

Synthesis of 4*H*-Cyclopenta[*c*]furans via Cooperative PdCl₂/FeCl₂ Catalyzed Cascade Cyclization Reaction Involving a Novel Acyl Rearrangement Process

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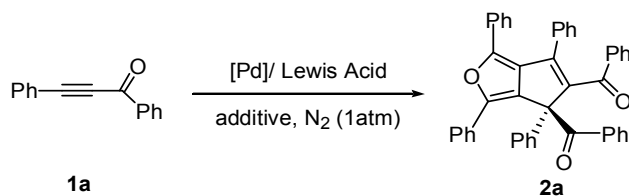
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A. General method

^1H and ^{13}C NMR spectra were recorded on BRUKER DRX-400 spectrometer using CDCl_3 as solvent and TMS as an internal standard. Chemical shifts are reported relative to CDCl_3 (^1H NMR 7.27; ^{13}C NMR 77.0). IR spectra were obtained as potassium bromide pellets or as liquid films between two potassium bromide pellets. High-resolution mass spectra (ESI TOF (+)) were measured on ThermoFisher Scientific LTQ Orbitrap XL.

B. Screening reaction conditions

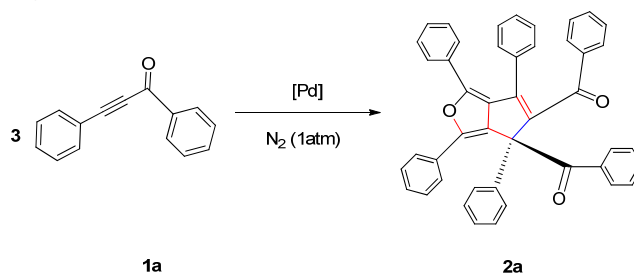
Table 1. Optimization of reaction conditions^[a]



Entry	Catalyst	Lewis Acid	Yield [%] ^[b]
1	-	-	none
2	PdCl_2	-	8
3	PdCl_2	$\text{Cu}(\text{OTf})_2$	47
4	PdCl_2	$\text{In}(\text{OTf})_3$	62
5	PdCl_2	$\text{Zn}(\text{OAc})_2$	50
6	PdCl_2	AgOTf	43
7	PdCl_2	FeCl_2	70
8	PdCl_2	FeCl_3	61
9	PdCl_2	$\text{Fe}(\text{OTf})_2$	65
10	PdCl_2	HCl	28
11	-	FeCl_2	none
12	$\text{Pd}(\text{OAc})_2$	FeCl_2	62
13	$\text{PdCl}_2/\text{PPh}_3$	FeCl_2	trace
14	$\text{PdCl}_2(\text{CH}_3\text{CN})_2$	FeCl_2	66
15	$\text{Pd}(\text{dba})_2$	FeCl_2	trace
16	$\text{Pd}(\text{PPh}_3)_4$	FeCl_2	none
17	PdCl_2	FeCl_2	51 ^[c] , 5 ^[d]

^aUnless otherwise specified, all the reactions were carried out with 1a (1 mmol), Pd catalyst (10 mol %), Lewis acid (5 mol %), additive LiCl (2 equiv) in xylene (3.0 mL) at 80 °C under 1 atm N_2 for 24 h. ^bIsolated yields. ^cThe reaction was carried out under an atmospheric air. [d] The reaction was carried out under an atmospheric of O_2 (1 atm).

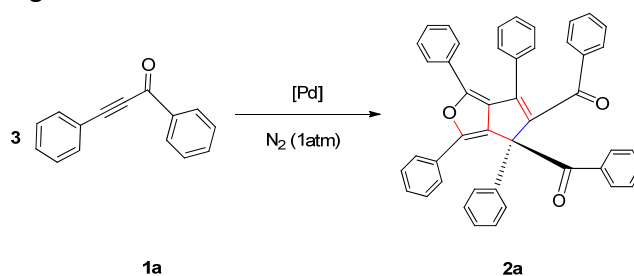
Table 2. Screening of Pd Catalyst for the Reaction^a



Entry	Catalyst	Lewis acid	Solvent	Yield[%] ^b
1	PdCl ₂ (Ph ₃ P) ₂	FeCl ₂	Xylene	trace
2	PdCl₂	FeCl₂	Xylene^c	70
3	PdBr ₂	FeCl ₂	Xylene	40
4	PdI ₂	FeCl ₂	Xylene	25
5	Pd(OH) ₂	FeCl ₂	Xylene	28

^aUnless otherwise specified, all the reactions were carried out with **1a** (1 mmol), Pd catalyst (10 mol %), Lewis acid FeCl₂ (5 mol %), additive LiCl (2 equiv), solvent (3.0 mL), at 80 °C, under 1atm N₂, for 24 h. ^bIsolated yields. ^cThe xylene used in the experiments was dried by 4 Å molecular sieves.

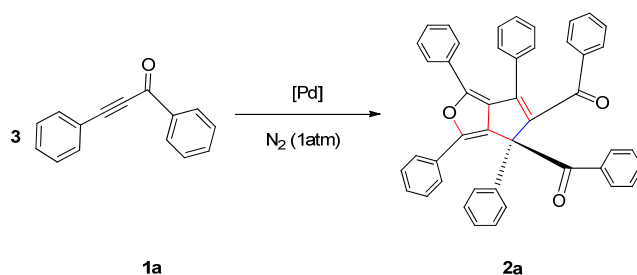
Table 3. Screening of Lewis acid for the Reaction^a



Entry	Catalyst	Lewis acid	Solvent	Yield[%] ^b
1	PdCl ₂	Zn(OTf) ₂	Xylene	45
2	PdCl ₂	NiCl ₂	Xylene ^c	30
3	PdCl ₂	TiCl ₄	Xylene	48
4	PdCl ₂	ZnBr ₂	Xylene	25
5	PdCl ₂	ZnCl ₂	Xylene	14
6	PdCl ₂	ZnI ₂	Xylene	18
7	PdCl ₂	AlCl ₃	Xylene	trace
8	PdCl ₂	HCl	Xylene	28
9	PdCl₂	FeCl₂	Xylene	70
10	PdCl ₂	none	Xylene	10

^aUnless otherwise specified, all the reactions were carried out with **1a** (1 mmol), Pd catalyst (10 mol %), Lewis acid (5 mol %), additive LiCl (2 equiv), solvent (3.0 mL), under 1atm N₂, at 80 °C, for 24 h. ^bIsolated yields. ^cThe xylene used in the experiments was dried by 4 Å molecular sieves.

Table 4. Screening of Additive, Solvent and Temperature for the Reaction^a



Entry	Catalyst	Additive	Solvent	T(°C)	Yield[%] ^b
1	PdCl ₂	LiCO ₃	Xylene ^c	80	25
2	PdCl ₂	NH ₄ Cl	Xylene	80	23
3	PdCl₂	LiCl	Xylene	80	70
4 ^d	PdCl ₂	LiCl	Xylene	80	58
5	PdCl ₂	LiCl	EtOH	80	trace
6	PdCl ₂	LiCl	DMF	80	10
7	PdCl ₂	LiCl	CH ₃ NO ₂	80	20
8	PdCl ₂	LiCl	CHCl ₃	80	30
9	PdCl ₂	LiCl	DMAP	80	10
10	PdCl ₂	LiCl	DMSO	80	15
11	PdCl ₂	LiCl	Xylene	60	52
12	PdCl ₂	LiCl	Xylene	100	54

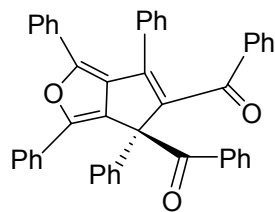
^aUnless otherwise specified, all the reactions were carried out with **1a** (1 mmol), Pd catalyst (10 mol %), Lewis acid FeCl₂ (5 mol %), additive (2 equiv), solvent (3.0 mL), under 1atm N₂, for 24 h. ^bIsolated yields. ^cThe xylene used in the experiments was dried by 4 Å molecular sieves. ^dThe reaction time was 12 h.

C. General procedure for substrate 2a-2m

A mixture of 1,3-diphenylprop-2-yn-1-one (1mmol), PdCl₂(10 mol %), FeCl₂ (5 mol %), LiCl (2 equiv) in xylene (3 mL) was added into a schlenk tube. The tube was then put into a 80 °C oil bath under magnetic stirring for 24 h under the atmosphere of N₂ (1atm). After the reaction was finished, the reaction mixture was cooled to room temperature, and extracted the crude product with ethyl acetate. The organic extract was concentrated in vacuum, and the resulting residue was purified by silica gel column chromatography using light petroleum ether/ethyl acetate as eluent to afford the desired products, which were further recrystallized from EtOAc/EtOH.

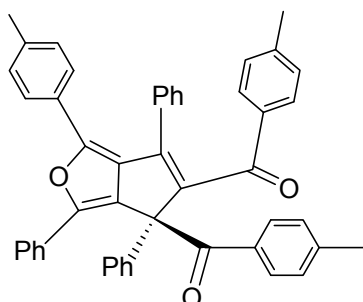
D. Analytical data for 2a-2m

(1,3,4,6-tetraphenyl-4*H*-cyclopenta[*c*]furan-4,5-diyl)bis(phenylmethanone) (**2a**)



m.p. 232-235 °C; IR (KBr): 3058, 1682, 1639, 1597, 1491, 1446, 1237, 1180, 799, 766, 692; ^1H NMR (400 MHz, CDCl_3) δ 7.72 (d, $J = 7.6$ Hz, 2H), 7.63 (d, $J = 7.6$ Hz, 2H), 7.53 (d, $J = 7.2$ Hz, 2H), 7.37–7.28 (m, 3H), 7.24–7.12 (m, 11H), 7.07–7.02 (m, 4H), 6.97–6.94 (m, 2H), 6.90–6.84 (m, 4H); ^{13}C NMR (100 MHz, CDCl_3) δ 195.59, 195.20, 149.11, 146.86, 145.73, 142.01, 139.14, 137.86, 135.15, 133.32, 132.87, 131.90, 131.04, 129.45, 128.90, 128.80, 128.70, 128.62, 128.33, 128.26, 128.07, 128.02, 127.69, 127.66, 127.40, 127.23, 127.11, 125.49, 69.82; HRMS (ESI): Anal. calcd. for $\text{C}_{45}\text{H}_{30}\text{NaO}_3$ m/z 641.2093 $[\text{M} + \text{Na}]^+$, found 641.2069.

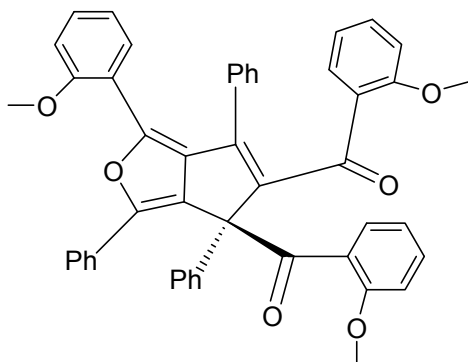
(3,4,6-triphenyl-1-(*p*-tolyl)-4*H*-cyclopenta[*c*]furan-4,5-diyl)bis(*p*-tolylmethanone (2b)



m.p. 219-220 °C; IR (KBr): 3058, 2921, 1682, 1638, 1605, 1498, 1237, 1180, 739, 698; ^1H NMR (400 MHz, CDCl_3) δ 7.72 (d, $J = 6.8$ Hz, 2H), 7.63 (d, $J = 7.2$ Hz, 2H), 7.50 (d, $J = 6.4$ Hz, 2H), 7.32–7.28 (m, 2H), 7.22–7.19 (m, 4H), 7.12–7.05 (m, 5H), 7.03–6.97 (m, 8H), 6.67 (d, $J = 8$ Hz, 2H), 2.33 (s, 3H), 2.29 (s, 3H), 2.10 (s, 3H); ^{13}C NMR (100 MHz, CDCl_3) δ 194.94, 194.75, 149.19, 146.42, 145.77, 142.62, 141.60, 140.88, 138.24, 136.34, 135.49, 135.30, 133.61, 132.26, 129.09, 128.97, 128.93, 128.76, 128.66, 128.54, 128.47, 128.40, 128.21, 128.09, 127.98, 127.77, 127.49, 127.41, 127.13, 126.86, 125.40, 69.84, 21.41, 21.36, 21.28; HRMS (ESI): Anal. calcd. for $\text{C}_{48}\text{H}_{36}\text{NaO}_3$ m/z 683.2562 $[\text{M} + \text{Na}]^+$, found 683.2549.

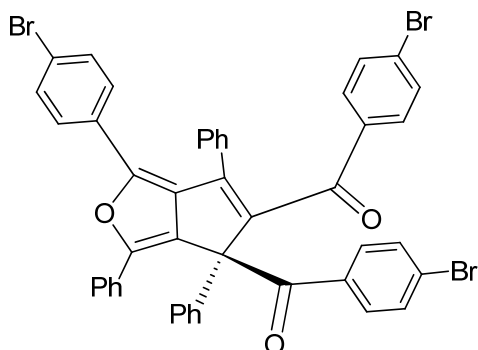
(1-(2-methoxyphenyl)-3,4,6-triphenyl-4*H*-cyclopenta[*c*]furan-4,5-diyl)bis((2-methoxyphenyl)methanone

oxyphenyl)methanone) (2c)



m.p. 218-220 °C; IR (KBr): 3060, 2936, 2836, 1703, 1602, 1490, 1459, 1282, 1251, 1024, 749, 696; ¹H NMR (400 MHz, CDCl₃) δ 7.78–7.75 (m, 1H), 7.73–7.71 (m, 2H), 7.67–7.65 (m, 2H), 7.48–7.45 (m, 1H), 7.29–7.23 (m, 6H), 7.21–7.16 (m, 4H), 6.94–6.82 (m, 4H), 6.75–6.70 (m, 5H), 6.64 (d, *J* = 8.4 Hz, 1H), 6.46 (d, *J* = 8.4 Hz, 1H), 6.42–6.38 (m, 1H), 6.26 (d, *J* = 8.4 Hz, 1H), 3.48 (s, 3H), 3.19 (s, 3H), 2.78 (s, 3H); ¹³C NMR (100 MHz, CDCl₃) δ 195.52, 193.89, 157.41, 156.57, 156.12, 148.67, 147.34, 145.42, 141.09, 134.86, 134.40, 133.79, 132.11, 130.05, 129.98, 129.93, 129.84, 129.67, 129.63, 128.97, 128.56, 128.14, 127.99, 127.73, 127.63, 127.18, 127.15, 126.57, 126.04, 125.54, 119.80, 119.37, 119.25, 118.25, 110.70, 110.25, 110.08, 70.92, 55.01, 54.89, 53.78; HRMS (ESI): Anal. calcd. for C₄₈H₃₆NaO₆ *m/z* 731.2410 [M + Na]⁺, found 731.2388.

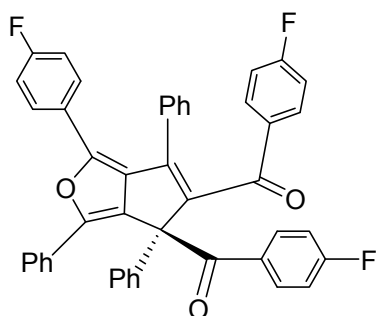
(1-(4-bromophenyl)-3,4,6-triphenyl-4H-cyclopenta[c]furan-4,5-diyl)bis((4-bromophenyl)methanone) (2d)



m.p. 191-195 °C; IR (KBr): IR (KBr): 3074, 2921, 1742, 1686, 1646, 1582, 1484, 1393, 1239, 1066, 1009, 831, 734, 702; ¹H NMR (400 MHz, CDCl₃) δ 7.60 (d, *J* = 8.0 Hz, 4H), 7.46–7.39 (m, 4H), 7.34–7.29 (m, 4H), 7.24–7.14 (m, 5H), 7.09–7.02 (m,

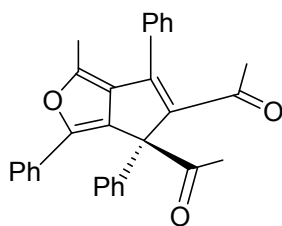
6H), 6.92–6.88 (m, 4H); ^{13}C NMR (100 MHz, CDCl_3) δ 194.10, 194.07, 148.91, 147.30, 144.84, 141.57, 137.64, 136.29, 134.67, 132.85, 132.77, 131.35, 131.05, 130.82, 130.21, 129.31, 129.22, 128.72, 128.67, 128.50, 128.43, 128.34, 128.08, 127.98, 127.31, 126.69, 126.10, 125.48, 122.63, 69.66; HRMS (ESI): Anal. calcd. for $\text{C}_{45}\text{H}_{27}\text{Br}_3\text{NaO}_3$ m/z 874.9408 $[\text{M} + \text{Na}]^+$, found 874.9420.

(1-(4-fluorophenyl)-3,4,6-triphenyl-4*H*-cyclopenta[*c*]furan-4,5-diyl)bis((4-fluorophenyl)methanone) (2e)



m.p. 210–213 °C; IR (KBr): 3070, 2922, 1687, 1644, 1596, 1501, 1233, 1156, 846, 741, 698, 604; ^1H NMR (400 MHz, CDCl_3) δ 7.78–7.75 (m, 2H), 7.59 (d, $J = 7.2$ Hz, 2H), 7.47–7.44 (m, 2H), 7.33–7.30 (m, 2H), 7.23–7.21 (m, 4H), 7.17–7.11 (m, 3H), 7.08–7.01 (m, 4H), 6.96–6.85 (m, 6H), 6.58–6.53 (m, 2H); ^{13}C NMR (100 MHz, CDCl_3) δ 193.84, 193.69, 166.17, 165.69, 163.87, 163.64, 163.19, 161.39, 148.81, 147.03, 144.97, 141.28, 135.21, 135.18, 134.95, 134.00, 133.97, 132.98, 132.16, 131.48, 131.38, 130.28, 130.19, 129.19, 129.11, 129.06, 128.73, 128.71, 128.57, 128.52, 128.45, 128.36, 128.25, 127.88, 126.82, 125.63, 125.60, 125.45, 115.41, 115.19, 114.97, 114.83, 114.75, 114.61, 69.79; HRMS (ESI): Anal. calcd. for $\text{C}_{45}\text{H}_{27}\text{NaO}_3$ m/z 695.1810 $[\text{M} + \text{Na}]^+$, found 695.1789.

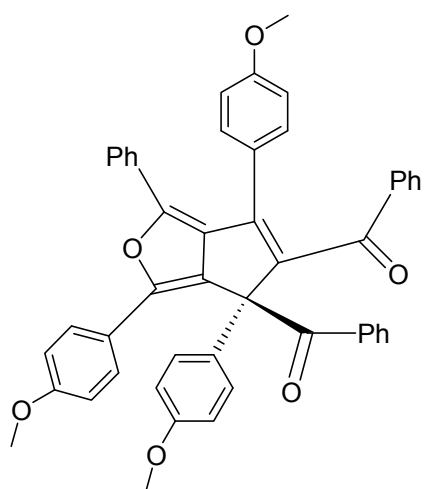
1,1'-(1-methyl-3,4,6-triphenyl-4*H*-cyclopenta[*c*]furan-4,5-diyl)diethanone (2f)



m.p. 139–140 °C; IR (KBr): 3064, 2921, 1710, 1638, 1549, 1495, 1166, 757, 729, 696; ^1H NMR (400 MHz, CDCl_3) δ 7.50 (d, $J = 6.8$ Hz, 3H), 7.40 (d, $J = 7.6$ Hz, 6H),

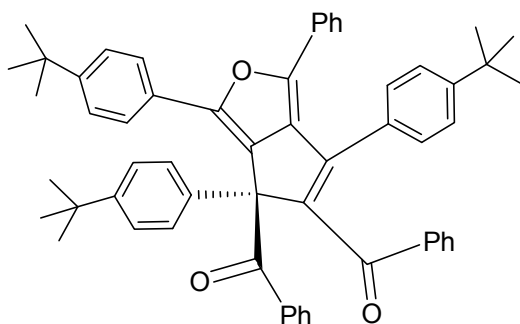
7.25–7.23 (m, 5H), 7.17–7.13(m, 1H), 2.24 (s, 3H), 2.11 (s, 3H), 1.69 (s, 3H); ^{13}C NMR (100 MHz, CDCl_3) δ 199.54, 198.73, 149.02, 145.78, 144.92, 143.95, 135.25, 133.69, 133.24, 129.32, 129.09, 128.94, 128.47, 128.07, 127.98, 127.49, 127.35, 124.87, 69.74, 30.52, 25.23, 12.78; HRMS (ESI): Anal. calcd. for $\text{C}_{30}\text{H}_{24}\text{NaO}_3$ m/z 455.1623 $[\text{M} + \text{Na}]^+$, found 455.1629.

(3,4,6-tris(4-methoxyphenyl)-1-phenyl-4*H*-cyclopenta[*c*]furan-4,5-diyl)bis(phenylmethanone) (2g)



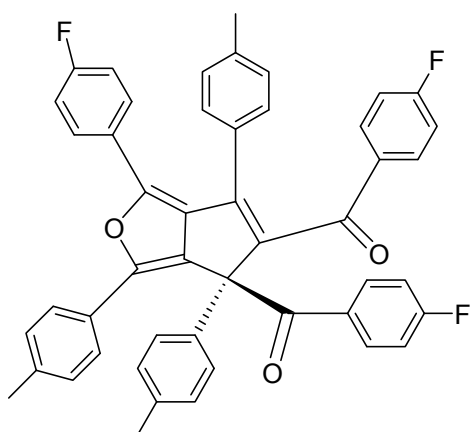
m.p. 224–226 °C; IR (KBr): 3064, 2937, 1608, 1509, 1460, 1253, 1179, 1030, 833, 796, 694; ^1H NMR (400 MHz, CDCl_3) δ 7.67 (d, $J = 7.6$ Hz, 2H), 7.57 (d, $J = 9.2$ Hz, 2H), 7.44 (d, $J = 8.8$ Hz, 2H), 7.35–7.31 (m, 1H), 7.24–7.16 (m, 7H), 7.11–7.07 (m, 3H), 6.91–6.84 (m, 4H), 6.80–6.75 (m, 4H), 6.46 (d, $J = 8.8$ Hz, 2H), 3.77 (s, 3H), 3.71 (s, 3H), 3.64 (s, 3H); ^{13}C NMR (100 MHz, CDCl_3) δ 196.38, 195.45, 159.79, 159.44, 158.79, 148.76, 146.89, 144.99, 141.98, 139.32, 137.93, 132.88, 131.77, 130.80, 130.49, 129.99, 129.75, 128.87, 128.05, 128.00, 127.62, 127.59, 127.44, 127.39, 127.27, 127.09, 125.69, 125.44, 121.88, 114.12, 113.62, 113.38, 69.03, 55.21, 55.09; HRMS (ESI): Anal. calcd. for $\text{C}_{48}\text{H}_{36}\text{NaO}_6$ m/z 731.2410 $[\text{M} + \text{Na}]^+$, found 731.2390.

(3,4,6-tri(4-(*tert*-butyl)phenyl)-1-phenyl-4*H*-cyclopenta[*c*]furan-4,5-diyl)bis(phenylmethanone) (2h)



m.p. 254-256 °C; IR (KBr): 3071, 2960, 1690, 1646, 1511, 1462, 1242, 751, 698;
 ^1H NMR (400 MHz, CDCl_3) δ 7.74 (d, $J = 7.2$ Hz, 2H), 7.60 (d, $J = 8.4$ Hz, 2H), 7.45 (d, $J = 8.4$ Hz, 2H), 7.37–7.34 (m, 3H), 7.26–7.23 (m, 5H), 7.20 (d, $J = 7.2$ Hz, 3H), 7.15–7.11 (m, 2H), 7.03–7.00 (m, 1H), 6.95 (d, $J = 8.0$ Hz, 4H), 6.84–6.78 (m, 4H), 1.29 (s, 9H), 1.22 (s, 9H), 1.15 (s, 9H); ^{13}C NMR (100 MHz, CDCl_3) δ 195.91, 195.44, 151.68, 151.01, 150.22, 149.47, 147.02, 145.38, 142.25, 139.28, 138.38, 133.14, 132.50, 131.33, 130.97, 130.52, 129.72, 128.72, 128.24, 127.99, 127.96, 127.78, 127.65, 127.13, 126.72, 126.24, 125.61, 125.34, 125.29, 124.71, 69.35, 34.66, 34.45, 34.35, 31.20, 31.15, 30.99; HRMS (ESI): Anal. calcd. for $\text{C}_{57}\text{H}_{54}\text{NaO}_3$ m/z 809.3971 $[\text{M} + \text{Na}]^+$, found 809.3938.

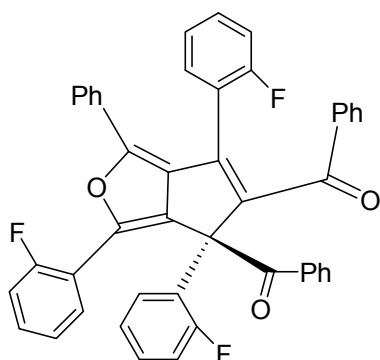
(1-(4-fluorophenyl)-3,4,6-tri-p-tolyl-4*H*-cyclopenta[*c*]furan-4,5-diyl)bis((4-fluorophenyl)methanone) (2i)



m.p. 235-337 °C; IR (KBr): 3063, 2930, 1698, 1640, 1510, 1451, 1210, 1137, 759, 692; ^1H NMR (400 MHz, CDCl_3) δ 7.77–7.74 (m, 2H), 7.50 (d, $J = 8.4$ Hz, 2H), 7.33 (d, $J = 8.4$ Hz, 2H), 7.19–7.16 (m, 2H), 7.14–7.09 (m, 4H), 7.01 (d, $J = 8.4$ Hz, 2H),

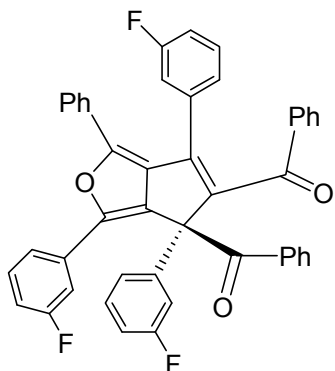
6.94–6.79 (m, 8H), 6.60–6.56 (m, 2H), 2.30 (s, 3H), 2.24 (s, 3H), 2.21 (s, 3H); ^{13}C NMR (100 MHz, CDCl_3) δ 194.16, 193.89, 166.12, 165.57, 163.72, 163.60, 163.07, 161.24, 148.52, 147.14, 144.46, 141.35, 139.04, 138.20, 137.33, 135.29, 135.26, 134.07, 134.04, 132.21, 131.97, 131.54, 131.45, 130.25, 130.16, 130.06, 129.38, 129.18, 129.10, 129.06, 128.88, 128.73, 128.40, 126.19, 125.95, 125.83, 125.80, 125.40, 115.27, 115.05, 114.84, 114.73, 114.62, 114.52, 69.44, 21.27, 21.14, 20.95; HRMS(ESI): Anal. calcd. for $\text{C}_{48}\text{H}_{33}\text{F}_3\text{NaO}_3$ m/z 737.2279 $[\text{M} + \text{Na}]^+$, found 737.2288.

(3,4,6-tri(2-fluorophenyl)-1-phenyl-4*H*-cyclopenta[*c*]furan-4,5-diyl)bis(phenylmethanone) (2j)



m.p. 203-204 °C; IR (KBr): 3064, 1683, 1655, 1489, 1448, 1235, 758, 693; ^1H NMR (400 MHz, CDCl_3) δ 7.71–7.66 (m, 3H), 7.40–7.34 (m, 2H), 7.26–6.82 (m, 22H), 6.73–6.69(m, 1H); ^{13}C NMR (100 MHz, CDCl_3) δ 193.85, 193.16, 162.45, 160.67, 160.46, 159.96, 158.20, 157.93, 148.30, 146.17, 142.64, 137.53, 136.56, 132.12, 131.36, 130.92, 130.84, 130.58, 130.40, 130.16, 130.08, 129.75, 129.66, 129.56, 128.63, 128.26, 128.21, 127.90, 127.70, 127.52, 126.36, 124.13, 124.10, 123.97, 123.93, 117.26, 117.14, 116.41, 116.26, 116.19, 116.03, 115.57, 115.37, 67.61; HRMS(ESI): Anal. calcd. for $\text{C}_{45}\text{H}_{27}\text{F}_3\text{NaO}_3$ m/z 695.1810 $[\text{M} + \text{Na}]^+$, found 695.1801.

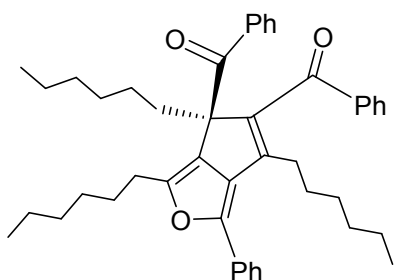
(3,4,6-tris(3-fluorophenyl)-1-phenyl-4*H*-cyclopenta[*c*]furan-4,5-diyl)bis(phenylmethanone) (2k)



m.p. 222-224 °C; IR (KBr): 3068, 1686, 1640, 1586, 1487, 1442, 1263, 876, 783, 694; ^1H NMR (400 MHz, CDCl_3) δ 7.66 (d, $J = 7.2$ Hz, 2H), 7.45–7.36 (m, 2H), 7.32–7.10 (m, 14H), 7.04 (d, $J = 7.6$ Hz, 2H), 6.97–6.89 (m, 5H), 6.78–6.73 (m, 1H), 6.67 (d, $J = 7.6$ Hz, 1H), 6.56 (d, $J = 9.2$ Hz, 1H); ^{13}C NMR (100 MHz, CDCl_3) δ 194.84, 194.40, 164.12, 163.79, 163.29, 161.68, 161.36, 160.82, 149.08, 146.56, 145.86, 145.83, 141.04, 141.02, 138.71, 137.50, 137.30, 137.22, 135.07, 134.99, 132.34, 132.24, 131.37, 130.50, 130.47, 130.41, 130.38, 130.01, 129.92, 129.87, 129.79, 128.93, 128.84, 128.65, 128.25, 127.84, 127.63, 127.51, 127.48, 127.33, 124.71, 124.68, 124.65, 124.62, 121.48, 121.45, 116.07, 115.84, 115.62, 115.61, 115.30, 115.09, 114.98, 114.78, 112.12, 111.88, 69.40; HRMS(ESI): Anal. calcd. for $\text{C}_{45}\text{H}_{27}\text{F}_3\text{NaO}_3$ m/z 695.1810 $[\text{M} + \text{Na}]^+$, found 695.1829.

(3,4,6-trihexyl-1-phenyl-4*H*-cyclopenta[*c*]furan-4,5-diyl)bis(phenylmethanone)

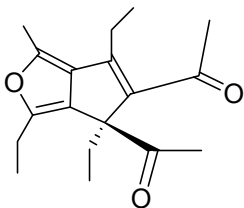
(21)



Buff oil; IR (KBr): 3063, 2926, 2860, 1712, 1653, 1591, 1455, 1329, 1236, 1173, 698; ^1H NMR (400 MHz, CDCl_3) δ 7.68–7.66 (m, 2H), 7.57–7.54 (m, 2H), 7.51–7.29 (m, 9H), 7.18–7.14 (m, 2H), 2.61–2.57 (m, 1H), 2.45–2.18 (m, 4H), 1.63–1.55 (m, 2H), 1.29–1.21 (m, 14H), 1.09–0.95 (m, 5H), 0.84–0.79 (m, 10H), 0.70 (t, $J = 7.2$ Hz, 3H); ^{13}C NMR (100 MHz, CDCl_3) δ 200.05, 193.62, 148.91, 147.73, 146.16, 144.96,

139.52, 139.08, 132.11, 131.96, 131.03, 130.71, 128.54, 128.51, 128.32, 128.01, 127.56, 127.49, 126.54, 63.26, 32.84, 31.66, 31.44, 30.99, 29.66, 29.55, 28.86, 28.54, 27.98, 26.76, 23.98, 22.54, 22.42, 22.12, 13.96, 13.94, 13.84; HRMS(ESI): Anal. calcd. for C₄₅H₅₄NaO₃ m/z 665.3971 [M + Na]⁺, found 665.3986.

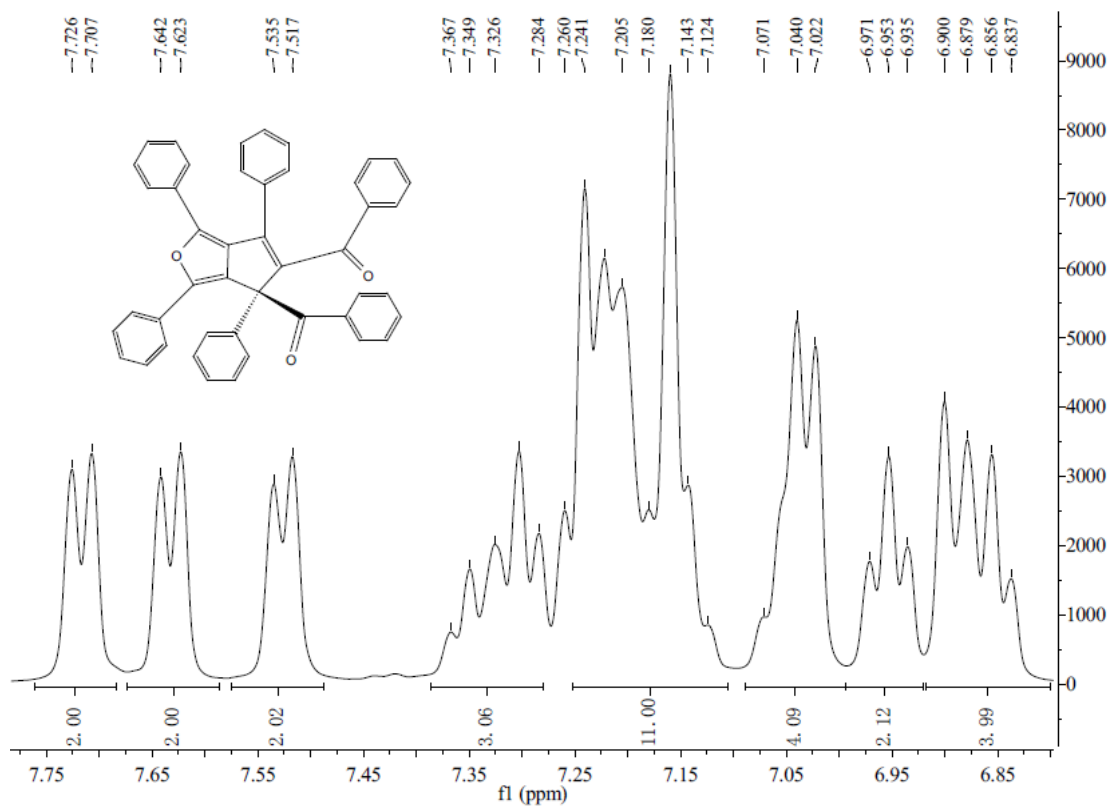
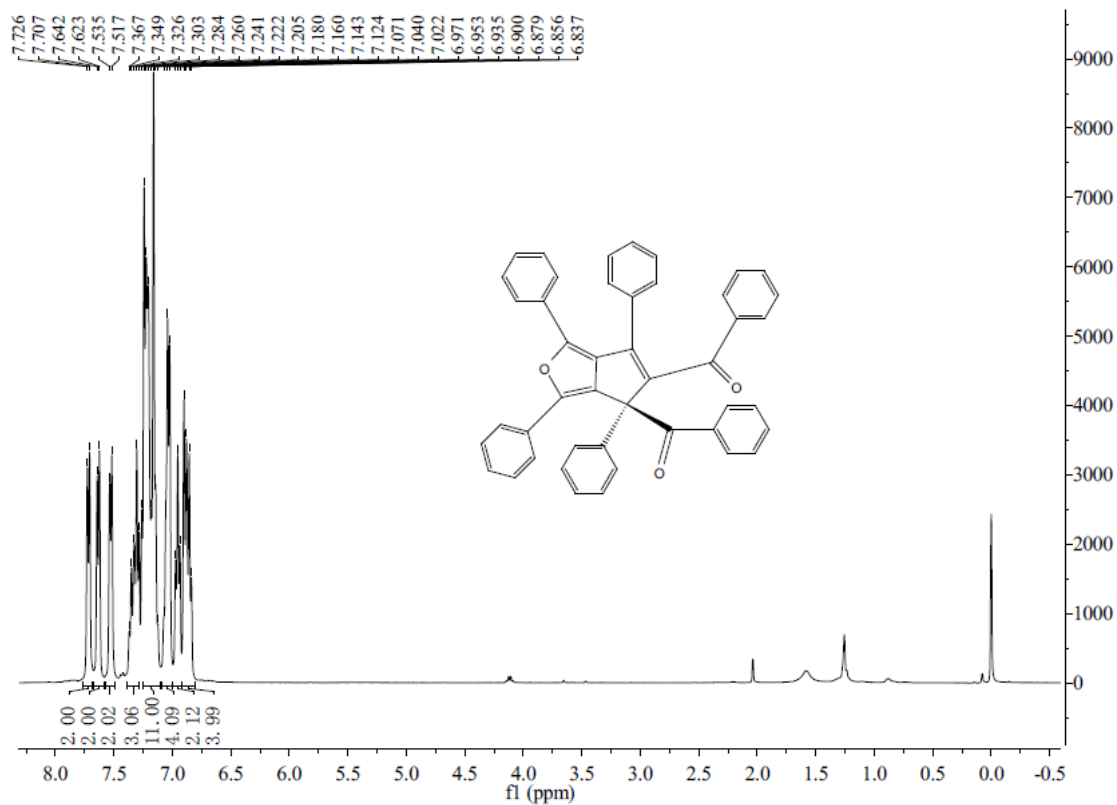
1,1'-(3,4,6-triethyl-1-methyl-4*H*-cyclopenta[*c*]furan-4,5-diyl)diethanone (2m)

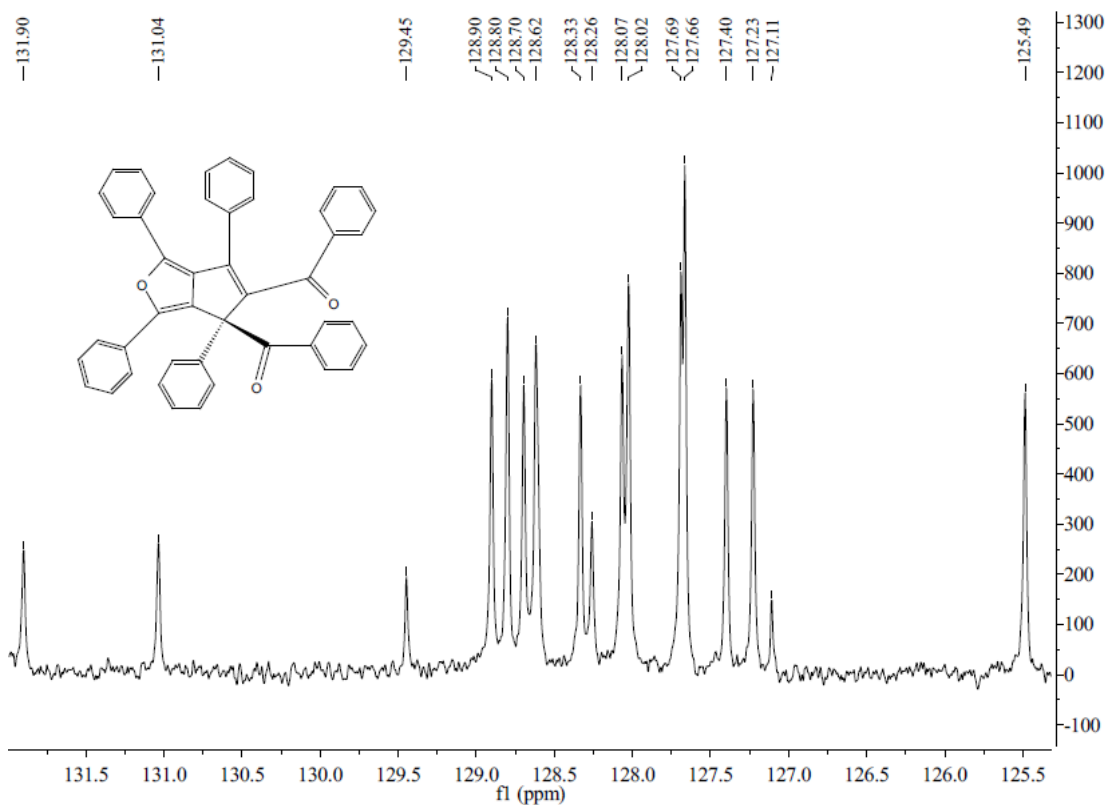
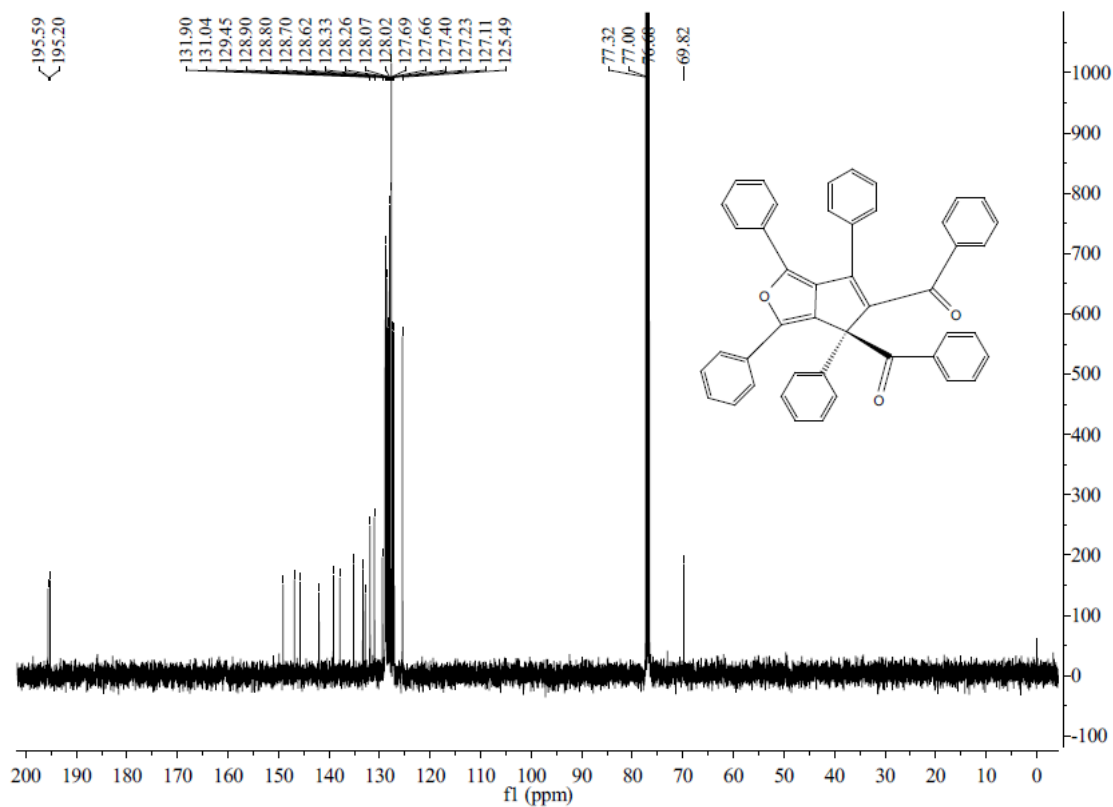


Buff oil; IR (KBr): 2976, 2938, 2882, 1710, 1361, 1254, 1172; ¹H NMR (400 MHz, CDCl₃) δ 2.89–2.83 (m, 2H), 2.45–2.38 (m, 8H), 2.15–2.09 (m, 1H), 1.98–1.93 (m, 1H), 1.74 (s, 3H), 1.29 (t, *J* = 7.6 Hz, 3H), 1.06 (t, *J* = 7.6 Hz, 3H), 0.44 (t, *J* = 7.6 Hz, 3H); ¹³C NMR (100 MHz, CDCl₃) δ 205.46, 195.76, 152.54, 147.52, 143.36, 142.66, 131.05, 123.52, 64.49, 29.89, 24.56, 23.98, 21.85, 19.97, 13.98, 13.15, 12.74, 8.24; HRMS (ESI): Anal. calcd. for C₁₈H₂₄ NaO₃ m/z 311.1623 [M + Na]⁺, found 311.1618.

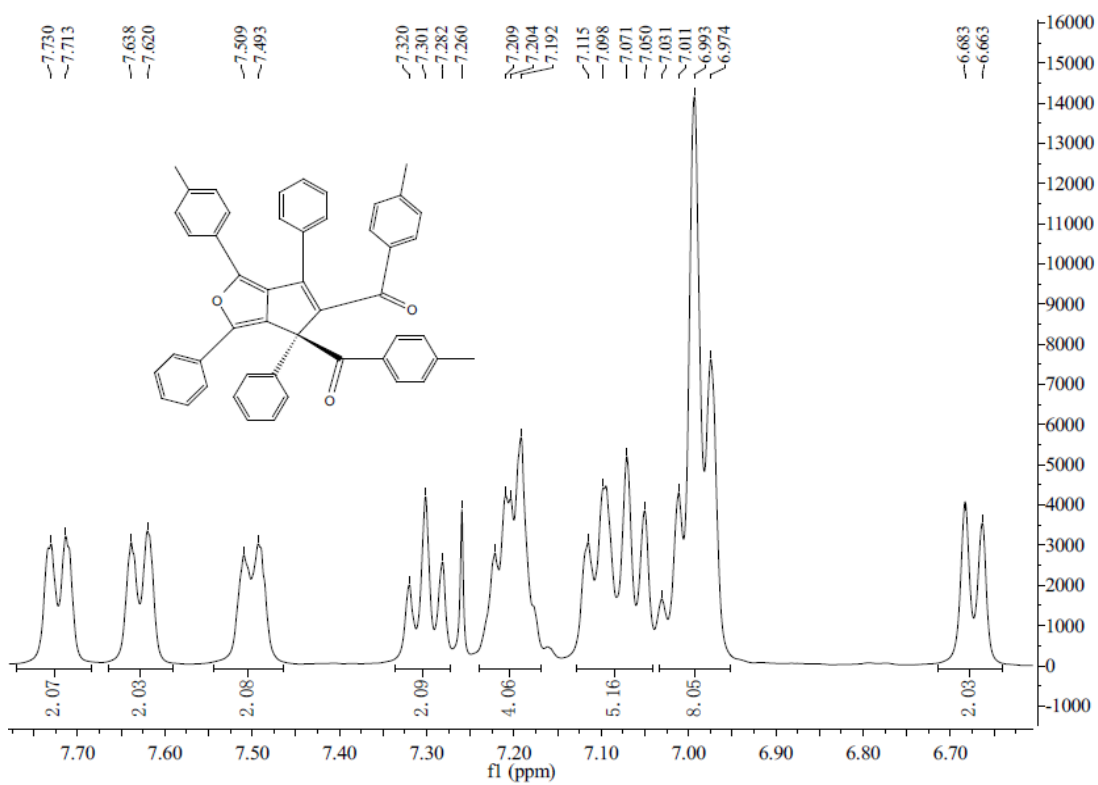
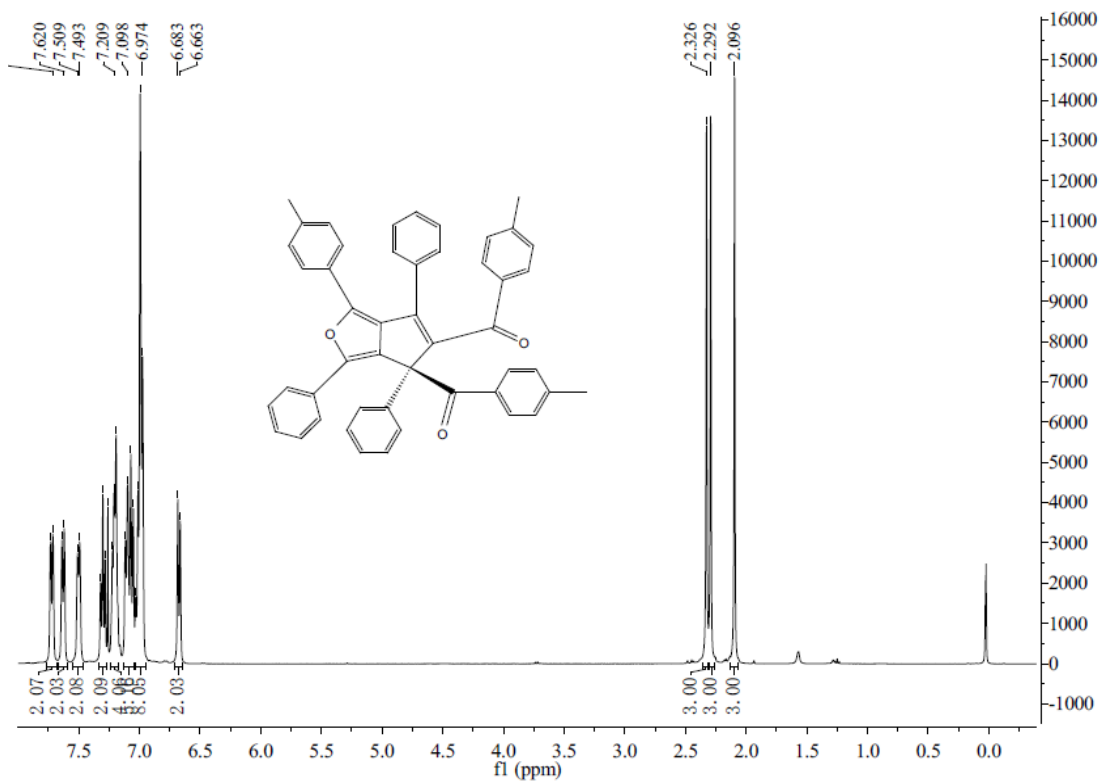
E. NMR spectra for 2a-2p

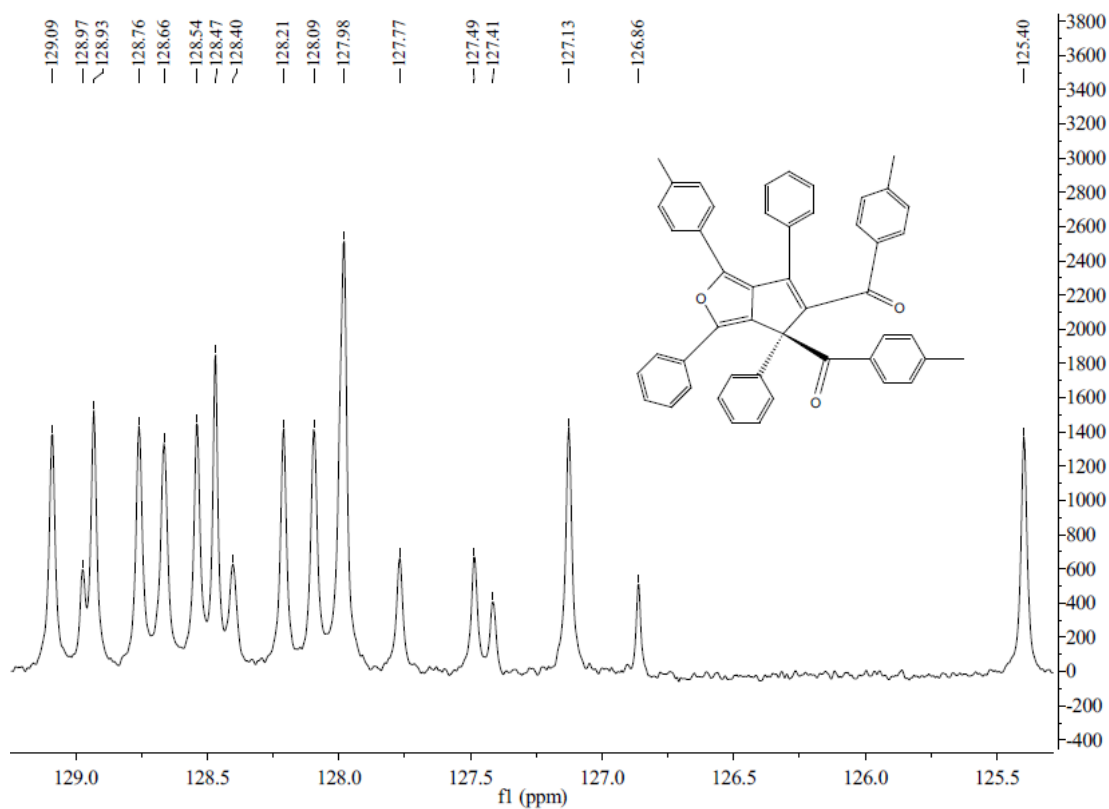
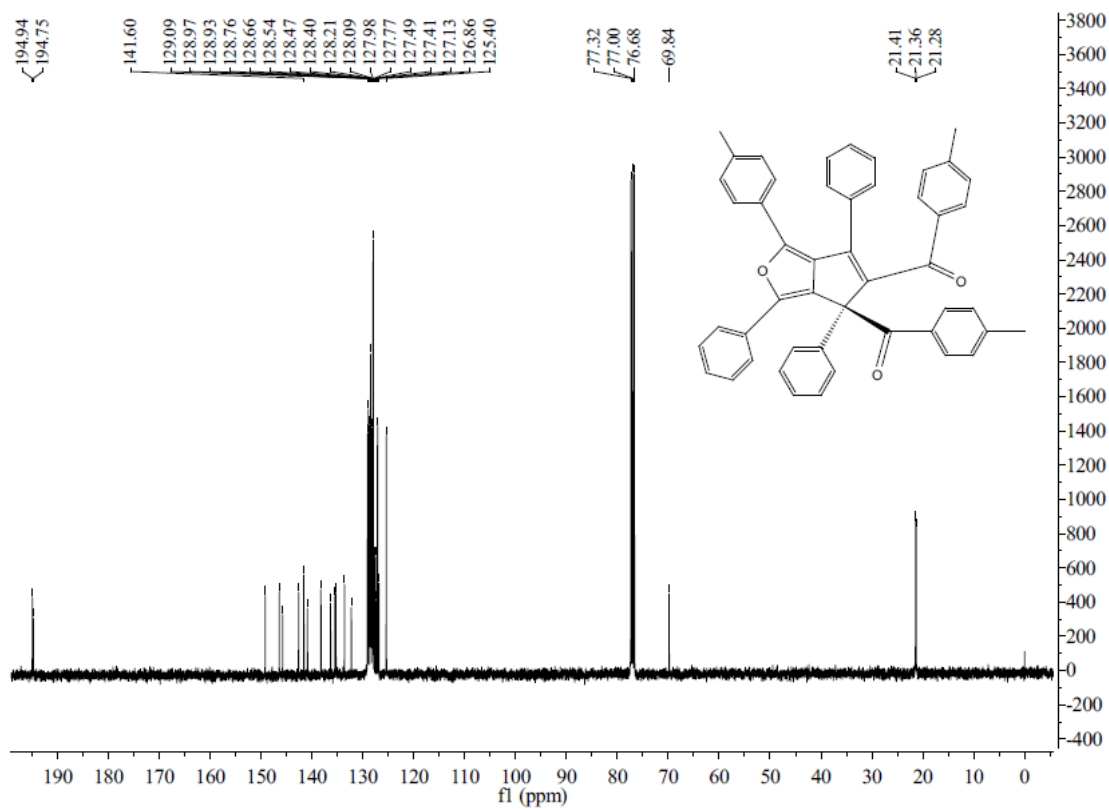
2a:



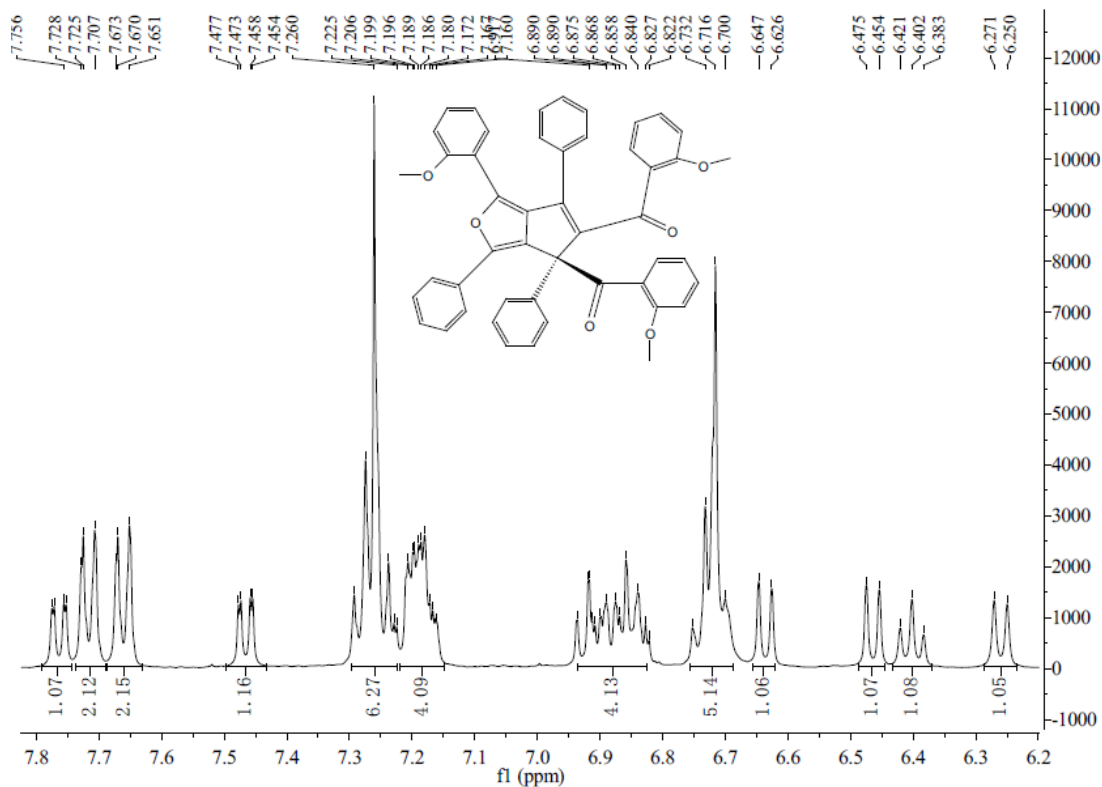
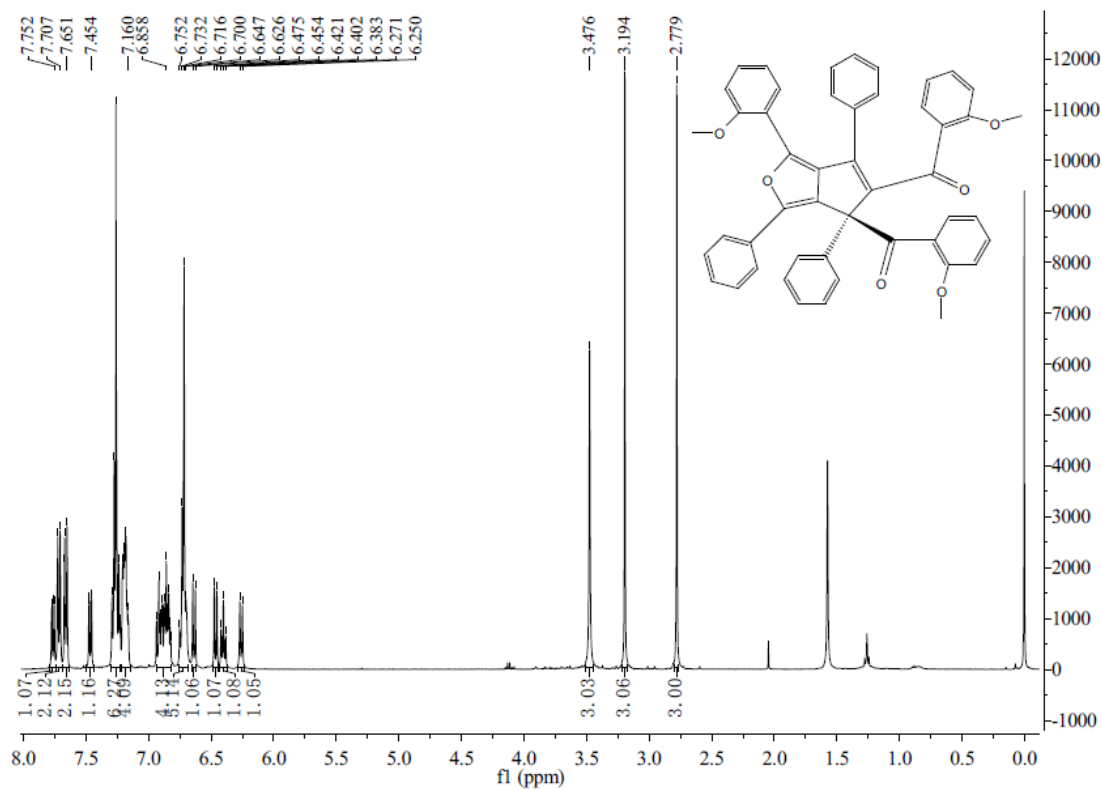


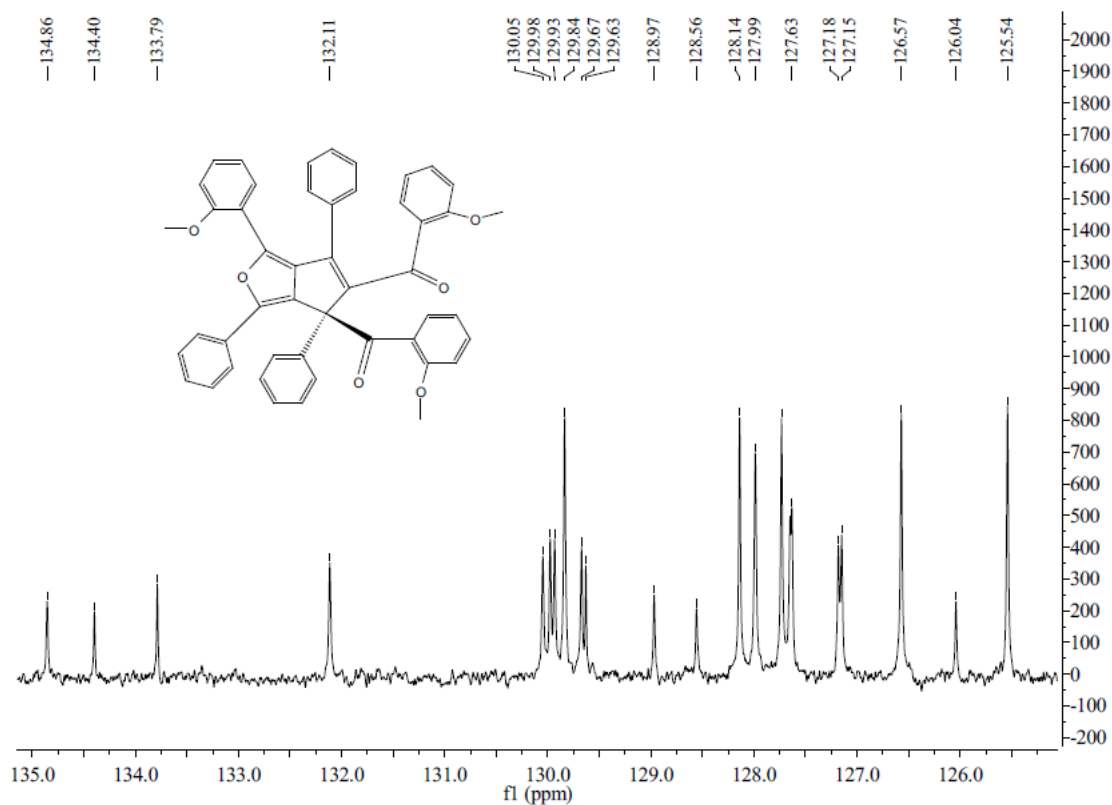
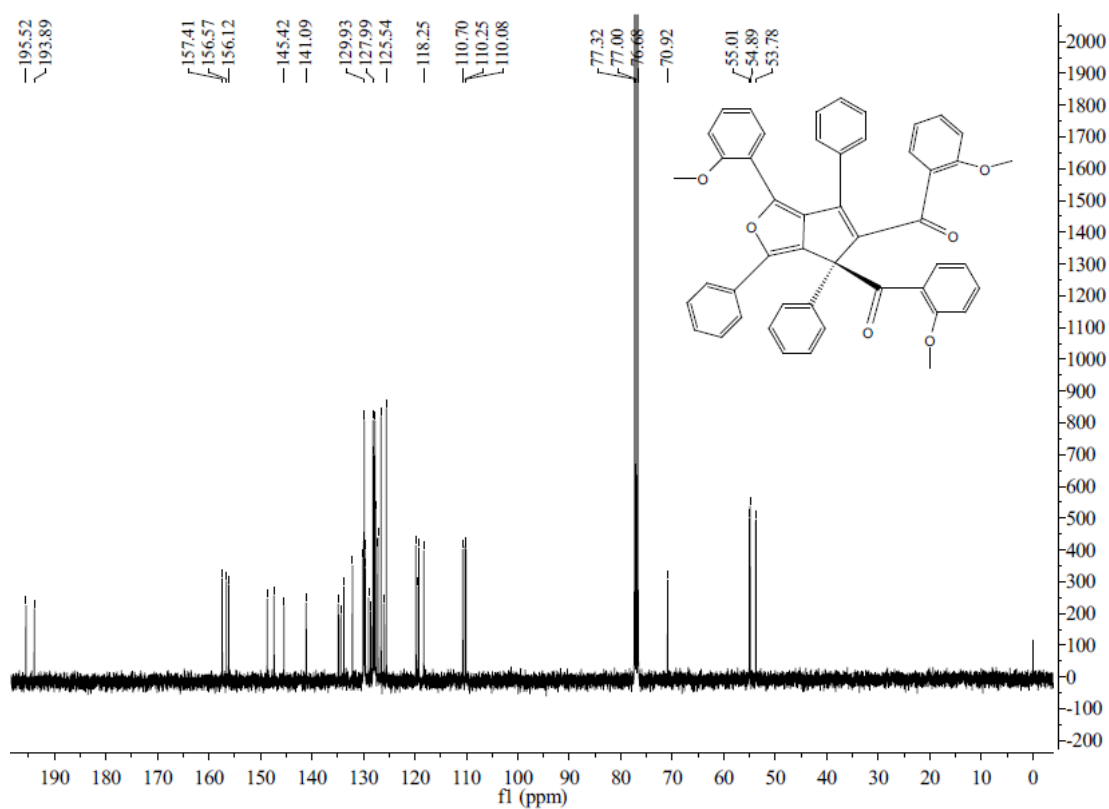
2b:



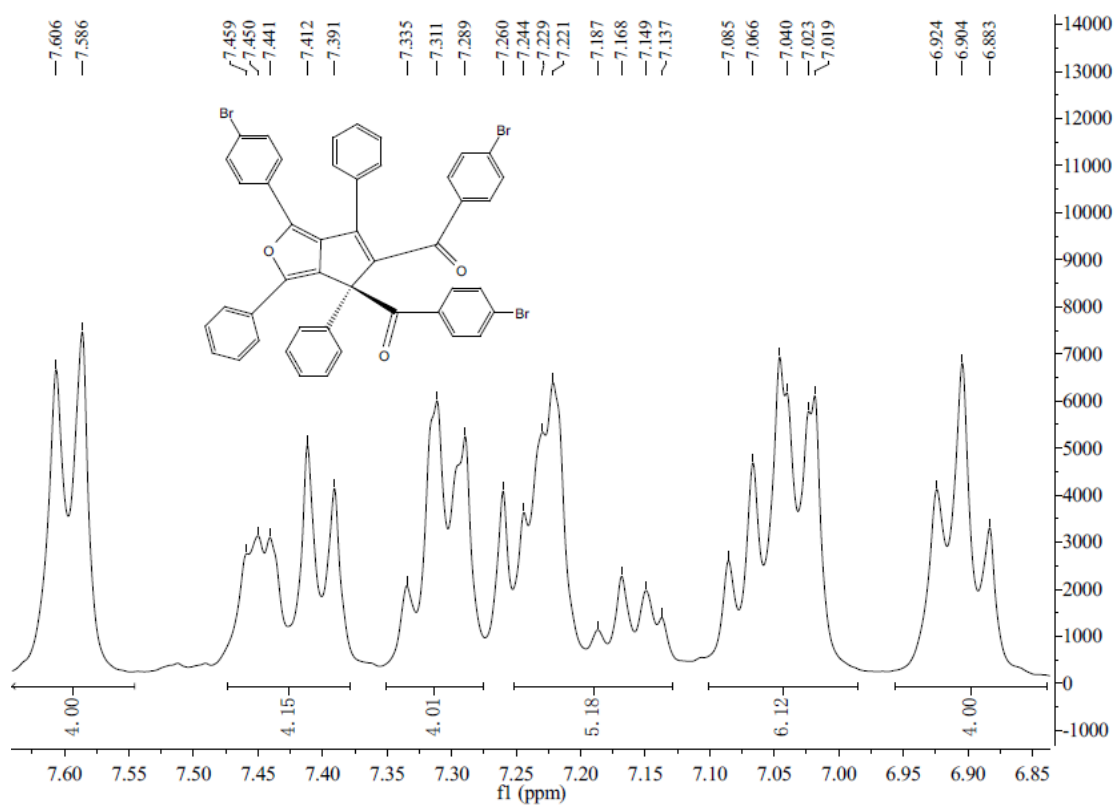
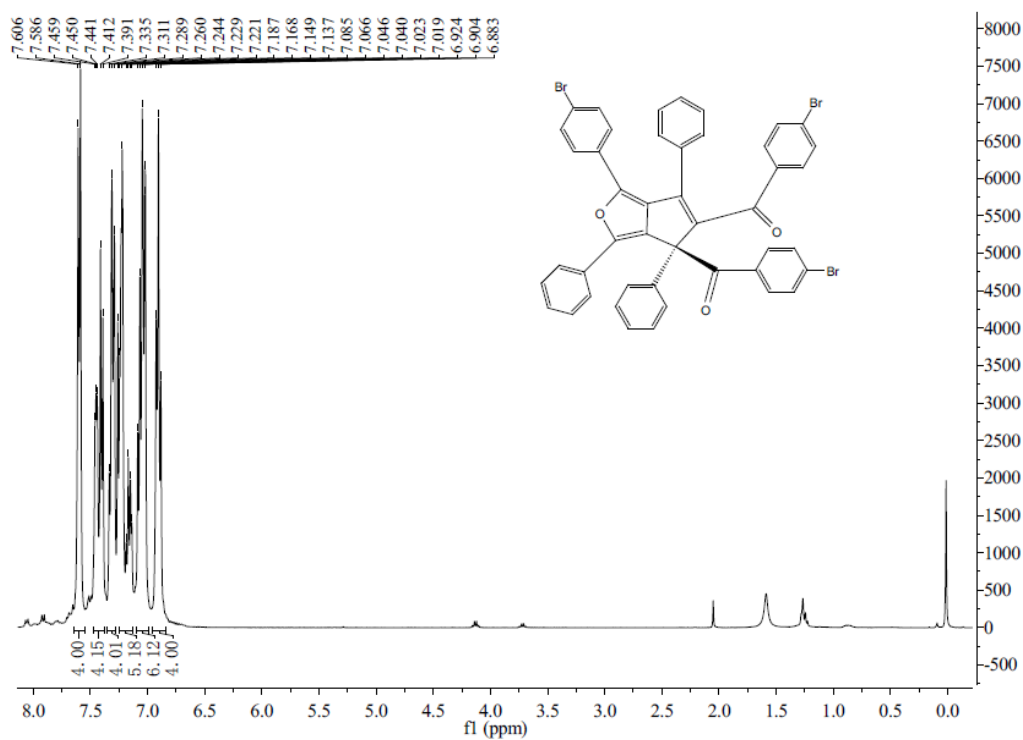


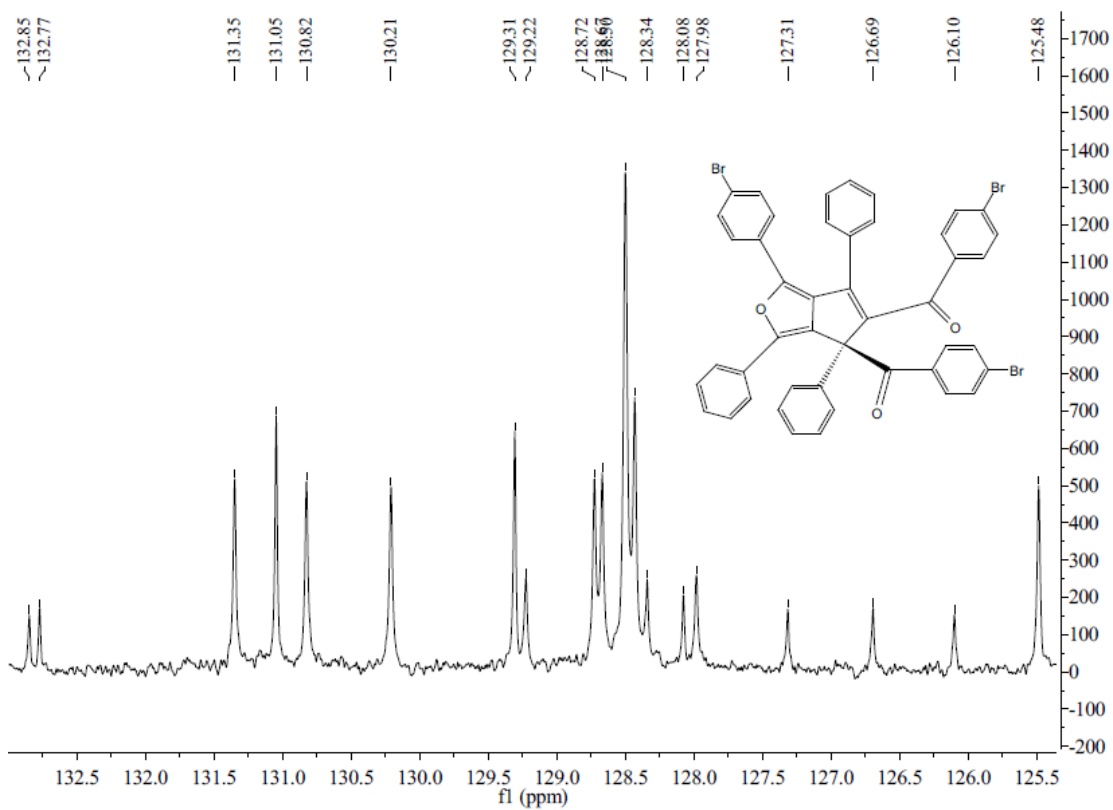
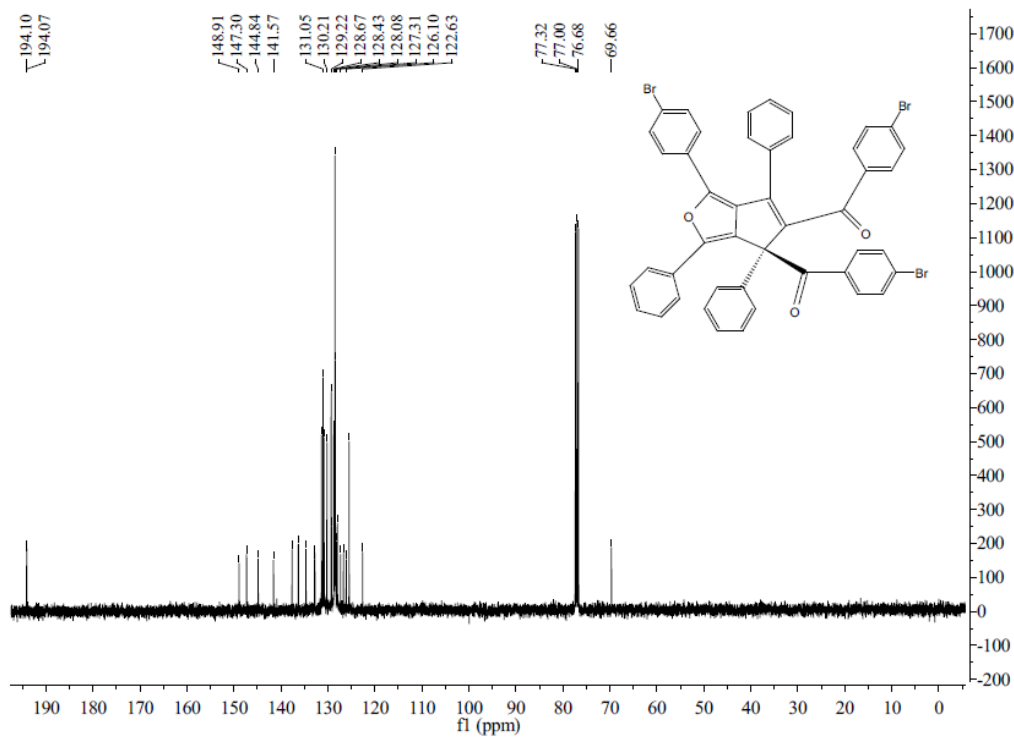
2c:



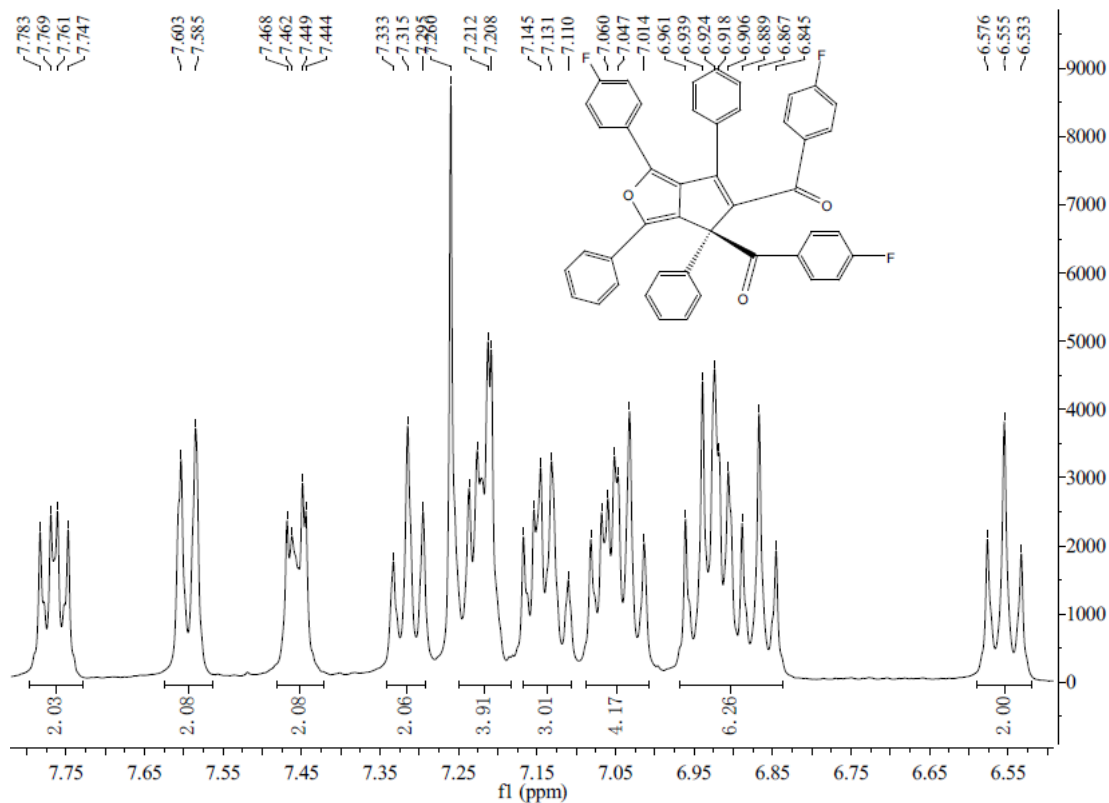
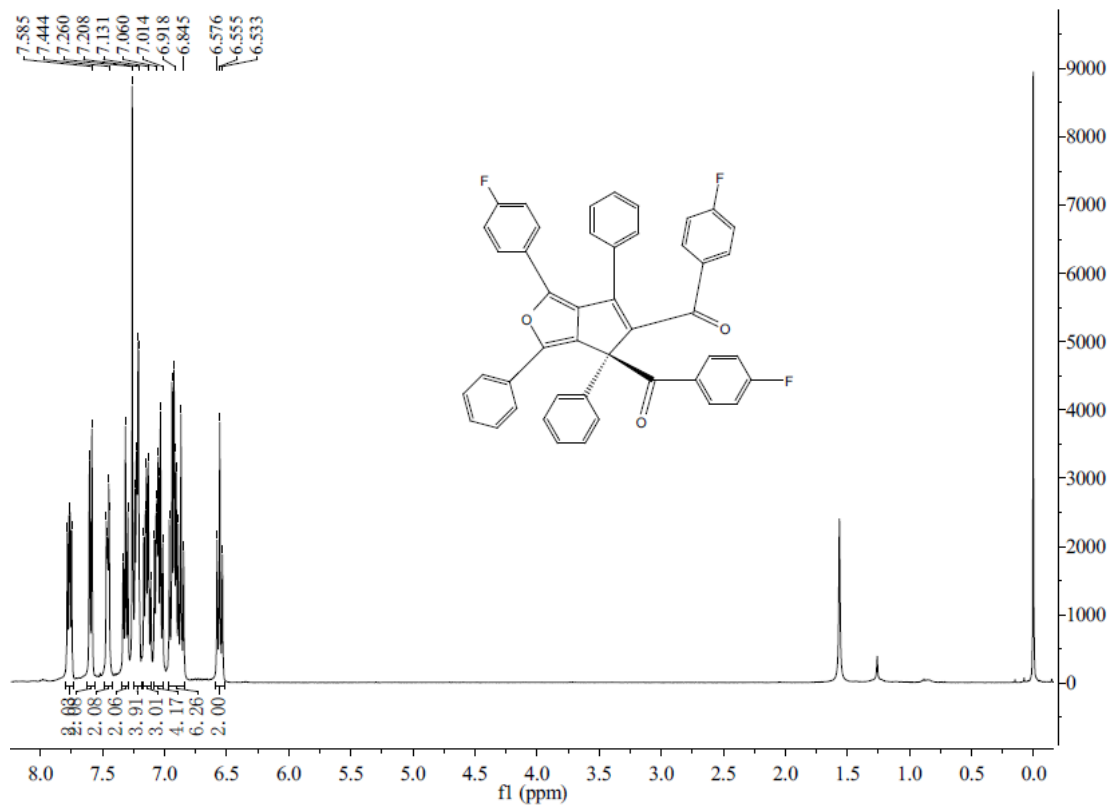


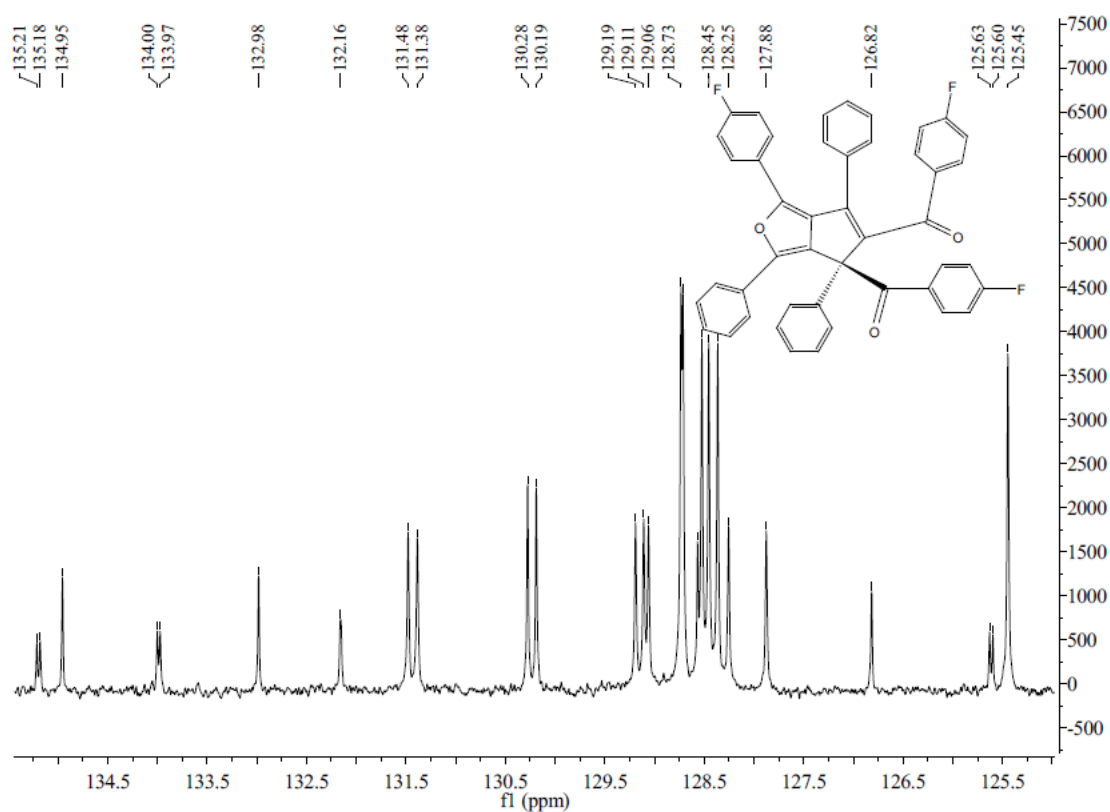
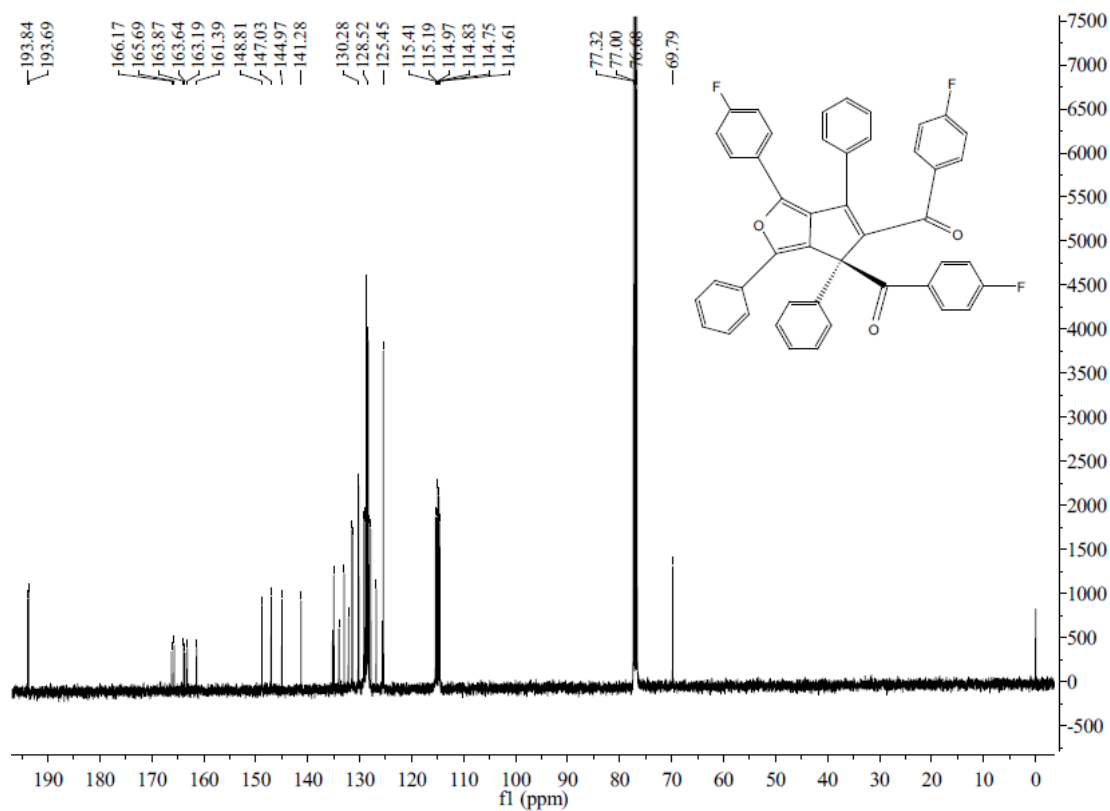
2d:

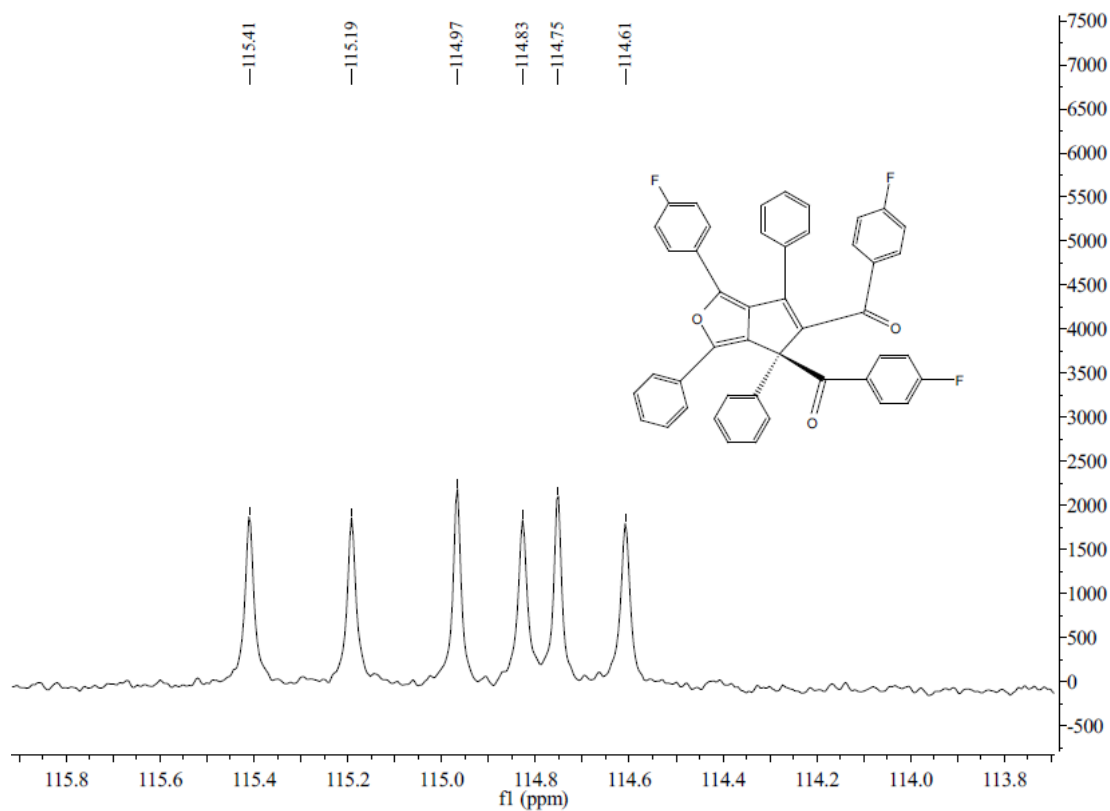




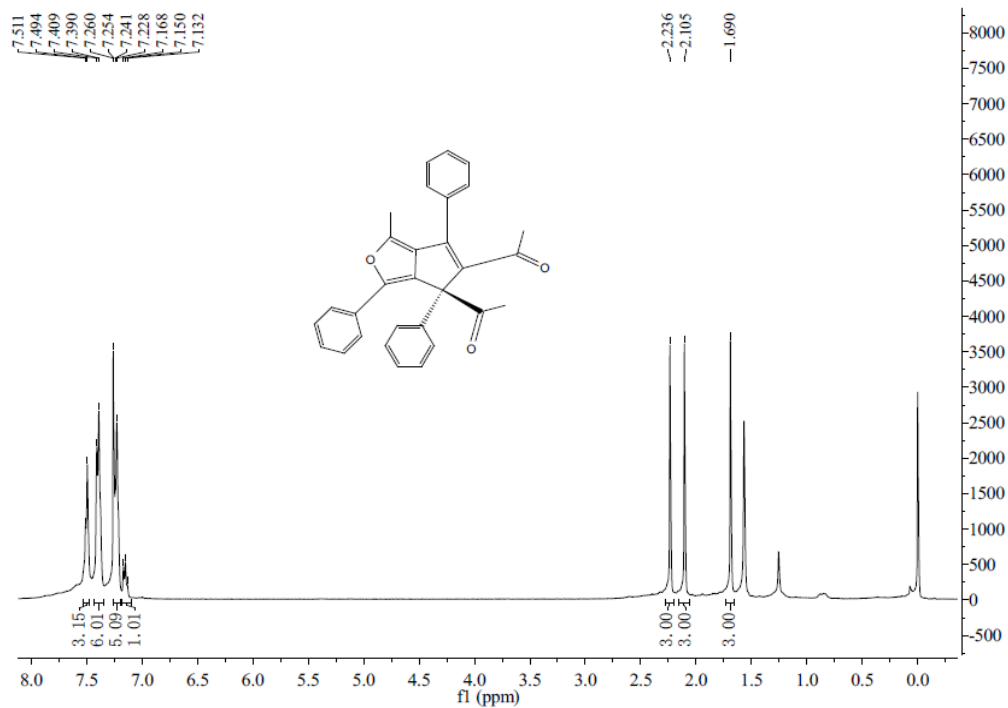
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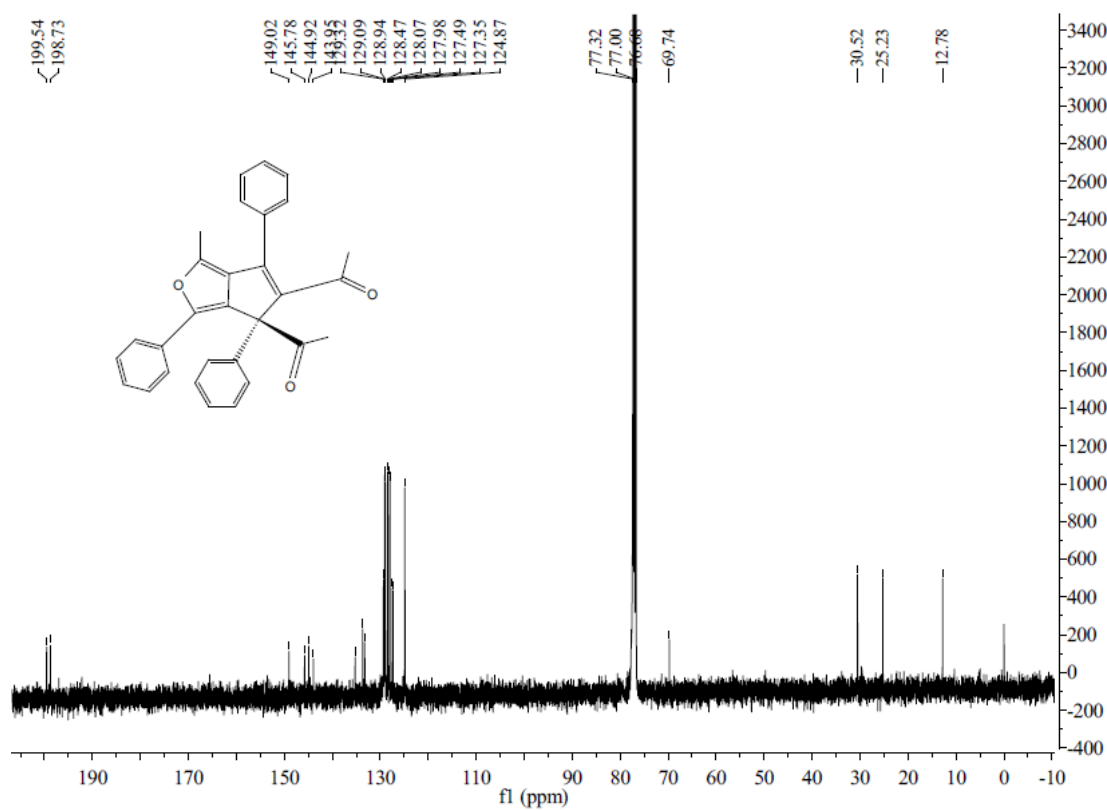
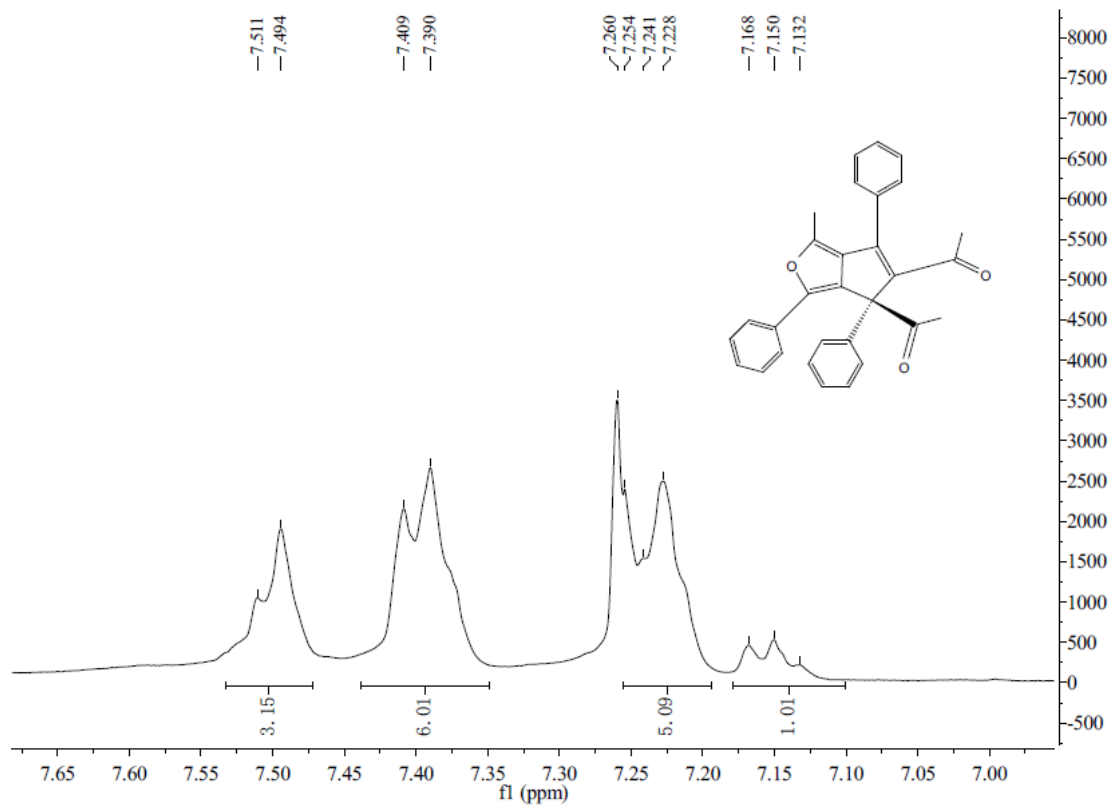


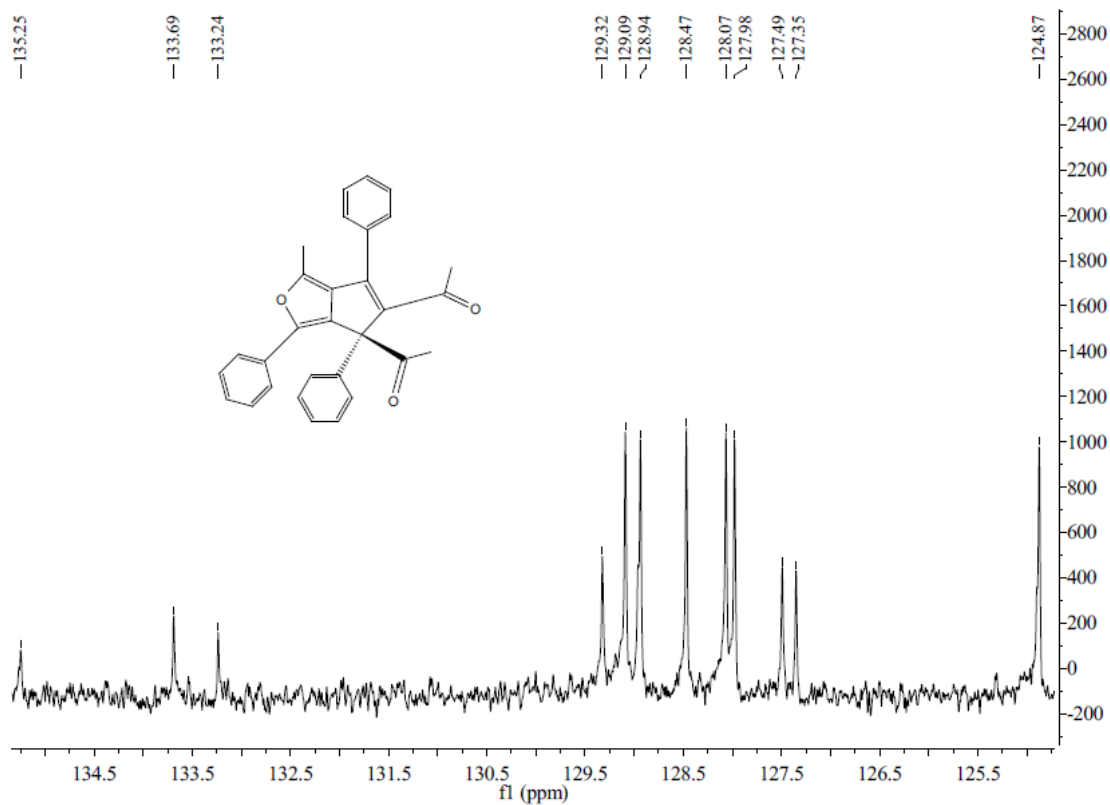




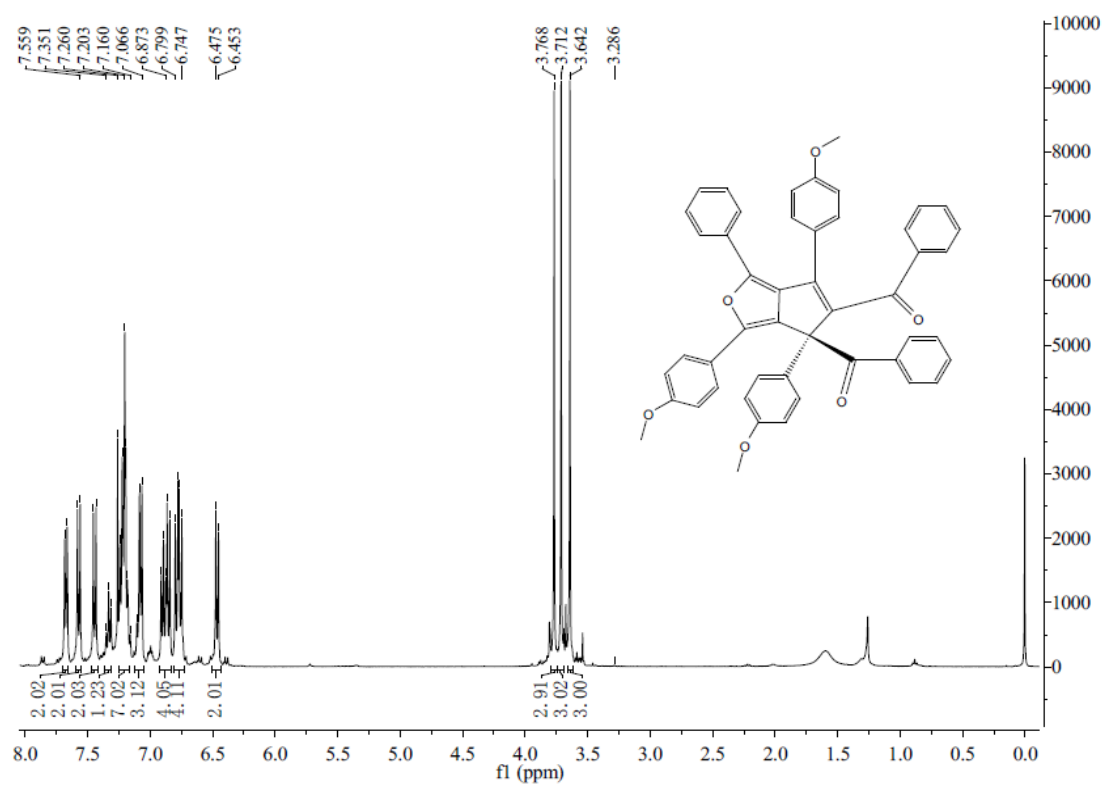
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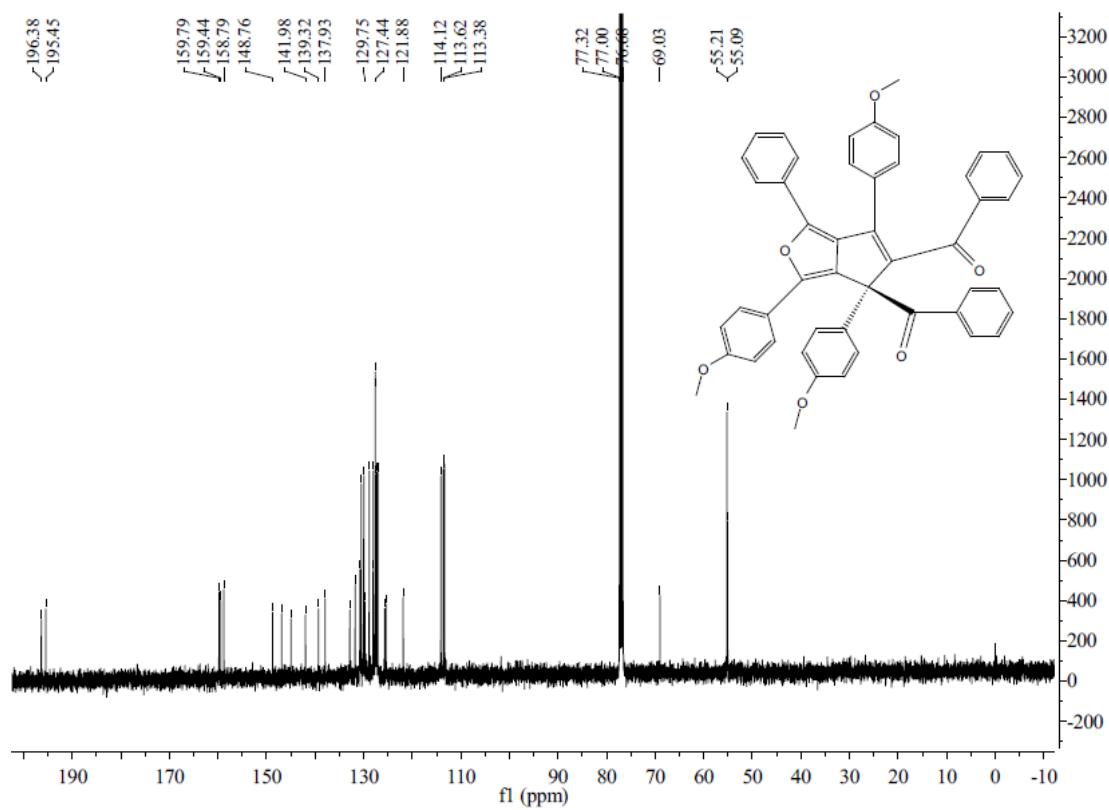
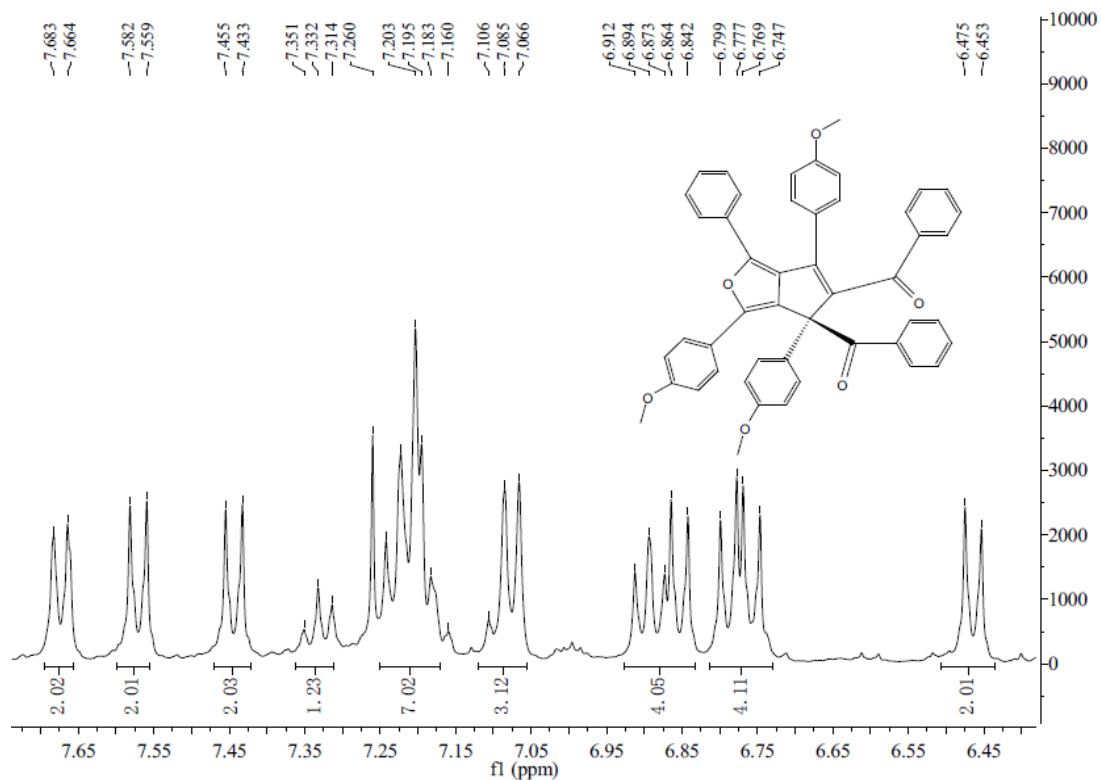


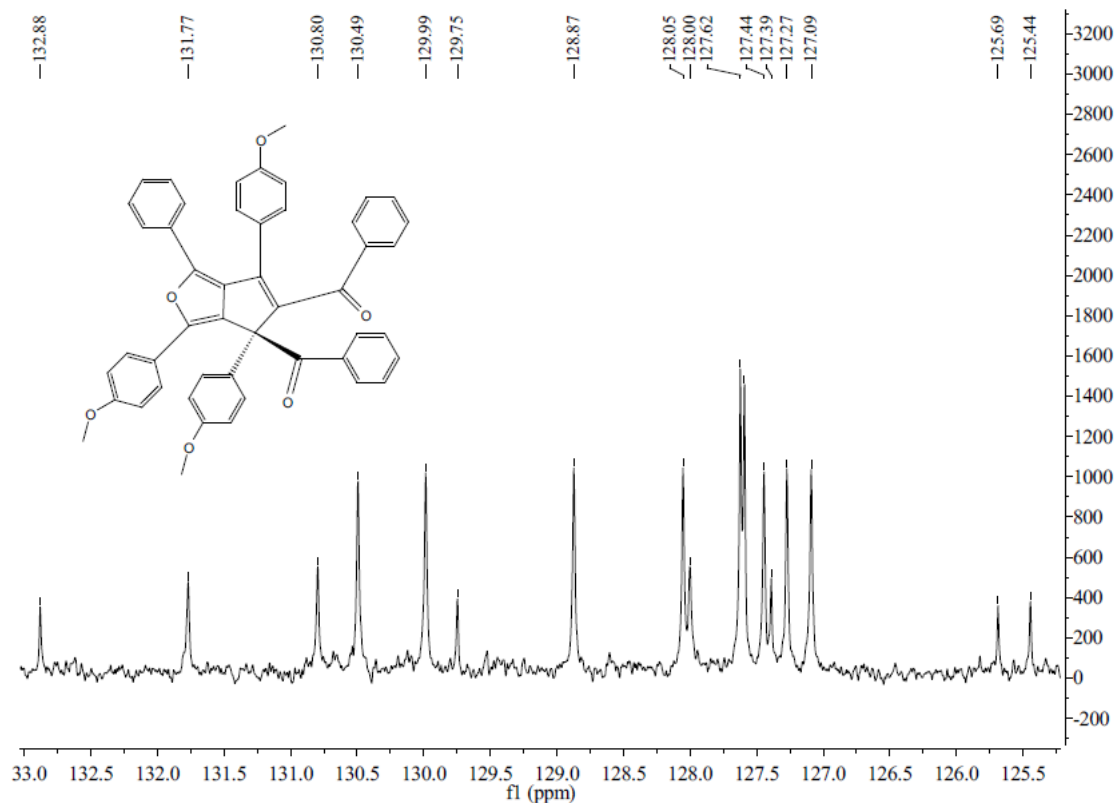




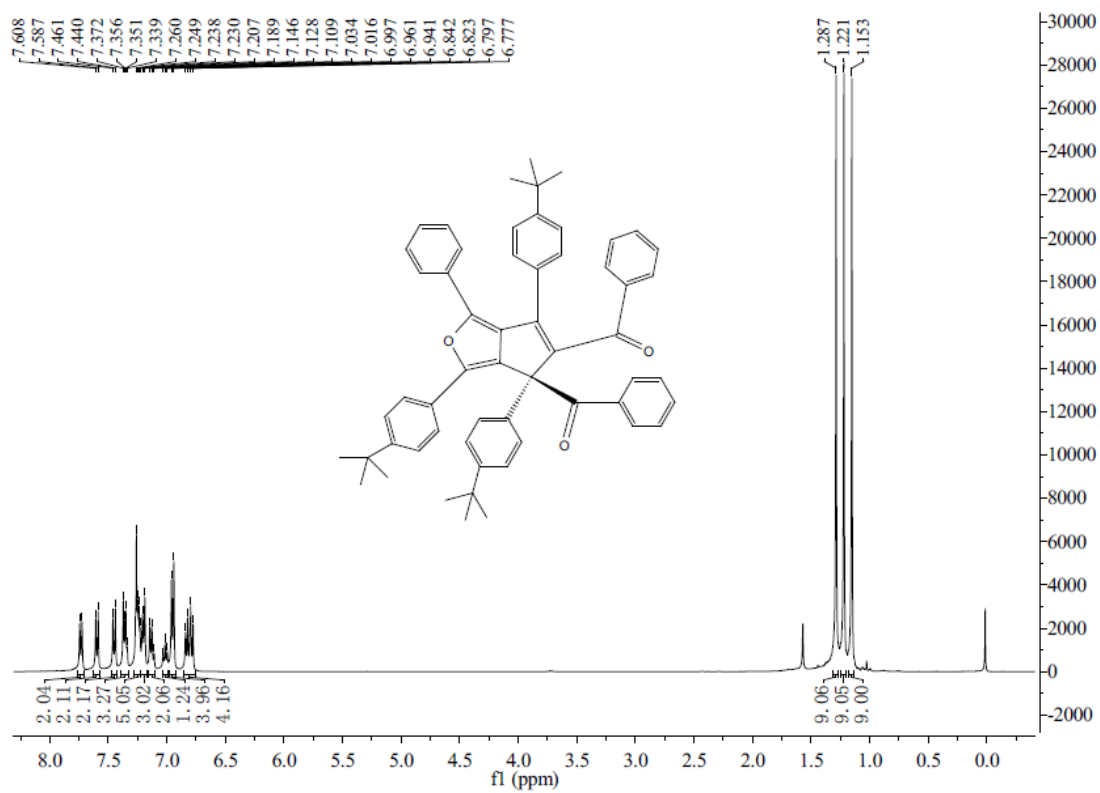
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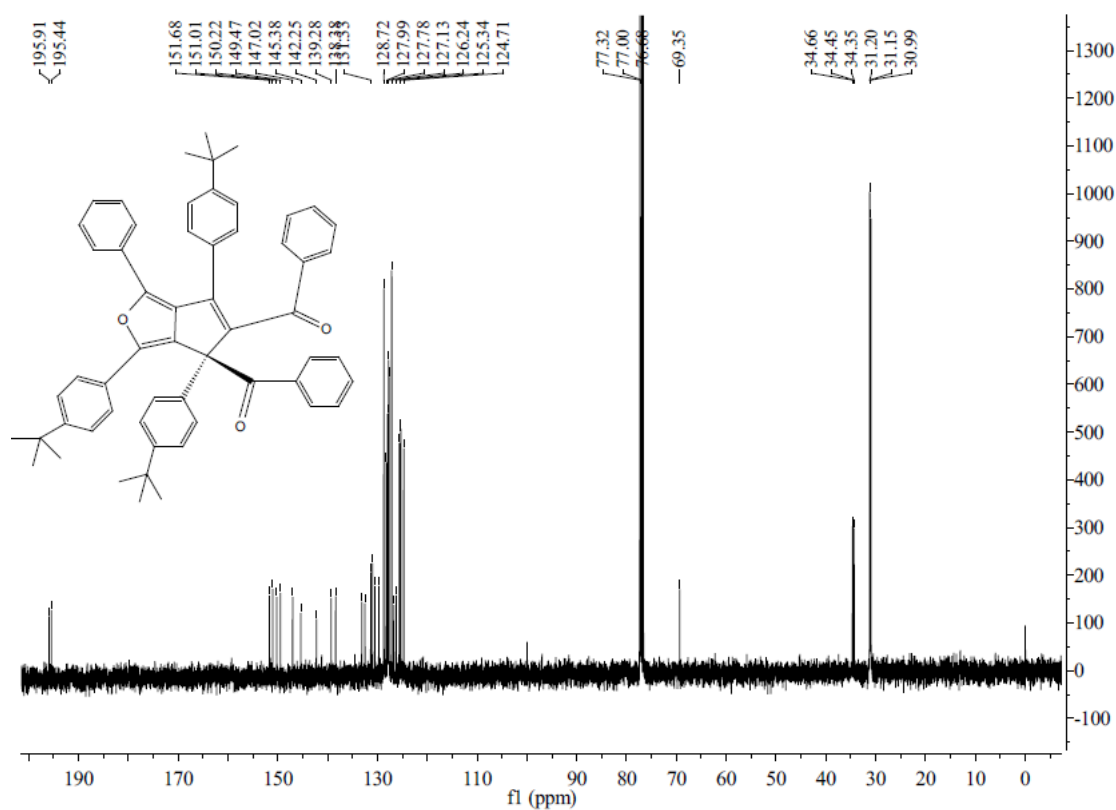
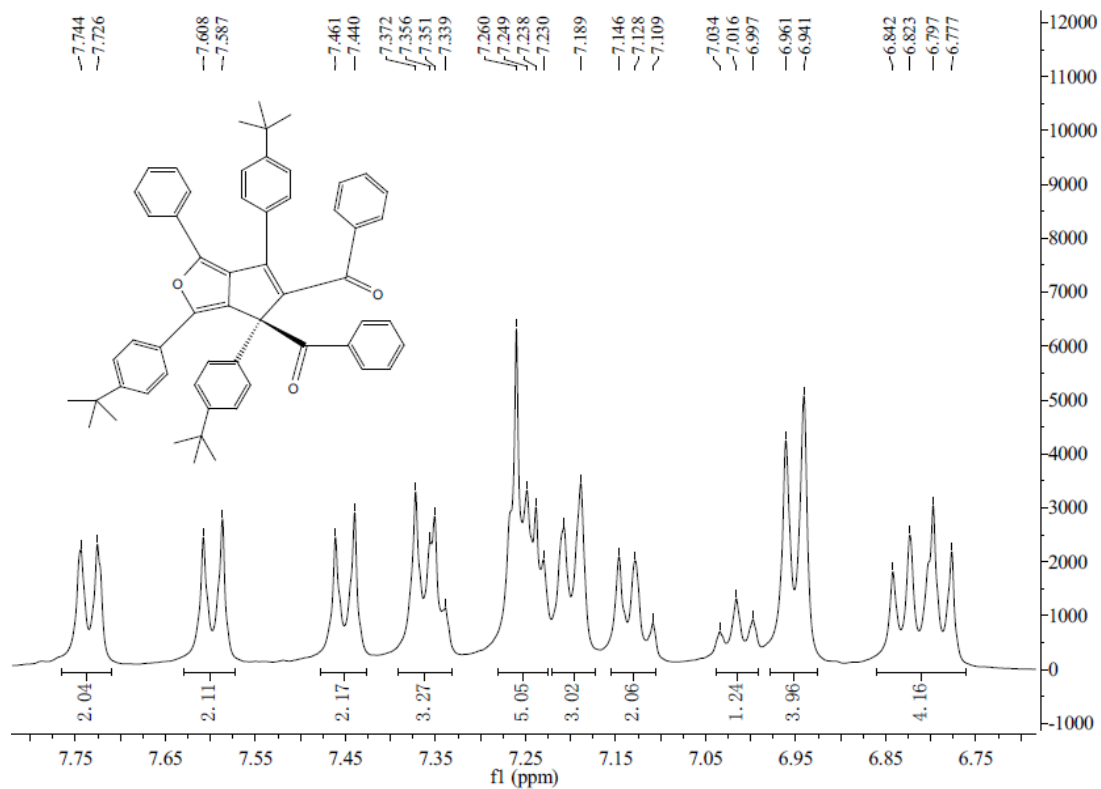


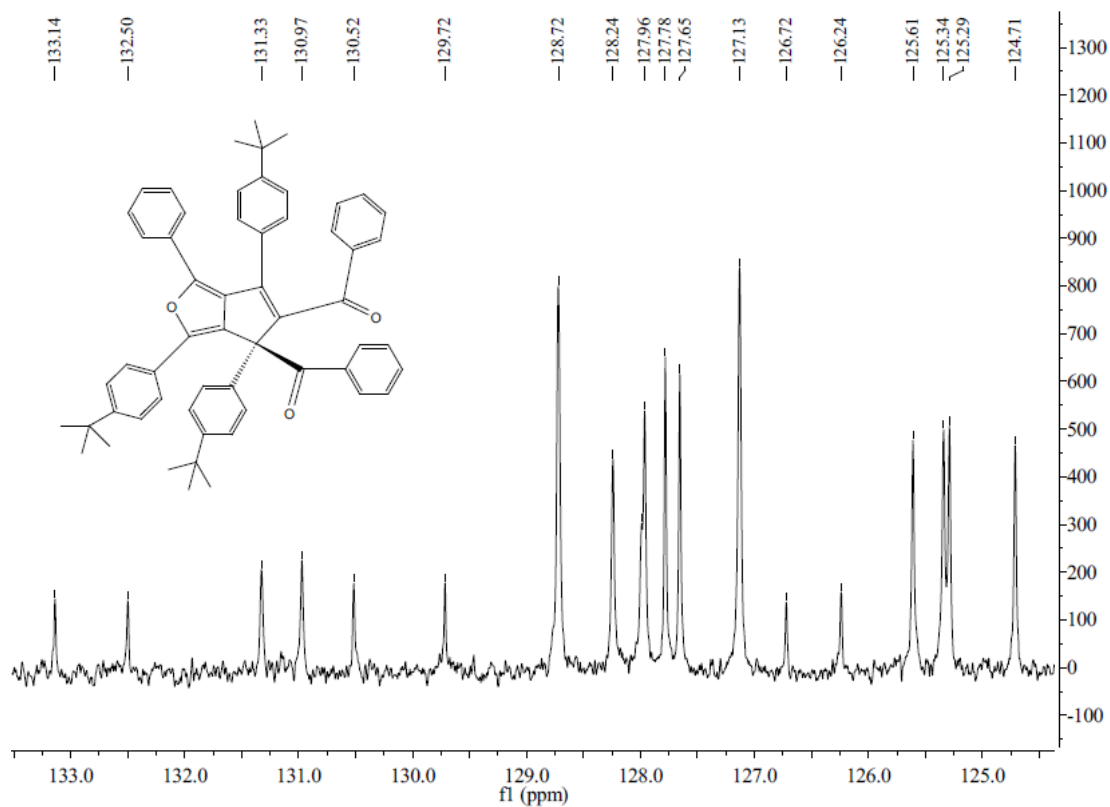




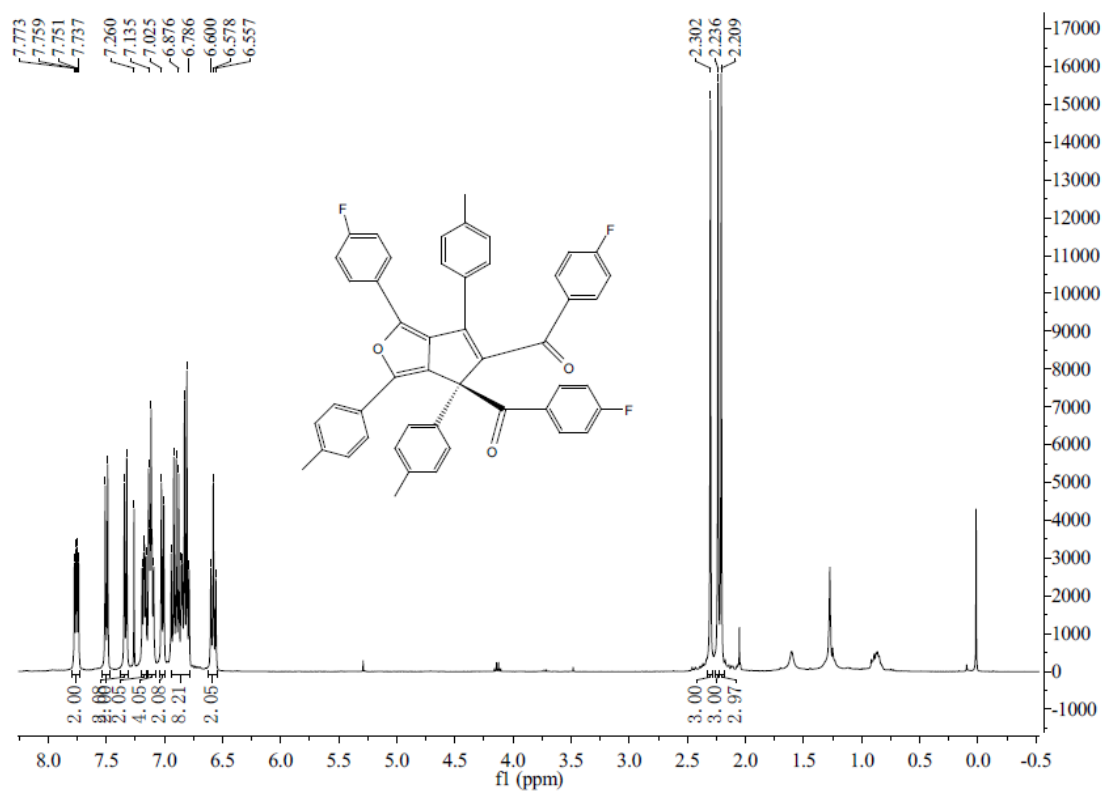
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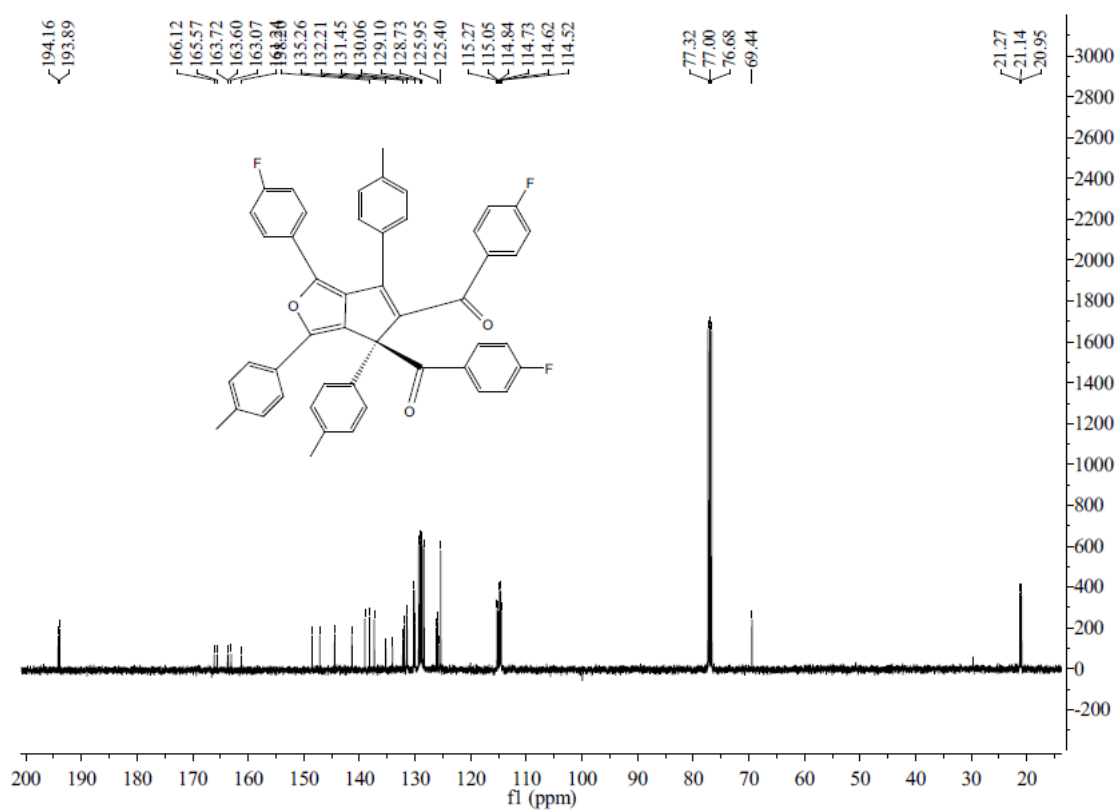
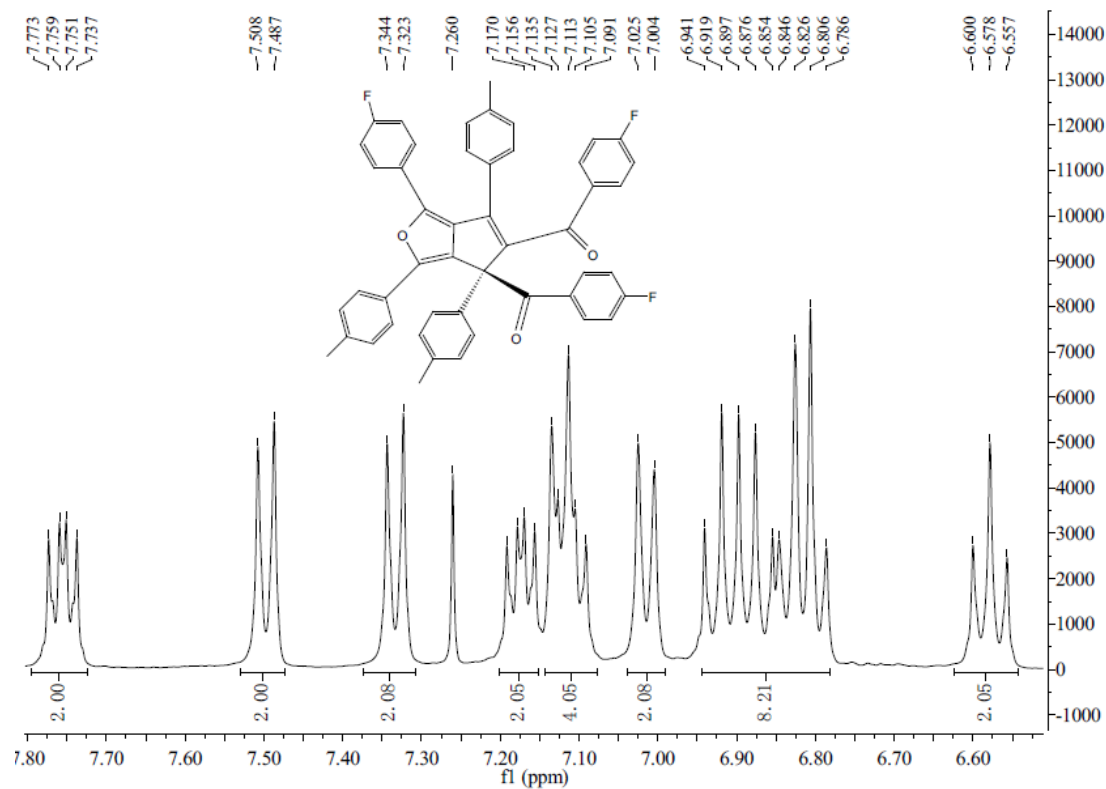


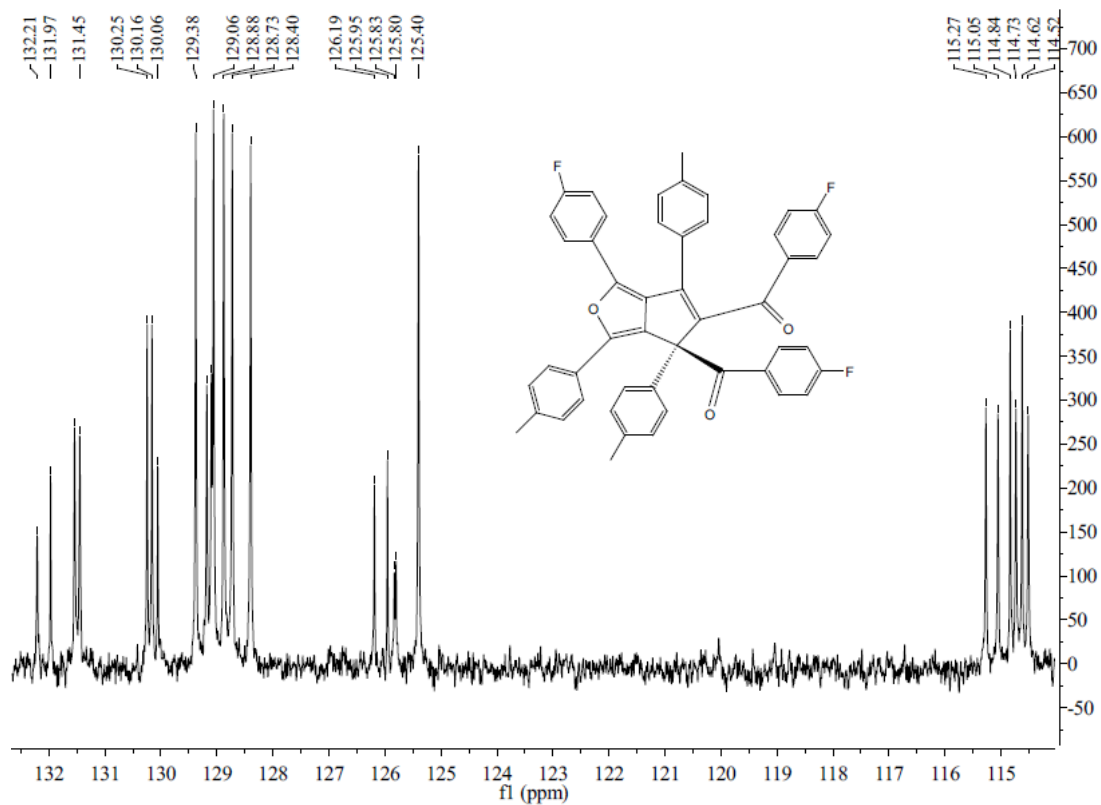




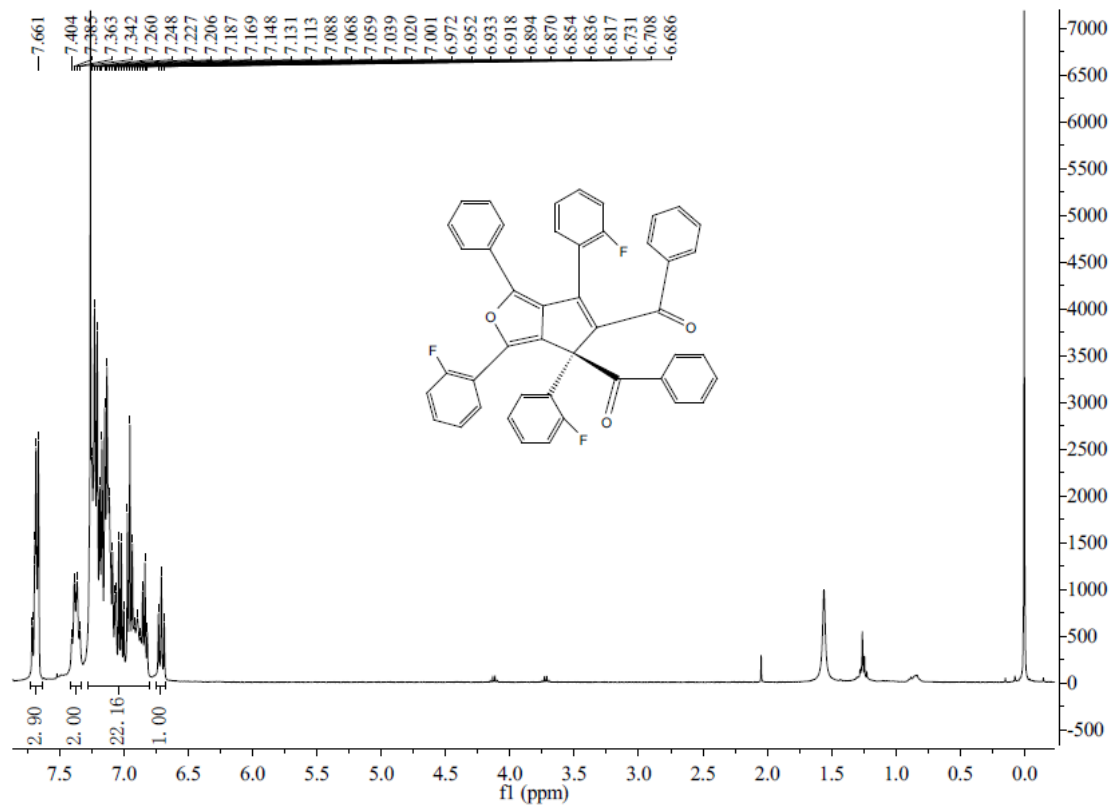
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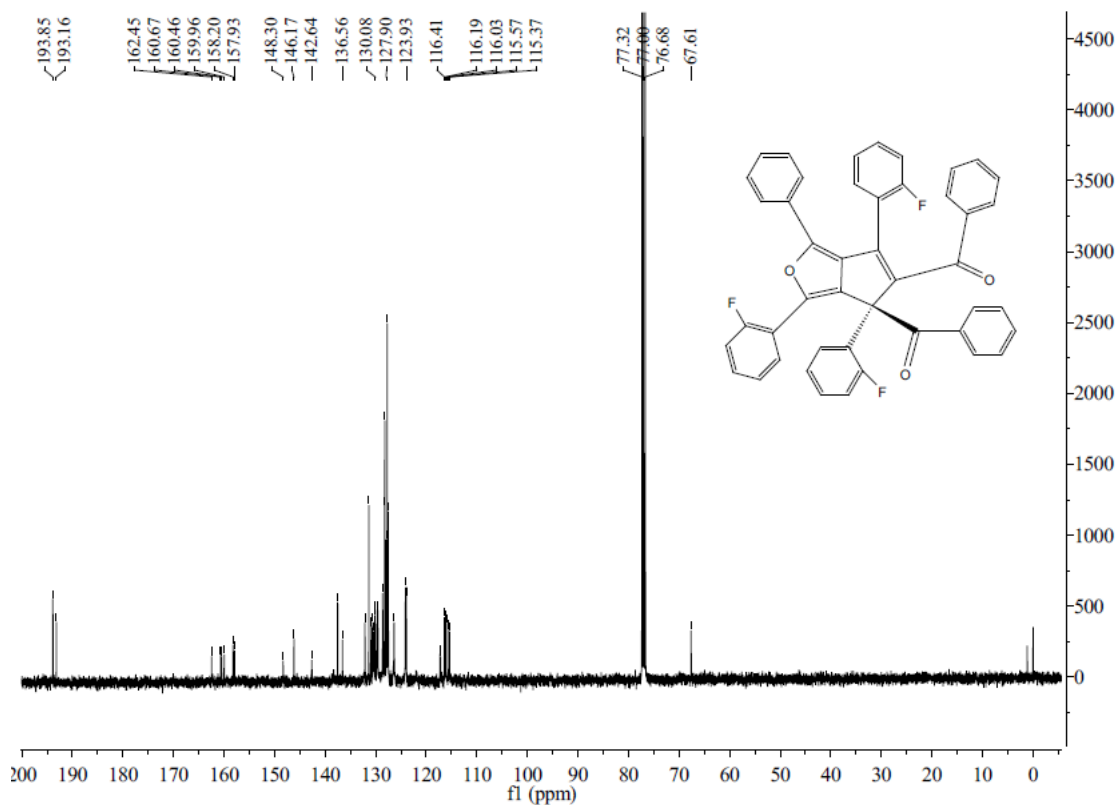
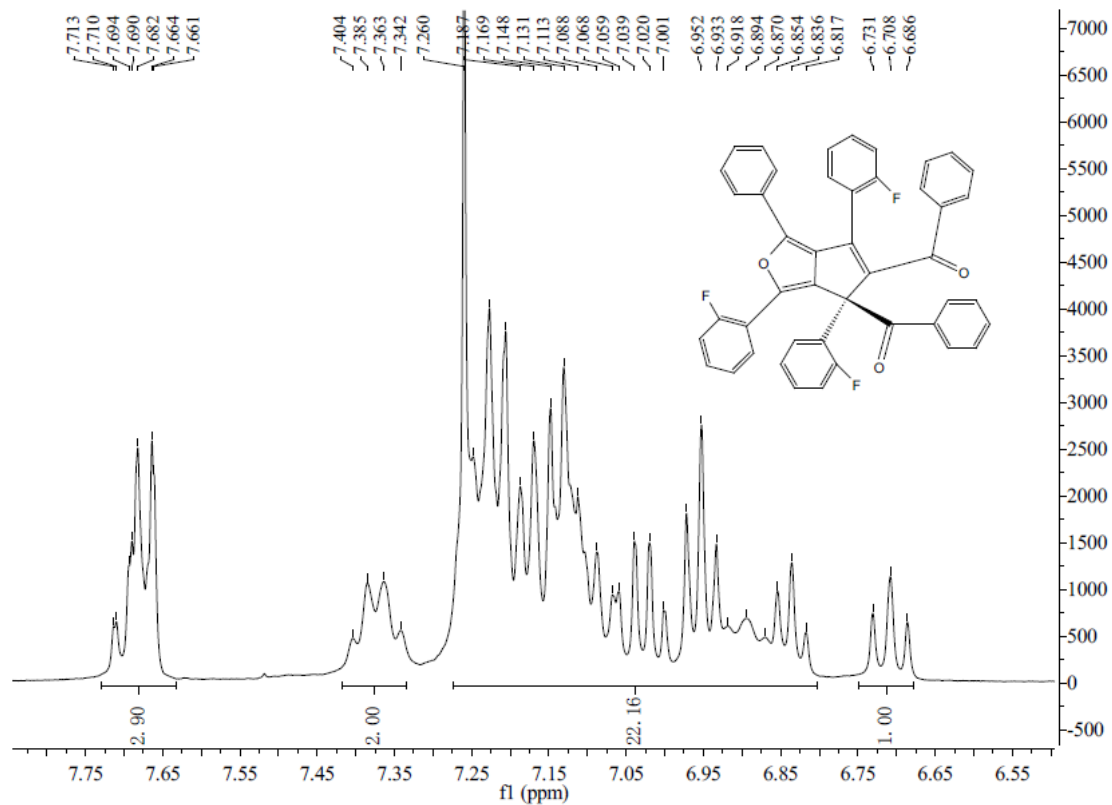


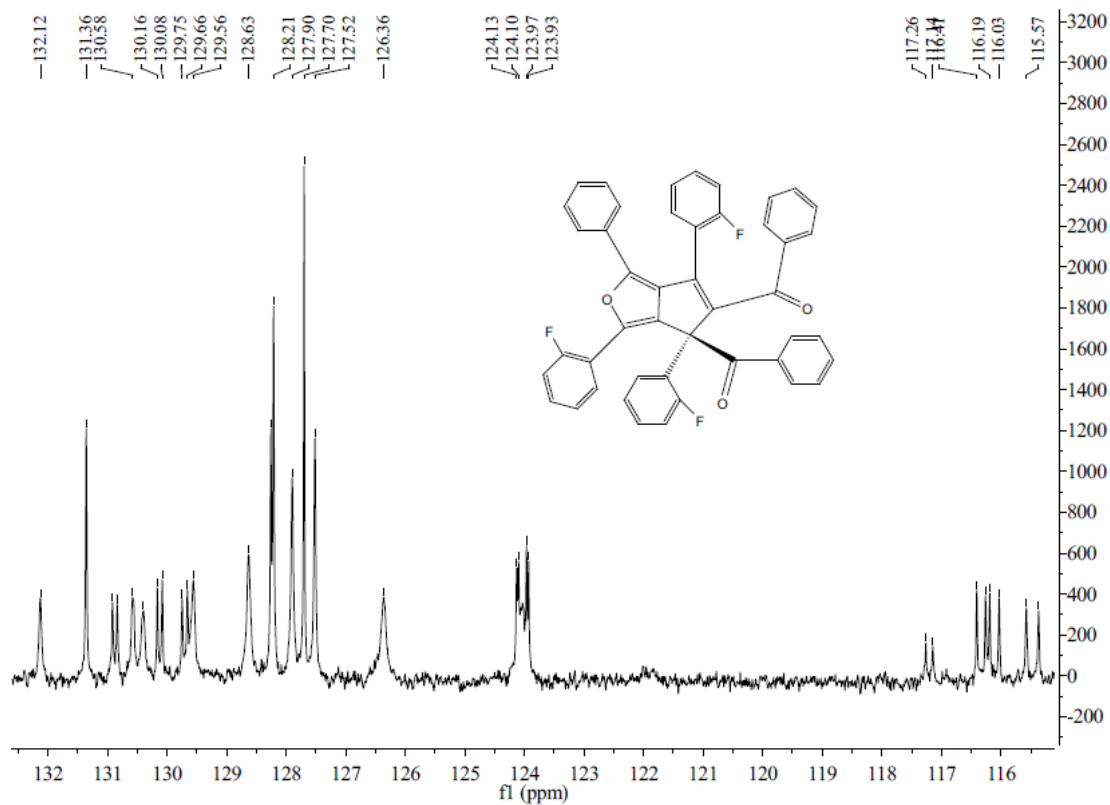




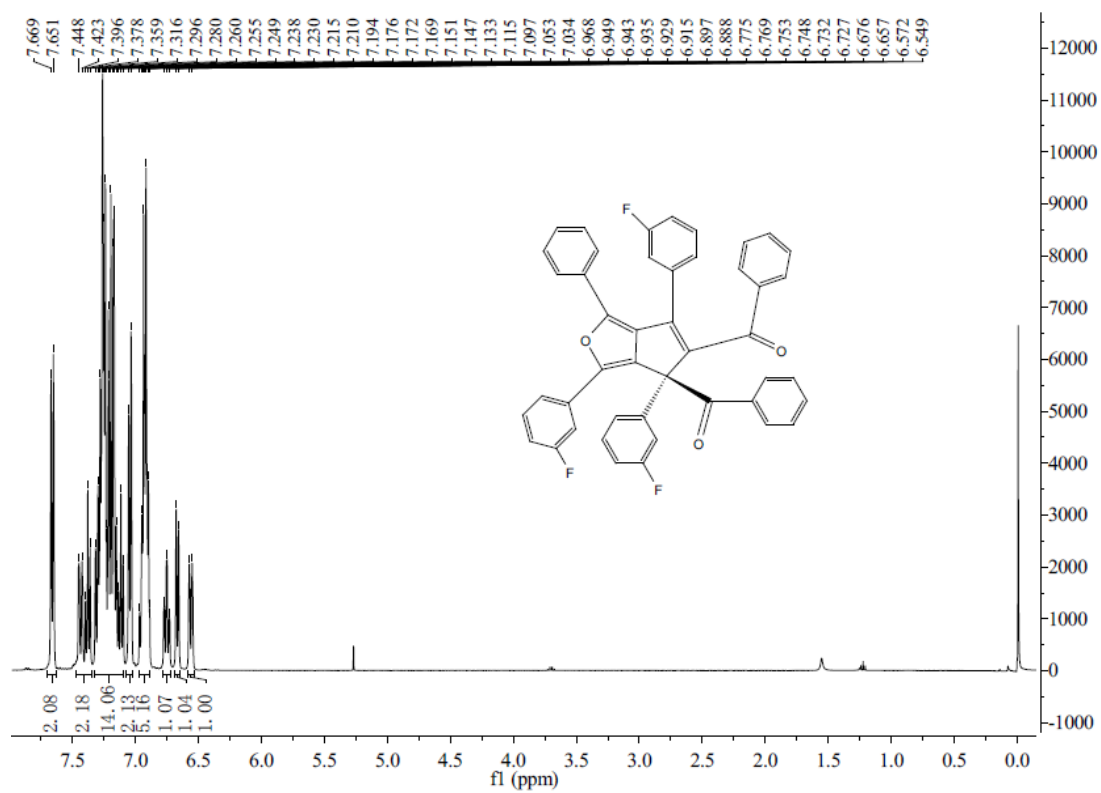
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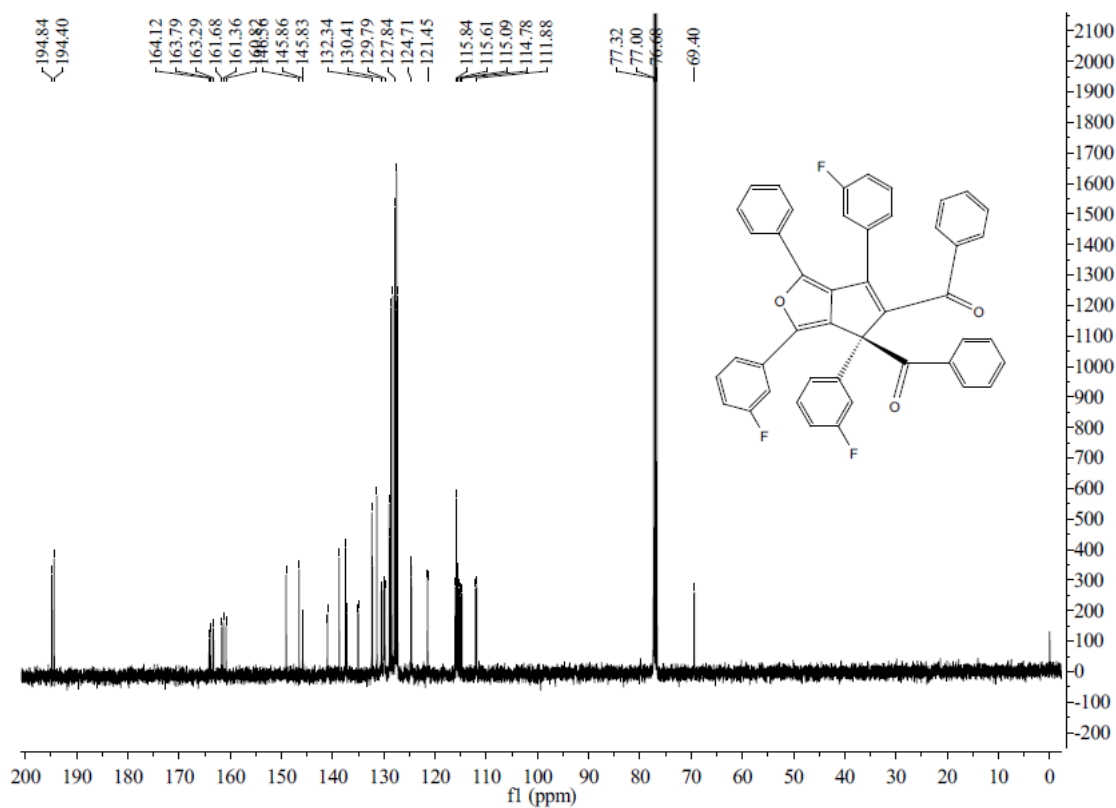
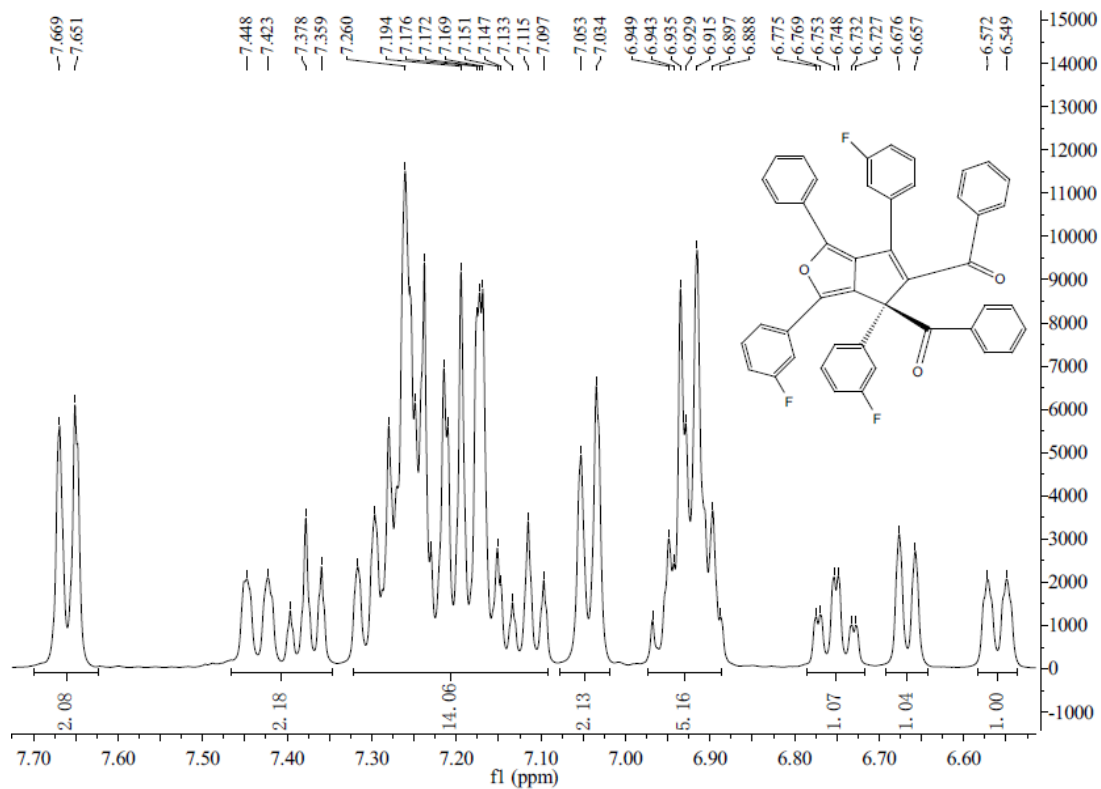


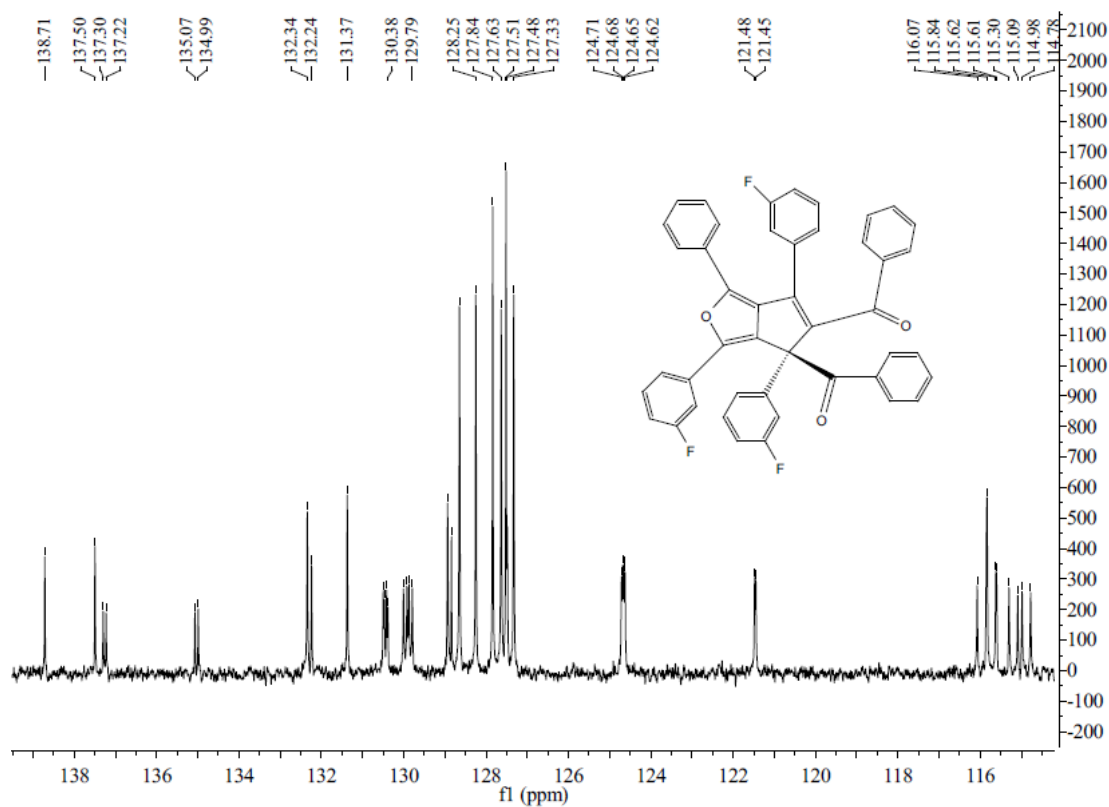




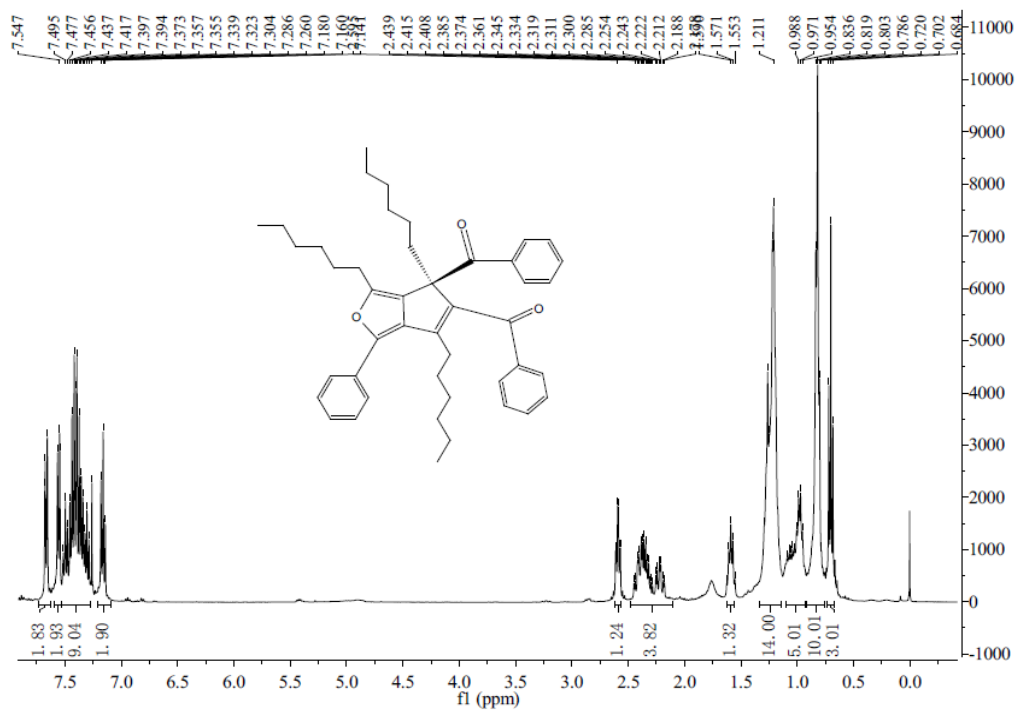
2k:

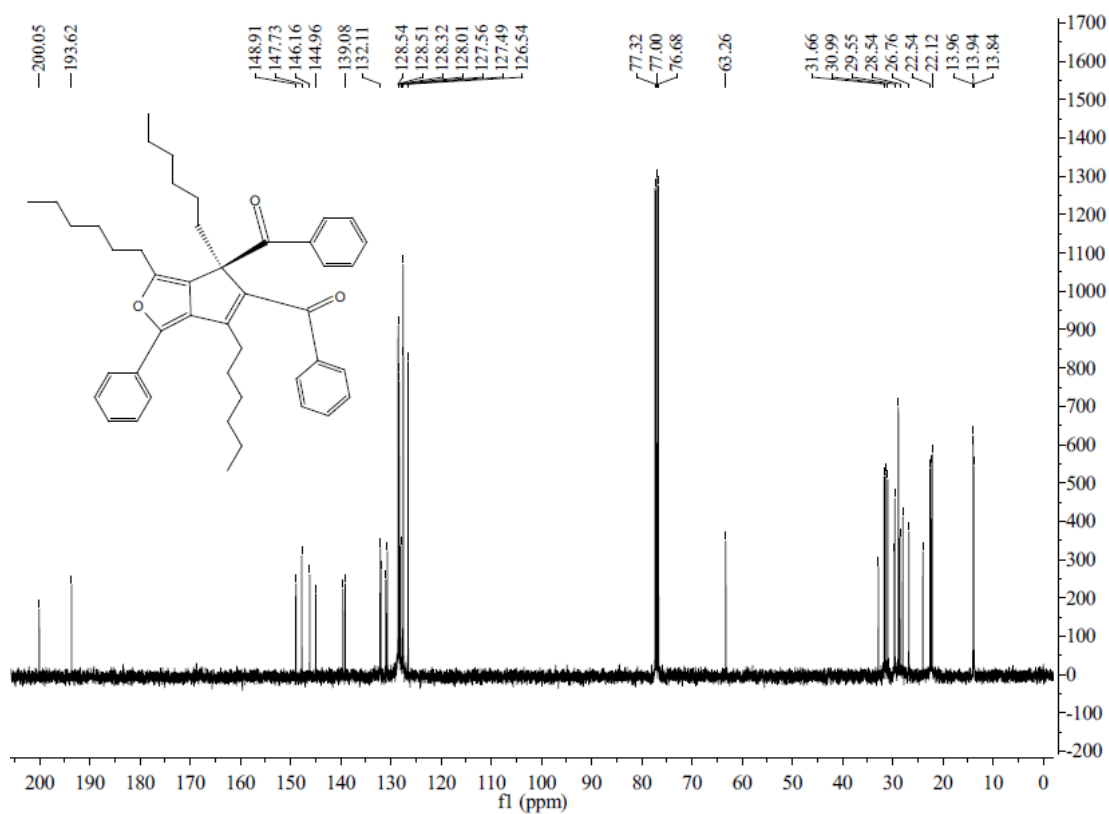
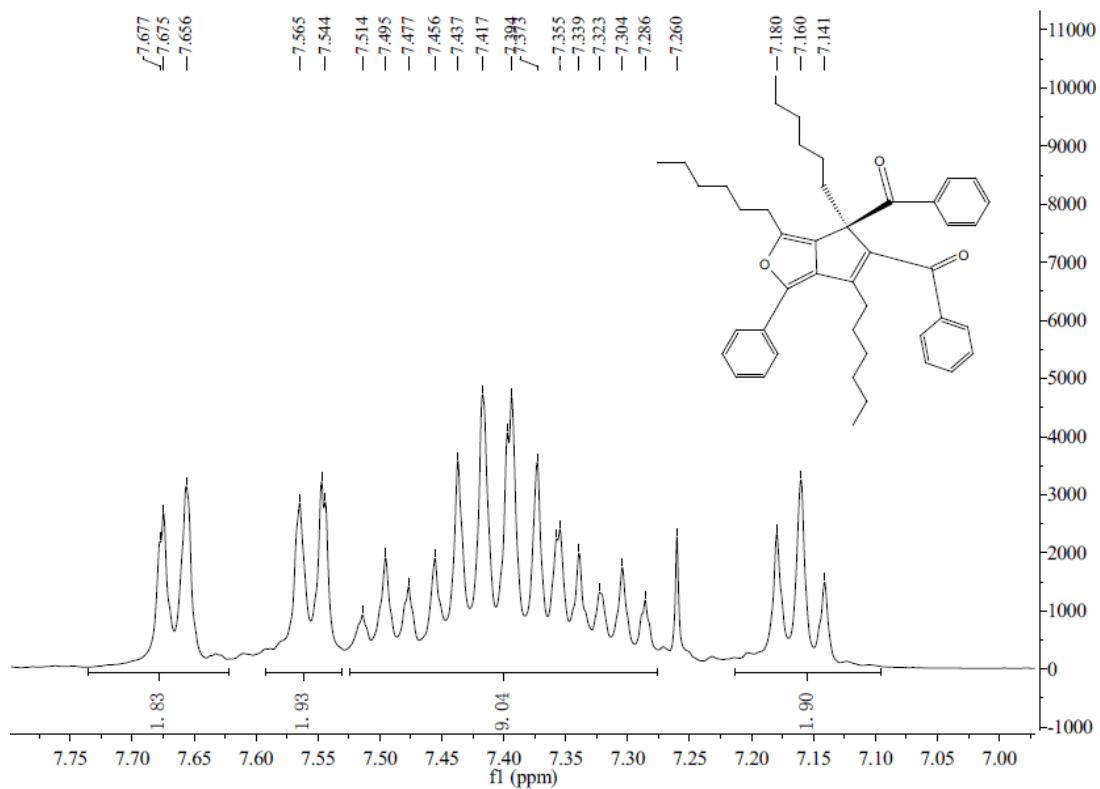


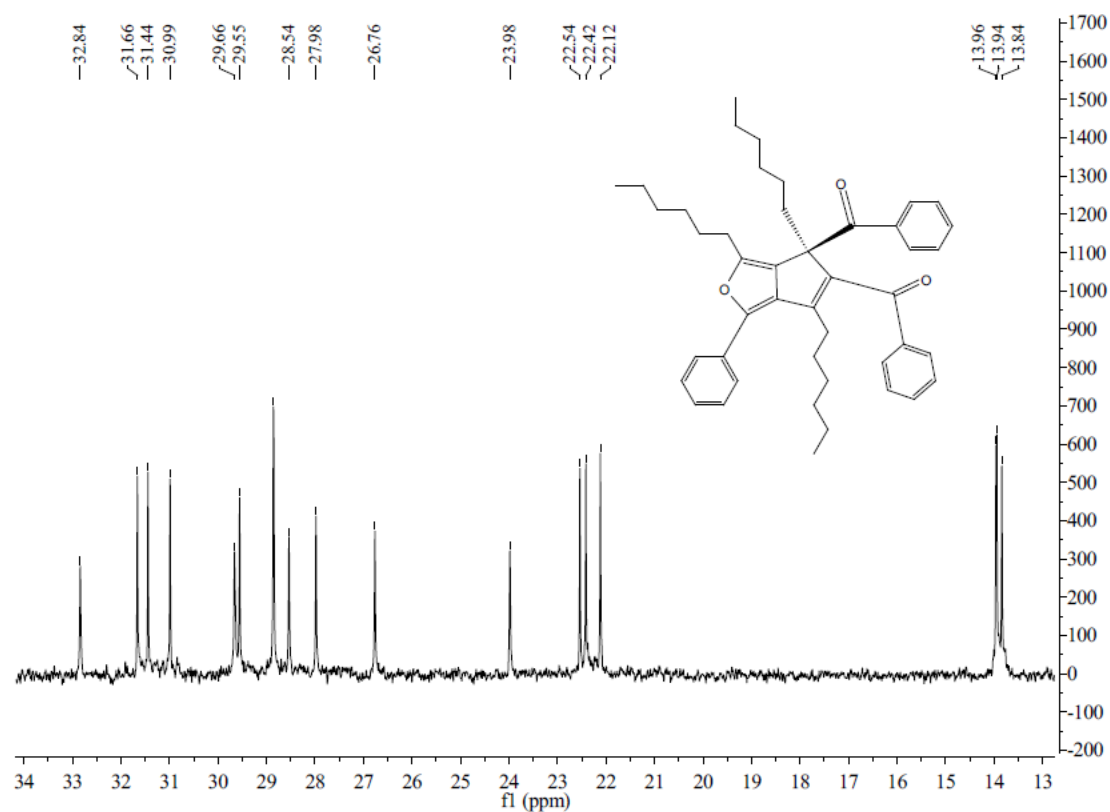
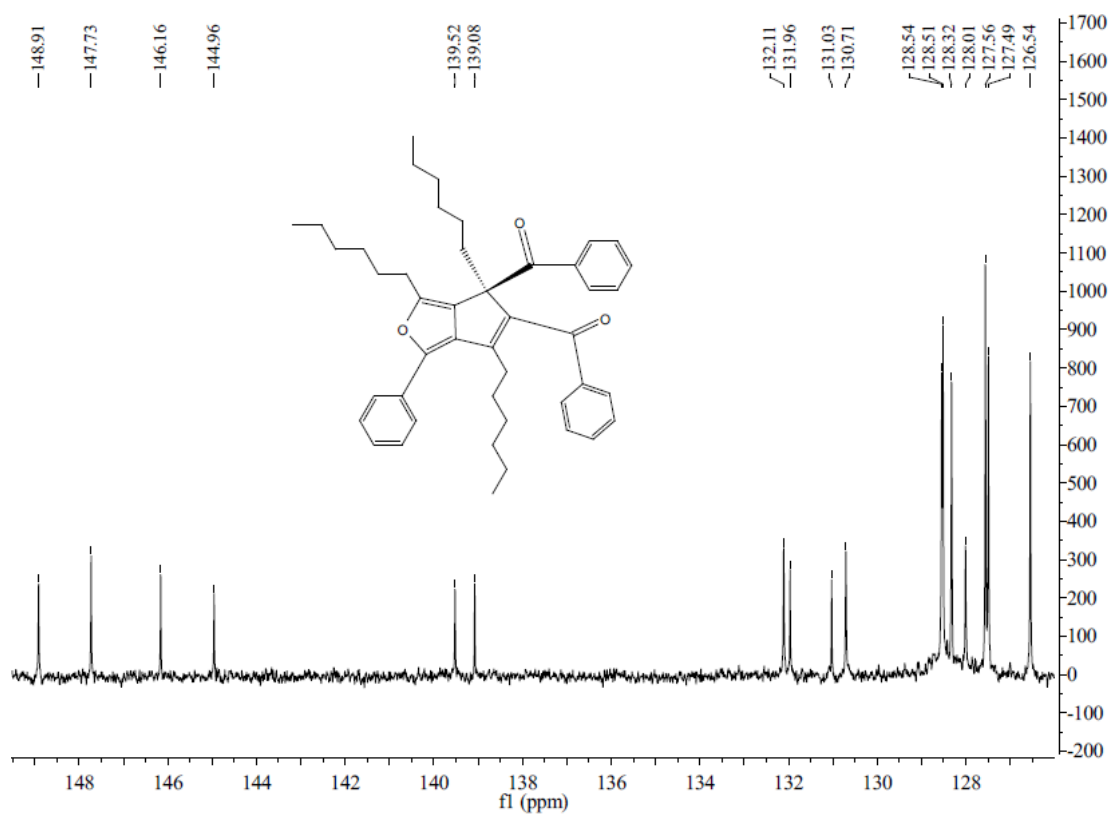




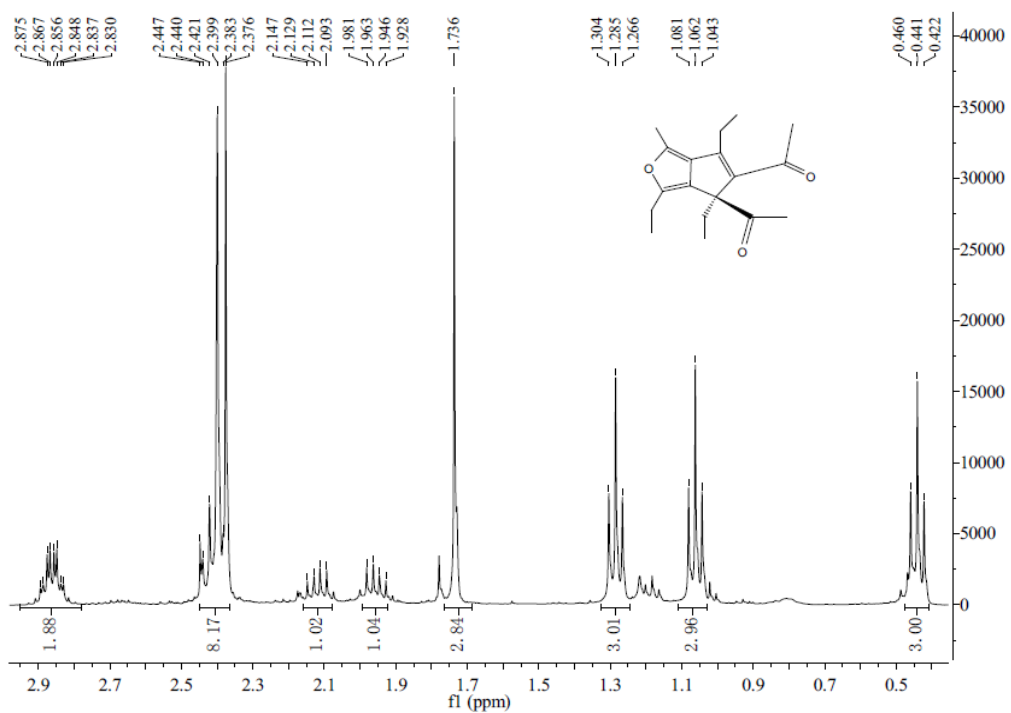
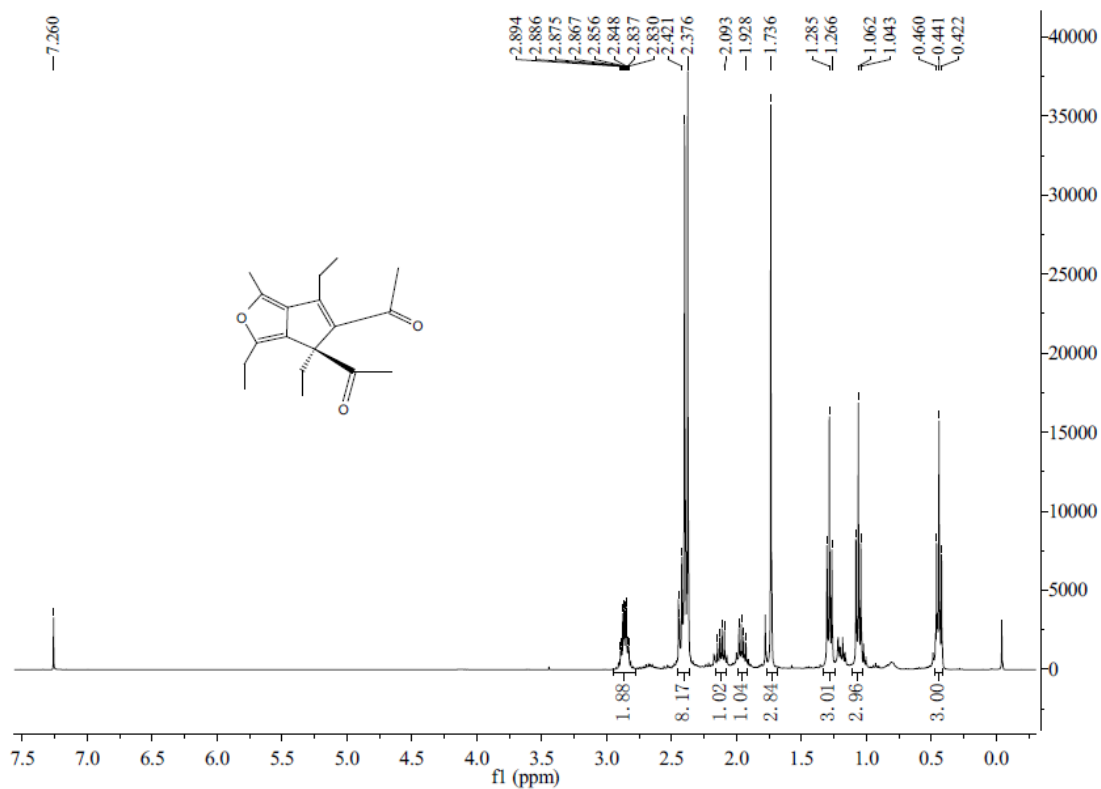
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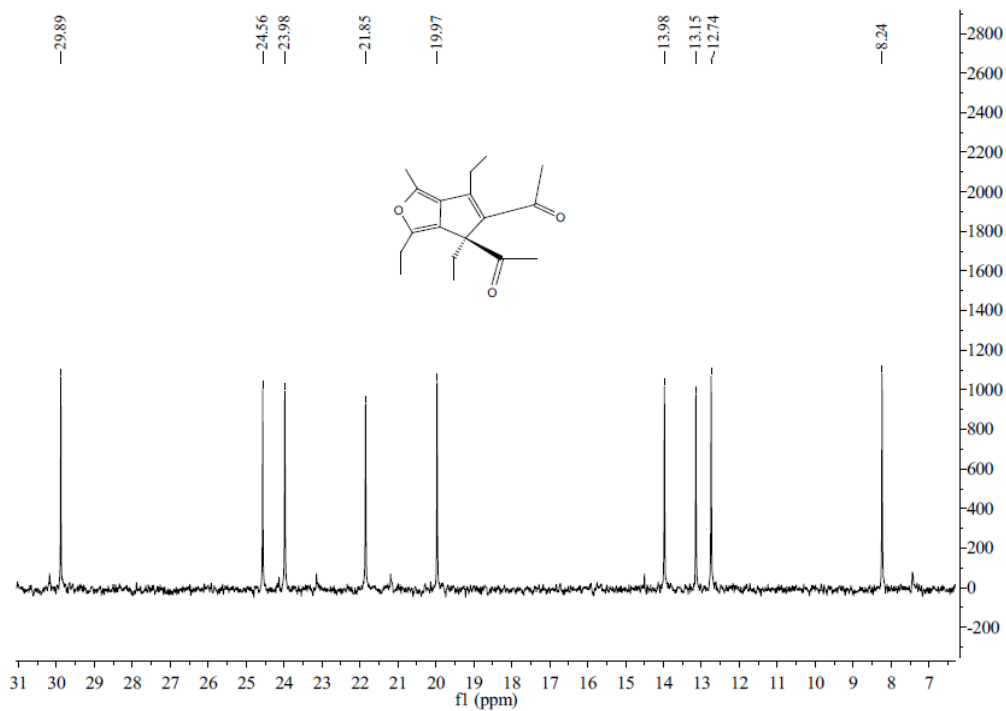
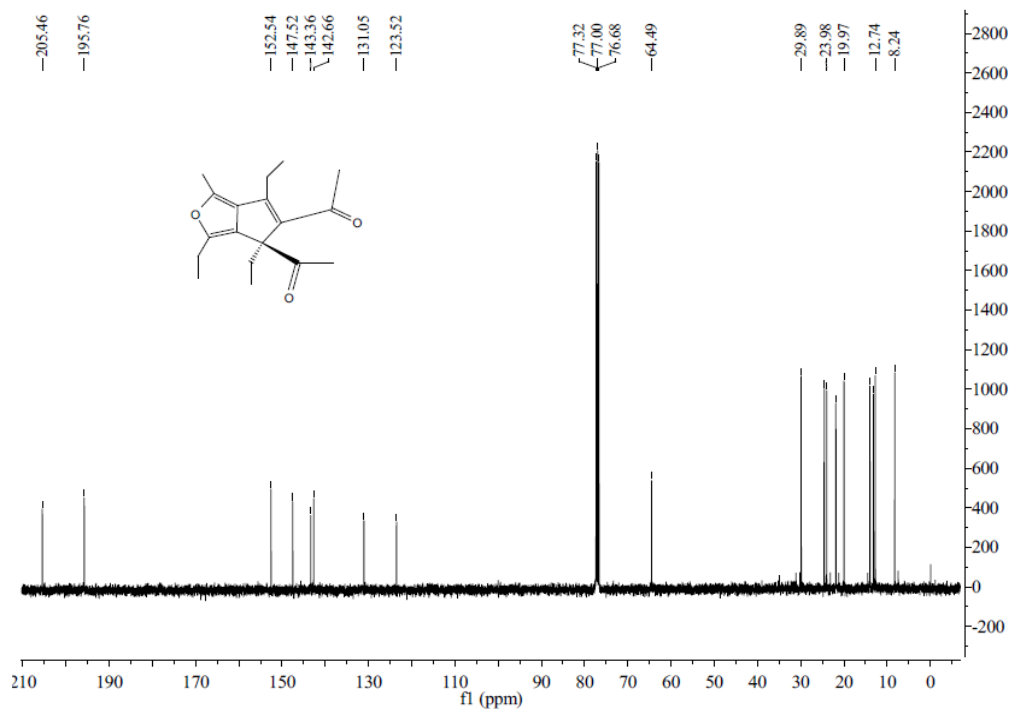






2m:





F. X-Ray Crystallographic Analysis for 2a and 2k

Table 1. Crystal data and structure refinement for compound **2a**.

Empirical formula	C ₄₅ H ₃₀ O ₃
Formula weight	618.69
Temperature	293(2) K
Wavelength	0.71073 Å
Crystal system	Monoclinic
space group	P21/c
Unit cell dimensions	a = 19.726(4) Å α = 90 deg. b = 9.4866(19) Å β = 119.02(3) deg. c = 20.005(4) Å γ = 90 deg.
Volume	3273.6(11) Å ³
Z	4
Calculated density	1.255 Mg/m ³
Absorption coefficient	0.077 mm ⁻¹
F(000)	1296
Crystal size	0.30 × 0.26 × 0.22 mm
Theta range for data collection	3.08 to 25.20 deg.
Limiting indices	-23 ≤ h ≤ 23, -11 ≤ k ≤ 10, -23 ≤ l ≤ 23
Reflections collected	24381
unique	5889 [R(int) = 0.0742]
Completeness to theta = 25.20	99.8 %
Max. and min. transmission	0.9832 and 0.9771
Refinement method	Full-matrix least-squares on F ²
Data / restraints / parameters	5889 / 42 / 434
Goodness-of-fit on F ²	0.934
Final R indices [I > 2σ(I)]	R ₁ = 0.0759, wR ₂ = 0.1881
R indices (all data)	R ₁ = 0.1492, wR ₂ = 0.2572
Extinction coefficient	0.016(3)

Table 2. Crystal data and structure refinement for compound **2k**.

Empirical formula	C ₄₅ H ₂₇ F ₃ O ₃
Formula weight	672.67
Temperature	293(2) K
Wavelength	0.71073 Å
Crystal system	P2(1)/c
space group	Monoclinic
Unit cell dimensions	a = 20.293(4) Å α = 90 deg. b = 9.2343(18) Å β = 117.20(3) deg. c = 20.400(4) Å γ = 90 deg.
Volume	3400.1(12) Å ³
Z	4
Calculated density	1.314 Mg/m ³
Absorption coefficient	0.093 mm ⁻¹
F(000)	1392

Crystal size	0.40 × 0.30 × 0.20 mm
Theta range for data collection	3.09 to 27.44 deg.
Limiting indices	-26 ≤ h ≤ 26, -11 ≤ k ≤ 11, -24 ≤ l ≤ 26
Reflections collected	32220
unique	7728 [R(int) = 0.0758]
Completeness to theta = 27.44	99.8 %
Max. and min. transmission	0.9817 and 0.9639
Refinement method	Full-matrix least-squares on F ²
Data / restraints / parameters	7728 / 0 / 461
Goodness-of-fit on F ²	0.972
Final R indices [I > 2σ(I)]	R ₁ = 0.0699, wR ₂ = 0.1848
R indices (all data)	R ₁ = 0.1562, wR ₂ = 0.2393
Extinction coefficient	0.0066(15)
Largest diff. peak and hole	0.668 and -0.291 e.Å ⁻³
