Supporting Information

Rhodium-Catalyzed C2 and C4 C-H Activation/Annulation of indoles with internal alkynes: A Facile Access to Substituted and Fused Carbazoles

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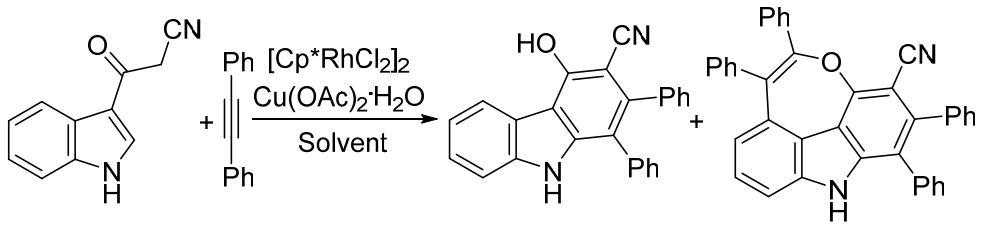
Contents

Experimental Section:

General Considerations. All reactions were carried out under argon atmosphere using standard Schlenk technique. ^{1}H NMR (400 MHz), ^{19}F (376 MHz), and ^{13}C NMR (100MHz) were recorded on Bruker AV400 NMR spectrometer with $CDCl_3$ as solvent. Chemical shifts of ^{1}H, ^{19}F, and ^{13}C NMR spectra are reported in parts per million (ppm). The residual solvent signals were used as references and the chemical shifts converted to the TMS scale ($CDCl_3$: δ_H = 7.26 ppm, δ_C = 77.00 ppm). All coupling constants (*J* values) were reported in Hertz (Hz). Multiplicities are reported as follows: singlet (s), doublet (d), doublet of doublets (dd), triplet (t), quartet (q), and multiplet (m). Column chromatography was performed on silica gel 200–300 mesh. Analytical thin-layer chromatography (TLC) was performed on pre-coated, glass-backed silica gel plates. Visualization of the developed chromatogram was performed by UV absorbance (254 nm). IR spectra were recorded as KBr disks on a Nicolet 380 FT-IR spectrometer. High-resolution mass spectrometry (HRMS) were done on Varian 7.0 T FTICR-mass spectrometer. $[Cp^*RhCl_2]_2$ was prepared from $RhCl_3.xH_2O$ following a literature procedure. [1] The substrates **1a-1l** was prepared according to the literature we reported before. [2] Unless otherwise noted below, all other compounds have been reported in the literature or are commercially available from Alfa Aesar China (Tianjin) Chemical Co., Ltd. without any further purification.

Table1 S1 Optimization studies[a, b]

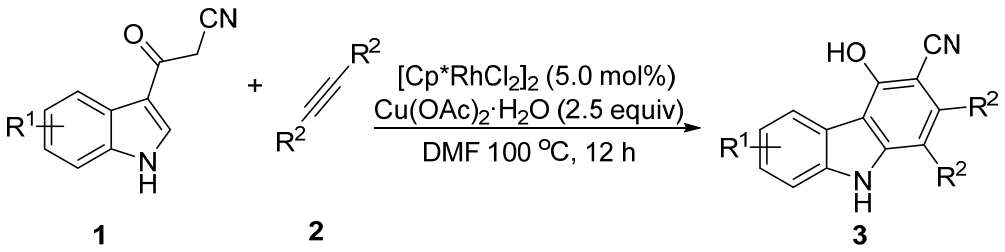


1a **2a** **3aa** **4aa**

entry	Ratio (**1a**:**2a**)	Solvent	Additive	T (°C)	Yield of **3aa** [%]	Yield of **4aa** [%]
1	1.1:1	DMF		100	55	7
2	***1.5:1***	***DMF***		***100***	***75***	***Trace***
3	1.5:1	CF_3CH_2OH		100	59	trace
4	1.5:1	NMP		100	33	trace
5	1.5:1	DMSO		100	20	trace
6	1.5:1	MeCN		100	24	trace
7	1.5:1	DMF	AcOH	100	74	trace
8	1.5:1	DMF	$MesCO_2H$	100	71	trace
9	1.5:1	DMF	NaOAc	100	61	trace
10	1.5:1	DMF	KOAc	100	57	trace
11[c]	1.5:1	DMF		100	trace	trace
12[d]	1.5:1	DMF		100	n.r.	n.r.
13[e]	1.5:1	DMF		100	n.r.	n.r.
14[f]	0.5:1	DMF		100	trace	53
15[f]	0.6:1	DMF		100	trace	65
16[f]	0.7:1	DMF		100	19	65
17[f]	***0.65:1***	***DMF***		***100***	***6***	***70***
18[f,g]	0.6:1	DMF	$AgSbF_6$	100	16	52
19[f]	0.65:1	DMF		120	trace	63

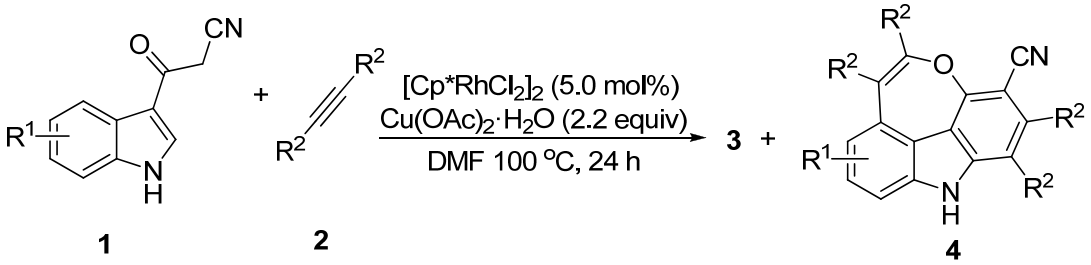
[a] Reaction conditions: **1a** (0.6–1.5 equiv.), **2a** (1.0 equiv.), [{Cp^*RhCl_2}$_2$] (5 mol %), $Cu(OAc)_2·H_2O$ (2.5 equiv.), additive (50 mol %), solvent (0.5 mL), 12 h, under Ar. [b] Yields of isolated products. [c] under air. [d] without [Cp^*RhCl_2]$_2$. [e] without $Cu(OAc)_2·H_2O$. [f] 24 h, $Cu(OAc)_2·H_2O$ (2.2 equiv.). [g] $AgSbF_6$ (20 mol %). n.r. = no reaction. Cp* = C_5Me_5, DMF = N,N-dimethylformamide..

General Procedure for the Rh(III)-Catalyzed Cascade Synthesis (A)



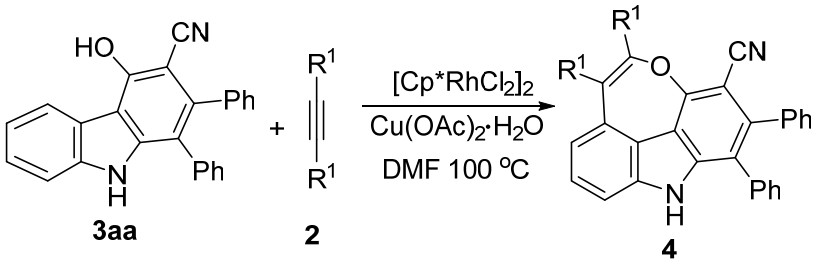
A mixture of substituted 3-(1H-indol-3-yl)-3-oxopropanenitrile (**1**) (0.3 mmol, 1.5 equiv), alkyne (**2**) (0.2 mmol, 1.0 equiv), $[Cp^*RhCl_2]_2$ (6.2 mg, 0.01 mmol, 5.0 mol %), and $Cu(OAc)_2 \cdot H_2O$ (100 mg, 0.5 mmol, 2.5 equiv) were weighted in a Schlenk tube equipped with a stir bar. Dry DMF (0.5 mL) was added and the mixture was stirred at 100 °C for 12 h under Ar atmosphere. Afterwards, it was diluted with CH_2Cl_2 and transferred to a round bottom flask. Silica was added to the flask and volatiles were evaporated under reduced pressure. The purification was performed by flash column chromatography on silica gel with EtOAc/petroleum ether.

General Procedure for the Rh(III)-Catalyzed Cascade Synthesis (B)



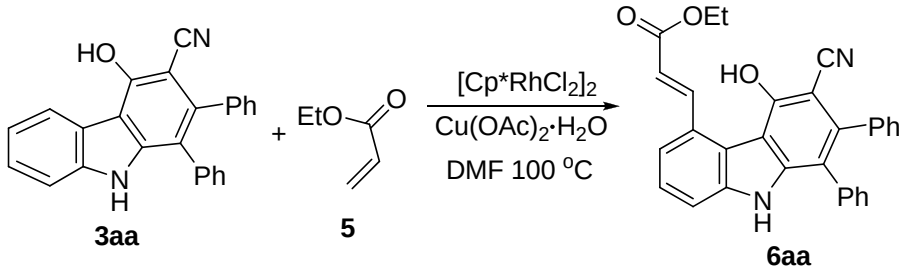
A mixture of substituted 3-(1H-indol-3-yl)-3-oxopropanenitrile (**1**) (0.195 mmol, 0.65 equiv), alkyne (**2**) (0.3 mmol, 1.0 equiv), $[Cp^*RhCl_2]_2$ (9.3 mg, 0.01 mmol, 5.0 mol %), and $Cu(OAc)_2 \cdot H_2O$ (132 mg, 0.66 mmol, 2.2 equiv) were weighted in a Schlenk tube equipped with a stir bar. Dry DMF (0.5 mL) was added and the mixture was stirred at 100 °C for 24 h under Ar atmosphere. Afterwards, it was diluted with CH_2Cl_2 and transferred to a round bottom flask. Silica was added to the flask and volatiles were evaporated under reduced pressure. The purification was performed by flash column chromatography on silica gel with DCE/petroleum ether.

General Procedure for the Rh(III)-Catalyzed Cascade Synthesis (C)



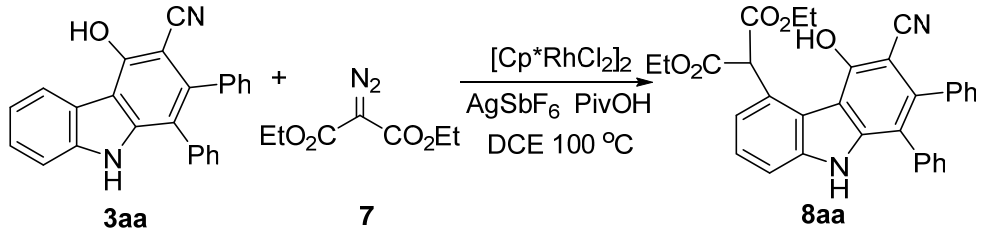
A mixture of substituted 4-hydroxy-1,2-diphenyl-9*H*-carbazole-3-carbonitrile (**3**) (0.12 mmol, 1.2 equiv), alkyne (**2**) (0.1 mmol, 1.0 equiv), $[Cp^*RhCl_2]_2$ (3.1 mg, 0.005 mmol, 5.0 mol %), and $Cu(OAc)_2 \cdot H_2O$ (50 mg, 0.25 mmol, 2.5 equiv) were weighted in a Schlenk tube equipped with a stir bar. Dry DMF (0.5 mL) was added and the mixture was stirred at 100 °C for 12 h under Ar atmosphere. Afterwards, it was diluted with CH_2Cl_2 and transferred to a round bottom flask. Silica was added to the flask and volatiles were evaporated under reduced pressure. The purification was performed by flash column chromatography on silica gel with EtOAc/petroleum ether.

General Procedure for the Rh(III)-Catalyzed Cascade Synthesis (D)



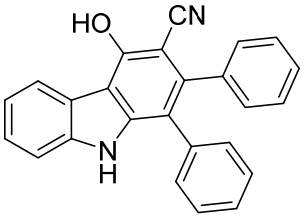
A mixture of substituted 4-hydroxy-1,2-diphenyl-9*H*-carbazole-3-carbonitrile (**3**) (0.1 mmol, 1.0 equiv), ethyl acrylate (**5**) (0.15 mmol, 1.0 equiv), $[Cp^*RhCl_2]_2$ (3.1 mg, 0.005 mmol, 5.0 mol %), and $Cu(OAc)_2 \cdot H_2O$ (50 mg, 0.25 mmol, 2.5 equiv) were weighted in a Schlenk tube equipped with a stir bar. Dry DMF (0.5 mL) was added and the mixture was stirred at 100 °C for 12 h under Ar atmosphere. Afterwards, it was diluted with CH_2Cl_2 and transferred to a round bottom flask. Silica was added to the flask and volatiles were evaporated under reduced pressure. The purification was performed by flash column chromatography on silica gel with EtOAc/petroleum ether.

General Procedure for the Rh(III)-Catalyzed Cascade Synthesis (E)



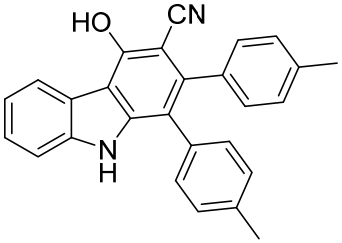
A mixture of substituted 4-hydroxy-1,2-diphenyl-9*H*-carbazole-3-carbonitrile (**3**) (0.1 mmol, 1.0 equiv), diethyl 2-diazomalonate (**7**) (0.15 mmol, 1.0 equiv), $[Cp^*RhCl_2]_2$ (3.1 mg, 0.005 mmol, 5.0 mol %), and $AgSbF_6$ (6.8 mg, 0.02 mmol, 20 mol %) were weighted in a Schlenk tube equipped with a stir bar. Dry DCE (0.5 mL) was added and the mixture was stirred at 100 °C for 12 h under Ar atmosphere. Afterwards, it was diluted with CH_2Cl_2 and transferred to a round bottom flask. Silica was added to the flask and volatiles were evaporated under reduced pressure. The purification was performed by flash column chromatography on silica gel with EtOAc/petroleum ether.

Characterization of Products 3, 4, 6, 8



4-Hydroxy-1,2-diphenyl-9H-carbazole-3-carbonitrile (3aa)

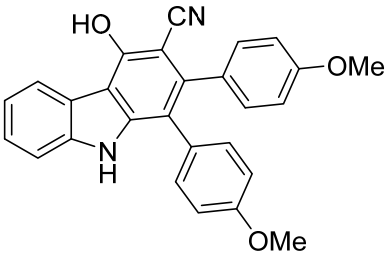
The title compound was isolated by column chromatography (eluent: EtOAc/petroleum ether = 1/5 to 1/2) as a yellow solid in 75% yield （54.3 mg, 0.150mmol）following the general procedure A. Mp: 244–246 °C. **^{1}H NMR (DMSO, 400 MHz):** δ 11.09 (s, 1H), 11.05 (d, J = 1.7 Hz, 1H), 8.32 (d, J = 7.8 Hz, 1H), 7.52 (d, J = 8.1 Hz, 1H), 7.42 – 7.37 (m, 1H), 7.33 – 7.11 (m, 11H).**^{13}C NMR (DMSO, 100 MHz):**δ 155.78, 141.99, 140.57, 139.81, 138.18, 135.69, 130.63, 130.27, 128.23, 127.47, 127.17, 126.96, 125.48, 122.18, 121.29, 119.91, 118.25, 117.73, 111.59, 111.32, 91.84. **HRMS (ESI):** Calcd for $C_{25}H_{17}N_2O$ $[M+H]^+$ 361.1335, found: 361.1334.



4-Hydroxy-1,2-di-p-tolyl-9*H*-carbazole-3-carbonitrile (3ab)

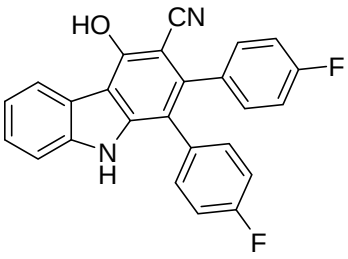
The title compound was isolated by column chromatography (eluent: EtOAc/petroleum ether = 1/5 to 1/2) as a yellow solid in 68% yield (53.2mg, 0.136 mmol) following the general procedure A. Mp: 260–262 °C. **^{1}H NMR (DMSO, 400 MHz):** δ

11.00 (s, 1H), 10.96 (s, 1H), 8.29 (d, *J* = 7.9 Hz, 1H), 7.50 (d, *J* = 8.1 Hz, 1H), 7.40 – 7.36 (m, 1H), 7.26 – 7.21 (m, 1H), 7.13 (d, *J* = 8.0 Hz, 2H), 7.10 – 7.01 (m, 6H), 2.29 (s, 3H), 2.27 (s, 3H). **^{13}C NMR (DMSO, 100 MHz):** δ 155.84, 142.40, 140.67, 139.98, 136.42, 136.13, 135.55, 133.01, 130.66, 130.34, 129.19, 128.37, 125.61, 122.34, 121.50, 120.06, 118.41, 118.03, 111.80, 111.37, 92.21, 20.92. **HRMS (ESI):** Calcd for $C_{27}H_{21}N_2O$ $[M+H]^+$ 389.1648, found: 389.1645.



4-Hydroxy-1,2-bis(4-methoxyphenyl)-9*H*-carbazole-3-carbonitrile (3ac)

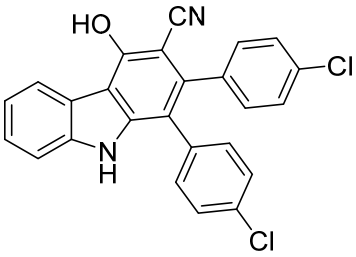
The title compound was isolated by column chromatography (eluent: EtOAc/petroleum ether = 1/5 to 1/1) as a yellow solid in 40% yield (33.6 mg, 0.080 mmol) following the general procedure A. Mp: 263–265 °C. **^{1}H NMR (DMSO, 400 MHz):** δ 10.99 (s, 1H), 10.90 (s, 1H), 8.29 (d, J = 7.9 Hz, 1H), 7.50 (d, J = 8.1 Hz, 1H), 7.39 (d, J = 7.4 Hz, 1H), 7.24 (d, J = 7.4 Hz, 1H), 7.09 (dd, J = 8.4, 3.9 Hz, 4H), 6.88 (d, J = 8.5 Hz, 2H), 6.81 (d, J = 8.5 Hz, 2H), 3.75 (s, 3H), 3.73 (s, 3H). **^{13}C NMR (DMSO, 100 MHz):** 13C NMR (101 MHz,) δ 158.54, 158.39, 155.96, 142.82, 140.74, 140.17, 132.13, 131.87, 130.86, 128.29, 125.78, 122.54, 121.76, 120.22, 118.52, 114.19, 113.36, 111.96, 111.49, 92.53, 55.32, 55.28. **HRMS (ESI):** Calcd for $C_{27}H_{21}N_2O_3$ $[M+H]^+$ 421.1547, found: 421.1545.



1,2-Bis(4-fluorophenyl)-4-hydroxy-9*H*-carbazole-3-carbonitrile (3ad)

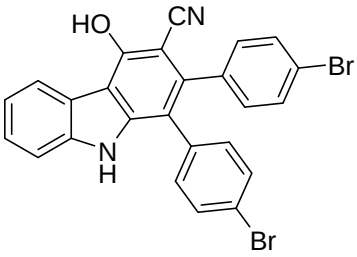
The title compound was isolated by column chromatography (eluent: EtOAc/petroleum ether = 1/5 to 1/2) as a yellow solid in 67% yield (52.9 mg, 0.134mmol) following the general procedure A. Mp: 238–241 °C. **^{1}H NMR (DMSO, 400 MHz):** δ 11.15 (s, 1H), 11.11 (s, 1H), 8.32 (d, J = 7.8 Hz, 1H), 7.51 (d, J = 8.1 Hz, 1H), 7.41 (s, 1H), 7.27 – 7.06 (m, 9H). **^{13}C NMR (DMSO, 100 MHz):** δ 162.47, 162.42, 160.04, 159.99, 155.81, 142.09, 139.77, 139.64, 134.36, 132.72, 132.63, 132.32, 132.23, 131.86, 125.58, 122.22, 121.25, 119.98, 117.60,

117.45, 115.28, 115.06, 114.58, 114.37, 111.49, 111.38, 91.78. **^{19}F NMR (DMSO, 376 MHz):** δ -114.74, -115.19. **HRMS (ESI):** Calcd for $C_{25}H_{15}F_2N_2O$ $[M+H]^+$ 397.1147, found: 397.1145.



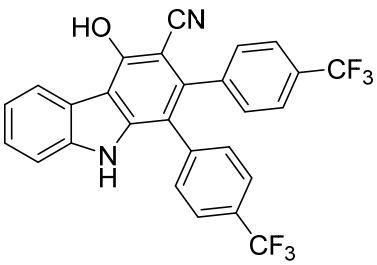
1,2-Bis(4-chlorophenyl)-4-hydroxy-9H-carbazole-3-carbonitrile (3ae)

The title compound was isolated by column chromatography (eluent: EtOAc/petroleum ether = 1/5 to 1/2) as a yellow solid in 62% yield (53.0 mg, 0.124 mmol) following the general procedure A. Mp: 250–252 °C. **^{1}H NMR (DMSO, 400 MHz):** δ 11.19 (s, 2H), 8.31 (d, J = 7.8 Hz, 1H), 7.49 (d, J = 8.1 Hz, 1H), 7.45 – 7.33 (m, 5H), 7.29 – 7.18 (m, 5H). **^{13}C NMR (DMSO, 100 MHz):** δ 156.00, 141.93, 139.79, 139.22, 136.86, 134.38, 132.54, 132.26, 132.10, 132.00, 128.44, 127.72, 125.69, 122.26, 121.20, 120.08, 117.55, 117.07, 111.49, 91.58. **HRMS (ESI):** Calcd for $C_{25}H_{15}Cl_2N_2O$ $[M+H]^+$ 429.0556, found: 429.0544.



1,2-Bis(4-bromophenyl)-4-hydroxy-9*H*-carbazole-3-carbonitrile (3af)

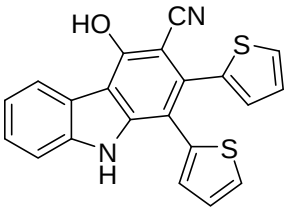
The title compound was isolated by column chromatography (eluent: EtOAc/petroleum ether = 1/5 to 1/2) as a yellow solid in 49% yield (50.5 mg 0.148 mmol) following the general procedure C. Mp: 251–254 °C. **^{1}H NMR (DMSO, 400 MHz):** ^{1}H NMR (400 MHz,) δ 11.19 (s, 2H), 8.31 (d, *J* = 7.7 Hz, 1H), 7.66 – 6.95 (m, 12H). **^{13}C NMR (DMSO, 100 MHz):** δ ^{1}H NMR (101 MHz,) δ 156.23, 142.08, 139.99, 139.36, 137.43, 134.96, 133.07, 132.61, 131.57, 130.85, 125.90, 122.45, 121.39, 121.19, 120.93, 120.29, 117.74, 117.20, 111.72, 91.74. **HRMS (ESI):** Calcd for $C_{25}H_{15}Br_2N_2O$ $[M+H]^+$ 516.9546, found: 516.9540.



4-Hydroxy-1,2-bis(4-(trifluoromethyl)phenyl)-9*H*-carbazole-3-carbonitrile (3ag)

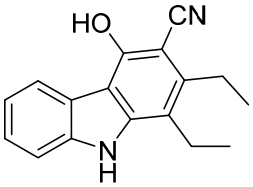
The title compound was isolated by column chromatography (eluent: EtOAc/petroleum ether = 1/5 to 1/2) as a yellow solid in 52% yield (51.8 mg, 0.104 mmol) following the general

procedure B. Mp: 228–230 °C. **^{1}H NMR (DMSO, 400 MHz):** δ 11.56 – 11.07 (m, 2H), 8.34 (d, *J* = 7.3 Hz, 1H), 7.72 – 7.61 (m, 4H), 7.55 – 7.37 (m, 6H), 7.32 – 7.23 (m, 1H). **^{13}C NMR (DMSO, 100 MHz):** δ 156.30, 142.09, 141.71, 139.85, 139.73, 139.06, 131.59, 131.20, 128.10, 127.89, 127.79, 127.58, 125.85, 125.51, 125.40, 125.21, 124.52, 122.80, 122.69, 122.33, 121.14, 120.22, 117.35, 116.87, 111.80, 111.56, 91.46. **^{19}F NMR (DMSO, 376 MHz):** δ -60.94, -60.98. **HRMS (ESI):** Calcd for $C_{27}H_{15}F_6N_2O$ $[M+H]^+$ 497.1083, found: 497.1076.



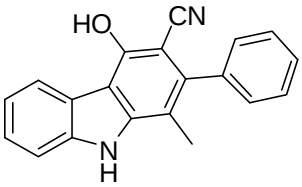
4-Hydroxy-1,2-di(thiophen-2-yl)-9*H*-carbazole-3-carbonitrile (3ah)

The title compound was isolated by column chromatography (eluent: EtOAc/petroleum ether = 1/5 to 1/2) as a yellow solid in 46% yield (34.3mg, 0.092 mmol) following the general procedure A. Mp: 227–229 °C. **^{1}H NMR (DMSO, 400 MHz):** δ 11.34 (s, 2H), 8.31 (d, *J* = 7.8 Hz, 1H), 7.63 – 7.55 (m, 3H), 7.46 – 7.40 (m, 1H), 7.27 (t, *J* = 7.5 Hz, 1H), 7.17 – 7.09 (m, 3H), 7.07 – 7.02 (m, 1H). **^{13}C NMR (DMSO, 100 MHz):** δ 156.37, 142.31, 139.79, 138.00, 135.58, 133.88, 129.57, 129.20, 127.95, 127.64, 127.14, 126.61, 125.91, 122.32, 121.17, 120.24, 117.20, 111.95, 111.80, 92.90. **HRMS (ESI):** Calcd for $C_{21}H_{13}N_2OS_2$ $[M+H]^+$ 373.0464, found: 373.0469.



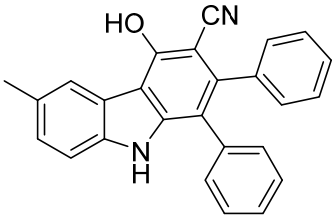
11-Methoxy-7,7-dimethyl-4,9-dioxo-1,2,4,5,6,7,8,9-octahydrobenzo[4,5]azepino[3,2,1-hi]indole-5-carbonitrile (3ai)

The title compound was isolated by column chromatography (eluent: EtOAc/petroleum ether = 1/5 to 1/2) as a yellow solid in 17% yield (9.0 mg, 0.034 mmol) following the general procedure A. Mp: 186–188 °C. **^{1}H NMR (DMSO, 400 MHz):** ^{1}H NMR (400 MHz,) δ 11.54 (s, 1H), 10.54 (s, 1H), 8.20 (d, *J* = 7.8 Hz, 1H), 7.51 (d, *J* = 8.1 Hz, 1H), 7.38 (s, 1H), 7.20 (d, *J* = 7.6 Hz, 1H), 2.94 – 2.82 (m, 4H), 1.26 – 1.19 (m, 6H). **^{13}C NMR (DMSO, 100 MHz):** ^{13}C NMR (101 MHz,) δ 154.69, 142.49, 140.52, 139.13, 124.81, 121.75, 121.38, 119.29, 117.75, 117.26, 110.69, 110.03, 90.73, 23.89, 19.75, 15.41, 14.62. **HRMS (ESI):** Calcd for $C_{17}H_{17}N_2O$ $[M+H]^+$ 265.1335, found: 265.1334.



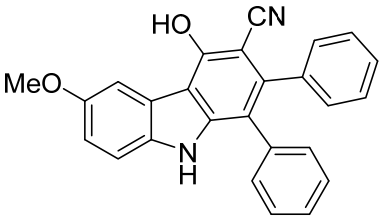
4-Hydroxy-1-methyl-2-phenyl-9H-carbazole-3-carbonitrile (3al)

The title compound was isolated by column chromatography (eluent: EtOAc/petroleum ether = 1/5 to 1/2) as a yellow solid in 16% yield (9.3 mg, 0.032 mmol) following the general procedure A. Mp: 206-208 °C. **^{1}H NMR (DMSO, 400 MHz):** δ 11.70 (s, 1H), 10.72 (s, 1H), 8.27 (d, *J* = 7.8 Hz, 1H), 7.58 – 7.42 (m, 5H), 7.36 (d, *J* = 6.9 Hz, 2H), 7.24 (t, *J* = 7.5 Hz, 1H), 2.21 (s, 3H). **^{13}C NMR (DMSO, 100 MHz):** δ 154.39, 142.70, 140.27, 139.30, 138.21, 129.36, 127.89, 127.44, 125.16, 122.05, 121.33, 119.56, 117.66, 111.42, 110.86, 110.67, 91.25, 13.91. **HRMS (ESI):** Calcd for $C_{20}H_{14}N_2NaO$ $[M+Na]^+$ 221.0998 found: 221.0999.



4-Hydroxy-6-methyl-1,2-diphenyl-9*H*-carbazole-3-carbonitrile (3ba)

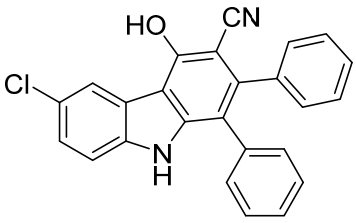
The title compound was isolated by column chromatography (eluent: EtOAc/petroleum ether = 1/5 to 1/2) as a yellow solid in 71% yield (53.3 mg, 0.142 mmol) following the general procedure A. Mp: 237–239 °C. **^{1}H NMR (DMSO, 400 MHz):** δ 10.95 (s, 2H), 8.11 (s, 1H), 7.40 (d, J = 8.2 Hz, 1H), 7.32 – 7.21 (m, 7H), 7.20 – 7.14 (m, 4H), 2.48 (s, 3H). **^{13}C NMR (DMSO, 100 MHz):** δ 155.79, 142.16, 140.34, 138.22, 138.03, 135.74, 130.63, 130.29, 128.60, 128.22, 127.46, 127.14, 126.93, 126.83, 121.98, 121.49, 118.23, 117.84, 111.30, 111.10, 91.50, 21.19. **HRMS (ESI):** Calcd for $C_{26}H_{19}N_2O$ $[M+H]^+$ 375.1492, found: 375.1487.



4-Hydroxy-6-methoxy-1,2-diphenyl-9*H*-carbazole-3-carbonitrile (3ca)

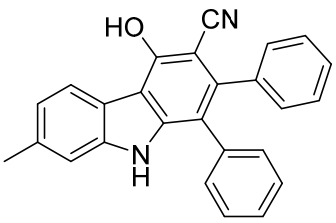
The title compound was isolated by column chromatography (eluent: EtOAc/petroleum ether = 1/5 to 1/2) as a yellow solid in 60% yield (47.1 mg, 0.120 mmol) following the general procedure A. Mp: 241–243 °C. **^{1}H NMR (DMSO, 400 MHz):** δ 11.00 (s, 1H), 10.92 (s, 1H), 7.85 (d, J = 2.4 Hz, 1H), 7.43 (d, J = 8.8 Hz, 1H), 7.36 – 7.14 (m, 10H), 7.06 (dd, J = 8.8, 2.5 Hz, 1H), 3.87 (s, 3H). **^{13}C NMR (DMSO, 100 MHz):** 1H NMR (400 MHz,) δ 11.00 (s, 1H), 10.92 (s, 1H), 7.85 (d, J = 2.4 Hz,

1H), 7.43 (d, J = 8.8 Hz, 1H), 7.36 – 7.14 (m, 10H), 7.06 (dd, J = 8.8, 2.5 Hz, 1H), 3.87 (s, 3H). **HRMS (ESI):** Calcd for $C_{26}H_{19}N_2O_2$ $[M+H]^+$ 391.1441, found: 391.1436.



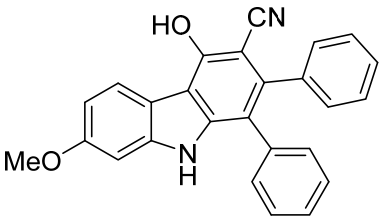
6-Chloro-4-hydroxy-1,2-diphenyl-9*H*-carbazole-3-carbonitrile (3da)

The title compound was isolated by column chromatography (eluent: EtOAc/petroleum ether = 1/5 to 1/2) as a yellow solid in 28% yield 22.4mg, 0.056 mmol) following the general procedure A. Mp: 263–266 °C. **^{1}H NMR (DMSO, 400 MHz):** δ 11.26 (s, 1H), 11.24 (s, 1H), 8.28 (s, 1H), 7.52 (d, J = 8.7 Hz, 1H), 7.46 – 7.41 (m, 1H), 7.35 – 7.14 (m, 10H). **^{13}C NMR (DMSO, 100 MHz):** δ 156.06, 142.58, 141.40, 138.35, 138.01, 135.43, 130.61, 130.21, 128.30, 127.53, 127.31, 127.11, 125.42, 124.12, 122.50, 121.26, 118.40, 117.54, 113.15, 110.59, 92.19. **HRMS (ESI):** Calcd for $C_{25}H_{16}ClN_2O$ $[M+H]^+$ 395.0946, found: 395.0943.



4-Hydroxy-7-methyl-1,2-diphenyl-9*H*-carbazole-3-carbonitrile (3ea)

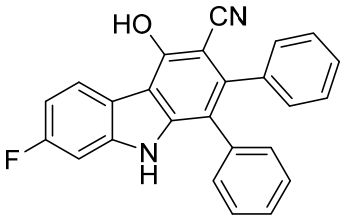
The title compound was isolated by column chromatography (eluent: EtOAc/petroleum ether = 1/5 to 1/2) as a yellow solid in 52% yield (38.9 mg, 0.104 mmol) following the general procedure A. Mp:232–234 °C. **^{1}H NMR (DMSO, 400 MHz):** δ 10.97 (s, 1H), 10.93 (s, 1H), 8.18 (d, J = 8.0 Hz, 1H), 7.31 – 7.21 (m, 7H), 7.19 – 7.14 (m, 4H), 7.08 (d, J = 8.0 Hz, 1H), 2.45 (s, 3H).**^{13}C NMR (DMSO, 100 MHz):** δ 155.50, 142.15, 140.48, 140.36, 138.43, 135.95, 135.22, 130.84, 130.49, 128.42, 127.65, 127.32, 127.14, 122.08, 121.66, 119.23, 118.44, 117.97, 111.71, 111.60, 92.01, 21.88. **HRMS (ESI):** Calcd for $C_{26}H_{19}N_2O$ $[M+H]^+$ 375.1492, found: 375.1491.



4-Hydroxy-7-methoxy-1,2-diphenyl-9*H*-carbazole-3-carbonitrile (3fa)

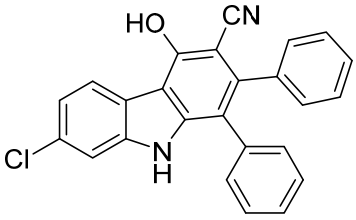
The title compound was isolated by column chromatography (eluent: EtOAc/petroleum ether = 1/5 to 1/2) as a yellow solid in 48% yield (37.6 mg, 0. 096 mmol) following the general procedure B. Mp: 257–259 °C. **^{1}H**

NMR (DMSO, 400 MHz): δ 10.96 (s, 1H), 10.85 (s, 1H), 8.18 (d, J = 8.6 Hz, 1H), 7.35 – 7.14 (m, 10H), 7.03 (d, J = 1.9 Hz, 1H), 6.88 (dd, J = 8.6, 2.1 Hz, 1H), 3.81 (s, 3H). **^{13}C NMR (DMSO, 100 MHz):** δ 158.16, 154.68, 141.97, 141.28, 139.43, 138.20, 135.73, 130.59, 130.32, 128.20, 127.43, 127.09, 126.89, 122.88, 118.13, 114.97, 111.49, 108.89, 95.17, 92.05, 55.06. **HRMS (ESI):** Calcd for $C_{26}H_{19}N_2O_2$ $[M+H]^+$ 391.1441, found: 391.1443.



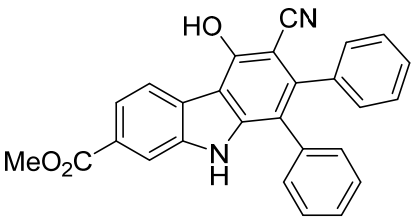
7-Fluoro-4-hydroxy-1,2-diphenyl-9H-carbazole-3-carbonitrile (3ga)

The title compound was isolated by column chromatography (eluent: EtOAc/petroleum ether = 1/5 to 1/2) as a yellow solid in 45% yield (34.1mg, 0.090 mmol) following the general procedure B. Mp: 270–272 °C. **^{1}H NMR (DMSO, 400 MHz):**.δ 11.16 (s, 1H), 11.15 – 10.97 (m, 1H), 8.36 – 8.22 (m, 1H), 7.32 – 7.21 (m, 7H), 7.17 (d, J = 5.5 Hz, 4H), 7.13 – 7.07 (m, 1H). **^{13}C NMR (DMSO, 100 MHz):** δ 161.90, 159.52, 155.33, 142.54, 140.61, 140.53, 140.48, 138.00, 135.48, 130.55, 130.22, 128.24, 127.46, 127.20, 127.02, 123.50, 123.39, 118.28, 118.02, 117.50, 111.00, 108.06, 107.82, 98.10, 97.83, 92.39. **^{19}F NMR (DMSO, 376 MHz):** δ -115.27. **HRMS (ESI):** Calcd for $C_{25}H_{16}FN_2O$ $[M+H]^+$ 379.1241, found: 379.1238.



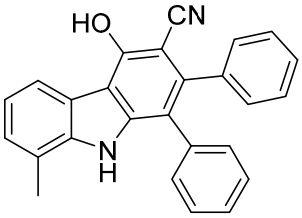
7-Chloro-4-hydroxy-1,2-diphenyl-9*H*-carbazole-3-carbonitrile (3ha)

The title compound was isolated by column chromatography (eluent: EtOAc/petroleum ether = 1/5 to 1/2) as a yellow solid in 50% yield (39.5mg, 0.100 mmol) following the general procedure B. Mp: 281–283 °C. **^{1}H NMR (DMSO, 400 MHz):** δ 11.24 (s, 1H), 11.19 (s, 1H), 8.28 (d, J = 8.4 Hz, 1H), 7.51 (s, 1H), 7.34 – 7.14 (m, 11H). **^{13}C NMR (DMSO, 100 MHz):** δ 155.71, 142.34, 141.18, 140.49, 137.97, 135.42, 130.58, 130.20, 129.88, 128.30, 127.50, 127.28, 127.11, 123.45, 120.19, 118.39, 117.45, 111.20, 110.89, 92.43. **HRMS (ESI):** Calcd for $C_{25}H_{16}ClN_2O$ $[M+H]^+$ 395.0946, found: 395.0942.



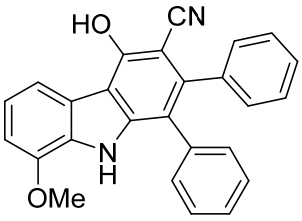
Methyl 6-cyano-5-hydroxy-7,8-diphenyl-9*H*-carbazole-2-carboxylate (3ia)

The title compound was isolated by column chromatography (eluent: EtOAc/petroleum ether = 1/5 to 1/2) as a yellow solid in 5% yield (8.3mg, 0.020 mmol) following the general procedure B. Mp: >300 °C. **^{1}H NMR (DMSO, 400 MHz):** 1H NMR (400 MHz,) δ 11.41 (s, 1H), 11.36 (s, 1H), 8.40 (d, J = 8.3 Hz, 1H), 8.17 (s, 1H), 7.88 (dd, J = 8.3, 0.8 Hz, 1H), 7.35 – 7.29 (m, 3H), 7.28 – 7.25 (m, 3H), 7.22 – 7.17 (m, 4H), 3.89 (s, 3H). **^{13}C NMR (DMSO, 100 MHz):** 13C NMR (101 MHz,) δ 166.65, 156.54, 143.28, 141.95, 139.25, 137.95, 135.36, 130.61, 130.17, 128.32, 127.53, 127.35, 127.14, 126.23, 125.12, 122.05, 120.66, 118.42, 112.97, 110.86, 92.20, 52.07. **HRMS (ESI):** Calcd for $C_{27}H_{19}N_2O_3$ $[M+H]^+$ 419.1390, found: 419.1398.



4-Hydroxy-8-methyl-1,2-diphenyl-9*H*-carbazole-3-carbonitrile (3ja)

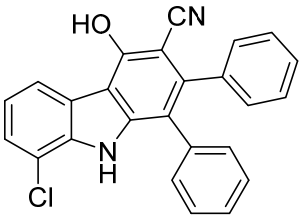
The title compound was isolated by column chromatography (eluent: EtOAc/petroleum ether = 1/5 to 1/2) as a yellow solid in 66% yield (49.3 mg, 0.132 mmol) following the general procedure A. Mp: 279–281°C. **^{1}H NMR (DMSO, 400 MHz):** δ 10.99 (s, 1H), 10.65 (s, 1H), 8.17 (d, J = 7.1 Hz, 1H), 7.31 – 7.09 (m, 12H), 2.50 (s, 3H). **^{13}C NMR (DMSO, 100 MHz):** δ 155.39, 141.91, 140.54, 138.68, 138.15, 135.40, 130.67, 129.99, 127.78, 127.16, 126.82, 126.68, 126.34, 121.16, 120.77, 120.01, 119.54, 118.55, 117.44, 111.81, 91.89, 17.32. **HRMS (ESI):** Calcd for $C_{26}H_{19}N_2O$ $[M+H]^+$ 375.1492, found: 375.1492.



4-Hydroxy-8-methoxy-1,2-diphenyl-9*H*-carbazole-3-carbonitrile (3ka)

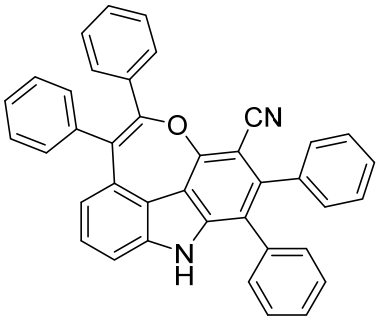
The title compound was isolated by column chromatography (eluent: EtOAc/petroleum ether = 1/5 to 1/2) as a yellow solid in 8% yield (4.7 mg, 0.012 mmol) following the general procedure B. Mp: 275–277 °C. **^{1}H NMR (DMSO, 400 MHz):** δ 11.18 – 10.92 (m, 1H), 10.86 (s, 1H), 7.91 (d, J = 7.7 Hz, 1H), 7.27 (d, J = 13.9 Hz, 1H), 7.32 – 7.08 (m, 11H), 7.02 (d, J = 7.8 Hz, 1H), 3.90 (s, 3H). **^{13}C NMR**

(DMSO, 100 MHz): δ 155.96, 145.80, 142.23, 140.80, 138.48, 135.74, 131.02, 130.42, 129.75, 128.21, 127.62, 127.30, 127.04, 122.96, 121.04, 119.26, 117.88, 114.87, 112.24, 106.82, 92.21, 55.47. **HRMS (ESI):** Calcd for $C_{26}H_{19}N_2O_2$ $[M+H]^+$ 391.1441, found: 391.1439.



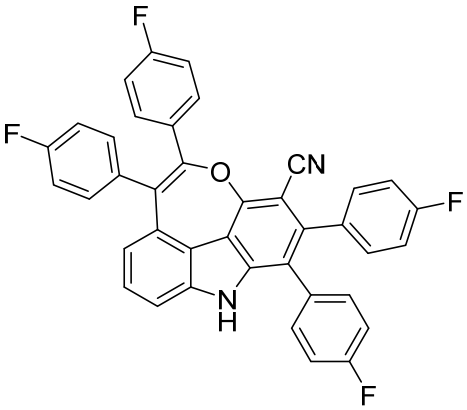
8-Chloro-4-hydroxy-1,2-diphenyl-9*H*-carbazole-3-carbonitrile (3la)

The title compound was isolated by column chromatography (eluent: EtOAc/petroleum ether = 1/5 to 1/2) as a yellow solid in 5% yield (2.96 mg, 0.0075 mmol) following the general procedure B. Mp: 256–258 °C. **^{1}H NMR (DMSO, 400 MHz):** δ 11.28 (s, 1H), 11.03 (s, 1H), 8.29 (d, J = 7.8 Hz, 1H), 7.49 (d, J = 7.5 Hz, 1H), 7.34 – 7.11 (m, 12H). **^{13}C NMR (DMSO, 100 MHz):** δ 155.99, 142.57, 142.02, 138.27, 136.82, 135.42, 131.02, 130.27, 128.15, 127.59, 127.37, 127.17, 125.66, 123.88, 121.45, 121.23, 119.38, 117.43, 115.72, 112.15, 93.14. **HRMS (ESI):** Calcd for $C_{25}H_{16}ClN_2O$ $[M+H]^+$ 395.0946, found: 395.0949.



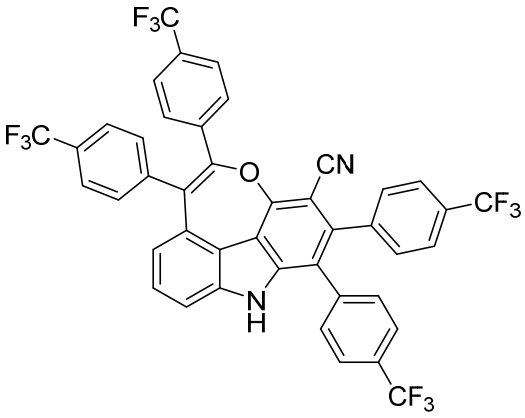
3-Chloro-5,6,9,10-tetraphenyl-4*H*-oxepino[2,3,4,5-*def*] carbazole-7-carbonitrile (4aa)

The title compound was isolated by column chromatography (eluent: EtOAc/petroleum ether = 1/5 to 1/2) as a yellow solid in 70% yield (56.3 mg, 0.105 mmol) following the general procedure B. Mp: > 300 °C. **^{1}H NMR ($CDCl_3$, 400 MHz):** δ 8.05 (s, 1H), 7.36 – 7.27 (m, 5H), 7.24 – 7.20 (m, 5H), 7.20 – 7.14 (m, 7H), 7.11 – 7.06 (m, 3H), 7.03 – 6.99 (m, 2H), 6.30 – 6.25 (m, 1H). **^{13}C NMR ($CDCl_3$, 100 MHz):** 1δ 156.04, 151.93, 142.38, 140.21, 139.18, 138.04, 137.74, 137.17, 135.28, 133.50, 131.96, 130.44, 130.07, 129.74, 128.81, 128.10, 127.82, 127.74, 127.69, 127.60, 127.30, 126.90, 122.43, 122.02, 121.48, 120.72, 115.83, 113.27, 110.98, 93.53. **HRMS (ESI):** Calcd for $C_{39}H_{28}N_3O$ $[M+NH_4]^+$ 554.2227, found: 554.2230.



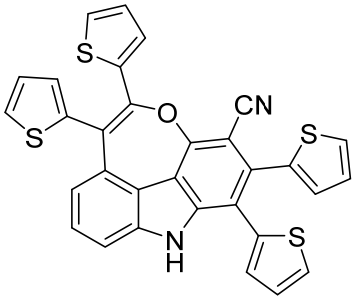
5,6,9,10-Tetrakis(4-fluorophenyl)-4*H*-oxepino[2,3,4,5-*def*]carbazole-7-carbonitrile (4ad)

The title compound was isolated by column chromatography (eluent: EtOAc/petroleum ether = 1/5 to 1/2) as a yellow solid in 63% yield (57.6 mg, 0.095mmol) following the general procedure B. Mp: > 300 °C. **^{1}H NMR (DMSO, 400 MHz):**δ 11.38 (s, 1H), 7.36 (dd, J = 8.5, 5.7 Hz, 2H), 7.25 – 7.16 (m, 9H), 7.13 – 7.06 (m, 5H), 7.01 (t, J = 8.8 Hz, 2H), 6.08 (d, J = 7.5 Hz, 1H). **^{13}C NMR (DMSO, 100 MHz):**δ 163.64, 163.24, 163.13, 161.17, 160.80, 160.70, 155.61, 151.04, 141.40, 139.93, 135.72, 135.38, 134.53, 134.46, 134.38, 133.44, 133.36, 133.29, 133.20, 132.90, 132.77, 132.69, 132.00, 128.37, 122.67, 121.94, 121.72, 120.87, 116.51, 116.44, 116.22, 116.18, 115.97, 115.81, 115.59, 115.52, 115.30, 113.59, 113.31, 92.52. **^{19}F NMR (DMSO, 376 MHz):** δ -112.89, -114.13, -114.55, -114.76. **HRMS (ESI):** Calcd for $C_{39}H_{24}F_4N_3O$ $[M+NH_4]^+$ 626.1850, found: 626.1851.



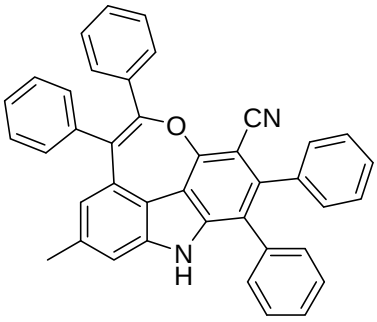
5,6,9,10-Tetrakis(4-(trifluoromethyl)phenyl)-4*H*-oxepino[2,3,4,5-*def*]carbazole-7-carbonitrile (4ag)

The title compound was isolated by column chromatography (eluent: EtOAc/petroleum ether = 1/5 to 1/2) as a yellow solid in 62% yield (74.8mg, 0.180 mmol) following the general procedure B. Mp: > 300 °C. **^{1}H NMR (DMSO, 400 MHz):** δ 8.13 – 8.05 (m, 8H), 8.01 – 7.91 (m, 8H), 7.73 (d, J = 8.2 Hz, 1H), 7.61 (s, 1H), 6.61 (d, J = 7.5 Hz, 1H). **^{13}C NMR (DMSO, 100 MHz):** δ 157.50, 152.44, 144.85, 143.86, 143.57, 142.70, 142.63, 141.35, 141.28, 134.75, 134.10, 133.46, 133.39, 132.67, 131.46, 131.28, 131.13, 130.81, 130.02, 127.58, 127.28, 126.87, 126.62, 125.02, 124.59, 123.84, 122.73, 122.69, 116.79, 115.27, 114.98, 94.75. **^{19}F NMR (DMSO, 376 MHz):** δ -63.03, -63.09, -63.25. **HRMS (ESI):** Calcd for $C_{39}H_{24}F_{12}N_3O$ $[M+NH_4]^+$ 826.1722, found: 826.1726.



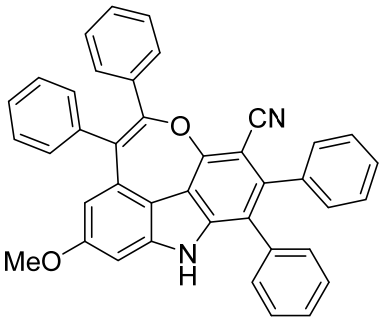
5,6,9,10-Tetra(thiophen-2-yl)-4*H*-oxepino[2,3,4,5-*def*] carbazole-7-carbonitrile (4ah)

The title compound was isolated by column chromatography (eluent: EtOAc/petroleum ether = 1/5 to 1/2) as a yellow solid in 39% yield (32.8 mg, 0.078 mmol) following the general procedure B. Mp: 280–282 °C. **^{1}H NMR (DMSO, 400 MHz):** δ 11.66 (s, 1H), 7.82 (d, J = 5.1 Hz, 1H), 7.68 – 7.54 (m, 4H), 7.30 (d, J = 8.1 Hz, 1H), 7.25 – 7.13 (m, 6H), 7.11 – 7.07 (m, 1H), 7.00 – 6.96 (m, 1H), 6.34 (d, J = 7.6 Hz, 1H). **^{13}C NMR (DMSO, 100 MHz):** δ 154.98, 145.80, 140.67, 139.31, 139.17, 138.67, 137.24, 134.75, 134.71, 132.42, 131.49, 130.51, 130.27, 129.54, 129.37, 128.71, 128.36, 128.15, 127.90, 127.33, 126.98, 126.15, 121.65, 119.18, 116.10, 115.30, 113.52, 112.91, 92.93. **HRMS (ESI):** Calcd for $C_{31}H_{20}N_3OS_4$ $[M+NH_4]^+$ 578.0484, found: 578.0477.



2-Methyl-5,6,9,10-tetraphenyl-4*H*-oxepino[2,3,4,5-*def*] carbazole-7-carbonitrile (4ea)

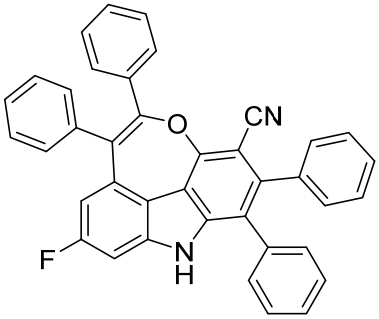
The title compound was isolated by column chromatography (eluent: EtOAc/petroleum ether = 1/5 to 1/2) as a yellow solid in 65% yield (53.6 mg, 0.097 mmol) following the general procedure B. Mp: 300–301 °C. **^{1}H NMR ($CDCl_3$, 400 MHz):** δ 7.94 (s, 1H), 7.35 – 7.26 (m, 5H), 7.24 – 7.13 (m, 12H), 7.08 (d, J = 6.6 Hz, 3H), 6.81 (s, 1H), 6.10 (s, 1H), 2.21 (s, 3H). **^{13}C NMR ($CDCl_3$, 100 MHz):** δ 155.62, 152.04, 141.88, 140.13, 139.15, 138.28, 138.18, 137.66, 137.26, 135.40, 132.99, 131.99, 130.48, 130.09, 129.74, 128.78, 128.05, 127.80, 127.67, 127.62, 127.54, 127.28, 126.87, 123.61, 122.32, 120.65, 119.24, 115.90, 113.31, 110.97, 93.36, 22.22. **HRMS (ESI):** Calcd for $C_{40}H_{27}N_2O$ $[M+H]^+$ 551.2118, found: 551.2125.



2-Methoxy-5,6,9,10-tetraphenyl-4*H*-oxepino[2,3,4,5-*def*] carbazole-7-carbonitrile (5fa)

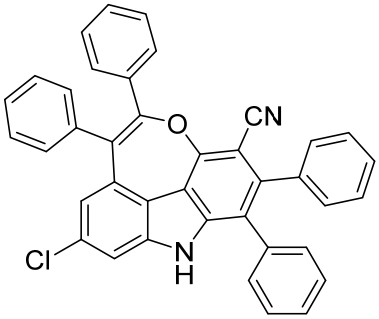
The title compound was isolated by column chromatography (eluent: EtOAc/petroleum ether = 1/5 to 1/2) as a yellow solid

in 57% yield (58.4 mg, 0.085 mmol) following the general procedure B. Mp: 277–278 °C. **^{1}H NMR ($CDCl_3$, 400 MHz):** δ 8.05 (s, 1H), 7.40 – 7.36 (m, 3H), 7.34 (d, J = 5.0 Hz, 2H), 7.27 (s, 4H), 7.26 – 7.19 (m, 7H), 7.15 (d, J = 6.1 Hz, 3H), 6.56 (s, 1H), 6.01 (s, 1H), 3.73 (s, 3H). **^{13}C NMR ($CDCl_3$, 100 MHz):** δ 160.28, 154.88, 152.65, 141.08, 140.11, 138.95, 138.88, 138.12, 137.25, 135.38, 134.14, 131.91, 130.51, 130.06, 129.70, 128.76, 128.09, 127.79, 127.69, 127.63, 127.52, 127.29, 126.94, 121.63, 120.63, 115.92, 115.07, 113.34, 112.28, 93.97, 55.44. **HRMS (ESI):** Calcd for $C_{40}H_{27}N_2O_2$ $[M+H]^+$ 567.2067, found: 567.2072.



2-Fluoro-5,6,9,10-tetraphenyl-4*H*-oxepino[2,3,4,5-*def*] carbazole-7-carbonitrile (4ga)

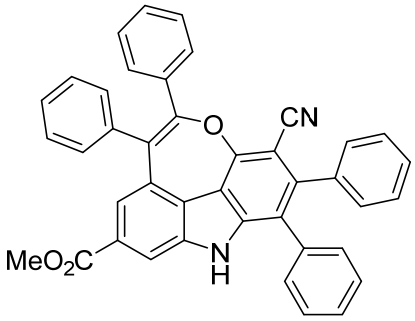
The title compound was isolated by column chromatography (eluent: EtOAc/petroleum ether = 1/5 to 1/2) as a yellow solid in 62% yield (51.5mg, 0.093 mmol) following the general procedure B. Mp: > 300 °C. **^{1}H NMR ($CDCl_3$, 400 MHz):** δ 8.06 (s, 1H), 7.35 – 7.26 (m, 5H), 7.25 – 7.12 (m, 12H), 7.09 (d, J = 4.6 Hz, 3H), 6.73 – 6.66 (m, 1H), 6.04 (d, J = 11.6 Hz, 1H). **^{13}C NMR ($CDCl_3$, 100 MHz):** δ 164.06, 161.66, 155.32, 153.10, 142.19, 140.65, 138.54, 138.07, 137.94, 137.79, 136.98, 135.03, 134.97, 134.87, 131.81, 130.41, 129.99, 129.64, 128.89, 128.31, 127.93, 127.87, 127.82, 127.73, 127.37, 127.20, 121.31, 120.92, 117.75, 115.61, 113.05, 110.80, 110.53, 97.71, 97.43, 93.99. **^{19}F NMR ($CDCl_3$, 376 MHz):** 19F NMR (376 MHz,) δ -112.58. **HRMS (ESI):** Calcd for $C_{39}H_{27}FN_3O$ $[M+NH_4]^+$ 572.2133, found: 572.2134.



2-Chloro-5,6,9,10-tetraphenyl-4*H*-oxepino[2,3,4,5-*def*] carbazole-7-carbonitrile (4ha)

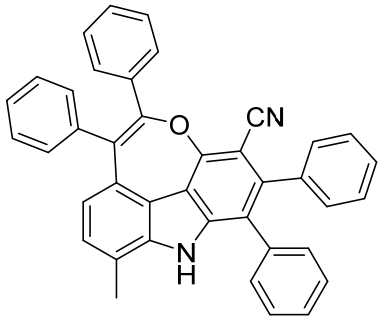
The title compound was isolated by column chromatography (eluent: EtOAc/petroleum ether = 1/5 to 1/2) as a white solid in 69% yield (59.2mg, 0.104 mmol) following the general procedure B. Mp: > 300 °C. **^{1}H NMR ($CDCl_3$, 400 MHz):** δ 8.14 (s, 1H), 7.35 – 7.29 (m, 5H), 7.27 – 7.21 (m, 6H), 7.20 – 7.15 (m, 5H), 7.15 – 7.13 (m, 1H), 7.10 (dd, J = 5.1, 1.9 Hz, 3H), 7.02 (d, J = 1.5 Hz, 1H), 6.26 (d, J = 1.5 Hz, 1H). **^{13}C**

NMR ($CDCl_3$, 100 MHz): δ 155.59, 153.05, 142.68, 140.51, 138.37, 138.08, 137.79, 136.94, 134.93, 134.49, 133.08, 131.79, 130.34, 129.99, 129.59, 128.85, 128.34, 127.87, 127.71, 127.34, 127.23, 122.32, 121.37, 120.98, 119.98, 115.60, 112.94, 110.89, 93.91. **HRMS (ESI):** Calcd for $C_{39}H_{27}ClN_3O$ $[M+NH_4]^+$ 588.1837, found: 588.1841.



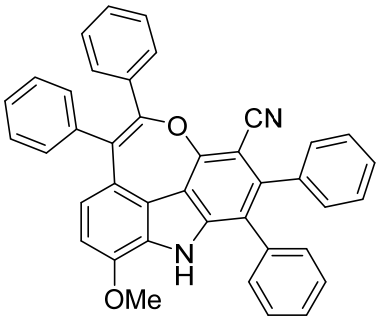
Methyl 7-cyano-5,6,9,10-tetraphenyl-4*H*-oxepino [2,3,4,5-*def*]carbazole-2-carboxylate (4ia)

The title compound was isolated by column chromatography (eluent: EtOAc/petroleum ether = 1/5 to 1/2) as a white solid in 68% yield (60.8mg, 0.0102 mmol) following the general procedure B. Mp: > 300 °C. **^{1}H NMR ($CDCl_3$, 400 MHz):** δ 8.26 (s, 1H), 7.80 (d, J = 1.0 Hz, 1H), 7.37 – 7.30 (m, 5H), 7.28 (s, 1H), 7.26 – 7.23 (m, 5H), 7.22 – 7.15 (m, 7H), 7.11 (dd, J = 5.2, 1.9 Hz, 3H), 7.01 (d, J = 1.0 Hz, 1H), 3.80 (s, 3H). **^{13}C NMR ($CDCl_3$, 100 MHz):**δ 166.89, 156.44, 152.48, 143.64, 141.50, 138.55, 137.85, 137.22, 136.90, 134.89, 133.34, 131.79, 130.31, 130.01, 129.69, 129.06, 128.90, 128.34, 127.90, 127.79, 127.35, 127.26, 125.15, 122.76, 122.10, 120.96, 115.49, 113.00, 112.86, 94.03, 52.20. **HRMS (ESI):** Calcd for $C_{41}H_{30}N_3O_3$ $[M+NH_4]^+$ 612.2282, found: 612.2292.



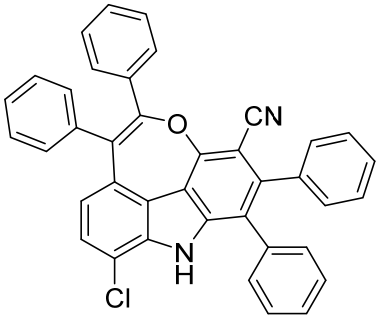
3-Methyl-5,6,9,10-tetraphenyl-4*H*-oxepino[2,3,4,5-*def*] carbazole-7-carbonitrile (4ja)

The title compound was isolated by column chromatography (eluent: EtOAc/petroleum ether = 1/5 to 1/2) as a white solid in 78% yield (64.1 mg, 0.116 mmol) following the general procedure B. Mp: > 300 °C. **^{1}H NMR ($CDCl_3$, 400 MHz):** δ 11.10 (s, 1H), 7.33 – 7.26 (m, 5H), 7.25 – 7.09 (m, 15H), 6.89 (d, J = 7.8 Hz, 1H), 6.04 (d, J = 7.7 Hz, 1H), 2.39 (s, 3H). **^{13}C NMR ($CDCl_3$, 100 MHz):** δ 154.73, 149.71, 141.60, 140.50, 138.73, 138.32, 137.88, 137.57, 134.82, 131.44, 130.59, 130.06, 129.64, 129.50, 128.05, 127.78, 127.54, 127.49, 127.34, 127.26, 126.89, 122.93, 122.60, 121.85, 121.53, 119.81, 115.66, 112.99, 91.80, 17.18. **HRMS (ESI):** Calcd for $C_{40}H_{30}N_3O$ $[M+NH_4]^+$ 568.2383, found: 568.2392.



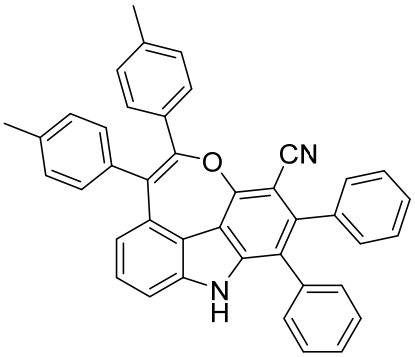
3-Methoxy-5,6,9,10-tetraphenyl-4*H*-oxepino[2,3,4,5-*def*] carbazole-7-carbonitrile (4ka)

The title compound was isolated by column chromatography (eluent: EtOAc/petroleum ether = 1/5 to 1/2) as a white solid in 77% yield (65.7 mg, 0.116 mmol) following the general procedure B. Mp: > 300 °C. **^{1}H NMR ($CDCl_3$, 400 MHz):** δ 8.15 (s, 1H), 7.36 – 7.27 (m, 5H), 7.24 – 7.14 (m, 12H), 7.09 (d, J = 7.3 Hz, 3H), 6.45 (d, J = 8.3 Hz, 1H), 6.21 (d, J = 8.2 Hz, 1H), 3.86 (s, 3H). **^{13}C NMR ($CDCl_3$, 100 MHz):** 13C NMR (101 MHz,) δ 156.05, 149.88, 145.76, 142.23, 139.82, 139.48, 138.20, 137.23, 135.28, 131.94, 130.47, 130.14, 129.84, 128.77, 128.02, 127.92, 127.80, 127.70, 127.54, 127.46, 127.25, 126.80, 125.84, 123.12, 122.42, 122.05, 120.78, 115.89, 113.31, 106.56, 93.53, 55.44. **HRMS (ESI):** Calcd for $C_{40}H_{30}N_3O_2$ $[M+NH_4]^+$ 584.2333, found: 584.2342.



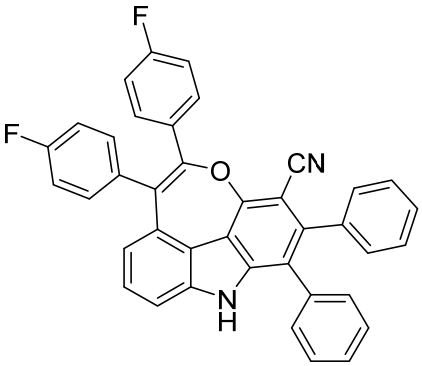
3-Chloro-5,6,9,10-tetraphenyl-4H-oxepino[2,3,4,5-def] carbazole-7-carbonitrile (4la)

The title compound was isolated by column chromatography (eluent: EtOAc/petroleum ether = 1/5 to 1/2) as a white solid in 60% yield (51.4 mg, 0.090 mmol) following the general procedure B. Mp: > 300 °C. **^{1}H NMR ($CDCl_3$, 400 MHz):** δ 11.39 (s, 1H), 7.37 – 7.07 (m, 20H), 6.92 (dd, J = 9.1, 1.7 Hz, 1H), 5.80 – 5.76 (m, 1H). **^{13}C NMR ($CDCl_3$, 100 MHz):** δ 162.89, 160.52, 154.12, 152.20, 141.32, 140.89, 139.40, 139.26, 137.88, 137.64, 137.19, 134.62, 133.75, 133.65, 131.33, 130.18, 130.09, 129.36, 128.34, 128.21, 127.87, 127.62, 127.56, 127.40, 127.34, 127.18, 121.59, 121.12, 116.56, 115.38, 112.08, 109.03, 108.75, 98.65, 98.39, 92.03. **HRMS (ESI):** Calcd for $C_{39}H_{27}ClN_3O$ $[M+NH_4]^+$ 588.1837, found: 588.1840.



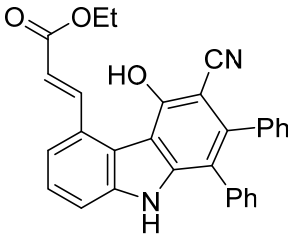
5,6-Diphenyl-9,10-di-p-tolyl-4H-oxepino[2,3,4,5-def] carbazole-7-carbonitrile (4ak)

The title compound was isolated by column chromatography (eluent: EtOAc/petroleum ether = 1/5 to 1/2) as a white solid in 94% yield (53.3 mg, 0.094 mmol) following the general procedure C. Mp: > 300 °C. **^{1}H NMR ($CDCl_3$, 400 MHz):** δ 8.00 (s, 1H), 7.33 – 7.27 (m, 3H), 7.24 – 7.14 (m, 8H), 7.09 – 6.99 (m, 6H), 6.90 (d, *J* = 8.1 Hz, 2H), 6.30 (dd, *J* = 5.7, 2.6 Hz, 1H), 2.31 (s, 3H), 2.22 (s, 3H). **^{13}C NMR ($CDCl_3$, 100 MHz):** δ 156.29, 151.70, 142.36, 140.18, 137.75, 137.37, 137.25, 136.44, 136.40, 135.37, 135.30, 133.91, 131.78, 131.42, 130.47, 130.10, 129.73, 129.06, 128.87, 128.80, 127.99, 127.81, 127.71, 127.57, 127.23, 122.35, 122.06, 121.53, 120.58, 115.93, 113.53, 110.68, 93.54, 29.69, 21.23. **HRMS (ESI):** Calcd for $C_{41}H_{28}N_2NaO$ $[M+Na]^+$ 587.2094, found: 587.2098.



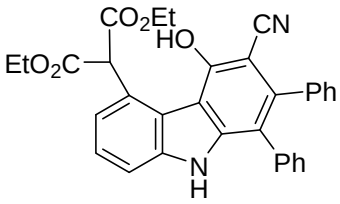
9,10-Bis(4-fluorophenyl)-5,6-diphenyl-4H-oxepino[2,3,4 ,5-def]carbazole-7-carbonitrile (4al)

The title compound was isolated by column chromatography (eluent: EtOAc/petroleum ether = 1/5 to 1/2) as a white solid in 89% yield (51.1 mg, 0.089 mmol) following the general procedure C. Mp: > 300 °C. **^{1}H NMR ($CDCl_3$, 400 MHz):** δ 8.07 (s, 1H), 7.33 – 7.28 (m, 5H), 7.24 – 7.21 (m, 3H), 7.19 – 7.10 (m, 6H), 7.07 – 7.02 (m, 2H), 6.94 (t, *J* = 8.6 Hz, 2H), 6.80 (t, *J* = 8.7 Hz, H), 6.25 (dd, *J* = 4.8, 3.5 Hz, 1H). **^{13}C NMR ($CDCl_3$, 100 MHz):** δ 163.04, 162.97, 160.52, 155.75, 151.04, 142.46, 140.25, 137.82, 137.07, 135.17, 135.02, 134.99, 134.12, 133.53, 133.45, 133.17, 131.66, 131.58, 130.40, 130.05, 128.85, 127.87, 127.83, 127.68, 127.37, 121.90, 121.77, 121.35, 120.93, 115.76, 115.44, 115.23, 114.66, 114.45, 113.17, 111.26, 93.61. **^{19}F NMR (DMSO, 376 MHz):** δ -117.33, -119.20. **HRMS (ESI):** Calcd for $C_{39}H_{22}F_2N_2NaO$ $[M+Na]^+$ 595.1592, found: 595.1598.



Ethyl (E)-3-(6-cyano-5-hydroxy-7,8-diphenyl-9H-carbazol-4-yl) acrylate (6aa)

The title compound was isolated by column chromatography (eluent: EtOAc/petroleum ether = 1/5 to 1/2) as a yellow solid in 38% yield (17.5 mg, 0.038 mmol) following the general procedure C. Mp: 250–252 °C. **^{1}H NMR ($CDCl_3$, 400 MHz):** δ 11.52 (s), 11.27 (s), 9.60 (d, *J* = 15.8 Hz), 7.68 (d, *J* = 7.4 Hz), 7.63 (d, *J* = 8.0 Hz), 7.45 (t, *J* = 7.7 Hz), 7.34 – 7.24 (m), 7.19 (d, *J* = 4.7 Hz), 6.56 (d, *J* = 15.8 Hz), 4.26 (q, *J* = 7.1 Hz), 1.33 (t, *J* = 7.0 Hz). **^{13}C NMR ($CDCl_3$, 100 MHz):** δ 166.51, 155.03, 147.02, 142.78, 141.36, 140.87, 137.92, 135.47, 130.75, 130.14, 129.08, 128.32, 127.51, 127.30, 127.17, 125.92, 120.61, 119.28, 118.50, 117.84, 113.54, 111.89, 93.25, 59.81, 14.30. **HRMS (ESI):** Calcd for $C_{30}H_{26}N_3O_3$ $[M+NH_4]^+$ 476.1969, found: 476.1974.



Diethyl 2-(6-cyano-5-hydroxy-7,8-diphenyl-9H-carbazol-4-yl) malonate (8aa)

The title compound was isolated by column chromatography (eluent: EtOAc/petroleum ether = 1/5 to 1/2) as a yellow solid in 37% yield (19.4 mg, 0.037 mmol) following the general procedure D. Mp: 216–218 °C. **^{1}H NMR ($CDCl_3$, 400 MHz):** δ 11.56 (s), 11.27 (s), 7.58 (d, *J* = 8.1 Hz), 7.45 (t, *J* = 7.8 Hz), 7.36 – 7.25 (m), 7.23 – 7.17 (m), 7.14 (d, *J* = 7.5 Hz), 6.78 (s), 4.30 – 4.17 (m), 1.25 (t, *J* = 7.1 Hz). **^{13}C NMR ($CDCl_3$, 100 MHz):** δ 166.51, 155.03, 147.02, 142.78, 141.36, 140.87, 137.92, 135.47, 130.75, 130.14, 129.08, 128.32, 127.51, 127.30, 127.17, 125.92, 120.61, 119.28, 118.50, 117.84, 113.54, 111.89, 93.25, 59.81, 14.30. **HRMS (ESI):** Calcd for $C_{32}H_{27}N_2O_5$ $[M+NH_4]^+$ 519.1914, found: 519.1915.

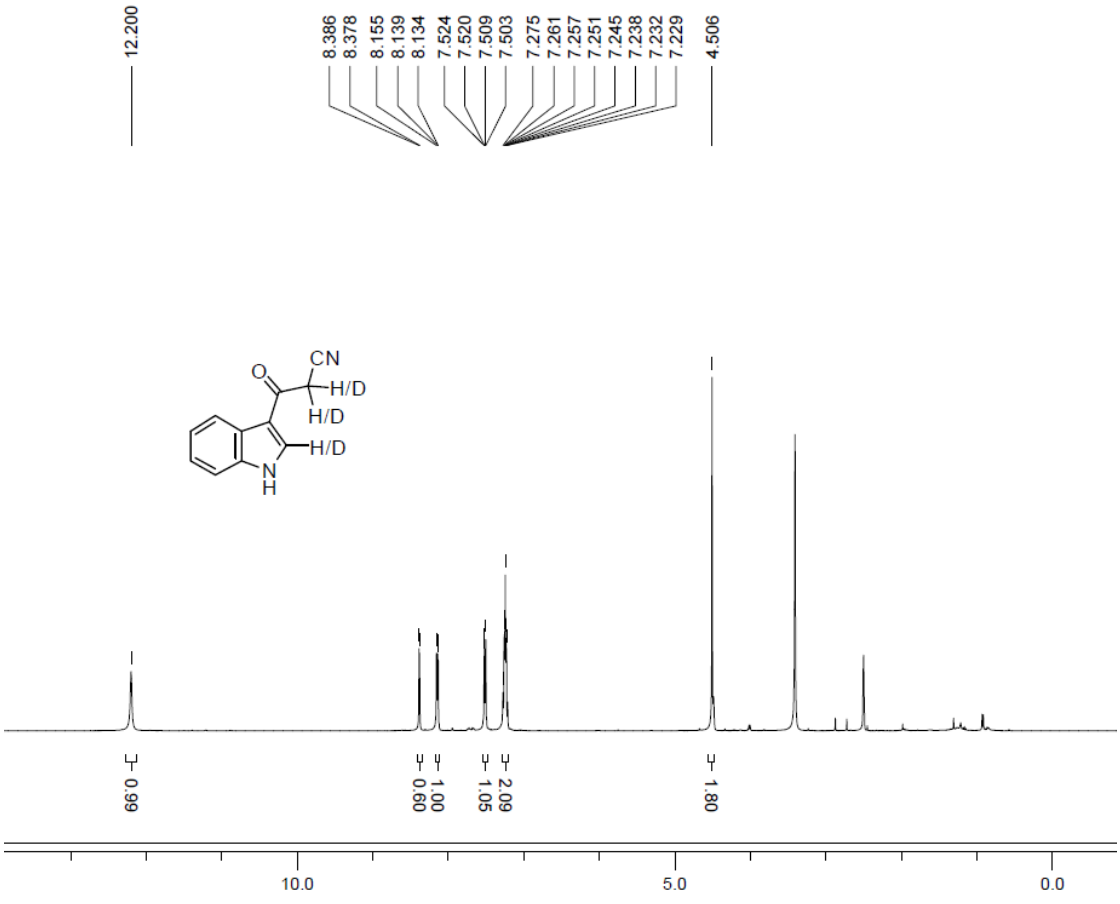
Mechanism Research:

Reaction (eq 3)

An oven-dried reaction vessel was charged with $[Cp^*RhCl_2]_2$ (6.2 mg, 0.01 mmol), $Cu(OAc)_2 \cdot H_2O$ (80 mg, 0.4 mmol), 4-hydroxy-1,2-diphenyl-9*H*-carbazole-3-carbonitrile **3aa** (86.4 mg, 0.24 mmol), alkyne (**2a**) (35.6 mg 0.2 mmol) DMF (0.5 mL) under Ar. The vessel was sealed and heated at 100 °C (oil bath) for 12 h. After removal of solvents, the residue was purified by flash column chromatography on silica gel (eluent: DCM/petroleum ether = 1:2). **4aa** was obtained in 93% yield.

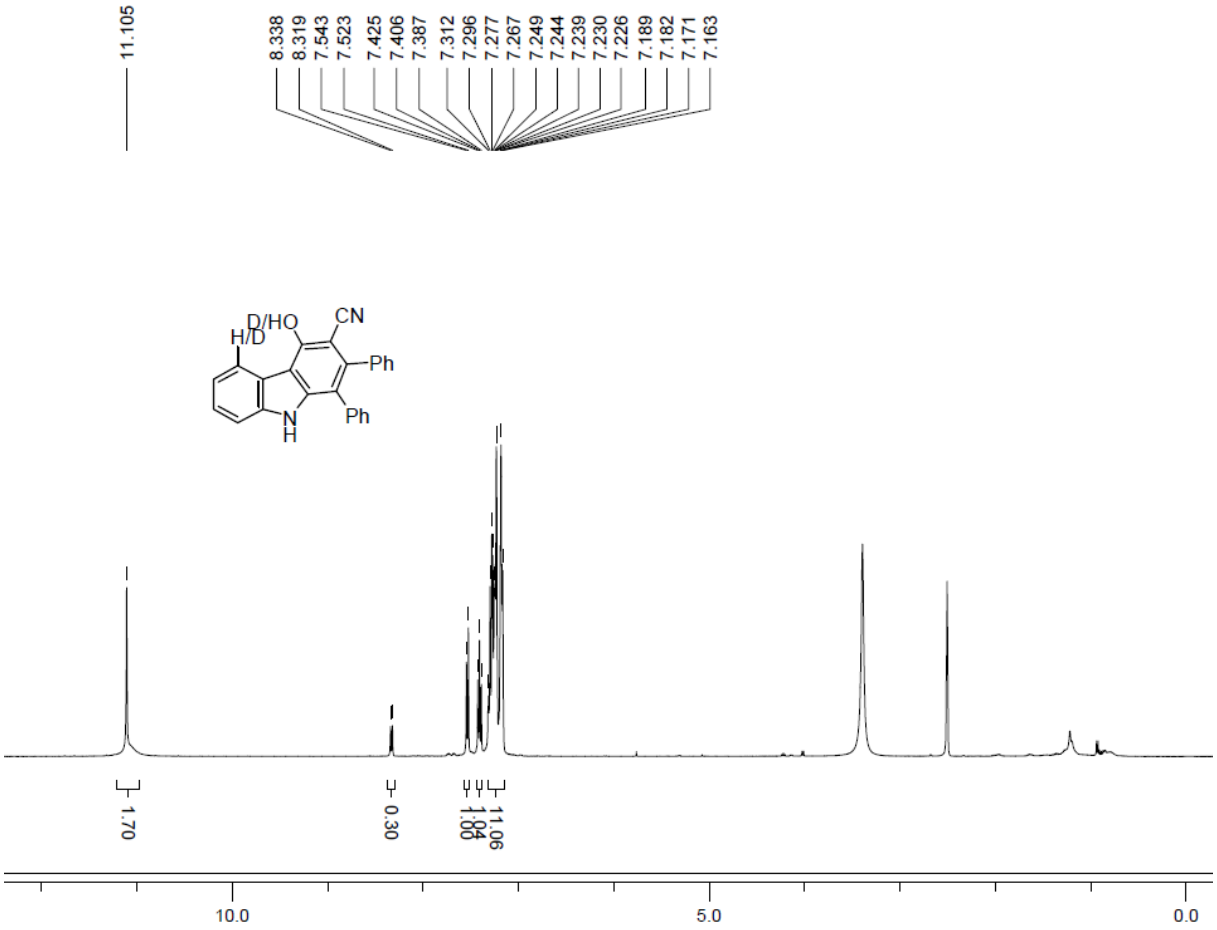
H/D Exchange Reaction (eq 5).

An oven-dried reaction vessel was charged with $[Cp^*RhCl_2]_2$ (6.2 mg, 0.01 mmol), $Cu(OAc)_2 \cdot H_2O$ (100 mg, 0.5 mmol), 3-(1*H*-indol-3-yl)-3-oxopropanenitrile **1a** (36.8 mg, 0.2 mmol), DMF (0.5 mL), and CD_3OD (0.15 mL) under Ar. The vessel was sealed and heated at 100 °C (oil bath) for 1 h. After removal of solvents, the residue was purified by flash column chromatography on silica gel (eluent: EtOAc/ petroleum ether = 1:2). **1a** was recovered in 90% yield.



H/D Exchange Reaction (eq 6).

An oven-dried reaction vessel was charged with $[Cp^*RhCl_2]_2$ (3.1 mg, 0.005 mmol), $Cu(OAc)_2 \cdot H_2O$ (50 mg, 0.25 mmol), 4-hydroxy-1,2-diphenyl-9*H*-carbazole-3-carbonitrile **3aa** (36.6 mg, 0.1 mmol), DMF (0.5 mL), and CD_3OD (0.15 mL) under Ar. The vessel was sealed and heated at 100 °C (oil bath) for 1 h. After removal of solvents, the residue was purified by flash column chromatography on silica gel (eluent: EtOAc/ petroleum ether = 1:2). **1a** was recovered in 90% yield.



X-ray crystallography:

CCDC-1537356 (**3ad**) and 1537357 (**4aa**), contain the supplementary crystallographic data. These data can be obtained free of charge from The Cambridge Crystallographic Data Centre via www.ccdc.cam.ac.uk/data_request/cif.

Figure S1. The molecular structure of **3ad**. Thermal ellipsoids are shown at the 30% level. Hydrogen atoms have been omitted for clarity.

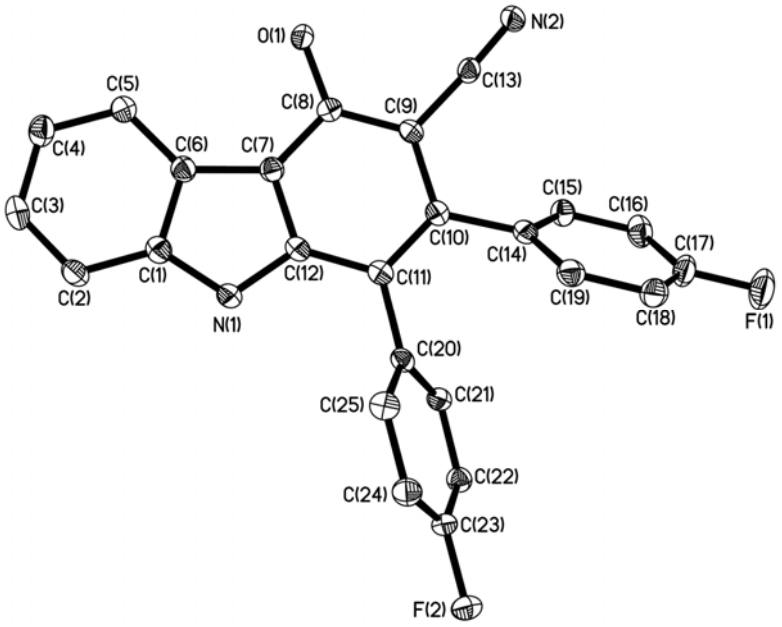
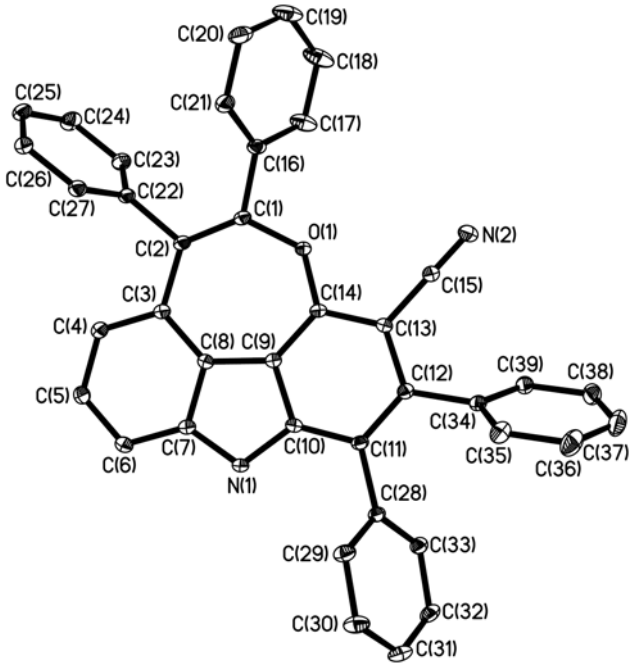


Figure S2. The molecular structure of **4aa**. Thermal ellipsoids are shown at the 30% level. Hydrogen atoms have been omitted for clarity.



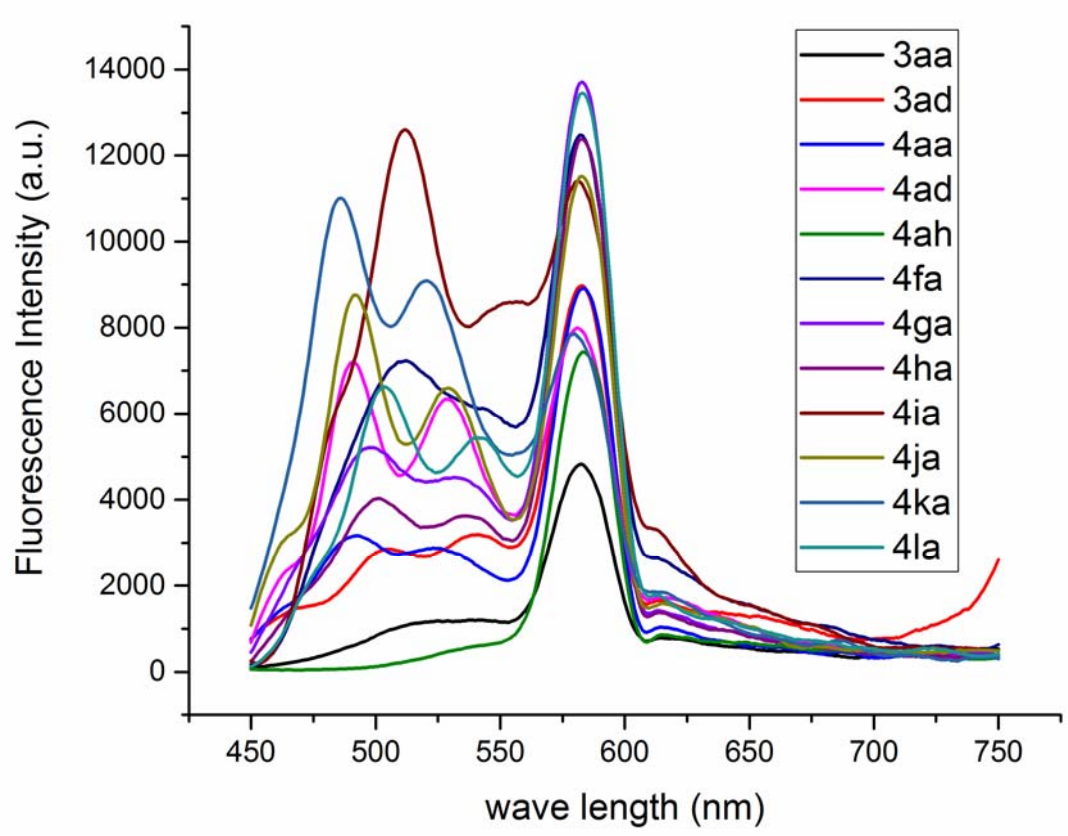
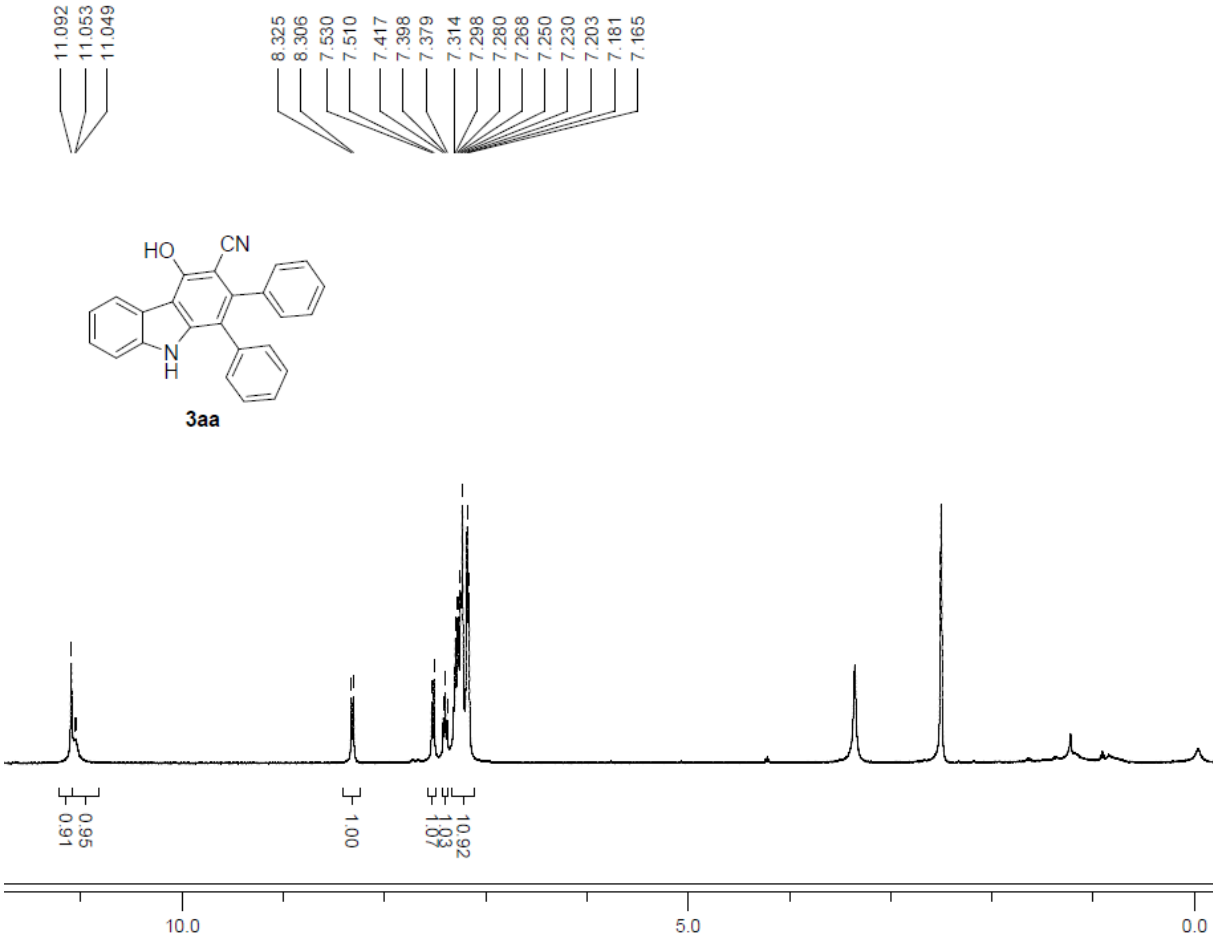
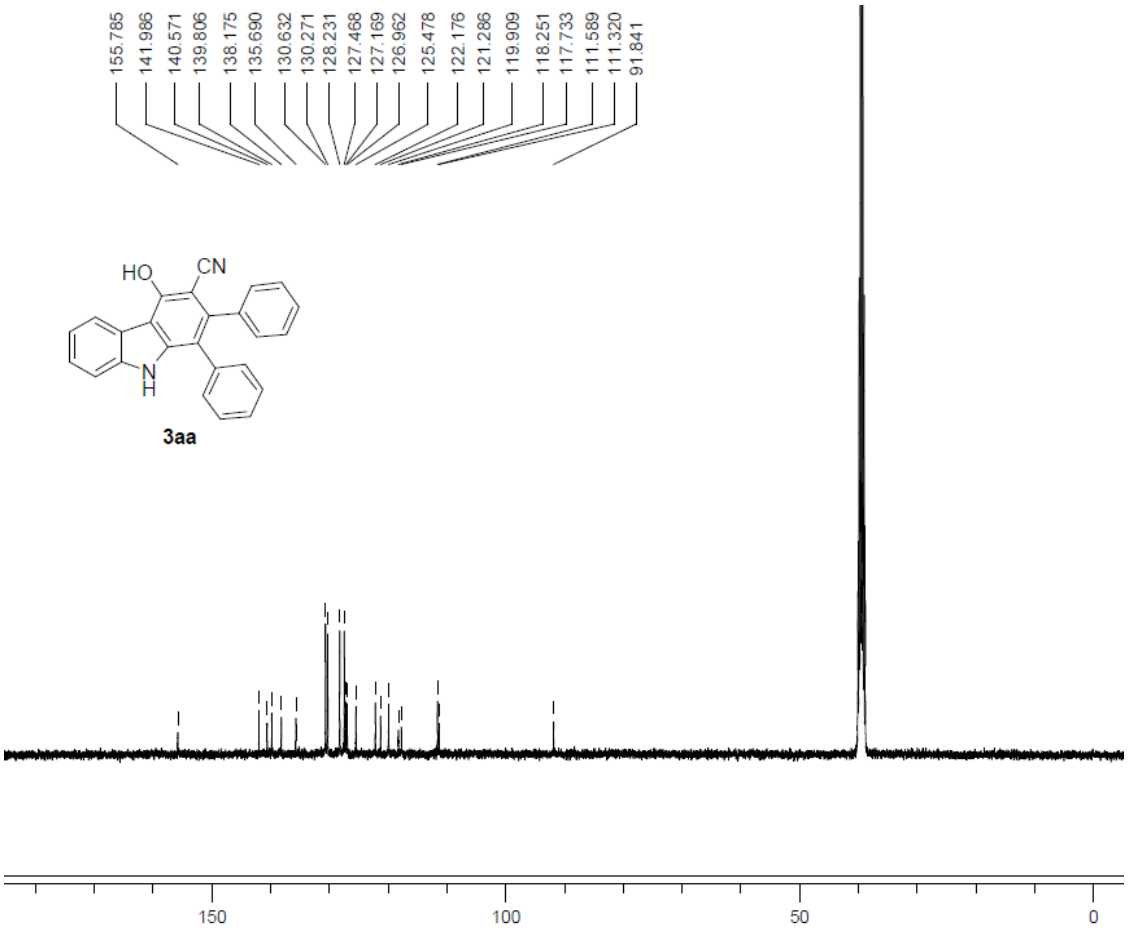


Figure S3. Fluorescence spectra of **3aa**,**3ad, 4aa, 4ah** and **4fa-4la** in the solid-state.

Spectral Copies of ^{1}H, ^{13}C, and ^{19}F NMR of Compounds Obtained in This Study

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122.176
121.286
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CN
N
H
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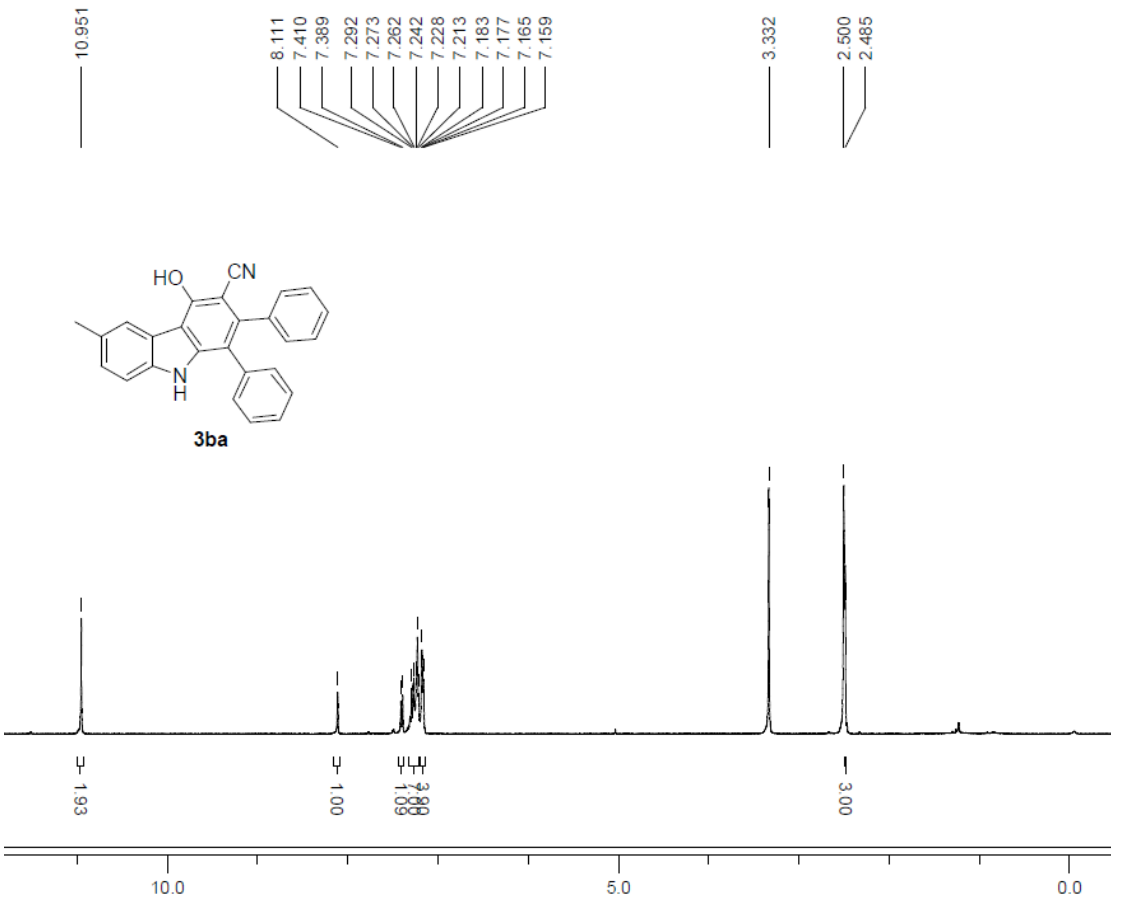
100
50
0

3aa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7.165
7.159
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H
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3.00
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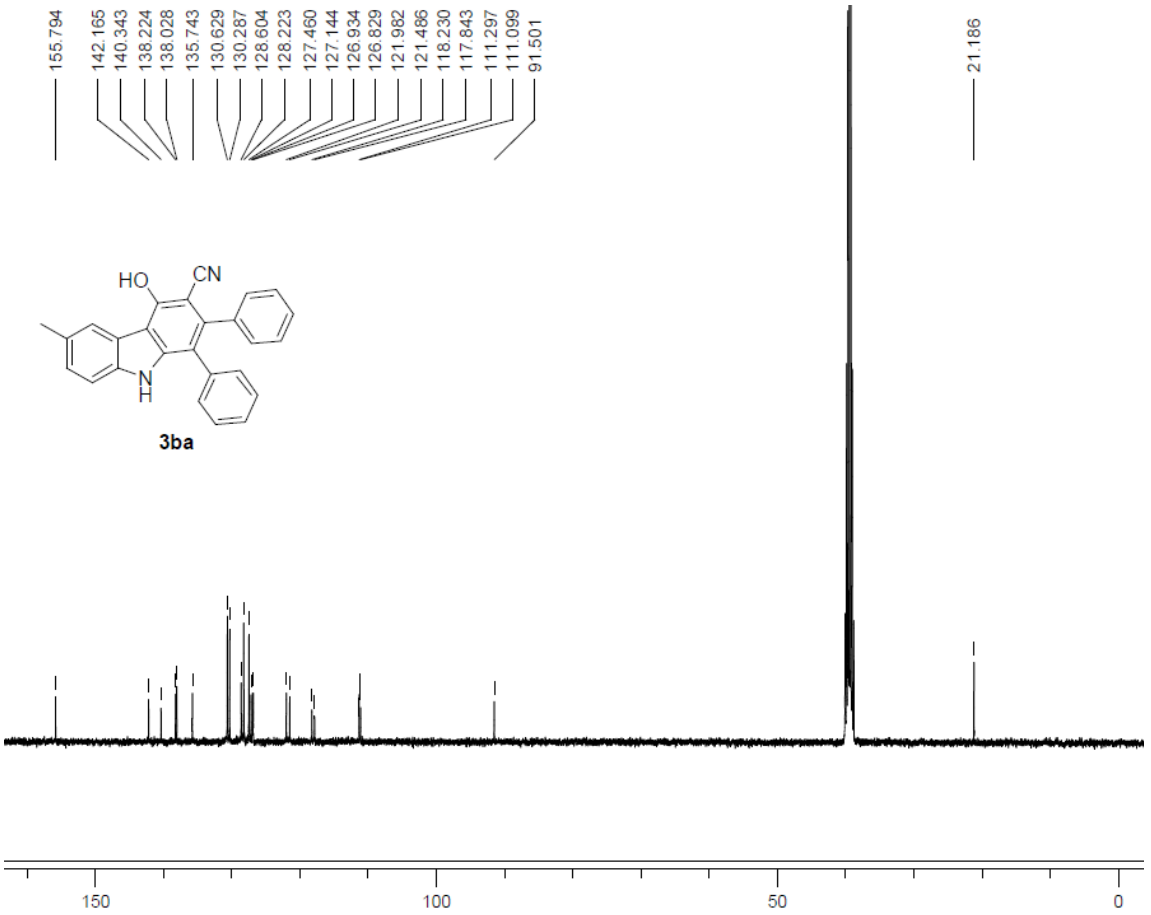
3ba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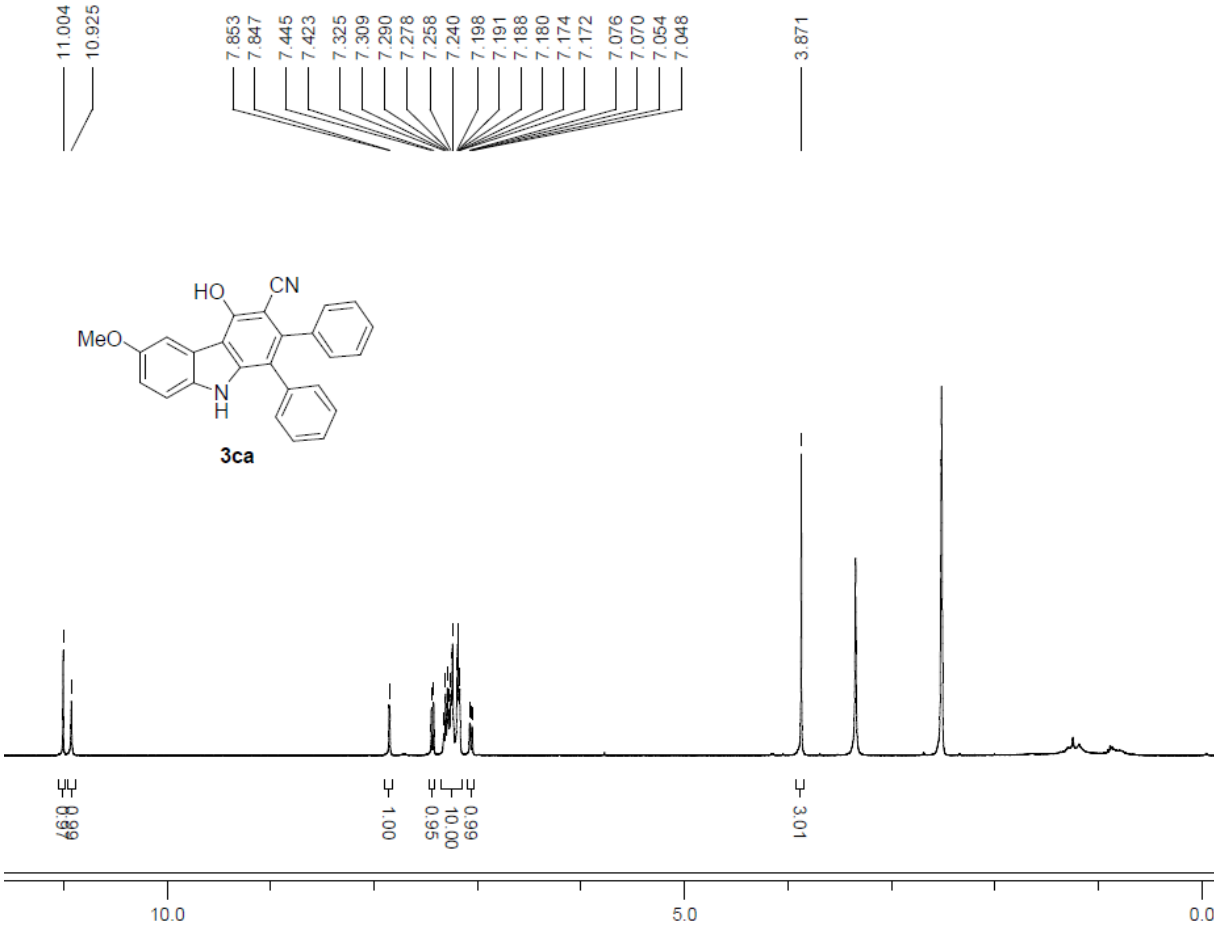
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MeO
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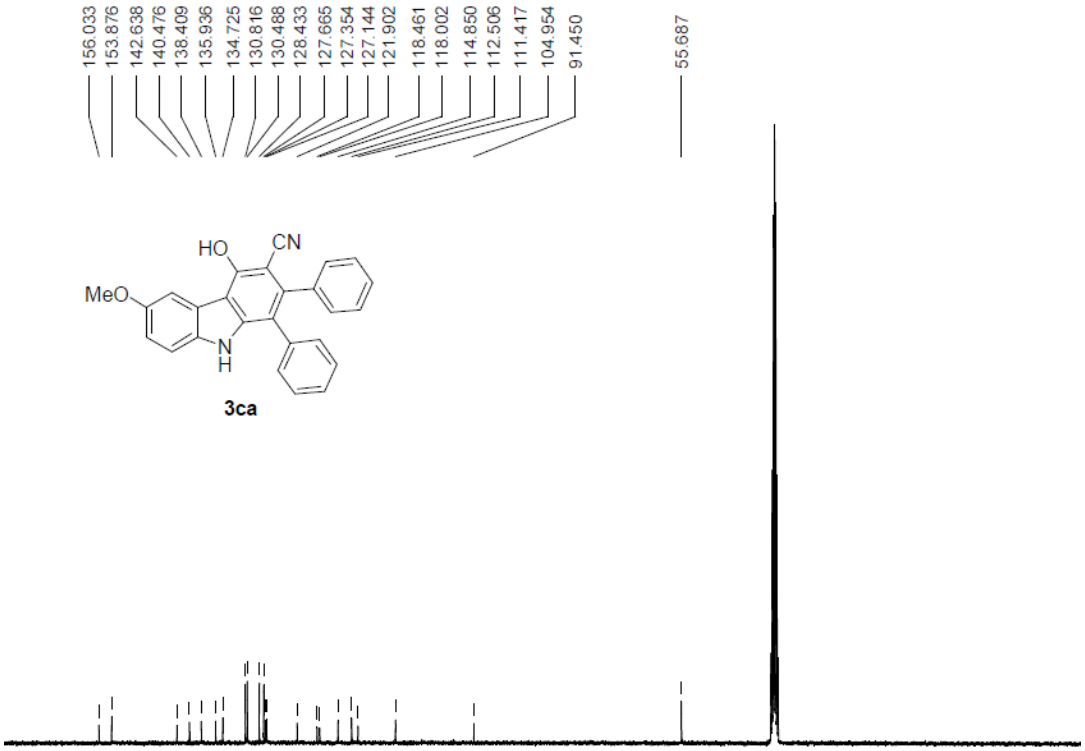
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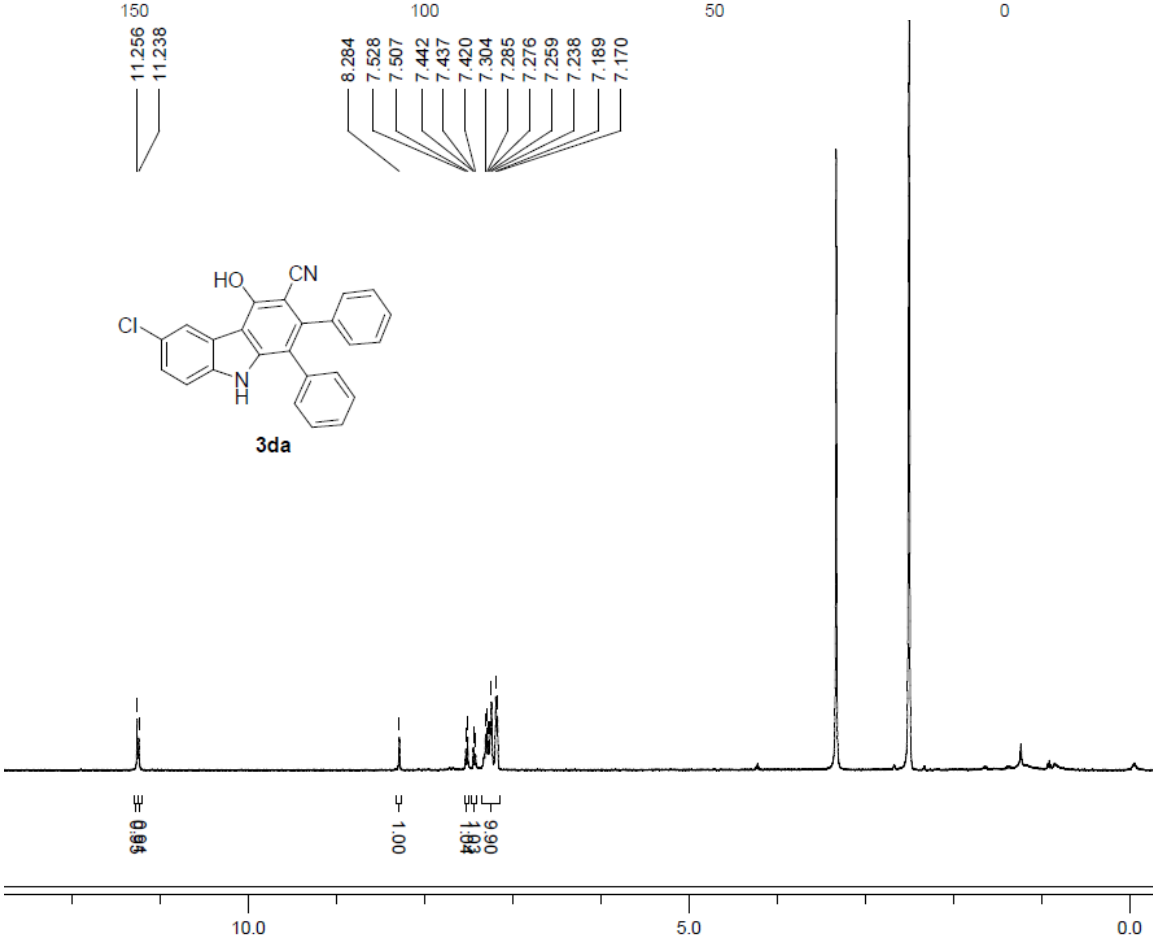
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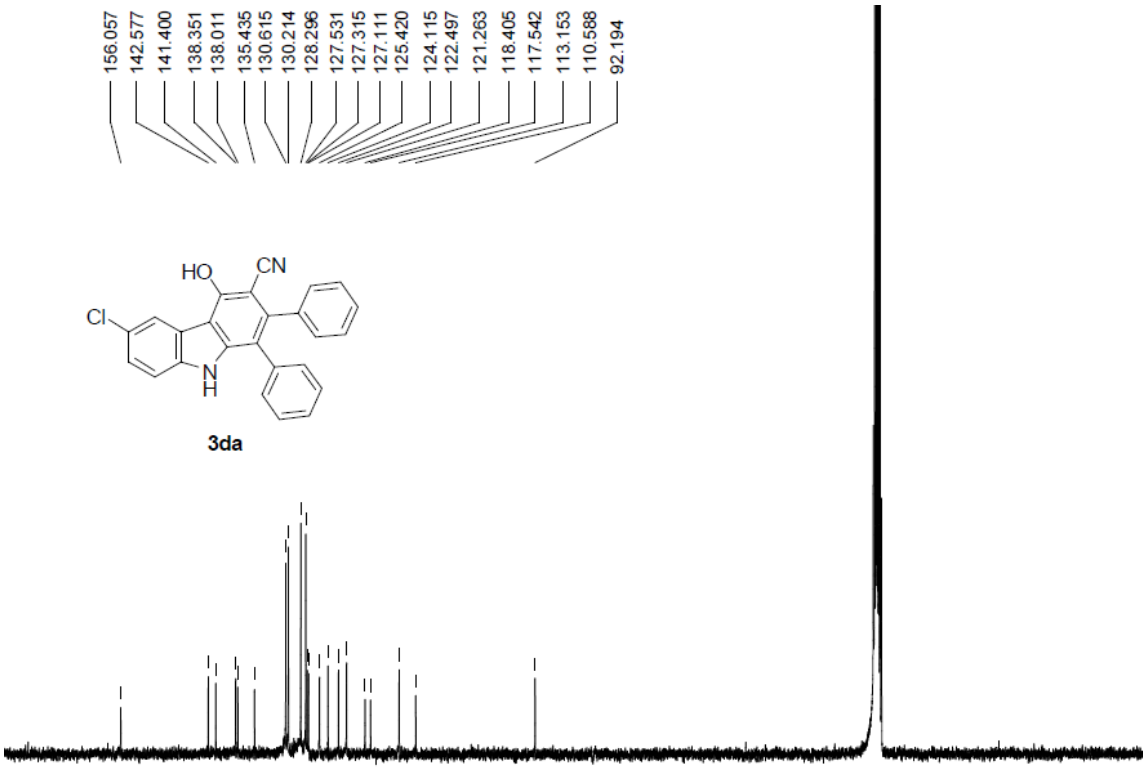
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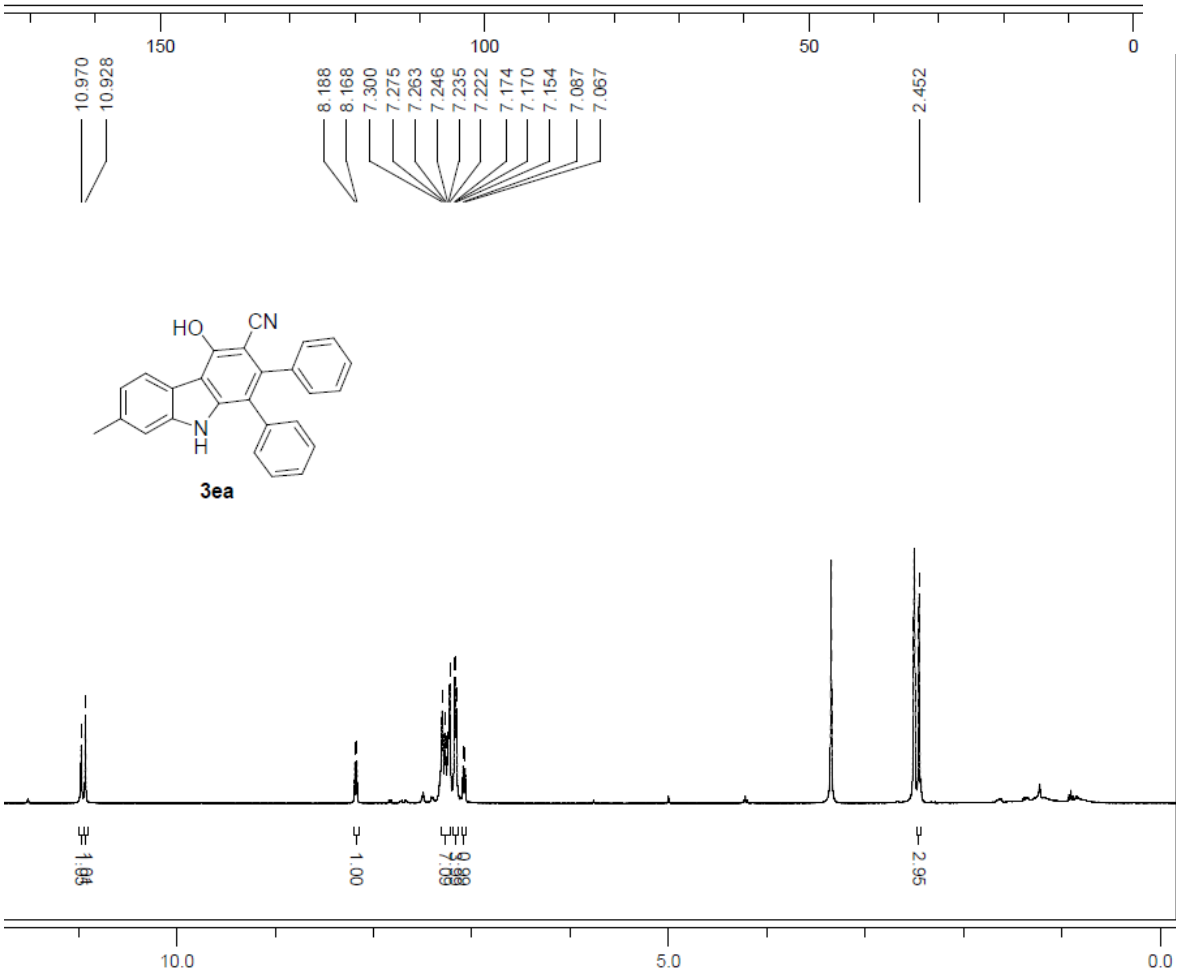
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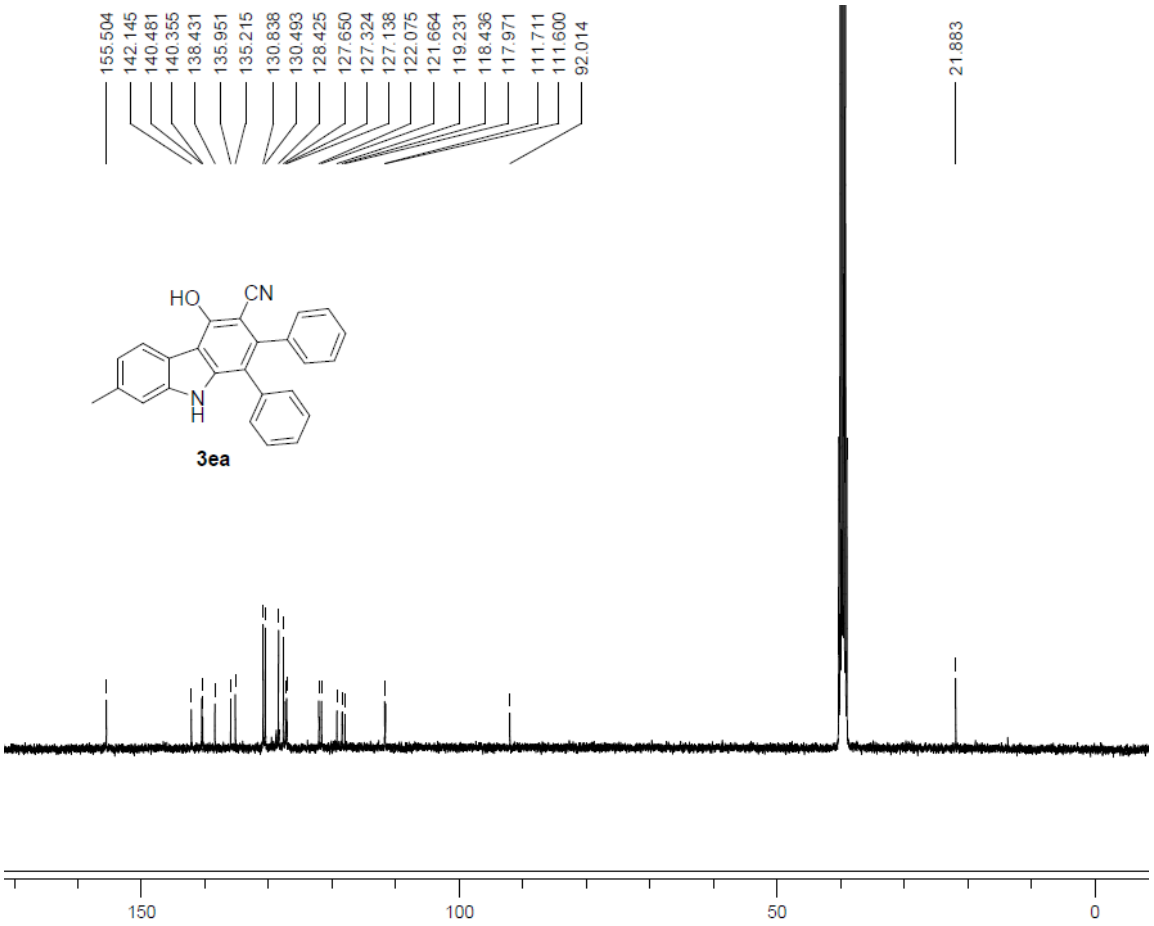
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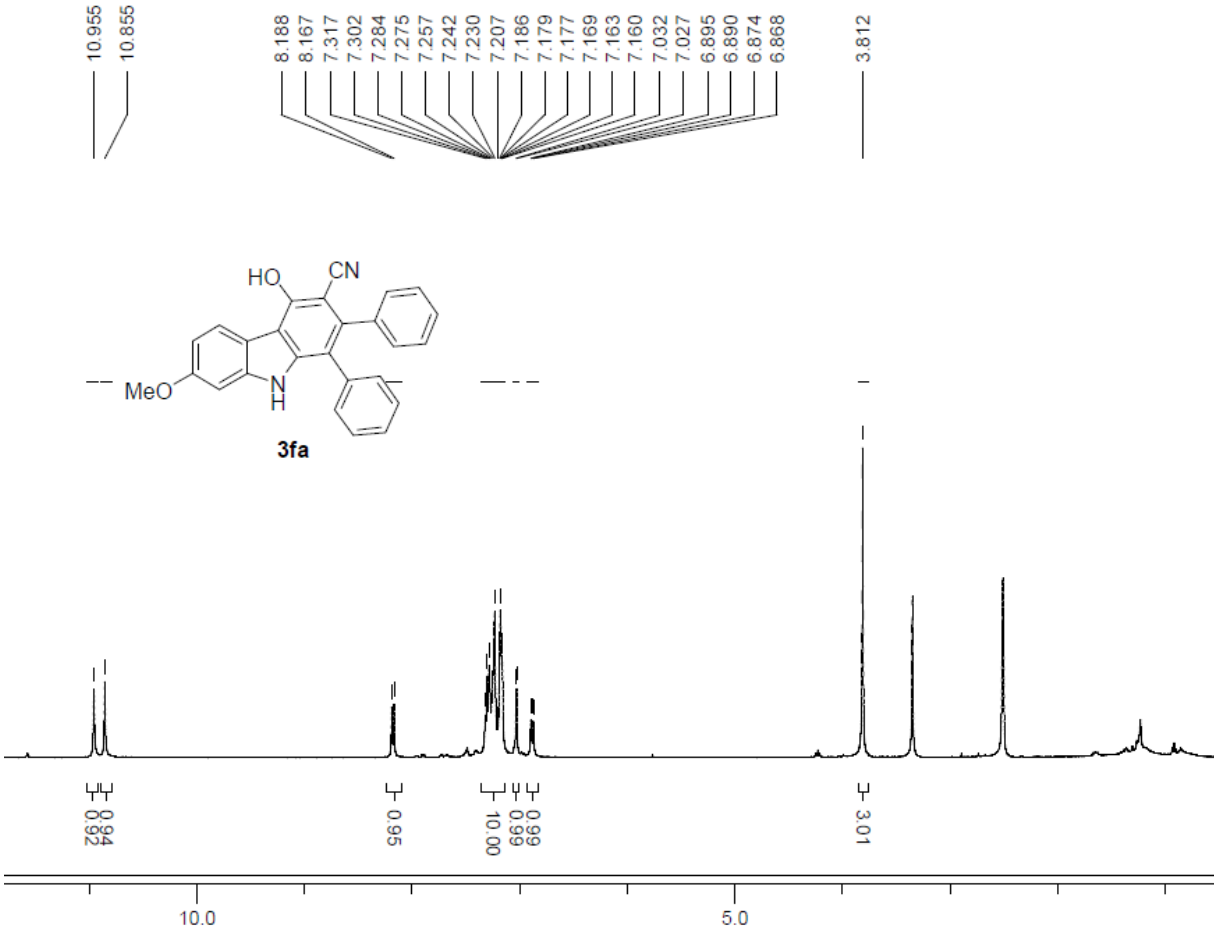
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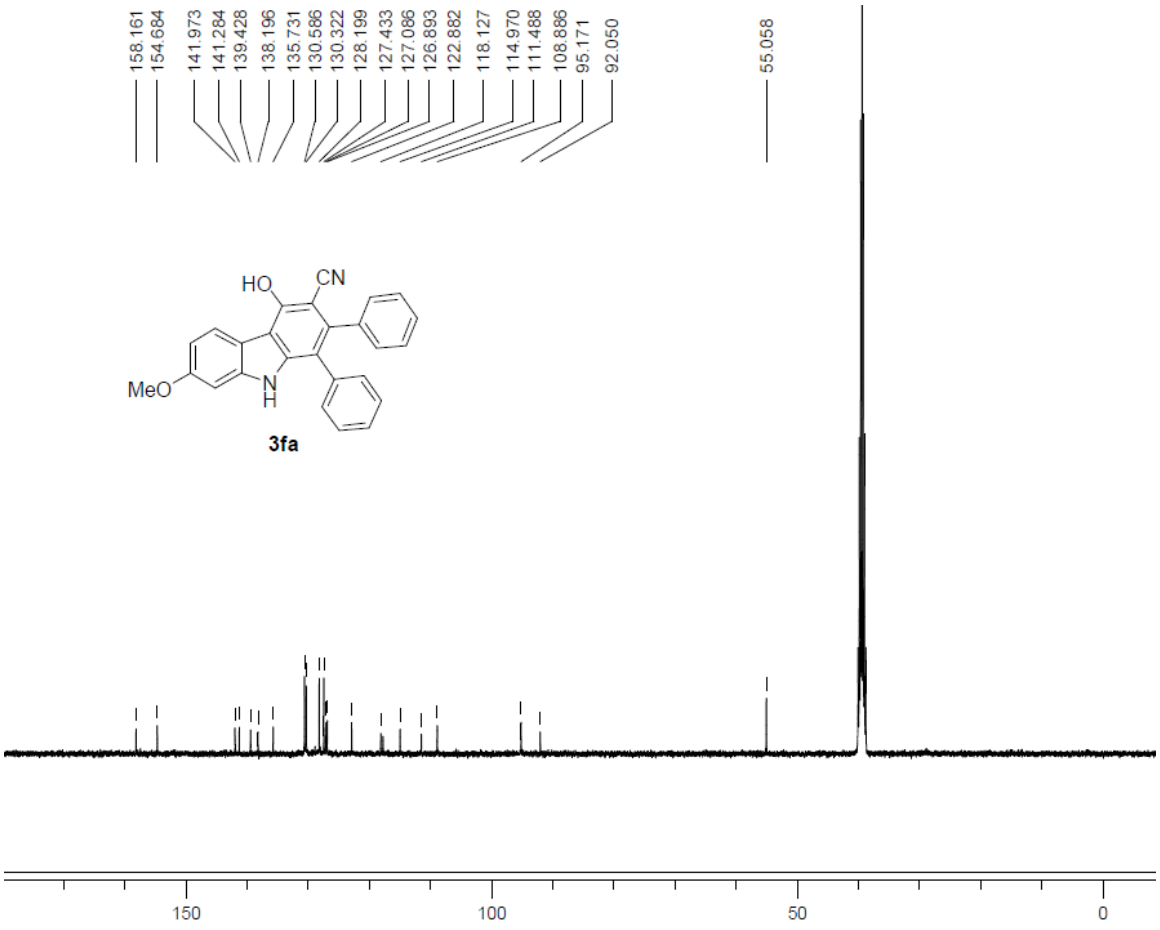
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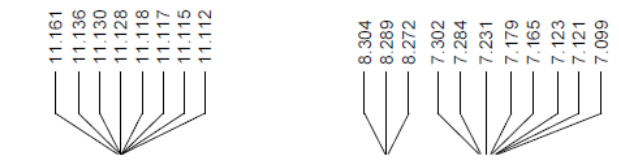
3fa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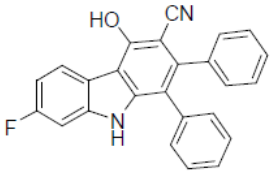
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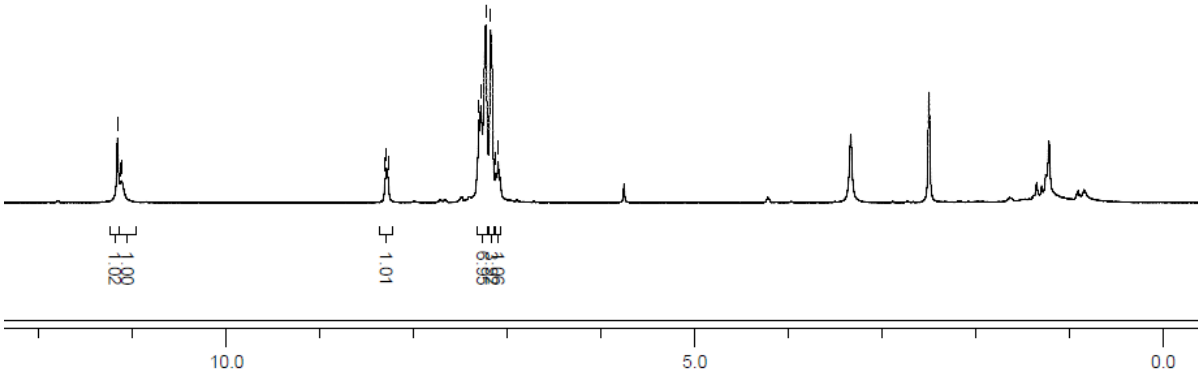
3ga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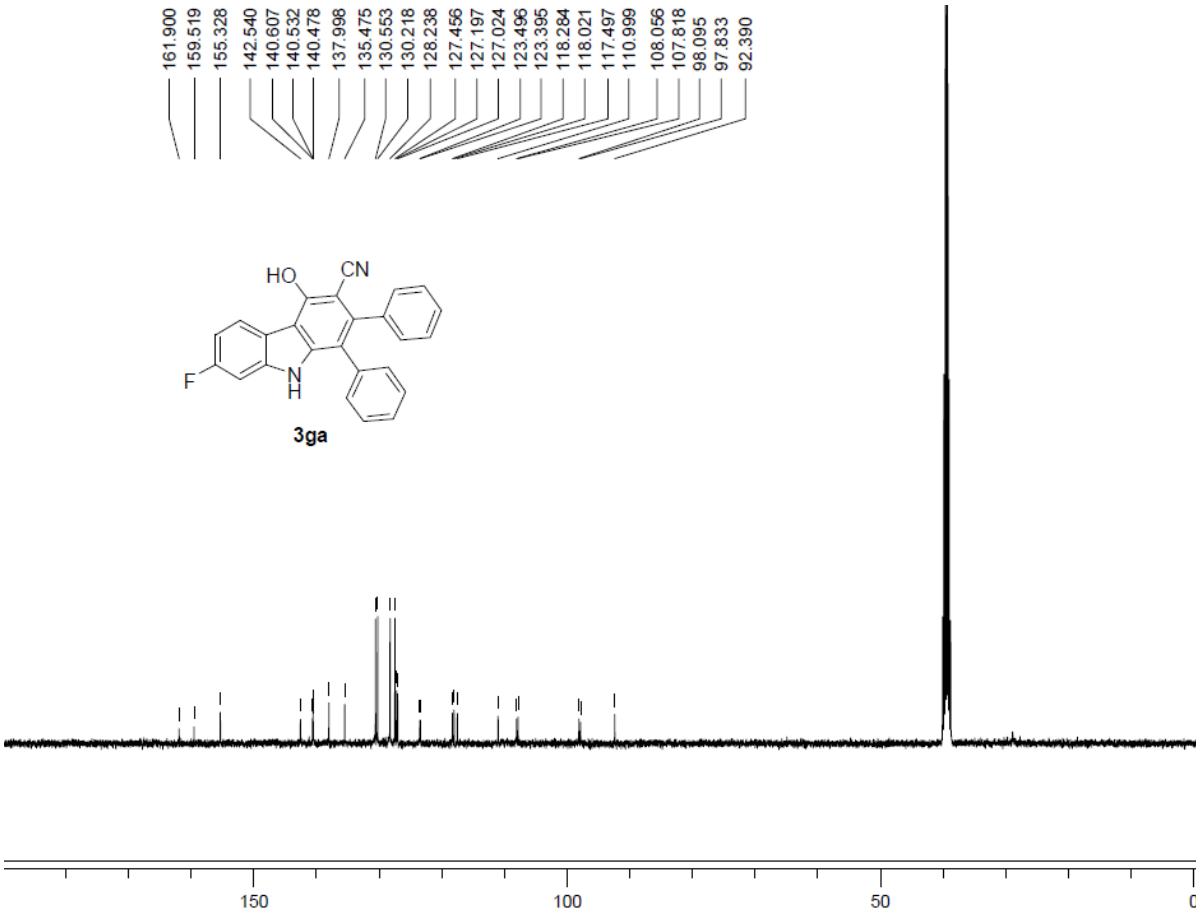
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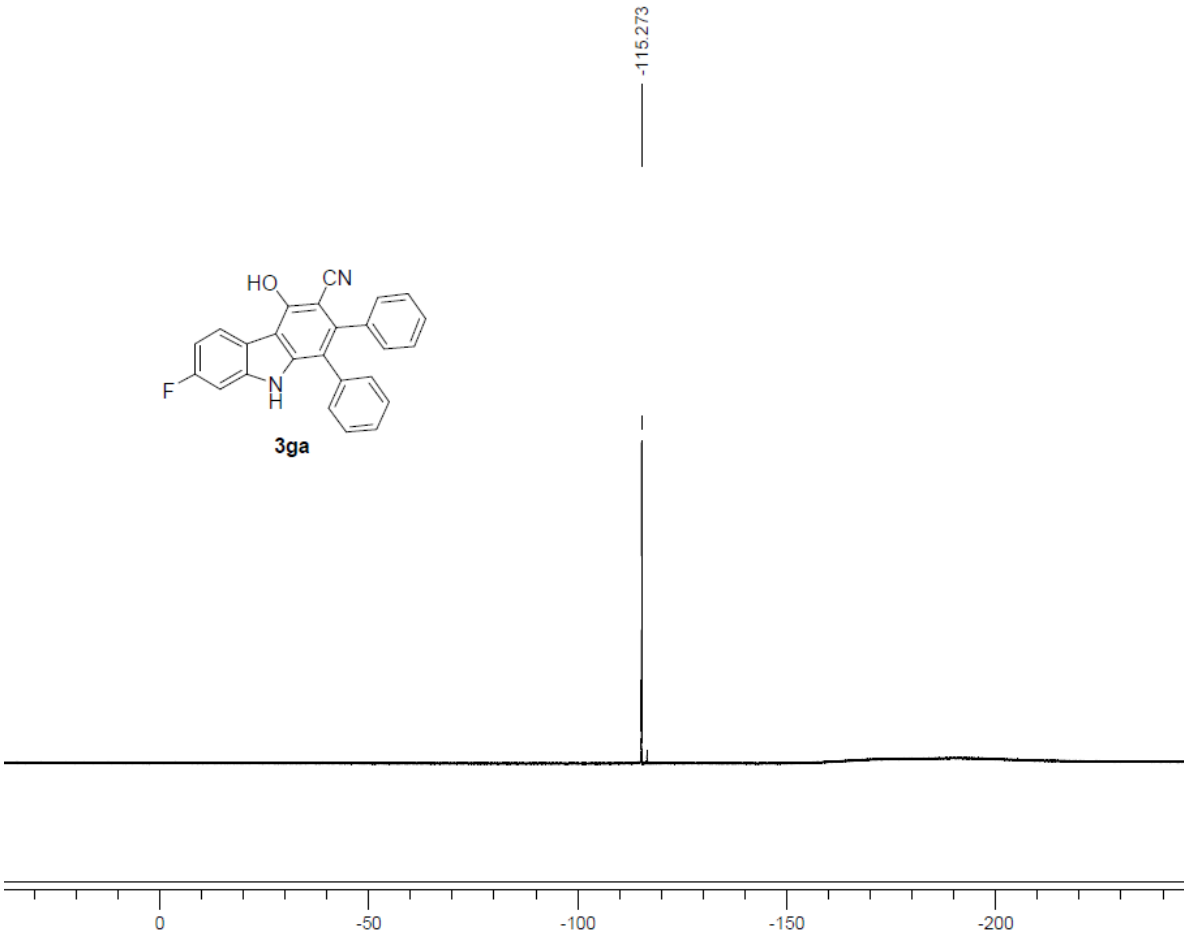
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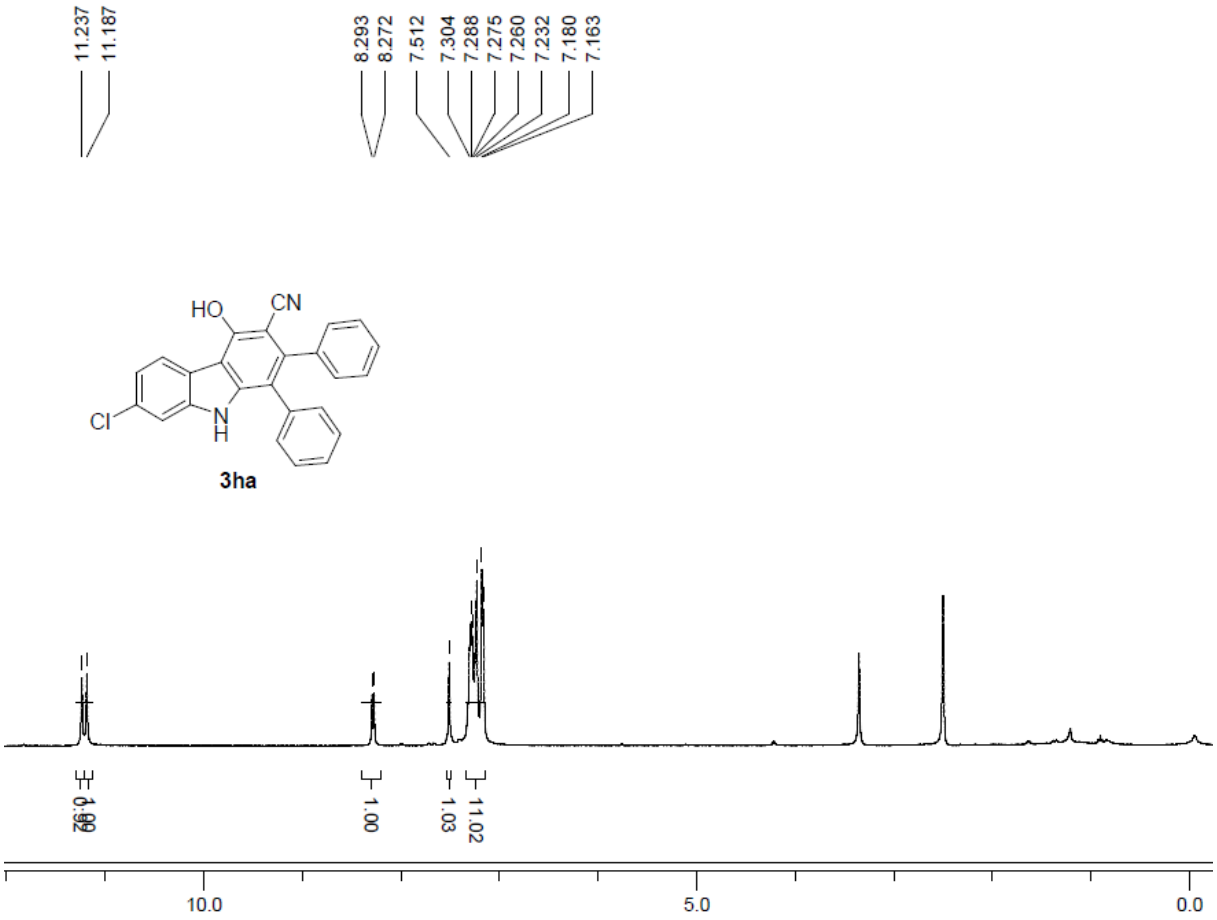
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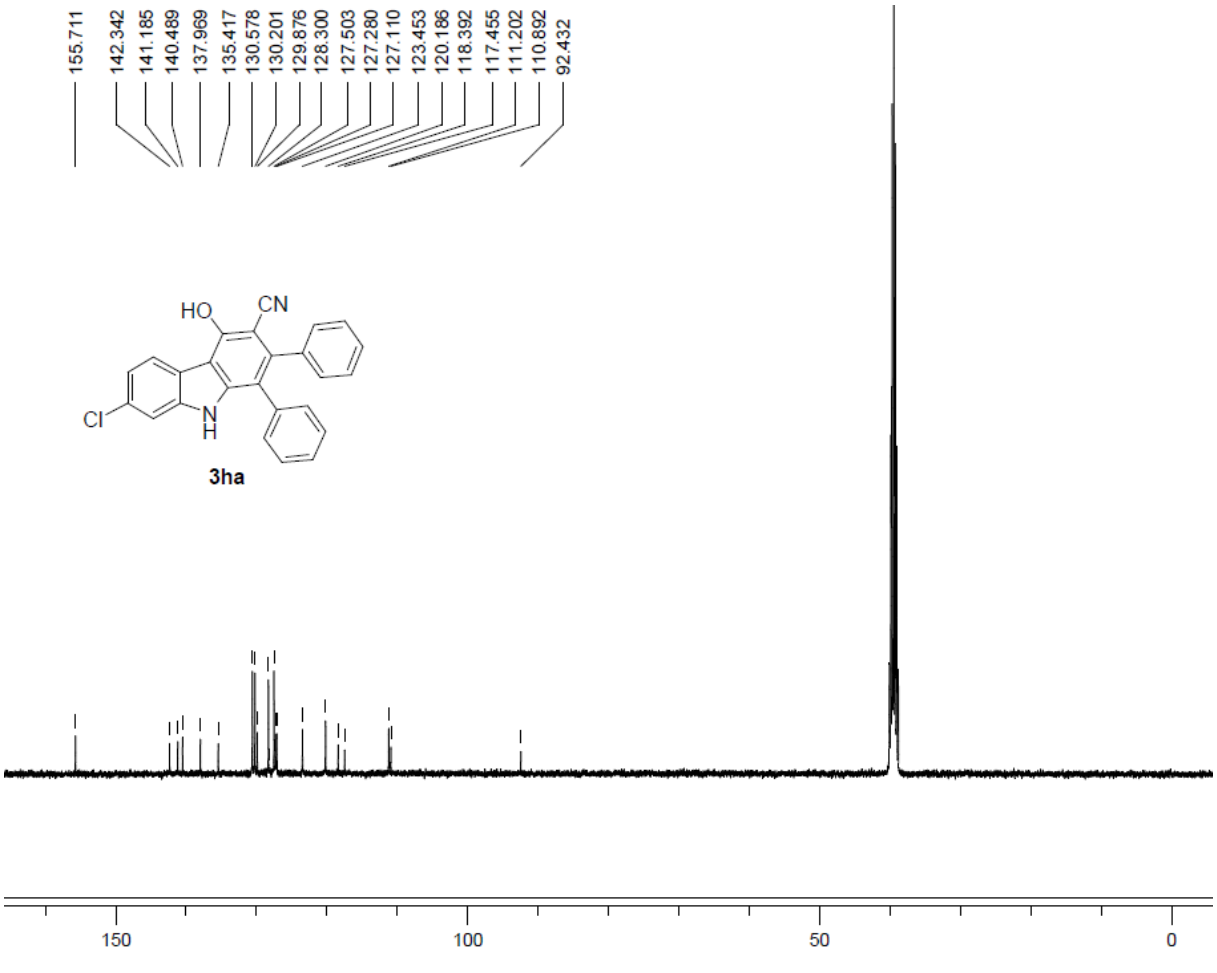
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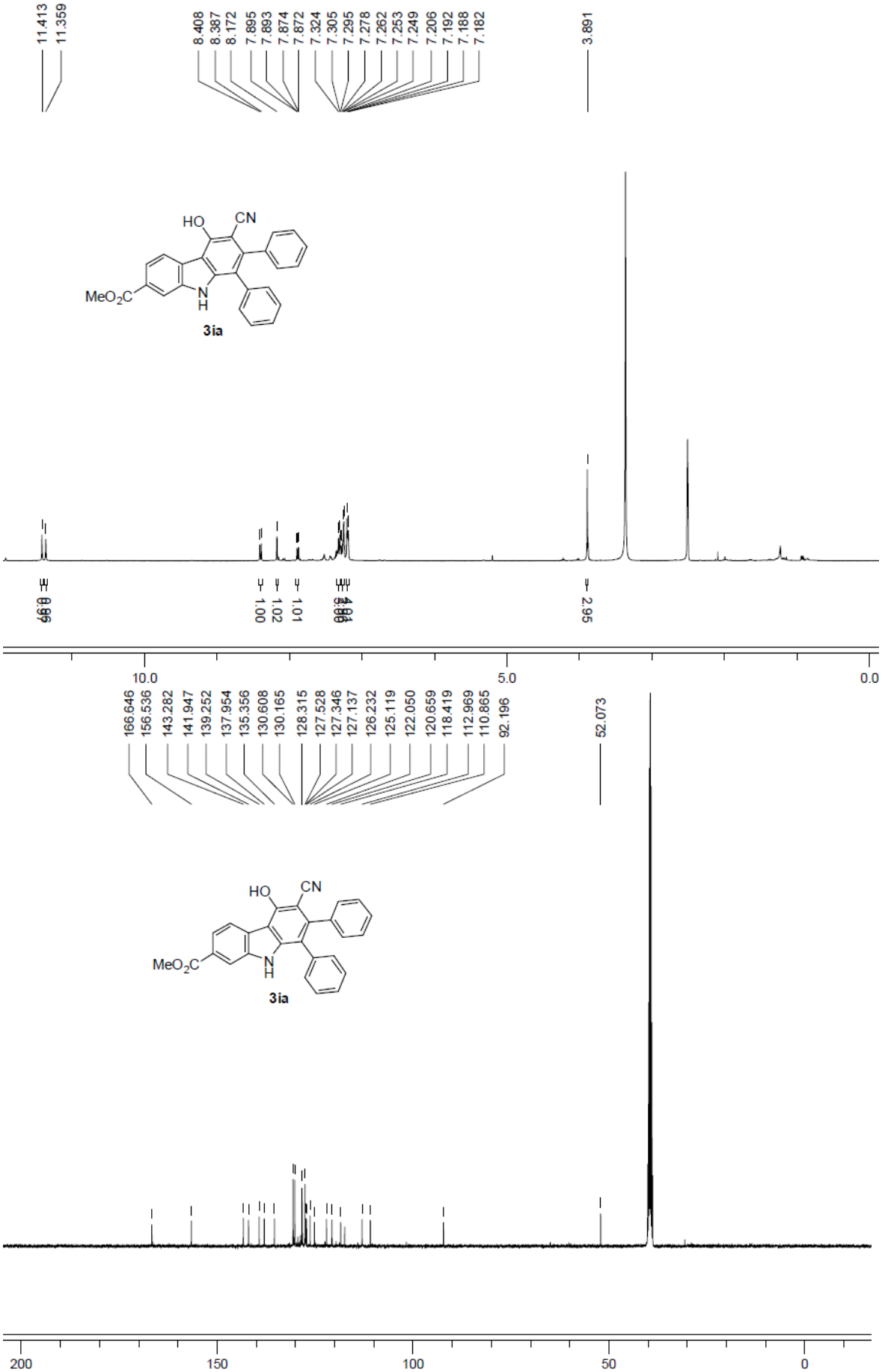
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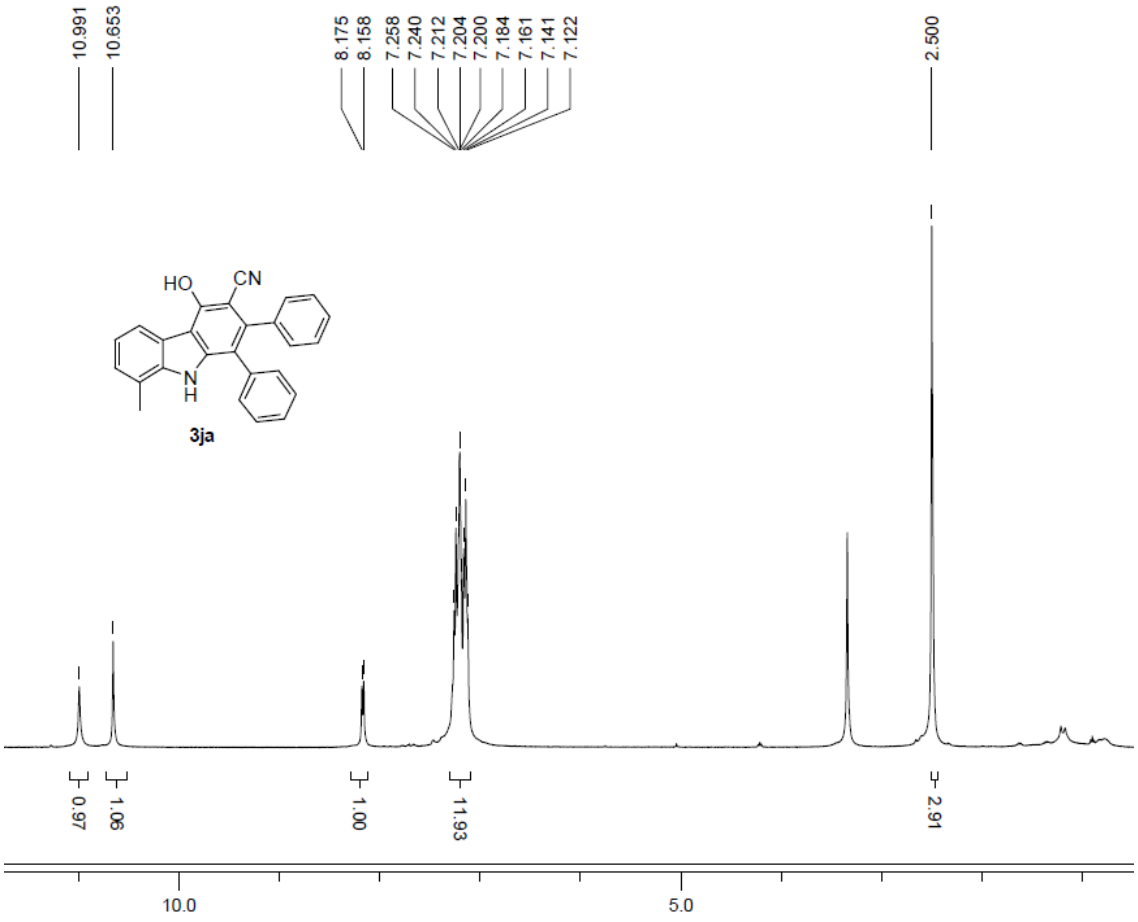
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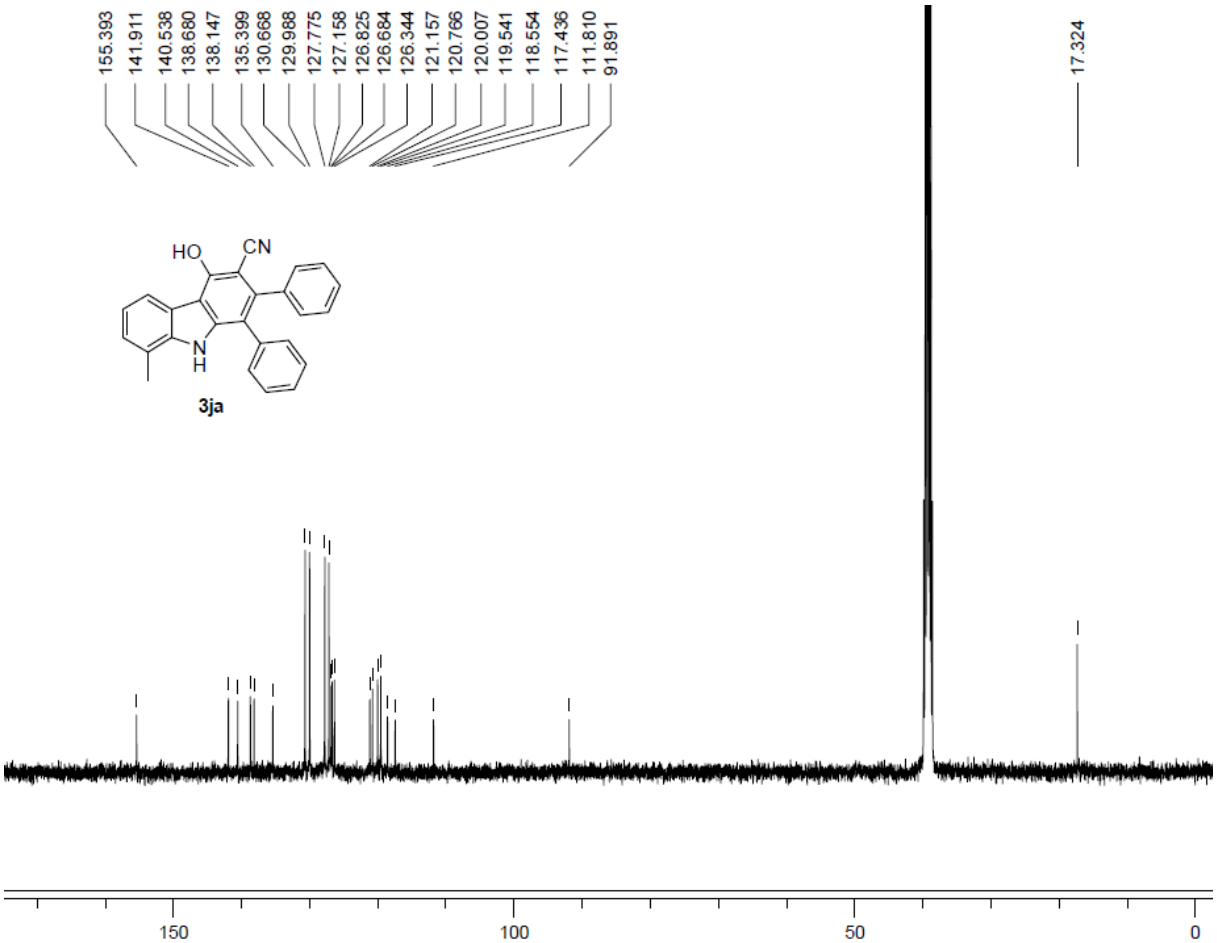
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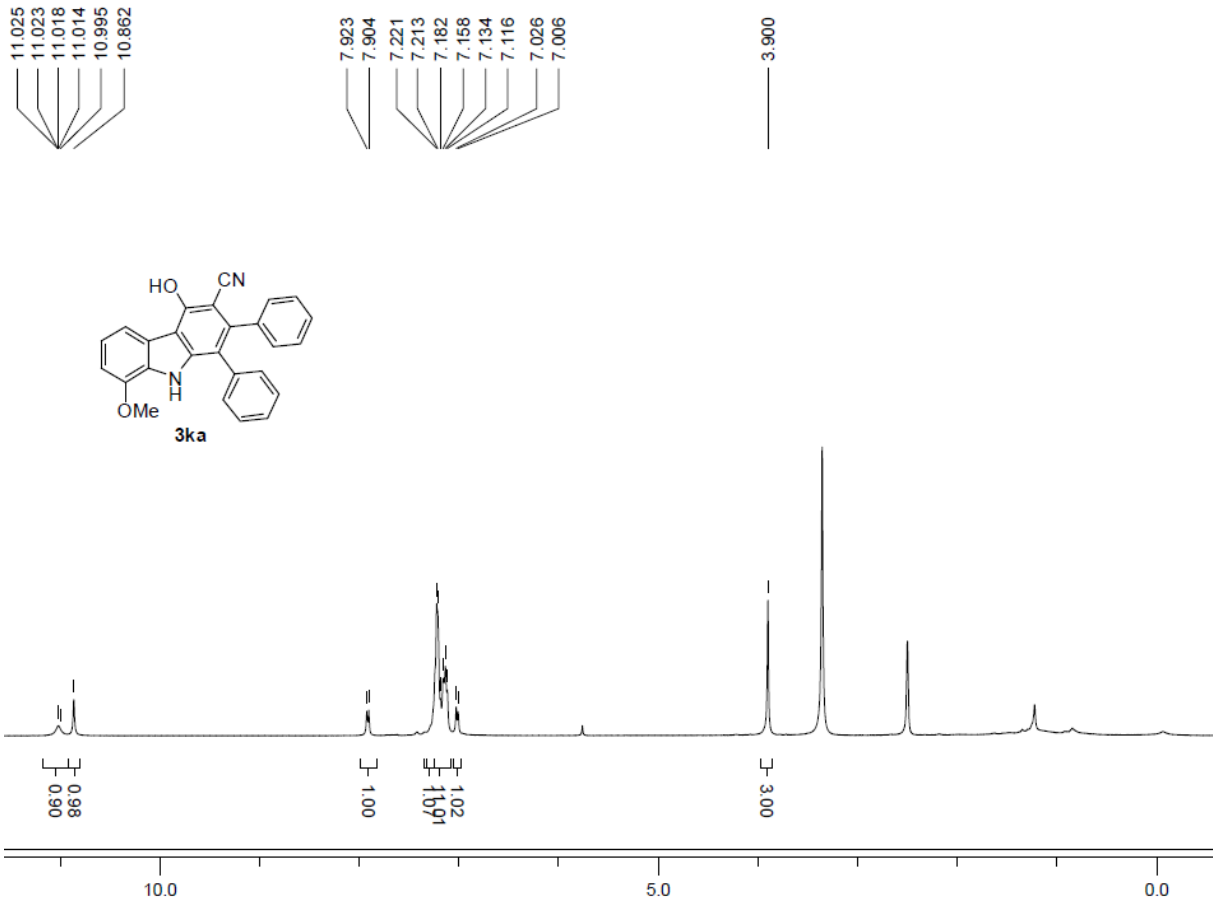
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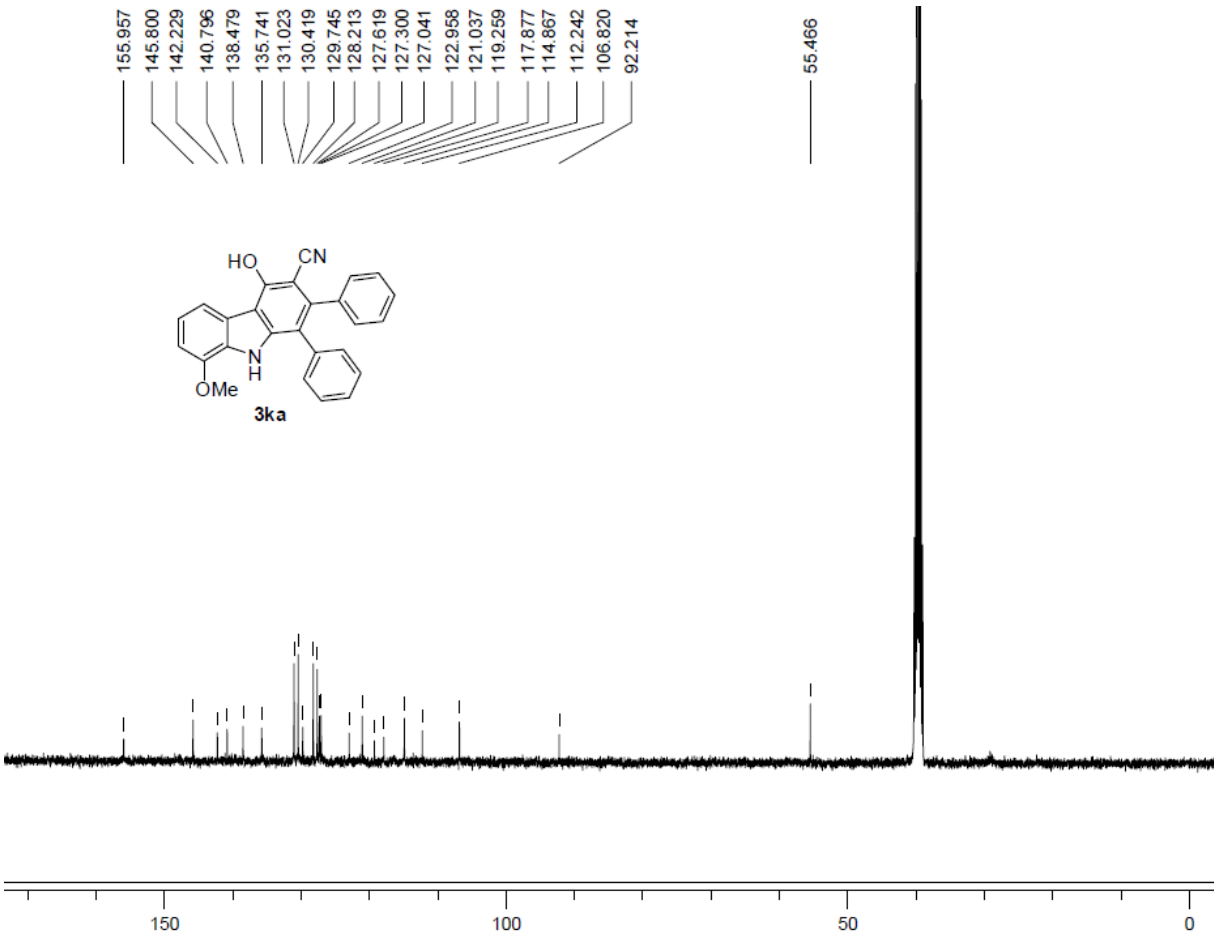
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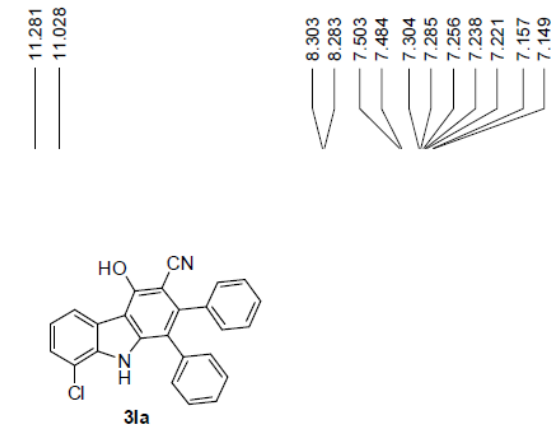
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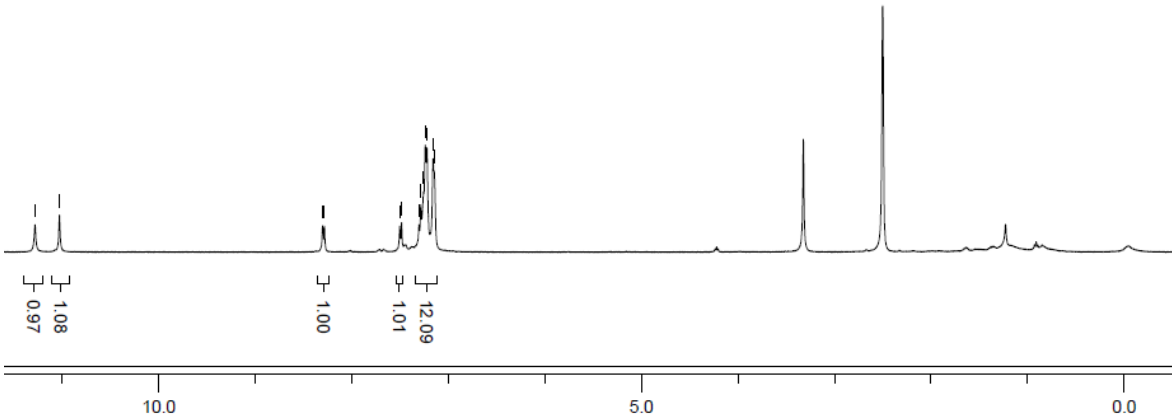
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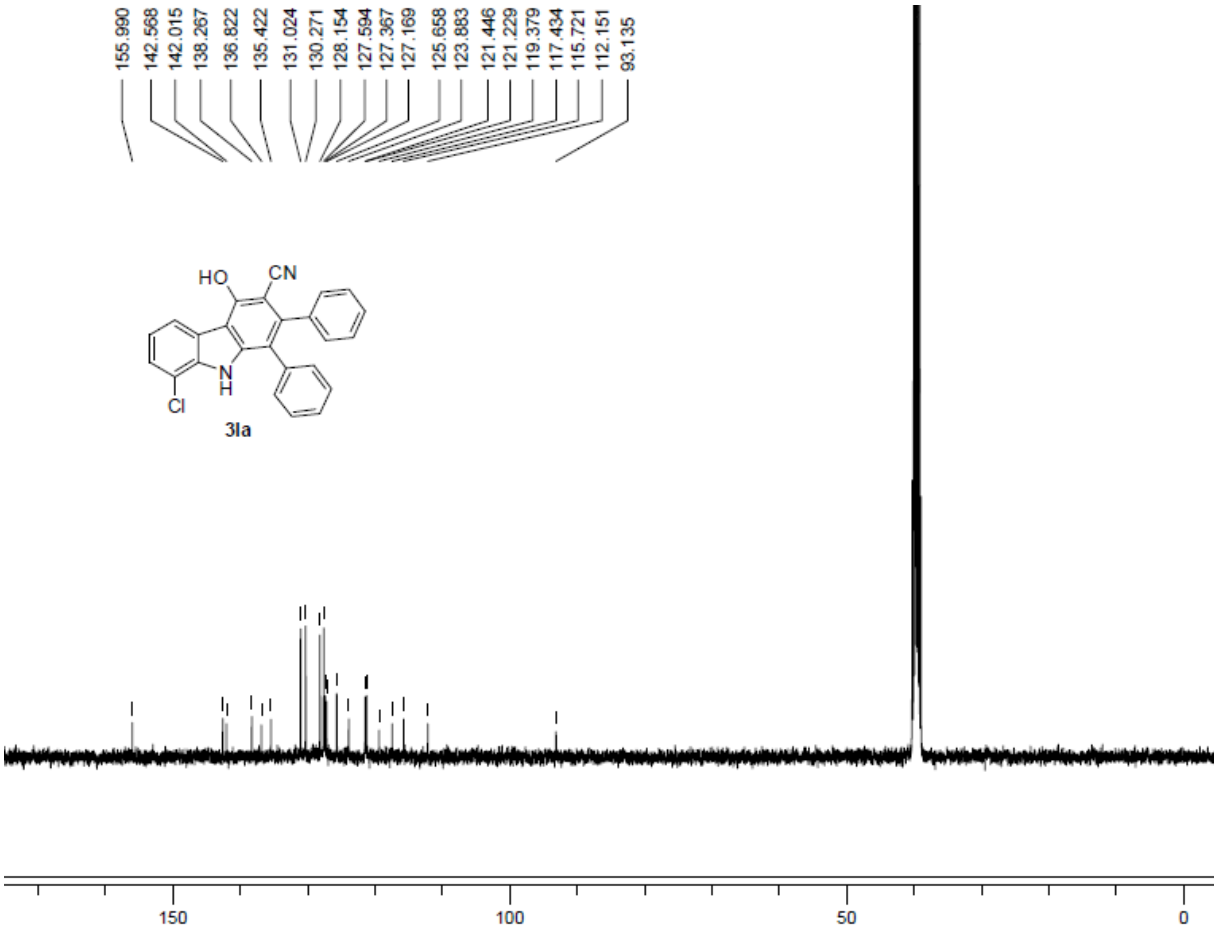
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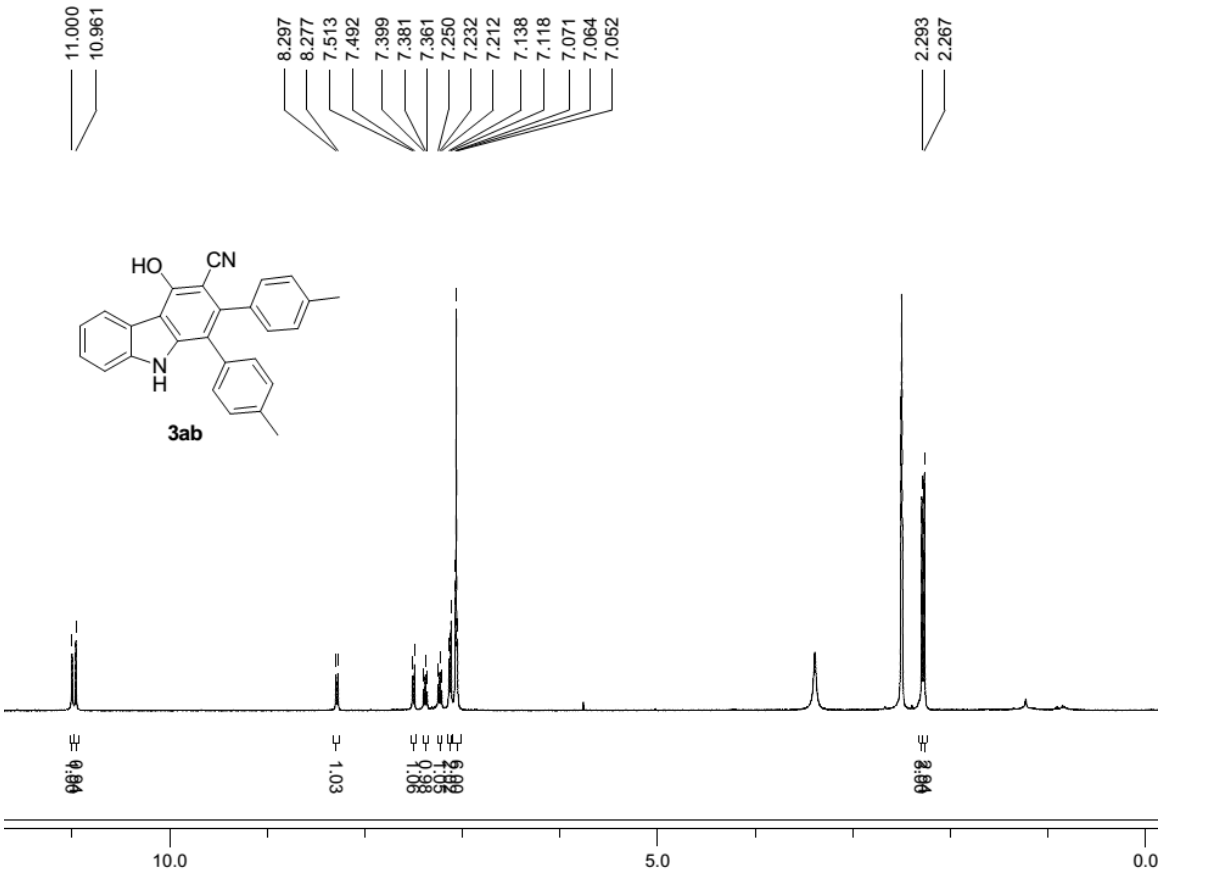
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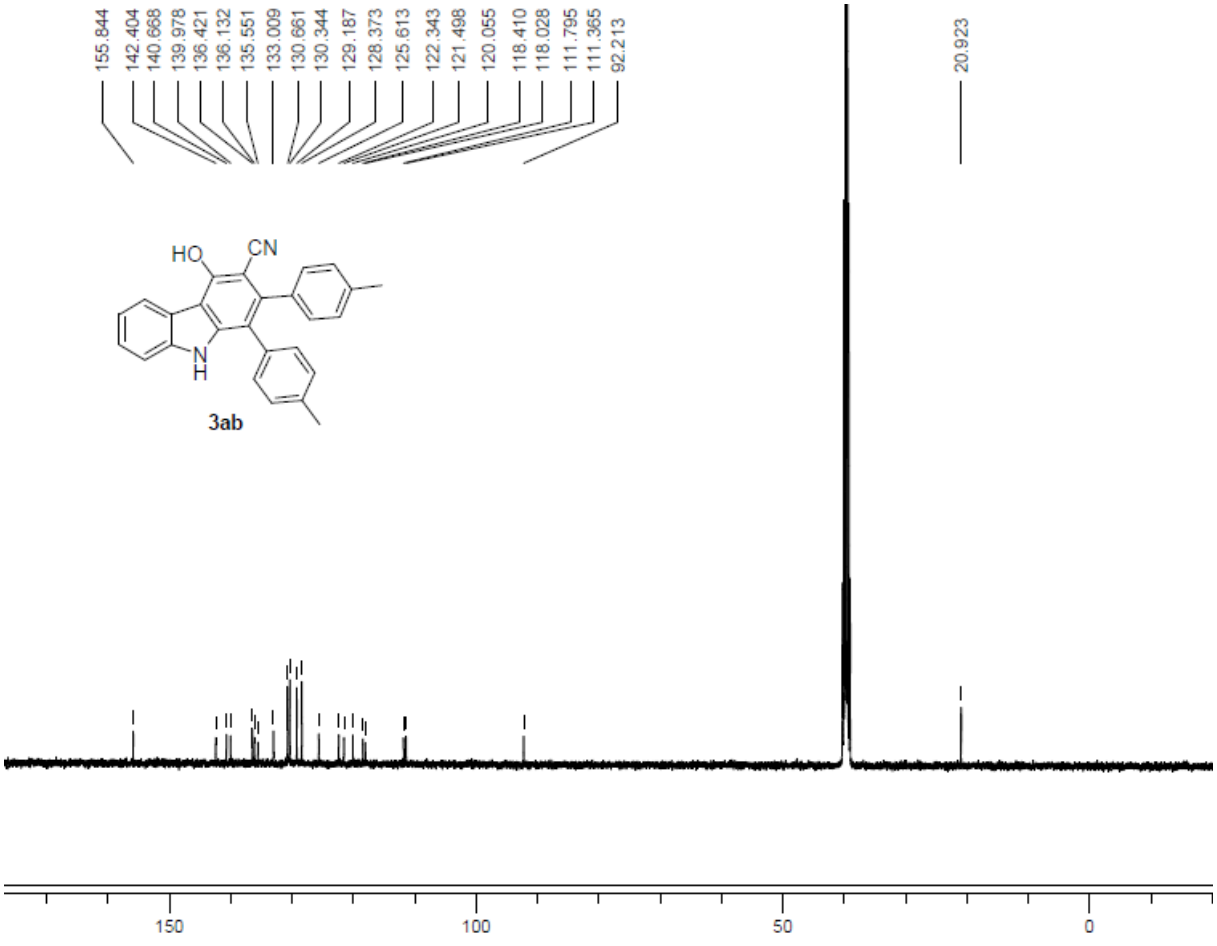
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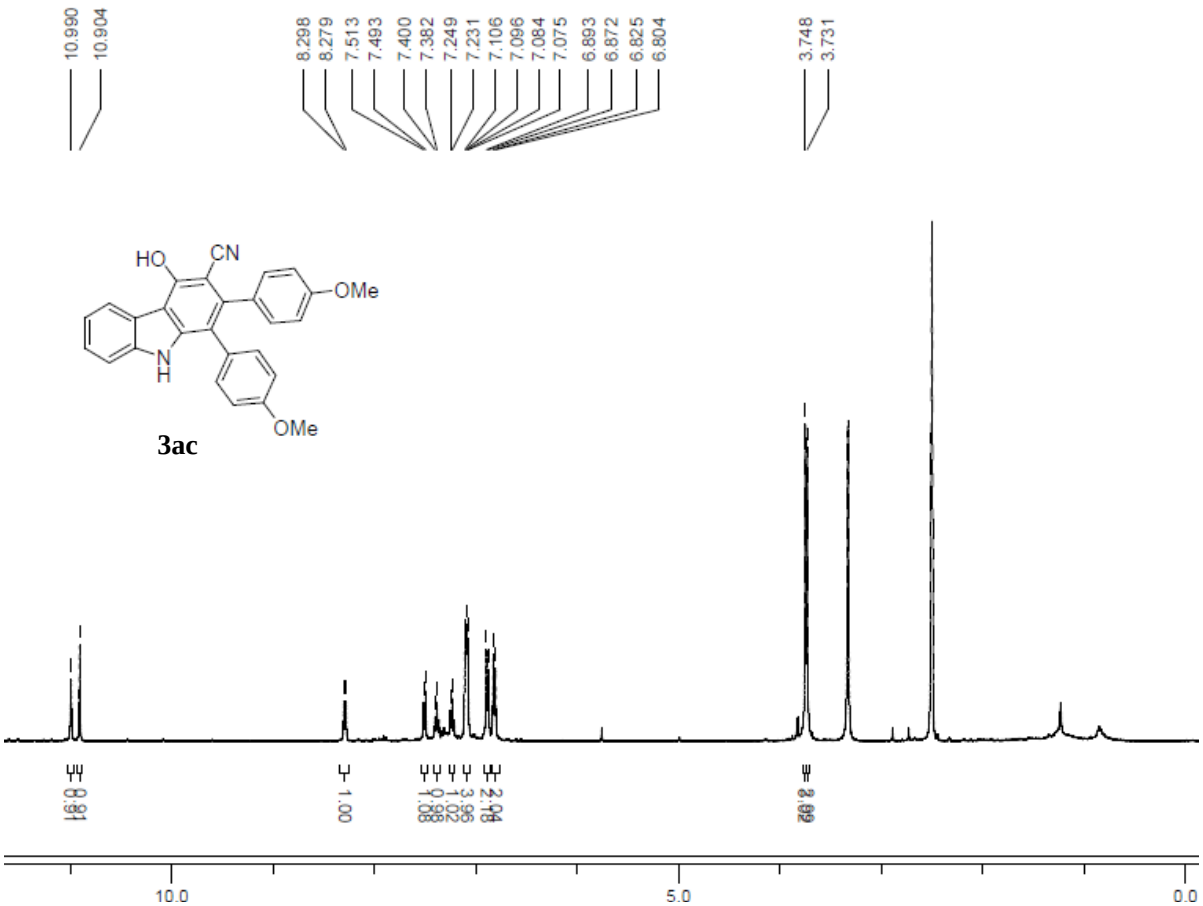
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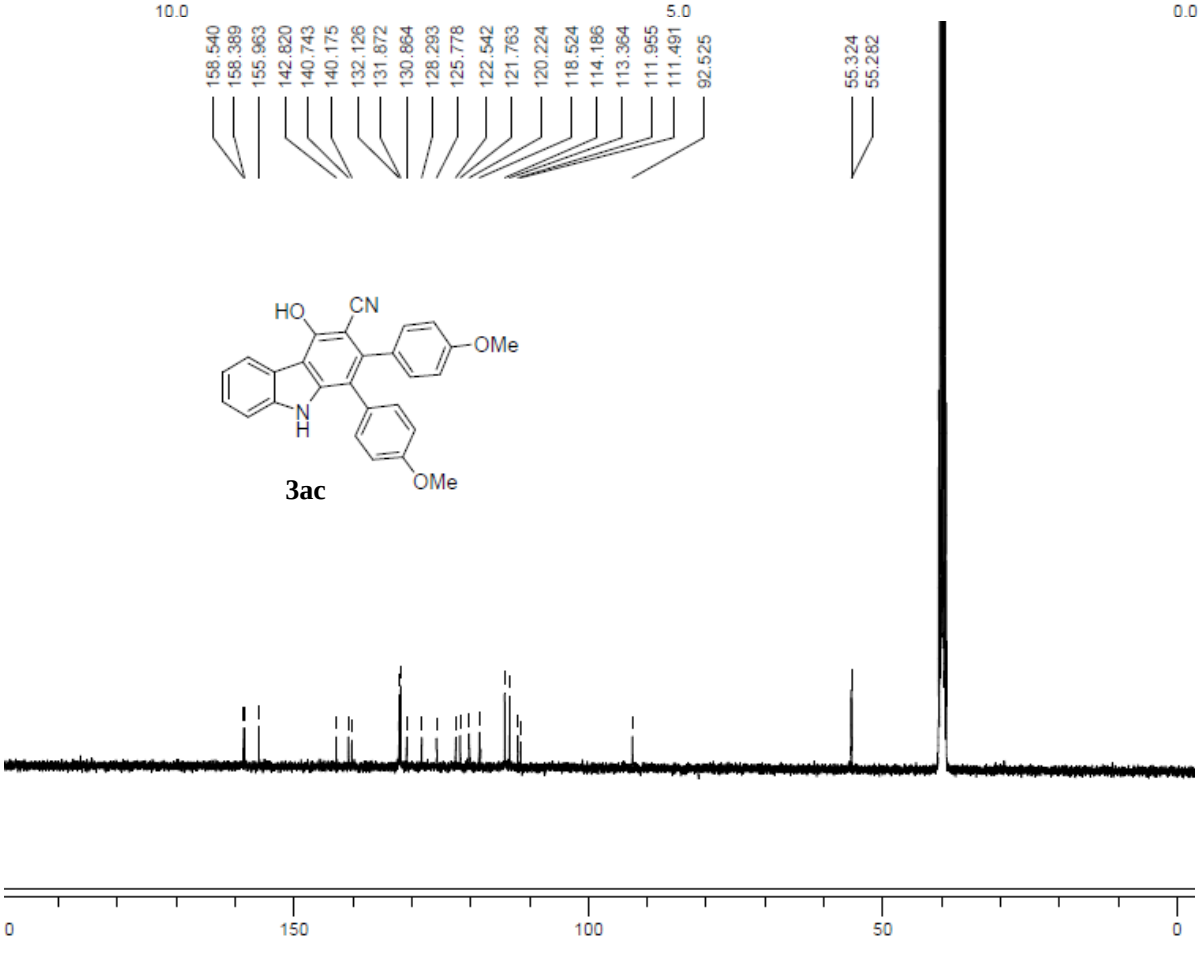
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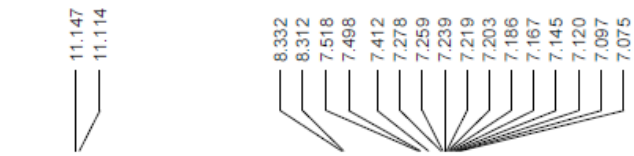
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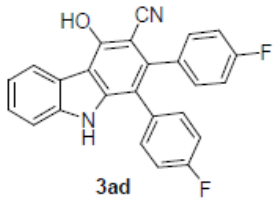
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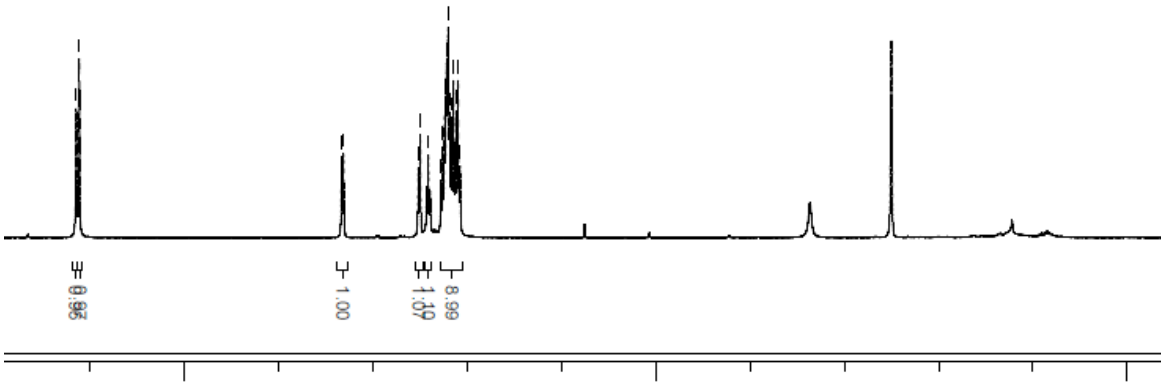
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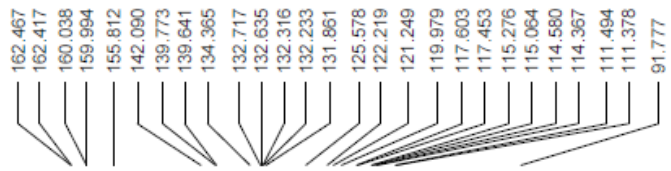
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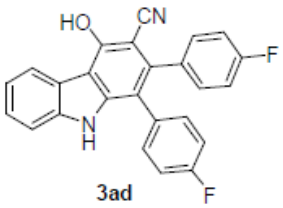
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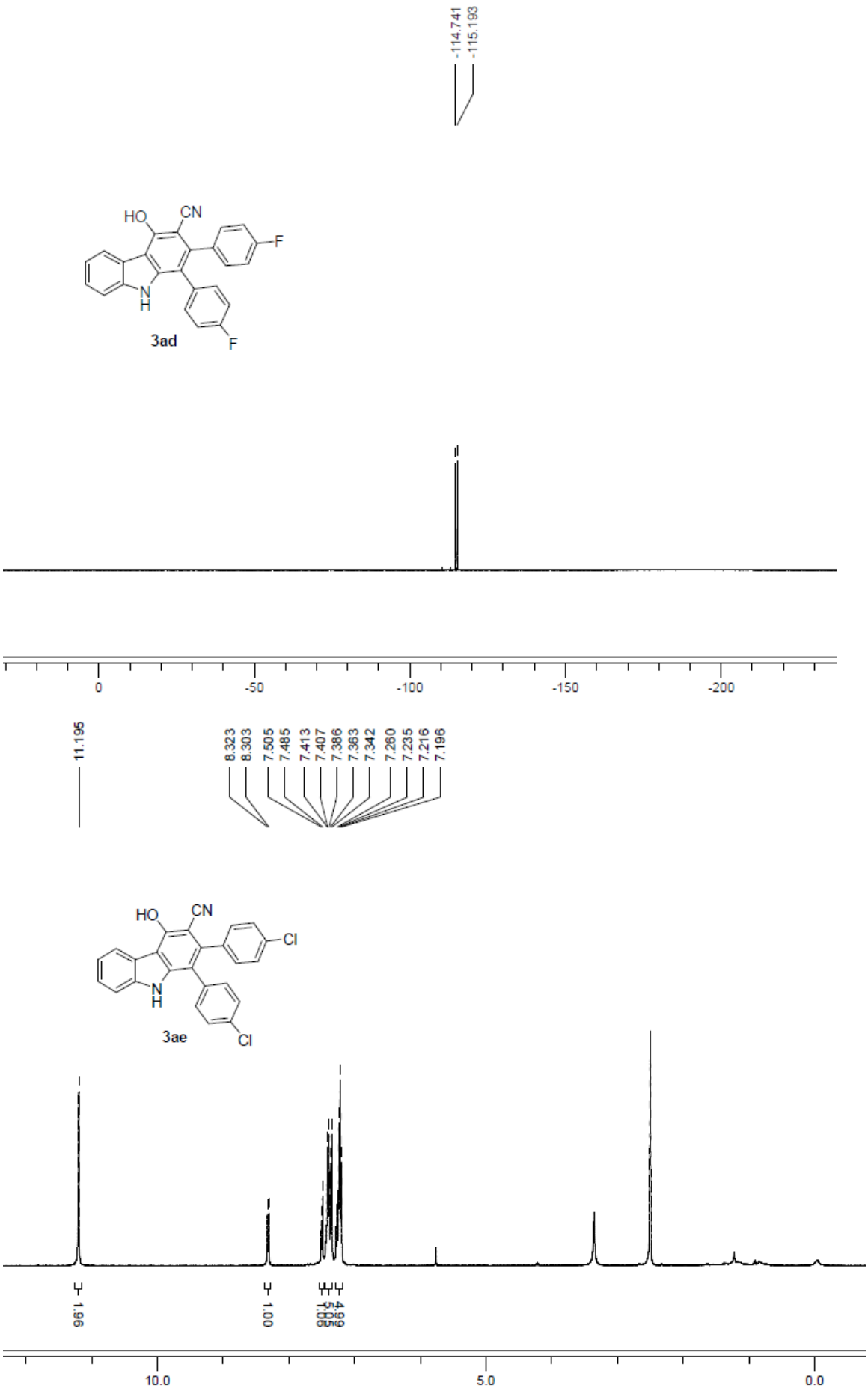
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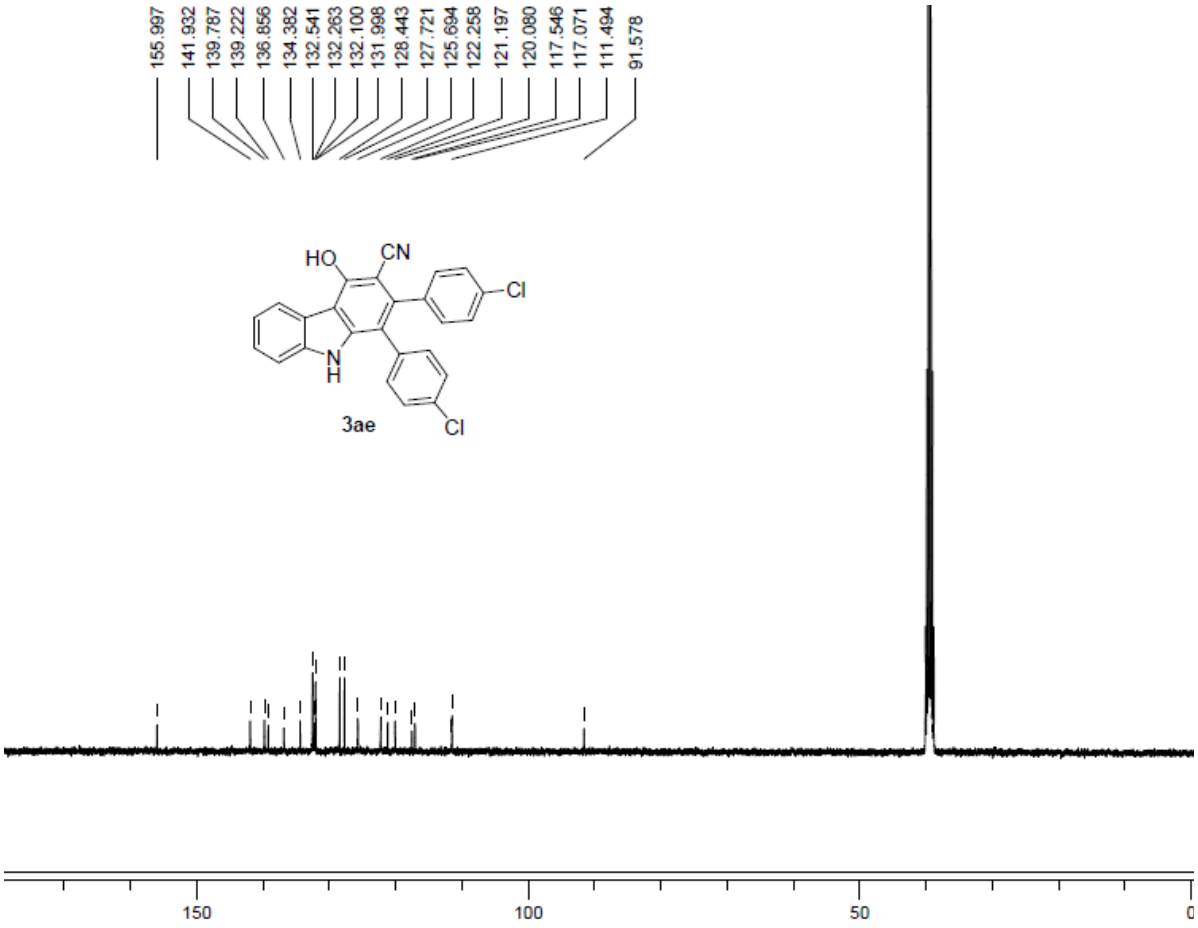
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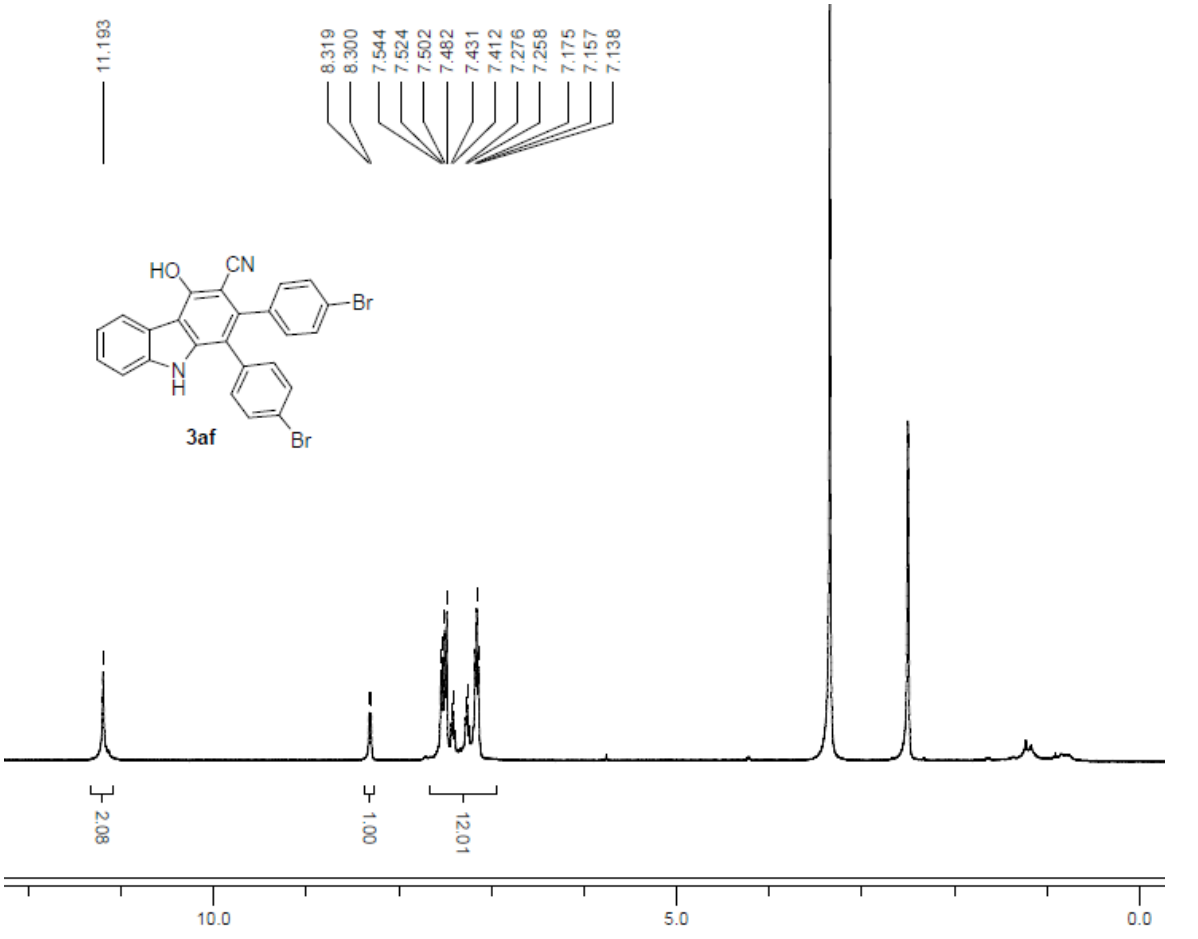
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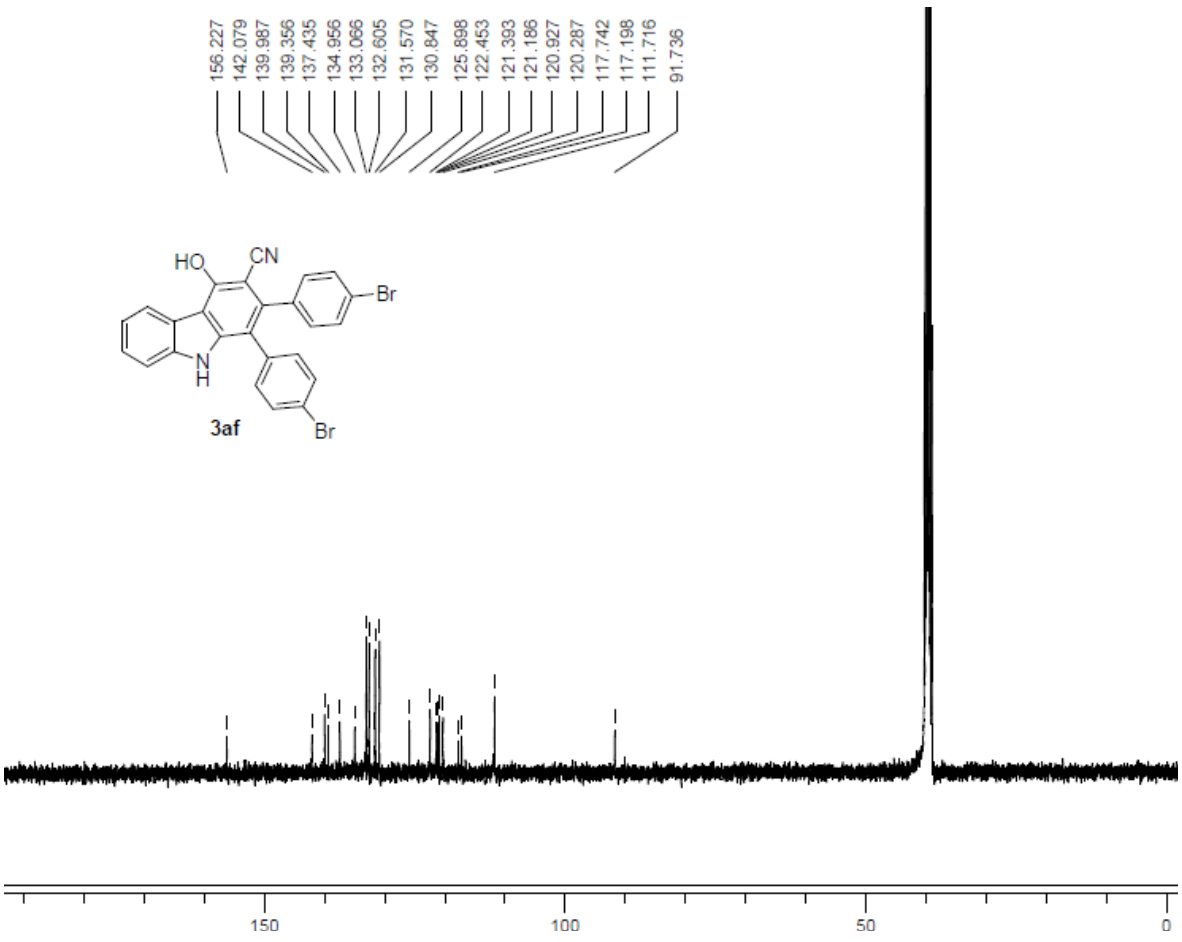
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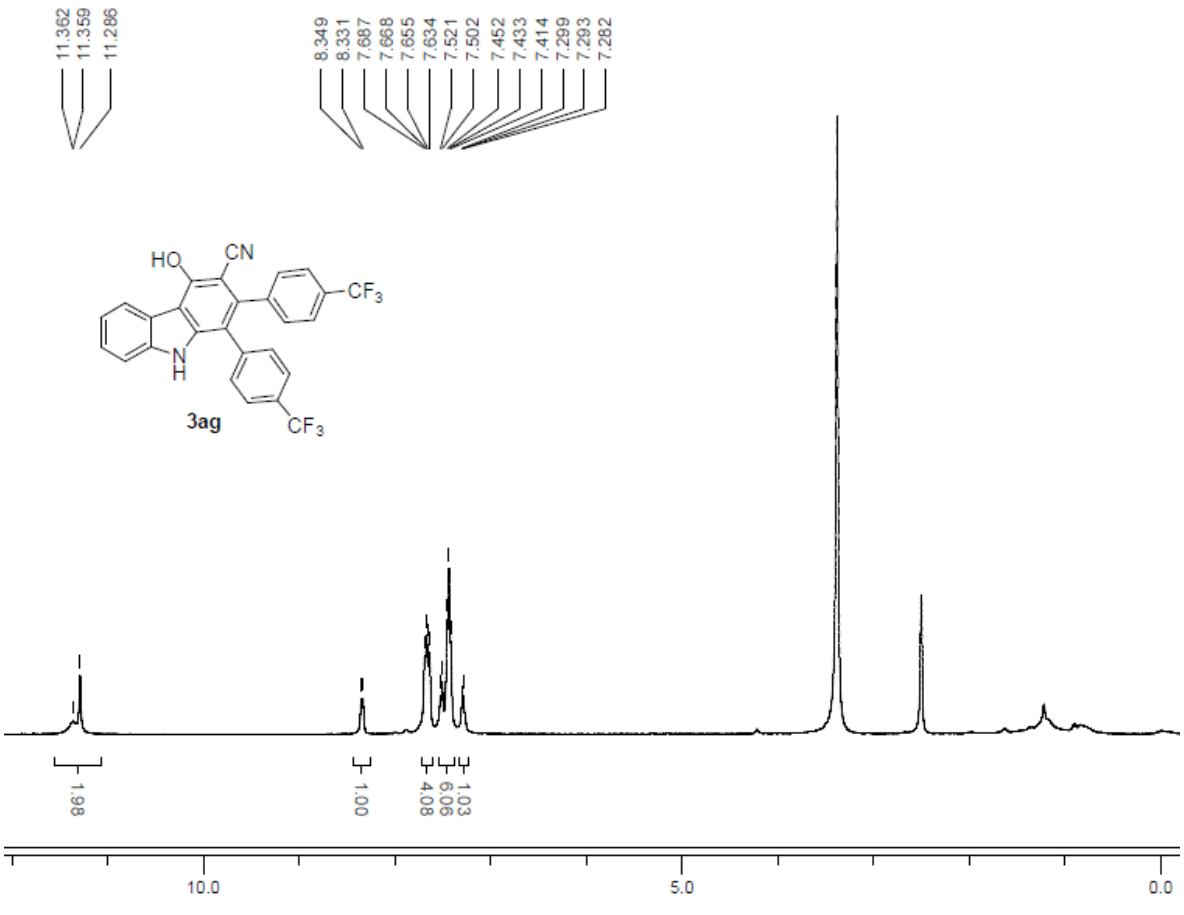
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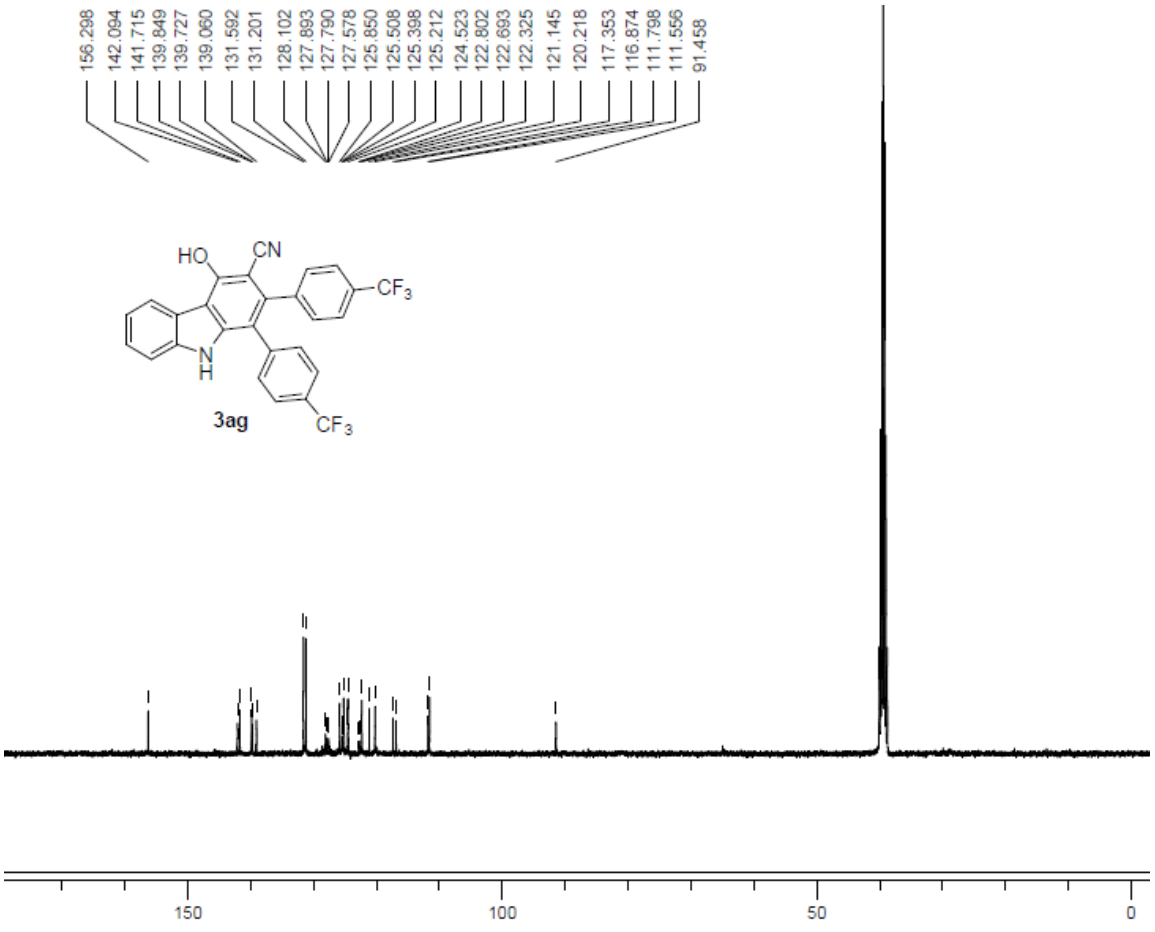
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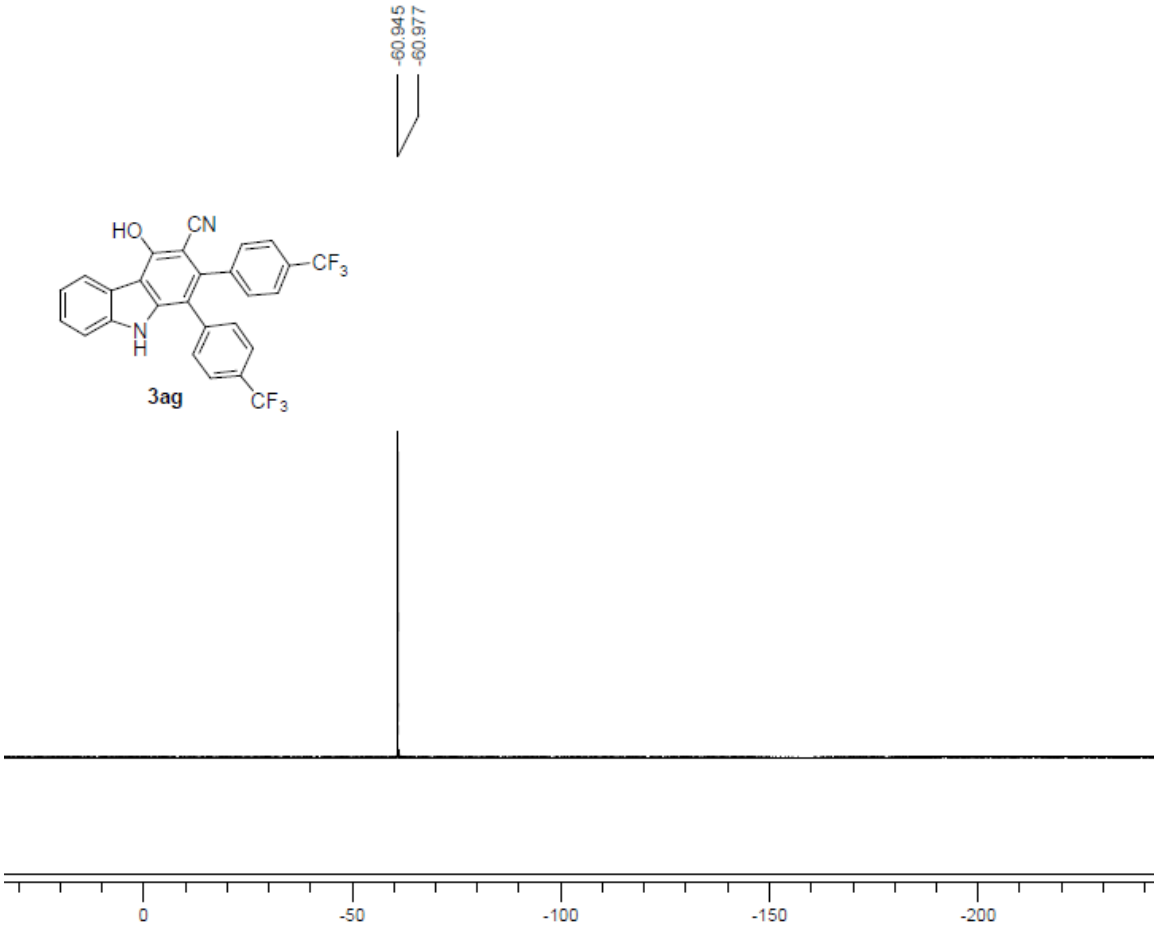
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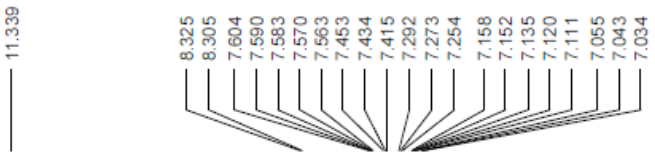
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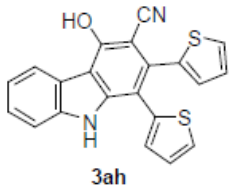
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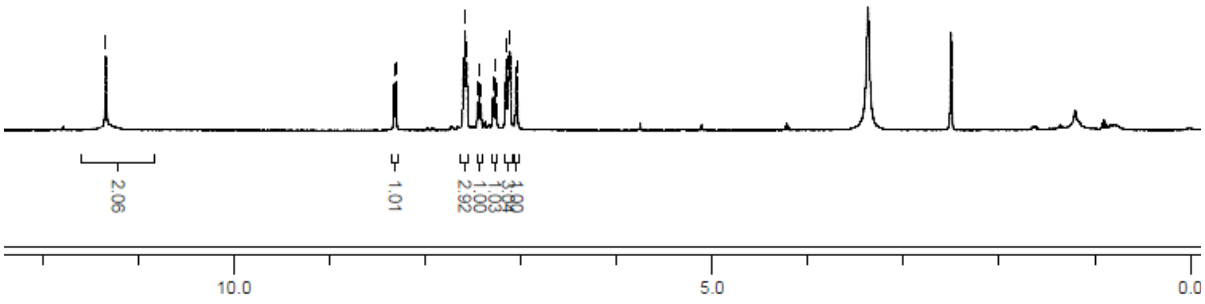
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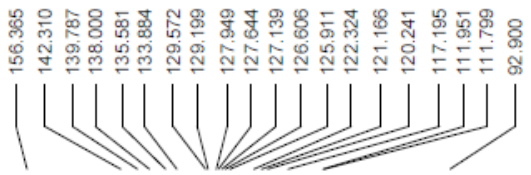
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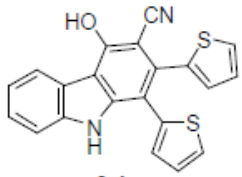
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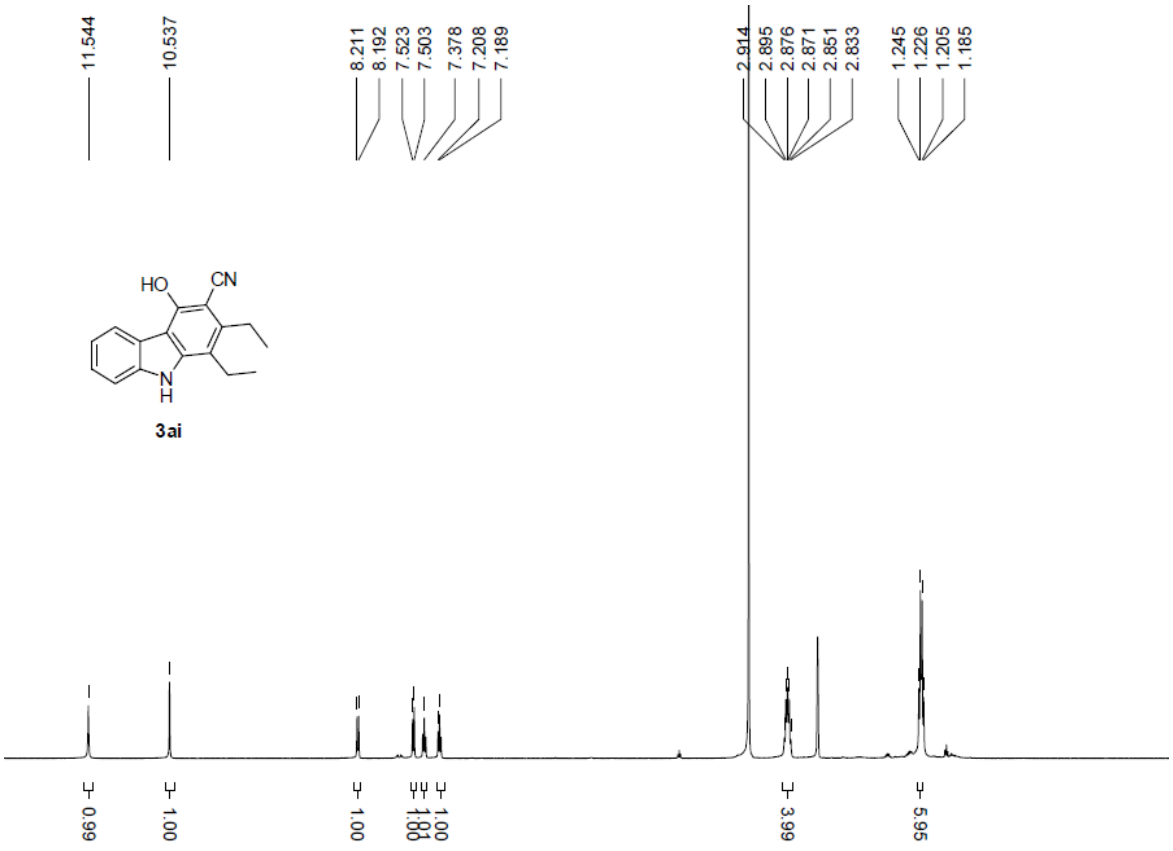
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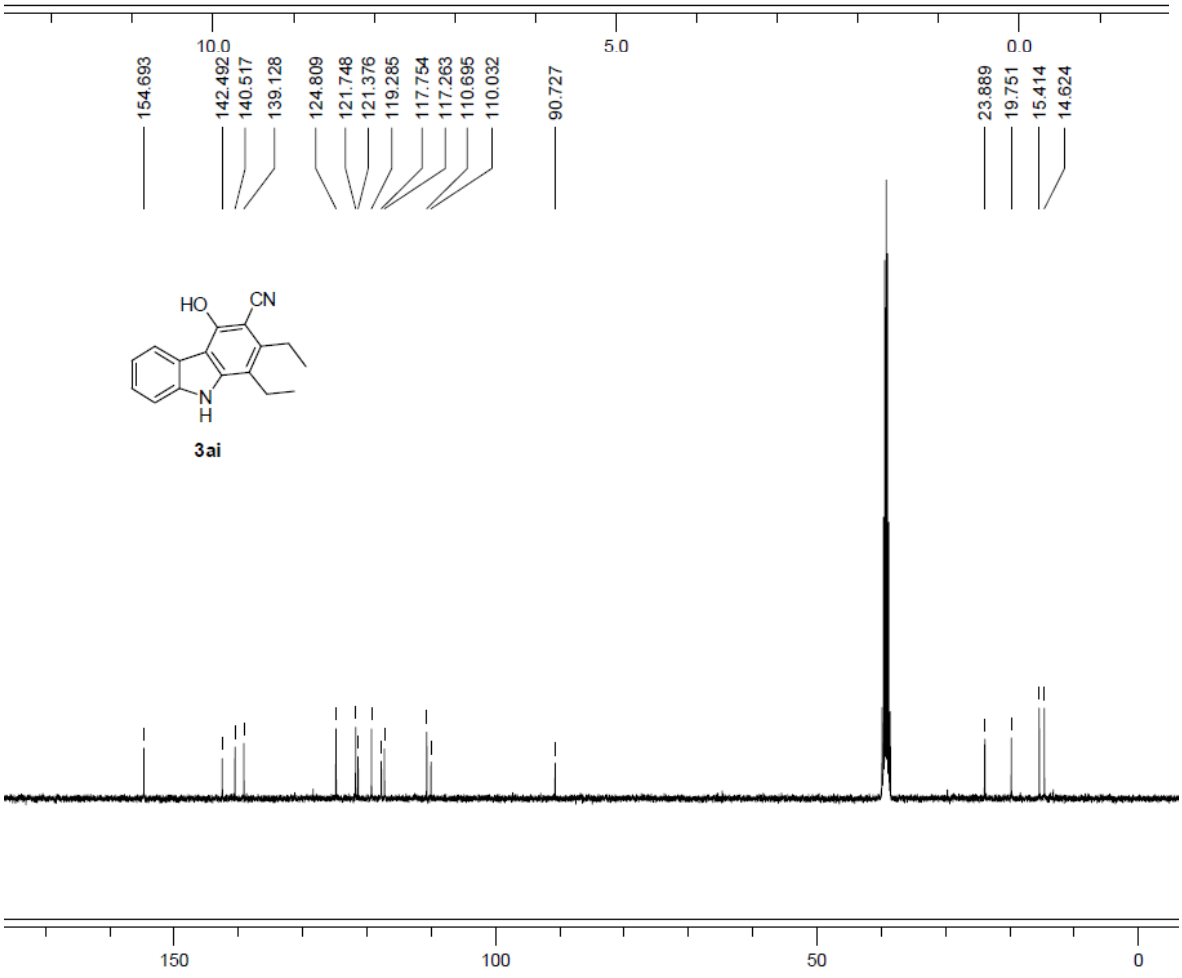
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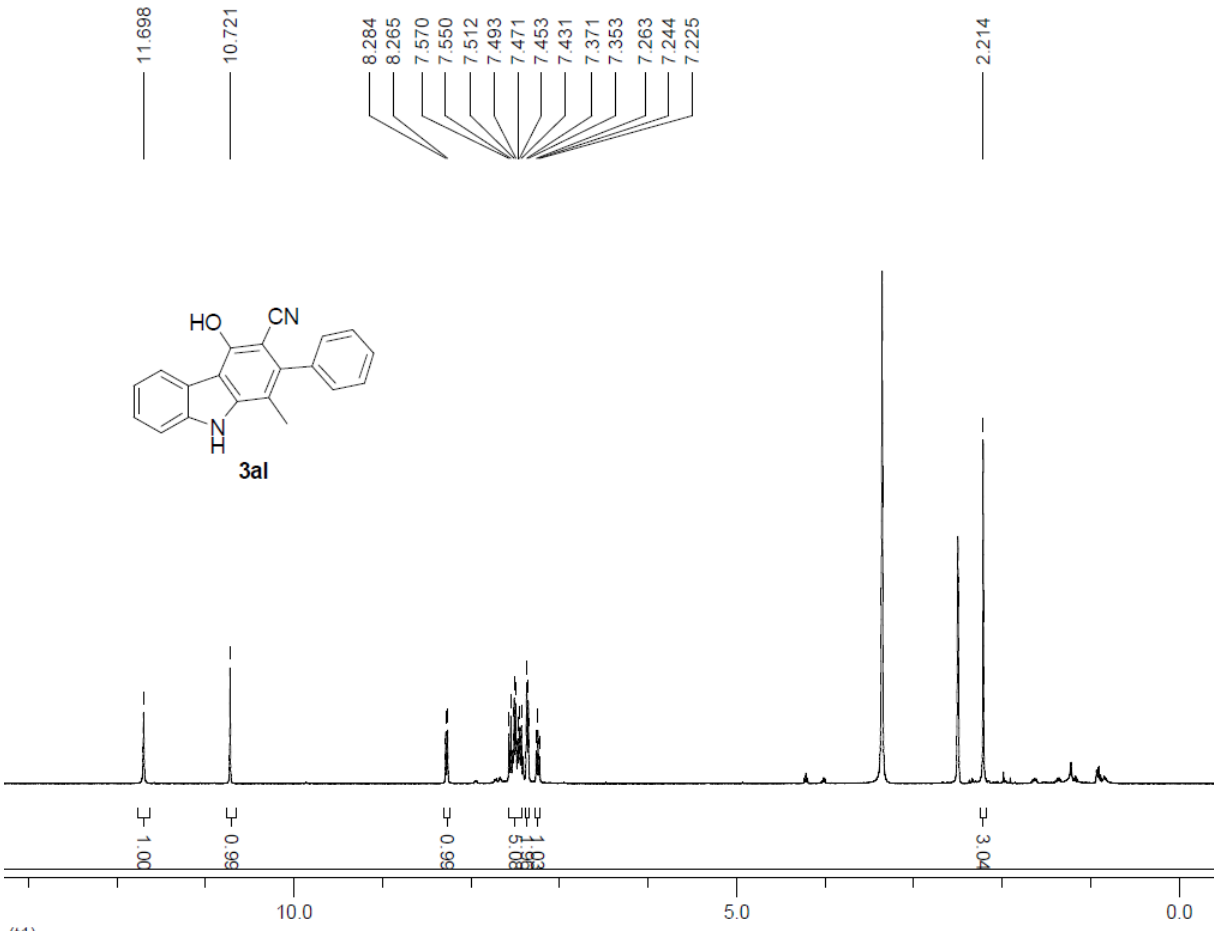
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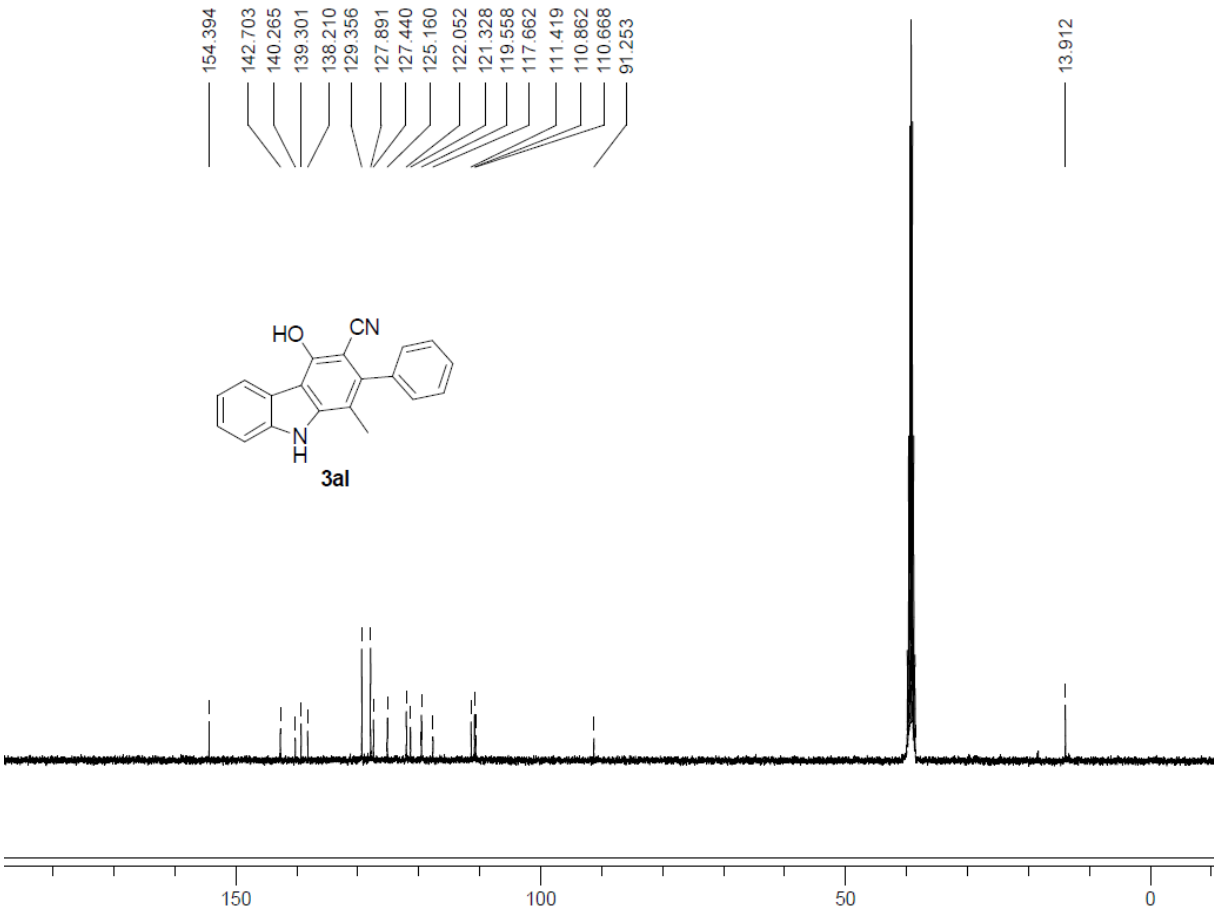
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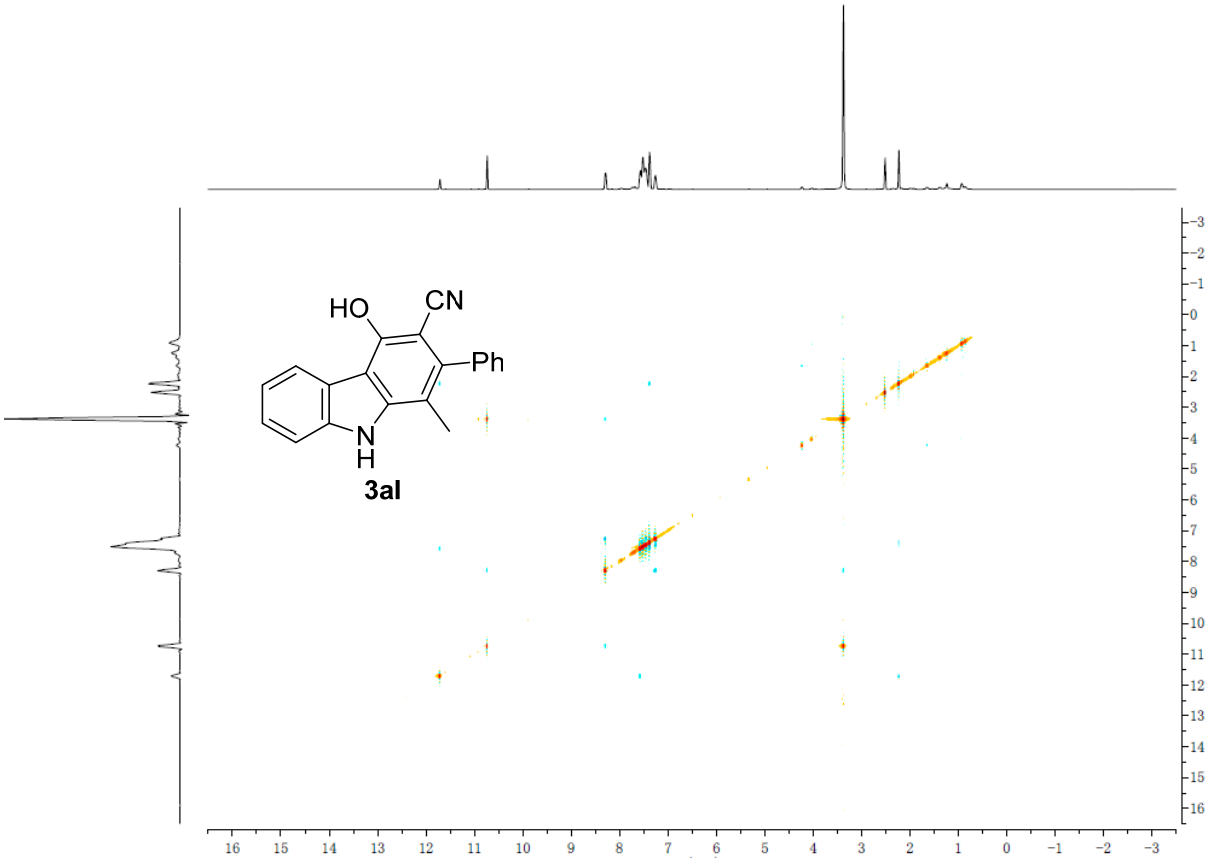
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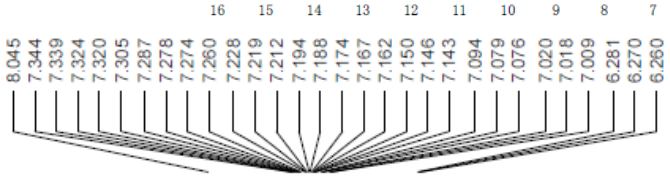
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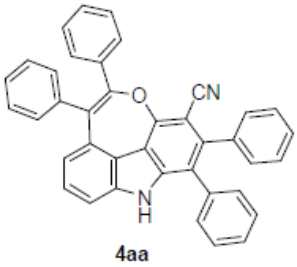
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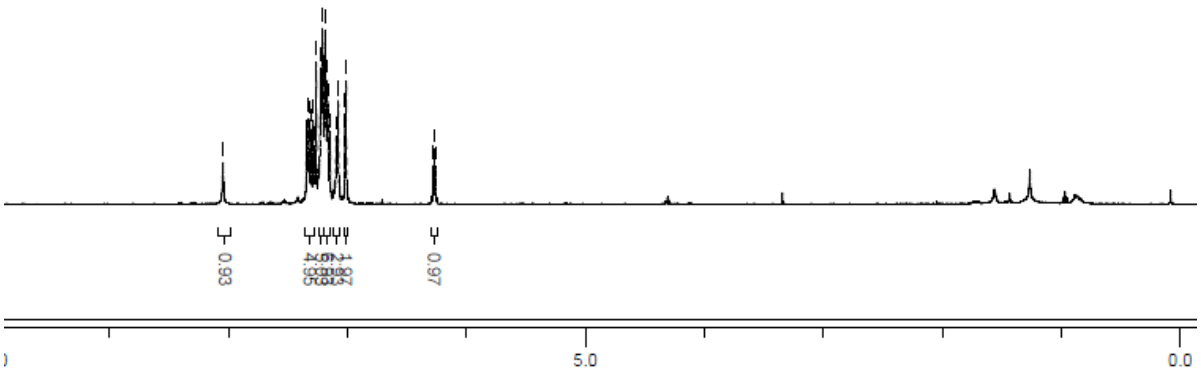
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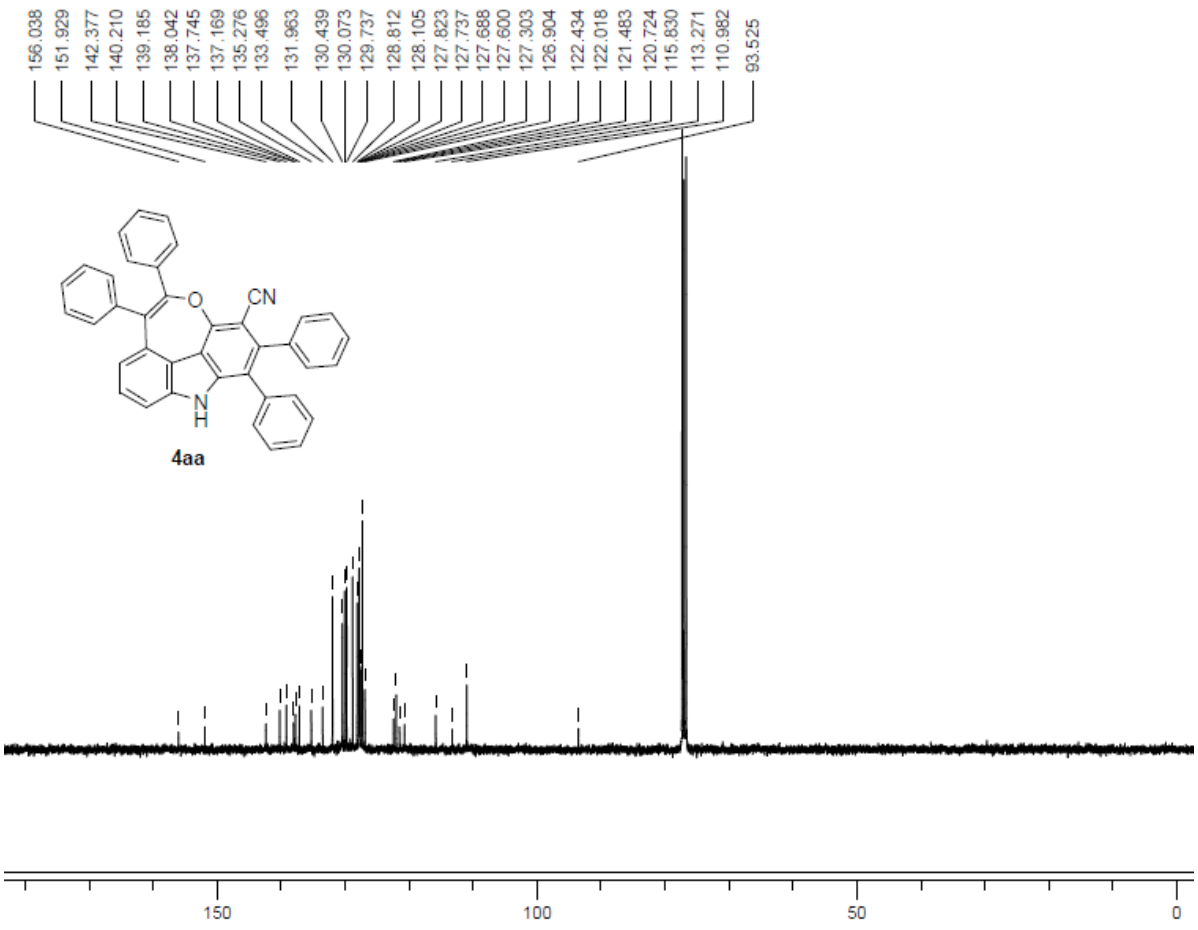
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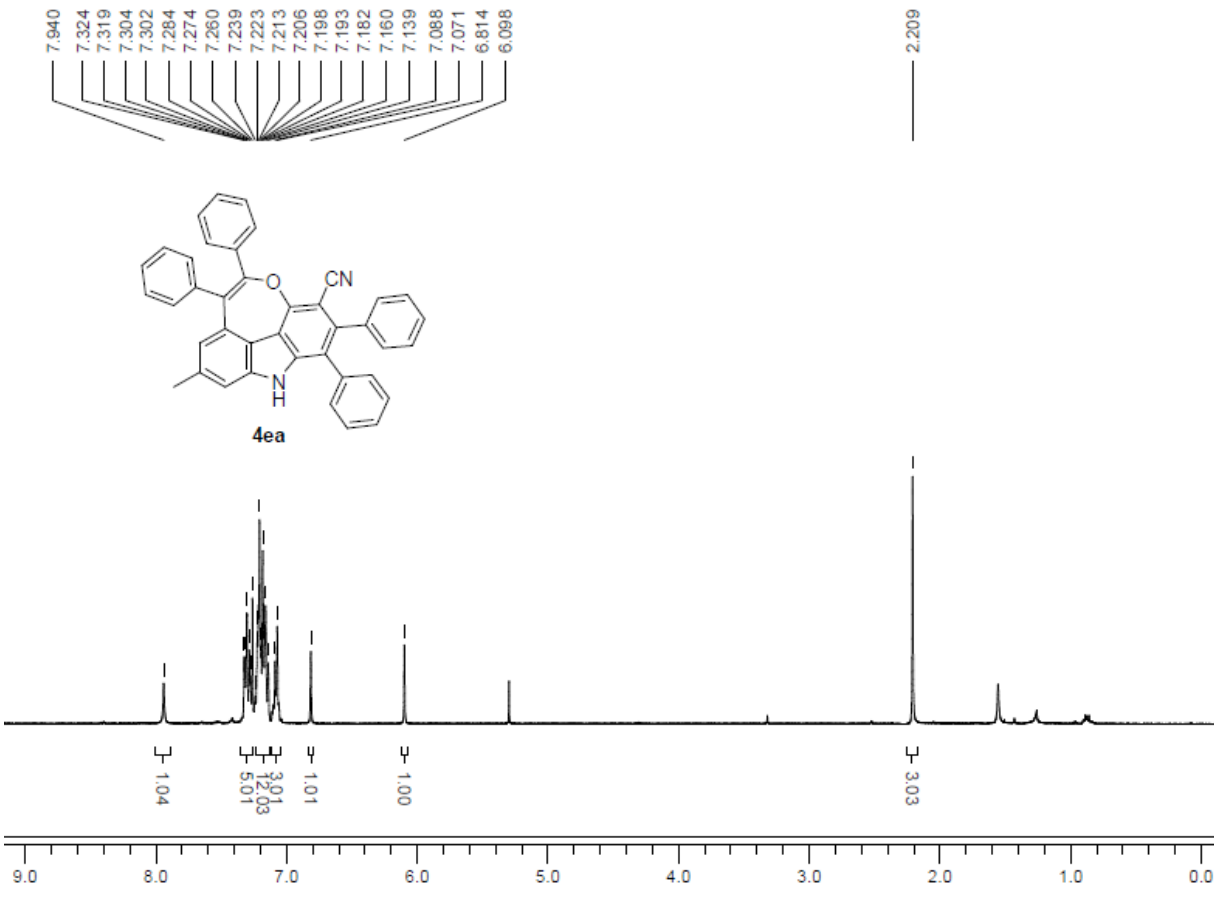
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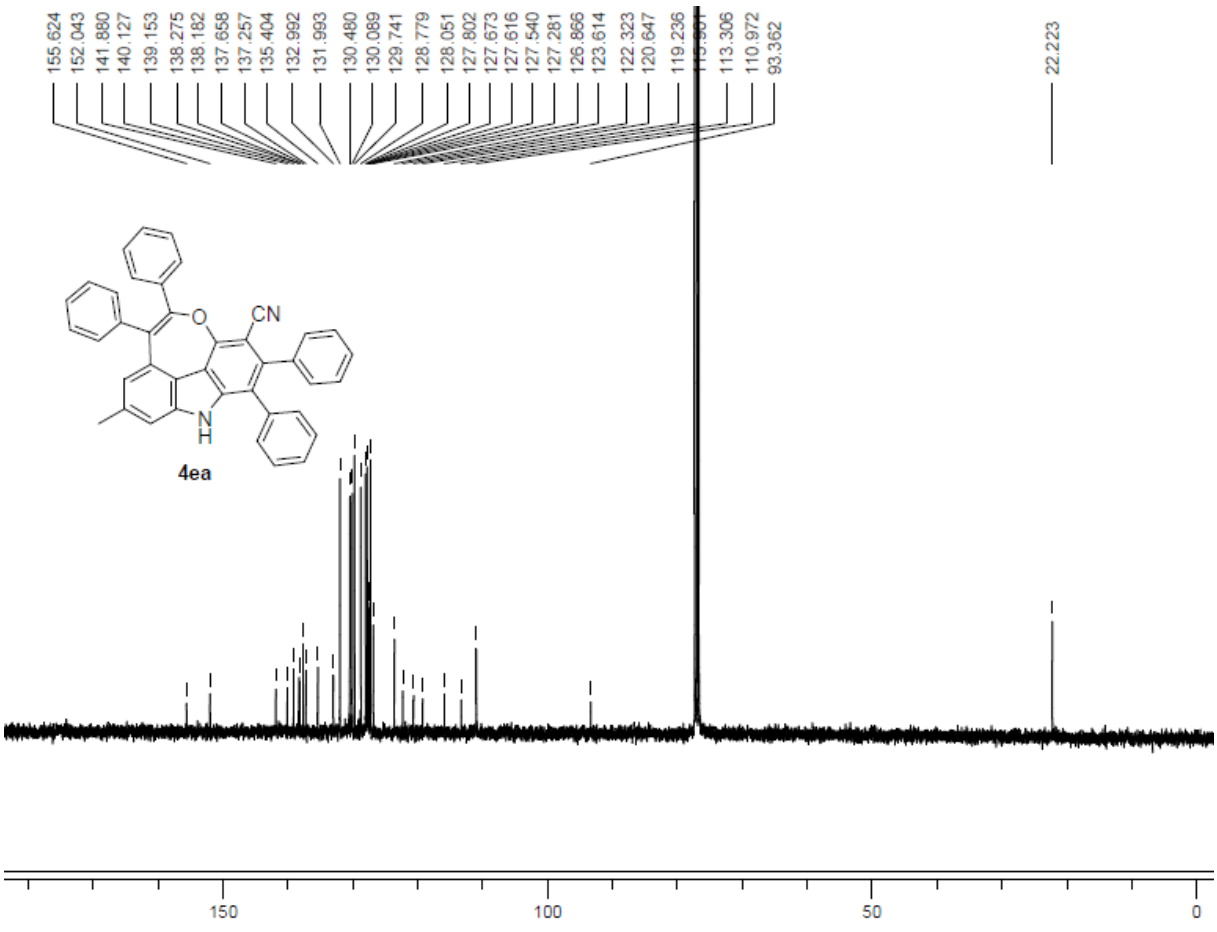
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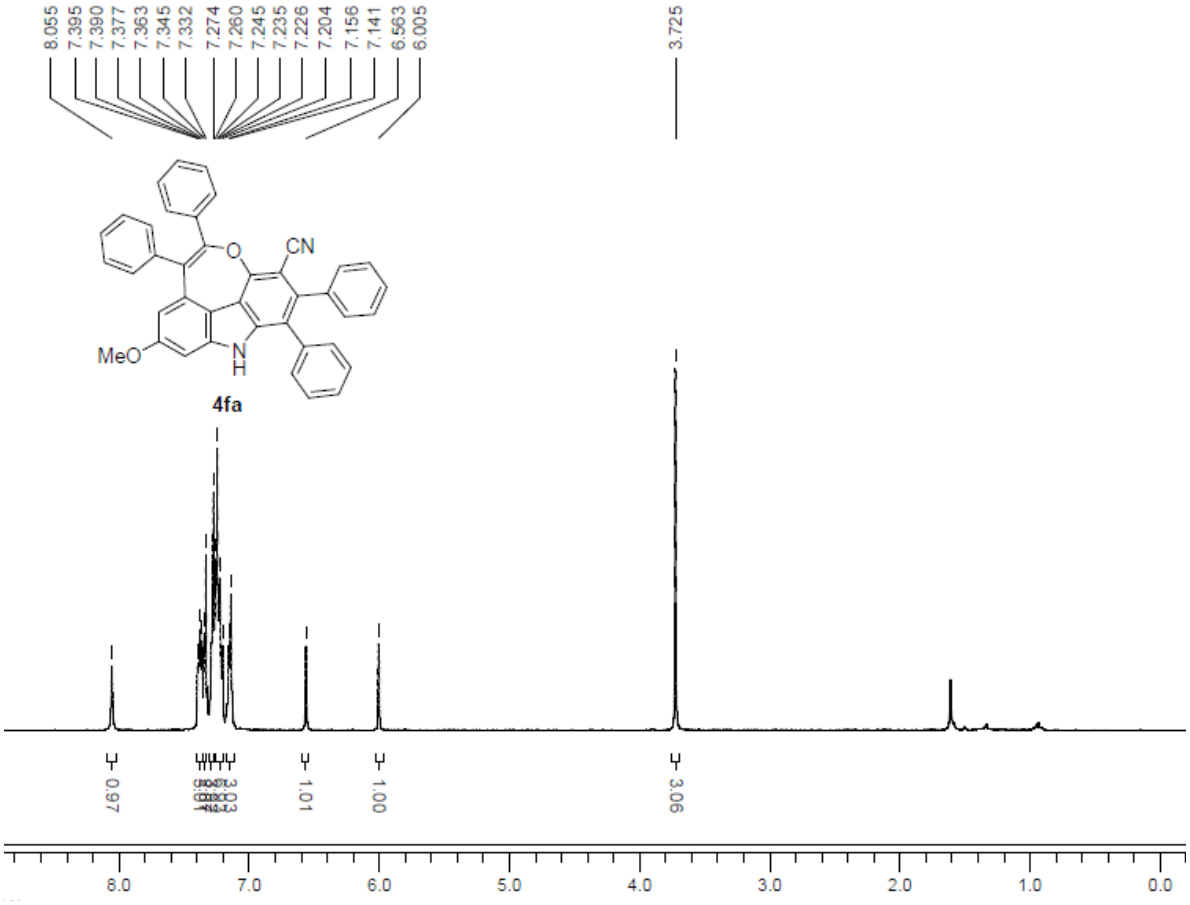
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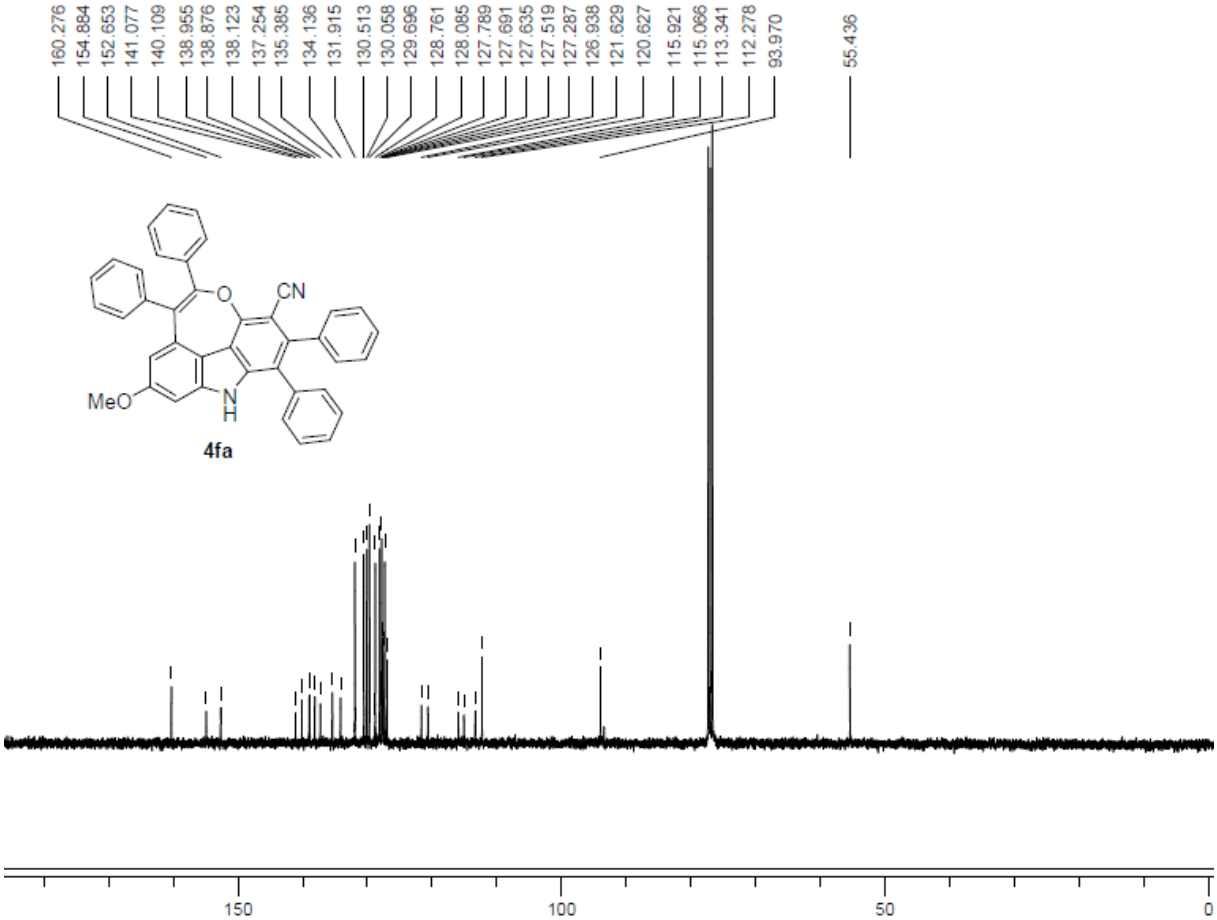
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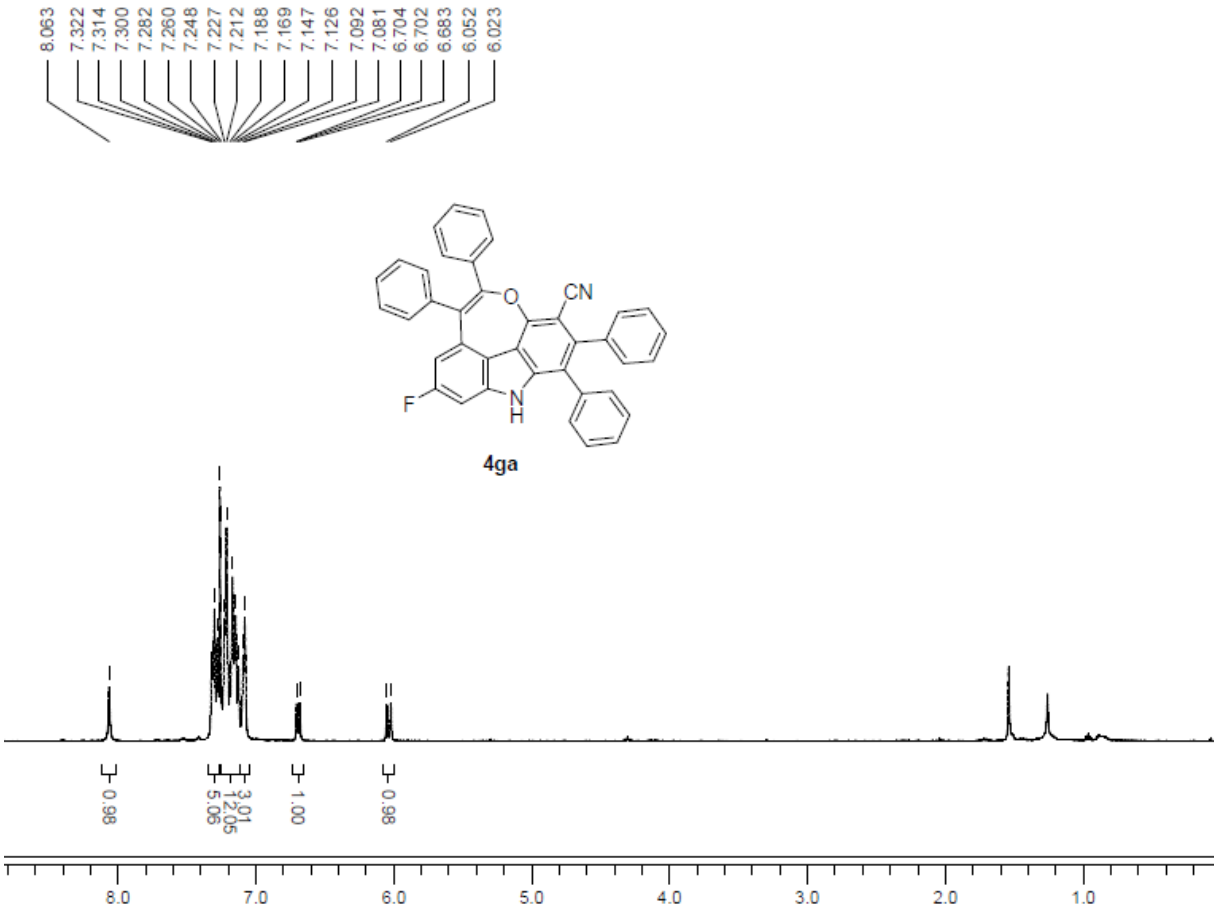
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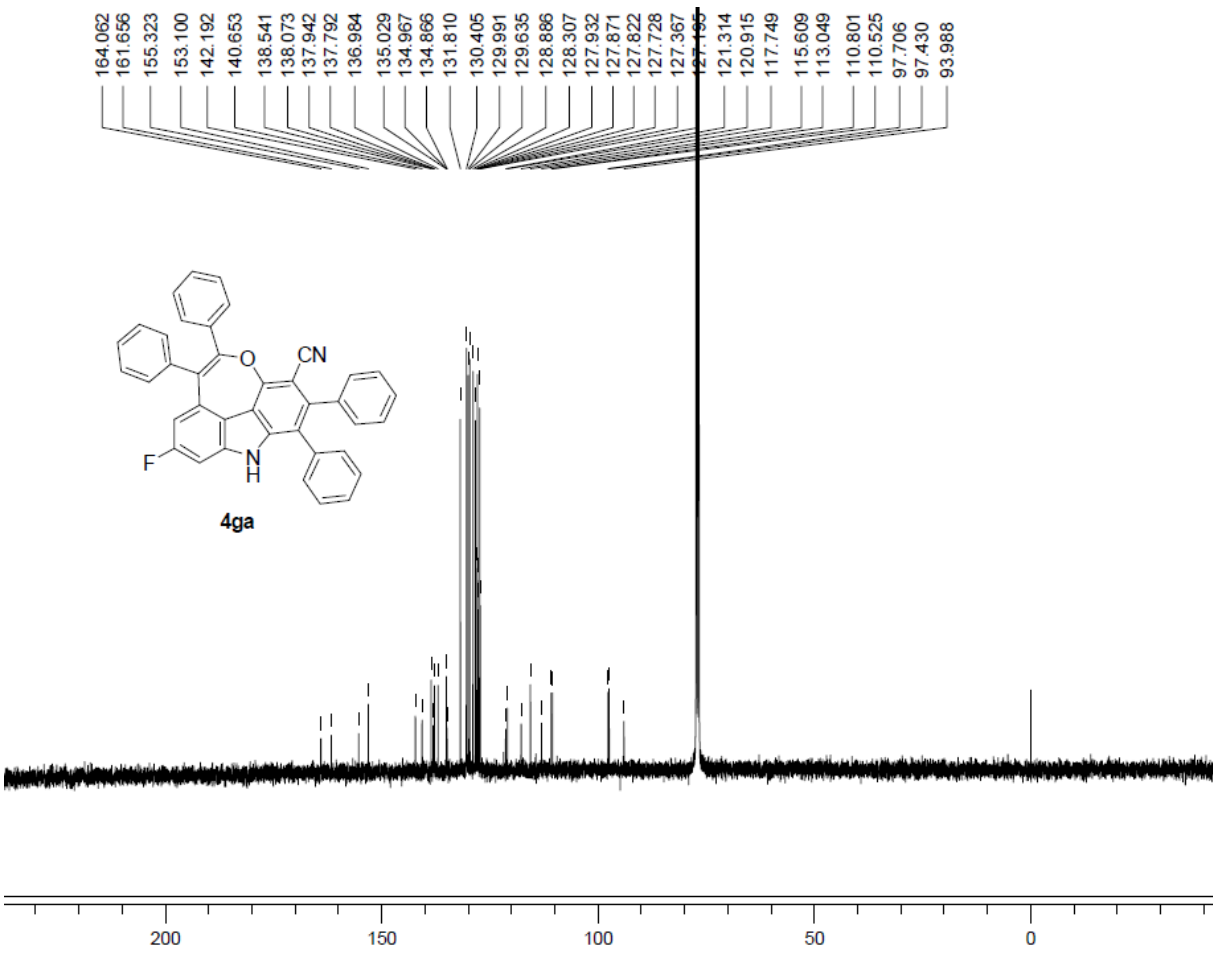
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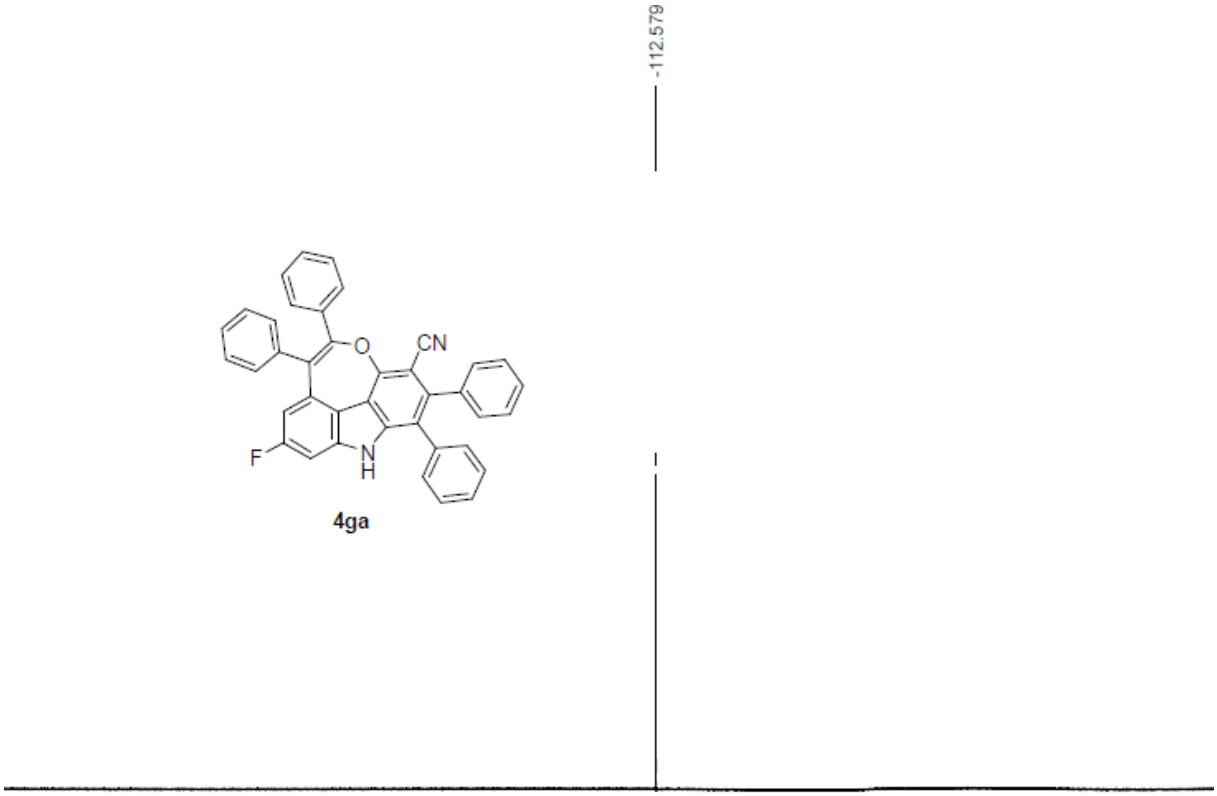
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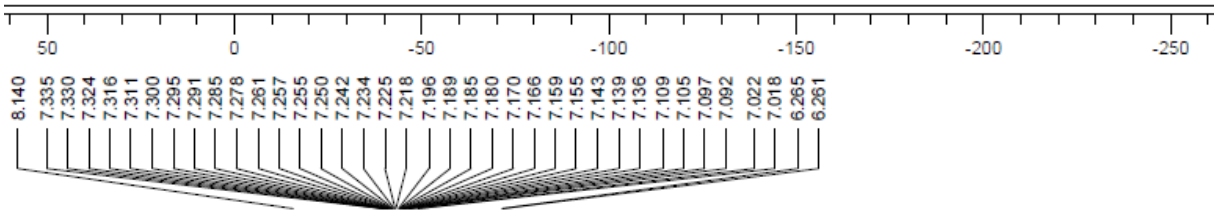
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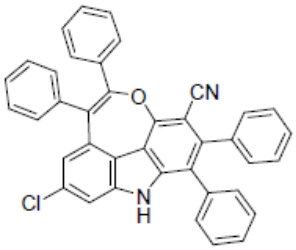
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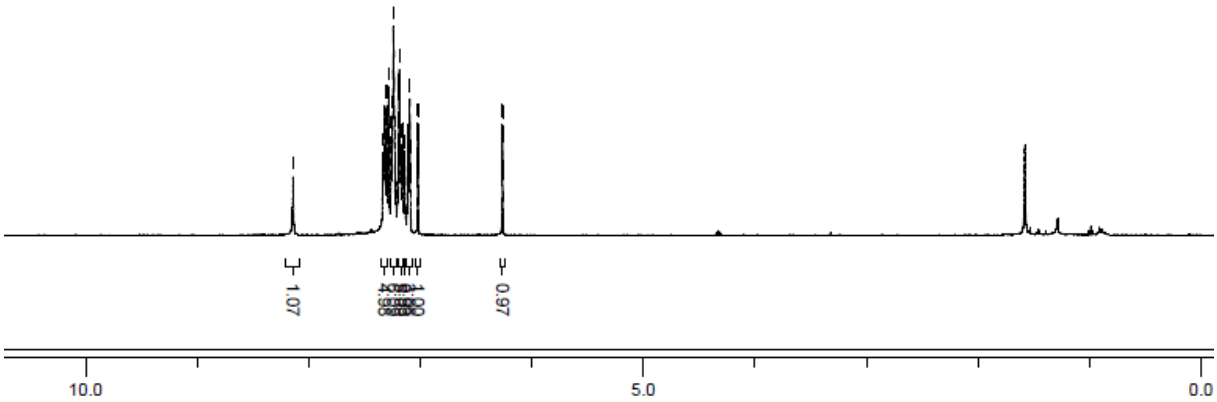
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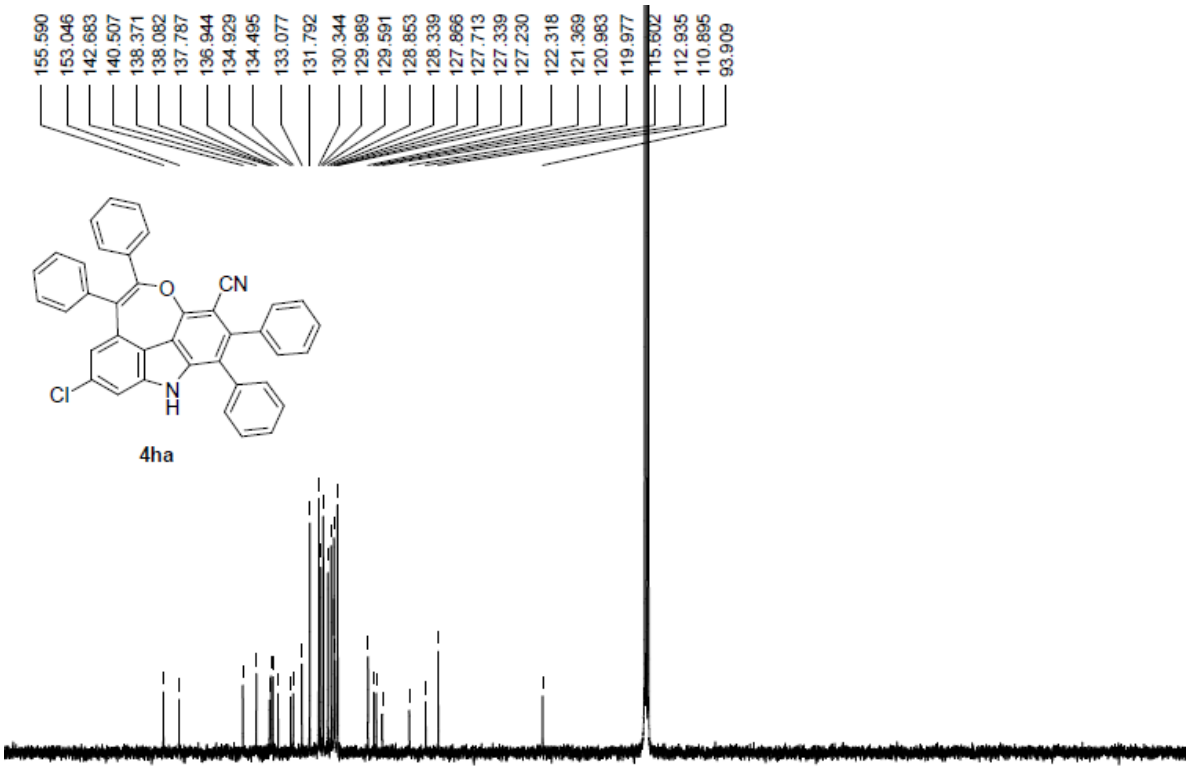
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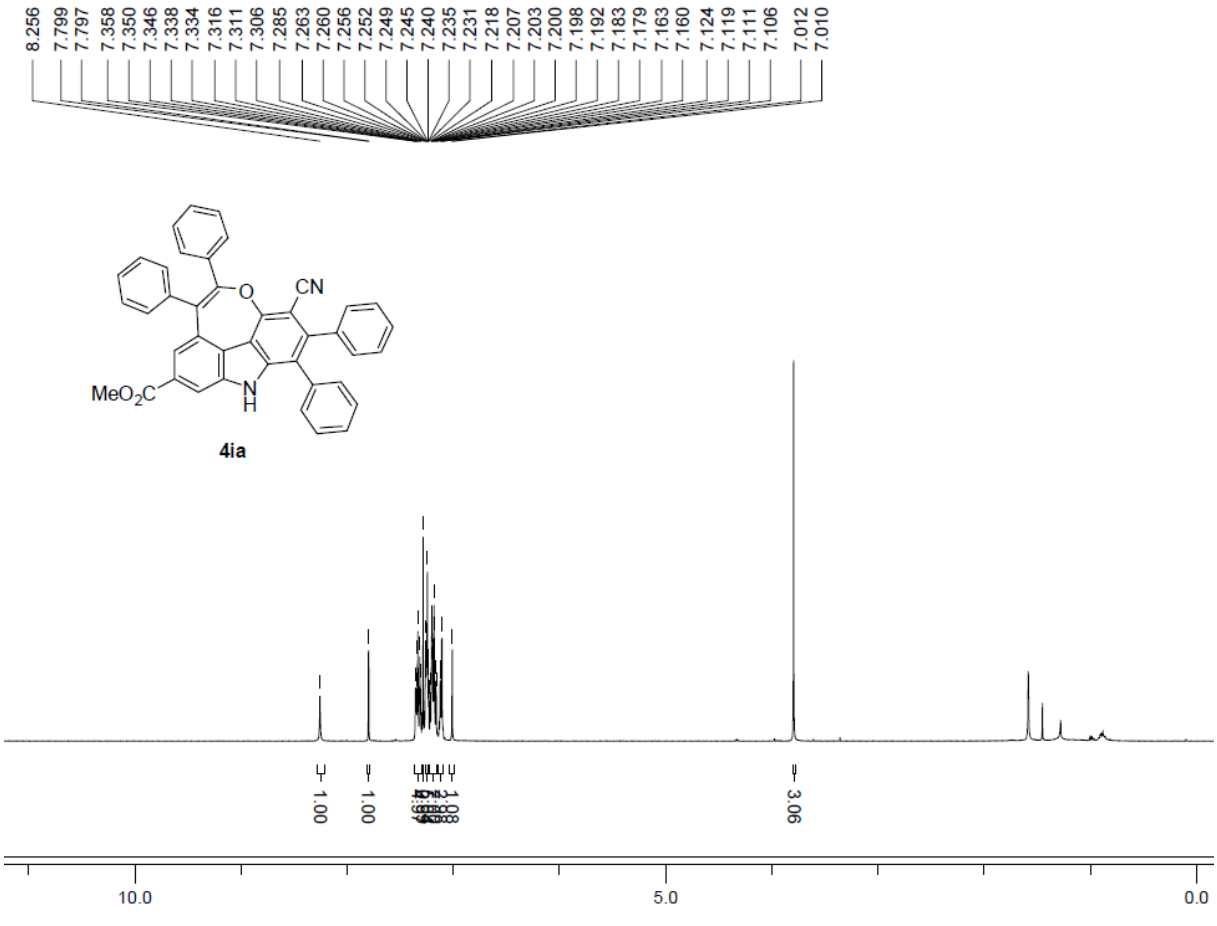
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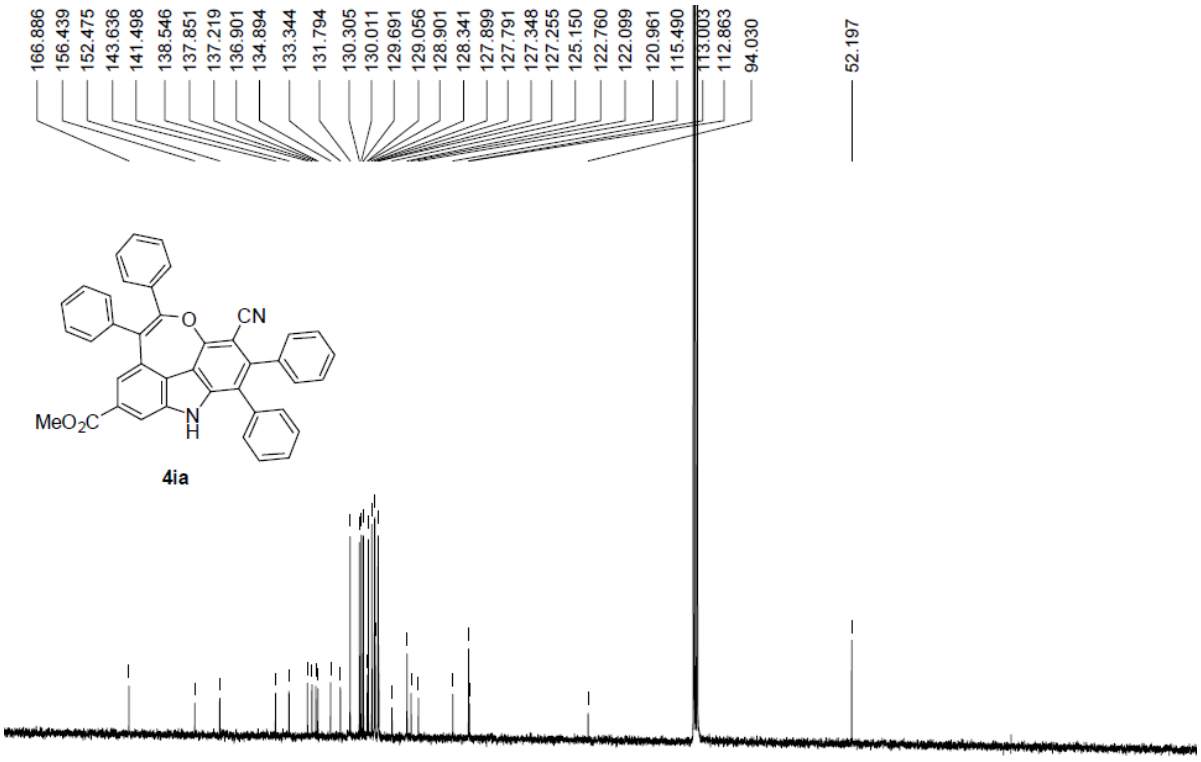
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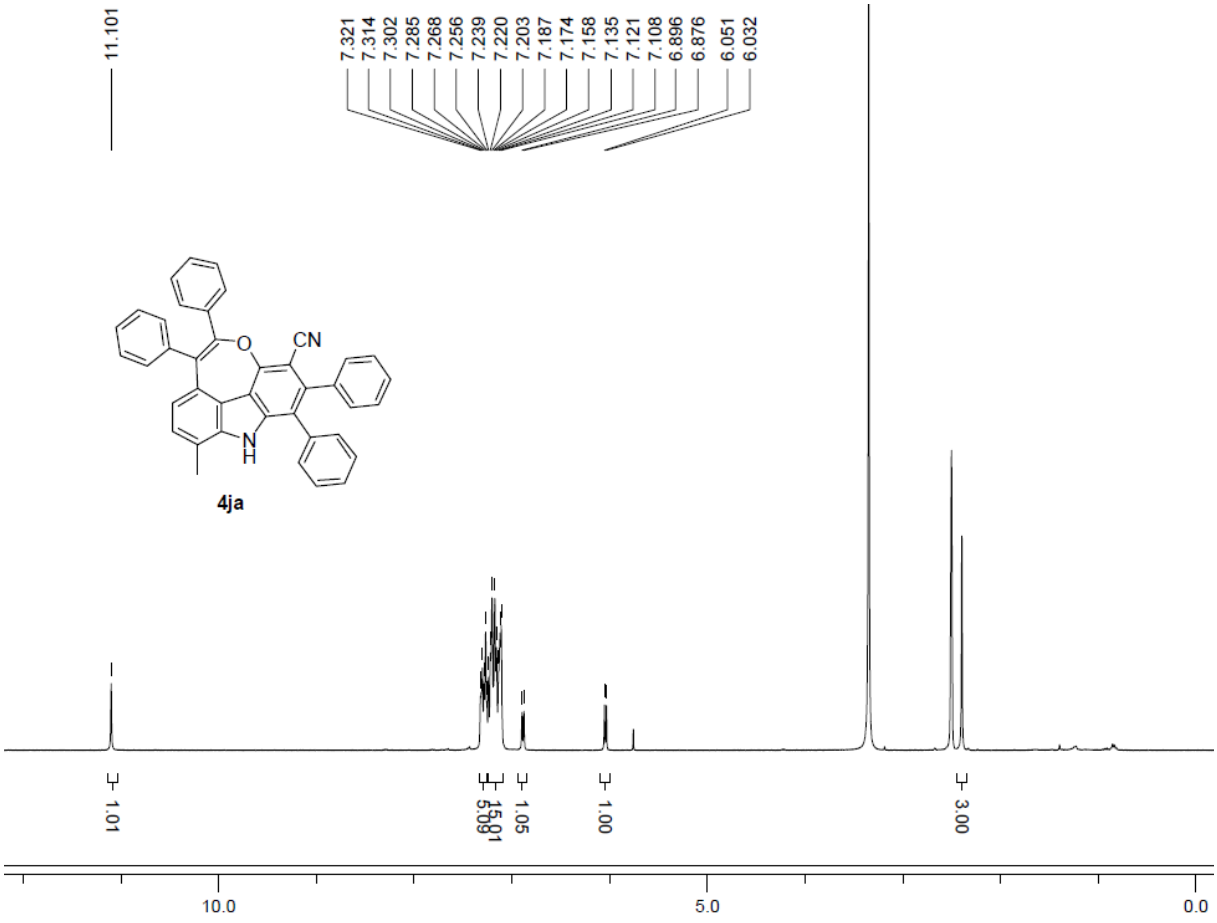
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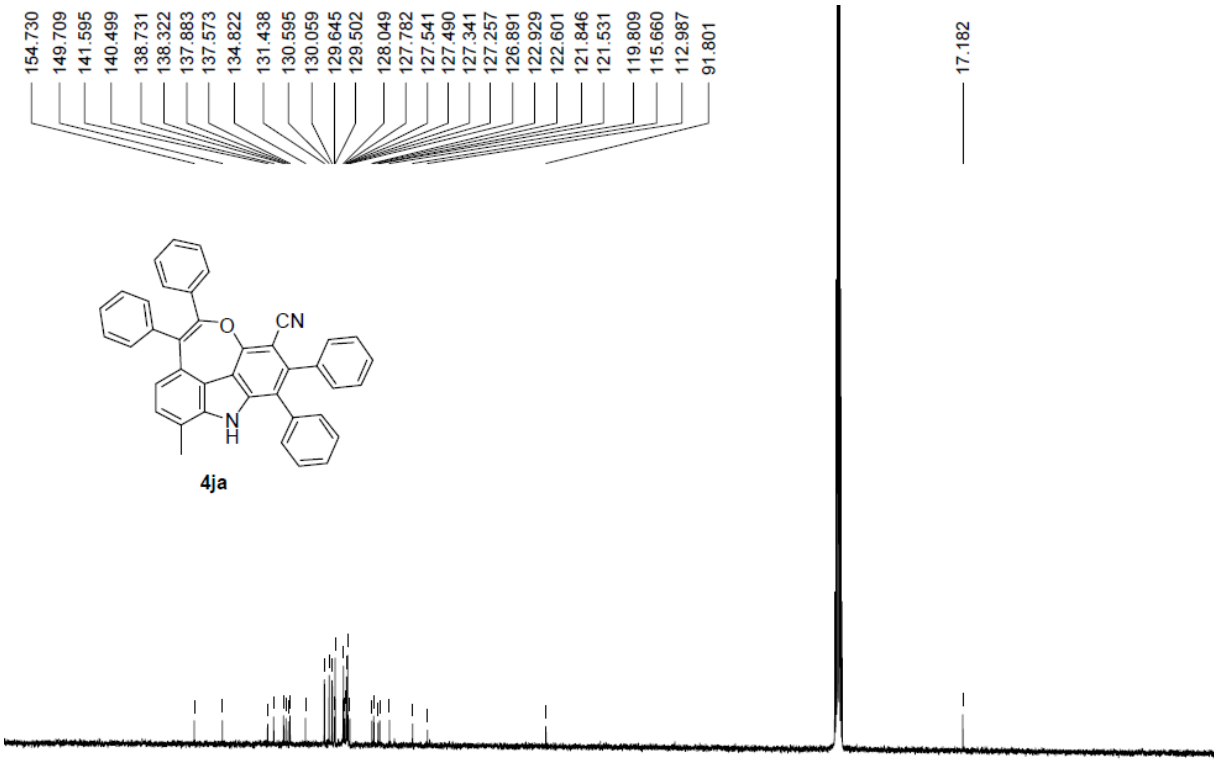
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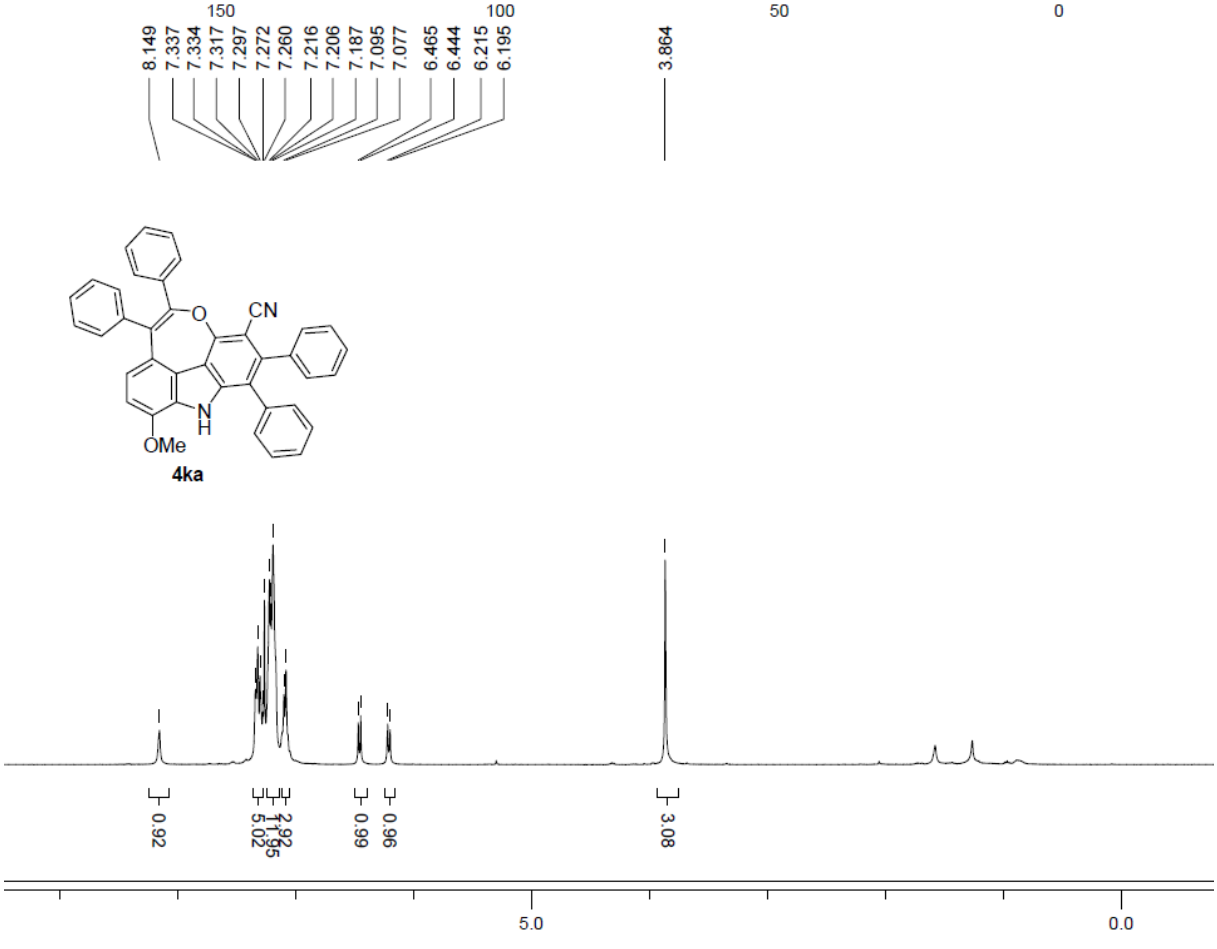
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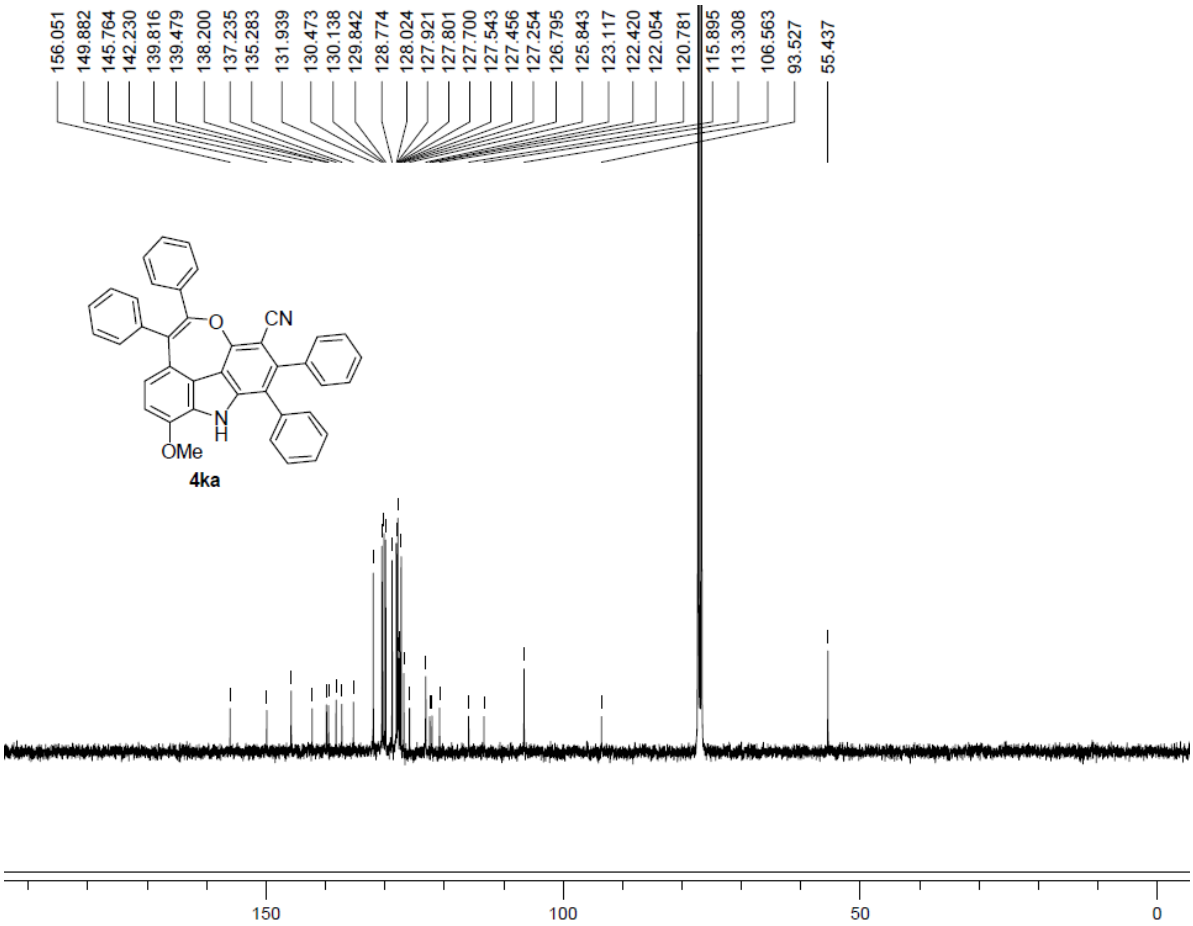
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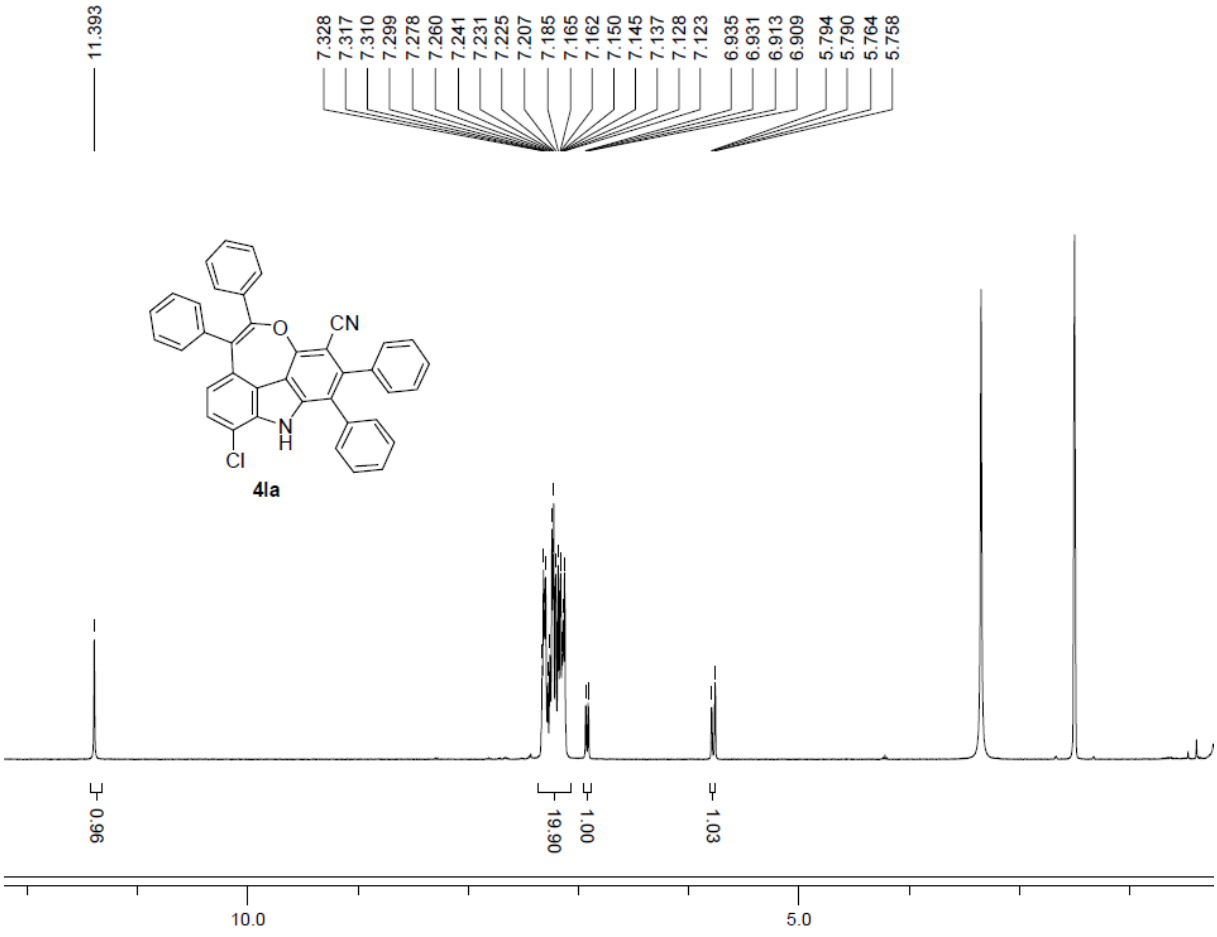
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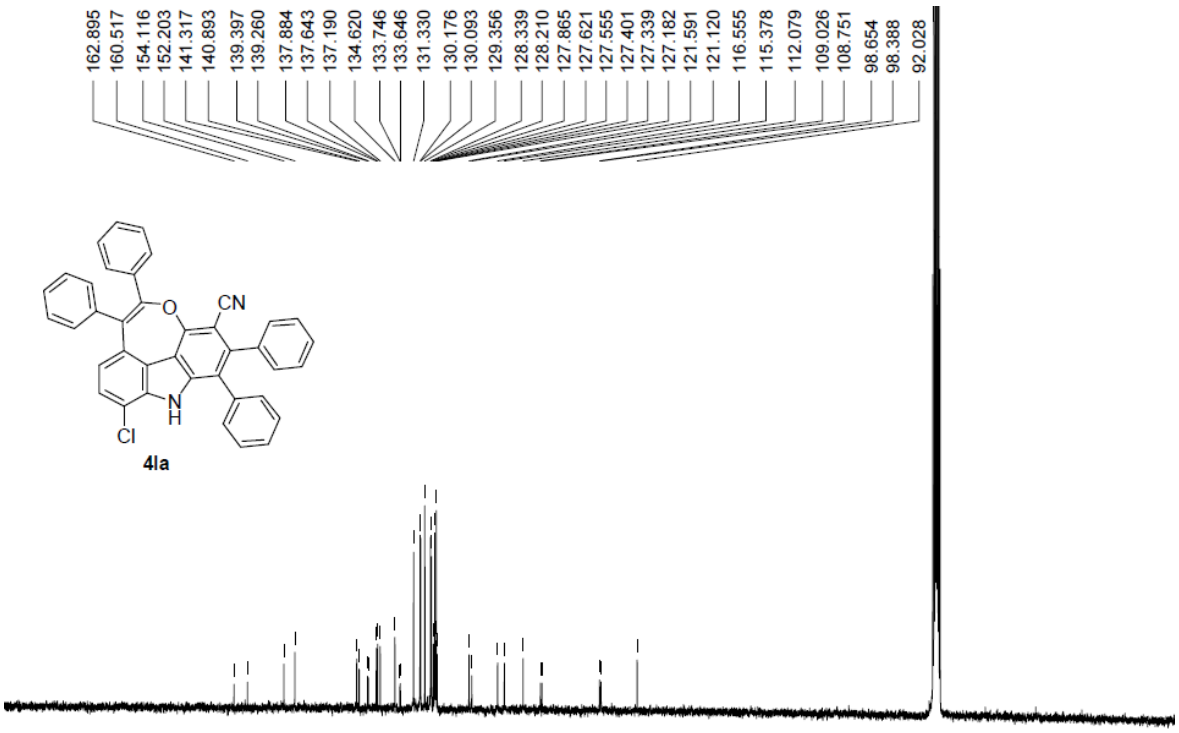
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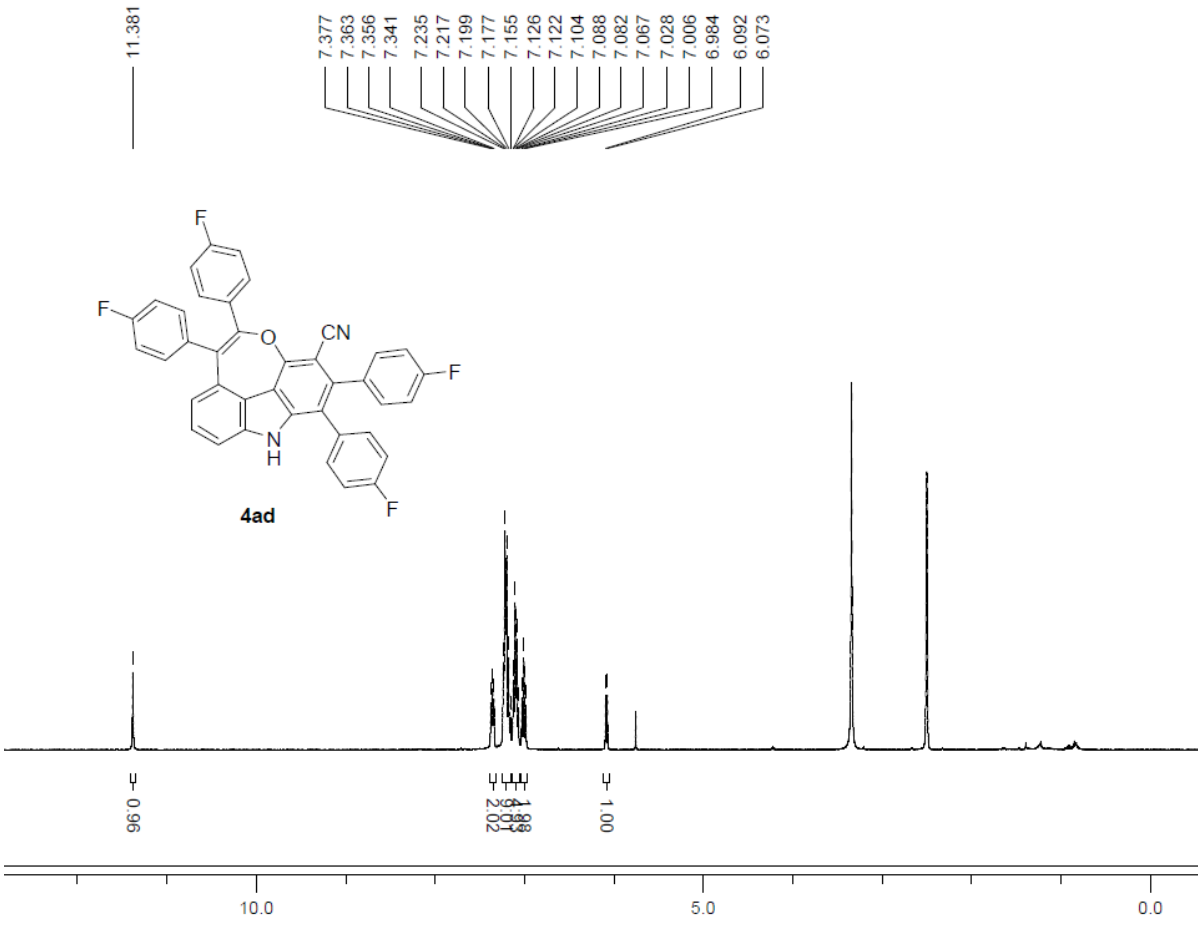
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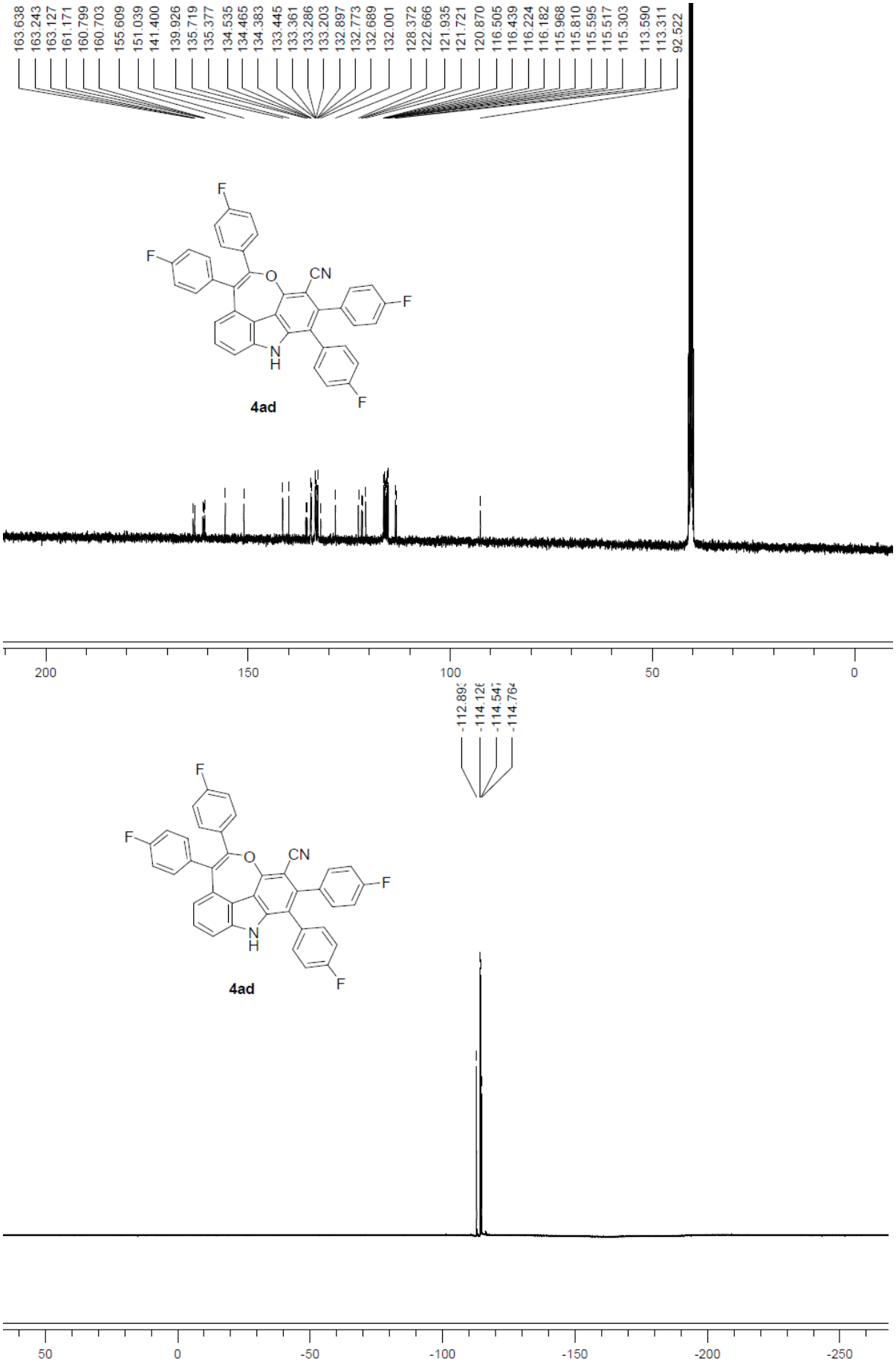
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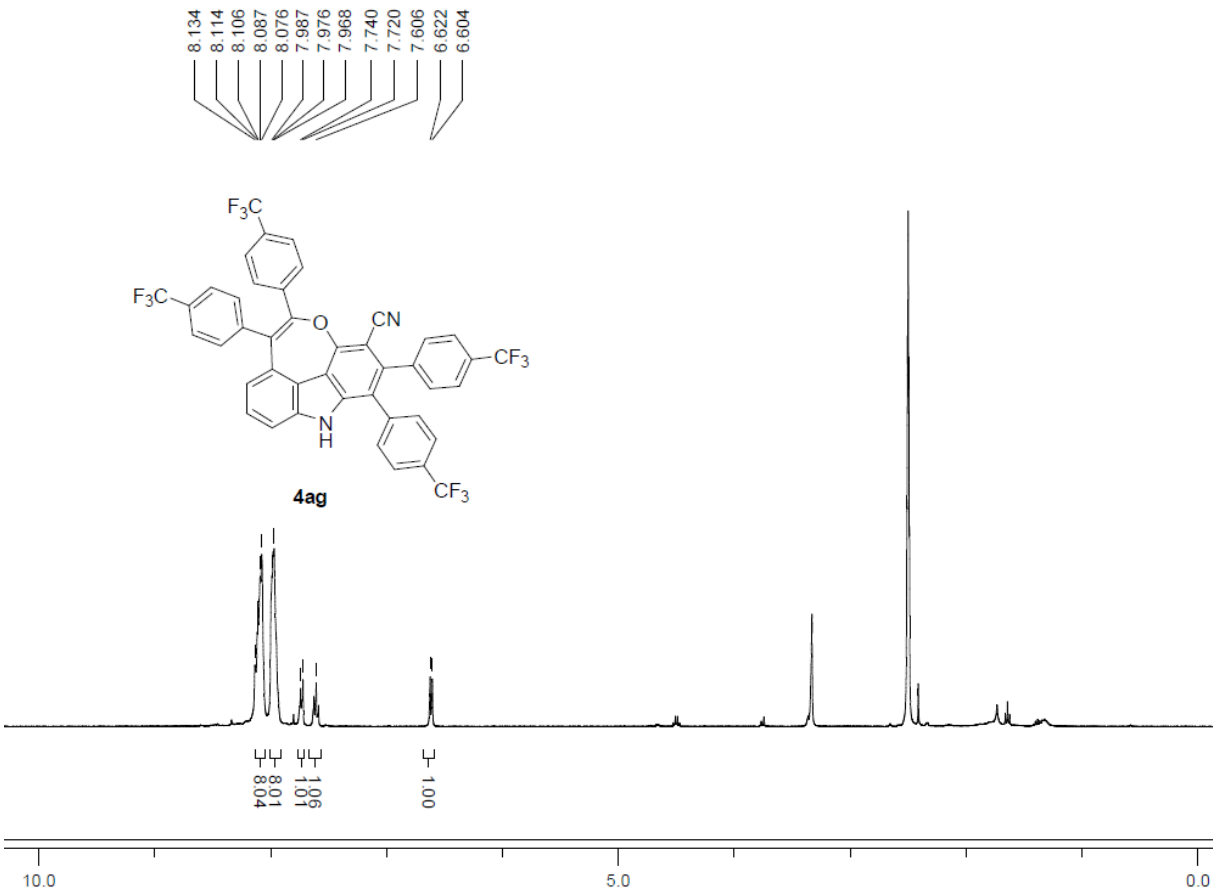
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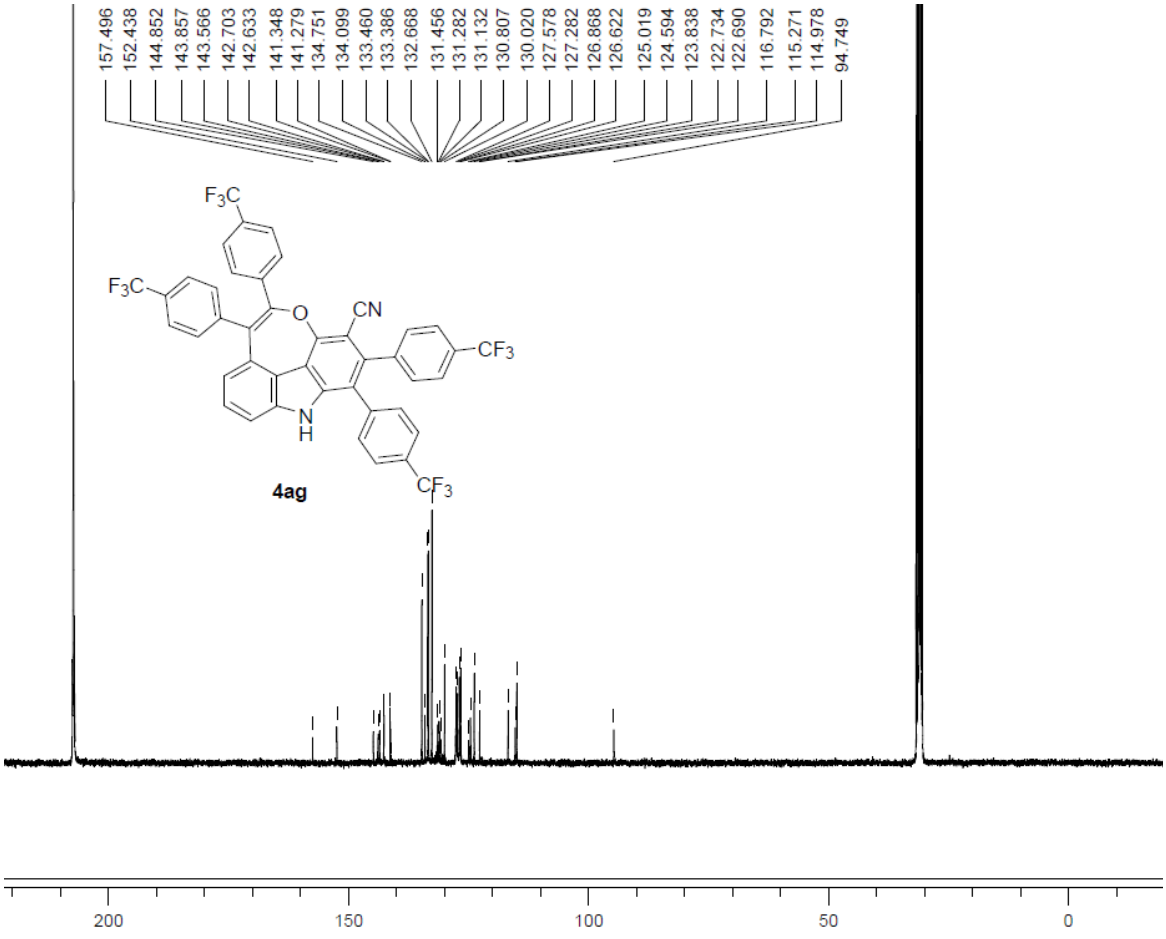
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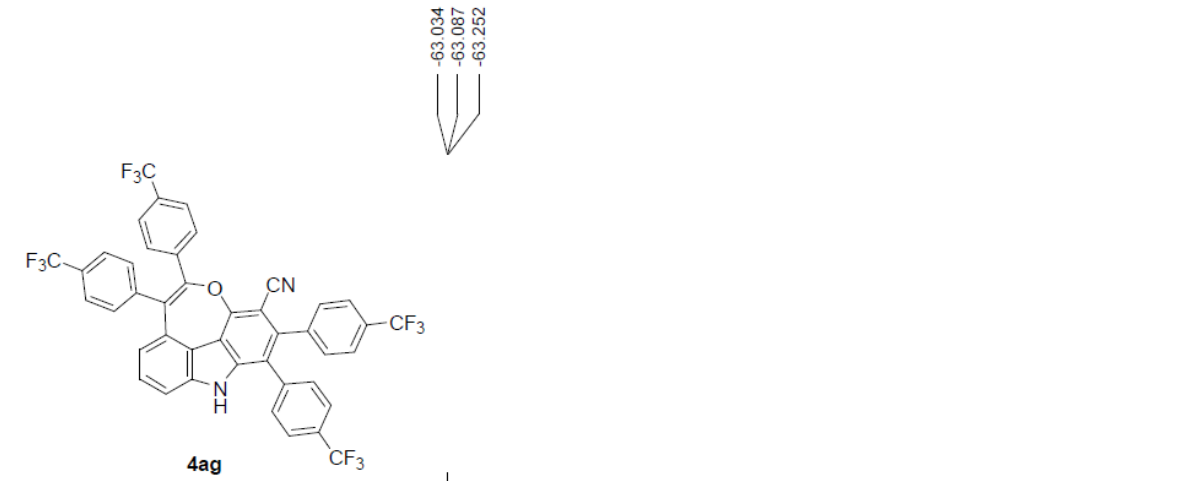
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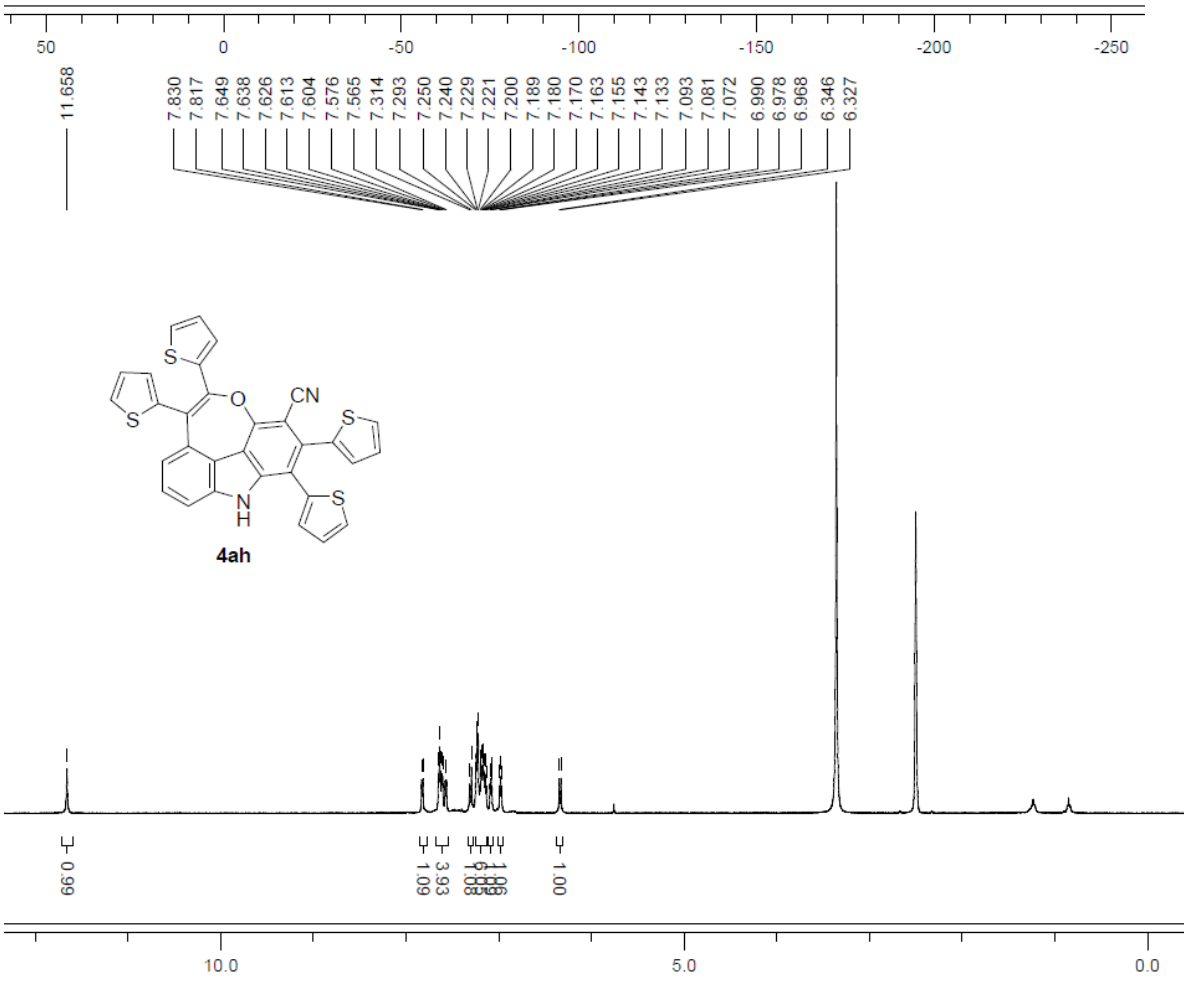
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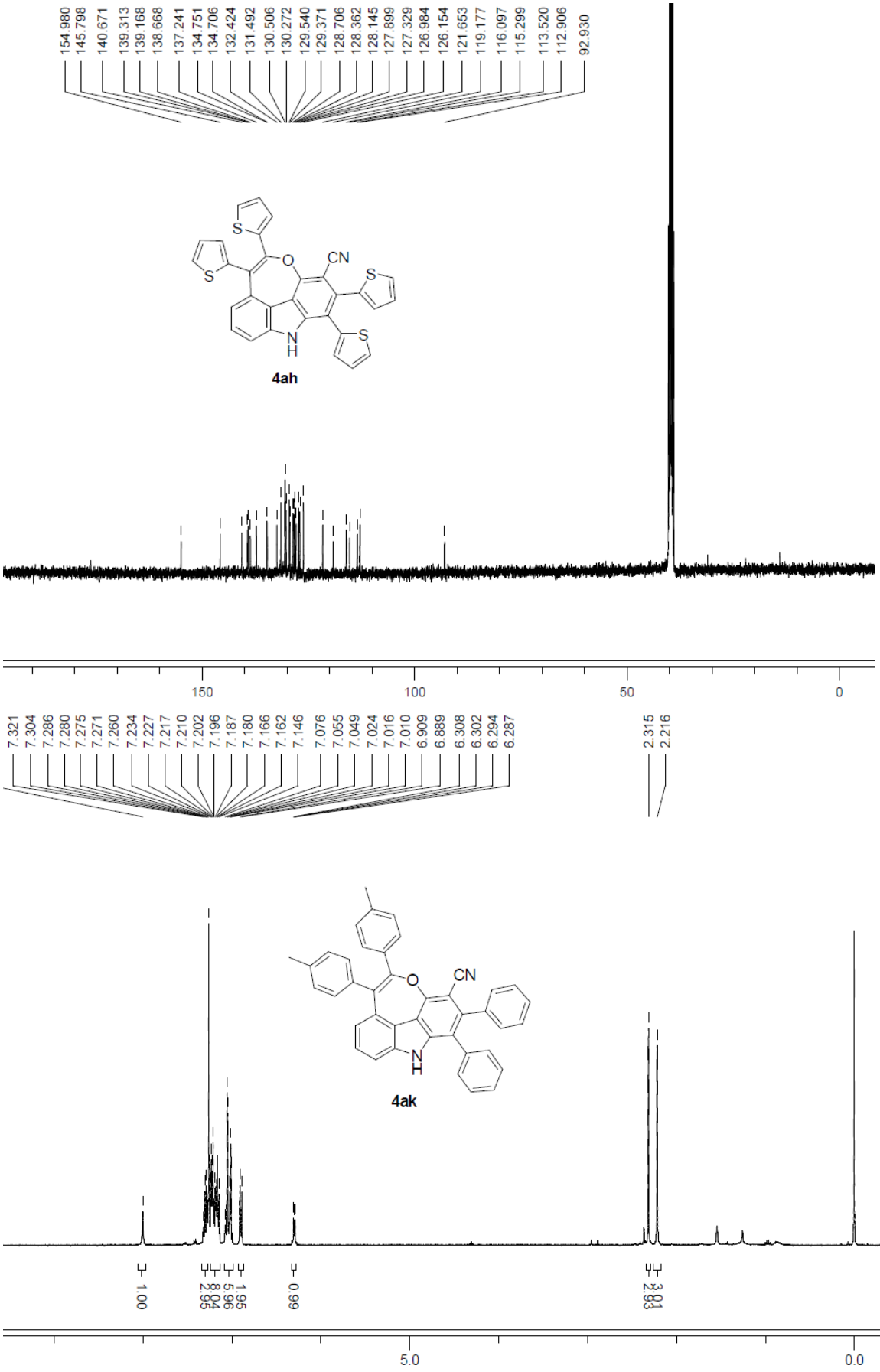
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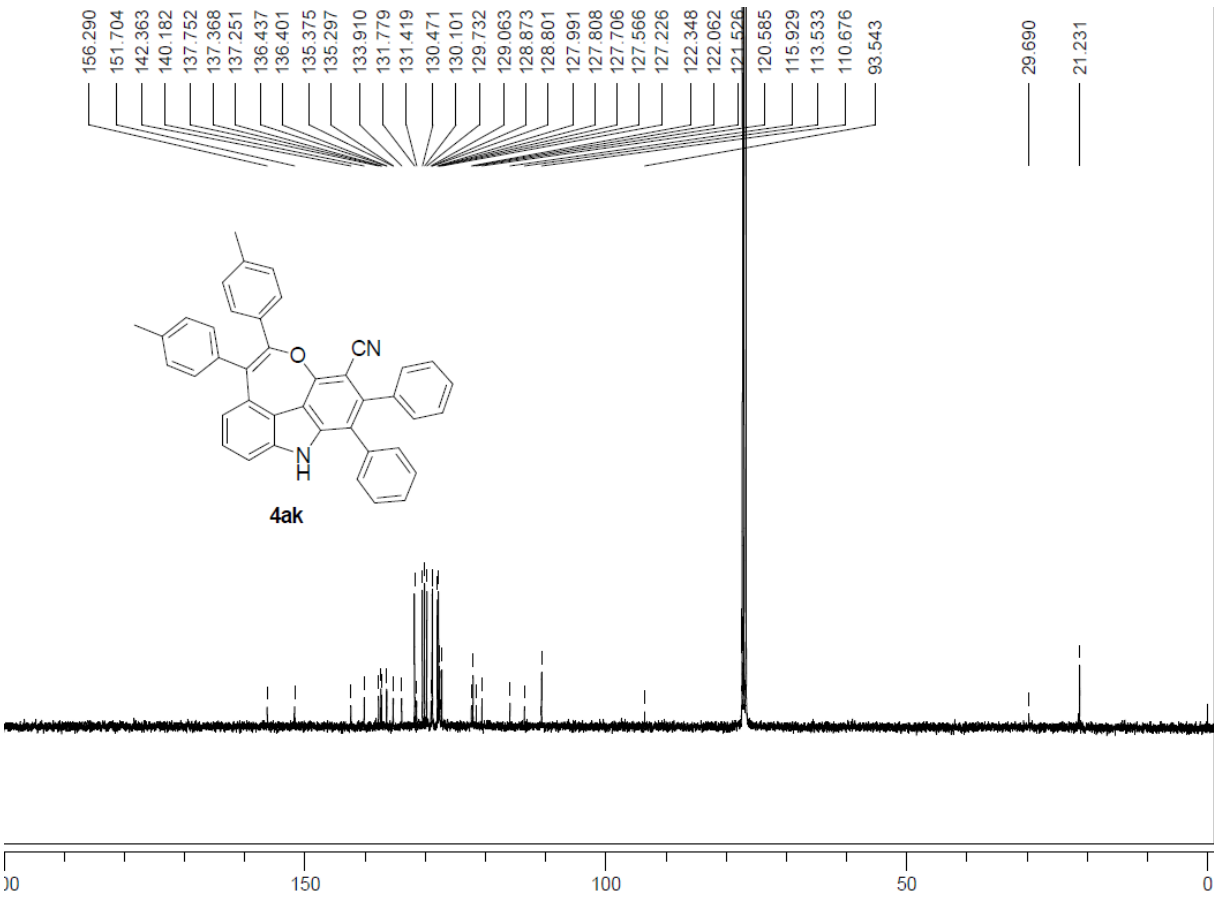
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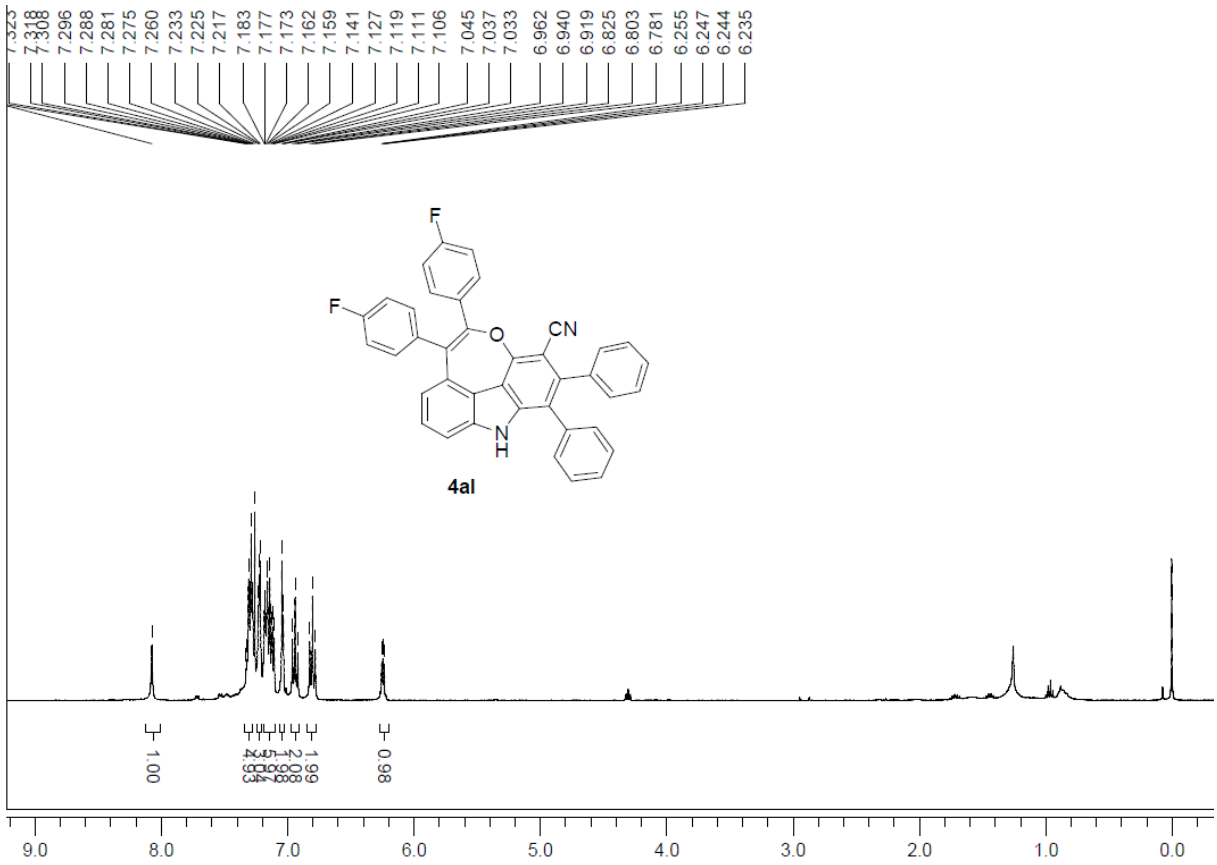
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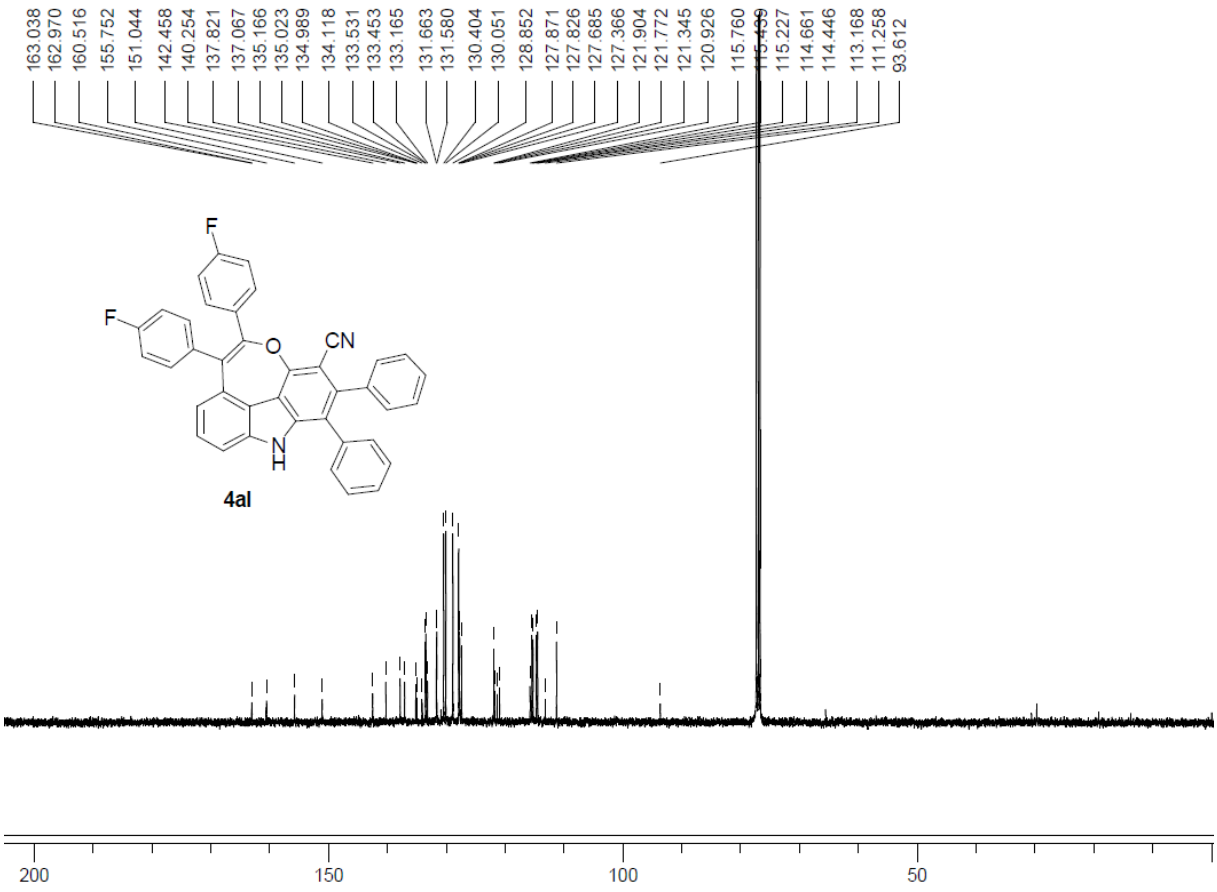
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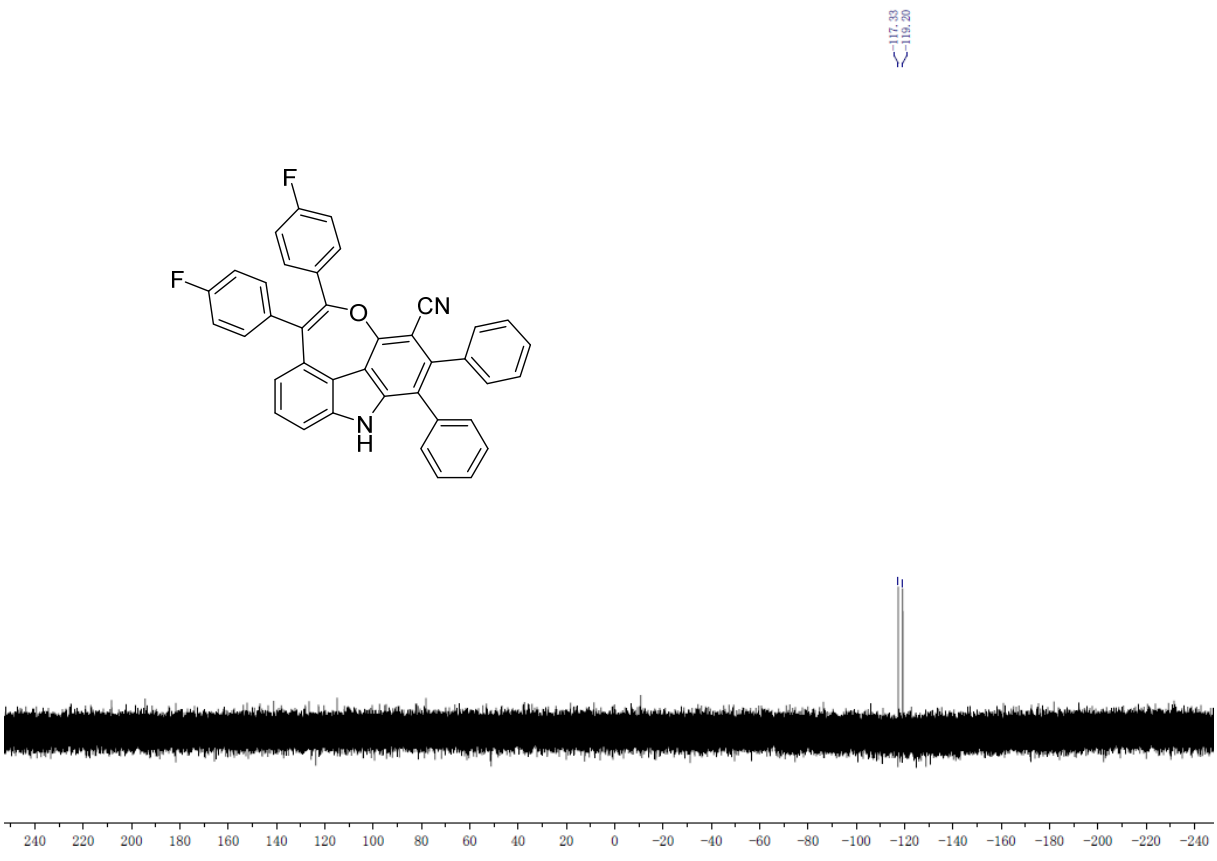
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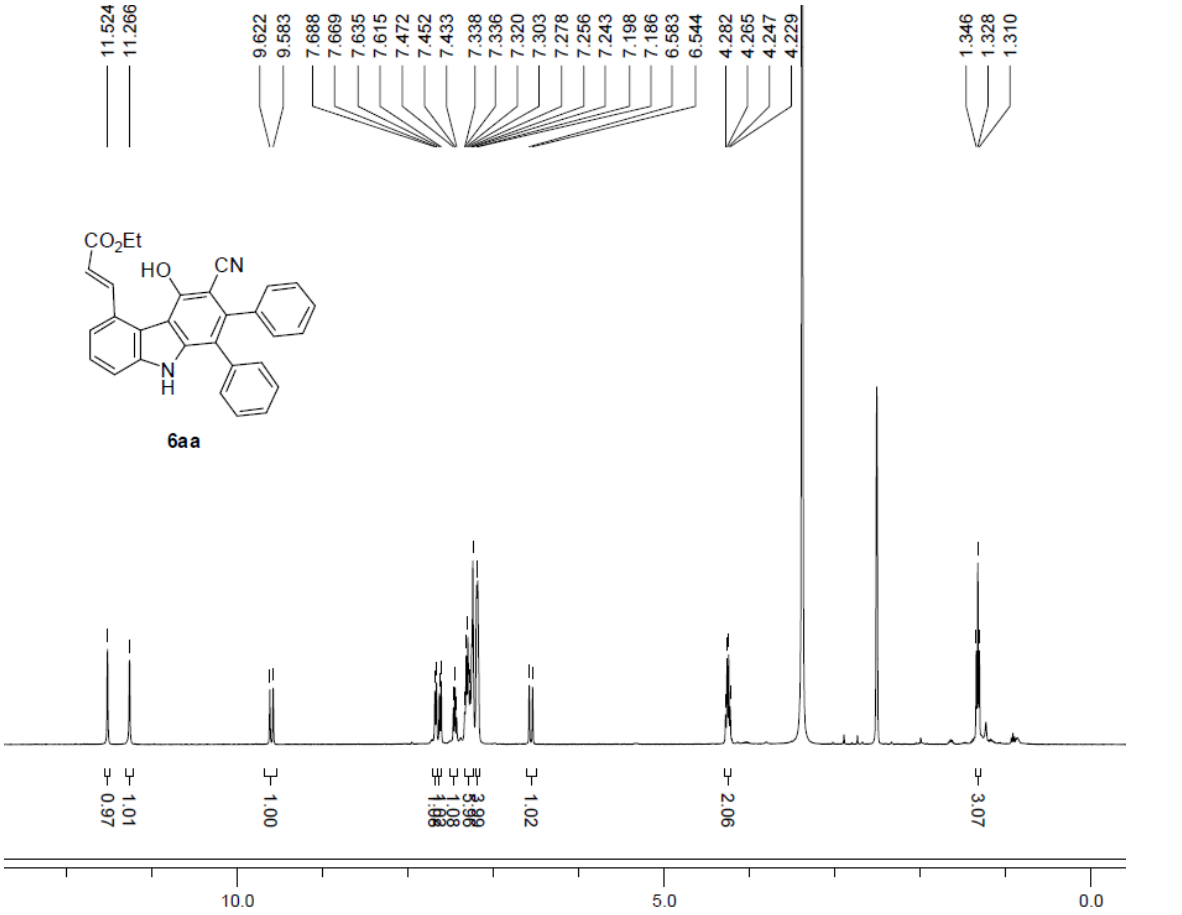
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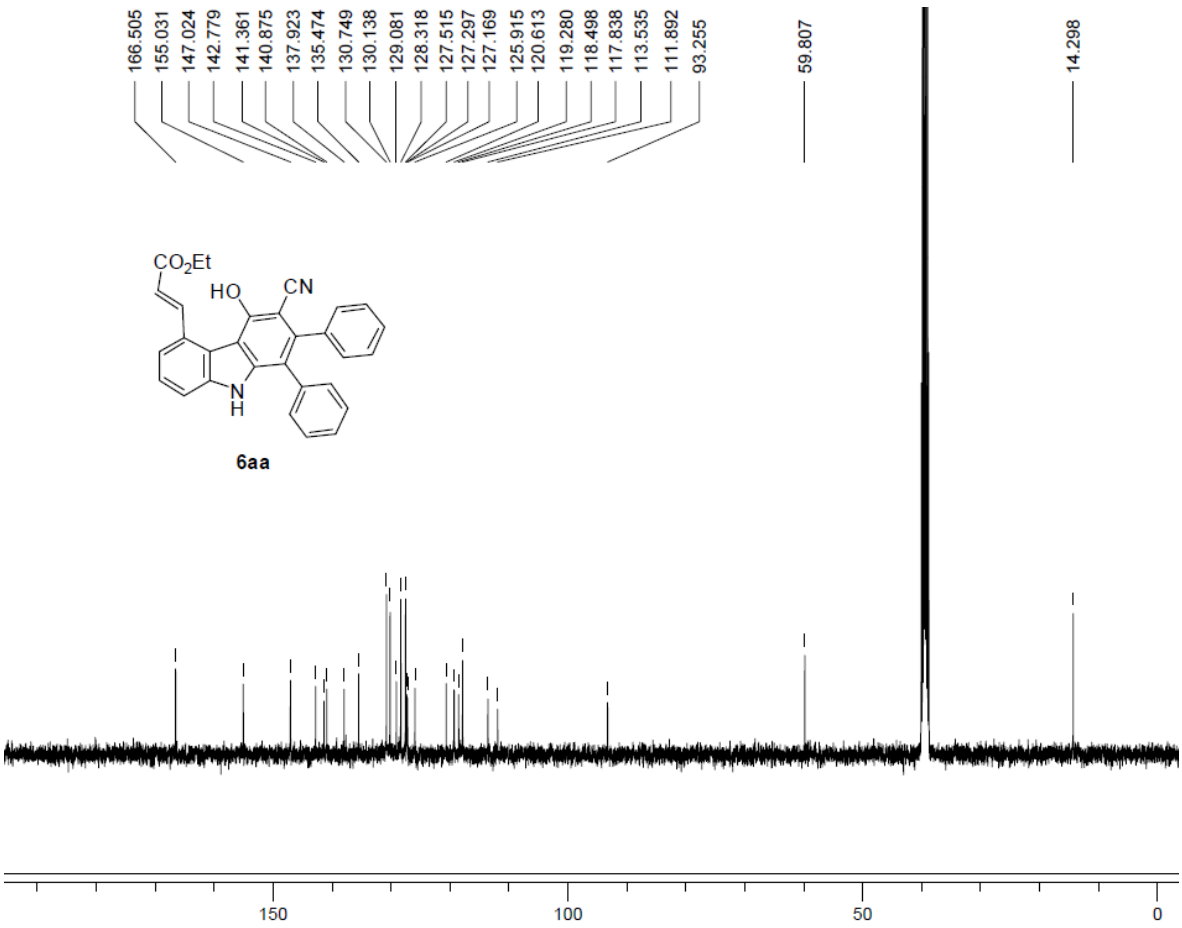
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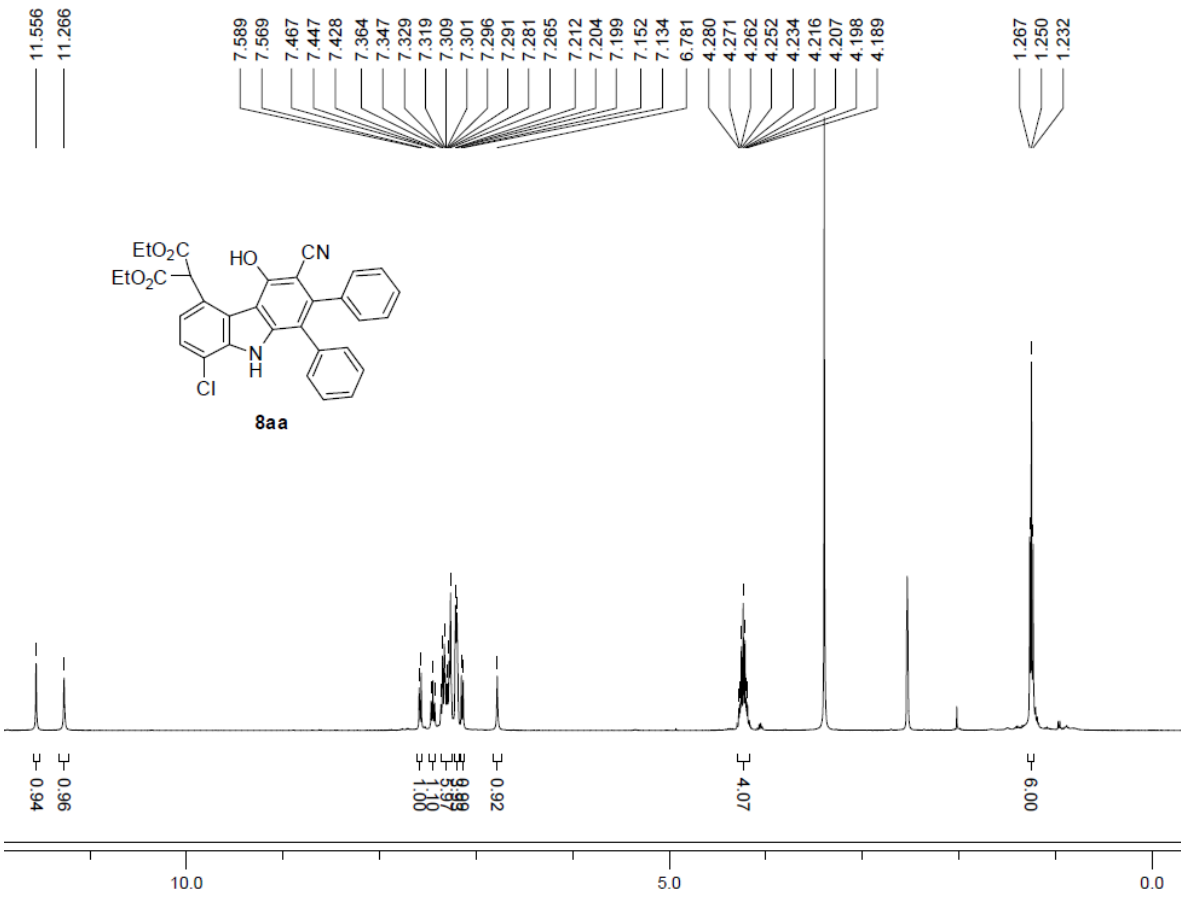
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7.447
7.428
7.364
7.347
7.329
7.319
7.309
7.301
7.296
7.291
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7.265
7.212
7.204
7.199
7.152
7.134
6.781
4.280
4.271
4.262
4.252
4.234
4.216
4.207
4.198
4.189
1.267
1.250
1.232
EtO2C
EtO2C
HO
CN
N
H
Cl
8aa
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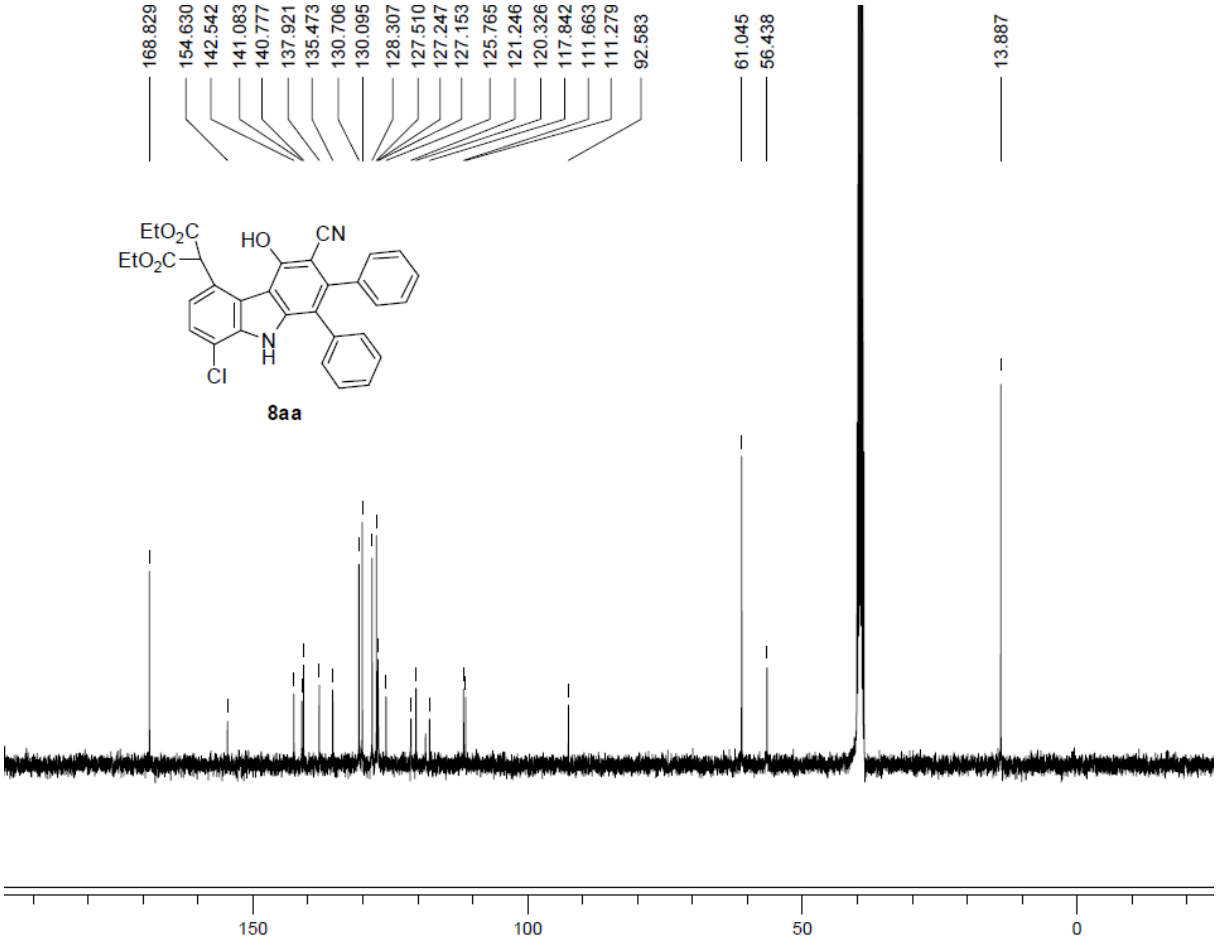
0.96
1.00
0.92
4.07
6.00
10.0
5.0
0.0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127.153
125.765
121.246
120.326
117.842
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111.279
92.583
61.045
56.438
13.887
EtO2C
EtO2C
HO
CN
N
H
Cl
8aa
150
100
50
0

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