Electronic Supplementary Material (ESI) for ChemComm.

Supporting Information

Rhodium-Catalyzed Multiple C−H Activation/Highly *meta*-Selective C−H Amination between Amidines and Alkynes

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Contents

1. General Information

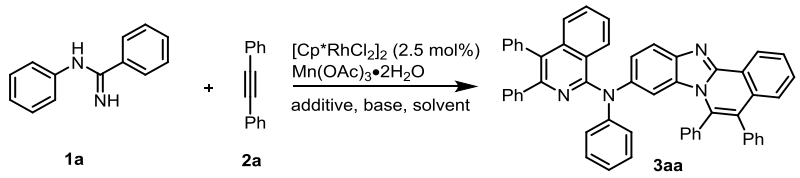
Unless otherwise noted, all the rhodium-catalyzed reactions were carried out under air condition. The commercially available chemicals and solvents were used as received without further purification. Alkynes were prepared according to the published procedure.[S1-S5] Amidines were obtained from corresponding nitriles and amines.[S6] The reactions were monitored by TLC using UV-light or by staining with iodine. Column chromatography was performed on silica gel (200-300 mesh). Single-crystal X-ray data in this work were collected on an Agilent Technologies SuperNova Single Crystal Diffractometer at different temperatures equipped with graphite-monochromatic Mo Kα or Cu Kα radiation (λ = 0.71073 Å or 1.54184 Å). The structures were solved by SHELXS (direct methods) and refined by SHELXL (full matrix least-squares techniques) in the Olex2 package.[S7] All non-hydrogen atoms were refined with anisotropic displacement parameters. Hydrogen atoms attached to carbon were placed in geometrically idealized positions and refined using a riding model. ^{1}H, ^{13}C, and ^{19}F NMR were recorded on a 600 or 400 MHz Bruker NMR spectrometer in $CDCl_3$ (7.26 ppm for ^{1}H and 77.16 ppm for ^{13}C) using tetramethylsilane (TMS) as the internal standard(s = singlet, d = doublet, t = triplet, q = quartet, dd = doublet of doublets, m = multiplet). High-resolution mass spectra HRMS data were obtained with Micromass HPLC–Q–TOF mass spectrometer.

2. Optimization of Reaction Conditions

To initiate our investigation, *N*-phenylbenzimidamide **1a** and diphenylacetylene **2a** were chosen as model substrates. The effect of varying different reaction parameters on the reaction efficiency was evaluated (Table S1). We first commence the reaction of **1a** (0.125 mmol) and **2a** (3 equiv) with $[Cp^*RhCl_2]_2$ as the catalyst precursor, and $Mn(OAc)_3•2H_2O$ as the oxidant in tert-amyl alcohol at 80 ℃. To our surprise, the reaction gave the heterocyclic product **3aa** in 24% yield, albeit with *N*-substituted 1-aminoisoquinolines side product (entry 1). Subsequent screening of solvents revealed that DCE performed the best with an increase in the yield to 44% (entries 2-7). Decreasing the amount of $Mn(OAc)_3•2H_2O$ to 2 equiv resulted in the formation of **3aa** in 27% yield, while increasing the loading of $Mn(OAc)_3•2H_2O$ to 8 equiv furnished **3aa** in 43% yield (entries 8-9). Interestingly, the yield of **3aa** could be increased to 64% upon the addition of PhCN

as the additive, which was proved to facilitate and stabilize the formation of the five-membered cyclometalated intermediate during the process. To our delight, the desired product **3aa** was obtained in 79% yield when 20 mol% KO^{t}Bu was used, whereas the yield of **3aa** dropped significantly upon further increasing the amount of KO^{t}Bu to 40 mol% (entries 11 and 12). Inspired by this result, we screened other bases, such as DBU and DMAP, but resulted in attenuated reactivity (entries 13 and 14). Conversely, 2,2-bipyridine and $PhNH_2$ failed to give desired product **3aa**. It is probably attributed to either chelation of the catalyst or competitive pyridine or NH_2-directed C-H bond activations (entries 15 and 16). Notably, $Mn(OAc)_3•2H_2O$ turned out to be an indispensable reaction parameter for this cascade, as no reaction proceeded in the absence of $Mn(OAc)_3•2H_2O$ or in the present of other oxidants (entries 17-21). Further optimization showed that the reaction did not occur without the $[Cp^*RhCl_2]_2$ (entry 22). Thus, the optimal reaction conditions were set as $[Cp^*RhCl_2]_2$ (2.5 mol%), $Mn(OAc)_3•2H_2O$ (6 equiv), PhCN (20 mol %), and KO^{t}Bu (20 mol %), in DCE at 40 ^{o}C for 48 h.

Table S1. Optimization of Reaction Conditions[a]



entry	oxidant	solvent	additive	yield (%)[b]
1	$Mn(OAc)_3\ 2H_2O$	tert amyl alcohol		24
2	$Mn(OAc)_3\ 2H_2O$	CF_3CH_2OH		ND
3	$Mn(OAc)_3\ 2H_2O$	NMP		N.D.
4	$Mn(OAc)_3\ 2H_2O$	DMF		N.D.
5	$Mn(OAc)_3\ 2H_2O$	CH_3CN		7
6	$Mn(OAc)_3\ 2H_2O$	dioxane		<5
7	$Mn(OAc)_3\ 2H_2O$	DCE		44
8[c]	$Mn(OAc)_3\ 2H_2O$	DCE		27
9[d]	$Mn(OAc)_3\ 2H_2O$	DCE		43
10[e]	$Mn(OAc)_3\ 2H_2O$	DCE	PhCN	64
11[e]	$Mn(OAc)_3\ 2H_2O$	DCE	PhCN/KO^{t}Bu	79
12[e,f]	$Mn(OAc)_3\ 2H_2O$	DCE	PhCN/KO^{t}Bu	49

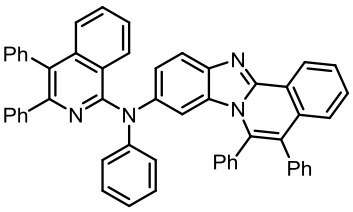
13[e]	$Mn(OAc)_3 \cdot 2H_2O$	DCE	PhCN/DBU	28
14[e]	$Mn(OAc)_3 \cdot 2H_2O$	DCE	PhCN/DMAP	42
15[e]	$Mn(OAc)_3 \cdot 2H_2O$	DCE	PhCN/2,2-bipyridin e	N.D.
16[e]	$Mn(OAc)_3 \cdot 2H_2O$	DCE	PhCN/$PhNH_2$	N.D.
17[e]	TBHP	DCE	PhCN/KO^{t}Bu	N.D.
18[e]	MnO_2	DCE	PhCN/KO^{t}Bu	N.D.
19[e]	BQ	DCE	PhCN/KO^{t}Bu	N.D.
20[e]	$Cu(OAc)_2$	DCE	PhCN/KO^{t}Bu	N.D.
21[e]	－－	DCE	PhCN/KO^{t}Bu	N.D.
22[e,g]	$Mn(OAc)_3 \cdot 2H_2O$	DCE	PhCN/KO^{t}Bu	N.D

Reaction conditions: [a] $[Cp^*RhCl_2]_2$ (0.0032 mmol, 2.5%), amidine **1a** (0.125 mmol, 24.5 mg), alkyne **2a** (0.375mmol, 66.8 mg), oxidant (6 equiv) base (20%), PhCN (20%, 25.6 uL), solvent (2 mL), 80 °C, 48 h. [b] Isolated yield. [c] $Mn(OAc)_3 \cdot 2H_2O$ (2 equiv). [d] $Mn(OAc)_3 \cdot 2H_2O$ (8 equiv). [e] Solvent (4 mL), 40 °C. [f] KO^{t}Bu (40%). [g] without $[Cp^*RhCl_2]_2$.

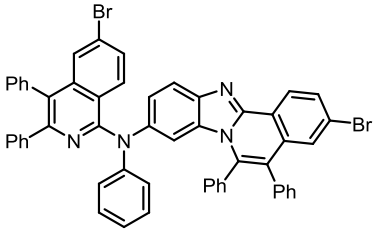
3. Procedure for Rh(III)-Catalyzed Cascade Reactions

A mixture of $[Cp^*RhCl_2]_2$ (0.0032 mmol, 2.5%), alkynes **2a-2o** (0.375 mmol), amidines **1a-1n** (0.125 mmol), $Mn(OAc)_3 \cdot 2H_2O$ (6 equiv, 201.1 mg), KO^{t}Bu (20%), PhCN (20%, 25.6 uL), DCE (4 mL) was stirred at 40 °C for 48 h. After cooling the reaction to room temperature, the solvent was removed under vacuum and the residue was purified by silica gel chromatography using petroleum ether/ethyl acetate = 10:1-4:1 to afford desired products.

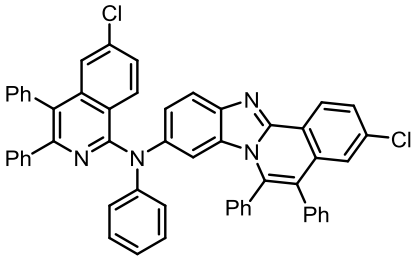
4. Characterization of Products



N-(3,4-diphenylisoquinolin-1-yl)-N,5,6-triphenylbenzo[4,5]imidazo[2,1-a]isoquinolin-9-amine (3aa). Yellow solid (isolated yield 79%). mp 187.5-188.2 ℃. Petroleum ether/ethyl acetate = 6:1. ^{1}H NMR (400 MHz, $CDCl_3$) δ = 9.00 (d, *J*=8.0 Hz, 1H), 7.96 (d, *J*=8.8 Hz, 1H), 7.72 (dd, *J*=16.6 Hz, 9.0 Hz, 3H), 7.58 (t, *J*=7.7 Hz, 1H), 7.50 (ddd, *J*=8.4 Hz, 6.9 Hz, 1.1 Hz , 1H), 7.48 – 7.41 (m, 4H), 7.37 (d, *J*=7.7 Hz, 2H), 7.32 (d, *J*=8.1 Hz, 1H), 7.28 – 7.20 (m, 6H), 7.19 – 7.13 (m, 4H), 7.13 – 7.07 (m, 3H), 7.07 – 6.99 (m, 5H), 6.80 (t, *J*=7.7 Hz, 2H), 6.71 (t, *J*=7.0 Hz, 1H), 5.51 (s, 1H). ^{13}C NMR (101 MHz, $CDCl_3$) δ = 170.3 156.8, 148.7, 148.3, 147.5, 142.8, 140.2, 139.3, 138.7, 137.8, 135.6, 135.0, 133.0, 132.4, 131.5, 131.5, 131.4, 131.4, 130.3, 129.9, 129.8, 129.0, 128.6, 128.3, 128.0, 127.9, 127.8, 127.5, 127.4, 127.2, 127.0, 126.4, 126.3, 126.2, 126.1, 124.9, 123.6, 123.0, 122.7, 122.2, 119.5, 119.5, 114.9, 110.0. HRMS Calculated for $C_{54}H_{37}N_4^+$, 741.3018, found 741.3013.

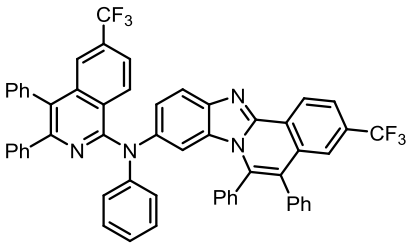


3-bromo-N-(6-bromo-3,4-diphenylisoquinolin-1-yl)-N,5,6-triphenylbenzo[4,5]imidazo[2,1-a]isoquinolin-9-amine (3ba). Yellow solid (isolated yield 72%). mp 121.6-123.5 ℃. Petroleum ether/ethyl acetate = 4:1. ^{1}H NMR (400 MHz, $CDCl_3$) δ = 8.88 (d, *J*=8.4 Hz, 1H), 7.96 (d, *J*=8.8 Hz, 1H), 7.85 – 7.79 (m, 2H), 7.59 (d, *J*=9.0 Hz, 1H), 7.49 – 7.43 (m, 4H), 7.41 (dd, *J*=8.8 Hz, 2.1 Hz, 1H), 7.35 – 7.30 (m, 3H), 7.26 (dd, *J*=9.7 Hz, 5.4 Hz, 5H), 7.15 (dd, *J*=7.6 Hz, 1.7 Hz, 2H), 7.13 – 7.08 (m, 5H), 7.07 – 7.03 (m, 3H), 6.99 (d, *J*=7.7 Hz, 2H), 6.85 (t, *J*=7.5 Hz, 2H), 6.77 (t, *J*=7.5 Hz, 1H), 5.50 (d, *J*=2.0 Hz, 1H). ^{13}C NMR (101 MHz, $CDCl_3$) δ = 185.0, 176.9, 169.6, 163.0, 156.8, 149.9, 148.0, 147.0, 145.5, 142.9, 140.6, 139.8, 137.1, 136.1, 135.5, 134.7, 133.9, 132.7, 131.4, 131.3, 131.3, 130.4, 130.4, 129.8, 129.7, 129.2, 128.8, 128.5, 128.4, 128.2, 128.0, 127.7, 127.6, 127.5, 127.3, 126.8, 126.6, 125.0, 123.9, 123.2, 122.6, 121.3, 119.6, 110.0. HRMS Calculated for $C_{54}H_{35}Br_2N_4^+$, 899.1228, found 899.1220.

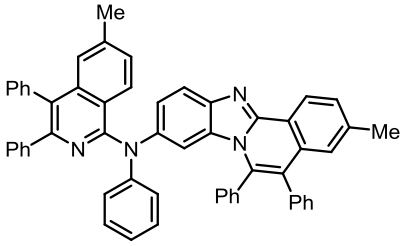


3-chloro-N-(6-chloro-3,4-diphenylisoquinolin-1-yl)-N,5,6-triphenylbenzo[4,5]imidazo[2,1-a]isoquinolin-9-amine (3ca). Yellow solid (isolated yield 57%). mp 131.3-132.5 ℃. Petroleum ether/ethyl acetate = 4:1. ^{1}H NMR (400 MHz, $CDCl_3$) δ = 8.93 (d, *J*=8.2 Hz, 1H), 7.93 (d, *J*=8.8 Hz, 1H), 7.63 (m, 3H), 7.47 – 7.40 (m, 3H), 7.38 (dd, *J*=8.8 Hz, 2.1 Hz, 1H), 7.30 (dd, *J*=7.5 Hz, 1.8 Hz, 2H), 7.27 – 7.19 (m, 6H), 7.17 – 6.99 (m, 11H), 6.96 (d, *J*=7.6 Hz, 2H), 6.82 (t, *J*=7.5 Hz, 2H), 6.74 (dd, *J*=8.5 Hz, 6.4 Hz, 1H), 5.48 (d, *J*=2.0 Hz, 1H). ^{13}C NMR (101 MHz, $CDCl_3$) δ = 164.8, 156.7, 149.9, 148.0, 143.0, 140.3, 139.8, 137.1, 136.2, 136.1, 134.7, 134.1, 133.9, 133.8, 132.7, 131.7, 131.3, 131.2, 130.3, 129.8, 129.6, 129.2, 128.8, 128.5, 128.4, 128.3, 128.2, 128.0, 127.7, 127.6, 127.5, 127.3, 127.1, 126.9, 126.6, 126.3, 125.8, 124.9, 123.9, 123.2, 122.6, 121.1, 119.5, 110.0. HRMS Calculated for $C_{54}H_{35}Cl_2N_4^+$, 809.2239, found 809.2195.

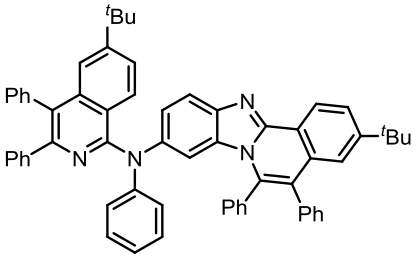
N-(3,4-diphenyl-6-(trifluoromethyl)isoquinolin-1-yl)-N,5,6-triphenyl-3-(trifluoromethyl)benzo[4,5]imidazo[2,1-a]isoquinolin-9-amine (3da). Yellow solid (isolated yield 59%). mp 113.2-114.5 ℃. Petroleum ether/ethyl acetate = 4:1. ^{1}H NMR (400 MHz, $CDCl_3$) δ = 9.11 (d, *J*=8.2 Hz, 1H), 8.03 – 7.94 (m, 2H), 7.90 (d, *J*=8.5 Hz, 1H), 7.83 (d, *J*=8.8 Hz, 1H), 7.57 (s, 1H), 7.48 – 7.37 (m, 5H), 7.31 (dd, *J*=7.2 Hz, 1.9 Hz, 2H), 7.28 – 7.21 (m, 6H), 7.16 – 7.06 (m, 8H), 7.03 (d, *J*=8.0 Hz, 2H), 6.97 (s, 1H), 6.81 (t, *J*=7.6 Hz, 2H), 6.73 (t, *J*=7.0 Hz, 1H), 5.53 (s, 1H). ^{13}C NMR (101 MHz, $CDCl_3$) δ = 196.4, 175.4, 156.7, 150.2, 147.9, 143.4 (d, *J* = 25.4 Hz), 139.6, 138.6, 136.7 136.3, 134.4, 133.31 (d, *J* = 23.1 Hz), 132.6, 132.3, 131.5, 130.3, 129.8 (d, *J* = 293.1 Hz), 129.8 (d, *J* = 291.9 Hz), 129.8, 129.3, 128.9, 128.5, 128.1, 127.9, 127.8, 127.6, 127.5, 127.4, 126.4, 126.3, 125.8, 125.3, 125.1, 124.12, 124.05, 123.8, 123.7, 123.7, 123.54, 123.52, 122.82 (d, *J* = 2.2 Hz), 122.4, 121.8 (d, *J* = 3.0 Hz), 120.0, 110.0, 100.0. ^{19}F NMR (376 MHz, $CDCl_3$) δ = -62.40, -62.94. HRMS Calculated for $C_{56}H_{35}F_6N_4^+$, 877.2766, found 877.2763.

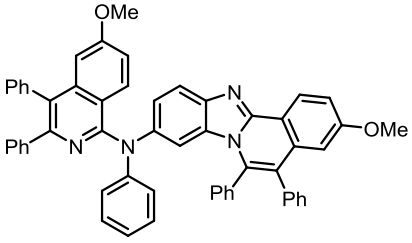


3-methyl-N-(6-methyl-3,4-diphenylisoquinolin-1-yl)-N,5,6-triphenylbenzo[4,5]imidazo[2,1-a]isoquinolin-9-amine (3ea). Yellow solid (isolated yield 60%). mp 229.0-230.6 ℃. Petroleum ether/ethyl acetate = 4:1. ^{1}H NMR (400 MHz, $CDCl_3$) δ = 8.83 (d, *J*=8.2, 1H), 7.88 (d, *J*=8.8, 1H), 7.60 (d, *J*=8.6, 1H), 7.50 (dd, *J*=8.3, 1.2, 1H), 7.45 – 7.34 (m, 5H), 7.31 (dd, *J*=7.6, 1.7, 2H), 7.20 (tt, *J*=8.4, 4.0, 5H), 7.12 (ddd, *J*=6.5, 6.0, 2.2, 4H), 7.07 – 6.93 (m, 10H), 6.77 (t, *J*=7.5, 2H), 6.69 (d, *J*=7.5, 1H), 5.47 (d, *J*=1.9, 1H), 2.40 (s, 3H), 2.35 (s, 3H). ^{13}C NMR (101 MHz, $CDCl_3$) δ = 156.7, 148.8, 148.4, 147.8, 142.5, 141.3, 140.4, 140.2, 140.0, 139.5, 138.1, 135.7, 135.1, 133.8, 133.2, 132.5, 132.1, 131.5, 131.4, 130.4, 129.9, 129.4, 129.0, 128.5, 128.4, 128.3, 128.0, 127.44, 127.38, 127.24, 127.17, 126.9, 126.2, 126.1, 124.9, 124.8, 123.5, 123.1, 122.5, 122.1, 121.3, 120.7, 119.3, 110.0, 22.12, 22.07. HRMS Calculated for $C_{56}H_{41}N_4^+$, 769.3331, found 769.3325.

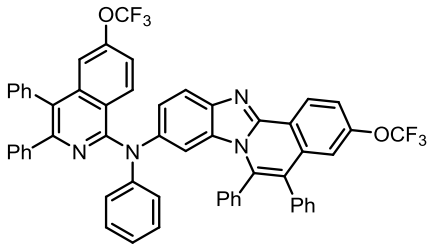


3-(tert-butyl)-N-(6-(tert-butyl)-3,4-diphenylisoquinolin-1-yl)-N,5,6-triphenylbenzo[4,5]imidazo[2,1-a]isoquinolin-9-amine (3fa). Yellow solid (isolated yield 61%). mp 198.6-199.8 ℃. Petroleum ether/ethyl acetate = 4:1. ^{1}H NMR (400 MHz, $CDCl_3$) δ = 8.89 (d, *J*=8.4 Hz, 1H), 7.90 (d, *J*=8.8 Hz, 1H), 7.75 (dd, *J*=8.5 Hz, 1.7 Hz, 1H), 7.61 (dd, *J*=5.4 Hz, 3.2, 2H), 7.44 – 7.36 (m, 4H), 7.36 – 7.26 (m, 4H), 7.24 – 7.16 (m, 5H), 7.16 – 7.09 (m, 4H), 7.08 – 7.02 (m, 3H), 6.99 (dt, *J*=6.9 Hz, 4.6, 5H), 6.74 (t, *J*=7.5 Hz, 2H), 6.65 (t, *J*=7.5 Hz, 1H), 5.46 (d, *J*=2.0 Hz, 1H), 1.26 (s, 9H), 1.23 (s, 9H). ^{13}C NMR (101 MHz, $CDCl_3$) δ = 156.3, 153.0, 152.7, 148.8, 148.3, 147.6, 147.5, 142.5, 140.5, 139.3, 138.0, 137.2, 135.6, 135.2, 134.9, 133.2, 132.3, 131.5, 131.38, 131.36, 130.3, 130.0, 128.9, 128.4, 128.2, 128.1, 128.0, 127.8, 127.4, 127.2, 127.1, 126.8, 126.0, 125.9, 125.0, 124.6, 123.5, 122.4, 122.0, 121.3, 121.1, 120.6, 119.3, 109.9, 35.2, 31.1, 30.9. HRMS Calculated for $C_{62}H_{53}N_4^+$, 853.4270, found 853.4265.

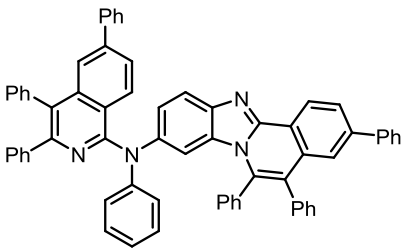


3-methoxy-N-(6-methoxy-3,4-diphenylisoquinolin-1-yl)-N,5,6-triphenylbenzo[4,5]imidazo[2,1-a]isoquinolin-9-amine (3ga). 

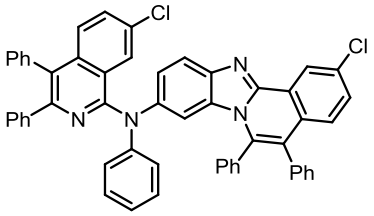
Yellow solid (isolated yield 42%). mp 193.6-194.5 ℃. Petroleum ether/ethyl acetate = 4:1. ^{1}H NMR (400 MHz, $CDCl_3$) δ = 8.90 (d, *J*=8.8 Hz, 1H), 7.88 (d, *J*=8.8 Hz, 1H), 7.62 (d, *J*=9.3 Hz, 1H), 7.44 – 7.26 (m, 7H), 7.25 – 7.16 (m, 5H), 7.16 – 7.09 (m, 4H), 7.07 – 6.93 (m, 8H), 6.92 (d, *J*=2.4 Hz, 1H), 6.88 – 6.76 (m, 3H), 6.71 (dd, *J*=14.4 Hz, 5.0 Hz, 2H), 5.46 (d, *J*=1.9 Hz, 1H), 3.74 (s, 3H), 3.69 (s, 3H). ^{13}C NMR (101 MHz, $CDCl_3$) δ = 167.3, 160.9, 160.3, 158.3, 156.5, 153.4, 151.1, 149.4, 148.3, 141.3, 140.4, 138.1, 135.5, 134.4, 133.1, 131.4, 131.3, 131.2, 130.3, 129.9, 128.9, 128.6, 128.3, 128.2, 128.0, 127.4, 127.3, 127.2, 126.9, 126.8, 123.4, 123.1, 122.4, 122.1, 119.0, 118.4, 118.1, 117.4, 116.8, 116.4, 110.0, 108.8, 107.3, 104.6, 55.3, 55.2. HRMS Calculated for $C_{56}H_{41}N_4O_2^+$, 801.3230, found 801.3224.

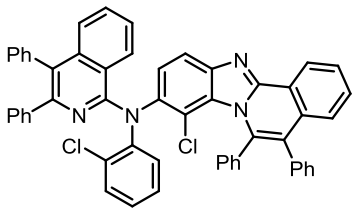
N-(3,4-diphenyl-6-(trifluoromethoxy)isoquinolin-1-yl)-N,5,6-triphenyl-3-(trifluoromethoxy)benzo[4,5]imidazo[2,1-a]isoquinolin-9-amine (3ha). 

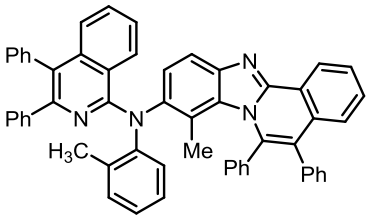
Yellow solid (isolated yield 63%). mp 79.9-81.2 ℃. Petroleum ether/ethyl acetate = 4:1. ^{1}H NMR (400 MHz, $CDCl_3$) δ = 9.03 (d, *J*=8.0 Hz, 1H), 7.94 (d, *J*=8.8 Hz, 1H), 7.74 (d, *J*=9.3 Hz, 1H), 7.54 (d, *J*=8.8 Hz, 1H), 7.48 – 7.36 (m, 5H), 7.30 (dd, *J*=7.5 Hz, 1.8 Hz, 2H), 7.26 – 7.18 (m, 5H), 7.15 – 7.04 (m, 10H), 7.03 – 6.95 (m, 4H), 6.80 (t, *J*=7.4 Hz, 2H), 6.72 (t, *J*=7.4 Hz, 1H), 5.47 (d, *J*=2.0 Hz, 1H). ^{13}C NMR (101 MHz, $CDCl_3$) δ = 156.6, 150.2, 150.0, 149.8, 148.0, 146.7, 143.0, 140.5, 139.7, 137.0, 136.3, 134.6, 134.1, 132.7, 131.7, 131.4, 131.2, 131.1, 130.3, 129.7, 129.5, 129.2, 129.0, 128.8, 128.4, 128.3, 128.2, 127.8, 127.7, 127.6, 127.5, 127.4, 127.1, 122.9 (dd, *J* = 258.5, 1.9 Hz), 124.0, 123.3, 122.9, 122.5, 121.0, 120.6, 119.7, 119.6, 117.79 (dd, *J* = 258.3, 2.2 Hz)., 117.8, 116.3, 109.9. ^{19}F NMR (376 MHz, $CDCl_3$) δ = -57.49, -57.58. HRMS Calculated for $C_{56}H_{35}N_4F_6O_2^+$, 909.2664, found 909.2659.

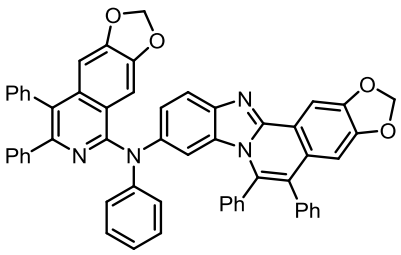
N,3,5,6-tetraphenyl-N-(3,4,6-triphenylisoquinolin-1-yl)benzo[4,5]imidazo[2,1-a]isoquinolin-9-amine (3ia). 

Yellow solid (isolated yield 49%). mp 225.2-226.5 ℃. Petroleum ether/ethyl acetate = 4:1. ^{1}H NMR (400 MHz, $CDCl_3$) δ = 9.04 (d, *J*=8.0 Hz, 1H), 7.94 (dd, *J*=12.7 Hz, 5.3 Hz, 2H), 7.86 (d, *J*=1.2 Hz, 1H), 7.77 (d, *J*=8.8 Hz, 1H), 7.55 – 7.47 (m, 6H), 7.46 – 7.30 (m, 13H), 7.24 – 7.11 (m, 8H), 7.08 (dd, *J*=10.3 Hz, 6.8 Hz, 3H), 7.03 (d, *J*=7.2 Hz, 5H), 6.80 (t, *J*=7.5 Hz, 2H), 6.71 (t, *J*=7.5 Hz, 1H), 5.53 (d, *J*=1.9 Hz, 1H). ^{13}C NMR (101 MHz, $CDCl_3$) δ = 160.7, 156.7 149.3, 148.3, 142.8, 142.2, 140.5, 140.33, 140.29, 139.7, 137.8, 135.4, 133.0, 132.9, 131.6, 131.4, 131.3, 130.4, 129.9, 129.6, 129.1, 128.94, 128.91, 128.83, 128.78, 128.6, 128.30, 128.28, 128.1, 128.04, 127.99, 127.8, 127.7, 127.5, 127.42, 127.38, 127.3, 127.1, 127.0, 126.9, 126.1, 125.9, 125.5, 124.6, 123.8, 123.7, 122.8, 122.3, 122.1, 119.5, 119.0, 110.0. HRMS Calculated for $C_{66}H_{45}N_4^+$, 893.3644, found 893.3636.

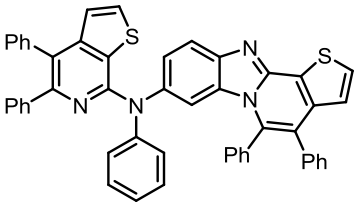
2-chloro-N-(7-chloro-3,4-diphenylisoquinolin-1-yl)-N,5,6-triphenylbenzo[4,5]imidazo[2,1-a]isoquinolin-9-amine (3ja). 
Yellow solid (isolated yield 54%). mp 182.6-183.9 ℃. Petroleum ether/ethyl acetate = 4:1. ^{1}H NMR (400 MHz, $CDCl_3$) δ = 8.94 (d, *J*=2.1, 1H), 7.92 (d, *J*=8.8, 1H), 7.69 (d, *J*=2.0, 1H), 7.59 (d, *J*=9.1, 1H), 7.46 (dd, *J*=8.7, 2.2, 1H), 7.44 – 7.35 (m, 5H), 7.29 (dd, *J*=7.4, 1.9, 2H), 7.23 (dd, *J*=8.2, 5.6, 6H), 7.15 – 6.99 (m, 10H), 6.94 (d, *J*=7.6, 2H), 6.82 (t, *J*=7.6, 2H), 6.71 (s, 1H), 5.50 (d, *J*=2.0, 1H). ^{13}C NMR (101 MHz, $CDCl_3$) δ = 149.1, 147.9, 142.7, 140.9, 139.8, 137.6, 137.3, 135.2, 133.9, 132.9, 132.0, 131.6, 131.3, 131.2, 130.6, 130.3, 129.9, 129.2, 128.7, 128.4, 128.3, 128.1, 128.0, 127.5, 127.4, 127.2, 125.1, 124.2, 123.6, 123.1, 122.7, 122.4, 120.0, 110.0. HRMS Calculated for $C_{54}H_{35}Cl_2N_4^+$, 809.2239, found 809.2244.

11-chloro-N-(2-chlorophenyl)-N-(3,4-diphenylisoquinolin-1-yl)-5,6-diphenylbenzo[4,5]imidazo[2,1-a]isoquinolin-9-amine (3ka). 
Yellow solid (isolated yield 51%). mp 206.8-209.6 ℃. Petroleum ether/ethyl acetate = 4:1. ^{1}H NMR (400 MHz, $CDCl_3$) δ = 9.11 (d, *J*=6.9 Hz, 1H), 7.72 – 7.62 (m, 3H), 7.61 – 7.49 (m, 1H), 7.48 – 7.35 (m, 5H), 7.34 – 7.26 (m, 3H), 7.25 – 7.17 (m, 5H), 7.17 – 7.08 (m, 6H), 7.08 – 7.00 (m, 4H), 7.00 – 6.94 (m, 2H), 6.85 (t, *J*=7.4 Hz, 1H), 6.78 (t, *J*=7.2 Hz, 2H), 5.32 (d, *J*=1.9 Hz, 1H). ^{13}C NMR (101 MHz, $CDCl_3$) δ = 171.2, 155.5, 148.0, 145.0, 142.7, 140.2, 139.1, 137.8, 136.0, 135.3, 134.8, 132.6, 132.4, 132.0, 131.4, 131.3, 131.0, 130.6, 130.3, 130.1, 129.9, 129.7, 129.6, 128.5, 128.4, 128.2, 128.0, 127.9, 127.7, 127.7, 127.4, 127.3, 126.9, 126.3, 126.18, 126.15, 126.1, 126.0, 125.5, 124.2, 124.13, 124.10, 122.8, 122.0, 121.1, 107.4. HRMS Calculated for $C_{54}H_{35}Cl_2N_4^+$, 809.2239, found 809.2233.

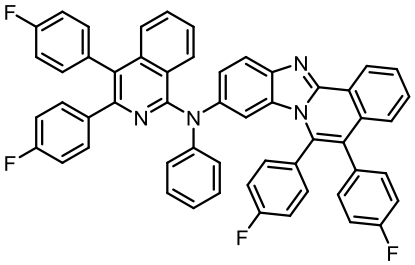
N-(3,4-diphenylisoquinolin-1-yl)-11-methyl-5,6-diphenyl-N-(o-tolyl)benzo[4,5]imidazo[2,1-a]isoquinolin-9-amine (3la). 
Yellow solid (isolated yield 41%). mp 205.7-207.1 ℃. Petroleum ether/ethyl acetate = 6:1. ^{1}H NMR (400 MHz, $CDCl_3$) δ 9.03 (s, 1H), 7.69 – 7.57 (m, 3H), 7.51 (t, *J* = 7.2 Hz, 1H), 7.45 – 7.36 (m, 4H), 7.31 (d, *J* = 6.4 Hz, 2H), 7.24 – 7.16 (m, 5H), 7.16 – 6.98 (m, 11H), 6.98 – 6.89 (m, 3H), 6.83 (t, *J* = 7.4 Hz, 1H), 6.75 (t, *J* = 7.2 Hz, 2H), 5.22 (d, *J* = 1.8 Hz, 1H), 2.80 (s, 3H), 1.95 (s, 3H). ^{13}C NMR (101 MHz, $CDCl_3$) δ = 156.5 147.9, 147.0, 146.7, 143.3, 140.4, 139.1, 138.2, 135.7, 135.1, 134.4, 133.0, 132.4, 132.2, 131.4, 131.3, 131.1, 131.0, 130.3, 130.0, 129.8, 129.6, 129.5, 129.3, 128.5, 128.2, 128.0, 127.9, 127.6, 127.3, 127.2, 127.1, 126.8, 126.5, 126.2, 126.1, 126.0, 125.7, 125.0, 123.1, 121.9, 121.8, 112.8, 106.3, 19.0, 17.3. HRMS Calculated for $C_{56}H_{41}N_4^+$, 769.3331, found 769.3326.

N-(7,8-diphenyl-[1,3]dioxolo[4,5-g]isoquinolin-5-yl)-N,5,6-triphenylbenzo[4,5]imidazo[2,1-a][1,3]dioxolo[4,5-g]isoquinolin-9-amine (3ma). 
Yellow solid (isolated yield 74%). mp 141.8-143.1 ℃. Petroleum ether/ethyl acetate = 4:1. ^{1}H NMR (400 MHz, $CDCl_3$) δ = 8.57 (d, *J*=8.4 Hz, 1H), 7.83 (d,

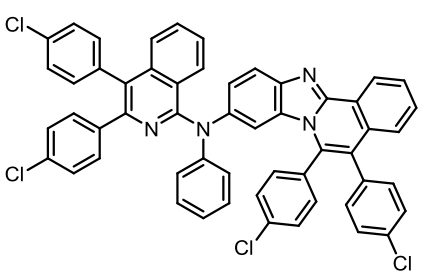
J=8.8 Hz, 1H), 7.43 (d, *J*=8.9 Hz, 1H), 7.35 – 7.26 (m, 6H), 7.24 – 7.16 (m, 3H), 7.14 – 7.07 (m, 5H), 7.07 – 6.97 (m, 8H), 6.96 – 6.88 (m, 3H), 6.83 (t, *J*=7.5 Hz, 2H), 6.74 (t, *J*=7.5 Hz, 1H), 5.81 (s, 2H), 5.75 (s, 2H), 5.38 (d, *J*=2.0 Hz, 1H). ^{13}C NMR (101 MHz, $CDCl_3$) δ = 157.0, 149.5, 148.9, 148.3, 147.4, 143.0, 142.5, 141.6, 140.1, 138.5, 136.5, 135.7, 132.7, 131.7, 131.2, 131.1, 130.3, 130.1, 129.0, 128.3, 128.1, 127.4, 127.3, 127.1, 127.0, 126.87, 126.86, 125.6, 123.6, 123.3, 122.5, 122.1, 121.9, 119.9, 119.819, 119.2, 119.1, 118.1, 117.0, 110.7, 110.1, 109.8, 101.4, 101.3. HRMS Calculated for $C_{56}H_{37}N_4O_4^+$, 829.2815, found 829.2809.



N-(4,5-diphenylthieno[2,3-c]pyridin-7-yl)-N,4,5-triphenylbenzo[4,5]imidazo[1,2-a]thieno[2,3-c]pyridin-8-amine (3na). Yellow solid (isolated yield 35%). mp 133.0-134.7 ℃. Petroleum ether/ethyl acetate = 4:1. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.92 (d, *J* = 8.8 Hz, 1H), 7.60 (d, *J* = 5.2 Hz, 1H), 7.43 (dd, *J* = 8.8 Hz, 2.0 Hz, 1H), 7.40 – 7.26 (m, 8H), 7.24 – 7.15 (m, 7H), 7.14 – 6.99 (m, 10H), 6.89 – 6.79 (m, 3H), 5.63 (d, *J* = 1.9 Hz, 1H). ^{13}C NMR (101 MHz, $CDCl_3$) δ = 151.5, 149.7, 149.3, 149.0, 148.7, 145.7, 142.1, 140.3, 139.9, 138.9, 138.7, 135.9, 134.9, 132.5, 131.7, 130.8, 130.7, 130.4, 130.1, 129.3, 128.8, 128.5, 128.5, 128.0, 127.6, 127.3, 127.1, 127.1, 126.2, 125.6, 125.4, 125.3, 125.1, 124.2, 123.8, 123.3, 121.5, 121.5, 119.2, 112.8. HRMS Calculated for $C_{50}H_{33}N_4S_2^+$, 753.2147, found 753.2141.



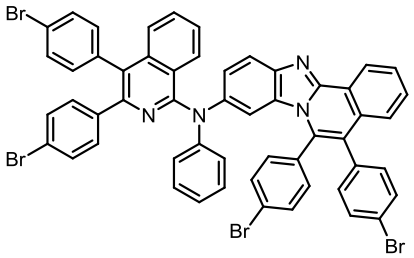
N-(3,4-bis(4-fluorophenyl)isoquinolin-1-yl)-5,6-bis(4-fluorophenyl)-N-phenylbenzo[4,5]imidazo[2,1-a]isoquinolin-9-amine (3ab). Yellow solid (isolated yield 70%). mp 188.8-190.3 ℃. Petroleum ether/ethyl acetate = 4:1. ^{1}H NMR (400 MHz, $CDCl_3$) δ = 8.97 (d, *J*=7.7 Hz, 1H), 7.94 (d, *J*=8.8 Hz, 1H), 7.69 (dd, *J*=7.8 Hz, 4.2 Hz, 2H), 7.64 – 7.53 (m, 2H), 7.51 – 7.45 (m, 1H), 7.36 (dd, *J*=8.8 Hz, 2.1 Hz, 1H), 7.33 – 7.19 (m, 2H), 7.16 – 7.03 (m, 7H), 7.03 – 6.89 (m, 6H), 6.75 (dd, *J*=12.2 Hz, 5.4 Hz, 2H), 6.50 (t, *J*=8.6 Hz, 2H), 5.73 (d, *J*=2.0 Hz, 1H). ^{13}C NMR (101 MHz, $CDCl_3$) δ =δ 162.28 (d, *J* = 250.4 Hz), 162.15 (d, *J* = 247.0 Hz), 161.98 (d, *J* = 247.1 Hz), 161.91 (d, *J* = 247.3 Hz), 156.7, 154.7, 148.3, 147.8, 147.5, 143.0, 139.2, 136.15 (d, *J* = 3.2 Hz), 134.2, 133.53 (d, *J* = 3.5 Hz), 133.04 (d, *J* = 8.1 Hz), 132.92 (d, *J* = 8.1 Hz), 132.2, 132.03 (d, *J* = 8.1 Hz), 131.80 (d, *J* = 8.3 Hz), 131.3, 129.9, 129.3, 129.1, 128.96 (d, *J* = 3.2 Hz), 128.8, 128.2, 126.5, 126.3, 126.18 (d, *J* = 2.9 Hz), 125.9, 124.9, 124.6, 123.6, 123.0, 122.5, 122.4, 119.7, 115.67 (d, *J* = 21.3 Hz), 115.65 (d, *J* = 21.8 Hz).115.23 (d, *J* = 21.4 Hz), 114.45 (d, *J* = 21.4 Hz), 109.4. ^{19}F NMR (376 MHz, $CDCl_3$) δ = -108.37, -109.39, -114.22, -114.54, -115.07. HRMS Calculated for $C_{54}H_{33}F_4N_4^+$, 813.2641, found 813.2636.



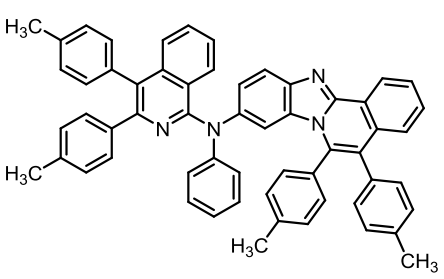
N-(3,4-bis(4-chlorophenyl)isoquinolin-1-yl)-5,6-bis(4-chlorophenyl)-N-phenylbenzo[4,5]imidazo[2,1-a]isoquinolin-9-amine (3ac). Yellow solid (isolated yield 46%). mp 125.3-126.6 ℃. Petroleum ether/ethyl acetate = 4:1. ^{1}H NMR (400 MHz, $CDCl_3$) δ = 9.00 (d, *J*=7.7 Hz, 1H), 7.93 (d,

J=8.8 Hz, 1H), 7.70 (dd, *J*=12.0 Hz, 6.0 Hz, 2H), 7.62 – 7.54 (m, 2H), 7.50 – 7.44 (m, 1H), 7.43 – 7.38 (m, 2H), 7.34 – 7.17 (m, 9H), 7.11 (t, *J*=7.4 Hz, 1H), 7.08 – 6.94 (m, 10H), 6.87 (d, *J*=8.4 Hz, 2H), 5.92 (d, *J*=1.9 Hz, 1H). ^{13}C NMR (101 MHz, $CDCl_3$) δ = 168.1, 156.9, 148.1, 147.2, 143.4, 139.0, 138.4, 136.0, 135.2, 133.8, 133.7, 133.6, 133.5, 133.2, 132.8, 132.6, 131.9, 131.6, 131.4, 131.1, 131.1, 130.1, 130.0, 129.3, 128.9, 128.9, 128.5, 128.4, 127.8, 126.4, 126.32, 126.29, 126.1, 125.9, 125.09, 125.08, 124.6, 123.9, 123.1, 123.0, 122.8, 122.2, 119.5, 109.9. HRMS Calculated for $C_{54}H_{33}Cl_4N_4^+$, 877.1459, found 877.1448.

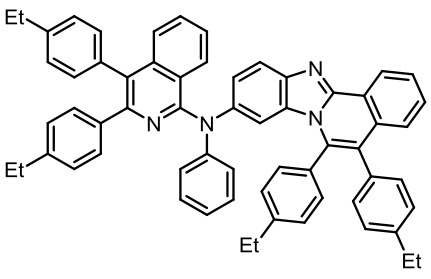
N-(3,4-bis(4-bromophenyl)isoquinolin-1-yl)-5,6-bis(4-bromophenyl)-N-phenylbenzo[4,5]imidazo[2,1-a]isoquinolin-9-amine (3ad). Yellow solid (isolated yield 33%). mp 257.2-258.6 ℃. Petroleum ether/ethyl acetate = 4:1. ^{1}H NMR (400 MHz, $CDCl_3$) δ = 8.94 (d, *J*=8.0 Hz, 1H), 7.89 (d, *J*=8.8 Hz, 1H), 7.69 (t, *J*=7.8 Hz, 2H), 7.54 (dd, *J*=10.5 Hz, 4.7 Hz, 4H), 7.45 (dd, *J*=8.2 Hz, 7.1 Hz, 1H), 7.39 (d, *J*=8.3 Hz, 2H), 7.31 – 7.15 (m, 9H), 7.12 (t, *J*=7.4 Hz, 1H), 7.05 (d, *J*=8.4 Hz, 2H), 7.02 – 6.90 (m, 8H), 5.96 (d, *J*=1.9 Hz, 1H). ^{13}C NMR (101 MHz, $CDCl_3$) δ = 157.0, 148.3, 147.7, 147.1, 143.2, 141.0, 138.93, 138.88, 136.6, 134.4, 133.9, 133.1, 133.0, 132.0, 131.9, 131.8, 131.7, 131.6, 131.5, 131.3, 130.7, 130.0, 129.9, 129.3, 128.2, 126.4, 126.2, 126.1, 125.9, 124.9, 124.6, 123.9, 123.5, 123.2, 123.0, 122.6, 122.2, 121.8, 121.7, 121.6, 119.8, 110.1. HRMS Calculated for $C_{54}H_{33}Br_4N_4^+$, 1052.9439, found 1052.9411.



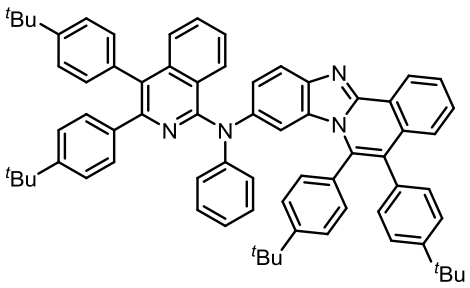
N-(3,4-di-p-tolylisoquinolin-1-yl)-N-phenyl-5,6-di-p-tolylbenzo[4,5]imidazo[2,1-a]isoquinolin-9-amine (3ae). Yellow solid (isolated yield 55%). mp 154.9-155.8 ℃. Petroleum ether/ethyl acetate = 4:1. ^{1}H NMR (400 MHz, $CDCl_3$) δ = 9.17 (d, *J*=7.4 Hz, 1H), 8.08 (d, *J*=8.8 Hz, 1H), 7.91 – 7.82 (m, 3H), 7.78 – 7.71 (m, 1H), 7.65 – 7.60 (m, 1H), 7.52 (d, *J*=8.1 Hz, 1H), 7.50 – 7.36 (m, 10H), 7.26 – 7.14 (m, 9H), 7.06 (d, *J*=8.0 Hz, 2H), 6.91 (d, *J*=7.8 Hz, 2H), 6.05 (d, *J*=1.9 Hz, 1H), 2.65 (s, 3H), 2.51 (s, 3H), 2.41 (s, 3H), 2.02 (s, 3H).^{13}C NMR (101 MHz, $CDCl_3$) δ = 156.6, 148.5, 148.4, 147.9, 142.8, 140.9, 139.4, 138.7, 137.4, 136.8, 136.6, 136.5, 135.3, 135.0, 132.8, 132.8, 131.7, 131.3, 131.2, 130.3, 130.2, 129.9, 129.5, 129.4, 129.3, 129.1, 128.9, 128.7, 128.2, 127.5, 127.1, 126.4, 126.21, 126.17, 125.8, 124.7, 123.7, 123.12, 123.10, 122.7, 122.6, 122.5, 119.4, 110.8. HRMS Calculated for $C_{58}H_{45}N_4^+$, 797.3644, found 797.3639.



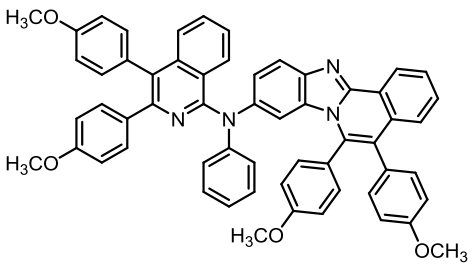
N-(3,4-bis(4-ethylphenyl)isoquinolin-1-yl)-5,6-bis(4-ethylphenyl)-N-phenylbenzo[4,5]imidazo[2,1-a]isoquinolin-9-amine (3af). Yellow solid (isolated yield 38%). mp 110.8-112.5 ℃. Petroleum ether/ethyl acetate = 4:1. ^{1}H NMR (400 MHz, $CDCl_3$) δ = 8.99 (d, *J*=7.9 Hz, 1H), 7.88 (d, *J*=8.8 Hz, 1H), 7.66 (dd, *J*=11.7 Hz, 4.6 Hz, 2H), 7.61 (d, *J*=8.5 Hz, 1H), 7.59 – 7.50 (m, 1H), 7.40 (ddd, *J*=8.3 Hz, 6.9 Hz, 1.1 Hz, 1H), 7.34 (d, *J*=8.1 Hz, 1H), 7.25 – 7.14 (m, 8H), 7.08 – 7.00 (m, 8H), 6.98 (t, *J*=7.3 Hz, 1H), 6.92 (d, *J*=7.6 Hz, 2H), 6.85 (d, *J*=8.2



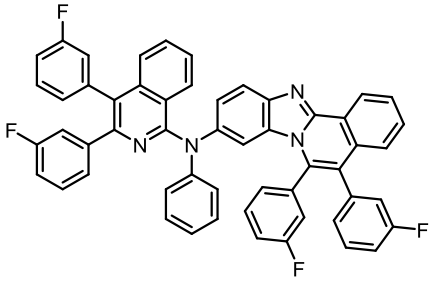
Hz, 2H), 6.74 (d, *J*=8.0 Hz, 2H), 5.96 (d, *J*=2.0 Hz, 1H), 2.73 (q, *J*=7.6 Hz, 2H), 2.58 (q, *J*=7.6 Hz, 2H), 2.48 (q, *J*=7.6 Hz, 2H), 2.12 (q, *J*=7.6 Hz, 2H), 1.31 (t, *J*=7.6 Hz, 3H), 1.18 (t, *J*=7.6 Hz, 3H), 1.09 (t, *J*=7.6 Hz, 3H), 0.88 (dd, *J*=7.2 Hz, 3.2 Hz, 3H). ^{13}C NMR (101 MHz, $CDCl_3$) δ = 158.6, 156.5, 148.6, 148.3, 147.7, 144.8, 143.1, 142.9, 142.8, 142.7, 140.4, 139.4, 137.6, 135.4, 135.1, 132.9, 132.8, 131.5, 131.3, 131.3, 130.4, 130.3, 130.0, 129.7, 129.4, 128.9, 128.0, 127.7, 127.3, 126.9, 126.4, 126.2, 126.1, 125.8, 124.9, 123.5, 123.4, 123.1, 122.8, 122.5, 122.4, 121.8, 119.2, 111.1, 28.6, 28.5, 28.4, 28.0, 15.5, 15.31, 15.28, 14.5. HRMS Calculated for $C_{62}H_{53}N_4^+$, 853.4270, found 853.4265.



N-(3,4-bis(4-(tert-butyl)phenyl)isoquinolin-1-yl)-5,6-bis(4-(tert-butyl)phenyl)-N-phenylbenzo[4,5]imidazo[2,1-a]isoquinolin-9-amine (3ag). Yellow solid (isolated yield 59%). mp 198.4-199.7 ℃. Petroleum ether/ethyl acetate = 4:1. ^{1}H NMR (400 MHz, $CDCl_3$) δ = 8.98 (d, *J*=7.8 Hz, 1H), 7.87 (d, *J*=8.7 Hz, 1H), 7.75 – 7.64 (m, 2H), 7.63 – 7.52 (m, 2H), 7.45 (d, *J*=7.9 Hz, 1H), 7.39 (dd, *J*=10.4 Hz, 4.8 Hz, 3H), 7.19 (dd, *J*=8.1 Hz, 4.0 Hz, 5H), 7.17 – 7.08 (m, 5H), 7.06 – 6.99 (m, 6H), 6.99 – 6.91 (m, 3H), 6.90 – 6.85 (m, 2H), 6.45 (d, *J*=1.9 Hz, 1H), 1.38 (s, 9H), 1.24 (s, 9H), 1.17 (s, 9H), 0.95 (s, 9H). ^{13}C NMR (101 MHz, $CDCl_3$) δ = 156.4, 154.7, 151.8, 150.1, 149.7, 149.6, 148.8, 148.3, 148.0, 142.3, 141.1, 139.4, 137.3, 135.5, 134.9, 132.7, 132.6, 131.6, 131.1, 131.0, 130.2, 129.9, 129.9, 129.6, 129.4, 128.8, 127.54, 127.52, 126.5, 126.3, 126.1, 125.8, 125.2, 124.9, 124.8, 124.5, 124.2, 123.8, 123.7, 123.0, 122.6, 122.1, 119.3, 111.7, 34.6, 34.4, 34.31, 34.29, 31.4, 31.23, 31.19, 30.9. HRMS Calculated for $C_{70}H_{69}N_4^+$, 965.5522, found 965.5517.

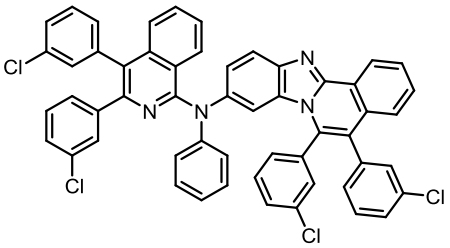


N-(3,4-bis(4-methoxyphenyl)isoquinolin-1-yl)-5,6-bis(4-methoxyphenyl)-N-phenylbenzo[4,5]imidazo[2,1-a]isoquinolin-9-amine (3ah). Yellow solid (isolated yield 34%). mp 146.4-147.9 ℃. Petroleum ether/ethyl acetate = 4:1. ^{1}H NMR (400 MHz, $CDCl_3$) δ = 8.99 (d, *J*=7.9 Hz, 1H), 7.91 (d, *J*=8.8 Hz, 1H), 7.65 (ddd, *J*=16.3 Hz, 11.2 Hz, 5.9 Hz, 3H), 7.58 – 7.50 (m, 1H), 7.41 (ddd, *J*=8.4 Hz, 6.8 Hz, 1.2 Hz, 1H), 7.35 – 7.24 (m, 4H), 7.24 – 7.13 (m, 3H), 7.11 – 7.05 (m, 2H), 7.05 – 6.92 (m, 9H), 6.80 – 6.72 (m, 2H), 6.63 – 6.54 (m, 2H), 6.41 – 6.33 (m, 2H), 5.93 (d, *J*=1.9 Hz, 1H), 3.87 (s, 3H), 3.76 (s, 3H), 3.68 (s, 3H), 3.40 (s, 3H). ^{13}C NMR (101 MHz, $CDCl_3$) δ = 159.4, 158.8, 158.6, 158.5, 156.4, 151.0, 148.4, 148.0, 147.40, 147.39, 143.0, 139.8, 135.2, 132.94, 132.92, 132.5, 132.4, 131.6, 131.5, 131.2, 130.3, 129.8, 129.4, 128.9, 127.9, 127.8, 126.8, 126.4, 126.2, 125.6, 125.3, 124.9, 124.0, 123.7, 122.8, 122.7, 122.3, 119.2, 114.1, 113.7, 113.4, 112.9, 112.4, 110.3, 55.3, 55.1, 55.1, 54.9. HRMS Calculated for $C_{58}H_{45}N_4O_4^+$, 861.3441, found 861.3436.

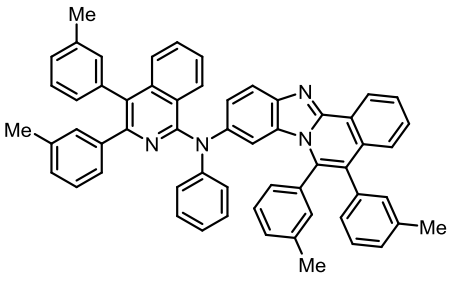


N-(3,4-bis(3-fluorophenyl)isoquinolin-1-yl)-5,6-bis(3-fluorophenyl)-N-phenylbenzo[4,5]imidazo[2,1-a]isoquinolin-9-amine (3ai). Yellow solid (isolated yield 60%). mp 102.8-104.6 ℃. Petroleum ether/ethyl acetate = 4:1. ^{1}H NMR (400 MHz, $CDCl_3$) δ = 8.97 (d, *J*=7.9 Hz, 1H), 7.94 (d, *J*=8.8 Hz, 1H), 7.79 – 7.67 (m, 2H), 7.64 – 7.54 (m, 2H),

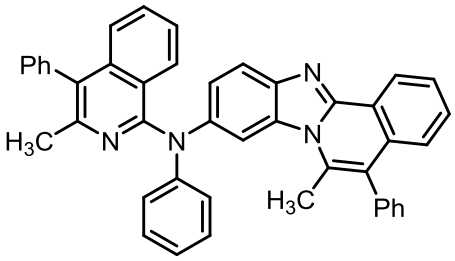
7.54 – 7.47 (m, 1H), 7.45 – 7.34 (m, 2H), 7.32 – 7.15 (m, 7H), 7.15 – 6.72 (m, 16H), 6.48 – 6.36 (m, 1H), 5.62 (d, *J*=2.0 Hz, 1H). ^{13}C NMR (101 MHz, $CDCl_3$) δ = 162.34 (d, *J* = 247.2 Hz), 162.18 (d, *J* = 244.5 Hz), 162.04 (d, *J* = 249.7 Hz), 162.00 (d, *J* = 249.1 Hz), 161.67 (d, *J* = 7.3 Hz), 157.1, 148.0, 147.3, 143.1, 142.14 (dd, *J* = 7.7, 1.5 Hz), 140.35 (d, *J* = 3.4 Hz), 139.64 (d, *J* = 7.9 Hz), 138.8, 137.36 (d, *J* = 8.0 Hz), 134.66 (d, *J* = 1.5 Hz), 134.6, 133.5, 131.7, 131.3, 130.3, 130.12 (d, *J* = 24.5 Hz), 130.2, 130.1, 129.78 (d, *J* = 5.4 Hz), 129.70 (d, *J* = 5.5 Hz), 129.2, 128.98 (d, *J* = 8.3 Hz), 128.3, 127.18, 127.16, 127.0, 126.8, 126.3, 126.1, 125.92 (d, *J* = 7.1 Hz), 125.0, 123.80, 123.75, 123.2, 123.0, 122.5, 119.8, 118.4, 118.2, 117.24 (d, *J* = 3.4 Hz), 117.07 (d, *J* = 22.8 Hz), 117.02 (d, *J* = 3.5 Hz), 116.1, 115.8, 115.64 (d, *J* = 1.5 Hz), 114.63 (d, *J* = 20.8 Hz), 114.18 (d, *J* = 21.3 Hz). ^{19}F NMR (376 MHz, $CDCl_3$) δ -110.11 (d, *J* = 120.6 Hz), -112.51 (dd, *J* = 46.8, 7.2 Hz), -112.87 (d, *J* = 88.3 Hz), -113.92 (d, *J* = 4.2 Hz). HRMS Calculated for $C_{54}H_{33}F_4N_4^+$, 813.2641, found 813.2638.

N-(3,4-bis(3-chlorophenyl)isoquinolin-1-yl)-5,6-bis(3-chlorophenyl)-N-phenylbenzo[4,5]imidazo[2,1-a]isoquinolin-9-amine (3aj). 

Yellow solid (isolated yield 64%). mp 129.4-130.6 ℃. Petroleum ether/ethyl acetate = 4:1. ^{1}H NMR (400 MHz, $CDCl_3$) δ = 8.94 (d, *J*=7.6 Hz, 1H), 7.92 (d, *J*=8.8 Hz, 1H), 7.80 (d, *J*=8.5 Hz, 1H), 7.69 (t, *J*=7.2 Hz, 1H), 7.63 – 7.47 (m, 3H), 7.37 (ddd, *J*=15.9 Hz, 8.3 Hz, 1.7 Hz, 4H), 7.32 – 7.27 (m, 1H), 7.24 – 7.05 (m, 11H), 7.04 – 6.90 (m, 6H), 6.75 (dd, *J*=8.5 Hz, 5.4 Hz, 2H), 5.71 (d, *J*=1.8 Hz, 1H). ^{13}C NMR (101 MHz, $CDCl_3$) δ = 157.2, 148.1, 147.6, 147.3, 143.0, 141.6, 140.8, 139.3, 138.8, 137.1, 134.6, 134.5, 134.3, 134.1, 134.0, 133.6, 133.5, 131.6, 131.4, 131.3, 131.2, 130.5, 130.3, 130.0, 129.9, 129.7, 129.6, 129.53, 129.50, 129.45, 129.2, 128.9, 128.8, 128.3, 128.3, 128.1, 127.9, 127.4, 126.9, 126.8, 126.3, 126.2, 125.9, 124.9, 124.0, 123.3, 123.3, 123.1, 122.5, 122.4, 119.9, 109.3. HRMS Calculated for $C_{54}H_{33}Cl_4N_4^+$, 877.1459, found 877.1458.

N-(3,4-di-m-tolylisoquinolin-1-yl)-N-phenyl-5,6-di-m-tolylbenzo[4,5]imidazo[2,1-a]isoquinolin-9-amine (3ak). 

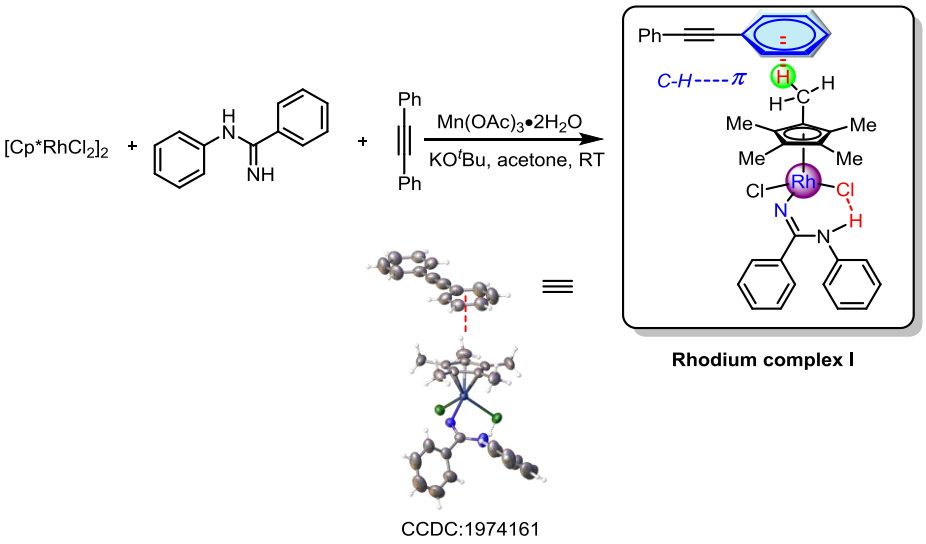
Yellow solid (isolated yield 66%). mp 99.8-100.7 ℃. Petroleum ether/ethyl acetate = 4:1. ^{1}H NMR (400 MHz, $CDCl_3$) δ = 8.97 (d, *J*=7.9 Hz, 1H), 7.92 (d, *J*=8.8 Hz, 1H), 7.74 (d, *J*=8.5 Hz, 1H), 7.70 – 7.63 (m, 2H), 7.54 (t, *J*=7.8 Hz, 1H), 7.47 (t, *J*=7.6 Hz, 1H), 7.39 (d, *J*=8.8 Hz, 1H), 7.36 – 7.16 (m, 7H), 7.15 – 6.83 (m, 13H), 6.79 (d, *J*=7.6 Hz, 1H), 6.62 (t, *J*=7.6 Hz, 1H), 6.52 – 6.40 (m, 1H), 5.58 (dd, *J*=8.7 Hz, 2.7 Hz, 1H), 2.43 – 2.29 (m, 3H), 2.23 (d, *J*=18.8 Hz, 3H), 2.09 (s, 3H), 1.88 (d, *J*=3.6 Hz, 3H). ^{13}C NMR (101 MHz, $CDCl_3$) δ = 156.6, 148.7, 148.4, 147.4, 142.8, 140.1, 139.3, 138.1, 138.01, 137.96, 137.9, 137.8, 137.5, 137.3, 136.8, 135.5, 135.1, 133.3, 132.9, 132.6, 132.6, 132.2, 132.0, 131.9, 131.6, 131.3, 130.7, 129.7, 129.6, 129.1, 128.9, 128.54, 128.47, 128.4, 128.3, 128.2, 128.0, 127.96, 127.9, 127.8, 127.7, 127.68, 127.6, 127.4, 127.2, 126.8, 126.4, 126.3, 126.1, 124.9, 123.5, 123.1, 122.5, 122.3, 119.3, 110.1, 21.52 (d, *J* = 6.6 Hz) , 21.4, 21.34 (d, *J* = 2.0 Hz), 21.2. HRMS Calculated for $C_{58}H_{45}N_4^+$, 797.3644, found 797.3639.

6-methyl-N-(3-methyl-4-phenylisoquinolin-1-yl)-N,5-diphenylbenzo[4,5]imidazo[2,1-a]isoquinolin-9-amine (3ap). 

Yellow solid (isolated yield 21%), Petroleum ether/ethyl acetate = 4:1. ^{1}H NMR (400 MHz, $CDCl_3$) δ = 8.96 (s, 1H), 8.11 (d, *J*=8.5, 1H), 7.85 (dd, *J*=9.1, 3.5, 2H), 7.69 (ddd, *J*=10.2, 9.7, 4.8, 4H), 7.49 – 7.44 (m, 2H), 7.41 – 7.26 (m, 6H), 7.20 – 7.13 (m, 2H), 7.09 – 7.03 (m, 2H), 6.92 (ddd, *J*=21.5, 16.1, 7.5, 5H), 6.79 (t, *J*=7.5, 1H), 2.79 (s, 3H), 2.19 (s, 3H). ^{13}C NMR (101 MHz, $CDCl_3$) δ = 155.5, 150.4, 148.2, 142.9, 140.8, 139.4, 134.5, 134.1, 133.7, 132.1, 131.3, 131.1, 130.2, 129.8, 129.4, 128.9, 128.7, 128.6, 127.9, 127.8, 127.8, 127.5, 127.0, 126.8, 126.2, 125.29, 125.28, 124.1, 124.0, 123.6, 123.2, 122.4, 121.6, 121.3, 119.1, 108.9, 29.7, 22.7.

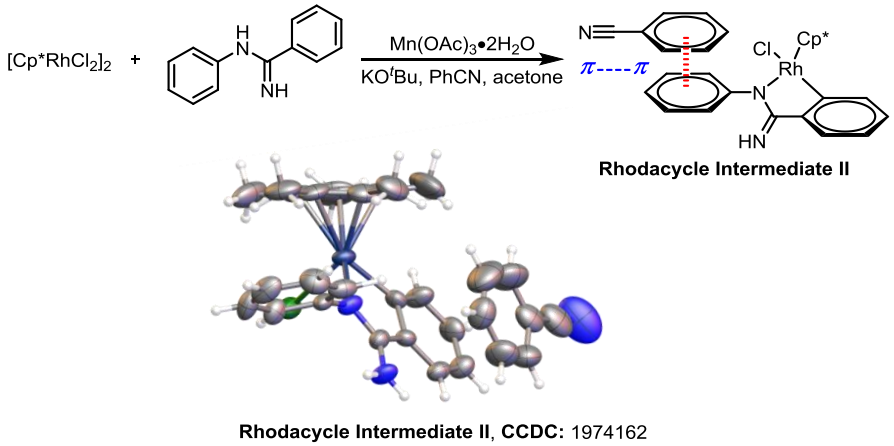
5. Procedures of mechanistic studies

5.1 Synthesis of Rh(III) complex I



N-phenylbenzimidamide **1a** (2.5 mg, 0.0125 mmol), $[RhCp^*Cl_2]_2$ (7.7 mg, 0.0125 mmol), 1,2-diphenylethyne **2a** (2.2 mg, 0.0125 mmol), $Mn(OAc)_3{\cdot}2H_2O$ (3.4 mg, 0.125 mmol), KO^tBu (1.4 mg, 0.0125 mmol), and acetone (2 mL) were charged into an oven dried reaction tube and then stirred for 5 min at room temperature under air atmosphere. The reaction mixture was recrystallized with n-petane to afford the intermediate **Rhodium complex I**, which was further confirmed by single-crystal X-ray crystallography.

5.2 Synthesis of Rhodacycle Intermediate II



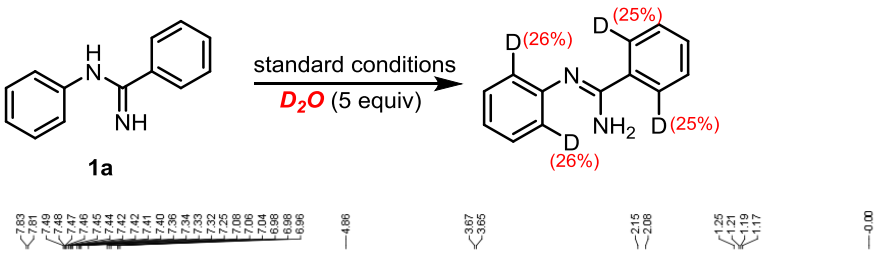
Rhodacycle Intermediate II, **CCDC:** 1974162

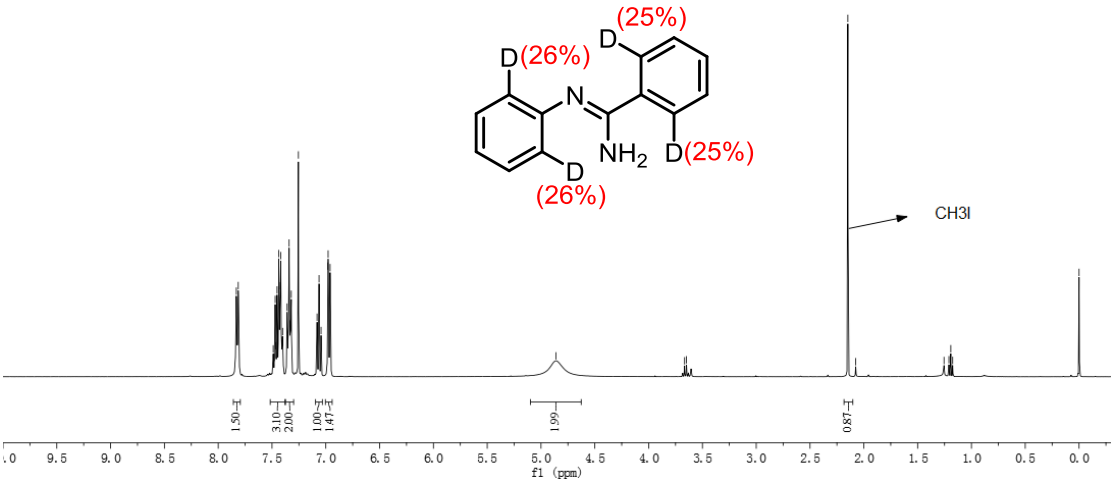
N-phenylbenzimidamide **1a** (2.5 mg, 0.0125 mmol), $[RhCp^*Cl_2]_2$ (7.7 mg, 0.0125 mmol), $Mn(OAc)_3{\cdot}2H_2O$ (3.4 mg, 0.125 mmol) and KO^tBu (1.4 mg, 0.0125 mmol), PhCN (2.6 uL, 0.025

mmol), and acetone (2 mL) were charged into an oven dried reaction tube and then stirred for 5 min at room temperature under air atmosphere. The reaction mixture was recrystallized with *n*-petane to afford the intermediate **Rhodacycle Intermediate II**, which was further confirmed by single-crystal X-ray crystallography.

5.3 H/D exchange experiment

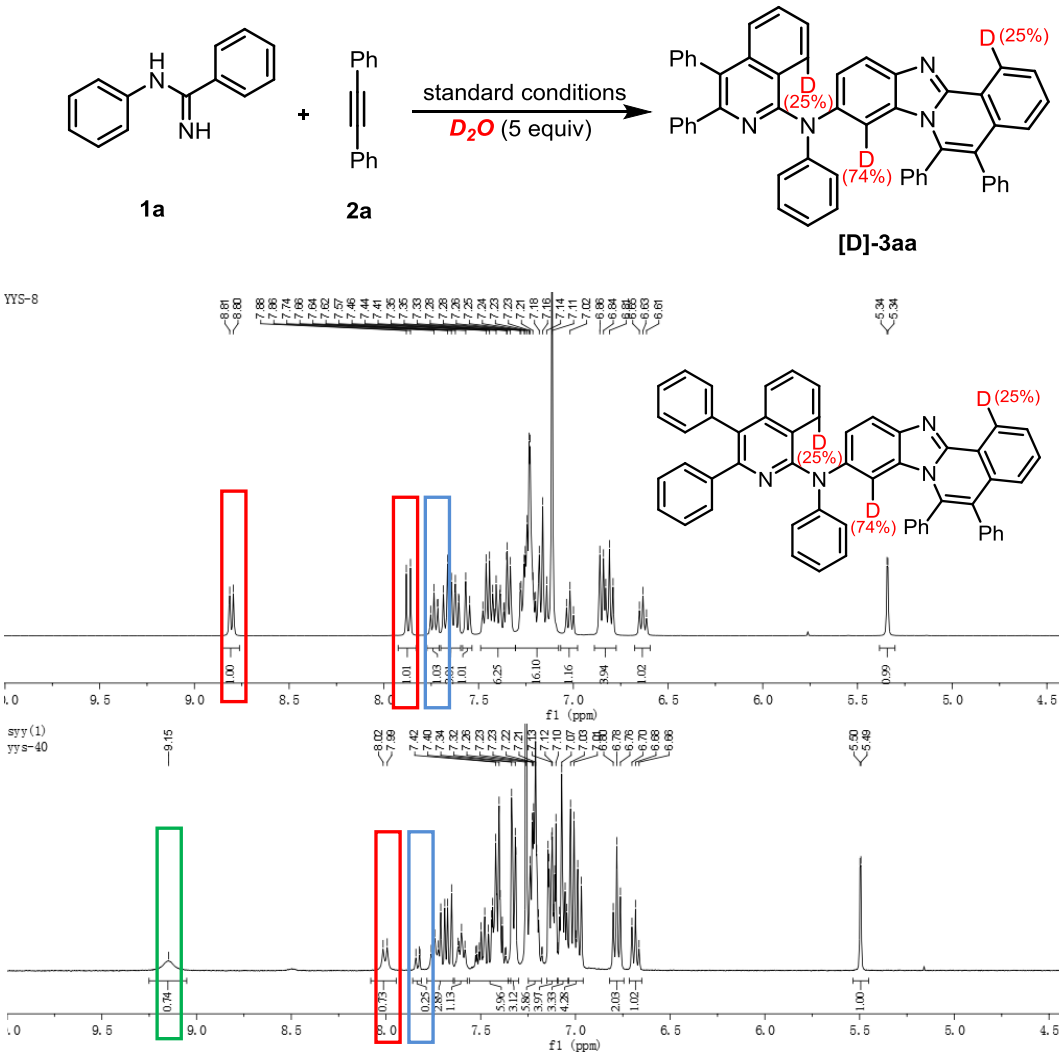
Under an atmospheric condition, amidine **1a** (24.5 mmol, 0.125 mmol), $Mn(OAc)_3 \cdot 2H_2O$ (6 equiv, 201.1 mg), KO^{t}Bu (20%), PhCN (20%, 25.6 uL), D_2O (5 equiv) and DCE (4 mL) were charged into a 25 mL vial equipped with a stir bar. The reaction mixture was stirred at 40 ^oC for 48 h. Solvent was removed under reduced pressure to leave a crude mixture, and the H/D exchange product was isolated.



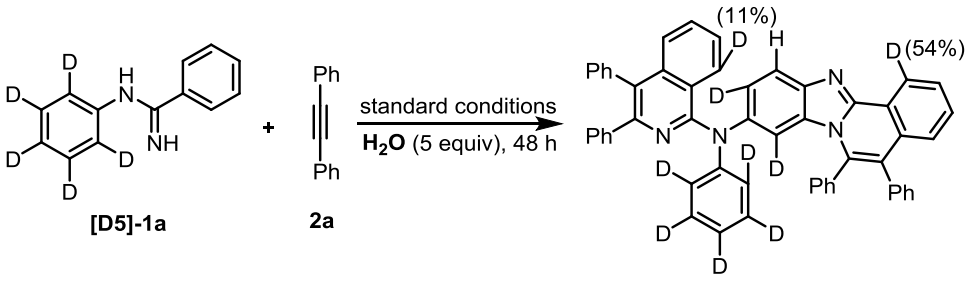


Under an atmospheric condition, amidine **1a** (24.5 mmol, 0.125 mmol), 1,2-diphenylethyne **2a** (0.375mmol, 66.8 mg), $Mn(OAc)_3 \cdot 2H_2O$ (6 equiv, 201.1 mg), KO^{t}Bu (20%), PhCN (20%, 25.6 uL), D_2O (5 equiv) and DCE (4 mL) were charged into a 25 mL vial. The reaction mixture was

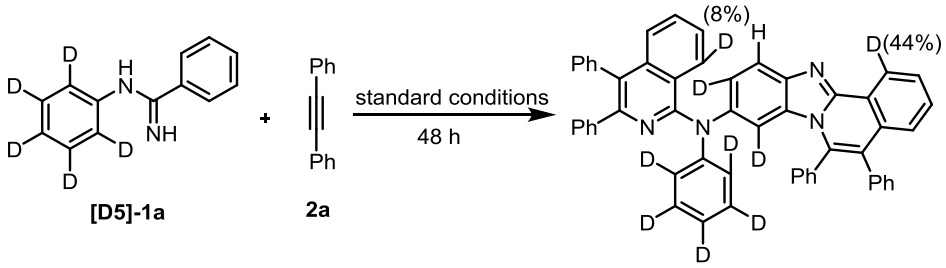
stirred at 40 °C for 48 h. Solvent was removed under reduced pressure to leave a crude mixture, and the **H/D exchange** product was isolated.

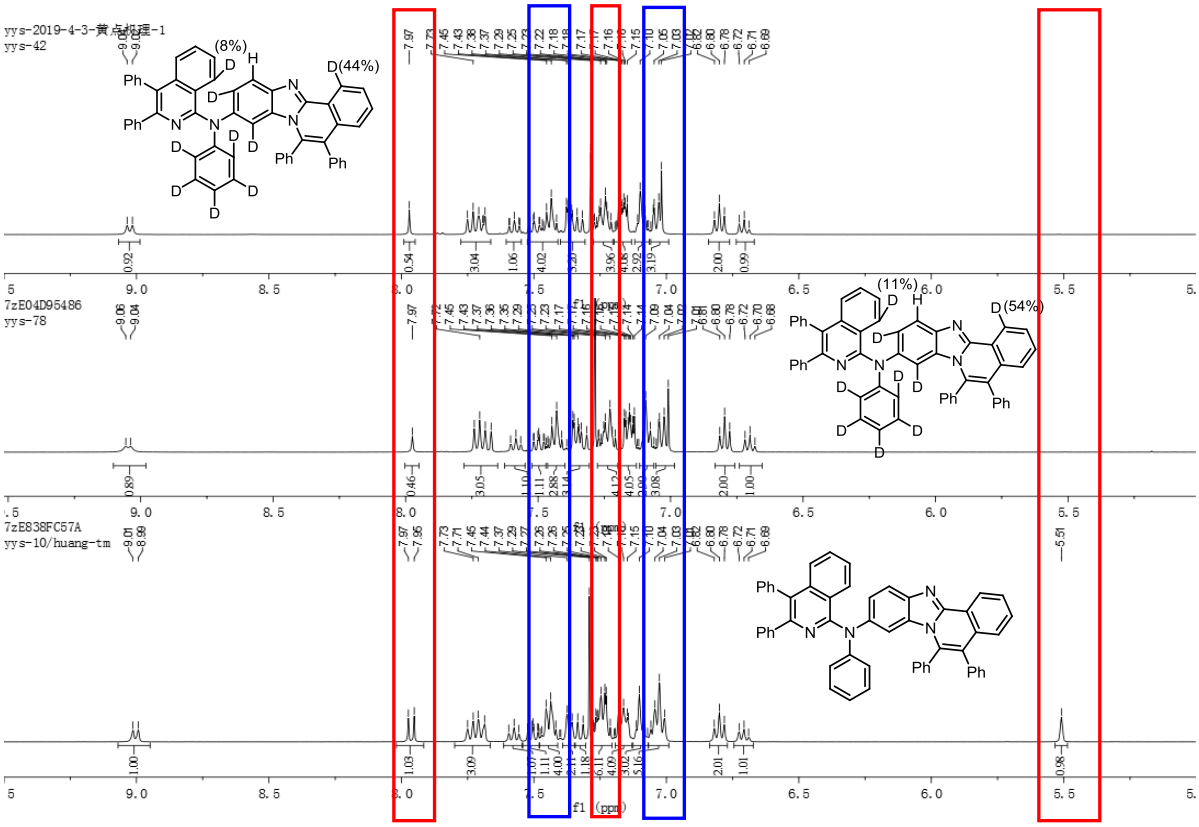


Under an atmospheric condition, [D_5]-**1a** (24.5 mg, 0.125 mmol), 1,2-diphenylethyne **2a** (0.375mmol, 66.8 mg), $Mn(OAc)_3$ $2H_2O$ (6 equiv, 201.1 mg), KO^{t}Bu (20%), PhCN (20%, 25.6 uL), H_2O (5 equiv) and DCE (4 mL) were charged into a 25 mL vial. The reaction mixture was stirred at 40 °C for 48 h. Solvent was removed under reduced pressure to leave a crude mixture, and the H/D exchange product was isolated in 63% yield. The corresponding product was determined by ^{1}H NMR using CH_3I (5.0 uL) as the internal standard.

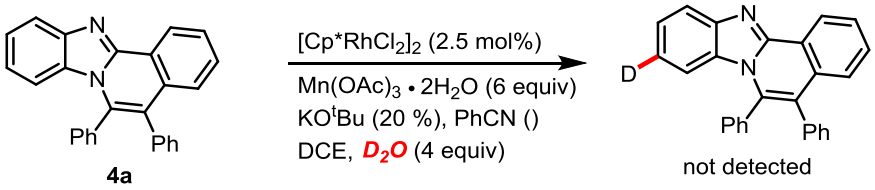


Under an atmospheric condition, [D_5]-**1a** (25.2 mg, 0.125 mmol), 1,2-diphenylethyne **2a** (0.375mmol, 66.8 mg), $Mn(OAc)_3$ $2H_2O$ (6 equiv, 201.1 mg), KO^{t}Bu (20%), PhCN (20%, 25.6 uL), and DCE (4 mL) were charged into a 25 mL vial equipped with a stir bar. The reaction mixture was stirred at 40 ^oC for 48 h, then the mixture was cooled and filtered through a short column of silica gel (eluent PE). Solvent was removed under reduced pressure to leave a crude mixture, and the H/D exchange product was isolated.

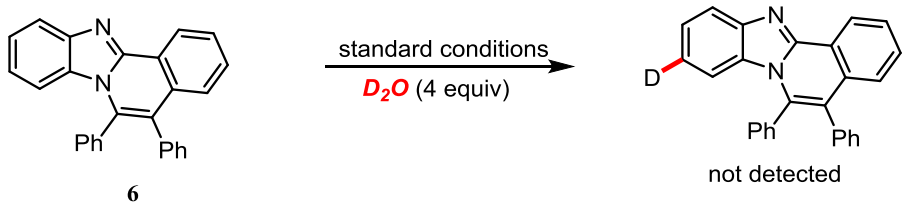




Under an atmospheric condition, 5,6-diphenylbenzo[4,5]imidazo[2,1-a]isoquinoline **6** (24.5 mmol, 0.125 mmol), $Mn(OAc)_3$ $2H_2O$ (6 equiv, 201.1 mg), KO^{t}Bu (20%), PhCN (20%, 25.6 uL), D_2O (4 equiv) and DCE (4 mL) were charged into a 25 mL vial. The reaction mixture was stirred at 40 ^oC for 48 h. Solvent was removed under reduced pressure to leave a crude mixture, and the H/D exchange product was not detected.



Reaction among **6** with 4 equiv of D_2O gave no H/D exchange, and **6** was recovered in 99% yield, suggesting that the meta C-H activation might not undergo CDM mechanism.

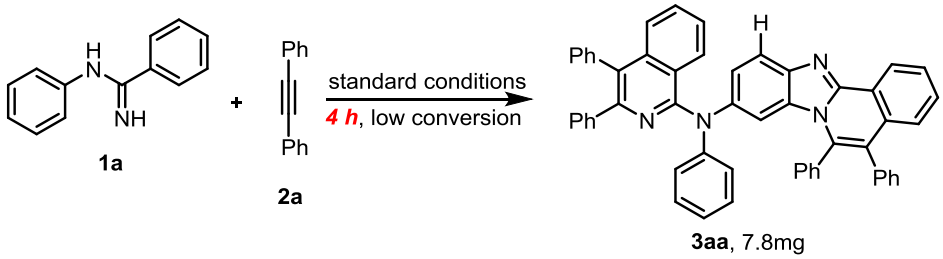


5.4 Kinetic Isotope Study

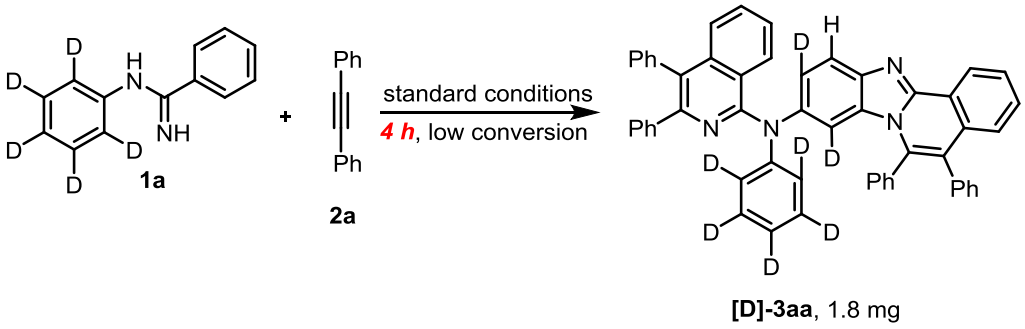
The kinetic isotope effect (KIE) was first investigated in parallel experiments between equimolar amounts of **1a** or **[D_5]-1a** and **2a** for 4 h, and a KIE of k_H/k_D =4.3:1 was observed. Subsequently, an intermolecular competition experiment was also conducted. However, an inseparable mixture was obtained.

5.4.1 In parallel experiments

Under an atmospheric condition, amidine **1a** (24.5 mg, 0.125 mmol), 1,2-diphenylethyne **2a** (0.375 mmol, 66.8 mg), $Mn(OAc)_3$ $2H_2O$ (6 equiv, 201.1 mg), KO^{t}Bu (20%), PhCN (20%, 25.6 uL), and DCE (4 mL) were charged into a 25 mL vial equipped with a stir bar. The reaction mixture was stirred at 40 ^oC for 4 h to keep low conversion, then the mixture was cooled and filtered through a short column of silica gel (eluent PE). Solvent was removed under reduced pressure to leave a crude mixture, and the product **3aa** was isolated (7.8 mg).



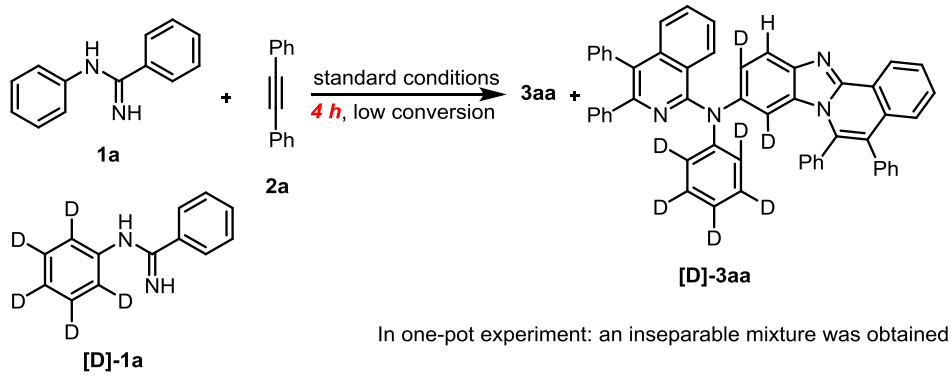
Under an atmospheric condition, [D_5]-**1a** (25.2 mg, 0.125 mmol), 1,2-diphenylethyne **2a** (0.375 mmol, 66.8 mg), $Mn(OAc)_3 \cdot 2H_2O$ (6 equiv, 201.1 mg), KO^{t}Bu (20%), PhCN (20%, 25.6 uL), and DCE (4 mL) were charged into a 25 mL vial equipped with a stir bar. The reaction mixture was stirred at 40 ^oC for 4 h, then the mixture was cooled and filtered through a short column of silica gel (eluent PE). Solvent was removed under reduced pressure to leave a crude mixture, and the product **3aa** was isolated (1.8 mg, <10% yield).

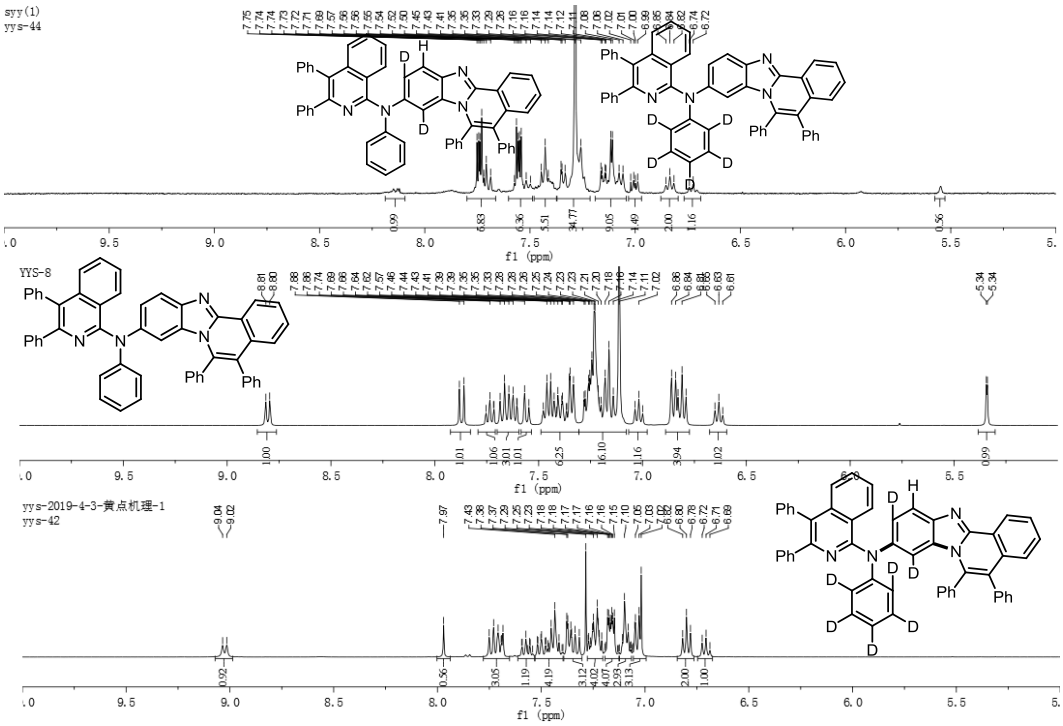


These two reactions were conducted at the same time in the same bath oil. Parallel competition: KIE =**3aa:[D_5]-3aa** = 7.8mg/1.8mg = 4.3.

5.4.2 In one-pot reactions

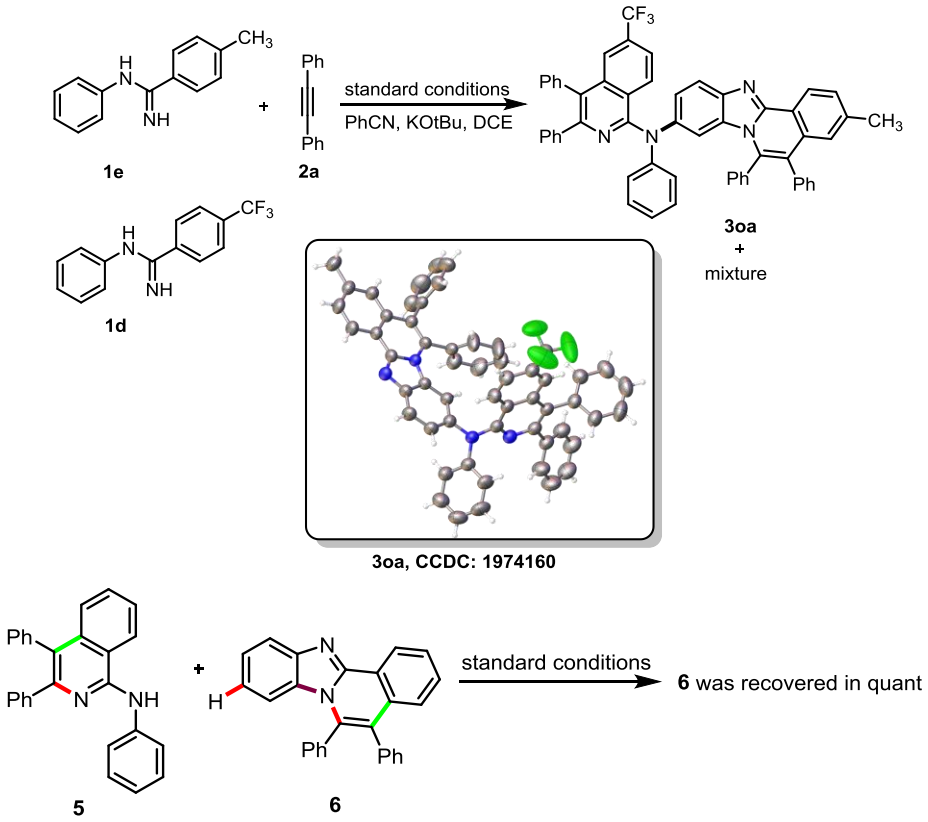
Without any particular precautions to extrude oxygen or moisture, a mixture of **1a** and **[D_5]-1a** (1:1 ratio, 0.25 mmol in total), 1,2-diphenylethyne **2a** (0.375 mmol, 66.8 mg), $Mn(OAc)_3 \cdot 2H_2O$ (6 equiv, 201.1 mg), KO^{t}Bu (20%), PhCN (20%, 25.6 uL), and DCE (4 mL) were charged into a 25 mL vial. The reaction mixture was stirred at 40 ^oC for 4 h, then the reaction mixture was filtered through a short column of silica gel (eluent PE). Solvent was removed under reduced pressure to leave a crude mixture, and an inseparable mixture was obtained.





5.5 Intermolecular Competitive Reaction

A mixture of **1e** and **1d** (1:1 ratio, 0.25 mmol in total), 1,2-diphenylethyne **2a** (0.375 mmol, 66.8 mg), $Mn(OAc)_3$ $2H_2O$ (6 equiv, 201.1 mg), KO^{t}Bu (20%), PhCN (20%, 25.6 uL), and DCE (4 mL) were charged into a 25 mL vial. The reaction mixture was stirred at 40 ^oC for 4 h, then the reaction mixture was filtered through a short column of silica gel (eluent PE). Solvent was removed under reduced pressure to leave a crude mixture, an inseparable mixture and a cross-coupling product **3oa** was obtained. The structure of **3oa** was further determined by X-ray crystallographic analysis. Then, subjecting N,3,4-triphenylisoquinolin-1-amine **5** and 5,6-diphenylbenzo[4,5]-imidazo[2,1-a]isoquinoline **6** to the reaction conditions, **6** was recovered in quant, suggesting that the intermolecular meta C-H amination might not occur at the last stage of the transformation.

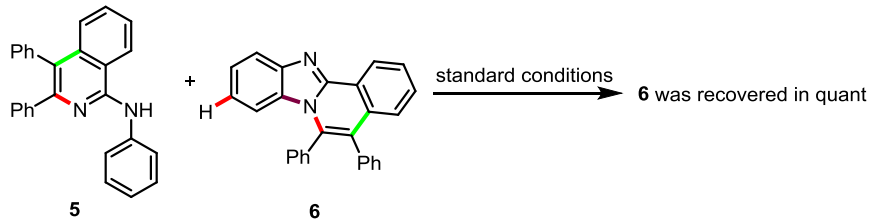


5.6 Radical Trapping experiments.

A mixture of **1a** (1:1 ratio, 0.25 mmol), 1,2-diphenylethyne **2a** (0.375 mmol, 66.8 mg), $Mn(OAc)_3$ $2H_2O$ (6 equiv, 201.1 mg), KO^{t}Bu (20%), PhCN (20%, 25.6 uL), TEMPO (1 equiv) and DCE (4 mL) were charged into a 25 mL vial. The reaction mixture was stirred at 40 ^oC for 48 h, the reaction mixture was filtered through a short column of silica gel (eluent PE). Solvent was removed under reduced pressure to leave a crude mixture, and the expected product was obtained in 20% yield.

5.7 Control experiment

5 and **6** were subjected to the reaction conditions for 48 h. After cooling the reaction to room temperature, the solvent was removed under vacuum and **6** was recovered in quant.

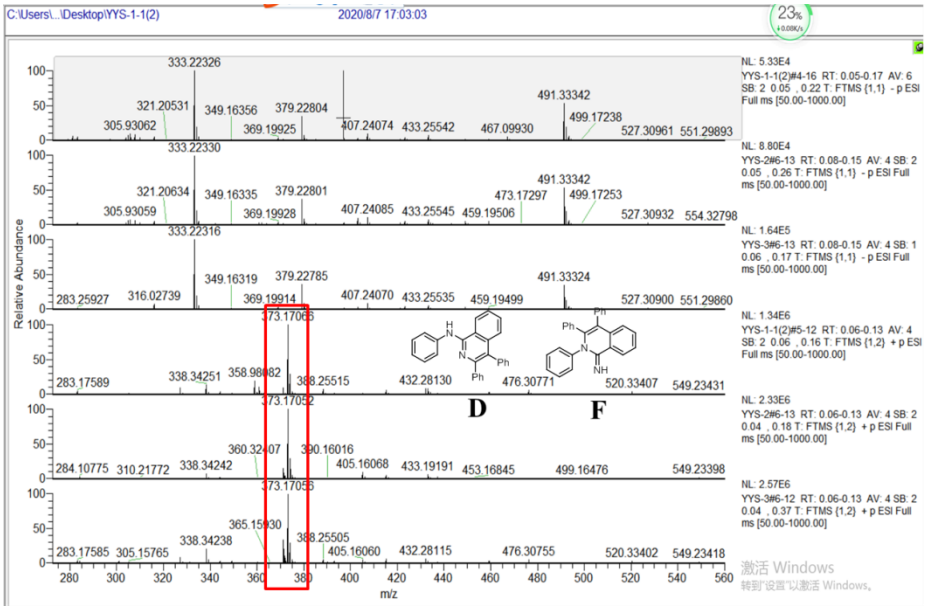


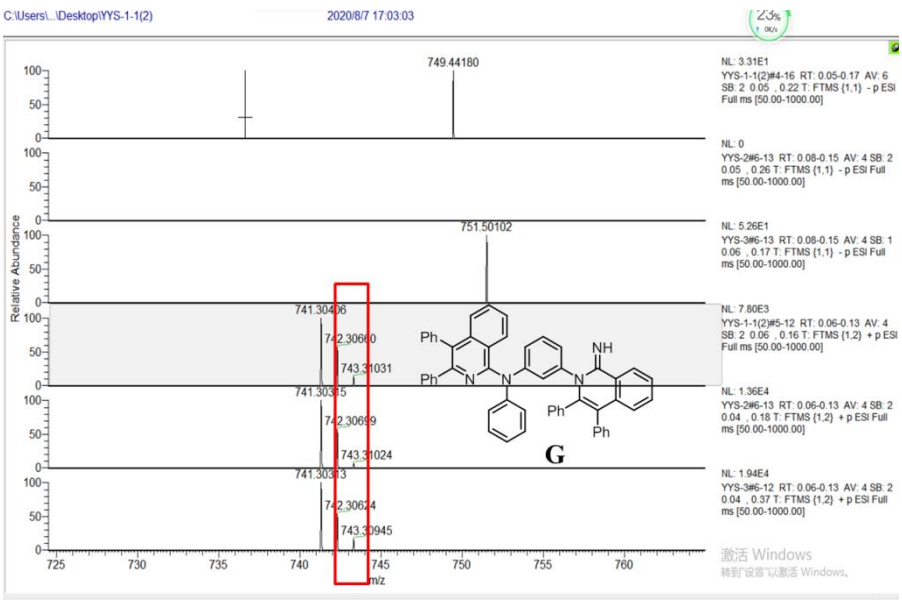
5.8 In-situ HRMS

Under an atmospheric condition, **1a** (25.2 mg, 0.125 mmol), 1,2-diphenylethyne **2a** (0.375 mmol, 66.8 mg), $Mn(OAc)_3 \cdot 2H_2O$ (6 equiv, 201.1 mg), KO^{t}Bu (20%), PhCN (20%, 25.6 uL), and DCE (4 mL) were charged into a 25 mL vial equipped with a stir bar. The reaction mixture was stirred at 40 ^oC for 4 h, then the mixture was cooled and the sample (YYS-1) was detected on UPLC-Exactive/UPLC-Exactive.

Under an atmospheric condition, **1a** (25.2 mg, 0.125 mmol), 1,2-diphenylethyne **2a** (0.375 mmol, 66.8 mg), $Mn(OAc)_3 \cdot 2H_2O$ (6 equiv, 201.1 mg), KO^{t}Bu (20%), PhCN (20%, 25.6 uL), and DCE (4 mL) were charged into a 25 mL vial equipped with a stir bar. The reaction mixture was stirred at 40 ^oC for 8 h, then the mixture was cooled and the sample (YYS-2) was detected on UPLC-Exactive/UPLC-Exactive.

Under an atmospheric condition, **1a** (25.2 mg, 0.125 mmol), 1,2-diphenylethyne **2a** (0.375 mmol, 66.8 mg), $Mn(OAc)_3 \cdot 2H_2O$ (6 equiv, 201.1 mg), KO^{t}Bu (20%), PhCN (20%, 25.6 uL), and DCE (4 mL) were charged into a 25 mL vial equipped with a stir bar. The reaction mixture was stirred at 40 ^oC for 24 h, then the mixture was cooled and the sample (YYS-3) was detected on UPLC-Exactive/UPLC-Exactive.




C:\Users\...\Desktop\YYS-1-1(2)
2020/8/7 17:03:03
749.44180
751.50102
741.30406
742.30660
743.31031
741.30315
742.30699
743.31024
741.30313
742.30624
743.30945
Relative Abundance
m/z
NL: 3.31E1
YYS-1-1(2)#4-16 RT: 0.05-0.17 AV: 6 SB: 2 0.05 , 0.22 T: FTMS {1,1} - p ESI Full ms [50.00-1000.00]
NL: 0
YYS-2#6-13 RT: 0.08-0.15 AV: 4 SB: 2 0.05 , 0.26 T: FTMS {1,1} - p ESI Full ms [50.00-1000.00]
NL: 5.26E1
YYS-3#6-13 RT: 0.08-0.15 AV: 4 SB: 1 0.06 , 0.17 T: FTMS {1,1} - p ESI Full ms [50.00-1000.00]
NL: 7.80E3
YYS-1-1(2)#5-12 RT: 0.06-0.13 AV: 4 SB: 2 0.06 , 0.16 T: FTMS {1,2} + p ESI Full ms [50.00-1000.00]
NL: 1.36E4
YYS-2#6-13 RT: 0.06-0.13 AV: 4 SB: 2 0.04 , 0.18 T: FTMS {1,2} + p ESI Full ms [50.00-1000.00]
NL: 1.94E4
YYS-3#6-12 RT: 0.06-0.13 AV: 4 SB: 2 0.04 , 0.37 T: FTMS {1,2} + p ESI Full ms [50.00-1000.00]
Ph
Ph
N
N
N
NH
Ph
Ph
G
激活 Windows
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6. References

(S1) Li, D.; Zeng, F. *Org. Lett.* **2017**, *19*, 6498−6501.

(S2) Martínez, A. M.; Echavarren, J.; Alonso, I.; Rodríguez, N.; Arrayás, R. G.; Carretero, J. C. *Chem. Sci.* **2015**, *6*, 5802–5814.

(S3) Mori, A.; Kawashima, J.; Shimada, T.; Suguro, M.; Hirabayashi, K.; Nishihara, Y. *Org. Lett.* **2000**, *2*, 2935-2937.

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(S5) Yamamoto, Y.; Kinpara, K.; Ogawa, R.; Nishiyama, H.; Itoh, K. *Chem.– Eur. J.* **2006**, *12*, 5618–5631.

(S6) Brasche, G.; Buchwald, S. L. *Angew. Chem., Int. Ed.* **2008**, *47*, 1932–1934.

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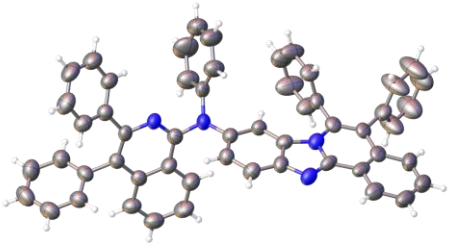
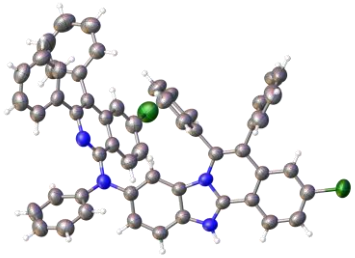
7. Single-Crystal X-Ray Crystallography

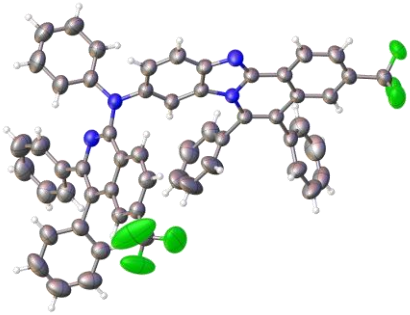
7.1 Crystal structures of targeted quinazolines (5 products). The displacement ellipsoids are drawn at the 30% probability.



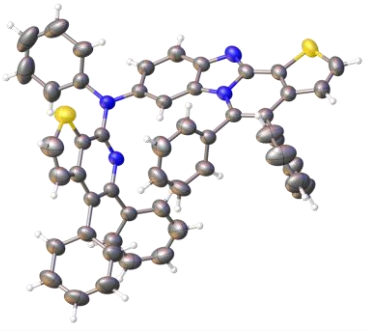
3aa, CCDC:1974156



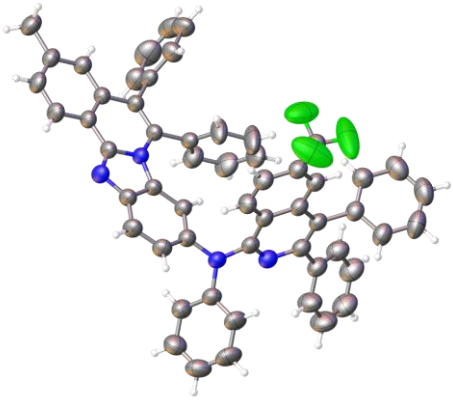
3ca, CCDC:1974157



3da, CCDC:1974158

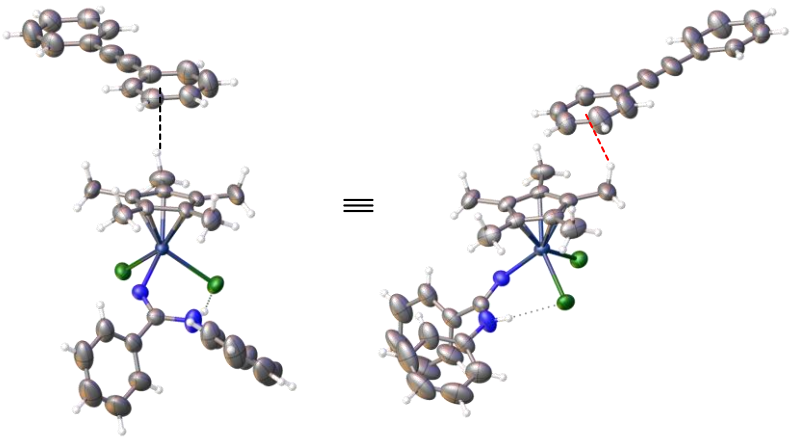


3na, CCDC:1974159



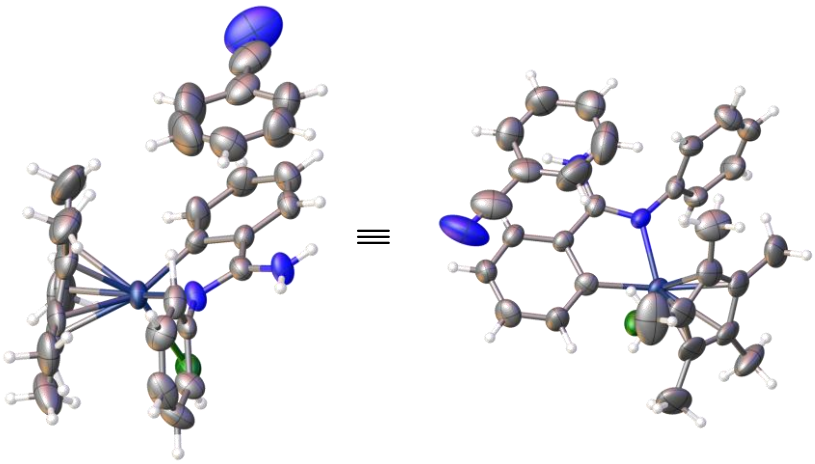
3oa, CCDC:1974160

7.2 Crystal structures of intermediate Rhodium-complex I (C: black; H: gray; Cl: green; N: light blue; Rh: navy bule). The displacement ellipsoids are drawn at the 30% probability.



Rhodium-complex I, CCDC:1974161

7.3 Crystal structures of intermediate Rhodacycle intermediate II (C: black; H: gray; Cl: green; N: light blue; Rh: navy bule). The displacement ellipsoids are drawn at the 30% probability.



Rhodacycle intermediate II, CCDC:1974162

Table S2. Crystal data and structure refinement details for targeted products, Rh(III) Complex I, and Rh(III) Complex II.

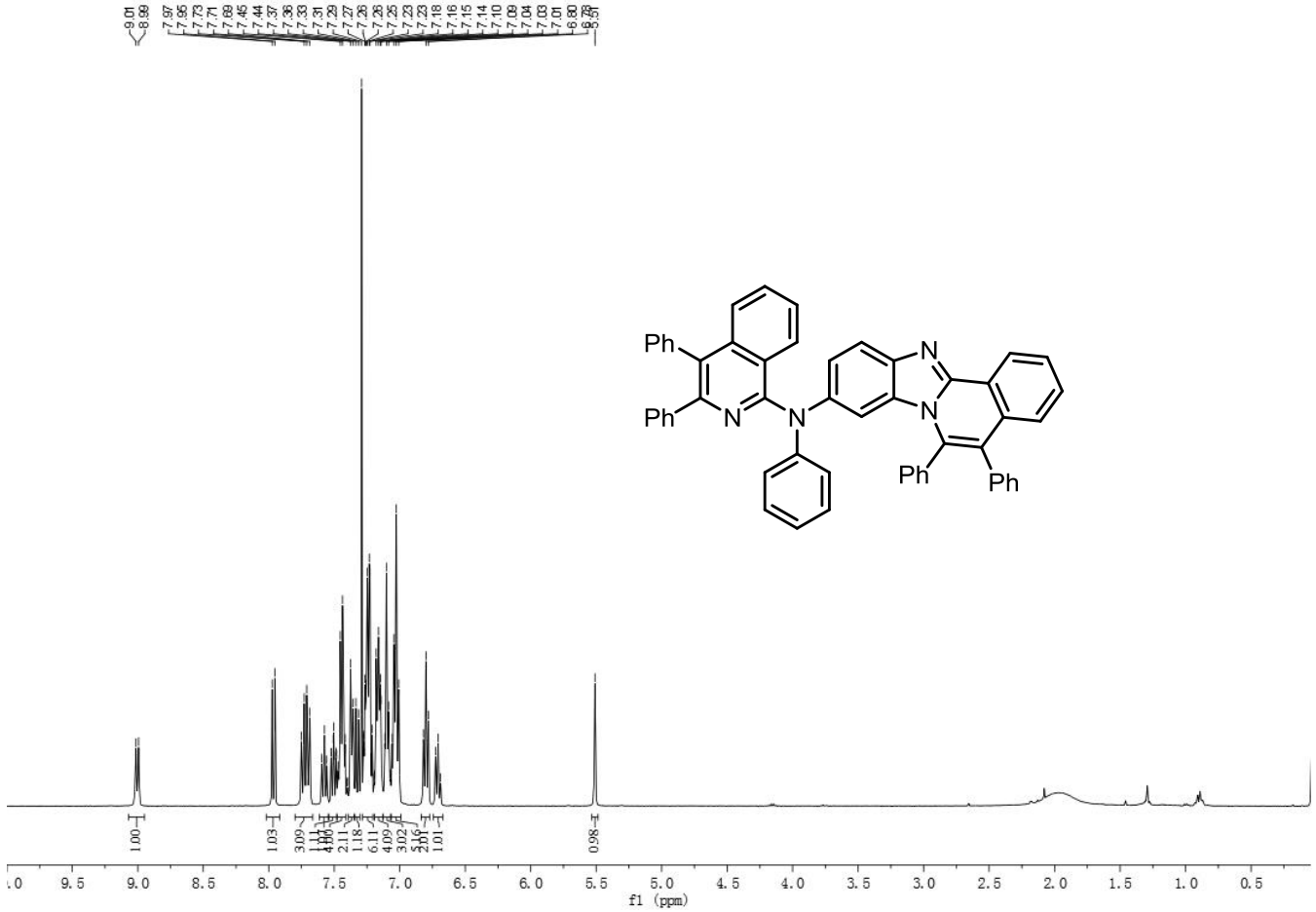
	3aa	**3ca**	**3da**	**3na**	**3oa**
Empirical formula	$C_{11}H_{10}NO$	$C_{10.8}H_7N_{0.8}Cl_{0.4}$	$C_{10.67}H_{6.48}N_{0.76}F_{1.14}$	$C_{11.11}H_{7.11}N_{0.89}S_{0.44}$	$C_{10.67}H_{7.05}N_{0.76}F_{0.57}Cl_{0.05}O_{0.05}$
Formula weight	155.98	162.15	167.02	167.31	159.19
Crystal system	monoclinic	monoclinic	monoclinic	triclinic	monoclinic
Space group	$P2_1/c$	$P2_1$	$P2_1/n$	P-1	$P2_1/n$
a / Å	13.1152(19)	13.3538(10)	15.7886(4)	9.8941(3)	15.7038(3)
b / Å	9.7918(10)	10.7542(10)	10.8211(3)	13.9468(4)	10.8165(2)
c / Å	33.822(4)	15.7395(12)	28.7265(8)	16.4764(5)	28.0637(6)
α / °	90	90	90	102.279(2)	90
β / °	91.189(12)	96.853(7)	90.484(3)	99.940(2)	90.879(2)
γ / °	90	90	90	97.712(2)	90
Volume / Å^3	4342.5(9)	2244.2(3)	4907.7(2)	2153.46(11)	4766.34(16)
Z	19	10	21	9	21
D / g cm^{-3}	1.1332	1.200	1.187	1.161	1.165
μ / mm^{-1}	0.513	1.609	0.712	1.407	0.745
F (000)	1556.4	842.0	1808.0	784.0	1737.0
R_{int}	0.0505	0.0508	0.0213	0.0175	0.0170
Goodness-of-fit on F^2	1.138	1.042	1.055	1.112	1.260
$R_1{}^a$ / $wR_2{}^b$ [$I > 2\sigma(I)$]	0.1265/0.3342	0.0836/0.2270	0.0859/0.2533	0.0655/0.2194	0.0902/0.2846
$R_1{}^a$ / $wR_2{}^b$ (all data)	0.2141/0.4339	0.0909/0.2423	0.0983/0.2739	0.0729/0.2324	0.1014/0.3053
CCDC number	1974156	1974157	1974158	1974159	1974160

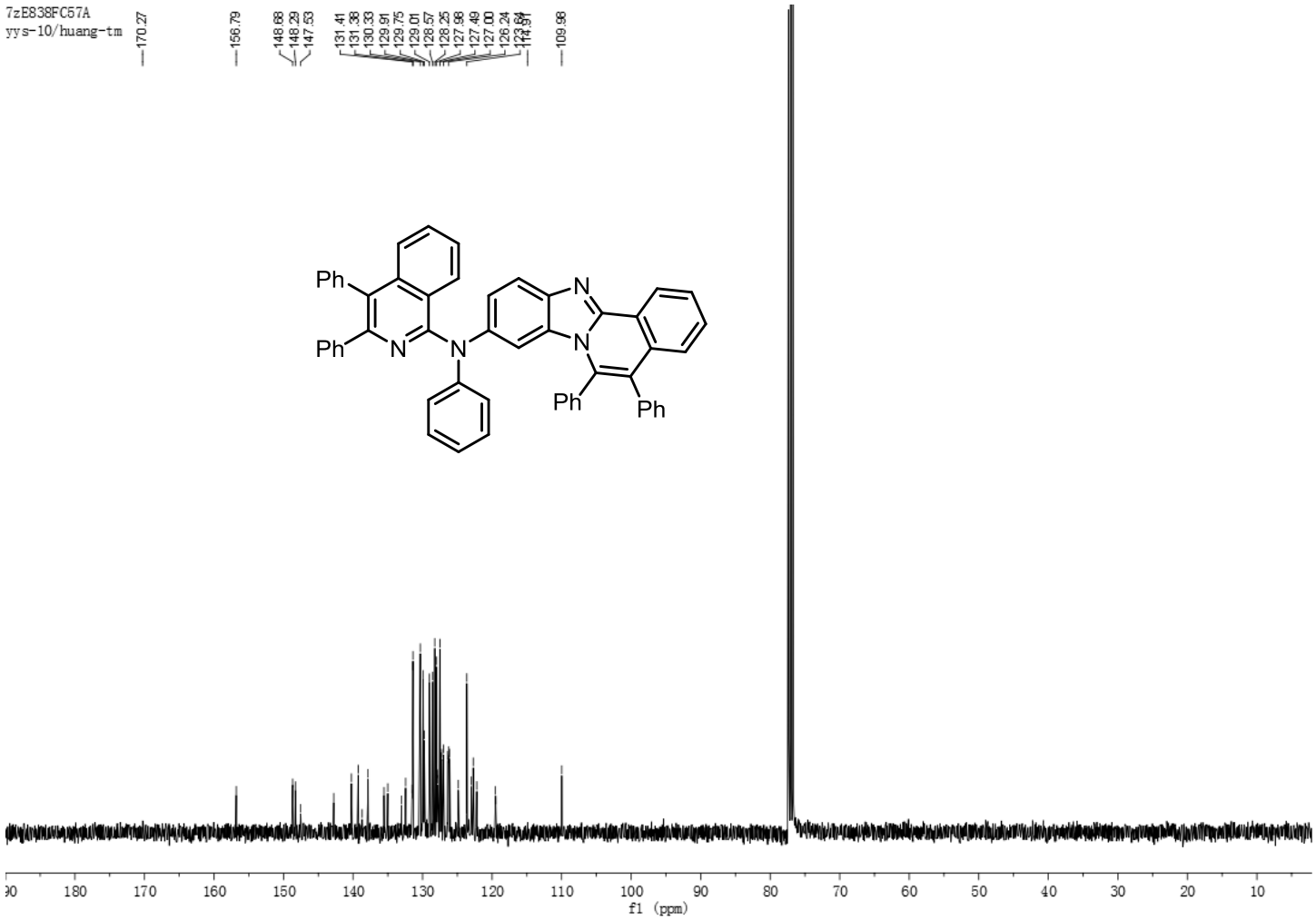
	Rh(III) complex II	Rh(III) complex I
Empirical formula	$C_{10.43}H_{10.78}N_{1.04}Rh_{0.35}Cl_{0.35}$	$C_{30}H_{31}N_3RhCl$
Formula weight	178.22	571.94
Crystal system	monoclinic	monoclinic
Space group	I2/a	C2/c
a / Å	22.2459(7)	30.7434(11)
b / Å	9.7093(4)	9.7093(4)
c / Å	25.0566(9)	22.2459(7)
α / °	90	90
β / °	99.165(3)	126.426(3)
γ / °	90	90
Volume / Å^3	5342.9(3)	5343.0(4)
Z	23	8
D / g cm^{-3}	1.274	1.422
μ / mm^{-1}	1.355	6.255
F (000)	2155.0	2352.0
R_{int}	0.0894	0.0894
Goodness-of-fit on F^2	1.955	1.316
$R_1{}^a$ / $wR_2{}^b$ [$I > 2\sigma(I)$]	0.0868/0.2267	0.0864/0.2632
$R_1{}^a$ / $wR_2{}^b$ (all data)	0.1199/0.2794	0.1193/ 0.3161
CCDC number	1974161	1974162

^{a} $R_1 = \Sigma||F_o| - |F_c||/\Sigma|F_o|$. ^{b} $wR_2 = |\Sigma w(|F_o|^2 - |F_c|^2)|/\Sigma|w(F_o)^2|^{1/2}$, where $w = 1/[\sigma^2(F_o{}^2) + (aP)^2 + bP]$. $P = (F_o{}^2 + 2F_c{}^2)/3$.

8. Copy of NMR (^{1}H, ^{13}C, ^{19}F) Spectra

Compound 3aa

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156.79
148.68
148.29
147.53
131.41
131.38
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129.75
129.01
128.57
128.25
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127.00
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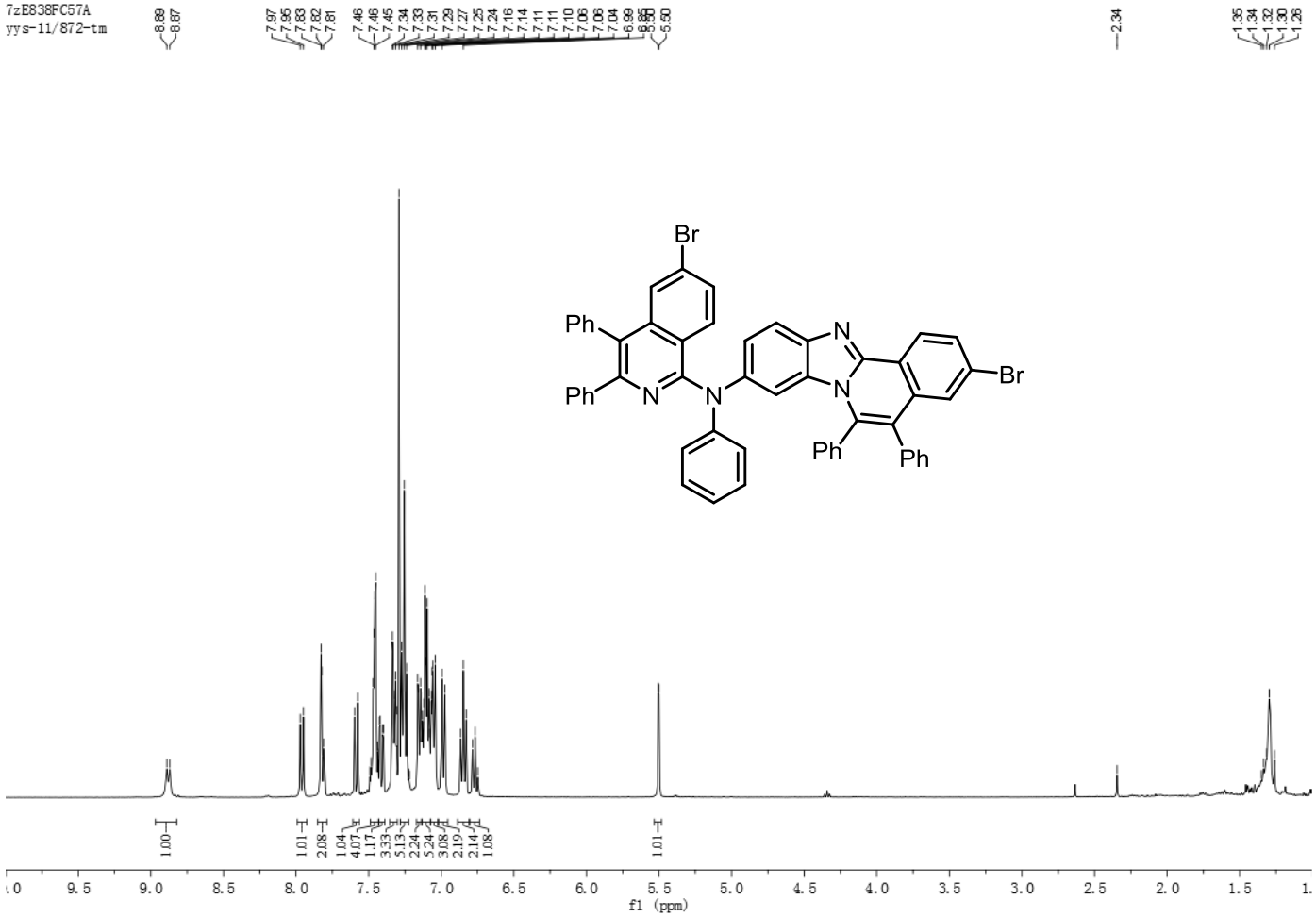
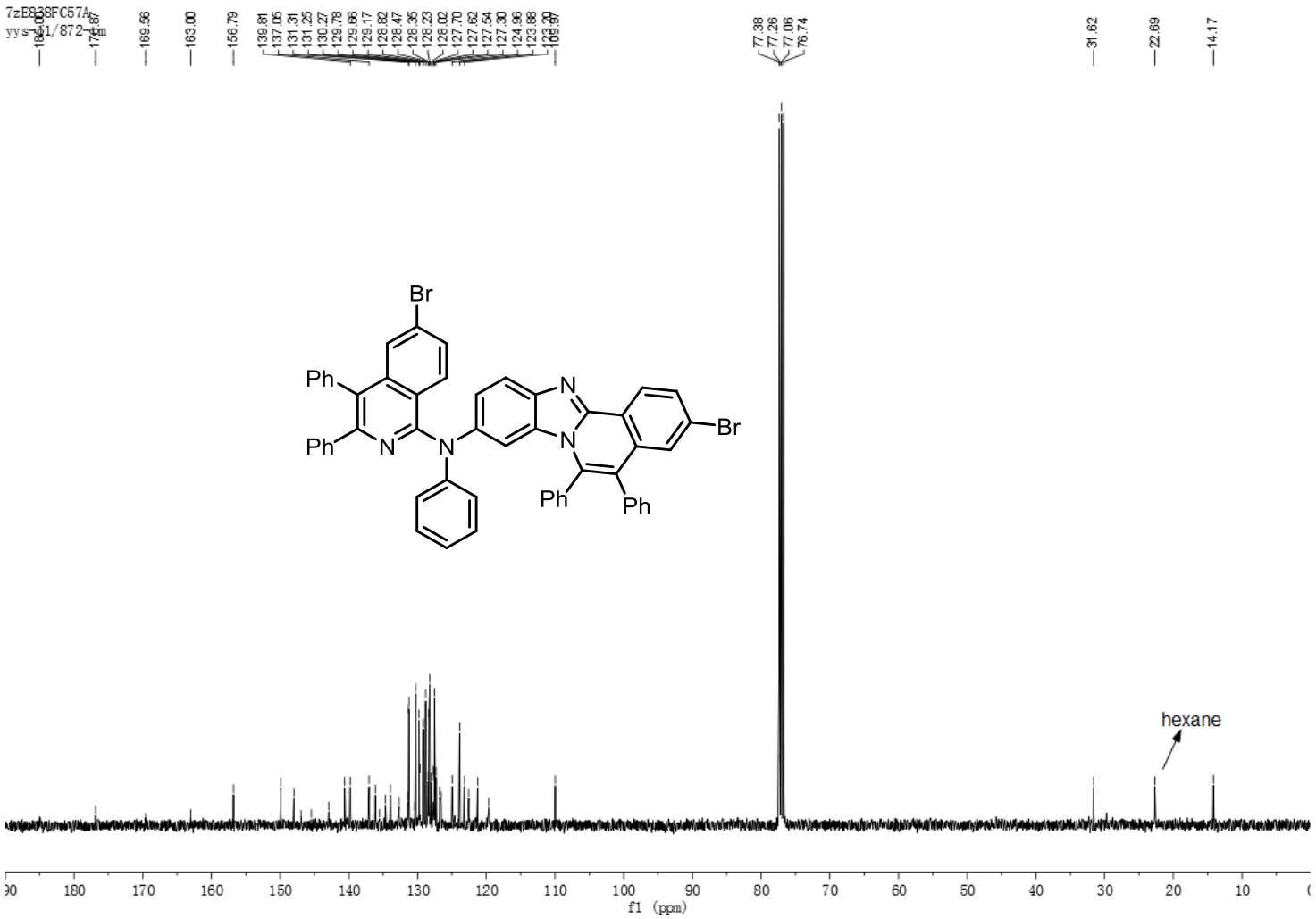
Ph
N
N
N
Ph
Ph
f1 (ppm)

Compound 3ba

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128.35
128.23
128.02
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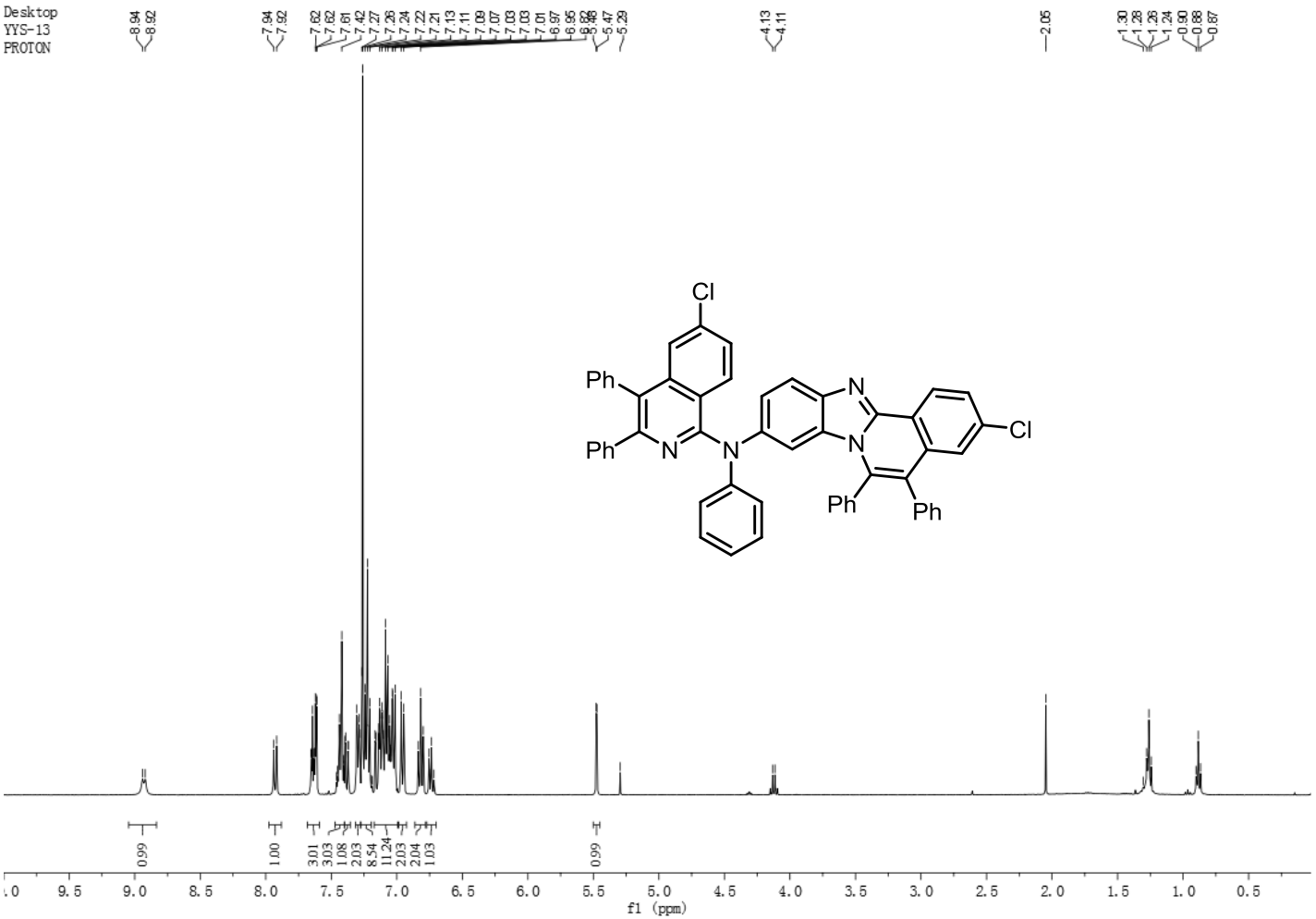
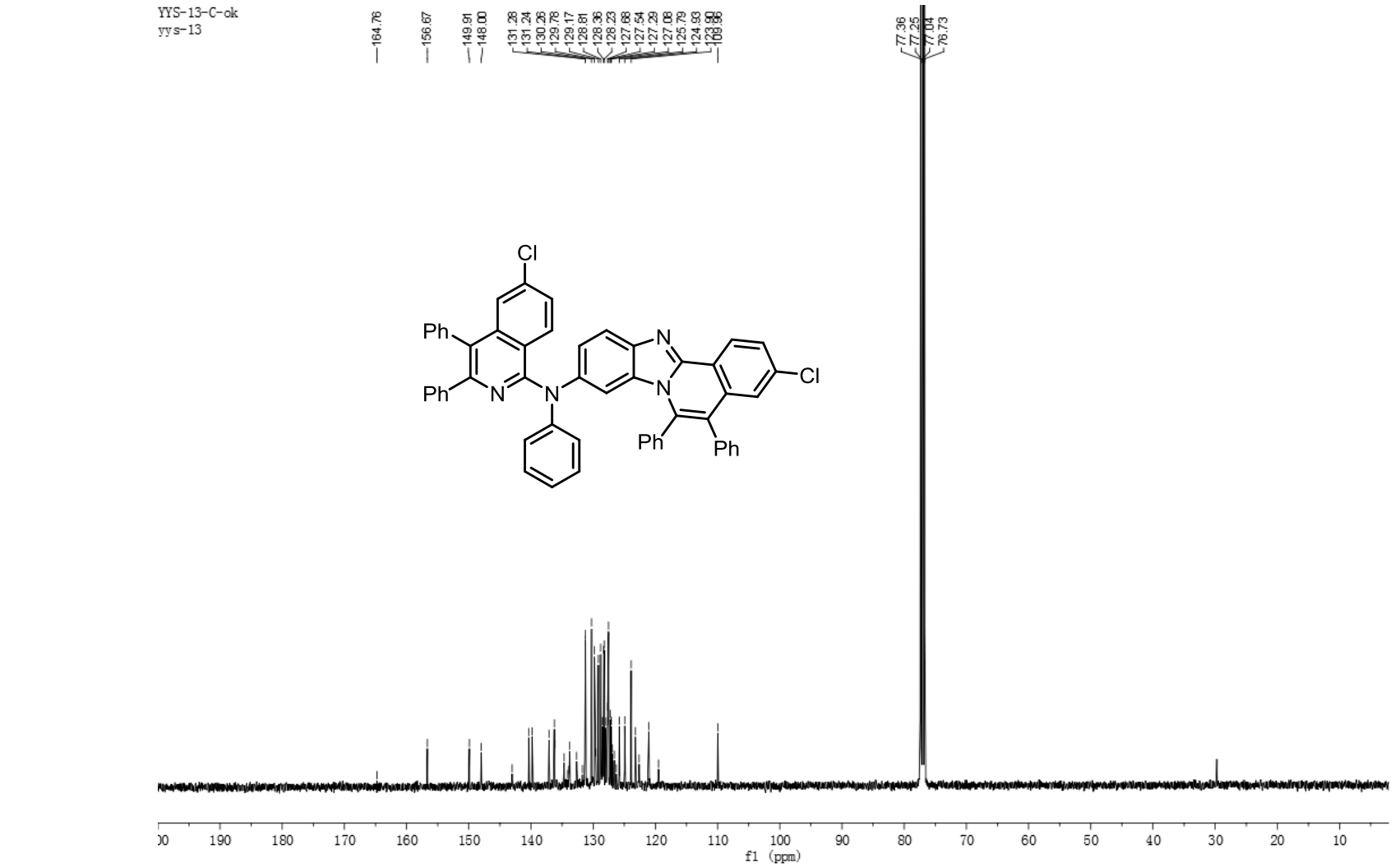
124.96
123.88
77.38
77.26
77.06
76.74
31.62
22.69
14.17
Br
Ph
Ph
N
N
N
Br
Ph
Ph
hexane
f1 (ppm)

Compound 3ca

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129.17
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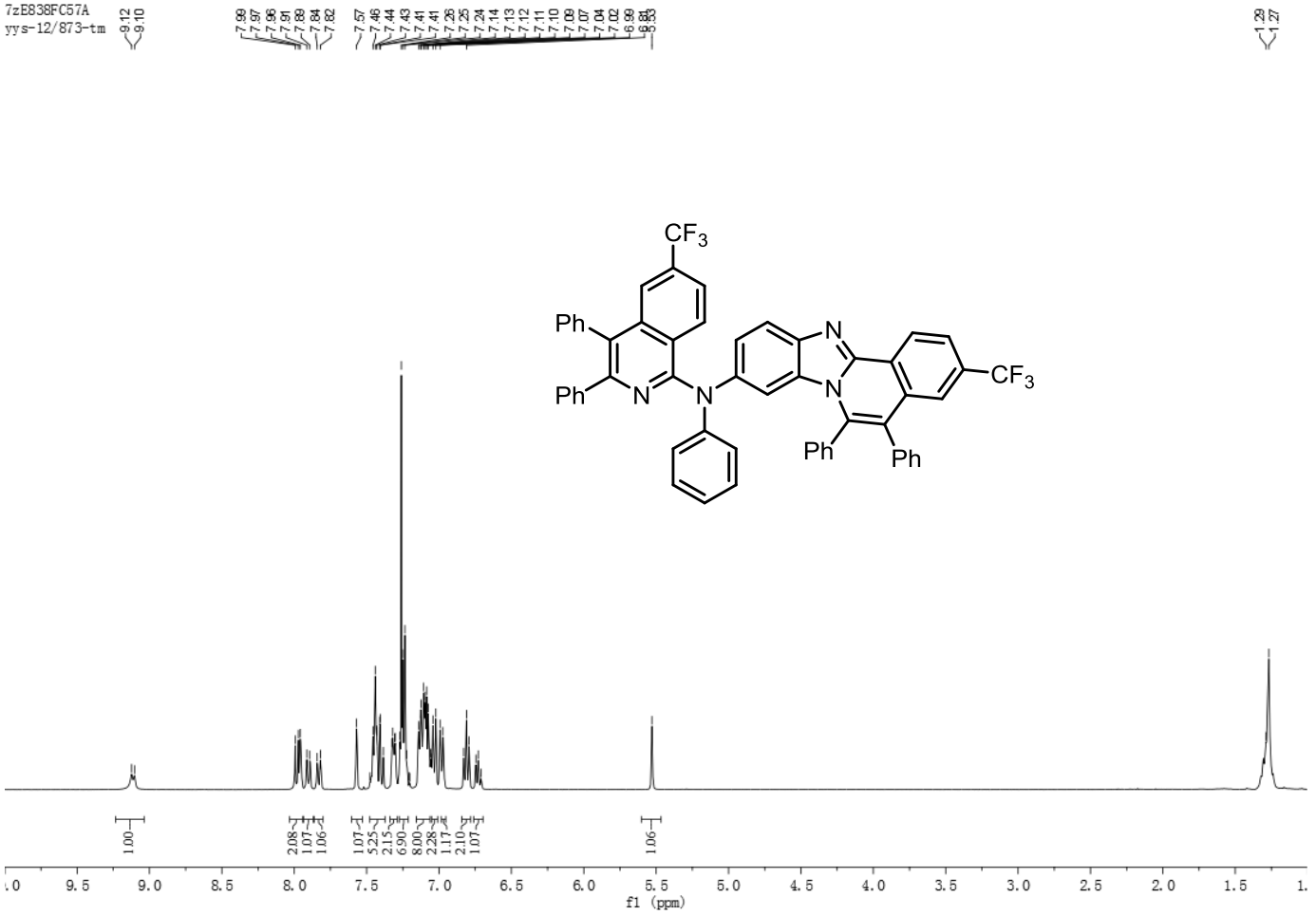
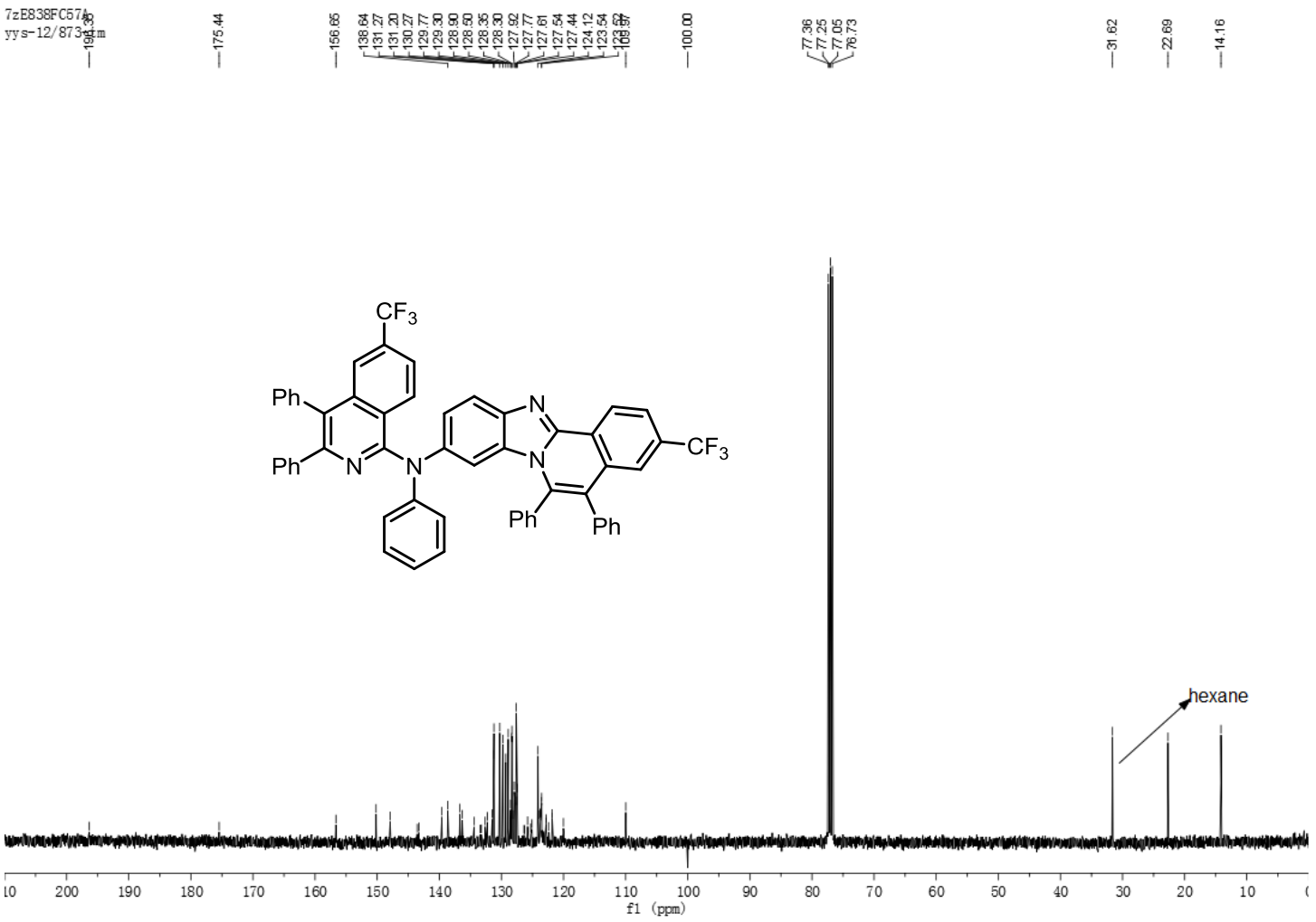
128.36
128.23
127.68
127.54
127.29
127.08
125.79
124.93
77.36
77.25
77.04
76.73
Cl
Ph
Ph
N
N
N
N
Cl
Ph
Ph
f1 (ppm)

Compound 3da

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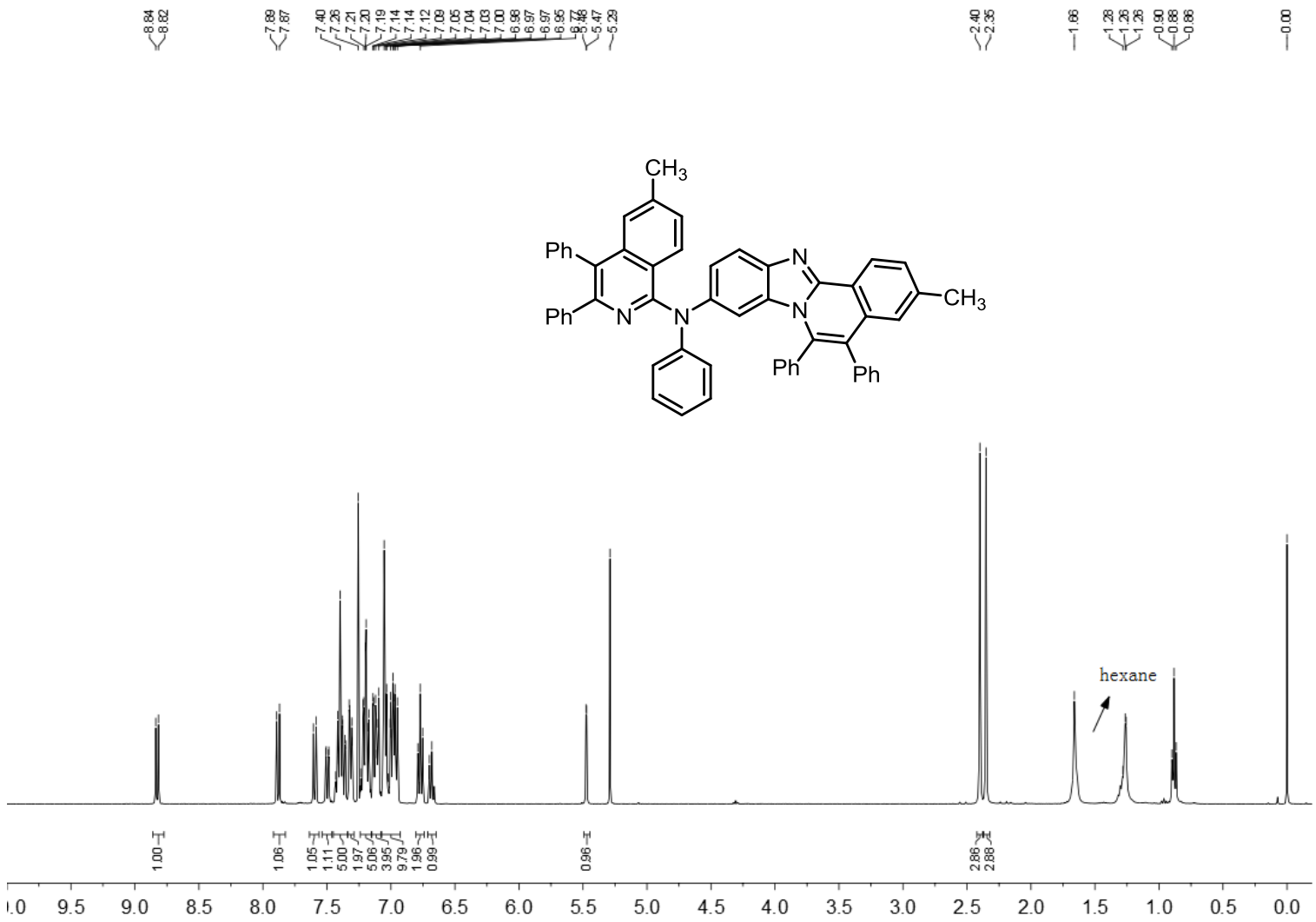
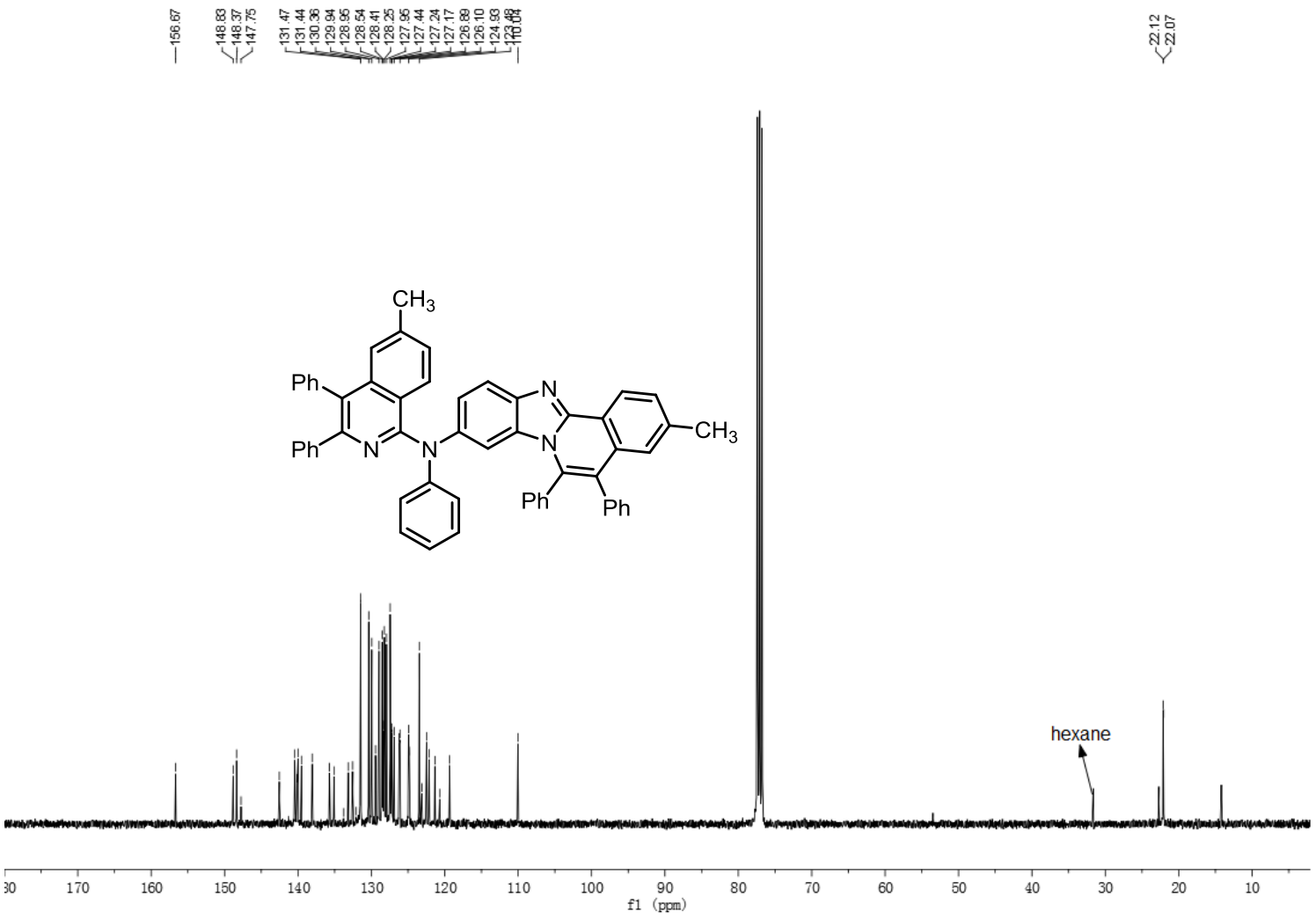
100.00
77.36
77.25
77.05
76.73
31.62
22.69
14.16
CF3
Ph
Ph
N
N
N
N
CF3
Ph
Ph
hexane
f1 (ppm)

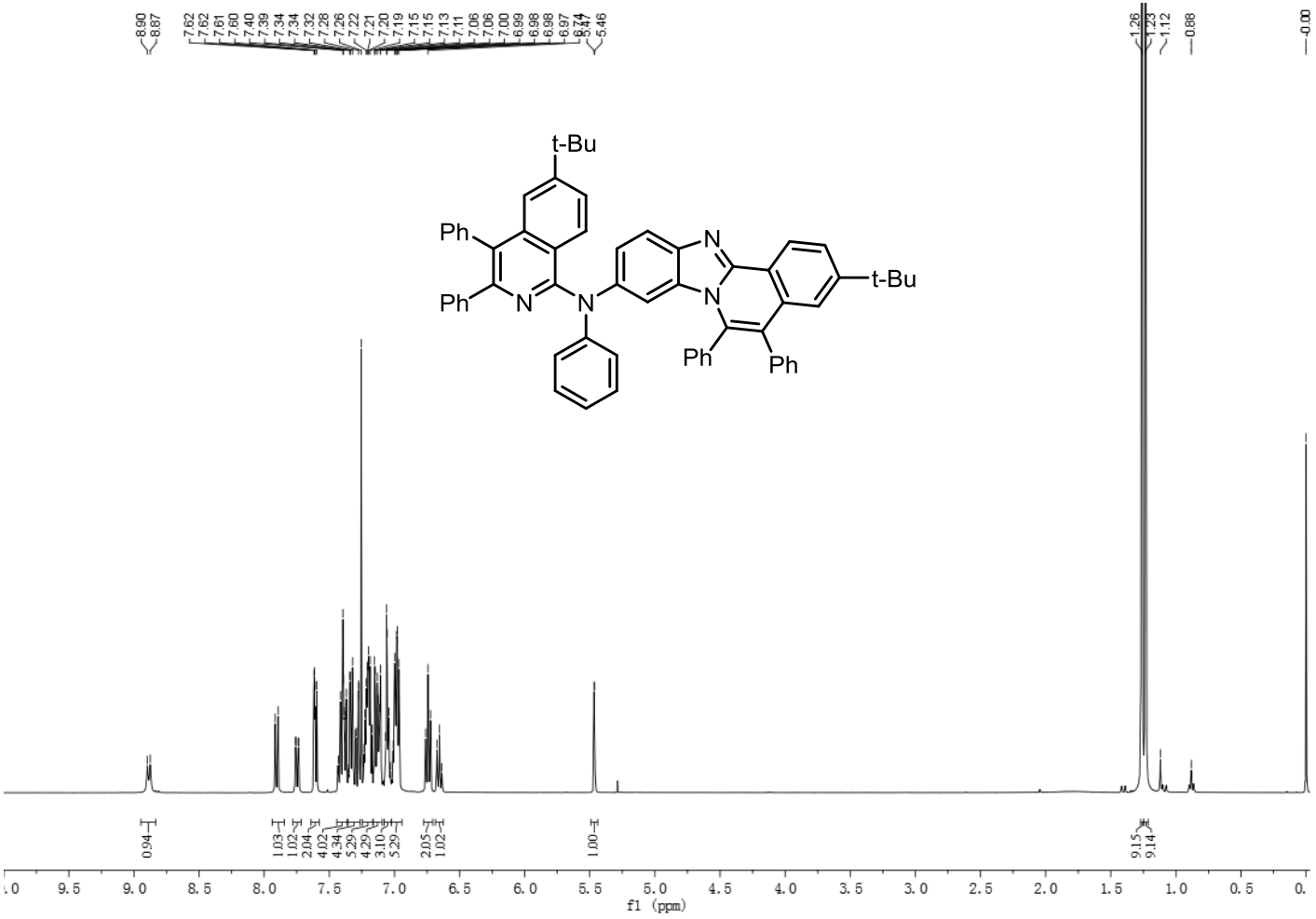

7zE838FC57A
yys-12/873-tm
-62.40
-62.94
CF3
Ph
Ph
N
N
N
CF3
Ph
Ph
10 0 -10 -20 -30 -40 -50 -60 -70 -80 -90 -100 -110 -120 -130 -140 -150 -160 -170 -180 -190 -200 -210
f1 (ppm)

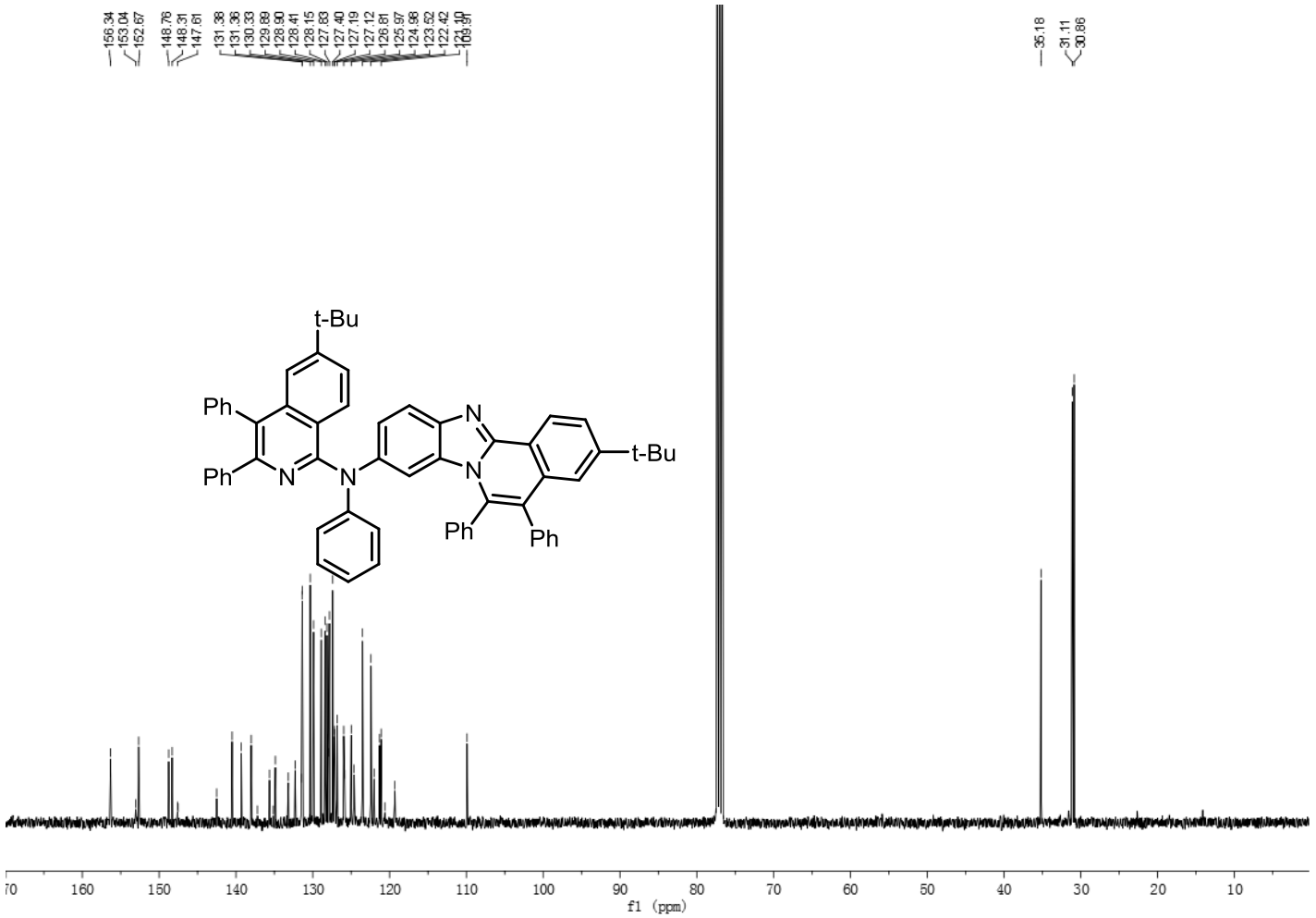
Compound 3ea



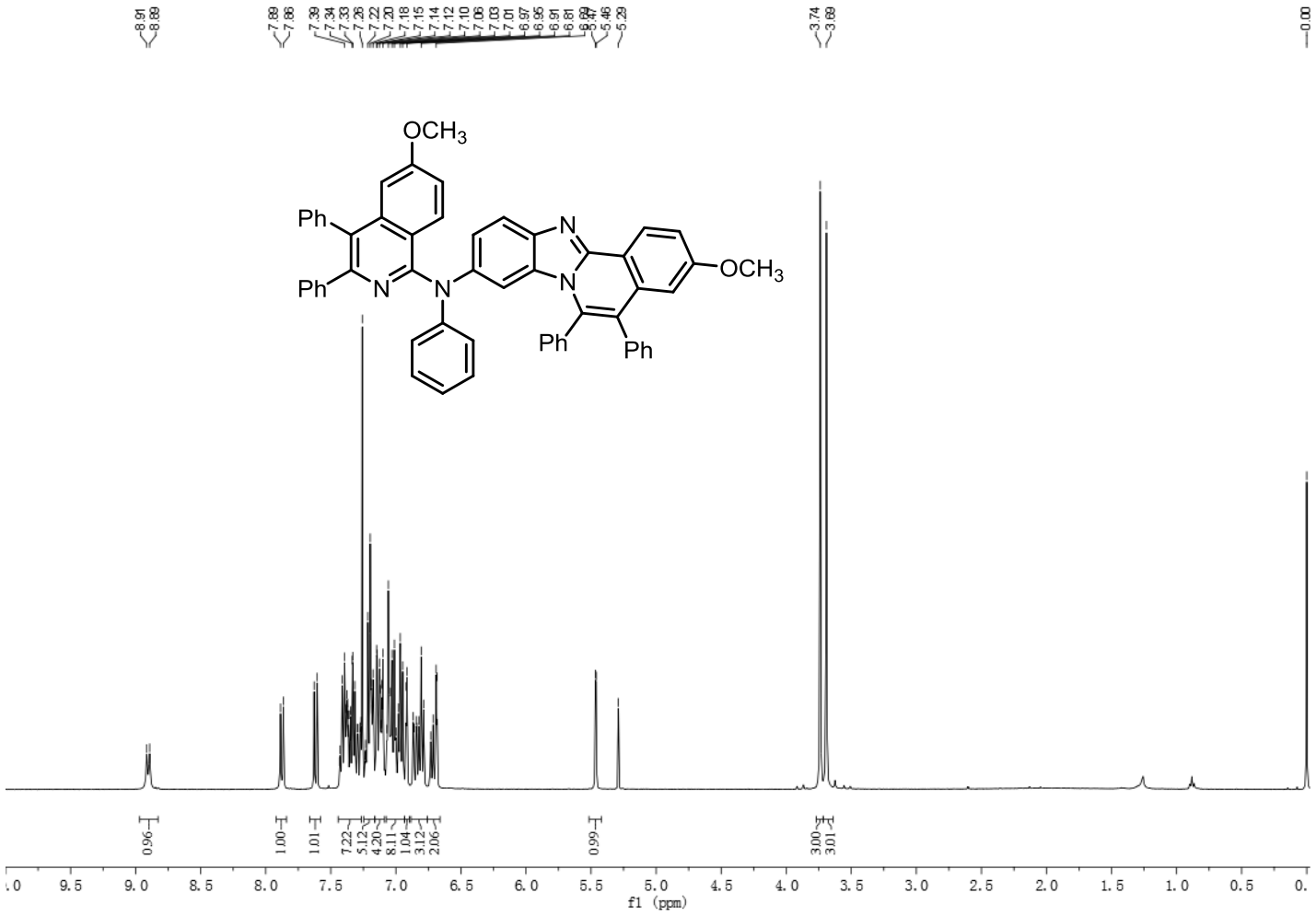

156.67
148.83
148.37
147.75
131.47
131.44
130.36
129.94
128.95
128.54
128.41
128.25
127.95
127.44
127.24
127.17
126.89
126.10
124.93
22.12
22.07
CH3
Ph
Ph
N
N
N
CH3
Ph
Ph
hexane
f1 (ppm)

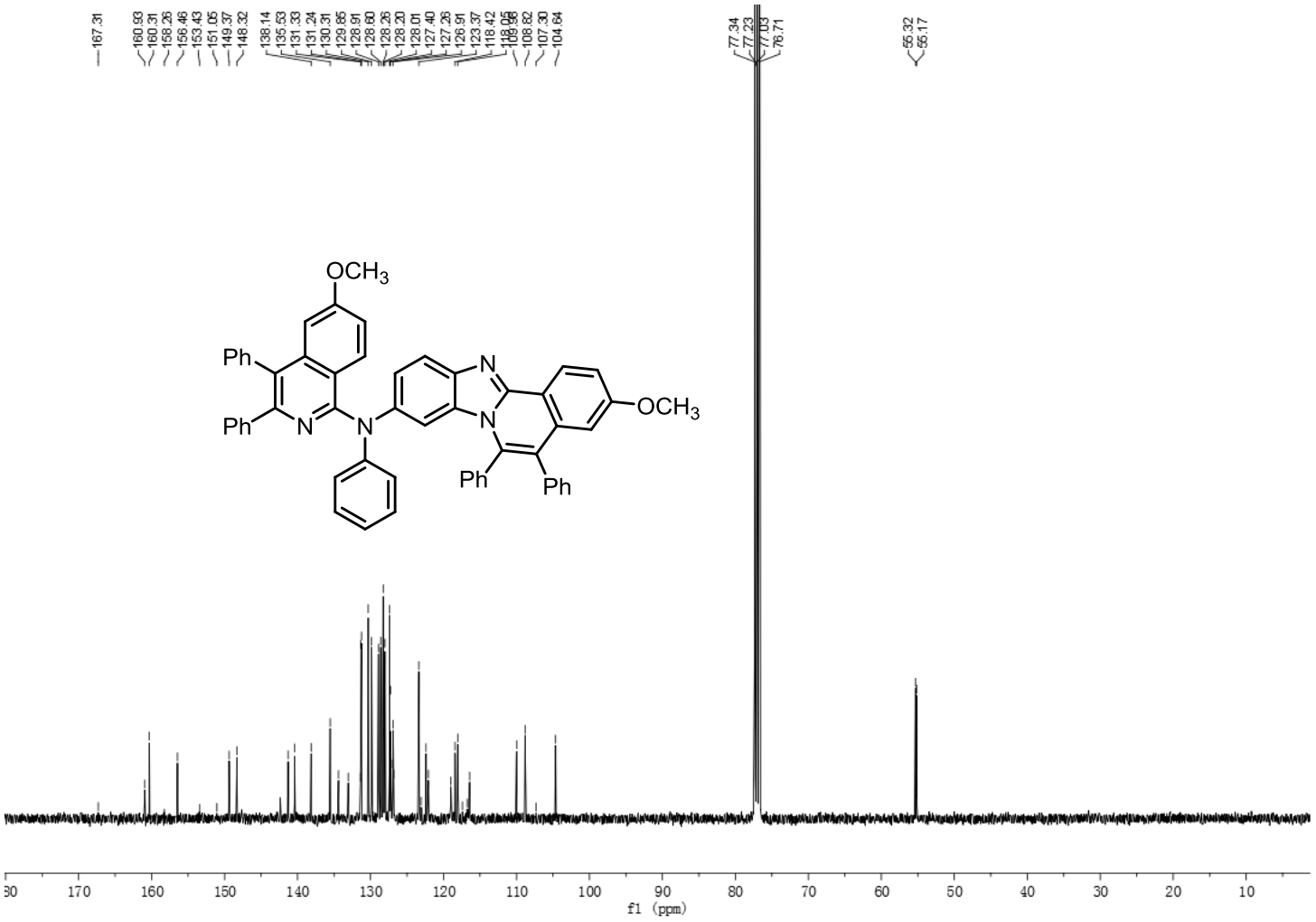
Compound 3fa



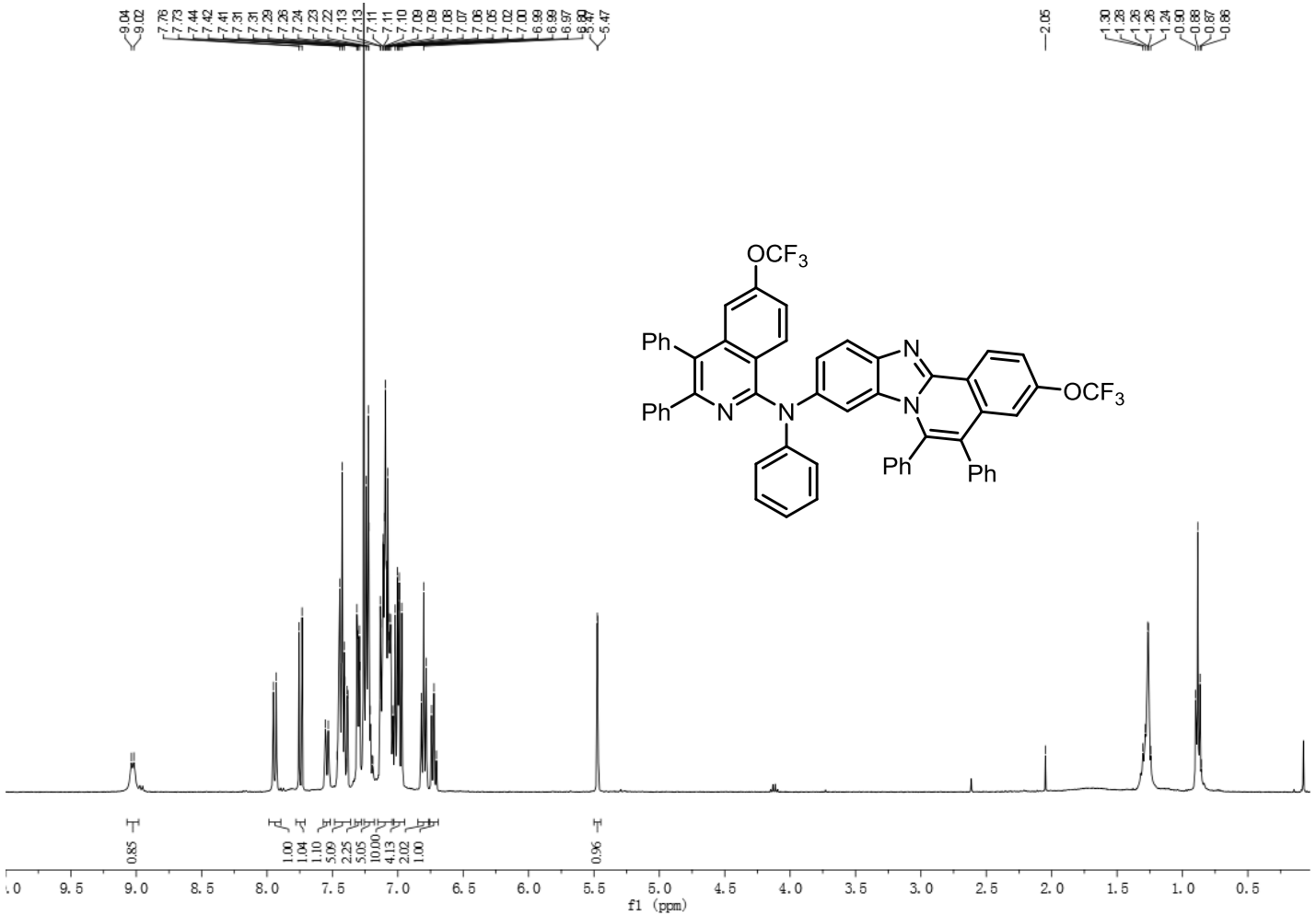

156.34
153.04
152.67
148.76
148.31
147.61
131.38
131.36
130.33
129.89
128.90
128.41
128.15
127.83
127.40
127.19
127.12
126.81
125.97
124.98
123.52
122.42
121.10
109.91
35.18
31.11
30.86
t-Bu
Ph
Ph
N
N
N
N
t-Bu
Ph
Ph
70
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
f1 (ppm)

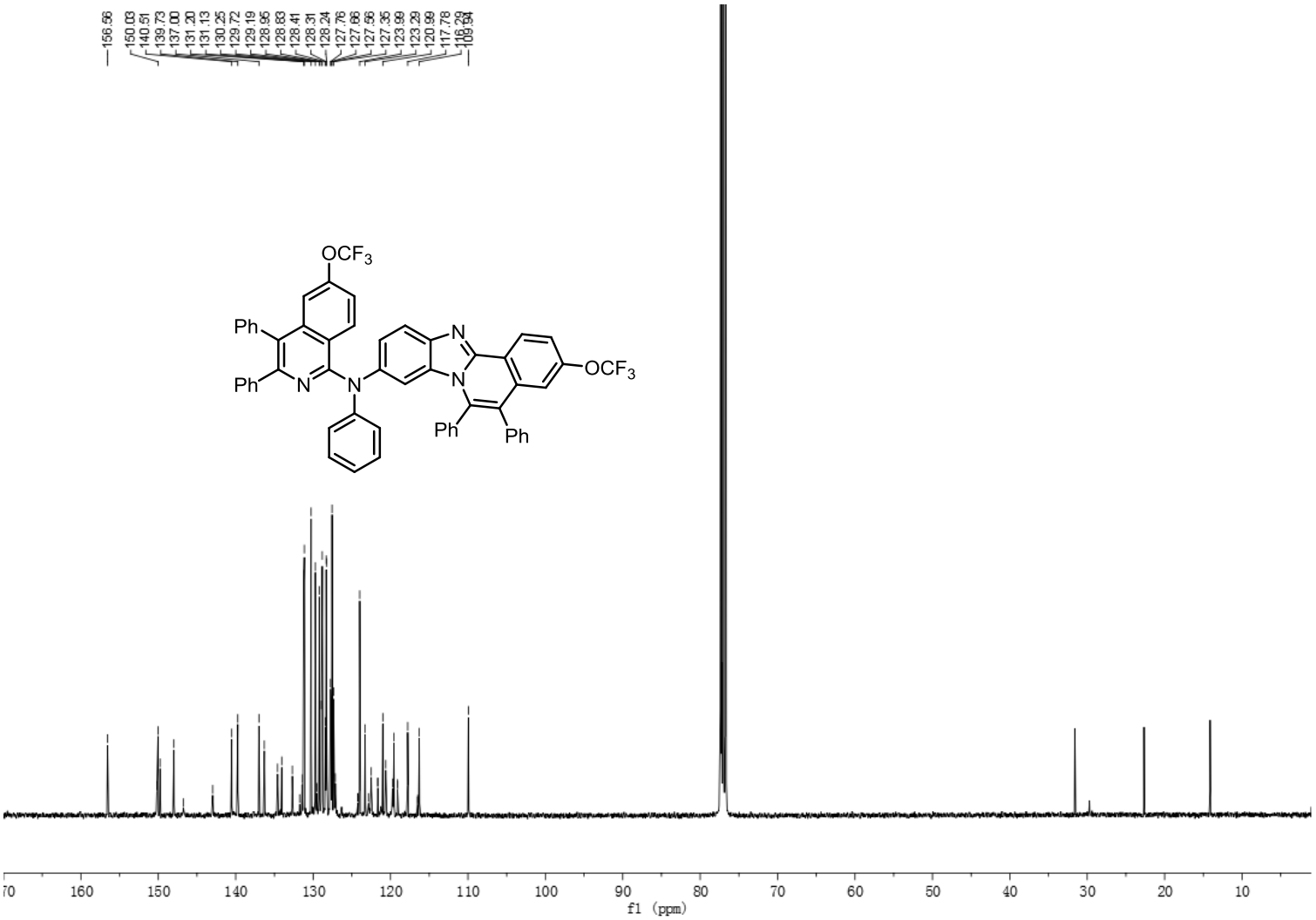
Compound 3ga

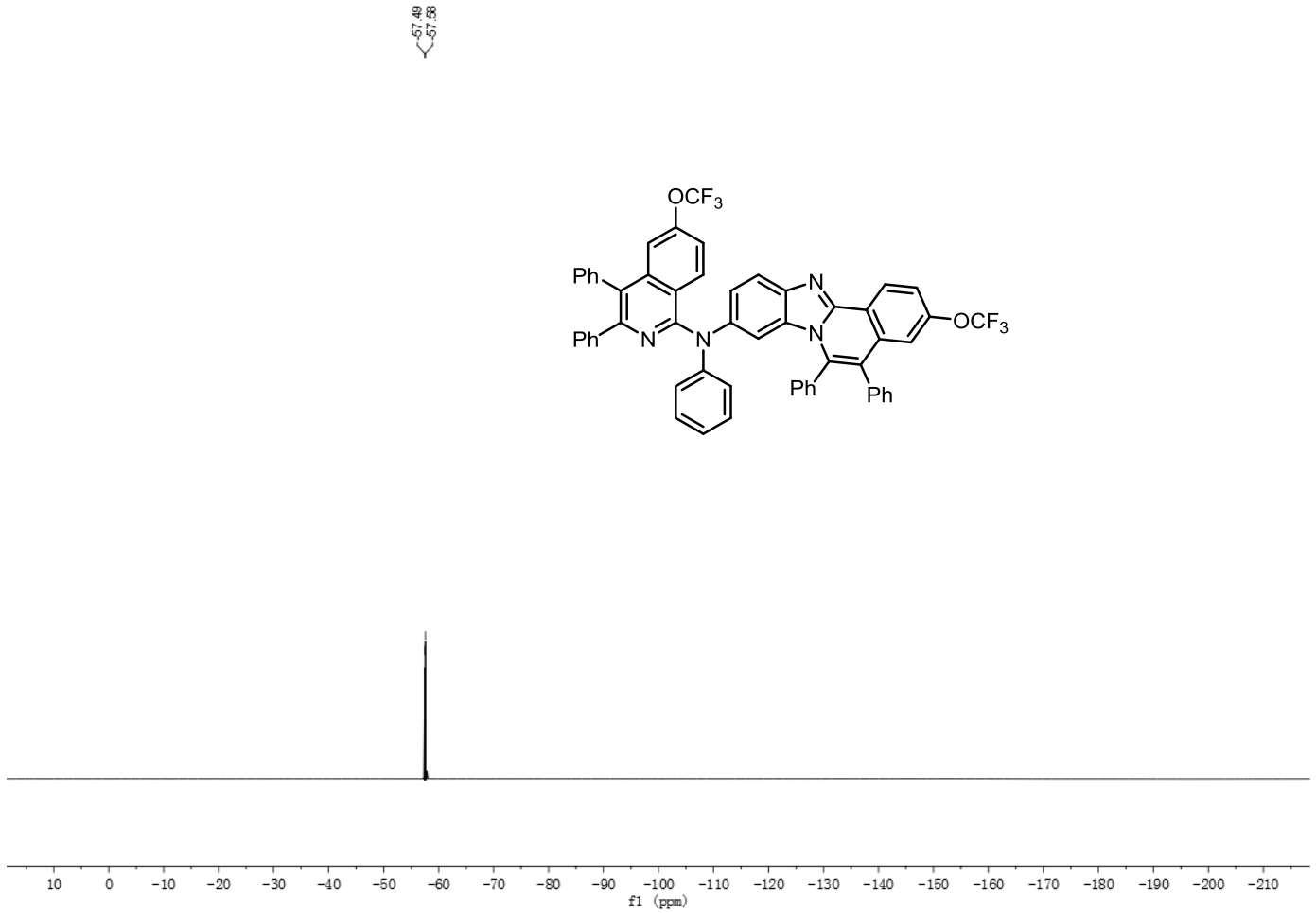



167.31
160.93
160.31
158.26
156.46
153.43
151.05
149.37
148.32
138.14
135.53
131.33
131.24
130.31
129.85
128.91
128.60
128.26
128.20
128.01
127.40
127.26
126.91
123.37
118.42
108.82
107.30
104.64
77.34
77.23
77.03
76.71
55.32
55.17
OCH3
Ph
Ph
N
N
N
N
OCH3
Ph
Ph
f1 (ppm)

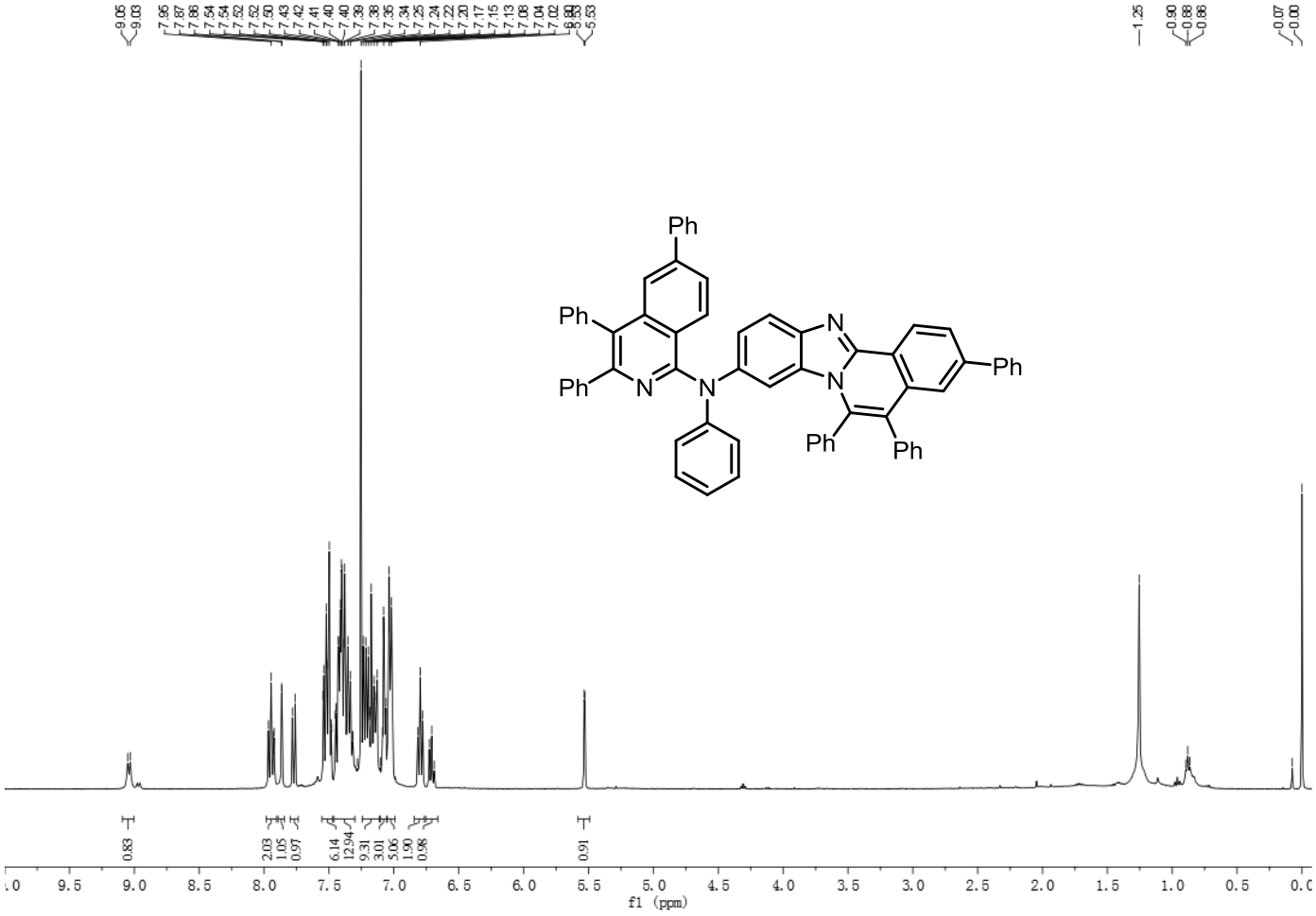
Compound 3ha

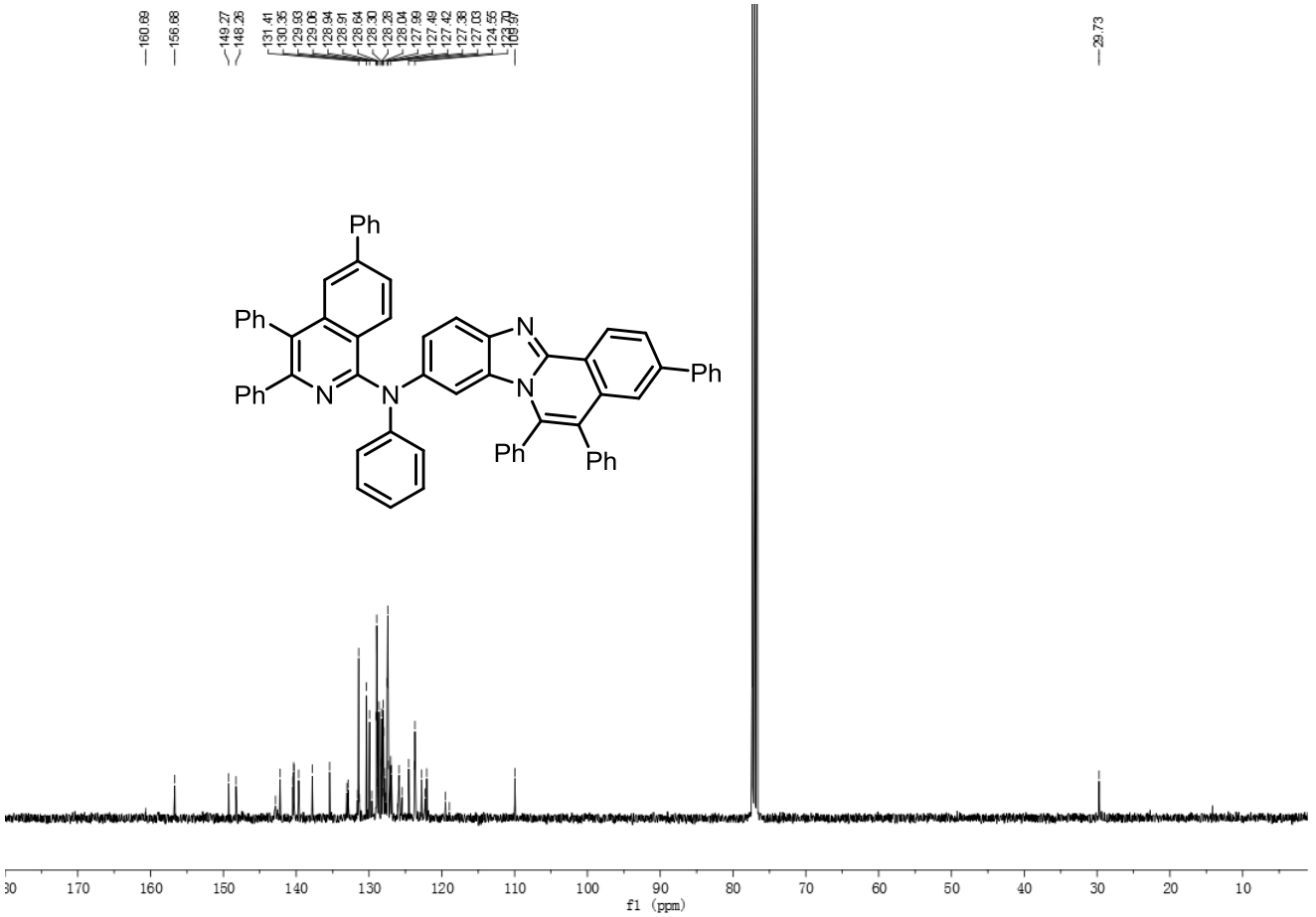



156.66
150.03
140.51
139.73
137.00
131.20
131.13
130.25
129.72
129.19
128.95
128.83
128.41
128.31
128.24
127.76
127.66
127.56
127.35
123.99
123.29
120.99
117.78
116.29
109.94
OCF3
Ph
Ph
N
N
N
N
OCF3
Ph
Ph
70
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
f1 (ppm)

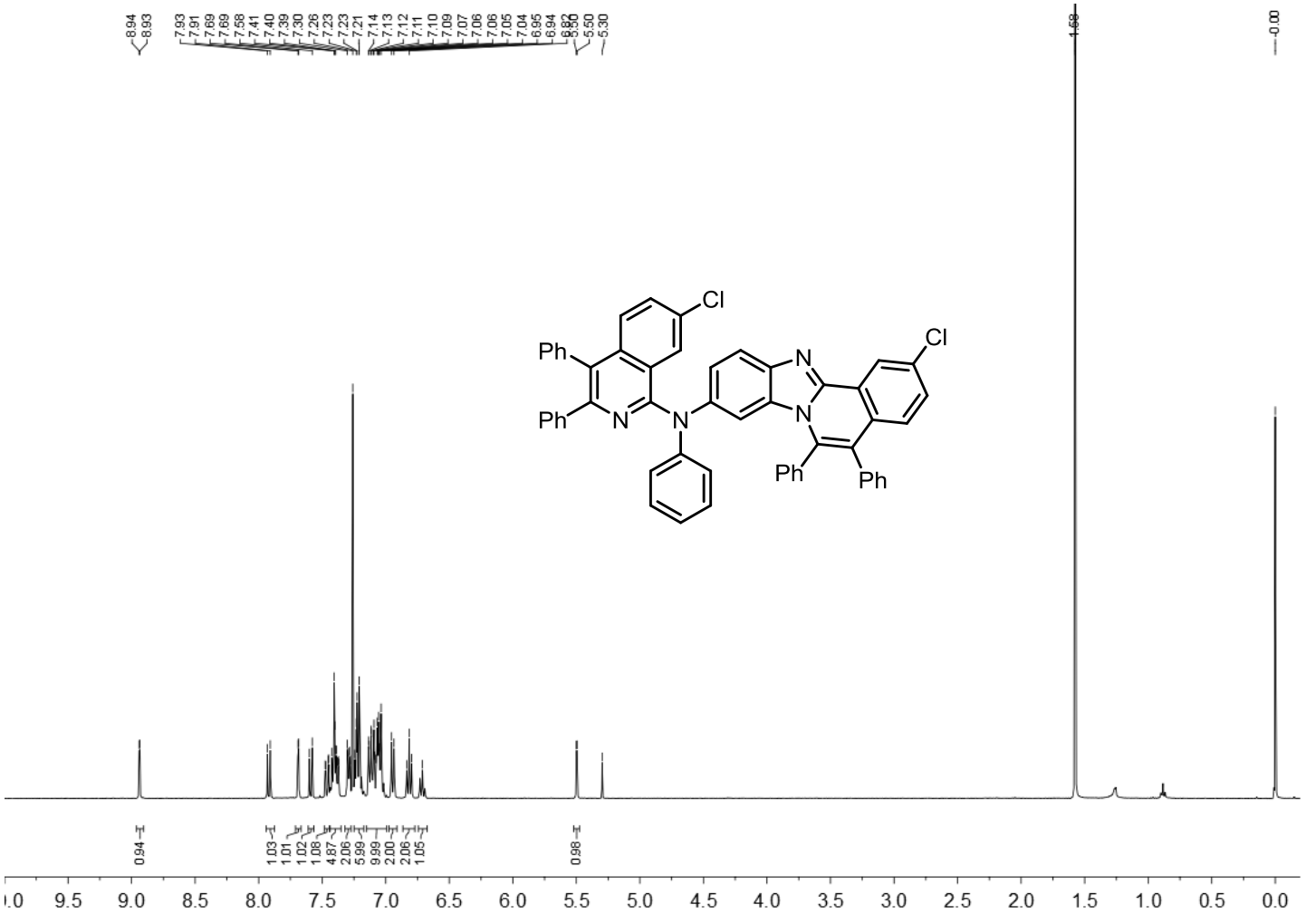

-57.49
-57.88
OCF3
Ph
Ph
N
N
N
N
OCF3
Ph
Ph
10 0 -10 -20 -30 -40 -50 -60 -70 -80 -90 -100 -110 -120 -130 -140 -150 -160 -170 -180 -190 -200 -210
f1 (ppm)

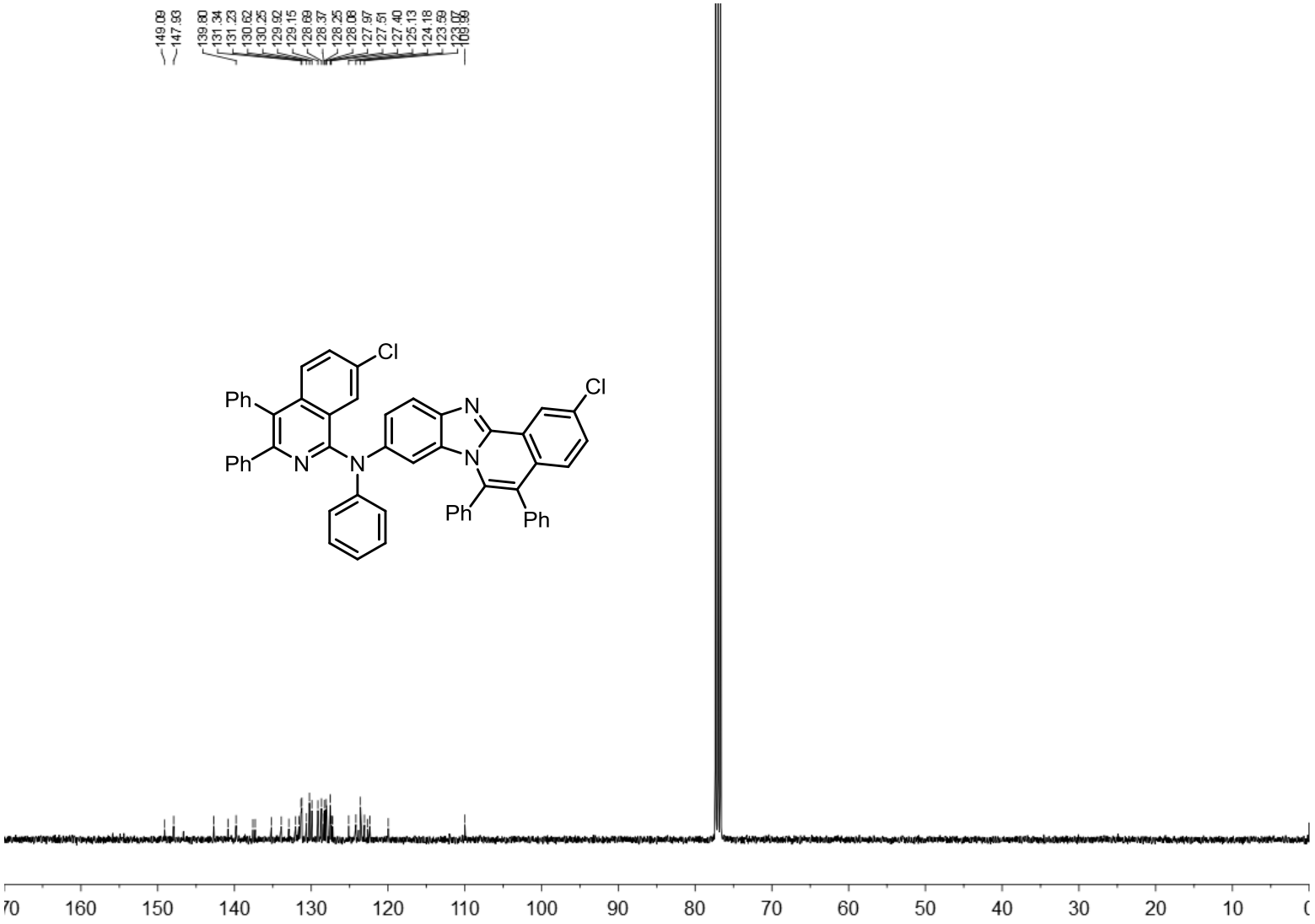
Compound 3ia



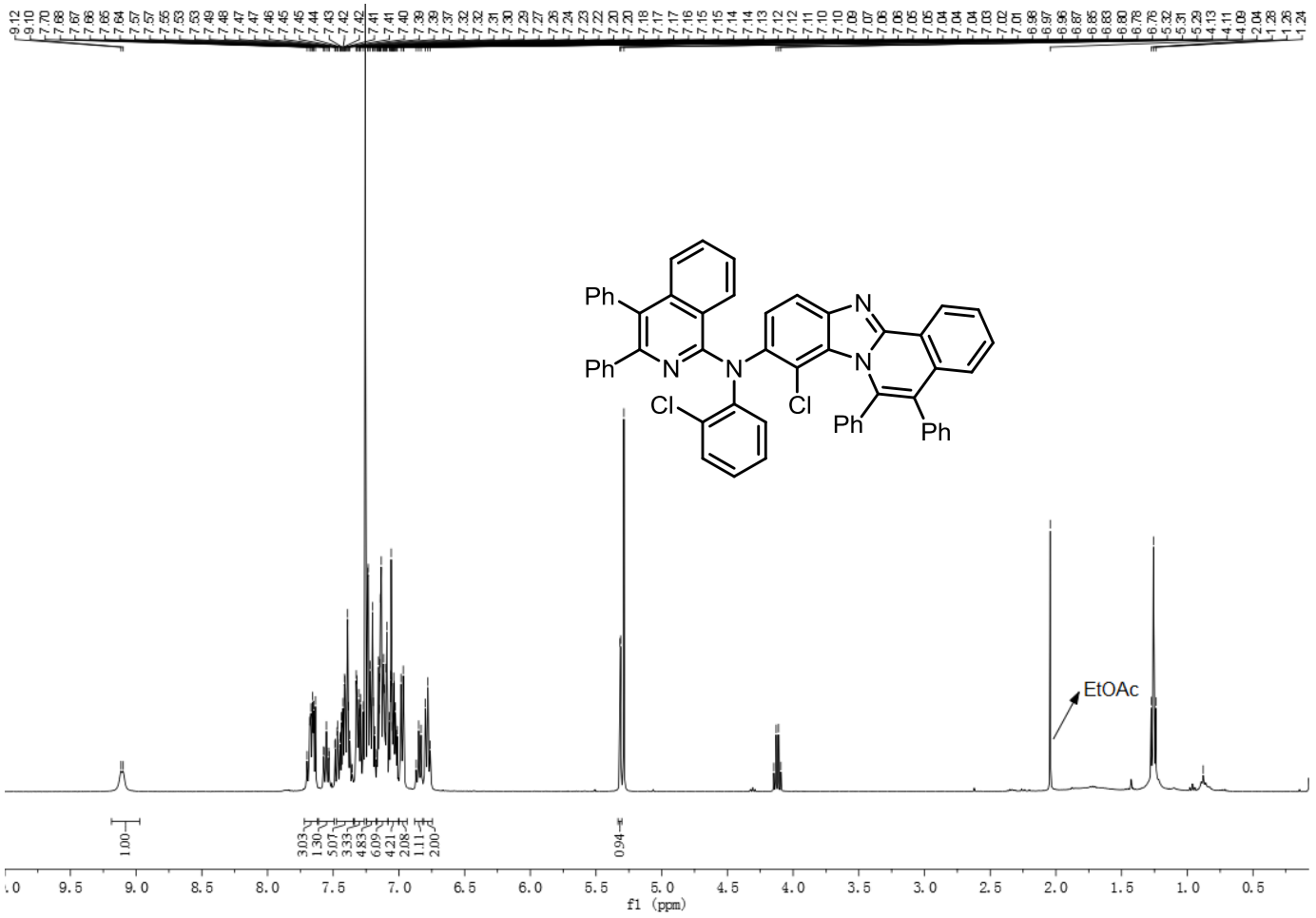

160.69
156.88
149.27
148.26
131.41
130.35
129.93
129.06
128.94
128.91
128.64
128.30
128.28
128.04
127.98
127.49
127.42
127.38
127.03
124.55
29.73
Ph
Ph
Ph
N
N
N
Ph
Ph
Ph
30
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
f1 (ppm)

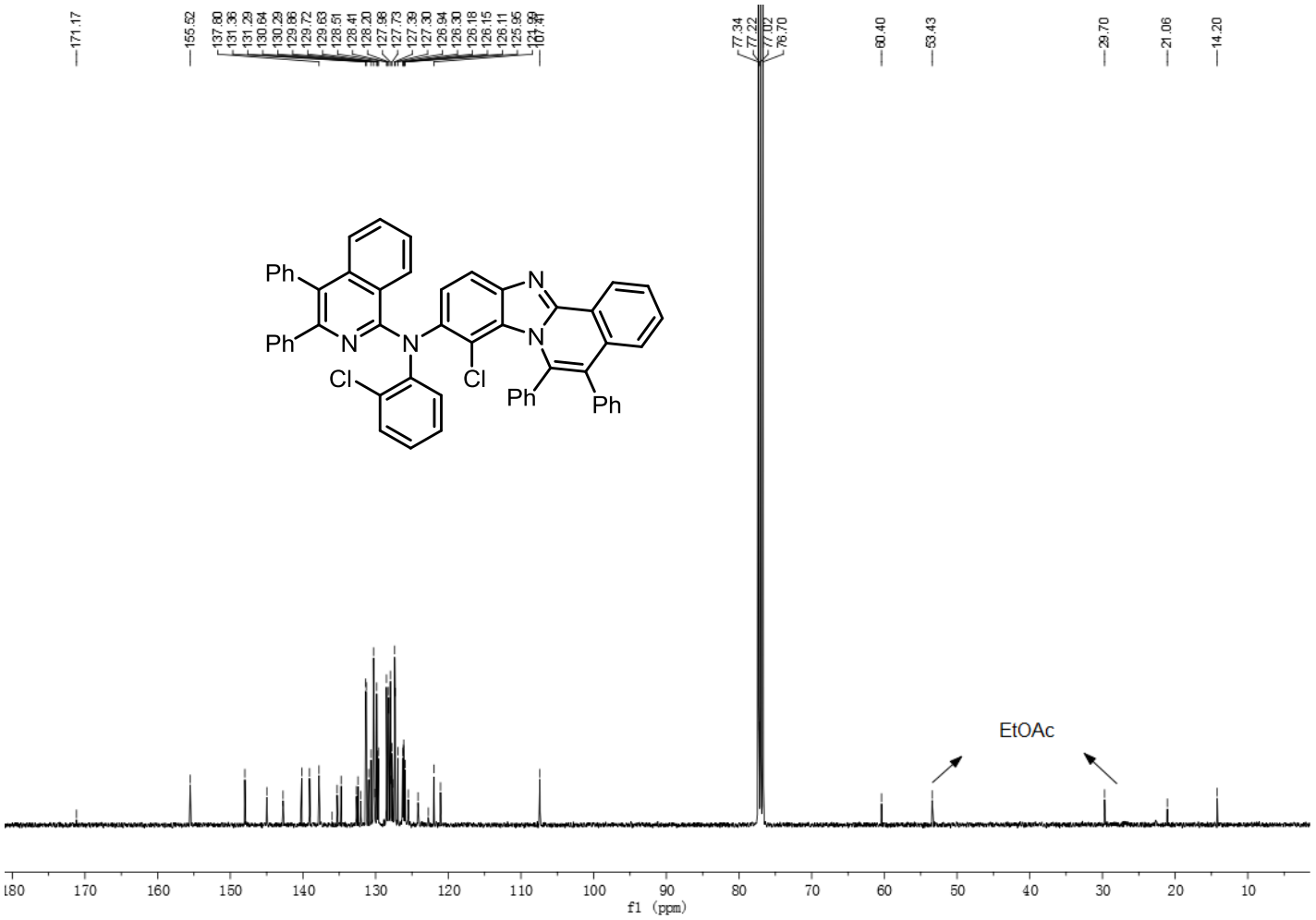
Compound 3ja



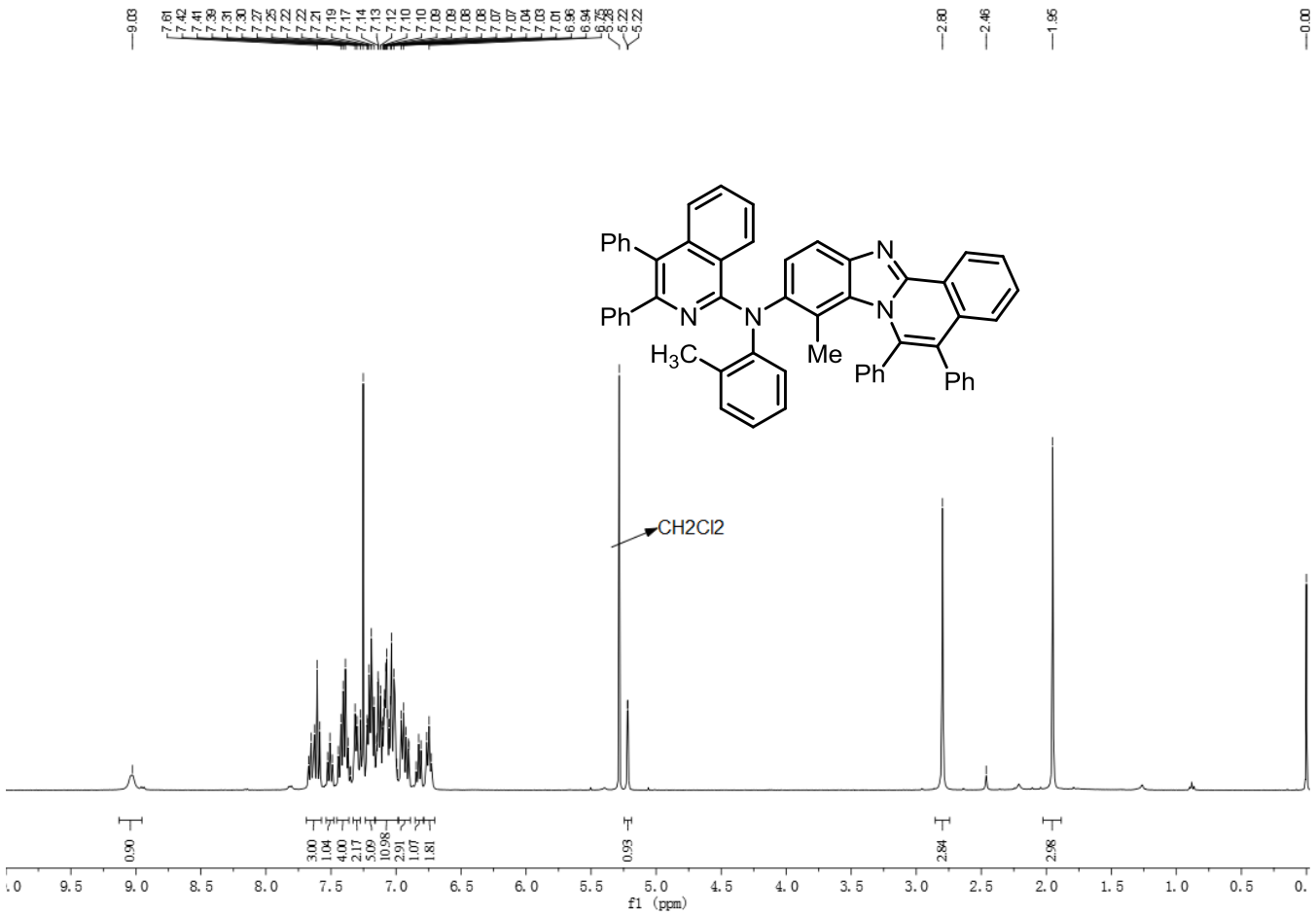

149.09
147.93
139.80
131.34
131.23
130.62
130.25
129.92
129.15
128.69
128.37
128.25
128.08
127.97
127.51
127.40
125.13
124.18
123.69
Cl
Ph
Ph
N
N
N
N
Cl
Ph
Ph
70
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10

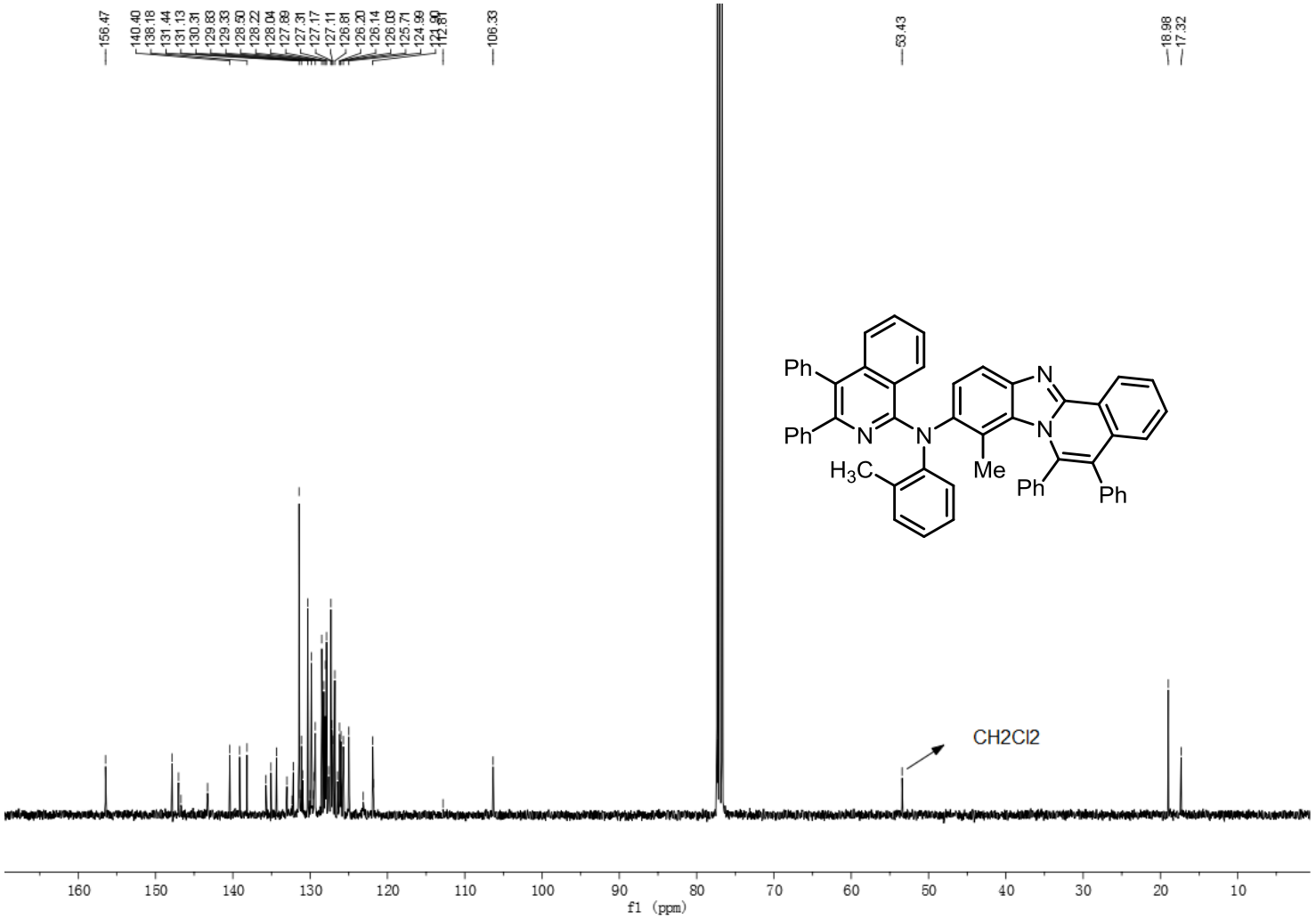
Compound 3ka



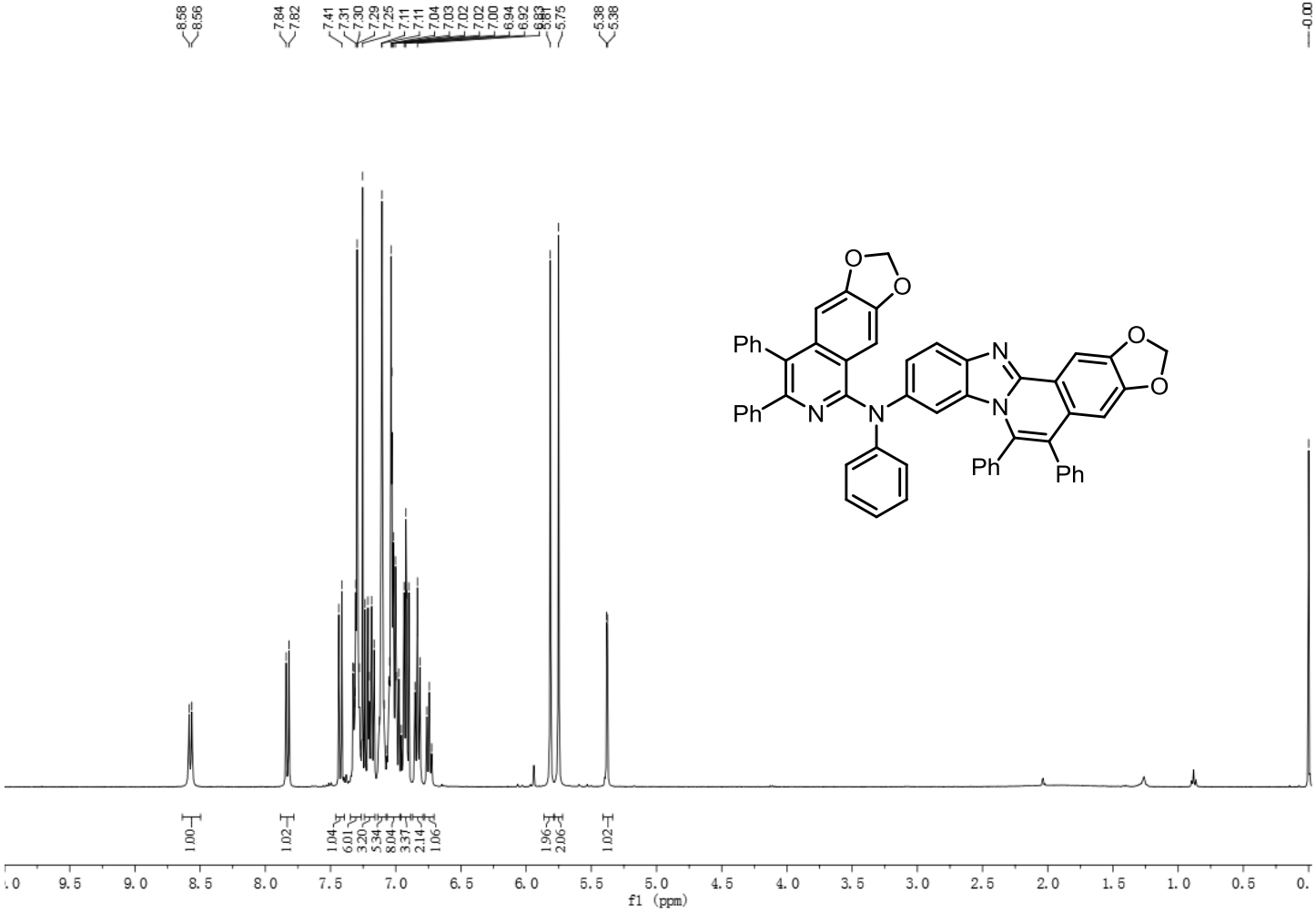

171.17
155.52
137.80
131.36
131.29
130.64
130.29
129.86
129.72
129.63
128.51
128.41
128.20
127.98
127.73
127.39
127.30
126.94
126.30
126.18
126.15
126.11
125.95
121.99
107.41
77.34
77.22
77.02
76.70
60.40
53.43
29.70
21.06
14.20
Ph
Ph
N
N
Cl
N
N
Cl
Ph
Ph
EtOAc
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
f1 (ppm)

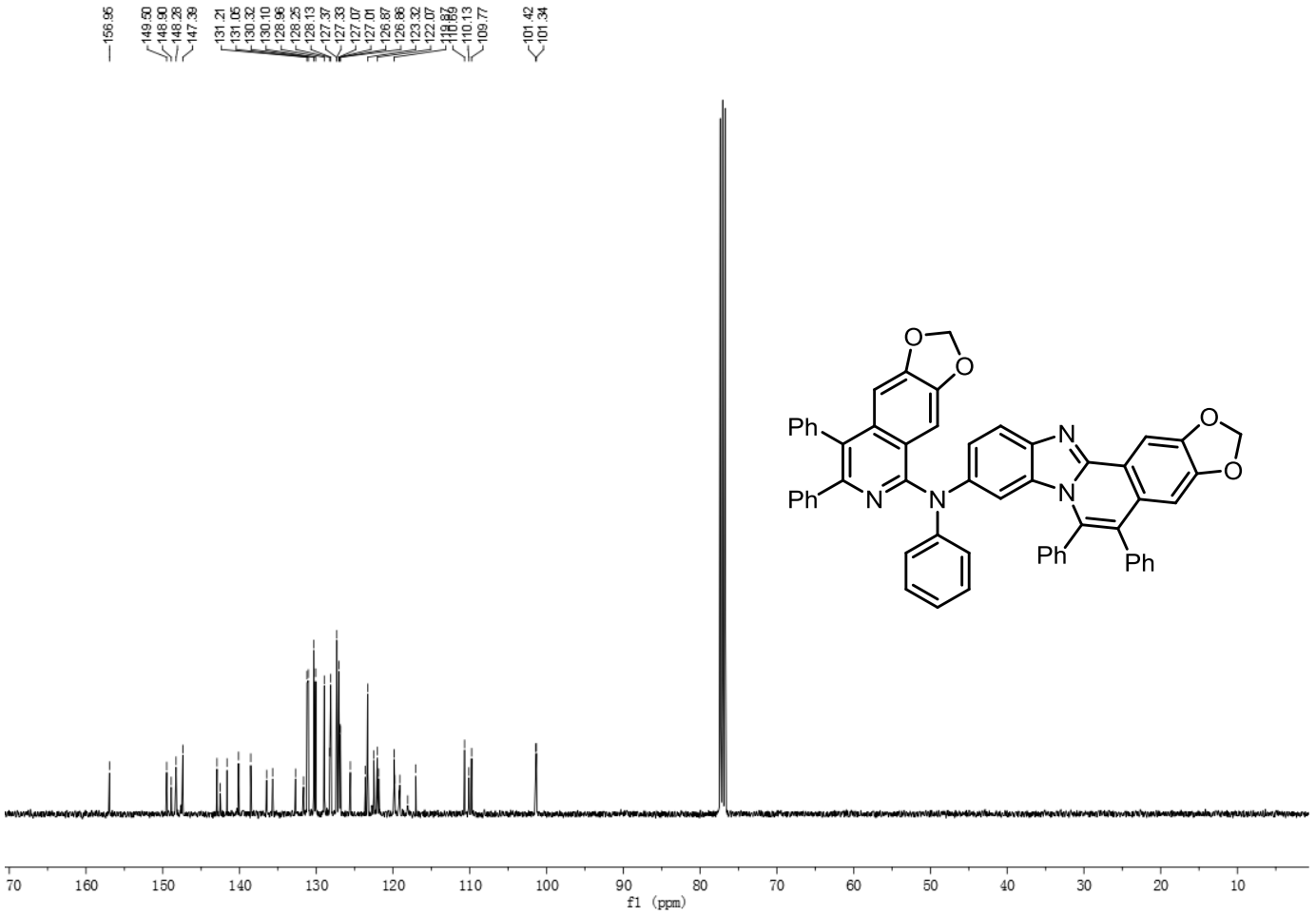
Compound 3la



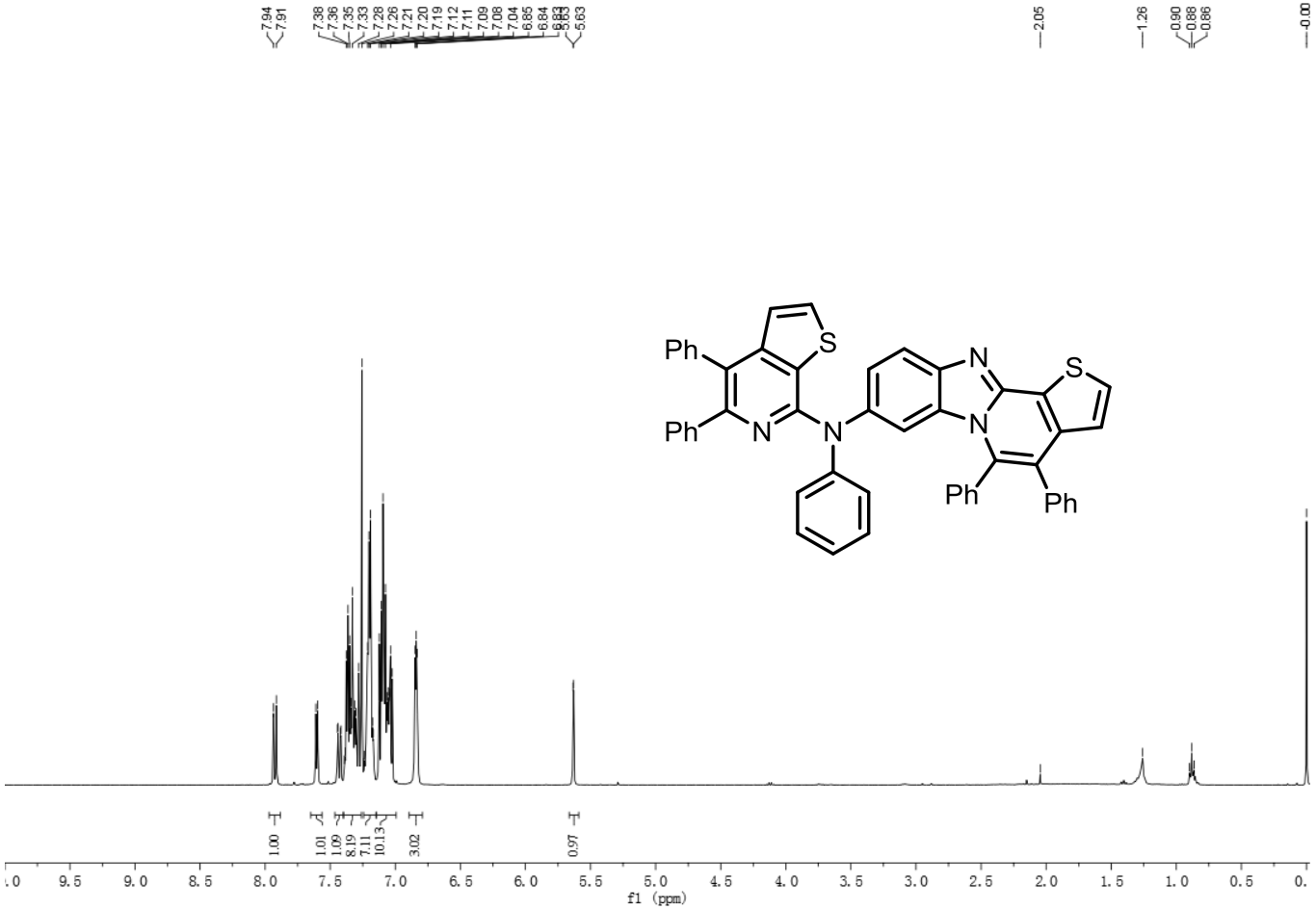

156.47
140.40
138.18
131.44
131.13
130.31
129.83
129.33
128.50
128.22
128.04
127.89
127.31
127.17
127.11
126.81
126.20
126.14
126.03
125.71
124.99
106.33
53.43
18.98
17.32
Ph
Ph
N
N
N
N
H3C
Me
Ph
Ph
CH2Cl2
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
f1 (ppm)

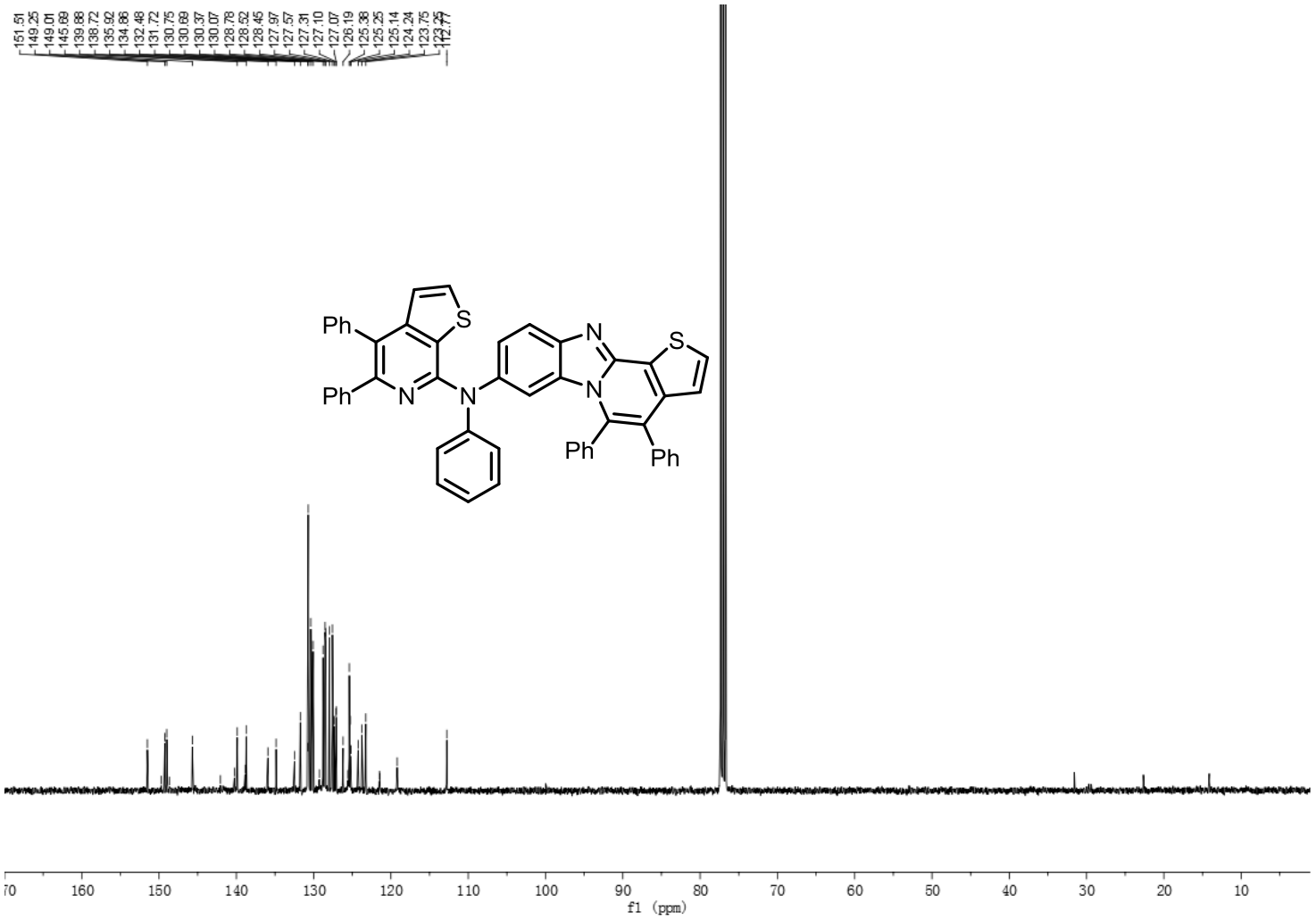
Compound 3ma



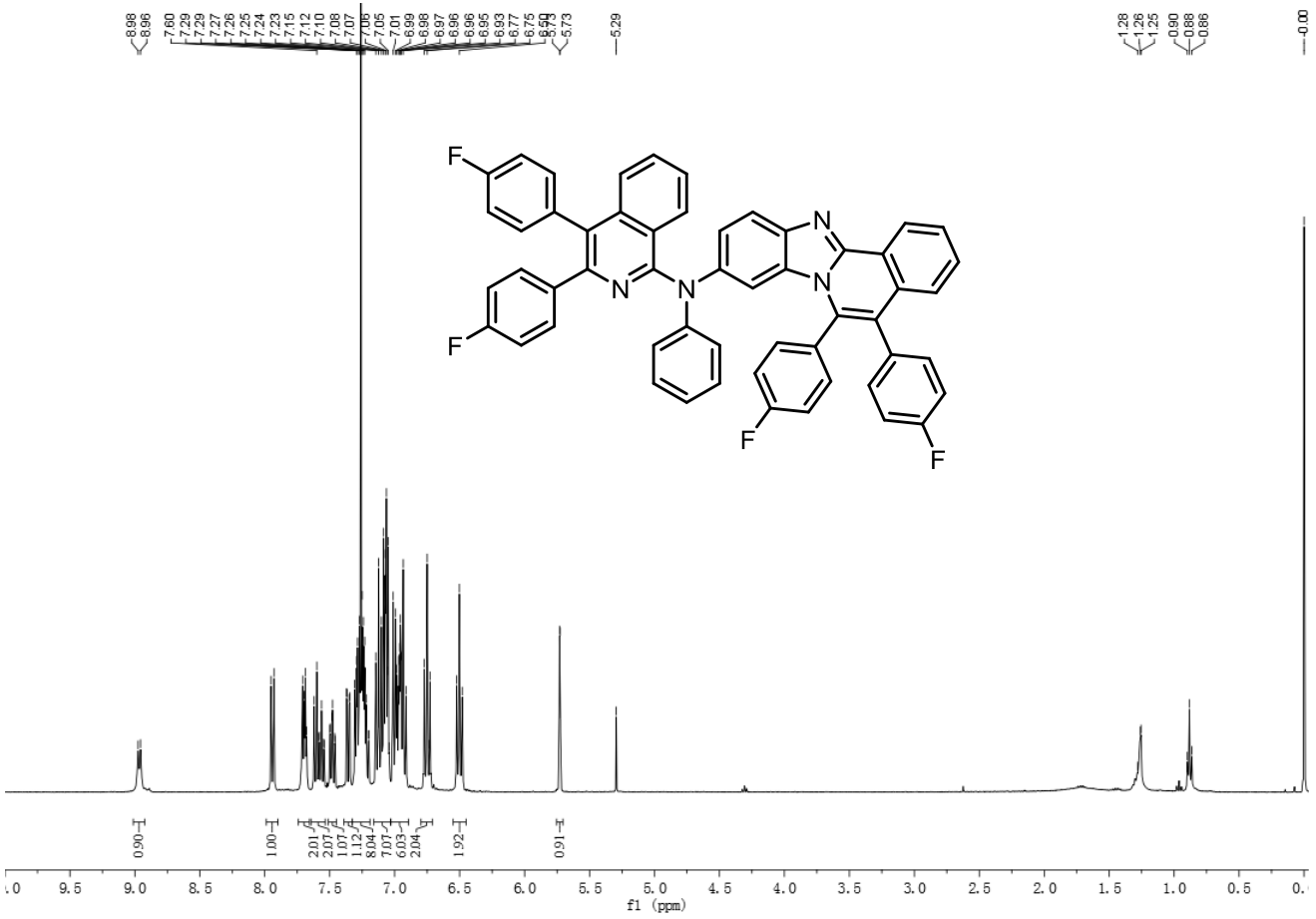

156.95
149.50
148.90
148.28
147.39
131.21
131.05
130.32
130.10
128.96
128.25
128.13
127.37
127.33
127.07
127.01
126.87
126.86
123.32
122.07
110.13
109.77
101.42
101.34
Ph
Ph
N
N
N
N
O
O
O
O
Ph
Ph
70
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
f1 (ppm)

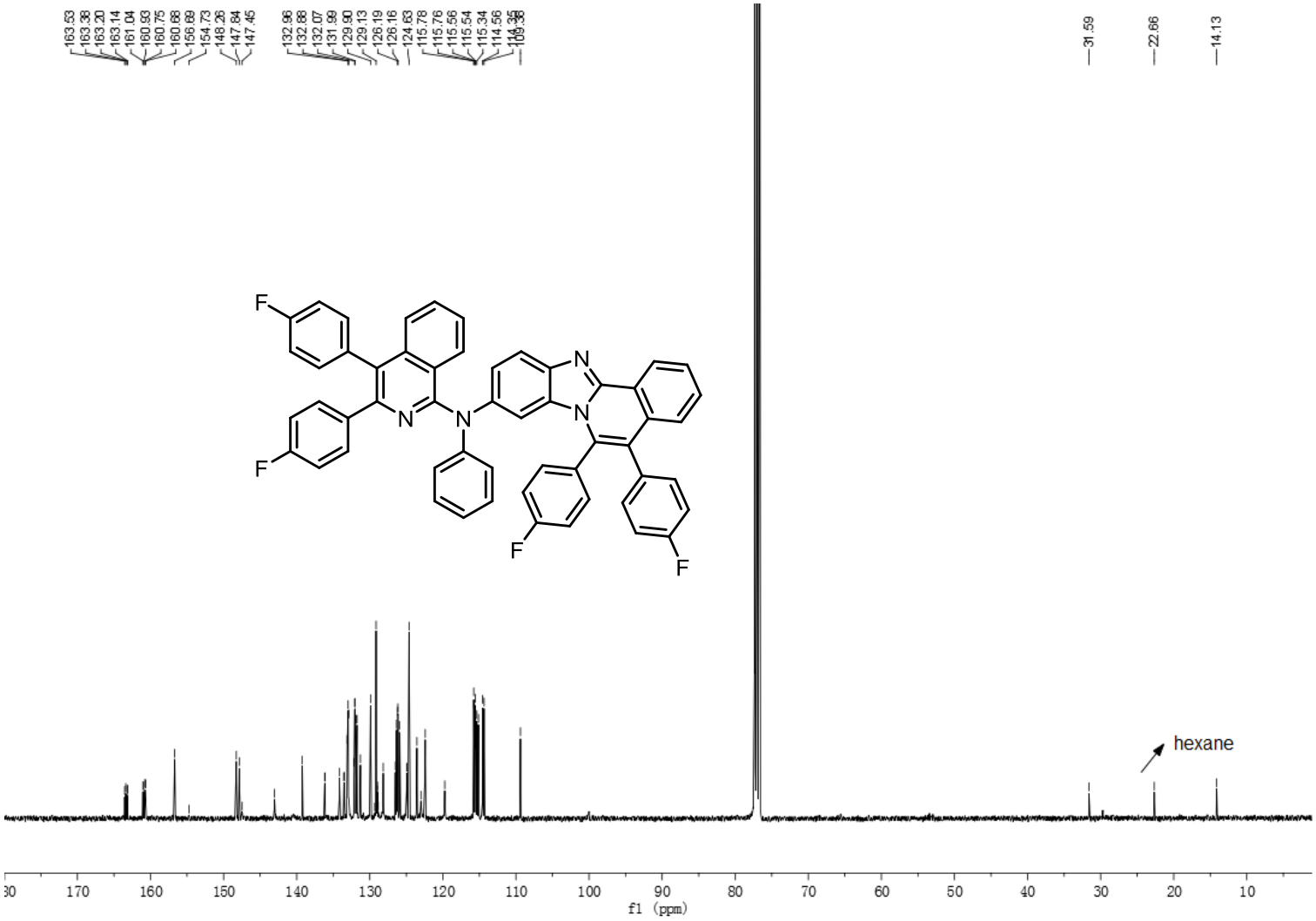
Compound 3na

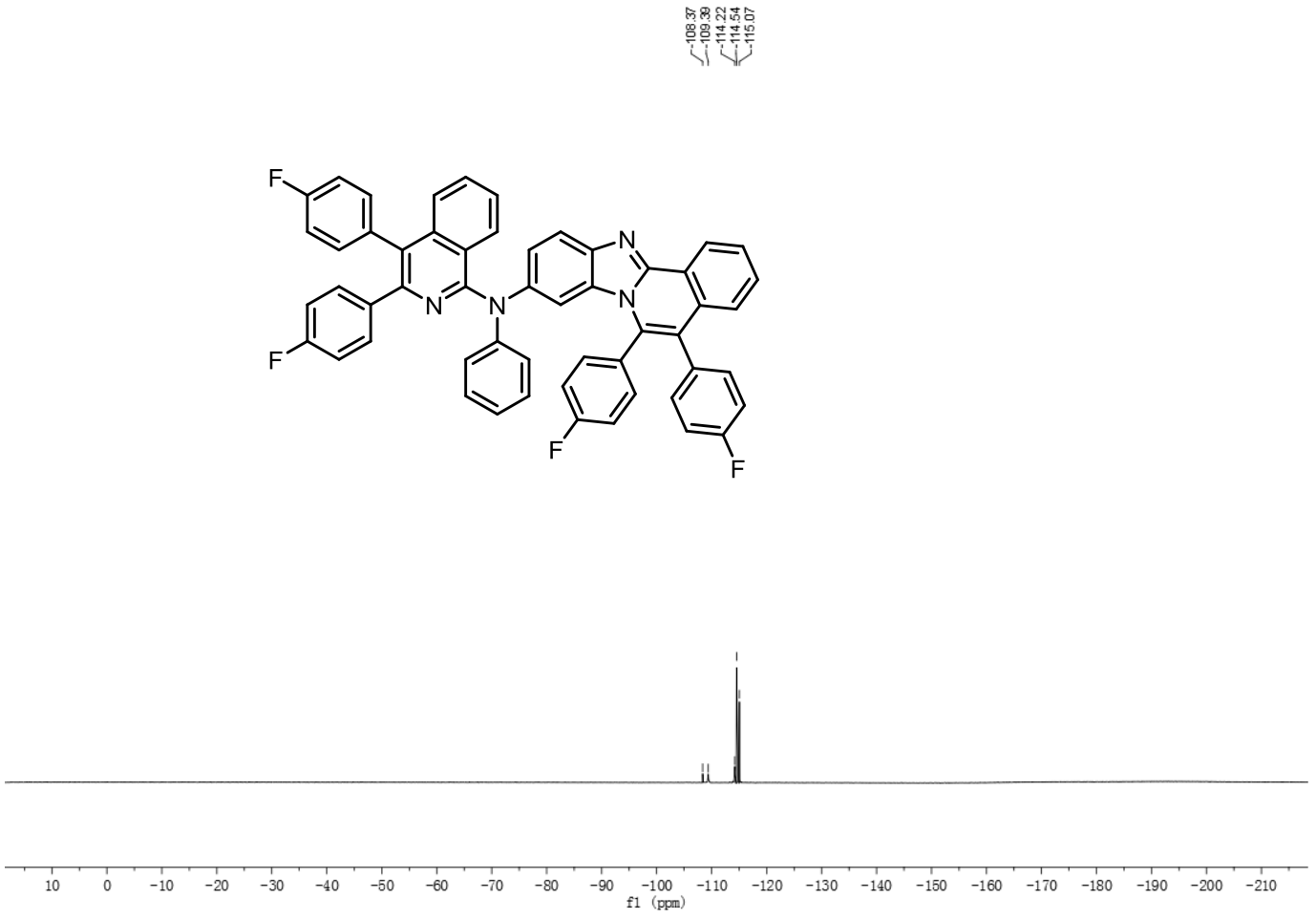



151.51
149.25
149.01
145.69
139.88
138.72
135.92
134.86
132.48
131.72
130.75
130.69
130.37
130.07
128.78
128.52
128.45
127.97
127.57
127.31
127.10
127.07
126.19
125.38
125.25
125.14
124.24
123.75
123.25
112.77
Ph
Ph
S
N
N
N
S
Ph
Ph
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
f1 (ppm)

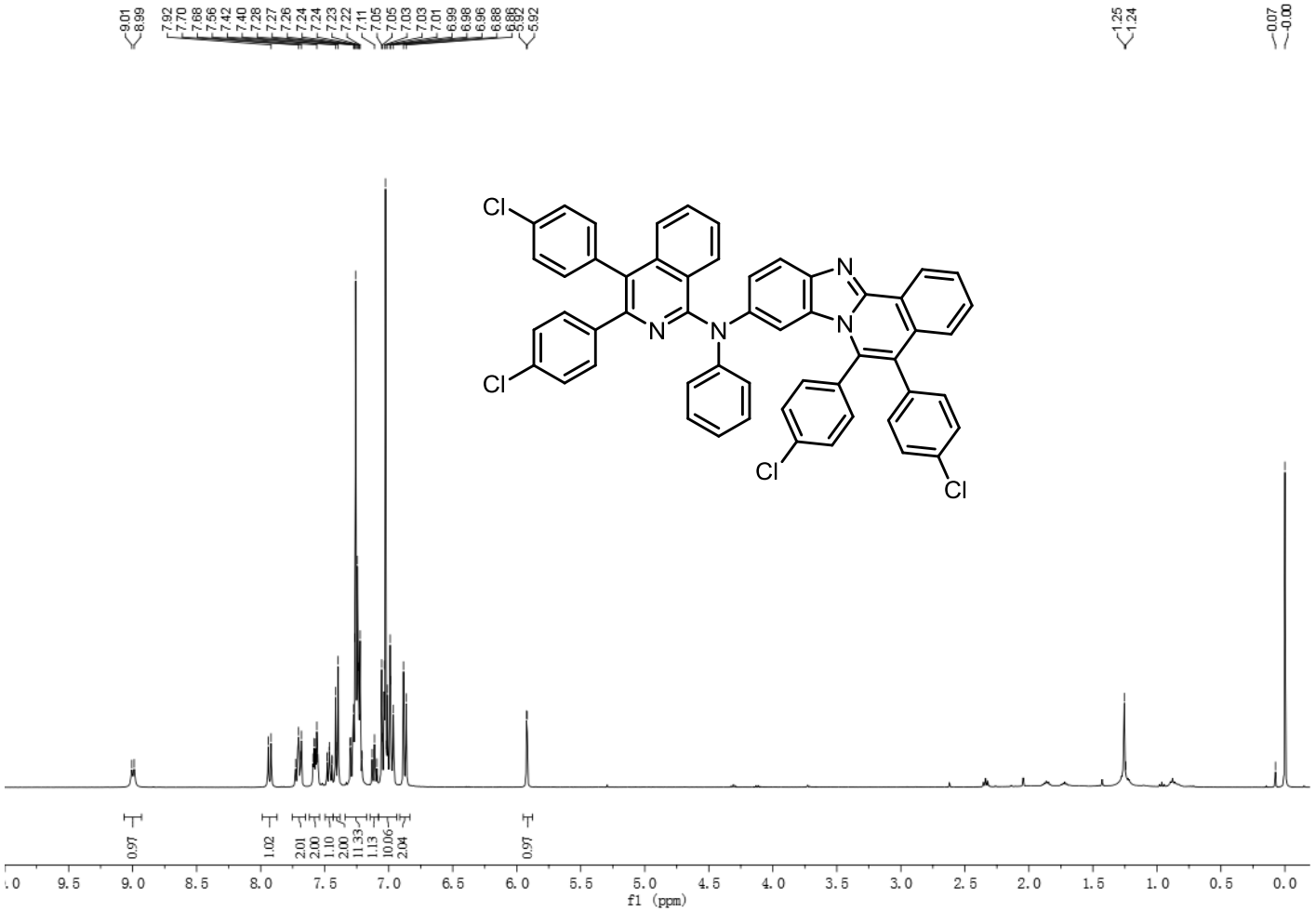
Compound 3ab

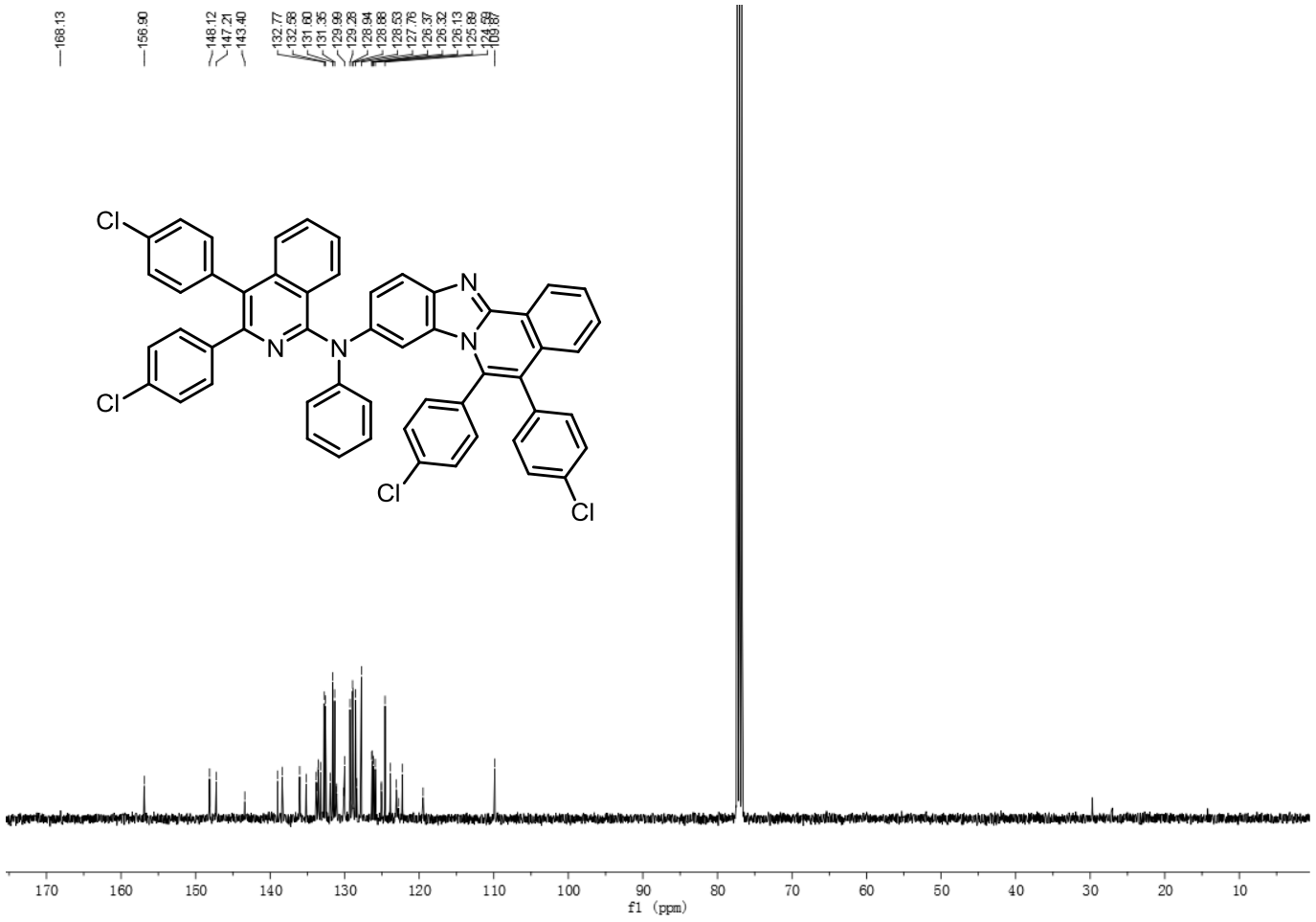



163.53
163.38
163.20
163.14
161.04
160.93
160.75
160.68
156.89
154.73
148.26
147.84
147.45
132.96
132.88
132.07
131.99
129.90
129.13
126.19
126.16
124.63
115.78
115.76
115.56
115.54
115.34
114.56
31.59
22.66
14.13
F
F
N
N
N
F
F
hexane
f1 (ppm)

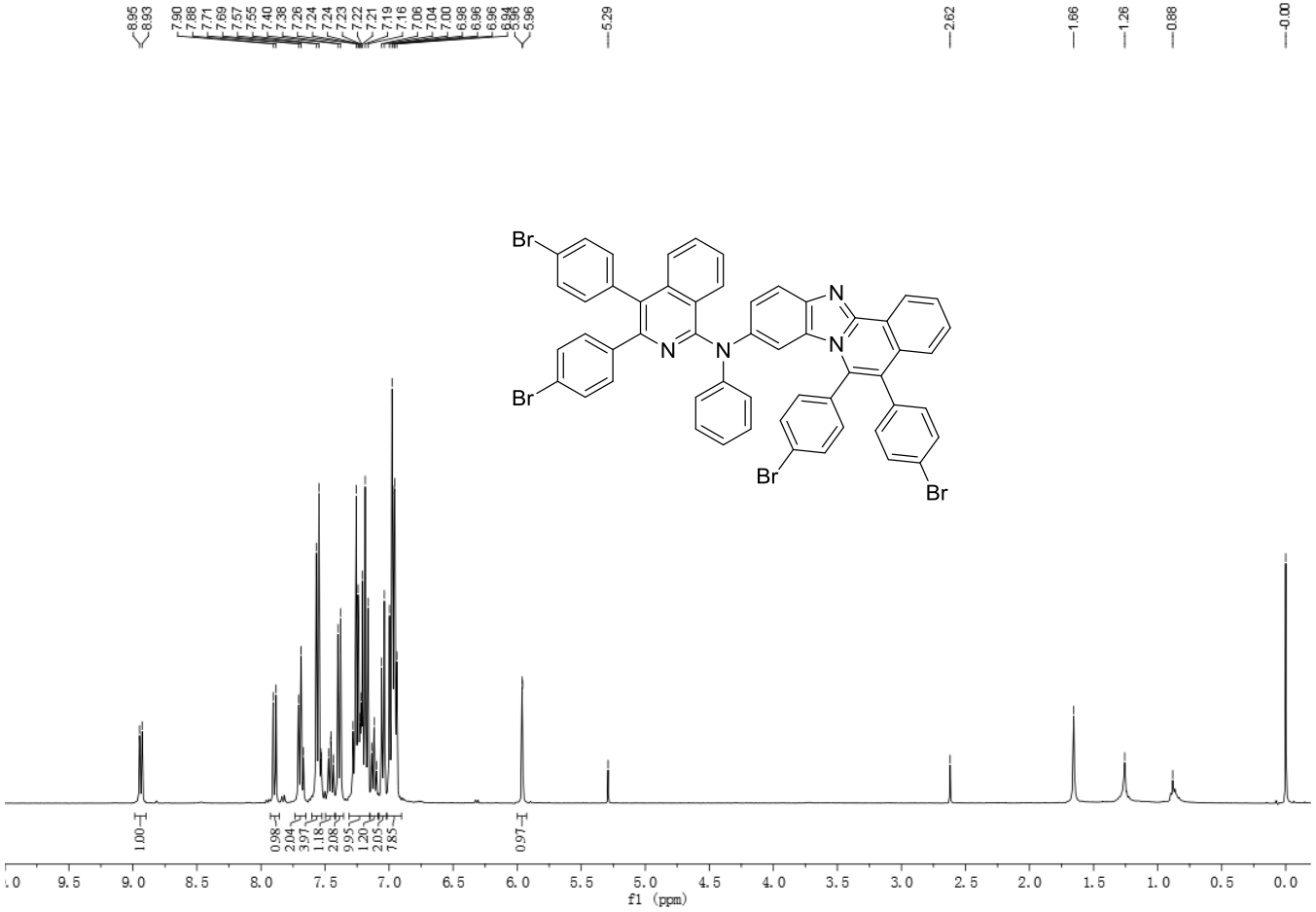

-108.37
-109.39
-114.22
-114.54
-115.07
F
F
N
N
N
F
F
10
0
-10
-20
-30
-40
-50
-60
-70
-80
-90
-100
-110
-120
-130
-140
-150
-160
-170
-180
-190
-200
-210
f1 (ppm)

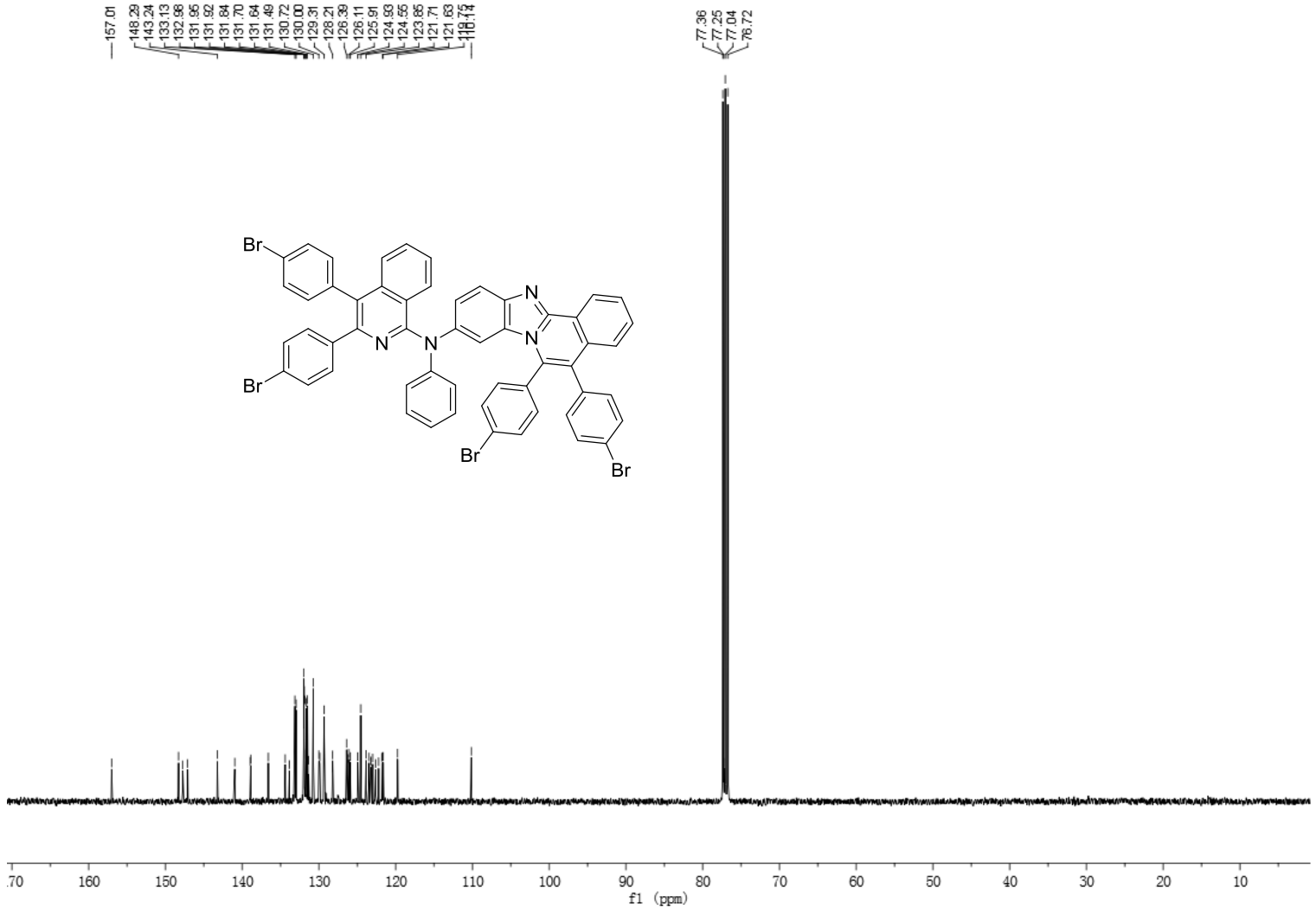
Compound 3ac



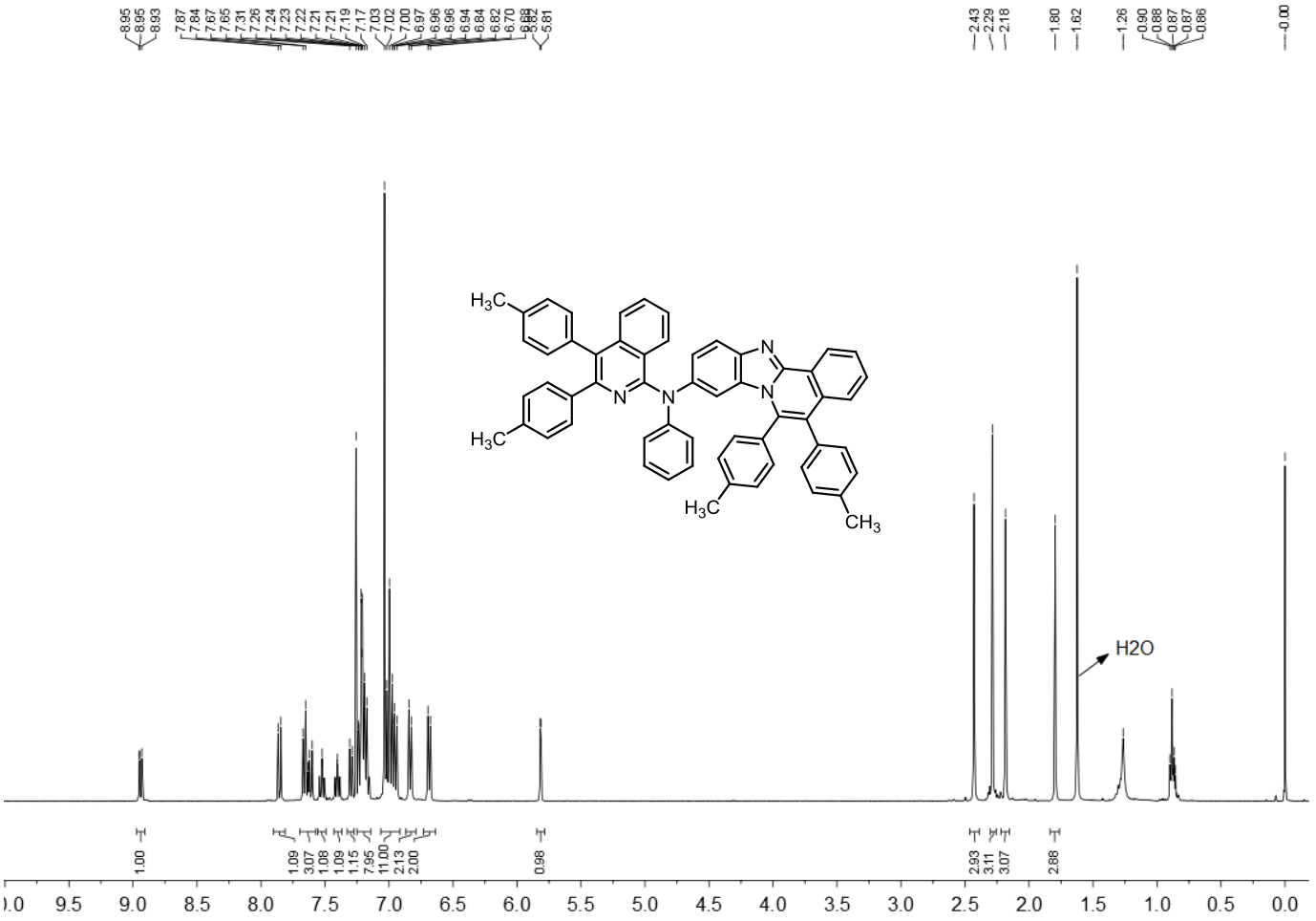

168.13
156.90
148.12
147.21
143.40
132.77
132.68
131.60
131.35
129.99
129.28
128.94
128.88
128.53
127.76
126.37
126.32
126.13
125.89
124.69
109.87
Cl
Cl
Cl
Cl
N
N
N
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
f1 (ppm)

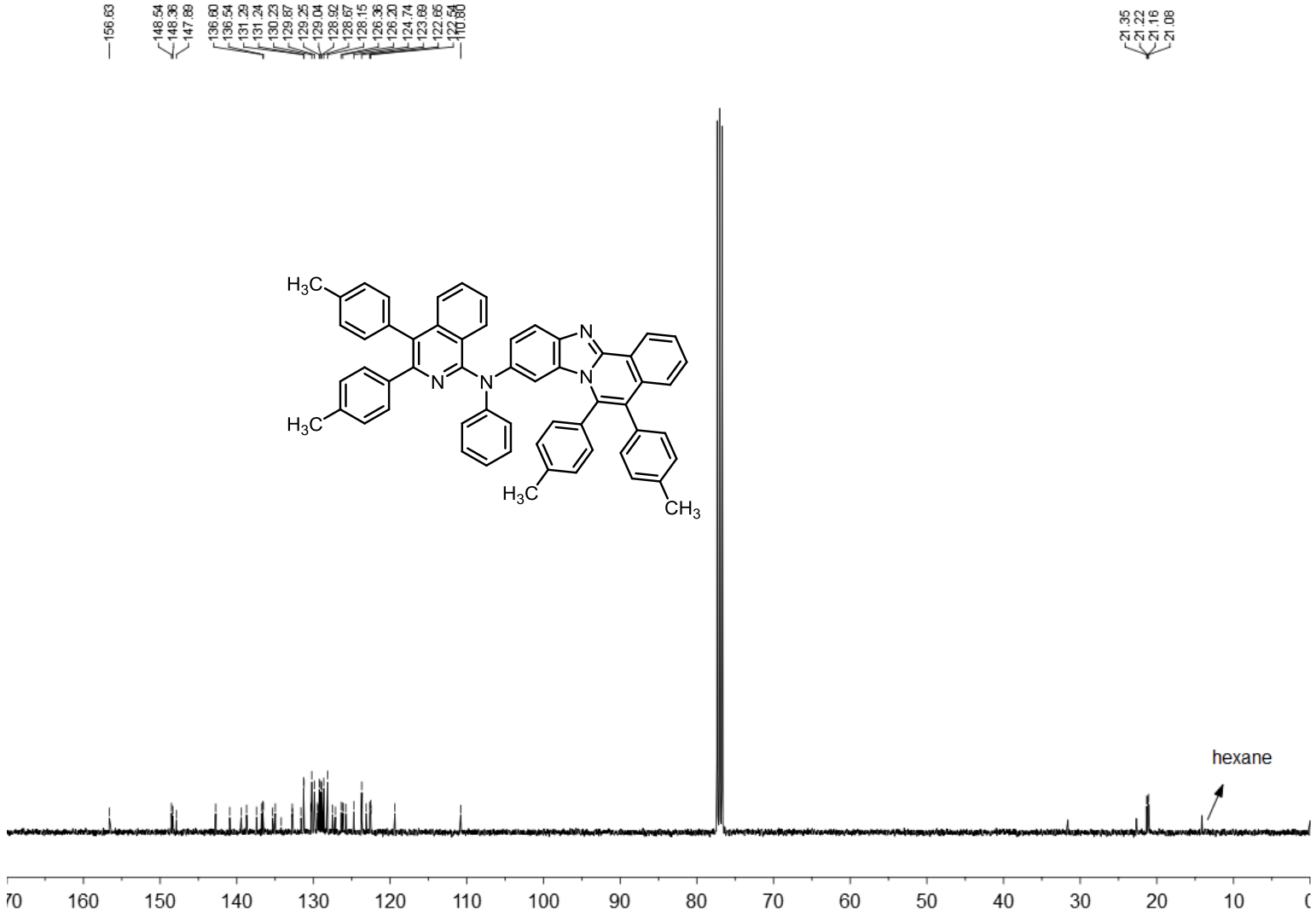
Compound 3ae



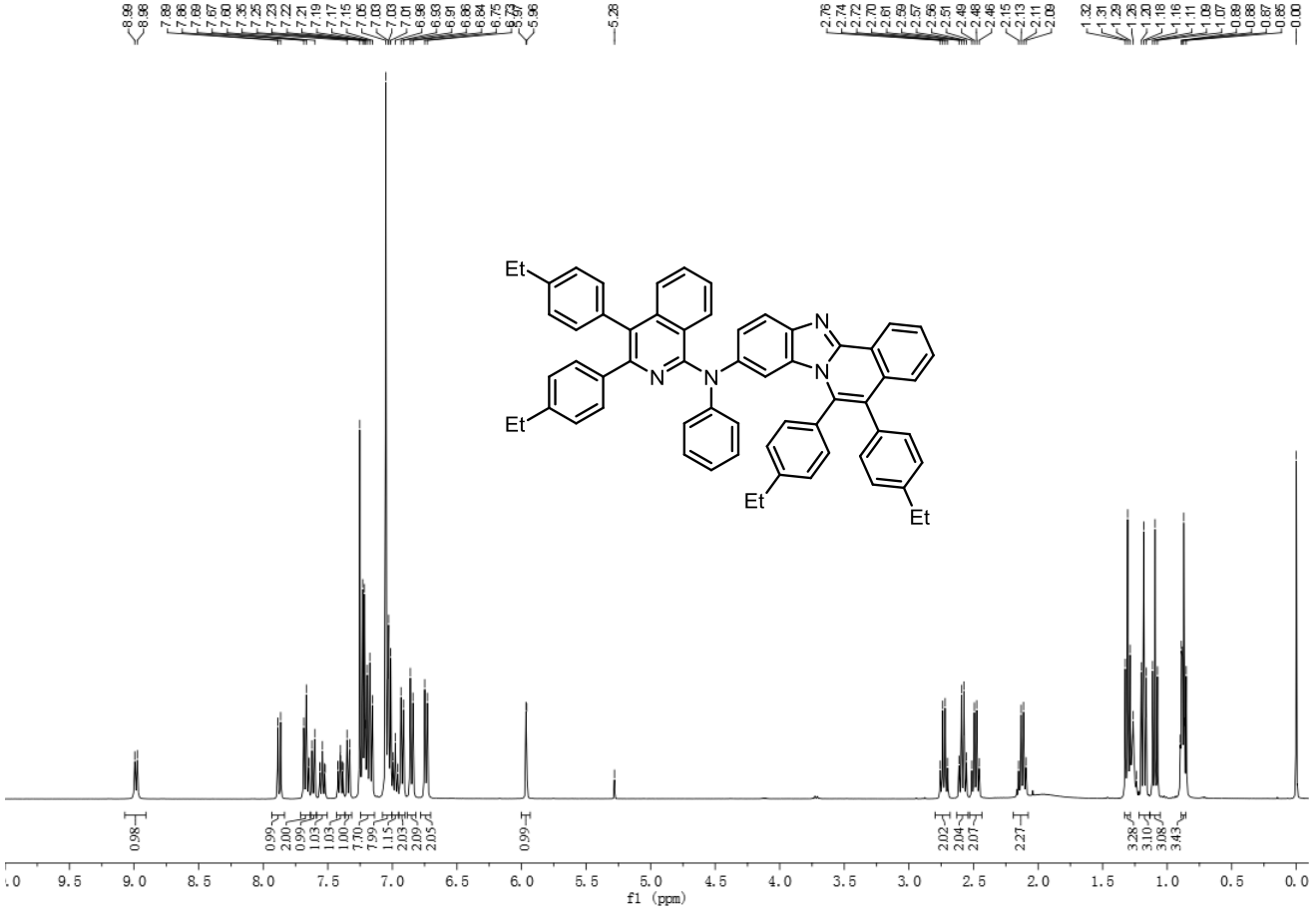

157.01
148.29
143.24
133.13
132.98
131.95
131.92
131.84
131.70
131.64
131.49
130.72
130.00
129.31
128.21
126.39
126.11
125.91
124.93
124.55
123.85
121.71
121.63
77.36
77.25
77.04
76.72
Br
Br
Br
Br
N
N
N
N
70
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
f1 (ppm)

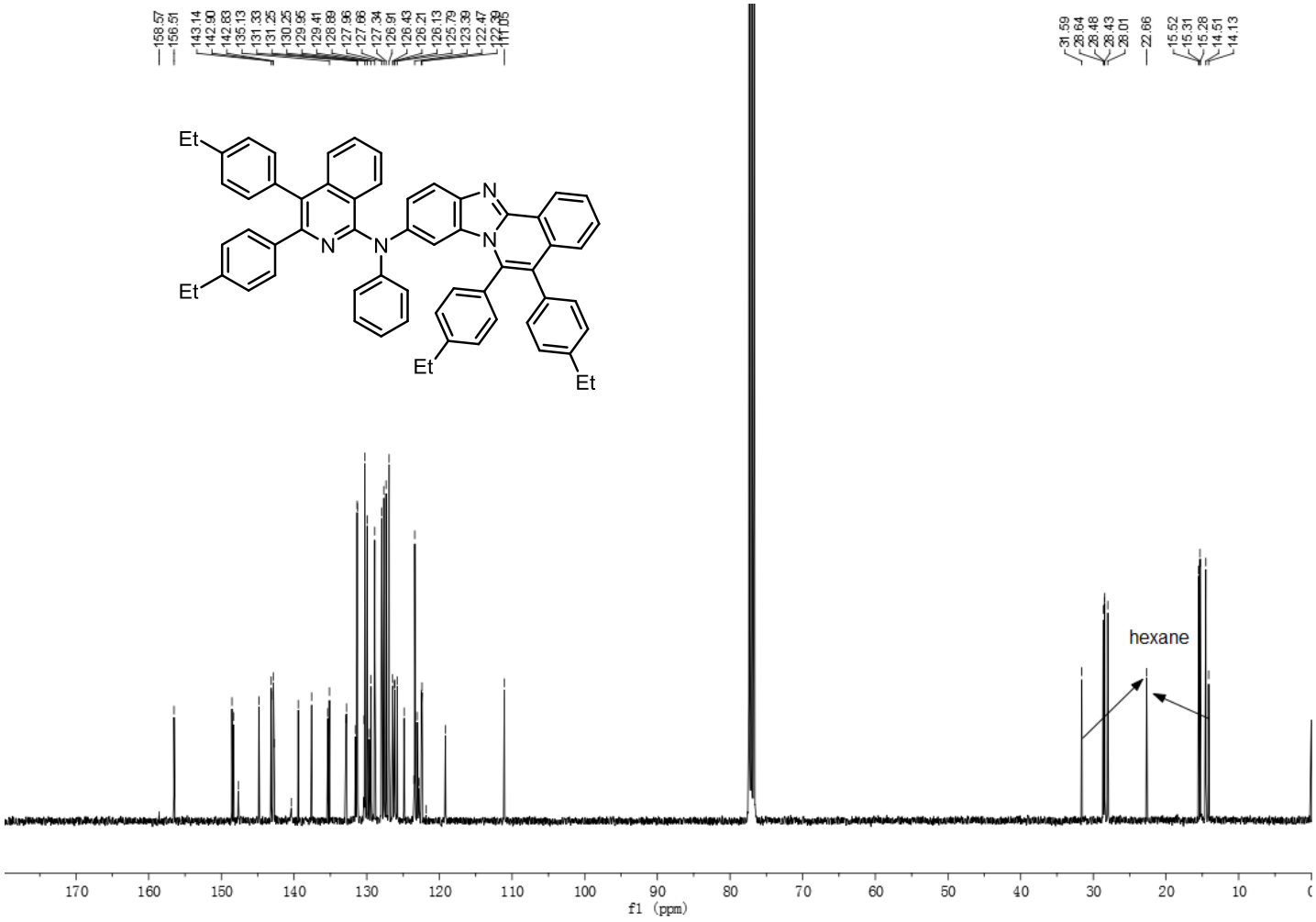
Compound 3ae



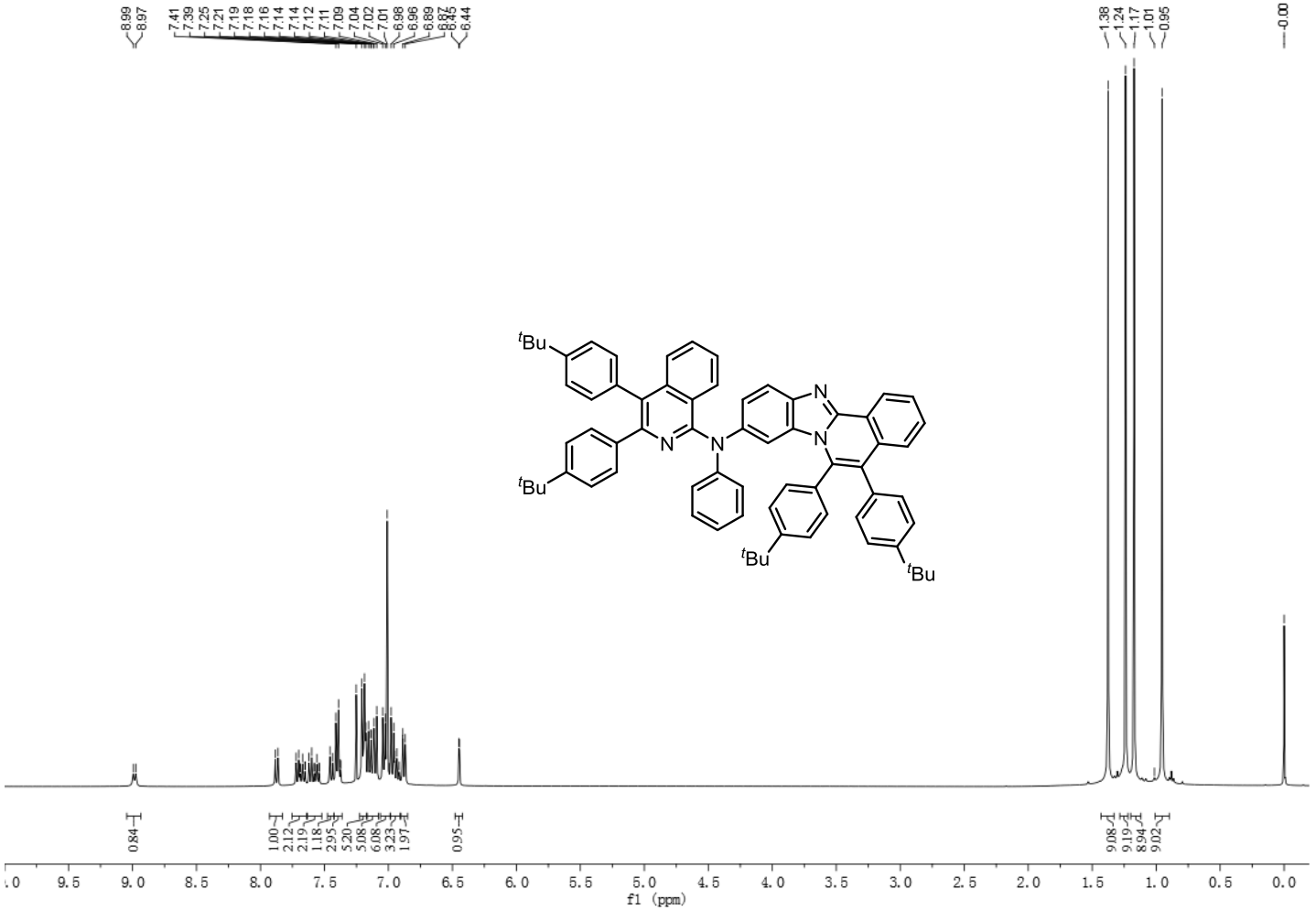

156.63
148.54
148.36
147.89
136.60
136.54
131.29
131.24
130.23
129.87
129.25
129.04
128.92
128.67
128.15
126.36
126.20
124.74
123.69
122.65
122.54
110.80
21.35
21.22
21.16
21.08
H3C
H3C
N
N
N
H3C
CH3
hexane
70
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0

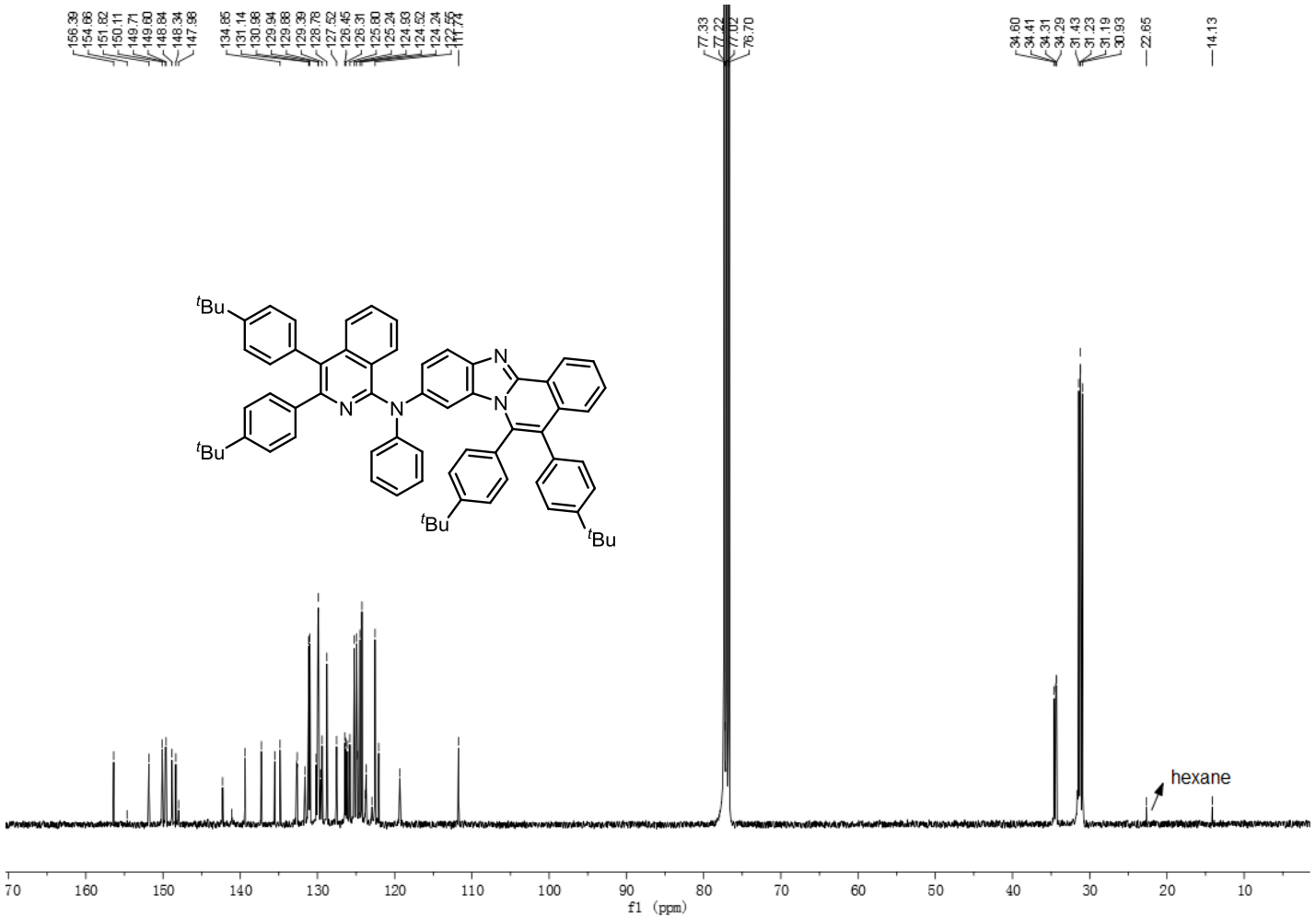
Compound 3af



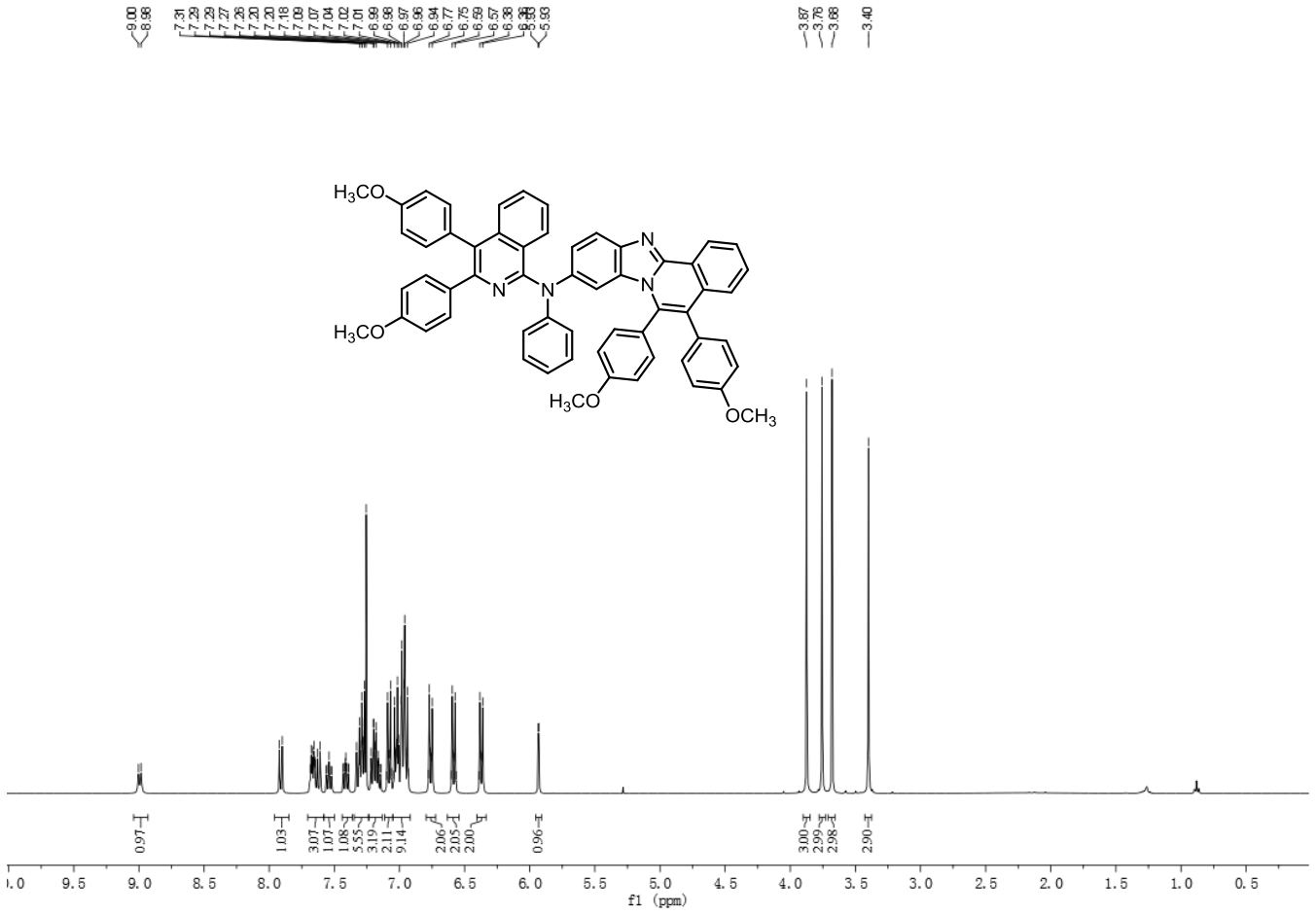

158.57
156.51
143.14
142.90
142.83
135.13
131.33
131.25
130.25
129.95
129.41
128.89
127.96
127.66
127.34
126.91
126.43
126.21
126.13
125.79
123.39
122.47
122.39
111.05
31.59
29.64
28.48
28.43
28.01
22.66
15.52
15.31
15.28
14.51
14.13
Et
Et
Et
Et
N
N
N
hexane
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
f1 (ppm)

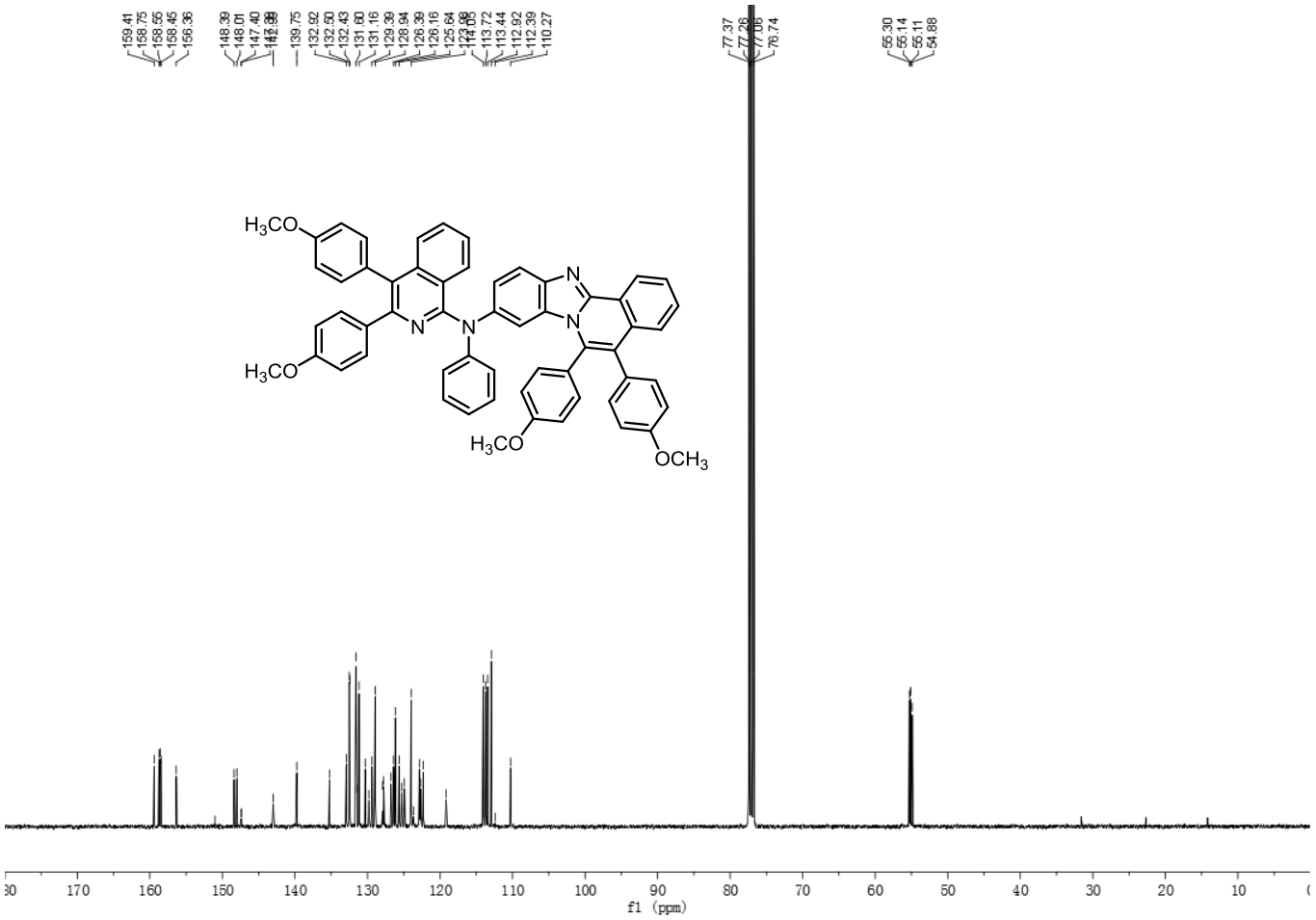
Compound 3ag



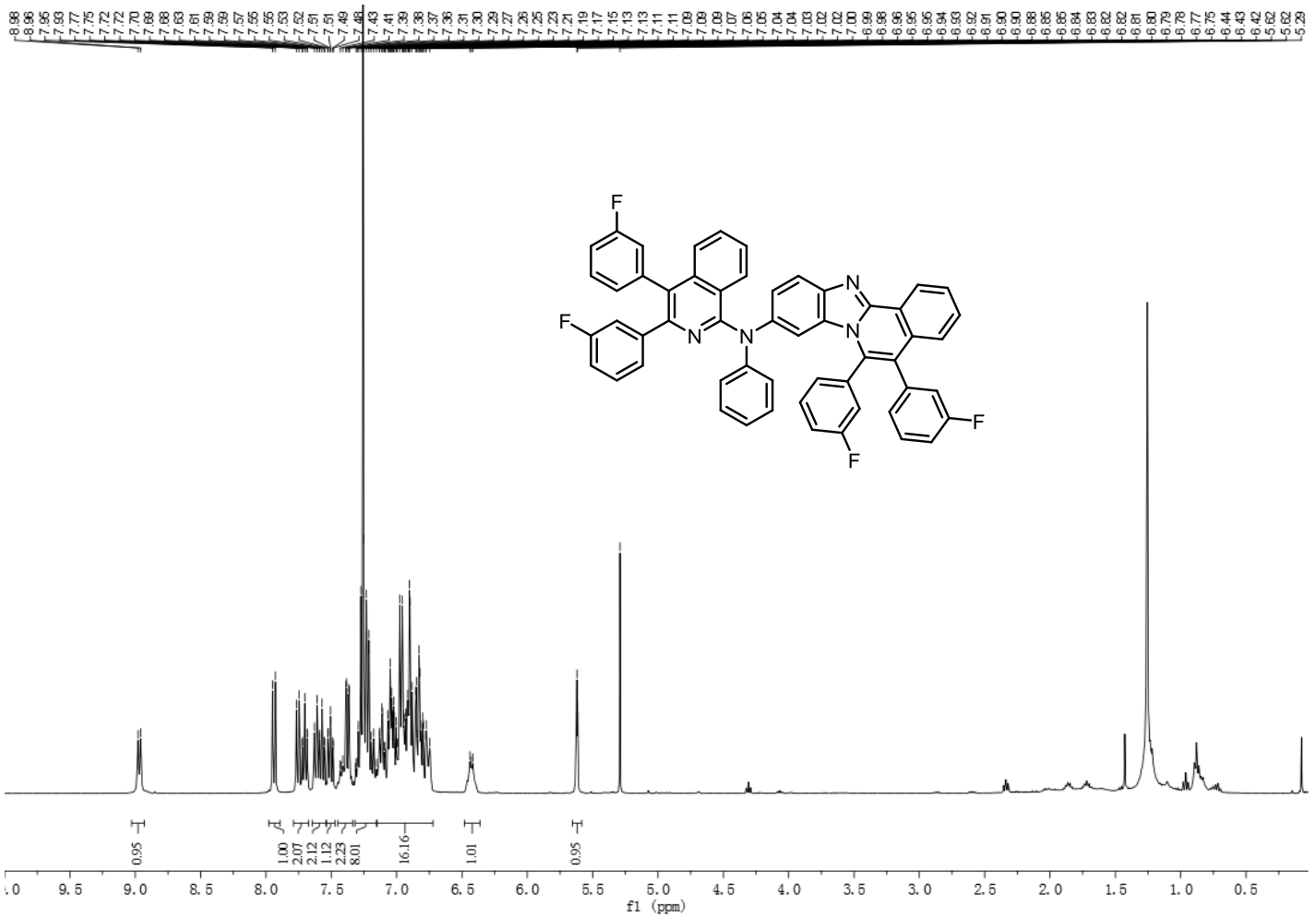

156.39
154.66
151.62
150.11
149.71
149.60
148.84
148.34
147.98
134.85
131.14
130.98
129.94
129.88
129.39
128.78
127.52
126.45
126.31
125.80
125.24
124.93
124.52
124.24
122.45
111.74
77.33
77.22
77.02
76.70
34.60
34.41
34.31
34.29
31.43
31.23
31.19
30.93
22.65
14.13
tBu
tBu
tBu
tBu
N
N
N
N
hexane
70
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
f1 (ppm)

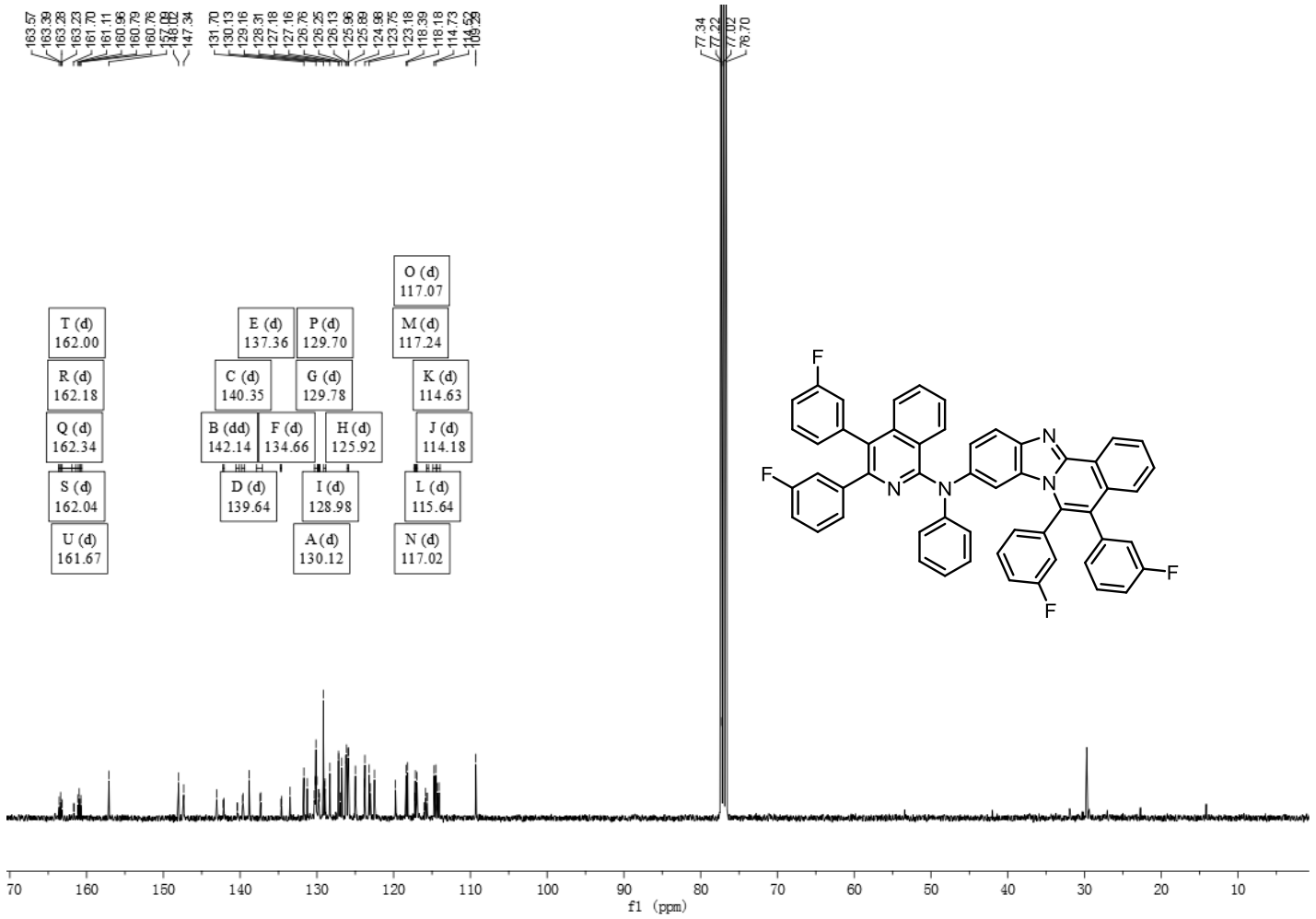
Compound 3ah

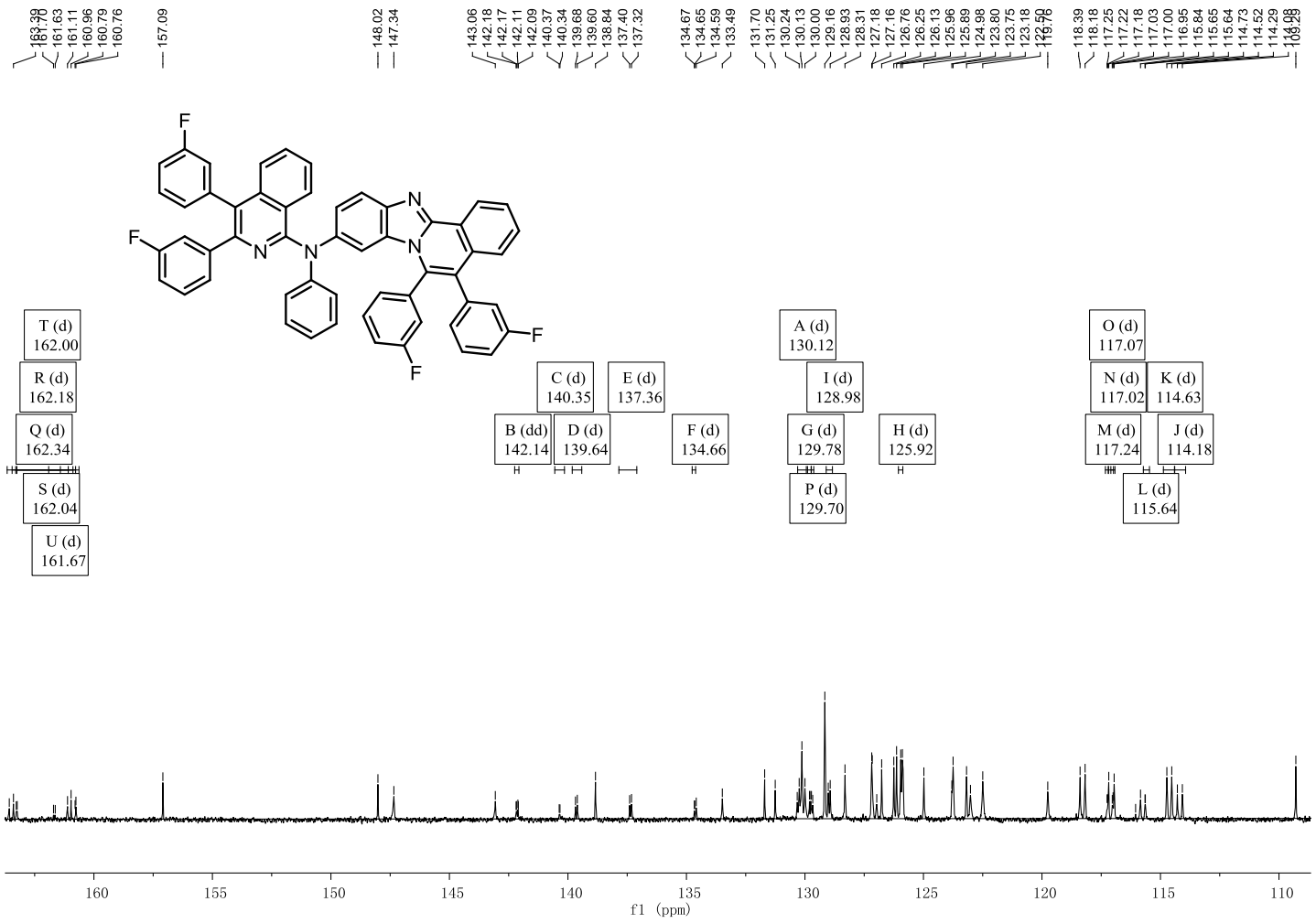



159.41
158.75
158.55
158.45
156.36
148.39
148.01
147.40
139.75
132.92
132.50
132.43
131.60
131.16
129.39
128.94
126.39
126.16
125.64
113.72
113.44
112.92
112.39
110.27
77.37
77.26
77.06
76.74
55.30
55.14
55.11
54.88
H3CO
H3CO
H3CO
OCH3
N
N
N
N
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
f1 (ppm)

Compound 3ai




T (d) 162.00
R (d) 162.18
Q (d) 162.34
S (d) 162.04
U (d) 161.67
E (d) 137.36
P (d) 129.70
C (d) 140.35
G (d) 129.78
B (dd) 142.14
F (d) 134.66
H (d) 125.92
D (d) 139.64
I (d) 128.98
A (d) 130.12
O (d) 117.07
M (d) 117.24
K (d) 114.63
J (d) 114.18
L (d) 115.64
N (d) 117.02
F
F
F
F
N
N
N
f1 (ppm)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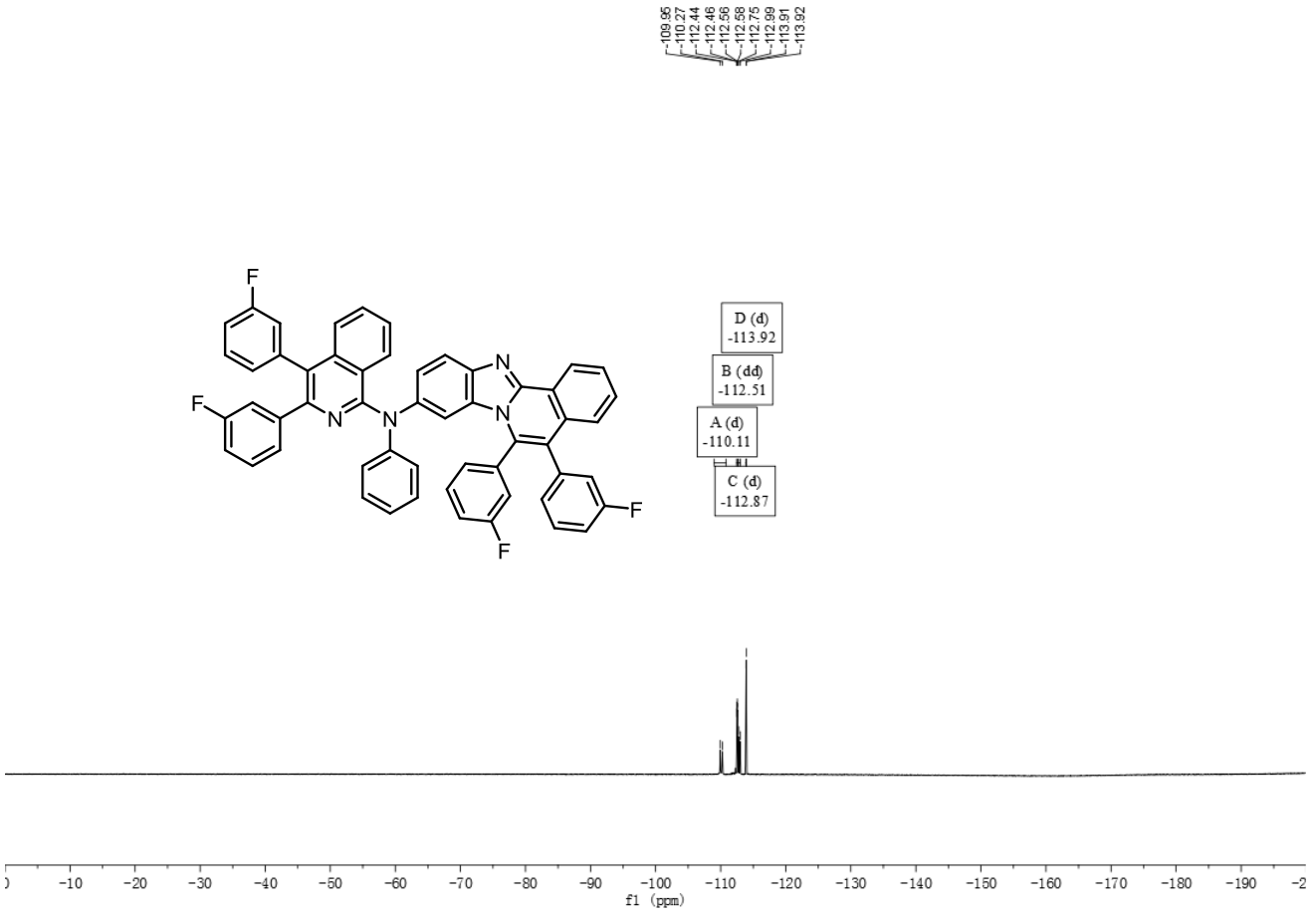
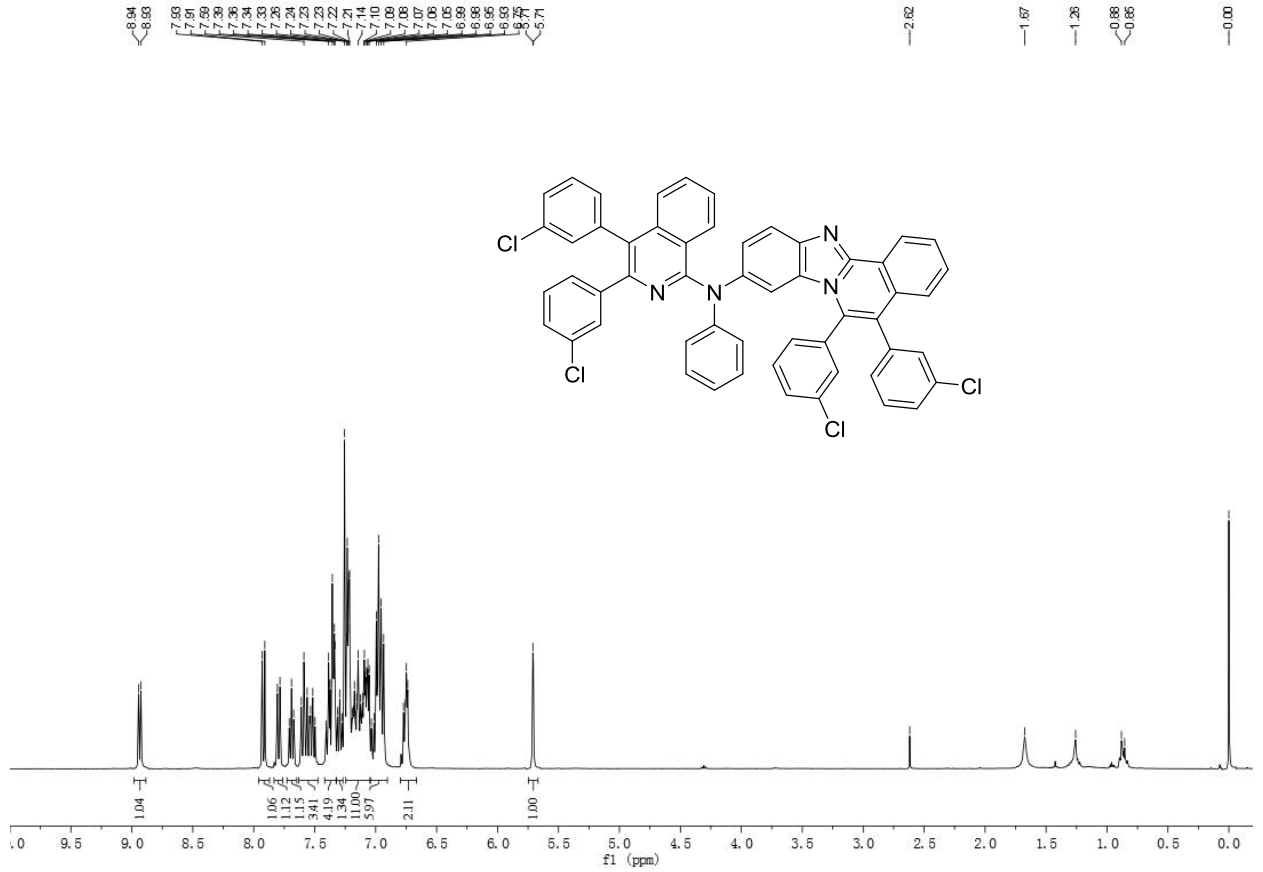
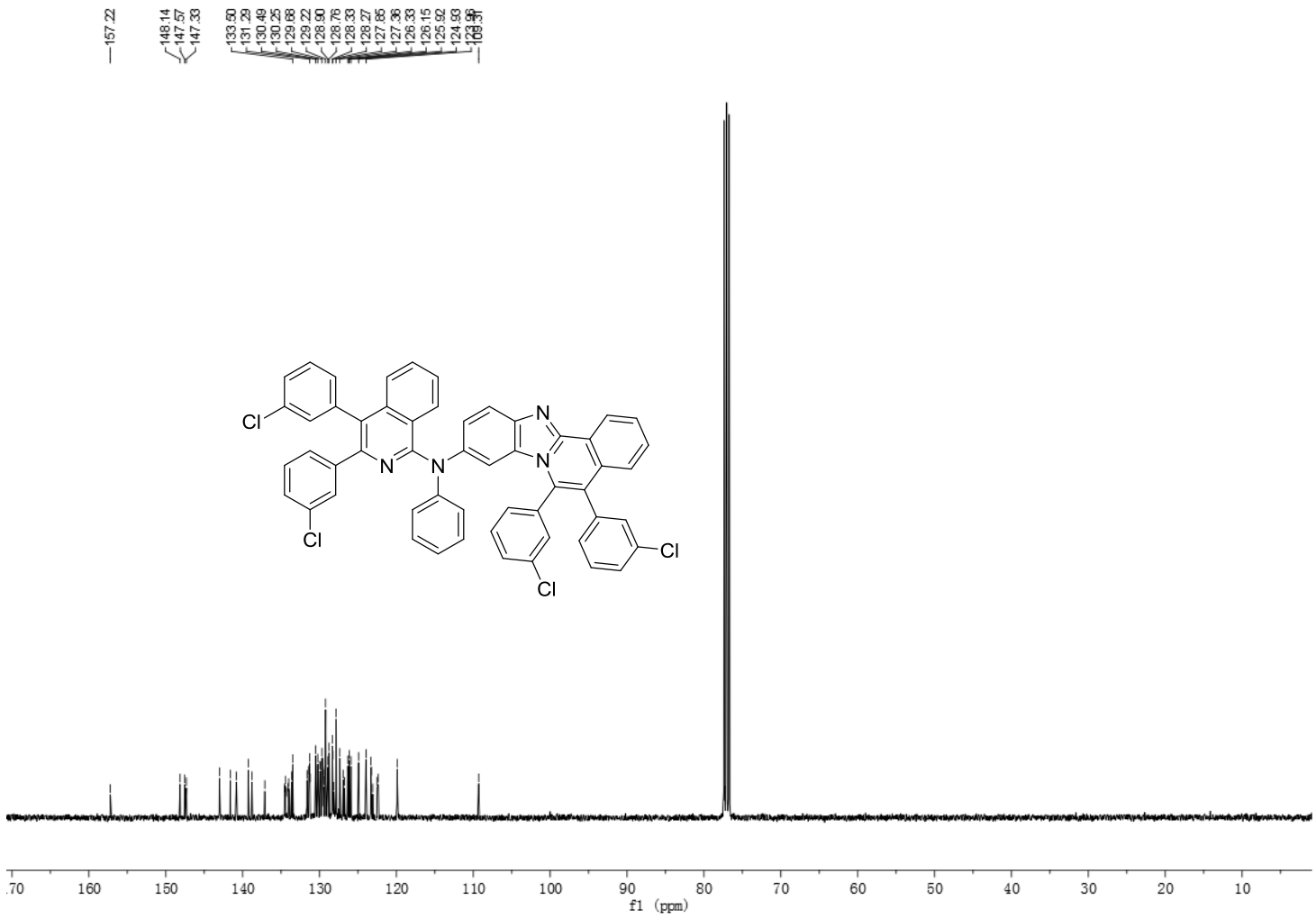
161.70
161.63
161.11
160.96
160.79
160.76
157.09
148.02
147.34
143.06
142.18
142.17
142.11
142.09
140.37
140.34
139.68
139.60
138.84
137.40
137.32
134.67
134.65
134.59
133.49
131.70
131.25
130.24
130.13
130.00
129.16
128.93
128.31
127.18
127.16
126.76
126.25
126.13
125.96
125.89
124.98
123.80
123.75
123.18
118.39
118.18
117.25
117.22
117.18
117.03
117.00
116.95
115.84
115.65
115.64
114.73
114.52
114.29
F
F
F
N
N
N
T (d)
162.00
R (d)
162.18
Q (d)
162.34
S (d)
162.04
U (d)
161.67
C (d)
140.35
E (d)
137.36
B (dd)
142.14
D (d)
139.64
F (d)
134.66
A (d)
130.12
I (d)
128.98
G (d)
129.78
H (d)
125.92
P (d)
129.70
O (d)
117.07
N (d)
117.02
K (d)
114.63
M (d)
117.24
J (d)
114.18
L (d)
115.64
160
155
150
145
140
135
130
125
120
115
110
f1 (ppm)

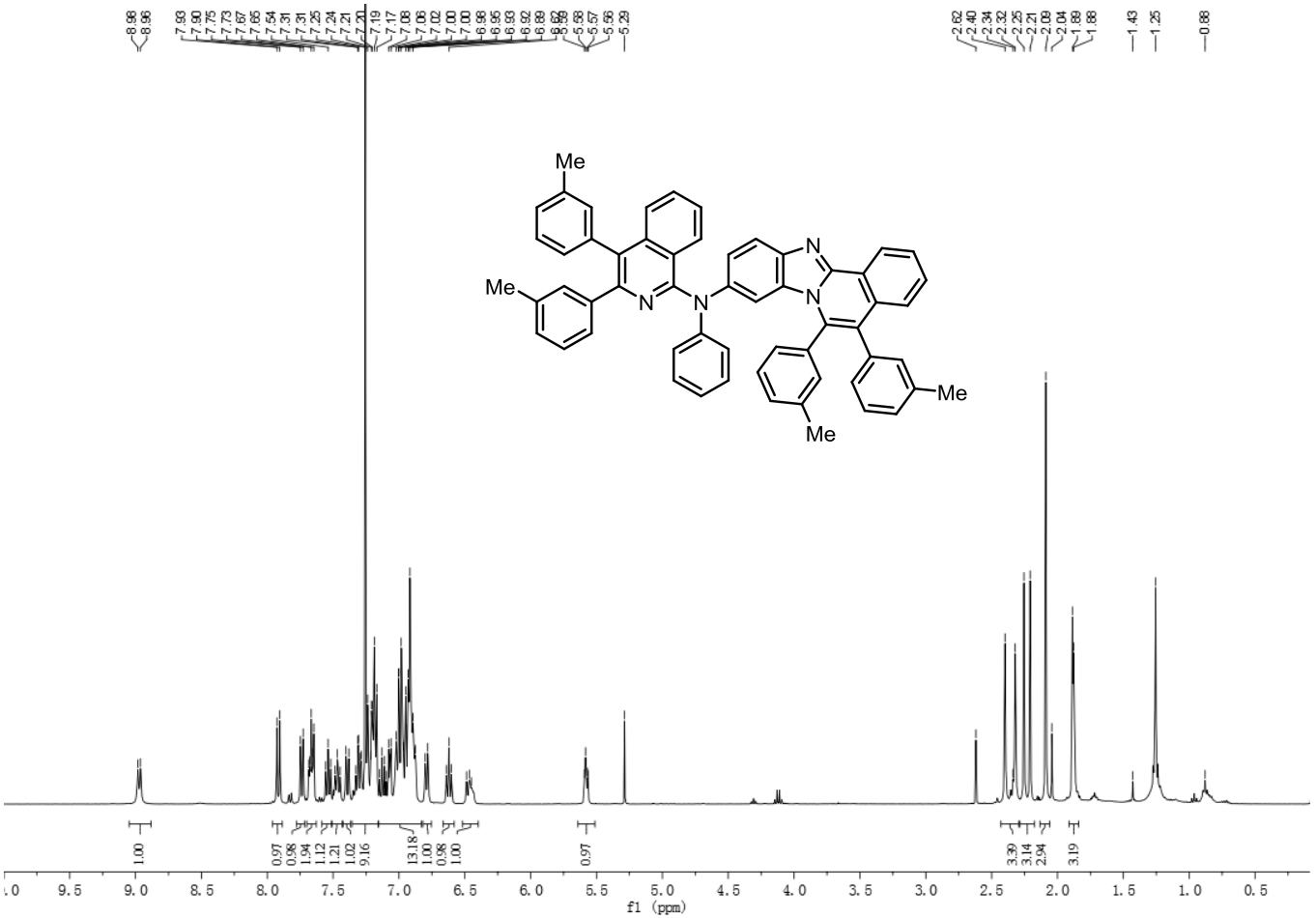

-109.95
-110.27
-112.44
-112.46
-112.56
-112.58
-112.75
-112.99
-113.91
-113.92
F
F
N
N
N
F
F
D (d)
-113.92
B (dd)
-112.51
A (d)
-110.11
C (d)
-112.87
-10
-20
-30
-40
-50
-60
-70
-80
-90
-100
-110
-120
-130
-140
-150
-160
-170
-180
-190
f1 (ppm)

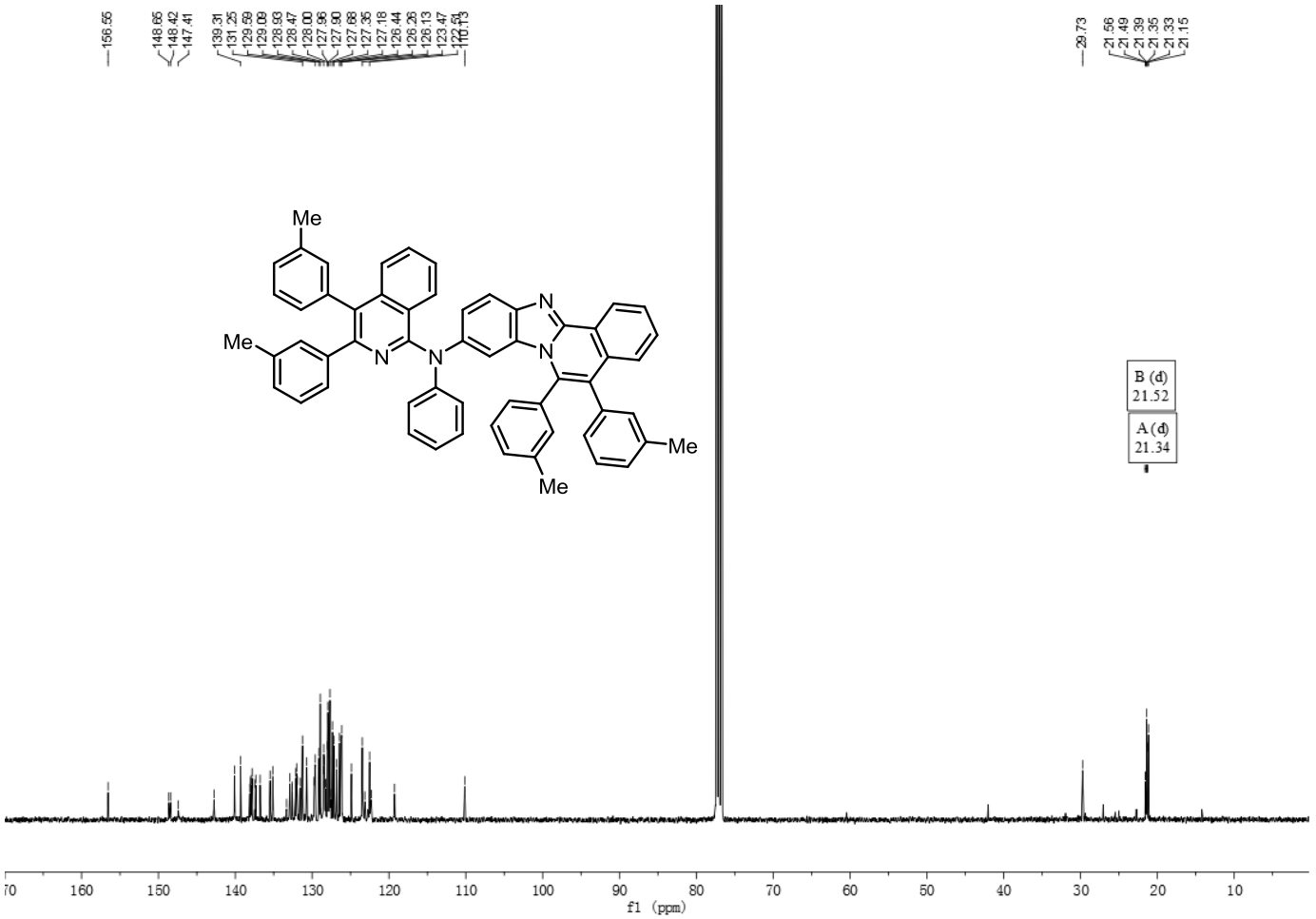
Compound 3aj



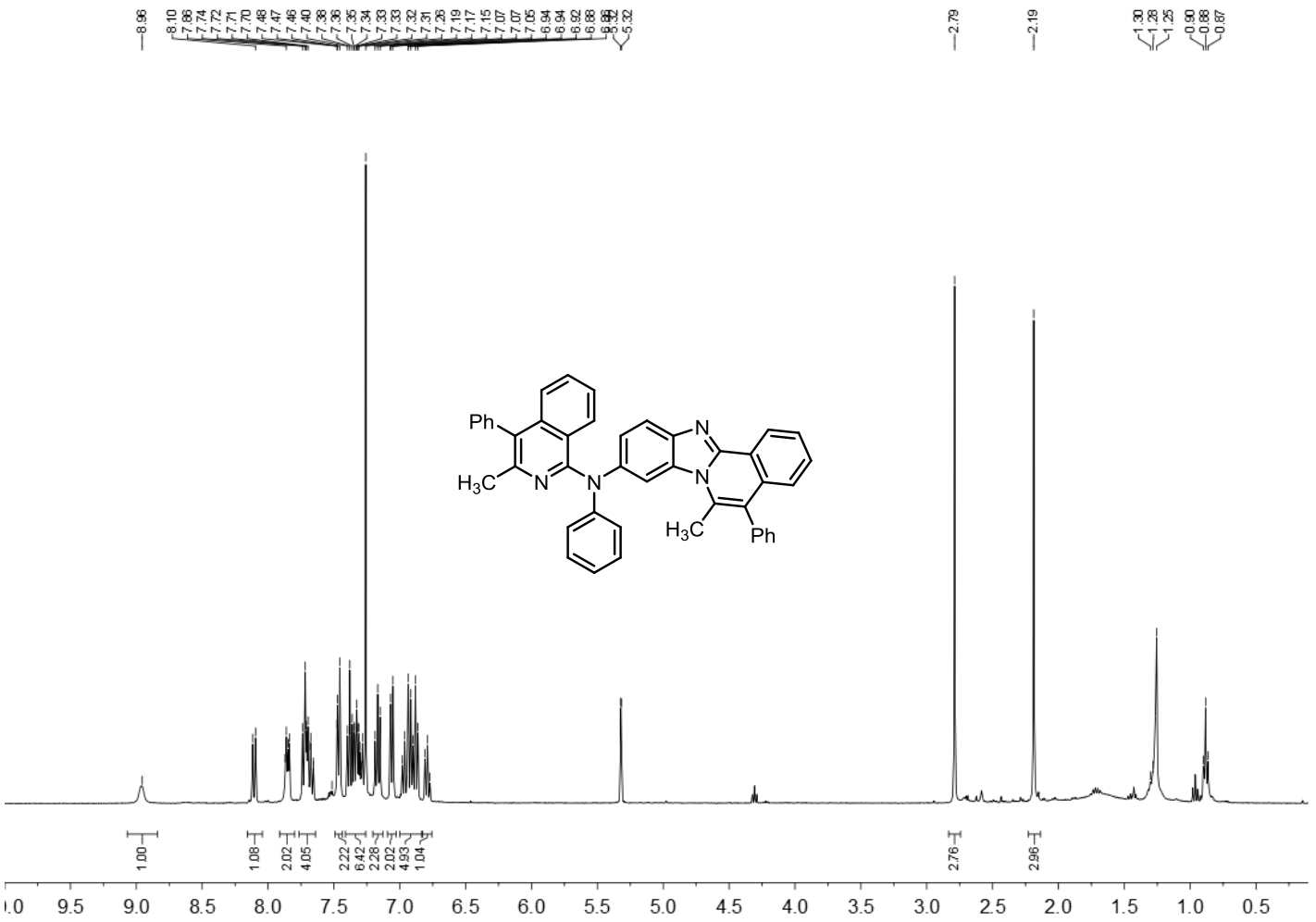

157.22
148.14
147.57
147.33
133.50
131.29
130.49
130.25
129.88
129.22
128.90
128.76
128.33
128.27
127.85
127.36
126.33
126.15
125.92
124.93
Cl
Cl
Cl
Cl
N
N
N
f1 (ppm)

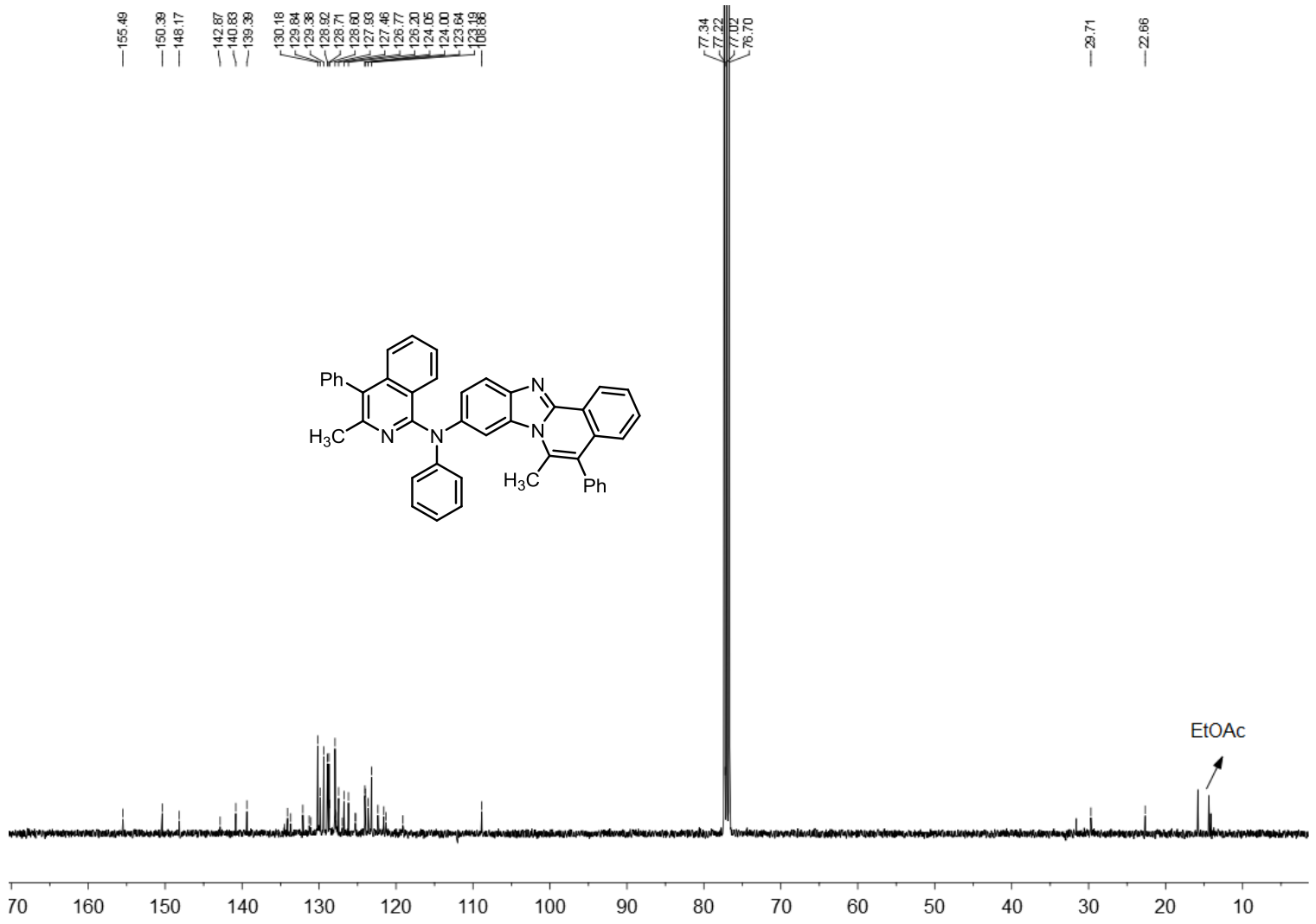
Compound 3ak




156.55
148.65
148.42
147.41
139.31
131.25
129.59
129.09
128.93
128.47
128.00
127.96
127.90
127.68
127.35
127.18
126.44
126.26
126.13
123.47
110.13
29.73
21.56
21.49
21.39
21.35
21.33
21.15
Me
Me
Me
Me
N
N
N
N
B (d)
21.52
A (d)
21.34
f1 (ppm)

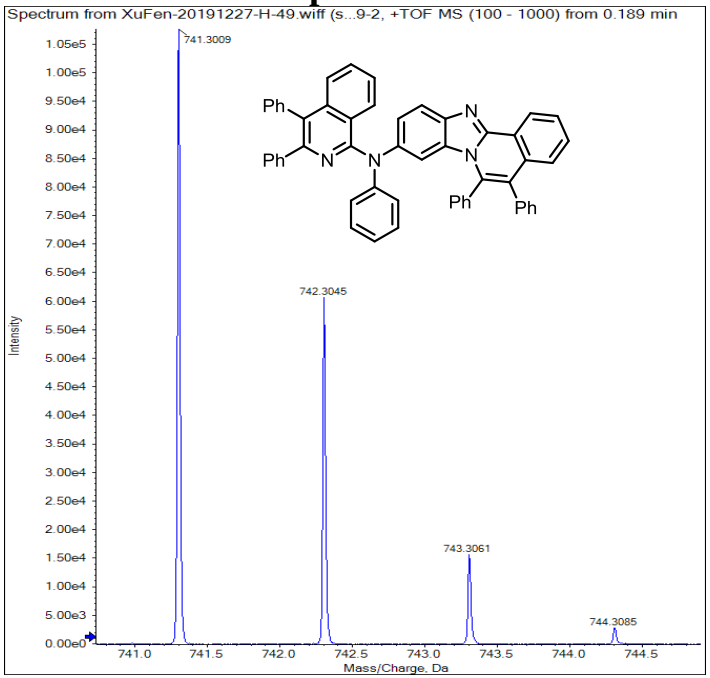
Compound 3ap



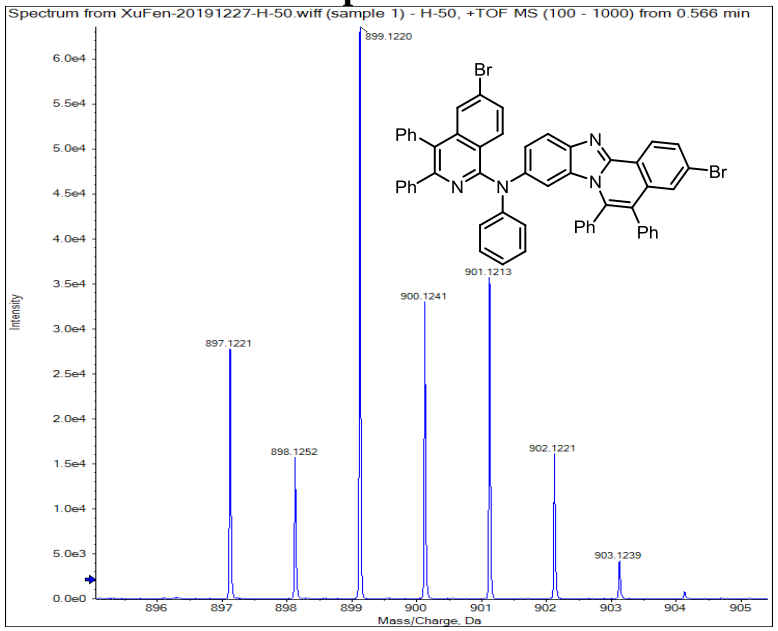

155.49
150.39
148.17
142.87
140.83
139.39
130.18
129.84
129.38
128.92
128.71
128.60
127.93
127.46
126.77
126.20
124.05
124.00
123.64
123.19
108.88
77.34
77.22
77.02
76.70
29.71
22.66
Ph
H3C
N
N
N
H3C
Ph
EtOAc
70
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10

9. Copy of HRMS Spectra

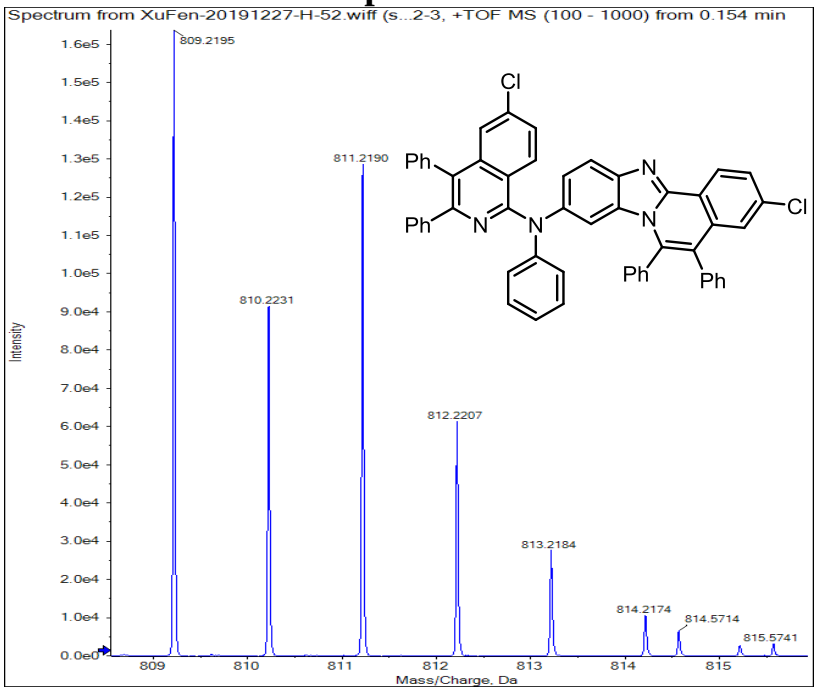
Compound 3aa



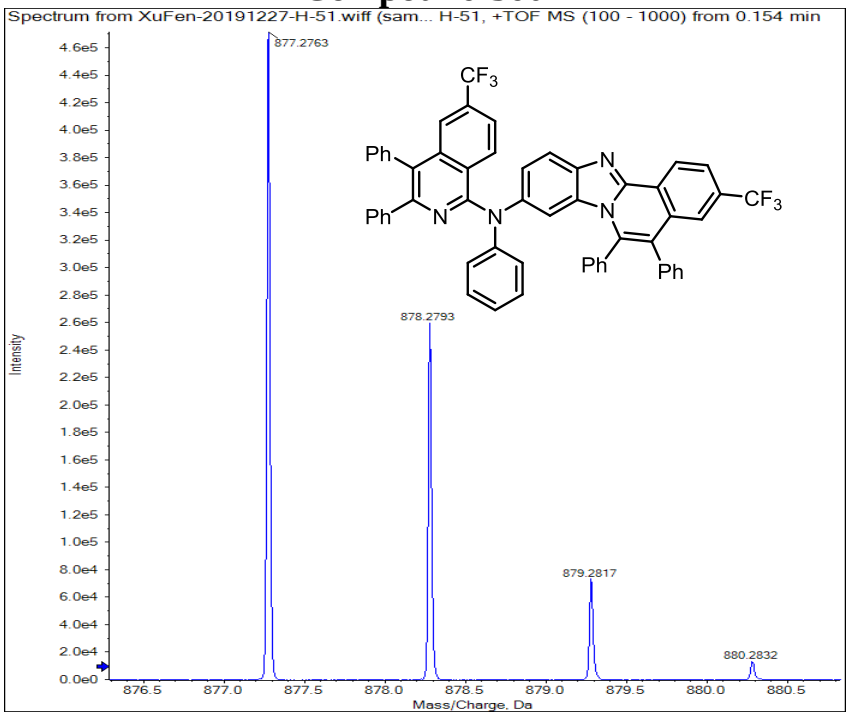
Compound 3ba



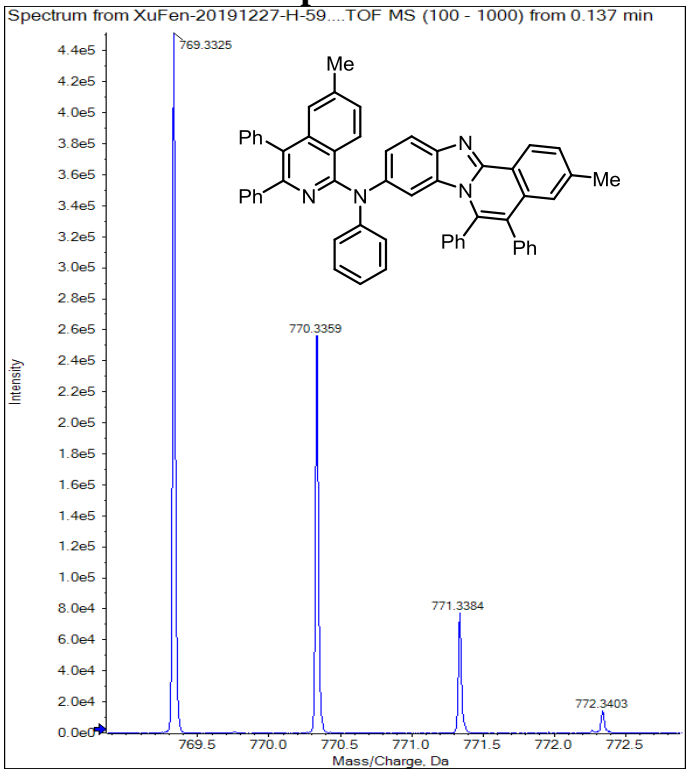
Compound 3ca



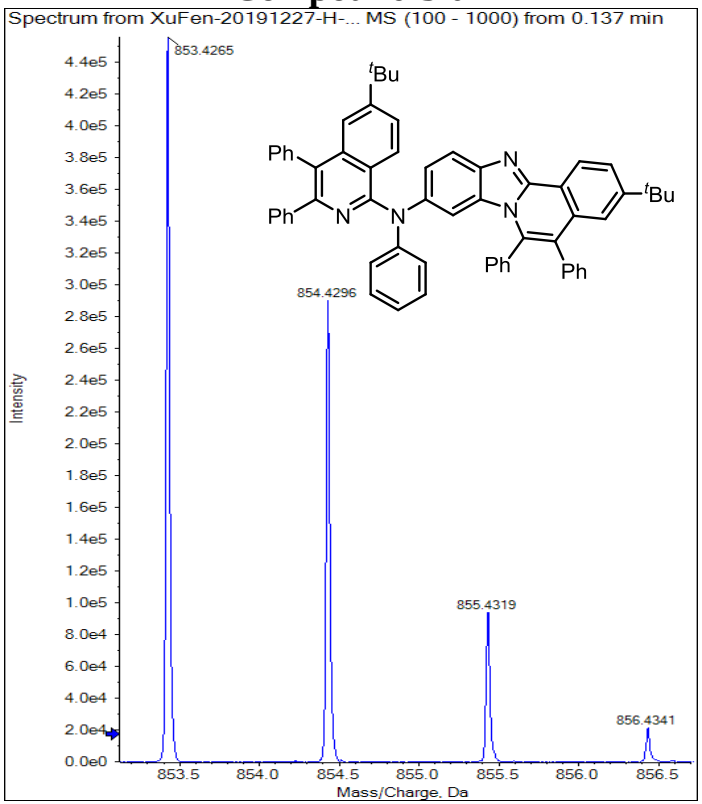
Compound 3da



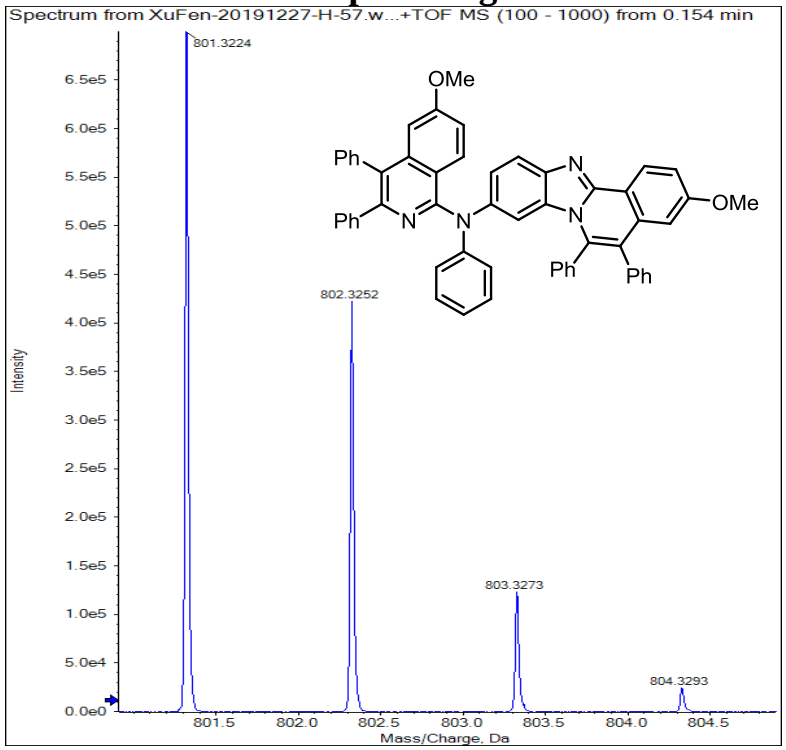
Compound 3ea



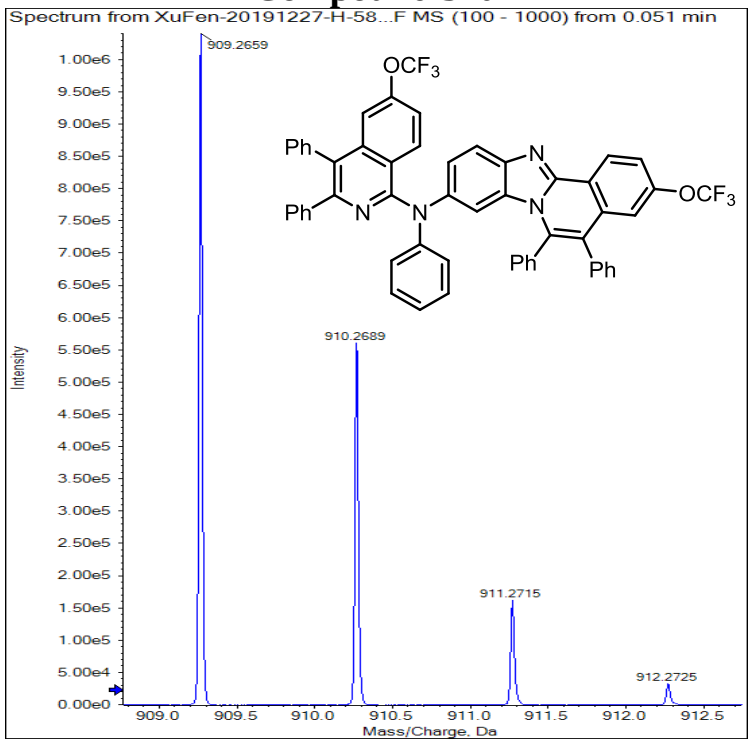
Compound 3fa



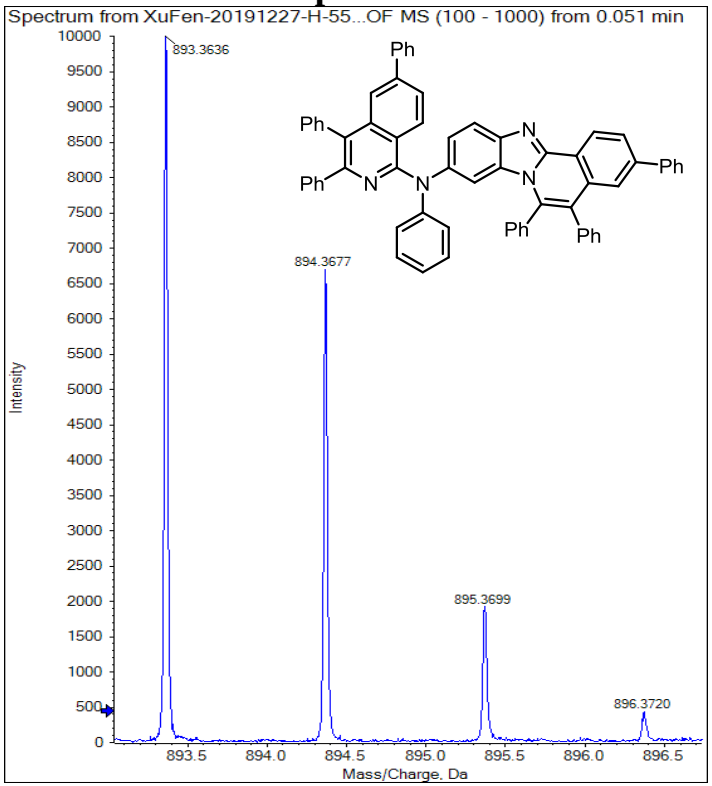
Compound 3ga



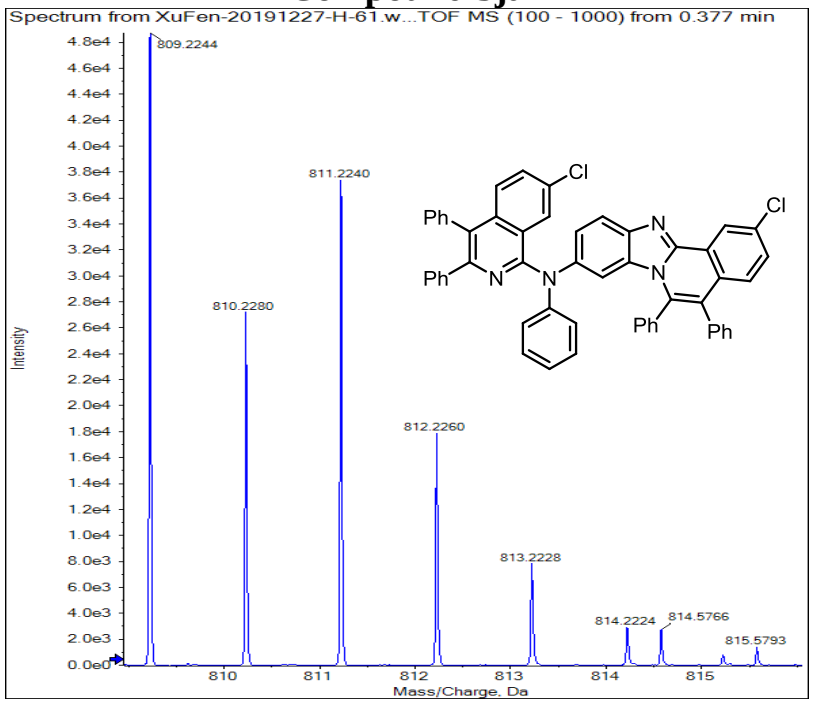
Compound 3ha



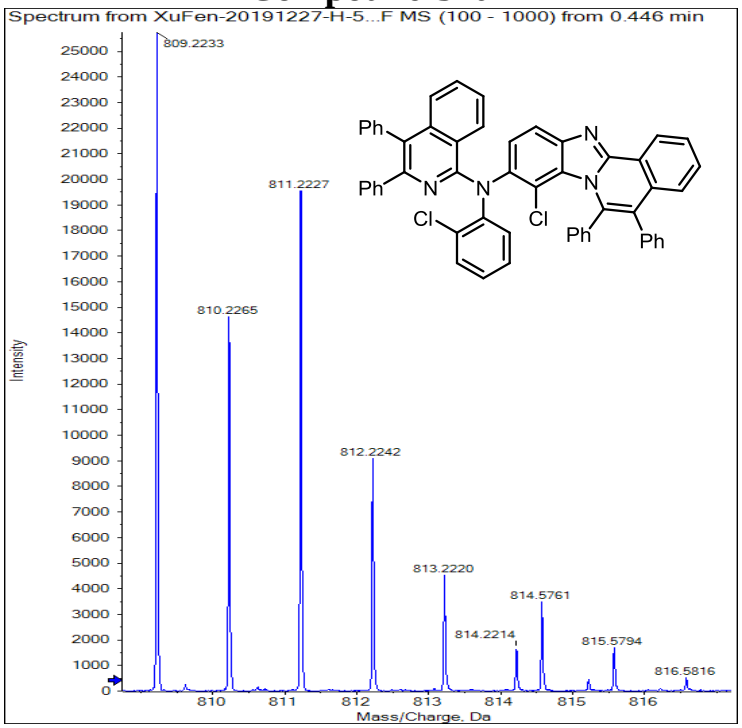
Compound 3ia



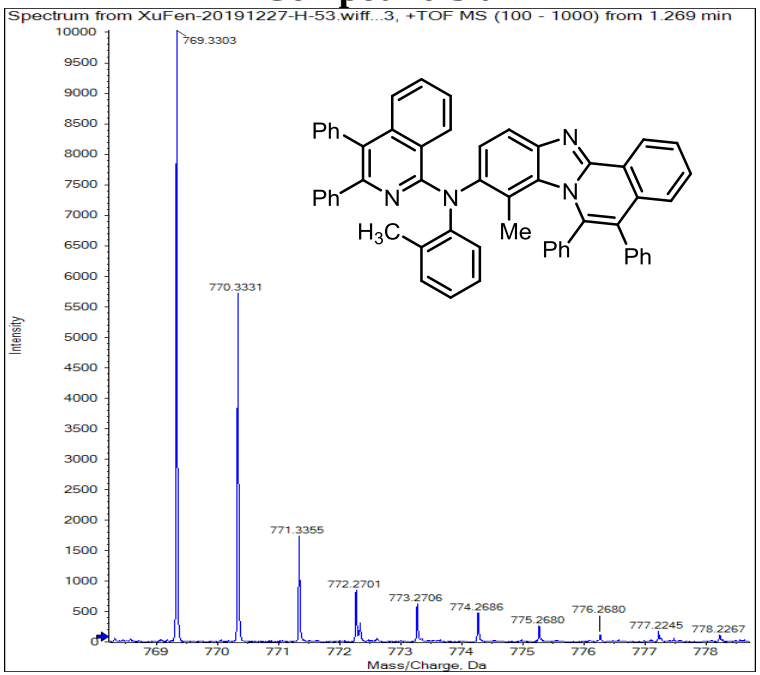
Compound 3ja



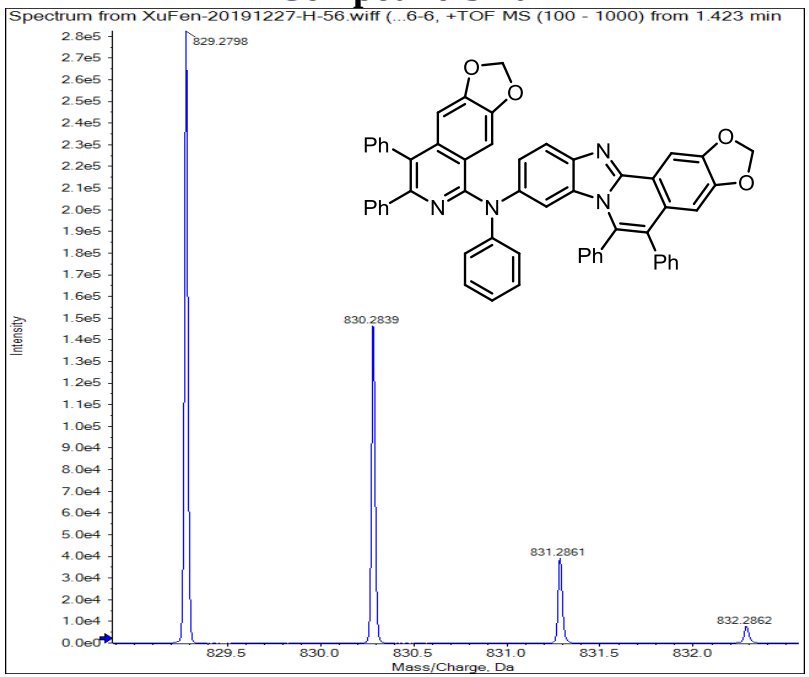
Compound 3ka



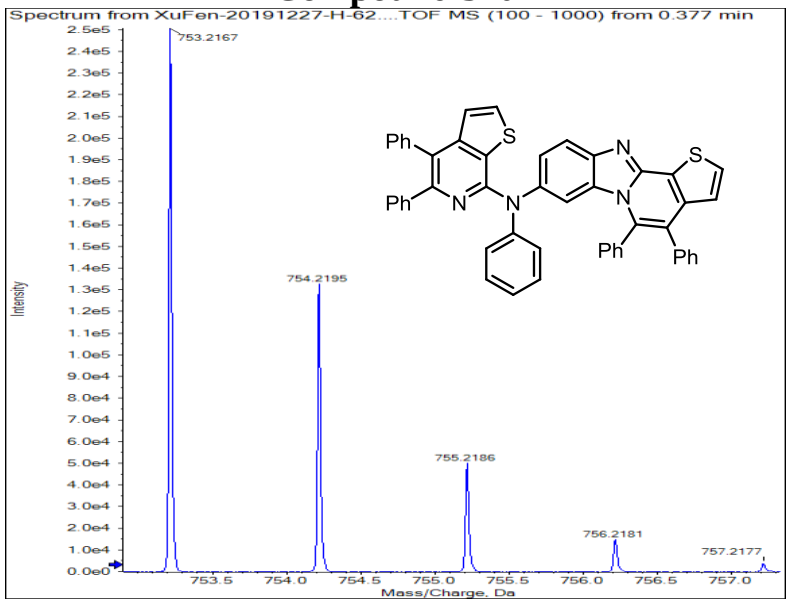
Compound 3la



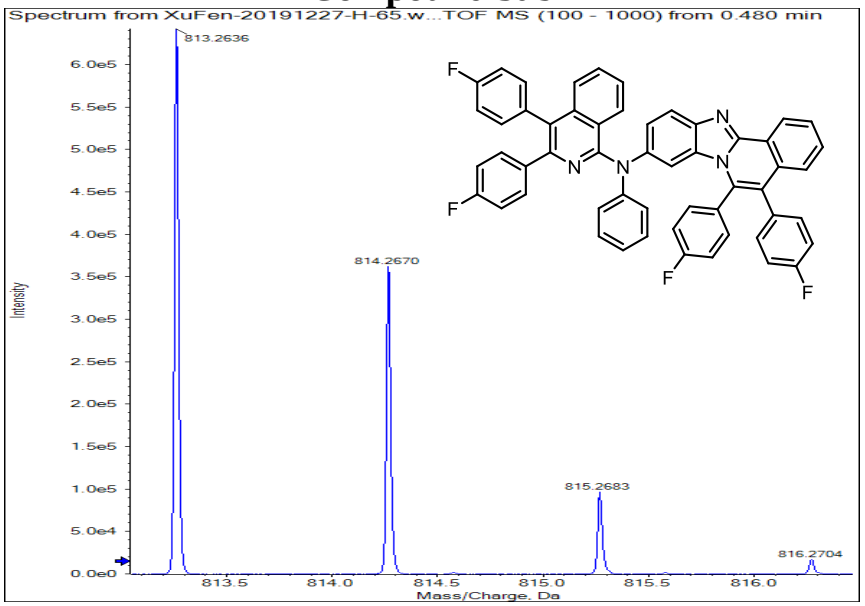
Compound 3ma



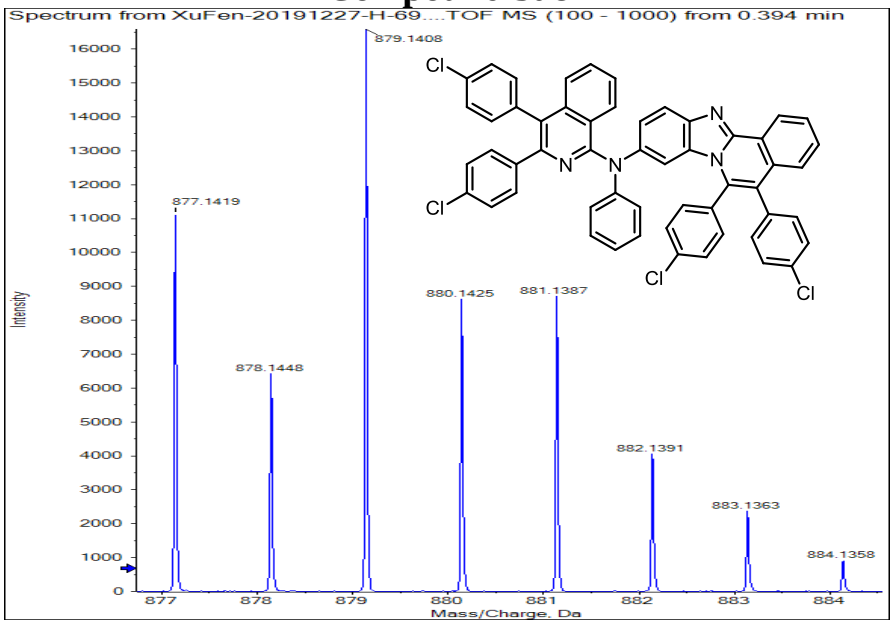
Compound 3na



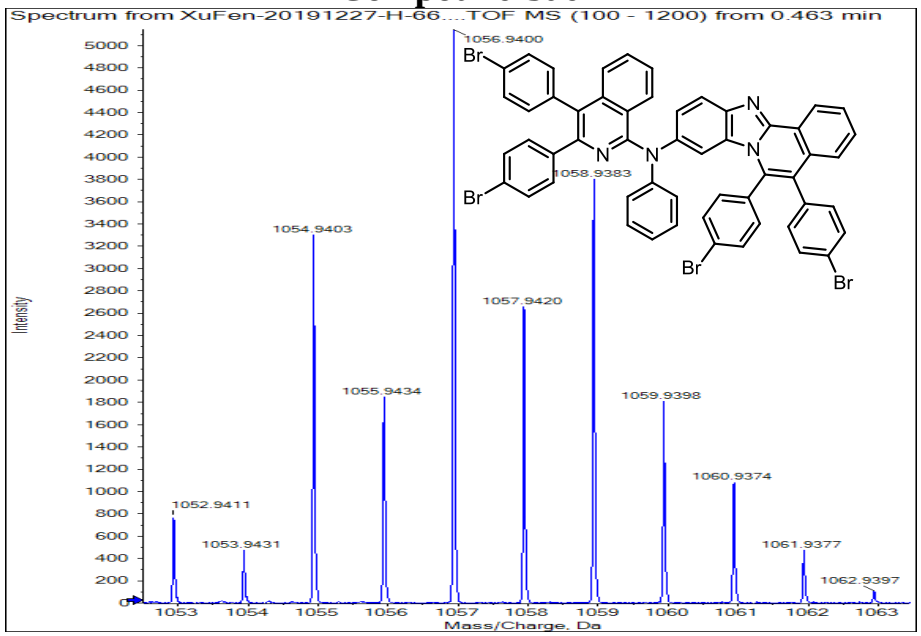
Compound 3ab



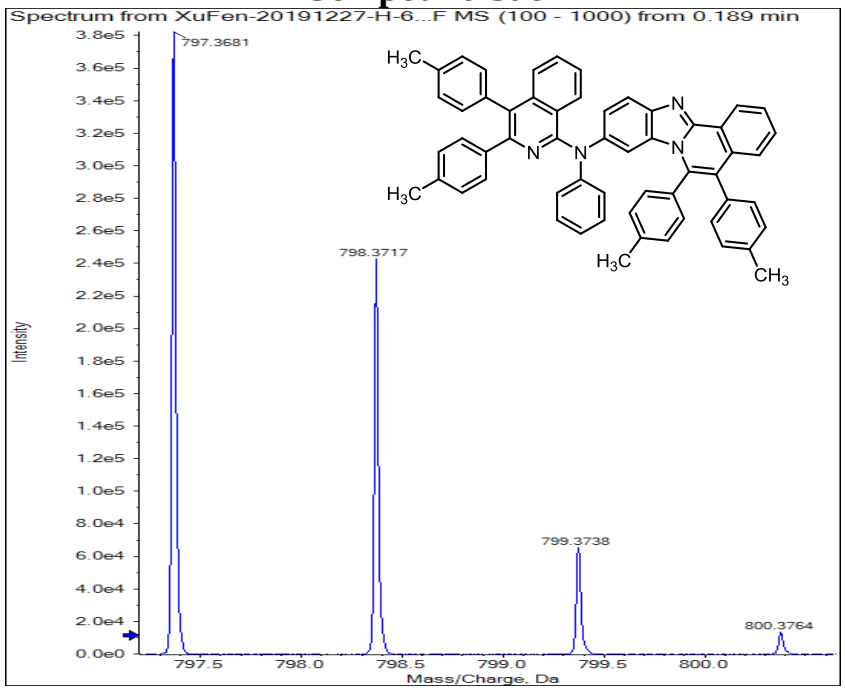
Compound 3ac



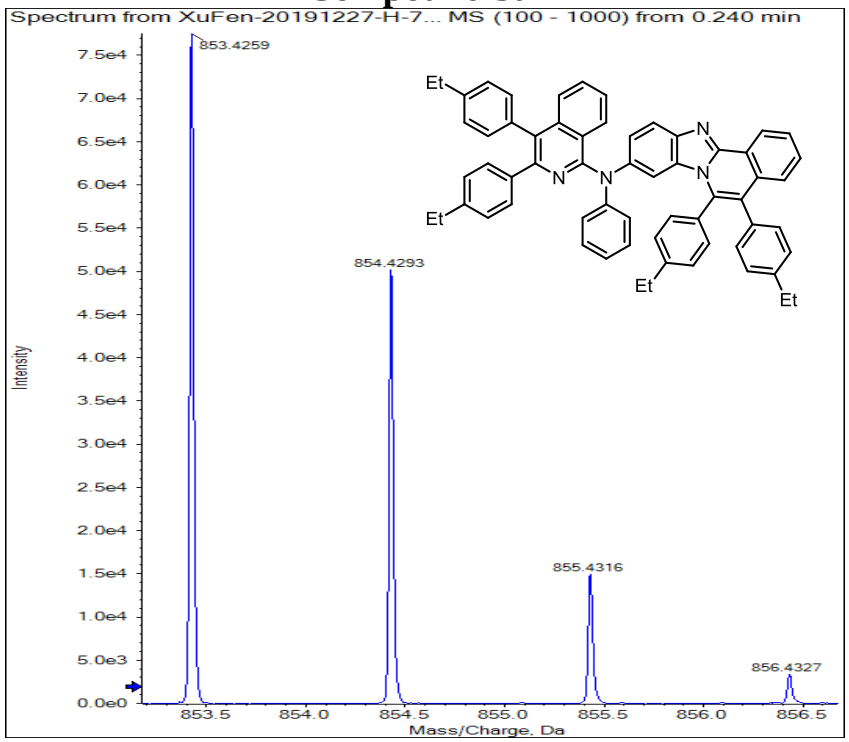
Compound 3ad



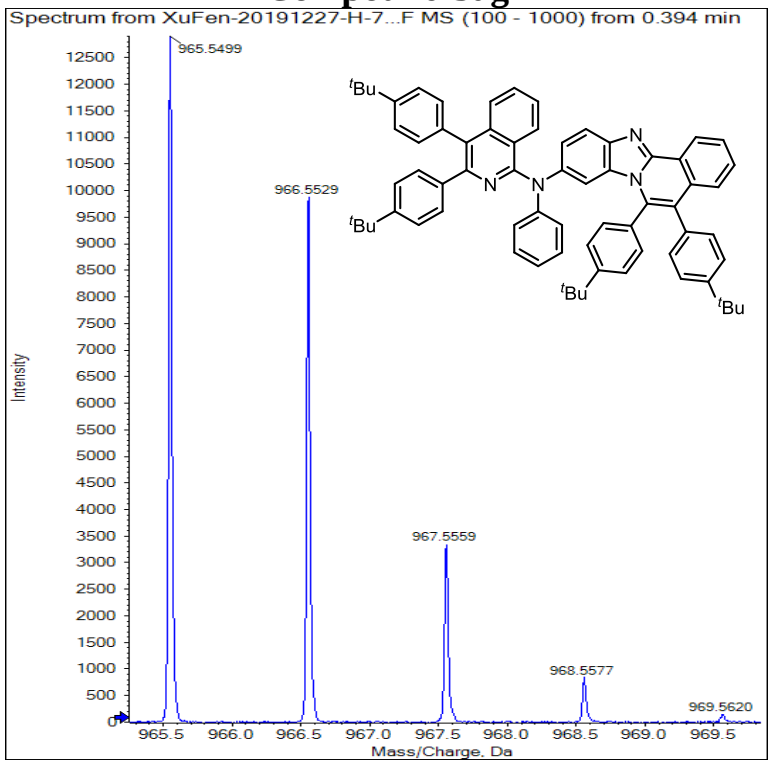
Compound 3ae



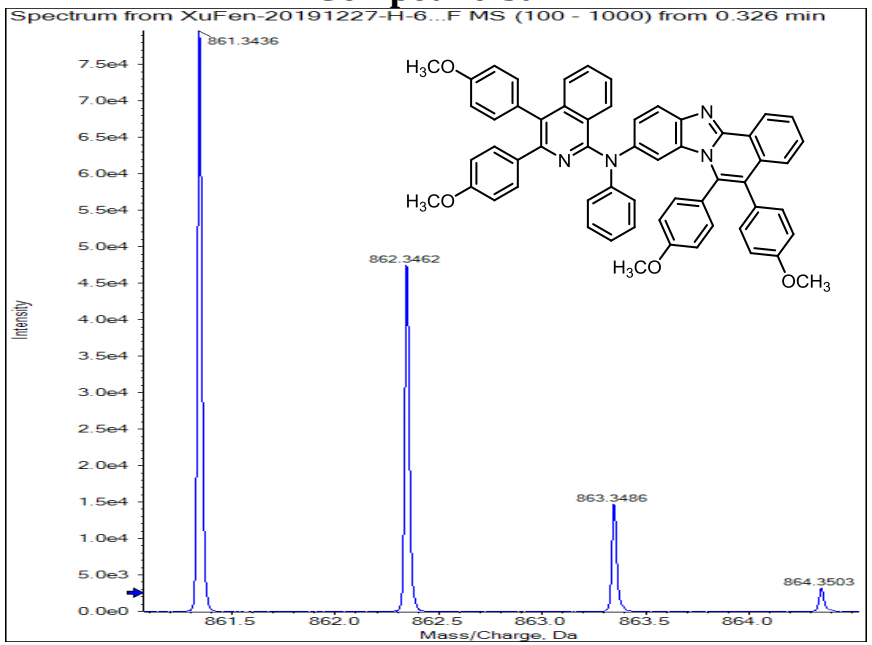
Compound 3af



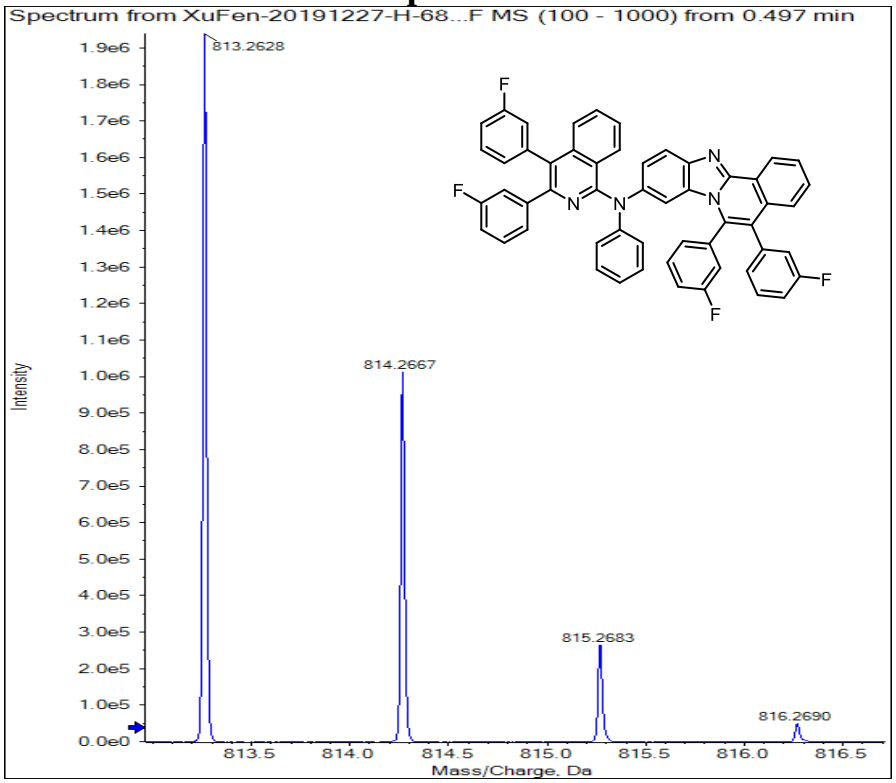
Compound 3ag



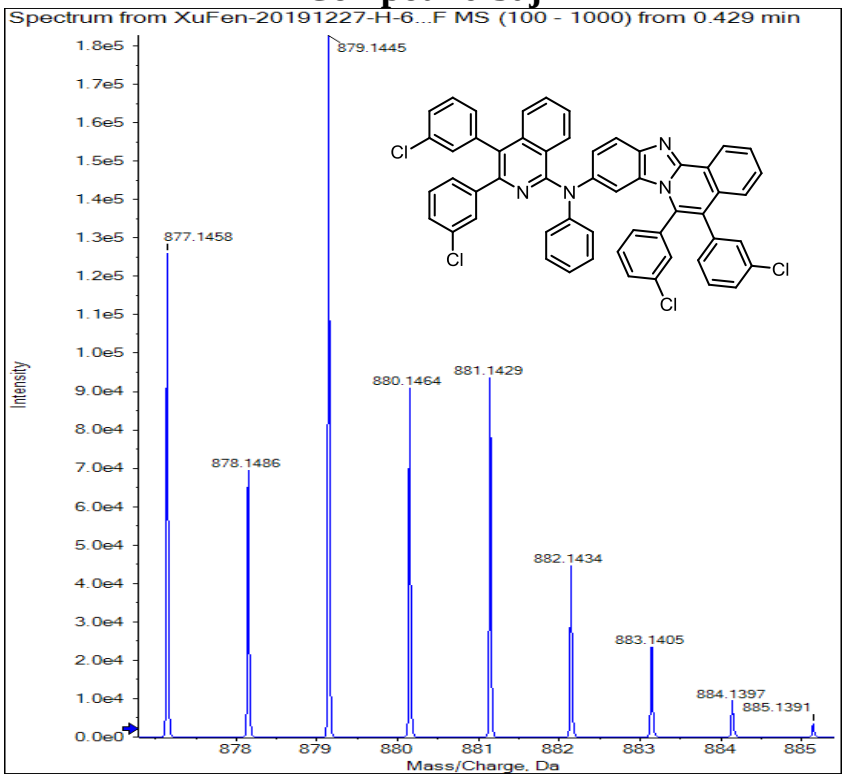
Compound 3ah



Compound 3ai



Compound 3aj



Compound 3ak