Rh(II)-catalyzed three-component reaction of 3-diazooxindoles with *N*,*N*-disubstituted anilines and glyoxylates for the synthesis of 3-aryl-3-substituted oxindoles

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Table of Contents

General Information and Materials **S2**

General Procedure for Optimization of Reaction Conditions **S3-S4**

Characterization Data of Compounds **S5-S13**

X-ray Diffraction Parameters and Data of *syn*-4d **S14**

NMR Spectra of Compounds **S15-S38**

General Information and Materials

All ^{1}H NMR (400 MHz) and ^{13}C NMR (100 MHz) and ^{19}F NMR (376 MHz) spectra were recorded on Brucker spectrometers in $CDCl_3$. Tetramethylsilane (TMS) served as an internal standard ($\delta = 0$) for ^{1}H NMR, and $CDCl_3$ was used as internal standard ($\delta = 77.0$) for ^{13}C NMR. Chemical shifts are reported in parts per million as follows: chemical shift, multiplicity (s =singlet, d = doublet, t = triplet, q = quartet, m = multiplet, br = broad). High-resolution mass spectrometry (HRMS) was performed on IonSpec FT-ICR or Waters Micromass Q-TOF micro Synapt High Definition Mass Spectrometer. HPLC analysis was performed on Dalian Elite (UV230+ UV/Vis Detector and P230P High Pressure Pump). Melting points were uncorrected. Single crystal X-ray diffraction data (*syn*-**4d**) were recorded on Bruker-AXS SMART APEX II single crystal X-ray diffractometer. Yields for all compounds were combined yields for all isomers unless otherwise indicated.

All reactions and manipulations were carried out under an argon atmosphere in a flame-dried or oven-dried flask containing magnetic stir bar. Dichloromethane (DCM), 1,2-dichloroethane (DCE), $CHCl_3$ and toluene was distilled over calcium hydride. Solvents for the column chromatography were distilled before use. 4 Å molecular sieves was dried in a Muffle furnace at 250 ^{o}C over 5 hrs.

General Procedure for Optimization of Reaction Conditions

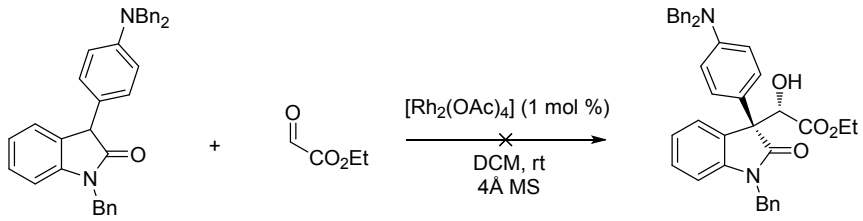
General procedure for optimization of reaction conditions (Table 1)

A mixture of $Rh_2(OAc)_4$ (0.001 mmol), **1a** (0.13 mmol) (as indicated in Table 1), **3a** (0.2 mmol) (50 wt. % solution in toluene)and 4 Å MS (100 mg) in 1mL of solvent under an argon atmosphere was stirred under T. Diazo compound **2a** (0.1 mmol) in 1 mL of solvent was then added over 1 h via a syringe pump. After completion of the addition, the reaction mixture was stirred for another 0.5 h, then filtrated and evaporated *in vacuo* to give the crude product. The crude products was purified by flash chromatography on silica gel (EtOAc/light petroleum ether = 1:10 ~ 1:5) to give the pure product.

General procedure for the preparation of products (Scheme 2)

A mixture of $Rh_2(OAc)_4$ (0.003 mmol), **1** (0.33 mmol), **3** (0.6 mmol)and 4 Å MS (100 mg) in 1 mL of DCM under an argon atmosphere was stirred at rt. Diazo compound **2** (0.3 mmol) in 1 mL or 2 mL of DCM was then added over 1 h via a syringe pump. After completion of the addition, the reaction mixture was stirred for another 0.5 h, then filtrated and evaporated *in vacuo* to give the crude product. The crude products was purified by flash chromatography on silica gel (EtOAc/light petroleum ether = 1:10 ~ 1:5) to give the pure product.

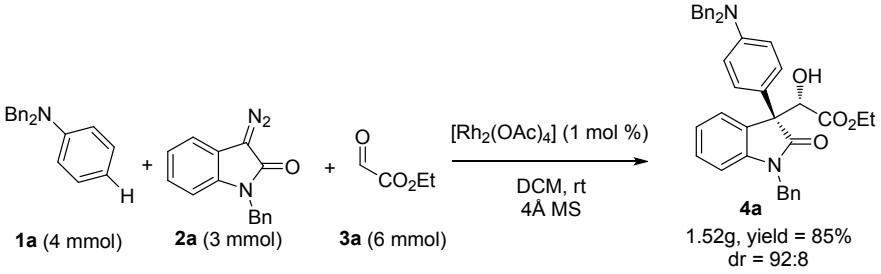
Procedure for the control experiment



5a (0.1 mmol) **3a** (0.2 mmol) **4a**

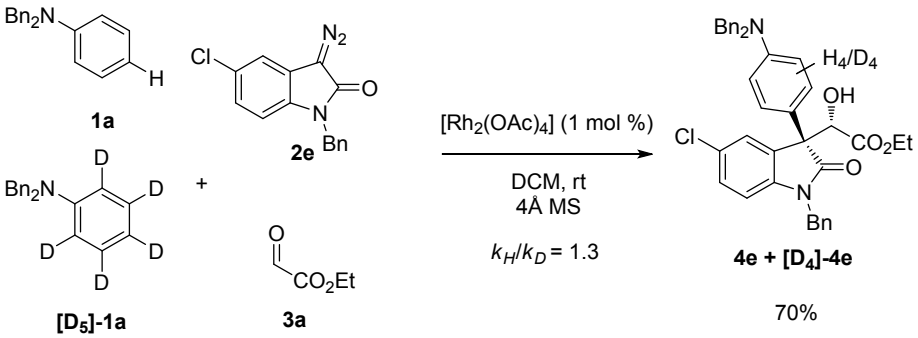
A mixture of $Rh_2(OAc)_4$ (0.001 mmol), **5a** (0.1 mmol), **3a** (0.2 mmol) and 4 Å MS (100 mg) in 1 mL of DCM under an argon atmosphere was stirred at rt for 2 h, the **4a** was not found.

Procedure for the gram-scale experiment



A mixture of $Rh_2(OAc)_4$ (0.03 mmol), **1a** (4 mmol), **3a** (6 mmol) (50 wt. % solution in toluene) and 4 Å MS (100 mg) in 3 mL of DCM under an argon atmosphere was stirred at rt. Diazo compound **2a** (3 mmol) in 2 mL of DCM was then added over 1 h via a syringe pump. After completion of the addition, the reaction mixture was stirred for another 0.5 h, then filtrated and evaporated in vacuo to give the crude product. The crude products was purified by flash chromatography on silica gel (EtOAc/light petroleum ether = 1:10 ~ 1:5) to give the pure product **4a** (1.52 g, 85%).

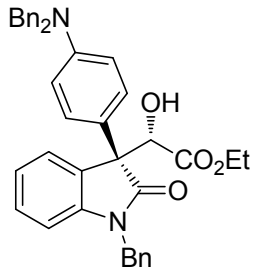
Procedure for intermolecular kinetic isotope effect experiment.



A mixture of $Rh_2(OAc)_4$ (0.003 mmol), **1a** (0.3 mmol), [D_5]-**1a** (0.3 mmol), **3a** (0.6 mmol)and 4 Å MS (100 mg) in 1 mL of DCM under an argon atmosphere was stirred at rt. Diazo compound **2** (0.33 mmol) in 1 mL of DCM was then added over 1 h via a syringe pump. After completion of the addition, the reaction mixture was stirred for another 0.5 h, then filtrated and evaporated *in vacuo* to give the crude product. The crude products was purified by flash chromatography on silica gel (EtOAc/light petroleum ether = 1:10 ~ 1:5) to give the crude product, the crude mixture was then subjected to ^{1}H NMR analysis for the determination of the ratio between **4e** and **4e-d$_4$**.

Characterization Data of Compounds

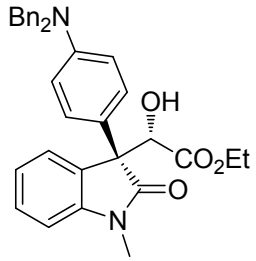
(S)-ethyl 2-((R)-1-benzyl-3-(4-(dibenzylamino)phenyl)-2-oxoindolin-3-yl)-2-hydroxyacetate



syn-**4a**

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.46 – 7.08 (m, 19H), 7.05 – 6.93 (m, 1H), 6.77 – 6.53 (m, 3H), 5.13 (d, *J* = 9.4 Hz, 1H), 5.05 (d, *J* = 15.8 Hz, 1H), 4.75 (d, *J* = 15.9 Hz, 1H), 4.62 (s, 4H), 4.09 – 3.83 (m, 2H), 3.53 (d, *J* = 9.4 Hz, 1H), 0.86 (t, *J* = 7.1 Hz, 3H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 177.29, 172.19, 148.49, 143.79, 138.49, 135.57, 128.82, 128.74, 128.68, 128.54, 127.51, 127.27, 127.24, 126.99, 126.64, 126.15, 123.43, 122.18, 112.24, 109.68, 75.43, 61.31, 58.55, 54.33, 44.07, 13.58. HRMS (ESI) Calcd. for $C_{39}H_{36}N_2NaO_4$ $(M+Na)^+$ 619.2573, found: 619.2542.

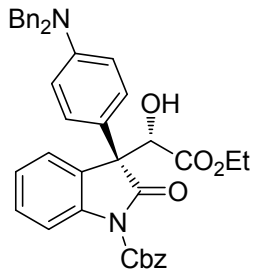
(S)-ethyl 2-((R)-3-(4-(dibenzylamino)phenyl)-1-methyl-2-oxoindolin-3-yl)-2-hydroxyacetate



syn-**4b**

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.35 – 7.26 (m, 7H), 7.25 – 7.17 (m, 7H), 7.11 – 7.03 (m, 1H), 6.85 (d, *J* = 7.8 Hz, 1H), 6.64 (d, *J* = 8.9 Hz, 2H), 5.03 (d, *J* = 9.7 Hz, 1H), 4.62 (s, 4H), 4.05 – 3.73 (m, 2H), 3.60 (d, *J* = 9.7 Hz, 1H), 3.20 (s, 3H), 0.88 (t, *J* = 7.1 Hz, 3H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 177.20, 172.06, 148.45, 144.61, 138.45, 128.94, 128.65, 128.47, 127.37, 126.96, 126.60, 126.04, 123.36, 122.20, 112.18, 108.52, 75.52, 61.19, 58.14, 54.31, 26.49, 13.60. HRMS (ESI) Calcd. for $C_{33}H_{32}N_2NaO_4$ $(M+Na)^+$ 543.2260, found: 543.2234.

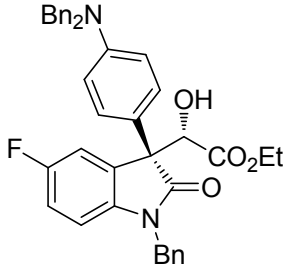
(R)-benzyl 3-(4-(dibenzylamino)phenyl)-3-((S)-2-ethoxy-1-hydroxy-2-oxoethyl)-2-oxoindoline-1-carboxylate



syn-**4c**

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.36 – 7.15 (m, 19H), 7.06 – 6.98 (m, 1H), 6.74 – 6.60 (m, 3H), 5.13 (d, *J* = 9.4 Hz, 1H), 5.05 (d, *J* = 15.9 Hz, 1H), 4.76 (d, *J* = 15.9 Hz, 1H), 4.63 (s, 4H), 4.04 – 3.84 (m, 2H), 3.51 (d, *J* = 9.4 Hz, 1H), 0.86 (t, *J* = 7.1 Hz, 3H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 176.89, 171.89, 148.27, 142.29, 135.09, 133.69, 129.36, 128.81, 128.69, 128.19, 127.66, 127.16, 126.48, 122.09, 116.03, 112.12, 110.51, 75.25, 61.48, 58.69, 52.70, 44.14, 13.55. HRMS (ESI) Calcd. for $C_{40}H_{36}N_2NaO_6$ $(M+Na)^+$ 663.2471, found: 663.2459.

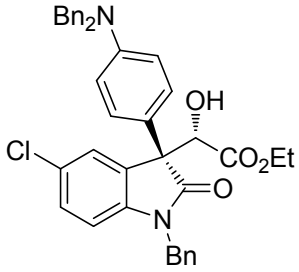
(S)-ethyl 2-((R)-1-benzyl-3-(4-(dibenzylamino)phenyl)-5-fluoro-2-oxoindolin-3-yl)-2-hydroxyacetate



syn-**4d**

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.35 – 7.26 (m, 10H), 7.25 – 7.18 (m, 7H), 6.98 – 6.91 (m, 1H), 6.90 – 6.83 (m, 1H), 6.68 (d, *J* = 8.3 Hz, 2H), 6.61 – 6.52 (m, 1H), 5.12 (d, *J* = 9.0 Hz, 1H), 5.05 (d, *J* = 15.9 Hz, 1H), 4.73 (d, *J* = 15.9 Hz, 1H), 4.64 (s, 4H), 4.04 – 3.89 (m, 2H), 3.49 (d, *J* = 9.1 Hz, 1H), 0.89 (t, *J* = 7.0 Hz, 3H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 176.49, 171.88, 152.68, 142.43, 139.79, 139.09, 135.02, 128.92, 128.83, 128.61, 128.28, 128.20, 128.15, 127.70, 127.63, 127.11, 126.76, 126.60, 120.13, 119.64, 111.63, 110.59, 75.23, 61.65, 59.25, 55.59, 44.17, 13.66. ^{19}F NMR (376 MHz, $CDCl_3$) δ -120.31. HRMS (ESI) Calcd. for $C_{39}H_{35}N_2NaO_4F$ $(M+Na)^+$ 637.2479, found: 637.2452.

(S)-ethyl 2-((R)-1-benzyl-5-chloro-3-(4-(dibenzylamino)phenyl)-2-oxoindolin-3-yl)-2-hydroxyacetate

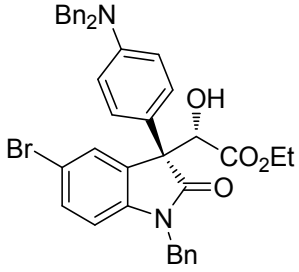


syn-**4e**

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.37 – 7.09 (m, 19H), 6.68 (d, *J* = 8.8 Hz, 2H), 6.57 (d, *J* = 8.3 Hz, 1H), 5.11 (d, *J* = 9.2 Hz, 1H), 5.06 (d, *J* = 15.9 Hz, 1H), 4.72 (d, *J* = 15.9 Hz, 1H), 4.64 (s, 4H),

4.06 – 3.75 (m, 2H), 3.49 (d, J = 9.2 Hz, 1H), 0.90 (t, J = 7.1 Hz, 3H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 176.82, 171.91, 148.62, 142.31, 138.34, 135.05, 129.18, 128.81, 128.73, 128.68, 128.37, 127.66, 127.63, 127.15, 127.00, 126.58, 126.48, 122.59, 112.29, 110.53, 75.19, 61.50, 58.76, 54.33, 44.15, 13.58. HRMS (ESI) Calcd. for $C_{39}H_{35}N_2NaO_4Cl$ $(M+Na)^+$ 653.2183, found: 653.2167.

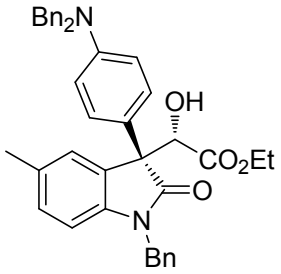
(S)-ethyl 2-((R)-1-benzyl-5-bromo-3-(4-(dibenzylamino)phenyl)-2-oxoindolin-3-yl)-2-hydroxyacetate



syn-**4f**

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.32 – 7.20 (m, 19H), 6.68 (d, J = 8.8 Hz, 2H), 6.53 (d, J = 8.2 Hz, 1H), 5.11 (d, J = 9.3 Hz, 1H), 5.05 (d, J = 15.9 Hz, 1H), 4.72 (d, J = 15.9 Hz, 1H), 4.65 (s, 4H), 4.19 – 3.80 (m, 2H), 3.49 (d, J = 9.3 Hz, 1H), 0.91 (t, J = 7.1 Hz, 3H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 171.87, 148.63, 142.78, 138.34, 135.01, 131.63, 129.60, 129.18, 128.81, 128.68, 128.36, 127.67, 127.15, 127.01, 126.58, 122.58, 114.93, 112.30, 111.04, 75.22, 61.51, 58.70, 54.33, 44.12, 13.60. HRMS (ESI) Calcd. for $C_{39}H_{35}N_2NaO_4Br$ $(M+Na)^+$ 697.1678, found: 697.1664.

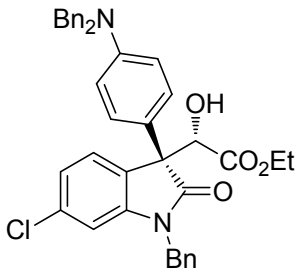
(S)-ethyl 2-((R)-1-benzyl-3-(4-(dibenzylamino)phenyl)-5-methyl-2-oxoindolin-3-yl)-2-hydroxyacetate



syn-**4g**

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.36 – 7.19 (m, 17H), 7.04 – 6.89 (m, 2H), 6.67 (d, J = 8.5 Hz, 2H), 6.55 (d, J = 7.9 Hz, 1H), 5.11 (d, J = 9.6 Hz, 1H), 5.02 (d, J = 15.8 Hz, 1H), 4.76 (d, J = 15.8 Hz, 1H), 4.63 (s, 4H), 4.07 – 3.80 (m, 2H), 3.60 (d, J = 9.6 Hz, 1H), 2.29 (s, 3H), 0.87 (t, J = 7.0 Hz, 3H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 177.26, 172.07, 148.45, 141.27, 138.48, 135.64, 131.64, 129.07, 128.67, 128.64, 128.48, 127.43, 127.21, 126.94, 126.82, 126.61, 123.67, 112.22, 109.37, 77.34, 77.02, 76.71, 75.46, 61.17, 58.40, 54.29, 44.05, 21.22, 13.55. HRMS (ESI) Calcd. for $C_{40}H_{38}N_2NaO_4$ $(M+Na)^+$ 633.2729, found: 633.2708.

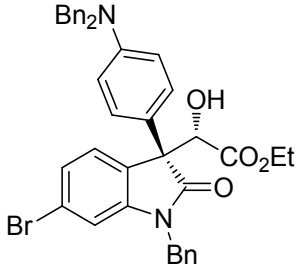
(S)-ethyl 2-((R)-1-benzyl-6-chloro-3-(4-(dibenzylamino)phenyl)-2-oxoindolin-3-yl)-2-hydroxyacetate



syn-**4h**

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.31 – 7.20 (m, 17H), 7.11 – 7.05 (m, 1H), 7.03 – 6.97 (m, 1H), 6.66 (d, *J* = 7.4 Hz, 3H), 5.11 (d, *J* = 9.1 Hz, 1H), 5.04 (d, *J* = 15.9 Hz, 1H), 4.73 – 4.60 (m, 5H), 4.10 – 3.85 (m, 2H), 3.33 (d, *J* = 9.1 Hz, 1H), 0.89 (t, *J* = 7.1 Hz, 3H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 177.15, 172.08, 148.57, 145.14, 138.36, 134.95, 134.71, 128.85, 128.66, 128.42, 127.70, 127.12, 127.04, 126.99, 126.58, 125.50, 122.62, 122.03, 112.23, 110.14, 75.16, 61.48, 58.48, 54.32, 44.13, 13.57. HRMS (ESI) Calcd. for $C_{39}H_{35}N_2NaO_4Cl$ $(M+Na)^+$ 653.2183, found: 653.2169.

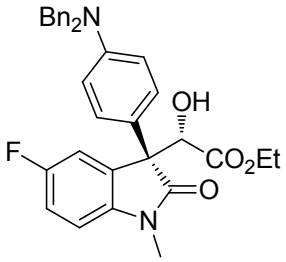
(S)-ethyl 2-((R)-1-benzyl-6-bromo-3-(4-(dibenzylamino)phenyl)-2-oxoindolin-3-yl)-2-hydroxyacetate



syn-**4i**

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.37 – 7.24 (m, 13H), 7.23 – 7.14 (m, 5H), 7.06 – 6.99 (m, 1H), 6.88 – 6.78 (m, 1H), 6.66 (d, *J* = 8.2 Hz, 2H), 5.11 (d, *J* = 8.8 Hz, 1H), 5.03 (d, *J* = 15.9 Hz, 1H), 4.77 – 4.58 (m, 5H), 4.08 – 3.83 (m, 2H), 3.33 (d, *J* = 8.9 Hz, 1H), 0.90 (t, *J* = 6.7 Hz, 3H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 177.03, 172.06, 148.57, 145.27, 138.35, 134.93, 128.85, 128.65, 128.40, 127.70, 127.39, 127.10, 126.99, 126.58, 126.08, 124.98, 122.56, 122.50, 112.88, 112.23, 75.09, 61.48, 58.55, 54.32, 44.11, 13.57. HRMS (ESI) Calcd. for $C_{39}H_{35}N_2NaO_4Br$ $(M+Na)^+$ 697.1678, found: 697.1649.

(S)-ethyl 2-((R)-3-(4-(dibenzylamino)phenyl)-5-fluoro-1-methyl-2-oxoindolin-3-yl)-2-hydroxyacetate

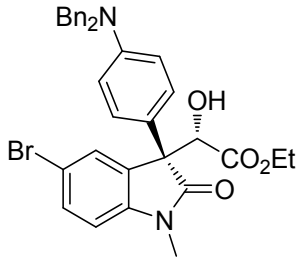


syn-**4j**

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.34 – 7.25 (m, 6H), 7.24 – 7.17 (m, 6H), 7.05 – 6.96 (m, 2H), 6.79 – 6.73 (m, 1H), 6.68 – 6.59 (m, 2H), 5.03 (d, *J* = 6.0 Hz, 1H), 4.62 (s, 4H), 4.02 – 3.85 (m, 2H), 3.60 (d, *J* = 7.6 Hz, 1H), 3.17 (s, 3H), 0.90 (t, *J* = 7.1 Hz, 3H). ^{13}C NMR (100 MHz, $CDCl_3$) δ

176.94, 171.90, 158.77 (d, J = 240.9 Hz), 148.56, 140.63, 138.36, 129.10, 129.02, 128.70, 128.33, 127.01, 126.63, 126.58, 122.69, 115.20 (d, J = 23.4 Hz), 114.26 (d, J = 25.2 Hz), 112.23, 108.91 (d, J = 8.1 Hz), 75.26, 61.38, 58.61, 54.34, 26.66, 13.63. ^{19}F NMR (376 MHz, $CDCl_3$) δ -120.26. HRMS (ESI) Calcd. for $C_{33}H_{32}N_2O_4F$ $(M+H)^+$ 539.2346, found: 539.2350.

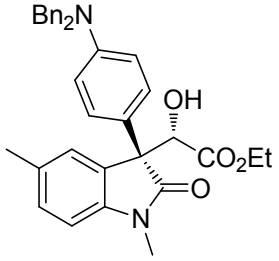
(S)-ethyl 2-((R)-5-bromo-3-(4-(dibenzylamino)phenyl)-1-methyl-2-oxoindolin-3-yl)-2-hydroxyacetate



syn-**4k**

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.48 – 7.39 (m, 1H), 7.36 – 7.16 (m, 13H), 6.72 (d, J = 8.3 Hz, 1H), 6.65 (d, J = 9.0 Hz, 2H), 5.01 (d, J = 9.5 Hz, 1H), 4.63 (s, 4H), 4.04 – 3.84 (m, 2H), 3.58 (d, J = 9.5 Hz, 1H), 3.17 (s, 3H), 0.92 (t, J = 7.1 Hz, 3H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 176.66, 171.80, 148.60, 143.67, 138.32, 131.77, 129.64, 129.13, 128.69, 128.33, 127.01, 126.56, 122.49, 114.90, 112.25, 109.89, 75.30, 61.42, 58.34, 54.33, 26.61, 13.64. HRMS (ESI) Calcd. for $C_{33}H_{31}N_2NaO_4Br$ $(M+Na)^+$ 621.1365, found: 621.1342.

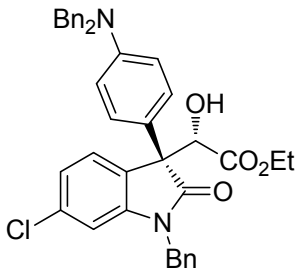
(S)-ethyl 2-((R)-3-(4-(dibenzylamino)phenyl)-1,5-dimethyl-2-oxoindolin-3-yl)-2-hydroxyacetate



syn-**4l**

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.35 – 7.16 (m, 12H), 7.10 (d, J = 7.8 Hz, 1H), 7.02 (s, 1H), 6.73 (d, J = 7.9 Hz, 1H), 6.65 (d, J = 8.9 Hz, 2H), 5.02 (d, J = 9.9 Hz, 1H), 4.62 (s, 4H), 4.02 – 3.81 (m, 2H), 3.73 (d, J = 9.9 Hz, 1H), 3.18 (s, 3H), 2.33 (s, 3H), 0.88 (t, J = 7.1 Hz, 3H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 177.21, 171.95, 148.42, 142.12, 138.46, 131.71, 129.18, 128.65, 128.43, 127.54, 126.94, 126.76, 126.58, 123.60, 112.15, 108.23, 75.59, 61.07, 57.97, 54.29, 26.51, 21.27, 13.60. HRMS (ESI) Calcd. for $C_{34}H_{35}N_2O_4$ $(M+H)^+$ 535.2597, found: 535.2586.

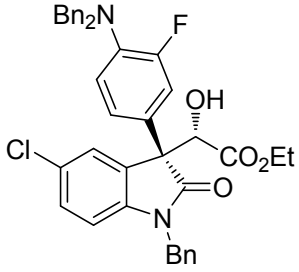
(S)-ethyl 2-((R)-1-benzyl-6-chloro-3-(4-(dibenzylamino)phenyl)-2-oxoindolin-3-yl)-2-hydroxyacetate



syn-**4m**

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.31 – 7.07 (m, 13H), 7.07 – 7.01 (m, 1H), 6.84 (s, 1H), 6.63 (d, *J* = 8.7 Hz, 2H), 5.01 (d, *J* = 9.2 Hz, 1H), 4.61 (s, 4H), 4.08 – 3.80 (m, 2H), 3.42 (d, *J* = 9.2 Hz, 1H), 3.14 (s, 3H), 0.90 (t, *J* = 7.1 Hz, 3H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 177.08, 172.04, 148.55, 146.02, 138.39, 134.89, 128.70, 128.43, 127.05, 127.02, 126.59, 125.55, 122.57, 121.99, 112.19, 109.25, 75.25, 61.42, 58.24, 54.35, 26.64, 13.66. HRMS (ESI) Calcd. for $C_{33}H_{32}N_2O_4Cl$ $(M+H)^+$ 555.2051, found: 555.2042.

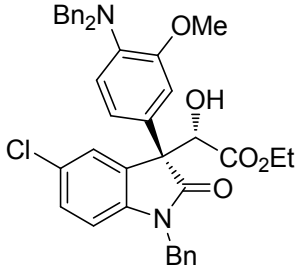
(S)-ethyl 2-((R)-1-benzyl-5-chloro-3-(4-(dibenzylamino)-3-fluorophenyl)-2-oxoindolin-3-yl)-2-hydroxyacetate



syn-**4n**

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.38 – 7.10 (m, 18H), 7.01 (d, *J* = 8.1 Hz, 1H), 6.77 (t, *J* = 8.9 Hz, 1H), 6.60 (d, *J* = 8.3 Hz, 1H), 5.15 – 4.95 (m, 2H), 4.73 (d, *J* = 15.9 Hz, 1H), 4.35 (s, 4H), 4.08 – 3.84 (m, 2H), 3.35 (d, *J* = 6.3 Hz, 1H), 0.85 (t, *J* = 7.1 Hz, 3H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 176.07, 171.70, 154.75 (d, *J* = 244.6 Hz), 142.48, 138.27, 134.88, 129.16, 128.86, 128.41, 128.15, 127.91, 127.80, 127.75, 127.62, 127.10, 126.44, 123.24 (d, *J* = 2.8 Hz), 120.07 (d, *J* = 3.6 Hz), 116.03 (d, *J* = 23.9 Hz), 110.76, 75.06, 61.79, 58.83, 55.61, 55.57, 44.23, 13.66. ^{19}F NMR (376 MHz, $CDCl_3$) δ -121.30. HRMS (ESI) Calcd. for $C_{39}H_{34}N_2NaO_4ClF$ $(M+Na)^+$ 671.2089, found: 671.2086.

(S)-ethyl 2-((R)-1-benzyl-5-chloro-3-(4-(dibenzylamino)-3-methoxyphenyl)-2-oxoindolin-3-yl)-2-hydroxyacetate

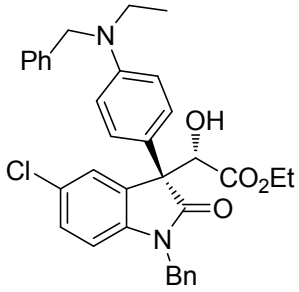


syn-**4o**

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.35 – 7.10 (m, 18H), 6.78 – 6.65 (m, 2H), 6.61 (d, *J* = 8.9 Hz, 1H),

5.14 (d, *J* = 8.9 Hz, 1H), 5.05 (d, *J* = 15.9 Hz, 1H), 4.76 (d, *J* = 15.9 Hz, 1H), 4.25 (s, 4H), 3.98 – 3.81 (m, 5H), 3.37 (d, *J* = 8.9 Hz, 1H), 0.82 (t, *J* = 7.1 Hz, 3H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 176.49, 171.89, 152.67, 142.42, 139.78, 139.08, 135.02, 128.93, 128.83, 128.60, 128.28, 128.15, 127.70, 127.62, 127.11, 126.77, 126.60, 120.11, 119.63, 111.61, 110.60, 75.22, 61.65, 59.25, 55.75, 55.59, 44.16, 13.67. HRMS (ESI) Calcd. for $C_{40}H_{37}N_2NaO_5Cl$ $(M+Na)^+$ 683.2289, found: 683.2283.

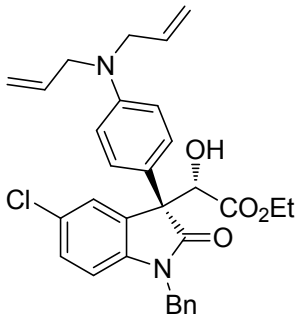
(S)-ethyl 2-((R)-1-benzyl-3-(4-(benzyl(ethyl)amino)phenyl)-5-chloro-2-oxoindolin-3-yl)-2-hydroxyacetate



syn-**4p**

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.33 – 7.12 (m, 14H), 6.69 – 6.53 (m, 3H), 5.12 (d, *J* = 9.3 Hz, 1H), 5.05 (d, *J* = 15.9 Hz, 1H), 4.75 (d, *J* = 15.9 Hz, 1H), 4.50 (s, 2H), 4.12 – 3.84 (m, 2H), 3.63 – 3.41 (m, 3H), 1.19 (t, *J* = 7.0 Hz, 3H), 0.90 (t, *J* = 7.1 Hz, 3H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 176.91, 171.90, 147.99, 142.28, 138.95, 135.10, 129.37, 128.82, 128.69, 128.58, 128.34, 127.66, 127.17, 126.85, 126.46, 121.84, 111.96, 110.52, 75.25, 61.49, 58.68, 53.84, 45.34, 44.14, 13.57, 12.13. HRMS (ESI) Calcd. for $C_{34}H_{33}N_2NaO_4Cl$ $(M+Na)^+$ 591.2027, found: 591.2010.

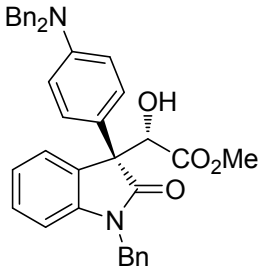
(S)-ethyl 2-((R)-1-benzyl-5-chloro-3-(4-(diallylamino)phenyl)-2-oxoindolin-3-yl)-2-hydroxyacetate



syn-**4q**

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.38 – 7.12 (m, 9H), 6.75 – 6.52 (m, 3H), 5.91 – 5.72 (m, 2H), 5.24 – 5.00 (m, 6H), 4.75 (d, *J* = 15.8 Hz, 1H), 4.08 – 3.83 (m, 6H), 3.54 (d, *J* = 9.2 Hz, 1H), 0.91 (t, *J* = 7.0 Hz, 3H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 176.89, 171.90, 148.27, 142.29, 135.09, 133.68, 129.35, 128.81, 128.70, 128.19, 127.66, 127.16, 126.48, 122.08, 116.03, 112.11, 110.52, 75.25, 61.48, 58.69, 52.70, 44.14, 13.56. HRMS (ESI) Calcd. for $C_{31}H_{31}N_2NaO_4Cl$ $(M+Na)^+$ 553.1870, found: 553.1862.

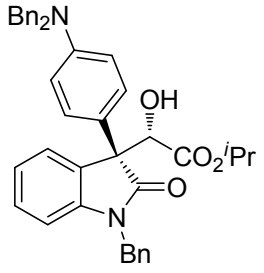
(S)-methyl 2-((R)-1-benzyl-3-(4-(dibenzylamino)phenyl)-2-oxoindolin-3-yl)-2-hydroxyacetate



syn-**4r**

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.37 – 7.10 (m, 19H), 7.02 (t, *J* = 7.5 Hz, 1H), 6.73 – 6.63 (m, 3H), 5.14 (d, *J* = 9.6 Hz, 1H), 5.04 (d, *J* = 15.8 Hz, 1H), 4.78 (d, *J* = 15.8 Hz, 1H), 4.62 (s, 4H), 3.70 (d, *J* = 9.6 Hz, 1H), 3.44 (s, 3H). ^{13}C NMR (101 MHz, CDCl3) δ 177.29, 172.44, 148.59, 143.61, 138.45, 135.54, 128.82, 128.75, 128.67, 128.36, 127.54, 127.28, 126.98, 126.67, 125.90, 123.44, 122.32, 112.39, 109.67, 75.57, 58.22, 54.28, 52.13, 44.08. HRMS (ESI) Calcd. for $C_{38}H_{34}N_2NaO_4$ $(M+Na)^+$ 605.2416, found: 605.2421.

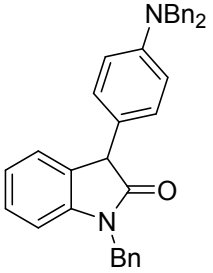
(S)-isopropyl 2-((R)-1-benzyl-3-(4-(dibenzylamino)phenyl)-2-oxoindolin-3-yl)-2-hydroxyacetate



syn-**4s**

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.35 – 7.13 (m, 19H), 7.01 (t, *J* = 7.5 Hz, 1H), 6.70 – 6.59 (m, 3H), 5.10 (d, *J* = 9.5 Hz, 1H), 5.04 (d, *J* = 15.9 Hz, 1H), 4.89 – 4.71 (m, 2H), 4.63 (s, 4H), 3.44 (d, *J* = 9.5 Hz, 1H), 1.07 (d, *J* = 6.2 Hz, 3H), 0.75 (d, *J* = 6.2 Hz, 3H). ^{13}C NMR (101 MHz, CDCl3) δ 177.33, 171.78, 148.43, 143.85, 138.49, 135.57, 128.80, 128.73, 128.67, 127.48, 127.19, 127.15, 126.97, 126.61, 126.30, 123.40, 122.11, 112.15, 109.66, 75.31, 69.29, 58.70, 54.34, 44.05, 21.55, 21.08. HRMS (ESI) Calcd. for $C_{40}H_{38}N_2NaO_4$ $(M+Na)^+$ 633.2729, found: 633.2739.

1-benzyl-3-(4-(dibenzylamino)phenyl)indolin-2-one

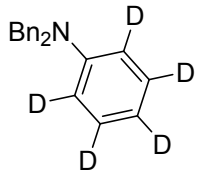


5a

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.36 – 7.27 (m, 8H), 7.27 – 7.20 (m, 7H), 7.18 – 7.12 (m, 2H), 7.03 – 6.94 (m, 3H), 6.75 – 6.63 (m, 3H), 5.07 – 4.80 (m, 2H), 4.62 (s, 4H), 4.58 (s, 1H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 176.84, 148.67, 143.54, 138.55, 136.05, 129.51, 129.20, 128.76, 128.67, 128.03, 127.56, 127.35, 126.93, 126.68, 125.15, 124.47, 122.59, 112.82, 109.07, 54.29, 51.22, 43.91.

HRMS (ESI) Calcd. for $C_{35}H_{30}N_2NaO$ $(M+Na)^+$ 517.2256, found: 517.2239.

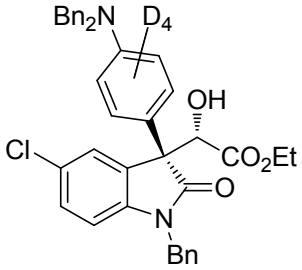
***N*,*N*-dibenzylaniline-*d*^{5}**



[D_5]-1a

^{1}H NMR (400 MHz, CDCl3) δ 8.71 – 6.60 (m, 10H), 4.64 (s, 4H). ^{13}C NMR (100 MHz, CDCl3) δ 149.14, 138.68, 128.68, 126.92, 126.72, 54.26. HRMS (ESI) Calcd. for $C_{20}H_{15}N_1D_5$ $(M+H)^+$ 279.1910, found: 279.1923.

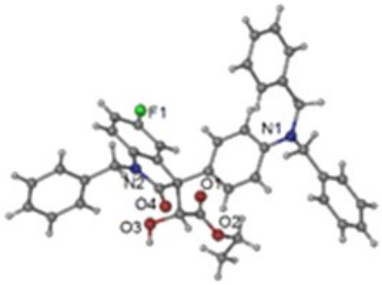
syn-**4e**-*d*^{4}



syn-[D_4]-**4e**

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.33 – 7.12 (m, 17H), 6.57 (d, *J* = 8.3 Hz, 1H), 5.22 – 4.97 (m, 2H), 4.86 – 4.49 (m, 5H), 4.15 – 3.79 (m, 2H), 3.48 (d, *J* = 9.1 Hz, 1H), 0.90 (t, *J* = 7.0 Hz, 3H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 176.82, 171.90, 148.51, 142.31, 138.35, 135.05, 129.17, 128.80, 128.67, 127.65, 127.14, 127.00, 126.57, 126.46, 122.39, 110.51, 75.21, 61.49, 58.71, 54.34, 44.14, 13.57. HRMS (ESI) Calcd. for $C_{39}H_{31}D_4N_2NaO_4Cl$ $(M+Na)^+$ 657.2434, found: 657.2433.

X-ray Diffraction Parameters and Data of *syn*-4d (CCDC 1480071)



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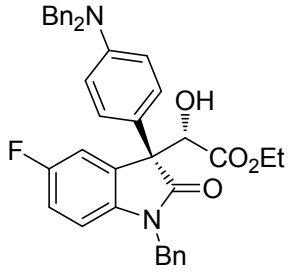


syn-**4d**

Bond precision: C-C = 0.0089 A Wavelength=0.71073

Cell: a=12.3506(5) b=15.0930(6) c=17.7124(7)
alpha=90 beta=100.508(2) gamma=90

Temperature: 296 K

	Calculated	Reported
Volume	3246.4(2)	3246.4(2)
Space group	P 21/n	P2(1)/n
Hall group	-P 2yn	?
Moiety formula	C39 H35 F N2 O4	?
Sum formula	C39 H35 F N2 O4	C39 H35 F N2 O4
Mr	614.69	614.69
Dx,g cm-3	1.258	1.258
Z	4	4
Mu (mm-1)	0.085	0.085
F000	1296.0	1296.0
F000'	1296.61	
h,k,lmax	14,17,21	14,17,21
Nref	5722	5716
Tmin,Tmax	0.979,0.991	0.977,0.991
Tmin'	0.976	

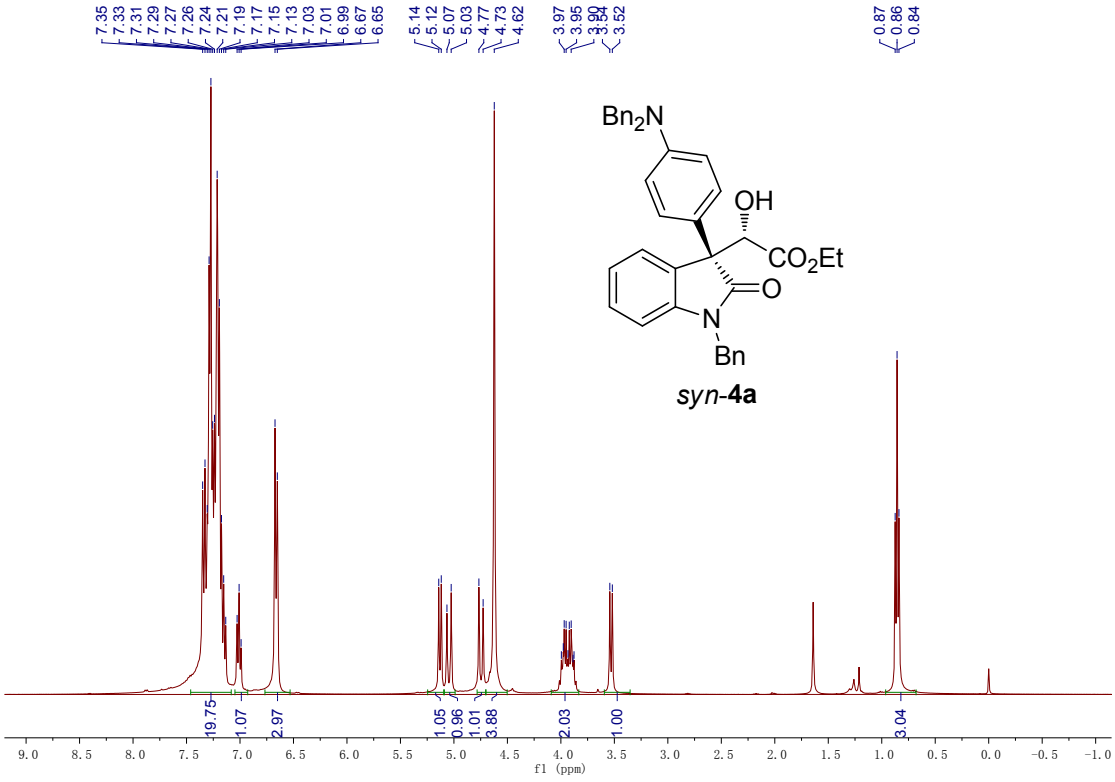
Correction method= # Reported T Limits: Tmin=0.977 Tmax=0.991
AbsCorr = MULTI-SCAN

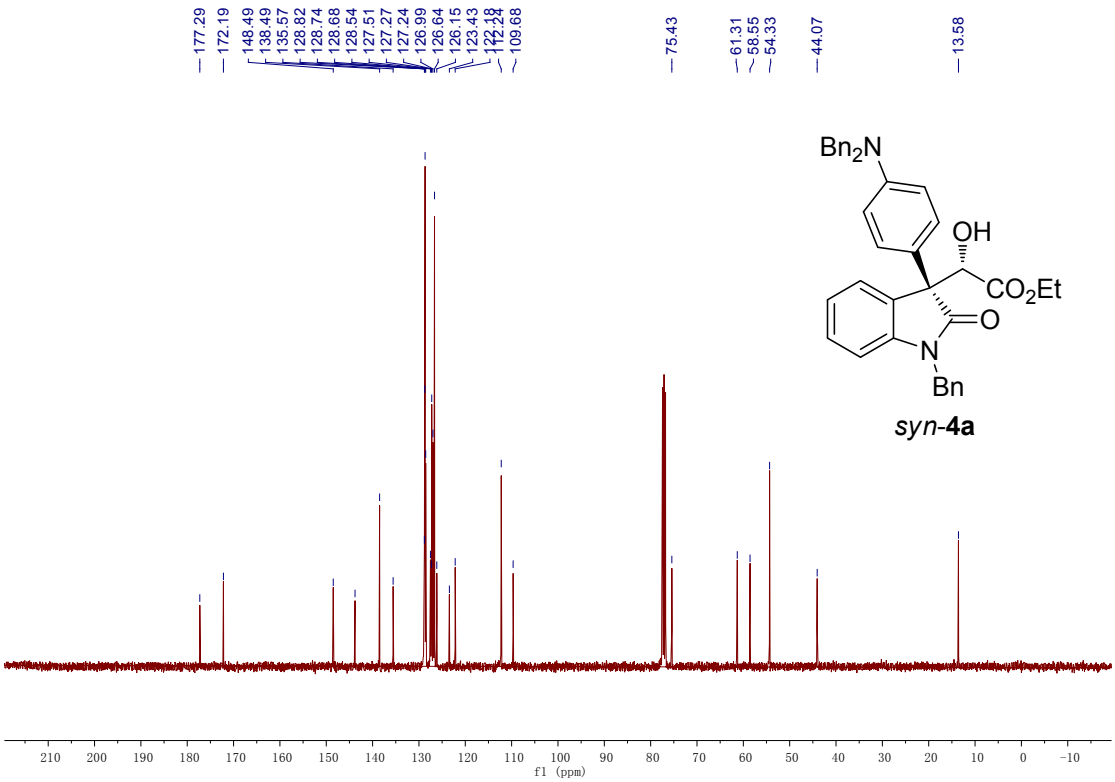
Data completeness= 0.999 Theta(max)= 25.010

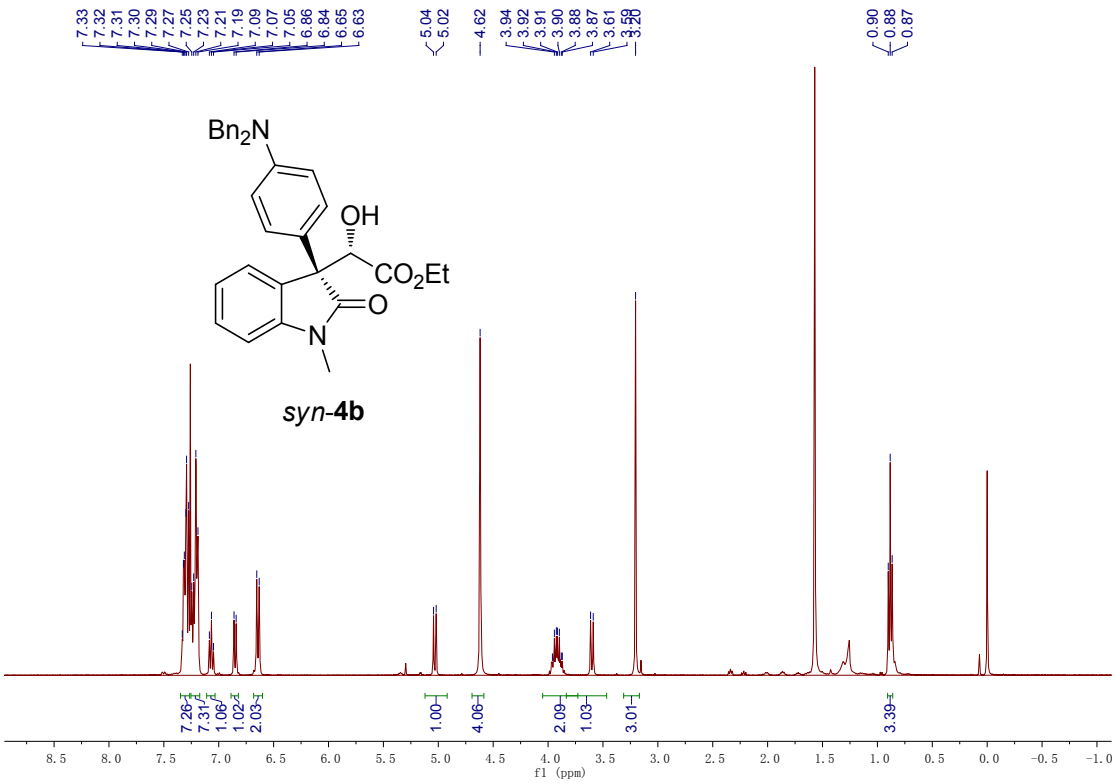
R(reflections)= 0.0818(2781) wR2(reflections)= 0.2925(5716)

S = 1.036 Npar= 404

NMR Spectra of Compounds



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6.86
6.84
6.65
6.63
5.04
5.02
4.62
3.94
3.92
3.91
3.90
3.88
3.87
3.61
3.59
3.20
0.90
0.88
0.87
Bn2N
OH
CO2Et
O
N
syn-4b
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1.02
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1.00
4.06
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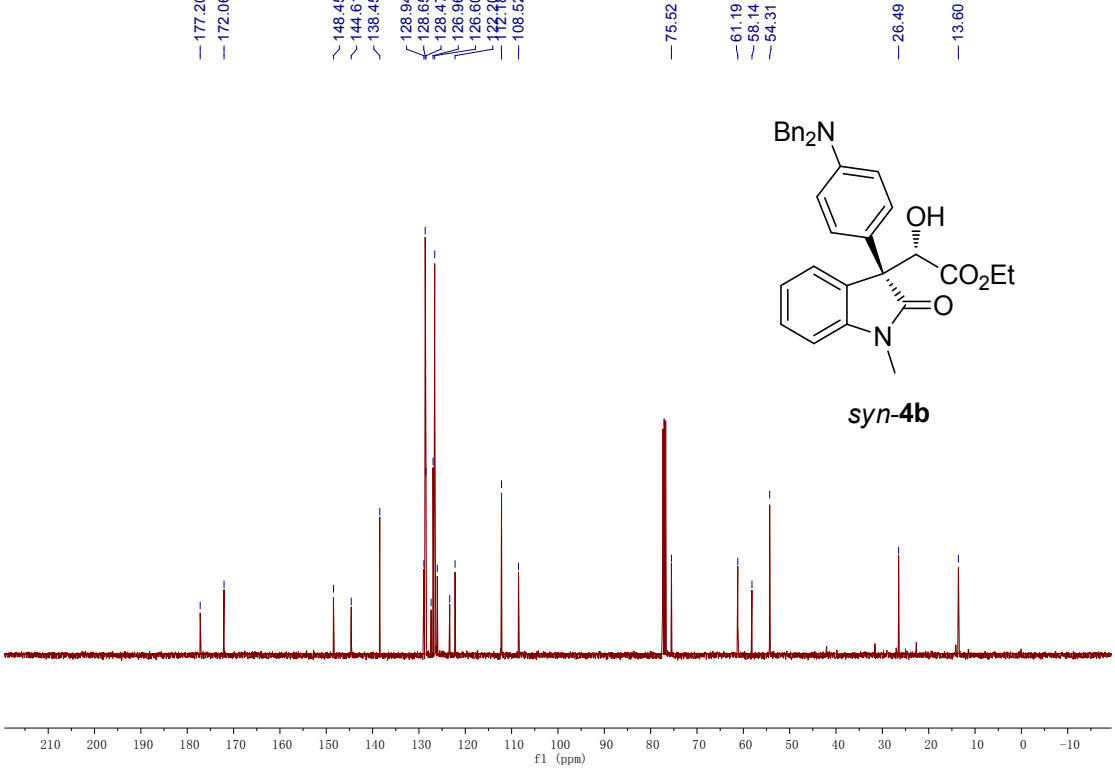
3.01
3.39
f1 (ppm)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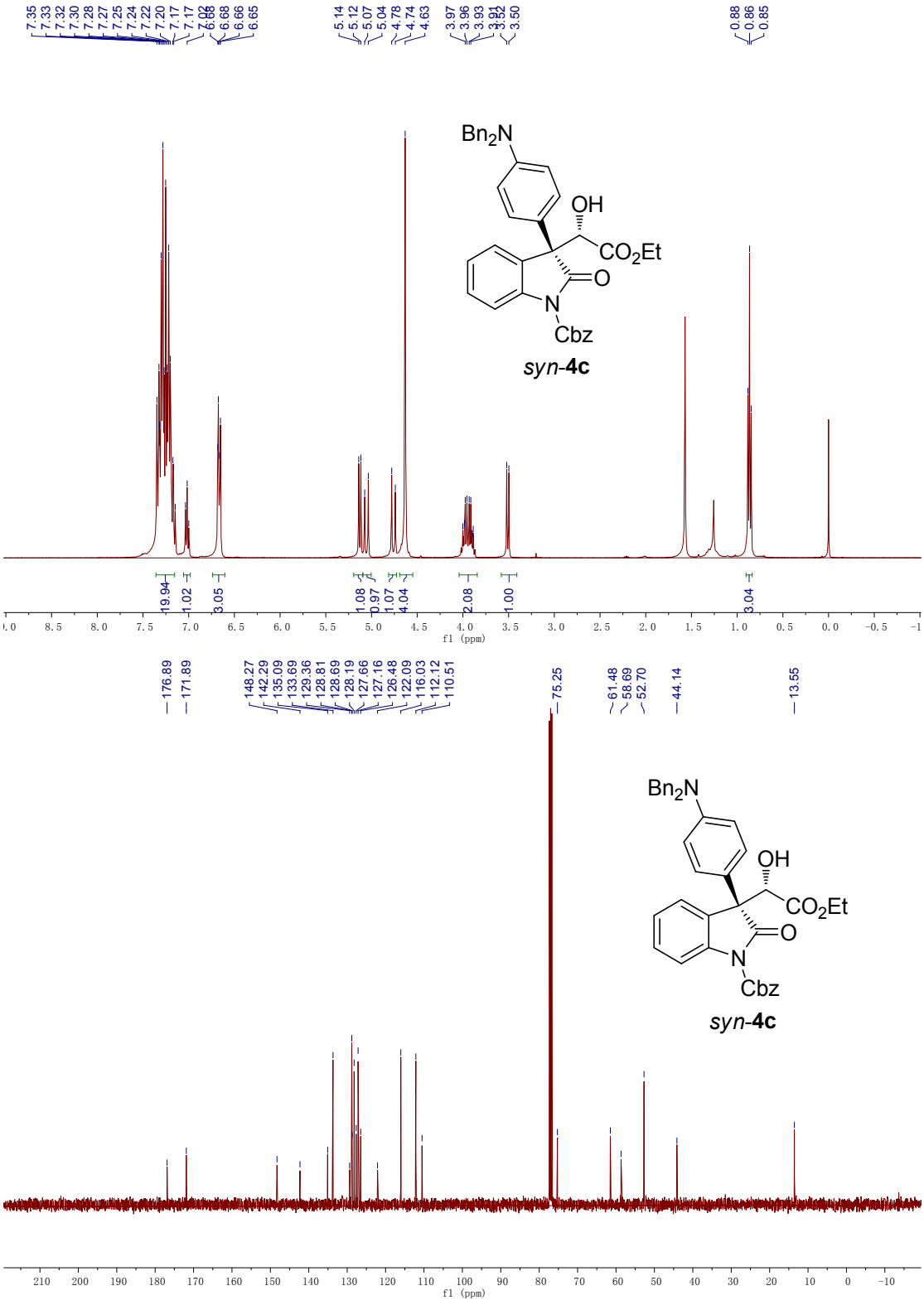
26.49
13.60
Bn2N
OH
CO2Et
O
N
syn-4b
f1 (ppm)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5.07
5.04
4.78
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4.63
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3.91
3.52
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0.85
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OH
CO2Et
O
N
Cbz
syn-4c
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1.02
3.05
1.08
0.97
1.07
4.04
2.08
1.00
3.04
f1 (ppm)
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171.89
148.27
142.29
135.09
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112.12
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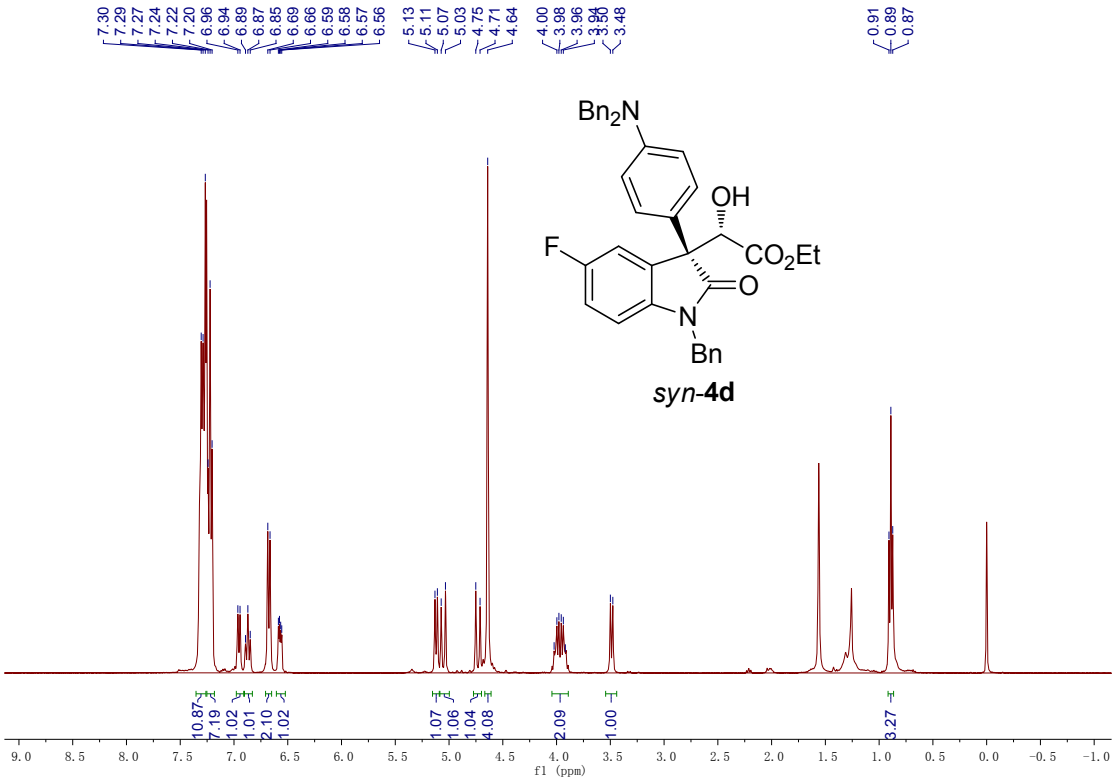
CO2Et
O
N
Cbz
syn-4c
f1 (ppm)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5.07
5.03
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4.64
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3.96
3.94
3.90
3.48
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0.87
Bn2N
OH
F
CO2Et
O
N
Bn
syn-4d
10.87
7.19
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1.01
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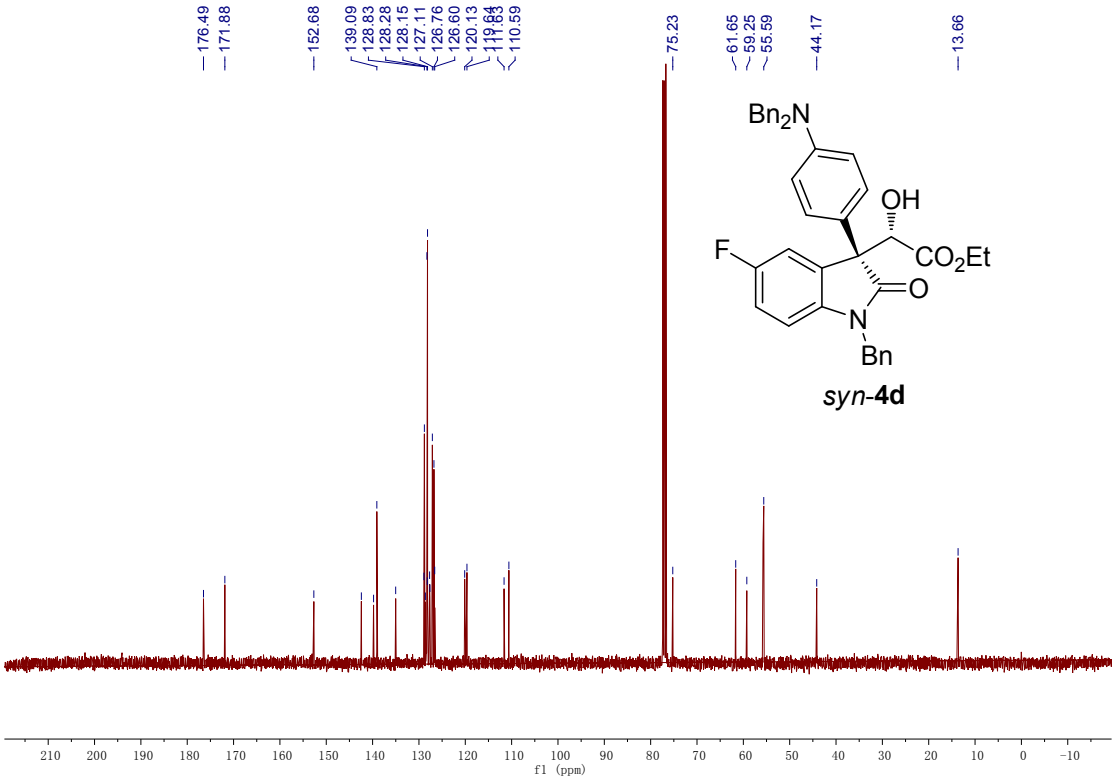
4.08
2.09
1.00
3.27
f1 (ppm)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139.09
128.83
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127.11
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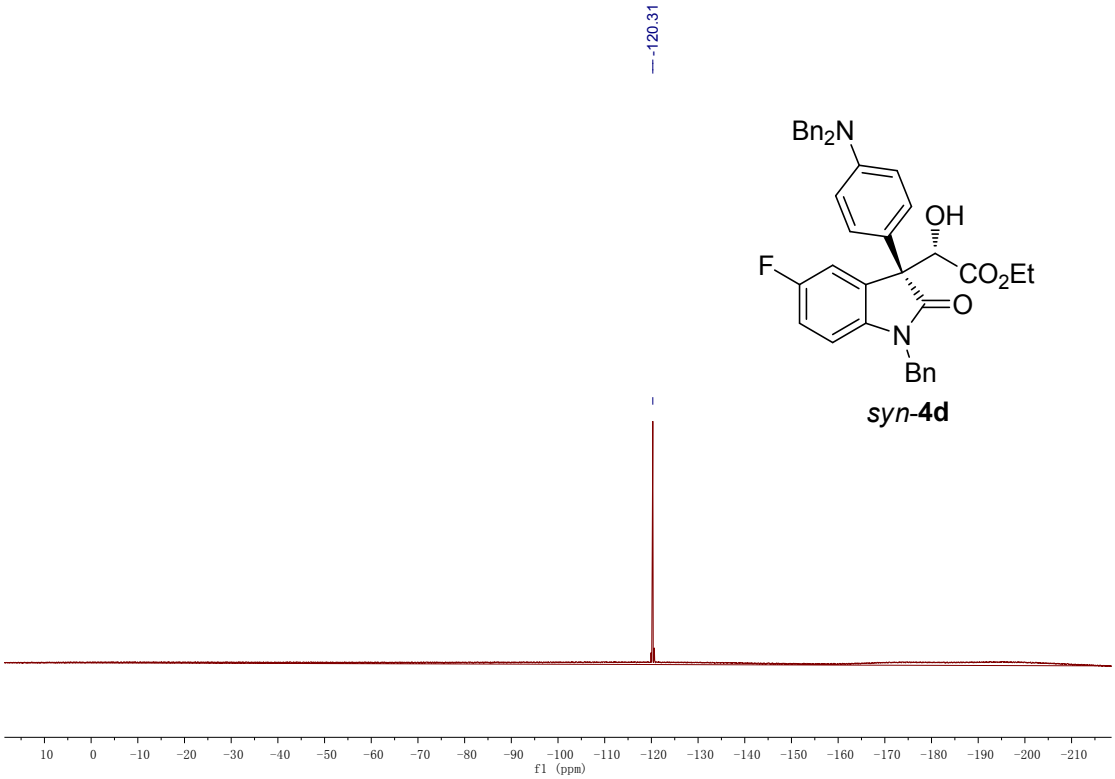
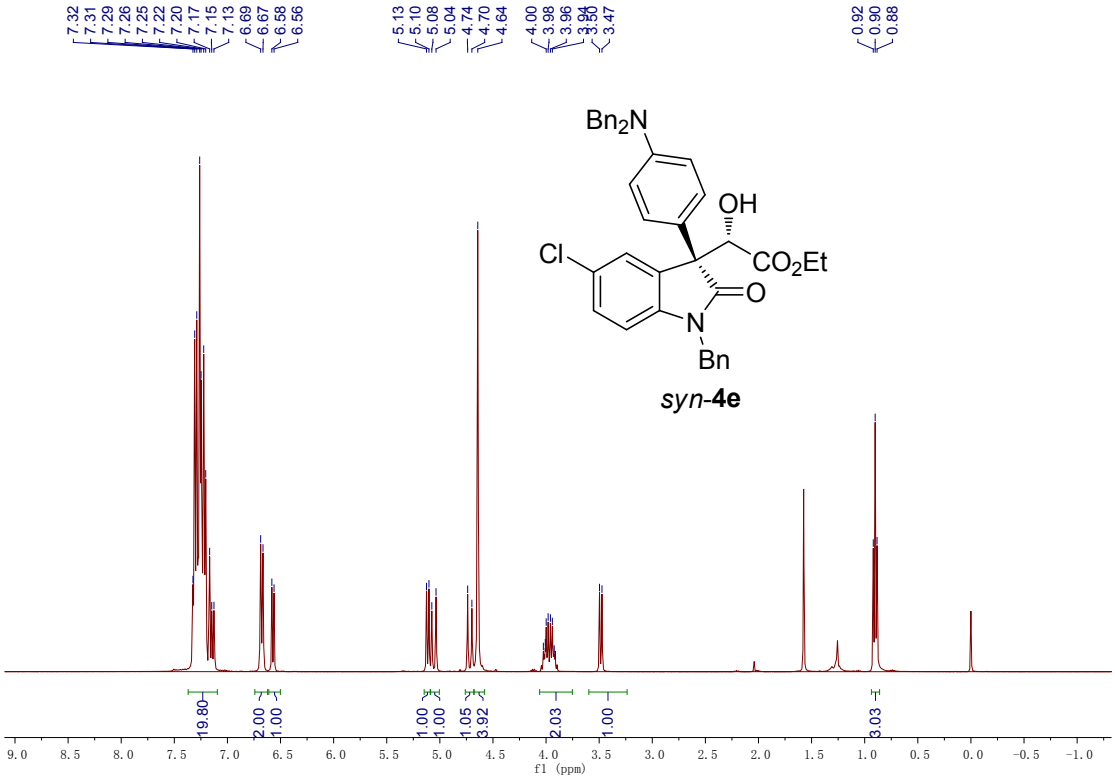
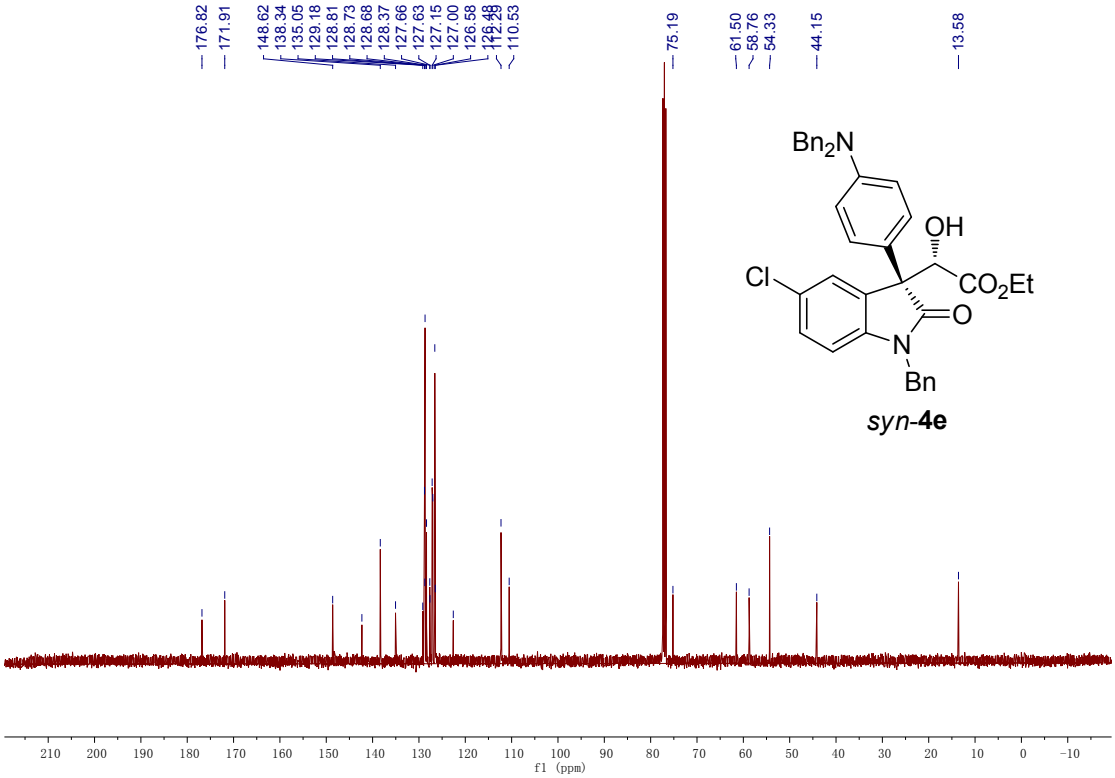
126.60
120.13
119.64
111.83
110.59
75.23
61.65
59.25
55.59
44.17
13.66
Bn2N
OH
F
CO2Et
O
N
Bn
syn-4d
f1 (ppm)

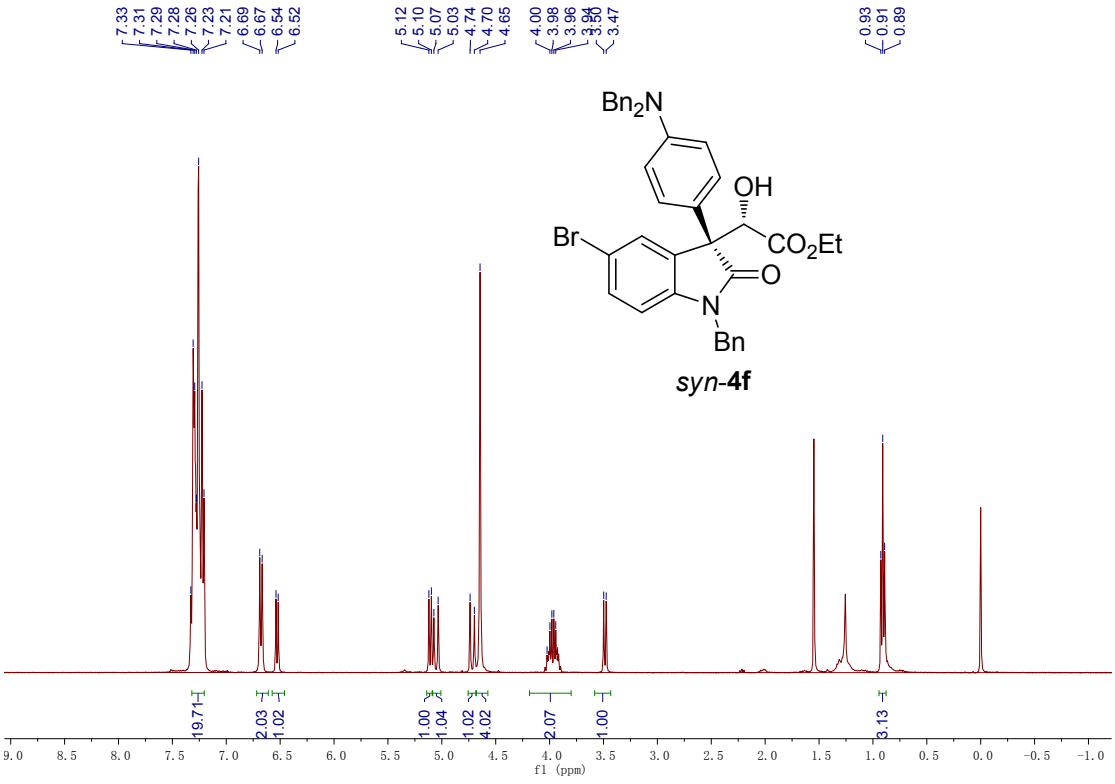

-120.31
Bn2N
OH
F
CO2Et
O
N
Bn
f1 (ppm)

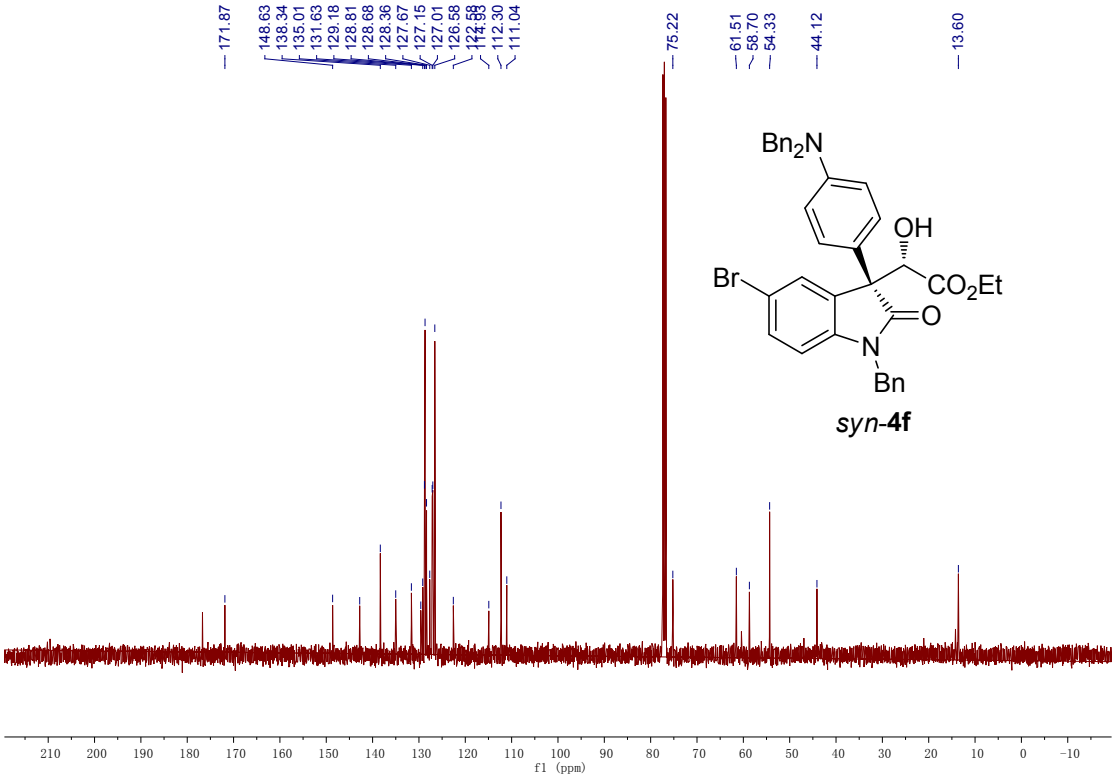
syn-**4d**


7.32
7.31
7.29
7.26
7.25
7.22
7.20
7.17
7.15
7.13
6.69
6.67
6.58
6.56
5.13
5.10
5.08
5.04
4.74
4.70
4.64
4.00
3.98
3.96
3.94
3.90
3.47
0.92
0.90
0.88
Bn2N
OH
Cl
CO2Et
O
N
Bn
19.80
2.00
1.00
1.00
1.00
1.05
3.92
2.03
1.00
3.03
f1 (ppm)

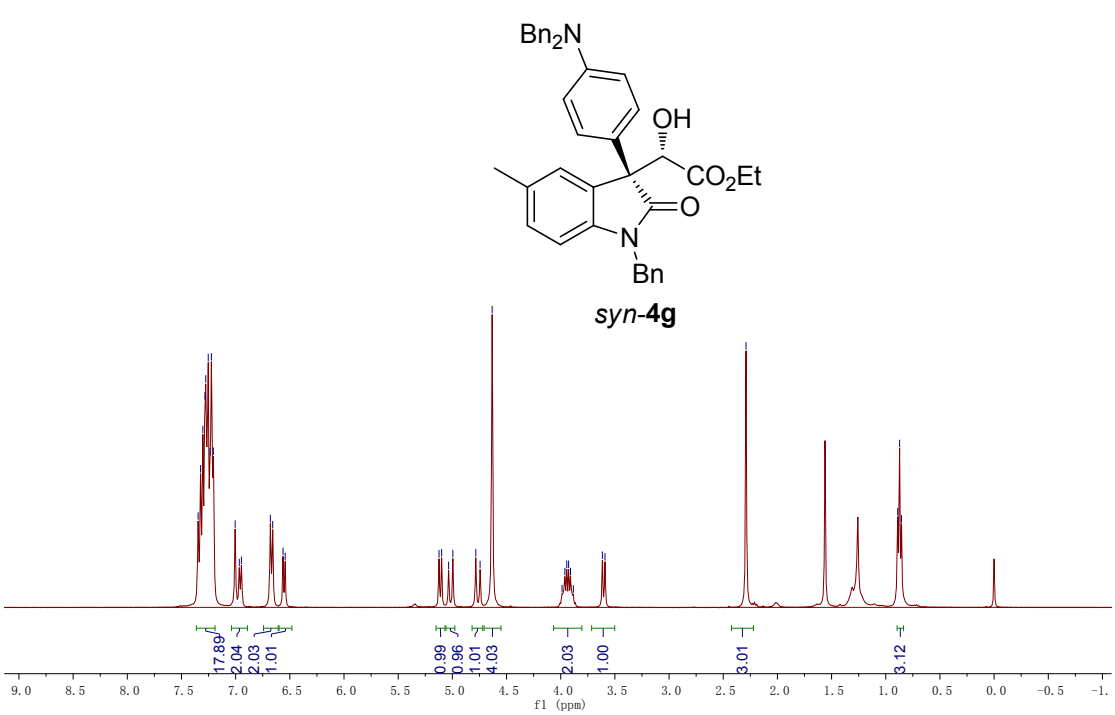
syn-**4e**


176.82
171.91
148.62
138.34
135.05
129.18
128.81
128.73
128.68
128.37
127.66
127.63
127.15
127.00
126.58
110.53
75.19
61.50
58.76
54.33
44.15
13.58
Bn2N
OH
Cl
CO2Et
O
N
Bn
syn-4e
f1 (ppm)

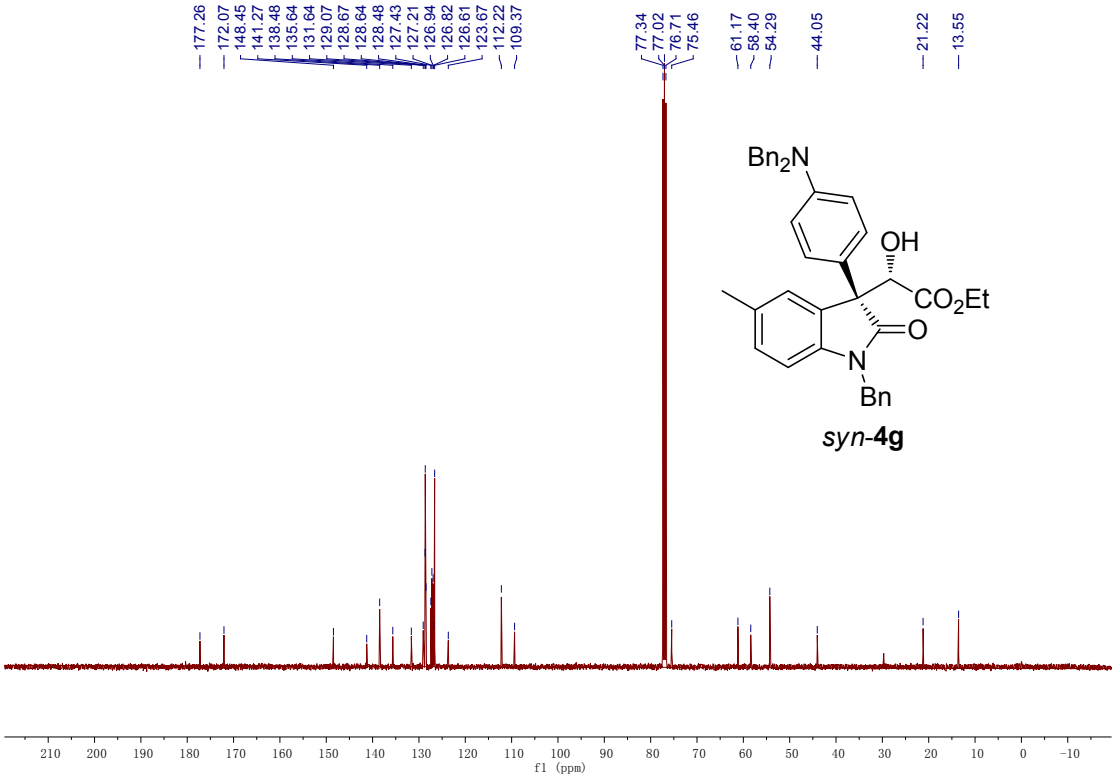

7.33
7.31
7.29
7.28
7.26
7.23
7.21
6.69
6.67
6.54
6.52
5.12
5.10
5.07
5.03
4.74
4.70
4.65
4.00
3.98
3.96
3.94
3.50
3.47
0.93
0.91
0.89
Bn2N
OH
Br
CO2Et
O
N
Bn
syn-4f
19.71
2.03
1.02
1.00
1.04
1.02
4.02
2.07
1.00
3.13
f1 (ppm)


171.87
148.63
138.34
135.01
131.63
129.18
128.81
128.68
128.36
127.67
127.15
127.01
126.58
112.30
111.04
75.22
61.51
58.70
54.33
44.12
13.60
Bn2N
OH
Br
CO2Et
O
N
Bn
f1 (ppm)

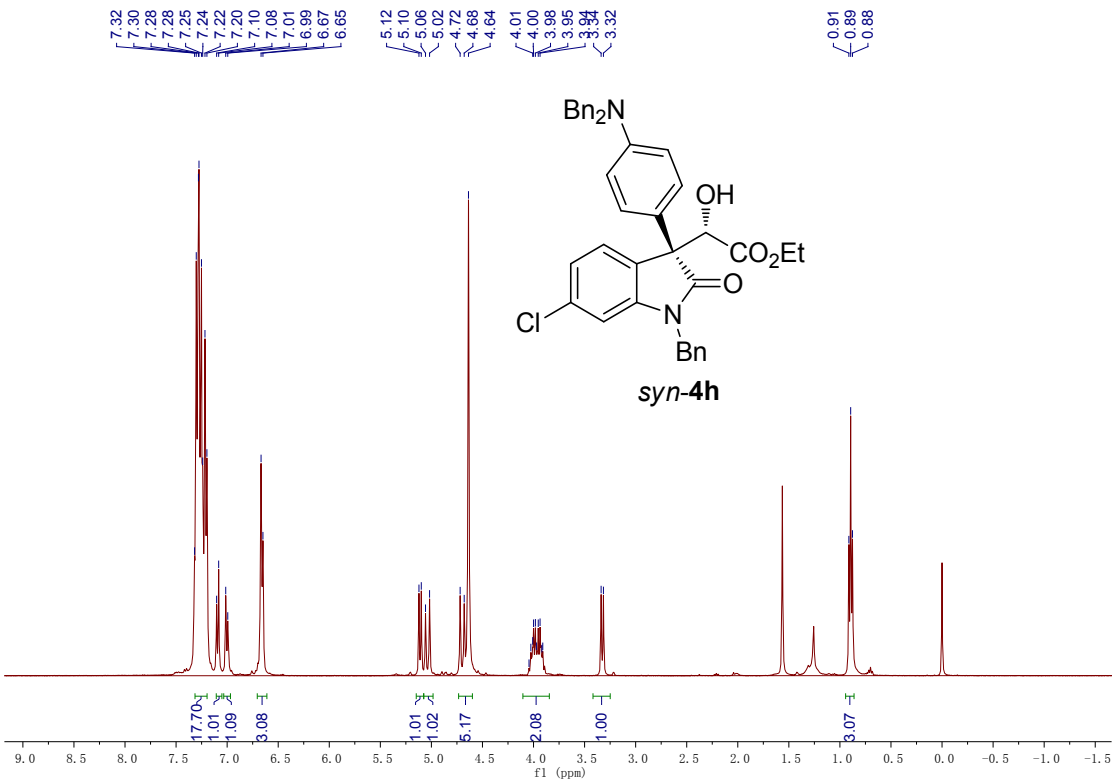
syn-**4f**


7.35
7.32
7.30
7.28
7.28
7.25
7.24
7.22
7.21
7.00
6.97
6.95
6.68
6.66
6.56
6.54
5.12
5.10
5.03
5.00
4.78
4.74
4.63
3.99
3.96
3.94
3.93
3.91
3.88
3.62
3.59
2.29
0.89
0.87
0.85
Bn2N
OH
CO2Et
O
N
Bn
17.89
2.04
2.03
1.01
0.99
0.96
1.01
4.03
2.03
1.00
3.01
3.12
f1 (ppm)

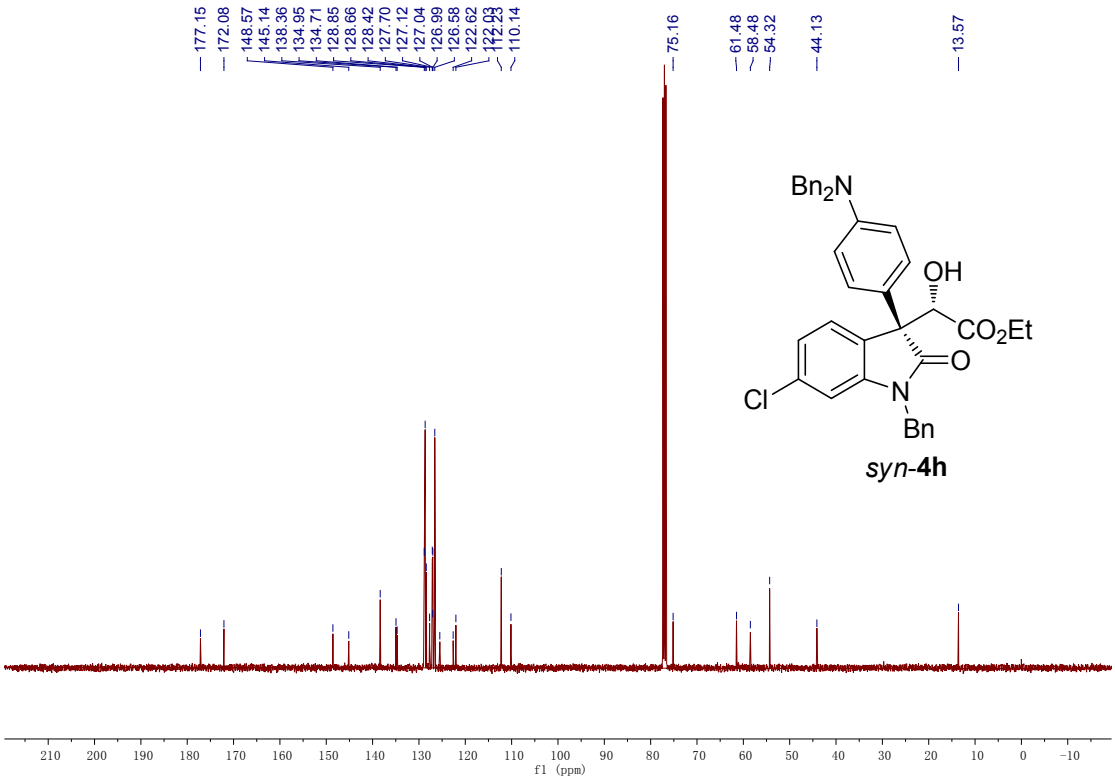
syn-**4g**

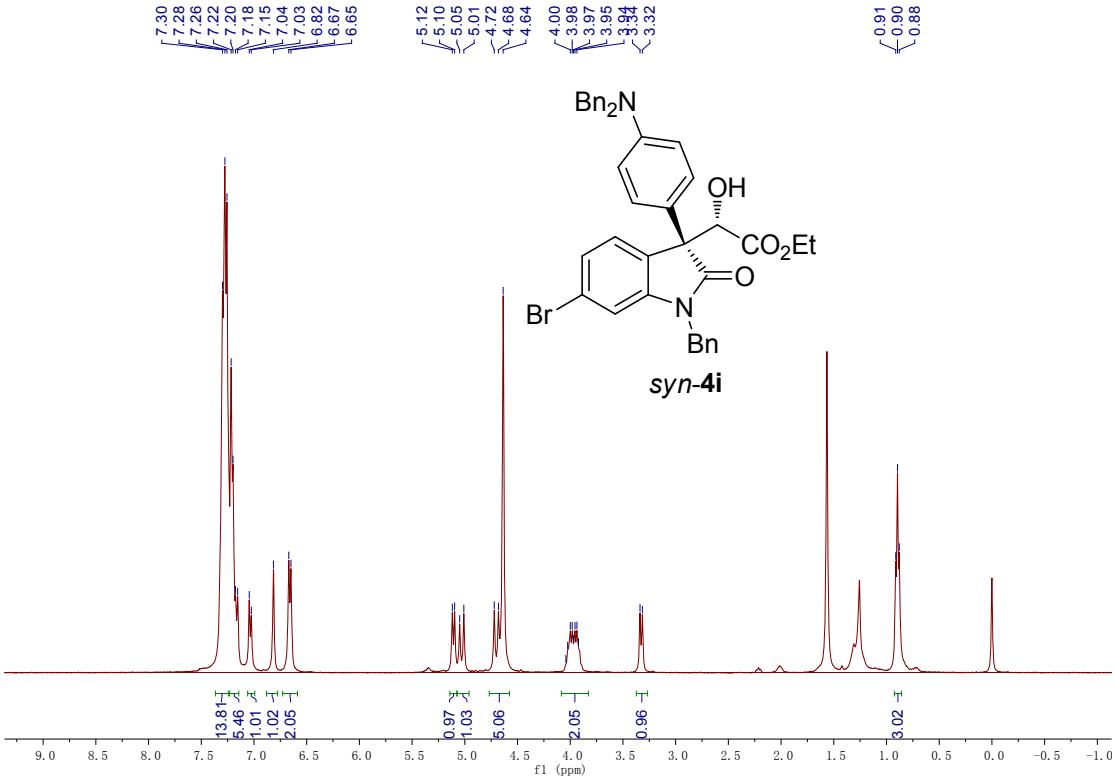

177.26
172.07
148.45
141.27
138.48
135.64
131.64
129.07
128.67
128.64
128.48
127.43
127.21
126.94
126.82
126.61
123.67
112.22
109.37
77.34
77.02
76.71
75.46
61.17
58.40
54.29
44.05
21.22
13.55
Bn2N
OH
CO2Et
O
N
Bn
f1 (ppm)

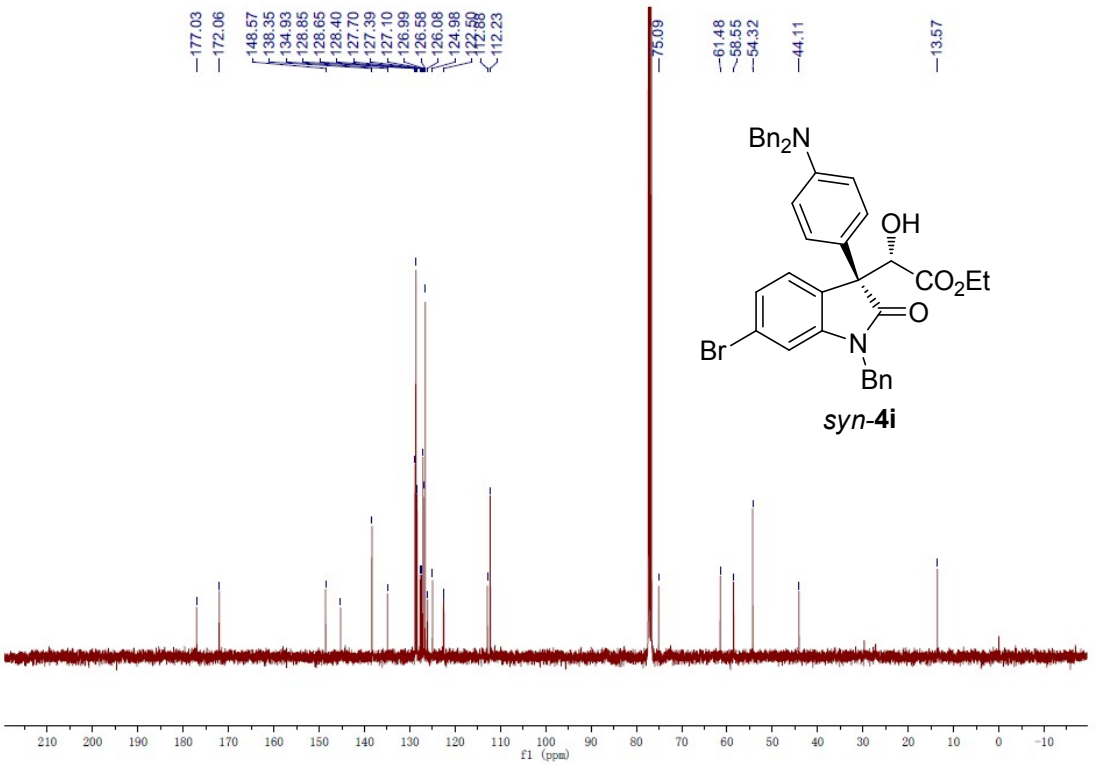
syn-**4g**


7.32
7.30
7.28
7.28
7.25
7.24
7.22
7.20
7.10
7.08
7.01
6.99
6.67
6.65
5.12
5.10
5.06
5.02
4.72
4.68
4.64
4.01
4.00
3.98
3.95
3.94
3.34
3.32
0.91
0.89
0.88
Bn2N
OH
CO2Et
O
Cl
N
Bn
17.70
1.01
1.09
3.08
1.01
1.02
5.17
2.08
1.00
3.07
f1 (ppm)

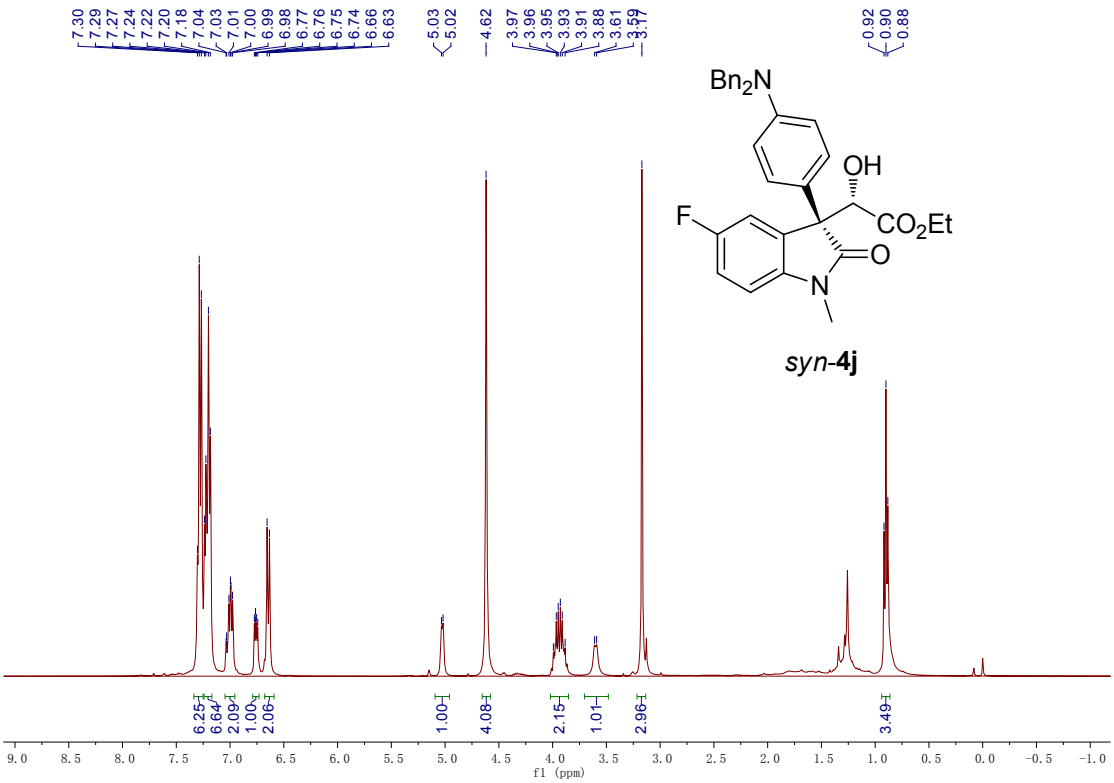
syn-**4h**


177.15
172.08
148.57
145.14
138.36
134.95
134.71
128.85
128.66
128.42
127.70
127.12
127.04
126.99
126.58
122.62
122.03
112.23
110.14
75.16
61.48
58.48
54.32
44.13
13.57
Bn2N
OH
CO2Et
O
N
Bn
Cl
syn-4h
f1 (ppm)

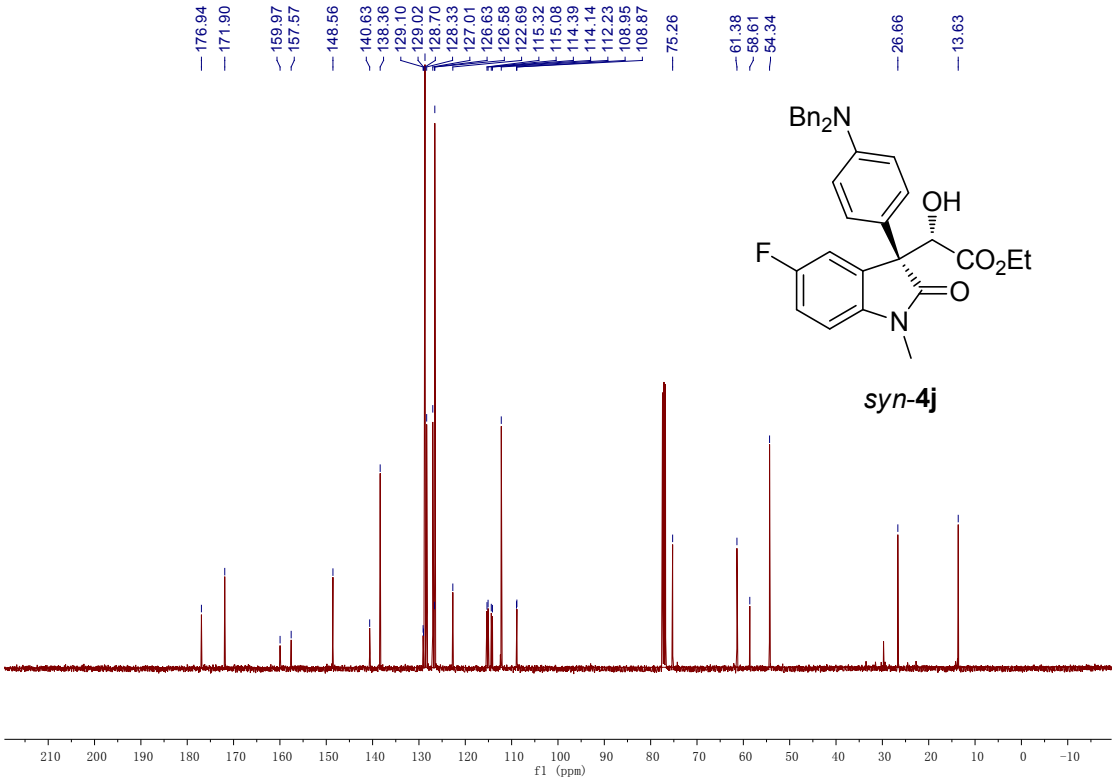

7.30
7.28
7.26
7.22
7.20
7.18
7.15
7.04
7.03
6.82
6.67
6.65
5.12
5.10
5.05
5.01
4.72
4.68
4.64
4.00
3.98
3.97
3.95
3.94
3.34
3.32
0.91
0.90
0.88
Bn2N
OH
CO2Et
O
N
Bn
Br
syn-4i
13.81
5.46
1.01
1.02
2.05
0.97
1.03
5.06
2.05
0.96
3.02
f1 (ppm)


177.03
172.06
148.57
138.35
134.93
128.85
128.65
128.40
127.70
127.39
127.10
126.99
126.58
126.08
124.98
122.50
112.88
112.23
75.09
61.48
58.55
54.32
44.11
13.57
Bn2N
OH
CO2Et
O
N
Br
Bn
f1 (ppm)

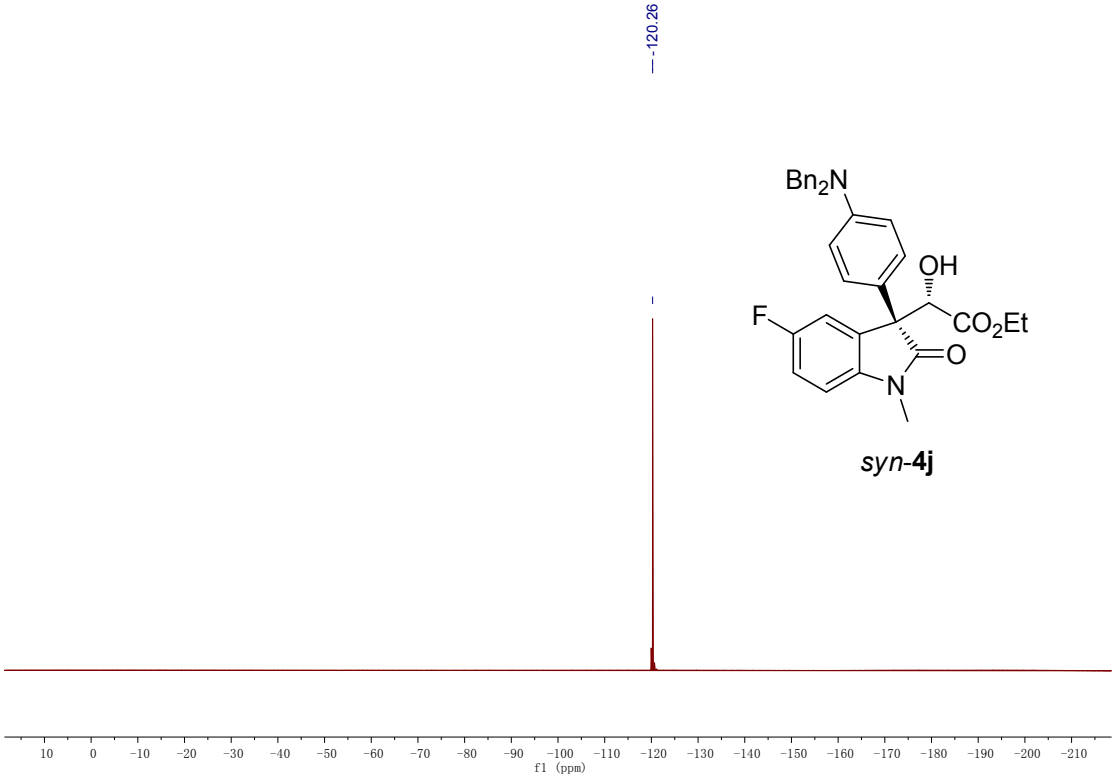
syn-**4i**


7.30
7.29
7.27
7.24
7.22
7.20
7.18
7.04
7.03
7.01
7.00
6.99
6.98
6.77
6.76
6.75
6.74
6.66
6.63
5.03
5.02
4.62
3.97
3.96
3.95
3.93
3.91
3.88
3.61
3.59
3.57
0.92
0.90
0.88
Bn2N
OH
CO2Et
F
O
N
6.25
6.64
2.09
1.00
2.06
1.00
4.08
2.15
1.01
2.96
3.49
f1 (ppm)

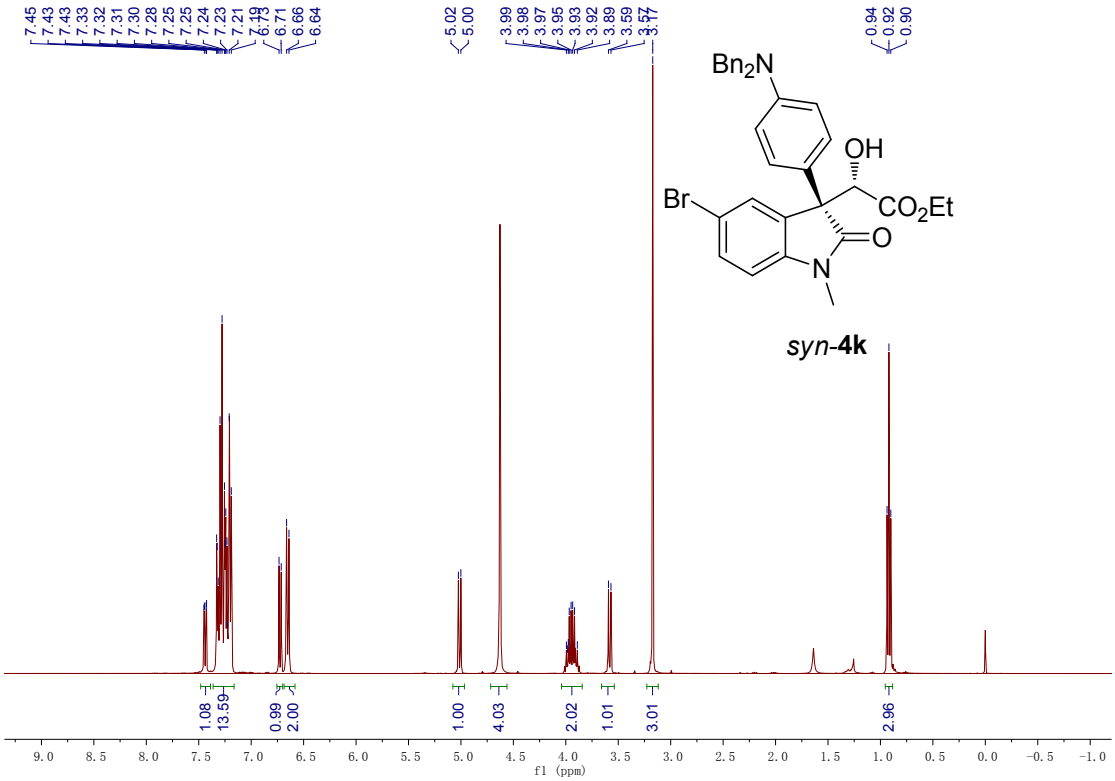
syn-**4j**

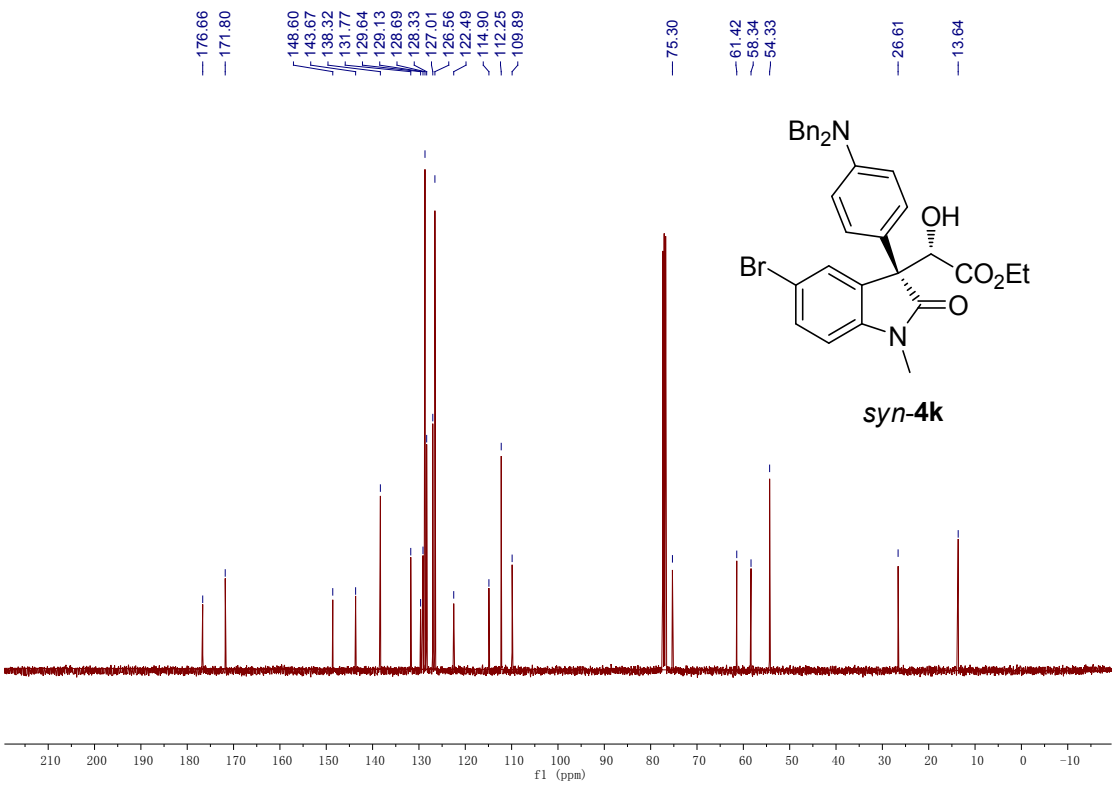

176.94
171.90
159.97
157.57
148.56
140.63
138.36
129.10
129.02
128.70
128.33
127.01
126.63
126.58
122.69
115.32
115.08
114.39
114.14
112.23
108.95
108.87
75.26
61.38
58.61
54.34
26.66
13.63
Bn2N
OH
F
CO2Et
O
N
210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 −10
f1 (ppm)

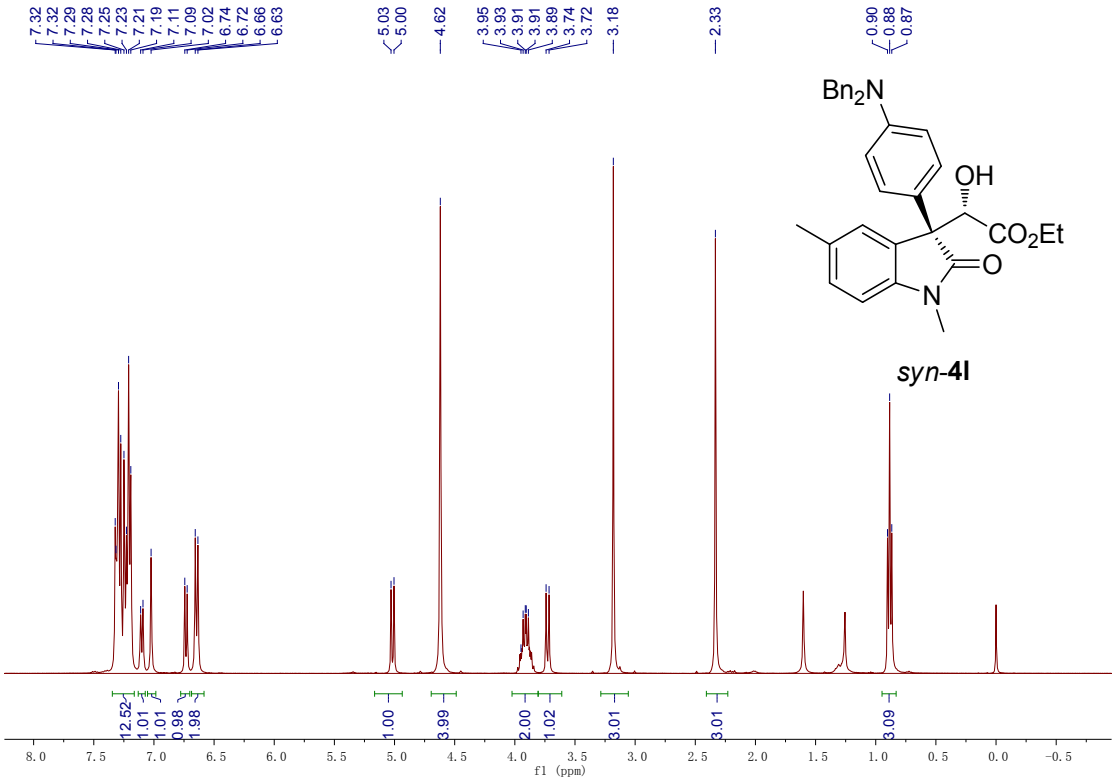
syn-**4j**


−120.26
Bn2N
OH
F
CO2Et
O
N
10 0 −10 −20 −30 −40 −50 −60 −70 −80 −90 −100 −110 −120 −130 −140 −150 −160 −170 −180 −190 −200 −210
f1 (ppm)

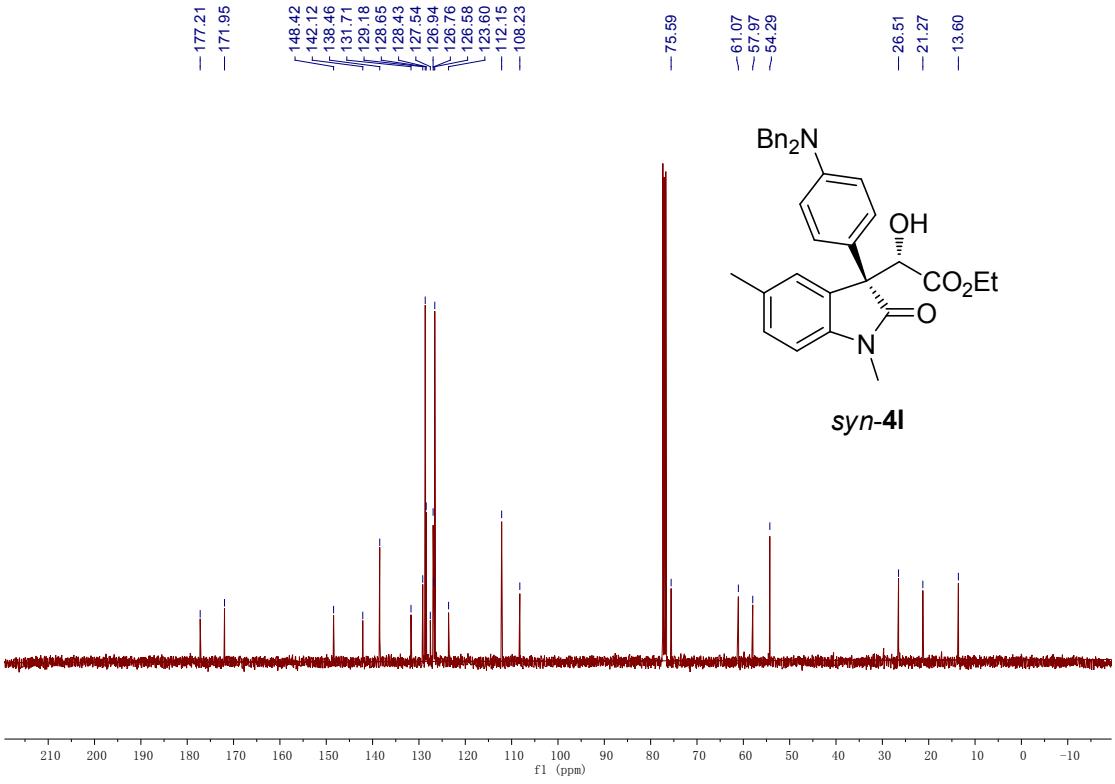
syn-**4j**


7.45
7.43
7.43
7.33
7.32
7.31
7.30
7.28
7.25
7.25
7.24
7.23
7.21
6.71
6.66
6.64
5.02
5.00
3.99
3.98
3.97
3.95
3.93
3.92
3.89
3.59
3.57
3.17
0.94
0.92
0.90
1.08
13.59
0.99
2.00
1.00
4.03
2.02
1.01
3.01
2.96
f1 (ppm)
Bn2N
OH
Br
CO2Et
O
N
syn-4k

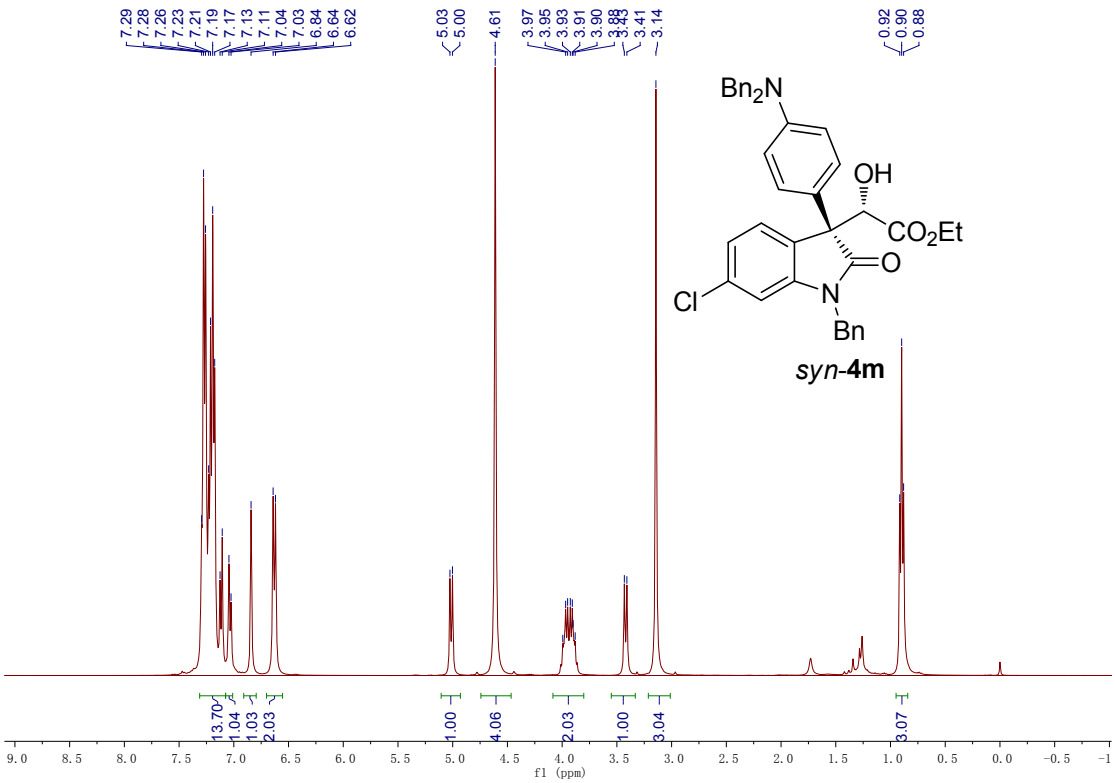

176.66
171.80
148.60
143.67
138.32
131.77
129.64
129.13
128.69
128.33
127.01
126.56
122.49
114.90
112.25
109.89
75.30
61.42
58.34
54.33
26.61
13.64
f1 (ppm)
Bn2N
OH
Br
CO2Et
O
N
syn-4k

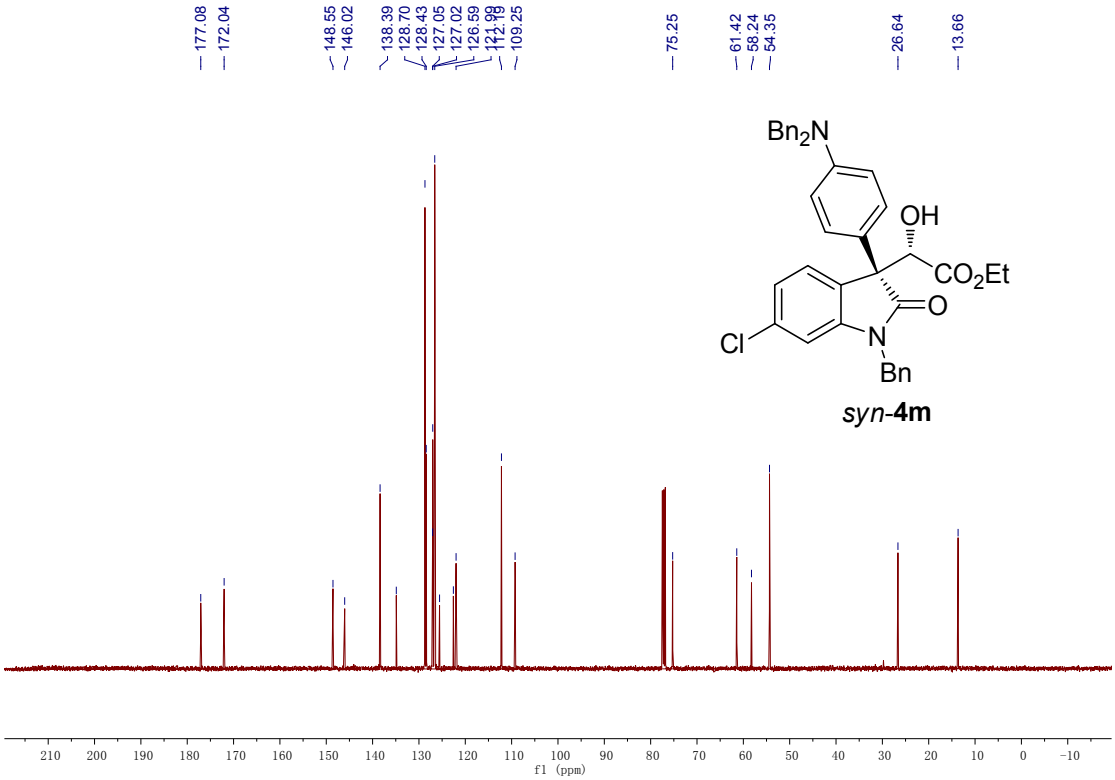

7.32
7.32
7.29
7.28
7.25
7.23
7.21
7.19
7.11
7.09
7.02
6.74
6.72
6.66
6.63
5.03
5.00
4.62
3.95
3.93
3.91
3.91
3.89
3.74
3.72
3.18
2.33
0.90
0.88
0.87
Bn2N
OH
CO2Et
O
N
12.52
1.01
1.01
0.98
1.98
1.00
3.99
2.00
1.02
3.01
3.01
3.09
f1 (ppm)

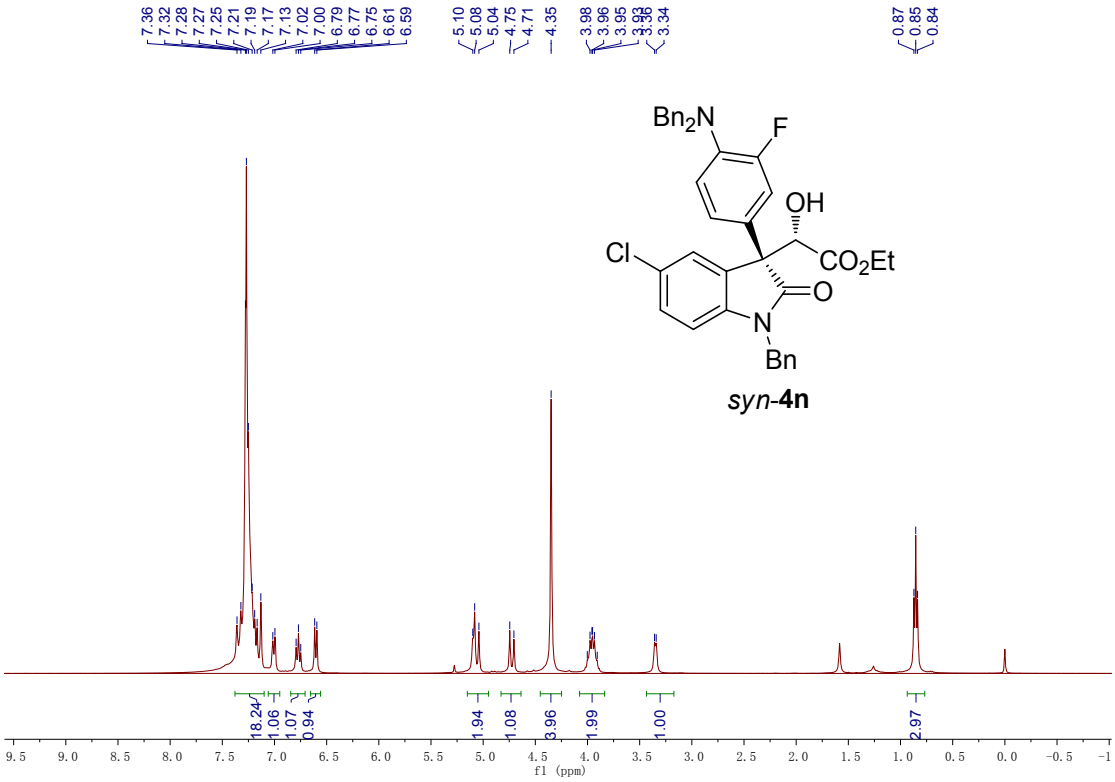
syn-**4l**


177.21
171.95
148.42
142.12
138.46
131.71
129.18
128.65
128.43
127.54
126.94
126.76
126.58
123.60
112.15
108.23
75.59
61.07
57.97
54.29
26.51
21.27
13.60
Bn2N
OH
CO2Et
O
N
f1 (ppm)

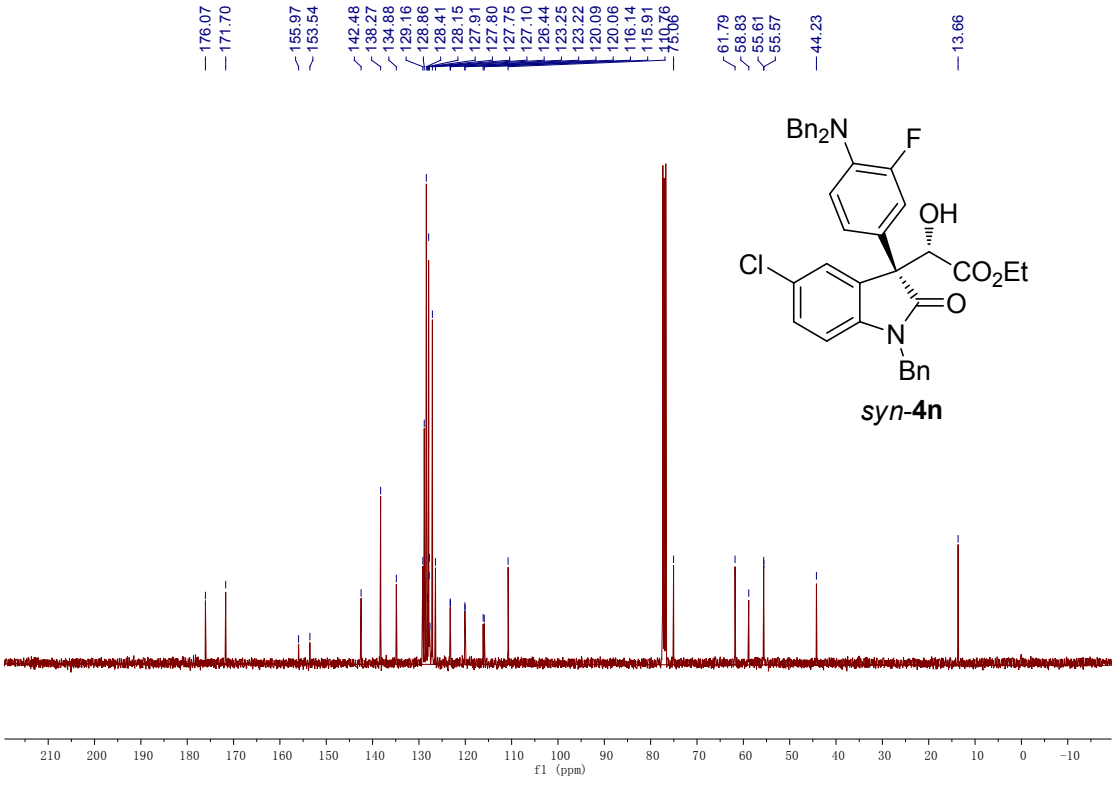
syn-**4l**


7.29
7.28
7.26
7.23
7.21
7.19
7.17
7.13
7.11
7.04
7.03
6.84
6.64
6.62
5.03
5.00
4.61
3.97
3.95
3.93
3.91
3.90
3.41
3.14
0.92
0.90
0.88
13.70
1.04
1.03
2.03
1.00
4.06
2.03
1.00
3.04
3.07
f1 (ppm)
Bn2N
OH
CO2Et
O
N
Cl
Bn
syn-4m

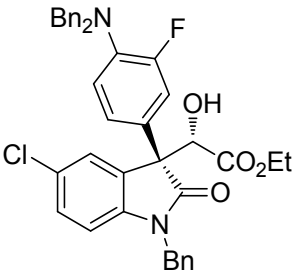

177.08
172.04
148.55
146.02
138.39
128.70
128.43
127.05
127.02
126.59
121.98
112.19
109.25
75.25
61.42
58.24
54.35
26.64
13.66
f1 (ppm)
Bn2N
OH
CO2Et
O
N
Cl
Bn
syn-4m


7.36
7.32
7.28
7.27
7.25
7.21
7.19
7.17
7.13
7.02
7.00
6.79
6.77
6.75
6.61
6.59
5.10
5.08
5.04
4.75
4.71
4.35
3.98
3.96
3.95
3.38
3.34
0.87
0.85
0.84
Bn2N
F
OH
Cl
CO2Et
O
N
Bn
18.24
1.06
1.07
0.94
1.94
1.08
3.96
1.99
1.00
2.97
f1 (ppm)

syn-**4n**

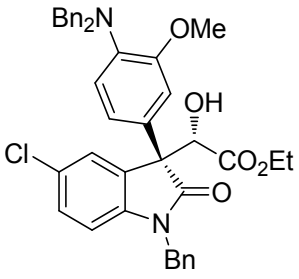

176.07
171.70
155.97
153.54
142.48
138.27
134.88
129.16
128.86
128.41
128.15
127.91
127.80
127.75
127.10
126.44
123.25
123.22
120.09
120.06
116.14
115.91
110.26
75.06
61.79
58.83
55.61
55.57
44.23
13.66
Bn2N
F
OH
Cl
CO2Et
O
N
Bn
f1 (ppm)

syn-**4n**


Bn2N
F
OH
Cl
CO2Et
O
N
Bn

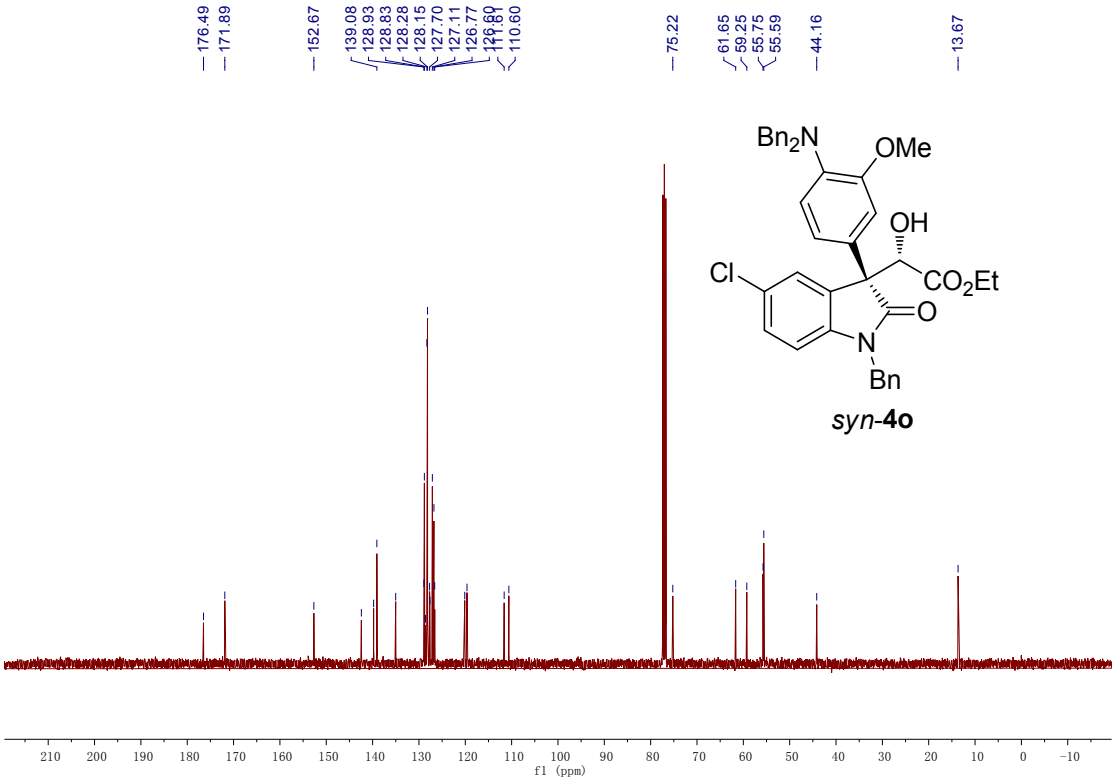
syn-**4n**

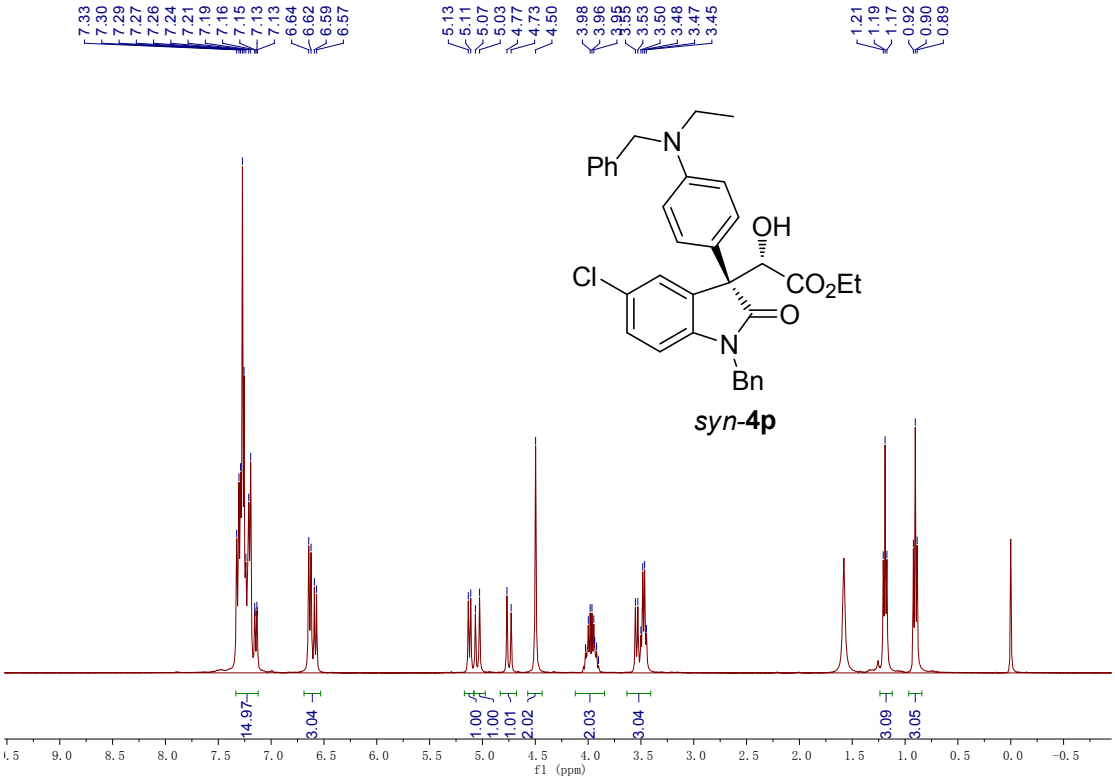
-121.30
10 0 -10 -20 -30 -40 -50 -60 -70 -80 -90 -100 -110 -120 -130 -140 -150 -160 -170 -180 -190 -200 -210
f1 (ppm)
7.32 7.30 7.29 7.26 7.25 7.23 7.20 7.18 7.17 7.17 7.16 6.73 6.70 6.68 6.62 6.59
5.16 5.13 5.07 5.03 4.78 4.74
4.25 3.95 3.93 3.91 3.36
0.84 0.82 0.80

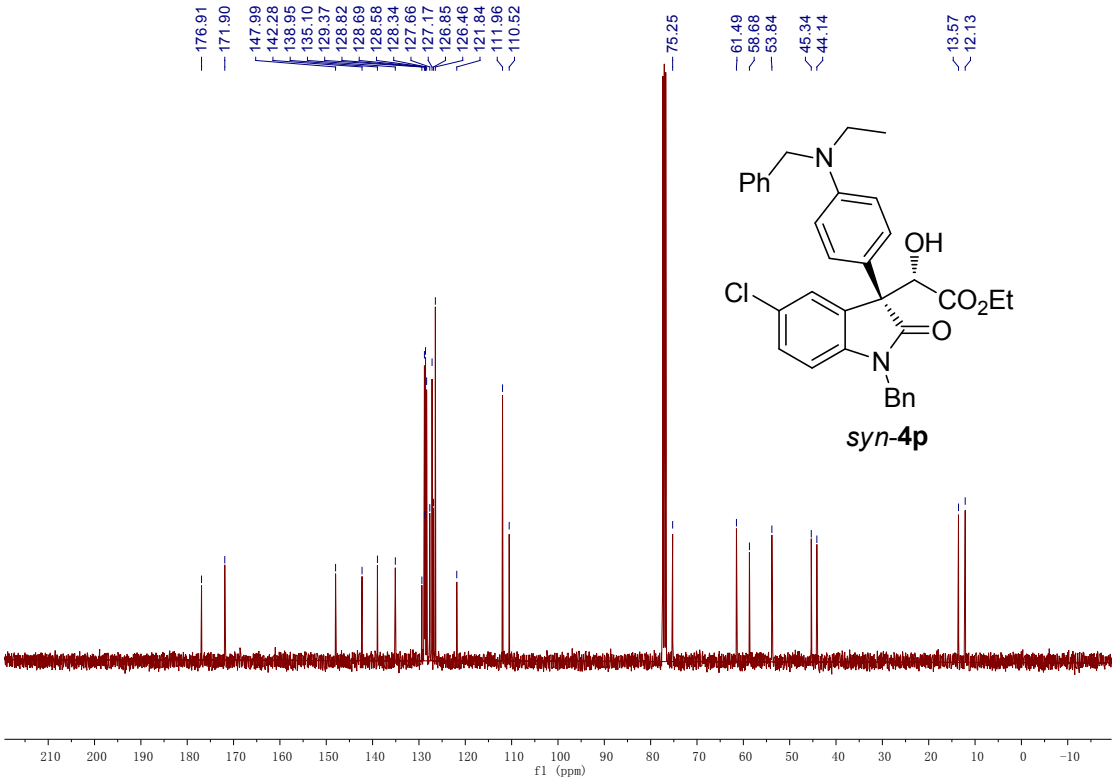

Bn2N
OMe
OH
Cl
CO2Et
O
N
Bn

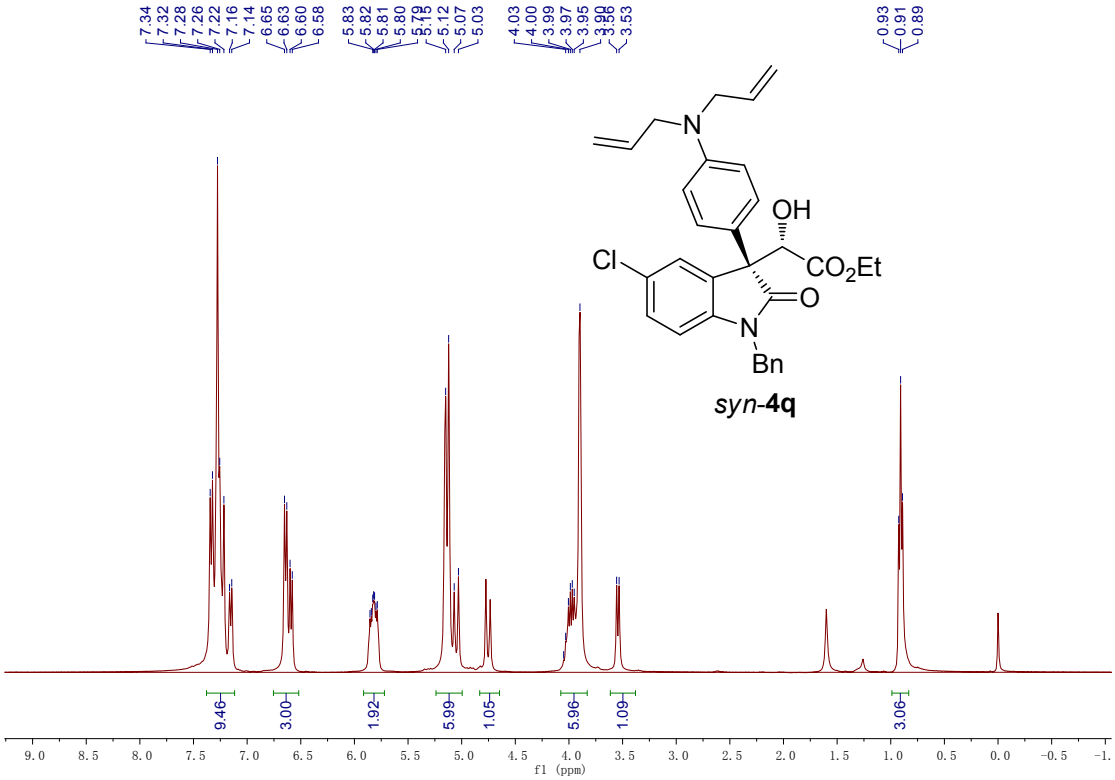
syn-**4o**

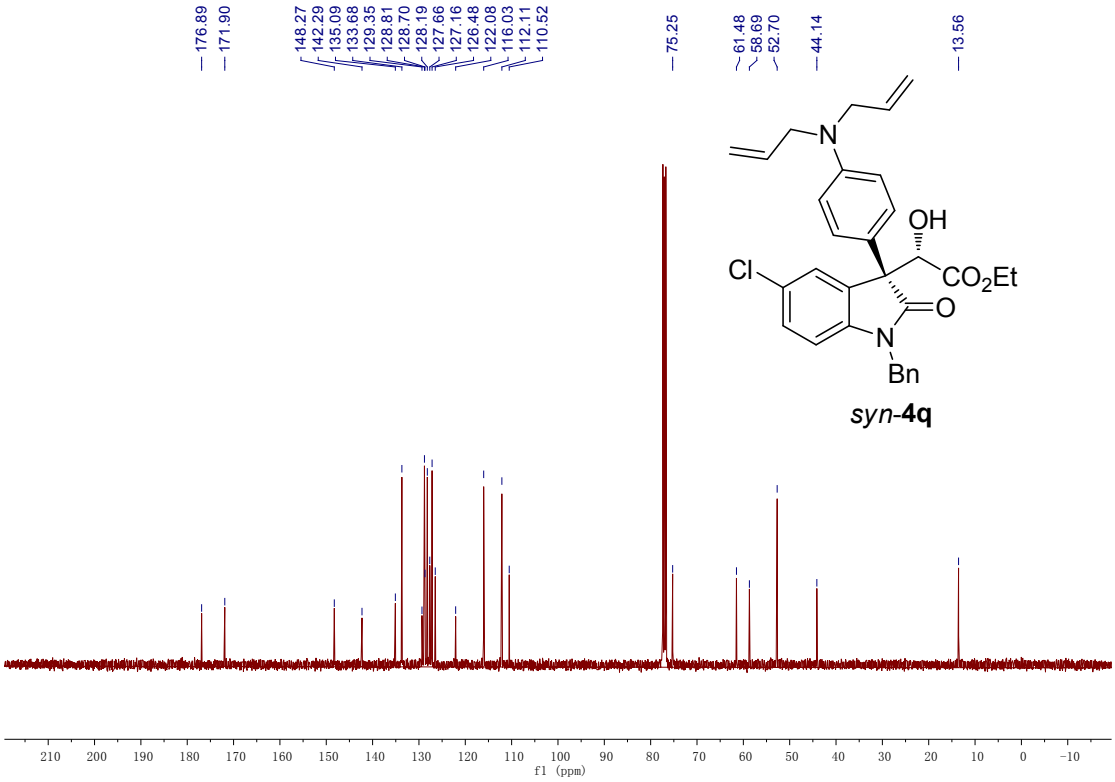
18.51 2.02 1.05 1.00 1.00 1.00 3.97 5.00 1.00 3.16
9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0 -0.5 -1.0
f1 (ppm)


176.49
171.89
152.67
139.08
128.93
128.83
128.28
128.15
127.70
127.11
126.77
126.60
111.81
110.60
75.22
61.65
59.25
55.75
55.59
44.16
13.67
Bn2N
OMe
OH
Cl
CO2Et
O
N
Bn
syn-4o
f1 (ppm)

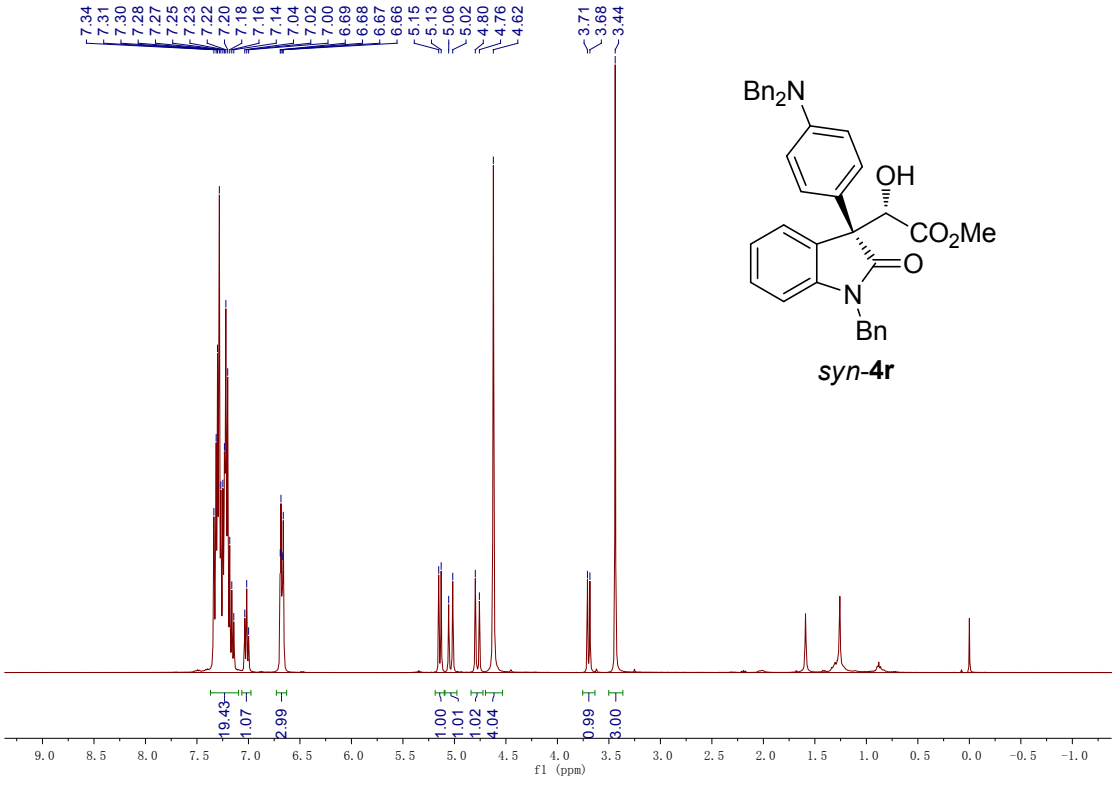

7.33
7.30
7.29
7.27
7.26
7.24
7.21
7.19
7.16
7.15
7.13
6.64
6.62
6.59
6.57
5.13
5.11
5.07
5.03
4.77
4.73
4.50
3.98
3.96
3.53
3.50
3.48
3.47
3.45
1.21
1.19
1.17
0.92
0.90
0.89
Ph
N
OH
Cl
CO2Et
O
N
Bn
syn-4p
14.97
3.04
1.00
1.00
1.01
2.02
2.03
3.04
3.09
3.05
f1 (ppm)


176.91
171.90
147.99
142.28
138.95
135.10
129.37
128.82
128.69
128.58
128.34
127.66
127.17
126.85
126.46
121.84
111.96
110.52
75.25
61.49
58.68
53.84
45.34
44.14
13.57
12.13
Ph
N
OH
Cl
CO2Et
O
N
Bn
syn-4p
f1 (ppm)

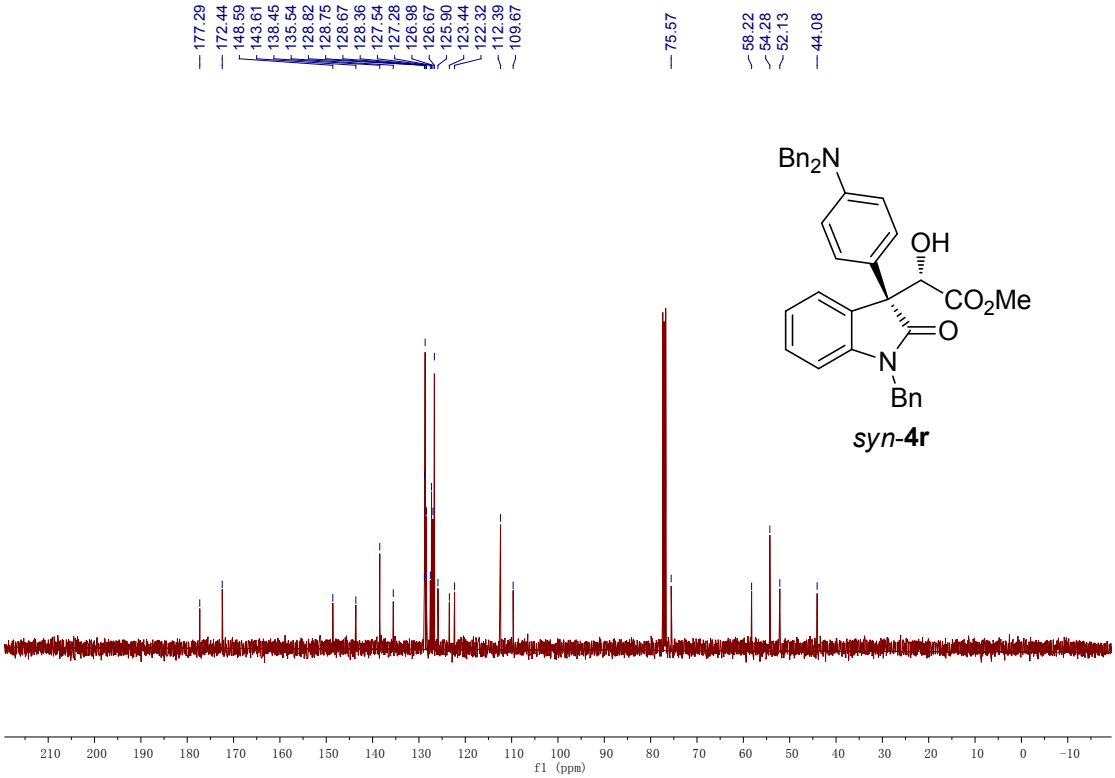

7.34
7.32
7.28
7.26
7.22
7.16
7.14
6.65
6.63
6.60
6.58
5.83
5.82
5.81
5.80
5.12
5.07
5.03
4.03
4.00
3.99
3.97
3.95
3.53
0.93
0.91
0.89
N
OH
Cl
CO2Et
O
N
Bn
syn-4q
9.46
3.00
1.92
5.99
1.05
5.96
1.09
3.06
f1 (ppm)


176.89
171.90
148.27
142.29
135.09
133.68
129.35
128.81
128.70
128.19
127.66
127.16
126.48
122.08
116.03
112.11
110.52
75.25
61.48
58.69
52.70
44.14
13.56
N
OH
Cl
CO2Et
O
N
Bn
f1 (ppm)

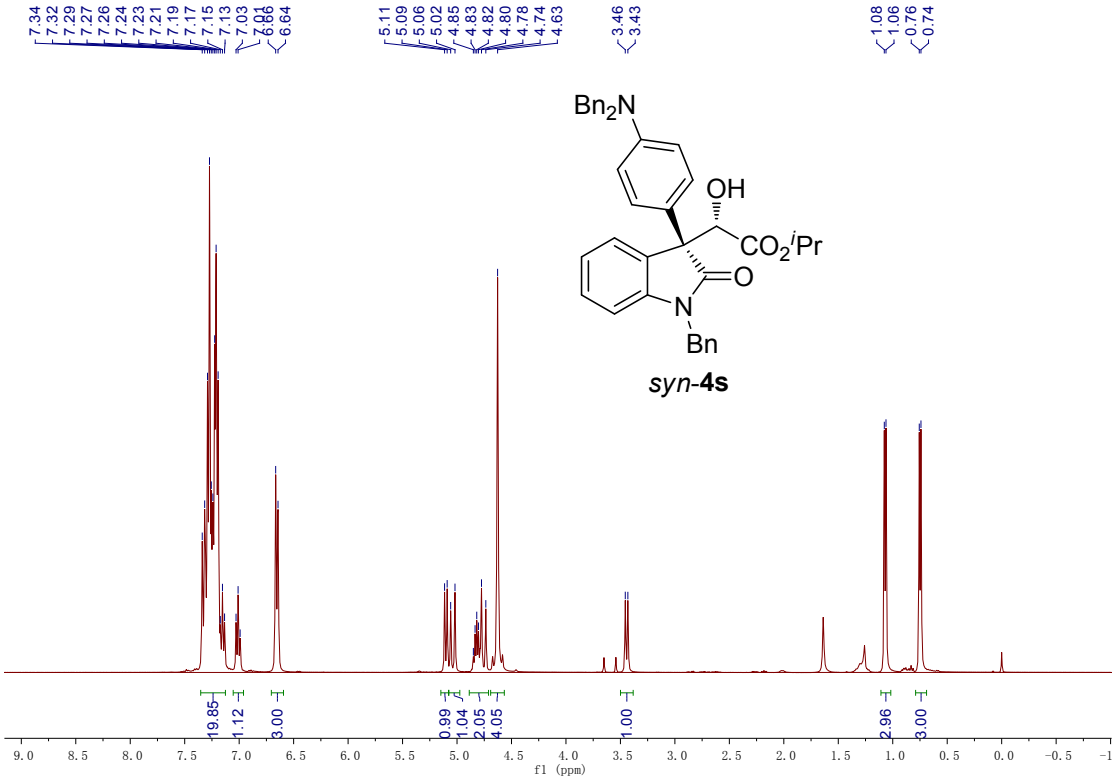
syn-**4q**


7.34
7.31
7.30
7.28
7.27
7.25
7.23
7.22
7.20
7.18
7.16
7.14
7.04
7.02
7.00
6.69
6.68
6.67
6.66
5.15
5.13
5.06
5.02
4.80
4.76
4.62
3.71
3.68
3.44
Bn2N
OH
CO2Me
O
N
Bn
19.43
1.07
2.99
1.00
1.01
1.02
4.04
0.99
3.00
f1 (ppm)

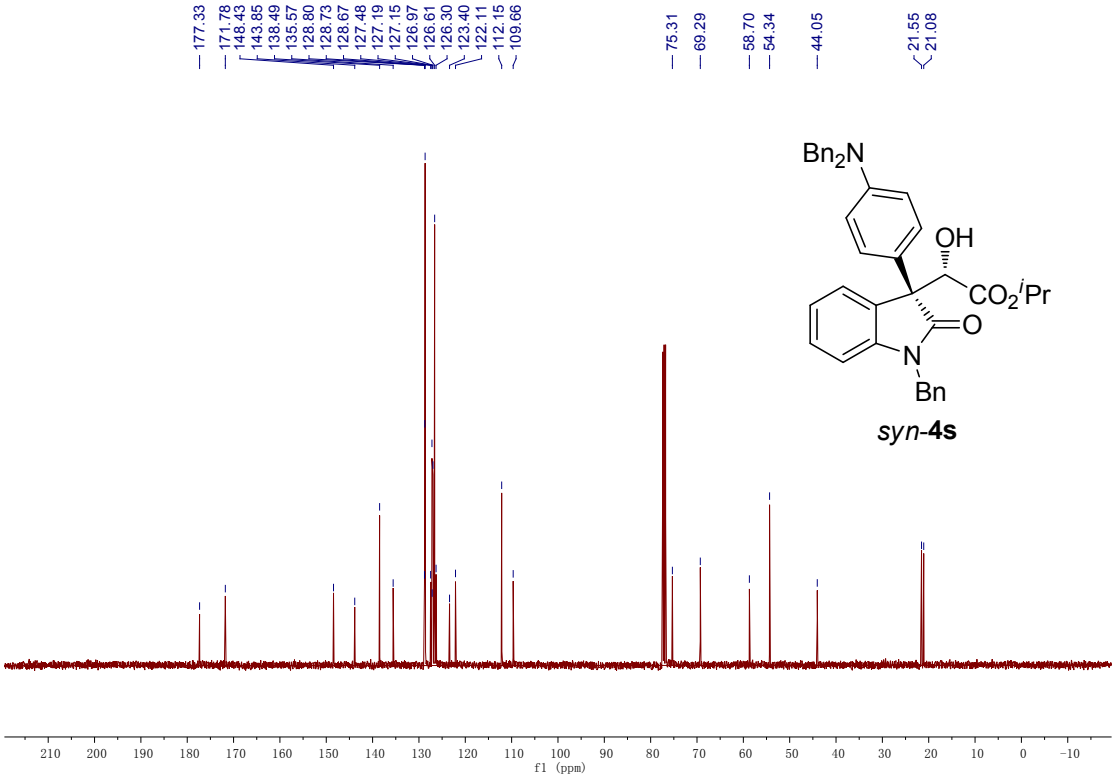
syn-**4r**


177.29
172.44
148.59
143.61
138.45
135.54
128.82
128.75
128.67
128.36
127.54
127.28
126.98
126.67
125.90
123.44
122.32
112.39
109.67
75.57
58.22
54.28
52.13
44.08
Bn2N
OH
CO2Me
O
N
Bn
f1 (ppm)

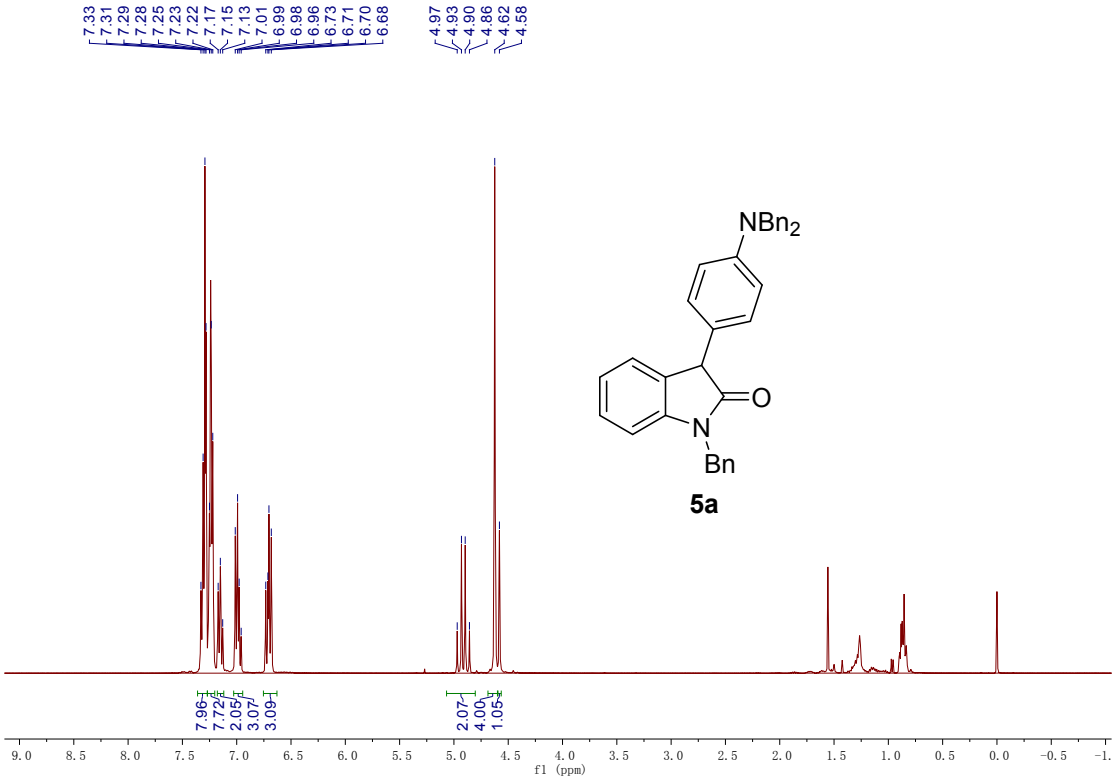
syn-**4r**


7.34
7.32
7.29
7.27
7.26
7.24
7.23
7.21
7.19
7.17
7.15
7.13
7.03
6.66
6.64
5.11
5.09
5.06
5.02
4.85
4.83
4.82
4.80
4.78
4.74
4.63
3.46
3.43
1.08
1.06
0.76
0.74
Bn2N
OH
CO2iPr
O
N
Bn
19.85
1.12
3.00
0.99
1.04
2.05
4.05
1.00
2.96
3.00
f1 (ppm)

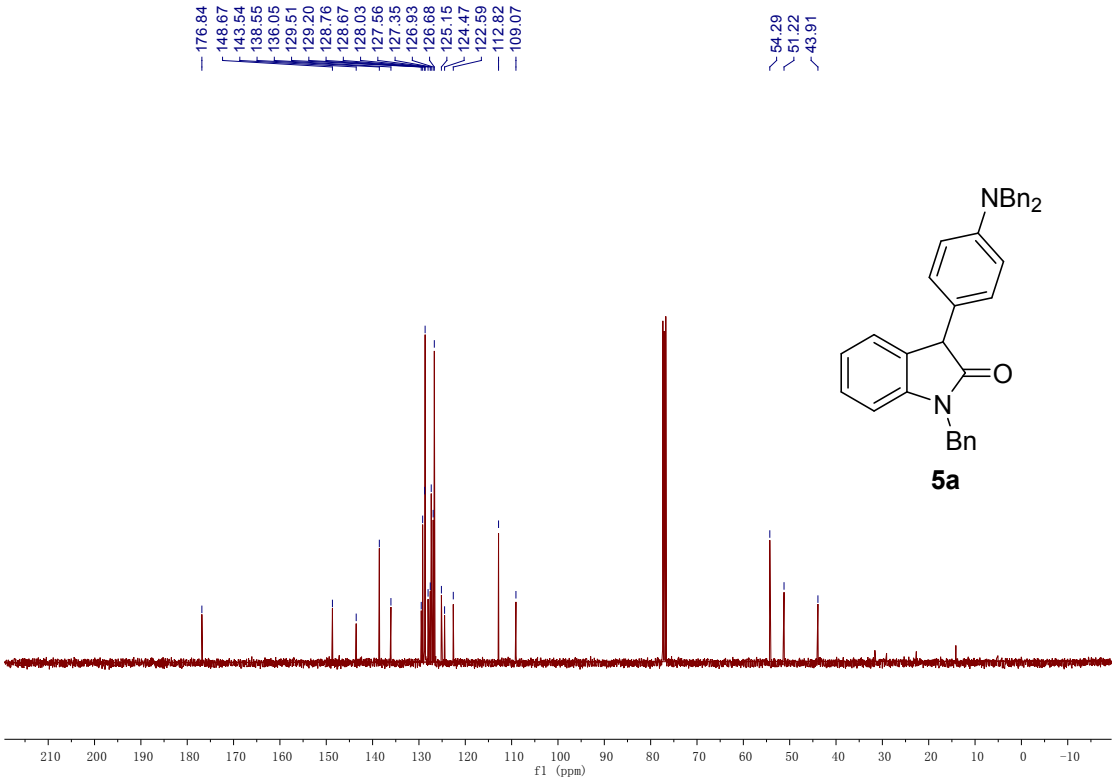
syn-**4s**

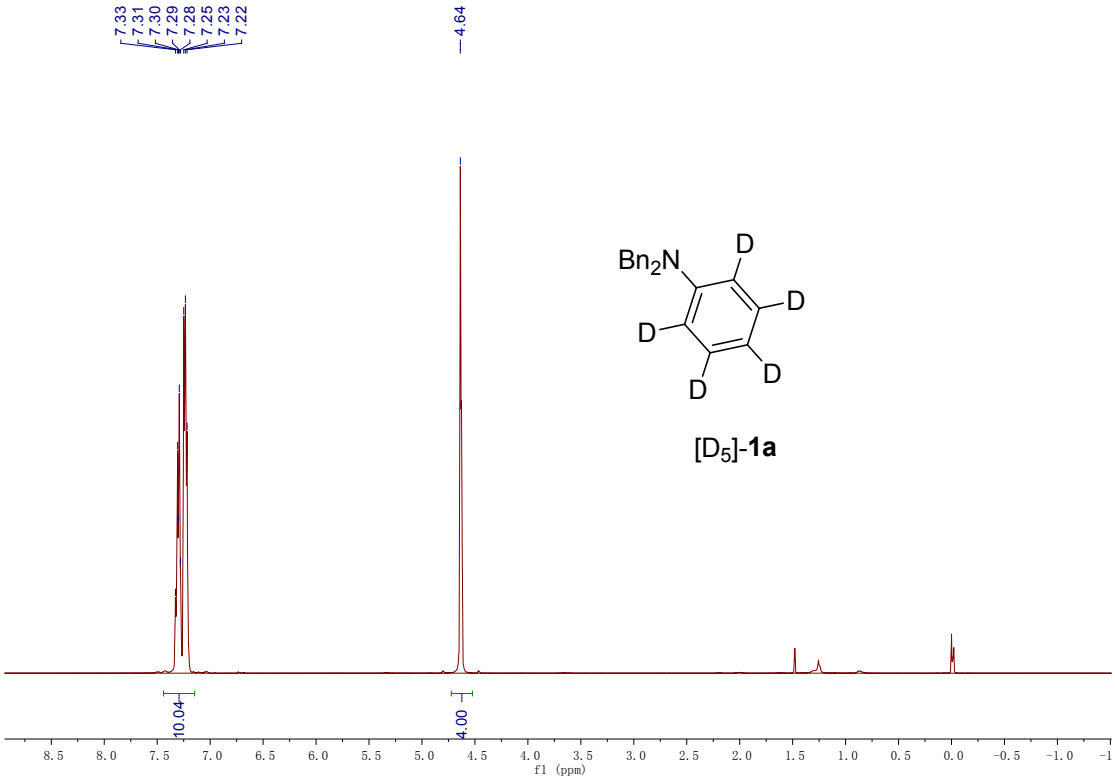

177.33
171.78
148.43
143.85
138.49
135.57
128.80
128.73
128.67
127.48
127.19
127.15
126.97
126.61
126.30
123.40
122.11
112.15
109.66
75.31
69.29
58.70
54.34
44.05
21.55
21.08
Bn2N
OH
CO2iPr
O
N
Bn
f1 (ppm)

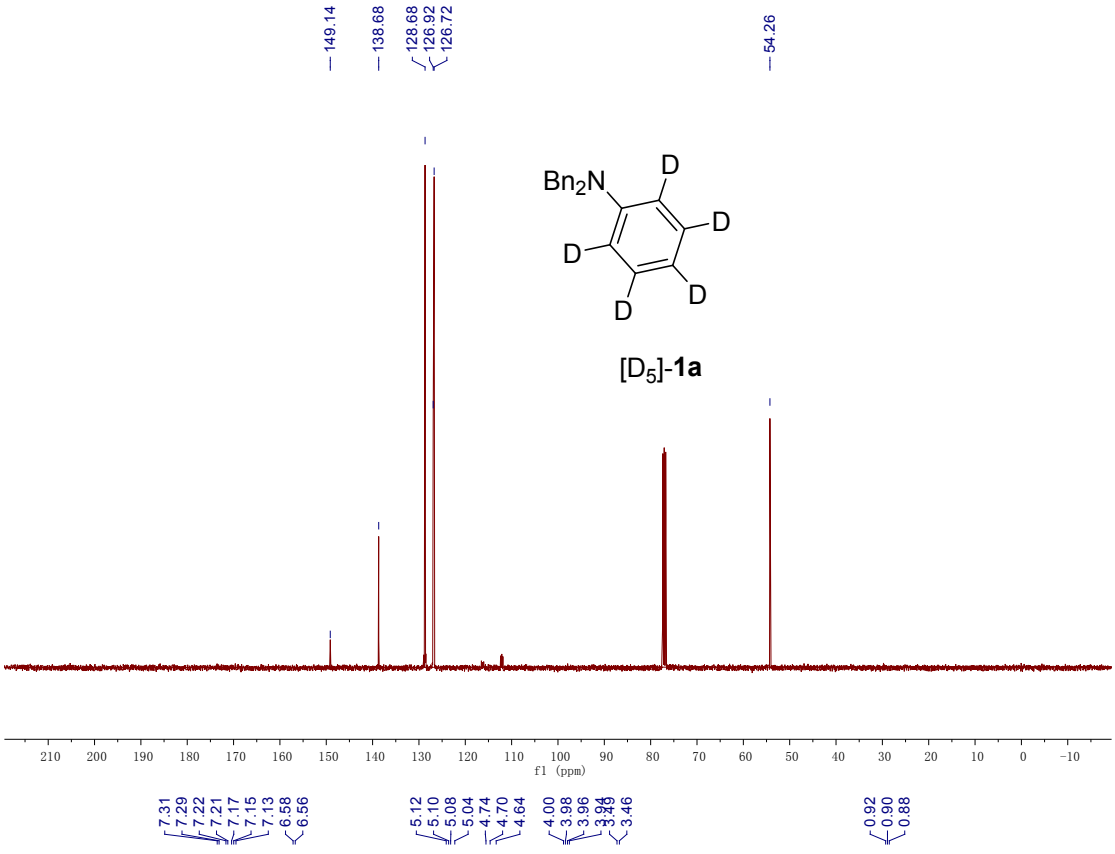
syn-**4s**

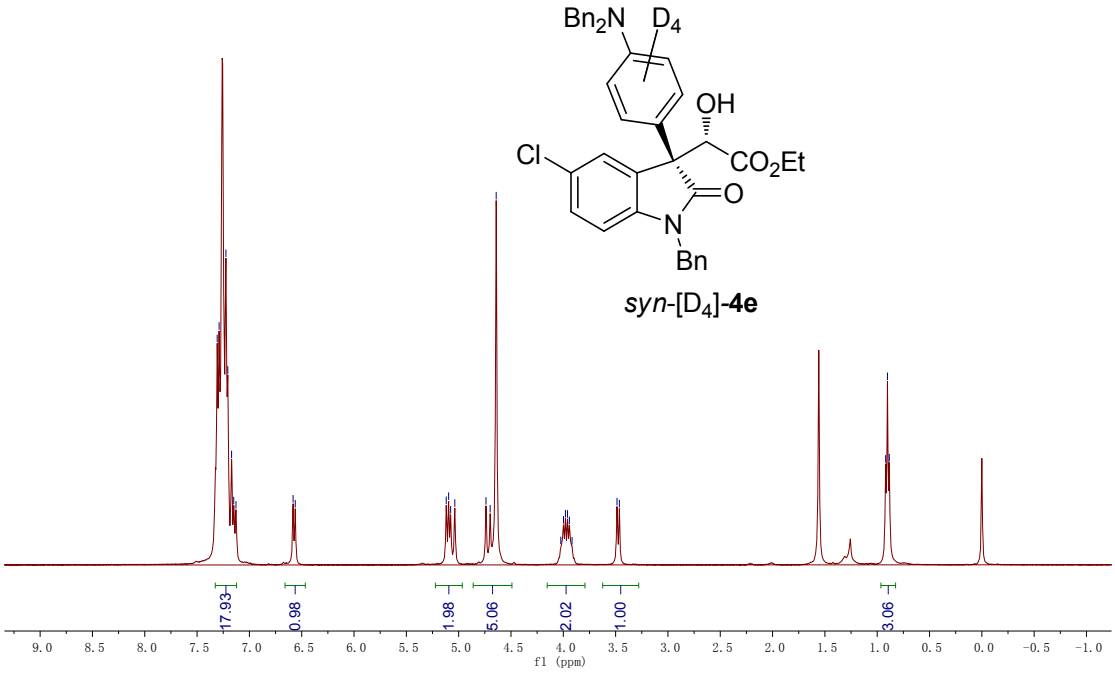

7.33
7.31
7.29
7.28
7.25
7.23
7.22
7.17
7.15
7.13
7.01
6.99
6.98
6.96
6.73
6.71
6.70
6.68
4.97
4.93
4.90
4.86
4.62
4.58
NBn2
O
N
Bn
7.96
7.72
2.05
3.07
3.09
2.07
4.00
1.05
f1 (ppm)

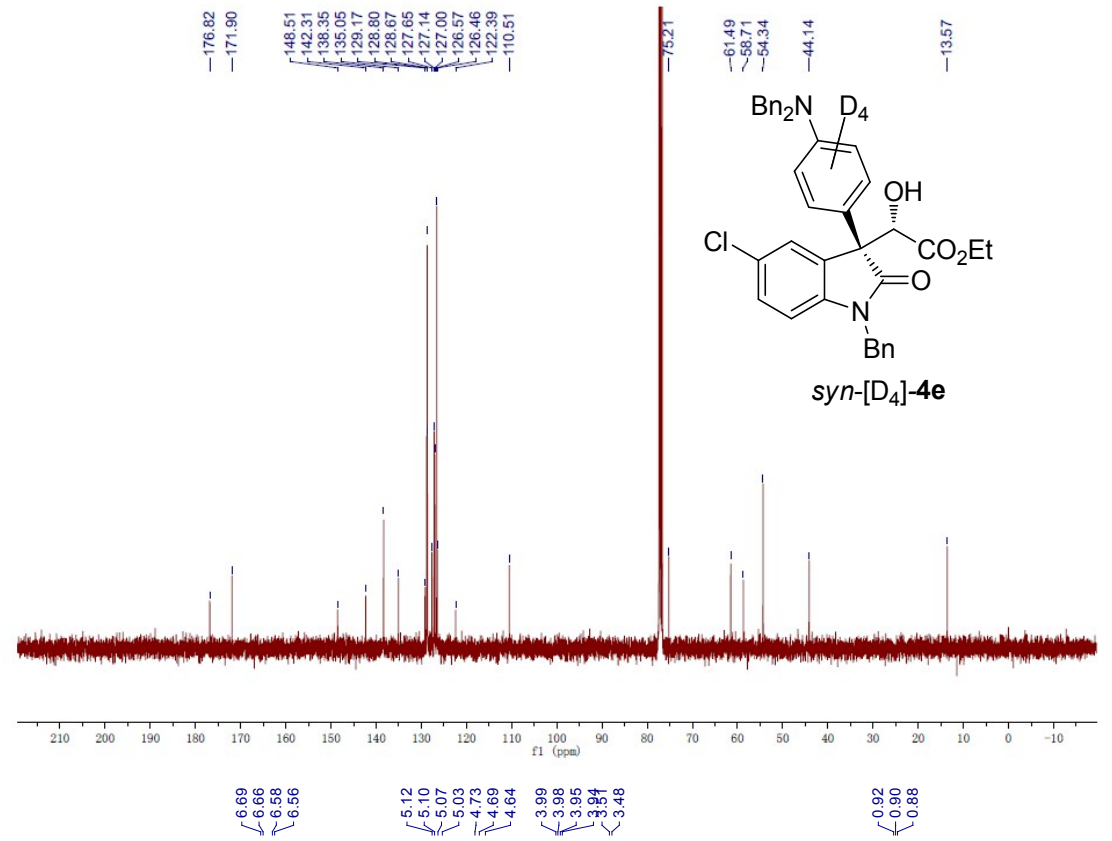
5a


176.84
148.67
143.54
138.55
136.05
129.51
129.20
128.76
128.67
128.03
127.56
127.35
126.93
126.68
125.15
124.47
122.59
112.82
109.07
54.29
51.22
43.91
NBn2
O
N
Bn
5a
f1 (ppm)

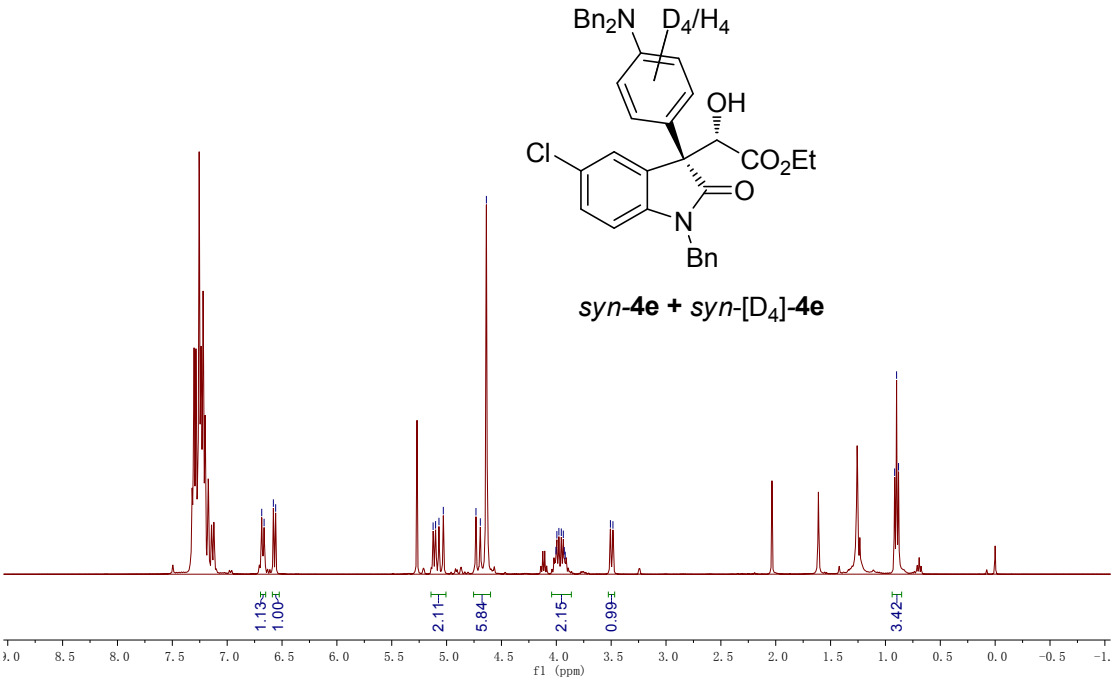

7.33
7.31
7.30
7.29
7.28
7.25
7.23
7.22
4.64
Bn2N
D
D
D
D
D
[D5]-1a
10.04
4.00
f1 (ppm)


149.14
138.68
128.68
126.92
126.72
54.26
Bn2N
D
D
D
D
D
[D5]-1a
f1 (ppm)
7.31
7.29
7.22
7.21
7.17
7.15
7.13
6.58
6.56
5.12
5.10
5.08
5.04
4.74
4.70
4.64
4.00
3.98
3.96
3.94
3.49
3.46
0.92
0.90
0.88


Bn2N
D4
OH
Cl
CO2Et
O
N
Bn
syn-[D4]-4e
17.93
0.98
1.98
5.06
2.02
1.00
3.06
f1 (ppm)



syn-[D_4]-**4e**



syn-**4e** + *syn*-[D_4]-**4e**