(***83 pages***)

Supporting Information For
Rhodium(III)-catalyzed C–H activation and intermolecular annulation with terminal alkynes: from indoles to carbazoles

Jinlong Jia,[a,b+] Jingjing Shi,[a+] Jie Zhou,[a,c] Xuelei Liu,[a] Yanling Song,[b] H. Eric Xu*[a,d] and Wei Yi*[a]

[a]*VARI/SIMM Center, Center for Structure and Function of Drug Targets, CAS-Key Laboratory of Receptor Research, Shanghai Institute of Materia Medica, Chinese Academy of Sciences, Shanghai 201203, P.R. China.*
Fax: +86-21-20231000-1715; Tel: 86-21-20231000-1715
[b]*College of Pharmaceutical and Biological Engineering, Shenyang University of Chemical Technology, Shenyang 110142, P.R. China*
[c]*School of Chemistry and Chemical Engineering, Sun Yat-sen University, Guangzhou 510275, P.R. China*
[d]*Laboratory of Structural Sciences, Program on Structural Biology and Drug Discovery, Van Andel Research Institute, Grand Rapids, Michigan 49503, USA*
E-mail: yiwei.simm@simm.ac.cn, eric.xu@simm.ac.cn
[+] *J. Jia and J. Shi contributed equally to this work.*

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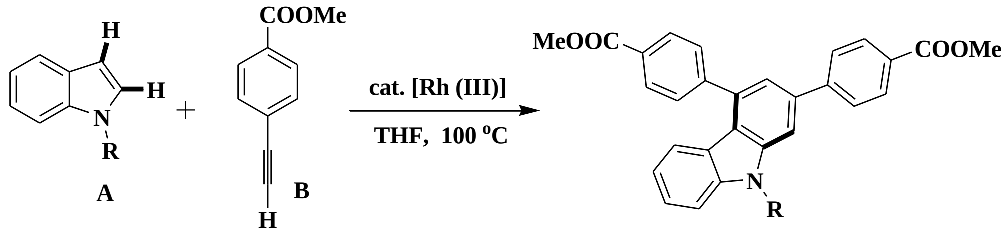
General methods and materials:

$[Cp^*RhCl_2]_2$ and $AgSbF_6$ were purchased from Adamas-beta and used without further purification. $[Cp^*Rh(MeCN)_3](SbF_6)_2$,[1] $[Cp^*Rh(OAc)_2]_2$[2] and substrates 1-(pyrimidin-2-yl)-1*H*-indoles[3-5] were synthesized according to published procedures. Other chemicals were purchased from commercial suppliers and were dried and purified when necessary. The water used was re-distillated and ion-free. Melting points were determined on a WRS-1B digital instrument without correction. ^{1}H and ^{13}C NMR spectra were recorded on Varian Mercury-Plus 400 NMR instruments (^{1}H 400 MHz; ^{13}C 100 MHz or ^{13}C 125 MHz) in $CDCl_3$. Abbreviations for data quoted are s, singlet; brs, broad singlet; d, doublet; t, triplet; dd, doublet of doublets; m, multiplet. Infrared Spectroscopy were recorded on Nicolet 6700 FT-IR spectrometer; Mass spectra and high-resolution mass spectra were measured on Thermo-DFS mass spectrometer. Thin-layer chromatographies were done on pre-coated silica gel 60 F254 plates (Merck). Silica gel 60H (200-300 mesh) manufactured by Qingdao Haiyang Chemical Group Co. (China) was used for general chromatography.

Preliminary optimization studies:



Effects of directing group, Rh(III) species and reaction stoichiometry

Standard procedure: substrate A (0.10 mmol, 1.0 equiv), substrate B (0.12 mmol, 1.2 equiv), THF (2.0 mL), 12 h, under air. Isolated yields were given.

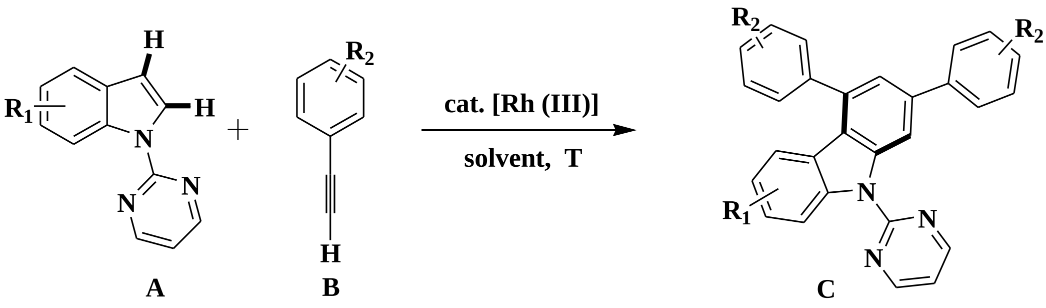
Table S1

Entry	R	Catalyst system (mol %)	Yield (%)
1	H	$[Cp^*Rh^{III}(MeCN)_3](SbF_6)_2$ (10)	0
2	Me	$[Cp^*Rh^{III}(MeCN)_3](SbF_6)_2$ (10)	0
3	Boc	$[Cp^*Rh^{III}(MeCN)_3](SbF_6)_2$ (10)	0
4	$CON(Me)_2$	$[Cp^*Rh^{III}(MeCN)_3](SbF_6)_2$ (10)	0
5	2-Pyrimidyl	$[Cp^*Rh^{III}(MeCN)_3](SbF_6)_2$ (10)	36
6[a]	2-Pyrimidyl	$[Cp^*Rh^{III}(MeCN)_3](SbF_6)_2$ (10)	51
7[a]	2-Pyrimidyl	$[Cp^*Rh(OAc)_2]_2$(10)	0
8[a]	2-Pyrimidyl	$[Cp^*RhCl_2]_2$(10)	0
9[a]	2-Pyrimidyl	$[Cp^*RhCl_2]_2$(10)+$Cu(OAc)_2$(100)	0
10[a]	2-Pyrimidyl	$[Cp^*RhCl_2]_2$(10)+AgOAc(100)	10

[a] A (0.10 mmol, 1.0 equiv) and B (0.22 mmol, 2.2 equiv) were used.

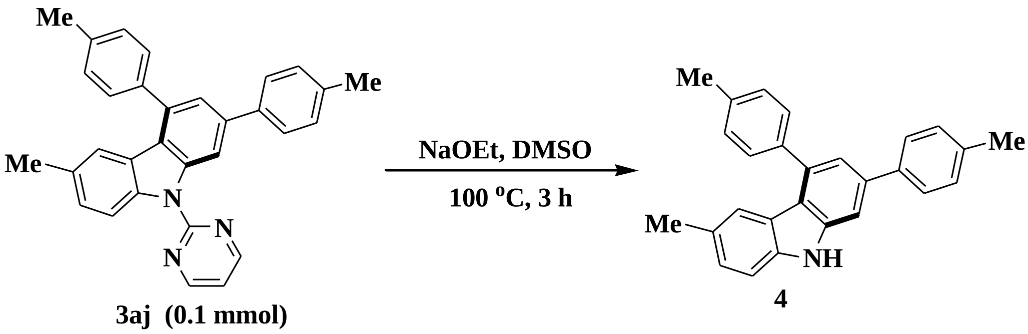
A survey of directing group revealed that the 2-pyrimidyl group was optimal for the reaction outcome (Table S1, entries 1-5). Screening of Rh(III) species showed that $[Cp^*Rh^{III}(MeCN)_3](SbF_6)_2$ complex was the most effective (Table S1, entries 6-10). Investigation of reaction stoichiometry demonstrated that the ratio of 1: 2.2 was better than that of 1: 1.2 (Table S1, entries 5-6). Based on these results, we carried out further reaction optimization including solvent, reaction temperature, catalyst loading, and concentration. For more detailed information, please see Table 1 in the main text.

General procedure for C–H activation and intermolecular annulation:



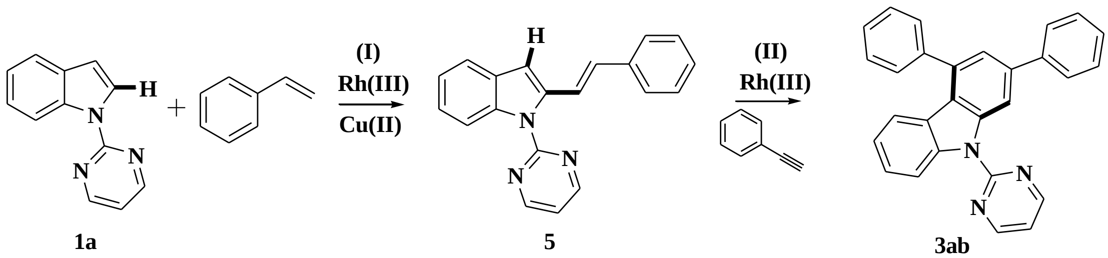
The mixture of $[Cp^*Rh(MeCN)_3][SbF_6]_2$ (8.3 mg, 0.01mmol, 10 mol%), substrate A (0.10 mmol, 1.0 equiv), substrate B (0.22 mmol, 2.2 equiv) and dioxane (2.0 mL) were stirred at 80 ℃ for 12 h under air. The resulting mixture was cooled to room temperature, silica gel column directly to give the desired products **3aa-3qa** and **3ab-3as**.

Procedure for deprotection:



A suspension of **3aj** (44 mg, 0.1 mmol) and NaOEt (34 mg, 0.5 mmol) in dry DMSO (1.0 mL) under N_2 was stirred at 100 ^{o}C until consumption of the starting material (3 h). It was allowed to reach room temperature, diluted with EtOAc (10 mL) and washed brine. The combined organic phase was dried (Na_2SO_4). After evaporation of the solvents under reduced pressure, the crude product was purified on a silica gel column to afford the desired free-NH carbazole **4**.

Procedure for the synthesis of 3ab *via* intermedicate 5:



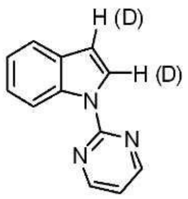
1a **5** **3ab**

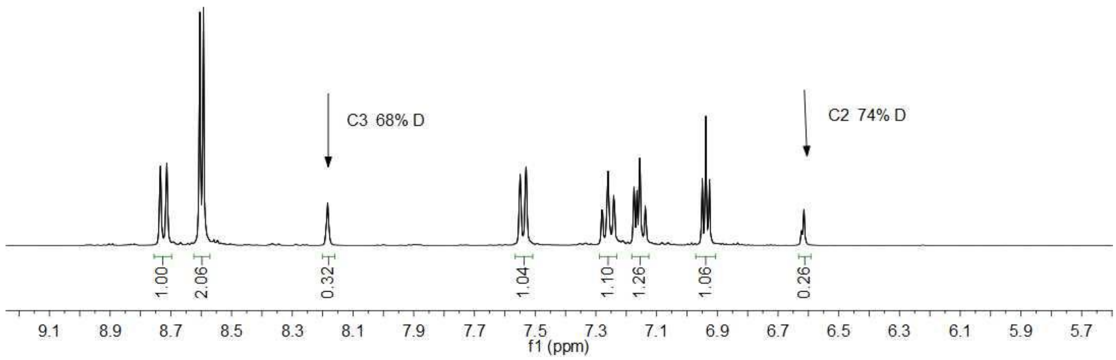
(**I**) C2-Alkenylated indole **5** was synthesized by the reported procedure[6] with slight modifications. Briefly, a mixture of **1a** (0.3 mmol, 1.0 equiv), $[Cp^*Rh(CH_3CN)_3][SbF_6]_2$ (5.00 mg, 0.006 mmol, 2.0 mol%), $Cu(OAc)_2{\cdot}H_2O$ (0.60 mmol, 2.0 equiv) and styrene (0.9 mmol, 3.0 equiv) was combined in a Schlenk tube followed by addition of THF (2.0 mL) under Ar. Then the reaction mixture was heated to 100 ^{o}C with stirring for 24 h. The resulting mixture was cooled to room temperature, silica gel column directly to give the desired intermedicate **5**.

(**II**) The mixture of $[Cp^*Rh(MeCN)_3][SbF_6]_2$ (8.3 mg, 0.01 mmol, 10 mol%), **5** (0.10 mmol, 1.0 equiv), phenylacetylene (0.12 mmol, 1.2 equiv) and dioxane (2.0 mL) were stirred at 80 ℃ for 2 h under air. The resulting mixture was cooled to room temperature, silica gel column directly to give the desired product **3ab** with 18% yield.

Procedure for estimation of the reversibility of the C−H activation step:

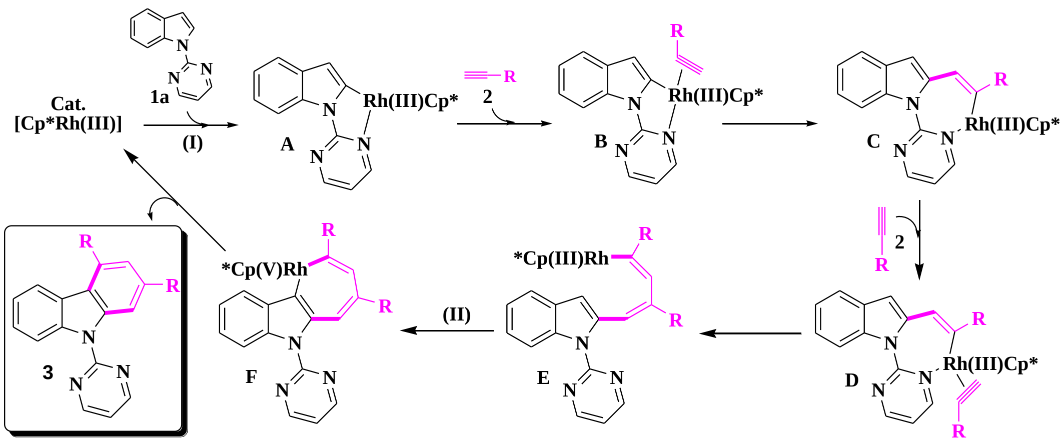
The mixture of $[Cp^*Rh(MeCN)_3][SbF_6]_2$ (8.3 mg, 0.01mmol, 0.10 equiv), **1a** (0.10 mmol, 1.0 equiv) and Dioxane/D_2O (2.0 mL, 20:1) were stirred at 80 ℃ for 1 h under air. The resulting mixture was cooled to room temperature, concentrated under reduced pressure and analyzed by ^{1}H NMR without purification. C2- and C3-positions of indole core were deuterated 74% and 68% respectively.





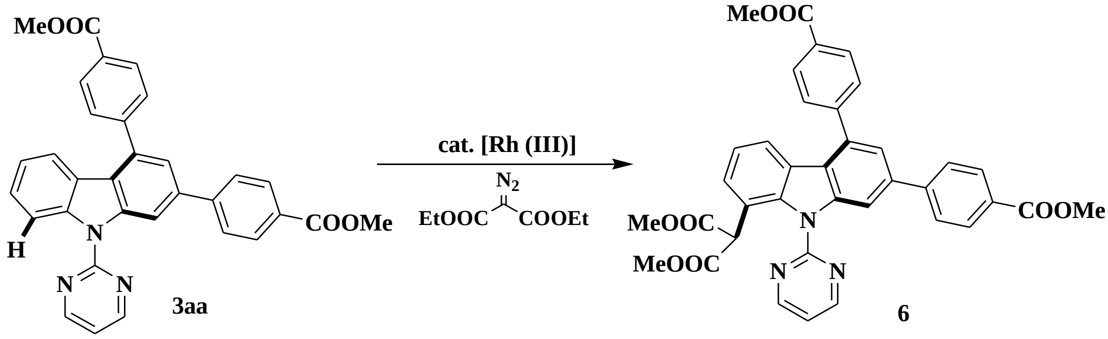
Proposed mechanism:

Taken together these results and literature precedent, a plausible reaction mechanism is proposed as bellow:



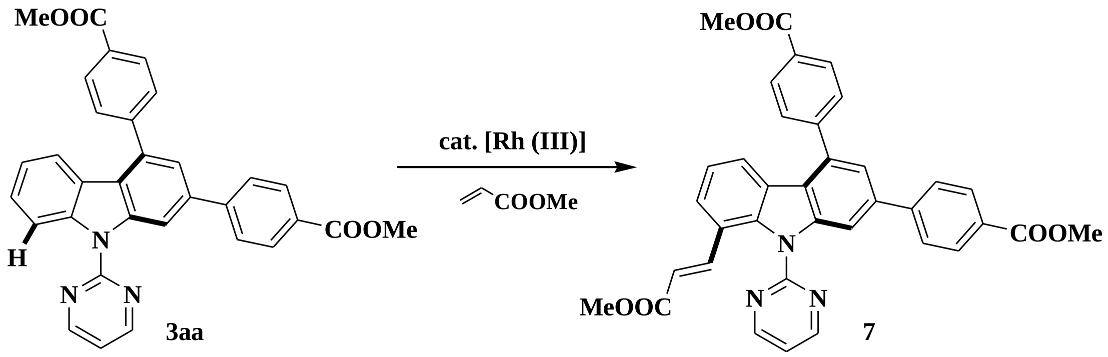
First, the coordination of C2-position of *N*-2-pyrimidyl indole **1a** to a [Cp*Rh(III)] species is the key step for the regioselective C2−H bond cleavage of indole to form a five-membered rhodacycle **A**. This rhodacycle can coordinate one equivalent of terminal alkyne **2** to afford **B**. Subsequently, insertion of alkyne **2** into the Rh−C bond gives a seven-membered rhodacycle **C**, followed by the coordination and the regionselective alkyne insertion once again to give **D** and **E**, respectively. Then intermedicate **E** undergoes further coordination with the C3-position of indole core to provide the seven-membered rhodacycle **F**. Reductive elimination[7] of **F** delivers the desired carbazoles **3** and the active Rh(III) catalyst.

Procedure for the synthesis of 6:



A mixture of **3aa** (0.1 mmol, 1.0 equiv), [Cp*RhCl$_2$]$_2$ (0.005 mmol, 5.0 mol%), AgSbF$_6$(0.01 mmol, 10 mol%) and diethyl 2-diazomalonate (0.12 mmol, 1.2 equiv) was combined in a Schlenk tube followed by addition of EtOH (1.0 mL). Then the reaction mixture was heated to 80 ^{o}C with stirring for 6 h. The resulting mixture was cooled to room temperature, silica gel column directly to give the desired product **6**.

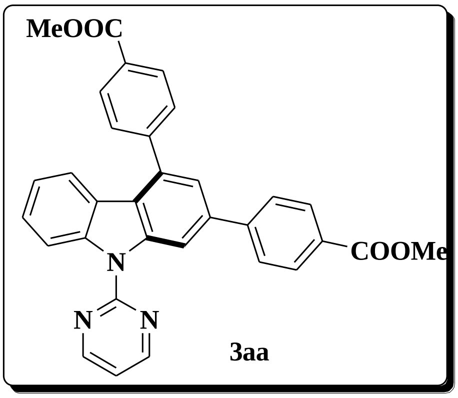
Procedure for the synthesis of 7:



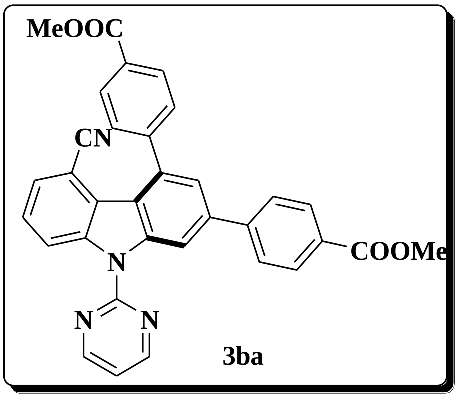
A mixture of **3aa** (0.1 mmol, 1.0 equiv), [Cp*RhCl$_2$]$_2$ (0.005 mmol, 5.0 mol%), AgSbF$_6$ (0.01 mmol, 10 mol%), Cu(OAc)$_2$ (0.1 mmol, 1.0 equiv) and methyl acrylate (0.12 mmol, 1.2 equiv) was combined in a Schlenk tube followed by addition of DMF (1.0 mL). Then the reaction mixture was heated to 80 ^{o}C with stirring for 8 h. It was allowed to reach room temperature, diluted with EtOAc (10 mL) and washed brine. The combined organic phase was dried (Na_2SO_4). After evaporation of the solvents under reduced pressure, the crude product was purified on a silica gel column to give the desired product **7**.

Characterizations of products 3aa-3qa, 3ab-3as and 4-7:

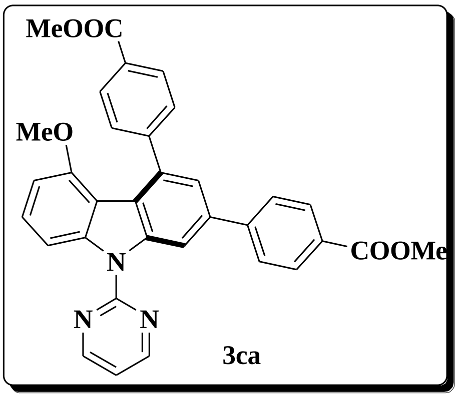
(The data of yield, Mp, ^{1}H NMR, ^{13}C NMR, IR and HRMS of each compound were given)



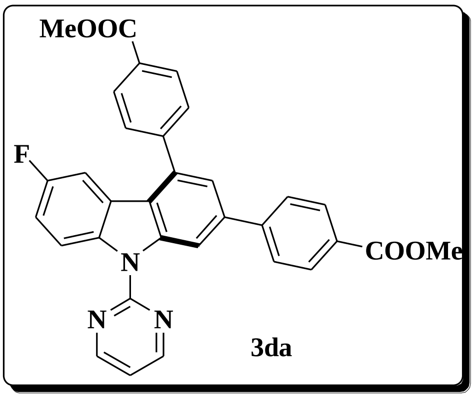
Yield 85%; Mp 180-181 °C; ^{1}H NMR (400 MHz, $CDCl_3$) δ: 9.18 (d, *J* = 1.4 Hz, 1H), 8.92 (d, *J* = 4.8 Hz, 2H), 8.81 (d, *J* = 8.4 Hz, 1H), 8.25 (d, *J* = 8.2 Hz, 2H), 8.15 (d, *J* = 8.4 Hz, 2H), 7.84 (d, *J* = 8.4 Hz, 2H), 7.74 (d, *J* = 8.2 Hz, 2H), 7.49 – 7.44 (m, 2H), 7.31 (d, *J* = 7.8 Hz, 1H), 7.22 (t, *J* = 4.8 Hz, 1H), 7.10 (t, *J* = 7.4 Hz, 1H), 4.02 (s, 3H), 3.97 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ: 167.1, 159.0, 158.1, 146.1, 145.6, 140.1, 140.0, 138.1, 136.4, 130.1, 129.9, 129.6, 129.5, 128.8, 127.5, 126.8, 124.6, 123.2, 122.7, 122.1, 121.9, 116.7, 115.7, 114.0, 52.3, 52.2; IR (ATR): 2949, 1718, 1606, 1577, 1562, 1486, 1454, 1430, 1332, 1280, 1187, 1105, 848, 769; HRMS (EI) calcd for $C_{32}H_{23}N_3O_4$: 513.1689 ($[M]^+$), found 513.1678 ($[M]^+$).



Yield 31%; Mp 245-246 °C; ^{1}H NMR (400 MHz, $CDCl_3$) δ: 9.06 (d, *J* = 1.6 Hz, 1H), 9.02 (dd, *J* = 8.2, 1.0 Hz, 1H), 8.98 (d, *J* = 4.8 Hz, 2H), 8.25 (d, *J* = 8.2 Hz, 2H), 8.17 (d, *J* = 8.4 Hz, 2H), 7.83 (d, *J* = 8.4 Hz, 2H), 7.73 (d, *J* = 8.2 Hz, 2H), 7.59 – 7.50 (m, 3H), 7.34 (t, *J* = 4.8 Hz, 1H), 3.98 (s, 3H) , 3.98 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ: 167.0, 166.9, 158.4, 158.2, 146.5, 145.3, 141.1, 140.5, 139.8, 137.8, 130.7, 130.2, 130.1, 130.1, 129.3, 129.2, 127.6, 126.3, 125.0, 124.3, 120.2, 119.5, 117.8, 117.2, 113.0, 105.7, 52.2, 52.1; IR (ATR): 2950, 2225, 1714, 1606, 1569, 1423, 1409, 1276, 1191, 1110, 856, 769; HRMS (EI) calcd for $C_{33}H_{22}N_4O_4$: 538.1641 ($[M]^+$), found 538.1641 ($[M]^+$).

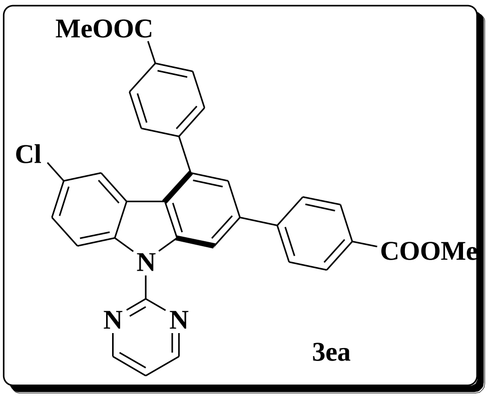


Yield 82%; Mp 210-211 °C; ^{1}H NMR (400 MHz, $CDCl_3$) δ: 9.02 (d, *J* = 1.2 Hz, 1H), 8.94 (d, *J* = 4.6 Hz, 2H), 8.29 (d, *J* = 8.4 Hz, 1H), 8.14 – 8.11 (m, 4H), 7.82 (d, *J* = 8.4 Hz, 2H), 7.56 (d, *J* = 8.2 Hz, 2H), 7.49 (d, *J* = 1.2 Hz, 1H), 7.41 (t, *J* = 8.2 Hz, 1H), 7.26 – 7.24 (m, 1H), 6.62 (d, *J* = 8.0 Hz, 1H), 3.99 (s, 3H), 3.95 (s, 3H), 3.18 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ: 165.4, 165.1, 156.7, 156.2, 152.6, 148.0, 144.0, 139.6, 137.9, 134.9, 134.9, 128.0, 127.1, 126.7, 126.1, 125.9, 125.9, 125.4, 122.3, 120.3, 115.1, 111.7, 110.4, 105.1, 101.4, 52.5, 50.1; IR (ATR): 3363, 2923, 2852, 1718, 1706, 1606, 1575, 1562, 1440, 1415, 1334, 1274, 1108, 848, 771; HRMS (EI) calcd for $C_{33}H_{25}N_3O_5$: 543.1794 ($[M]^+$), found 543.1792 ($[M]^+$).



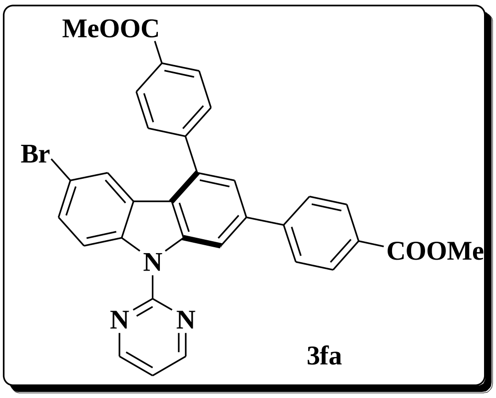
3da

Yield 88%; Mp 179-180 °C; ^{1}H NMR (400 MHz, $CDCl_3$) δ: 9.22 (s, 1H), 8.92 – 8.83 (m, 3H), 8.27 (d, *J* = 7.2 Hz, 2H), 8.17 (d, *J* = 7.6 Hz, 2H), 7.85 (d, *J* = 7.6 Hz, 2H), 7.72 (d, *J* = 7.2 Hz, 2H), 7.49 (s, 1H), 7.27 – 7.12 (m, 2H), 6.96 (d, *J* = 8.4 Hz, 1H), 4.04 (s, 3H), 3.98 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ: 167.0, 166.9, 158.8, 158.1, 158.0 (d, *J* = 167.7 Hz), 145.9, 145.0, 140.8, 138.7, 136.5, 136.3, 130.1, 130.1, 129.9, 129.3, 129.0, 127.6, 125.5 (d, *J* = 9.6 Hz), 123.2, 122.0 (d, *J* = 3.6 Hz), 116.9 (d, *J* = 8.4 Hz), 116.7, 114.4, 114.2 (d, *J* = 24.1 Hz), 107.7 (d, *J* = 25.1 Hz), 52.3, 52.2; IR (ATR): 3359, 3187, 2921, 2850, 1722, 1658, 1633, 1432, 1276, 1187, 1101, 1018, 850, 771; HRMS (EI) calcd for $C_{32}H_{22}FN_3O_4$: 531.1594 ($[M]^+$), found 531.1597 ($[M]^+$).



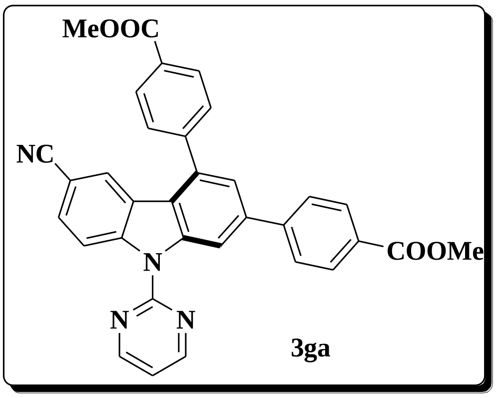
3ea

Yield 86%; Mp 222-223 °C; ^{1}H NMR (400 MHz, $CDCl_3$) δ: 9.20 (d, *J* = 1.6 Hz, 1H), 8.92 (d, *J* = 4.8 Hz, 2H), 8.79 (d, *J* = 9.0 Hz, 1H), 8.28 (d, *J* = 8.2 Hz, 2H), 8.17 (d, *J* = 8.4 Hz, 2H), 7.84 (d, *J* = 8.4 Hz, 2H), 7.73 (d, *J* = 8.2 Hz, 2H), 7.50 (d, *J* = 1.6 Hz, 1H), 7.41 (dd, *J* = 9.0, 2.0 Hz, 1H), 7.30 (d, *J* = 2.0 Hz, 1H), 7.25 (t, *J* = 4.8 Hz, 1H), 4.04 (s, 3H), 3.98 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ: 167.0, 166.9, 158.7, 158.1, 145.9, 145.0, 140.5, 138.8, 138.3, 136.6, 130.2, 130.1, 129.9, 129.3, 129.0, 127.6, 127.5, 126.8, 125.9, 123.5, 121.6, 121.4, 116.9, 116.8, 114.3, 52.3, 52.2; IR (ATR): 2950, 2991, 2850, 1725, 1608, 1577, 1563, 1450, 1425, 1278, 1187, 1103, 846, 767; HRMS (EI) calcd for $C_{32}H_{22}ClN_3O_4$: 547.1299, 549.1269 ($[M]^+$), found 547.1290, 549.1266 ($[M]^+$).



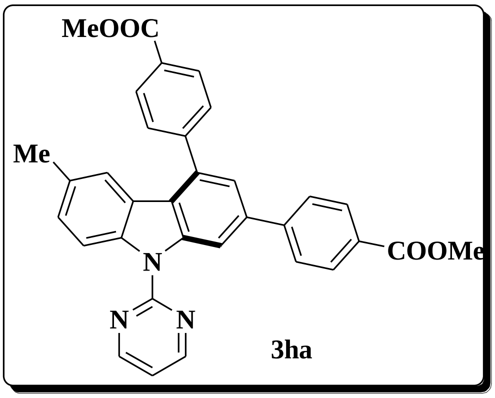
3fa

Yield 79%; Mp 231-232 °C; ^{1}H NMR (400 MHz, $CDCl_3$) δ: 9.17 (d, *J* = 1.6 Hz, 1H), 8.89 (d, *J* = 4.8 Hz, 2H), 8.71 (d, *J* = 9.0 Hz, 1H), 8.26 (d, *J* = 8.2 Hz, 2H), 8.15 (d, *J* = 8.4 Hz, 2H), 7.82 (d, *J* = 8.4 Hz, 2H), 7.71 (d, *J* = 8.2 Hz, 2H), 7.52 (dd, *J* = 9.0, 2.0 Hz, 1H), 7.47 (d, *J* = 1.6 Hz, 1H), 7.44 (d, *J* = 2.0 Hz, 1H), 7.22 (t, *J* = 4.8 Hz, 1H), 4.02 (s, 3H), 3.96 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ: 167.0, 167.0, 158.7, 158.2, 145.8, 145.0, 140.4, 138.8, 138.7, 136.6, 130.2, 130.1, 129.9, 129.5, 129.3, 129.0, 127.6, 126.4, 124.4, 123.6, 121.4, 117.3, 116.9, 115.1, 114.2, 52.3, 52.2; IR (ATR): 2950, 1720, 1608, 1579, 1562, 1481, 1448, 1425, 1407, 1282, 1214, 1189, 1112, 1016, 846, 767; HRMS (EI) calcd for $C_{32}H_{22}BrN_3O_4$: 591.0794, 593.0773 ($[M]^+$), found 591.0787, 593.0776 ($[M]^+$).



3ga

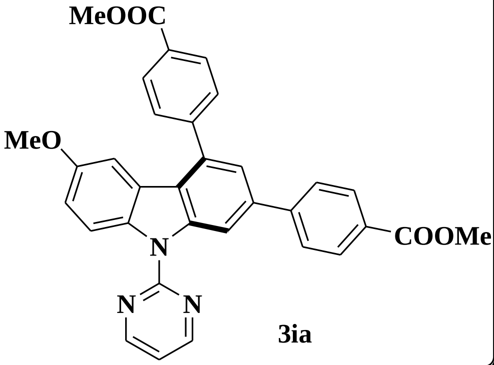
Yield 38%; Mp 279-280 °C; ^{1}H NMR (400 MHz, $CDCl_3$) δ: 9.13 (d, *J* = 1.4 Hz, 1H), 8.96 (d, *J* = 4.8 Hz, 2H), 8.88 (d, *J* = 8.8 Hz, 1H), 8.28 (d, *J* = 8.2 Hz, 2H), 8.16 (d, *J* = 8.4 Hz, 2H), 7.82 (d, *J* = 8.4 Hz, 2H), 7.75 – 7.66 (m, 3H), 7.62 (d, *J* = 1.2 Hz, 1H), 7.53 (d, *J* = 1.4 Hz, 1H), 7.32 (t, *J* = 4.8 Hz, 1H), 4.04 (s, 3H), 3.97 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ: 166.9, 166.7, 158.4, 145.5, 144.5, 141.9, 140.6, 139.6, 136.9, 130.3, 130.3, 130.2, 129.9, 129.3, 129.1, 127.6, 126.1, 124.8, 124.1, 121.1, 119.8, 117.7, 116.4, 114.1, 105.2, 52.3, 52.2; IR (ATR): 2952, 2223, 1727, 1606, 1573, 1484, 1454, 1427, 1274, 1187, 1103, 846, 767; HRMS (EI) calcd for $C_{33}H_{22}N_4O_4$: 583.1641 ($[M]^+$), found 583.1640 ($[M]^+$).



3ha

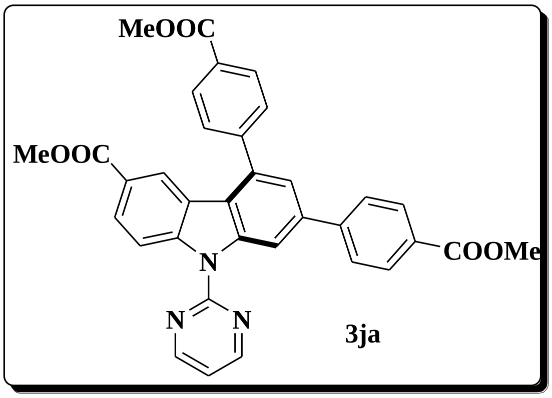
Yield 84%; Mp 164-165 °C; ^{1}H NMR (400 MHz, $CDCl_3$) δ: 9.21 (s, 1H), 8.91 (s, 2H), 8.72 (d, *J* = 8.0 Hz, 1H), 8.27 (d, *J* = 7.2 Hz, 2H), 8.16 (d, *J* = 7.2 Hz, 2H), 7.85 (d, *J* = 7.2 Hz, 2H), 7.76 (d, *J* = 7.2 Hz, 2H), 7.47 (s, 1H), 7.30 – 7.08 (m, 3H), 4.04 (s, 3H), 3.98 (s, 3H), 2.32 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ: 167.1, 159.0, 158.0, 146.2, 145.8, 140.3, 138.2, 137.9, 136.3, 131.5, 130.1, 129.9, 129.6, 129.5, 128.8, 128.1, 127.5, 124.7, 123.2, 122.6, 121.9, 116.4, 115.5, 114.1, 52.3, 52.1, 21.5; IR (ATR):

3355, 3954, 2923, 2852, 1714, 1606, 1579, 1477, 1430, 1324, 1272, 1213, 1178, 1105, 857, 775; HRMS (EI) calcd for $C_{33}H_{25}N_3O_4$: 527.1845 ($[M]^+$), found 527.1845 ($[M]^+$).



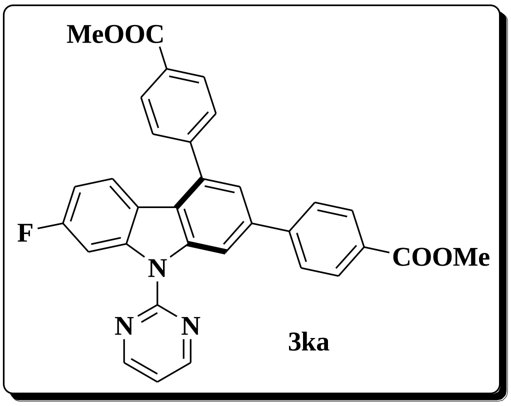
3ia

Yield 85%; Mp 164-165 °C; ^{1}H NMR (400 MHz, $CDCl_3$) δ: 9.23 (d, *J* = 1.6 Hz, 1H), 8.88 (d, *J* = 4.8 Hz, 2H), 8.77 (d, *J* = 9.2 Hz, 1H), 8.24 (d, *J* = 8.4 Hz, 2H), 8.15 (d, *J* = 8.4 Hz, 2H), 7.84 (d, *J* = 8.4 Hz, 2H), 7.74 (d, *J* = 8.4 Hz, 2H), 7.46 (d, *J* = 1.6 Hz, 1H), 7.17 (t, *J* = 4.8 Hz, 1H), 7.06 (dd, *J* = 9.2, 2.6 Hz, 1H), 6.77 (d, *J* = 2.6 Hz, 1H), 4.00 (s, 3H), 3.96 (s, 3H), 3.60 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ: 167.1, 167.0, 159.0, 158.0, 155.0, 146.1, 145.5, 140.6, 138.1, 136.2, 134.7, 130.1, 129.8, 129.6, 128.8, 127.5, 125.4, 123.0, 122.6, 116.9, 116.2, 114.9, 114.5, 105.1, 55.4, 52.3, 52.2, 29.7; IR (ATR): 3363, 3193, 2921, 2852, 1720, 1658, 1606, 1581, 1481, 1432, 1274, 1214, 1105, 1043, 852, 794; HRMS (EI) calcd for $C_{33}H_{25}N_3O_5$: 543.1794 ($[M]^+$), found 543.1797 ($[M]^+$).

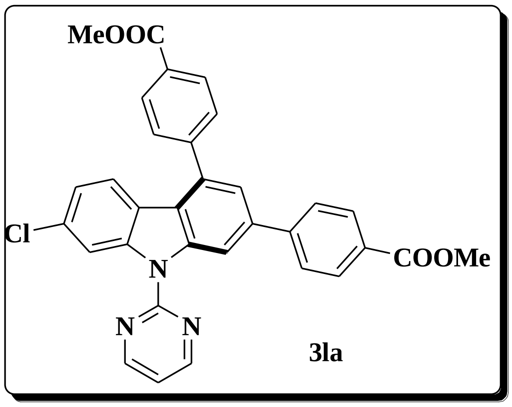


3ja

Yield 71%; Mp 246-247 °C; ^{1}H NMR (400 MHz, $CDCl_3$) δ: 9.10 (d, *J* = 1.4 Hz, 1H), 8.91 (d, *J* = 4.8 Hz, 2H), 8.77 (d, *J* = 8.8 Hz, 1H), 8.27 (d, *J* = 8.2 Hz, 2H), 8.18 – 8.04 (m, 4H), 7.81 (d, *J* = 8.4 Hz, 2H), 7.74 (d, *J* = 8.2 Hz, 2H), 7.51 (d, *J* = 1.4 Hz, 1H), 7.27 – 7.20 (m, 1H), 4.01 (s, 3H), 3.95 (s, 3H), 3.82 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ: 167.1, 167.0, 166.9, 158.6, 158.2, 145.8, 145.0, 142.7, 140.7, 138.7, 136.7, 130.2, 130.1, 129.9, 129.4, 129.0, 128.1, 127.6, 124.3, 123.9, 123.8, 123.7, 122.2, 117.3, 115.2, 114.1, 52.3, 52.2, 52.0; IR (ATR): 2950, 1720, 1606, 1583, 1563, 1482, 1454, 1427, 1309, 1276, 1103, 850, 767; HRMS (EI) calcd for $C_{34}H_{25}N_3O_6$: 571.1743 ($[M]^+$), found 571.1740 ($[M]^+$).

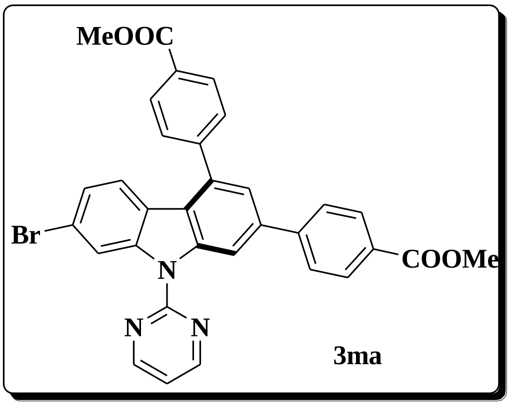


Yield 89%; Mp 197-198 °C; ^{1}H NMR (400 MHz, $CDCl_3$) δ: 9.18 (d, *J* = 1.2 Hz, 1H), 8.90 (d, *J* = 4.8 Hz, 2H), 8.60 (dd, *J* = 11.2, 2.2 Hz, 1H), 8.25 (d, *J* = 8.0 Hz, 2H), 8.15 (d, *J* = 8.2 Hz, 2H), 7.82 (d, *J* = 8.2 Hz, 2H), 7.71 (d, *J* = 8.0 Hz, 2H), 7.47 (d, *J* = 1.2 Hz, 1H), 7.23 – 7.19 (m, 2H), 6.83 (td, *J* = 8.8, 2.2 Hz, 1H), 4.03 (s, 3H), 3.97 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ: 167.0, 167.0, 162.1 (d, *J* = 242.5 Hz), 158.8, 158.1, 145.9, 145.4, 140.7 (d, *J* = 13.0 Hz), 140.5 (d, *J* = 1.8 Hz), 137.8, 135.8, 130.1, 130.0, 129.7, 129.4, 128.9, 127.5, 123.4, 122.6 (d, *J* = 9.9 Hz), 122.2, 120.9, 116.8, 114.3, 110.0 (d, *J* = 23.8 Hz), 103.4 (d, *J* = 29.4 Hz), 52.3, 52.2; IR (ATR): 3396, 2918, 2805, 1718, 1644, 1604, 1577, 1563, 1430, 1280, 1186, 1101, 850, 808, 769; HRMS (EI) calcd for $C_{32}H_{22}FN_3O_4$: 531.1594 ($[M]^+$), found 531.1589 ($[M]^+$).



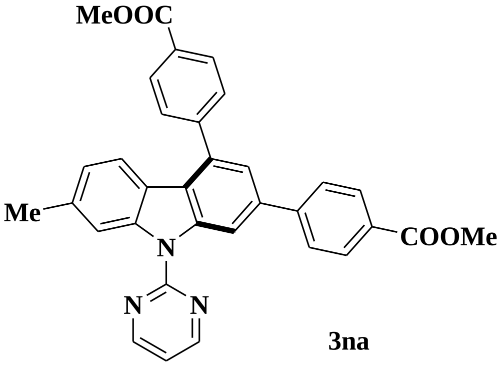
3la

Yield 73%; Mp 192-193 °C; ^{1}H NMR (400 MHz, CDCl$_3$) δ: 9.13 (d, *J* = 1.6 Hz, 1H), 8.88 (d, *J* = 4.8 Hz, 2H), 8.85 (d, *J* = 1.6 Hz, 1H), 8.20 (d, *J* = 8.4 Hz, 2H), 8.11 (d, *J* = 8.4 Hz, 2H), 7.78 (d, *J* = 8.4 Hz, 2H), 7.66 (d, *J* = 8.4 Hz, 2H), 7.44 (d, *J* = 1.6 Hz, 1H), 7.20 (t, *J* = 4.8 Hz, 1H), 7.15 (d, *J* = 8.4 Hz, 1H), 7.02 (dd, *J* = 8.4, 2.0 Hz, 1H), 3.98 (s, 3H), 3.93 (s, 3H); ^{13}C NMR (100 MHz, CDCl$_3$) δ: 167.0, 167.0, 158.7, 158.2, 145.9, 145.2, 140.5, 140.3, 138.4, 136.2, 132.6, 130.1, 130.0, 129.8, 129.4, 129.0, 127.5, 123.5, 123.1, 122.6, 122.5, 122.0, 116.9, 116.0, 114.3, 52.3, 52.2; IR (ATR): 3357, 2923, 2852, 1720, 1658, 1631, 1604, 1577, 1428, 1280, 1186, 1108, 962, 769; HRMS (EI) calcd for $C_{32}H_{22}ClN_3O_4$: 547.1299, 549.1269 ([M]$^+$), found 547.1303, 549.1298 ([M]$^+$).



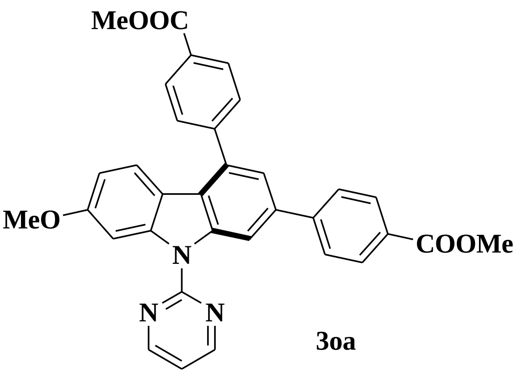
3ma

Yield 77%; Mp 199-200 °C; ^{1}H NMR (400 MHz, CDCl$_3$) δ: 9.11 (s, 1H), 8.99 (s, 1H), 8.86 (d, *J* = 4.0 Hz, 2H), 8.19 (d, *J* = 7.6 Hz, 2H), 8.10 (d, *J* = 7.6 Hz, 2H), 7.77 (d, *J* = 7.6 Hz, 2H), 7.64 (d, *J* = 7.6 Hz, 2H), 7.42 (s, 1H), 7.23 – 7.02 (m, 3H), 3.98 (s, 3H), 3.93 (s, 3H); ^{13}C NMR (100 MHz, CDCl$_3$) δ: 167.0, 167.0, 158.6, 158.1, 145.8, 145.2, 140.6, 140.1, 138.5, 136.3, 130.1, 130.0, 129.8, 129.4, 129.0, 127.5, 125.3, 123.5, 122.7, 122.0, 120.6, 118.9, 116.9, 114.3, 52.3, 52.2; IR (ATR): 3359, 3191, 2921, 2850, 1722, 1606, 1577, 1421, 1276, 1106, 815, 771; HRMS (EI) calcd for $C_{32}H_{22}BrN_3O_4$: 591.0794, 593.0773 ($[M]^+$), found 591.0794, 593.0780 ($[M]^+$).



3na

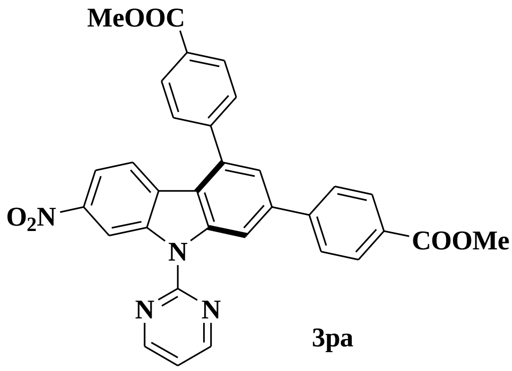
Yield 86%; Mp 153-154 °C; ^{1}H NMR (400 MHz, $CDCl_3$) δ: 9.13 (s, 1H), 8.94 (d, *J* = 4.8 Hz, 2H), 8.61 (s, 1H), 8.25 (d, *J* = 8.0 Hz, 2H), 8.16 (d, *J* = 8.2 Hz, 2H), 7.85 (d, *J* = 8.2 Hz, 2H), 7.75 (d, *J* = 8.0 Hz, 2H), 7.48 (s, 1H), 7.42 – 7.30 (m, 2H), 6.94 (d, *J* = 8.0 Hz, 1H), 4.03 (s, 3H), 3.98 (s, 3H), 2.54 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ: 167.1, 158.9, 158.1, 146.2, 145.7, 140.4, 140.1, 137.6, 137.2, 135.9, 130.3, 130.1, 129.9, 129.6, 129.5, 128.8, 127.5, 123.5, 123.1, 122.8, 122.2, 121.6, 116.6, 115.6, 113.9, 52.3, 52.1, 22.3; IR (ATR): 2923, 2852, 1720, 1606, 1577, 1563, 1432, 1276, 1187, 1110, 769; HRMS (EI) calcd for $C_{33}H_{25}N_3O_4$: 527.1845 ($[M]^+$), found 527.1837 ($[M]^+$).



3oa

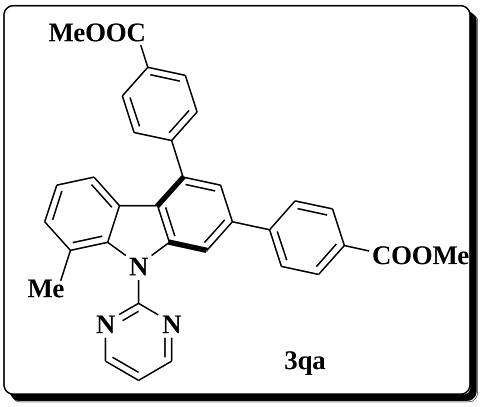
Yield 81%; Mp 183- 184 °C; ^{1}H NMR (400 MHz, $CDCl_3$) δ: 9.15 (d, *J* = 1.6 Hz, 1H), 8.93 (d, *J* = 4.8 Hz, 2H), 8.44 (d, *J* = 2.4 Hz, 1H), 8.25 (d, *J* = 8.4 Hz, 2H), 8.16 (d, *J*

= 8.4 Hz, 2H), 7.85 (d, *J* = 8.4 Hz, 2H), 7.75 (d, *J* = 8.4 Hz, 2H), 7.48 (d, *J* = 1.6 Hz, 1H), 7.25 – 7.20 (m, 2H), 6.73 (dd, *J* = 8.8, 2.4 Hz, 1H), 4.03 (s, 3H), 3.98 (s, 3H), 3.93 (s, 3H); ^{13}C NMR (125 MHz, $CDCl_3$) δ: 167.1, 167.1, 159.4, 159.0, 158.1, 146.2, 145.7, 141.5, 140.2, 136.9, 135.3, 130.1, 129.9, 129.5, 129.5, 128.7, 127.5, 123.2, 122.9, 122.5, 118.3, 116.6, 114.0, 110.0, 100.7, 55.7, 52.3, 52.2; IR (ATR): 2950, 2852, 1720, 1606, 1577, 1432, 1272, 1193, 1114, 852, 767; HRMS (EI) calcd for $C_{33}H_{25}N_3O_5$: 543.1794 ($[M]^+$), found 543.1788 ($[M]^+$).



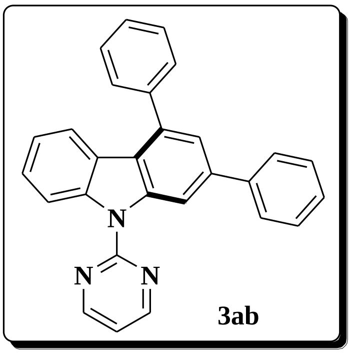
3pa

Yield 69%; Mp 272-273 ^{o}C; ^{1}H NMR (400 MHz, $CDCl_3$) δ: 9.77 (d, *J* = 1.6 Hz, 1H), 9.25 (s, 1H), 8.99 (d, *J* = 4.8 Hz, 2H), 8.28 (d, *J* = 8.0 Hz, 2H), 8.19 (d, *J* = 8.0 Hz, 2H), 7.98 (dd, *J* = 8.8, 1.6 Hz, 1H), 7.85 (d, *J* = 8.0 Hz, 2H), 7.72 (d, *J* = 8.0 Hz, 2H), 7.56 (s, 1H), 7.42 – 7.30 (m, 2H), 4.05 (s, 3H), 3.99 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ: 166.9, 166.8, 158.5, 158.4, 146.3, 145.4, 144.6, 142.0, 140.3, 139.1, 137.5, 130.2, 130.2, 129.6, 129.4, 129.3, 127.6, 123.9, 121.6, 121.0, 117.5, 117.3, 114.5, 112.2, 52.4, 52.2; IR (ATR): 2919, 1720, 1608, 1577, 1515, 1486, 1427, 1340, 1276, 1112, 854, 769; HRMS (EI) calcd for $C_{32}H_{22}N_4O_6$: 558.1539 ($[M]^+$), found 558.1535 ($[M]^+$).



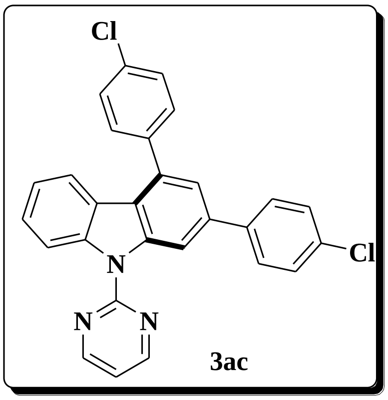
3qa

Yield 62%; Mp 170-171 °C; ^{1}H NMR (400 MHz, $CDCl_3$) δ: 8.98 (d, *J* = 4.8 Hz, 2H), 8.31 (s, 1H), 8.26 (d, *J* = 8.0 Hz, 2H), 8.13 (d, *J* = 8.0 Hz, 2H), 7.79 – 7.75 (m, 4H), 7.46 (s, 1H), 7.36 (t, *J* = 4.8 Hz, 1H), 7.28 – 7.24 (d, *J* = 18.1 Hz, 2H), 7.04 (t, *J* = 7.6 Hz, 1H), 4.03 (s, 3H), 3.97 (s, 3H), 2.18 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ: 167.1, 167.0, 158.8, 158.7, 145.9, 145.6, 142.3, 140.1, 138.1, 136.7, 130.1, 129.9, 129.6, 129.6, 129.5, 128.8, 127.4, 125.1, 123.6, 122.9, 122.5, 122.0, 120.0, 118.5, 110.2, 100.0, 52.3, 52.1, 21.1; IR (ATR): 3359, 2921, 2852, 1720, 1660, 1631, 1563, 1457, 1425, 1282, 1110, 775; HRMS (EI) calcd for $C_{33}H_{25}N_3O_4$: 527.1845 ($[M]^+$), found 527.1853 ($[M]^+$).



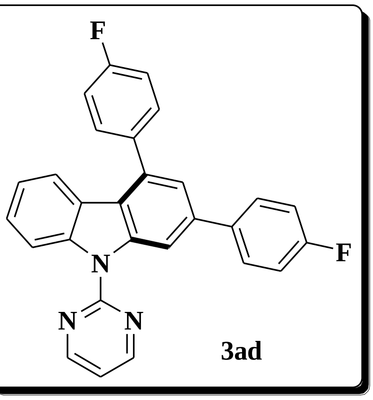
3ab

Yield 75%; Mp 166-167 °C; ^{1}H NMR (400 MHz, $CDCl_3$) δ: 9.14 (d, *J* = 1.6 Hz, 1H), 8.91 (d, *J* = 4.8 Hz, 2H), 8.82 (d, *J* = 8.4 Hz, 1H), 7.83 – 7.78 (m, 2H), 7.68 (dd, *J* = 8.0, 1.6 Hz, 2H), 7.62 – 7.35 (m, 9H), 7.19 (t, *J* = 4.8 Hz, 1H), 7.14 – 7.08 (m, 1H); ^{13}C NMR (100 MHz, $CDCl_3$) δ: 159.1, 158.0, 141.9, 141.1, 140.1, 139.9, 139.4, 137.3, 129.4, 128.8, 128.6, 127.7, 127.2, 126.3, 125.2, 123.6, 122.3, 122.0, 121.9, 116.4, 115.4, 113.3; IR (ATR): 2956, 2921, 2852, 1660, 1581, 1562, 1450, 1425, 1332, 800, 750; HRMS (EI) calcd for $C_{28}H_{19}N_3$: 397.1579 ($[M]^+$), found 397.1569 ($[M]^+$).



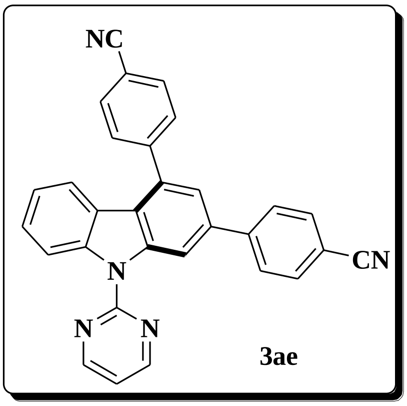
3ac

Yield 62%; Mp 186-187 °C; ^{1}H NMR (400 MHz, $CDCl_3$) δ: 9.07 (d, *J* = 1.6 Hz, 1H), 8.91 (d, *J* = 4.8 Hz, 2H), 8.80 (d, *J* = 8.4 Hz, 1H), 7.72 – 7.66 (m, 2H), 7.60 – 7.52 (m, 4H), 7.49 – 7.43 (m, 3H), 7.38 (d, *J* = 1.6 Hz, 1H), 7.35 (d, *J* = 7.6 Hz, 1H), 7.21 (t, *J* = 4.8 Hz, 1H), 7.16 – 7.10 (m, 1H); ^{13}C NMR (100 MHz, $CDCl_3$) δ: 159.0, 158.1, 140.2, 140.1, 139.9, 139.4, 138.1, 136.1, 133.9, 133.4, 130.7, 128.9, 128.9, 128.8, 126.6, 124.7, 123.2, 122.4, 122.1, 121.8, 116.6, 115.6, 113.4; IR (ATR): 2923, 1579, 1563, 1496, 1452, 1421, 1332, 1089, 835, 752; HRMS (EI) calcd for $C_{28}H_{17}Cl_2N_3$: 465.0800, 467.0770, 469.0741 ($[M]^+$), found 465.0810, 467.0782, 469.0751 ($[M]^+$).



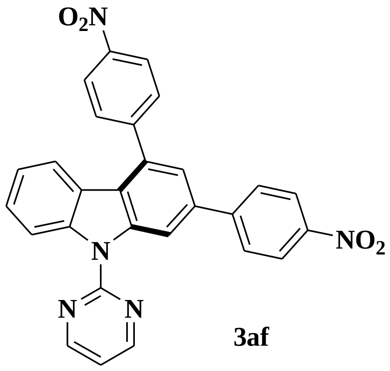
3ad

Yield 82%; Mp 162-163 °C; H NMR (400 MHz, $CDCl_3$) δ: 9.05 (d, *J* = 1.6 Hz, 1H), 8.91 (d, *J* = 4.8 Hz, 2H), 8.80 (d, *J* = 8.4 Hz, 1H), 7.78 – 7.70 (m, 2H), 7.63 – 7.58 (m, 2H), 7.48 – 7.42 (m, 1H), 7.39 (d, *J* = 1.6 Hz, 1H), 7.32 (d, *J* = 7.6 Hz, 1H), 7.29 – 7.23 (m, 3H), 7.21 – 7.10 (m, 4H); ^{13}C NMR (100 MHz, $CDCl_3$) δ: 162.6 (d, *J* = 246.3 Hz), 162.5 (d, *J* = 246.1 Hz), 159.0, 158.1, 140.1, 139.9, 138.4, 137.9 (d, *J* = 3.2 Hz), 136.9 (d, *J* = 3.5 Hz), 136.3, 131.0 (d, *J* = 8.0 Hz), 129.2 (d, *J* = 8.0 Hz), 126.5, 124.9, 123.4, 122.3, 122.0, 121.7, 116.5, 115.7 (d, *J* = 7.7 Hz), 115.5, 115.5 (d, *J* = 7.7 Hz), 113.3; IR (ATR): 3367, 2921, 2852, 1600, 1579, 1511, 1452, 1423, 1330, 1220, 1159, 833, 750; HRMS (EI) calcd for $C_{28}H_{17}F_2N_3$: 433.1391 ($[M]^+$), found 433.1388 ($[M]^+$).



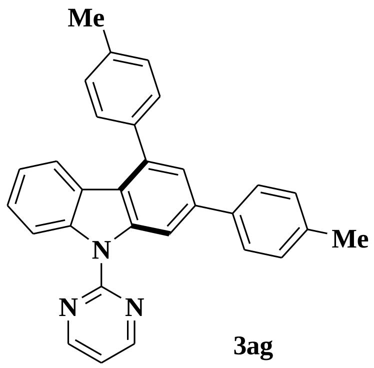
3ae

Yield 58%; Mp 218-219 °C; ^{1}H NMR (400 MHz, $CDCl_3$) δ: 9.19 (s, 1H), 8.94 (d, *J* = 4.0 Hz, 2H), 8.85 (d, *J* = 8.2 Hz, 1H), 7.97 – 7.72 (m, 8H), 7.51 (t, *J* = 7.2 Hz, 1H), 7.41 (s, 1H), 7.26 (m, 2H), 7.16 (t, *J* = 7.2 Hz, 1H); ^{13}C NMR (100 MHz, $CDCl_3$) δ: 158.8, 158.2, 145.9, 145.5, 140.2, 140.1, 137.3, 135.5, 132.7, 132.5, 130.2, 128.2, 127.3, 124.1, 122.9, 122.3, 121.7, 119.0, 118.8, 116.9, 115.9, 114.4, 111.9, 111.0; IR (ATR): 3359, 2921, 2852, 2223, 1741, 1658, 1633, 1602, 1577, 1562, 1452, 1425, 1403, 1334, 835, 756; HRMS (EI) calcd for $C_{30}H_{17}N_5$: 447.1484 ($[M]^+$), found 447.1489 ($[M]^+$).



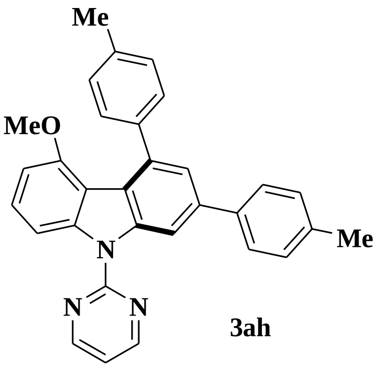
3af

Yield 88%; Mp 187-188 °C; H NMR (400 MHz, $CDCl_3$) δ: 9.25 (s, 1H), 8.96 (d, *J* = 4.8 Hz, 2H), 8.86 (d, *J* = 8.4 Hz, 1H), 8.47 (d, *J* = 8.4 Hz, 2H), 8.37 (d, *J* = 8.6 Hz, 2H), 7.93 (d, *J* = 8.6 Hz, 2H), 7.86 (d, *J* = 8.4 Hz, 2H), 7.53 (t, *J* = 7.6 Hz, 1H), 7.48 (s, 1H), 7.31 – 7.27 (m, 2H), 7.16 (t, *J* = 7.6 Hz, 1H); ^{13}C NMR (100 MHz, $CDCl_3$) δ: 158.8, 158.2, 147.9, 147.8, 147.4, 147.1, 140.2, 140.1, 136.9, 135.2, 130.4, 128.3, 127.4, 124.2, 124.0, 124.0, 123.1, 123.0, 122.4, 121.7, 117.0, 116.0, 114.8; IR (ATR): 1594, 1579, 1562, 1513, 1454, 1430, 1342, 1106, 844, 752; HRMS (EI) calcd for $C_{28}H_{17}N_5O_4$: 487.1281 ($[M]^+$), found 487.1285 ($[M]^+$).



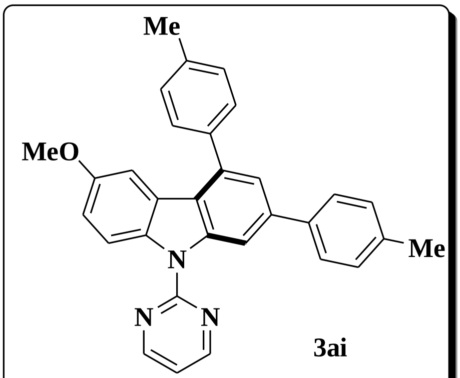
3ag

Yield 81%; Mp 122-123 °C; ^{1}H NMR (400 MHz, $CDCl_3$) δ: 9.09 (d, *J* = 1.6 Hz, 1H), 8.91 (d, *J* = 4.8 Hz, 2H), 8.80 (d, *J* = 8.2 Hz, 1H), 7.69 (d, *J* = 8.2 Hz, 2H), 7.56 (d, *J* = 8.0 Hz, 2H), 7.48 (d, *J* = 1.6 Hz, 1H), 7.46 – 7.35 (m, 4H), 7.31 (d, *J* = 8.0 Hz, 2H), 7.19 (t, *J* = 4.8 Hz, 1H), 7.11 (t, *J* = 7.6 Hz, 1H), 2.54 (s, 3H), 2.45 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ: 159.1, 158.0, 140.1, 139.8, 139.3, 139.1, 138.2, 137.4, 137.3, 136.9, 129.5, 129.2, 127.5, 126.1, 125.3, 123.6, 122.1, 122.0, 121.8, 116.3, 115.4, 112.9, 21.4, 21.2; IR (ATR): 2958, 2919, 2850, 1727, 1662, 1581, 1562, 1454, 1432, 1334, 1261, 1020, 821, 800, 752; HRMS (EI) calcd for $C_{30}H_{23}N_3$: 425.1892 ($[M]^+$), found 425.1890 ($[M]^+$).



3ah

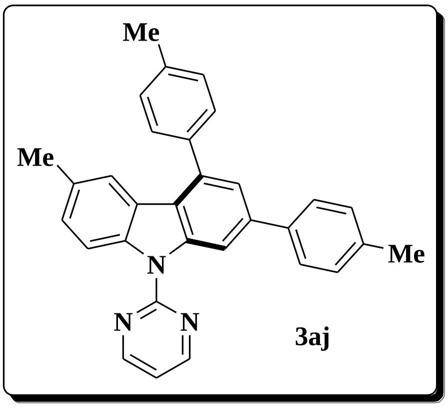
Yield 63%; Mp 197-198 °C; ^{1}H NMR (400 MHz, $CDCl_3$) δ: 8.92 – 8.90 (m, 3H), 8.27 (d, *J* = 8.2 Hz, 1H), 7.66 (d, *J* = 8.0 Hz, 2H), 7.50 (d, *J* = 1.6 Hz, 1H), 7.42 – 7.34 (m, 3H), 7.28 – 7.19 (m, 5H), 6.62 (d, *J* = 7.9 Hz, 1H), 3.24 (s, 3H), 2.48 (s, 3H), 2.42 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ: 158.9, 158.2, 154.7, 142.6, 141.5, 140.0, 138.9, 138.2, 137.9, 136.8, 135.4, 129.4, 129.0, 127.4, 127.4, 127.1, 124.8, 121.8, 116.8, 114.3, 111.3, 107.0, 103.5, 54.8, 21.3, 21.1; IR (ATR): 2921, 1575, 1560, 1513, 1427, 1413, 1338, 1297, 1278, 1110, 813; HRMS (EI) calcd for $C_{31}H_{25}N_3O$: 455.1998 ($[M]^+$), found 455.1992 ($[M]^+$).



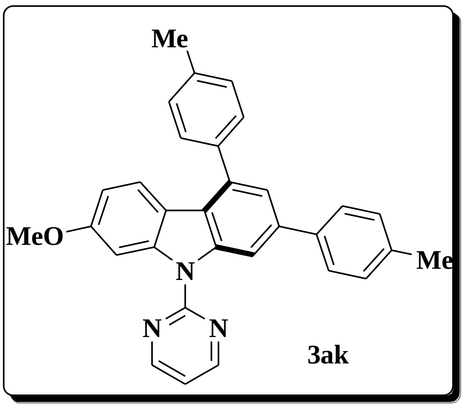
3ai

Yield 78%; Mp 158-159 °C; ^{1}H NMR (400 MHz, $CDCl_3$) δ: 9.14 (d, *J* = 1.2 Hz, 1H), 8.85 (d, *J* = 4.8 Hz, 2H), 8.75 (d, *J* = 9.0 Hz, 1H), 7.69 (d, *J* = 8.0 Hz, 2H), 7.55 (d, *J* = 7.8 Hz, 2H), 7.46 (d, *J* = 1.2 Hz, 1H), 7.37 (d, *J* = 7.8 Hz, 2H), 7.30 (d, *J* = 8.0 Hz, 2H), 7.12 (t, *J* = 4.8 Hz, 1H), 7.03 (dd, *J* = 9.0, 2.6 Hz, 1H), 6.85 (d, *J* = 2.6 Hz, 1H), 3.64 (s, 3H), 2.51 (s, 3H), 2.43 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ: 159.1, 157.9, 154.9, 140.6, 139.6, 139.1, 138.0, 137.4, 137.2, 136.9, 134.5, 129.5, 129.4, 129.1, 127.5, 126.2, 123.2, 122.1, 116.6, 115.9, 114.1, 113.4, 105.3, 55.3, 21.4, 21.2; IR

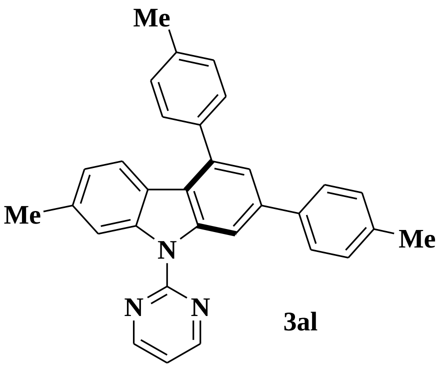
(ATR): 2921, 1579, 1558, 1475, 1450, 1427, 1330, 1290, 1218, 1045, 802; HRMS (EI) calcd for $C_{31}H_{25}N_3O$: 455.1998 ($[M]^+$), found 455.1998 ($[M]^+$).



Yield 71%; Mp 158-159 °C; ^{1}H NMR (400 MHz, $CDCl_3$) δ: 9.11 (d, *J* = 1.6 Hz, 1H), 8.88 (d, *J* = 4.8 Hz, 2H), 8.70 (d, *J* = 8.4 Hz, 1H), 7.70 (d, *J* = 8.0 Hz, 2H), 7.57 (d, *J* = 8.0 Hz, 2H), 7.46 (d, *J* = 1.6 Hz, 1H), 7.39 (d, *J* = 7.8 Hz, 2H), 7.31 (d, *J* = 8.0 Hz, 2H), 7.27 – 7.23 (m, 2H), 7.15 (t, *J* = 4.8 Hz, 1H), 2.55 (s, 3H), 2.45 (s, 3H), 2.34 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ: 159.2, 157.9, 140.3, 139.1, 138.3, 138.0, 137.3, 137.3, 136.8, 131.1, 129.4, 129.2, 129.1, 127.5, 127.4, 125.5, 123.5, 122.1, 122.1, 116.1, 115.2, 113.0, 21.5, 21.4, 21.2; IR (ATR): 2919, 2852, 1579, 1564, 1489, 1423, 1326, 1270, 1148, 1045, 809; HRMS (EI) calcd for $C_{31}H_{25}N_3$: 439.2048 ($[M]^+$), found 439.2044 ($[M]^+$).

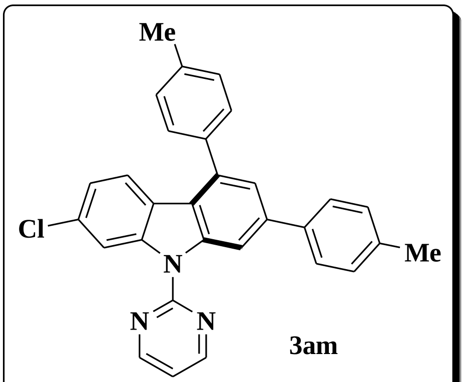


Yield 65%; Mp 115-116 °C; ^{1}H NMR (400 MHz, $CDCl_3$) δ: 9.04 (d, *J* = 1.2 Hz, 1H), 8.88 (d, *J* = 4.8 Hz, 2H), 8.43 (d, *J* = 2.0 Hz, 1H), 7.67 (d, *J* = 8.0 Hz, 2H), 7.54 (d, *J* = 7.8 Hz, 2H), 7.44 (d, *J* = 1.2 Hz, 1H), 7.37 (d, *J* = 7.8 Hz, 2H), 7.32 – 7.27 (m, 3H), 7.16 (t, *J* = 4.8 Hz, 1H), 6.73 (dd, *J* = 8.8, 2.0 Hz, 1H), 3.92 (s, 3H), 2.52 (s, 3H), 2.43 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ: 159.2, 158.9, 158.0, 141.2, 140.2, 139.2, 138.3, 138.2, 137.3, 136.7, 136.3, 129.4, 129.2, 129.2, 127.5, 123.5, 122.4, 122.3, 119.1, 116.3, 113.0, 109.5, 100.7, 55.7, 21.4, 21.1; IR (ATR): 2921, 2852, 1619, 1598, 1579, 1562, 1515, 1467, 1427, 1340, 1276, 1193, 1160, 1141, 1043, 811; HRMS (EI) calcd for $C_{31}H_{25}N_3O$: 455.1998 ($[M]^+$), found 455.2003 ($[M]^+$).



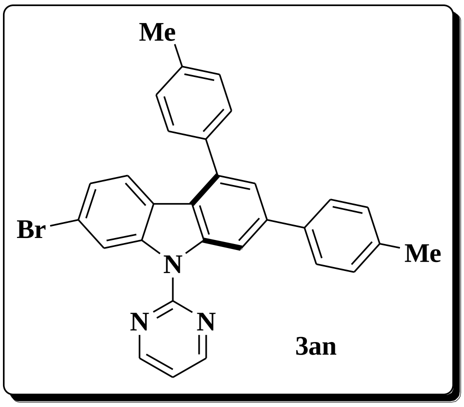
3al

Yield 61%; Mp 109-110 ^oC; ^{1}H NMR (400 MHz, $CDCl_3$) δ: 9.02 (s, 1H), 8.90 (d, *J* = 4.8 Hz, 2H), 8.58 (s, 1H), 7.68 (d, *J* = 8.0 Hz, 2H), 7.55 (d, *J* = 7.8 Hz, 2H), 7.45 (s, 1H), 7.37 (d, *J* = 7.6 Hz, 2H), 7.30 (d, *J* = 7.8 Hz, 3H), 7.17 (t, *J* = 4.8 Hz, 1H), 6.93 (d, *J* = 8.0 Hz, 1H), 2.53 (m, 6H), 2.43 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ: 159.1, 158.0, 140.2, 140.1, 139.2, 138.8, 138.3, 137.3, 136.9, 136.8, 136.3, 129.4, 129.2, 129.2, 127.5, 123.5, 123.2, 122.9, 122.2, 121.6, 116.3, 115.4, 112.8, 22.3, 21.4, 21.2; IR (ATR): 3359, 2919, 2850, 1658, 1631, 1575, 1562, 1513, 1423, 1324, 1265, 1141, 812; HRMS (EI) calcd for $C_{31}H_{25}N_3$: 439.2048 ($[M]^+$), found 439.2040 ($[M]^+$).



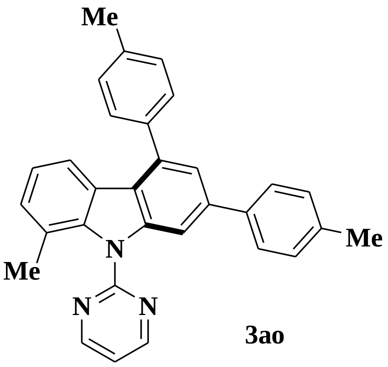
3am

Yield 75%; Mp 143-144 °C; ^{1}H NMR (400 MHz, $CDCl_3$) δ: 9.08 (d, *J* = 1.2 Hz, 1H), 8.88 (d, *J* = 4.8 Hz, 3H), 7.68 (d, *J* = 8.0 Hz, 2H), 7.52 (d, *J* = 7.8 Hz, 2H), 7.47 (d, *J* = 1.2 Hz, 1H), 7.37 (d, *J* = 7.8 Hz, 2H), 7.31 (d, *J* = 8.0 Hz, 3H), 7.17 (t, *J* = 4.8 Hz, 1H), 7.08 (dd, *J* = 8.4, 1.8 Hz, 1H), 2.53 (s, 3H), 2.44 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ: 158.8, 158.1, 140.4, 140.3, 139.7, 138.9, 137.8, 137.6, 137.2, 137.1, 131.8, 129.5, 129.4, 129.1, 127.5, 123.9, 123.8, 122.5, 122.3, 121.5, 116.6, 115.8, 113.2, 21.4, 21.2; IR (ATR): 2917, 1646, 1595, 1579, 1560, 1515, 1484, 1432, 1390, 1326, 962, 808; HRMS (EI) calcd for $C_{30}H_{22}ClN_3$: 459.1502, 461.1473 $[M]^+$), found 459.1494, 461.1497 ($[M]^+$).



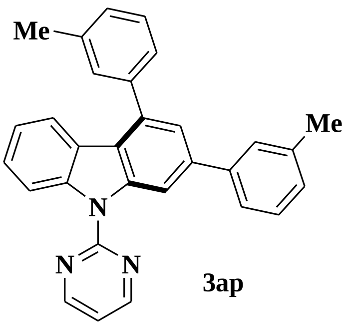
3an

Yield 80%; Mp 128-129 °C; ^{1}H NMR (400 MHz, $CDCl_3$) δ: 9.07 (d, *J* = 1.2 Hz, 1H), 9.03 (d, *J* = 1.2 Hz, 1H), 8.89 (d, *J* = 4.8 Hz, 2H), 7.67 (d, *J* = 8.0 Hz, 2H), 7.51 (d, *J* = 8.0 Hz, 2H), 7.46 (d, *J* = 1.2 Hz, 1H), 7.37 (d, *J* = 7.8 Hz, 2H), 7.30 (d, *J* = 8.0 Hz, 2H), 7.26 – 7.18 (m, 3H), 2.52 (s, 3H), 2.43 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ: 158.8, 158.1, 140.5, 140.2, 139.8, 138.9, 137.8, 137.6, 137.3, 137.1, 129.5, 129.3, 129.1, 127.5, 125.0, 124.3, 123.8, 122.9, 121.5, 119.9, 118.6, 116.7, 113.2, 21.4, 21.2; IR (ATR): 3359, 2921, 2852, 1660, 1633, 1577, 1560, 1515, 1482, 1430, 1326, 1139, 954, 809; HRMS (EI) calcd for $C_{30}H_{22}BrN_3$: 503.0997, 505.0977 $[M]^+$), found 503.0998, 505.0969 ($[M]^+$).



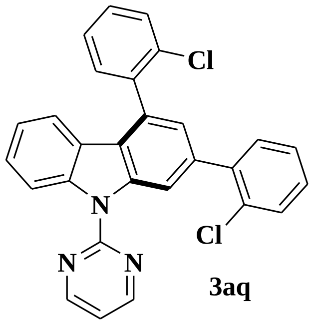
3ao

Yield 55%; Mp 170-171 °C; ^{1}H NMR (400 MHz, $CDCl_3$) δ: 8.95 (d, *J* = 4.8 Hz, 2H), 8.24 (d, *J* = 1.6 Hz, 1H), 7.62 (d, *J* = 8.0 Hz, 2H), 7.56 (d, *J* = 8.0 Hz, 2H), 7.43 (d, *J* = 1.6 Hz, 1H), 7.39 – 7.26 (m, 6H), 7.21 (d, *J* = 7.2 Hz, 1H), 7.04 (t, *J* = 7.6 Hz, 1H), 2.53 (s, 3H), 2.42 (s, 3H), 2.18 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ: 159.0, 158.6, 142.4, 139.9, 139.3, 138.9, 138.1, 137.6, 137.3, 136.9, 129.4, 129.2, 129.2, 129.0, 127.4, 125.9, 123.4, 123.3, 122.0, 121.8, 120.1, 118.1, 109.1, 21.4, 21.1, 21.0; IR (ATR): 3359, 2291, 2852, 1658, 1633, 1563, 1515, 1455, 1415, 1315, 1226, 1108, 815; HRMS (EI) calcd for $C_{31}H_{25}N_3$: 439.2048 [M]$^+$), found 439.2046 ([M]$^+$).



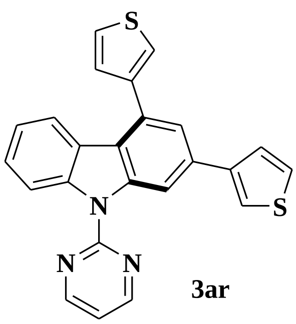
3ap

Yield 67%; Mp 132-133 °C; ^{1}H NMR (400 MHz, $CDCl_3$) δ: 9.11 (s, 1H), 8.91 (d, *J* = 4.8 Hz, 2H), 8.82 (d, *J* = 8.4 Hz, 1H), 7.62 (d, *J* = 5.6 Hz, 2H), 7.55 – 7.33 (m, 8H), 7.24 – 7.11 (m, 3H), 2.52 (s, 3H), 2.49 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ: 159.1, 158.0, 141.9, 141.1, 140.1, 139.9, 139.5, 138.3, 138.2, 137.4, 130.0, 128.7, 128.5, 128.4, 127.9, 126.4, 126.2, 125.3, 124.9, 123.6, 122.2, 122.0, 121.9, 116.4, 115.4, 113.2, 21.6, 21.6; IR (ATR): 3073, 2923, 2852, 1579, 1560, 1496, 1452, 0425, 1334, 1311, 1220, 875, 794; HRMS (EI) calcd for $C_{30}H_{23}N_3$: 425.1892 [M]$^+$), found 425.1898 ([M]$^+$).



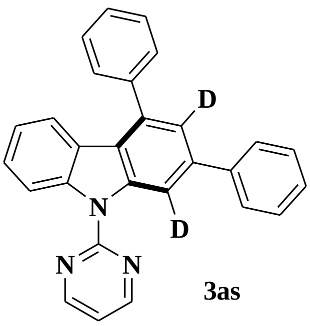
3aq

Yield 61%; Mp 135-136 °C; ^{1}H NMR (400 MHz, $CDCl_3$) δ: 9.08 (s, 1H), 8.88 – 8.84 (m, 3H), 7.71 – 7.54 (m, 4H), 7.41 – 7.32 (m, 3H), 7.43 – 7.31 (m, 3H), 7.18 – 7.09 (m, 2H), 7.06 (d, *J* = 7.9 Hz, 1H); ^{13}C NMR (100 MHz, $CDCl_3$) δ: 159.0, 158.0, 141.1, 139.8, 139.5, 139.1, 137.2, 134.0, 133.1, 132.9, 132.0, 131.5, 130.0, 129.8, 129.4, 128.5, 127.0, 126.8, 126.6, 125.5, 125.1, 123.0, 122.3, 121.4, 116.4, 116.3, 115.7; IR (ATR): 2921, 2850, 1660, 1633, 1581, 1563, 1494, 1450, 1423, 1400, 1332, 1141, 800, 756; HRMS (EI) calcd for $C_{28}H_{17}Cl_2N_3$: 465.0800, 467.0770, 469.0741 $[M]^+$), found 465.0800, 467.0792, 469.0764 ($[M]^+$).



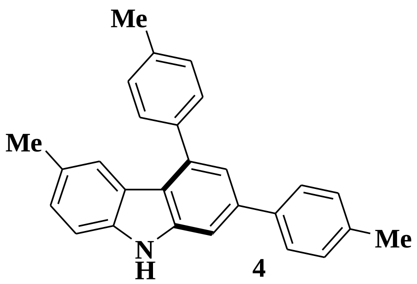
3ar

Yield 58%; Mp 236-237 °C; ^{1}H NMR (400 MHz, $CDCl_3$) δ: 9.12 (d, *J* = 1.6 Hz, 1H), 8.92 (d, *J* = 4.8 Hz, 2H), 8.81 (d, *J* = 8.2 Hz, 1H), 7.62 (dd, *J* = 3.0, 1.2 Hz, 1H), 7.57 – 7.55 (m, 3H), 7.52 (dd, *J* = 3.0, 1.2 Hz, 1H), 7.50 – 7.43 (m, 3H), 7.40 (dd, *J* = 4.8, 1.2 Hz, 1H), 7.22 – 7.15 (m, 2H); ^{13}C NMR (100 MHz, $CDCl_3$) δ: 159.1, 158.0, 143.0, 141.3, 140.0, 139.8, 133.9, 132.0, 129.2, 126.9, 126.3, 126.1, 125.7, 125.2, 123.2, 123.1, 122.7, 122.1, 121.8, 120.6, 116.4, 115.5, 112.8; IR (ATR): 1592, 1575, 1560, 1523, 1490, 1452, 1421, 786, 748; HRMS (EI) calcd for $C_{24}H_{15}N_3S_2$: 409.0707 $[M]^+$), found 409.0702 ($[M]^+$).



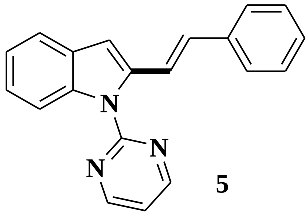
3as

Yield 69%; Mp 178-179 °C; ^{1}H NMR (400 MHz, $CDCl_3$) δ: 8.91 (d, *J* = 4.8 Hz, 2H), 8.82 (d, *J* = 8.4 Hz, 1H), 7.85 – 7.78 (m, 2H), 7.70 – 7.68 (m, 2H), 7.63 – 7.34 (m, 8H), 7.19 (t, *J* = 4.8 Hz, 1H), 7.14 – 7.08 (m, 1H); ^{13}C NMR (100 MHz, $CDCl_3$) δ: 159.1, 158.0, 141.3, 141.1, 140.0, 139.9, 139.2, 137.3, 129.4, 128.8, 128.6, 127.7, 127.2, 126.3, 125.2, 122.3, 122.0, 121.9, 116.4, 115.5; IR (ATR): 2919, 1850, 1581, 1562, 1459, 1444, 1427, 1386, 1330, 800, 750; HRMS (EI) calcd for $C_{28}H_{17}D_2N_3$: 399.1705 $[M]^+$), found 399.1707 ($[M]^+$).



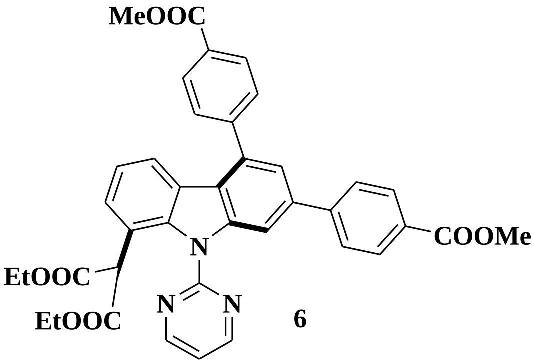
4

Yield 85 %; Mp 190-191 °C; ^{1}H NMR (400 MHz, $CDCl_3$) δ: 7.95 (brs, 1H), 7.54 – 7.50 (m, 4H), 7.46 (d, *J* = 0.8 Hz, 1H), 7.32 – 7.23 (m, 4H), 7.21 – 7.17 (dm, 3H), 7.09 (d, *J* = 8.0 Hz, 1H), 2.43 (s, 3H), 2.33 (s, 3H), 2.27 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ: 140.9, 138.8, 138.8, 138.4, 138.4, 137.8, 137.3, 136.9, 129.5, 129.1, 129.1, 128.3, 127.3, 126.9, 123.1, 122.4, 120.7, 119.8, 110.1, 107.5, 21.6, 21.4, 21.1; IR (ATR): 3454, 3022, 2952, 2920, 2864, 1608, 1576, 1558, 1516, 1479, 1442, 1325, 1302, 820, 810. HRMS (EI) calcd for $C_{27}H_{23}N$: 361.1830 ($[M]^+$), found 361.1833 ($[M]^+$).



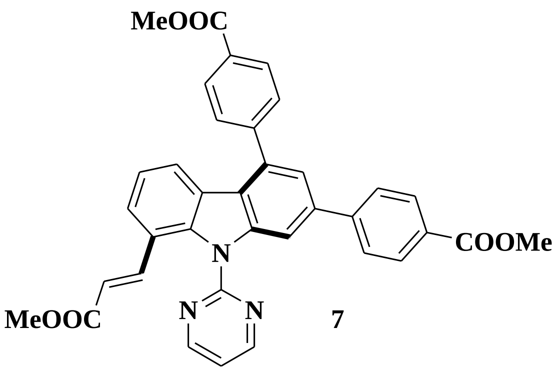
5

Yield 79%; Mp 89-90 °C; ^{1}H NMR (400 MHz, $CDCl_3$) δ: 8.87 (d, *J* = 4.8 Hz, 2H), 8.33 (d, *J* = 8.2 Hz, 1H), 7.73 (d, *J* = 16.0 Hz, 1H), 7.67 – 7.62 (m, 1H), 7.53 (d, *J* = 7.3 Hz, 2H), 7.38 (t, *J* = 7.6 Hz, 2H), 7.33 – 7.16 (m, 5H), 7.05 (s, 1H); ^{13}C NMR (100 MHz, $CDCl_3$) δ: 158.3, 158.2, 138.8, 137.5, 137.4, 129.7, 129.4, 128.7, 127.6, 126.6, 123.6, 122.4, 120.7, 120.4, 117.3, 114.0, 105.3; IR (ATR): 3052, 2962, 1562, 1450, 1425, 1348, 1261, 1089, 1018, 802; HRMS (EI) calcd for $C_{20}H_{15}N_3$: 297.1266 ($[M]^+$), found 297.1273 ($[M]^+$).



6

Yield 62%; Mp 122-123 °C; ^{1}H NMR (400 MHz, $CDCl_3$) δ: 8.85 (d, *J* = 4.8 Hz, 2H), 8.64 (d, *J* = 1.6 Hz, 1H), 8.26 (d, *J* = 8.4 Hz, 2H), 8.15 (d, *J* = 8.4 Hz, 2H), 7.80 (d, *J* = 8.4 Hz, 2H), 7.72 (d, *J* = 8.4 Hz, 2H), 7.58 (d, *J* = 6.8 Hz, 1H), 7.48 (d, *J* = 1.6 Hz, 1H), 7.32 – 7.26 (m, 2H), 7.16 (t, *J* = 7.8 Hz, 1H), 4.60 (s, 1H), 4.28 – 4.15 (m, 4H), 4.03 (s, 3H), 3.97 (s, 3H), 1.24 (t, *J* = 7.2 Hz, 6H); ^{13}C NMR (100 MHz, $CDCl_3$) δ: 168.3, 167.0, 167.0, 159.2, 158.9, 145.8, 145.3, 142.4, 139.3, 138.5, 136.6, 130.1, 130.0, 129.7, 129.4, 129.0, 128.8, 127.5, 126.6, 123.6, 122.8, 122.7, 122.1, 119.9, 118.1, 111.6, 61.9, 55.7, 52.3, 52.2, 14.0; IR (ATR): 3361, 3191, 2921, 2852, 1724, 1564, 1413, 1280, 1189, 1112, 1020, 854, 773; HRMS (EI) calcd for $C_{39}H_{33}N_3O_8$: 671.2268 ($[M]^+$), found 671.2269 ($[M]^+$).



7

Yield 81%; Mp 102- 103 °C; ^{1}H NMR (400 MHz, $CDCl_3$) δ: 8.83 (d, *J* = 4.8 Hz, 2H), 8.37 (d, *J* = 1.4 Hz, 1H), 8.17 (d, *J* = 8.2 Hz, 2H), 8.05 (d, *J* = 8.4 Hz, 2H), 7.70 (d, *J* = 8.4 Hz, 2H), 7.66 (d, *J* = 8.2 Hz, 2H), 7.51 (d, *J* = 7.6 Hz, 1H), 7.41 (d, *J* = 1.4 Hz, 1H), 7.33 – 7.26 (m, 3H), 7.03 (t, *J* = 7.8 Hz, 1H), 6.21 (d, *J* = 15.8 Hz, 1H), 3.94 (s, 3H), 3.88 (s, 3H), 3.64 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ: 167.2, 167.0, 167.0, 158.9, 158.9, 145.7, 145.3, 143.0, 142.0, 139.0, 138.8, 136.8, 130.1, 130.0, 129.8, 129.4, 129.0, 127.5, 126.2, 125.8, 123.9, 123.3, 122.1, 121.9, 121.3, 118.9, 116.7, 110.7, 52.3, 52.2, 51.5; IR (ATR): 2919, 2850, 1720, 1633, 1608, 1563, 1434, 1413, 1305, 1278, 1168, 1105, 852, 771; HRMS (EI) calcd for $C_{36}H_{27}N_3O_6$: 597.1900 ($[M]^+$), found 597.1897 ($[M]^+$).

References:

1 Y. Li, B. J. Li, W. H. Wang, W. P. Huang, X. S. Zhang, K. Chen and Z. J. Shi, *Angew. Chem., Int. Ed.*, 2011, **50**, 2115.

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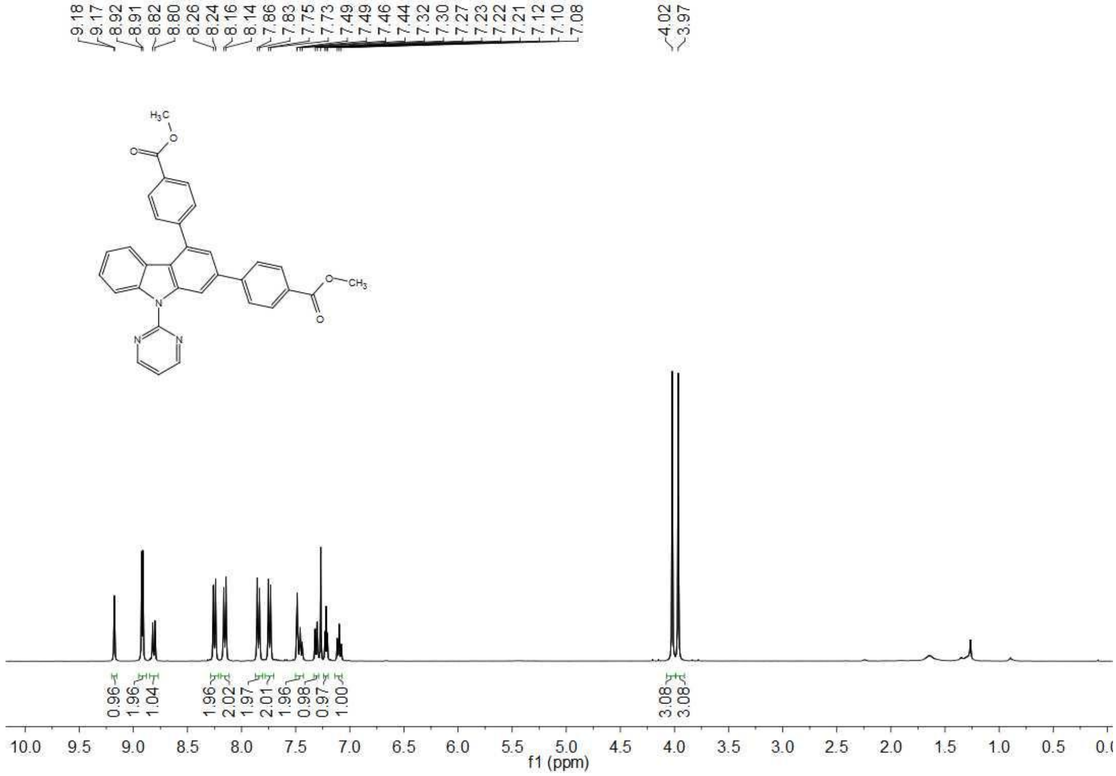
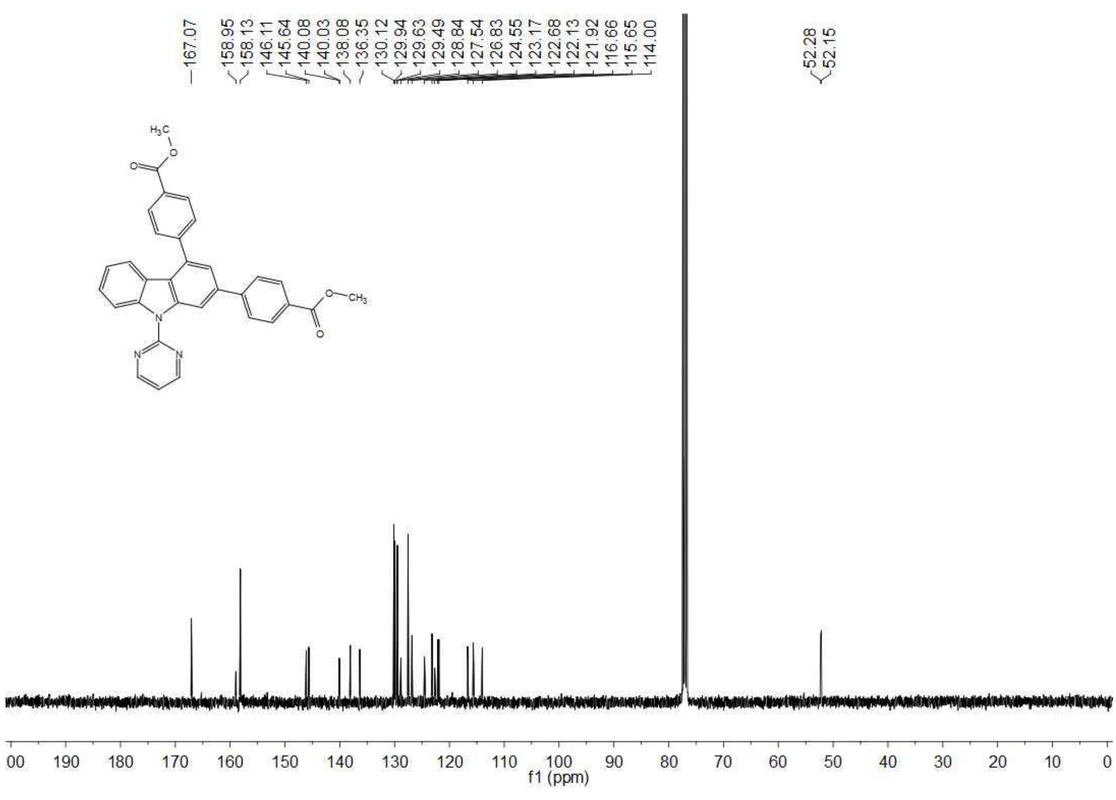
^{1}H and ^{13}C NMR spectra of products 3aa-3qa, 3ba-3sa and 4-7:

3aa





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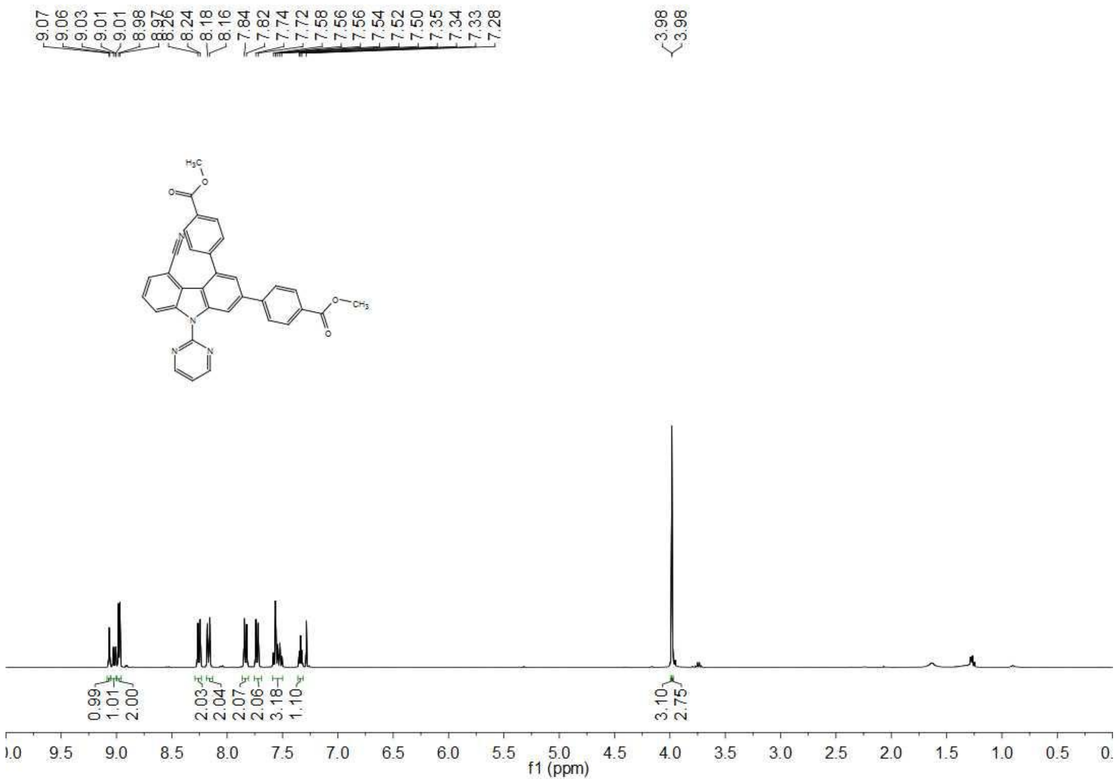
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7.56
7.56
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7.50
7.35
7.34
7.33
7.28
3.98
3.98
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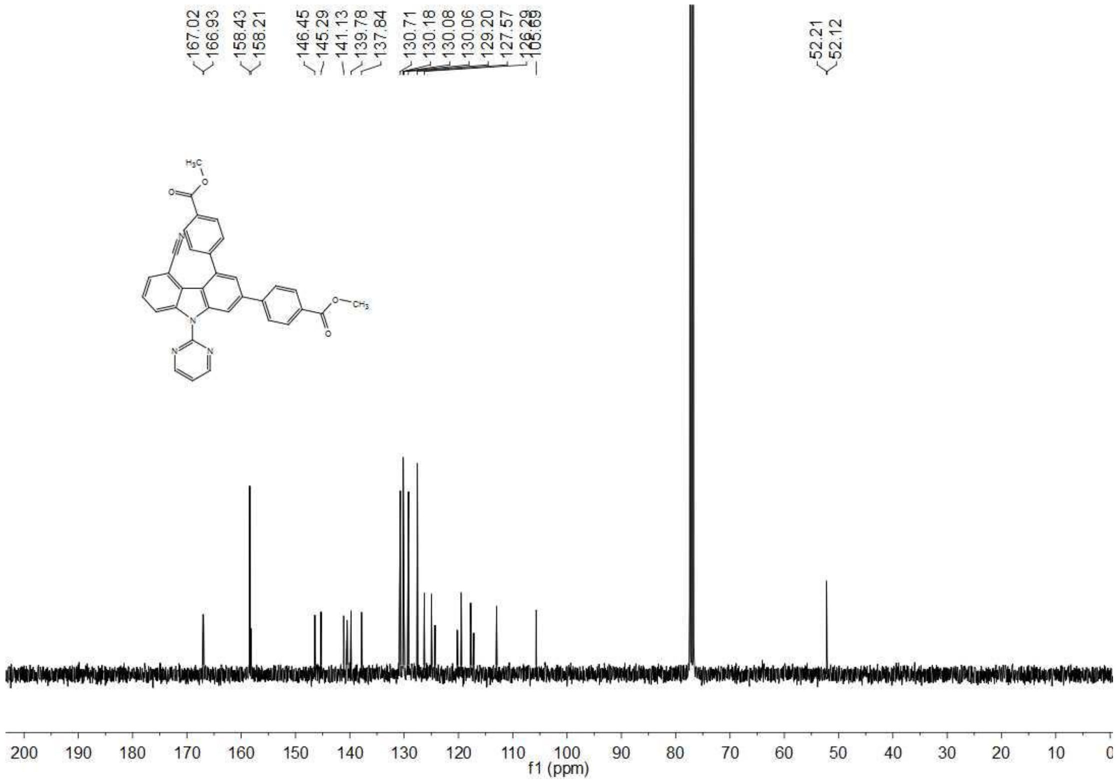
f1 (ppm)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f1 (ppm)

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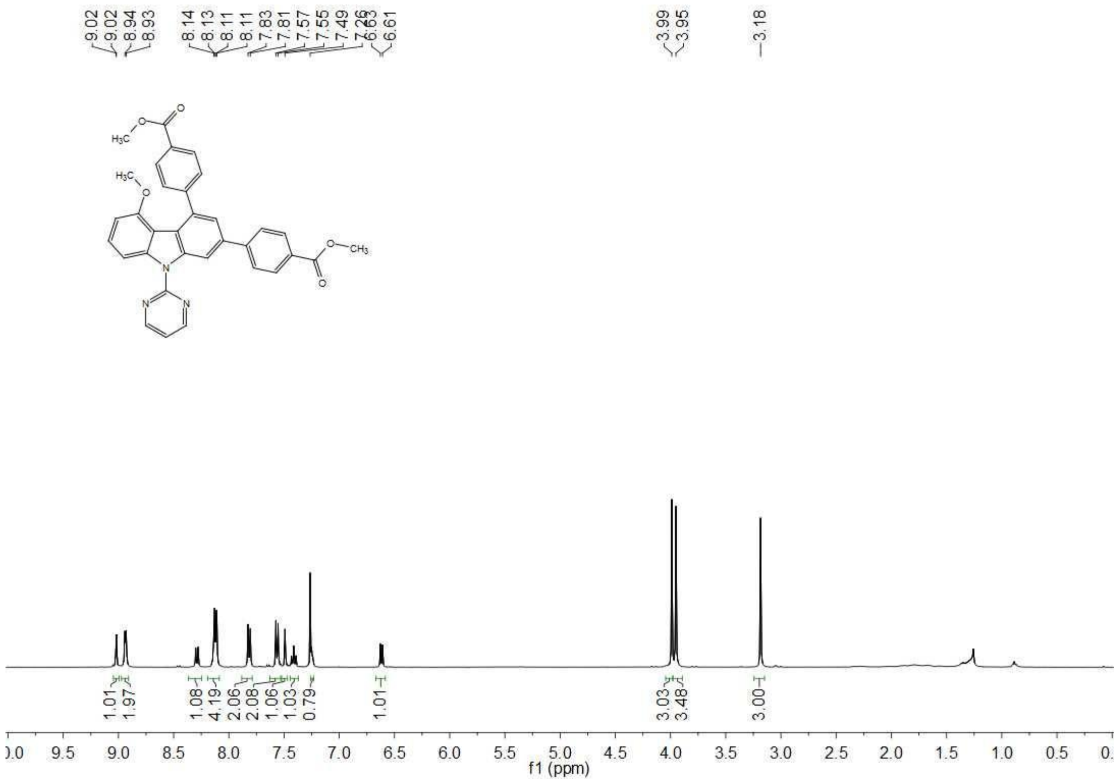

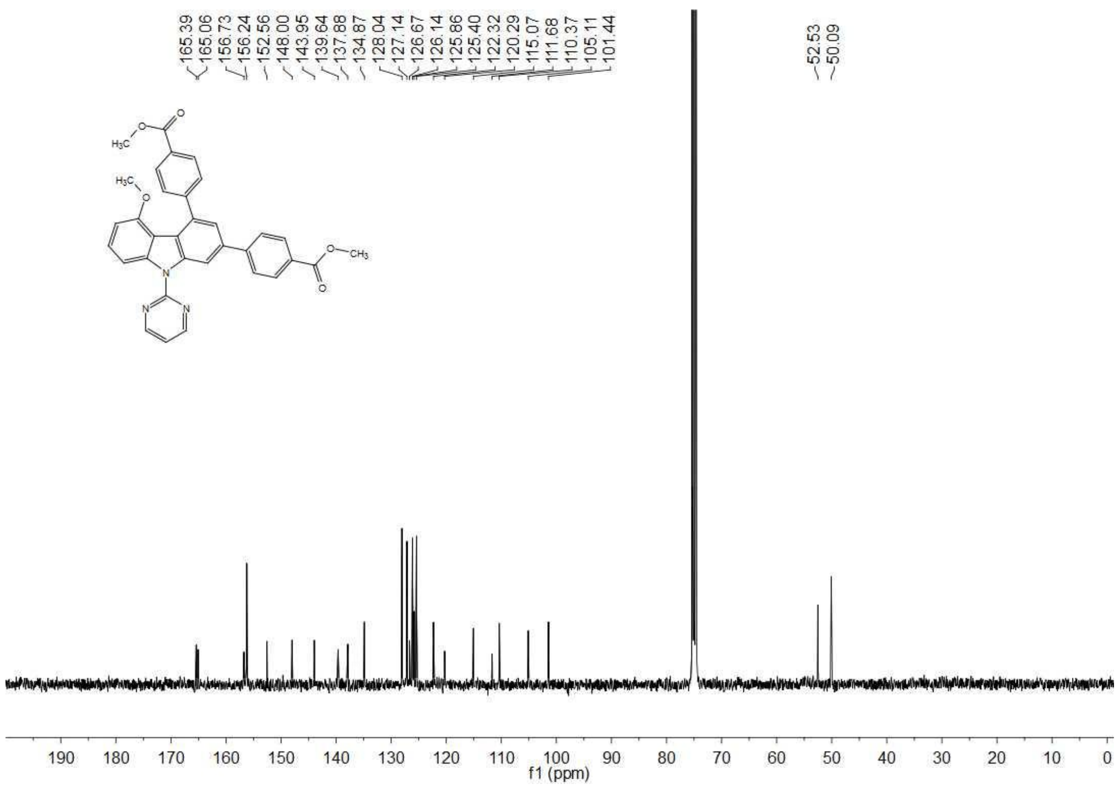

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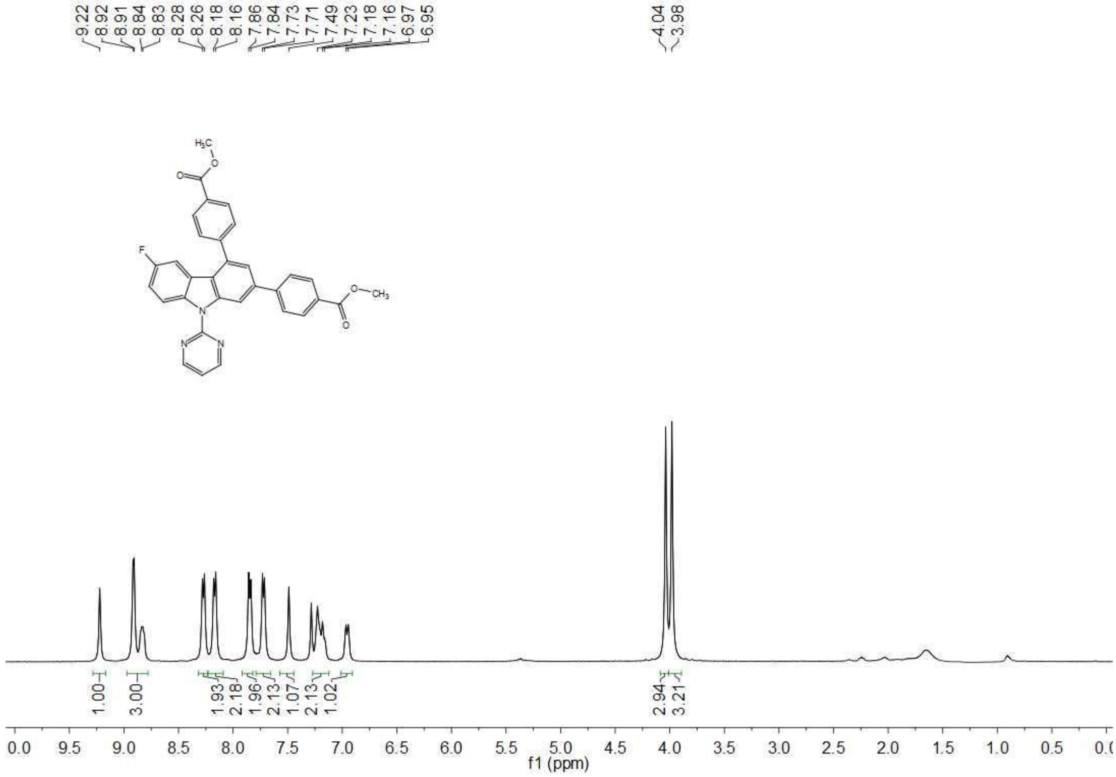
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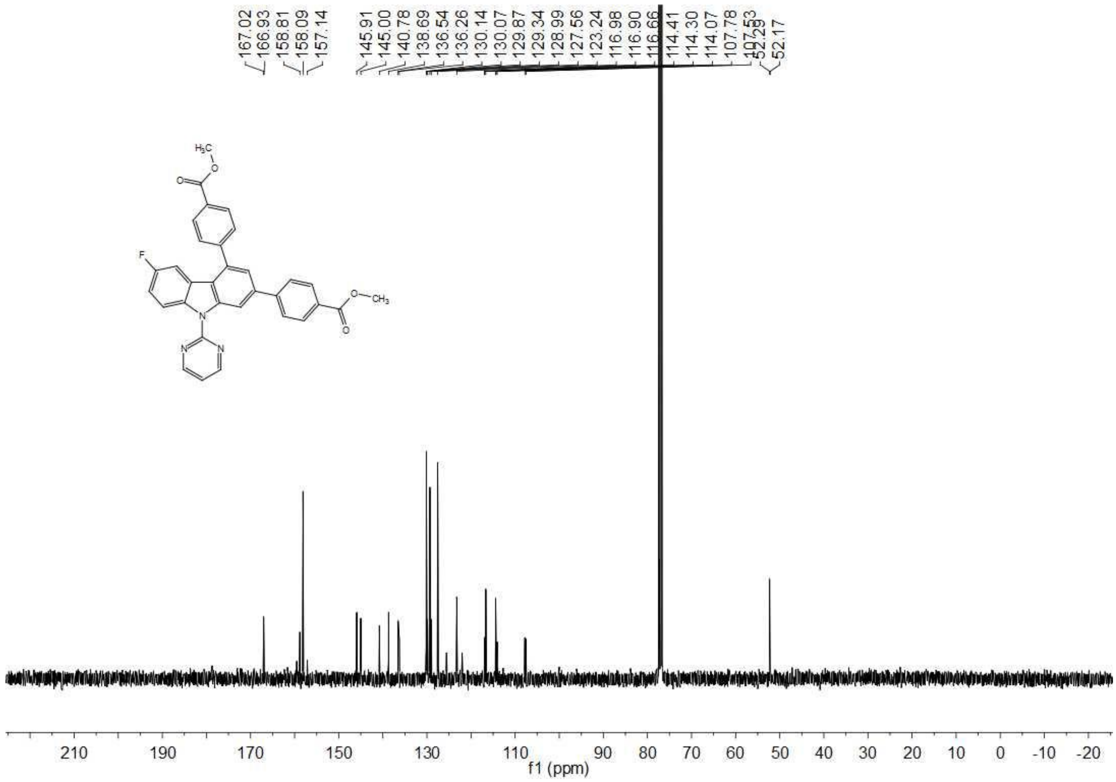
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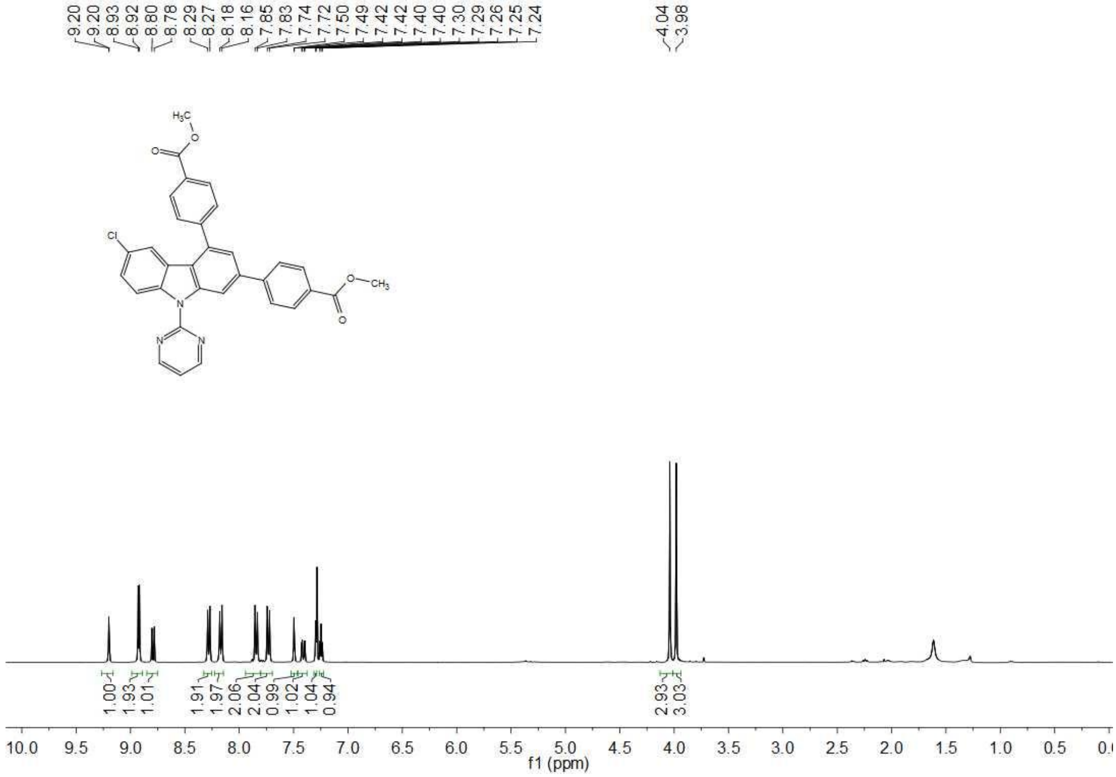

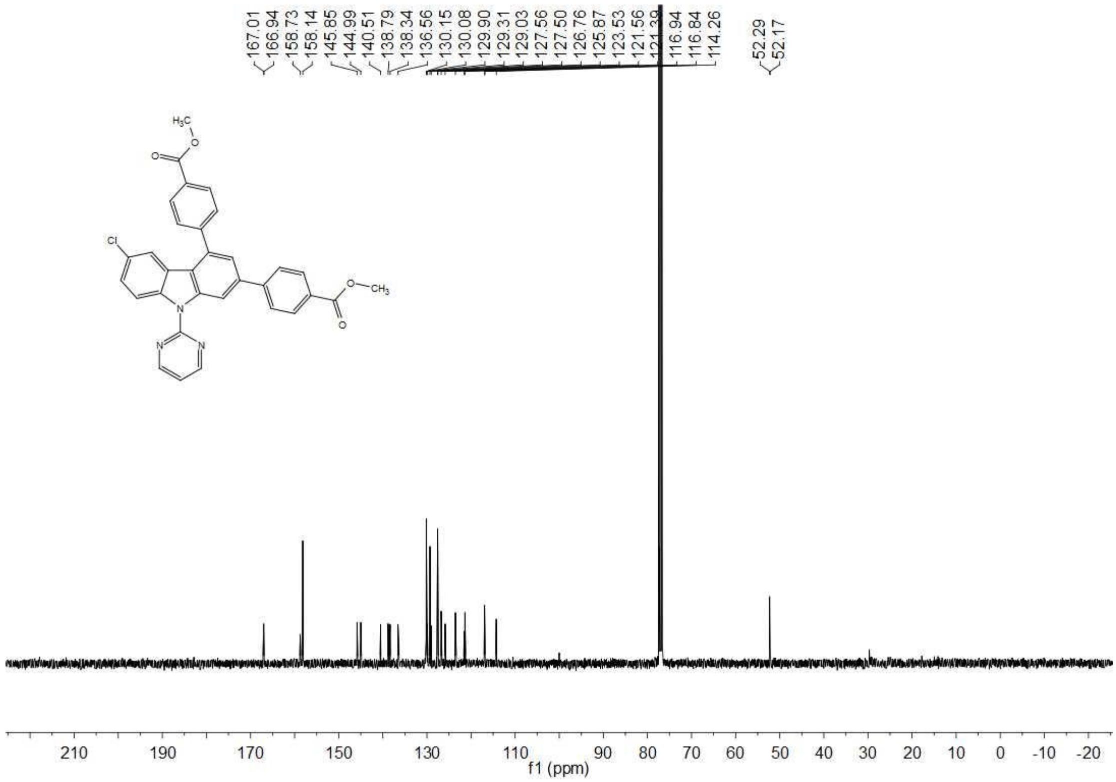

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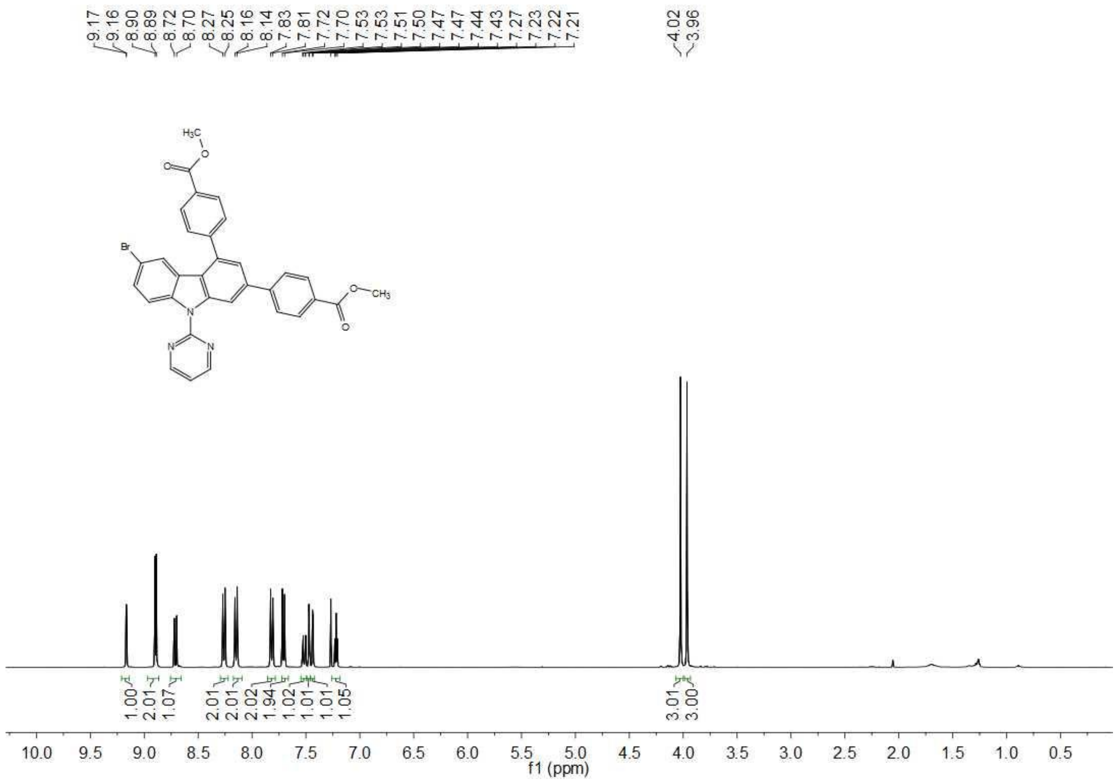

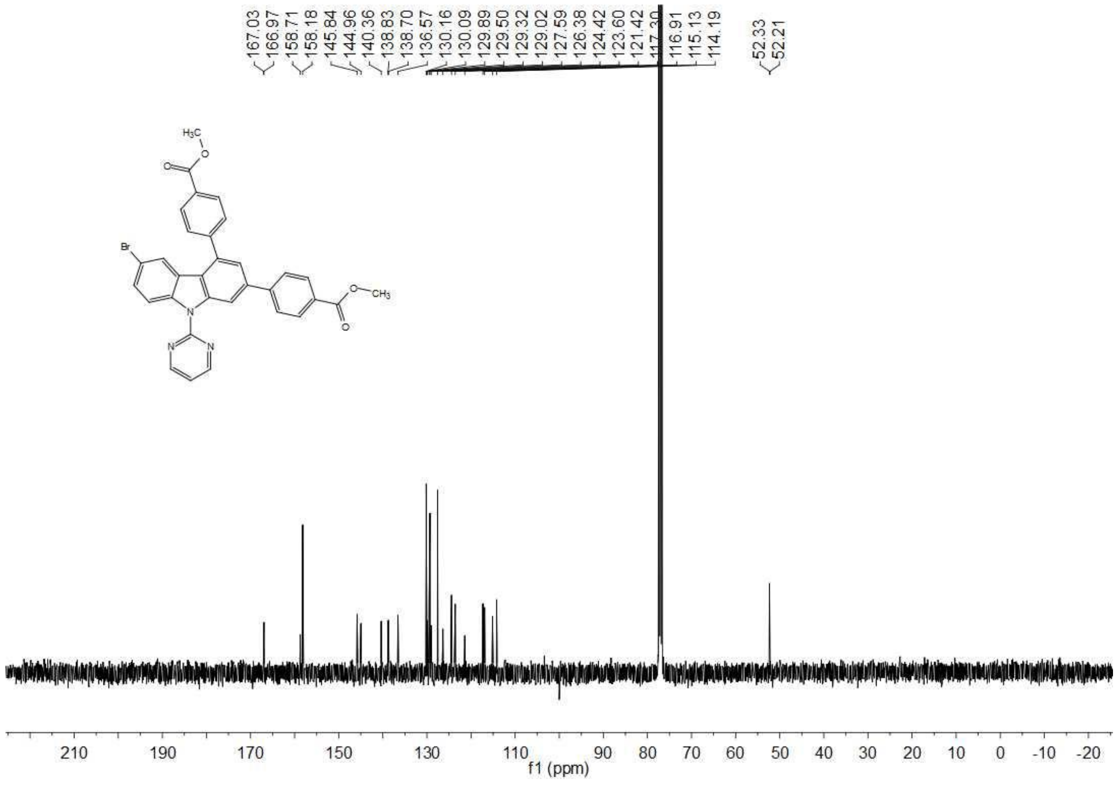

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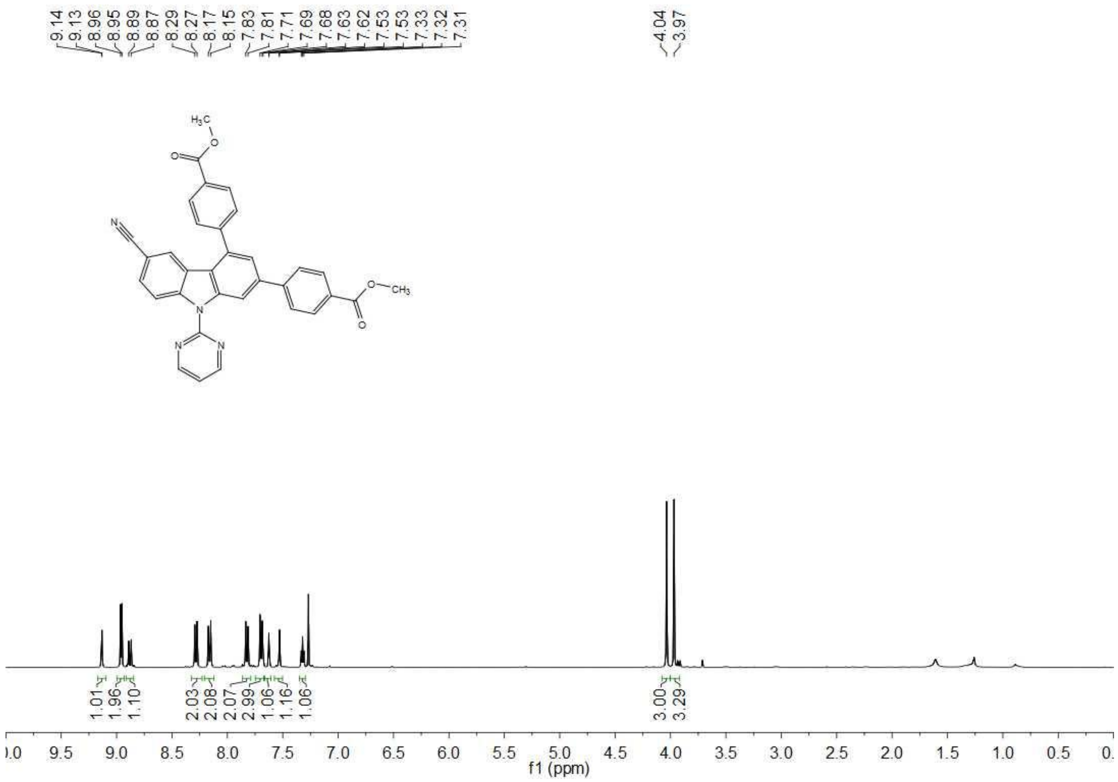
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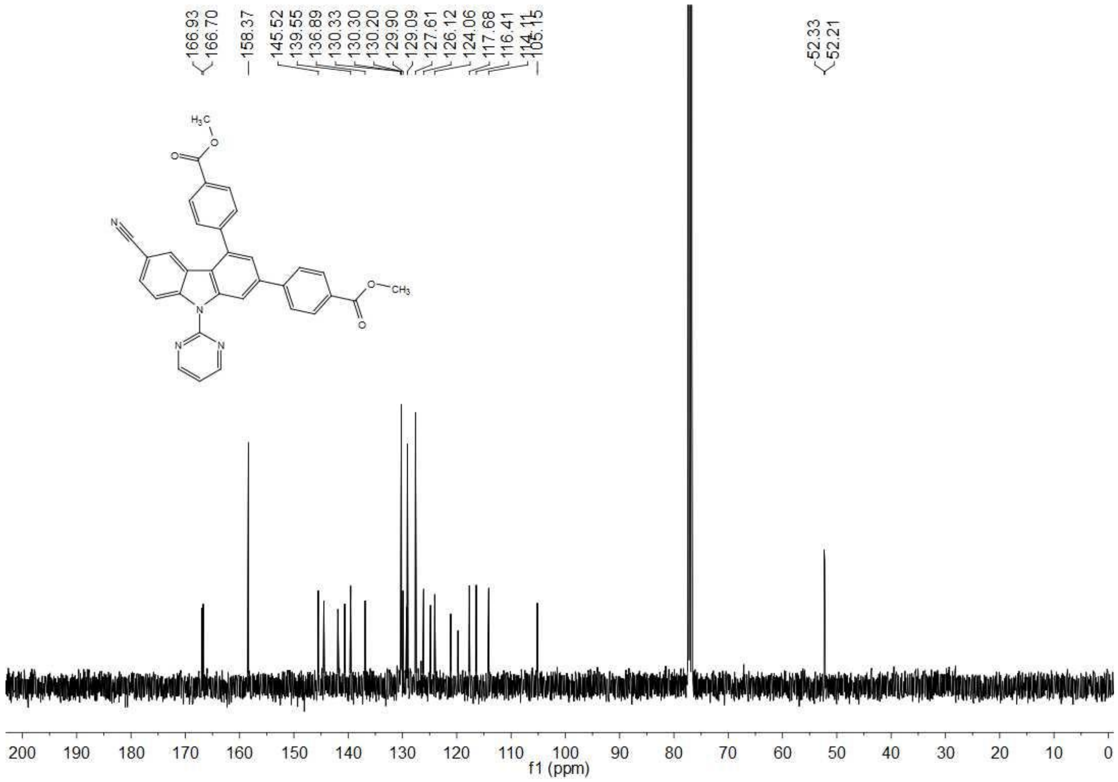
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f1 (ppm)

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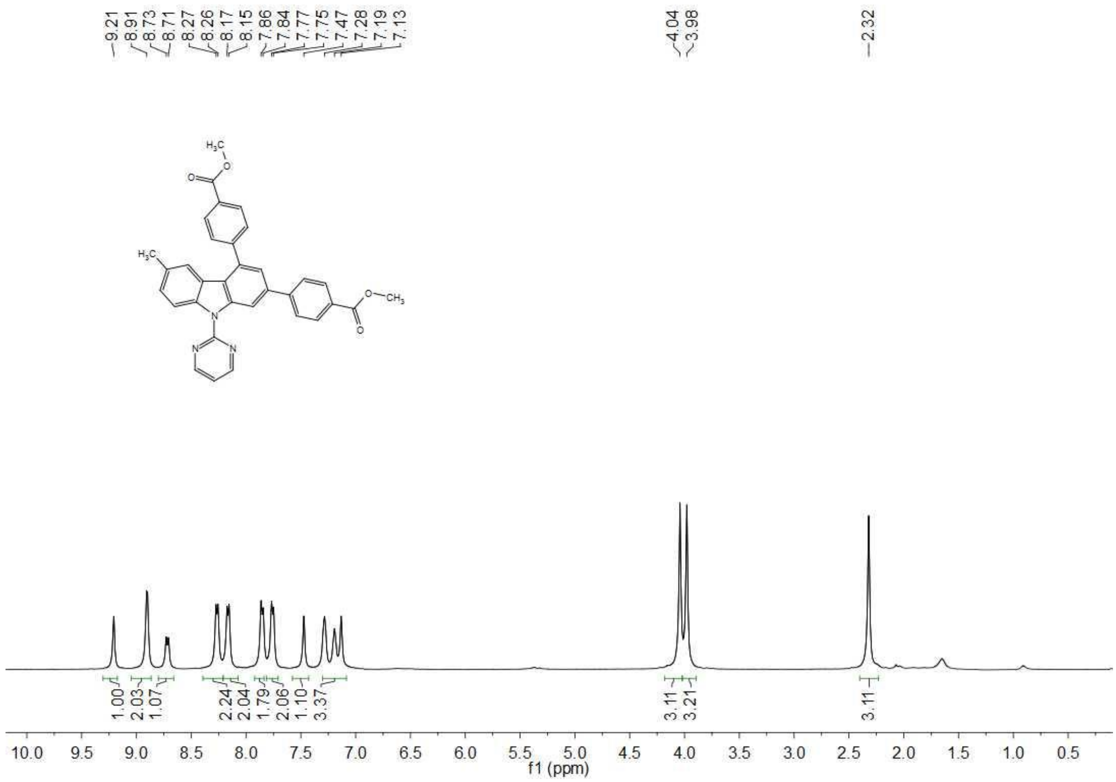

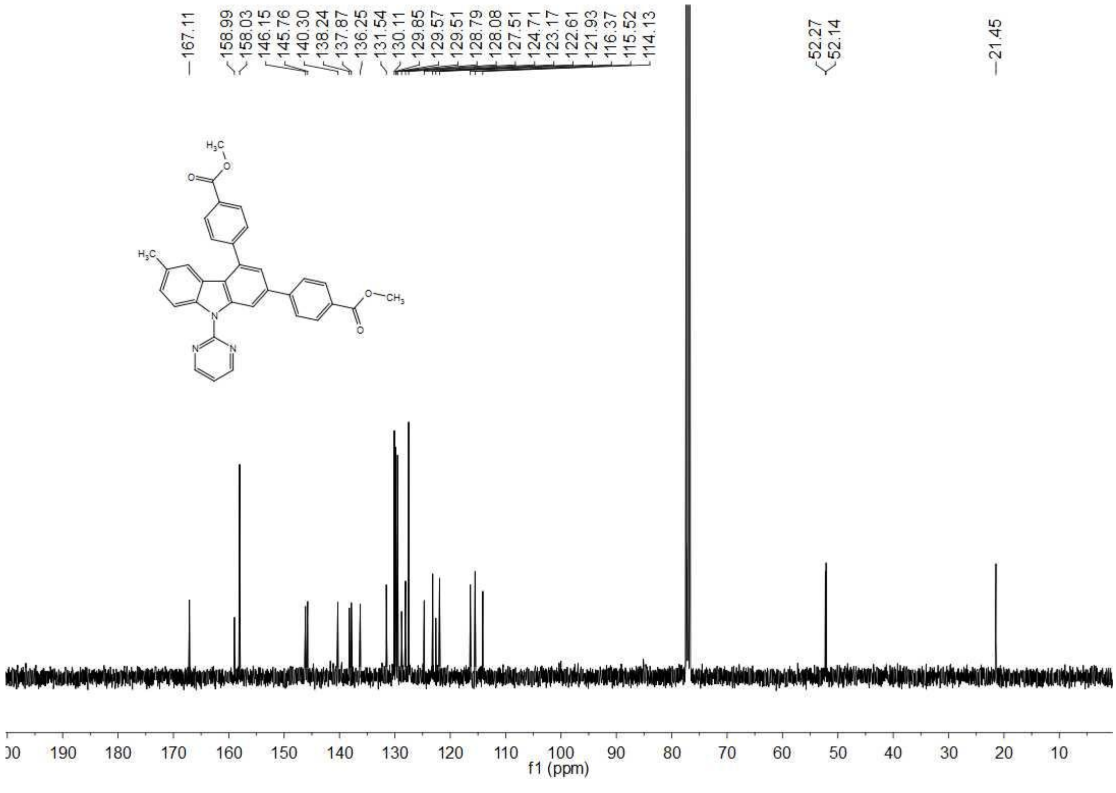

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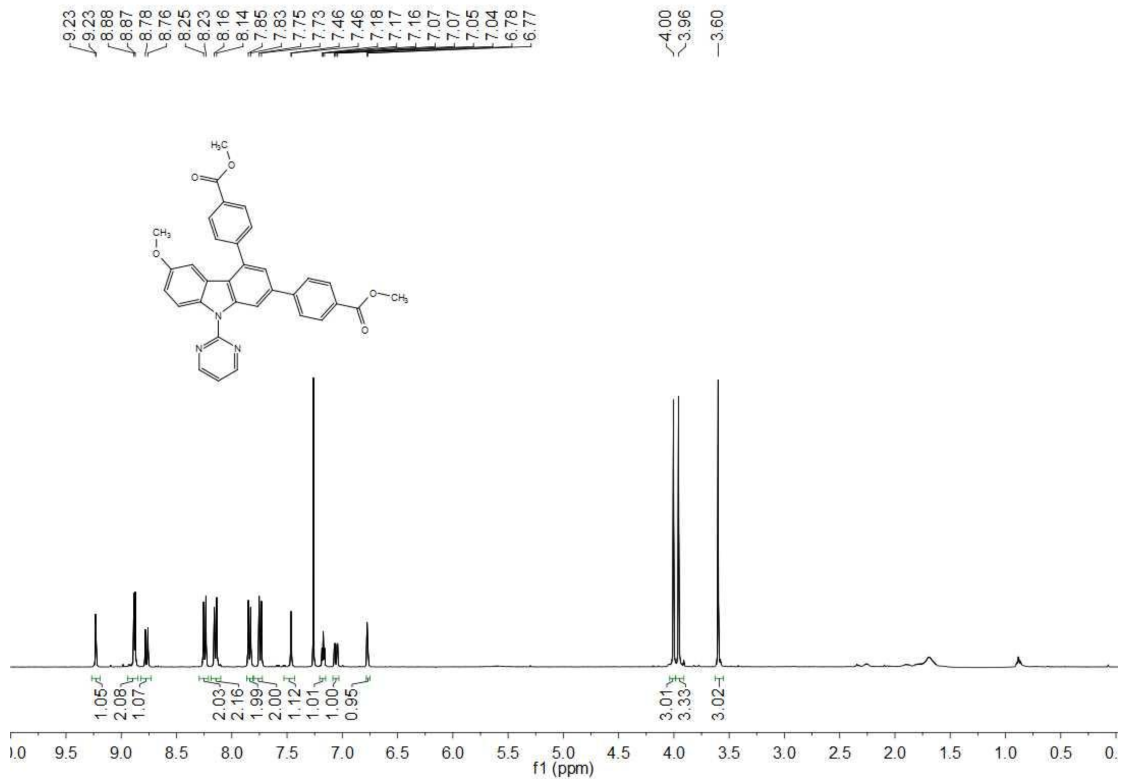
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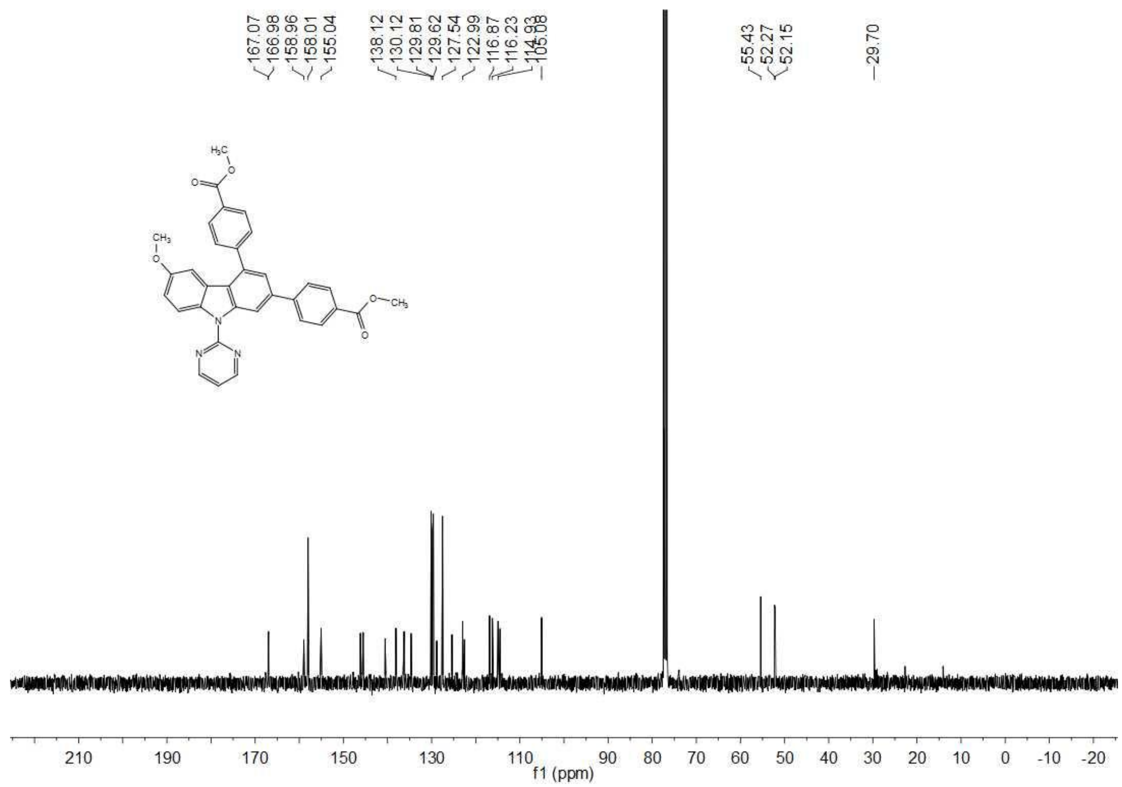
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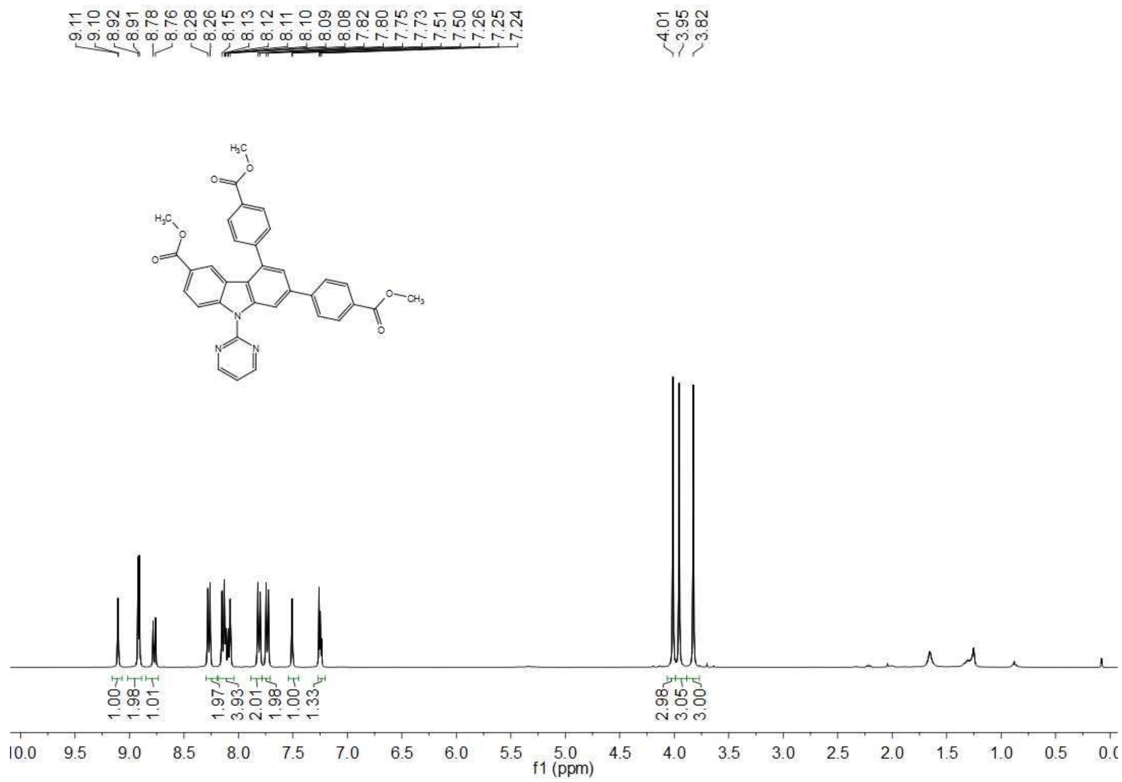

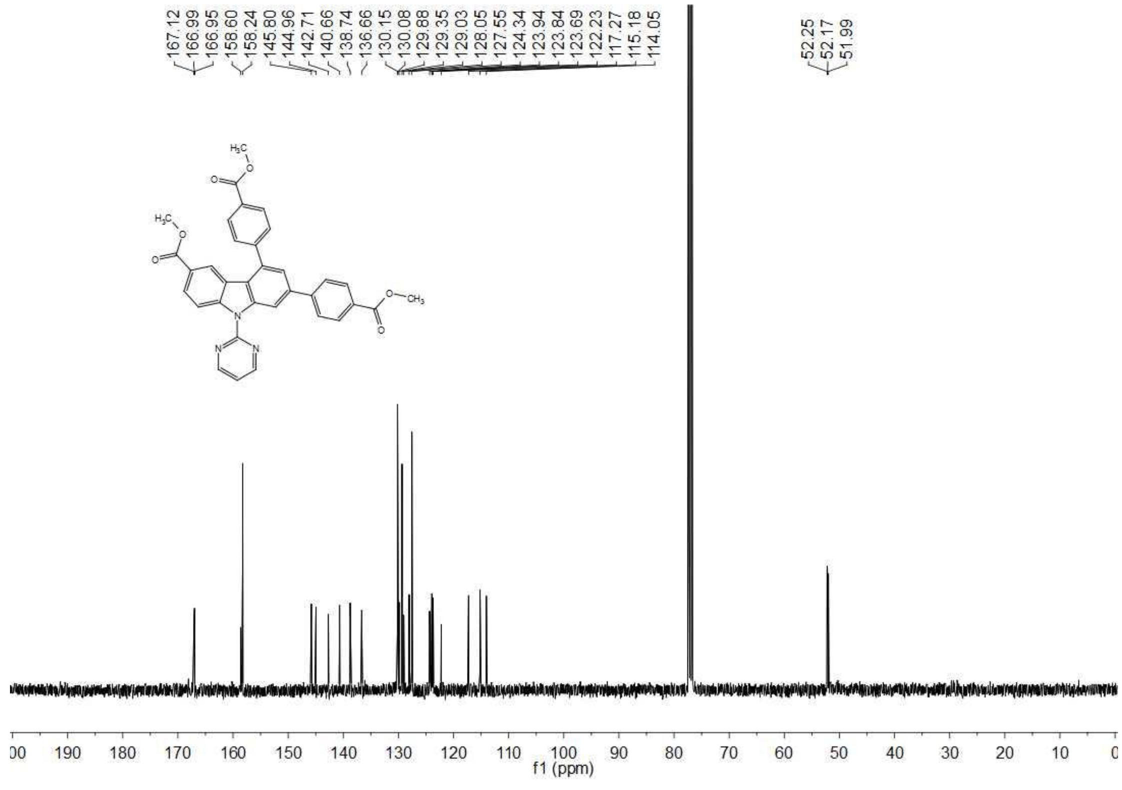

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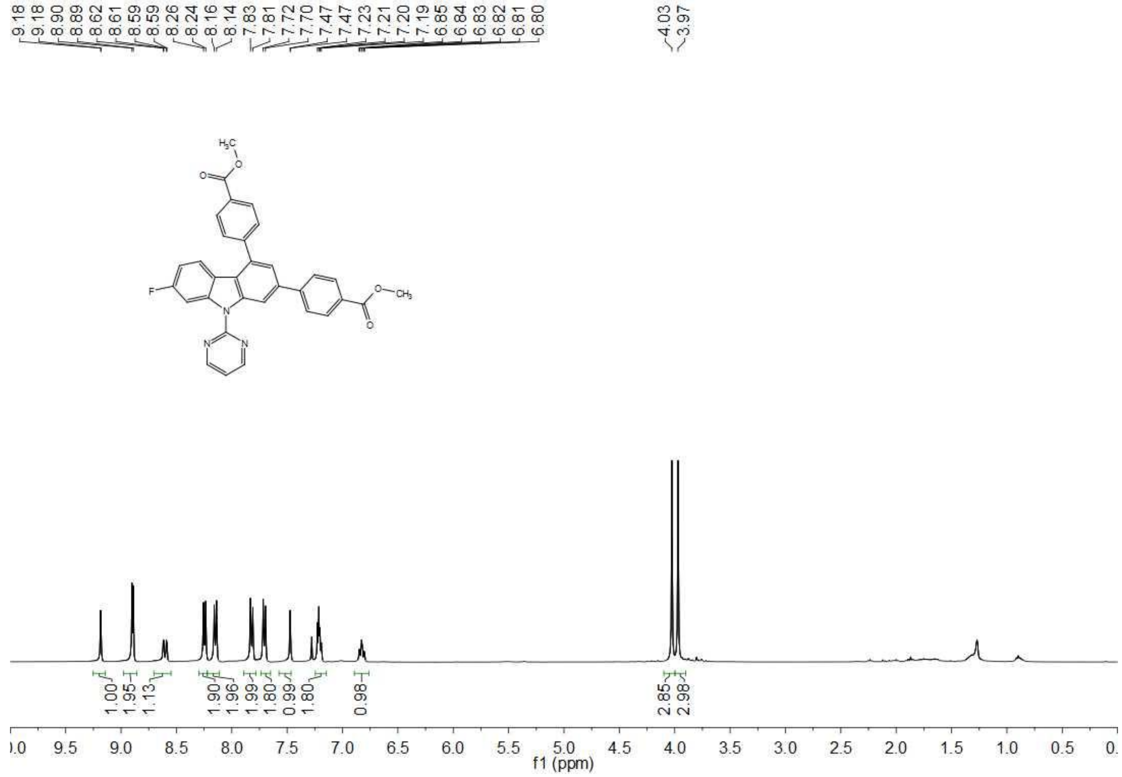

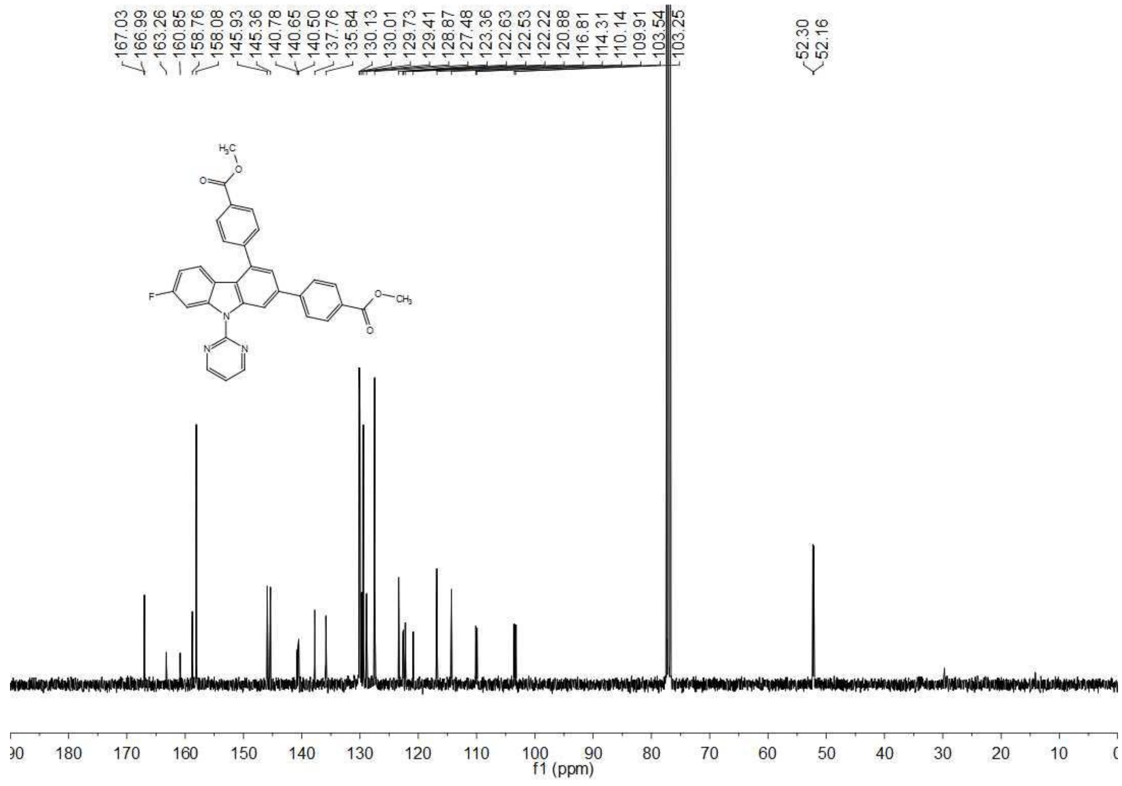

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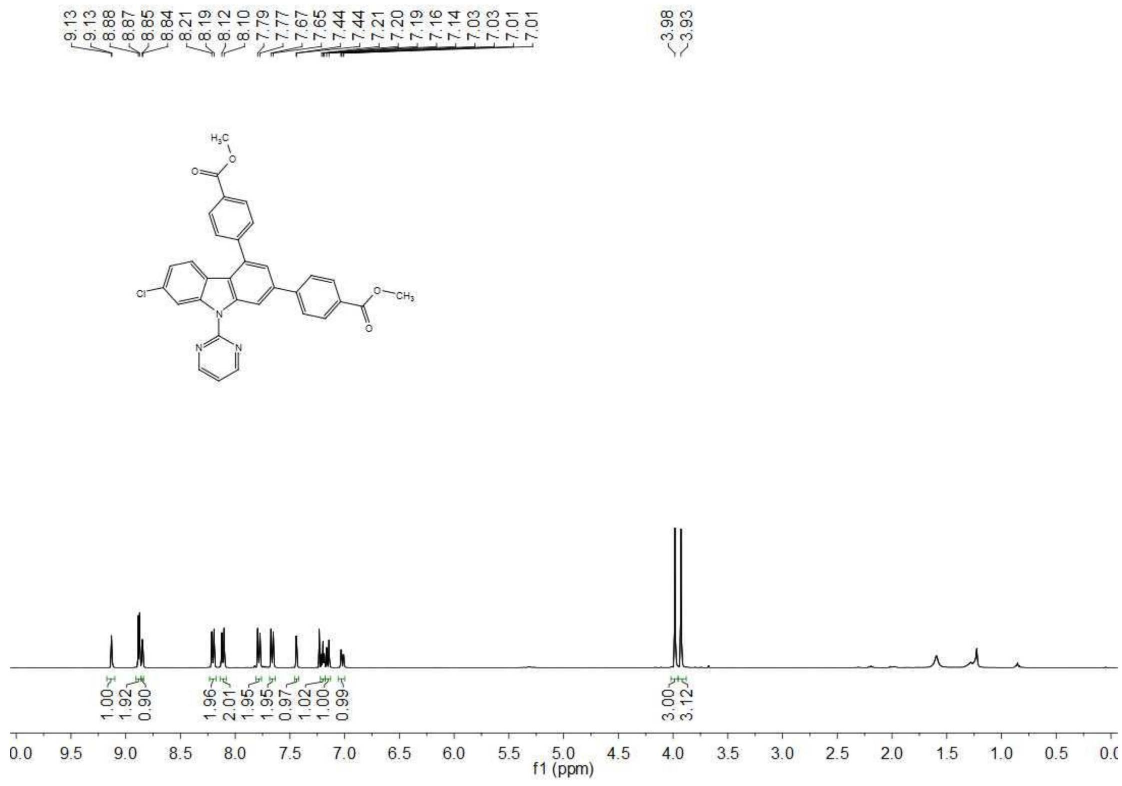

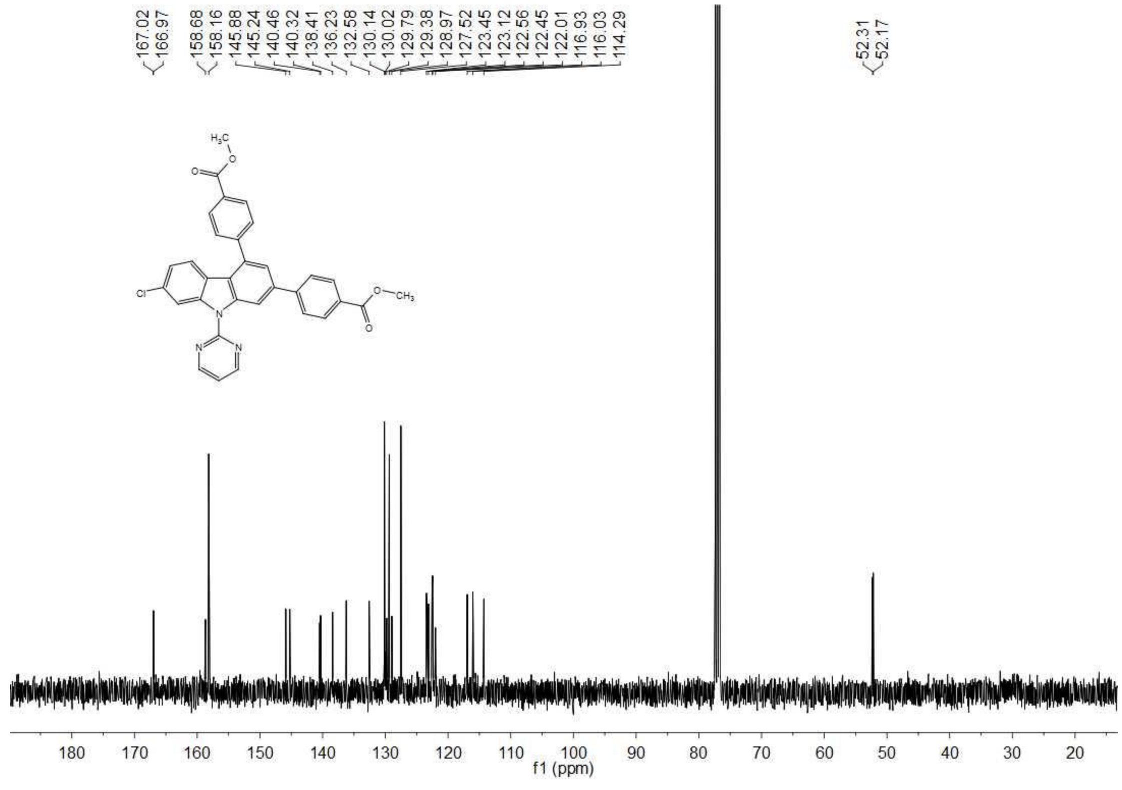

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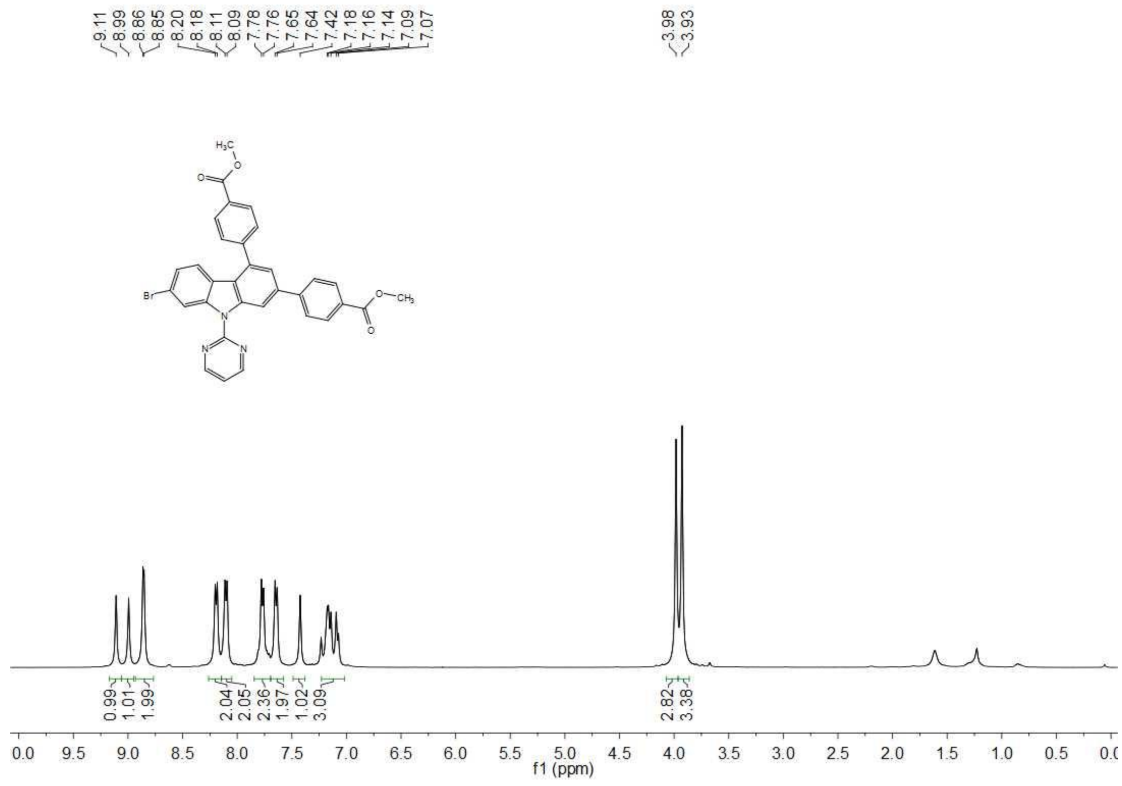
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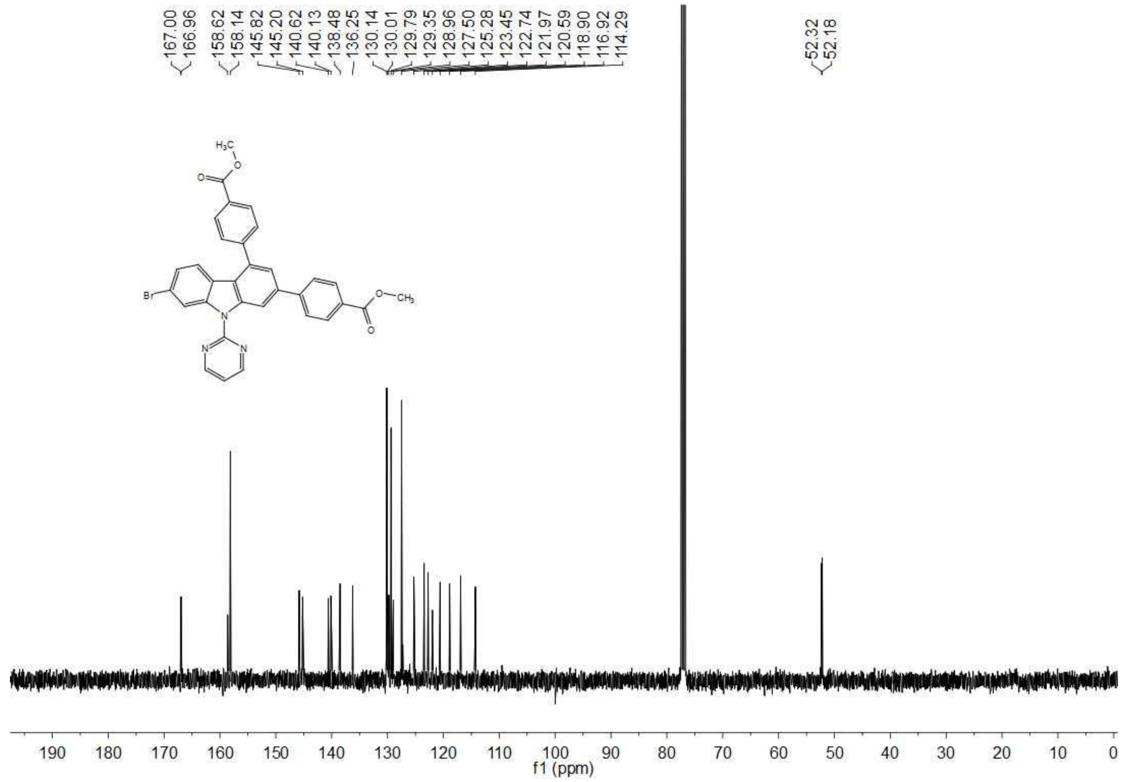
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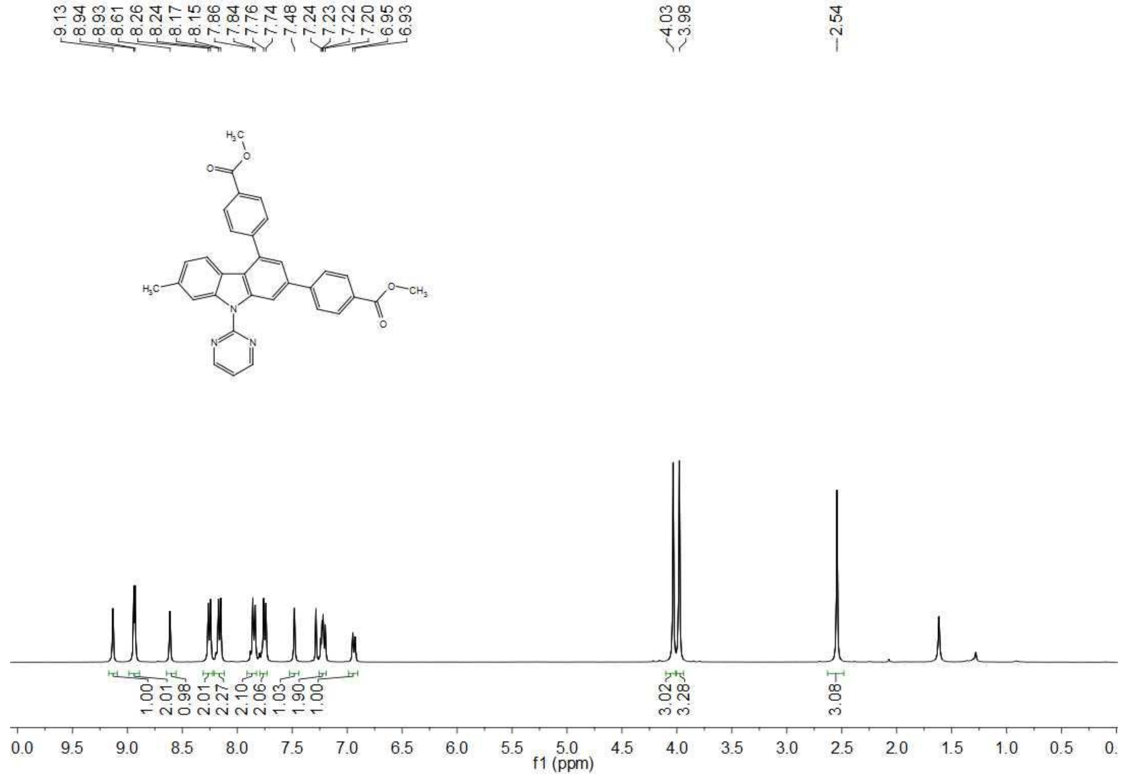
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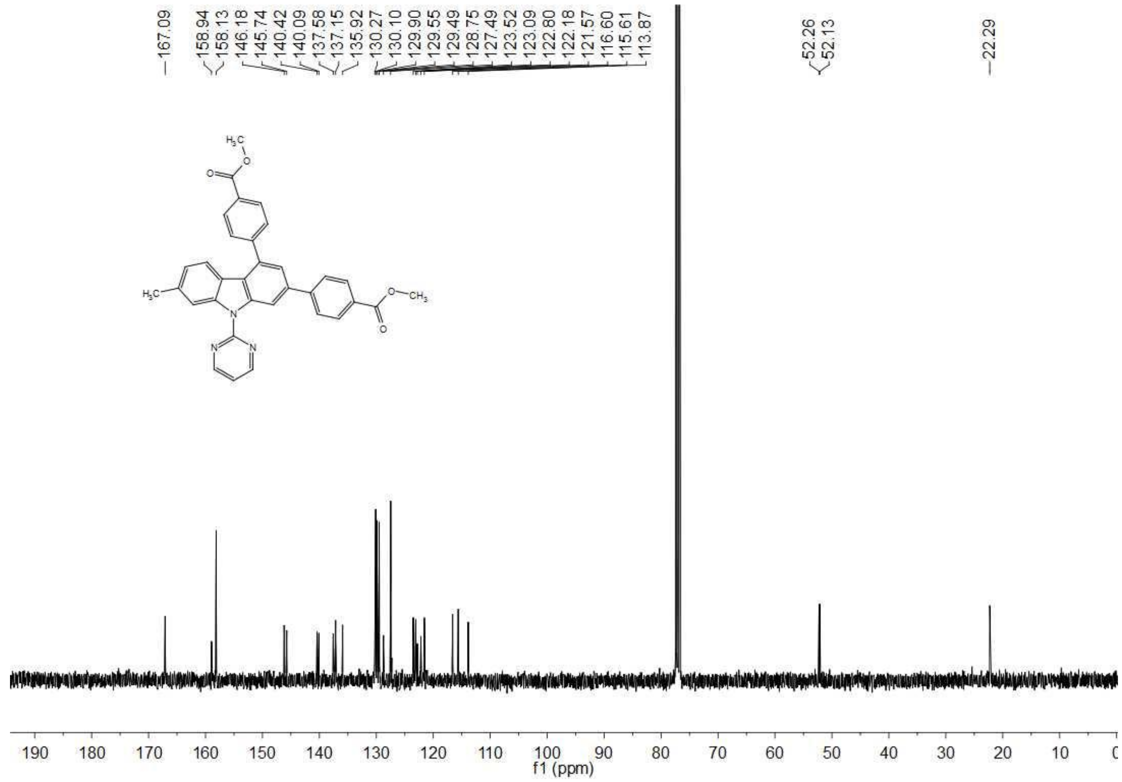
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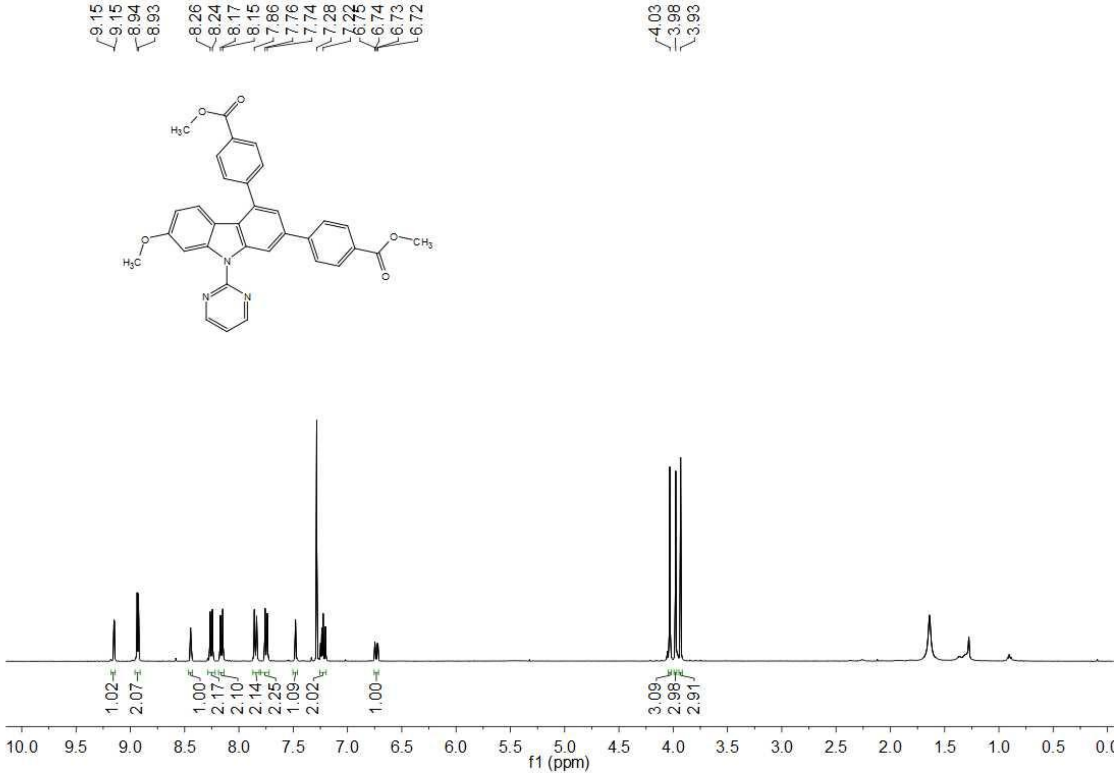
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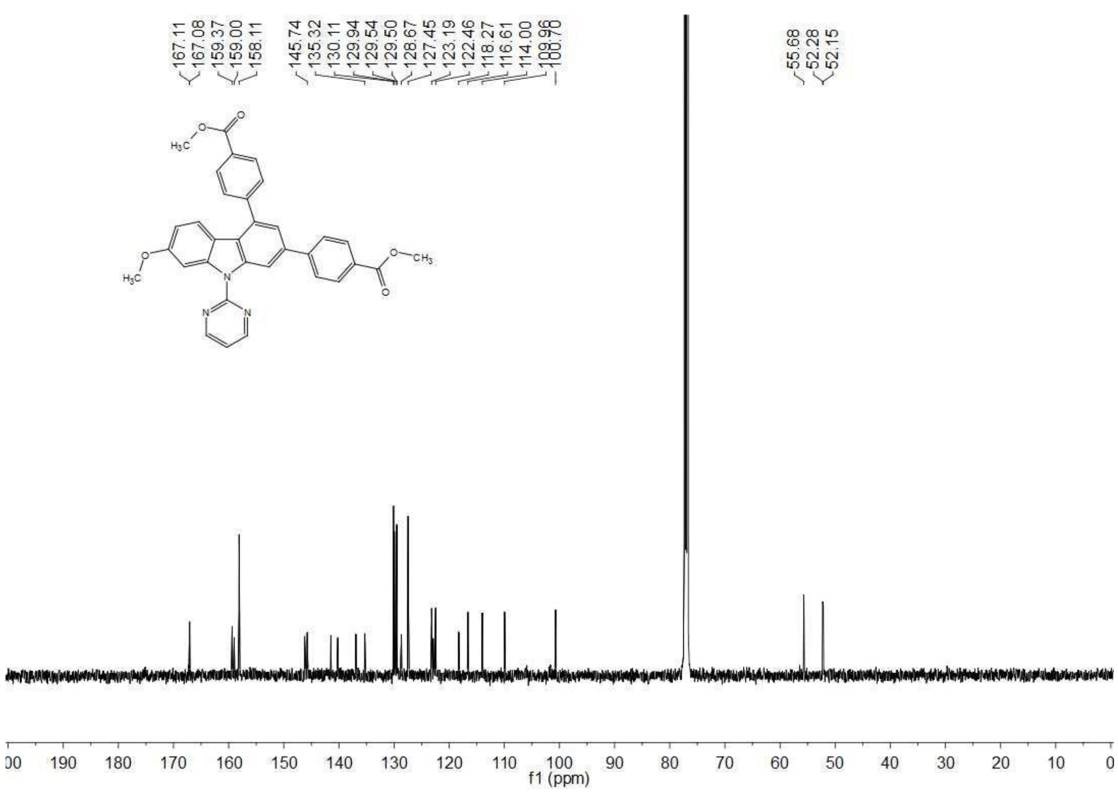
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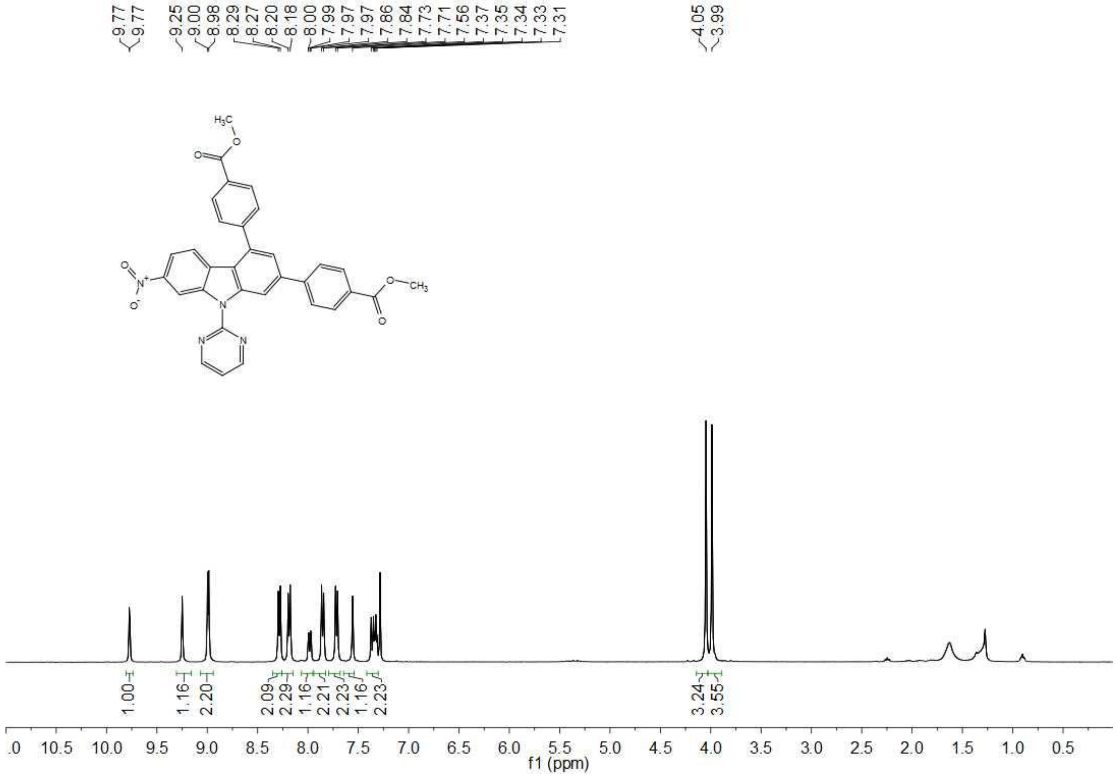

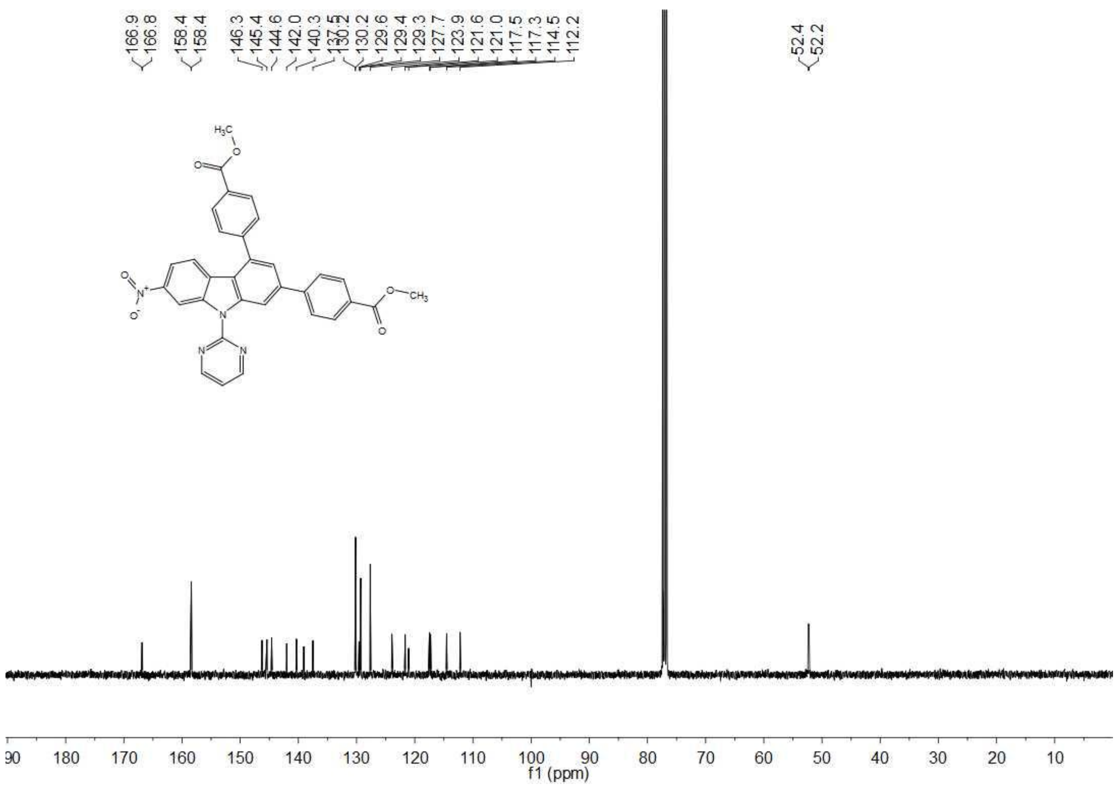

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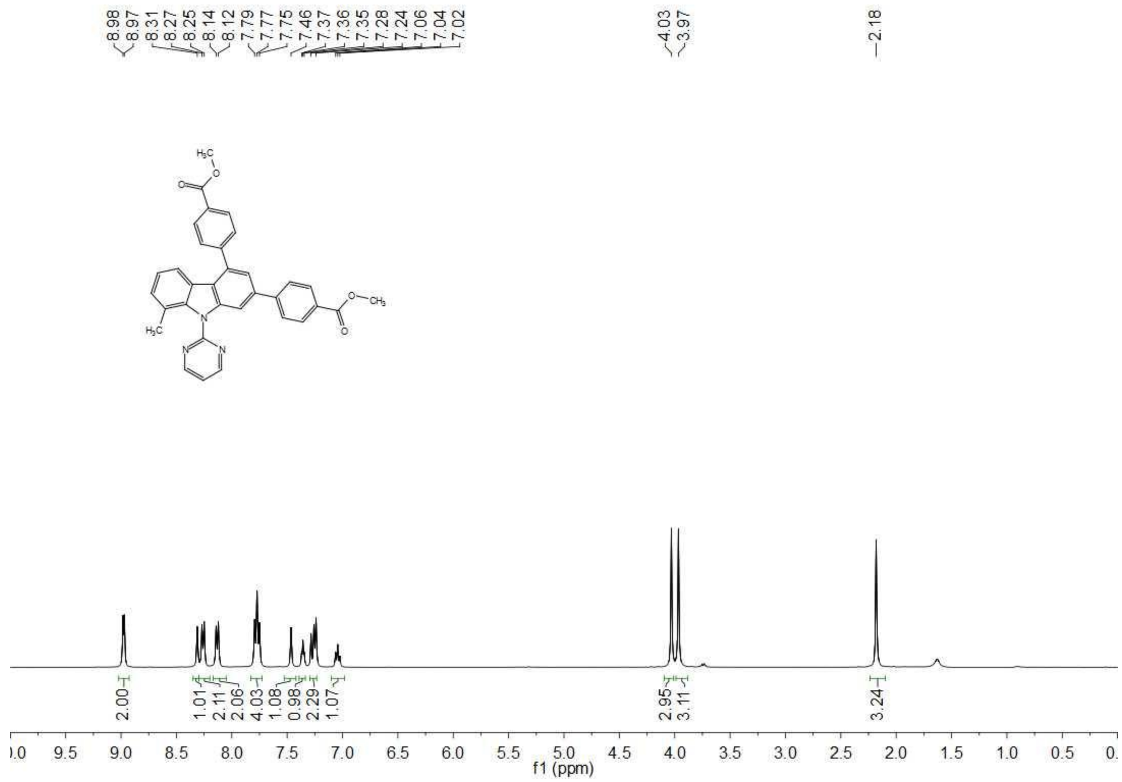

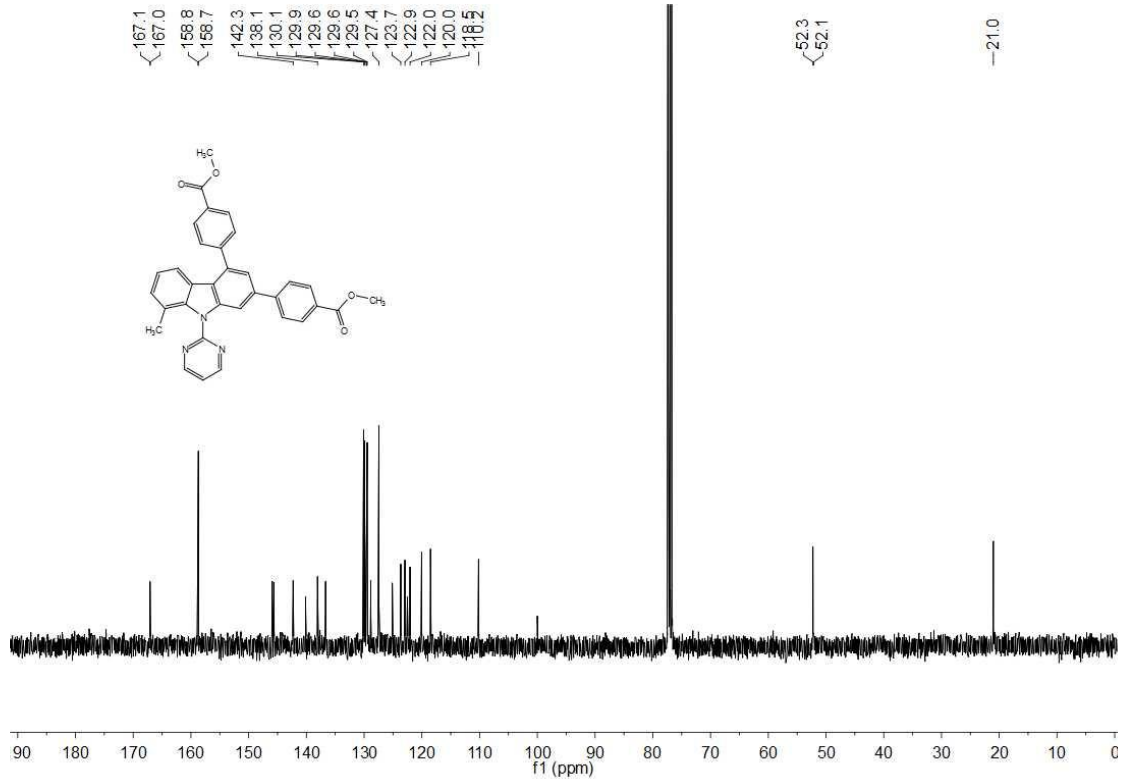

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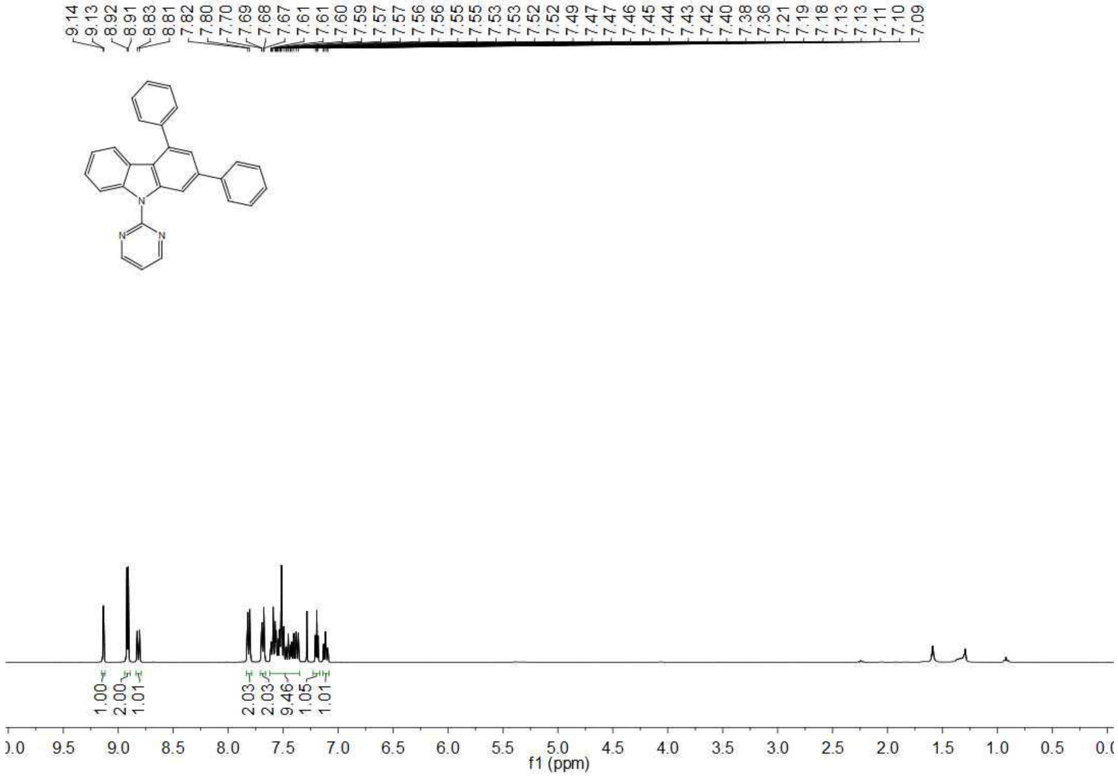
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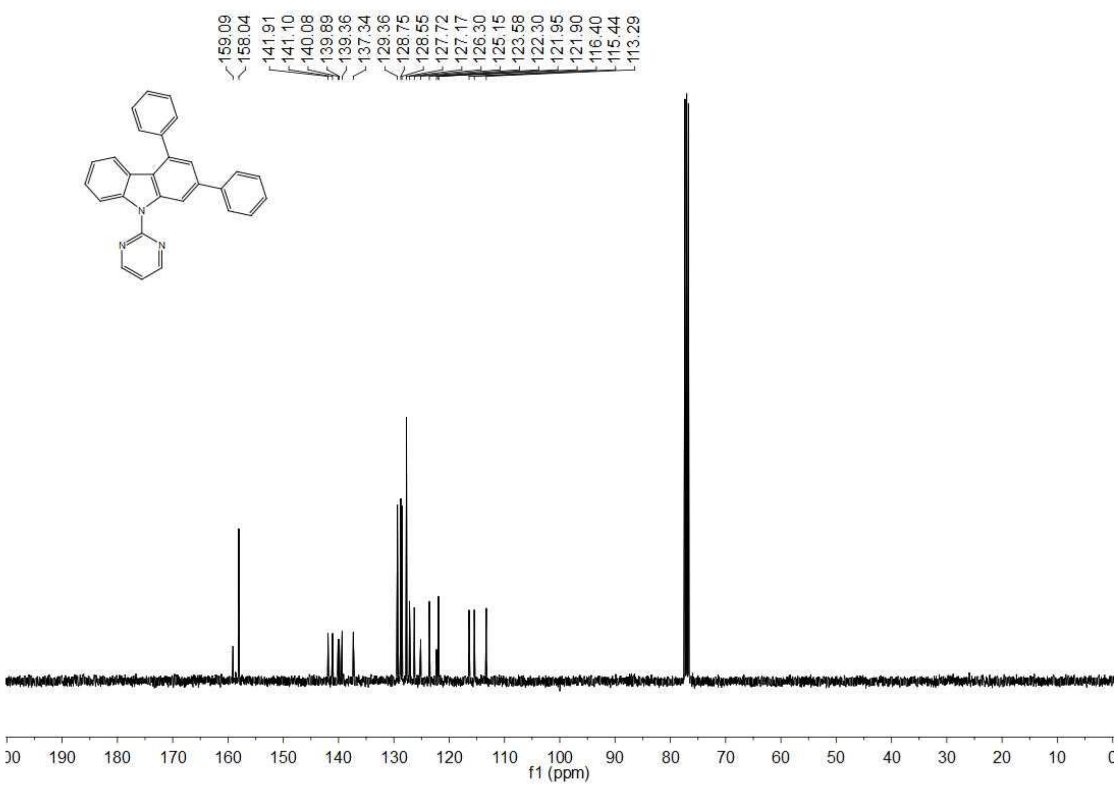
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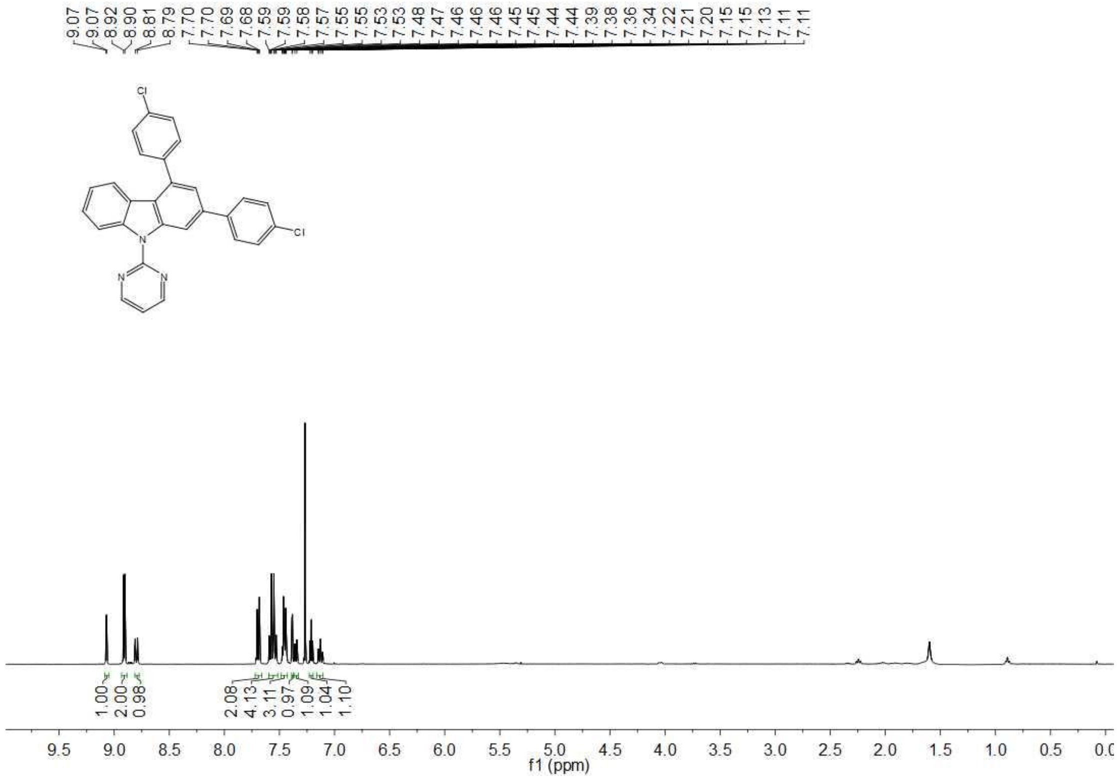

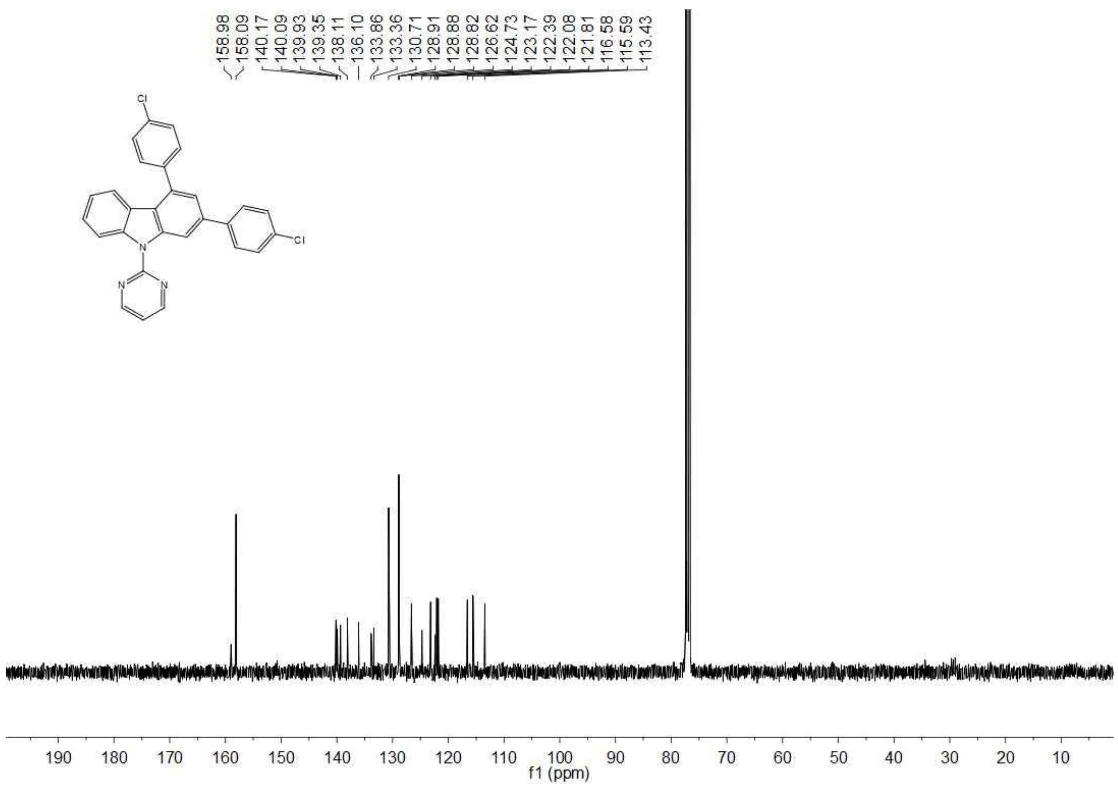

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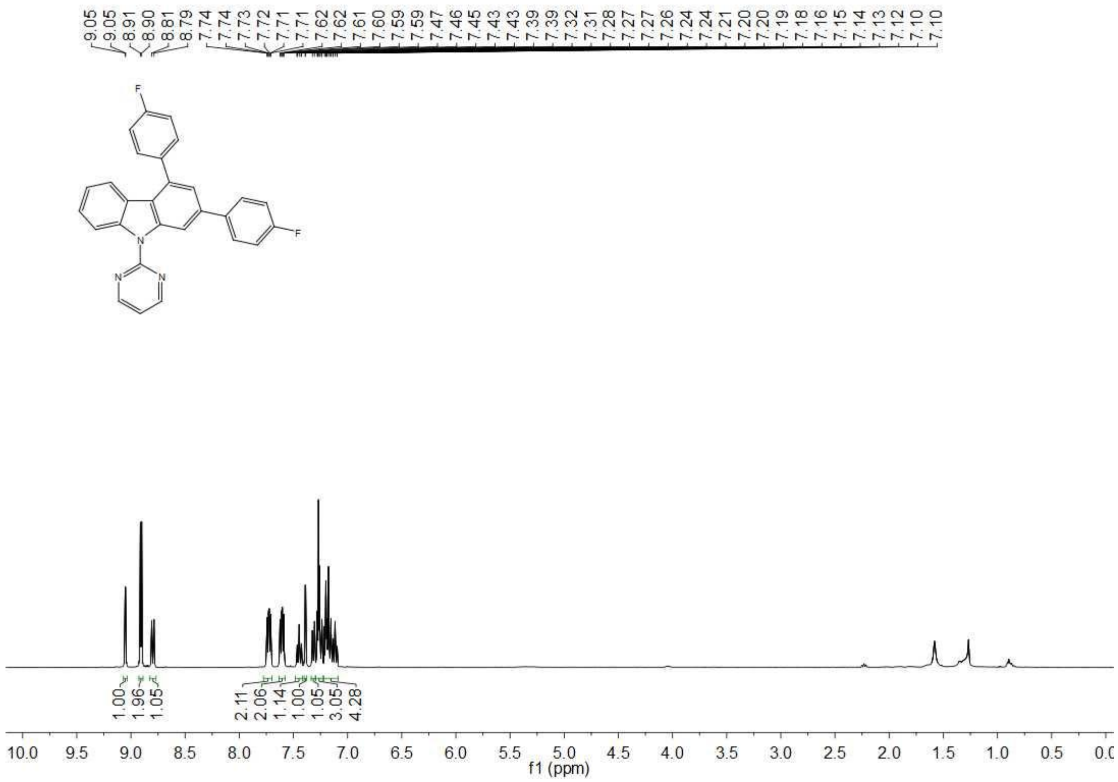

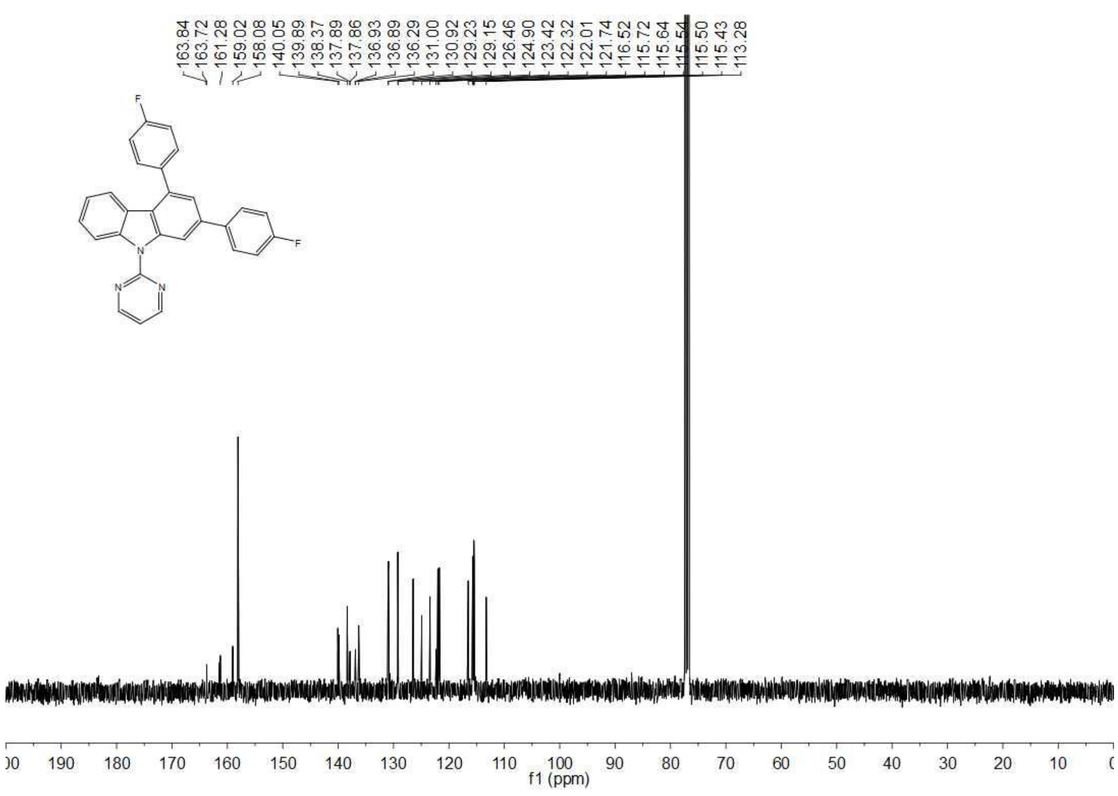

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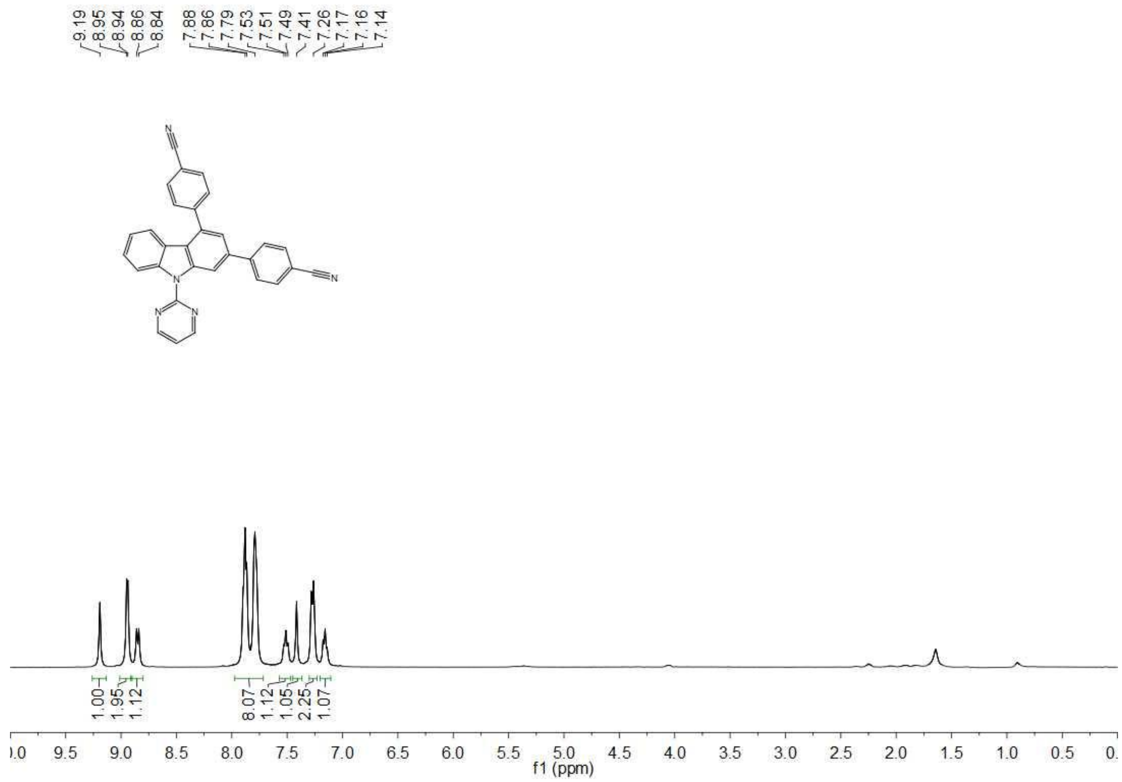
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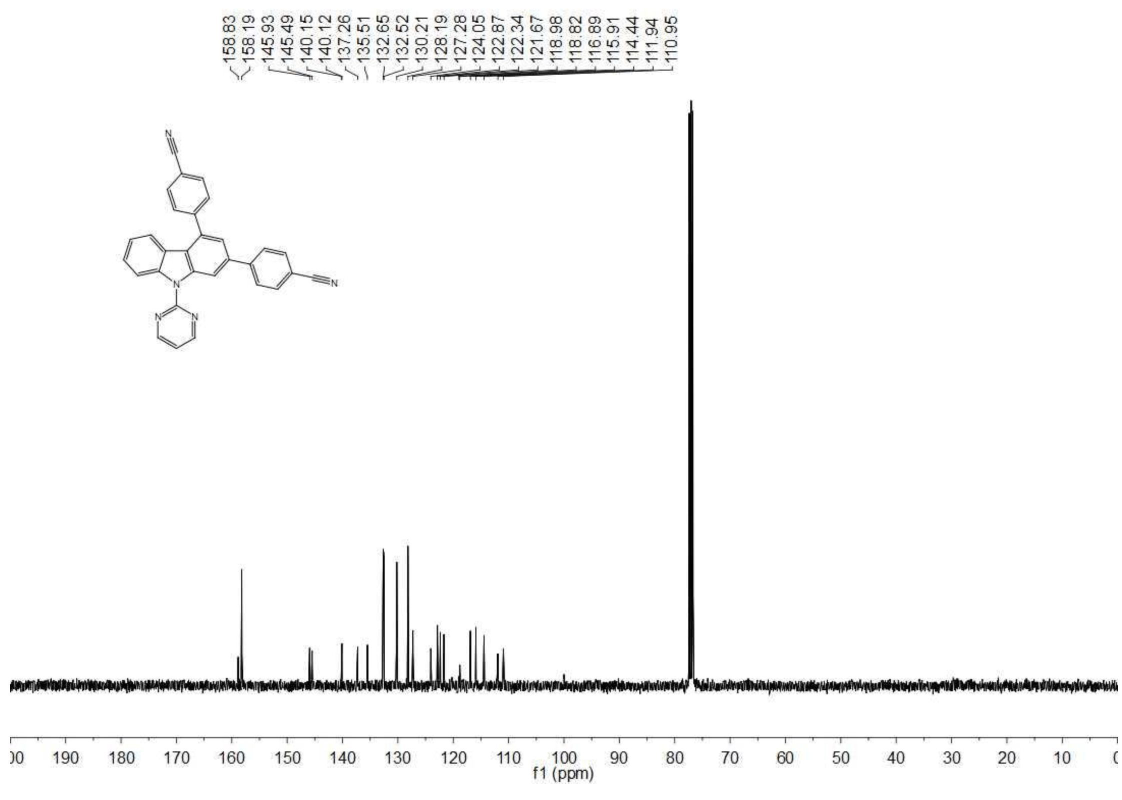
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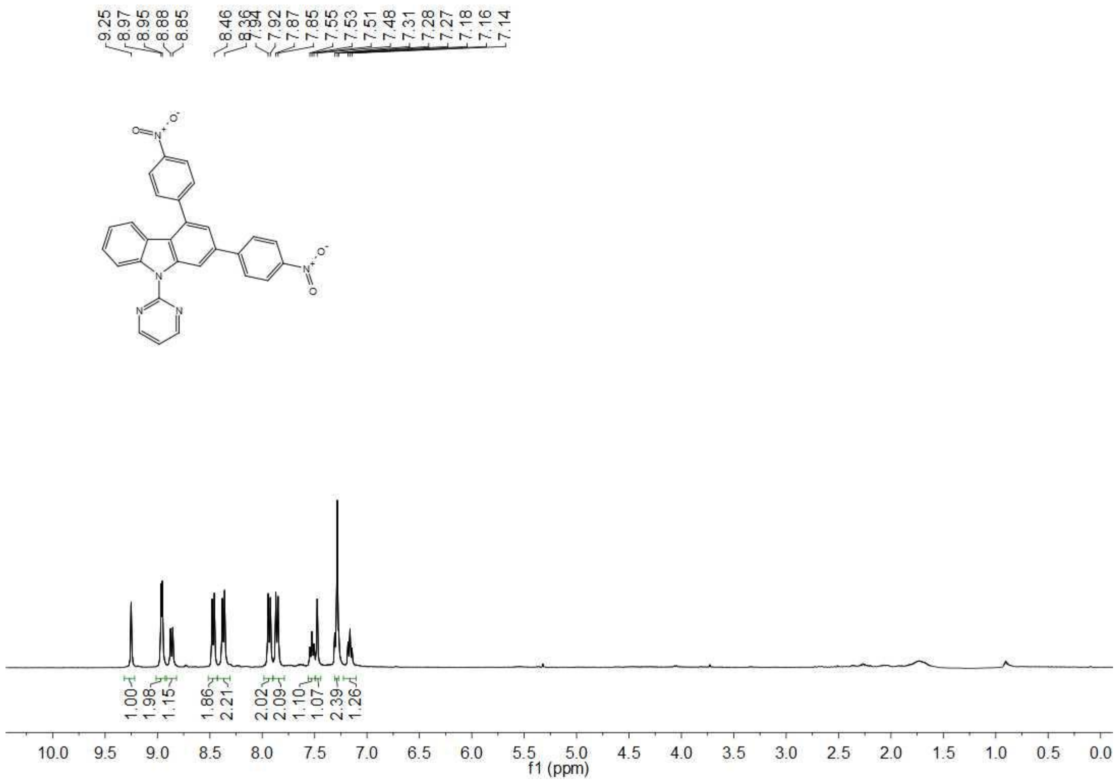
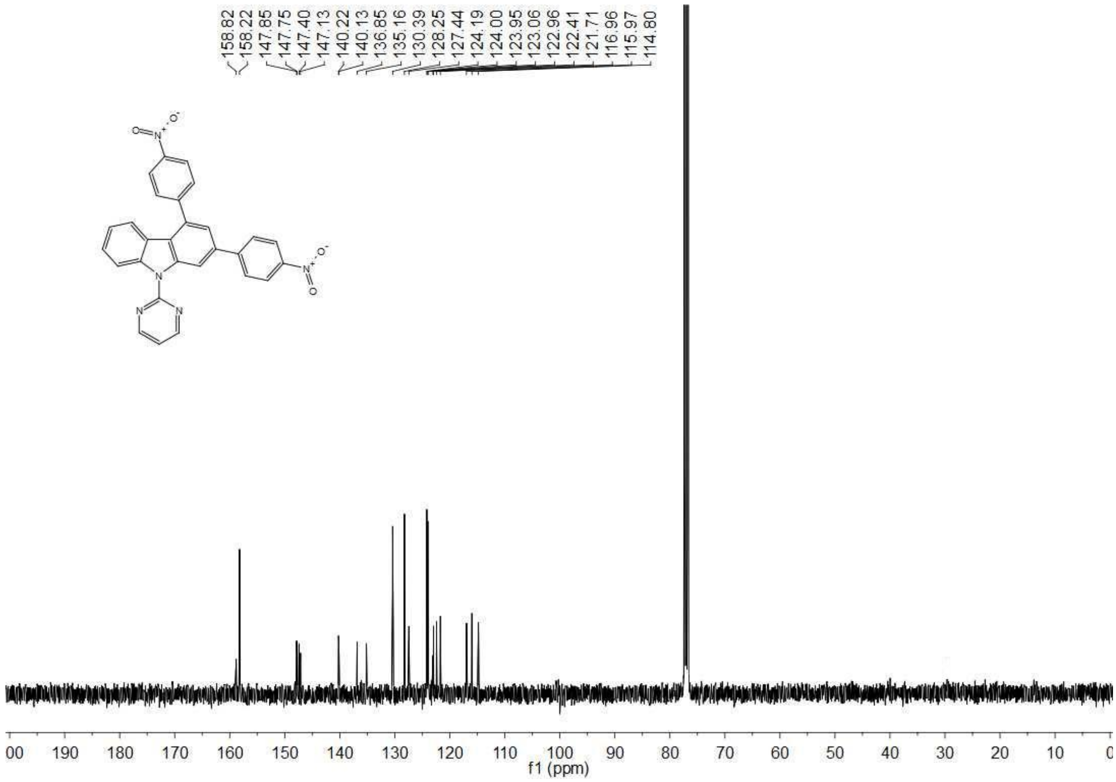
132.52
130.21
128.19
127.28
124.05
122.87
122.34
121.67
118.98
118.82
116.89
115.91
114.44
111.94
110.95
f1 (ppm)

3af



9.25
8.97
8.95
8.88
8.85
8.46
8.36
7.94
7.92
7.87
7.85
7.55
7.53
7.51
7.48
7.31
7.28
7.27
7.18
7.16
7.14
1.00
1.98
1.15
1.86
2.21
2.02
2.09
1.10
1.07
2.39
1.26
10.0 9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0
f1 (ppm)



158.82
158.22
147.85
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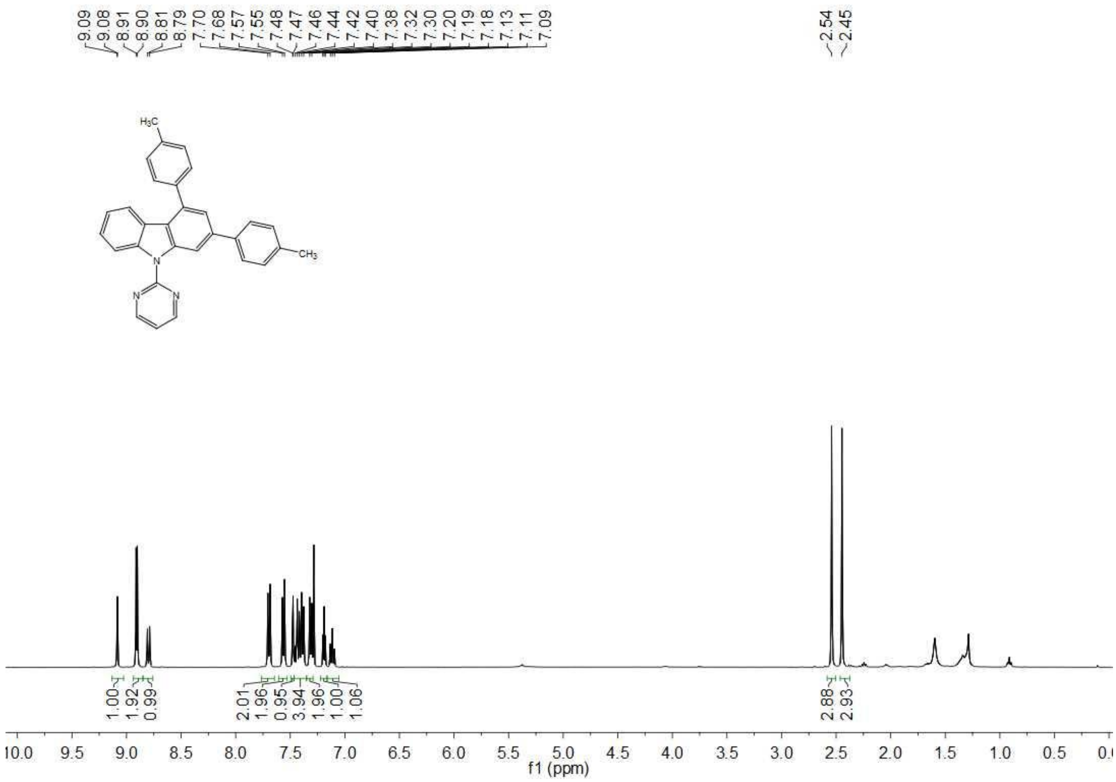
147.40
147.13
140.22
140.13
136.85
135.16
130.39
128.25
127.44
124.19
124.00
123.95
123.06
122.96
122.41
121.71
116.96
115.97
114.80
00 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0
f1 (ppm)

3ag



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9.08
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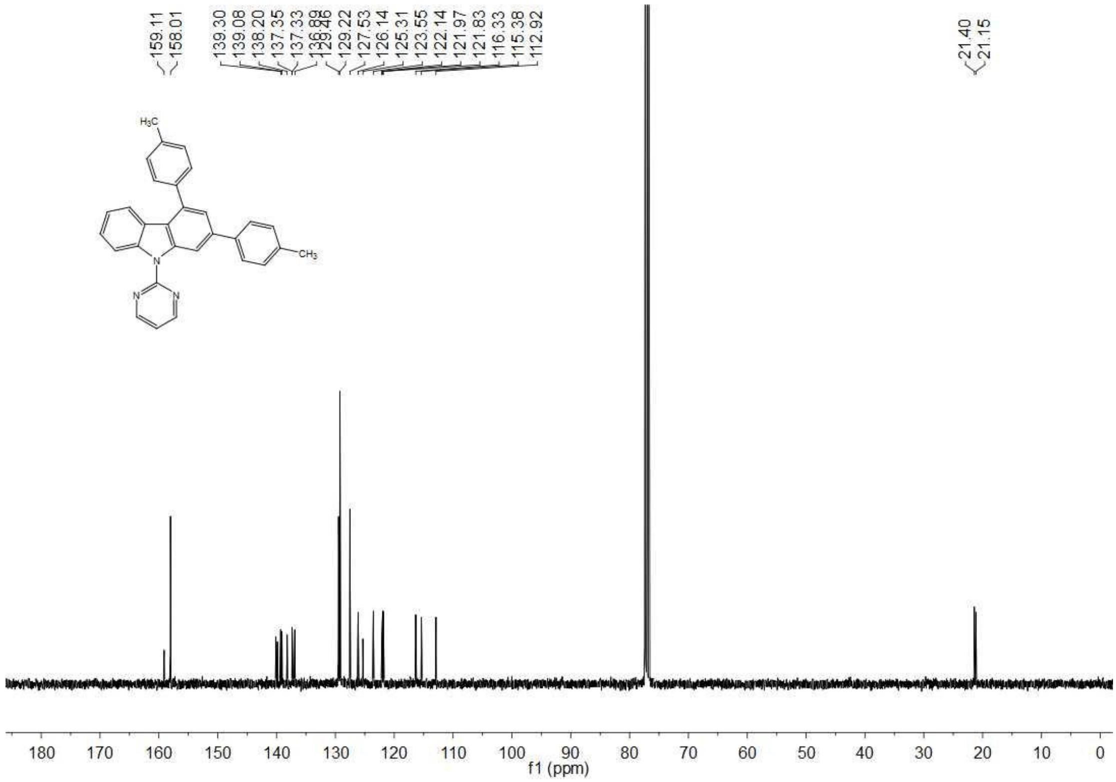
8.79
7.70
7.68
7.57
7.55
7.48
7.47
7.46
7.44
7.42
7.40
7.38
7.32
7.30
7.20
7.19
7.18
7.13
7.11
7.09
2.54
2.45
H3C
CH3
N
1.00
1.92
0.99
2.01
1.96
0.95
3.94
1.96
1.00
1.06
2.88
2.93
10.0 9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5
f1 (ppm)



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158.01
139.30
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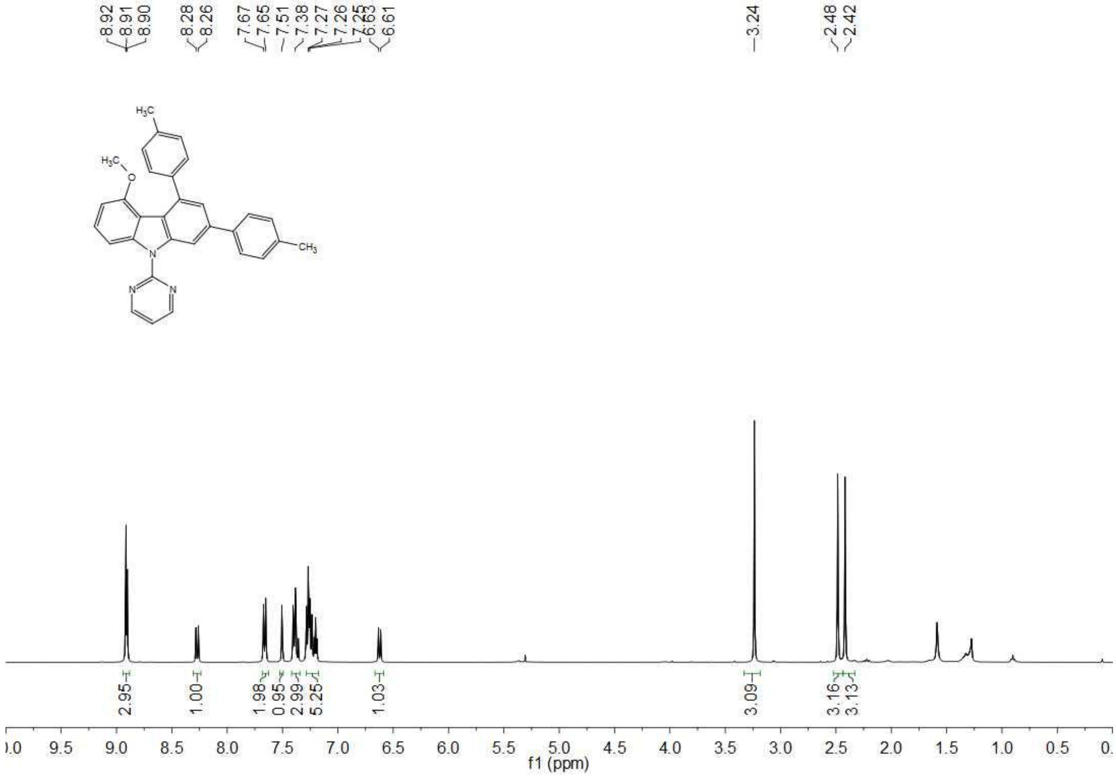
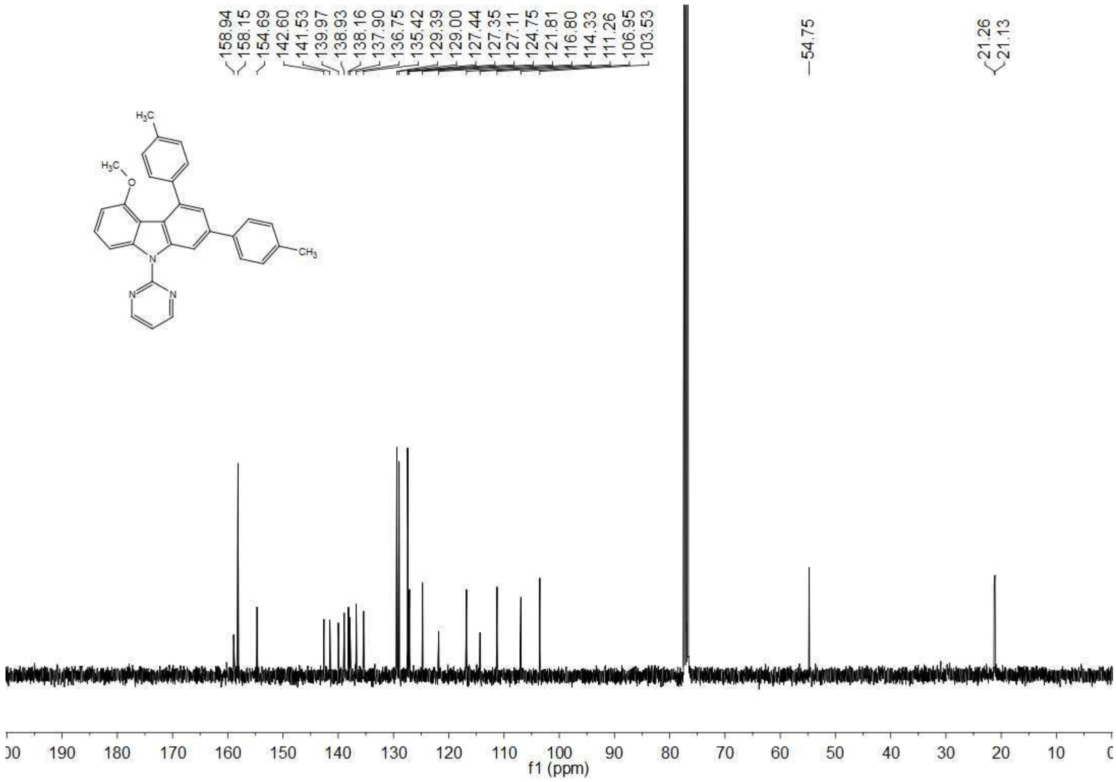
138.20
137.35
137.33
129.22
127.53
126.14
125.31
123.55
122.14
121.97
121.83
116.33
115.38
112.92
21.40
21.15
H3C
CH3
N
180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0
f1 (ppm)

3ah


8.92
8.91
8.90
8.28
8.26
7.67
7.65
7.51
7.38
7.27
7.26
7.25
6.63
6.61
3.24
2.48
2.42
H3C
H3C
O
N
N
N
CH3
2.95
1.00
1.98
0.95
2.99
5.25
1.03
3.09
3.16
3.13
f1 (ppm)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158.15
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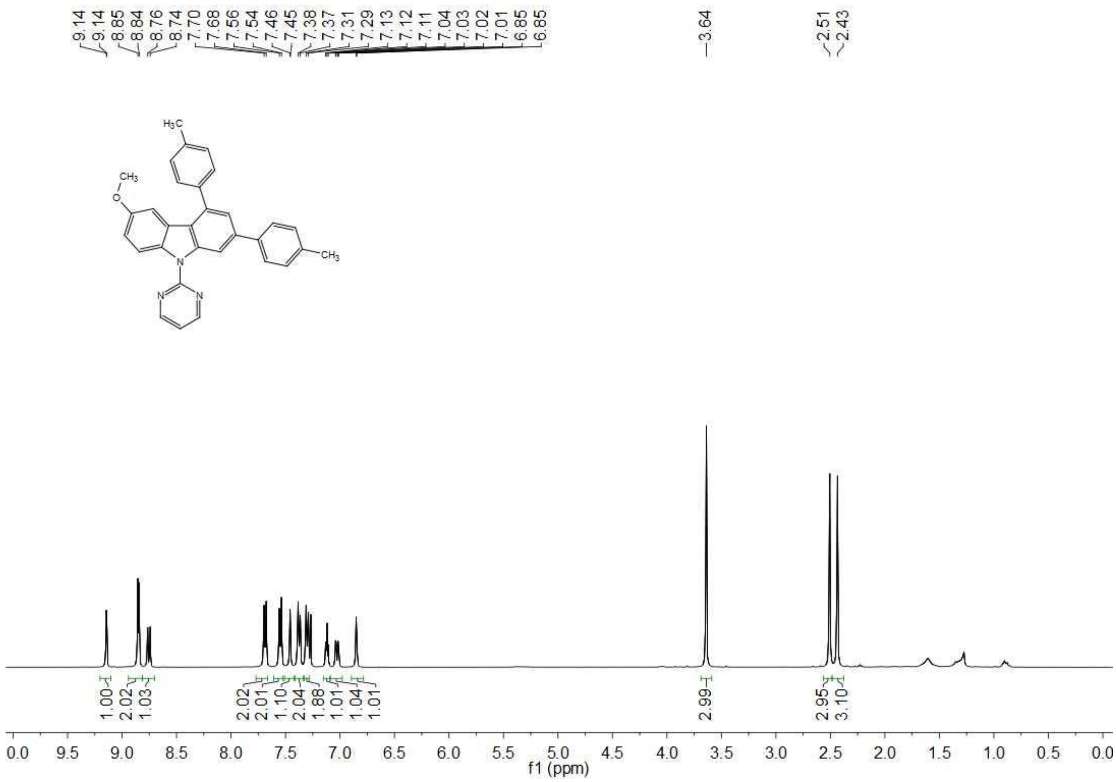
142.60
141.53
139.97
138.93
138.16
137.90
136.75
135.42
129.39
129.00
127.44
127.35
127.11
124.75
121.81
116.80
114.33
111.26
106.95
103.53
54.75
21.26
21.13
H3C
H3C
O
N
N
N
CH3
f1 (ppm)

3ai


9.14
9.14
8.85
8.84
8.76
8.74
7.70
7.68
7.56
7.54
7.46
7.45
7.38
7.37
7.31
7.29
7.13
7.12
7.11
7.04
7.03
7.02
7.01
6.85
6.85
3.64
2.51
2.43
1.00
2.02
1.03
2.02
2.01
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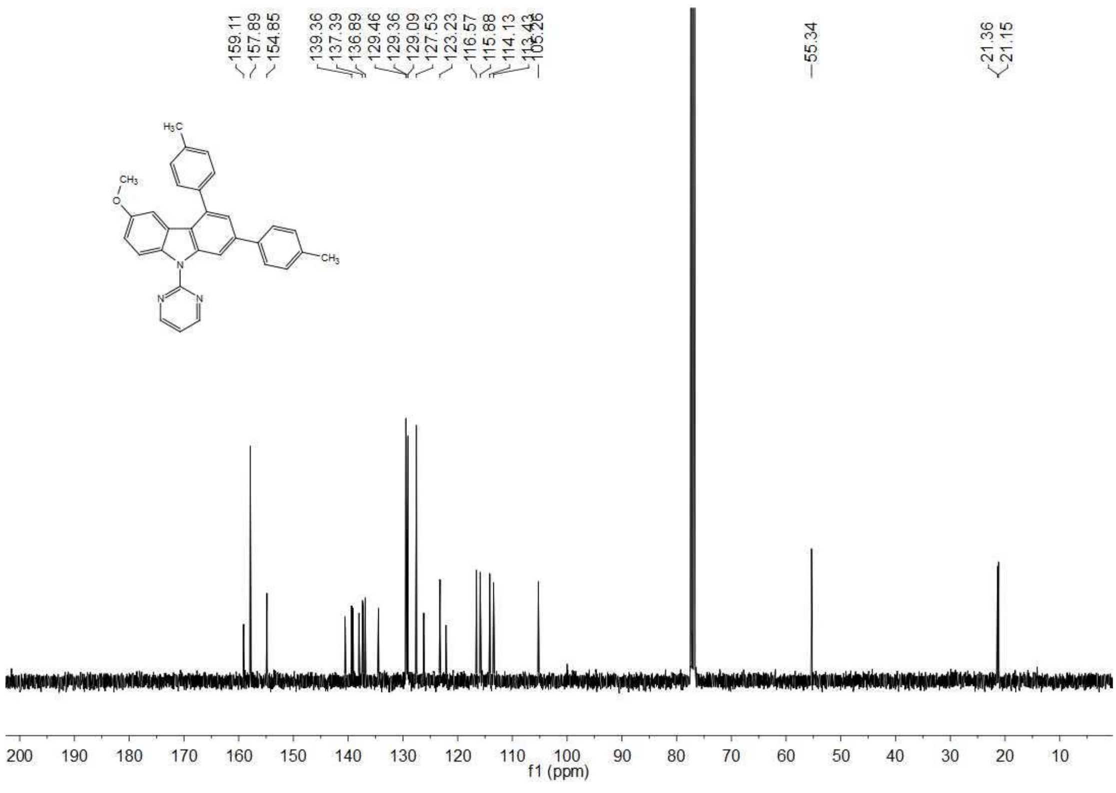
2.04
1.88
1.01
1.04
1.01
2.99
2.95
3.10
f1 (ppm)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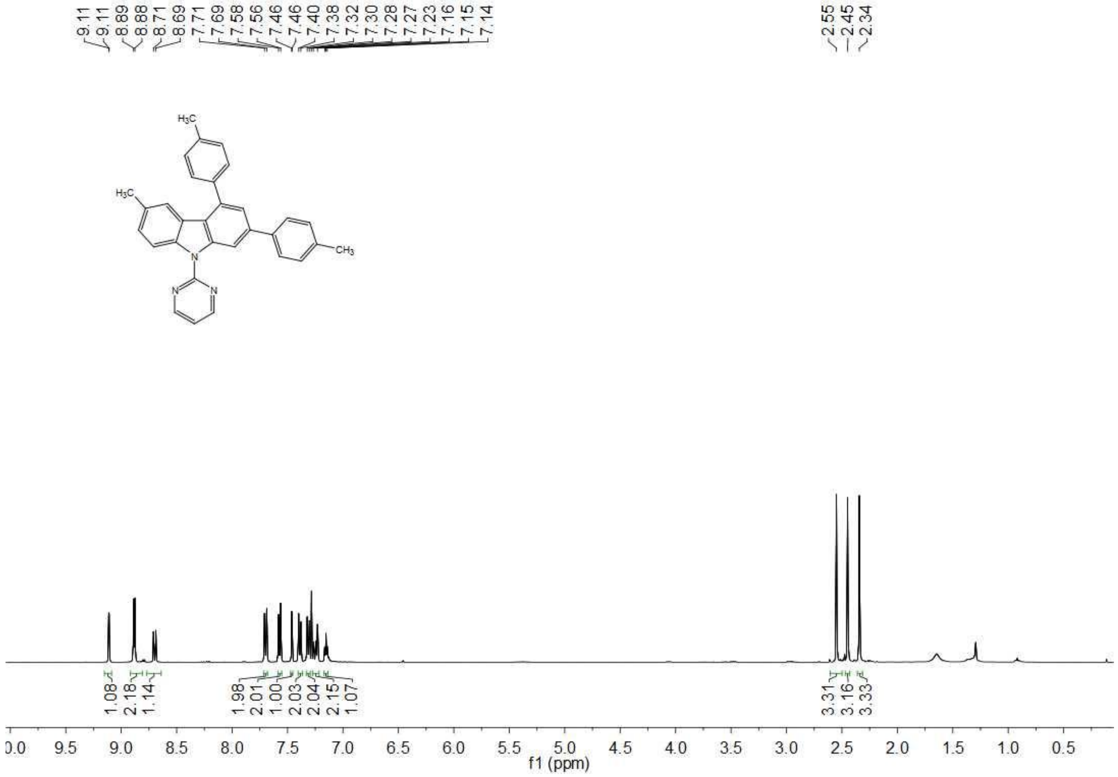
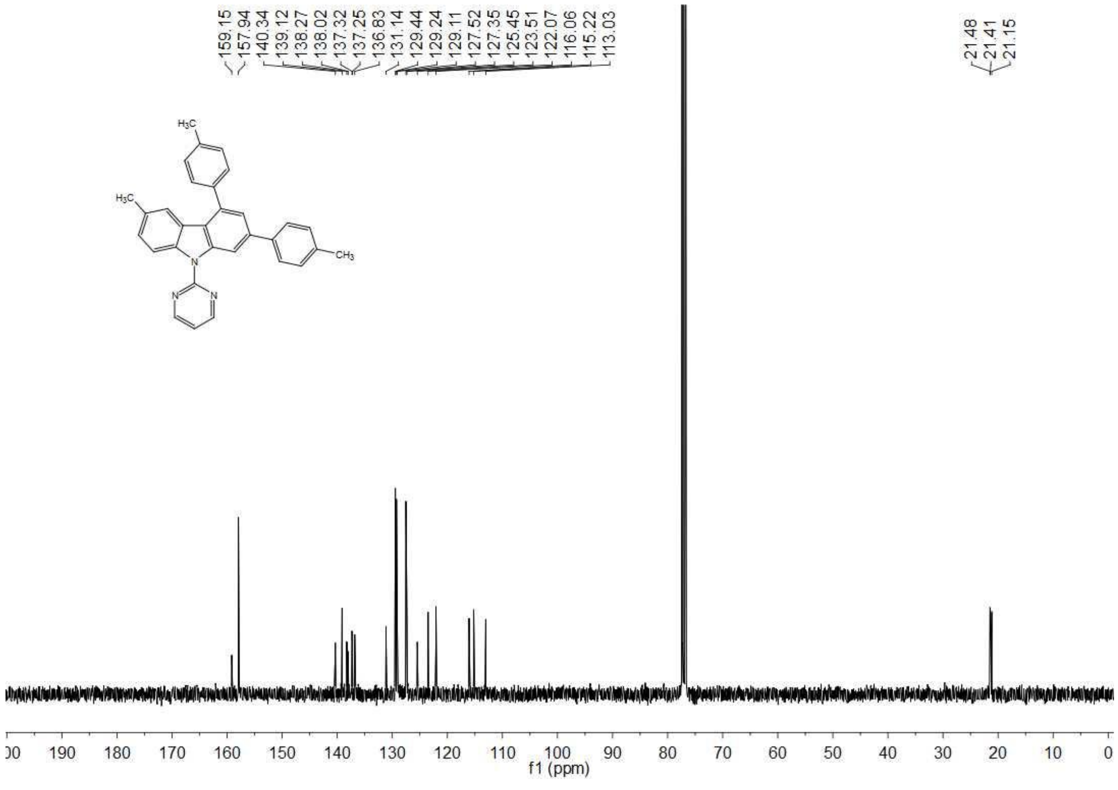
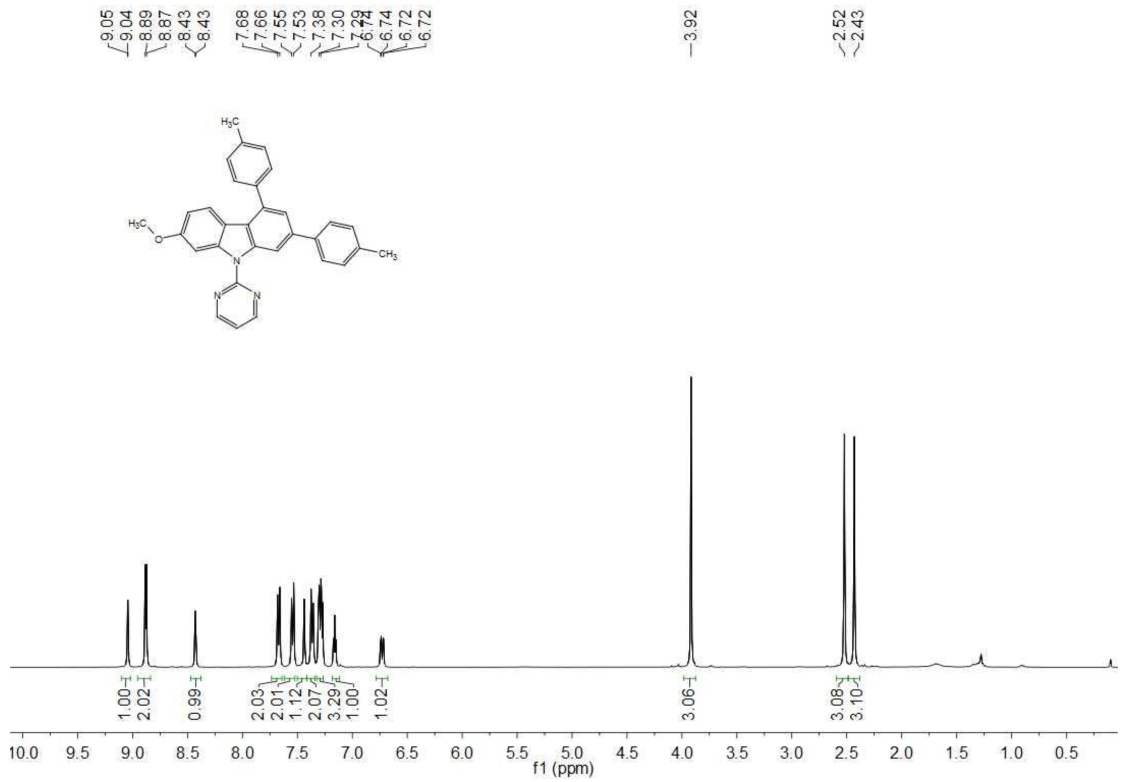
157.89
154.85
139.36
137.39
136.89
129.46
129.36
129.09
127.53
123.23
116.57
115.88
114.13
113.43
105.26
55.34
21.36
21.15
f1 (ppm)

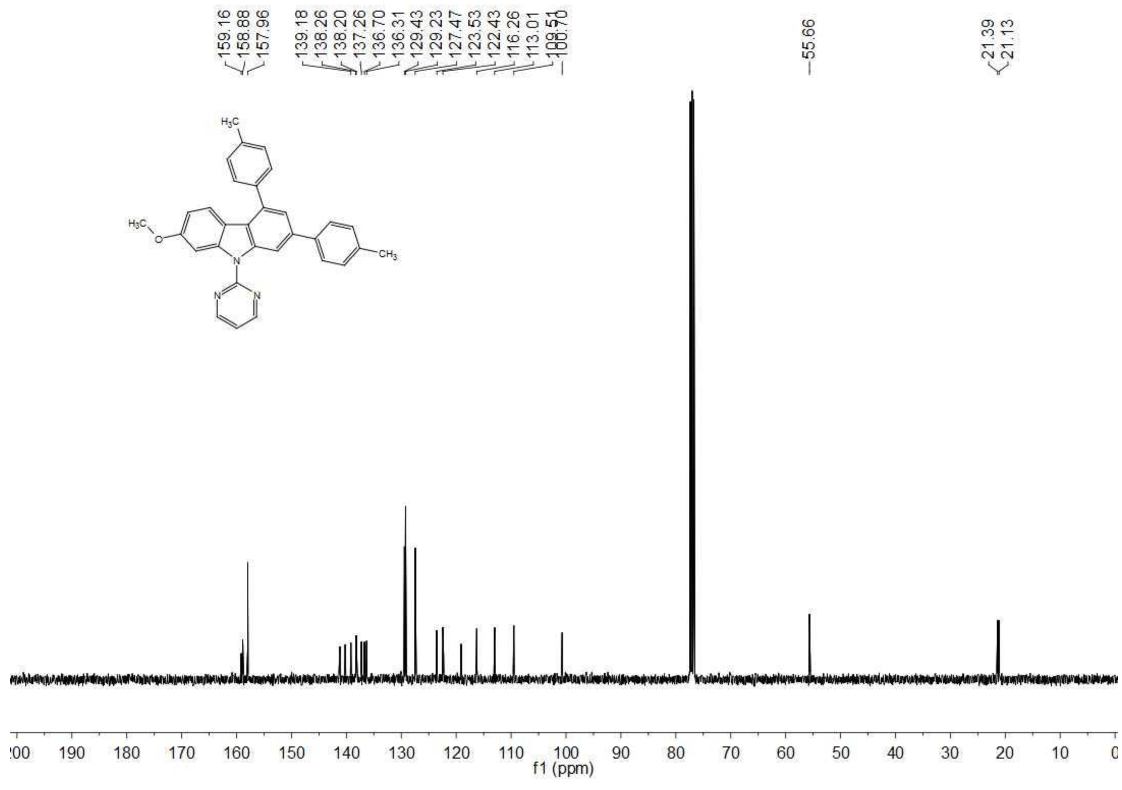
3aj





3ak


9.05
9.04
8.89
8.87
8.43
8.43
7.68
7.66
7.55
7.53
7.38
7.30
6.74
6.74
6.72
6.72
3.92
2.52
2.43
1.00
2.02
0.99
2.03
2.01
1.12
2.07
3.29
1.00
1.02
3.06
3.08
3.10
f1 (ppm)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158.88
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138.20
137.26
136.70
136.31
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129.23
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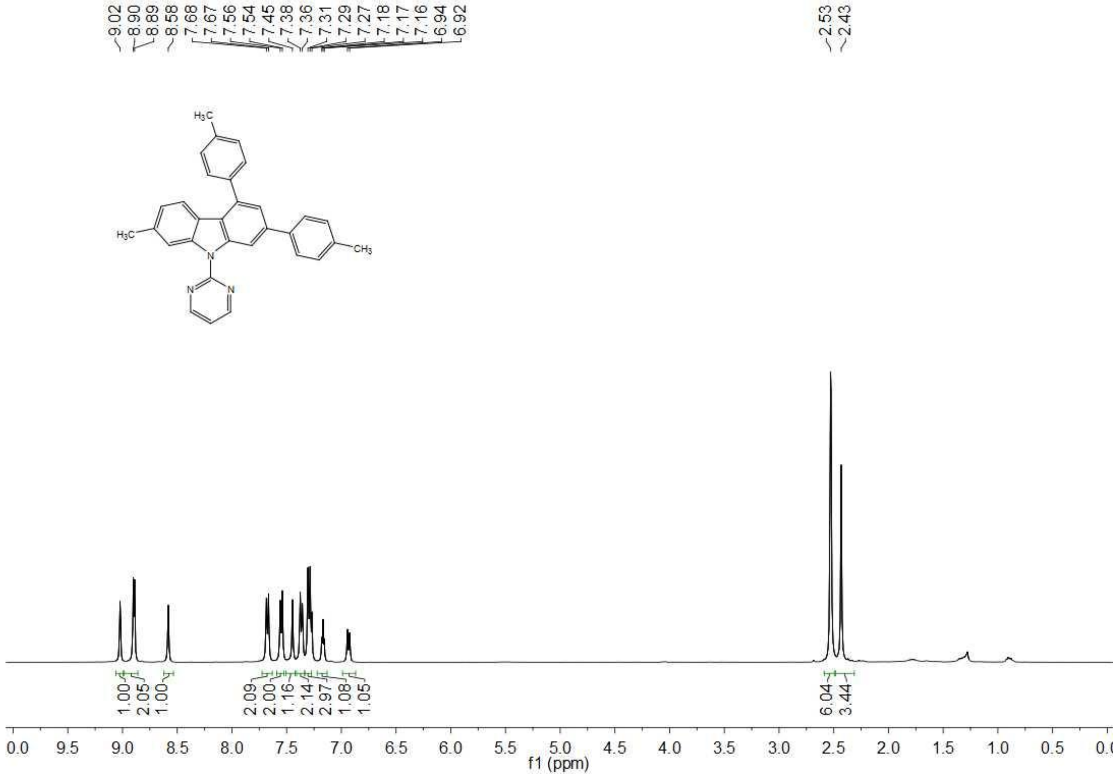
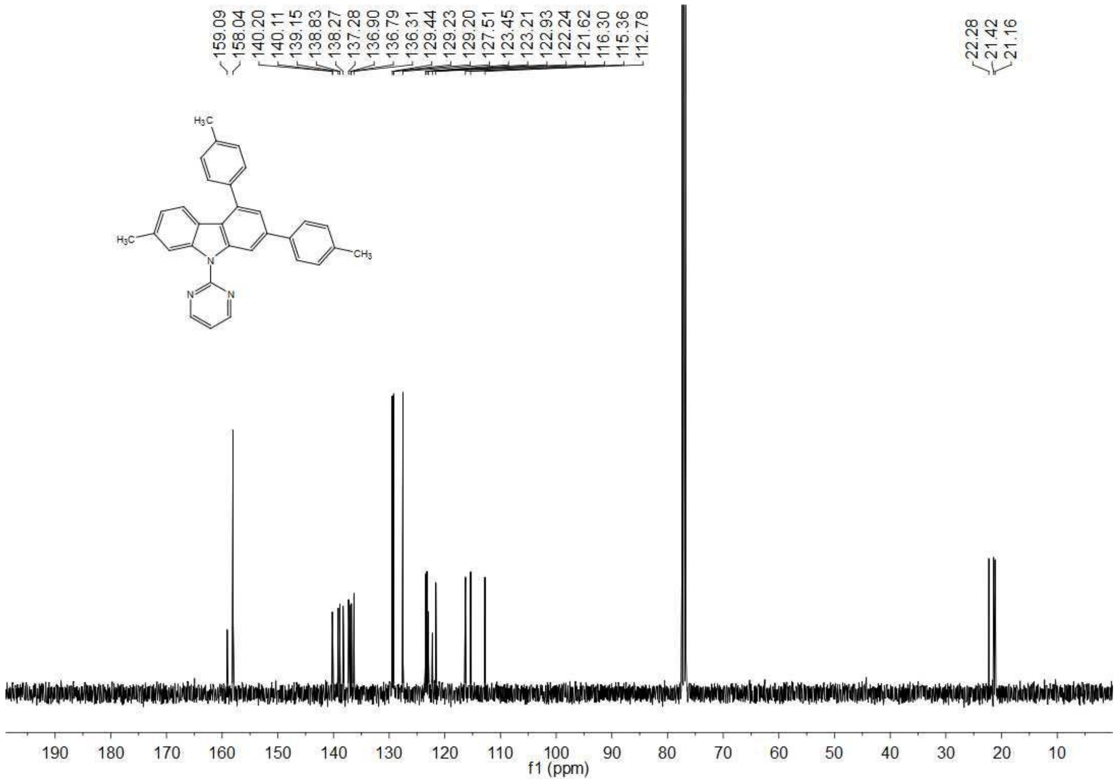
123.53
122.43
116.26
113.01
55.66
21.39
21.13
f1 (ppm)

3al


9.02
8.90
8.89
8.58
7.68
7.67
7.56
7.54
7.45
7.38
7.36
7.31
7.29
7.27
7.18
7.17
7.16
6.94
6.92
2.53
2.43
1.00
2.05
1.00
2.09
2.00
1.16
2.14
2.97
1.08
1.05
6.04
3.44
f1 (ppm)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158.04
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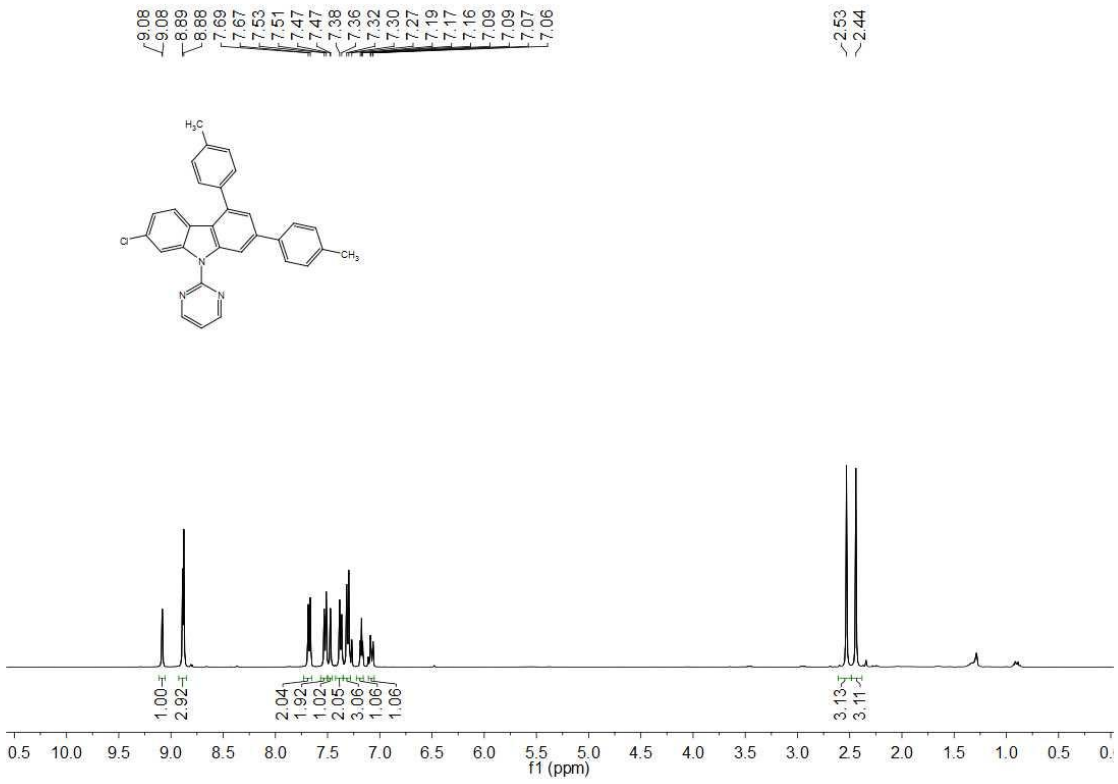
140.11
139.15
138.83
138.27
137.28
136.90
136.79
136.31
129.44
129.23
129.20
127.51
123.45
123.21
122.93
122.24
121.62
116.30
115.36
112.78
22.28
21.42
21.16
f1 (ppm)

3am



9.08
9.08
8.89
8.88
7.69
7.67
7.53
7.51
7.47
7.47
7.38
7.36
7.32
7.30
7.27
7.19
7.17
7.16
7.09
7.09
7.07
7.06
2.53
2.44
H3C
Cl
N
N
N
CH3
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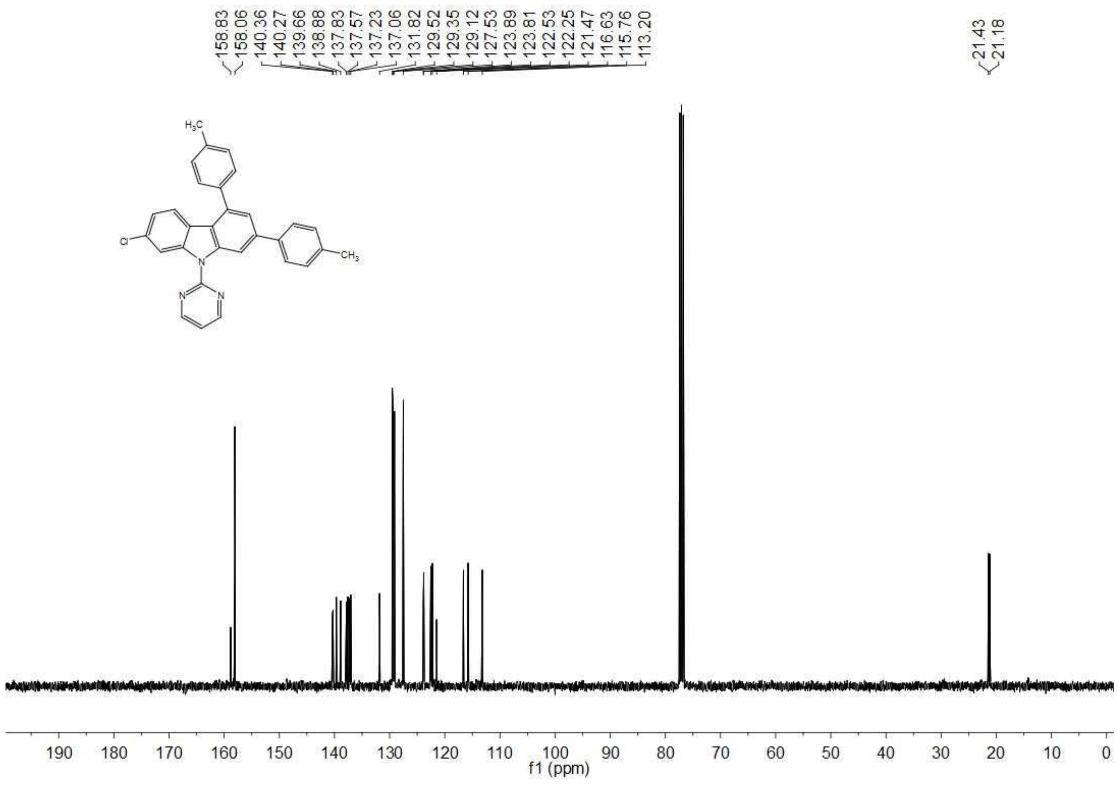
3.13
3.11
f1 (ppm)



158.83
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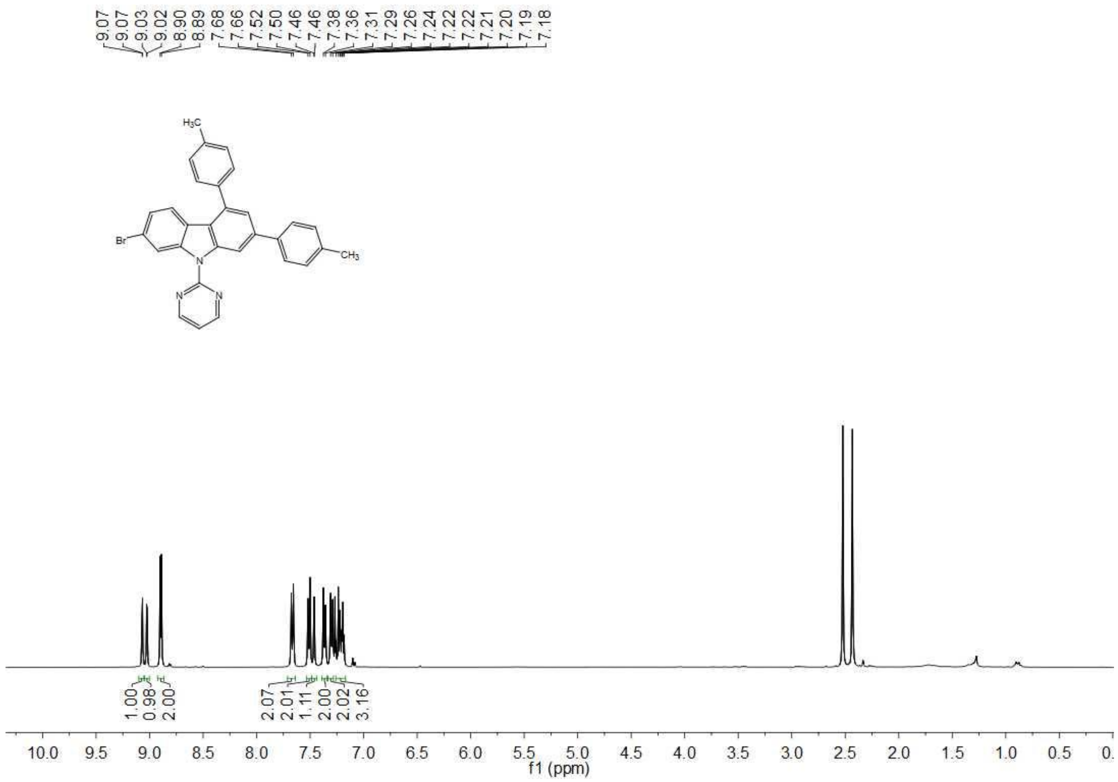
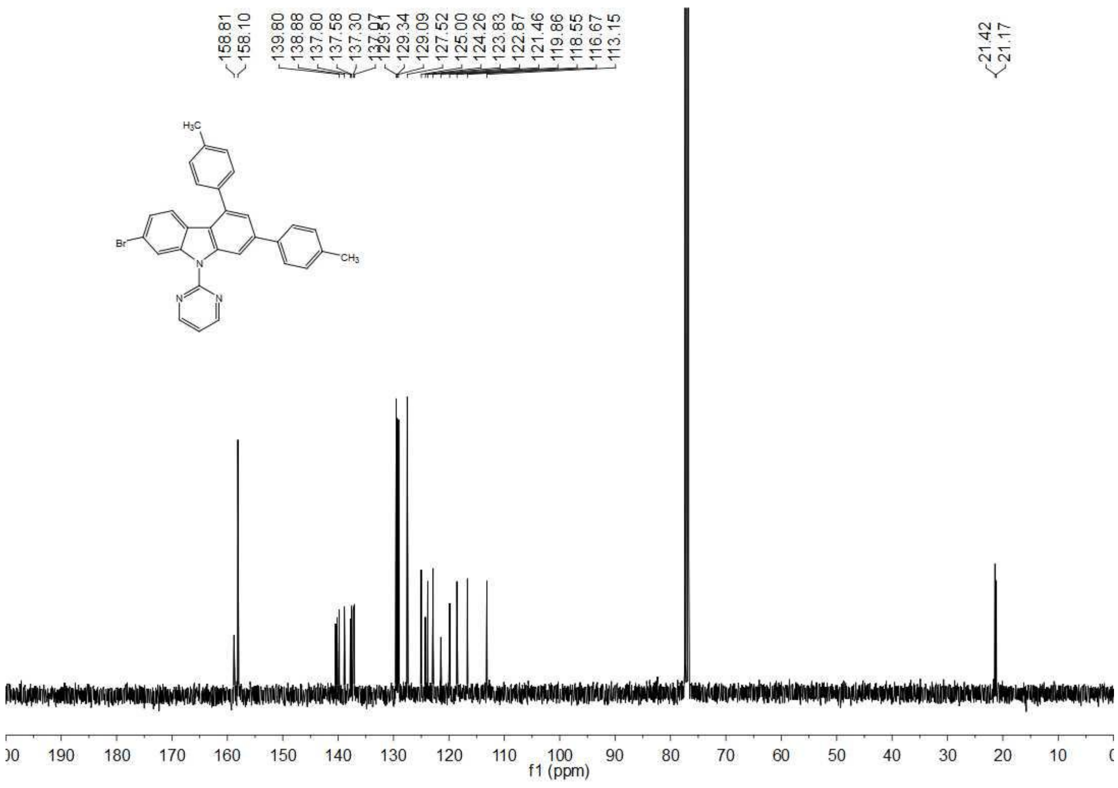
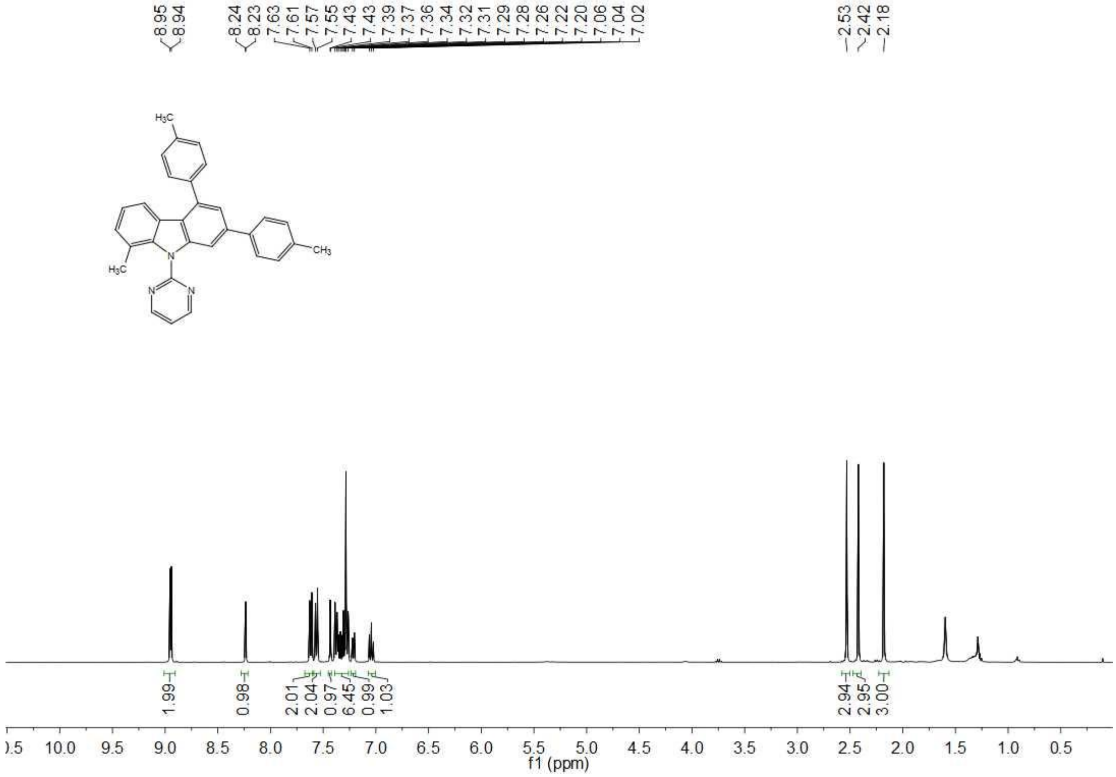
138.88
137.83
137.57
137.23
137.06
131.82
129.52
129.35
129.12
127.53
123.89
123.81
122.53
122.25
121.47
116.63
115.76
113.20
21.43
21.18
H3C
Cl
N
N
N
CH3
f1 (ppm)

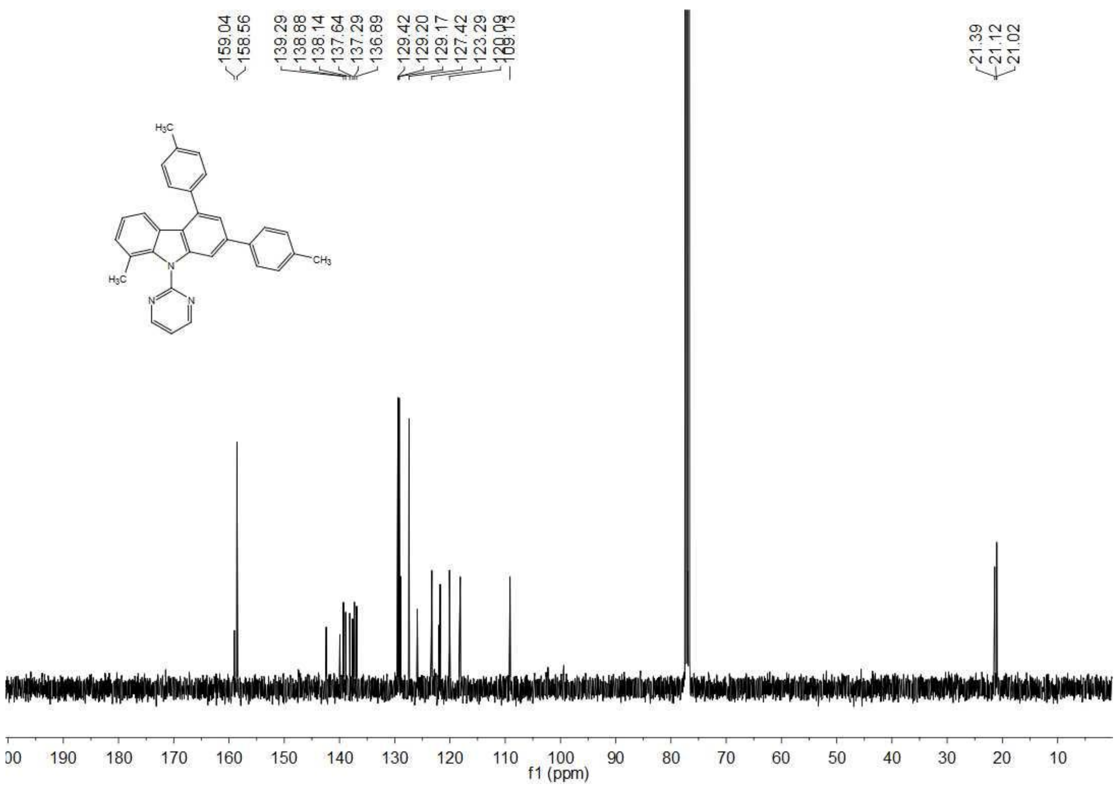
3an





3ao





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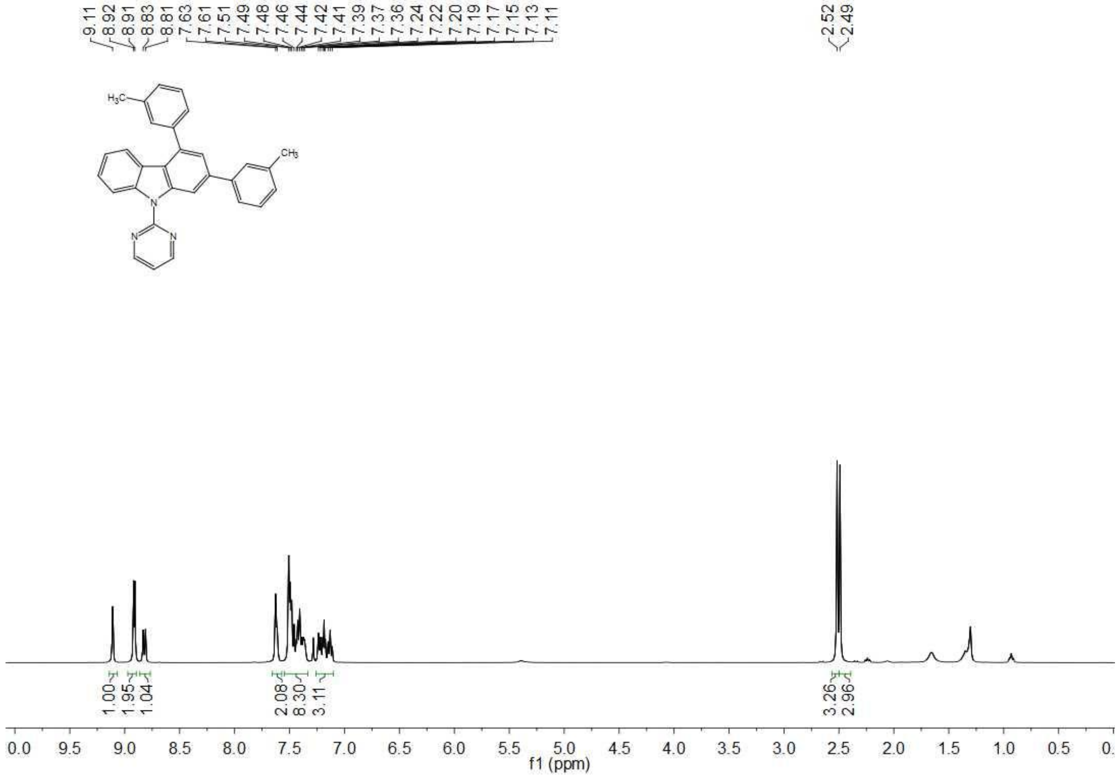
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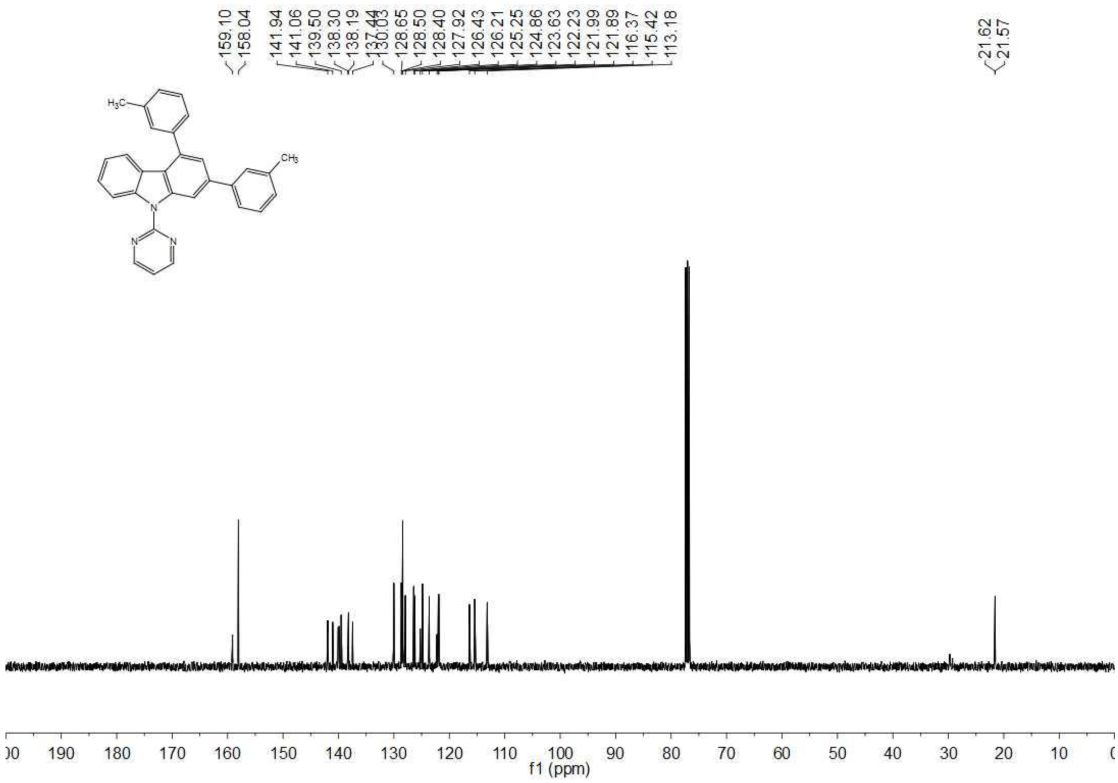
8.92
8.91
8.83
8.81
7.63
7.61
7.51
7.49
7.48
7.46
7.44
7.42
7.41
7.39
7.37
7.36
7.24
7.22
7.20
7.19
7.17
7.15
7.13
7.11
2.52
2.49
H_3C
CH_3
N
N
N
1.00
1.95
1.04
2.08
8.30
3.11
3.26
2.96
f1 (ppm)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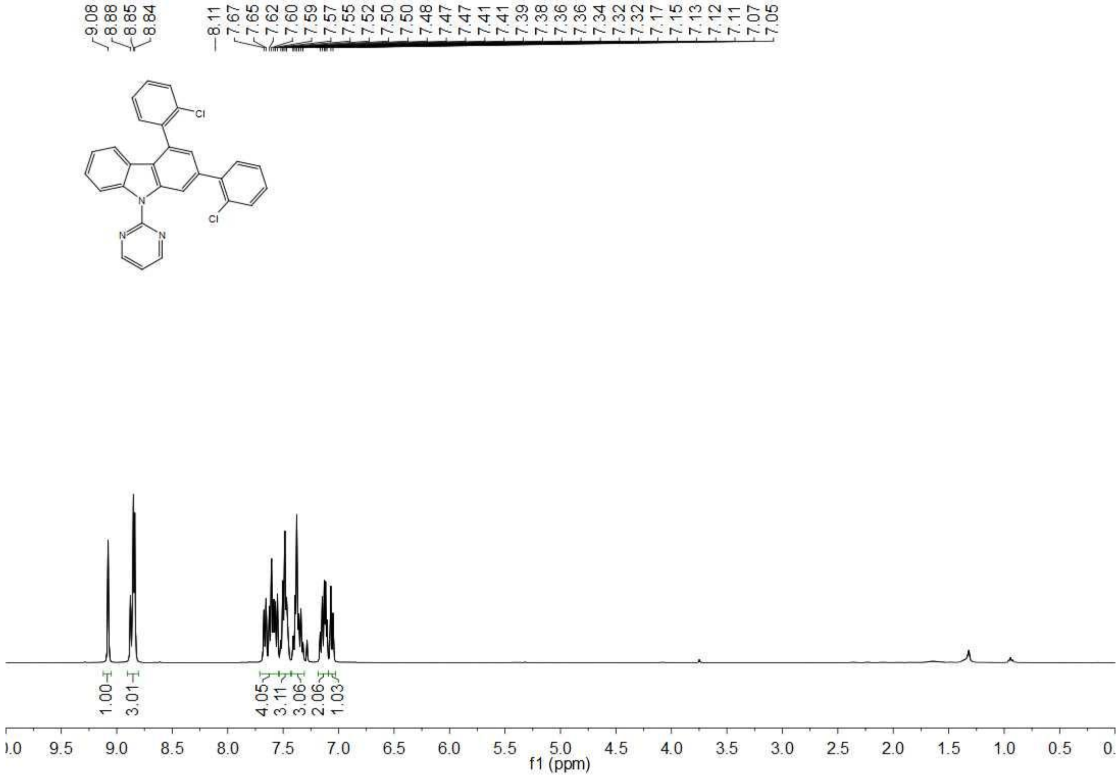
138.30
138.19
128.65
128.50
128.40
127.92
126.43
126.21
125.25
124.86
123.63
122.23
121.99
121.89
116.37
115.42
113.18
21.62
21.57
H_3C
CH_3
N
N
N
f1 (ppm)

3aq



9.08
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7.67
7.65
7.62
7.60
7.59
7.57
7.55
7.52
7.50
7.50
7.48
7.47
7.47
7.41
7.41
7.39
7.38
7.36
7.36
7.34
7.32
7.32
7.17
7.15
7.13
7.12
7.11
7.07
7.05
Cl
Cl
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N
N
1.00
3.01
4.05
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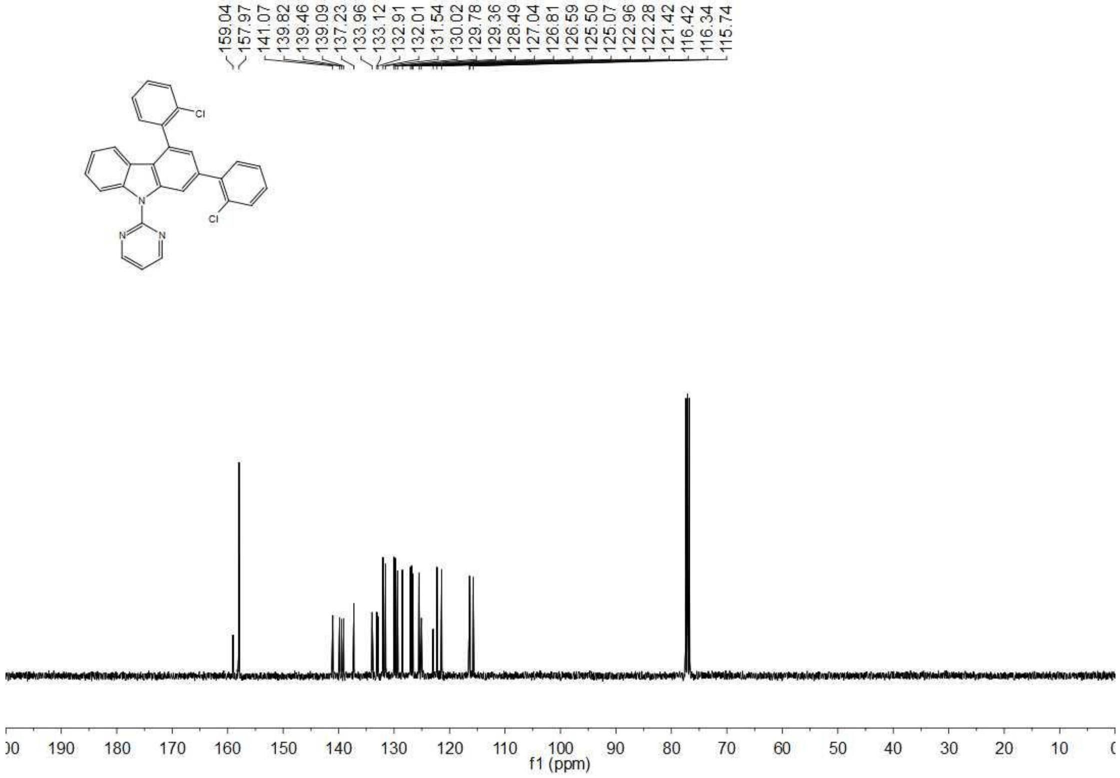
3.06
2.06
1.03
f1 (ppm)



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139.09
137.23
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132.91
132.01
131.54
130.02
129.78
129.36
128.49
127.04
126.81
126.59
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125.07
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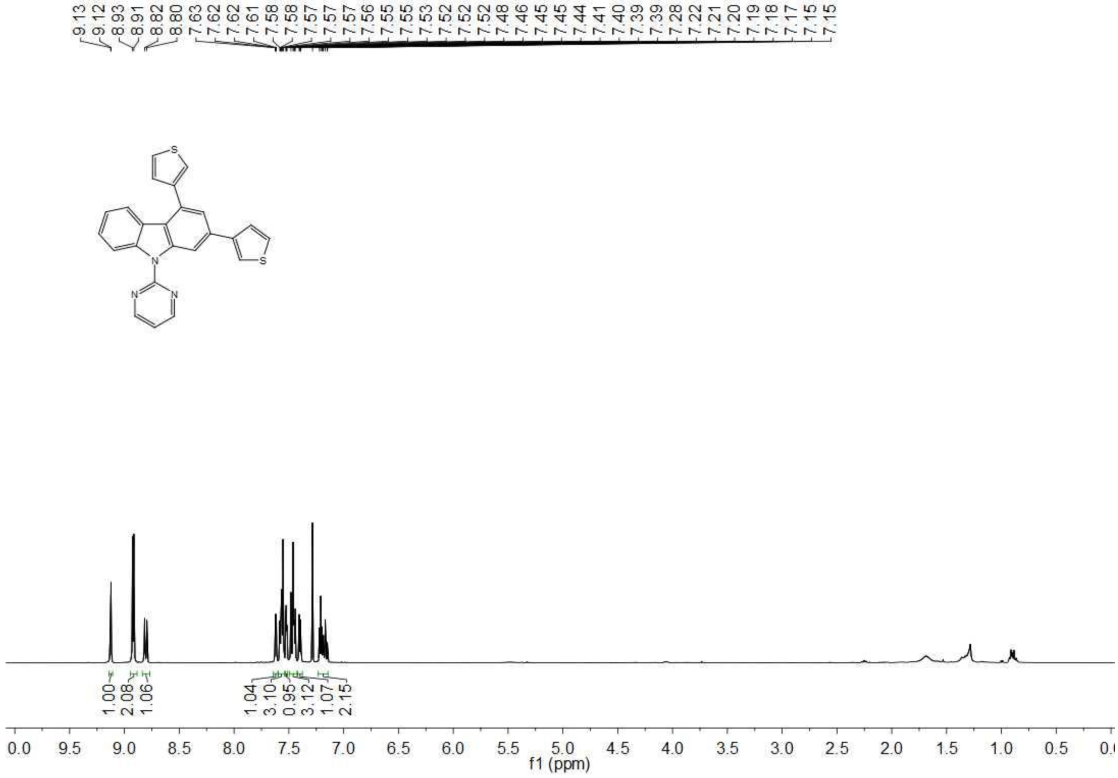
122.28
121.42
116.34
115.74
Cl
Cl
N
N
N
f1 (ppm)

3ar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7.57
7.57
7.56
7.55
7.55
7.53
7.52
7.52
7.52
7.48
7.46
7.45
7.45
7.44
7.41
7.40
7.39
7.39
7.28
7.22
7.21
7.20
7.19
7.18
7.17
7.15
7.15
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2.08
1.06
1.04
3.10
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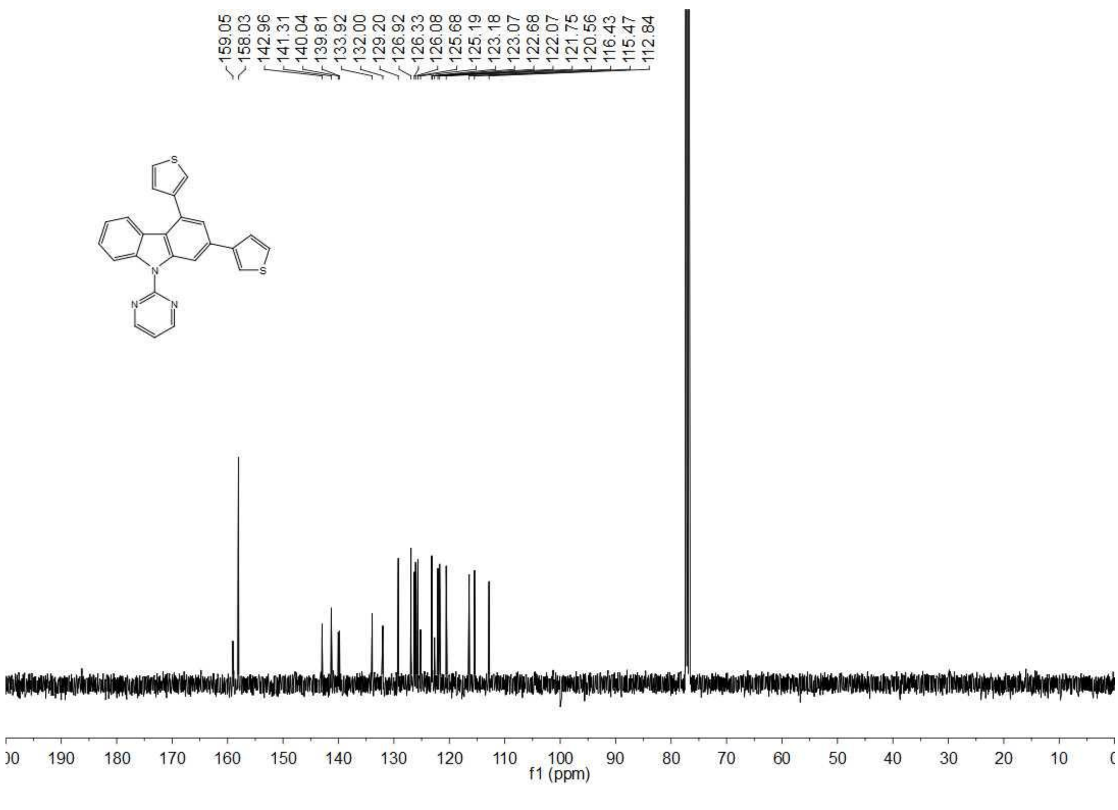
3.12
1.07
2.15
f1 (ppm)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132.00
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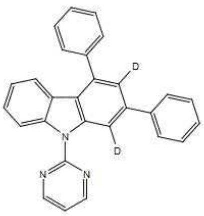
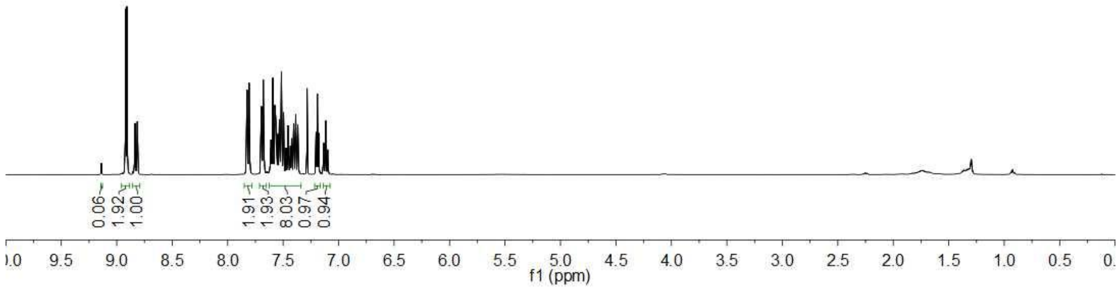
126.92
126.33
126.08
125.68
125.19
123.18
123.07
122.68
122.07
121.75
120.56
116.43
115.47
112.84
f1 (ppm)

3as


D
D
N
N
N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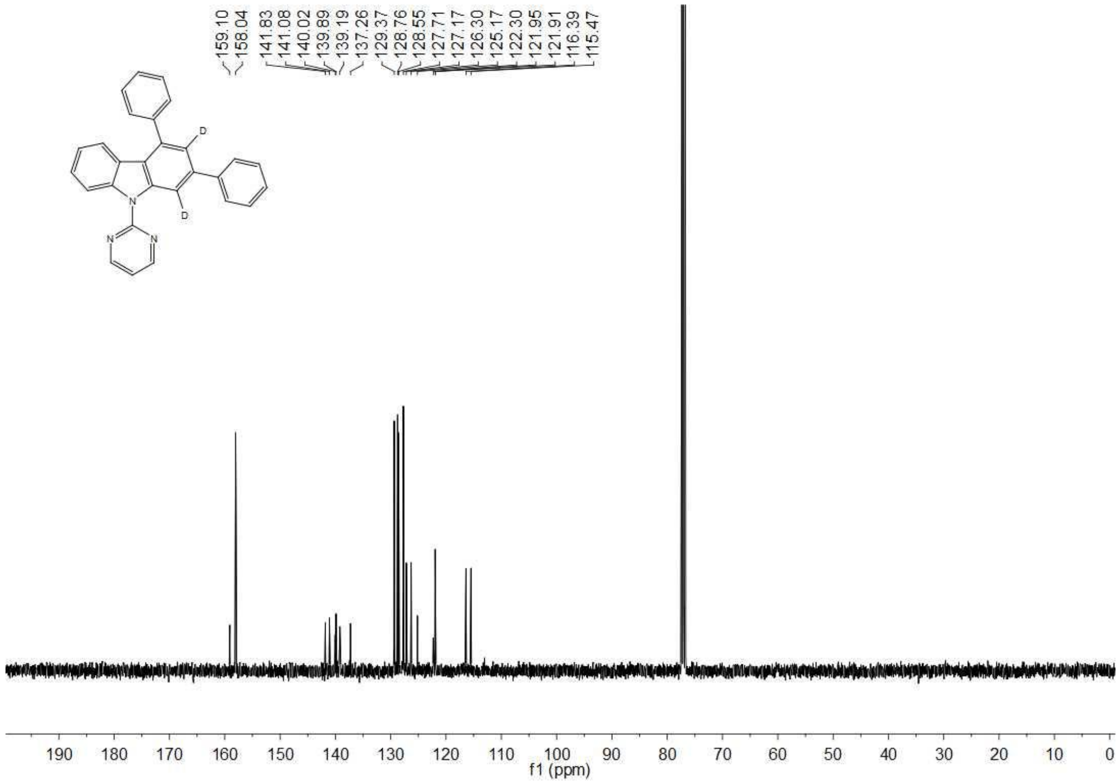
0.94
f1 (ppm)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158.04
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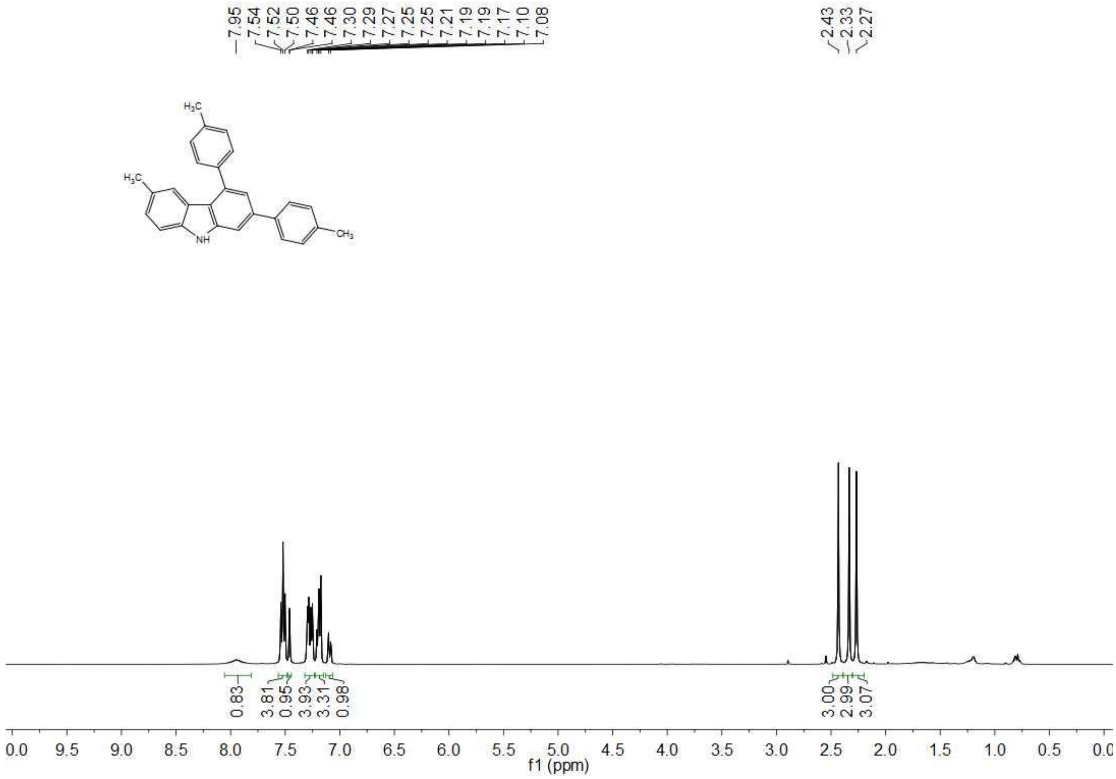
139.89
139.19
137.26
129.37
128.76
128.55
127.71
127.17
126.30
125.17
122.30
121.95
121.91
116.39
115.47
D
D
N
N
N
f1 (ppm)

4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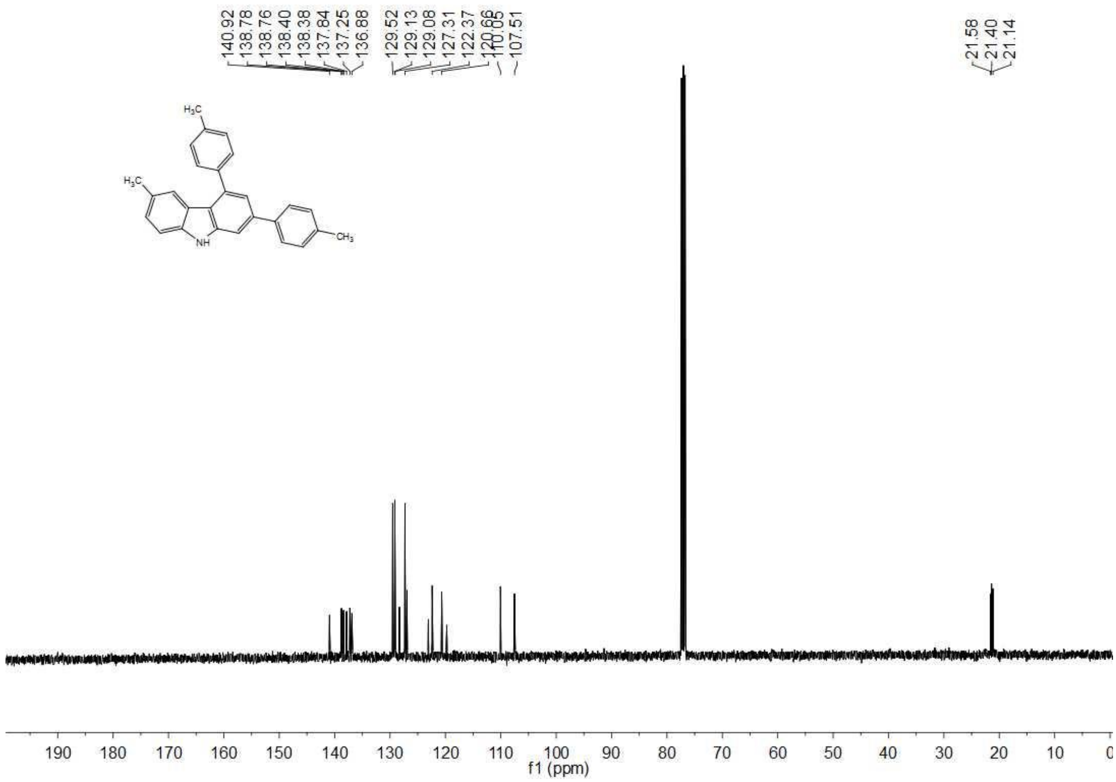
7.30
7.29
7.27
7.25
7.25
7.21
7.19
7.19
7.17
7.10
7.08
2.43
2.33
2.27
0.83
3.81
0.95
3.93
3.31
0.98
3.00
2.99
3.07
f1 (ppm)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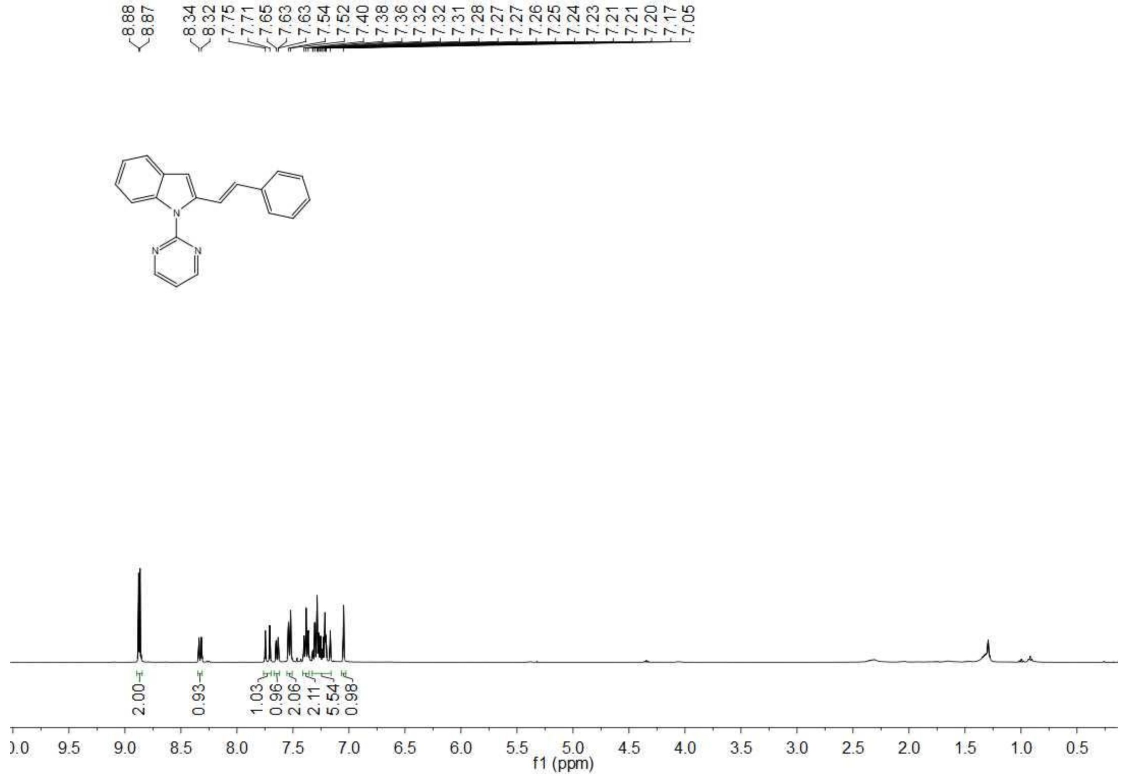
138.38
137.84
137.25
136.88
129.52
129.13
129.08
127.31
122.37
120.66
110.05
107.51
21.58
21.40
21.14
f1 (ppm)

5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7.71
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7.63
7.63
7.54
7.52
7.40
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7.36
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7.31
7.28
7.27
7.27
7.26
7.25
7.24
7.23
7.21
7.21
7.20
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2.11
5.54
0.98
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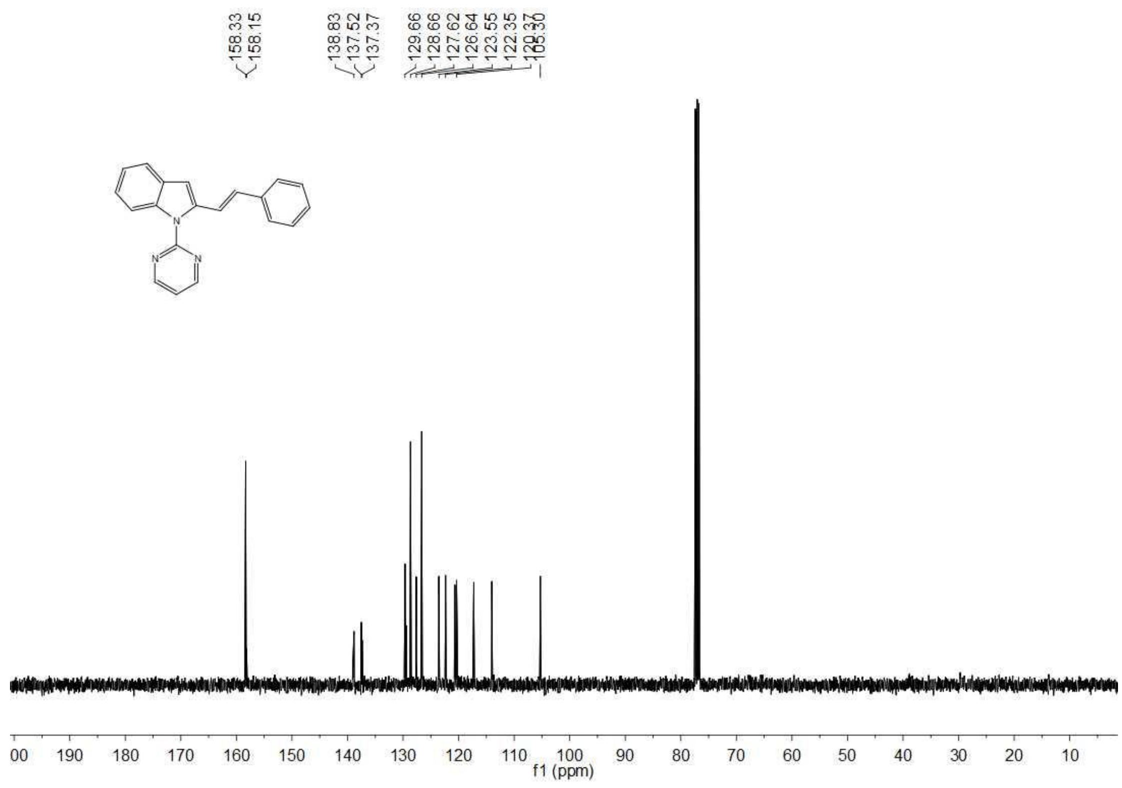
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127.62
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123.55
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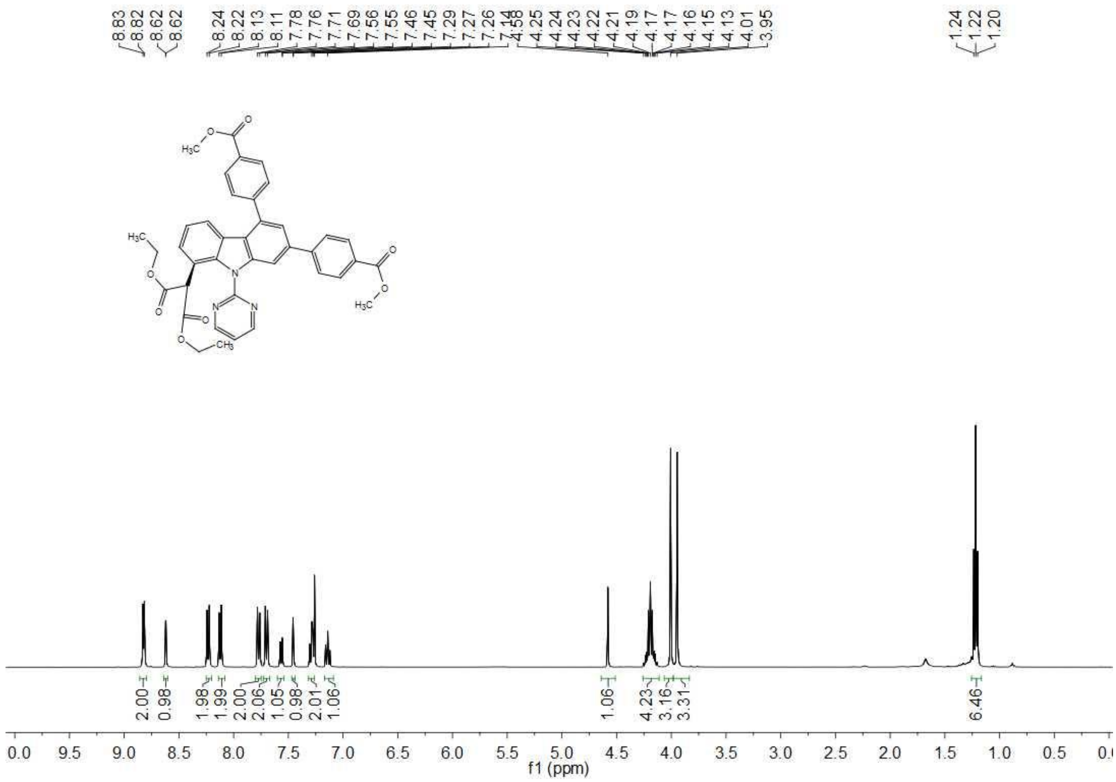
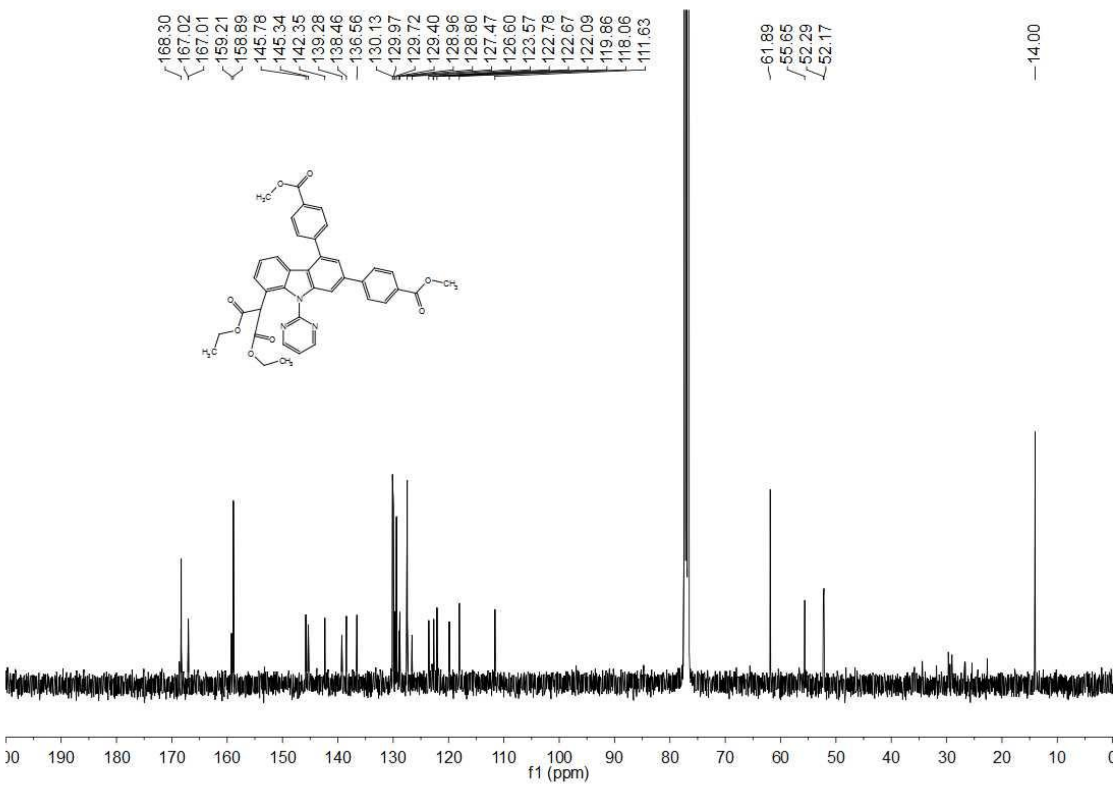
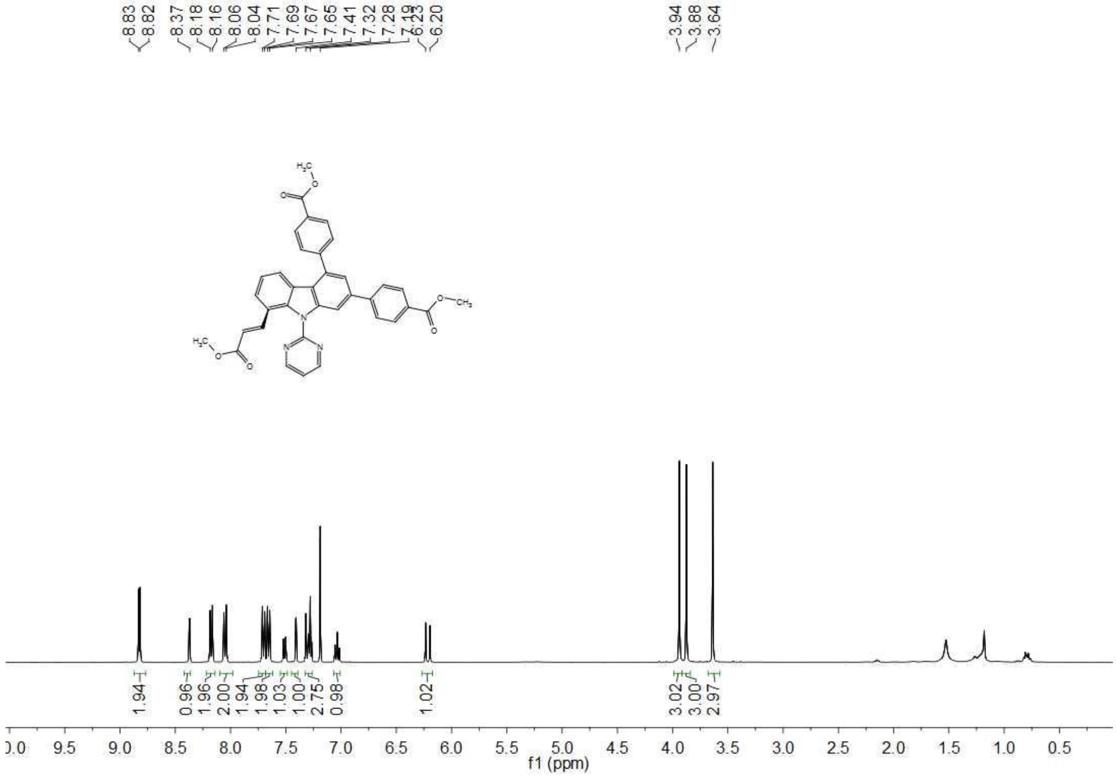
120.37
105.30
N
f1 (ppm)

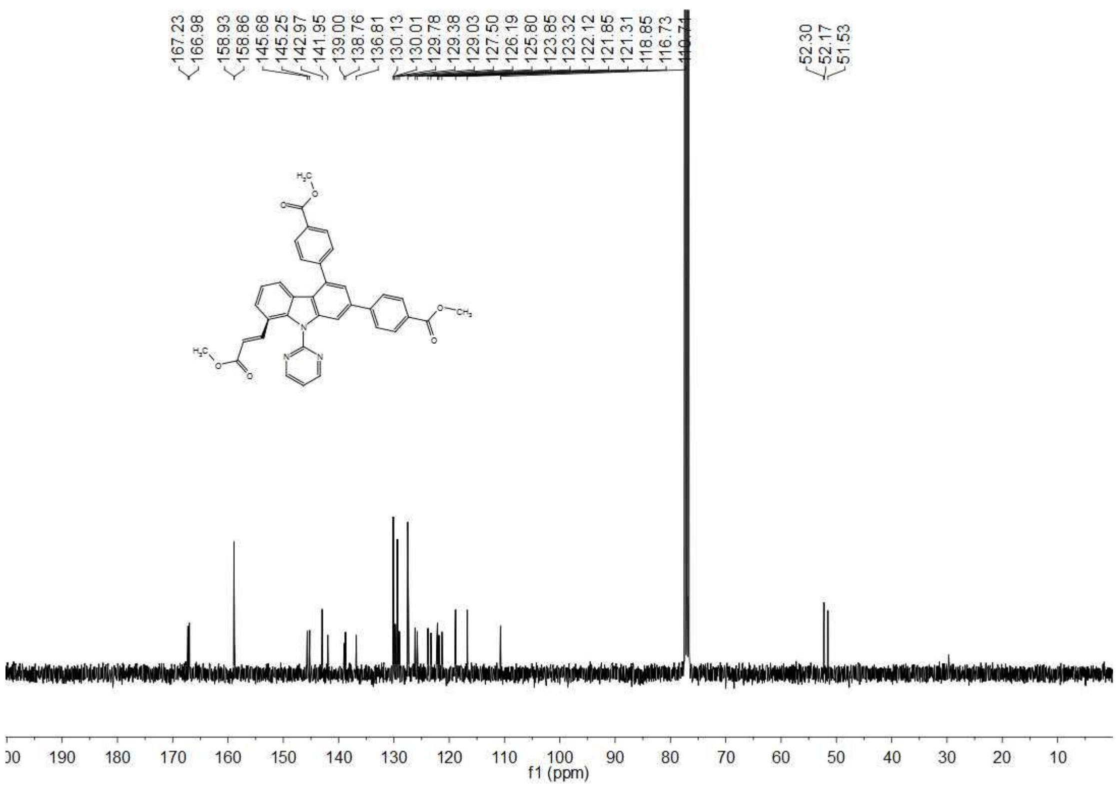
6



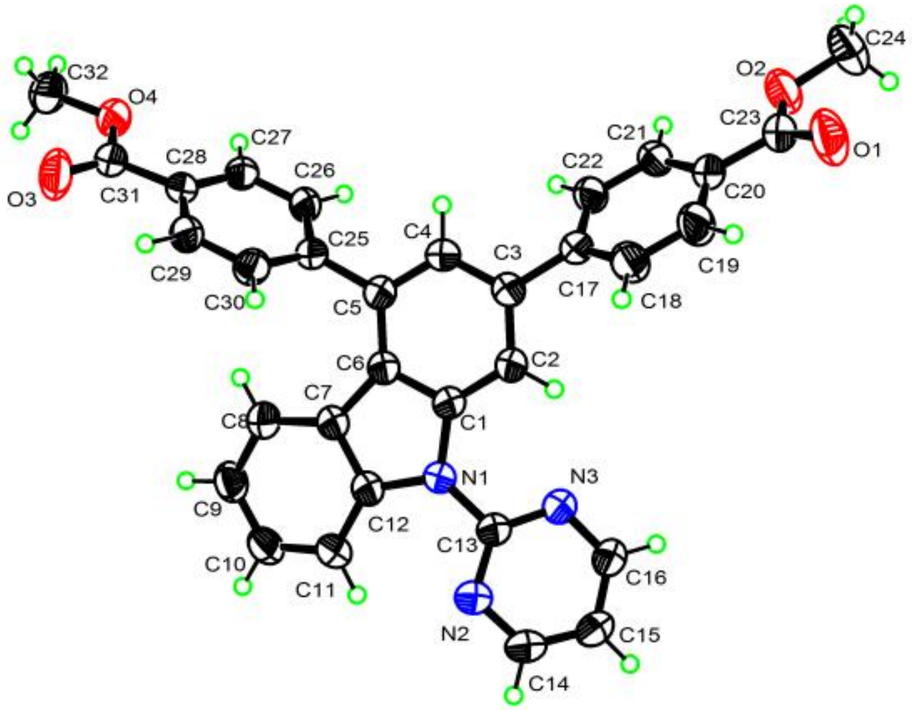


7





Crystal data and structure refinement for 3aa (CCDC: 1036782):



Computing details

Data collection: Bruker *APEX2*; cell refinement: Bruker *SAINT*; data reduction: Bruker *SAINT*; program(s) used to solve structure: *SHELXS97* (Sheldrick, 2008); program(s) used to refine structure: *SHELXL97* (Sheldrick, 2008); molecular graphics: Bruker *SHELXTL*; software used to prepare material for publication: Bruker *SHELXTL*.

Crystal data

$C_{32}H_{23}N_3O_4$	*F*(000) = 1072
M_r = 513.53	D_x = 1.386 Mg m^{-3} D_m = 1.30 Mg m^{-3} D_m measured by not measured
Monoclinic, $P2_1/c$	Mo *K* radiation, = 0.71073 Å
a = 27.800 (4) Å	Cell parameters from 6169 reflections
b = 8.1692 (14) Å	= 4.5–54.9 °
c = 10.9466 (18) Å	= 0.09 mm^{-1}

= 98.172 (6)°	T = 296 K
V = 2460.8 (7) Å^3	Prism, colorless
Z = 4	0.3 × 0.2 × 0.05 mm

Data collection

Bruker APEX-II CCD diffractometer	5660 independent reflections
Radiation source: fine-focus sealed tube	3975 reflections with $I > 2$ (I)
graphite	R_{int} = 0.022
and scans	$_{max}$ = 27.6°, $_{min}$ = 0.7 °
Absorption correction: multi-scan *SADABS*	h = -36 31
T_{min} = 0.653, T_{max} = 0.746	k = -10 8
21239 measured reflections	l = -14 13

Refinement

Refinement on F^2	Primary atom site location: structure-invariant direct methods
Least-squares matrix: full	Secondary atom site location: difference Fourier map
$R[F^2 > 2 (F^2)]$ = 0.043	Hydrogen site location: inferred from neighbouring sites
$wR(F^2)$ = 0.123	H atoms treated by a mixture of independent and constrained refinement
S = 1.02	$w = 1/[^2(F_o^2) + (0.0579P)^2 + 0.4381P]$ where $P = (F_o^2 + 2F_c^2)/3$
5660 reflections	$(/)_{max} < 0.001$
354 parameters	$_{max}$ = 0.17 e Å^{-3}
0 restraints	$_{min}$ = -0.17 e Å^{-3}

Special details

Geometry. All esds (except the esd in the dihedral angle between two l.s. planes) are estimated using the full covariance matrix. The cell esds are taken into account individually in the estimation of esds in distances, angles and torsion angles; correlations between esds in cell parameters are only used when they are defined by crystal symmetry. An approximate (isotropic) treatment of cell esds is used for estimating esds involving l.s. planes.

Refinement. Refinement of F^2 against ALL reflections. The weighted R-factor wR and goodness of fit S are based on F^2, conventional R-factors R are based on F, with F set to zero for negative F^2. The threshold expression of $F^2 > 2\mathrm{sigma}(F^2)$ is used only for calculating R-factors(gt) etc. and is not relevant to the choice of reflections for refinement. R-factors based on F^2 are statistically about twice as large as those based on F, and R- factors based on ALL data will be even larger.

Fractional atomic coordinates and isotropic or equivalent isotropic displacement parameters (Å^2)

	x	*y*	*z*	U_{iso}*/U_{eq}
O2	-0.01038 (4)	0.41094 (17)	-0.22099 (11)	0.0653 (3)
O4	0.45312 (4)	0.45390 (15)	-0.19307 (10)	0.0563 (3)
O3	0.48647 (4)	0.2820 (2)	-0.04748 (12)	0.0795 (4)
O1	-0.03253 (4)	0.2247 (2)	-0.09118 (13)	0.0874 (5)
N1	0.25590 (4)	0.52710 (16)	0.44386 (10)	0.0439 (3)
N3	0.17873 (5)	0.6014 (2)	0.48261 (11)	0.0585 (4)
N2	0.24370 (5)	0.5754 (2)	0.64580 (12)	0.0631 (4)
C24	-0.05767 (7)	0.4022 (3)	-0.2931 (2)	0.0788 (6)
H24A	-0.0629	0.2940	-0.3267	0.118*
H24B	-0.0597	0.4802	-0.3592	0.118*
H24C	-0.0820	0.4263	-0.2417	0.118*
C23	-0.00232 (6)	0.3148 (2)	-0.12236 (15)	0.0537 (4)
C20	0.04793 (5)	0.3322 (2)	-0.05728 (13)	0.0462 (4)
C19	0.06138 (6)	0.2506 (2)	0.05293 (15)	0.0613 (5)
H19	0.0390	0.1846	0.0851	0.074*
C18	0.10781 (6)	0.2665 (2)	0.11533 (15)	0.0583 (5)

H18	0.1162	0.2120	0.1899	0.070*
C17	0.14239 (5)	0.3625 (2)	0.06902 (13)	0.0435 (3)
C3	0.19162 (5)	0.38882 (19)	0.13763 (13)	0.0433 (3)
C4	0.23259 (5)	0.38409 (19)	0.07685 (13)	0.0443 (4)
H4	0.2286	0.3580	-0.0067	0.053*
C5	0.27893 (5)	0.41700 (18)	0.13687 (13)	0.0407 (3)
C25	0.32188 (5)	0.39751 (18)	0.07100 (13)	0.0396 (3)
C30	0.35926 (6)	0.2920 (2)	0.11723 (13)	0.0471 (4)
H30	0.3564	0.2293	0.1868	0.056*
C29	0.40044 (5)	0.2791 (2)	0.06130 (13)	0.0464 (4)
H29	0.4251	0.2079	0.0935	0.056*
C28	0.40548 (5)	0.37107 (19)	-0.04267 (12)	0.0403 (3)
C31	0.45230 (5)	0.3618 (2)	-0.09271 (14)	0.0473 (4)
C32	0.49838 (6)	0.4582 (3)	-0.24321 (18)	0.0672 (5)
H32A	0.5235	0.5018	-0.1826	0.101*
H32B	0.4948	0.5263	-0.3154	0.101*
H32C	0.5070	0.3493	-0.2650	0.101*
C26	0.32605 (5)	0.48262 (19)	-0.03675 (13)	0.0440 (4)
H26	0.3006	0.5488	-0.0719	0.053*
C27	0.36748 (5)	0.47063 (19)	-0.09259 (13)	0.0440 (4)
H27	0.3698	0.5298	-0.1641	0.053*
C2	0.19652 (5)	0.4282 (2)	0.26263 (13)	0.0451 (4)
H2	0.1699	0.4257	0.3052	0.054*
C1	0.24221 (5)	0.47123 (19)	0.32187 (12)	0.0412 (3)
C12	0.30656 (5)	0.55879 (19)	0.45964 (13)	0.0422 (3)
C7	0.32432 (5)	0.52473 (18)	0.34857 (13)	0.0412 (3)
C6	0.28365 (5)	0.46625 (18)	0.26123 (13)	0.0401 (3)
C8	0.37312 (5)	0.5572 (2)	0.33978 (15)	0.0480 (4)
H8	0.3854	0.5371	0.2665	0.058*
C9	0.40266 (6)	0.6190 (2)	0.44055 (15)	0.0538 (4)
H9	0.4352	0.6404	0.4355	0.065*
C10	0.38433 (6)	0.6498 (2)	0.54951 (15)	0.0541 (4)

H10	0.4050	0.6910	0.6167	0.065*
C11	0.33648 (6)	0.6215 (2)	0.56157 (14)	0.0494 (4)
H11	0.3246	0.6433	0.6351	0.059*
C13	0.22435 (5)	0.56886 (19)	0.52825 (13)	0.0433 (4)
C16	0.14992 (6)	0.6454 (3)	0.56508 (15)	0.0622 (5)
H16	0.1173	0.6664	0.5373	0.075*
C15	0.16618 (6)	0.6608 (2)	0.68730 (15)	0.0595 (5)
H15	0.1459	0.6938	0.7433	0.071*
C14	0.21352 (7)	0.6254 (3)	0.72315 (15)	0.0694 (5)
H14	0.2258	0.6363	0.8063	0.083*
C21	0.08212 (5)	0.4273 (2)	-0.10487 (14)	0.0484 (4)
H21	0.0736	0.4826	-0.1790	0.058*
C22	0.12881 (5)	0.4406 (2)	-0.04283 (14)	0.0492 (4)
H22	0.1515	0.5030	-0.0768	0.059*

Atomic displacement parameters (Å^2)

	U^{11}	U^{22}	U^{33}	U^{12}	U^{13}	U^{23}
O2	0.0423 (6)	0.0863 (9)	0.0630 (8)	-0.0093 (6)	-0.0066 (5)	0.0063 (7)
O4	0.0425 (6)	0.0793 (8)	0.0494 (6)	0.0002 (6)	0.0140 (5)	0.0023 (6)
O3	0.0477 (7)	0.1137 (12)	0.0791 (9)	0.0314 (7)	0.0166 (6)	0.0196 (8)
O1	0.0446 (7)	0.1260 (13)	0.0890 (10)	-0.0278 (8)	0.0009 (7)	0.0238 (9)
N1	0.0359 (6)	0.0613 (8)	0.0342 (6)	0.0012 (6)	0.0039 (5)	-0.0035 (6)
N3	0.0420 (8)	0.0936 (12)	0.0401 (7)	0.0109 (7)	0.0064 (6)	-0.0013 (7)
N2	0.0502 (8)	0.1011 (12)	0.0375 (7)	0.0108 (8)	0.0041 (6)	-0.0036 (7)
C24	0.0491 (11)	0.0966 (16)	0.0829 (14)	-0.0048 (10)	-0.0176 (10)	0.0045 (12)
C23	0.0386 (9)	0.0717 (12)	0.0514 (9)	-0.0055 (8)	0.0090 (7)	-0.0066 (8)

C20	0.0354 (8)	0.0597 (10)	0.0440 (8)	-0.0049 (7)	0.0081 (6)	-0.0074 (7)
C19	0.0449 (9)	0.0844 (13)	0.0550 (10)	-0.0195 (9)	0.0081 (8)	0.0085 (9)
C18	0.0485 (9)	0.0789 (13)	0.0466 (9)	-0.0111 (8)	0.0037 (7)	0.0129 (8)
C17	0.0372 (8)	0.0551 (9)	0.0386 (7)	-0.0023 (7)	0.0074 (6)	-0.0062 (7)
C3	0.0374 (8)	0.0526 (9)	0.0394 (7)	-0.0013 (6)	0.0036 (6)	-0.0010 (7)
C4	0.0414 (8)	0.0550 (9)	0.0364 (7)	-0.0007 (7)	0.0051 (6)	-0.0050 (7)
C5	0.0375 (8)	0.0465 (8)	0.0387 (7)	0.0019 (6)	0.0070 (6)	-0.0001 (6)
C25	0.0359 (7)	0.0464 (8)	0.0365 (7)	-0.0004 (6)	0.0051 (6)	-0.0058 (6)
C30	0.0482 (9)	0.0528 (9)	0.0409 (8)	0.0073 (7)	0.0087 (6)	0.0086 (7)
C29	0.0422 (8)	0.0517 (9)	0.0445 (8)	0.0124 (7)	0.0036 (6)	0.0028 (7)
C28	0.0358 (8)	0.0480 (8)	0.0363 (7)	0.0017 (6)	0.0028 (6)	-0.0076 (6)
C31	0.0379 (8)	0.0601 (10)	0.0438 (8)	0.0023 (7)	0.0055 (7)	-0.0088 (7)
C32	0.0471 (10)	0.0922 (15)	0.0665 (11)	-0.0136 (9)	0.0223 (8)	-0.0069 (10)
C26	0.0370 (8)	0.0539 (9)	0.0403 (8)	0.0100 (7)	0.0025 (6)	0.0039 (7)
C27	0.0419 (8)	0.0548 (9)	0.0356 (7)	0.0037 (7)	0.0062 (6)	0.0031 (7)
C2	0.0347 (8)	0.0618 (10)	0.0396 (8)	-0.0009 (7)	0.0074 (6)	-0.0010 (7)
C1	0.0377 (8)	0.0510 (9)	0.0351 (7)	0.0026 (6)	0.0059 (6)	-0.0007 (6)
C12	0.0364 (8)	0.0483 (9)	0.0409 (8)	0.0032 (6)	0.0027 (6)	0.0015 (6)
C7	0.0362 (8)	0.0469 (8)	0.0399 (7)	0.0023 (6)	0.0031 (6)	0.0010 (6)
C6	0.0358 (8)	0.0461 (8)	0.0383 (7)	0.0015 (6)	0.0049 (6)	0.0008 (6)
C8	0.0395 (8)	0.0549 (10)	0.0500 (9)	-0.0018 (7)	0.0076 (7)	-0.0025 (7)
C9	0.0370 (8)	0.0608	0.0623	-0.0049	0.0023 (7)	-0.0037

		(11)	(10)	(7)		(8)
C10	0.0443 (9)	0.0623 (11)	0.0520 (9)	-0.0019 (8)	-0.0052 (7)	-0.0064 (8)
C11	0.0446 (9)	0.0603 (10)	0.0414 (8)	0.0024 (7)	-0.0008 (6)	-0.0039 (7)
C13	0.0415 (8)	0.0533 (9)	0.0354 (7)	0.0021 (7)	0.0067 (6)	0.0013 (6)
C16	0.0432 (9)	0.0961 (14)	0.0484 (9)	0.0124 (9)	0.0109 (7)	-0.0004 (9)
C15	0.0541 (10)	0.0837 (13)	0.0436 (9)	0.0095 (9)	0.0173 (7)	-0.0025 (8)
C14	0.0619 (11)	0.1114 (17)	0.0351 (8)	0.0102 (11)	0.0073 (8)	-0.0062 (9)
C21	0.0410 (8)	0.0633 (10)	0.0402 (8)	-0.0065 (7)	0.0037 (6)	0.0006 (7)
C22	0.0396 (8)	0.0654 (11)	0.0431 (8)	-0.0123 (7)	0.0073 (6)	0.0009 (7)

Geometric parameters (Å, °)

O2—C23	1.328 (2)	C30—H30	0.9300
O2—C24	1.436 (2)	C29—C28	1.387 (2)
O4—C31	1.3346 (19)	C29—H29	0.9300
O4—C32	1.4428 (19)	C28—C27	1.383 (2)
O3—C31	1.1992 (19)	C28—C31	1.484 (2)
O1—C23	1.202 (2)	C32—H32A	0.9600
N1—C13	1.4033 (18)	C32—H32B	0.9600
N1—C1	1.4113 (18)	C32—H32C	0.9600
N1—C12	1.4181 (18)	C26—C27	1.382 (2)
N3—C13	1.3223 (19)	C26—H26	0.9300
N3—C16	1.3385 (19)	C27—H27	0.9300
N2—C13	1.3234 (19)	C2—C1	1.387 (2)
N2—C14	1.337 (2)	C2—H2	0.9300
C24—H24A	0.9600	C1—C6	1.4096 (19)
C24—H24B	0.9600	C12—C11	1.391 (2)
C24—H24C	0.9600	C12—C7	1.404 (2)

C23—C20	1.482 (2)	C7—C8	1.399 (2)
C20—C19	1.382 (2)	C7—C6	1.454 (2)
C20—C21	1.386 (2)	C8—C9	1.375 (2)
C19—C18	1.378 (2)	C8—H8	0.9300
C19—H19	0.9300	C9—C10	1.385 (2)
C18—C17	1.391 (2)	C9—H9	0.9300
C18—H18	0.9300	C10—C11	1.375 (2)
C17—C22	1.384 (2)	C10—H10	0.9300
C17—C3	1.480 (2)	C11—H11	0.9300
C3—C2	1.393 (2)	C16—C15	1.356 (2)
C3—C4	1.399 (2)	C16—H16	0.9300
C4—C5	1.387 (2)	C15—C14	1.350 (2)
C4—H4	0.9300	C15—H15	0.9300
C5—C6	1.408 (2)	C14—H14	0.9300
C5—C25	1.4886 (19)	C21—C22	1.381 (2)
C25—C26	1.388 (2)	C21—H21	0.9300
C25—C30	1.389 (2)	C22—H22	0.9300
C30—C29	1.377 (2)		
C23—O2—C24	116.92 (14)	O4—C32—H32C	109.5
C31—O4—C32	116.40 (13)	H32A—C32—H32C	109.5
C13—N1—C1	126.29 (12)	H32B—C32—H32C	109.5
C13—N1—C12	125.33 (12)	C27—C26—C25	121.05 (14)
C1—N1—C12	107.68 (11)	C27—C26—H26	119.5
C13—N3—C16	115.66 (13)	C25—C26—H26	119.5
C13—N2—C14	115.03 (14)	C26—C27—C28	120.32 (14)
O2—C24—H24A	109.5	C26—C27—H27	119.8
O2—C24—H24B	109.5	C28—C27—H27	119.8
H24A—C24—H24B	109.5	C1—C2—C3	118.23 (13)
O2—C24—H24C	109.5	C1—C2—H2	120.9

H24A—C24—H24C	109.5	C3—C2—H2	120.9
H24B—C24—H24C	109.5	C2—C1—C6	121.87 (13)
O1—C23—O2	123.30 (15)	C2—C1—N1	129.06 (13)
O1—C23—C20	124.80 (17)	C6—C1—N1	109.06 (12)
O2—C23—C20	111.89 (14)	C11—C12—C7	121.59 (14)
C19—C20—C21	118.93 (14)	C11—C12—N1	129.43 (14)
C19—C20—C23	119.54 (14)	C7—C12—N1	108.90 (12)
C21—C20—C23	121.53 (15)	C8—C7—C12	119.08 (13)
C18—C19—C20	120.35 (15)	C8—C7—C6	133.48 (14)
C18—C19—H19	119.8	C12—C7—C6	107.36 (12)
C20—C19—H19	119.8	C5—C6—C1	119.57 (13)
C19—C18—C17	121.32 (15)	C5—C6—C7	133.39 (13)
C19—C18—H18	119.3	C1—C6—C7	106.98 (12)
C17—C18—H18	119.3	C9—C8—C7	119.28 (15)
C22—C17—C18	117.79 (14)	C9—C8—H8	120.4
C22—C17—C3	119.88 (13)	C7—C8—H8	120.4
C18—C17—C3	122.27 (14)	C8—C9—C10	120.44 (15)
C2—C3—C4	120.06 (13)	C8—C9—H9	119.8
C2—C3—C17	119.08 (13)	C10—C9—H9	119.8
C4—C3—C17	120.75 (13)	C11—C10—C9	122.12 (15)
C5—C4—C3	122.26 (13)	C11—C10—H10	118.9
C5—C4—H4	118.9	C9—C10—H10	118.9
C3—C4—H4	118.9	C10—C11—C12	117.48 (15)
C4—C5—C6	117.79 (13)	C10—C11—H11	121.3
C4—C5—C25	120.33 (13)	C12—C11—H11	121.3
C6—C5—C25	121.87 (13)	N3—C13—N2	126.49 (14)
C26—C25—C30	118.16 (13)	N3—C13—N1	117.12 (13)
C26—C25—C5	121.85 (13)	N2—C13—N1	116.38 (13)
C30—C25—C5	119.99 (13)	N3—C16—C15	122.87 (16)
C29—C30—C25	120.77 (14)	N3—C16—H16	118.6
C29—C30—H30	119.6	C15—C16—H16	118.6

C25—C30—H30	119.6	C14—C15—C16	116.20 (15)
C30—C29—C28	120.70 (14)	C14—C15—H15	121.9
C30—C29—H29	119.6	C16—C15—H15	121.9
C28—C29—H29	119.6	N2—C14—C15	123.68 (16)
C27—C28—C29	118.83 (13)	N2—C14—H14	118.2
C27—C28—C31	123.03 (14)	C15—C14—H14	118.2
C29—C28—C31	118.10 (13)	C22—C21—C20	120.40 (15)
O3—C31—O4	122.75 (14)	C22—C21—H21	119.8
O3—C31—C28	124.07 (15)	C20—C21—H21	119.8
O4—C31—C28	113.18 (13)	C21—C22—C17	121.19 (14)
O4—C32—H32A	109.5	C21—C22—H22	119.4
O4—C32—H32B	109.5	C17—C22—H22	119.4
H32A—C32—H32B	109.5		
C24—O2—C23—O1	-0.9 (3)	C12—N1—C1—C6	0.45 (16)
C24—O2—C23—C20	178.76 (15)	C13—N1—C12—C11	6.4 (3)
O1—C23—C20—C19	-5.4 (3)	C1—N1—C12—C11	177.24 (16)
O2—C23—C20—C19	174.94 (16)	C13—N1—C12—C7	-170.30 (14)
O1—C23—C20—C21	174.00 (18)	C1—N1—C12—C7	0.55 (17)
O2—C23—C20—C21	-5.7 (2)	C11—C12—C7—C8	-1.0 (2)
C21—C20—C19—C18	1.2 (3)	N1—C12—C7—C8	175.95 (14)
C23—C20—C19—C18	-179.37 (17)	C11—C12—C7—C6	-178.30 (14)
C20—C19—C18—C17	-0.8 (3)	N1—C12—C7—C6	-1.31 (17)
C19—C18—C17—C22	-0.7 (3)	C4—C5—C6—C1	3.6 (2)

C19—C18—C17—C3	176.57 (16)	C25—C5—C6—C1	-175.36 (14)
C22—C17—C3—C2	130.93 (17)	C4—C5—C6—C7	-173.15 (16)
C18—C17—C3—C2	-46.2 (2)	C25—C5—C6—C7	7.9 (3)
C22—C17—C3—C4	-45.3 (2)	C2—C1—C6—C5	0.3 (2)
C18—C17—C3—C4	137.57 (17)	N1—C1—C6—C5	-178.80 (13)
C2—C3—C4—C5	0.2 (2)	C2—C1—C6—C7	177.81 (14)
C17—C3—C4—C5	176.39 (14)	N1—C1—C6—C7	-1.24 (17)
C3—C4—C5—C6	-3.9 (2)	C8—C7—C6—C5	1.9 (3)
C3—C4—C5—C25	175.09 (14)	C12—C7—C6—C5	178.64 (16)
C4—C5—C25—C26	58.1 (2)	C8—C7—C6—C1	-175.13 (17)
C6—C5—C25—C26	-122.95 (17)	C12—C7—C6—C1	1.56 (17)
C4—C5—C25—C30	-122.01 (16)	C12—C7—C8—C9	1.0 (2)
C6—C5—C25—C30	57.0 (2)	C6—C7—C8—C9	177.42 (17)
C26—C25—C30—C29	3.5 (2)	C7—C8—C9—C10	-0.3 (3)
C5—C25—C30—C29	-176.45 (14)	C8—C9—C10—C11	-0.4 (3)
C25—C30—C29—C28	-0.1 (2)	C9—C10—C11—C12	0.4 (3)
C30—C29—C28—C27	-2.9 (2)	C7—C12—C11—C10	0.3 (2)
C30—C29—C28—C31	175.16 (14)	N1—C12—C11—C10	-176.01 (15)
C32—O4—C31—O3	-2.2 (2)	C16—N3—C13—N2	0.1 (3)
C32—O4—C31—	176.76 (13)	C16—N3—C13—	-178.15 (16)

C28		N1	
C27—C28—C31—O3	176.46 (16)	C14—N2—C13—N3	-2.3 (3)
C29—C28—C31—O3	-1.5 (2)	C14—N2—C13—N1	176.03 (17)
C27—C28—C31—O4	-2.5 (2)	C1—N1—C13—N3	-19.3 (2)
C29—C28—C31—O4	179.54 (14)	C12—N1—C13—N3	149.89 (15)
C30—C25—C26—C27	-3.9 (2)	C1—N1—C13—N2	162.28 (16)
C5—C25—C26—C27	176.03 (14)	C12—N1—C13—N2	-28.6 (2)
C25—C26—C27—C28	0.9 (2)	C13—N3—C16—C15	1.8 (3)
C29—C28—C27—C26	2.5 (2)	N3—C16—C15—C14	-1.5 (3)
C31—C28—C27—C26	-175.48 (14)	C13—N2—C14—C15	2.6 (3)
C4—C3—C2—C1	3.7 (2)	C16—C15—C14—N2	-0.9 (3)
C17—C3—C2—C1	-172.52 (14)	C19—C20—C21—C22	-0.2 (2)
C3—C2—C1—C6	-3.9 (2)	C23—C20—C21—C22	-179.55 (15)
C3—C2—C1—N1	174.90 (15)	C20—C21—C22—C17	-1.4 (2)
C13—N1—C1—C2	-7.8 (3)	C18—C17—C22—C21	1.7 (2)
C12—N1—C1—C2	-178.51 (16)	C3—C17—C22—C21	-175.55 (14)
C13—N1—C1—C6	171.19 (14)		