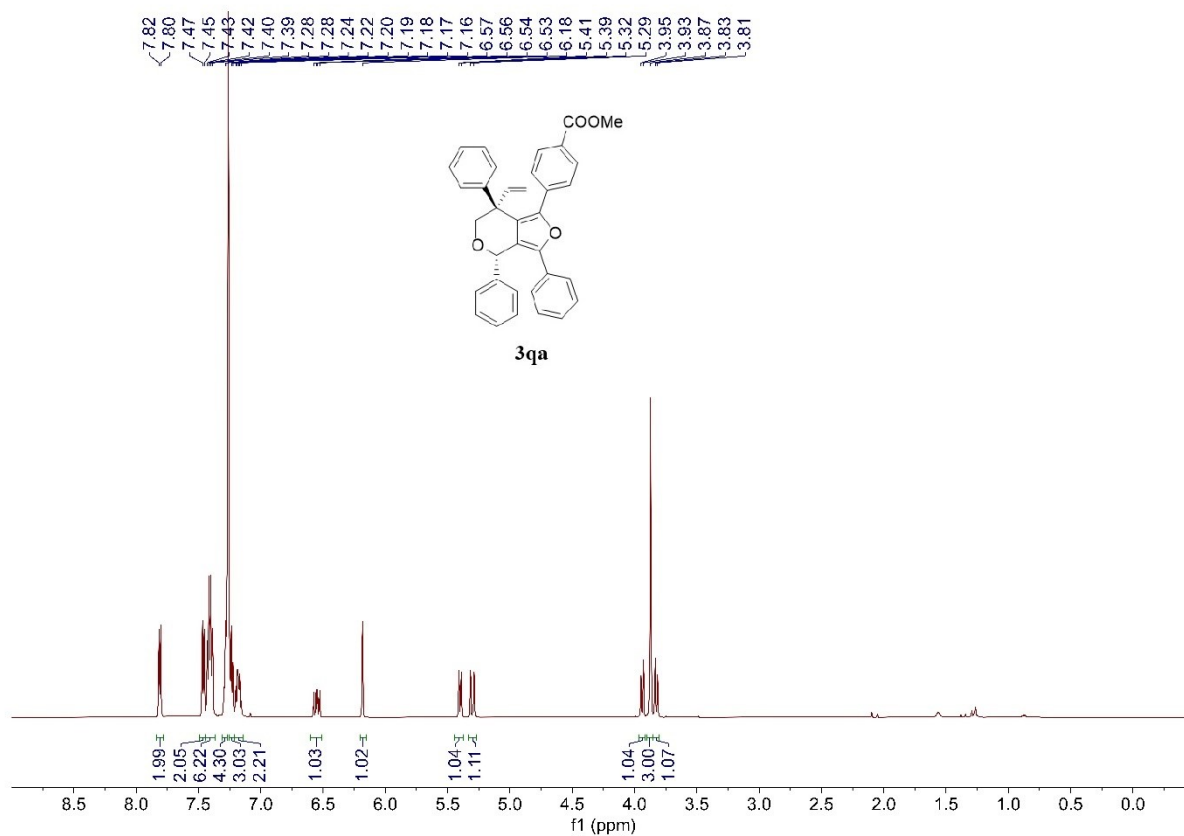
^1H NMR (600 MHz, CDCl_3) for **3pa**



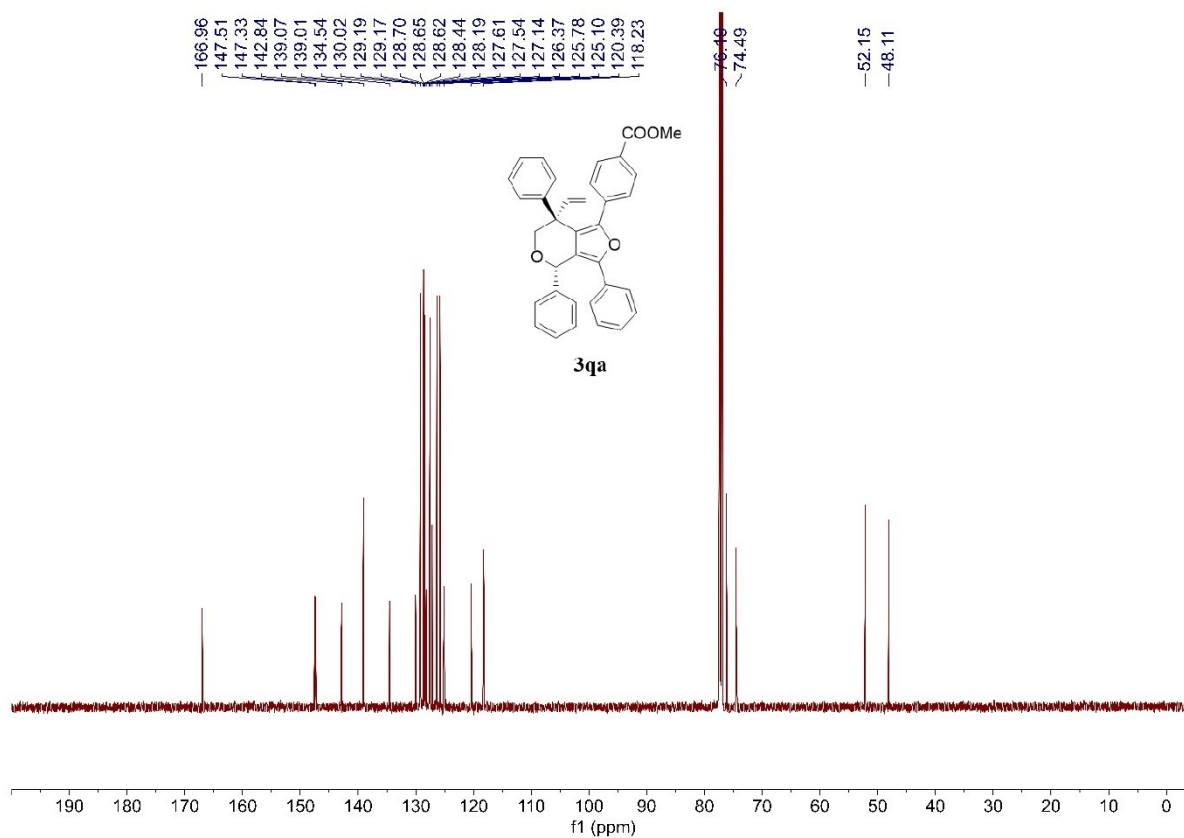
$^{13}\text{C}\{^1\text{H}\}$ NMR (151 MHz, CDCl_3) for **3pa**



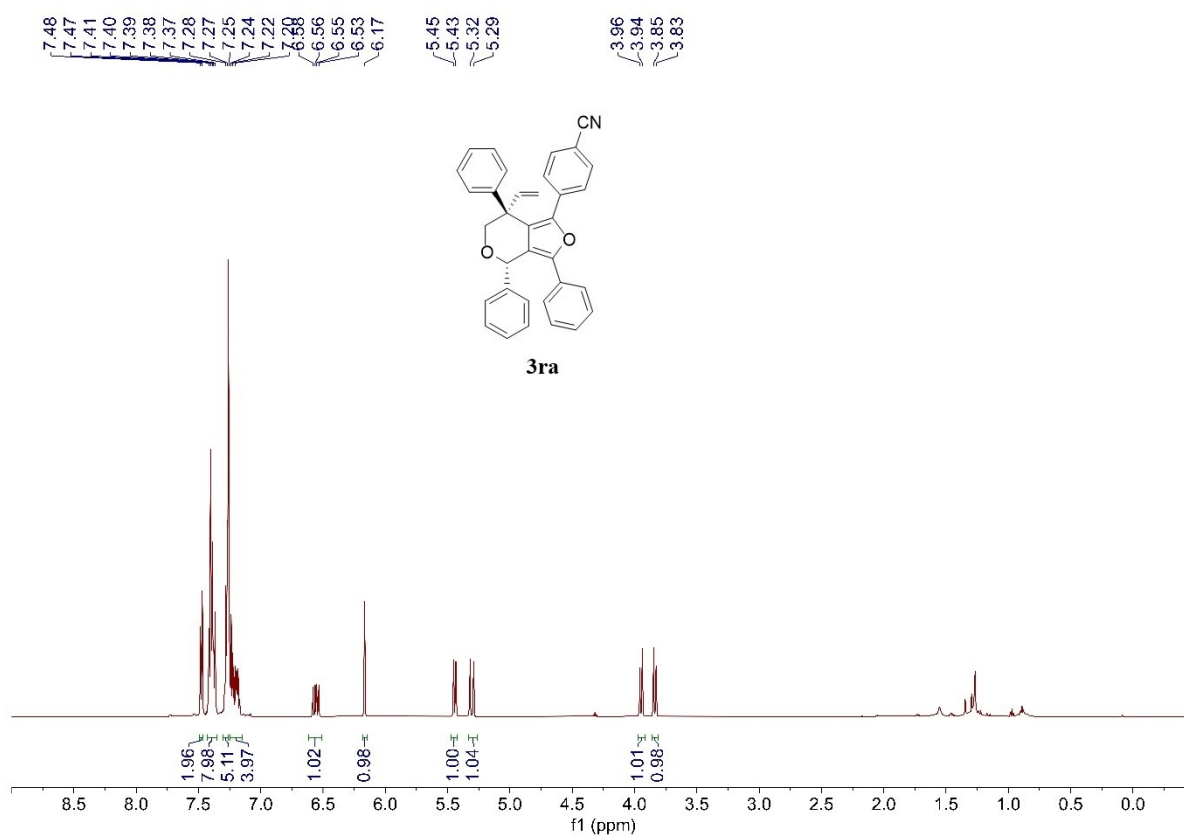
^1H NMR (600 MHz, CDCl_3) for **3qa**



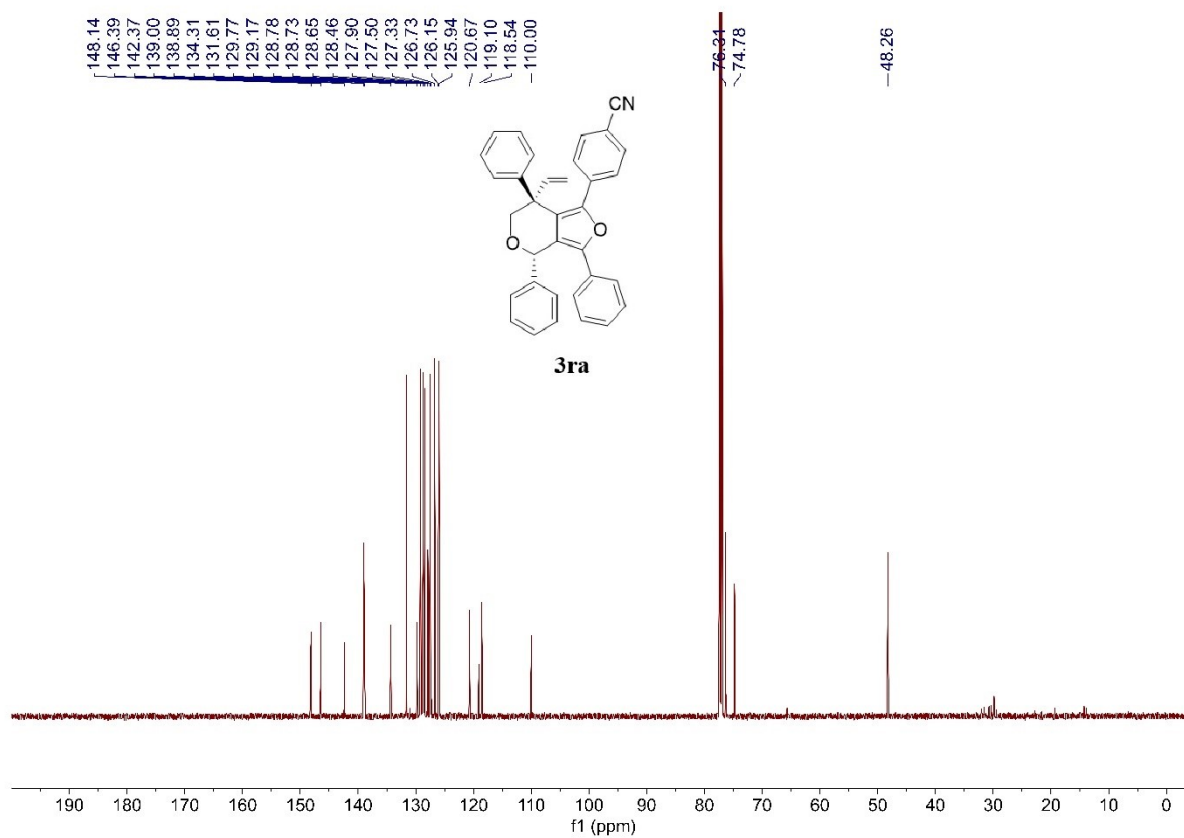
$^{13}\text{C}\{^1\text{H}\}$ NMR (151 MHz, CDCl_3) for **3qa**



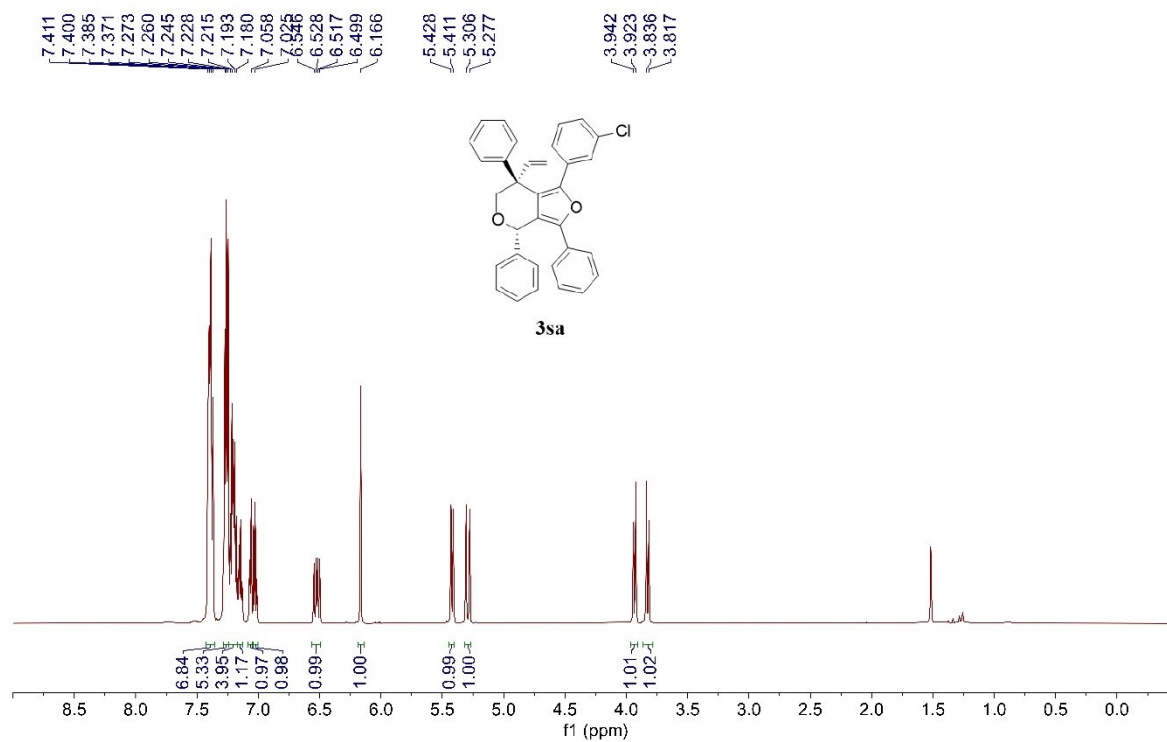
^1H NMR (600 MHz, CDCl_3) for **3ra**



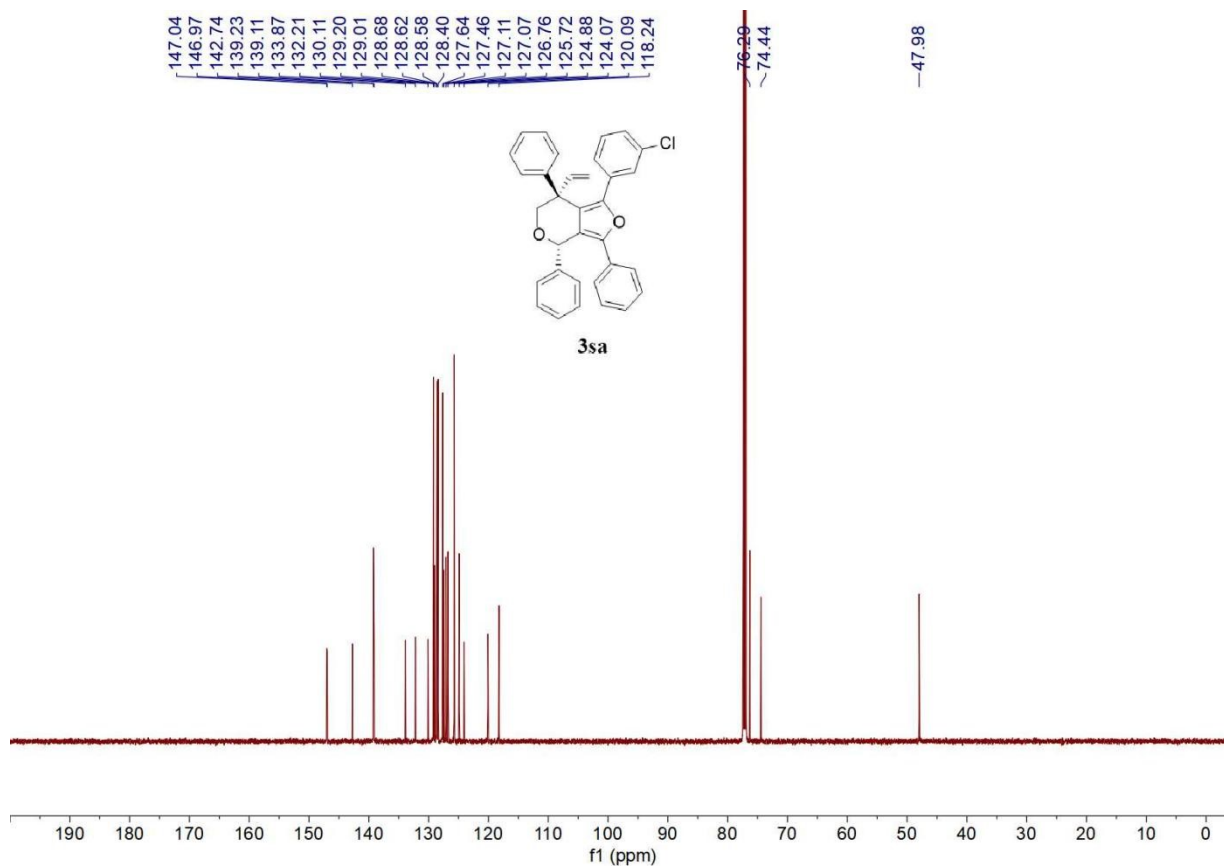
$^{13}\text{C}\{^1\text{H}\}$ NMR (151 MHz, CDCl_3) for **3ra**



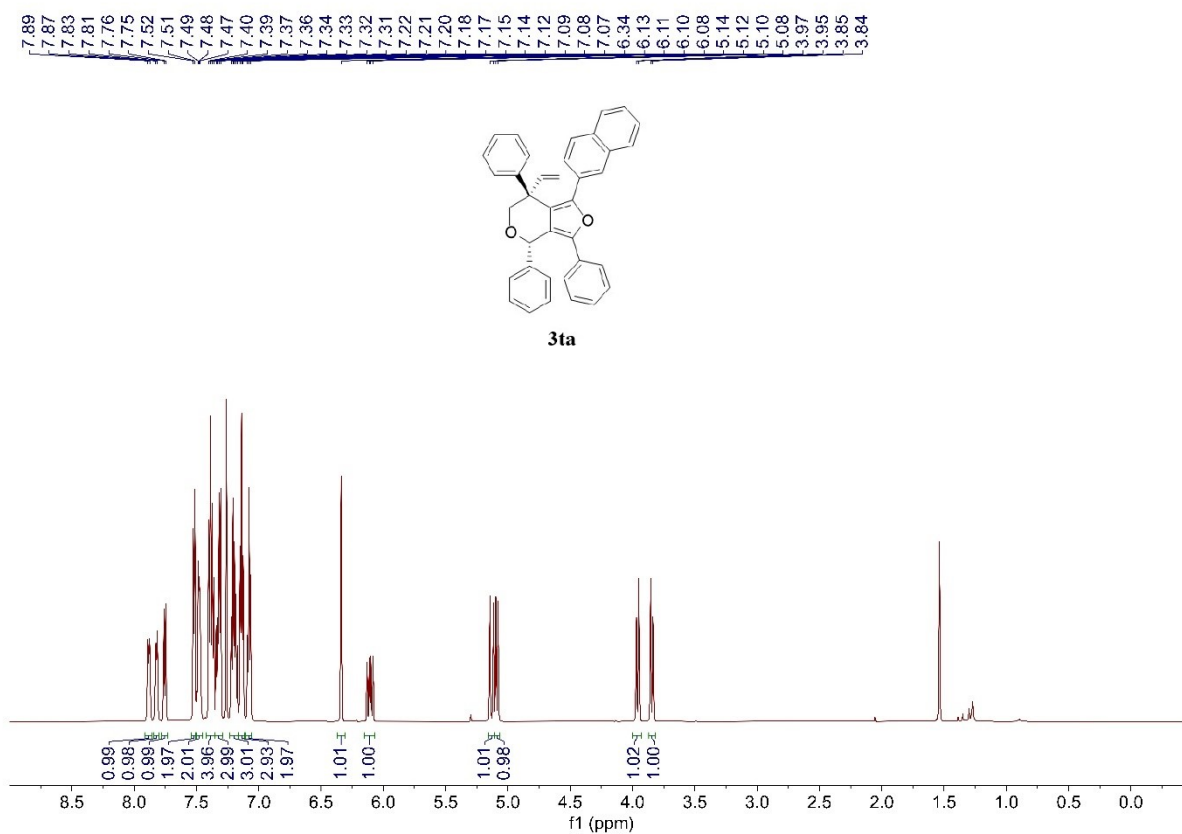
^1H NMR (600 MHz, CDCl_3) for **3sa**



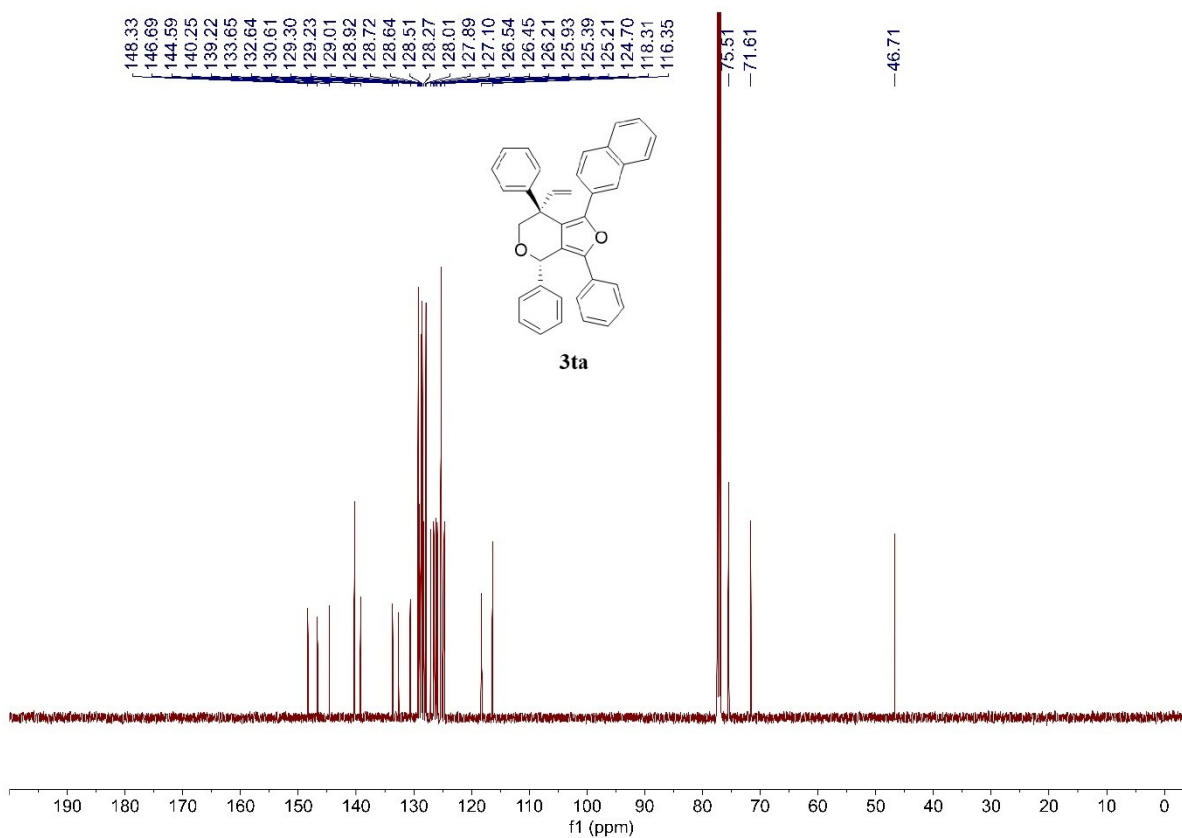
$^{13}\text{C}\{^1\text{H}\}$ NMR (151 MHz, CDCl_3) for **3sa**



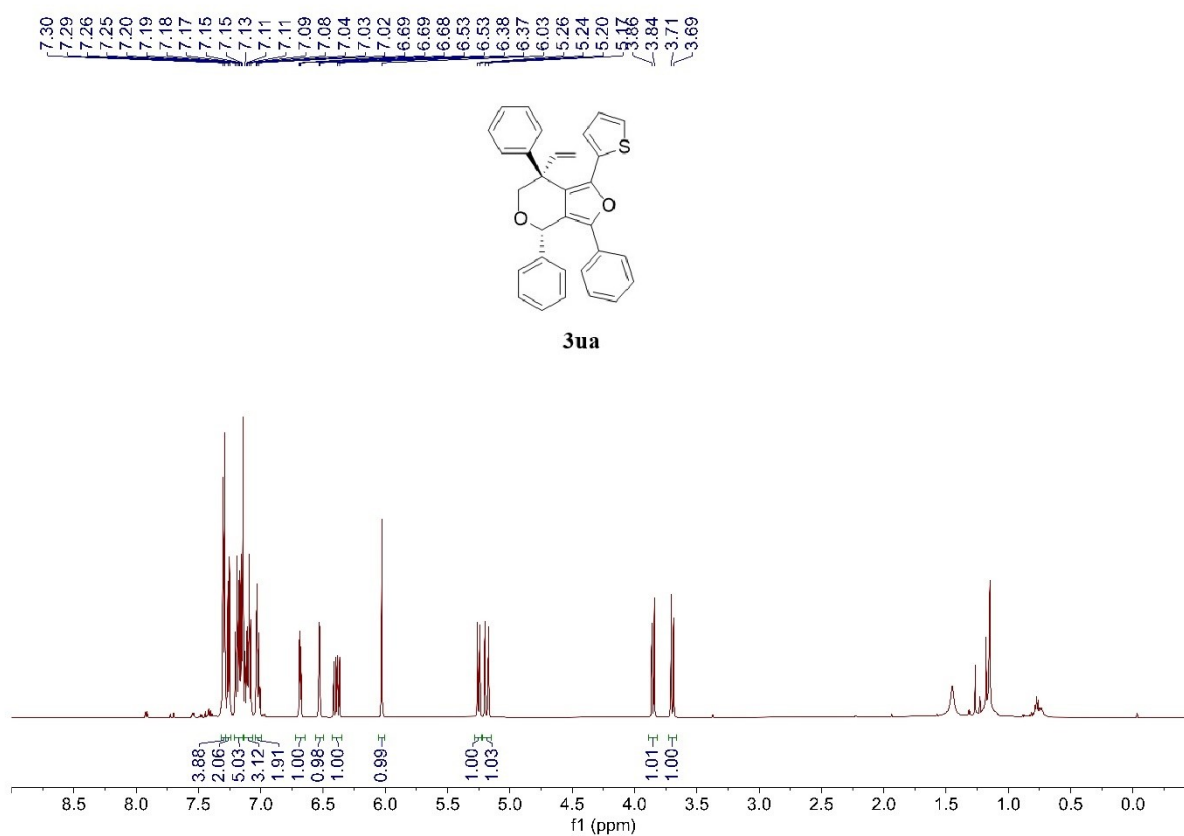
^1H NMR (600 MHz, CDCl_3) for **3ta**



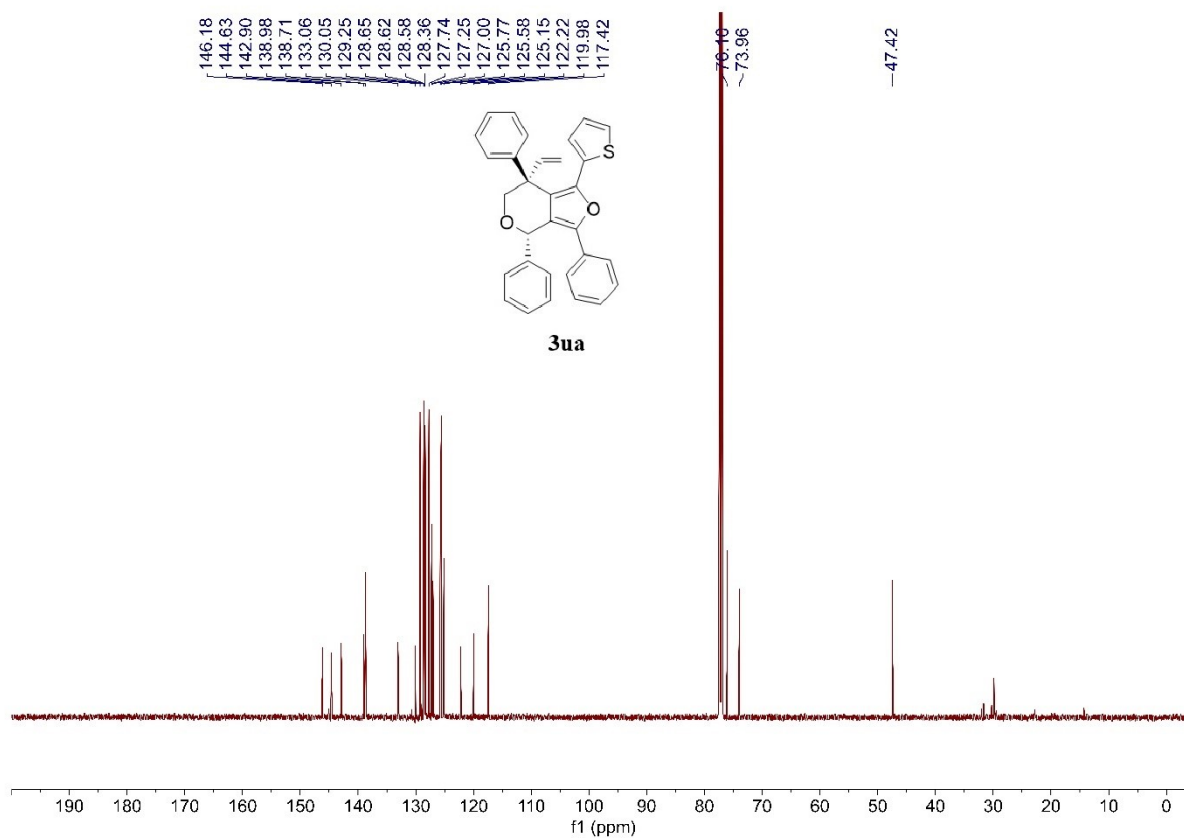
$^{13}\text{C}\{^1\text{H}\}$ NMR (151 MHz, CDCl_3) for **3ta**



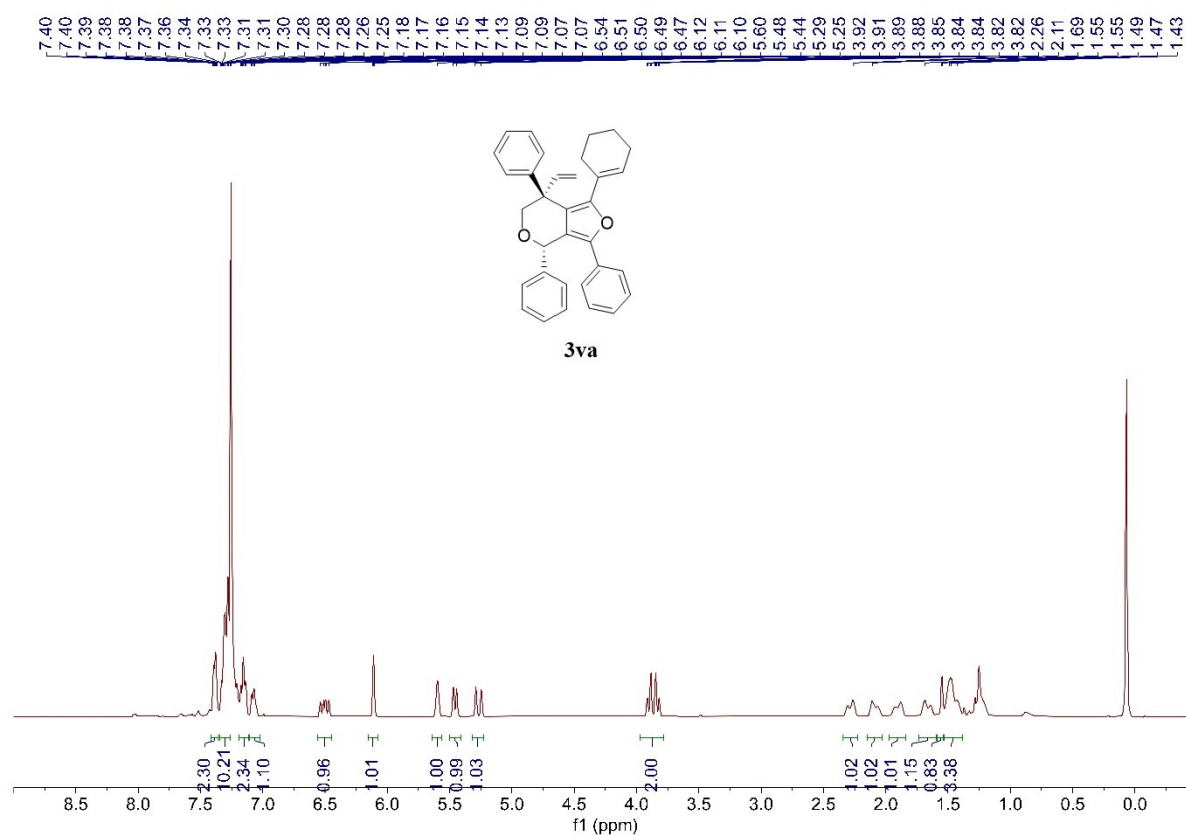
^1H NMR (600 MHz, CDCl_3) for **3ua**



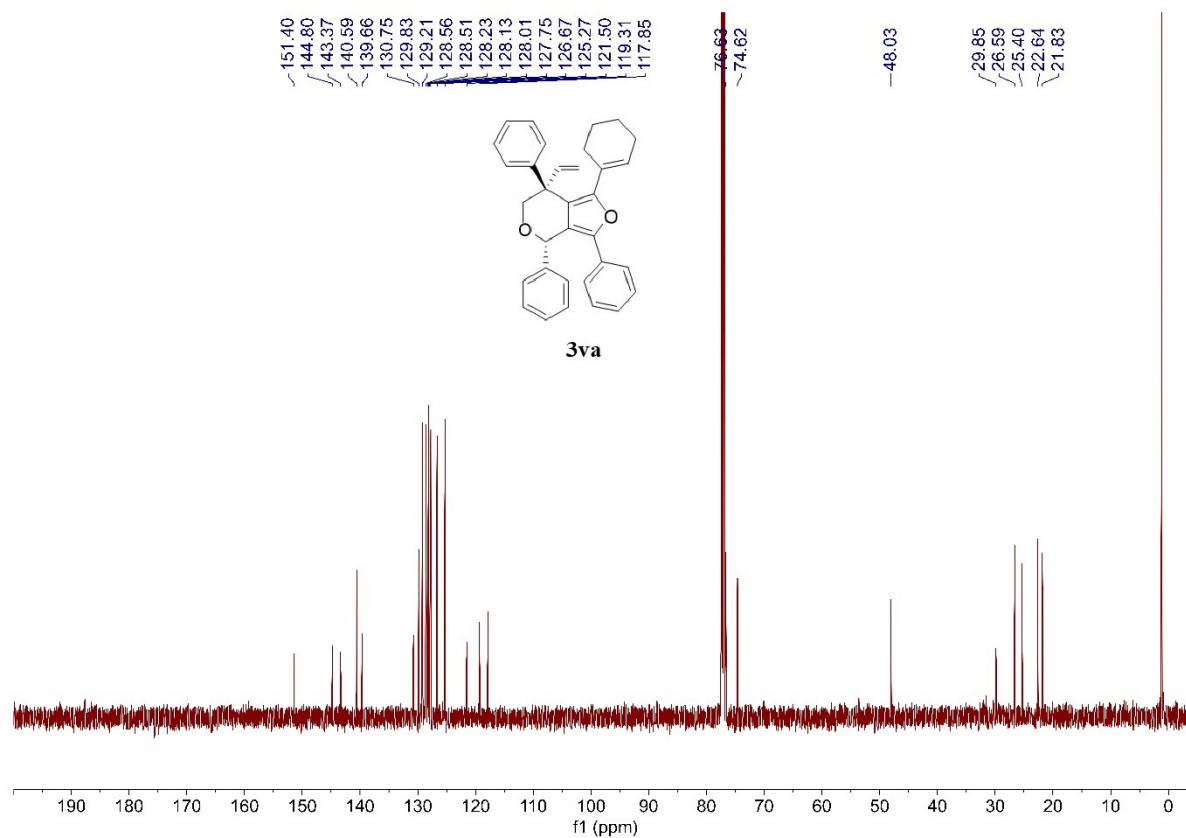
$^{13}\text{C}\{^1\text{H}\}$ NMR (151 MHz, CDCl_3) for **3ua**



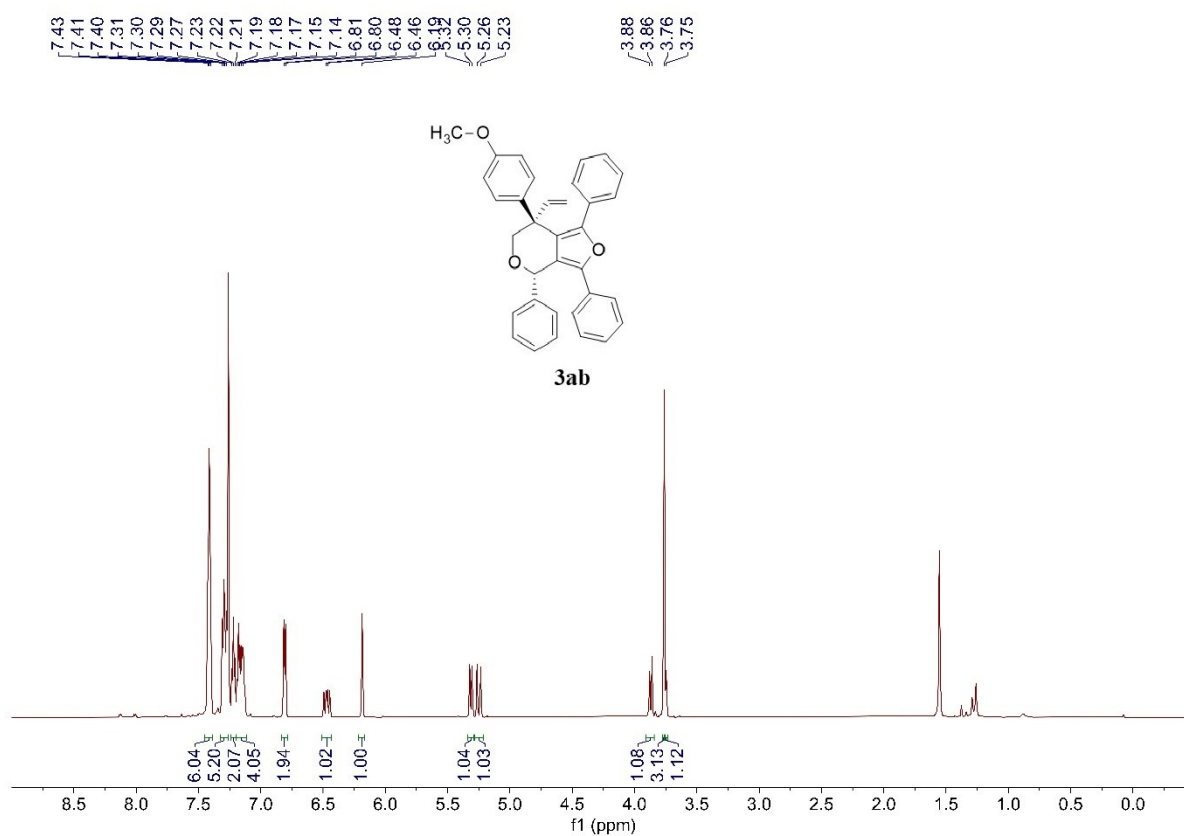
^1H NMR (400 MHz, CDCl_3) for **3va**



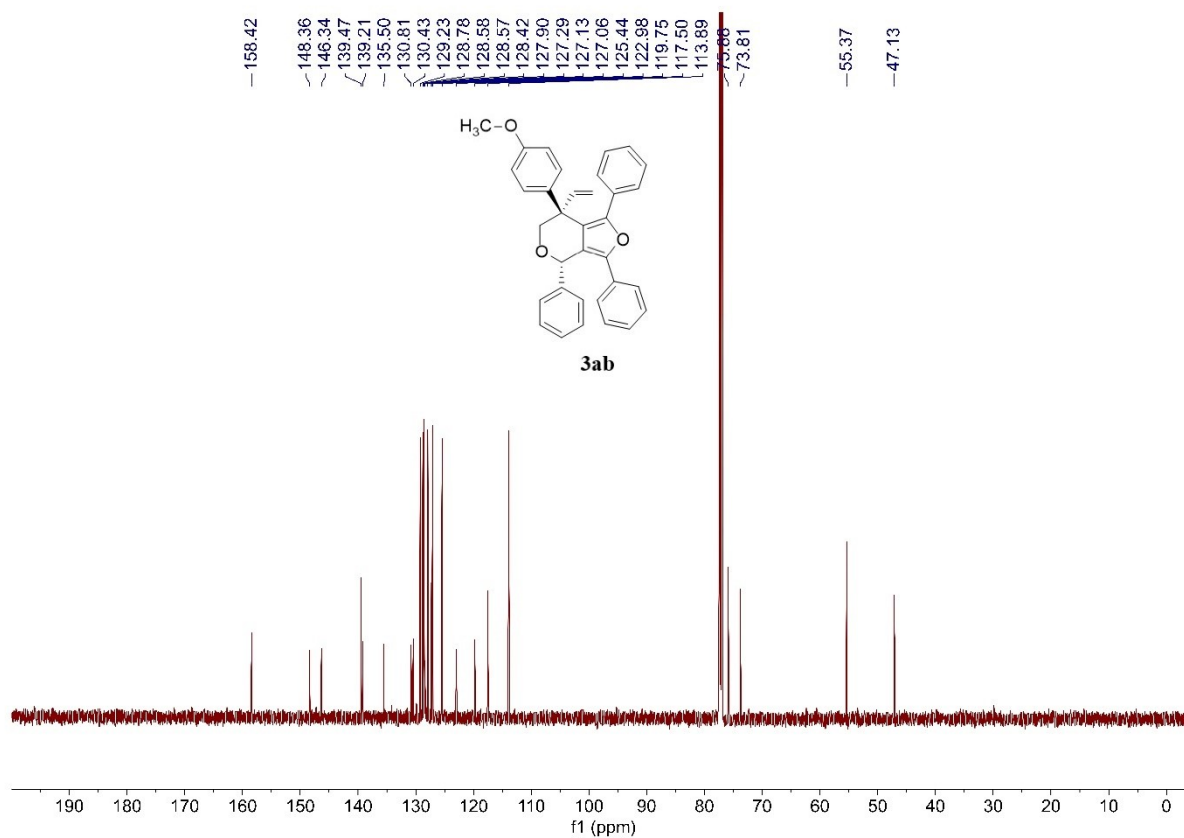
$^{13}\text{C}\{^1\text{H}\}$ NMR (151 MHz, CDCl_3) for **3va**



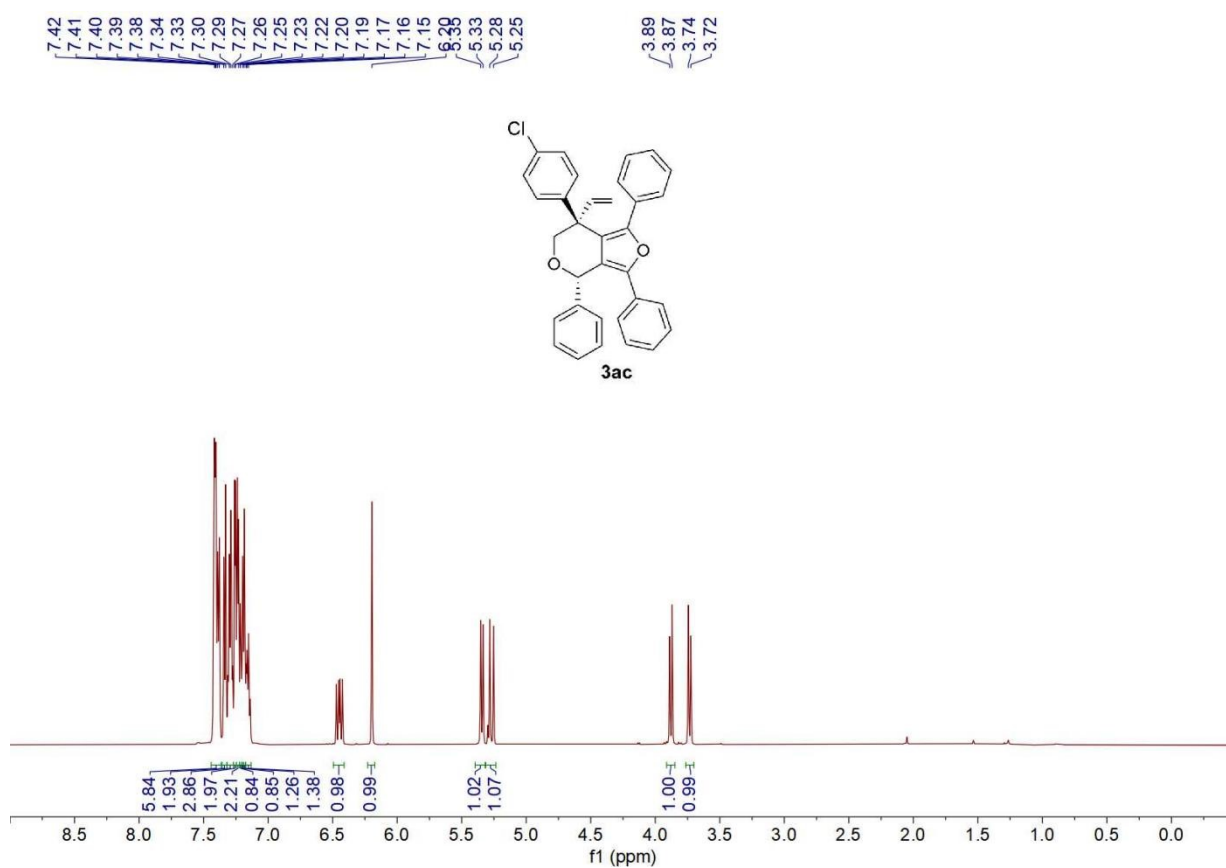
^1H NMR (600 MHz, CDCl_3) for **3ab**



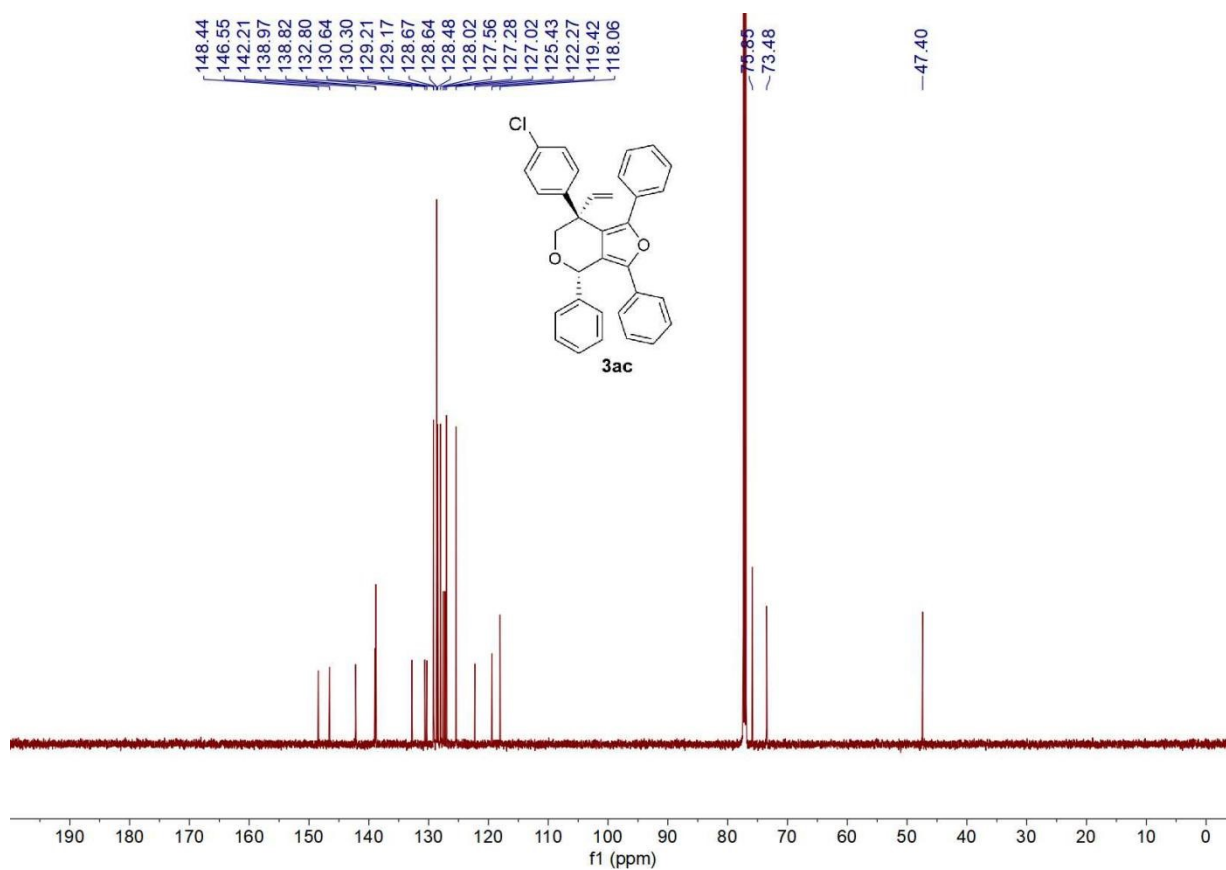
$^{13}\text{C}\{^1\text{H}\}$ NMR (151 MHz, CDCl_3) for **3ab**



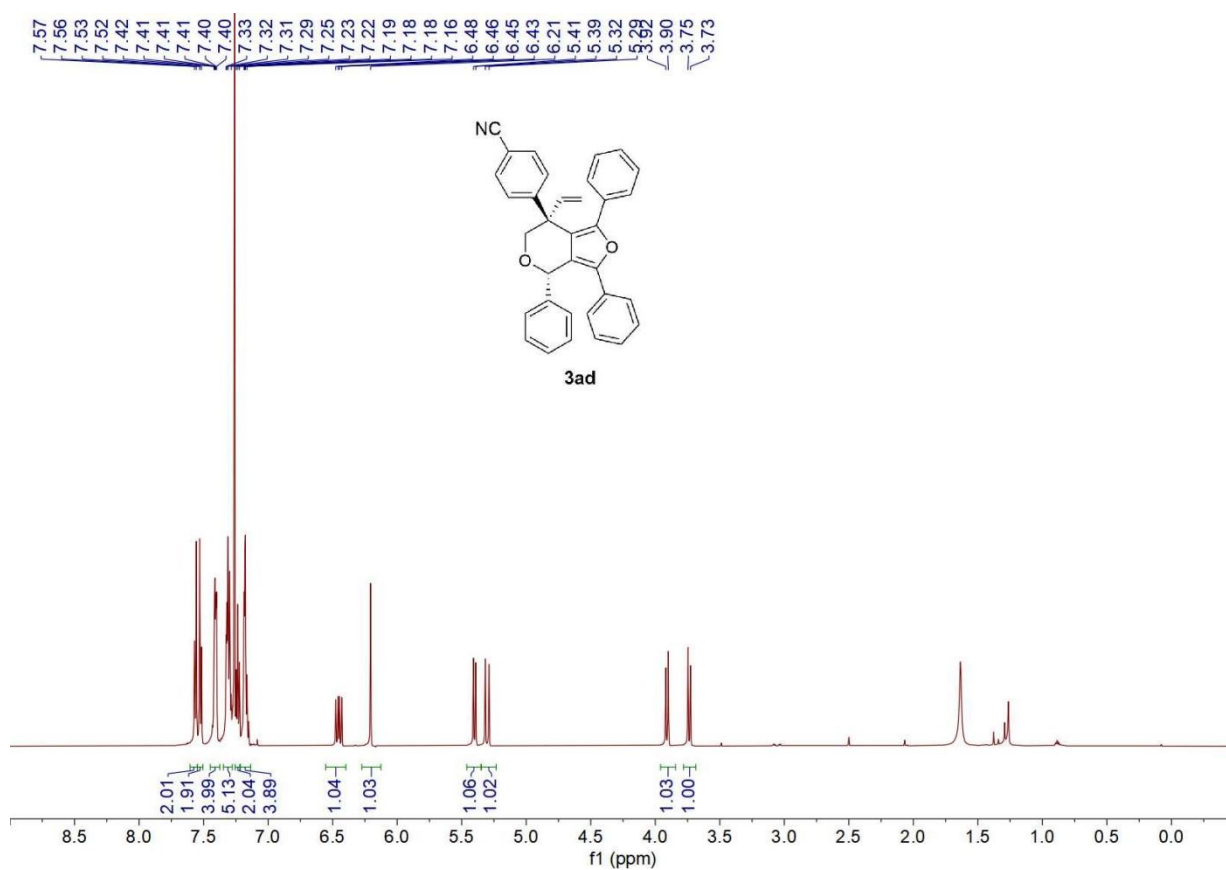
^1H NMR (600 MHz, CDCl_3) for **3ac**



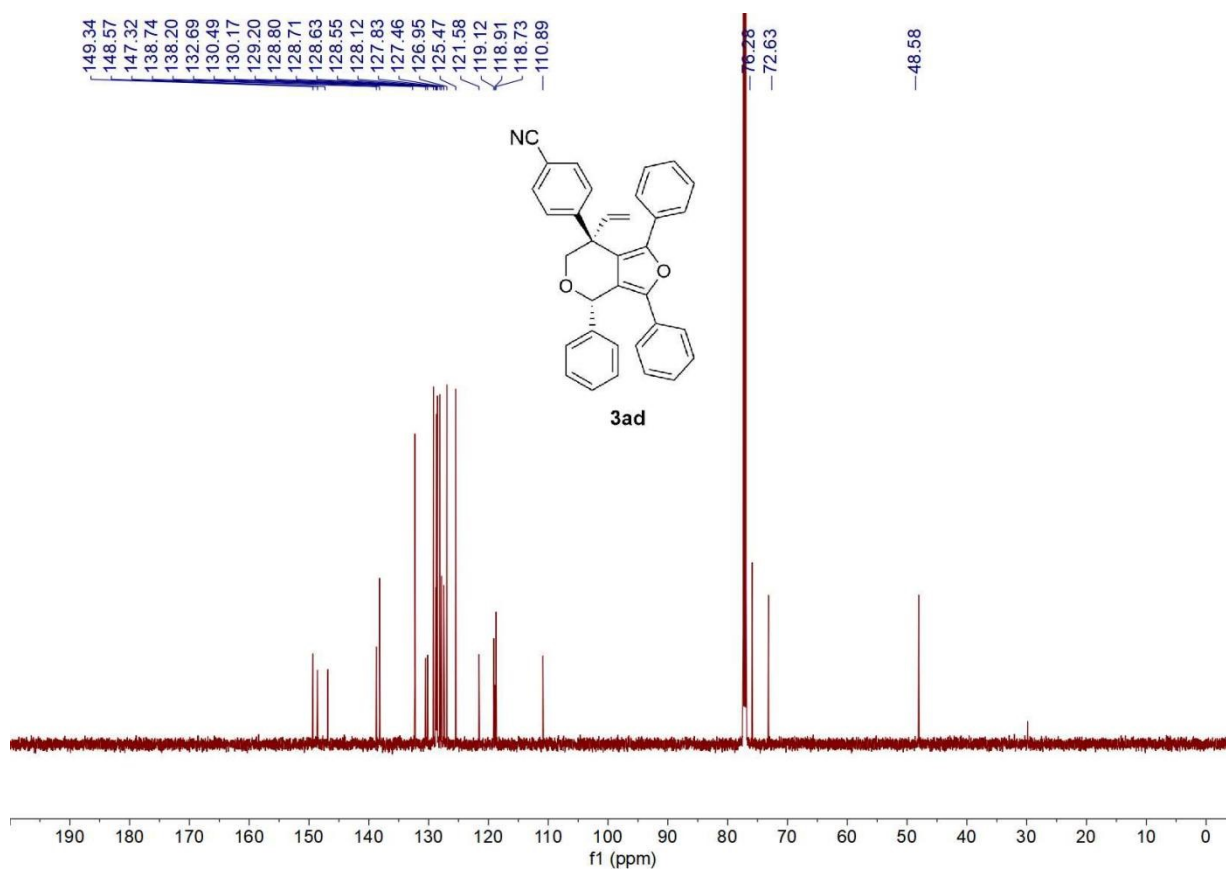
$^{13}\text{C}\{^1\text{H}\}$ NMR (151 MHz, CDCl_3) for **3ac**



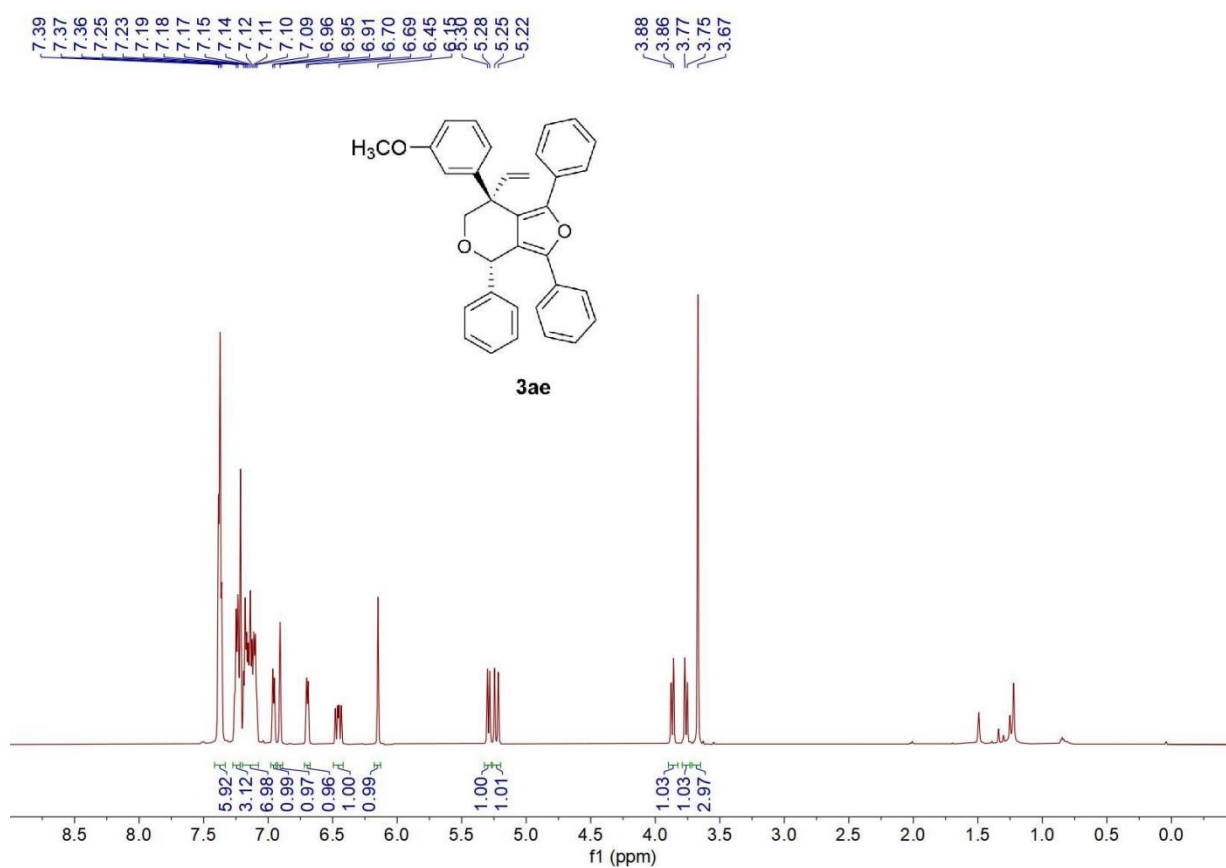
^1H NMR (600 MHz, CDCl_3) for **3ad**



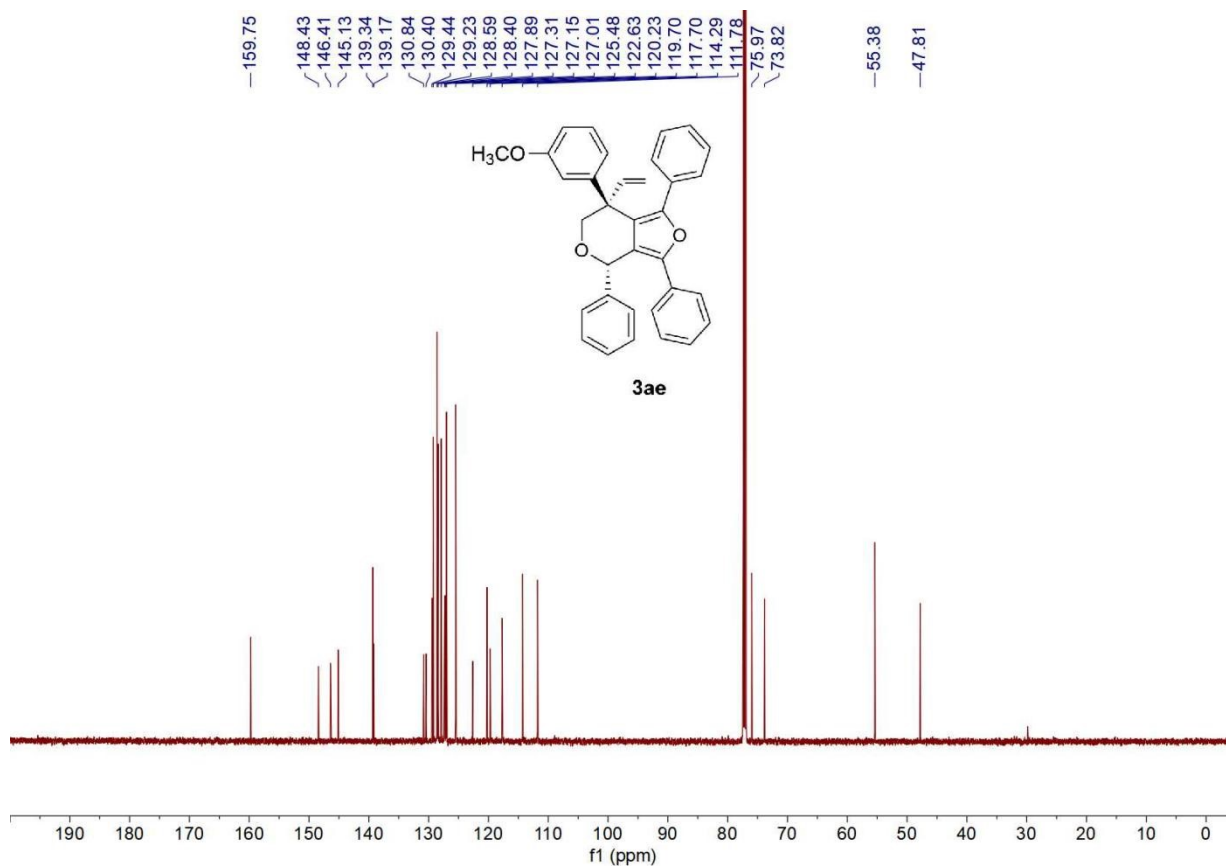
$^{13}\text{C}\{^1\text{H}\}$ NMR (151 MHz, CDCl_3) for **3ad**



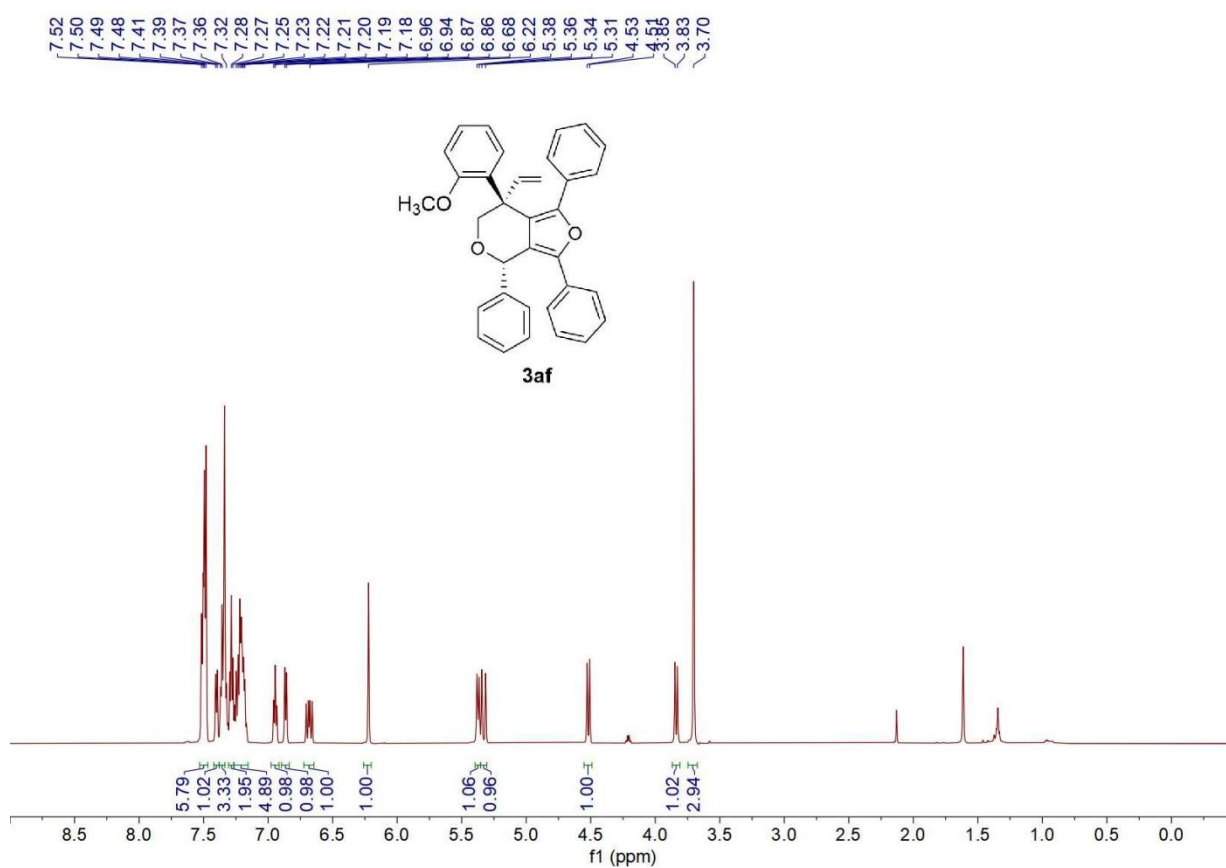
^1H NMR (600 MHz, CDCl_3) for **3ae**



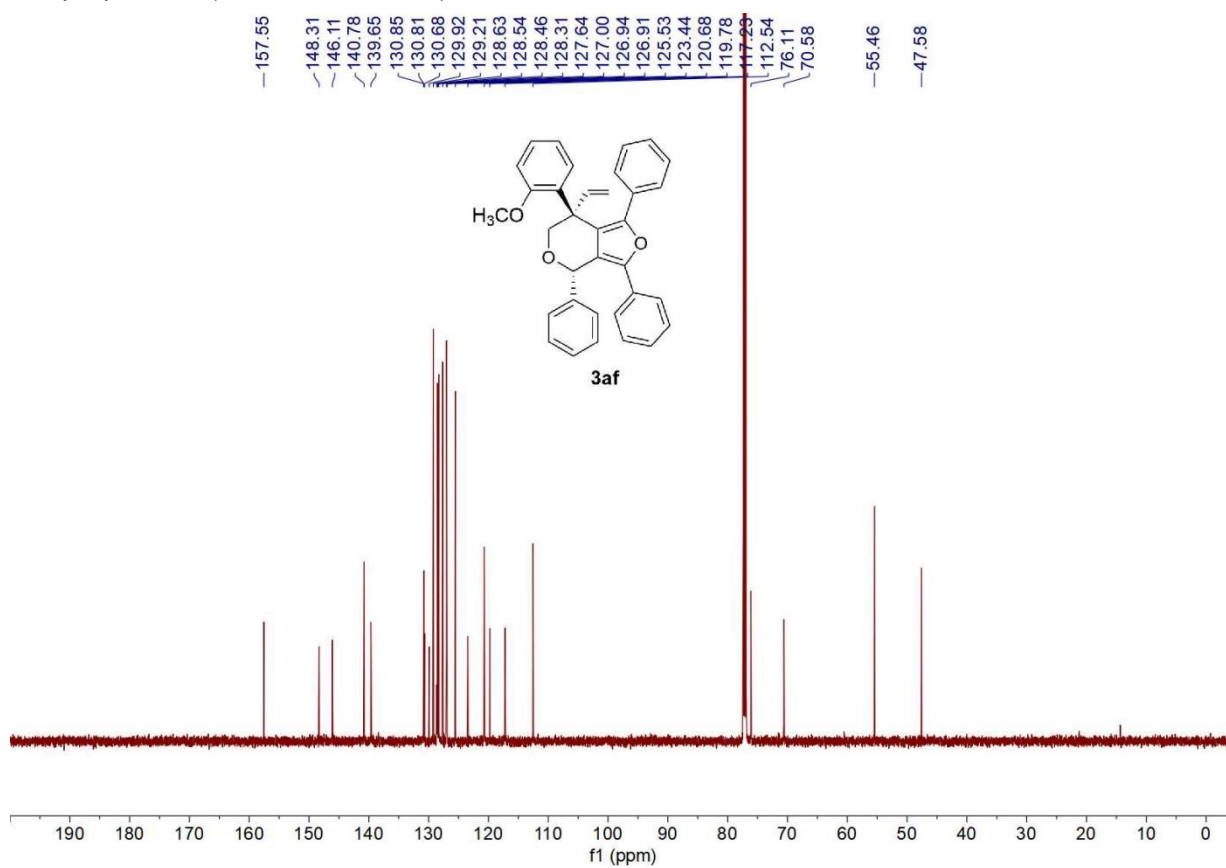
$^{13}\text{C}\{^1\text{H}\}$ NMR (151 MHz, CDCl_3) for **3ae**



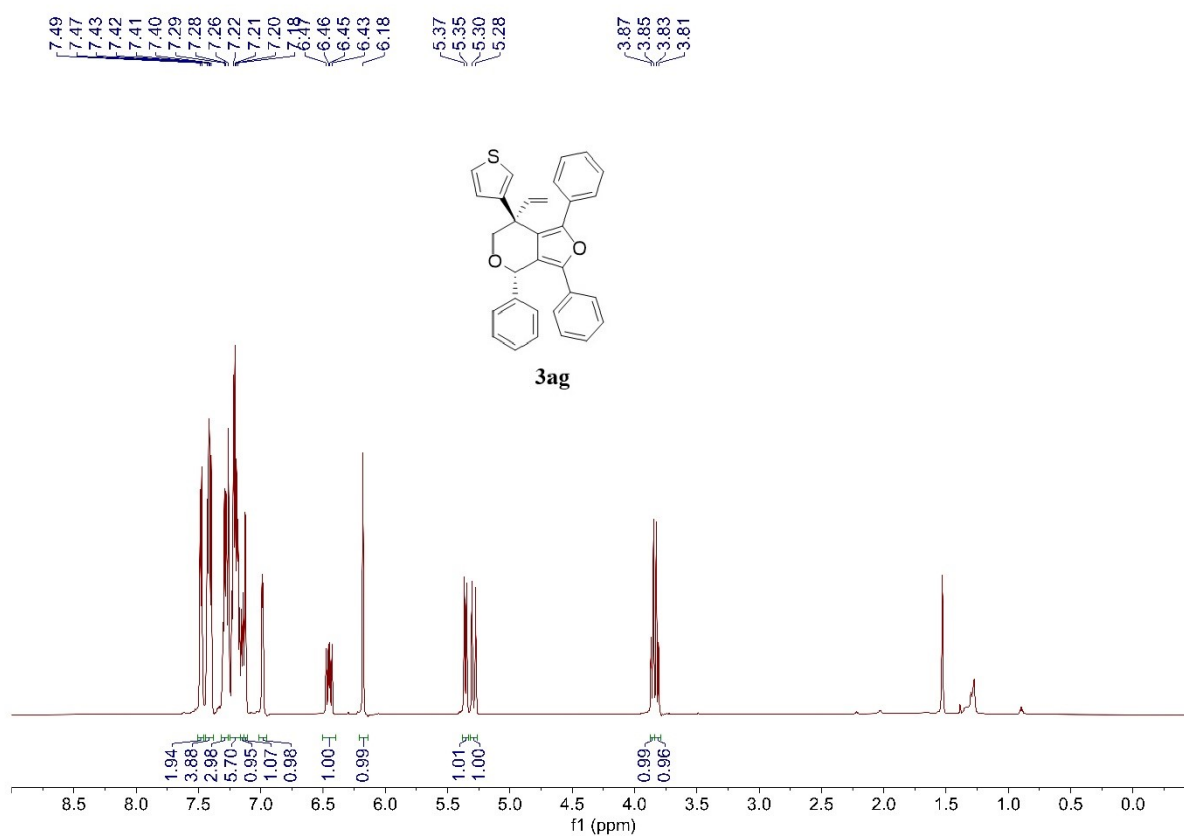
^1H NMR (600 MHz, CDCl_3) for **3af**



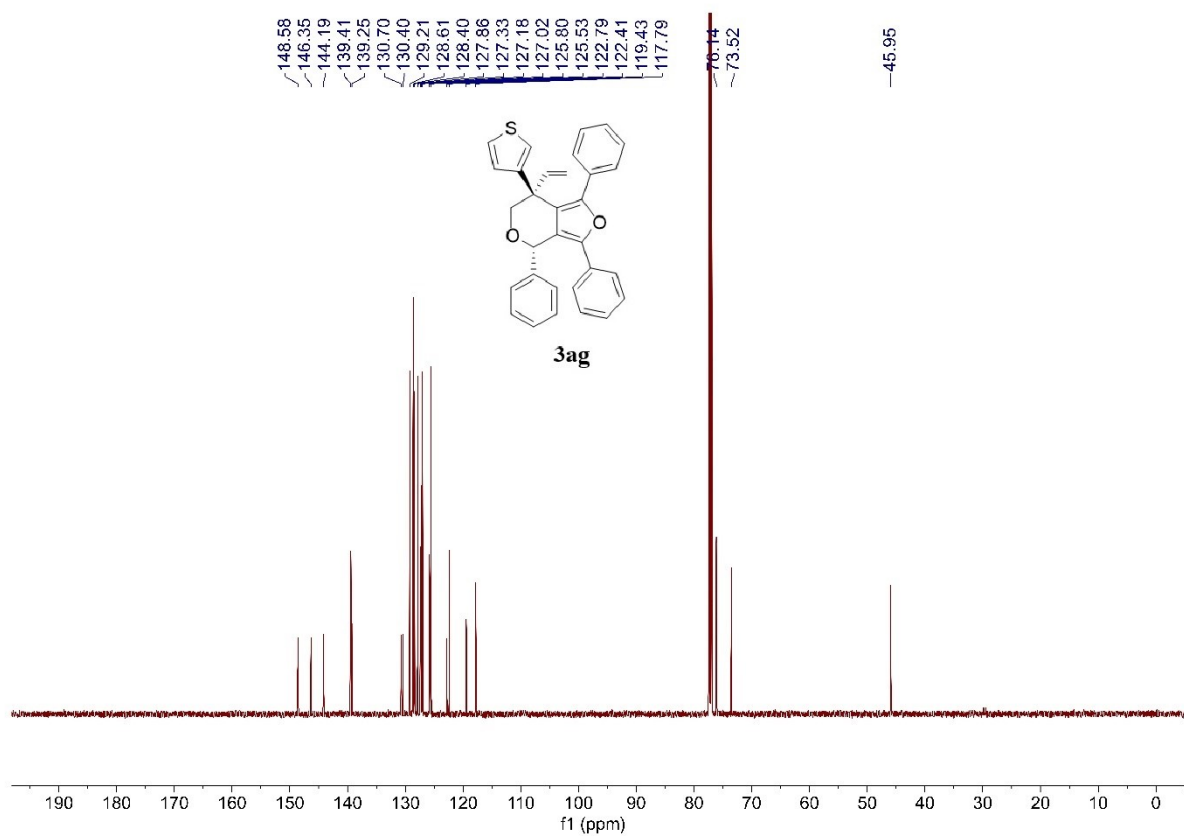
$^{13}\text{C}\{^1\text{H}\}$ NMR (151 MHz, CDCl_3) for **3af**



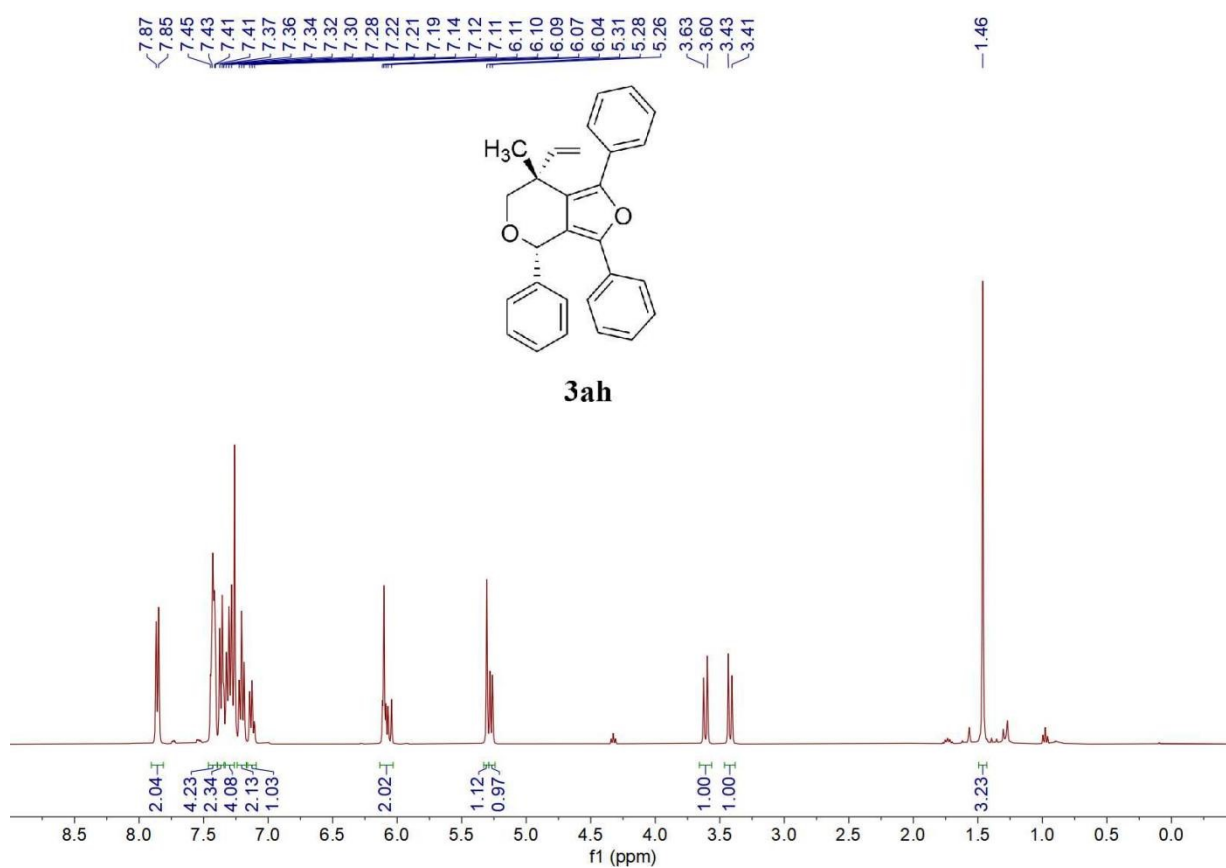
^1H NMR (600 MHz, CDCl_3) for **3ag**



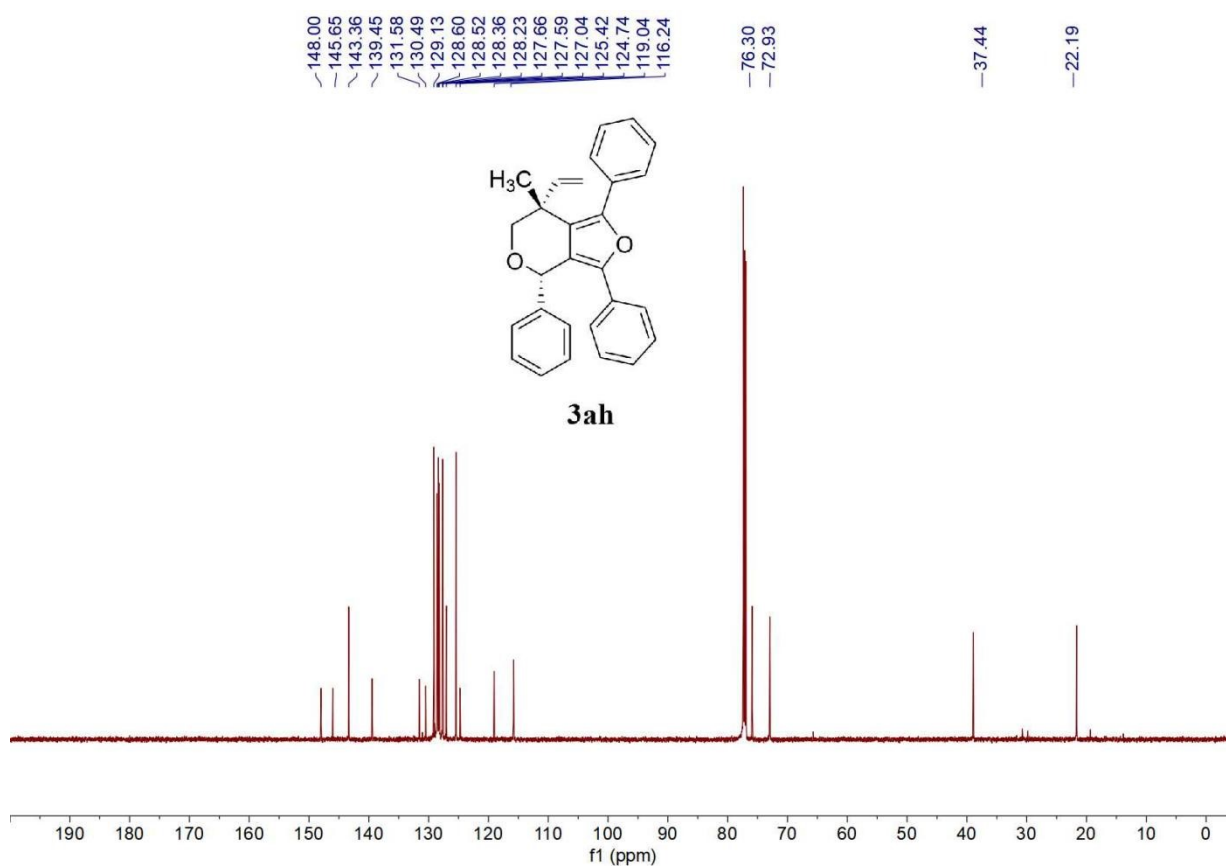
$^{13}\text{C}\{^1\text{H}\}$ NMR (151 MHz, CDCl_3) for **3ag**



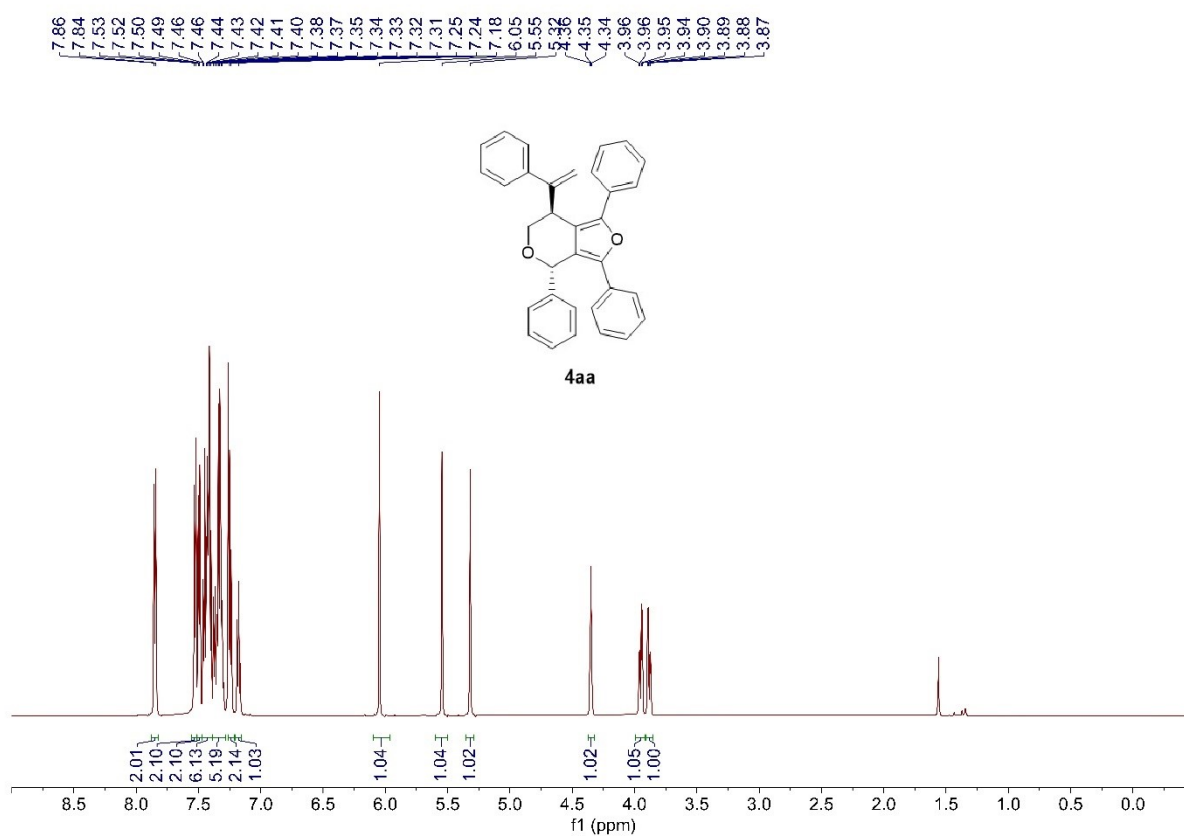
^1H NMR (400 MHz, CDCl_3) for **3ah**



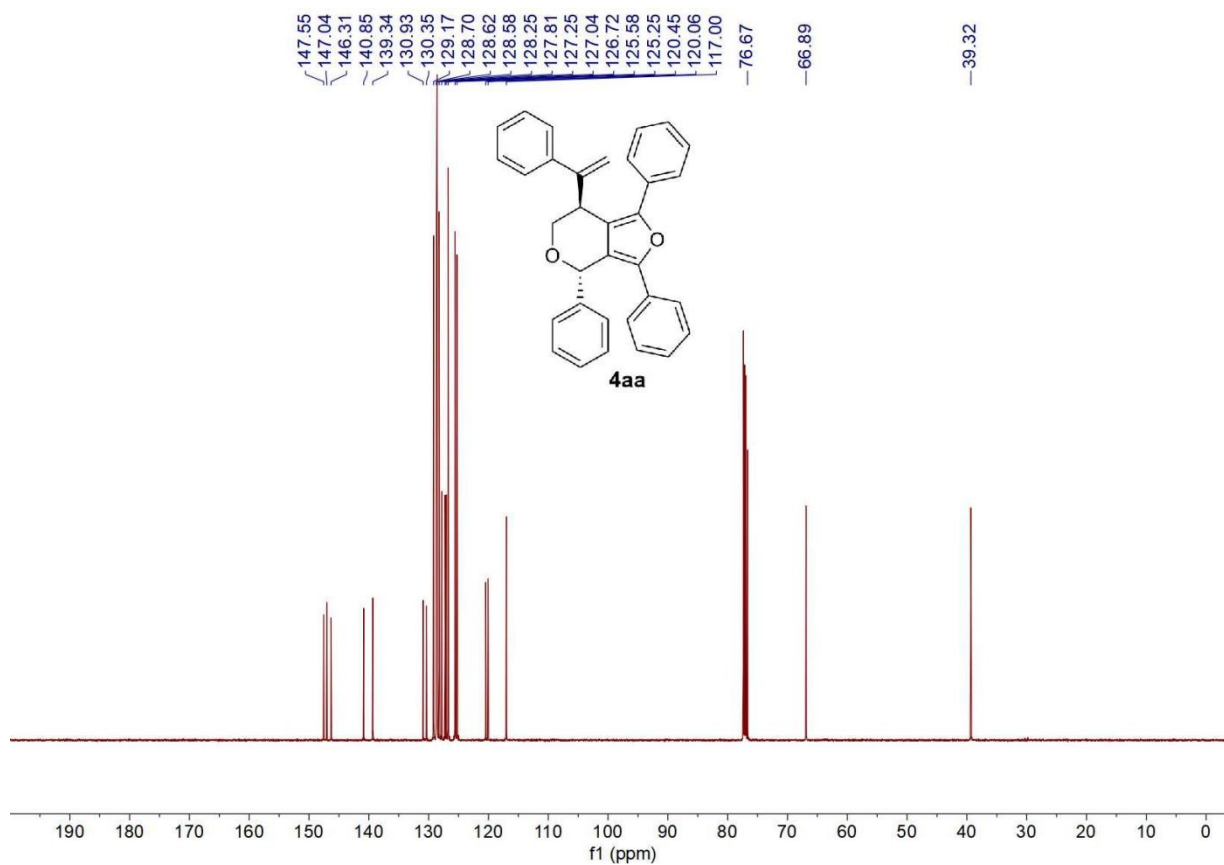
$^{13}\text{C}\{^1\text{H}\}$ NMR (151 MHz, CDCl_3) for **3ah**



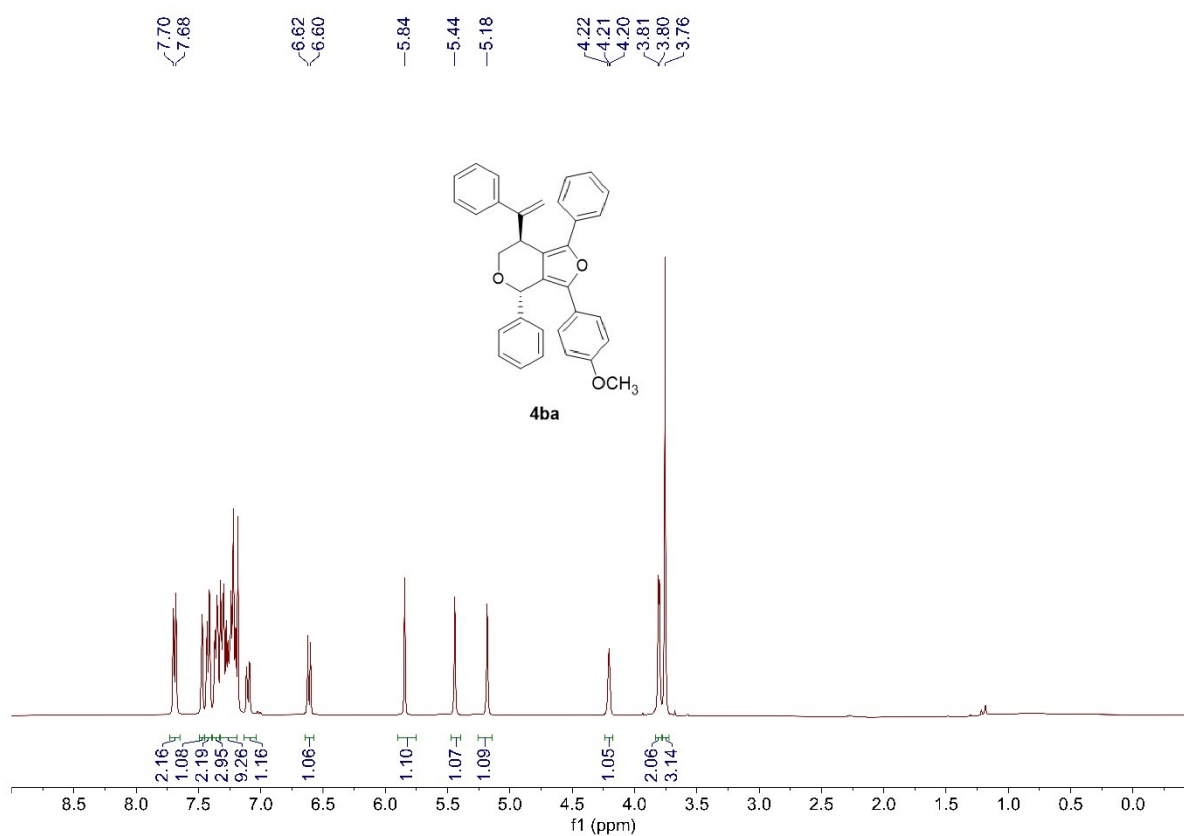
^1H NMR (600 MHz, CDCl_3) for **4aa**



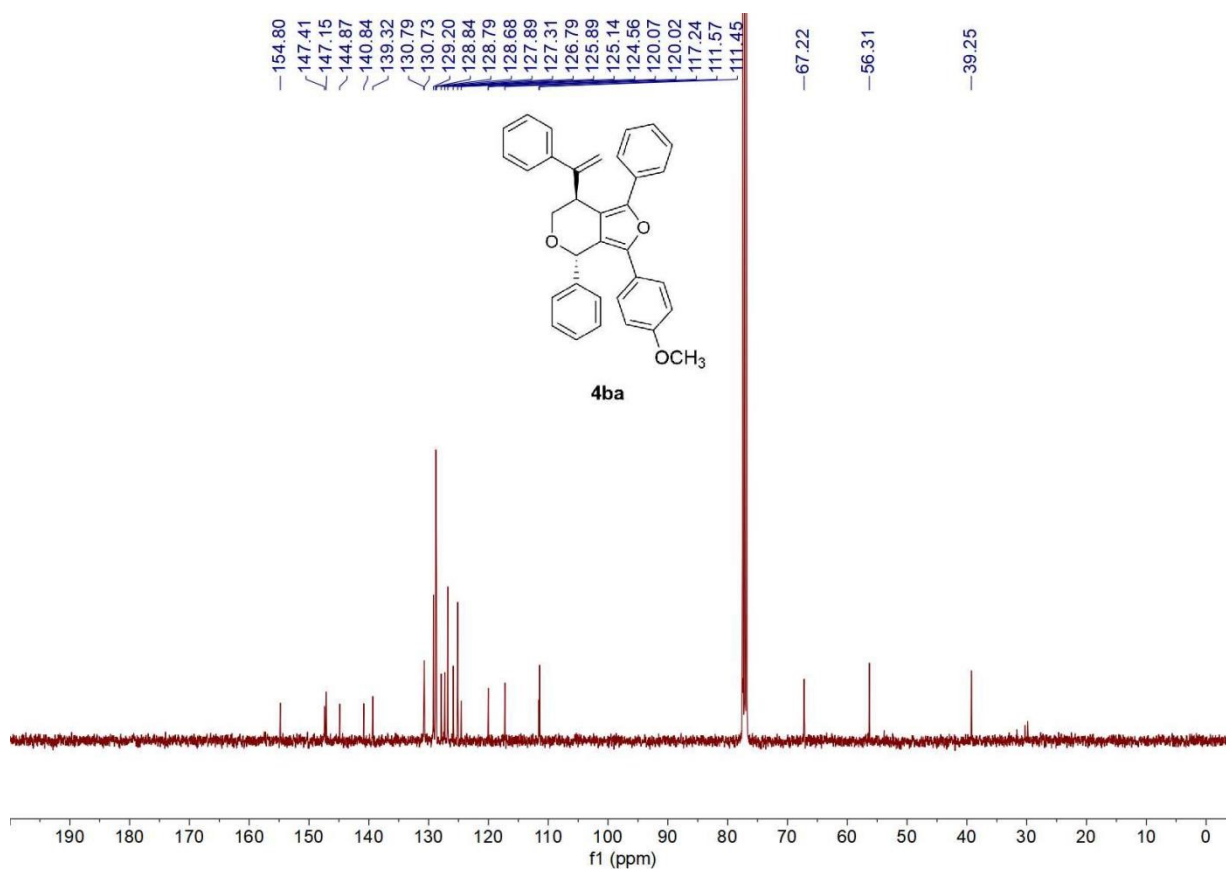
$^{13}\text{C}\{^1\text{H}\}$ NMR (151 MHz, CDCl_3) for **4aa**



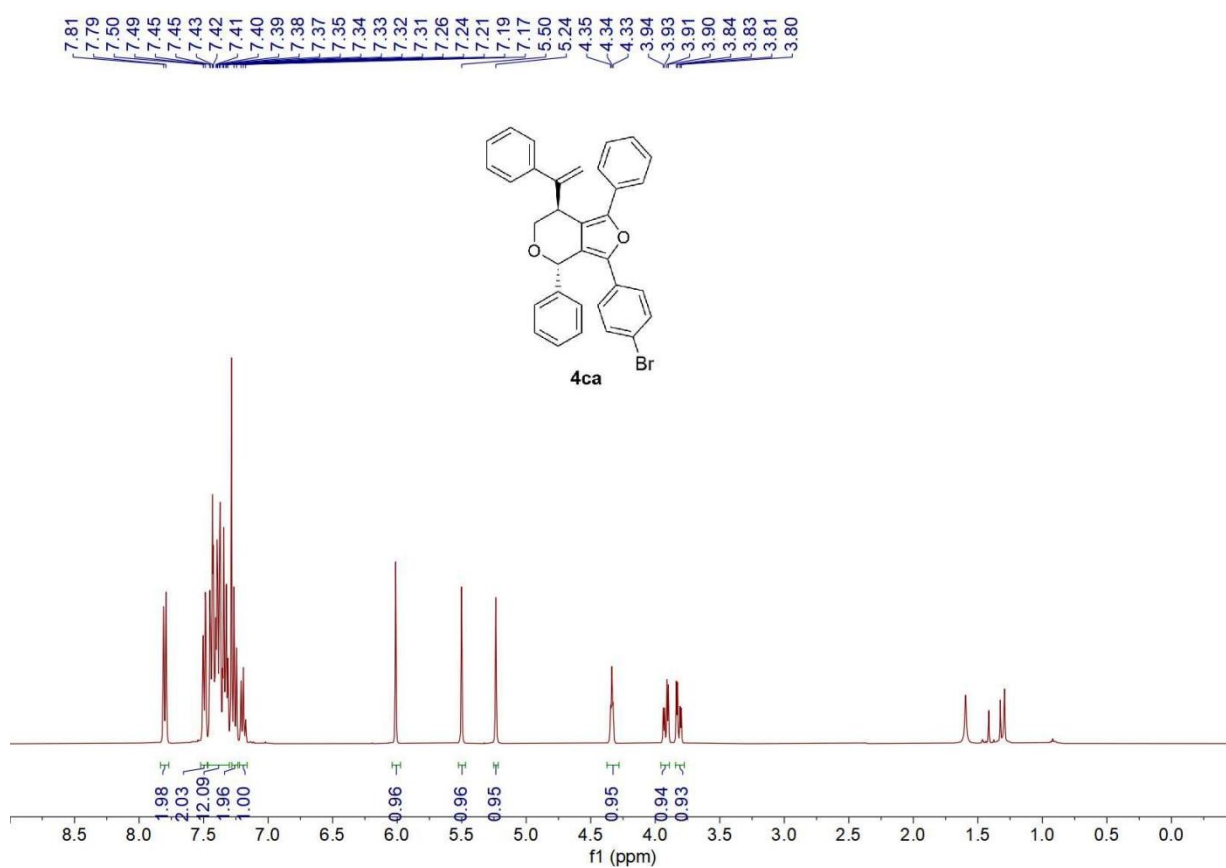
^1H NMR (400 MHz, CDCl_3) for **4ba**



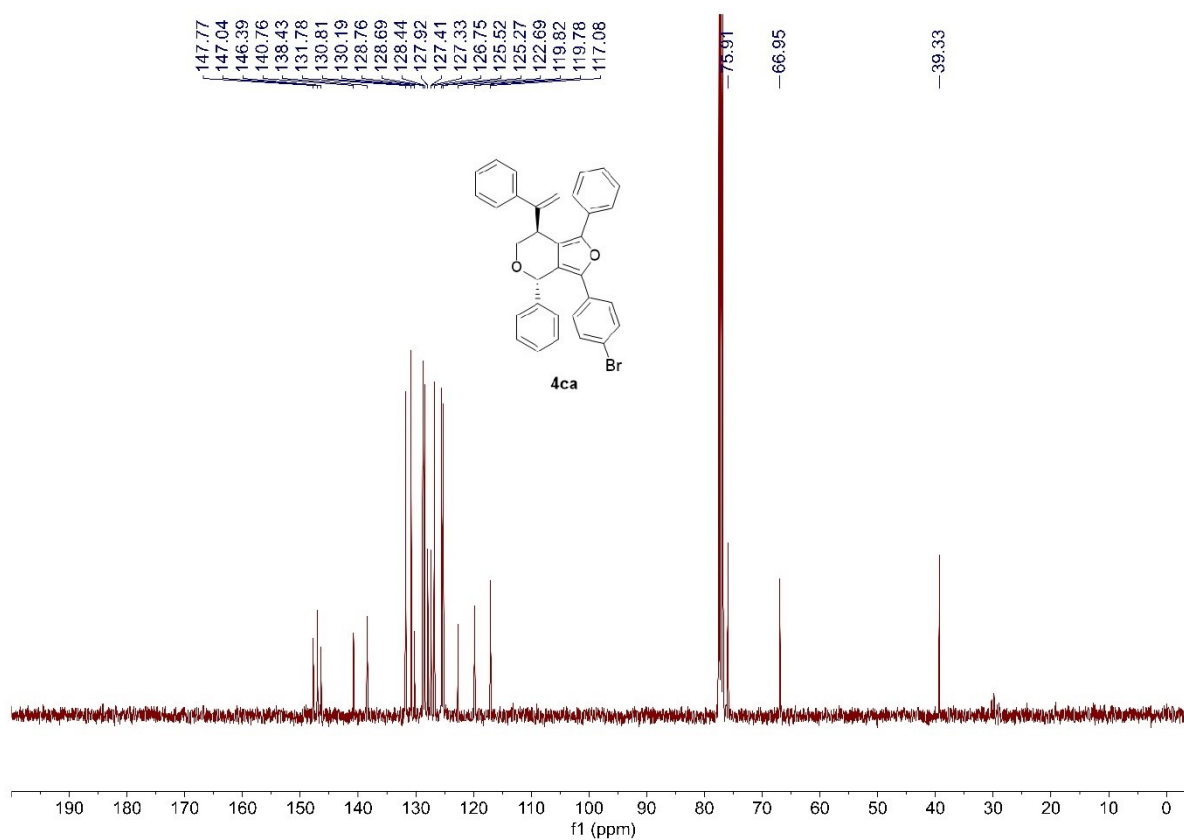
$^{13}\text{C}\{^1\text{H}\}$ NMR (101 MHz, CDCl_3) for **4ba**



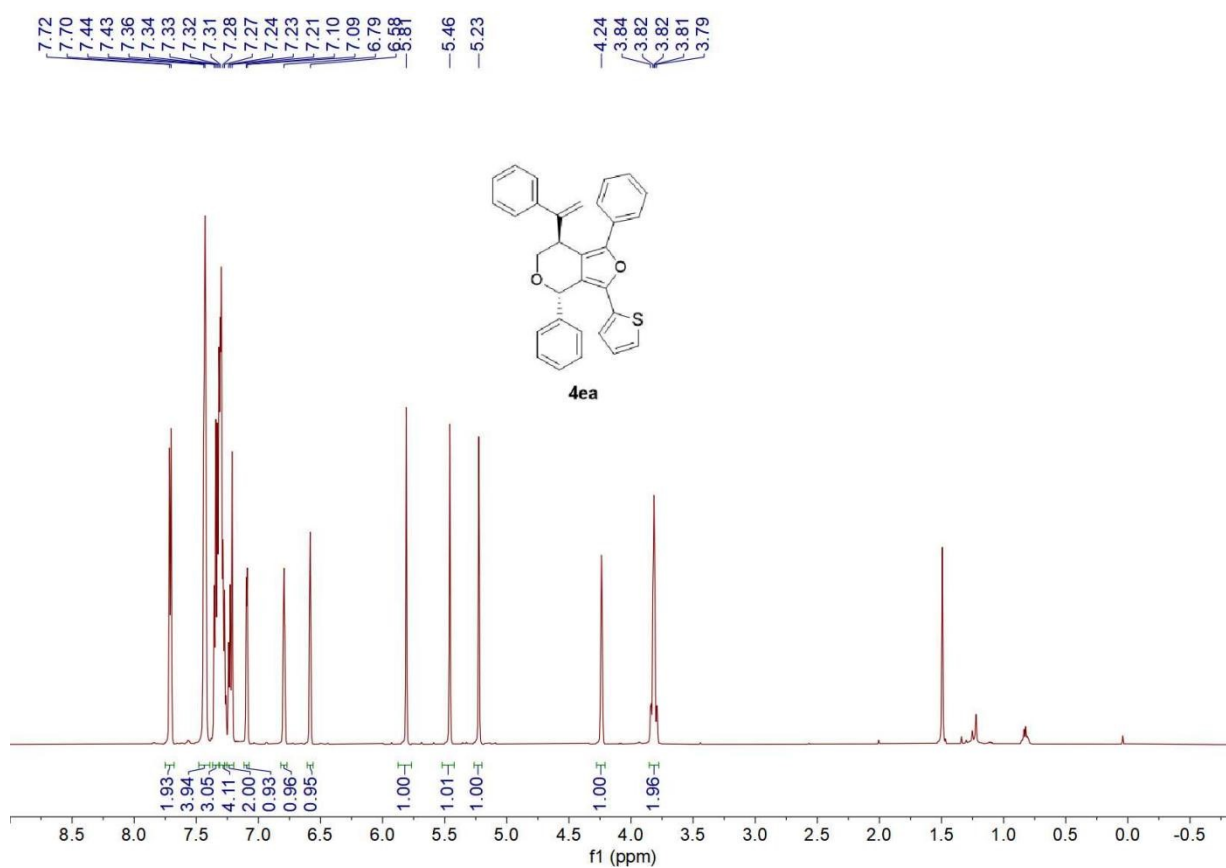
^1H NMR (400 MHz, CDCl_3) for **4ca**



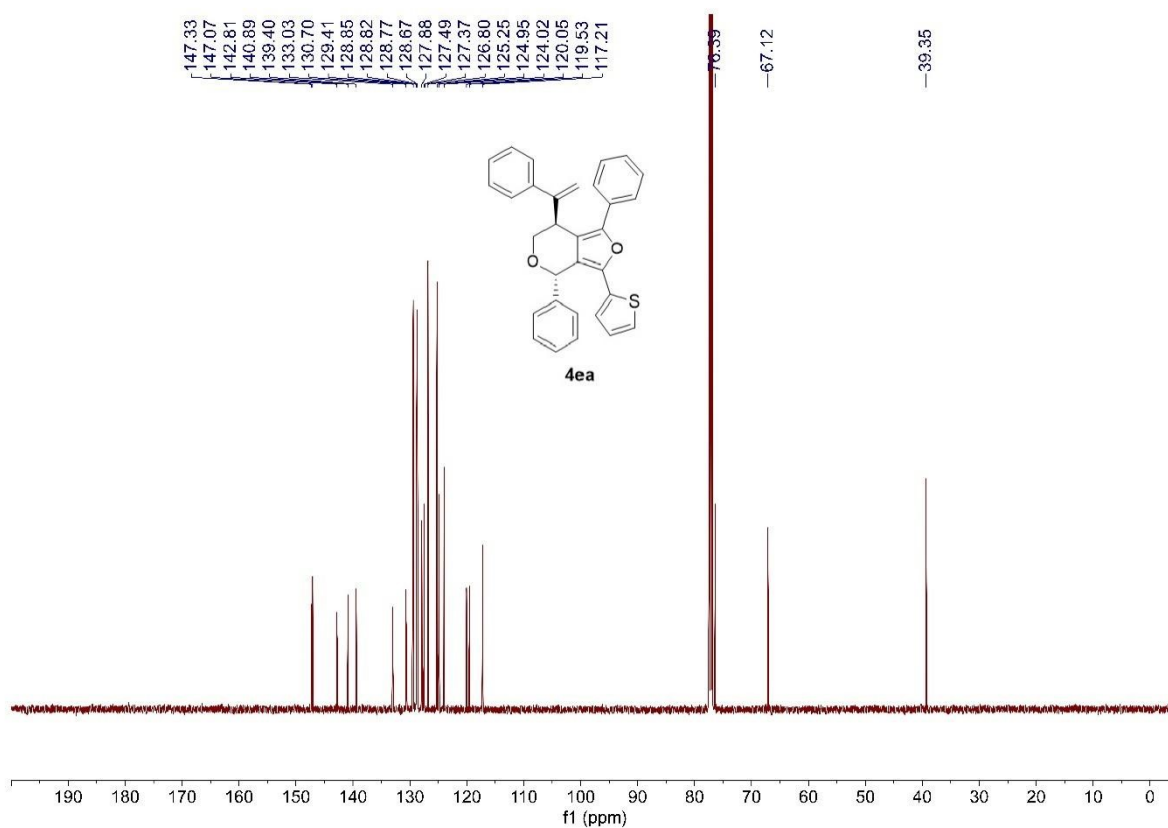
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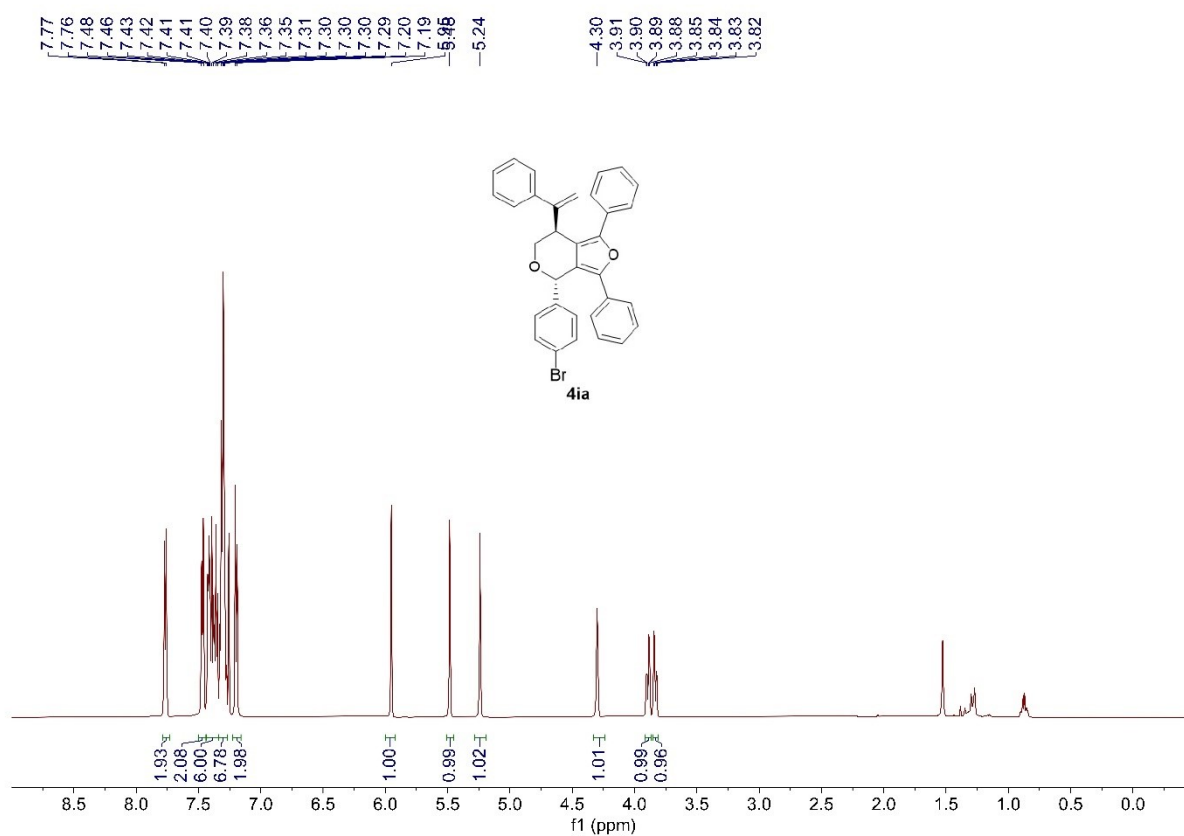
^1H NMR (600 MHz, CDCl_3) for **4ea**



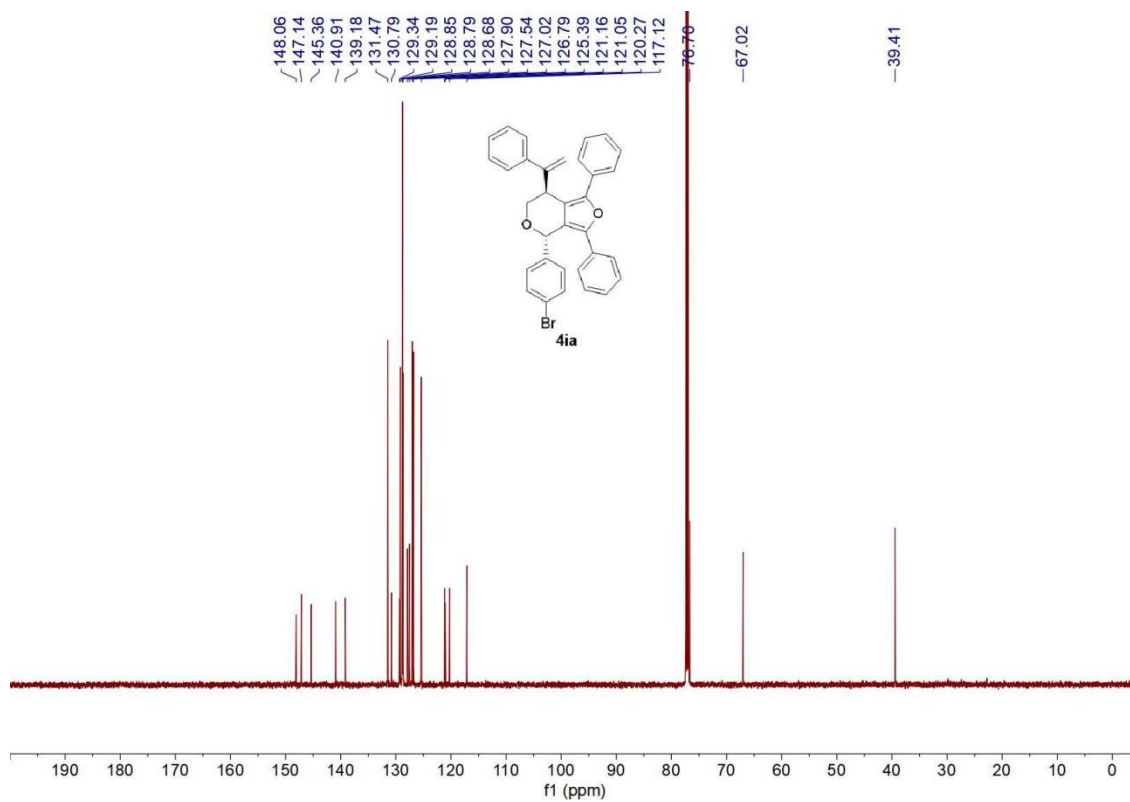
$^{13}\text{C}\{^1\text{H}\}$ NMR (151 MHz, CDCl_3) for **4ea**



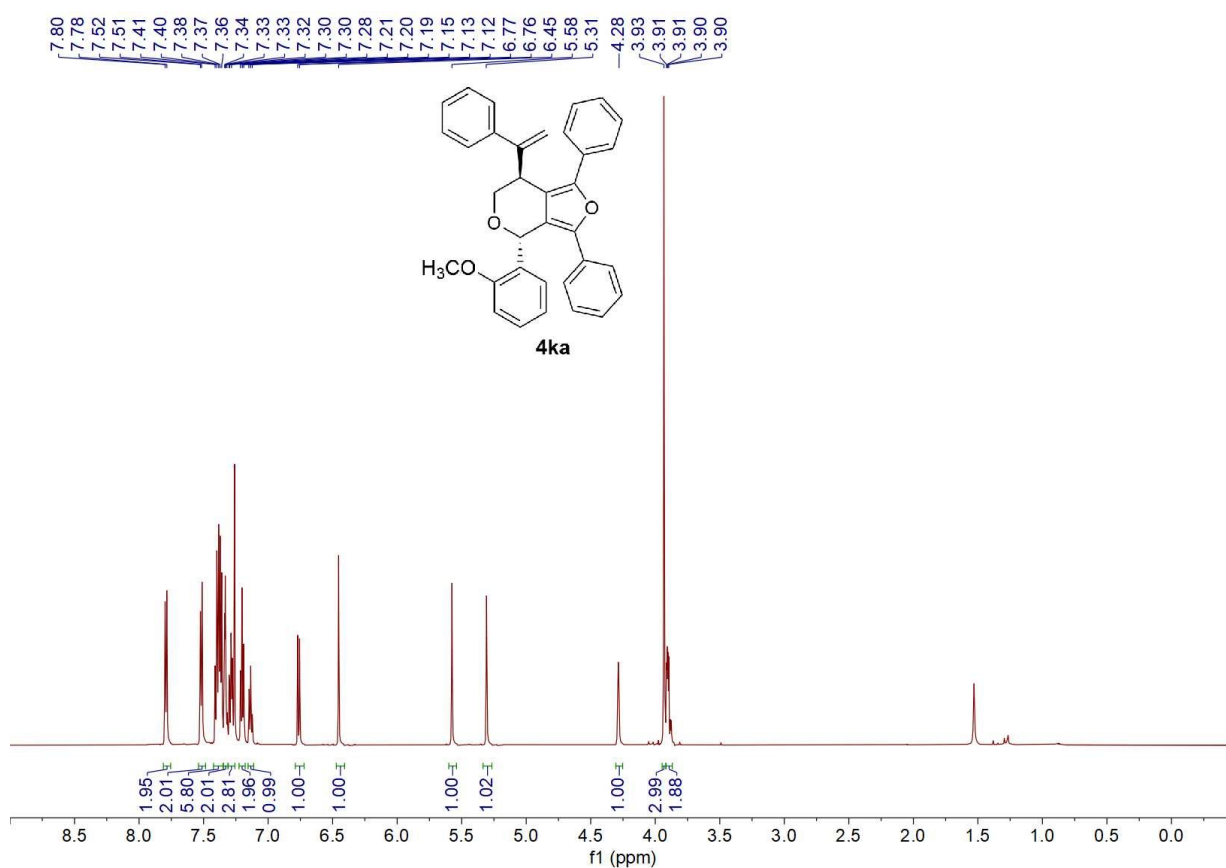
^1H NMR (600 MHz, CDCl_3) for **4ia**



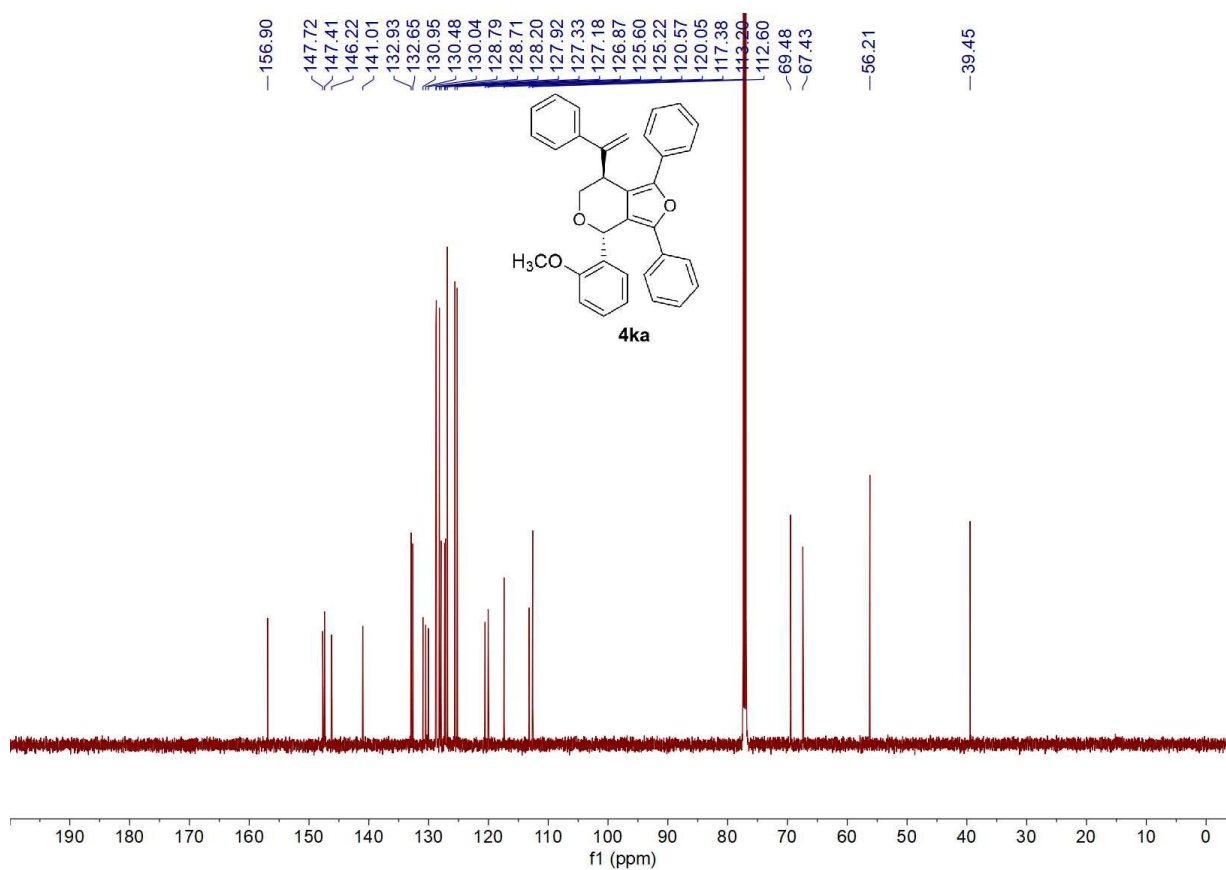
$^{13}\text{C}\{^1\text{H}\}$ NMR (151 MHz, CDCl_3) for **4ia**



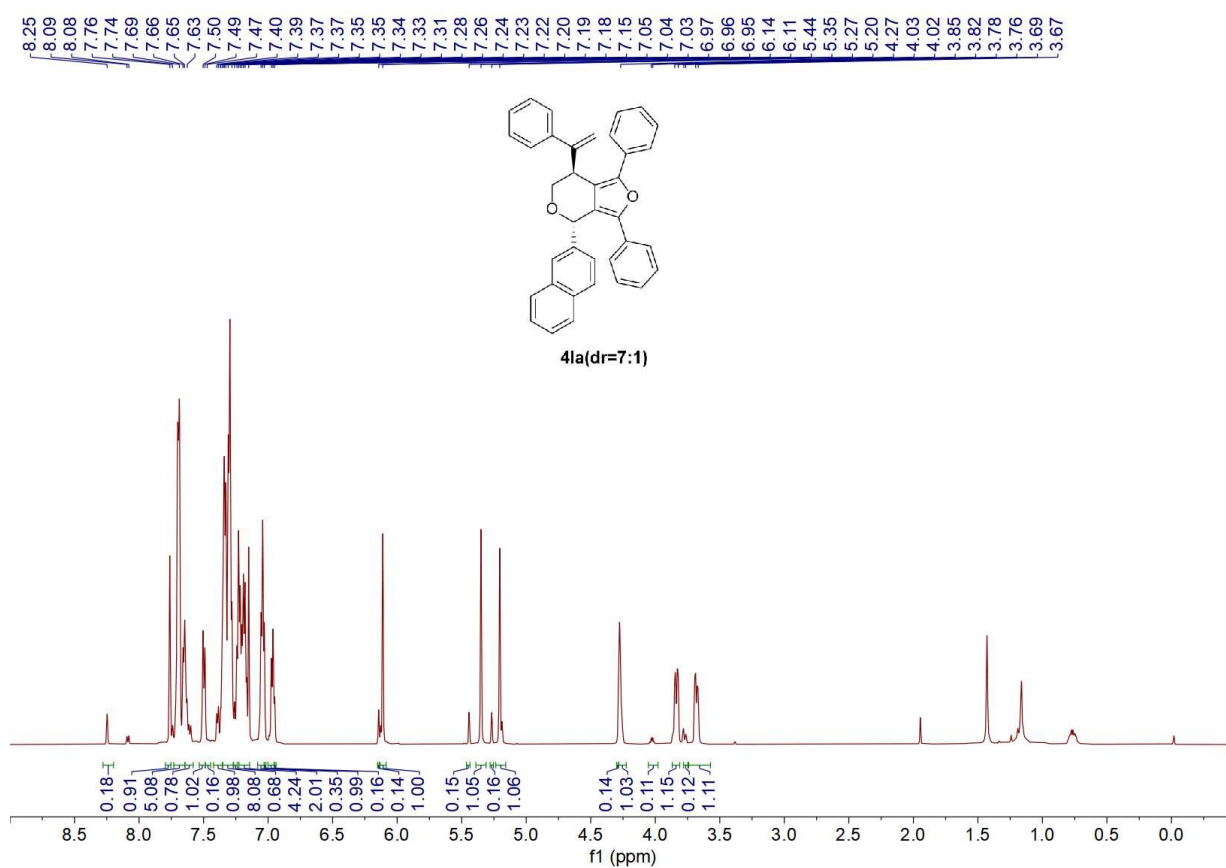
^1H NMR (600 MHz, CDCl_3) for **4ka**



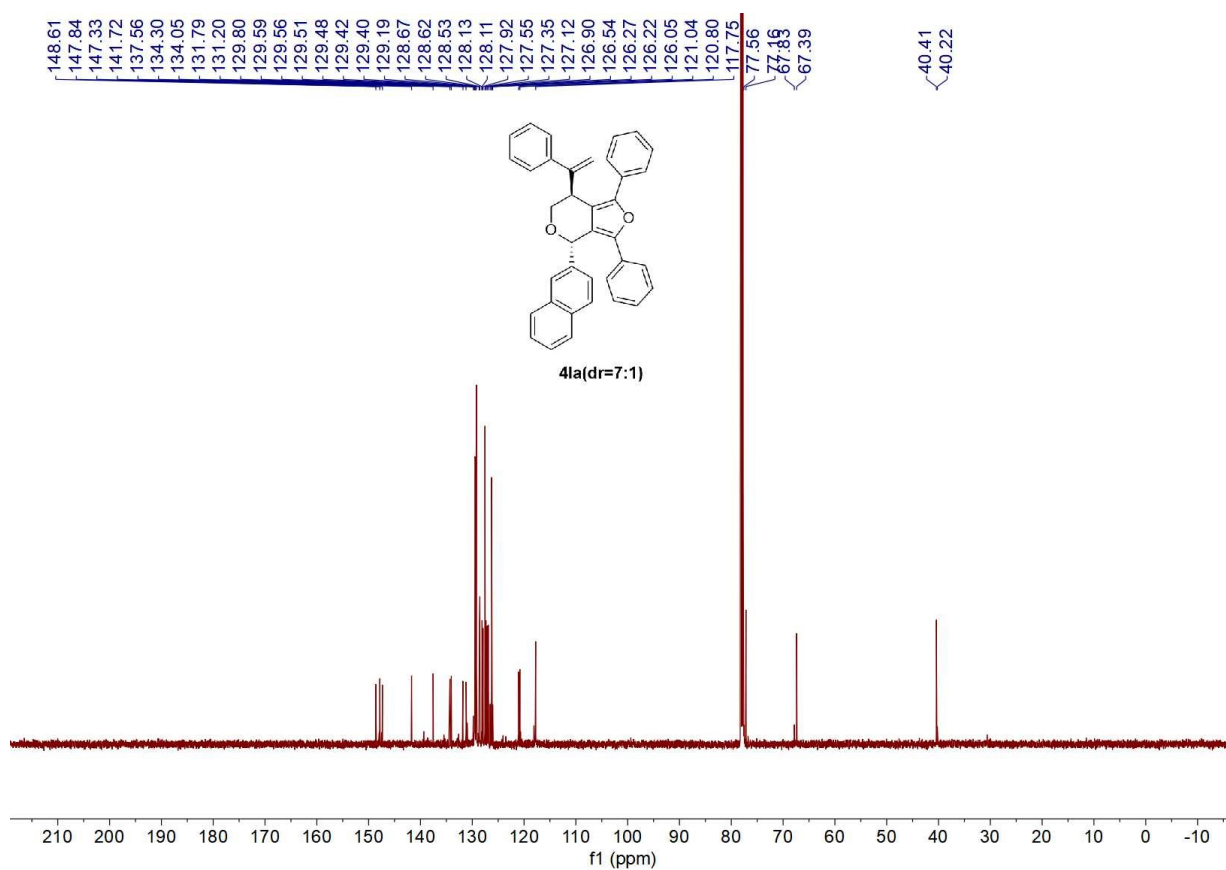
$^{13}\text{C}\{^1\text{H}\}$ NMR (151 MHz, CDCl_3) for **4ka**



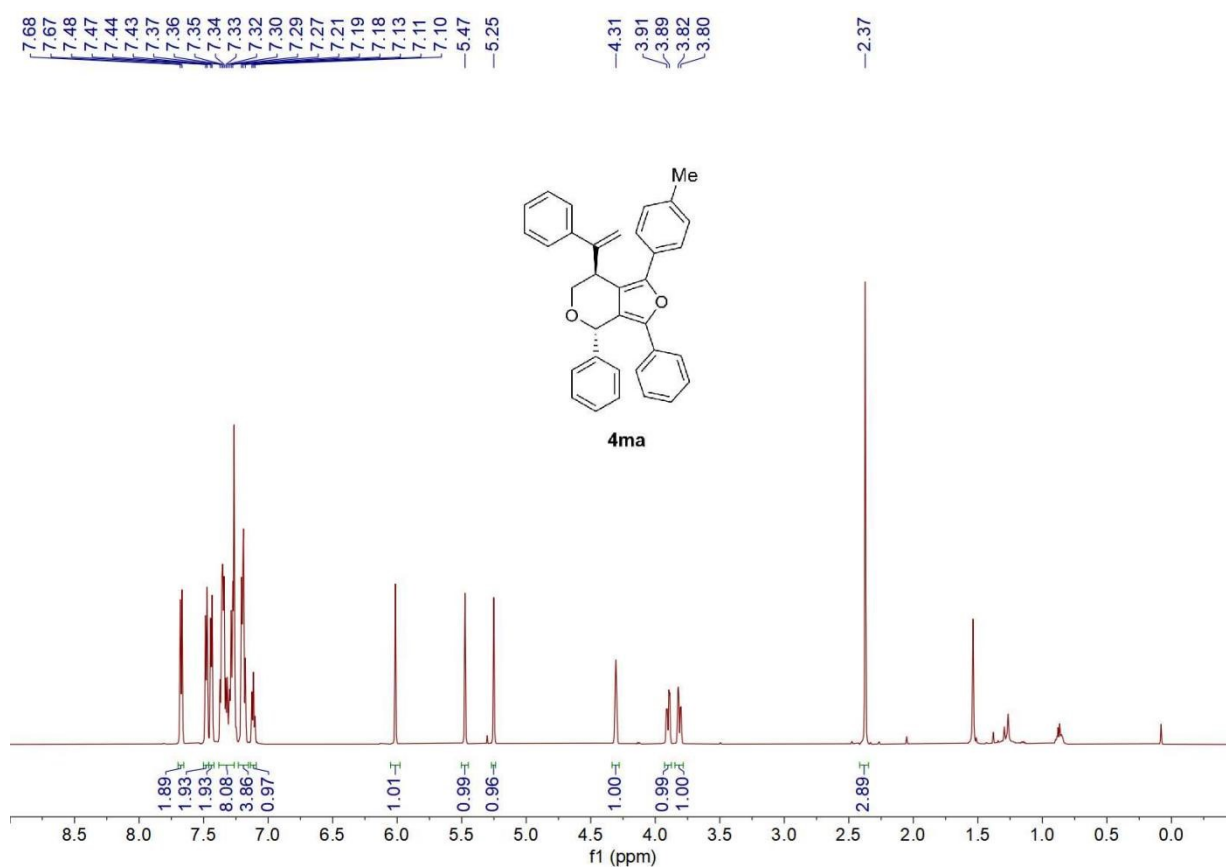
^1H NMR (600 MHz, CDCl_3) for **4la**



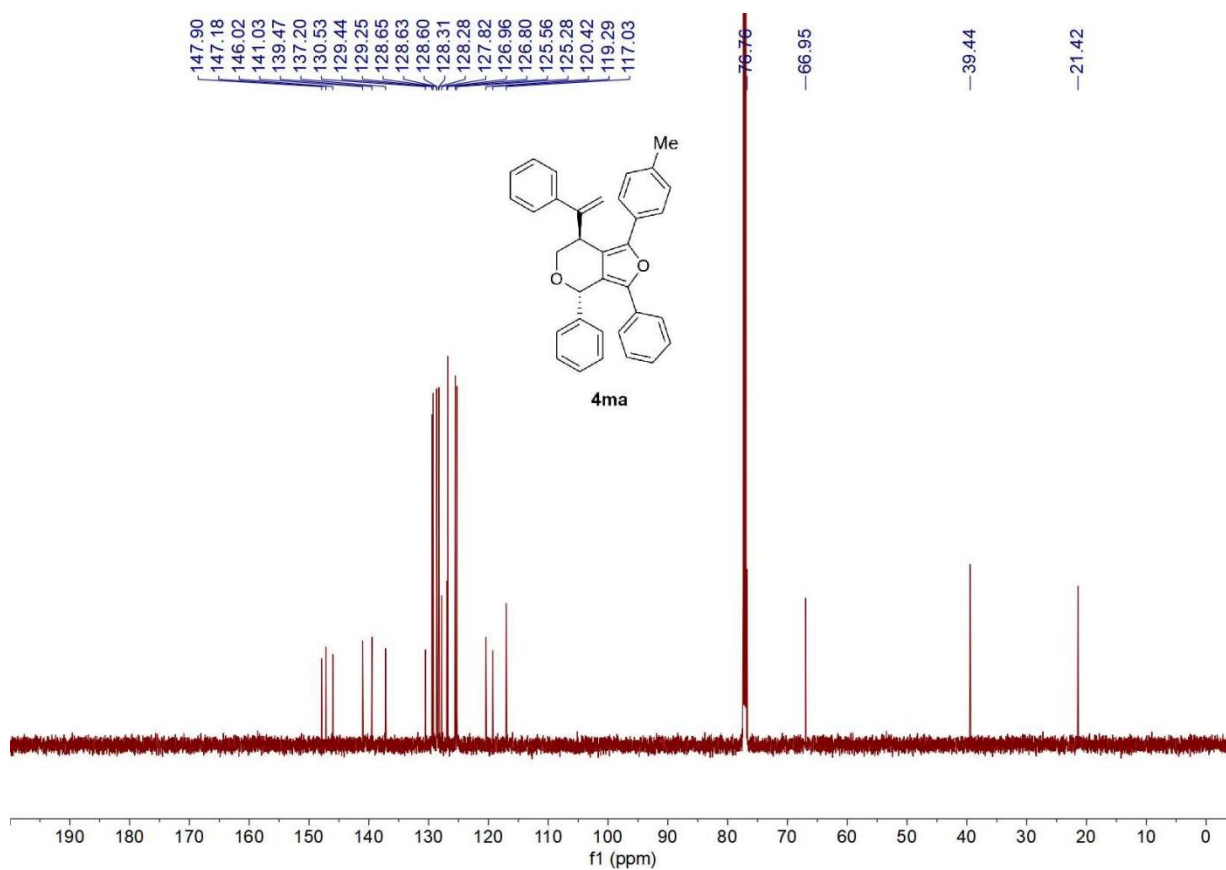
$^{13}\text{C}\{^1\text{H}\}$ NMR (151 MHz, CDCl_3) for **4la**



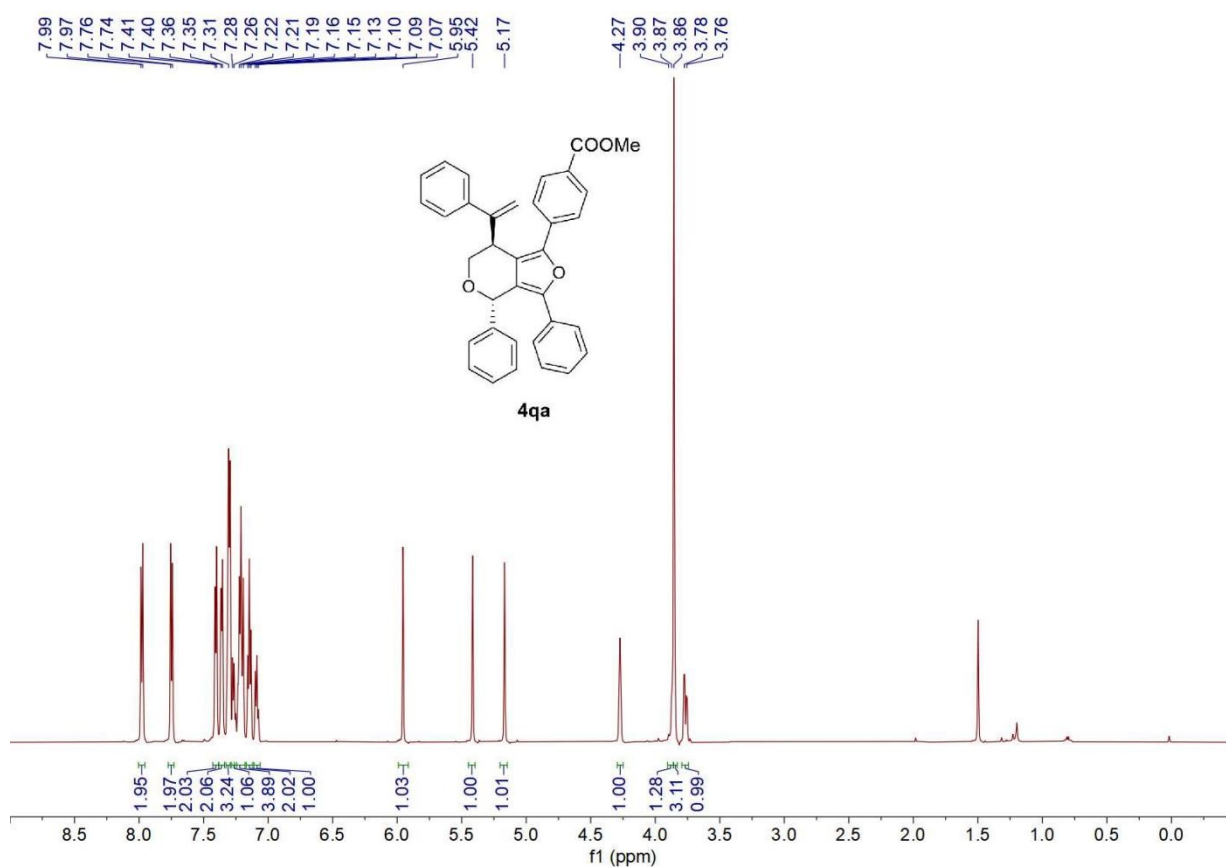
^1H NMR (600 MHz, CDCl_3) for **4ma**



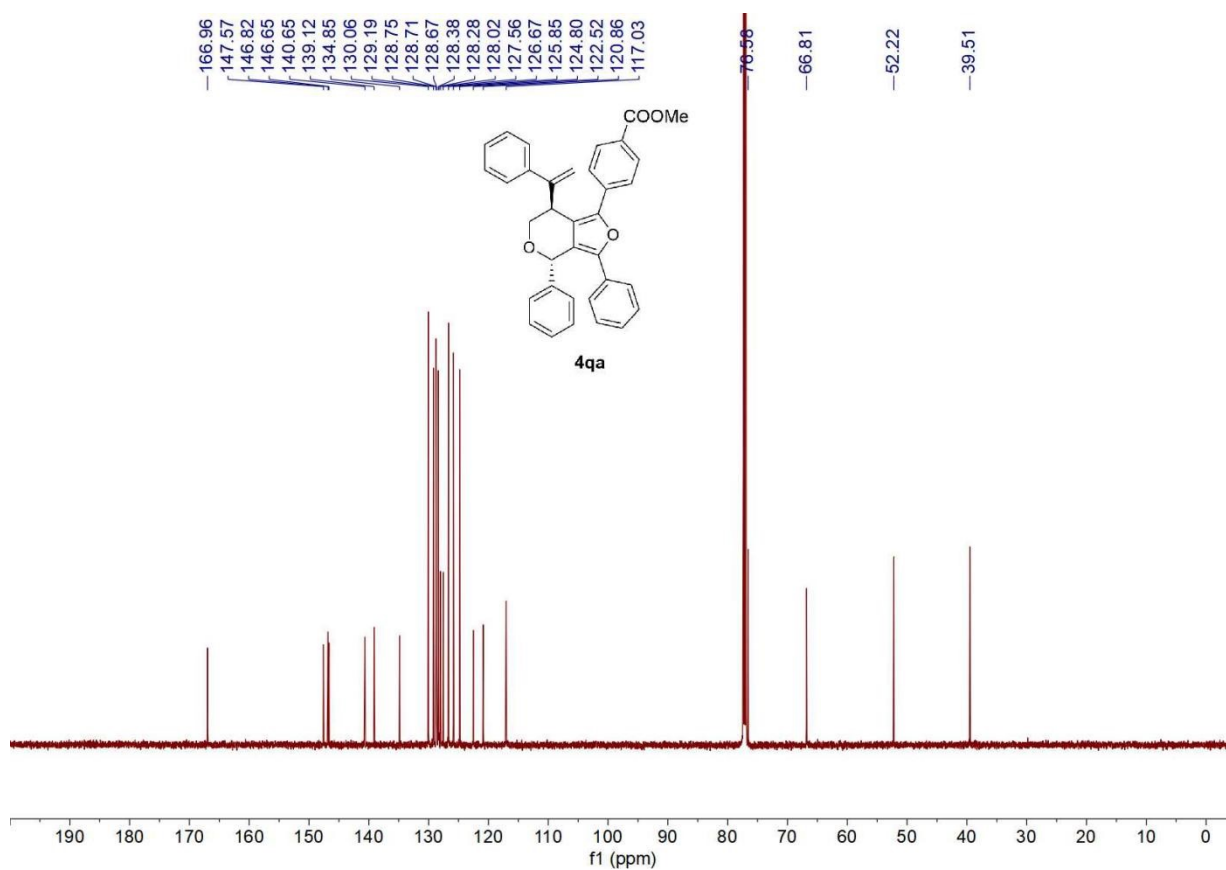
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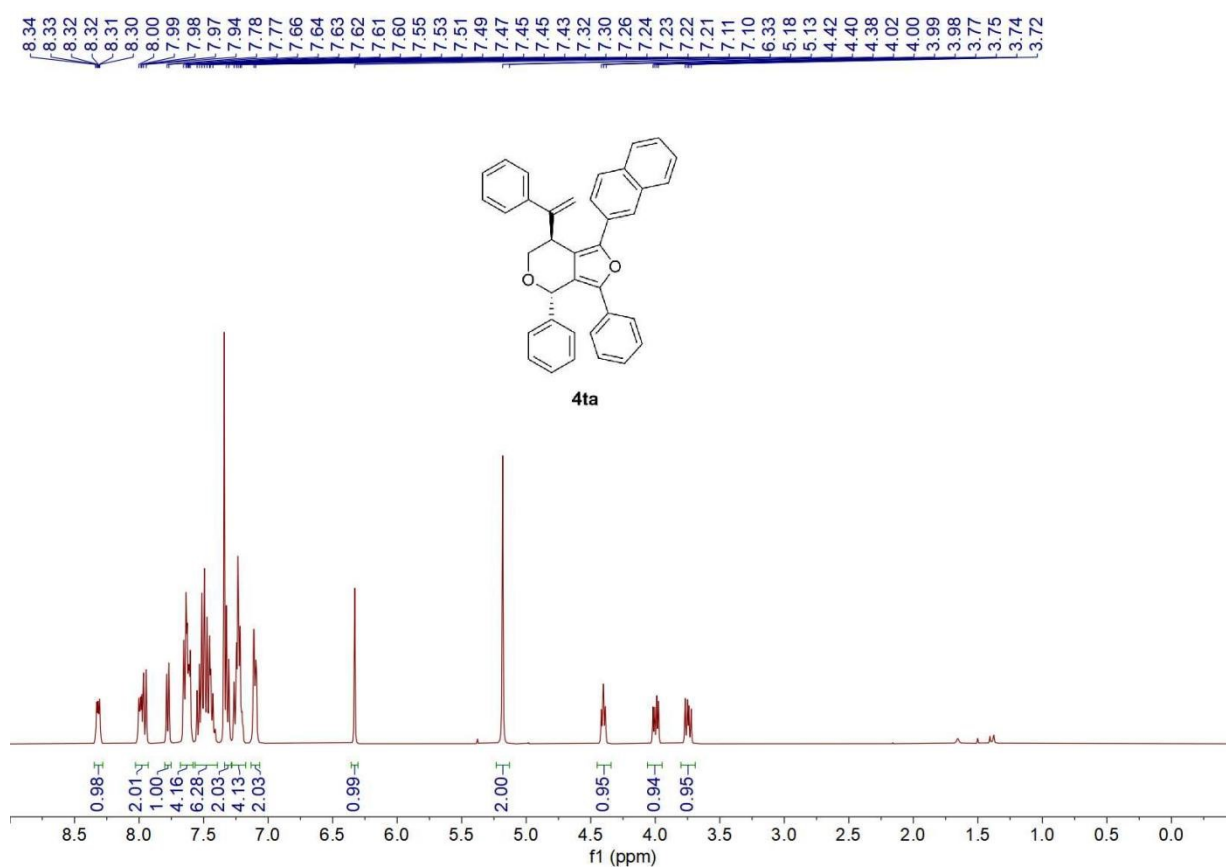
^1H NMR (600 MHz, CDCl_3) for **4qa**



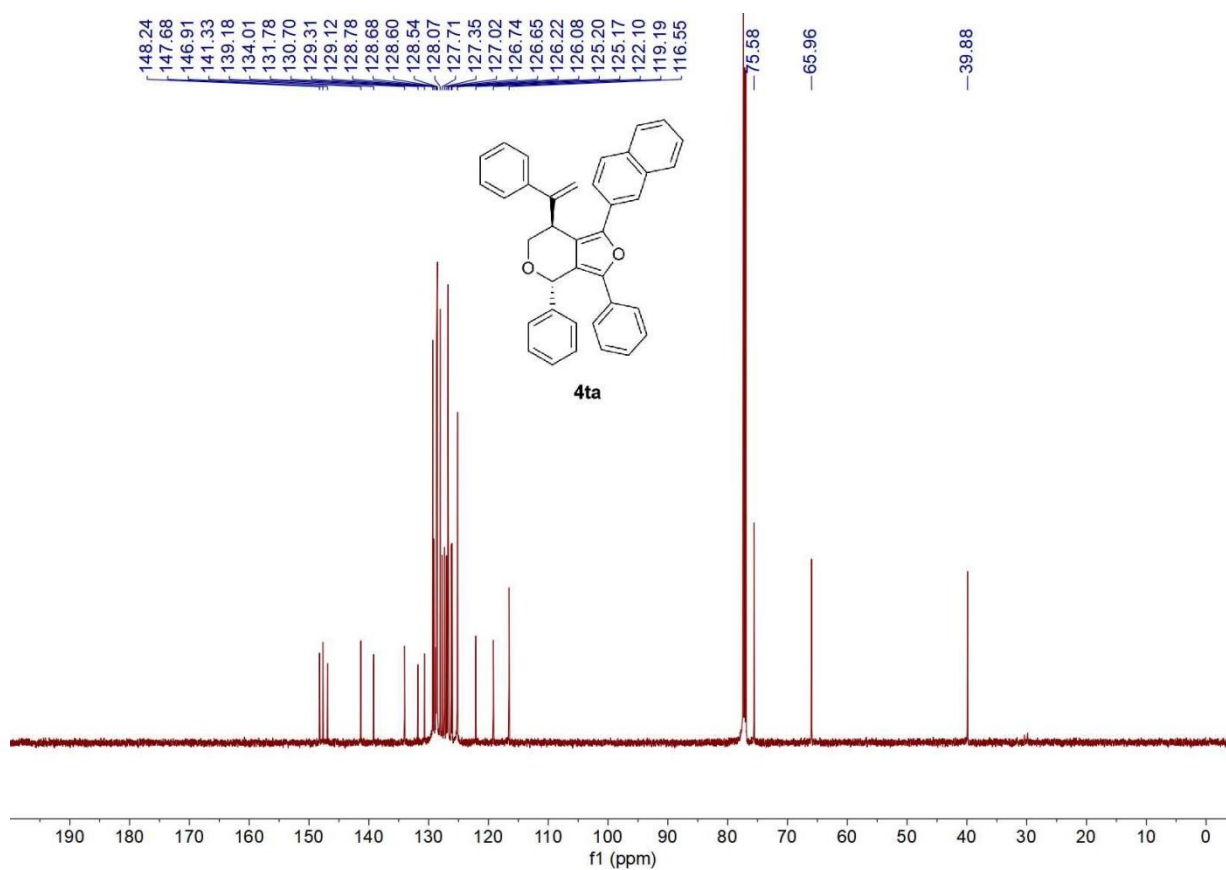
$^{13}\text{C}\{^1\text{H}\}$ NMR (151 MHz, CDCl_3) for **4qa**



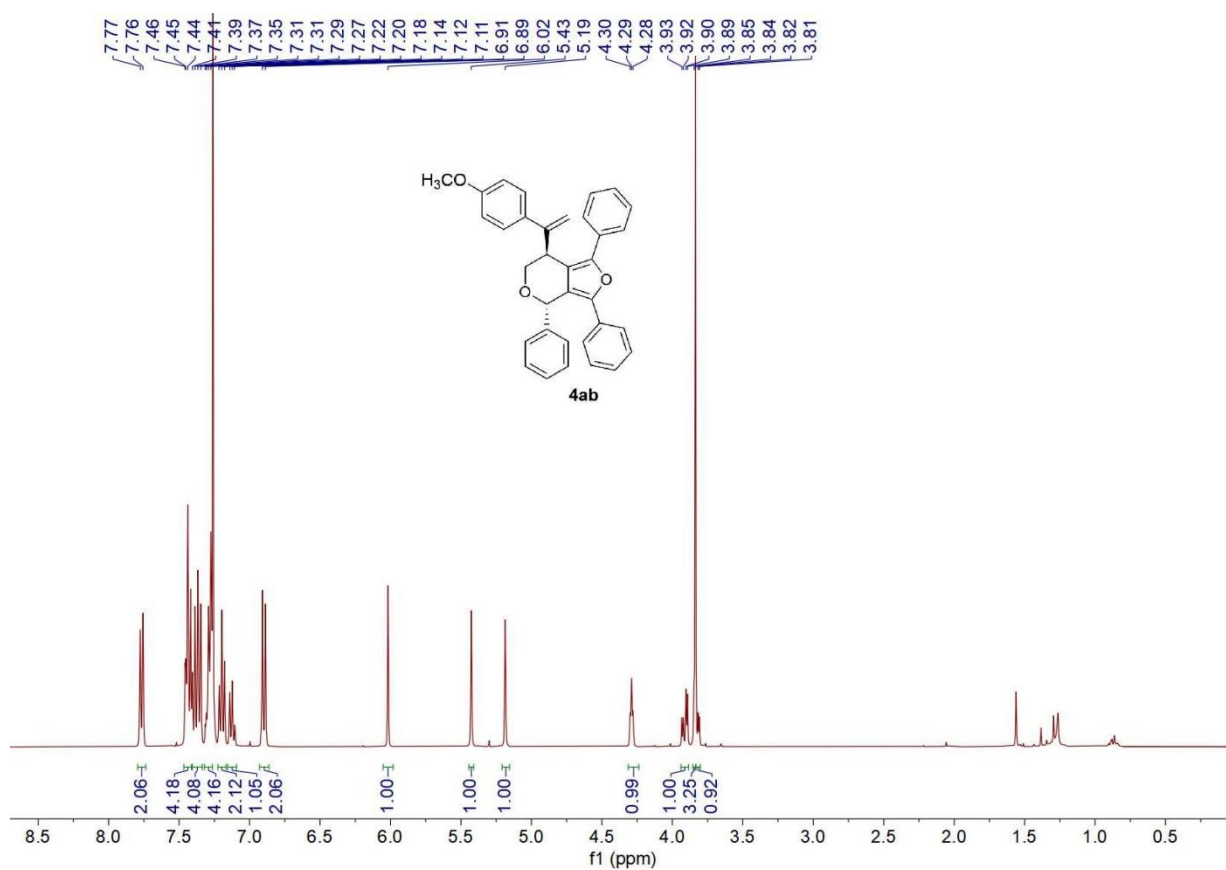
^1H NMR (600 MHz, CDCl_3) for **4ta**



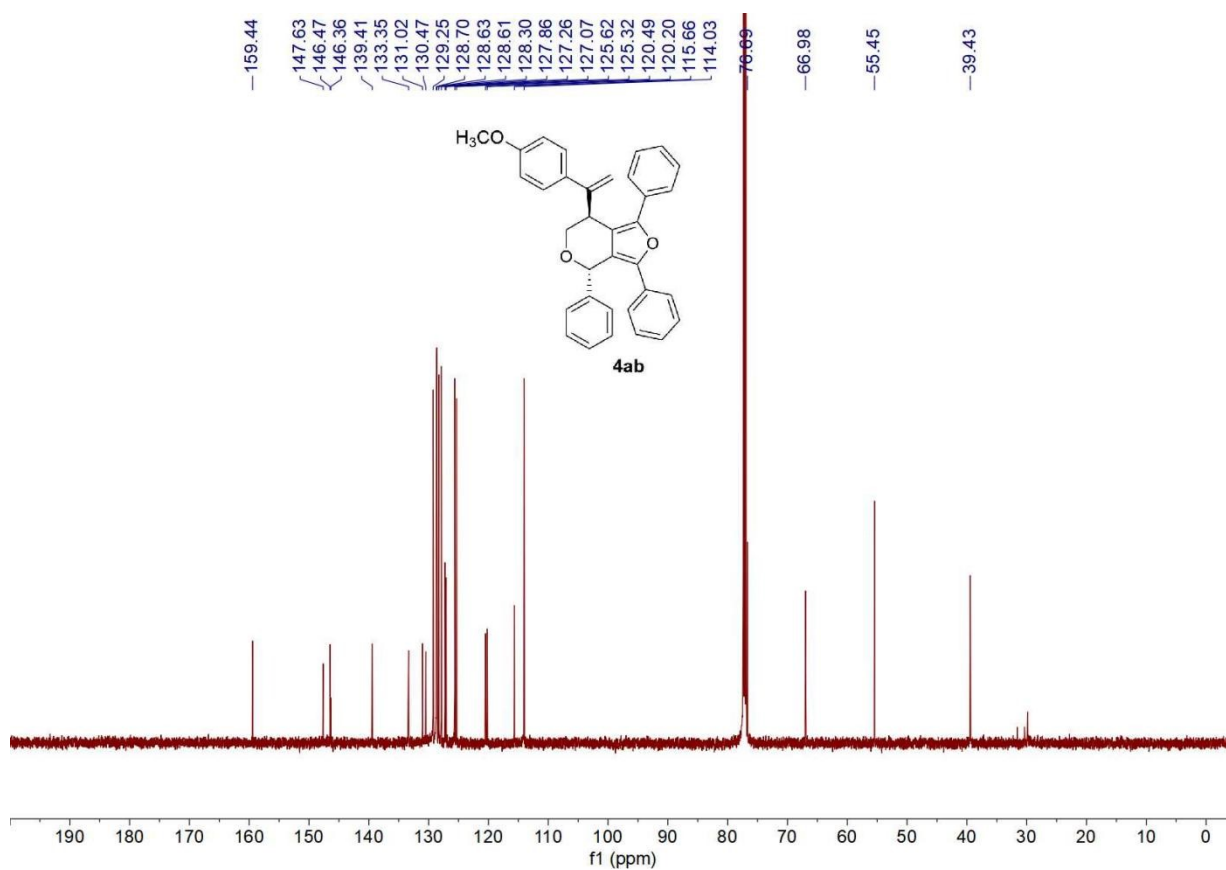
$^{13}\text{C}\{^1\text{H}\}$ NMR (151 MHz, CDCl_3) for **4ta**



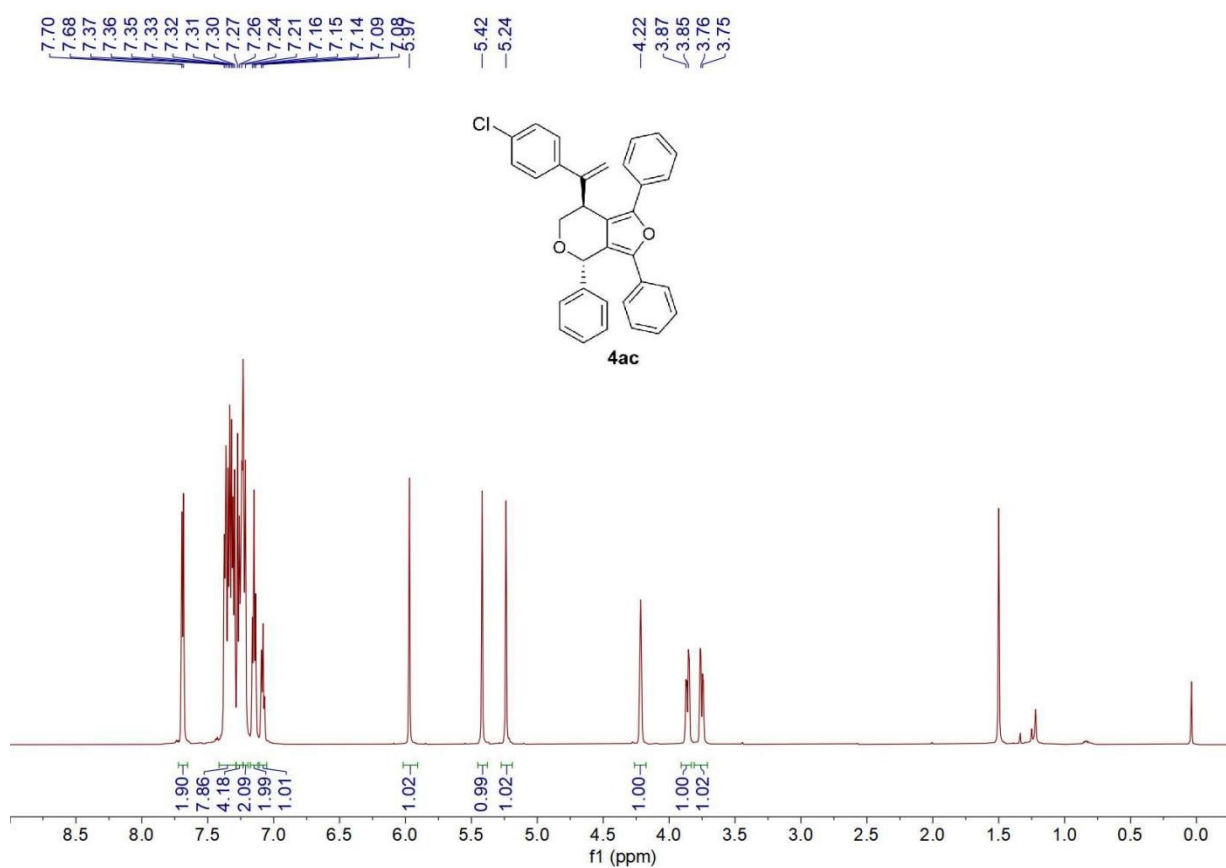
^1H NMR (600 MHz, CDCl_3) for **4ab**



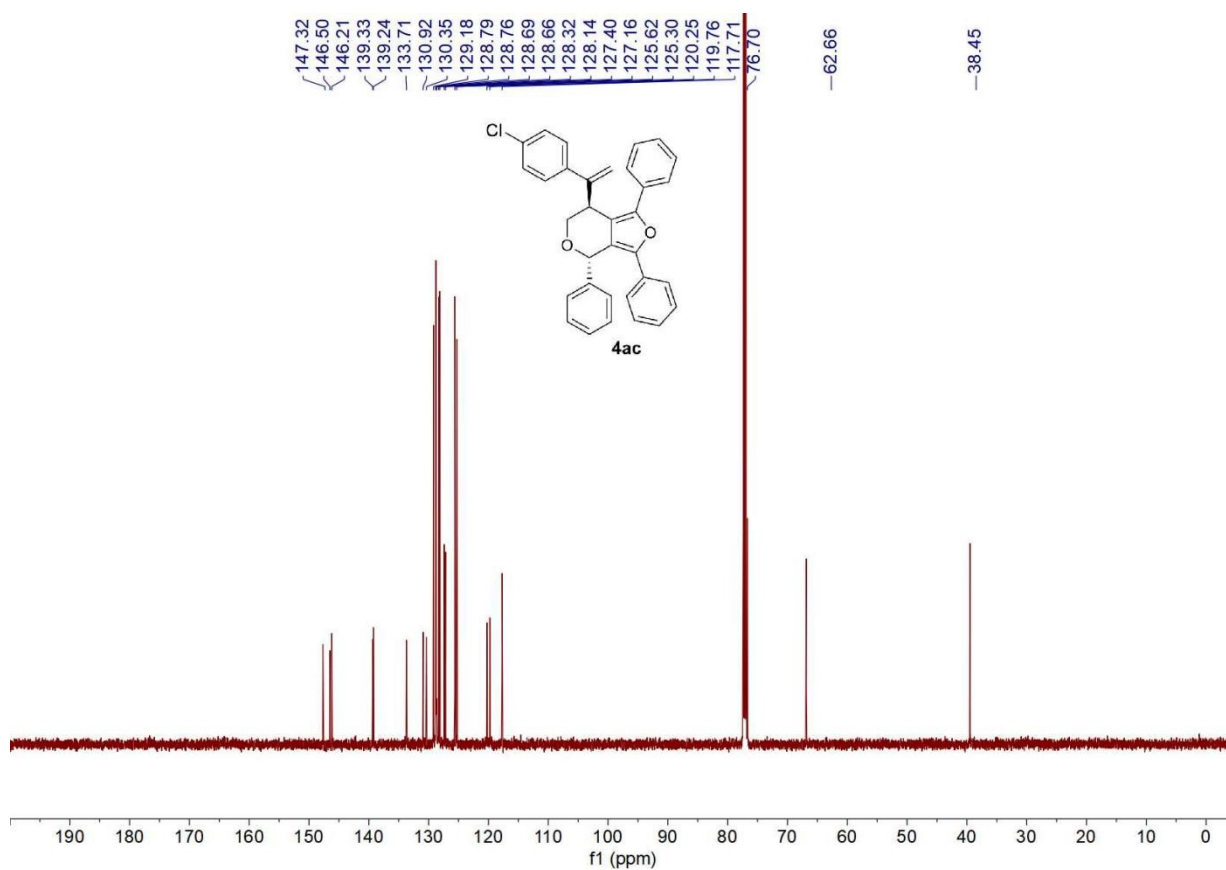
$^{13}\text{C}\{^1\text{H}\}$ NMR (151 MHz, CDCl_3) for **4ab**



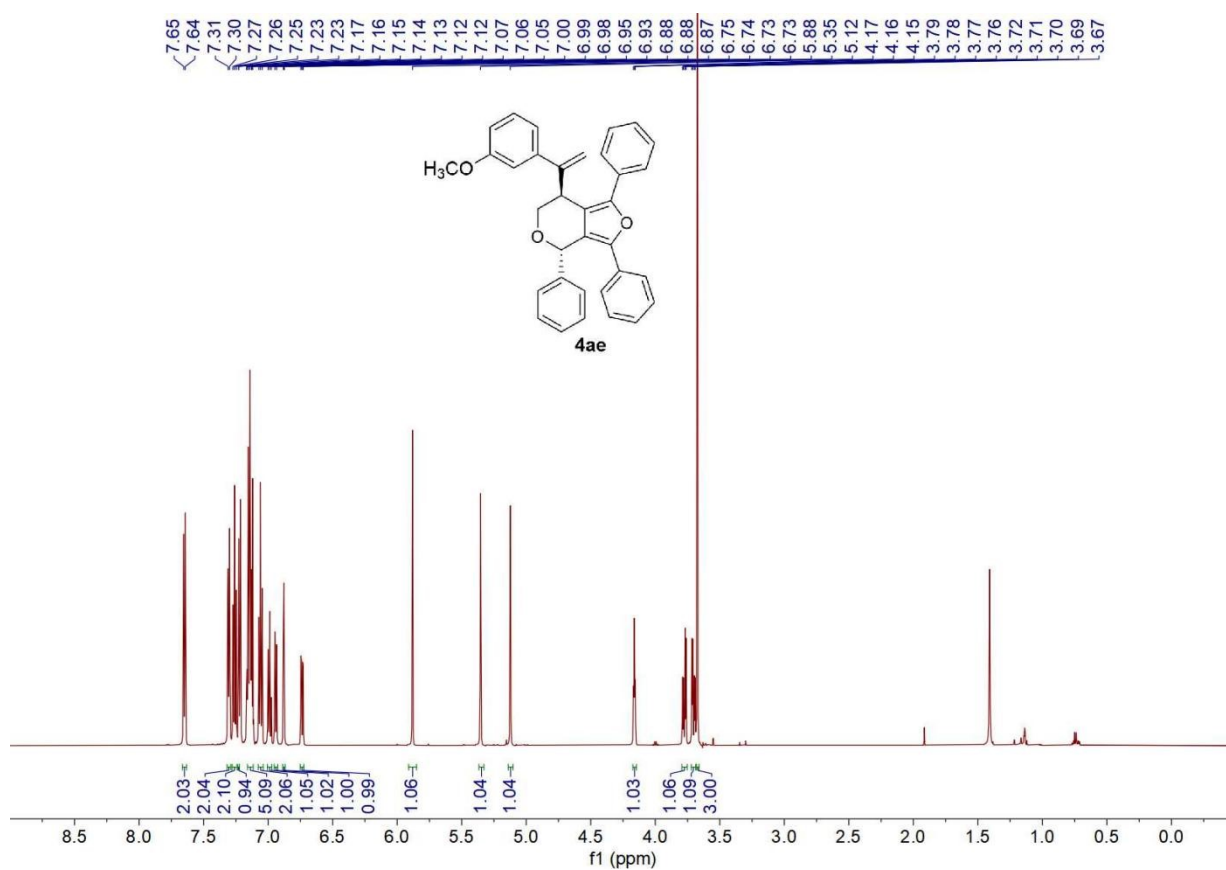
^1H NMR (600 MHz, CDCl_3) for **4ac**



$^{13}\text{C}\{^1\text{H}\}$ NMR (151 MHz, CDCl_3) for **4ac**



^1H NMR (600 MHz, CDCl_3) for **4ae**



$^{13}\text{C}\{^1\text{H}\}$ NMR (151 MHz, CDCl_3) for **4ae**

