Electronic Supplementary Information

Facile single-step synthesis of pentaaryl-substituted pyrano[3,2-*b*] pyrrol-5(1*H*)-ones showing aggregation-induced emission

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1. General information

Unless stated otherwise, all reagents and solvents were obtained from commercial sources and used without further purification. 2,3-Diaryl cyclopropenones were prepared according to literature procedures.[1] Reactions were monitored by thin-layer chromatographic (TLC) analysis. Column chromatography was performed using silica gel (200–300 mesh). ^{1}H spectra were recorded in $CDCl_3$ or DMSO-d_6 on a Bruker Avance II 300 MHz NMR spectrometer and resonances (δ) are given in parts per million relative to tetramethylsilane (internal standard). Data are reported as follows: chemical shift, multiplicity (s = singlet, d = doublet, t = triplet, m = multiplet), coupling constants (Hz) and integration. ^{13}C spectra were recorded in $CDCl_3$ or DMSO-d_6 on a 75 MHz NMR spectrometer and resonances (δ) are given in ppm. IR spectra were recorded on a Nicolet 5700 FTIR infrared spectrometer as KBr pellets with absorption in cm^{-1}. Melting points were determined using an uncorrected X-4 apparatus. High-resolution mass spectrometry (HRMS) data were obtained on an Agilent QTOF 6540 MS/Thermo Scientific LTQ Orbitrap XL equipped with an electrospray source. The X-ray crystal structure determination was performed using a Bruker SMART APEX CCD system. The UV-vis absorption data were determined on a METASH UV spectrometer, and the PL emission data were determined on a Shimadzu RF-6000 fluorescence spectrometer. Density Functional Theory (DFT) calculations were optimized on a Gaussian 16 program B3LYP/6-31G(d) basis group.

2. General procedures for the synthesis of products 4-12

2.1 Synthesis of products 4-6

A 25 mL sealed tube was charged with isatins **1** (0.2 mmol, 1.0 equiv.), 2,3-diaryl cyclopropenones **2** (0.4 mmol, 2.0 equiv.) and alkyl bromides **3** (0.5 mmol, 2.5 equiv.), then DBU (0.4 mmol, 2.0 equiv.) and ^{i}PrOH (3 mL) was added. The resulting mixture was stirred at 100 °C for 3 h. Upon completion of the reaction, the solvent was evaporated under reduced pressure and the residue was purified by column chromatography on silica gel (eluent: petroleum ether/EtOAc/DCM = 15:1:1~10:1:1) to afford the desired products **4-6**.

2.2 Synthesis of products 7 and 8[2]

A pressure tube was charged with **5f** (138.9 mg, 0.2 mmol), aromatic boronic acids (0.3 mmol, 1.5 equiv.), $Pd(PPh_3)_4$ (11.6 mg, 0.01 mmol) and Na_2CO_3 (106.0 mg, 1.0 mmol), then a mixture of toluene (1.0 mL) and H_2O (0.5 mL) was added as the solvent. The reaction was heated to reflux for 12 h under a nitrogen atmosphere. On completion, the reaction mixture was diluted with EtOAc (50 mL) and washed with brine (40 mL). The organic extracts were dried over anhydrous Na_2SO_4 and filtered. Concentration of the solution by rotary evaporation under reduced pressure gave a residue, which was purified by column chromatography on silica gel (eluent: petroleum ether/EtOAc = 5:1) to afford the desired products **7** (156.3 mg, 91% yield) and **8** (135.2 mg, 87% yield) as yellow solids, respectively.

2.3 Synthesis of product 9[3]

According to the literature procedures, a mixture of **5h** (132.1 mg, 0.2 mmol), stannous chloride (151.7 mg, 0.8 mmol), and hydrochloric acid (29.2 mg, 0.8 mmol) in ethanol (2 mL) was stirred at 90 °C for 10 h. After completion of the reaction, the solvent was volatilized and the crude product was separated by column chromatography on silica gel (eluent: petroleum ether/ EtOAc = 3:1) to provide product **9** as a yellow solid (99.7 mg, 79% yield).

2.4 Synthesis of product 10[2]

A pressure tube was charged with compound **6e** (130.4 mg, 0.14 mmol), (4-(diphenylamino)phenyl)boronic acid (242.8 mg, 0.84 mmol), $Pd(PPh_3)_4$ (32.4 mg, 0.028 mmol) and Na_2CO_3 (296.8 mg, 2.8 mmol), then a mixture of toluene (1.4 mL) and H_2O (0.7 mL) was added as the solvent. The reaction was heated to reflux for 12 h under a nitrogen atmosphere. On completion, the resulting mixture was diluted with EtOAc (50 mL) and washed with brine (40 mL). The organic extracts were dried over anhydrous Na_2SO_4 and concentrated under reduced pressure. The residue was purified by column chromatography on silica gel (eluent: petroleum ether/EtOAc/DCM = 5:1:1) to give product **10** as a bright yellow solid (189.1 mg, 85% yield).

2.5 Synthesis of product 11

A 25 mL sealed tube was charged with isatin (**1a**) (29.4 mg, 0.2 mmol) and 2,3-diphenyl cyclopropenone (**2a**) (82.5 mg, 0.4 mmol), then DBU (60.9 mg, 0.4 mmol) and ^{i}PrOH (3 mL) was added. The resulting mixture was stirred at 100 °C for 3 h. Upon completion of the reaction, the solvent was evaporated under reduced pressure and the residue was purified by column chromatography on silica gel (eluent: DCM/EtOAc = 3:1) to afford the desired product **11** as a yellow solid (62.7 mg, 56% yield).

2.6 Synthesis of product 12[4]

An oven-dried vessel was charged with the 2-(5-oxo-2,3,6,7-tetraphenylpyrano[3,2-*b*]pyrrol-1(5*H*)-yl)benzoic acid (**11**) (559.6 mg, 1.0 mmol), Cu_2O (7.2 mg, 0.05 mmol) and 1,10-phenanthroline (18.0 mg, 0.1 mmol). After flushing the vessel with alternating vacuum and nitrogen purge cycles, a solution of NMP (1.5 mL) and quinoline (0.5 mL) was added by syringe. The resulting mixture was stirred at 170 °C and monitored by TLC until full conversion, poured into aqueous HCl (5 N , 2 mL) and extracted with EtOAc (3 × 50 mL). The combined organic layers were washed with aqueous $NaHCO_3$ (30 mL) and brine (50 mL), dried over anhydrous Na_2SO_4, and filtered. Concentration of the solution under reduced pressure gave a residue, which was purified by column chromatography on silica gel (eluent: petroleum ether/EtOAc = 5:1) to afford the desired product **12** as a yellow solid (376.4 mg, 73% yield).

2.7 Scale-up synthesis of product 4b

A 250 mL vessel tube was charged with isatin (**1a**) (0.59 g, 4.0 mmol),

2,3-diphenyl cyclopropenone (**2a**) (1.65 g, 8.0 mmol) and 1-bromobutane (**3b**) (1.37 g, 10.0 mmol), then DBU (1.22 g, 8.0 mmol) and ^{i}PrOH (40 mL) was added. The resulting mixture was stirred at 100 °C for 3 h. Upon completion of the reaction, the solvent was evaporated under reduced pressure and the residue was purified by column chromatography on silica gel (eluent: petroleum ether/EtOAc/DCM = 10:1:1) to afford the desired product **4b** as a yellow solid (1.87 g, 76% yield).

3. Crystal data of products 4b and 6c

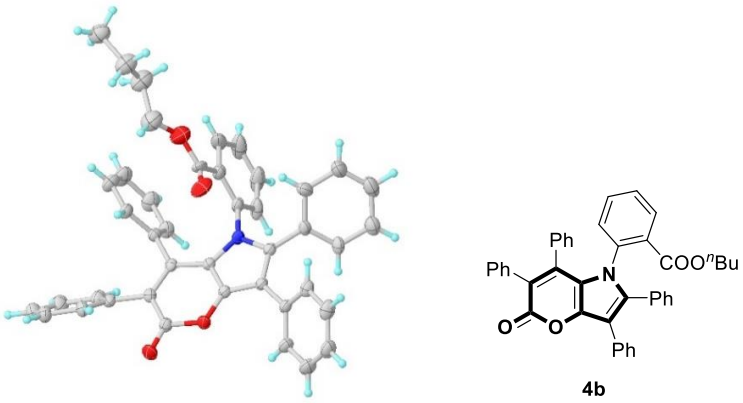


Figure S1. X-ray crystal structure of **4b** with 30% probability ellipsoids

Sample preparation: In a 10 mL glass bottle, 15 mg of pure **4b** was completely dissolved in the mixed solvent of 2 mL EtOAc and 2 mL CH_2Cl_2 at room temperature, and then 1 mL of n-hexane was added slowly. After slow evaporation of the solvent at room temperature, some light yellow transparent crystals were obtained.

Crystal measurement: The crystals were mounted on a glass fiber for diffraction experiments. Intensity data were collected on a Bruker SMART APEX CCD diffractometer with Mo Kα radiation (0.71073 Å) at room temperature. Thermal ellipsoids are drawn at 30% probability level.

Table S1. Crystal data and structure refinement for **4b**

Empirical formula	$C_{42}H_{33}NO_4$ (**CCDC**: 2327902)	
Formula weight	615.73	
Temperature	296(2) K	
Wavelength	0.71073 Å	
Crystal system	Triclinic	
Space group	P-1	
Unit cell dimensions	a = 11.128(8) Å	α = 73.175(16)°
	b =11.730(8) Å	β = 81.066(17)°
	c = 14.406(10) Å	γ = 65.706(16)°

Volume	1639(2) Å^3
Z	2
Density (calculated)	1.241 Mg/m^3
Absorption coefficient	0.079 mm^{-1}
F(000）	642
Crystal size	0.220×0.200×0.180 mm^3
Theta range for data collection	2.308 to 25.041°
Index ranges	-13 ≤ h ≤ 13, -13 ≤ k ≤ 13，-16 ≤ l ≤ 17
Reflections collected	27572
Independent reflections	5708 [R(int) = 0.0986]
Completeness to theta = 25.041°	98.6 %
Absorption correction	Semi-empirical from equivalents
Refinement method	Full-matrix least-squares on F^2
Data / restraints / parameters	5708 / 143 / 461
Goodness-of-fit on F^2	1.070
Final R indices [I>2sigma(I)]	R_1 = 0.0942, wR_2 = 0.2308
R indices (all data)	R_1 = 0.2022, wR_2 = 0.2924
Extinction coefficient	n/a
Largest diff. peak and hole	0.473 and -0.503 e.Å^{-3}

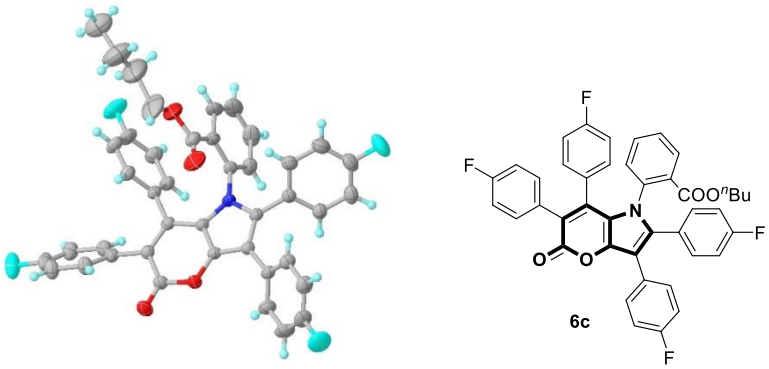


Figure S2. X-ray crystal structure of **6c** with 30% probability ellipsoids

Sample preparation: In a 10 mL glass bottle, 15 mg of pure **6c** was completely dissolved in the mixed solvent of 1 mL EtOAc and 3 mL CH_2Cl_2 at room temperature, and then 2 mL of n-hexane was added slowly. After slow evaporation of the solvent at room temperature, some light yellow transparent crystals were obtained.

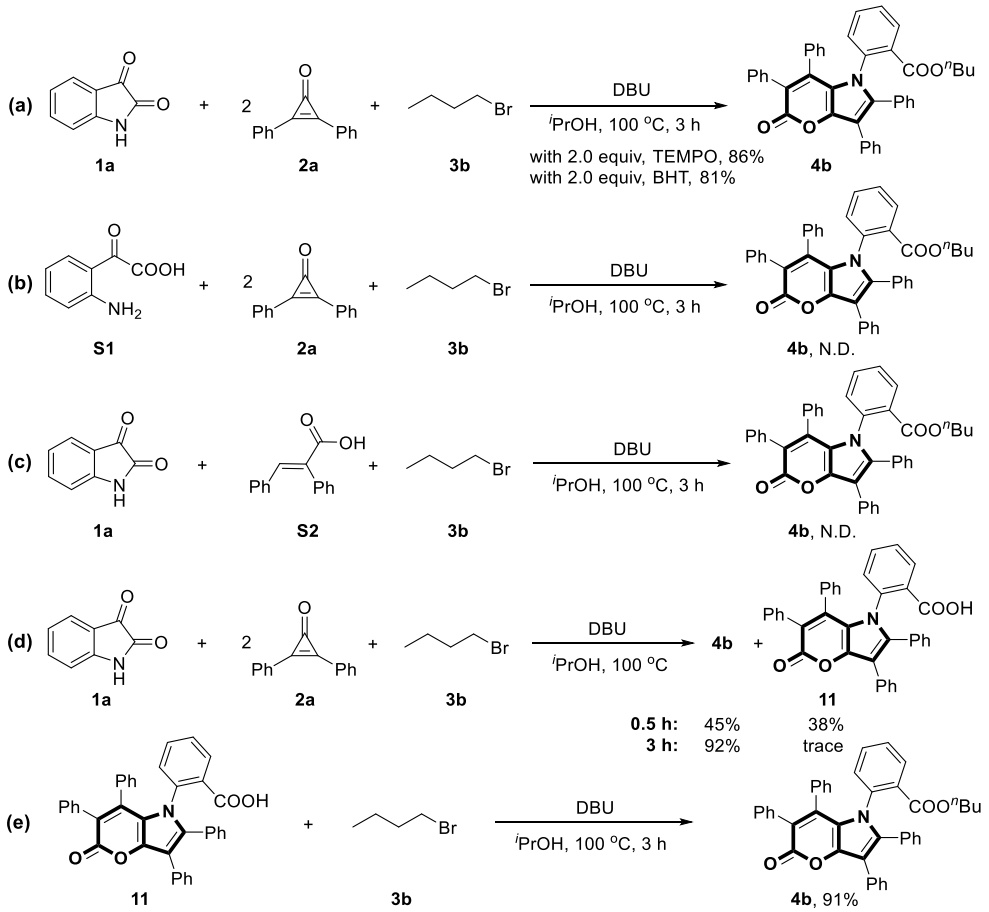
Crystal measurement: The crystals were mounted on a glass fiber for diffraction experiments. Intensity data were collected on a Bruker SMART APEX CCD diffractometer with Mo Kα radiation (0.71073 Å) at room temperature. Thermal ellipsoids are drawn at 30% probability level.

Table S2. Crystal data and structure refinement for **6c**

Empirical formula	$C_{42}H_{29}F_4NO_4$ (**CCDC**: 2298102)	
Formula weight	687.66	
Temperature	293(2) K	
Wavelength	0.71073 Å	
Crystal system	Monoclinic	
Space group	P-1	
Unit cell dimensions	a = 11.3020(3) Å	α = 76.589(2)°
	b = 12.0469(3) Å	β = 79.961(2)°
	c = 14.3021(4) Å	γ = 66.586(3)°
Volume	1730.84(9) Å^3	
Z	2	
Density (calculated)	1.319 mg/m^3	
Absorption coefficient	0.829 mm^{-1}	
F(000）	712.0	
Crystal size	0.25 × 0.18 ×0.15 mm^3	
Theta range for data collection	6.38 to 136.544°	
Index ranges	-13 ≤ h ≤ 13, -14 ≤ k ≤ 14，-17 ≤ l ≤ 15	
Reflections collected	16350	
Independent reflections	6295 [Rint = 0.0368, Rsigma = 0.0335]	
Absorption correction	Semi-empirical from equivalents	
Max. and min. transmission	0.982 and 0.982	
Refinement method	Full-matrix least-squares on F^2	
Data / restraints / parameters	6295/51/462	
Goodness-of-fit on F^2	1.656	
Final R indices [I>2sigma(I)]	R_1 = 0.0900, wR_2 = 0.2619	
R indices (all data)	R_1 = 0.0994, wR_2 = 0.2739	
Largest diff. peak and hole	1.45 and -0.61 e.Å^{-3}	

4. Preliminary mechanistic investigations

To gain insights into the reaction mechanism, several control experiments were conducted. Initially, the reaction of isatin (**1a**), 2,3-diphenyl cyclopropenone (**2a**), and 1-bromobutane (**3b**) was performed in the presence of radical inhibitors (2.0 equiv. of TEMPO or BHT), which still gave the desired product **4b** in 86% and 81% yields, showing that a radical process might not be involved (Scheme S1, a). Given that both isatin (**1a**) and 2,3-diphenyl cyclopropenone (**2a**) are susceptible to ring opening by hydrolysis under the prevailing conditions, an attempt was made to perform the reaction using 2-(2-aminophenyl)-2-oxoacetic acid (**S1**) or 2,3-diphenylacrylic acid (**S2**) as a substrate. However, no corresponding product **4b** was obtained. The results demonstrated that neither **S1** nor **S2** were possible intermediates (Scheme S1, b and c). When the reaction of isatin (**1a**), 2,3-diphenyl cyclopropenone (**2a**), and 1-bromobutane (**3b**) under standard conditions was terminated at 0.5 h, product **4b** was obtained in 45% yield, accompanied by the generation of 2-(5-oxo-2,3,6,7-tetraphenylpyrano[3,2-*b*]pyrrol-1(5*H*)-yl)benzoic acid (**11**) in 38% yield. After prolonging the reaction to 3 h, **11** had disappeared, while the yield of **4b** was increased to 92%. In the following experiments, **11** was isolated and reacted independently with 1-bromobutane (**3b**) under the optimized conditions, resulting in the successful conversion to product **4b** in 91% yield. These results demonstrated that **11** might be an intermediate in this transformation (Scheme S1, d and e).



Scheme S1. Control experiments

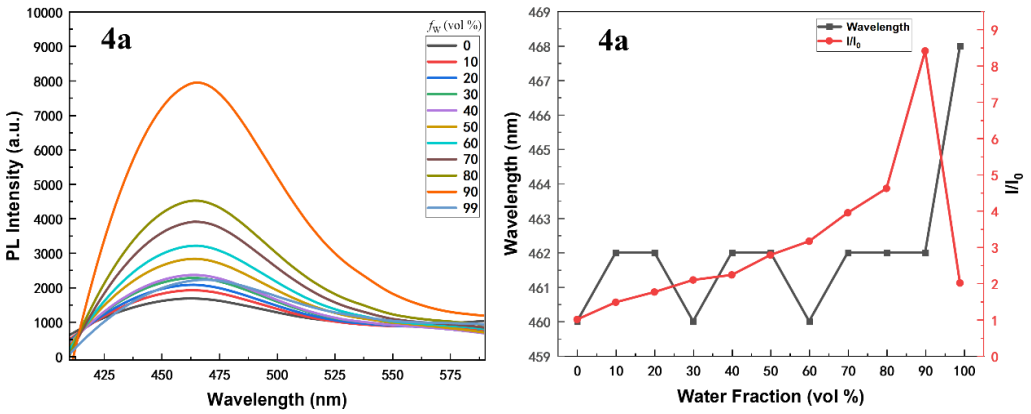
5. Supplementary spectra data and HOMO−LUMO energies

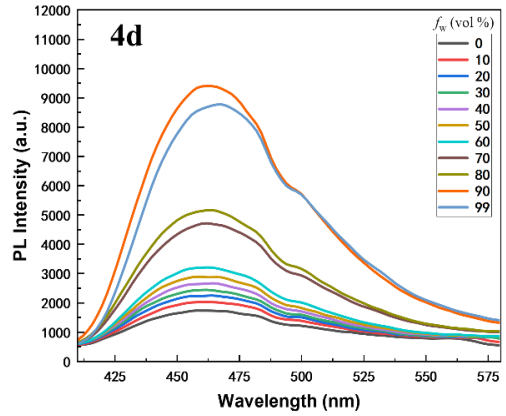
Table S3. Photophysical properties and HOMO−LUMO energies of the selected compounds

Compounds	λ_{abs}[a] nm	λ_{em}[a] nm	Stokes shift cm^{-1} (nm)	molar abs coeff. ε_{max} $M^{-1}\cdot cm^{-1}$	Φ_F/THF[b] %	HOMO[c] eV	LUMO[c] eV	E_g eV
4a	379	462	4740 (83)	34709	1.10	-5.27	-1.59	3.67
4b	378	460	4716 (82)	34639	0.93	-5.17	-1.56	3.61
4d	379	462	4740 (83)	32885	1.12	-5.16	-1.54	3.62
4k	378	460	4716 (82)	29680	1.24	-5.22	-2.01	3.21
5b	377	460	4786 (83)	29976	2.84	-5.14	-1.51	3.63
5c	378	460	4716 (82)	28734	2.19	-5.11	-1.46	3.65
5d	376	460	4857 (84)	26155	2.18	-5.22	-1.73	3.49
5k	378	462	4810 (84)	29790	2.30	-5.12	-1.49	3.63
6a	378	466	4996 (88)	23330	2.99	-5.03	-1.49	3.54
6c	374	460	4999 (86)	23440	3.14	-5.39	-1.75	3.64
6d	378	466	4996 (88)	19338	3.63	-5.54	-1.97	3.57
7	361	448	5379 (87)	95407	1.52	-5.13	-1.56	3.57
9	377	462	4880 (85)	38426	1.38	-5.06	-1.42	3.64
10	343, 396	500	5253 (104)	83130	52.4	-4.72	-1.60	3.12

[a] In THF solution at RT (10^{-5} mol/L); [b] Quinine sulfate (Φ = 0.55) used as a standard; [c] DFT calculations were performed at the B3LYP/6-31G(d) level using the Gaussian 16 package.

6. Emission spectra of the selected compounds in THF/H_2O mixtures

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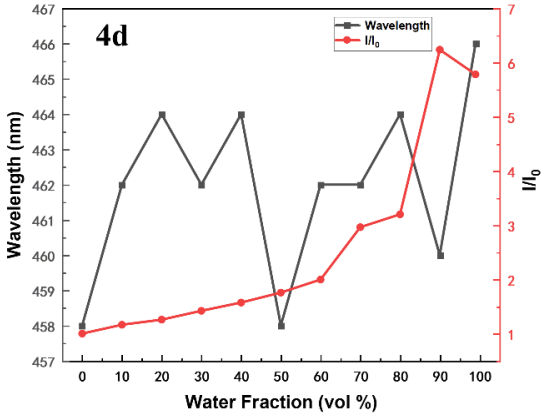
f_w (vol %)
0
10
20
30
40
50
60
70
80
90
99
PL Intensity (a.u.)
Wavelength (nm)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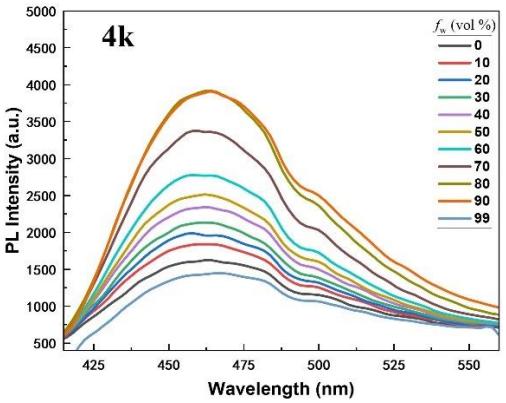
Wavelength
I/I0
Wavelength (nm)
I/I0
Water Fraction (vol %)


4k
f_w (vol %)
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10
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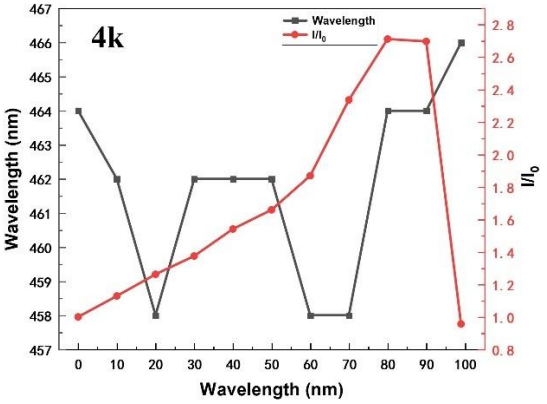
30
40
50
60
70
80
90
99
PL Intensity (a.u.)
Wavelength (nm)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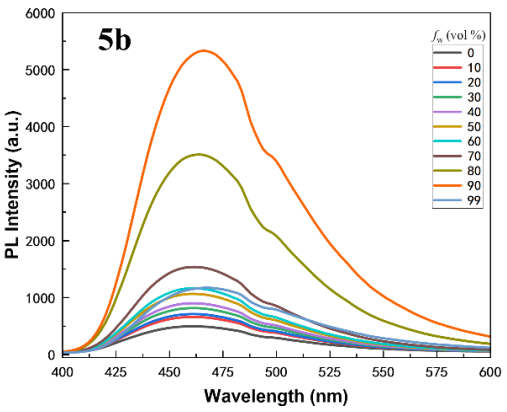
Wavelength
I/I0
Wavelength (nm)
I/I0
Wavelength (nm)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f_w (vol %)
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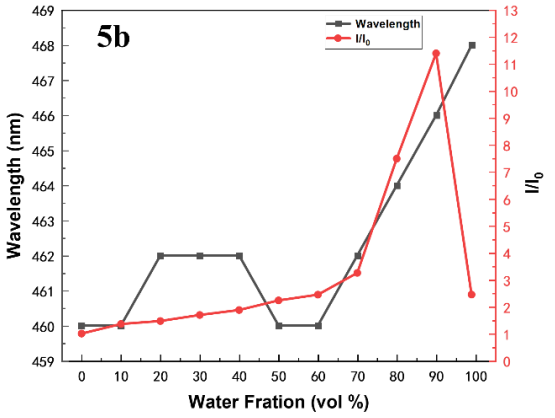
PL Intensity (a.u.)
Wavelength (nm)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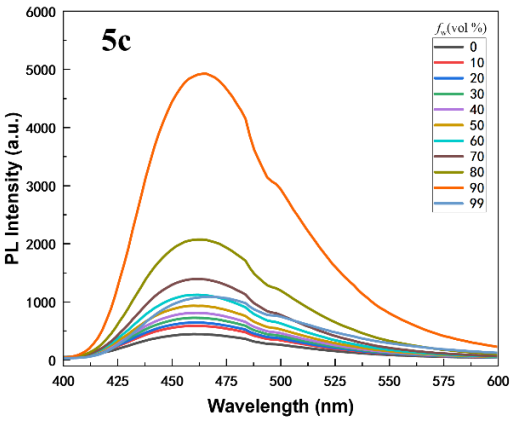
Wavelength
I/I0
Wavelength (nm)
I/I0
Water Fration (vol %)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f_w (vol %)
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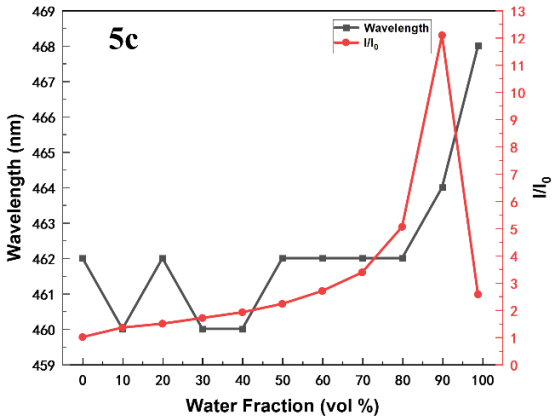
99
PL Intensity (a.u.)
Wavelength (nm)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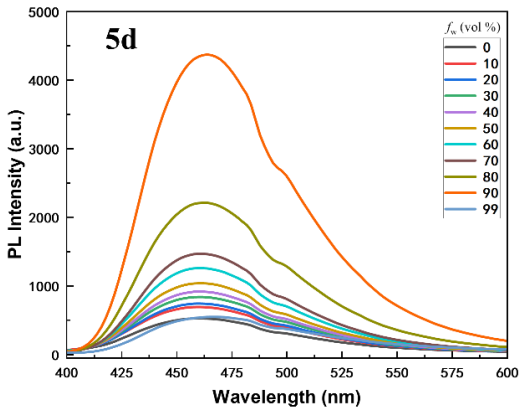
Wavelength
I/I0
Wavelength (nm)
I/I0
Water Fraction (vol %)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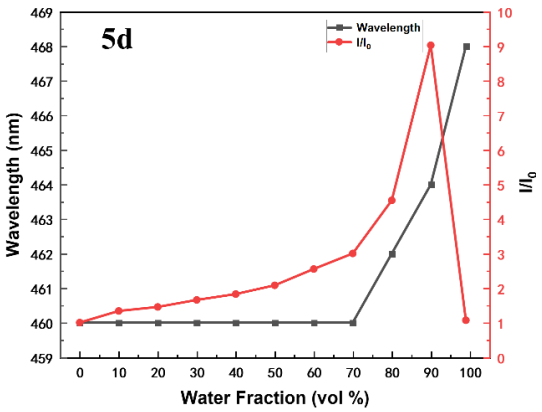
PL Intensity (a.u.)
Wavelength (nm)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Wavelength
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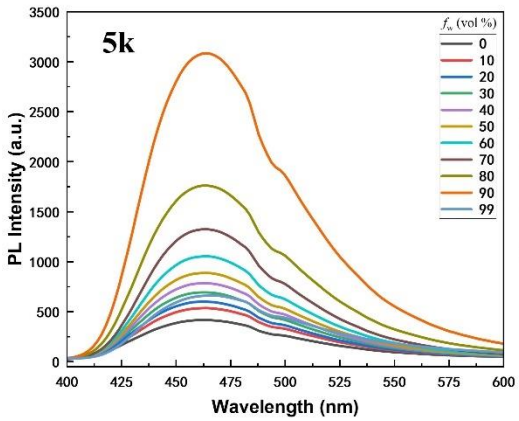
Wavelength (nm)
I/I0
Water Fraction (vol %)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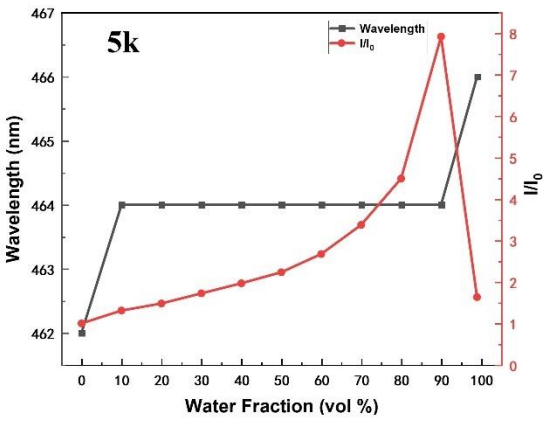
PL Intensity (a.u.)
Wavelength (nm)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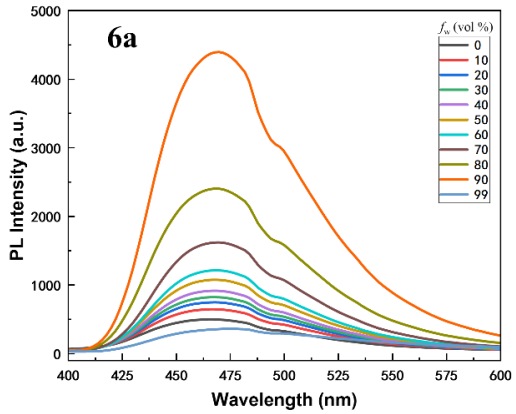
Wavelength
I/I0
Wavelength (nm)
I/I0
Water Fraction (vol %)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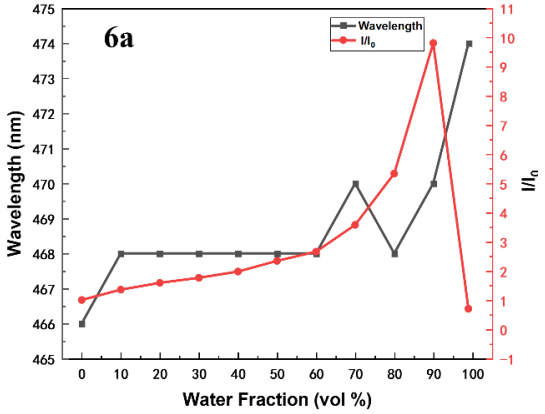
PL Intensity (a.u.)
Wavelength (nm)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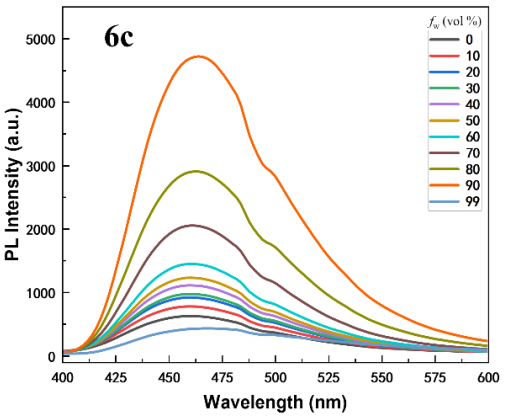
Wavelength
I/I0
Wavelength (nm)
I/I0
Water Fraction (vol %)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f_w (vol %)
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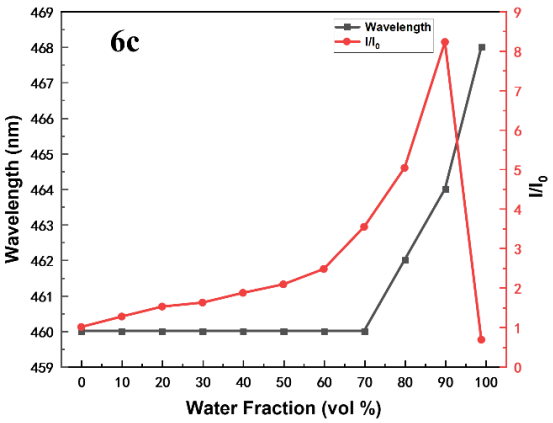
99
PL Intensity (a.u.)
Wavelength (nm)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Wavelength
I/I0
Wavelength (nm)
I/I0
Water Fraction (vol %)

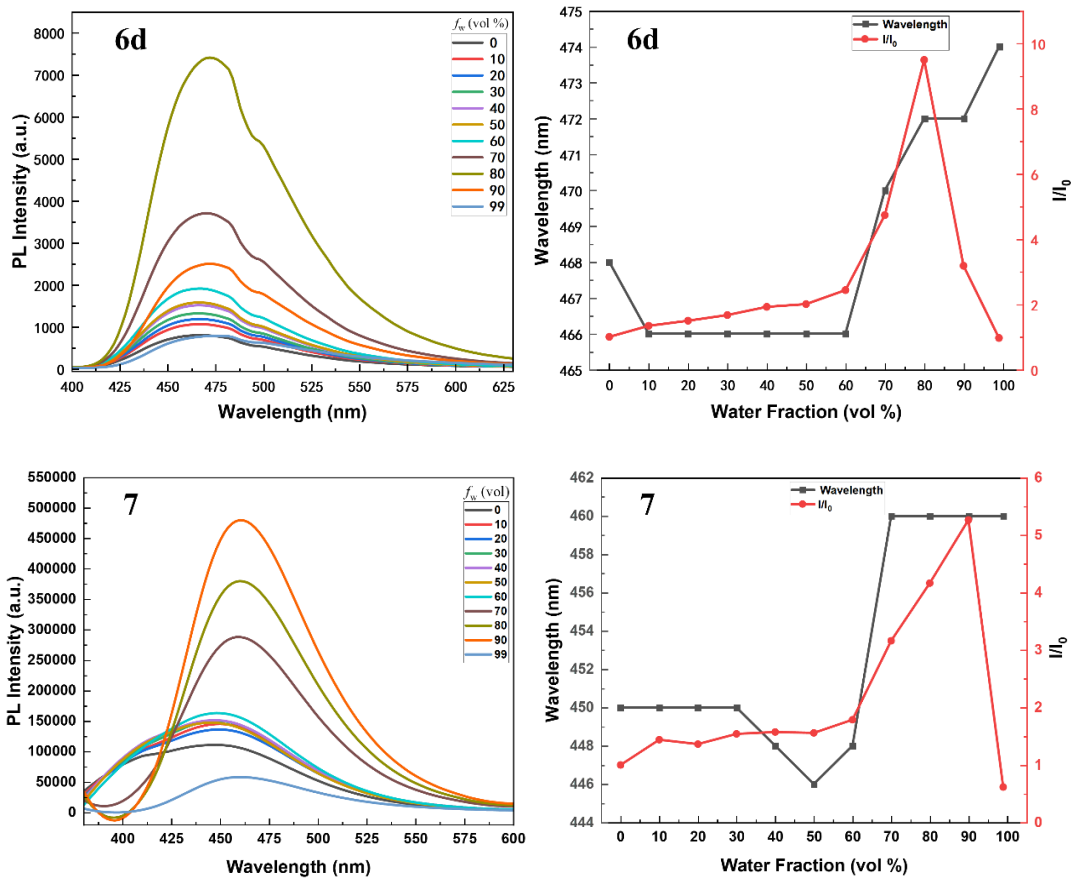
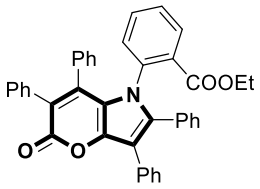


Figure S3. Fluorescence spectra of the selected compounds in THF/H_2O mixtures with different water fractions (left); Plot of wavelength and ratio of maximum fluorescence intensity of the selected compounds *vs*. water fraction (right). I_0 = emission intensity in pure THF solution, λ_{ex} = 375 nm, concentration: 10^{-5} mol/L.

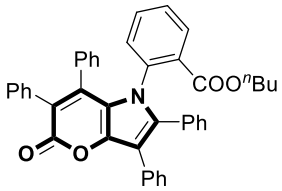
7. Characterization data of compounds 4-12



Ethyl 2-(5-oxo-2,3,6,7-tetraphenylpyrano[3,2-*b*]pyrrol-1(5*H*)-yl)benzoate (4a)

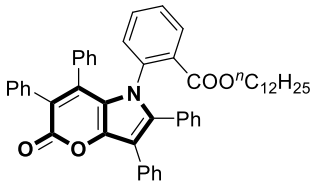
Yellow solid; 88% yield; m.p. 246–247 °C; IR (KBr, cm^{-1}) *v*: 3052, 1698, 1565, 1513, 1468, 1377, 1262, 1085, 874, 764, 699; ^1H NMR (300 MHz, $CDCl_3$) δ (ppm) 7.43 (t, *J* = 8.7 Hz, 3H), 7.27–7.19 (m, 3H), 7.08–6.65 (m, 18H), 4.13 (d, *J* = 6.6 Hz, 2H), 1.20 (t, *J* = 6.9 Hz, 3H); ^{13}C NMR (75 MHz, $CDCl_3$) δ (ppm) 164.6, 162.6, 145.1, 145.0, 137.6, 136.6, 134.8, 132.8, 131.6, 131.1, 130.9, 130.5, 130.1, 129.8, 129.4, 128.8, 128.7, 128.2, 128.1, 128.1, 128.0, 127.5, 127.2, 127.2, 127.1, 126.7, 126.4,

119.1, 117.8, 111.3, 61.3, 14.0; HRMS (ESI): *m/z* $[M + H]^+$ calcd for $C_{40}H_{30}NO_4$: 588.2169, found: 588.2174.



Butyl 2-(5-oxo-2,3,6,7-tetraphenylpyrano[3,2-*b*]pyrrol-1(5*H*)-yl)benzoate (4b)

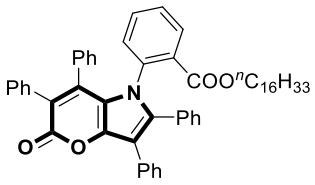
Yellow solid; 92% yield; m.p. 209–210 °C; IR (KBr, cm^{-1}) *v*: 2960, 1700, 1513, 1468, 1379, 1259, 1084, 873, 706; ^1H NMR (300 MHz, $CDCl_3$) δ (ppm) 7.46 (d, *J* = 6.9 Hz, 1H), 7.41 (d, *J* = 7.5 Hz, 2H), 7.30–7.19 (m, 3H), 7.16–6.98 (m, 10H), 6.90–6.65 (m, 8H), 4.09 (t, *J* = 6.6 Hz, 2H), 1.59–1.50 (m, 2H), 1.38–1.26 (m, 2H), 0.91 (t, *J* = 7.2 Hz, 3H); ^{13}C NMR (75 MHz, $CDCl_3$) δ (ppm) 164.8, 162.5, 145.1, 145.0, 137.6, 136.7, 134.8, 132.9, 131.6, 131.1, 130.9, 130.7, 130.1, 129.8, 129.4, 128.8, 128.7, 128.2, 128.2, 128.1, 128.0, 127.5, 127.21, 127.17, 126.8, 126.4, 119.2, 117.8, 111.3, 65.4, 30.5, 19.2, 13.7; HRMS (ESI): *m/z* $[M + H]^+$ calcd for $C_{42}H_{34}NO_4$: 616.2482, found: 616.2482.



Dodecyl 2-(5-oxo-2,3,6,7-tetraphenylpyrano[3,2-*b*]pyrrol-1(5*H*)-yl)benzoate (4c)

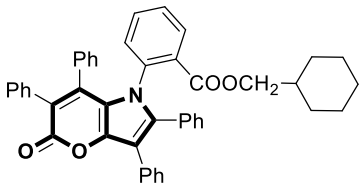
Yellow solid; 81% yield; m.p. 105–107 °C; IR (KBr, cm^{-1}) *v*: 2924, 1698, 1512, 1378, 1288, 1125, 873, 699; ^1H NMR (300 MHz, $CDCl_3$) δ (ppm) 7.47–7.40 (m, 3H), 7.26 (t, *J* = 7.2 Hz, 2H), 7.20 (d, *J* = 6.9 Hz, 1H), 7.16–6.97 (m, 10H), 6.90–6.65 (m, 8H), 4.07 (t, *J* = 6.6 Hz, 2H), 1.56–1.54 (m, 2H), 1.26–1.22 (m, 18H), 0.87 (t, *J* = 6.6 Hz, 3H); ^{13}C NMR (75 MHz, $CDCl_3$) δ (ppm) 164.7, 162.4, 145.0, 144.9, 137.5, 136.6, 134.8, 132.9, 131.6, 131.1, 130.9, 130.6, 130.1, 129.7, 129.3, 128.8, 128.7, 128.2, 128.1, 128.0, 127.4, 127.2, 127.1, 126.7, 126.4, 119.1, 117.7, 111.2, 65.6, 31.8, 31.5,

29.6, 29.5, 29.5, 29.3, 29.2, 28.4, 26.0, 22.6, 14.1; HRMS (ESI): *m/z* $[M + H]^+$ calcd for $C_{50}H_{50}NO_4$: 728.3734, found: 728.3730.



Hexadecyl 2-(5-oxo-2,3,6,7-tetraphenylpyrano[3,2-*b*]pyrrol-1(5*H*)-yl)benzoate (4d)

Yellow solid; 83% yield; m.p. 92–93 °C; IR (KBr, cm^{-1}) *v*: 2917, 2850, 1699, 1511, 1468, 1375, 1243, 1117, 873, 765, 698; ^1H NMR (300 MHz, $CDCl_3$) δ (ppm) 7.46 (dd, J_1 = 1.7 Hz, J_2 = 7.6 Hz, 1H), 7.41 (d, J = 7.2 Hz, 2H), 7.30–7.20 (m, 3H), 7.13–6.95 (m, 10H), 6.90–6.64 (m, 8H), 4.07 (t, J = 6.6 Hz, 2H), 1.58–1.54 (m, 2H), 1.26–1.21 (m, 26H), 0.88 (t, J = 6.6 Hz, 3H); ^{13}C NMR (75 MHz, $CDCl_3$) δ (ppm) 164.8, 162.5, 145.02, 144.99, 137.6, 136.7, 134.8, 132.9, 131.59, 131.56, 131.1, 130.92, 130.90, 130.6, 130.2, 129.8, 129.4, 128.9, 128.7, 128.23, 128.15, 128.0, 127.5, 127.22, 127.17, 126.8, 126.4, 119.2, 117.8, 111.3, 65.6, 31.9, 29.69, 29.68, 29.65, 29.64, 29.60, 29.58, 29.5, 29.4, 29.2, 28.4, 26.0, 22.7, 14.1; HRMS (ESI): *m/z* $[M + H]^+$ calcd for $C_{54}H_{58}NO_4$: 784.4360, found: 784.4352.

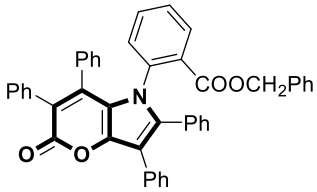


Cyclohexylmethyl

2-(5-oxo-2,3,6,7-tetraphenylpyrano[3,2-*b*]pyrrol-1(5*H*)-yl)benzoate (4e)

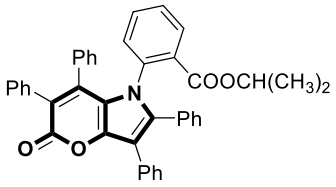
Yellow solid; 81% yield; m.p. 243–244 °C; IR (KBr, cm^{-1}) *v*: 2924, 2847, 1703, 1514, 1378, 1298, 1248, 1127, 868, 699; ^1H NMR (300 MHz, $CDCl_3$) δ (ppm) 7.49 (dd, J_1 = 1.5 Hz, J_2 = 7.6 Hz, 1H), 7.41 (d, J = 7.2 Hz, 2H), 7.30–7.18 (m, 3H), 7.15–6.95 (m, 10H), 6.88–6.64 (m, 8H), 3.96–3.84 (m, 2H), 1.70–1.53 (m, 6H), 1.26–1.11 (m, 3H), 0.98–0.86 (m, 2H); ^{13}C NMR (75 MHz, $CDCl_3$) δ (ppm) 165.0, 162.4, 145.1, 145.0,

137.59, 136.62, 134.8, 132.9, 131.62, 131.57, 131.0, 130.9, 130.8, 130.1, 129.8, 129.4, 128.8, 128.5, 128.24, 128.18, 128.1, 127.5, 127.23, 127.20, 126.8, 126.4, 119.3, 117.8, 111.3, 71.1, 37.1, 29.9, 29.6, 26.1, 25.7, 25.6; HRMS (ESI): *m/z* $[M + H]^+$ calcd for $C_{45}H_{38}NO_4$: 656.2795, found: 656.2789.



Benzyl 2-(5-oxo-2,3,6,7-tetraphenylpyrano[3,2-*b*]pyrrol-1(5*H*)-yl)benzoate (4f)

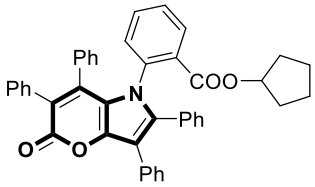
Yellow solid; 84% yield; m.p. 236–237 °C; IR (KBr, cm^{-1}) *v*: 3053, 1703, 1600, 1513, 1457, 1379, 1283, 1127, 1074, 876, 707; ^1H NMR (300 MHz, $CDCl_3$) δ (ppm) 7.49 (d, *J* = 6.9 Hz, 1H), 7.35–7.20 (m, 10H), 7.15–6.95 (m, 10H), 6.88–6.76 (m, 4H), 6.71 (t, *J* = 7.2 Hz, 1H), 6.62 (d, *J* = 6.9 Hz, 2H), 6.48 (d, *J* = 7.5 Hz, 1H), 5.23 (d, *J* = 12.0 Hz, 1H), 4.99 (d, *J* = 12.0 Hz, 1H); ^{13}C NMR (75 MHz, $CDCl_3$) δ (ppm) 164.6, 162.4, 144.80, 144.78, 137.4, 136.8, 134.8, 134.5, 132.8, 131.8, 131.7, 131.0, 130.91, 130.88, 130.2, 129.7, 129.3, 128.9, 128.74, 128.69, 128.6, 128.2, 128.13, 128.08, 127.4, 127.2, 127.13, 127.10, 126.7, 126.4, 119.1, 117.8, 111.1, 67.7; HRMS (ESI): *m/z* $[M + H]^+$ calcd for $C_{45}H_{32}NO_4$: 650.2326, found: 650.2341.



Isopropyl 2-(5-oxo-2,3,6,7-tetraphenylpyrano[3,2-*b*]pyrrol-1(5*H*)-yl)benzoate (4g)

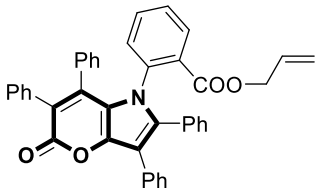
Yellow solid; 79% yield; m.p. 234–235 °C; IR (KBr, cm^{-1}) *v*: 3052, 2977, 1700, 1513, 1467, 1380, 1268, 1108, 874, 698; ^1H NMR (300 MHz, $CDCl_3$) δ (ppm) 7.47–7.40 (m, 3H), 7.30–7.20 (m, 3H), 7.13–7.00 (m, 10H), 6.93 (d, *J* = 7.2 Hz, 2H), 6.87–6.78 (m, 2H), 6.73 (t, *J* = 6.6 Hz, 2H), 6.65 (t, *J* = 7.5 Hz, 2H), 5.09–5.01 (m, 1H), 1.20–1.16 (m, 6H); ^{13}C NMR (75 MHz, $CDCl_3$) δ (ppm) 164.2, 162.6, 145.2, 144.9, 137.5, 136.4,

134.8, 132.6, 131.6, 131.5, 131.0, 130.93, 130.88, 130.5, 130.2, 129.4, 128.9, 128.7, 128.3, 128.18, 128.16, 128.0, 127.5, 127.2, 127.1, 126.8, 126.4, 119.2, 118.1, 111.2, 68.9, 21.8, 21.7; HRMS (ESI): *m/z* $[M + H]^+$ calcd for $C_{41}H_{32}NO_4$: 602.2326, found: 602.2325.



Cyclopentyl 2-(5-oxo-2,3,6,7-tetraphenylpyrano[3,2-*b*]pyrrol-1(5*H*)-yl)benzoate (4h)

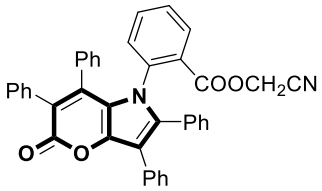
Yellow solid; 78% yield; m.p. 253–254 °C; IR (KBr, cm^{-1}) *v*: 3053, 2960, 1700, 1513, 1468, 1380, 1259, 1084, 873, 706; ^1H NMR (300 MHz, $CDCl_3$) δ (ppm) 7.46–7.39 (m, 3H), 7.30–7.23 (m, 3H), 7.12–7.03 (m, 10H), 6.91 (d, J = 7.2 H_Z, 2H), 6.82 (t, J = 7.8 Hz, 2H), 6.76–6.66 (m, 4H), 5.23–5.22 (m, 1H), 1.86–1.85 (m, 2H), 1.59–1.58 (m, 6H); ^{13}C NMR (75 MHz, $CDCl_3$) δ (ppm) 164.6, 162.5, 145.1, 144.8, 137.4, 136.3, 134.8, 132.6, 131.5, 131.00, 130.97, 130.85, 130.80, 130.3, 130.1, 129.3, 128.9, 128.6, 128.2, 128.14, 128.05, 127.5, 127.24, 127.21, 127.1, 126.8, 126.4, 119.2, 117.8, 111.1, 78.3, 32.6, 32.5, 23.62, 23.56; HRMS (ESI): *m/z* $[M + H]^+$ calcd for $C_{43}H_{34}NO_4$: 628.2482, found: 628.2479.



Allyl 2-(5-oxo-2,3,6,7-tetraphenylpyrano[3,2-*b*]pyrrol-1(5*H*)-yl)benzoate (4j)

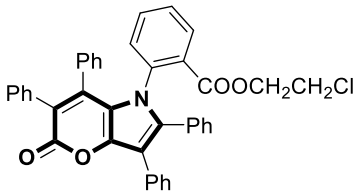
Yellow solid; 68% yield; m.p. 261–262 °C; IR (KBr, cm^{-1}) *v*: 3051, 2977, 1700, 1513, 1467, 1380, 1286, 1108, 874, 698; ^1H NMR (300 MHz, $CDCl_3$) δ (ppm) 7.47–7.40 (m, 3H), 7.29–7.19 (m, 3H), 7.15–7.00 (m, 10H), 6.91–6.64 (m, 8H), 5.88–5.75 (m, 1H), 5.30 (t, J = 8.1 H_Z, 2H), 4.63–4.50 (m, 2H); ^{13}C NMR (75 MHz, $CDCl_3$) δ (ppm) 164.2, 162.5, 145.01, 144.97, 137.6, 136.8, 134.8, 132.8, 131.7, 131.6, 131.3, 131.0,

130.9, 130.5, 130.1, 129.5, 129.3, 128.8, 128.7, 128.2, 128.12, 128.06, 128.0, 127.4, 127.2, 127.1, 126.7, 126.4, 119.4, 119.1, 117.8, 111.3, 66.1; HRMS (ESI): *m/z* [M + H]$^+$ calcd for $C_{41}H_{30}NO_4$: 600.2169, found: 600.2164.



Cyanomethyl 2-(5-oxo-2,3,6,7-tetraphenylpyrano[3,2-*b*]pyrrol-1(5*H*)-yl)benzoate (4k)

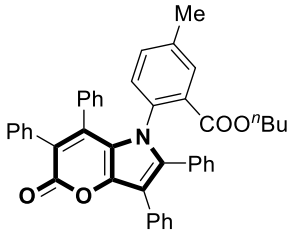
Yellow solid; 65% yield; m.p. 235–237 °C; IR (KBr, cm^{-1}) *v*: 3058, 1745, 1698, 1541, 1512, 1378, 1242, 1086, 874, 765, 701; ^{1}H NMR (300 MHz, $CDCl_3$) δ (ppm) 7.43 (t, *J* = 7.2 Hz, 3H), 7.30–7.20 (m, 3H), 7.15–7.05 (m, 10H), 6.93–6.67 (m, 8H), 4.70 (d, *J* = 1.5 Hz, 2H); ^{13}C NMR (75 MHz, $CDCl_3$) δ (ppm) 162.5, 162.4, 145.1, 144.6, 137.6, 137.2, 134.7, 132.90, 132.87, 132.1, 131.1, 130.9, 130.7, 130.6, 130.0, 129.4, 128.9, 128.6, 128.3, 128.24, 128.17, 127.5, 127.38, 127.35, 127.3, 126.9, 126.8, 126.6, 119.6, 117.5, 113.9, 111.9, 48.7; HRMS (ESI): *m/z* [M + H]$^+$ calcd for $C_{40}H_{27}N_2O_4$: 599.1965, found: 599.1972.



2-Chloroethyl 2-(5-oxo-2,3,6,7-tetraphenylpyrano[3,2-*b*]pyrrol-1(5*H*)-yl)benzoate (4l)

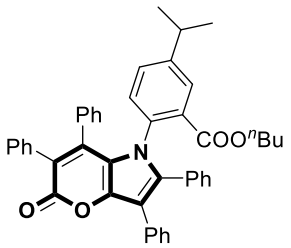
Yellow solid; 61% yield; m.p. 222–224 °C; IR (KBr, cm^{-1}) *v*: 3052, 1953, 1705, 1580, 1512, 1494, 1441, 1379, 1262, 1138, 1091, 872, 764, 707, 698; ^{1}H NMR (300 MHz, $CDCl_3$) δ (ppm) 7.51–7.48 (m, 1H), 7.42 (d, *J* = 7.2 Hz, 2H), 7.29–7.19 (m, 3H), 7.13–7.03 (m, 10H), 6.88 (d, *J* = 6.9 Hz, 3H), 6.82–6.65 (m, 5H), 4.34–4.31 (m, 2H), 3.63–3.60 (m, 2H); ^{13}C NMR (75 MHz, $CDCl_3$) δ (ppm) 164.2, 162.5, 144.94, 144.88, 137.4, 136.9, 134.8, 132.9, 132.0, 131.7, 131.0, 130.9, 130.83, 130.78, 130.1, 129.3,

128.9, 128.8, 128.7, 128.3, 128.2, 128.14, 128.06, 127.4, 127.3, 127.23, 127.19, 126.8, 126.5, 119.4, 117.9, 111.3, 65.0, 41.5; HRMS (ESI): *m/z* $[M + H]^+$ calcd for $C_{40}H_{29}ClNO_4$: 622.1780, found: 622.1783.



Butyl 5-methyl-2-(5-oxo-2,3,6,7-tetraphenylpyrano[3,2-*b*]pyrrol-1(5*H*)-yl) benzoate (5a)

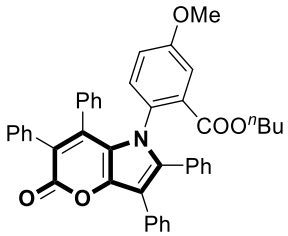
Yellow solid; 78% yield; m.p. 208–209 °C; IR (KBr, cm^{-1}) *v*: 3055, 2956, 1700, 1503, 1379, 1293, 1246, 1197, 1133, 878, 699; ^1H NMR (300 MHz, $CDCl_3$) δ (ppm) 7.40 (d, *J* = 7.2 Hz, 2H), 7.29–7.19 (m, 4H), 7.16–7.05 (m, 8H), 6.90 (d, *J* = 7.2 Hz, 2H), 6.84 (d, *J* = 6.9 Hz, 1H), 6.79–6.63 (m, 6H), 4.14–4.00 (m, 2H), 2.16 (s, 3H), 1.58–1.49 (m, 2H), 1.35–1.26 (m, 2H), 0.90 (t, *J* = 7.2 Hz, 3H); ^{13}C NMR (75 MHz, $CDCl_3$) δ (ppm) 165.0, 162.5, 145.1, 144.9, 138.2, 137.6, 134.8, 134.0, 133.0, 132.2, 131.3, 131.1, 131.03, 130.95, 130.9, 130.2, 129.33, 129.25, 128.9, 128.7, 128.2, 128.1, 128.0, 127.4, 127.10, 127.07, 126.70, 126.65, 126.3, 119.1, 117.9, 111.1, 65.3, 30.5, 20.7, 19.2, 13.7; HRMS (ESI): *m/z* $[M + H]^+$ calcd for $C_{43}H_{36}NO_4$: 630.2639, found: 630.2635.



Butyl 5-isopropyl-2-(5-oxo-2,3,6,7-tetraphenylpyrano[3,2-*b*]pyrrol-1(5*H*)-yl) benzoate (5b)

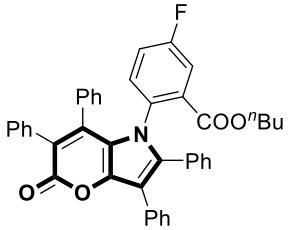
Yellow solid; 79% yield; m.p. 187–188 °C; IR (KBr, cm^{-1}) *v*: 3060, 2958, 1719, 1564, 1515, 1382, 1288, 1247, 1205, 880, 697; ^1H NMR (300 MHz, $CDCl_3$) δ (ppm) 7.40 (d, *J* = 7.2 Hz, 2H), 7.31–7.25 (m, 3H), 7.21 (d, *J* = 7.2 Hz, 1H), 7.13–7.03 (m, 8H), 6.88 (d, *J* = 7.2 Hz, 2H), 6.83–6.68 (m, 5H), 6.63 (d, *J* = 3.3 Hz, 2H), 4.14–4.01 (m, 2H),

2.77–2.68 (m, 1H), 1.58–1.49 (m, 2H), 1.38–1.26 (m, 2H), 1.12 (d, J = 6.9 Hz, 6H), 0.91 (t, J = 7.5 Hz, 3H); ^{13}C NMR (75 MHz, $CDCl_3$) δ (ppm) 165.2, 162.5, 148.9, 145.1, 144.9, 137.6, 134.9, 134.1, 133.0, 131.4, 131.1, 131.0, 130.9, 130.2, 129.6, 129.44, 129.40, 128.9, 128.8, 128.7, 128.2, 128.1, 128.0, 127.5, 127.2, 127.14, 127.10, 126.7, 126.4, 119.1, 117.8, 111.1, 65.4, 33.5, 30.5, 23.6, 23.5, 19.2, 13.7; HRMS (ESI): *m/z* $[M + H]^+$ calcd for $C_{45}H_{40}NO_4$: 658.2952, found: 658.2949.



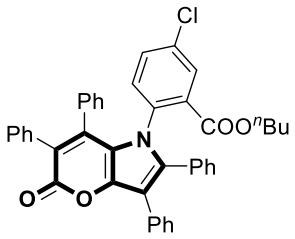
Butyl 5-methoxy-2-(5-oxo-2,3,6,7-tetraphenylpyrano[3,2-*b*]pyrrol-1(5*H*)-yl) benzoate (5c)

Yellow solid; 84% yield; m.p. 171–172 ^{o}C; IR (KBr, cm^{-1}) *v*: 3059, 2959, 1701, 1502, 1467, 1286, 1075, 876, 699; ^{1}H NMR (300 MHz, $CDCl_3$) δ (ppm) 7.40 (d, J = 7.2 Hz, 2H), 7.29–7.24 (m, 2H), 7.20 (d, J = 6.9 Hz, 1H), 7.17–7.05 (m, 8H), 6.96–6.68 (m, 8H), 6.62 (d, J = 7.5 Hz, 1H), 6.47 (dd, J_1 = 2.8 Hz, J_2 = 8.7 Hz, 1H), 4.13–4.03 (m, 2H), 3.67 (s, 3H), 1.58–1.49 (m, 2H), 1.37–1.28 (m, 2H), 0.90 (t, J = 7.2 Hz, 3H); ^{13}C NMR (75 MHz, $CDCl_3$) δ (ppm) 164.7, 162.5, 158.9, 145.2, 144.8, 137.8, 134.8, 133.0, 132.5, 131.04, 130.96, 130.9, 130.5, 130.2, 129.3, 129.2, 128.9, 128.7, 128.2, 128.11, 128.06, 127.5, 127.19, 127.18, 126.9, 126.7, 126.4, 119.1, 117.9, 117.4, 115.2, 111.0, 65.5, 55.5, 30.4, 19.2, 13.7; HRMS (ESI): *m/z* $[M + H]^+$ calcd for $C_{43}H_{36}NO_5$: 646.2588, found: 646.2585.



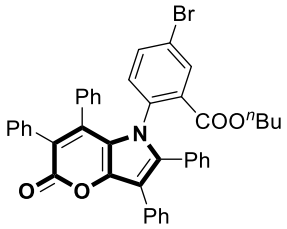
Butyl 5-fluoro-2-(5-oxo-2,3,6,7-tetraphenylpyrano[3,2-*b*]pyrrol-1(5*H*)-yl) benzoate (5d)

Yellow solid; 78% yield; m.p. 219–221 °C; IR (KBr, cm^{-1}) *v*: 3414, 3070, 2952, 1696, 1566, 1515, 1421, 1381, 1270, 1073, 878, 700; ^{1}H NMR (300 MHz, $CDCl_3$) δ (ppm) 7.40 (d, *J* = 6.9 Hz, 2H), 7.30–7.03 (m, 12H), 6.94–6.80 (m, 5H), 6.76–6.62 (m, 4H), 4.14–4.05 (m, 2H), 1.58–1.52 (m, 2H), 1.36–1.26 (m, 2H), 0.91 (t, *J* = 7.5 Hz, 3H); ^{13}C NMR (75 MHz, $CDCl_3$) δ (ppm) 163.6, 162.4, 161.1 (d, $J_{C\text{-}F}$ = 249.0 Hz), 145.0, 144.8, 137.6, 134.6, 133.3 (d, $J_{C\text{-}F}$ = 8.3 Hz), 132.9, 132.8 (d, $J_{C\text{-}F}$ = 3.3 Hz), 131.6 (d, $J_{C\text{-}F}$ = 8.3 Hz), 131.0, 130.9, 130.7, 130.0, 129.3, 128.9, 128.7, 128.32, 128.26, 128.2, 127.3, 127.3, 126.9, 126.5, 119.4, 118.5 (d, $J_{C\text{-}F}$ = 22.5 Hz), 117.9, 117.5 (d, $J_{C\text{-}F}$ = 24.8 Hz), 111.5, 65.8, 30.4, 19.2, 13.7; HRMS (ESI): *m/z* $[M + H]^+$ calcd for $C_{42}H_{33}FNO_4$: 634.2388, found: 634.2382.



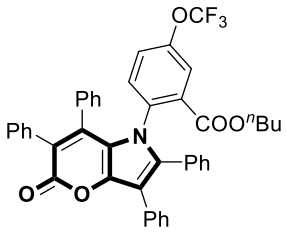
Butyl 5-chloro-2-(5-oxo-2,3,6,7-tetraphenylpyrano[3,2-*b*]pyrrol-1(5*H*)-yl) benzoate (5e)

Yellow solid; 79% yield; m.p. 211–212 °C; IR (KBr, cm^{-1}) *v*: 3063, 2950, 2870, 1698, 1513, 1468, 1409, 1284, 1261, 877, 699; ^{1}H NMR (300 MHz, $CDCl_3$) δ (ppm) 7.41–7.39 (m, 3H), 7.29–7.22 (m, 3H), 7.20–7.06 (m, 8H), 6.97–6.68 (m, 8H), 6.62 (d, *J* = 7.8 Hz, 1H), 4.11–4.06 (m, 2H), 1.59–1.50 (m, 2H), 1.38–1.26 (m, 2H), 0.91 (t, *J* = 7.5 Hz, 3H); ^{13}C NMR (75 MHz, $CDCl_3$) δ (ppm) 163.6, 162.3, 145.0, 144.7, 137.4, 135.2, 134.6, 134.1, 132.9, 132.7, 131.4, 131.0, 130.9, 130.8, 130.6, 130.4, 129.8, 129.3, 128.9, 128.7, 128.4, 128.24, 128.22, 127.5, 127.4, 127.2, 126.9, 126.5, 119.4, 117.9, 111.6, 65.8, 30.4, 19.1, 13.7; HRMS (ESI): *m/z* $[M + H]^+$ calcd for $C_{42}H_{33}ClNO_4$: 650.2093, found: 650.2092.



Butyl 5-bromo-2-(5-oxo-2,3,6,7-tetraphenylpyrano[3,2-*b*]pyrrol-1(5*H*)-yl) benzoate (5f)

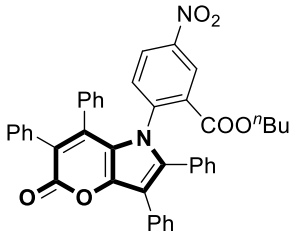
Yellow solid; 80% yield; m.p. 203–205 ^{o}C; IR (KBr, cm^{-1}) *v*: 3062, 2960, 2873, 1700, 1468, 1244, 877, 698; ^{1}H NMR (300 MHz, $CDCl_3$) δ (ppm) 7.55 (d, J = 2.1 Hz, 1H), 7.39 (d, J = 7.2 Hz, 2H), 7.30–7.03 (m, 12H), 6.96 (t, J = 7.5 Hz, 1H), 6.90–6.82 (m, 3H), 6.75–6.67 (m, 3H), 6.62 (d, J = 7.8 Hz, 1H), 4.11–4.06 (m, 2H), 1.59–1.50 (m, 2H), 1.37–1.26 (m, 2H), 0.91 (t, J = 7.5 Hz, 3H); ^{13}C NMR (75 MHz, $CDCl_3$) δ (ppm) 163.5, 162.4, 145.0, 144.7, 137.3, 135.8, 134.6, 134.4, 133.4, 132.89, 132.85, 131.1, 131.0, 130.9, 130.6, 129.8, 129.3, 128.9, 128.7, 128.4, 128.3, 127.52, 127.45, 127.4, 127.1, 126.9, 126.6, 122.0, 119.4, 117.9, 111.6, 65.8, 30.4, 19.2, 13.7; HRMS (ESI): *m/z* $[M + H]^+$ calcd for $C_{42}H_{33}BrNO_4$: 694.1587, found: 694.1584.



Butyl 2-(5-oxo-2,3,6,7-tetraphenylpyrano[3,2-*b*]pyrrol-1(5*H*)-yl)-5-(trifluoromethoxy)benzoate (5g)

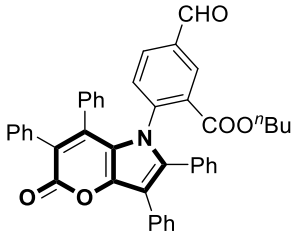
Yellow solid; 74% yield; m.p. 188–189 ^{o}C; IR (KBr, cm^{-1}) *v*: 3062, 2961, 2875, 1699, 1498, 1468, 1380, 1268, 1213, 878, 699; ^{1}H NMR (300 MHz, $CDCl_3$) δ (ppm) 7.40 (d, J = 6.9 Hz, 2H), 7.30–7.03 (m, 12H), 6.92–6.80 (m, 6H), 6.70 (t, J = 7.5 Hz, 2H), 6.63 (d, J = 7.5 Hz, 1H), 4.13–4.08 (m, 2H), 1.60–1.51 (m, 2H), 1.38–1.26 (m, 2H), 0.91 (t, J = 7.2 Hz, 3H); ^{13}C NMR (75 MHz, $CDCl_3$) δ (ppm) 163.4, 162.3, 147.93, 147.90, 145.0, 144.7, 137.4, 135.3, 134.5, 133.0, 132.8, 131.4, 131.0, 130.8, 130.6, 129.8, 129.3, 128.9, 128.7, 128.4, 128.3, 128.2, 127.5, 127.44, 127.35, 126.9, 126.6, 123.7,

123.0, 121.8, 119.49, 119.48, 118.4, 118.0, 111.7, 65.9, 30.4, 19.2, 13.7; HRMS (ESI): *m/z* $[M + H]^+$ calcd for $C_{43}H_{33}F_3NO_5$: 700.2305, found: 700.2300.



Butyl 5-nitro-2-(5-oxo-2,3,6,7-tetraphenylpyrano[3,2-*b*]pyrrol-1(5*H*)-yl)benzoate (5h)

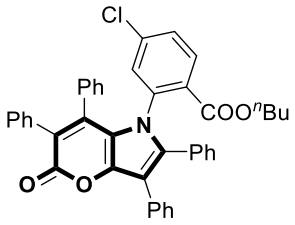
Yellow solid; 67% yield; m.p. 225–227 °C; IR (KBr, cm^{-1}) *v*: 3064, 2957, 2870, 1700, 1530, 1469, 1347, 1267, 1139, 1074, 879, 699; ^1H NMR (300 MHz, $CDCl_3$) δ (ppm) 8.24 (d, J = 2.4 Hz, 1H), 7.77 (dd, J_1 = 2.4 Hz, J_2 = 8.4 Hz, 1H), 7.40 (d, J = 6.9 Hz, 2H), 7.31–6.99 (m, 12H), 6.89–6.80 (m, 4H), 6.72 (d, J = 7.5 Hz, 1H), 6.66 (d, J = 5.7 Hz, 2H), 4.14 (t, J = 6.6 Hz, 2H), 1.61–1.54 (m, 2H), 1.40–1.28 (m, 2H), 0.93 (t, J = 7.5 Hz, 3H); ^{13}C NMR (75 MHz, $CDCl_3$) δ (ppm) 162.8, 162.1, 146.3, 145.3, 144.1, 142.3, 137.1, 134.2, 132.9, 132.7, 131.1, 130.9, 130.8, 130.2, 129.4, 129.3, 129.0, 128.74, 128.72, 128.5, 128.4, 127.64, 127.60, 127.55, 127.5, 127.1, 126.8, 125.49, 125.46, 119.8, 118.0, 112.4, 66.3, 30.4, 19.2, 13.7; HRMS (ESI): *m/z* $[M + H]^+$ calcd for $C_{42}H_{33}N_2O_6$: 661.2333, found: 661.2331.



Butyl 5-formyl-2-(5-oxo-2,3,6,7-tetraphenylpyrano[3,2-*b*]pyrrol-1(5*H*)-yl) benzoate (5i)

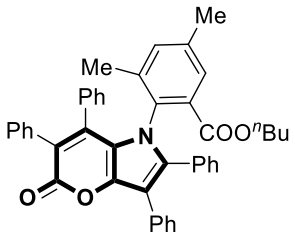
Yellow solid; 81% yield; m.p. 217–219 °C; IR (KBr, cm^{-1}) *v*: 3076, 3012, 2856, 1751, 1629, 1518, 1337 1225, 1182, 1074, 825, 763; ^1H NMR (300 MHz, $CDCl_3$) δ (ppm) 9.83 (s, 1H), 7.92 (d, J = 1.5 Hz, 1H), 7.48 (dd, J_1 = 1.8 Hz, J_2 = 8.1 Hz, 1H), 7.40 (d, J = 6.9 Hz, 2H), 7.30–7.21 (m, 3H), 7.19–6.99 (m, 9H), 6.88 (d, J = 7.5 Hz, 2H),

6.84–6.70 (m, 3H), 6.67–6.59 (m, 2H), 4.13 (t, J = 6.6 Hz, 2H), 1.62–1.53 (m, 2H), 1.42–1.28 (m, 2H), 0.92 (t, J = 7.5 Hz, 3H); ^{13}C NMR (75 MHz, $CDCl_3$) δ (ppm) 190.0, 163.7, 162.2, 145.1, 144.5, 141.7, 137.2, 135.0, 134.4, 132.8, 132.5, 132.2, 132.1, 131.0, 130.9, 130.8, 130.6, 130.4, 129.6, 129.3, 128.9, 128.6, 128.5, 128.2, 127.5, 127.4, 127.4, 127.3, 126.9, 126.6, 119.4, 117.8, 111.9, 65.8, 30.4, 19.1, 13.6; HRMS (ESI): *m/z* $[M + H]^+$ calcd for $C_{43}H_{34}NO_5$: 644.2431, found: 644.2449.



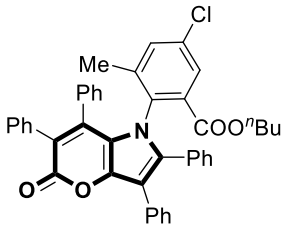
Butyl 4-chloro-2-(5-oxo-2,3,6,7-tetraphenylpyrano[3,2-*b*]pyrrol-1(5*H*)-yl) benzoate (5j)

Yellow solid; 77% yield; m.p. 210–212 ^{o}C; IR (KBr, cm^{-1}) *v*: 2071, 2959, 1729, 1703, 1597, 1465, 1419, 1307, 1252, 1126, 875, 777, 696; ^{1}H NMR (300 MHz, $CDCl_3$) δ (ppm) 7.39 (d, J = 7.8 Hz, 3H), 7.29–7.22 (m, 3H), 7.20–7.08 (m, 8H), 6.98 (t, J = 7.5 Hz, 2H), 6.89–6.79 (m, 5H), 6.67–6.63 (m, 2H), 4.12–4.03 (m, 2H), 1.59–1.50 (m, 2H), 1.38–1.26 (m, 2H), 0.92 (t, J = 7.2 Hz, 3H); ^{13}C NMR (75 MHz, $CDCl_3$) δ (ppm) 164.1, 162.3, 145.0, 144.7, 137.6, 137.5, 137.4, 134.5, 132.7, 131.9, 131.6, 130.9, 130.8, 130.6, 129.7, 129.3, 128.8, 128.5, 128.37, 128.35, 128.3, 128.2, 128.0, 127.7, 127.5, 127.4, 127.3, 126.9, 126.5, 119.4, 117.7, 111.6, 65.6, 30.4, 19.2, 13.7; HRMS (ESI): *m/z* $[M + H]^+$ calcd for $C_{42}H_{33}ClNO_4$: 650.2093, found: 650.2088.



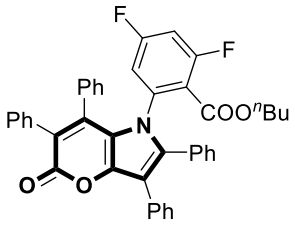
Butyl 3,5-dimethyl-2-(5-oxo-2,3,6,7-tetraphenylpyrano[3,2-*b*]pyrrol-1(5*H*)-yl) benzoate (5k)

Yellow solid; 71% yield; m.p. 214–215 °C; IR (KBr, cm^{-1}) *v*: 3421, 3059, 2955, 1704, 1516, 1468, 1370, 1308, 1246, 1212, 1118, 877, 781, 698; ^{1}H NMR (300 MHz, $CDCl_3$) δ (ppm) 7.41 (d, *J* = 7.2 Hz, 2H), 7.29–7.16 (m, 4H), 7.14–7.05 (m, 8H), 6.91 (d, *J* = 7.2 Hz, 2H), 6.86–6.81 (m, 1H), 6.73–6.63 (m, 5H), 4.10 (t, *J* = 6.6 Hz, 2H), 2.11 (s, 3H), 1.86 (s, 3H), 1.58–1.49 (m, 2H), 1.37–1.26 (m, 2H), 0.89 (t, *J* = 7.5 Hz, 3H); ^{13}C NMR (75 MHz, $CDCl_3$) δ (ppm) 165.5, 162.6, 145.2, 145.0, 138.4, 137.7, 136.8, 134.9, 134.6, 133.1, 132.6, 131.1, 130.42, 130.37, 130.0, 129.4, 128.9, 128.2, 128.03, 127.95, 127.4, 126.82, 126.76, 126.7, 126.3, 119.2, 116.8, 111.2, 65.3, 30.5, 20.6, 19.2, 18.0, 13.7; HRMS (ESI): *m/z* $[M + H]^+$ calcd for $C_{44}H_{38}NO_4$: 644.2795, found: 644.2790.



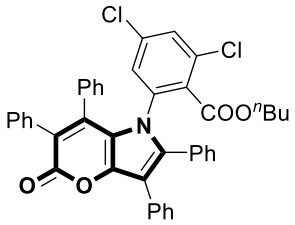
Butyl 5-chloro-3-methyl-2-(5-oxo-2,3,6,7-tetraphenylpyrano[3,2-*b*]pyrrol-1(5*H*)-yl)benzoate (5l)

Yellow solid; 49% yield; m.p. 249–251 °C; IR (KBr, cm^{-1}) *v*: 3666, 3059, 2957, 2931, 2864, 1706, 1544, 1464, 1283, 1184, 878, 698; ^{1}H NMR (300 MHz, $CDCl_3$) δ (ppm) 7.41 (d, *J* = 7.2 Hz, 2H), 7.33–7.03 (m, 12H), 6.96–6.86 (m, 4H), 6.80–6.74 (m, 2H), 6.67 (t, *J* = 8.4 Hz, 2H), 4.12 (t, *J* = 6.6 Hz, 2H), 1.89 (s, 3H), 1.61–1.50 (m, 2H), 1.38–1.26 (m, 2H), 0.90 (t, *J* = 7.2 Hz, 3H); ^{13}C NMR (75 MHz, $CDCl_3$) δ (ppm) 164.1, 162.4, 145.1, 144.8, 140.0, 136.6, 134.7, 134.4, 134.2, 133.5, 132.4, 131.7, 131.0, 130.7, 130.4, 130.1, 129.4, 128.8, 128.7, 128.5, 128.3, 127.9, 127.5, 127.3, 127.1, 127.0, 126.9, 126.5, 119.5, 116.7, 111.7, 65.8, 30.5, 19.2, 18.1, 13.7; HRMS (ESI): *m/z* $[M + H]^+$ calcd for $C_{43}H_{35}ClNO_4$: 664.2249, found: 664.2246.



Butyl 2,4-difluoro-6-(5-oxo-2,3,6,7-tetraphenylpyrano[3,2-*b*]pyrrol-1(5*H*)-yl) benzoate (5m)

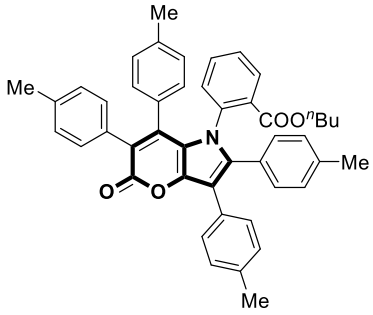
Yellow solid; 80% yield; m.p. 214–216 ^{o}C; IR (KBr, cm^{-1}) *v*: 3725, 3057, 2961, 1698, 1604, 1509, 1468, 1440, 1323, 1273, 1132, 1010, 887, 696; ^{1}H NMR (300 MHz, $CDCl_3$) δ (ppm) 7.36 (d, J = 6.9 H_Z, 2H), 7.30–7.08 (m, 11H), 7.03–6.91 (m, 5H), 6.85–6.77 (m, 2H), 6.54–6.47 (m, 1H), 6.42 (d, J = 8.1 Hz, 1H), 4.16–4.08 (m, 1H), 4.02–3.94 (m, 1H), 1.60–1.48 (m, 2H), 1.39–1.26 (m, 2H), 0.91 (t, J = 7.5 Hz, 3H); ^{13}C NMR (75 MHz, $CDCl_3$) δ (ppm) 162.3 (dd, $J_{C\text{-}F}$ = 254.3 Hz, $J_{C\text{-}F}$ = 15.0 Hz), 162.2, 160.5 (dd, $J_{C\text{-}F}$ = 258.0 Hz, $J_{C\text{-}F}$ = 14.3 Hz), 161.3, 145.1, 144.6, 138.5 (dd, $J_{C\text{-}F}$ = 13.5 Hz, $J_{C\text{-}F}$ = 6.0 Hz), 137.3, 134.4, 132.9, 130.9, 130.8, 130.3, 129.4, 129.1, 128.8, 128.7, 128.6, 128.3, 127.6, 127.3 (dd, $J_{C\text{-}F}$ = 29.2 Hz, $J_{C\text{-}F}$ = 29.3 Hz), 127.0, 119.9, 118.3, 117.7 (dd, $J_{C\text{-}F}$ = 14.3 Hz, $J_{C\text{-}F}$ = 4.5 Hz), 115.3 (dd, $J_{C\text{-}F}$ = 23.3 Hz, $J_{C\text{-}F}$ = 3.8 Hz), 112.1, 105.3, 105.0, 104.6, 65.9, 31.5, 19.1, 13.7; HRMS (ESI): *m/z* [M + H]$^{+}$ calcd for $C_{42}H_{32}F_2NO_4$: 652.2294, found: 652.2292.



Butyl 2,4-dichloro-6-(5-oxo-2,3,6,7-tetraphenylpyrano[3,2-*b*]pyrrol-1(5*H*)-yl) benzoate (5n)

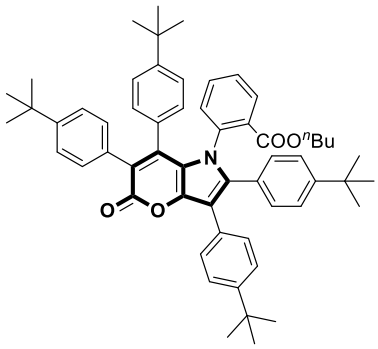
Yellow solid; 79% yield; m.p. 207–209 ^{o}C; IR (KBr, cm^{-1}) *v*: 3725, 3084, 2956, 1706, 1587, 1514, 1417, 1276, 1119, 1020, 874, 698; ^{1}H NMR (300 MHz, $CDCl_3$) δ (ppm) 7.34 (d, J = 6.9 H_Z, 2H), 7.30–7.03 (m, 13H), 7.00–6.93 (m, 4H), 6.86 (d, J = 7.5 Hz, 1H), 6.82–6.78 (m, 2H), 4.19–4.11 (m, 1H), 4.03–3.95 (m, 1H), 1.58–1.51 (m, 2H), 1.40–1.27 (m, 2H), 0.92 (t, J = 7.5 Hz, 3H); ^{13}C NMR (75 MHz, $CDCl_3$) δ (ppm)

162.9, 162.2, 145.0, 144.9, 137.7, 136.7, 135.1, 134.4, 132.6, 132.4, 131.6, 131.1, 130.9, 130.3, 130.1, 129.9, 129.4, 128.9, 128.7, 128.6, 128.3, 128.2, 127.9, 127.6, 127.4, 127.0, 126.9, 120.1, 118.8, 112.3, 66.2, 30.3, 19.1, 13.7; HRMS (ESI): *m/z* [M + H]$^+$ calcd for $C_{42}H_{32}Cl_2NO_4$: 684.1703, found: 684.1695.



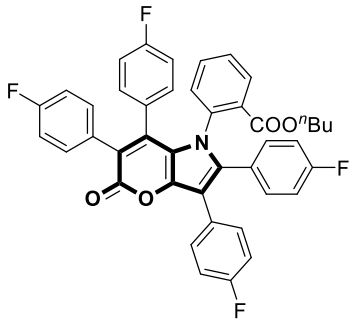
Butyl 2-(5-oxo-2,3,6,7-tetra-*p*-tolylpyrano[3,2-*b*]pyrrol-1(5*H*)-yl)benzoate (6a)

Yellow solid; 85% yield; m.p. 242–243 ^{o}C; IR (KBr, cm^{-1}) *v*: 3380, 2955, 2869, 1563, 1519, 1454, 1285, 1245, 1121, 818; ^{1}H NMR (300 MHz, $CDCl_3$) δ (ppm) 7.47 (dd, J_1 = 1.5 Hz, J_2 = 7.8 Hz, 1H), 7.28 (d, J = 6.6 Hz, 3H), 7.09–6.73 (m, 12H), 6.57 (s, 2H), 6.50 (d, J = 7.8 Hz, 1H), 6.40 (d, J = 7.8 Hz, 1H), 4.13–3.99 (m, 2H), 2.32 (s, 3H), 2.20 (s, 3H), 2.19 (s, 3H), 2.06 (s, 3H), 1.54–1.47 (m, 2H), 1.33–1.26 (m, 2H), 0.89 (t, J = 7.2 Hz, 3H); ^{13}C NMR (75 MHz, $CDCl_3$) δ (ppm) 165.0, 162.8, 145.0, 144.8, 137.9, 137.4, 137.0, 136.7, 136.2, 135.9, 132.0, 131.7, 131.4, 130.9, 130.7, 130.6, 130.1, 129.9, 129.2, 128.9, 128.8, 128.7, 128.5, 128.3, 128.1, 127.9, 127.30, 127.27, 118.7, 118.1, 111.0, 65.3, 30.5, 21.24, 21.19, 21.0, 19.2, 13.7; HRMS (ESI): *m/z* [M + H]$^+$ calcd for $C_{46}H_{42}NO_4$: 672.3108, found: 672.3120.



Butyl 2-(2,3,6,7-tetrakis(4-(*tert*-butyl)phenyl)-5-oxopyrano[3,2-*b*]pyrrol-1(5*H*)-yl) benzoate (6b)

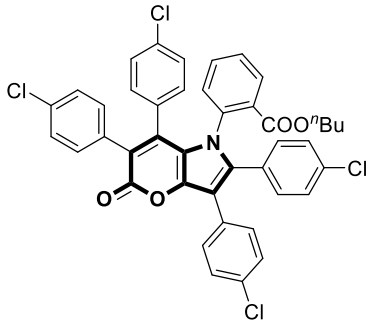
Yellow solid; 75% yield; m.p. 75–76 °C; IR (KBr, cm^{-1}) *v*: 3344, 2963, 2051, 2024, 1706, 1607, 1385, 1101, 620; ^1H NMR (300 MHz, $CDCl_3$) δ (ppm) 7.44 (dd, J_1 = 2.1 Hz, J_2 = 7.2 Hz, 1H), 7.37–7.27 (m, 4H), 7.06 (t, *J* = 7.5 Hz, 4H), 7.00–6.92 (m, 4H), 6.84–6.72 (m, 4H), 6.62 (d, *J* = 8.4 Hz, 1H), 6.56–6.49 (m, 2H), 4.13–3.99 (m, 2H), 1.57–1.48 (m, 2H), 1.31 (s, 9H), 1.29–1.28 (m, 2H), 1.19 (s, 9H), 1.17 (s, 9H), 1.10 (s, 9H), 0.90 (t, *J* = 7.2 Hz, 3H); ^{13}C NMR (75 MHz, $CDCl_3$) δ (ppm) 164.9, 162.8, 150.9, 149.6, 149.1, 148.9, 145.3, 145.0, 137.4, 137.1, 131.9, 131.8, 131.3, 130.7, 130.5, 130.2, 129.9, 128.9, 128.6, 128.4, 128.1, 127.7, 127.3, 125.1, 124.8, 124.2, 123.8, 118.8, 117.9, 111.0, 65.2, 34.47, 34.45, 34.3, 34.2, 31.3, 31.2, 31.1, 31.0, 30.5, 29.7, 19.2, 13.7; HRMS (ESI): *m/z* $[M + H]^+$ calcd for $C_{58}H_{66}NO_4$: 840.4986, found: 840.4985.



Butyl 2-(2,3,6,7-tetrakis(4-fluorophenyl)-5-oxopyrano[3,2-*b*]pyrrol-1(5*H*)-yl) benzoate (6c)

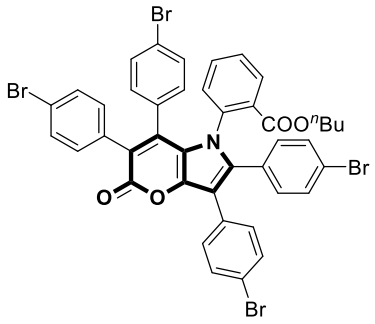
Yellow solid; 75% yield; m.p. 195–197 °C; IR (KBr, cm^{-1}) *v*: 2963, 1704, 1602, 1514, 1224, 1159, 842; ^1H NMR (300 MHz, $CDCl_3$) δ (ppm) 7.52 (dd, J_1 = 1.5 Hz, J_2 = 7.8 Hz, 1H), 7.36–7.31 (m, 2H), 7.18–6.96 (m, 6H), 6.88–6.75 (m, 7H), 6.67–6.60 (m, 2H), 6.50 (t, *J* = 8.7 Hz, 1H), 6.38 (t, *J* = 8.7 Hz, 1H), 4.08 (t, *J* = 6.6 Hz, 2H), 1.59–1.50 (m, 2H), 1.36–1.26 (m, 2H), 0.91 (t, *J* = 7.5 Hz, 3H); ^{13}C NMR (75 MHz, $CDCl_3$) δ (ppm) 164.6, 162.4 (d, $J_{C\text{-}F}$ = 248.3 Hz), 162.19, 162.18, 161.6 (d, $J_{C\text{-}F}$ = 247.5 Hz), 161.5 (d, $J_{C\text{-}F}$ = 243.8 Hz), 144.8, 144.2, 136.5, 136.4, 132.7 (d, $J_{C\text{-}F}$ = 8.3 Hz), 131.1 (d, $J_{C\text{-}F}$ = 24.0 Hz), 131.0, 130.9 (d, $J_{C\text{-}F}$ = 8.3 Hz), 130.5 (d, $J_{C\text{-}F}$ = 8.3 Hz), 130.4 (d, $J_{C\text{-}F}$ = 8.0 Hz), 130.3 (d, $J_{C\text{-}F}$ = 3.3 Hz), 129.9, 128.7 (d, $J_{C\text{-}F}$ = 3.3 Hz), 128.5, 126.5 (d, $J_{C\text{-}F}$ = 3.0 Hz), 125.9 (d, $J_{C\text{-}F}$ = 3.0 Hz), 118.6, 117.7, 115.5 (d, $J_{C\text{-}F}$ = 21.8

Hz), 115.4 (d, $J_{C\text{-}F}$ = 21.0 Hz), 114.8 (d, $J_{C\text{-}F}$ = 21.8 Hz), 114.7, 114.4, 110.7, 65.4, 30.5, 19.2, 13.7; HRMS (ESI): *m/z* $[M + H]^+$ calcd for $C_{42}H_{30}F_4NO_4$: 688.2105, found: 688.2117.



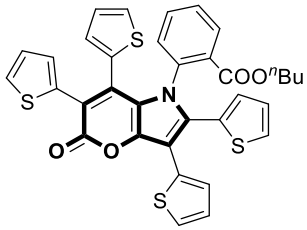
Butyl 2-(2,3,6,7-tetrakis(4-chlorophenyl)-5-oxopyrano[3,2-*b*]pyrrol-1(5*H*)-yl) benzoate (6d)

Yellow solid; 78% yield; m.p. 220–221 °C; IR (KBr, cm^{-1}) *v*: 2950, 2868, 1703, 1513, 1274, 1090, 1015, 740; ^1H NMR (300 MHz, $CDCl_3$) δ (ppm) 7.54 (dd, J_1 = 1.2 Hz, J_2 = 7.8 Hz, 1H), 7.32–7.25 (m, 4H), 7.20 (t, *J* = 7.8 Hz, 1H), 7.13–7.05 (m, 5H), 6.96 (d, *J* = 8.4 Hz, 2H), 6.82–6.77 (m, 4H), 6.67–6.56 (m, 3H), 4.07 (t, *J* = 6.6 Hz, 2H), 1.56–1.49 (m, 2H), 1.37–1.27 (m, 2H), 0.91 (t, *J* = 7.5 Hz, 3H); ^{13}C NMR (75 MHz, $CDCl_3$) δ (ppm) 164.4, 161.8, 144.9, 143.8, 136.5, 136.3, 134.8, 133.8, 133.2, 132.72, 132.69, 132.3, 132.04, 131.96, 131.4, 130.93, 130.90, 130.5, 130.0, 129.9, 129.8, 128.9, 128.7, 128.7, 128.5, 128.2, 128.1, 127.8, 118.5, 117.8, 110.6, 65.5, 30.5, 19.2, 13.7; HRMS (ESI): *m/z* $[M + H]^+$ calcd for $C_{42}H_{30}Cl_4NO_4$: 754.0894, found: 754.0916.



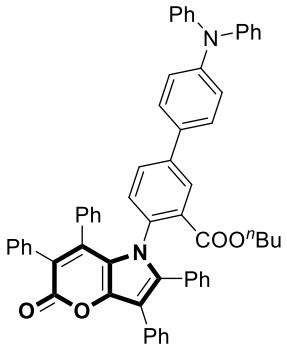
Butyl 2-(2,3,6,7-tetrakis(4-bromophenyl)-5-oxopyrano[3,2-*b*]pyrrol-1(5*H*)-yl) benzoate (6e)

Yellow solid; 51% yield; m.p. 221–223 °C; IR (KBr, cm^{-1}) *v*: 3426, 3067, 2957, 2929, 2871, 2025, 1707, 1453, 1375, 1102, 1011; ^1H NMR (300 MHz, $CDCl_3$) δ (ppm) 7.54 (dd, J_1 = 1.8 Hz, J_2 = 7.8 Hz, 1H), 7.42 (d, J = 8.4 Hz, 2H), 7.28–7.20 (m, 7H), 7.12–7.07 (m, 1H), 6.96–6.89 (m, 3H), 6.80 (d, J = 7.8 Hz, 2H), 6.73 (d, J = 8.4 Hz, 2H), 6.56–6.49 (m, 2H), 4.06 (t, J = 6.9 Hz, 2H), 1.59–1.49 (m, 2H), 1.35–1.25 (m, 2H), 0.91 (t, J = 7.5 Hz, 3H); ^{13}C NMR (75 MHz, $CDCl_3$) δ (ppm) 164.4, 161.7, 144.8, 143.7, 136.5, 136.1, 133.1, 132.6, 132.2, 132.0, 131.57, 131.56, 131.4, 131.3, 130.94, 130.88, 130.8, 130.7, 130.2, 130.0, 129.7, 129.3, 128.5, 128.4, 123.1, 122.1, 121.4, 120.8, 118.3, 117.8, 110.5, 65.4, 30.4, 19.2, 13.7; HRMS (ESI): *m/z* $[M + H]^+$ calcd for $C_{42}H_{30}Br_4NO_4$: 931.8862, found: 931.8867.



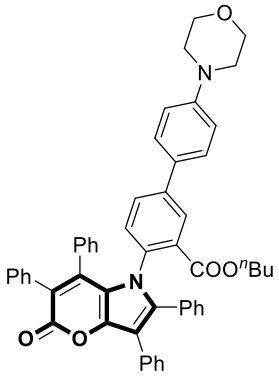
Butyl 2-(5-oxo-2,3,6,7-tetra(thiophen-2-yl)pyrano[3,2-*b*]pyrrol-1(5*H*)-yl)benzoate (6f)

Yellow solid; 83% yield; m.p. 235–236 °C; IR (KBr, cm^{-1}) *v*: 3263, 3012, 2913, 2852, 2130, 1843, 1526, 1367, 1135, 872; ^1H NMR (300 MHz, $CDCl_3$) δ (ppm) 7.70–7.66 (m, 1H), 7.53 (d, J = 3.0 Hz, 1H), 7.29 (d, J = 4.8 Hz, 1H), 7.21–7.17 (m, 4H), 7.06–6.99 (m, 3H), 6.93 (d, J = 3.3 Hz, 1H), 6.87–6.81 (m, 3H), 6.44–6.41 (m, 2H), 4.17–4.07 (m, 2H), 1.55–1.46 (m, 2H), 1.34–1.21 (m, 2H), 0.86 (t, J = 7.5 Hz, 3H); ^{13}C NMR (75 MHz, $CDCl_3$) δ (ppm) 164.6, 160.8, 142.9, 137.3, 136.0, 135.2, 132.1, 131.9, 131.5, 131.3, 130.9, 130.3, 130.0, 129.7, 129.5, 129.32, 129.30, 128.6, 127.8, 126.90, 126.87, 126.6, 126.5, 125.9, 124.5, 118.7, 114.9, 107.5, 65.4, 30.4, 19.1, 13.6; HRMS (ESI): *m/z* $[M + H]^+$ calcd for $C_{34}H_{26}NO_4S_4$: 640.0739, found: 640.0754.



Butyl 4'-(diphenylamino)-4-(5-oxo-2,3,6,7-tetraphenylpyrano[3,2-*b*]pyrrol-1(5*H*)-yl)-[1,1'-biphenyl]-3-carboxylate (7)

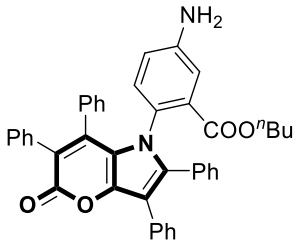
Yellow solid; 91% yield; m.p. 211–212 °C; IR (KBr, cm^{-1}) *v*: 3175, 3032, 2946, 2915, 2863, 2122, 1809, 1641, 1523, 1216, 1187; ^{1}H NMR (300 MHz, $CDCl_3$) δ (ppm) 7.62 (s, 1H), 7.42 (d, *J* = 7.5 Hz, 2H), 7.30–7.20 (m, 9H), 7.13–7.07 (m, 17H), 6.94 (d, *J* = 7.2 Hz, 2H), 6.86–6.66 (m, 6H), 4.13–4.06 (m, 2H), 1.60–1.51 (m, 2H), 1.36–1.26 (m, 2H), 0.91 (t, *J* = 7.2 Hz, 3H); ^{13}C NMR (75 MHz, $CDCl_3$) δ (ppm) 164.9, 162.5, 148.0, 147.3, 145.1, 145.0, 140.3, 137.6, 135.0, 134.8, 133.1, 132.1, 131.8, 131.1, 130.9, 130.2, 129.9, 129.4, 129.3, 129.2, 128.9, 128.8, 128.6, 128.2, 128.1, 127.5, 127.3, 127.2, 126.9, 126.8, 126.4, 124.7, 123.4, 123.1, 119.2, 118.0, 111.3, 65.4, 30.5, 19.2, 13.7; HRMS (ESI): *m/z* $[M + H]^+$ calcd for $C_{60}H_{47}N_2O_4$: 859.3530, found: 859.3528.



Butyl 4'-morpholino-4-(5-oxo-2,3,6,7-tetraphenylpyrano[3,2-*b*]pyrrol-1(5*H*)-yl)-[1,1'-biphenyl]-3-carboxylate (8)

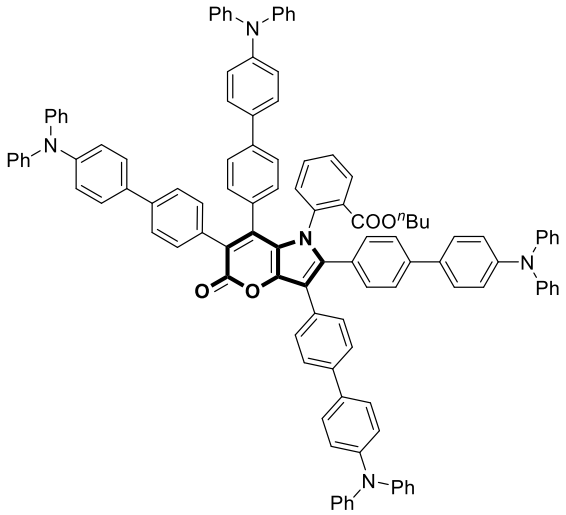
Yellow solid; 87% yield; m.p. 218–219 °C; IR (KBr, cm^{-1}) *v*: 2942, 2906, 2782, 2132, 1812, 1539, 1285, 1176, 1032; ^{1}H NMR (300 MHz, $CDCl_3$) δ (ppm) 7.62 (s, 1H), 7.42 (d, *J* = 7.5 Hz, 2H), 7.34 (d, *J* = 8.4 Hz, 2H), 7.27 (t, *J* = 7.5 Hz, 2H), 7.21 (d, *J* =

6.9 Hz, 1H), 7.17–7.06 (m, 9H), 6.96–6.93 (m, 4H), 6.85–6.65 (m, 6H), 4.15–4.06 (m, 2H), 3.87 (t, *J* = 4.2 Hz, 4H), 3.21 (t, *J* = 4.2 Hz, 4H), 1.56–1.51 (m, 2H), 1.38–1.26 (m, 2H), 0.91 (t, *J* = 7.5 Hz, 3H); ^{13}C NMR (75 MHz, $CDCl_3$) δ (ppm) 165.0, 162.5, 151.0, 145.1, 144.9, 140.4, 137.6, 134.8, 134.7, 133.0, 131.8, 131.0, 130.9, 130.1, 129.8, 129.7, 129.3, 129.0, 128.9, 128.7, 128.3, 128.21, 128.17, 128.1, 127.53, 127.45, 127.23, 127.16, 126.8, 126.7, 126.4, 119.1, 118.0, 115.4, 111.2, 66.7, 65.4, 48.7, 30.5, 19.2, 13.7; HRMS (ESI): *m/z* $[M + H]^+$ calcd for $C_{52}H_{45}N_2O_5$: 777.3323, found: 777.3320.



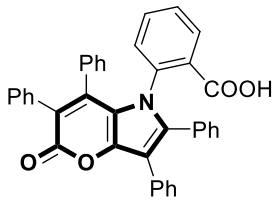
Butyl 5-amino-2-(5-oxo-2,3,6,7-tetraphenylpyrano[3,2-*b*]pyrrol-1(5*H*)-yl) benzoate (9)

Yellow solid; 79% yield; m.p. 242–243 ^{o}C; IR (KBr, cm^{-1}) *v*: 3432, 3318, 2953, 2865, 2036, 1689, 1472, 1321, 1143, 1068; ^{1}H NMR (300 MHz, $CDCl_3$) δ (ppm) 7.39 (d, *J* = 7.2 H_Z, 2H), 7.26 (t, *J* = 7.5 Hz, 2H), 7.19 (d, *J* = 7.2 Hz, 1H), 7.16–7.04 (m, 8H), 6.91–6.80 (m, 5H), 6.75–6.68 (m, 2H), 6.64–6.57 (m, 2H), 6.32 (d, *J* = 7.5 Hz, 1H), 4.22(s, 2H), 4.09–4.00 (m, 2H), 1.56–1.47 (m, 2H), 1.34–1.26 (m, 2H), 0.89 (t, *J* = 7.2 Hz, 3H); ^{13}C NMR (75 MHz, $CDCl_3$) δ (ppm) 164.8, 163.0, 145.7, 144.8, 138.2, 134.8, 132.8, 132.3, 131.1, 131.0, 130.9, 130.13, 130.05, 129.3, 128.8, 128.6, 128.2, 128.1, 128.0, 127.5, 127.2, 127.0, 126.8, 126.4, 118.6, 118.1, 110.9, 65.3, 30.4, 19.2, 13.7; HRMS (ESI): *m/z* $[M + H]^+$ calcd for $C_{42}H_{35}N_2O_4$: 631.2591, found: 631.2601.



Butyl 2-(2,3,6,7-tetrakis(4'-(diphenylamino)-[1,1'-biphenyl]-4-yl)-5-oxopyrano [3,2-*b*]pyrrol-1(5*H*)-yl)benzoate (10)

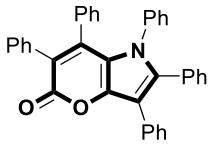
Bright yellow solid; 85% yield; m.p. 206–207 ^{o}C; IR (KBr, cm^{-1}) *v*: 3156, 3051, 2934, 2912, 2849, 2127, 1795, 1558, 1357, 1285, 1139; ^{1}H NMR (300 MHz, $CDCl_3$) δ (ppm) 7.51–7.45 (m, 7H), 7.37–7.31 (m, 7H), 7.26–7.19 (m, 20H), 7.12–6.96 (m, 38H), 6.89–6.83 (m, 2H), 6.75 (d, *J* = 7.8 Hz, 2H), 4.15–4.08 (m, 2H), 1.62–1.52 (m, 2H), 1.38–1.28 (m, 2H), 0.91 (t, *J* = 7.5 Hz, 3H); ^{13}C NMR (75 MHz, $CDCl_3$) δ (ppm) 164.8, 162.5, 147.60, 147.56, 147.44, 147.40, 147.3, 147.0, 146.9, 145.0, 144.8, 139.8, 139.2, 138.7, 138.3, 137.4, 136.9, 134.7, 134.6, 133.8, 133.4, 131.7, 131.5, 131.4, 131.3, 130.8, 129.8, 129.7, 129.5, 129.22, 129.18, 128.5, 127.8, 127.5, 127.4, 127.3, 126.4, 125.9, 125.7, 125.4, 124.4, 124.34, 124.27, 124.2, 123.9, 123.8, 123.7, 123.5, 123.02, 122.98, 122.8, 118.6, 118.3, 111.0, 65.4, 30.5, 19.3, 13.8; HRMS (ESI): *m/z* $[M + H]^+$ calcd for $C_{114}H_{86}N_5O_4$: 1588.6674, found: 1588.6668.



2-(5-oxo-2,3,6,7-tetraphenylpyrano[3,2-*b*]pyrrol-1(5*H*)-yl)Benzoic acid (11)

Yellow solid; 56% yield; m.p. >300 ^{o}C; IR (KBr, cm^{-1}) *v*: 3453, 3057, 2539, 1694, 1602, 1580, 1564, 1541, 1467, 1418, 1379, 1305, 718; ^{1}H NMR (300 MHz, DMSO-d_6) δ (ppm) 12.87 (s, 1H), 7.37–7.24 (m, 6H), 7.14–6.99 (m, 13H), 6.82–6.79 (m, 3H),

6.66–6.65 (m, 2H); ^{13}C NMR (75 MHz, DMSO-d_6) δ (ppm) 165.4, 161.4, 145.5, 143.9, 137.8, 135.9, 134.9, 132.2, 131.9, 131.5, 130.9, 130.7, 130.2, 129.9, 129.8, 128.81, 128.77, 128.3, 128.1, 128.0, 127.3, 127.1, 126.9, 126.6, 126.5, 118.1, 117.2, 110.0; HRMS (ESI): *m/z* $[M + H]^+$ calcd for $C_{38}H_{26}NO_4$: 560.1856, found: 560.1864.



1,2,3,6,7-Pentaphenylpyrano[3,2-*b*]pyrrol-5(1*H*)-one (12)

Yellow solid; 73% yield; m.p. 193–194 ^{o}C; IR (KBr, cm^{-1}) *v*: 2987, 1705, 1643, 1526, 1215, 1180, 973, 826; ^{1}H NMR (300 MHz, $CDCl_3$) δ (ppm) 7.40 (d, J = 7.2 H_Z, 2H), 7.27–7.17 (m, 3H), 7.10–7.05 (m, 8H), 6.95 (d, J = 7.2 H_Z, 2H), 6.90–6.65 (m, 10H); ^{13}C NMR (75 MHz, $CDCl_3$) δ (ppm) 162.4, 145.2, 144.8, 137.8, 136.5, 134.7, 132.9, 131.00, 130.96, 130.8, 130.2, 129.4, 129.0, 128.8, 128.1, 127.9, 127.7, 127.34, 127.26, 127.03, 127.00, 126.6, 126.4, 119.2, 117.4, 111.0; HRMS (ESI): *m/z* $[M + H]^+$ calcd for $C_{37}H_{26}NO_2$: 516.1958, found: 516.1958.

8. References

[1] (a) Nacsa, E. D.; Lambert, T. H. *Org. Lett.* **2013**, *15*, 38–41. (b) Miao, W. H.; Gao, W. X.; Huang, X. B.; Liu, M. C.; Zhou, Y. B.; Wu, H. Y. *Org. Lett.* **2021**, *23*, 9425–9430.

[2] Liao, G.; Zhang, T.; Jin, L.; Wang, B.; Xu, C.; Lan, Y.; Zhao, Y.; Shi, B. *Angew. Chem. Int. Ed.* **2022**, *61*, e202115221.

[3] Zhai, X. Y.; Wang, W.; Xiao, K.; Zhao, L. *Inorg. Chem.* **2023**, *62*, 6147–6154.

[4] Gooßen, L.; Rodríguez, N.; Linder, C.; Lange, P.; Fromm, A. *ChemCatChem* **2010**, *2*, 430–442.

9. Copies of the ^{1}H and ^{13}C NMR Spectra

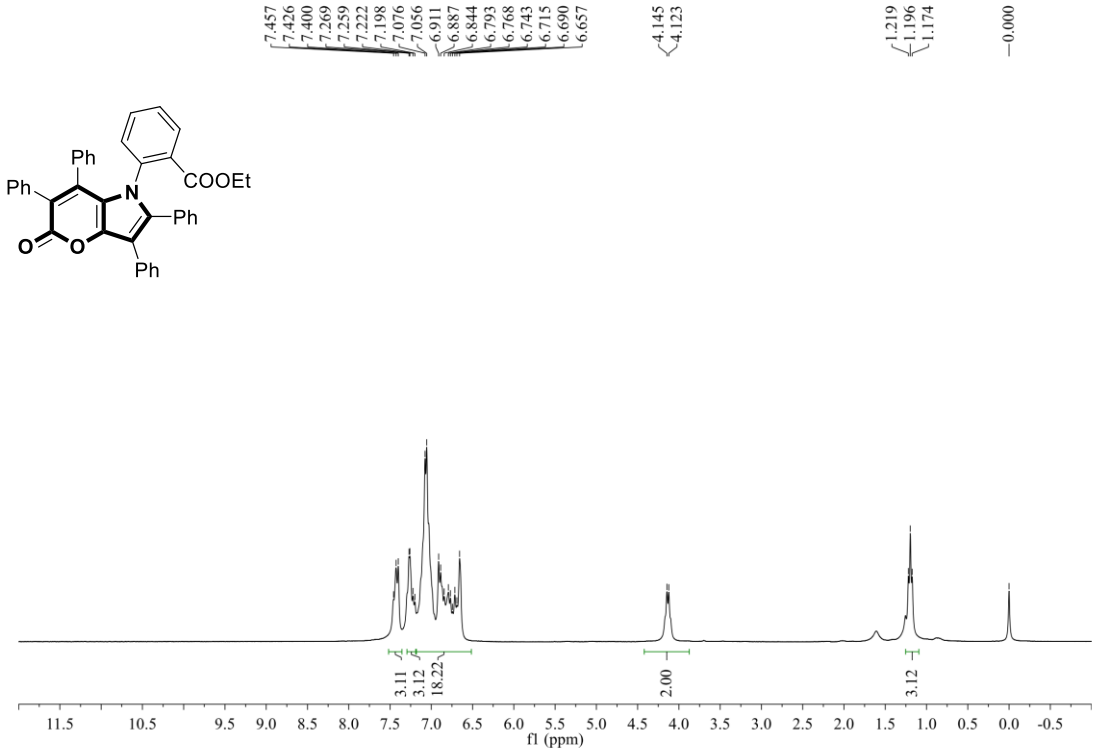


Figure S4. ^{1}H NMR spectrum of compound **4a** (300 MHz, $CDCl_3$)

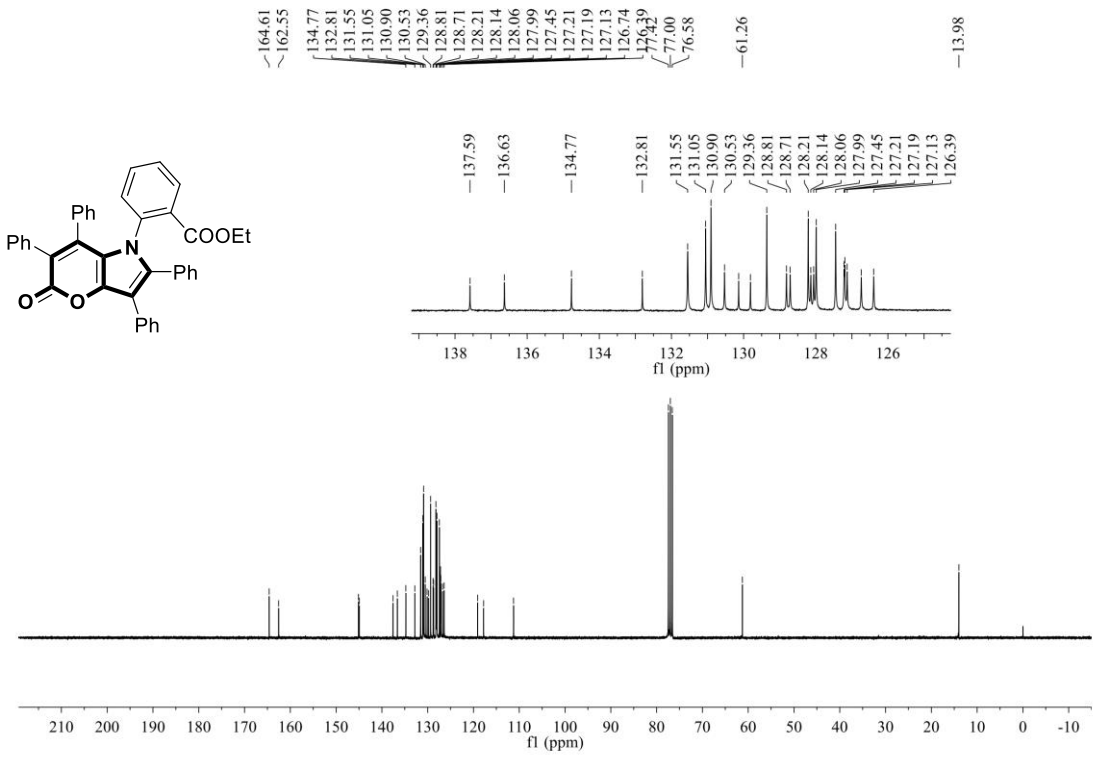


Figure S5. ^{13}C NMR spectrum of compound **4a** (75 MHz, $CDCl_3$)

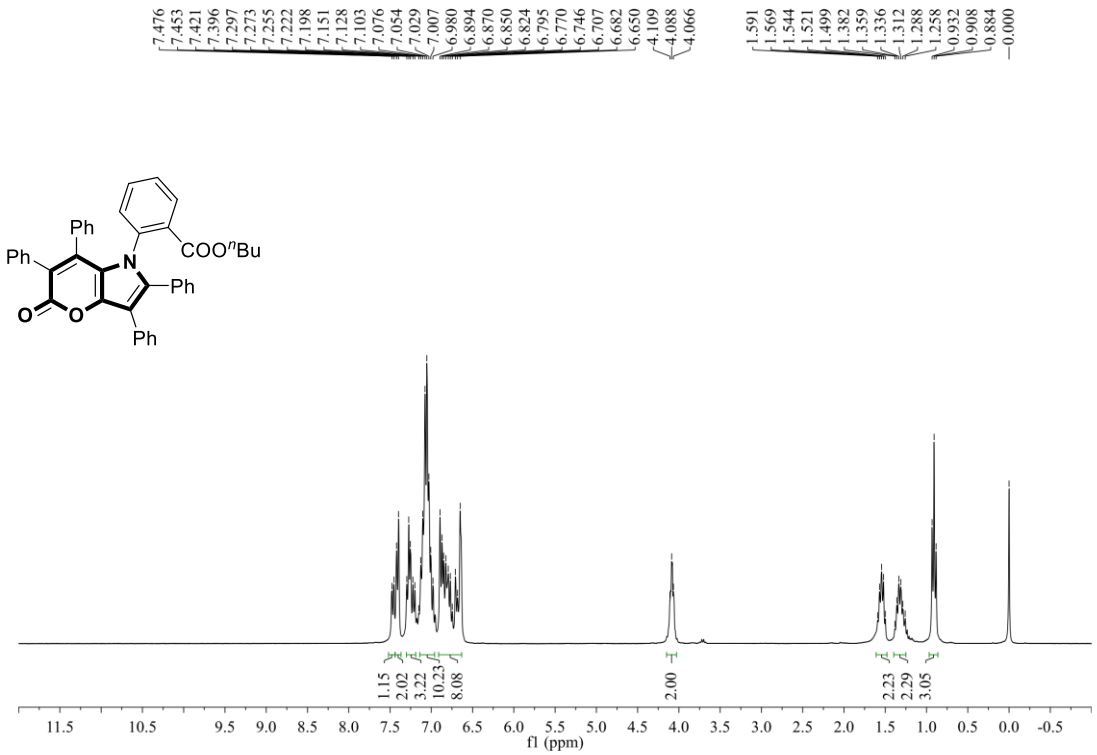


Figure S6. ^{1}H NMR spectrum of compound **4b** (300 MHz, $CDCl_3$)

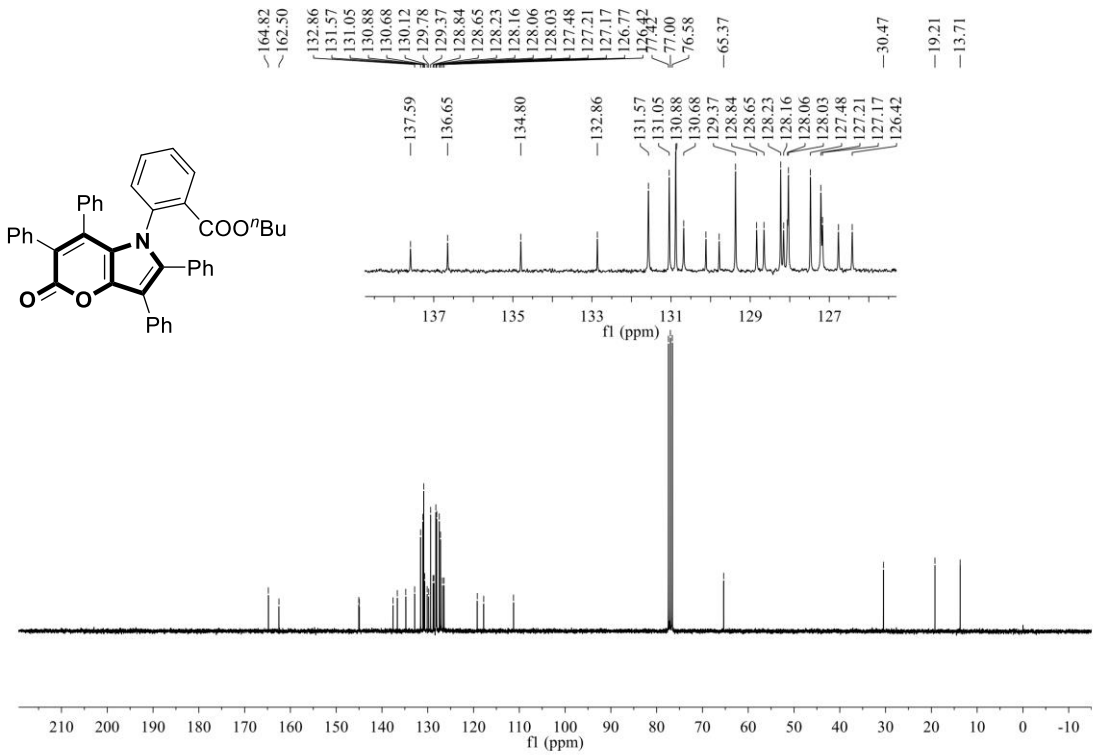


Figure S7. ^{13}C NMR spectrum of compound **4b** (75 MHz, $CDCl_3$)

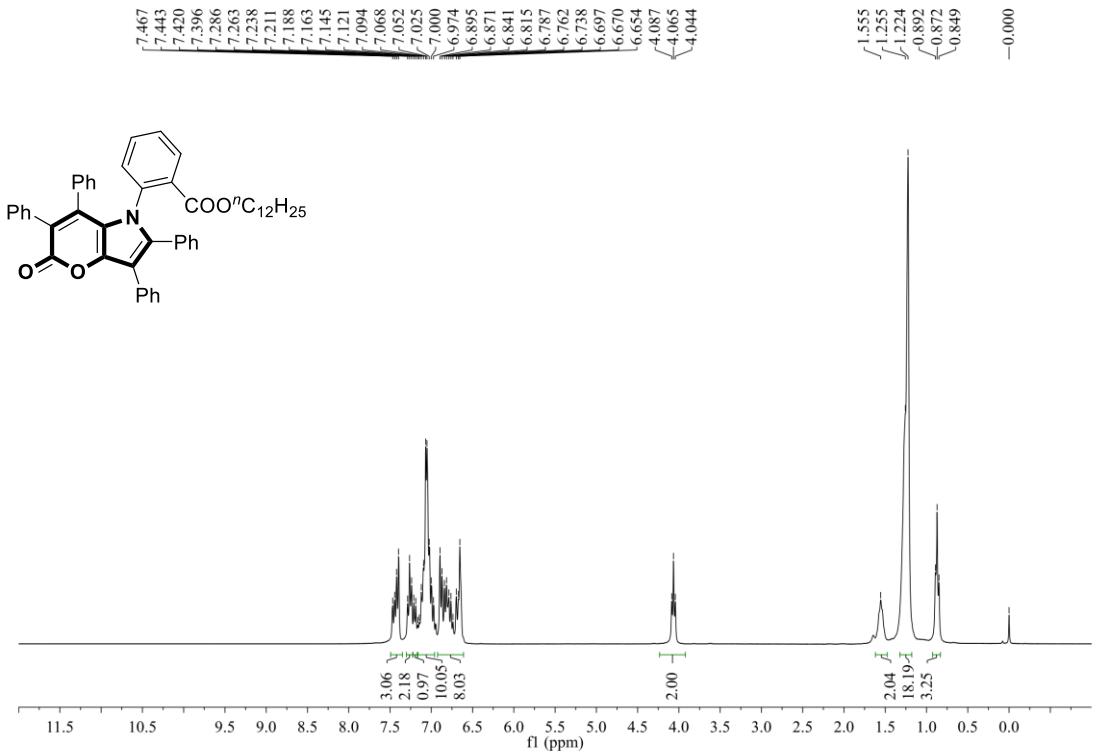


Figure S8. ^{1}H NMR spectrum of compound **4c** (300 MHz, $CDCl_3$)

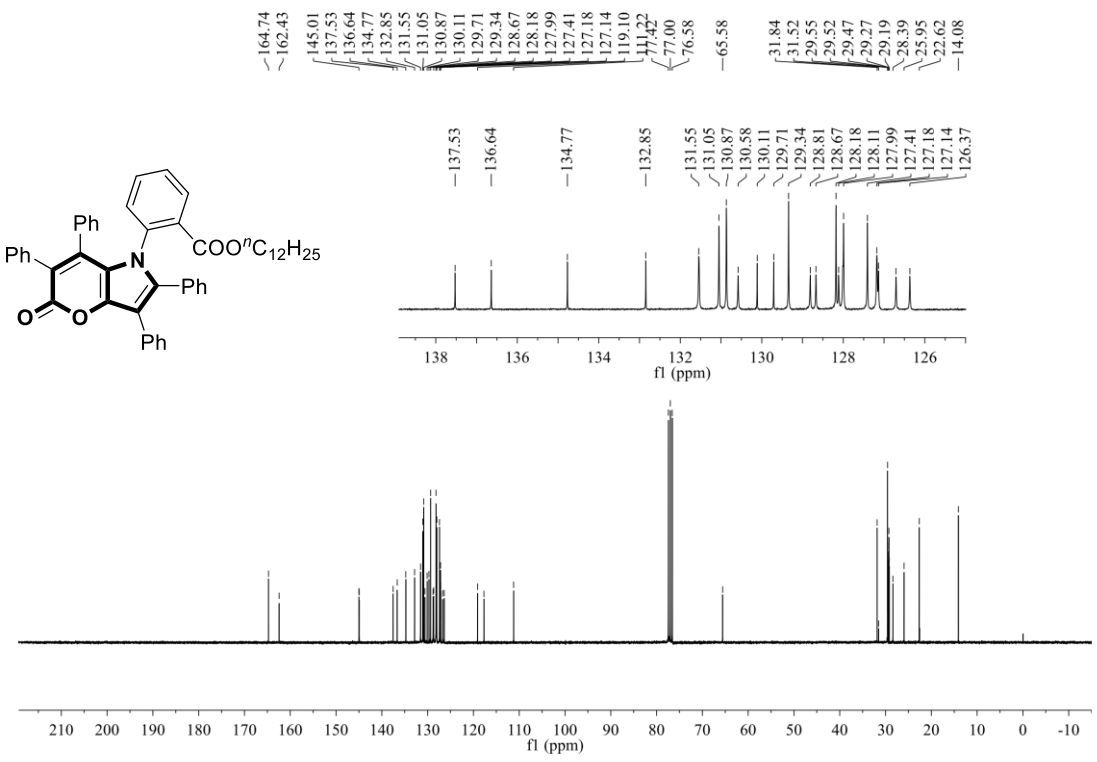


Figure S9. ^{13}C NMR spectrum of compound **4c** (75 MHz, $CDCl_3$)

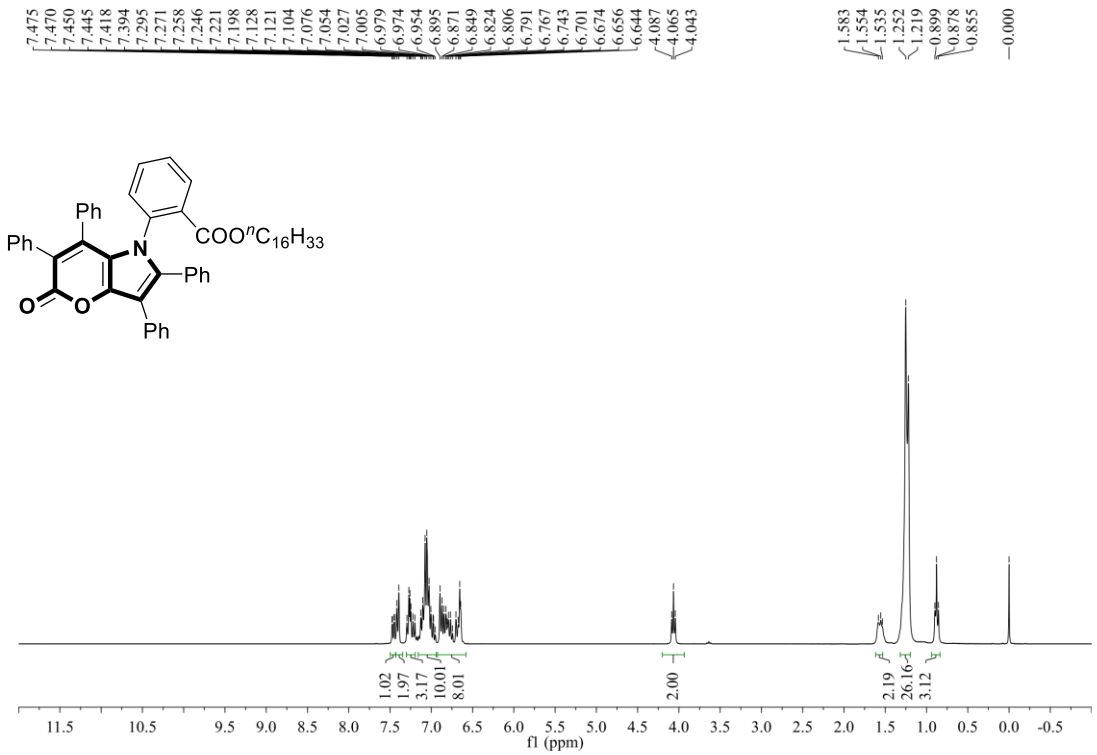


Figure S10. ^{1}H NMR spectrum of compound **4d** (300 MHz, $CDCl_3$)

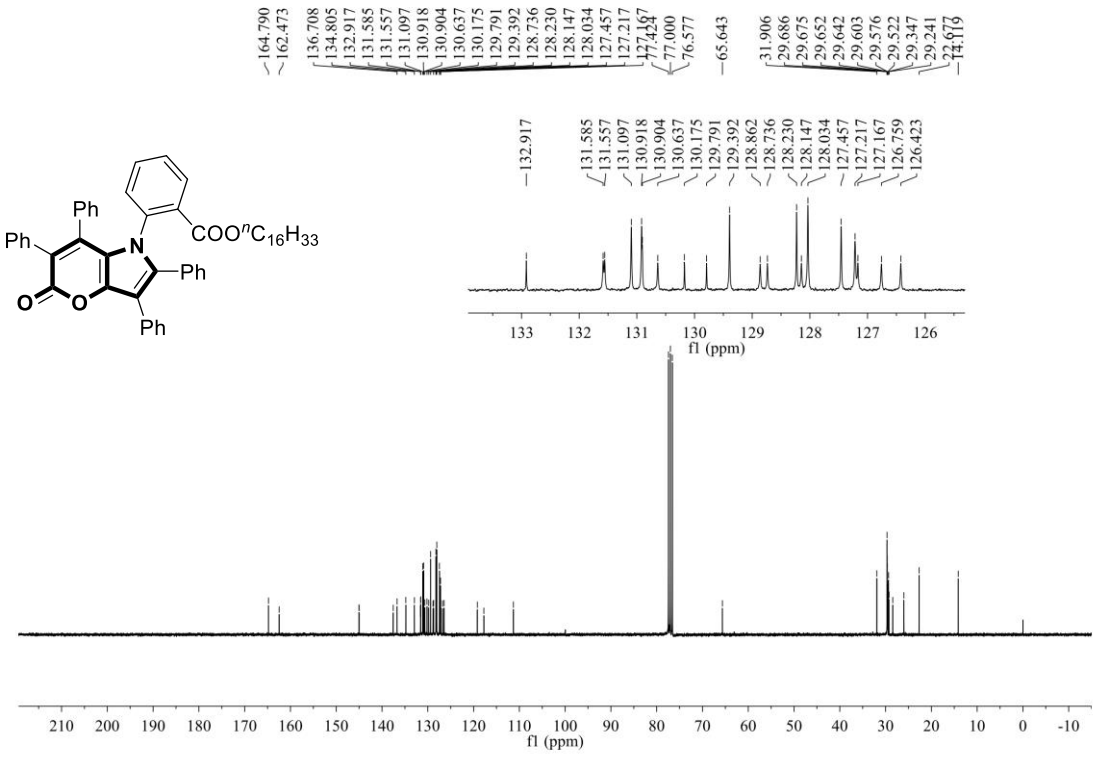


Figure S11. ^{13}C NMR spectrum of compound **4d** (75 MHz, $CDCl_3$)

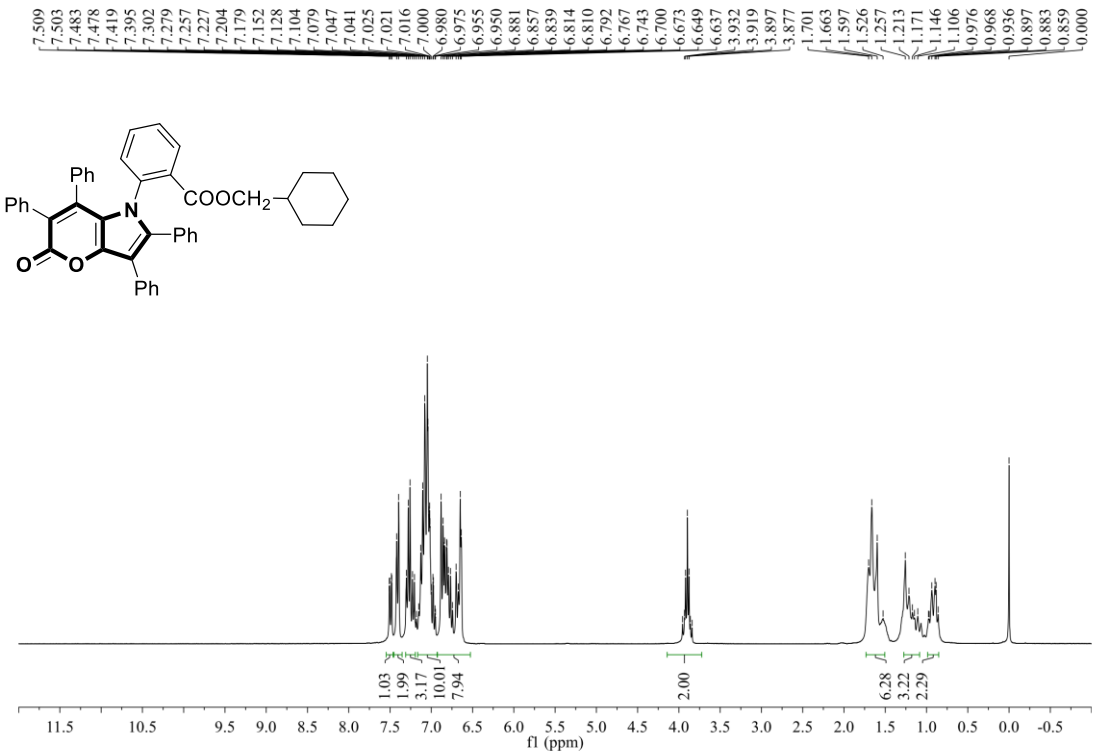


Figure S12. ^{1}H NMR spectrum of compound **4e** (300 MHz, $CDCl_3$)

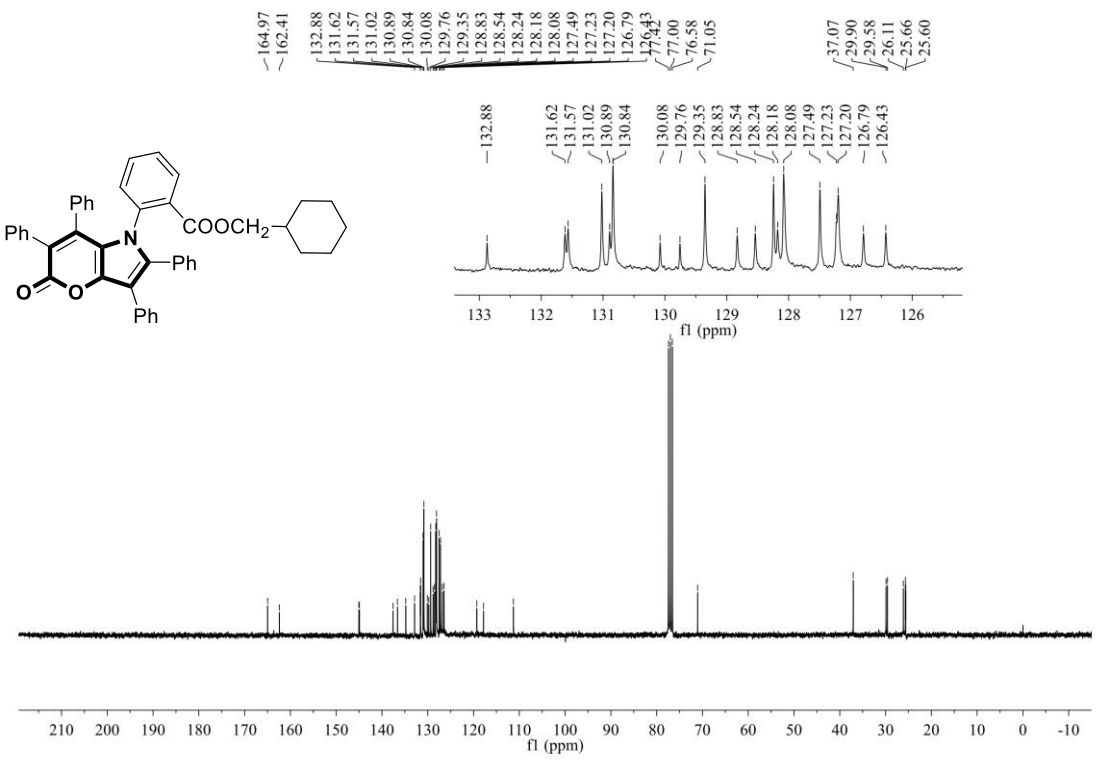


Figure S13. ^{13}C NMR spectrum of compound **4e** (75 MHz, $CDCl_3$)

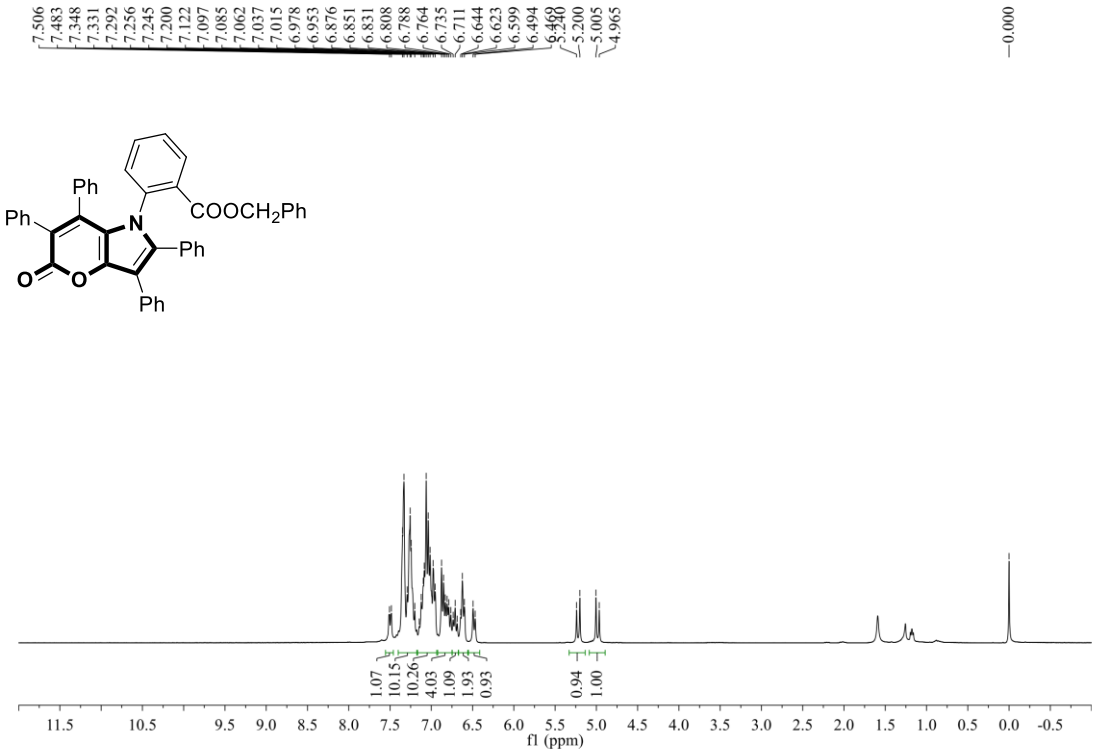


Figure S14. ^{1}H NMR spectrum of compound **4f** (300 MHz, $CDCl_3$)

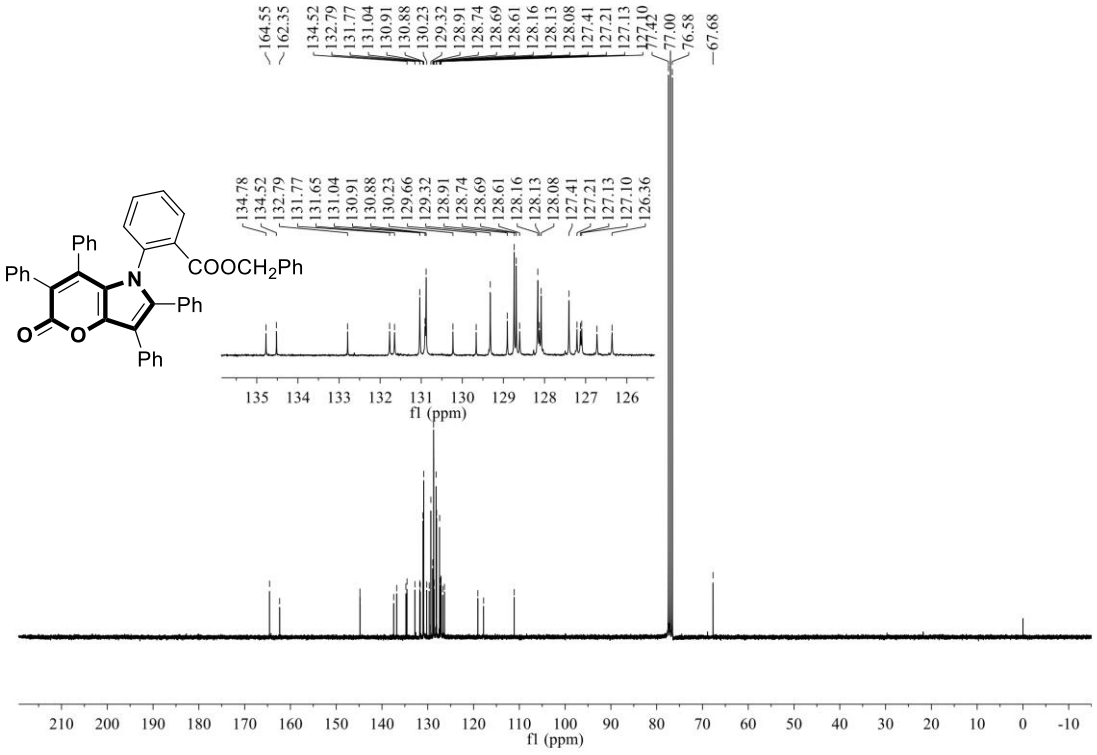


Figure S15. ^{13}C NMR spectrum of compound **4f** (75 MHz, $CDCl_3$)

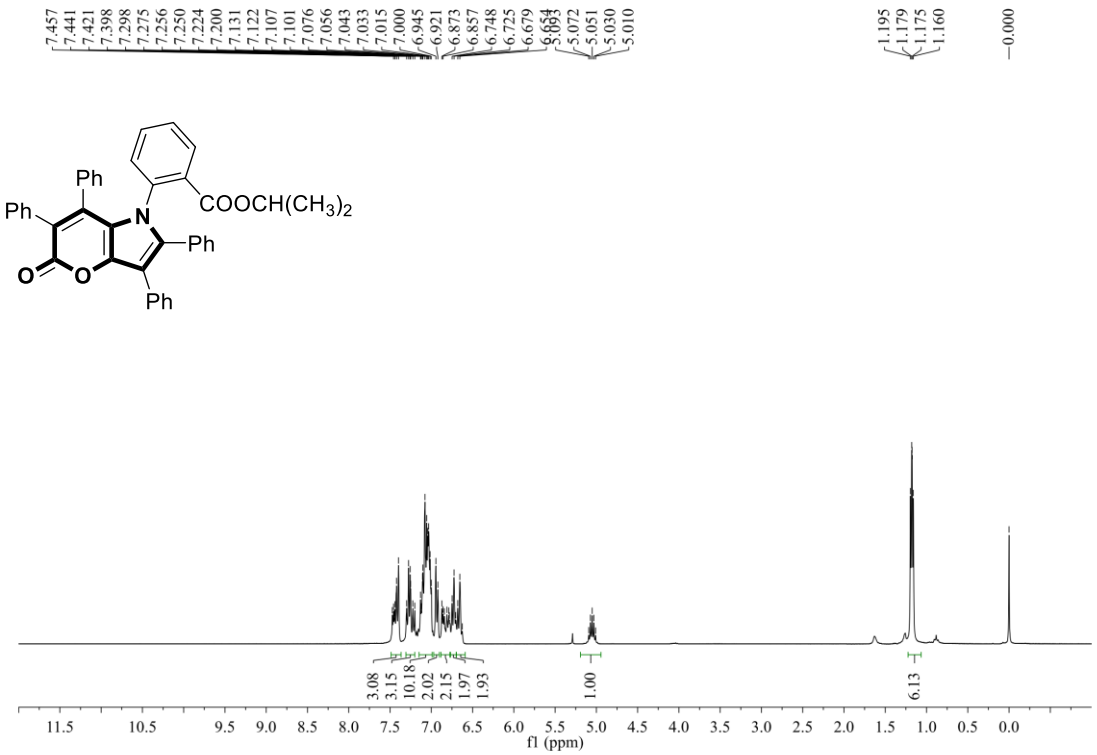


Figure S16. ^{1}H NMR spectrum of compound **4g** (300 MHz, $CDCl_3$)

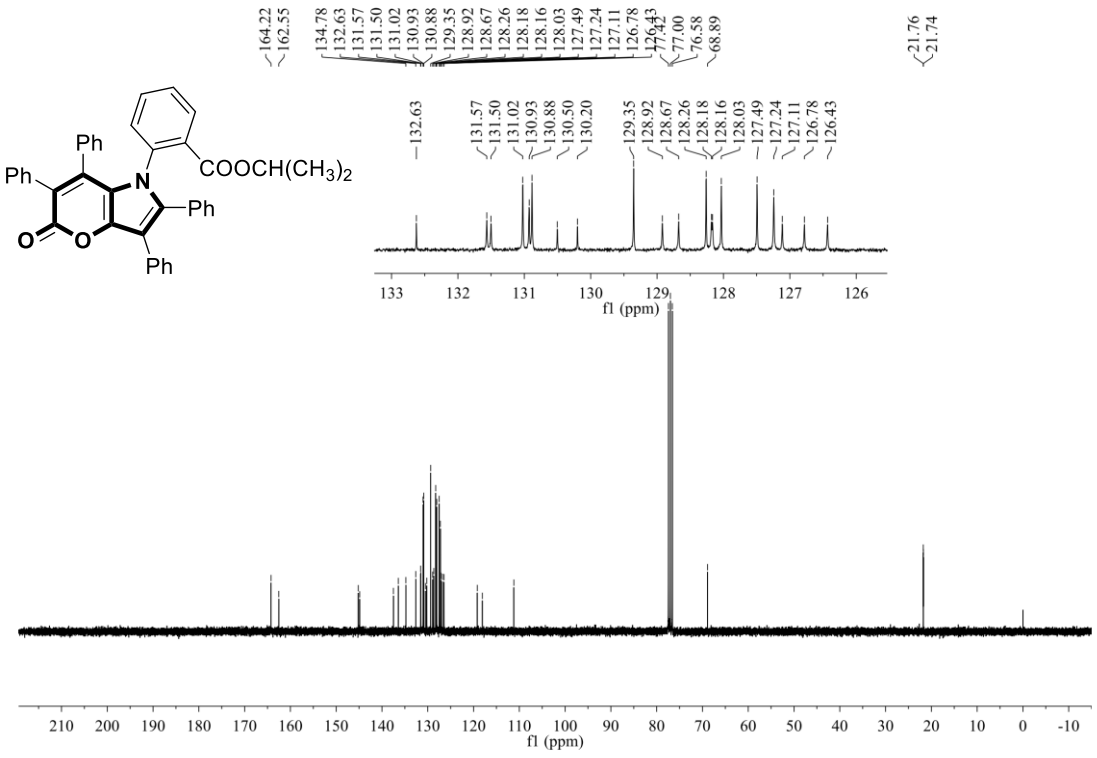


Figure S17. ^{13}C NMR spectrum of compound **4g** (75 MHz, $CDCl_3$)

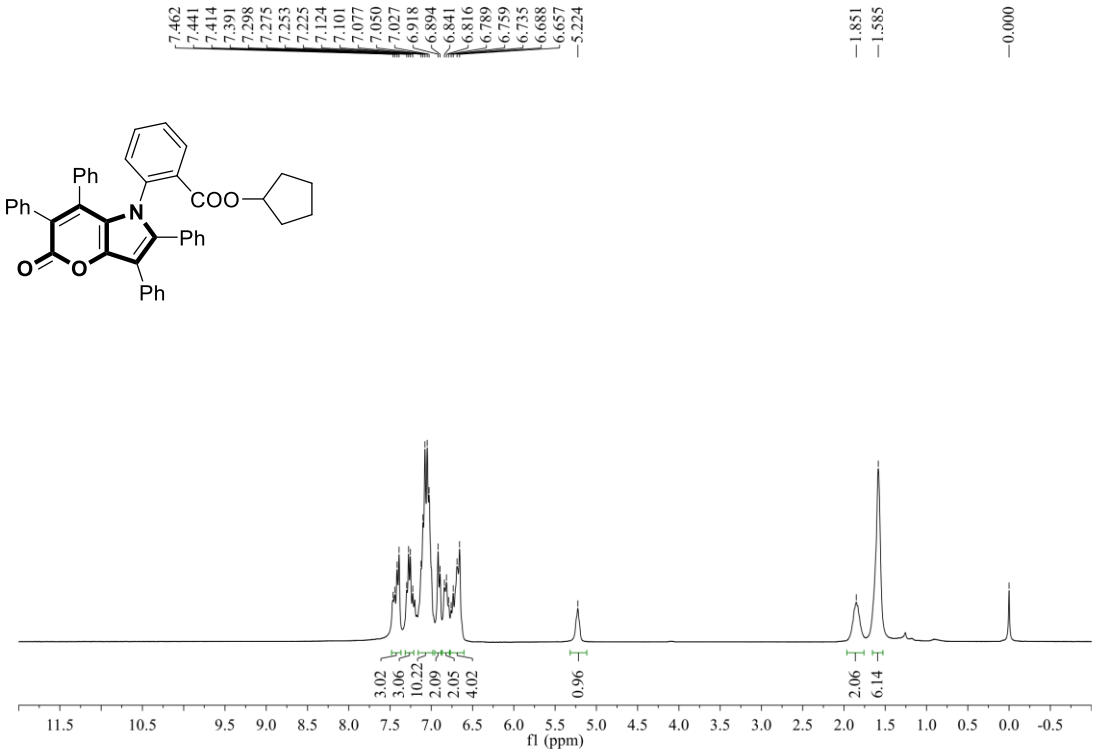


Figure S18. ^{1}H NMR spectrum of compound **4h** (300 MHz, $CDCl_3$)

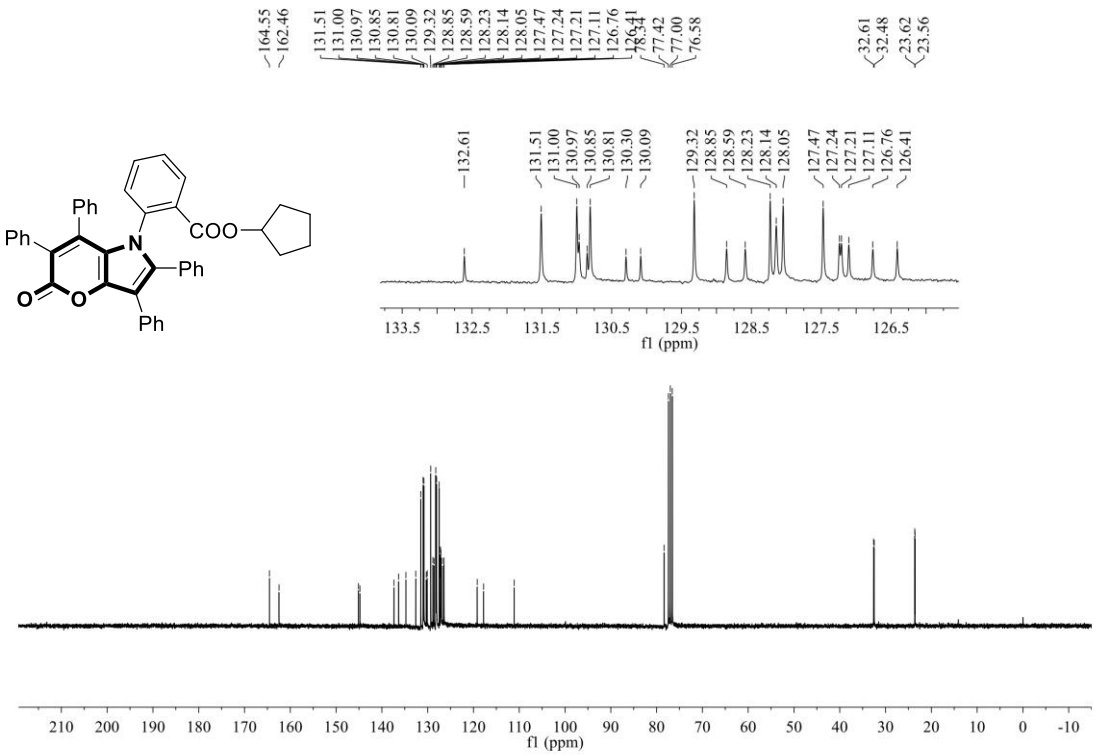


Figure S19. ^{13}C NMR spectrum of compound **4h** (75 MHz, $CDCl_3$)

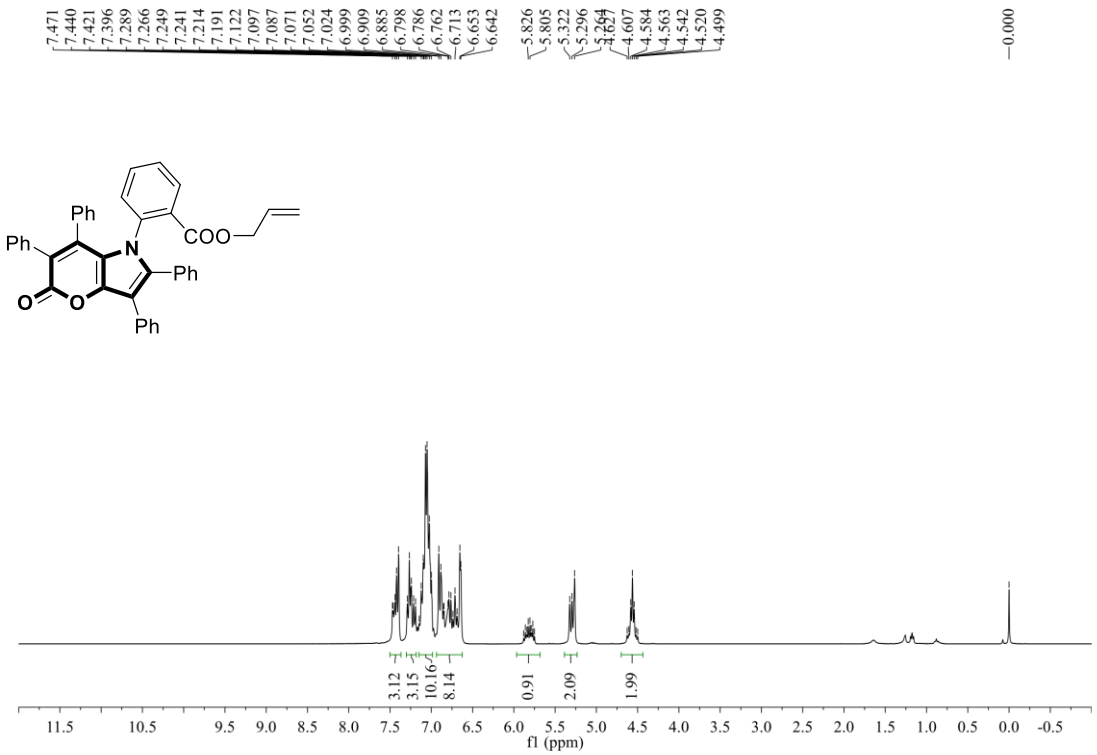


Figure S20. ^{1}H NMR spectrum of compound **4j** (300 MHz, $CDCl_3$)

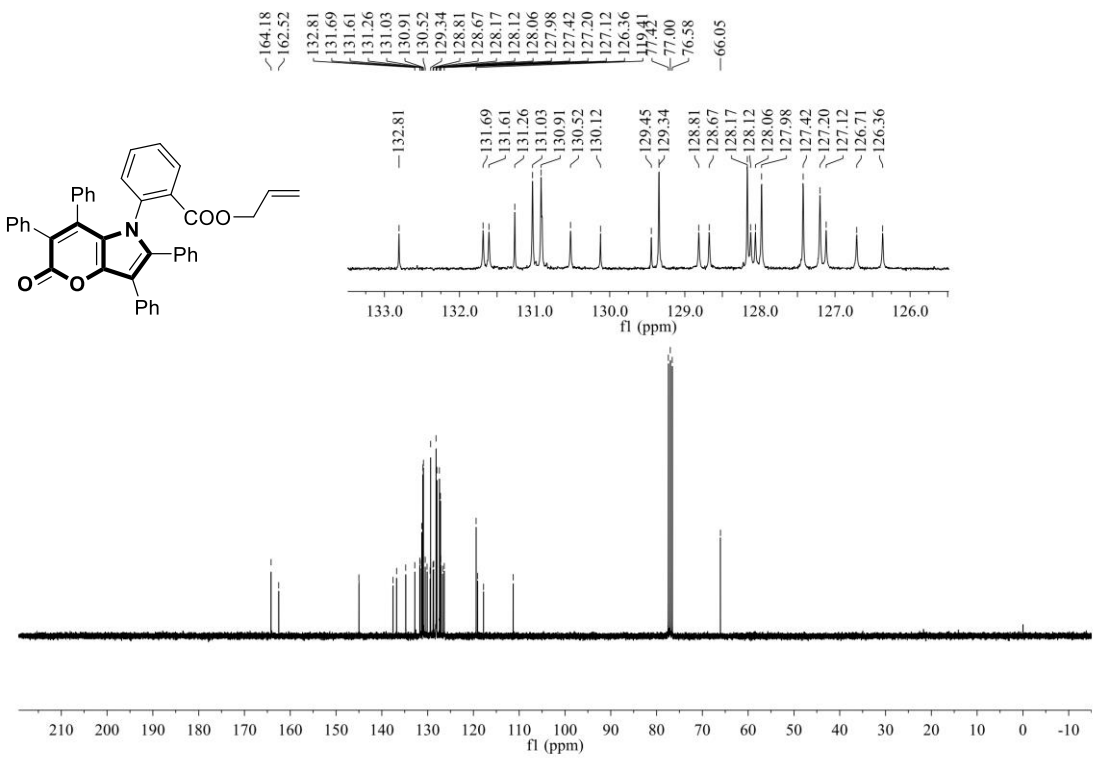


Figure S21. ^{13}C NMR spectrum of compound **4j** (75 MHz, $CDCl_3$)

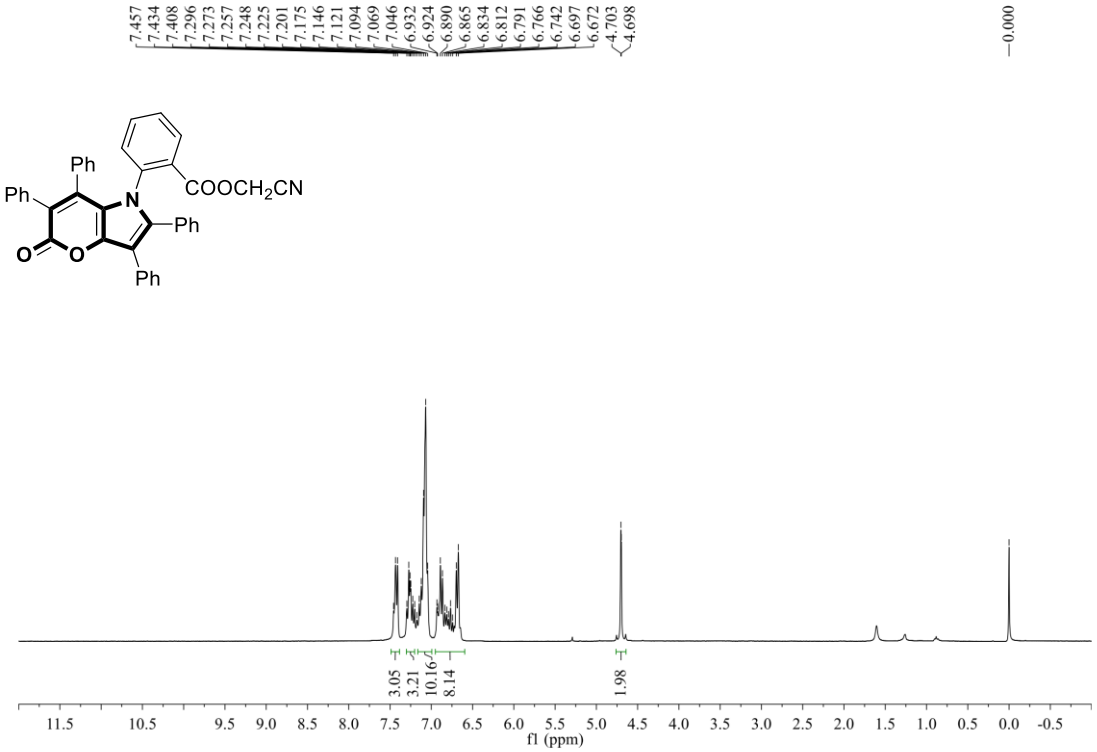


Figure S22. ^{1}H NMR spectrum of compound **4k** (300 MHz, $CDCl_3$)

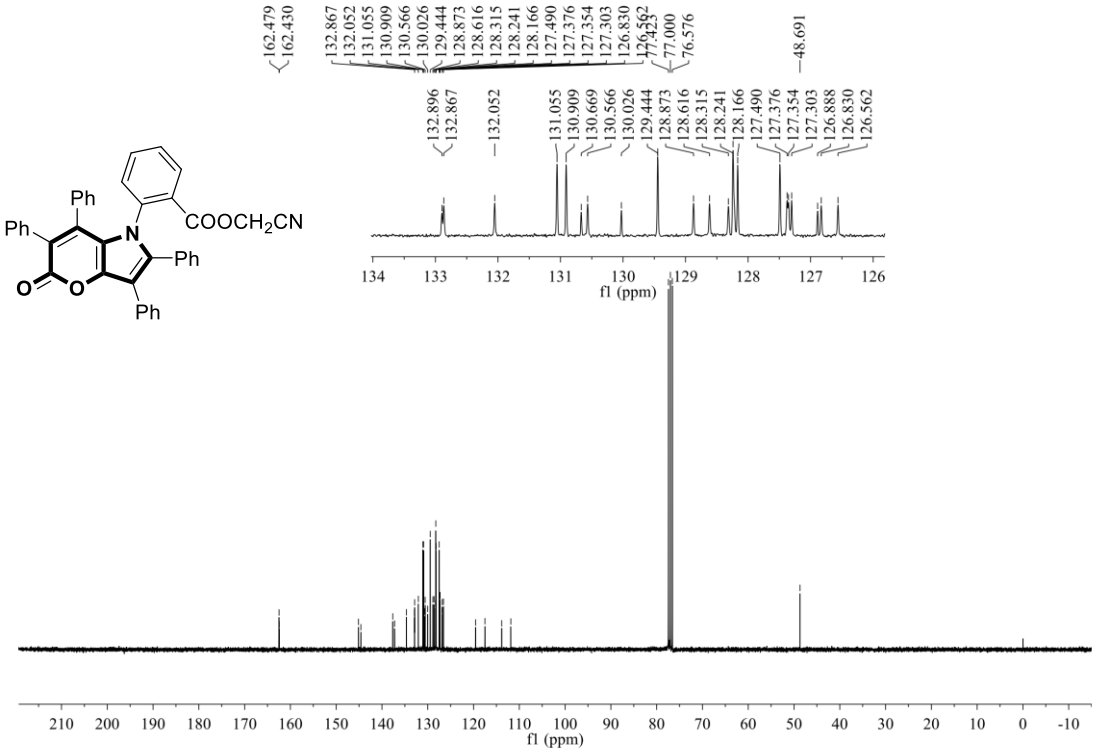


Figure S23. ^{13}C NMR spectrum of compound **4k** (75 MHz, $CDCl_3$)

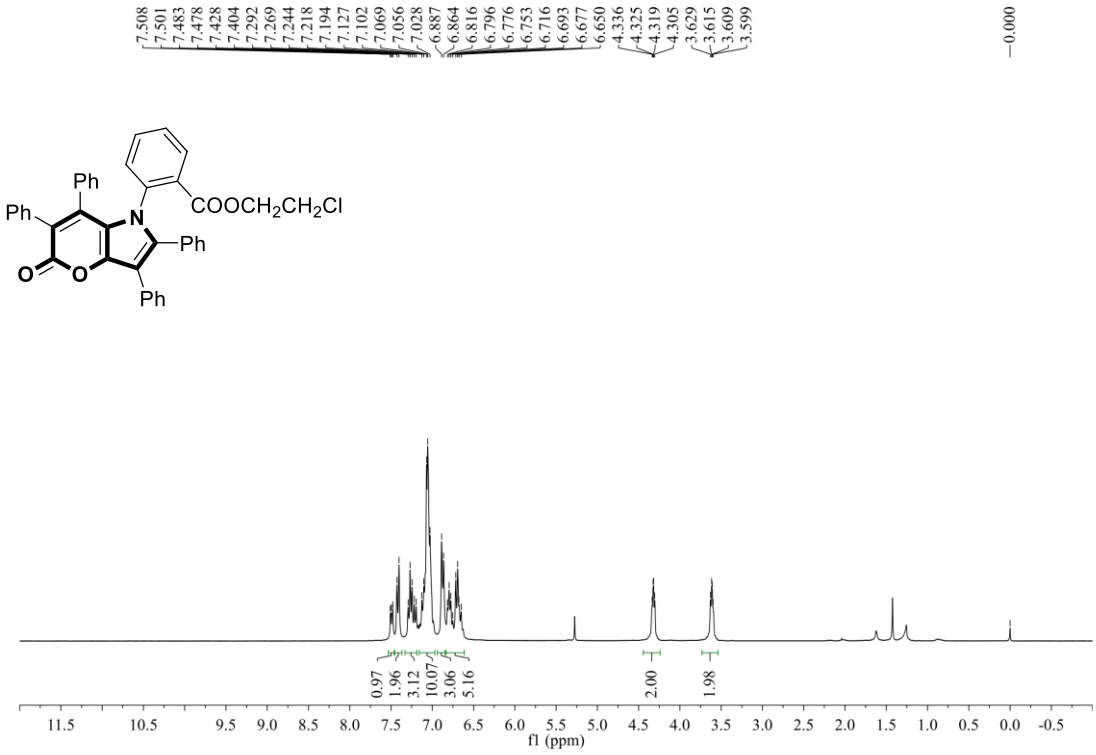


Figure S24. ^{1}H NMR spectrum of compound **4l** (300 MHz, $CDCl_3$)

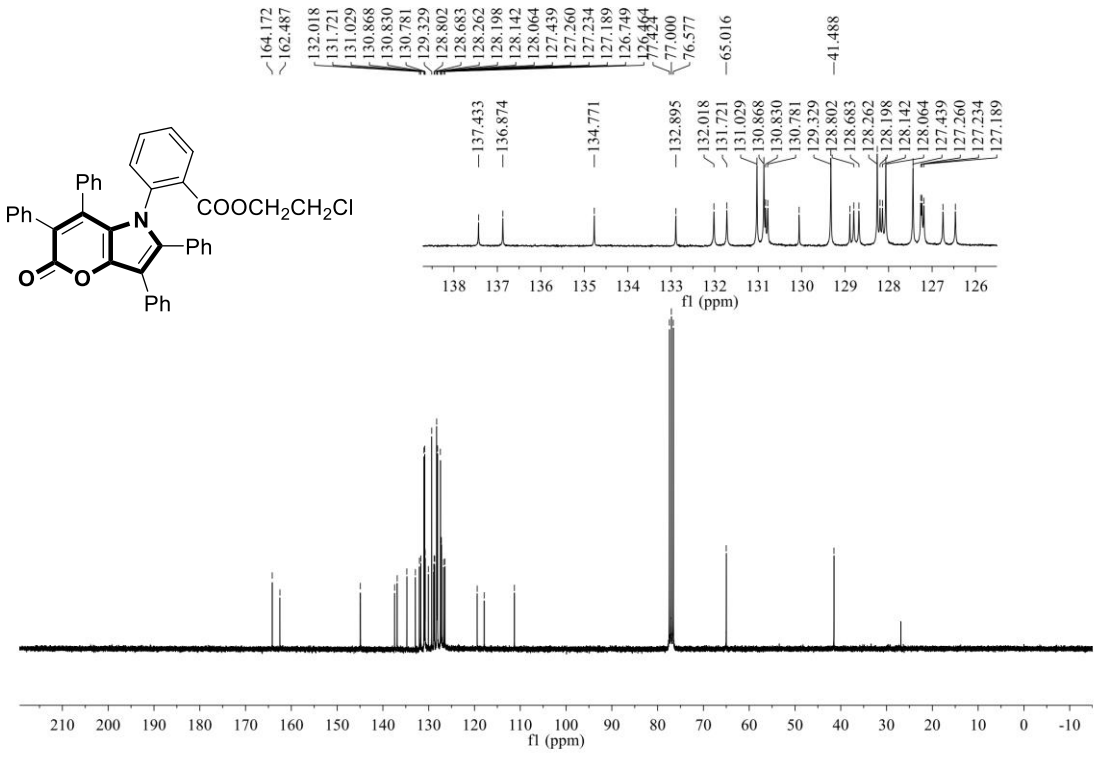


Figure S25. ^{13}C NMR spectrum of compound **4l** (75 MHz, $CDCl_3$)

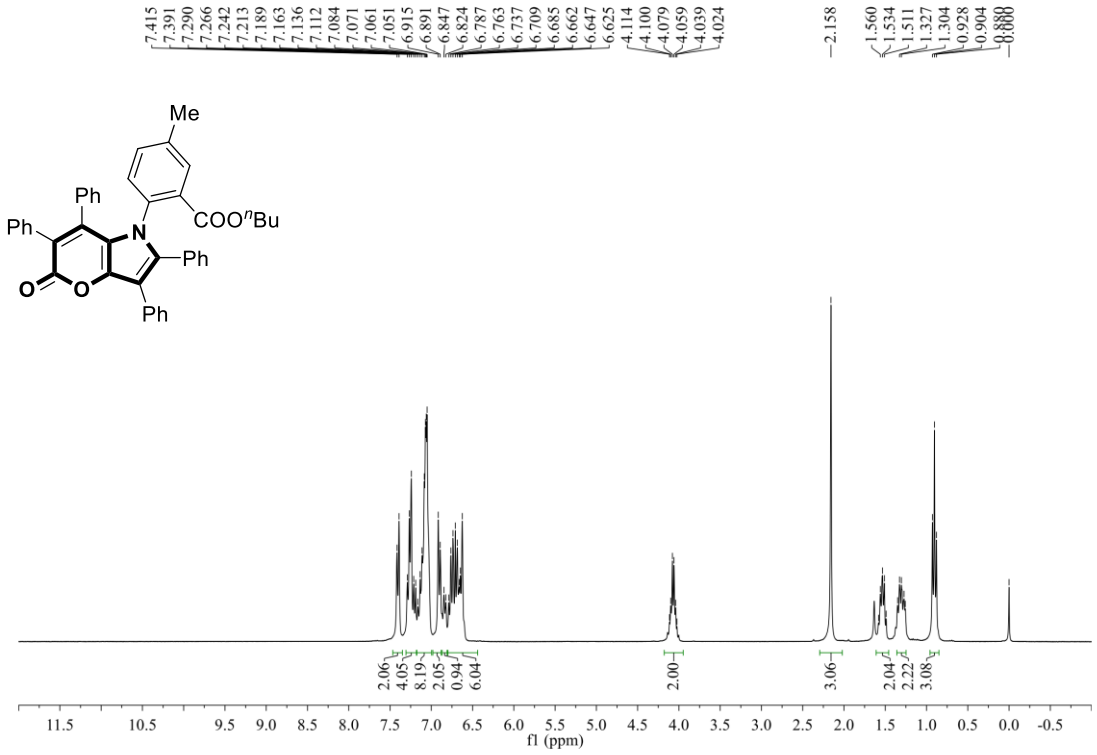


Figure S26. ^{1}H NMR spectrum of compound **5a** (300 MHz, $CDCl_3$)

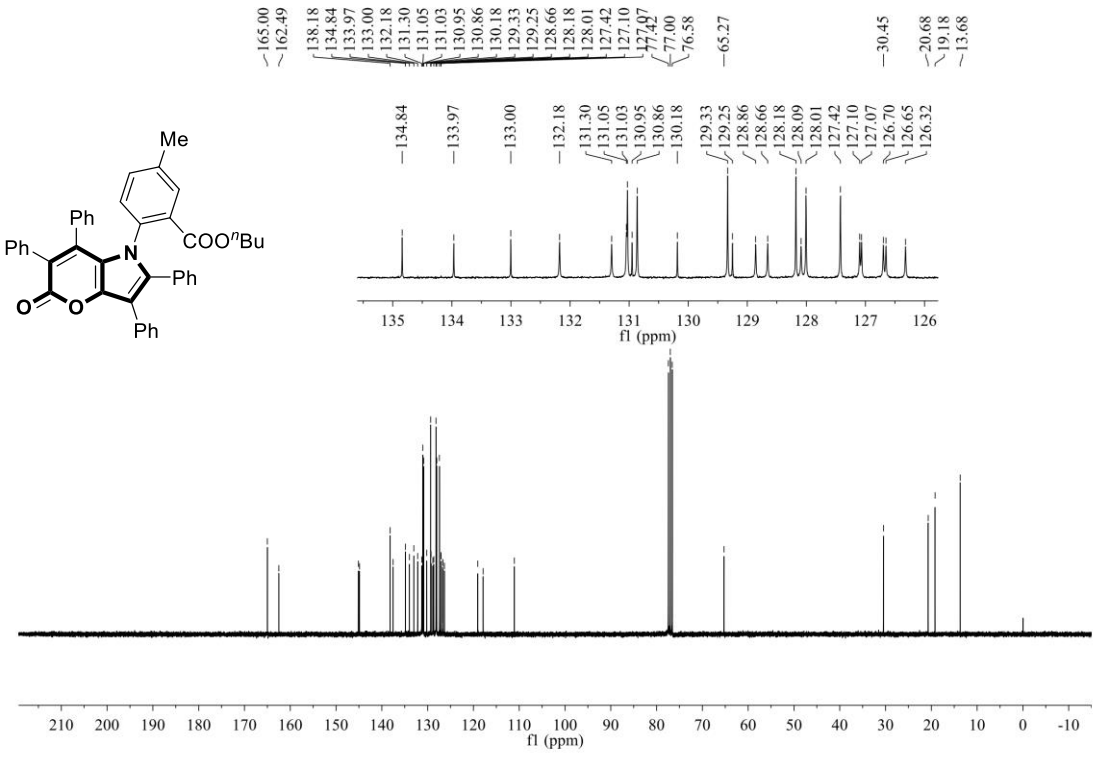


Figure S27. ^{13}C NMR spectrum of compound **5a** (75 MHz, $CDCl_3$)

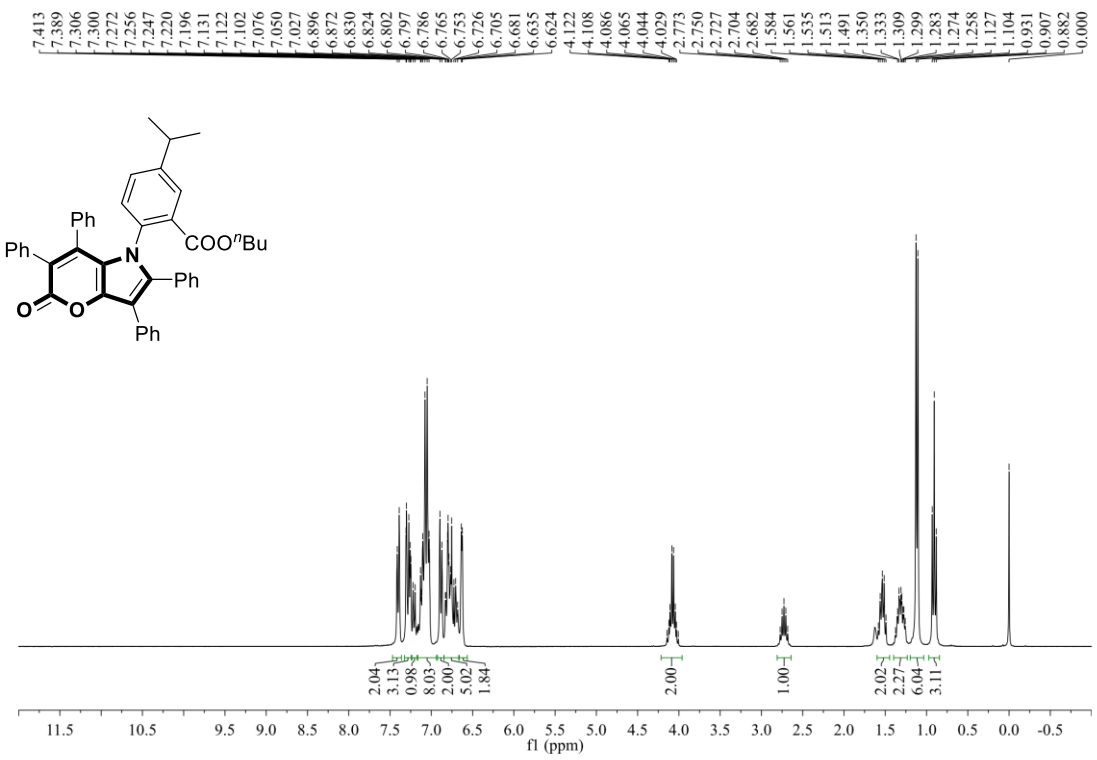


Figure S28. ^{1}H NMR spectrum of compound **5b** (300 MHz, $CDCl_3$)

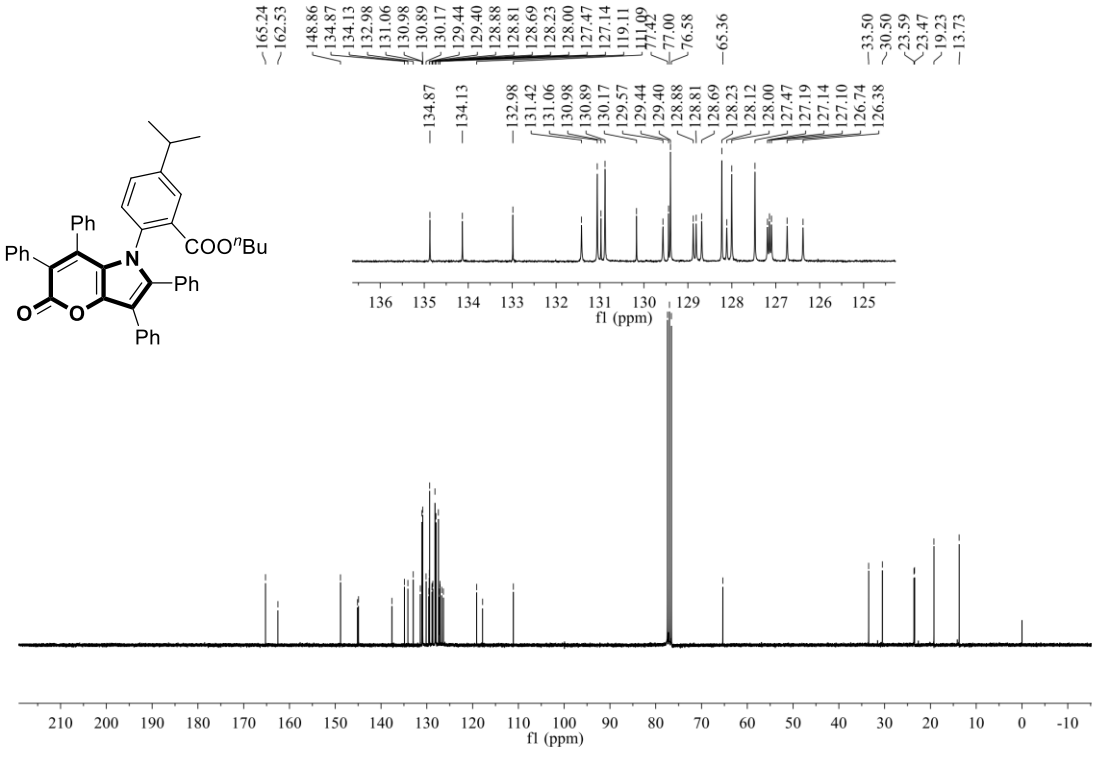


Figure S29. ^{13}C NMR spectrum of compound **5b** (75 MHz, $CDCl_3$)

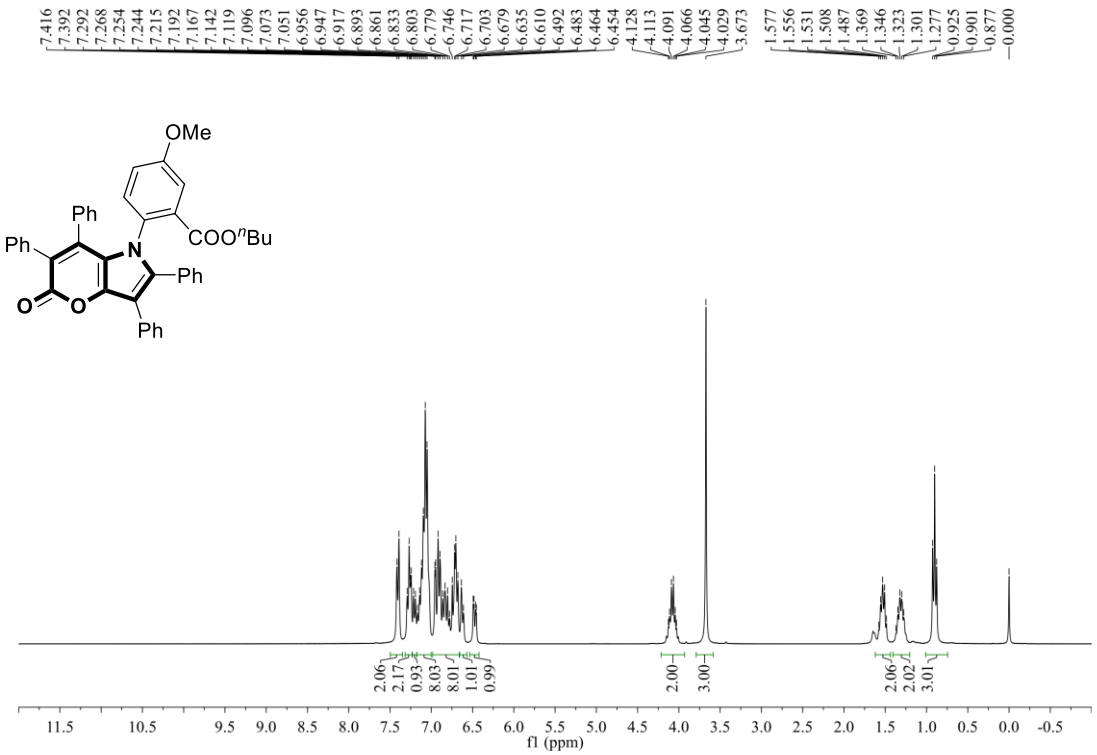


Figure S30. ^{1}H NMR spectrum of compound **5c** (300 MHz, $CDCl_3$)

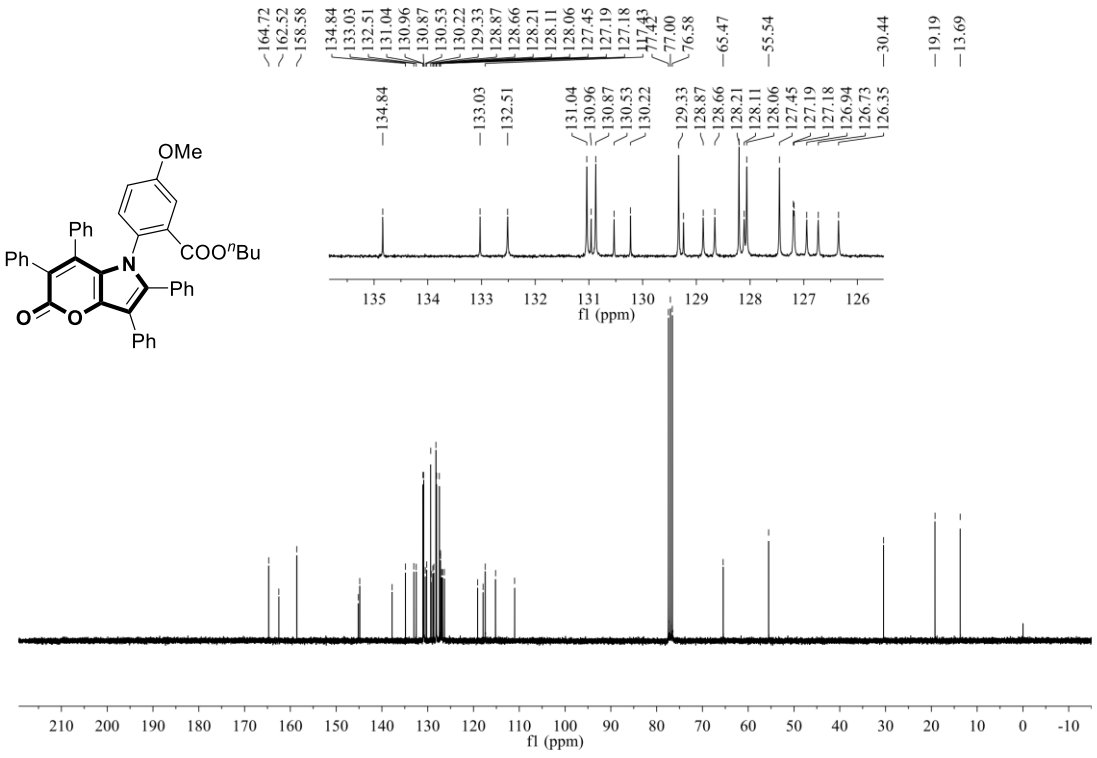


Figure S31. ^{13}C NMR spectrum of compound **5c** (75 MHz, $CDCl_3$)

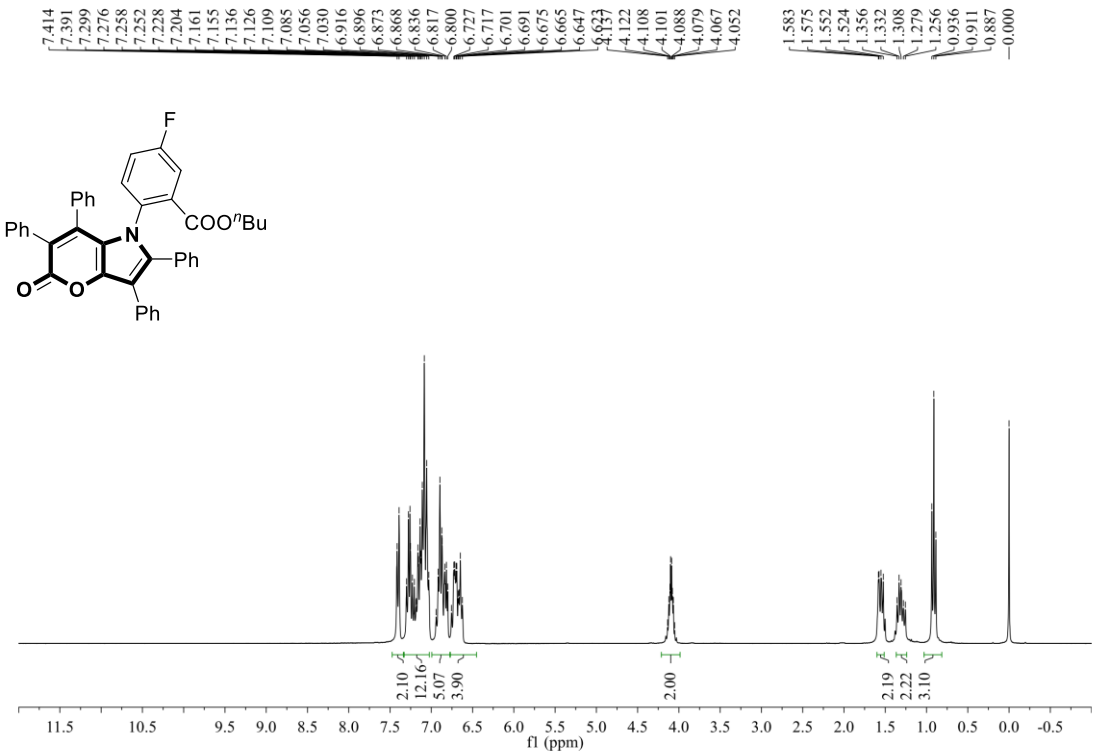


Figure S32. ^{1}H NMR spectrum of compound **5d** (300 MHz, $CDCl_3$)

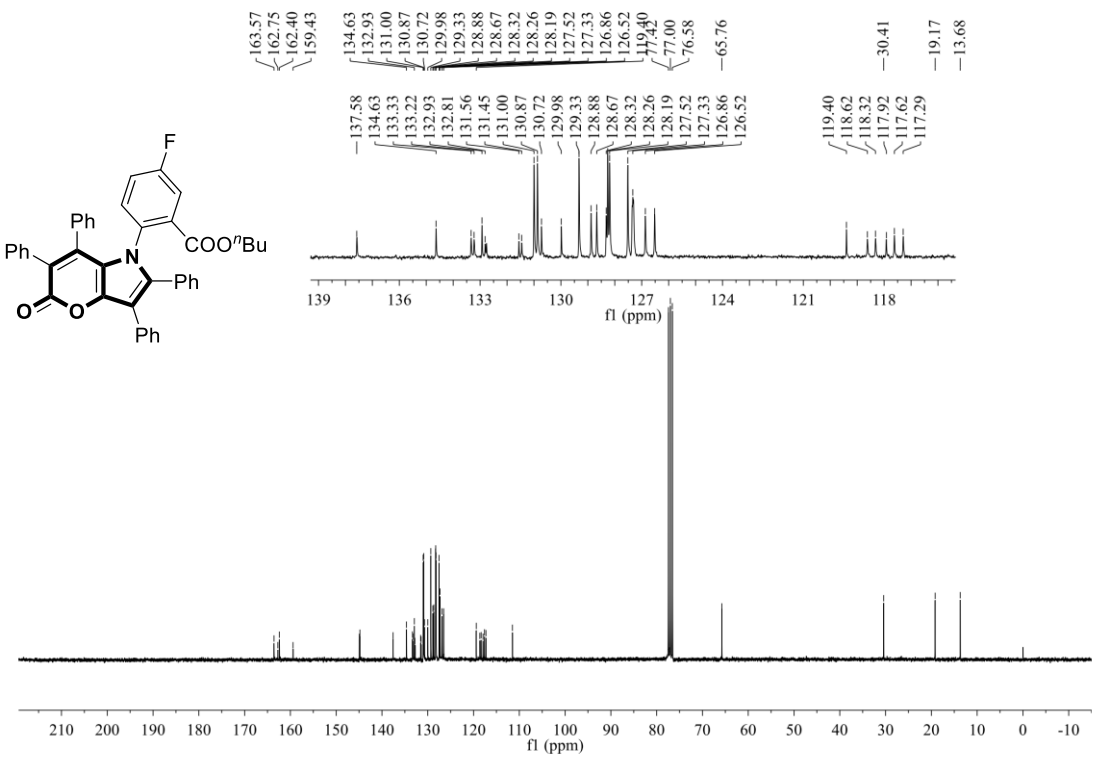


Figure S33. ^{13}C NMR spectrum of compound **5d** (75 MHz, $CDCl_3$)

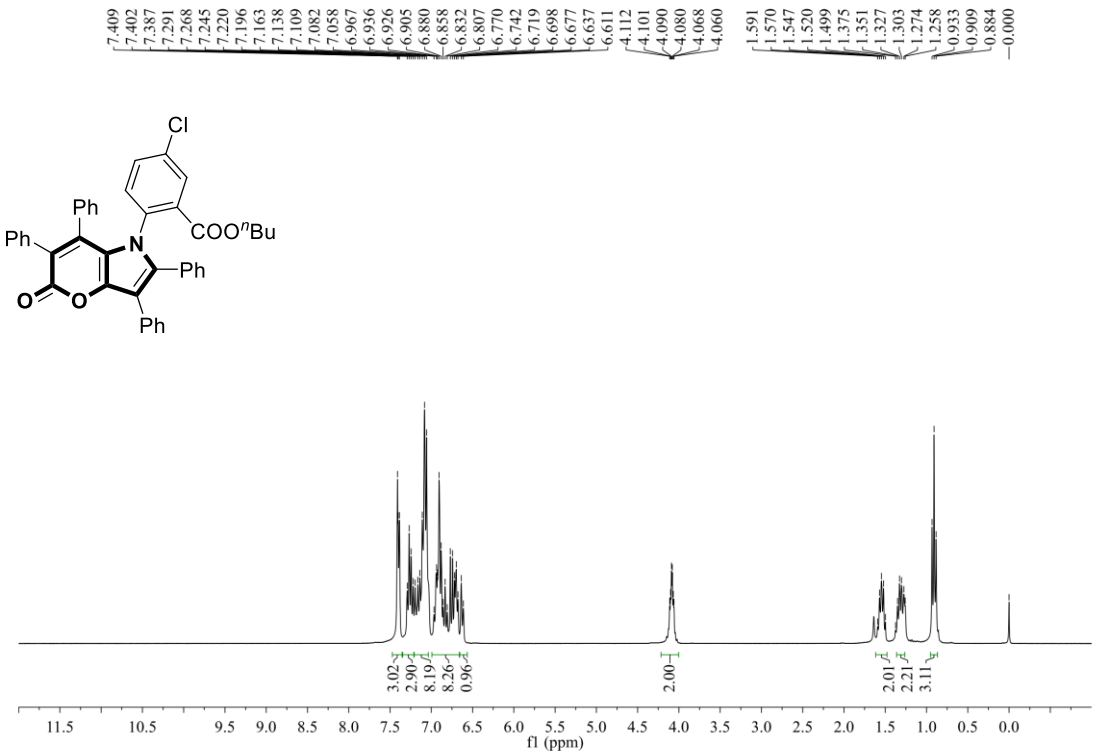


Figure S34. ^{1}H NMR spectrum of compound **5e** (300 MHz, $CDCl_3$)

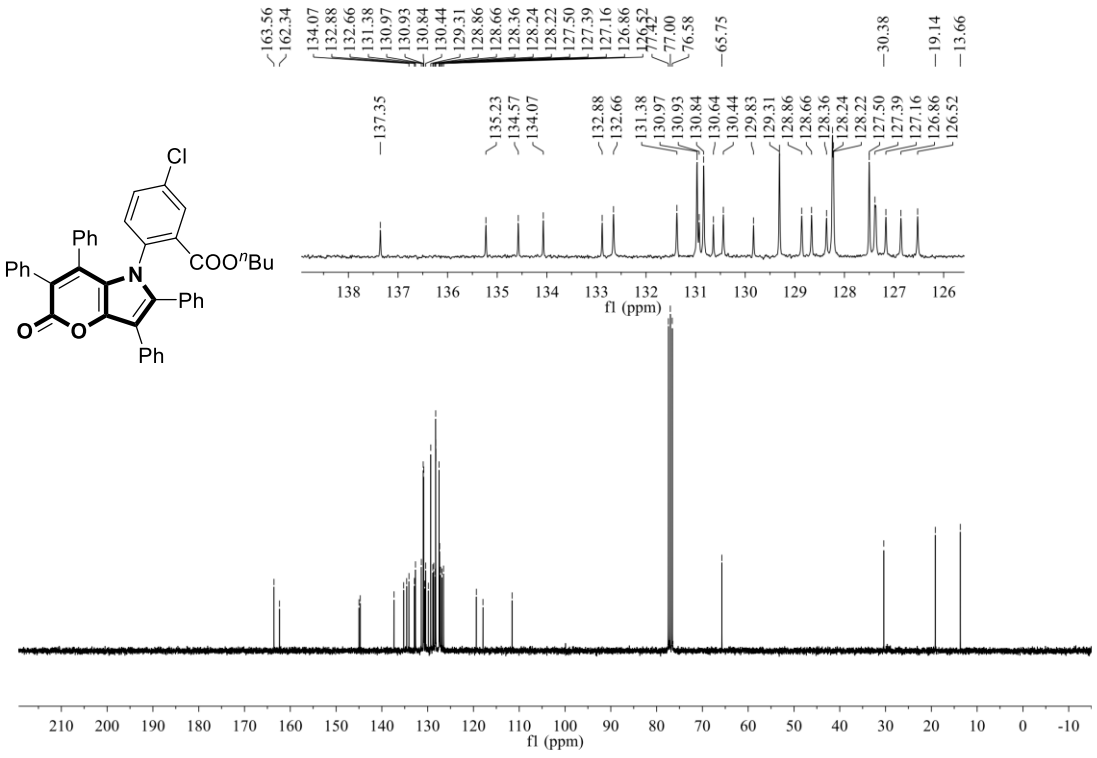


Figure S35. ^{13}C NMR spectrum of compound **5e** (75 MHz, $CDCl_3$)

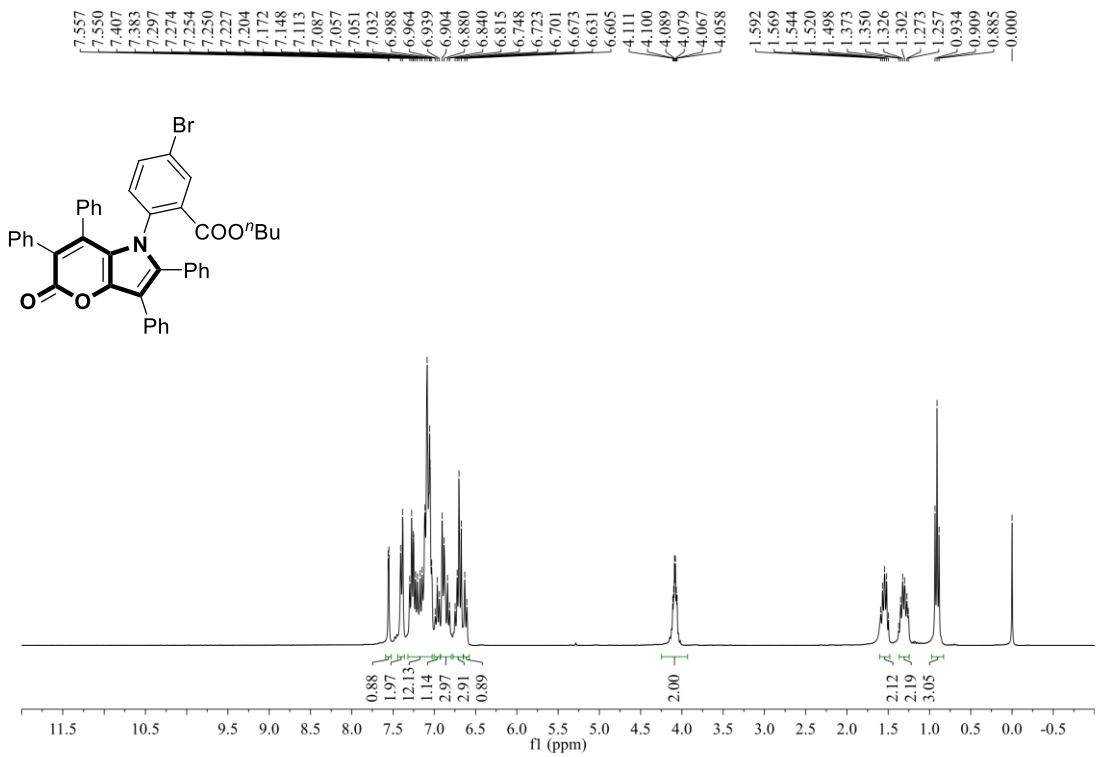


Figure S36. ^{1}H NMR spectrum of compound **5f** (300 MHz, $CDCl_3$)

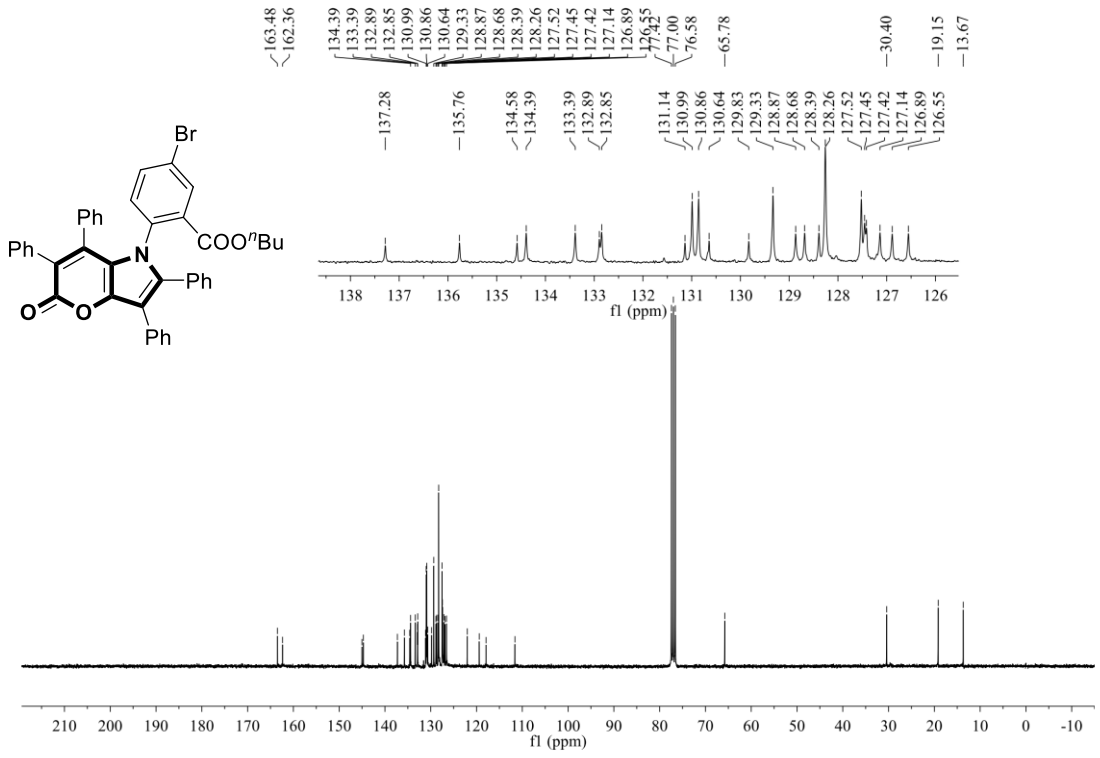


Figure S37. ^{13}C NMR spectrum of compound **5f** (75 MHz, $CDCl_3$)

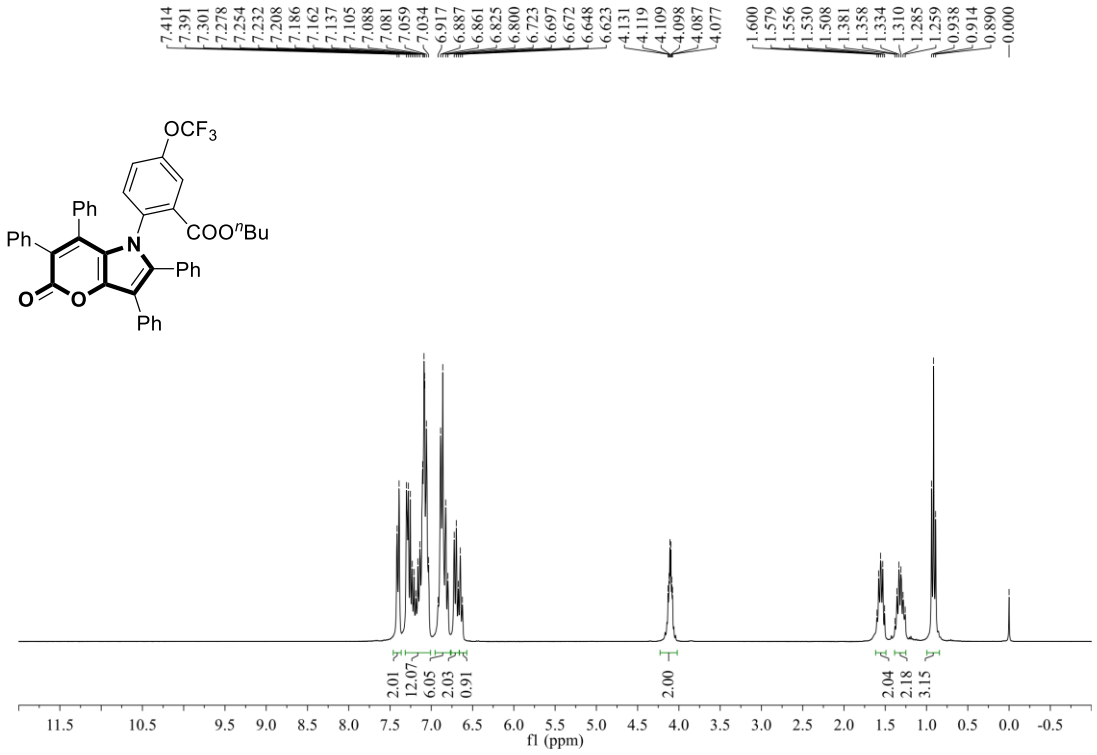


Figure S38. ^{1}H NMR spectrum of compound **5g** (300 MHz, $CDCl_3$)

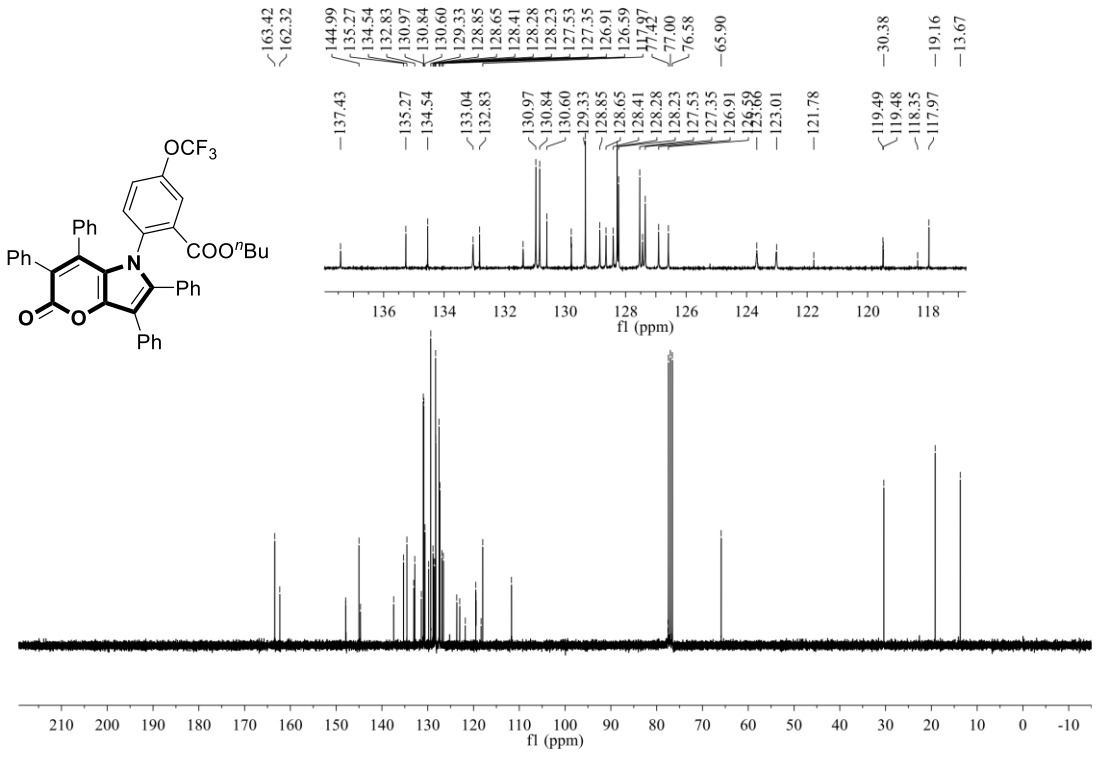


Figure S39. ^{13}C NMR spectrum of compound **5g** (75 MHz, $CDCl_3$)

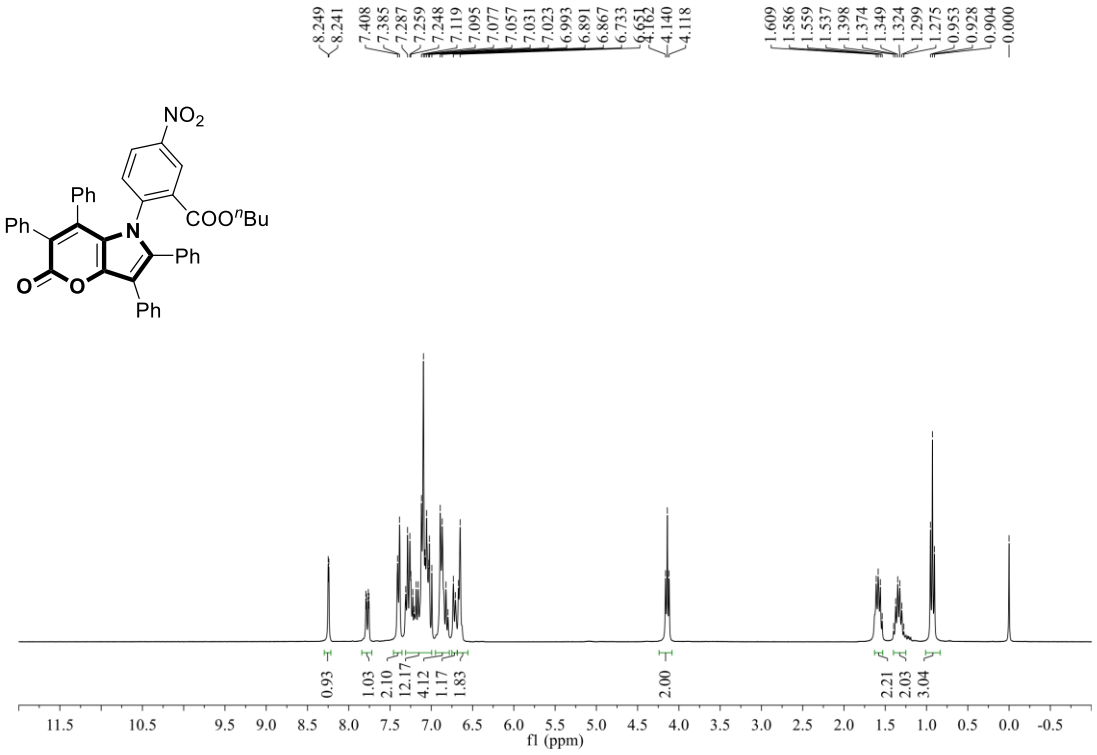


Figure S40. ^{1}H NMR spectrum of compound **5h** (300 MHz, $CDCl_3$)

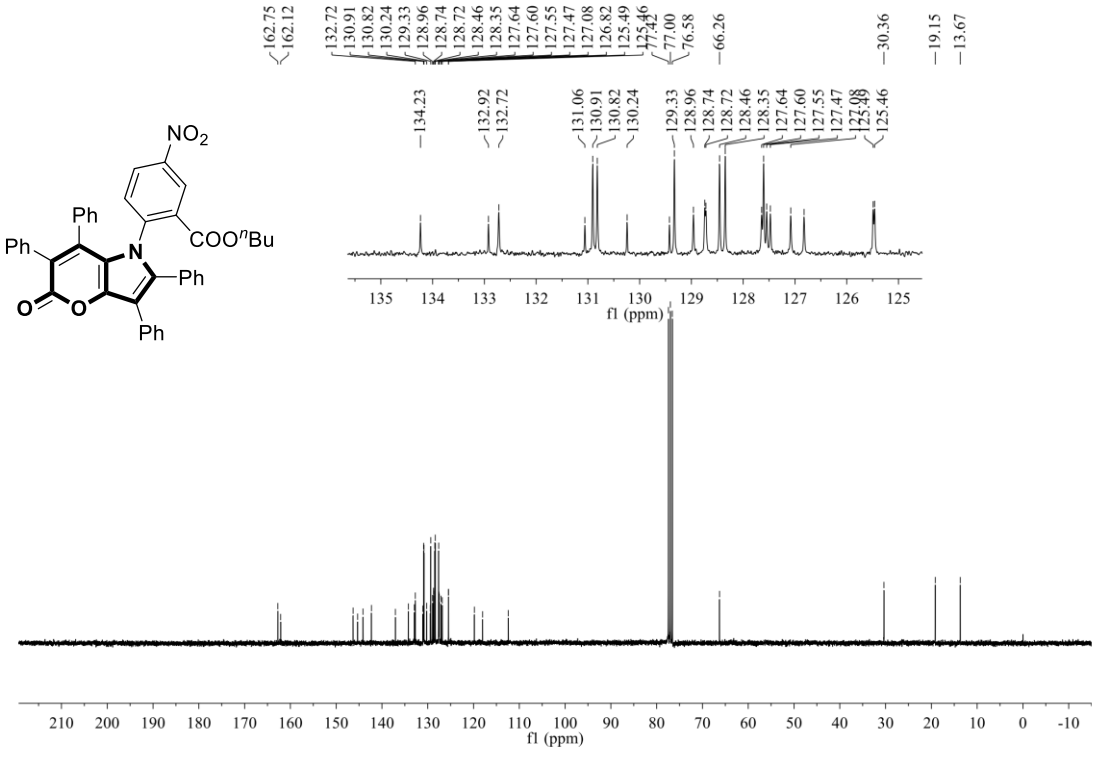


Figure S41. ^{13}C NMR spectrum of compound **5h** (75 MHz, $CDCl_3$)

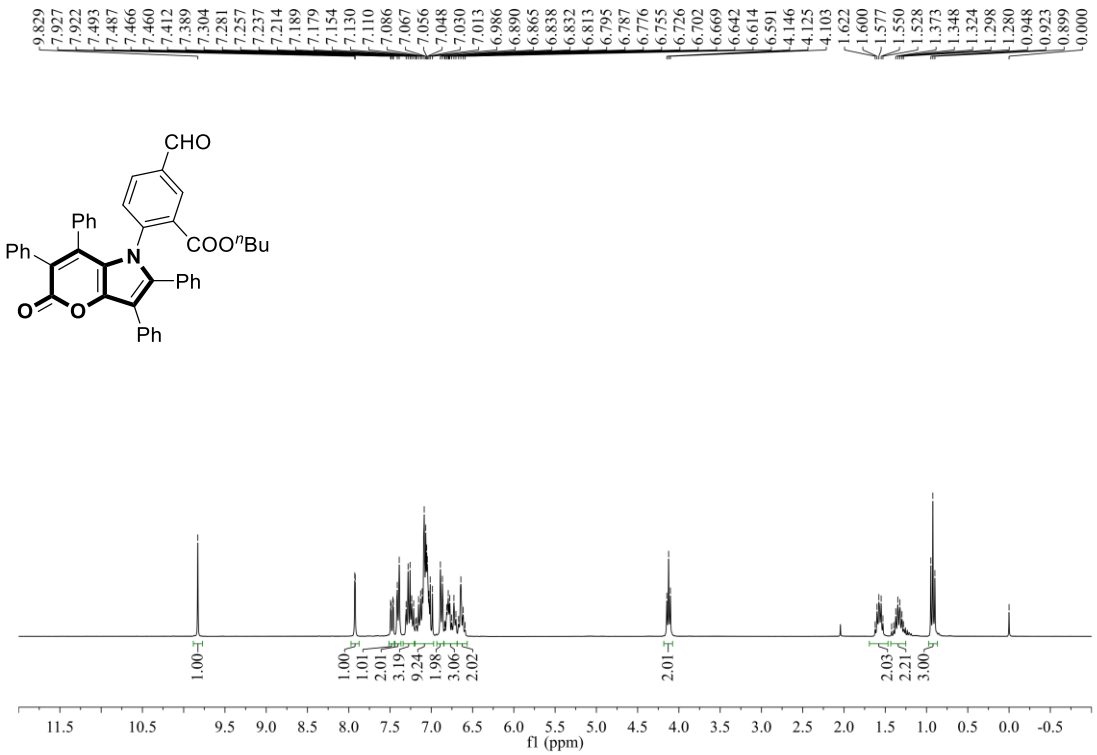


Figure S42. ^{1}H NMR spectrum of compound **5i** (300 MHz, $CDCl_3$)

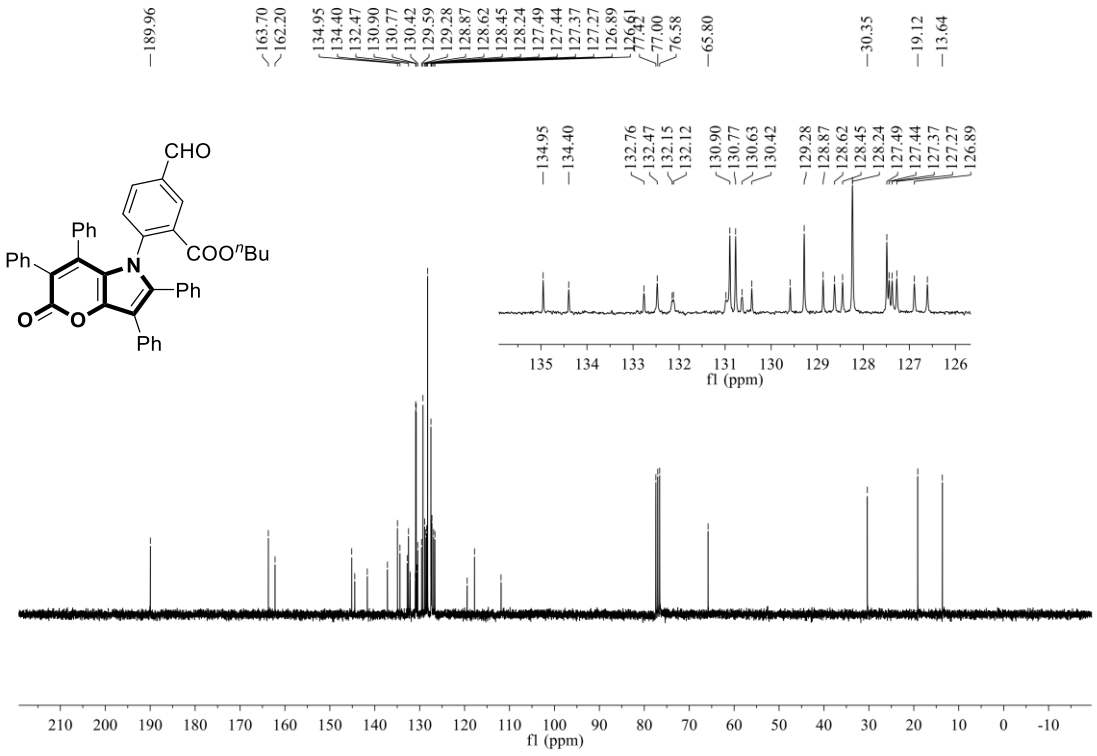


Figure S43. ^{13}C NMR spectrum of compound **5i** (75 MHz, $CDCl_3$)

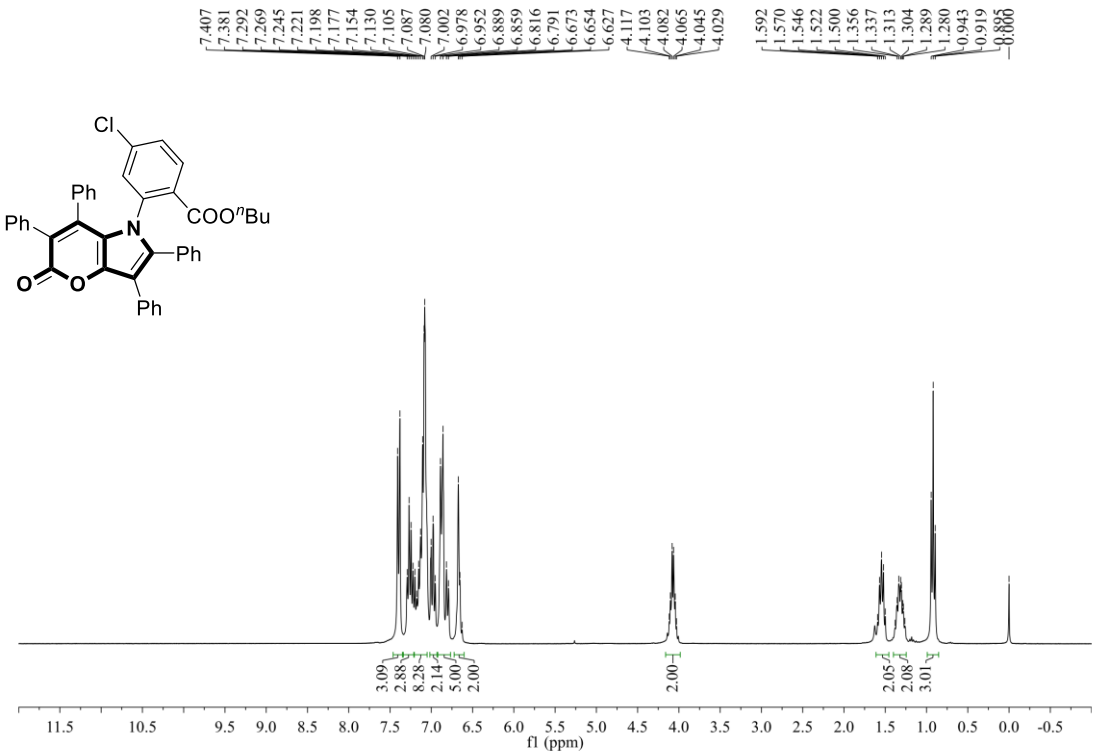


Figure S44. ^{1}H NMR spectrum of compound **5j** (300 MHz, $CDCl_3$)

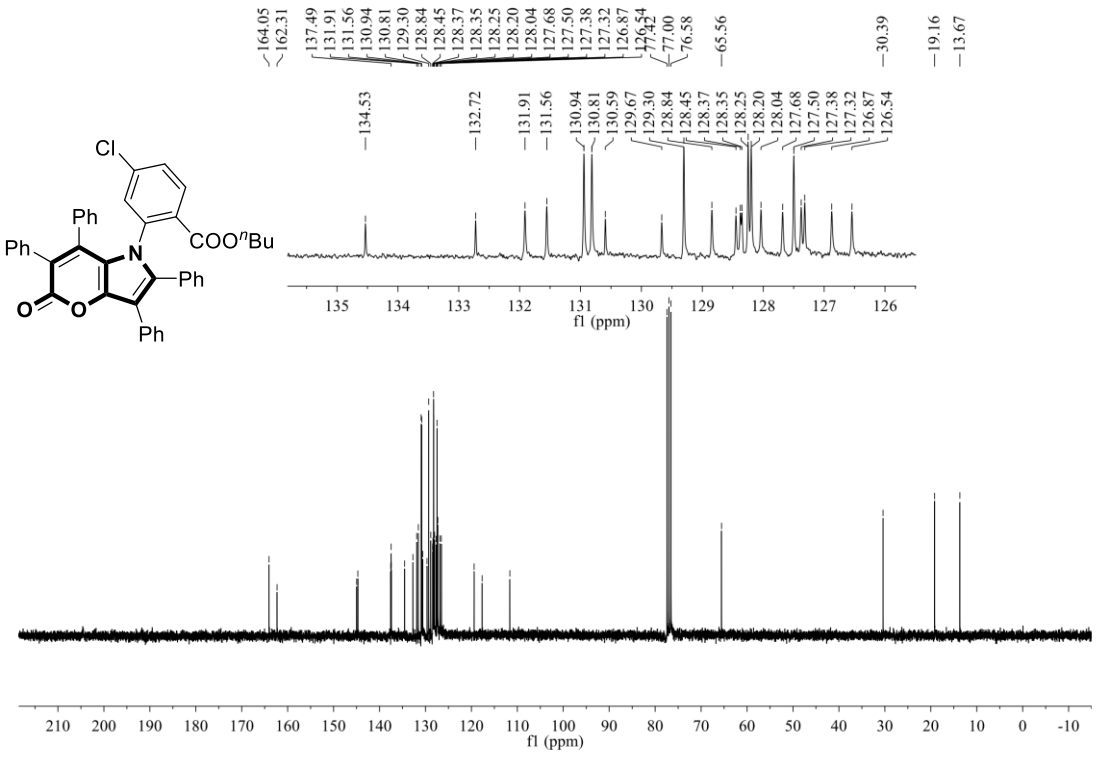


Figure S45. ^{13}C NMR spectrum of compound **5j** (75 MHz, $CDCl_3$)

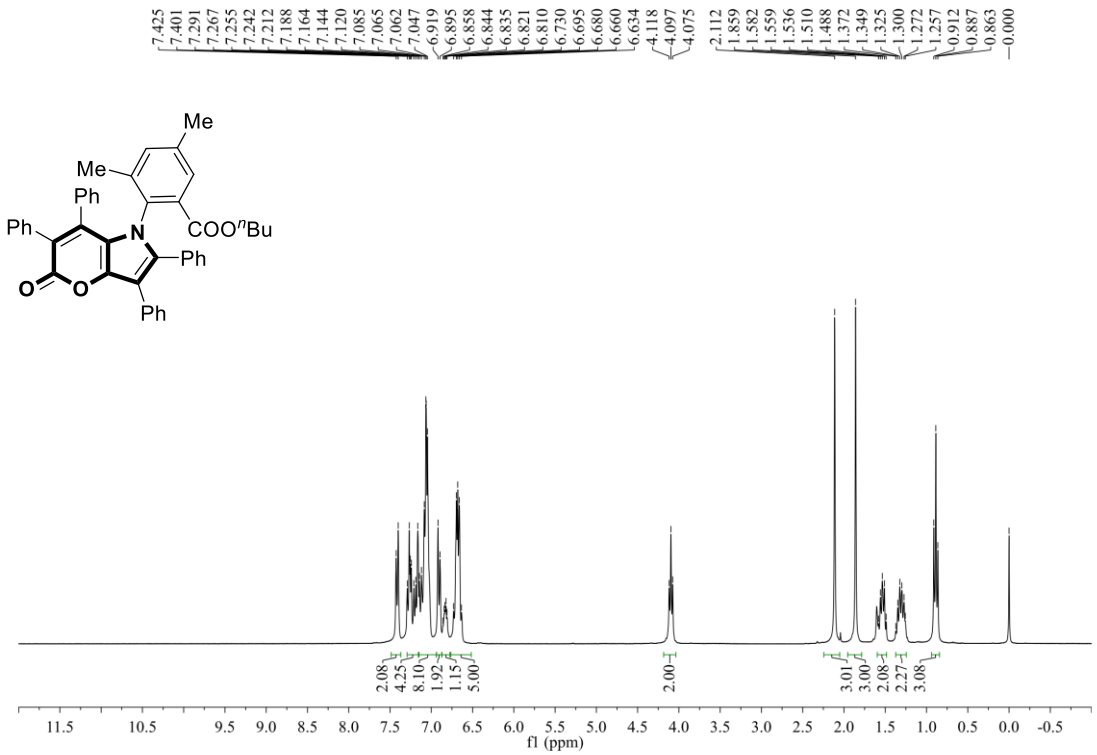


Figure S46. ^{1}H NMR spectrum of compound **5k** (300 MHz, $CDCl_3$)

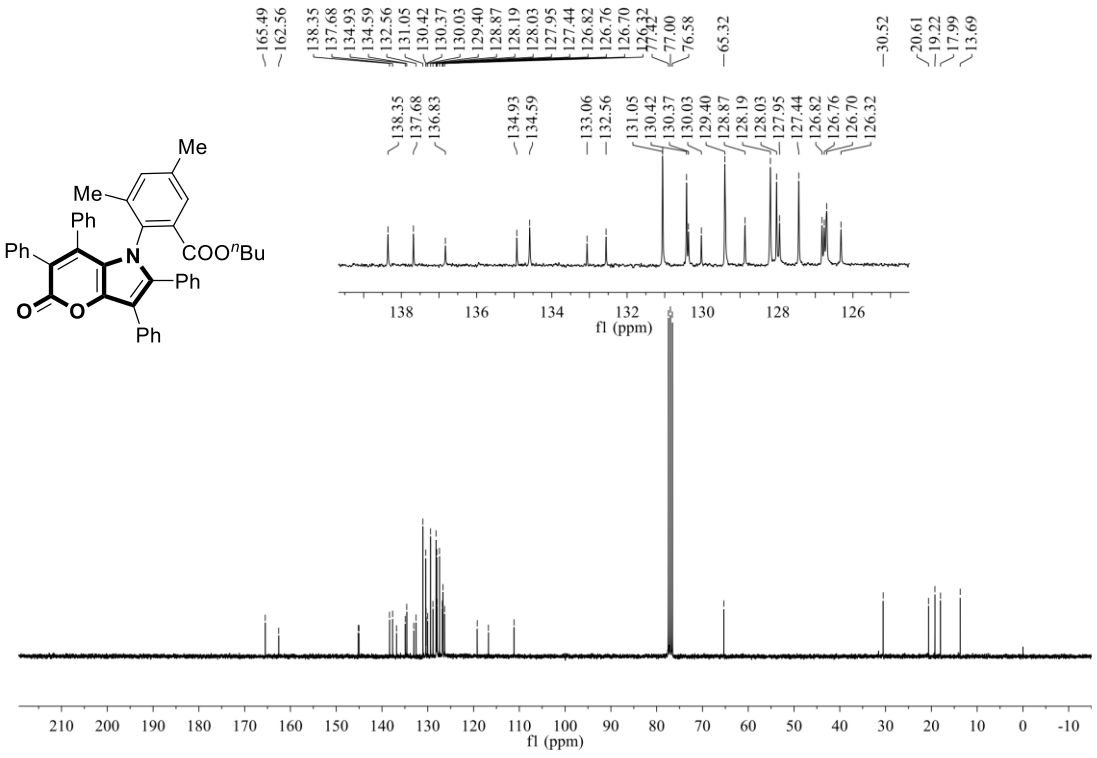


Figure S47. ^{13}C NMR spectrum of compound **5k** (75 MHz, $CDCl_3$)

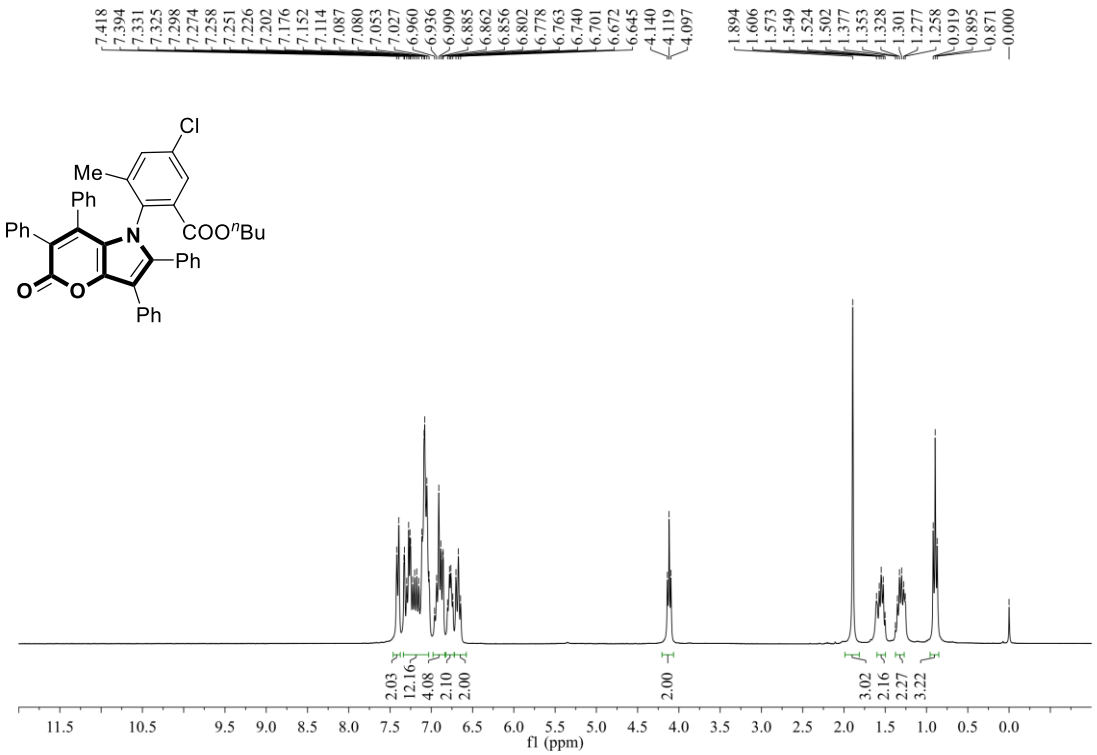


Figure S48. ^{1}H NMR spectrum of compound **5l** (300 MHz, $CDCl_3$)

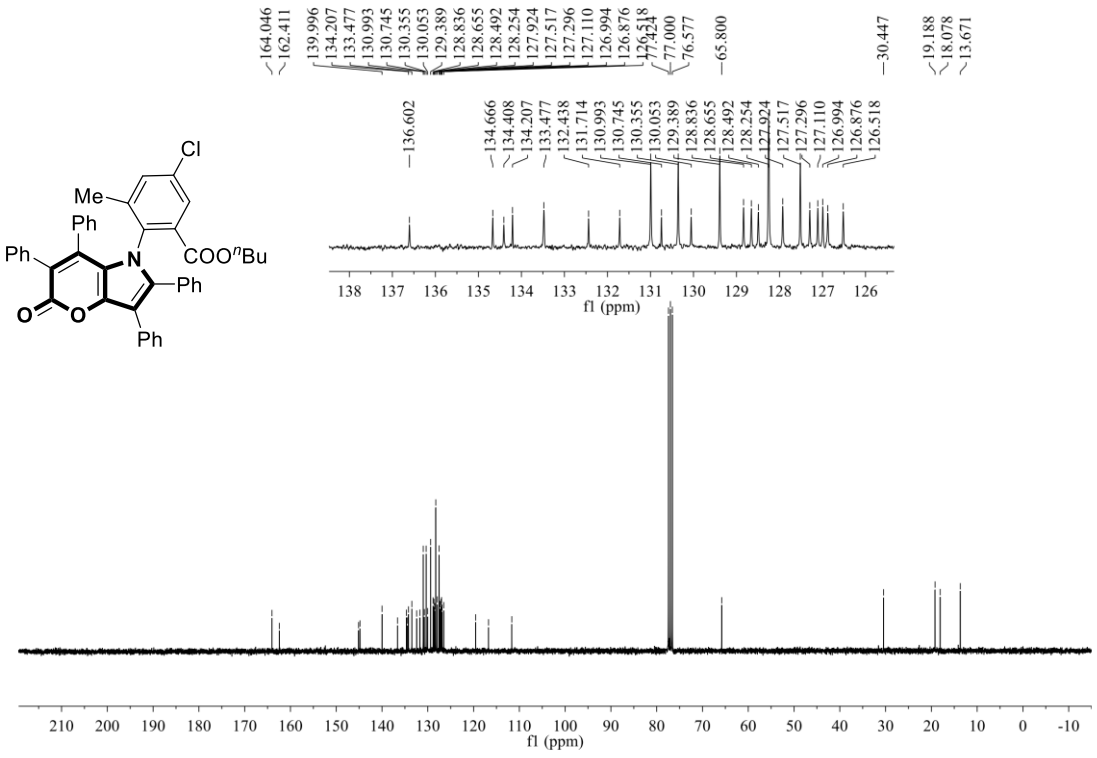


Figure S49. ^{13}C NMR spectrum of compound **5l** (75 MHz, $CDCl_3$)

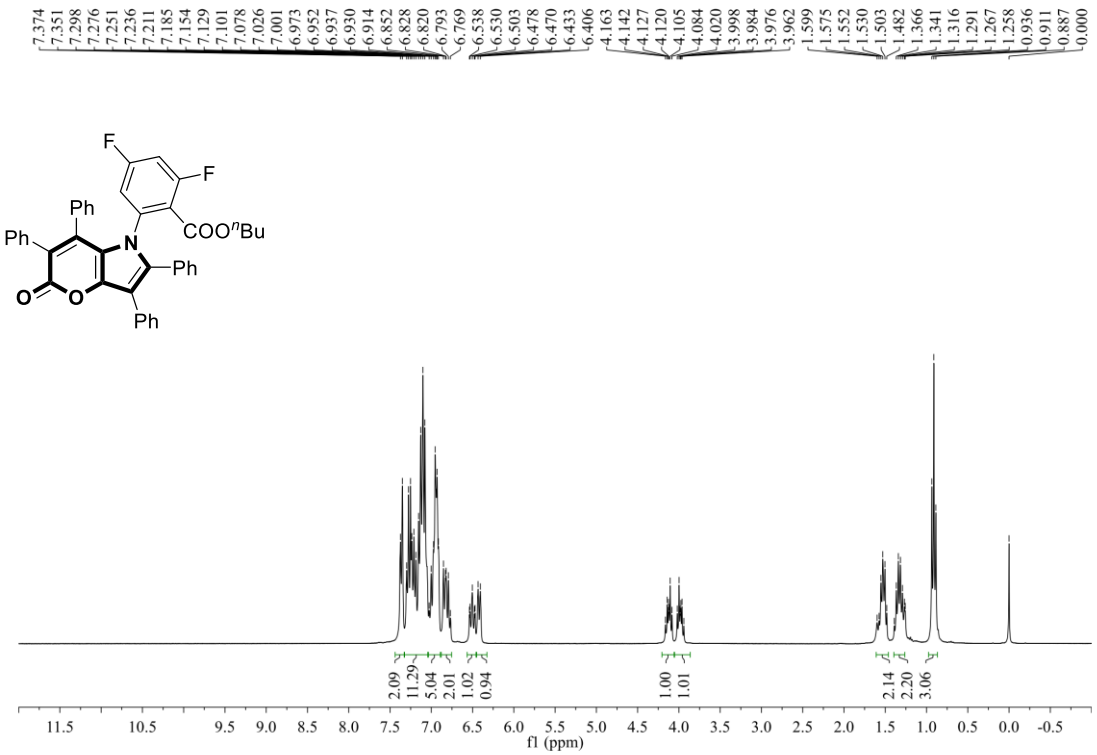


Figure S50. ^{1}H NMR spectrum of compound **5m** (300 MHz, $CDCl_3$)

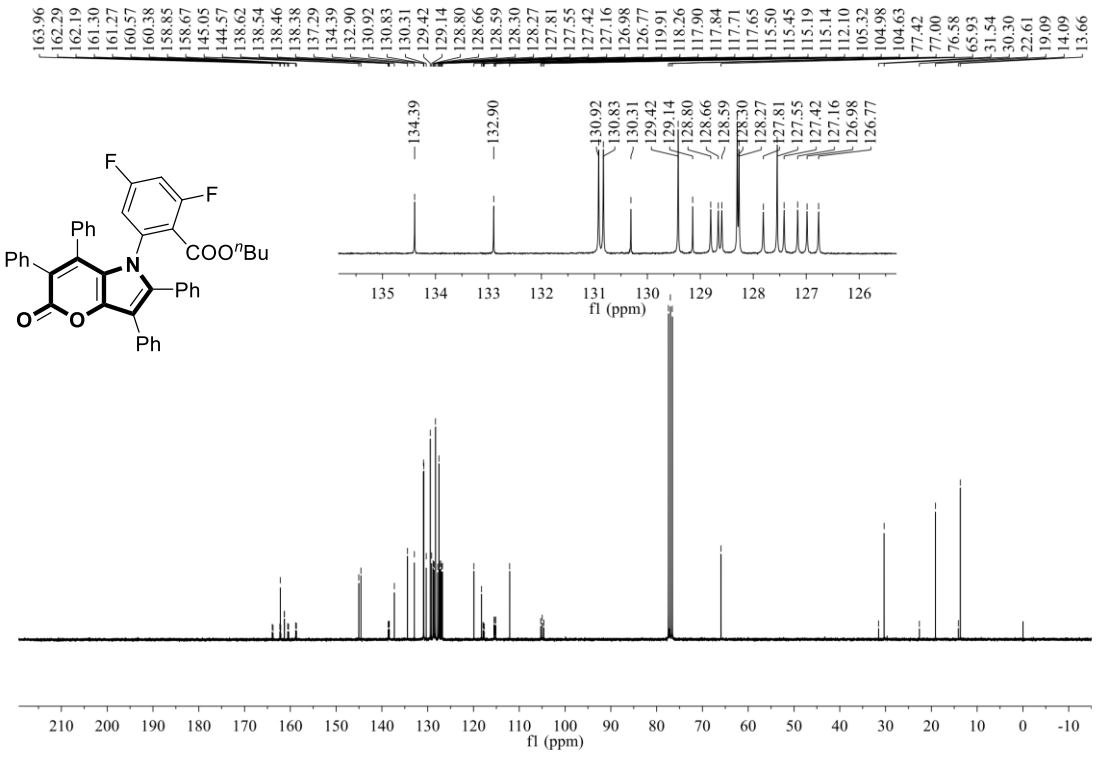


Figure S51. ^{13}C NMR spectrum of compound **5m** (75 MHz, $CDCl_3$)

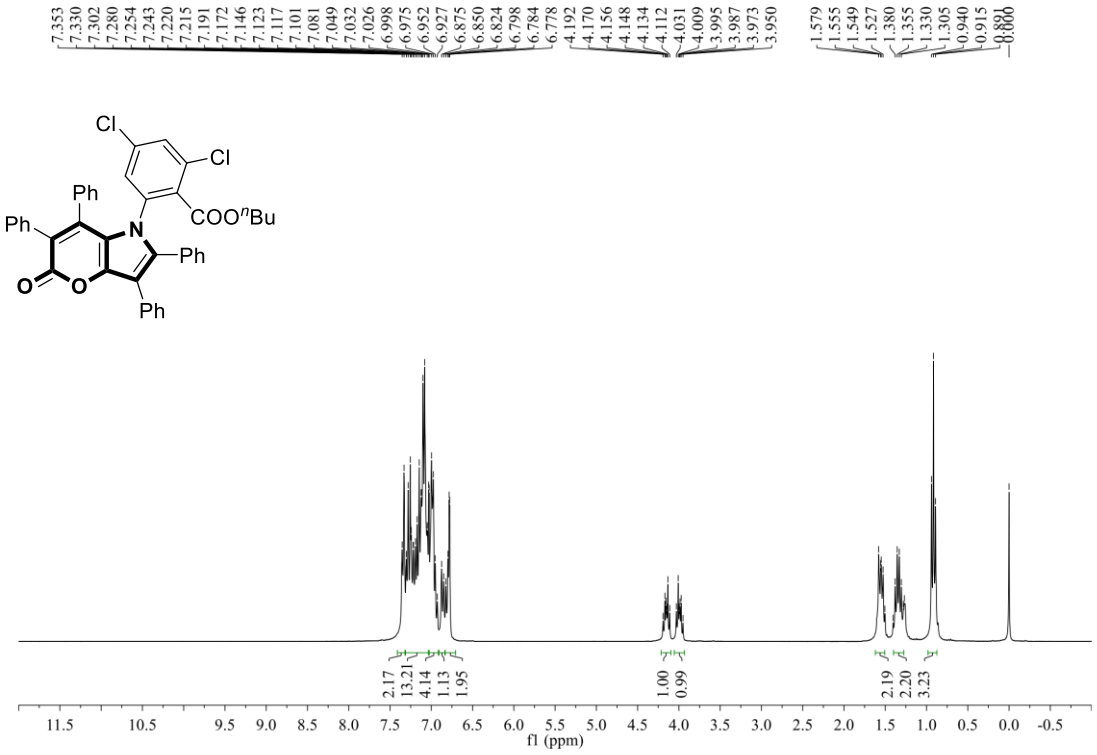


Figure S52. ^{1}H NMR spectrum of compound **5n** (300 MHz, $CDCl_3$)

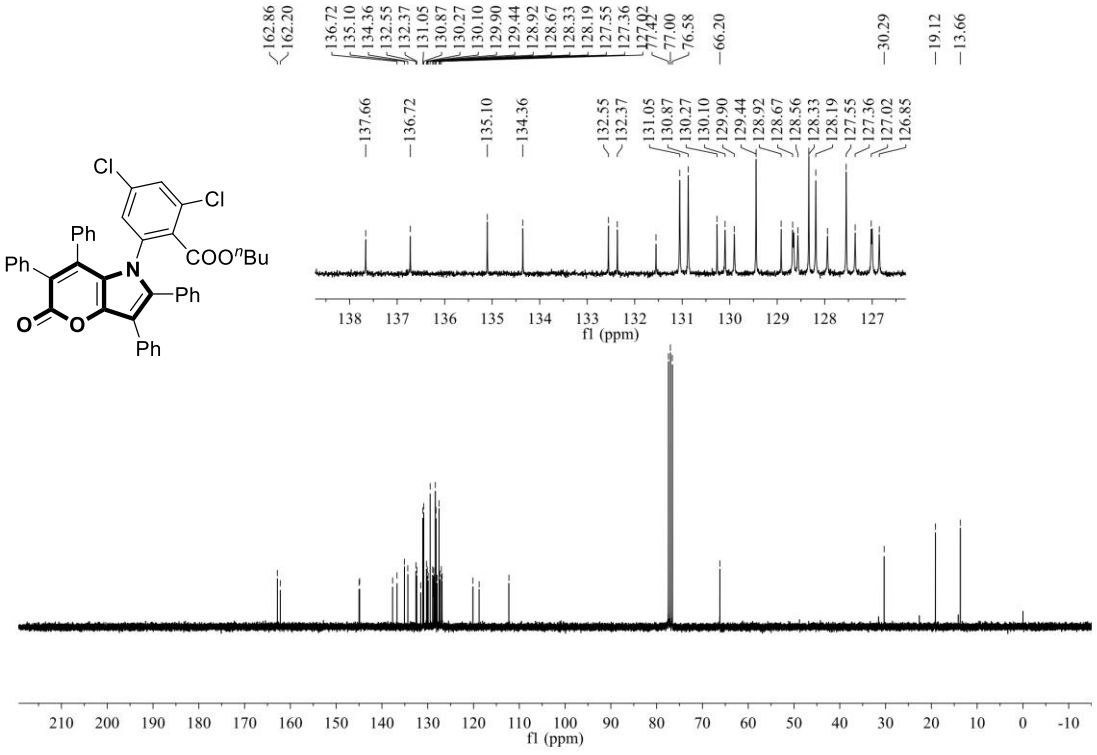


Figure S53. ^{13}C NMR spectrum of compound **5n** (75 MHz, $CDCl_3$)

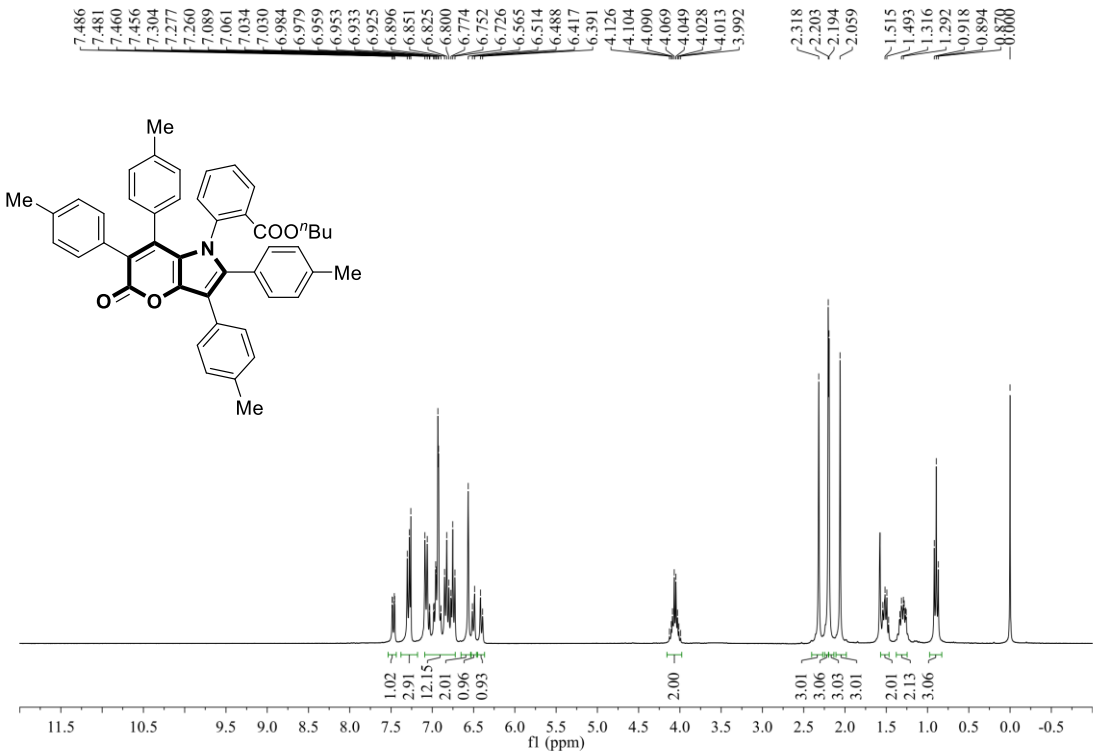


Figure S54. ^{1}H NMR spectrum of compound **6a** (300 MHz, $CDCl_3$)

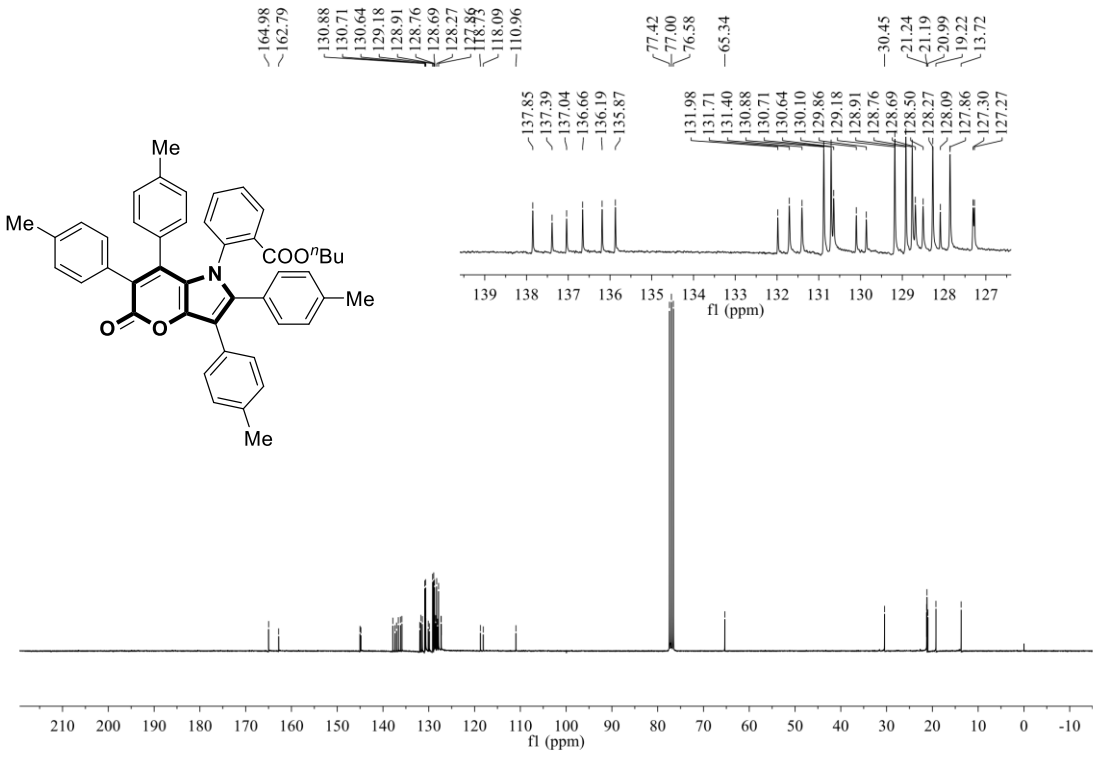


Figure S55. ^{13}C NMR spectrum of compound **6a** (75 MHz, $CDCl_3$)

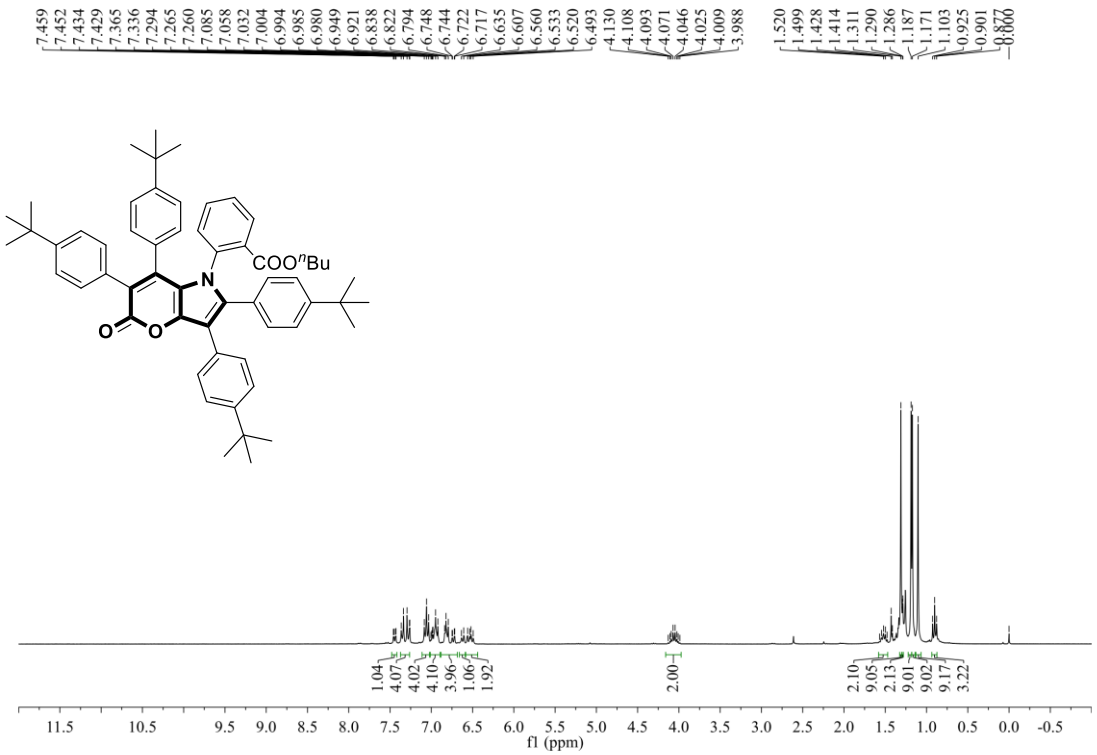


Figure S56. ^{1}H NMR spectrum of compound **6b** (300 MHz, $CDCl_3$)

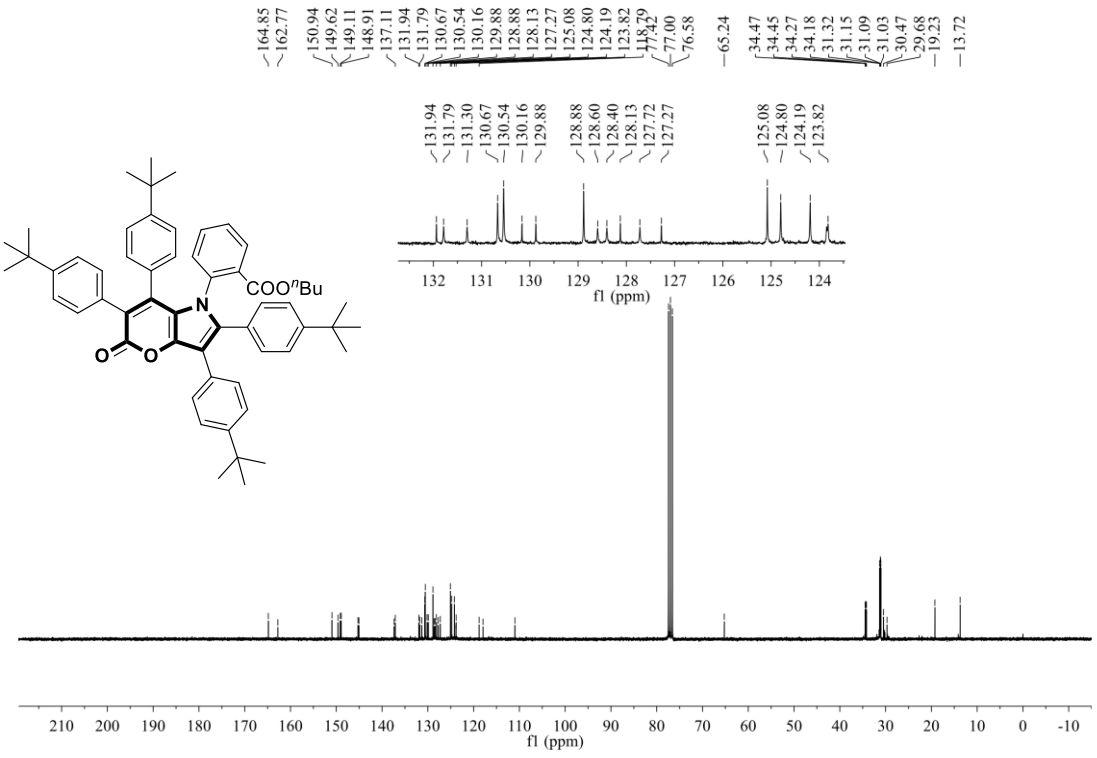


Figure S57. ^{13}C NMR spectrum of compound **6b** (75 MHz, $CDCl_3$)

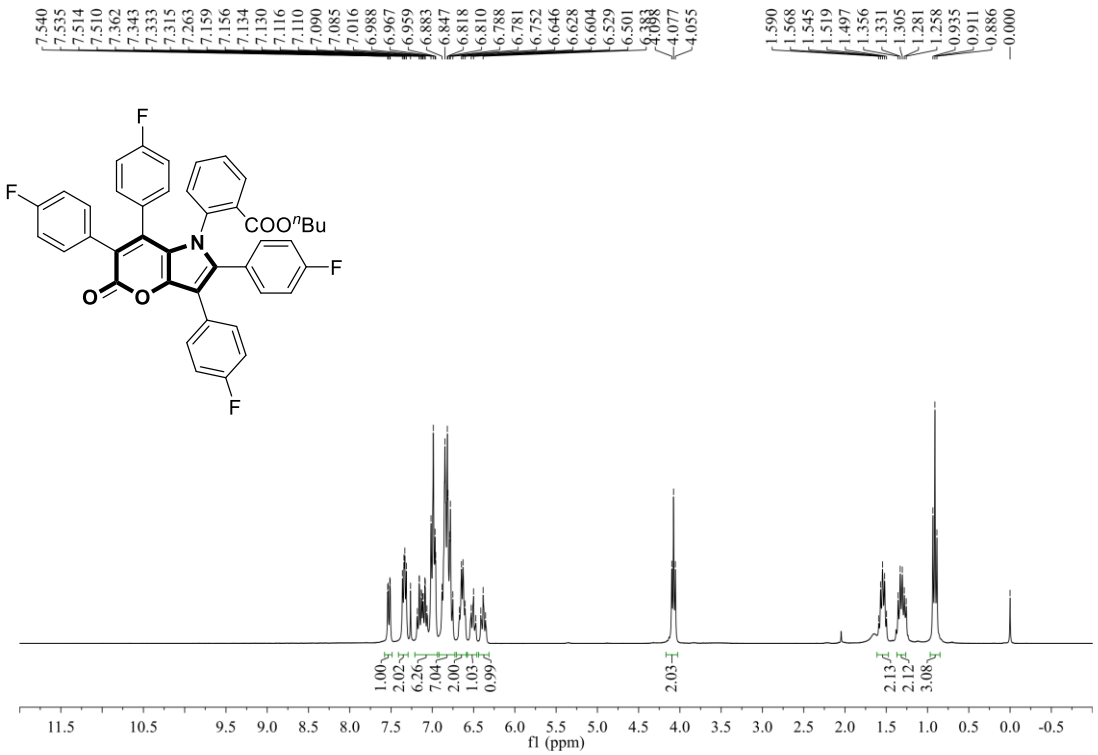


Figure S58. ^{1}H NMR spectrum of compound **6c** (300 MHz, $CDCl_3$)

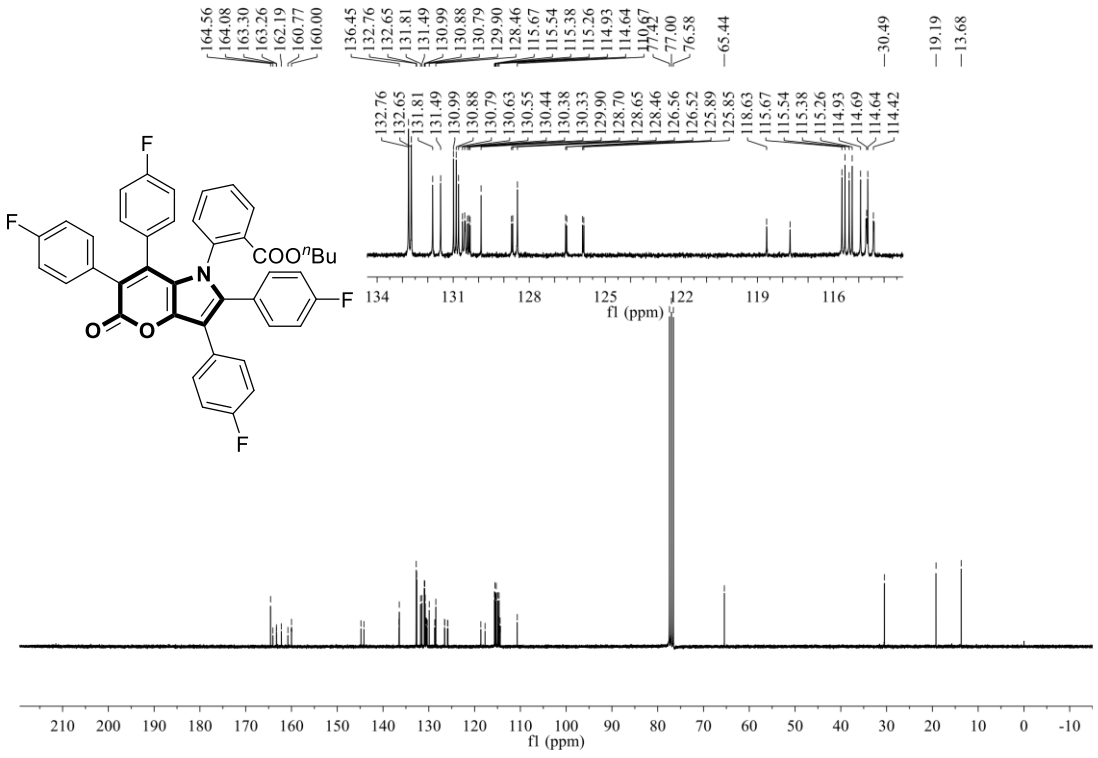


Figure S59. ^{13}C NMR spectrum of compound **6c** (75 MHz, $CDCl_3$)

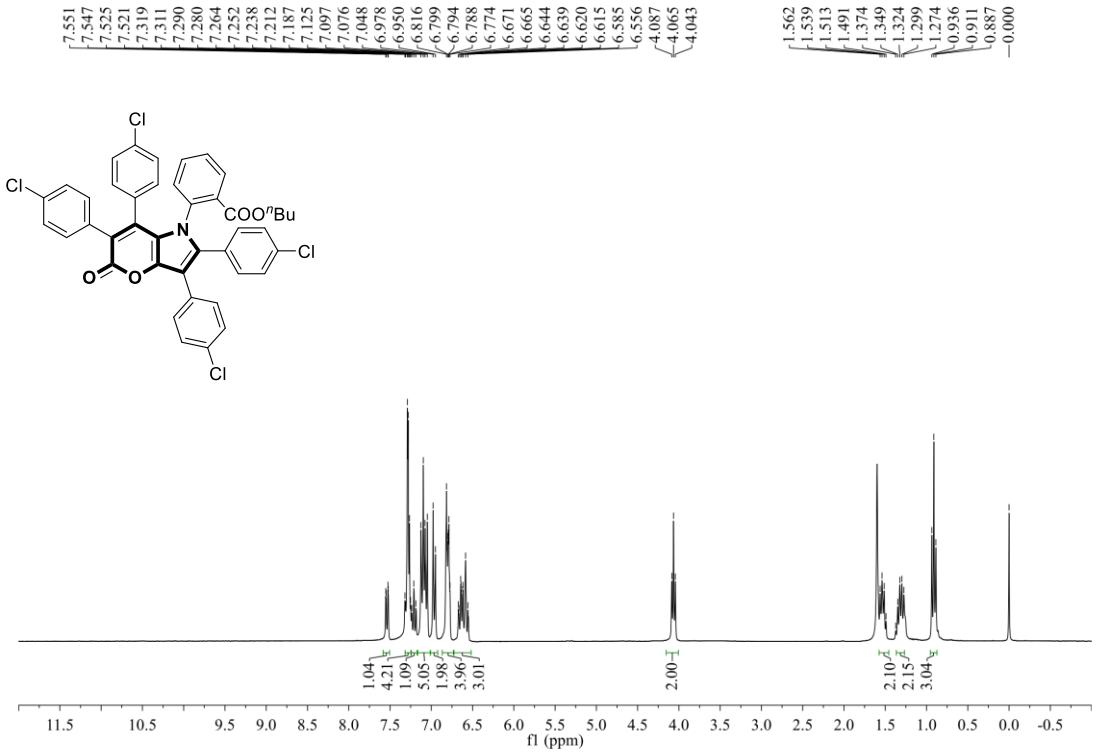


Figure S60. ^{1}H NMR spectrum of compound **6d** (300 MHz, $CDCl_3$)

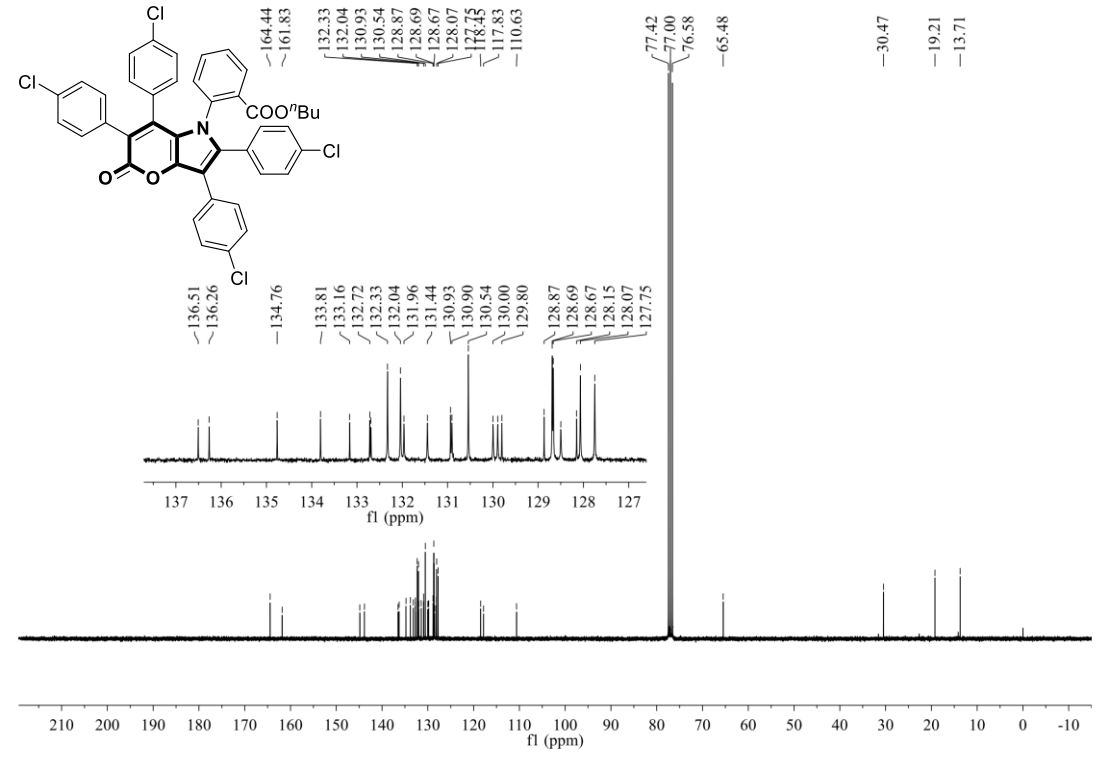


Figure S61. ^{13}C NMR spectrum of compound **6d** (75 MHz, $CDCl_3$)

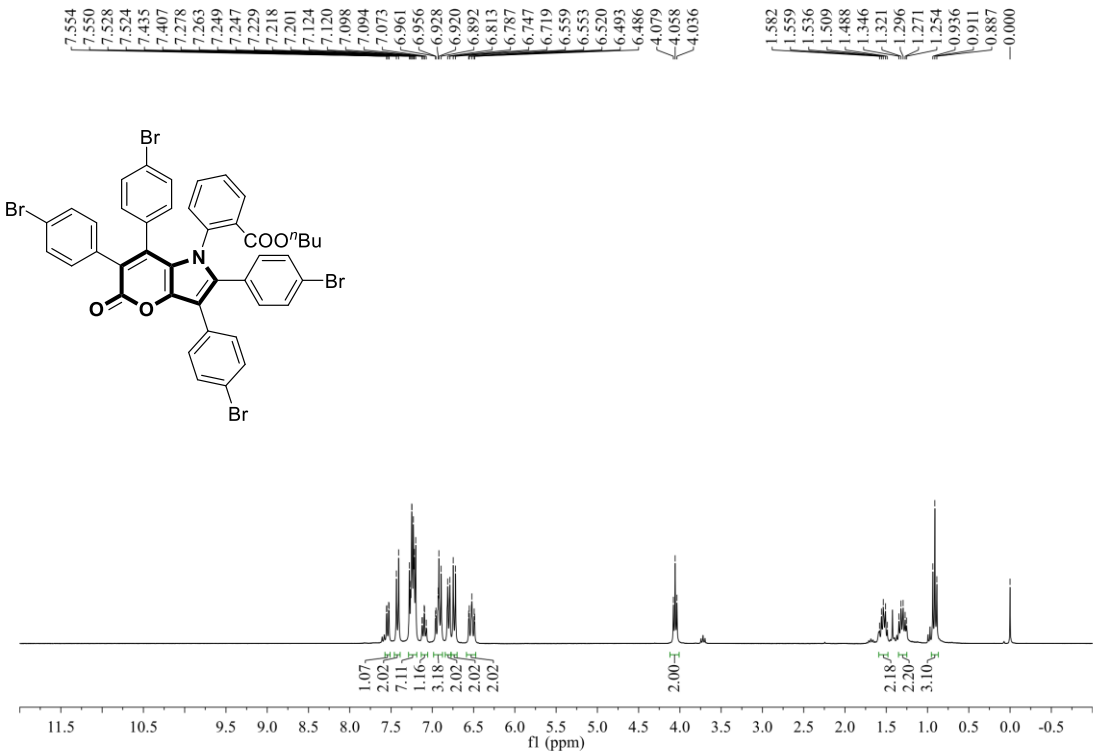


Figure S62. ^{1}H NMR spectrum of compound **6e** (300 MHz, $CDCl_3$)

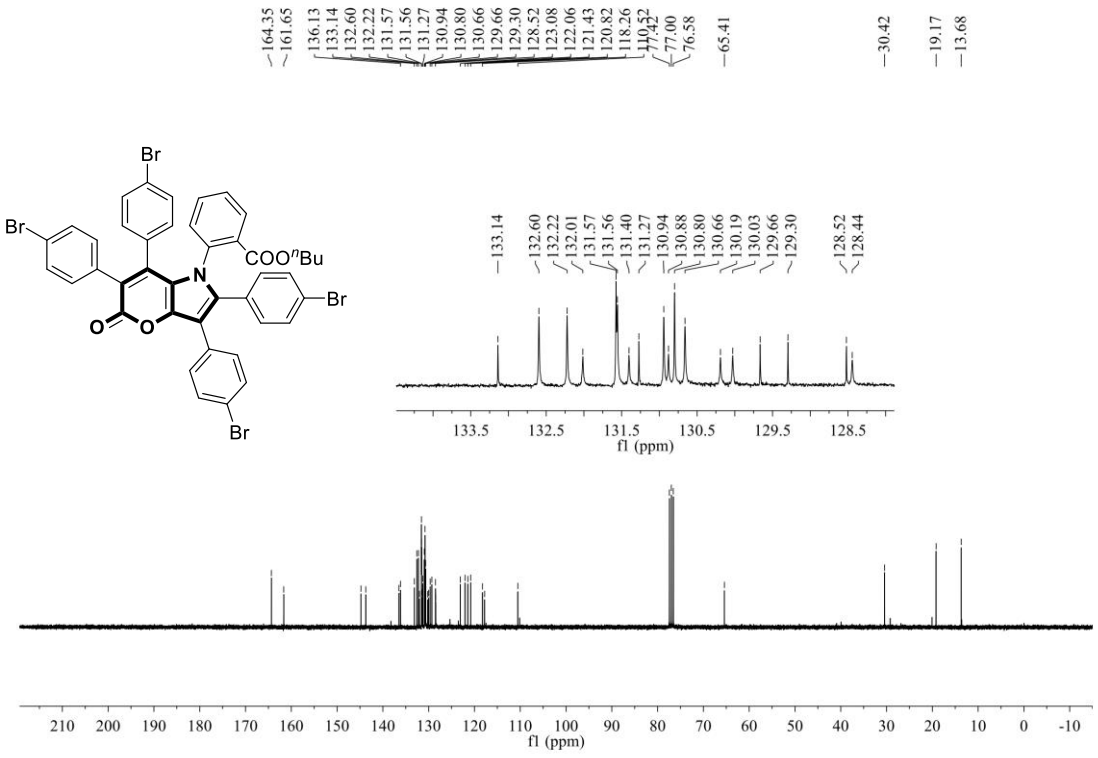


Figure S63. ^{13}C NMR spectrum of compound **6e** (75 MHz, $CDCl_3$)

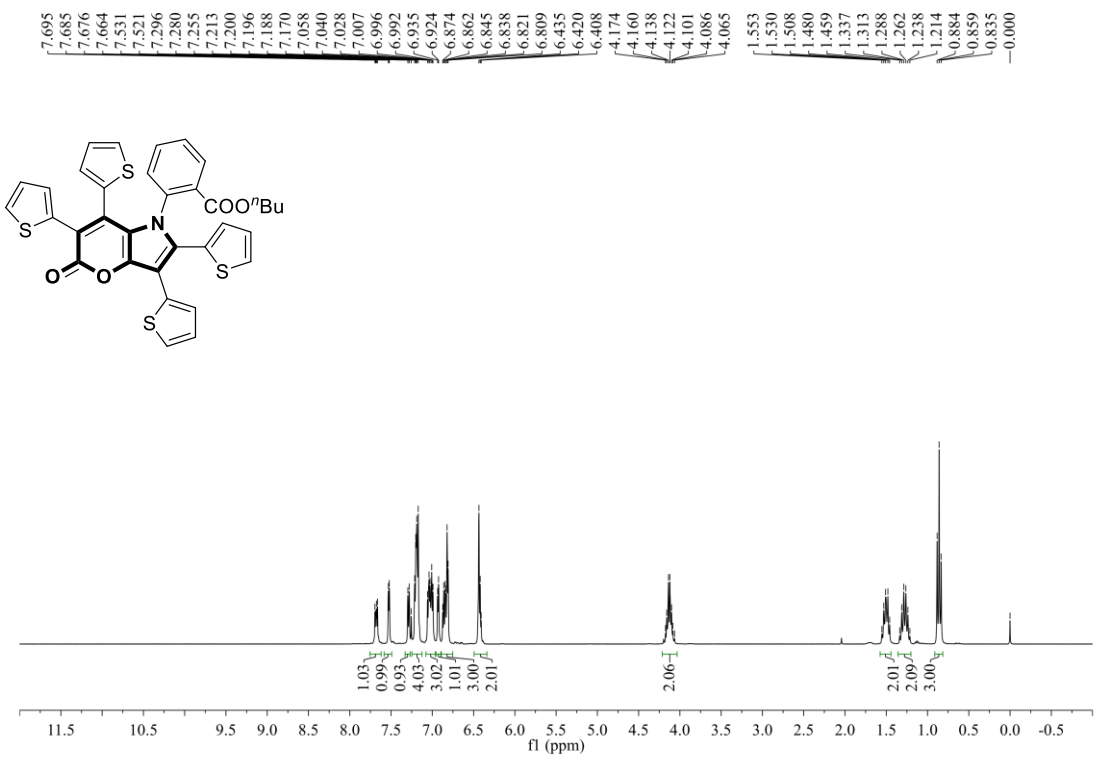


Figure S64. ^{1}H NMR spectrum of compound **6f** (300 MHz, $CDCl_3$)

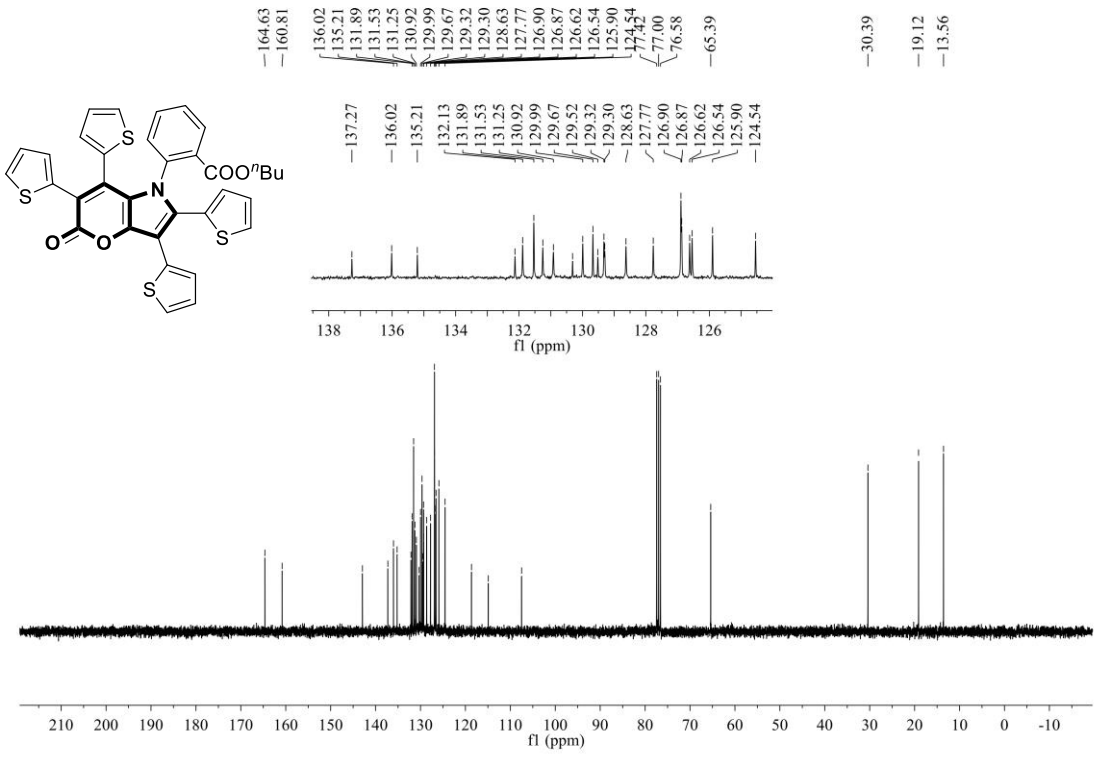


Figure S65. ^{13}C NMR spectrum of compound **6f** (75 MHz, $CDCl_3$)

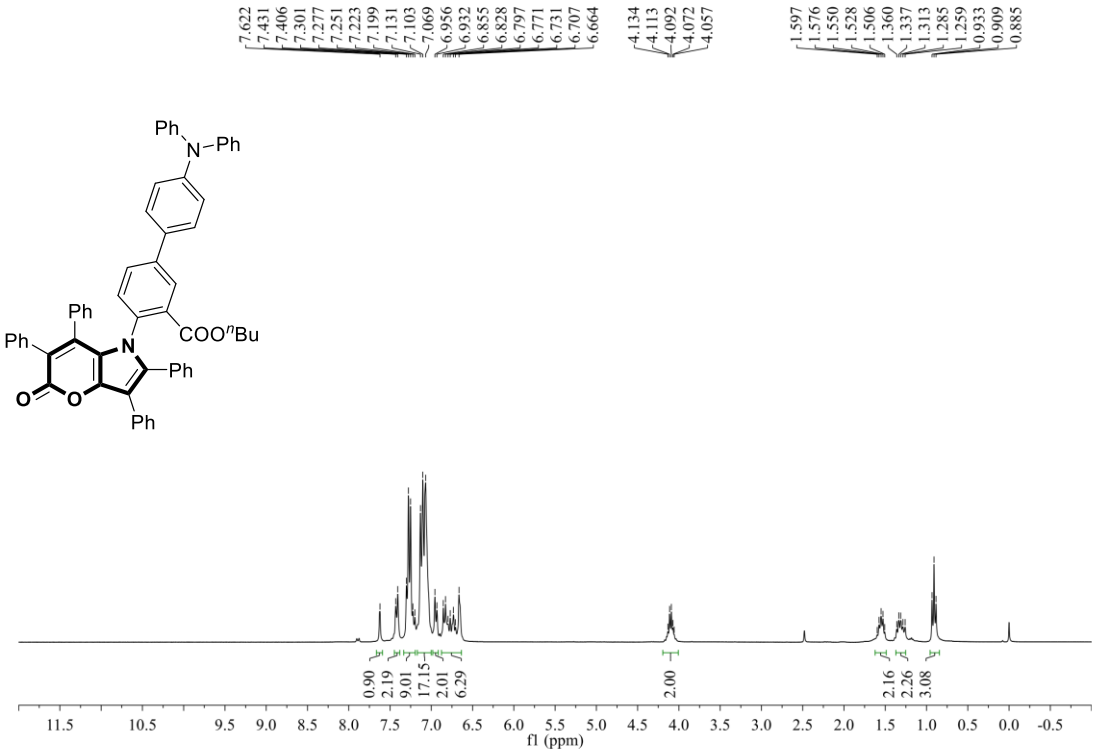


Figure S66. ^{1}H NMR spectrum of compound **7** (300 MHz, $CDCl_3$)

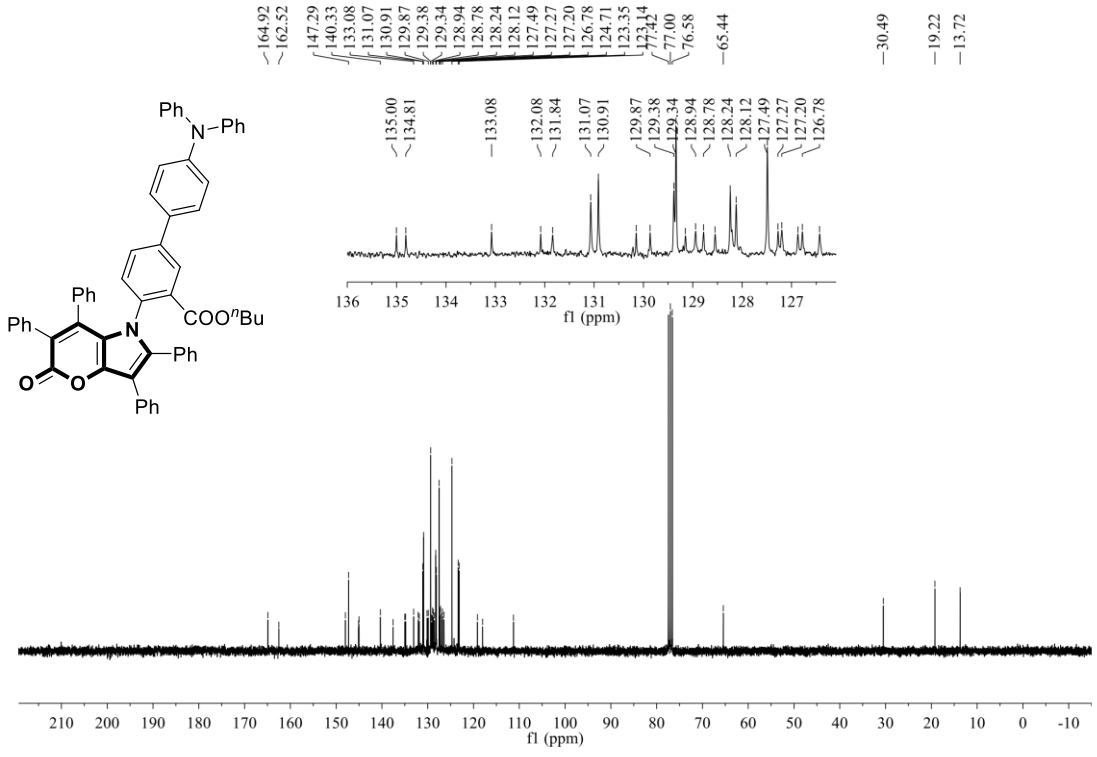


Figure S67. ^{13}C NMR spectrum of compound **7** (75 MHz, $CDCl_3$)

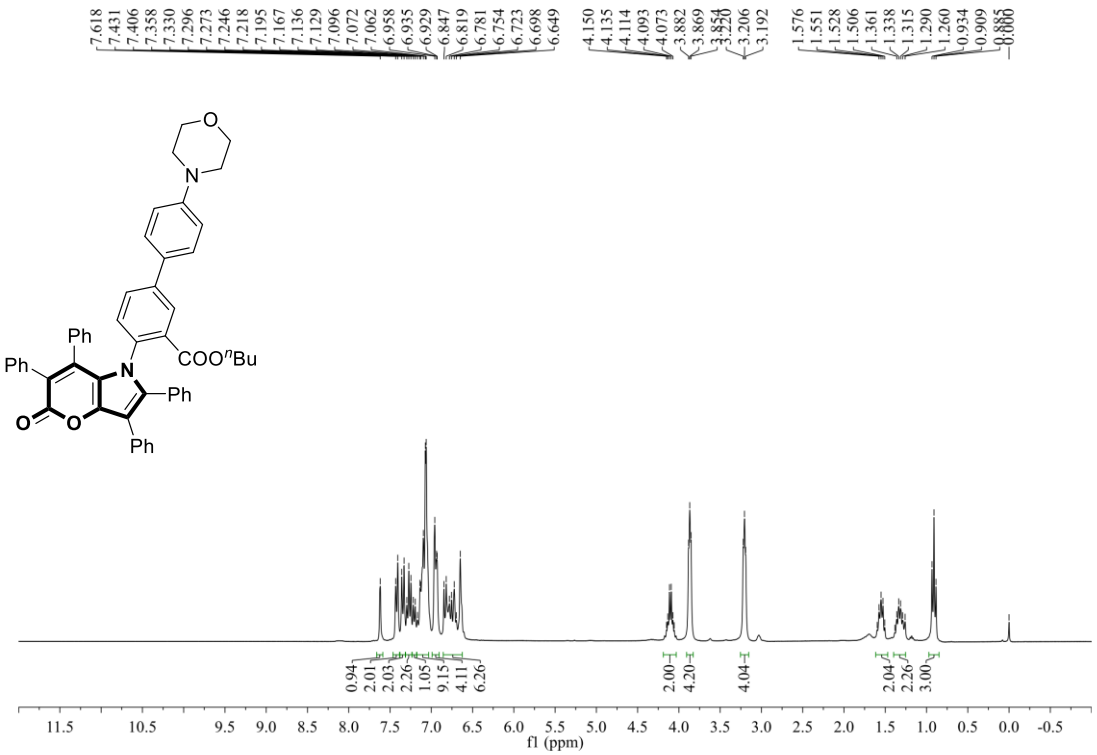


Figure S68. ^{1}H NMR spectrum of compound **8** (300 MHz, $CDCl_3$)

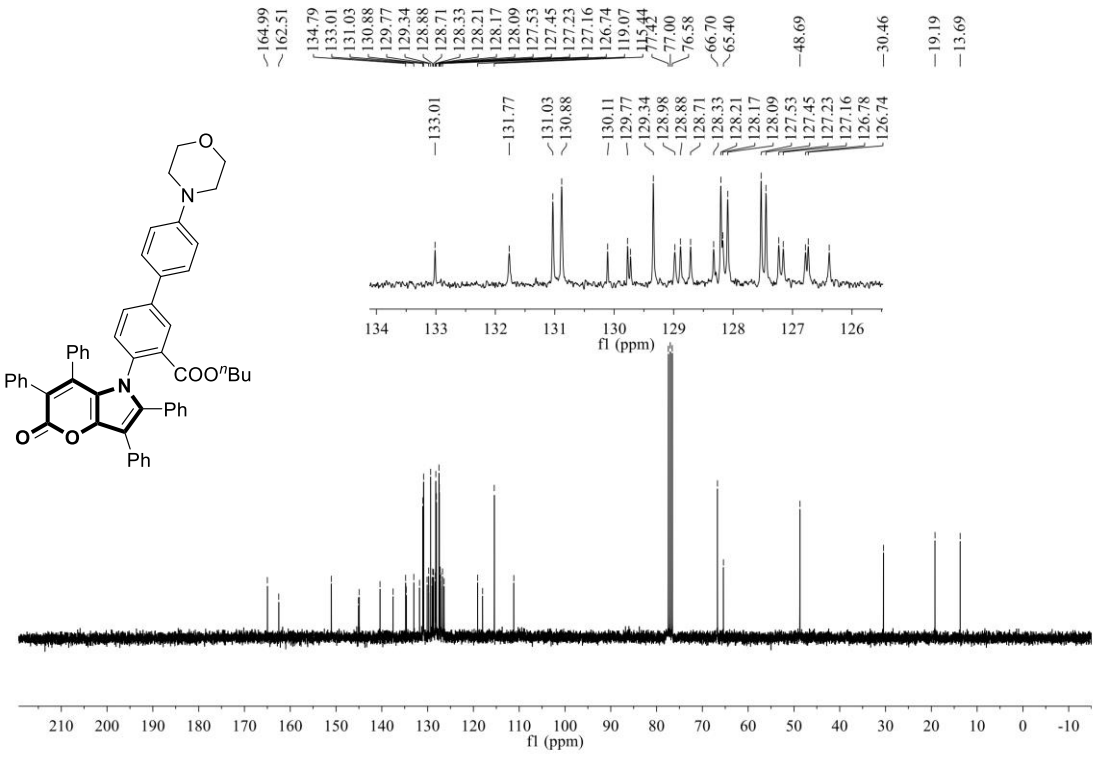


Figure S69. ^{13}C NMR spectrum of compound **8** (75 MHz, $CDCl_3$)

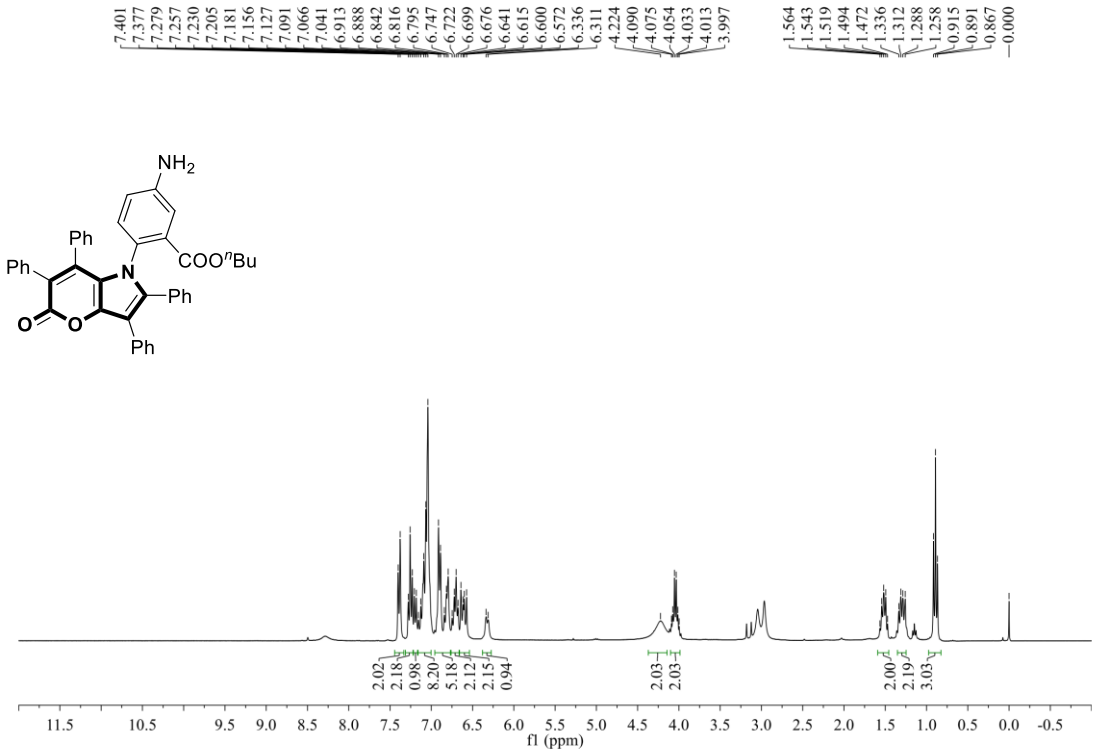


Figure S70. ^{1}H NMR spectrum of compound **9** (300 MHz, $CDCl_3$)

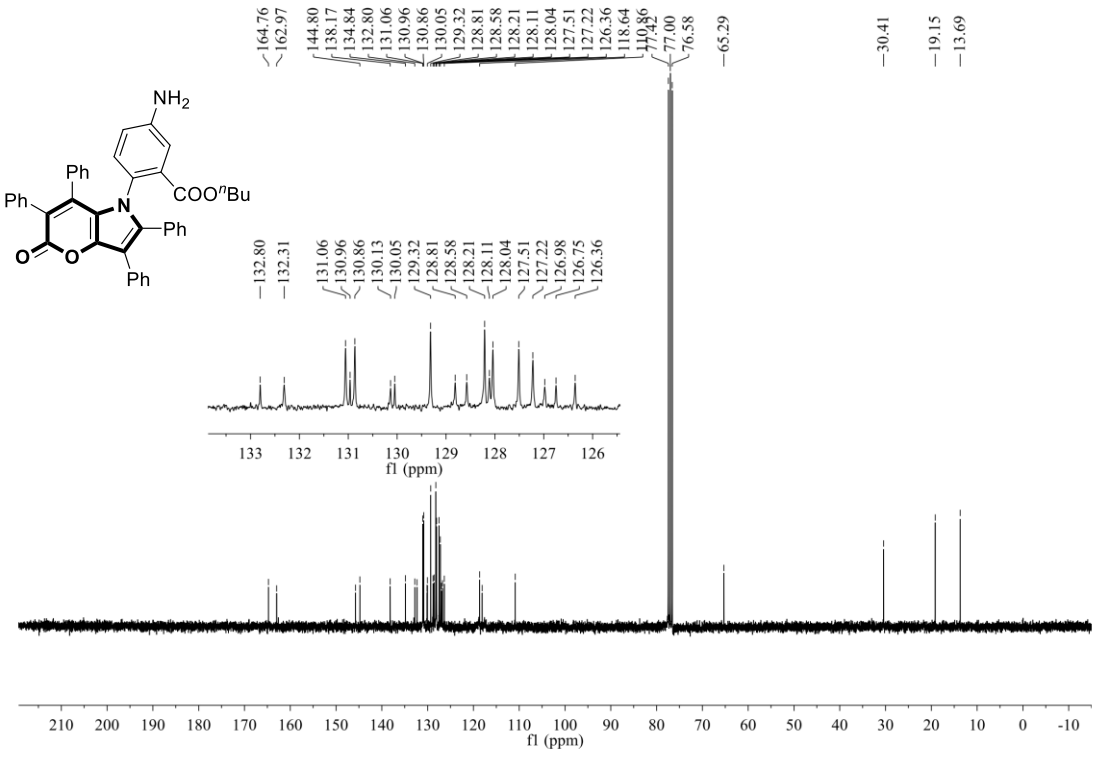


Figure S71. ^{13}C NMR spectrum of compound **9** (75 MHz, $CDCl_3$)

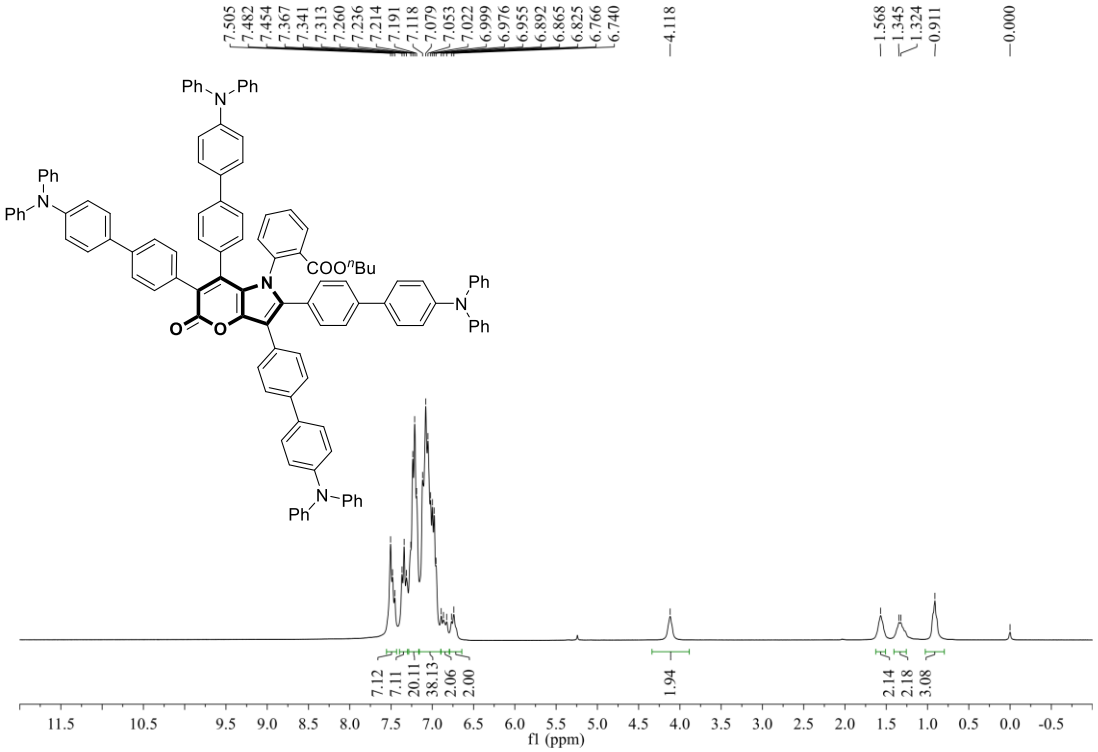


Figure S72. ^{1}H NMR spectrum of compound **10** (300 MHz, $CDCl_3$)

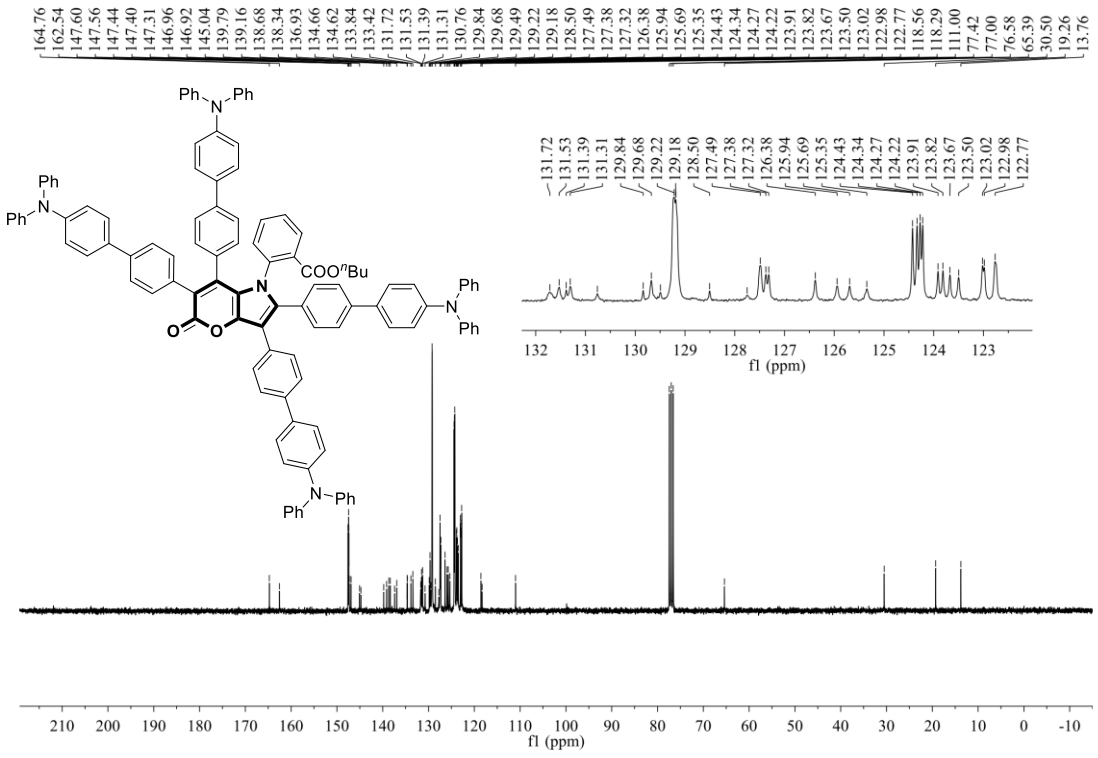


Figure S73. ^{13}C NMR spectrum of compound **10** (75 MHz, $CDCl_3$)

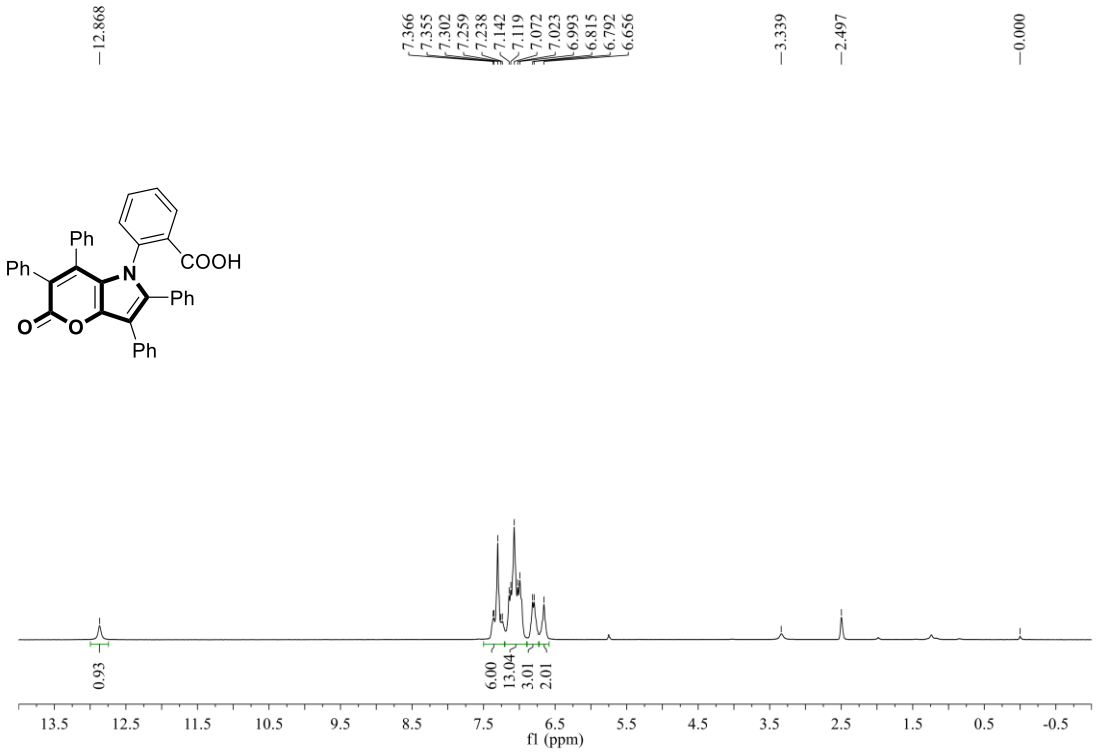


Figure S74. ^{1}H NMR spectrum of compound **11** (300 MHz, DMSO-d_6)

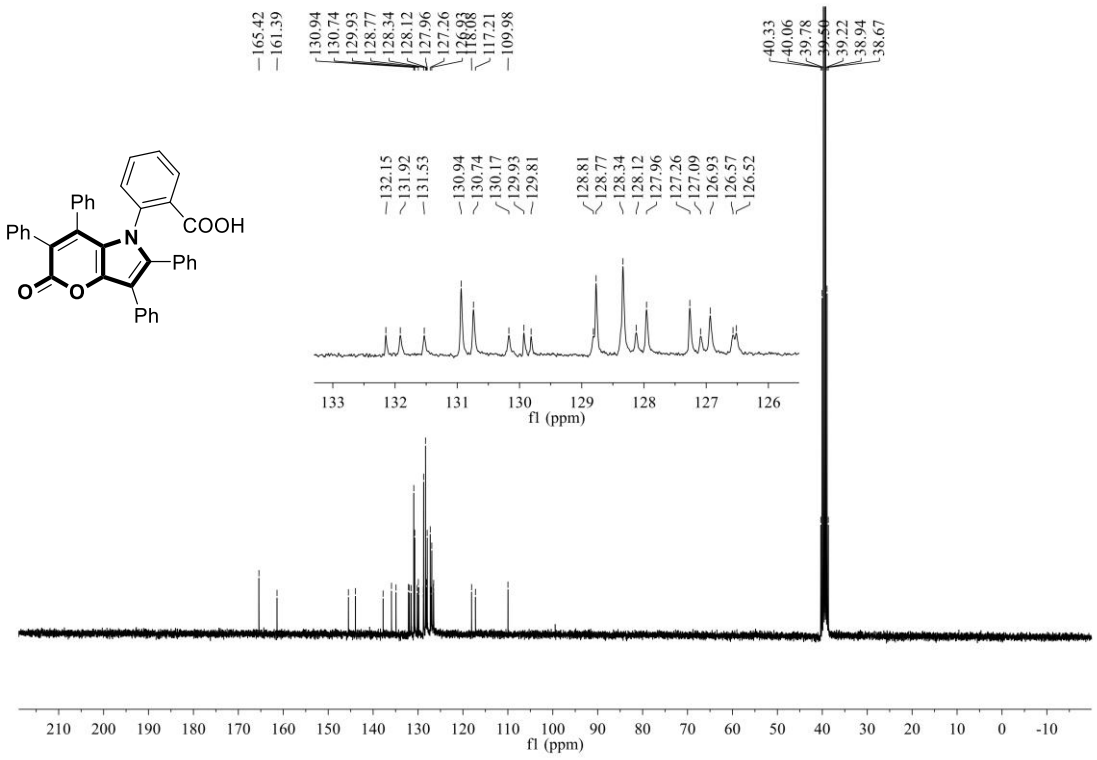


Figure S75. ^{13}C NMR spectrum of compound **11** (75 MHz, DMSO-d_6)

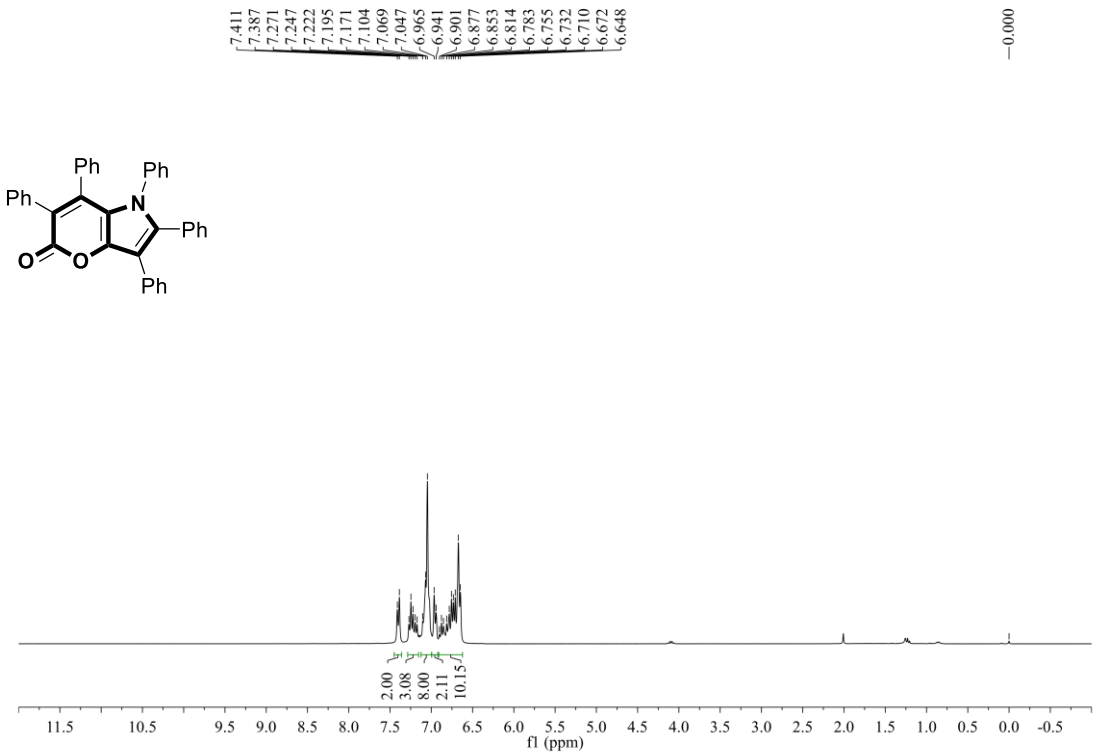


Figure S76. ^{1}H NMR spectrum of compound **12** (300 MHz, $CDCl_3$)

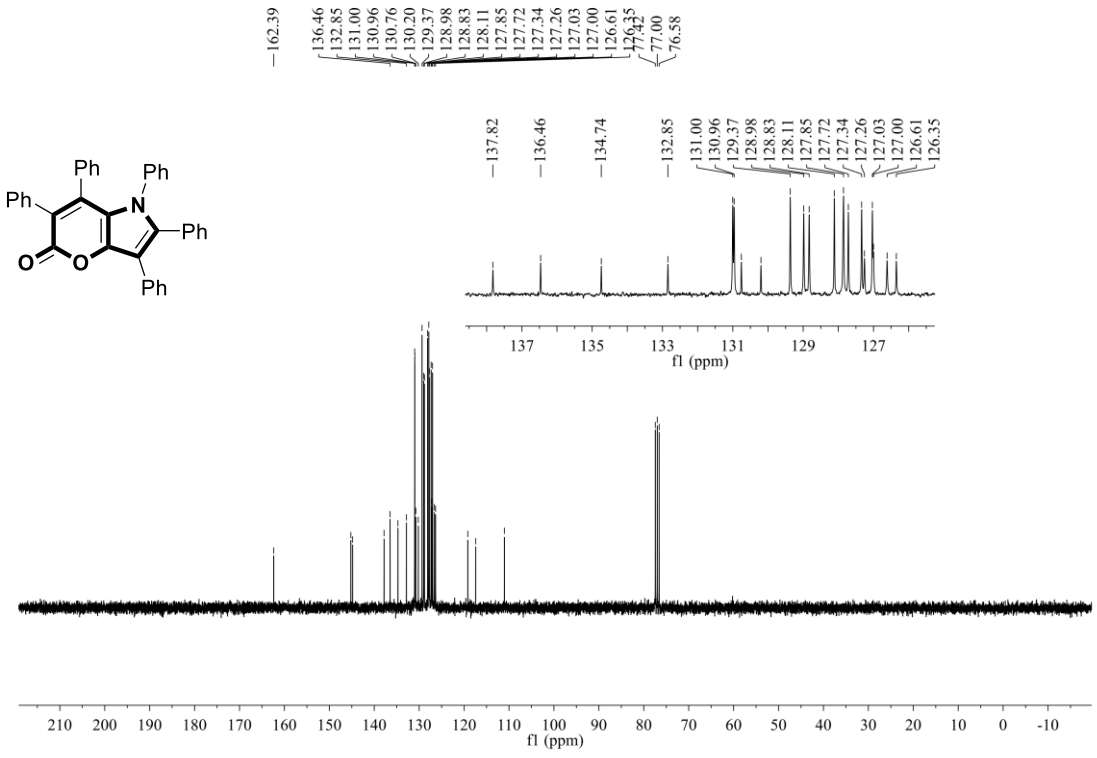


Figure S77. ^{13}C NMR spectrum of compound **12** (75 MHz, $CDCl_3$)