Supporting Information:

Organocatalytic Stereocontrolled Synthesis of 3,3'- Pyrrolidinyl Spirooxindoles by [3+2] Annulation of Isocyanoesters with Methyleneindolinones

Liang-Liang Wang,[†,‡] Jian-Fei Bai,[†,‡] Lin Peng,[†,‡] Liang-Wen Qi,[†,‡] Li-Na Jia,[†,‡] Yun-Long Guo,[†,‡] Xi-Ya Luo,[†,‡] Xiao-Ying Xu,*[,†] and Li-Xin Wang*[,†]

[†]*Key Laboratory of Asymmetric Synthesis and Chirotechnology of Sichuan Province, Chengdu Institute of Organic Chemistry, Chinese Academy of Sciences,Chengdu 610041, China;* [‡] *Graduate University of Chinese Academy of Science, Beijing, China. E-mail: wlxioc@cioc.ac.cn; xuxy@cioc.ac.cn.*

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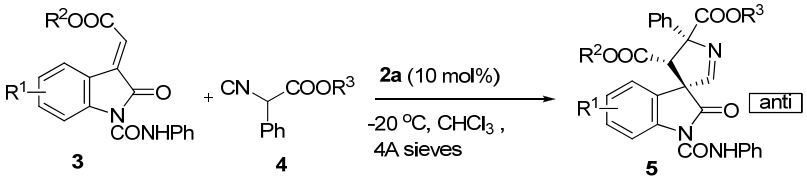
1. General methods

Commercial grade solvent was dried and purified by standard procedures as specified in Purification of Laboratory Chemicals, 4th Ed (Armarego, W. L. F.; Perrin, D. D. Butterworth Heinemann: 1997). NMR spectra were recorded with tetramethylsilane as the internal standard. ^{1}H NMR spectra were recorded at 300 MHz, and ^{13}C NMR spectra were recorded at 75 MHz (Bruker Avance). ^{1}H NMR chemical shifts (δ) are reported in ppm relative to tetramethylsilane (TMS) with the solvent signal as the internal standard ($CDCl_3$ at 7.26 ppm, $(CD_3)_2SO$ at 2.50 ppm). ^{13}C NMR chemical shifts are reported in ppm from tetramethylsilane (TMS) with the solvent resonance as the internal standard ($CDCl_3$ at 77.00 ppm, $(CD_3)_2SO$ at 39.52 ppm). Data are given as: s (singlet), d (doublet), t (triplet), q (quartet), dd (double of doublet) or m (multiplets), coupling constants (Hz) and integration. Flash column chromatography was carried out using silica gel eluting with ethyl acetate and petroleum ether. High-resolution mass spectra were obtained with the Q-TOF-Premier mass spectrometer. Reactions were monitored by TLC and visualized with ultraviolet light. Enantiomeric excess was determined by HPLC analysis on chiralpak AD-H, or OD-H columns. IR spectra were recorded on a ThermoFisher Nicolet Avatar 360 FTIR spectrometer on a KBr beamsplitter. Optical rotations are reported as follows: $[\alpha]^{20}_{D}$ (C in g/per 100 mL, DCM).

2. Typical Procedure for the Asymmetric [3+2] Cycloaddition Reaction with N-phenyl amide protected Methyleneindolinones

All starting materials were purchased from commercial supplier and used without further purification. Substrates **3, 4** were prepared according to literature methods,[1] purified by chromatography.

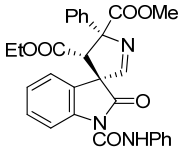
1. (a) B. Tan, N. R. Candeias and C. F. Barbas III., *J. Am. Chem. Soc*., 2011, **133**, 4672; (b) J. Song, C. Guo, P. H. Chen, J. Yu, S. W. Luo and L. Z. Gong, *Chem. Eur. J.*, 2011, **17**, 7786.



Typical Procedure for synthesis of 5a-l: Methyleneindolinones **3 (**0.2 mmol**)** and Isocyanoesters **4 (**0.3 mmol**)** were dissolved in 1.0 mL $CHCl_3$, and 4 Å MS (200 mg) was added. When the mixture was cooled to -20 °C, catalyst **2a** (10 % mmol) was added. After stirred for the indicated time, the reaction mixture was directly subjected

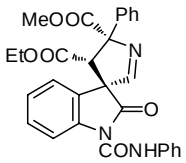
to flash column chromatography on silica gel (petroleum ether/ethyl acetate) to afford the corresponding pure products **5**.

(3R, 4'S, 5'R)-4'-ethyl 5'-methyl 2-oxo-5'-phenyl-1-(phenylcarbamoyl)-4',5' dihydrospiro[indoline-3,3'-pyrrole]-4',5'-dicarboxylate (5a)



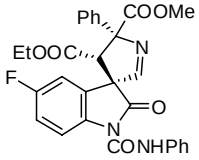
White solid, $[\alpha]_D^{20}$ = -132.8 (*c* 1.16, DCM), 60 % yield, 2.7:1 dr, 95 % ee; HPLC: Chiralcel AD-H column, hexane/i-PrOH = 85/15, flow rate 1.0 mL/min, UV detection at 220 nm, t_{major} = 23.3 min, t_{minor} = 25.7 min; ^{1}H NMR ($CDCl_3$, 300 MHz) δ 0.78 (t, J = 7.1 Hz, 3H), 3.55-3.67 (m, 2H), 3.83 (s, 3H), 4.83 (s, 1H), 7.11-7.19 (m, 3H), 7.34-7.37 (m, 6H), 7.51-7.57 (m, 3H), 7.63-7.66 (m, 2H), 8.35 (d, J = 8.3 Hz, 1H), 10.30 (s, 1H); ^{13}C NMR ($CDCl_3$, 75 MHz) δ 13.4, 53.5, 59.9, 60.8, 69.4, 89.4, 116.6, 120.7, 122.4, 124.8, 125.0, 126.1, 126.3, 128.2 (2C), 129.0, 130.4, 136.5, 138.3, 140.9, 148.4, 161.8, 166.8, 171.8, 176.0; HRMS (ESI) Calcd. For C29H25N3O6 $[M+Na]^+$: 534.1636, Found: 524.1641; IR (KBr) ν 3253.3, 1736.1, 1599.0, 1552.9, 1447.8, 1242.0, 1166.0, 1022.8, 759.6, 694.4 cm^{-1}.

(3R,4'S,5'S)-diethyl 2-oxo-5'-phenyl-1-(phenylcarbamoyl)-4',5'-dihydrospiro-[indoline-3,3'-pyrrole]-4',5'-dicarboxylate (5a')



^{1}H NMR ($CDCl_3$, 300 MHz) δ 0.72 (t, J = 7.1 Hz, 3H), 3.76-3.92 (m, 5H), 4.21 (s, 1H), 7.15 (t, J = 7.5 Hz, 1H), 7.24-7.29 (m, 1H), 7.33-7.45 (m, 7H), 7.54 (d, J = 8.3 Hz, 2H), 7.61-7.63 (m, 2H), 7.82 (d, J = 7.7 Hz, 1H), 8.39 (d, J = 8.2 Hz, 1H), 10.43 (s, 1H); ^{13}C NMR ($CDCl_3$, 75 MHz) δ 13.3, 53.4, 61.5, 62.9, 70.9, 88.0, 116.5, 120.5, 123.7, 124.8, 125.6, 126.3, 126.8, 127.9, 128.3, 129.1, 130.1, 136.7, 140.4, 141.8, 148.6, 161.1, 167.8, 171.0, 177.5; HRMS (ESI) Calcd. for C29H25N3O6 $[M+Na]^+$: 534.1636, Found: 534.1641 ;

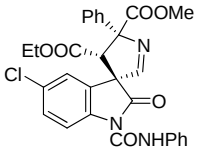
(3R,4'S,5'R)-4'-ethyl 5'-methyl 5-fluoro- 2-oxo- 5'-phenyl-1 -(phenylcarbamoyl) - 4',5' - dihydrospiro[indoline-3,3'-pyrrole]-4',5'-dicarboxylate (5b)



White solid, $[\alpha]_D^{20}$ = - 127.8 (*c* 1.03, DCM), 53% yield, 6.2:1 dr, 92 % ee; HPLC: Chiralcel AD-H column, hexane/i-PrOH = 85/15, flow rate 1.0 mL/min, UV detection at 220 nm, t_{major} = 25.2 min, t_{minor} = 20.4 min; ^{1}H NMR ($CDCl_3$, 300 MHz) δ 0.84 (t, J = 7.1 Hz, 3H), 3.61-3.70 (m, 2H), 3.85 (s, 3H), 4.83 (s, 1H), 6.96-6.98 (m, 1H), 7.12-7.21 (m, 2H), 7.36-7.40 (m, 5H), 7.52-7.56 (m, 3H), 7.63 (d, J = 7.4 Hz, 2H), 8.34-8.37 (m, 1H), 10.24 (s, 1H); ^{13}C NMR ($CDCl_3$, 75 MHz) δ 13.5, 53.7, 60.1, 61.2, 69.4, 89.7, 114.1 (d, J = 26.1 Hz, 1C), 117.1 (d, J = 22.5 Hz, 1C), 118.0 (d, J = 7.7 Hz, 1C), 120.5, 120.9, 125.1, 126.3, 128.4, 128.5, 129.2, 136.4, 136.9, 138.2, 148.4, 159.9 (d, J = 243.7 Hz, 1C), 161.3, 166.8, 171.7, 175.7; HRMS (ESI) Calcd. for C29H24FN3O6

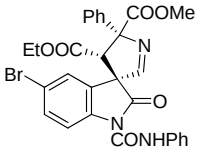
$[M+H]^+$: 530.1722, Found: 530.1712; IR (KBr) *v* 3254.0, 1736.5, 1600.4, 1555.5, 1481.1, 1447.9, 1292.4, 1240.9, 1160.7, 754.9 cm^{-1}.

(3R,4'S,5'R)-4'-ethyl 5'-methyl 5-chloro-2-oxo-5'-phenyl-1-(phenylcarbamoyl) -4',5'-dihydrospiro[indoline-3,3'-pyrrole]-4',5'-dicarboxylate (5c)



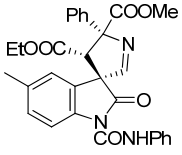
White solid, $[\alpha]_D^{20}$ = - 93.2 (*c* 1.20, DCM), 61 % yield, 7.0:1 dr, 92 % ee; HPLC: Chiralcel AD-H column, hexane/i-PrOH = 85/15, flow rate 1.0 mL/min, UV detection at 220 nm, t_{major} = 30.8 min, t_{minor} = 22.4 min; ^{1}H NMR ($CDCl_3$, 300 MHz) δ 0.83 (t, *J* = 7.1 Hz, 3H), 3.60-3.70 (m, 2H), 3.85 (s, 3H), 4.82 (s, 1H), 7.16-7.21 (m, 2H), 7.35-7.42 (m, 6H), 7.52-7.56 (m, 3H), 7.64 (d, *J* = 6.8 Hz, 2H), 8.32 (d, *J* = 8.9 Hz, 1H), 10.2 (s, 1H); ^{13}C NMR ($CDCl_3$, 75 MHz) δ 13.5, 53.7, 60.3, 61.3, 69.2, 89.7, 117.9, 120.9, 124.1, 125.1, 126.3, 126.6, 128.4, 128.7, 129.2, 130.5, 130.8, 136.3, 138.2, 139.4, 148.3, 161.1, 166.8, 171.6, 175.5; HRMS (ESI) Calcd. for C29H24ClN3O6 $[M+H]^+$: 546.1426, Found: 546.1429; IR (KBr) *v* 3248.9, 1734.9, 1600.3, 1556.7, 1466.1, 1293.0, 1239.4, 1164.5, 756.3, 691.7 cm^{-1}.

(3R,4'S,5'R)-4'-ethyl 5'-methyl 5-bromo-2-oxo-5'-phenyl- 1-(phenylcarbamoyl) -4',5'-dihydrospiro[indoline-3,3'-pyrrole]-4',5'-dicarboxylate (5d)



White solid, $[\alpha]_D^{20}$ = - 96.6 (*c* 1.36, DCM), 64 % yield, 8.0:1 dr, 94 % ee; HPLC: Chiralcel AD-H column, hexane/i-PrOH = 85/15, flow rate 1.0 mL/min, UV detection at 220 nm, t_{major} = 33.5 min, t_{minor} = 24.1 min; ^{1}H NMR (DMSO, 300 MHz) δ 0.77 (t, *J* = 7.1 Hz, 3H), 3.53-3.59 (m, 2H), 3.71 (s, 3H), 4.80 (s, 1H), 7.12 (s, 1H), 7.18 (d, *J* = 7.4 Hz, 1H), 7.36-7.49 (m, 7H), 7.59-7.66 (m, 3H), 7.82 (s, 1H), 7.93 (d, *J* = 8.7 Hz, 1H), 10.29 (s, 1H); ^{13}C NMR (DMSO, 75 MHz) δ 13.2, 53.1, 59.5, 60.5, 68.6, 89.0, 116.0, 116.8, 120.2, 124.5, 125.4, 126.2, 128.2, 128.2, 129.0, 129.1, 132.5, 136.9, 138.6, 140.2, 147.8, 163.1, 166.9, 171.2, 174.0; HRMS (ESI) Calcd. for C29H24BrN3O6 $[M+H]^+$: 590.0929, Found: 590.0910; IR (KBr) *v* 3248.0, 1733.4, 1600.5, 1557.0, 1463.8, 1293.4, 1239.5, 1164.8, 756.1, 691.6 cm^{-1}.

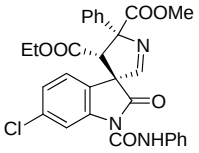
(3R,4'S,5'R)-4'-ethyl 5'-methyl 5-methyl-2-oxo-5'-phenyl- 1- (phenylcarbamoyl) -4',5'-dihydrospiro[indoline-3,3'-pyrrole]-4',5'-dicarboxylate (5e)



White solid, $[\alpha]_D^{20}$ = - 132.7 (*c* 1.10, DCM), 61 % yield, 7.2:1 dr, 97 % ee; HPLC: Chiralcel AD-H column, hexane/i-PrOH = 85/15, flow rate 1.0 mL/min, UV detection at 220 nm, t_{major} = 24.7 min, t_{minor} = 20.7 min; ^{1}H NMR ($CDCl_3$, 300 MHz) δ 0.79 (t, *J* = 7.11 Hz, 3H), 2.25(s, 3H), 3.57-3.72 (m, 2H), 3.84 (s, 3H), 4.80 (s, 1H), 6.99 (s, 1H), 7.15-7.22 (m, 2H), 7.34-7.40 (m, 5H), 7.52-7.57 (m, 3H), 7.66 (d, *J* = 6.9 Hz, 2H), 8.22 (d, *J* = 8.3 Hz, 1H), 10.30 (s, 1H); ^{13}C NMR ($CDCl_3$, 75 MHz) δ 13.5, 20.9, 53.6, 60.1, 60.9, 69.5, 89.4, 116.4, 120.8, 122.4, 124.9, 126.3, 126.7, 128.2, 128.3, 128.6, 129.1, 130.9,

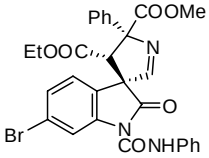
134.9, 136.6, 138.6, 148.6, 162.1, 167.0, 171.9, 176.1; HRMS (ESI) Calcd. for C30 H27N3O6 $[M+H]^+$: 526.1973, Found: 526.1970; IR (KBr) *v* 3252.3, 1735.7, 1598.7, 1555.7, 1487.8, 1447.8, 1307.9, 1158.1, 755.3, 695.1 cm^{-1}.

(3R,4'S,5'R)-4'-ethyl 5'-methyl 6-chloro-2-oxo-5'-phenyl-1-(phenylcarbamoyl) -4',5'-dihydrospiro[indoline-3,3'-pyrrole]-4',5'-dicarboxylate (5f)



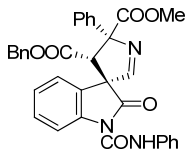
White solid, $[\alpha]_D^{20}$ = - 132.4 (*c* 0.48, DCM), 53 % yield, 5.1:1 dr, 92 % ee; HPLC: Chiralcel AD-H column, hexane/i-PrOH = 85/15, flow rate 1.0 mL/min, UV detection at 220 nm, t_{major} = 18.6 min, t_{minor} = 21.8 min; ^{1}H NMR ($CDCl_3$, 300 MHz) δ 0.84 (t, *J* = 7.1, 3H), 3.57-3.68 (m, 2H), 3.84 (s, 3H), 4.81 (s, 1H), 7.12 (s, 2H), 7.17-7.22 (m, 1H), 7.32-7.42 (m, 5H),7.50 (s, 1H), 7.56 (d, *J* = 8.0 Hz, 2H), 7.62 (d, *J* = 6.9 Hz, 2H), 8.45 (s, 1H), 10.23 (s, 1H); ^{13}C NMR ($CDCl_3$, 75 MHz) δ 13.5, 53.6, 60.0, 61.1, 69.2, 89.7, 117.4, 120.9, 125.1, 125.2, 126.4, 127.3, 128.4, 128.5, 129.2, 136.3, 136.6, 138.2, 141.7, 148.2, 161.3, 166.9, 171.7, 176.0 (one carbon missing); HRMS (ESI) Calcd. for C29 H24ClN3O6 $[M+H]^+$: 546.1426, Found: 546.1422; IR (KBr) *v* 3258.5, 1738.3, 1598.4, 1553.0, 1448.0, 1287.9, 1165.3, 1023.6, 756.1, 694.7 cm^{-1}.

(3R,4'S,5'R)-4'-ethyl 5'-methyl 6-bromo-2-oxo-5'-phenyl-1-(phenylcarbamoyl) -4',5'-dihydrospiro[indoline-3,3'-pyrrole]-4',5'-dicarboxylate (5g)



White solid, $[\alpha]_D^{20}$ = - 100.3 (*c* 0.51, DCM), 50 % yield, 3.9:1 dr, 90 % ee; HPLC: Chiralcel AD-H column, hexane/i-PrOH = 85/15, flow rate 1.0 mL/min, UV detection at 220 nm, t_{major} = 18.3 min, t_{minor} = 21.9 min; ^{1}H NMR ($CDCl_3$, 300 MHz) δ 0.84 (t, *J* = 7.1 Hz, 3H), 3.58-3.70 (m, 2H), 3.84 (s, 3H), 4.81(s, 1H), 7.06 (d, *J* = 8.3 Hz, 1H), 7.19-7.29 (m, 2H), 7,37-7.42 (m, 5H), 7.50 (s, 1H), 7.55 (d, *J* = 7.6 Hz, 2H), 7.60-7.63 (m, 2H), 8.61 (s, 1H), 10.22 (1H); ^{13}C NMR ($CDCl_3$, 75 MHz) δ 13.5, 53.7, 60.0, 61.2, 69.2, 89.7, 120.2, 120.9, 121.3, 124.6, 125.2, 126.3, 127.6, 128.2, 128.4, 128.5, 129.2, 136.3, 138.1, 141.8, 148.2, 161.3, 166.9, 171.7, 175.8; HRMS (ESI) Calcd. for C29H24BrN3O6 $[M+H]^+$: 590.0921, Found: 590.0911; IR (KBr) *v* 3250.5, 1739.2, 1682.5, 1597.4, 1552.3, 1447.9, 1287.6, 1160.4, 754.2, 694.2 cm^{-1}.

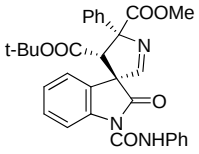
(3R,4'S,5'R)-4'-benzyl 5'-methyl 2-oxo-5'-phenyl-1-(phenylcarbamoyl) -4',5'-dihydrospiro-[indoline-3,3'-pyrrole]-4',5'-dicarboxylate (5h)



White solid, $[\alpha]_D^{20}$ = - 149.7 (*c* 0.88, DCM), 45 % yield, 3.2:1 dr, 95 % ee; HPLC: Chiralcel AD-H column, hexane/i-PrOH = 85/15, flow rate 1.0 mL/min, UV detection at 220 nm, t_{major} = 49.7 min, t_{minor} = 42.9 min; ^{1}H NMR ($CDCl_3$, 300 MHz) δ 3.84 (s, 3H), 4.45 (d, *J* = 12.0 Hz, 1H), 4.63 (d, *J* = 12.0 Hz, 1H), 4.90 (s, 1H), 6.91-6.94 (m, 2H), 6.99-7.05 (m, 1H), 7.10-7.13 (m, 1H), 7.16-7.23 (m, 5H), 7.34-7.41 (m, 6H), 7.52-7.57 (m, 2H), 7.61-7.63 (m, 2H), 8.34 (d, *J* = 8.2 Hz, 1H), 10.28 (s, 1H); ^{13}C NMR ($CDCl_3$, 75

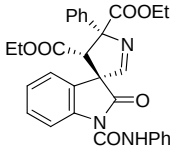
MHz) δ 53.6, 59.9, 66.9, 69.5, 89.6, 116.8, 120.9, 122.3, 124.9, 125.1, 126.3, 126.4, 128.3, 128.4, 128.5, 128.9, 129.0, 129.1, 130.5, 134.4, 136.6, 138.3, 140.9, 148.5, 161.8, 166.8, 171.8, 176.1; HRMS (ESI) Calcd. for C34H27N3O6 $[M+H]^+$: 547.1973,Found: 574.1971; IR (KBr) ν 3253.1, 1731.9, 1598.8, 1477.1, 1464.1, 1447.8, 1259.9, 1166.8, 757.7, 695.6 cm^{-1}.

(3R,4'S,5'R)-4'-tert-butyl 5'-methyl 2-oxo-5'-phenyl-1-(phenylcarbamoyl) -4',5'-dihydrospiro[indoline-3,3'-pyrrole]-4',5'-dicarboxylate (5i)



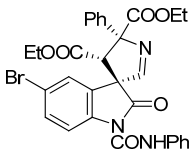
White solid, $[\alpha]_D^{20}$ = - 131.0 (*c* 0.75, DCM), 41 % yield, 2.8:1 dr, 96 % ee; HPLC: Chiralcel OD-H column, hexane/i-PrOH = 85/15, flow rate 1.0 mL/min, UV detection at 220 nm, t_{major} = 9.2 min, t_{minor} = 18.6 min; ^{1}H NMR ($CDCl_3$, 300 MHz) δ 0.96 (s, 9H), 3.84 (s, 3H), 4.69 (s, 1H), 7.10 (t, *J* = 7.6 Hz, 1H), 7.18 (t, *J* = 7.5 Hz, 1H), 7.25 (s, 1H), 7.34-7.44 (m, 6H), 7.55-7.59 (m, 3H), 7.68 (d, *J* = 7.2 Hz, 2H), 8.37 (d, *J* = 8.3 Hz, 1H), 10.34 (s, 1H); ^{13}C NMR ($CDCl_3$, 75 MHz) δ 27.3, 53.5, 60.4, 69.6, 82.5, 89.3, 116.6, 120.9, 122.5, 124.9, 125.0, 126.8, 127.0, 128.2, 128.3, 129.1, 130.4, 136.6, 138.3, 141.0, 148.7, 162.0, 166.0, 172.1, 176.4; HRMS (ESI) Calcd. for C31H29N3O6 $[M+H]^+$: 540.2129, Found: 540.2111; IR (KBr) ν 3251.7, 1737.9, 1599.1, 1555.6, 1477.8, 1464.8, 1311.0, 1278.0, 758.2, 694.5 cm^{-1}.

(3R,4'S,5'R)-diethyl 2-oxo-5'-phenyl- 1-(phenylcarbamoyl)-4',5'- dihydrospiro [indoline-3,3'-pyrrole]-4',5'-dicarboxylate (5j)



White solid, $[\alpha]_D^{20}$ = - 149.5 (*c* 0.79, DCM), 41 % yield, 3.0:1 dr, 96 % ee; HPLC: Chiralcel AD-H column, hexane/i-PrOH = 85/15, flow rate 1.0 mL/min, UV detection at 220 nm, t_{major} = 18.2 min, t_{minor} = 20.5 min; ^{1}H NMR ($CDCl_3$, 300 MHz) δ 0.78 (t, *J* = 7.1 Hz, 3H), 1.29(t, *J* = 7.1 Hz, 3H), 3.59-3.65 (m, 2H), 4.29-4.36 (m, 2H), 4.84 (s, 1H), 7.09-7.20 (m, 3H), 7.34-7.43 (m, 6H), 7.53-7.58 (m, 3H), 7.63 (d, *J* = 7.0 Hz, 2H), 8.37 (d, *J* = 8.2 Hz, 1H), 10.35 (s, 1H); ^{13}C NMR ($CDCl_3$, 75 MHz) δ 13.5, 13.9, 59.8, 60.9, 62.6, 69.5, 89.6, 116.7, 120.7, 122.5, 124.9, 125.1, 126.3, 126.4, 128.3, 128.6, 129.1, 130.5, 136.6, 138.5, 140.9, 148.6, 161.7, 167.0, 171.2, 176.2; HRMS (ESI) Calcd. for C30H27N3O6 $[M+Na]^+$: 548.1792, Found: 548.1794; IR (KBr) ν 3252.9, 1736.6, 1599.0, 1555.5, 1464.5, 1310.4, 1278.1, 1166.4, 760.3, 694.2 cm^{-1}.

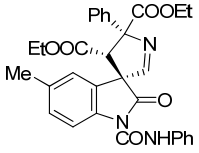
(3R,4'S,5'R)-diethyl-5-bromo-2-oxo-5'-phenyl-1-(phenylcarbamoyl)-4',5'- dihydr -ospiro-[indoline-3,3'-pyrrole]-4',5'-dicarboxylate (5k)



White solid, $[\alpha]_D^{20}$ = - 70.5 (*c* 1.08, DCM), 50 % yield, 5.6:1 dr, 94 % ee; HPLC: Chiralcel AD-H column, hexane/i-PrOH = 85/15, flow rate 1.0 mL/min, UV detection at 220 nm, t_{major} = 26.7 min, t_{minor} = 21.6 min; ^{1}H NMR ($CDCl_3$, 300 MHz) δ 0.83 (t, *J* = 7.0 Hz, 3H), 1.22-1.34 (m, 3H), 3.64 (t, *J* = 6.1 Hz, 2H), 4.31 (t, *J* = 7.2 Hz, 2H), 4.83 (s, 1H),

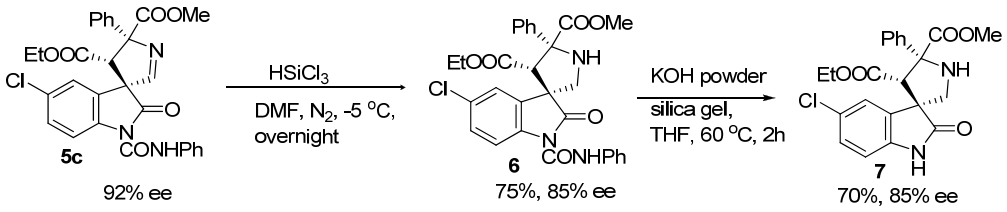
7.18 (t, *J* = 7.3 Hz, 1H), 7.35-7.40 (m, 6H), 7.53 (d, *J* = 8.8 Hz, 4H), 7.63 (d, *J* = 6.8 Hz, 2H), 8.26 (d, *J* = 8.7 Hz,1H), 10.24 (s, 1H); ^{13}C NMR ($CDCl_3$, 75 MHz) δ 13.5, 13.9, 60.2, 61.2, 62.7, 69.1, 89.8, 118.1, 118.2 120.8, 124.6, 125.1, 126.3, 127.4, 128.3, 129.2, 129.4, 133.4, 136.4, 138.5, 139.9, 148.3, 160.8, 166.9, 171.0, 175.5; HRMS (ESI) Calcd. for C30H26Br3NO6 $[M+Na]^+$ 626.0897, Found: 626.0906; IR (KBr) *v* 3249.3, 1738.2, 1559.0, 1552.5, 1470.0, 1447.9, 1292.9, 1240.8, 754.7, 694.7 cm^{-1}.

(3R,4'S,5'R)-diethyl 5-methyl-2-oxo-5'-phenyl-1-(phenylcarbamoyl)-4',5'-dihydro -spiro[indoline-3,3'-pyrrole]-4',5'-dicarboxylate (5l)



White solid, $[\alpha]_D^{20}$ = - 108.8 (*c* 0.92, DCM), 54 % yield, 3.0:1 dr, 95 % ee; HPLC: Chiralcel AD-H column, hexane/i-PrOH = 85/15, flow rate 1.0 mL/min, UV detection at 220 nm, t_{major} = 21.5 min, t_{minor} = 17.9 min; ^{1}H NMR ($CDCl_3$, 300 MHz) δ 0.78 (t, *J* = 7.1 Hz, 3H), 1.29 (t, *J* = 7.2 Hz, 3H), 2.25 (s, 3H), 3.59-3.63 (m, 2H), 4.27-4.36 (m, 2H), 4.81 (s, 1H), 6.99 (s, 1H), 7.15-7.22 (m, 2H), 7.36-7.40 (m, 5H), 7.52-7.57 (m, 3H), 7.65 (d, *J* = 7.2 Hz, 2H), 8.22 (d, *J* = 8.5 Hz, 1H), 10.34 (s, 1H); ^{13}C NMR ($CDCl_3$, 75 MHz) δ 13.5, 13.9, 20.9, 60.0, 60.9, 62.6, 69.5, 89.5, 116.4, 120.7, 122.5, 124.8, 126.4, 126.8, 128.1, 128.2, 129.1, 130.9, 134.9, 136.7, 138.5, 138.7, 148.6, 161.8, 167.0, 171.2, 176.2; HRMS (ESI) Calcd. for C31H29N3O6 $[M+Na]^+$: 562.1949, Found: 562.1949; IR (KBr) *v* 3249.6, 1732.1, 1598.9, 1556.2, 1487.3, 1447.7, 1297.9, 1180.8, 754.4, 695.2 cm^{-1}.

3. Synhesis of 7 and 8

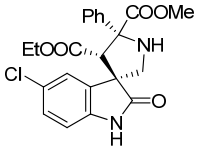


Procedure for reduction and deprotection of 5c:

To a solution of **5c** (80 mg, 92 % ee**)** in DMF (3.0 mL) charged with N_2 at -5 °C, $HSiCl_3$ (0.3 mL) was added. After stirred overnight, the reaction mixture was poured into saturated $NaHCO_3$ aq. and stirred for another 0.5 h at room temperature, then extracted with CH_2Cl_2. Organic layer was dried over anhydrous Na_2SO_4, concentrated under vacuum and purified by flash column chromatography on silica gel to give the white solid **6** in 75 % yield, 85 % ee.

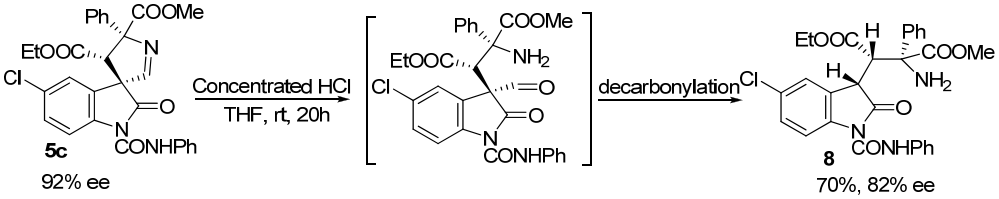
To a solution of **6** (60 mg) in THF (3 mL), KOH (103 mg) and silica gel (366 mg) were added, the reaction mixture was stirred at 60 °C for 2 h, then evaporated the solvent and purified by flash column chromatography on silica gel to give the white solid **7** in 70 % yield, 85 % ee.

(3R,4'S,5'R)-4'-ethyl 5'-methyl 5-chloro-2-oxo-5'-phenylspiro[indoline- 3,3'-pyrrolidine]- 4',5'-dicarboxylate (7)



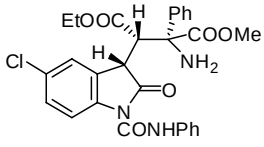
HPLC: Chiralcel AD-H column, hexane/i-PrOH = 85/15, flow rate 1.0 mL/min, UV detection at 220 nm, t_{major} = 8.4 min, t_{minor} = 7.3 min; ^{1}H NMR ($CDCl_3$, 300 MHz) δ 0.85 (t, J = 7.1 Hz, 3H), 3.55 (d, J = 11.5 Hz, 1H), 3.61-3.73 (m, 3H), 3.79 (s, 3H), 4.47 (s, 1H), 6.81 (d, J = 8.8 Hz, 1H), 7.18 (d, J = 6.2 Hz, 2H), 7.24-7.35 (m, 3H), 7.70 (d, J = 7.1 Hz, 2H), 8.56 (s, 1H);^{13}C NMR (DMSO, 75 MHz) δ 13.2, 52.9, 55.6, 57.1, 60.0, 60.3, 75.9, 110.8, 125.0, 125.3, 126.2, 127.5, 127.9, 128.3, 130.5, 140.0, 141.1, 168.2, 173.5, 178.8; HRMS (ESI) Calcd. for $C_{22}H_{21}ClN_2O_5$ $[M+Na]^+$: 429.1212, Found: 429.1200.

Procedure for synthesis of 8:



To a solution of **5c (**43 mg, 92 % ee**)** in THF (1.0 mL), concentrated HCl (1.0 mL) was added and stirred at room temperature for 20 h, then the reaction mixture were poured into saturated $NaHCO_3$ aq. and stirred for another 0.5 h at room temperature, extracted with CH_2Cl_2. Organic layer was dried over anhydrous Na_2SO_4, concentrated under vacuum and purified by flash column chromatography on silica gel to give the white solid **8** in 70% yield, 82 % ee.

(2R,3S)-4-ethyl 1-methyl 2-amino-3- (5-chloro- 2-oxo -1- (phenylcarbamoyl) -2,3,3a,7a-tetrahydro-1H-indol-3-yl)-2-phenylsuccinate (8)

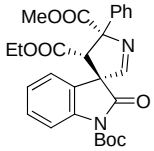


White solid, 70 % yield, 82 % ee. $[\alpha]_D^{20}$ = + 3.0 (c 0.13, DCM); HPLC: Chiralcel AD-H column, hexane/i-PrOH = 85/15, flow rate 1.0 mL/min, UV detection at 220 nm, t_{major} = 15.2 min, t_{minor} = 52.6 min; ^{1}H NMR ($CDCl_3$, 300 MHz) δ 0.94-0.98 (m, 3H), 3.59-3.67 (m, 4H), 3.72-3.80 (m, 1H), 4.34 (d, J = 8.6 Hz, 1H), 4.61 (d, J = 8.6 Hz, 1H), 6.99-7.04 (m, 1H), 7.21-7.47 (m, 11H), 7.85-7.95 (m, 2H); (**8**+D_2O) ^{1}H NMR ($CDCl_3$, 300 MHz) δ 0.93-0.98 (m, 3H), 3.61-3.81 (m, 5H), 4.34 (d, J = 7.6 Hz, 1H), 4.60 (d, J = 8.3 Hz, 1H), 6.99-7.04 (m, 1H), 7.12-7.34 (m, 11H), 7.47 (d, J = 8.1 Hz, 1H); ^{13}C NMR ($CDCl_3$, 75 MHz) δ 13.5, 47.7, 53.8, 54.3, 61.8, 69.1, 119.2, 122.9, 125.8, 128.7, 128.9, 129.2, 129.3, 130.1, 130.5, 132.1, 133.9, 135.4, 135.6, 138.9, 154.2, 169.4, 172.2, 176.1; HRMS (ESI) Calcd. for $C_{28}H_{26}N_3O_6$ $[M+H]^+$: 536.1583, Found: 536.1578.

4. Typical Procedure for [3+2] Cycloaddition Reaction with N-Boc protected Methyleneindolinones

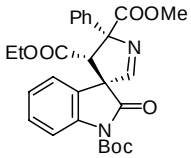
Typical Procedure for synthesis of 5m-y: Methyleneindolinones **3** (0.2 mmol) and Isocyanoesters **4** (0.22 mmol) were dissolved in 1.0 mL $CHCl_3$, and 4 Å MS (200 mg) was added. When the mixture was cooled to -20 °C, catalyst **2a** (10% mmol) was added. After stirred for the indicated time, the reaction mixture was directly subjected to flash column chromatography on silica gel (petroleum ether/ethyl acetate) to afford the corresponding pure products **5**.

(3R,4'S,5'S)-1-tert-butyl 4'-ethyl 5'-methyl 2-oxo-5'-phenyl-4',5'-dihydrospiro [indoline-3,3'-pyrrole]-1,4',5'-tricarboxylate (5m)



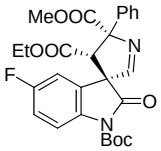
White solid, $[\alpha]_D^{20}$ = - 10.6 (*c* 0.68, DCM), 53 % yield, 3.0:1 dr, 99 % ee; HPLC: Chiralcel AD-H column, hexane/i-PrOH = 85/15, flow rate 1.0 mL/min, UV detection at 220 nm, t_{major} = 5.6 min, t_{minor} = 6.8 min; ^{1}H NMR ($CDCl_3$, 300 MHz) δ 0.73 (t, *J* = 7.1 Hz, 3H), 1.62 (s, 9H), 3.75-3.88 (m, 5H), 4.19 (s, 1H), 7.21-7.23 (m, 1H), 7.31-7.42 (m, 5H), 7.56-7.59 (m, 2H), 7.76 (d, *J* = 7.7 Hz, 1H), 7.93 (d, *J* = 8.1 Hz, 1H); ^{13}C NMR ($CDCl_3$, 75 MHz) *δ* 13.3, 28.0, 53.3, 61.2 62.7, 70.3, 85.1, 87.7, 114.9, 123.8, 125.1, 126.5, 126.8, 127.8, 128.2, 129.7, 139.9, 141.7, 148.7, 161.8, 168.1, 171.3, 173.1; HRMS (ESI) Calcd. for C27H28N2O7 $[M+H]^+$: 493.1969, Found: 493.1971; IR (KBr) *v* 3444.1, 2983.8, 1761.7, 1735.6, 1347.3, 1293.2, 1260.4, 1147.1, 1007.0, 780.4 cm^{-1}.

(3R,4'S,5'R)-1-tert-butyl 4'-ethyl 5'-methyl 2-oxo-5'-phenyl-4',5'-dihydrospiro [indoline-3,3'-pyrrole]-1,4',5'-tricarboxylate (5m')



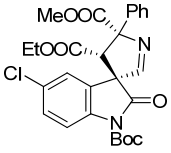
^{1}H NMR ($CDCl_3$, 300 MHz) δ 0.77 (t, *J* = 7.1 Hz, 3H), 1.65 (s, 9H), 3.53-3.62 (m, 2H), 3.80 (s, 3H), 4.78 (s, 1H), 7.05-7.11 (m, 2H), 7.33-7.37 (m, 4H), 7.48 (s, 1H), 7.62-7.65 (m, 2H), 7.86 (d, *J* = 8.3 Hz, 1H); ^{13}C NMR ($CDCl_3$, 75 MHz) *δ* 13.4, 28.0, 53.5, 60.1, 60.7, 68.8, 85.3, 89.1, 115.1, 122.5, 124.6, 126.4, 126.5, 128.1, 128.2, 130.1, 138.6, 140.4, 148.5, 162.5, 167.2, 171.5, 171.8.

(3R,4'S,5'S)-1-tert-butyl 4'-ethyl 5'-methyl 5-fluoro-2-oxo-5'-phenyl -4',5'-dihydrospiro[indoline-3,3'-pyrrole]-1,4',5'-tricarboxylate (5n)



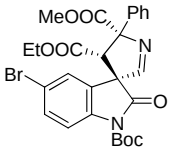
White solid, $[\alpha]_D^{20}$ = - 8.0 (*c* 1.28, DCM), 56 % yield, 4.9:1 dr, > 99 % ee; HPLC: Chiralcel AD-H column, hexane/i-PrOH = 85/15, flow rate 1.0 mL/min, UV detection at 220 nm, t_{major} = 5.6 min, t_{minor} = 5.0 min; ^{1}H NMR ($CDCl_3$, 300 MHz) δ 0.80 (t, *J* = 7.1, 3H), 1.61 (s, 9H), 3.82-3.96 (m, 5H), 4.19 (s, 1H), 7.09-7.10 (m, 1H), 7.32-7.40 (m, 4H), 7.56 (d, *J* = 6.9 Hz, 2H), 7.62-7.65 (m, 1H), 7.92-7.97 (m, 1H); ^{13}C NMR ($CDCl_3$, 75 MHz) *δ* 13.4, 28.0, 53.4, 61.4, 62.7, 70.3, 85.3, 87.9, 114.3 (d, *J* = 26.0 Hz, 1C), 116.1(d, *J* = 7.7 Hz, 1C), 116.4, 125.7 (d, *J* = 9.0 Hz, 1C), 126.8, 128.0 (d, *J* = 28.8 Hz , 1C), 135.8, 135.9, 141.4, 148.7, 160.0 (d, *J* = 242.9 Hz, 1C), 161.4, 167.9, 171.1, 172.8; HRMS (ESI) Calcd. for C27H27FN2O7 $[M+H]^+$: 511.1875, Found: 511.1861; IR (KBr) *v* 3452.9, 2982.9, 1762.3, 1733.3, 1481.3, 1369.3, 1305.7, 1290.1, 1147.9, 835.5 cm^{-1}.

(3R,4'S,5'S)-1-tert-butyl 4'-ethyl 5'-methyl 5-chloro-2-oxo-5'-phenyl-4',5'-dihydrospiro[indoline-3,3'-pyrrole]-1,4',5'-tricarboxylate (5o)



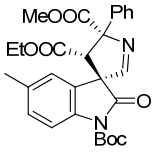
White solid, $[\alpha]_D^{20}$ = + 44.0 (*c* 0.21, DCM), 58 % yield, 4.5:1 dr, 99 % ee; HPLC: Chiralcel AD-H column, hexane/i-PrOH = 85/15, flow rate 1.0 mL/min, UV detection at 220 nm, t_{major} = 6.7 min, t_{minor} = 5.6 min; ^{1}H NMR ($CDCl_3$, 300 MHz) δ 0.81(t, *J* = 7.2 Hz, 3H), 1.61(s, 9H), 3.80-3.98 (m, 5H), 4.17 (s, 1H), 7.29-7.39 (m, 5H), 7.56 (d, *J* = 7.4 Hz, 2H), 7.81 (s, 1H), 7.91 (d, *J* = 8.7 Hz, 1H); ^{13}C NMR ($CDCl_3$, 75 MHz) *δ* 13.4, 28.0, 53.3, 61.4, 62.8, 70.1, 85.5, 88.0, 116.1, 125.7, 126.8, 126.9, 127.9, 128.2, 129.7, 130.6, 138.5, 141.5, 148.6, 161.3, 167.8, 170.9, 172.5; HRMS (ESI) Calcd. for C27H27ClN2O7 $[M+H]^+$: 527.1580, Found: 527.1553; IR (KBr) *v* 3458.6, 2981.8, 1765.6, 1732.4, 1471.1, 1337.2, 1290.5, 1261.9, 1149.7, 835.3 cm^{-1}.

(3R,4'S,5'S)-1-tert-butyl 4'-ethyl 5'-methyl 5-bromo-2-oxo-5'-phenyl-4',5'-dihydrospiro[indoline-3,3'-pyrrole]-1,4',5'-tricarboxylate (5p)



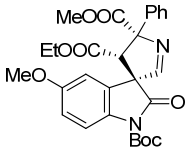
White solid, $[\alpha]_D^{20}$ = + 51 (*c* 0.15, DCM), 50 % yield, 3.9:1 dr, > 99 % ee; HPLC: Chiralcel AD-H column, hexane/i-PrOH = 85/15, flow rate 1.0 mL/min, UV detection at 220 nm, t_{major} = 7.4 min, t_{minor} = 6.1 min; ^{1}H NMR ($CDCl_3$, 300 MHz) δ 0.81 (d, *J* = 7.1 Hz, 3H), 1.61 (s, 9H), 3.79-3.99 (m, 5H), 4.17 (s, 1H), 7.29-7.39 (m, 4H), 7.51-7.57 (m, 3H), 7.85 (d, *J* = 8.7 Hz, 1H), 7.93 (s, 1H); ^{13}C NMR ($CDCl_3$, 75 MHz) *δ* 13.4, 28.0, 53.4, 61.4, 62.8, 70.0, 85.5, 88.0, 116.5, 118.0, 126.0, 126.8, 127.9, 128.2, 129.6, 132.6, 139.0, 141.5, 148.6, 161.3, 167.8, 170.8, 172.4; HRMS (ESI) Calcd. for C27H27BrN2O7 $[M+H]^+$: 571.1074, Found: 571.1062; IR (KBr) *v* 3373.4, 2981.0, 1765.6, 1732.3, 1468.1, 1337.3, 1291.1, 1151.4, 833.2, 702.6 cm^{-1}.

(3R,4'S,5'S)-1-tert-butyl 4'-ethyl 5'-methyl 5-methyl-2-oxo-5'-phenyl-4',5'-dihydrospiro[indoline-3,3'-pyrrole]-1,4',5'-tricarboxylate (5q)



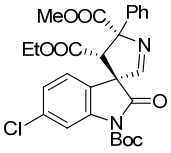
White solid, $[\alpha]_D^{20}$ = + 20.0 (*c* 0.80, DCM), 50 % yield, 2.0:1 dr, 98 % ee; HPLC: Chiralcel AD-H column, hexane/i-PrOH = 85/15, flow rate 1.0 mL/min, UV detection at 220 nm, t_{major} = 6.4 min, t_{minor} = 5.6 min; ^{1}H NMR ($CDCl_3$, 300 MHz) δ 0.75 (t, *J* = 7.1 Hz, 3H), 1.61 (s, 9H), 2.36 (s, 3H), 3.76-3.90 (m, 5H), 4.19 (s, 1H), 7.19 (d, *J* = 8.1 Hz, 1H), 7.31-7.39 (m, 4H), 7.53-7.58 (m, 3H), 7.80 (d, *J* = 8.3 Hz, 1H); ^{13}C NMR ($CDCl_3$, 75 MHz) *δ* 13.3, 21.2, 28.0, 53.1, 61.1, 62.7, 70.4, 84.9, 87.6, 114.7, 123.7, 126.8, 127.0, 127.7, 128.2, 130.1, 134.6, 137.5, 141.8, 148.8, 162.0, 168.1, 171.1, 173.2; HRMS (ESI) Calcd. for C28H30N2O7 $[M+H]^+$: 507.2126, Found: 507.2119; IR (KBr) *v* 3453.9, 2956.8, 1760.0, 1731.9, 1491.0, 1367.9, 1258.6, 1197.8, 1137.4, 830.8 cm^{-1}.

(3R,4'S,5'S)-1-tert-butyl 4'-ethyl 5'-methyl 5-methoxy-2-oxo-5'-phenyl-4',5'-dihydrospiro[indoline-3,3'-pyrrole]-1,4',5'-tricarboxylate (5r)



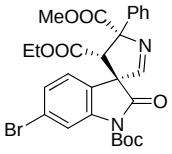
White solid, $[\alpha]_D^{20}$ = + 21.3 (*c* 0.70, DCM), 45 % yield, 2.3:1 dr, > 99 % ee; HPLC: Chiralcel AD-H column, hexane/i-PrOH = 85/15, flow rate 1.0 mL/min, UV detection at 220 nm, t_{major} = 7.8 min, t_{minor} = 6.7 min; ^{1}H NMR ($CDCl_3$, 300 MHz) δ 0.77 (t, *J* = 7.1 Hz, 3H), 1.61 (s, 9H), 3.77-3.91 (m, 8H), 4.19 (s, 1H), 6.90 (dd, J_1 = 2.7 Hz, J_2 = 8.9 Hz, 1H), 7.31-7.38 (m, 4H), 7.41-7.46 (m, 1H), 7.56 (d, *J* = 6.9 Hz, 2H), 7.84 (d, *J* = 8.9 Hz, 1H); ^{13}C NMR ($CDCl_3$, 75 MHz) *δ* 13.4, 28.0, 53.2, 55.7, 61.2, 62.8, 70.7, 84.8, 87.7, 112.1, 115.4, 115.8, 125.0, 126.9, 127.7, 128.2, 133.2, 141.8, 148.9, 157.3, 161.9, 168.1, 171.2, 173.1; HRMS (ESI) Calcd. for C28H30N2O8 $[M+Na]^+$: 523.2075, Found: 523.2065; IR (KBr) *v* 3452.4, 2981.6, 1759.9, 1731.6, 1485.9, 1293.1, 1254.8, 1201.3, 1153.1, 702.0 cm^{-1}.

(3R,4'S,5'S)-1-tert-butyl 4'-ethyl 5'-methyl 6-chloro-2-oxo-5'-phenyl-4',5'-dihydrospiro[indoline-3,3'-pyrrole]-1,4',5'-tricarboxylate (5s)



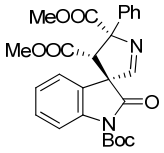
White solid, $[\alpha]_D^{20}$ = + 7.2 (*c* 0.93, DCM), 51 % yield, 4.1:1 dr, 98 % ee; HPLC: Chiralcel AD-H column, hexane/i-PrOH = 85/15, flow rate 1.0 mL/min, UV detection at 220 nm, t_{major} = 6.4 min, t_{minor} = 5.1 min; ^{1}H NMR ($CDCl_3$, 300 MHz) δ 0.82 (t, *J* = 7.1 Hz, 3H), 1.62 (s, 9H), 3.78 (s, 3H), 3.80-3.93 (m, 2H), 4.16 (s, 1H), 7.19 (dd, J_1 = 2.0 Hz, J_2 = 8.3 Hz, 1H), 7.32-7.39 (m, 4H), 7.54-7.58 (m, 2H), 7.74 (d, *J* = 8.3 Hz, 1H), 8.03 (s, 1H); ^{13}C NMR ($CDCl_3$, 75 MHz) *δ* 13.4, 27.9, 53.4, 61.4, 62.7, 69.9, 85.6, 87.8, 115.6, 122.2, 125.1, 126.8, 127.6, 127.8, 128.2, 135.7, 140.7, 141.4, 148.5, 161.3, 167.9, 171.3, 172.7; HRMS (ESI) Calcd. for C27H27ClN2O7 $[M+H]^+$: 527.1580, Found: 527.1562; IR (KBr) *v* 3368.4, 2981.9, 1766.1, 1736.3, 1371.2, 1343.9, 1288.1, 1252.7, 1149.7, 701.4 cm^{-1}.

(3R,4'S,5'S)-1-tert-butyl 4'-ethyl 5'-methyl 6-bromo-2-oxo-5'-phenyl-4',5'-dihydrospiro[indoline-3,3'-pyrrole]-1,4',5'-tricarboxylate (5t)



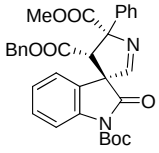
White solid, $[\alpha]_D^{20}$ = + 11.2 (*c* 1.08, DCM), 55 % yield, 4.0:1 dr, 99 % ee; HPLC: Chiralcel AD-H column, hexane/i-PrOH = 85/15, flow rate 1.0 mL/min, UV detection at 220 nm, t_{major} = 5.3 min, t_{minor} = 6.6 min; ^{1}H NMR ($CDCl_3$, 300 MHz) δ 0.82 (t, *J* = 7.1 Hz, 3H), 1.62 (s, 9H), 3.80 (s, 3H), 3.82-3.93 (m, 2H), 4.16 (s, 1H), 7.29-7.40 (m, 5H), 7.54-7.57 (m, 2H), 7.68 (d, *J* = 8.2 Hz, 1H), 8.18 (s, 1H); ^{13}C NMR ($CDCl_3$, 75 MHz) *δ* 13.4, 27.9, 53.4, 61.4, 62.7, 70.0, 85.6, 87.9, 118.4, 122.8, 123.6, 126.8, 126.8, 127.9, 128.1, 128.2, 140.8, 141.4, 148.5, 161.2, 167.9, 171.3, 172.6; HRMS (ESI) Calcd. for C27 H27BrN2O7 $[M+Ha]^+$: 571.1074, Found: 571.1072; IR (KBr) *v* 3456.7, 2984.1, 1766.6, 1736.7, 1479.1, 1372.1, 1342.7, 1286.6, 1253.5, 793.1 cm^{-1}.

(3R,4'S,5'S)-1-tert-butyl 4',5'-dimethyl 2-oxo-5'-phenyl-4',5'- dihydrospiro [indoline-3,3'-pyrrole]- 1,4',5'-tricarboxylate (5u)



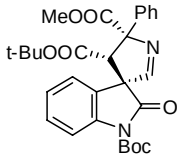
White solid, $[\alpha]_D^{20}$ = + 0.8 (*c* 0.94, DCM), 58 % yield, 3.5:1 dr, > 99 % ee; HPLC: Chiralcel AD-H column, hexane/i-PrOH = 85/15, flow rate 1.0 mL/min, UV detection at 220 nm, t_{major} = 6.9 min, t_{minor} = 8.8 min; ^{1}H NMR ($CDCl_3$, 300 MHz) δ 1.62 (s. 9H), 3.35 (s, 3H), 3.82 (s, 3H), 4.22 (s, 1H), 7.19-7.24 (m, 1H), 7.32-7.42 (m, 5H), 7.56 (d, *J* = 7.7 Hz, 2H), 7.68 (d, *J* = 7.6 Hz, 1H), 7.94 (d, *J* = 8.2 Hz, 1H); ^{13}C NMR ($CDCl_3$, 75 MHz) *δ* 28.0, 52.1, 53.3, 62.4, 70.3, 85.1, 88.0, 114.9, 123.6, 125.1, 126.3, 126.8, 127.8, 128.2, 129.8, 139.6, 141.5, 148.7, 161.8, 168.7, 171.3, 172.9; HRMS (ESI) Calcd. for C26H26N2O7 $[M+H]^+$: 479.1813; Found: 479.1806; IR (KBr) *v* 2986.8, 1759.2, 1726.8, 1478.3, 1346.4, 1292.3, 1252.3, 1151.2, 773.3, 704.0 cm^{-1}.

(3R,4'S,5'S)-4'-benzyl 1-tert-butyl 5'-methyl 2-oxo-5'-phenyl-4',5'-dihydrospiro [indoline-3,3'-pyrrole]-1,4',5'-tricarboxylate (5v)



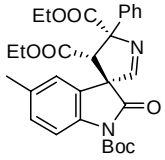
White solid, $[\alpha]_D^{20}$ = - 16.1 (*c* 0.71, DCM), 44 % yield, 2.4:1 dr, > 99 % ee; HPLC: Chiralcel AD-H column, hexane/i-PrOH = 85/15, flow rate 1.0 mL/min, UV detection at 220 nm, t_{major} = 7.8 min, t_{minor} = 5.4 min; ^{1}H NMR ($CDCl_3$, 300 MHz) δ 1.58 (s, 9H), 3.79 (s, 3H), 4.25 (s, 1H), 4.65 (d, *J* = 11.9 Hz, 1H), 4.84 (d, *J* = 11.9 Hz, 1H), 6.88 (d, *J* = 6.8 Hz, 2H) 7.16-7.25 (m, 4H), 7.28-7.36 (m, 5H), 7.55 (d, *J* = 6.9 Hz, 2H), 7.74 (d, *J* = 7.6 Hz, 1H), 7.86 (d, *J* = 8.2 Hz, 1H); ^{13}C NMR ($CDCl_3$, 75 MHz) *δ* 27.9, 53.3, 62.6, 67.4, 70.3, 84.9, 87.8, 115.1, 123.5, 125.1, 126.4, 126.8, 127.8, 128.1, 128.2, 128.3, 128.4, 129.8, 134.3, 139.8, 141.6, 148.6, 161.9, 168.0, 171.2, 172.9; HRMS (ESI) Calcd. for C32H30N2O7 $[M+H]^+$: 555.2126, Found: 555.2109; IR (KBr) *v* 3457.6, 2989.1, 1758.1, 1737.6, 1497.6, 1344.3, 1255.8, 1173.5, 755.0, 697.6 cm^{-1}.

(3R,4'S,5'S)-1,4'-di-tert-butyl 5'-methyl 2-oxo-5'- phenyl-4',5'- dihydrospiro [indoline-3,3'-pyrrole]-1,4',5'-tricarboxylate (5w)



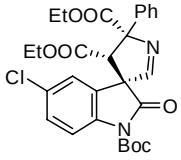
White solid, $[\alpha]_D^{20}$ = - 35.3 (*c* 0.83, DCM), 50 % yield, 1.9:1 dr, > 99 % ee; HPLC: Chiralcel AD-H column, hexane/i-PrOH = 85/15, flow rate 1.0 mL/min, UV detection at 220 nm, t_{major} = 4.2 min, t_{minor} = 5.2 min; ^{1}H NMR ($CDCl_3$, 300 MHz) δ 1.01 (s, 9H), 1.61 (s, 9H), 3.81 (s, 3H), 4.14 (s, 1H), 7.21-7.43 (m, 6H), 7.56 (d, *J* = 7.0, 2H), 7.93 (s, 2H); ^{13}C NMR ($CDCl_3$, 75 MHz) *δ* 27.2, 27.9, 53.2, 64.1, 70.3, 82.3, 84.9, 87.0, 114.9, 124.3, 125.1, 126.8, 126.9, 127.6, 128.1, 129.7, 140.2, 142.1, 148.8, 161.9, 166.9, 171.3, 173.5; HRMS (ESI) Calcd. for C29H32N2O7 $[M+Na]^+$: 543.2102, Found: 543.2089; IR (KBr) *v* 3445.4, 2958.8, 1758.8, 1731.5, 1478.0, 1370.6, 1344.8, 1253.5, 1149.6, 747.8 cm^{-1}.

(3R,4'S,5'S)-1-tert-butyl 4',5'-diethyl 5-methyl-2-oxo-5'-phenyl-4',5'-dihydrospiro [indoline-3,3'-pyrrole]-1,4',5'-tricarboxylate (5x)



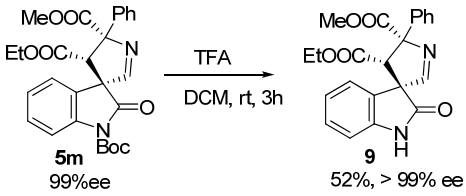
White solid, $[\alpha]_D^{20}$ = + 19.9 (*c* 1.10, DCM), 65 % yield, 4.4:1 dr, > 99 % ee; HPLC: Chiralcel AD-H column, hexane/i-PrOH = 85/15, flow rate 1.0 mL/min, UV detection at 220 nm, t_{major} = 5.9 min, t_{minor} = 5.3 min; ^{1}H NMR ($CDCl_3$, 300 MHz) δ 0.77 (t, *J* = 7.1 Hz, 3H), 1.28 (t , *J* = 7.1 Hz, 3H), 1.61 (s, 9H), 2.35 (s, 3H), 3.77-3.91 (m, 2H), 4.17 (s, 1H), 4.26-4.35 (m, 2H), 7.18 (d, *J* = 8.3 Hz, 1H), 7.29-7.38 (m, 4H), 7.53-7.58 (m, 3H), 7.80 (d, *J* = 8.3 Hz, 1H); ^{13}C NMR ($CDCl_3$, 75 MHz) *δ* 13.3, 13.9, 21.1, 27.9, 61.0, 62.3, 62.6, 70.3, 84.8, 87.8, 114.7, 123.8, 126.8, 126.9, 127.6, 128.1, 130.1, 134.6, 137.5, 142.0, 148.8, 161.9, 168.0, 170.5, 173.2; HRMS (ESI) Calcd. for C29H32N2O7 $[M+H]^+$: 521.2282, Found: 521.2274; IR (KBr) *v* 3444.8, 2980.3, 1758.7, 1728.4, 1492.4, 1320.6, 1292.2, 1198.3, 1138.5, 830.6 cm^{-1}.

(3R,4'S,5'S)-1-tert-butyl 4',5'-diethyl 5-chloro-2-oxo- 5'-phenyl- 4',5'-dihydrospiro[indoline-3,3'-pyrrole]-1,4',5'-tricarboxylate (5y)



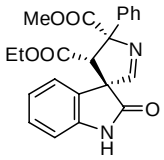
White solid, $[\alpha]_D^{20}$ = + 44.0 (*c* 0.31, DCM), 62 % yield, 5.1:1 dr, 97 % ee; HPLC: Chiralcel AD-H column, hexane/i-PrOH = 85/15, flow rate 1.0 mL/min, UV detection at 220 nm, t_{major} = 6.2 min, t_{minor} = 5.4 min; 1H NMR (CDCl3, 300 MHz) δ 0.82 (t, *J* = 7.1 Hz, 3H), 1.30 (t, *J* = 7.1 Hz, 3H), 1.61 (s, 9H), 3.81-3.99 (m, 2H), 4.16 (s, 1H), 4.27-4.37 (m, 2H), 7.29-7.39 (m, 5H), 7.55 (d, *J* = 7.1 Hz, 2H), 7.81 (s, 1H), 7.91 (d, *J* = 8.7 Hz, 1H); ^{13}C NMR ($CDCl_3$, 75 MHz) *δ* 13.4, 13.9, 27.9, 61.3, 62.7, 70.0, 85.4, 88.1, 116.1, 125.8, 126.7, 126.8, 127.8, 128.1, 129.6, 130.5, 138.4, 141.6, 148.6, 161.3, 167.7, 170.3, 172.5; HRMS (ESI) Calcd. for C28H29ClN2O7 $[M+H]^+$: 541.1736, Found: 541.1732; IR (KBr) *v* 3446.5, 2980.1, 1764.1, 1724.3, 1338.2, 1289.5, 1259.4, 1185.1, 1150.2, 836.5 cm^{-1}.

5. Depretection of [3+2] cycloadduct



Procedure for deprotection of 5m: TFA (0.4 mL) was added to a solution of **5m** (80 mg, 99% ee) in DCM (0.6 mL) and stirred for 4h at room temperature, then the reaction mixture was poured into saturated $NaHCO_3$ aq. and extracted with CH_2Cl_2. Organic layer was dried over anhydrous Na_2SO_4, concentrated under vacuum and purified by flash column chromatography on silica gel to give the white solid **9** in 52 % yield, 82 % ee.

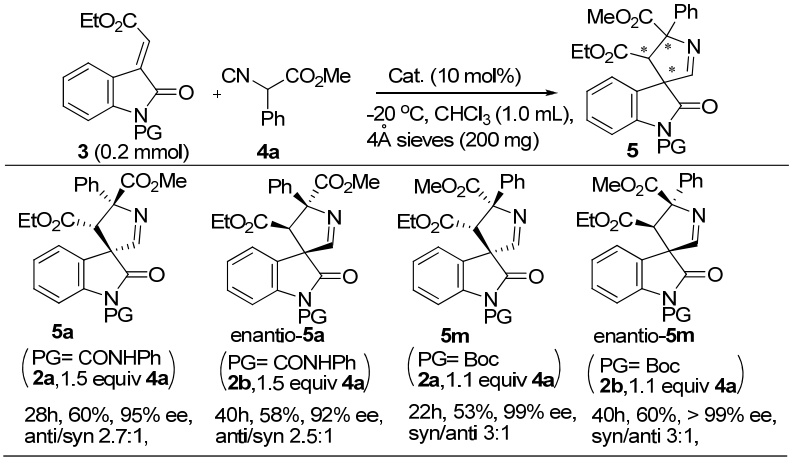
(3R,4'S,5'S)-4'-ethyl 5'-methyl 2-oxo-5'-phenyl-4',5'-dihydrospiro [indoline- 3,3'-pyrrole]-4',5'-dicarboxylate (9)



White solid, 52 % yield; 99 % ee; HPLC: Chiralcel AD-H column, hexane/i-PrOH = 50/50, flow rate 0.6 mL/min, UV detection at 220 nm, t_{major} = 15.8 min, t_{minor} = 7.3 min; ^{1}H NMR ($CDCl_3$, 300 MHz) δ 0.72 (t, J = 7.1 Hz, 3H), 3.76-3.93 (m, 5H), 4.17 (s, 1H), 6.86 (d, J = 7.6 Hz, 1H), 7.07 (t, J = 7.6 Hz, 1H), 7.24-7.29 (m, 1H), 7.32-7.42 (m, 4H), 7.64 (d, J = 7.1 Hz, 2H), 7.68(d, J = 7.5 Hz, 1H), 8.76(s, 1H); ^{13}C NMR ($CDCl_3$, 75 MHz) δ 13.4, 53.3, 61.1, 61.5, 70.1, 87.8, 109.9, 123.3, 125.2, 126.9, 127.1, 127.7, 128.2, 129.6, 140.9, 141.9, 162.7, 168.5, 171.4, 176.2; HRMS (ESI) Calcd. for C22H20N2O5 $[M+H]^+$: 393.1445, Found: 393.1446.

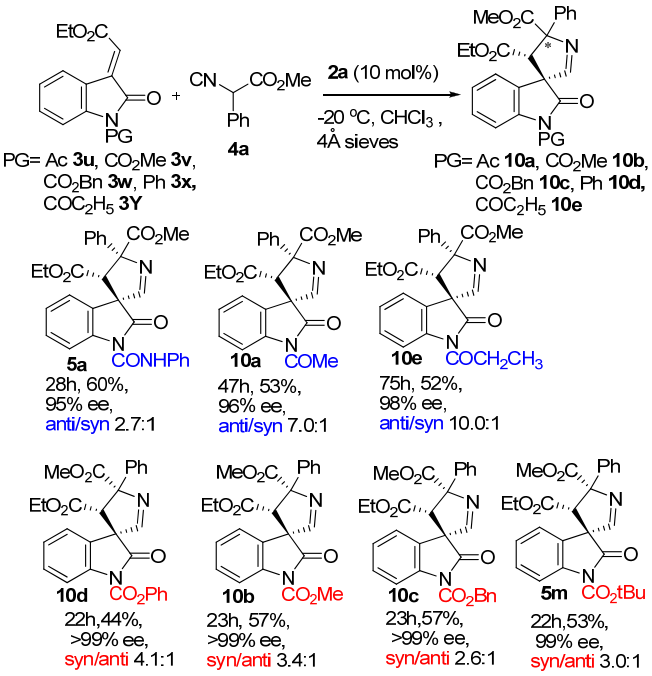
6. Controlled syntheses of enantio- and diastereomers.

we could access four stereoisomers by changing N-protecting groups and catalysts. Under the optimized reaction condition, catalyst **2b**, the pseudo-enantiomer of **2a**, could promoted the cycloaddtion reaction smoothly, affording the desired enantiomers in a high level of enantiocontrol.



7. Control experiment for testing the effect of N-protecting group on the diasteroselectivity and proposed mechanism.

To investigate the origin of diastereochemical switch, a variety of N-protecting groups were introduced to methyleneindolinones as shown in Scheme 3. We find that N-acetyl group provides anti- product with the same stereochemistry as N-phenylamide group (**10a** vs **5a**), indicating that N-H bonding on phenylamide group isn't the essential factor for determining the diasteroselectivity. In contrast, insertion of an oxygen atom to acetyl reverses the diastereoselectivity (syn-**10b** vs anti-**10a**), revealing the oxygen of the alkoxycarbonyl group may play a key role on diastereoselection switch. Steric hindrance of N-protecting groups might not predominate the diasteroselectivity switch because phenylamide group has a semblable size as phenoxycarbonyl group while producing contrary diastereoselectivity (**5a** vs **10d**) and also propionyl group leads to different diastereoselectivity compared to methoxycarbonyl group notwithstanding they have analogical steric hindrance (**10e** vs **10b**). Therefore, on the basis of the analysis above, we hypothesize that electronic effect of oxygen atom on alkoxycarbonyl - or phenoxycarbonyl protecting group rather than steric hindrance effect may play a crucial role in determining diastereochemical switch.



Scheme 3. Control experiment for testing the effect of N-protecting group

A plausible mechanism is proposed in Figure 4. The reaction is initiated through enolization of isocyanoesters by deprotonation at its α-carbon atom by tertiary amine moiety of catalyst, and electron-poor methyleneindolinone is activated by hydrogen-

binding interaction between carbonyl group in the indolinone and thiourea moiety of catalyst. The Re face of methyleneindolinone is approached by in situ generated enolate, and synchronously proton transfer occurs in the conjugated addition step, and subsequent intramolecular cyclization leads to product. The protecting group induced switch of disatereoselectivity can be explained by transition states TS1-TS3. When using N-phenylamide or N-acetyl protecting group, a thermodynamically controlled stable anti- product is generated through TS1. However, when N-alkoxycarbonyl or phenoxycarbonyl is employed, the [3+2] cycloaddition reaction takes place in a kinetically controlled manner and provided syn- products through TS2 because TS3 is disfavored for the electron-repulsion between N-carboxylic esters moieties and electron-rich enolate. The highly asymmetric induction arises from hydrogen-binding interaction between catalyst and both of methyleneindolinone and enolized isocyanoester.

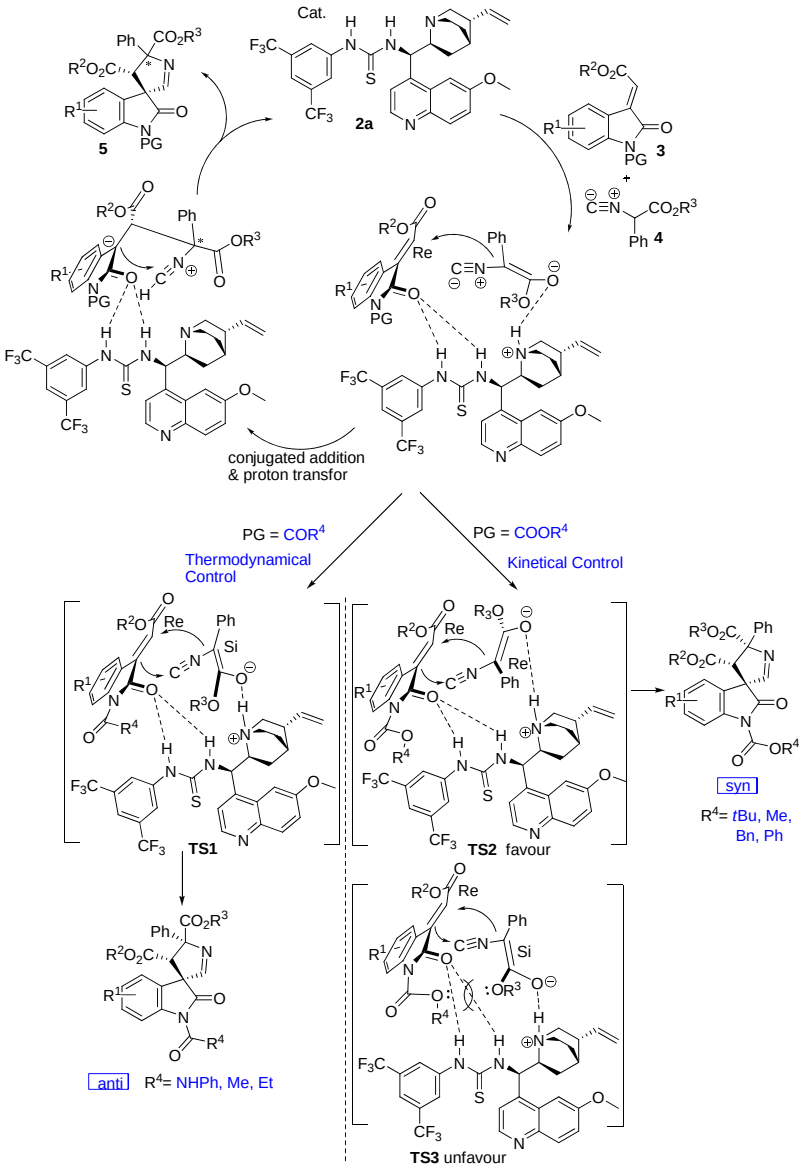
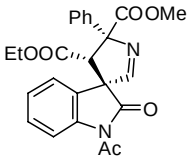


Figure 4. Proposed Mechanism.

Procedure for the synthesis of 10a-e

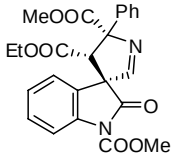
Methyleneindolinones **3** (0.2 mmol) and Isocyanoesters **4a** (0.3 mmol) were dissolved in 1.0 mL $CHCl_3$, and 4 Å MS (200 mg) was added. When the mixture was cooled to -20 ^oC, catalyst **2a** (10 mol%) was added. After stirred for the indicated time, the reaction mixture was directly subjected to flash column chromatography on silica gel (petroleum ether / ethyl acetate) to afford the pure products **10**.

(3R,4'S,5'R)-4'-ethyl 5'-methyl 1-acetyl-2-oxo-5'-phenyl-4',5'-dihydrospiro [indoline - 3,3'-pyrrole]-4',5'-dicarboxylate (10a)



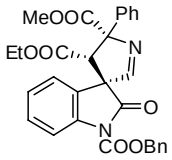
White solid, $[\alpha]_D^{20}$ = - 87.2 (*c* 0.52, DCM), 53 % yield, anti/syn 7.0:1, 96 % ee; HPLC: Chiralcel AD-H column, hexane/i-PrOH = 85/15, flow rate 1.0 mL/min, UV detection at 220 nm, t_{major} = 12.2 min, t_{minor} = 17.2 min; ^1H NMR ($CDCl_3$, 300 MHz) δ 0.76 (t, *J* = 7.1 Hz, 3H), 2.68 (s, 3H), 3.52-3.64 (m, 2H), 3.81 (s, 3H), 4.76 (s, 1H), 7.11-7.18 (m, 2H), 7.32-7.41 (m, 4H), 7.52 (s, 1H), 7.62-7.65 (m, 2H), 8.25 (d, *J* = 8.2 Hz, 1H); ^{13}C NMR ($CDCl_3$, 75 MHz) *δ* 13.4, 26.7, 53.5, 60.3, 60.8, 68.9, 89.2, 116.6, 122.8, 125.3, 126.2, 126.3, 128.2, 128.3, 130.3, 138.5, 140.8, 162.3, 167.0, 170.4, 171.8, 174.1; HRMS (ESI) Calcd. for C24H22N2O6 $[M+H]^+$: 435.1551, Found: 435.1551; IR (KBr) *v* 3431.4, 2949.9, 1749.5, 1732.1, 1464.6, 1271.2, 1222.9, 1177.7, 1020.8, 777.6 cm^{-1}.

(3R,4'S,5'S)-4'-ethyl 1,5'-dimethyl 2-oxo-5'-phenyl-4',5'-dihydrospiro [indoline-3,3'-pyrrole]-1,4',5'-tricarboxylate (10b)



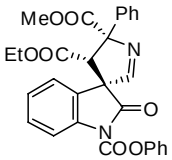
White solid, $[\alpha]_D^{20}$ = - 18.0 (*c* 0.97, DCM), 57 % yield, syn/anti 3.4:1, > 99 % ee; HPLC: Chiralcel AD-H column, hexane/i-PrOH = 85/15, flow rate 1.0 mL/min, UV detection at 220 nm, t_{major} = 15.2 min, t_{minor} = 16.8 min; ^1H NMR ($CDCl_3$, 300 MHz) δ 0.71 (t, *J* = 7.1 Hz, 3H), 3.74-3.88 (m, 5H), 4.01 (s, 3H), 4.17 (s, 1H), 7.23-7.24 (m, 1H), 7.34-7.42 (m, 5H), 7.55-7.58 (m, 2H), 7.75-7.78 (m, 1H), 7.98 (d, *J* = 8.1 Hz, 1H); ^{13}C NMR ($CDCl_3$, 75 MHz) *δ* 13.3, 53.3, 54.2, 61.3, 62.9, 70.2, 87.8, 114.9, 123.8, 125.4, 126.5, 126.7, 127.8, 128.2, 129.9, 139.4, 141.6, 150.9, 161.5, 167.9, 171.2, 173.1; HRMS (ESI) Calcd. for C24H22N2O7 $[M+Na]^+$: 473.1319, Found: 473.1310; IR (KBr) *v* 3372.8, 2956.2, 1738.3, 1481.0, 1350.0, 1294.3, 1243.7, 1169.1, 1014.7, 770.8 cm^{-1}.

(3R,4'S,5'S)-1-benzyl 4'-ethyl 5'-methyl 2-oxo-5'-phenyl-4',5'-dihydrospiro[indoline-3,3'-pyrrole]-1,4',5'-tricarboxylate (10c)



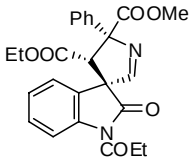
White solid, $[\alpha]_D^{20}$ = - 32.6 (*c* 0.78, DCM), 57 % yield, syn/anti 2.6:1, > 99 % ee; HPLC: Chiralcel AD-H column, hexane/i-PrOH = 85/15, flow rate 1.0 mL/min, UV detection at 220 nm, t_{major} = 15.6 min, t_{minor} = 38.2 min; ^{1}H NMR ($CDCl_3$, 300 MHz) δ 0.69 (t, *J* = 7.1 Hz, 3H), 3.71-3.88 (m, 5H), 4.19 (s, 1H), 5.39-5.48 (m, 2H), 7.23-7.26 (m, 1H), 7.33-7.43 (m, 8H), 7.47 (d, *J* = 6.4 Hz, 2H), 7.57 (d, *J* = 6.8 Hz, 2H), 7.79 (d, *J* = 7.5 Hz, 1H), 7.99 (d, *J* = 8.1 Hz, 1H); ^{13}C NMR ($CDCl_3$, 75 MHz) *δ* 13.3, 53.3, 61.3, 62.8, 69.1, 70.2, 87.7, 114.9, 123.9, 125.4, 126.6, 126.8, 127.8, 128.1, 128.2, 128.6, 128.7, 129.9, 134.4, 139.4, 141.6, 150.3, 161.5, 167.9, 171.2, 172.9; HRMS (ESI) Calcd. for C30H26N2O7 $[M+Na]^+$: 549.1632, Found: 549.1624; IR (KBr) *v* 3444.2, 2918.3, 1769.9, 1740.5, 1730.6, 1385.7, 1347.1, 1256.5, 1172.4, 774.6 cm^{-1}.

(3R,4'S,5'S)-4'-ethyl 5'-methyl 1-phenyl 2-oxo-5'-phenyl-4',5'- dihydrospiro [indoline-3,3'-pyrrole] -1,4',5'-tricarboxylate (10d)



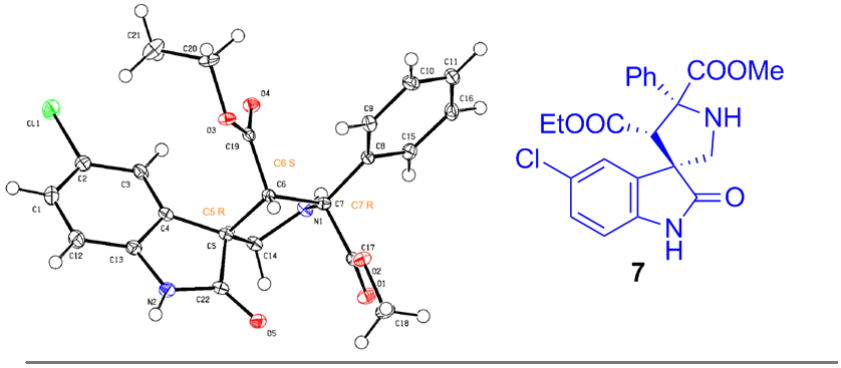
White solid, $[\alpha]_D^{20}$ = - 16.4 (*c* 0.40, DCM), 44 % yield, syn/anti 4.1:1, > 99 % ee; HPLC: Chiralcel AD-H column, hexane/i-PrOH = 85/15, flow rate 1.0 mL/min, UV detection at 220 nm, t_{major} = 27.0 min, t_{minor} = 20.2 min; ^{1}H NMR ($CDCl_3$, 300 MHz) δ 0.77 (t, *J* = 7.1 Hz, 3H), 3.75-3.93 (m, 5H), 4.25 (s, 1H), 7.28-7.46 (m, 11H), 7.58 (d, *J* = 7.0 Hz, 2H), 7.83 (d, *J* = 7.6 Hz, 1H), 8.03 (d, *J* = 8.1 Hz, 1H); ^{13}C NMR ($CDCl_3$, 75 MHz) *δ* 13.4, 53.3, 61.4, 63.0, 70.3, 87.9, 115.1, 121.2, 124.0, 125.7, 126.6, 126.7, 126.8, 127.9, 128.3, 129.7, 130.1, 139.2, 141.6, 149.8, 150.0, 161.4, 167.9, 171.2, 173.0; HRMS (ESI) Calcd. for C29H24N2O7 $[M+Na]^+$: 535.1476, Found: 535.1475; IR (KBr) *v* 3471.1, 2948.4, 1766.5, 1747.1, 1478.3, 1371.3, 1352.2, 1221.3, 1011.6, 761.3 cm^{-1}.;

(3R,4'S,5'R)-4'-ethyl 5'-methyl 2-oxo-5'-phenyl-1-propionyl-4',5'- dihydrospiro [indoline-3,3'-pyrrole]-4',5'-dicarboxylate (10e)



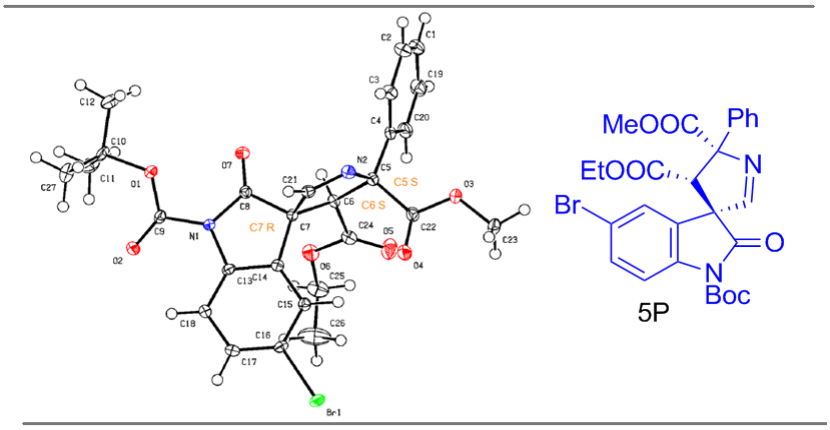
White solid, 52 % yield, anti/syn 10.0:1, 98 % ee; HPLC: Chiralcel AD-H column, hexane/i-PrOH = 85/15, flow rate 1.0 mL/min, UV detection at 220 nm, t_{major} = 10.1 min, t_{minor} = 17.3 min; ^{1}H NMR ($CDCl_3$, 300 MHz) δ 0.75 (t, *J* = 7.2 Hz, 3H), δ 1.24 (t, *J* = 7.2 Hz, 3H), 3.02-3.12 (m, 2H), 3.51-3.63 (m, 2H), 3.81 (s, 3H), 4.74 (s, 1H), 7.08-7.17 (m, 2H), 7.30-7.40 (m, 4H), 7.52 (s, 1H), 7.63 (d, *J* = 6.9 Hz, 2H), 8.27 (d, *J* = 8.3 Hz, 1H); ^{13}C NMR ($CDCl_3$, 75 MHz) *δ* 8.2, 13.4, 32.0, 53.2, 60.3, 60.8, 68.9, 89.1, 116.6, 122.8, 125.2, 126.2, 126.3, 128.2, 128.3, 130.3, 138.5, 141.0, 162.4, 167.1, 171.8, 174.0, 174.5; HRMS (ESI) Calcd. for C25H24N2O6 $[M+Na]^+$: 471.1527, Found: 471.1527; IR (KBr) *v* 3411.3, 2981.7, 1754.9, 1734.9, 1464.1, 1264.1, 1181.2, 1068.8, 1025.2, 762.2 cm^{-1}.

8. Crystal data for 7, 5p and 5m



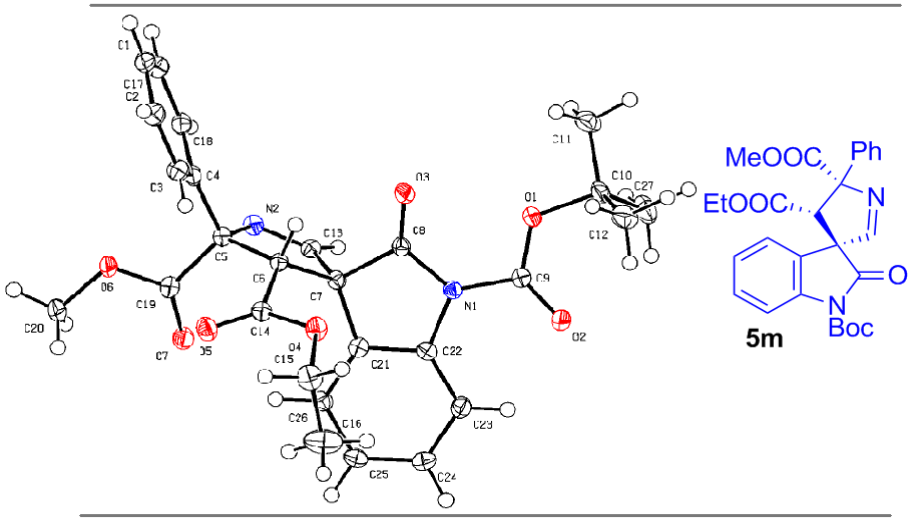
Crystal data and structure refinement for 7: (CDCC number: CCDC 849672)

Identification code	**7**
Empirical formula	C22 H21ClN2O5
Formula weight	428.86
Temperature	100(2) K
Wavelength	0.71073 A
Crystal system, space group	Monoclinic, P 21
Unit cell dimensions	a = 12.6866(15) A alpha = 90 deg. b = 5.7581(7) A beta = 113.145(2) deg. c = 14.9160(18) A gamma = 90 deg.
Volume	1001.9(2) A^3
Z, Calculated density	2, 1.422 Mg/m^3
Absorption coefficient	0.229 mm^-1
F(000)	448
Crystal size	0.80 x 0.19 x 0.06 mm
Theta range for data collection	1.48 to 30.08 deg.
Limiting indices	-17<=h<=17, -7<=k<=8, -21<=l<=20
Reflections collected / unique	10651 / 5461 [R(int) = 0.0226]
Completeness to theta = 30.08	95.8 %
Absorption correction	Semi-empirical from equivalents
Max. and min. transmission	0.9864 and 0.8382
Refinement method	Full-matrix least-squares on F^2
Data / restraints / parameters	5461 / 1 / 273
Goodness-of-fit on F^2	1.051
Final R indices [I>2sigma(I)]	R1 = 0.0338, wR2 = 0.0860
R indices (all data)	R1 = 0.0366, wR2 = 0.0878
Absolute structure parameter	0.00(5)
Largest diff. peak and hole	0.535 and -0.629 e.A^-3



Crystal data and structure refinement for 5P: (CDCC number: CCDC 849673)

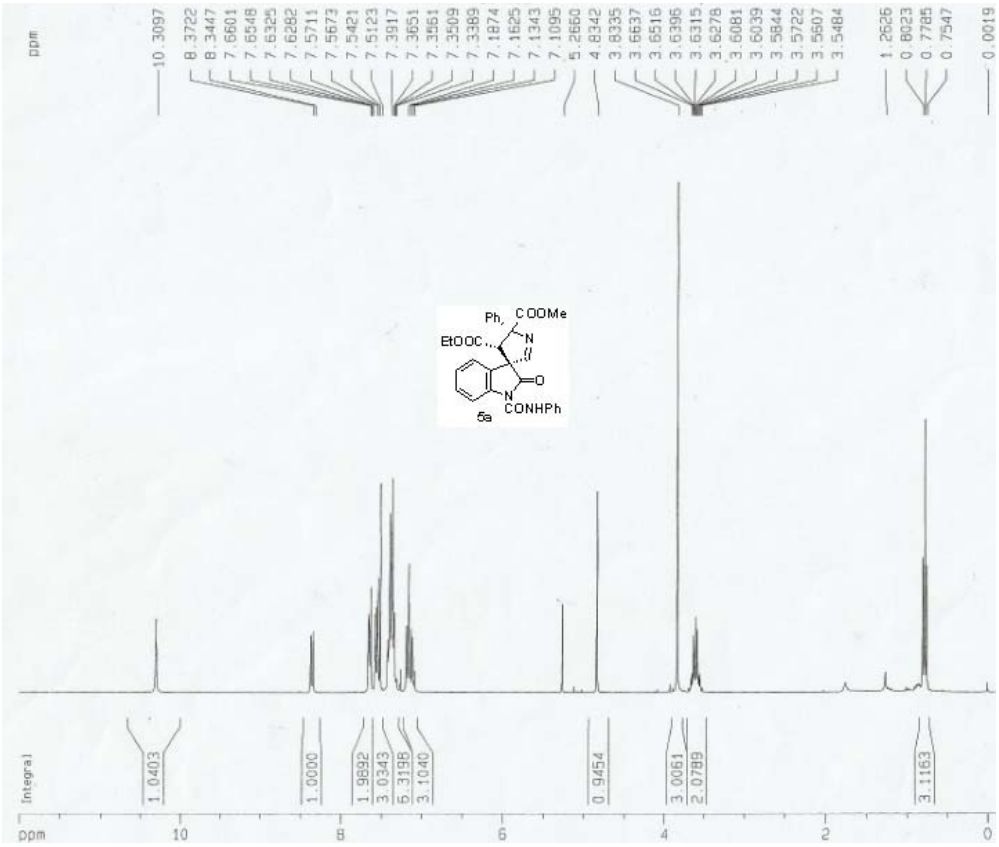
Identification code	**5P**
Empirical formula	C27 H27BrN2O7
Formula weight	571.42
Temperature	100(2) K
Wavelength	0.71073 A
Crystal system, space group	Orthorhombic, P 21 21 21
Unit cell dimensions	a = 11.9894(7) A alpha = 90 deg. b = 13.0968(8) A beta = 90 deg. c = 17.2527(10) A gamma = 90 deg.
Volume	2709.1(3) A^3
Z, Calculated density	4, 1.401 Mg/m^3
Absorption coefficient	1.564 mm^-1
F(000)	1176
Crystal size	0.35 x 0.32 x 0.25 mm
Theta range for data collection	1.95 to 30.03 deg.
Limiting indices	-16<=h<=16, -18<=k<=15, -24<=l<=24
Reflections collected / unique	28898 / 7693 [R(int) = 0.0300]
Completeness to theta = 30.03	99.1 %
Absorption correction	Semi-empirical from equivalents
Max. and min. transmission	0.6958 and 0.6105
Refinement method	Full-matrix least-squares on F^2
Data / restraints / parameters	7693 / 0 / 340
Goodness-of-fit on F^2	0.994
Final R indices [I>2sigma(I)]	R1 = 0.0224, wR2 = 0.0519
R indices (all data)	R1 = 0.0273, wR2 = 0.0529
Absolute structure parameter	0.006(4)
Extinction coefficient	0.0004(2)
Largest diff. peak and hole	0.342 and -0.232 e.A^-3

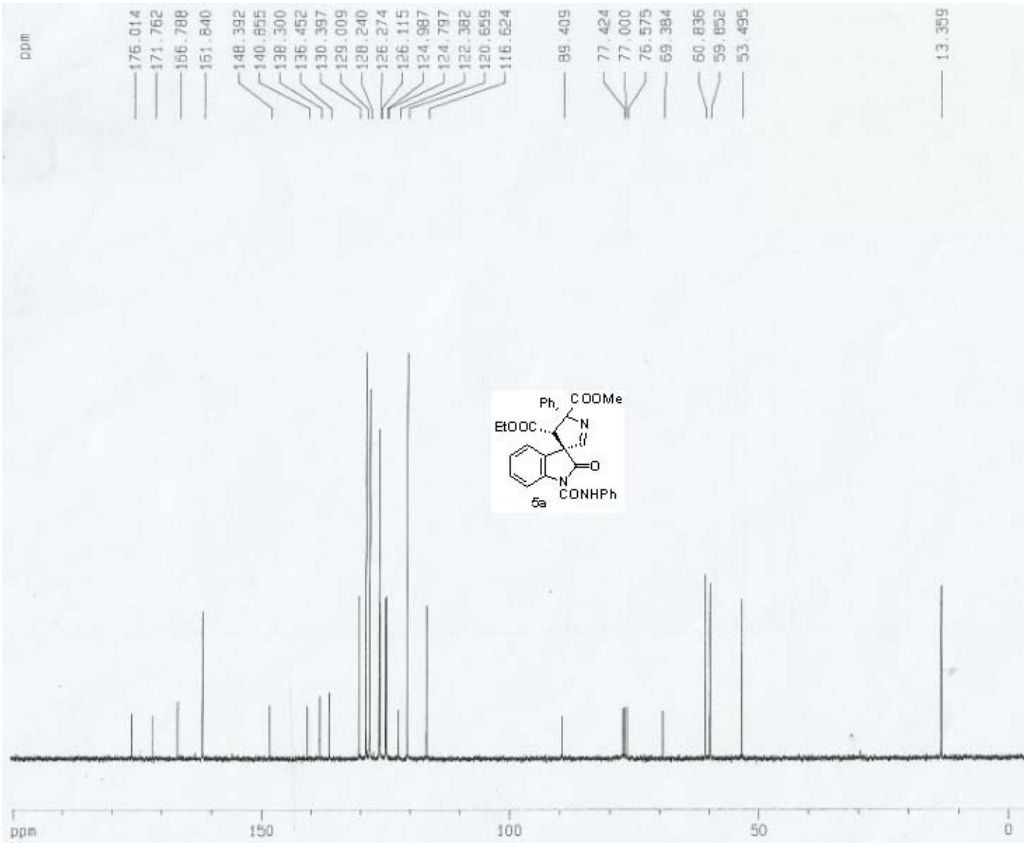


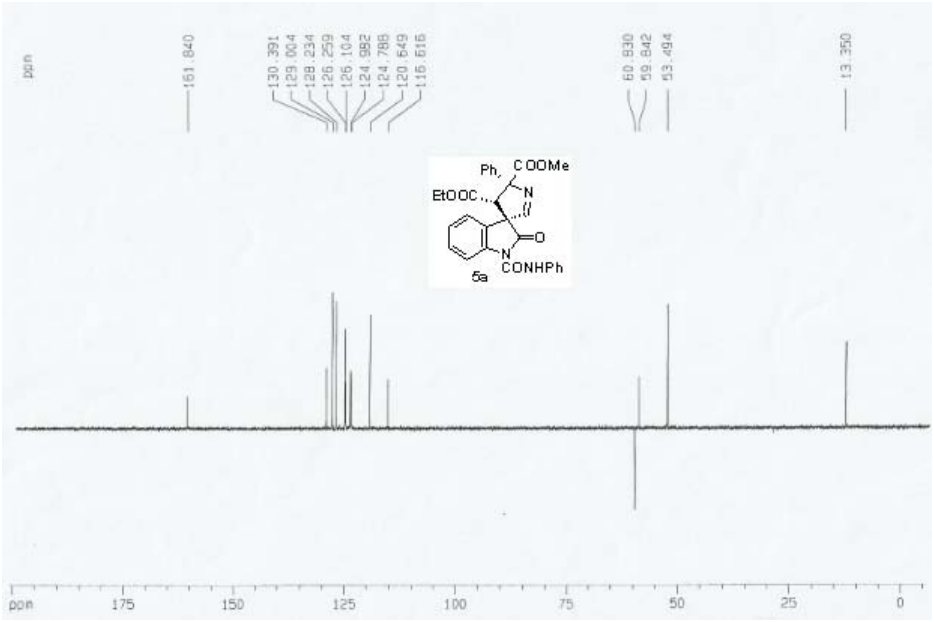
Crystal data and structure refinement for 5m: (CDCC number: CCDC 849674)

Identification code	**5m**
Empirical formula	C27 H28N2O7
Formula weight	492.51
Temperature	100(2) K
Wavelength	1.54178 A
Crystal system, space group	Orthorhombic, P 21 21 21
Unit cell dimensions	a = 12.0989(2) A alpha = 90 deg. b = 12.7731(2) A beta = 90 deg. c = 16.3369(3) A gamma = 90 deg.
Volume	2524.71(7) A^3
Z, Calculated density	4, 1.296 Mg/m^3
Absorption coefficient	0.779 mm^-1
F(000)	1040
Crystal size	0.88 x 0.55 x 0.50 mm
Theta range for data collection	5.42 to 69.52 deg.
Limiting indices	9<=h<=14, -15<=k<=14, -19<=l<=19
Reflections collected / unique	11751 / 4463 [R(int) = 0.0289]
Completeness to theta = 69.52	96.7 %
Absorption correction	None
Refinement method	Full-matrix least-squares on F^2
Data / restraints / parameters	4463 / 0 / 331
Goodness-of-fit on F^2	1.168
Final R indices [I>2sigma(I)]	R1 = 0.0326, wR2 = 0.0844
R indices (all data)	R1 = 0.0326, wR2 = 0.0844
Absolute structure parameter	0.11(13)
Extinction coefficient	0.0116(5)
Largest diff. peak and hole	0.379 and -0.289 e.A^-3

9. NMR spectra



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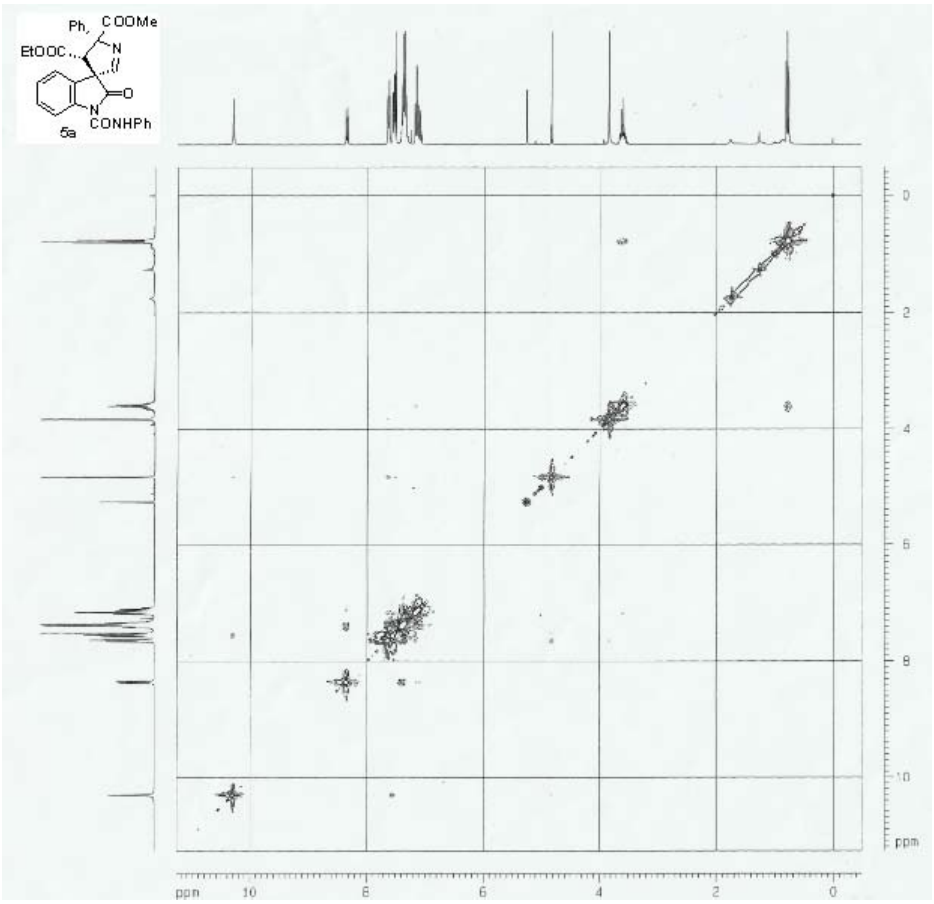
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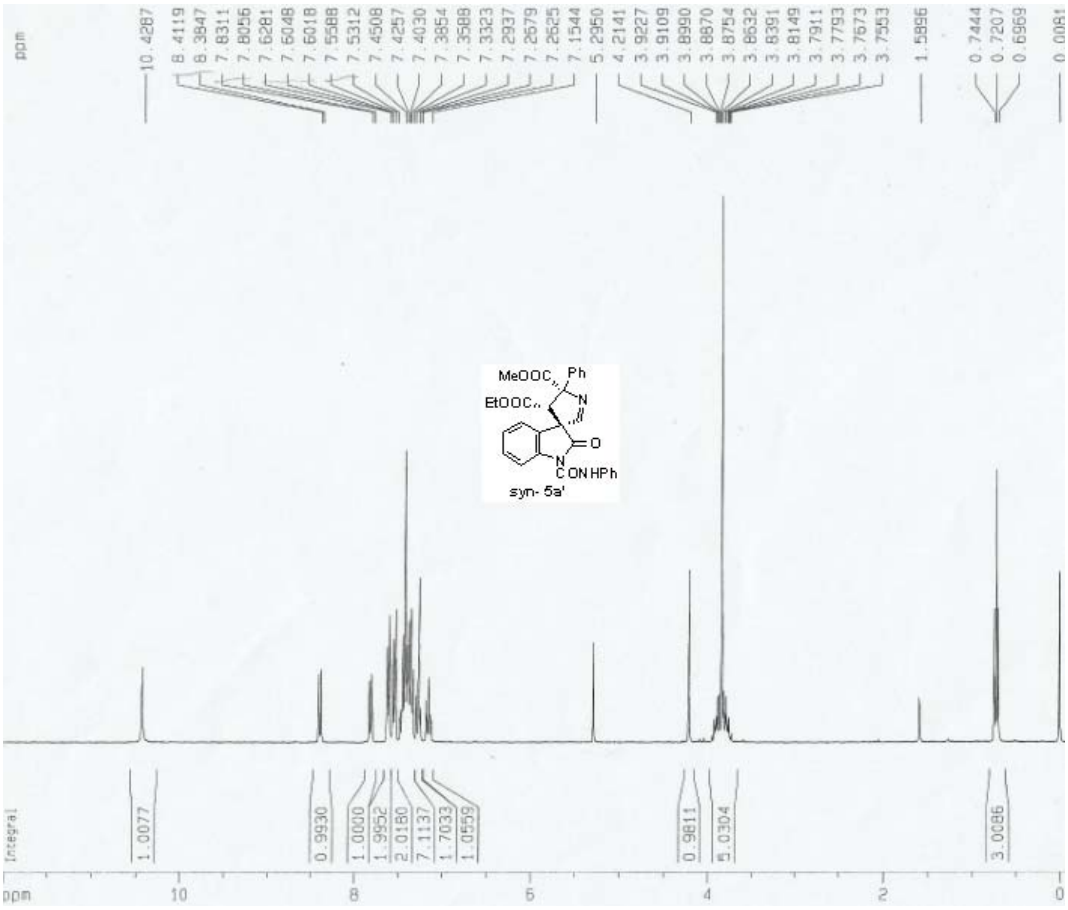
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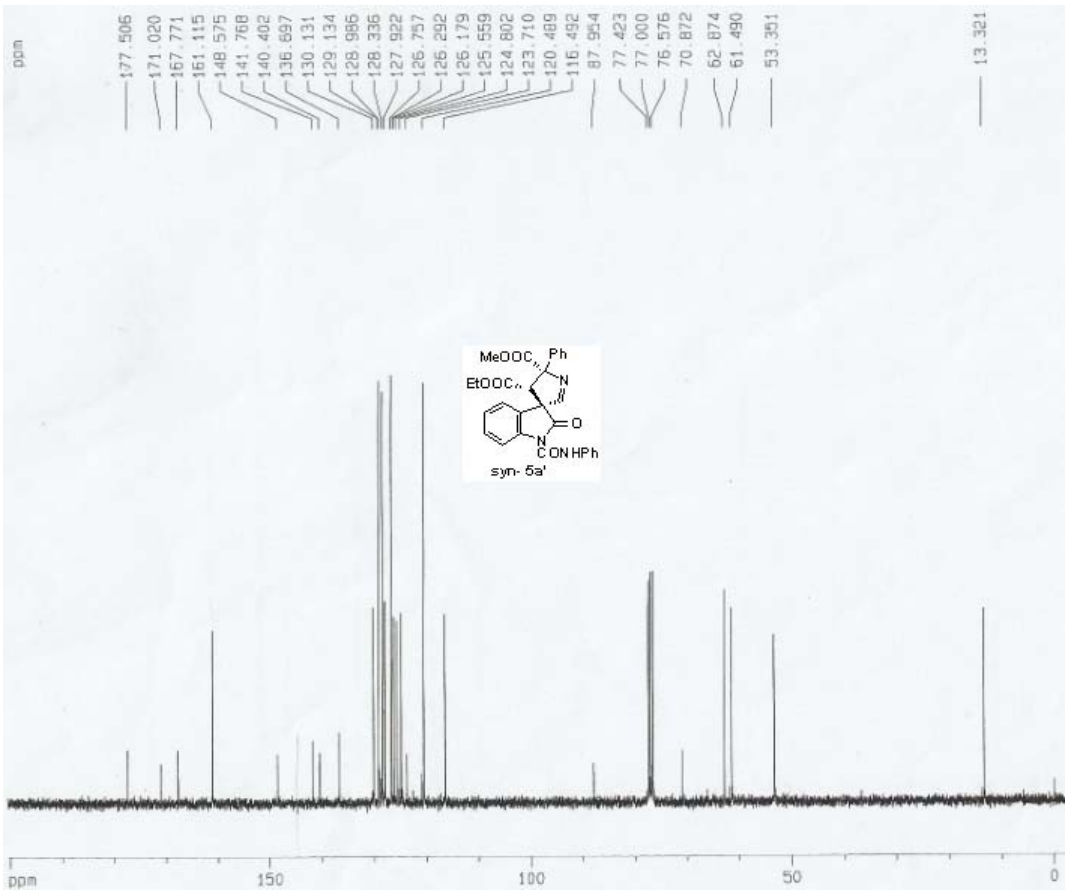
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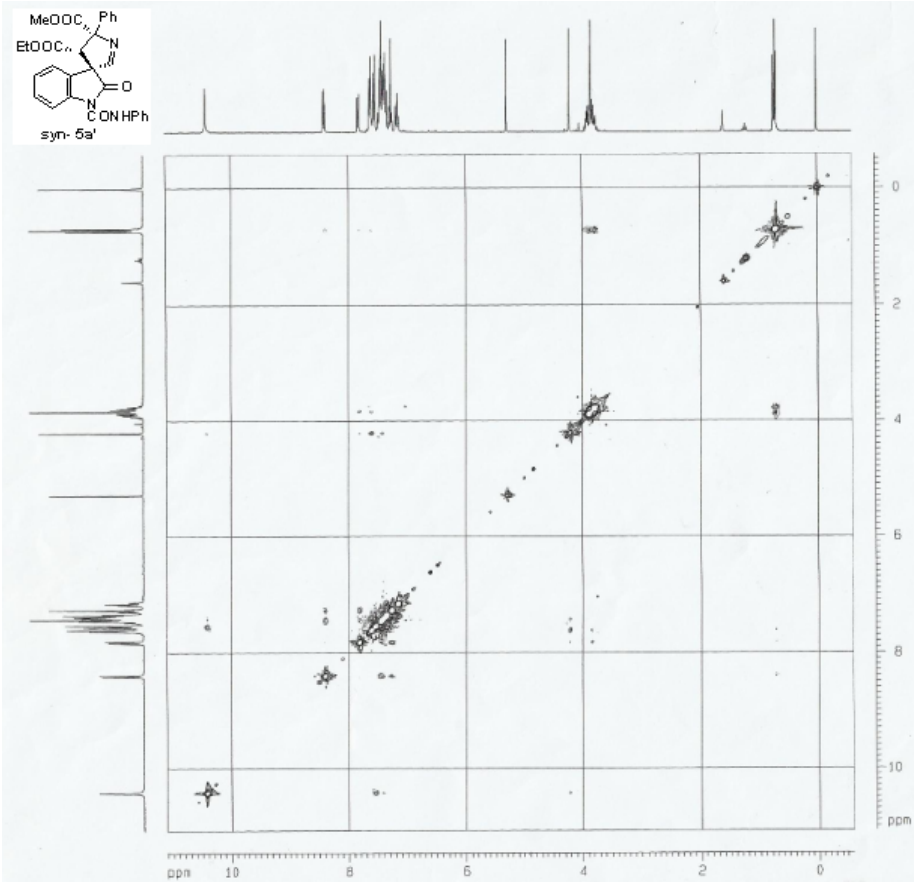
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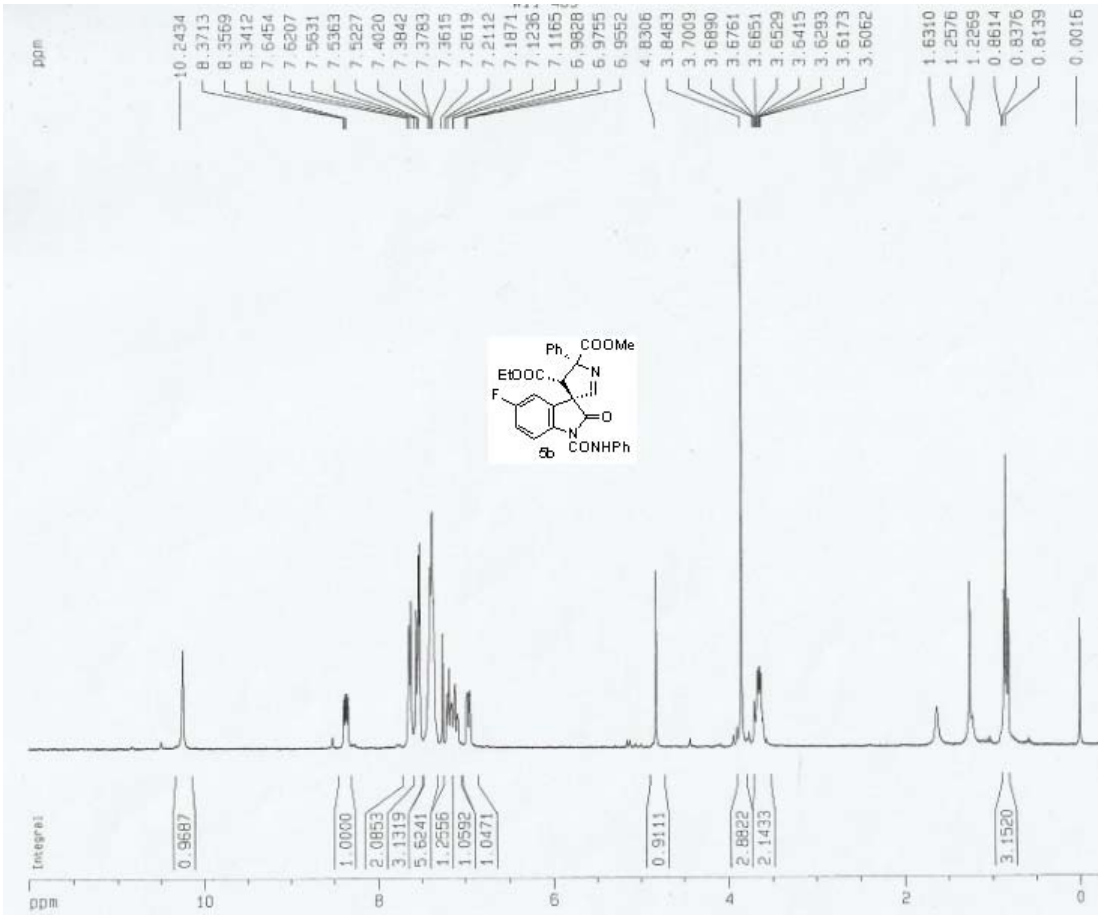
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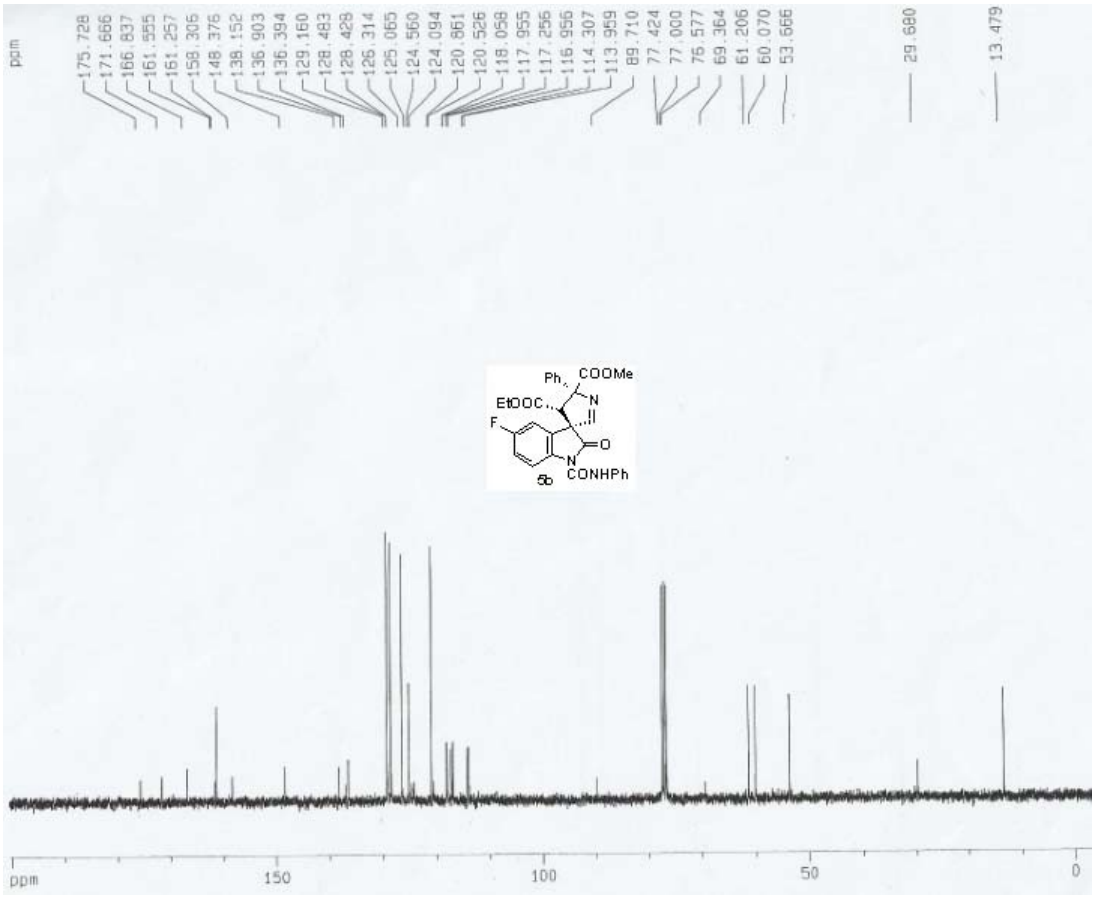
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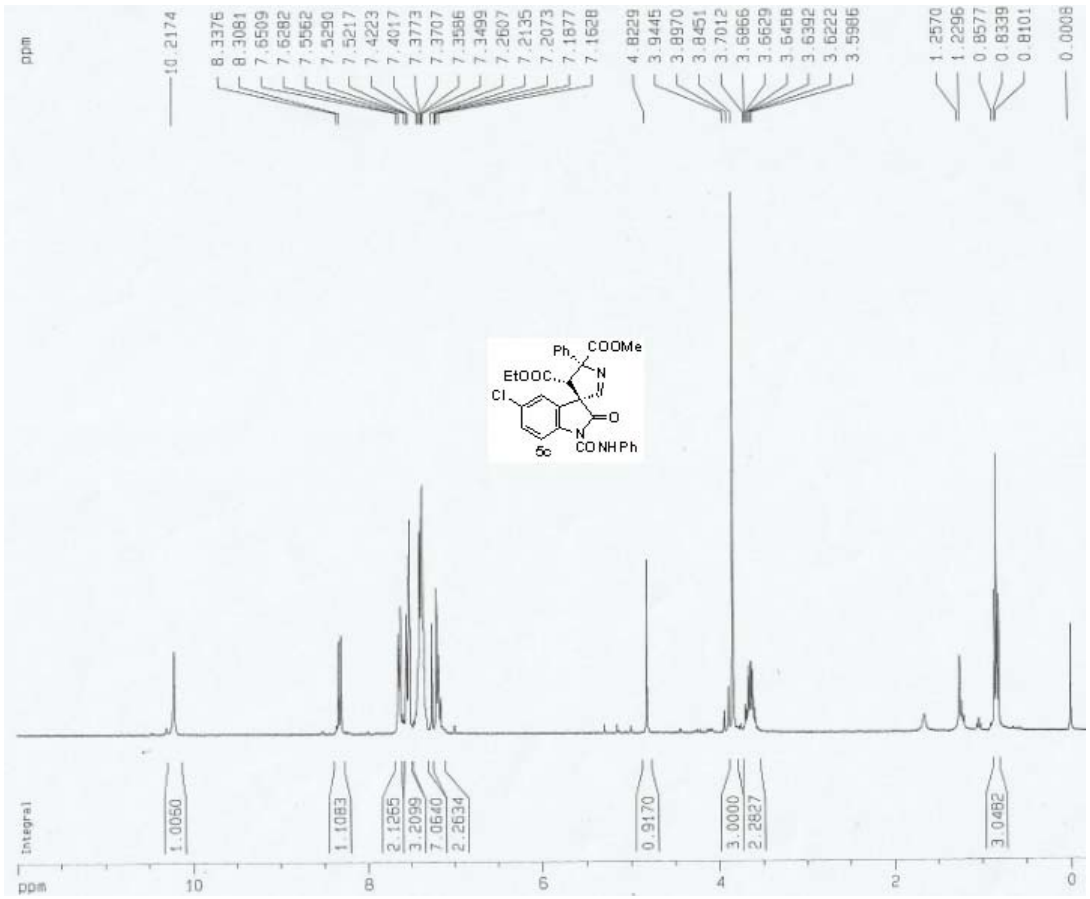
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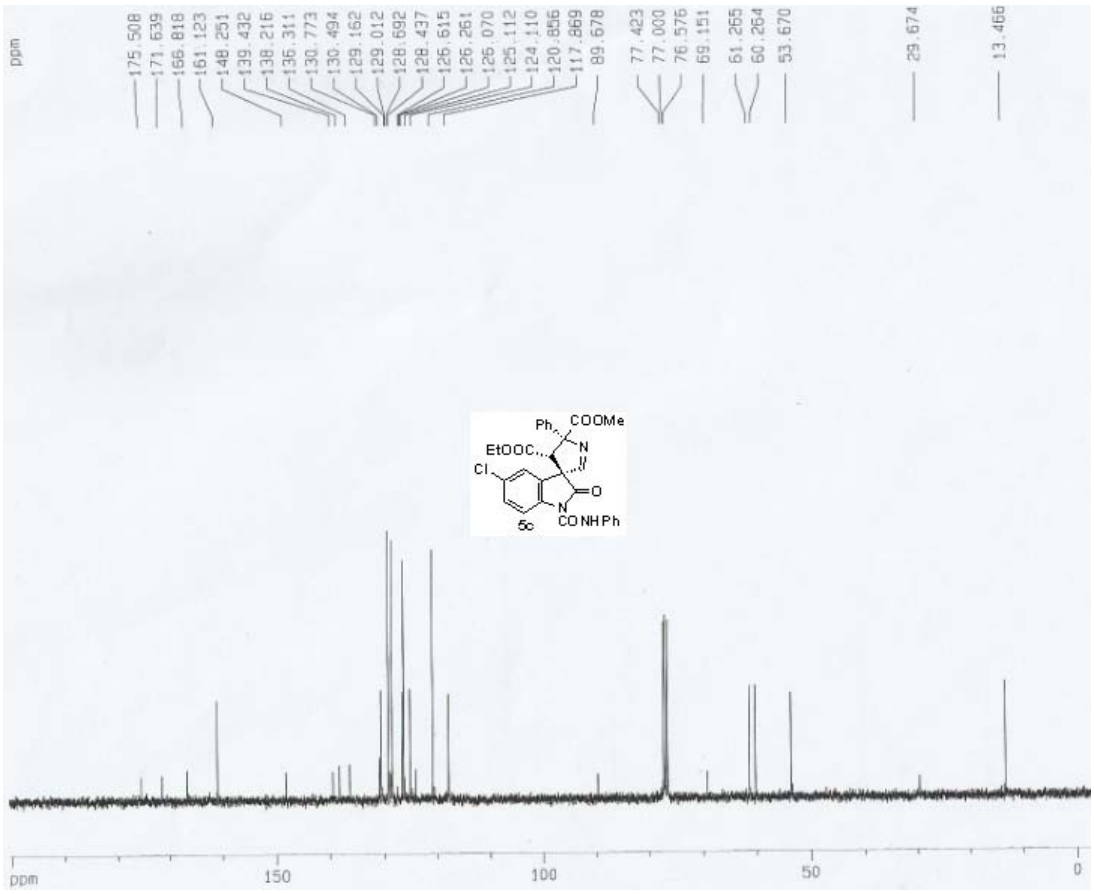
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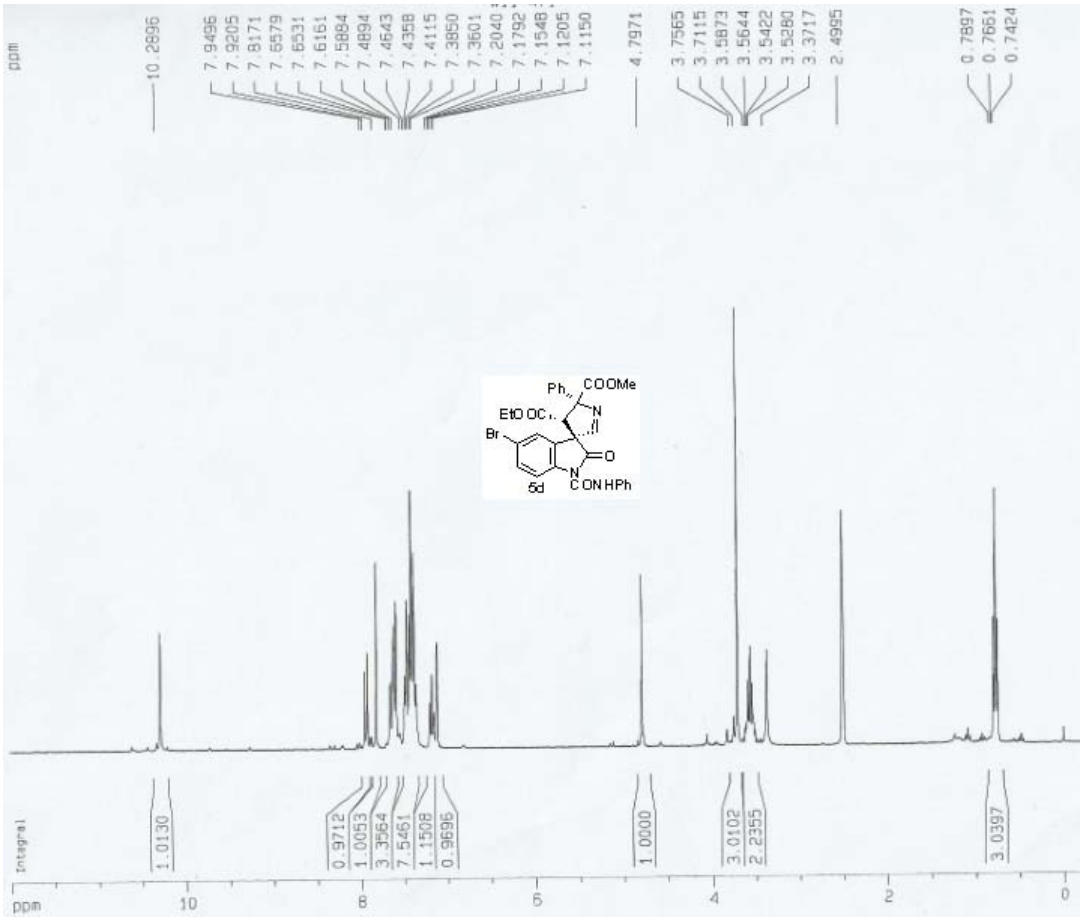
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1.1508
0.9696
1.0000
3.0102
2.2355
3.0397
ppm
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4
2
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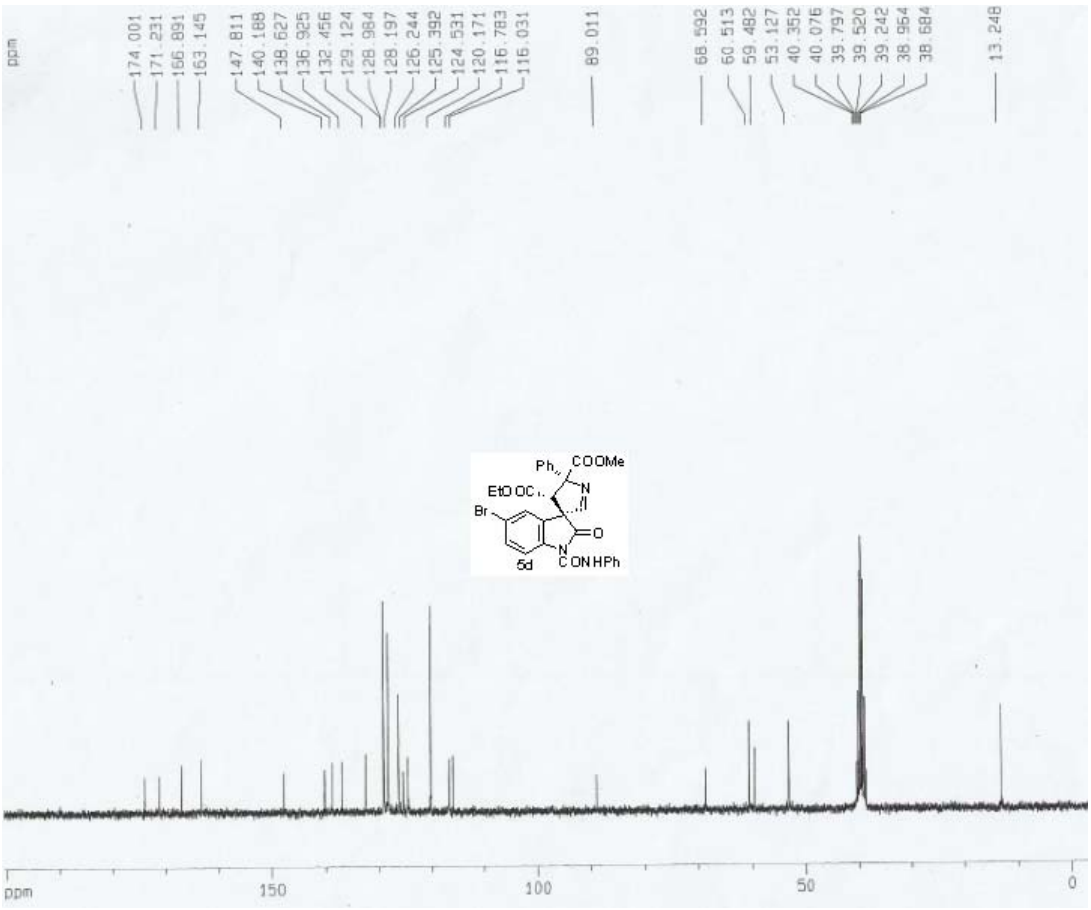
COOMe
EtOOC
N
Br
O
N
CONHPh
5d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166.891
163.145
147.811
140.188
138.627
136.925
132.456
129.124
128.984
128.197
126.244
125.392
124.531
120.171
116.783
116.031
89.011
68.592
60.513
59.482
53.127
40.352
40.076
39.797
39.520
39.242
38.964
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Ph
COOMe
EtOOC
N
Br
O
N
CONHPh
5d
ppm
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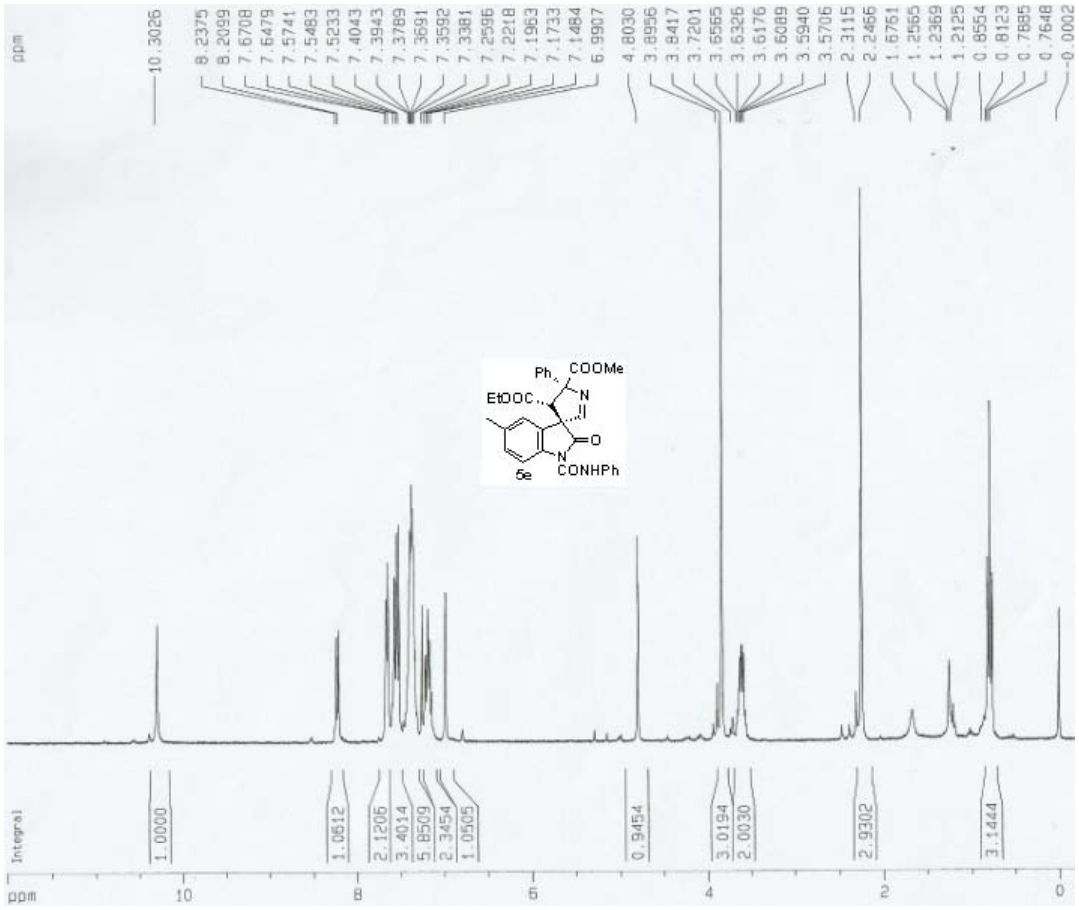
100
50
0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7.5741
7.5483
7.5233
7.4043
7.3943
7.3789
7.3691
7.3592
7.3381
7.2596
7.2218
7.1963
7.1733
7.1484
6.9907
4.8030
3.8956
3.8417
3.7201
3.5565
3.5326
3.6176
3.6089
3.5940
3.5706
2.3115
2.2466
1.6751
1.2565
1.2369
1.2125
0.8554
0.8123
0.7885
0.7648
0.0002
Ph
COOMe
EtOOC
N
O
N
CONHPh
5e
Integral
1.0000
1.0612
2.1206
3.4014
5.8509
2.3454
1.0505
0.9454
3.0194
2.0030
2.9302
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8
6
4
2
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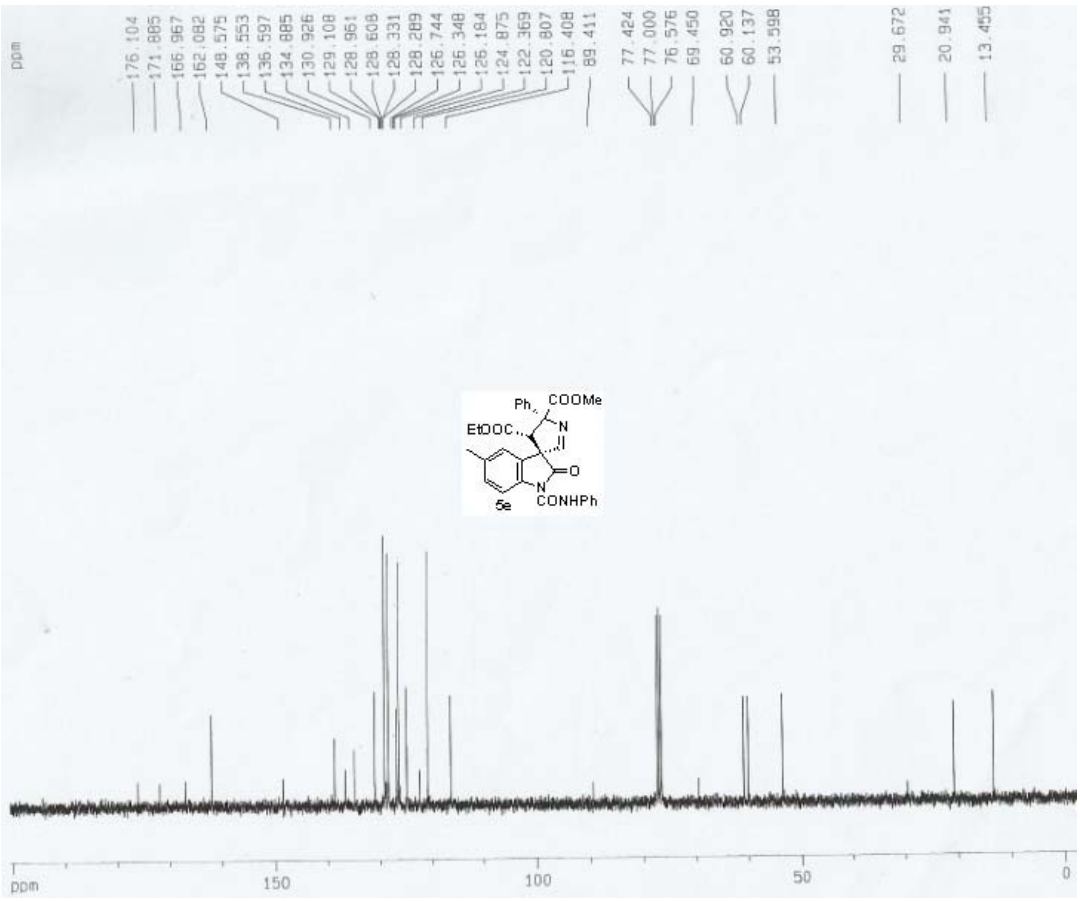
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129.108
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128.331
128.289
126.744
126.348
126.184
124.875
122.369
120.807
116.408
89.411
77.424
77.000
76.576
69.450
60.920
60.137
53.598
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EtOOC
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O
N
CONHPh
5e
ppm
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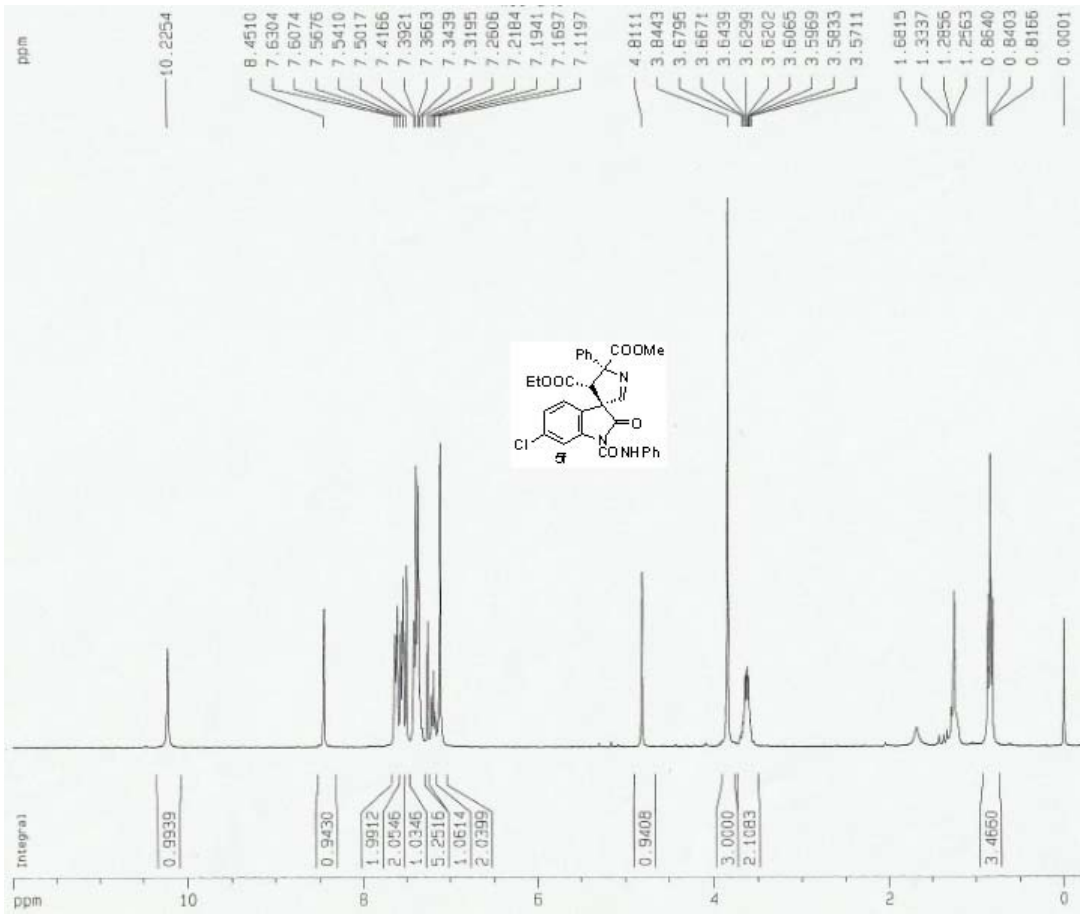
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7.3663
7.3439
7.3195
7.2606
7.1197
4.8111
3.8443
3.6795
3.6671
3.6439
3.6299
3.6202
3.6065
3.5969
3.5833
3.5711
1.6815
1.3337
1.2856
1.2563
0.8640
0.8403
0.8165
0.0001
Ph
COOMe
EtOOC
N
O
Cl
N
CONHPh
Integral
0.9939
0.9430
1.9912
2.0546
1.0346
5.2516
1.0614
2.0399
0.9408
3.0000
2.1083
3.4650
ppm
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8
6
4
2
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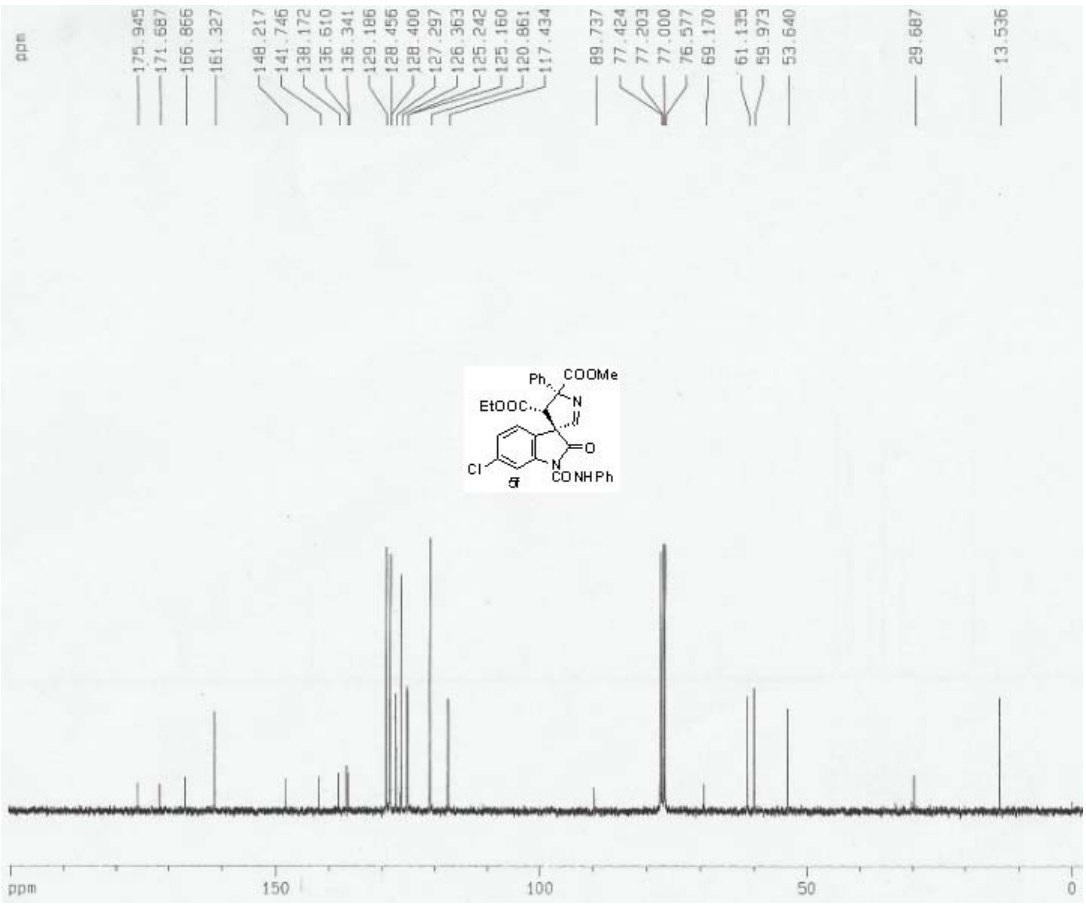
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129.186
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127.297
126.363
125.242
125.160
120.861
117.434
89.737
77.424
77.203
77.000
76.577
69.170
61.135
59.973
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Ph
COOMe
EtOOC
N
O
Cl
N
CONHPh
ppm
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50
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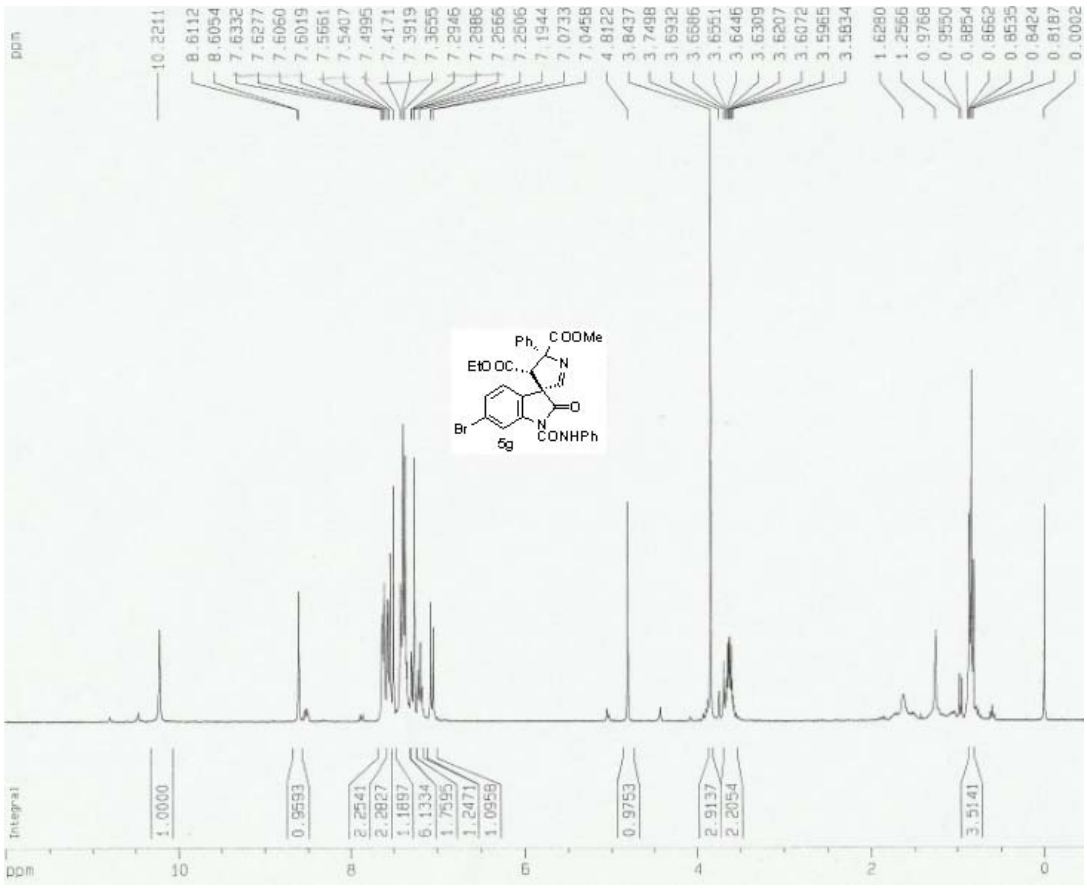
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7.6060
7.6019
7.5661
7.5407
7.4995
7.4171
7.3919
7.3655
7.2946
7.2886
7.2666
7.2506
7.1944
7.0733
7.0458
4.8122
3.8437
3.7498
3.6932
3.6686
3.6551
3.6446
3.6309
3.6207
3.6072
3.5965
3.5834
1.6280
1.2566
0.9768
0.9550
0.8854
0.8652
0.8535
0.8424
0.8187
0.0002
Ph
COOMe
EtOOC
N
O
Br
N
CONHPh
5g
Integral
1.0000
0.9593
2.2541
2.2827
1.1697
6.1334
1.7595
1.2471
1.0958
0.9753
2.9137
2.2054
3.5141
ppm
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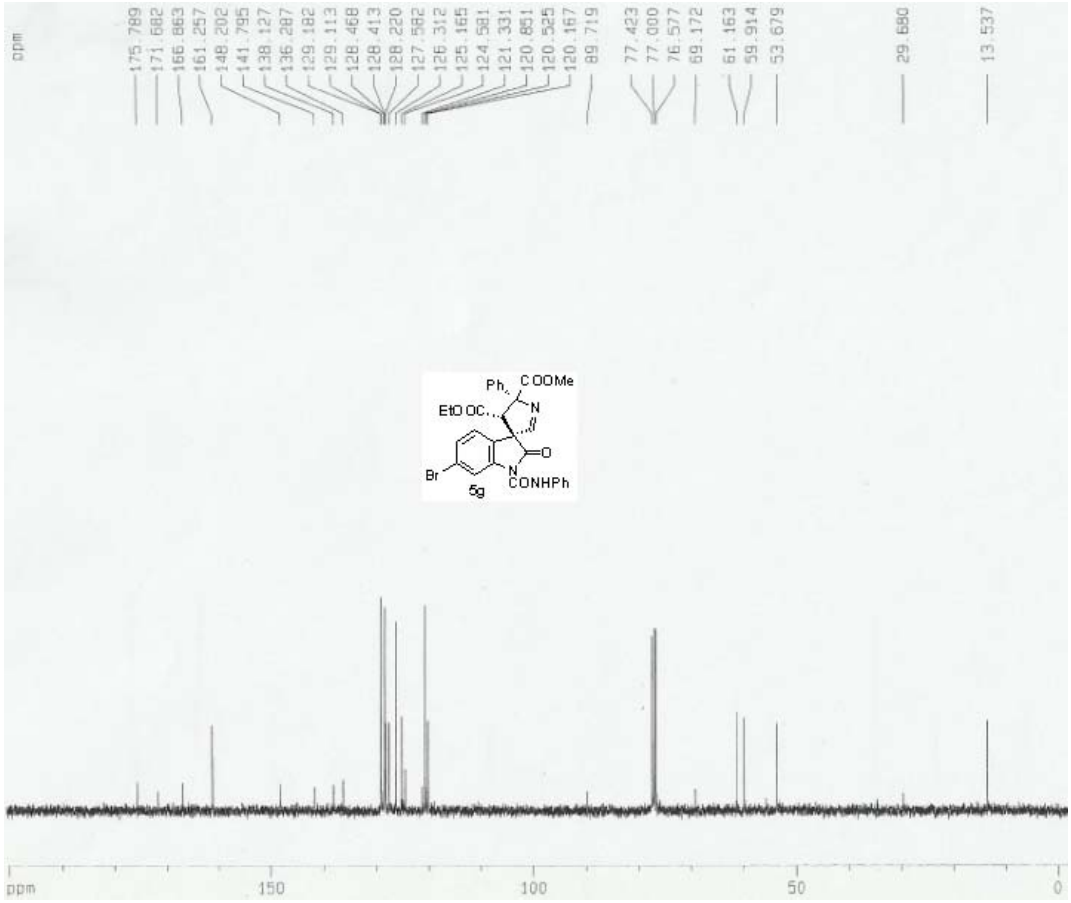
8
6
4
2
0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141.795
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136.287
129.182
129.113
128.468
128.413
128.220
127.562
126.312
125.165
124.581
121.331
120.851
120.525
120.167
89.719
77.423
77.000
76.577
69.172
61.163
59.914
53.679
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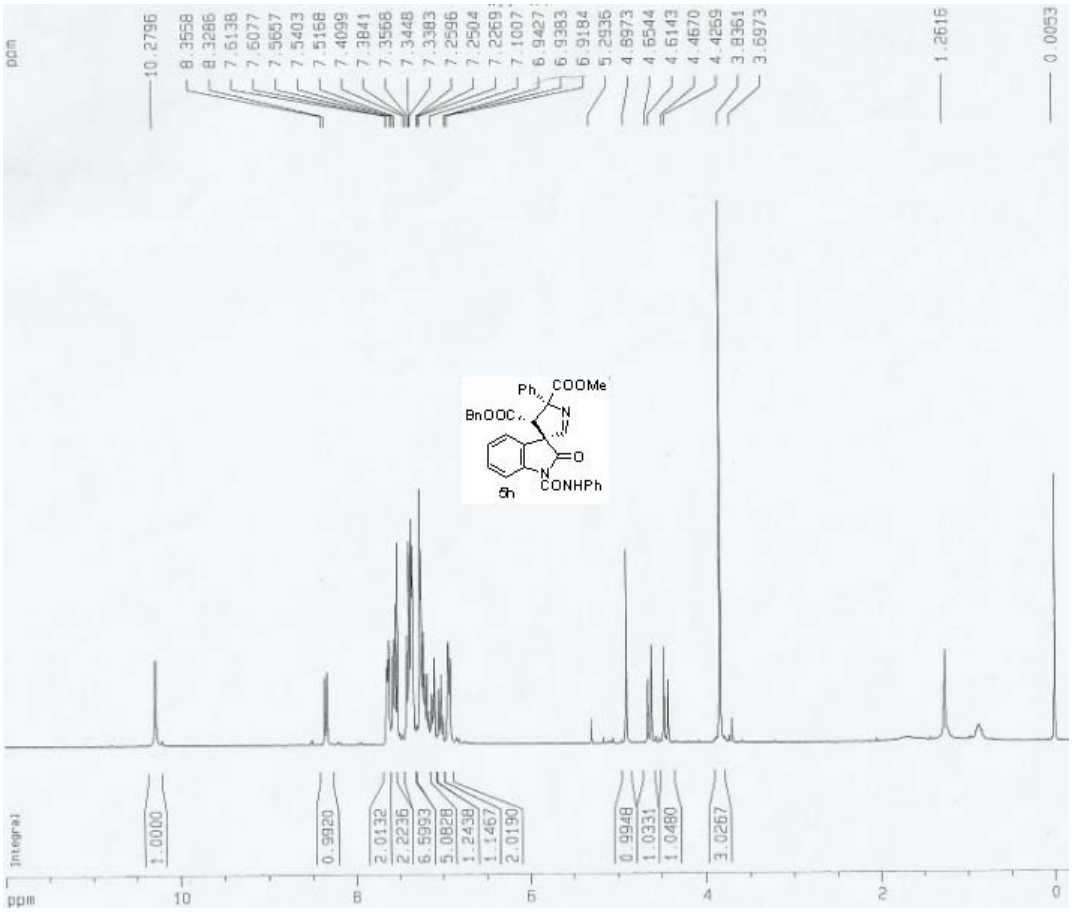
Ph
COOMe
EtOOC
N
O
Br
N
CONHPh
5g
ppm
150
100
50
0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7.5168
7.4099
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7.3566
7.3448
7.3383
7.2596
7.2504
7.2269
7.1007
6.9427
6.9383
6.9184
5.2936
4.8973
4.6544
4.6143
4.4670
4.4259
3.8361
3.6973
1.2616
0.0053
Ph
COOMe
BnOOC
N
O
N
CONHPh
5h
Integral
1.0000
0.9920
2.0132
2.2236
6.5993
5.0828
1.2438
1.1467
2.0190
0.9948
1.0331
1.0480
3.0267
ppm
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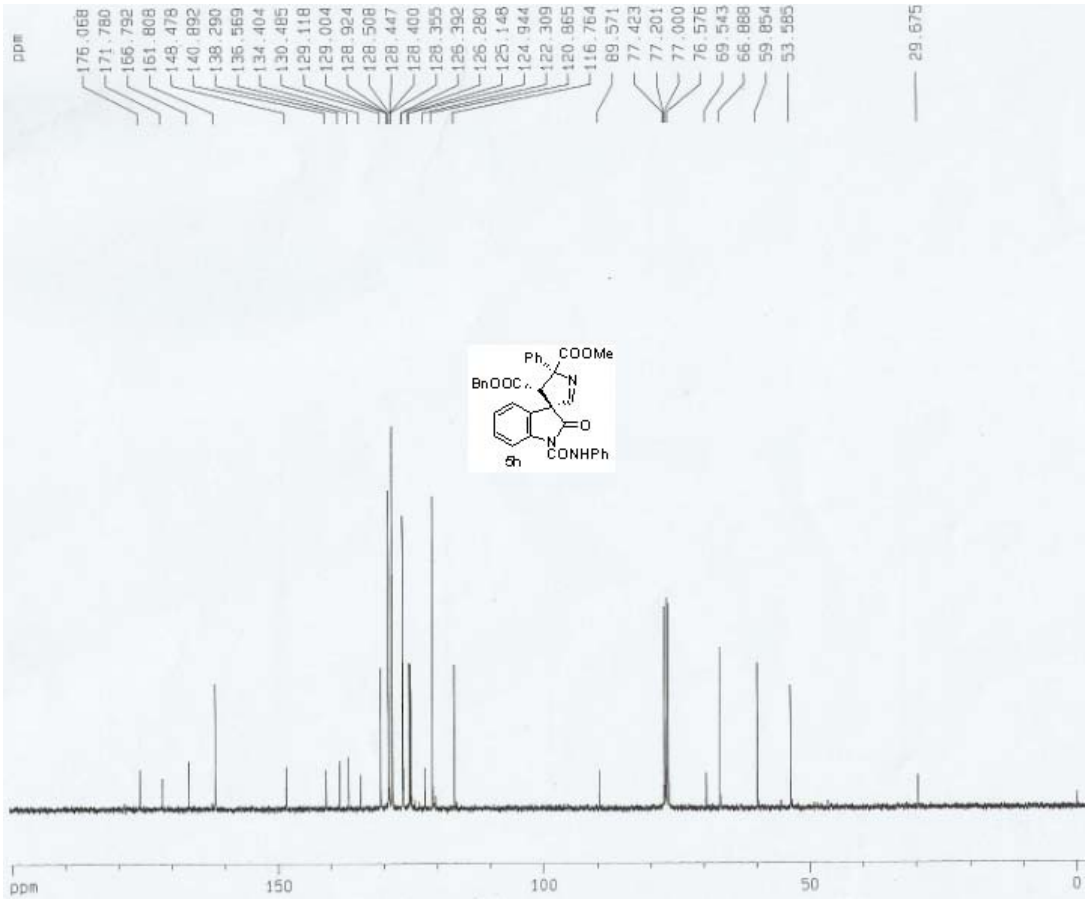
8
6
4
2
0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135.569
134.404
130.485
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129.004
128.924
128.508
128.447
128.400
128.355
126.392
126.280
125.148
124.944
122.309
120.965
116.764
89.571
77.423
77.201
77.000
76.576
69.543
66.888
59.854
53.585
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Ph
COOMe
BnOOC
N
O
N
CONHPh
5h
ppm
150
100
50
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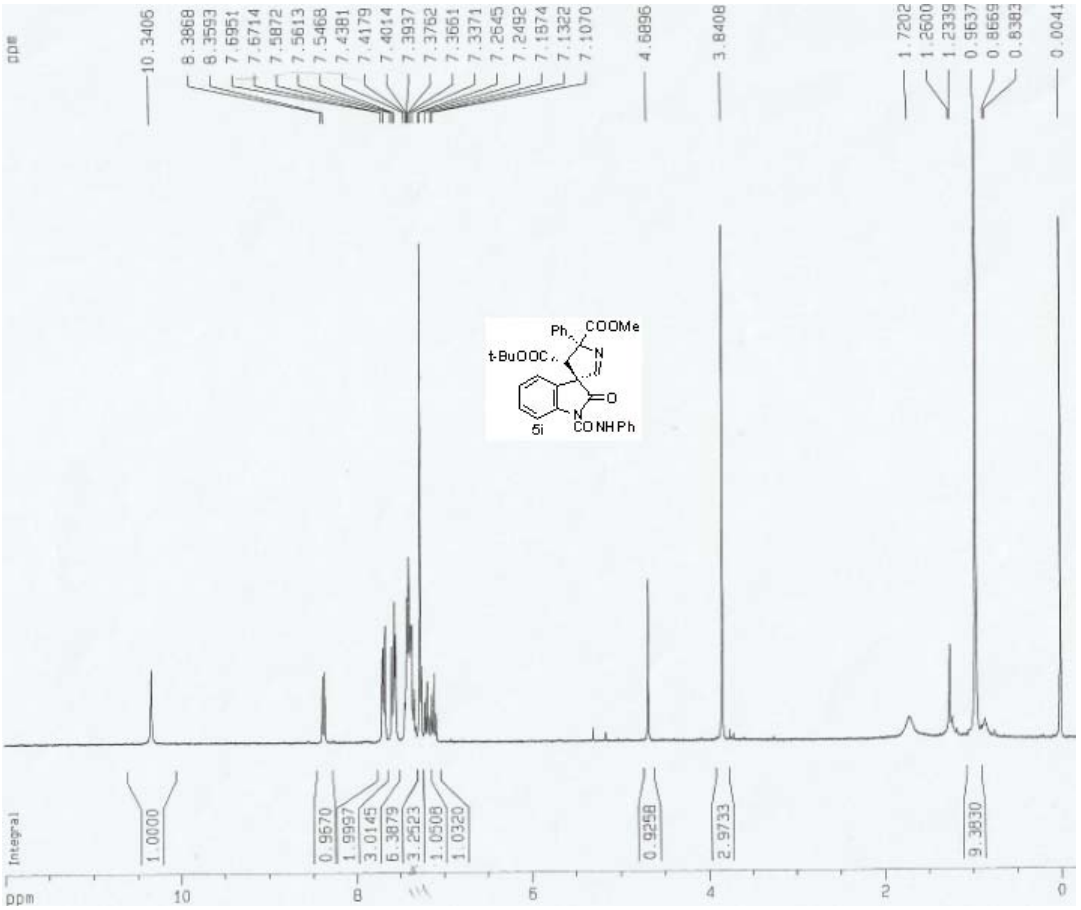
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7.6714
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7.5468
7.4381
7.4179
7.4014
7.3937
7.3762
7.3661
7.3371
7.2645
7.2492
7.1874
7.1322
7.1070
4.6896
3.8408
1.7202
1.2600
1.2339
0.9637
0.8669
0.8383
0.0041
Ph
COOMe
t-BuOOC
N
O
N
CONHPh
5i
Integral
1.0000
0.9570
1.9997
3.0145
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1.0320
0.9258
2.9733
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ppm
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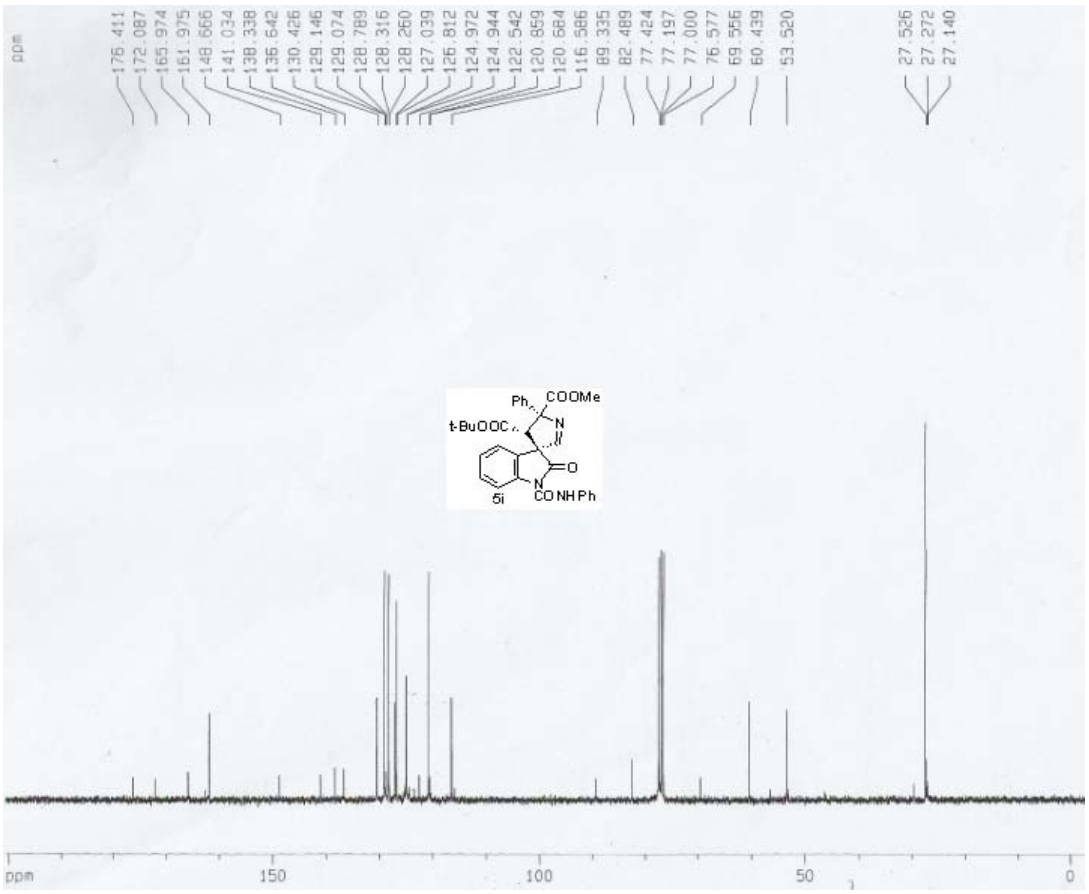
8
5
4
2
0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128.789
128.316
128.260
127.039
126.812
124.972
124.944
122.542
120.859
120.684
116.586
89.335
82.489
77.424
77.197
77.000
76.577
69.556
60.439
53.520
27.526
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Ph
COOMe
t-BuOOC
N
O
N
CONHPh
5i
ppm
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100
50
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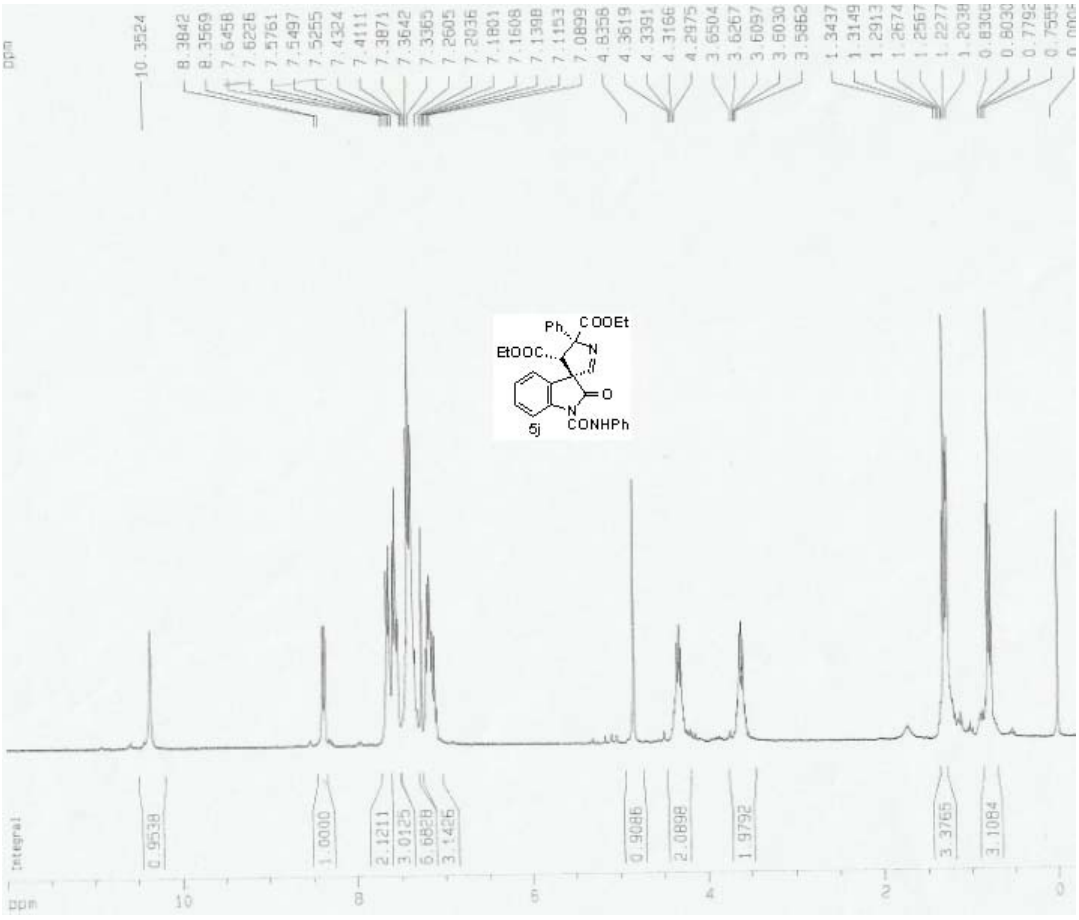
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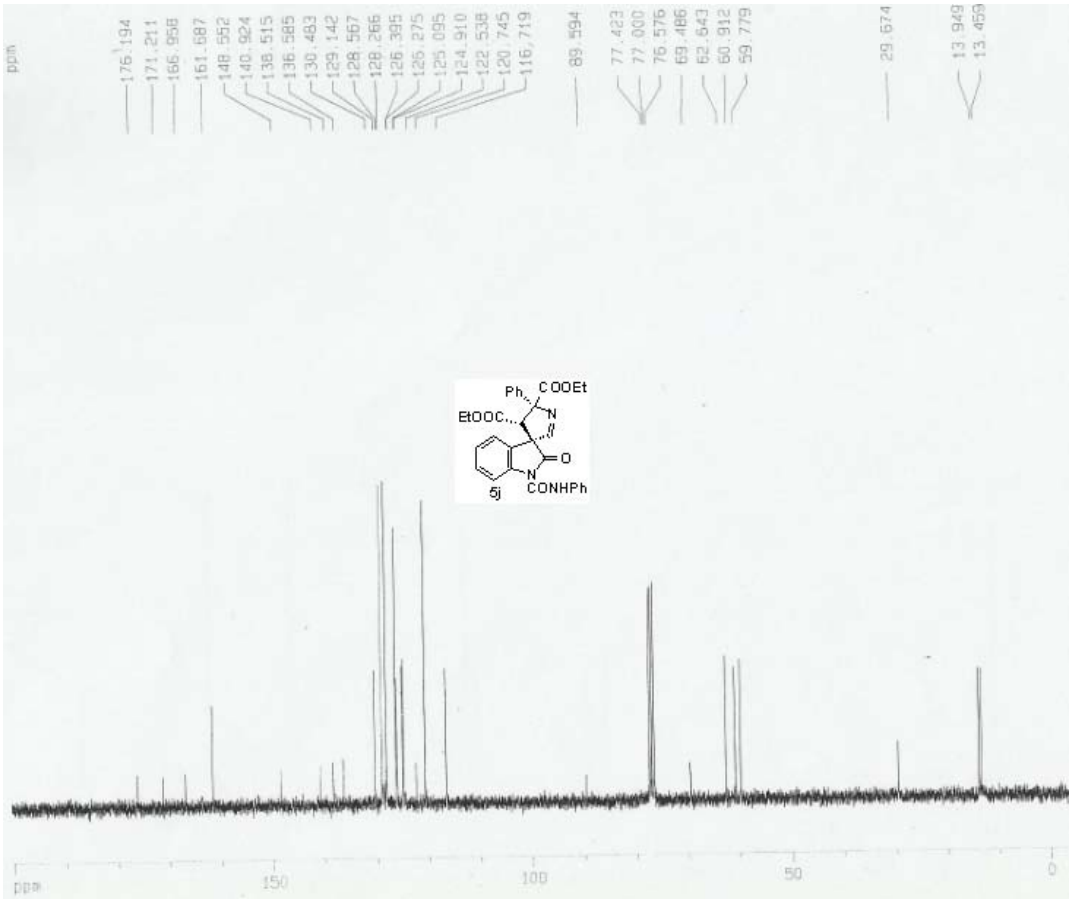
N
O
N
CONHPh
5j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EtOOC
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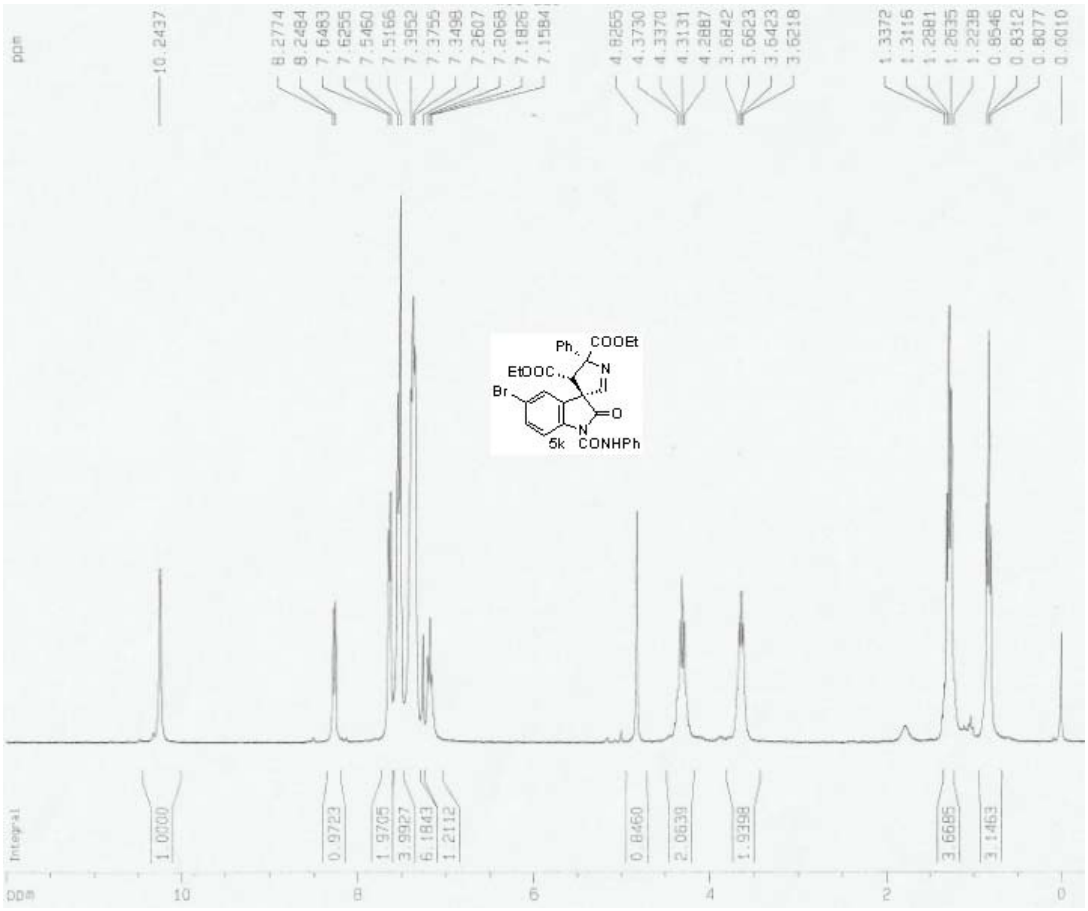
O
N
CONHPh
5j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7.3952
7.3755
7.3498
7.2607
7.2068
7.1826
7.1584
4.8265
4.3730
4.3370
4.3131
4.2887
3.6842
3.6623
3.6423
3.6218
1.3372
1.3115
1.2881
1.2635
1.2239
0.8546
0.8312
0.8077
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COOEt
EtOOC
N
Br
O
N
5k
CONHPh
Integral
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1.9705
3.9927
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6
4
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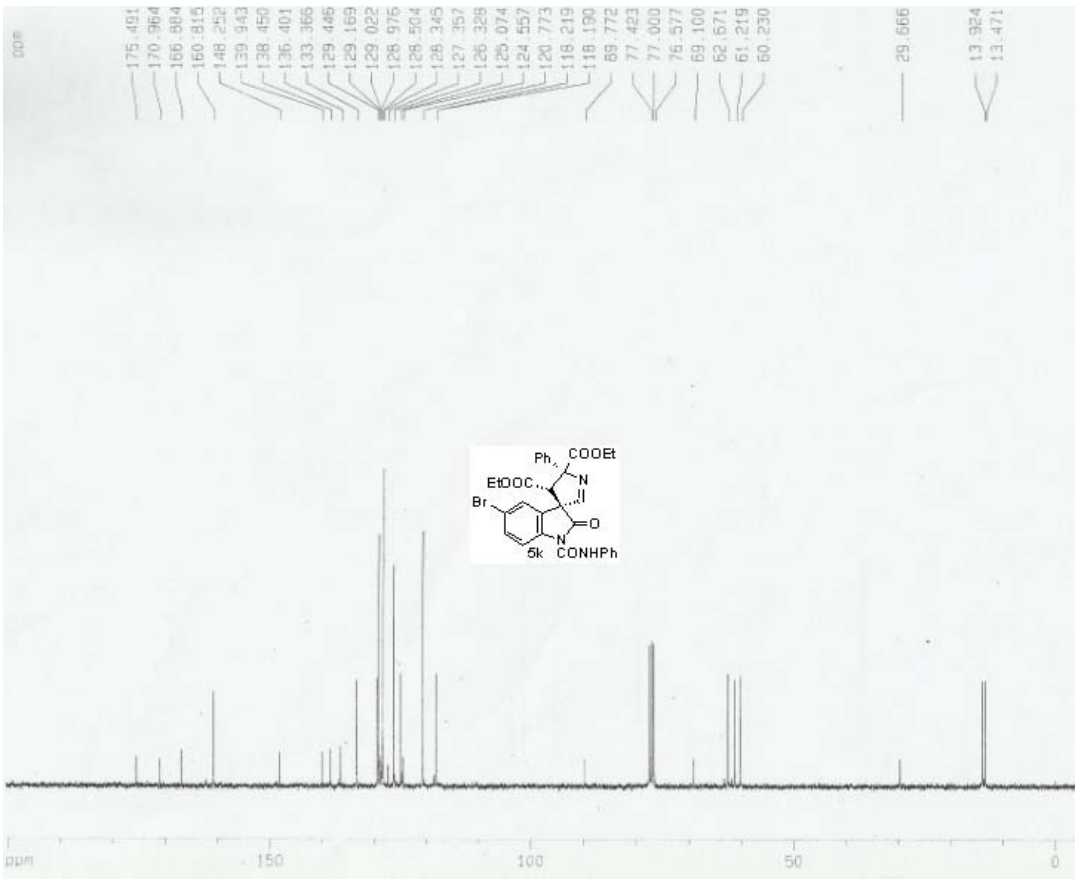
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129.169
129.022
128.976
128.504
128.345
127.357
126.328
125.074
124.557
120.773
118.219
118.190
89.772
77.423
77.000
76.577
69.100
62.671
61.219
60.230
29.666
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Ph
COOEt
EtOOC
N
Br
O
N
5k
CONHPh
ppm
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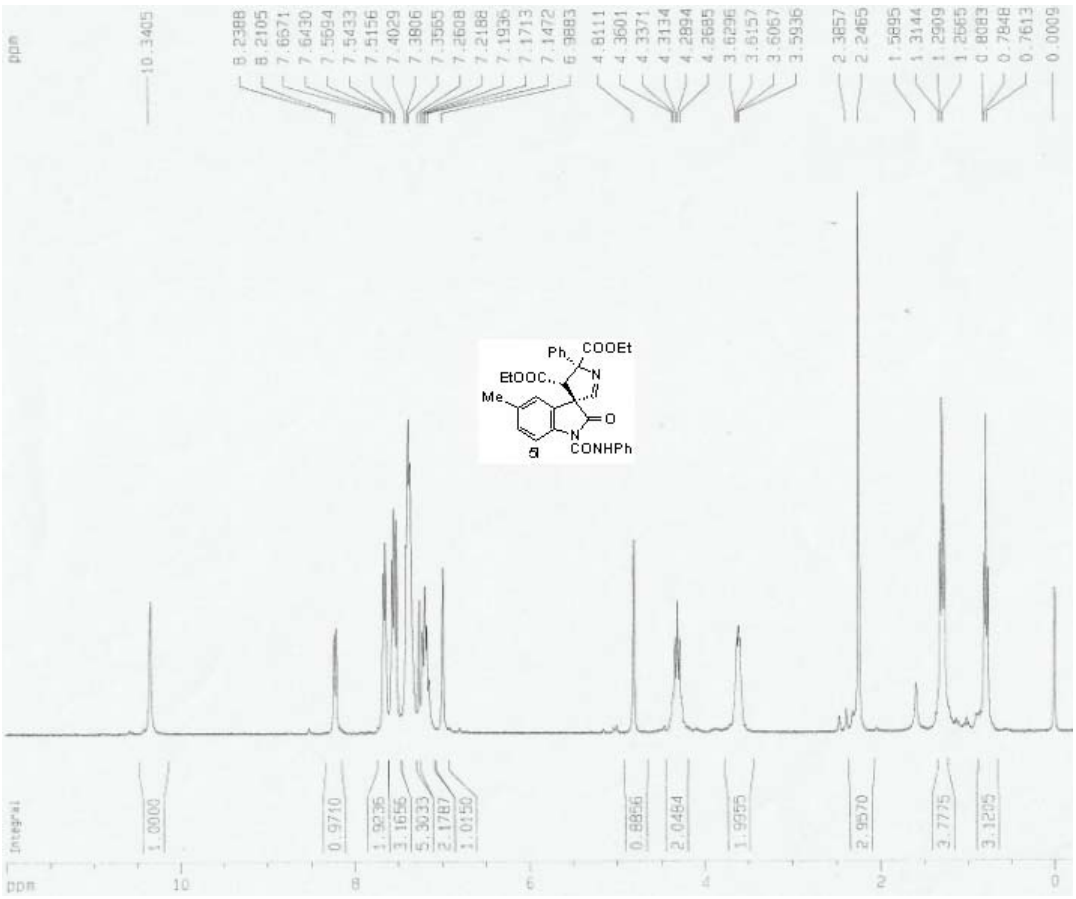
100
50
0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7.4029
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7.3565
7.2608
7.2188
7.1936
7.1713
7.1472
6.9883
4.8111
4.3601
4.3371
4.3134
4.2894
4.2685
3.6296
3.6157
3.6067
3.5936
2.3857
2.2465
1.5695
1.3144
1.2909
1.2565
0.8083
0.7848
0.7613
0.0009
Integral
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3.1656
5.3033
2.1787
1.0150
0.8856
2.0464
1.9995
2.9570
3.7775
3.1205
ppm
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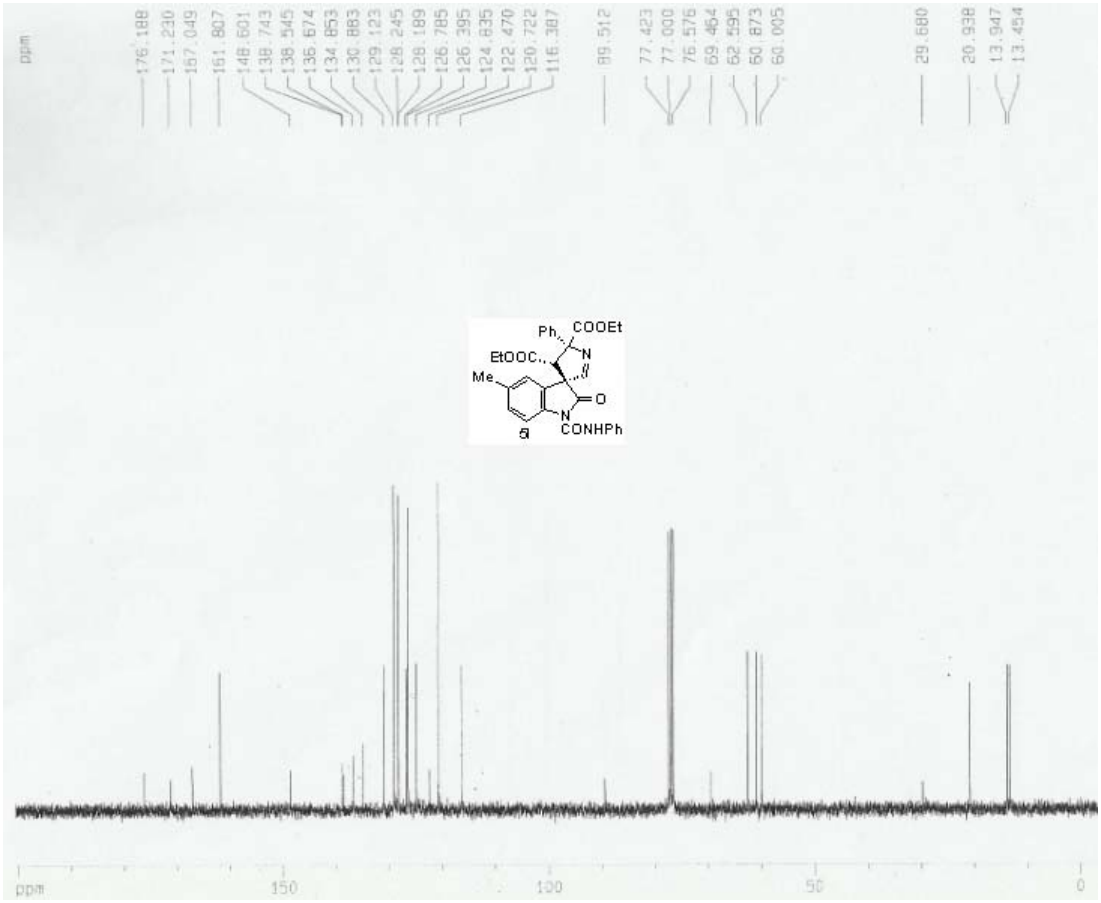
8
6
4
2
0
Ph
COOEt
EtOOC
N
Me
O
N
CONHPh
a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128.189
126.785
126.395
124.635
122.470
120.722
116.387
89.512
77.423
77.000
76.576
69.464
62.595
60.873
60.005
29.680
20.938
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ppm
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100
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0
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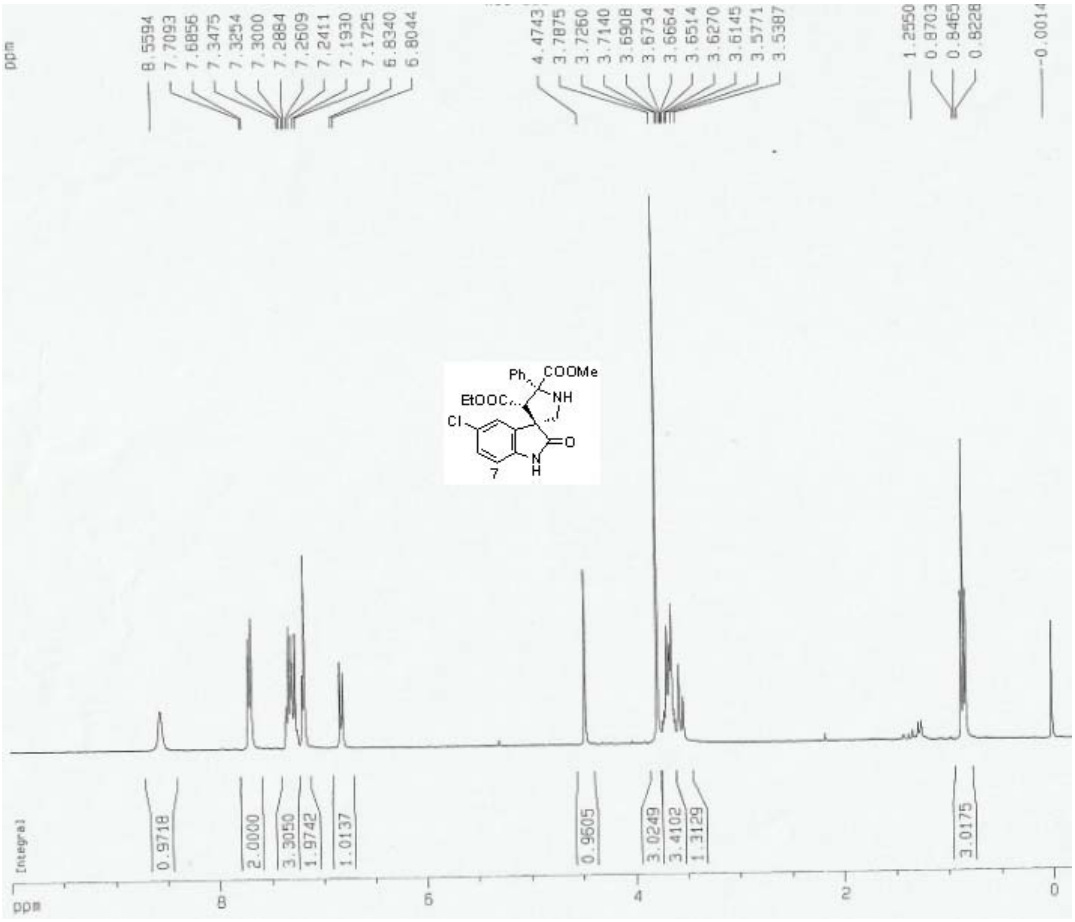
EtOOC
N
Me
O
N
CONHPh
a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7.1725
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6.8044
4.4743
3.7875
3.7260
3.7140
3.6908
3.6734
3.6664
3.6514
3.6270
3.6145
3.5771
3.5387
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0.8703
0.8465
0.8228
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Ph
COOMe
EtOOC
NH
Cl
O
N
H
7
Integral
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ppm
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6
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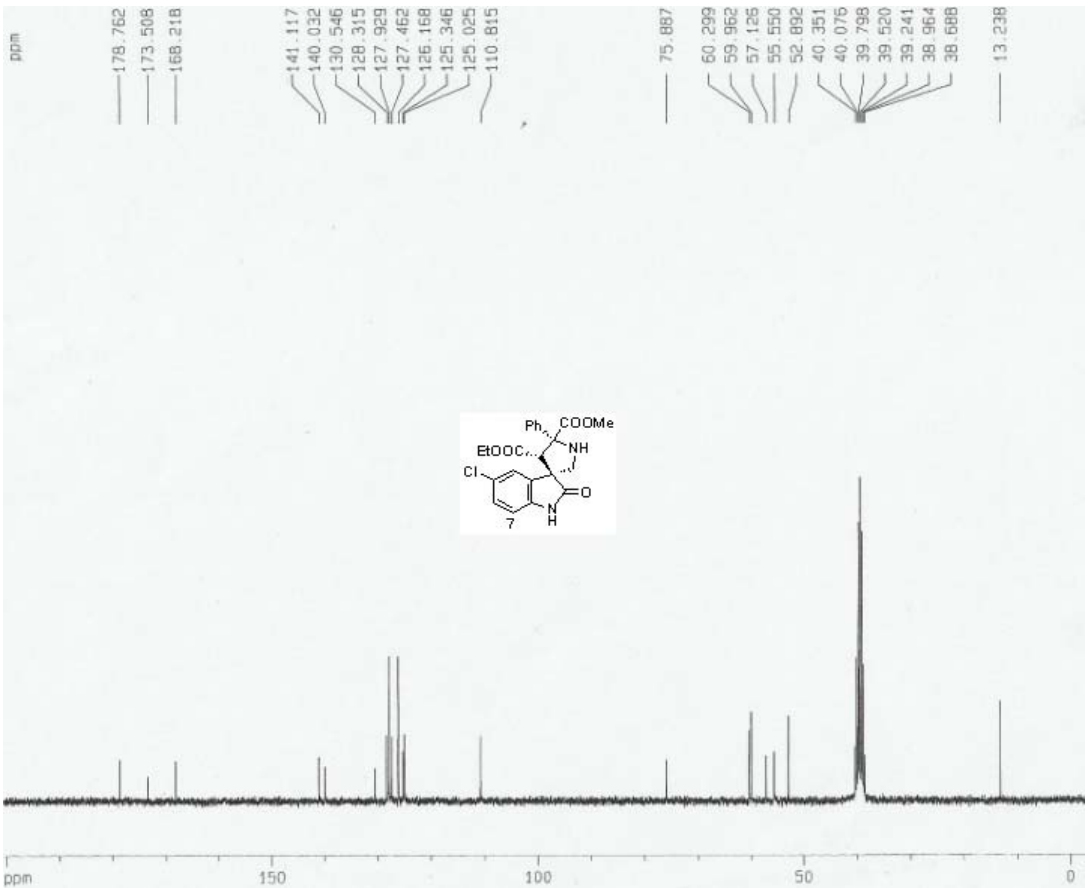
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127.462
126.168
125.346
125.025
110.815
75.887
60.299
59.962
57.125
55.550
52.892
40.351
40.075
39.798
39.520
39.241
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Ph
COOMe
EtOOC
NH
Cl
O
N
H
7
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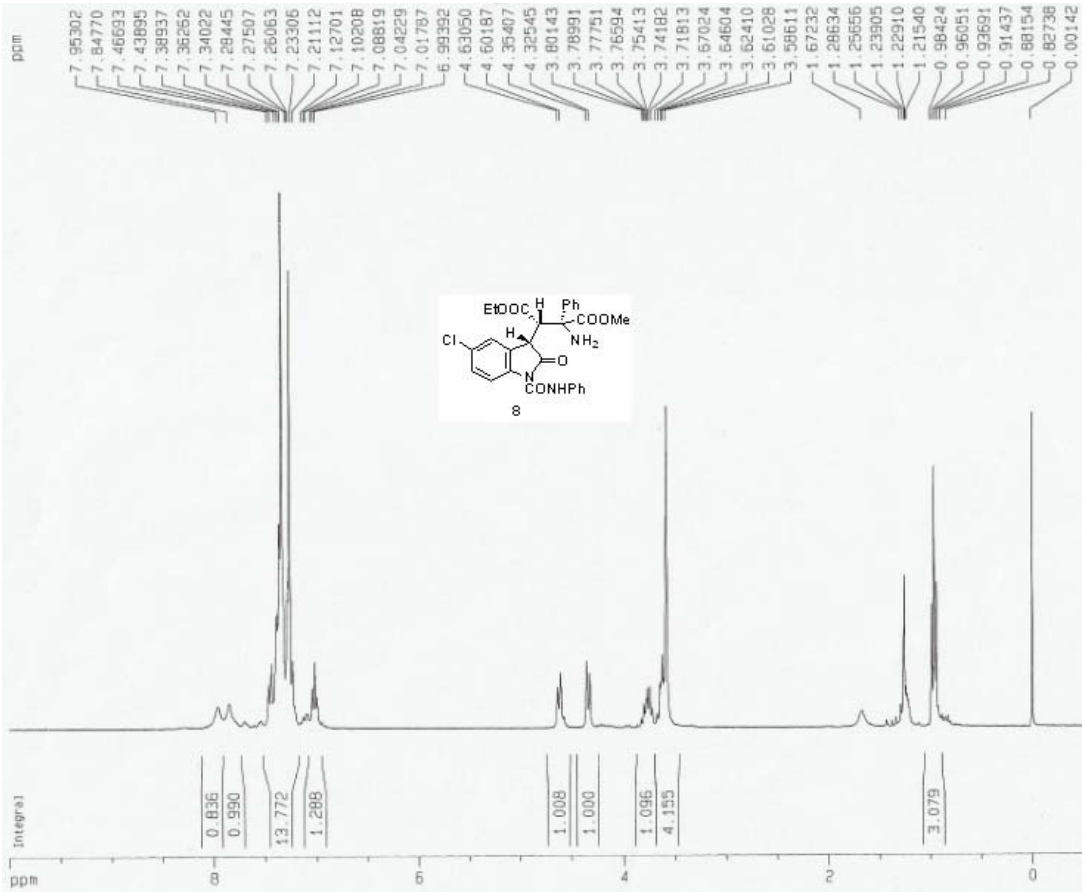
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7.27507
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7.23306
7.21112
7.12701
7.10208
7.08819
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6.99392
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4.32545
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3.62410
3.61028
3.59611
1.67232
1.28634
1.25656
1.23905
1.22910
1.21540
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0.96051
0.93691
0.91437
0.88154
0.82738
0.00142
EtOOC
H
Ph
COOMe
NH2
Cl
H
O
N
CONHPh
8
Integral
0.836
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1.288
1.008
1.000
1.096
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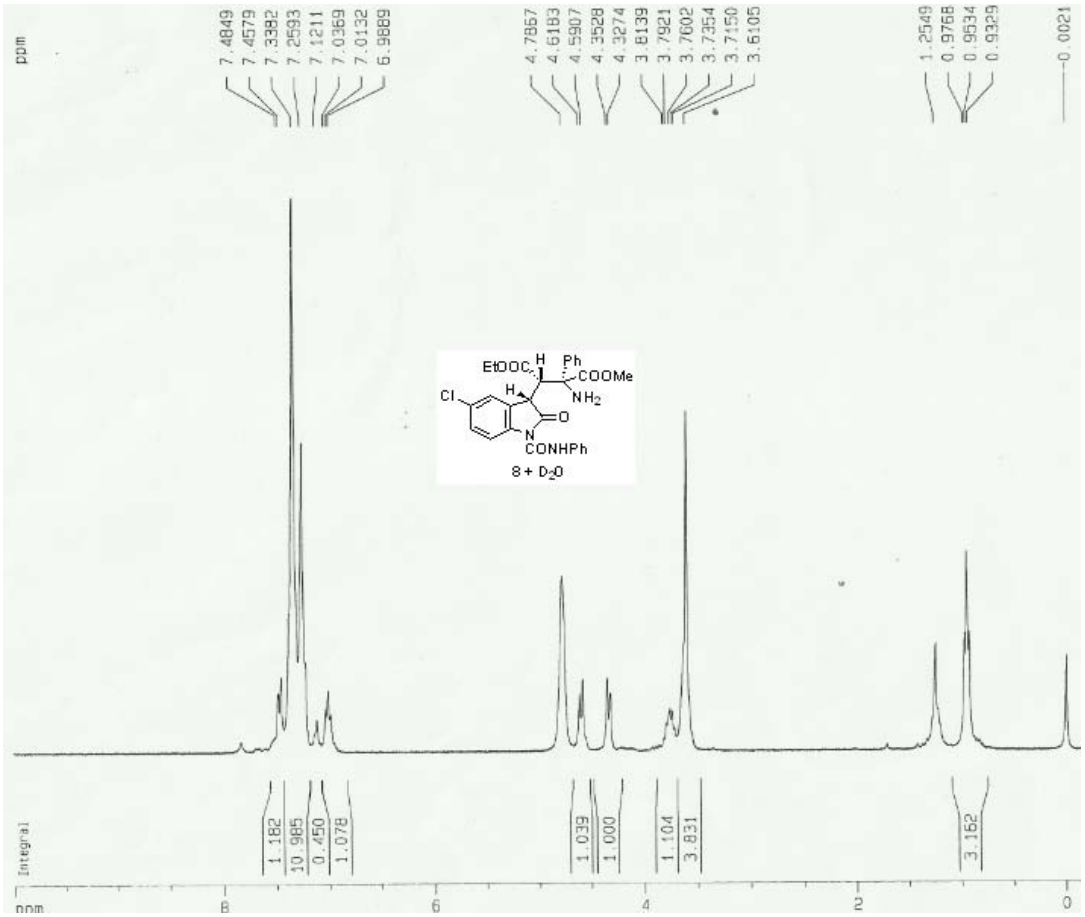
3.079
ppm
8
6
4
2
0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4.7857
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4.5907
4.3528
4.3274
3.8139
3.7921
3.7602
3.7354
3.7150
3.6105
1.2549
0.9768
0.9534
0.9329
0.0021
EtOOC
H
Ph
COOMe
NH2
Cl
H
O
N
CONHPh
8 + D2O
Integral
1.182
10.985
0.450
1.078
1.039
1.000
1.104
3.831
3.162
ppm
8
6
4
2
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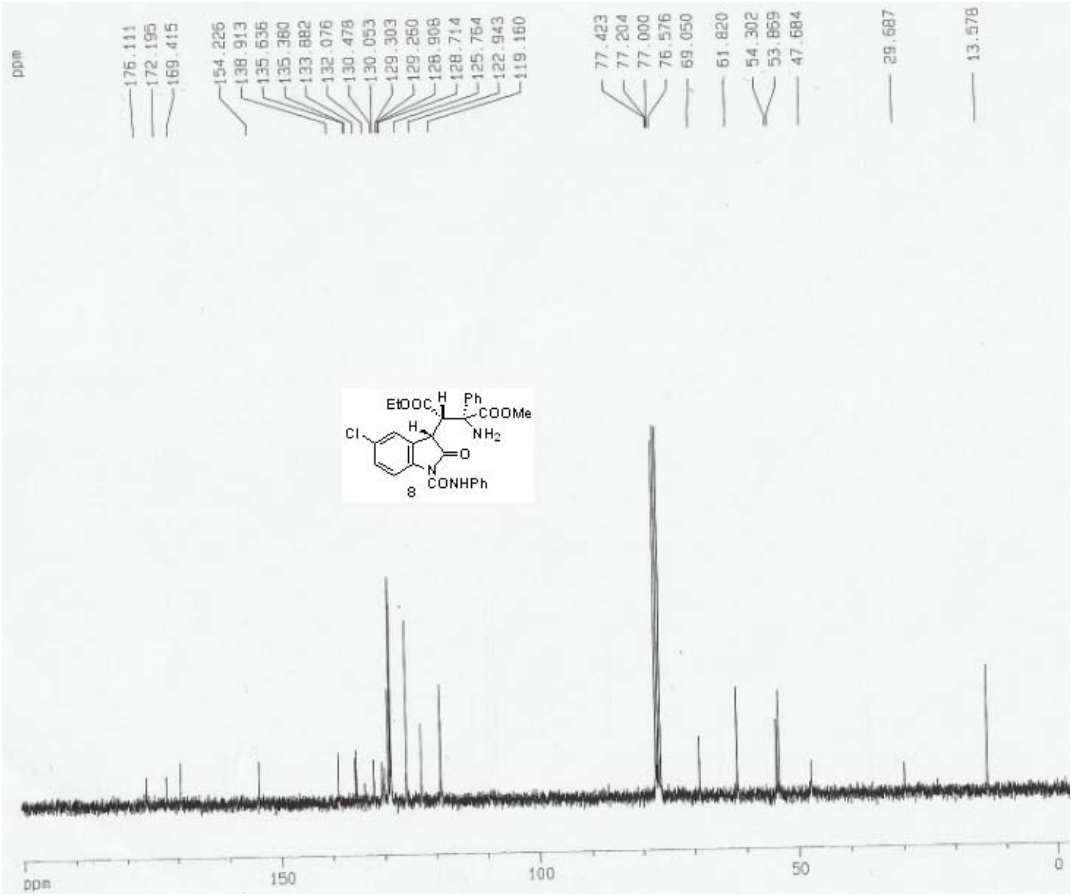
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135.380
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132.076
130.478
130.053
129.303
129.260
128.908
128.714
125.764
122.943
119.160
77.423
77.204
77.000
76.576
69.050
61.820
54.302
53.869
47.684
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H
Ph
COOMe
NH2
Cl
O
N
CONHPh
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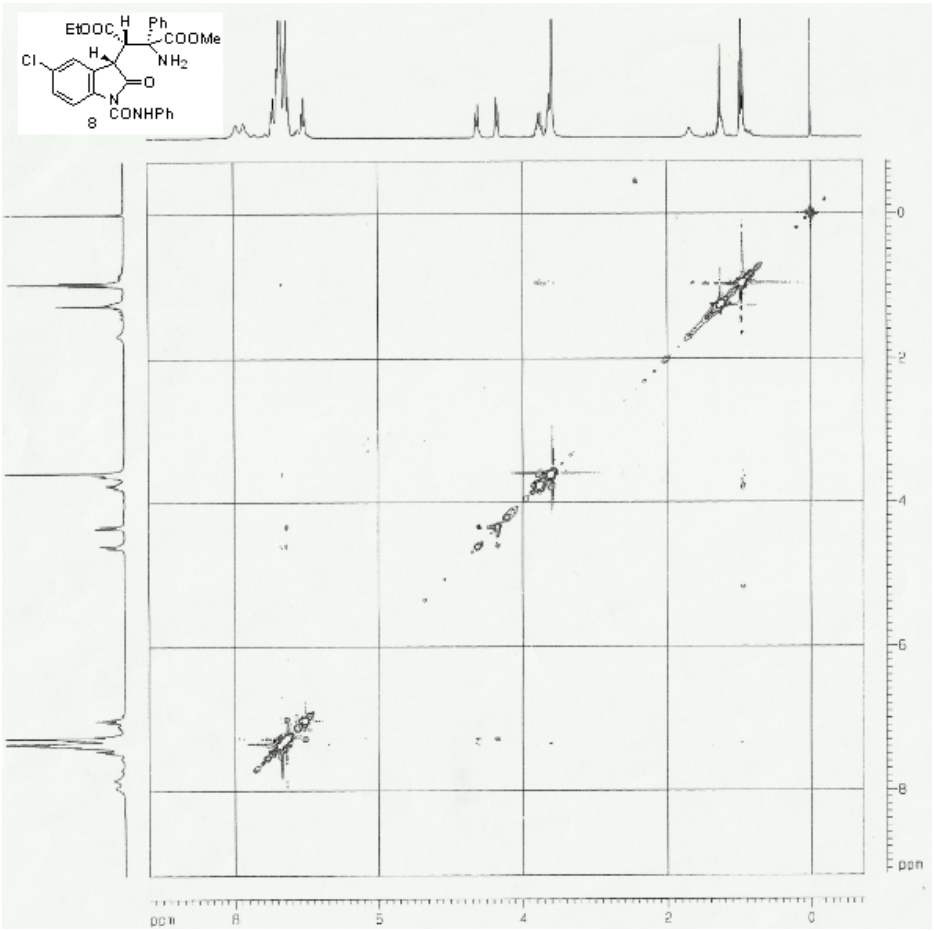
50
0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ppm
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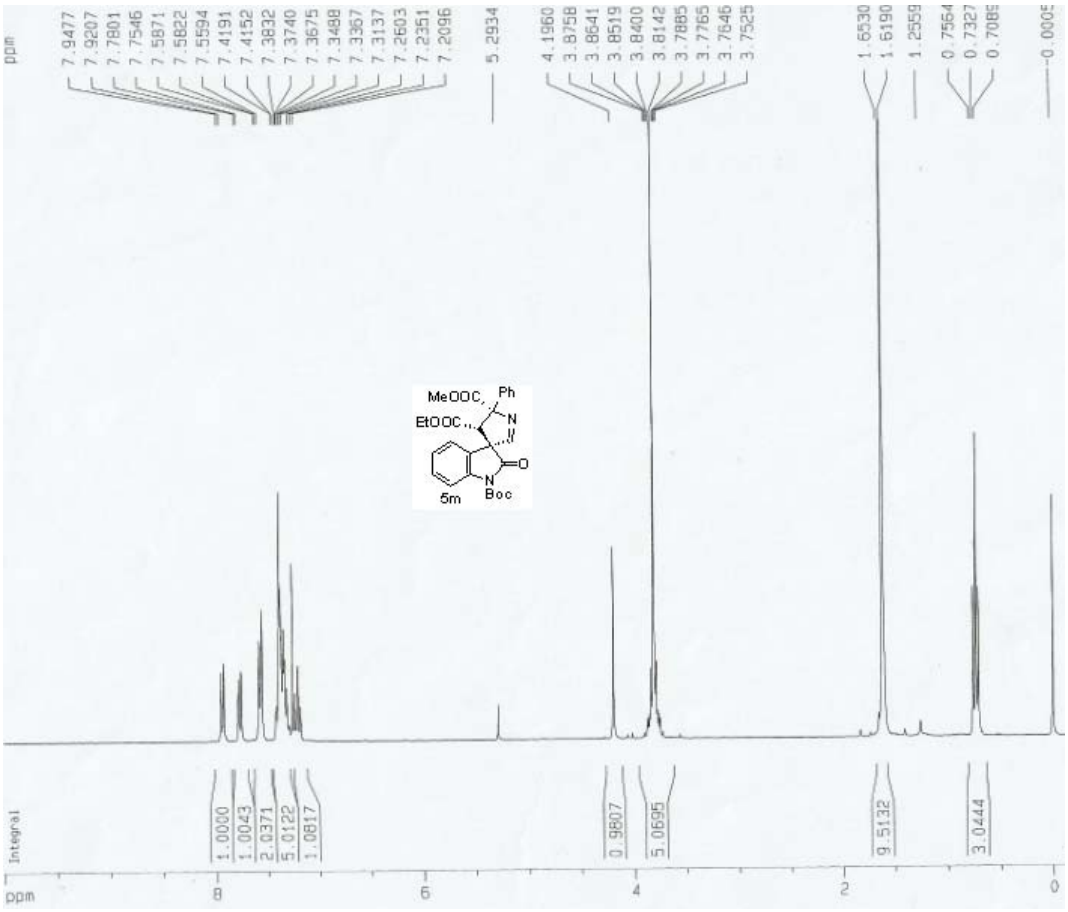
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7.3740
7.3675
7.3488
7.3357
7.3137
7.2603
7.2351
7.2096
5.2934
4.1960
3.8758
3.8641
3.8519
3.8400
3.8142
3.7885
3.7765
3.7646
3.7525
1.6530
1.6190
1.2559
0.7564
0.7327
0.7085
-0.0005
MeOOC
Ph
EtOOC
N
O
N
Boc
5m
Integral
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1.0043
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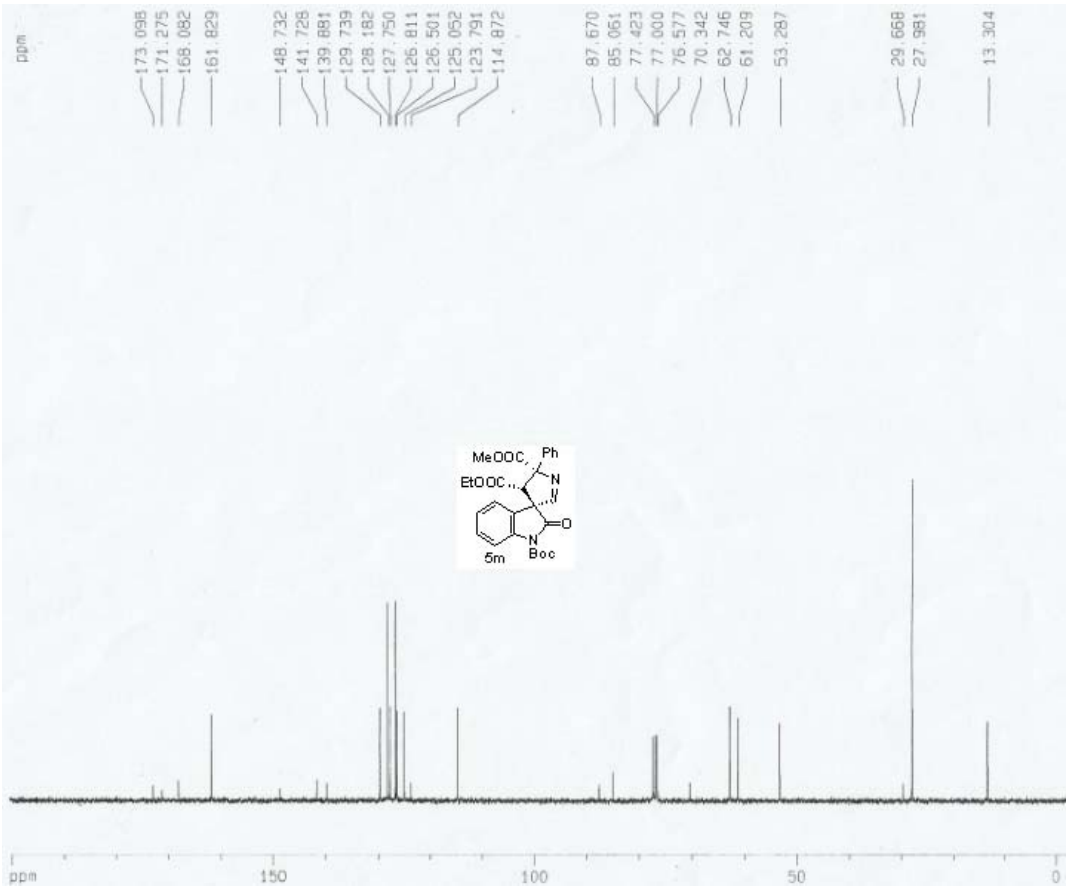
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126.811
126.501
125.052
123.791
114.872
87.670
85.061
77.423
77.000
76.577
70.342
62.746
61.209
53.287
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Boc
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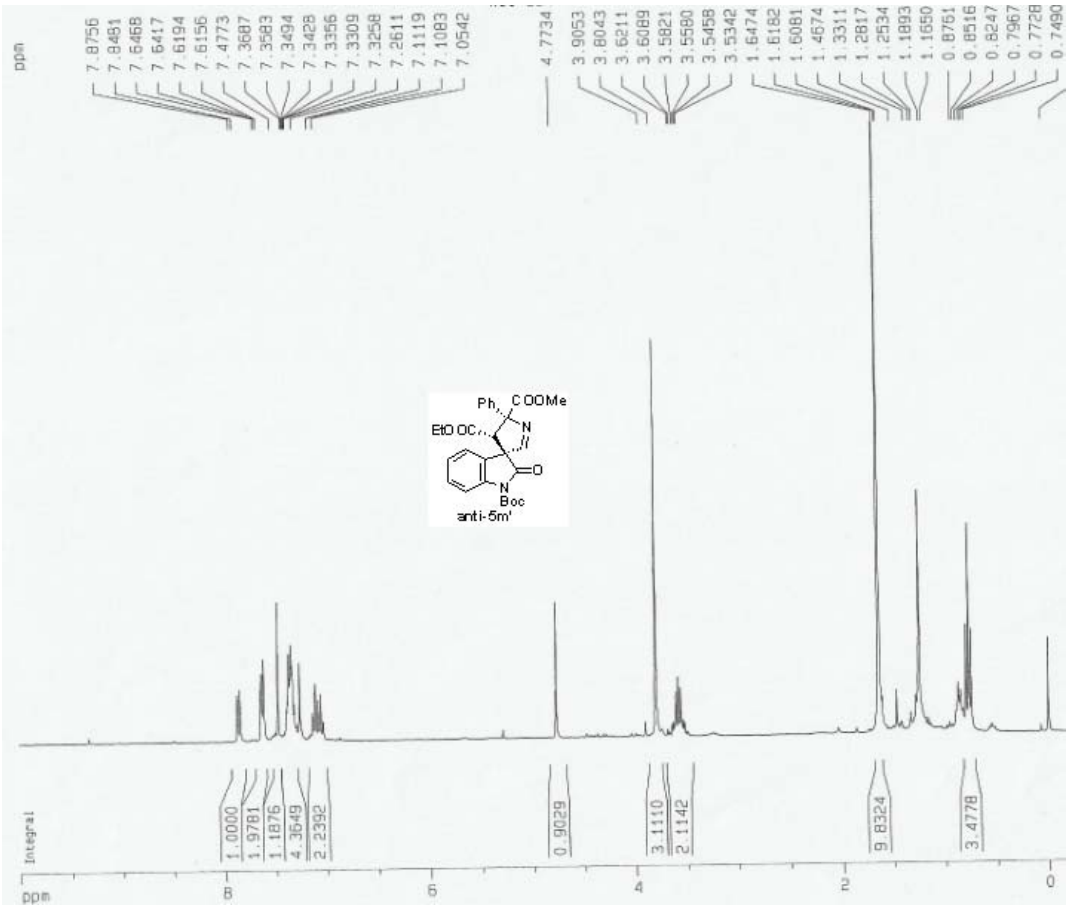
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7.3428
7.3356
7.3309
7.3258
7.2611
7.1119
7.1083
7.0542
4.7734
3.9053
3.8043
3.6211
3.6089
3.5821
3.5580
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3.5342
1.6474
1.6182
1.6081
1.4674
1.3311
1.2817
1.2534
1.1893
1.1650
0.8761
0.8516
0.8247
0.7967
0.7728
0.7490
Ph
COOMe
EtO OC
N
O
N
Boc
anti-5m'
Integral
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1.9781
1.1876
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3.4778
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4
2
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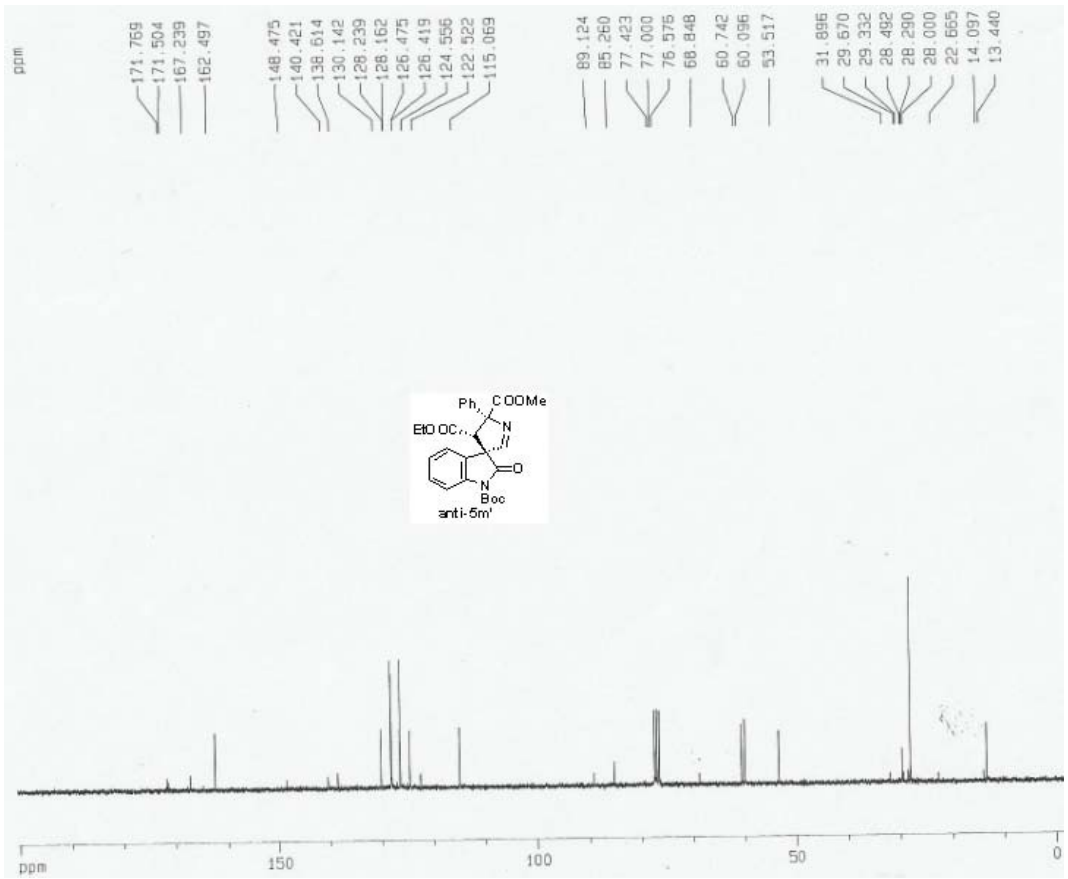
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128.162
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126.419
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122.522
115.069
89.124
85.260
77.423
77.000
76.576
68.848
60.742
60.096
53.517
31.896
29.670
29.332
28.492
28.290
28.000
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Ph
COOMe
EtO OC
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O
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Boc
anti-5m'
ppm
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100
50
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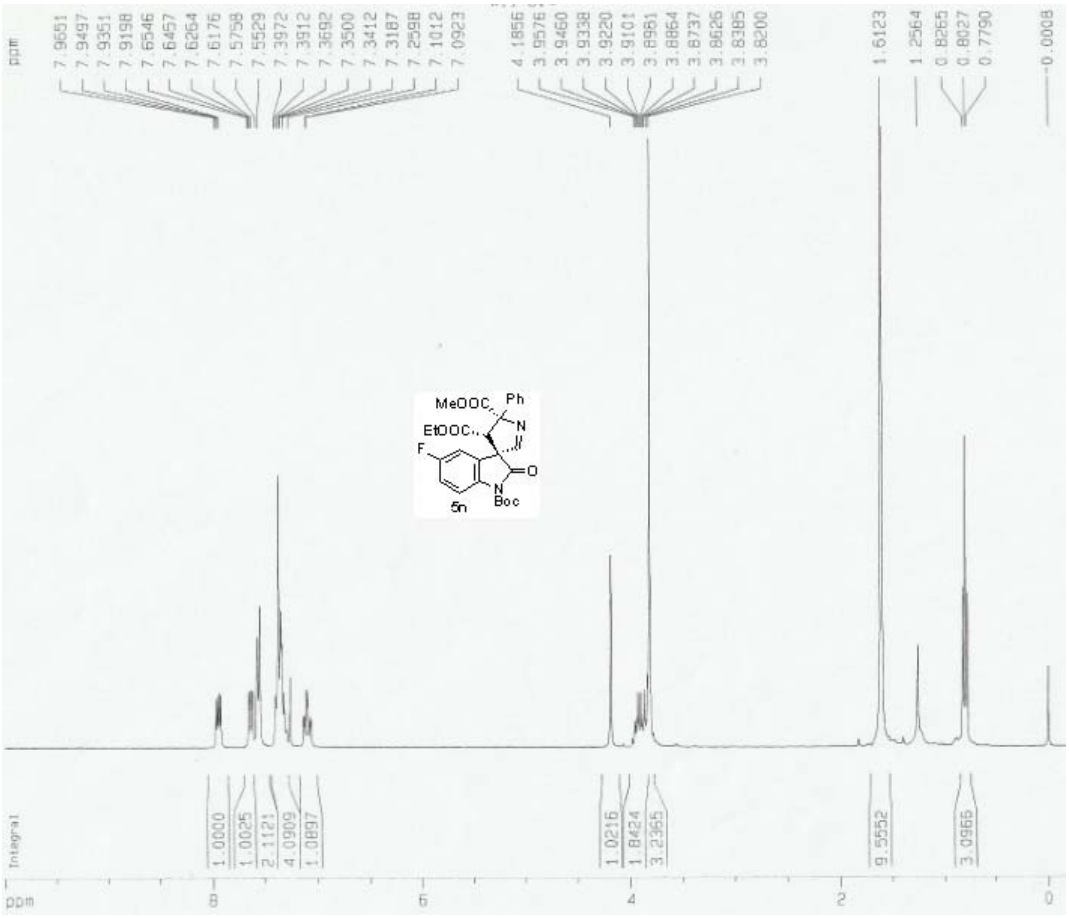
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7.6176
7.5758
7.5529
7.3972
7.3912
7.3692
7.3500
7.3412
7.3187
7.2598
7.1012
7.0923
4.1856
3.9576
3.9460
3.9338
3.9220
3.9101
3.8981
3.8864
3.8737
3.8626
3.8385
3.8200
1.6123
1.2564
0.8265
0.8027
0.7790
0.0008
MeOOC
Ph
EtOOC
N
F
O
N
Boc
5n
Integral
1.0000
1.0025
2.1121
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3.0966
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4
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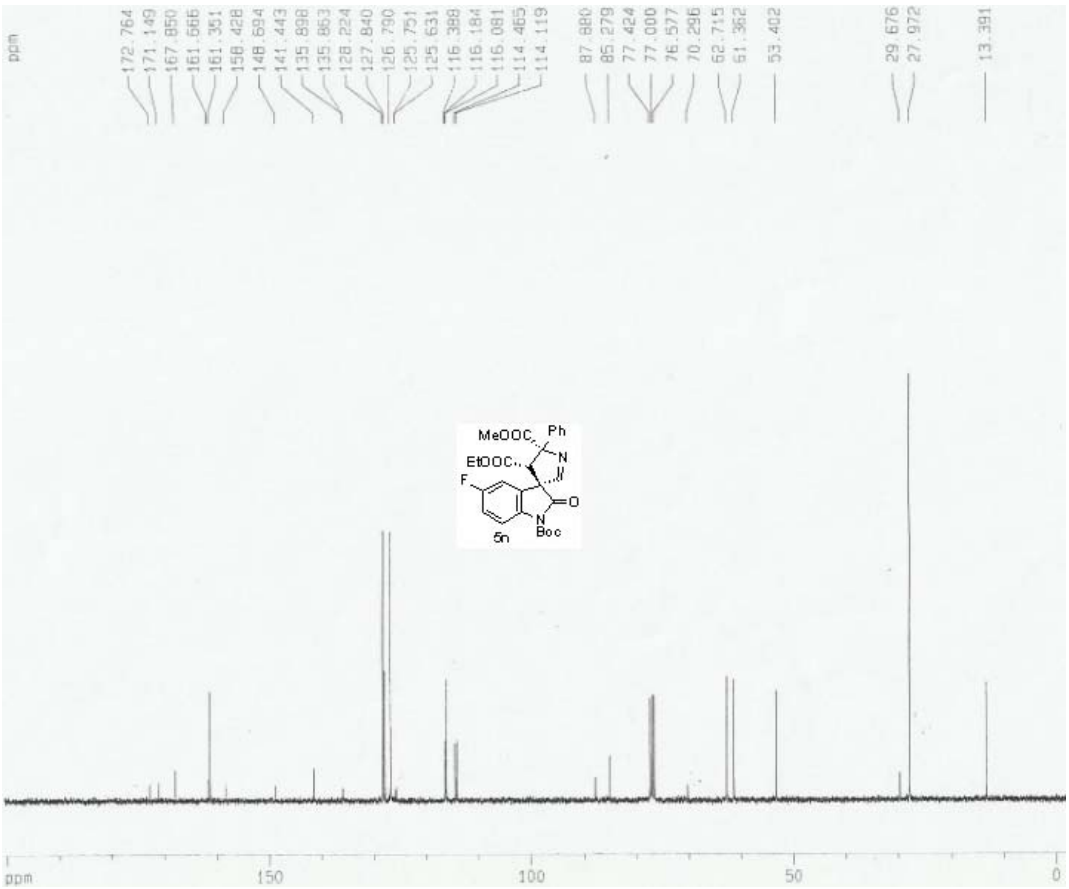
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125.751
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116.388
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116.081
114.465
114.119
87.880
85.279
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77.000
76.577
70.296
62.715
61.362
53.402
29.676
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Boc
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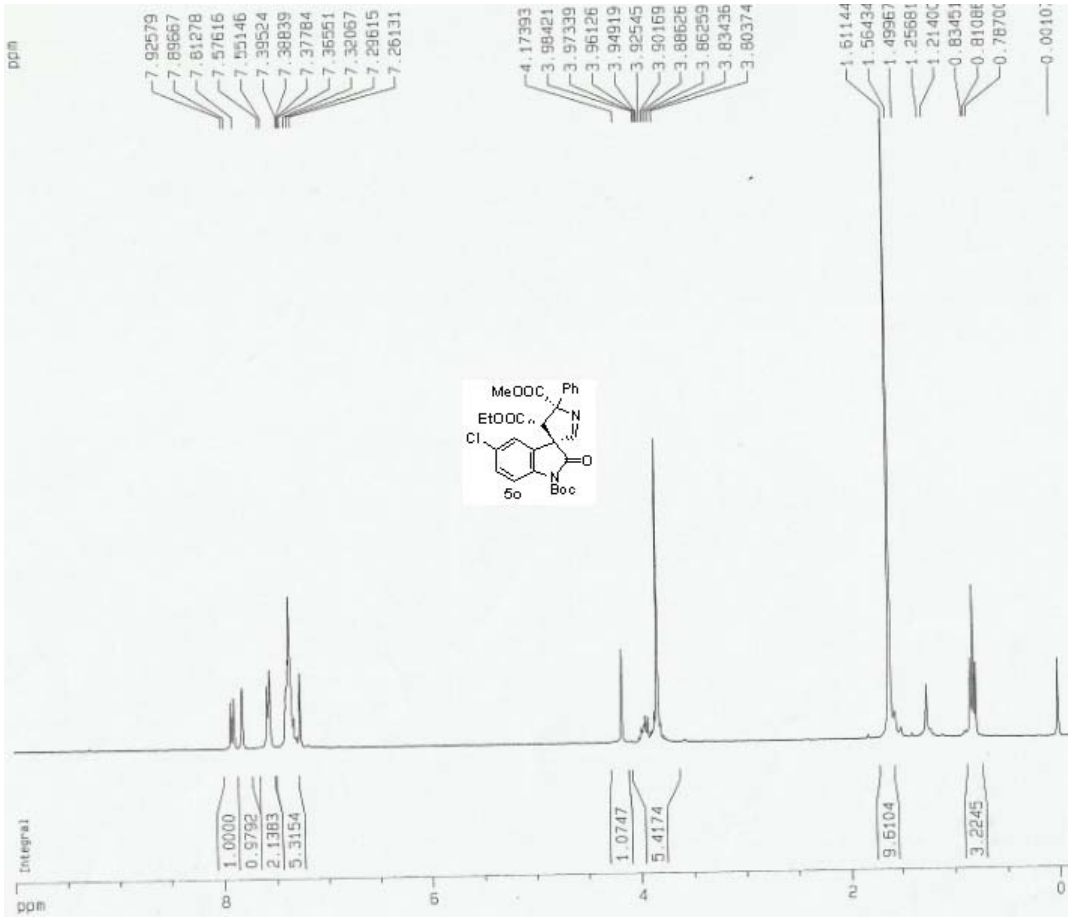
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7.29615
7.26131
4.17393
3.98421
3.97339
3.96126
3.94919
3.92545
3.90169
3.88626
3.86299
3.83436
3.80374
1.61144
1.56434
1.49967
1.25681
1.21402
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0.81088
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Ph
EtOOC
Cl
N
O
N
Boc
5o
Integral
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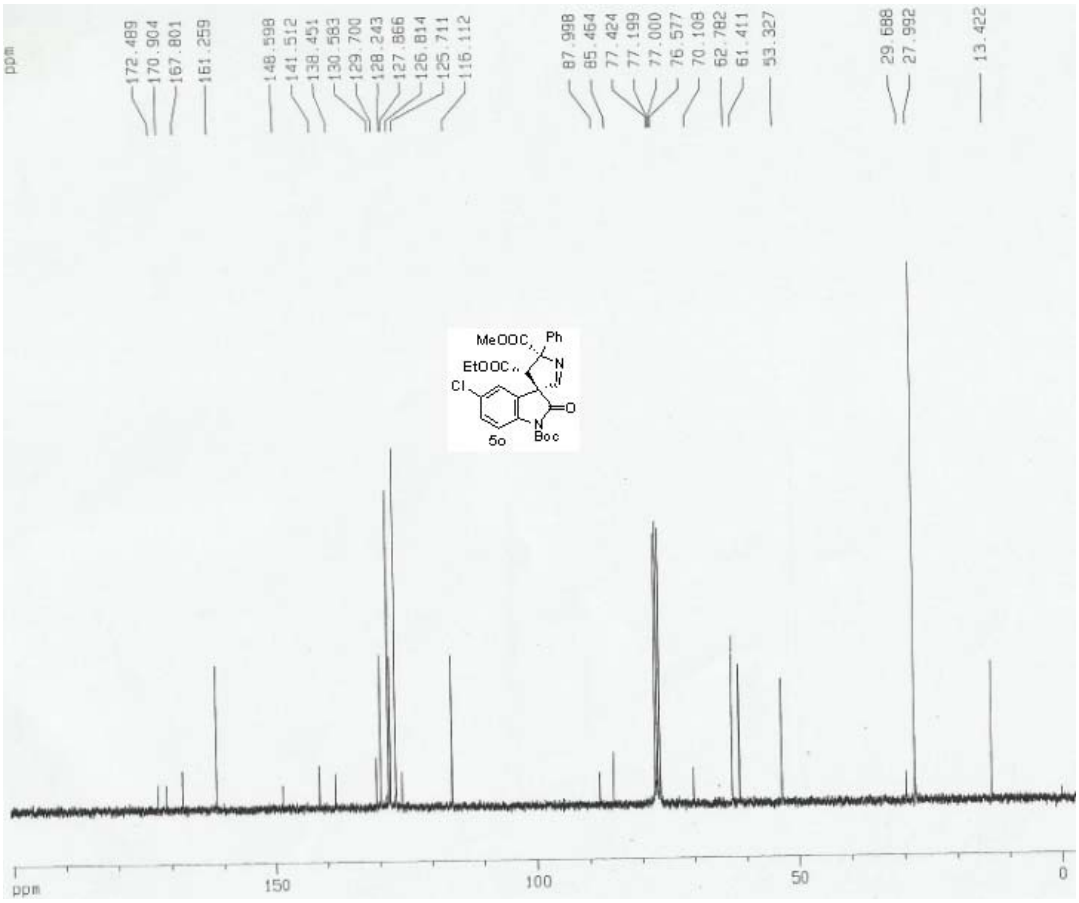
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125.711
116.112
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77.424
77.199
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53.327
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Cl
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N
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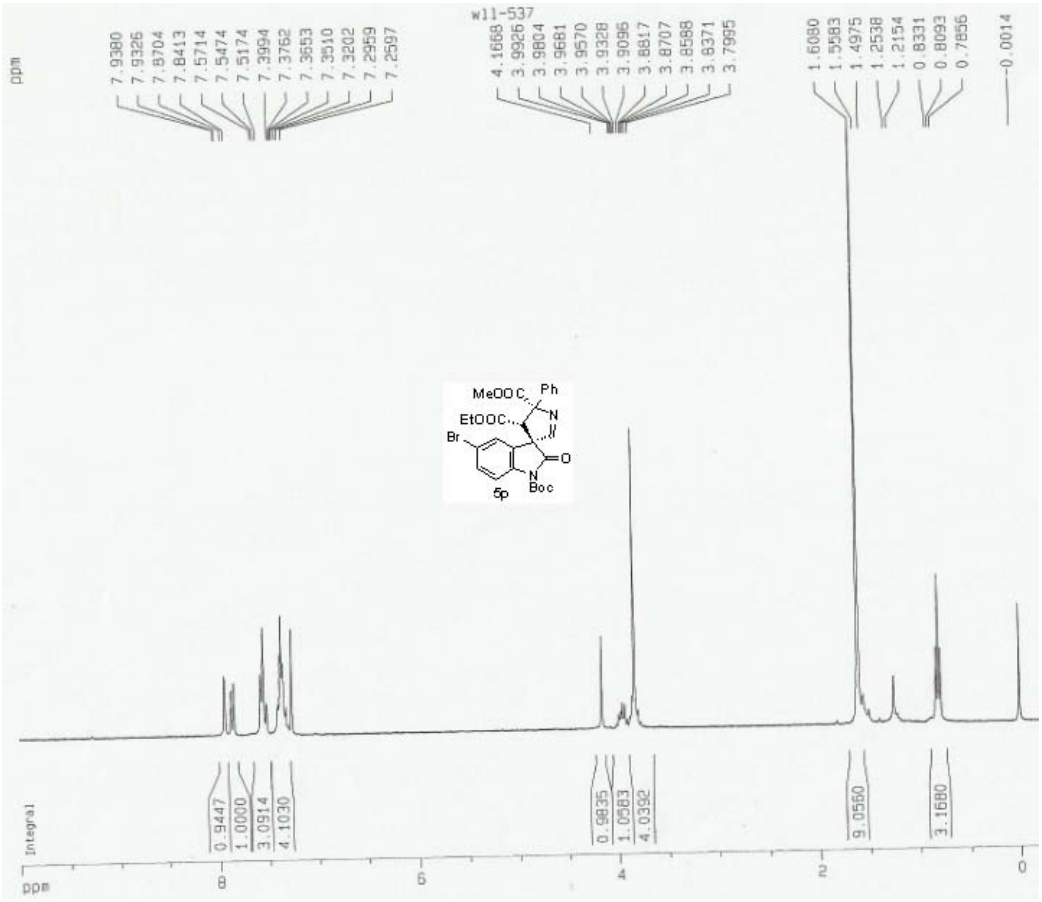
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7.3762
7.3653
7.3510
7.3202
7.2959
7.2597
4.1668
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3.9804
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3.9570
3.9328
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3.8707
3.8588
3.8371
3.7995
1.6080
1.5583
1.4975
1.2538
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Ph
EtOOC
Br
O
N
Boc
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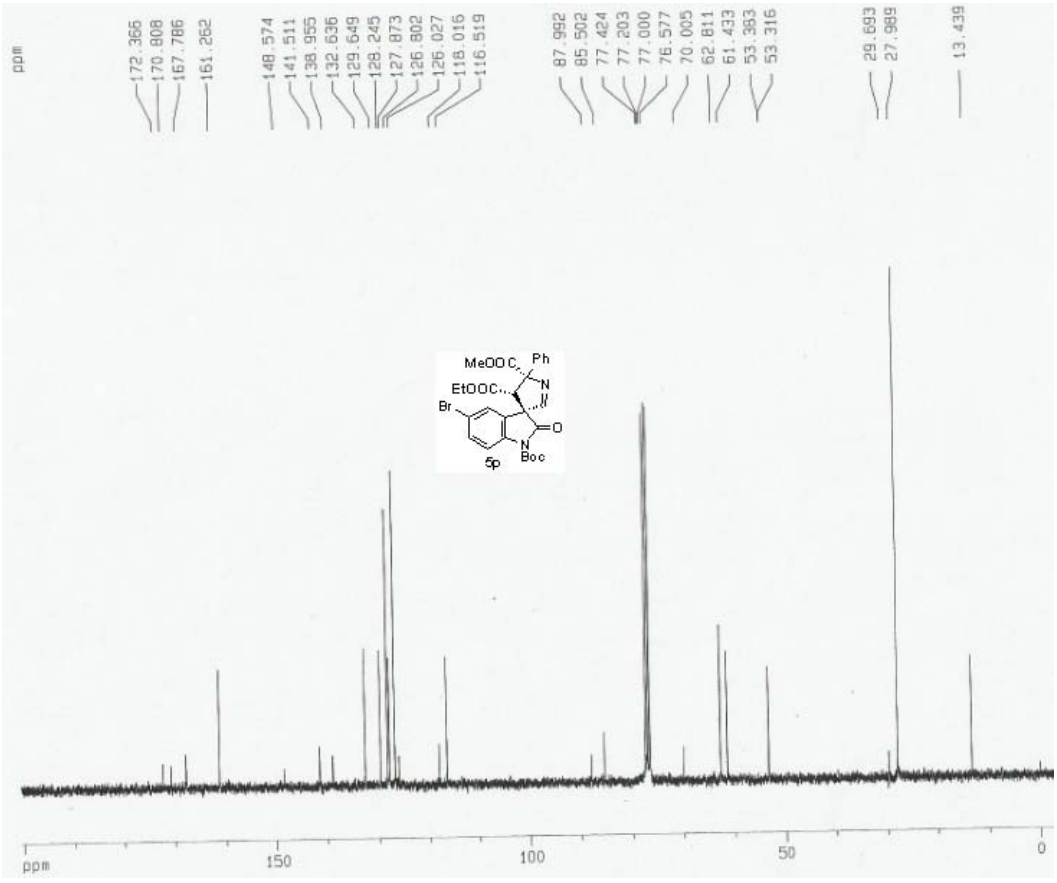
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85.502
77.424
77.203
77.000
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Boc
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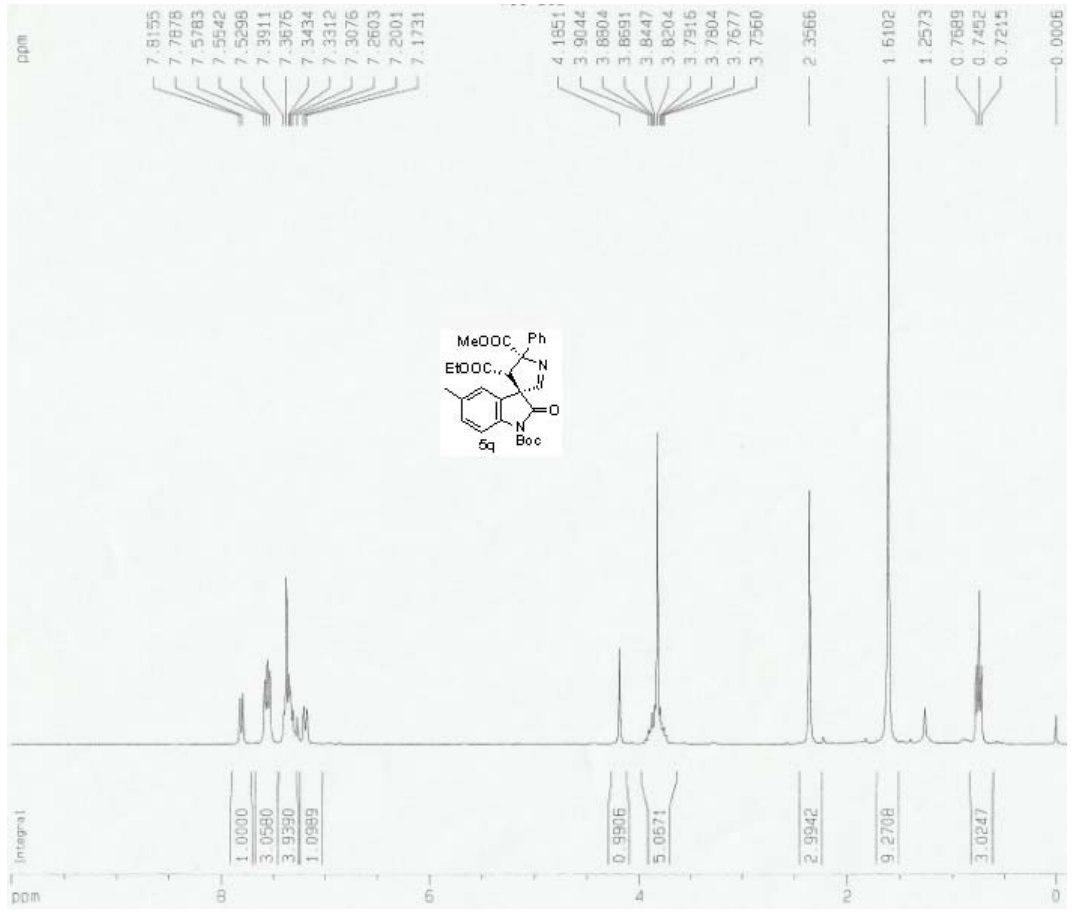
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3.8447
3.8204
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Ph
EtOOC
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O
N
Boc
5q
Integral
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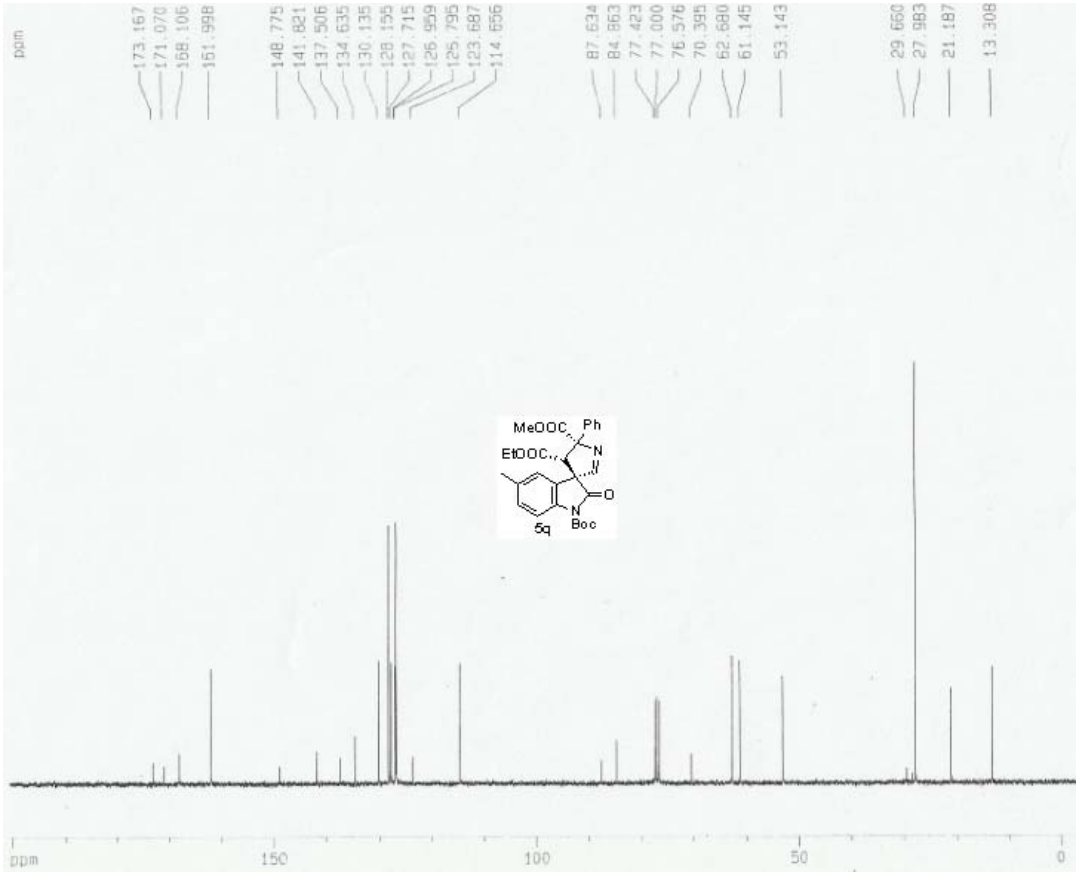
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126.959
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123.687
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77.000
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70.395
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53.143
29.660
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Ph
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Boc
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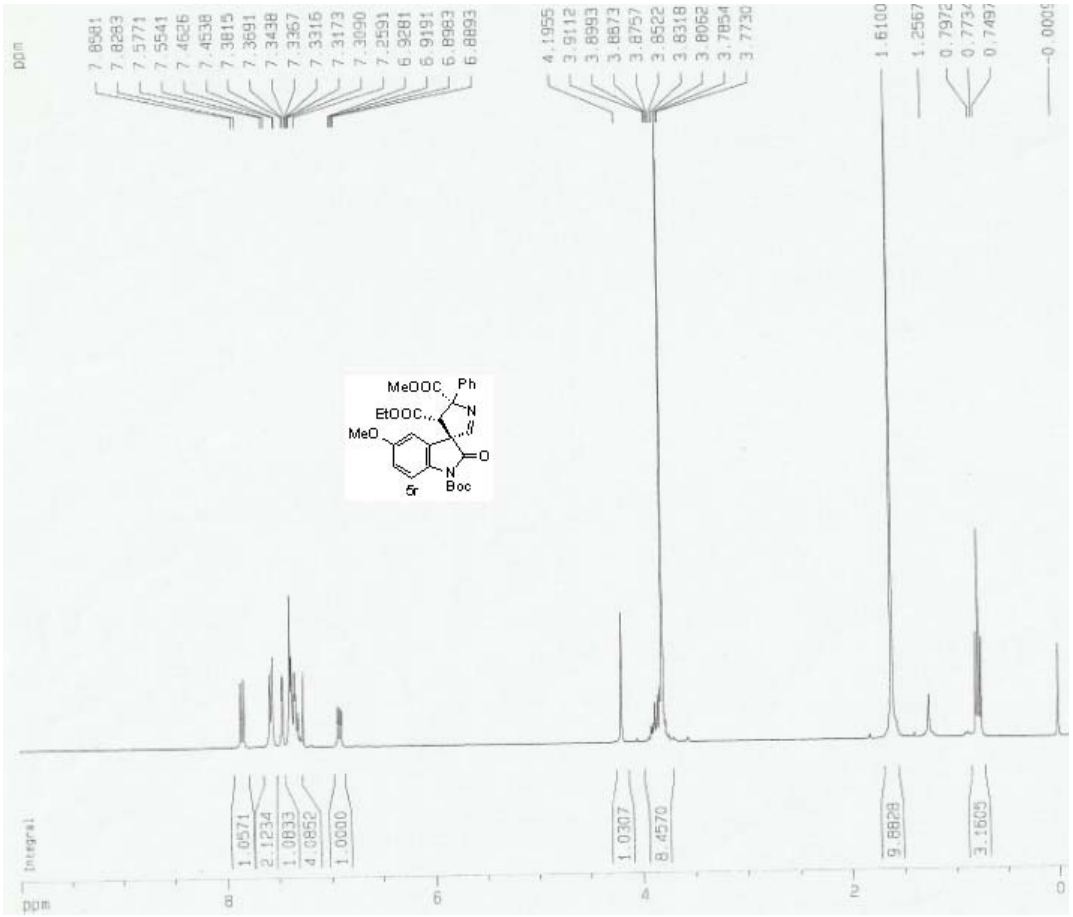
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Boc
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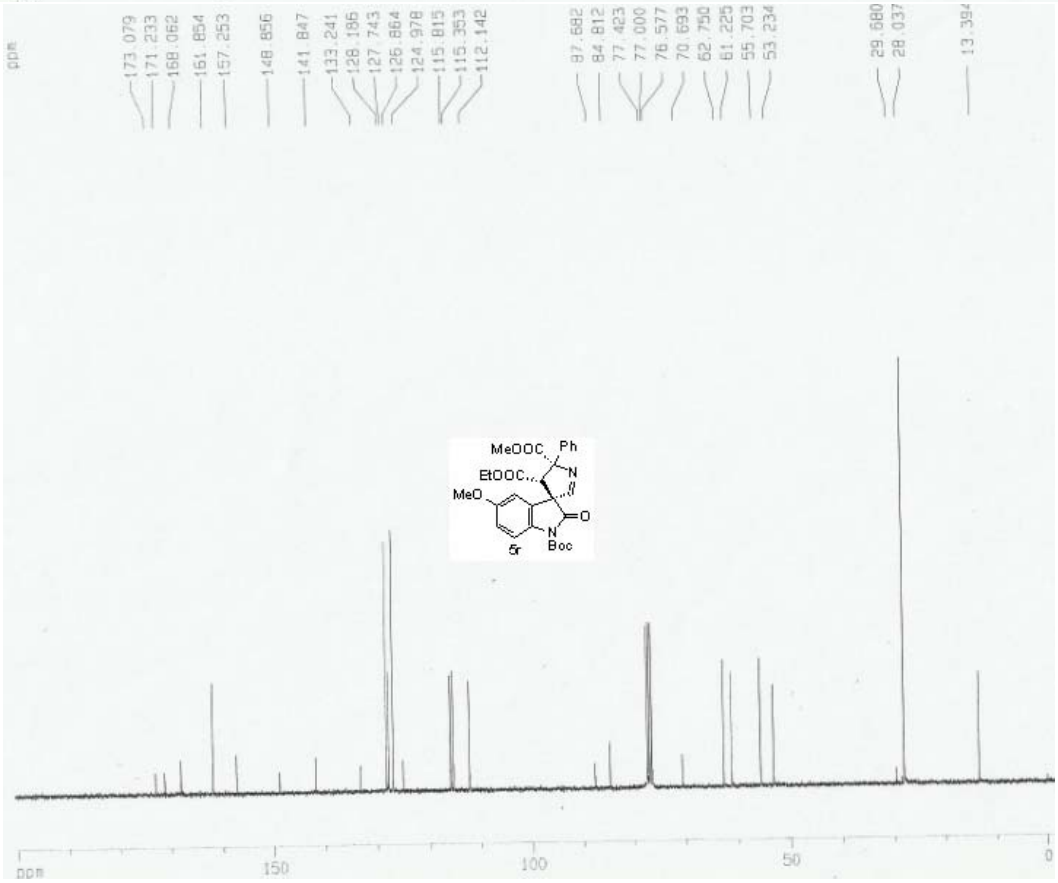
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Boc
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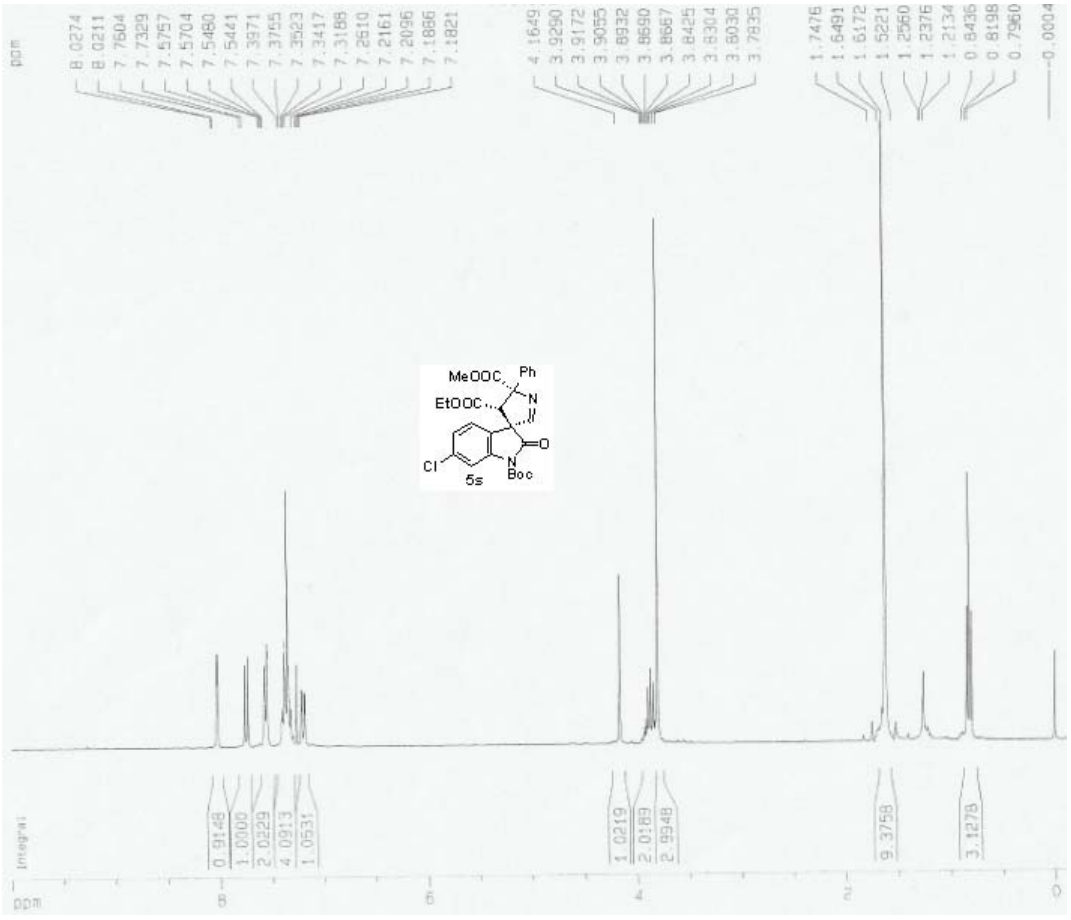
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O
Cl
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Boc
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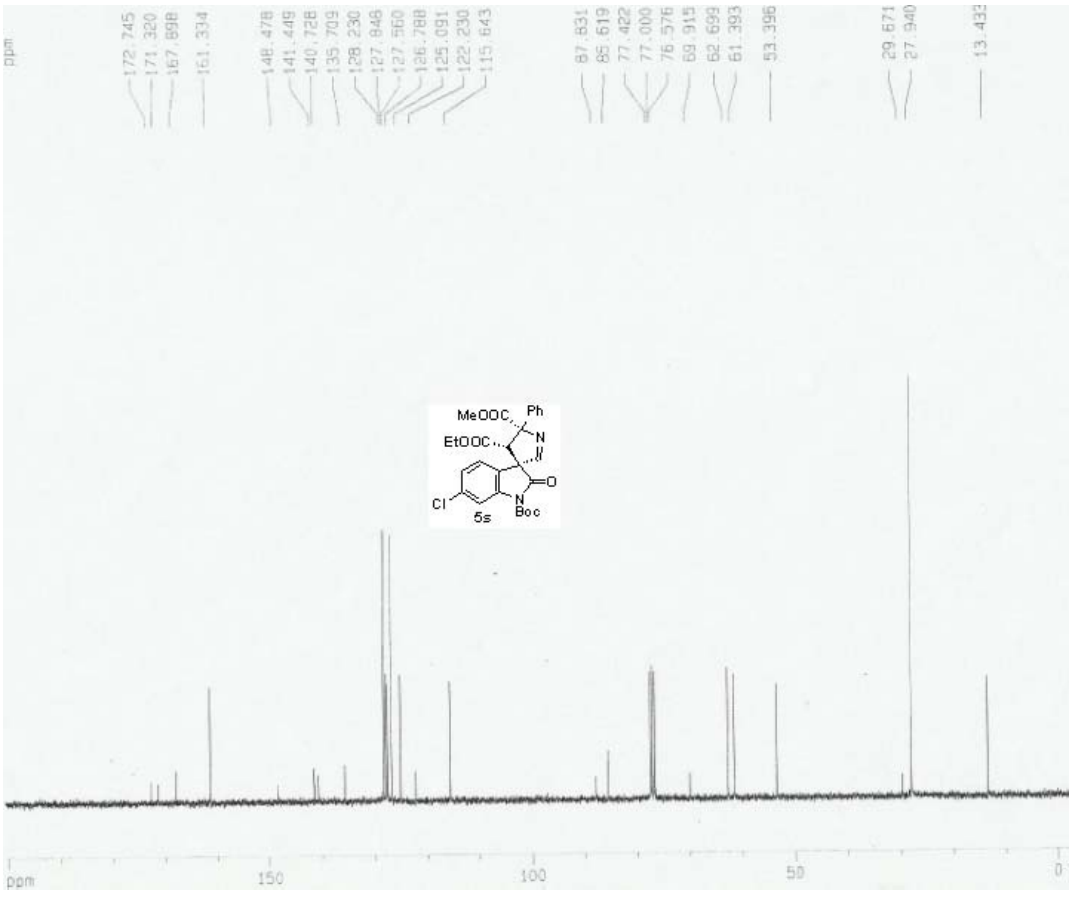
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Cl
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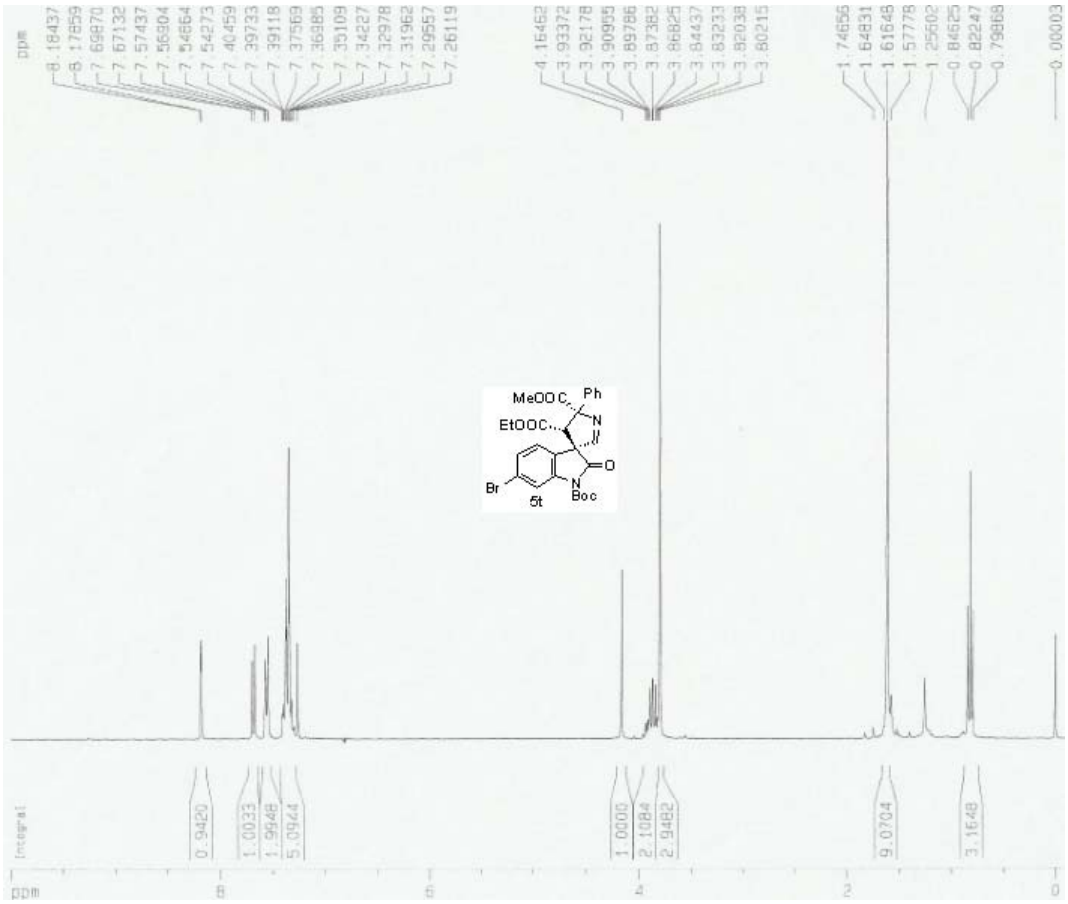
Boc
5s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O
Br
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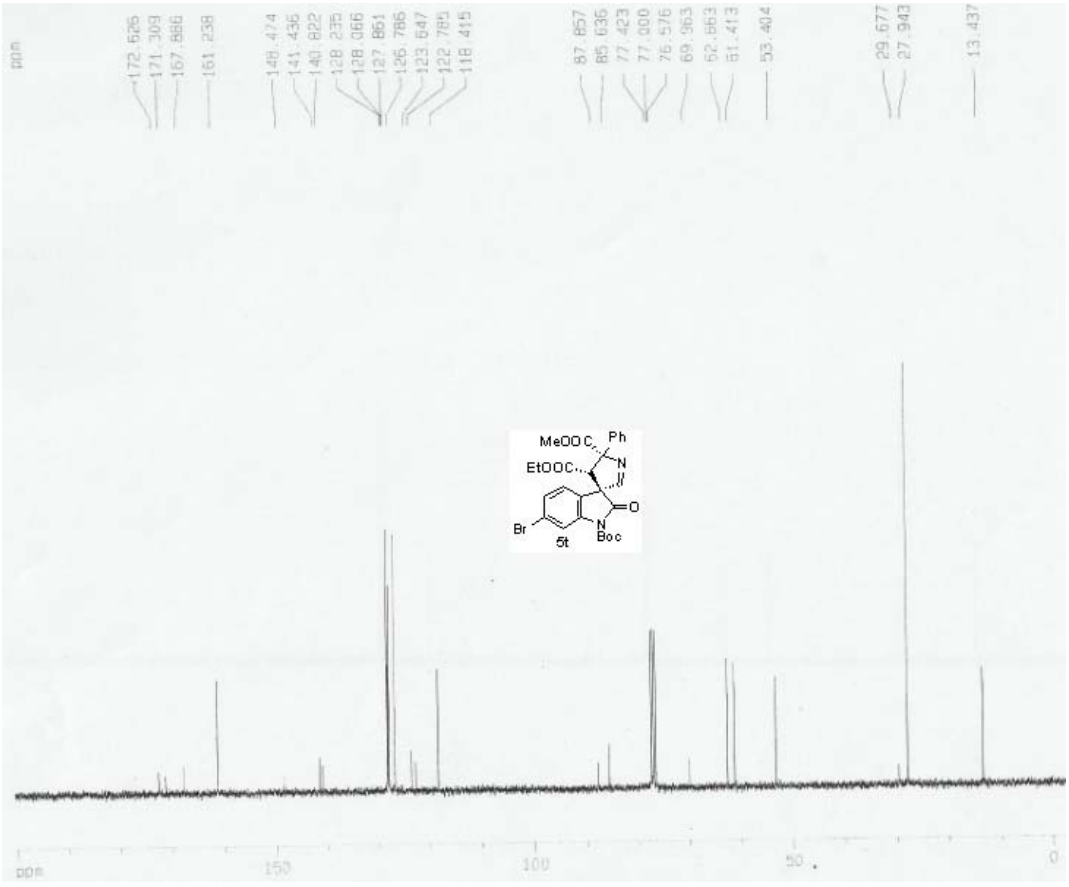
Boc
5t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Boc
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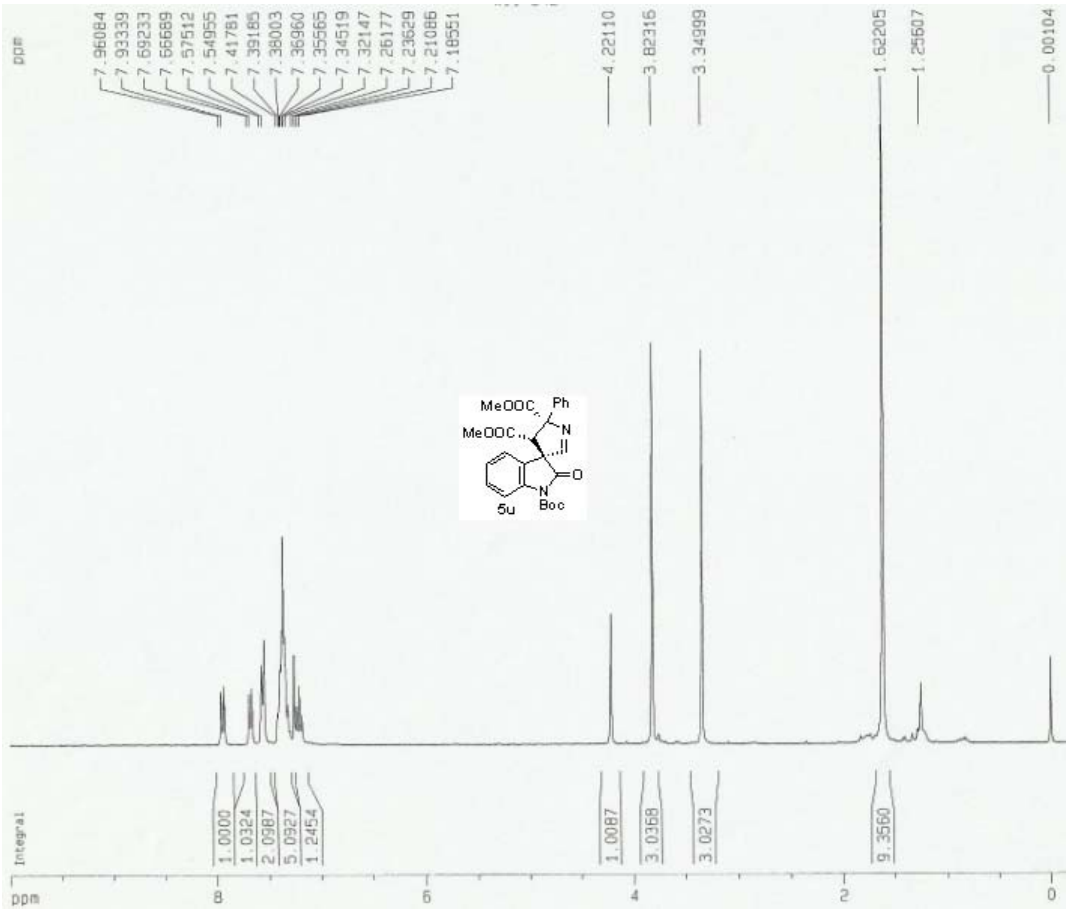
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7.32147
7.26177
7.23629
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7.18551
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MeOOC
Ph
MeOOC
N
O
N
Boc
5u
Integral
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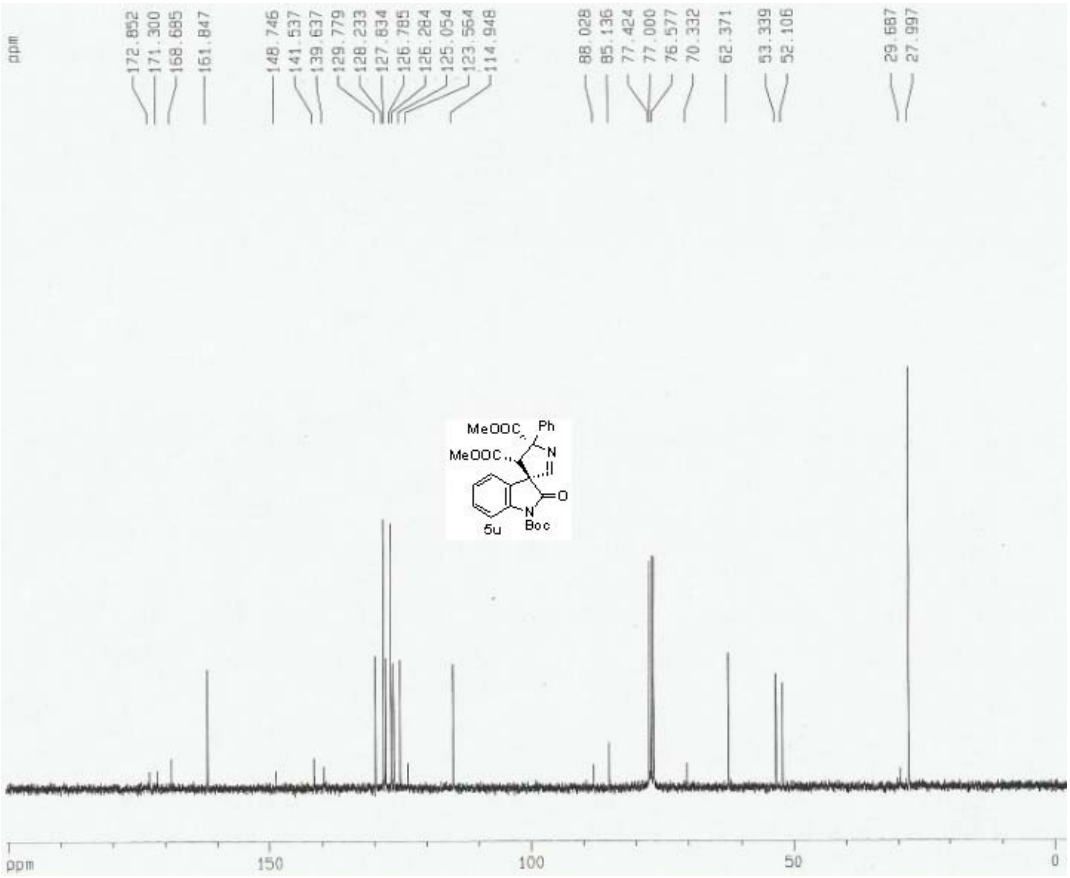
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123.564
114.948
88.028
85.136
77.424
77.000
76.577
70.332
62.371
53.339
52.106
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27.997
MeOOC
Ph
MeOOC
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O
N
Boc
5u
ppm
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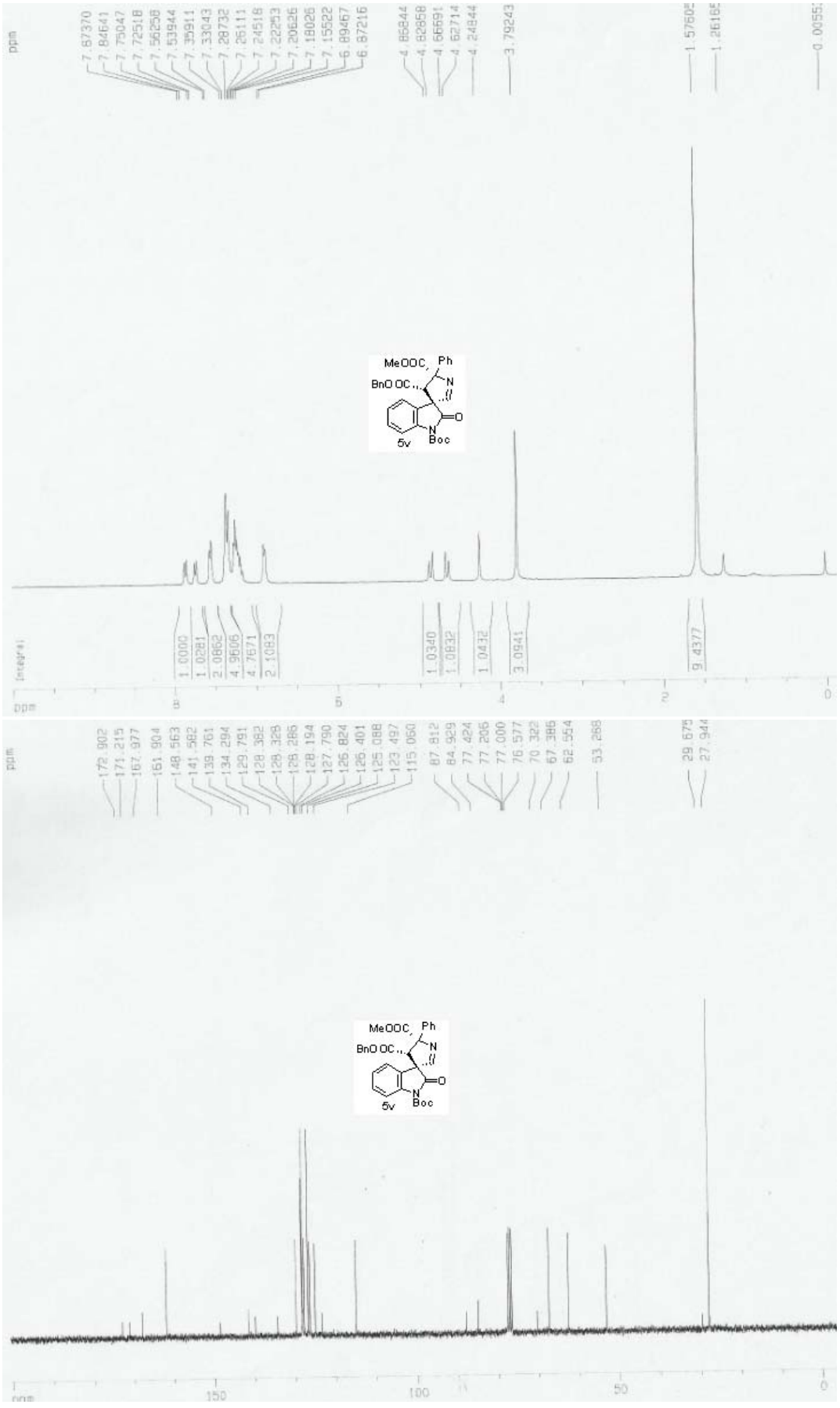
100
50
0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O
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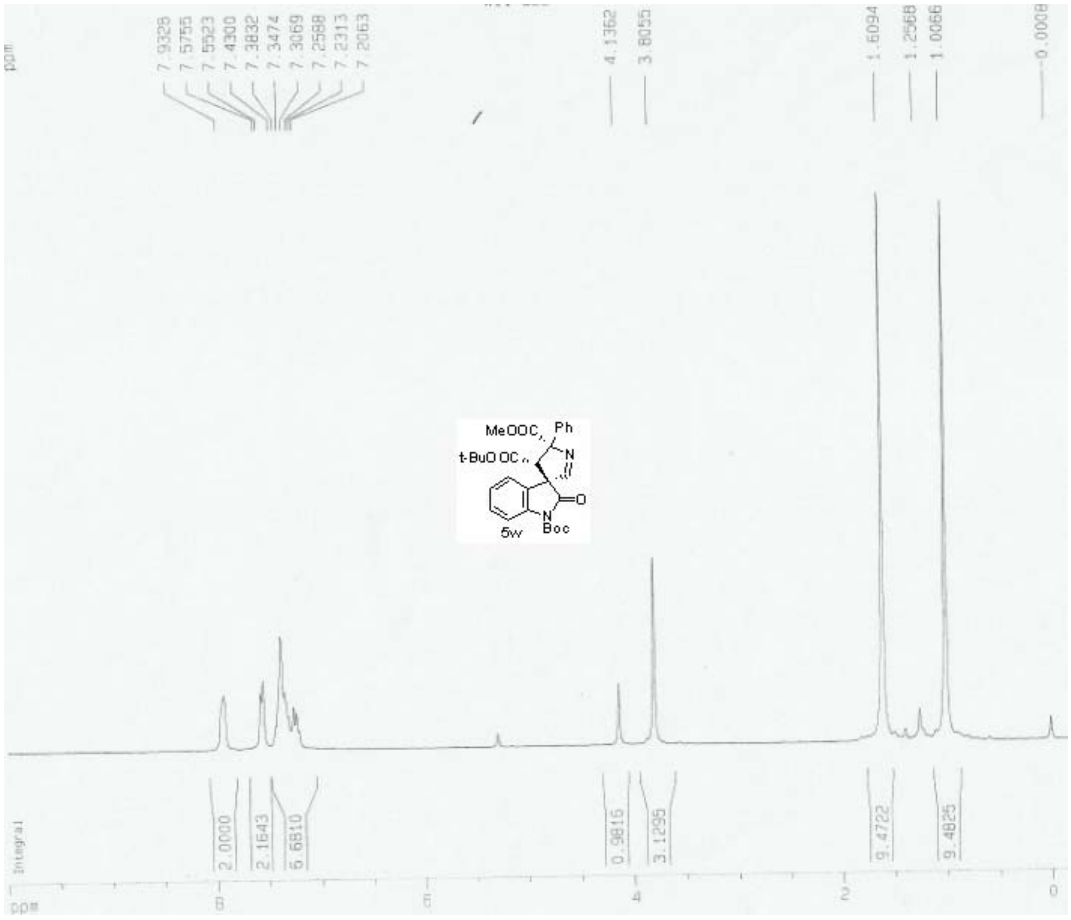
Boc
5v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7.2313
7.2063
4.1362
3.8055
1.6094
1.2568
1.0066
0.0008
MeOOC
Ph
t-BuO OC
N
O
N
Boc
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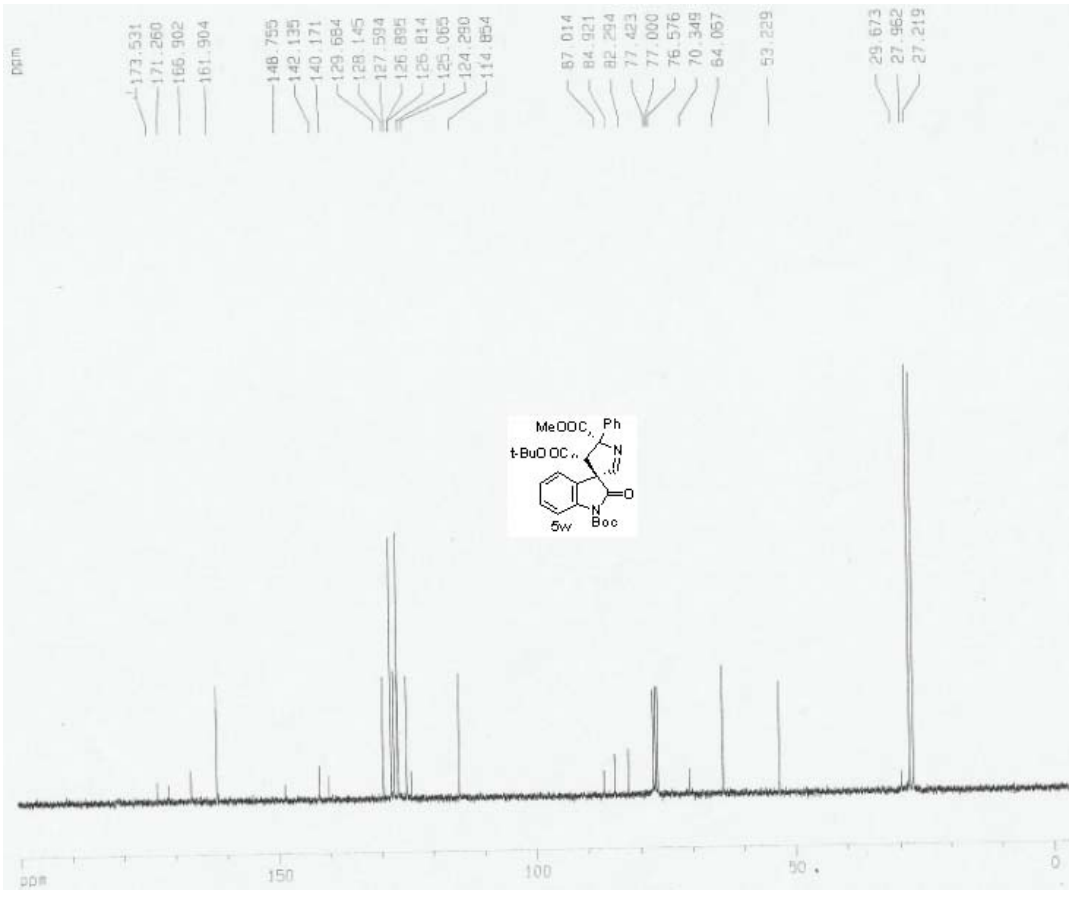
9.4825
Integral
ppm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166.902
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127.594
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125.065
124.290
114.854
87.014
84.921
82.294
77.423
77.000
76.576
70.349
64.057
53.229
29.673
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MeOOC
Ph
t-BuO OC
N
O
N
Boc
5w
ppm
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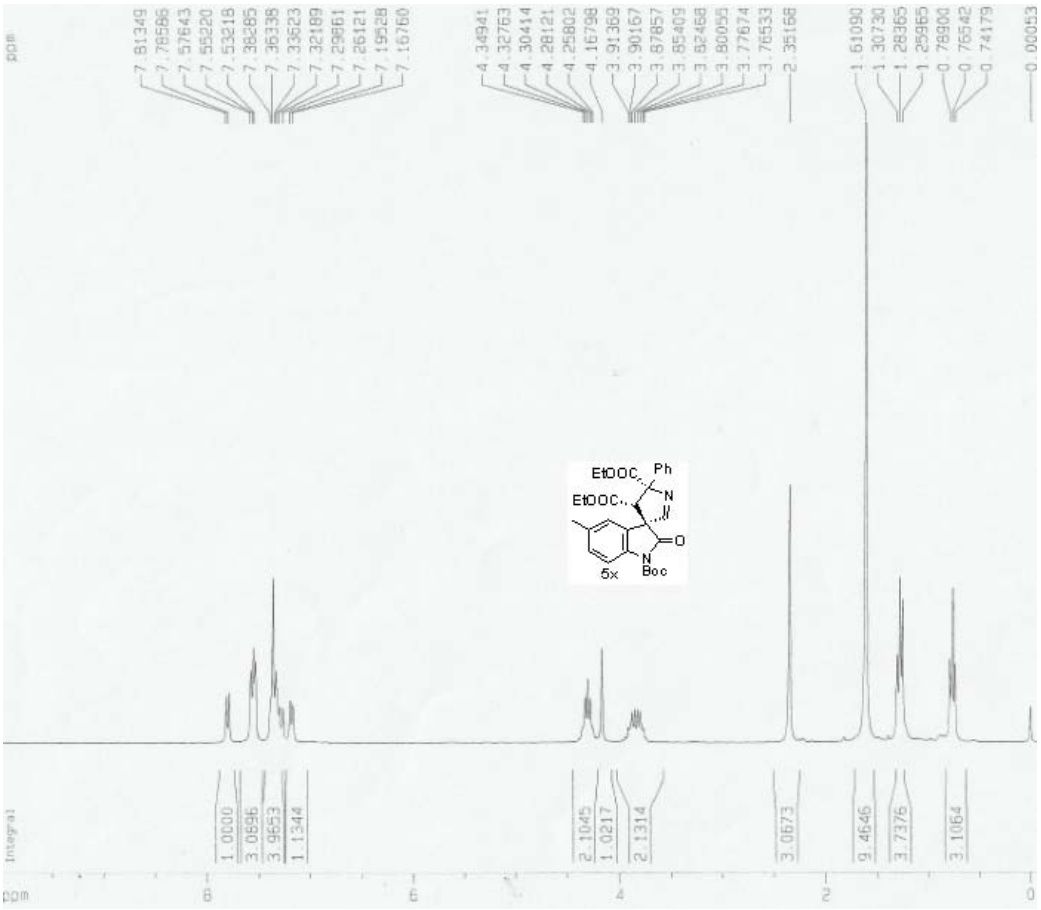
100
50
0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3.82458
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3.76533
2.35168
1.61090
1.30730
1.28365
1.25965
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EtOOC
Ph
EtOOC
N
O
N
Boc
5x
Integral
1.0000
3.0696
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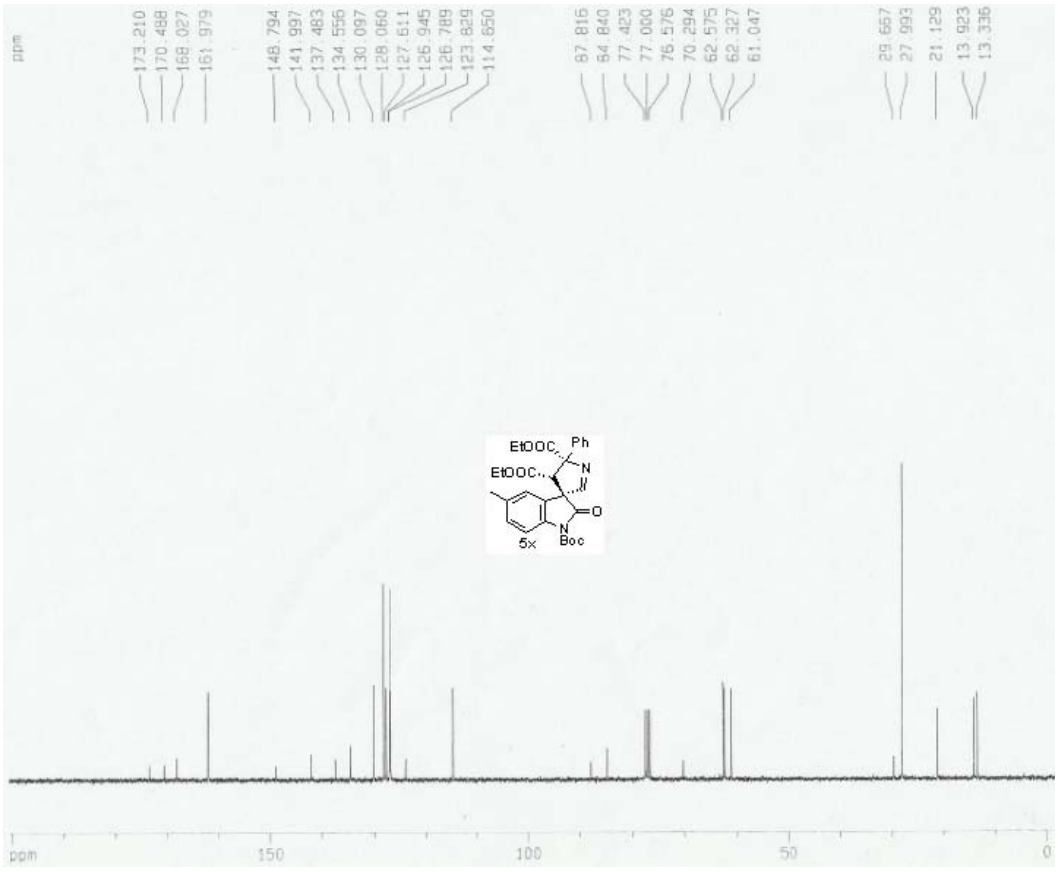
2.1045
1.0217
2.1314
3.0673
9.4646
3.7376
3.1064
ppm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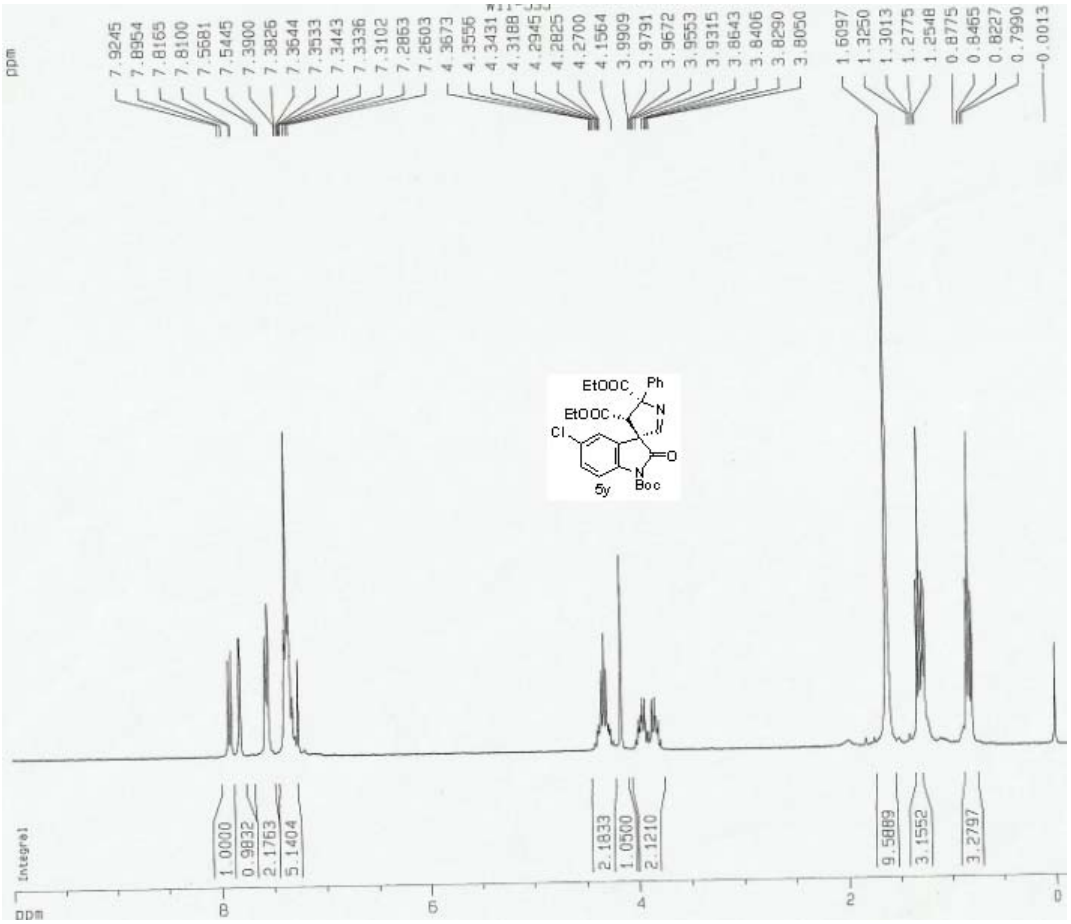
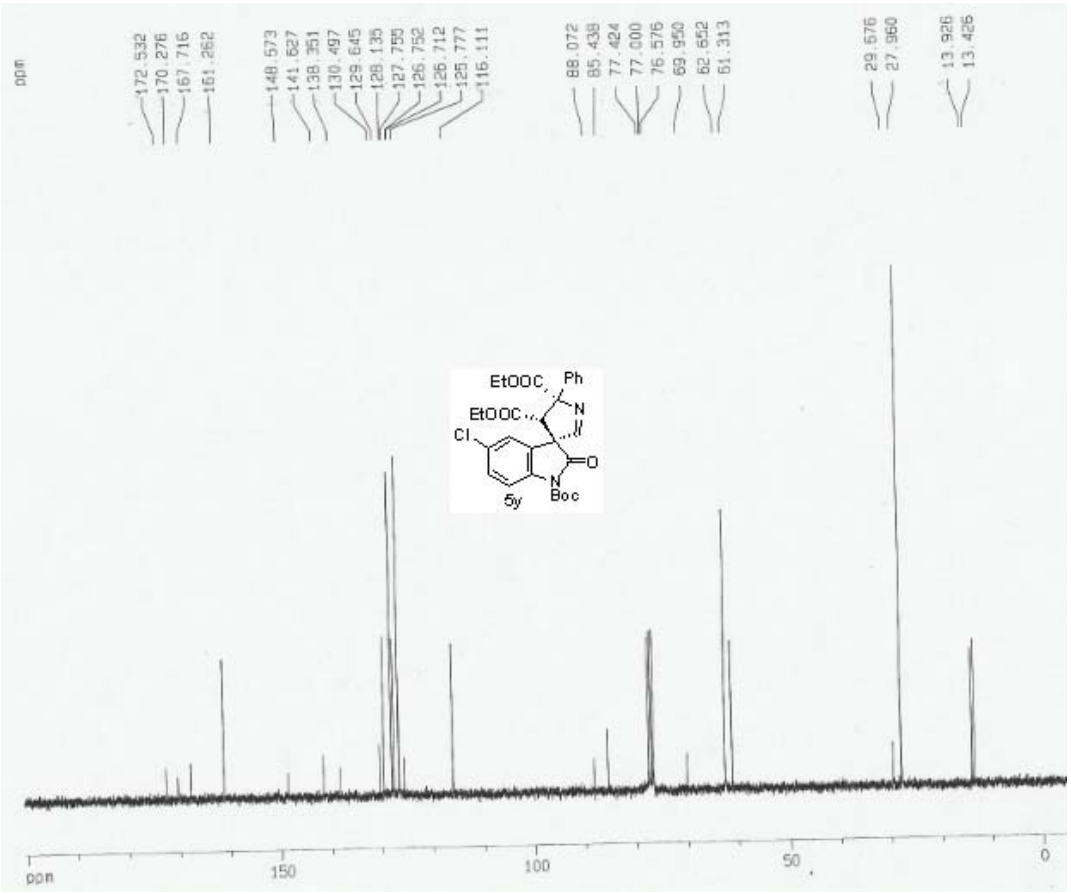
173.210
170.488
168.027
161.979
148.794
141.997
137.483
134.556
130.097
128.060
127.611
126.945
126.789
123.829
114.850
87.816
84.840
77.423
77.000
76.576
70.294
62.575
62.327
61.047
29.667
27.993
21.129
13.923
13.336
EtOOC
Ph
EtOOC
N
O
N
Boc
5x
ppm
150
100
50
0


ppm
7.9245
7.8954
7.8165
7.8100
7.5681
7.5445
7.3900
7.3826
7.3644
7.3533
7.3443
7.3336
7.3102
7.2863
7.2603
4.3673
4.3556
4.3431
4.3188
4.2945
4.2825
4.2700
4.1564
3.9909
3.9791
3.9672
3.9553
3.9315
3.8643
3.8406
3.8290
3.8050
1.6097
1.3250
1.3013
1.2775
1.2548
0.8775
0.8465
0.8227
0.7990
-0.0013
EtOOC
Ph
EtOOC
N
Cl
O
N
Boc
5y
Integral
1.0000
0.9832
2.1763
5.1404
2.1833
1.0560
2.1210
9.5889
3.1552
3.2797
ppm
8
6
4
2
0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172.532
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167.716
161.262
148.573
141.627
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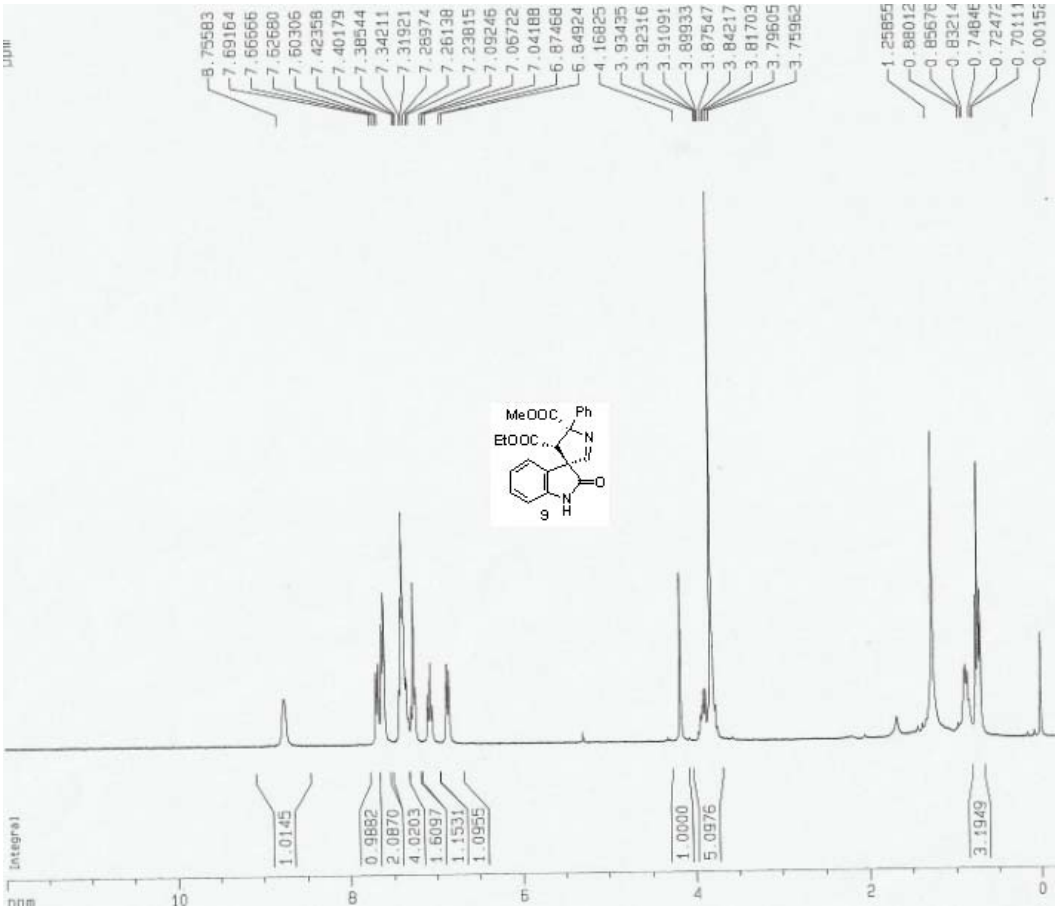
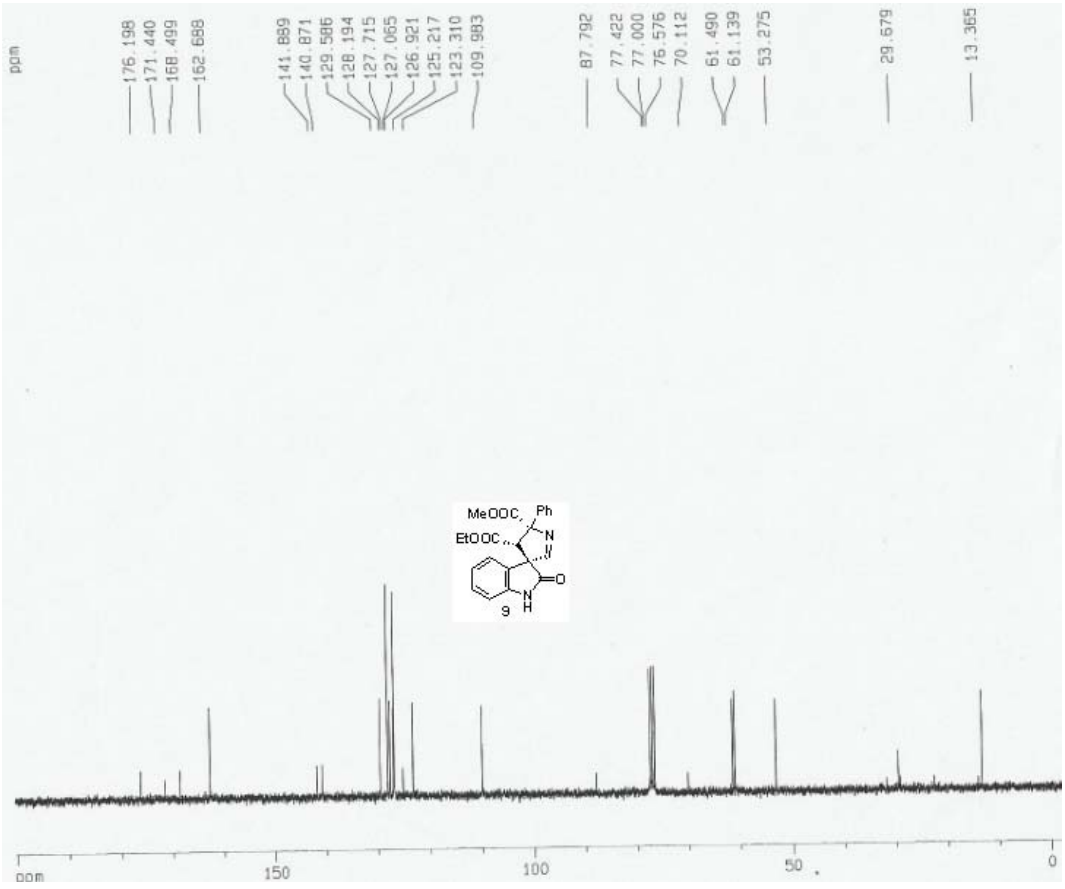
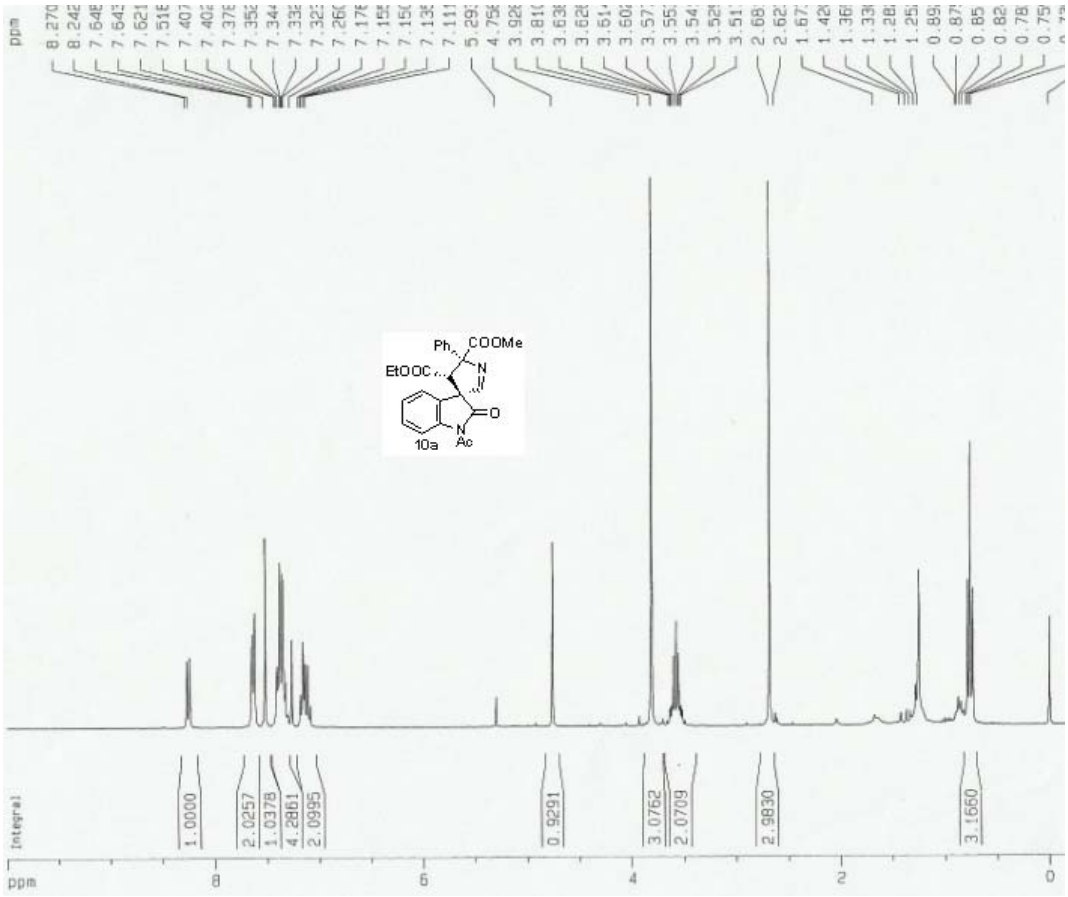
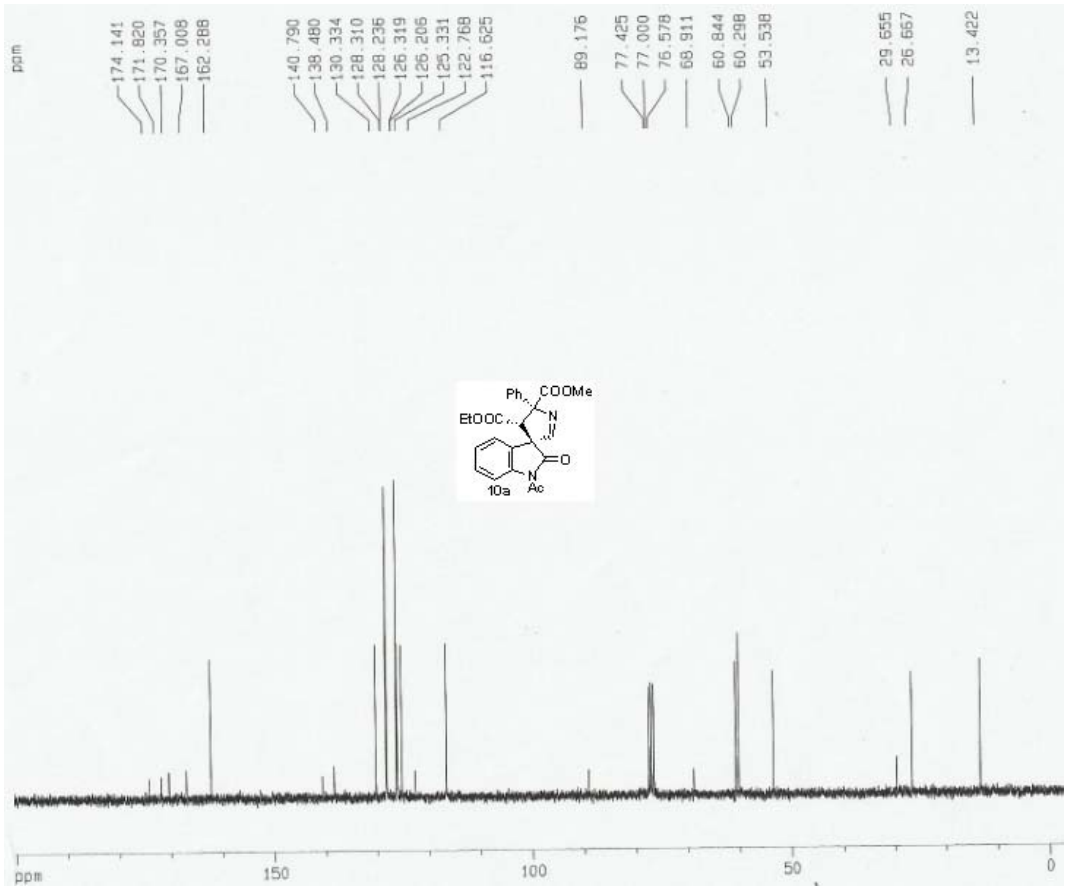
130.497
129.645
128.135
127.755
126.752
126.712
125.777
116.111
88.072
85.438
77.424
77.000
76.576
69.950
62.652
61.313
29.576
27.960
13.926
13.426
EtOOC
Ph
EtOOC
N
Cl
O
N
Boc
5y
ppm
150
100
50
0


8.75583
7.69164
7.66666
7.62680
7.60305
7.42358
7.40179
7.38544
7.34211
7.31921
7.28974
7.26138
7.23815
7.09245
7.06722
7.04188
6.87468
6.84924
4.16825
3.93435
3.92316
3.91091
3.89933
3.87547
3.84217
3.81703
3.79605
3.75962
1.25855
0.88012
0.85678
0.83214
0.74848
0.72472
0.70111
0.00152
MeOOC
Ph
EtOOC
N
O
N
H
9
Integral
1.0145
0.9882
2.0870
4.0203
1.6097
1.1531
1.0955
1.0000
5.0976
3.1949
ppm
10
8
6
4
2
0


ppm
176.198
171.440
168.499
162.688
141.889
140.871
129.586
128.194
127.715
127.065
126.921
125.217
123.310
109.983
87.792
77.422
77.000
76.576
70.112
61.490
61.139
53.275
29.679
13.365
MeOOC
Ph
EtOOC
N
O
N
H
9
ppm
150
100
50
0


ppm
Ph
COOMe
EtOOC
N
O
N
Ac
10a
[integral]
1.0000
2.0257
1.0378
4.2861
2.0995
0.9291
3.0762
2.0709
2.9830
3.1660
ppm
8
6
4
2
0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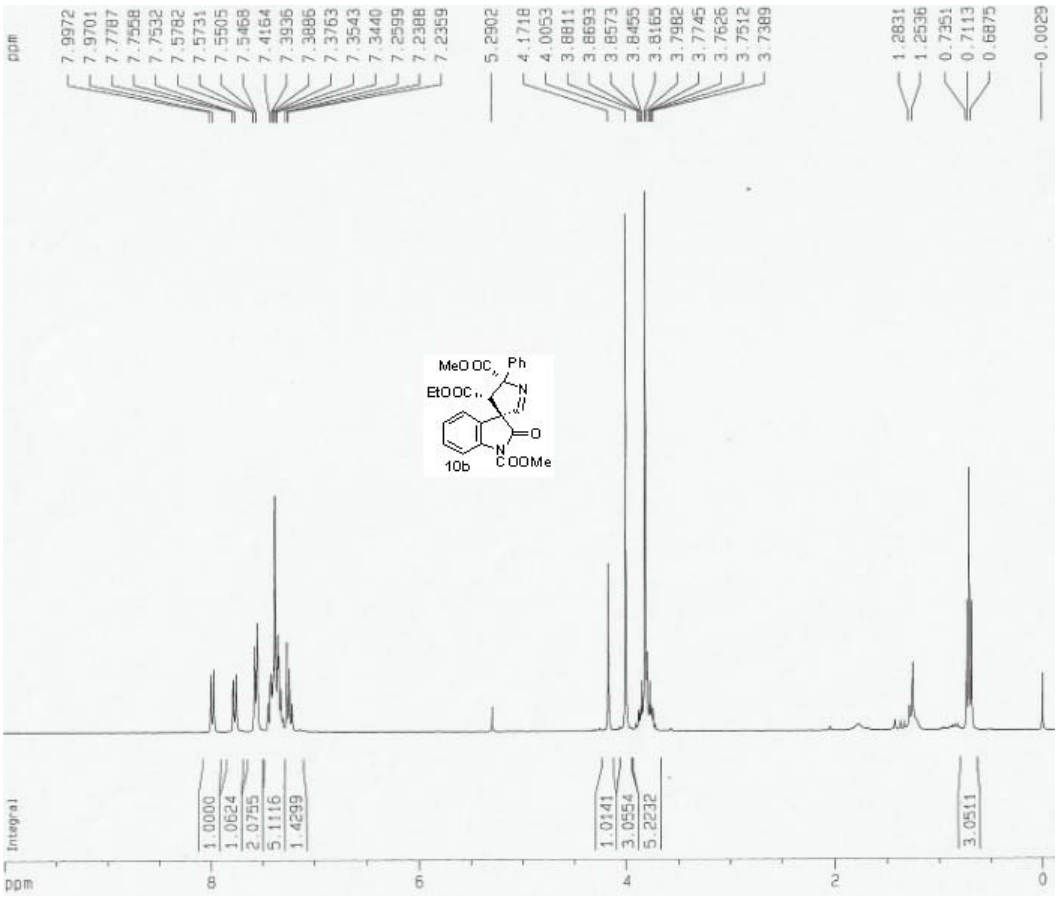
174.141
171.820
170.357
167.008
162.288
140.790
138.480
130.334
128.310
128.236
126.319
126.205
125.331
122.768
116.625
89.176
77.425
77.000
76.578
68.911
60.844
60.298
53.538
29.655
26.667
13.422
Ph
COOMe
EtOOC
N
O
N
Ac
10a
ppm
150
100
50
0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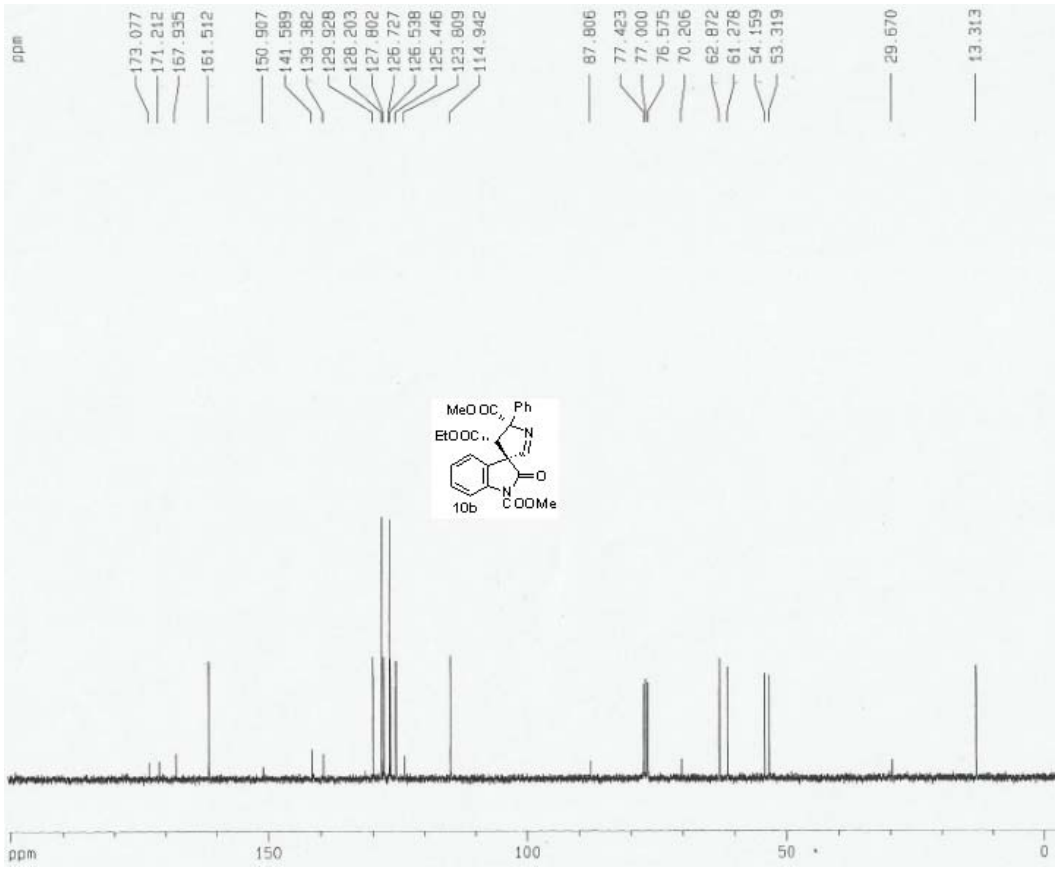
7.9972
7.9701
7.7787
7.7558
7.7532
7.5782
7.5731
7.5505
7.5468
7.4164
7.3936
7.3886
7.3763
7.3543
7.3440
7.2599
7.2388
7.2359
5.2902
4.1718
4.0053
3.8811
3.8693
3.8573
3.8455
3.8165
3.7982
3.7745
3.7625
3.7512
3.7389
1.2831
1.2536
0.7351
0.7113
0.6875
0.0029
MeO OC
Ph
EtOOC
N
O
N
COOMe
10b
Integral
1.0000
1.0624
2.0755
5.1116
1.4299
1.0141
3.0554
5.2232
3.0511
ppm
8
6
4
2
0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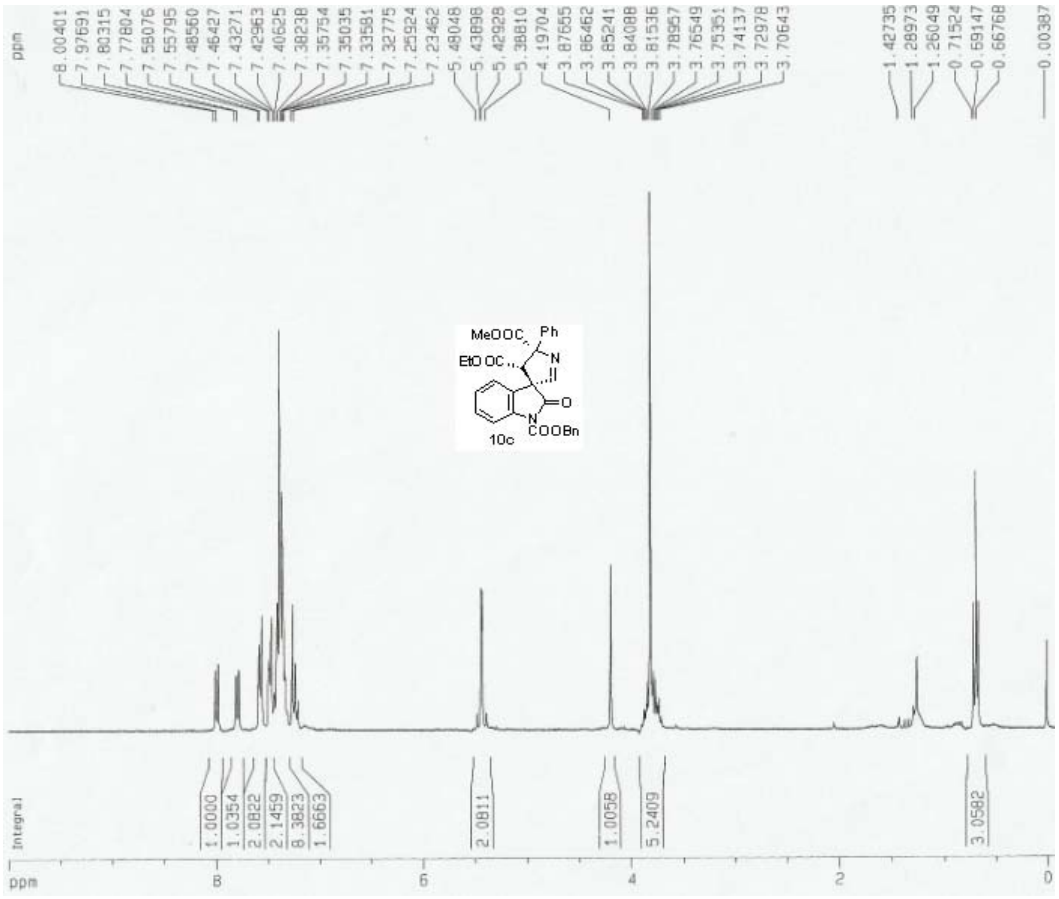
167.935
161.512
150.907
141.589
139.382
129.928
128.203
127.802
126.727
126.538
125.446
123.809
114.942
87.806
77.423
77.000
76.575
70.206
62.872
61.278
54.159
53.319
29.670
13.313
MeO OC
Ph
EtOOC
N
O
N
COOMe
10b
ppm
150
100
50
0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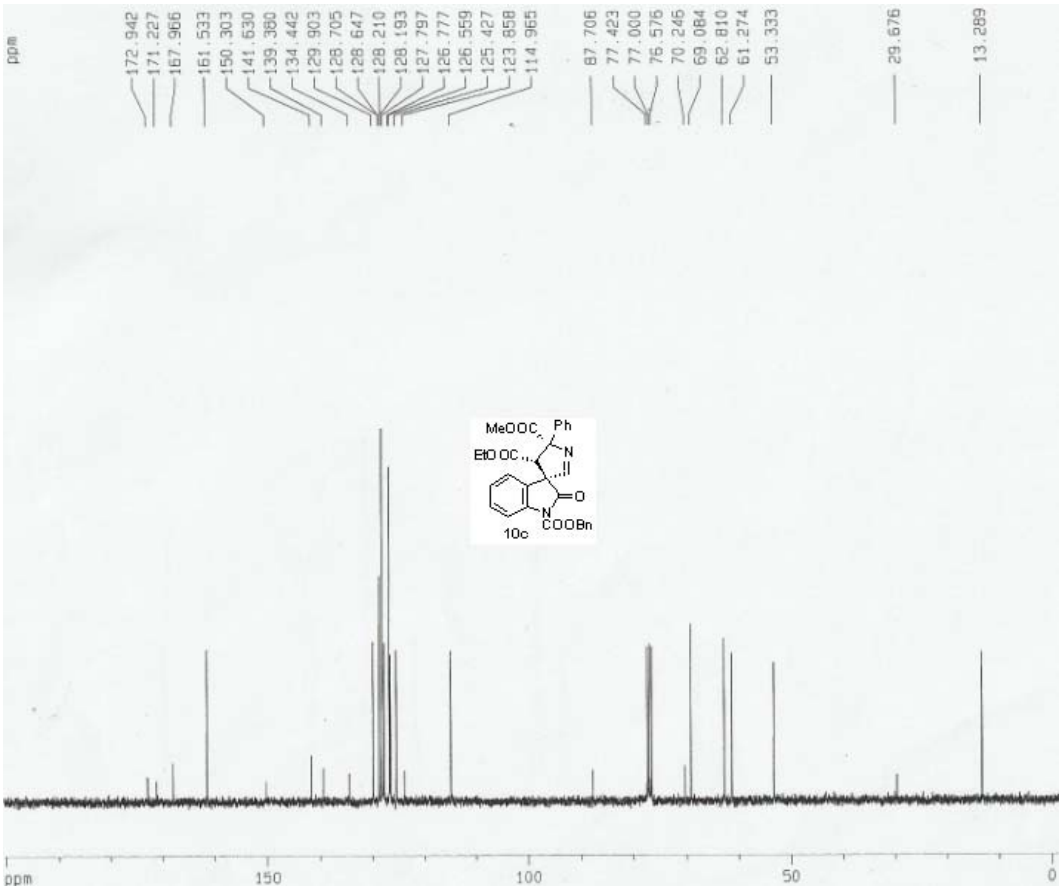
7.80315
7.77804
7.55076
7.55795
7.48560
7.46427
7.43271
7.42963
7.40625
7.38238
7.35754
7.35035
7.33581
7.32775
7.25924
7.23462
5.48048
5.43898
5.42928
5.38810
4.19704
3.87655
3.86462
3.85241
3.84088
3.81536
3.78957
3.76549
3.75351
3.74137
3.72978
3.70643
1.42735
1.28973
1.26049
0.71524
0.69147
0.66768
0.00387
MeOOC
Ph
EtO OC
N
O
N
COOBn
10c
Integral
1.0000
1.0354
2.0822
2.1459
8.3823
1.6663
2.0811
1.0058
5.2409
3.0582
ppm
8
6
4
2
0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167.966
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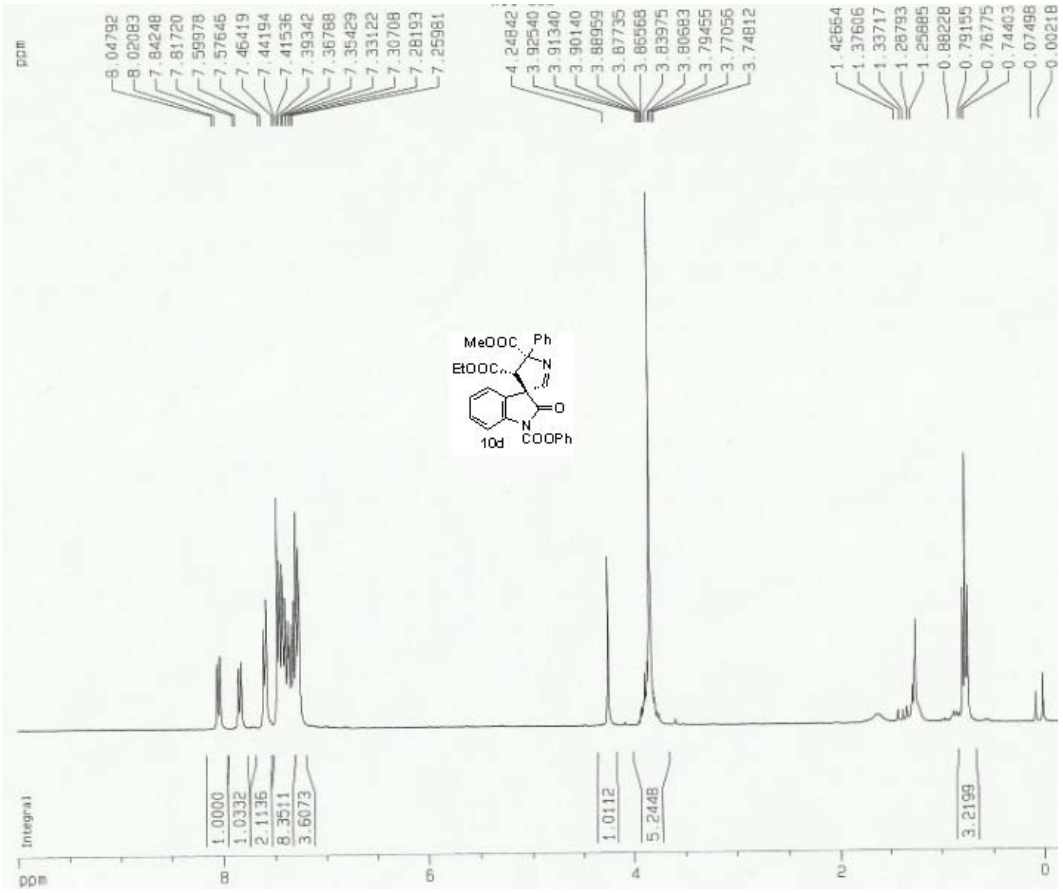
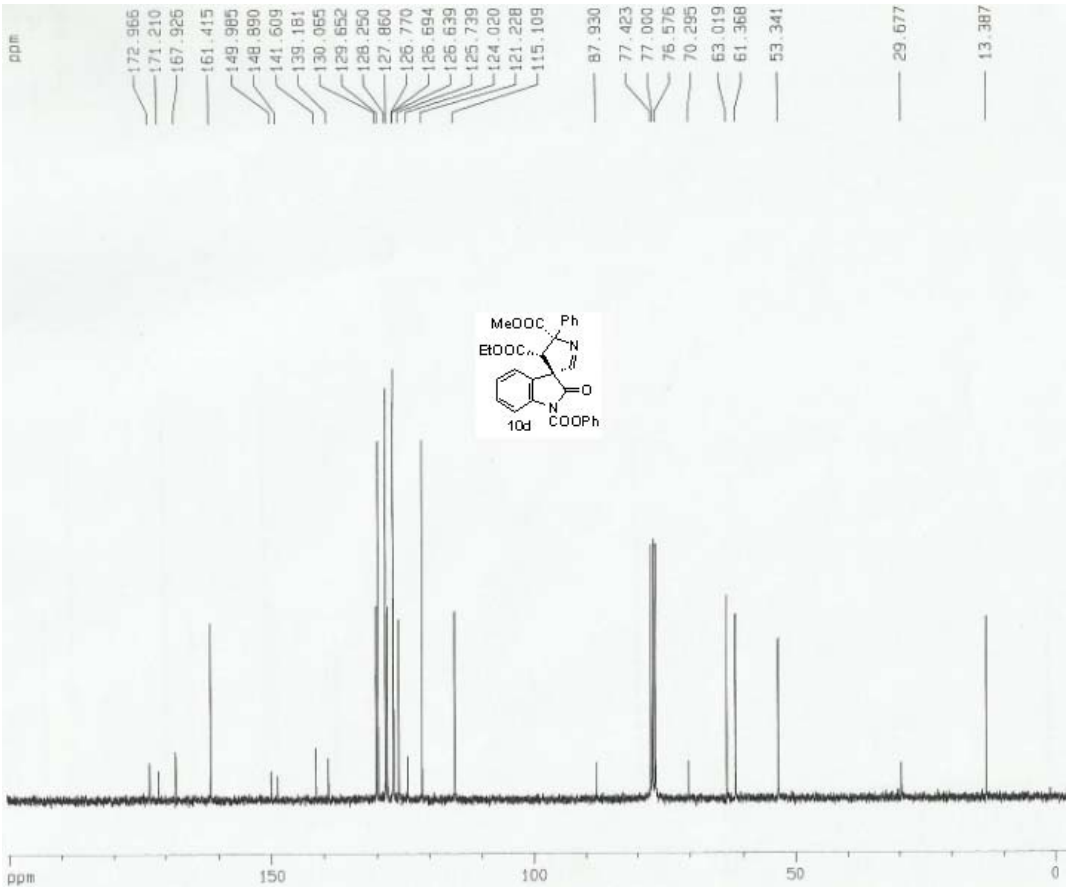
150.303
141.630
139.380
134.442
129.903
128.705
128.647
128.210
128.193
127.797
126.777
126.559
125.427
123.858
114.965
87.706
77.423
77.000
76.576
70.246
69.084
62.810
61.274
53.333
29.676
13.289
MeOOC
Ph
EtO OC
N
O
N
COOBn
10c
ppm
150
100
50
0


ppm
8.04792
8.02083
7.84248
7.81720
7.59978
7.57645
7.46419
7.44194
7.41536
7.39342
7.36788
7.35429
7.33122
7.30708
7.28193
7.25981
4.24842
3.92540
3.91340
3.90140
3.88959
3.87735
3.86568
3.83975
3.80683
3.79455
3.77056
3.74812
1.42664
1.37606
1.33717
1.28793
1.25885
0.88228
0.79155
0.76775
0.74403
0.07498
0.00218
MeOOC
Ph
EtOOC
N
O
N
COOPh
10d
Integral
1.0000
1.0332
2.1136
8.3511
3.6073
1.0112
5.2448
3.2199
ppm
8
6
4
2
0


ppm
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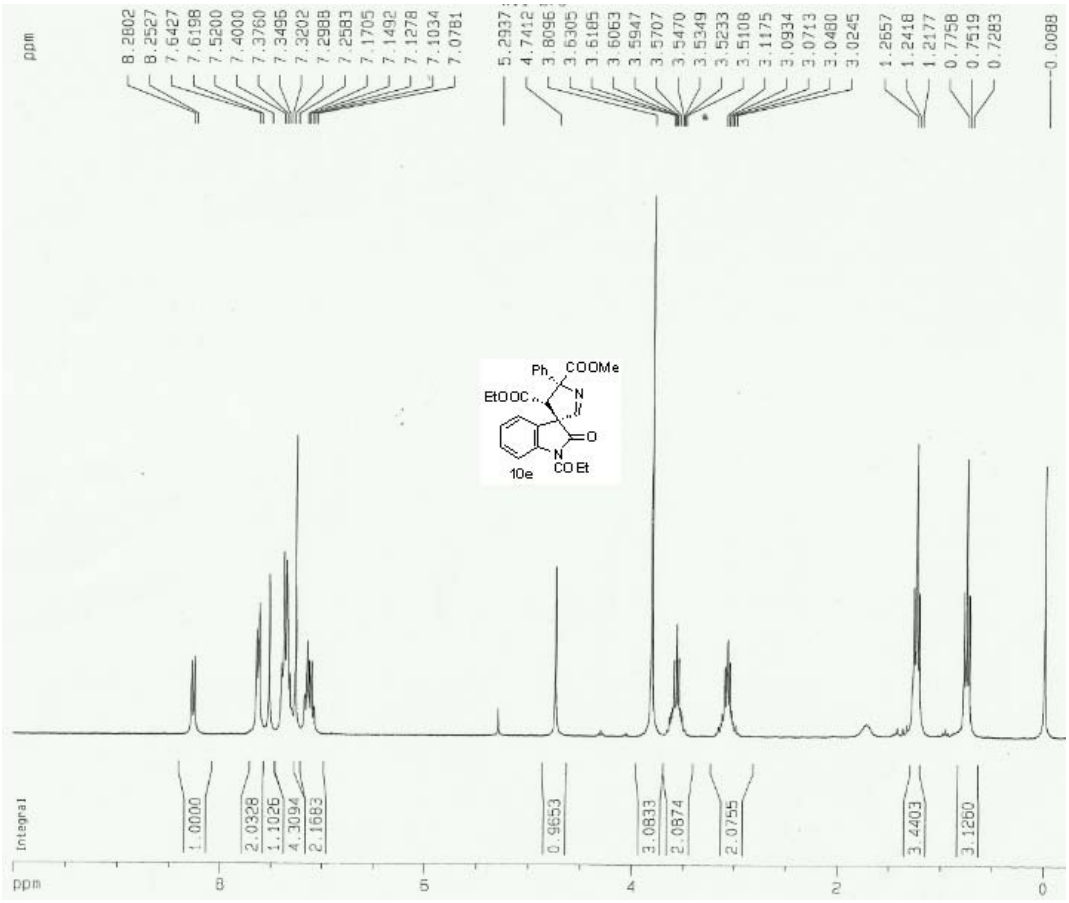
167.926
161.415
149.985
148.890
141.609
139.181
130.065
129.652
128.250
127.860
126.770
126.694
126.639
125.739
124.020
121.228
115.109
87.930
77.423
77.000
76.576
70.295
63.019
61.368
53.341
29.677
13.387
MeOOC
Ph
EtOOC
N
O
N
COOPh
10d
ppm
150
100
50
0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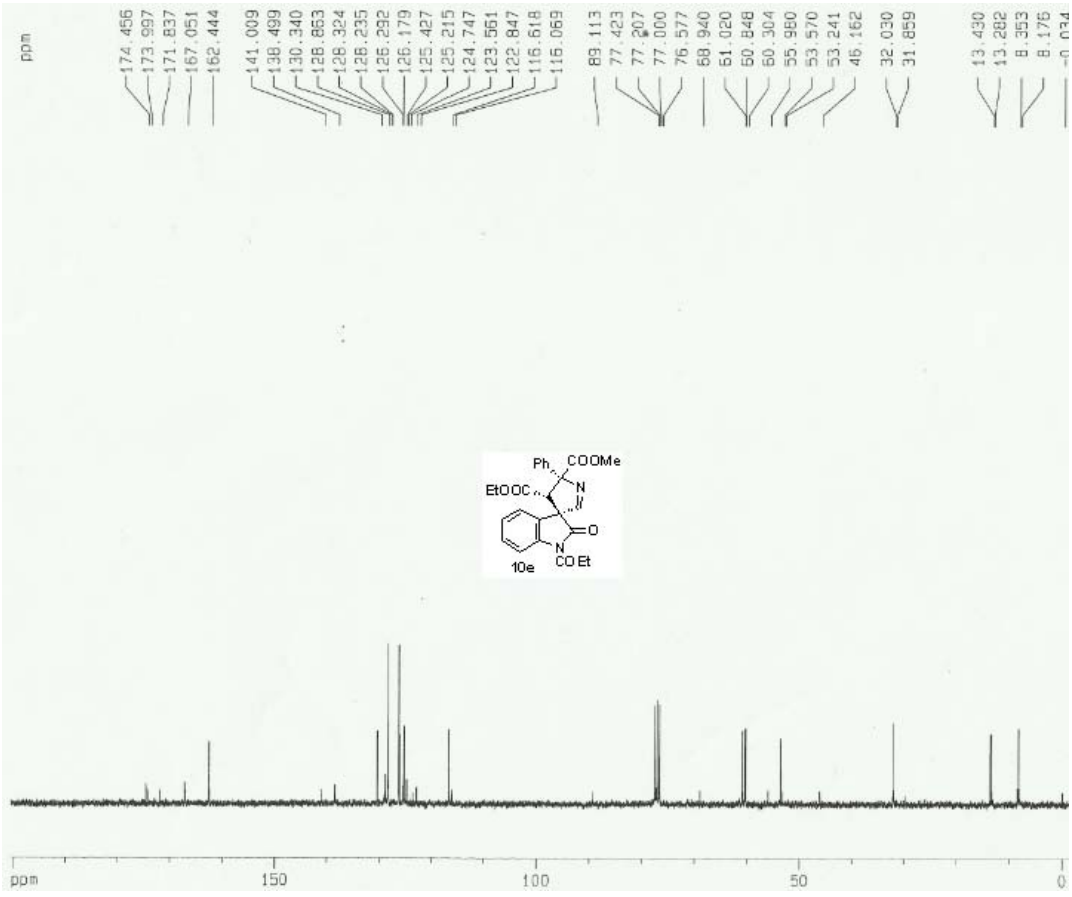
7.5200
7.4000
7.3760
7.3495
7.3202
7.2988
7.2583
7.1705
7.1492
7.1278
7.1034
7.0781
5.2937
4.7412
3.8096
3.6305
3.6185
3.6063
3.5947
3.5707
3.5470
3.5349
3.5233
3.5108
3.1175
3.0934
3.0713
3.0480
3.0245
1.2657
1.2418
1.2177
0.7758
0.7519
0.7283
0.0088
Integral
1.0000
2.0328
1.1026
4.3094
2.1683
0.9653
3.0833
2.0874
2.0755
3.4403
3.1260
ppm
8
6
4
2
0
Ph
COOMe
EtOOC
N
O
N
CO Et
10e


ppm
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171.837
167.051
162.444
141.009
138.499
130.340
128.863
128.324
128.235
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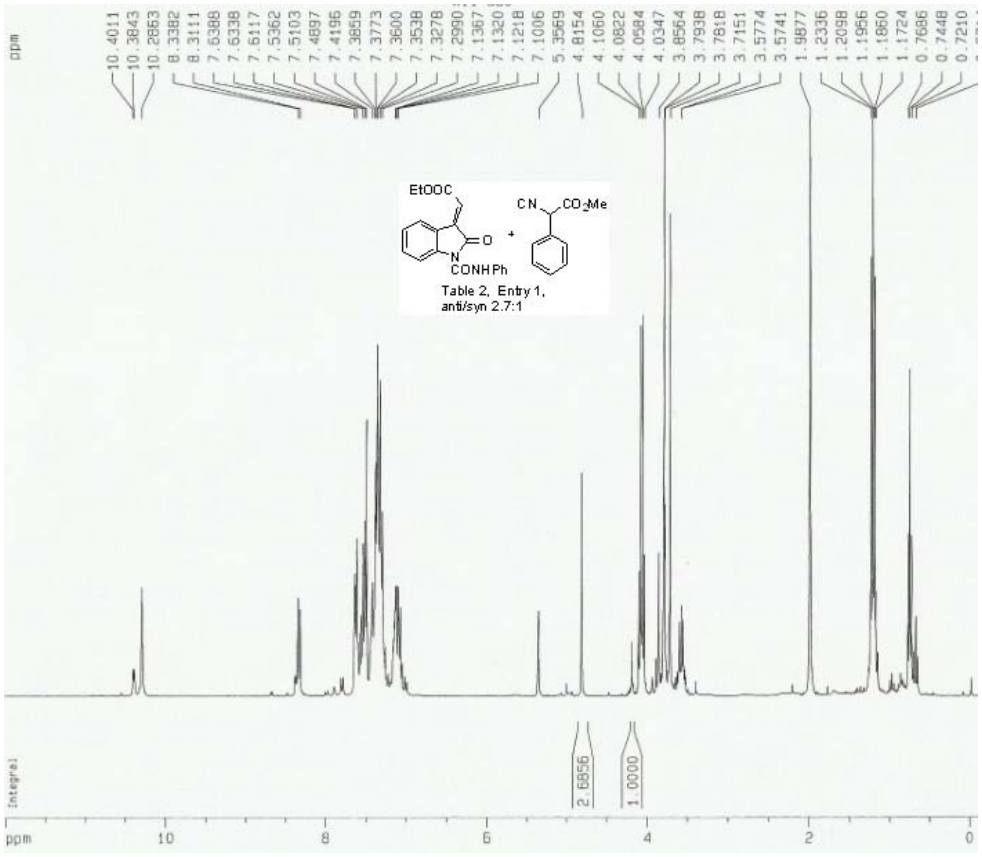
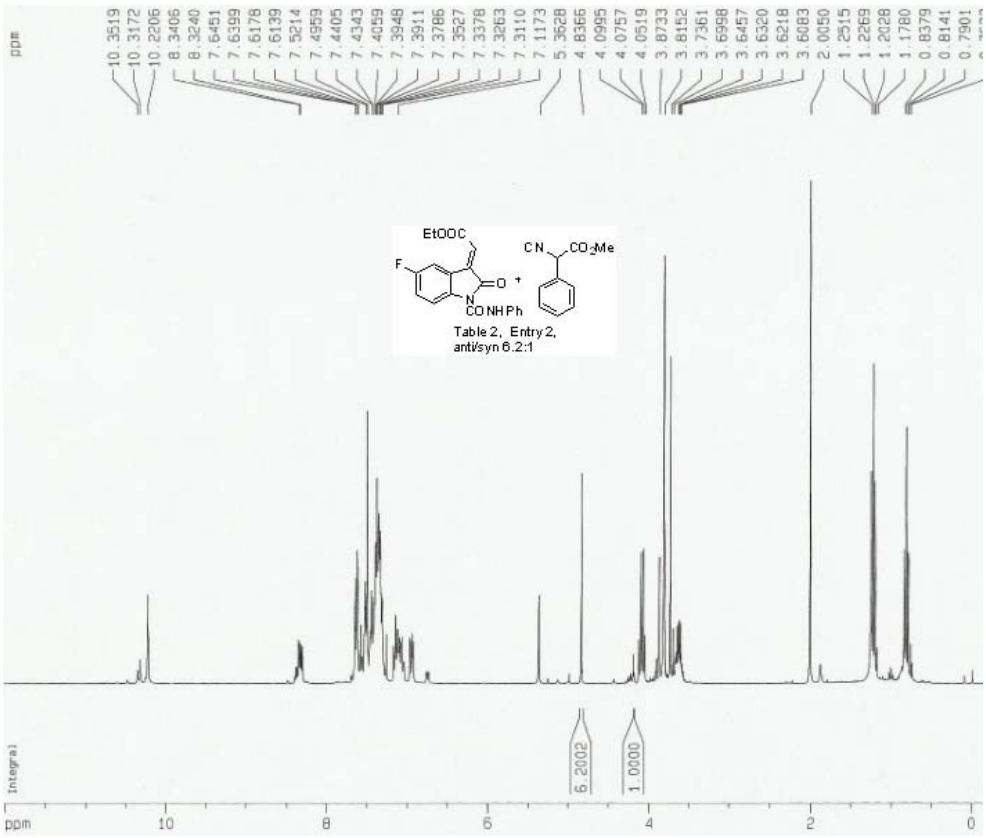
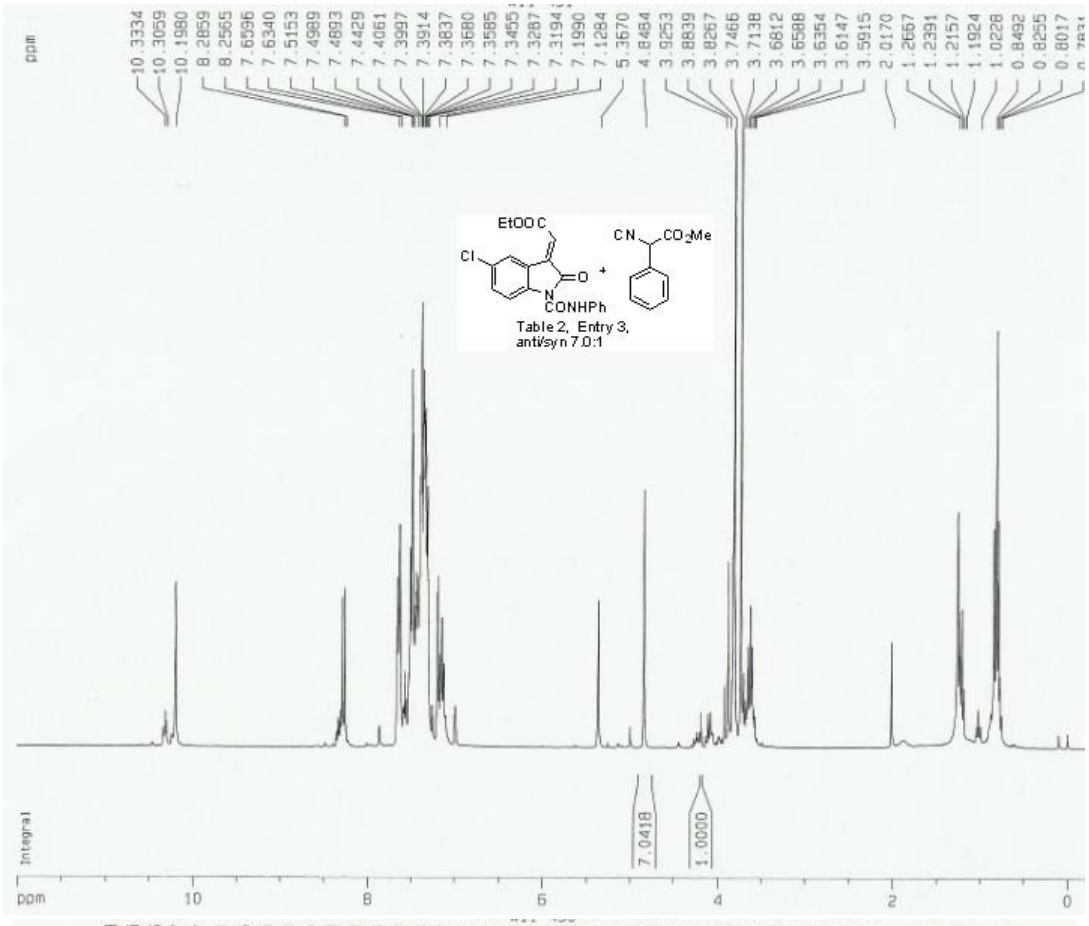
125.427
125.215
124.747
123.561
122.847
116.618
116.069
89.113
77.423
77.207
77.000
76.577
68.940
61.020
60.848
60.304
55.980
53.570
53.241
46.162
32.030
31.859
13.430
13.282
8.353
8.175
ppm
150
100
50
0
Ph
COOMe
EtOOC
N
O
N
CO Et
10e

10. Crude NMR spectra of some reaction mixtures






EtOOC
Cl
CONHPh
CN
CO2Me
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anti/syn 7.0:1
Integral
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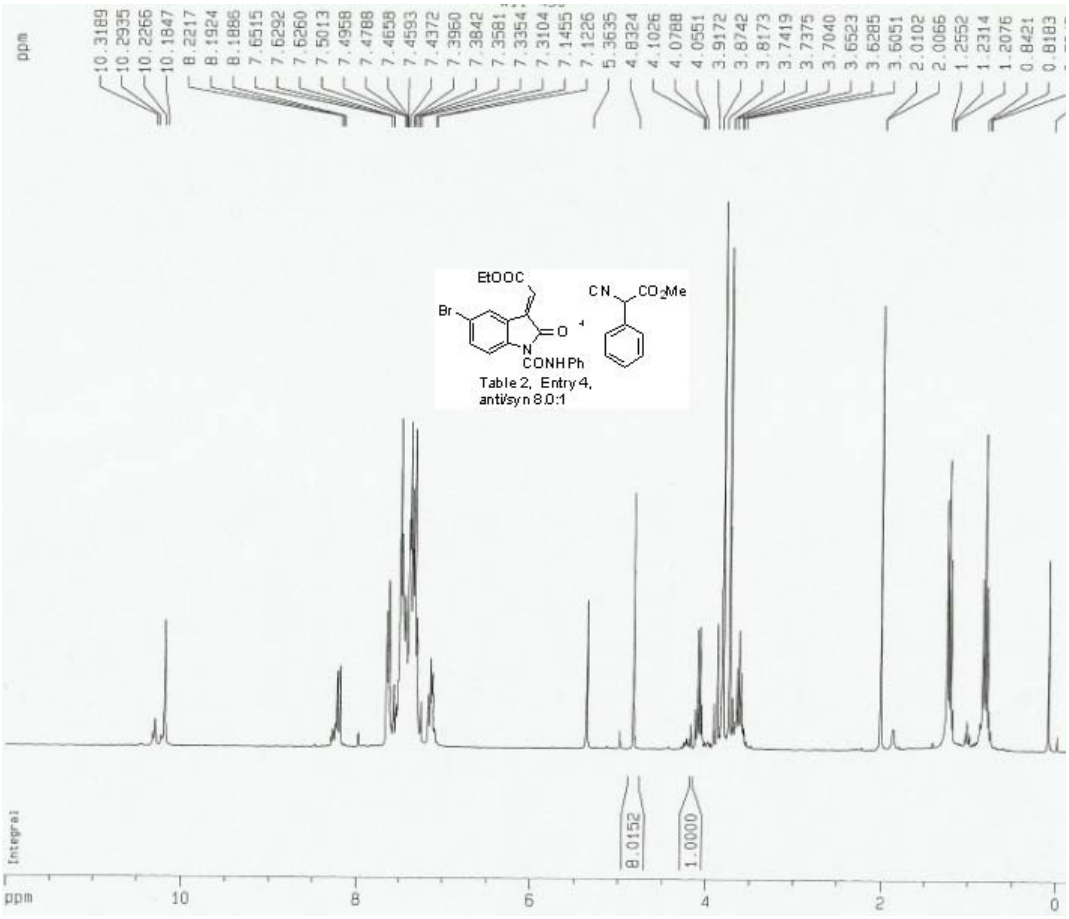
1.0000
ppm


EtOOC
Br
CONHPh
CN
CO2Me
Table 2, Entry 4,
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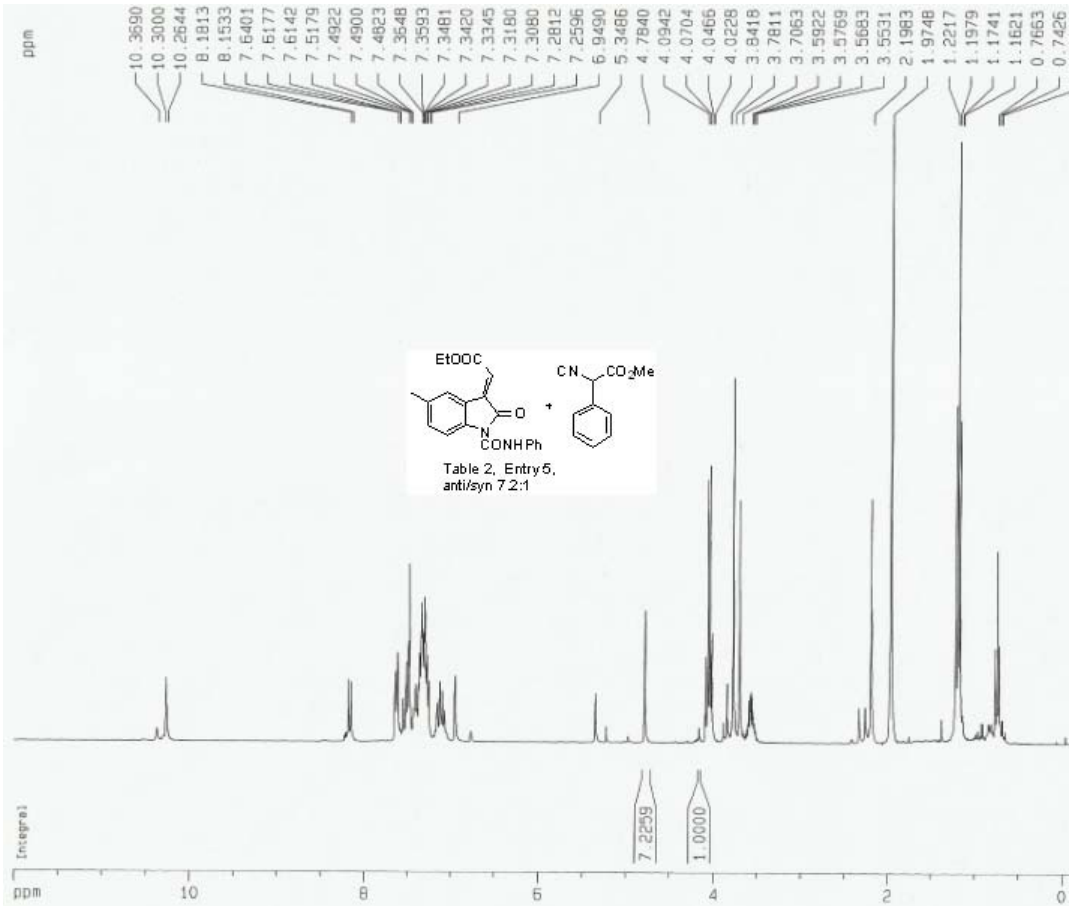
Integral
8.0152
1.0000
ppm


EtOOC
CN
CO2Me
O
N
CONHPh
Table 2, Entry 5,
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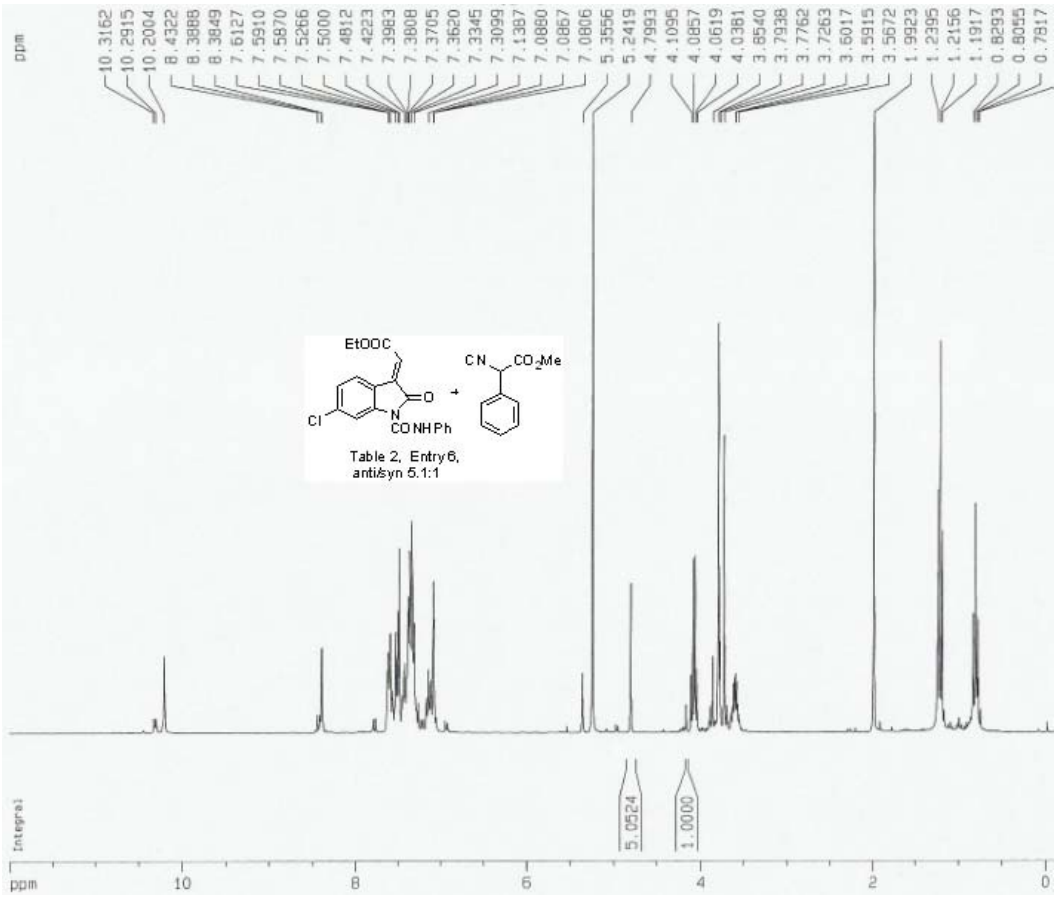
EtOOC
CN
CO2Me
Cl
O
N
CONHPh
Table 2, Entry 6,
anti/syn 5.1:1
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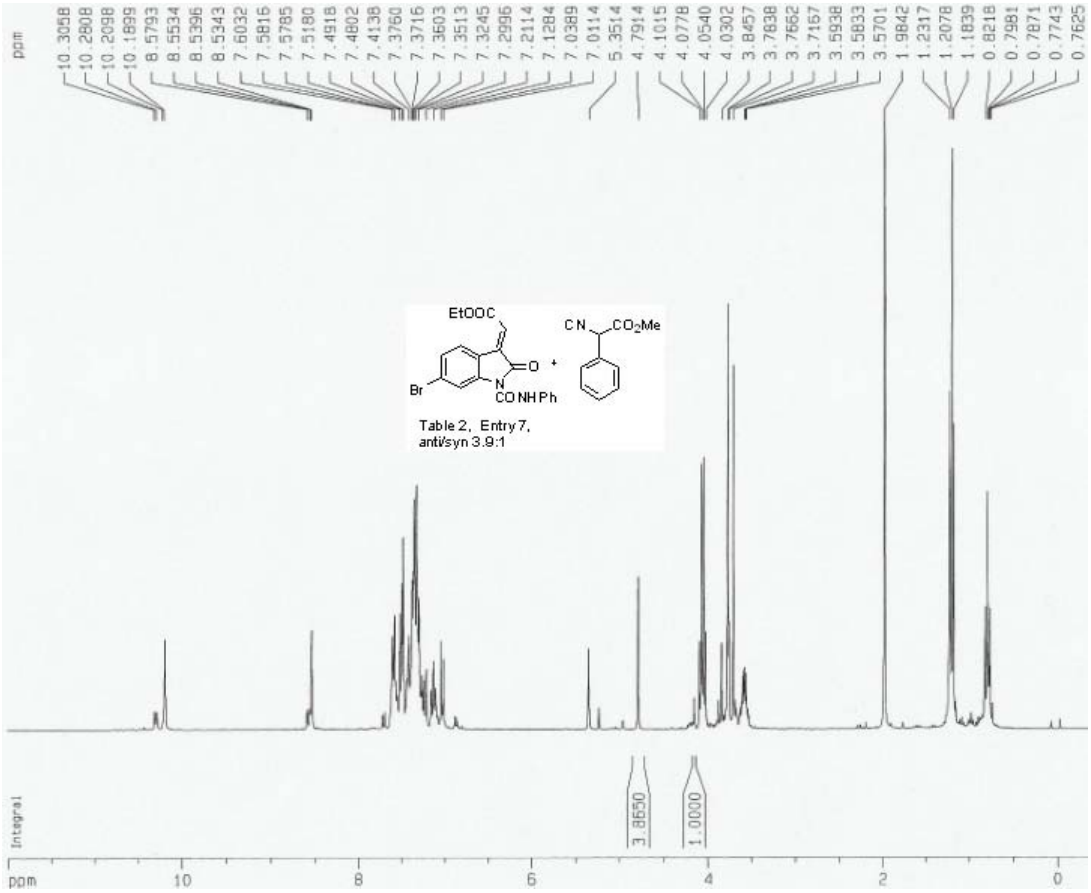
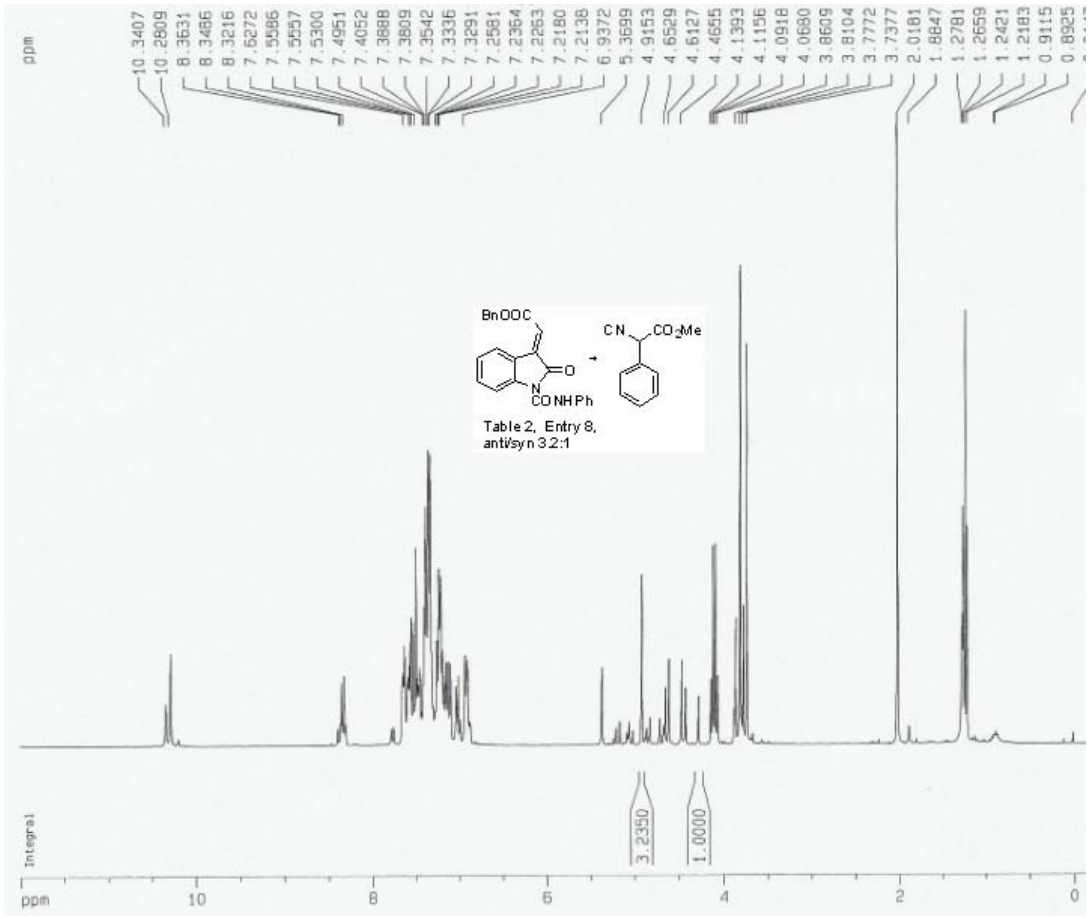
1.0000


EtOOC
Br
CONHPh
CN
CO2Me
Table 2, Entry 7,
anti/syn 3.9:1
3.8650
1.0000


BnOOC
CONHPh
CN
CO2Me
Table 2, Entry 8,
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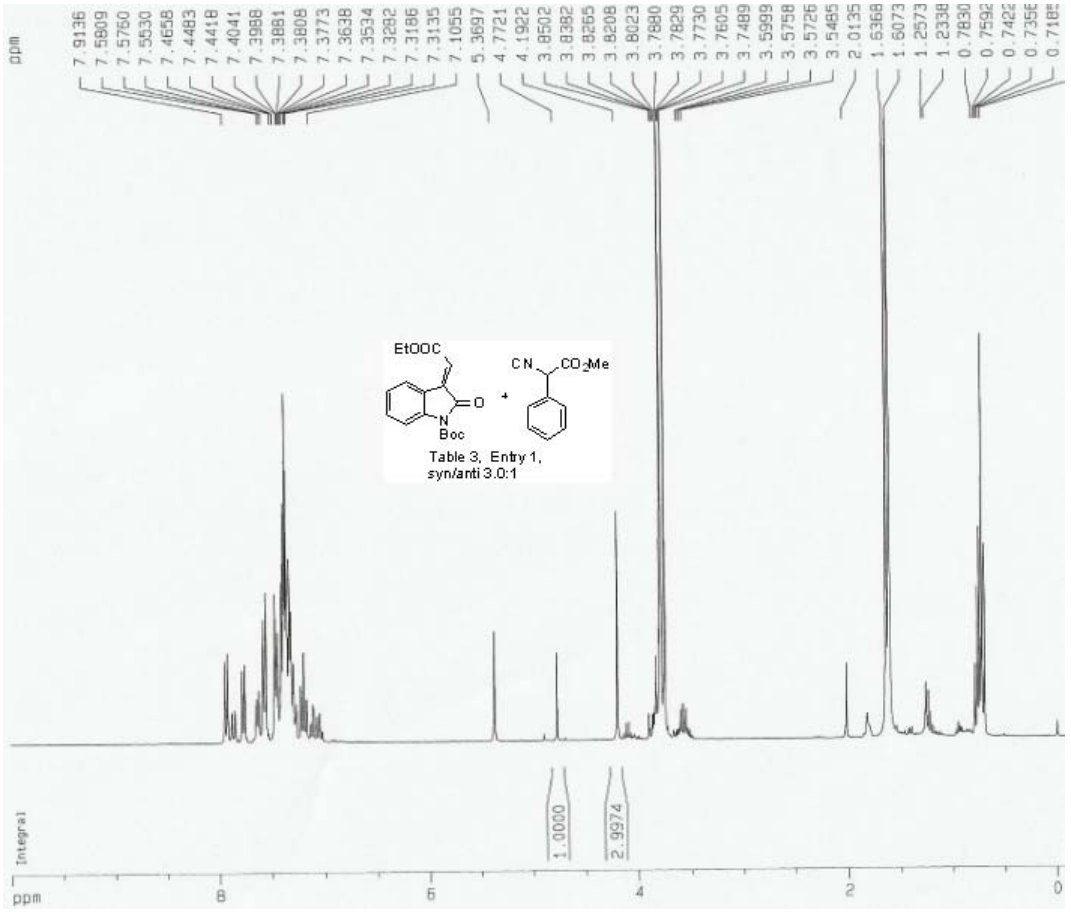
1.0000


EtOOC
CN
CO2Me
O
N
Boc
Table 3, Entry 1,
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Integral
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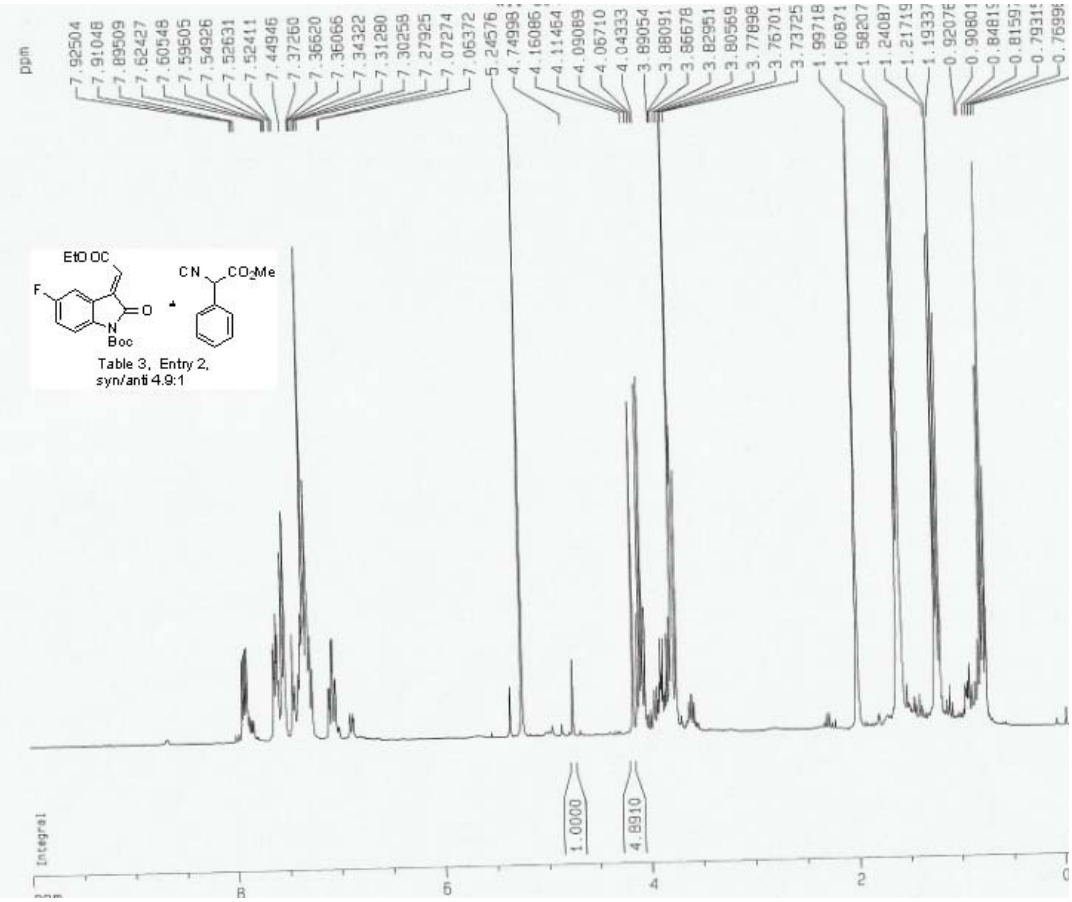
2.9974
ppm


EtOOC
F
CN
CO2Me
O
N
Boc
Table 3, Entry 2,
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Integral
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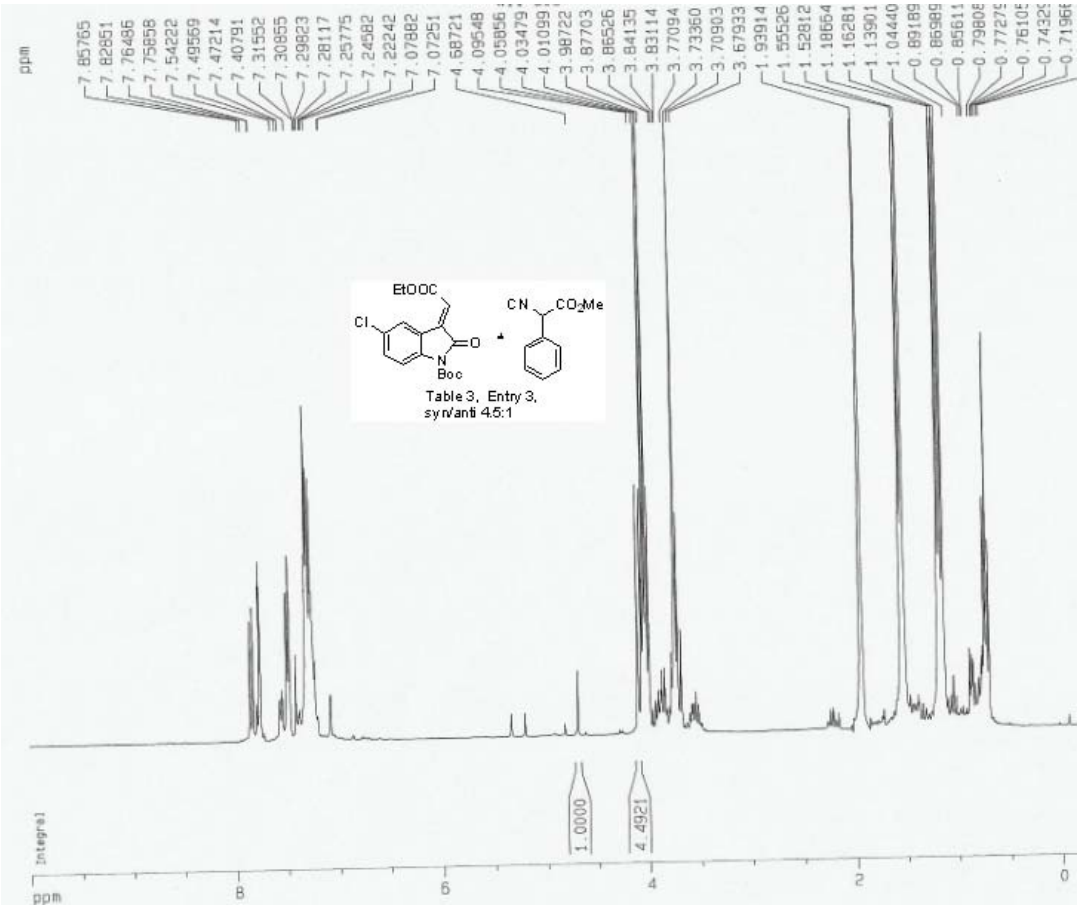
4.8910
ppm


EtOOC
Cl
N
Boc
CN
CO2Me
Table 3, Entry 3,
syn/anti 4.5:1
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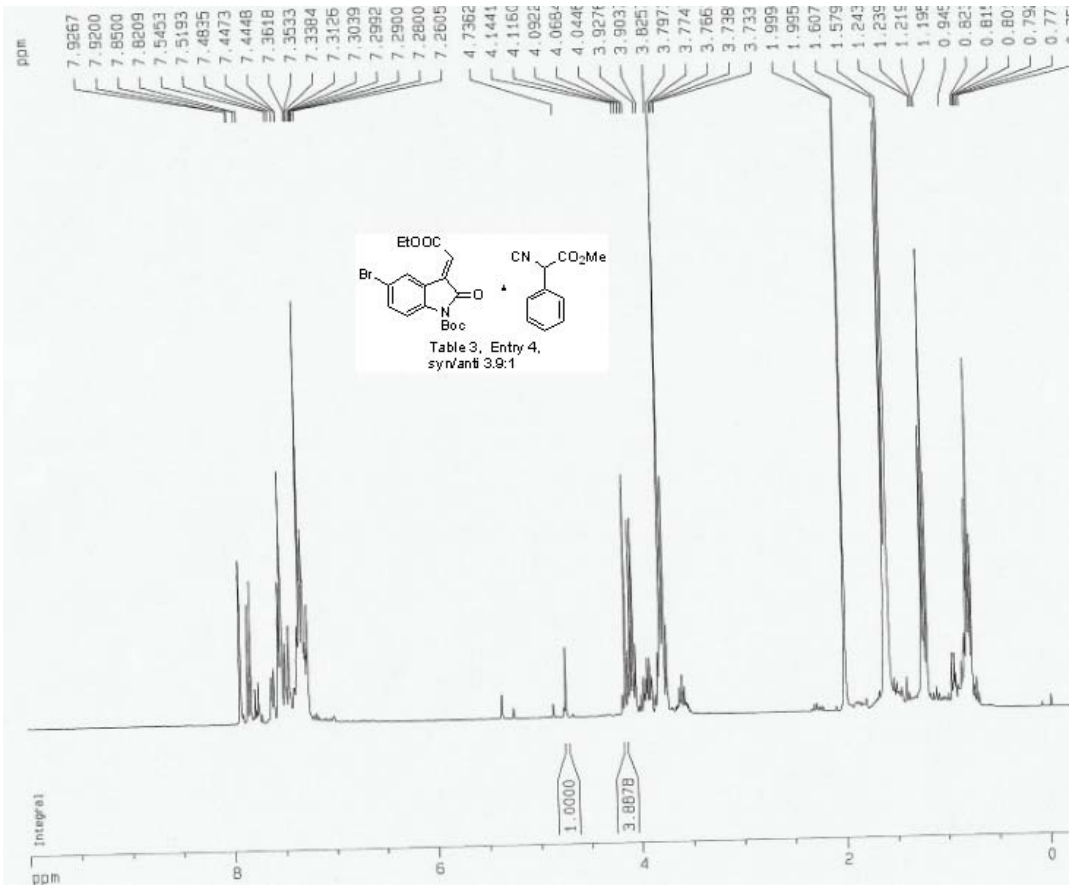
4.4921
Integral
ppm


EtOOC
Br
N
Boc
CN
CO2Me
Table 3, Entry 4,
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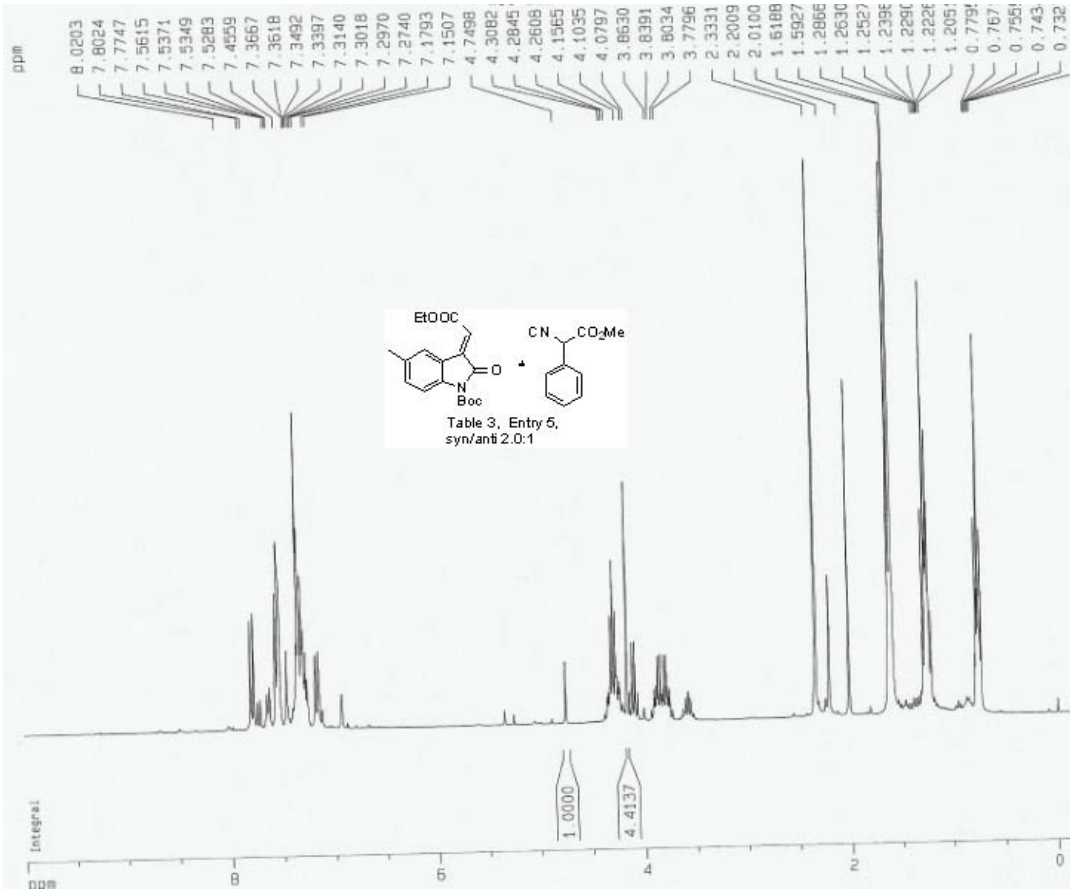
3.8878
Integral
ppm


EtOOC
CN
CO2Me
O
N
Boc
Table 3, Entry 5,
syn/anti 2.0:1
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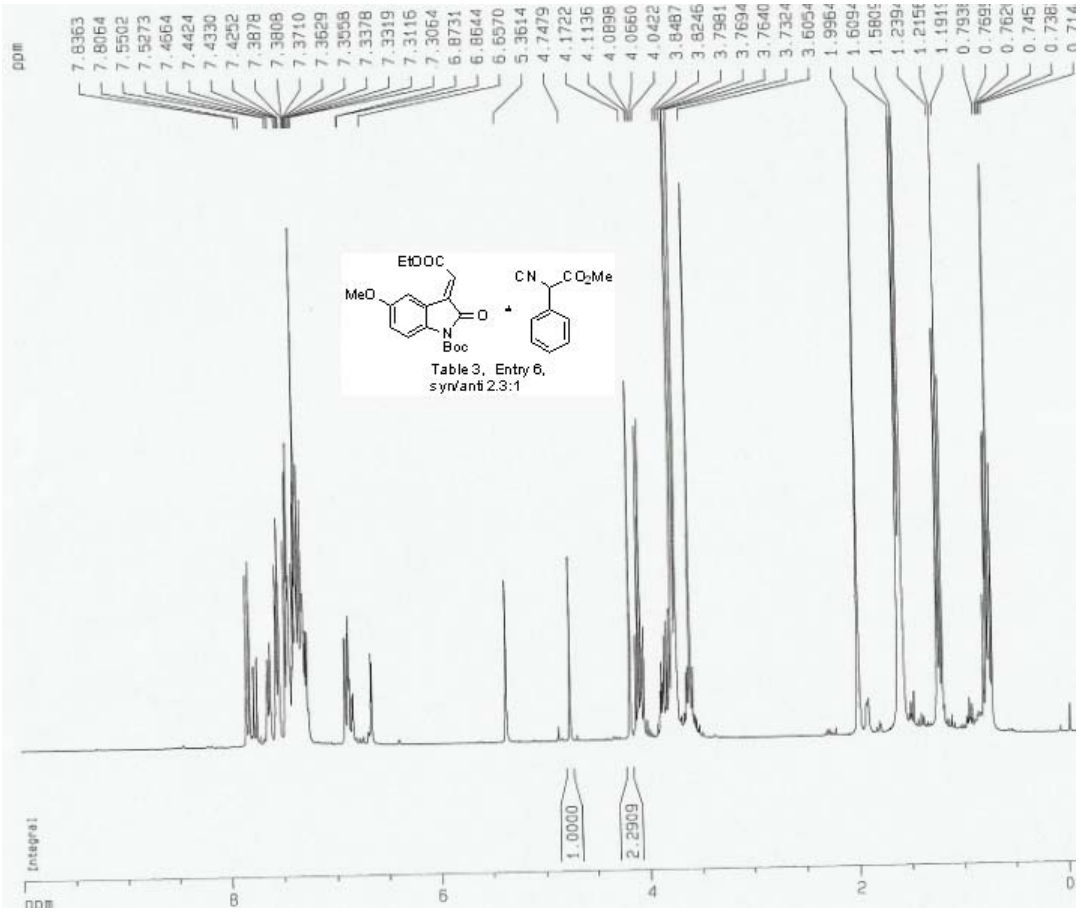
4.4137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MeO
CN
CO2Me
O
N
Boc
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syn/anti 2.3:1
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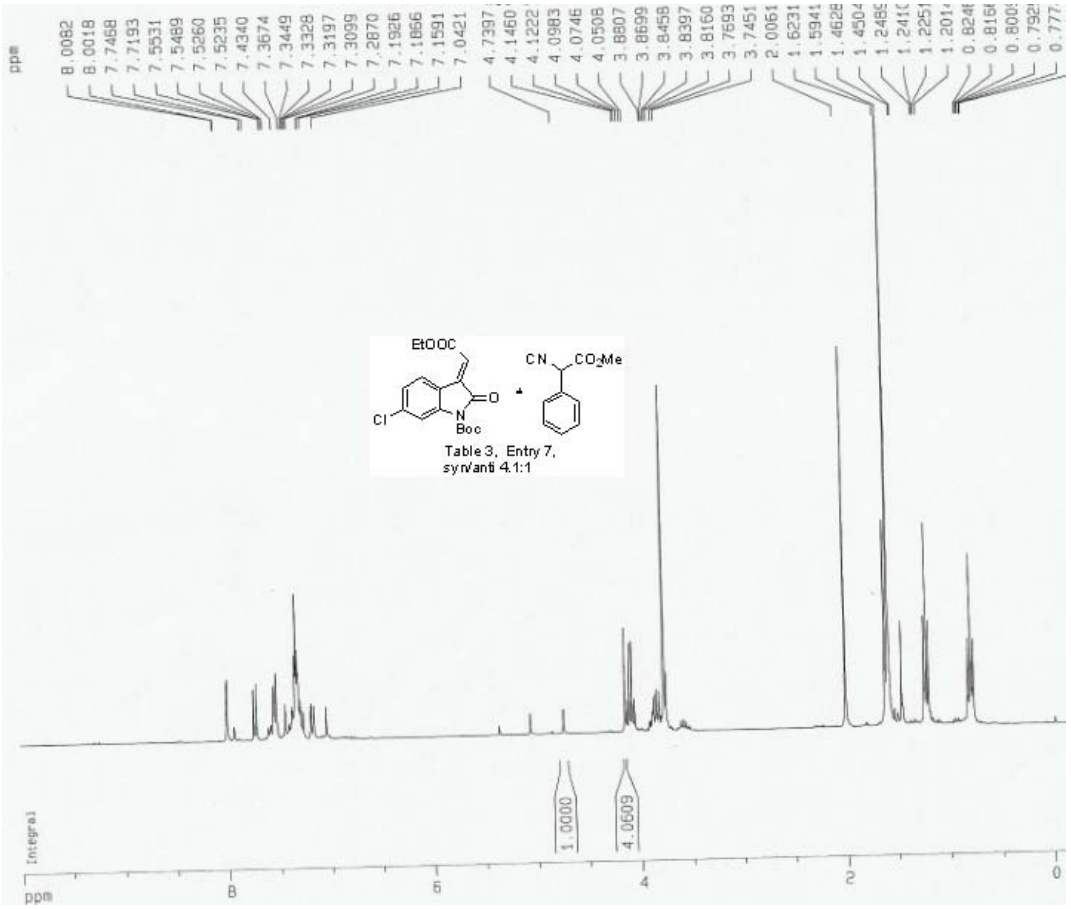
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CN
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Cl
O
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Boc
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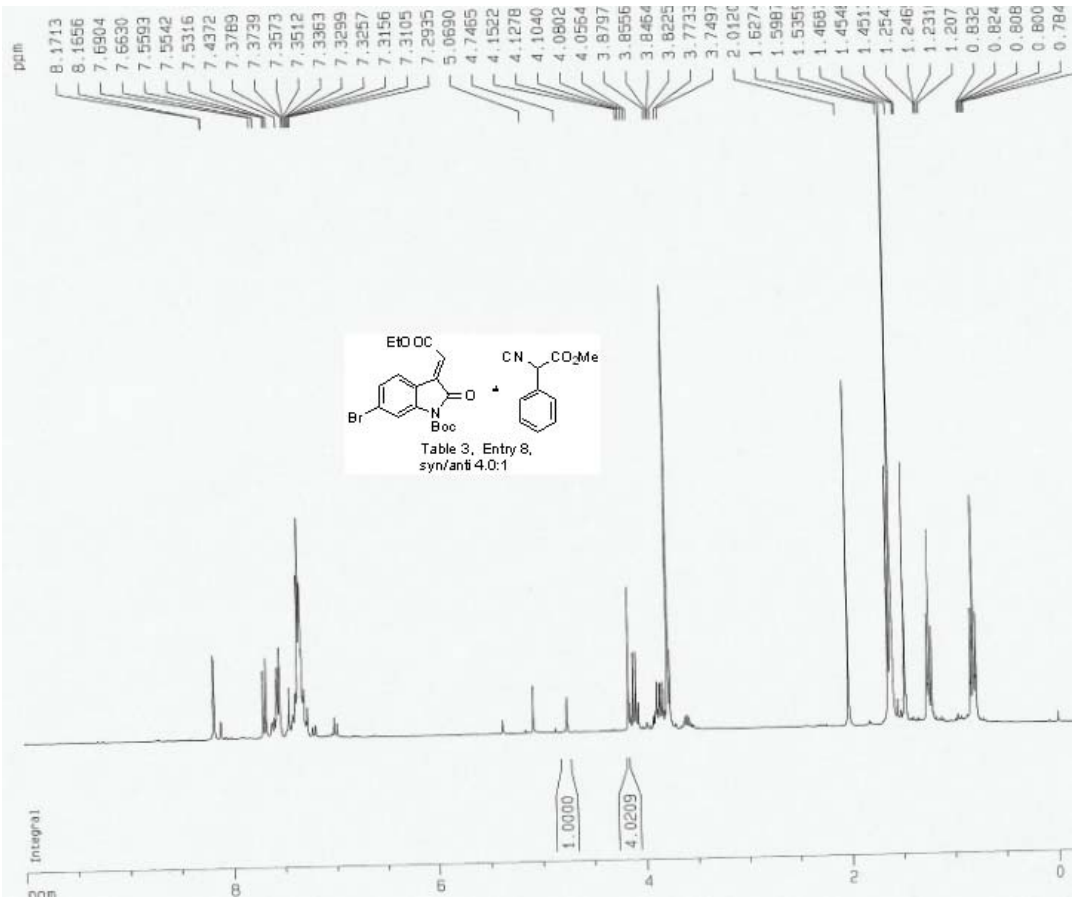
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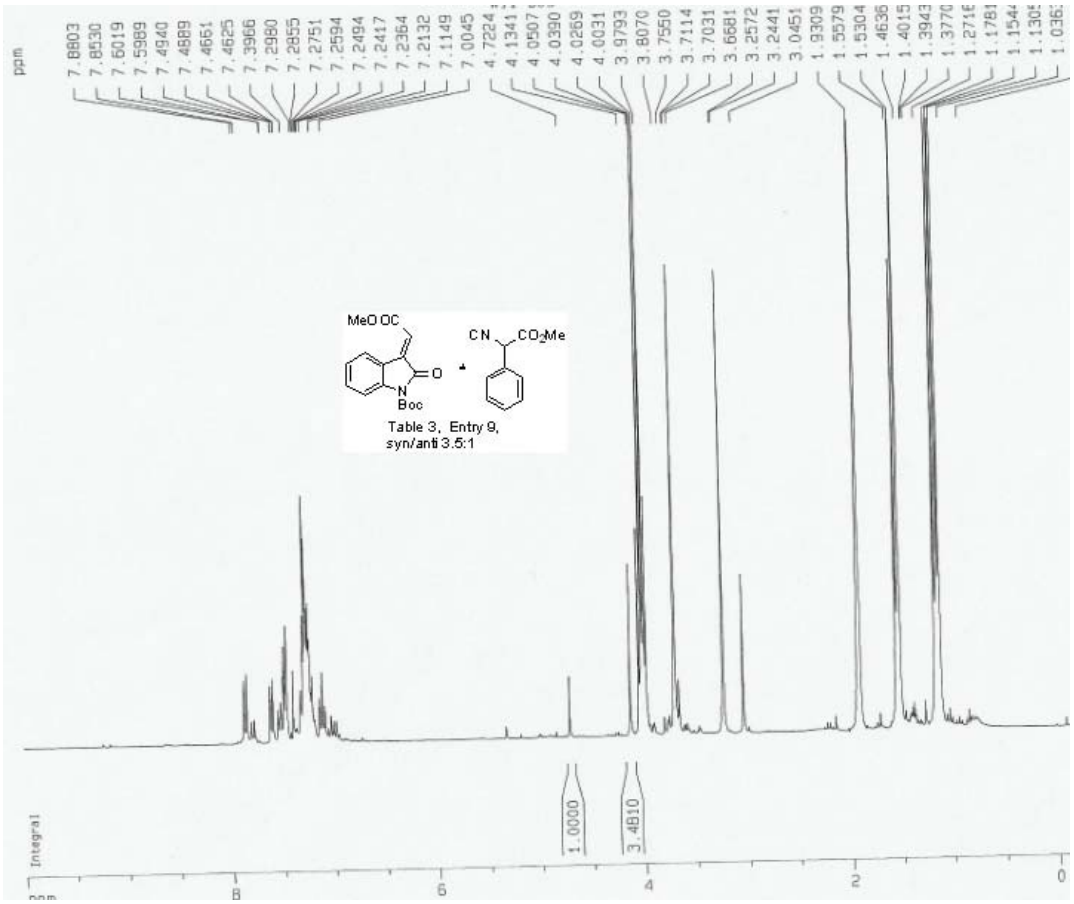
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CN
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O
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Boc
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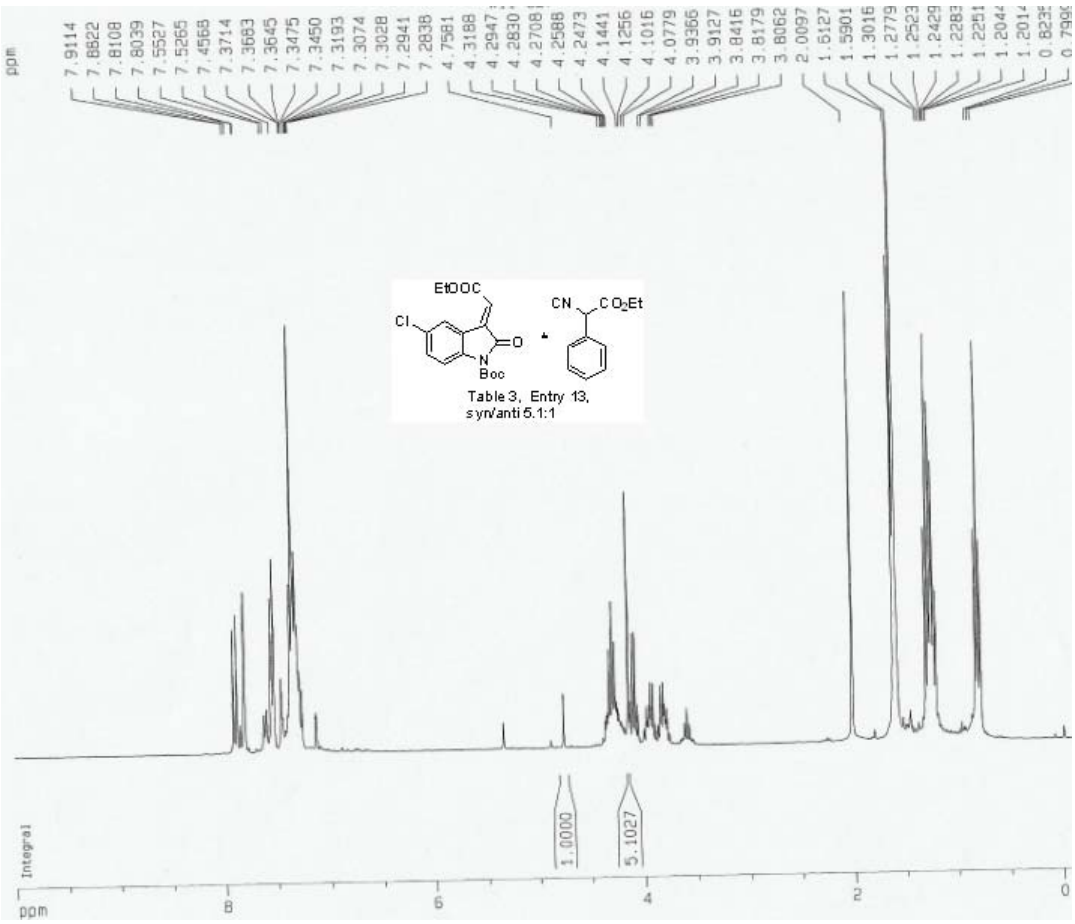
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O
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Boc
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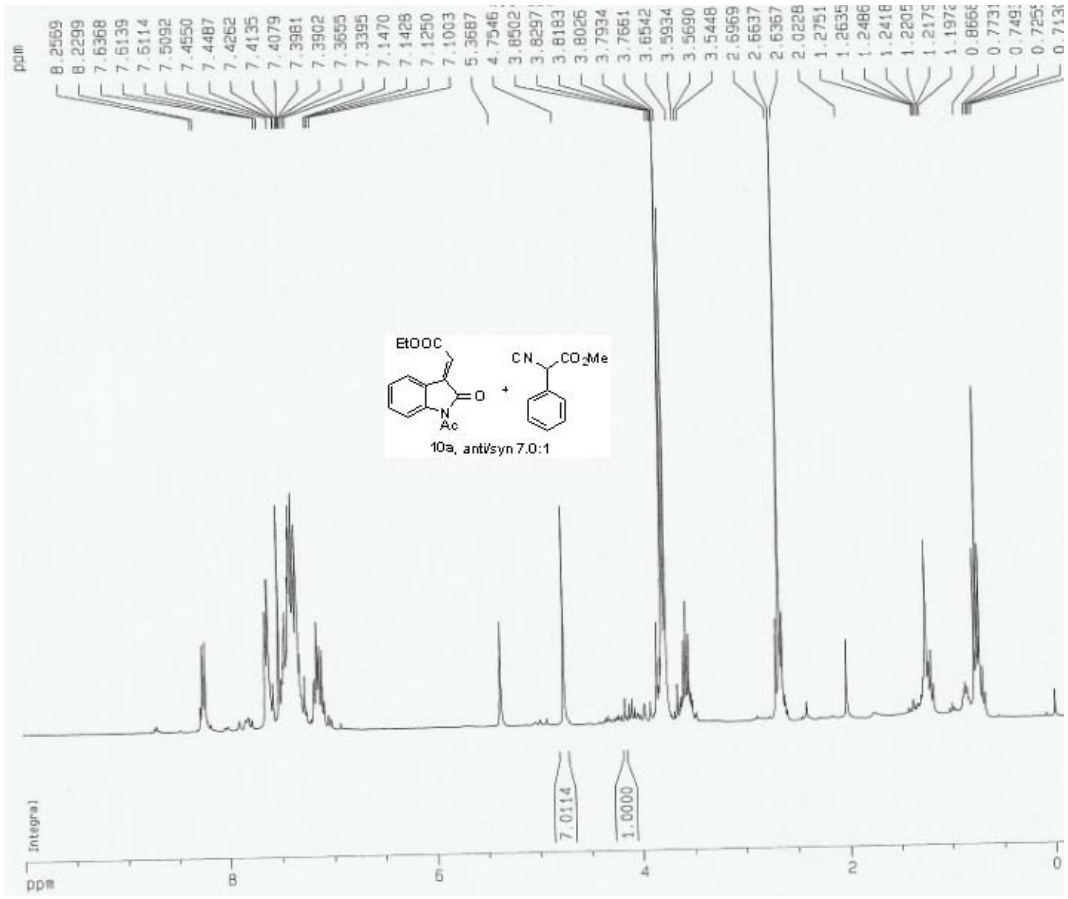
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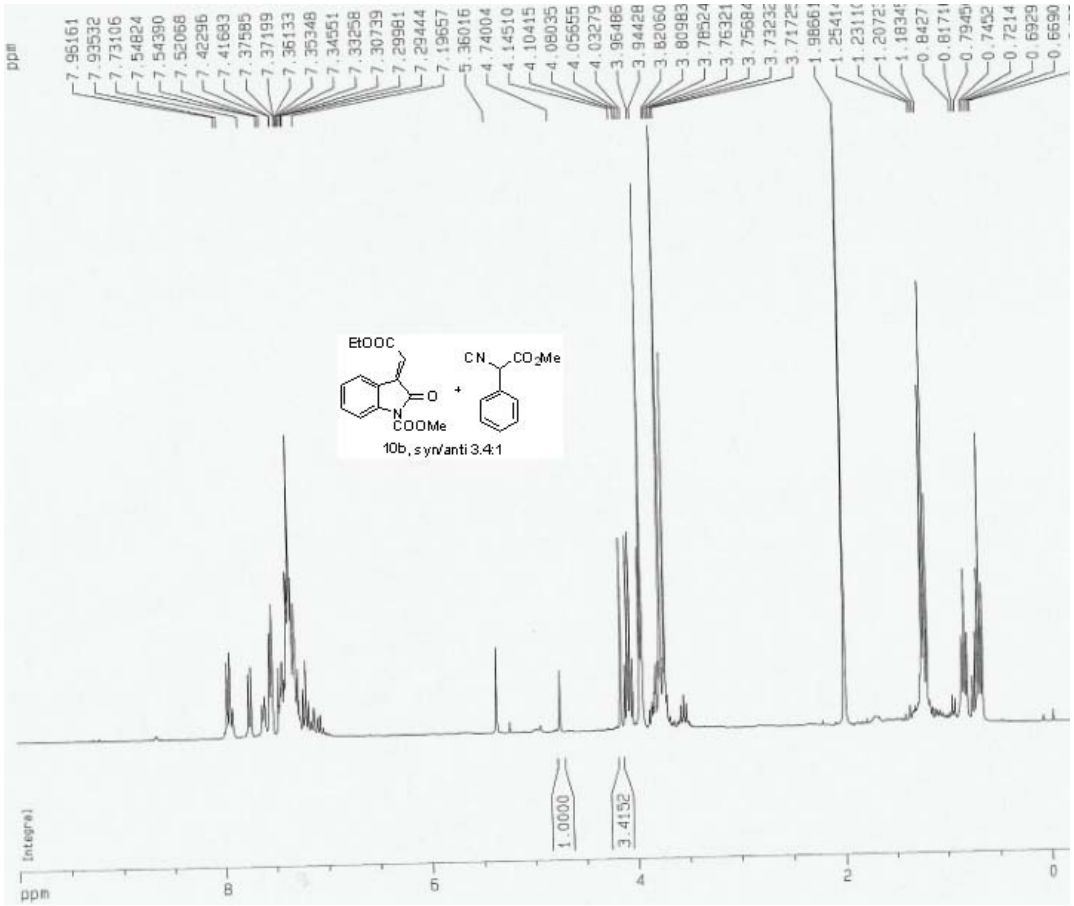
CN
CO2Me
O
N
Ac
10a, anti/syn 7.0:1
7.0114
1.0000
Integral
ppm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COOMe
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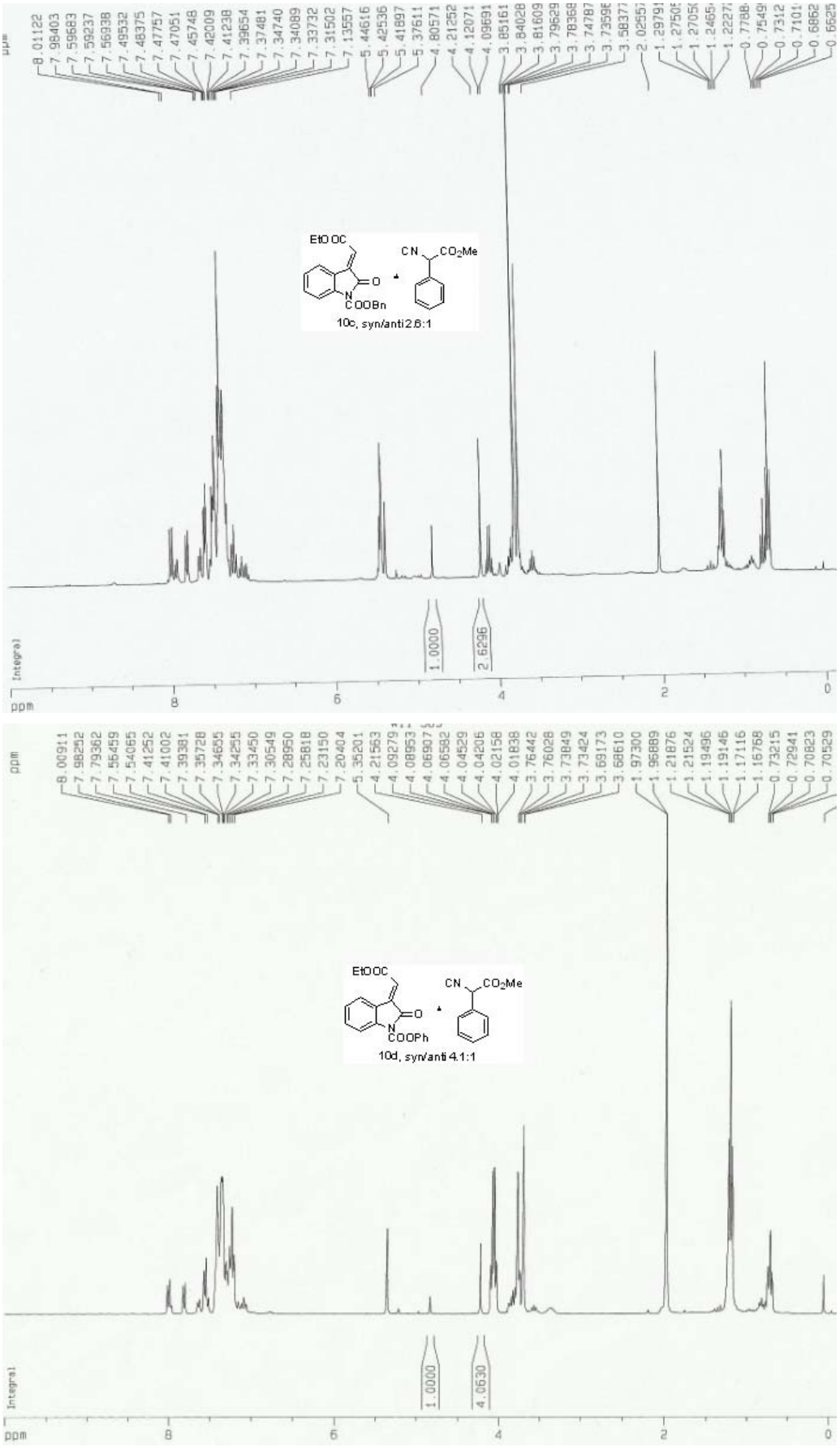
ppm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O
N
COOBn
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ppm
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COOPh
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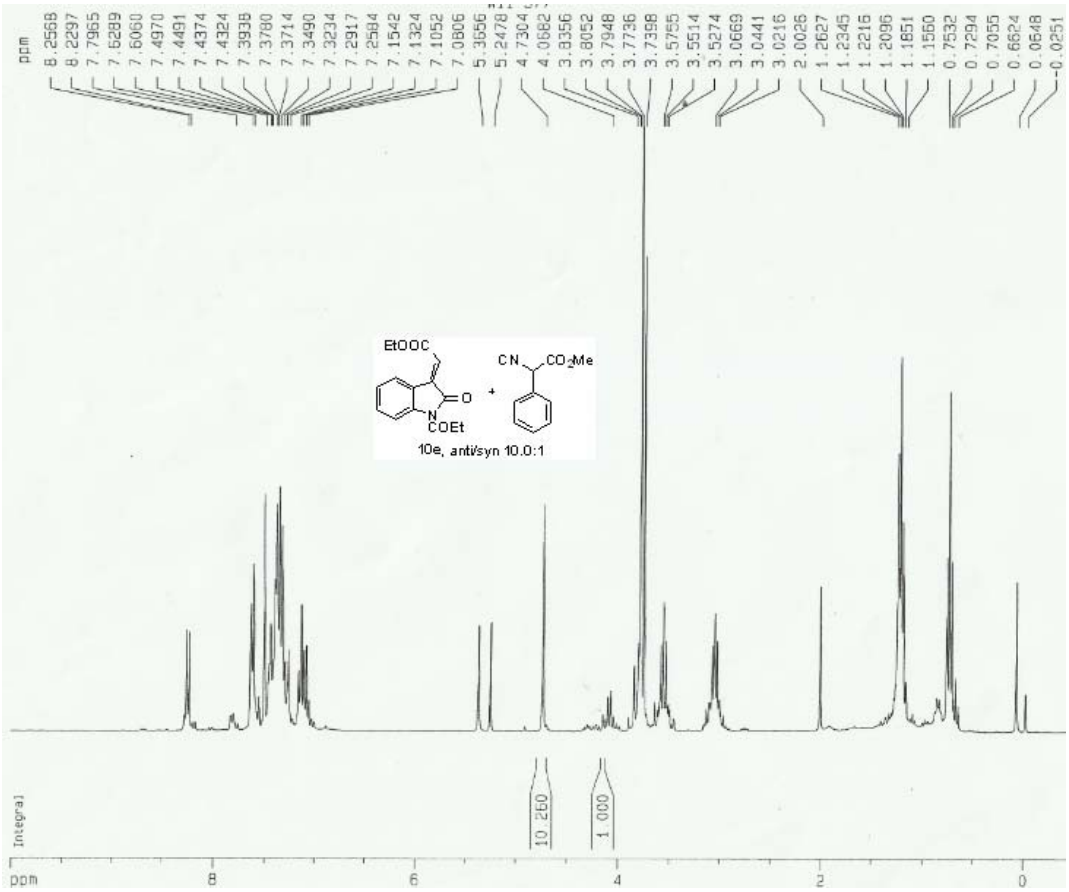
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3.7398
3.5755
3.5514
3.5274
3.0669
3.0441
3.0216
2.0026
1.2627
1.2345
1.2216
1.2096
1.1851
1.1560
0.7532
0.7294
0.7055
0.6624
0.0548
-0.0251
EtOOC
O
N
COEt
CN
CO2Me
10e, anti/syn 10.0:1
Integral
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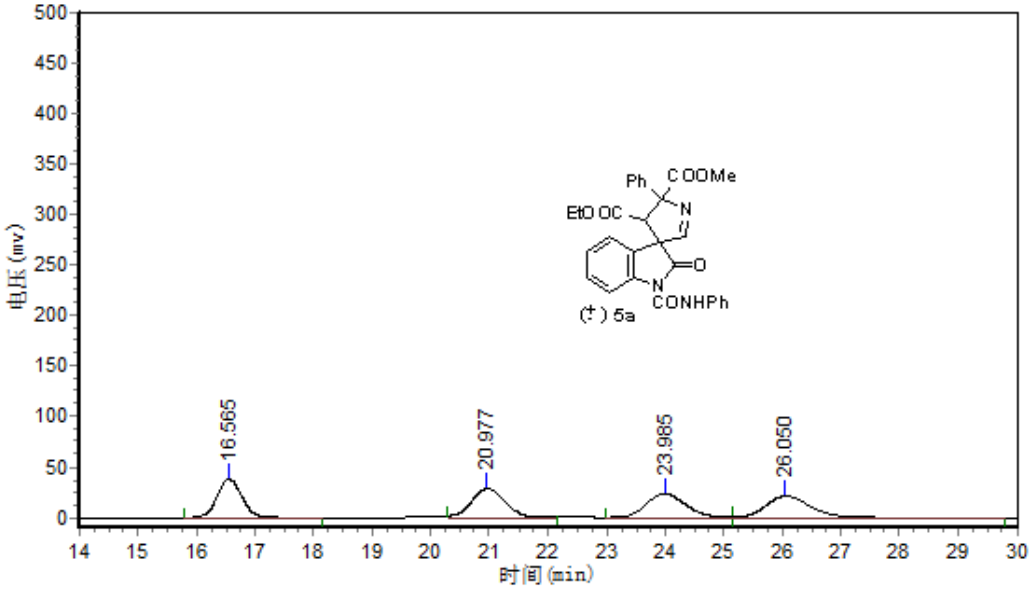
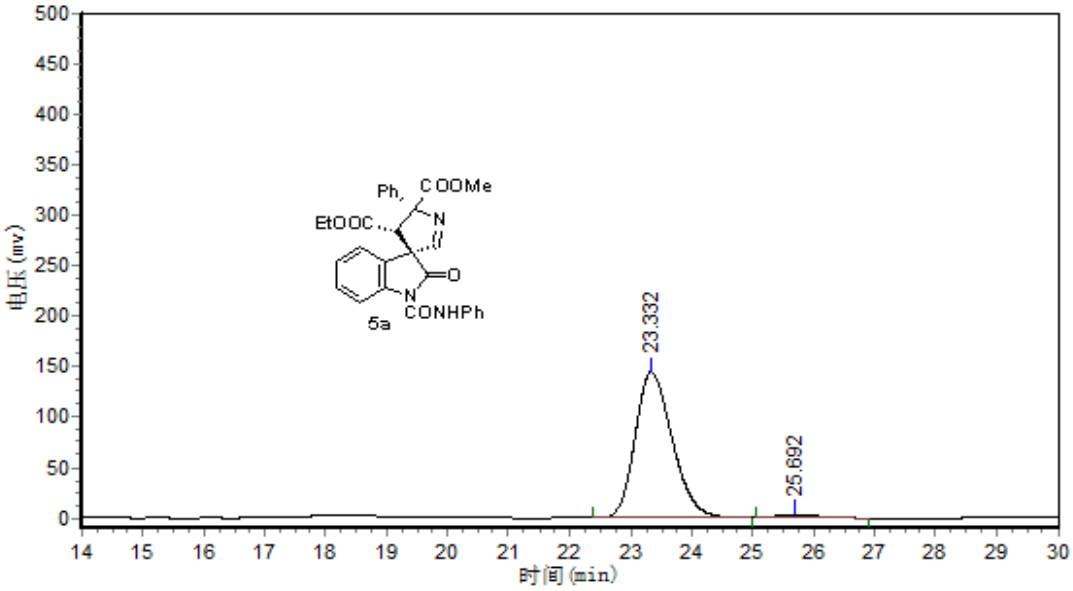
1.000
ppm
8
6
4
2
0

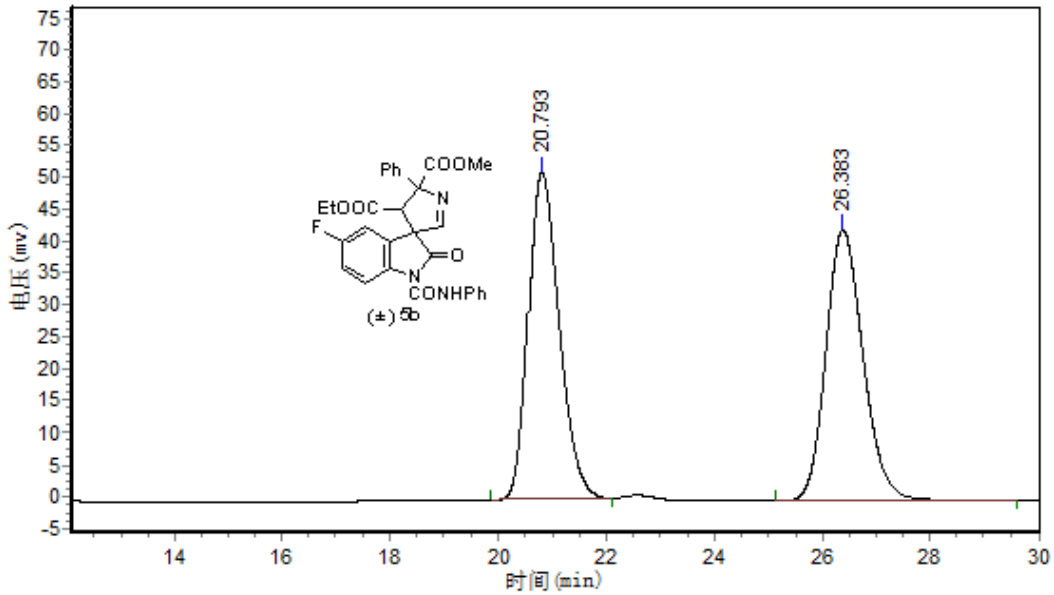
11. HPLC chromatograms



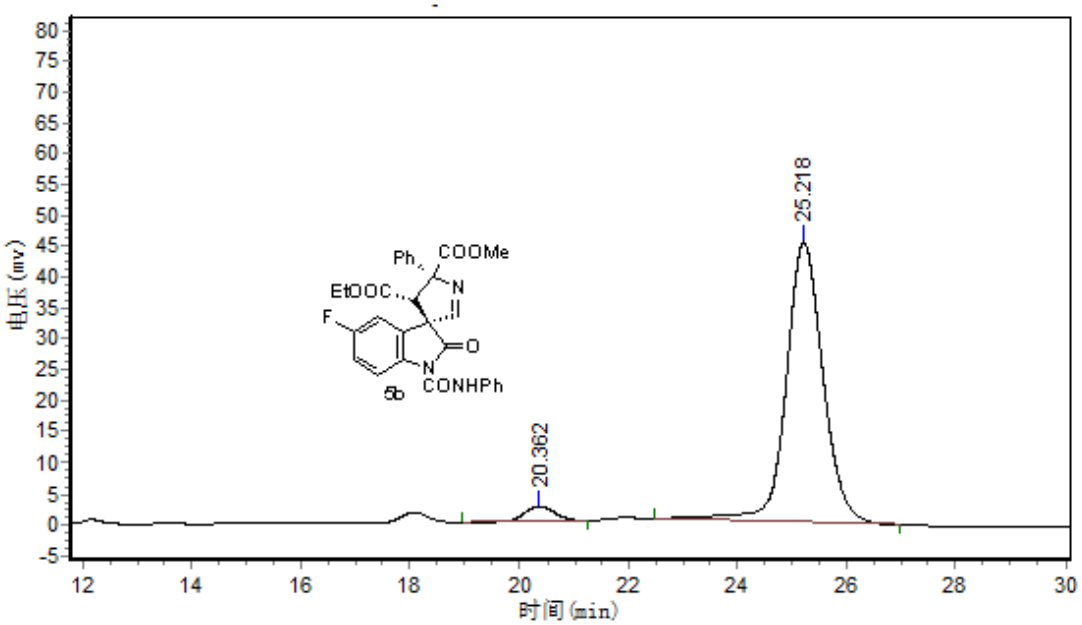
Peak	RT(min)	Height (mV*sec)	Area (mv)	Area (%)
1	16.565	37905.676	1094234.750	24.7666
2	20.977	28768.531	1117601.000	25.2955
3	23.985	23446.813	1093660.375	24.7536
4	26.050	21355.797	1112686.750	25.1843
		111476.816	4418182.875	100.0000



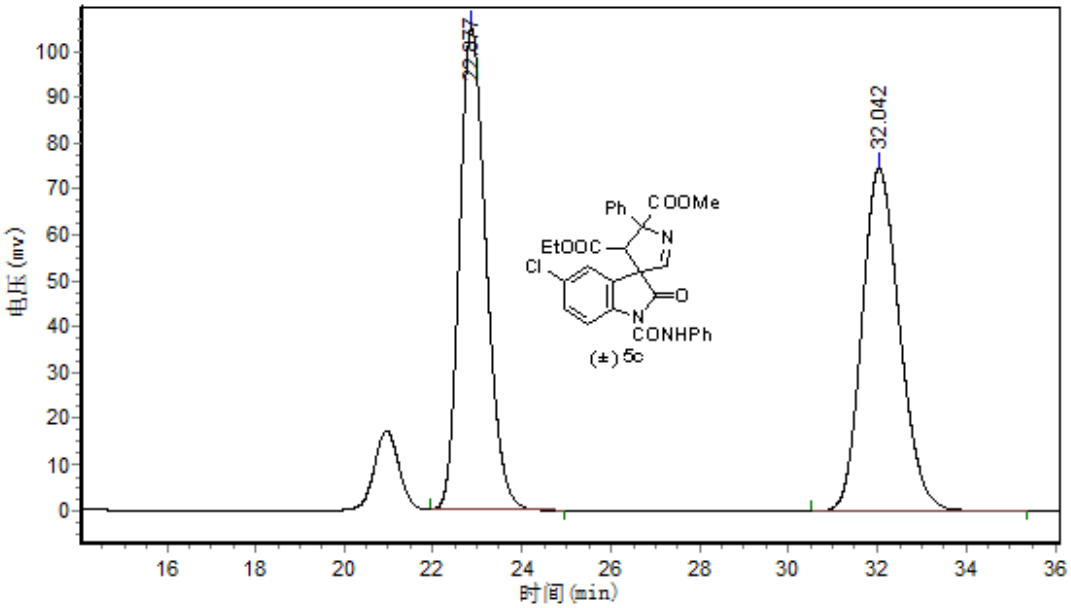
Peak	RT(min)	Height (mV*sec)	Area (mv)	Area (%)
1	23.332	143800.078	6071338.000	97.6543
2	25.692	3330.723	145834.641	2.3457
Total		147130.801	6217172.641	100.0000



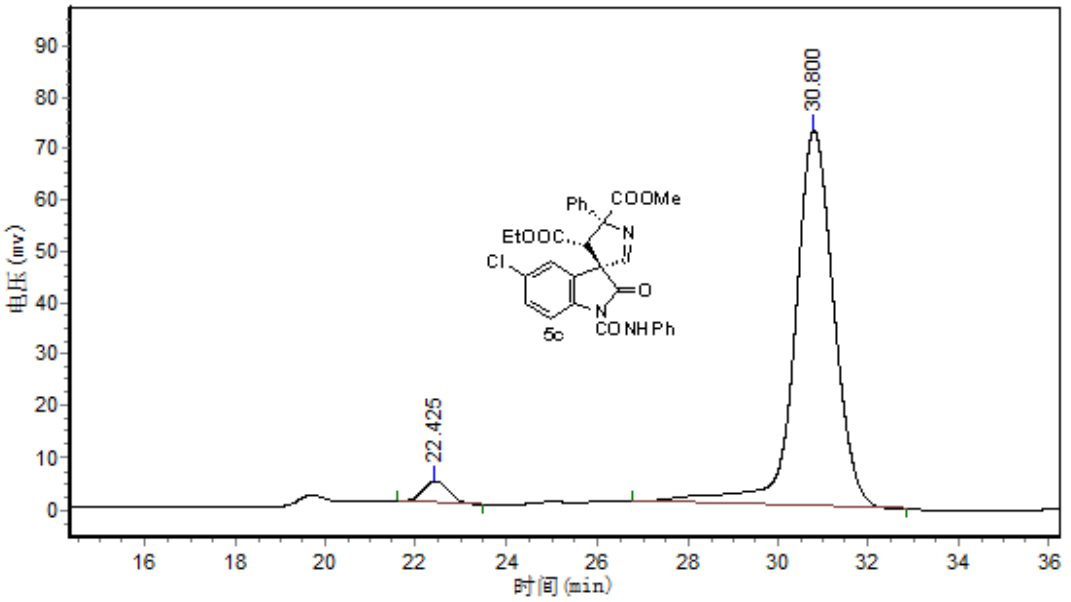
Peak	RT(min)	Height (mV*sec)	Area (mv)	Area (%)
1	20.793	51284.625	1992551.250	49.6723
2	26.383	42269.238	2018843.625	50.3277
Total		93553.863	4011394.875	100.0000



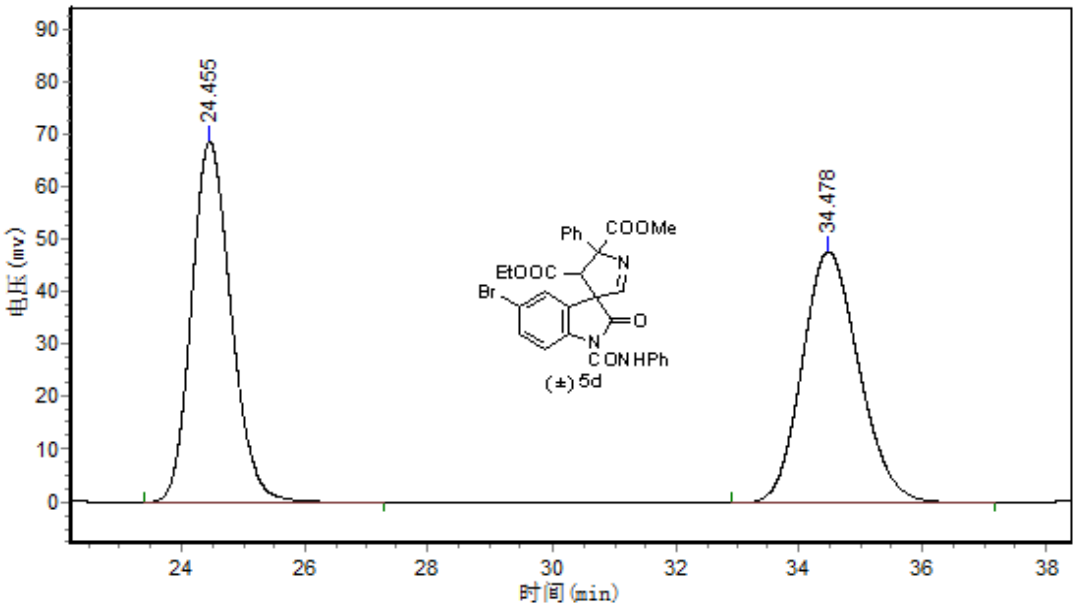
Peak	RT(min)	Height (mV*sec)	Area (mv)	Area (%)
1	20.362	2379.588	85937.188	3.8790
2	25.218	45189.094	2129531.750	96.1210
Total		47568.682	2215468.938	100.0000



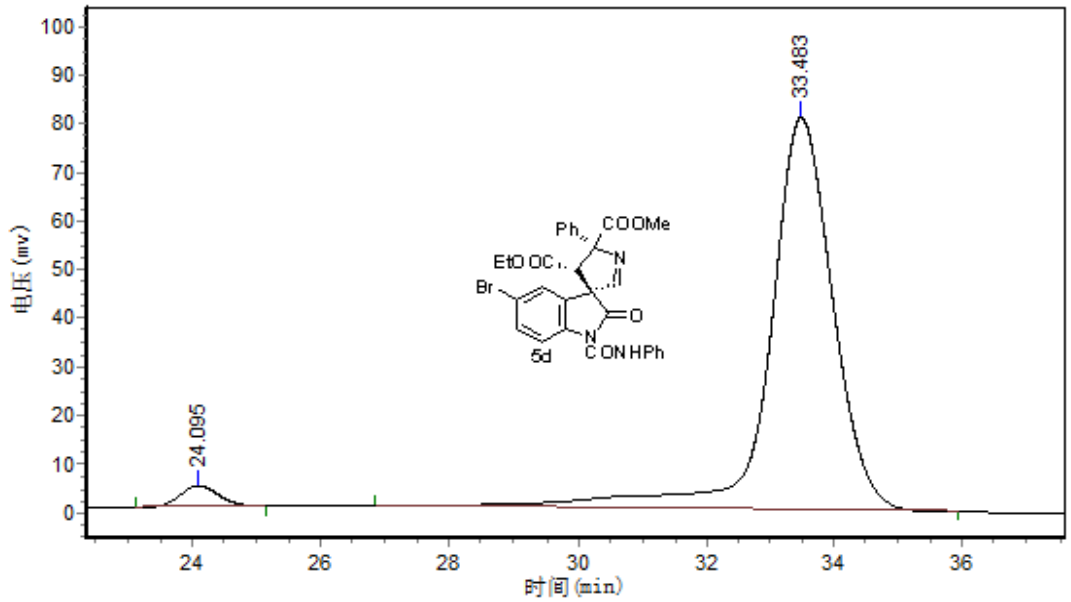
Peak	RT(min)	Height (mV*sec)	Area (mv)	Area (%)
1	22.877	105031.117	4392084.000	50.0909
2	32.042	74432.430	4376136.500	49.9091
Total		179463.547	8768220.500	100.0000



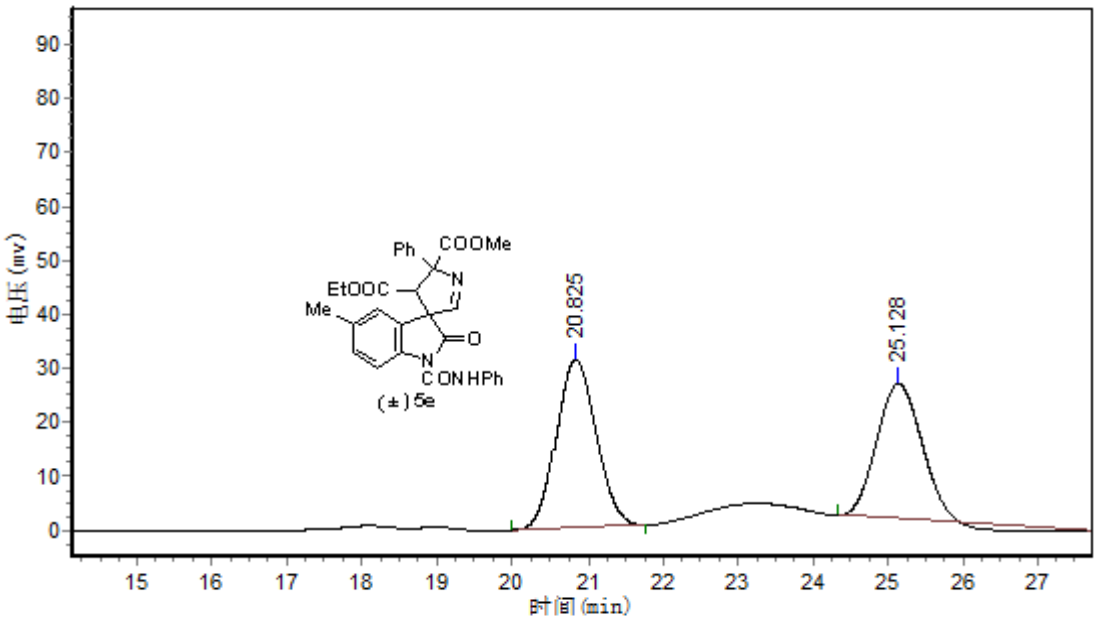
Peak	RT(min)	Height (mV*sec)	Area (mv)	Area (%)
1	22.425	4195.461	167183.609	3.6553
2	30.800	72924.266	4406505.500	96.3447
Total		77119.727	4573689.109	100.0000



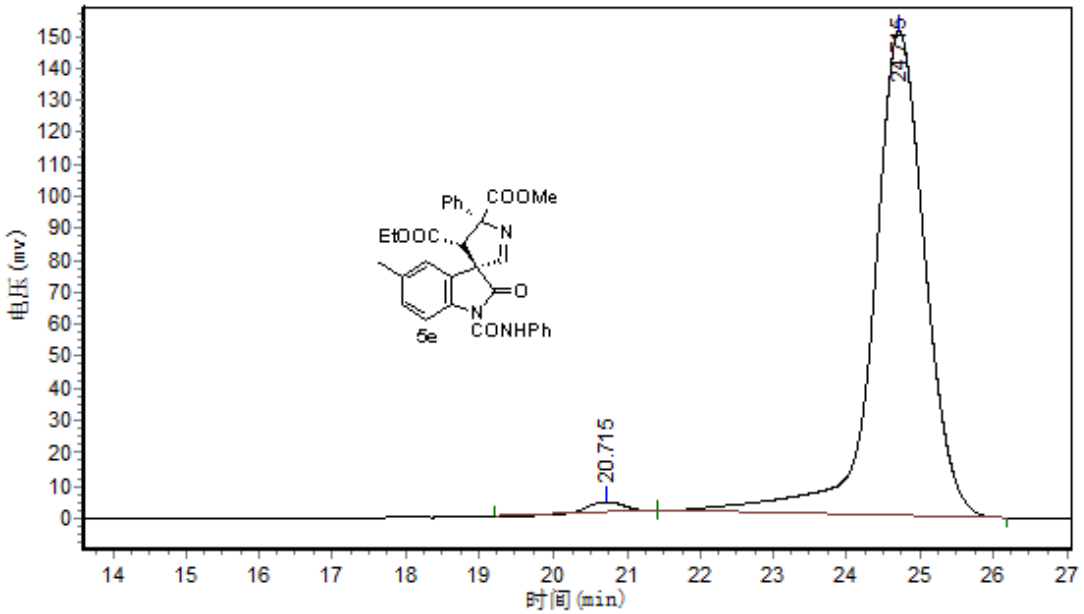
Peak	RT(min)	Height (mV*sec)	Area (mv)	Area (%)
1	24.455	68570.836	3057200.500	50.1990
2	34.478	47622.379	3032962.000	49.8010
Total		116193.215	6090162.500	100.0000



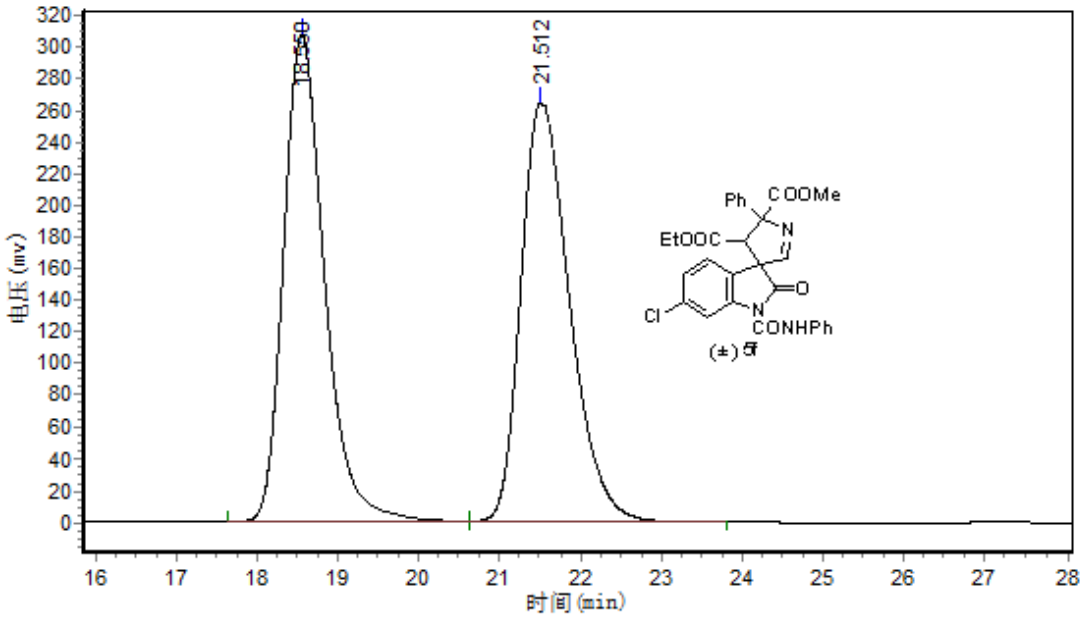
Peak	RT(min)	Height (mV*sec)	Area (mv)	Area (%)
1	24.095	4267.167	178185.297	3.0818
2	33.483	80557.641	5603751.000	96.9182
Total		84824.807	5781936.297	100.0000



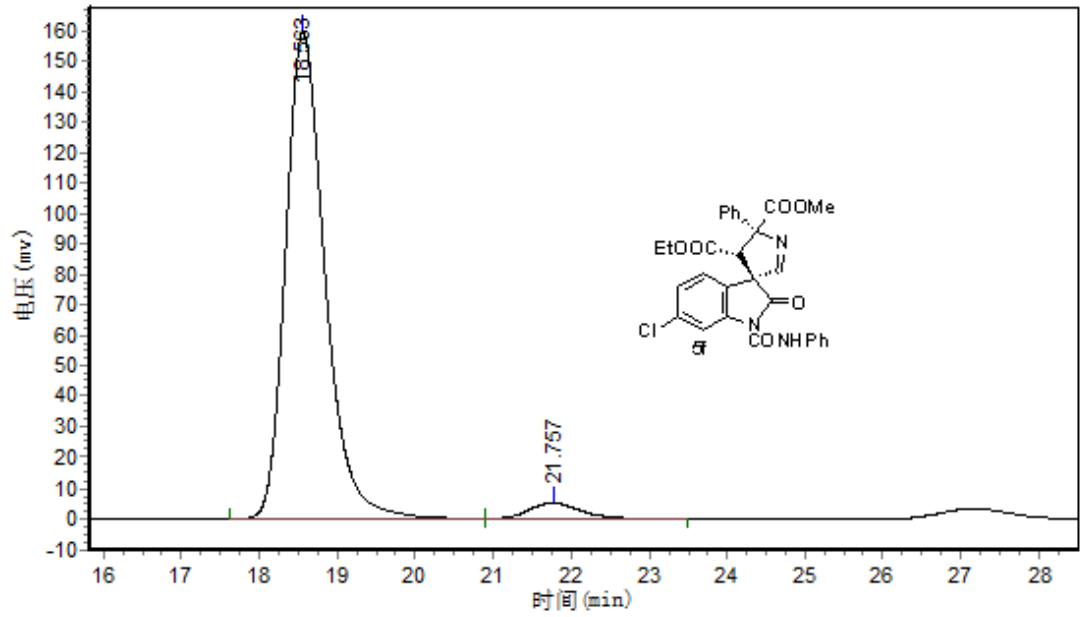
Peak	RT(min)	Height (mV*sec)	Area (mv)	Area (%)
1	20.825	31054.678	1127797.125	52.9331
2	25.128	25038.318	1002812.375	47.0669
Total		56092.996	2130609.500	100.0000



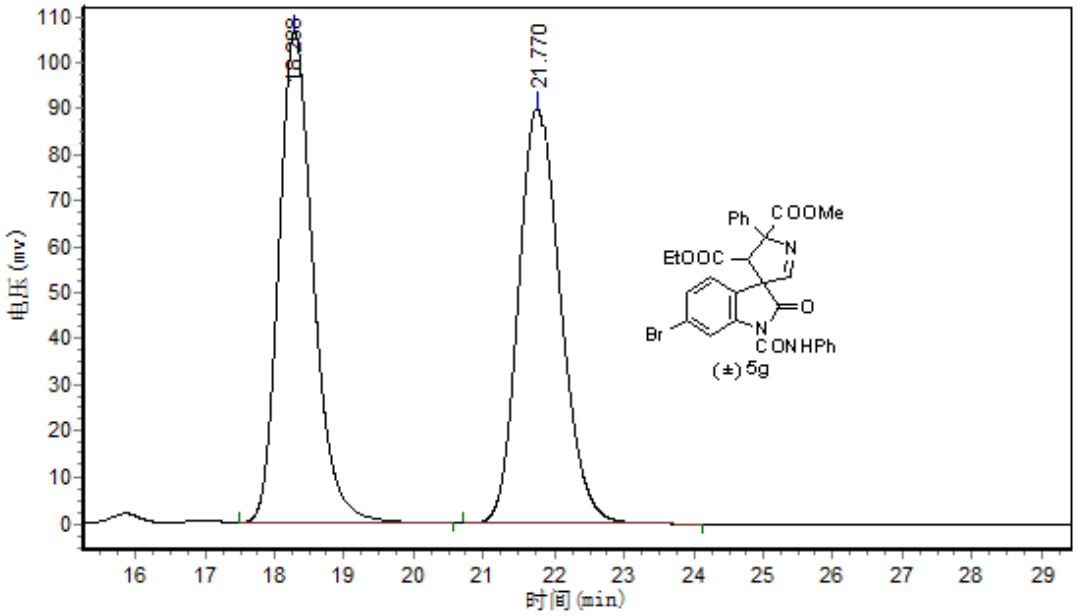
Peak	RT(min)	Height (mV*sec)	Area (mv)	Area (%)
1	20.715	3447.264	117242.883	1.5637
2	24.715	150746.875	7380481.500	98.4363
Total		154194.139	7497724.383	100.0000



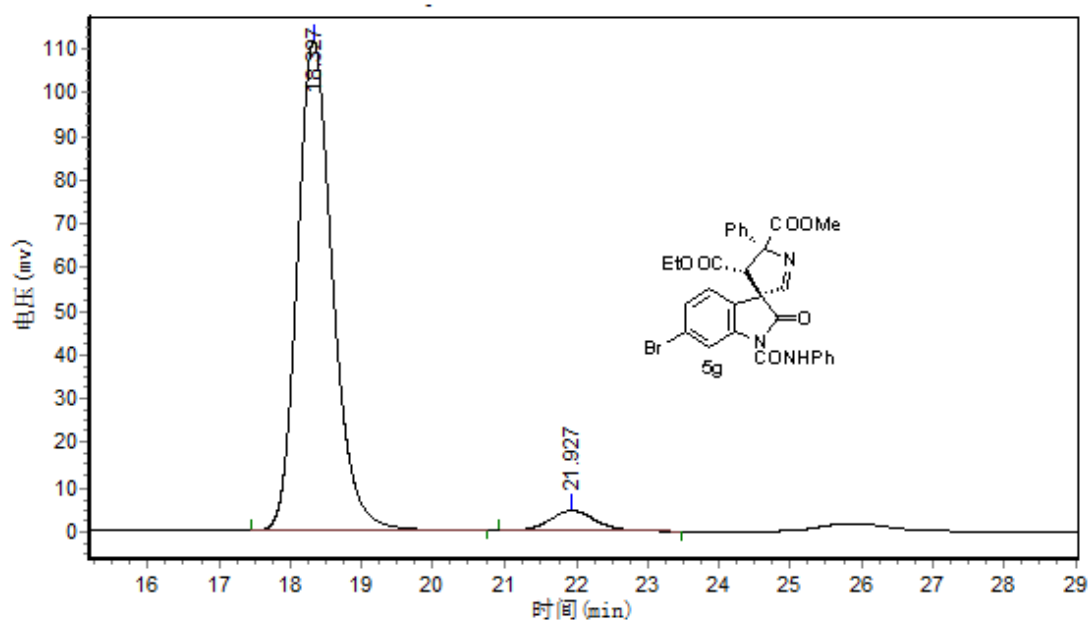
Peak	RT(min)	Height (mV*sec)	Area (mv)	Area (%)
1	18.550	306966.969	10733722.000	50.0942
2	21.512	263570.500	10693347.000	49.9058
Total		570537.469	21427069.000	100.0000



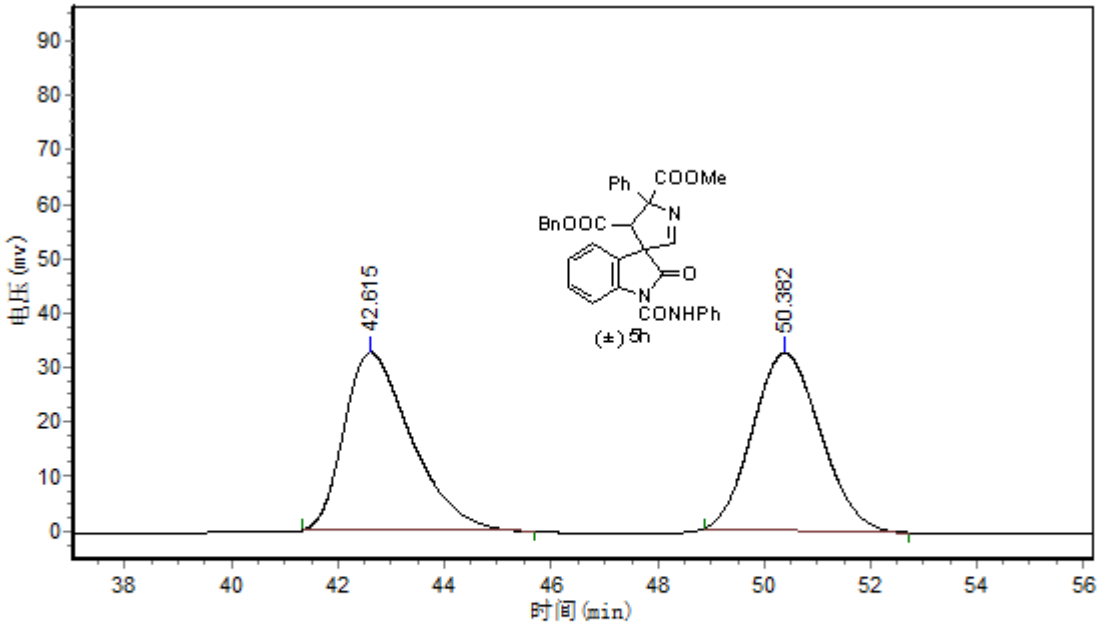
Peak	RT(min)	Height (mV*sec)	Area (mv)	Area (%)
1	18.563	159247.859	5575109.500	96.0695
2	21.757	5103.224	228094.219	3.9305
Total		164351.083	5803203.719	100.0000



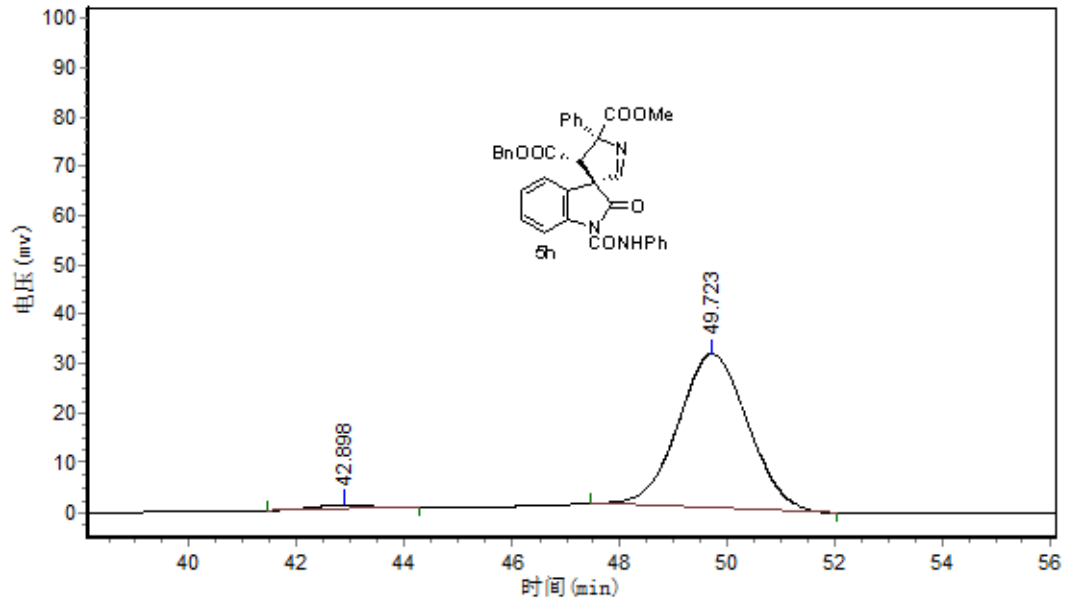
Peak	RT(min)	Height (mV*sec)	Area (mv)	Area (%)
1	18.288	106438.484	3649017.250	49.9248
2	21.770	90224.547	3660003.500	50.0752
Total		196663.031	7309020.750	100.0000



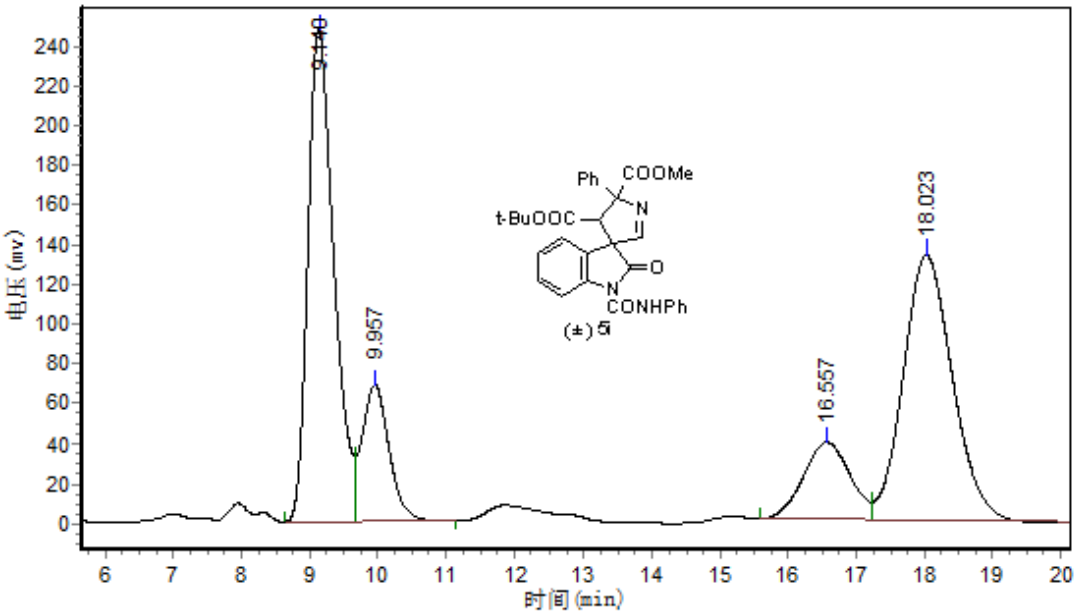
Peak	RT(min)	Height (mV*sec)	Area (mv)	Area (%)
1	18.327	111524.969	3811691.000	95.0409
2	21.927	4571.558	198887.641	4.9591
Total		116096.527	4010578.641	100.0000



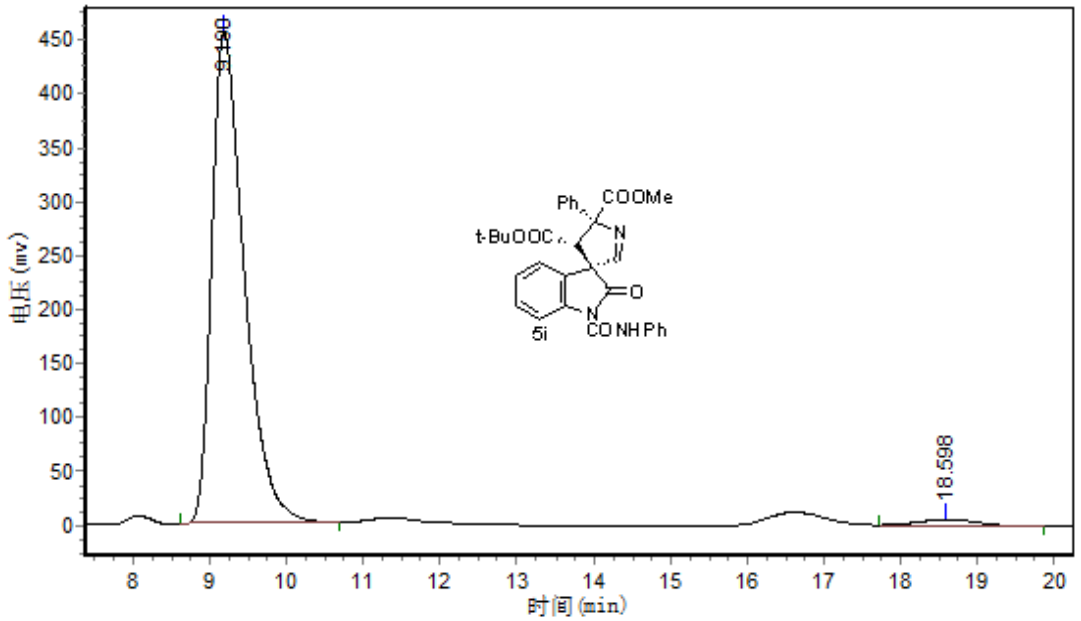
Peak	RT(min)	Height (mV*sec)	Area (mv)	Area (%)
1	42.615	32647.080	2872390.000	50.2313
2	50.382	32295.061	2845938.500	49.7687
Total		64942.141	5718328.500	100.0000



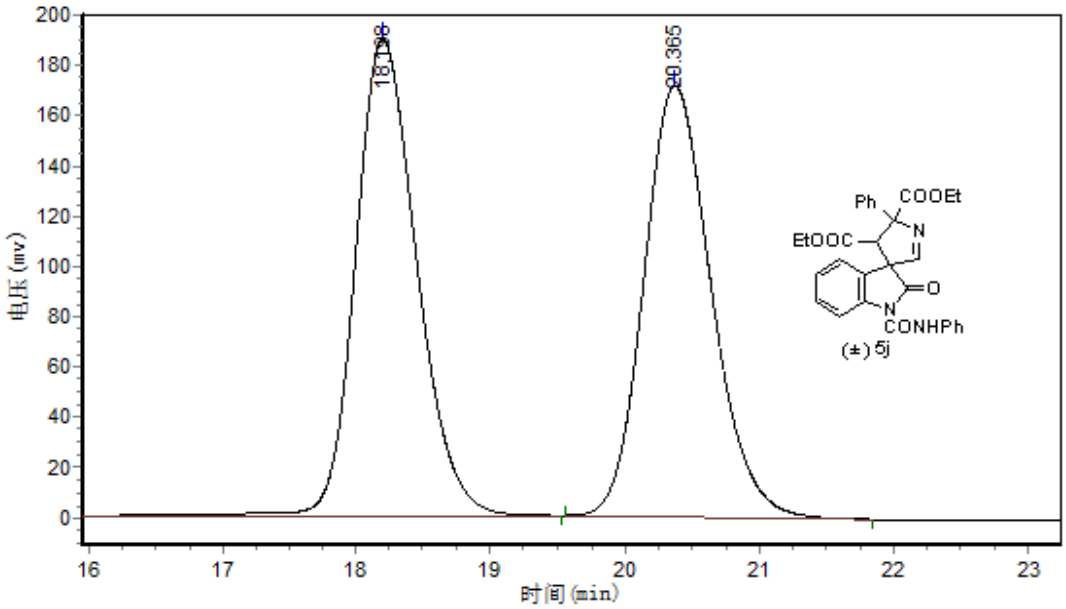
Peak	RT(min)	Height (mV*sec)	Area (mv)	Area (%)
1	42.898	851.628	71838.250	2.5099
2	49.723	31003.703	2790391.000	97.4901
Total		31855.331	2862229.250	100.0000



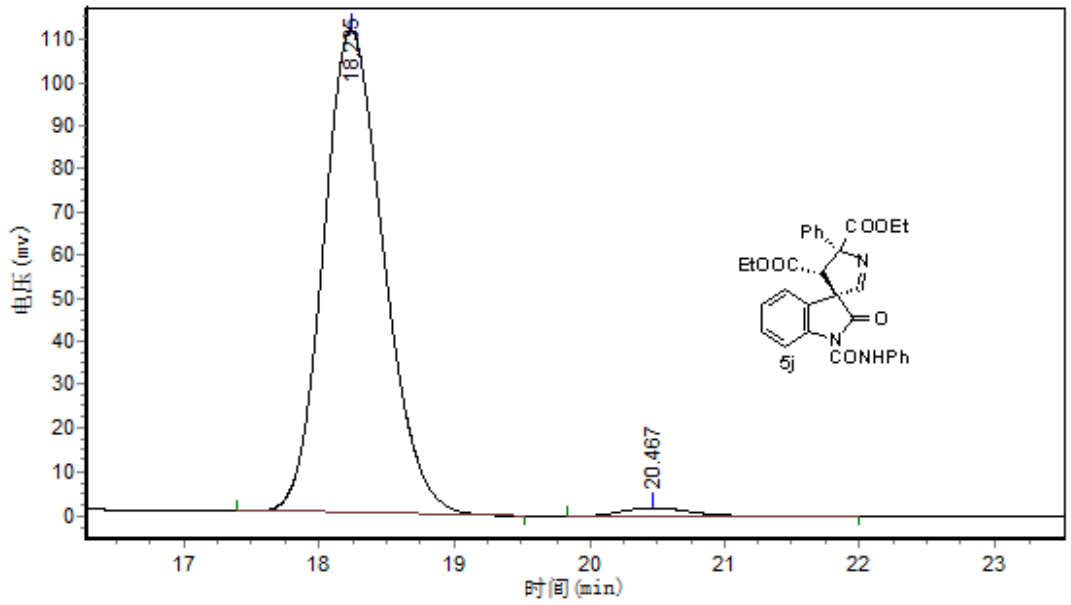
Peak	RT(min)	Height (mV*sec)	Area (mv)	Area (%)
1	9.140	247280.266	6547052.000	37.8430
2	9.957	68353.148	1858813.000	10.7442
3	16.557	40054.820	2024179.500	11.7001
4	18.023	134321.703	6870512.000	39.7127
Total		490009.938	17300556.500	100.0000



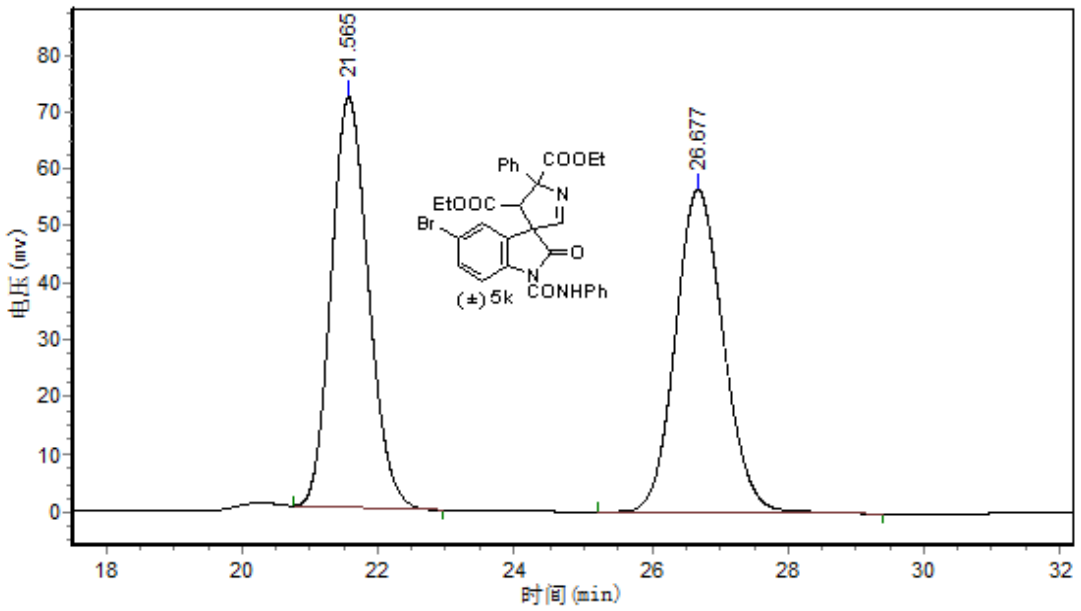
Peak	RT(min)	Height (mV*sec)	Area (mv)	Area (%)
1	9.190	454958.250	13408914.000	97.7741
2	18.598	5785.685	305264.313	2.2259
Total		460743.935	13714178.313	100.0000



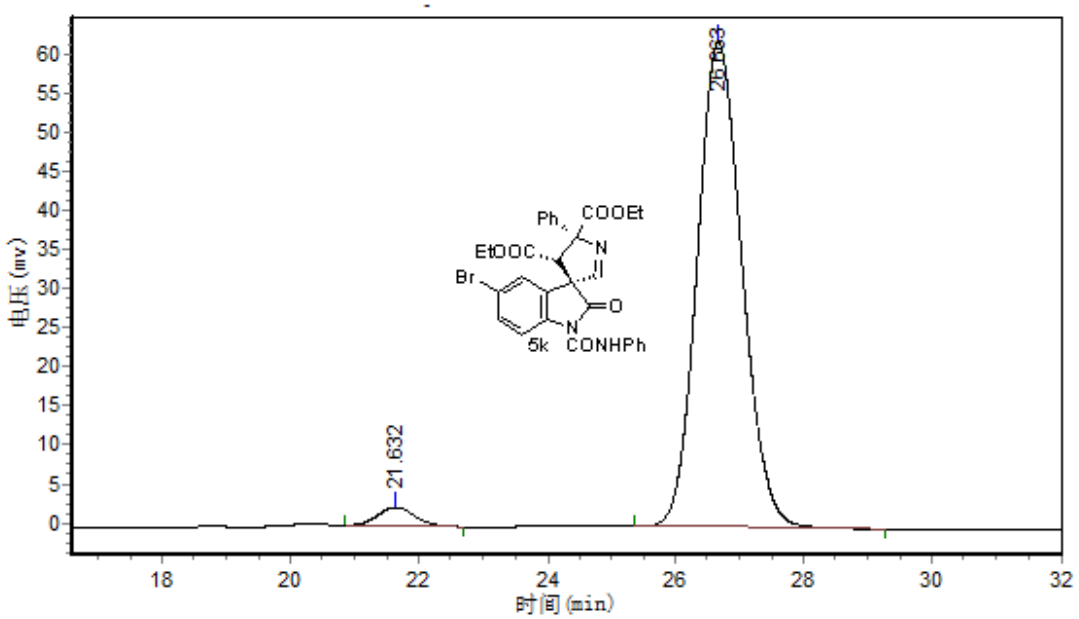
Peak	RT(min)	Height (mV*sec)	Area (mv)	Area (%)
1	18.198	189452.578	5995672.000	50.1431
2	20.365	171479.031	5961447.500	49.8569
Total		360931.609	11957119.500	100.0000



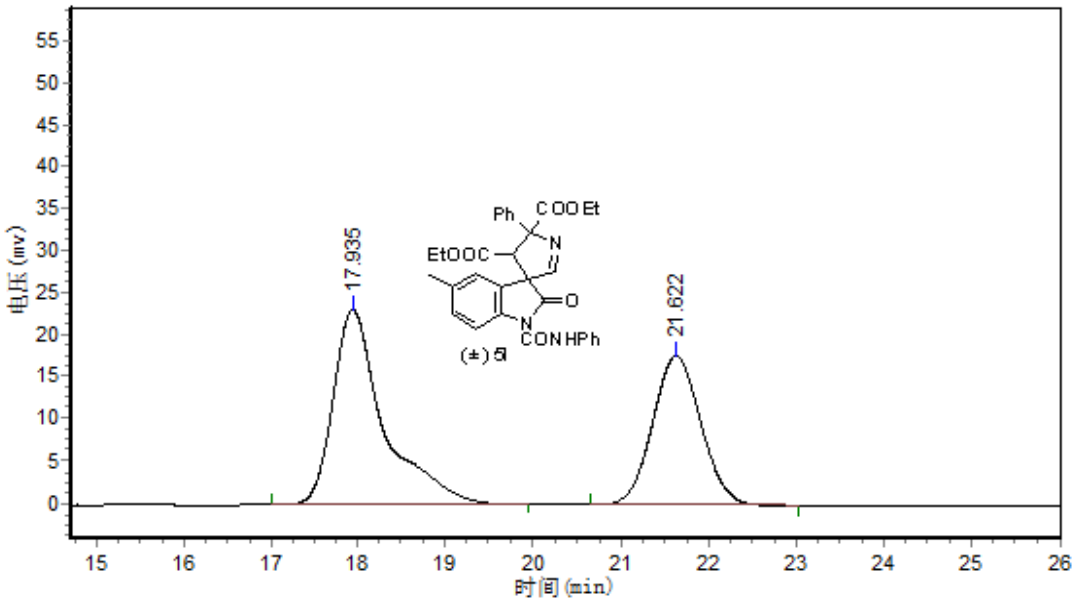
Peak	RT(min)	Height (mV*sec)	Area (mv)	Area (%)
1	18.235	111762.008	3465848.000	97.7291
2	20.467	2081.581	80533.555	2.2709
Total		113843.589	3546381.555	100.0000



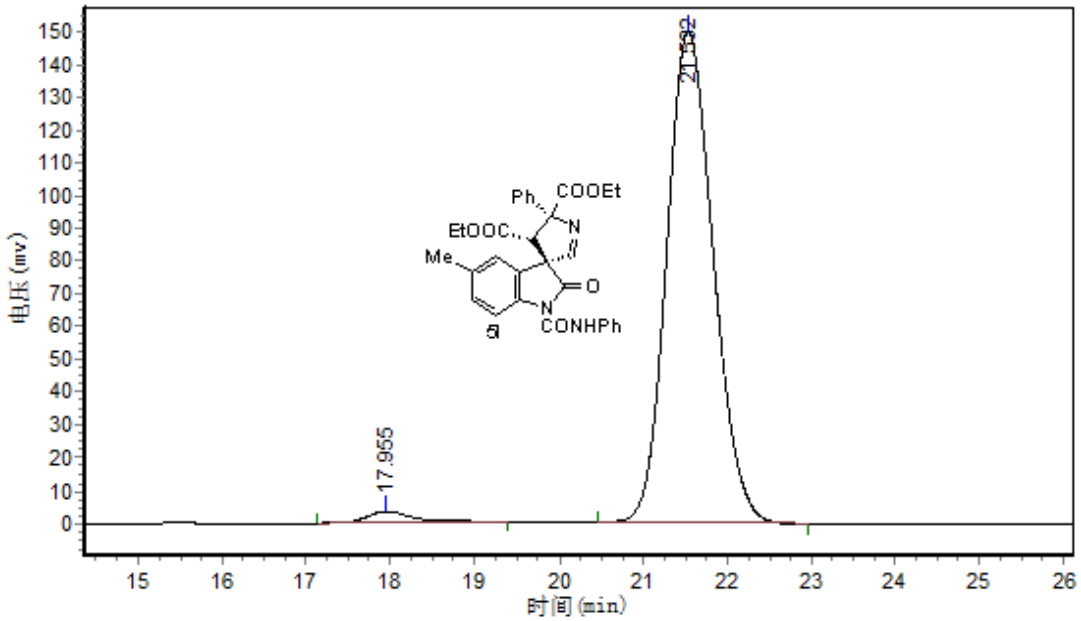
Peak	RT(min)	Height (mV*sec)	Area (mv)	Area (%)
	21.565	71754.602	2734495.000	49.7634
	26.677	56404.441	2760496.750	50.2366
Total		128159.043	5494991.750	100.0000



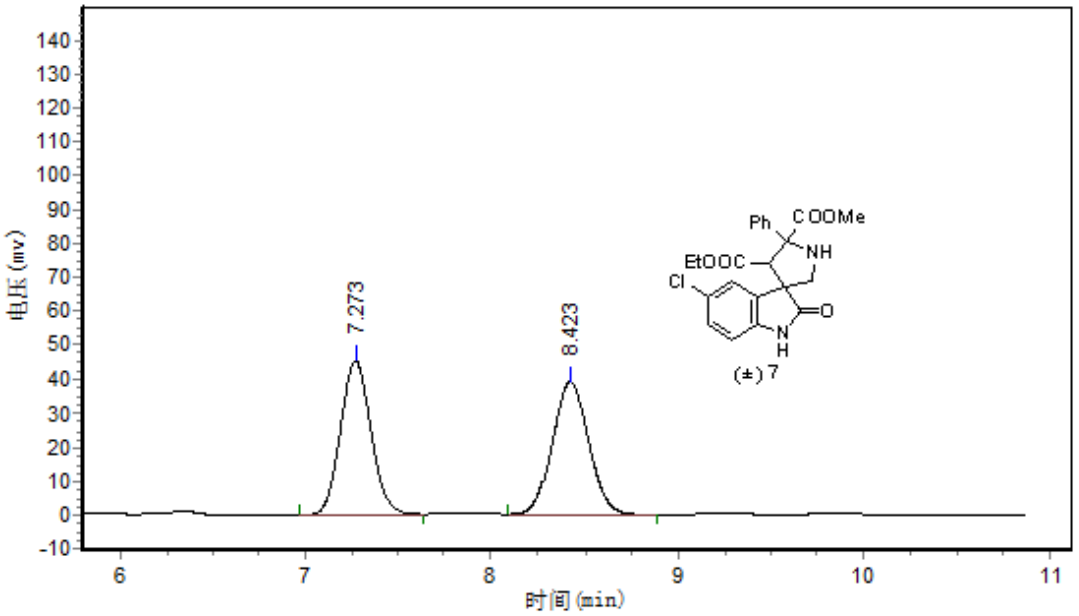
Peak	RT(min)	Height (mV*sec)	Area (mv)	Area (%)
1	21.632	2356.087	94071.602	3.0268
2	26.663	62162.621	3013922.500	96.9732
Total		64518.708	3107994.102	100.0000



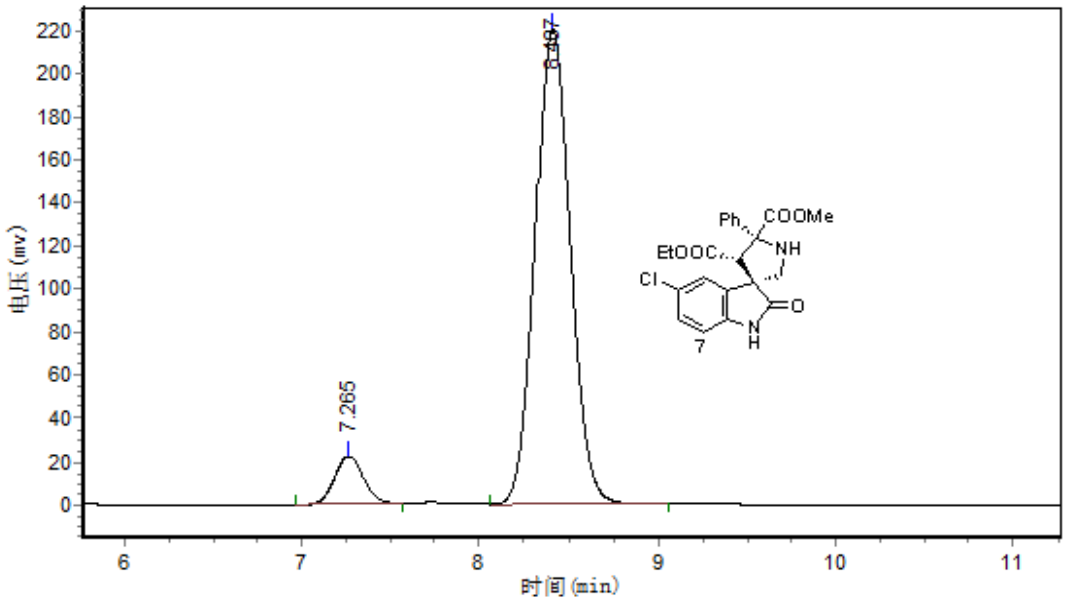
Peak	RT(min)	Height (mV*sec)	Area (mv)	Area (%)
1	17.935	23093.631	919285.875	57.5885
2	21.622	17628.676	677014.563	42.4115
Total		40722.307	1596300.438	100.0000



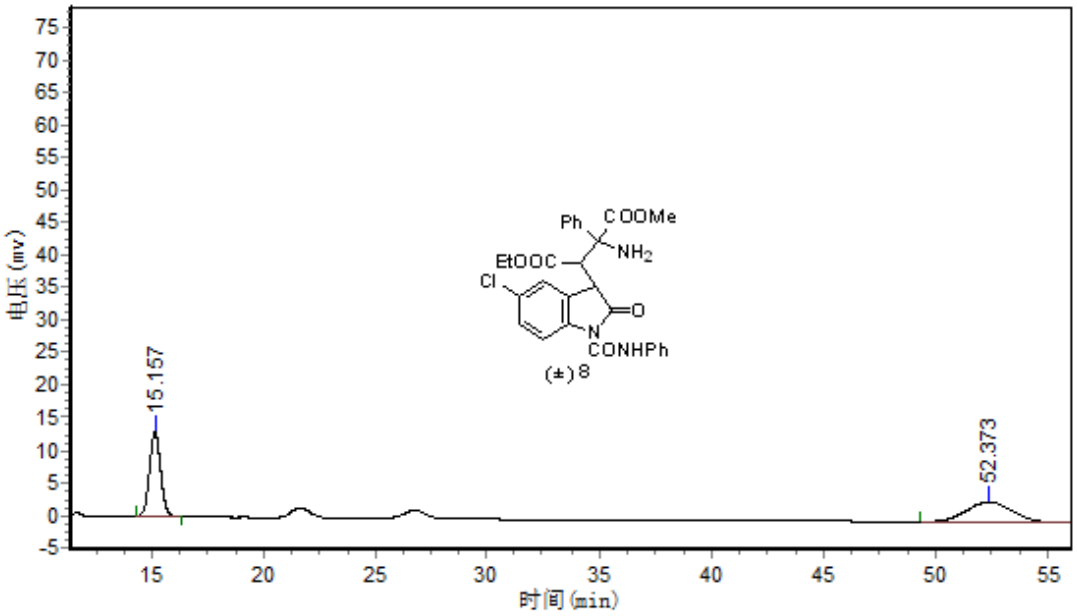
Peak	RT(min)	Height (mV*sec)	Area (mv)	Area (%)
1	17.955	3496.978	137352.500	2.3361
2	21.532	149674.828	5742213.500	97.6639
Total		153171.806	5879566.000	100.0000



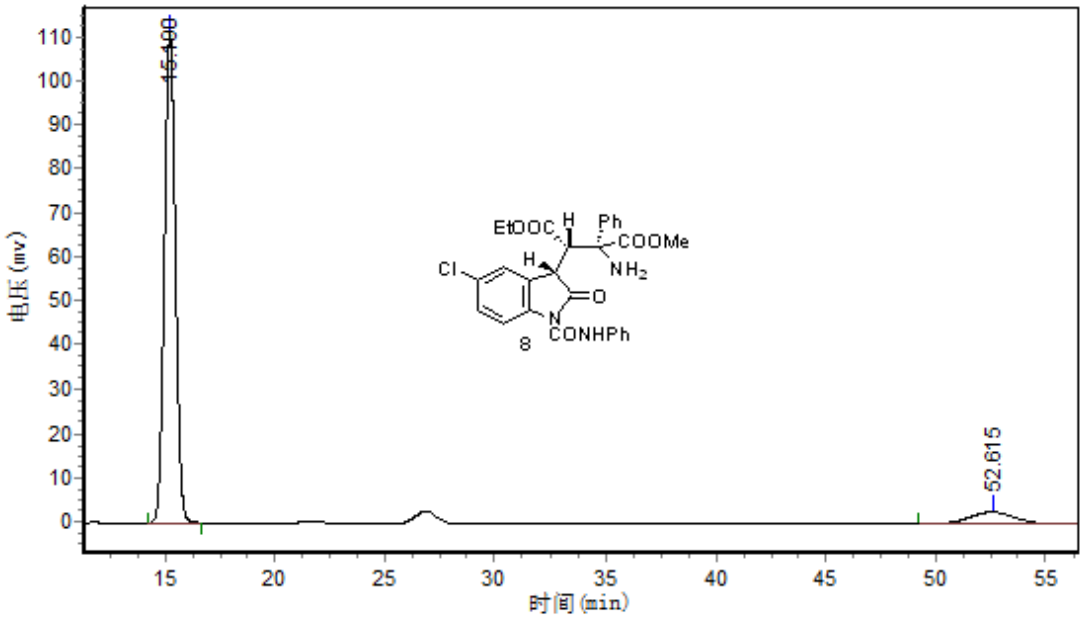
Peak	RT(min)	Height (mV*sec)	Area (mv)	Area (%)
1	7.273	45180.051	513398.906	49.6814
2	8.423	38732.949	519983.656	50.3186
Total		83913.000	1033382.563	100.0000



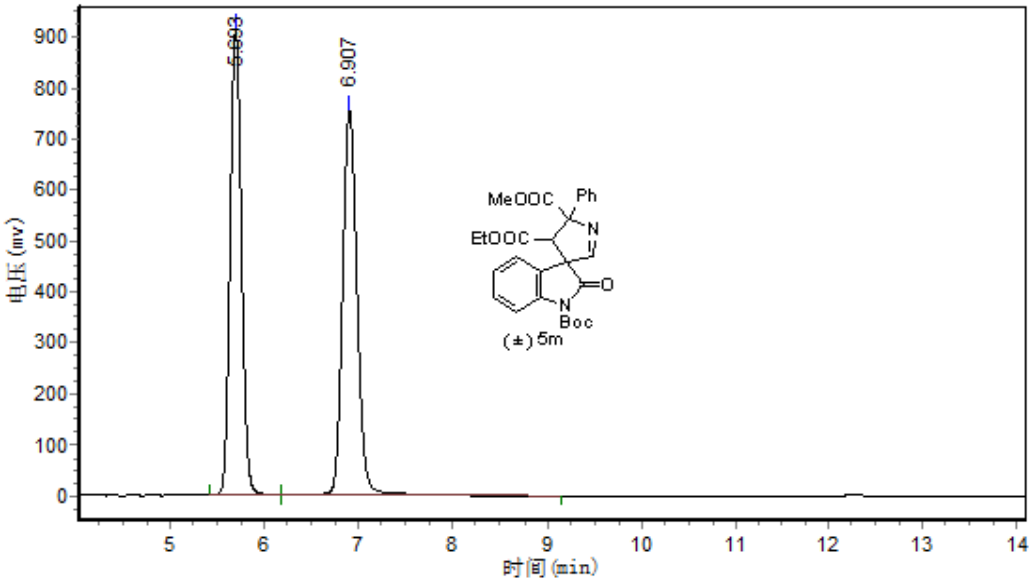
Peak	RT(min)	Height (mV*sec)	Area (mv)	Area (%)
1	7.265	22155.500	245143.703	7.6331
2	8.407	220185.797	2966459.500	92.3669
Total		242341.297	3211603.203	100.0000



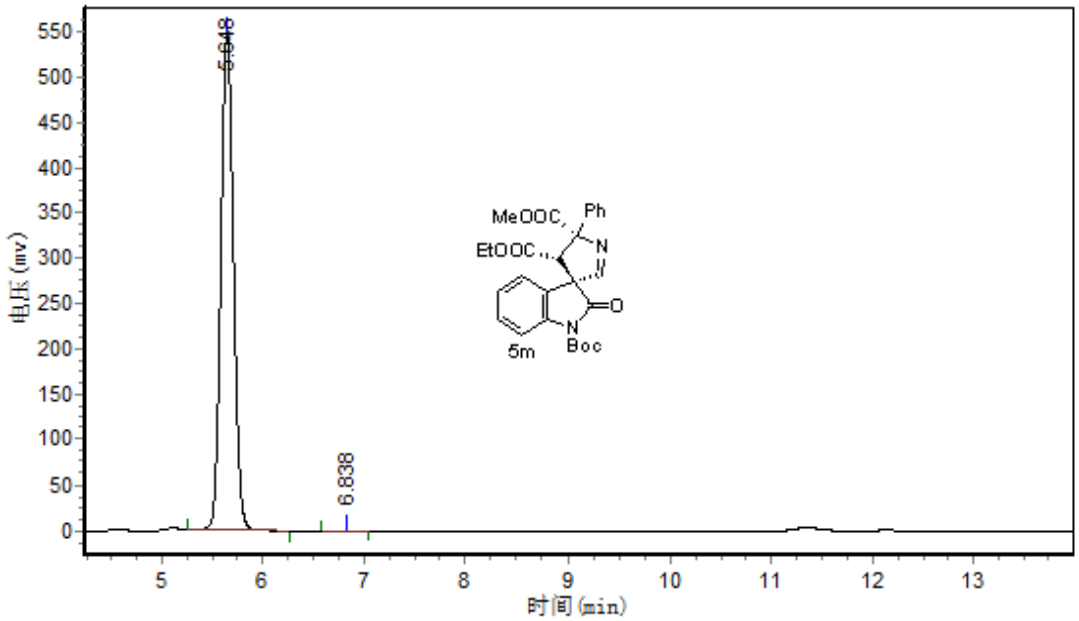
Peak	RT(min)	Height (mV*sec)	Area (mv)	Area (%)
1	15.157	13030.481	446826.594	50.4341
2	52.373	3078.477	439135.000	49.5659
Total		16108.958	885961.594	100.0000



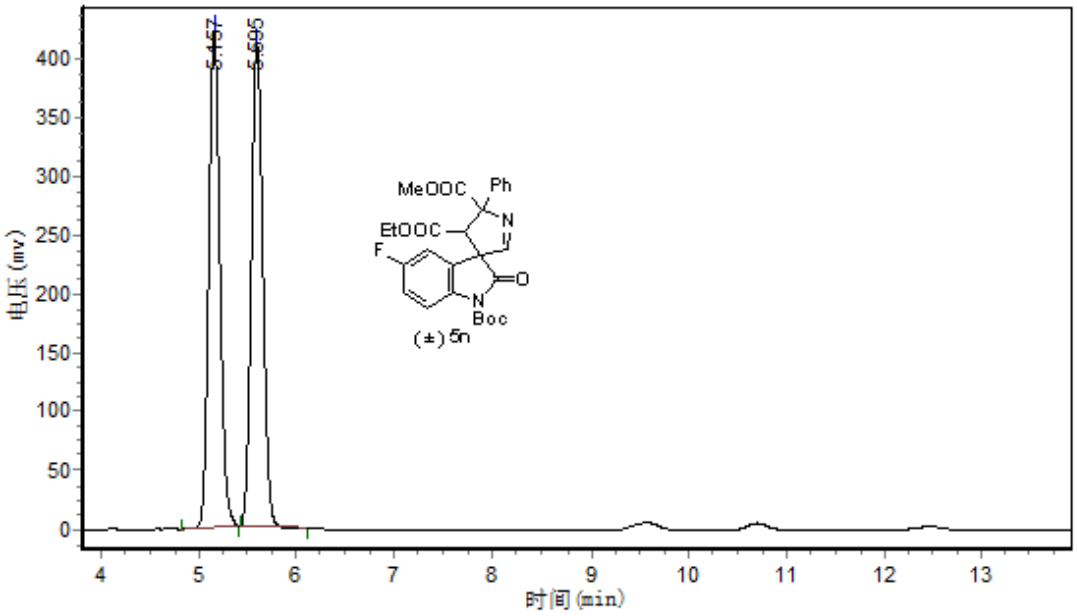
Peak	RT(min)	Height (mV*sec)	Area (mv)	Area (%)
1	15.190	111202.586	3860450.000	90.7233
2	52.615	2685.767	394741.906	9.2767
Total		113888.353	4255191.906	100.0000



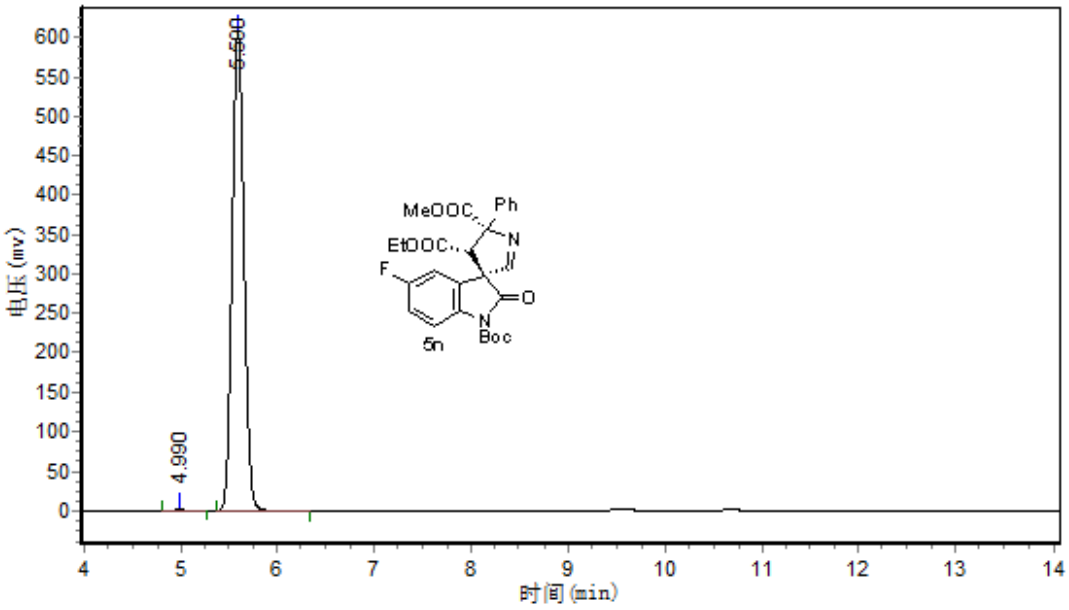
Peak	RT (min)	Height (mV*sec)	Area (mv)	Area (%)
1	5.693	910882.375	7666944.000	48.6063
2	6.907	749523.938	8106628.500	51.3937
Total		1660406.313	15773572.500	100.0000



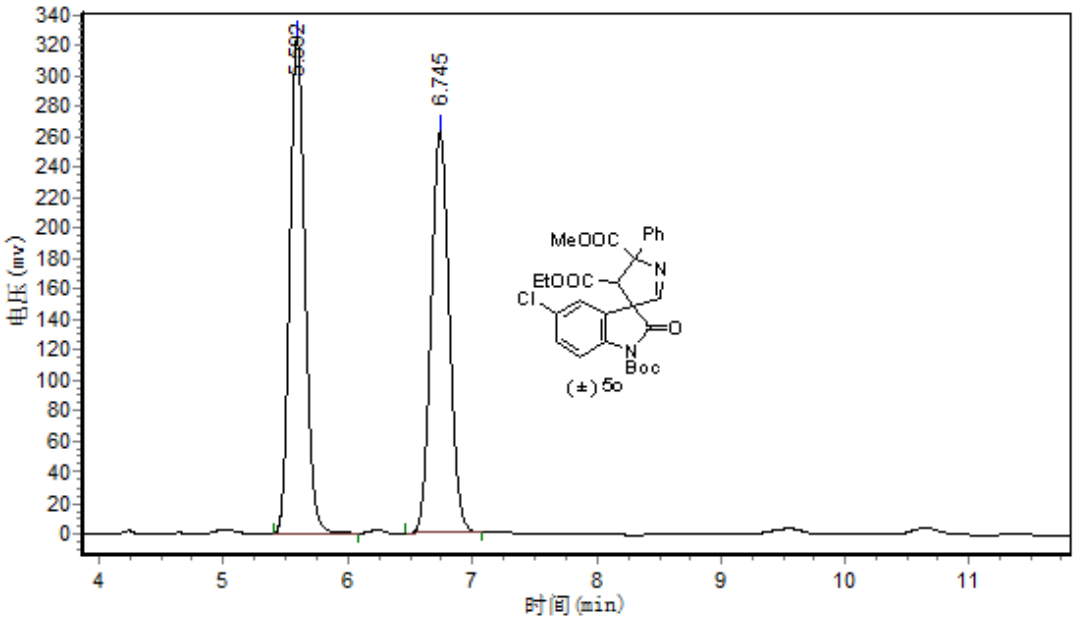
Peak	RT (min)	Height (mV*sec)	Area (mv)	Area (%)
1	5.648	547862.188	4721960.000	99.9412
2	6.838	258.790	2776.000	0.0588
Total		548120.977	4724736.000	100.0000



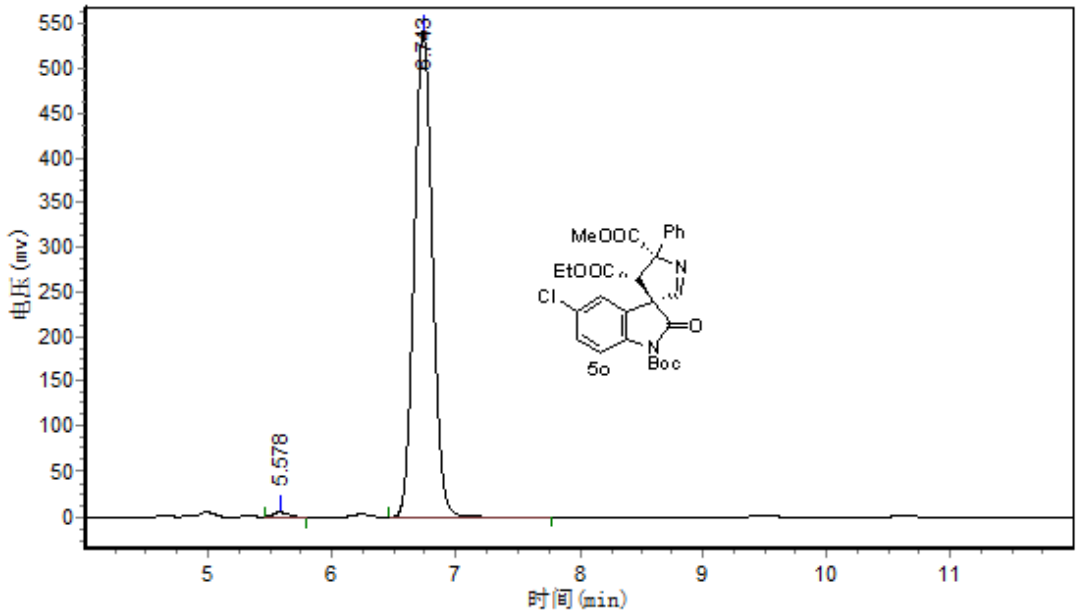
Peak	RT (min)	Height (mV*sec)	Area (mv)	Area (%)
1	5.157	421270.781	3310919.750	49.7380
2	5.595	409125.906	3345804.750	50.2620
Total		830396.688	6656724.500	100.0000



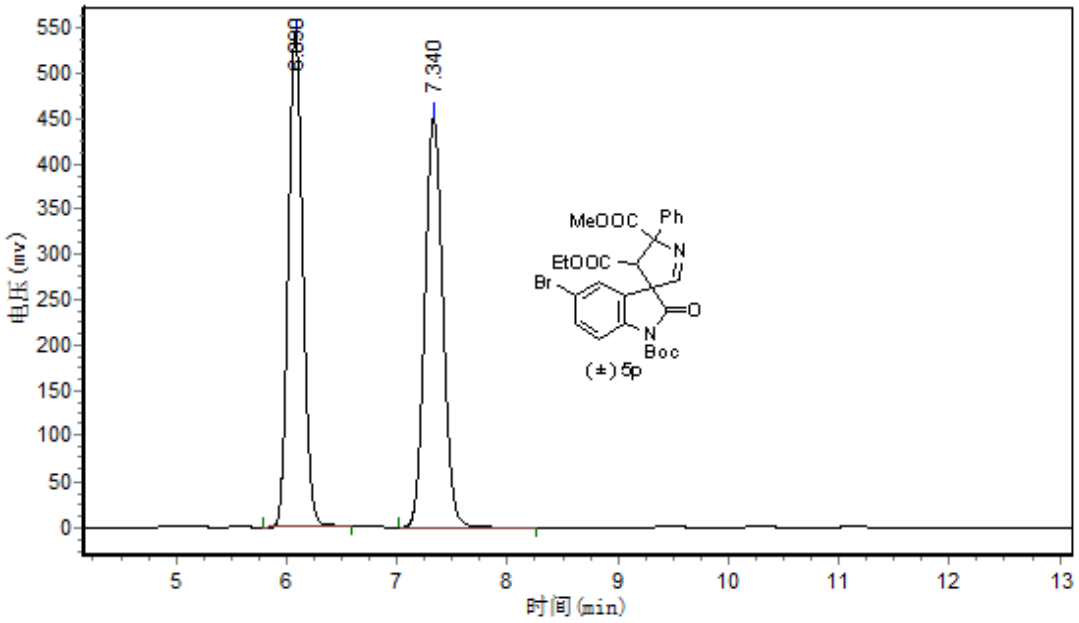
Peak	RT (min)	Height (mV*sec)	Area (mv)	Area (%)
1	4.990	2892.436	24491.500	0.4731
2	5.590	606606.188	5152842.000	99.5269
Total		609498.624	5177333.500	100.0000



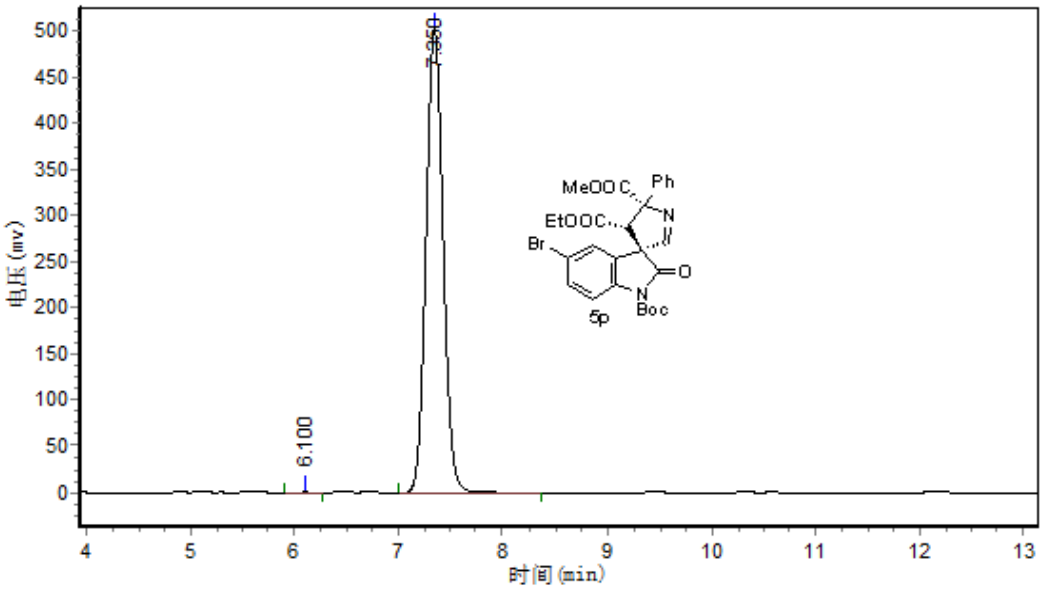
Peak	RT (min)	Height (mV*sec)	Area (mv)	Area (%)
1	5.592	324834.375	2759153.000	50.8642
2	6.745	262410.188	2665397.750	49.1358
Total		587244.563	5424550.750	100.0000



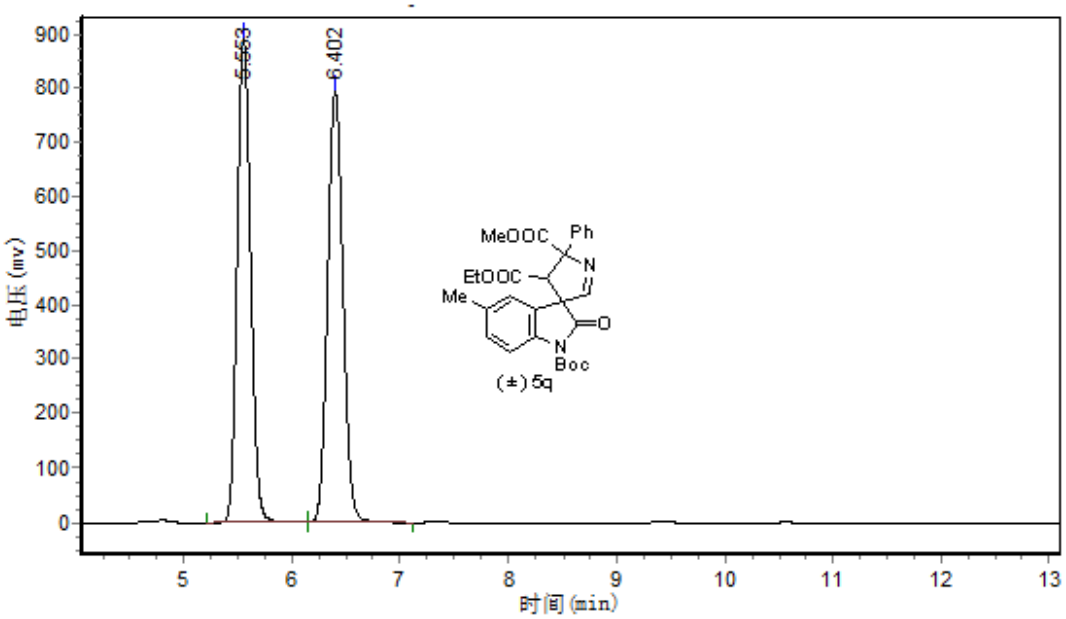
Peak	RT (min)	Height (mV*sec)	Area (mv)	Area (%)
1	5.578	5176.458	42082.102	0.7496
2	6.743	541956.938	5571485.500	99.2504
Total		547133.395	5613567.602	100.0000



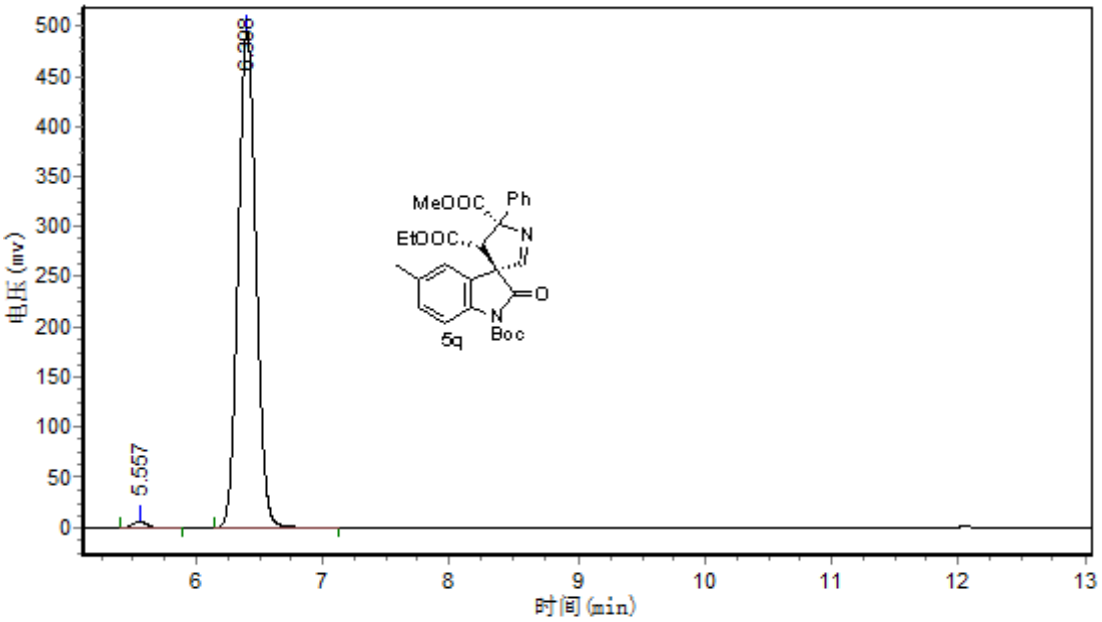
Peak	RT (min)	Height (mV*sec)	Area (mv)	Area (%)
1	6.090	543311.813	4994482.500	49.3457
2	7.340	450272.844	5126933.500	50.6543
Total		993584.656	10121416.000	100.0000



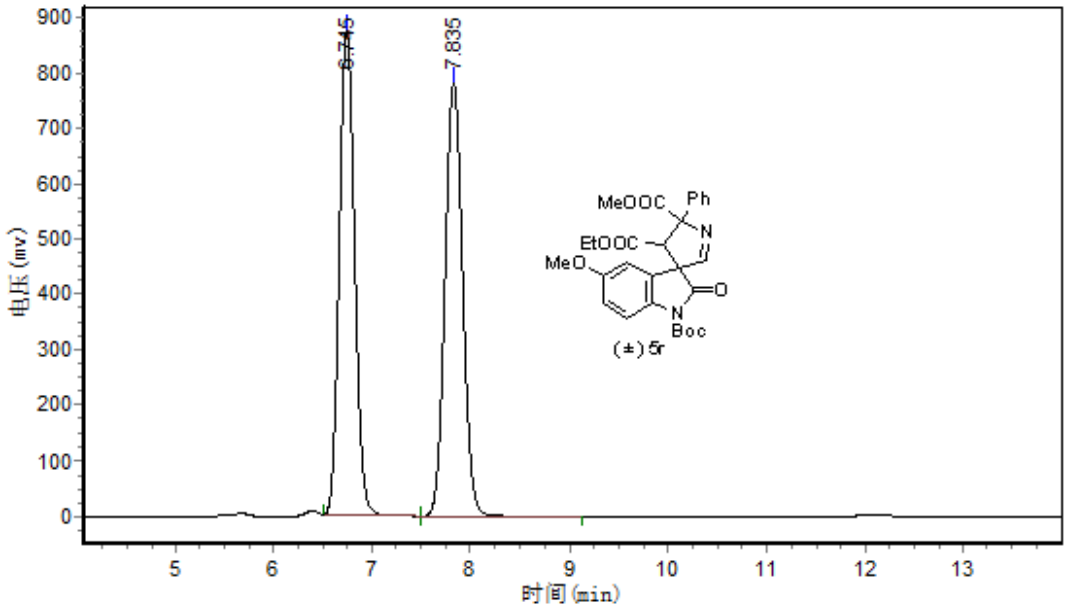
Peak	RT (min)	Height (mV*sec)	Area (mv)	Area (%)
1	6.100	537.430	4966.550	0.0868
2	7.350	502474.688	5718979.500	99.9132
Total		503012.117	5723946.050	100.0000



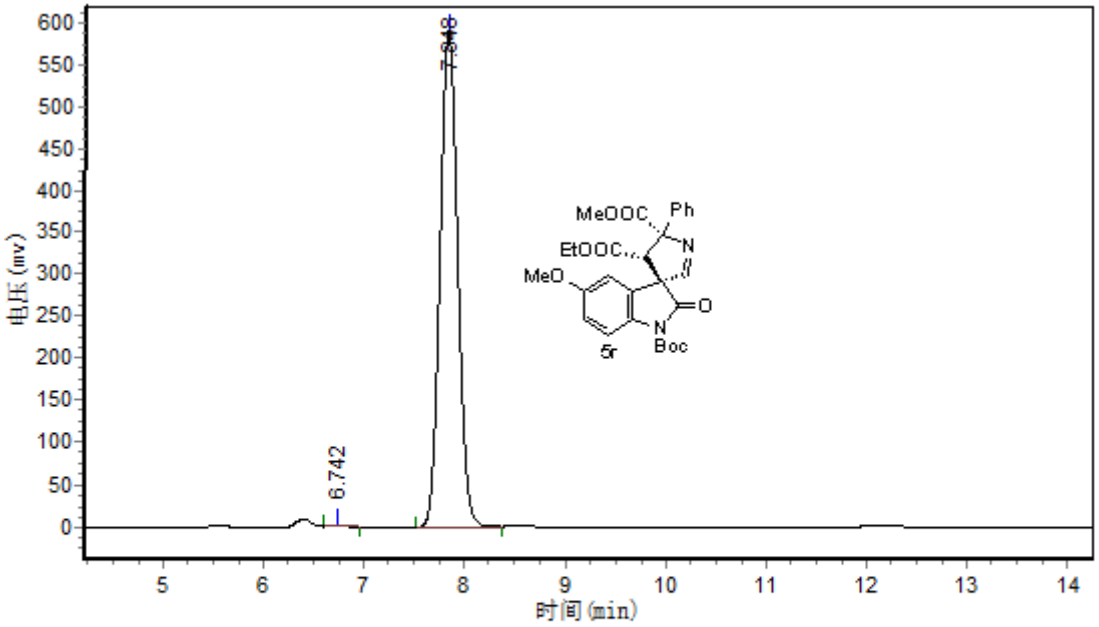
Peak	RT (min)	Height (mV*sec)	Area (mv)	Area (%)
1	5.553	889423.563	7725985.000	49.5476
2	6.402	793380.188	7867078.000	50.4524
Total		1682803.750	15593063.000	100.0000



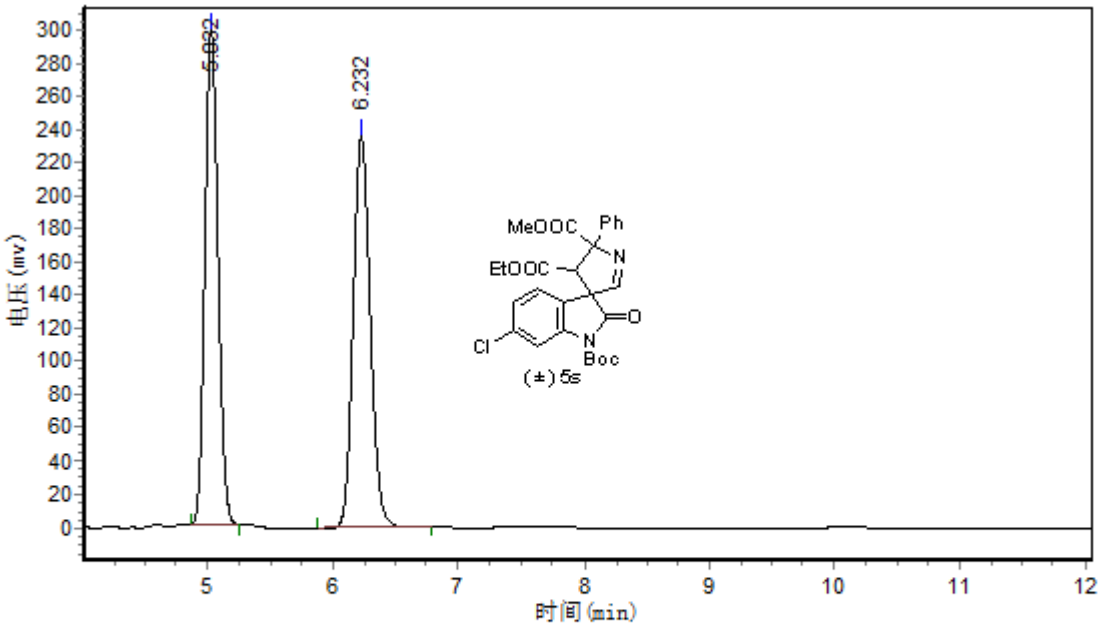
Peak	RT (min)	Height (mV*sec)	Area (mv)	Area (%)
1	5.557	6371.119	53076.449	1.0780
2	6.398	494300.156	4870454.000	98.9220
Total		500671.275	4923530.449	100.0000



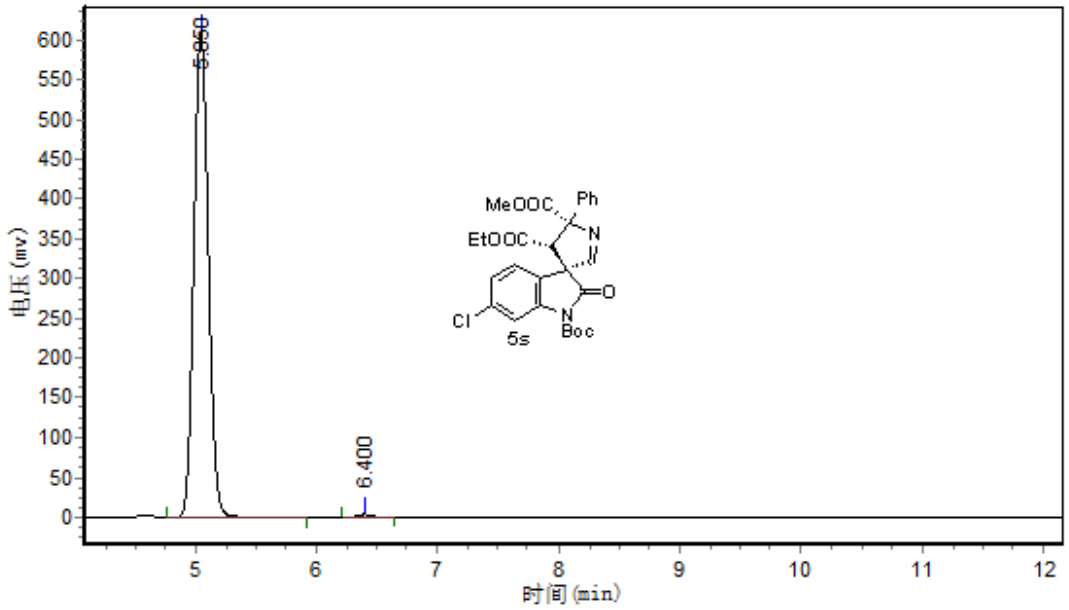
Peak	RT (min)	Height (mV*sec)	Area (mv)	Area (%)
1	6.745	873762.063	9441674.000	49.3410
2	7.835	781146.250	9693898.000	50.6590
		1654908.313	19135572.000	100.0000



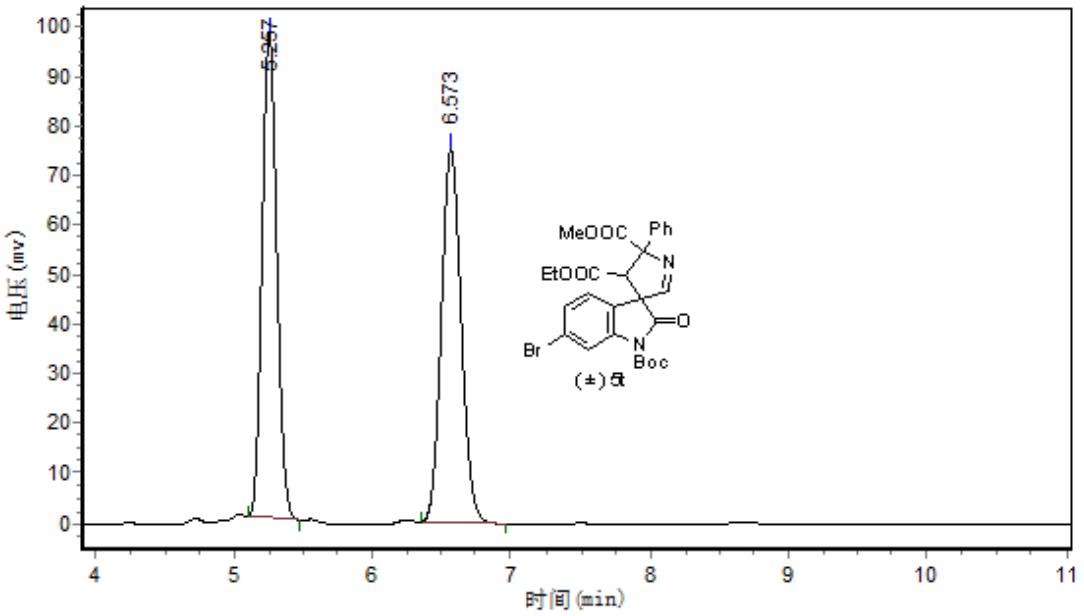
Peak	RT (min)	Height (mV*sec)	Area (mv)	Area (%)
1	6.742	818.380	8391.801	0.1165
2	7.848	588858.563	7192784.500	99.8835
Total		589676.942	7201176.301	100.0000



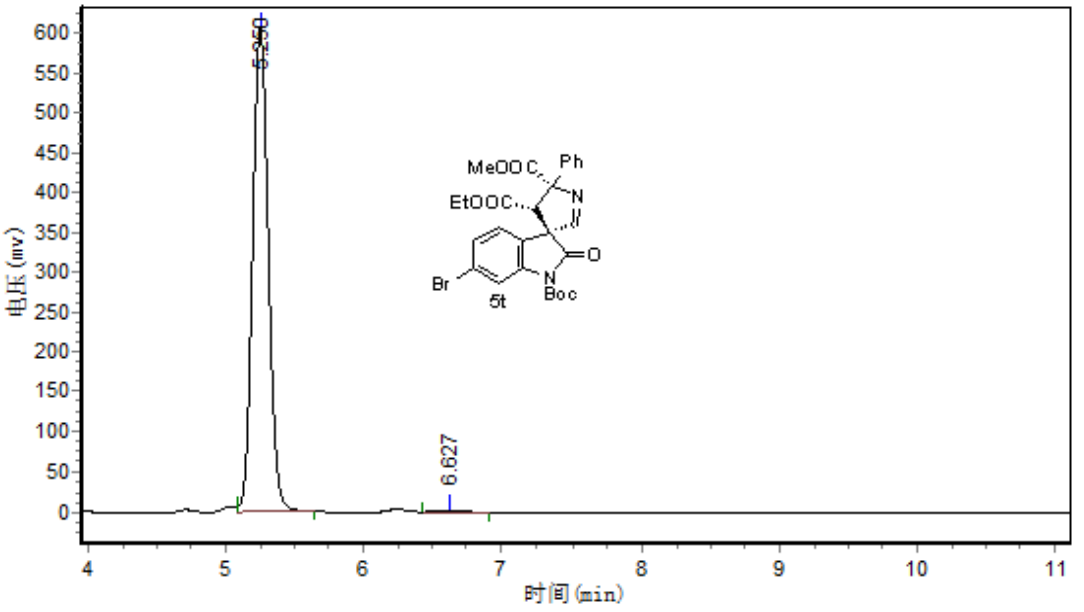
Peak	RT (min)	Height (mV*sec)	Area (mv)	Area (%)
1	5.032	297694.594	2169815.750	49.2395
2	6.232	235492.125	2236842.000	50.7605
Total		533186.719	4406657.750	100.0000



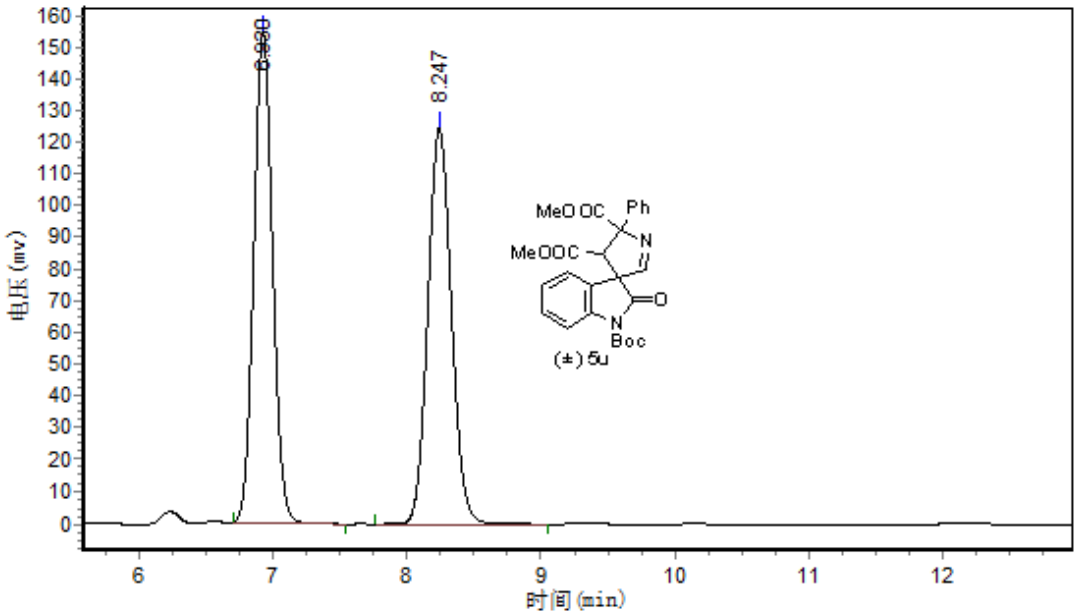
Peak	RT (min)	Height (mV*sec)	Area (mv)	Area (%)
1	5.050	610165.000	5100944.500	99.1396
2	6.400	4573.827	44268.203	0.8604
Total		614738.827	5145212.703	100.0000



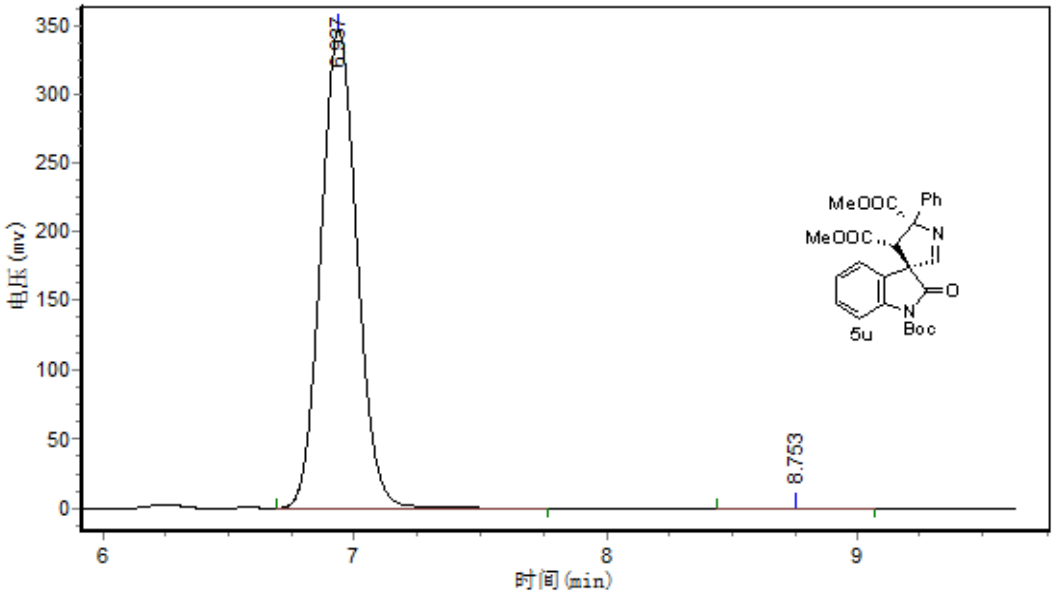
Peak	RT (min)	Height (mV*sec)	Area (mv)	Area (%)
1	5.257	97876.500	722467.313	49.1948
2	6.573	75057.375	746118.875	50.8052
Total		172933.875	1468586.188	100.0000



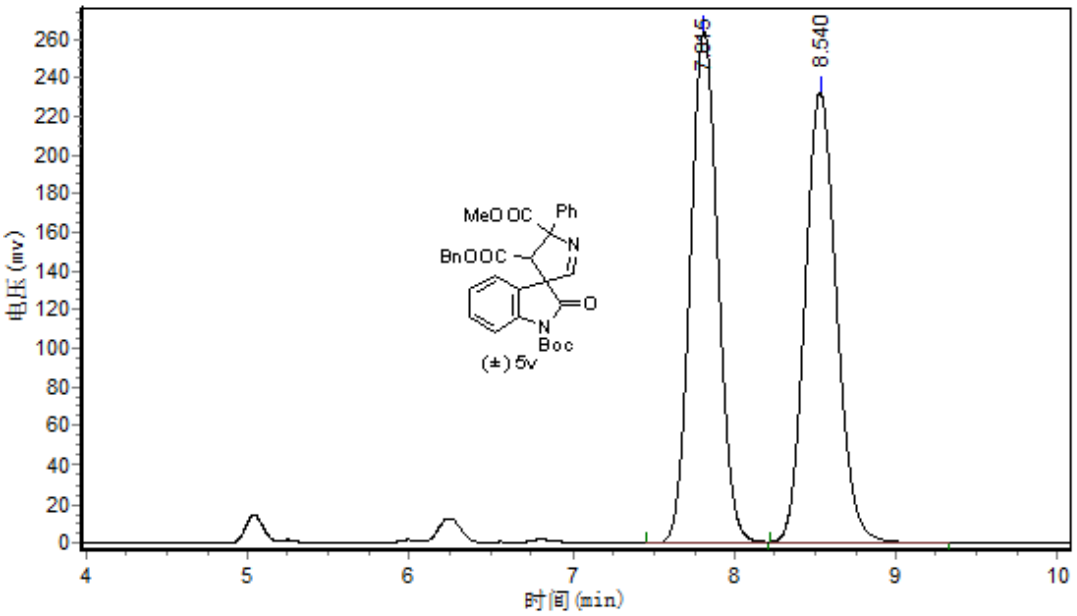
Peak	RT (min)	Height (mV*sec)	Area (mv)	Area (%)
1	5.250	604457.313	4789188.000	99.2692
2	6.627	2779.772	35259.000	0.7308
Total		607237.085	4824447.000	100.0000



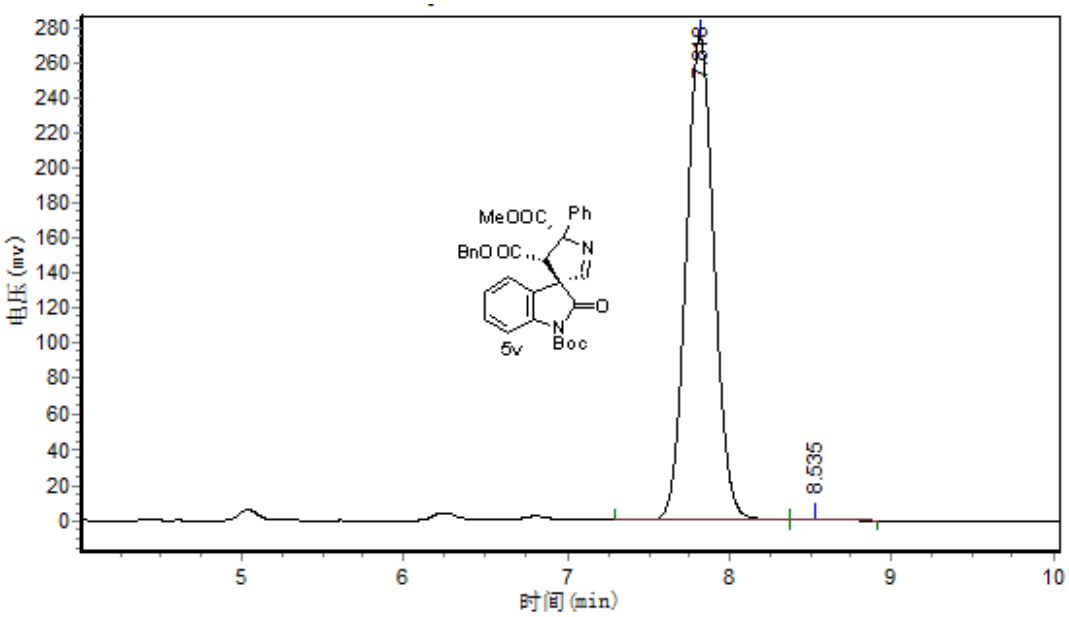
Peak	RT (min)	Height (mV*sec)	Area (mv)	Area (%)
1	6.930	154340.641	1510187.625	49.9061
2	8.247	124329.258	1515869.000	50.0939
		278669.898	3026056.625	100.0000



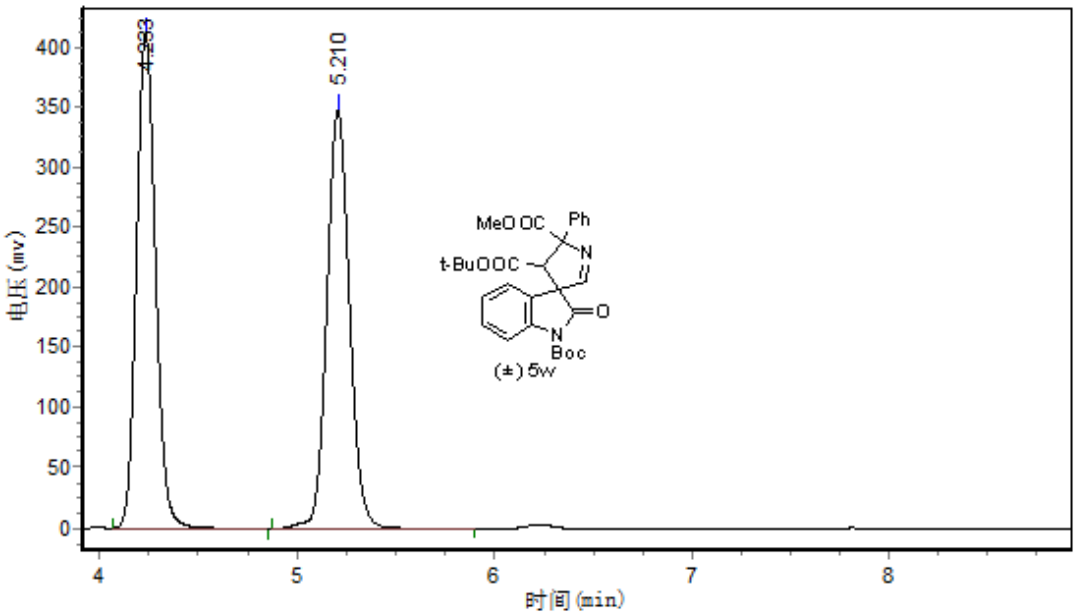
Peak	RT (min)	Height (mV*sec)	Area (mv)	Area (%)
1	6.937	346338.438	3474611.750	99.9179
2	8.753	194.152	2854.250	0.0821
Total		346532.590	3477466.000	100.0000



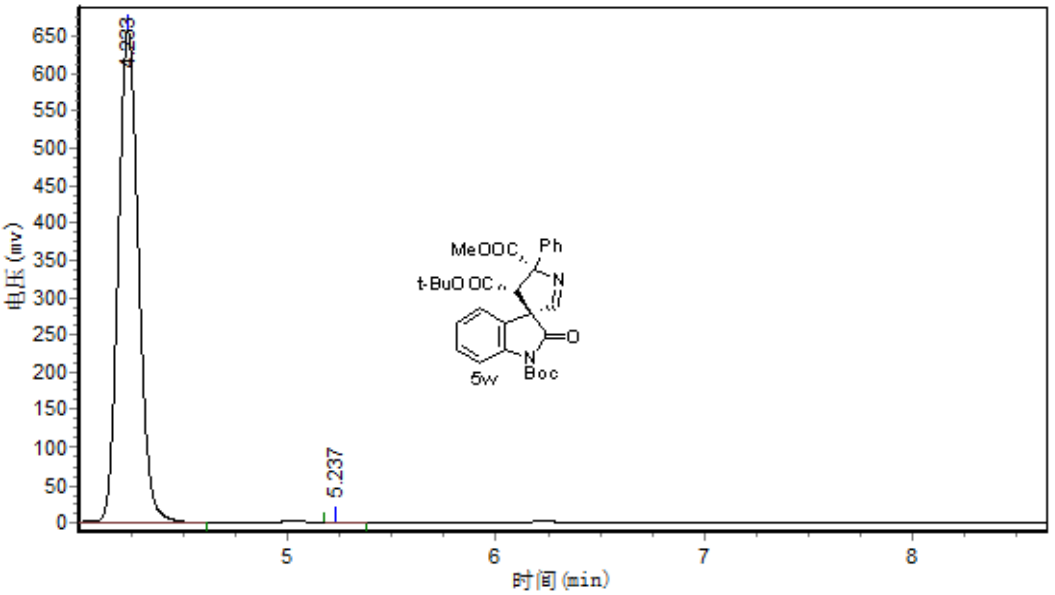
Peak	RT (min)	Height (mV*sec)	Area (mv)	Area (%)
1	7.815	263353.813	3135132.750	50.0290
2	8.540	231839.578	3131497.250	49.9710
Total		495193.391	6266630.000	100.0000



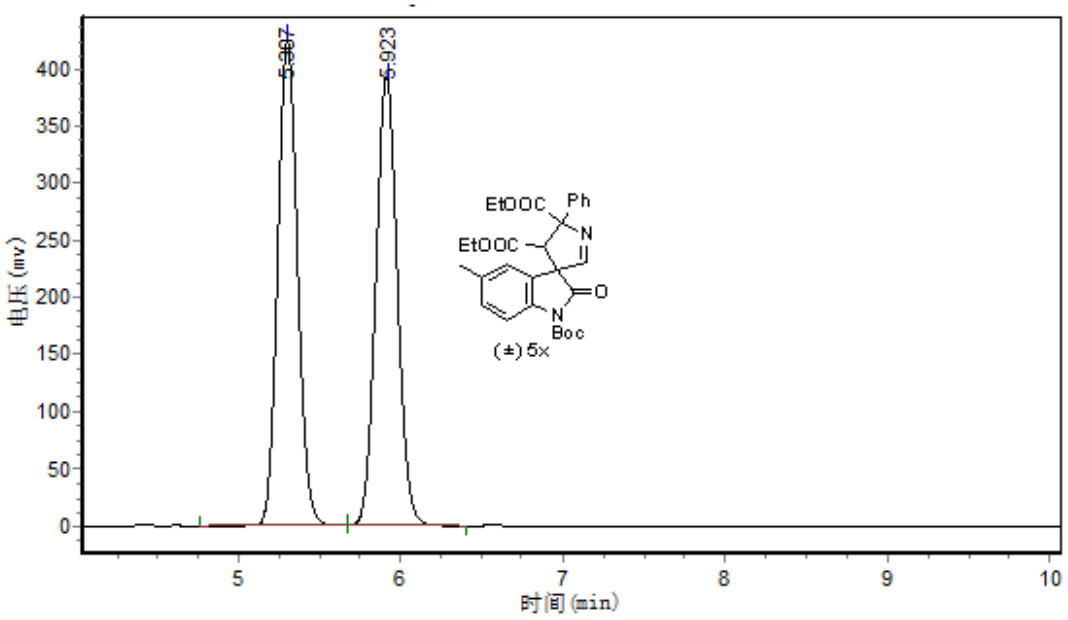
Peak	RT (min)	Height (mV*sec)	Area (mv)	Area (%)
1	7.818	274572.719	3291457.250	99.7680
2	8.535	584.211	7654.599	0.2320
Total		275156.930	3299111.849	100.0000



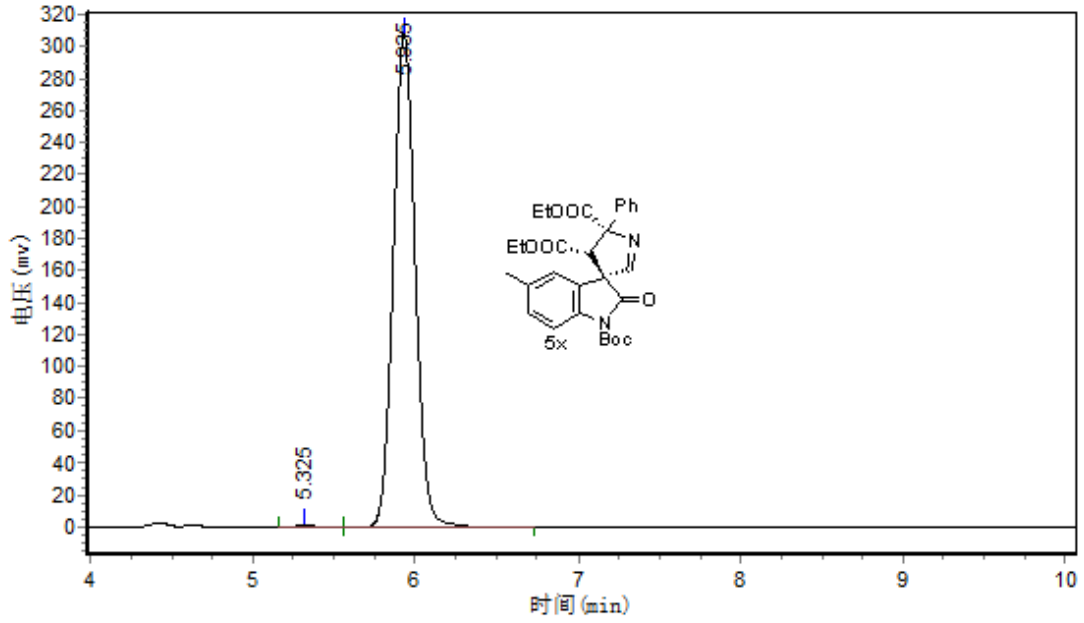
Peak	RT (min)	Height (mV*sec)	Area (mv)	Area (%)
1	4.233	410936.594	2748585.250	49.7452
2	5.210	346910.594	2776741.500	50.2548
Total		757847.188	5525326.750	100.0000



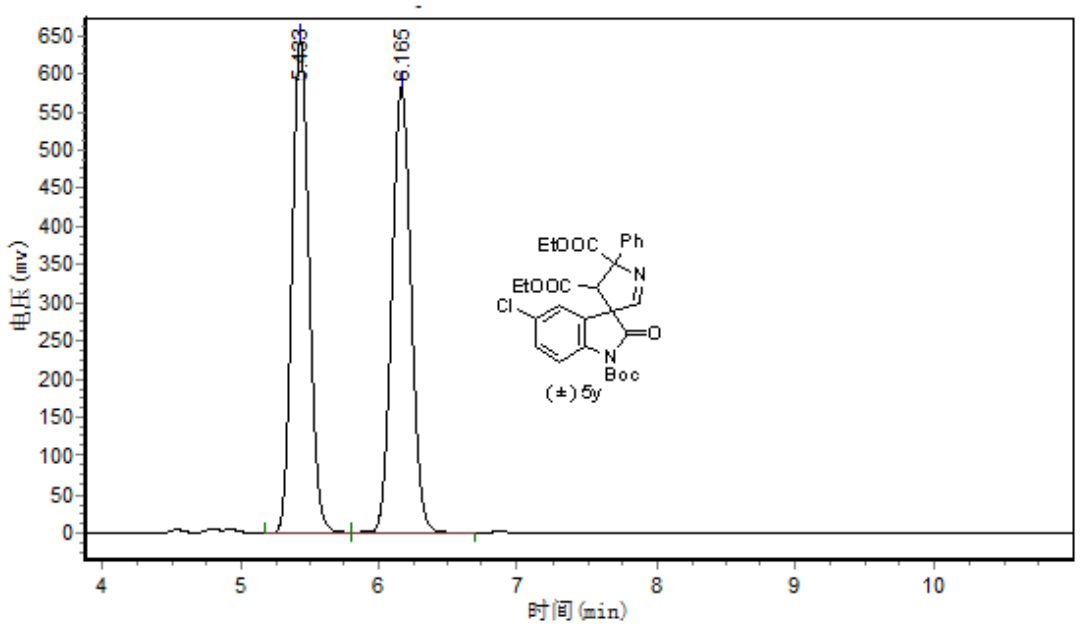
Peak	RT (min)	Height (mV*sec)	Area (mv)	Area (%)
1	4.233	657298.063	4454729.500	99.9152
2	5.237	620.318	3781.600	0.0848
Total		657918.380	4458511.100	100.0000



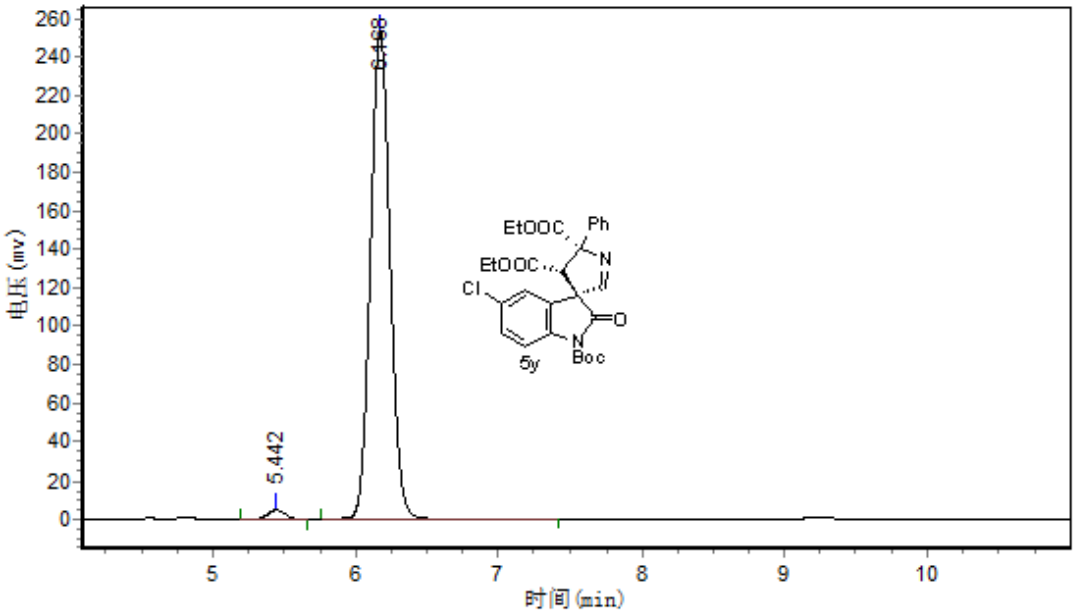
Peak	RT (min)	Height (mV*sec)	Area (mv)	Area (%)
1	5.307	424349.969	3596397.750	49.8614
2	5.923	390232.344	3616390.250	50.1386
		814582.313	7212788.000	100.0000



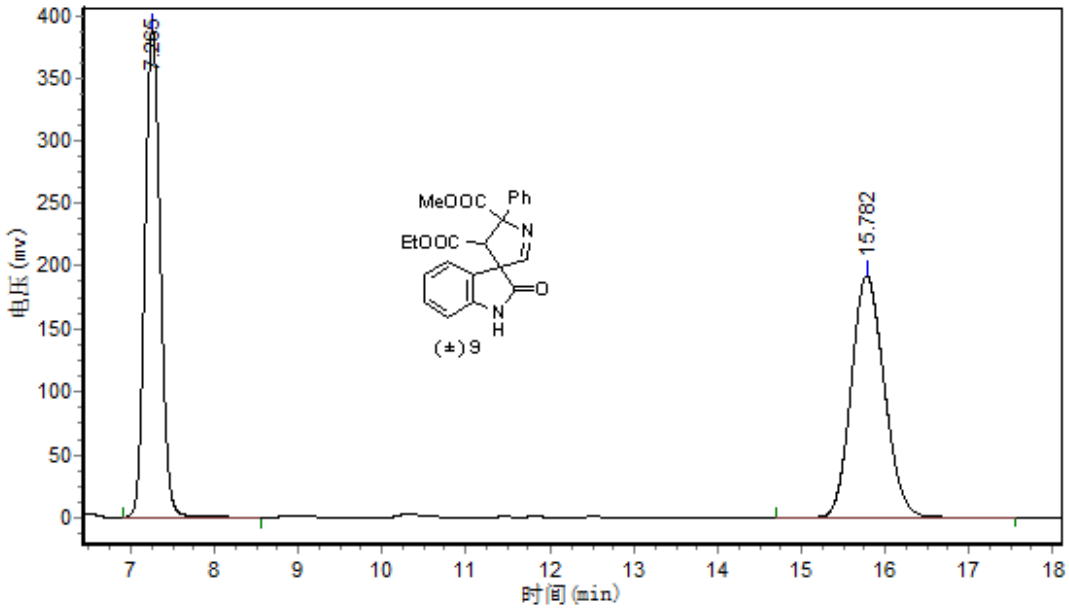
Peak	RT (min)	Height (mV*sec)	Area (mv)	Area (%)
1	5.325	1151.685	9538.250	0.3305
2	5.935	307735.875	2876559.500	99.6695
Total		308887.560	2886097.750	100.0000



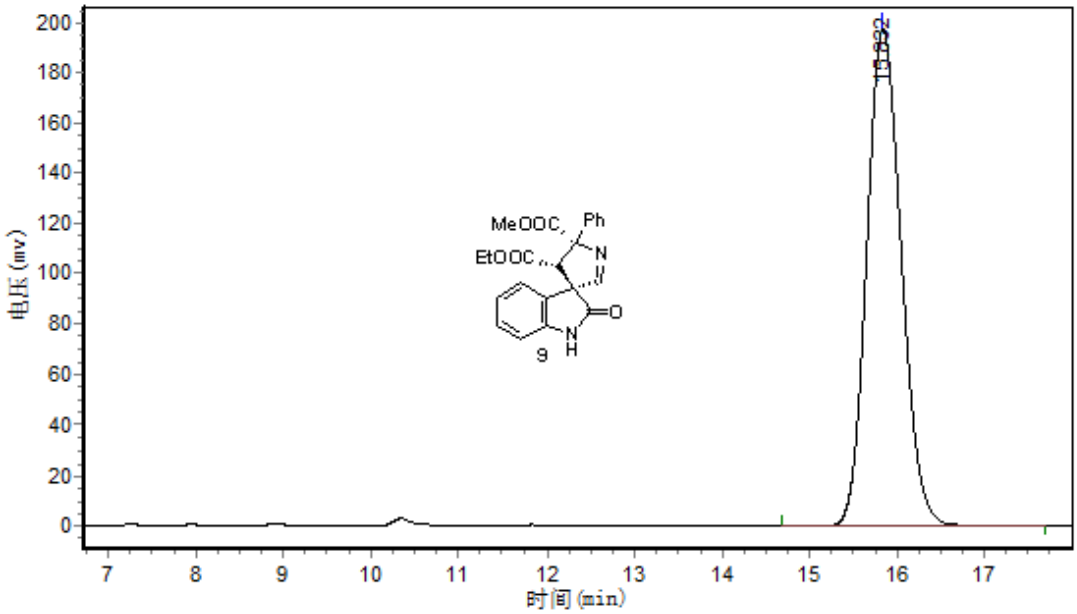
Peak	RT (min)	Height (mV*sec)	Area (mv)	Area (%)
1	5.433	641759.375	5482226.000	49.5347
2	6.165	579541.063	5585226.500	50.4653
Total		1221300.438	11067452.500	100.0000



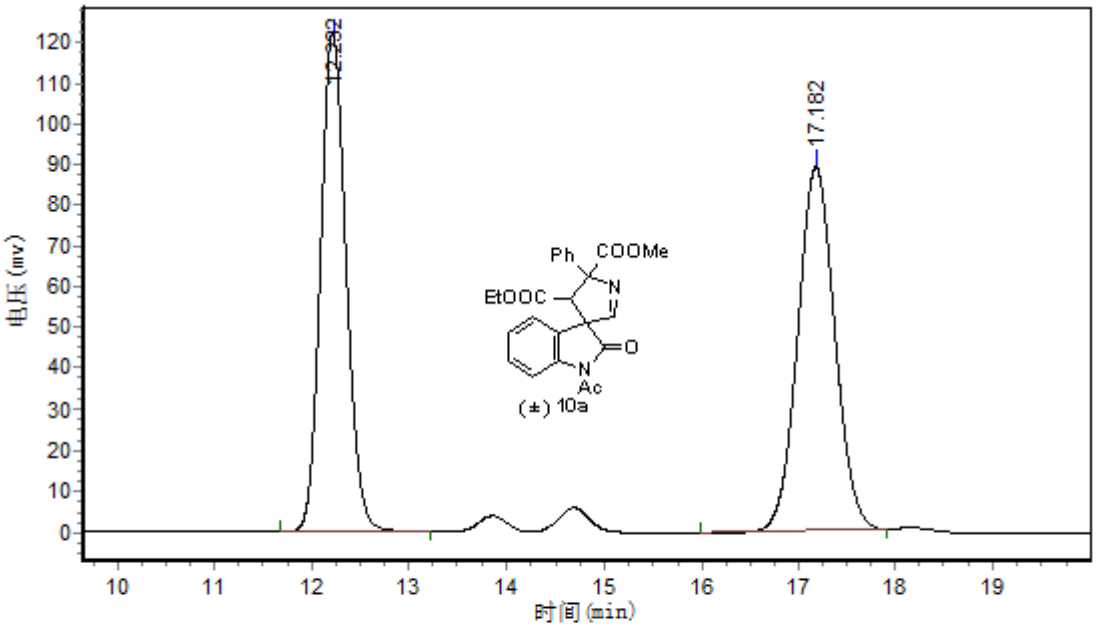
Peak	RT (min)	Height (mV*sec)	Area (mv)	Area (%)
1	5.442	5018.313	44354.449	1.7979
2	6.168	252858.156	2422658.250	98.2021
Total		257876.469	2467012.699	100.0000



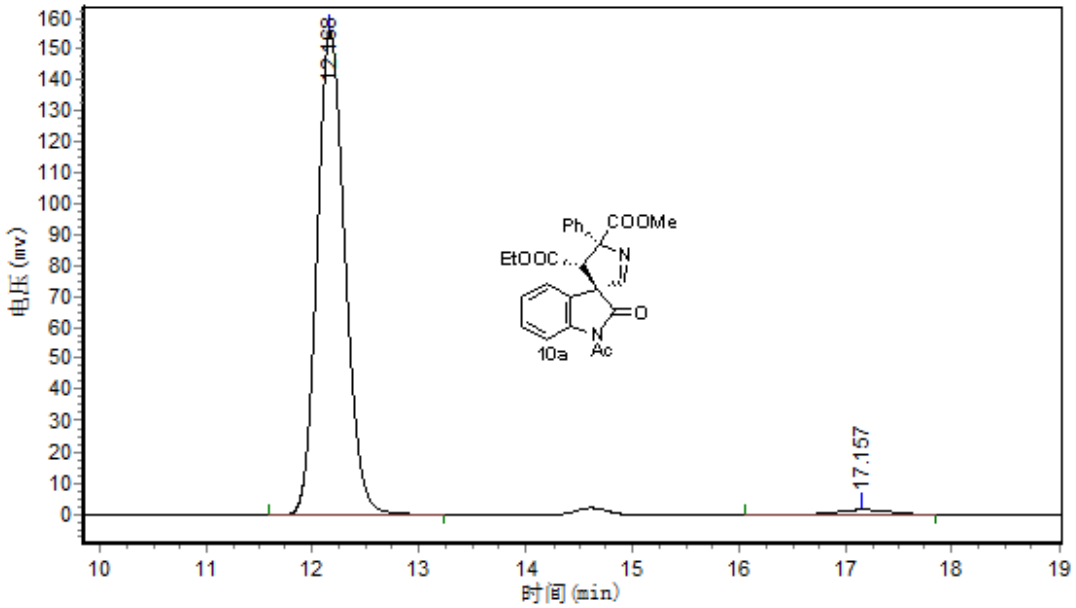
Peak	RT (min)	Height (mV*sec)	Area (mv)	Area
1	7.265	388925.875	4949920.500	48.4890
2	15.782	192355.281	5258424.000	51.5110
Total		581281.156	10208344.500	100.0000



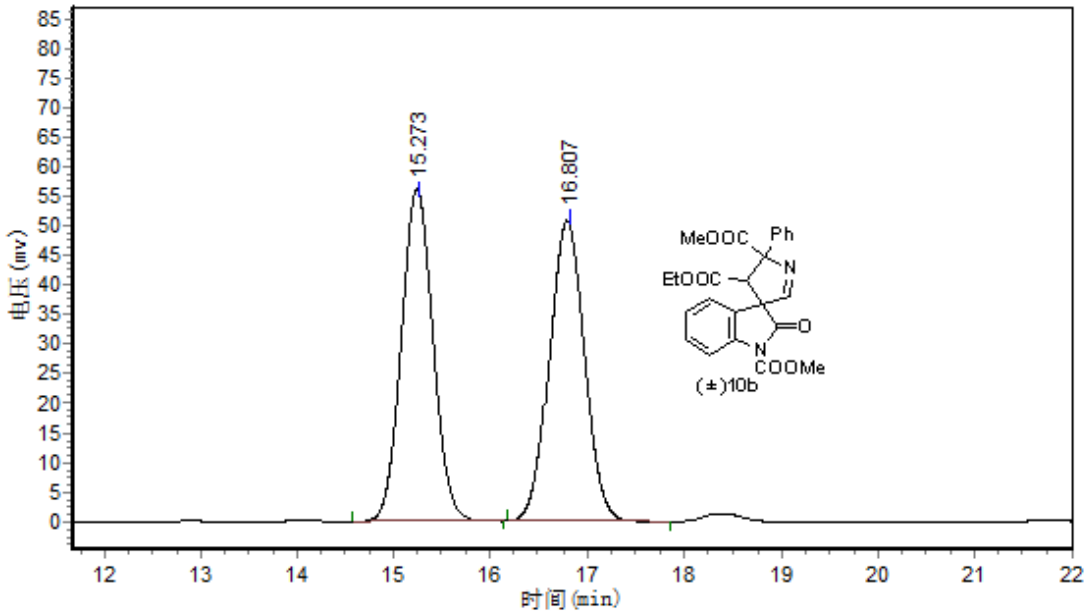
Peak	RT (min)	Height (mV*sec)	Area (mv)	Area
1	15.832	197113.266	5408722.500	100.0000
		197113.266	5408722.500	100.0000



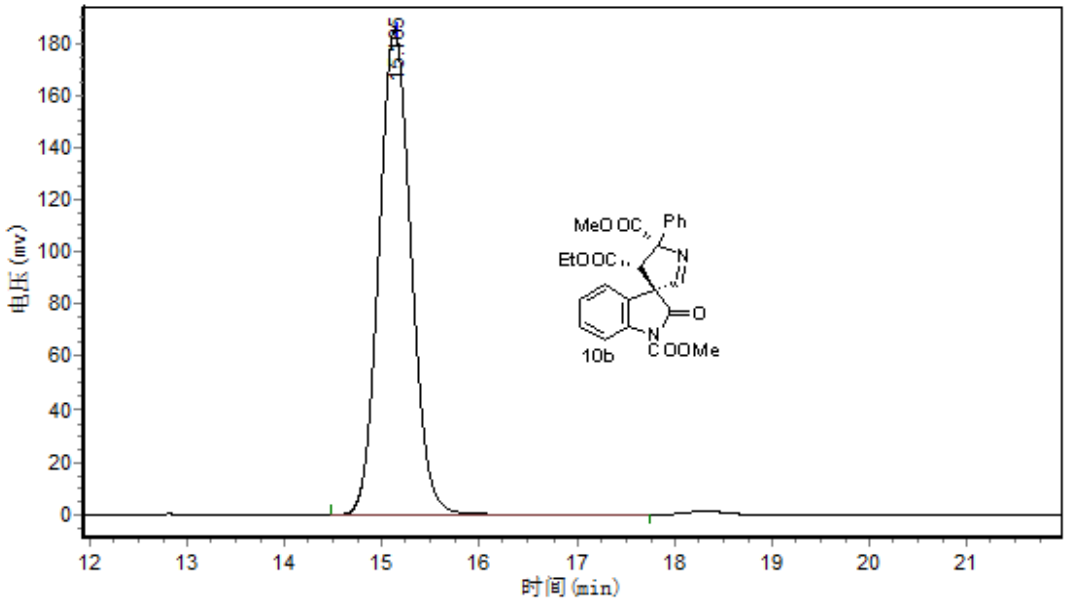
Peak	RT (min)	Height (mV*sec)	Area (mv)	Area
1	12.232	122275.680	2237302.500	48.7687
2	17.182	89018.273	2350276.250	51.2313
Total		211293.953	4587578.750	100.0000



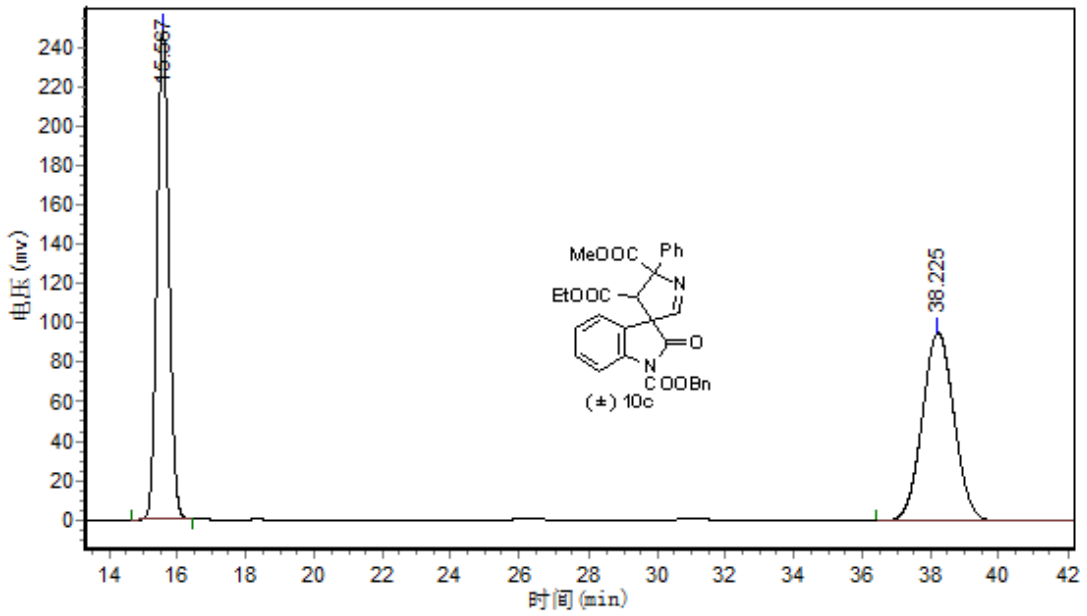
Peak	RT (min)	Height (mV*sec)	Area (mv)	Area
1	12.168	155753.094	2836946.250	97.8831
2	17.157	1700.820	61354.801	2.1169
Total		157453.914	2898301.051	100.0000



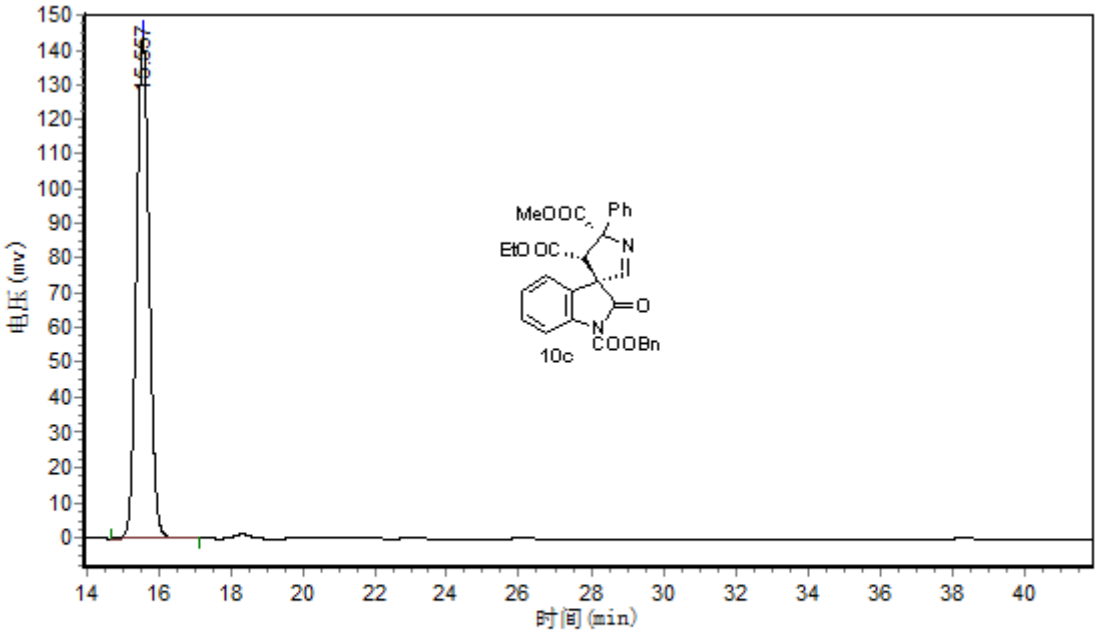
Peak	RT (min)	Height (mV*sec)	Area (mv)	Area
1	15.273	55758.574	1280426.750	50.2205
2	16.807	50609.180	1269183.500	49.7795
Total		106367.754	2549610.250	100.0000



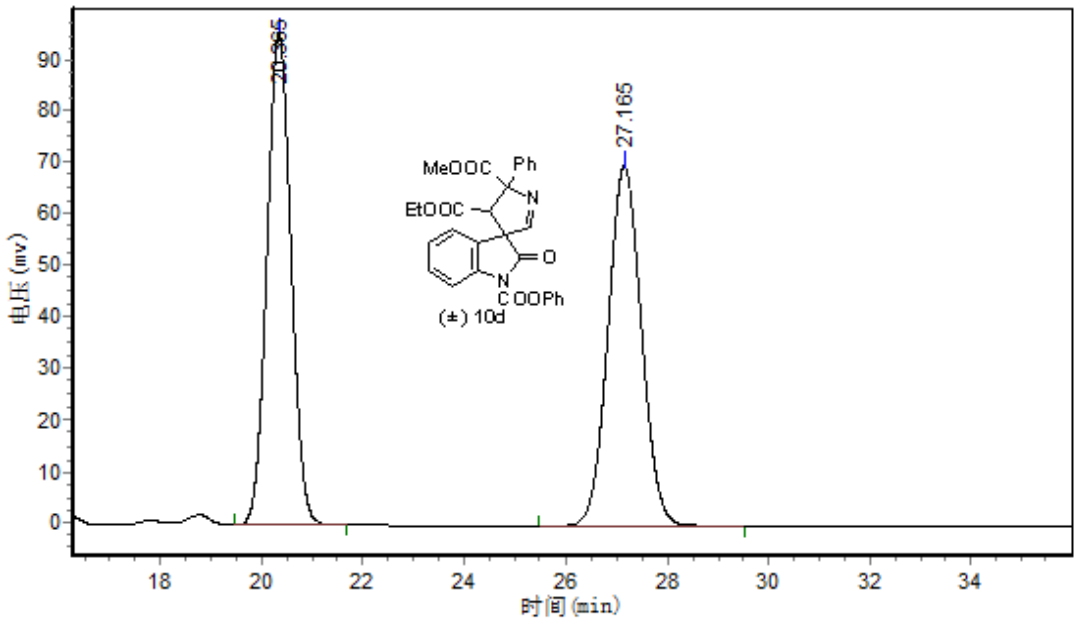
Peak	RT (min)	Height (mV*sec)	Area (mv)	Area
1	15.165	184269.156	4236623.500	100.0000
		184269.156	4236623.500	100.0000



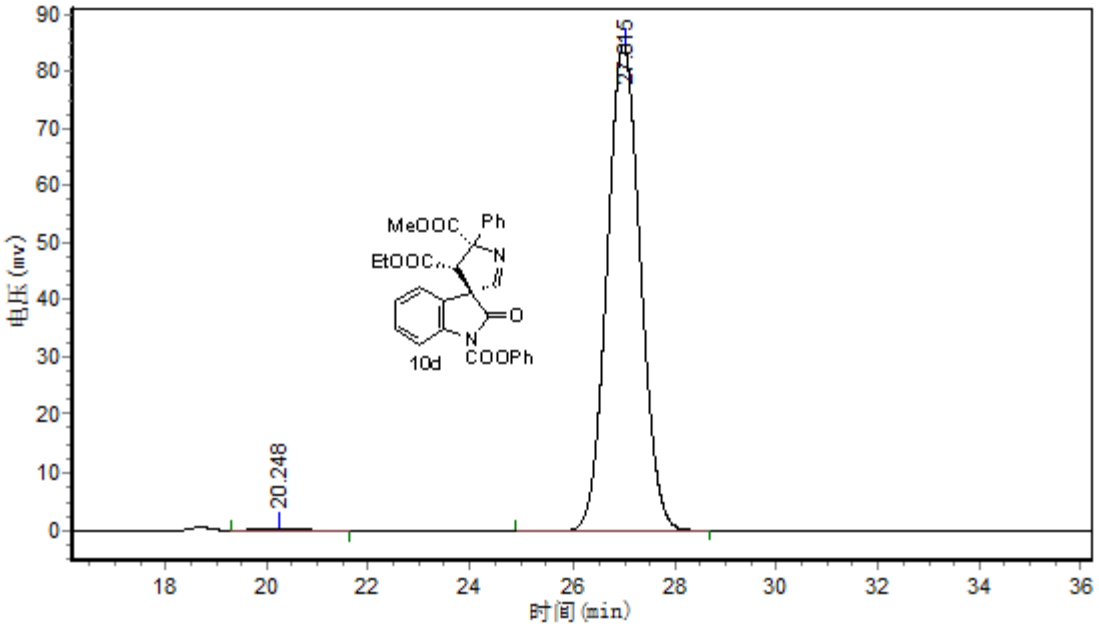
Peak	RT (min)	Height (mV*sec)	Area (mv)	Area
1	15.567	247806.438	6090049.000	49.7579
2	38.225	95357.438	6149318.500	50.2421
Total		343163.875	12239367.500	100.0000



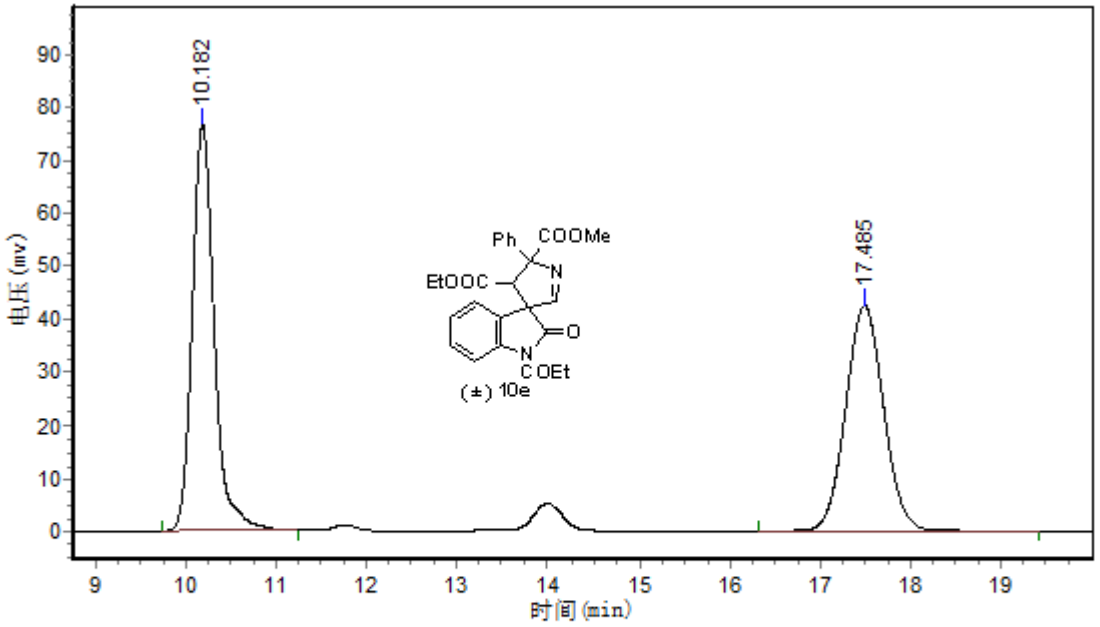
Peak	RT (min)	Height (mV*sec)	Area (mv)	Area
1	15.567	143041.313	3531550.000	100.0000
Total		143041.313	3531550.000	100.0000



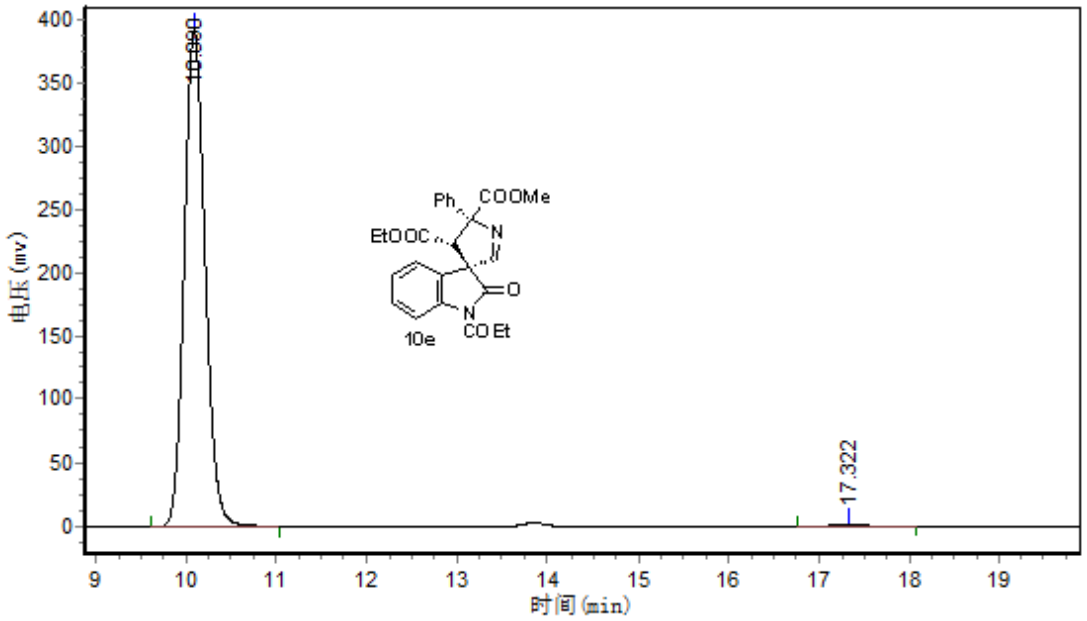
Peak	RT (min)	Height (mV*sec)	Area (mv)	Area
1	20.365	95535.594	3150955.250	49.6884
2	27.165	69642.719	3190470.250	50.3116
Total		165178.313	6341425.500	100.0000



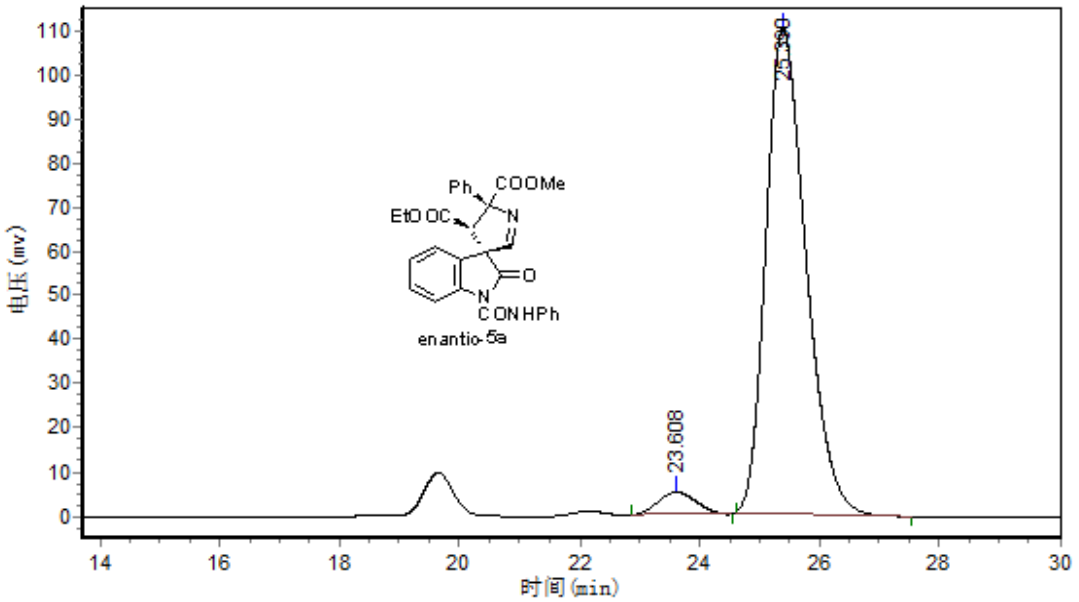
Peak	RT (min)	Height (mV*sec)	Area (mv)	Area
1	20.248	340.343	19123.600	0.4914
2	27.015	84780.383	3872360.000	99.5086
Total		85120.726	3891483.600	100.0000



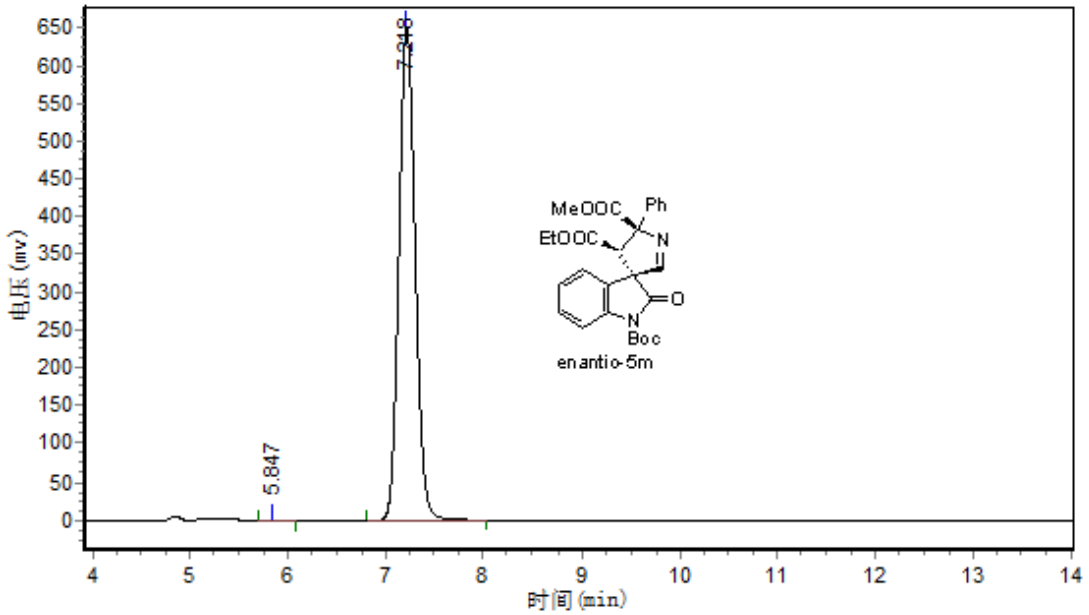
Peak	RT(min)	Height (mV*sec)	Area (mv)	Area (%)
1	10.182	76529.453	1291107.875	51.2492
2	17.485	42275.773	1228166.625	48.7508
Total		118805.227	2519274.500	100.0000



Peak	RT(min)	Height (mV*sec)	Area (mv)	Area (%)
1	10.090	392813.813	6281463.500	98.8101
2	17.322	2635.552	75640.672	1.1899
Total		395449.365	6357104.172	100.0000



Peak	RT (min)	Height (mV*sec)	Area (mv)	Area
1	23.608	5063.918	222469.000	4.1886
2	25.390	109805.508	5088841.500	95.8114
Total		114869.426	5311310.500	100.0000



Peak	RT (min)	Height (mV*sec)	Area (mv)	Area
1	5.847	628.021	5366.900	0.0713
2	7.218	649879.938	7526480.500	99.9287
Total		650507.959	7531847.400	100.0000