Asymmetric Construction of Quaternary Stereocenters by Direct Organocatalytic Amination of 3-Substituted Oxindoles

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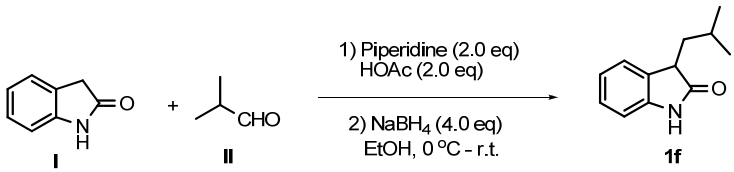
General: Reactions were monitored by thin layer chromatography using UV light to visualize the course of reaction. Purification of reaction products was carried out by flash chromatography on silica gel. Chemical yields refer to pure isolated substances. ^{1}H and ^{13}C NMR spectra were obtained using a Bruker DPX-300 spectrometer. Chemical shifts are reported in ppm from tetramethylsilane with the solvent resonance as the internal standard. The following abbreviations were used to designate chemical shift mutiplicities: s = singlet, d = doublet, t = triplet, q = quartet, h = heptet, m = multiplet, br = broad.

All reactions were run under nitrogen except noted. Anhydrous ether, THF and toluene were prepared by distillation over sodium-benzophenone ketyl prior to use. Anhydrous halogenated solvents were prepared by first distillation over P_2O_5 and then from CaH_2. Catalyst **5-7** and $(DHQ)_2PHAL$ were purchased from Aldrich. Catalysts **4**[1] and $(QD)_2PYR$[2] were prepared using a literature method. 3-prochiral oxindoles **1**[3] were prepared according to literature report or by a modified method.

Preparation of Substrates.

Substrate **1f** was prepared according to a modified method of literature report.[3]

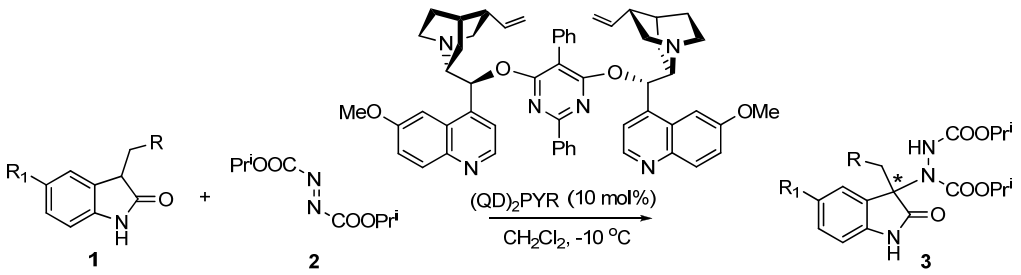


To a solution of oxindole **I** (0.8 g, 9.0 mmol) and isobutylaldehyde (0.9 g, 9.9 mmol) in 9.0

[1] B. Vakulya, S. Varga, A. Csámpai, T. Soós, *Org. Lett.* **2005**, *7*, 1967.
[2] a) G. A. Crispino, K.-S. Jeong, H. C. Kolb, Z.-M. Wang, D. Xu, K. B. Sharpless, *J. Org. Chem.* **1993**, *58*, 3785. b) T. Seitz, J. Baudoux, H. Bekolo, D. Cahard, J.-C. Plaquevent, M.-C. Lasne, J. Rouden, *Tetrahderon* **2006**, *62*, 6155.
[3] a) P. Galzerano, G. Bencivenni, F. Pesciaioli, A. Mazzanti, B. Giannichi, L. Sambri, G. Bartoli, P. Melchiorre, *Chem. Eur. J.*. **2009**, *15*, 7846. b) G. Lakshmaiah, T. Kawabata, M. Shang, K. Fuji, *J. Org. Chem.* **1999**, *64*, 1699.

mL of absolute ethanol was added piperidine (1.8 mL, 18.0 mmol) and HOAc (1.1 mL, 18.0 mmol). The resulting mixture was refluxed till TLC analysis showed the full conversion of oxindole. Then the reaction mixture was cooled to 0°C, and $NaBH_4$ (380.0 mg, 9.9 mmol) and 10.0 mL of ethanol were added. After the completion of reduction by TLC analysis, most of the ethanol was evaporated and 20 mL of saturated NH_4Cl was added. The reaction mixture was extracted with CH_2Cl_2 (3 × 30.0 mL). The combined organic phases were washed with water and brine, and then concentrated, followed by purification on a short SiO_2 column (CH_2Cl_2/EtOAc, from 50/1 to 25/1) afforded 0.7 g of the oxindole **1f**[4] in 61% yield. ^{1}H NMR (300 MHz, $CDCl_3$): δ 8.02 (s, br, 1H), 7.18-7.26 (m, 2H), 6.99-7.04 (m, 1H), 6.88 (d, J = 7.5 Hz, 1H), 3.48 (t, J = 6.9 Hz, 1H), 1.99-2.12 (m, 1H), 1.82-1.92 (m, 1H), 1.64-1.74 (m, 1H), 0.96-1.01 (m, 6H); ^{13}C NMR (75 MHz, $CDCl_3$): δ 181.4, 141.4, 130.2, 127.7, 124.3, 122.0, 109.8, 44.3, 39.8, 25.2, 22.9, 22.0.

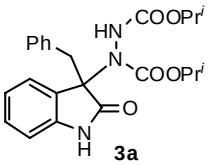
General Procedure for the Organocatalytic amination reaction.



To a schlenk tube was added $(QD)_2PYR$ (22.0 mg, 0.025 mmol) and 3-prochiral oxindole **1** (0.25 mmol), followed by 2.5 mL of anhydrous CH_2Cl_2. The thus formed solution was cooled to -10 °C for 15 minutes, and then DIAD **2** (0.3 mmol) was added. The resulting mixture was stirring at -10 °C till full conversion of the oxindole **1**. The reaction mixture was directly subjected for column chromatographic purification on a short SiO_2 column (10%~20% Et_2O in dichloromethane), affording the desired product. The racemate samples of product **3** were prepared using DABCO or Et_3N as the catalyst.

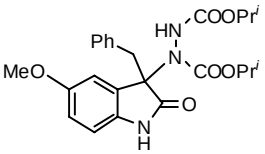
It should be noted that due to the distinct presence of rotameric isomers, the ^{1}H NMR and ^{13}C NMR contained extra peaks, as reported in the related work.[5]

[4] V. Balazs, S. Gyula, *Eur. J. Org. Chem.* **2003**, 3991.
[5] a) R. Matsubara, S. Kobayashi, *Angew. Chem. Int. Ed.* **2006**, *45*, 7993. b) T. B. Poulsen, C. Alemparte, K. A. Jørgensen, *J. Am. Chem. Soc.* **2005**, *127*, 11614. c) S. Saaby, M. Bella, K. A. Jørgensen, *J. Am. Chem. Soc.,* 2004, **126**, 8120.

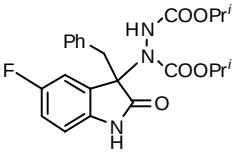


3a

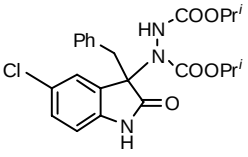
Column chromatography afforded the desired product **3a** in 98% yield as white solid. HPLC analysis (Chiralcel AD-H, 10% ^{i}PrOH/hexane, 1.0 mL/min, 230 nm; t_r (major) = 32.30 min, t_r (minor) = 9.86 min) gave the isomeric composition of the product: 93.9% ee. $[\alpha]_D^{20}$ = +46.5 (c = 1.26, $CHCl_3$). ^{1}H NMR (300 MHz, $CDCl_3$): see below. ^{13}C NMR ($CDCl_3$, 75 MHz) δ 178.17, 157.10, 153.71, 140.45, 132.61, 130.39, 128.58, 127.34, 126.76, 124.92, 122.70, 109.28, 70.73, 70.28, 70.06, 41.74, 22.05, 21.91, 21.57, 21.41; MS (EI): 425 (M^+, 11), 426 [$(M+H)^+$, 3], 162 (100), 206 (96), 248 (82), 222 (69), 223 (41), 145 (37); HRMS (EI): Exact mass calcd for $C_{23}H_{27}N_3O_5$ $[M]^+$: 425.1951 Found: 425.1951.



Column chromatography afforded the desired product **3b** in 90% yield as white solid. HPLC analysis (Chiralcel OD-H + OD-H, 10% ^{i}PrOH/hexane, 0.9 mL/min, 254 nm; t_r (major) = 14.07 min, t_r (minor) = 17.69 min) gave the isomeric composition of the product: 91.2% ee. $[\alpha]_D^{20}$ = +86.0 (c = 1.07, $CHCl_3$). ^{1}H NMR (300 MHz, $CDCl_3$):see below. ^{13}C NMR ($CDCl_3$, 75 MHz): δ 178.07, 156.90, 156.01, 153.74, 133.75, 132.67, 131.60, 130.40, 127.38, 126.76, 113.81, 111.44, 109.67, 70.74, 70.61, 69.93, 55.83, 41.78, 22.06, 21.90, 21.61, 21.48; MS (EI): 425 (M^+, 11), 426 [$(M+H)^+$, 3], 162 (100), 206 (96), 248 (82), 222 (69), 223 (41), 145 (37); HRMS (EI): Exact mass calcd for $C_{24}H_{29}N_3O_6$ $[M]^+$: 455.2056, Found: 455.2057.

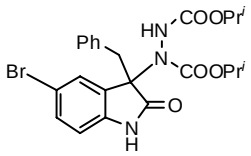


Column chromatography afforded the desired product **3c** in 96% yield as white solid. HPLC analysis (Chiralcel AD-H, 10% ^{i}PrOH/hexane, 1.0 mL/min, 254 nm; t_r (major) = 35.17 min, t_r (minor) = 11.39 min) gave the isomeric composition of the product: 90.2% ee. $[\alpha]_D^{20}$ = +42.8 (c = 0.93, $CHCl_3$). ^{1}H NMR (300 MHz, $CDCl_3$): see below. ^{13}C NMR ($CDCl_3$, 75 MHz): see below. MS (EI): 443 (M^+, 10), 444 [$(M+H)^+$, 3], 180 (100), 224 (87), 43 (80), 266 (44), 163 (35), 240 (33); HRMS (EI): Exact mass calcd for $C_{23}H_{26}N_3O_5F$ $[M]^+$: 443.1856, Found: 443.1857.

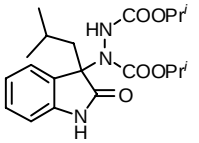


Column chromatography afforded the desired product **3d** in 92% yield as white solid. HPLC analysis (Chiralcel AD-H, 10% ^{i}PrOH/hexane, 1.0 mL/min, 254 nm; t_r (major) = 35.31 min, t_r (minor) = 12.99 min) gave the isomeric composition of the product: 89.0% ee. $[\alpha]_D^{20}$ = +100.0 (c = 0.95, $CHCl_3$). ^{1}H NMR

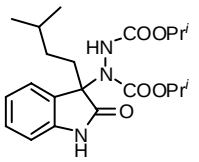
(300 MHz, $CDCl_3$): see below. ^{13}C NMR ($CDCl_3$, 75 MHz): see below. MS (EI): 459 (M^+, 10), 460 [$(M+H)^+$, 3], 43 (100), 240 (91), 196 (86), 282 (45), 57 (44), 91 (39); HRMS (EI): Exact mass calcd for $C_{23}H_{26}N_3O_5Cl$ $[M]^+$: 459.1561, Found: 459.1557.



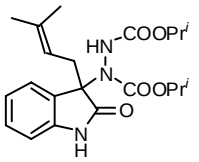
Column chromatography afforded the desired product **3e** in 95% yield as white solid. HPLC analysis (Chiralcel AD-H, 10% ^{i}PrOH/hexane, 1.0 mL/min, 254 nm; t_r (major) = 37.99 min, t_r (minor) = 15.52 min) gave the isomeric composition of the product: 90.6% ee. $[\alpha]_D^{20}$ = +99.4 (c = 1.16, $CHCl_3$). ^1H NMR (300 MHz, $CDCl_3$): see below. ^{13}C NMR ($CDCl_3$, 75 MHz): see below. MS (EI): 504 (M^+, 2), 505 [$(M+H)^+$, 6], 43 (100), 284 (53), 240 (50), 286 (50), 242 (48), 91 (38); HRMS (EI): Exact mass calcd for $C_{23}H_{26}N_3O_5Br$ $[M]^+$: 503.1056, Found: 503.1043.



Column chromatography afforded the desired product **3f** in 97% yield as white solid. HPLC analysis (Chiralcel AD-H, 10% ^{i}PrOH/hexane, 1.0 mL/min, 254 nm; t_r (major) = 21.90 min, t_r (minor) = 12.31 min) gave the isomeric composition of the product: 90.2% ee. $[\alpha]_D^{20}$ = -4.9 (c = 1.14, $CHCl_3$). ^1H NMR (300 MHz, $CDCl_3$): see below. ^{13}C NMR ($CDCl_3$, 75 MHz): see below. MS (EI): 391 (M^+, 3), 392 [$(M+H)^+$, 1], 146 (100), 189 (77), 43 (39), 188 (30), 160 (22), 132 (20); HRMS (EI): Exact mass calcd for $C_{20}H_{29}N_3O_5$ $[M]^+$: 391.2107, Found: 391.2104.

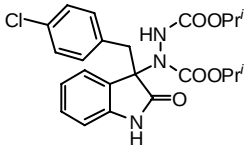


Column chromatography afforded the desired product **3g** in 92% yield as white solid. HPLC analysis (Chiralcel AD-H, 10% ^{i}PrOH/hexane, 1.0 mL/min, 254 nm; t_r (major) = 19.73 min, t_r (minor) = 10.85 min) gave the isomeric composition of the product: 86.0% ee. $[\alpha]_D^{20}$ = -3.5 (c = 3.80, $CHCl_3$). ^1H NMR (300 MHz, $CDCl_3$): see below. ^{13}C NMR ($CDCl_3$, 75 MHz): δ 179.45, 156.91, 153.86, 140.68, 131.09, 128.31, 124.46, 122.83, 109.49, 70.57, 69.86, 69.40, 33.66, 31.16, 27.97, 22.32, 22.15, 21.96, 21.86, 21.55, 21.39; MS (EI): 405 (M^+, 5), 406 [$(M+H)^+$, 1], 203 (100), 146 (84), 43 (47), 202 (41), 130 (20), 132 (20); HRMS (EI): Exact mass calcd for $C_{21}H_{31}N_3O_5$ $[M]^+$: 405.2264, Found: 405.2263.

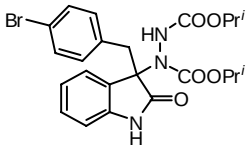


Column chromatography afforded the desired product **3h** in 96% yield as white solid. HPLC analysis (Chiralcel AD-H, 10% ^{i}PrOH/hexane, 1.0 mL/min, 230 nm; t_r (major) = 18.42 min, t_r (minor) = 11.22 min) gave the isomeric

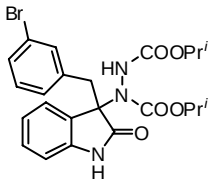
composition of the product: 83.7% ee. $[\alpha]_D^{20}$ = -28.5 (c = 4.60, $CHCl_3$). ^1H NMR (300 MHz, $CDCl_3$): see below. ^{13}C NMR ($CDCl_3$, 75 MHz): δ 179.21, 156.81, 153.79, 140.42, 136.51, 130.98, 128.27, 124.74, 122.57, 115.26, 109.34, 70.60, 70.32, 69.85, 69.26, 34.55, 25.74, 22.24, 21.97, 21.86, 21.54, 21.33, 17.77; MS (EI): 403 (M^+, 0.3), 404 [$(M+H)^+$, 0.2], 162 (100), 199 (67), 206 (60), 200 (41), 145 (38), 43 (33); HRMS (EI): Exact mass calcd for $C_{21}H_{29}N_3O_5$ $[M]^+$: 403.2107, Found: 403.2102.



Column chromatography afforded the desired product **3i** in 97% yield as white solid. HPLC analysis (Chiralcel OD-H, 10% ^{i}PrOH/hexane, 1.0 mL/min, 230 nm; t_r (major) = 5.03 min, t_r (minor) = 8.19 min) gave the isomeric composition of the product: 90.2% ee. $[\alpha]_D^{20}$ = +48.3 (c = 3.19, $CHCl_3$). ^1H NMR (300 MHz, $CDCl_3$): see below. ^{13}C NMR ($CDCl_3$, 75 MHz): see below. MS (EI): 459 (M^+, 3), 460 [$(M+H)^+$, 1], 162 (100), 206 (90), 248 (67), 43 (45), 256 (39), 145 (36); HRMS (EI): Exact mass calcd for $C_{23}H_{26}N_3O_5Cl$ $[M]^+$: 459.1561, Found: 459.1562.

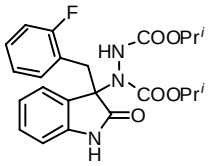


Column chromatography afforded the desired product **3j** in 95% yield as white solid. HPLC analysis (Chiralcel OD-H, 10% ^{i}PrOH/hexane, 1.0 mL/min, 230 nm; t_r (major) = 5.01 min, t_r (minor) = 8.30 min) gave the isomeric composition of the product: 81.8% ee. $[\alpha]_D^{20}$ = +46.7 (c = 2.02, $CHCl_3$). ^1H NMR (300 MHz, $CDCl_3$): see below. ^{13}C NMR ($CDCl_3$, 75 MHz): δ 177.52, 157.04, 153.62, 140.20, 132.09, 132.03, 131.74, 130.57, 129.94, 128. 85, 124.89, 122.89, 121.14, 109.35, 70.93, 70.28, 69.87, 69.87, 41.13, 22.06, 21.91, 21.62, 21.46; MS (EI): 505 [$(M+H)^+$, 1], 505 [$(M-H)^-$, 1], 162 (100), 206 (90), 248 (71), 43 (64), 145 (36), 57 (29); HRMS (EI): Exact mass calcd for $C_{23}H_{26}N_3O_5Br$ $[M]^+$: 503.1056, Found: 503.1043.

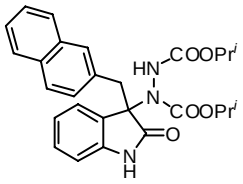


Column chromatography afforded the desired product **3k** in 97% yield as white solid. HPLC analysis (Chiralcel OD-H + OD-H, 5% ^{i}PrOH/hexane, 1.0 mL/min, 254 nm; t_r (major) = 21.63 min, t_r (minor) = 26.55 min) gave the isomeric composition of the product: 88.0% ee. $[\alpha]_D^{20}$ = +24.5 (c = 5.58, $CHCl_3$). ^1H NMR (300 MHz, $CDCl_3$): see below. ^{13}C NMR ($CDCl_3$, 75 MHz): δ 177.82, 157.03, 153.60, 140.24, 135.06, 133.30, 129.88, 129.07, 128.87, 124.84, 122.81, 121.19, 109.43, 70.82, 70.16, 70.00, 41.24, 22.00, 21.86, 21.55, 21.39; MS (EI): 505 [$(M+H)^+$, 2], 505 [$(M-H)^-$, 2], 162

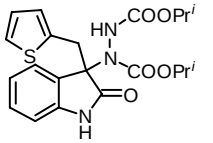
(100), 206 (94), 248 (78), 43 (69), 145 (32), 301 (27); HRMS (EI): Exact mass calcd for $C_{23}H_{26}N_3O_5Br$ $[M]^+$: 503.1056, Found: 503.1049.



Column chromatography afforded the desired product **3l** in 96% yield as white solid. HPLC analysis (Chiralcel AD-H, 10% ^{i}PrOH/hexane, 1.0 mL/min, 230 nm; t_r (major) = 32.31 min, t_r (minor) = 12.76 min) gave the isomeric composition of the product: 90.5% ee. $[\alpha]_D^{20}$ = +39.4 (c = 1.08, $CHCl_3$). ^{1}H NMR (300 MHz, $CDCl_3$): see below. ^{13}C NMR ($CDCl_3$, 75 MHz): see below. MS (EI): 443 (M^+, 7), 444 [$(M+H)^+$, 2], 162 (100), 206 (81), 248 (66), 43 (65), 240 (55), 241 (42); HRMS (EI): Exact mass calcd for $C_{23}H_{26}N_3O_5F$ $[M]^+$: 443.1856, Found: 443.1851.



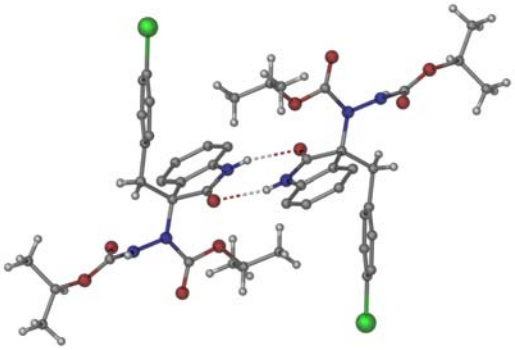
Column chromatography afforded the desired product **3m** in 97% yield as white solid. HPLC analysis (Chiralcel OD-H + OD-H, 5% ^{i}PrOH/hexane, 1.0 mL/min, 254 nm; t_r (major) = 24.04 min, t_r (minor) = 32.31 min) gave the isomeric composition of the product: 92.8% ee. $[\alpha]_D^{20}$ = +65.8 (c = 1.74, $CHCl_3$). ^{1}H NMR (300 MHz, $CDCl_3$): see below. ^{13}C NMR ($CDCl_3$, 75 MHz): see below. MS (EI): 475 [M^+, 0.1], 162 (100), 271 (97), 206 (80), 141 (61), 272 (57), 43 (51), 248 (37); HRMS (EI): Exact mass calcd for $C_{27}H_{29}N_3O_5$ $[M]^+$: 475.2107, Found: 475.2106.

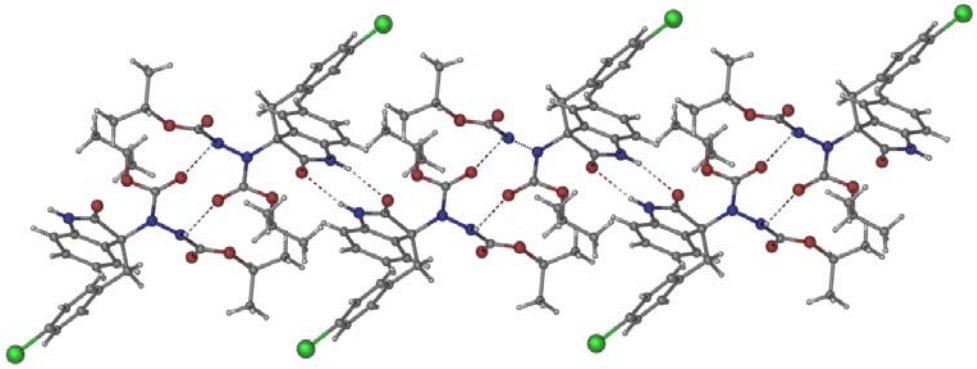


Column chromatography afforded the desired product **3n** in 95% yield as white solid. HPLC analysis (Chiralcel AD-H, 15% ^{i}PrOH/hexane, 1.0 mL/min, 254 nm; t_r (major) = 15.46 min, t_r (minor) = 7.75 min) gave the isomeric composition of the product: 86.0% ee. $[\alpha]_D^{20}$ = +3.73 (c = 5.87, $CHCl_3$). ^{1}H NMR (300 MHz, $CDCl_3$): see below. ^{13}C NMR ($CDCl_3$, 75 MHz): see below. MS (EI): 431 (M^+, 0.3), 432 [$(M+H)^+$, 0.1], 162 (100), 227 (87), 206 (65), 228 (40), 145 (37), 248 (36); HRMS (EI): Exact mass calcd for $C_{21}H_{25}N_3O_5S$ $[M]^+$: 431.1515, Found: 431.1514.

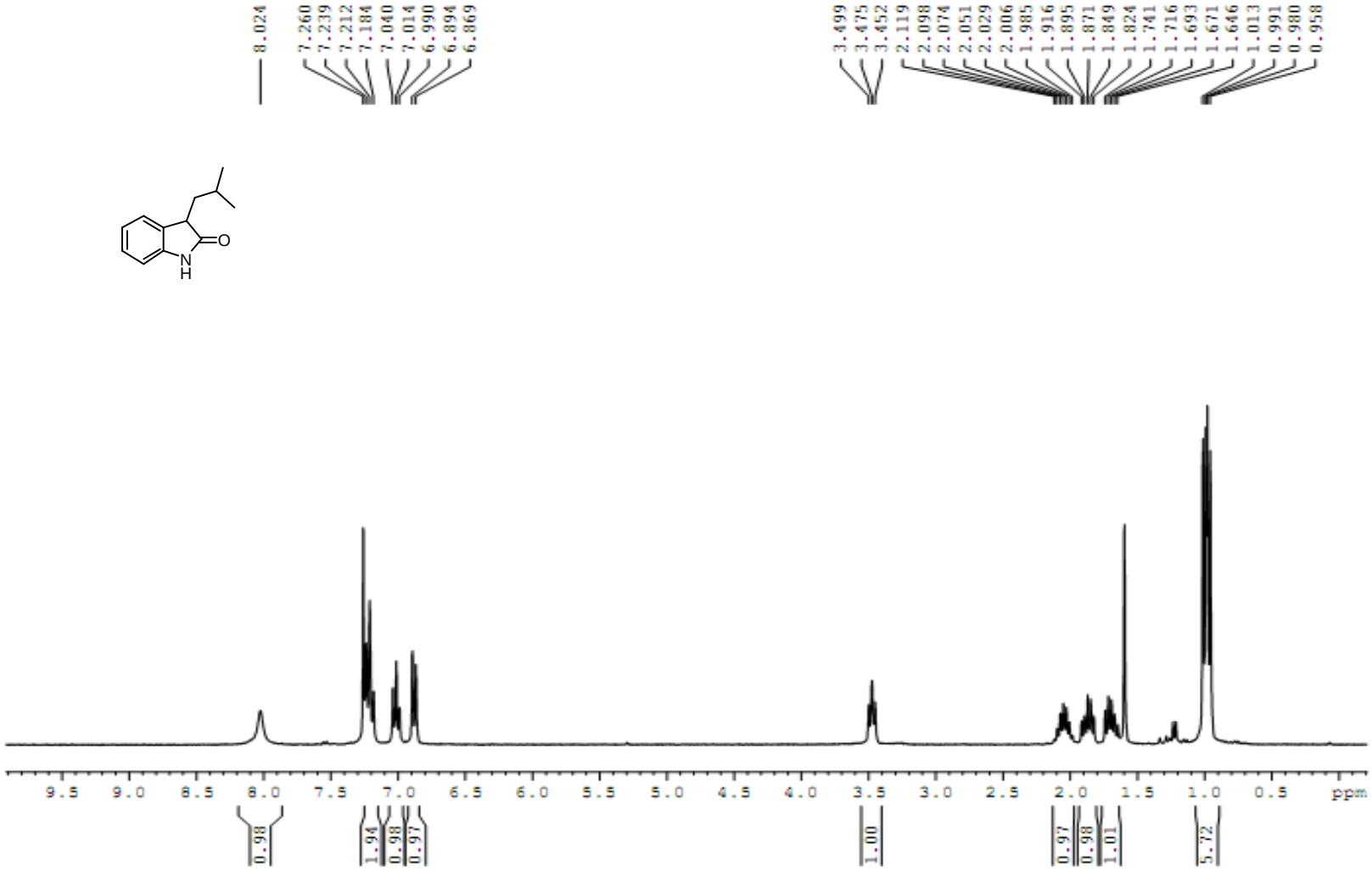
Single-Crystal X-ray Crystollgraphy[6]

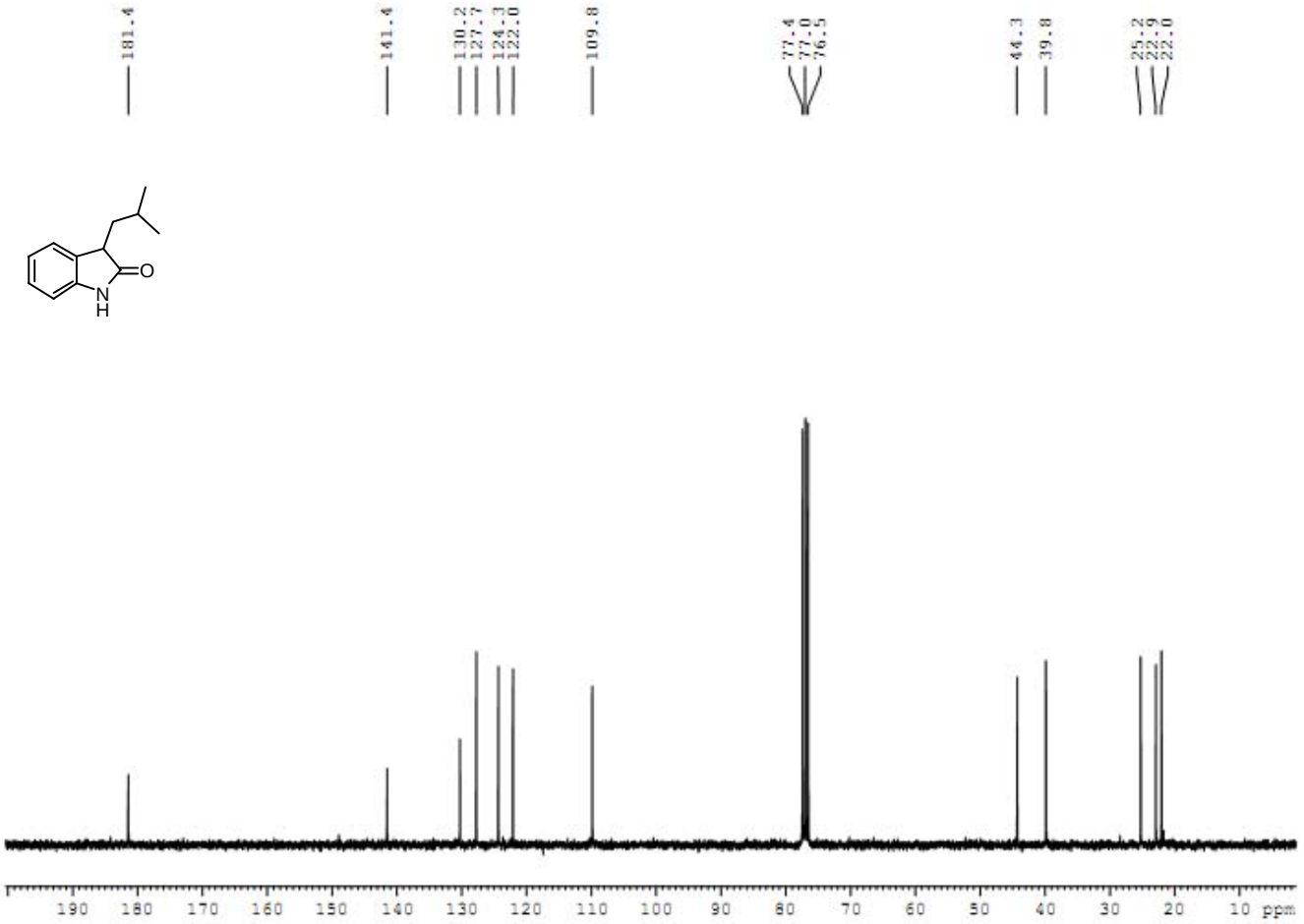
Data intensity of **3j** was collected using a Bruker SMART APEX II (Mo radiation) at 173 K in a cold nitrogen stream. The X-ray condition of was 50 kV × 30 mA. Data collection and reduction were done by using the Bruker ApexII software package. The structures were solved by direct methods and refined by full-matrix least-squares on F^2 with anisotropic displacement parameters for non-H atoms using SHELX-97. Hydrogen atoms were added at their geometrically idea positions and refined isotropically. Crystal data for **3j**: $C_{23}H_{26}BrN_3O_5$, T = 173 K, Triclinic, space group $P\bar{1}$ (No. 2), a = 9.0411(3) Å, b = 12.0586(4) Å, c = 12.8583(4) Å, α = 115.626 (1), β = 92.778 (1), γ = 107.037 (1), V = 1183.27(7) Å^3. Z = 2, d_{calc} = 1.416 mg/m^3 and μ = 1.775 mm^{-1}. Total number of reflections 13845 (R_{int} = 0.0198), R_1 = 0.0404, wR_2 = 0.1107 (all data), GOF = 1.027, and 289 parameters.

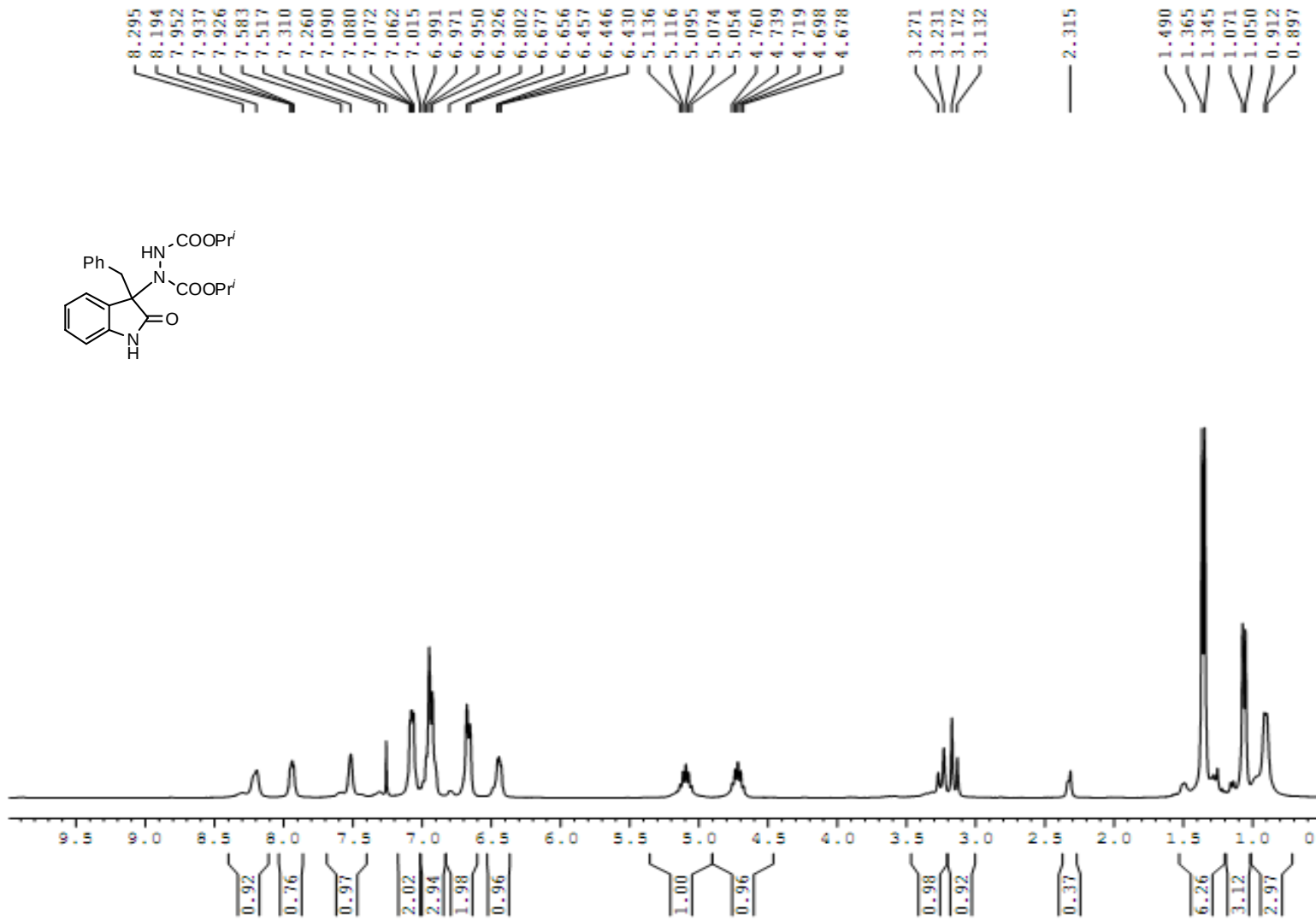


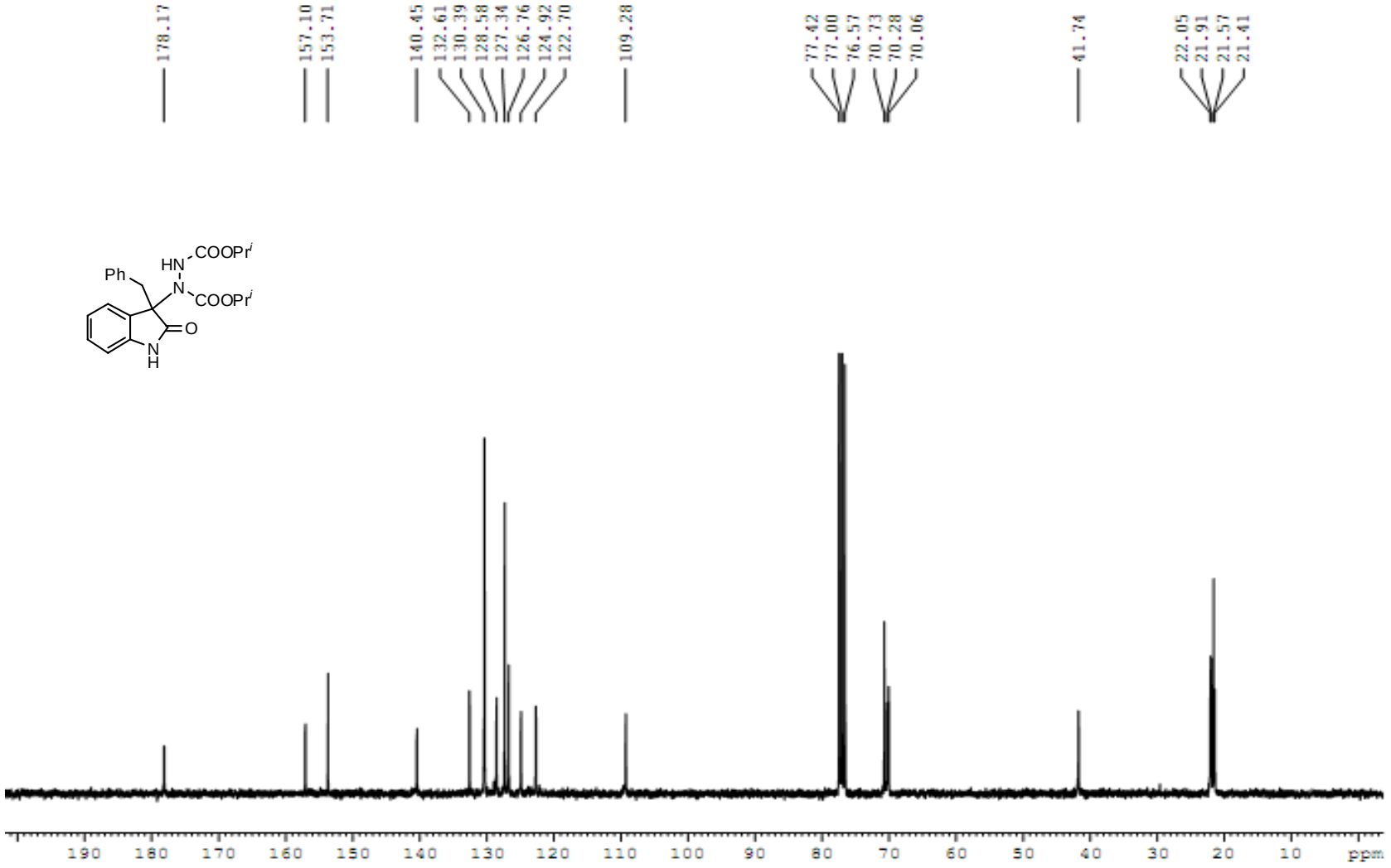


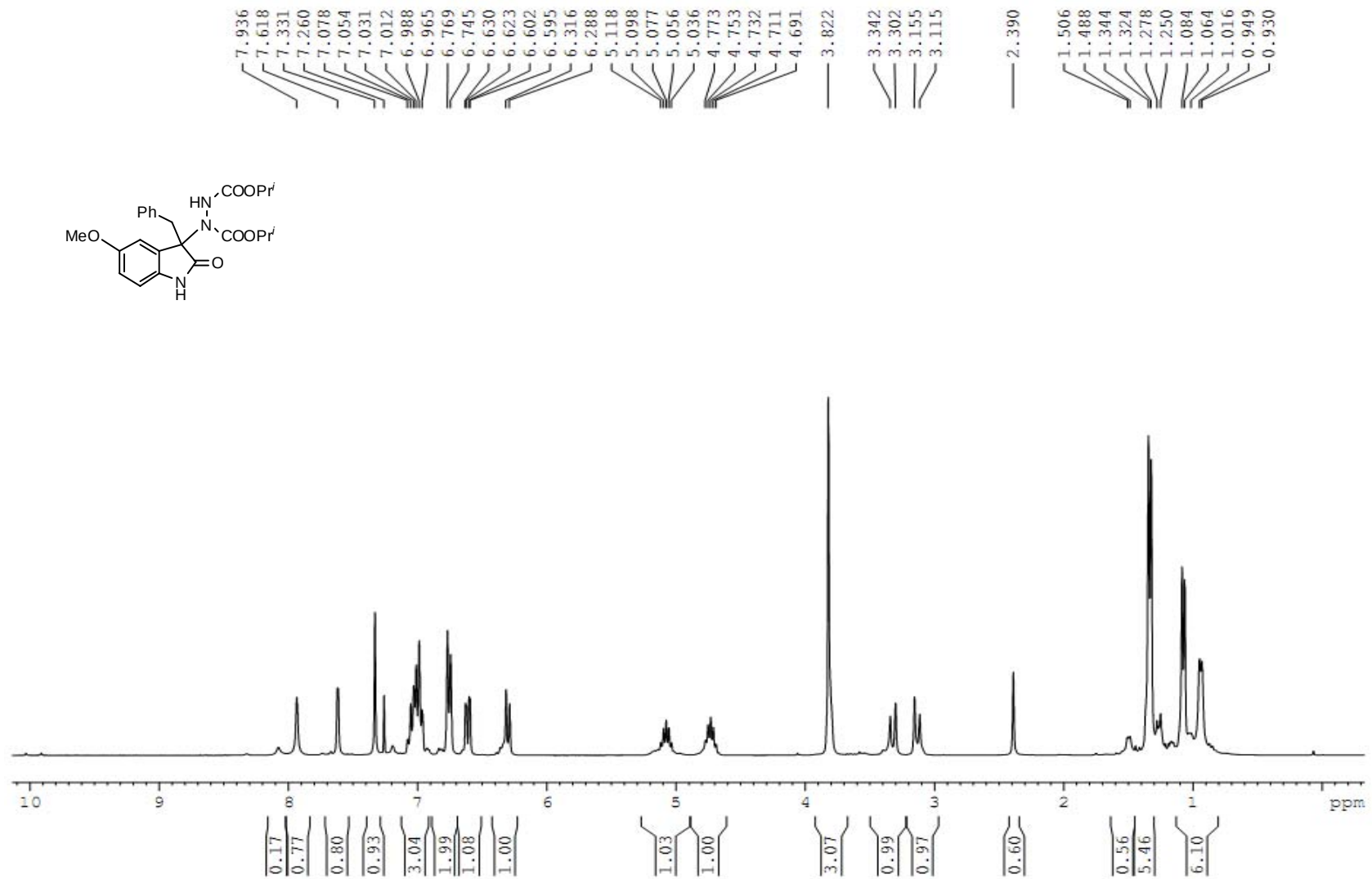
[6] Supplementary crystallographic data have been deposited at the Cambridge Crystallographic Data Center. (CCDC 739060)

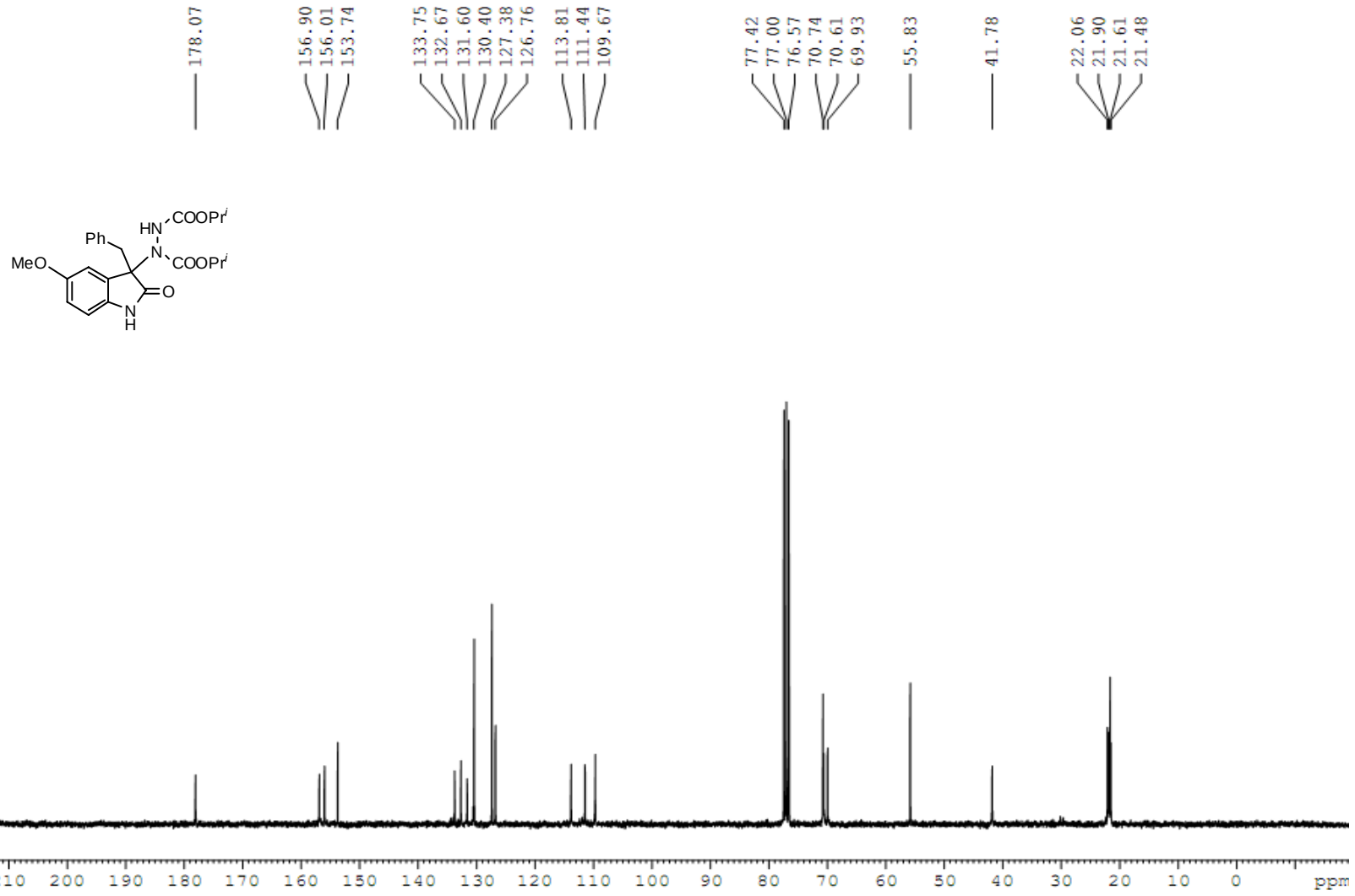


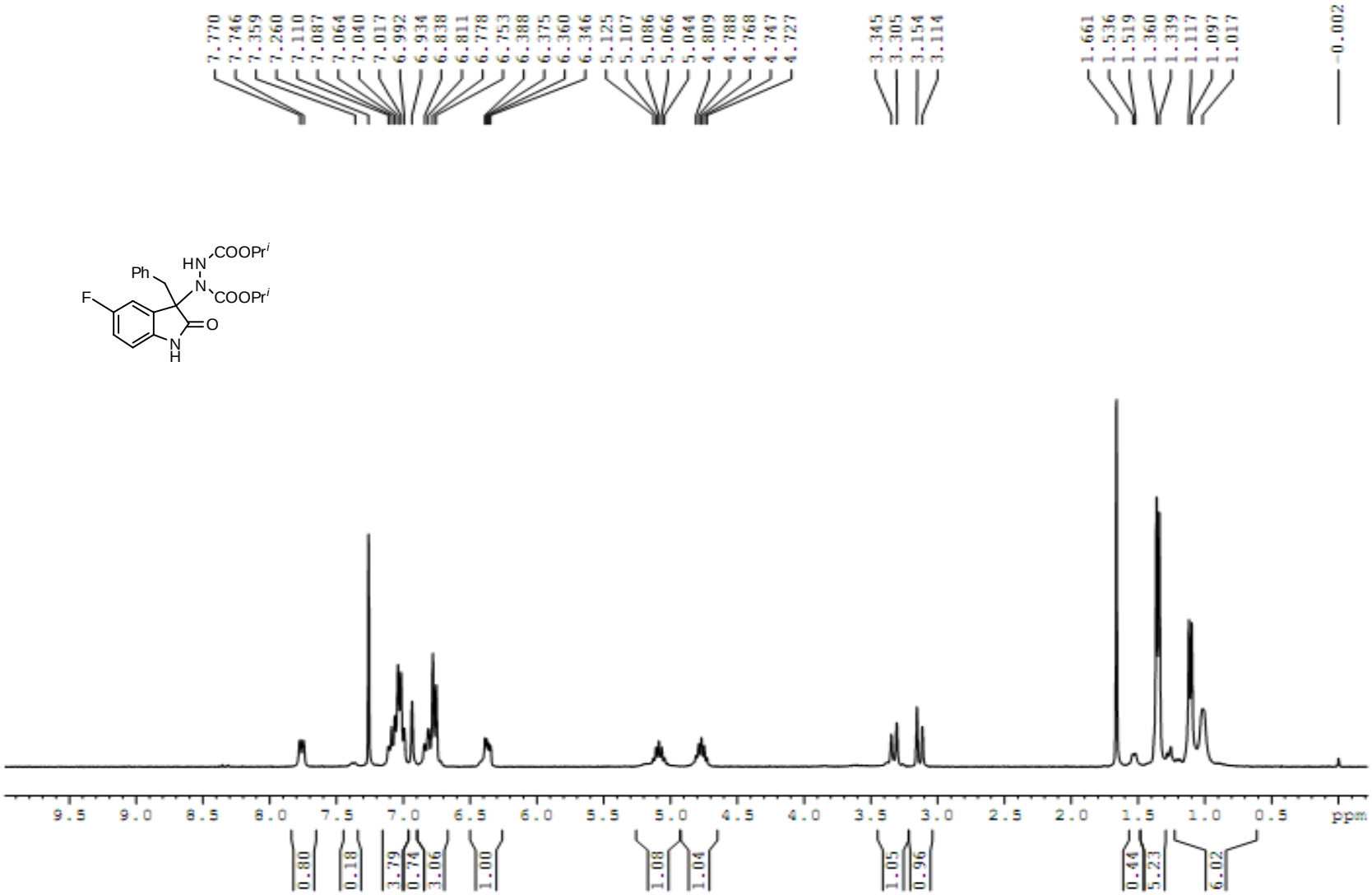








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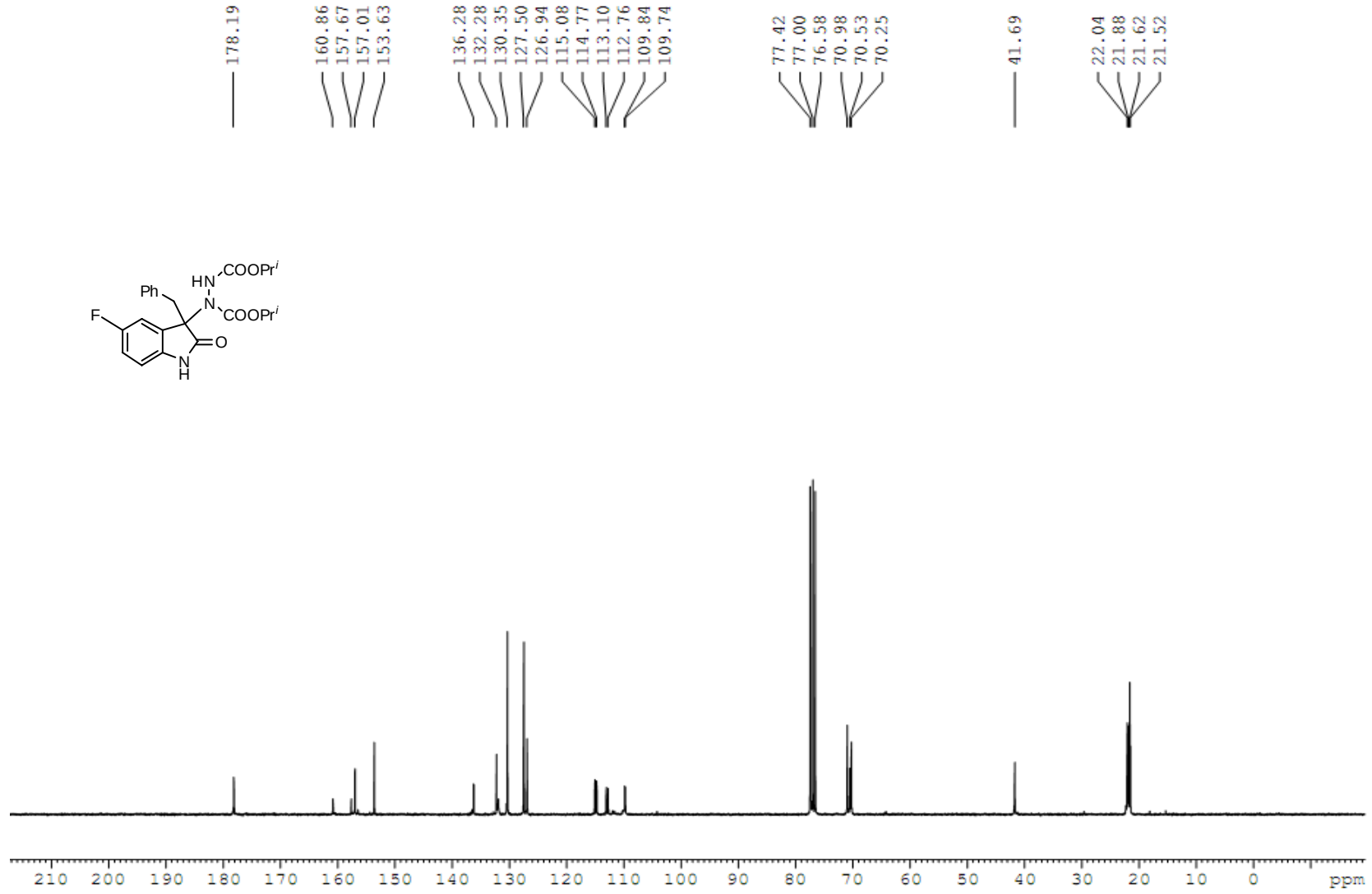

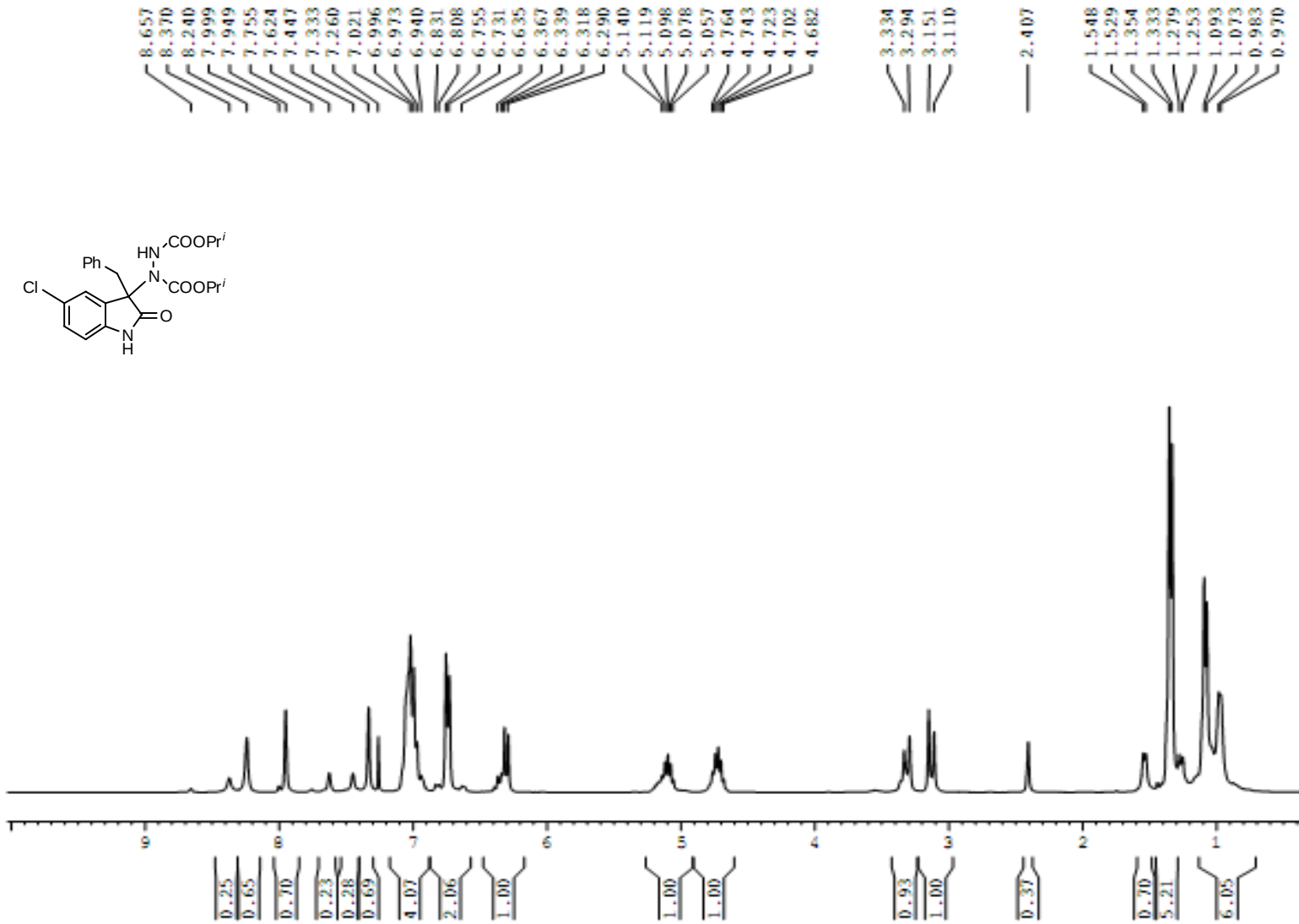

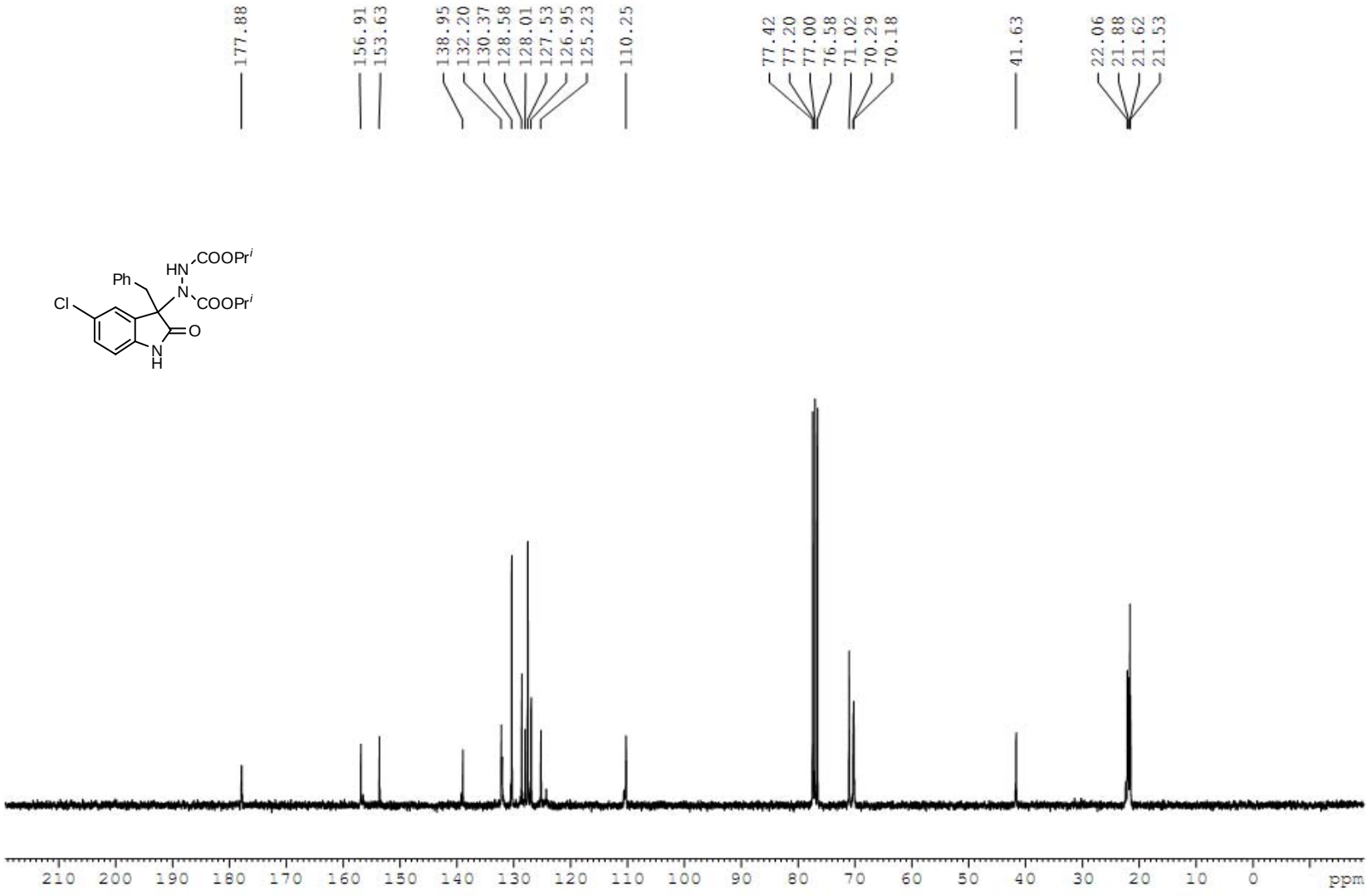

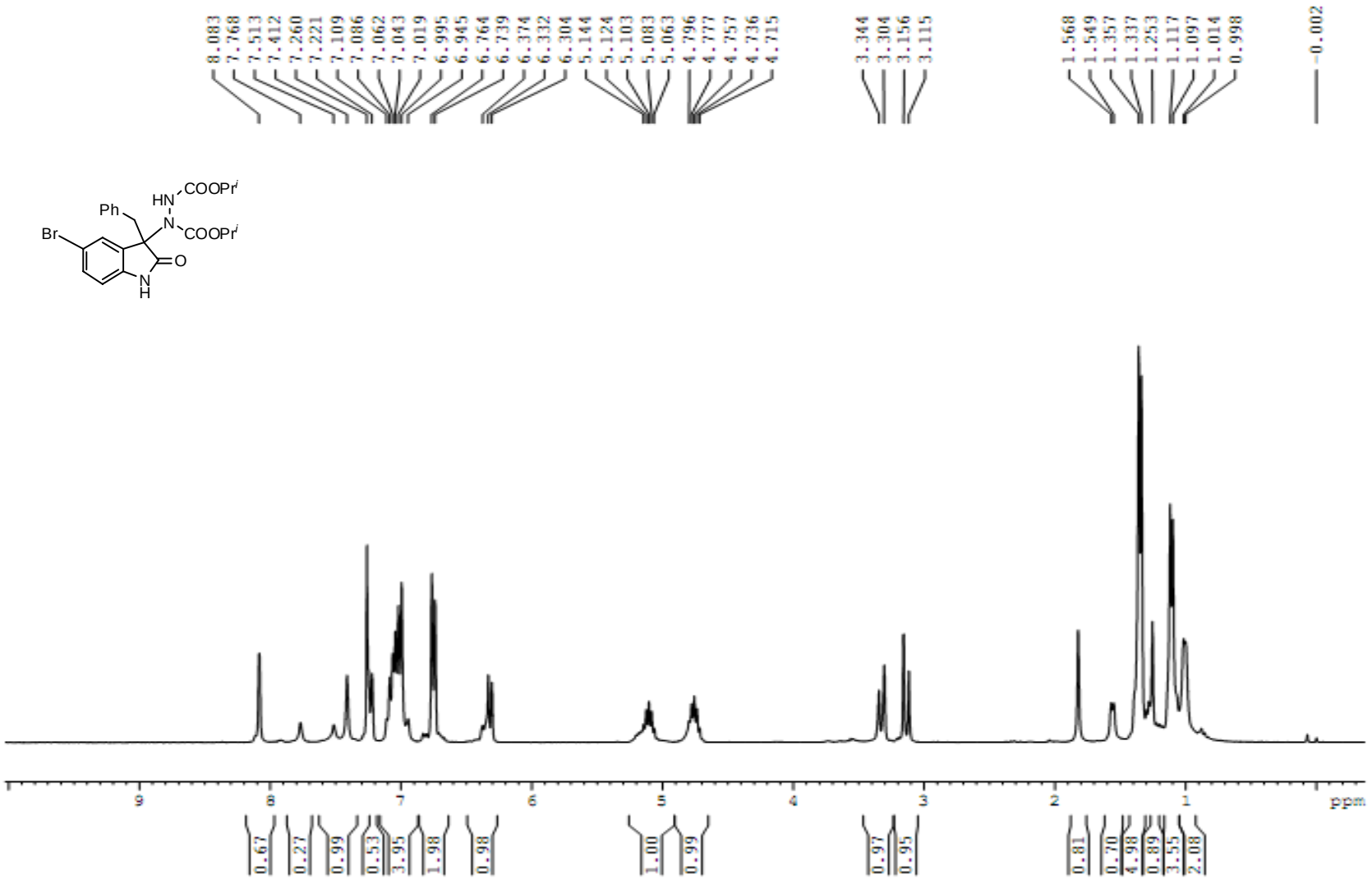

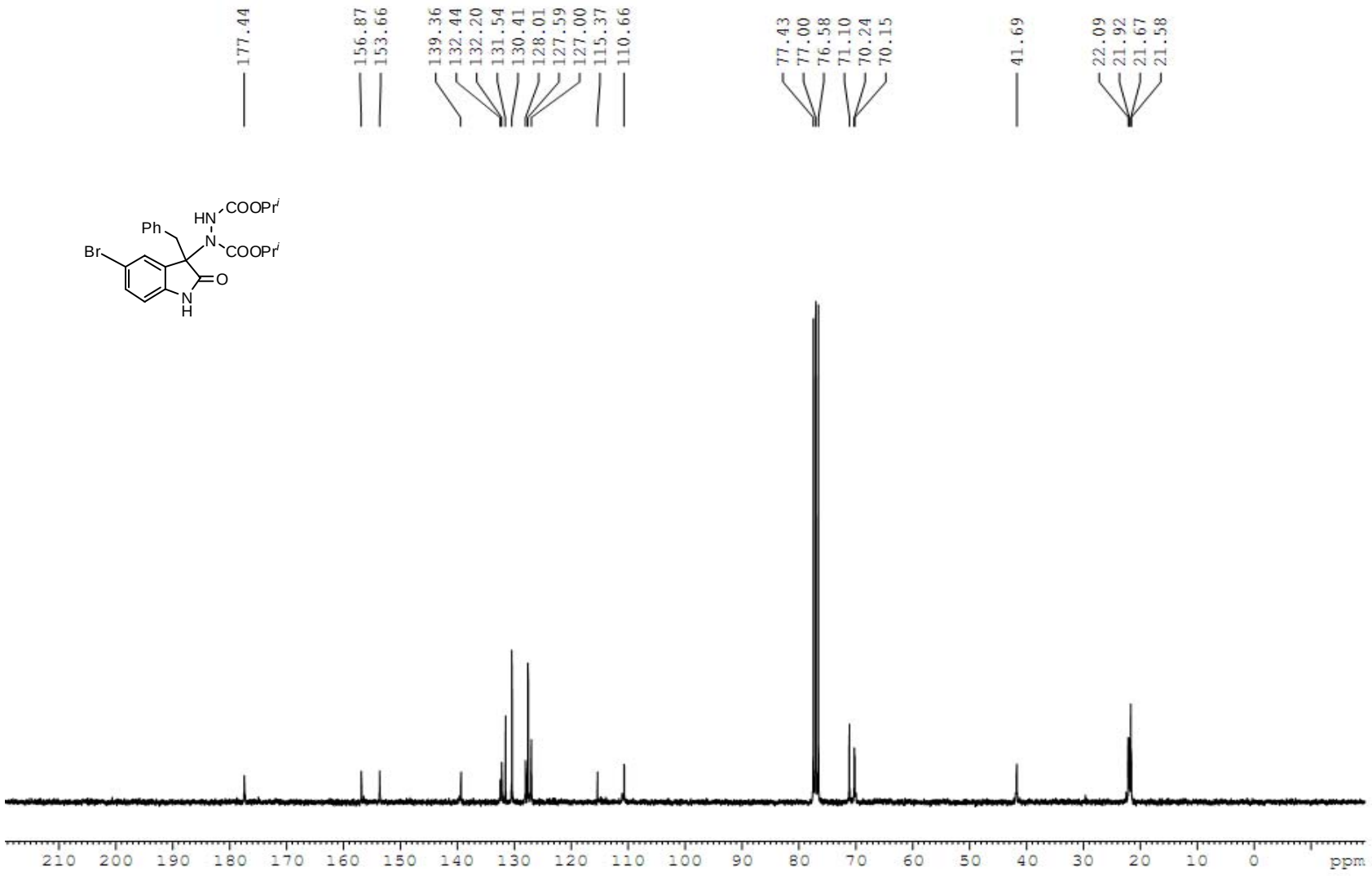

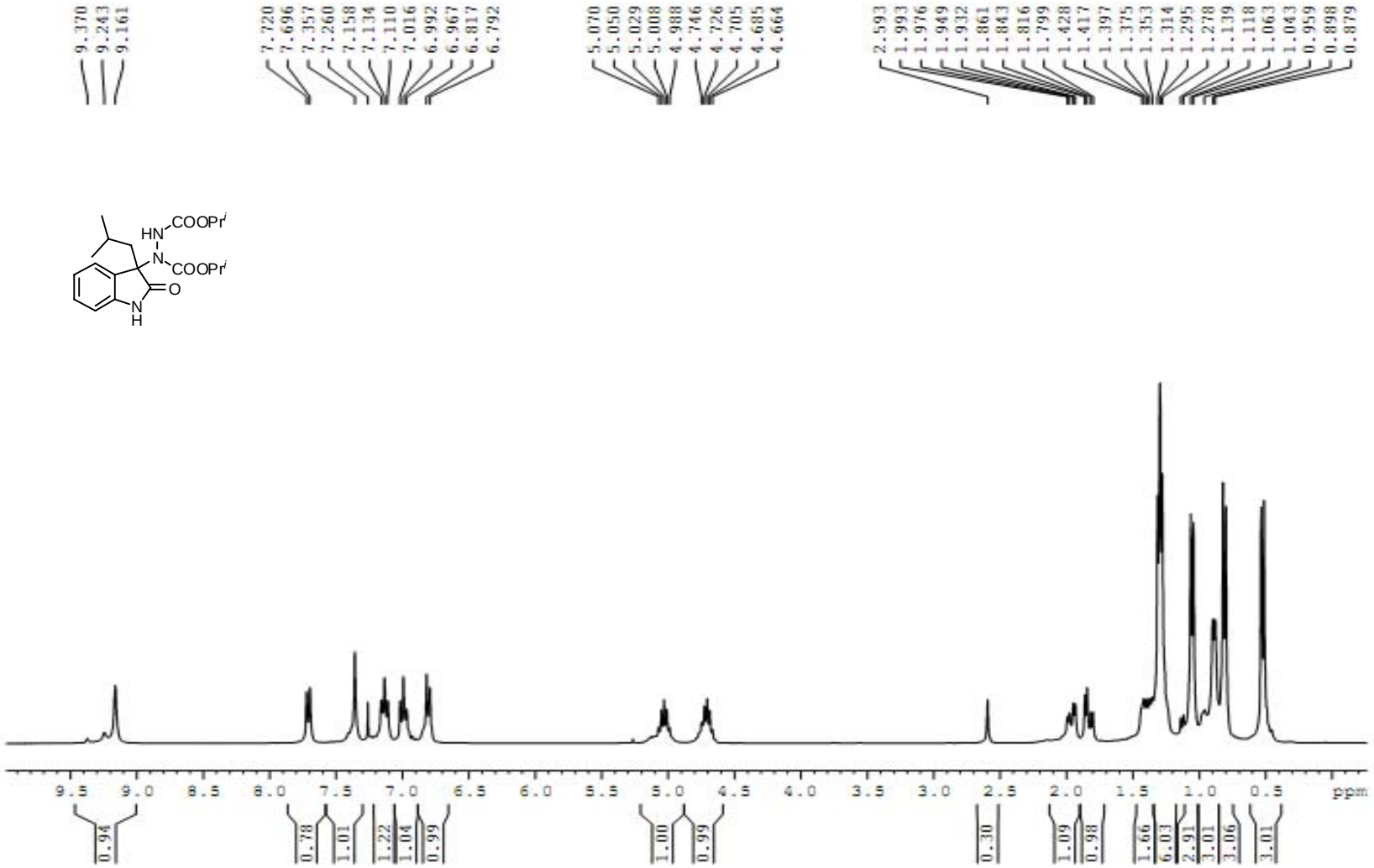
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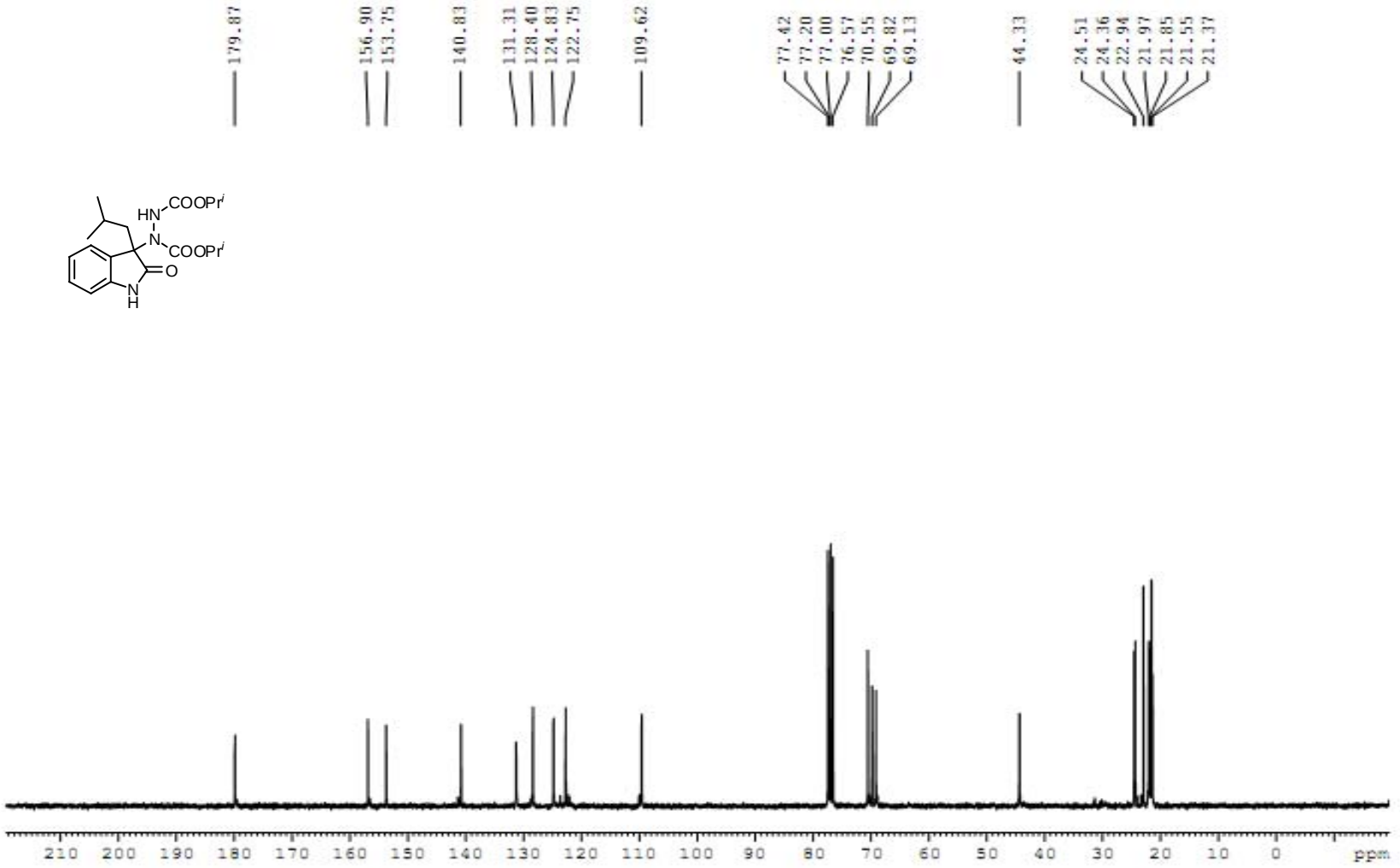

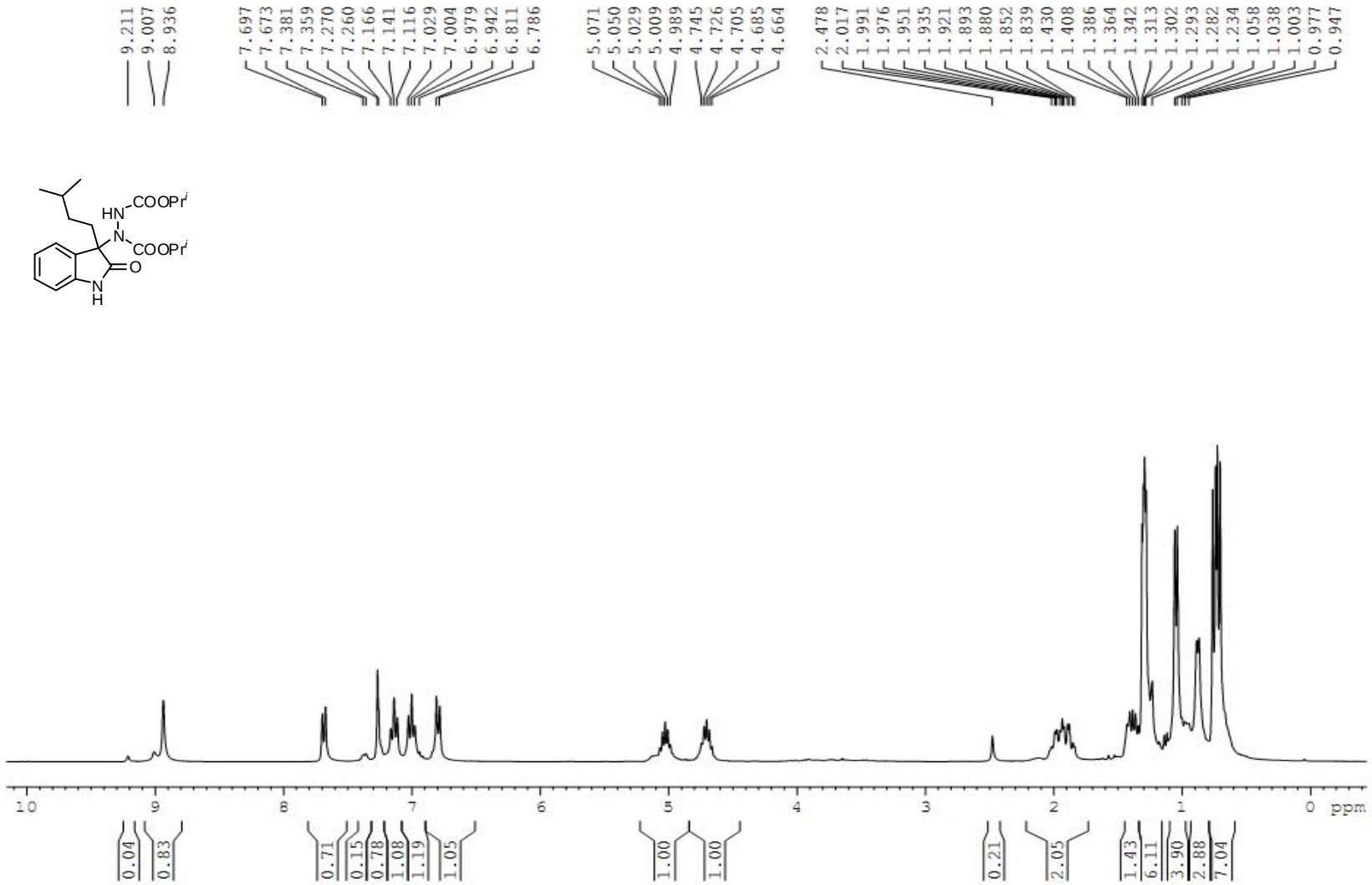

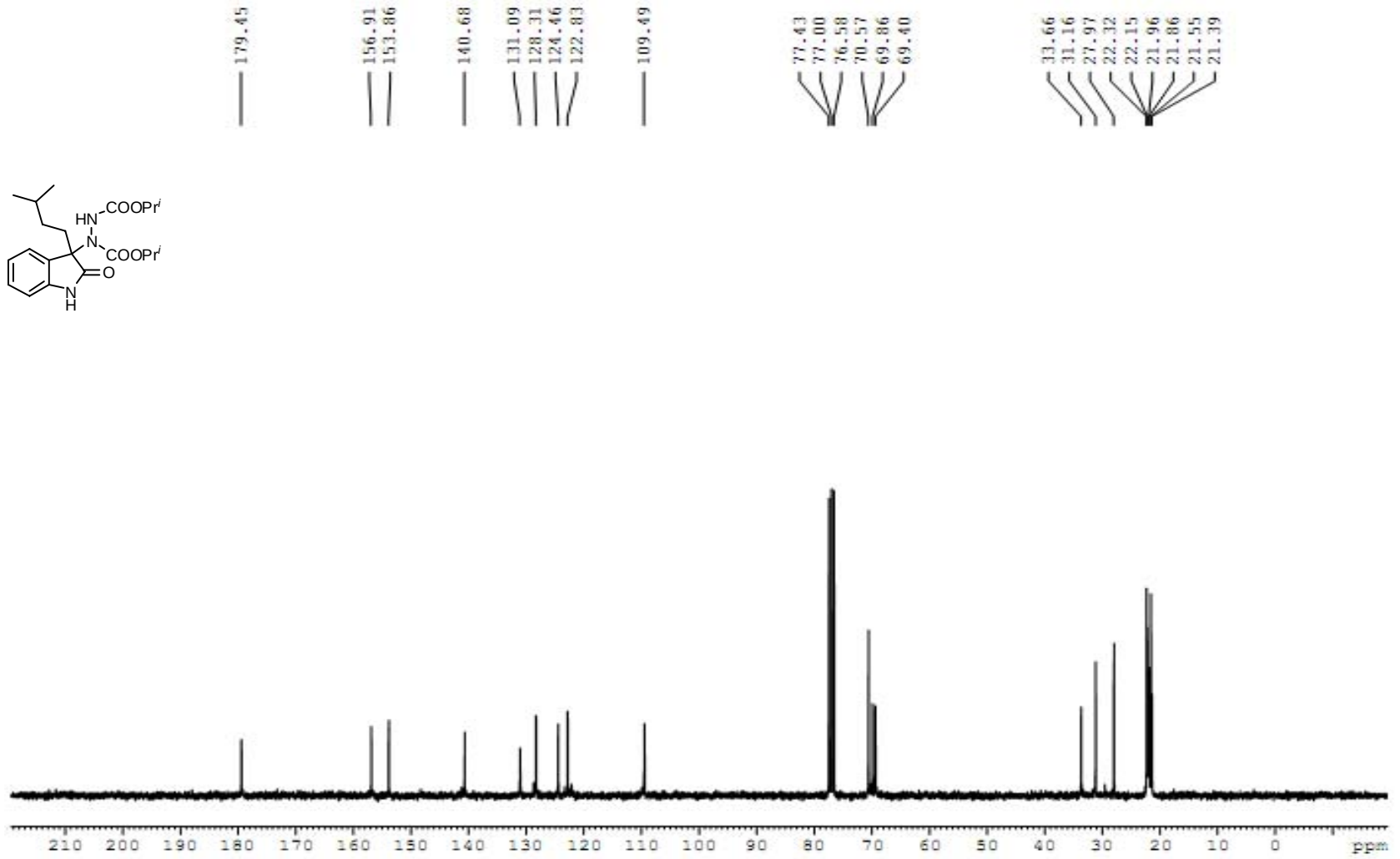

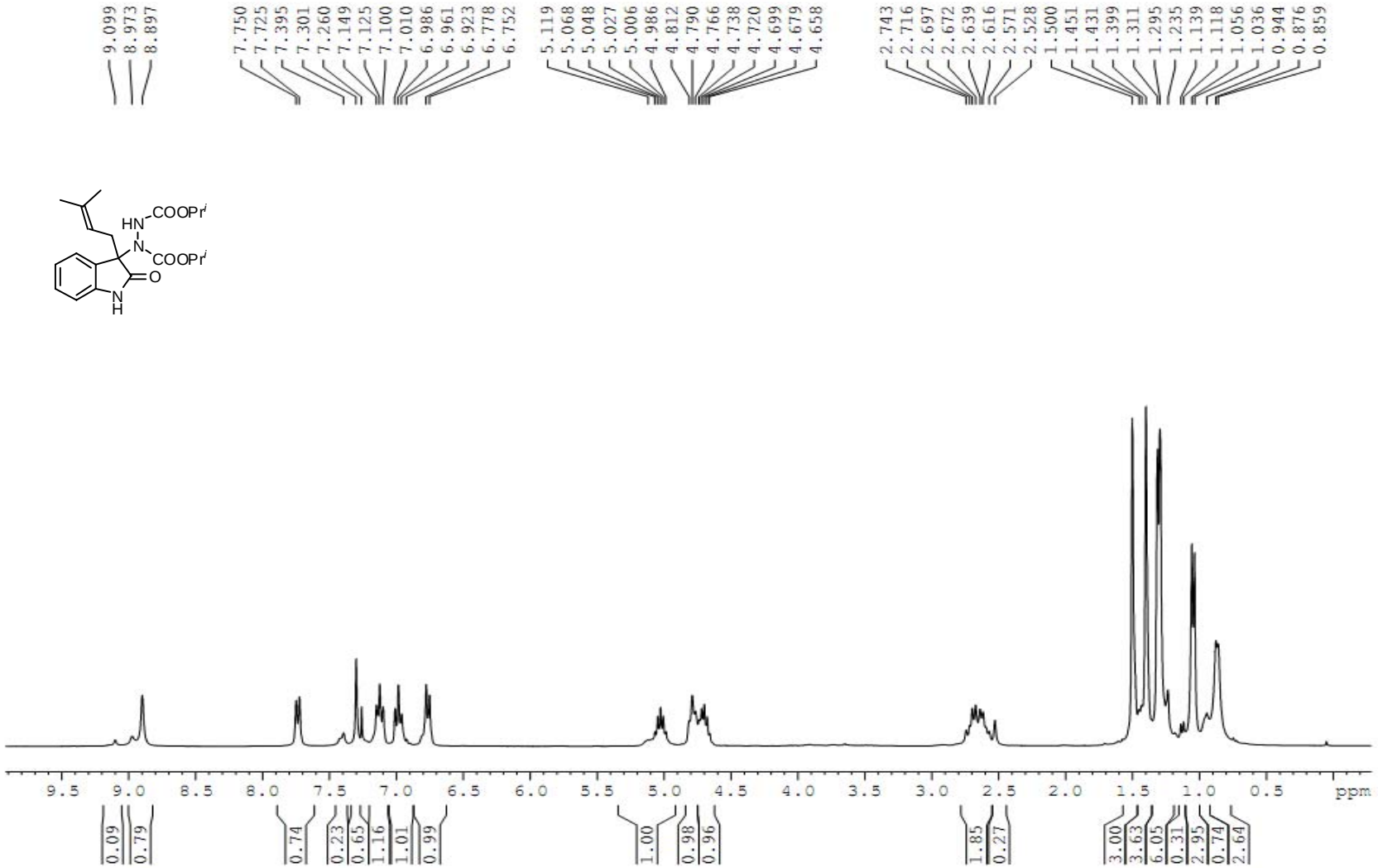
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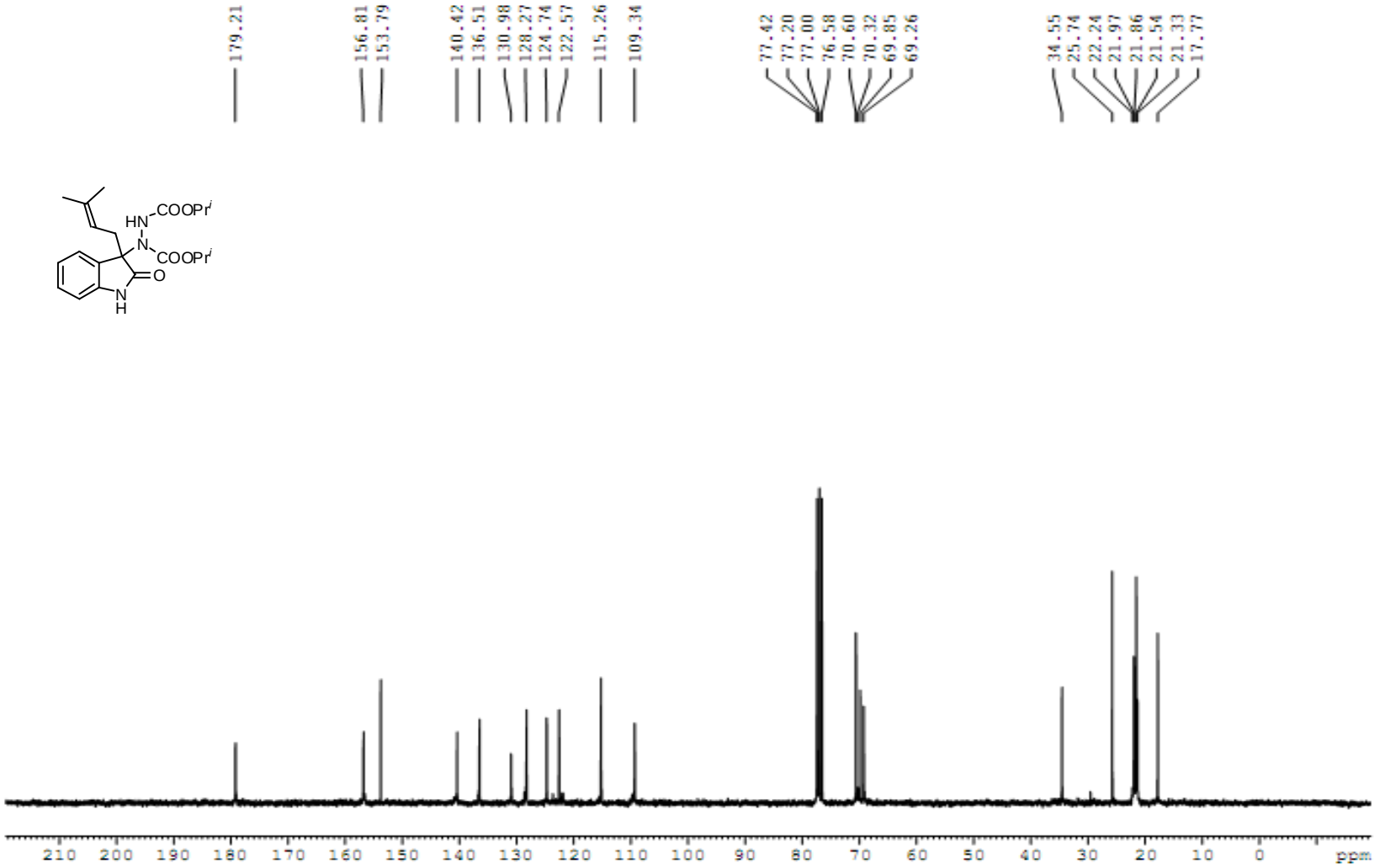

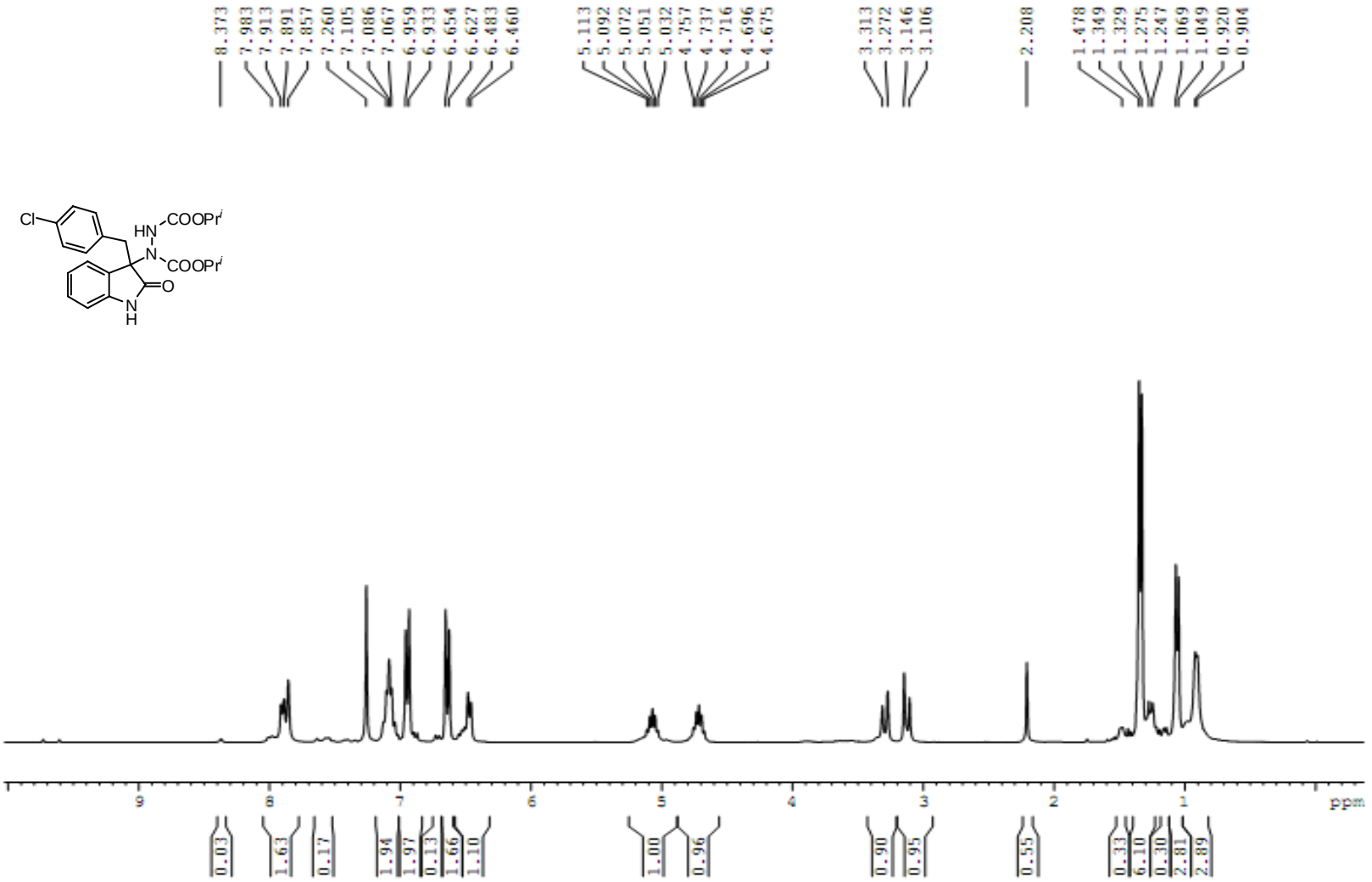

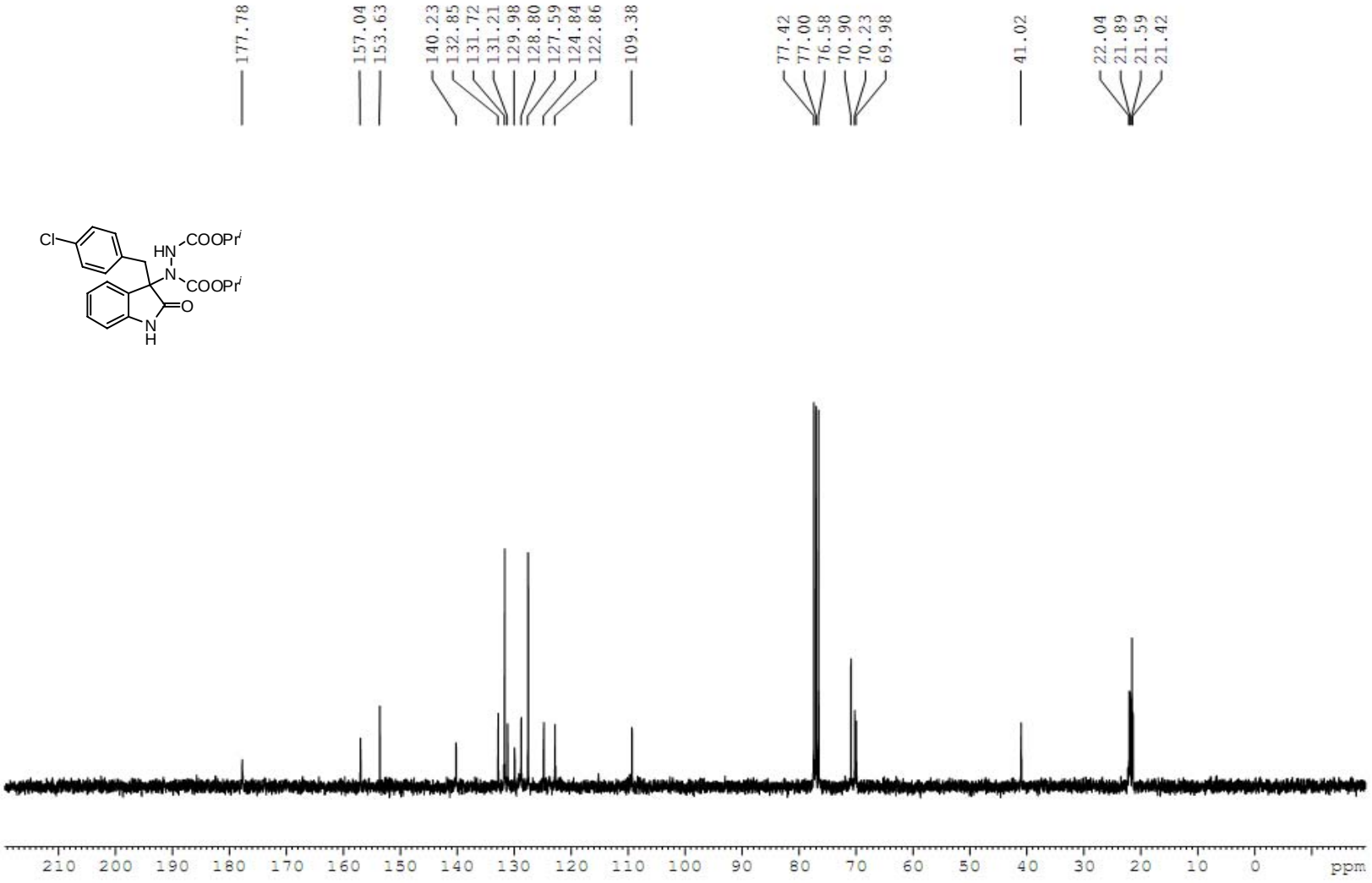

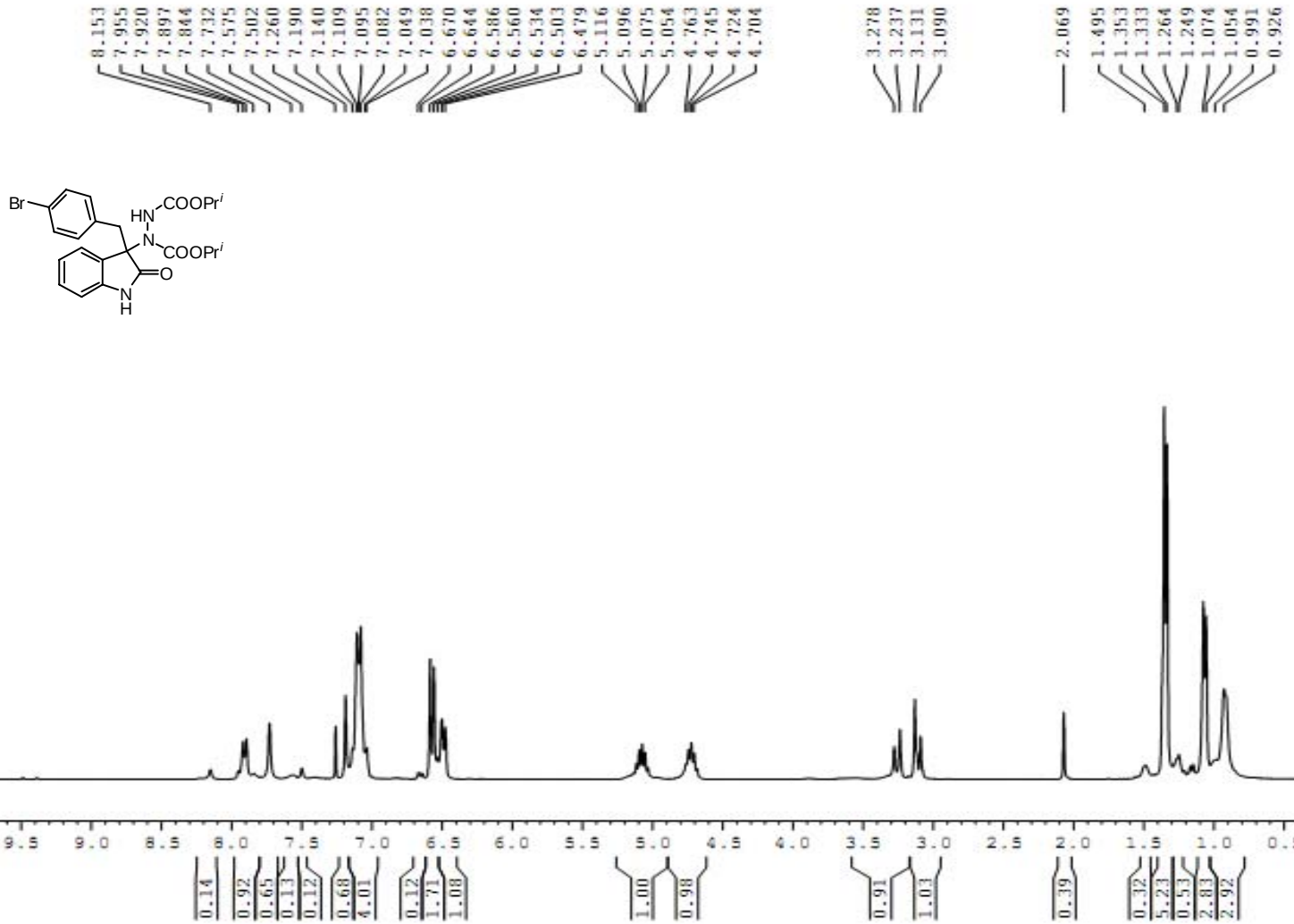

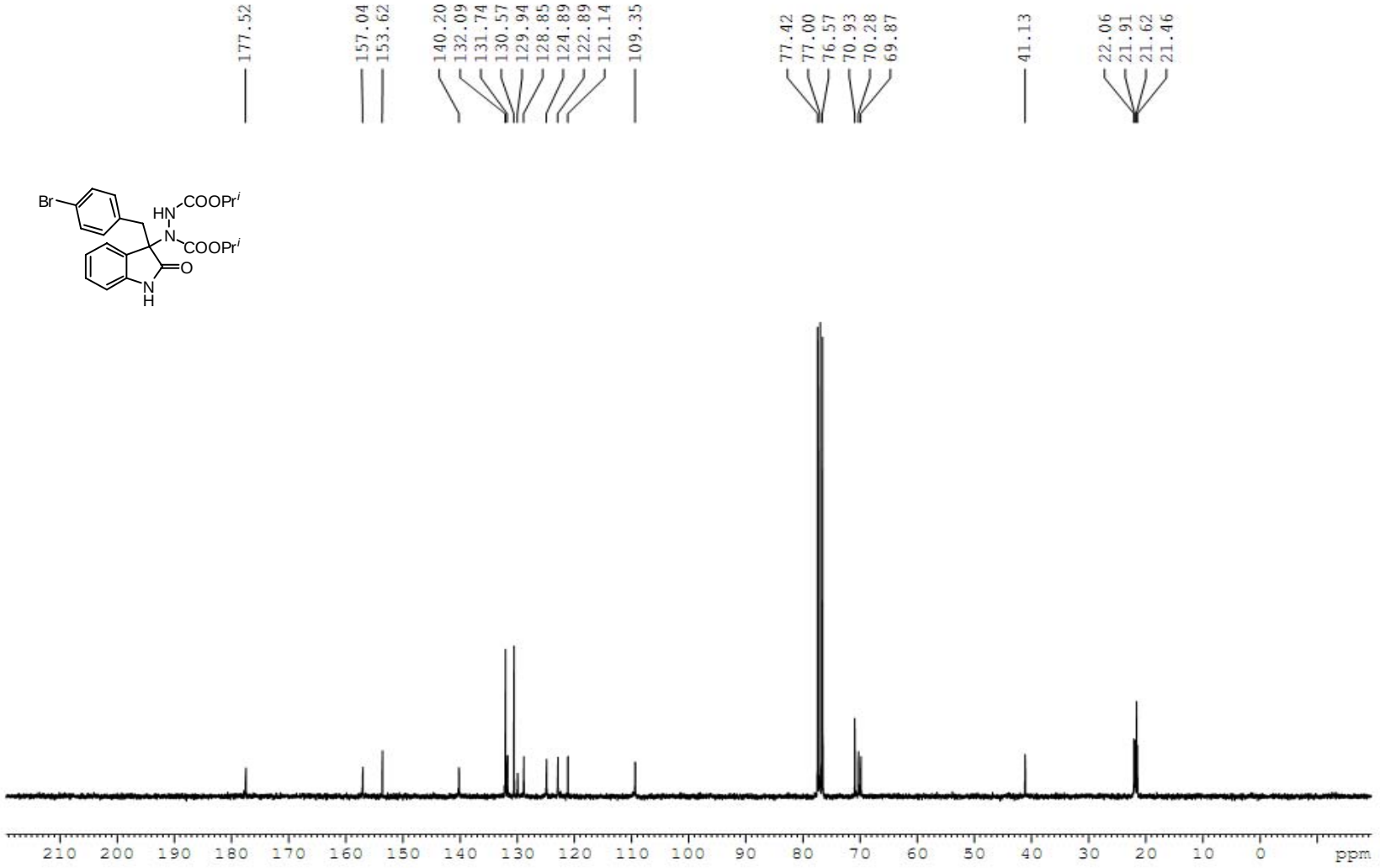

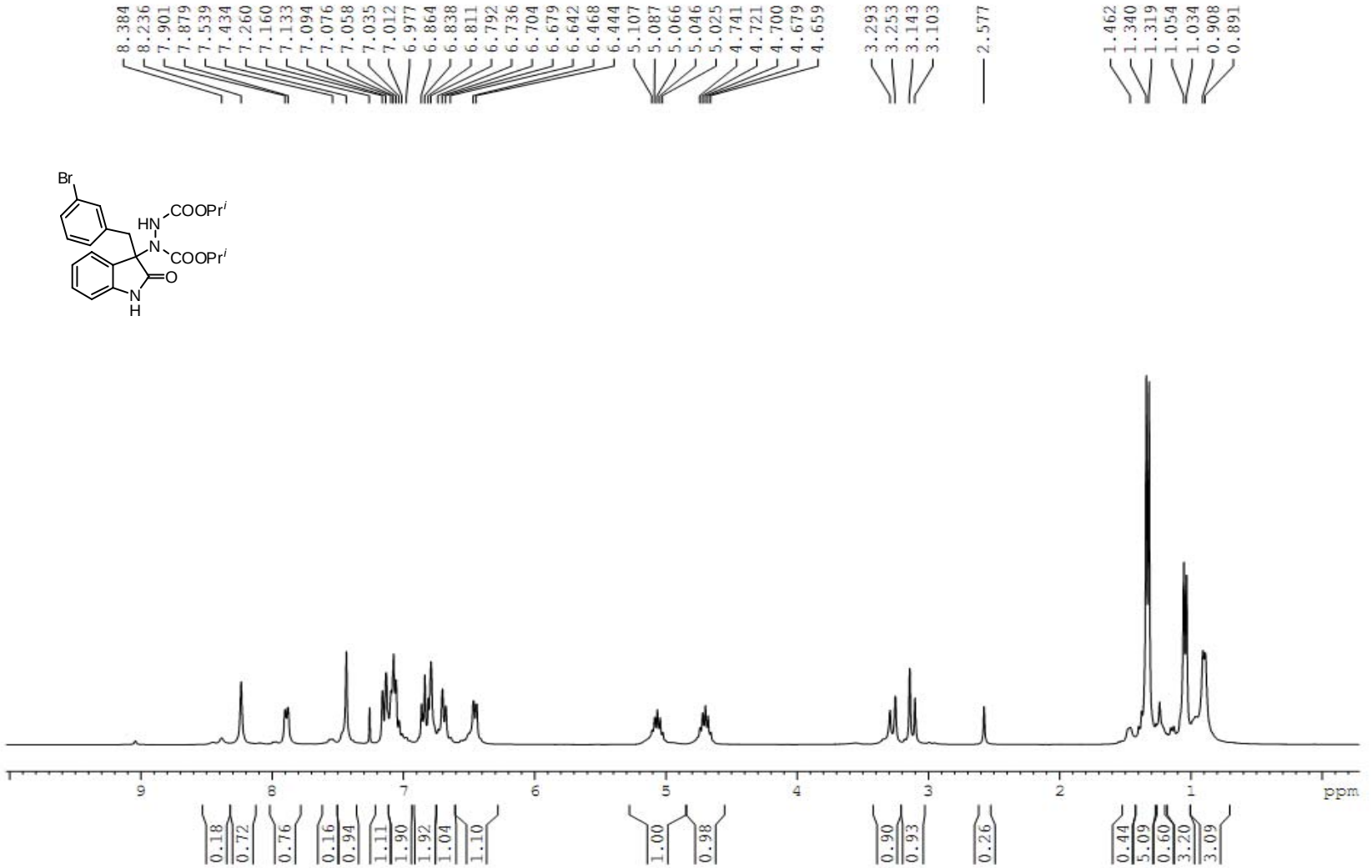

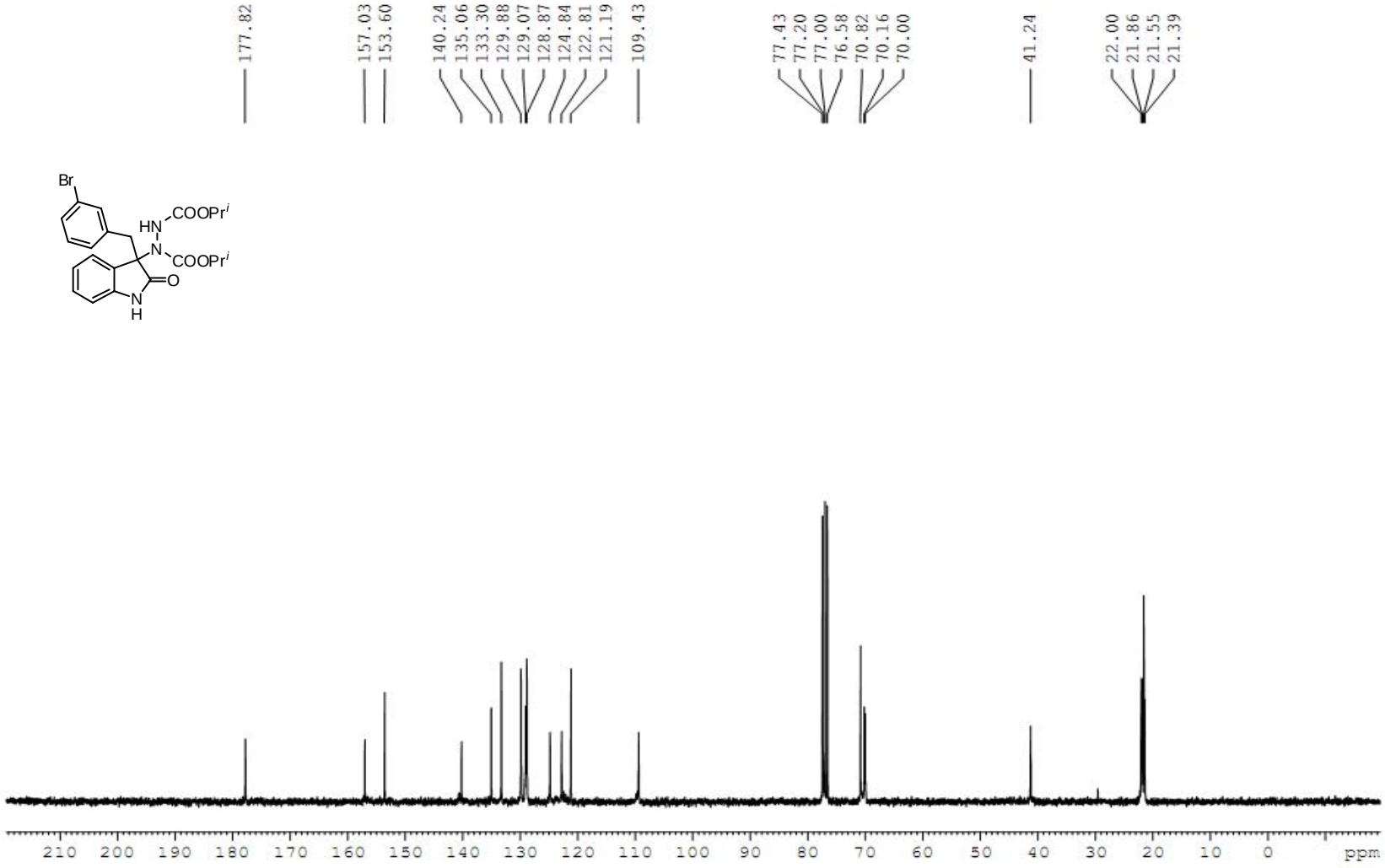

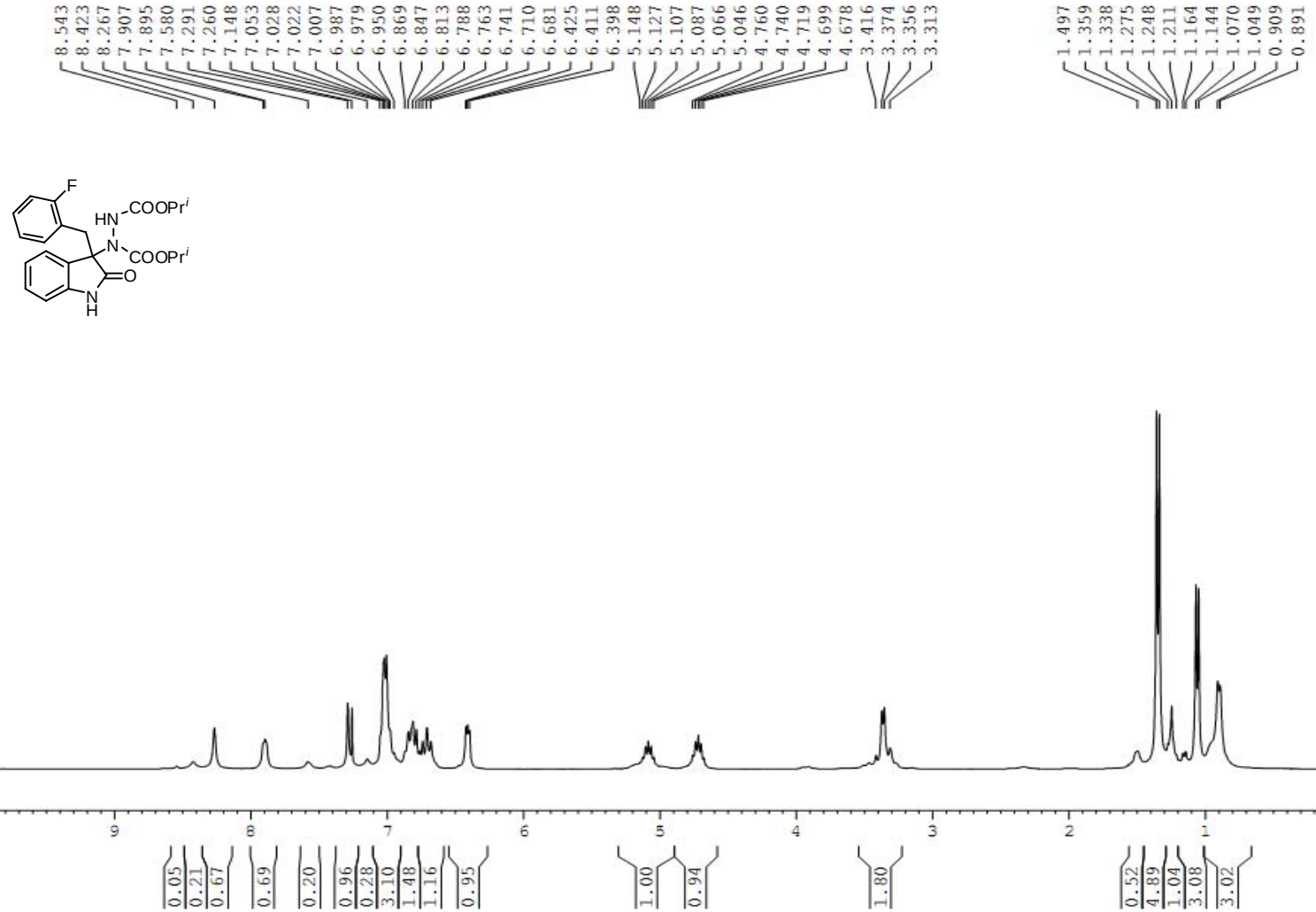

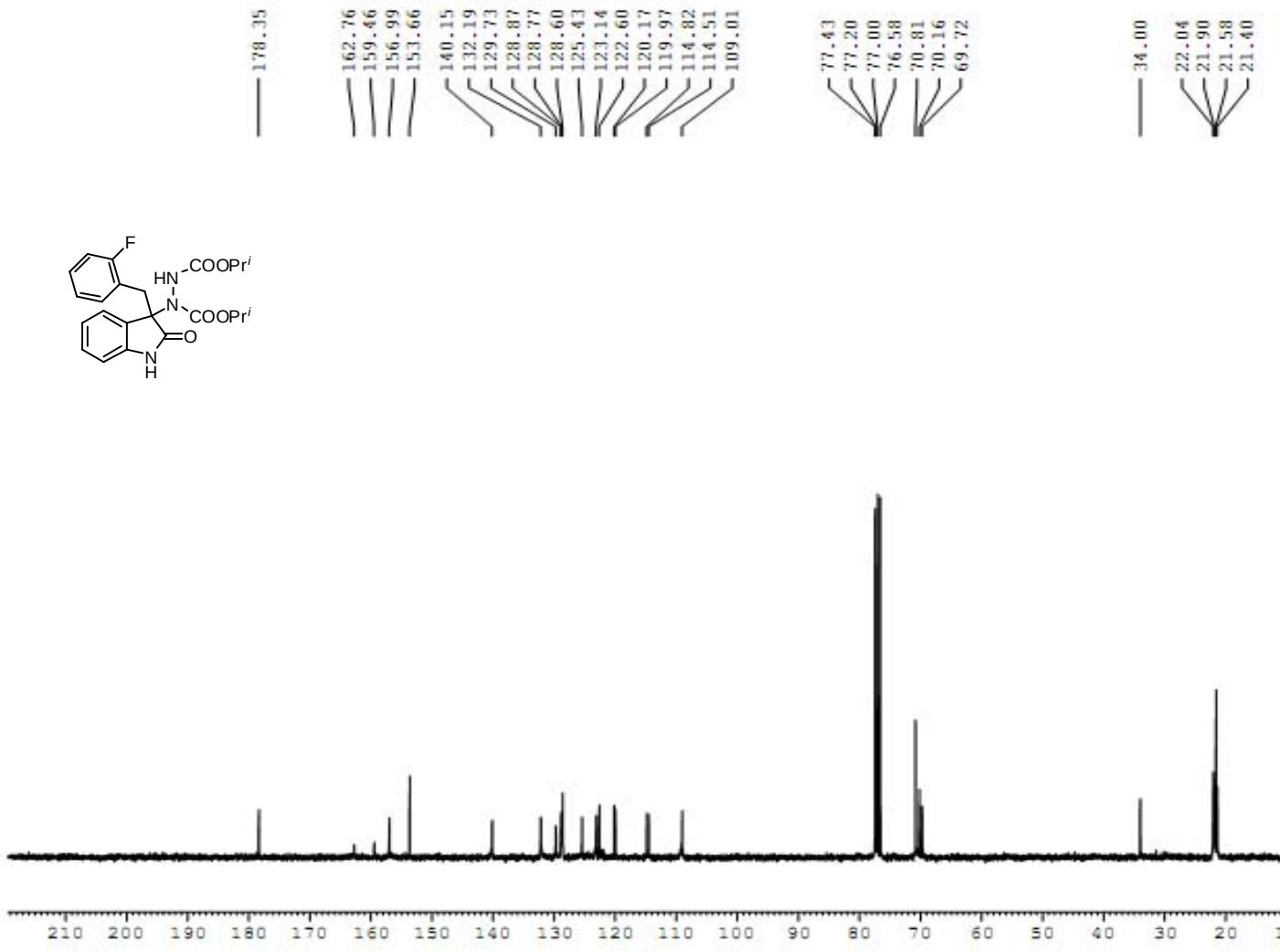

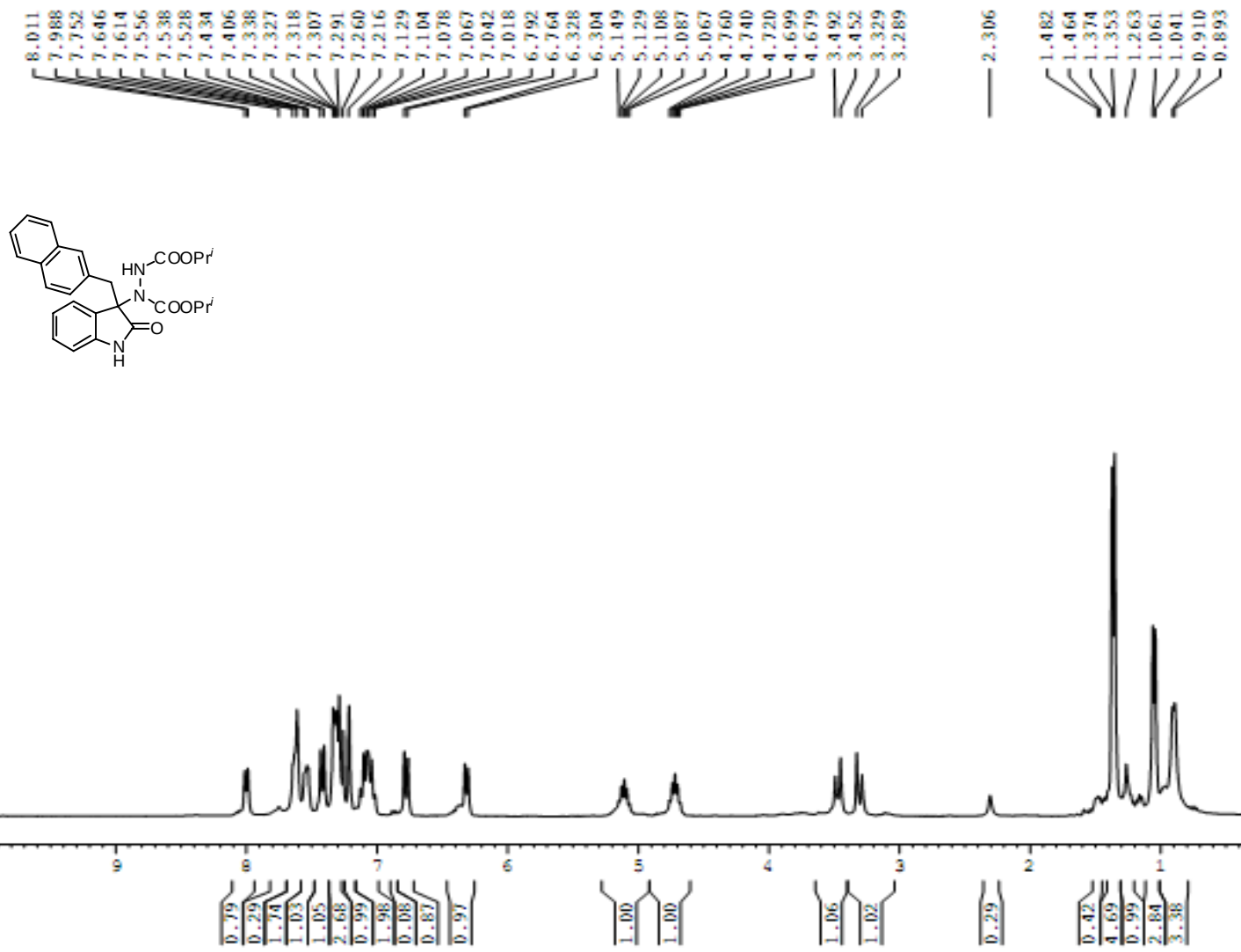

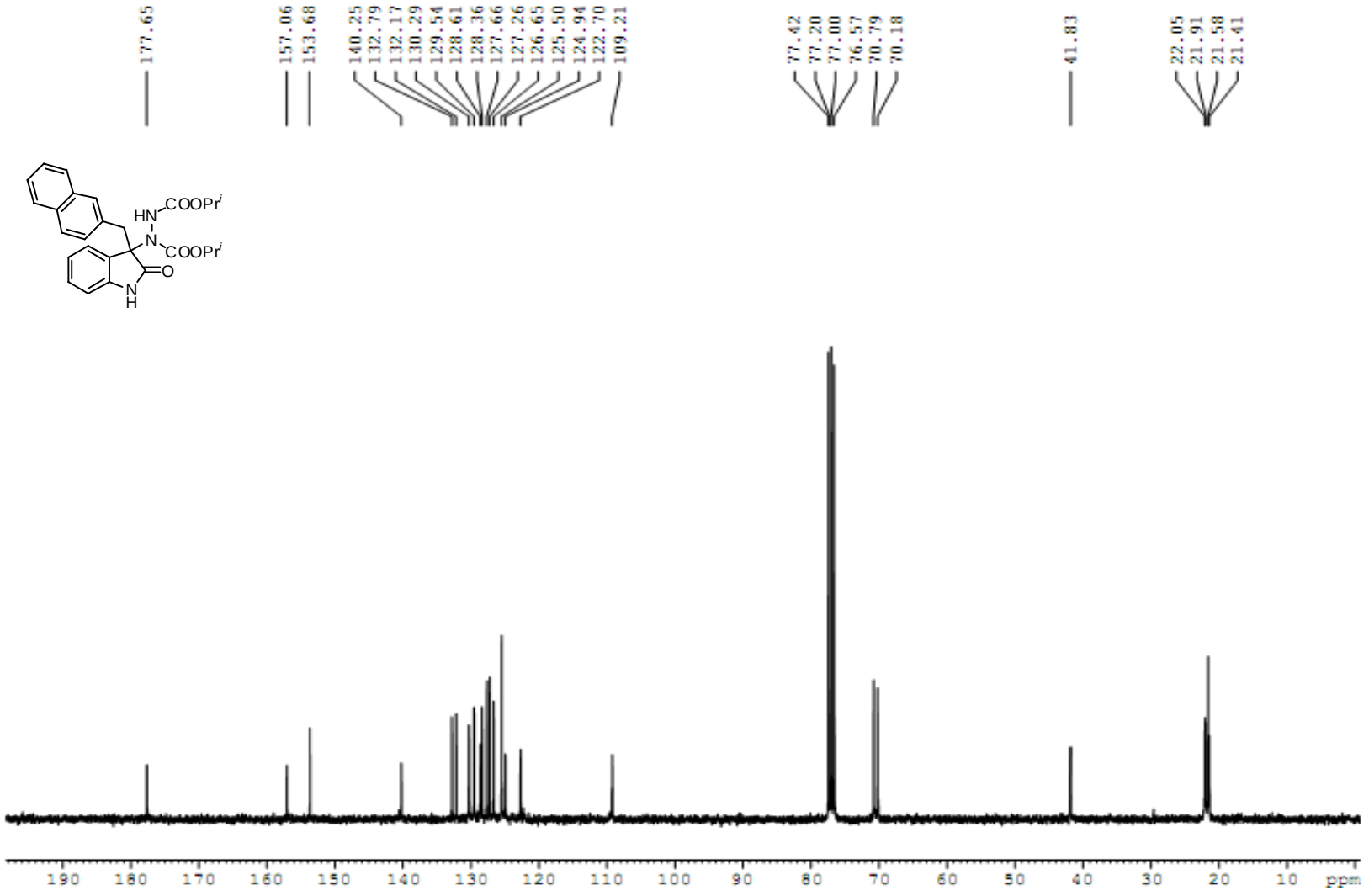

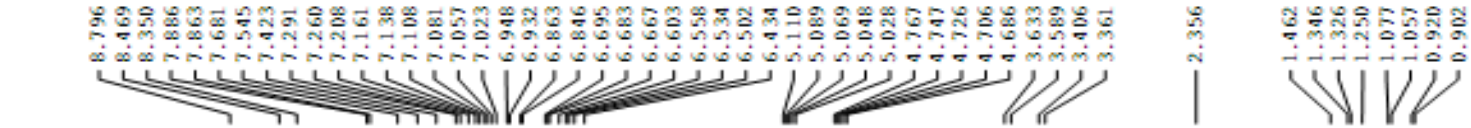

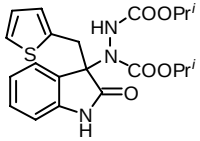

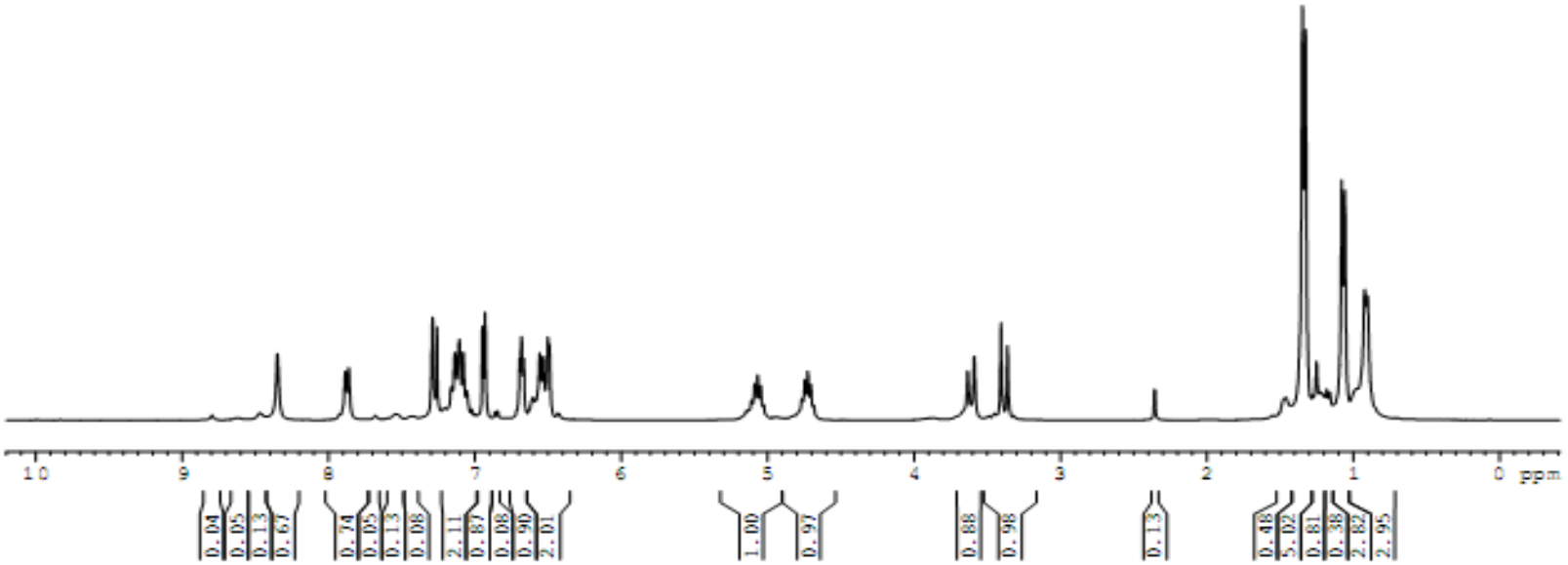

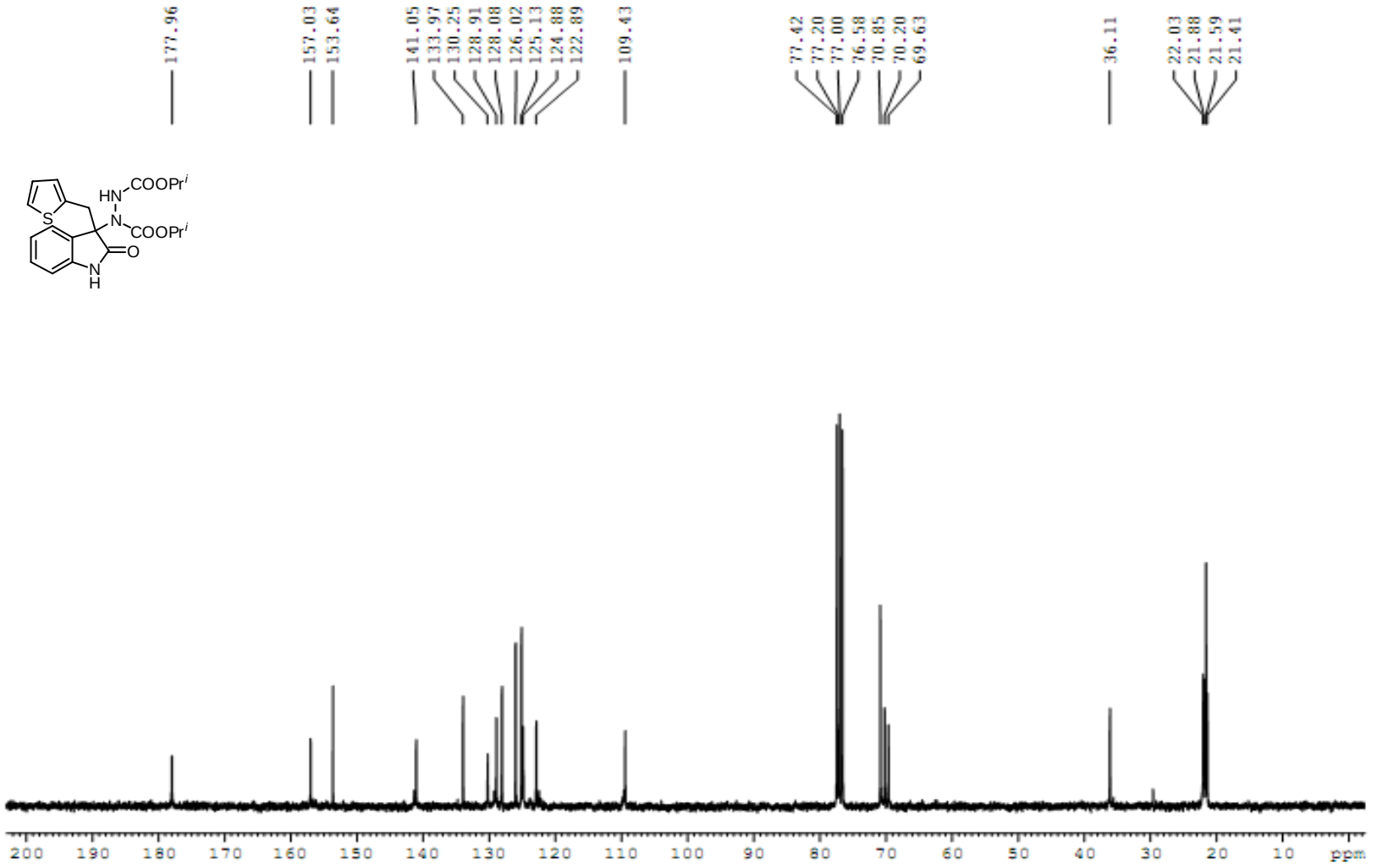

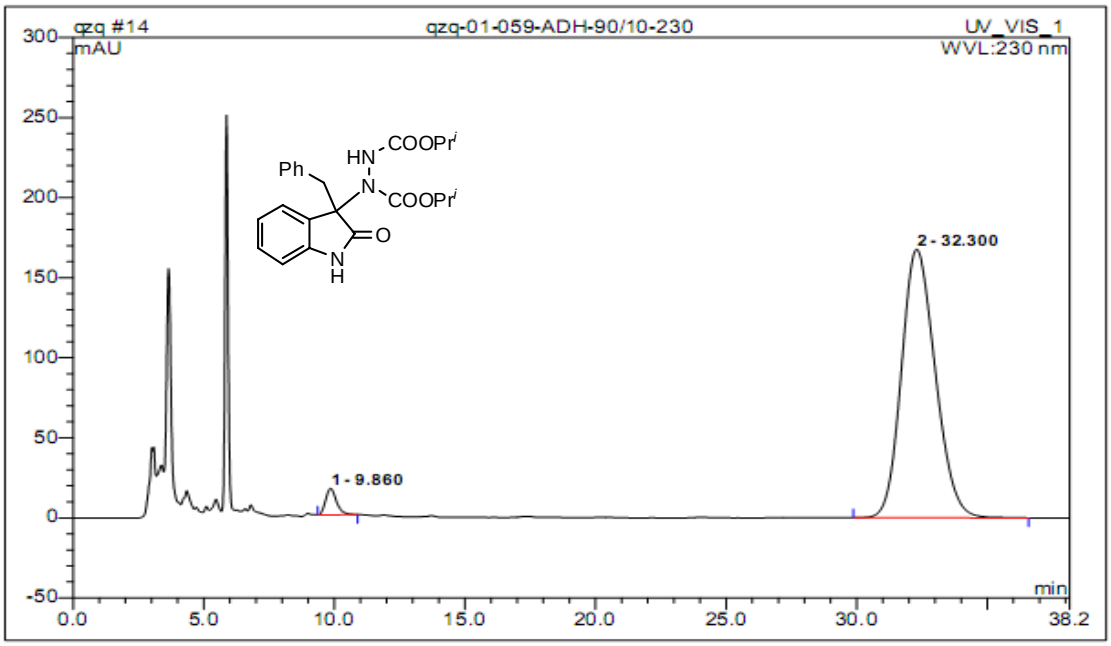

No.	Ret.Time min	Peak Name	Height mAU	Area mAU*min	Rel.Area %	Amount	Type
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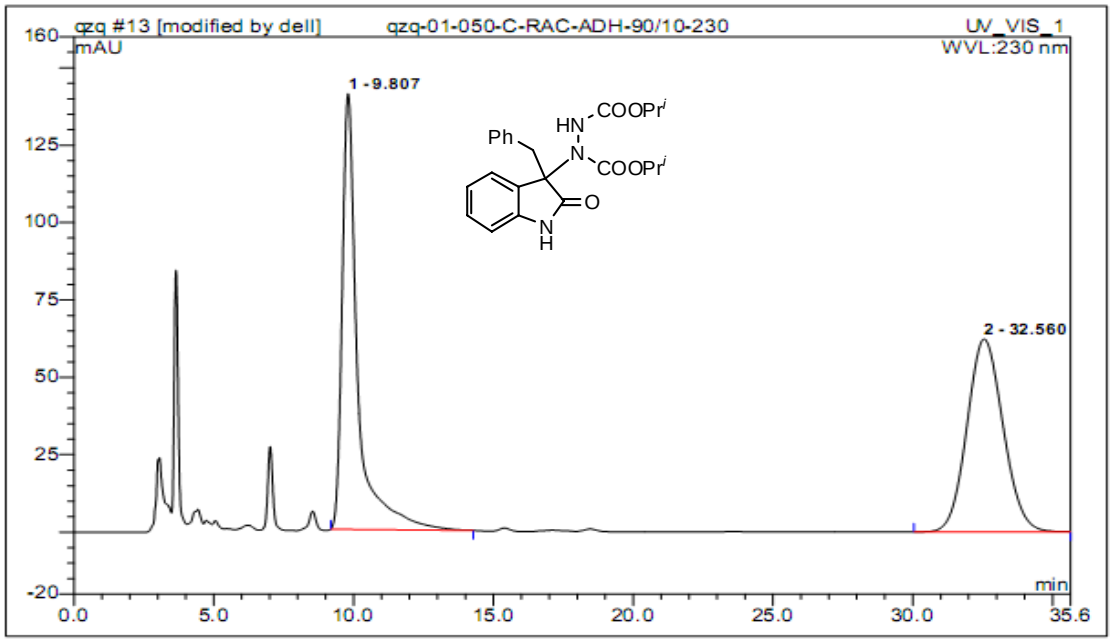

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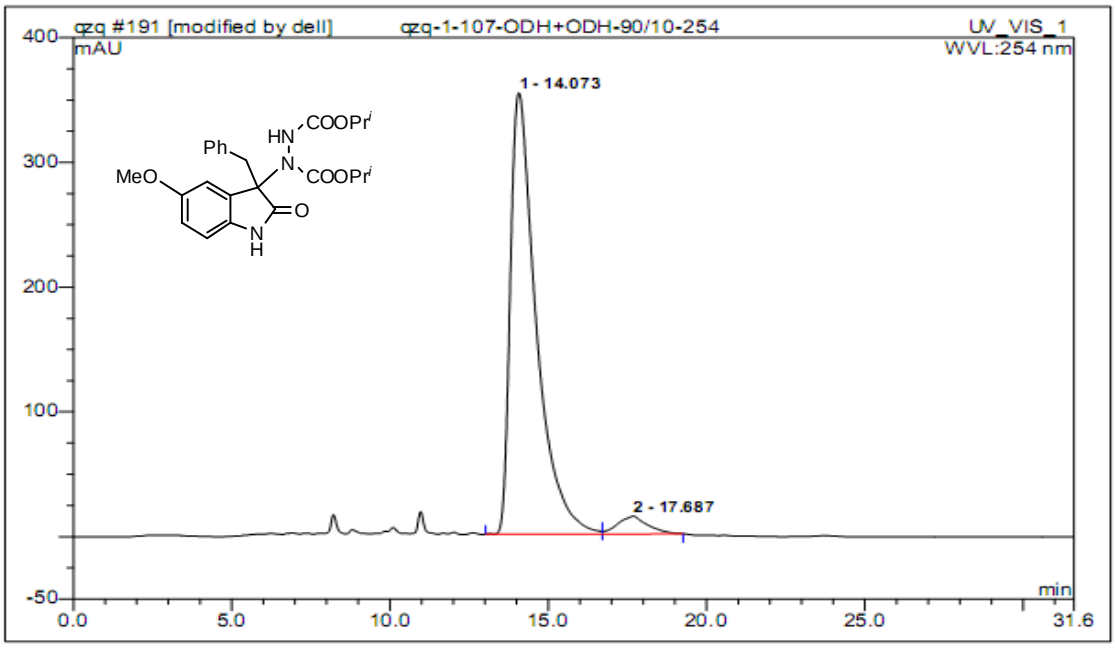

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1	14.07	n.a.	353.720	334.792	95.60	n.a.	BM *
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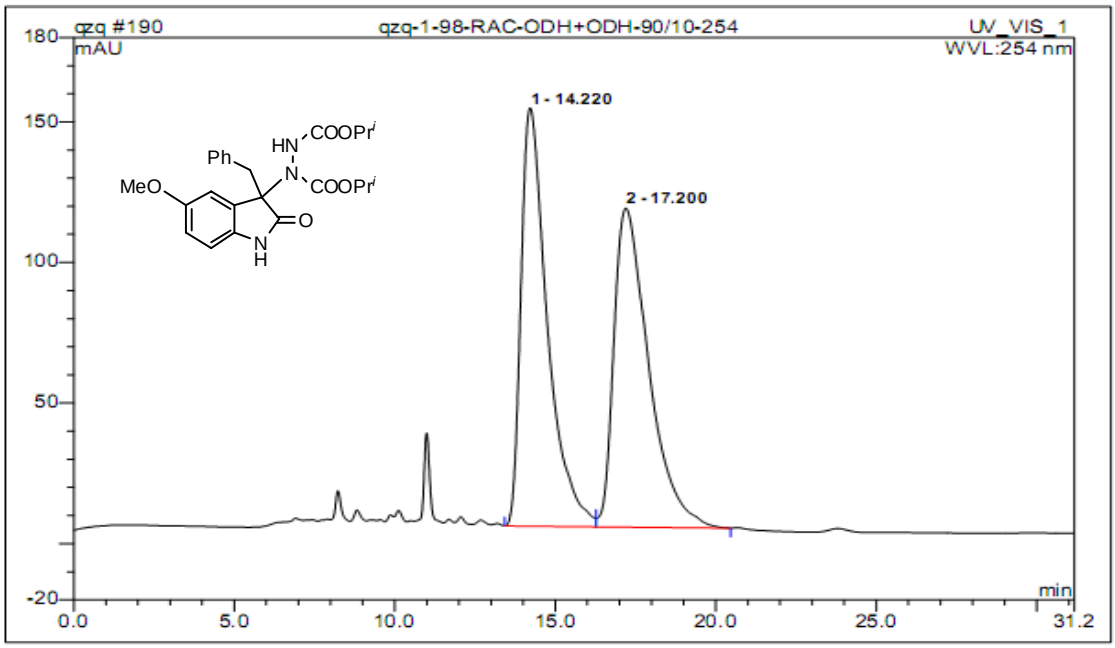
Total:			367.936	350.194	100.00	0.000	



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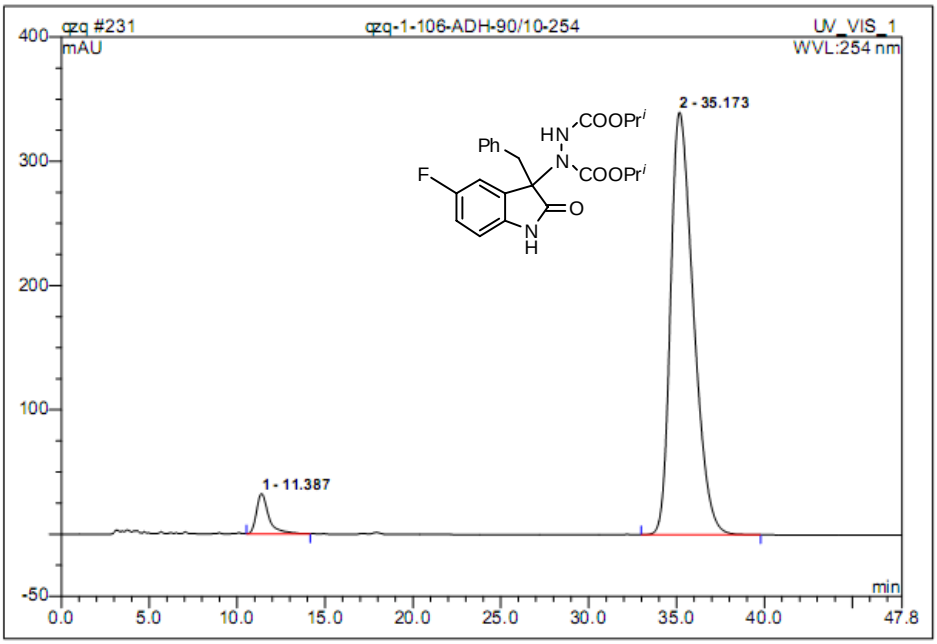

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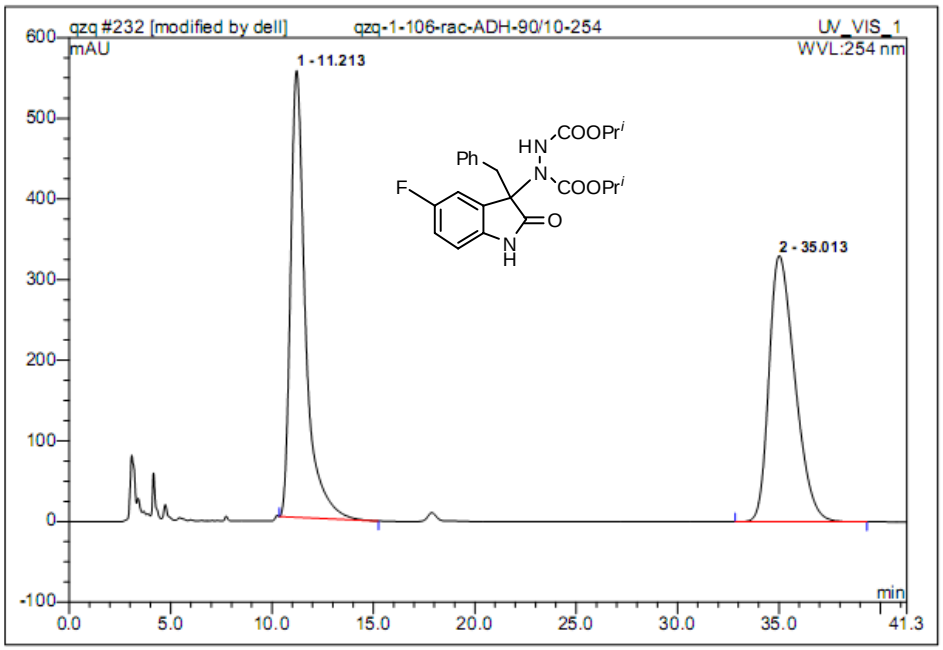

No.	Ret.Time min	Peak Name	Height mAU	Area mAU*min	Rel.Area %	Amount	Type
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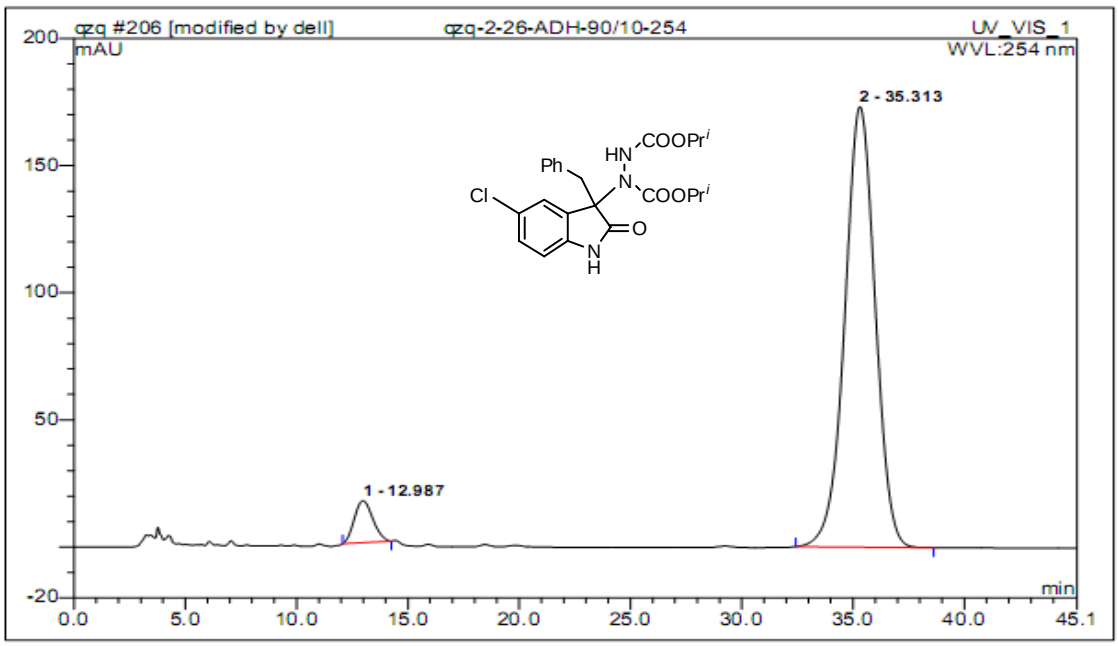

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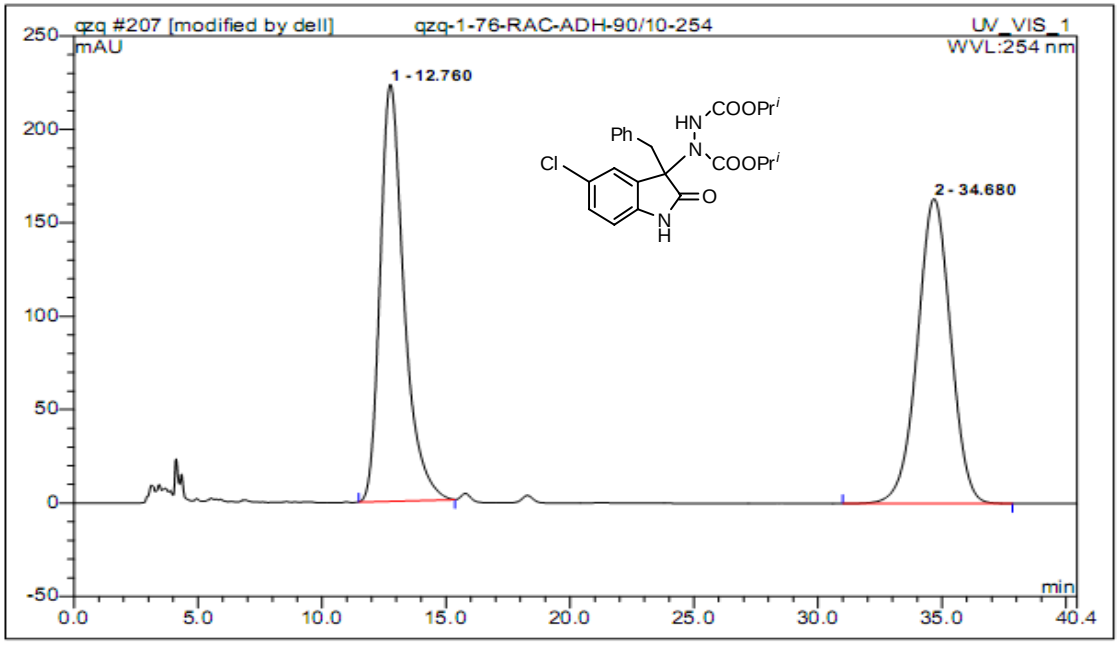
Total:			189.741	290.307	100.00	0.000	



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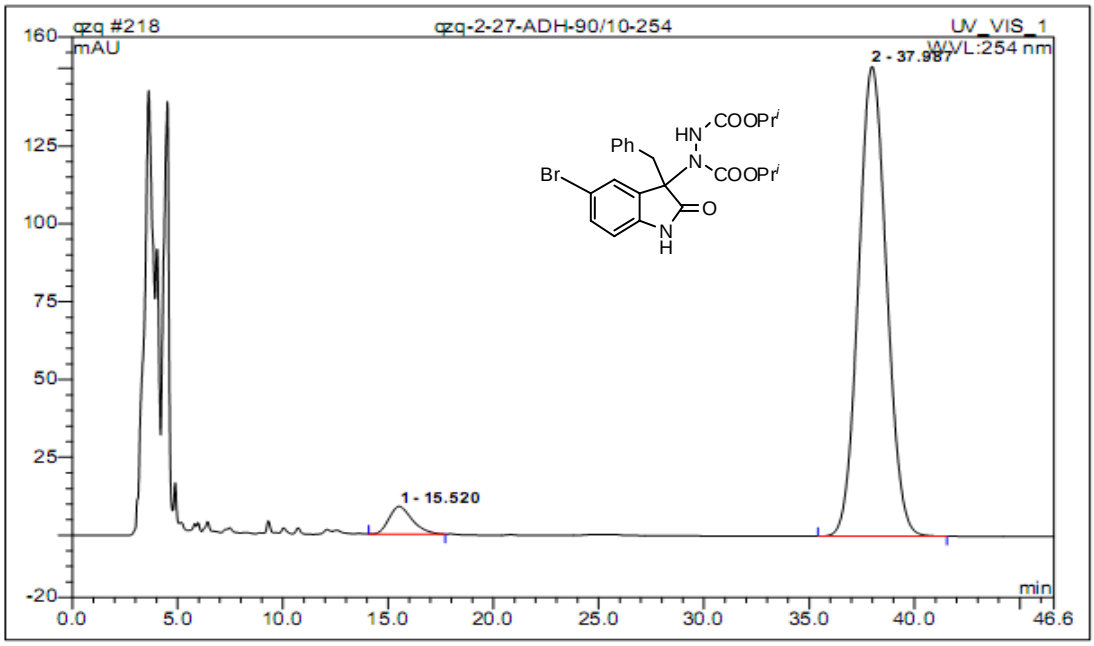
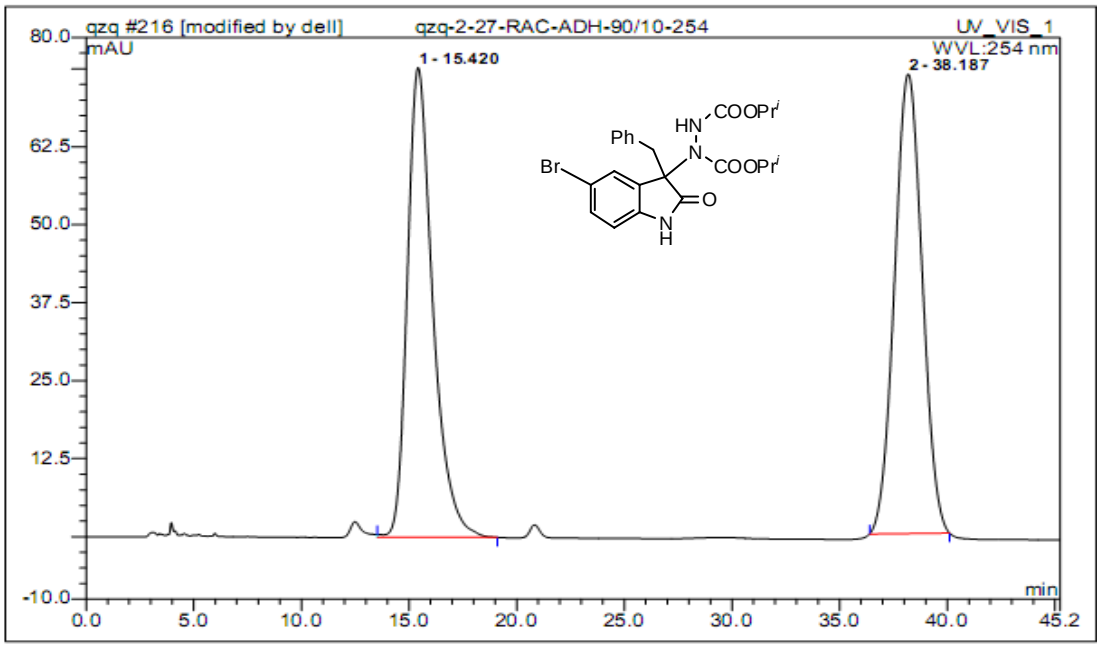
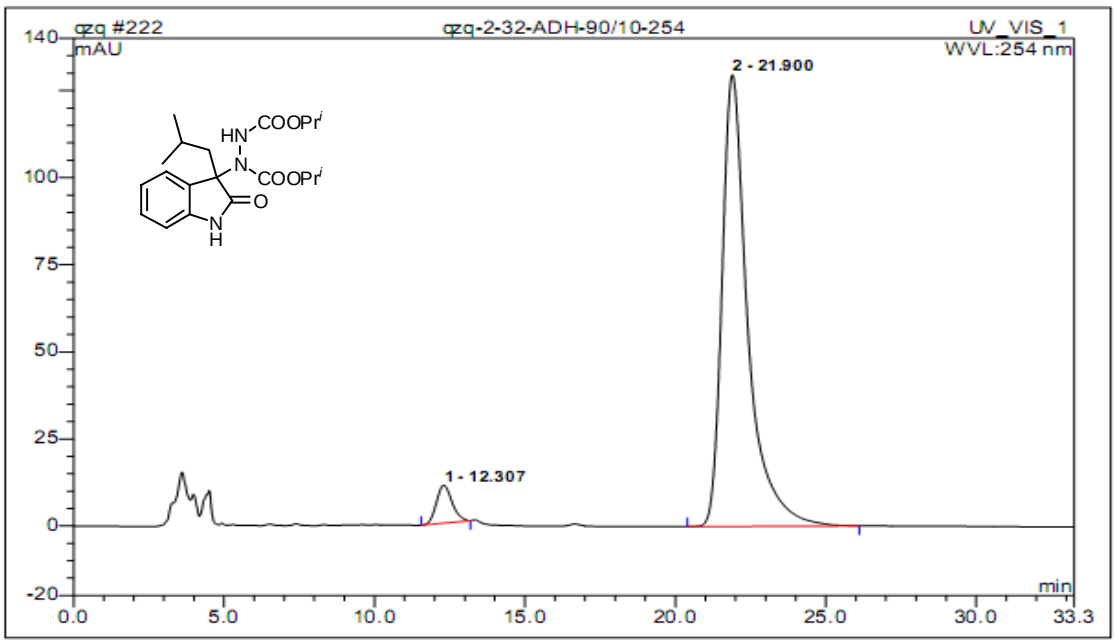
1	12.76	n.a.	223.059	249.001	49.53	n.a.	BMB*
2	34.68	n.a.	163.046	253.697	50.47	n.a.	BMB
Total:			386.105	502.698	100.00	0.000	



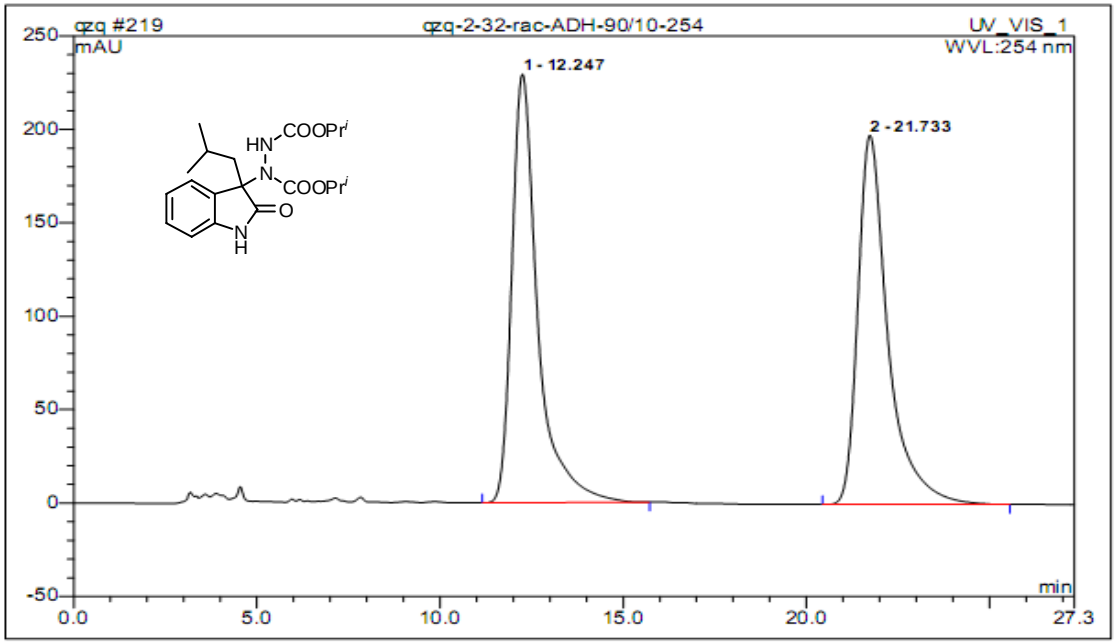
No.	Ret.Time min	Peak Name	Height mAU	Area mAU*min	Rel.Area %	Amount	Type
1	15.52	n.a.	8.891	11.437	4.69	n.a.	BMB
2	37.99	n.a.	150.860	232.628	95.31	n.a.	BMB
Total:			159.751	244.065	100.00	0.000	



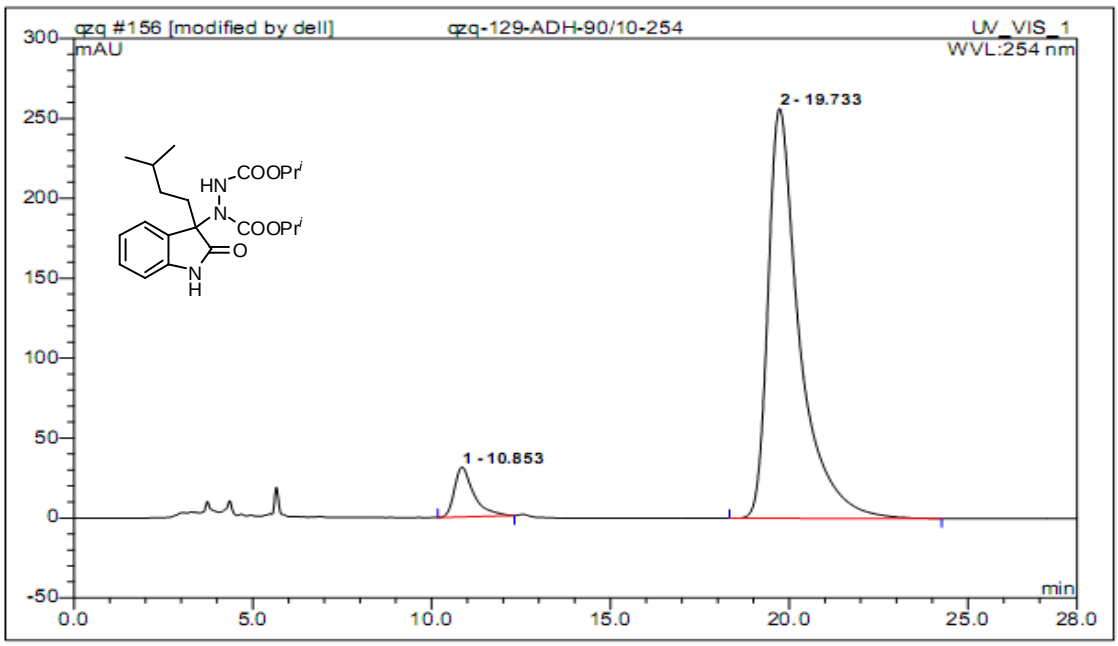
No.	Ret.Time min	Peak Name	Height mAU	Area mAU*min	Rel.Area %	Amount	Type
1	15.42	n.a.	75.268	103.370	48.50	n.a.	MB*
2	38.19	n.a.	73.615	109.777	51.50	n.a.	BMB*
Total:			148.883	213.147	100.00	0.000	



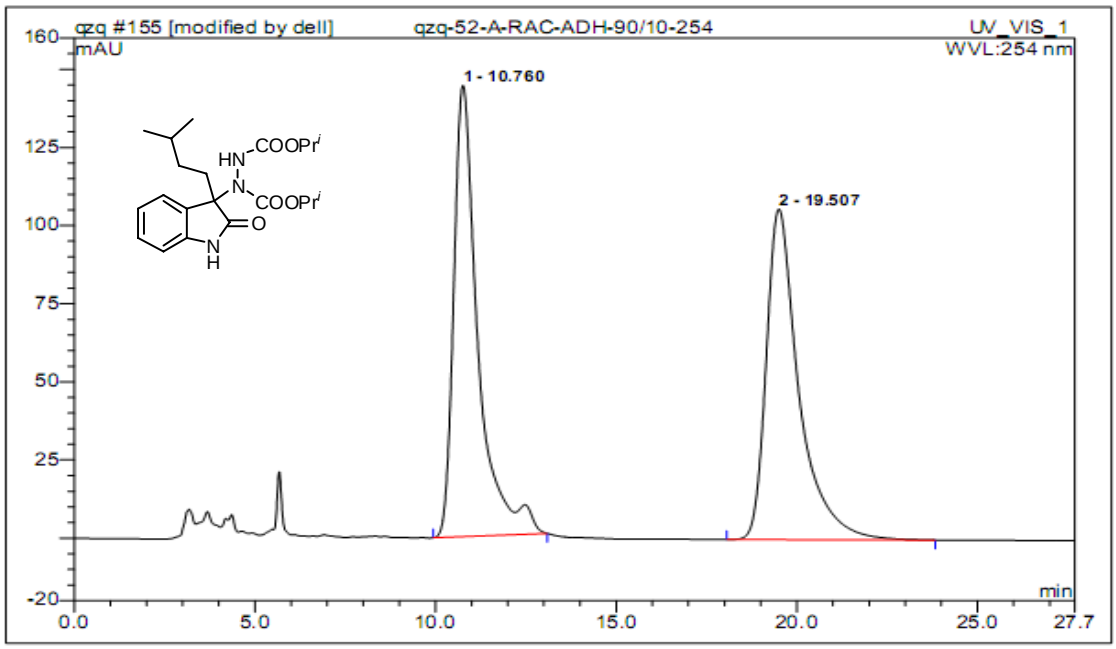
No.	Ret.Time min	Peak Name	Height mAU	Area mAU*min	Rel.Area %	Amount	Type
1	12.31	n.a.	10.839	6.571	4.86	n.a.	BMB
2	21.90	n.a.	129.632	128.586	95.14	n.a.	BMB
Total:			140.472	135.157	100.00	0.000	



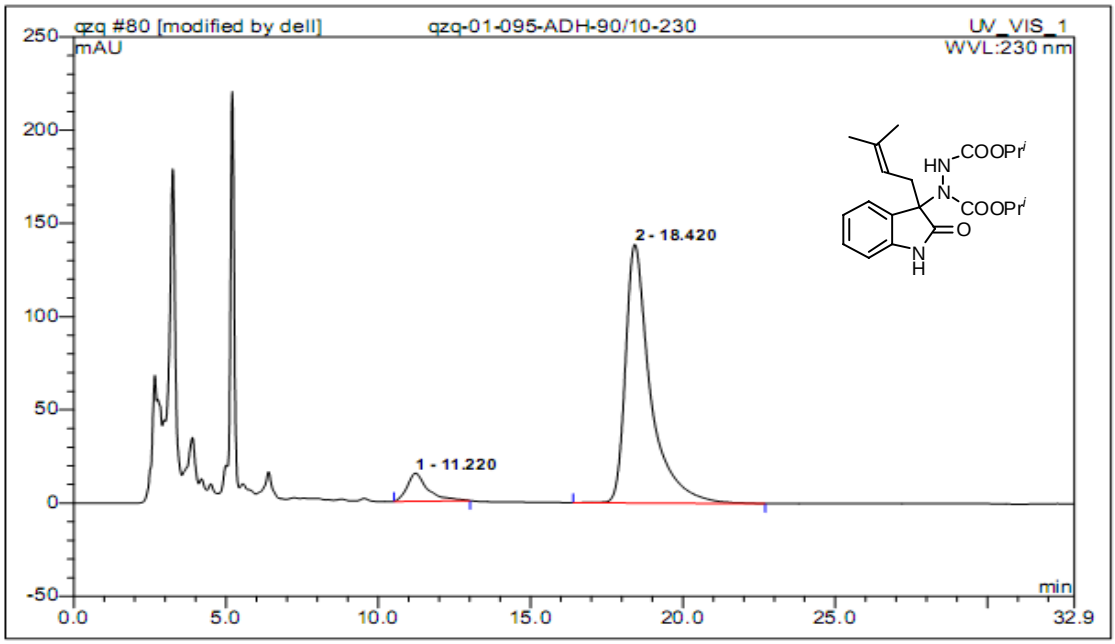
No.	Ret.Time min	Peak Name	Height mAU	Area mAU*min	Rel.Area %	Amount	Type
1	12.25	n.a.	229.326	187.895	49.92	n.a.	BMB
2	21.73	n.a.	197.577	188.489	50.08	n.a.	BMB
Total:			426.903	376.384	100.00	0.000	



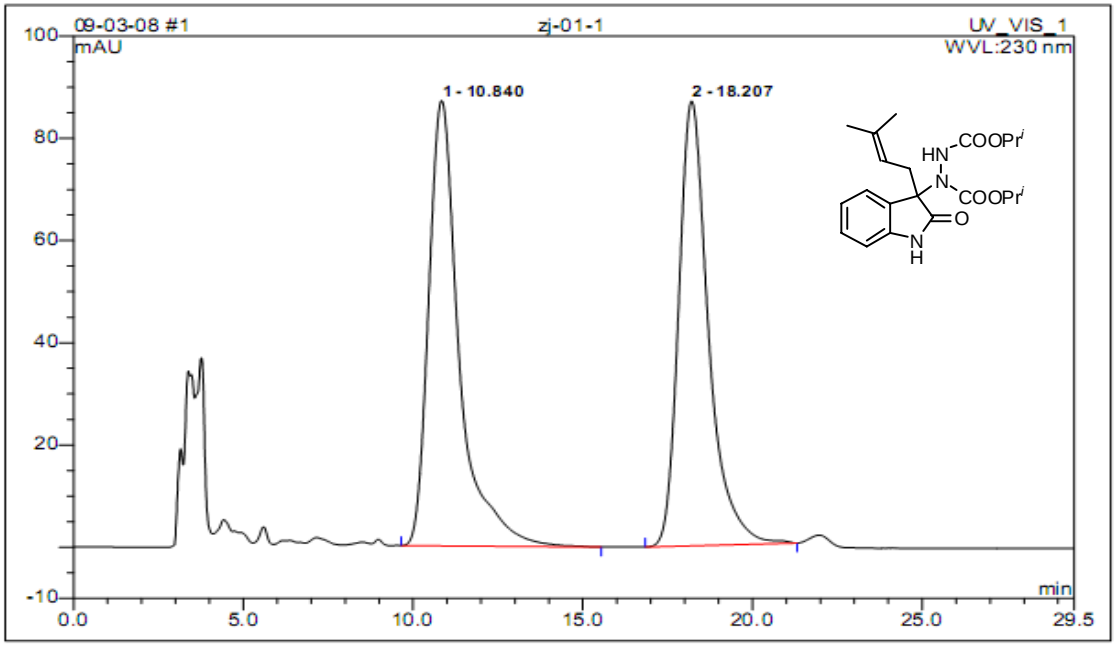
No.	Ret.Time min	Peak Name	Height mAU	Area mAU*min	Rel.Area %	Amount	Type
1	10.85	n.a.	31.183	19.617	6.99	n.a.	BMB
2	19.73	n.a.	256.323	260.916	93.01	n.a.	BMB
Total:			287.506	280.533	100.00	0.000	



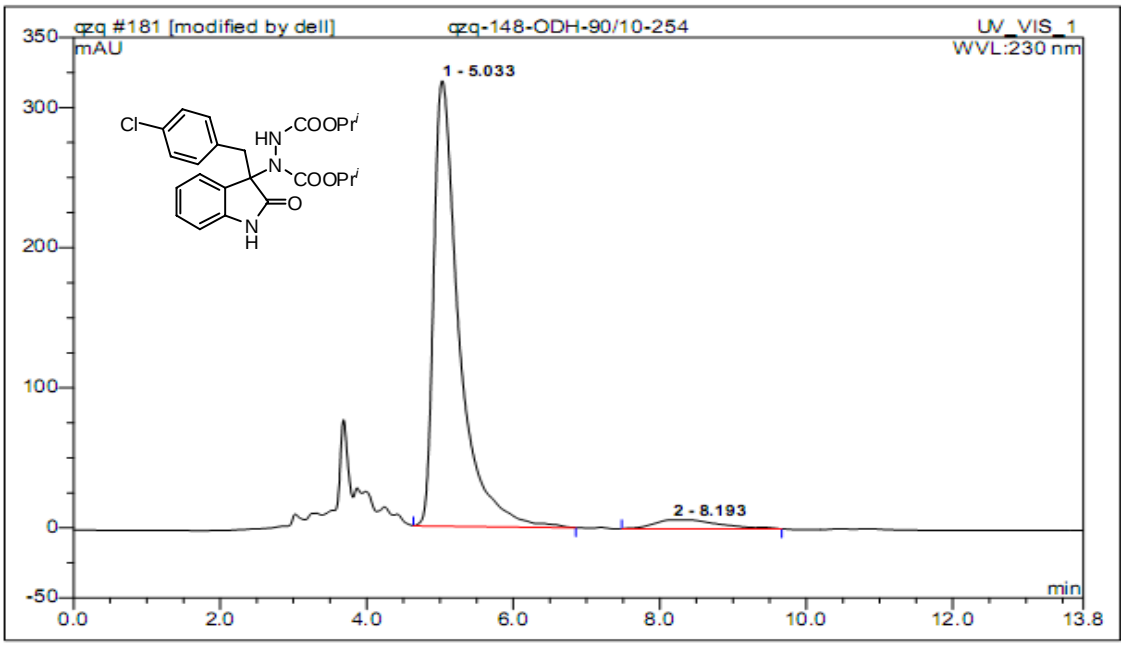
No.	Ret.Time min	Peak Name	Height mAU	Area mAU*min	Rel.Area %	Amount	Type
1	10.76	n.a.	144.423	112.302	50.38	n.a.	BMB*
2	19.51	n.a.	105.741	110.623	49.62	n.a.	BMB
Total:			250.164	222.926	100.00	0.000	



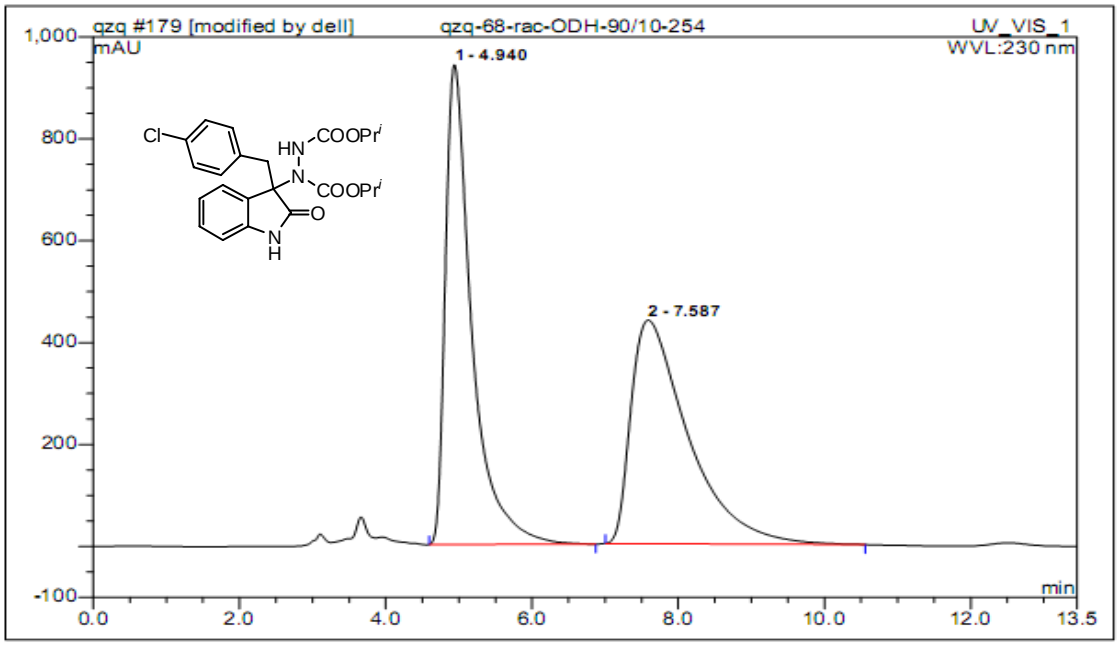
No.	Ret.Time min	Peak Name	Height mAU	Area mAU*min	Rel.Area %	Amount	Type
1	11.22	n.a.	14.979	11.671	8.13	n.a.	BMB*
2	18.42	n.a.	138.569	131.868	91.87	n.a.	BMB
Total:			153.548	143.539	100.00	0.000	



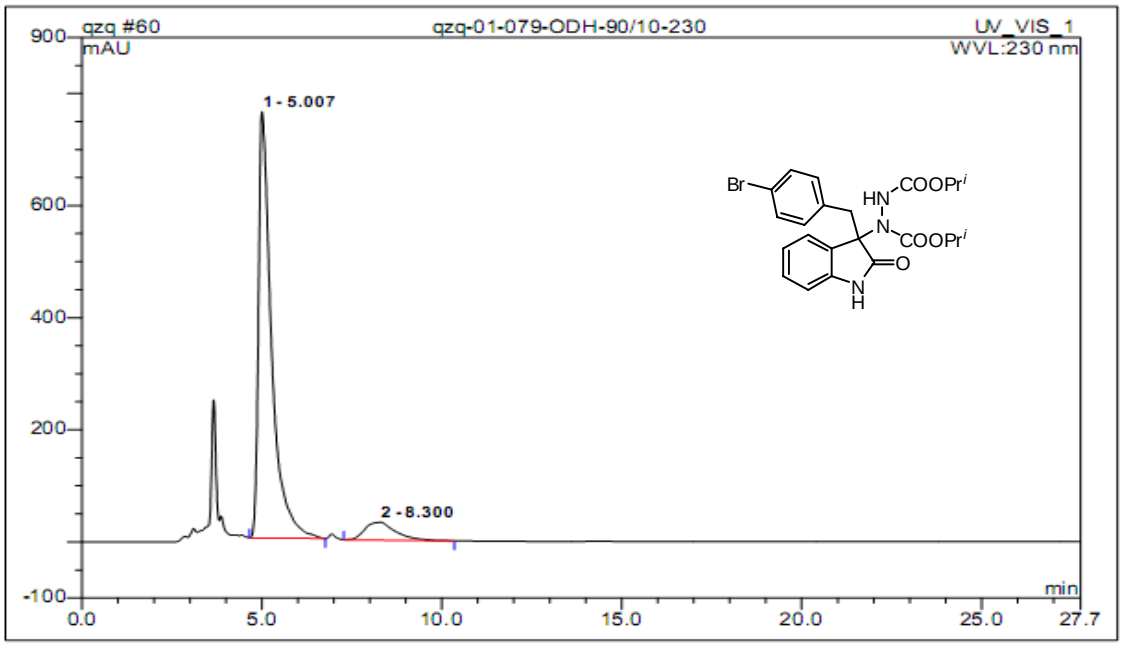
No.	Ret.Time min	Peak Name	Height mAU	Area mAU*min	Rel.Area %	Amount	Type
1	10.84	n.a.	87.101	90.977	50.69	n.a.	BMB
2	18.21	n.a.	87.001	88.501	49.31	n.a.	BMB
Total:			174.102	179.478	100.00	0.000	



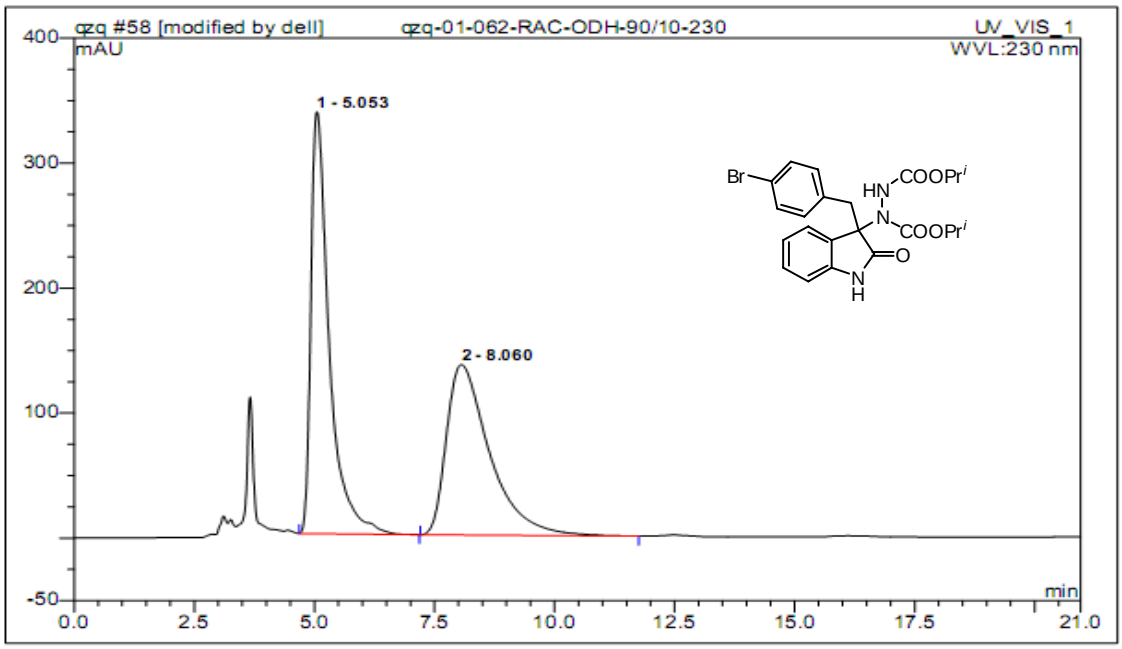
No.	Ret.Time min	Peak Name	Height mAU	Area mAU*min	Rel.Area %	Amount	Type
1	5.03	n.a.	317.837	127.073	95.10	n.a.	BMB*
2	8.19	n.a.	6.352	6.554	4.90	n.a.	BMB*
Total:			324.189	133.626	100.00	0.000	



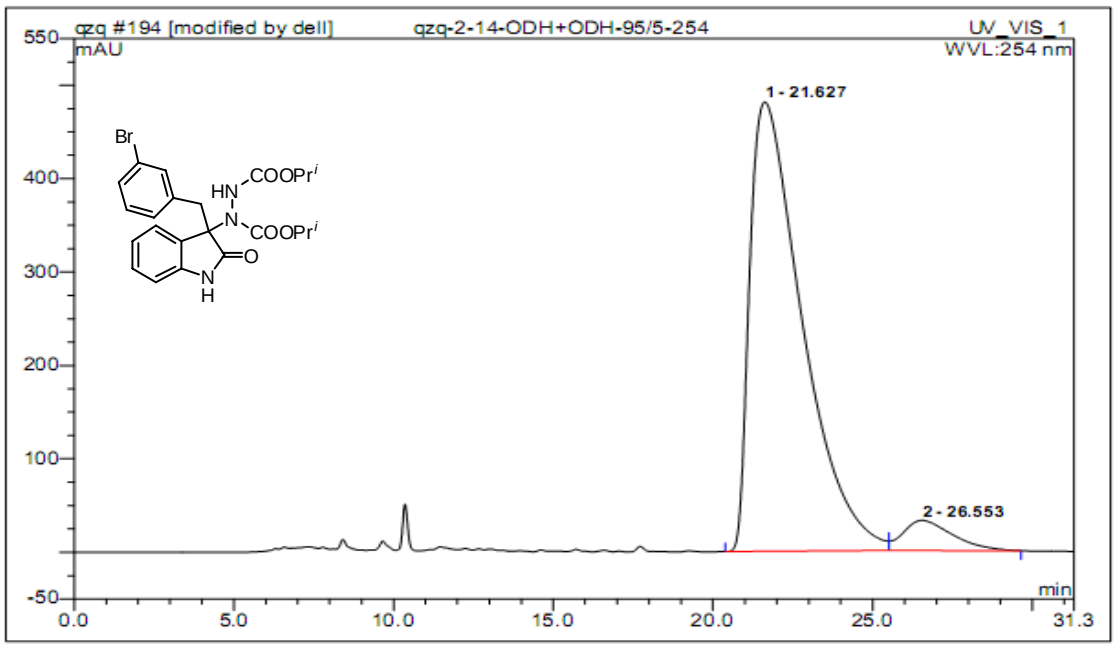
No.	Ret.Time min	Peak Name	Height mAU	Area mAU*min	Rel.Area %	Amount	Type
1	4.94	n.a.	941.314	394.712	49.82	n.a.	BMB*
2	7.59	n.a.	438.501	397.634	50.18	n.a.	BMB*
Total:			1379.815	792.346	100.00	0.000	



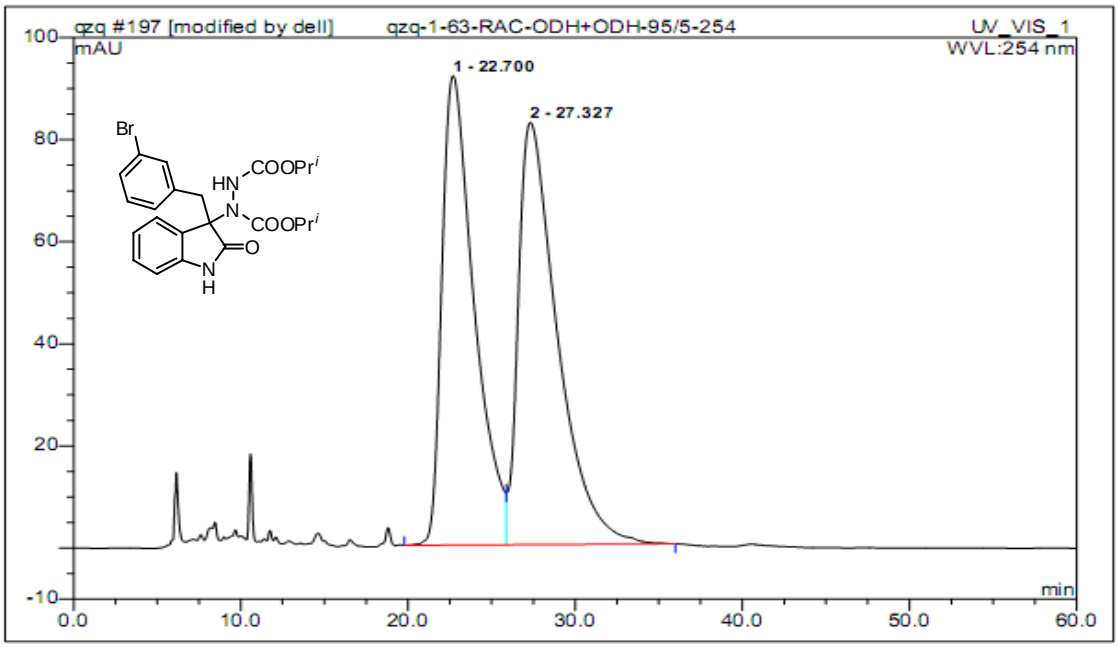
No.	Ret.Time min	Peak Name	Height mAU	Area mAU*min	Rel.Area %	Amount	Type
1	5.01	n.a.	760.618	319.033	90.88	n.a.	BMB
2	8.30	n.a.	31.992	32.021	9.12	n.a.	BMB
Total:			792.610	351.054	100.00	0.000	



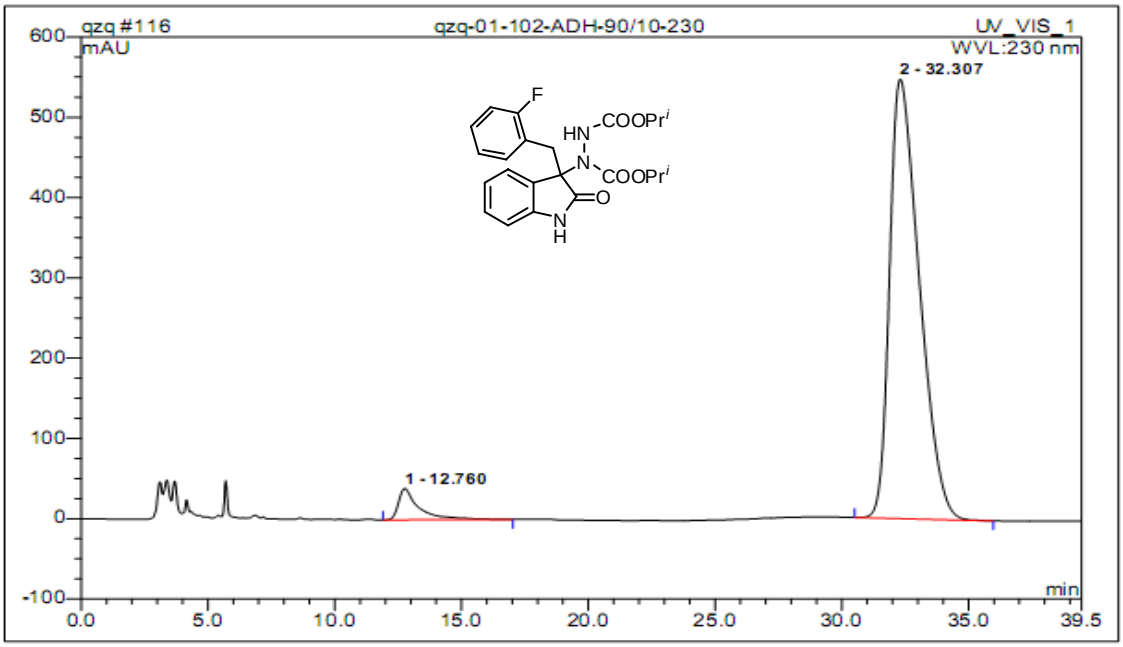
No.	Ret.Time min	Peak Name	Height mAU	Area mAU*min	Rel.Area %	Amount	Type
1	5.05	n.a.	337.298	148.981	51.15	n.a.	BMB*
2	8.06	n.a.	136.296	142.299	48.85	n.a.	BMB
Total:			473.594	291.280	100.00	0.000	



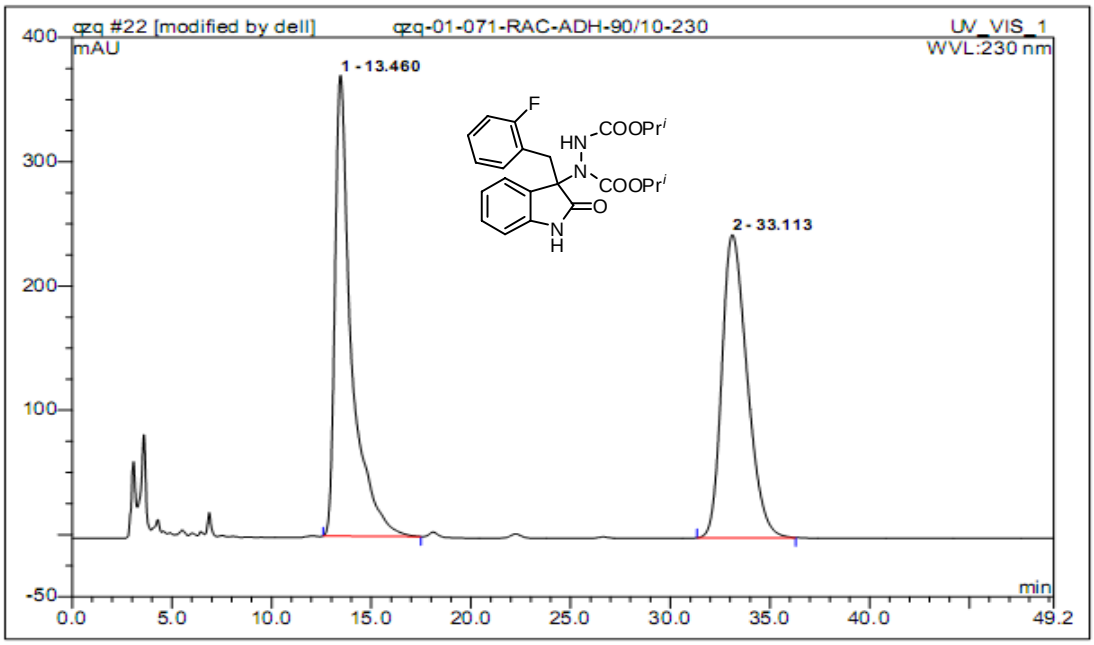
No.	Ret.Time min	Peak Name	Height mAU	Area mAU*min	Rel.Area %	Amount	Type
1	21.63	n.a.	481.097	914.648	94.06	n.a.	BM *
2	26.55	n.a.	32.035	57.775	5.94	n.a.	MB*
Total:			513.132	972.423	100.00	0.000	



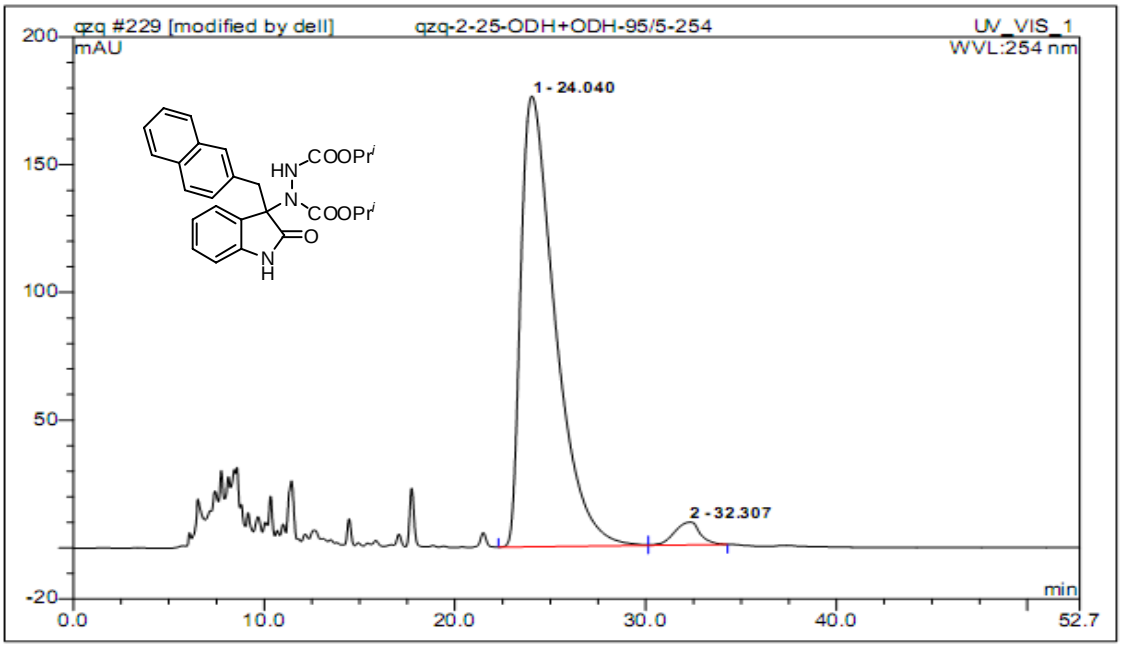
No.	Ret.Time min	Peak Name	Height mAU	Area mAU*min	Rel.Area %	Amount	Type
1	22.70	n.a.	91.934	205.792	47.87	n.a.	BM *
2	27.33	n.a.	82.731	224.104	52.13	n.a.	MB*
Total:			174.664	429.896	100.00	0.000	



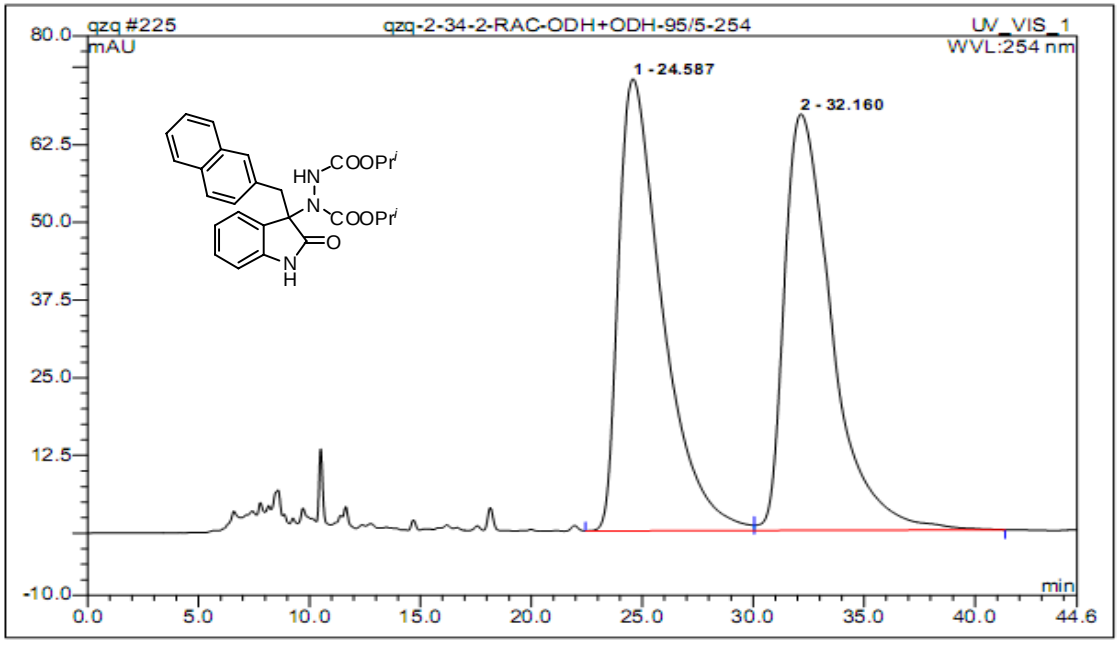
No.	Ret.Time min	Peak Name	Height mAU	Area mAU*min	Rel.Area %	Amount	Type
1	12.76	n.a.	38.925	36.884	4.73	n.a.	BMB
2	32.31	n.a.	547.214	743.515	95.27	n.a.	BMB
Total:			586.139	780.399	100.00	0.000	



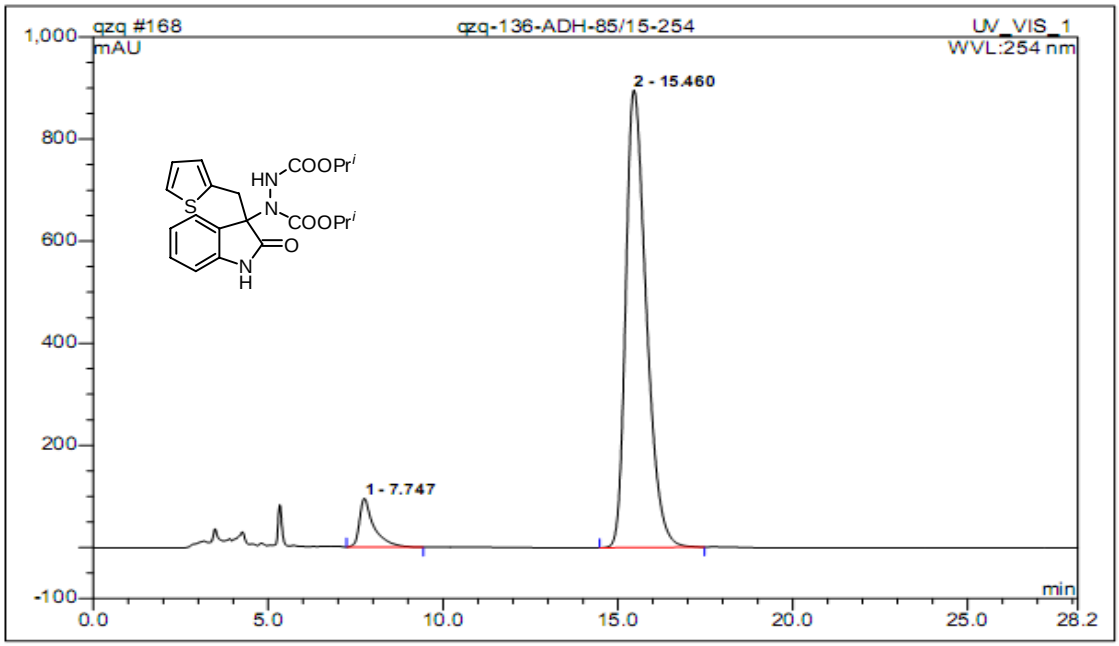
No.	Ret.Time min	Peak Name	Height mAU	Area mAU*min	Rel.Area %	Amount	Type
1	13.46	n.a.	370.706	355.834	49.90	n.a.	BMB*
2	33.11	n.a.	243.610	357.259	50.10	n.a.	BMB*
Total:			614.316	713.093	100.00	0.000	



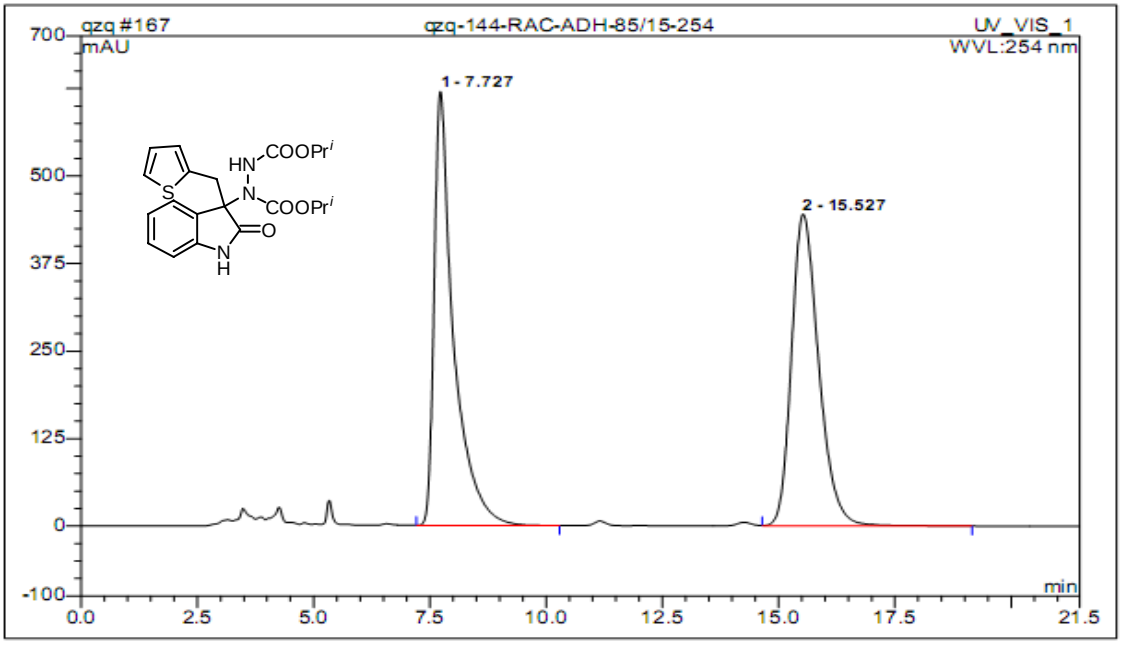
No.	Ret.Time min	Peak Name	Height mAU	Area mAU*min	Rel.Area %	Amount	Type
1	24.04	n.a.	176.439	366.769	96.38	n.a.	BM
2	32.31	n.a.	8.866	13.778	3.62	n.a.	MB
Total:			185.305	380.547	100.00	0.000	



No.	Ret.Time min	Peak Name	Height mAU	Area mAU*min	Rel.Area %	Amount	Type
1	24.59	n.a.	72.702	166.365	50.02	n.a.	BM
2	32.16	n.a.	66.954	166.228	49.98	n.a.	MB
Total:			139.656	332.593	100.00	0.000	



No.	Ret.Time min	Peak Name	Height mAU	Area mAU*min	Rel.Area %	Amount	Type
1	7.75	n.a.	95.048	45.667	6.97	n.a.	BMB
2	15.46	n.a.	895.947	609.170	93.03	n.a.	BMB
Total:			990.994	654.837	100.00	0.000	



No.	Ret.Time min	Peak Name	Height mAU	Area mAU*min	Rel.Area %	Amount	Type
1	7.73	n.a.	620.040	300.389	49.88	n.a.	BMB
2	15.53	n.a.	445.122	301.810	50.12	n.a.	BMB
Total:			1065.162	602.199	100.00	0.000	