One-pot and metal-free synthesis of atropisomeric carbazolyl-indoles by a facile [4+2]-benzannulation in ethanol and investigation of their photoluminescence property

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Supporting Information

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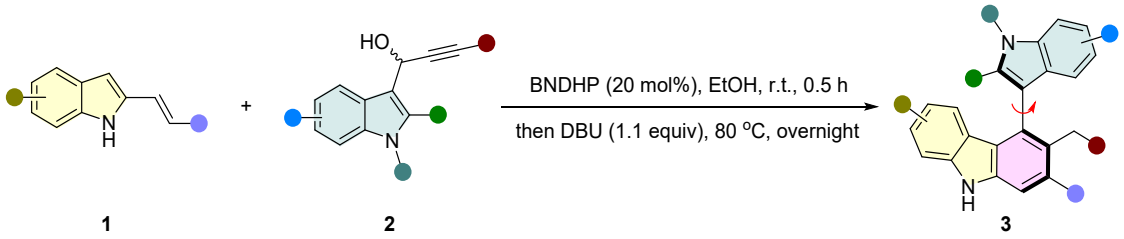
1. General Information

High Performance Liquid Chromatography (HPLC) was analyzed by chiral column in comparison with authentic racemates, using a Daicel Chiralpak AD-H Column (250 × 4.6 mm), Daicel Chiralpak OD-H Column (250 × 4.6 mm), and UV detection was performed at 220 nm or 254 nm. Nuclear magnetic resonance (NMR) spectra were recorded in $CDCl_3$ or DMSO-d_6 on Bruker 600 or 700 MHz NMR instrument (at 600, or 700 MHz for ^1H, and at 150, or 175 for ^{13}C). Protonchemical shifts are reported in parts per million (δ scale). The ^1H NMR chemical shifts are reported in ppm with the internal TMS signal at 0.0 ppm as standard. The ^{13}C NMR chemical shifts were given using $CDCl_3$ or DMSO-d_6 as the internal standard ($CDCl_3$: δ = 77.00 ppm, DMSO-d_6: δ = 39.52 ppm). Data are reported as follows: chemical shift [multiplicity (s = singlet, d = doublet, t = triplet, q = quartet, m = multiplet), coupling constant(s) (Hz), integration]. High-resolution mass spectra (HRMS) were obtained using Agilent P/N G1969-90010. High-resolution mass spectra were reported for the molecular ion $[M+H]^+$ or $[M+Na]^+$. X-ray diffraction experiment was carried out on Agilent Gemini or Agilent D8 QUEST and the data obtained were deposited at the Cambridge Crystallographic Data Centre. UV detection was performed at 254 nm. Column UV detection was performed at 254 nm. Column chromatography was performed on silica gel (200–300 mesh) using an eluent of ethyl acetate and petroleum ether. TLC was performed on glass-backed silica plates; products were visualized using UV light. All reagents and solvents were obtained from commercial sources and used without further purification. Oil baths were used as the heat source. Melting points were recorded on BUCHI Melting Point M-565 instrument. 2-indolyl acrylate **1**[1-4] and propargylic alcohol **2**[5,6] were prepared according to the literature procedures. The detail characterization of new compounds is shown as following. All UV-vis absorption spectra and fluorescence emission spectra were performed on a TU-1901 spectrophotometer (Persee, China) and a F-380 fluorescence spectrophotometer (Gangdong SCI.&TECH, China), respectively.

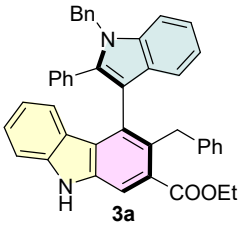
2. General Procedure for Synthesis of Compound 3



1 2 3

To a dry flask, absolute ethyl alcohol (1.0 mL) was added to a mixture of 2-indolyl acrylate **1** (0.1 mmol), propargylic alcohol **2** (0.1 mmol) and (±)-1,1′-binaphthyl-2,2′-diylhydrogenphosphate (BNDHP) (20 mol%). Then, the mixture was stirred at room temperature for 0.5 h. After 0.5 h, DBU (1.1 equiv.) was added to the mixture and the mixture continued to be stirred at 80 ℃ overnight. The reaction mixture was monitored by TLC, the solvent was evaporated under reduced pressure and the residue was purified by flash column chromatography to yield the corresponding product **3**.

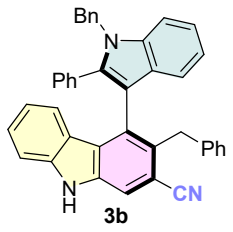
ethyl 3-benzyl-4-(1-benzyl-2-phenyl-1*H*-indol-3-yl)-9*H*-carbazole-2-carboxylate (3a)



3a

The residue was purified by a silica gel flash chromatography (PE/EA = 5/1) giving the product **3a** as a white solid in 90% yield (55.1 mg), m.p. 126-129 ℃. ^{1}H NMR (600 MHz, Chloroform-*d*) δ 8.19 (s, 1H), 7.88 (s, 1H), 7.39 (d, *J* = 8.1 Hz, 1H), 7.35 (d, *J* = 8.3 Hz, 1H), 7.33 – 7.30 (m, 1H), 7.30 – 7.26 (m, 2H), 7.24 (d, *J* = 7.9 Hz, 1H), 7.18 (t, *J* = 7.2 Hz, 1H), 7.13 – 7.04 (m, 4H), 7.00 – 6.87 (m, 8H), 6.83 (d, *J* = 7.8 Hz, 1H), 6.79 (t, *J* = 7.4 Hz, 1H), 6.60 – 6.55 (m, 2H), 5.44 (d, *J* = 16.6 Hz, 1H), 5.39 (d, *J* = 16.6 Hz, 1H), 4.36 (d, *J* = 16.0 Hz, 1H), 4.20 (d, *J* = 16.0 Hz, 1H), 4.09 – 3.99 (m, 2H), 1.09 (t, *J* = 7.1 Hz, 3H). ^{13}C NMR (151 MHz, Chloroform-d) δ 169.1, 142.2, 140.9, 138.3, 138.0, 137.2, 137.1, 132.1, 131.4, 130.6, 129.9, 129.9, 128.7, 128.37, 128.3, 128.1, 127.7, 127.5, 127.3, 126.9, 126.4, 126.3, 124.7, 123.1, 122.9, 122.4, 120.3, 120.1, 119.6, 112.8, 112.2, 110.5, 110.4, 60.9, 47.9, 35.6, 14.0. HRMS (ESI-TOF) m/z: $[M+Na]^+$ Calcd for $C_{43}H_{34}N_2NaO_2^+$ 633.2512, found 633.2511.

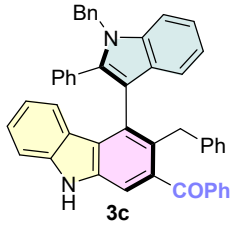
3-benzyl-4-(1-benzyl-2-phenyl-1*H*-indol-3-yl)-9*H*-carbazole-2-carbonitrile (3b)



3b

The residue was purified by a silica gel flash chromatography (PE/EA = 5/1) giving the product **3b** as a white solid in 90% yield (50.8 mg), m.p. 138-140 °C. ^{1}H NMR (600 MHz, Chloroform-*d*) δ 8.22 (s, 1H), 7.68 (s, 1H), 7.39 – 7.31 (m, 3H), 7.29 (dd, *J* = 8.1, 6.4 Hz, 2H), 7.27 – 7.23 (m, 1H), 7.18 (t, *J* = 7.1 Hz, 1H), 7.14 – 7.06 (m, 3H), 7.01 – 6.95 (m, 3H), 6.95 – 6.91 (m, 4H), 6.87 (d, *J* = 7.3 Hz, 3H), 6.81 (t, *J* = 7.2 Hz, 1H), 6.75 – 6.67 (m, 2H), 5.46 (d, *J* = 16.6 Hz, 1H), 5.41 (d, *J* = 16.6 Hz, 1H), 4.15 (d, *J* = 15.5 Hz, 1H), 4.03 (d, *J* = 15.5 Hz, 1H). ^{13}C NMR (151 MHz, Chloroform-d) δ 141.0, 139.9, 138.1, 138.9, 137.3, 137.0, 135.0, 131.1, 131.0, 129.7, 128.7, 128.5, 128.3, 128.2, 128.0, 127.9, 127.8, 127.4, 127.3, 126.3, 125.6, 123.1, 122.6, 120.5, 120.0, 119.9, 119.8, 114.9, 111.6, 110.7, 110.6, 110.0, 48.0, 37.1. HRMS (ESI-TOF) m/z: $[M+Na]^+$ Calcd for $C_{41}H_{29}N_3Na^+$ 586.2254, found 586.2256.

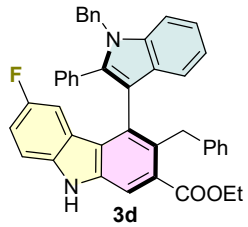
(3-benzyl-4-(1-benzyl-2-phenyl-1*H*-indol-3-yl)-9*H*-carbazol-2-yl)(phenyl)methanone (3c)



3c

The residue was purified by a silica gel flash chromatography (PE/EA = 5/1) giving the product **3c** as a brown oil in 75% yield (48.0 mg). ^{1}H NMR (600 MHz, Chloroform-*d*) δ ^{1}H NMR (600 MHz, Chloroform-*d*) δ 8.23 (s, 1H), 7.48 – 7.42 (m, 3H), 7.41 – 7.36 (m, 2H), 7.33 (dd, *J* = 12.8, 8.1 Hz, 2H), 7.31 – 7.27 (m, 2H), 7.26 – 7.19 (m, 4H), 7.18 – 7.15 (m, 1H), 7.13 – 7.06 (m, 6H), 6.96 – 6.89 (m, 2H), 6.81 (t, *J* = 7.6 Hz, 1H), 6.77 – 6.75 (m, 2H), 6.57 – 6.43 (m, 2H), 5.50 (d, *J* = 16.6 Hz, 1H), 5.44 (d, *J* = 16.7 Hz, 1H), 3.93 (d, *J* = 15.7 Hz, 1H), 3.68 (d, *J* = 15.8 Hz, 1H). ^{13}C NMR (151 MHz, Chloroform-*d*) δ 199.0, 141.4, 140.6, 138.3, 138.2, 138.0, 137.8, 137.3, 137.1, 132.6, 131.7, 131.2, 130.1, 130.0, 130.0, 129.0, 128.7, 128.3, 128.0, 127.8, 127.5, 127.3, 126.3, 126.0, 125.8, 125.0, 123.2, 122.8, 122.4, 120.3, 120.2, 119.6, 112.9, 110.8, 110.5, 110.4, 48.0, 35.9. HRMS (ESI-TOF) m/z: $[M+Na]^+$ Calcd for $C_{47}H_{34}N_2NaO^+$ 665.2563, found 665.2559.

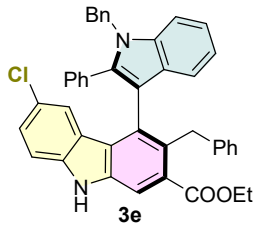
ethyl 3-benzyl-4-(1-benzyl-2-phenyl-1*H*-indol-3-yl)-6-fluoro-9*H*-carbazole-2-carboxylate (3d)



3d

The residue was purified by a silica gel flash chromatography (PE/EA = 5/1) giving the product **3d** as a white solid in 96% yield (60.6 mg), m.p. 116 -118 ℃. ^{1}H NMR (700 MHz, Chloroform-*d*) δ 8.08 (s, 1H), 7.77 (s, 1H), 7.26 (d, *J* = 8.3 Hz, 1H), 7.24 – 7.19 (m, 3H), 7.18 – 7.15 (m, 1H), 7.11 (t, *J* = 7.6 Hz, 1H), 7.04 – 6.95 (m, 5H), 6.91 (t, *J* = 7.4 Hz, 1H), 6.89 – 6.81 (m, 7H), 6.55 – 6.51 (m, 2H), 6.46 (d, *J* = 8.0 Hz, 1H), 5.36 (d, *J* = 16.7 Hz, 1H), 5.32 (d, *J* = 16.7 Hz, 1H), 4.31 (d, *J* = 16.0 Hz, 1H), 4.15 (d, *J* = 16.0 Hz, 1H), 4.05 – 3.90 (m, 2H), 1.02 (t, *J* = 7.1 Hz, 3H). ^{13}C NMR (176 MHz, Chloroform-d) δ 168.1, 156.9, 155.5, 141.0, 137.1 (d, *J* = 3.3 Hz), 137.0, 136.2, 136.1,131.0, 130.2, 129.9, 129.6, 128.8, 127.8, 127.3, 127.1, 126.8, 126.5, 126.2, 125.4 (d, *J* = 4.3 Hz), 125.1, 123.8, 122.6 (d, *J* = 10.1 Hz), 121.6, 119.4, 118.9, 113.2 (d, *J* = 26.0 Hz), 111.4, 111.1, 109.9 (d, *J* = 9.2 Hz), 109.6, 107.1 (d, *J* = 24.8 Hz), 59.9, 46.9, 34.6, 12.9. HRMS (ESI-TOF) m/z: $[M+Na]^+$ Calcd for $C_{43}H_{33}FN_2NaO_2^+$ 651.2418, found 651.2428.

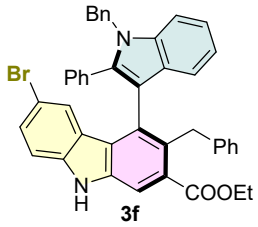
ethyl 3-benzyl-4-(1-benzyl-2-phenyl-1*H*-indol-3-yl)-6-chloro-9*H*-carbazole-2-carboxylate (3e)



3e

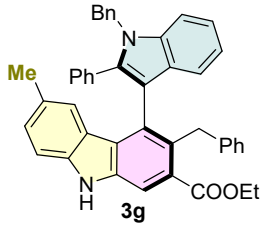
The residue was purified by a silica gel flash chromatography (PE/EA = 5/1) giving the product **3e** as a white solid in 95% yield (61.3 mg), m.p. 115-117 ℃. ^{1}H NMR (700 MHz, Chloroform-*d*) δ 8.09 (s, 1H), 7.75 (s, 1H), 7.27 – 7.22 (m, 3H), 7.18 – 7.15 (m, 3H), 7.11 (t, *J* = 7.6 Hz, 1H), 7.07 (d, *J* = 7.6 Hz, 2H), 7.04 (d, *J* = 7.9 Hz, 1H), 6.98 (t, *J* = 7.1 Hz, 1H), 6.93 (t, *J* = 7.5 Hz, 1H), 6.90 – 6.83 (m, 7H), 6.80 (s, 1H), 6.58 (d, *J* = 7.8 Hz, 2H), 5.37 (d, *J* = 16.8 Hz, 1H), 5.32 (d, *J* = 16.8 Hz, 1H), 4.36 (d, *J* = 16.0 Hz, 1H), 4.19 (d, *J* = 16.0 Hz, 1H), 4.02 – 3.92 (m, 2H), 1.03 (t, *J* = 7.1 Hz, 3H). ^{13}C NMR (176 MHz, Chloroform-*d*) δ 168.1, 141.0, 138.0, 137.1, 137.0, 136.6, 136.2, 131.3, 130.2, 129.9, 129.7, 128.8, 127.9, 127.3, 127.0, 127.0, 126.8, 126.6, 126.2, 125.4, 125.0, 124.6, 123.9, 123.8, 123.1, 121.6, 121.2, 119.4, 118.9, 111.3, 111.0, 110.33, 109.7, 60.0, 47.0, 34.6, 12.9. HRMS (ESI-TOF) m/z: $[M+Na]^+$ Calcd for $C_{43}H_{33}ClN_2NaO_2^+$ 667.2123, found 667.2121.

ethyl 3-benzyl-4-(1-benzyl-2-phenyl-1*H*-indol-3-yl)-6-bromo-9*H*-carbazole-2-carboxylate (3f)



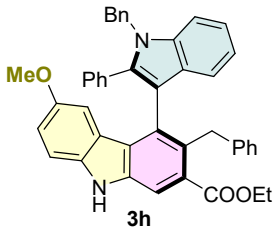
The residue was purified by a silica gel flash chromatography (PE/EA = 5/1) giving the product **3f** as a white solid in 94% yield (65.1 mg), m.p. 108-110 °C. ^{1}H NMR (600 MHz, Chloroform-*d*) δ 8.15 (s, 1H), 7.82 (s, 1H), 7.38 – 7.32 (m, 3H), 7.31 (d, *J* = 8.2 Hz, 1H), 7.25 – 7.23 (m, 1H), 7.21 – 7.18 (m, 2H), 7.16 (d, *J* = 7.7 Hz, 2H), 7.12 (d, *J* = 7.9 Hz, 1H), 7.06 – 7.03 (m, 2H), 7.02 – 6.99 (m, 1H), 6.98 – 6.91 (m, 7H), 6.66 (d, *J* = 6.8 Hz, 2H), 5.45 (d, *J* = 16.8 Hz, 1H), 5.39 (d, *J* = 16.8 Hz, 1H), 4.44 (d, *J* = 16.0 Hz, 1H), 4.27 (d, *J* = 16.0 Hz, 1H), 4.10 – 4.00 (m, 2H), 1.12 (t, *J* = 7.1 Hz, 3H). ^{13}C NMR (151 MHz, Chloroform-*d*) δ 169.1, 142.0, 139.3, 138.2, 138.0, 137.5, 137.2, 132.4, 131.2, 131.0, 130.8, 129.8, 129.0, 128.9, 128.4, 128.1, 128.0, 127.8, 127.6, 127.2, 126.1, 125.4, 125.3, 124.9, 124.8, 122.6, 120.5, 119.9, 112.3, 112.3, 112.0, 111.8, 110.7, 61.0, 48.0, 35.6, 14.0. HRMS (ESI-TOF) m/z: $[M+Na]^+$ Calcd for $C_{43}H_{33}BrN_2NaO_2^+$ 711.1618, found 711.1617.

ethyl 3-benzyl-4-(1-benzyl-2-phenyl-1*H*-indol-3-yl)-6-methyl-9*H*-carbazole-2-carboxylate (3g)



The residue was purified by a silica gel flash chromatography (PE/EA = 5/1) giving the product **3g** as a white solid in 96% yield (60.1 mg), m.p. 126-128 °C. ^{1}H NMR (600 MHz, Chloroform-*d*) δ 8.08 (s, 1H), 7.84 (d, *J* = 3.3 Hz, 1H), 7.34 – 7.31 (m, 1H), 7.30 – 7.22 (m, 4H), 7.19 – 7.15 (m, 1H), 7.15 – 7.09 (m, 4H), 7.07 – 7.03 (m, 1H), 6.99 – 6.96 (m, 1H), 6.96 – 6.90 (m, 7H), 6.68 (s, 1H), 6.60 (s, 2H), 5.46 (d, *J* = 16.6 Hz, 1H), 5.39 (d, *J* = 16.7 Hz, 1H), 4.38 (d, *J* = 16.0 Hz, 1H), 4.21 (d, *J* = 16.0 Hz, 1H), 4.09 – 3.95 (m, 2H), 2.10 (s, 3H), 1.09 (td, *J* = 7.1, 3.1 Hz, 3H). ^{13}C NMR (151 MHz, Chloroform-*d*) δ 169.2, 142.3, 139.1, 138.3, 138.0, 137.4, 137.1, 131.8, 131.4, 130.5, 129.9, 129.7, 128.7, 128.5, 128.4, 128.3, 128.1, 127.7, 127.7, 127.5, 127.2, 126.6, 126.3, 124.7, 123.3, 122.7, 122.3, 120.2, 120.1, 112.8, 112.2, 110.41, 110.0, 60.8, 47.8, 35.6, 21.5, 14.0. HRMS (ESI-TOF) m/z: $[M+Na]^+$ Calcd for $C_{43}H_{36}N_2NaO_2^+$ 647.2669, found 647.2671.

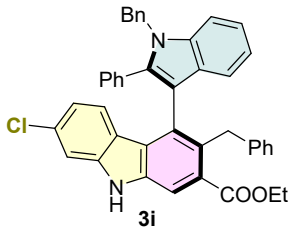
ethyl 3-benzyl-4-(1-benzyl-2-phenyl-1*H*-indol-3-yl)-6-methoxy-9*H*-carbazole-2-carboxylate (3h)



3h

The residue was purified by a silica gel flash chromatography (PE/EA = 5/1) giving the product **3h** as a white solid in 85% yield (54.7 mg), m.p. 123-125 ℃. ^{1}H NMR (700 MHz, Chloroform-*d*) δ 8.00 (s, 1H), 7.77 (s, 1H), 7.25 (d, *J* = 8.3 Hz, 1H), 7.21 (d, *J* = 8.8 Hz, 1H), 7.20 – 7.18 (m, 2H), 7.17 – 7.14 (m, 1H), 7.08 (t, *J* = 7.6 Hz, 1H), 7.05 – 7.01 (m, 4H), 6.92 (t, *J* = 7.5 Hz, 2H), 6.91 – 6.86 (m, 4H), 6.83 (d, *J* = 6.5 Hz, 3H), 6.53 (d, *J* = 7.1 Hz, 2H), 6.14 (s, 1H), 5.38 (d, *J* = 16.5 Hz, 1H), 5.29 (d, *J* = 16.5 Hz, 1H), 4.27 (d, *J* = 15.9 Hz, 1H), 4.14 (d, *J* = 15.9 Hz, 1H), 3.99 – 3.91 (m, 2H), 2.98 (s, 3H), 1.02 (t, *J* = 7.1 Hz, 3H). ^{13}C NMR (176 MHz, Chloroform-*d*) δ 168.1, 152.6, 141.3, 137.0, 137.0, 136.8, 135.9, 134.8, 130.5, 130.4, 129.4, 129.0, 128.9, 127.7, 127.3, 127.3, 127.2, 126.8, 126.5, 126.3, 125.6, 125.4, 123.6, 122.4, 121.4, 119.4, 119.3, 115.0, 111.6, 111.4, 109.92, 109.32, 104.3, 59.8, 54.1, 46.8, 34.6, 12.9. HRMS (ESI-TOF) m/z: $[M+Na]^+$ Calcd for $C_{44}H_{36}N_2NaO_3^+$ 663.2618, found 663.2627.

ethyl 3-benzyl-4-(1-benzyl-2-phenyl-1*H*-indol-3-yl)-7-chloro-9*H*-carbazole-2-carboxylate (3i)

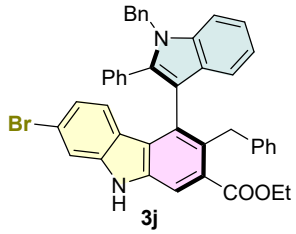


3i

The residue was purified by a silica gel flash chromatography (PE/EA = 5/1) giving the product **3i** as a white solid in 83% yield (53.7 mg), m.p. 126-128 ℃. ^{1}H NMR (700 MHz, Chloroform-*d*) δ 8.23 (s, 1H), 7.85 (s, 1H), 7.38 – 7.33 (m, 2H), 7.28 (t, *J* = 7.2 Hz, 2H), 7.26 – 7.24 (m, 1H), 7.18 (t, *J* = 7.6 Hz, 1H), 7.10 – 7.04 (m, 4H), 6.96 (q, *J* = 7.2 Hz, 3H), 6.92 – 6.87 (m, 5H), 6.74 (d, *J* = 8.5 Hz, 1H), 6.68 (d, *J* = 8.5 Hz, 1H), 6.59 – 6.55 (m, 2H), 5.42 (d, *J* = 16.5 Hz, 1H), 5.38 (d, *J* = 16.5 Hz, 1H), 4.36 (d, *J* = 15.9 Hz, 1H), 4.20 (d, *J* = 15.9 Hz, 1H), 4.09 – 3.99 (m, 2H), 1.09 (t, *J* = 7.1 Hz, 3H). ^{13}C NMR (176 MHz, Chloroform-*d*) δ 169.0, 142.0, 141.3, 138.2, 138.0, 137.3, 137.2, 132.6, 132.1, 131.2, 130.6, 130.3, 129.8, 128.7, 128.3, 128.2, 128.1, 127.8, 127.55, 127.4, 126.3, 126.3, 124.8, 123.5, 122.5, 121.7, 120.4, 120.2, 119.9, 112.5, 112.3, 110.6, 110.5, 61.0, 47.9, 35.6, 13.9. HRMS (ESI-TOF) m/z: $[M+Na]^+$ Calcd for $C_{43}H_{33}ClN_2NaO_2^+$ 667.2123, found

667.2125.

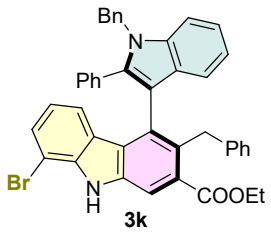
ethyl 3-benzyl-4-(1-benzyl-2-phenyl-1*H*-indol-3-yl)-7-bromo-9*H*-carbazole-2-carboxylate (3j)



3j

The residue was purified by a silica gel flash chromatography (PE/EA = 5/1) giving the product **3j** as a white solid in 93% yield (64.0 mg), m.p. 111-113 ℃. ^{1}H NMR (600 MHz, Chloroform-*d*) δ 8.24 (s, 1H), 7.86 (s, 1H), 7.51 (s, 1H), 7.36 (d, *J* = 8.3 Hz, 1H), 7.30 – 7.24 (m, 3H), 7.21 – 7.16 (m, 1H), 7.11 – 7.04 (m, 4H), 6.96 (td, *J* = 7.7, 2.8 Hz, 3H), 6.94 – 6.85 (m, 6H), 6.63 (d, *J* = 8.5 Hz, 1H), 6.61 – 6.55 (m, 2H), 5.43 (d, *J* = 16.5 Hz, 1H), 5.38 (d, *J* = 16.5 Hz, 1H), 4.35 (d, *J* = 15.9 Hz, 1H), 4.20 (d, *J* = 16.0 Hz, 1H), 4.10 – 3.99 (m, 2H), 1.09 (t, *J* = 7.1 Hz, 3H). ^{13}C NMR (151 MHz, Chloroform-*d*) δ 169.0, 142.0, 141.6, 138.2, 138.0, 137.2, 137.1, 132.6, 131.2, 130.7, 130.5, 129.8, 128.7, 128.3, 128.2, 128.1, 127.8, 127.6, 127.4, 126.3, 126.3, 124.8, 123.8, 122.89, 122.5, 122.0, 120.4, 120.1, 119.9, 113.5, 112.4, 112.3, 110.6, 61.0, 47.9, 35.6, 13.9. HRMS (ESI-TOF) m/z: $[M+Na]^+$ Calcd for $C_{43}H_{33}BrN_2NaO_2^+$ 711.1618, found 711.1623.

ethyl 3-benzyl-4-(1-benzyl-2-phenyl-1*H*-indol-3-yl)-8-bromo-9*H*-carbazole-2-carboxylate (3k)

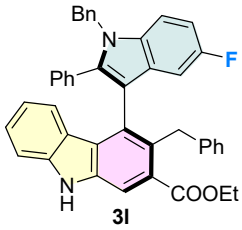


3k

The residue was purified by a silica gel flash chromatography (PE/EA = 5/1) giving the product **3k** as a white solid in 94% yield (65.0 mg), m.p. 110-112 ℃. ^{1}H NMR (600 MHz, Chloroform-*d*) δ 8.33 (s, 1H), 7.89 (s, 1H), 7.39 (d, *J* = 7.6 Hz, 1H), 7.28 (d, *J* = 8.3 Hz, 1H), 7.22 – 7.16 (m, 3H), 7.11 (t, *J* = 7.6 Hz, 1H), 7.03 – 7.00 (m, 3H), 6.98 (d, *J* = 7.9 Hz, 1H), 6.88 (t, *J* = 7.8 Hz, 3H), 6.85 – 6.80 (m, 5H), 6.67 (d, *J* = 7.9 Hz, 1H), 6.60 (t, *J* = 7.8 Hz, 1H), 6.52 – 6.48 (m, 2H), 5.36 (d, *J* = 16.6 Hz, 1H), 5.31 (d, *J* = 16.6 Hz, 1H), 4.29 (d, *J* = 16.0 Hz, 1H), 4.13 (d, *J* = 16.0 Hz, 1H), 4.03 – 3.94 (m, 2H), 1.03 (t, *J* = 7.1 Hz, 3H). ^{13}C NMR (151 MHz, Chloroform-*d*) δ 168.9, 141.9, 139.4, 138.2, 138.1, 137.2, 136.7, 132.8, 131.2, 131.2, 130.7, 129.8, 128.7, 128.4, 128.3, 128.2, 128.2, 127.8, 127.6, 127.3, 127.2, 126.4, 124.8, 124.4, 122.5, 121.8, 120.7, 120.4, 120.0, 112.7, 112.4, 110.6, 103.9, 61.0, 47.9,

35.6, 14.0. HRMS (ESI-TOF) m/z: $[M+Na]^+$ Calcd for $C_{43}H_{33}BrN_2NaO_2^+$ 711.1618, found 711.1618.

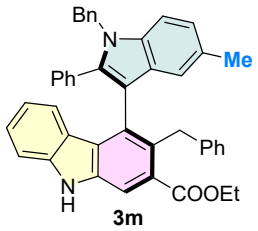
ethyl 3-benzyl-4-(1-benzyl-5-fluoro-2-phenyl-1*H*-indol-3-yl)-9*H*-carbazole-2-carboxylate (3l)



3l

The residue was purified by a silica gel flash chromatography (PE/EA = 5/1) giving the product **3l** as a white solid in 94% yield (59.2 mg), m.p. 104-106 °C. ^{1}H NMR (700 MHz, Chloroform-*d*) δ 8.14 (s, 1H), 7.84 (s, 1H), 7.36 (d, *J* = 8.1 Hz, 1H), 7.29 – 7.26 (m, 1H), 7.23 (t, *J* = 7.5 Hz, 2H), 7.20 – 7.15 (m, 3H), 7.04 – 6.99 (m, 3H), 6.90 (t, *J* = 7.6 Hz, 2H), 6.87 – 6.81 (m, 6H), 6.75 (d, *J* = 4.1 Hz, 2H), 6.58 – 6.56 (m, 1H), 6.52 – 6.49 (m, 2H), 5.36 (d, *J* = 16.6 Hz, 1H), 5.29 (d, *J* = 16.6 Hz, 1H), 4.23 (d, *J* = 15.9 Hz, 1H), 4.14 (d, *J* = 15.9 Hz, 1H), 4.04 – 3.97 (m, 2H), 1.05 (t, *J* = 7.0 Hz, 3H). ^{13}C NMR (176 MHz, Chloroform-*d*) δ 167.99, 157.89, 156.55, 140.999, 139.87, 138.60, 136.95, 136.06, 132.64, 131.06, 130.07, 128.97 (d, *J* = 11.9 Hz), 128.27, 127.70, 127.20, 127.19, 126.91, 126.61, 126.51, 126.40, 125.80, 125.38, 125.26, 124.99, 127.73, 121.95, 121.67, 118.61, 111.85 (d, *J* = 4.4 Hz), 111.34, 110.16 (d, *J* = 9.5 Hz), 109.73 (d, *J* = 26.4 Hz), 109.48, 103.80 (d, *J* = 23.5 Hz), 59.89, 47.12, 34.58, 12.96. HRMS (ESI-TOF) m/z: $[M+Na]^+$ Calcd for $C_{43}H_{33}FN_2NaO_2^+$ 651.2418, found 651.2427.

ethyl 3-benzyl-4-(1-benzyl-5-methyl-2-phenyl-1*H*-indol-3-yl)-9*H*-carbazole-2-carboxylate (3m)

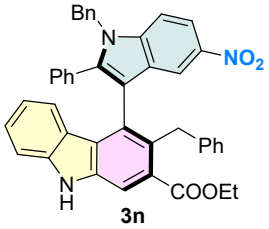


3m

The residue was purified by a silica gel flash chromatography (PE/EA = 5/1) giving the product **3m** as a white solid in 87% yield (54.5 mg), m.p. 106-108 °C. ^{1}H NMR (700 MHz, Chloroform-*d*) δ 8.10 (s, 1H), 7.82 (s, 1H), 7.32 (d, *J* = 8.1 Hz, 1H), 7.25 (t, *J* = 7.6 Hz, 1H), 7.21 (t, *J* = 7.2 Hz, 2H), 7.19 – 7.14 (m, 3H), 7.02 (d, *J* = 7.6 Hz, 2H), 6.98 (t, *J* = 7.2 Hz, 1H), 6.92 (d, *J* = 8.4 Hz, 1H), 6.84 (t, *J* = 7.8 Hz, 2H), 6.82 (d, *J* = 6.4 Hz, 5H), 6.77 – 6.73 (m, 2H), 6.49 (d, *J* = 4.8 Hz, 2H), 5.33 (d, *J* = 16.5 Hz, 1H), 5.28 (d, *J* = 16.5 Hz, 1H), 4.30 (d, *J* = 15.9 Hz, 1H), 4.15 (d, *J* = 16.0 Hz, 1H), 4.02 – 3.94 (m, 2H), 2.15 (s, 3H), 1.03 (t, *J* = 7.2 Hz, 3H).

^{13}C NMR (176 MHz, Chloroform-*d*) δ 169.2, 142.2, 140.9, 138.4, 138.0, 137.1, 135.7, 132.2, 131.5, 131.0, 129.9, 129.9, 129.4, 128.6, 128.6, 128.3, 128.1, 127.6, 127.5, 127.2, 127.1, 126.4, 126.3, 124.6, 124.0, 123.2, 123.0, 119.8, 119.6, 112.4, 112.2, 110.4, 110.1, 60.9, 47.9, 35.7, 21.3, 14.0. HRMS (ESI-TOF) m/z: $[M+Na]^+$ Calcd for $C_{43}H_{36}N_2NaO_2^+$ 647.2669, found 647.2670.

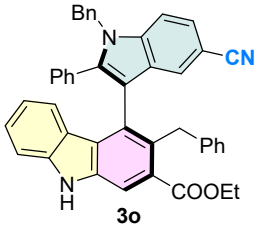
ethyl 3-benzyl-4-(1-benzyl-5-nitro-2-phenyl-1*H*-indol-3-yl)-9*H*-carbazole-2-carboxylate (3n)



3n

The residue was purified by a silica gel flash chromatography (PE/EA = 5/1) giving the product **3n** as a white solid in 89% yield (58.5 mg), m.p. 114-116 °C. ^{1}H NMR (700 MHz, Chloroform-*d*) δ 8.24 (s, 1H), 7.93 (d, *J* = 17.3 Hz, 2H), 7.70 (s, 1H), 7.37 (s, 1H), 7.30 – 7.20 (m, 5H), 7.19 (s, 1H), 7.09 (s, 1H), 7.02 – 6.88 (m, 6H), 6.82 – 6.69 (m, 4H), 6.62 (s, 1H), 6.52 (s, 2H), 5.43 (d, *J* = 14.9 Hz, 1H), 5.35 (d, *J* = 14.4 Hz, 1H), 4.22 (d, *J* = 14.6 Hz, 1H), 4.13 – 4.02 (m, 3H), 1.13 – 1.07 (m, 3H). ^{13}C NMR (176 MHz, Chloroform-*d*) δ 168.8, 142.1, 141.7, 141.1, 140.9, 139.9, 137.2, 137.0, 132.14, 130.2, 130.0, 129.6, 129.0, 128.6, 128.5, 128.1, 127.9, 127.7, 127.6, 127.0, 126.7, 126.3, 124.9, 122.6, 122.2, 119.7, 118.0, 117.2, 115.31, 112.9, 110.8, 110.4, 61.1, 48.4, 35.9, 14.1. HRMS (ESI-TOF) m/z: $[M+Na]^+$ Calcd for $C_{43}H_{33}N_3NaO_4^+$ 678.2363, found 678.2372.

ethyl 3-benzyl-4-(1-benzyl-5-cyano-2-phenyl-1*H*-indol-3-yl)-9*H*-carbazole-2-carboxylate (3o)

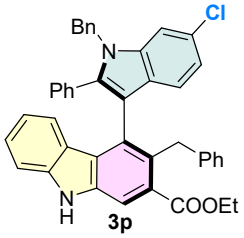


3o

The residue was purified by a silica gel flash chromatography (PE/EA = 5/1) giving the product **3o** as a white solid in 91% yield (58.1 mg), m.p. 132-134 °C. ^{1}H NMR (700 MHz, Chloroform-*d*) δ 8.22 (s, 1H), 7.90 (s, 1H), 7.38 (d, *J* = 8.1 Hz, 1H), 7.30 – 7.27 (m, 3H), 7.25 – 7.22 (m, 2H), 7.19 (s, 1H), 7.14 (s, 1H), 7.08 (t, *J* = 7.1 Hz, 1H), 6.99 (d, *J* = 7.4 Hz, 2H), 6.94 (t, *J* = 7.7 Hz, 2H), 6.89 (d, *J* = 7.9 Hz, 2H), 6.83 (d, *J* = 5.2 Hz, 3H), 6.73 (t, *J* = 7.5 Hz, 1H), 6.61 (d, *J* = 8.0 Hz, 1H), 6.52 – 6.48 (m, 2H), 5.40 (d, *J* = 16.5 Hz, 1H), 5.34 (d, *J* = 16.5 Hz, 1H), 4.18 (d, *J* = 15.8 Hz, 1H), 4.10 – 4.03 (m, 3H), 1.09 (t, *J* = 7.1 Hz, 3H). ^{13}C NMR (176 MHz, Chloroform-*d*)

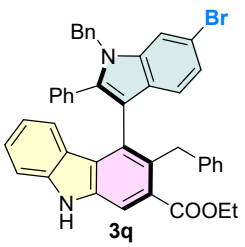
δ 168.8, 141.7, 141.0, 140.1, 138.6, 137.2, 137.1, 132.1, 130.3, 130.0, 129.7, 128.9, 128.9, 128.5, 128.5, 128.1, 128.1, 127.8, 127.6, 126.8, 126.7, 126.3, 125.5, 125.3, 125.0, 122.6, 122.2, 120.4, 119.7, 113.7, 112.7, 111.3, 110.8, 103.3, 61.1, 48.2, 35.7, 14.1. HRMS (ESI-TOF) m/z: $[M+Na]^+$ Calcd for $C_{44}H_{33}N_3NaO_2^+$ 658.2465, found 658.2471.

ethyl 3-benzyl-4-(1-benzyl-6-chloro-2-phenyl-1*H*-indol-3-yl)-9*H*-carbazole-2-carboxylate (3p)



The residue was purified by a silica gel flash chromatography (PE/EA = 5/1) giving the product **3p** as a white solid in 87% yield (56.2 mg), m.p. 104-106 °C. ^{1}H NMR (700 MHz, Chloroform-*d*) δ 8.14 (s, 1H), 7.83 (s, 1H), 7.35 (d, *J* = 8.1 Hz, 1H), 7.27 (d, *J* = 7.7 Hz, 1H), 7.23 (t, *J* = 7.4 Hz, 2H), 7.21 – 7.17 (m, 2H), 7.04 – 6.98 (m, 3H), 6.90 – 6.86 (m, 3H), 6.85 – 6.80 (m, 6H), 6.76 (t, *J* = 7.5 Hz, 1H), 6.73 (d, *J* = 7.9 Hz, 1H), 6.51 – 6.48 (m, 2H), 5.33 (d, *J* = 16.6 Hz, 1H), 5.26 (d, *J* = 16.6 Hz, 1H), 4.23 (d, *J* = 15.9 Hz, 1H), 4.11 (d, *J* = 15.9 Hz, 1H), 4.03 – 3.94 (m, 2H), 1.03 (t, *J* = 7.1 Hz, 3H). ^{13}C NMR (176 MHz, Chloroform-*d*) δ 169.0, 142.0, 140.9, 138.7, 137.7, 137.6, 137.1, 132.0, 130.9, 130.0, 129.9, 129.8, 128.8, 128.2, 128.2, 128.2, 128.0, 127.6, 127.5, 126.9, 126.9, 126.5, 126.3, 124.8, 122.9, 122.7, 121.1, 121.0, 119.7, 113.0, 112.4, 110.5, 110.5, 60.9, 48.0, 35.6, 14.0. HRMS (ESI-TOF) m/z: $[M+Na]^+$ Calcd for $C_{43}H_{33}ClN_2NaO_2^+$ 667.2123, found 667.2124.

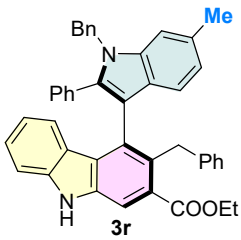
ethyl 3-benzyl-4-(1-benzyl-6-bromo-2-phenyl-1*H*-indol-3-yl)-9*H*-carbazole-2-carboxylate (3q)



The residue was purified by a silica gel flash chromatography (PE/EA = 5/1) giving the product **3q** as a white solid in 97% yield (66.7 mg), m.p. 110-112 °C. ^{1}H NMR (700 MHz, Chloroform-*d*) δ 8.14 (s, 1H), 7.83 (s, 1H), 7.43 (s, 1H), 7.34 (s, 1H), 7.30 – 7.15 (m, 5H), 6.98 (d, *J* = 31.0 Hz, 4H), 6.85 (d, *J* = 30.0 Hz, 8H), 6.74 (d, *J* = 21.7 Hz, 2H), 6.49 (s, 2H), 5.33 (d, *J* = 16.2 Hz, 1H), 5.26 (d, *J* = 13.5 Hz, 1H), 4.23 (d, *J* = 15.7 Hz, 1H), 4.11 (d, *J* = 15.6 Hz, 1H), 4.04 – 3.93 (m, 2H), 1.03 (s, 3H). ^{13}C NMR (176 MHz, Chloroform-*d*) δ 169.0, 142.0, 140.9, 138.7, 138.0, 137.7, 137.1,

132.0, 130.9, 123.0, 129.9, 129.8, 128.8, 128.2, 128.0, 127.6, 127.5, 127.2, 126.9, 126.5, 126.3, 124.8, 123.7, 122.9, 122.7, 121.3, 119.7, 116.0, 113.4, 113.1, 112.4, 110.6, 61.0, 48.0, 35.6, 14.0. HRMS (ESI-TOF) m/z: $[M+Na]^+$ Calcd for $C_{43}H_{33}BrN_2NaO_2^+$ 711.1618, found 711.1620.

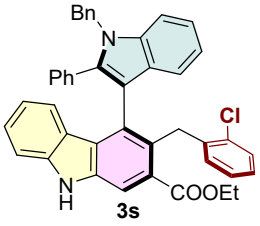
ethyl 3-benzyl-4-(1-benzyl-6-methyl-2-phenyl-1*H*-indol-3-yl)-9*H*-carbazole-2-carboxylate (3r)



3r

The residue was purified by a silica gel flash chromatography (PE/EA = 5/1) giving the product **3r** as a white solid in 89% yield (55.6 mg), m.p. 126-128 °C. ^{1}H NMR (600 MHz, Chloroform-*d*) δ 8.17 (s, 1H), 7.87 (s, 1H), 7.40 (d, *J* = 8.1 Hz, 1H), 7.33 – 7.27 (m, 3H), 7.24 (d, *J* = 7.3 Hz, 1H), 7.15 (s, 1H), 7.10 (d, *J* = 7.3 Hz, 2H), 7.05 (t, *J* = 7.2 Hz, 1H), 6.99 (d, *J* = 8.0 Hz, 1H), 6.94 – 6.87 (m, 8H), 6.81 (t, *J* = 8.3 Hz, 2H), 6.59 – 6.54 (m, 2H), 5.40 (d, *J* = 16.6 Hz, 1H), 5.35 (d, *J* = 16.6 Hz, 1H), 4.38 (d, *J* = 16.0 Hz, 1H), 4.19 (d, *J* = 16.0 Hz, 1H), 4.07 – 3.97 (m, 2H), 2.43 (s, 3H), 1.08 (t, *J* = 7.1 Hz, 3H). ^{13}C NMR (151 MHz, Chloroform-*d*) δ 169.1, 142.3, 140.8, 138.4, 137.7, 137.4, 137.0, 132.2, 132.0, 131.5, 130.8, 129.9, 129.9, 128.6, 128.3, 128.0, 127.5, 127.2, 126.9, 126.3, 126.3, 126.2, 124.6, 123.2, 122.9, 122.1, 119.7, 119.6, 112.7, 112.2, 110.4, 110.4, 60.8, 47.7, 35.6, 22.0, 14.0. HRMS (ESI-TOF) m/z: $[M+Na]^+$ Calcd for $C_{43}H_{36}N_2NaO_2^+$ 647.2669, found 647.2678.

ethyl 4-(1-benzyl-2-phenyl-1*H*-indol-3-yl)-3-(2-chlorobenzyl)-9*H*-carbazole-2-carboxylate (3s)

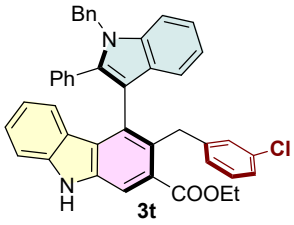


3s

The residue was purified by a silica gel flash chromatography (PE/EA = 5/1) giving the product **3s** as a white solid in 97% yield (62.8 mg), m.p. 121-123 °C. ^{1}H NMR (700 MHz, Chloroform-*d*) δ 8.30 (s, 1H), 8.05 (s, 1H), 7.42 (d, *J* = 8.1 Hz, 1H), 7.33 (t, *J* = 7.5 Hz, 1H), 7.31 – 7.27 (m, 3H), 7.24 (d, *J* = 7.5 Hz, 1H), 7.14 (t, *J* = 7.6 Hz, 1H), 7.11 (d, *J* = 7.9 Hz, 1H), 7.06 (d, *J* = 7.5 Hz, 2H), 7.03 – 6.99 (m, 2H), 6.93 – 6.85 (m, 5H), 6.85 – 6.79 (m, 3H), 6.57 (t, *J* = 7.6 Hz, 1H), 6.11 (d, *J* = 7.8 Hz, 1H), 5.43 (d, *J* = 16.7 Hz, 1H), 5.37 (d, *J* = 16.7 Hz, 1H), 4.46 (d, *J* = 17.1 Hz, 1H), 4.20 (d, *J* = 17.1 Hz, 1H), 4.10 – 4.01 (m, 2H), 1.05 (t, *J* = 7.1 Hz, 3H). ^{13}C NMR (176

MHz, Chloroform-*d*) δ 168.8, 141.0, 139.9, 138.2, 137.8, 137.3, 137.1, 133.2, 131.3, 131.2, 130.6, 129.7, 129.5, 128.8, 128.7, 128.2, 128.1, 128.1, 127.7, 127.5, 127.2, 126.5, 126.2, 126.2, 125.8, 123.0, 122.9, 122.3, 120.2, 120.0, 119.7, 112.8, 112.4, 110.5, 110.4, 61.0, 47.8, 33.8, 13.8. HRMS (ESI-TOF) m/z: $[M+Na]^+$ Calcd for $C_{43}H_{33}ClN_2NaO_2^+$ 667.2123, found 667.2127.

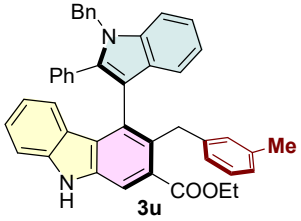
ethyl 4-(1-benzyl-2-phenyl-1*H*-indol-3-yl)-3-(3-chlorobenzyl)-9*H*-carbazole-2-carboxylate (3t)



3t

The residue was purified by a silica gel flash chromatography (PE/EA = 5/1) giving the product **3t** as a white solid in 92% yield (59.6 mg), m.p. 111-113 ℃. ^{1}H NMR (700 MHz, Chloroform-*d*) δ 8.16 (s, 1H), 7.87 (s, 1H), 7.32 (d, *J* = 8.1 Hz, 1H), 7.28 (d, *J* = 8.3 Hz, 1H), 7.23 (dt, *J* = 18.8, 7.4 Hz, 3H), 7.19 – 7.15 (m, 1H), 7.10 (t, *J* = 7.6 Hz, 1H), 7.00 (dd, *J* = 15.4, 7.5 Hz, 3H), 6.95 (d, *J* = 7.9 Hz, 1H), 6.89 – 6.83 (m, 3H), 6.82 – 6.77 (m, 3H), 6.76 (d, *J* = 7.9 Hz, 1H), 6.72 (t, *J* = 7.7 Hz, 2H), 6.46 (s, 1H), 6.37 (d, *J* = 7.7 Hz, 1H), 5.37 (d, *J* = 16.5 Hz, 1H), 5.31 (d, *J* = 16.5 Hz, 1H), 4.25 (d, *J* = 16.1 Hz, 1H), 4.11 (d, *J* = 16.1 Hz, 1H), 4.08 – 3.99 (m, 2H), 1.06 (t, *J* = 7.1 Hz, 3H).^{13}C NMR (176 MHz, Chloroform-*d*) δ 167.8, 143.3, 139.9, 137.2, 136.9, 136.2, 136.2, 132.3, 130.09, 130.0, 129.8, 128.7, 128.4, 127.7, 127.6, 127.2, 127.1, 127.1, 126.9, 126.3, 126.2, 125.4, 125.3, 125.3, 123.9, 122.0, 121.8, 121.4, 119.29, 118.9, 118.7, 111.6, 111.5, 109.5, 109.4, 59.9, 46.9, 34.4, 13.0. HRMS (ESI-TOF) m/z: $[M+Na]^+$ Calcd for $C_{43}H_{33}ClN_2NaO_2^+$ 667.2123, found 667.2125.

ethyl 4-(1-benzyl-2-phenyl-1*H*-indol-3-yl)-3-(3-methylbenzyl)-9*H*-carbazole-2-carboxylate (3u)

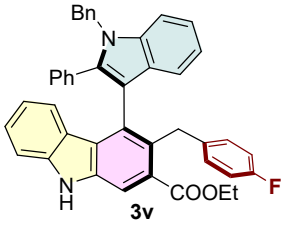


3u

The residue was purified by a silica gel flash chromatography (PE/EA = 5/1) giving the product **3u** as a white solid in 87% yield (54.2 mg), m.p. 109-111 ℃. ^{1}H NMR (700 MHz, Chloroform-*d*) δ 8.19 (s, 1H), 7.86 (s, 1H), 7.38 (d, *J* = 8.1 Hz, 1H), 7.34 (d, *J* = 8.3 Hz, 1H), 7.32 – 7.26 (m, 3H), 7.24 (d, *J* = 7.1 Hz, 1H), 7.17 (t, *J* = 7.6 Hz, 1H), 7.10 (d, *J* = 7.5 Hz, 2H), 7.08 – 7.04 (m,

2H), 6.98 – 6.91 (m, 5H), 6.84 (d, *J* = 8.0 Hz, 1H), 6.82 – 6.78 (m, 2H), 6.71 (d, *J* = 7.5 Hz, 1H), 6.41 (d, *J* = 7.7 Hz, 1H), 6.38 (s, 1H), 5.43 (d, *J* = 16.6 Hz, 1H), 5.38 (d, *J* = 16.6 Hz, 1H), 4.30 (d, *J* = 15.9 Hz, 1H), 4.18 (d, *J* = 15.9 Hz, 1H), 4.10 – 4.00 (m, 2H), 2.02 (s, 3H), 1.11 (t, *J* = 7.1 Hz, 3H). ^{13}C NMR (176 MHz, Chloroform-*d*) δ 169.2, 142.0, 140.9, 138.3, 138.0, 137.2, 137.0, 136.8, 132.1, 131.3, 130.6, 130.0, 129.9, 129.1, 128.7, 128.4, 128.0, 127.7, 127.4, 127.3, 126.9, 126.3, 126.2, 125.5, 125.5, 123.1, 122.8, 122.4, 120.2, 120.1, 119.6, 112.9, 112.1, 110.5, 110.4, 60.9, 47.9, 35.5, 21.3, 14.0. HRMS (ESI-TOF) m/z: $[M+Na]^+$ Calcd for $C_{43}H_{36}N_2NaO_2^+$ 647.2669, found 647.2673.

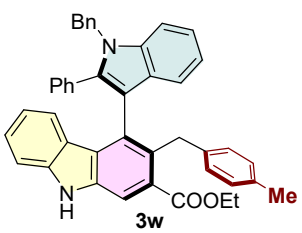
ethyl 4-(1-benzyl-2-phenyl-1*H*-indol-3-yl)-3-(4-fluorobenzyl)-9*H*-carbazole-2-carboxylate (3v)



3v

The residue was purified by a silica gel flash chromatography (PE/EA = 5/1) giving the product **3v** as a white solid in 92% yield (58.1 mg), m.p. 117-119 °C. ^{1}H NMR (700 MHz, Chloroform-*d*) δ 8.23 (s, 1H), 7.91 (s, 1H), 7.38 (dd, *J* = 11.8, 8.2 Hz, 2H), 7.31 (ddd, *J* = 8.2, 7.0, 1.3 Hz, 1H), 7.29 – 7.26 (m, 2H), 7.26 – 7.22 (m, 1H), 7.18 (t, *J* = 7.7 Hz, 1H), 7.10 – 7.05 (m, 3H), 7.03 (d, *J* = 7.9 Hz, 1H), 6.96 – 6.92 (m, 3H), 6.90 – 6.87 (m, 2H), 6.82 (d, *J* = 7.7 Hz, 1H), 6.79 (t, *J* = 7.5 Hz, 1H), 6.54 (t, *J* = 8.8 Hz, 2H), 6.46 (dd, *J* = 8.5, 5.6 Hz, 2H), 5.45 (d, *J* = 16.5 Hz, 1H), 5.39 (d, *J* = 16.5 Hz, 1H), 4.31 (d, *J* = 15.8 Hz, 1H), 4.13 (d, *J* = 15.8 Hz, 1H), 4.12 – 4.04 (m, 2H), 1.13 (t, *J* = 7.1 Hz, 3H). ^{13}C NMR (176 MHz, Chloroform-*d*) δ 169.0, 160.5 (d, *J* = 241.7 Hz), 140.9, 138.2, 137.9, 137.8 (d, *J* = 2.9 Hz), 137.2, 137.1, 131.9, 131.3, 130.6, 129.8, 129.6, 129.4, 129.4, 128.7, 128.3, 128.1, 127.7, 127.3, 127.2, 126.4, 126.4, 123.0, 122.8, 122.5, 120.3, 120.0, 119.7, 114.1 (d, *J* = 21.1 Hz), 112.8, 112.4, 110.5 (d, *J* = 10.1 Hz), 60.9, 47.9, 34.8, 14.0. HRMS (ESI-TOF) m/z: $[M+Na]^+$ Calcd for $C_{43}H_{33}FN_2NaO_2^+$ 651.2418, found 651.2427.

ethyl 4-(1-benzyl-2-phenyl-1*H*-indol-3-yl)-3-(4-methylbenzyl)-9*H*-carbazole-2-carboxylate (3w)

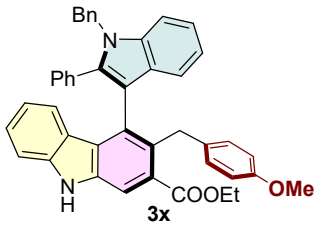


3w

The residue was purified by a silica gel flash chromatography (PE/EA = 5/1) giving the product **3w** as a white solid in 85%

yield (53.3 mg), m.p. 125-127 °C. ^{1}H NMR (700 MHz, Chloroform-*d*) δ 8.18 (s, 1H), 7.85 (s, 1H), 7.38 (d, *J* = 8.1 Hz, 1H), 7.35 (d, *J* = 8.3 Hz, 1H), 7.33 – 7.26 (m, 3H), 7.24 (d, *J* = 7.2 Hz, 1H), 7.17 (t, *J* = 7.6 Hz, 1H), 7.12 – 7.05 (m, 4H), 6.97 – 6.89 (m, 5H), 6.83 (d, *J* = 7.9 Hz, 1H), 6.79 (t, *J* = 7.5 Hz, 1H), 6.70 (d, *J* = 7.8 Hz, 2H), 6.46 (d, *J* = 7.7 Hz, 2H), 5.44 (d, *J* = 16.6 Hz, 1H), 5.39 (d, *J* = 16.6 Hz, 1H), 4.31 (d, *J* = 15.8 Hz, 1H), 4.14 (d, *J* = 15.8 Hz, 1H), 4.10 – 4.00 (m, 2H), 2.15 (s, 3H), 1.12 (t, *J* = 7.1 Hz, 3H). ^{13}C NMR (176 MHz, Chloroform-*d*) δ 169.2, 140.8, 139.1, 138.3, 138.0, 137.2, 137.0, 133.9, 132.4, 131.4, 130.5, 130.0, 129.9, 128.7, 128.4, 128.2, 128.2, 128.0, 127.64, 127.3, 126.8, 126.4, 126.2, 123.1, 122.8, 122.3, 120.2, 120.1, 119.5, 112.9, 112.1, 110.5 110.4, 60.9, 47.9, 35.2, 20.8, 14.0. HRMS (ESI-TOF) m/z: $[M+Na]^+$ Calcd for $C_{43}H_{36}N_2NaO_2^+$ 647.2669, found 647.2679.

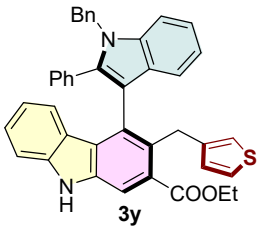
ethyl 4-(1-benzyl-2-phenyl-1*H*-indol-3-yl)-3-(4-methoxybenzyl)-9*H*-carbazole-2-carboxylate (3x)



3x

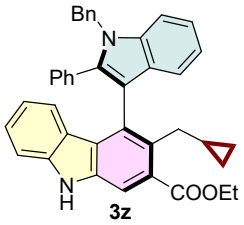
The residue was purified by a silica gel flash chromatography (PE/EA = 5/1) giving the product **3x** as a white solid in 68% yield (43.3 mg), m.p. 122-124 °C. ^{1}H NMR (600 MHz, Chloroform-*d*) δ 8.20 (d, *J* = 5.9 Hz, 1H), 7.86 (s, 1H), 7.39 (d, *J* = 8.1 Hz, 1H), 7.36 (d, *J* = 8.3 Hz, 1H), 7.33 – 7.26 (m, 3H), 7.25 (d, *J* = 7.9 Hz, 2H), 7.18 (t, *J* = 7.6 Hz, 1H), 7.12 – 7.05 (m, 4H), 6.98 – 6.91 (m, 5H), 6.83 (d, *J* = 8.0 Hz, 1H), 6.79 (t, *J* = 7.5 Hz, 1H), 6.49 – 6.42 (m, 4H), 5.45 (d, *J* = 16.5 Hz, 1H), 5.39 (d, *J* = 16.6 Hz, 1H), 4.27 (d, *J* = 15.7 Hz, 1H), 4.14 – 4.02 (m, 3H), 3.65 (s, 3H), 1.14 (t, *J* = 7.1 Hz, 3H). ^{13}C NMR (151 MHz, Chloroform-*d*) δ 169.2, 156.9, 140.9, 138.3, 138.0, 137.2, 137.0, 134.4, 132.5, 131.4, 130.5, 130.0, 129.9, 129.2, 128.7, 128.4, 128.1, 127.7, 127.3, 126.9, 126.4, 126.3, 123.1, 122.8, 122.4, 120.3, 120.1, 119.6, 113.0, 112.9, 112.1, 110.5, 110.4, 60.9, 55.2, 47.9, 34.7, 14.0. HRMS (ESI-TOF) m/z: $[M+Na]^+$ Calcd for $C_{44}H_{36}N_2NaO_3^+$ 663.2618, found 663.2625.

ethyl 4-(1-benzyl-2-phenyl-1*H*-indol-3-yl)-3-(thiophen-3-ylmethyl)-9*H*-carbazole-2-carboxylate (3y)



The residue was purified by a silica gel flash chromatography (PE/EA = 5/1) giving the product **3y** as a white solid in 95% yield (58.7 mg), m.p. 104-106 °C. ^{1}H NMR (700 MHz, Chloroform-*d*) δ 8.12 (s, 1H), 7.80 (s, 1H), 7.30 (dd, *J* = 8.2, 4.7 Hz, 2H), 7.25 – 7.19 (m, 3H), 7.18 – 7.15 (m, 1H), 7.12 (t, *J* = 7.7 Hz, 1H), 7.03 (d, *J* = 7.6 Hz, 2H), 7.01 – 6.97 (m, 2H), 6.91 – 6.83 (m, 6H), 6.76 (d, *J* = 8.0 Hz, 1H), 6.72 (t, *J* = 7.5 Hz, 1H), 6.38 (d, *J* = 5.0 Hz, 1H), 6.07 – 6.04 (m, 1H), 5.38 (d, *J* = 16.5 Hz, 1H), 5.33 (d, *J* = 16.5 Hz, 1H), 4.27 (d, *J* = 15.7 Hz, 1H), 4.11 – 4.01 (m, 3H), 1.10 (t, *J* = 7.4 Hz, 3H). ^{13}C NMR (176 MHz, Chloroform-*d*) δ 168.2, 141.7, 139.8, 137.2, 137.1, 136.2, 136.0, 131.1, 130.3, 129.0, 128.8, 128.5, 127.6, 127.4, 127.3, 127.1, 126.7, 126.3, 125.8, 125.3, 125.3, 122.8, 122.1, 121.8, 121.4, 119.3, 119.2, 119.0, 118.5, 111.8, 111.3, 109.5, 109.4, 59.9, 46.9, 29.8, 13.0. HRMS (ESI-TOF) m/z: $[M+Na]^+$ Calcd for $C_{41}H_{32}N_2NaO_2S^+$ 639.2077, found 639.2078.

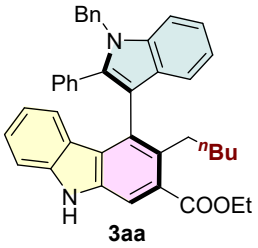
ethyl 4-(1-benzyl-2-phenyl-1*H*-indol-3-yl)-3-(cyclopropylmethyl)-9*H*-carbazole-2-carboxylate (3z)



The residue was purified by a silica gel flash chromatography (PE/EA = 5/1) giving the product **3z** as a colorless oil in 44% yield (25.0 mg). ^{1}H NMR (600 MHz, Chloroform-*d*) δ 8.10 (s, 1H), 7.87 (s, 1H), 7.39 (d, *J* = 8.3 Hz, 1H), 7.34 (d, *J* = 8.1 Hz, 1H), 7.32 – 7.27 (m, 3H), 7.26 – 7.23 (m, 1H), 7.22 – 7.18 (m, 1H), 7.14 – 7.09 (m, 5H), 7.09 – 7.06 (m, 1H), 7.02 (t, *J* = 7.4 Hz, 2H), 6.98 (t, *J* = 7.2 Hz, 1H), 6.76 (d, *J* = 4.0 Hz, 2H), 5.53 (d, *J* = 16.6 Hz, 1H), 5.46 (d, *J* = 16.6 Hz, 1H), 4.38 (d, *J* = 7.1 Hz, 1H), 4.36 (d, *J* = 7.1 Hz, 1H), 2.99 (dd, *J* = 13.9, 5.7 Hz, 1H), 2.67 (dd, *J* = 13.9, 7.4 Hz, 1H), 1.40 (t, *J* = 7.1 Hz, 3H), 0.59 (qq, *J* = 7.9, 5.2 Hz, 1H), 0.18 – 0.10 (m, 1H), 0.07 – 0.00 (m, 1H), -0.11 – -0.18 (m, 1H), -0.27 – -0.33 (m, 1H). ^{13}C NMR (151 MHz, Chloroform-*d*) δ 169.8, 140.9, 138.4, 137.6, 137.3, 136.8, 134.5, 131.6, 129.8, 129.5, 129.0, 128.9, 128.7, 128.1, 127.8, 127.3, 126.8, 126.3, 126.2, 123.1, 122.9, 122.4, 120.4, 120.3, 119.4, 113.4, 112.1, 110.5, 110.3, 61.0, 48.0, 33.7, 14.3,

12.8, 5.3, 4.7.HRMS (ESI-TOF) m/z: $[M+Na]^+$ Calcd for $C_{40}H_{34}N_2NaO_2^+$ 597.2512, found 597.2520.

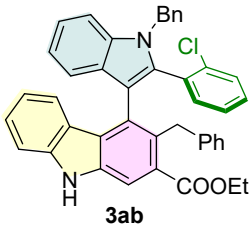
ethyl 4-(1-benzyl-2-phenyl-1*H*-indol-3-yl)-3-pentyl-9*H*-carbazole-2-carboxylate (3aa)



3aa

The residue was purified by a silica gel flash chromatography (PE/EA = 5/1) giving the product **3aa** as a colorless oil in 78% yield (46.1 mg). ^{1}H NMR (600 MHz, Chloroform-*d*) δ 8.12 (s, 1H), 7.92 (s, 1H), 7.39 (d, *J* = 2.7 Hz, 1H), 7.37 (d, *J* = 2.9 Hz, 1H), 7.33 – 7.28 (m, 3H), 7.28 – 7.24 (m, 2H), 7.22 – 7.18 (m, 1H), 7.13 (d, *J* = 7.2 Hz, 2H), 7.12 – 7.09 (m, 3H), 7.07 – 7.02 (m, 3H), 6.97 (t, *J* = 7.4 Hz, 1H), 6.80 – 6.75 (m, 2H), 5.55 (d, *J* = 16.7 Hz, 1H), 5.48 (d, *J* = 16.7 Hz, 1H), 4.37 (qd, *J* = 7.1, 1.6 Hz, 2H), 2.83 (td, *J* = 11.9, 11.1, 4.7 Hz, 1H), 2.76 – 2.66 (m, 1H), 1.39 (t, *J* = 7.1 Hz, 3H), 1.22 – 1.13 (m, 1H), 1.09 – 0.95 (m, 5H), 0.66 (t, *J* = 6.7 Hz, 3H).^{13}C NMR (151 MHz, Chloroform-*d*) δ 169.3, 141.0, 138.4, 137.4, 137.3, 136.6, 135.6, 131.7, 129.7, 129.4, 128.7, 128.5, 128.2, 127.8, 127.3, 127.2, 126.3, 126.2, 123.1, 122.9, 122.4, 120.2, 119.5, 113.2, 112.3, 110.4, 110.3, 60.9, 48.0, 32.6, 31.6, 30.6, 22.2, 14.3, 14.0. HRMS (ESI-TOF) m/z: $[M+Na]^+$ Calcd for $C_{41}H_{38}N_2NaO_2^+$ 613.2825, found 613.2825.

ethyl 3-benzyl-4-(1-benzyl-2-(2-chlorophenyl)-1*H*-indol-3-yl)-9*H*-carbazole-2-carboxylate (3ab)

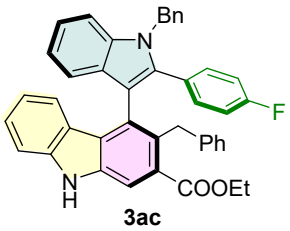


3ab

The residue was purified by a silica gel flash chromatography (PE/EA = 5/1) giving the product **3ab** as a white solid in 84% yield (54.5 mg), m.p. 126-128 ℃. ^{1}H NMR (600 MHz, Chloroform-*d*) δ 8.16 (s, 1H), 7.77 (s, 1H), 7.36 (d, *J* = 9.0 Hz, 2H), 7.26 (t, *J* = 7.2 Hz, 1H), 7.18 (s, 1H), 7.14 – 7.08 (m, 5H), 6.98 (d, *J* = 7.9 Hz, 3H), 6.84 (dt, *J* = 14.4, 7.3 Hz, 4H), 6.71 (q, *J* = 8.1, 7.3 Hz, 2H), 6.66 (q, *J* = 8.2 Hz, 1H), 6.60 (d, *J* = 7.9 Hz, 1H), 6.43 (d, *J* = 6.6 Hz, 2H), 5.41 (d, *J* = 16.2 Hz, 1H), 5.10 (d, *J* = 16.2 Hz, 1H), 4.34 (d, *J* = 16.3 Hz, 1H), 4.24 (d, *J* = 16.2 Hz, 1H), 3.93 – 3.82 (m, 2H), 0.96 (t, *J* = 7.1 Hz, 3H). ^{13}C NMR (151 MHz, Chloroform-*d*) δ 169.2, 142.7, 138.2, 136.9, 136.7, 135.0, 134.7, 132.9, 132.4, 130.7, 130.1, 130.0,

129.8, 129.7, 128.5, 128.4, 128.1, 127.4, 127.4, 126.8, 126.7, 126.3, 126.3, 124.5, 123.1, 122.8, 122.6, 120.3, 120.1, 119.6, 113.7, 112.4, 110.6, 110.5, 60.9, 48.2, 35.6, 13.9. HRMS (ESI-TOF) m/z: $[M+Na]^+$ Calcd for $C_{43}H_{33}ClN_2NaO_2^+$ 667.2123, found 667.2128.

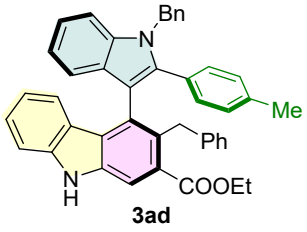
ethyl 3-benzyl-4-(1-benzyl-2-(4-fluorophenyl)-1*H*-indol-3-yl)-9*H*-carbazole-2-carboxylate (3ac)



3ac

The residue was purified by a silica gel flash chromatography (PE/EA = 5/1) giving the product **3ac** as a white solid in 98% yield (61.3 mg), m.p. 102-104 ℃. ^{1}H NMR (700 MHz, Chloroform-*d*) δ 8.16 (s, 1H), 7.85 (s, 1H), 7.33 (d, *J* = 8.1 Hz, 1H), 7.30 (d, *J* = 8.3 Hz, 1H), 7.26 – 7.23 (m, 1H), 7.23 – 7.20 (m, 2H), 7.19 – 7.16 (m, 2H), 7.15 – 7.11 (m, 1H), 7.03 (d, *J* = 7.9 Hz, 1H), 7.00 (d, *J* = 7.8 Hz, 2H), 6.91 (t, *J* = 7.5 Hz, 1H), 6.86 – 6.82 (m, 3H), 6.74 – 6.69 (m, 4H), 6.54 – 6.47 (m, 4H), 5.32 (d, *J* = 16.6 Hz, 1H), 5.29 (d, *J* = 16.6 Hz, 1H), 4.34 (d, *J* = 16.0 Hz, 1H), 4.10 (d, *J* = 16.0 Hz, 1H), 4.04 – 3.95 (m, 2H), 1.03 (t, *J* = 7.1 Hz, 3H). ^{13}C NMR (176 MHz, Chloroform-*d*) δ 169.1, 163.0, 161.6, 142.1, 140.9, 138.1, 137.2, 137.1, 137.0, 131.9, 131.6 (d, *J* = 8.2 Hz), 130.4, 130.0, 128.7, 128.2, 128.1, 127.6, 127.4, 127.3 (d, *J* = 3.2 Hz), 126.9, 126.4, 126.3, 124.8, 123.0, 122.7, 122.6, 120.4, 120.1, 119.7, 115.1 (d, *J* = 21.5 Hz), 113.1, 112.4, 110.5, 110.5, 61.0, 47.8, 35.6, 14.0. HRMS (ESI-TOF) m/z: $[M+Na]^+$ Calcd for $C_{43}H_{33}FN_2NaO_2^+$ 651.2418, found 651.2424.

ethyl 3-benzyl-4-(1-benzyl-2-(p-tolyl)-1*H*-indol-3-yl)-9*H*-carbazole-2-carboxylate (3ad)

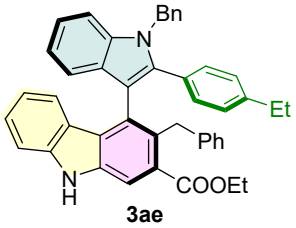


3ad

The residue was purified by a silica gel flash chromatography (PE/EA = 5/1) giving the product **3ad** as a white solid in 99% yield (62.1 mg), m.p. 114-116 ℃. ^{1}H NMR (700 MHz, Chloroform-*d*) δ 8.12 (s, 1H), 7.80 (s, 1H), 7.32 (d, *J* = 8.1 Hz, 1H), 7.27 – 7.23 (m, 2H), 7.23 – 7.20 (m, 2H), 7.18 – 7.15 (m, 1H), 7.09 (t, *J* = 7.6 Hz, 1H), 7.04 (d, *J* = 7.6 Hz, 2H), 6.99 (d, *J* = 7.9 Hz, 1H), 6.87 (t, *J* = 7.5 Hz, 1H), 6.83 (d, *J* = 4.8 Hz, 3H), 6.77 – 6.71 (m, 4H), 6.67 (d, *J* = 7.7 Hz, 2H), 6.50 (d, *J* = 4.4 Hz, 2H), 5.37 (d, *J* = 16.6 Hz, 1H),

5.30 (d, *J* = 16.6 Hz, 1H), 4.28 (d, *J* = 16.0 Hz, 1H), 4.13 (d, *J* = 16.0 Hz, 1H), 4.01 – 3.91 (m, 2H), 2.09 (s, 3H), 1.02 (t, *J* = 7.1 Hz, 3H).^{13}C NMR (176 MHz, Chloroform-d) δ 169.2, 142.3, 140.9, 138.4, 138.2, 137.5, 137.1, 137.1, 132.0, 130.8, 130.0, 129.8, 128.9, 128.7, 128.5, 128.4, 128.3, 127.4, 127.3, 126.9, 126.4, 126.3, 124.6, 123.2, 122.9, 122.2, 120.2, 120.0, 119.6, 112.6, 112.2, 110.5, 110.4, 60.9, 47.9, 35.6, 21.2, 14.0. HRMS (ESI-TOF) m/z: $[M+Na]^+$ Calcd for $C_{43}H_{36}N_2NaO_2^+$ 647.2669, found 647.2666.

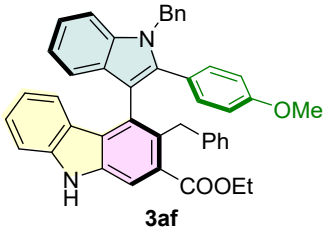
ethyl 3-benzyl-4-(1-benzyl-2-(4-ethylphenyl)-1*H*-indol-3-yl)-9*H*-carbazole-2-carboxylate (3ae)



3ae

The residue was purified by a silica gel flash chromatography (PE/EA = 5/1) giving the product **3ae** as a white solid in 92% yield (58.5 mg), m.p. 112-114 °C. ^{1}H NMR (700 MHz, Chloroform-*d*) δ 8.11 (s, 1H), 7.81 (s, 1H), 7.33 (d, *J* = 8.2 Hz, 1H), 7.27 – 7.24 (m, 2H), 7.24 – 7.20 (m, 2H), 7.17 (t, *J* = 7.3 Hz, 1H), 7.09 (t, *J* = 7.7 Hz, 1H), 7.04 (d, *J* = 7.3 Hz, 2H), 6.99 (d, *J* = 7.9 Hz, 1H), 6.87 (t, *J* = 7.2 Hz, 1H), 6.82 (dd, *J* = 5.2, 1.9 Hz, 3H), 6.77 (d, *J* = 8.2 Hz, 3H), 6.74 – 6.69 (m, 3H), 6.50 – 6.46 (m, 2H), 5.38 (d, *J* = 16.6 Hz, 1H), 5.31 (d, *J* = 16.6 Hz, 1H), 4.28 (d, *J* = 16.0 Hz, 1H), 4.13 (d, *J* = 16.0 Hz, 1H), 4.01 – 3.91 (m, 2H), 2.40 (q, *J* = 7.6 Hz, 2H), 1.05 – 1.01 (m, 6H). ^{13}C NMR (176 MHz, Chloroform-*d*) δ 169.2, 143.6, 142.3, 140.9, 138.4, 138.2, 137.1, 137.1, 132.1, 130.9, 130.0, 129.8, 128.7, 128.6, 128.5, 128.3, 127.7, 127.5, 127.2, 127.0, 126.4, 126.3, 124.6, 123.2, 122.9, 122.2, 120.2, 120.0, 119.6, 112.5, 112.1, 110.5, 110.4, 60.9, 47.9, 35.6, 28.5, 15.1, 14.0 HRMS (ESI-TOF) m/z: $[M+Na]^+$ Calcd for $C_{45}H_{38}N_2NaO_2^+$ 661.2825, found 661.2835.

ethyl 3-benzyl-4-(1-benzyl-2-(4-methoxyphenyl)-1*H*-indol-3-yl)-9*H*-carbazole-2-carboxylate (3af)

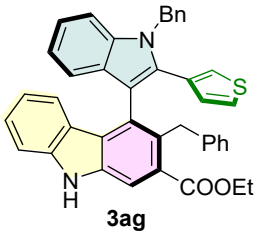


3af

The residue was purified by a silica gel flash chromatography (PE/EA = 5/1) giving the product **3af** as a white solid in 47% yield (30.2 mg), m.p. 111-113 °C. ^{1}H NMR (600 MHz, Chloroform-*d*) δ 8.11 (s, 1H), 7.83 (s, 1H), 7.35 (d, *J* = 8.0 Hz, 1H), 7.28 – 7.24 (m, 2H), 7.23 – 7.20 (m, 2H), 7.18 – 7.16 (m, 1H), 7.09 (t, *J* = 7.6 Hz, 1H), 7.03 (d, *J* = 7.2 Hz, 2H),

7.00 (d, *J* = 7.9 Hz, 1H), 6.88 (t, *J* = 7.5 Hz, 1H), 6.85 – 6.83 (m, 3H), 6.76 – 6.72 (m, 4H), 6.52 – 6.49 (m, 2H), 6.41 – 6.38 (m, 2H), 5.36 (d, *J* = 16.6 Hz, 1H), 5.30 (d, *J* = 16.6 Hz, 1H), 4.31 (d, *J* = 16.0 Hz, 1H), 4.13 (d, *J* = 16.0 Hz, 1H), 4.03 – 3.92 (m, 2H), 3.58 (s, 3H), 1.03 (t, *J* = 7.1 Hz, 3H). ^{13}C NMR (151 MHz, Chloroform-*d*) δ 169.2, 159.1, 142.3, 140.9, 138.4, 138.0, 137.1, 132.0, 131.1, 130.9, 130.0, 128.8, 128.7, 128.4, 128.3, 127.5, 127.3, 127.0, 126.3, 126.3, 124.7, 123.7, 123.2, 122.9, 122.2, 120.2, 119.9, 119.6, 113.6, 112.4, 112.1, 110.40, 60.9, 55.0, 47.8, 35.6, 14.0. HRMS (ESI-TOF) m/z: $[M+Na]^+$ Calcd for $C_{44}H_{36}N_2NaO_3^+$ 663.2618, found 663.2628.

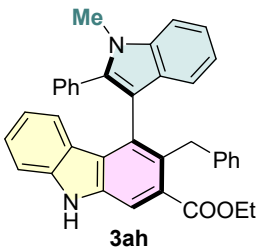
ethyl 3-benzyl-4-(1-benzyl-2-(thiophen-3-yl)-1*H*-indol-3-yl)-9*H*-carbazole-2-carboxylate (3ag)



3ag

The residue was purified by a silica gel flash chromatography (PE/EA = 5/1) giving the product **3ag** as a white solid in 54% yield (33.5 mg), m.p. 90-92 ℃. ^{1}H NMR (600 MHz, Chloroform-*d*) δ 8.14 (s, 1H), 7.88 (s, 1H), 7.34 (d, *J* = 8.1 Hz, 1H), 7.28 – 7.23 (m, 4H), 7.20 (d, *J* = 7.2 Hz, 1H), 7.12 (t, *J* = 7.6 Hz, 1H), 7.07 – 7.03 (m, 3H), 6.91 (t, *J* = 7.4 Hz, 1H), 6.86 – 6.81 (m, 4H), 6.77 (d, *J* = 7.9 Hz, 1H), 6.72 (t, *J* = 7.5 Hz, 1H), 6.57 – 6.54 (m, 1H), 6.53 – 6.49 (m, 2H), 6.46 – 6.42 (m, 1H), 5.42 (d, *J* = 16.7 Hz, 1H), 5.37 (d, *J* = 16.9 Hz, 1H), 4.36 (d, *J* = 15.9 Hz, 1H), 4.11 – 4.00 (m, 3H), 1.07 (t, *J* = 7.1 Hz, 3H). ^{13}C NMR (151 MHz, Chloroform-*d*) δ 169.1, 142.2, 140.9, 138.3, 137.2, 137.1, 133.3, 132.2, 131.4, 130.8, 130.0, 128.8, 128.4, 128.2, 128.1, 127.6, 127.3, 127.0, 126.4, 126.2, 125.0, 125.0, 124.7, 123.1, 122.8, 122.5, 120.3, 120.0, 119.7, 112.8, 112.3, 110.5, 110.2, 61.0, 47.9, 35.6, 14.0. HRMS (ESI-TOF) m/z: $[M+Na]^+$ Calcd for $C_{41}H_{32}N_2NaO_2S^+$ 639.2077, found 639.2084.

ethyl 3-benzyl-4-(1-methyl-2-phenyl-1*H*-indol-3-yl)-9*H*-carbazole-2-carboxylate (3ah)

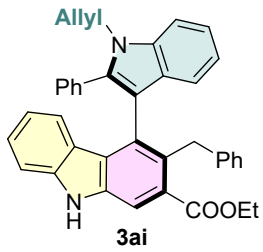


3ah

The residue was purified by a silica gel flash chromatography (PE/EA = 5/1) giving the product **3ah** as a white solid in 97% yield (51.6 mg), m.p. 115-117 ℃. ^{1}H NMR (600 MHz, Chloroform-*d*) δ 8.19 (s, 1H), 7.86 (s, 1H), 7.48 (d, *J* = 8.2 Hz,

1H), 7.38 (d, *J* = 8.0 Hz, 1H), 7.33 – 7.26 (m, 2H), 7.14 – 7.06 (m, 2H), 7.04 – 6.96 (m, 5H), 6.91 – 6.87 (m, 3H), 6.85 – 6.78 (m, 2H), 6.57 – 6.52 (m, 2H), 4.32 (d, *J* = 16.0 Hz, 1H), 4.15 (d, *J* = 16.0 Hz, 1H), 4.07 – 3.95 (m, 2H), 3.81 (s, 3H), 1.08 (t, *J* = 7.1 Hz, 3H). ^{13}C NMR (151 MHz, Chloroform-*d*) δ 169.2, 142.3, 140.8, 137.9, 137.6, 137.0, 132.1, 131.5, 130.7, 130.0, 128.3, 128.0, 128.0, 127.6, 127.5, 126.9, 126.2, 124.6, 123.2, 122.8, 122.1, 120.0, 120.0, 119.6, 112.2, 112.0, 110.4, 109.4, 60.8, 35.5, 31.4, 14.0. HRMS (ESI-TOF) m/z: $[M+Na]^+$ Calcd for $C_{37}H_{30}N_2NaO_2^+$ 557.2199, found 557.2206.

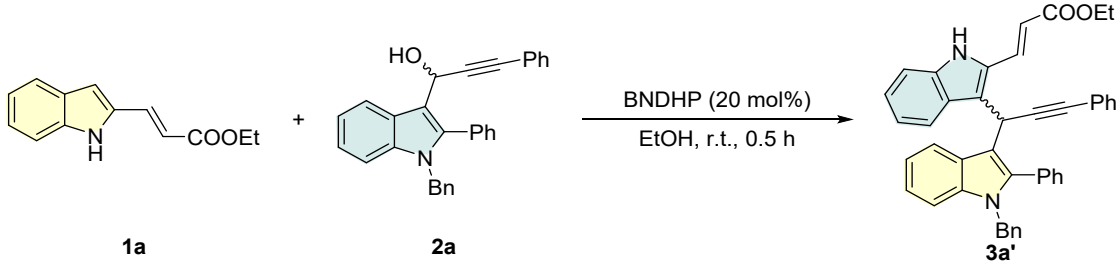
ethyl 4-(1-allyl-2-phenyl-1*H*-indol-3-yl)-3-benzyl-9*H*-carbazole-2-carboxylate (3ai)



3ai

The residue was purified by a silica gel flash chromatography (PE/EA = 5/1) giving the product **3ai** as a white solid in 88% yield (49.6 mg), m.p. 106-108 ℃. ^{1}H NMR (700 MHz, Chloroform-*d*) δ 8.11 (s, 1H), 7.78 (s, 1H), 7.36 (d, *J* = 8.3 Hz, 1H), 7.29 (d, *J* = 8.1 Hz, 1H), 7.24 – 7.20 (m, 1H), 7.18 – 7.14 (m, 1H), 7.04 – 6.99 (m, 2H), 6.95 – 6.87 (m, 5H), 6.85 – 6.81 (m, 3H), 6.77 – 6.73 (m, 2H), 6.51 (s, 2H), 5.97 – 5.89 (m, 1H), 5.16 (d, *J* = 10.4 Hz, 1H), 5.01 (d, *J* = 17.2 Hz, 1H), 4.71 (qd, *J* = 17.5, 4.3 Hz, 2H), 4.27 (d, *J* = 16.0 Hz, 1H), 4.12 (d, *J* = 15.9 Hz, 1H), 4.01 – 3.91 (m, 2H), 1.02 (t, *J* = 7.1 Hz, 3H). ^{13}C NMR (176 MHz, Chloroform-*d*) δ 168.2, 141.2, 139.8, 136.7, 136.0, 132.9, 131.0, 130.4, 129.7, 128.9, 128.8, 127.3, 127.2, 127.0, 126.7, 126.5, 125.8, 125.2, 123.7, 122.1, 121.7, 121.2, 119.1, 119.1, 118.5, 115.4, 111.4, 111.2, 109.4, 109.2, 59.8, 45.6, 34.6, 12.9. HRMS (ESI-TOF) m/z: $[M+Na]^+$ Calcd for $C_{39}H_{32}N_2NaO_2^+$ 583.2356, found 583.2353.

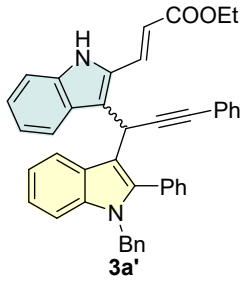
3. Synthesis of Intermediate 3a'



1a **2a** **3a'**

To a dry flask, absolute ethyl alcohol (1.0 mL) was added to a mixture of 2-indolyl acrylate **1a** (0.1 mmol), propargylic alcohol **2a** (0.1 mmol) and (±)-1,1′-binaphthyl-2,2′-diylhydrogenphosphate (BNDHP) (20 mol%). Then, the mixture was stirred at room temperature for 0.5 h. The reaction mixture was monitored by TLC, the solvent was evaporated under reduced pressure and the residue was purified by flash column chromatography to yield the intermediate **3a'** (58.1 mg, 95% yield).

ethyl (*E*)-3-(3-(1-(1-benzyl-2-phenyl-1*H*-indol-3-yl)-3-phenylprop-2-yn-1-yl)-1*H*-indol-2-yl)acrylate (3a')



3a'

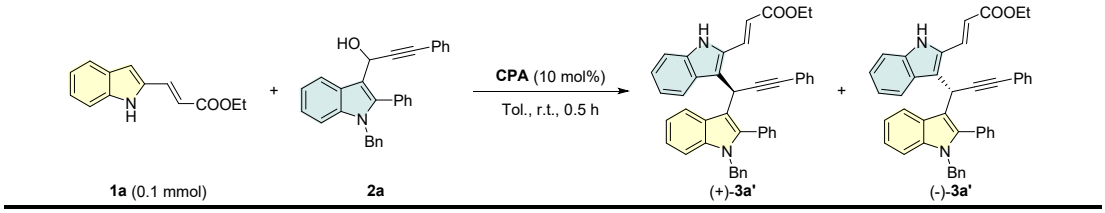
The residue was purified by a silica gel flash chromatography (PE/EA = 5/1) giving the product **3a'** as a white solid in 95% yield (58.1 mg), m.p. 127-129 °C. ^{1}H NMR (600 MHz, Chloroform-*d*) δ 8.13 (d, *J* = 16.2 Hz, 1H), 8.07 (s, 1H), 7.99 (d, *J* = 7.8 Hz, 1H), 7.54 (d, *J* = 7.8 Hz, 1H), 7.51 – 7.48 (m, 2H), 7.32 – 7.26 (m, 7H), 7.23 (d, *J* = 7.8 Hz, 1H), 7.18 (m, 5H), 7.13 (t, *J* = 8.4 Hz, 1H), 7.09 (t, *J* = 8.4 Hz, 1H), 6.93 – 6.89 (m, 3H), 6.01 (d, *J* = 16.2 Hz, 1H), 5.91 (s, 1H), 5.16 (s, 2H), 4.19 (m, 2H), 1.23 (t, *J* = 7.2 Hz, 3H). ^{13}C NMR (150 MHz, Chloroform-*d*) δ 166.6, 138.2, 138.1, 136.9, 136.7, 132.7, 131.7, 131.2, 130.8, 129.7, 128.6, 128.4, 128.1,127.8, 127.1, 126.8, 126.0, 124.6, 123.8, 122.0, 121.2, 120.4, 120.3, 120.1, 120.0, 115.2, 112.4, 110.8, 110.4, 90.6, 83.2, 60.4, 47.4, 27.0, 14.3. HRMS (ESI-TOF) m/z: $[M+Na]^+$ Calcd for $C_{43}H_{34}N_2NaO_2^+$ 633.2512, found 633.2510.

4. Screening of Catalysts for Atropselective Synthesis of Axially Chiral Carbazolyl-Indole 3a

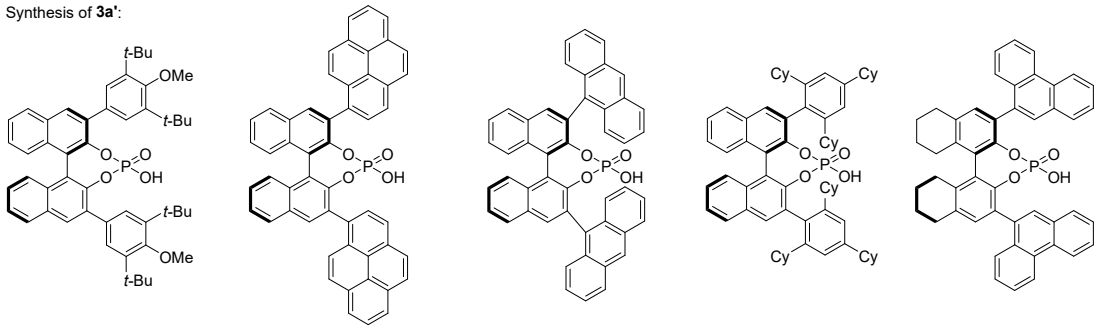
To screen the catalysts for atropselective synthesis of axially chiral carbazolyl-indole **3a**, the reaction was processed as below. To a dry flask, dry toluene (1.0 mL) was added to a mixture of 2-indolyl acrylate **1** (0.1 mmol), propargylic alcohol **2** (0.1 mmol) and corresponding chiral phosphoric acid (CPA) (10 mol%). Then, the mixture was stirred at room temperature for 0.5 h and monitored by TLC. After the consumption of **1a**, intermediate **3a'** was obtained by purified through flash column chromatography. The enantioselectivity ratio of intermediate **3a'** was determined by HPLC on a

Chiralpak AD-H column at 254 nm (n-hexane/2-propanol = 80/20, 1 mL/min).

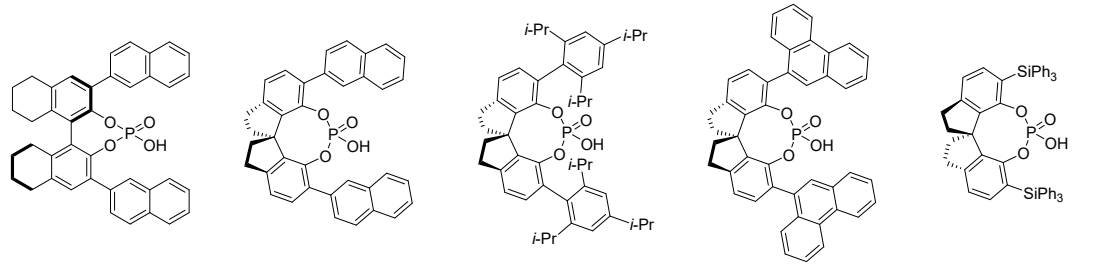
After screening out the optimal chiral phosphoric acid (**CPA6**), the intermediate **3a'** (55 mg, 8:92 er), prepared by **CPA6**, was straightly used in next cyclization. Corresponding base (15.3mg, 1.1 equiv.) was added to the mixture of **3a'** in dry toluene (1.0 mL) and the mixture was stirred at corresponding temperature for 2 h or 12 h. The final product **3a** was obtained by purified through flash column chromatography. The enantiomeric excess value of carbazolyl-indole **3a** was determined by HPLC on a Chiralpak OD-H column at 254 nm (n-hexane/2-propanol = 90/10, 1 mL/min, t_{major} = 10.08 min, t_{minor} = 12.59 min).



Synthesis of **3a'**:

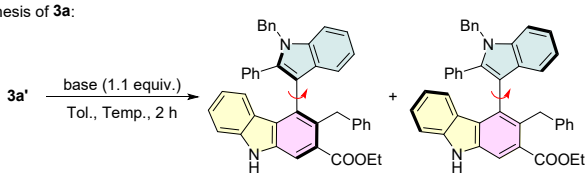


CPA1, 86%, 13:87 er | **CPA2**, 89%, 12:88 er | **CPA3**, 89%, 17:83 er | **CPA4**, 81%, 62:38 er | **CPA5**, 91%, 14:86 er



CPA6, 91%, 8:92 er | **CPA7**, 90%, 9:91 er | **CPA8**, 83%, 49:51 er | **CPA9**, 91%, 61:39 er | **CPA10**, 81%, 49:51 er

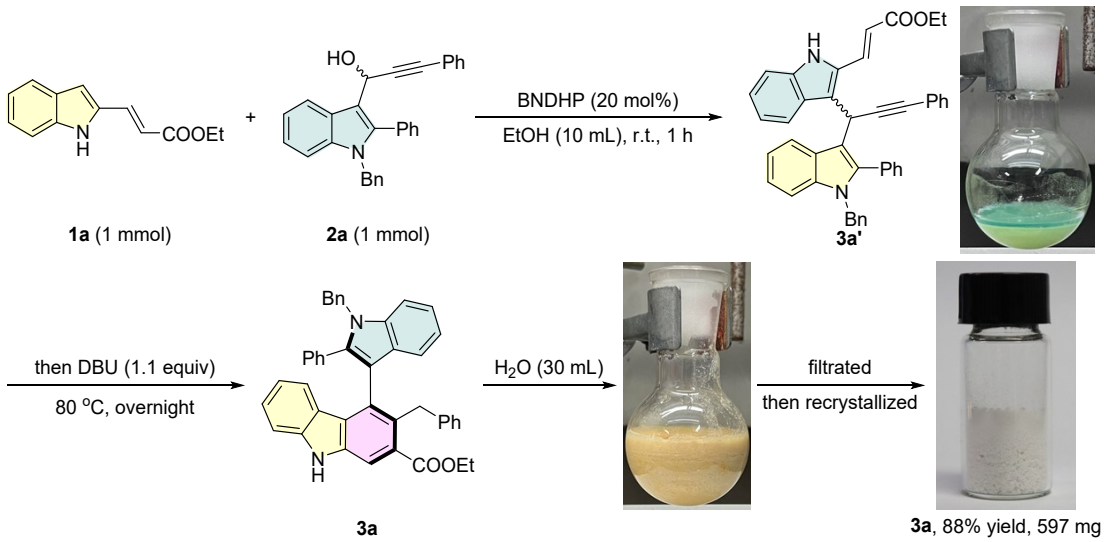
Synthesis of **3a**:



Entry	Base	Yield of **3a** (%)	Temp (°C)	E.r. value of **3a**
1	**DBU**	**94**	**40**	**69:31**
2	TEA	N.R.	40	-
3[a]	K_2CO_3	72	r.t.	63:37
4[a]	K_2CO_3	trace	0	-

[a] The reaction was conducted for 12 h.

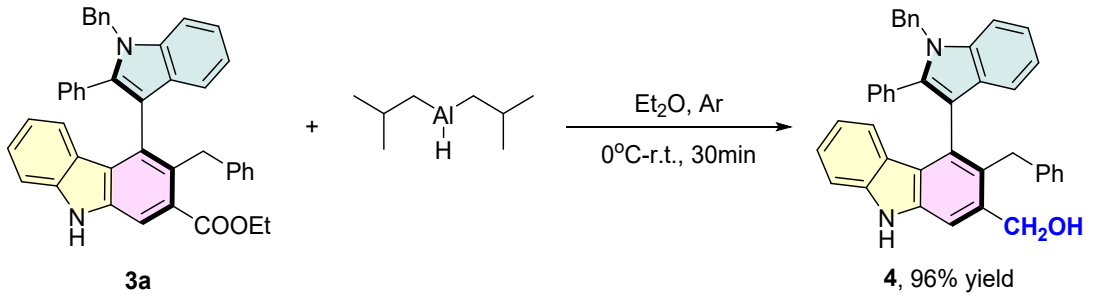
5. The Scale-Up Reaction



To a dry flask, absolute ethyl alcohol (10.0 mL) was added to a mixture of 2-indolyl acrylate **1a** (1 mmol), propargylic alcohol **2a** (1 mmol) and (±)-1,1′-binaphthyl-2,2′-diylhydrogenphosphate (BNDHP) (20 mol%). Then, the mixture was stirred at room temperature for 1 h. After 1 h, DBU (1.1 equiv.) was added to the mixture and the mixture continued to be stirred at 80 ℃ overnight and monitored by TLC. After completion of the reaction, deionized water (30 mL) was poured into the mixture, and the crude product **3a** precipitated. After filtration, the crude product was recrystallized by isopropanol and hexane to afford pure product **3a** (88% yield, 597 mg).

6. Synthetic Transformations of 3a

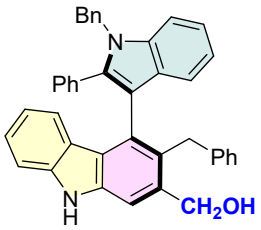
6.1 Procedure for Synthesis of Compound 4



To a solution of **3a** (61.8 mg, 0.1 mmol) in absolute ethyl ether (2.0 mL), diisobutylaluminium hydride (2mL, 1M in hexanes, 0.2 mmol) was added at 0 ℃ under argon atmosphere. Then, the mixture was stirred at room temperature for 0.5 h and monitored by TLC. After the consumption of **3a**, the mixture was quenched by 0.5 mL

deionized water. The solvent was removed in vacuo and the residue was purified by flash column chromatography on silica gel to give the final products **4** (54.8 mg, 96% yield) as a white solid.

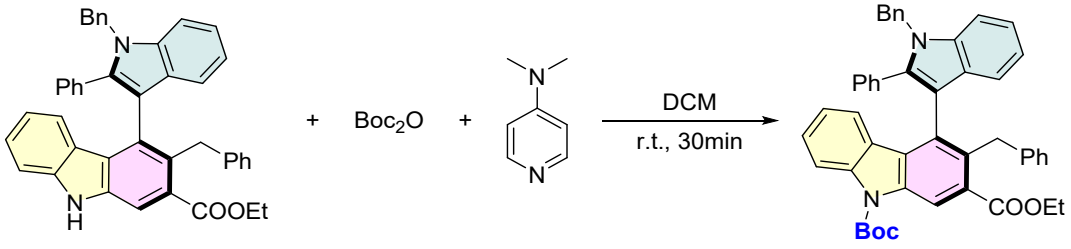
(3-benzyl-4-(1-benzyl-2-phenyl-1*H*-indol-3-yl)-9*H*-carbazol-2-yl)methanol



4

The residue was purified by a silica gel flash chromatography (PE/EA = 2/1) giving the product **4** as a white solid in 96% yield (54.8 mg), m.p. 128.6-130.8 ℃. ^{1}H NMR (600 MHz, Chloroform-*d*) δ 8.08 (s, 1H), 7.53 (s, 1H), 7.37 (d, *J* = 8.4, 1H), 7.35 (d, *J* = 8.4, 1H), 7.30 – 7.25 (m, 3H), 7.25 – 7.21 (m, 2H), 7.17 (t, *J* = 7.2 Hz, 1H), 7.10 – 7.07 (m, 4H), 6.98 – 6.91 (m, 9H), 6.83 – 6.77 (m, 2H), 6.61 (d, *J* = 6.6 Hz, 2H), 5.46 (d, *J* = 16.8, 1H), 5.39 (d, *J* = 16.2, 1H), 4.56 (d, *J* = 13.2 Hz, 1H), 4.52 (d, *J* = 13.8 Hz, 1H), 4.03 (d, *J* = 16.8 Hz, 1H), 3.90 (d, *J* = 16.8 Hz, 1H). ^{13}C NMR (150 MHz, Chloroform-*d*) δ 141.8, 140.0, 138.3, 138.1, 137.9, 137.2, 131.6, 130.0, 129.8, 129.4, 128.6, 128.5, 128.2, 128.1, 127.9, 127.6, 127.3, 126.37, 125.2, 125.1, 123.9, 123.6, 122.3, 122.2, 120.2, 120.1, 119.3, 113.5, 110.5, 110.2, 109.8, 64.0, 47.9, 34.9. HRMS (ESI-TOF) m/z: $[M+Na]^+$ Calcd for $C_{41}H_{32}N_2NaO^+$ 591.2407, found 591.2412.

6.2 Procedure for Synthesis of Compound 5

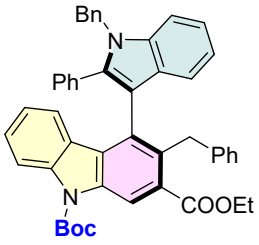


3a **5**, 98% yield

To a dry flask, di-tert-butyl dicarbonate (32.7 mg, 0.15 mmol) was added to a mixture of **3a** (61.1 mg, 0.10 mmol) and DMAP (1.2 mg, 0.01 mmol) in DCM (2 mL). Then, the mixture was stirred at room temperature for 0.5 h and monitored by TLC. After completion of the reaction, the solvent was removed in vacuo and the residue was purified by flash column chromatography on silica gel to give the final products **5** (70 mg, 98% yield) as a white solid.

9-(tert-butyl) 2-ethyl 3-benzyl-4-(1-benzyl-2-phenyl-1*H*-indol-3-yl)-9*H*-carbazole-

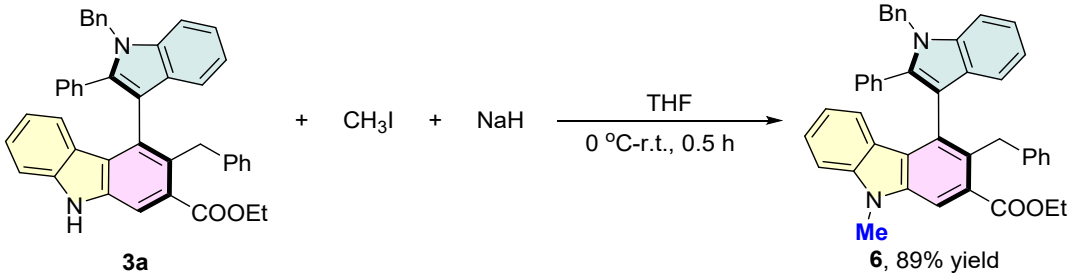
2,9-dicarboxylate



5

The residue was purified by a silica gel flash chromatography (PE/EA = 10/1) giving the product **5** as a white solid in 98% yield (70.0 mg), m.p. 127.6-129.9 ℃. ^{1}H NMR (700 MHz, Chloroform-*d*) δ 8.80 (s, 1H), 8.37 (d, *J* = 8.4 Hz, 1H), 7.36 (m, 2H), 7.28 (t, *J* = 7.0 Hz, 2H), 7.25 – 7.23 (m, 1H), 7.18 (t, *J* = 7.7 Hz, 1H), 7.10 – 7.08 (m, 3H), 7.04 (d, *J* = 8.4 Hz, 1H), 6.98 – 6.94 (m, 3H), 6.92 – 6.86 (m, 6H), 6.76 (d, *J* = 7.7 Hz, 1H), 6.58 – 6.57 (m, 2H), 5.42 (d, *J* = 16.1 Hz, 1H), 5.37 (d, *J* = 16.8 Hz, 1H), 4.35 (d, *J* = 16.8 Hz, 1H), 4.19 (d, *J* = 15.4 Hz, 1H), 4.09 – 4.04 (m, 2H), 1.78 (s, 9H), 1.11 (t, *J* = 7.0 Hz, 3H). ^{13}C NMR (176 MHz, Chloroform-*d*) δ 168.7, 150.9, 141.5, 139.8, 138.1, 138.0, 137.2, 136.3, 136.2, 131.1, 130.8, 130.4, 129.8, 129.0, 128.7, 128.3, 128.2, 128.1, 127.8, 127.6, 127.4, 127.3, 126.3, 125.4, 128.8, 123.1, 122.6, 122.5, 120.4, 119.9, 117.5, 115.8, 112.1, 110.6, 84.2, 60.9, 47.9, 35.4, 28.4, 14.0. HRMS (ESI-TOF) m/z: $[M+Na]^+$ Calcd for $C_{48}H_{42}N_2NaO_4^+$ 733.3037, found 733.3035.

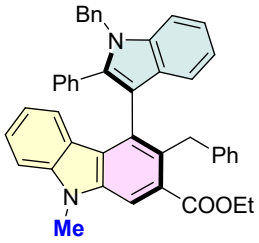
6.3 Procedure for Synthesis of Compound 6



3a **6**, 89% yield

To a dry flask, **3a** (61.1 mg, 0.10 mmol) was dissolved in THF (1 mL) and then was added to a mixture of NaH (4.8 mg, 0.20 mmol) in THF (1 mL). Next, the mixture was stirred at 0 ℃ for 15 min. After 15 min, iodomethane (21.3 mg, 0.15 mmol) was added to mixture and the reaction continued to be stirred at room temperature for 0.5 h. After completion of the reaction, the solvent was removed in vacuo and the residue was purified by flash column chromatography on silica gel to give the final products **6** (55.1 mg, 89% yield) as a white solid.

ethyl 3-benzyl-4-(1-benzyl-2-phenyl-1*H*-indol-3-yl)-9-methyl-9*H*-carbazole-2-carboxylate



6

The residue was purified by a silica gel flash chromatography (PE/EA = 10/1) giving the product **6** as a white solid in 89% yield (55.1 mg), m.p. 119.2-121.6 ℃. ^{1}H NMR (700 MHz, Chloroform-*d*) δ 7.86 (s, 1H), 7.38 (d, *J* = 4.2 Hz, 2H), 7.35 (d, *J* = 8.4 Hz, 1H), 7.28 (t, *J* = 7.7 Hz, 2H), 7.25 – 7.23 (m, 1H), 7.17 (t, *J* = 7.7 Hz, 1H), 7.10 (d, *J* = 7.7 Hz, 2H), 7.08 – 7.05 (m, 2H), 6.95 – 6.91 (m, 5H), 6.90 – 6.89 (m, 3H), 6.86 (d, *J* = 7.7 Hz, 1H), 6.81 – 6.79 (m, 1H), 6.57 (s, 2H), 5.44 (d, *J* = 16.8 Hz, 1H), 5.39 (d, *J* = 16.1 Hz, 1H), 4.36 (d, *J* = 16.1 Hz, 1H), 4.20 (d, *J* = 16.1 Hz, 1H), 4.10 – 4.01 (m, 2H), 3.91 (s, 3H), 1.10 (t, *J* = 7.0 Hz, 3H).^{13}C NMR (176 MHz, Chloroform-*d*) δ 169.4, 142.3, 142.3, 138.6, 138.3, 138.0, 137.2, 131.4, 131.4, 130.6, 129.9 ,129.8, 128.7, 128.4, 128.3, 128.1, 127.7, 127.5, 127.3, 126.4, 126.2, 126.1, 124.6, 122.9, 122.5, 122.4, 120.2, 120.1, 119.1, 112.9, 110.5, 110.1, 108.2, 60.9, 47.9, 35.6, 29.2, 14.0. HRMS (ESI-TOF) m/z: $[M+Na]^+$ Calcd for $C_{44}H_{36}N_2NaO_2^+$ 647.2669, found 647.2665.

6.4 Thermal stability experiments

3a (1 mg, 60:40 er) dissolved in *m*-xylene (1.0 mL) for **3a**. The vial was fitted with a puncturable sealed cap and placed into an aluminum heating block. The experiment was performed at 80 ℃. At given time, a small aliquot (one microliter) was removed from the vial and concentrated in an HPLC vial. The residue was dissolved in a 10% iso-propanol/hexanes solution (1.0 mL) and injected into in the HPLC system, equipped with a Chiralpak OD-H column (n-hexane/2-propanol = 90/10, flow rate = 1 mL/min, 25 ℃). The timepoints and corresponding enantiomeric excess of the entire system was plotted to determine an observed rate constant. The rotational barrier ($\Delta G^{\neq}_{ent}$), rate constants for enantiomerization (k_{ent}) and racemization (k_{rac}), and halflife for racemization ($t_{1/2rac}$) were calculated based on the following Eyring equations[7]:

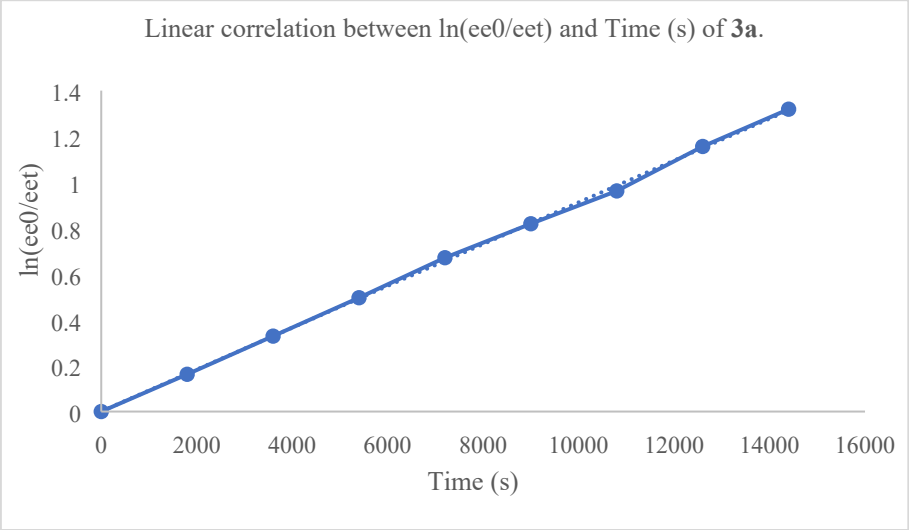
$$t_{1/2rac} = \ln 2 / k_{rac}$$

$$\Delta G^{\neq}_{ent} = RT\ln(k_{ent}h/k_BT)$$

where the transmission coefficient κ is set as 1, Boltzmann constant $k_B = 1.3806503\times10^{-23}$ J/K, Planck constant $h = 6.62606876 \times 10^{-34}$ J·s, idea gas constant R = 8.314472 J/(mol·K).

Table S1. Change of enantiomer ratio with time for **3a** (80 °C in *m*-Xylene)

Time (s)	ee	First order racemization $\ln(ee_0/ee_t)$
0	20	0
1800	17	0.162519
3600	14.39	0.328998
5400	12.17	0.496527
7200	10.22	0.671076
9000	8.82	0.819195
10800	7.64	0.962366
12600	6.3	1.15633
14400	5.35	1.319



$k_{racemization}$ (80 °C) = 0.000091174418625 s^{-1}

$k_{enantiomerization}$ (80 °C) = 0.000045587209313 s^{-1}

Employing the Eyring equation:

$$\Delta G^{\neq}_{ent} = RTln(\frac{k_B \times T}{k_{ent} \times h})$$

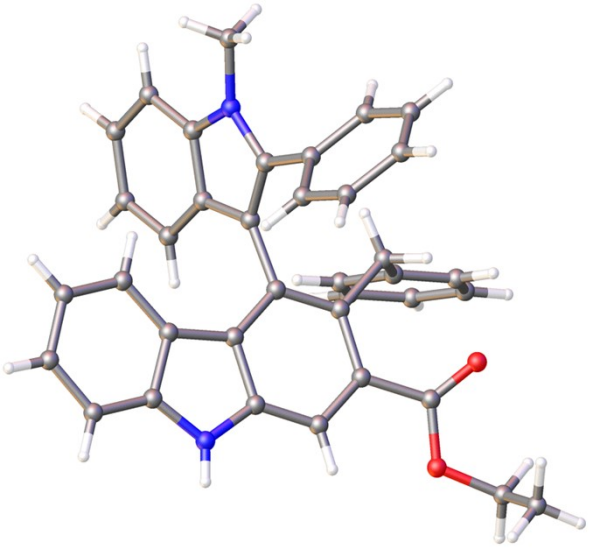
$$\Delta G^{\neq}_{ent} = 8.314\ J{\cdot}mol^{-1} \times 353.15\ K \times ln(\frac{1.381 \times 10^{-23}\ J{\cdot}K^{-1} \times 353.15\ K}{4.55872 \times 10^{-5} \times 6.626 \times 10^{-34}\ J{\cdot}S})$$

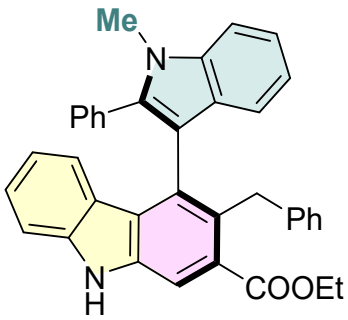
$$\Delta G^{\neq}_{ent} = 116.34\ kJ \cdot mol^{-1} = 27.830\ \text{kcal} \cdot mol^{-1}$$

$$T_{1/2} = \frac{ln\,2}{k_{racemization}} = 2.11\ \text{h}$$

7. X-ray Crystal Structures of 3ah

To a 5 mL tube containing **3ah** (20 mg) was added ethyl acetate (3 mL). A clear solution was obtained through ultrasound treatment and was kept at room temperature and **3ah** crystals were obtained after the solvent evaporated, which were characterized by single crystal X-ray diffraction. X-ray diffraction experiment was carried out on an Agilent D8 QUEST and the data obtained were deposited at the Cambridge Crystallographic Data Centre. The crystal structure was solved by Olex2 with the SHELXT structure solution program using Intrinsic Phasing and refined with the SHELXL refinement package using Least Squares minimisation. CCDC 2295497 (**3ah**) contains the supplementary crystallographic data for this paper. X-ray crystal structure of **3ah** with the ellipsoid contour at 50% probability levels.





3ah, CCDC 2295497

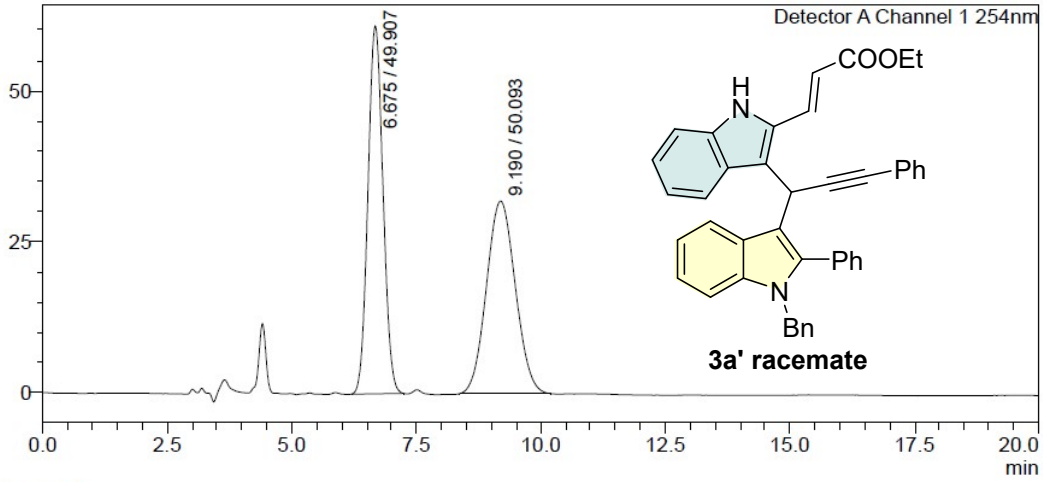
Identification code	**3ah**
Empirical formula	$C_{37}H_{30}N_2O_2$
Formula weight	534.63
Temperature/K	293.15
Crystal system	monoclinic
Space group	P 1 21/c 1
a/Å	14.5252(4)
b/Å	12.5893(3)

c/Å	16.5370(5)
α/°	90
β/°	107.271(2)
γ/°	90
Volume/Å^3	2887.6 (14)
Z	4
ρ_{calc}g/cm^3	1.230
μ/mm^{-1}	0.596
F(000)	1128
2Θ range for data collection/°	3.19 to 68.35
Index ranges	$-17 \leq h \leq 15$, $-15 \leq k \leq 14$, $-19 \leq l \leq 19$
Reflections collected	19415
Independent reflections	5212 [R_{int} = 0.0672]
Data/restraints/parameters	5212/0/376
Goodness-of-fit on F^2	1.198
Final R indexes [I>=2σ (I)]	R_1 = 0.0627, wR_2 = 0.1399
Final R indexes [all data]	R_1 = 0.1098, wR_2 = 0.1651
Largest diff. peak and hole / eÅ^{-3}	0.364 and -0.221
R.M.S. deviation from mean / eÅ^{-3}	0.041

8. HPLC Spectra for Screening of Catalysts

8.1 HPLC Spectra of Intermediate 3a'

Racemic 3a': HPLC (Chiralpak AD-H column, n-hexane/2-propanol = 80/20, flow rate = 1 mL/min, λ = 254 nm) t_R = 6.675 min (minor), 9.190 min (major)

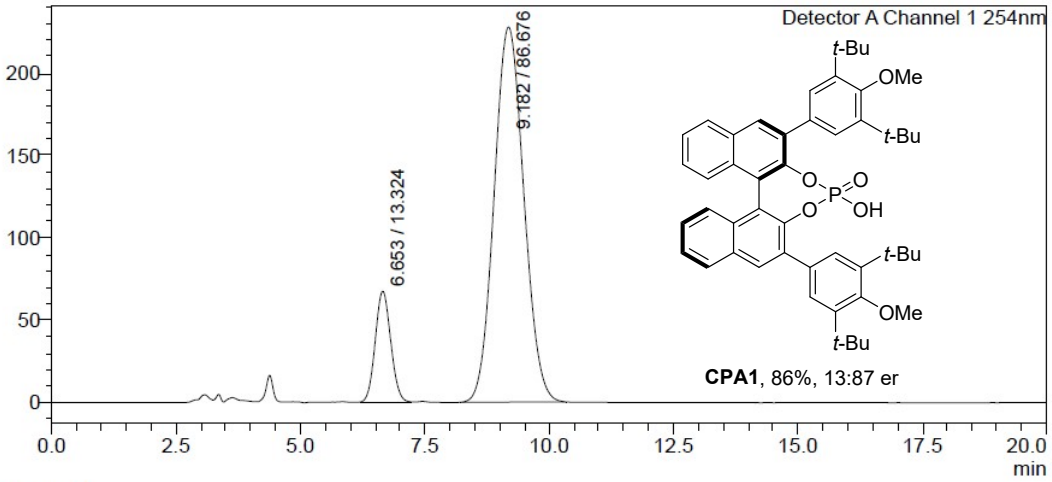


<Peak Table>

Detector A Channel 1 254nm

Peak#	Ret. Time	Area	Height	Conc.	Unit	Mark	Name
1	6.675	1283703	60994	49.907		M	
2	9.190	1288469	31942	50.093		M	
Total		2572172	92936				

CPA1: HPLC (Chiralpak AD-H column, n-hexane/2-propanol = 80/20, flow rate = 1 mL/min, λ = 254 nm) t_R = 6.653 min (minor), 9.182 min (major)

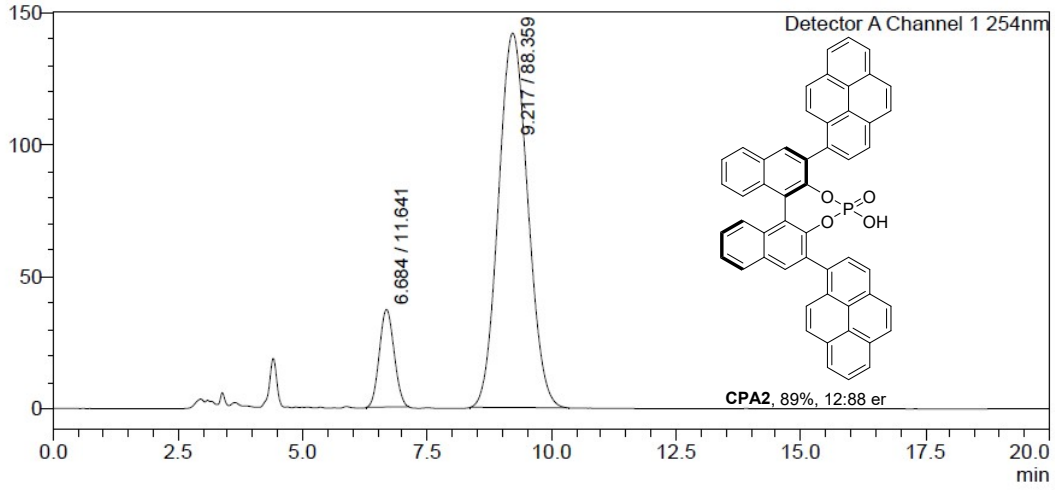


<Peak Table>

Detector A Channel 1 254nm

Peak#	Ret. Time	Area	Height	Conc.	Unit	Mark	Name
1	6.653	1452748	67235	13.324		M	
2	9.182	9450590	227687	86.676		M	
Total		10903338	294921				

CPA2: HPLC (Chiralpak AD-H column, n-hexane/2-propanol = 80/20, flow rate = 1 mL/min, λ = 254 nm) t_R = 6.684 min (minor), 9.217 min (major)

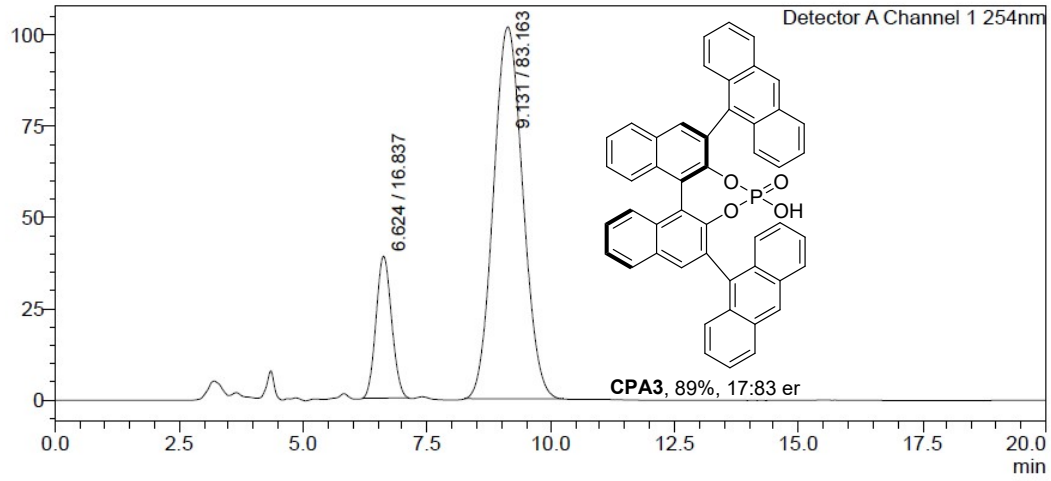


<Peak Table>

Detector A Channel 1 254nm

Peak#	Ret. Time	Area	Height	Conc.	Unit	Mark	Name
1	6.684	763748	37047	11.641		M	
2	9.217	5797274	141990	88.359		M	
Total		6561022	179037				

CPA3: HPLC (Chiralpak AD-H column, n-hexane/2-propanol = 80/20, flow rate = 1 mL/min, λ = 254 nm) t_R = 6.624 min (minor), 9.131 min (major)

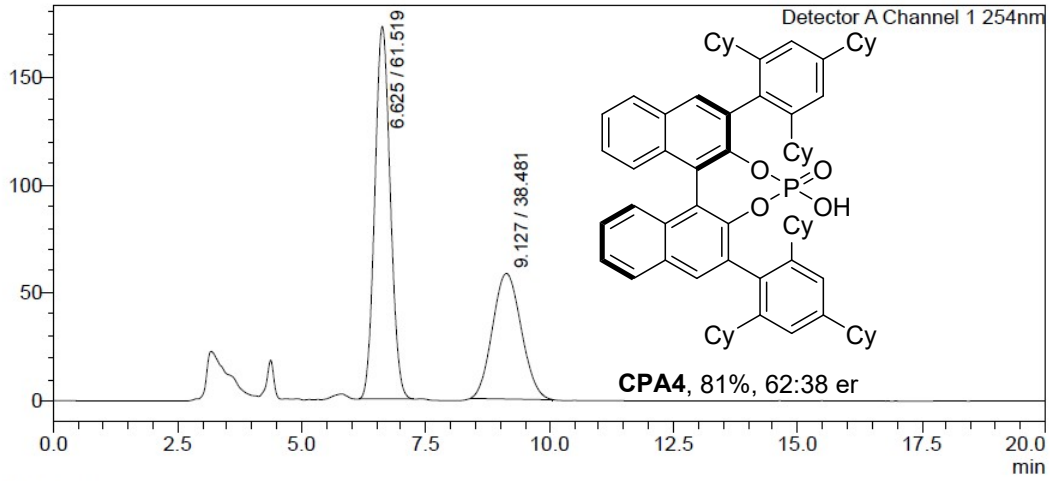


<Peak Table>

Detector A Channel 1 254nm

Peak#	Ret. Time	Area	Height	Conc.	Unit	Mark	Name
1	6.624	852332	38918	16.837		M	
2	9.131	4210052	101934	83.163		M	
Total		5062384	140852				

CPA4: HPLC (Chiralpak AD-H column, n-hexane/2-propanol = 80/20, flow rate = 1 mL/min, λ = 254 nm) t_R = 6.625 min (major), 9.127 min (minor)

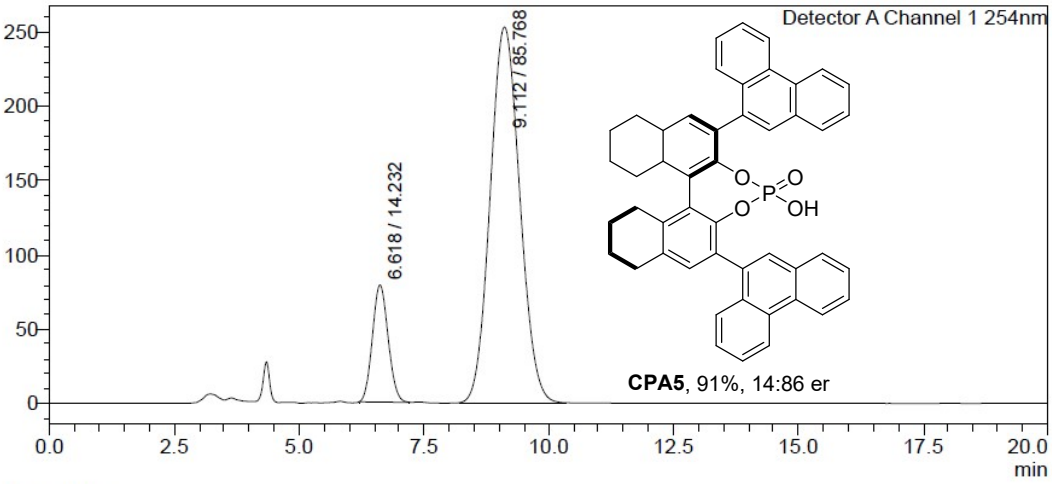


<Peak Table>

Detector A Channel 1 254nm

Peak#	Ret. Time	Area	Height	Conc.	Unit	Mark	Name
1	6.625	3762724	172835	61.519		M	
2	9.127	2353670	58236	38.481		M	
Total		6116394	231071				

CPA5: HPLC (Chiralpak AD-H column, n-hexane/2-propanol = 80/20, flow rate = 1 mL/min, λ = 254 nm) t_R = 6.618 min (minor), 9.112 min (major)

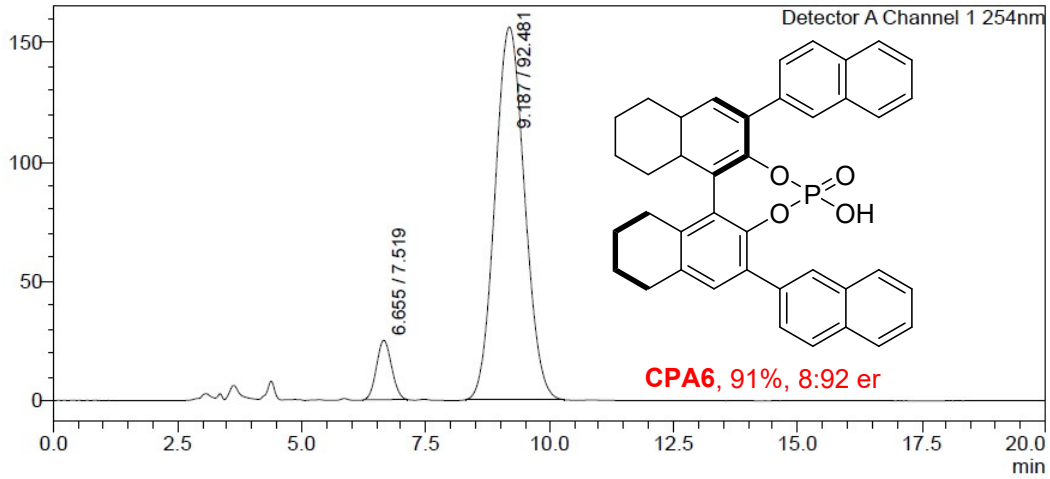


<Peak Table>

Detector A Channel 1 254nm

Peak#	Ret. Time	Area	Height	Conc.	Unit	Mark	Name
1	6.618	1730603	78837	14.232		M	
2	9.112	10429285	252902	85.768		M	
Total		12159888	331739				

CPA6: HPLC (Chiralpak AD-H column, n-hexane/2-propanol = 80/20, flow rate = 1 mL/min, λ = 254 nm) t_R = 6.655 min (major), 9.187 min (minor)

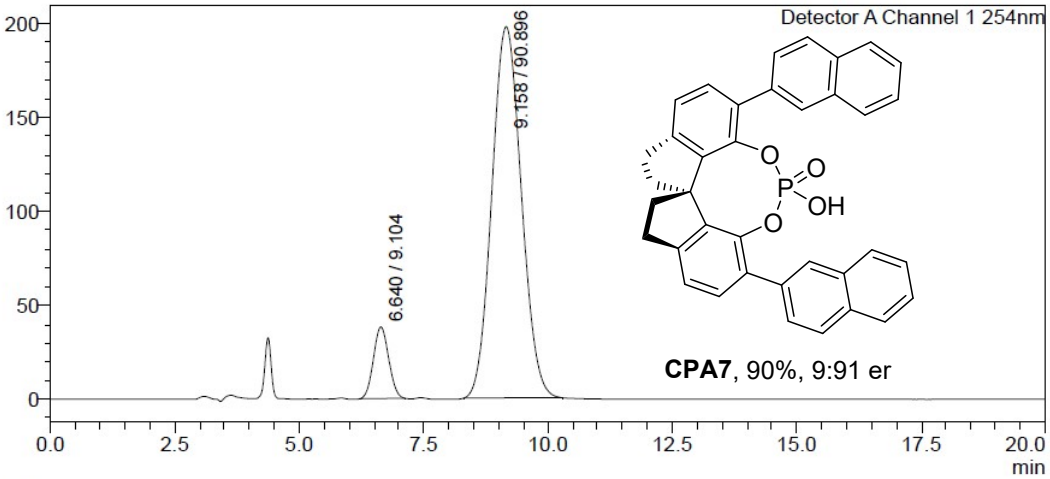


<Peak Table>

Detector A Channel 1 254nm

Peak#	Ret. Time	Area	Height	Conc.	Unit	Mark	Name
1	6.655	525801	24835	7.519		M	
2	9.187	6467347	156280	92.481		M	
Total		6993147	181115				

CPA7: HPLC (Chiralpak AD-H column, n-hexane/2-propanol = 80/20, flow rate = 1 mL/min, λ = 254 nm) t_R = 6.640 min (minor), 9.158 min (major)

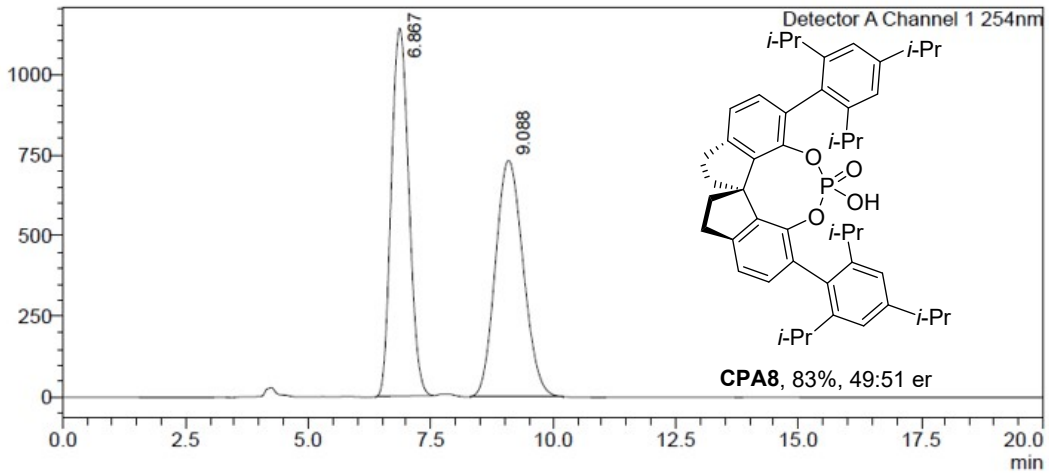


<Peak Table>

Detector A Channel 1 254nm

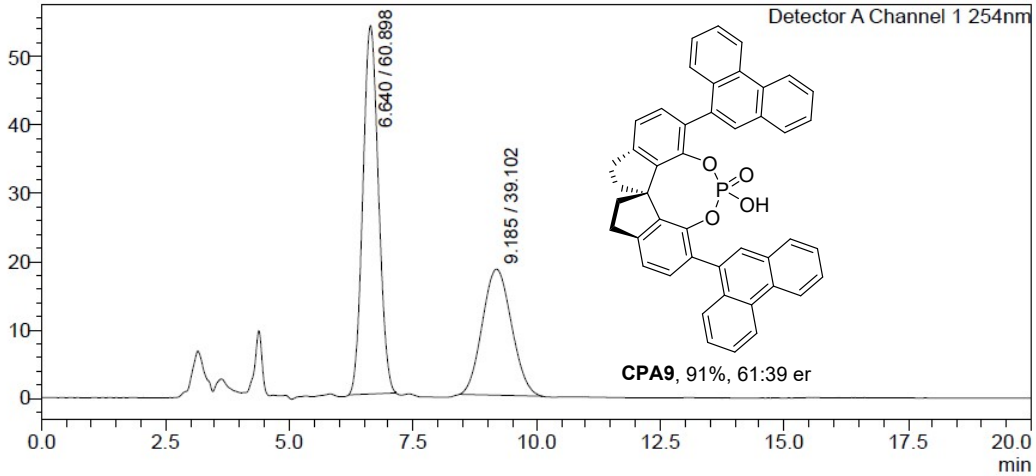
Peak#	Ret. Time	Area	Height	Conc.	Unit	Mark	Name
1	6.640	815299	38137	9.104		M	
2	9.158	8139653	197669	90.896		M	
Total		8954952	235806				

CPA8: HPLC (Chiralpak AD-H column, n-hexane/2-propanol = 80/20, flow rate = 1 mL/min, λ = 254 nm) t_R = 6.867 min (minor), 9.088 min (major)



Peak#	Ret. Time	Area	Height	Conc.	Unit	Mark	Name
1	6.867	28297499	1137728	49.508		M	
2	9.088	28859755	730508	50.492		M	
Total		57157254	1868236				

CPA9: HPLC (Chiralpak AD-H column, n-hexane/2-propanol = 80/20, flow rate = 1 mL/min, λ = 254 nm) t_R = 6.640 min (major), 9.185 min (minor)

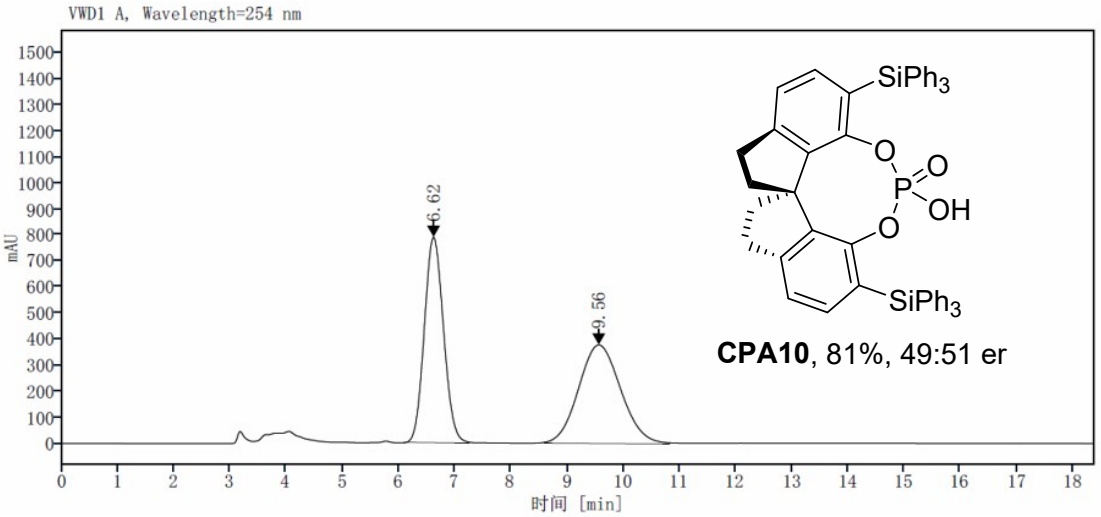


<Peak Table>

Detector A Channel 1 254nm

Peak#	Ret. Time	Area	Height	Conc.	Unit	Mark	Name
1	6.640	1189459	54144	60.898		M	
2	9.185	763751	18536	39.102		M	
Total		1953210	72680				

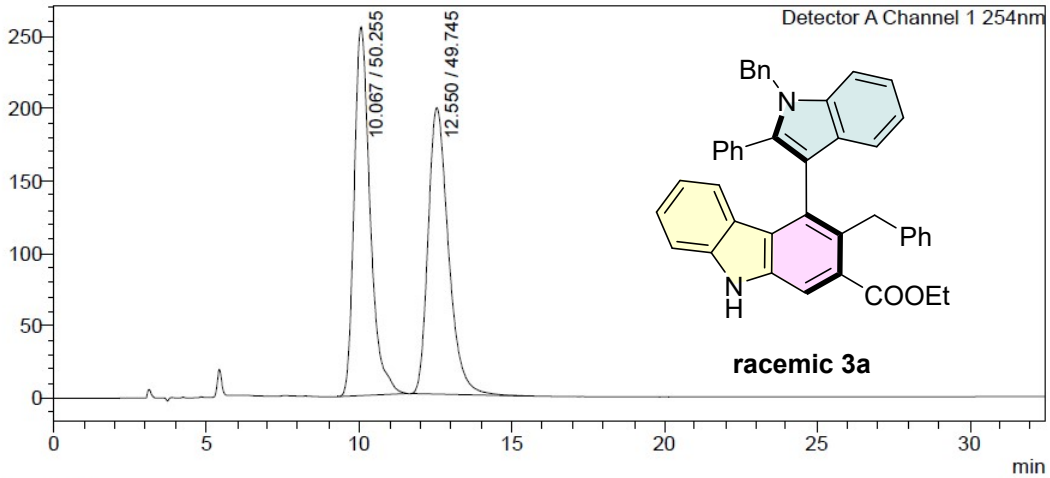
CPA10: HPLC (Chiralpak AD-H column, n-hexane/2-propanol = 80/20, flow rate = 1 mL/min, λ = 254 nm) t_R = 6.620 min (major), 9.560 min (minor)



保留时间 [min]	峰面积	峰宽 (50%)	峰面积%
6.620	18728.1367	0.372	48.7056
9.560	19723.5801	0.812	51.2944
总和	38451.7168		

8.2 HPLC Spectra of compound 3a

Racemic 3a: (Chiralpak OD-H column n-hexane/2-propanol = 90/10, flow rate = 1 mL/min) t_R= 10.067 min (major), 12.550 min (minor).

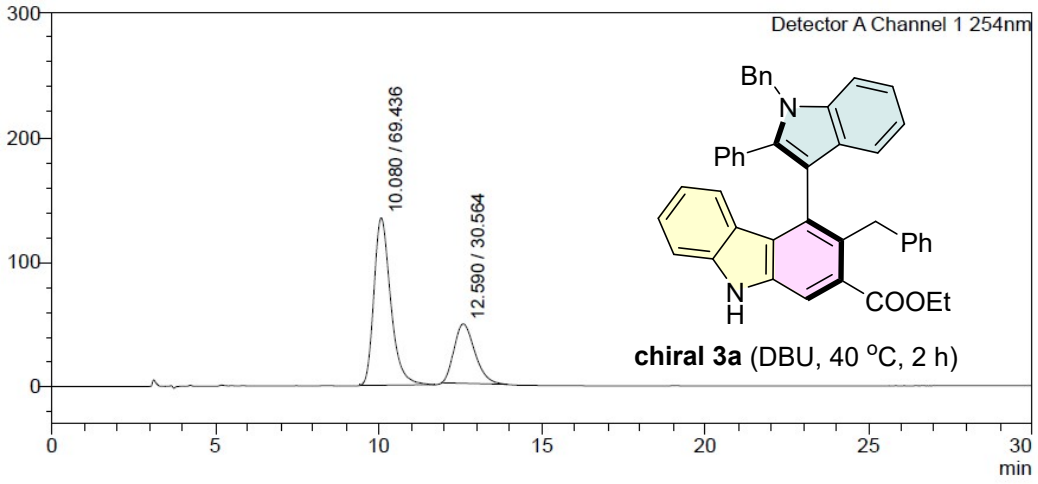


<Peak Table>

Detector A Channel 1 254nm

Peak#	Ret. Time	Area	Height	Conc.	Unit	Mark	Name
1	10.067	9248093	254647	50.255		M	
2	12.550	9154182	197826	49.745		M	
Total		18402275	452473				

Chiral 3a (DBU, 40 °C, 2 h): (Chiralpak OD-H column n-hexane/2-propanol = 90/10, flow rate = 1 mL/min) t_R= 10.080 min (major), 12.590 min (minor).

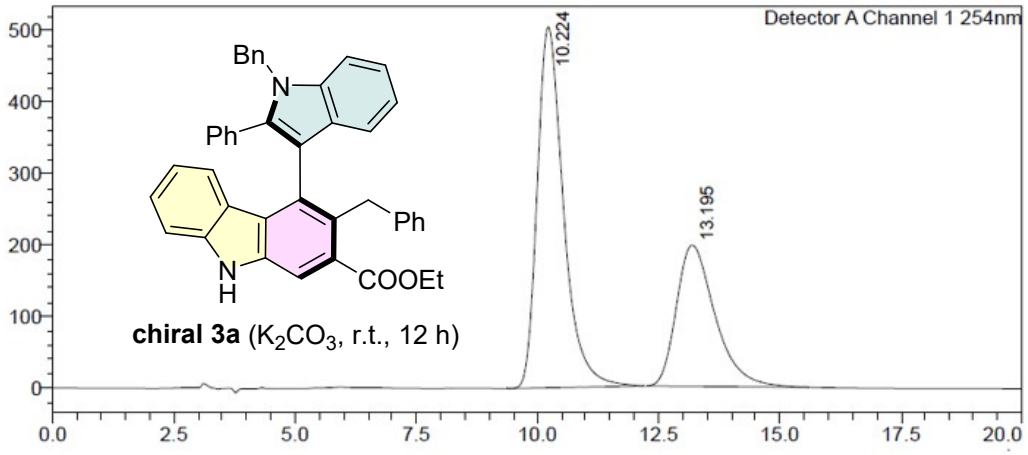


<Peak Table>

Detector A Channel 1 254nm

Peak#	Ret. Time	Area	Height	Conc.	Unit	Mark	Name
1	10.080	4818186	134396	69.436		M	
2	12.590	2120873	47770	30.564		M	
Total		6939058	182166				

Chiral 3a (K_2CO_3, r.t., 12 h): (Chiralpak OD-H column n-hexane/2-propanol = 90/10, flow rate = 1 mL/min) t_R= 10.224 min (major), 13.195 min (minor).



Peak#	Ret. Time	Area	Height	Conc.	Unit	Mark	Name
1	10.224	19077199	505249	63.491		M	
2	13.195	10969884	197602	36.509		M	
Total		30047083	702851				

9. UV-Vis Absorption Spectroscopy, Fluorescence Emission Spectroscopy and Fluorescence Quantum Yields

Sample preparation of UV-Vis Absorption Spectroscopy: To a 10 mL of volumetric flask was added **3e** or other products (0.01 mmol). Subsequently, draw 30 μL of this solution using a pipette and dilute it with DCM to 3 mL. The flask with solution was shaken several times for using.

Quantum yield determination[8]: To a 10 mL of volumetric flask was added **3e** or other products (0.01 mmol). Subsequently, draw 1.5 μL of this solution using a pipette and dilute it with DCM to 3 mL. The flask with solution was shaken several times for using. All the quantum yields of samples were determined based on 5.0 x 10^{-7} mol/L quinine sulfate in 0.5 M H_2SO_4 ($\Phi = 0.52$). Fluorescence emission of all the samples were measured in DCM, c = 0.5 μM, excited at 302 nm with 10 nm EX slit and 10.0 nm EM slit.

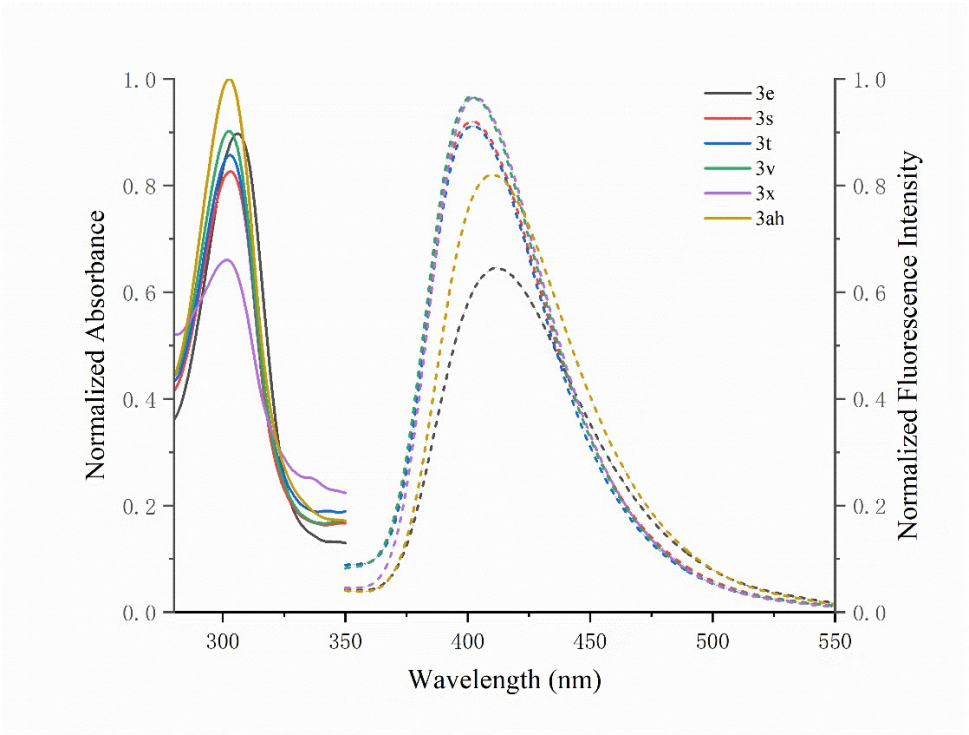


Figure S1. UV-Vis absorption spectra (solid line) and fluorescence emission spectra (dashed line) of **3e**, **3s**, **3t**, **3v**, **3x** and **3ah**.

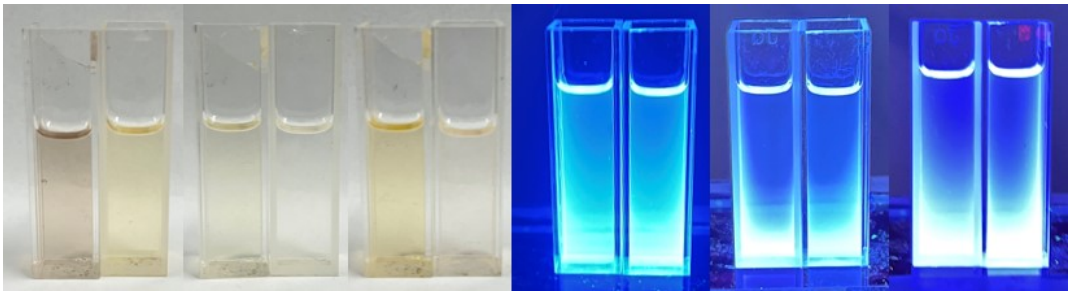
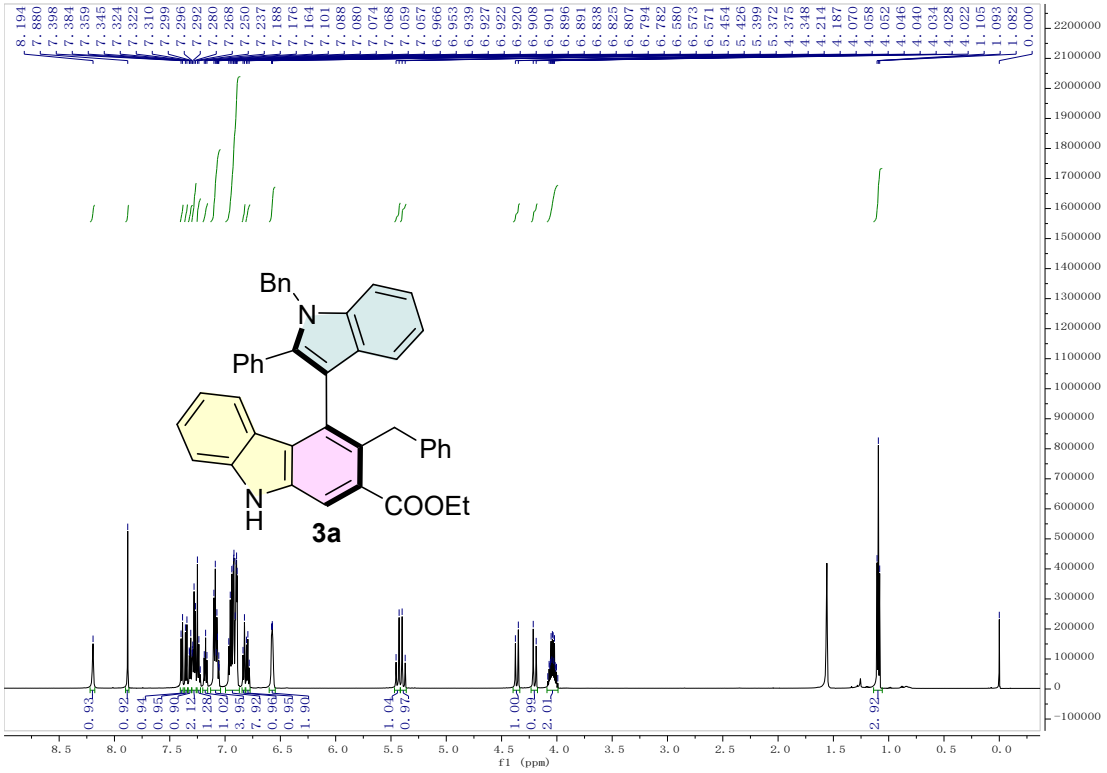
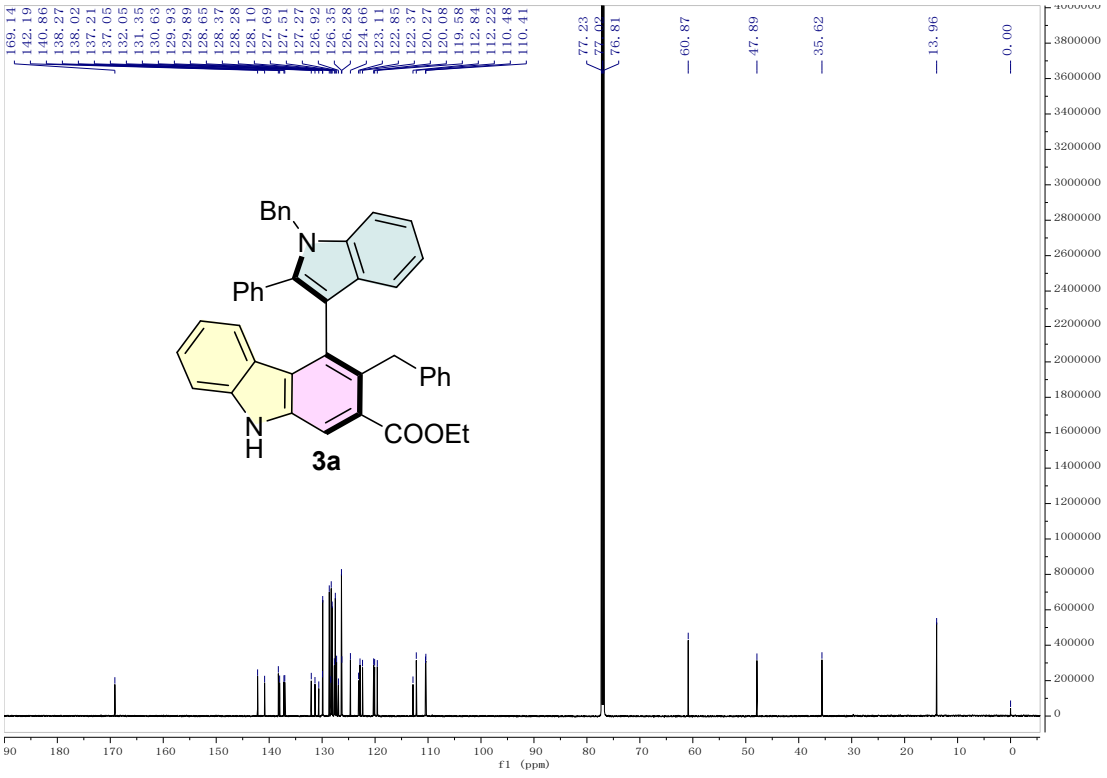
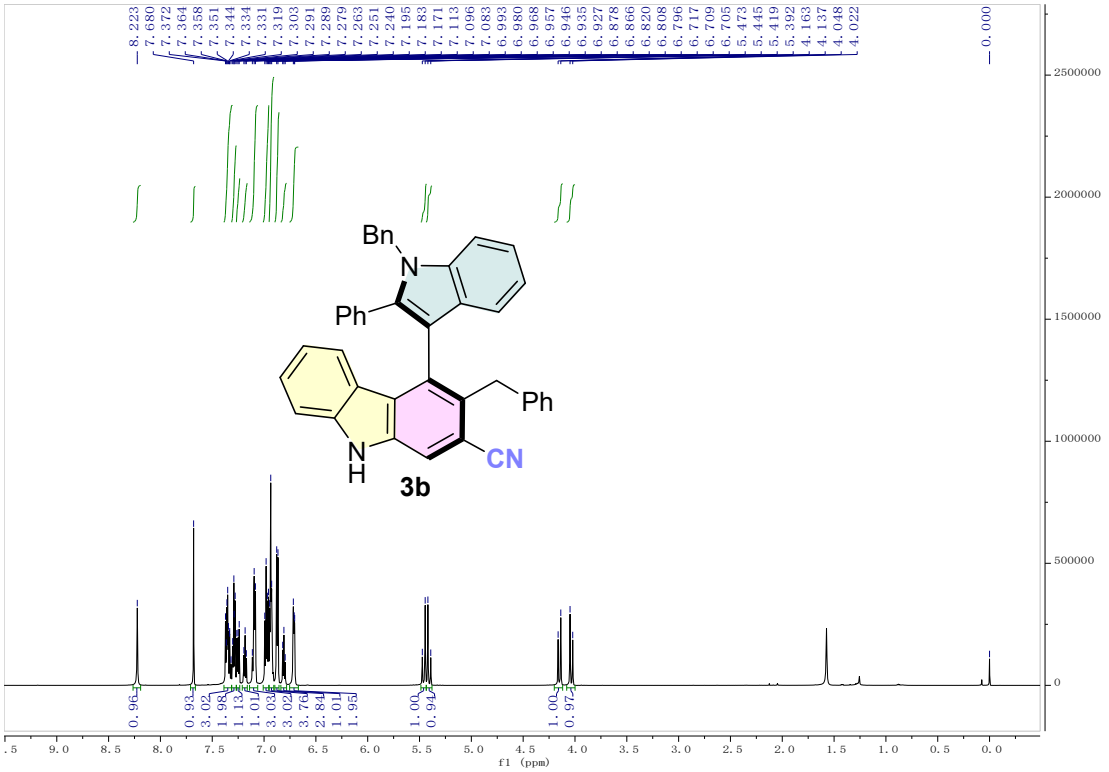


Figure S2. Fluorescence emission, without 365 UV light (lift), with 365nm UV light (right) (from left to right: **3v**, **3t**, **3x**, **3s**, **3e** and **3ah**)

10.NMR Spectra of Compound 3



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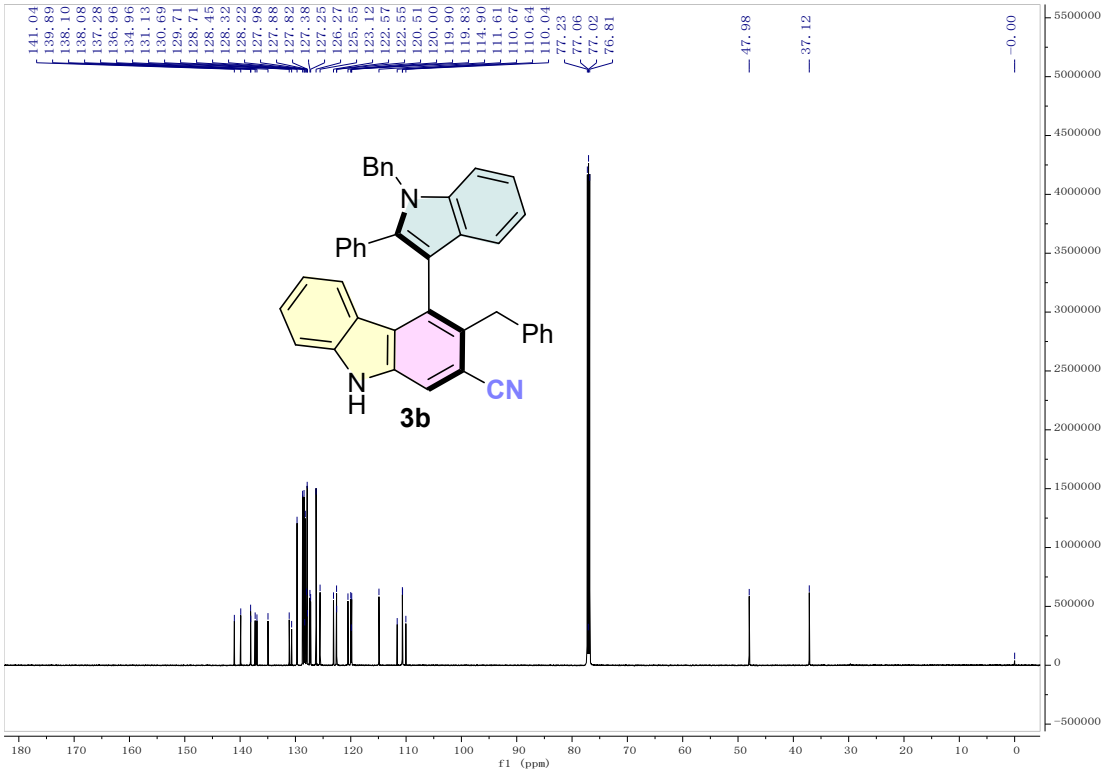
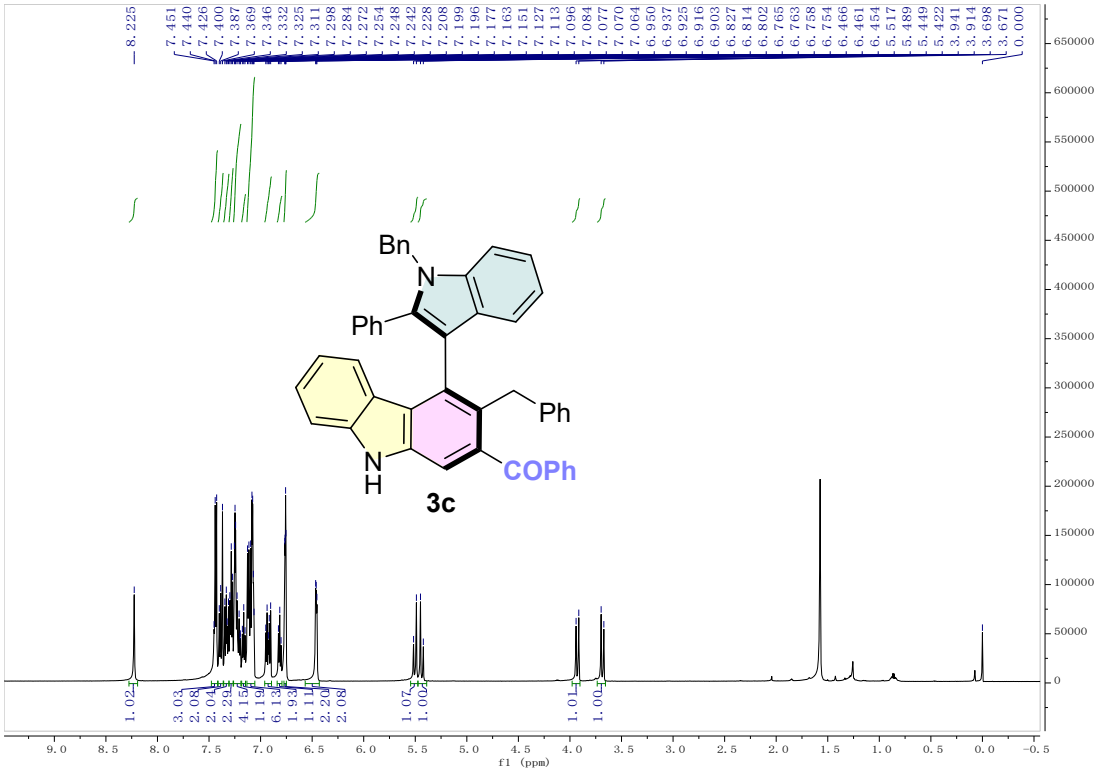
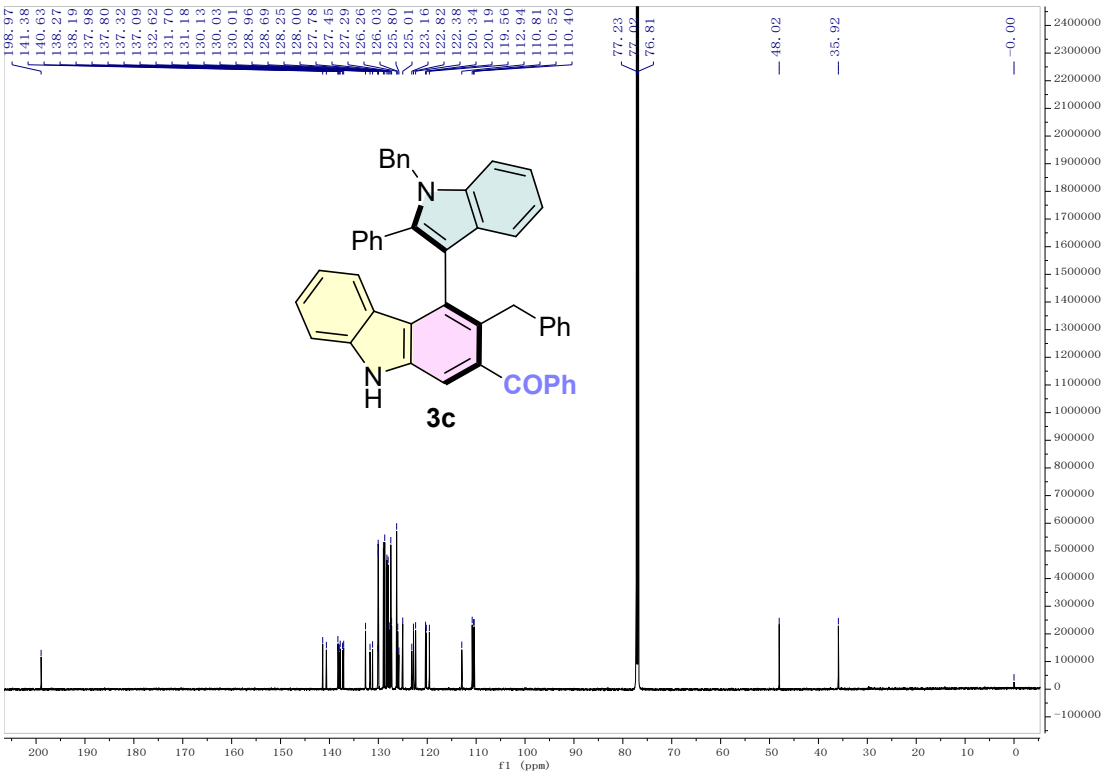
N
Ph
Ph
CN
N
H
3b
f1 (ppm)


Bn
N
Ph
Ph
CN
N
H
3b
f1 (ppm)


Bn
N
Ph
Ph
N
H
COPh
3c
f1 (ppm)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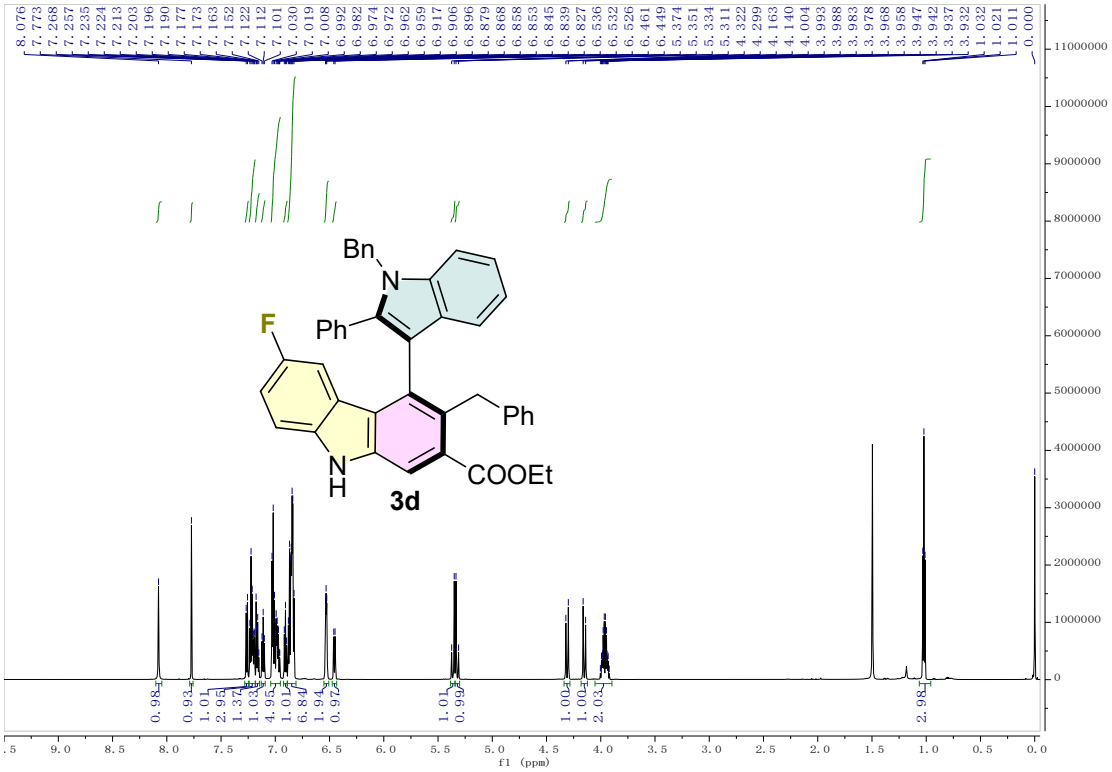
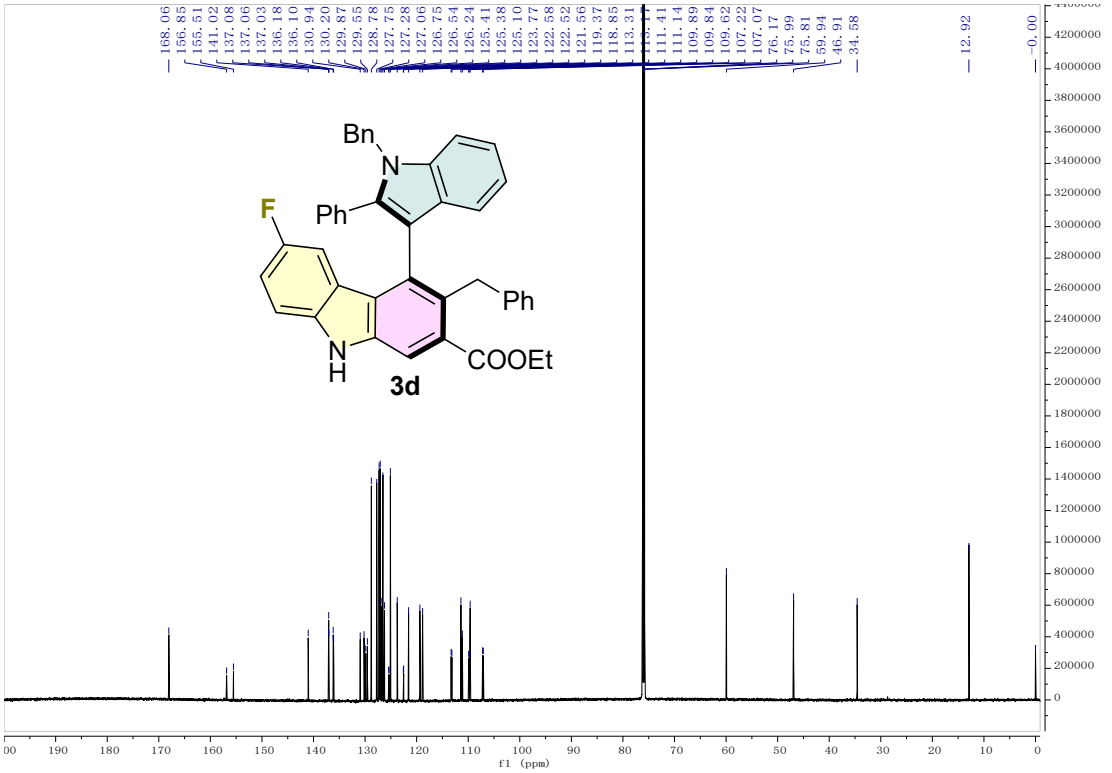
N
Ph
Ph
N
H
COPh
3c
f1 (ppm)


Bn
N
Ph
F
Ph
N
H
COOEt
3d
f1 (ppm)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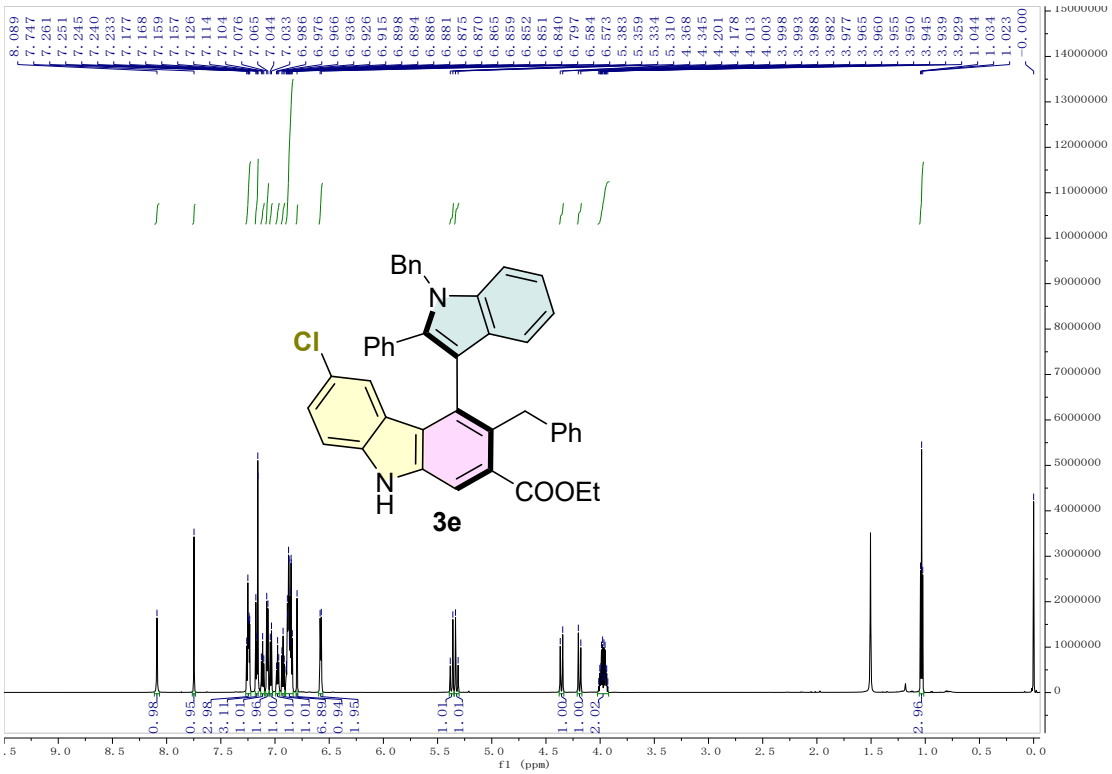
Ph
N
H
COOEt
3d
f1 (ppm)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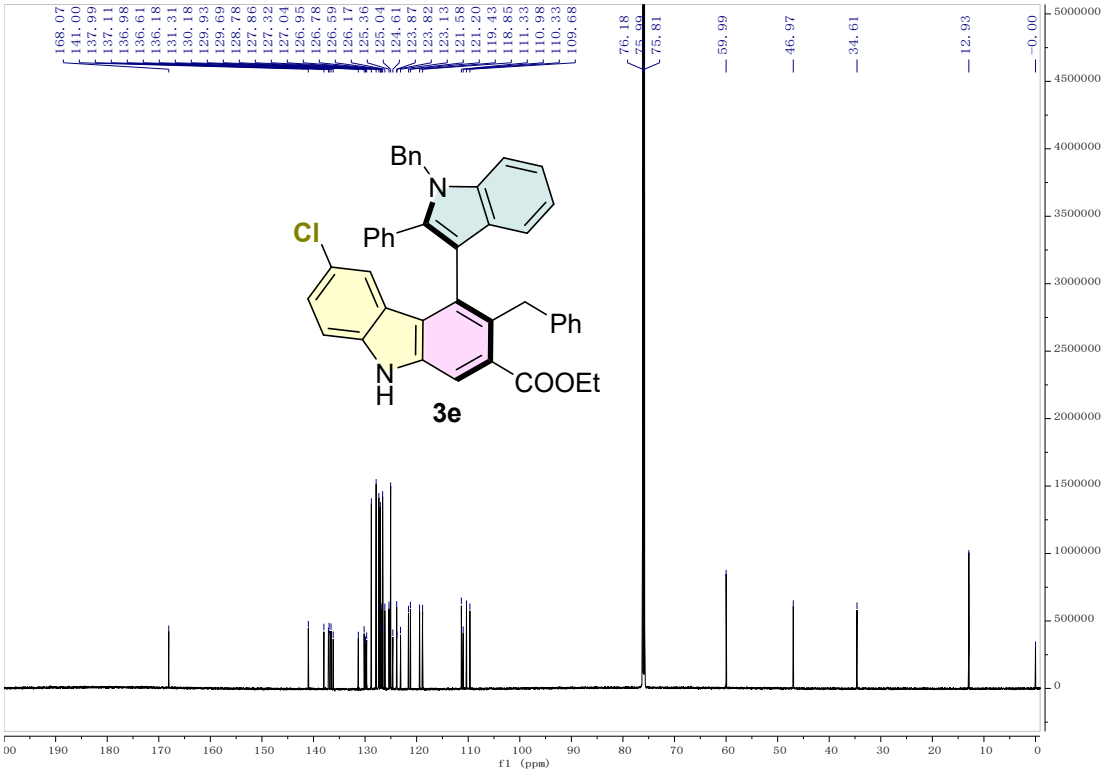
Cl
Ph
Ph
N
H
COOEt
3e
f1 (ppm)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Ph
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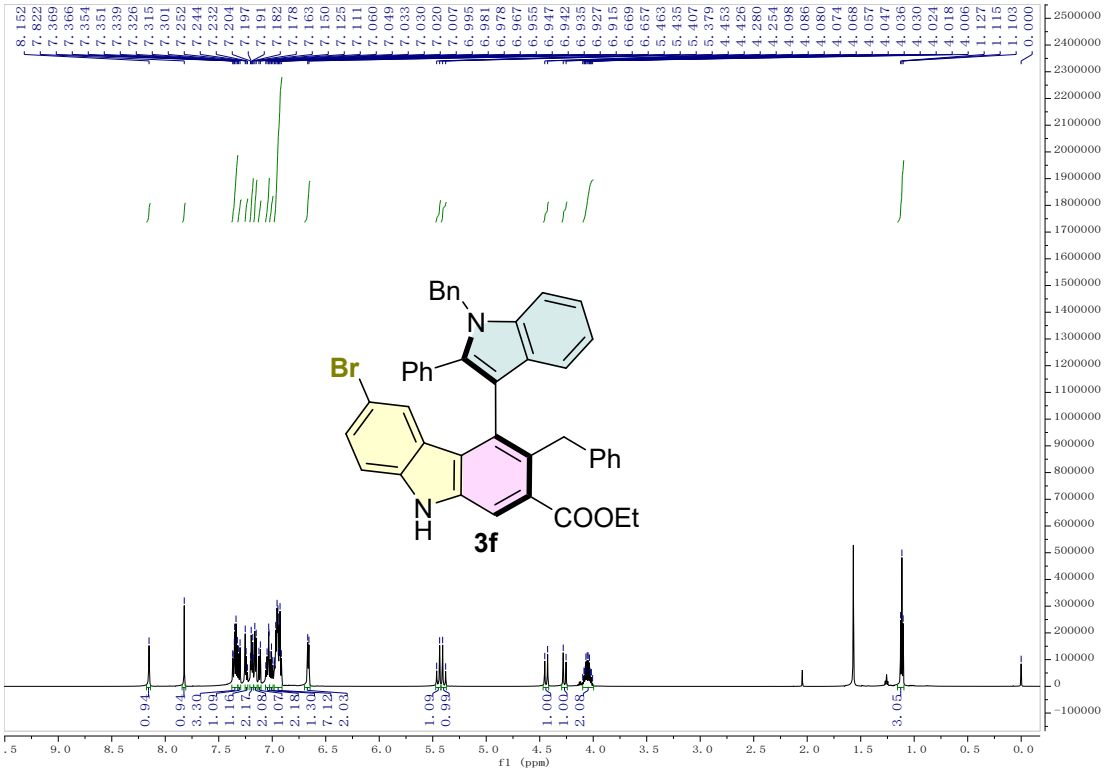
H
COOEt
3e
f1 (ppm)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Ph
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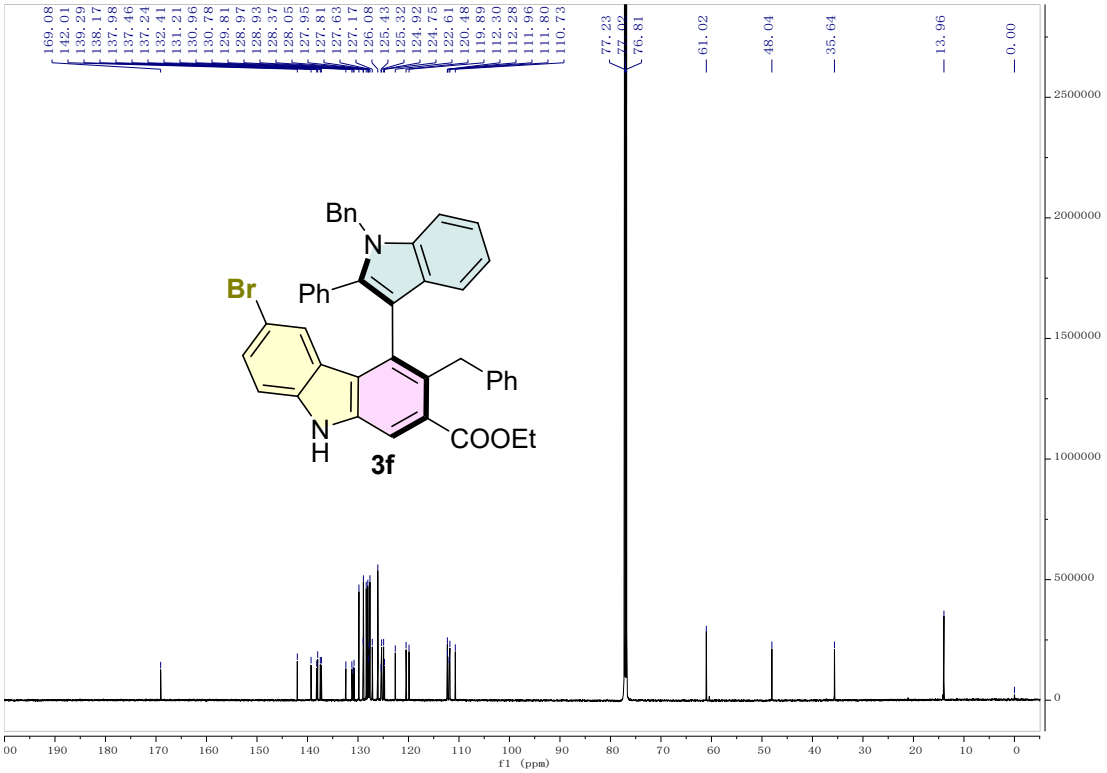
COOEt
3f
f1 (ppm)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Ph
Ph
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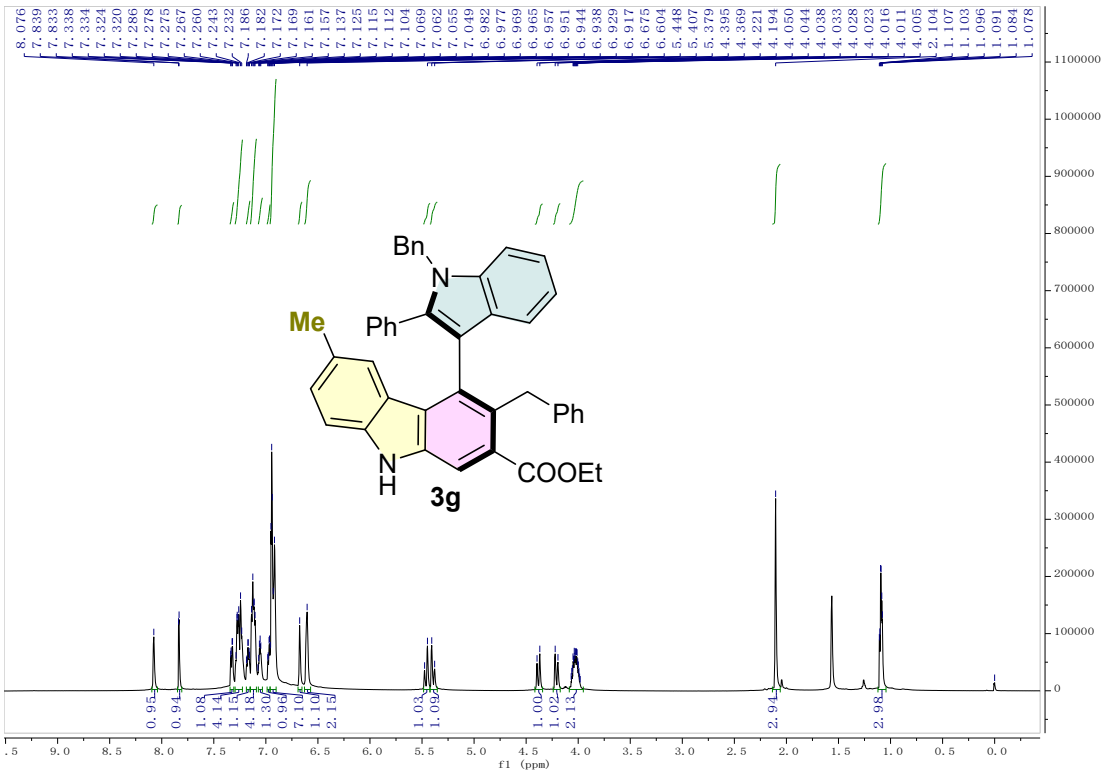
H
COOEt
3f
f1 (ppm)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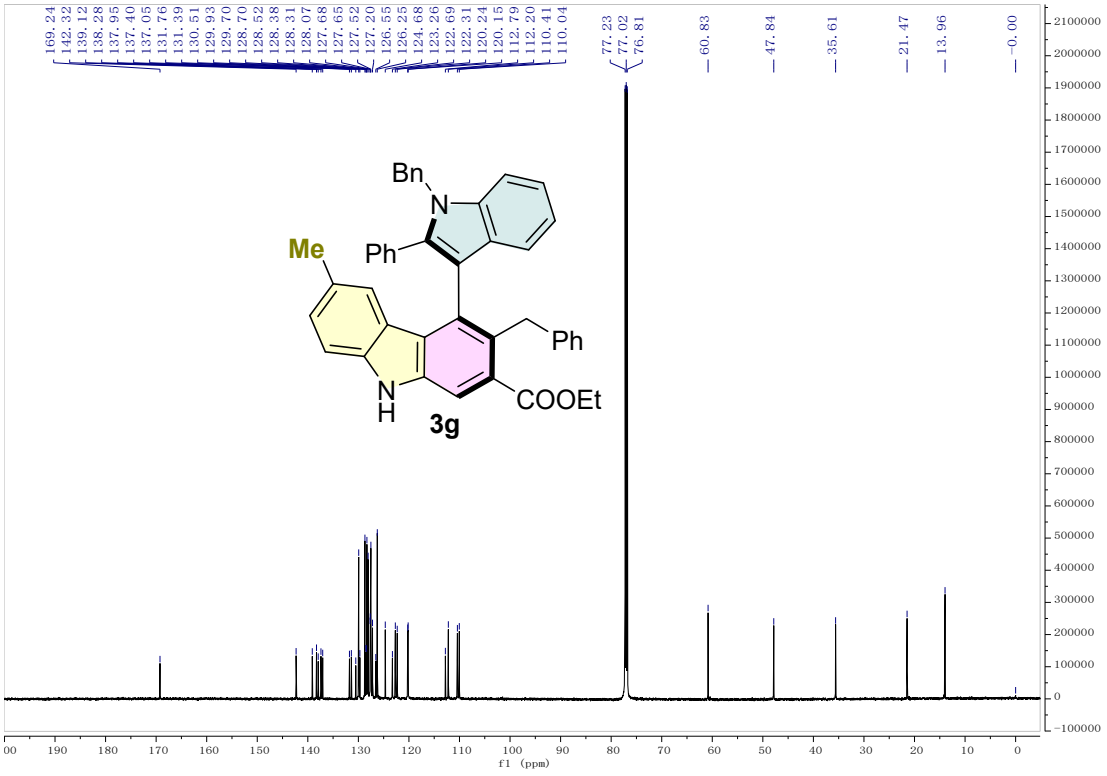
Me
Ph
Ph
N
H
COOEt
3g
f1 (ppm)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Ph
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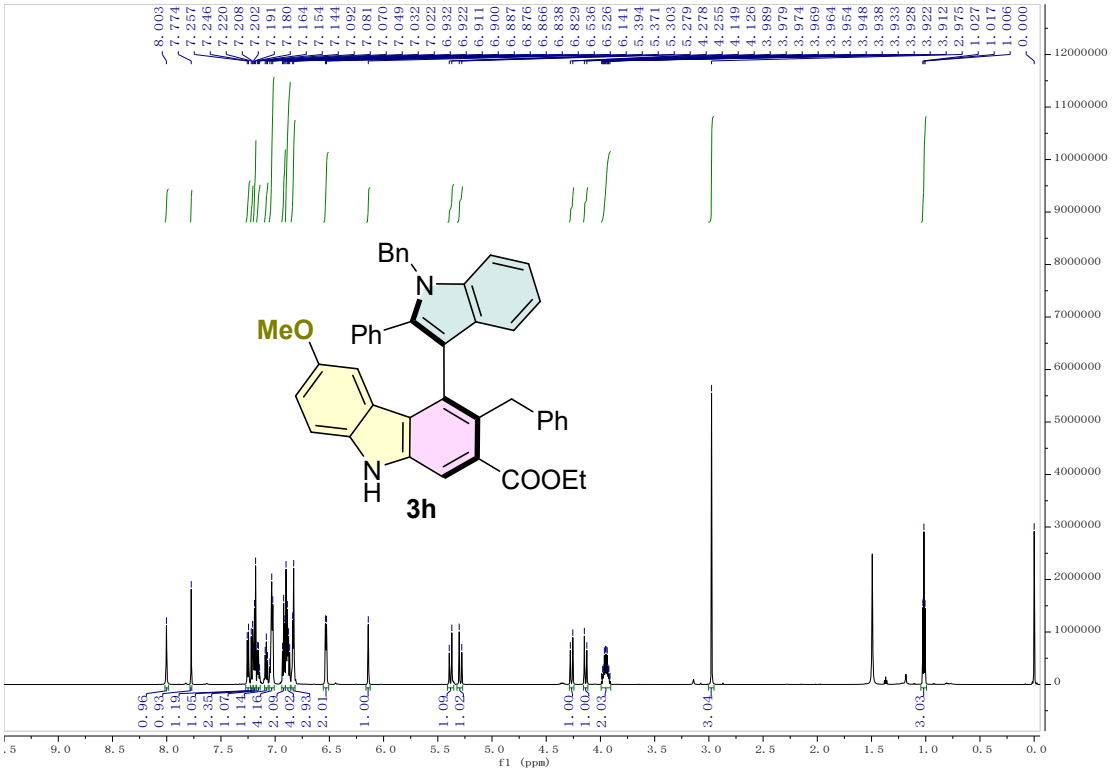
H
COOEt
3g
f1 (ppm)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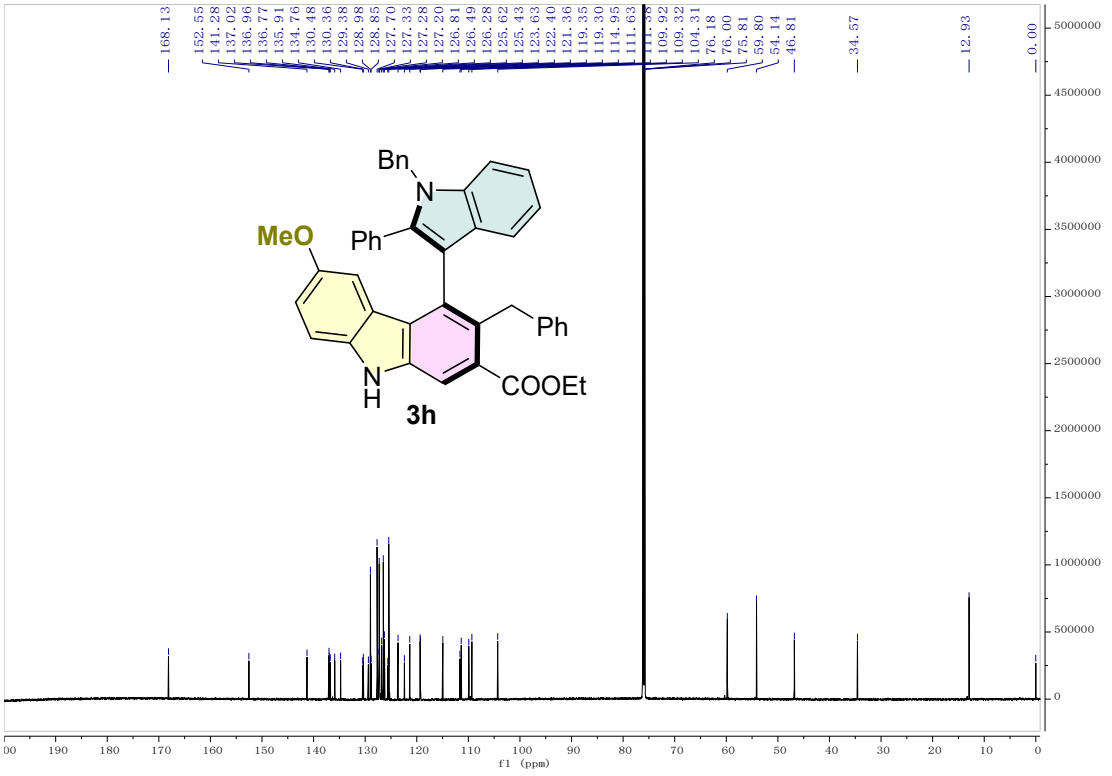
Ph
Ph
N
H
COOEt
3h
f1 (ppm)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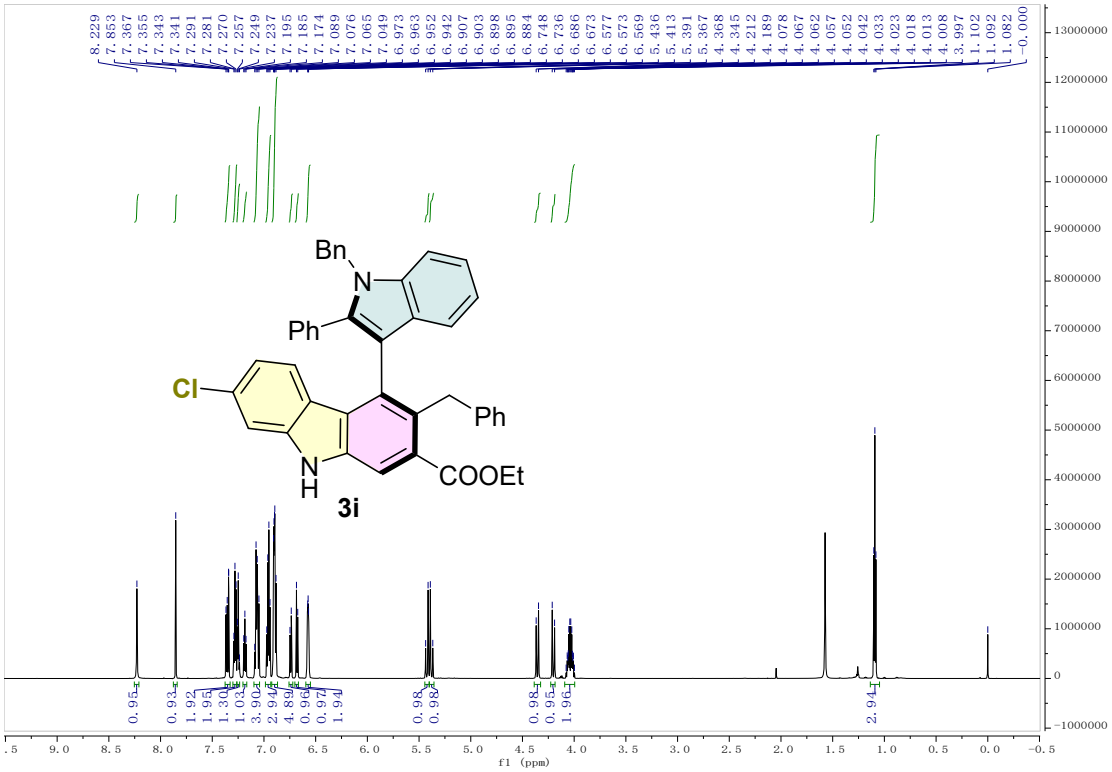
MeO
Ph
Ph
N
H
COOEt
3h
f1 (ppm)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Ph
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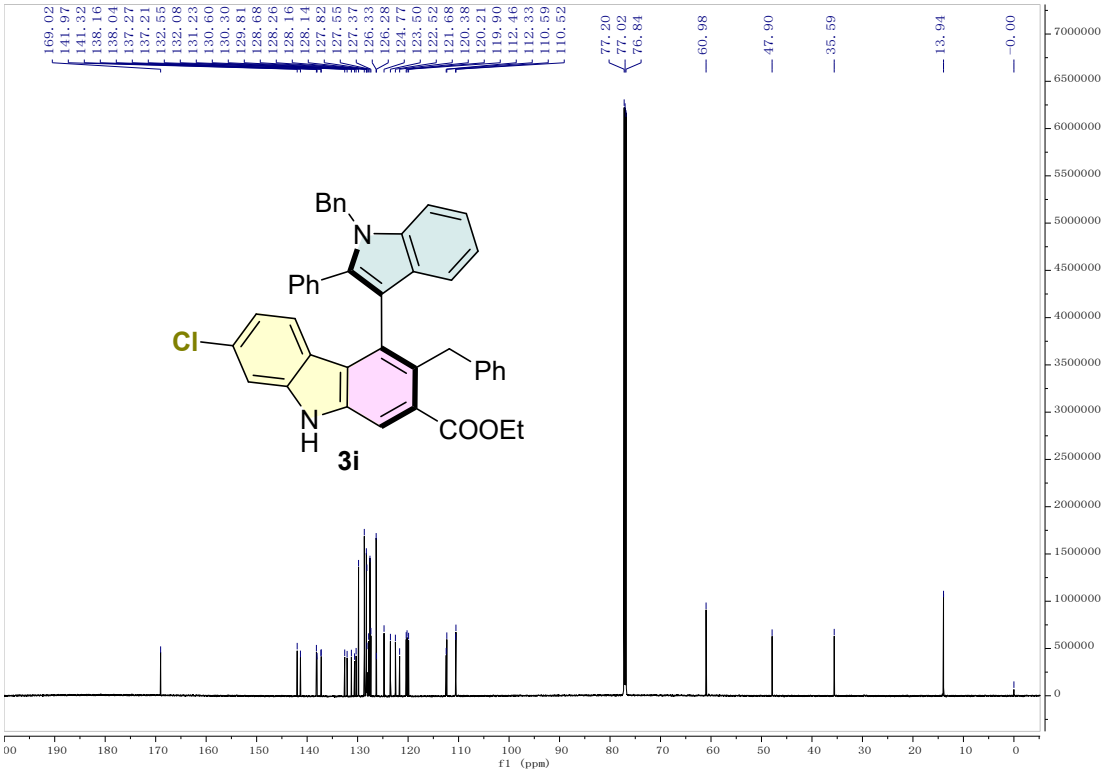
H
COOEt
3i
f1 (ppm)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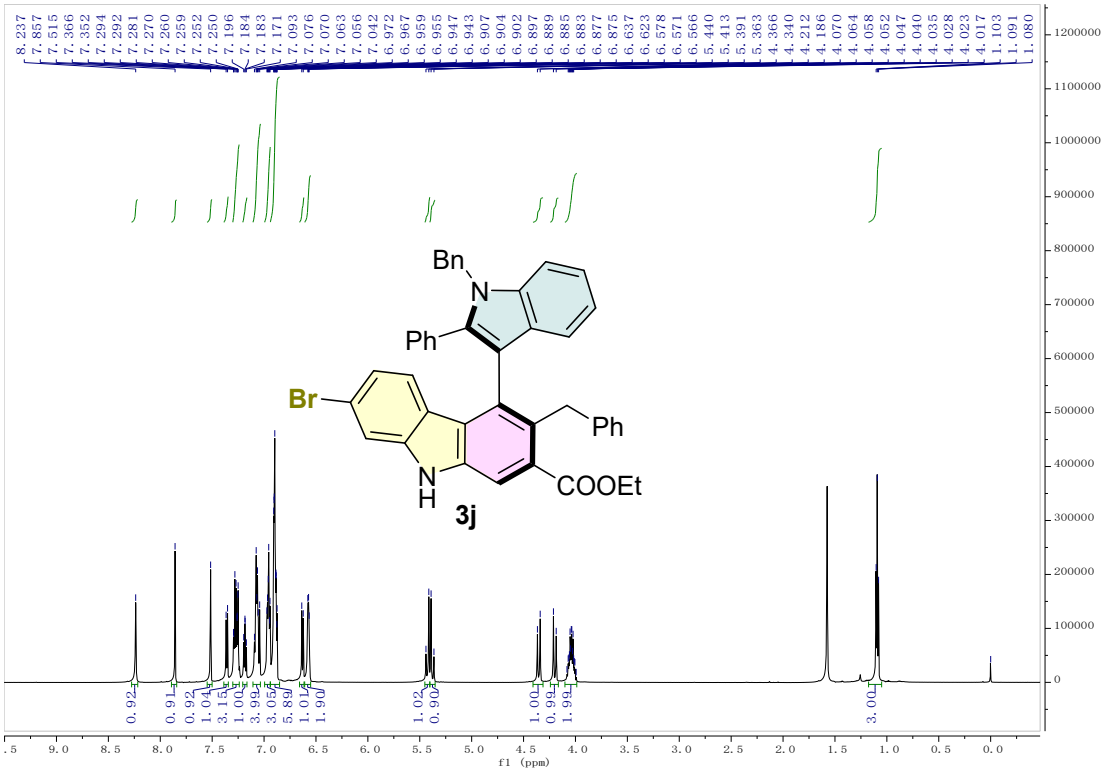
Ph
Cl
Ph
N
H
COOEt
3i
f1 (ppm)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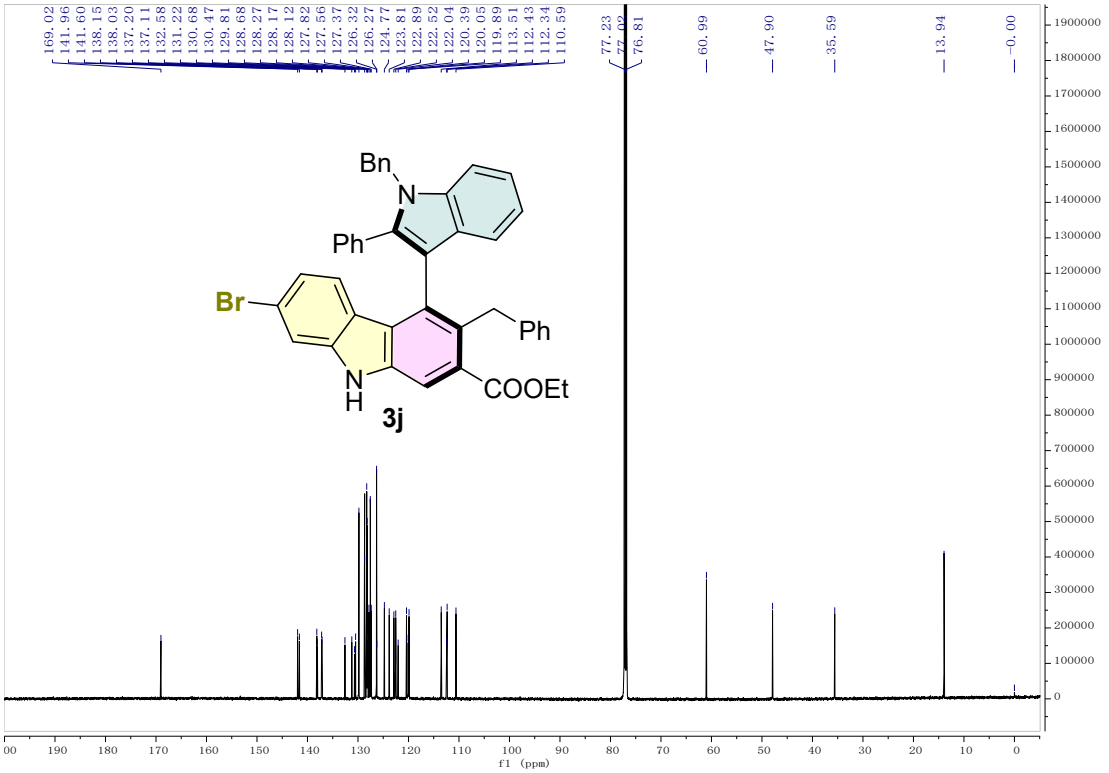
Ph
Br
Ph
N
H
COOEt
3j
f1 (ppm)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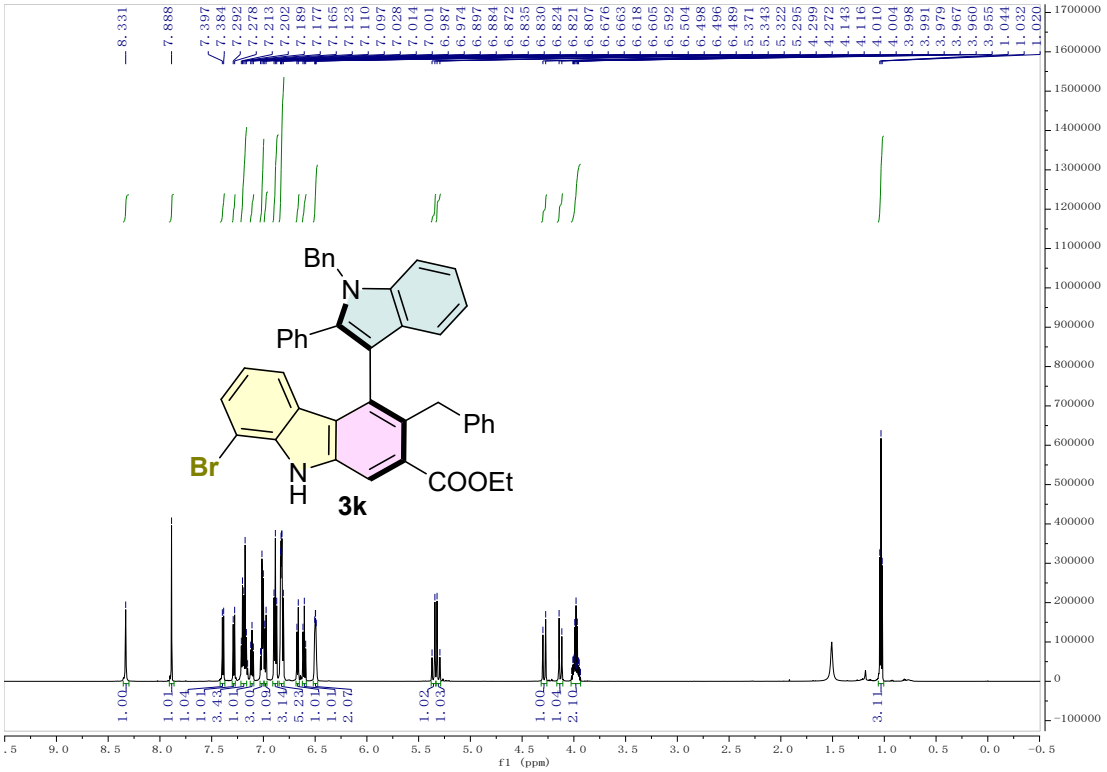
Br
Ph
N
H
COOEt
3j
f1 (ppm)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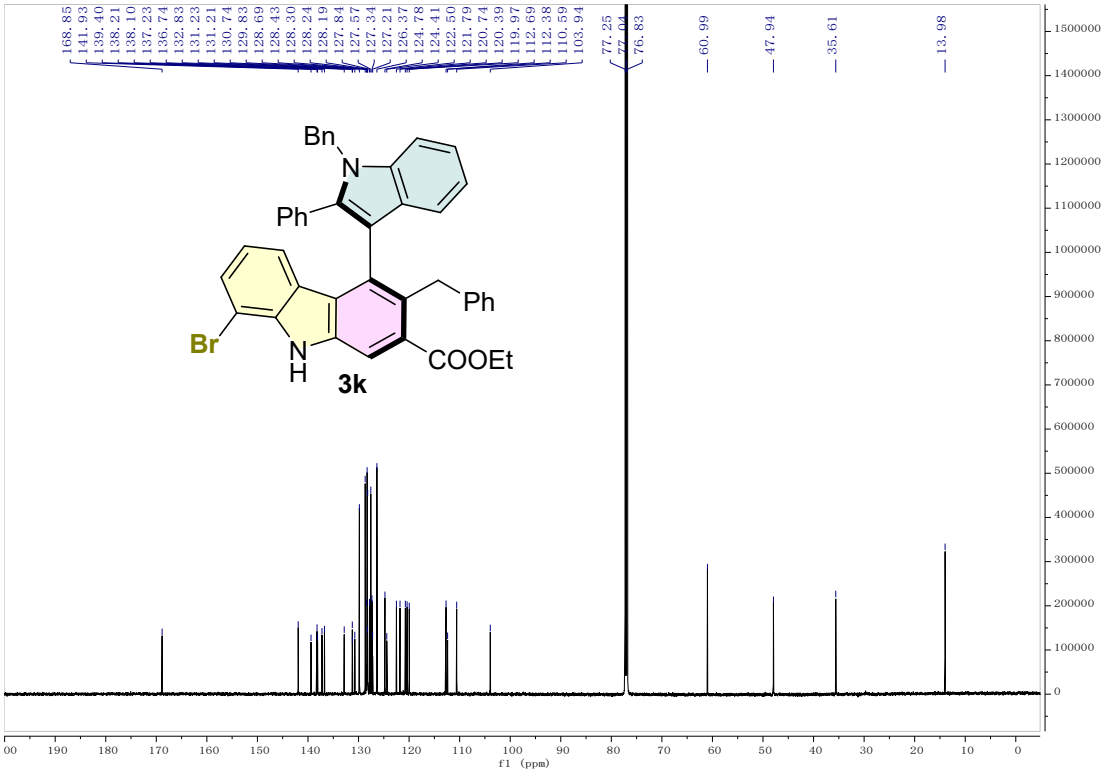
Ph
Br
N
H
COOEt
3k
f1 (ppm)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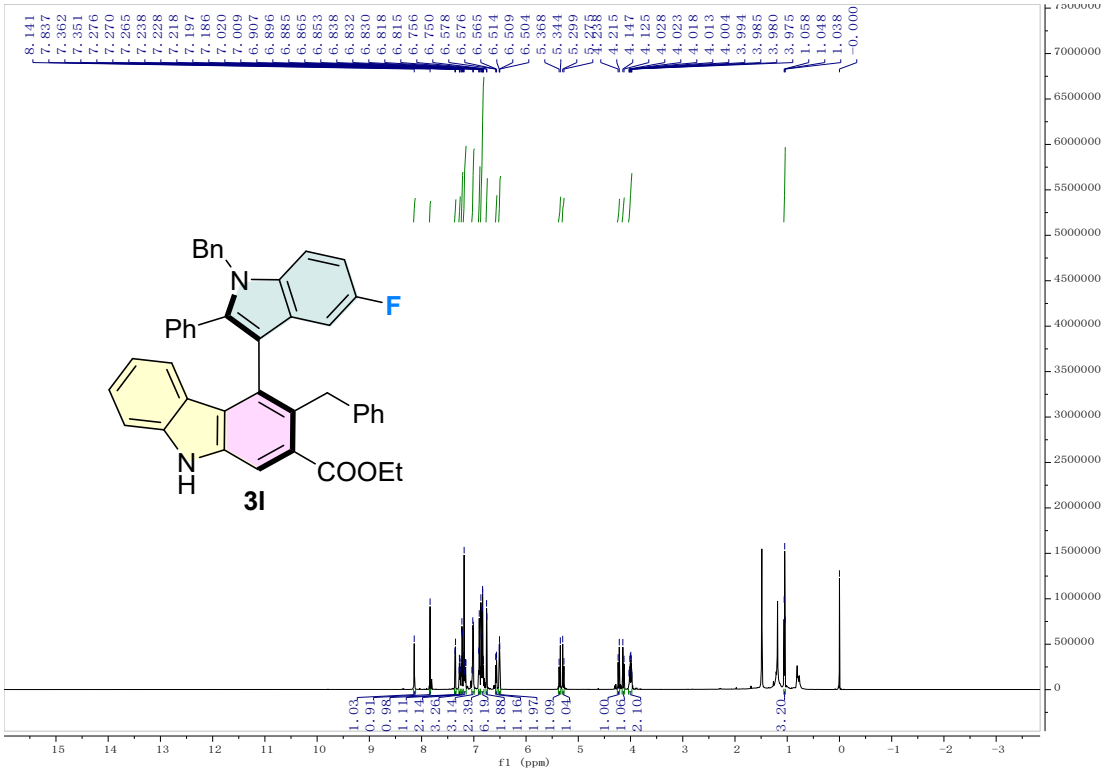
Ph
Br
N
H
COOEt
3k
f1 (ppm)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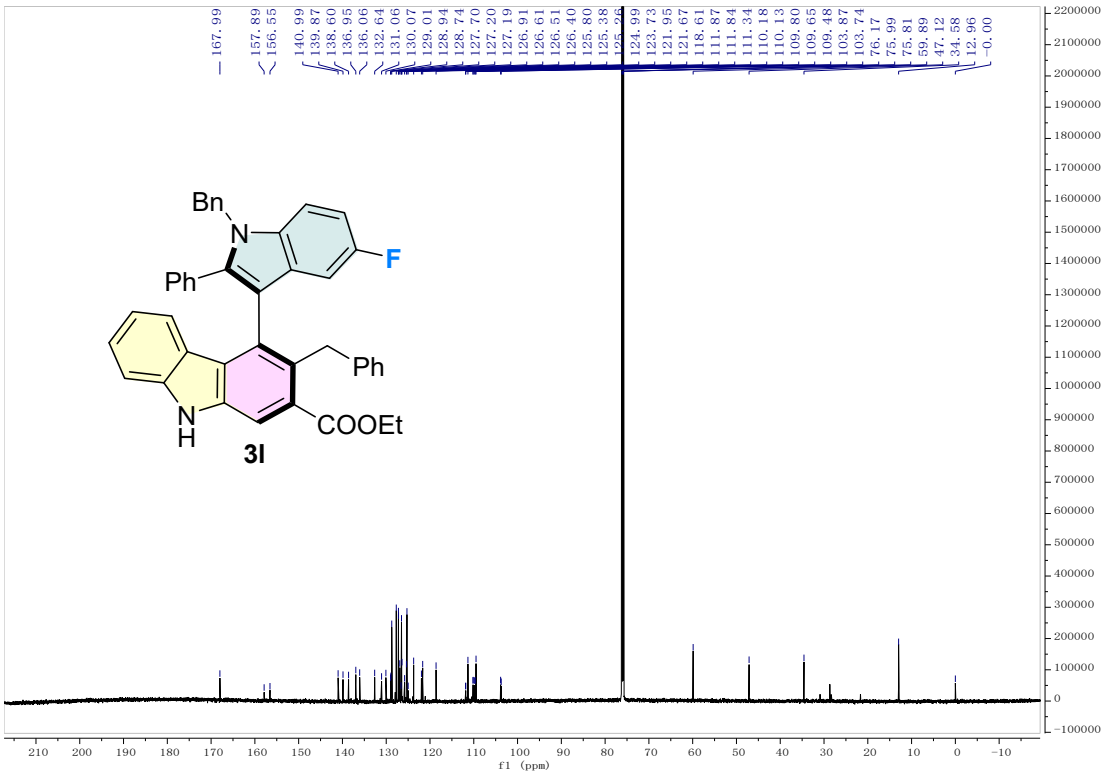
F
Ph
Ph
N
H
COOEt
3l
f1 (ppm)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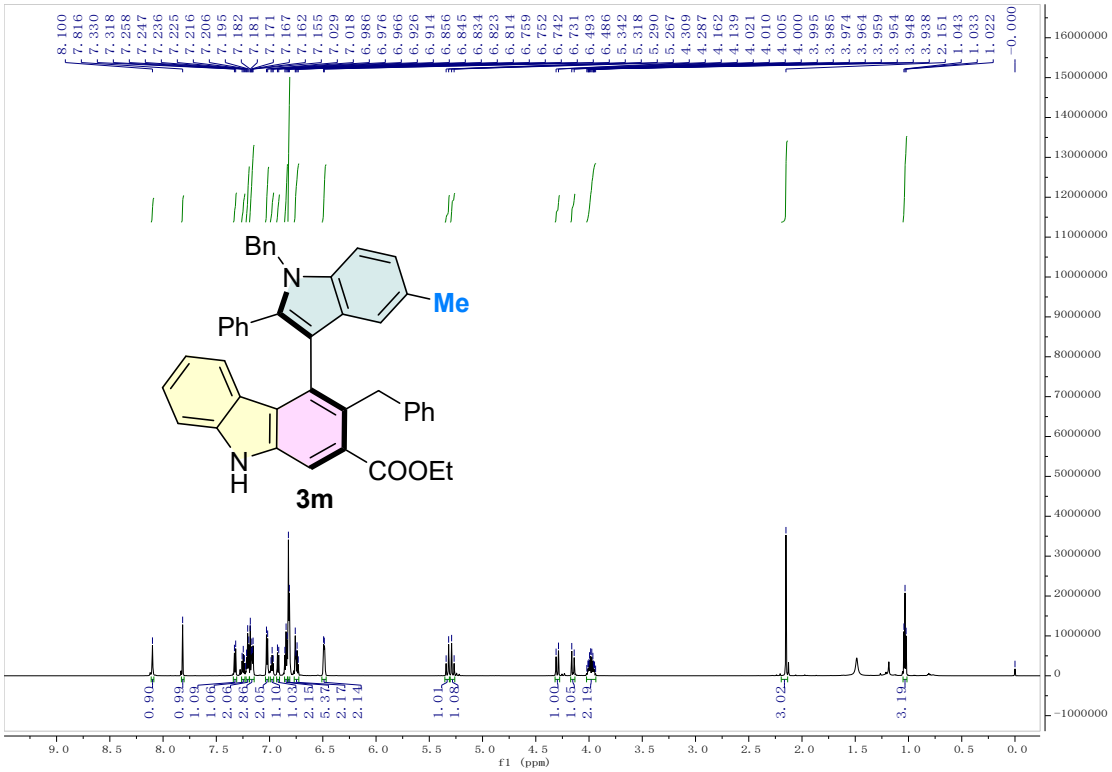
F
Ph
Ph
N
H
COOEt
3l
f1 (ppm)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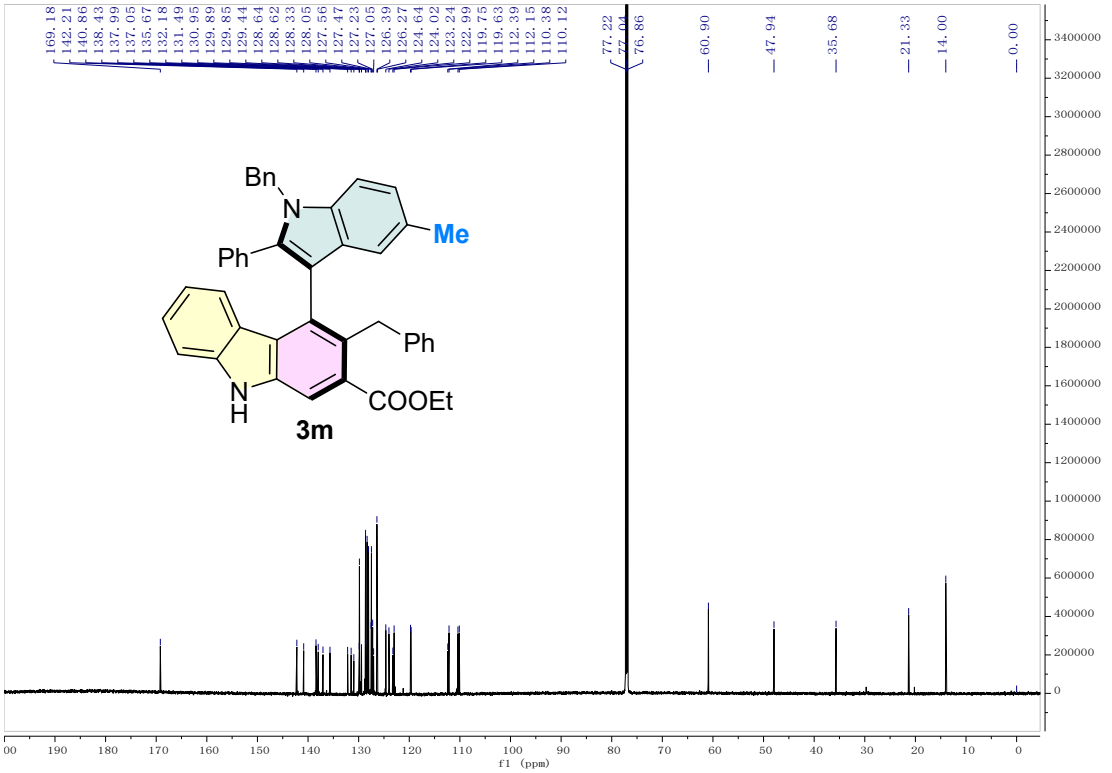
Ph
Me
Ph
N
H
COOEt
3m
f1 (ppm)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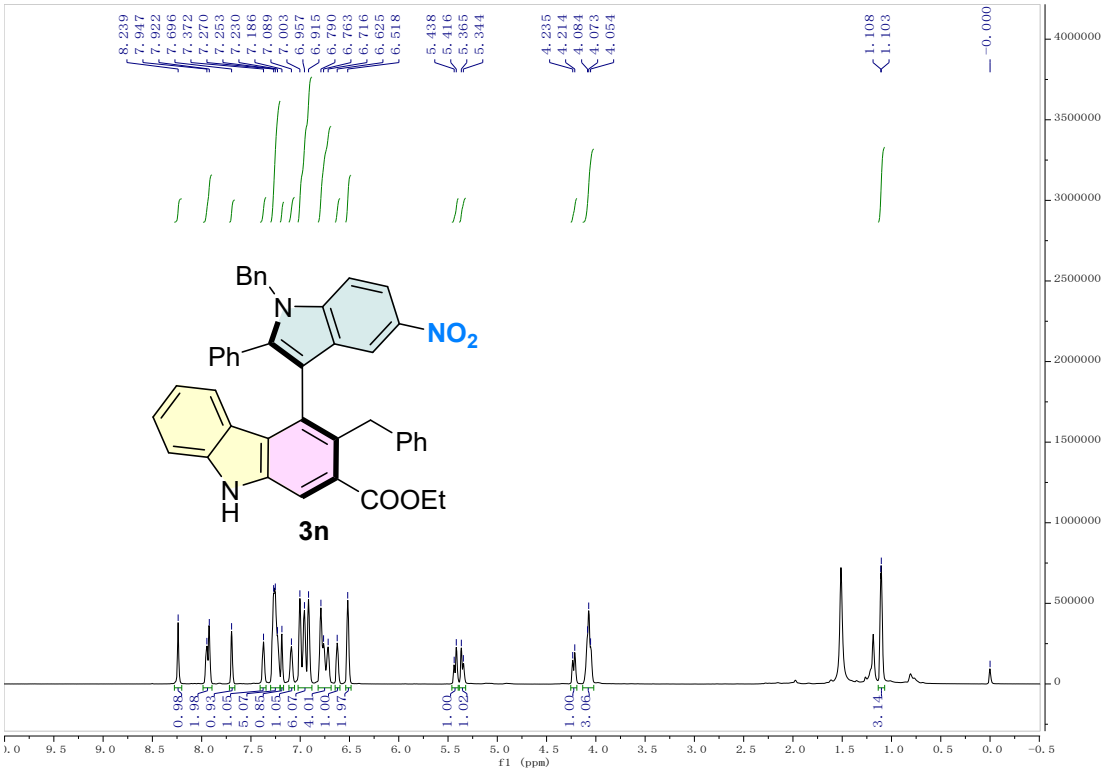
Ph
Me
Ph
N
H
COOEt
3m
f1 (ppm)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7.922
7.696
7.372
7.270
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7.230
7.186
7.089
7.003
6.957
6.915
6.790
6.763
6.716
6.625
6.518
5.438
5.416
5.365
5.344
4.235
4.214
4.084
4.073
4.054
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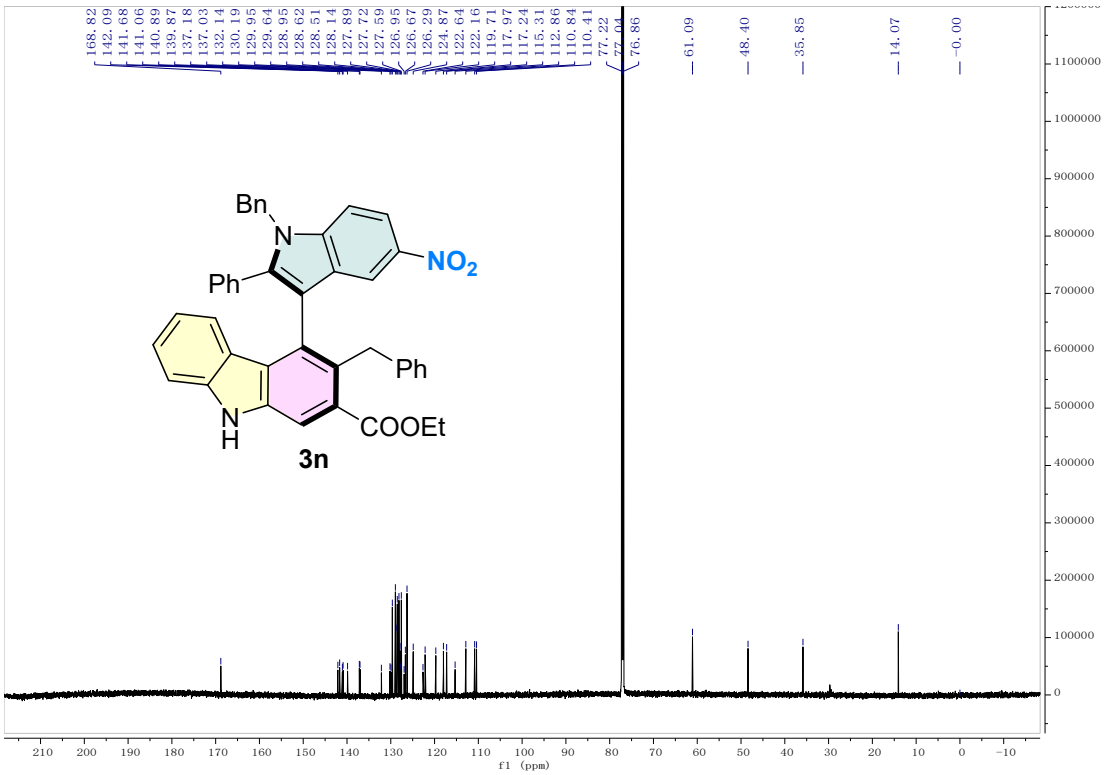
1.103
-0.000
Bn
N
NO2
Ph
Ph
N
H
COOEt
3n
f1 (ppm)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141.06
140.89
139.87
137.18
137.03
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130.19
129.95
129.64
128.95
128.62
128.51
128.14
127.89
127.72
127.59
126.95
126.67
126.29
124.87
122.64
122.16
119.71
117.97
117.24
115.31
112.86
110.84
110.41
77.22
77.04
76.86
61.09
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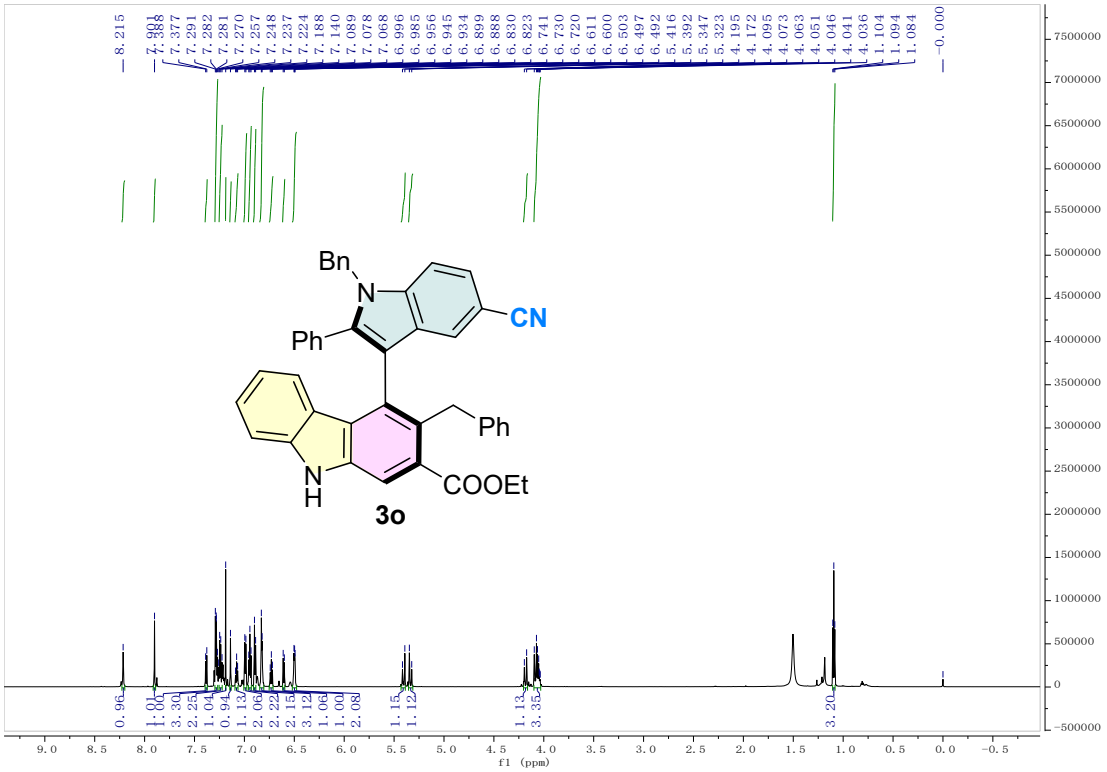
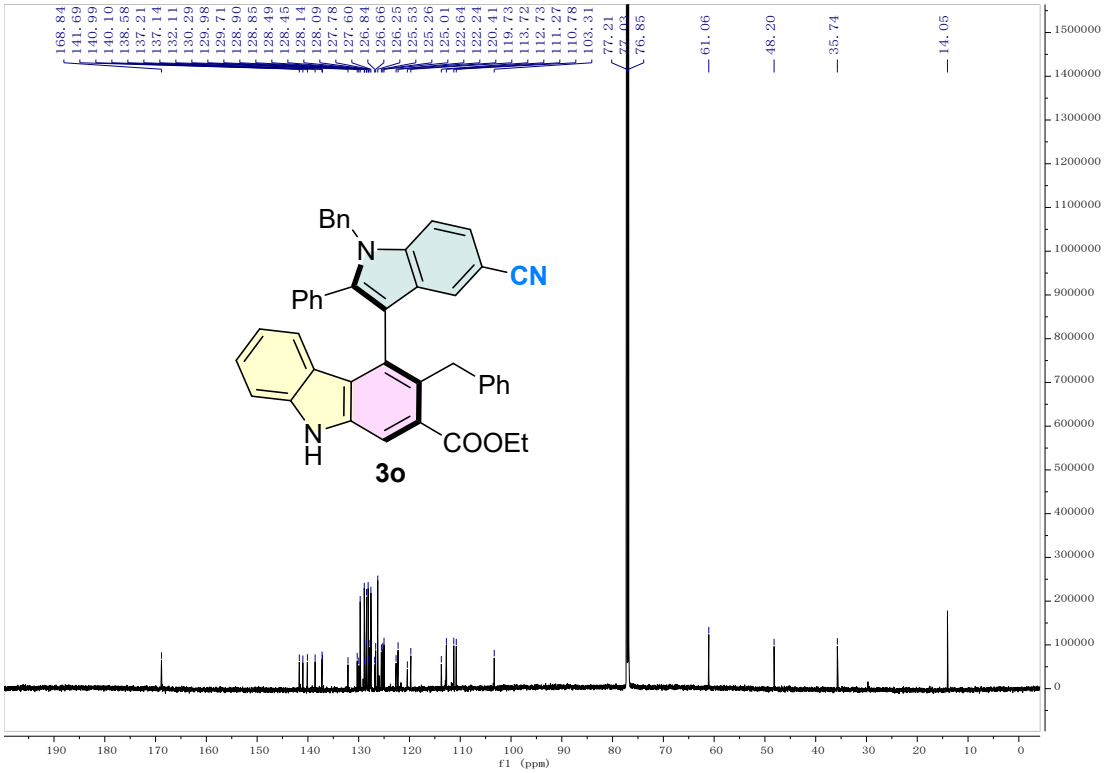
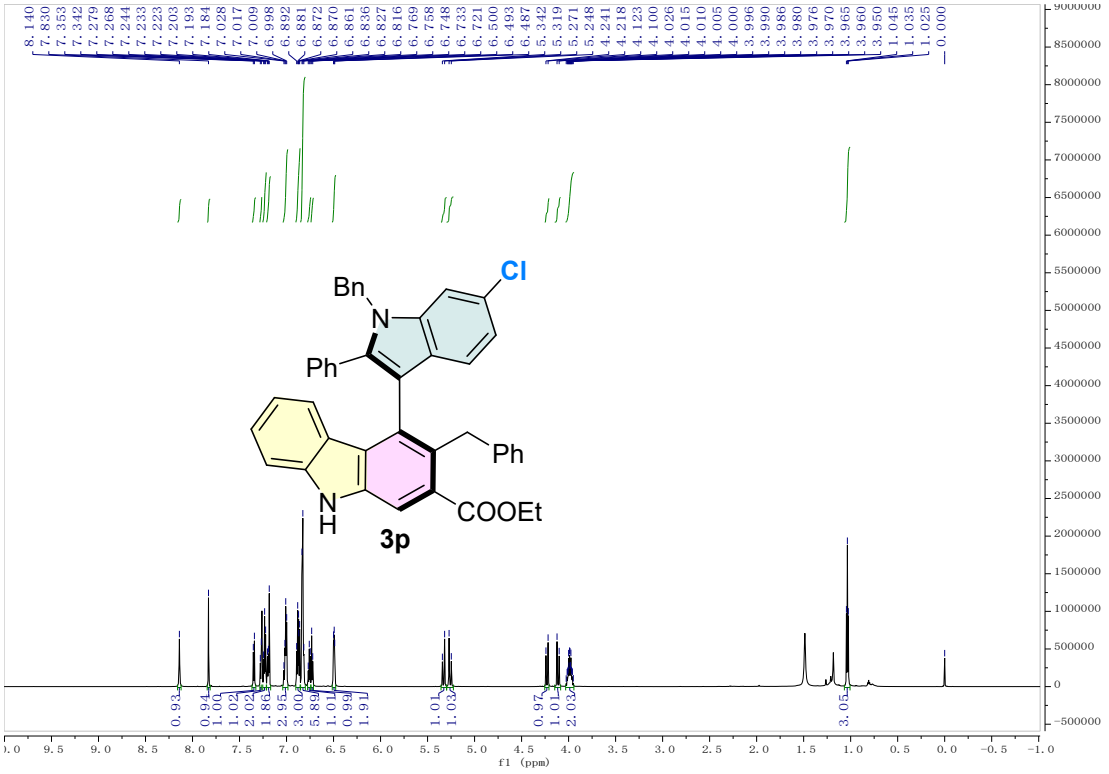
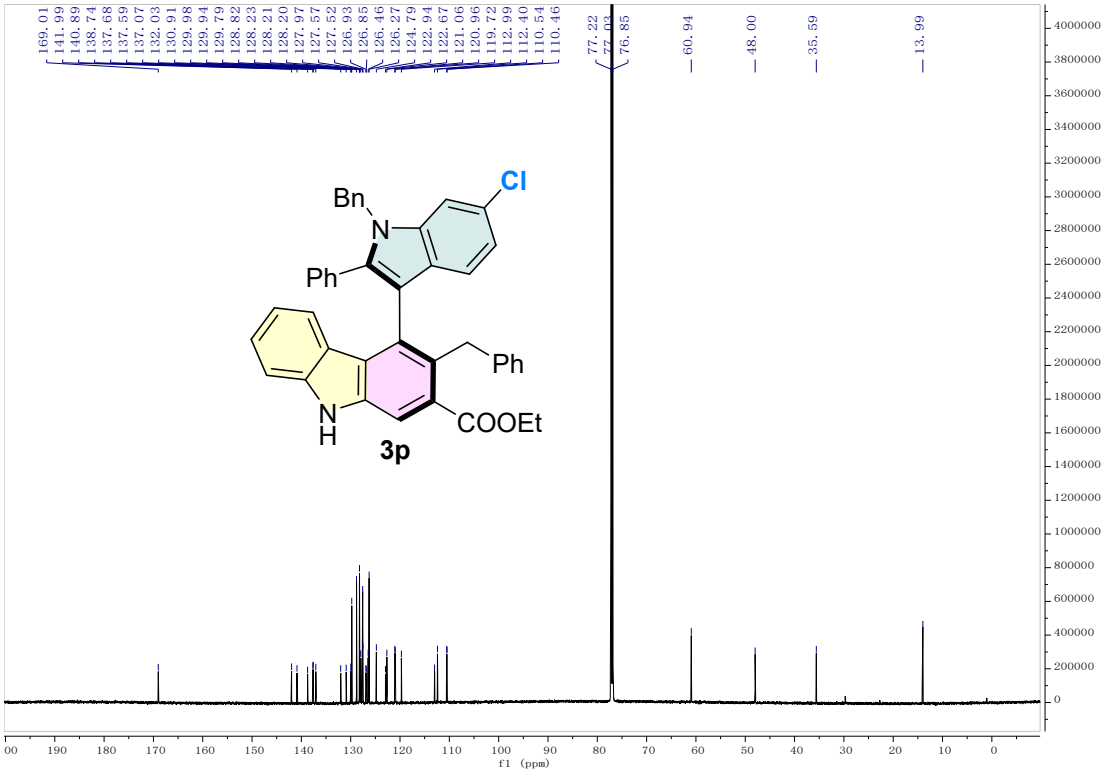
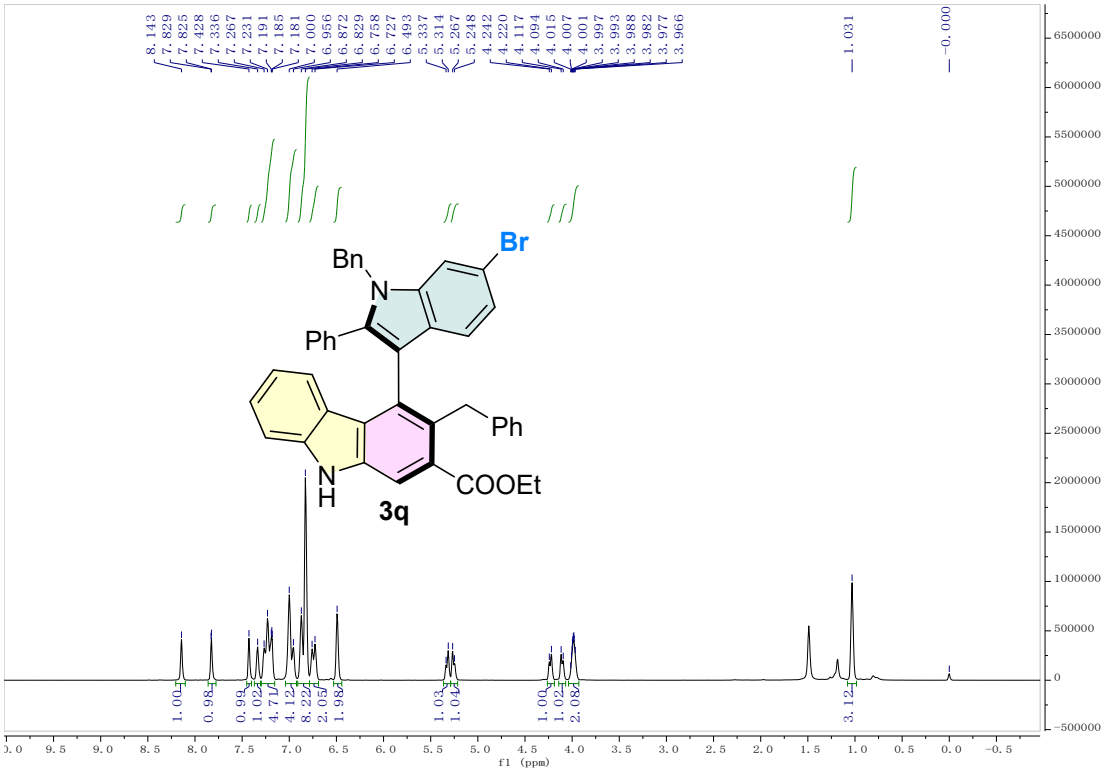
35.85
14.07
-0.00
Bn
N
NO2
Ph
Ph
N
H
COOEt
3n
f1 (ppm)

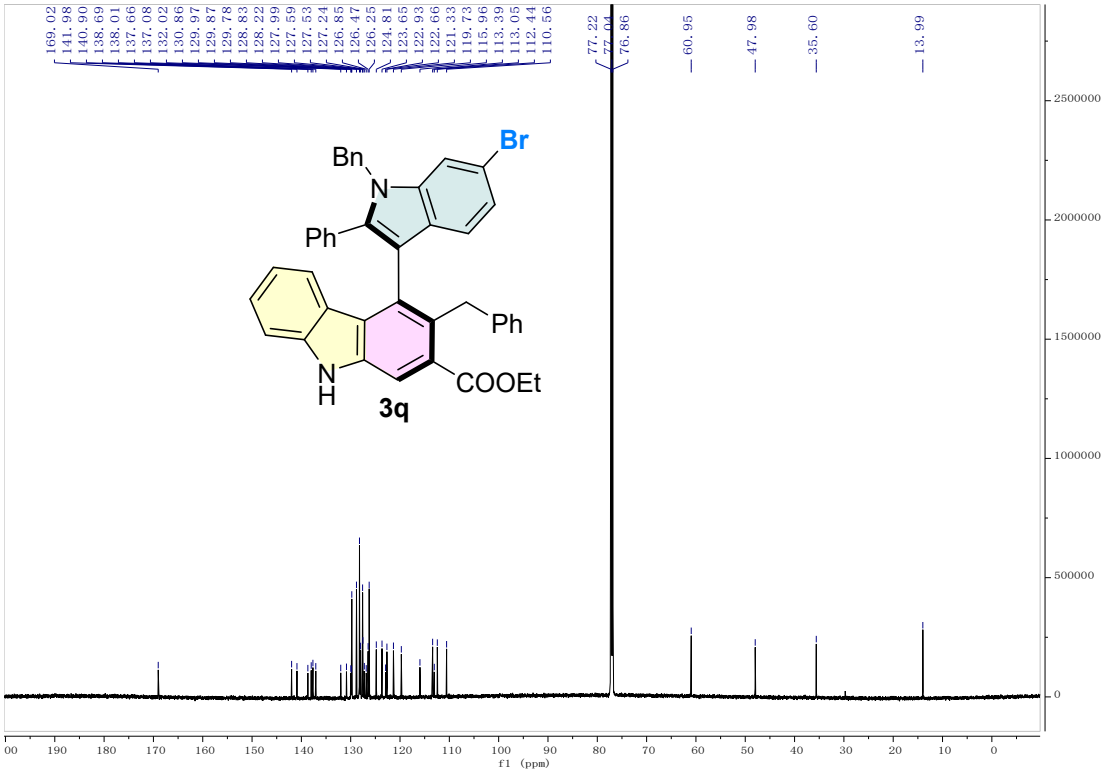

Bn
N
CN
Ph
Ph
N
H
COOEt
3o
f1 (ppm)

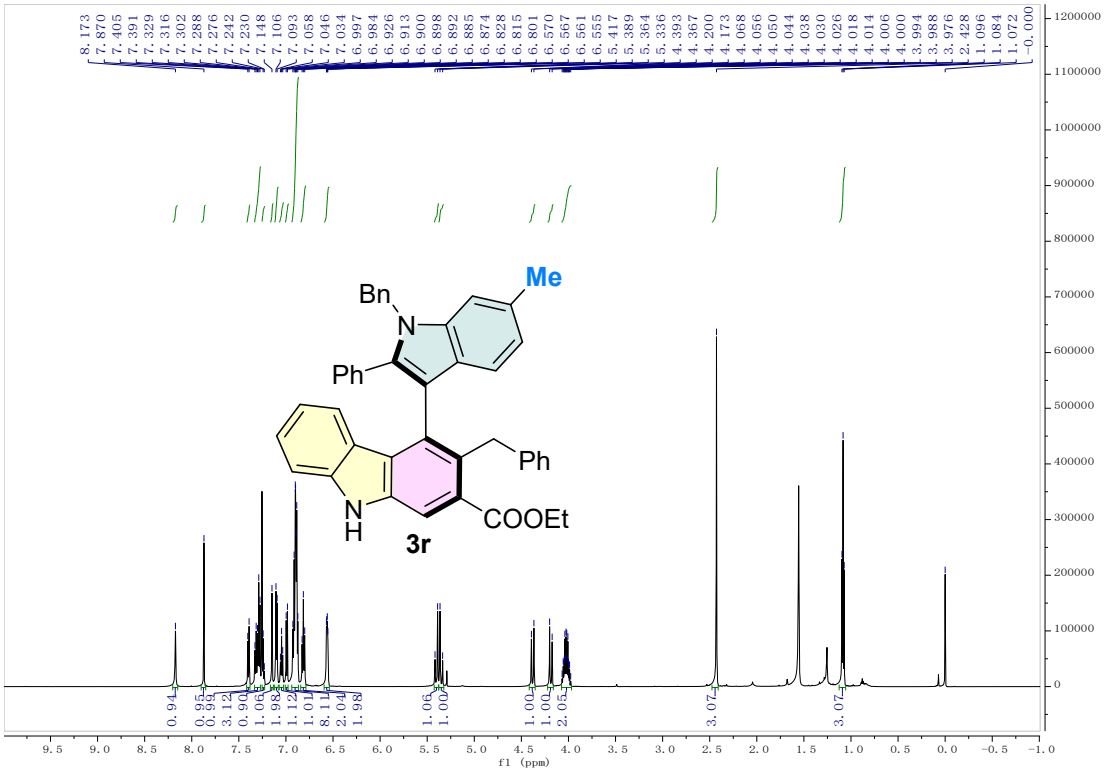

Bn
N
CN
Ph
Ph
N
H
COOEt
3o
f1 (ppm)

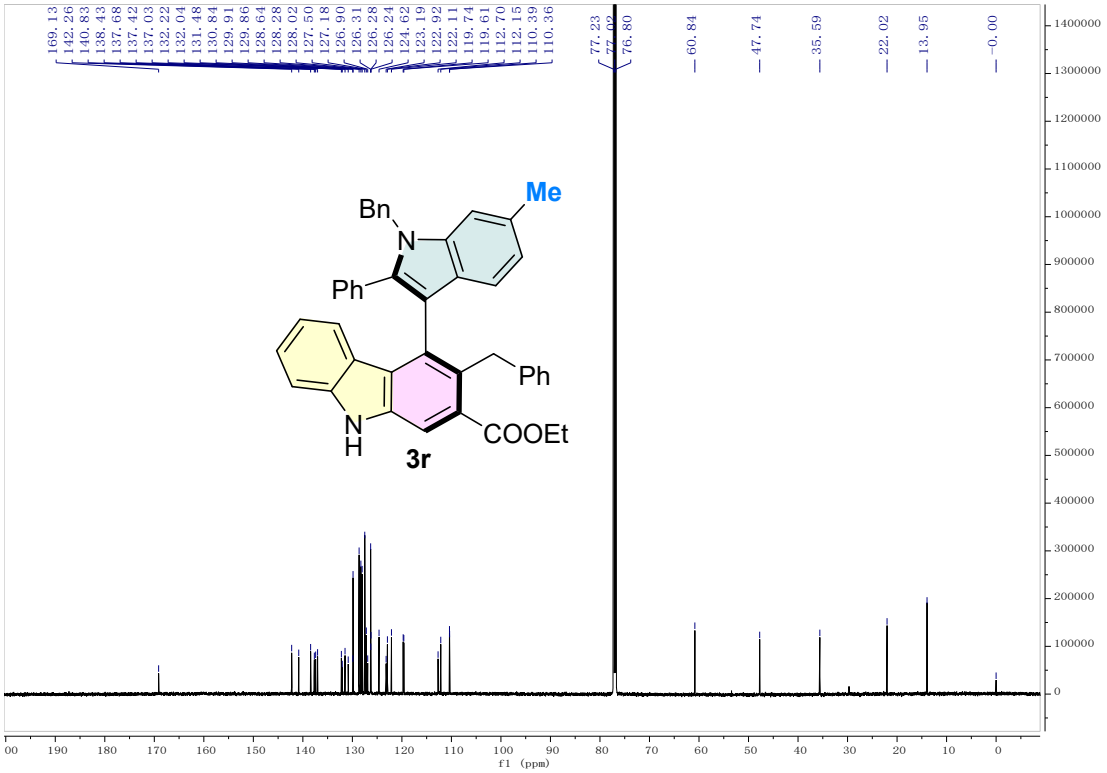

Cl
Bn
N
Ph
Ph
N
H
COOEt
3p
f1 (ppm)

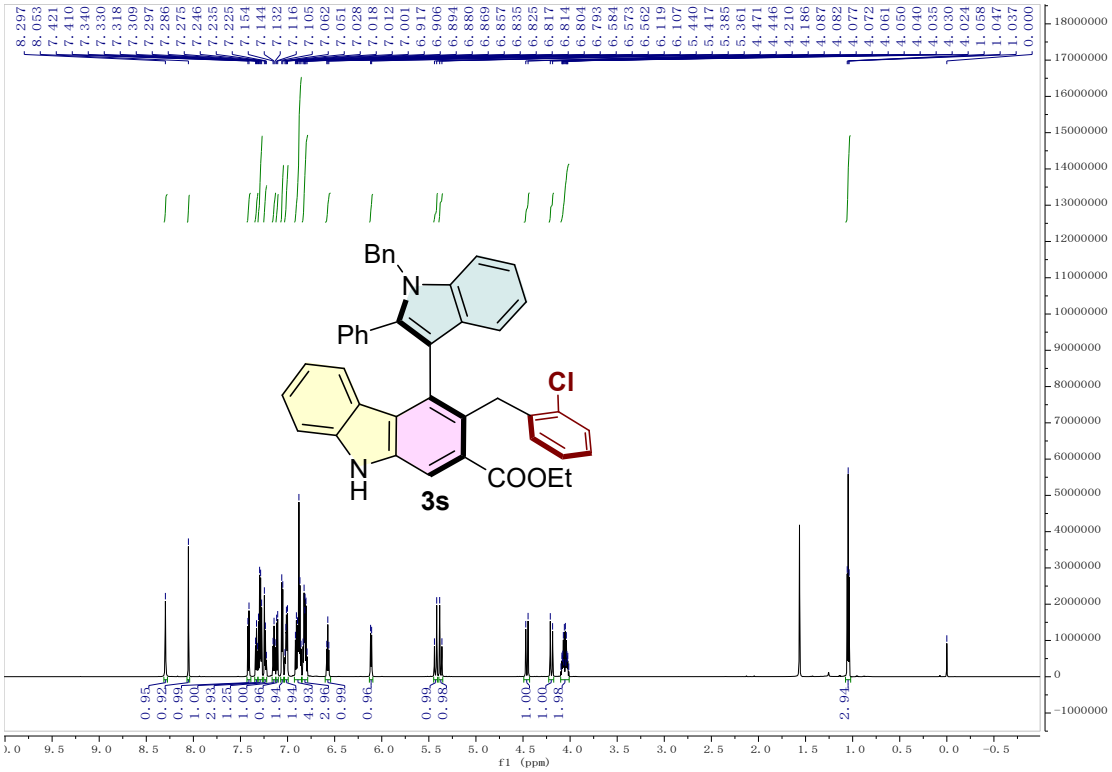

Cl
Bn
N
Ph
Ph
N
H
COOEt
3p
f1 (ppm)

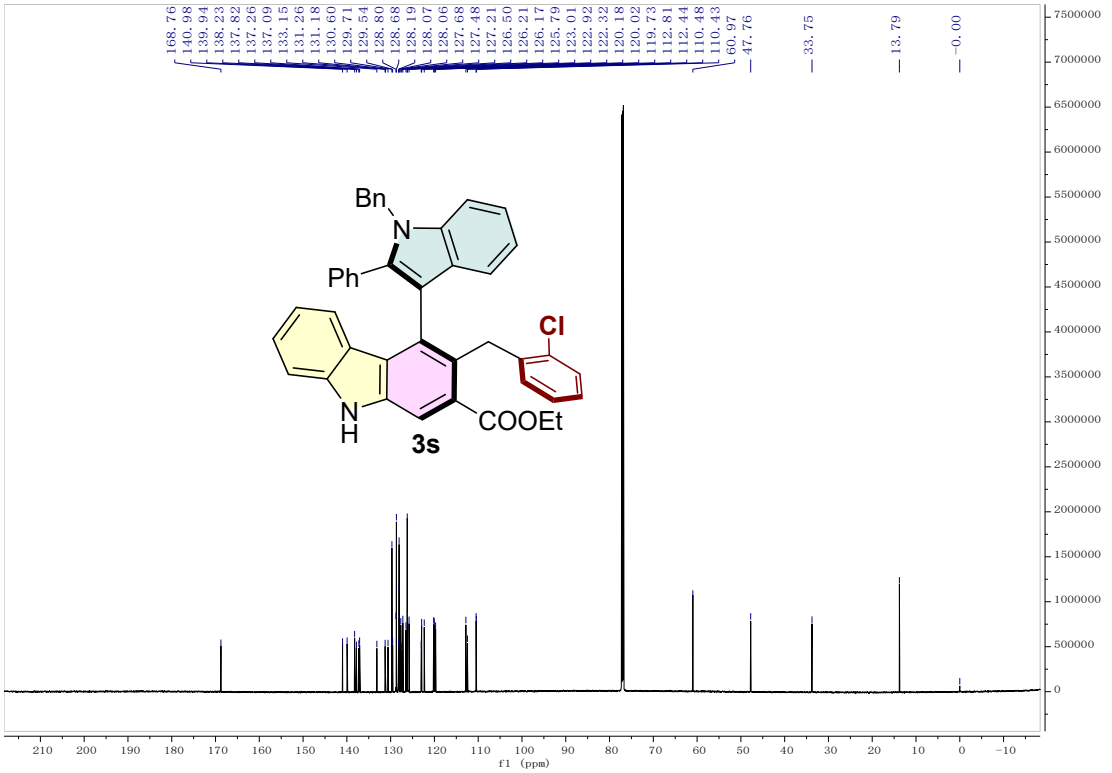

Br
Bn
N
Ph
Ph
N
H
COOEt
3q
f1 (ppm)


Br
Bn
N
Ph
Ph
N
H
COOEt
3q
f1 (ppm)


Me
Bn
N
Ph
Ph
N
H
COOEt
3r
f1 (ppm)


Me
Bn
N
Ph
Ph
N
H
COOEt
3r
f1 (ppm)


Bn
N
Ph
Cl
N
H
COOEt
3s
f1 (ppm)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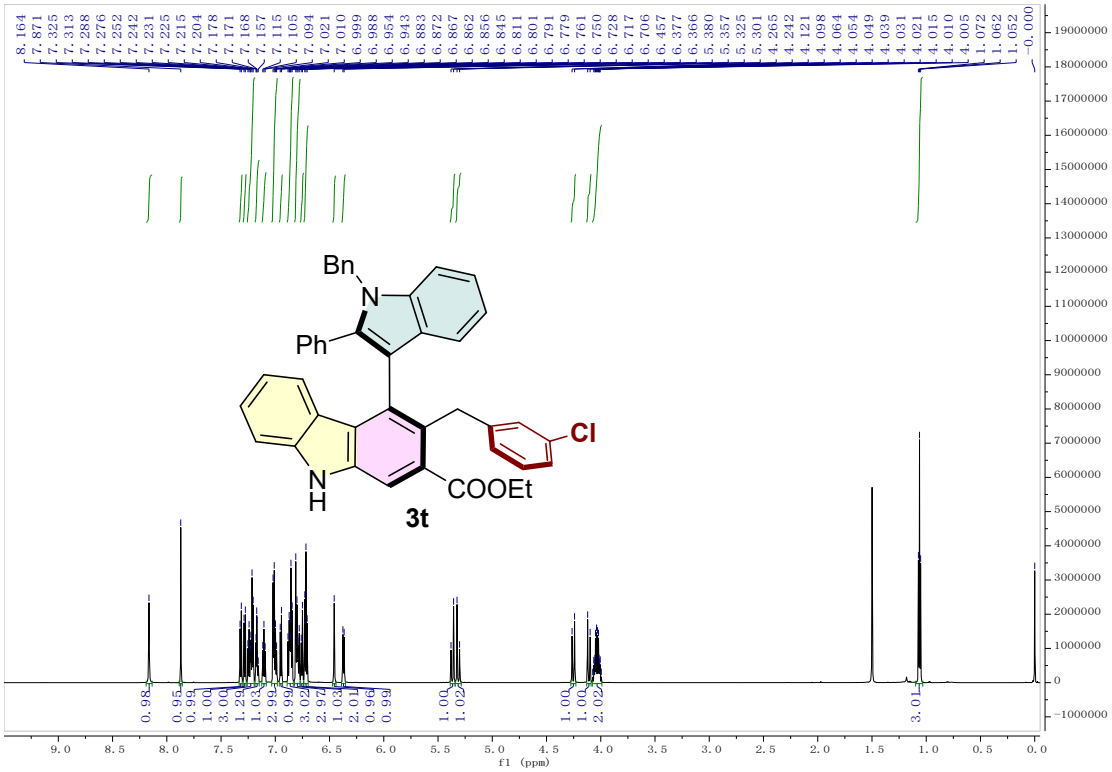
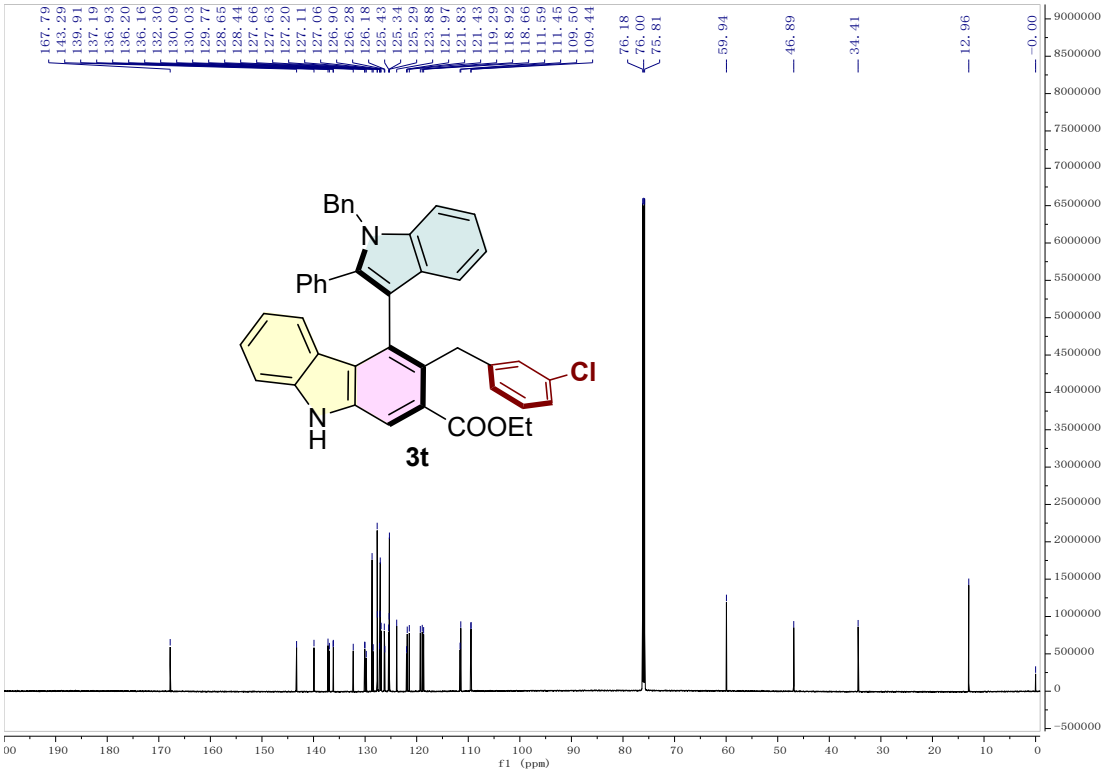
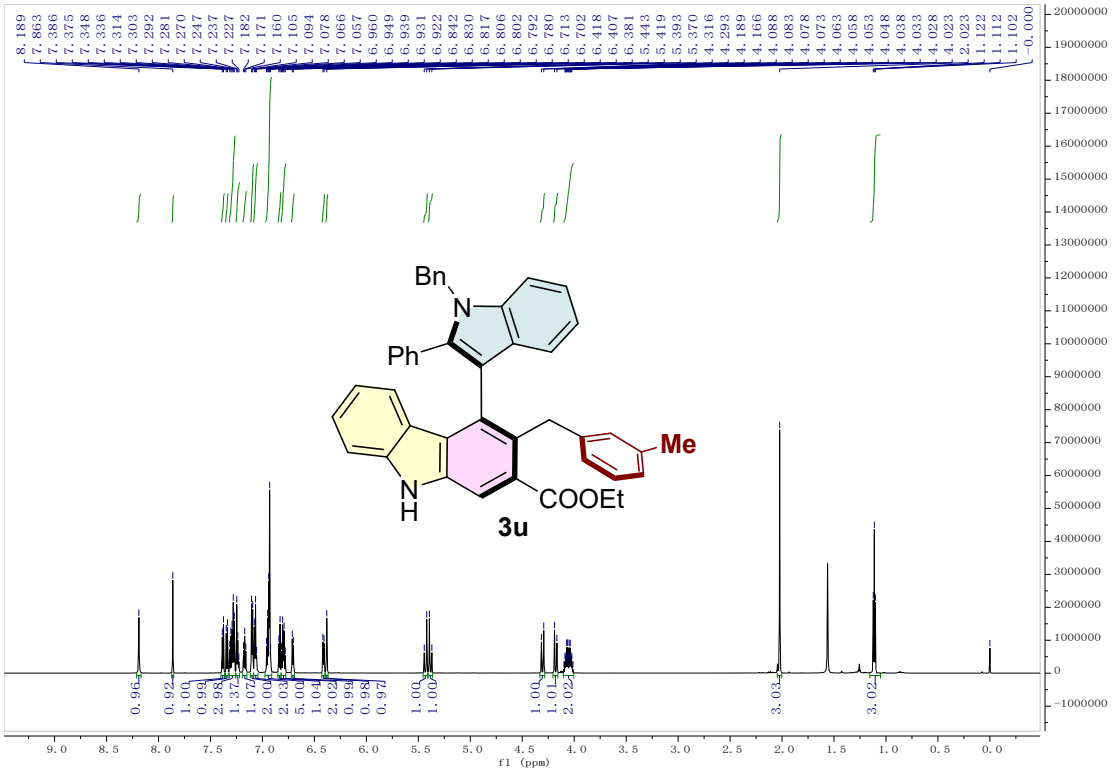
Ph
Cl
N
H
COOEt
3s
f1 (ppm)


Bn
N
Ph
Cl
N
H
COOEt
3t
f1 (ppm)


Bn
N
Ph
Cl
N
H
COOEt
3t
f1 (ppm)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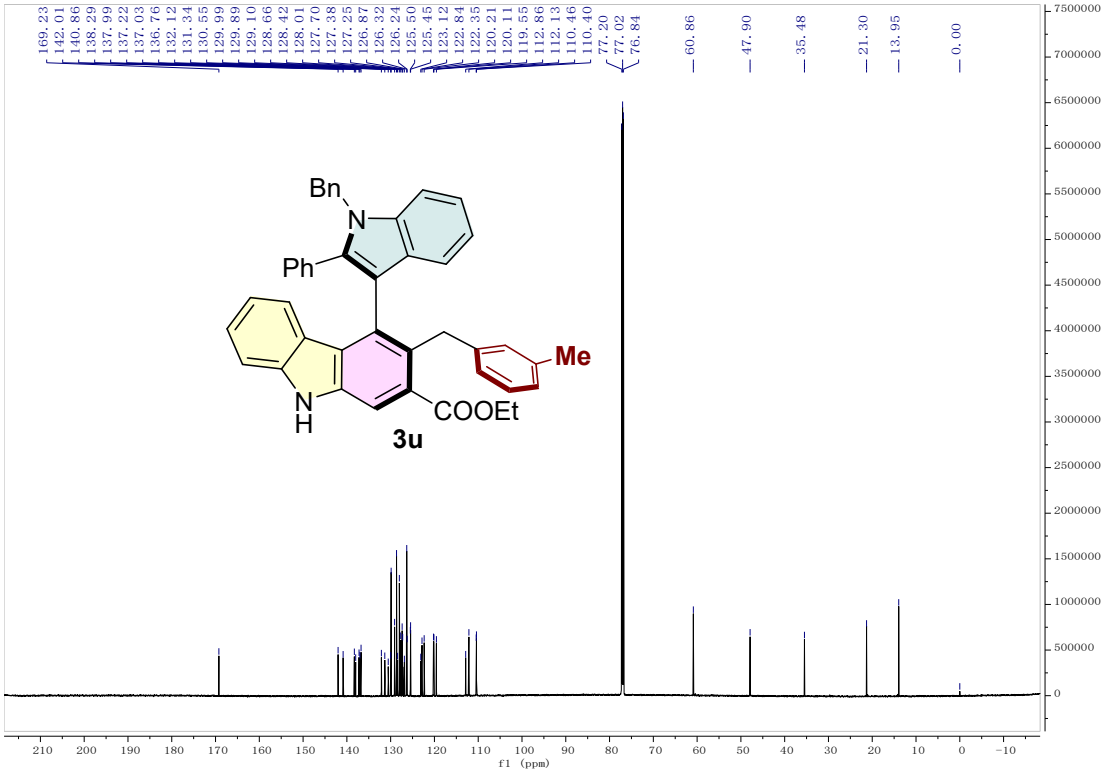
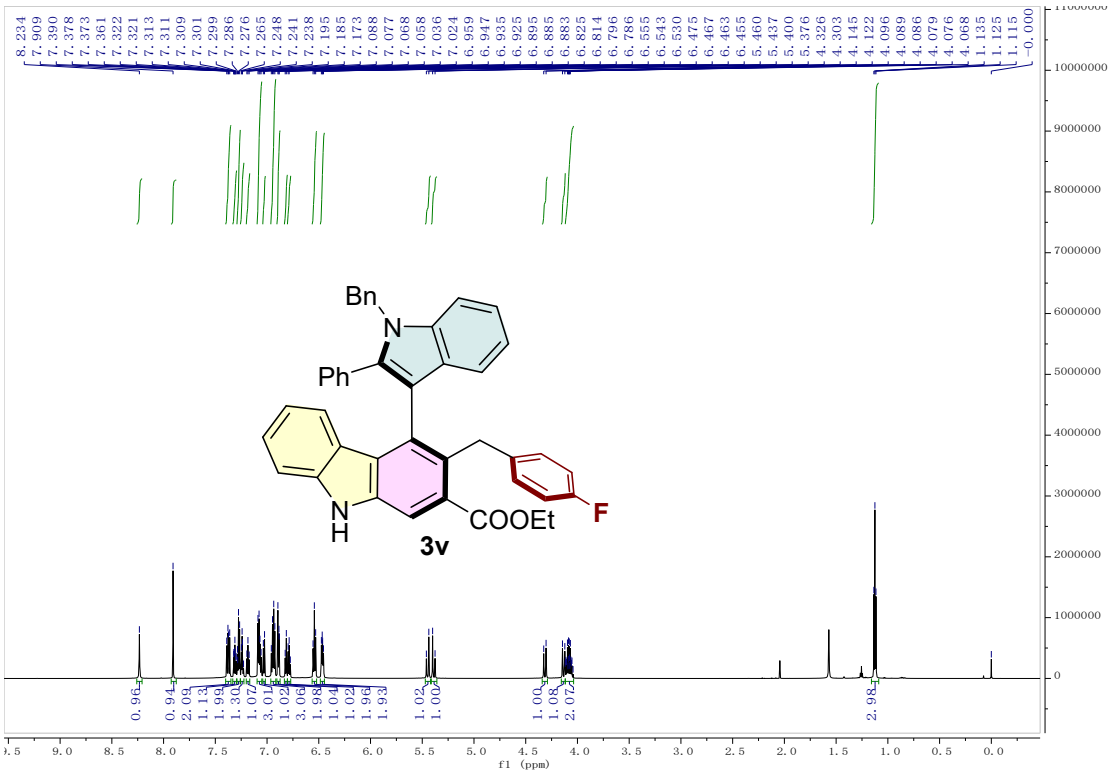
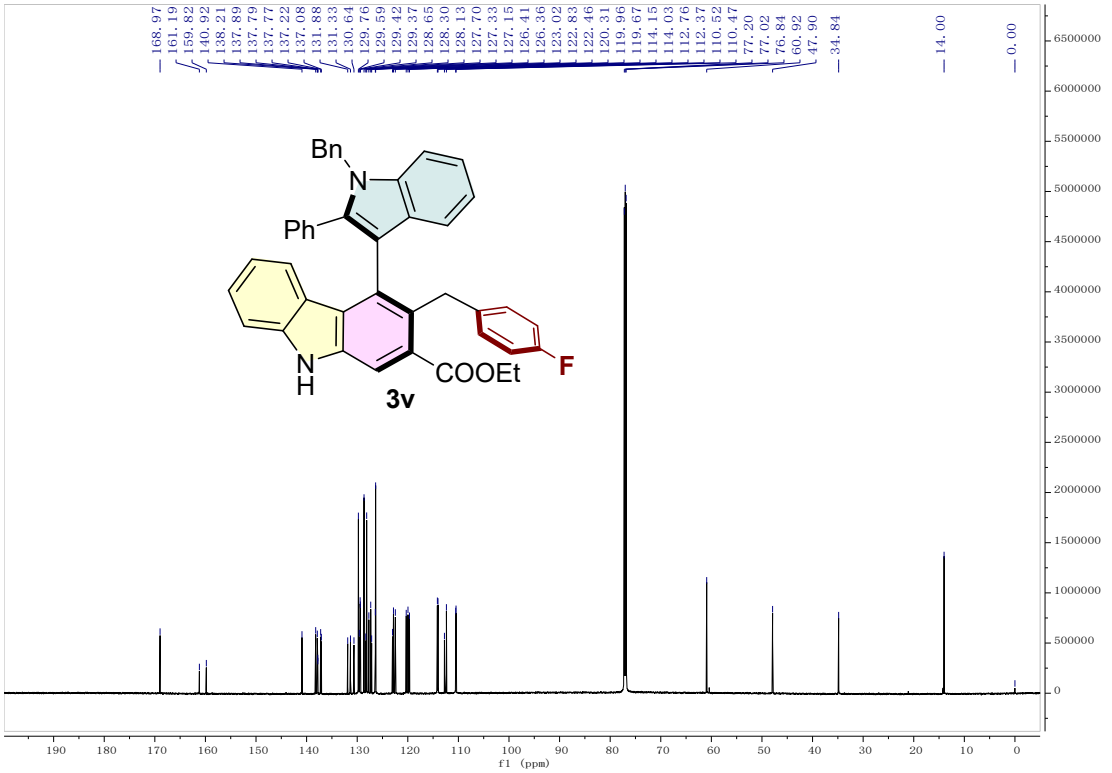
Ph
Me
N
H
COOEt
3u
f1 (ppm)


Bn
N
Ph
Me
N
H
COOEt
3u
f1 (ppm)


Bn
N
Ph
N
H
COOEt
F
3v
f1 (ppm)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N
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COOEt
F
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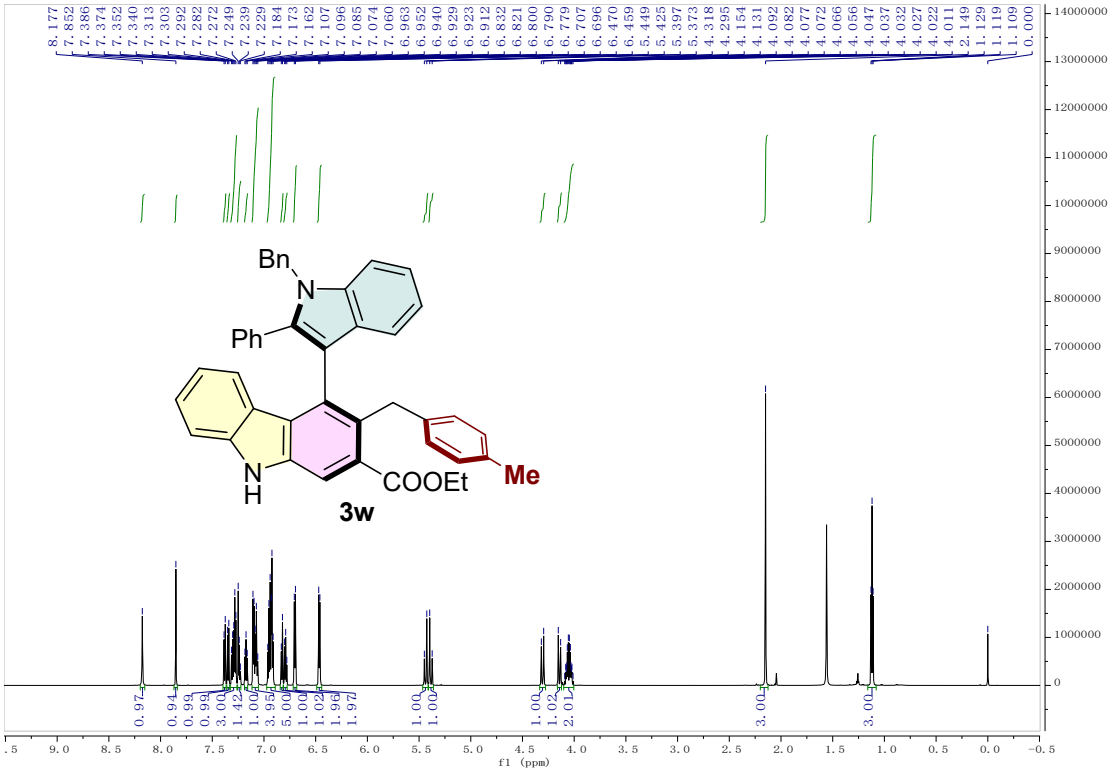
f1 (ppm)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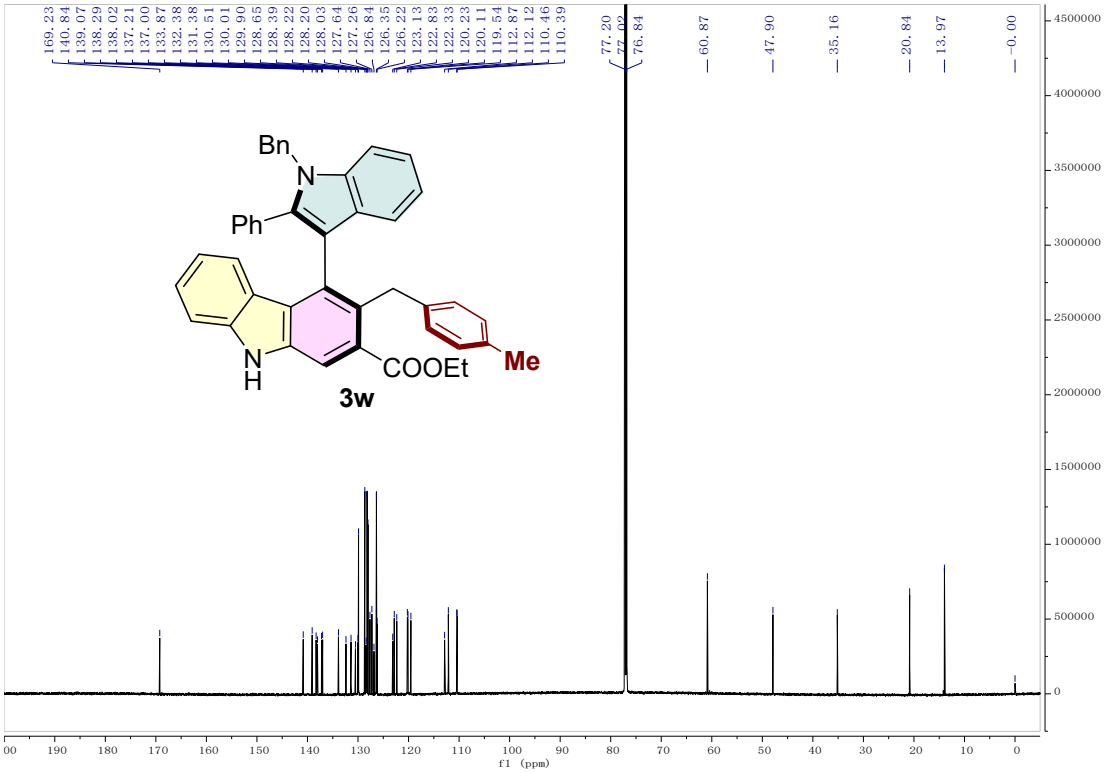
f1 (ppm)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H
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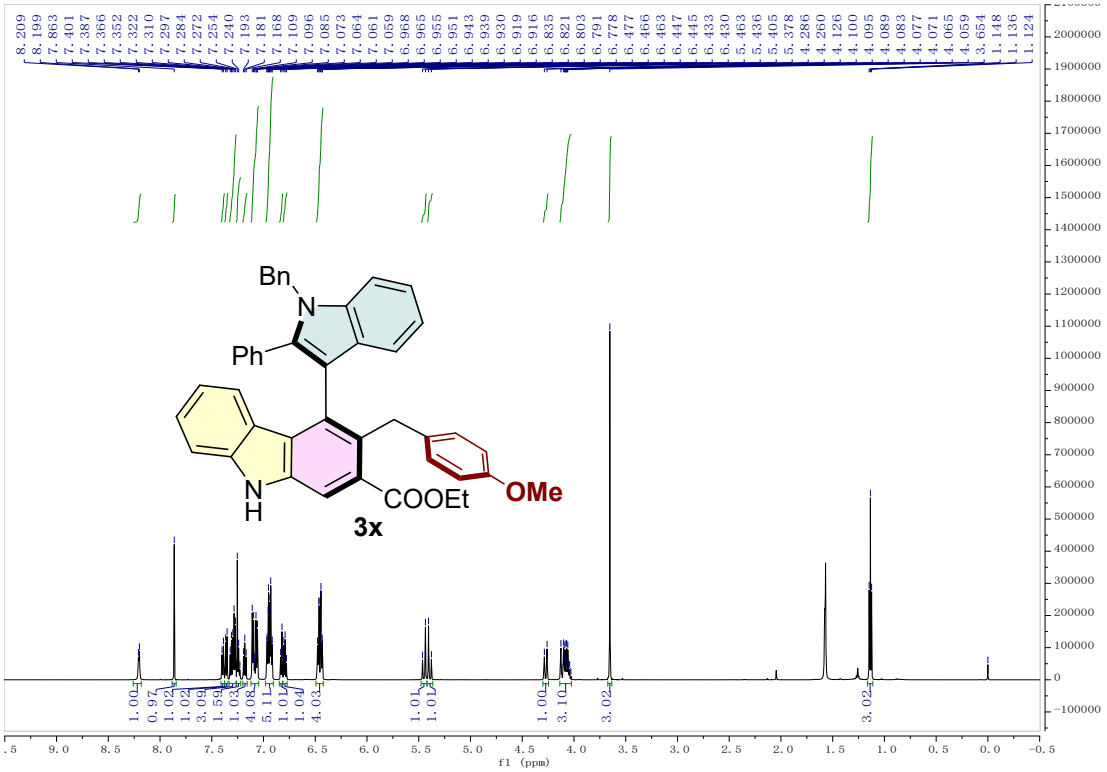
Me
3w
f1 (ppm)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OMe
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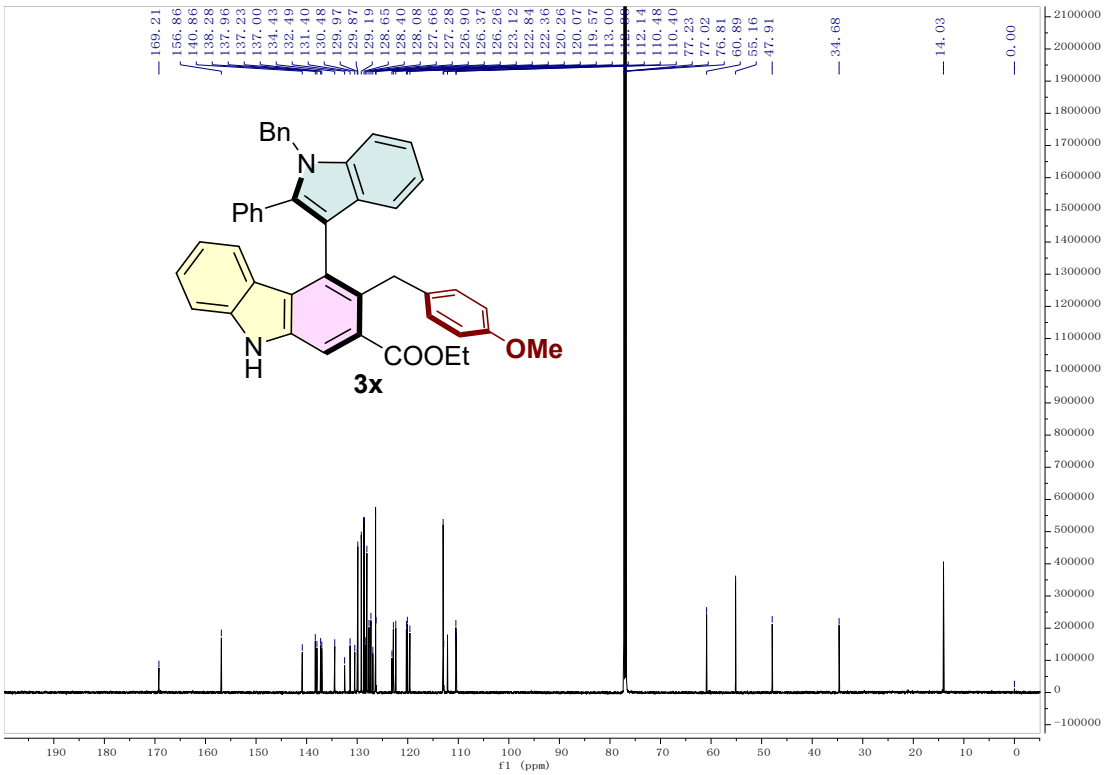
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OMe
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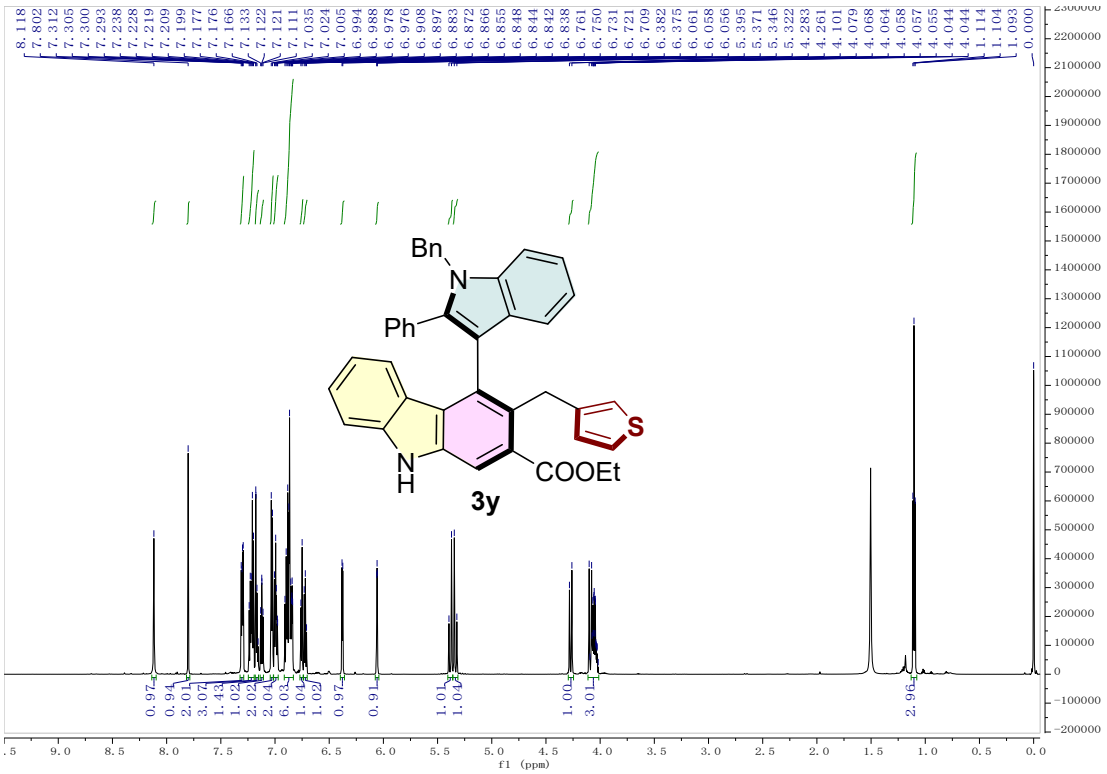
f1 (ppm)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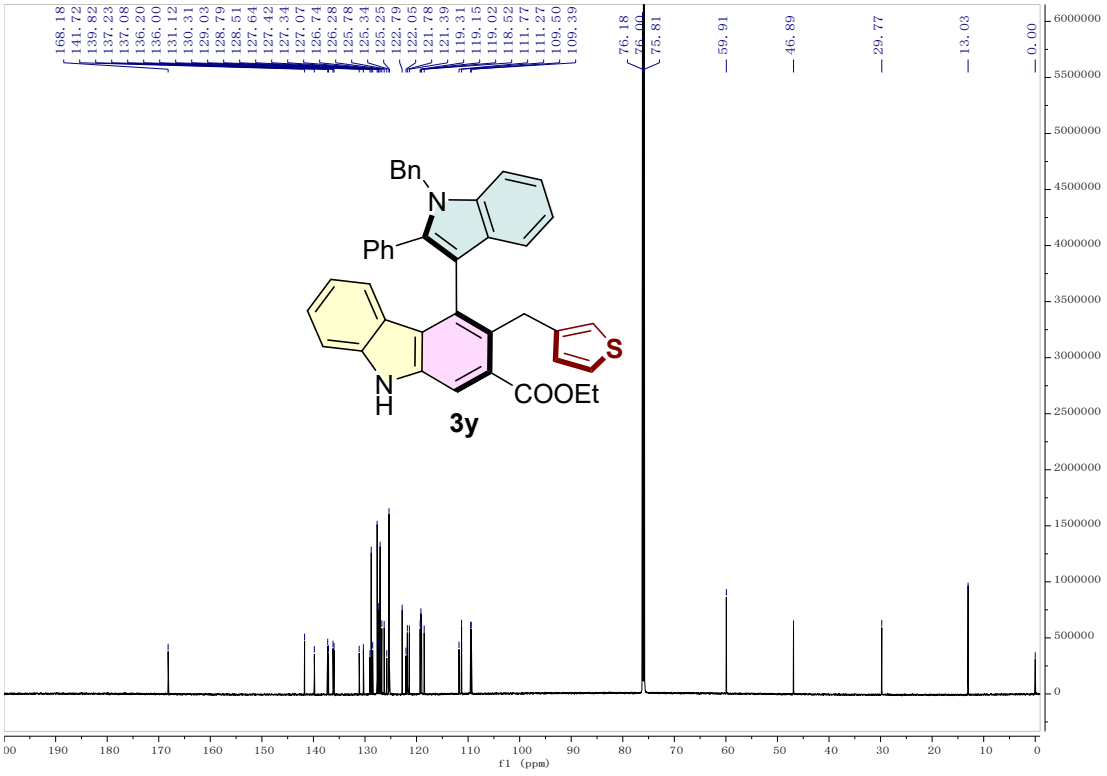
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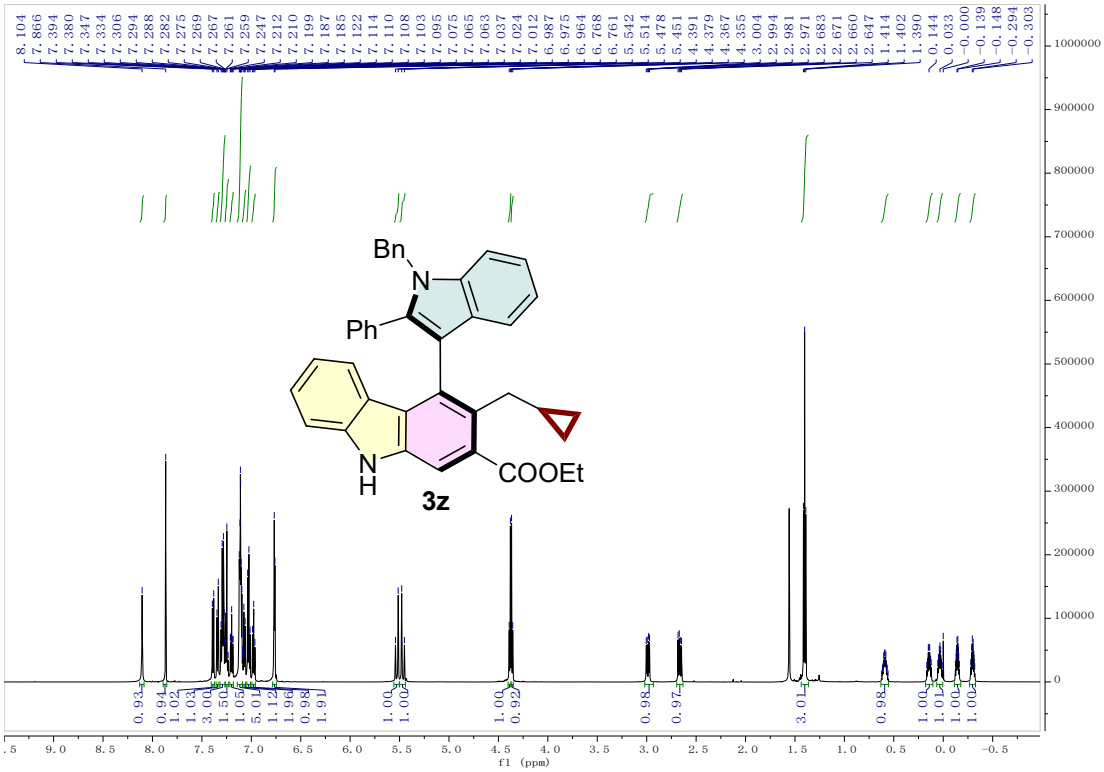
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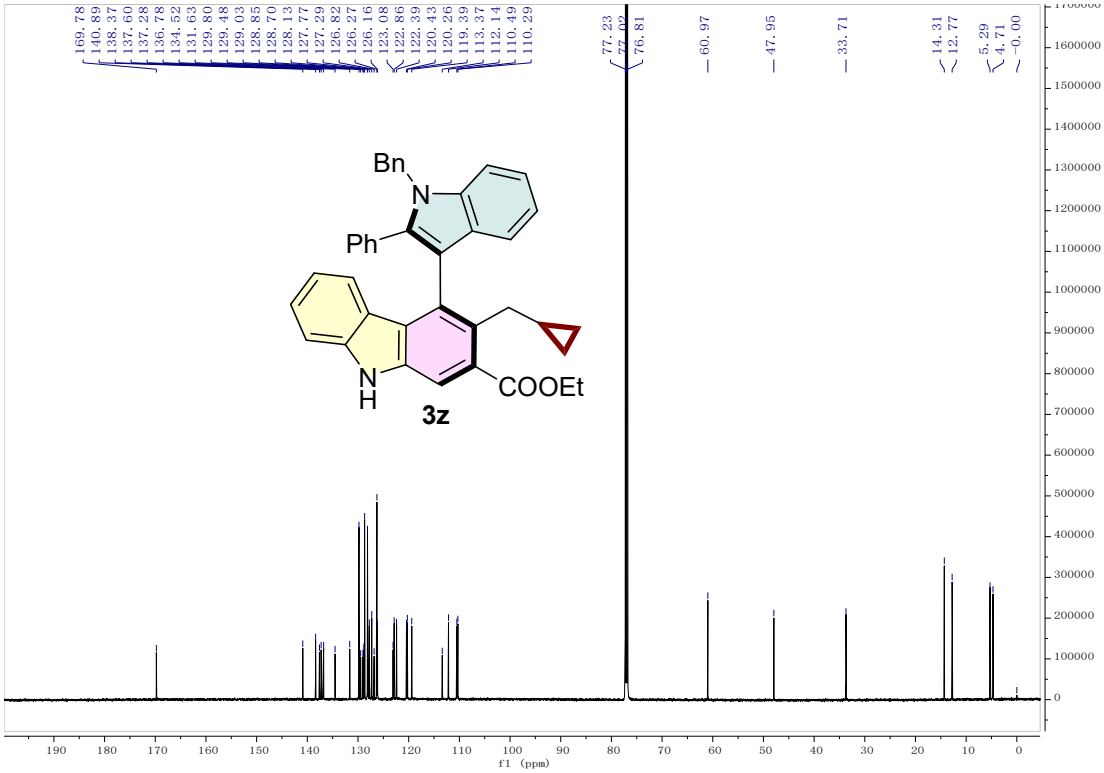
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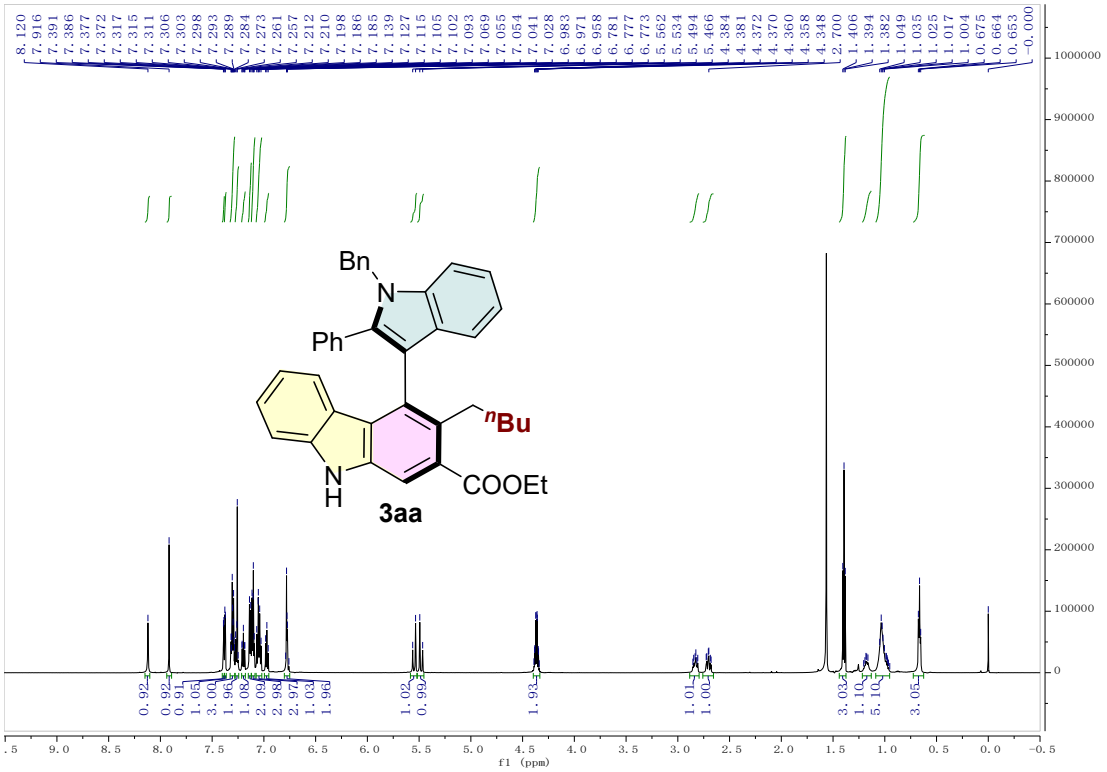
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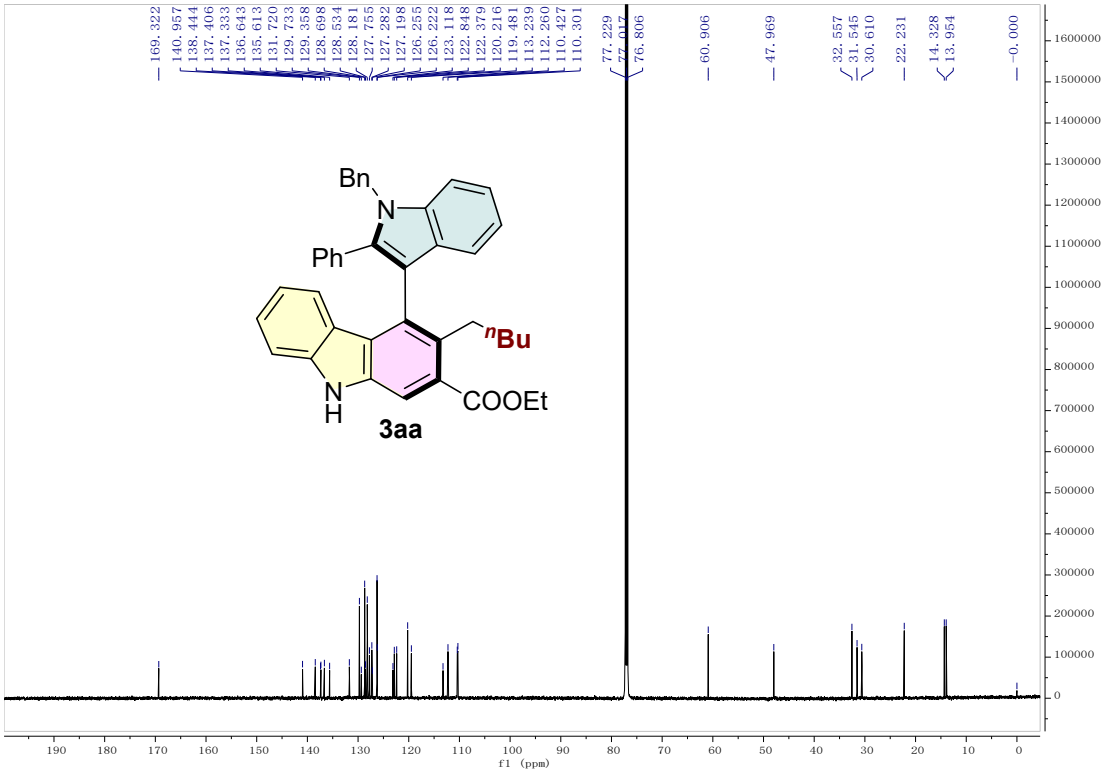
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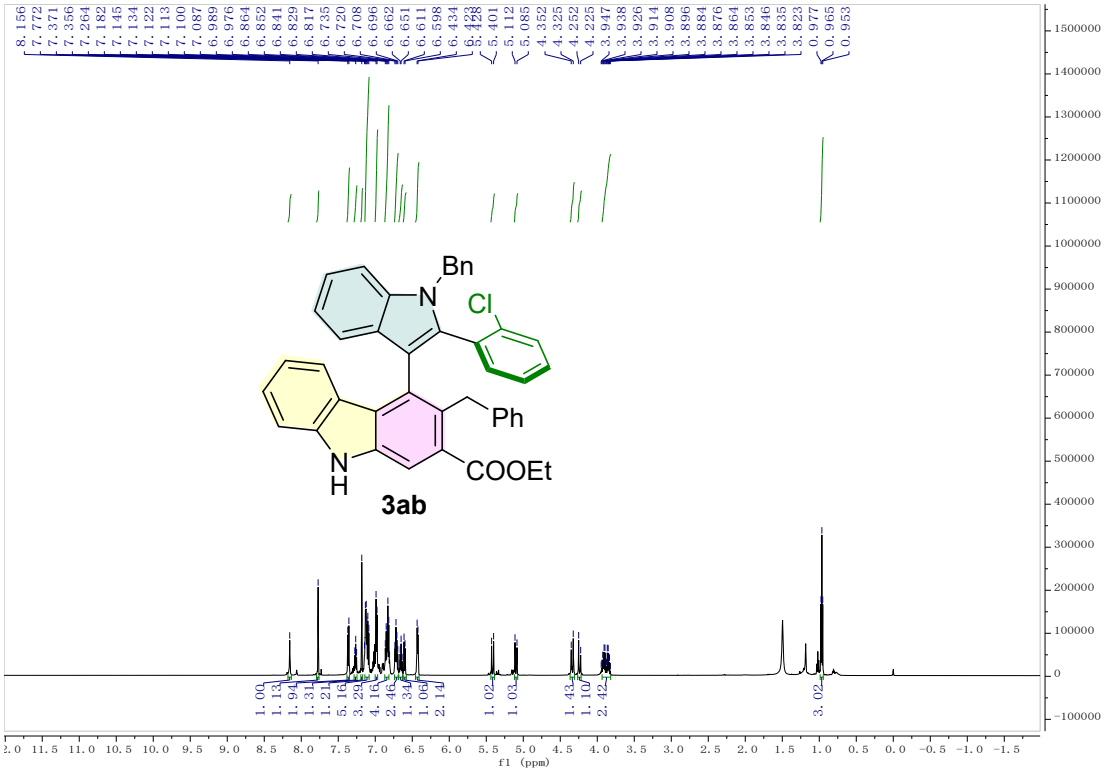
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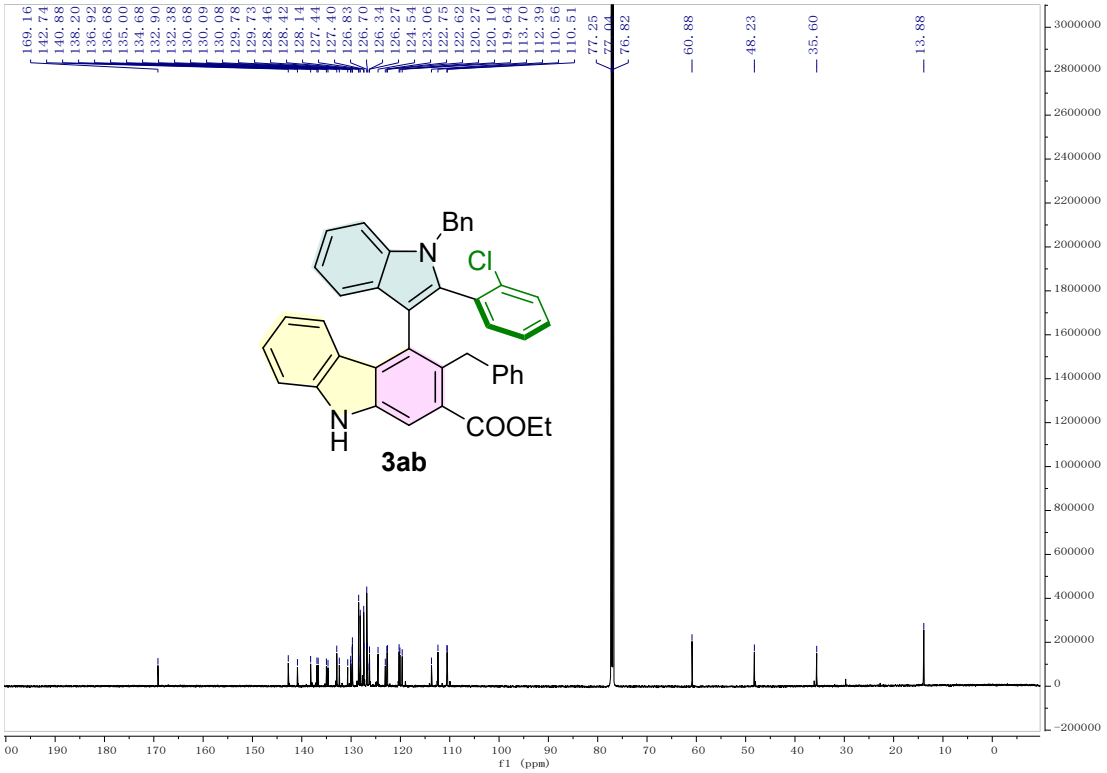
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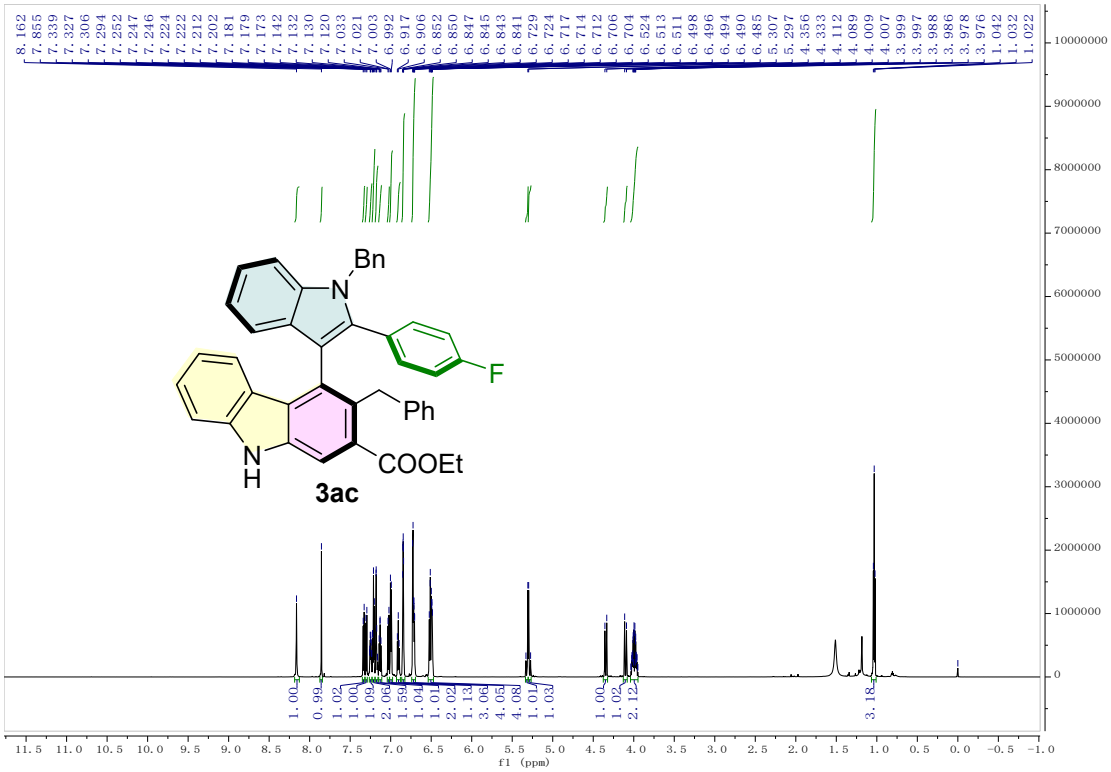
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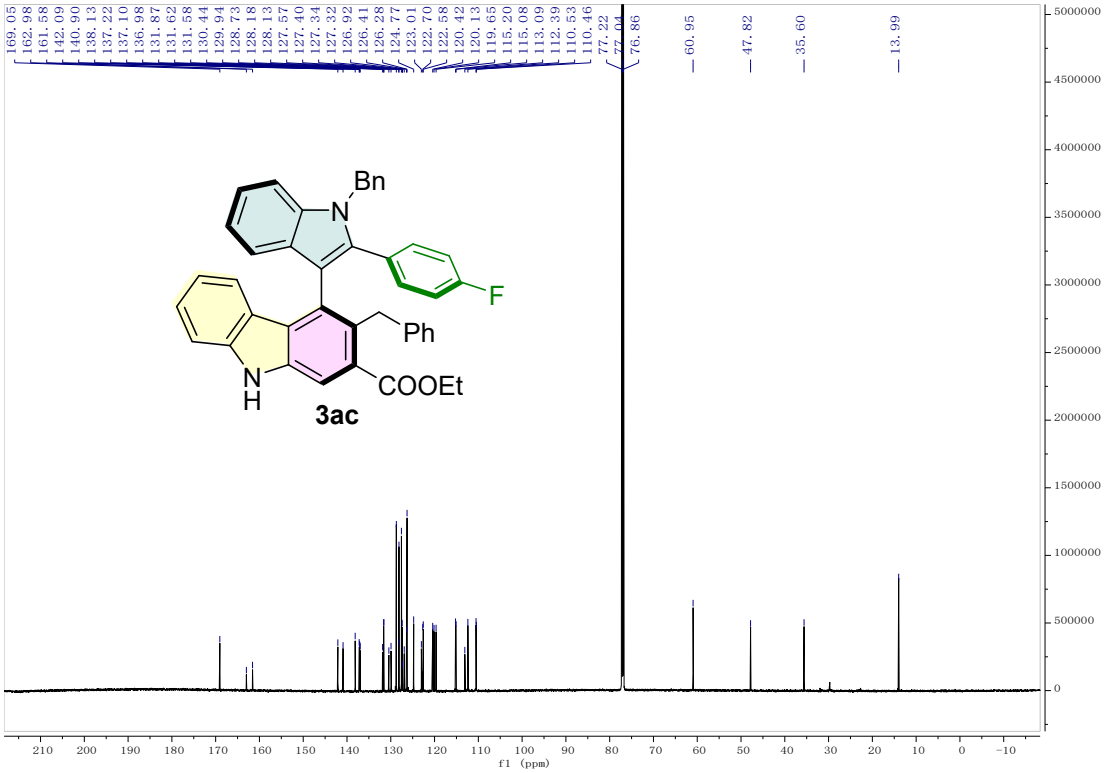
f1 (ppm)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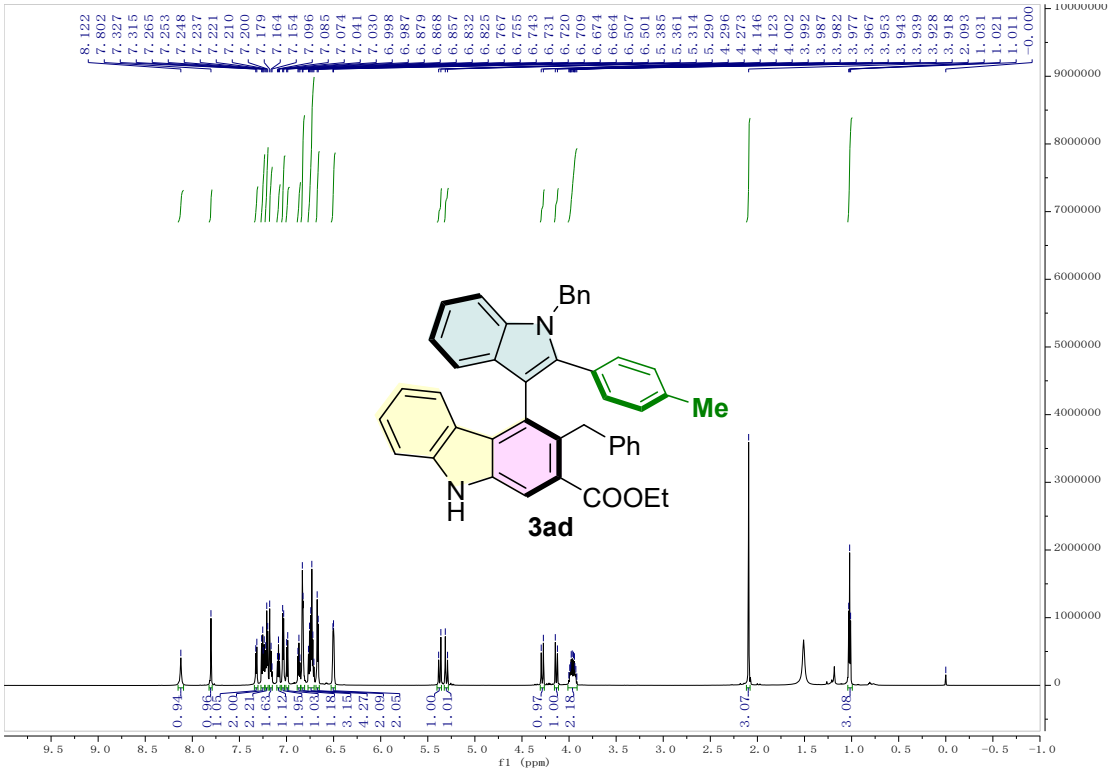
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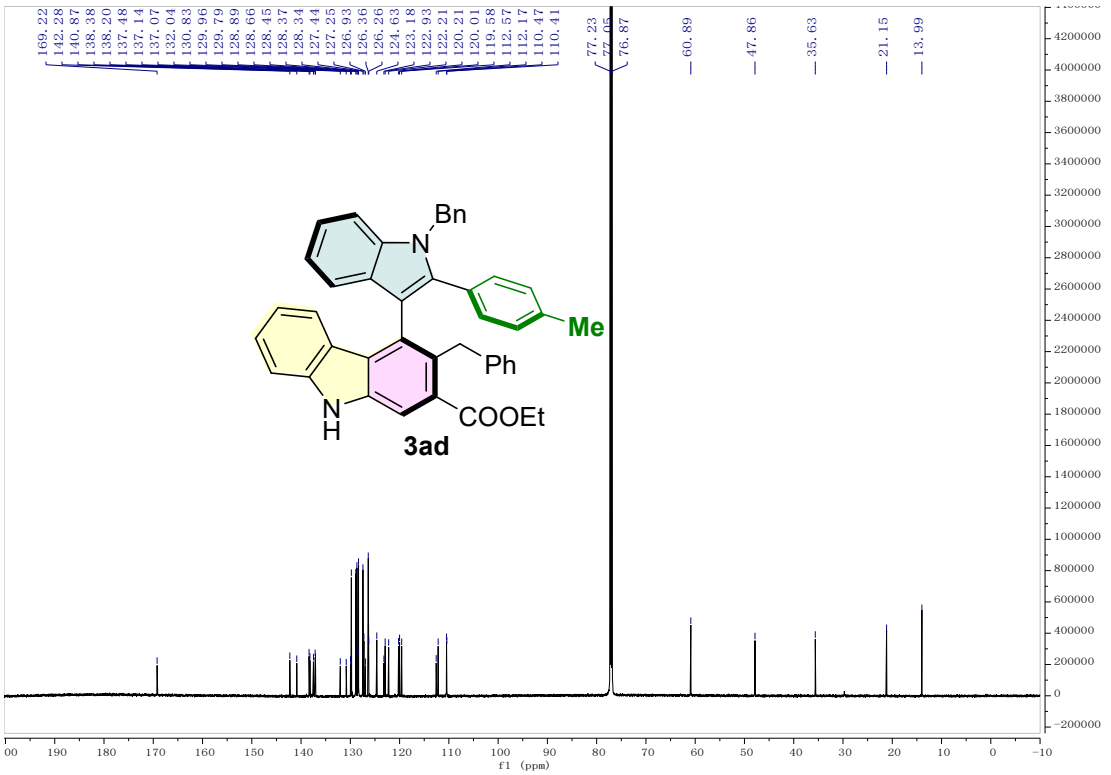
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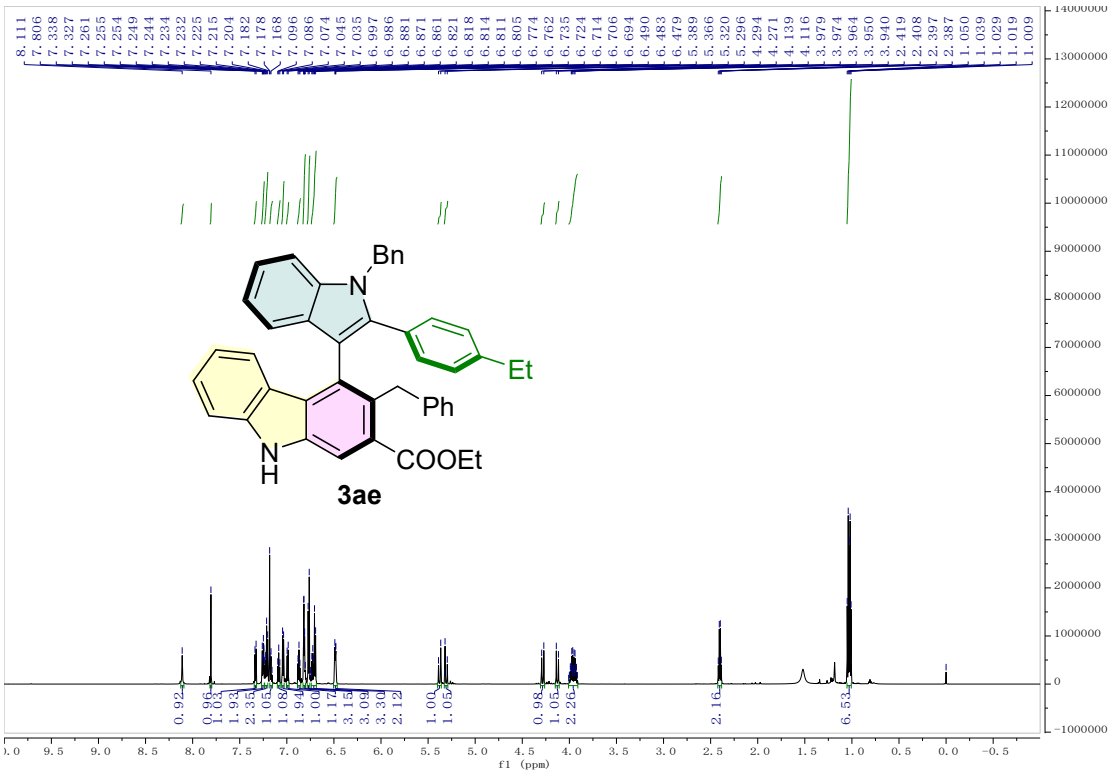
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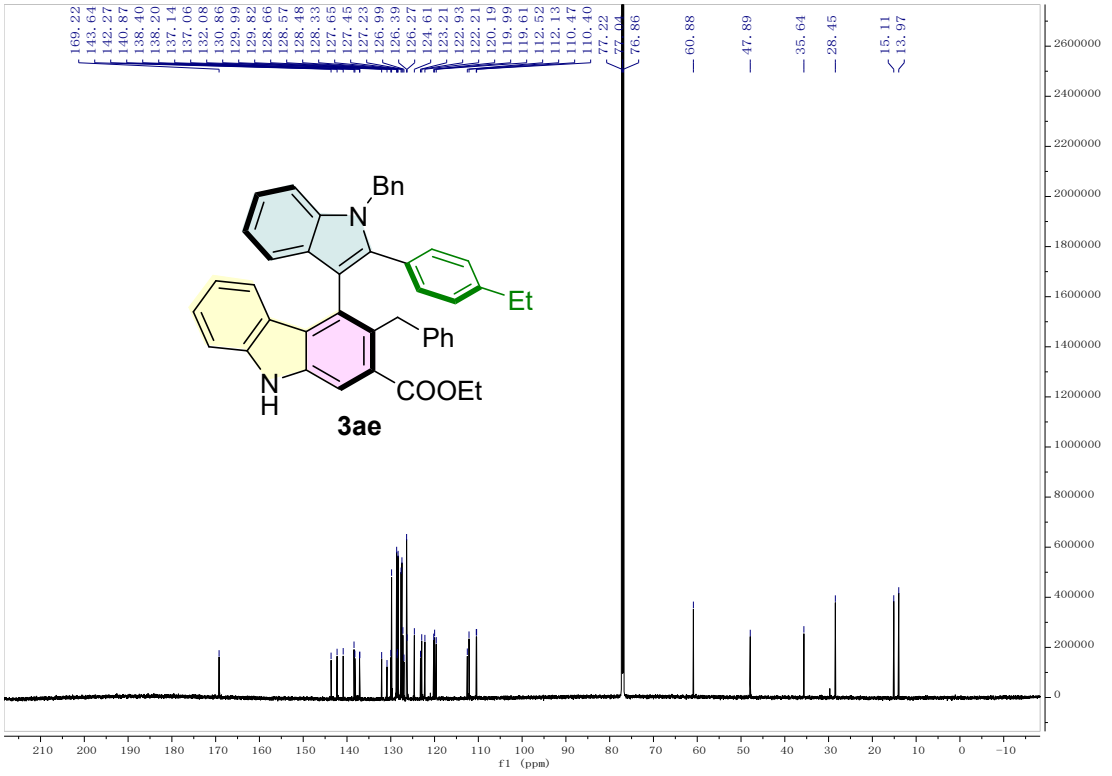
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COOEt
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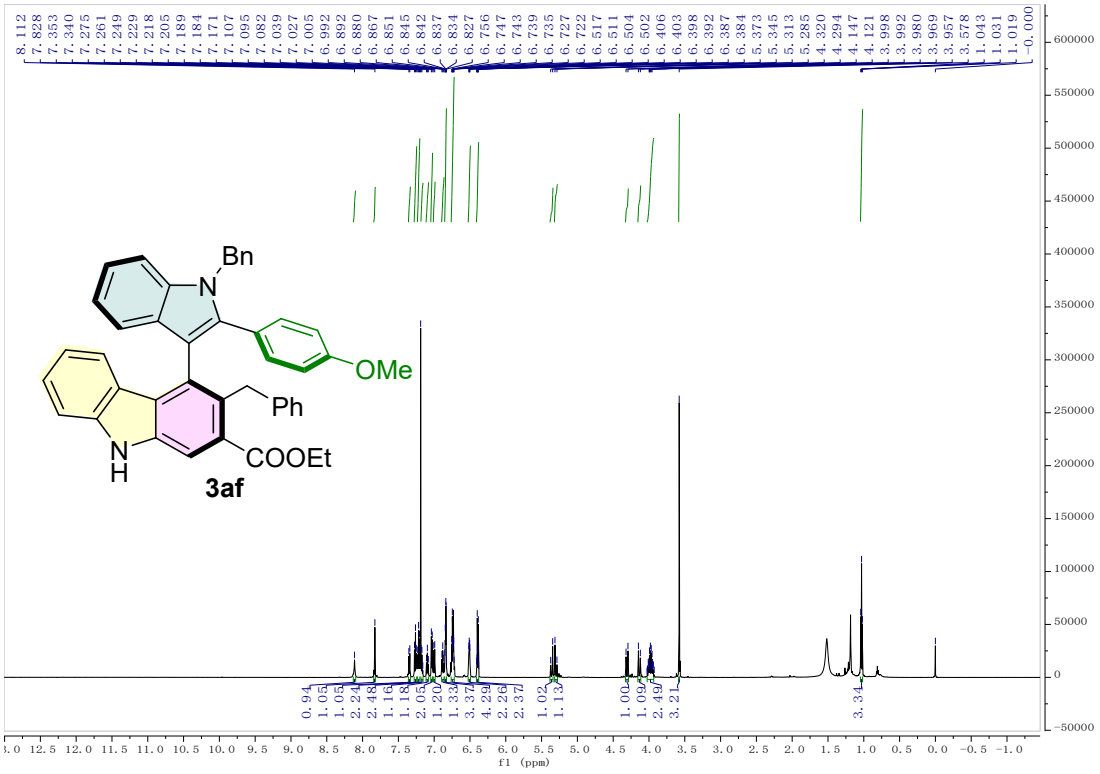
f1 (ppm)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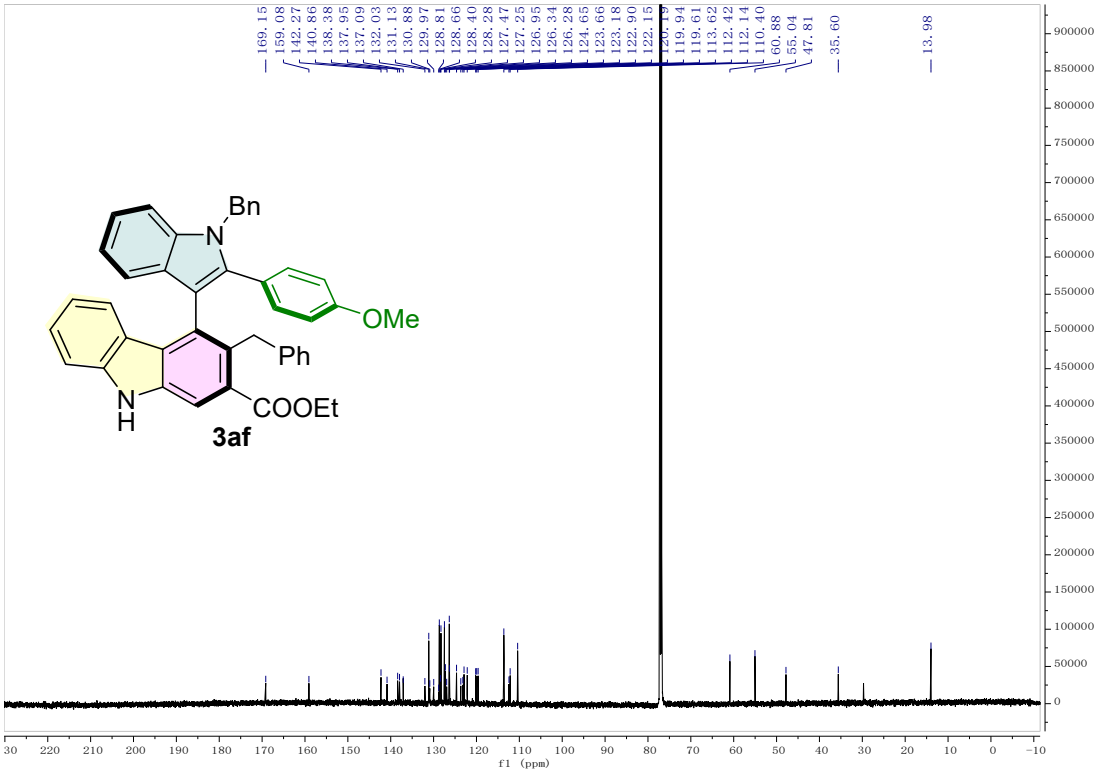
f1 (ppm)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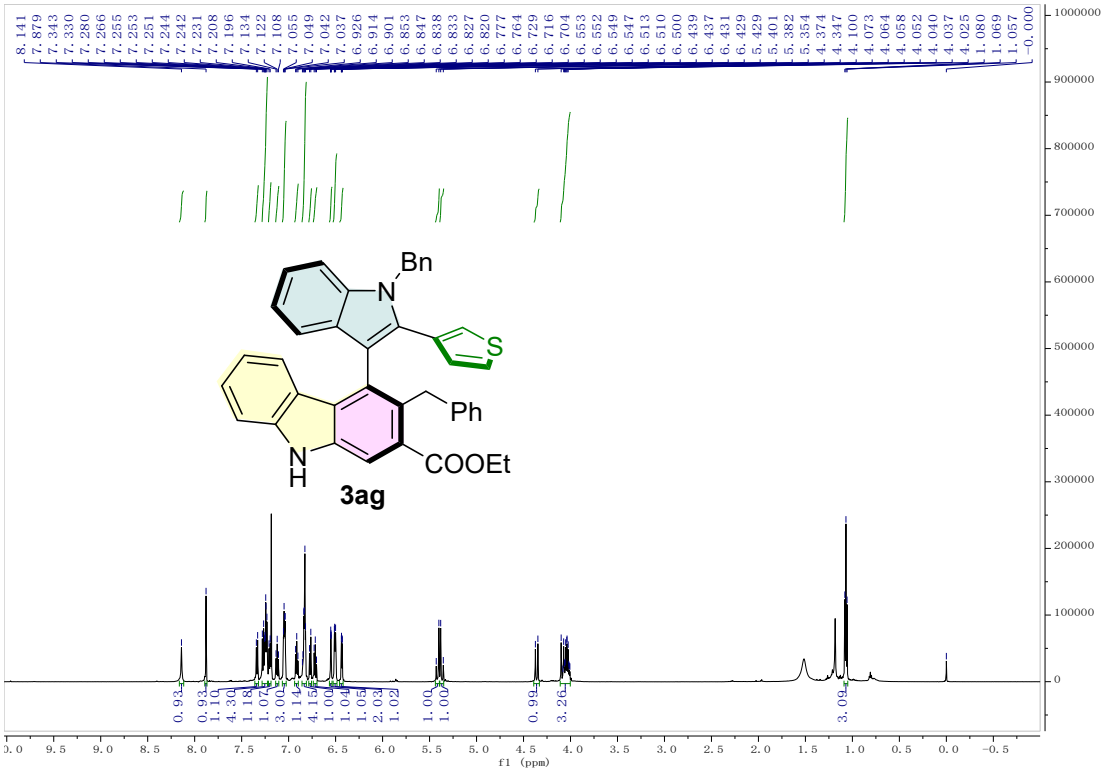
Bn
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COOEt
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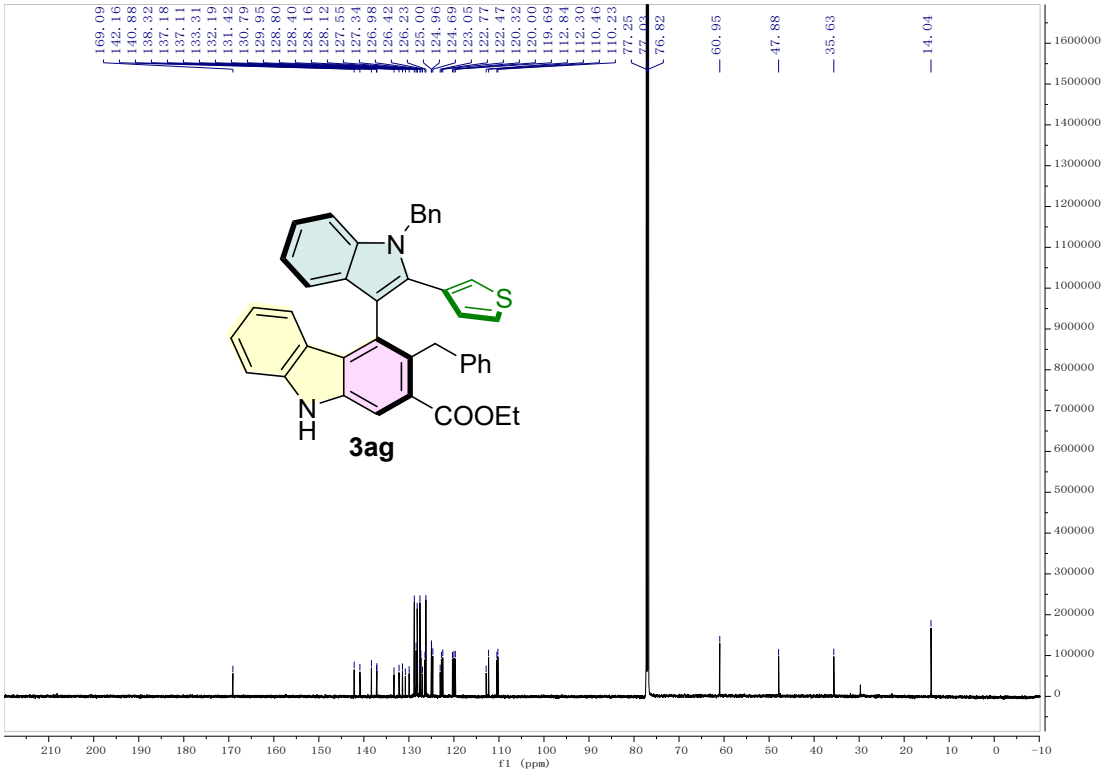
Bn
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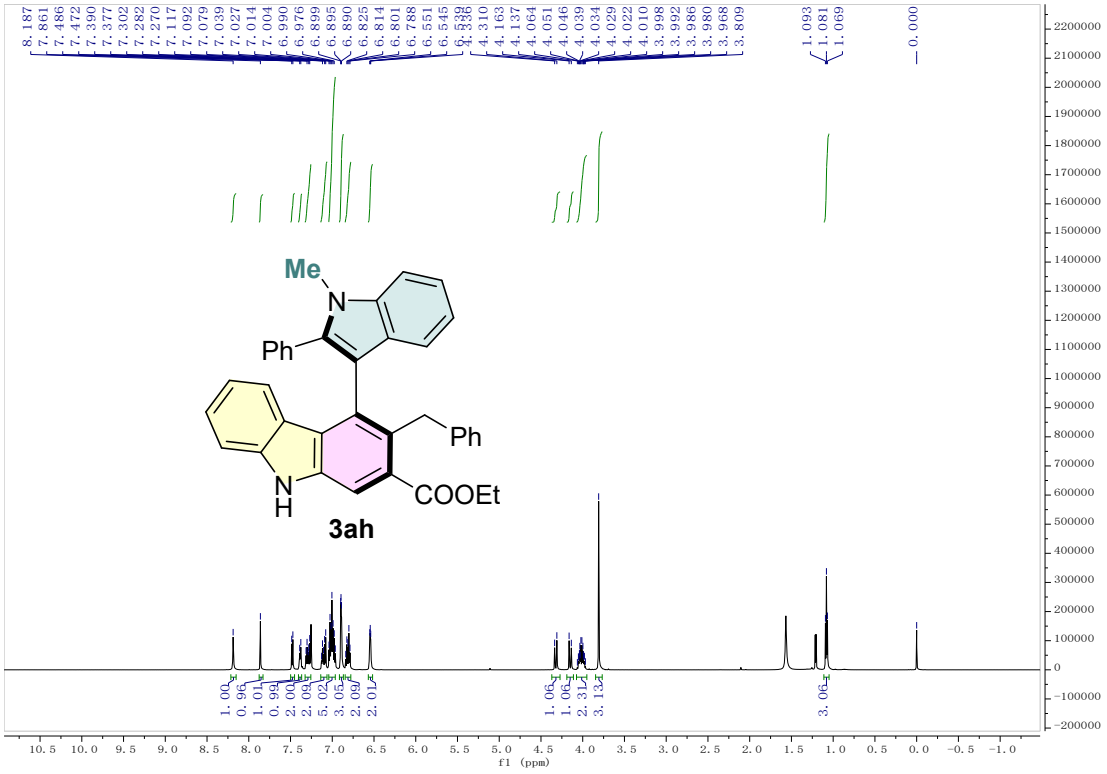
f1 (ppm)


Me
N
Ph
Ph
N
H
COOEt
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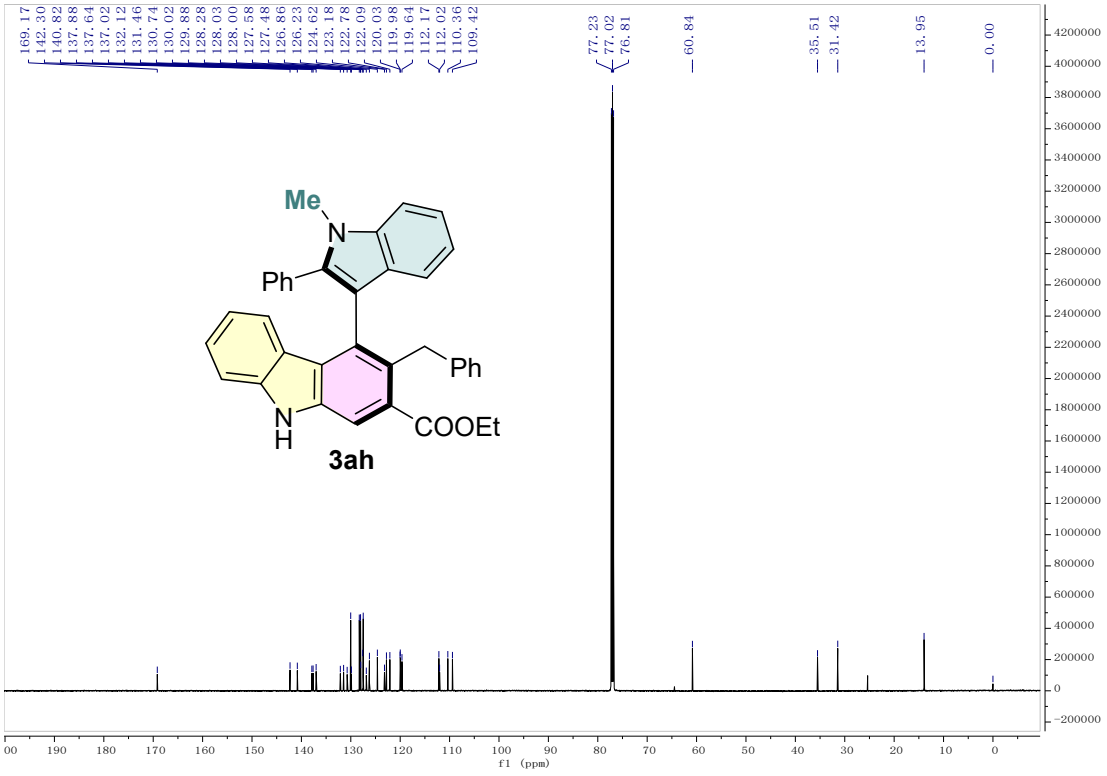
f1 (ppm)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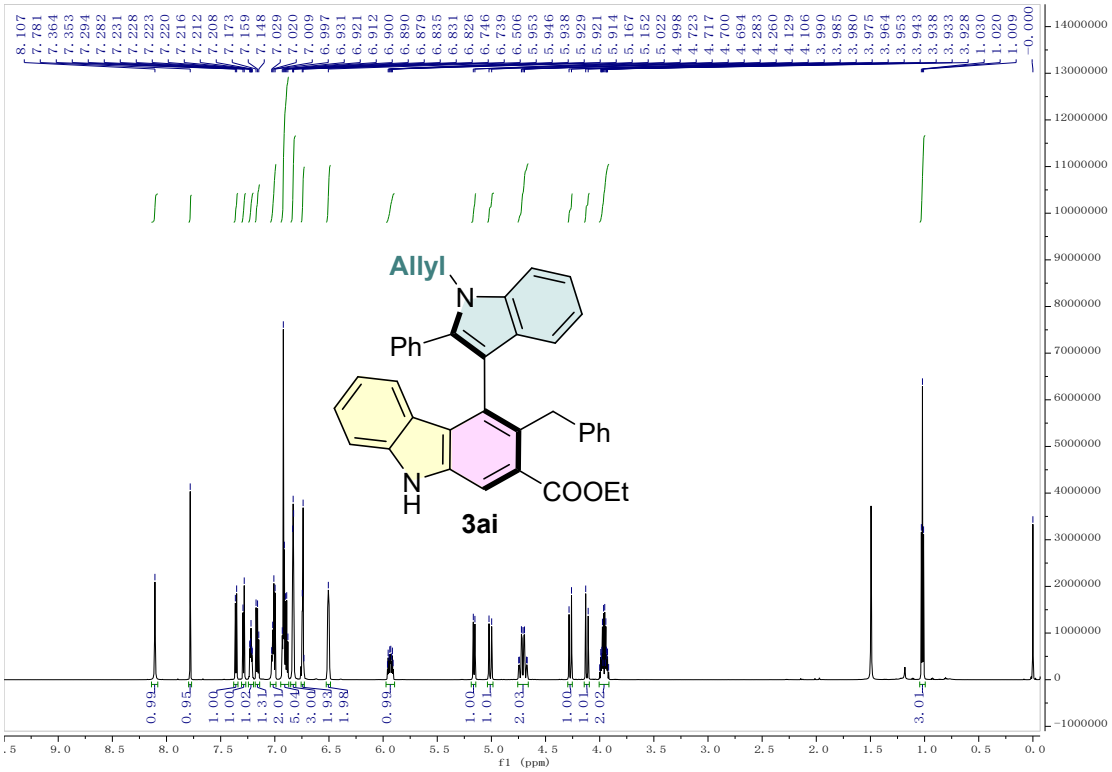
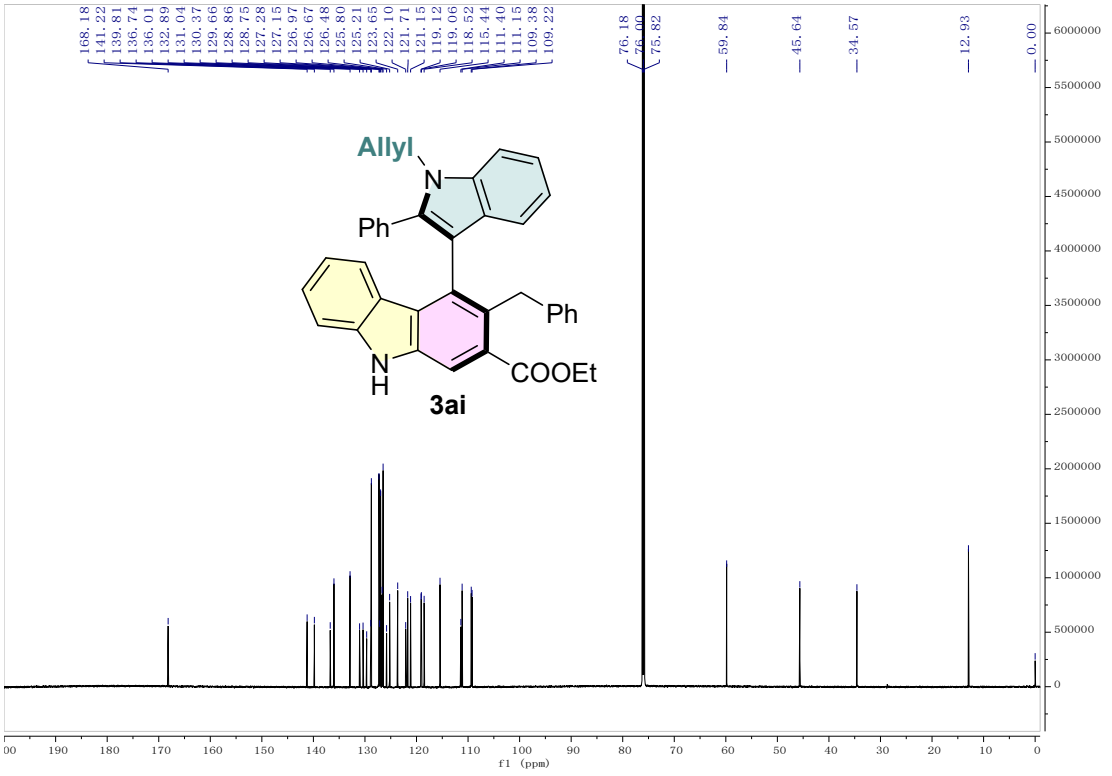
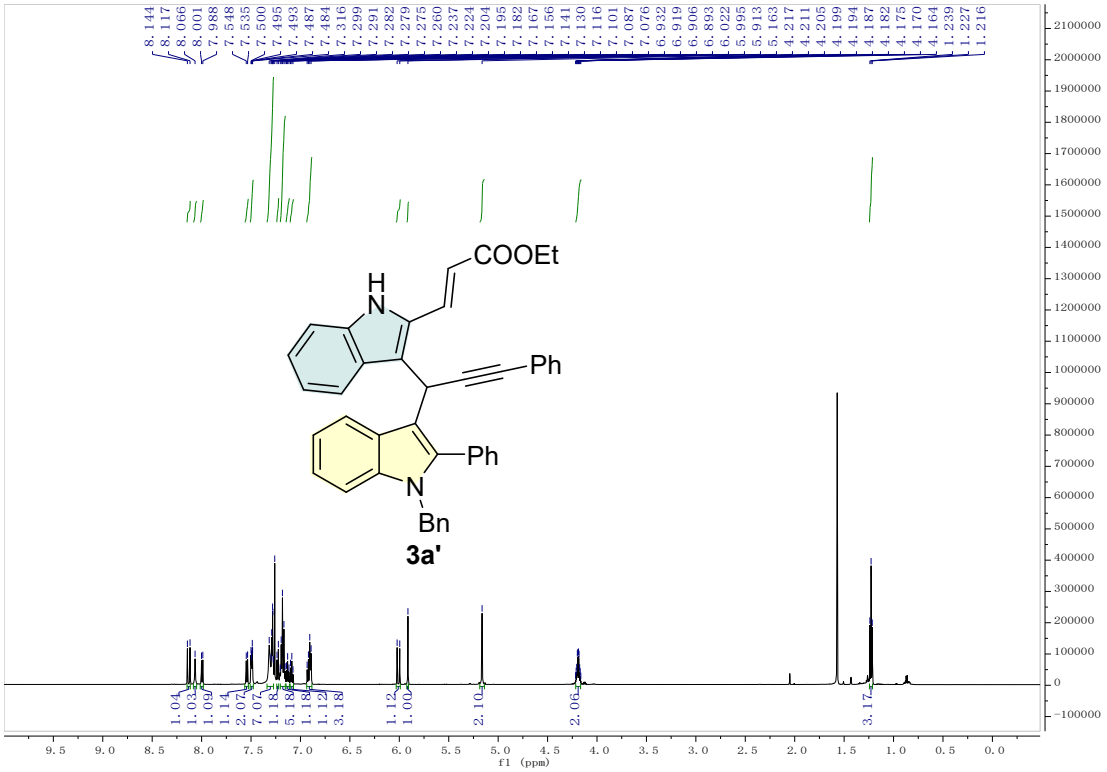
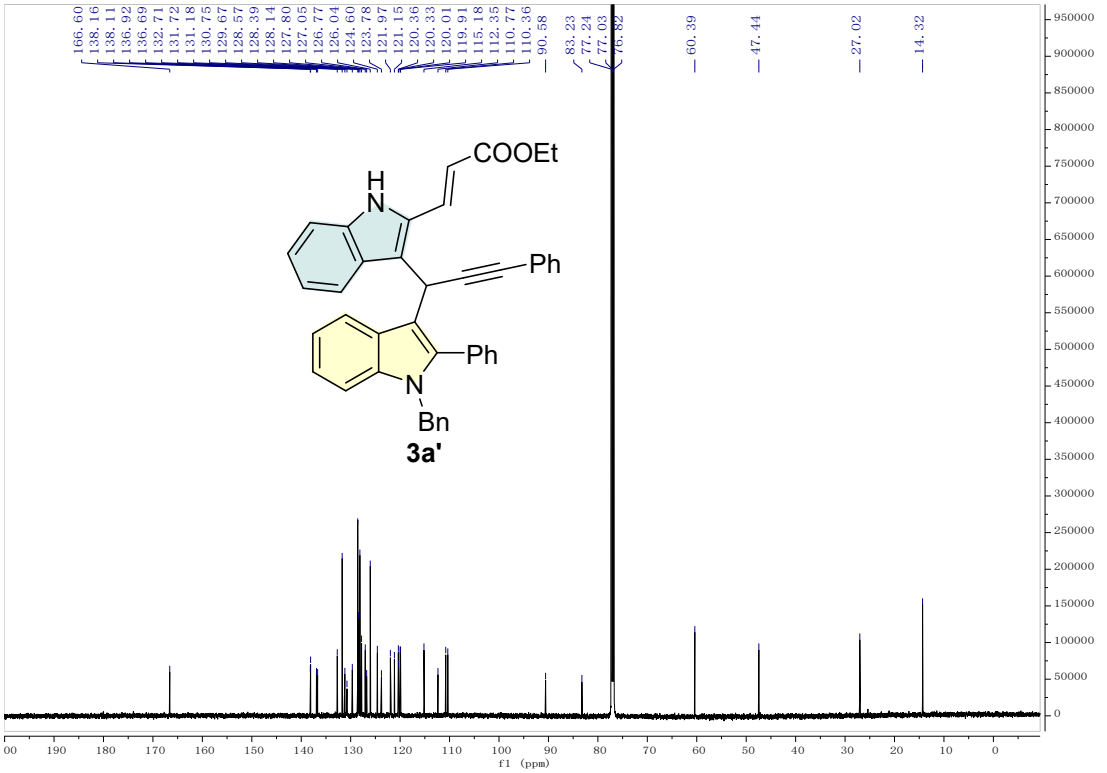
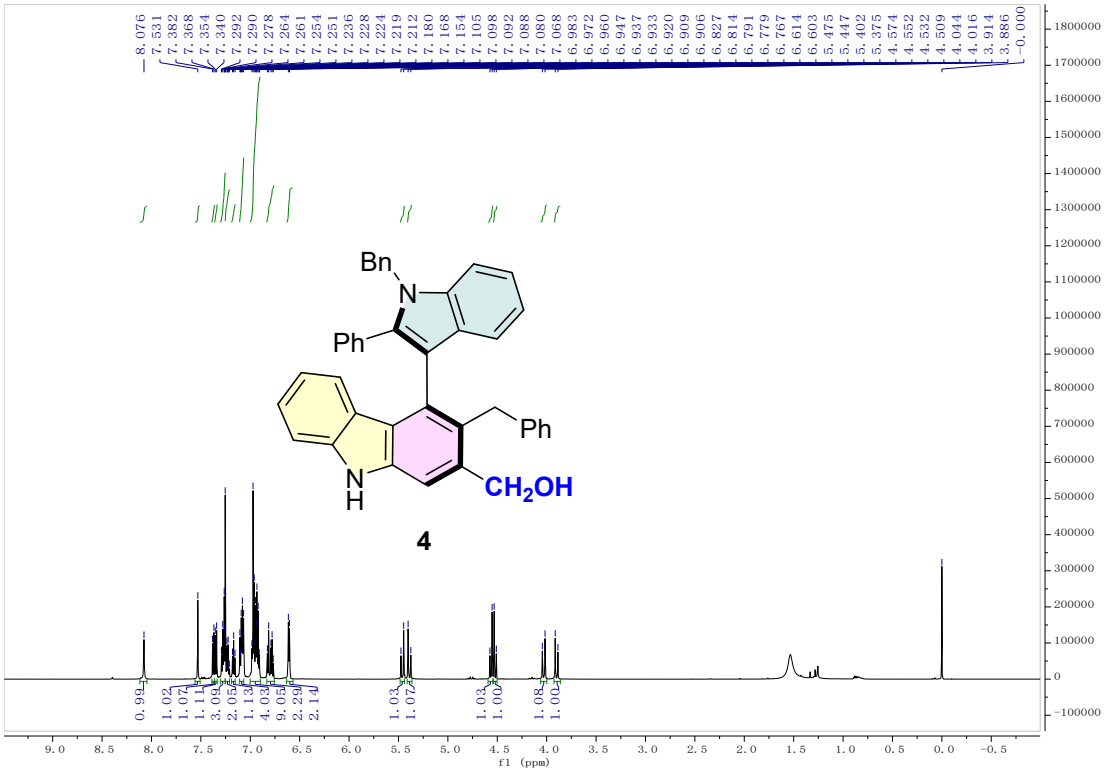
Ph
Ph
N
H
COOEt
3ah
f1 (ppm)


Allyl
N
Ph
Ph
N
H
COOEt
3ai
f1 (ppm)


Allyl
N
Ph
Ph
N
H
COOEt
3ai
f1 (ppm)


COOEt
H
N
Ph
Ph
N
Bn
3a'
f1 (ppm)


COOEt
H
N
Ph
Ph
N
Bn
3a'
f1 (ppm)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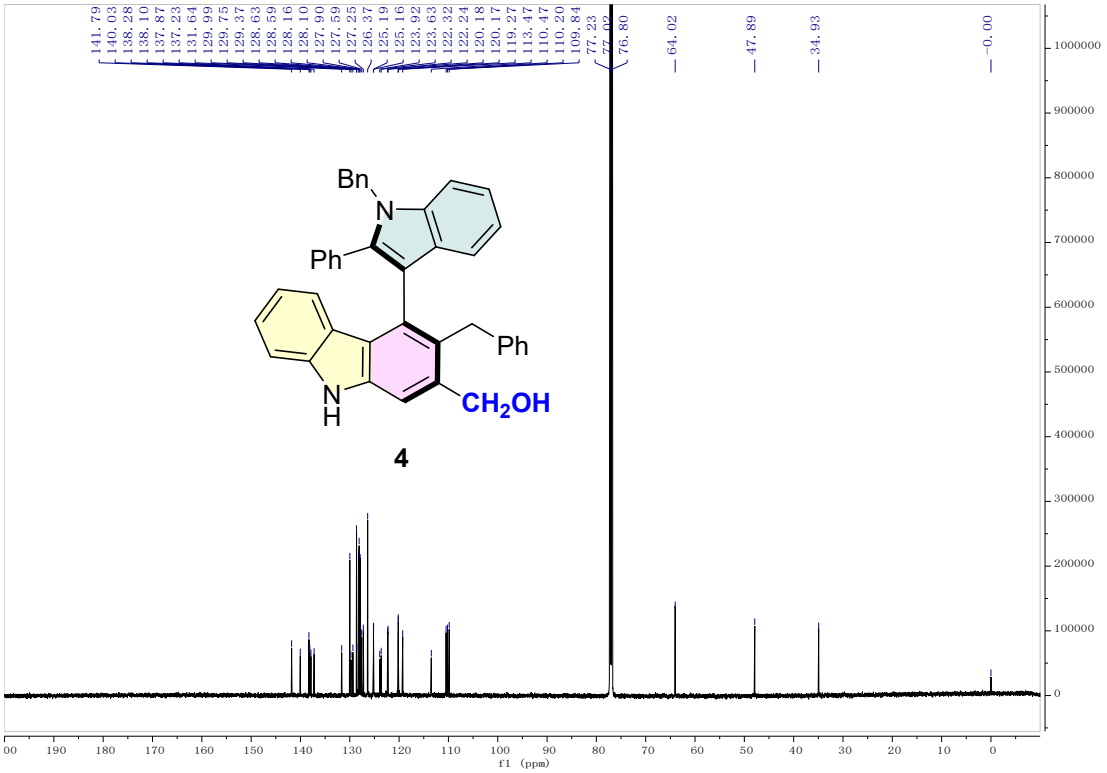
N
Ph
Ph
N
H
CH2OH
4
f1 (ppm)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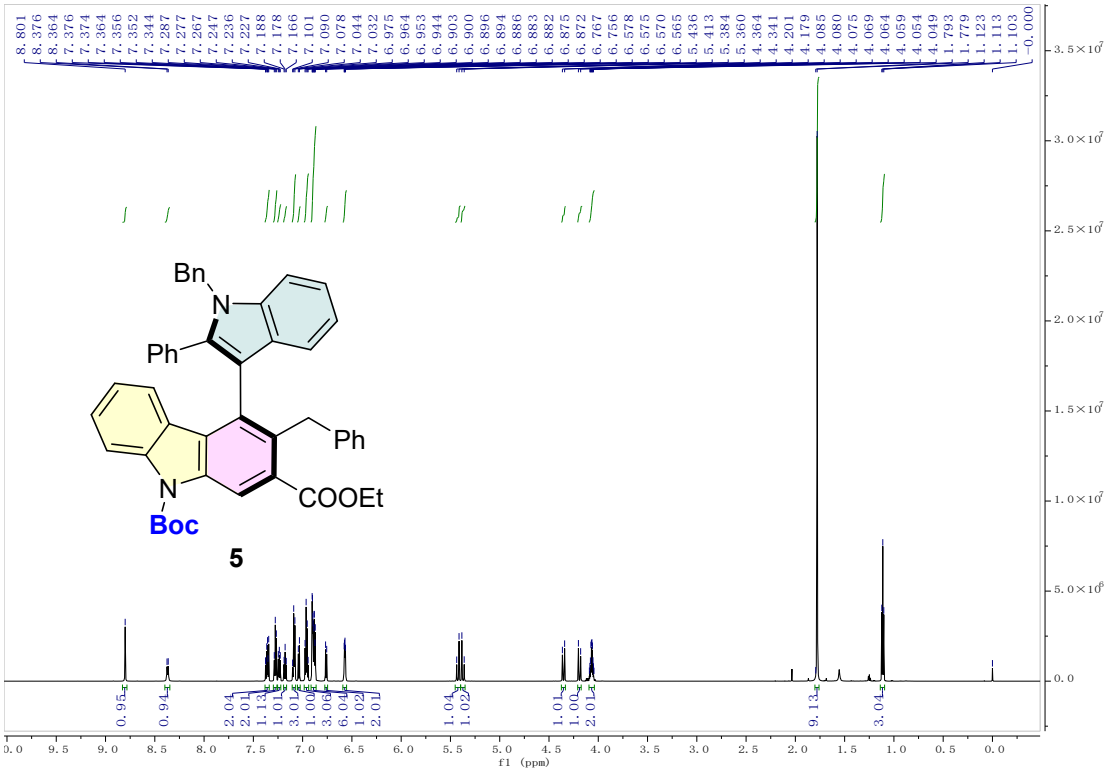
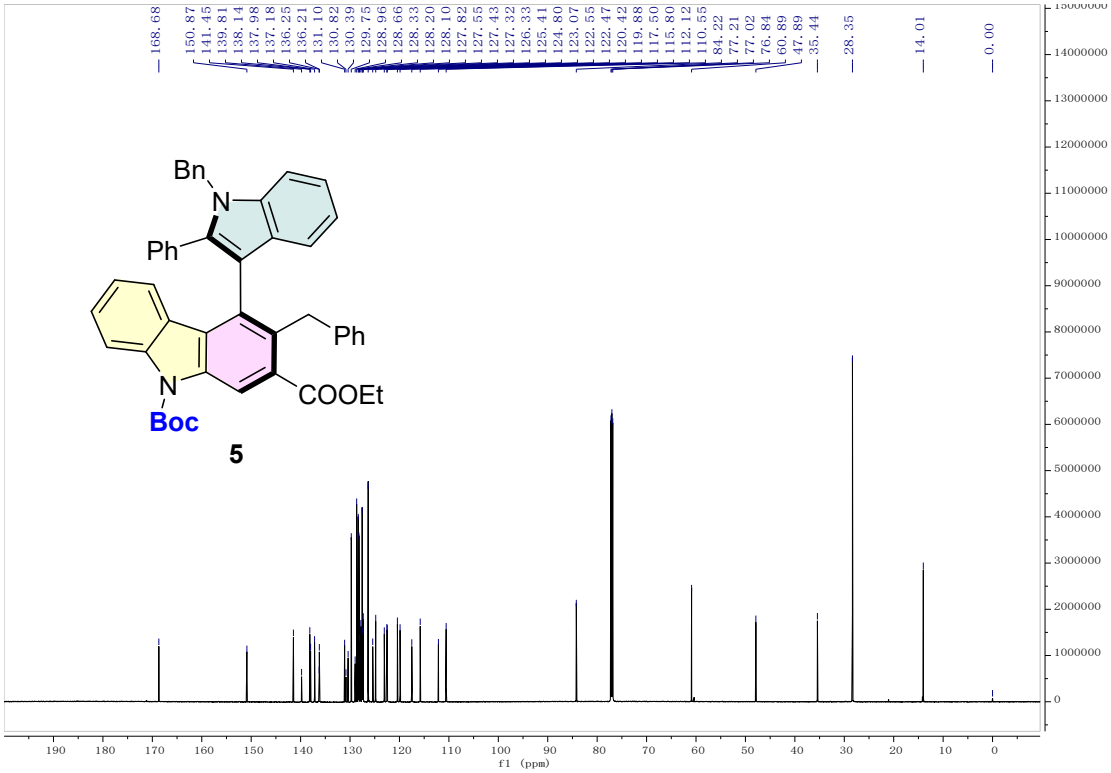
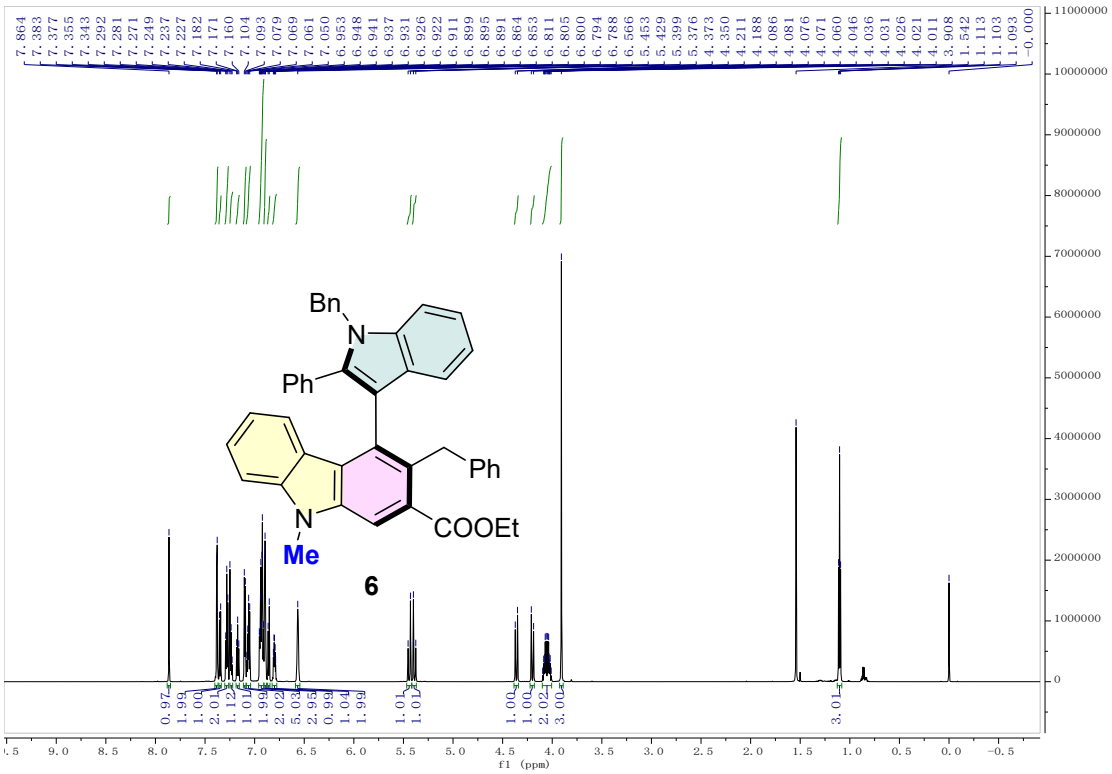
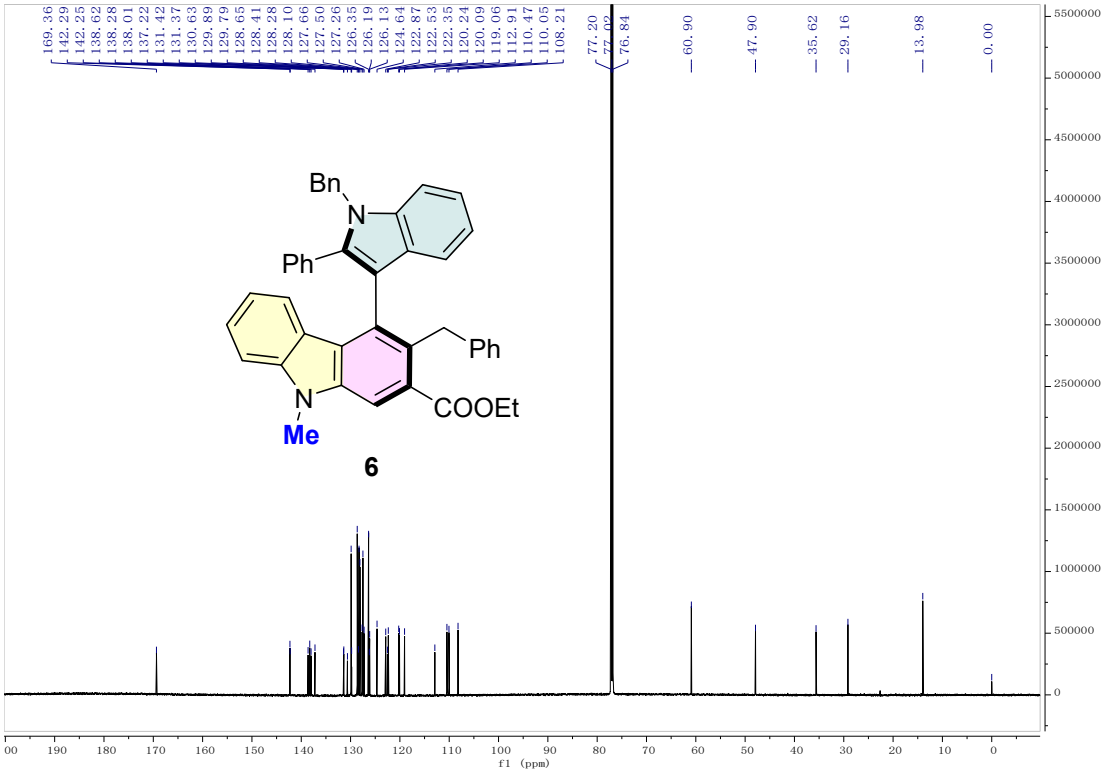
N
Ph
Ph
N
H
CH2OH
4
f1 (ppm)


Bn
N
Ph
Ph
N
COOEt
Boc
5
f1 (ppm)


Bn
N
Ph
Ph
N
COOEt
Boc
5
f1 (ppm)


Bn
N
Ph
Ph
N
COOEt
Me
6
f1 (ppm)


Bn
N
Ph
Ph
N
COOEt
Me
6
f1 (ppm)

11. Reference

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