Supporting Information

Cascade C-N Bond Cleavage of Amides / Intramolecular Amination Reactions: An Atom Economical Way to α-Cabolin-4-ones

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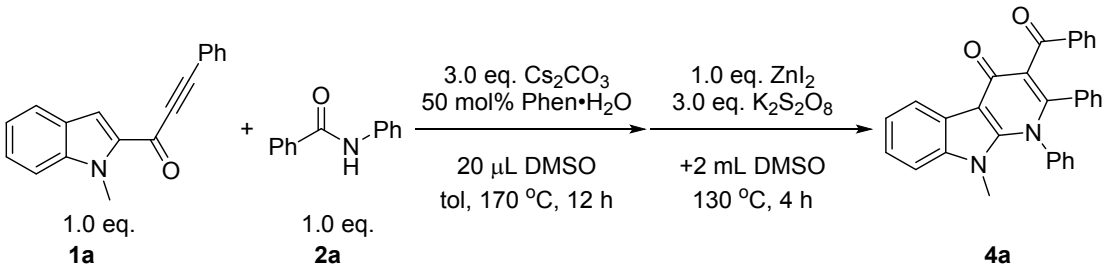
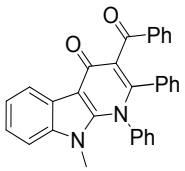
1. General Methods

All reactions were carried out under air. Toluene was prepared by distillation from sodium using benzophenone as indicator. Unless noted, all commercial reagents were used without further purification. Reactions were monitored by thin layer chromatography. Purification of reaction products was carried out by flash chromatography on silica gel (300~400 mesh). ^{1}H NMR spectra were recorded at 400 MHz or 600 MHz, ^{13}C NMR spectra were recorded at 100 MHz or 150 MHz, and in $CDCl_3$ or d^6-DMSO (containing 0.03% TMS) solutions. ^{1}H NMR spectra was recorded with tetramethylsilane (δ = 0.00 ppm) as internal reference; ^{13}C NMR spectra was recorded with $CDCl_3$ (δ = 77.00 ppm) or d^6-DMSO (δ = 39.52 ppm) as internal reference. High-resolution mass spectra were performed on a mass spectrometer with a TOF (for EI or ESI) or FT-ICR (for MALDI) analyzer. Single crystal X-ray diffraction data was collected in Bruker SMARTAPEX diffractiometers.

2. Preparation and Characterization of α-Cabolinone 4



In a dried sealed tube ynone **1a** (0.2 mmol, 51.9 mg), *N*-phenylbenzamide **2a** (0.2 mmol, 39.4 mg), 1,10-phenanthroline hydrate (0.1 mmol, 19.8 mg), cesium carbonate (0.6 mmol, 195.6 mg), toluene (2 mL) and dimethyl sulfoxide (20 μL) were added, and the mixture was heated at 170 °C for 12 h. After the reaction was complete as monitored by thin-layer chromatography, a portion of dimethyl sulfoxide (2 mL) was added to the reaction mixture, then vigorously stir until all the preticipates were dissolved. Zinc iodide (0.2 mmol, 63.8 mg), potassium persulfate (0.6 mmol, 162.2 mg) were added, and the mixture was heated at 130 °C for 4 h. After the reaction was complete as monitored by thin-layer chromatography, the reaction mixture was then quenched by water (20 mL), a portion of ethyl acetate (20 mL) was added and the combined organic layer was washed with water (50 mL), saturated sodium thiosulfate solution (50 mL), brine (50 mL). Combined aqueous phase was extracted with dichloromethane until all dissolvable preticipates were dissolved. The combined organic phase was dried over with anhydrous Na_2SO_4, filtered, and concentrated under reduced pressure, Purification by chromatography on silica gel (petroleum ether / ethyl acetate = 1/1) afforded desired compound **4a**.



4a

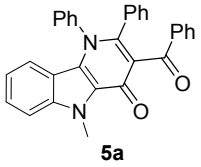
3-benzoyl-9-methyl-1,2-diphenyl-1,9-dihydro-4H-pyrido[2,3-b]indol-4-one (4a)

Light yellow solid, 78 % yield (71 mg); mp 273-275 ^{o}C.

^{1}H NMR ($CDCl_3$, 400 MHz) δ 3.00 (s, 3H), 6.92-7.05 (m, 5H), 7.18-7.25 (m, 3H), 7.28-7.38 (m, 7H), 7.39-7.47 (m, 1H), 7.85 (d, J = 8.0 Hz, 2H), 8.56 (d, J = 6.0 Hz, 1H).

^{13}C NMR ($CDCl_3$, 100 MHz) δ 31.66, 108.60, 108.75, 122.35, 122.55, 122.70, 124.36, 127.12, 127.68, 128.46, 128.82, 129.42, 129.58, 129.96, 130.56, 130.81, 131.80, 132.98, 137.40, 138.13, 138.25, 144.21, 146.59, 173.50, 196.06.

HRMS (ESI) calcd for $C_{31}H_{23}N_2O_2$, $[M+H]^+$: 455.1754, found: 455.1761.



5a

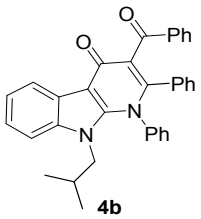
3-benzoyl-5-methyl-1,2-diphenyl-1,5-dihydro-4H-pyrido[3,2-b]indol-4-one (5a)

White solid, 34% yield (31 mg); mp 277-279 ^{o}C.

^{1}H NMR ($CDCl_3$, 400 MHz) δ 4.41 (s, 3H), 6.02 (d, J = 8.0 Hz, 1H), 6.80-6.89 (m, 1H), 6.94-7.15 (m, 5H), 7.26-7.31 (m, 2H), 7.32-7.52 (m, 8H), 7.89 (d, J = 7.6 Hz, 2H).

^{13}C NMR ($CDCl_3$, 100 MHz) δ 31.12, 110.12, 116.23, 119.85, 121.29, 126.71, 127.00, 127.13, 127.71, 128.55, 128.85, 128.94, 129.47, 129.63, 129.75, 129.81, 130.78, 132.01, 133.04, 138.45, 139.71, 139.84, 146.73, 169.23, 196.52.

HRMS (ESI) calcd for $C_{31}H_{23}N_2O_2$, $[M+H]^+$: 455.1754, found: 455.1763.



4b

3-benzoyl-9-isobutyl-1,2-diphenyl-1,9-dihydro-4H-pyrido[2,3-b]indol-4-one (4b)

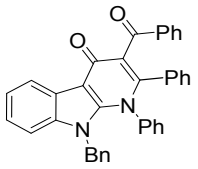
Brown solid, 47 % yield (47 mg); mp 257-259 ^{o}C.

^{1}H NMR ($CDCl_3$, 400 MHz) δ 0.52 (d, J = 6.8 Hz, 6H), 1.75-1.87 (m, 1H), 3.17 (d, J = 7.6 Hz, 2H), 6.92-7.07 (m, 5H), 7.18 (d, J = 7.2 Hz, 2H), 7.27-7.39 (m, 8H), 7.40-7.47 (m, 1H), 7.85 (d, J = 7.6 Hz, 2H), 8.57 (d, J = 7.6 Hz, 1H).

^{13}C NMR ($CDCl_3$, 100 MHz) δ 19.53, 29.14, 50.67, 109.42, 110.07, 122.30, 122.59, 122.78,

124.20, 127.36, 127.63, 128.44, 128.83, 129.41, 129.58, 129.72, 130.01, 130.76, 131.85, 133.04, 137.47, 138.10, 138.13, 144.47, 147.00, 173.72, 196.17.

HRMS (ESI) calcd for $C_{34}H_{29}N_2O_2$, $[M+H]^+$: 497.2224, found: 497.2222.



4c

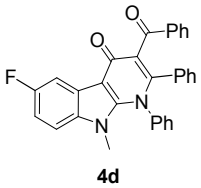
3-benzoyl-9-benzyl-1,2-diphenyl-1,9-dihydro-4H-pyrido[2,3-b]indol-4-one (4c)

Light yellow solid, 65 % yield (69 mg); mp 274-276 °C.

^{1}H NMR ($CDCl_3$, 400 MHz) δ 4.73 (s, 2H), 6.48 (d, J = 7.2 Hz, 2H), 6.84-6.97 (m, 7H), 6.97-7.04 (m, 2H), 7.08-7.21 (m, 5H), 7.27-7.39 (m, 4H), 7.40-7.47 (m, 1H), 7.86 (d, J = 8.0 Hz, 2H), 8.64 (d, J = 7.6 Hz, 1H).

^{13}C NMR ($CDCl_3$, 100 MHz) δ 47.50, 109.25, 109.38, 122.73, 122.79, 122.91, 124.76, 125.21, 127.32, 127.53, 128.45, 128.68, 128.74, 129.17, 129.44, 129.83, 130.21, 130.78, 131.67, 133.02, 136.26, 137.29, 137.40, 138.19, 143.82, 146.95, 173.62, 196.09.

HRMS (ESI) calcd for $C_{37}H_{26}N_2NaO_2$, $[M+Na]^+$: 553.1886, found: 553.1890.



4d

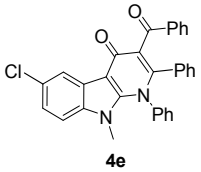
3-benzoyl-6-fluoro-9-methyl-1,2-diphenyl-1,9-dihydro-4H-pyrido[2,3-b]indol-4-one (4d)

Brown solid, 73 % yield (69 mg); mp 289-291 °C.

^{1}H NMR ($CDCl_3$, 400 MHz) δ 2.98 (s, 3H), 6.90-7.12 (m, 7H), 7.21-7.39 (m, 7H), 7.39-7.48 (m, 1H), 7.83 (d, J = 8.0 Hz, 2H), 8.14 (dd, J_1 = 9.2 Hz, J_2 = 2.4 Hz, 1H).

^{13}C NMR ($CDCl_3$, 100 MHz) δ 31.86, 107.62 (d, J = 25.0 Hz), 108.21 (d, J = 3.9 Hz), 109.74 (d, J = 9.5 Hz), 111.87 (d, J = 25.9 Hz), 123.10 (d, J = 11.4 Hz), 126.84, 127.69, 128.46, 128.86, 129.36, 129.60, 130.04, 130.56, 130.79, 131.64, 133.02, 133.68, 137.80, 138.16, 144.71, 146.94, 159.16 (d, J = 236.7 Hz), 173.34, 195.87.

HRMS (ESI) calcd for $C_{30}H_{21}FN_2NaO_2$, $[M+Na]^+$: 495.1479, found: 495.1479.



4e

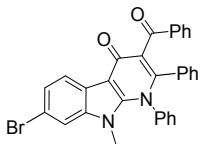
3-benzoyl-6-chloro-9-methyl-1,2-diphenyl-1,9-dihydro-4H-pyrido[2,3-b]indol-4-one (4e)

White solid, 62% yield (61 mg); mp 321-323 °C.

^{1}H NMR ($CDCl_3$, 400 MHz) δ 2.97 (s, 3H), 6.93-7.06 (m, 6H), 7.17 (dd, J_1 = 8.8 Hz, J_2 = 2.0 Hz, 1H), 7.25-7.36 (m, 7H), 7.40-7.47 (m, 1H), 7.83 (d, J = 7.6 Hz, 2H), 8.47 (d, J = 2.4 Hz, 1H).

^{13}C NMR ($CDCl_3$, 100 MHz) δ 31.86, 107.74, 109.99, 121.53, 123.56, 124.20, 126.92, 127.60, 127.70, 128.46, 128.86, 129.35, 129.59, 130.08, 130.61, 130.77, 131.56, 133.02, 135.70, 137.65, 138.14, 144.46, 147.10, 173.27, 195.84.

HRMS (ESI) calcd for $C_{31}H_{21}ClN_2NaO_2$, $[M+Na]^+$: 511.1184, found 511.1187.



4f

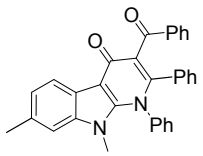
3-benzoyl-7-bromo-9-methyl-1,2-diphenyl-1,9-dihydro-4H-pyrido[2,3-b]indol-4-one (4f)

Yellow solid, 68% yield (68 mg); mp 349-351 °C.

^{1}H NMR (DMSO-d^6, 400 MHz) δ 2.97 (s, 3H), 6.96-7.05 (m, 3H), 7.15 (d, J = 7.2 Hz, 2H), 7.32-7.39 (m, 3H), 7.40-7.47 (m, 3H), 7.52-7.59 (m, 1H), 7.62-7.69 (m, 2H), 7.81-7.89 (m, 3H), 8.18 (d, J = 8.4 Hz, 1H).

^{13}C NMR (DMSO-d^6, 100 MHz) δ 31.95, 107.13, 113.31, 116.74, 121.35, 122.44, 125.00, 125.98, 127.51, 128.86, 128.95, 129.43, 130.34, 130.99, 131.45, 131.88, 133.57, 137.60, 137.89, 138.50, 144.60, 146.82, 172.66, 195.89.

HRMS (ESI) calcd for $C_{31}H_{21}BrN_2NaO_2$, $[M+Na]^+$: 555.0679, found: 555.0684.



4g

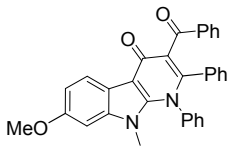
3-benzoyl-7,9-dimethyl-1,2-diphenyl-1,9-dihydro-4H-pyrido[2,3-b]indol-4-one (4g)

Light yellow solid, 87% yield (82 mg); mp 179-181 °C.

^{1}H NMR ($CDCl_3$, 400 MHz) δ 2.50 (s, 3H), 2.98 (s, 3H), 6.89-7.08 (m, 6H), 7.16 (d, J = 8.0 Hz, 1H), 7.19-7.26 (m, 2H), 7.28- 7.37 (m, 5H), 7.39-7.49 (m, 1H), 7.85 (d, J = 8.0 Hz, 2H), 8.42 (d, J = 8.0 Hz, 1H).

^{13}C NMR ($CDCl_3$, 100 MHz) δ 21.92, 31.56, 108.74, 108.99, 120.33, 122.28, 123.86, 127.05, 127.66, 128.45, 128.79, 129.42, 129.56, 129.92, 130.53, 130.84, 131.86, 132.94, 134.54, 137.82, 138.20, 138.29, 144.07, 146.33, 173.32, 196.18.

HRMS (ESI) calcd for $C_{32}H_{24}N_2NaO_2$, $[M+Na]^+$: 491.1730, found 491.1730.



4h

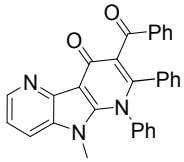
3-benzoyl-6-methoxy-9-methyl-1,2-diphenyl-1,9-dihydro-4H-pyrido[2,3-b]indol-4-one (4h)

Brown solid, 61% yield (59 mg); mp 286-288 °C.

^{1}H NMR ($CDCl_3$, 400 MHz) δ 2.94 (s, 3H), 3.87 (s, 3H), 6.88-7.04 (m, 6H), 7.07 (d, *J* = 8.8 Hz, 1H), 7.20-7.36 (m, 7H), 7.38-7.47 (m, 1H), 7.85 (d, *J* = 7.6 Hz, 2H), 8.08 (s, 1H).

^{13}C NMR ($CDCl_3$, 100 MHz) δ 31.64, 55.65, 103.90, 108.47, 109.67, 114.07, 123.10, 126.58, 127.61, 128.42, 128.75, 129.30, 129.49, 129.90, 130.53, 130.74, 131.72, 131.89, 132.93, 137.90, 138.24, 144.14, 146.54, 155.93, 173.52, 196.03.

HRMS (ESI) calcd for $C_{32}H_{24}N_2NaO_3$, $[M+Na]^+$: 507.1679, found 507.1676.



4i

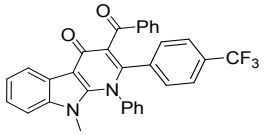
3-benzoyl-9-methyl-1,2-diphenyl-1,9-dihydro-4H-pyrrolo[2,3-b:5,4-b']dipyridin-4-one (4i)

White solid, 59% yield (54 mg); mp 275-277 °C.

^{1}H NMR ($CDCl_3$, 400 MHz) δ 3.17 (s, 3H), 6.91-7.08 (m, 5H), 7.22-7.38 (m, 8H), 7.40-7.48 (m, 1H), 7.84 (d, *J* = 7.6 Hz, 2H), 8.37 (d, *J* = 4.4 Hz, 1H), 8.72 (d, *J* = 7.6 Hz, 1H).

^{13}C NMR ($CDCl_3$, 100 MHz) δ 29.88, 106.37, 115.82, 118.52, 127.36, 127.72, 128.49, 128.96, 129.35, 129.52, 130.21, 130.24, 130.66, 130.73, 131.48, 133.10, 137.62, 138.07, 144.25, 144.40, 147.13, 148.51, 173.38, 195.62.

HRMS (ESI) calcd for $C_{30}H_{21}N_3NaO_2$, $[M+Na]^+$: 478.1526, found: 478.1527.



4j

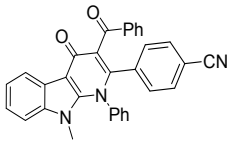
3-benzoyl-9-methyl-1-phenyl-2-(4-(trifluoromethyl)phenyl)-1,9-dihydro-4H-pyrido[2,3-b] indol-4-one (4j)

White solid, 76% yield (80 mg); mp 289-291 °C.

^{1}H NMR ($CDCl_3$, 400 MHz) δ 2.94 (s, 3H), 7.08 (d, *J* = 4.4 Hz, 1H), 7.13-7.38 (m, 13H), 7.40-7.49 (m, 1H), 7.84 (d, *J* = 8.0 Hz, 2H), 8.46-8.61 (m, 1H).

^{13}C NMR ($CDCl_3$, 100 MHz) δ 31.61, 108.51, 108.83, 122.24, 122.27, 122.47, 123.59 (q, *J* = 272.6 Hz), 124.38, 124.63 (q, *J* = 3.9 Hz), 127.06, 128.59, 129.33, 129.76, 130.31, 130.52, 130.65

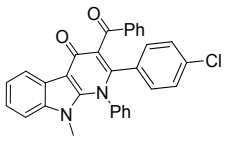
(q, J = 32.6 Hz), 131.35, 133.28, 135.54, 137.31, 137.60, 138.03, 143.95, 145.10, 173.12, 195.97.
HRMS (ESI) calcd for $C_{32}H_{21}F_3N_2NaO_2$, $[M+Na]^+$: 545.1447, found: 545.1448.



4k

4-(3-benzoyl-9-methyl-4-oxo-1-phenyl-4,9-dihydro-1H-pyrido[2,3-b]indol-2-yl) benzonitrile (4k)

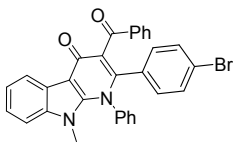
Light yellow solid, 57% yield (55 mg); mp 302-304 °C.
^{1}H NMR ($CDCl_3$, 400 MHz) δ 2.93 (s, 3H), 7.02 (d, J = 7.6 Hz, 1H), 7.17 (d, J = 8.0 Hz, 2H), 7.20-7.40 (m, 11H), 7.43-7.51 (m, 1H), 7.82 (d, J = 8.0 Hz, 2H), 8.50 (d, J = 7.2 Hz, 1H).
^{13}C NMR ($CDCl_3$, 100 MHz) δ 31.61, 108.52, 108.86, 112.64, 118.06, 122.20, 122.27, 122.41, 124.43, 126.98, 128.68, 129.34, 129.85, 130.47, 130.58, 131.44, 131.72, 133.44, 136.58, 137.31, 137.51, 137.93, 143.85, 144.61, 172.95, 195.84.
HRMS (ESI) calcd for $C_{32}H_{21}N_3NaO_2$, $[M+Na]^+$: 502.1526, found: 502.1532.



4l

3-benzoyl-2-(4-chlorophenyl)-9-methyl-1-phenyl-1,9-dihydro-4H-pyrido[2,3-b]indol-4-one (4l)

Light yellow solid, 76% yield (74 mg); mp 268-269 °C.
^{1}H NMR ($CDCl_3$, 400 MHz) δ 2.97 (s, 3H), 6.96 (s, 4H), 7.10-7.18 (m, 1H), 7.21-7.28 (m, 2H), 7.28-7.40 (m, 7H), 7.42-7.49 (m, 1H), 7.85 (d, J = 7.6 Hz, 2H), 8.48-8.57 (m, 1H).
^{13}C NMR ($CDCl_3$, 100 MHz) δ 31.63, 108.60, 108.80, 122.37, 122.43, 122.55, 124.44, 127.23, 128.08, 128.60, 129.41, 129.78, 130.24, 130.28, 130.52, 132.15, 133.24, 135.09, 137.38, 137.86, 138.06, 144.11, 145.39, 173.29, 196.01.
HRMS (ESI) calcd for $C_{31}H_{21}ClN_2NaO_2$, $[M+Na]^+$: 511.1184, found 511.1184.



4m

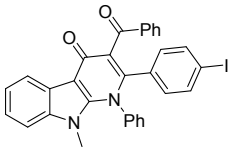
3-benzoyl-2-(4-bromophenyl)-9-methyl-1-phenyl-1,9-dihydro-4H-pyrido[2,3-b]indol-4-one (4m)

Light yellow solid, 71% yield (76 mg); mp 292-294 °C.

^{1}H NMR (DMSO-d^6, 400 MHz) δ 2.99 (s, 3H), 7.14 (d, J = 8.4 Hz, 2H), 7.21-7.32 (m, 3H), 7.34-7.49 (m, 6H), 7.50-7.61 (m, 2H), 7.63-7.72 (m, 2H), 7.87 (d, J = 8.0 Hz, 2H), 8.27 (d, J = 8.0 Hz, 1H).

^{13}C NMR (DMSO-d^6, 100 MHz) δ 31.62, 107.52, 110.16, 120.98, 122.09, 122.24, 122.54, 124.28, 125.96, 128.88, 129.42, 129.57, 130.43, 130.58, 131.39, 133.08, 133.60, 137.43, 137.71, 137.95, 144.26, 145.30, 172.61, 196.14.

HRMS (ESI) calcd for $C_{31}H_{21}BrN_2NaO_2$, $[M+Na]^+$: 555.0679, found: 555.0686.



4n

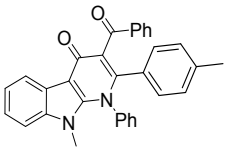
3-benzoyl-2-(4-iodophenyl)-9-methyl-1-phenyl-1,9-dihydro-4H-pyrido[2,3-b]indol-4-one(4n)

Light yellow solid, 59% yield (64 mg); mp 311-313 °C.

^{1}H NMR ($CDCl_3$, 500 MHz) δ 2.97 (s, 3H), 6.76 (d, J = 5.0 Hz, 2H), 7.15 (d, J = 10.0 Hz, 1H), 7.22-7.25 (m, 2H), 7.30-7.37 (m, 9H), 7.43-7.48 (m, 1H), 7.84 (d, J = 10.0 Hz, 2H), 8.51-8.54 (m, 1H).

^{13}C NMR ($CDCl_3$, 125 MHz) δ 31.84, 95.27, 108.50, 108.64, 122.19, 122.28, 122.38, 124.24, 126.96, 128.37, 129.19, 129.57, 130.02, 130.27, 131.14, 132.16, 132.98, 136.68, 137.11, 137.62, 137.83, 143.83, 145.19, 172.85, 195.41.

HRMS (ESI) calcd for $C_{31}H_{21}IN_2NaO_2$, $[M+Na]^+$: 603.0540, found 603.0533.



4o

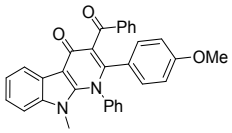
3-benzoyl-9-methyl-1-phenyl-2-(p-tolyl)-1,9-dihydro-4H-pyrido[2,3-b]indol-4-one (4o)

Light yellow solid, 68% yield (64 mg); mp 289-291 °C.

^{1}H NMR ($CDCl_3$, 400 MHz) δ 2.10 (s, 3H), 2.98 (s, 3H), 6.76 (d, J = 8.0 Hz, 2H), 6.88 (d, J = 8.0 Hz, 2H), 7.19 (d, J = 7.6 Hz, 1H), 7.22-7.26 (m, 2H), 7.27-7.38 (m, 7H), 7.40-7.48 (m, 1H), 7.86 (d, J = 8.0 Hz, 2H), 8.54 (d, J = 7.6 Hz, 1H).

^{13}C NMR ($CDCl_3$, 100 MHz) δ 20.85, 31.63, 108.54, 108.74, 122.29, 122.48, 122.67, 124.31, 127.08, 128.40, 128.43, 128.77, 129.44, 129.54, 129.90, 130.54, 130.59, 132.93, 137.40, 138.16 138.26, 138.73, 144.26, 146.85, 173.55, 196.17.

HRMS (ESI) calcd for $C_{32}H_{24}N_2NaO_2$, $[M+Na]^+$: 491.1730, found 491.1724.



4p

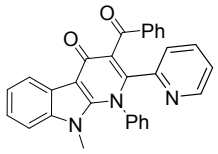
3-benzoyl-2-(4-methoxyphenyl)-9-methyl-1-phenyl-1,9-dihydro-4H-pyrido[2,3-b]indol-4-one (4p)

Light yellow solid, 80% yield (78 mg); mp 294-296 °C.

^{1}H NMR ($CDCl_3$, 400 MHz) δ 2.97 (s, 3H), 3.58 (s, 3H), 6.47 (d, J = 8.0 Hz, 2H), 6.90 (d, J = 8.4 Hz, 2H), 7.11-7.38 (m, 10H), 7.39-7.49 (m, 1H), 7.85 (d, J = 7.6 Hz, 2H), 8.46-8.61 (m, 1H).

^{13}C NMR ($CDCl_3$, 100 MHz) δ 31.65, 54.85, 108.58, 108.72, 113.10, 122.32, 122.53, 122.73, 123.97, 124.31, 127.38, 128.47, 129.44, 129.61, 129.91, 130.57, 132.15, 132.95, 137.43, 138.29, 144.34, 146.56, 159.70, 173.57, 196.17.

HRMS (ESI) calcd for $C_{32}H_{24}N_2NaO_3$, $[M+Na]^+$: 507.1679, found 507.1672.



4q

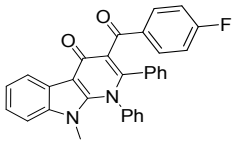
3-benzoyl-9-methyl-1-phenyl-2-(pyridin-2-yl)-1,9-dihydro-4H-pyrido[2,3-b]indol-4-one (4q)

Yellow solid, 52% yield (47 mg); mp 277-279 °C.

^{1}H NMR ($CDCl_3$, 400 MHz) δ 3.01 (s, 3H), 6.92 (dd, J_1 = 7.6 Hz, J_2 = 4.8 Hz, 1H), 7.21 (d, J = 7.6 Hz, 2H), 7.27-7.47 (m, 11H), 7.88 (d, J = 7.6 Hz, 2H), 8.23 (d, J = 4.8 Hz, 1H), 8.54 (d, J = 7.6 Hz, 1H).

^{13}C NMR ($CDCl_3$, 100 MHz) δ 31.59, 108.79, 108.87, 122.34, 122.53, 122.67, 123.26, 124.40, 126.93, 127.26, 128.47, 129.42, 129.55, 130.02, 130.62, 133.02, 135.86, 137.43, 138.00, 138.12, 144.17, 145.52, 149.03, 151.16, 173.47, 196.18.

HRMS (ESI) calcd for $C_{30}H_{21}N_3NaO_2$, $[M+Na]^+$: 478.1526, found 478.1525.



4r

3-(4-fluorobenzoyl)-9-methyl-1,2-diphenyl-1,9-dihydro-4H-pyrido[2,3-b]indol-4-one (4r)

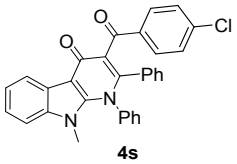
Light yellow solid, 84% yield (80 mg); mp 290-292 °C.

^{1}H NMR ($CDCl_3$, 400 MHz) δ 2.98 (s, 3H), 6.89-7.07 (m, 7H), 7.18 (d, J = 8.0 Hz, 1H), 7.21-7.28 (m, 2H), 7.28-7.39 (m, 5H), 7.87 (dd, J_1 = 8.4 Hz, J_2 = 5.6 Hz, 2H), 8.53 (d, J = 7.2 Hz, 1H).

^{13}C NMR ($CDCl_3$, 100 MHz) δ 31.64, 108.58, 108.82, 115.51 (d, J = 22.0 Hz), 122.35, 122.39,

122.56, 124.44, 126.66, 127.72, 128.90, 129.58, 130.03, 130.52, 130.73, 131.70, 132.03 (d, J = 9.4 Hz), 134.72 (d, J = 2.9 Hz), 137.42, 137.95, 144.16, 146.73, 165.91 (d, J = 253.6 Hz), 173.35, 194.48.

HRMS (ESI) calcd for $C_{31}H_{21}FN_2NaO_2$, $[M+Na]^+$: 495.1479, found 495.1482.



4s

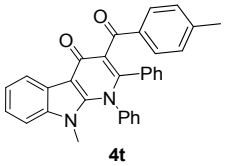
3-(4-chlorobenzoyl)-9-methyl-1,2-diphenyl-1,9-dihydro-4H-pyrido[2,3-b]indol-4-one (4s)

Light yellow solid, 86% yield (84 mg); mp 271-273 °C.

^{1}H NMR ($CDCl_3$, 400 MHz) δ 2.98 (s, 3H), 6.94-7.08 (m, 5H), 7.17 (d, J = 7.6 Hz, 1H), 7.21-7.39 (m, 9H), 7.78 (d, J = 8.4 Hz, 2H), 8.53 (dd, J_1 = 5.6 Hz, J_2 = 2.8 Hz, 1H).

^{13}C NMR ($CDCl_3$, 100 MHz) δ 31.64, 108.59, 108.82, 122.35, 122.40, 122.56, 124.43, 126.53, 127.76, 128.81, 128.93, 129.59, 130.03, 130.53, 130.71, 130.78, 131.68, 136.69, 137.41, 137.95, 139.28, 144.13, 146.90, 173.34, 194.88.

HRMS (ESI) calcd for $C_{31}H_{21}ClN_2NaO_2$, $[M+Na]^+$: 511.1184, found 511.1188.



4t

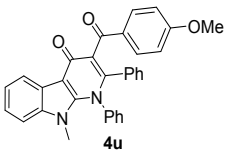
9-methyl-3-(4-methylbenzoyl)-1,2-diphenyl-1,9-dihydro-4H-pyrido[2,3-b]indol-4-one (4t)

Light yellow solid, 79% yield (74 mg); mp 264-266 °C.

^{1}H NMR ($CDCl_3$, 400 MHz) δ 2.31 (s, 3H), 2.96 (s, 3H), 6.90-7.04 (m, 5H), 7.09 (d, J = 8.0 Hz, 2H), 7.13-7.19 (m, 1H), 7.20-7.35 (m, 7H), 7.74 (d, J = 8.0 Hz, 2H), 8.54 (dd, J_1 = 5.6 Hz, J_2 = 2.4 Hz, 1H).

^{13}C NMR ($CDCl_3$, 100 MHz) δ 21.31, 31.58, 108.47, 108.75, 122.18, 122.35, 122.60, 124.25, 127.08, 127.59, 128.69, 129.15, 129.49, 129.52, 129.89, 130.51, 130.75, 131.79, 135.79, 137.36, 138.00, 143.72, 144.15, 146.47, 173.45, 195.58.

HRMS (ESI) calcd for $C_{32}H_{24}N_2NaO_2$, $[M+Na]^+$: 491.1730, found 491.1728.



4u

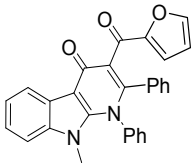
3-(4-methoxybenzoyl)-9-methyl-1,2-diphenyl-1,9-dihydro-4H-pyrido[2,3-b]indol-4-one (4u)

Dark yellow solid, 47% yield (46 mg); mp 268-270 °C.

^{1}H NMR ($CDCl_3$, 400 MHz) δ 3.00 (s, 3H), 3.79 (s, 3H), 6.80 (d, *J* = 8.4 Hz, 2H), 6.90-7.10 (m, 5H), 7.16-7.26 (m, 3H), 7.28-7.40 (m, 5H), 7.83 (d, *J* = 8.8 Hz, 2H), 8.56 (d, *J* = 7.2 Hz, 1H).

^{13}C NMR ($CDCl_3$, 100 MHz) δ 31.64, 55.22, 108.58, 108.73, 113.67, 122.34, 122.54, 122.69, 124.35, 127.20, 127.66, 128.77, 129.55, 129.93, 130.55, 130.78, 131.45, 131.86, 131.89, 137.41, 138.15, 144.22, 146.37, 163.68, 173.53, 194.44.

HRMS (ESI) calcd for $C_{32}H_{24}N_2NaO_3$, $[M+Na]^+$: 507.1679, found 507.1677.



4v

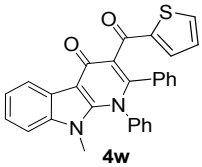
3-(furan-2-carbonyl)-9-methyl-1,2-diphenyl-1,9-dihydro-4H-pyrido[2,3-b]indol-4-one (4v)

Brown solid, 50% yield (44 mg); mp 268-270 ^{o}C.

^{1}H NMR ($CDCl_3$, 400 MHz) δ 2.99 (s, 3H), 6.41 (d, *J* = 1.6 Hz, 1H), 6.96-7.12 (m, 6H), 7.20 (d, *J* = 7.6 Hz, 1H), 7.22-7.28 (m, 2H), 7.29-7.38 (m, 5H), 7.46 (s, 1H), 8.56 (d, *J* = 6.8 Hz, 1H).

^{13}C NMR ($CDCl_3$, 100 MHz) δ 31.65, 108.68, 108.78, 112.39, 119.06, 122.36, 122.53, 122.65, 124.38, 126.14, 127.73, 128.95, 129.59, 130.01, 130.57, 130.76, 131.65, 137.38, 138.02, 144.12, 146.71, 147.09, 153.99, 173.23, 183.06.

HRMS (ESI) calcd for $C_{29}H_{20}N_2NaO_3$, $[M+Na]^+$: 467.1366, found 467.1366.



4w

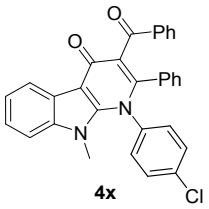
9-methyl-1,2-diphenyl-3-(thiophene-2-carbonyl)-1,9-dihydro-4H-pyrido[2,3-b]indol-4-one (4w)

Brown solid, 51% yield (47 mg); mp 317-319 ^{o}C.

^{1}H NMR ($CDCl_3$, 400 MHz) δ 2.98 (s, 3H), 6.87-7.10 (m, 6H), 7.12-7.19 (m, 1H), 7.20-7.40 (m, 7H), 7.49 (d, *J* = 4.8 Hz, 1H), 7.63 (d, *J* = 2.8 Hz, 1H), 8.49-8.63 (m, 1H).

^{13}C NMR ($CDCl_3$, 100 MHz) δ 31.64, 108.64, 108.78, 122.26, 122.42, 122.66, 124.30, 127.05, 127.67, 128.07, 128.84, 129.55, 129.96, 130.57, 130.91, 131.65, 133.95, 134.35, 137.36, 138.01, 144.08, 145.63, 146.74, 173.12, 187.71.

HRMS (ESI) calcd for $C_{29}H_{20}N_2NaO_2S$, $[M+Na]^+$: 483.1138, found: 483.1142.



4x

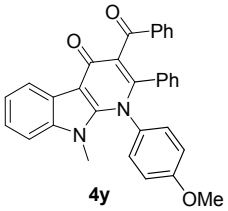
3-benzoyl-1-(4-chlorophenyl)-9-methyl-2-phenyl-1,9-dihydro-4H-pyrido[2,3-b]indol-4-one (4x)

Yellow solid, 75% yield (73 mg); mp 277-279 °C.

^{1}H NMR ($CDCl_3$, 400 MHz) δ 2.98 (s, 3H), 6.91-7.11 (m, 6H), 7.19 (d, *J* = 8.4 Hz, 2H), 7.22-7.33 (m, 6H), 7.36-7.44 (m, 1H), 7.81 (d, *J* = 7.6 Hz, 2H), 8.46-8.55 (m, 1H).

^{13}C NMR ($CDCl_3$, 100 MHz) δ 31.86, 108.38, 108.82, 122.18, 122.21, 122.47, 124.30, 127.02, 127.86, 128.43, 128.98, 129.34, 129.68, 130.73, 131.42, 131.87, 133.01, 135.93, 136.48, 137.22, 138.05, 143.92, 146.40, 173.34, 195.91.

HRMS (ESI) calcd for $C_{31}H_{21}ClN_2NaO_2$, $[M+Na]^+$: 511.1184, found 511.1185.



4y

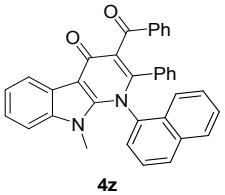
3-benzoyl-1-(4-methoxyphenyl)-9-methyl-2-phenyl-1,9-dihydro-4H-pyrido[2,3-b]indol-4-one (4y)

Yellow solid, 69% yield (66 mg); mp 291-293 °C.

^{1}H NMR ($CDCl_3$, 400 MHz) δ 3.01 (s, 3H), 3.75 (s, 3H), 6.79 (d, *J* = 8.8 Hz, 2H), 6.93-7.06 (m, 5H), 7.09-7.21 (m, 3H), 7.24-7.35 (m, 4H), 7.37-7.45 (m, 1H), 7.83 (d, *J* = 8.0 Hz, 2H), 8.54 (dd, J_1 = 5.6 Hz, J_2 = 2.4 Hz, 1H).

^{13}C NMR ($CDCl_3$, 100 MHz) δ 31.62, 55.36, 108.47, 108.75, 114.43, 122.18, 122.37, 122.67, 124.24, 126.96, 127.66, 128.40, 128.72, 129.37, 130.34, 130.74, 131.57, 131.91, 132.89, 137.37, 138.28, 144.40, 147.04, 160.35, 173.41, 196.13.

HRMS (ESI) calcd for $C_{32}H_{25}N_2O_3$, $[M+H]^+$: 485.1860, found 485.1860.



4z

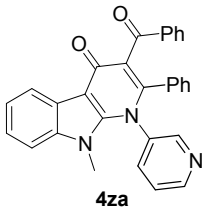
3-benzoyl-9-methyl-1-(naphthalen-1-yl)-2-phenyl-1,9-dihydro-4H-pyrido[2,3-b]indol-4-one (4z)

Light yellow solid, 71% yield (72 mg); mp 175-178 °C.

^{1}H NMR (DMSO-d^6, 400 MHz) δ 2.68 (s, 3H), 6.53-6.65 (m, 1H), 6.70 (d, J = 8.0 Hz, 1H), 6.88 (t, J = 7.6 Hz, 1H), 6.93-7.04 (m, 1H), 7.28-7.68 (m, 11H), 7.89 (d, J = 8.0 Hz, 2H), 7.95-8.08 (m, 3H), 8.34 (d, J = 7.6 Hz, 1H).

^{13}C NMR (DMSO-d^6, 100 MHz) δ 31.04, 107.36, 110.19, 121.10, 122.19, 122.23, 122.29, 124.35, 125.39, 126.37, 126.99, 127.28, 127.57, 128.92, 128.98, 129.04, 129.20, 129.43, 130.88, 131.06, 131.40, 131.53, 131.74, 133.44, 133.57, 137.32, 137.92, 144.52, 146.91, 172.98, 195.93.

HRMS (ESI) calcd for $C_{35}H_{24}N_2NaO_2$, $[M+Na]^+$: 527.1730, found 527.1730.



4za

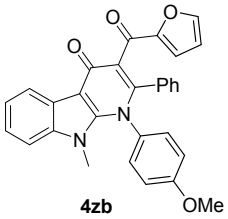
3-benzoyl-9-methyl-2-phenyl-1-(pyridin-3-yl)-1,9-dihydro-4H-pyrido[2,3-b]indol-4-one (4za)

Brown solid, 80% yield (73 mg); mp 253-255 ^{o}C.

^{1}H NMR ($CDCl_3$, 400 MHz) δ 2.99 (s, 3H), 6.90-7.14 (m, 6H), 7.19-7.35 (m, 5H), 4.39-7.48 (m, 1H), 7.66 (d, J = 8.0 Hz, 1H), 7.83 (d, J = 8.0 Hz, 2H), 8.43-8.61 (m, 3H).

^{13}C NMR ($CDCl_3$, 100 MHz) δ 32.37, 108.56, 108.87, 122.32, 122.47, 122.50, 124.07, 124.52, 127.37, 128.17, 128.52, 129.25, 129.38, 130.78, 131.21, 133.17, 135.32, 137.18, 137.98, 138.03, 143.99, 146.42, 150.80, 150.90, 173.43, 195.72.

HRMS (ESI) calcd for $C_{30}H_{21}N_3NaO_2$, $[M+Na]^+$: 478.1526, found 478.1528.



4zb

3-(furan-2-carbonyl)-1-(4-methoxyphenyl)-9-methyl-2-phenyl-1,9-dihydro-4H-pyrido[2,3-b]indol-4-one (4zb)

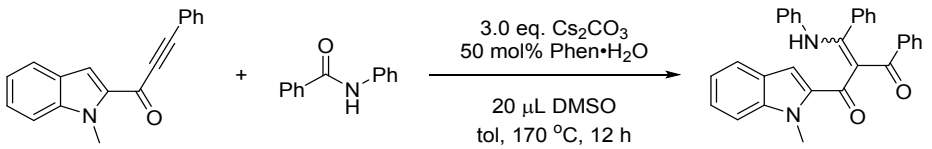
Dark yellow solid, 64% yield (60 mg); mp 286-288 ^{o}C.

^{1}H NMR ($CDCl_3$, 400 MHz) δ 2.99 (s, 3H), 3.76 (s, 3H), 6.38 (d, J = 1.6 Hz, 1H), 6.79 (d, J = 8.8 Hz, 2H), 6.96-7.09 (m, 6H), 7.09-7.19 (m, 3H), 7.23-7.33 (m, 2H), 7.43 (s, 1H), 8.48-8.59 (m, 1H).

^{13}C NMR ($CDCl_3$, 100 MHz) δ 31.59, 55.36, 108.47, 108.76, 112.30, 114.42, 118.99, 122.10, 122.31, 122.64, 124.17, 126.00, 127.69, 128.81, 130.24, 130.67, 131.59, 131.78, 137.28, 144.24, 146.59, 147.51, 153.99, 160.34, 173.13, 183.09.

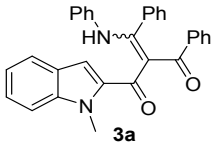
HRMS (ESI) calcd for $C_{30}H_{22}N_2NaO_4$, $[M+Na]^+$: 497.1472, found: 497.1469.

3. Control experiments



1.0 eq. **1a** 1.0 eq. **2a** **3a**

In a dried sealed tube ynone **1a** (0.2 mmol, 51.9 mg), *N*-phenylbenzamide **2a** (0.2 mmol, 39.4 mg), 1,10-phenanthroline hydrate (0.1 mmol, 19.8 mg), cesium carbonate (0.6 mmol, 195.6 mg), toluene (2 mL) and dimethyl sulfoxide (20 μL) were added, and the mixture was heated at 170 °C for 12 h. After the reaction was complete as monitored by thin-layer chromatography, the reaction mixture was then quenched by water (20 mL), a portion of ethyl acetate (20 mL) was added and the combined organic layer was washed with water (50 mL), brine (50 mL). Combined aqueous phase was extracted with ethyl acetate (50 mL× 2). The combined organic phase was dried over with anhydrous Na_2SO_4, filtered, and concentrated under reduced pressure, Purification by chromatography on silica gel (petroleum ether / ethyl acetate = 8/1) afforded desired compound **3a**.



3a

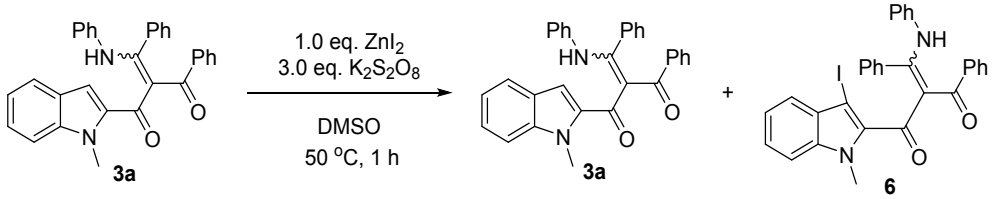
1-(1-methyl-1H-indol-2-yl)-3-phenyl-2-(phenyl(phenylamino)methylene)propane-1,3-dione (3a)

Light yellow solid, 91 % yield (83 mg); mp 214-216 °C.

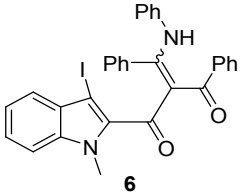
^{1}H NMR ($CDCl_3$, 400 MHz) Obtained as 3.7:1 isomer, Major isomer: δ 3.58 (s, 3H), 6.81 (d, *J* = 8.0 Hz, 2H), 6.96-7.53 (m, 17H), 7.56 (d, *J* = 8.0 Hz, 1H), 13.77 (s, 1H); minor isomer: δ 3.87 (s, *3*H), 6.62 (s, 1H), 7.44 (d, *J* = 8.0 Hz, 1H), 7.67 (d, *J* = 8.0 Hz, 2H), 13.61 (s, 1H); other peaks are overlapped with the other isomer.

^{13}C NMR (100 MHz, $CDCl_3$) δ 30.77, 31.10, 108.37, 109.71, 110.00, 112.32, 114.08, 120.07, 120.37, 122.45, 122.84, 124.19, 124.40, 124.54, 125.24, 125.54, 125.62, 125.89, 126.50, 127.29, 128.02, 128.08, 128.28, 128.40, 128.99, 129.19, 129.30, 129.56, 129.70, 130.15, 131.97, 133.01, 133.16, 138.48, 138.69, 139.11, 139.96, 140.08, 141.38, 142.53, 164.26, 164.79, 185.90, 189.31, 194.66, 196.66.

HRMS (ESI) calcd for $C_{31}H_{24}N_2NaO_2$, $[M+Na]^+$: 479.1730, found: 479.1737.



In a Schlenk tube intermediate **3a** (0.2 mmol, 91.3 mg), zinc iodide (0.2 mmol, 63.8 mg), potassium persulfate (0.6 mmol, 162.8 mg) and dimethyl sulfoxide (2 mL) were added, and the mixture was heated at 50 °C. After the reaction was heated at 50°C for 1 h, the reaction mixture was then quenched by water (10 mL), a portion of ethyl acetate (20 mL) was added and the combined organic layer was washed with water (50 mL), saturated sodium thiosulfate solution (50 mL), brine (50 mL). Combined aqueous phase was extracted with ethyl acetate (50 mL× 2). The combined organic phase was dried over with anhydrous Na_2SO_4, filtered, and concentrated under reduced pressure, Purification by chromatography on silica gel (petroleum ether / ethyl acetate = 6/1) afforded compound **3a** (13.7 mg, 15%) and compound **6** (63.4 mg, 54%).



6

1-(3-iodo-1-methyl-1H-indol-2-yl)-3-phenyl-2-(phenyl(phenylamino)methylene)propane-1,3-dione (6)

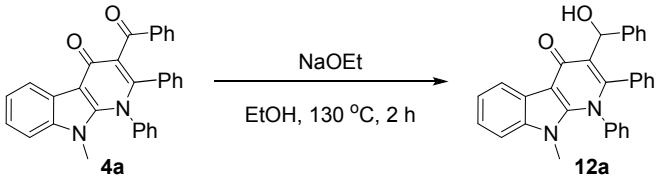
Yellow solid, 54% yield (63 mg); mp 210-212 °C.

^{1}H NMR (400 MHz, $CDCl_3$) Obtained as 7:1 isomer, Major isomer: δ 3.54 (s, 3H), 6.81 (d, J = 8.0 Hz, 2H), 6.89-7.38 (m, 14H), 7.40 (d, J = 8.4 Hz, 1H), 7.43-7.52 (m, 2H), 14.04 (s, 1H); minor isomer: δ 3.75 (s, 3H) ; other peaks are overlapped with the other isomer.

^{13}C NMR (100 MHz, $CDCl_3$) δ 31.71, 66.95, 109.94, 114.90, 120.82, 121.21, 123.72, 124.71, 125.00, 125.96, 126.06, 126.23, 127.01, 127.86, 127.92, 128.49, 128.58, 129.01, 129.20, 129.57, 129.65, 129.77, 129.96, 133.20, 138.27, 139.14, 139.40, 142.48, 165.88, 188.50, 194.93.

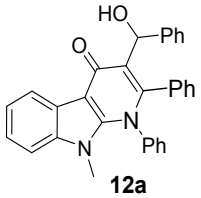
HRMS (ESI) calcd for $C_{31}H_{23}IN_2NaO_2$, $[M+Na]^+$: 605.0696, found: 605.0701.

4. Transformations of 4a



4a **12a**

In a dried sealed tube **4a** (0.2 mmol, 91.3 mg), NaOEt / EtOH (20%, 1 mL) was added, and then mixture was heated at 130 °C for 2 h. After the reaction was complete as monitored by thin-layer chromatography, the reaction mixture was then quenched by water (10 mL), a portion of ethyl acetate (10 mL) was added and the combined organic layer was washed with water (20 mL), brine (20 mL). The combined organic phase was dried over with anhydrous Na_2SO_4, filtered, and concentrated under reduced pressure, purification by chromatography on silica gel (petroleum ether / ethyl acetate = 5/1) to give the final product as a yellow solid.



12a

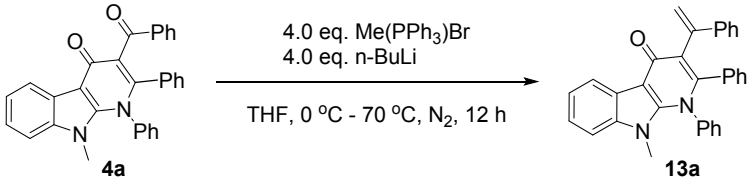
3-(hydroxy(phenyl)methyl)-9-methyl-1,2-diphenyl-1,9-dihydro-4H-pyrido[2,3-b]indol-4-one (12a)

Yellow solid, 73% yield (67 mg); mp 260-262 °C.

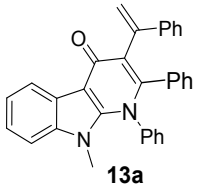
^{1}H NMR ($CDCl_3$, 600 MHz) δ 2.94 (s, 3H), 5.20 (s, 1H), 6.83 (d, J = 7.2 Hz, 1H), 7.05-7.08 (m, 1H), 7.13-7.23 (m, 9H), 7.26-7.38 (m, 8H), 8.55 (d, J = 7.2 Hz, 1H).

^{13}C NMR ($CDCl_3$, 150 MHz) δ 176.20, 145.88, 144.62, 143.91, 138.18, 137.23, 132.31, 130.73, 130.21, 130.11, 129.60, 129.27, 129.10, 128.70, 128.21, 127.94, 127.66, 126.71, 126.42, 124.25, 123.40, 122.15, 122.06, 108.57, 108.46, 74.72, 31.61.

HRMS (ESI) calcd for $C_{31}H_{25}N_2O_2$, $[M+H]^+$: 457.1911, found: 457.1914.



To a solution of methyltriphenylphosphonium bromide (284 mg, 0.8 mmol, 4.0 equiv) in anhydrous THF (2 mL), n-BuLi (0.32 mL, 2.5 M in hexane, 0.8 mmol, 4.0 equiv) was added at 0 °C. The resulting mixture was stirred at 0 °C for 90 min. A solution of **4a** (91.3 mg, 0.2 mmol, 1.0 equiv) in THF was then added and warmed to 70 °C and stirred for 12 h. The resulting mixture was quenched with a saturated solution of NH_4Cl and extracted with ethyl acetate (10 mL × 3). The combined organic layers were washed with brine and dried over with anhydrous Na_2SO_4, filtered, and concentrated under reduced pressure. Purification by column chromatography with petroleum ether / ethyl acetate = 2/1 as the eluent to give the final product as a white solid.



13a

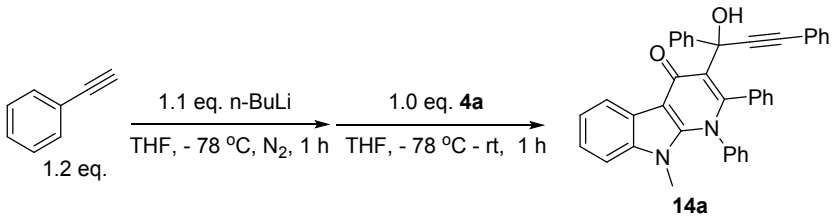
9-methyl-1,2-diphenyl-3-(1-phenylvinyl)-1,9-dihydro-4H-pyrido[2,3-b]indol-4-one (13a)

White solid, 78% yield (71 mg); mp 273-275 °C.

^{1}H NMR ($CDCl_3$, 600 MHz) δ 2.99 (s, 3H), 5.14 (s, 1H), 5.65 (s, 1H), 6.74-7.05 (m, 5H), 7.09-7.17 (m, 3H), 7.18-7.35 (m, 10H), 8.59-8.67 (m, 1H).

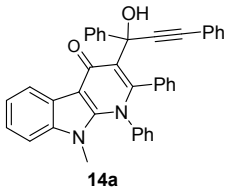
^{13}C NMR ($CDCl_3$, 150 MHz) δ 174.19, 146,56, 144.03, 142.87, 141.36, 138.82, 137.18, 133.73, 130.54, 130.35, 129.31, 129.13, 127.82, 127.69, 127.45, 127.06, 126.80, 126.12, 123.78, 122.94, 122.42, 121.96, 118.42, 108.32, 108.07, 31.74.

HRMS (ESI) calcd for $C_{32}H_{25}N_2O$, $[M+H]^+$: 453.1961, found: 453.1961.



14a

To a solution of ethynylbenzene (29 μL, 0.26 mmol) in anhydrous THF (2 mL), n-BuLi (2.5M, 0.24 mmol, 0.1 mL) was added at -78 °C. The resulting mixture was stirred at -78 °C for 40 min, then the **4a** (91.3 mg, 0.2 mmol) was added and the reaction temperature was raised to room temperature till **4a** disappeared by TLC analysis. The resulting mixture was quenched with a saturated solution of NH_4Cl and extracted with ethyl acetate (10 mL × 3). The combined organic layers were washed with brine and dried over with anhydrous Na_2SO_4, filtered, and concentrated under reduced pressure. Purification by column chromatography with petroleum ether / ethyl acetate = 1/1 as the eluent to give the final product as a white solid.



14a

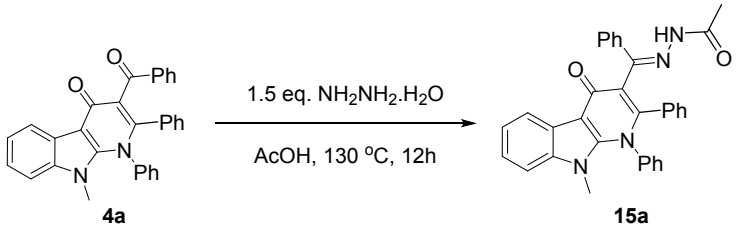
3-(1-hydroxy-1,3-diphenylprop-2-yn-1-yl)-9-methyl-1,2-diphenyl-1,9-dihydro-4H-pyrido[2,3-b]indol-4-one (14a)

White solid, 72% yield (80 mg); mp 255-257 °C.

^{1}H NMR ($CDCl_3$, 600 MHz) δ 2.86 (s, 3H), 5.96 (d, *J* = 7.2 Hz, 1H), 6.44-6.49 (m, 1H), 6.82-6.86 (m, 1H), 6.89-6.95 (m, 2H), 6.96-7.02 (m, 3H), 7.13-7.16 (m, 1H), 7.18-7.23 (m, 4H), 7.25-7.28 (m, 3H), 7.33 (d, *J* = 7.2 Hz, 2H), 7.37-7.42 (m, 4H), 8.64-8.68 (m, 1H), 11.23 (s, 1H).

^{13}C NMR ($CDCl_3$, 150 MHz) δ 177.51, 147,76, 145.90, 143.54, 137.93, 132.29, 131.98, 131.50, 131.31, 130.77, 130.42, 129.48, 129.05, 128.79, 127.97, 127.84, 127.56, 127.48, 126.76, 126.63, 126.52, 126.34, 125.11, 124.55, 123.51, 122.45, 122.33, 122.29, 108.66, 108.47, 92.75, 87.20, 75.79, 31.49.

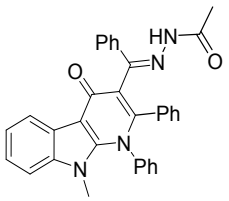
HRMS (ESI) calcd for $C_{39}H_{29}N_2O_2$, $[M+H]^+$: 557.2224, found: 557.2239.



4a **15a**

In a dried sealed tube **4a** (0.2 mmol, 91.3 mg), AcOH (1 mL), $NH_2NH_2.H_2O$ (85%, 0.2 mmol, 19 μL) was added, and then the mixture was heated at 130 °C for 12 h. After the reaction was

complete as monitored by thin-layer chromatography, the reaction mixture was then quenched by water (10 mL), a portion of ethyl acetate (10 mL) was added and the combined organic layer was washed with saturated solution of $NaHCO_3$ (20 mL), water (20 mL), brine (20 mL). The combined organic phase was dried over with anhydrous Na_2SO_4, filtered, and concentrated under reduced pressure, purification by chromatography on silica gel (ethyl acetate) to give the final product as a white solid.



15a

3-((E)-(((Z)-ethylidene)hydrazono)(phenyl)methyl)-9-methyl-1,2-diphenyl-1,9-dihydro-4H-pyrido[2,3-b]indol-4-one (15a)

White solid, 87% yield (89 mg); mp 283-285 ^{o}C.

^{1}H NMR ($CDCl_3$, 600 MHz) δ 2.25 (s, 3H), 3.06 (s, 3H), 6.61 (d, *J* = 7.8 Hz, 1H), 6.75-6.85 (m, 1H), 7.00-7.10 (m, 3H), 7.19-7.27 (m, 4H), 7.28-7.45 (m, 7H), 7.48-7.56 (m, 2H), 8.58 (d, *J* = 7.2 Hz, 1H), 8.80 (s, 1H).

^{13}C NMR ($CDCl_3$, 150 MHz) δ 173.13, 171.88, 147.89, 146.91, 144.12, 137.85, 137.50, 137.28, 131.66, 130.19, 130.08, 129.91, 129.56, 129.35, 129.33, 128.96, 128.89, 128.82, 128.01, 127.56, 127.29, 126.68, 124.60, 122.63, 122.54, 122.31, 117.79, 108.70, 108.63, 31.94, 20.58.

HRMS (ESI) calcd for $C_{33}H_{26}N_4O_2$, $[M+Na]^+$: 533.1948, found: 533.1944.

5. Computational methods

All DFT calculations were conducted with Gaussian 09 program, 'Ultrafine' grid and SMD solvation model (solvent = dimethylsulfoxide). Geometry optimization, frequency analysis and intrinsic reaction coordinate analysis were performed with B3LYP method and basis set Lanl2DZ for Zn, Cs, I and 6-31G(d) for the other elements. The optimized structures have no imaginary frequency for energy minima and only one imaginary frequency for the transition states. Based on the optimized structures, solution-phase single-point energies were calculated with B3LYP-D3 method larger basis sets of SDD for Zn, Cs, I and 6-311++G (d, p) for the other elements. The thermodynamic correction obtained from frequency analysis was added to the solution-phase single-point energies to get the solution-phase Gibbs free energies which were used for mechanistic discussion.

Note that the geometry optimization of **TS1** and **TS5** did not reach all convergence criteria though much effect has been devoted to the geometry optimization. This is possibly because the potential energy curve for step is too abrupt. To estimate the energy of **TS1** and **TS5**, we directly performed frequency analysis (still got only one imaginary frequency with the proper vibration

direction) and solution-phase single-point energy calculation when the changes of the energy of transition state oscillates with setting the maximum size of optimization step to be 0.03 bohr.

Table S2. Calculated thermodynamic corrections (ΔG_{cor}), solution-phase single point energies (E_{sol}) and solution-phase Gibbs free energies (ΔG_{sol}) (in Hartree).

	ΔG_{cor}	ΔE_{sol}	ΔG_{sol}
3a	0.40846	-1456.175618	-1455.767158
CO_3^{2-}	-0.011265	-264.1152742	-264.1265392
HCO_3^-	0.000518	-264.645238	-264.64472
7	0.39654	-1455.689431	-1455.292891
I_2	-0.025533	-22.8389178	-22.8644508
8	0.387228	-1478.562556	-1478.175328
TS1	0.385884	-1478.55251	-1478.166626
I^-	-0.016848	-11.60716715	-11.62401515
9	0.396695	-1466.987906	-1466.591211
10	0.380192	-1466.463811	-1466.083619
TS2	0.382074	-1466.447954	-1466.06588
11	0.386917	-1454.870734	-1454.483817
TS3	0.386899	-1454.856577	-1454.469678
pro	0.390518	-1454.980704	-1454.590186
12	0.385833	-1705.856392	-1705.470559
TS4	0.384422	-1705.8376	-1705.453178
13	0.392793	-1466.952411	-1466.559618
TS5	0.395012	-1466.917727	-1466.522715

Cartesian coordinates of all calculated intermediates and transition states (in angstrom)

3a

C	3.25853900	-1.89358400	-0.22909700
C	3.98859800	-0.79166500	-0.76659000
C	5.39351000	-0.76664600	-0.76989700
C	6.05476900	-1.87095700	-0.24765200
C	5.34777500	-2.98039300	0.27600200
C	3.96127300	-3.00154200	0.28956800
C	1.88015600	-1.56418300	-0.35894000
C	1.80035500	-0.31722700	-0.96045300
H	5.94488400	0.08021900	-1.16647100
H	7.14157200	-1.88404600	-0.24070000
H	5.90514000	-3.82394200	0.67448200
H	3.42092100	-3.85223700	0.69727700
H	1.03679900	-2.17843900	-0.07606700
N	3.09187100	0.14522200	-1.22586800
C	3.48967900	1.46417300	-1.70583200
H	3.83016500	2.09268600	-0.87483100
H	4.30656600	1.35598700	-2.42557100
H	2.64187300	1.93087800	-2.19990900
C	0.56758800	0.37529000	-1.39393700
O	0.57378800	1.18598900	-2.32356000
C	-0.71387700	-0.01877400	-0.72152000
C	-1.80532400	-0.35463900	-1.67520000
C	-0.84328800	-0.09948900	0.65562500
C	-1.89286200	-0.91579700	1.32291500
C	-2.23041000	-2.18662400	0.82548000
C	-2.52289100	-0.45279800	2.49242800
C	-3.18651200	-2.96791600	1.47388200
H	-1.72612000	-2.57175600	-0.05514100
C	-3.48218500	-1.23409700	3.13509400
H	-2.27689700	0.53074500	2.88231200
C	-3.81654800	-2.49317800	2.62743900
H	-3.43196400	-3.95171600	1.08368900
H	-3.97226700	-0.85863500	4.02914600
H	-4.56180200	-3.10293600	3.13095200
N	0.00929500	0.51010800	1.54422600

H	0.07188500	0.06907800	2.45560700
C	0.79019900	1.68182000	1.41645900
C	1.92738300	1.80192300	2.23134000
C	0.42144200	2.75026300	0.58328300
C	2.68521400	2.97259700	2.21180100
H	2.20931400	0.97537400	2.87854100
C	1.19242700	3.91248900	0.56691300
H	-0.46257600	2.67826200	-0.03992600
C	2.32618700	4.03382600	1.37599400
H	3.56095100	3.05085100	2.85045100
H	0.89395300	4.73424400	-0.07871400
H	2.91817900	4.94441700	1.35799300
O	-1.55191100	-0.95746800	-2.72125100
C	-3.21714100	0.10303200	-1.42446600
C	-3.52211100	1.22832300	-0.64320000
C	-4.26005900	-0.57535600	-2.07732700
C	-4.84349400	1.66063500	-0.51248600
H	-2.72689900	1.77965300	-0.15129100
C	-5.57999200	-0.15432300	-1.93354500
H	-4.01814400	-1.43474700	-2.69478700
C	-5.87493200	0.96732300	-1.15033300
H	-5.06633700	2.54022100	0.08559600
H	-6.37948200	-0.69553900	-2.43264700
H	-6.90370200	1.30087500	-1.04249700

CO_3^{2-}

C	-0.00036300	0.00010700	0.00031300
O	0.61095300	1.15361400	0.00000100
O	-1.30471200	-0.04797800	-0.00021500
O	0.69403100	-1.10571500	-0.00002100

HCO_3^-

C	-0.14777200	0.06485200	0.00004100
O	0.08085900	1.29754100	0.00005600
O	-1.21398800	-0.57704400	-0.00002100
O	1.02565700	-0.75611600	-0.00009300
H	1.74640500	-0.10416300	0.00021100

7

C	-3.22494200	1.82103000	-0.35788100
C	-3.95241600	0.63767100	-0.68657700
C	-5.35210900	0.58021300	-0.60018700
C	-6.02056400	1.72748900	-0.18379700
C	-5.31885800	2.91061700	0.14135700
C	-3.93284200	2.96661700	0.05737900
C	-1.84461400	1.51166600	-0.55311800
C	-1.76162800	0.19962400	-0.98223800
H	-5.89884300	-0.32290000	-0.85534400
H	-7.10514800	1.71443500	-0.11151100
H	-5.87565200	3.78774500	0.46150500
H	-3.39891300	3.87973100	0.31057100
H	-1.00525000	2.17871100	-0.41233000
N	-3.04915500	-0.33068000	-1.06743000
C	-3.43233100	-1.68506500	-1.44154200
H	-4.19654300	-2.05001400	-0.74881700
H	-3.83590600	-1.71139100	-2.46054200
H	-2.56381300	-2.33672300	-1.39827000
C	-0.55675600	-0.53713800	-1.49948300
O	-0.73723700	-1.27190500	-2.48650500
C	0.73928100	-0.26059600	-0.88868000
C	1.91873200	-0.34512500	-1.73785900
C	0.82207600	0.11862300	0.52463600
C	1.70476500	1.27179200	0.92737600
C	1.97177600	2.33092700	0.04415300
C	2.23546600	1.34036800	2.22757200
C	2.74130700	3.42494500	0.44766100
H	1.56352700	2.30286100	-0.96120700
C	3.01187300	2.42600200	2.62957500
H	2.03296800	0.52717700	2.91752100
C	3.26722800	3.47591600	1.74049100
H	2.92677500	4.23854800	-0.24906100
H	3.42106800	2.45378400	3.63649000
H	3.87056800	4.32415700	2.05364800
N	0.13872500	-0.38284700	1.52118400
C	-0.62605100	-1.55405200	1.47545600
C	-1.86079700	-1.55475100	2.15890500
C	-0.17879800	-2.77635400	0.92593500
C	-2.62677500	-2.71501400	2.26912300
H	-2.20440100	-0.62374600	2.60258100
C	-0.93899000	-3.93891700	1.05934100
H	0.77053200	-2.81315200	0.40272100
C	-2.17077000	-3.91894500	1.72247600
H	-3.57733200	-2.68080700	2.79650700
H	-0.56348200	-4.86975800	0.63992900
H	-2.75945500	-4.82733000	1.81879900
O	1.88849200	-0.30386200	-2.98162400
C	3.30083100	-0.52296300	-1.12354800
C	4.39754700	0.03298100	-1.80335700

C	3.55004200	-1.29900600	0.01827600
C	5.69977800	-0.15306700	-1.34214000
H	4.20935600	0.61185200	-2.70247100
C	4.85630300	-1.50658400	0.47193100
H	2.72539800	-1.75648100	0.55494900
C	5.93471800	-0.92896000	-0.20138700
H	6.53337200	0.30056500	-1.87296900
H	5.02950200	-2.12237200	1.35112700
H	6.94973600	-1.08372100	0.15583700

I_2

I	0.00000000	0.00000000	1.43061700
I	0.00000000	0.00000000	-1.43061700

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C	1.05231400	2.63309200	1.09627000
C	0.64696700	3.49788800	0.07176900
C	0.89259800	4.86514500	0.08935600
C	1.57240900	5.36392000	1.20614700
C	1.97661800	4.51806200	2.24827700
C	1.72638100	3.14201600	2.20248200
C	0.64040800	1.26651400	0.70252900
C	-0.13729200	1.46721800	-0.54857200
H	0.57164800	5.51930400	-0.71388100
H	1.78584300	6.42700000	1.26442800
H	2.49549500	4.93764800	3.10506600
H	2.05562500	2.48854000	3.00453900
H	0.20967500	0.60402900	1.44631400
N	-0.05358100	2.73601000	-0.90641100
C	-0.58599900	3.35870100	-2.11983300
H	-1.22635100	4.19426400	-1.83084200
H	0.25371800	3.73038400	-2.71389700
H	-1.14241600	2.62395200	-2.69167700
C	-0.75459400	0.38655300	-1.43337300
O	-0.34676700	0.42187800	-2.60904900
C	-1.62988400	-0.55673400	-0.81063800
C	-1.91402400	-1.81645500	-1.50266600
C	-2.16618300	-0.24876300	0.52759900
C	-2.00002800	-1.25709000	1.62712700
C	-0.96981800	-2.21237300	1.59421200
C	-2.86055700	-1.23769000	2.74014400
C	-0.80310200	-3.11886500	2.64360600
H	-0.28603600	-2.23597900	0.75182600
C	-2.69907700	-2.14630600	3.78353300
H	-3.65992900	-0.50428700	2.77075600
C	-1.66782300	-3.09145800	3.73980300
H	0.00523300	-3.84430400	2.60432800
H	-3.38023000	-2.12229000	4.63038000
H	-1.54167700	-3.80021700	4.55409100
N	-2.70561300	0.87848100	0.90646700
C	-3.19989900	1.89774000	0.07868200
C	-3.15049700	3.20935400	0.59583100
C	-3.87048400	1.69514700	-1.14794300
C	-3.72423800	4.27890800	-0.09037700
H	-2.66021300	3.36725800	1.55272800
C	-4.46403200	2.76624900	-1.81667200
H	-3.94098900	0.69787400	-1.56665300
C	-4.38923400	4.06459500	-1.30200800
H	-3.66619400	5.27933100	0.33146000
H	-4.99043500	2.58211800	-2.75027200
H	-4.85139000	4.89350600	-1.83116900
O	-1.24512400	-2.22969000	-2.46051600
C	-3.08102500	-2.68588000	-1.06835000
C	-2.95663400	-4.07335700	-1.25258500
C	-4.29918000	-2.18164100	-0.58805400
C	-4.00654400	-4.93543400	-0.94197000
H	-2.02255000	-4.46271900	-1.64519500
C	-5.36119600	-3.04234700	-0.29560700
H	-4.43646700	-1.11410900	-0.45471600
C	-5.21678500	-4.42084500	-0.46412500
H	-3.88551800	-6.00736600	-1.07676500
H	-6.30229100	-2.63247200	0.06209900
H	-6.04077200	-5.08958300	-0.22893600
I	2.51659100	0.03602300	0.10906300
I	5.46658500	-1.82255100	-0.58841100

TS1

C	0.95072600	2.70776900	1.03338200
C	0.59314800	3.47479600	-0.08458000
C	0.85457500	4.83646200	-0.17324600
C	1.48496600	5.43222000	0.92642000
C	1.83145100	4.68601200	2.06029800
C	1.57402900	3.31169000	2.12118200
C	0.57132200	1.30625500	0.74742800
C	-0.22010900	1.40563700	-0.52068200
H	0.58009300	5.41923400	-1.04587200
H	1.70393100	6.49563500	0.89666300
H	2.31164600	5.17893400	2.90037500

H	1.86282400	2.72875200	2.99064500
H	0.17265300	0.68611700	1.53927400
N	-0.06698500	2.63594400	-1.02164700
C	-0.48628000	3.12962200	-2.33484400
H	-1.02077300	4.07245600	-2.20709000
H	0.40028200	3.29420100	-2.95521700
H	-1.13482400	2.40224200	-2.81265400
C	-0.68264300	0.23070200	-1.36223700
O	-0.29812700	0.15549700	-2.52823800
C	-1.51216700	-0.72480900	-0.63562700
C	-1.47011200	-2.14939400	-1.07316600
C	-2.15265900	-0.17767900	0.48223500
C	-2.56316100	-0.98051000	1.66509800
C	-1.86098400	-2.13383900	2.06012000
C	-3.65548900	-0.55341100	2.44224000
C	-2.25400800	-2.84959400	3.19084700
H	-0.98575900	-2.45381300	1.50369300
C	-4.05540700	-1.27730800	3.56351100
H	-4.19269200	0.34423400	2.15295000
C	-3.35541900	-2.42792600	3.94077000
H	-1.69437900	-3.73098200	3.49164100
H	-4.90977800	-0.94314100	4.14586100
H	-3.66189300	-2.98777000	4.82033300
N	-2.25593300	1.17612300	0.63048400
C	-2.98866800	2.01177400	-0.20339800
C	-2.96029100	3.39517100	0.09710900
C	-3.80125200	1.59207100	-1.28560200
C	-3.69106900	4.31298500	-0.65351400
H	-2.36201400	3.72397000	0.94190800
C	-4.53673600	2.51861300	-2.02272400
H	-3.85673800	0.54057600	-1.54448200
C	-4.48399600	3.88472000	-1.72392000
H	-3.64798000	5.36859100	-0.39564300
H	-5.16019600	2.16674000	-2.84159700
H	-5.06017600	4.59874300	-2.30579400
O	-0.42670400	-2.62158600	-1.52581800
C	-2.70080400	-3.01453900	-1.02529300
C	-2.52222400	-4.40497100	-1.13096800
C	-4.00529500	-2.50380100	-0.94397800
C	-3.61782100	-5.26428200	-1.13907100
H	-1.51261400	-4.79596900	-1.20422600
C	-5.10466300	-3.36417300	-0.96456300
H	-4.17085900	-1.43479300	-0.87447700
C	-4.91454700	-4.74487900	-1.05720500
H	-3.46384900	-6.33771900	-1.21007100
H	-6.10961500	-2.95459200	-0.90961100
H	-5.77115500	-5.41365000	-1.06757600
I	2.52339800	0.10273500	0.26974500
I	5.85691200	-1.85586800	-0.36058600

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C	-3.29376200	0.16743100	0.28924400
C	-2.92494400	0.28539600	1.64549400
C	-3.83201900	0.76804000	2.59558800
C	-5.10932300	1.12772100	2.15423500
C	-5.48147600	1.02133400	0.80624500
C	-4.56910800	0.53323800	-0.13423900
C	-2.13872300	-0.36667900	-0.46217200
C	-0.95748900	-0.31148800	0.55940400
H	-3.55473200	0.87089600	3.63963100
H	-5.82647500	1.50724400	2.87767700
H	-6.47864700	1.31646300	0.49354000
H	-4.85014800	0.43175900	-1.17901200
N	-1.61582400	-0.12503300	1.83064500
C	-0.89600700	0.01870000	3.08169500
H	-0.64181500	1.06456900	3.30461900
H	-1.50554200	-0.37315600	3.90202100
H	0.02703400	-0.56317700	3.04357200
C	0.03733000	-1.52677500	0.58689300
O	-0.26570900	-2.60448200	1.07179400
C	1.30785500	-1.05286900	0.08340000
C	2.48460200	-1.94474700	-0.05334200
C	1.20316100	0.31659400	-0.13674700
C	2.27393100	1.19833200	-0.64980500
C	2.97946600	0.83036900	-1.80691400
C	2.61368500	2.38716500	0.01821100
C	4.00300500	1.64459500	-2.29251800
H	2.71289200	-0.08018000	-2.33496500
C	3.64881700	3.18734600	-0.46266100
H	2.08299000	2.67251300	0.92090400
C	4.34200400	2.82127300	-1.62052500
H	4.53555200	1.35711100	-3.19465300
H	3.91436700	4.09768500	0.06743700
H	5.14365100	3.45097400	-1.99656600
N	-0.03458100	0.81366800	0.17096200
C	-0.52297900	2.10143800	-0.23762900
C	-0.97249100	3.00352200	0.73340700
C	-0.56650700	2.45103500	-1.59446700

C	-1.47337200	4.24776500	0.34519700
H	-0.91786300	2.73736600	1.78362800
C	-1.05765300	3.70111400	-1.97311000
H	-0.21281600	1.74933700	-2.34367900
C	-1.51609300	4.59976300	-1.00608000
H	-1.82117900	4.94474300	1.10254100
H	-1.08602900	3.96862200	-3.02572000
H	-1.90142400	5.57077200	-1.30448300
O	2.35508700	-3.04272700	-0.59338800
C	3.81404300	-1.54992200	0.52003200
C	4.97150900	-2.16112200	0.00930700
C	3.93035100	-0.65779300	1.59720700
C	6.22174400	-1.86971000	0.54956700
H	4.87507400	-2.86059500	-0.81519400
C	5.18183900	-0.37949000	2.14963800
H	3.04205200	-0.19803700	2.01876300
C	6.32902400	-0.97887300	1.62359900
H	7.11259400	-2.33719400	0.13868200
H	5.26040800	0.30329200	2.99130000
H	7.30347000	-0.75578600	2.05004100
H	-1.89943500	0.11080600	-1.40573700
I	-2.65393700	-2.45858500	-1.32229800

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C	-3.48231300	-0.59021800	0.44685800
C	-3.07646100	-0.73717700	1.81468600
C	-3.96966700	-1.06521800	2.82079700
C	-5.32928300	-1.27508500	2.48154900
C	-5.74251500	-1.15663000	1.15583000
C	-4.83315000	-0.81703900	0.13521300
C	-2.33774700	-0.15012000	-0.28276000
C	-1.12447200	-0.38735900	0.57096300
H	-3.63464000	-1.19051400	3.84752100
H	-6.03848800	-1.54856900	3.25889500
H	-6.78332600	-1.34141000	0.89598800
H	-5.16957500	-0.76118400	-0.89780300
N	-1.70443300	-0.47979500	1.90751100
C	-0.91350700	-0.91920100	3.04079700
H	-1.36297700	-0.55105700	3.96878200
H	-0.82790000	-2.01431600	3.10581800
H	0.09127800	-0.49273700	2.97020500
C	-0.20552100	-1.61696800	0.23396200
O	-0.61807900	-2.76732600	0.31850500
C	1.12638900	-1.12228000	-0.06734200
C	2.24597900	-2.01219600	-0.41702400
C	1.10847700	0.27049800	0.07763700
C	2.24322300	1.18094800	-0.20499100
C	2.94493200	1.06587500	-1.41568100
C	2.64135900	2.15003000	0.73114700
C	4.02137200	1.91148900	-1.68766200
H	2.63532800	0.32783800	-2.14939300
C	3.72779500	2.98118300	0.46179800
H	2.11123200	2.24014400	1.67414300
C	4.41756400	2.86733100	-0.74922400
H	4.55026800	1.82129300	-2.63243500
H	4.03574300	3.71851400	1.19800600
H	5.25968500	3.52108500	-0.95956700
N	-0.09214200	0.74784400	0.49154600
C	-0.51634800	2.10977000	0.43082400
C	-1.01908400	2.71707900	1.58895300
C	-0.47291200	2.83203100	-0.76974300
C	-1.46872600	4.03863700	1.54461400
H	-1.05028500	2.15569100	2.51664500
C	-0.91015600	4.15664300	-0.80334500
H	-0.09988900	2.35428000	-1.67005800
C	-1.41143500	4.76372600	0.35183700
H	-1.85579800	4.50303600	2.44771100
H	-0.86826700	4.71088000	-1.73728000
H	-1.75576000	5.79392000	0.32176500
O	2.07163000	-2.96400800	-1.18332800
C	3.60089900	-1.82961800	0.21473000
C	4.72354200	-2.34707100	-0.45263100
C	3.77311700	-1.23955500	1.47621800
C	5.99274800	-2.25322500	0.11446100
H	4.58474800	-2.81786900	-1.42095400
C	5.04221400	-1.16133400	2.05344900
H	2.91207900	-0.85997400	2.01731000
C	6.15497100	-1.66063500	1.37172700
H	6.85552400	-2.64426300	-0.41859900
H	5.16121400	-0.71266700	3.03618000
H	7.14346200	-1.59213800	1.81842600
I	-2.20101400	-0.65795300	-2.42777300

TS2

C	3.26829700	-1.42291600	0.10224000
C	2.87370600	-1.83196500	-1.20534100
C	3.73820400	-2.51942000	-2.05747600
C	5.05331000	-2.75923800	-1.62379900

C	5.48128900	-2.31982200	-0.36600000
C	4.59735900	-1.65478300	0.49350500
C	2.11220400	-0.95447400	0.85017200
C	0.96705300	-0.92533500	-0.23274400
H	3.41797600	-2.83703400	-3.04600500
H	5.74189800	-3.28670800	-2.27945500
H	6.50556300	-2.50074000	-0.04870300
H	4.93933400	-1.31310700	1.46774800
N	1.57140100	-1.42720800	-1.45763300
C	0.77053800	-1.97751500	-2.53406600
H	1.30382600	-1.88303900	-3.48666400
H	0.52356800	-3.03726000	-2.37580400
H	-0.16031900	-1.40964600	-2.61882000
C	-0.09830500	-1.92249300	0.33592300
O	0.11277400	-3.12148600	0.46431700
C	-1.32222800	-1.17005700	0.55306200
C	-2.52906000	-1.77278300	1.16189900
C	-1.13281100	0.10178900	0.02331000
C	-2.17694000	1.15318500	-0.04121500
C	-2.84401500	1.53961600	1.13150100
C	-2.54055700	1.73801300	-1.26549100
C	-3.84916000	2.50720400	1.08231600
H	-2.56391400	1.09462100	2.08163700
C	-3.55674400	2.69131500	-1.31144100
H	-2.03760900	1.43761500	-2.17951500
C	-4.20913700	3.08293200	-0.13806500
H	-4.35131700	2.80713300	1.99790800
H	-3.83862500	3.13008800	-2.26461600
H	-4.99509500	3.83235500	-0.17650100
N	0.13746900	0.30075400	-0.45393200
C	0.63231700	1.53097700	-0.99557600
C	1.32061900	1.53986800	-2.21752400
C	0.41678300	2.74626000	-0.32570900
C	1.79235900	2.74289000	-2.74954600
H	1.48633200	0.61434000	-2.75208900
C	0.86690700	3.94466000	-0.87681000
H	-0.09553000	2.75207200	0.62870100
C	1.56386700	3.95017700	-2.08839000
H	2.32808300	2.72981000	-3.69504900
H	0.68680700	4.87501400	-0.34472100
H	1.92355100	4.88471100	-2.51024200
O	-2.42576400	-2.42412600	2.20256800
C	-3.87071200	-1.66978900	0.49260400
C	-5.02390200	-1.84348800	1.27634400
C	-4.00849600	-1.49199900	-0.89247500
C	-6.28832000	-1.81411600	0.69259700
H	-4.91201300	-1.99742600	2.34513300
C	-5.27489900	-1.48071500	-1.48028800
H	-3.12534200	-1.38351900	-1.51389900
C	-6.41639200	-1.63399600	-0.68934200
H	-7.17420900	-1.93529300	1.31041400
H	-5.36969400	-1.35376900	-2.55540900
H	-7.40204300	-1.61689100	-1.14697800
I	2.67607200	1.13250700	1.97327800

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C	-3.65917000	-0.89545100	-0.80861900
C	-3.55243000	-1.22586600	0.59598500
C	-4.62040200	-1.83072400	1.29461100
C	-5.79026100	-2.04547300	0.58910800
C	-5.94148600	-1.70265100	-0.78648200
C	-4.89414400	-1.13791600	-1.47759300
C	-2.47065600	-0.33722800	-1.31402200
C	-1.55549900	-0.47900700	-0.13388000
H	-4.53687100	-2.10604100	2.34094700
H	-6.63427700	-2.49668900	1.10503700
H	-6.88830700	-1.90323600	-1.27853000
H	-4.98358100	-0.88022300	-2.52972800
N	-2.33720900	-0.85285800	1.05203800
C	-1.74911000	-1.25489300	2.31971300
H	-2.47000400	-1.09195000	3.12532100
H	-1.45255600	-2.31152400	2.31313400
H	-0.87000300	-0.63564700	2.51275400
C	-0.58805400	-1.69103600	-0.53991000
O	-0.96894400	-2.84193500	-0.62931800
C	0.73465300	-1.10600300	-0.62191100
C	1.92289400	-1.92657700	-0.96521600
C	0.65269100	0.23926700	-0.27232200
C	1.75730100	1.21903500	-0.27544600
C	2.61860900	1.29867700	-1.38215100
C	1.96571500	2.06691900	0.82603600
C	3.66559700	2.22035600	-1.38920000
H	2.45347900	0.65774500	-2.24276300
C	3.02431500	2.97334300	0.81955700
H	1.31300100	2.00153400	1.69074700
C	3.87262200	3.05595700	-0.28884500
H	4.31948900	2.28399700	-2.25431100
H	3.18648400	3.61579000	1.68038500

H	4.69197200	3.76961000	-0.29392400
N	-0.61470500	0.61748700	0.08442400
C	-1.11525600	1.96779400	0.07384000
C	-1.75139300	2.45776300	1.21855000
C	-1.00811300	2.76350600	-1.07307400
C	-2.27908000	3.75113500	1.21514600
H	-1.82404300	1.83409400	2.10397300
C	-1.52496300	4.05952500	-1.06256000
H	-0.52837500	2.36678600	-1.96191600
C	-2.16332100	4.55466300	0.07845000
H	-2.77212600	4.13127500	2.10550600
H	-1.43714900	4.67801200	-1.95150000
H	-2.56858900	5.56271800	0.08056000
O	1.85754500	-2.72650000	-1.89728400
C	3.17765300	-1.83485100	-0.14770400
C	4.38442500	-2.25526400	-0.73185400
C	3.17417600	-1.42303100	1.19407400
C	5.56774000	-2.24140200	0.00235900
H	4.37931600	-2.58593600	-1.76565800
C	4.35756900	-1.42608600	1.93451700
H	2.24509800	-1.12192500	1.66758000
C	5.55611400	-1.82763800	1.33918200
H	6.49831600	-2.55530200	-0.46284700
H	4.34288600	-1.11696300	2.97607300
H	6.47799800	-1.82211800	1.91470800

TS3

C	-3.52989800	-1.03408700	-0.77974800
C	-3.63582200	-1.01953000	0.64747500
C	-4.74243900	-1.56263000	1.32136000
C	-5.75695100	-2.09720700	0.53738300
C	-5.68514200	-2.11770300	-0.87610100
C	-4.57910400	-1.59986100	-1.53296000
C	-2.29116900	-0.42835900	-1.20032500
C	-1.68209000	-0.15397200	0.05761200
H	-4.81059700	-1.55907000	2.40493200
H	-6.63438900	-2.51420500	1.02522200
H	-6.50416700	-2.55243000	-1.44199100
H	-4.51184700	-1.62063300	-2.61790300
N	-2.50978900	-0.42724500	1.16631800
C	-2.11471000	-0.45101600	2.56628800
H	-2.88565000	0.02049300	3.18297000
H	-1.95753800	-1.47984200	2.91151300
H	-1.18410000	0.10750000	2.67763800
C	-0.78174100	-1.60366500	-0.55929400
O	-1.16461800	-2.74495500	-0.48269200
C	0.56181300	-1.05689000	-0.62060500
C	1.68927500	-1.96594100	-0.97746400
C	0.61158500	0.26868100	-0.23369300
C	1.80594500	1.13637100	-0.25760200
C	2.64600200	1.14621100	-1.38338100
C	2.12188300	1.94673900	0.84705400
C	3.78105500	1.95652400	-1.40403000
H	2.39759300	0.53909900	-2.24859600
C	3.26449800	2.74393600	0.82542200
H	1.48567700	1.93422900	1.72632900
C	4.09369200	2.75410600	-0.30052600
H	4.41875600	1.96567300	-2.28336000
H	3.50833300	3.35710700	1.68838000
H	4.98060400	3.38154700	-0.31663600
N	-0.59251600	0.78202100	0.19897600
C	-0.94000000	2.18192500	0.03961600
C	-1.39440900	2.89790200	1.14942800
C	-0.86186800	2.79280600	-1.21688500
C	-1.76450500	4.23688700	1.00177100
H	-1.44956800	2.41453500	2.11942600
C	-1.22267500	4.13362600	-1.35365700
H	-0.52726600	2.21948700	-2.07575000
C	-1.67599400	4.85712500	-0.24645400
H	-2.11554100	4.79407800	1.86579600
H	-1.15680900	4.60977000	-2.32796800
H	-1.96043600	5.89980900	-0.35762700
O	1.57537300	-2.71356000	-1.94602500
C	2.92528400	-2.01223700	-0.13191300
C	4.10625000	-2.51309400	-0.70534600
C	2.92097500	-1.65163000	1.22471700
C	5.26660500	-2.62809800	0.05585400
H	4.10015100	-2.80312500	-1.75126800
C	4.07977100	-1.78520800	1.99127700
H	2.00859600	-1.28931800	1.68768400
C	5.25489700	-2.26525400	1.40746800
H	6.17918300	-3.00291200	-0.39964400
H	4.06434000	-1.51548700	3.04368000
H	6.15871800	-2.36035900	2.00340000

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C	-2.63231500	-2.29688100	-0.25055600
C	-3.67966700	-1.40851900	0.09809400

C	-4.99465400	-1.85707200	0.25879300
C	-5.24112900	-3.21805800	0.07405200
C	-4.20876100	-4.11231600	-0.26579400
C	-2.90149600	-3.66194700	-0.43143600
C	-1.43867900	-1.50304800	-0.33984000
C	-1.80455800	-0.18196900	-0.05315600
H	-5.80720700	-1.18400100	0.51162000
H	-6.25511800	-3.59043300	0.19289000
H	-4.43754600	-5.16589500	-0.40305300
H	-2.09637400	-4.33843600	-0.69712000
N	-3.15592100	-0.11423800	0.22889300
C	-3.98633300	1.03387100	0.58887400
H	-4.19290200	1.66571800	-0.27929700
H	-4.92957700	0.65575400	0.98207000
H	-3.51234400	1.62805700	1.36889800
C	-0.08674400	-1.87839900	-0.65060100
O	0.27780900	-3.03937300	-0.92935400
C	0.84413000	-0.74545200	-0.63002600
C	2.26818100	-1.05405800	-1.03645500
C	0.44526900	0.53993000	-0.37022600
C	1.43252000	1.66493900	-0.37796500
C	1.52742200	2.53089100	-1.47763100
C	2.31712300	1.82310800	0.69876500
C	2.48648000	3.54417000	-1.49339500
H	0.85792200	2.40402800	-2.32297100
C	3.27466000	2.84024900	0.68101300
H	2.25527000	1.15048600	1.54929100
C	3.36024300	3.70300300	-0.41359400
H	2.55410400	4.20709300	-2.35180500
H	3.95287300	2.95483500	1.52224600
H	4.10665500	4.49276200	-0.42836700
N	-0.88729800	0.85087500	-0.07049600
C	-1.25015500	2.22385700	0.22889800
C	-1.05926900	2.71886400	1.52098900
C	-1.77422400	3.03348100	-0.78034000
C	-1.40987300	4.03982900	1.80607200
H	-0.64926000	2.07338300	2.29152900
C	-2.12523300	4.35272600	-0.48593500
H	-1.90734700	2.63278400	-1.78046900
C	-1.94500100	4.85573600	0.80506200
H	-1.26686900	4.42850500	2.81024200
H	-2.53652400	4.98566800	-1.26701200
H	-2.21829800	5.88271900	1.03060000
O	2.67785400	-0.72249700	-2.14267500
C	3.14913100	-1.78596900	-0.07583700
C	4.43613100	-2.16365400	-0.49543000
C	2.74014600	-2.08427400	1.23369700
C	5.29524200	-2.82923900	0.37482000
H	4.74610100	-1.92698400	-1.50825200
C	3.60268500	-2.74895000	2.10622400
H	1.75094700	-1.79324100	1.57256100
C	4.87957300	-3.12303000	1.67863100
H	6.28800500	-3.11959600	0.04159500
H	3.27928700	-2.97458600	3.11867600
H	5.55036100	-3.64103700	2.35898100

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C	0.99212500	2.89454400	0.54689400
C	0.93081900	2.88397600	-0.87746400
C	1.32995900	3.98540700	-1.64728700
C	1.80821900	5.10435600	-0.97052400
C	1.88679100	5.13109900	0.43894600
C	1.48415700	4.03954500	1.20117600
C	0.49225500	1.62378100	0.98618000
C	0.14264900	0.91049400	-0.14392200
H	1.26922100	3.97023000	-2.73153100
H	2.12609200	5.97434200	-1.53922000
H	2.26633400	6.02159800	0.93344500
H	1.54333700	4.06934300	2.28654300
N	0.43513800	1.65740100	-1.27724400
C	0.10175200	1.30692900	-2.64808700
H	-0.78622300	1.85237200	-2.98616500
H	0.94240600	1.54260100	-3.30706500
H	-0.09836800	0.23665400	-2.71132100
C	-0.24430300	-0.53759800	-0.21254300
O	0.75193500	-1.34851200	-0.39989200
C	-1.56177900	-0.96415400	-0.05794200
C	-1.83755500	-2.43026400	0.03501900
C	-2.67120200	-0.00662900	0.05732600
C	-3.80815400	-0.39484900	0.96378700
C	-3.54812800	-0.91771400	2.24125200
C	-5.14370600	-0.25828100	0.54828100
C	-4.59735600	-1.27573500	3.09067500
H	-2.52098900	-1.03256100	2.57457100
C	-6.19026400	-0.63234900	1.39027000
H	-5.36109000	0.12663000	-0.44321000
C	-5.92081000	-1.13733000	2.66647800
H	-4.37906000	-1.66606200	4.08121600

H	-7.21747300	-0.53255000	1.04953800
H	-6.73801500	-1.42414900	3.32301000
N	-2.62438400	1.11059100	-0.60396500
C	-3.45386900	2.21465100	-0.36402500
C	-4.08081700	2.83687000	-1.46170000
C	-3.58238800	2.80922100	0.90771200
C	-4.84441500	3.99002700	-1.28570900
H	-3.96400500	2.39587900	-2.44847400
C	-4.33346500	3.97372500	1.07213400
H	-3.07715700	2.36043800	1.75785900
C	-4.97601400	4.56772400	-0.01820200
H	-5.33109400	4.44556600	-2.14477500
H	-4.41538300	4.41939900	2.06076400
H	-5.56143700	5.47334300	0.11538000
O	-1.16810300	-3.19149600	0.73185600
C	-2.96112200	-3.00240800	-0.79251700
C	-3.50731500	-4.24295400	-0.42372400
C	-3.43151400	-2.37087100	-1.95492600
C	-4.51597400	-4.82892400	-1.18530600
H	-3.13164500	-4.73389600	0.46861800
C	-4.43188500	-2.96524200	-2.72729500
H	-3.00669100	-1.42163000	-2.26592500
C	-4.98029500	-4.19075800	-2.34124000
H	-4.94024100	-5.78273900	-0.88267100
H	-4.78108700	-2.47188800	-3.63049300
H	-5.76411200	-4.64899200	-2.93873700
H	0.39072800	1.27463800	2.00542300
Zn	2.64264800	-0.60104700	0.06931600
I	3.93567700	-0.89578400	2.70188800
I	4.64228900	-0.88102200	-2.06784600

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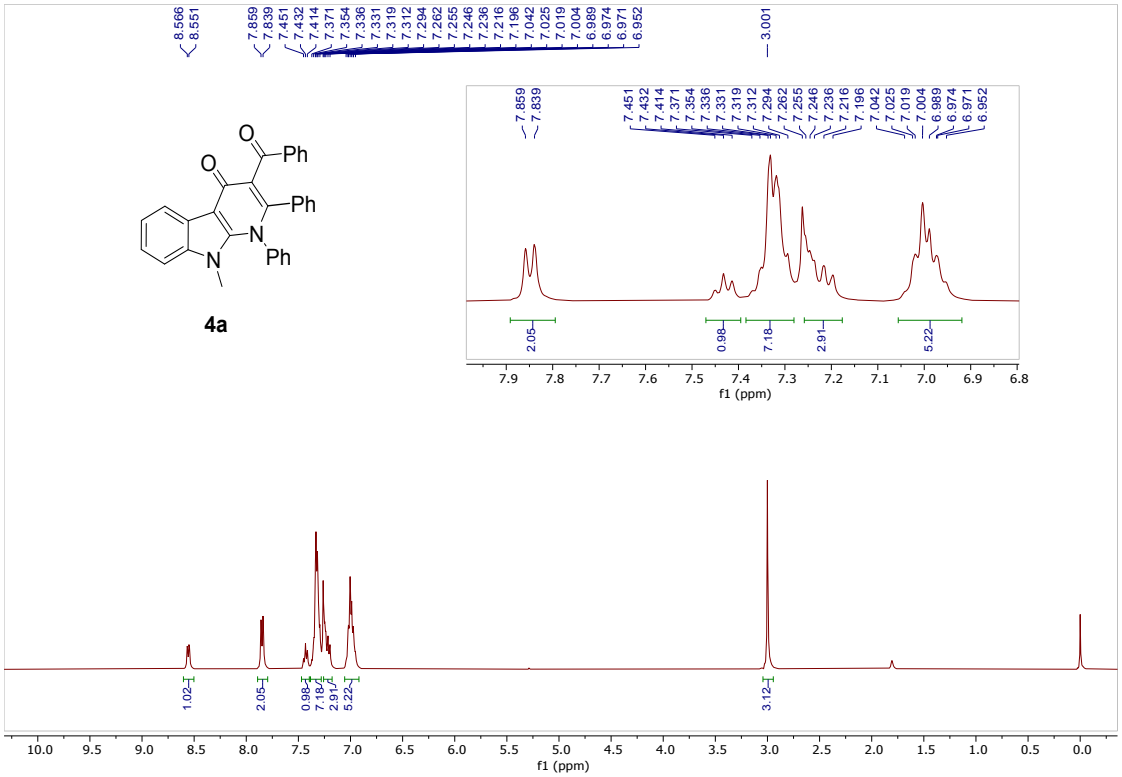
C	-3.30776400	-0.41171000	-1.88988700
C	-3.96466100	-1.30489600	-0.99147800
C	-5.35831800	-1.48684400	-1.01512600
C	-6.08027600	-0.76728500	-1.95771400
C	-5.44565000	0.11907500	-2.86253500
C	-4.07206100	0.30205000	-2.83788100
C	-1.92305400	-0.47170300	-1.57450500
C	-1.76743500	-1.37391400	-0.53012100
H	-5.85315200	-2.16612300	-0.32804600
H	-7.15931300	-0.88835300	-2.00461900
H	-6.05044300	0.66106300	-3.58454100
H	-3.58783800	0.98405200	-3.53213800
H	-1.12141900	0.05830400	-2.06839100
N	-3.02055500	-1.88587400	-0.17957300
C	-3.35908000	-2.81185700	0.89636300
H	-4.07533600	-2.34497200	1.58019100
H	-3.80920900	-3.72059000	0.48125600
H	-2.45469700	-3.08089100	1.43360700
C	-0.49528700	-1.81960400	0.05332000
O	-0.38714800	-2.84162700	0.73312100
C	0.74412500	-1.03028600	-0.30056500
C	1.74468800	-1.87235400	-1.03331300
C	0.92392000	0.29920500	0.00342800
C	2.01559600	1.10644700	-0.60366500
C	2.26800100	1.04901500	-1.98379600
C	2.81038600	1.94090700	0.20205900
C	3.30119500	1.80117800	-2.54524600
H	1.64255100	0.43129500	-2.62129100
C	3.84805100	2.68213200	-0.35851300
H	2.61619900	1.99321400	1.26916700
C	4.09505600	2.61533100	-1.73433300
H	3.48115300	1.75537500	-3.61574300
H	4.46543400	3.31226300	0.27589800
H	4.90081800	3.19896900	-2.17134800
N	0.12096800	0.96225500	0.92825900
C	-0.44147000	0.35877900	2.09284300
C	-1.81503000	0.37078300	2.36988300
C	0.44332900	-0.21605700	3.02187000
C	-2.29527800	-0.20021500	3.55025800
H	-2.50495800	0.82660900	1.66806100
C	-0.04766100	-0.80420900	4.18628000
H	1.51080200	-0.19197400	2.82759700
C	-1.41860400	-0.79709300	4.45939000
H	-3.36237700	-0.17891700	3.75438400
H	0.64884500	-1.24902400	4.89197700
H	-1.79764700	-1.24159100	5.37528500
O	1.34714600	-2.59003100	-1.95210000
C	3.18481200	-1.91352900	-0.62438000
C	4.13620400	-2.34569300	-1.56385400
C	3.59667700	-1.62475200	0.68515500
C	5.47757300	-2.45963000	-1.20759200
H	3.80988300	-2.58325800	-2.57153700
C	4.93845600	-1.75783900	1.04645900
H	2.86495600	-1.32304600	1.42705400
C	5.88145200	-2.16663200	0.10022000
H	6.20898700	-2.78035100	-1.94451600

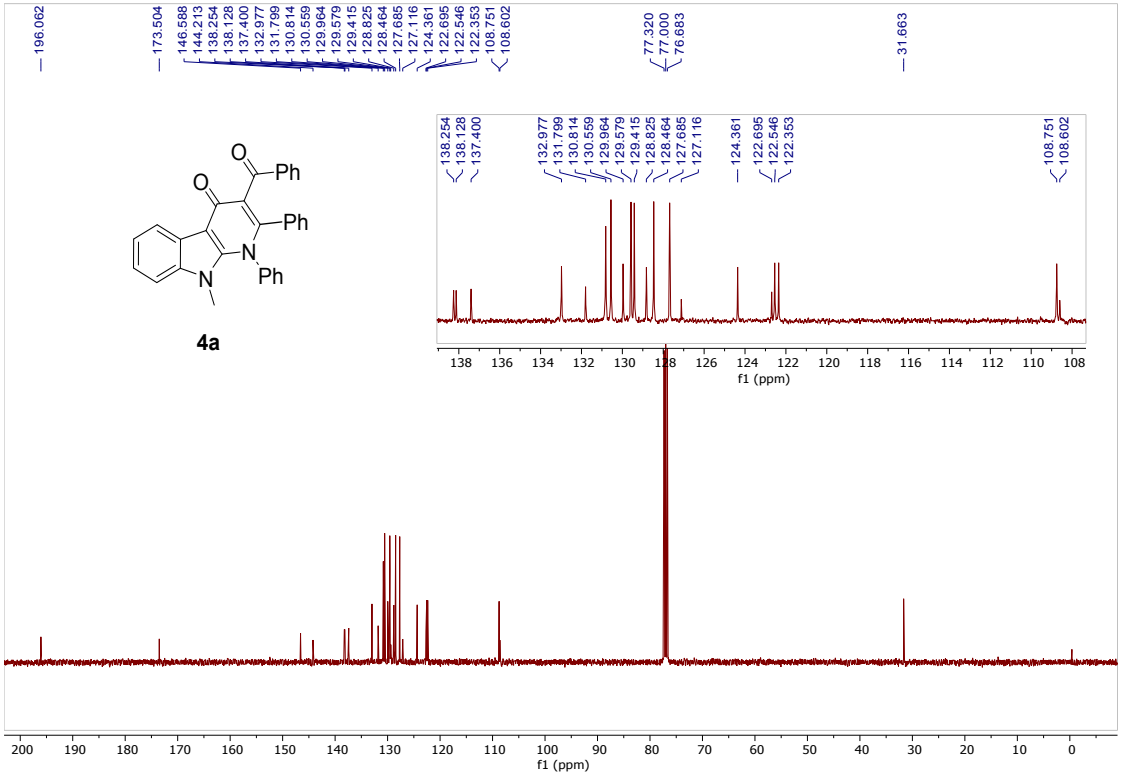
H	5.24610700	-1.54357500	2.06631900
H	6.92729300	-2.26119000	0.38025100
I	-0.67239300	2.87167000	0.36234000

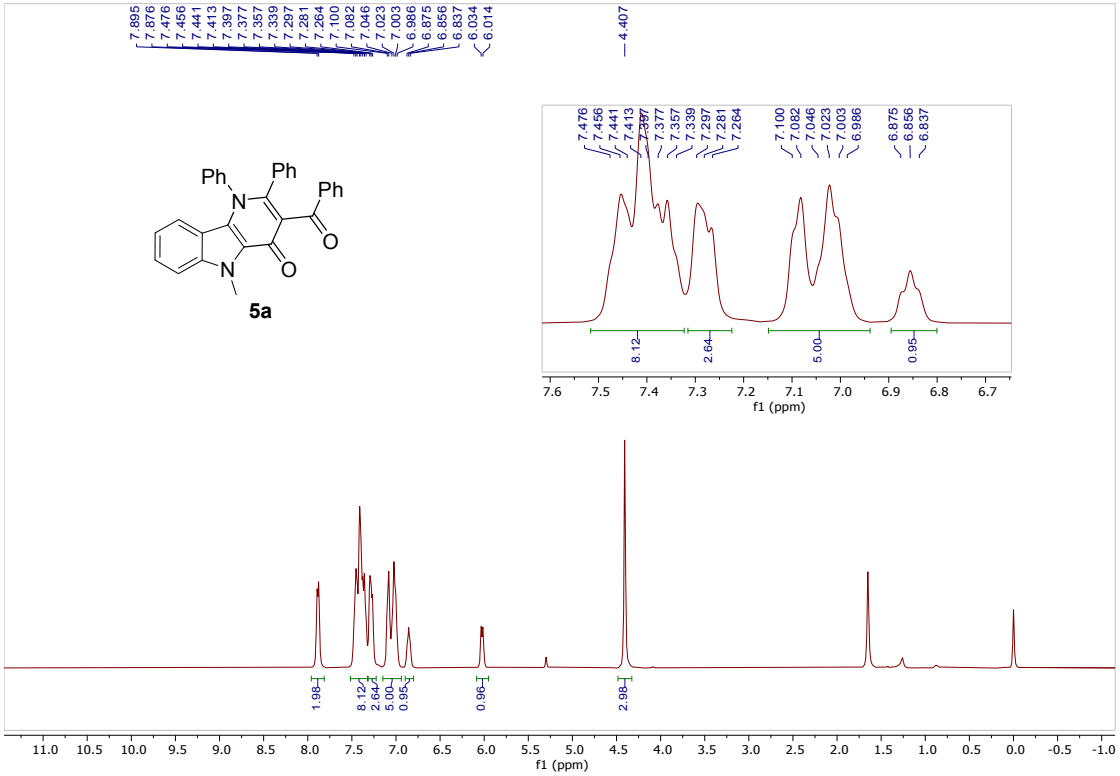
TS5

C	-3.34328300	-0.81932500	-1.65535000
C	-3.62878700	-1.48529200	-0.42677000
C	-4.93795500	-1.74478300	-0.00867800
C	-5.97735900	-1.33036500	-0.84222000
C	-5.71753700	-0.66863100	-2.06024000
C	-4.41383300	-0.40753200	-2.47232900
C	-1.92241500	-0.73203100	-1.75319000
C	-1.38538100	-1.29721000	-0.59343800
H	-5.14317700	-2.25976500	0.92528500
H	-7.00525000	-1.52616900	-0.54833400
H	-6.55106300	-0.35910900	-2.68578300
H	-4.22231400	0.10449500	-3.41230800
H	-1.34463500	-0.33332500	-2.57533400
N	-2.42361500	-1.79251900	0.18702600
C	-2.30960200	-2.68519700	1.33250100
H	-3.03388500	-2.39555100	2.09805100
H	-2.49903800	-3.72408300	1.03811700
H	-1.31066600	-2.61706700	1.76030900
C	-0.02999300	-1.92049400	-0.56662900
O	0.13636800	-3.12835800	-0.44418600
C	1.08142200	-0.95868800	-0.72626200
C	2.30043500	-1.44252300	-1.47250500
C	0.84933000	0.28122500	-0.21108700
C	1.78356400	1.42309400	-0.33540200
C	2.00132400	2.32953100	0.72029300
C	2.46917400	1.62300800	-1.54886700
C	2.90257600	3.38114400	0.57347300
H	1.47537200	2.20893900	1.66038100
C	3.36199400	2.68424600	-1.69451300
H	2.27354400	0.97338400	-2.39497500
C	3.58788200	3.56147800	-0.63203700
H	3.06776700	4.06365700	1.40235700
H	3.87278400	2.82895200	-2.64227300
H	4.28592500	4.38651600	-0.74394800
N	-0.44432100	0.38043800	0.42171200
C	-0.49416500	0.25859500	1.84661400
C	-1.74165300	0.38299200	2.49246200
C	0.62632600	-0.11793500	2.61087700
C	-1.85837300	0.13034400	3.85422100
H	-2.61265100	0.68941900	1.92488600
C	0.49429600	-0.38602400	3.97485100
H	1.59972500	-0.21424900	2.14662600
C	-0.74298800	-0.26064500	4.60559900
H	-2.82738700	0.23895400	4.33336200
H	1.37212500	-0.68230500	4.54231000
H	-0.83980300	-0.45635400	5.66959700
O	2.15359500	-1.74165200	-2.65373600
C	3.60952200	-1.59805300	-0.78367200
C	4.77371400	-1.70221700	-1.56545800
C	3.70386100	-1.69992900	0.61278300
C	6.01232700	-1.88105700	-0.95685100
H	4.69210600	-1.63149800	-2.64548700
C	4.94497800	-1.89554500	1.21934600
H	2.80744100	-1.65753000	1.22182700
C	6.09959900	-1.97861000	0.43722400
H	6.91082300	-1.94666300	-1.56411100
H	5.00981800	-1.98496700	2.30000500
H	7.06679900	-2.12215600	0.91137400
I	-1.46948200	2.32074900	-0.30279600

6. Copies of Spectra of New Products



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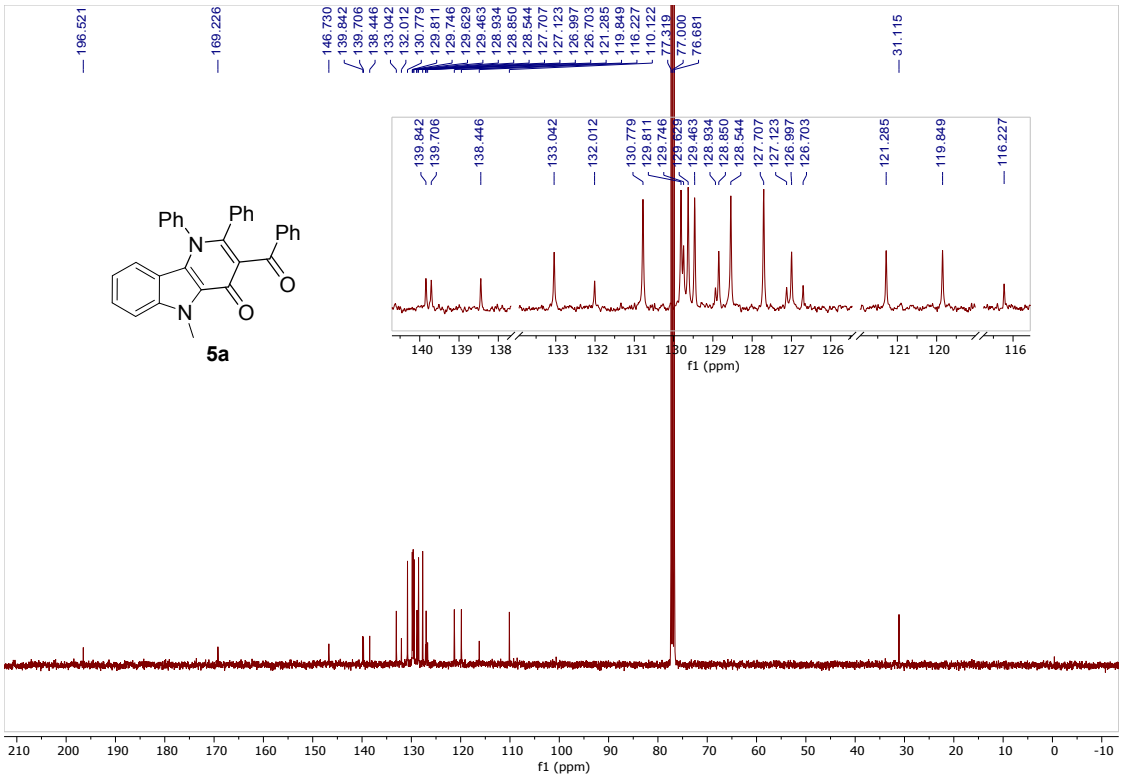
7.082
7.046
7.023
7.003
6.986
6.875
6.856
6.837
6.034
6.014
4.407
Ph
Ph
Ph
N
O
O
N
5a
8.12
2.64
5.00
0.95
f1 (ppm)
1.98
8.12
2.64
5.00
0.95
0.96
2.98
f1 (ppm)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132.012
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129.746
129.629
129.463
128.934
128.850
128.544
127.707
127.123
126.997
126.703
121.285
119.849
116.227
110.122
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77.000
76.681
31.115
Ph
Ph
Ph
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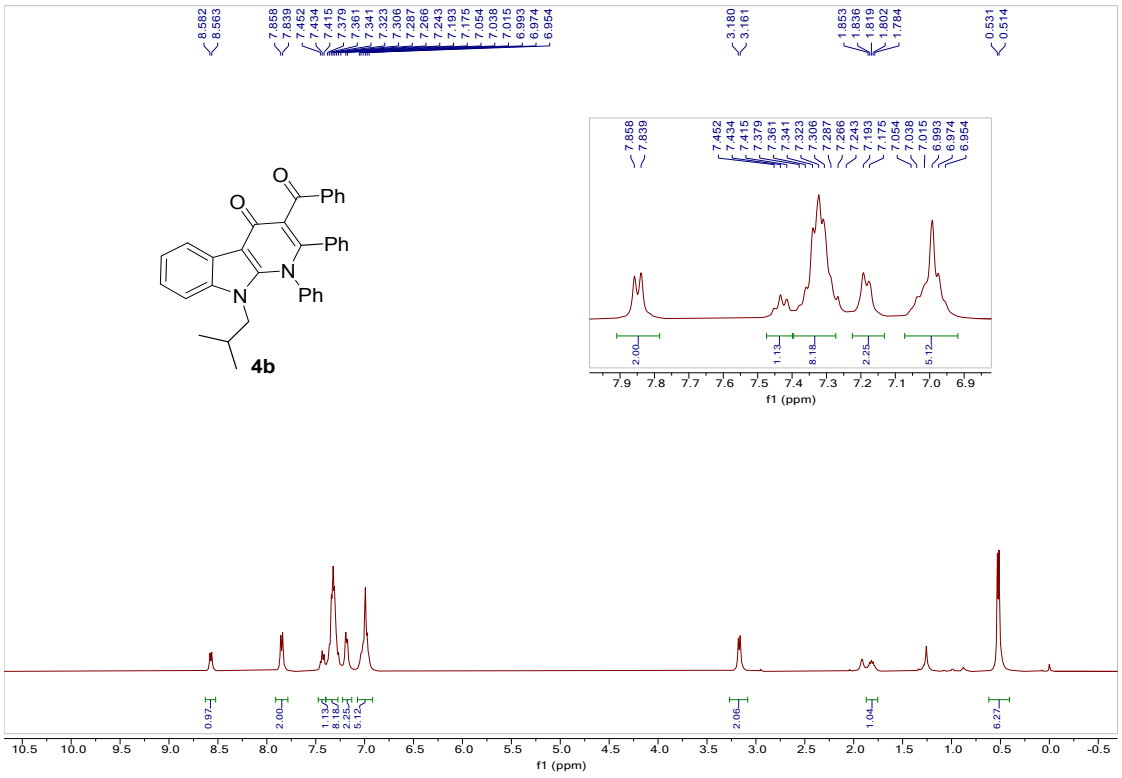
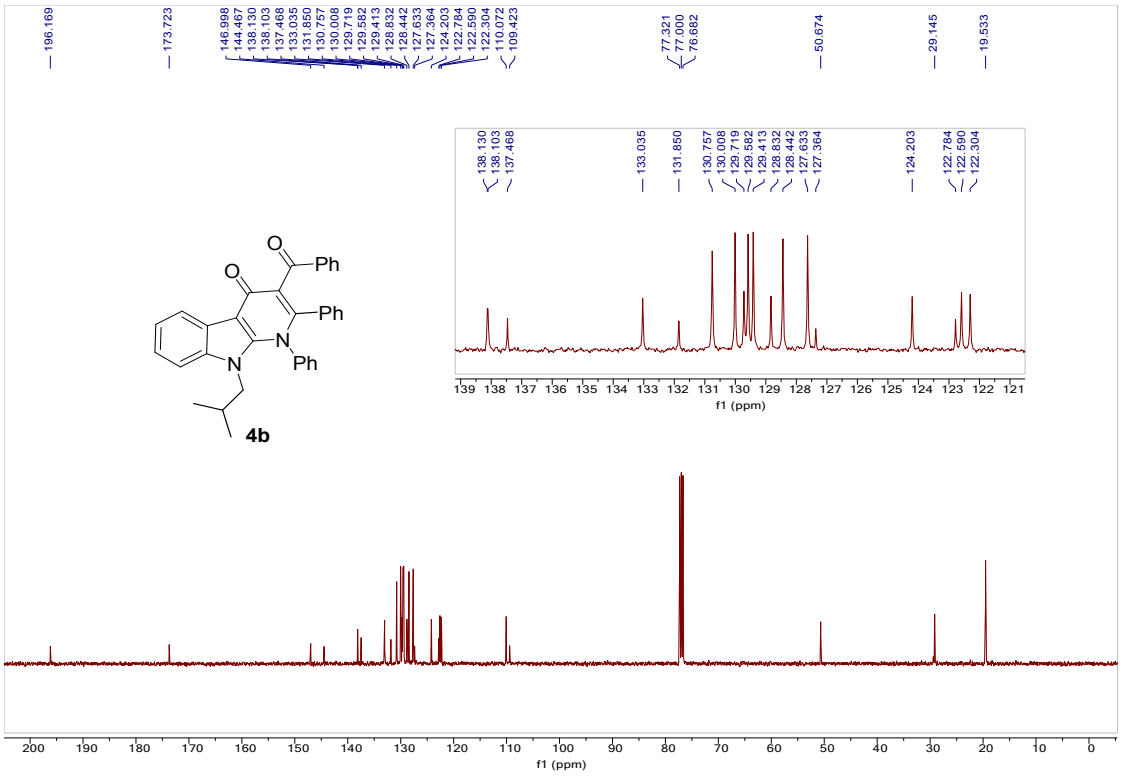
O
O
N
5a
f1 (ppm)
f1 (ppm)


4b
f1 (ppm)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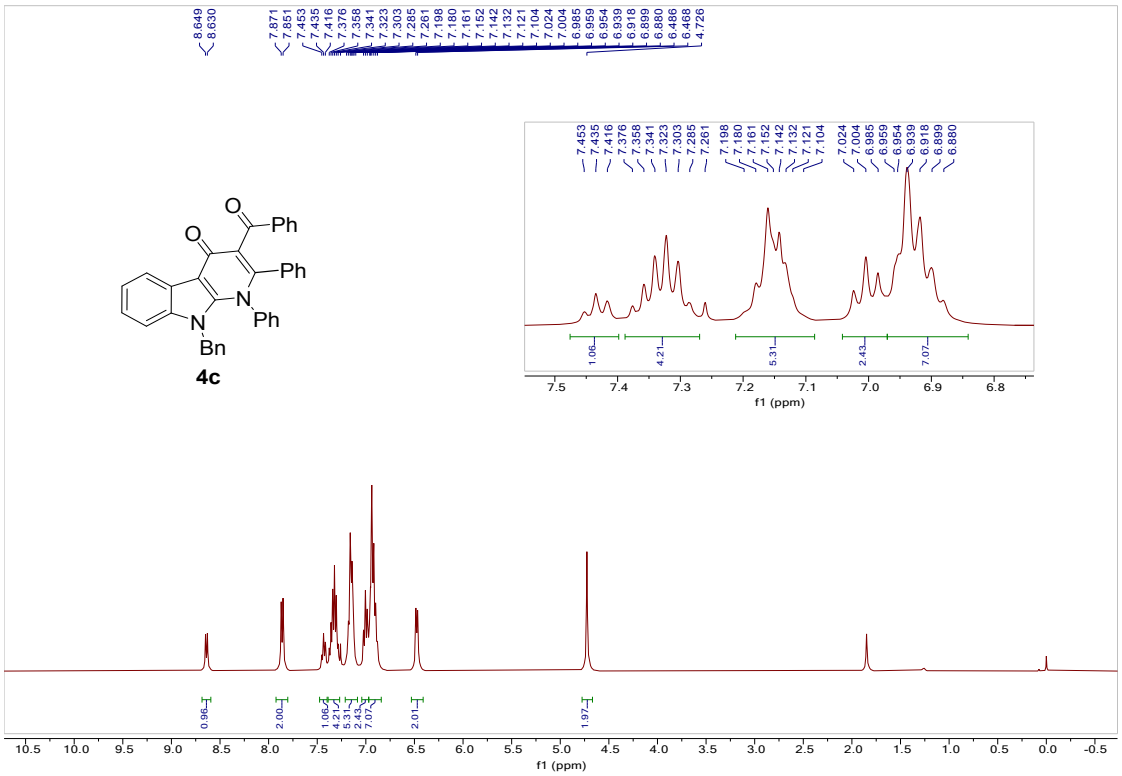
f1 (ppm)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7.376
7.358
7.341
7.323
7.303
7.285
7.261
7.198
7.180
7.161
7.152
7.142
7.132
7.121
7.104
7.024
7.004
6.985
6.959
6.954
6.939
6.918
6.899
6.880
6.486
6.468
4.726
O
O
Ph
Ph
N
N
Ph
Bn
4c
1.06
4.21
5.31
2.43
7.07
f1 (ppm)
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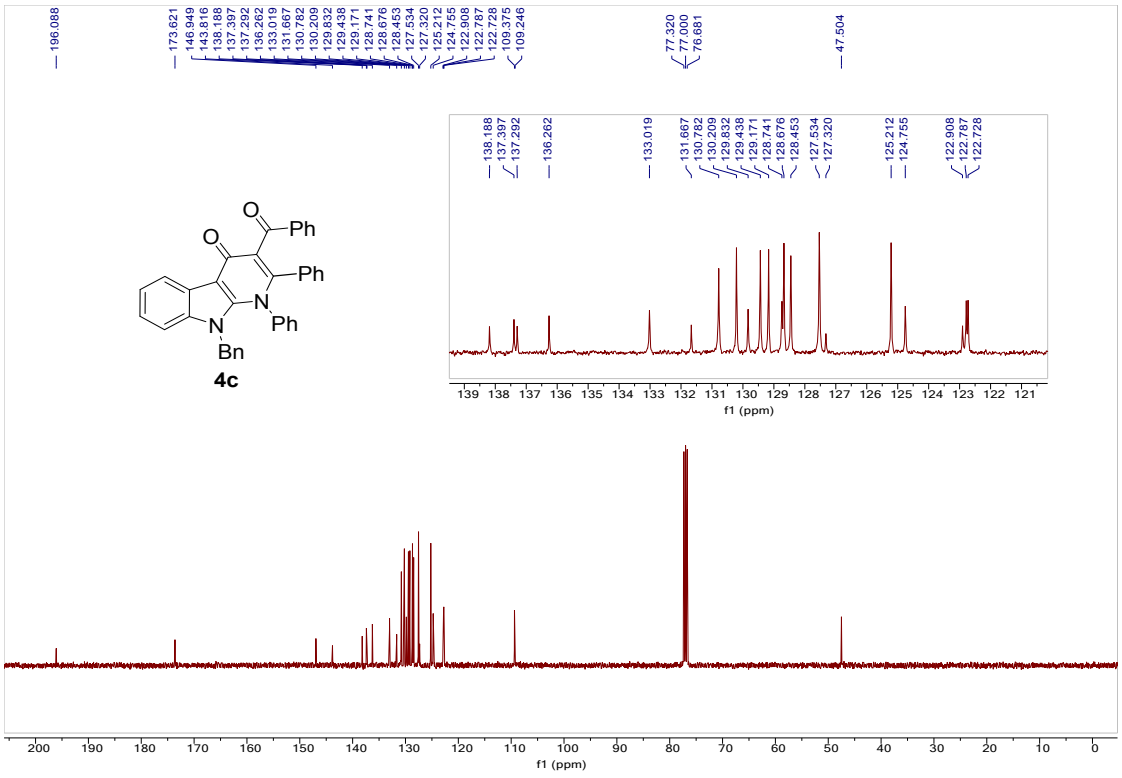
2.00
1.06
4.27
5.31
2.43
7.07
2.01
1.97
f1 (ppm)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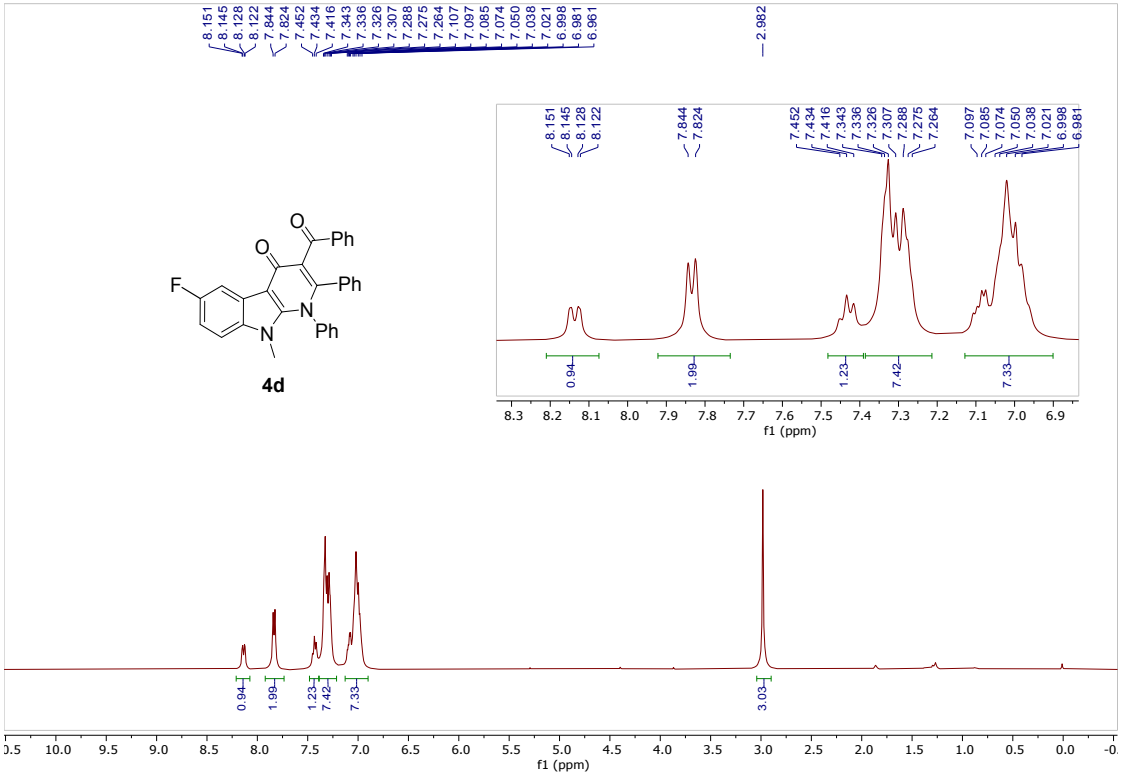
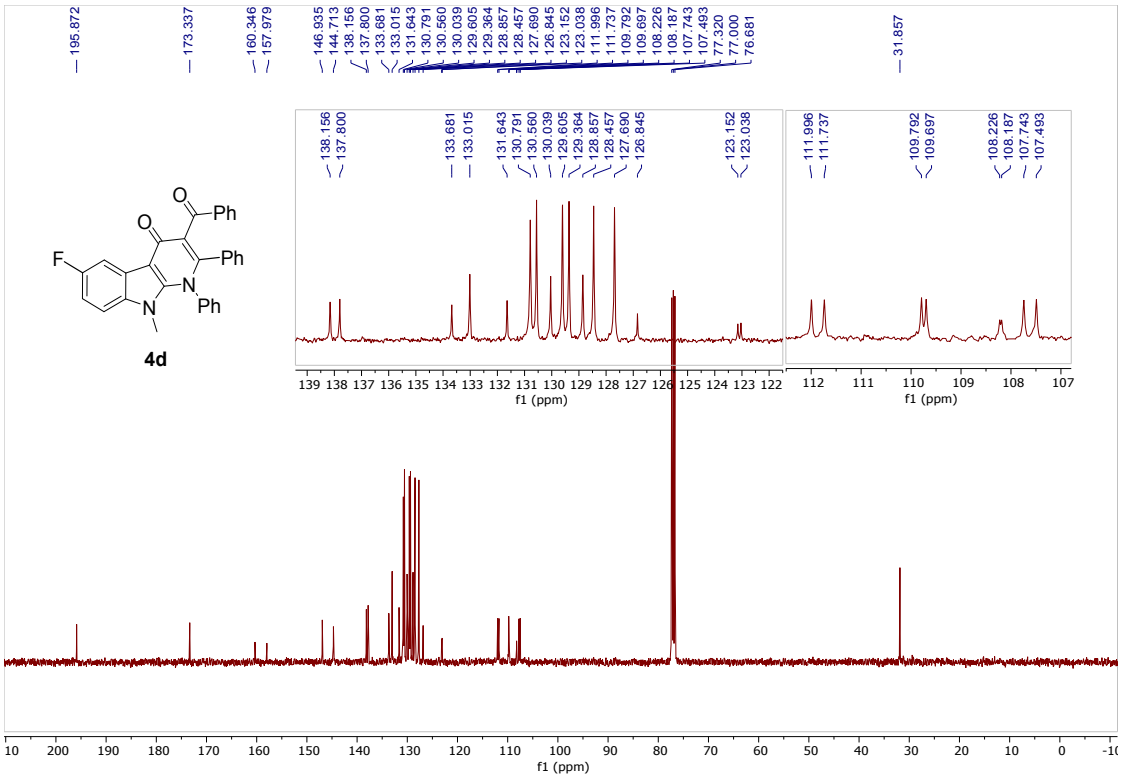
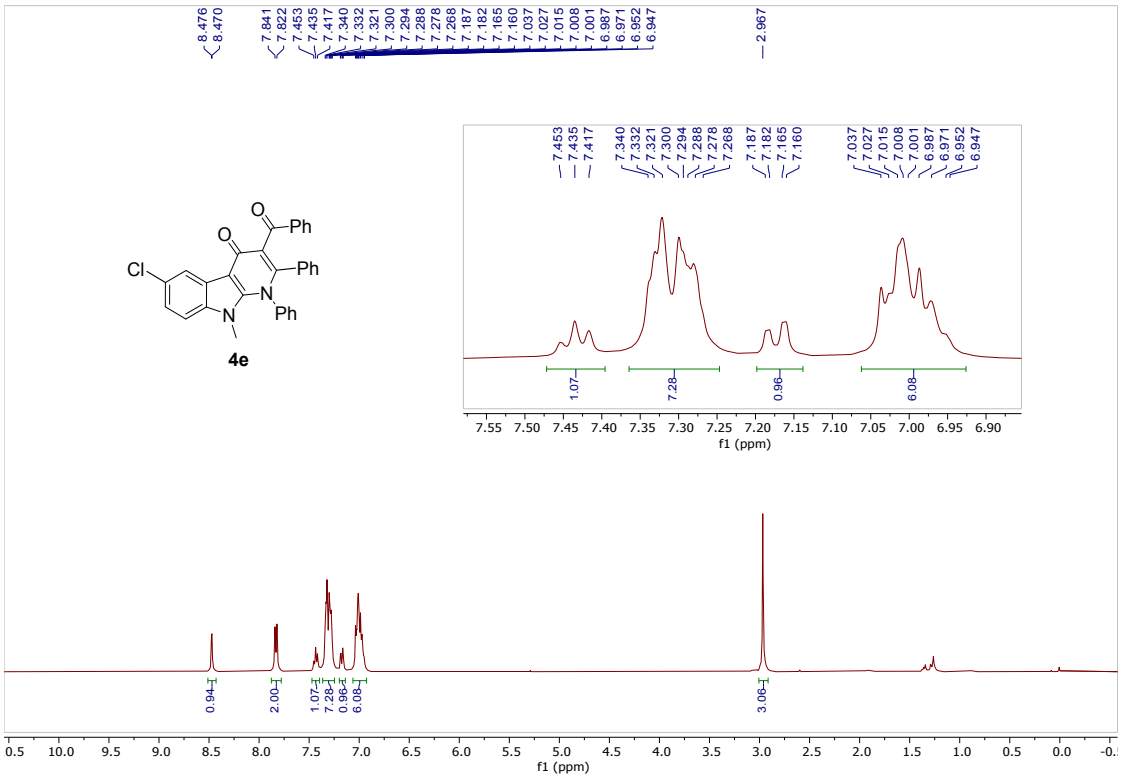
137.292
136.262
133.019
131.667
130.782
130.209
129.832
129.438
129.171
128.741
128.676
128.453
127.534
127.320
125.212
124.755
122.908
122.787
122.728
109.375
109.246
77.320
77.000
76.681
47.504
O
O
Ph
Ph
N
N
Ph
Bn
4c
f1 (ppm)
f1 (ppm)


4d
f1 (ppm)


4d
f1 (ppm)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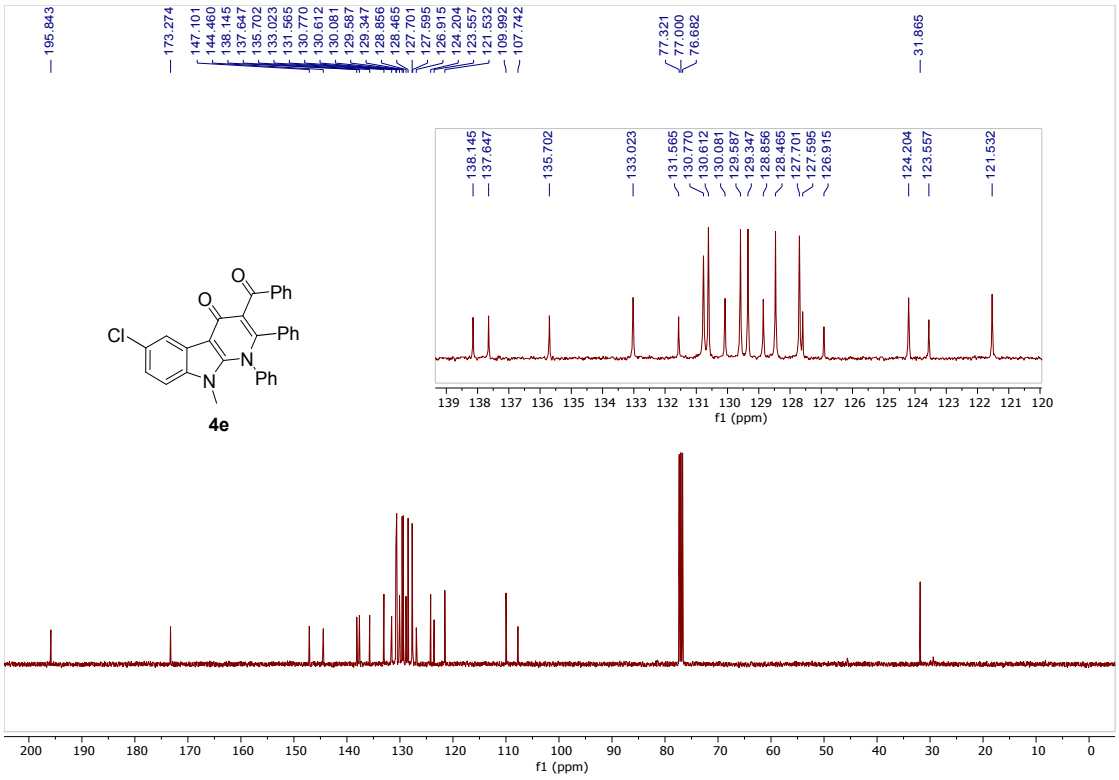
7.435
7.417
7.340
7.332
7.321
7.300
7.294
7.288
7.278
7.268
7.187
7.182
7.165
7.160
7.037
7.027
7.015
7.008
7.001
6.987
6.971
6.952
6.947
2.967
Cl
O
Ph
Ph
N
Ph
4e
1.07
7.28
0.96
6.08
0.94
2.00
1.07
7.28
0.96
6.08
3.06
f1 (ppm)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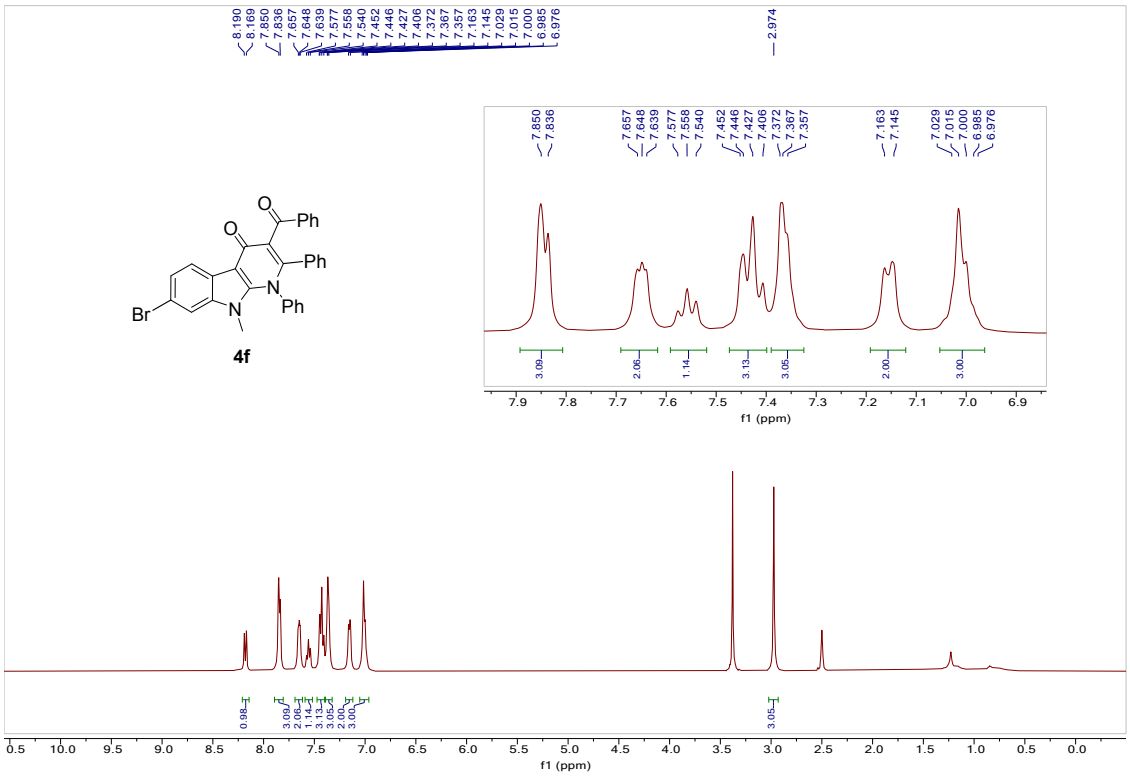
147.101
144.460
138.145
137.647
135.702
133.023
131.565
130.770
130.612
130.081
129.587
129.347
128.856
128.465
127.701
127.595
126.915
124.204
123.557
121.532
109.992
107.742
77.321
77.000
76.682
31.865
Cl
O
Ph
Ph
N
Ph
4e
f1 (ppm)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8.169
7.850
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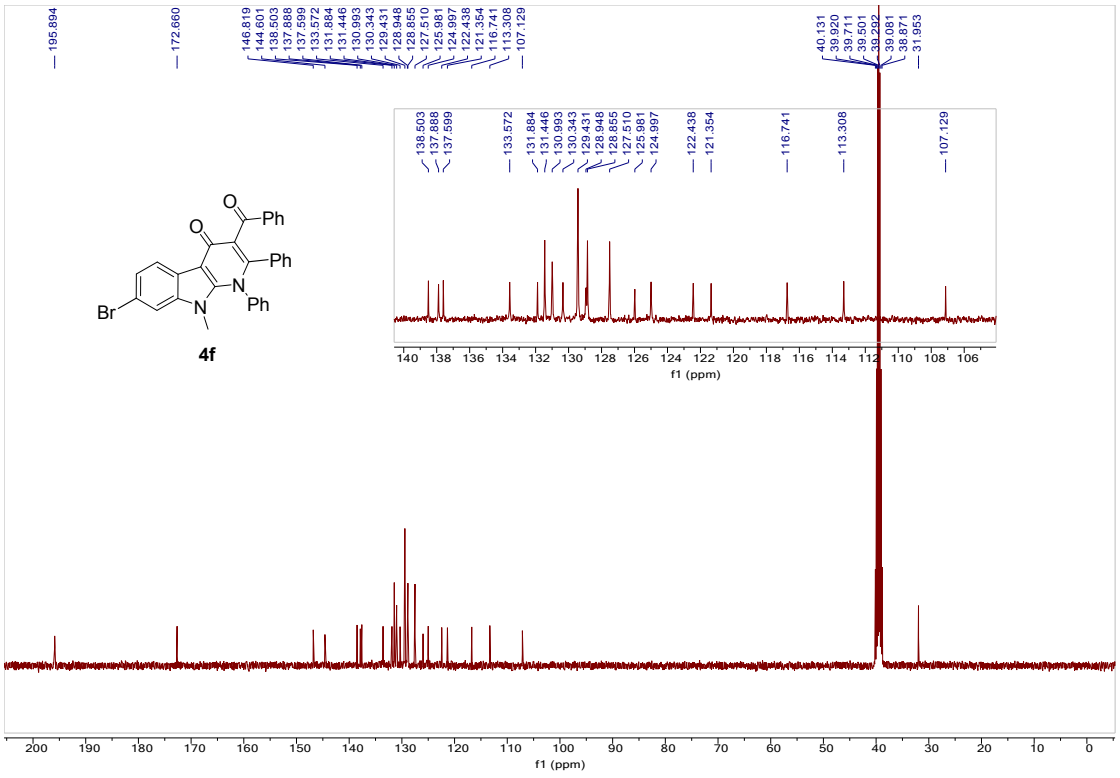
7.657
7.648
7.639
7.577
7.558
7.540
7.452
7.446
7.427
7.406
7.372
7.367
7.357
7.163
7.145
7.029
7.015
7.000
6.985
6.976
2.974
O
Ph
O
Ph
N
Ph
Br
4f
3.09
2.06
1.14
3.13
3.05
2.00
3.00
f1 (ppm)
0.98
3.08
2.06
1.14
3.13
3.05
2.00
3.00
3.05
f1 (ppm)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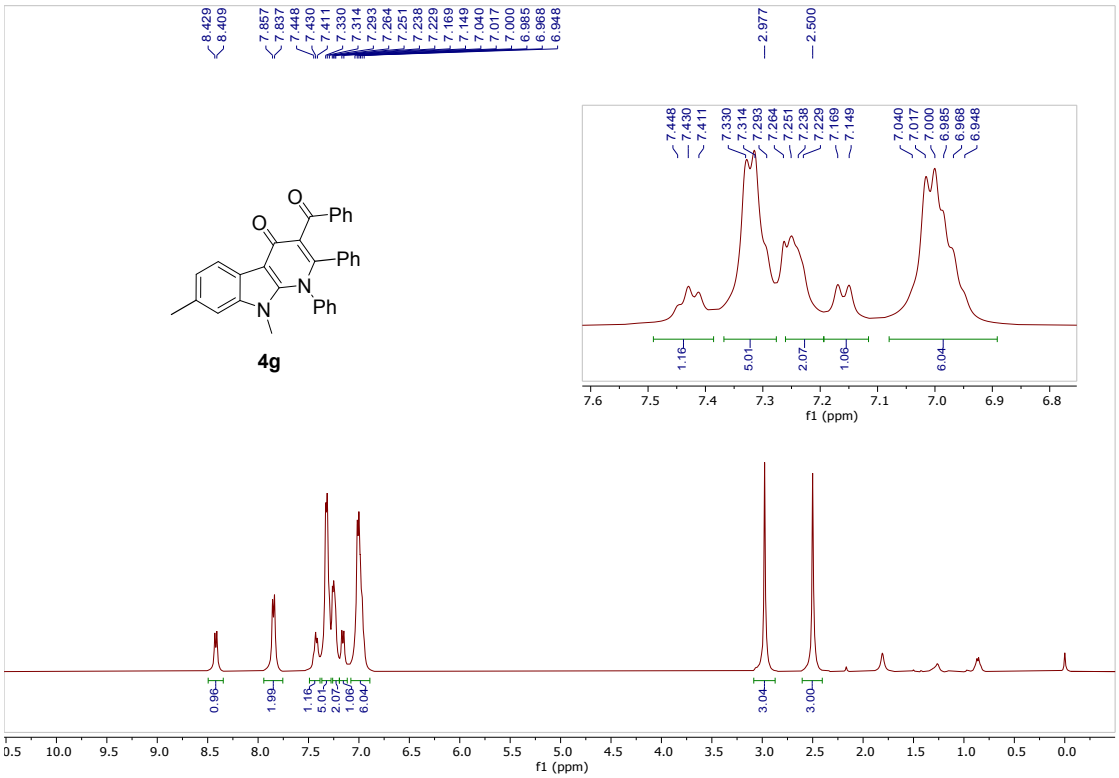
137.599
133.572
131.884
131.446
130.993
130.343
129.431
128.948
128.855
127.510
125.981
124.997
122.438
121.354
116.741
113.308
107.129
40.131
39.920
39.711
39.501
39.292
39.081
38.871
31.953
O
Ph
O
Ph
N
Ph
Br
4f
f1 (ppm)
f1 (ppm)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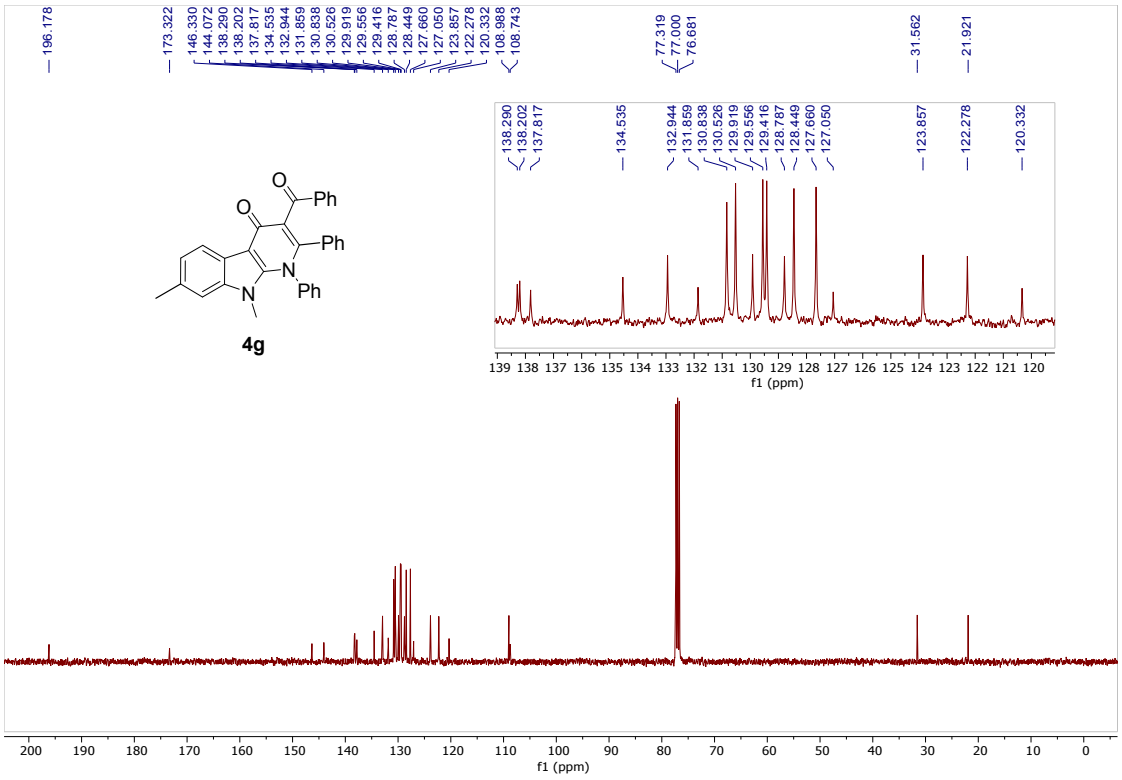
8.409
7.857
7.837
7.448
7.430
7.411
7.330
7.314
7.293
7.264
7.251
7.238
7.229
7.169
7.149
7.040
7.017
7.000
6.985
6.968
6.948
2.977
2.500
O
O
Ph
Ph
N
N
Ph
4g
1.16
5.01
2.07
1.06
6.04
0.96
1.99
3.04
3.00
f1 (ppm)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144.072
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138.202
137.817
134.535
132.944
131.859
130.838
130.526
129.919
129.556
129.416
128.787
128.449
127.660
127.050
123.857
122.278
120.332
108.988
108.743
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77.000
76.681
31.562
21.921
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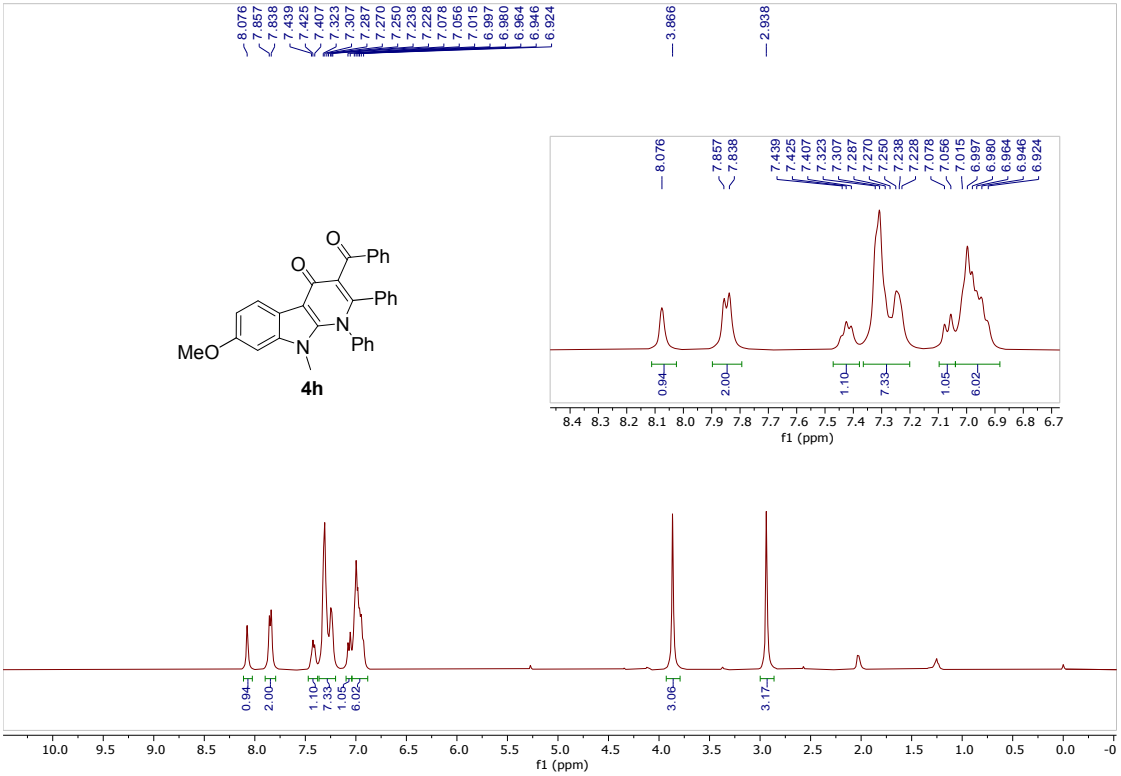
O
Ph
Ph
N
N
Ph
4g
f1 (ppm)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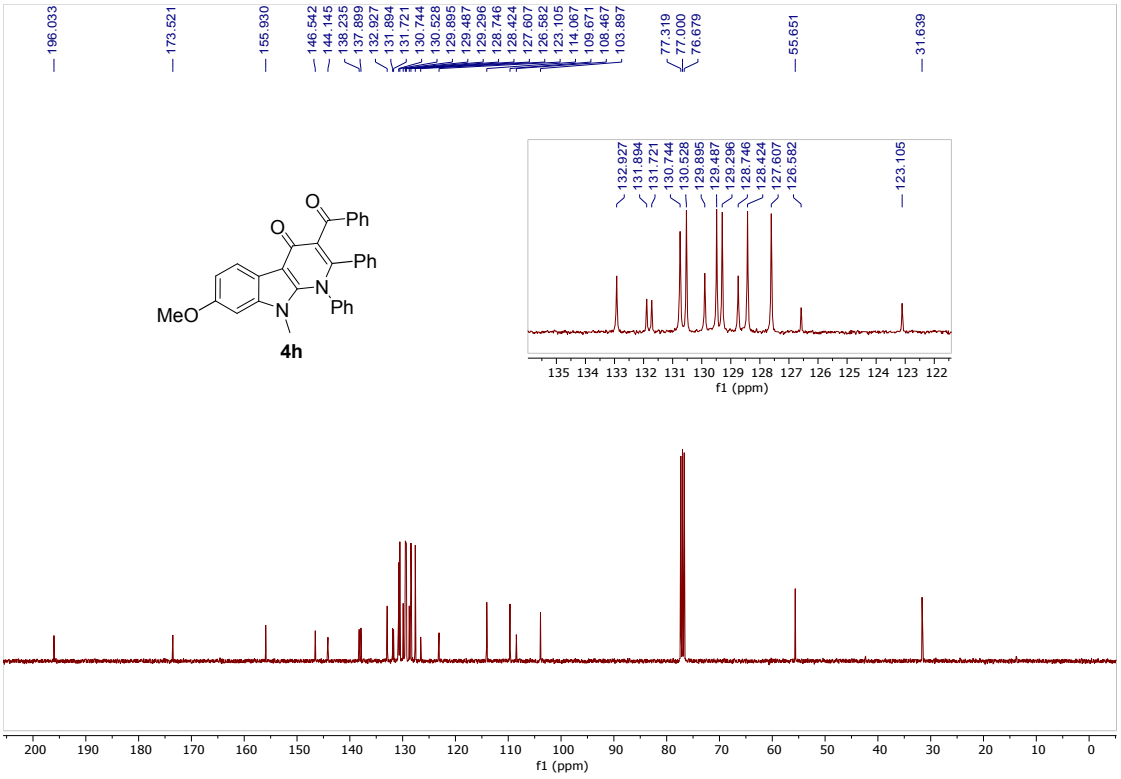
7.857
7.838
7.439
7.425
7.407
7.323
7.307
7.287
7.270
7.250
7.238
7.228
7.078
7.056
7.015
6.997
6.980
6.964
6.946
6.924
3.866
2.938
O
Ph
O
Ph
N
Ph
MeO
4h
0.94
2.00
1.10
7.33
1.05
6.02
3.06
3.17
f1 (ppm)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132.927
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130.528
129.895
129.487
129.296
128.746
128.424
127.607
126.582
123.105
114.067
109.671
108.467
103.897
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77.000
76.679
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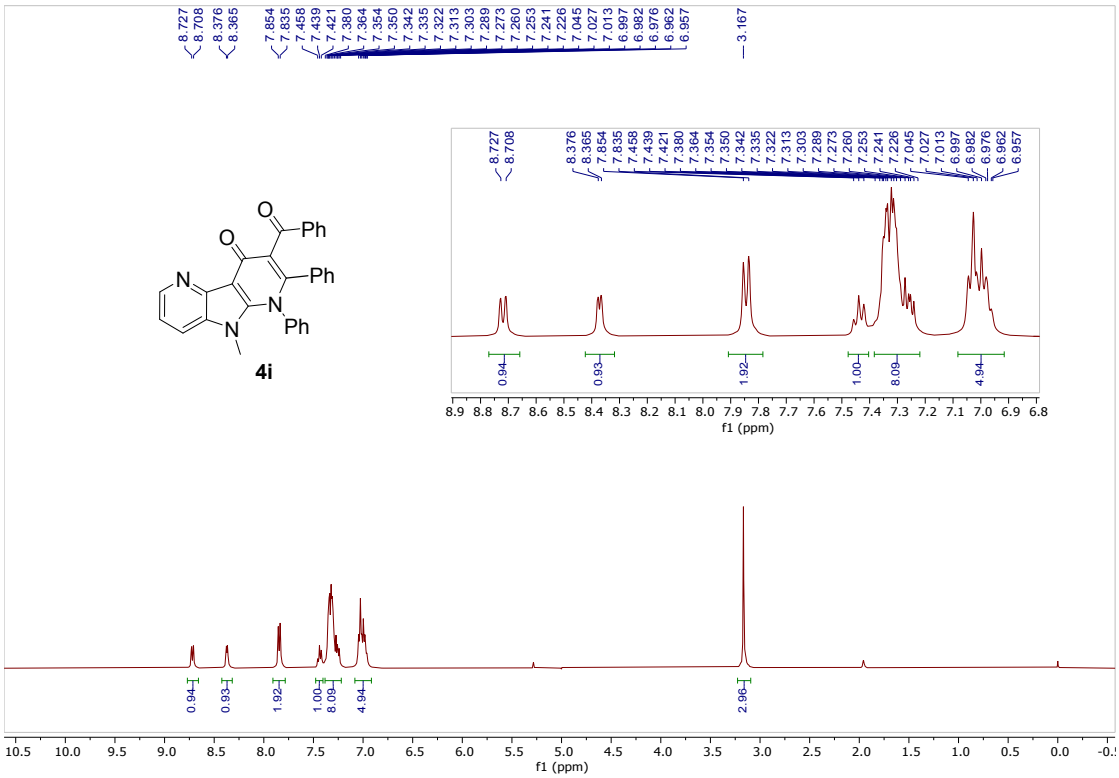
Ph
O
Ph
N
Ph
MeO
4h
f1 (ppm)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7.439
7.421
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7.354
7.350
7.342
7.335
7.322
7.313
7.303
7.289
7.273
7.260
7.253
7.241
7.226
7.045
7.027
7.013
6.997
6.982
6.976
6.962
6.957
3.167
O
Ph
O
Ph
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N
Ph
N
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0.93
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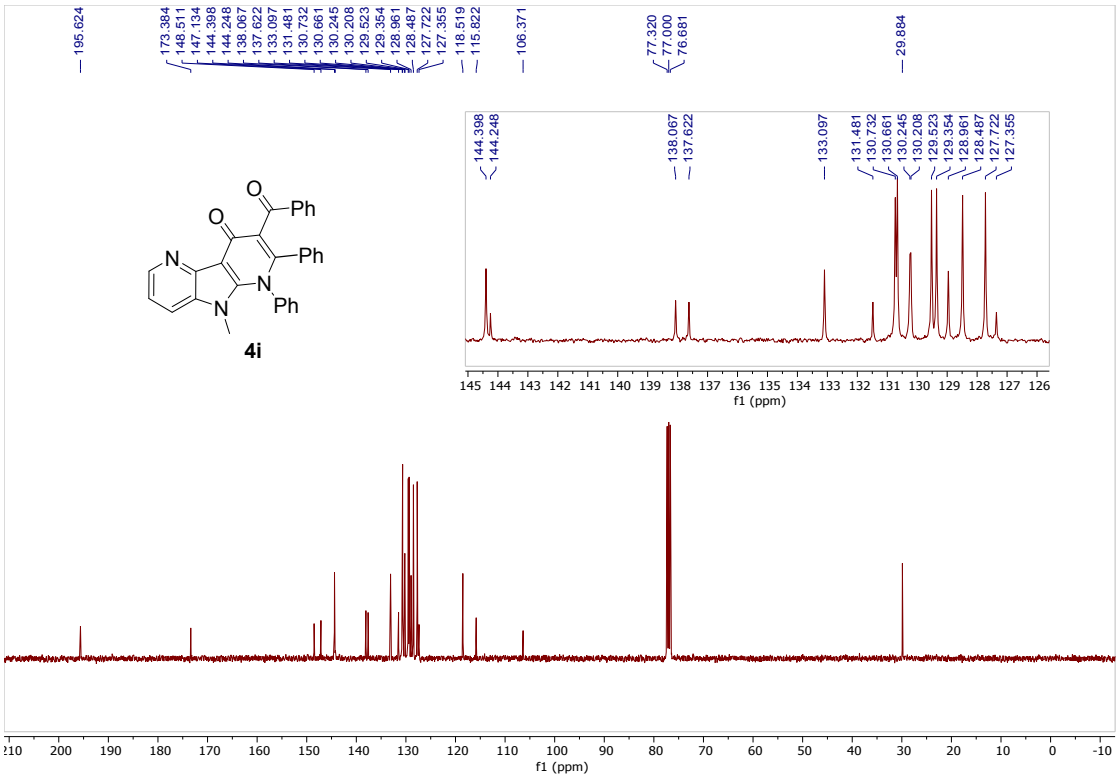
4.94
2.96
f1 (ppm)

4i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130.732
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130.245
130.208
129.523
129.354
128.961
128.487
127.722
127.355
118.519
115.822
106.371
77.320
77.000
76.681
29.884
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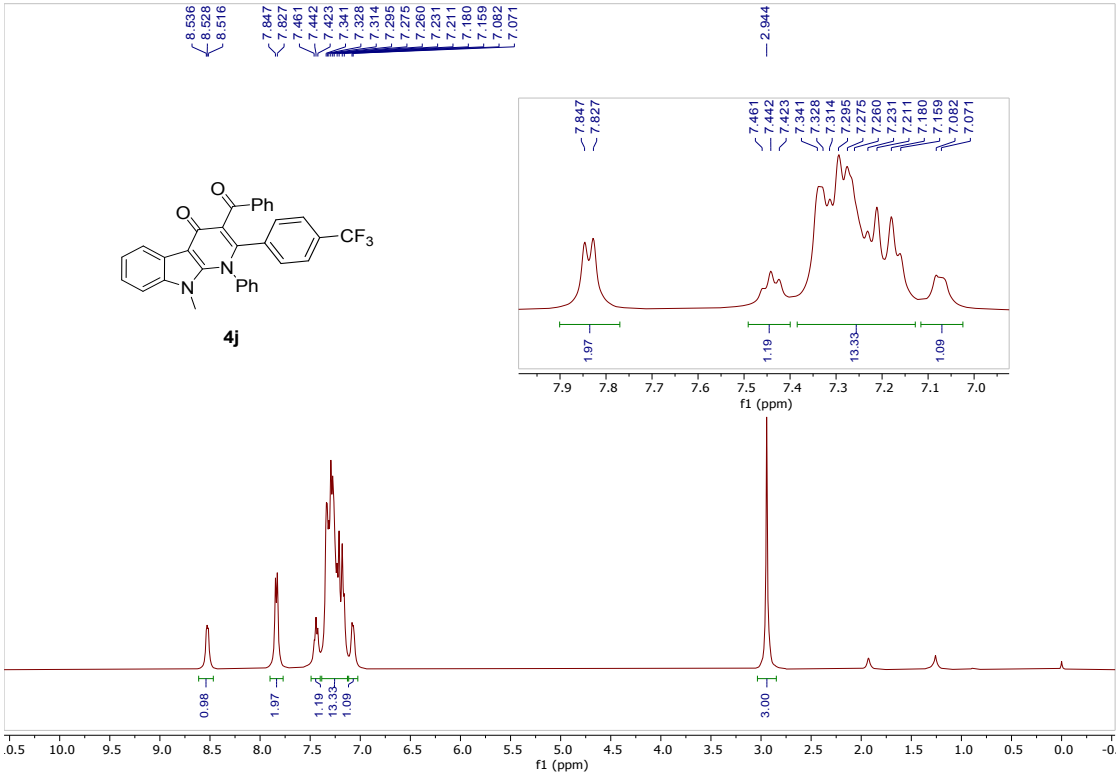
Ph
O
Ph
N
N
Ph
N
f1 (ppm)

4i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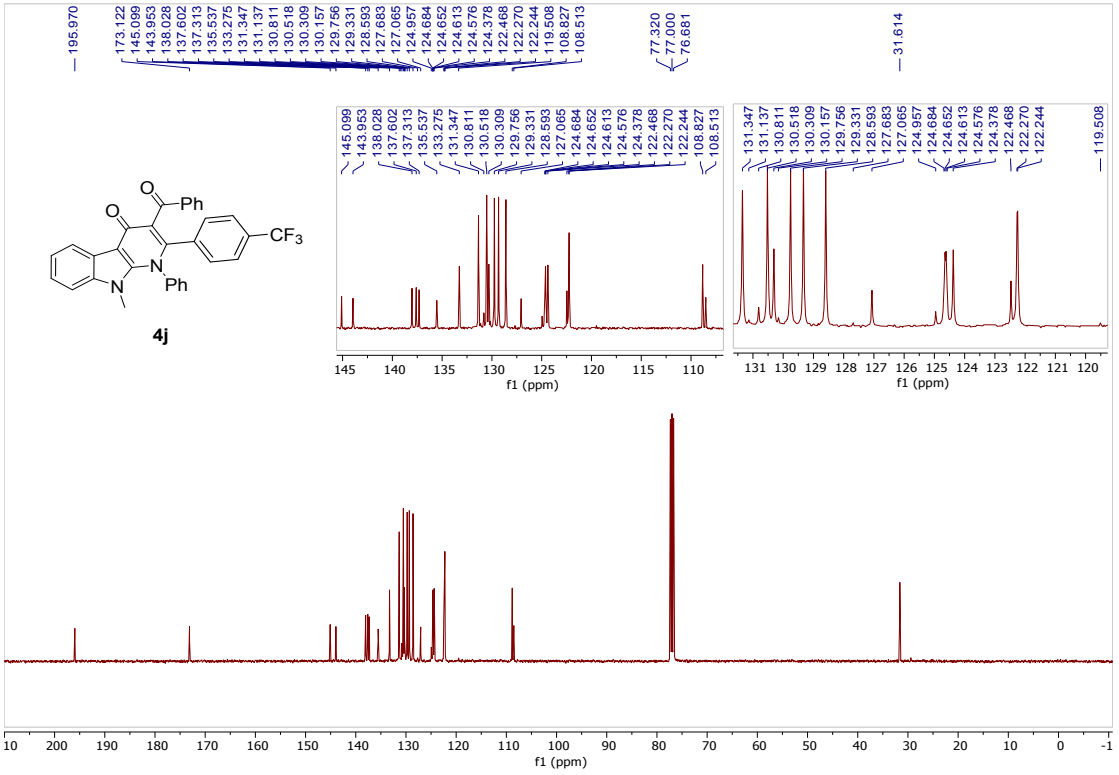
7.442
7.423
7.341
7.328
7.314
7.295
7.275
7.260
7.231
7.211
7.180
7.159
7.082
7.071
2.944
O
Ph
O
CF3
N
Ph
N
4j
1.97
1.19
13.33
1.09
f1 (ppm)
0.98
1.97
1.19
13.33
1.09
3.00
f1 (ppm)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135.537
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131.137
130.811
130.518
130.309
130.157
129.756
129.331
128.593
127.683
127.065
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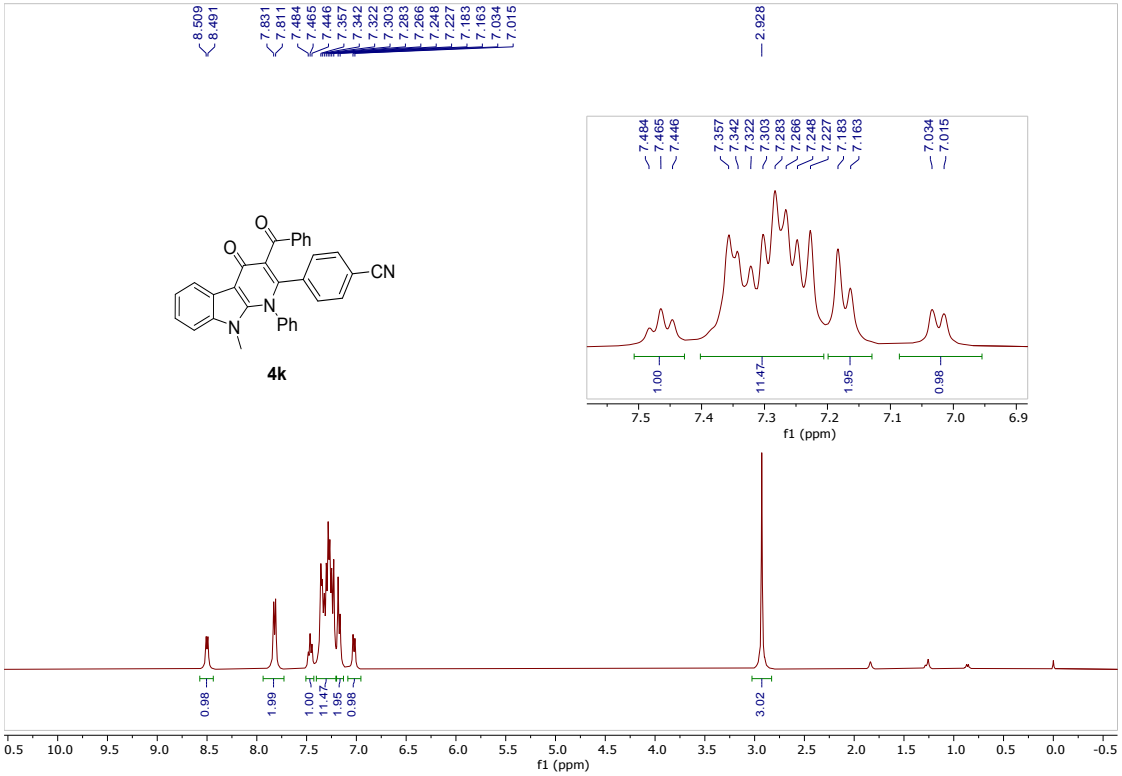
124.684
124.652
124.613
124.576
124.378
122.468
122.270
122.244
119.508
108.827
108.513
77.320
77.000
76.681
31.614
O
Ph
O
CF3
N
Ph
N
4j
f1 (ppm)
f1 (ppm)
f1 (ppm)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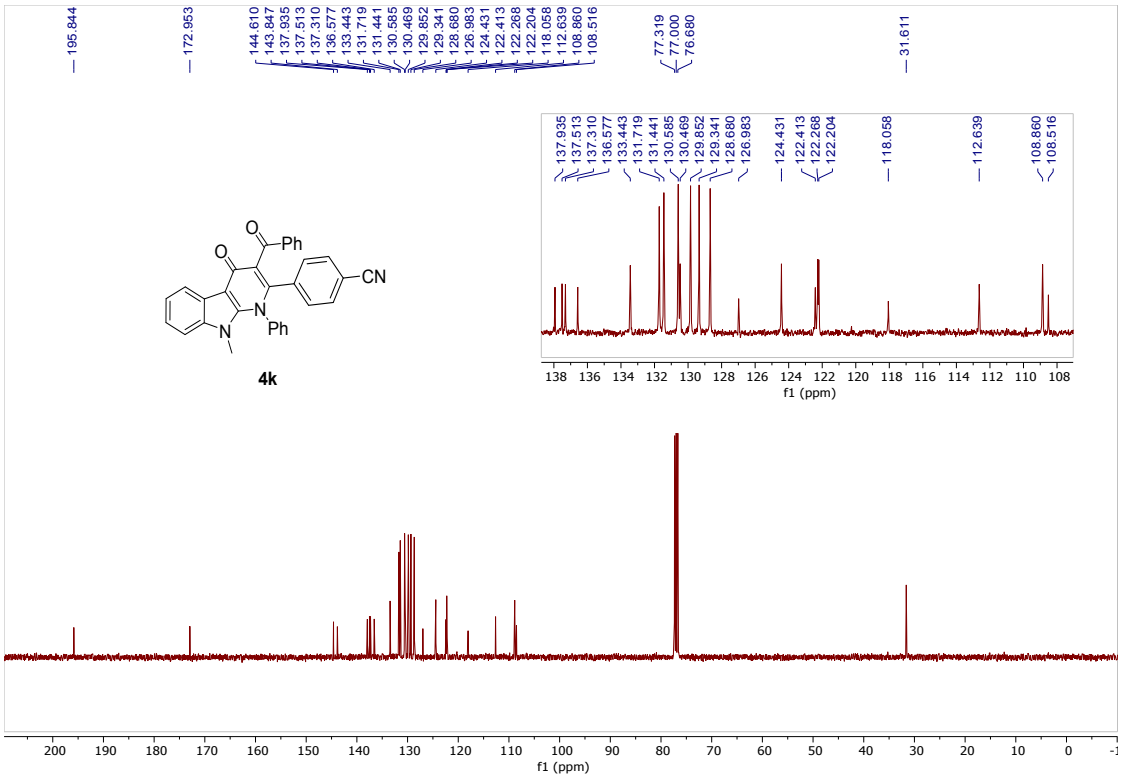
7.465
7.446
7.357
7.342
7.322
7.303
7.283
7.266
7.248
7.227
7.183
7.163
7.034
7.015
2.928
O
Ph
O
CN
N
Ph
4k
1.00
11.47
1.95
0.98
f1 (ppm)
0.98
1.99
1.00
11.47
1.95
0.98
3.02
f1 (ppm)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131.441
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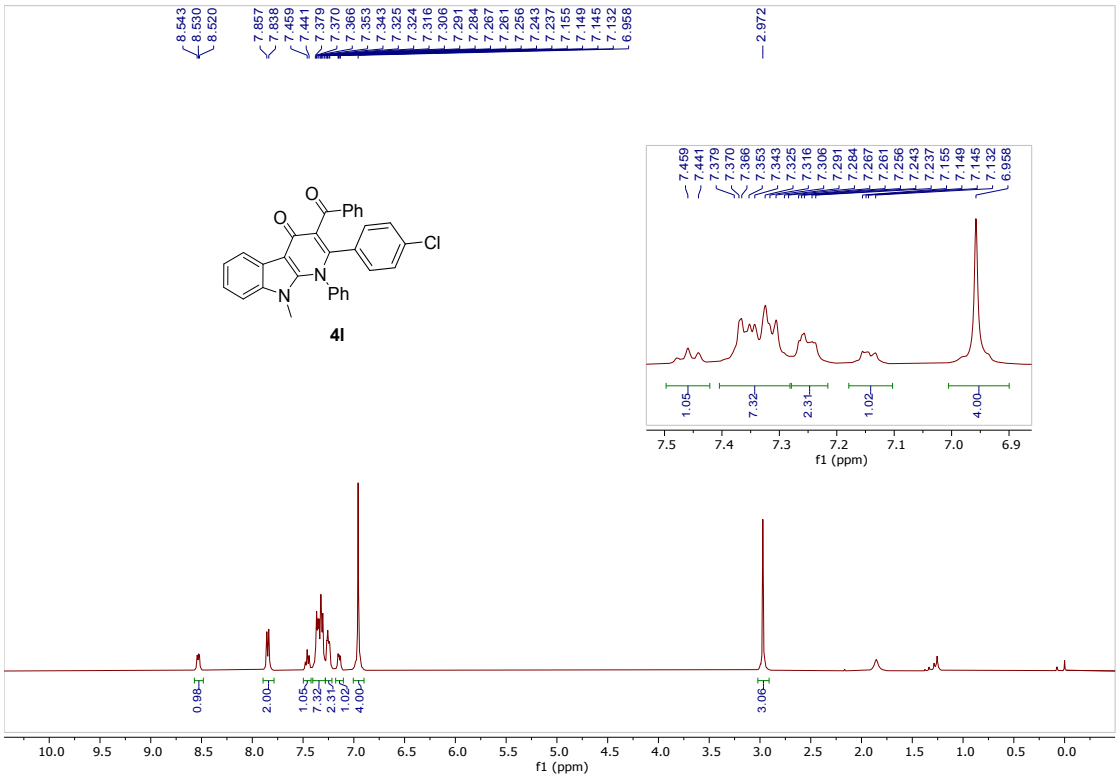
130.469
129.852
129.341
128.680
126.983
126.880
124.431
122.413
122.268
122.204
118.058
112.639
108.860
108.516
77.319
77.000
76.680
31.611
O
Ph
O
CN
N
Ph
4k
f1 (ppm)
f1 (ppm)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7.366
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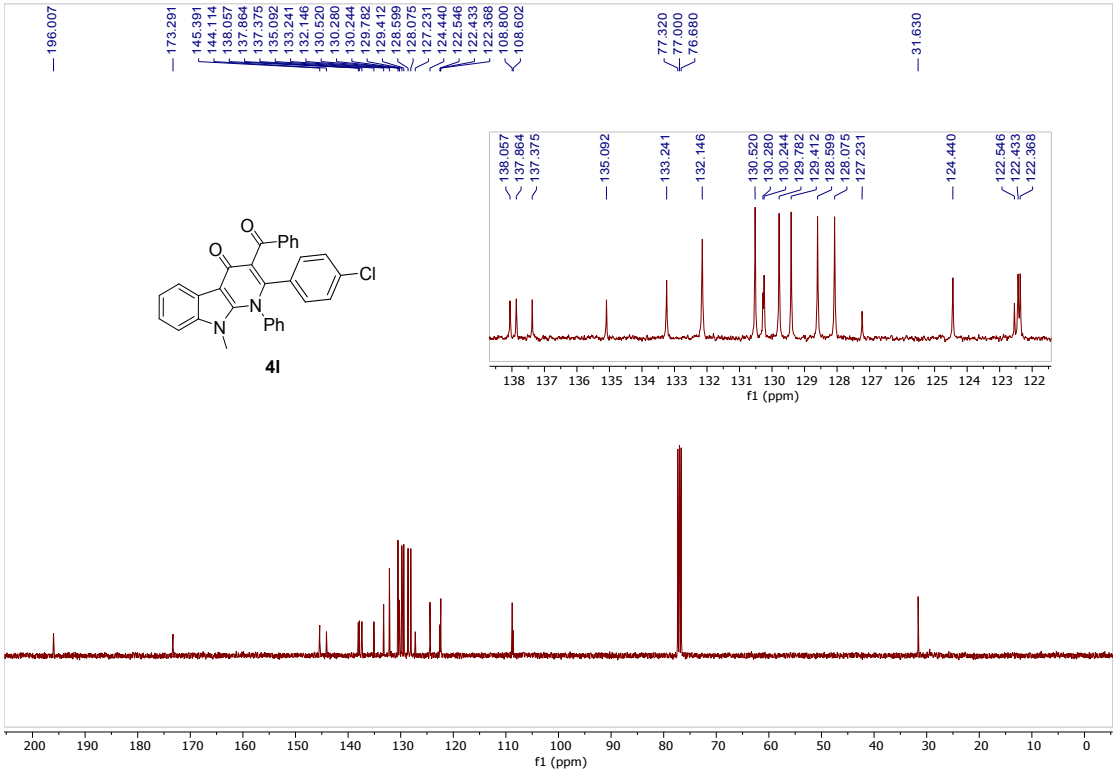
7.343
7.325
7.324
7.316
7.306
7.291
7.284
7.267
7.261
7.256
7.243
7.237
7.155
7.149
7.145
7.132
6.958
2.972
O
Ph
O
Cl
N
N
Ph
4l
1.05
7.32
2.31
1.02
4.00
f1 (ppm)
0.98
2.00
3.06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135.092
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132.146
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130.280
130.244
129.782
129.412
128.599
128.075
127.231
124.440
122.546
122.433
122.368
108.800
108.602
77.320
77.000
76.680
31.630
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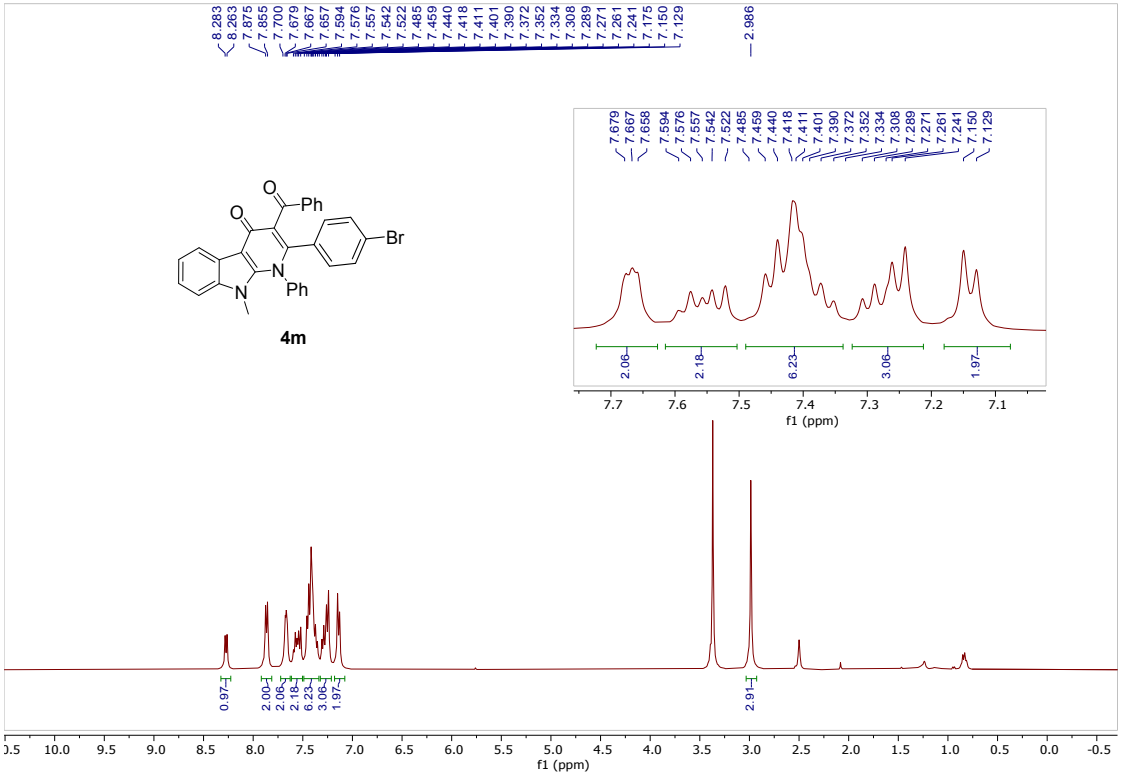
Ph
O
Cl
N
N
Ph
4l
f1 (ppm)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7.679
7.667
7.657
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7.576
7.557
7.542
7.522
7.485
7.459
7.440
7.418
7.411
7.401
7.390
7.372
7.352
7.334
7.308
7.289
7.271
7.261
7.241
7.175
7.150
7.129
2.986
O
Ph
O
Br
N
Ph
N
4m
2.06
2.18
6.23
3.06
1.97
f1 (ppm)
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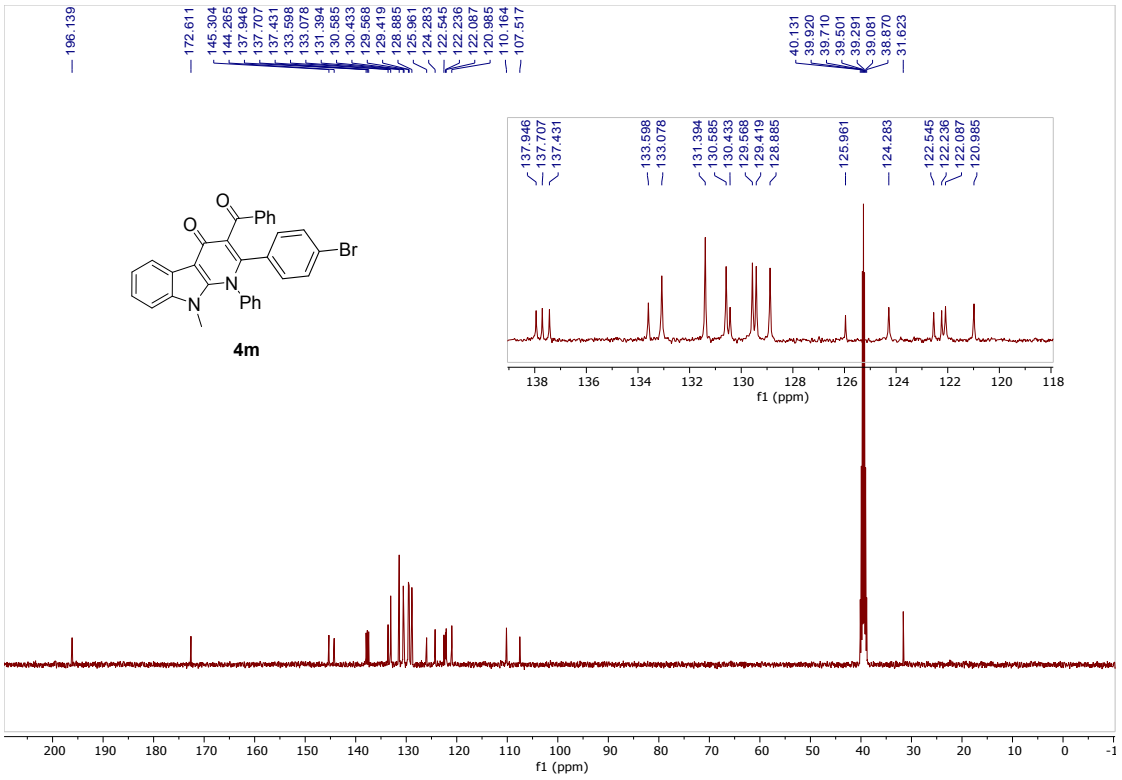
2.18
6.23
3.06
1.97
2.91
f1 (ppm)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144.265
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137.707
137.431
133.598
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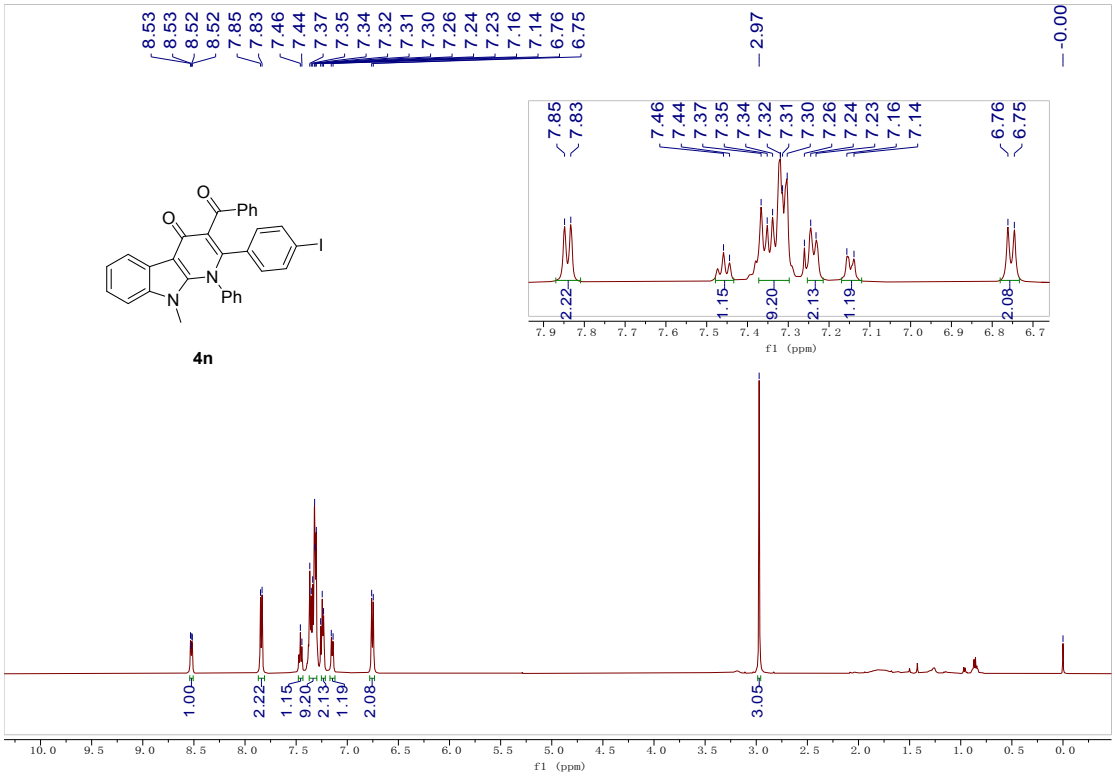
131.394
130.585
130.433
129.568
129.419
128.885
125.961
124.283
122.545
122.236
122.087
120.985
110.164
107.517
40.131
39.920
39.710
39.501
39.291
39.081
38.870
31.623
O
Ph
O
Br
N
Ph
N
4m
f1 (ppm)
f1 (ppm)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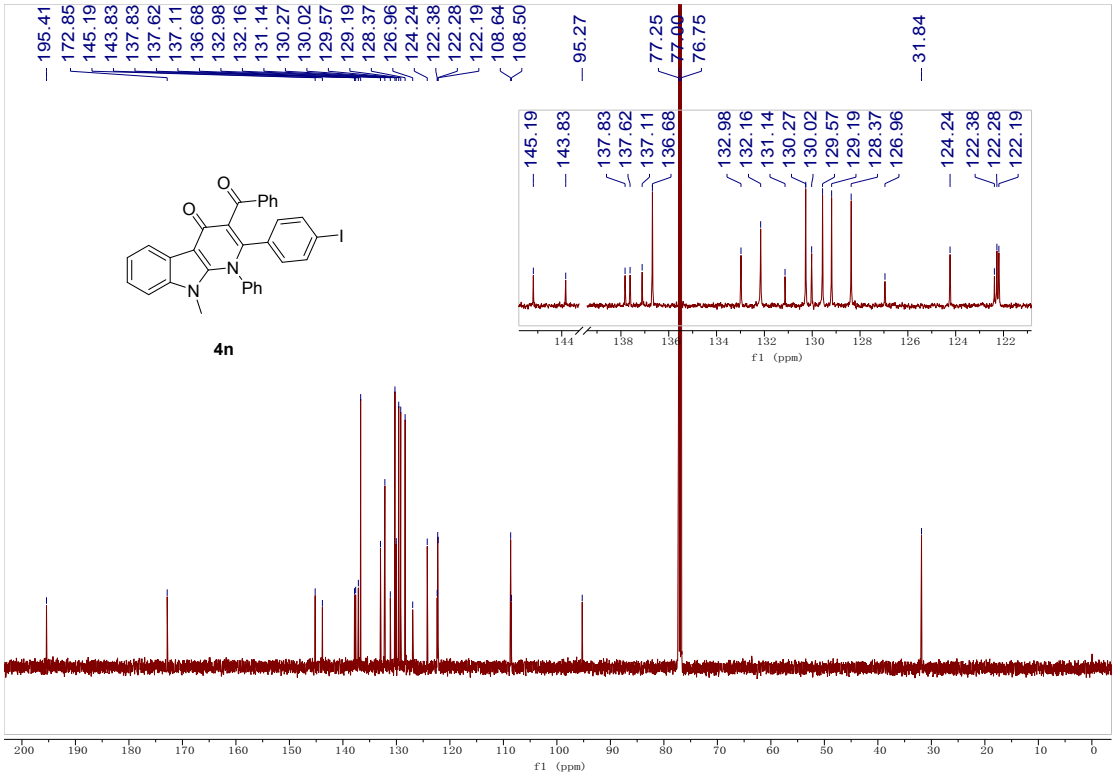
7.44
7.37
7.35
7.34
7.32
7.31
7.30
7.26
7.24
7.23
7.16
7.14
6.76
6.75
2.97
-0.00
O
Ph
O
I
N
Ph
N
4n
1.00
2.22
1.15
9.20
2.13
1.19
2.08
3.05
f1 (ppm)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131.14
130.27
130.02
129.57
129.19
128.37
126.96
124.24
122.38
122.28
122.19
108.64
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77.00
76.75
31.84
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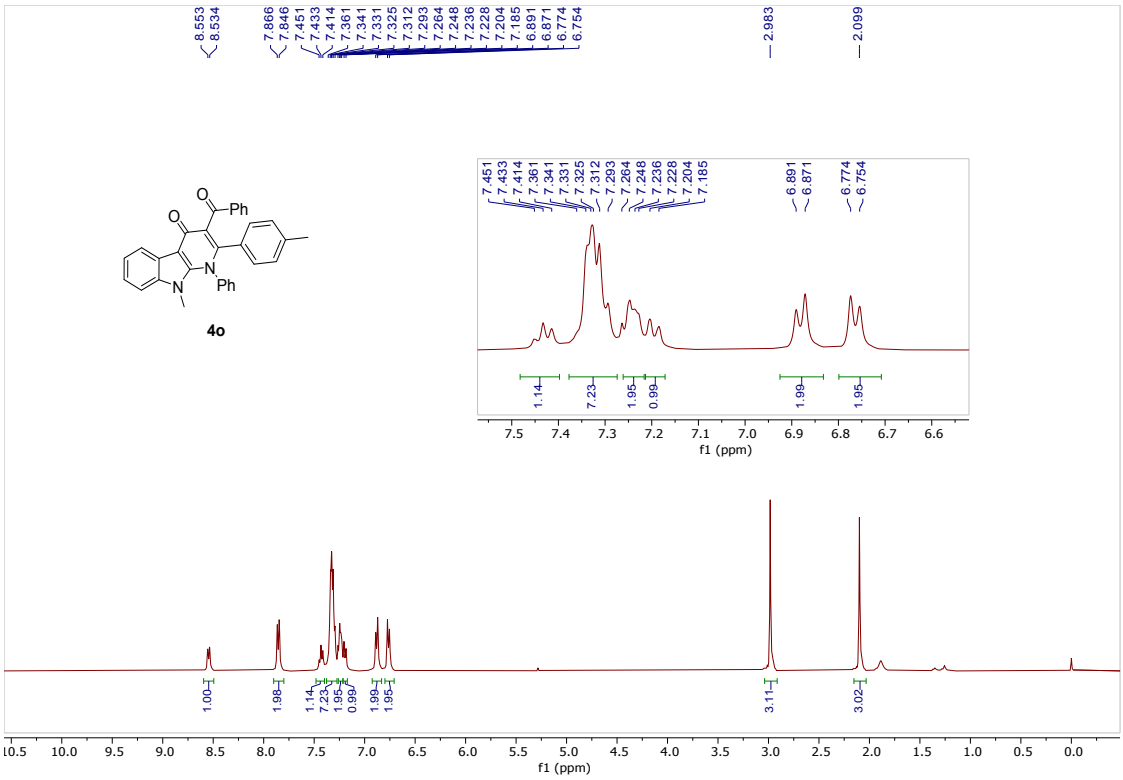
Ph
O
I
N
Ph
N
4n
f1 (ppm)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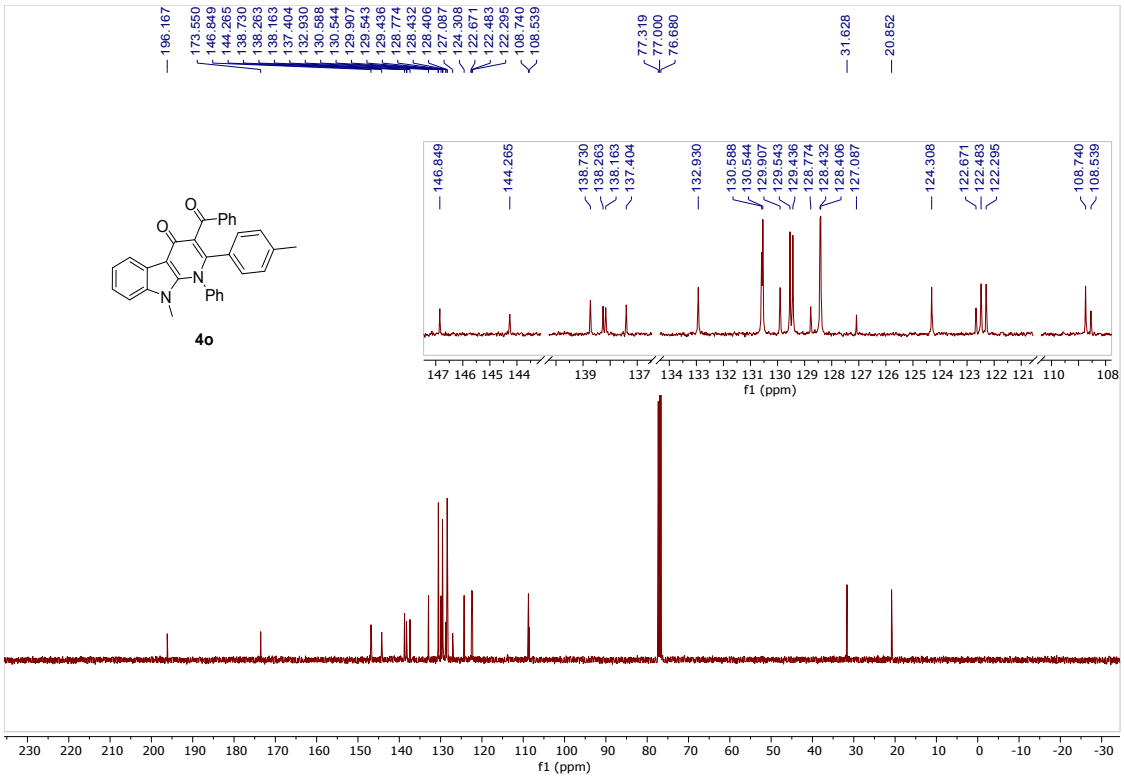
7.325
7.312
7.293
7.264
7.248
7.236
7.228
7.204
7.185
6.891
6.871
6.774
6.754
2.983
2.099
O
Ph
O
N
N
Ph
4o
1.14
7.23
1.95
0.99
1.99
1.95
f1 (ppm)
1.00
1.98
1.14
7.23
1.95
0.99
1.99
1.95
3.11
3.02
f1 (ppm)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137.404
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129.907
129.543
129.436
128.774
128.432
128.406
127.087
124.308
122.671
122.483
122.295
108.740
108.539
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77.000
76.680
31.628
20.852
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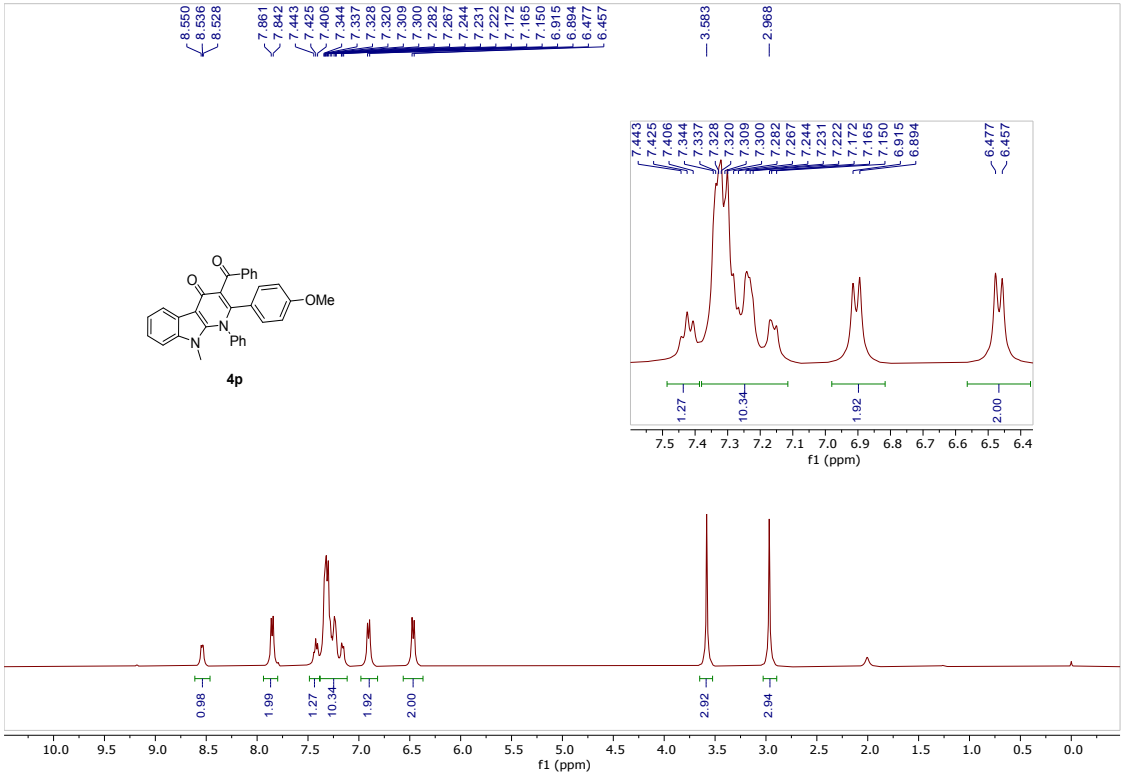
Ph
O
N
N
Ph
4o
f1 (ppm)
f1 (ppm)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7.406
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7.309
7.300
7.282
7.267
7.244
7.231
7.222
7.172
7.165
7.150
6.915
6.894
6.477
6.457
3.583
2.968
Ph
O
OMe
N
Ph
4p
1.27
10.34
1.92
2.00
f1 (ppm)
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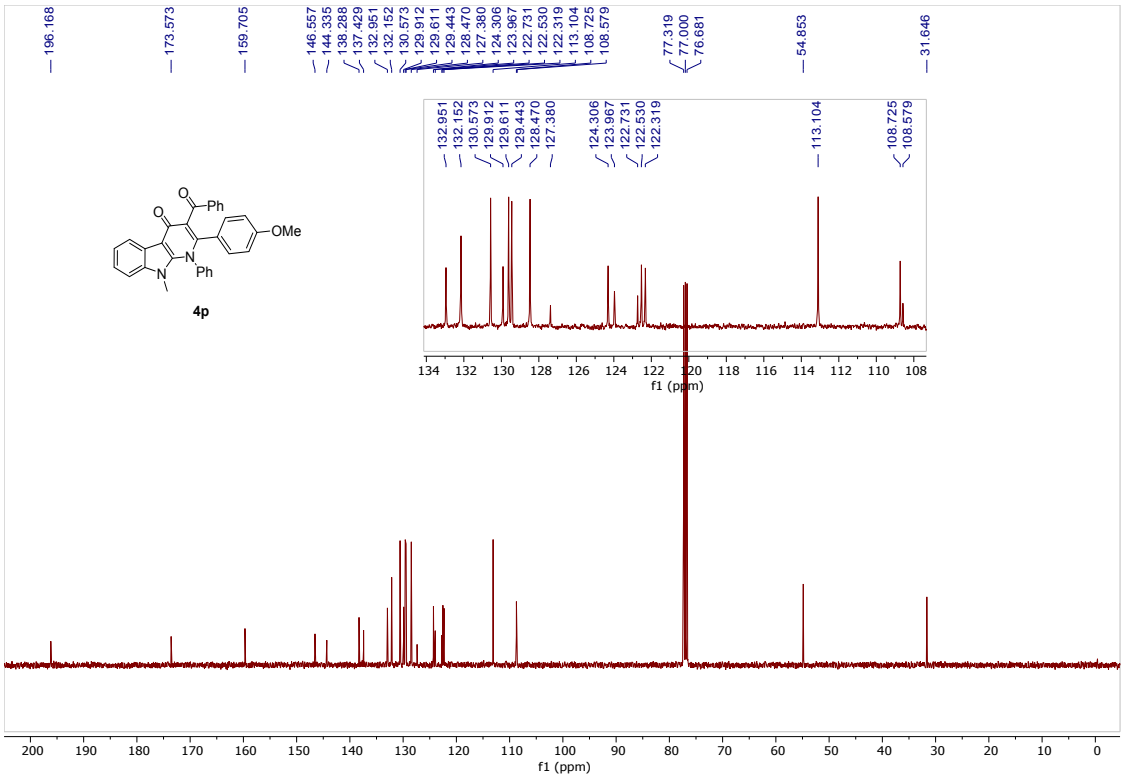
1.99
1.27
10.34
1.92
2.00
2.92
2.94
f1 (ppm)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127.380
124.306
123.967
122.731
122.530
122.319
113.104
108.725
108.579
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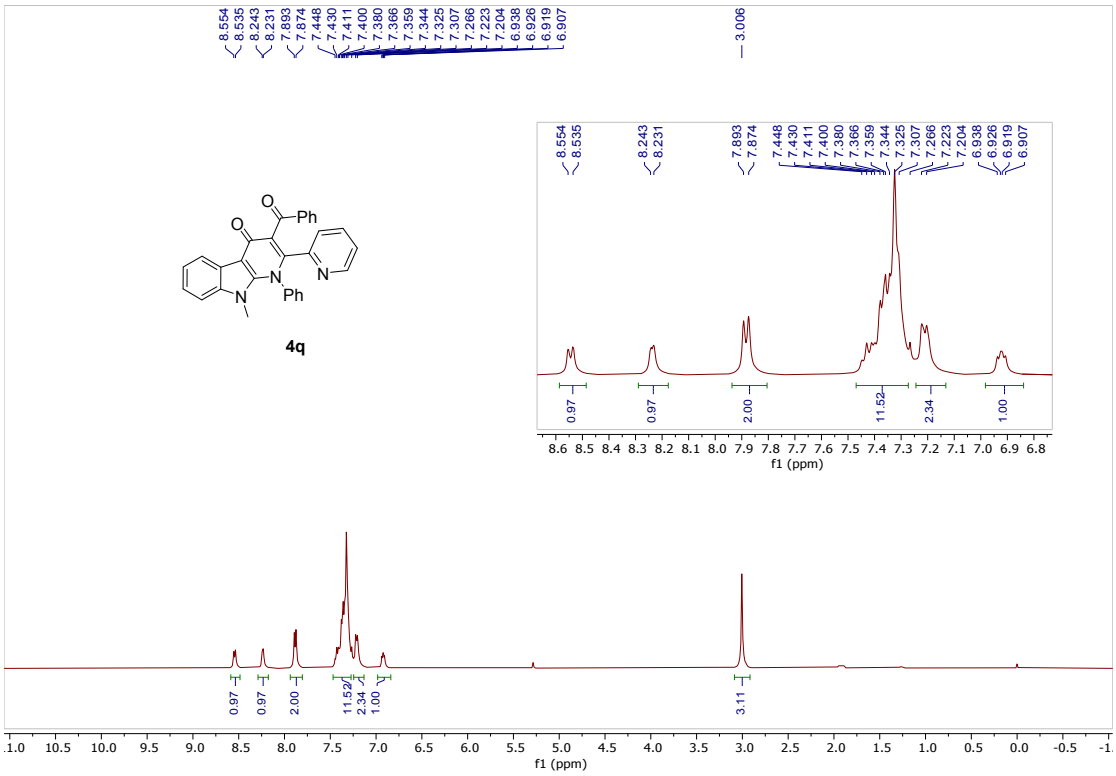
77.000
76.681
54.853
31.646
O
Ph
OMe
N
Ph
4p
f1 (ppm)
f1 (ppm)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7.307
7.266
7.223
7.204
6.938
6.926
6.919
6.907
3.006
O
Ph
O
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N
Ph
4q
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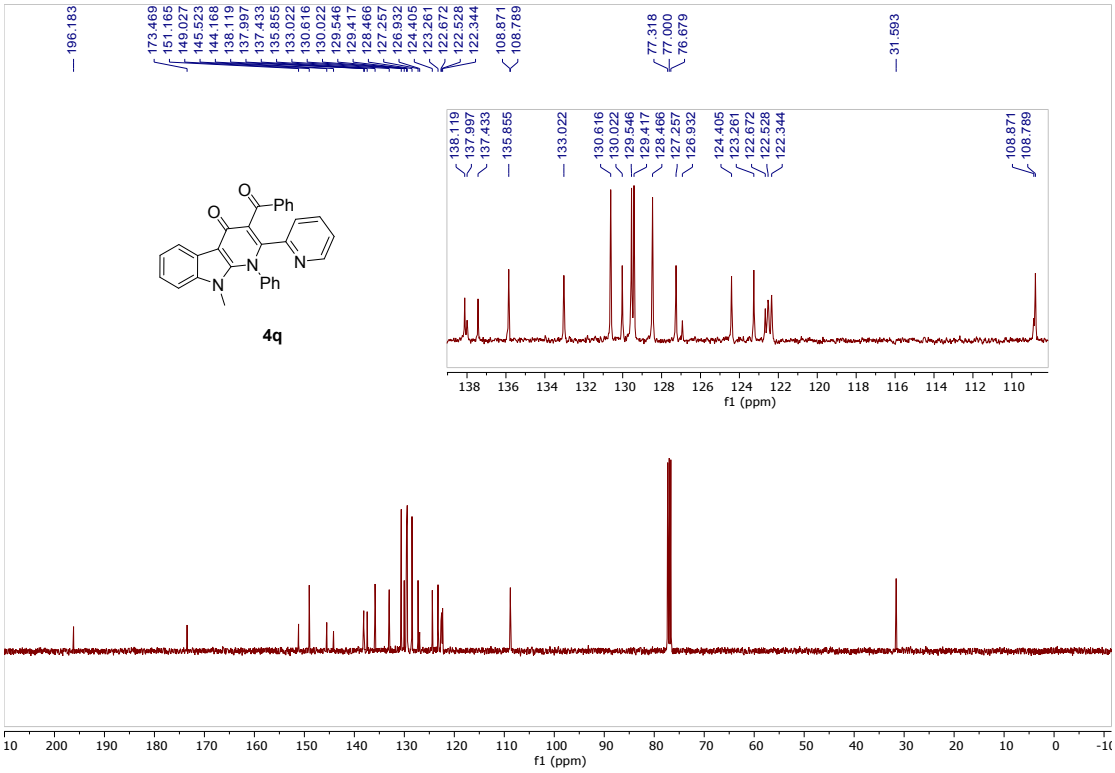
2.34
1.00
3.11
f1 (ppm)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137.997
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130.022
129.546
129.417
128.466
127.257
126.932
124.405
123.261
122.672
122.528
122.344
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77.318
77.000
76.679
31.593
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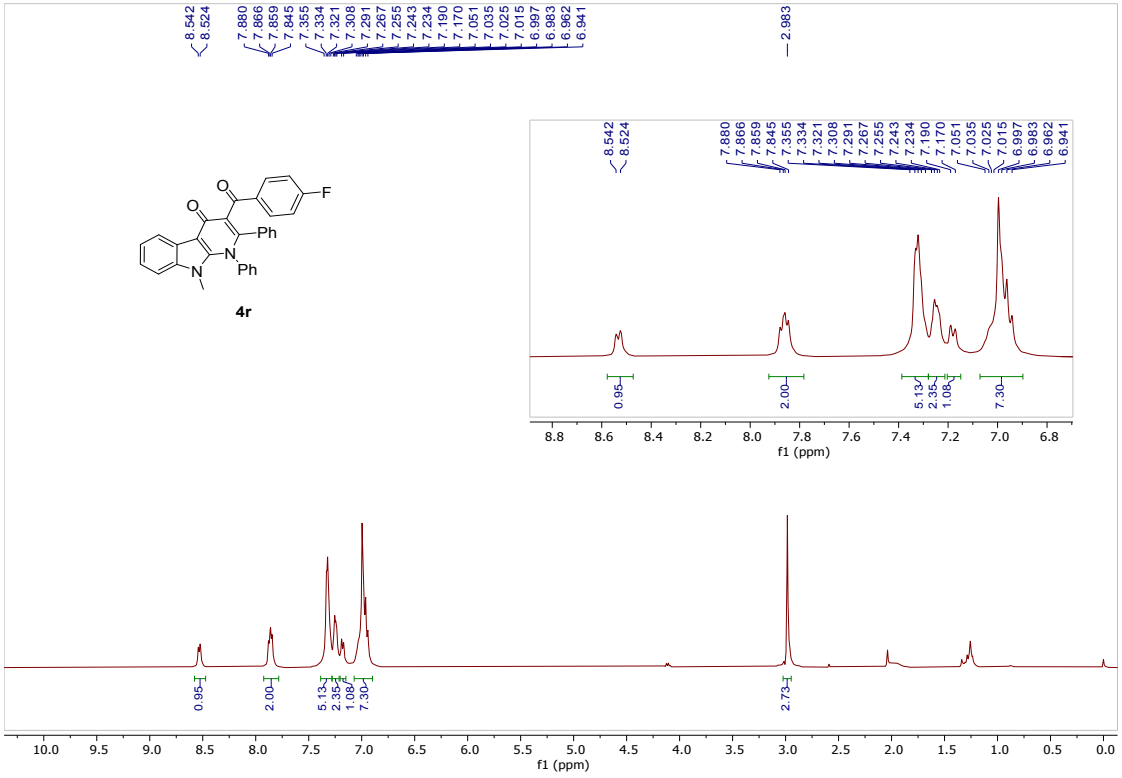
Ph
O
N
N
Ph
4q
f1 (ppm)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7.334
7.321
7.308
7.291
7.267
7.255
7.243
7.234
7.190
7.170
7.051
7.035
7.025
7.015
6.997
6.983
6.962
6.941
2.983
O
O
F
Ph
N
Ph
4r
0.95
2.00
5.13
2.35
1.08
7.30
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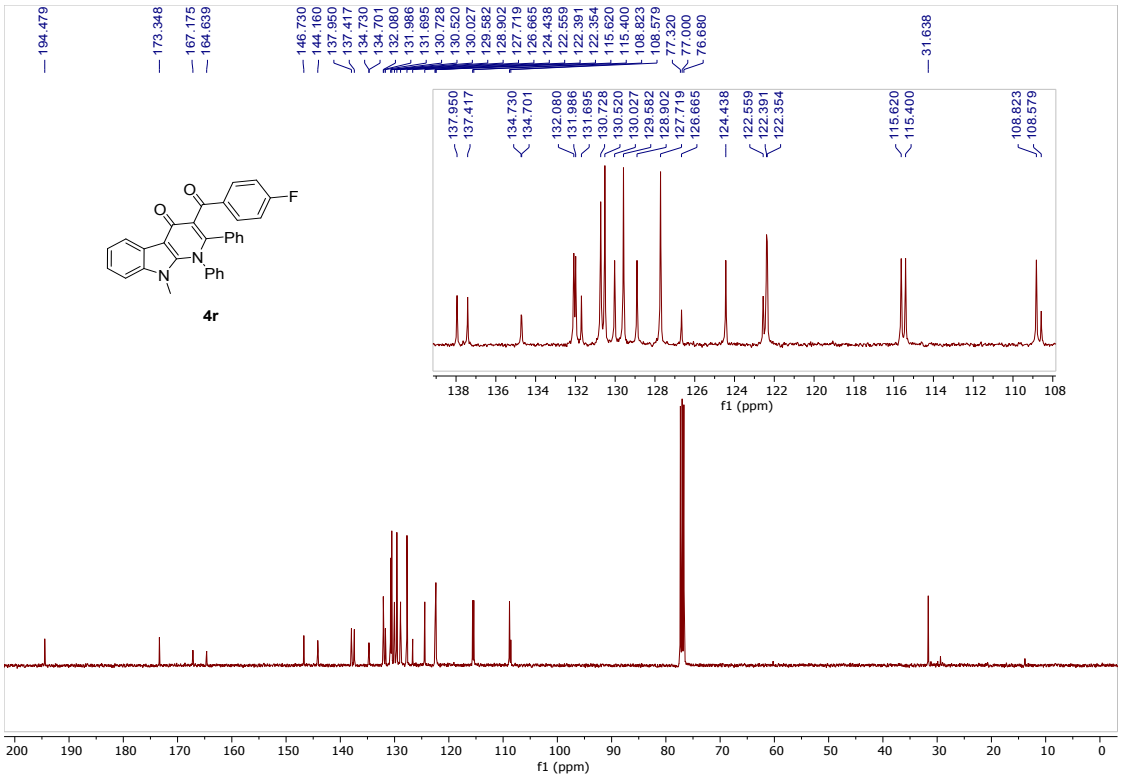
f1 (ppm)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130.520
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128.902
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126.665
124.438
122.559
122.391
122.354
115.620
115.400
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77.000
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31.638
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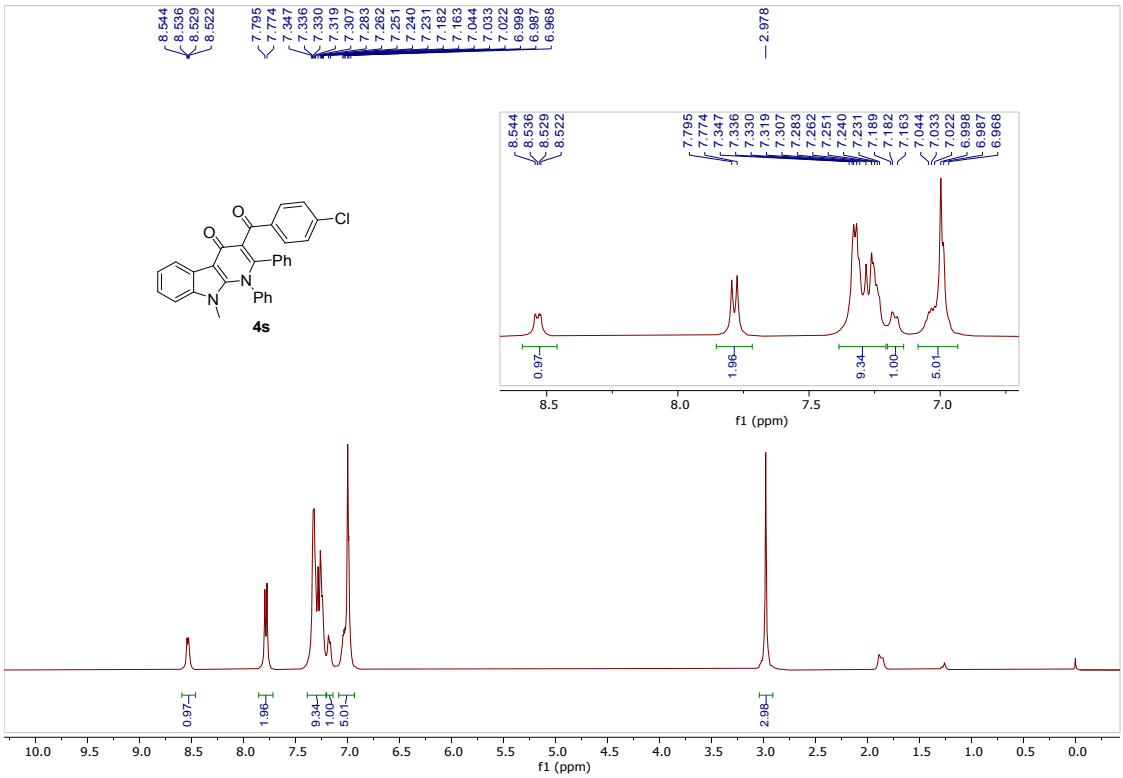
O
F
Ph
N
Ph
4r
f1 (ppm)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7.307
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7.262
7.251
7.240
7.231
7.182
7.163
7.044
7.033
7.022
6.998
6.987
6.968
2.978
Cl
O
O
Ph
N
Ph
N
4s
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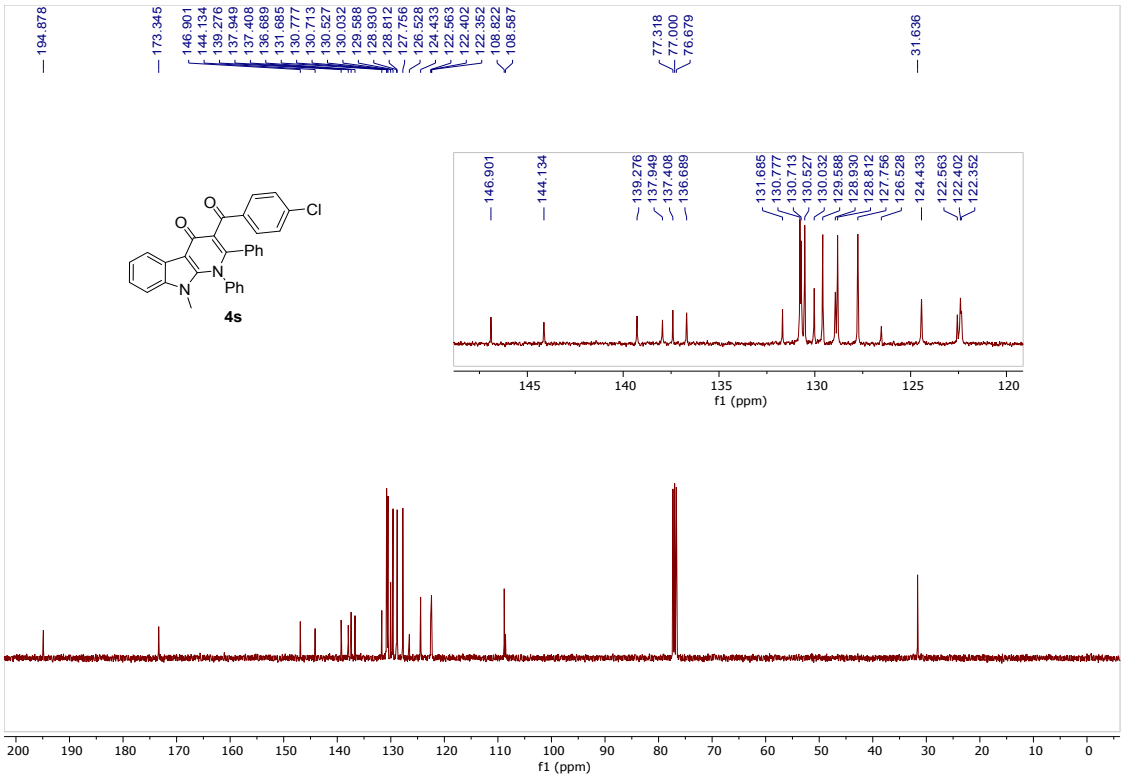
1.00
5.01
2.98
f1 (ppm)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128.930
128.812
127.756
126.528
124.433
122.563
122.402
122.352
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108.587
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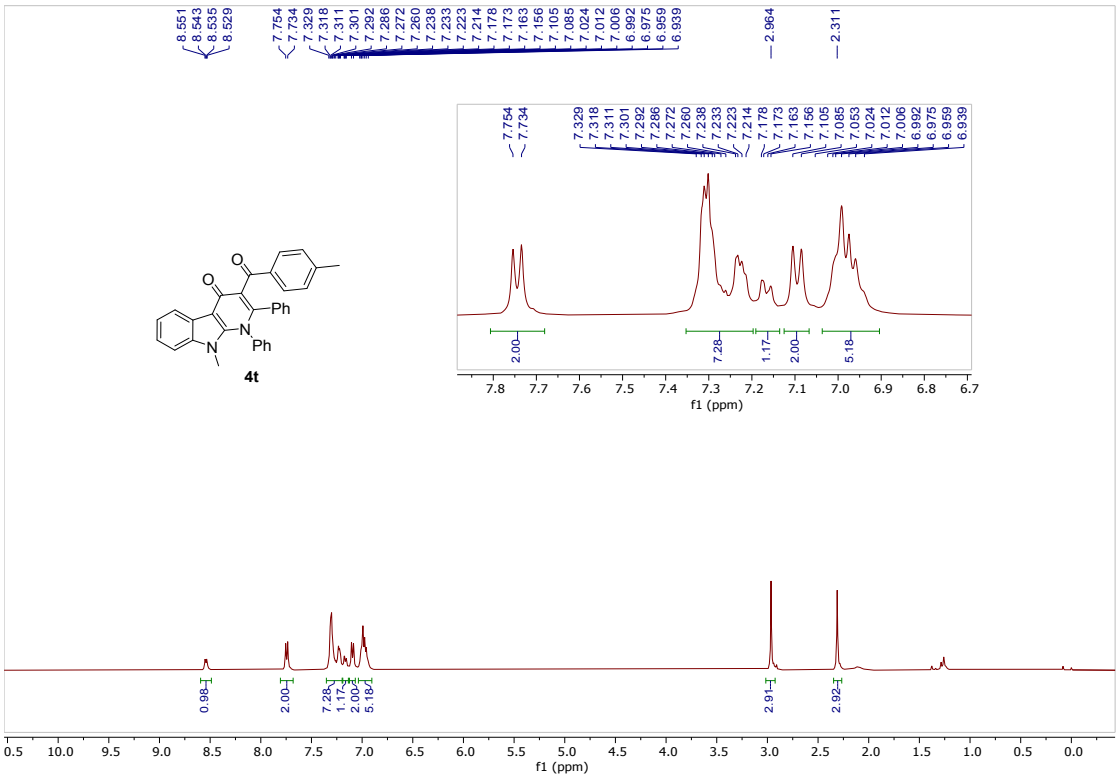
77.000
76.679
31.636
Cl
O
O
Ph
N
Ph
N
4s
f1 (ppm)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7.260
7.238
7.233
7.223
7.214
7.178
7.173
7.163
7.156
7.105
7.085
7.024
7.012
7.006
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6.975
6.959
6.939
2.964
2.311
Ph
Ph
4t
2.00
7.28
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5.18
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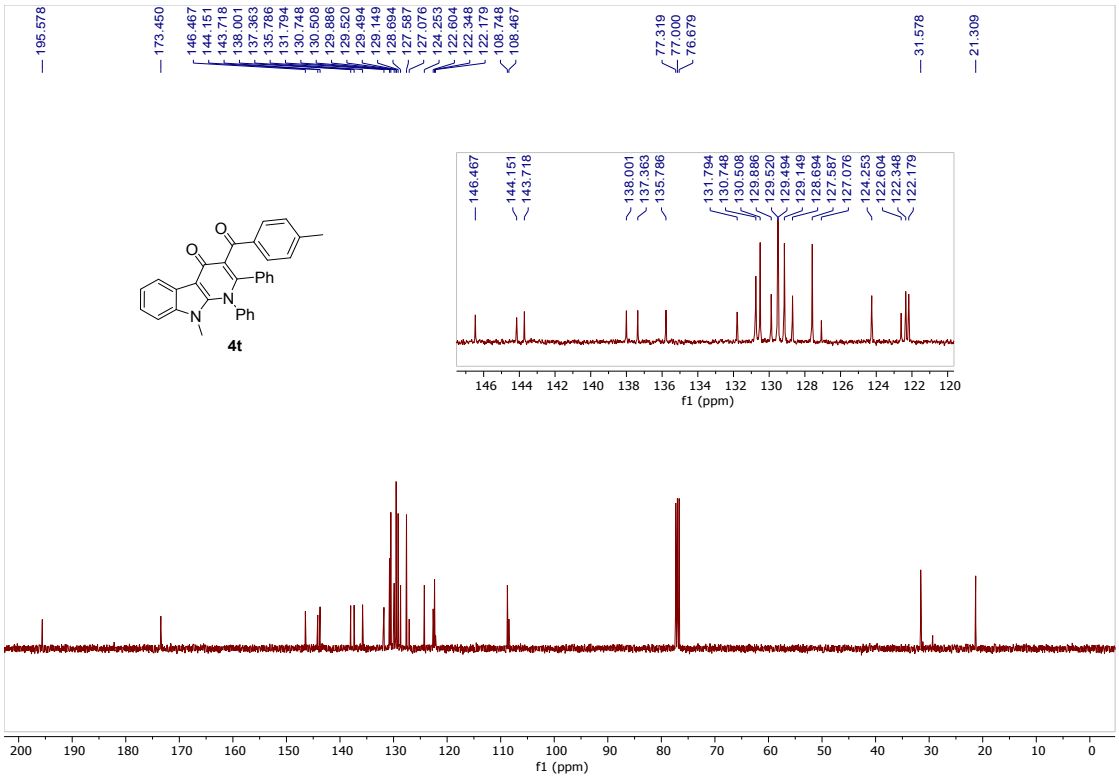
2.92
f1 (ppm)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129.149
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127.076
124.253
122.604
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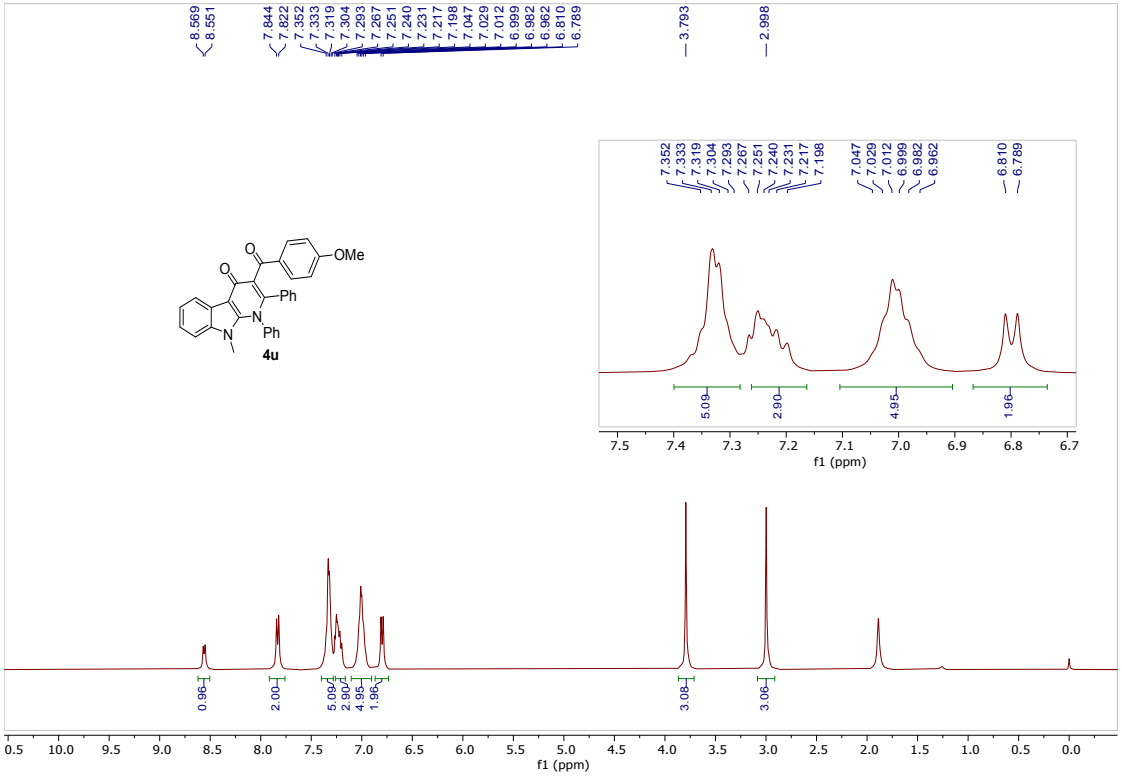
77.000
76.679
31.578
21.309
Ph
Ph
4t
f1 (ppm)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7.231
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7.198
7.047
7.029
7.012
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6.982
6.962
6.810
6.789
3.793
2.998
OMe
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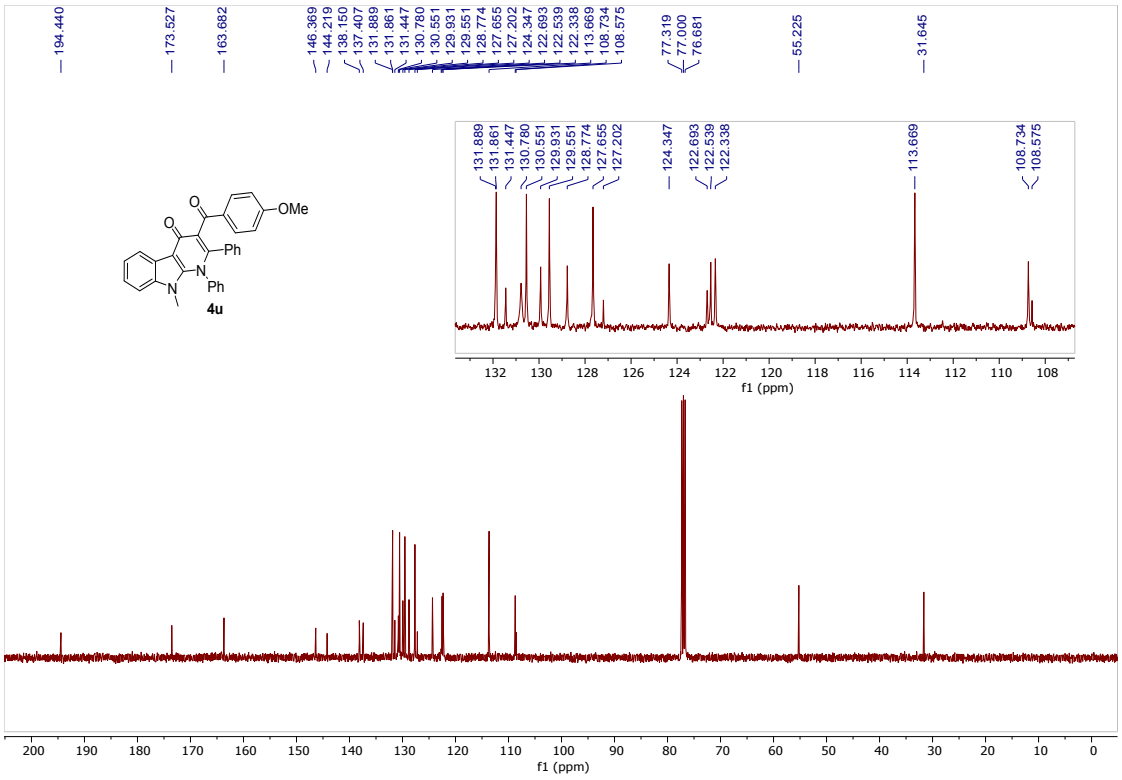
2.00
3.08
3.06
f1 (ppm)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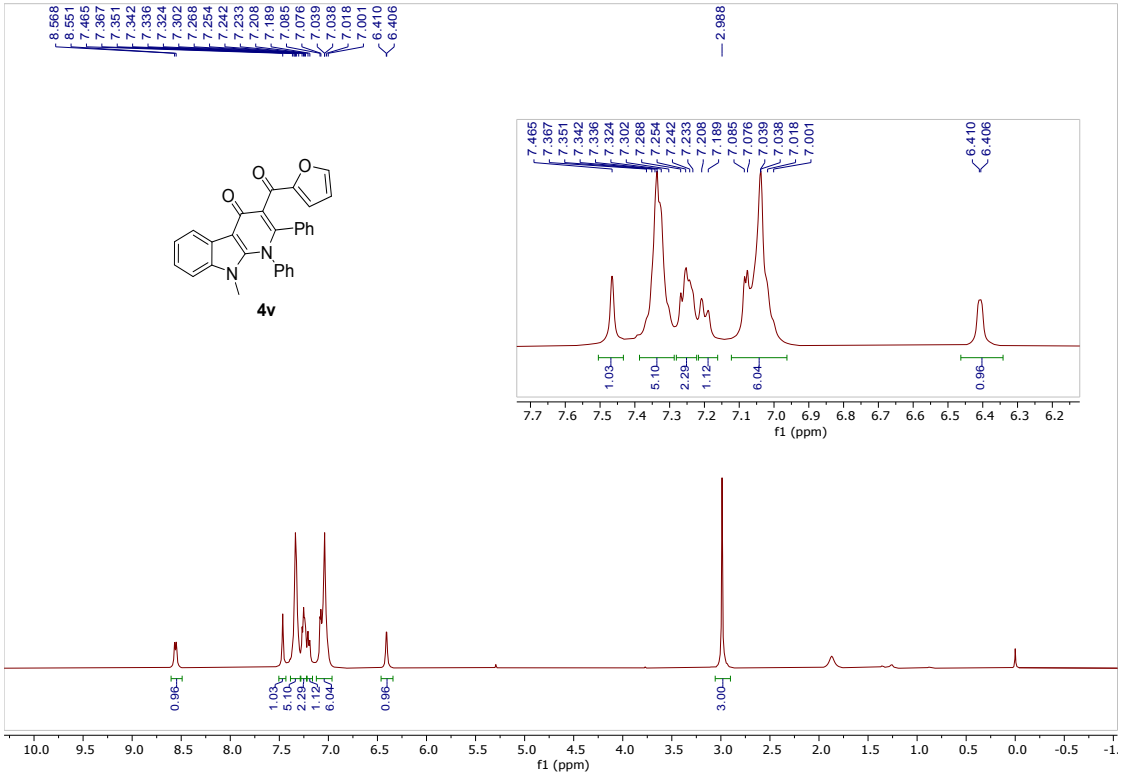
OMe
Ph
N
Ph
4u
f1 (ppm)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7.233
7.208
7.189
7.085
7.076
7.039
7.038
7.018
7.001
6.410
6.406
2.988
O
O
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Ph
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4v
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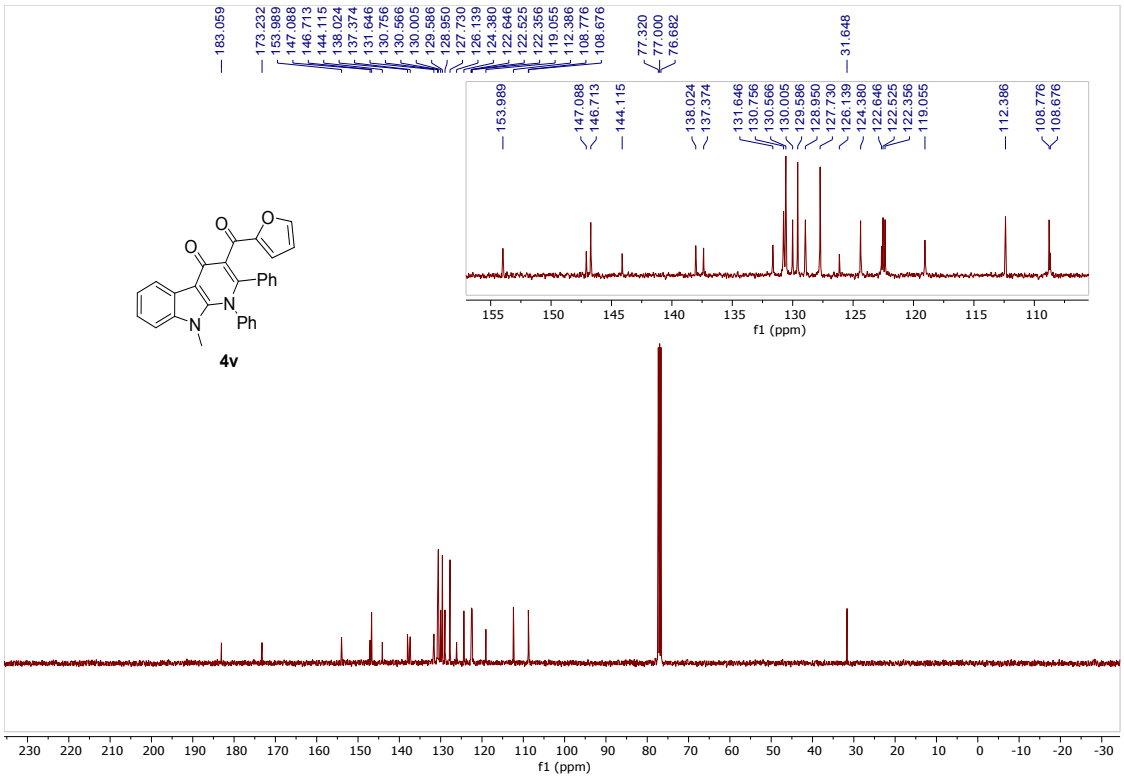
3.00
f1 (ppm)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126.139
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122.646
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112.386
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Ph
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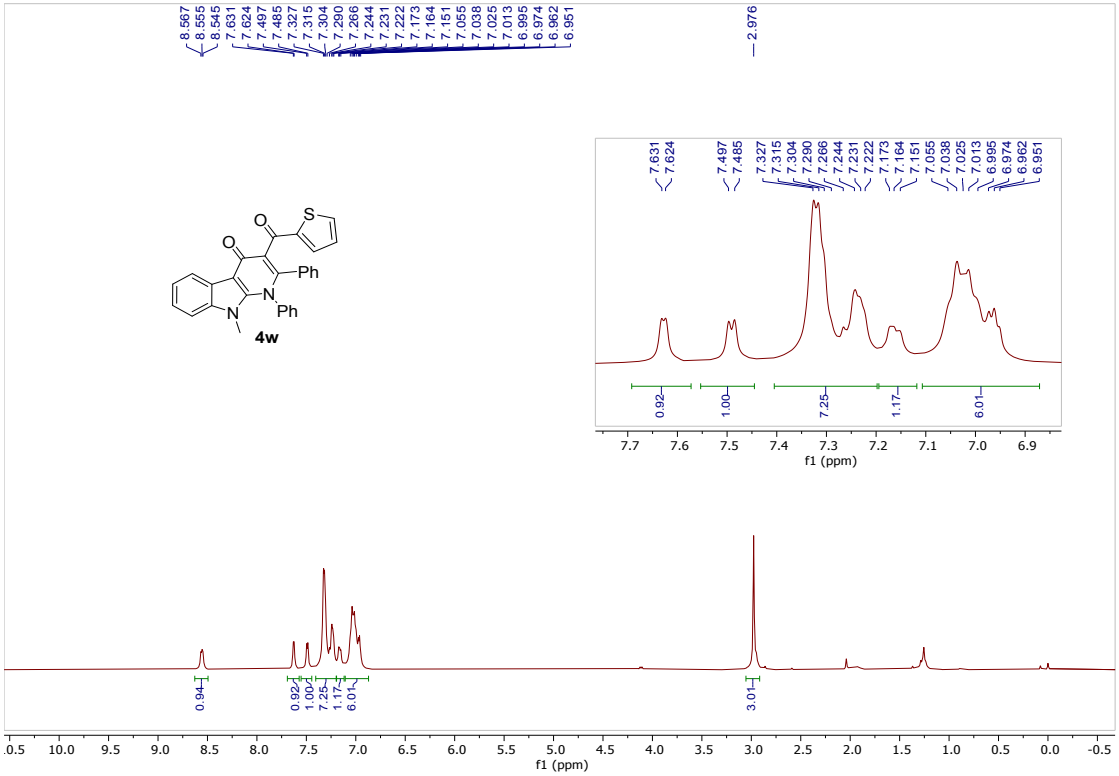
Ph
N
4v
f1 (ppm)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7.266
7.244
7.231
7.222
7.173
7.164
7.151
7.055
7.038
7.025
7.013
6.995
6.974
6.962
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4w
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0.92
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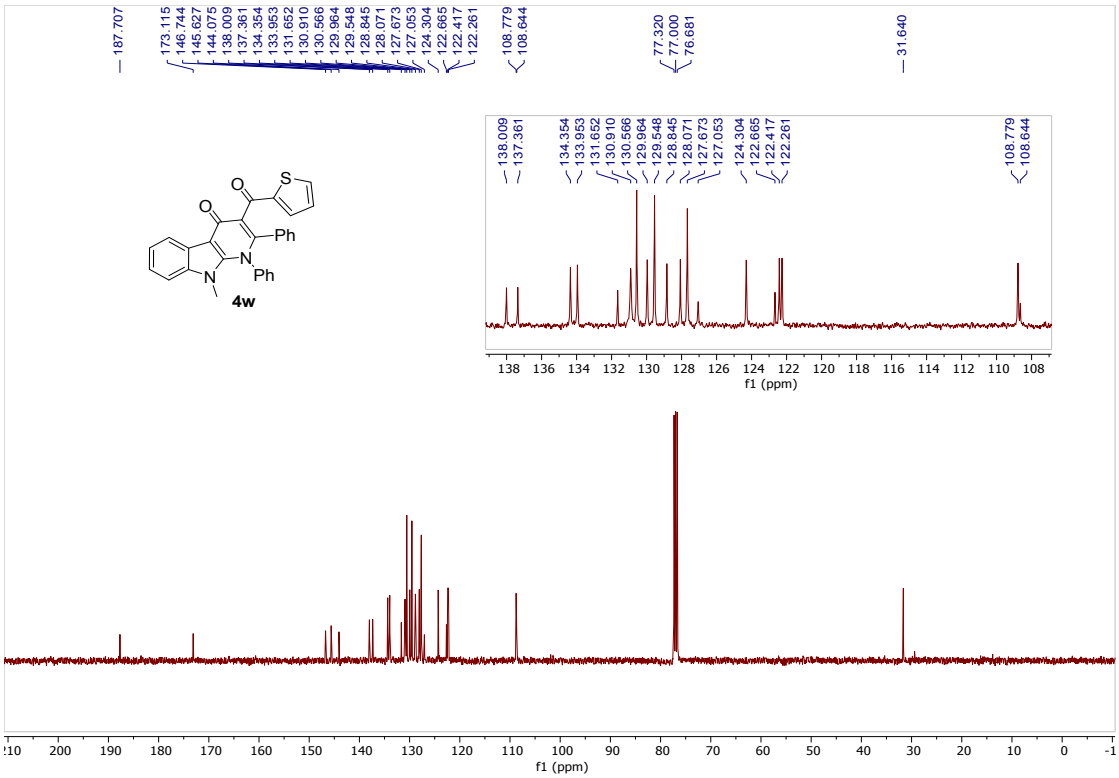
3.01
f1 (ppm)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128.071
127.673
127.053
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122.417
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108.644
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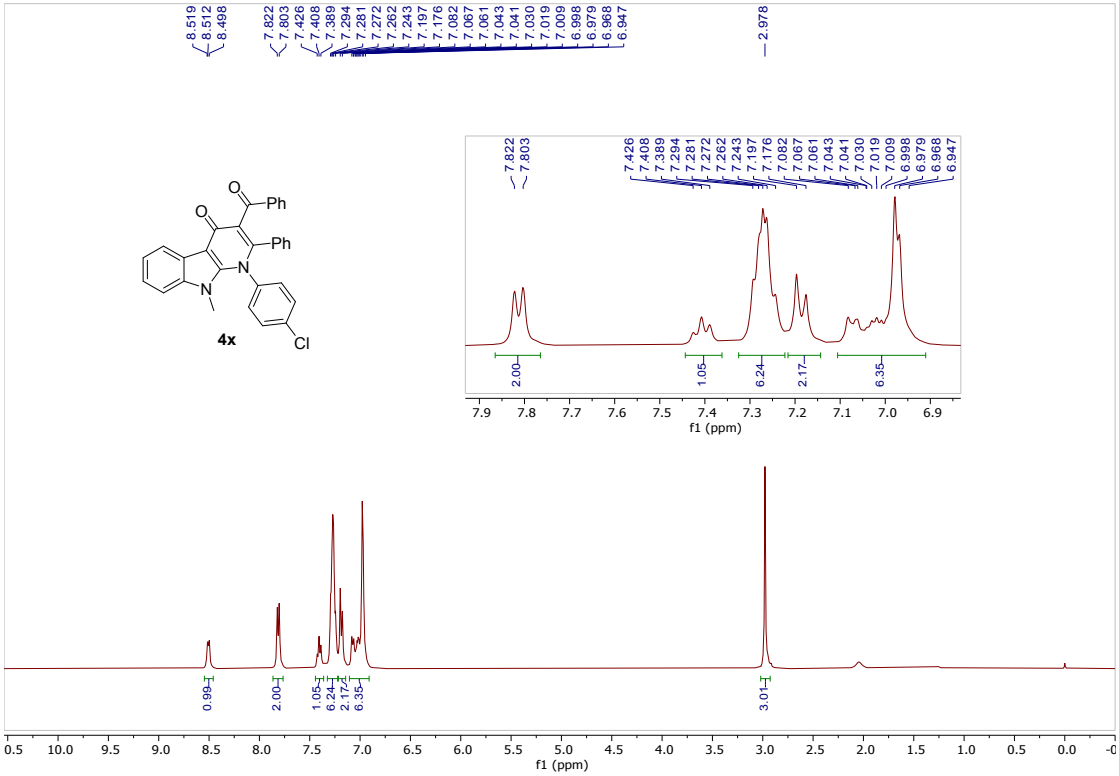
4w
f1 (ppm)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7.243
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7.082
7.067
7.061
7.043
7.041
7.030
7.019
7.009
6.998
6.979
6.968
6.947
2.978
Ph
O
Ph
N
N
Cl
4x
2.00
1.05
6.24
2.17
6.35
f1 (ppm)
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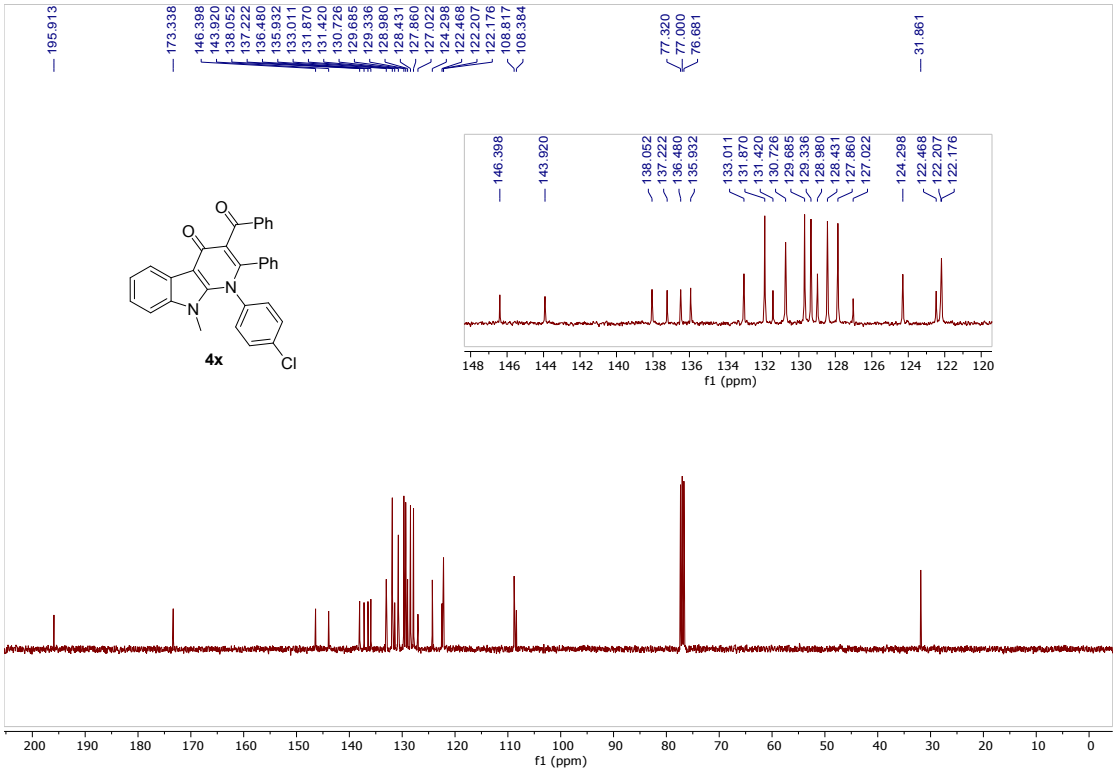
2.00
1.05
6.24
2.17
6.35
3.01
f1 (ppm)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128.431
127.860
127.022
124.298
122.468
122.207
122.176
108.817
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76.681
31.861
Ph
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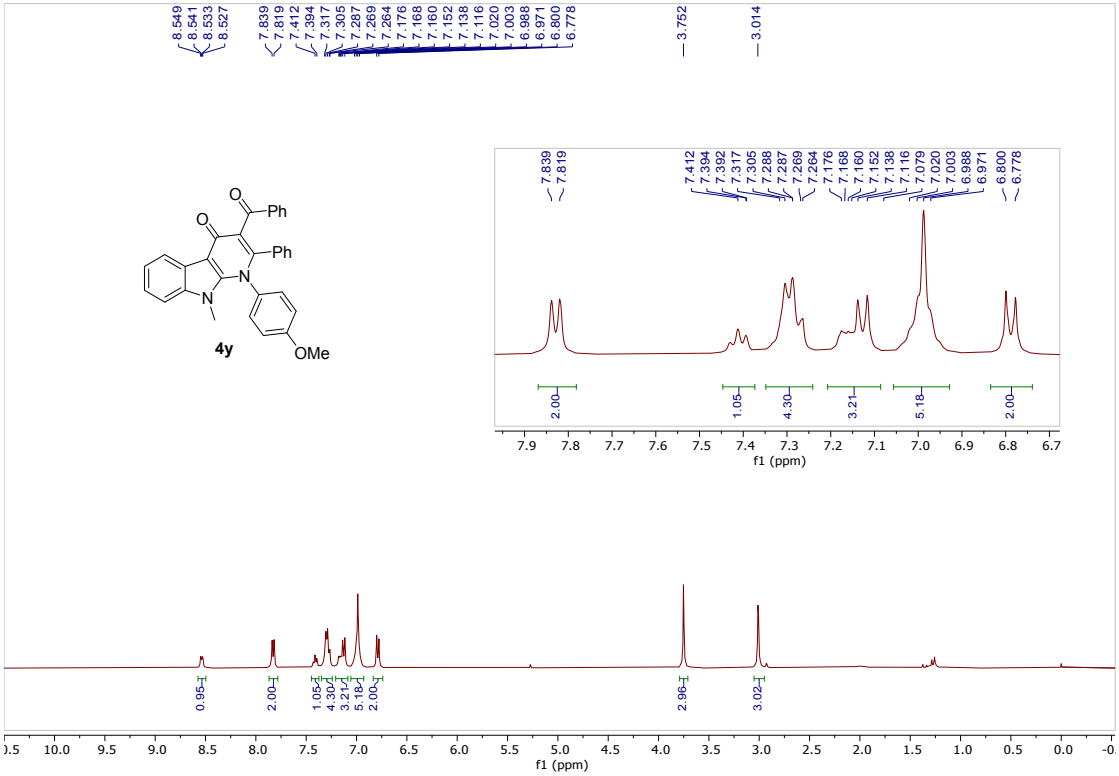
N
Cl
4x
f1 (ppm)
f1 (ppm)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7.176
7.168
7.160
7.152
7.138
7.116
7.020
7.003
6.988
6.971
6.800
6.778
3.752
3.014
O
Ph
O
Ph
N
N
OMe
4y
2.00
1.05
4.30
3.21
5.18
2.00
f1 (ppm)
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1.05
4.30
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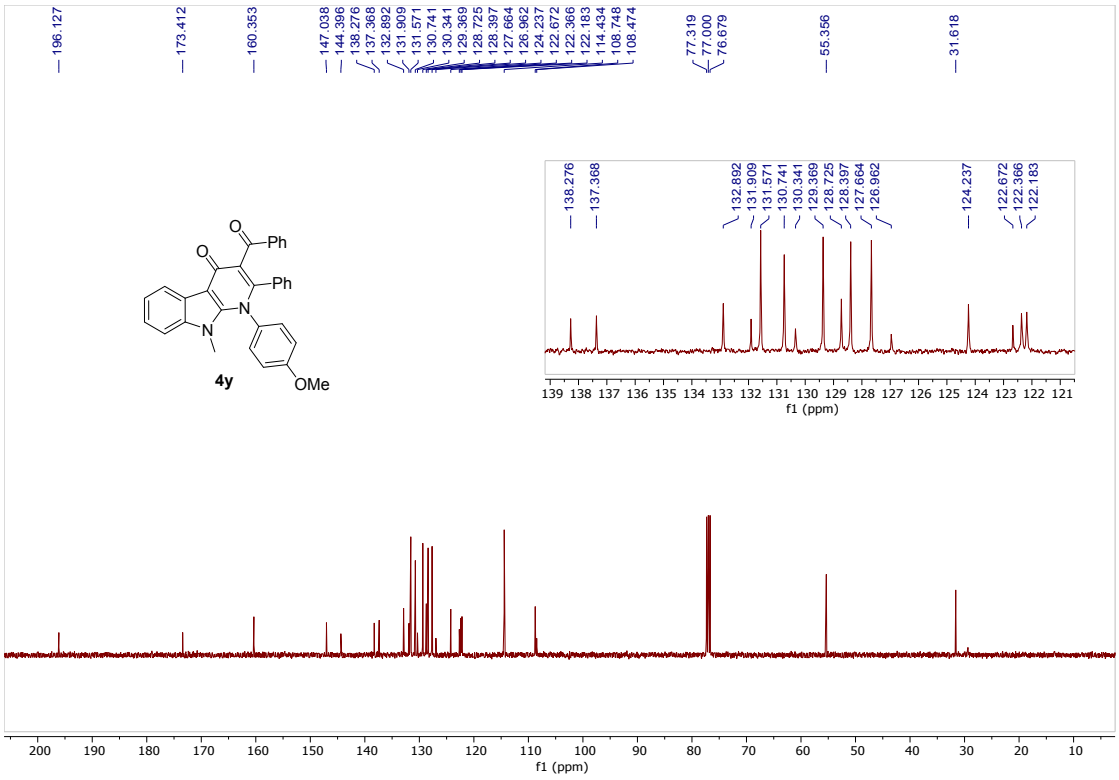
5.18
2.00
2.96
3.02
f1 (ppm)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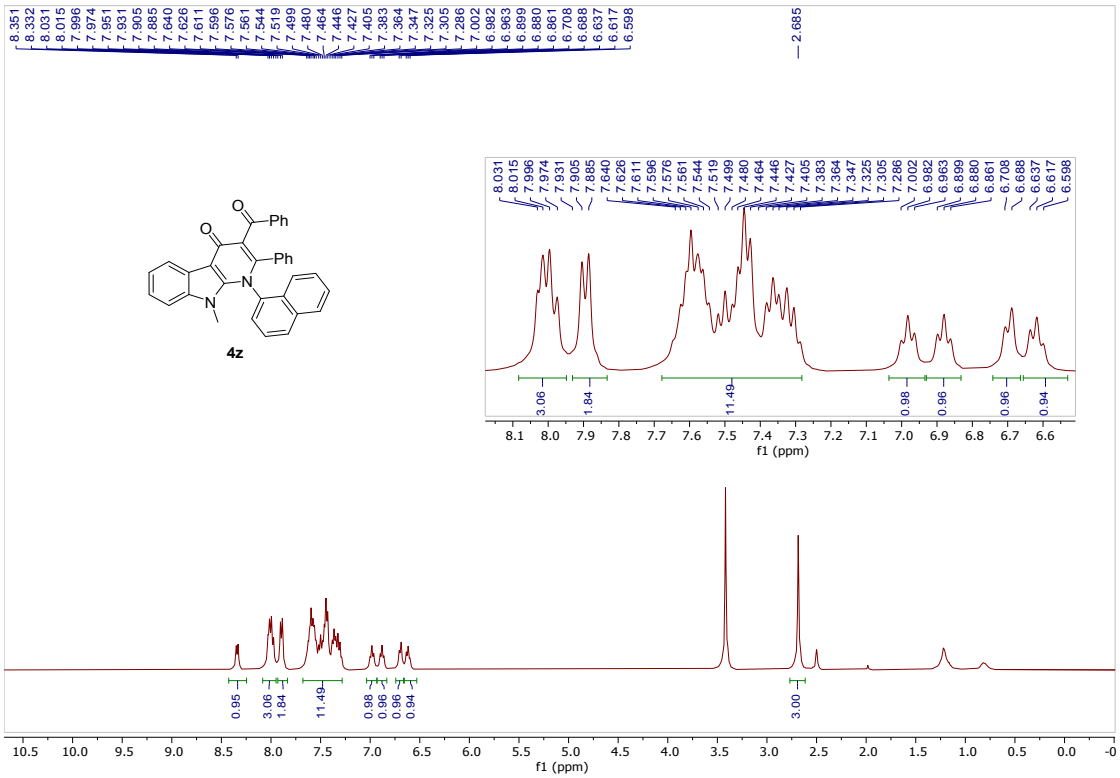
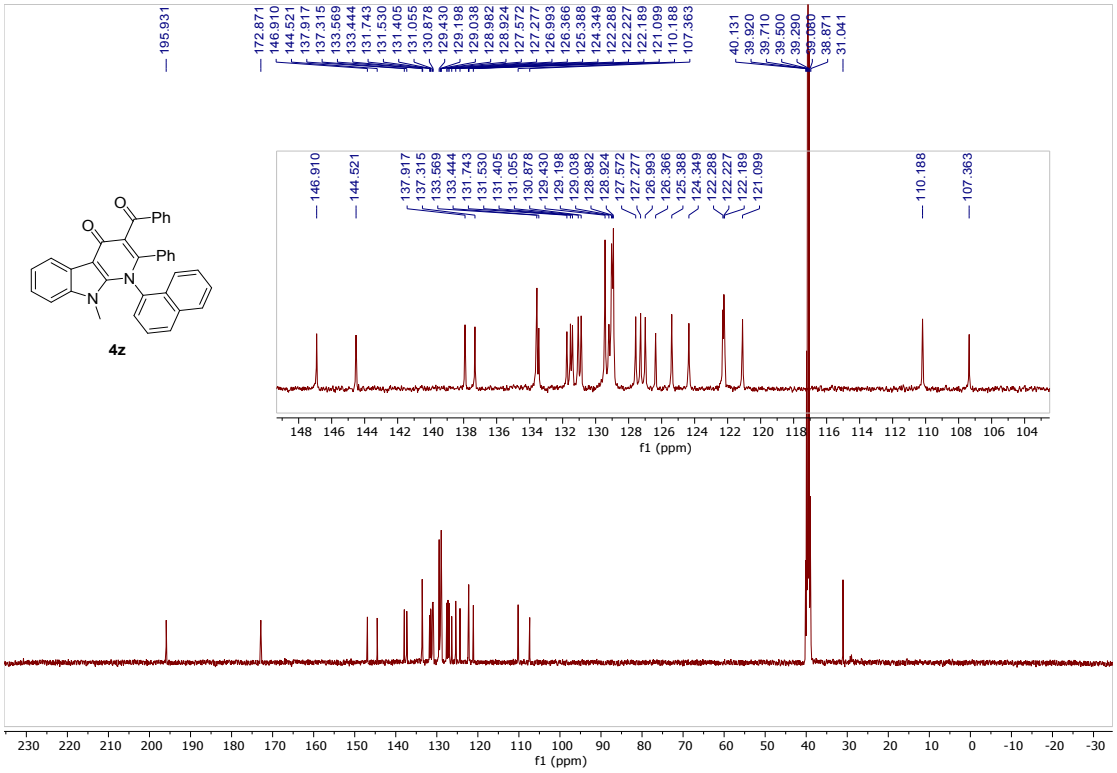
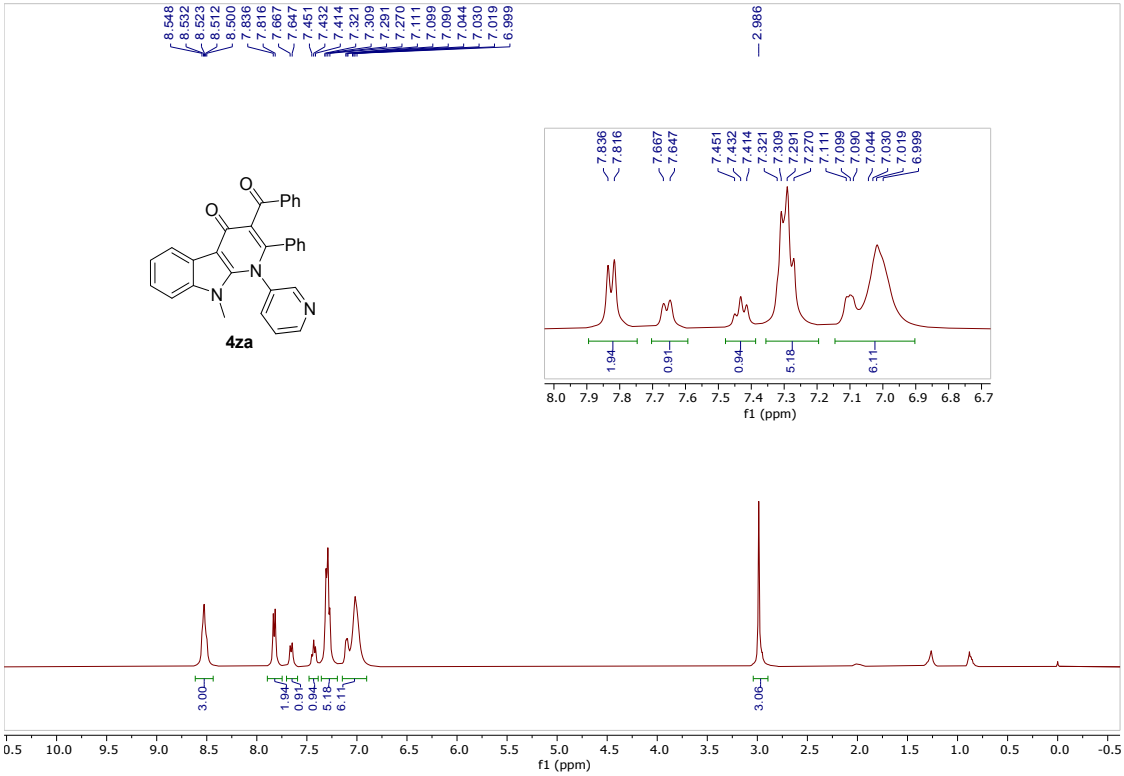
122.366
122.183
114.434
108.748
108.474
77.319
77.000
76.679
55.356
31.618
O
Ph
O
Ph
N
N
OMe
4y
f1 (ppm)
f1 (ppm)


4z
f1 (ppm)


4z
f1 (ppm)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7.432
7.414
7.321
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7.291
7.270
7.111
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7.044
7.030
7.019
6.999
2.986
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Ph
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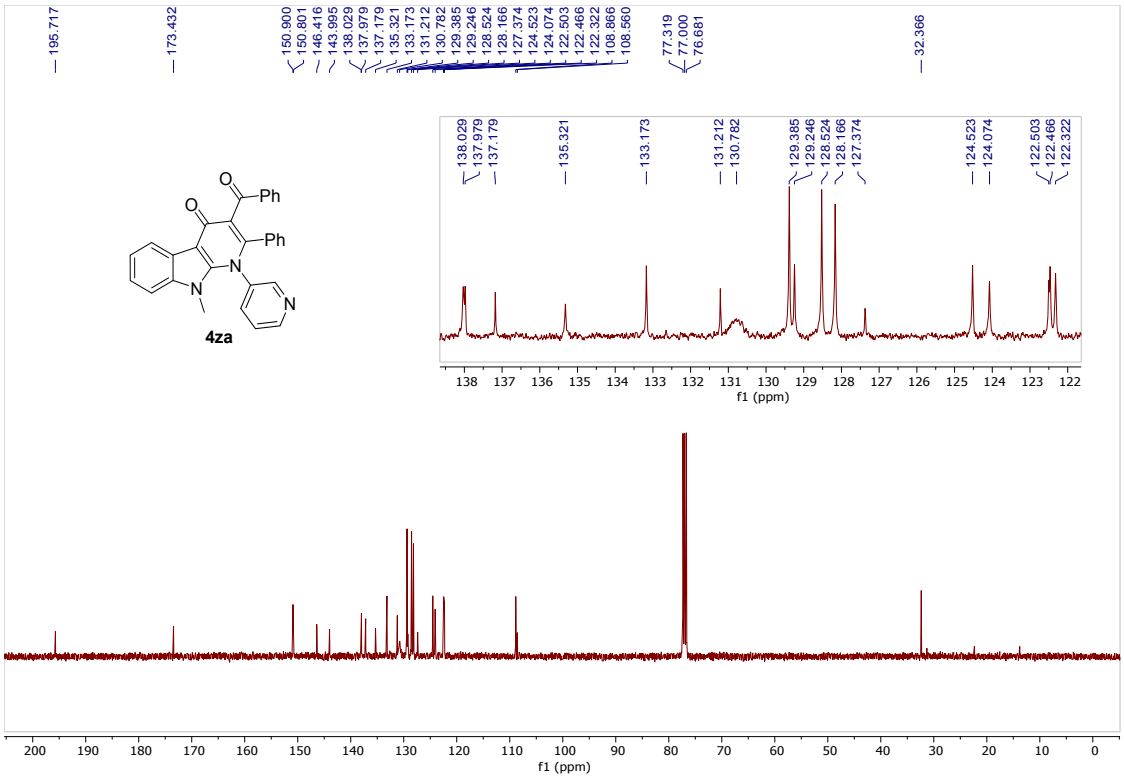
3.06
f1 (ppm)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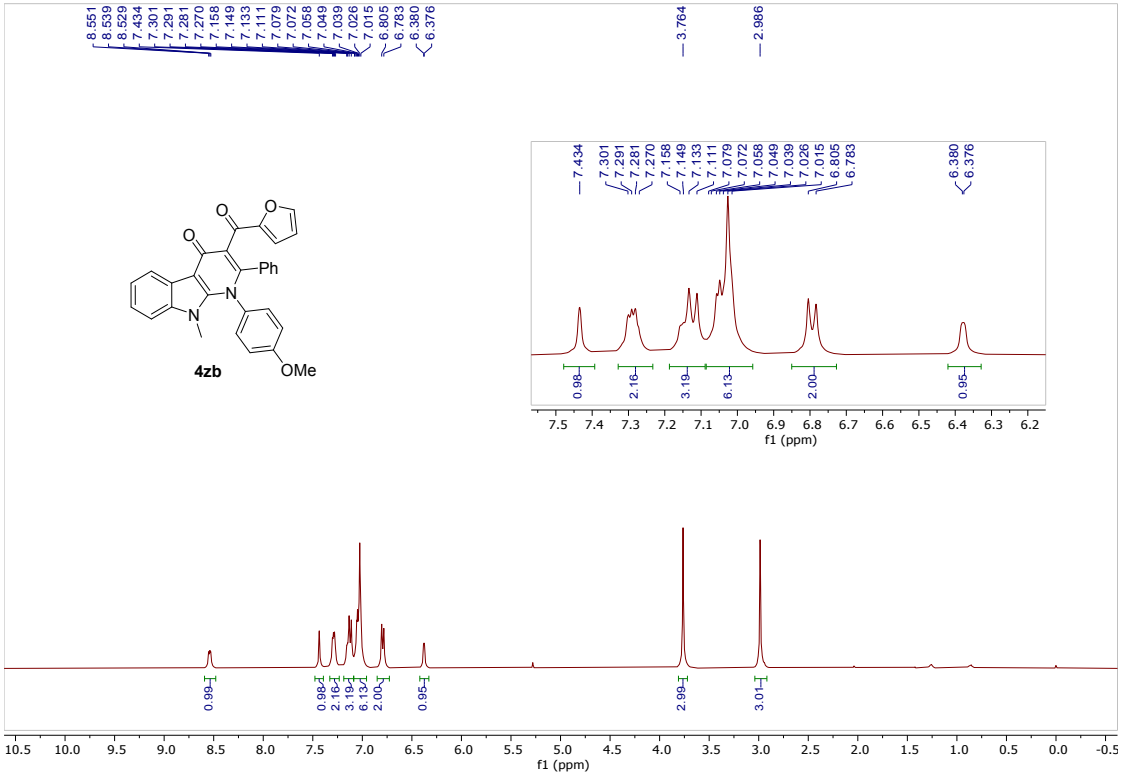
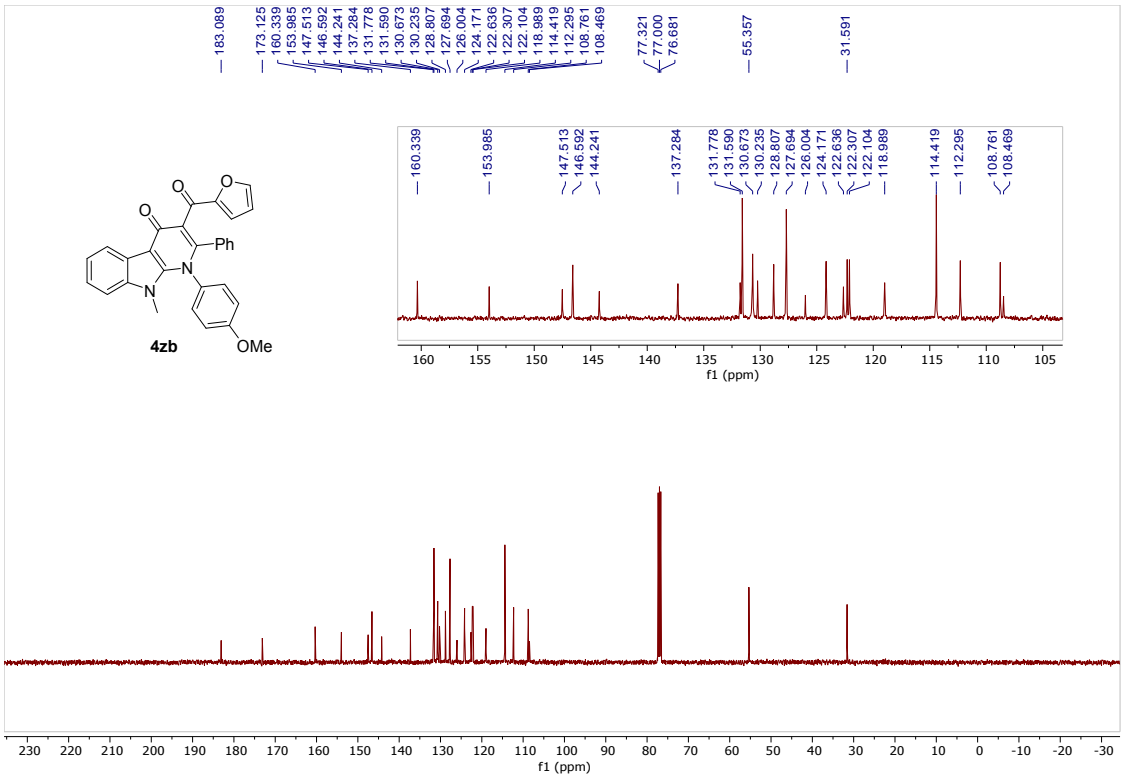
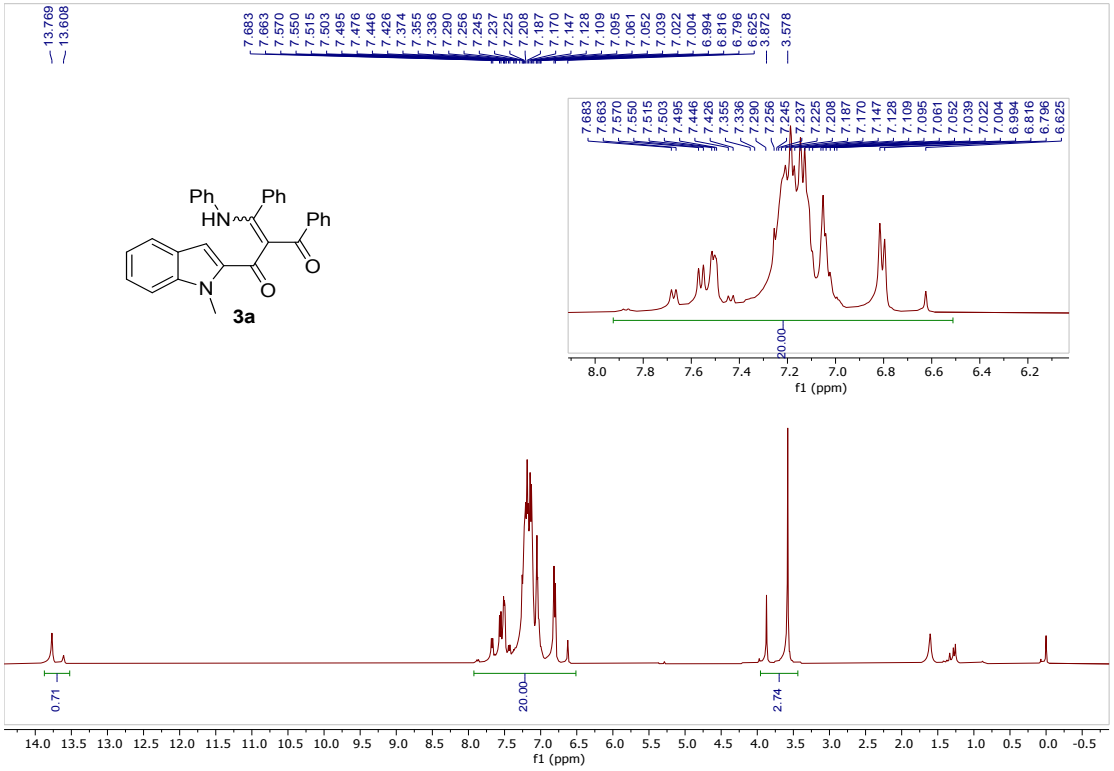
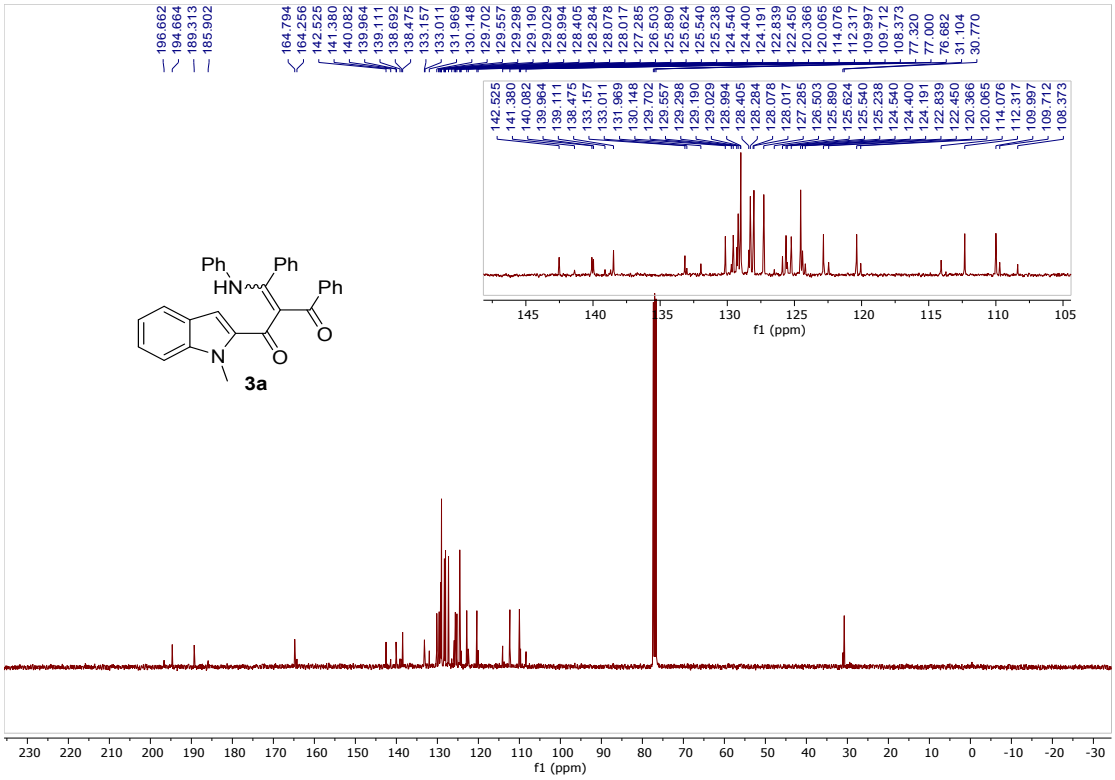
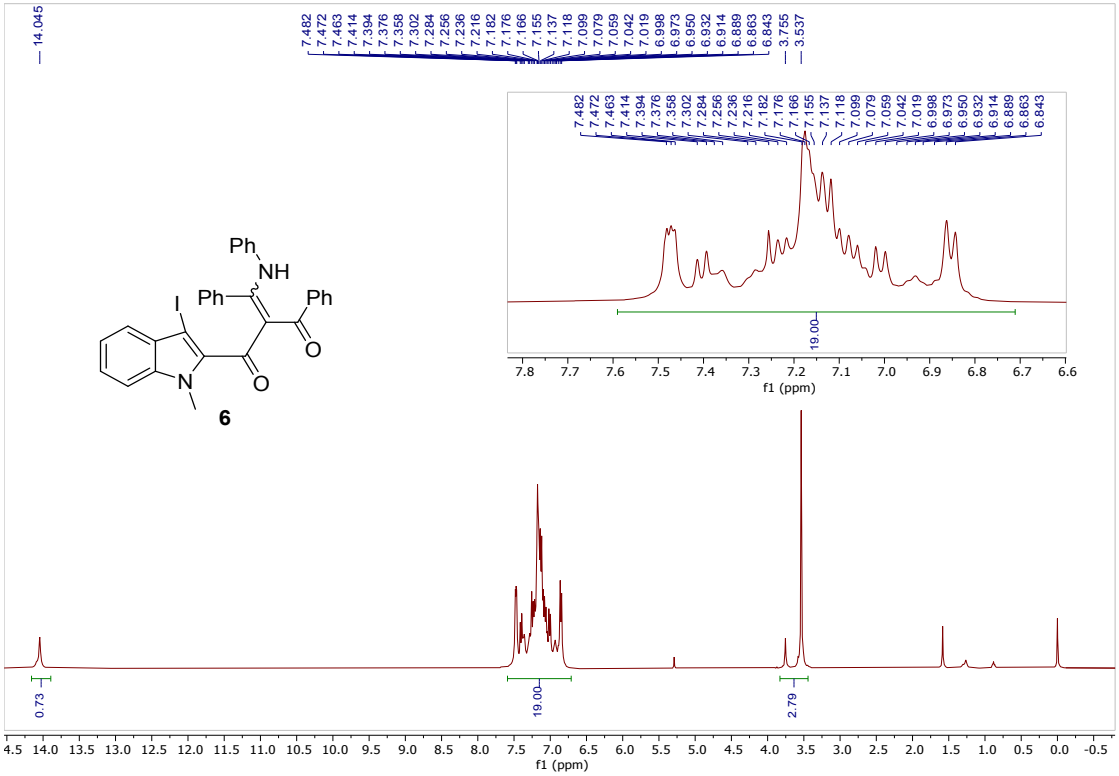
150.801
146.416
143.995
138.029
137.979
137.179
135.321
133.173
131.212
130.782
129.385
129.246
128.524
128.166
127.374
124.523
124.074
122.503
122.466
122.322
108.866
108.560
77.319
77.000
76.681
32.366
O
Ph
O
Ph
N
N
N
4za
f1 (ppm)

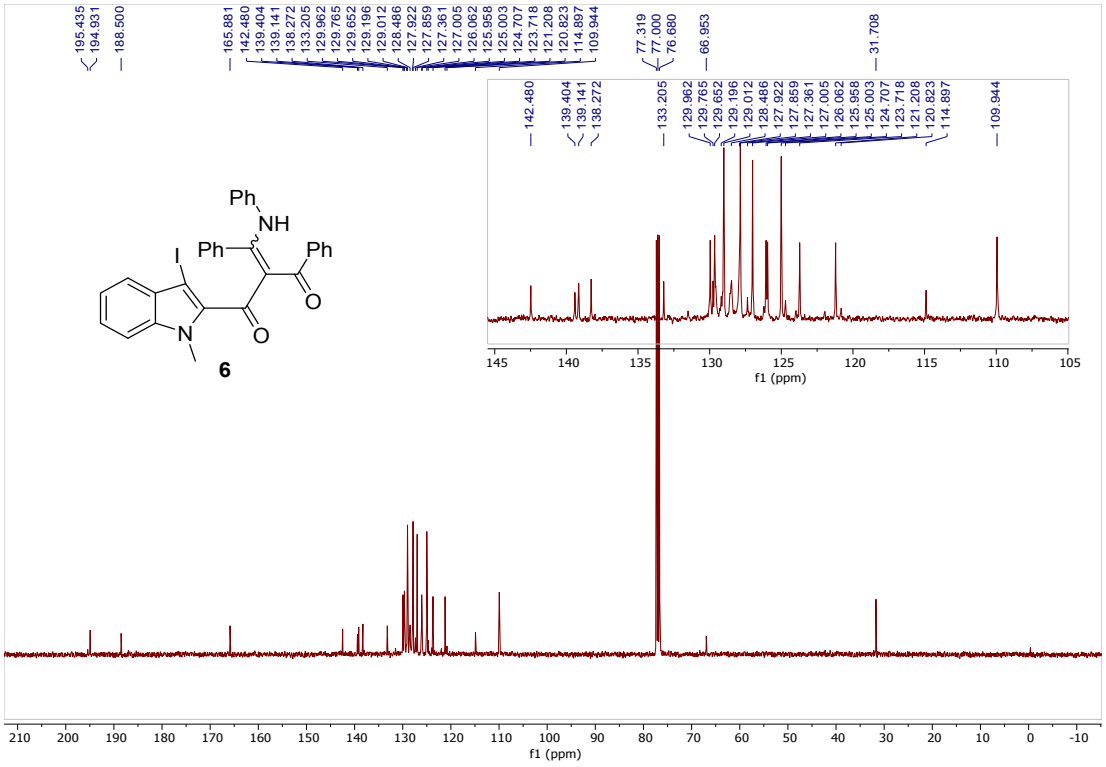

8.551
8.539
8.529
7.434
7.301
7.291
7.281
7.270
7.158
7.149
7.133
7.111
7.079
7.072
7.058
7.049
7.039
7.026
7.015
6.805
6.783
6.380
6.376
3.764
2.986
4zb
OMe
Ph
0.99
0.98
2.16
3.19
6.13
2.00
0.95
2.99
3.01
f1 (ppm)

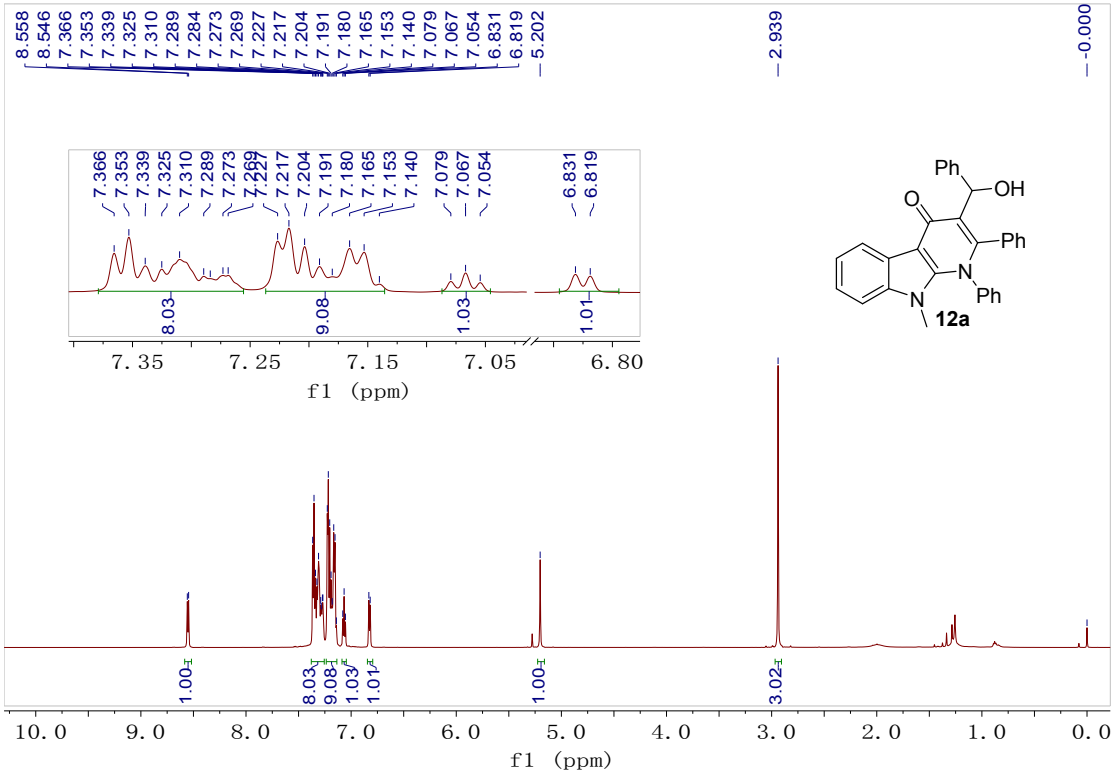

183.089
173.125
160.339
153.985
147.513
146.592
144.241
137.284
131.778
131.590
130.673
130.235
128.807
127.694
126.004
124.171
122.636
122.307
122.104
118.989
114.419
112.295
108.761
108.469
77.321
77.000
76.681
55.357
31.591
4zb
OMe
Ph
f1 (ppm)


13.769
13.608
7.683
7.663
7.570
7.550
7.515
7.503
7.495
7.476
7.446
7.426
7.374
7.355
7.336
7.290
7.256
7.245
7.237
7.225
7.208
7.187
7.170
7.147
7.128
7.109
7.095
7.061
7.052
7.039
7.022
7.004
6.994
6.816
6.796
6.625
3.872
3.578
Ph
HN
Ph
Ph
O
N
O
3a
20.00
f1 (ppm)
0.71
20.00
2.74
f1 (ppm)


196.662
194.664
189.313
185.902
164.794
164.256
142.525
141.380
140.082
139.964
139.111
138.692
138.475
133.157
133.011
131.969
130.148
129.702
129.557
129.298
129.190
129.029
128.994
128.405
128.284
128.078
128.017
127.285
126.503
125.890
125.624
125.540
125.238
124.540
124.400
124.191
122.839
122.450
120.366
120.065
114.076
112.317
109.997
109.712
108.373
77.320
77.000
76.682
31.104
30.770
Ph
HN
Ph
Ph
O
N
O
3a
f1 (ppm)
f1 (ppm)


Ph
NH
Ph
Ph
I
O
O
N
6
f1 (ppm)


Ph
NH
Ph
Ph
I
O
O
N
6
f1 (ppm)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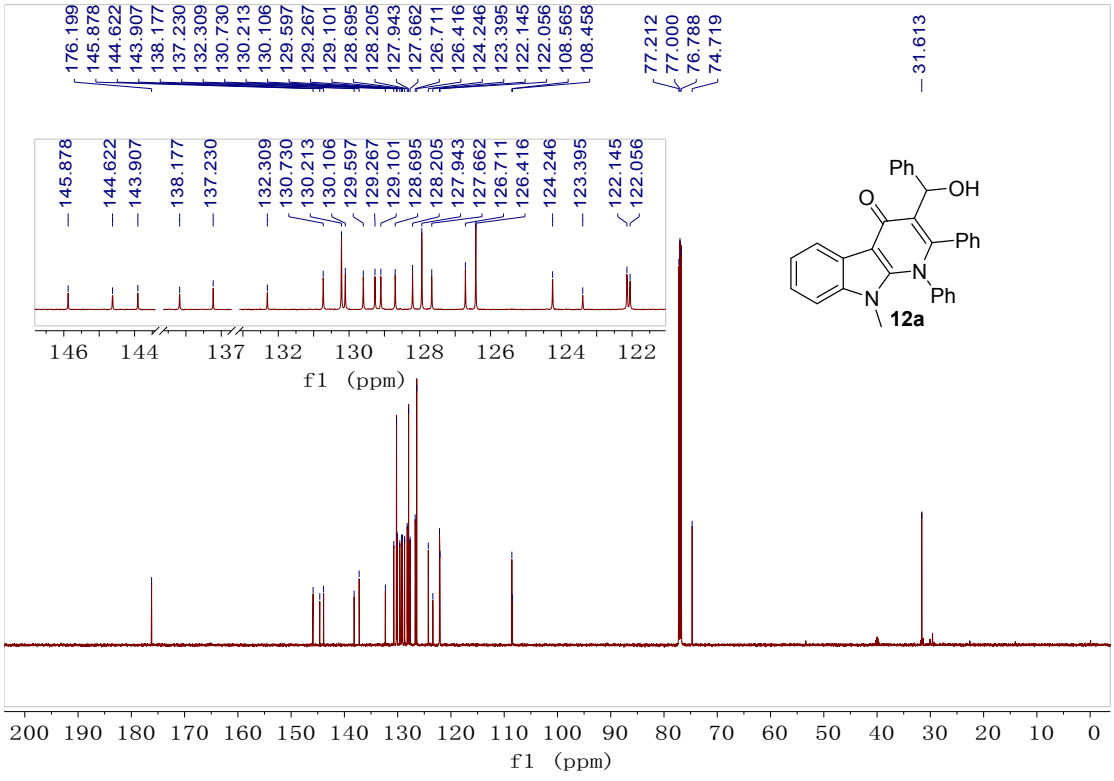
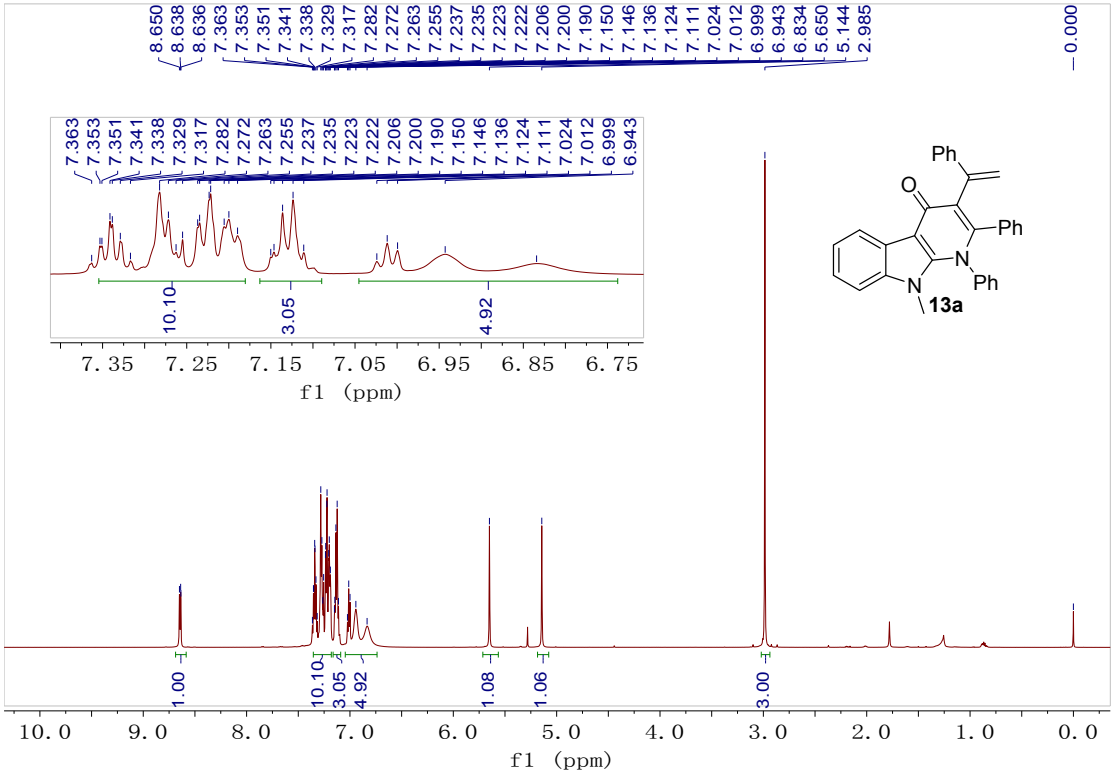
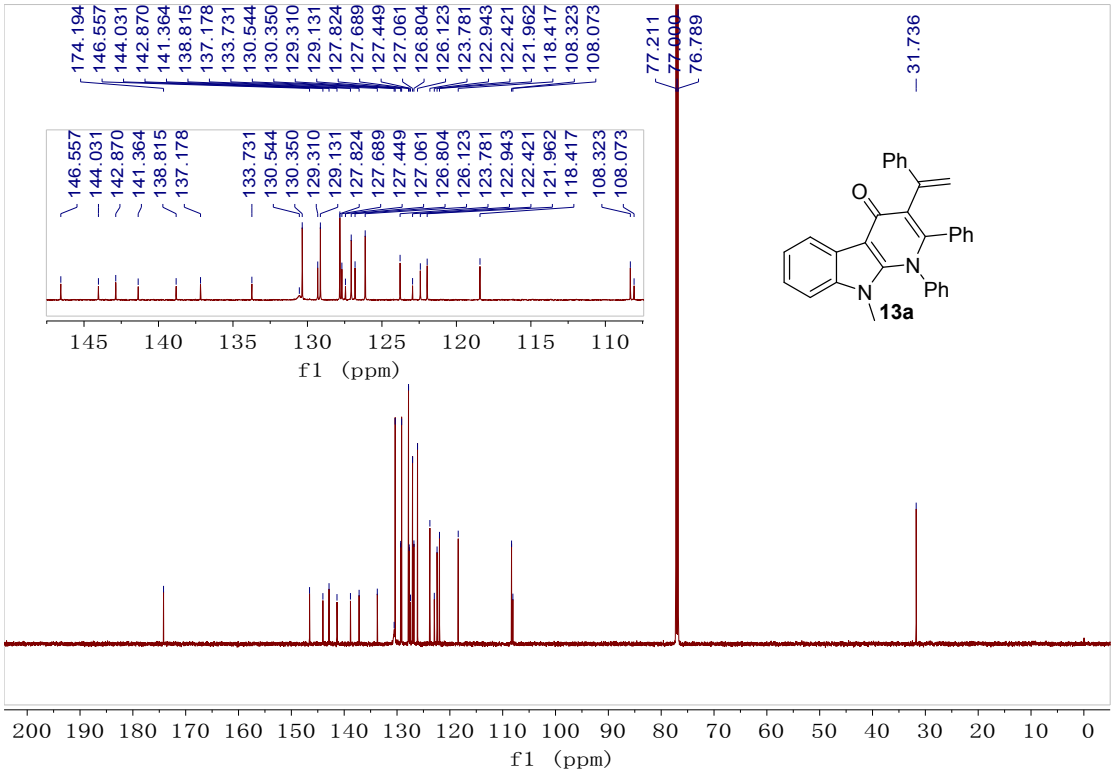
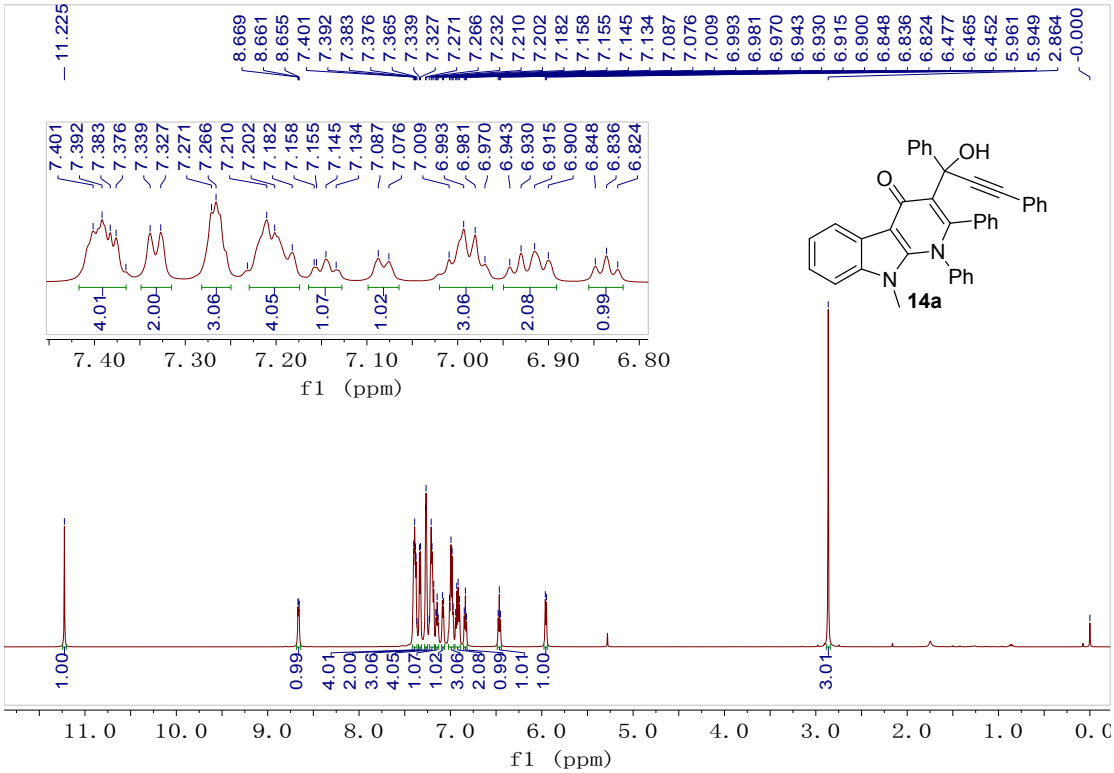
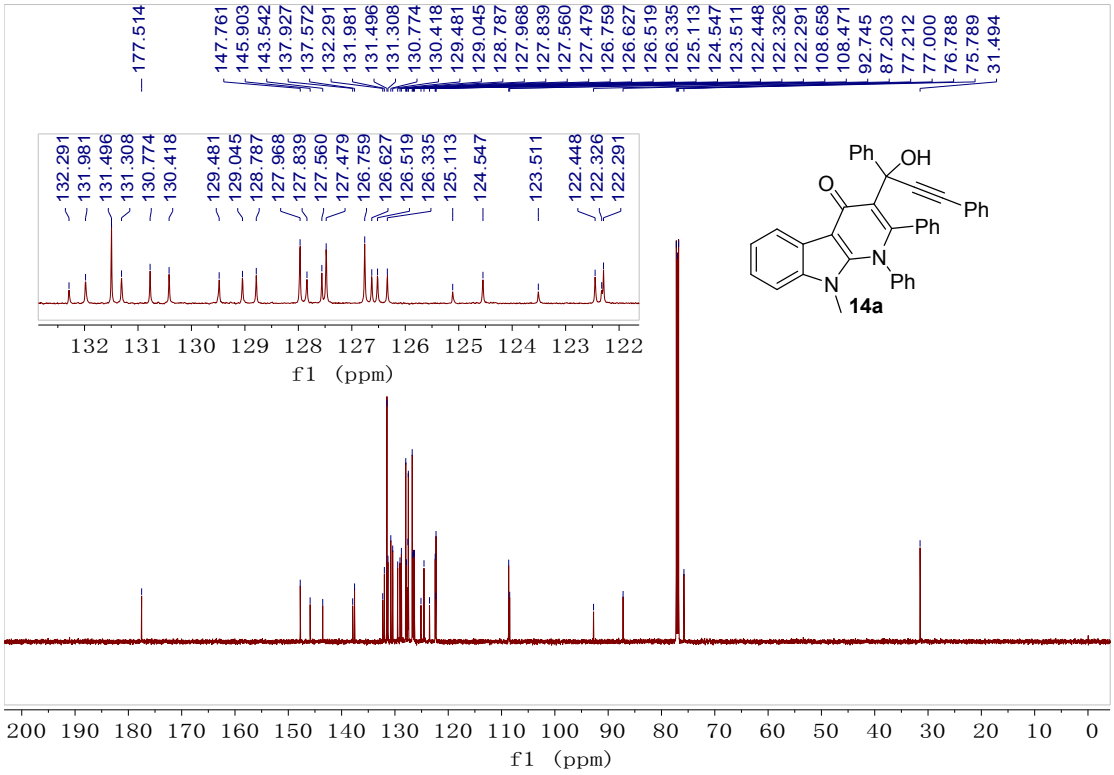
8.546
7.366
7.353
7.339
7.325
7.310
7.289
7.284
7.273
7.269
7.227
7.217
7.204
7.191
7.180
7.165
7.153
7.140
7.079
7.067
7.054
6.831
6.819
5.202
2.939
-0.000
8.03
9.08
1.03
1.01
1.00
3.02
Ph
OH
O
Ph
N
Ph
12a
f1 (ppm)

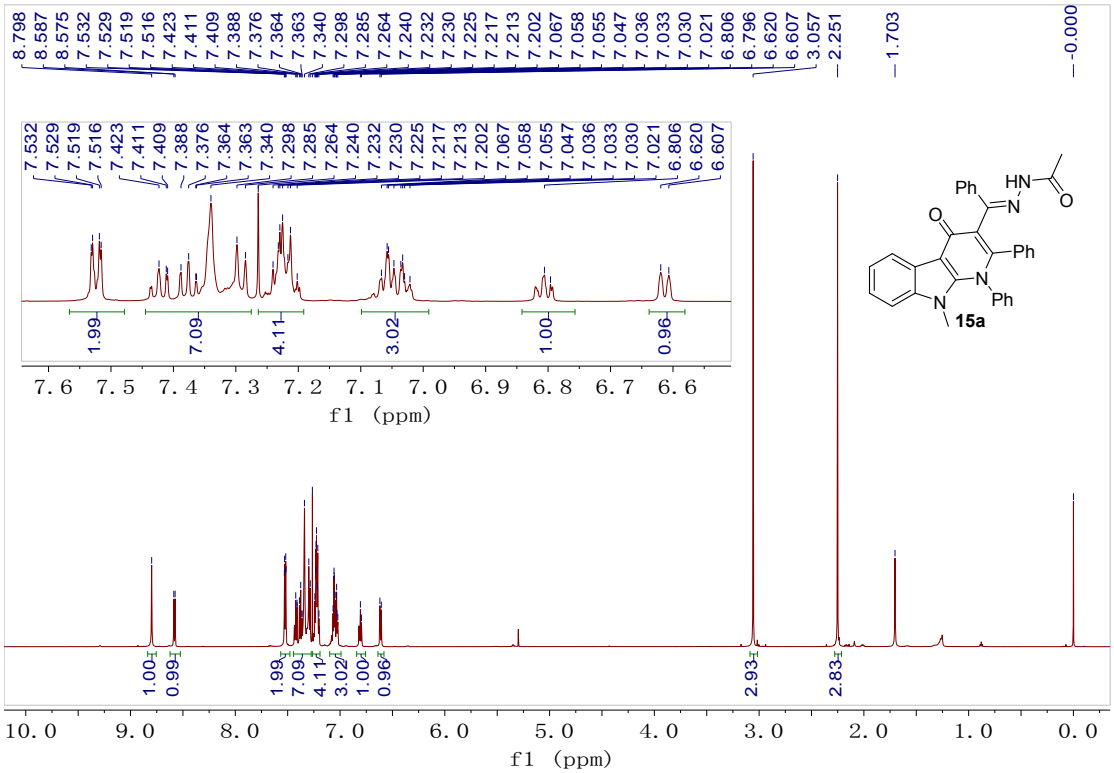

176.199
145.878
144.622
143.907
138.177
137.230
132.309
130.730
130.213
130.106
129.597
129.267
129.101
128.695
128.205
127.943
127.662
126.711
126.416
124.246
123.395
122.145
122.056
108.565
108.458
77.212
77.000
76.788
74.719
31.613
Ph
OH
O
Ph
N
Ph
12a
f1 (ppm)

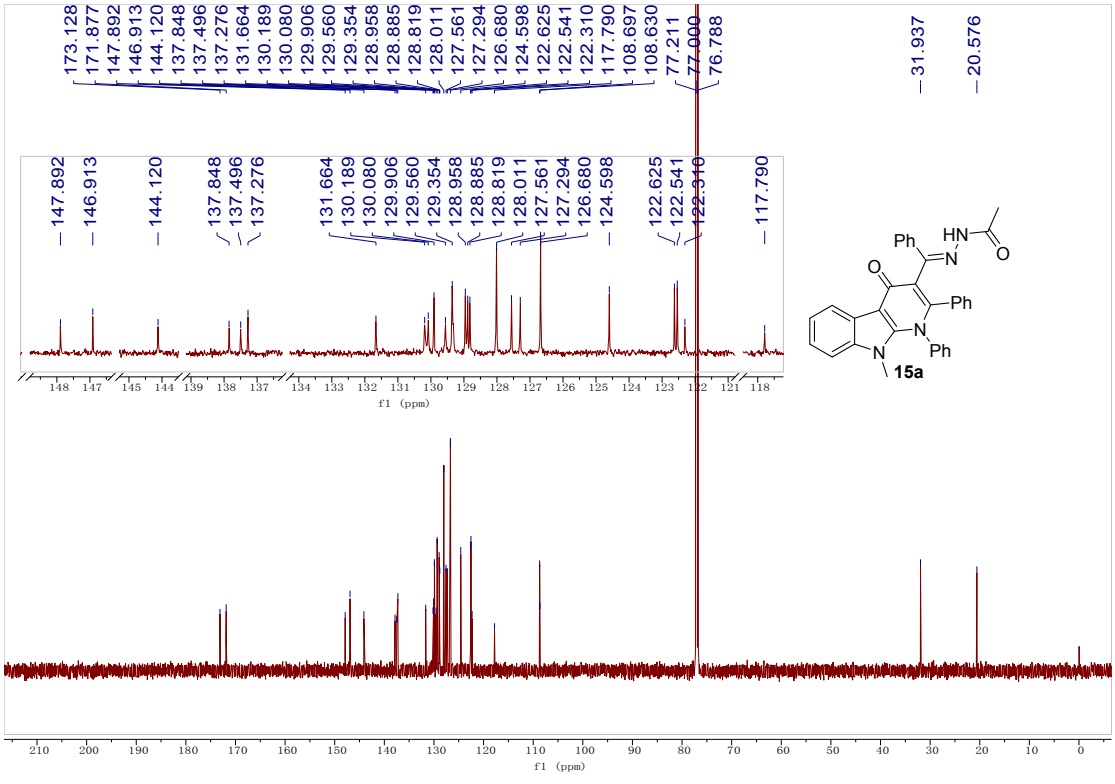

8.650 8.638 8.636 7.363 7.353 7.351 7.341 7.338 7.329 7.317 7.282 7.272 7.263 7.255 7.237 7.235 7.223 7.222 7.206 7.200 7.190 7.150 7.146 7.136 7.124 7.111 7.024 7.012 6.999 6.943 6.834 5.650 5.144 2.985 0.000
10.10 3.05 4.92
7.35 7.25 7.15 7.05 6.95 6.85 6.75
f1 (ppm)
Ph O Ph N Ph N 13a
1.00 10.10 3.05 4.92 1.08 1.06 3.00
10.0 9.0 8.0 7.0 6.0 5.0 4.0 3.0 2.0 1.0 0.0
f1 (ppm)


174.194 146.557 144.031 142.870 141.364 138.815 137.178 133.731 130.544 130.350 129.310 129.131 127.824 127.689 127.449 127.061 126.804 126.123 123.781 122.943 122.421 121.962 118.417 108.323 108.073 77.211 77.000 76.789 31.736
145 140 135 130 125 120 115 110
f1 (ppm)
Ph O Ph N Ph N 13a
200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0
f1 (ppm)

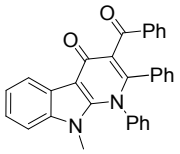

11.225
8.669
8.661
8.655
7.401
7.392
7.383
7.376
7.365
7.339
7.327
7.271
7.266
7.232
7.210
7.202
7.182
7.158
7.155
7.145
7.134
7.087
7.076
7.009
6.993
6.981
6.970
6.943
6.930
6.915
6.900
6.848
6.836
6.824
6.477
6.465
6.452
5.961
5.949
2.864
-0.000
4.01
2.00
3.06
4.05
1.07
1.02
3.06
2.08
0.99
7.40
7.30
7.20
7.10
7.00
6.90
6.80
f1 (ppm)
Ph
OH
O
Ph
Ph
N
N
Ph
14a
1.00
0.99
4.01
2.00
3.06
4.05
1.07
1.02
3.06
2.08
0.99
1.01
1.00
3.01
11.0
10.0
9.0
8.0
7.0
6.0
5.0
4.0
3.0
2.0
1.0
f1 (ppm)


177.514
147.761
145.903
143.542
137.927
137.572
132.291
131.981
131.496
131.308
130.774
130.418
129.481
129.045
128.787
127.968
127.839
127.560
127.479
126.759
126.627
126.519
126.335
125.113
124.547
123.511
122.448
122.326
122.291
108.658
108.471
92.745
87.203
77.212
77.000
76.788
75.789
31.494
132
131
130
129
128
127
126
125
124
123
122
f1 (ppm)
Ph
OH
O
Ph
Ph
N
N
Ph
14a
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
f1 (ppm)


f1 (ppm)
15a

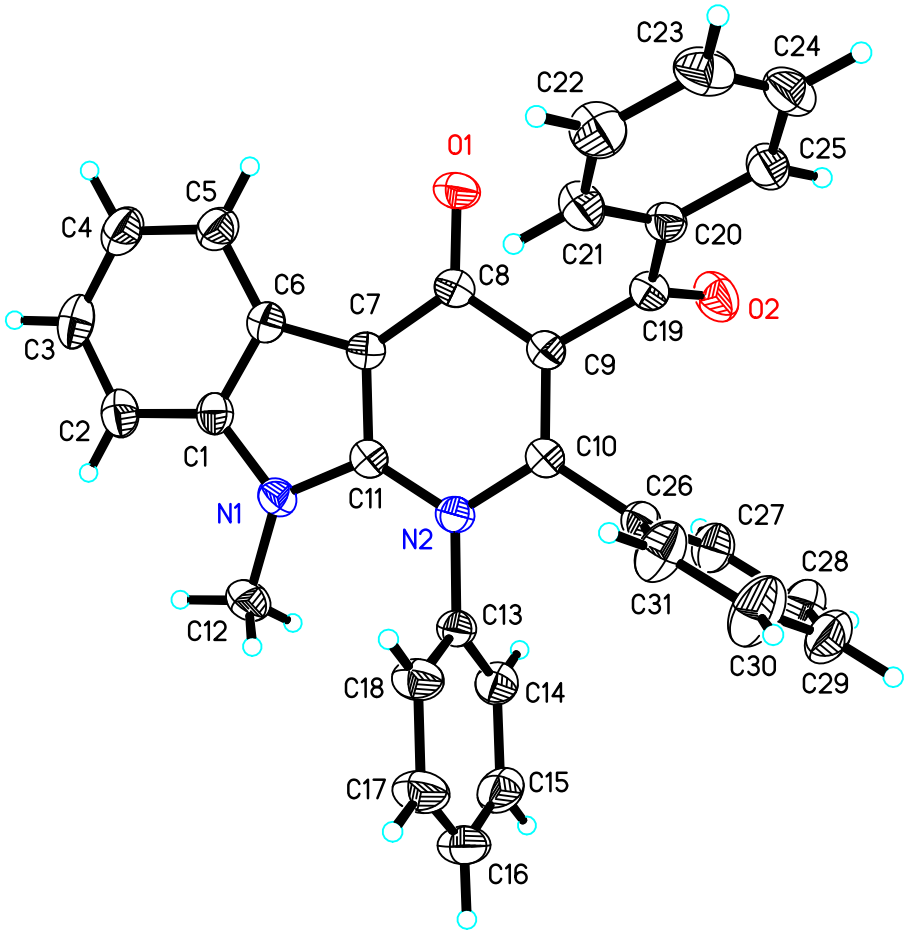

f1 (ppm)
15a

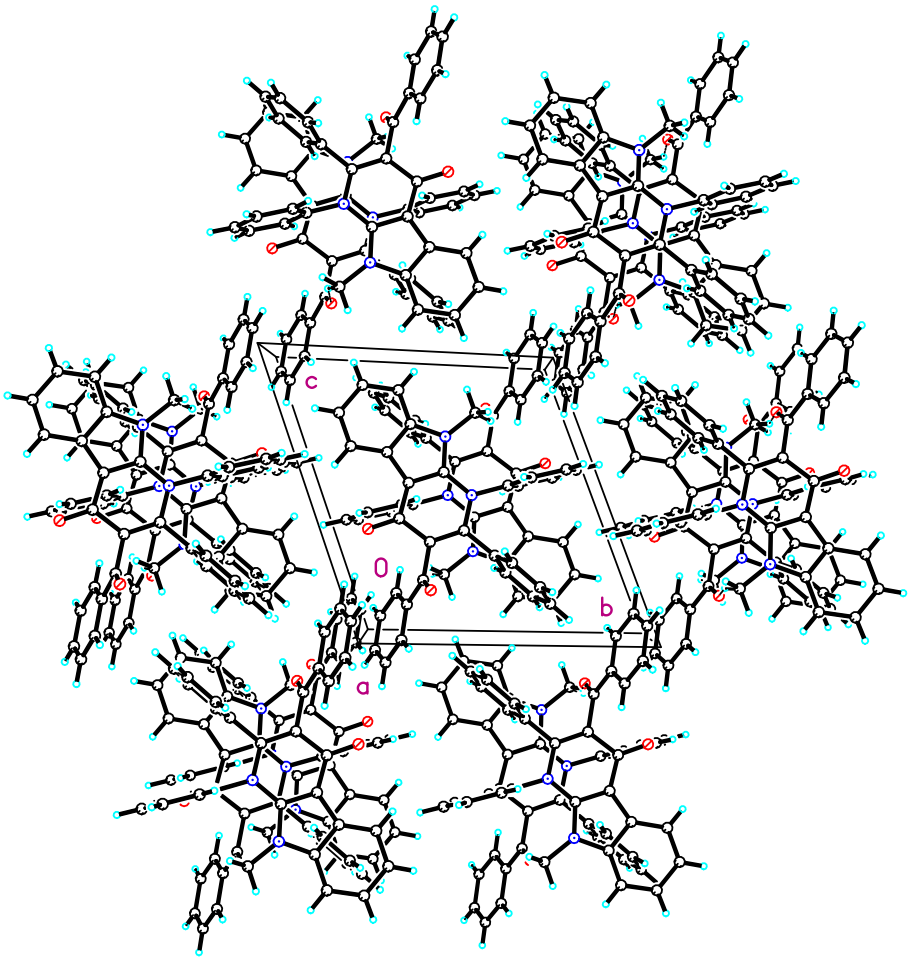
7. X-ray Crystallography of Compounds 4a, 5a, 6
3-benzoyl-9-methyl-1,2-diphenyl-1,9-dihydro-4H-pyrido[2,3-b]indol-4-one (4a, CCDC 1905133)
(Ortep ellipsoids are depicted at the 50% level)



Crystal data and structure refinement for **4a**

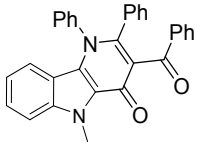
Idenfication code	**4a**
Empirical formula	$C_{31}H_{22}N_2O_2$
Formula weight	454.50
Temperature	296(2) K
Wavelength	0.71073 Å
Crystal system	Triclinic
Space group	P-1
Unit cell dimensions	a = 9.937(2) Å α= 103.522(6)°. b = 11.632(2) Å β= 107.357(6)°. c = 12.077(2) Å γ= 108.565(6)°.
Volume	1176.8(4) $Å^3$
Z	2
Density (calculated)	1.283 Mg/m^3
Absorption coefficient	0.081 mm^{-1}
F(000)	476
Crystal size	0.200 x 0.170 x 0.130 mm^3
Theta range for data collection	2.364 to 25.999°.
Index ranges	-12<=h<=12, -14<=k<=14, -14<=l<=14
Reflections collected	20851
Independent reflections	4594 [R(int) = 0.0434]
Completeness to theta = 25.242°	99.3 %
Absorption correction	Semi-empirical from equivalents
Max. and min. transmission	0.7456 and 0.6319
Refinement method	Full-matrix least-squares on F^2
Data / restraints / parameters	4594 / 1 / 318
Goodness-of-fit on F^2	1.042
Final R indices [I>2sigma(I)]	R1 = 0.0444, wR2 = 0.1175
R indices (all data)	R1 = 0.0560, wR2 = 0.1286
Extinction coefficient	0.068(9)
Largest diff. peak and hole	0.205 and -0.155 $e.Å^{-3}$


C23
C24
C22
C25
O1
C5
C4
C21
C20
C8
C6
C7
O2
C19
C3
C9
C2
C1
C10
C26
C11
N1
C27
N2
C28
C31
C12
C13
C30
C18
C14
C29
C17
C15
C16


c
0
b
a

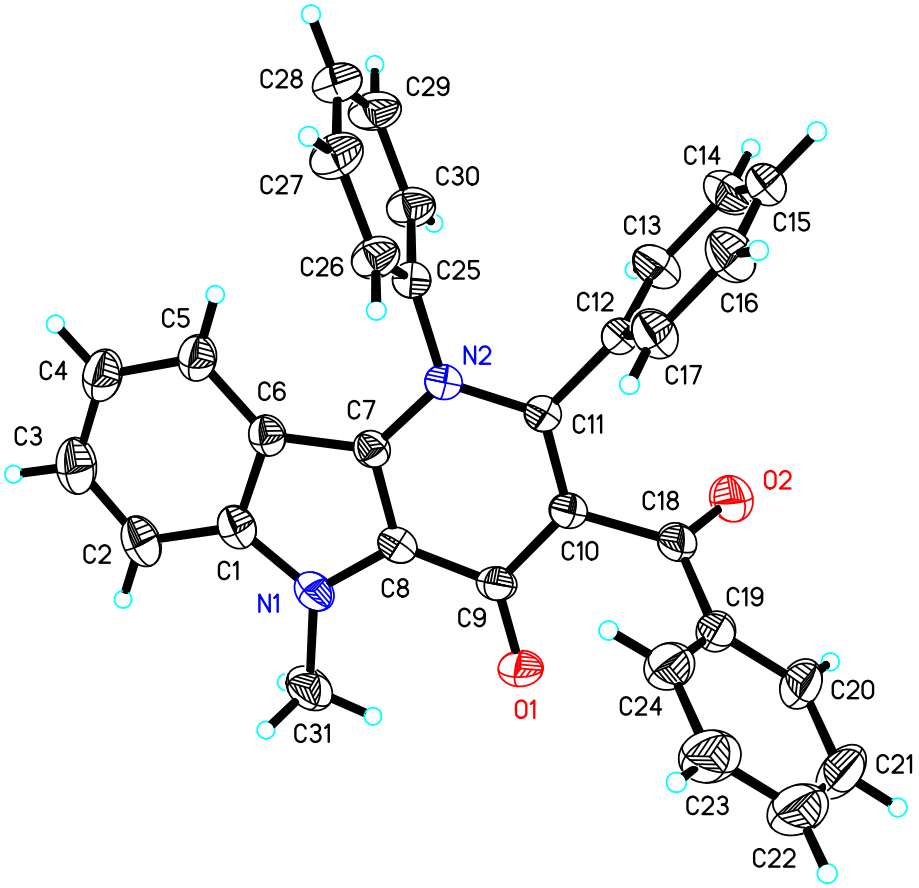
3-benzoyl-5-methyl-1,2-diphenyl-1,5-dihydro-4H-pyrido[3,2-b]indol-4-one (5a, CCDC 1905134)

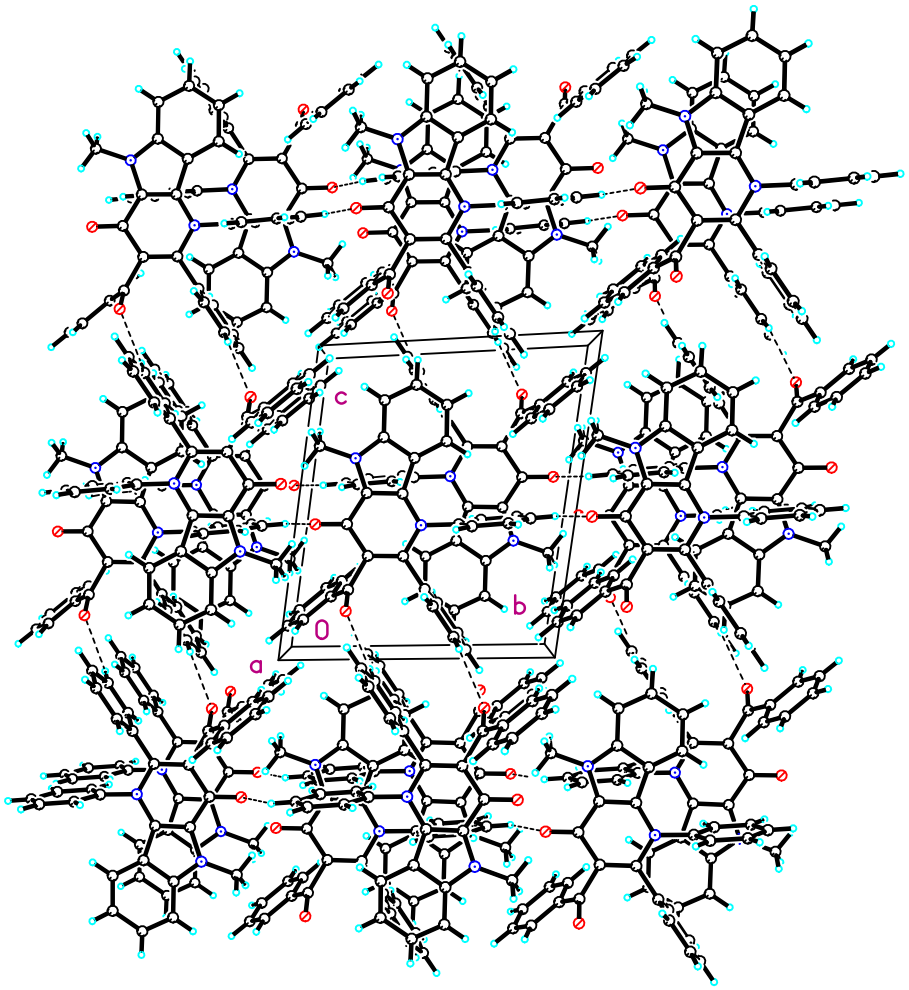
(Ortep ellipsoids are depicted at the 50% level)



Crystal data and structure refinement for **5a**

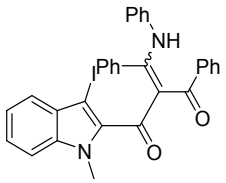
Idenfication code	**5a**
Empirical formula	$C_{31}H_{22}N_2O_2$
Formula weight	454.50
Temperature	296(2) K
Wavelength	0.71073 Å
Crystal system	Triclinic
Space group	P-1
Unit cell dimensions	a = 9.8266(3) Å α= 77.5020(10)°. b = 11.0583(3) Åβ= 79.6760(10)°. c = 12.1317(4) Åγ= 69.1700(10)°.
Volume	1195.36(6) $Å^3$
Z	2
Density (calculated)	1.263 Mg/m^3
Absorption coefficient	0.079mm^{-1}
F(000)	476
Crystal size	0.200 x 0.160 x 0.110 mm^3
Theta range for data collection	2.416 to 26.000°.
Index ranges	-12<=h<=12, -13<=k<=13, -14<=l<=14
Reflections collected	17427
Independent reflections	4671 [R(int) = 0.0537]
Completeness to theta = 25.242°	99.5 %
Absorption correction	Semi-empirical from equivalents
Max. and min. transmission	0.7456 and 0.6660
Refinement method	Full-matrix least-squares on F^2
Data / restraints / parameters	4671 / 0 / 318
Goodness-of-fit on F^2	1.055
Final R indices [I>2sigma(I)]	R1 = 0.0627, wR2 = 0.1766
R indices (all data)	R1 = 0.0878, wR2 = 0.2007
Extinction coefficient	0.036(12)
Largest diff. peak and hole	0.236 and -0.237 e.$Å^{-3}$


C28
C29
C27
C30
C26
C25
C14
C15
C13
C16
C12
C17
C5
N2
C4
C6
C7
C11
C3
O2
C18
C2
C1
C10
N1
C8
C19
C9
O1
C24
C20
C31
C21
C23
C22


c
b
0
a

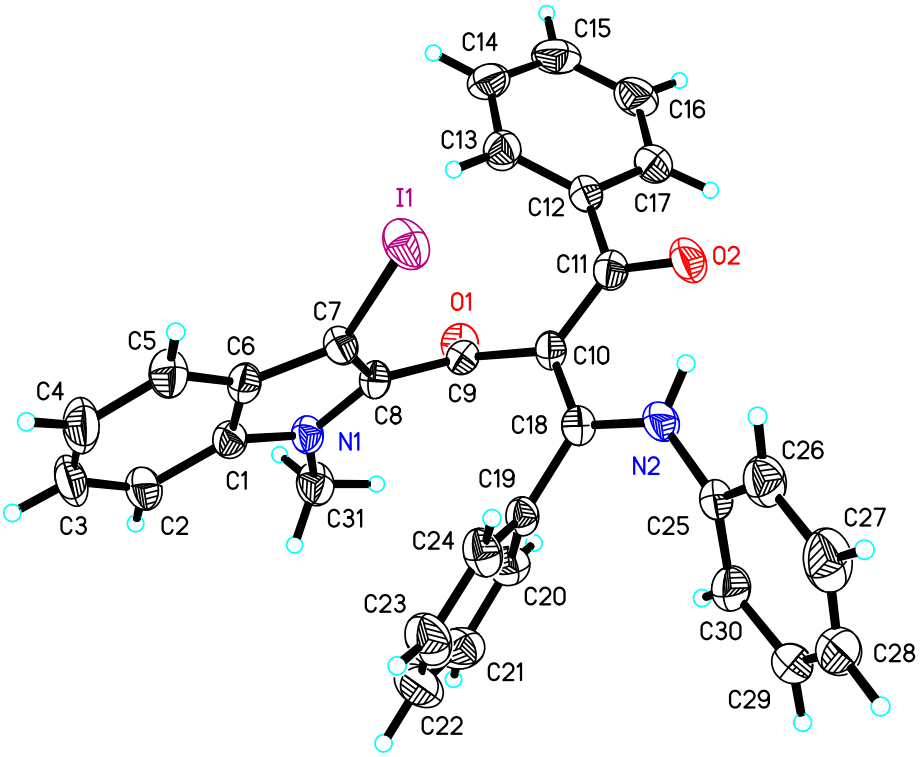
1-(3-iodo-1-methyl-1H-indol-2-yl)-3-phenyl-2-(phenyl(phenylamino)methylene) propane-1,3-dione (6, CCDC 1916642)

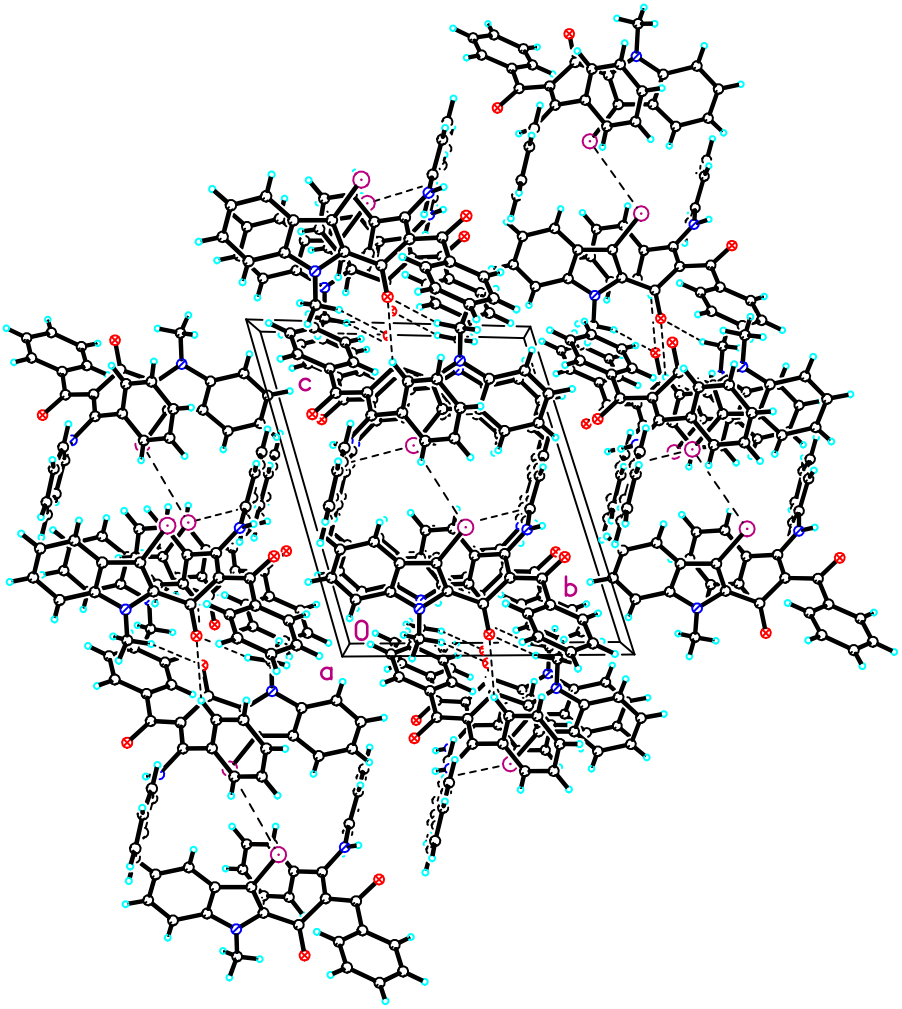
(Ortep ellipsoids are depicted at the 50% level)



Crystal data and structure refinement for **6**

Idenfication code	**6**
Empirical formula	$C_{31}H_{23}IN_2O_2$
Formula weight	582.41
Temperature	293(2) K
Wavelength	0.71073 Å
Crystal system	Triclinic
Space group	P-1
Unit cell dimensions	a = 9.1580(5) Å α= 100.582(2)°. b = 11.6088(7) Åβ= 108.208(2)°. c = 14.1255(8) Åγ= 106.392(2)°.
Volume	1306.25(13) $Å^3$
Z	2
Density (calculated)	1.481 Mg/m^3
Absorption coefficient	1.256mm^{-1}
F(000)	584
Crystal size	0.1500.11 x 0.05mm^3
Theta range for data collection	2.093 to 25.999°.
Index ranges	-11<=h<=11, -14<=k<=14, -17<=l<=17
Reflections collected	18716
Independent reflections	5130 [R(int) = 0.0550]
Completeness to theta = 25.242°	99.8 %
Absorption correction	Semi-empirical from equivalents
Max. and min. transmission	0.7456 and 0.5579
Refinement method	Full-matrix least-squares on F^2
Data / restraints / parameters	5130 / 0 / 327
Goodness-of-fit on F^2	1.067
Final R indices [I>2sigma(I)]	R1 = 0.0487, wR2 = 0.1423
R indices (all data)	R1 = 0.0688, wR2 = 0.1635
Largest diff. peak and hole	0.649 and -0.768 e.$Å^{-3}$


C14
C15
C16
C13
C12
C17
I1
C11
O2
C7
O1
C5
C6
C10
C4
C8
C9
C18
N1
N2
C26
C1
C19
C31
C3
C2
C24
C25
C27
C20
C23
C30
C28
C21
C29
C22


c
b
0
a