

Supporting Information for

ArPNO Catalyzed Acylative Kinetic Resolutions of Tertiary Alcohols: Access to 3-Hydroxy-3-Substituted Oxindoles

Min Yang, Yu-Lin Gao, Ming-Sheng Xie* and Hai-Ming Guo*

[†]NMPA Key Laboratory for Research and Evaluation of Innovative Drug, Key Laboratory of Green Chemical Media and Reactions, Ministry of Education, Collaborative Innovation Center of Henan Province for Green Manufacturing of Fine Chemicals, School of Chemistry and Chemical Engineering, Henan Normal University, Xinxiang, Henan 453007, China.

E-mail: xiemingsheng@htu.edu.cn; ghm@htu.edu.cn

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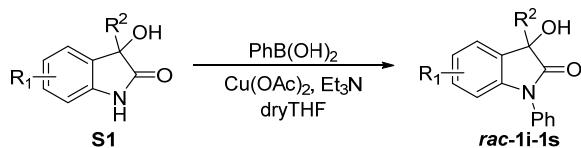
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1. General information

All reactions were carried out in oven-dried tube, and monitored by thin layer chromatography (TLC). All reagents were reagent grade quality and purchased from commercial sources unless otherwise indicated. ^1H NMR spectra were recorded on commercial instruments (400/600 MHz). Data are reported as follows: chemical shift, multiplicity (s = singlet, d = doublet, t = triplet, sep = septet, br = broad, m = multiplet), coupling constants (Hz), integration. ^{13}C NMR data were collected on commercial instruments (100/150 MHz) with complete proton decoupling. Chemical shifts are reported in ppm from the tetramethylsilane with the solvent resonance as internal standard. Coupling constants (J) are reported in Hz. Enantiomer excesses were determined by chiral HPLC analysis on Chiralcel ODH/IA/ID in comparison with the authentic racemates. Chiral HPLC analysis recorded on Thermo scientific Dionex Ultimate 3000. Optical rotations were reported as follows: $[\alpha]_D^T$ (c: = g/100mL, in solvent). Optical rotations recorded on Autopol Automatic Polarimeter. All products were further characterized by high-resolution mass spectra (HRMS). The HRMS was obtained using a Q-TOF instrument equipped with an ESI source. All the solvents were purified by usual methods before use. The starting materials **rac-1a-1f**^[1], **rac-1t**^[1] and **rac-1g**^[2] were prepared according to the literature procedures. Catalyst **6a-6g** were prepared according to the literature procedures^[3].

2. Synthesis of starting materials

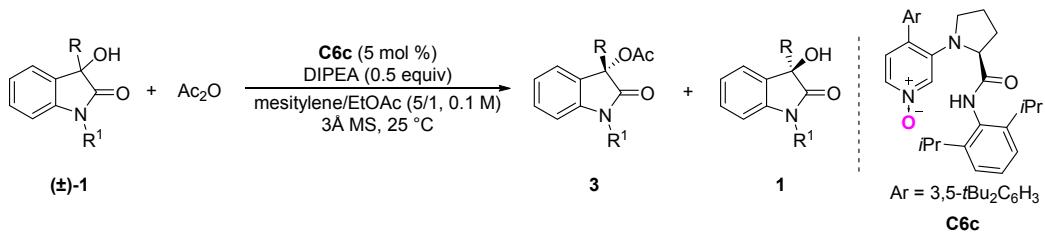
Synthesis of substrates *rac*-**1i-1s**, **1h**



Materials **S1** were prepared according to the literature^[1].

According to reference^[4], material **S1** (3.0 mmol), PhB(OH)₂ (683.8 mg, 4.5 mmol), Cu(OAc)₂ (598.9 mg, 3.0 mmol) and Et₃N (834 μL, 6.0 mmol) were dissolved in THF (30 mL). The reaction was stirred at room temperature under anhydrous conditions. After the reaction was complete (monitoring by TLC), the reaction mixture was filtered through a pad of celite. The solids were washed with EtOAc for many times. The residue was purified by flash column chromatography on silica gel (eluent: ether/ethyl acetate = 9/1 to 4/1, v/v) to give *rac*-**1i-1s** as white solids.

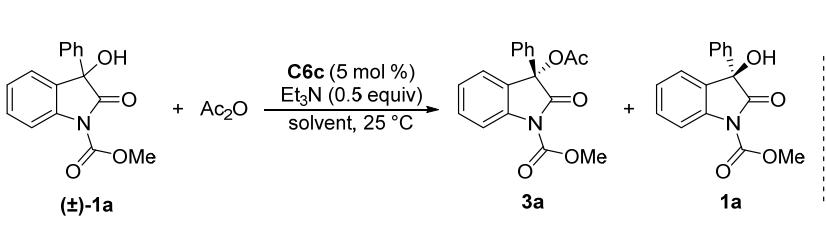
3. General procedure for kinetic resolution of 3-hydroxy-3-substituted oxindole



In a test tube, (\pm)-**1** (0.1 mmol), **C6c** (2.7 mg, 5 mol %), and 3 Å MS (10 mg) were added. Then, mesitylene/EtOAc (5/1, v/v, 1 mL), DIPEA (6.5 mg, 0.5 equiv), and acetic anhydride (15.3 mg, 1.5 equiv) were added successively. The reaction was stirred under air at 25 °C for 35-60 h. After the reaction was complete (monitoring by TLC), the reaction solution was quenched with methanol. Subsequently, the reaction mixture was concentrated under vacuum. The residue was purified by flash column chromatography on silica gel (eluent: ether/ethyl acetate = 15/1 to 5/1, v/v) to give the recovered alcohol **1a-t** and acylated products **3a-t**. The enantiomeric ratios of **1a-t** and **3a-t** were determined by chiral HPLC analysis. Conversion was determined by enantiomeric excess (ee) of **1** and **3**. *s*-Factors were calculated by Kagan's equation^[5].

4. Screening of the solvent

Table S1 Screening of the solvents^a



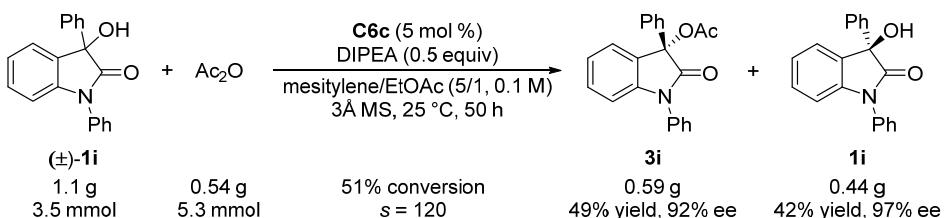
The reaction scheme shows the conversion of (±)-1a to 3a and 1a. (±)-1a reacts with Ac₂O in the presence of C6c (5 mol %) and Et₃N (0.5 equiv) in a solvent at 25 °C for 10 hours. The products are 3a and 1a. A detailed description of the catalyst C6c is shown on the right, featuring a quaternary ammonium salt core with an imidazolidine ring substituted with an iPr group and an amide group.

| entry | solvent | t (h) | ee (3a) (%) ^b | ee (1a) (%) ^b | conv (%) ^c | <i>s</i> ^d |
|-------|------------------------|-------|-----------------------------|-----------------------------|-----------------------|-----------------------|
| 1 | toluene | 10 | 89 | - | - | - |
| 2 | PhF | 10 | 80 | - | - | - |
| 3 | PhCF ₃ | 10 | 78 | - | - | - |
| 4 | mesitylene | 10 | 91 | - | - | - |
| 5 | mesitylene/EtOAc = 1:1 | 10 | 83 | 17 | 17 | 13 |
| 6 | mesitylene/EtOAc = 2:1 | 10 | 87 | 25 | 22 | 21 |
| 7 | mesitylene/EtOAc = 4:1 | 21 | 84 | 37 | 31 | 15 |
| 8 | mesitylene/EtOAc = 5:1 | 21 | 87 | 37 | 30 | 29 |
| 9 | mesitylene/EtOAc = 5:1 | 36 | 84 | 58 | 41 | 20 |
| 10 | mesitylene/EtOAc = 6:1 | 36 | 83 | 50 | 38 | 16 |
| 11 | mesitylene/EtOAc = 5:1 | 72 | 81 | 77 | 49 | 22 |

^aReaction conditions: (±)-1a (0.1 mmol), Ac₂O (0.75 equiv), C6c (5 mol %), Et₃N (0.5 equiv), solvent (1 mL) under air at 25 °C. ^bDetermined by chiral HPLC analysis. ^cConversion was determined by enantiomeric excess (ee) of 1a and 3a. ^d*s*-Factors were calculated by Kagan's equation.^[5]

Note: Due to the poor solubility of alcohol 1a in toluene, PhF, PhCF₃ and mesitylene, the ee value of recovered alcohol 1a could not be determined accurately, and only the ee value ester product 3a could be provided.

5. Gram-scale synthesis of 1i

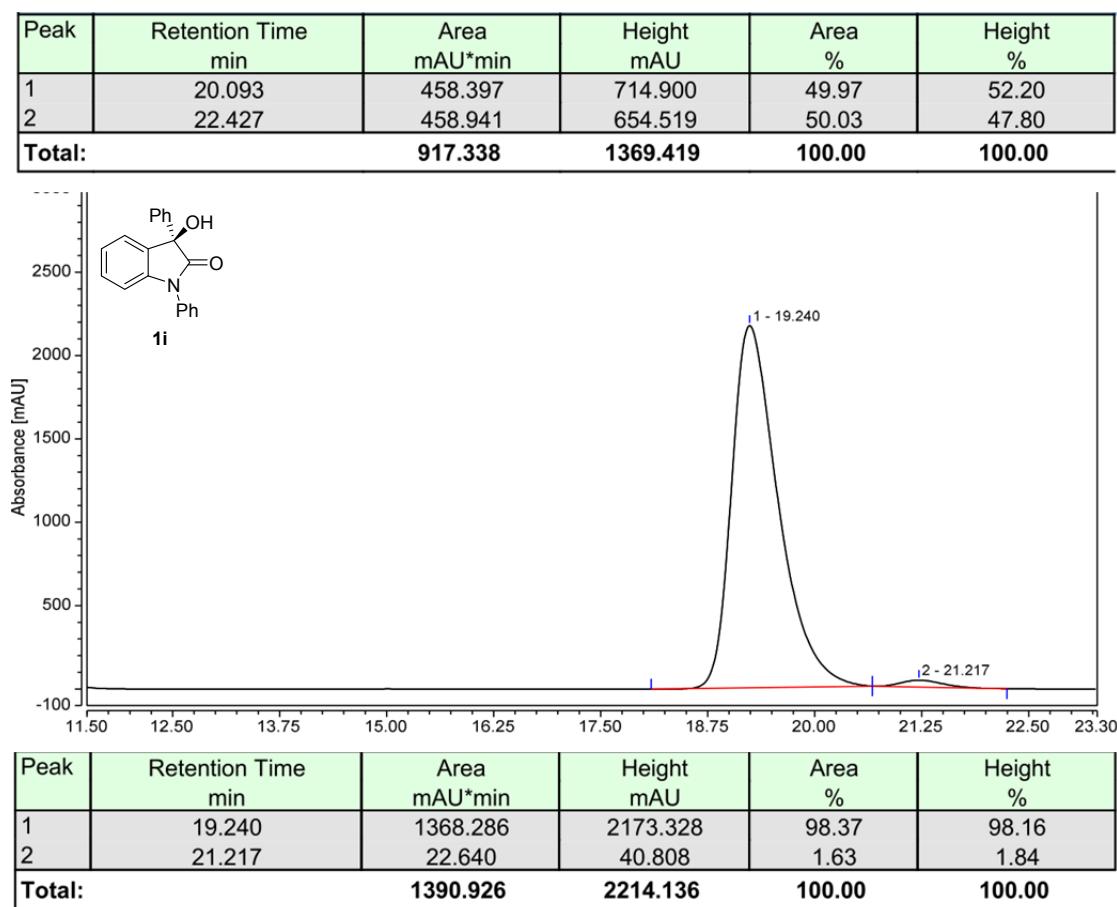
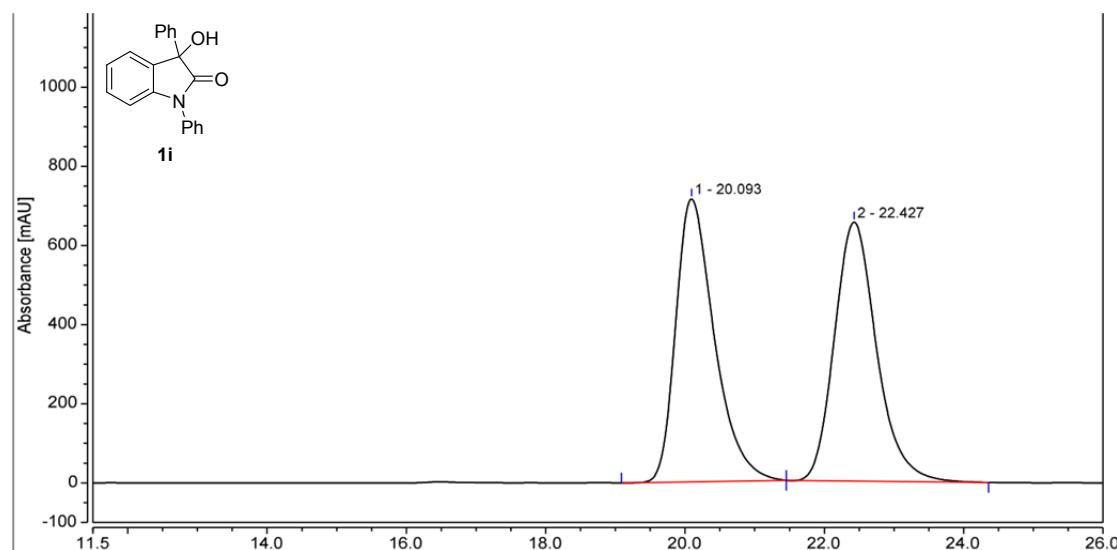


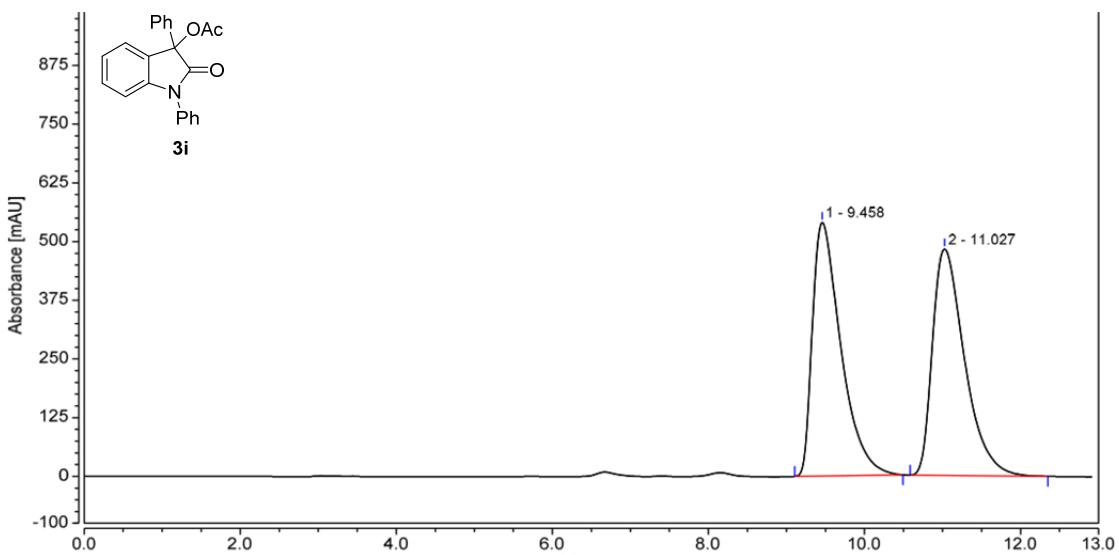
Scheme S4

In a round-bottomed flask, (±)-1i (1.054 g, 3.5 mmol), C6c (2.7 mg, 5 mol %), and 3 Å MS (10 mg) were added. Then, mesitylene/EtOAc (5/1, v/v, 35 mL), DIPEA (226.2 mg, 1.7 mmol), and acetic anhydride (0.536 g, 5.3 mmol) were added successively. The reaction was stirred under air at 25 °C for 50 h. After the reaction was complete (monitoring by TLC), The reaction solution was

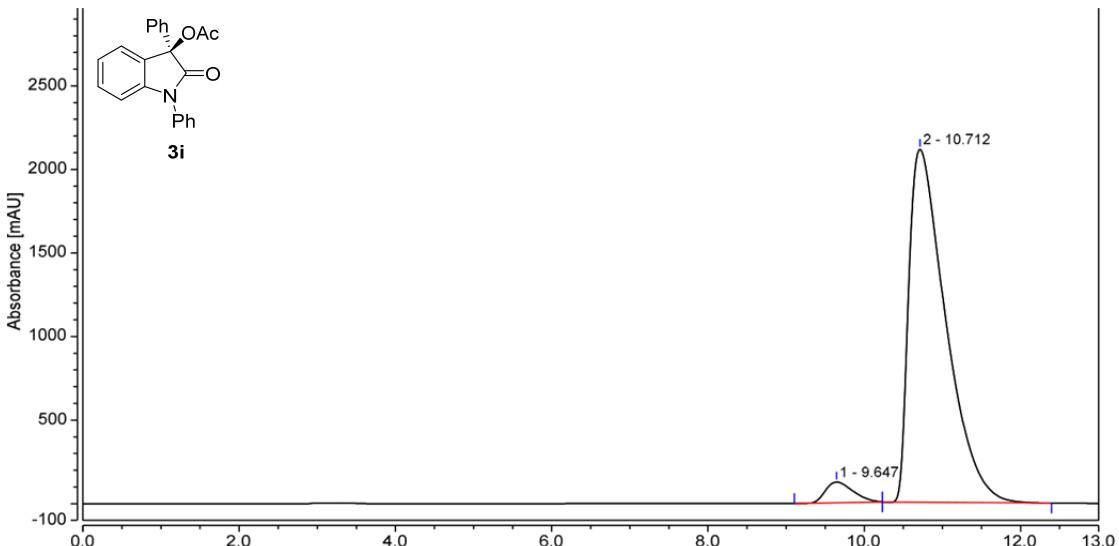
quenched with methanol. Subsequently, the reaction mixture was concentrated under vacuum. The residue was purified by flash column chromatography on silica gel (eluent: ether/ethyl acetate = 15/1 to 5/1, v/v) to give the recovered alcohol **1i** (0.4395 g, 42% yield, 97% ee) and acylated products **3i** (0.5865 g, 49% yield, 92% ee). The enantiomeric ratios of **1i** and **3i** were determined by chiral HPLC analysis. Conversion was determined by enantiomeric excess (ee) of **1** and **3**. s-Factors were calculated by Kagan's equation.^[5]

Figure S1. HPLC spectra of **1i/3i** on a gram-scale





| Peak | Retention Time min | Area mAU*min | Height mAU | Area % | Height % |
|---------------|-----------------------|-----------------|-----------------|---------------|---------------|
| 1 | 9.458 | 228.468 | 540.519 | 49.85 | 52.83 |
| 2 | 11.027 | 229.859 | 482.641 | 50.15 | 47.17 |
| Total: | | 458.327 | 1023.159 | 100.00 | 100.00 |



| Peak | Retention Time min | Area mAU*min | Height mAU | Area % | Height % |
|---------------|-----------------------|-----------------|-----------------|---------------|---------------|
| 1 | 9.647 | 51.336 | 124.683 | 4.26 | 5.57 |
| 2 | 10.712 | 1153.594 | 2112.366 | 95.74 | 94.43 |
| Total: | | 1204.930 | 2237.049 | 100.00 | 100.00 |

6. The X-ray data for product 3i

Recrystallization in petroleum ether/ethyl acetate afforded crystals suitable for X-ray analysis.

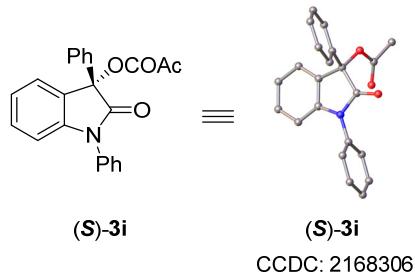


Table S1 Crystal data and structure refinement for 3i.

| Identification code | 3i |
|---|---|
| Empirical formula | C ₂₂ H ₁₇ NO ₃ |
| Formula weight | 343.39 |
| Temperature/K | 189.99(10) |
| Crystal system | orthorhombic |
| Space group | P2 ₁ 2 ₁ 2 ₁ |
| a/Å | 8.30180(10) |
| b/Å | 10.53570(10) |
| c/Å | 20.17220(10) |
| α/° | 90 |
| β/° | 90 |
| γ/° | 90 |
| Volume/Å ³ | 1764.37(3) |
| Z | 4 |
| ρ _{calcd} /cm ³ | 1.2926 |
| μ/mm ⁻¹ | 0.697 |
| F(000) | 722.3 |
| Crystal size/mm ³ | 0.09 × 0.06 × 0.04 |
| Radiation | Cu Kα (λ = 1.54184) |
| 2Θ range for data collection/° | 8.76 to 143.14 |
| Index ranges | -10 ≤ h ≤ 9, -12 ≤ k ≤ 12, -24 ≤ l ≤ 24 |
| Reflections collected | 22801 |
| Independent reflections | 3414 [R _{int} = 0.0336, R _{sigma} = 0.0176] |
| Data/restraints/parameters | 3414/0/236 |
| Goodness-of-fit on F ² | 1.103 |
| Final R indexes [I>=2σ (I)] | R ₁ = 0.0340, wR ₂ = 0.0863 |
| Final R indexes [all data] | R ₁ = 0.0345, wR ₂ = 0.0868 |
| Largest diff. peak/hole / e Å ⁻³ | 0.13/-0.26 |
| Flack parameter | -0.14(13) |

7. HRMS analysis

A mixture of **C6c** and acetic anhydride was stirred in mesitylene/EtOAc (5/1, v/v, 0.5 mL) at rt for 16 h.

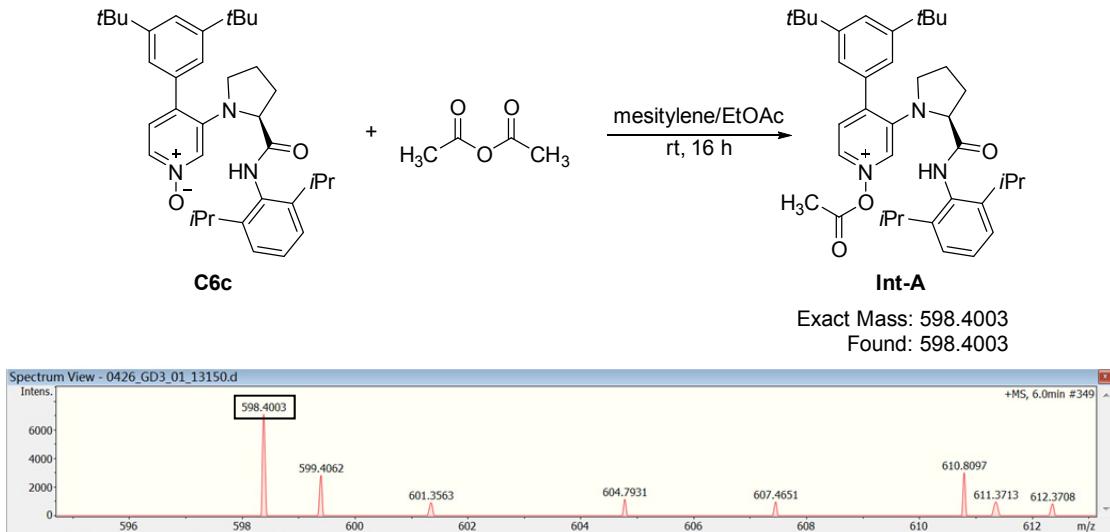
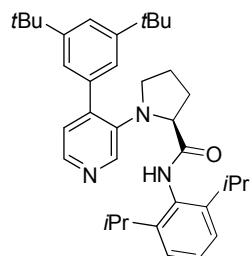


Figure S2. HRMS experiment

8. The analytical and spectral characterization data for Catalyst **7c**, **6h**, **6i**

(*S*)-1-(4-(3,5-Di-*tert*-butylphenyl)pyridin-3-yl)-N-(2,6-diisopropylphenyl)pyrrolidine-2-carboxamide (**C7c**)



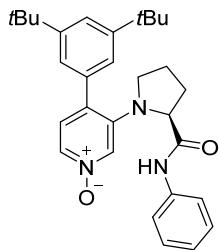
White solid, m.p.: 77.3–79.0 °C. $R_f = 0.35$ ($\text{CH}_2\text{Cl}_2/\text{MeOH}$, 30/1, v/v). $[\alpha]_{\text{D}}^{26} = -64.6$ ($c = 0.07$, CHCl_3).

$^1\text{H NMR}$ (600 MHz, CDCl_3) δ 8.52 (s, 1H), 8.34 (d, $J = 4.8$ Hz, 1H), 7.68 (s, 1H), 7.26 (t, $J = 8.4$ Hz, 3H), 7.21 (d, $J = 4.8$ Hz, 1H), 7.12 (d, $J = 7.8$ Hz, 2H), 4.33 (t, $J = 7.8$ Hz, 2H), 3.26 – 3.22 (m, 1H), 2.89 – 2.85 (m, 2H), 2.55 – 2.49 (m, 2H), 2.11 – 2.05 (m, 1H), 1.93 – 1.85 (m, 2H), 1.30 (s, 18H), 1.00 – 0.86 (m, 12H).

¹³C NMR (150 MHz, CDCl₃) δ 172.3, 151.5, 146.3, 143.3, 142.4, 141.2, 139.7, 138.6, 130.3, 128.5, 125.8, 123.4, 122.5, 122.0, 64.2, 54.5, 35.0, 31.6, 31.5, 28.7, 25.1, 23.5.

HRMS (ESI): exact mass calcd for C₃₆H₄₉N₃NaO⁺ (M+Na)⁺ requires m/z 562.3768, found m/z 562.3761.

(S)-4-(3,5-Di-*tert*-butylphenyl)-3-(2-(phenylcarbamoyl)pyrrolidin-1-yl)pyridine 1-oxide (C6h)



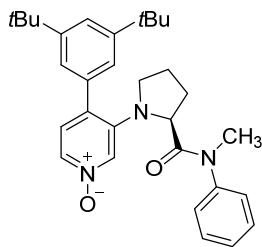
White solid, m.p.: 135.6–138.3 °C. R_f = 0.19 (CH₂Cl₂/MeOH, 30/1, v/v). [α]_D²⁵ = -45.3 (c = 0.08, CHCl₃).

¹H NMR (600 MHz, CDCl₃) δ 8.82 (s, 1H), 8.35 (d, J = 7.8 Hz, 1H), 7.86 (dd, J = 6.6, 1.8 Hz, 1H), 7.46 (t, J = 7.8 Hz, 1H), 7.32 (d, J = 1.8 Hz, 2H), 7.24 (d, J = 7.2 Hz, 2H), 7.15 – 7.11 (m, 3H), 6.97 (t, J = 7.2 Hz, 1H), 4.24 (t, J = 7.2 Hz, 1H), 3.27 – 3.23 (m, 1H), 2.91 – 2.87 (m, 1H), 2.39 – 2.34 (m, 1H), 2.10 – 2.04 (m, 1H), 1.94 – 1.90 (m, 1H), 1.83 – 1.78 (m, 1H), 1.35 (s, 18H).

¹³C NMR (150 MHz, CDCl₃) δ 170.4, 151.4, 145.0, 137.7, 137.4, 132.3, 130.8, 129.5, 128.9, 128.3, 124.2, 123.1, 122.2, 119.8, 64.3, 54.9, 35.1, 31.7, 31.6, 25.2.

HRMS (ESI): exact mass calcd for C₃₀H₃₇N₃NaO₂⁺ (M+Na)⁺ requires m/z 494.2778, found m/z 494.2776.

(S)-4-(3,5-Di-*tert*-butylphenyl)-3-(2-(methyl(phenyl)carbamoyl)pyrrolidin-1-yl)pyridine 1-oxide (C6i)



White solid, m.p.: 97.9–101.2 °C. R_f = 0.24 (CH₂Cl₂/MeOH, 30/1, v/v). [α]_D²⁵ = +34.7 (c = 0.2, CHCl₃).

¹H NMR (600 MHz, CDCl₃) δ 7.92 (s, 1H), 7.79 (d, *J* = 4.8 Hz, 1H), 7.48 (s, 1H), 7.38 (s, 2H), 7.30 – 7.28 (m, 3H), 7.03 (d, *J* = 4.8 Hz, 1H), 6.70 (s, 2H), 4.28 (t, *J* = 7.2 Hz, 1H), 3.35 – 3.31 (m, 1H), 3.12 (s, 2H), 3.08 (t, *J* = 7.8 Hz, 1H), 1.85 – 1.81 (m, 1H), 1.76 – 1.69 (m, 1H), 1.68 – 1.56 (m, 1H), 1.33 (s, 18H).

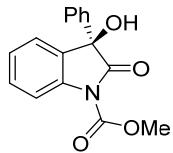
¹³C NMR (150 MHz, CDCl₃) δ 171.8, 151.1, 144.3, 142.6, 137.9, 129.9, 129.8, 129.3, 128.9, 127.9, 127.5, 122.9, 121.7, 59.3, 51.5, 37.8, 35.0, 31.5, 31.2, 24.4.

HRMS (ESI): exact mass calcd for C₃₁H₃₉N₃NaO₂⁺ (M+Na)⁺ requires m/z 508.2934, found m/z 508.2931.

9. The analytical and spectral characterization data for products

(R)-Methyl 3-hydroxy-2-oxo-3-phenylindoline-1-carboxylate (1a)

(Known compound, see: H. Mandai, R. Shiimoto, K. Fujii, K. Mitsudo and S. Suga, *Org. Lett.*, 2021, **23**, 1169.)



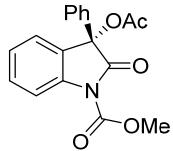
White solid (10.6 mg, 37% yield, 96% ee). m.p.: 145.6–147.5 °C. R_f = 0.24 (Pet/EtOAc, 5/1, v/v).

HPLC CHIRALCEL ODH, *n*-hexane/2-propanol = 90/10, flow rate = 1.0 mL/min, λ = 256 nm, retention time: 11.438 min, 14.042 min; [α]_D²⁵ = +64.6 (c = 0.5, CHCl₃).

¹H NMR (600 MHz, CDCl₃) δ 7.97 (d, *J* = 7.8 Hz, 1H), 7.40 (t, *J* = 7.2 Hz, 1H), 7.34 – 7.30 (m, 6H), 7.21 (t, *J* = 7.8 Hz, 1H), 3.95 (s, 1H), 3.89 (br, 1H).

HRMS (ESI): exact mass calcd for C₁₆H₁₃NNaO₄⁺ (M+Na)⁺ requires m/z 306.0737, found m/z 306.0736.

(S)-Methyl 3-(acetoxy)-2-oxo-3-phenylindoline-1-carboxylate (3a)



White solid (17.5 mg, 54% yield, 83% ee). m.p.: 159.7–162.6 °C. $R_f = +0.44$ (Pet/EtOAc, 5/1, v/v).

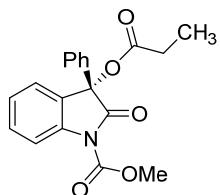
HPLC CHIRALCEL ODH, *n*-hexane/2-propanol = 90/10, flow rate = 1.0 mL/min, $\lambda = 256$ nm, retention time: 9.302 min, 20.263 min. $[\alpha]_D^{25} = 68.8$ ($c = 0.4$, CHCl_3).

$^1\text{H NMR}$ (600 MHz, CDCl_3) δ 8.08 (d, $J = 8.4$ Hz, 1H), 7.48 – 7.45 (m, 1H), 7.35 – 7.30 (m, 5H), 7.27 – 7.25 (m, 2H), 3.96 (s, 3H), 2.17 (s, 3H).

$^{13}\text{C NMR}$ (150 MHz, CDCl_3) δ 171.6, 169.5, 151.5, 140.3, 135.8, 130.6, 129.4, 128.78, 128.75, 127.2, 124.1, 115.6, 80.9, 54.0, 20.7.

HRMS (ESI): exact mass calcd for $\text{C}_{18}\text{H}_{15}\text{NNaO}_5^+$ ($\text{M}+\text{Na}$) $^+$ requires m/z 348.0842, found m/z 348.0843.

(S)-Methyl 3-(propionyloxy)-2-oxo-3-phenylindoline-1-carboxylate (3b)



White solid, m.p.: 138.2–140.8 °C. $R_f = 0.47$ (Pet/EtOAc, 5/1, v/v);

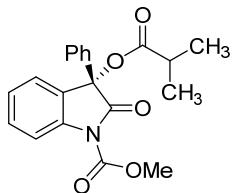
$^1\text{H NMR}$ (600 MHz, CDCl_3) δ 8.07 (d, $J = 8.4$ Hz, 1H), 7.48 – 7.45 (m, 1H), 7.35 – 7.29 (m, 5H), 7.25 – 7.21 (m, 2H), 3.96 (s, 3H), 2.71 (sep, $J = 7.2$ Hz, 1H), 1.24 (d, $J = 6.6$ Hz, 3H), 1.18 (d, $J = 7.2$ Hz, 3H).

$^{13}\text{C NMR}$ (150 MHz, CDCl_3) δ 173.0, 171.6, 151.5, 140.3, 135.9, 130.6, 129.4, 128.8, 127.3, 126.7, 125.5, 124.0, 115.6, 80.7, 54.0, 27.3, 8.8.

HRMS (ESI): exact mass calcd for $\text{C}_{19}\text{H}_{17}\text{NNaO}_5^+$ ($\text{M}+\text{Na}$) $^+$ requires m/z 362.0999, found m/z 362.0999.

(S)-methyl 3-(isobutyryloxy)-2-oxo-3-phenylindoline-1-carboxylate (3c)

(Known compound, see: H. Mandai, R. Shiomoto, K. Fujii, K. Mitsudo and S. Suga, *Org. Lett.*, 2021, **23**, 1169.)

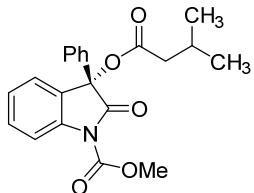


White solid, m.p.: 103.2–106.3 °C. $R_f = 0.51$ (Pet/EtOAc, 5/1, v/v).

$^1\text{H NMR}$ (600 MHz, CDCl₃) δ 8.07 (d, $J = 8.4$ Hz, 1H), 7.48 – 7.45 (m, 1H), 7.35 – 7.29 (m, 5H), 7.25 – 7.21 (m, 2H), 3.96 (s, 1H), 2.71 (sep, $J = 7.0$ Hz, 1H), 1.24 (d, $J = 6.6$ Hz, 3H), 1.18 (d, $J = 7.2$ Hz, 3H).

HRMS (ESI): exact mass calcd for C₂₀H₁₉NNaO₅⁺ (M+Na)⁺ requires m/z 376.1155, found m/z 376.1158.

(S)-Methyl 3-((3-methylbutanoyl)oxy)-2-oxo-3-phenylindoline-1-carboxylate (3d)



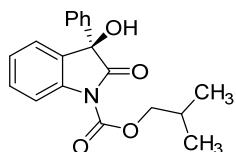
White solid, m.p.: 90.6–92.4 °C. $R_f = 0.49$ (Pet/EtOAc, 5/1, v/v).

$^1\text{H NMR}$ (600 MHz, CDCl₃) δ 8.07 (d, $J = 8.4$ Hz, 1H), 7.47 – 7.45 (m, 1H), 7.35 – 7.29 (m, 5H), 7.25 – 7.23 (m, 2H), 3.96 (s, 3H), 2.33 (dd, $J = 14.4, 7.2$ Hz, 1H), 2.28 (dd, $J = 15, 7.2$ Hz, 1H), 2.14 (sep, $J = 7.2$ Hz, 1H), 0.97 (dd, $J = 8.4, 6.6$ Hz, 6H).

$^{13}\text{C NMR}$ (150 MHz, CDCl₃) δ 171.7, 171.6, 151.5, 140.4, 136.0, 130.6, 129.4, 128.8, 127.4, 126.8, 125.4, 124.0, 115.7, 80.8, 54.1, 43.0, 26.1, 22.5.

HRMS (ESI): exact mass calcd for C₂₁H₂₁NNaO₅⁺ (M+Na)⁺ requires m/z 390.1312, found m/z 390.1314.

(R)-Isobutyl -3-hydroxy-2-oxo-3-phenylindoline-1-carboxylate (1e)



White solid (12.2 mg, 38% yield, 98% ee). m.p.: 118.7-120.2 °C. $R_f = 0.23$ (Pet/EtOAc, 5/1, v/v).

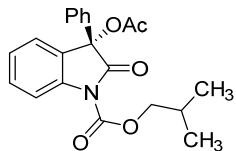
HPLC CHIRALCEL ID, *n*-hexane/2-propanol = 90/10, flow rate = 1.0 mL/min, $\lambda = 256$ nm, retention time: 8.992 min, 11.087 min. $[\alpha]_D^{25} = +40.0$ ($c = 0.6$, CHCl₃).

¹H NMR (600 MHz, CDCl₃) δ 8.00 (d, $J = 7.8$ Hz, 1H), 7.42 (td, $J = 7.8, 1.8$ Hz, 1H), 7.37 – 7.32 (m, 6H), 7.23 (td, $J = 7.2, 1.2$ Hz, 1H), 4.21 (dd, $J = 10.8, 6.6$ Hz, 1H), 4.15 (dd, $J = 10.8, 6.6$ Hz, 1H), 3.34 (br, 1H), 2.11 (sep, $J = 7.2$ Hz, 1H), 1.03 (dd, $J = 6.6, 2.4$ Hz, 6H).

¹³C NMR (150 MHz, CDCl₃) δ 175.7, 151.0, 139.8, 130.5, 128.9, 128.8, 125.7, 125.6, 115.6, 77.9, 73.7, 27.9, 19.1.

HRMS (ESI): exact mass calcd for C₁₉H₁₉NNaO₄⁺ (M+Na)⁺ requires m/z 348.1206, found m/z 349.1209.

(S)-Isobutyl -3-acetoxy-2-oxo-3-phenylindoline-1-carboxylate (3e)



Colorless oil (16.7 mg, 45% yield, 80% ee). $R_f = 0.43$ (Pet/EtOAc, 5/1, v/v).

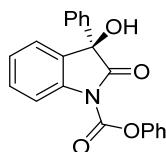
HPLC CHIRALCEL ODH, *n*-hexane/2-propanol = 90/10, flow rate = 1.0 mL/min, $\lambda = 256$ nm, retention time: 5.903 min, 7.880 min. $[\alpha]_D^{25} = +54.7$ ($c = 0.3$, CHCl₃).

¹H NMR (600 MHz, CDCl₃) δ 8.06 (d, $J = 8.4$ Hz, 1H), 7.47 – 7.44 (m, 1H), 7.34 – 7.30 (m, 5H), 7.26 – 7.22 (m, 2H), 4.18 (dd, $J = 10.8, 6.6$ Hz, 1H), 4.10 (dd, $J = 10.2, 6.6$ Hz, 1H), 2.16 (s, 3H), 2.08 (sep, $J = 6.6$ Hz, 1H), 0.99 (dd, $J = 6.6, 3$ Hz, 6H).

¹³C NMR (150 MHz, CDCl₃) δ 171.3, 169.4, 151.1, 140.5, 136.0, 130.6, 129.4, 128.8, 127.2, 126.7, 125.3, 124.1, 115.6, 80.9, 73.4, 27.8, 20.7, 19.14, 19.10;

HRMS (ESI): exact mass calcd for C₂₁H₂₁NNaO₅⁺ (M+Na)⁺ requires m/z 390.1312, found m/z 390.1316.

(R)-Phenyl 3-hydroxy-2-oxo-3-phenylindoline-1-carboxylate (1f)



White solid (14.0 mg, 41% yield, 94% ee). m.p.: 109.8–113.8 °C. $R_f = 0.32$ (Pet/EtOAc, 5/1, v/v).

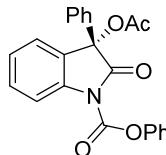
HPLC CHIRALCEL ODH, *n*-hexane/2-propanol = 90/10, flow rate = 1.0 mL/min, $\lambda = 256$ nm, retention time: 20.018 min, 24.643 min. $[\alpha]_D^{25} = +29.5$ ($c = 0.3$, CHCl₃).

¹H NMR (600 MHz, CDCl₃) δ 8.01 (d, $J = 8.4$ Hz, 1H), 7.41 – 7.35 (m, 5H), 7.32 – 7.29 (m, 4H), 7.27 – 7.25 (m, 4H), 3.87 (br, 1H).

¹³C NMR (150 MHz, CDCl₃) δ 175.6, 150.1, 149.4, 139.5, 139.0, 130.6, 130.3, 129.7, 129.0, 128.9, 126.7, 126.1, 125.8, 125.3, 115.8, 78.0.

HRMS (ESI): exact mass calcd for C₁₄H₁₁NSNaO₄⁺ (M+Na)⁺ requires m/z 368.0893, found m/z 368.0896.

(S)-Phenyl 3-acetoxy-2-oxo-3-phenylindoline-1-carboxylate (3f)



White solid (19.3 mg, 50% yield, 67% ee). m.p.: 173.9–177.6 °C. $R_f = 0.52$ (Pet/EtOAc, 5/1, v/v).

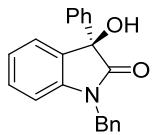
HPLC CHIRALCEL ODH, *n*-hexane/2-propanol = 90/10, flow rate = 1.0 mL/min, $\lambda = 256$ nm, retention time: 9.660 min, 10.730 min. $[\alpha]_D^{25} = +45.8$ ($c = 0.4$, CHCl₃).

¹H NMR (600 MHz, CDCl₃) δ 8.11 – 8.09 (m, 1H), 7.50 – 7.47 (m, 1H), 7.41 – 7.35 (m, 7H), 7.41 – 7.35 (m, 5H), 2.21 (s, 3H).

¹³C NMR (150 MHz, CDCl₃) δ 171.2, 169.6, 150.2, 149.5, 140.1, 135.7, 130.8, 129.63, 129.60, 128.9, 127.3, 126.5, 125.8, 124.2, 121.7, 115.8, 80.9, 20.8;

HRMS (ESI): exact mass calcd for C₂₃H₁₉NNaO₄⁺ (M+Na)⁺ requires m/z 410.0999, found m/z 410.0989.

(R)-1-Benzyl-3-hydroxy-3-phenylindolin-2-one (1g)



White solid (11.4 mg, 36% yield, 69% ee). m.p.: 143.1-143.9 °C. $R_f = 0.19$ (Pet/EtOAc, 5/1, v/v).

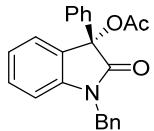
HPLC CHIRALCEL ODH, *n*-hexane/2-propanol = 90/10, flow rate = 1.0 mL/min, $\lambda = 256$ nm, retention time: 11.607 min, 13.375 min. $[\alpha]_D^{25} = +16.5$ ($c = 0.6$, CHCl₃).

¹H NMR (600 MHz, CDCl₃) δ 7.40 – 7.38 (m, 2H), 7.33 – 7.23 (m, 9H), 7.19 (td, $J = 7.8, 1.2$ Hz, 1H), 7.01 (td, $J = 7.8, 1.2$ Hz, 1H), 6.76 (d, $J = 7.8$ Hz, 1H), 5.01 (d, $J = 15.6$ Hz, 1H), 4.78 (d, $J = 15.6$ Hz, 1H), 3.88 (br, 1H).

¹³C NMR (150 MHz, CDCl₃) δ 177.9, 142.7, 140.3, 135.5, 131.9, 129.8, 129.0, 128.7, 128.4, 127.9, 127.4, 125.5, 125.1, 123.7, 109.9, 78.1, 44.1.

HRMS (ESI): exact mass calcd for C₂₁H₁₇NNaO₂⁺ (M+Na)⁺ requires m/z 338.1151, found m/z 338.1149.

(S)-1-Benzyl-2-oxo-3-phenylindolin-3-yl acetate (3g)



White solid (14.7 mg, 41% yield, 81% ee). m.p.: 137.2-139.3 °C. $R_f = 0.40$ (Pet/EtOAc, 5/1, v/v).

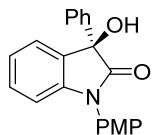
HPLC CHIRALCEL ODH, *n*-hexane/2-propanol = 90/10, flow rate = 1.0 mL/min, $\lambda = 256$ nm, retention time: 9.900 min, 12.222 min. $[\alpha]_D^{25} = +25.6$ ($c = 0.3$, CHCl₃).

¹H NMR (600 MHz, CDCl₃) δ 7.38 – 7.36 (m, 2H), 7.35 – 7.28 (m, 7H), 7.25 – 7.21 (m, 3H), 7.05 (td, $J = 7.8, 1.2$ Hz, 1H), 6.71 (d, $J = 7.8$ Hz, 1H), 4.92 (dd, $J = 21.6, 16.2$ Hz, 2H), 2.19 (s, 3H).

¹³C NMR (150 MHz, CDCl₃) δ 174.1, 169.2, 143.7, 136.7, 135.6, 130.1, 129.1, 128.8, 128.7, 128.3, 127.7, 127.3, 126.4, 124.2, 123.2, 109.9, 81.4, 44.3, 21.0.

HRMS (ESI): exact mass calcd for C₂₃H₁₉NNaO₃⁺ (M+Na)⁺ requires m/z 380.1257, found m/z 380.1255.

(R)-3-Hydroxy-1-(4-methoxyphenyl)-3-phenylindolin-2-one (1h)



White solid (10.6 mg, 32% yield, 85% ee). m.p.: 181.2-184.4 °C. $R_f = 0.21$ (Pet/EtOAc, 5/1, v/v).

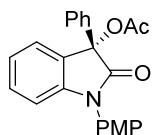
HPLC CHIRALCEL ODH, *n*-hexane/2-propanol = 90/10, flow rate = 1.0 mL/min, $\lambda = 256$ nm, retention time: 16.365 min, 20.872 min. $[\alpha]_D^{25} = +28.0$ ($c = 0.5$, CHCl₃).

¹H NMR (600 MHz, CDCl₃) δ 7.49 – 7.47 (m, 2H), 7.37 – 7.31 (m, 6H), 7.27 – 7.25 (m, 1H), 7.09 (t, $J = 7.2$ Hz, 1H), 7.04 (d, $J = 9.0$ Hz, 2H), 6.82 (d, $J = 7.8$ Hz, 1H), 3.86 (s, 3H), 3.36 (br, 1H).

¹³C NMR (150 MHz, CDCl₃) δ 177.2, 159.5, 144.1, 131.3, 129.9, 128.9, 128.5, 128.0, 126.7, 125.4, 125.3, 124.0, 115.2, 110.1, 78.2, 55.7.

HRMS (ESI): exact mass calcd for C₂₁H₁₇NNaO₃⁺ (M+Na)⁺ requires m/z 354.1101, found m/z 354.1095.

(S)-1-(4-Methoxyphenyl)-2-oxo-3-phenylindolin-3-yl acetate (3h)



White solid (16.1 mg, 43% yield, 77% ee). m.p.: 163.8-167.1 °C. $R_f = 0.43$ (Pet/EtOAc, 5/1, v/v).

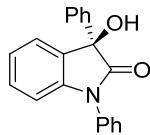
HPLC CHIRALCEL ODH, *n*-hexane/2-propanol = 90/10, flow rate = 1.0 mL/min, $\lambda = 256$ nm, retention time: 14.178 min, 20.467 min. $[\alpha]_D^{25} = +33.8$ ($c = 0.5$, CHCl₃).

¹H NMR (600 MHz, CDCl₃) δ 7.49 – 7.48 (m, 2H), 7.38 – 7.35 (m, 5H), 7.32 – 7.29 (m, 2H), 7.13 (t, $J = 7.2$ Hz, 1H), 7.02 (d, $J = 9.0$ Hz, 1H), 6.78 (d, $J = 8.4$ Hz, 1H), 3.84 (s, 3H), 2.21 (s, 3H).

¹³C NMR (150 MHz, CDCl₃) δ 173.8, 169.4, 159.5, 145.5, 136.5, 130.1, 129.0, 128.7, 128.4, 128.0, 127.3, 126.5, 124.4, 123.4, 115.0, 109.9, 81.3, 55.6, 21.0;

HRMS (ESI): exact mass calcd for C₂₃H₁₉NNaO₄⁺ (M+Na)⁺ requires m/z 396.1206, found m/z 396.1198.

(R)-3-Hydroxy-1,3-diphenylindolin-2-one (1i)



White solid (13.7 mg, 45% yield, 97% ee). m.p.: 166.0–169.6 °C. $R_f = 0.23$ (Pet/EtOAc, 5/1, v/v).

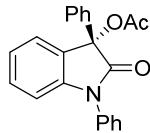
HPLC CHIRALCEL IA, *n*-hexane/2-propanol = 90/10, flow rate = 1.0 mL/min, $\lambda = 256$ nm, retention time: 19.536 min, 21.868 min. $[\alpha]_D^{25} = +140.2$ ($c = 0.4$, CHCl₃).

¹H NMR (600 MHz, CDCl₃) δ 7.51 (t, $J = 7.2$ Hz, 2H), 7.47 – 7.39 (m, 5H), 7.35 – 7.28 (m, 4H), 7.24 (d, $J = 9.0$ Hz, 1H), 3.36 (br, 1H).

¹³C NMR (150 MHz, CDCl₃) δ 177.0, 143.6, 140.5, 134.1, 131.5, 129.9, 129.8, 128.9, 128.5, 128.4, 126.6, 125.4, 124.1, 110.1, 78.2.

HRMS (ESI): exact mass calcd for C₂₀H₁₅NNaO₂⁺ (M+Na)⁺ requires m/z 324.0995, found m/z 324.0995.

(S)-2-Oxo-1,3-diphenylindolin-3-yl acetate (3i)



White solid (16.9 mg, 49% yield, 95% ee). m.p.: 145.9–149.6 °C. $R_f = 0.48$ (Pet/EtOAc, 5/1, v/v).

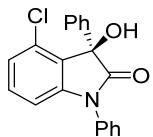
HPLC CHIRALCEL ODH, *n*-hexane/2-propanol = 90/10, flow rate = 1.0 mL/min, $\lambda = 256$ nm, retention time: 9.727 min, 10.500 min. $[\alpha]_D^{25} = +72.5$ ($c = 0.4$, CHCl₃).

¹H NMR (600 MHz, CDCl₃) δ 7.53 – 7.47 (m, 6H), 7.43 – 7.38 (m, 4H), 7.34 – 7.32 (m, 2H), 7.15 (t, $J = 7.2$ Hz, 1H), 6.86 (d, $J = 8.4$ Hz, 1H), 2.22 (s, 3H).

¹³C NMR (150 MHz, CDCl₃) δ 173.5, 169.4, 145.0, 136.5, 134.7, 130.1, 129.7, 129.1, 128.7, 128.4, 128.1, 126.7, 126.5, 124.5, 123.5, 109.9, 81.3, 20.9.

HRMS (ESI): exact mass calcd for C₂₂H₁₇NNaO₃⁺ (M+Na)⁺ requires m/z 366.1101, found m/z 366.1098.

(R)-4-Chloro-3-hydroxy-1,3-diphenylindolin-2-one (1j)



White solid (13.7 mg, 41% yield, 99% ee). m.p.: 179.0–182.6 °C. $R_f = 0.32$ (Pet/EtOAc, 5/1, v/v).

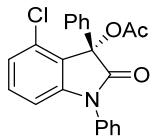
HPLC CHIRALCEL ODH, *n*-hexane/2-propanol = 90/10, flow rate = 1.0 mL/min, $\lambda = 256$ nm, retention time: 10.328 min, 12.397 min. $[\alpha]_D^{25} = -9.3$ ($c = 0.4$, CHCl_3).

$^1\text{H NMR}$ (600 MHz, CDCl_3) δ 7.52 (t, $J = 7.8$ Hz, 2H), 7.48 – 7.46 (m, 2H), 7.44 – 7.35 (m, 6H), 7.25 (t, $J = 7.8$ Hz, 1H), 7.08 (d, $J = 7.8$ Hz, 1H), 6.81 (d, $J = 7.8$ Hz, 1H), 3.57 (br, 1H).

$^{13}\text{C NMR}$ (150 MHz, CDCl_3) δ 175.4, 145.6, 138.1, 133.8, 132.3, 131.2, 130.0, 128.8, 128.7, 128.1, 126.6, 125.6, 124.9, 108.6, 78.7.

HRMS (ESI): exact mass calcd for $\text{C}_{20}\text{H}_{14}\text{ClNNaO}_2^+$ ($\text{M}+\text{Na}$) $^+$ requires m/z 358.0605, found m/z 358.0606.

(S)-4-Chloro-2-oxo-1,3-diphenylindolin-3-yl acetate (3j)



White solid (19.7 mg, 52% yield, 83% ee). m.p.: 163.3–167.0 °C. $R_f = 0.48$ (Pet/EtOAc, 5/1, v/v).

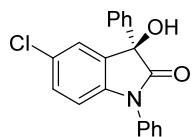
HPLC CHIRALCEL ODH, *n*-hexane/2-propanol = 90/10, flow rate = 1.0 mL/min, $\lambda = 256$ nm, retention time: 7.642 min, 8.897 min. $[\alpha]_D^{25} = +74.1$ ($c = 0.5$, CHCl_3).

$^1\text{H NMR}$ (600 MHz, CDCl_3) δ 7.54 – 7.48 (m, 4H), 7.45 – 7.40 (m, 6H), 7.28 (t, $J = 3.6$ Hz, 1H), 7.09 (d, $J = 7.8$ Hz, 1H), 6.76 (d, $J = 7.8$ Hz, 1H), 2.29 (s, 3H).

$^{13}\text{C NMR}$ (150 MHz, CDCl_3) δ 172.9, 169.7, 146.8, 134.4, 134.2, 131.4, 131.3, 129.8, 129.3, 128.9, 128.7, 127.1, 126.1, 124.9, 124.4, 108.4, 81.4, 20.5.

HRMS (ESI): exact mass calcd for $\text{C}_{22}\text{H}_{16}\text{ClNNaO}_3^+$ ($\text{M}+\text{Na}$) $^+$ requires m/z 400.0711, found m/z 400.0713.

(R)-5-Chloro-3-hydroxy-1,3-diphenylindolin-2-one (1k)



White solid (14.7 mg, 44% yield, 99% ee). m.p.: 175.9–179.6 °C. $R_f = 0.24$ (Pet/EtOAc, 5/1, v/v).

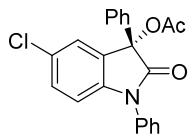
HPLC CHIRALCEL ODH, *n*-hexane/2-propanol = 90/10, flow rate = 1.0 mL/min, $\lambda = 256$ nm, retention time: 9.260 min, 14.766 min. $[\alpha]_D^{25} = +54.9$ ($c = 0.4$, CHCl₃).

¹H NMR (600 MHz, CDCl₃) δ 7.54 (t, $J = 7.8$ Hz, 2H), 7.47 – 7.42 (m, 5H), 7.39 – 7.34 (m, 3H), 7.31 (d, $J = 2.4$ Hz, 1H), 7.31 (dd, $J = 8.4, 1.8$ Hz, 1H), 6.82 (d, $J = 8.4$ Hz, 1H), 3.85 (br, 1H).

¹³C NMR (150 MHz, CDCl₃) δ 176.7, 142.0, 139.9, 133.8, 133.1, 130.0, 129.9, 129.8, 129.4, 129.0, 128.8, 128.7, 126.5, 125.8, 125.3, 111.2, 78.2.

HRMS (ESI): exact mass calcd for C₂₀H₁₄ClNNaO₂⁺ (M+Na)⁺ requires m/z 358.0605, found m/z 358.0603.

(S)-5-Chloro-2-oxo-1,3-diphenylindolin-3-yl acetate (3k)



White solid (18.9 mg, 50% yield, 90% ee). m.p.: 172.6–176.5 °C. $R_f = 0.44$ (Pet/EtOAc, 5/1, v/v).

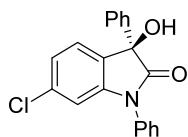
HPLC CHIRALCEL ID, *n*-hexane/2-propanol = 90/10, flow rate = 1.0 mL/min, $\lambda = 256$ nm, retention time: 13.750 min, 21.401 min. $[\alpha]_D^{25} = +43.9$ ($c = 0.5$, CHCl₃).

¹H NMR (600 MHz, CDCl₃) δ 7.53 – 7.50 (m, 2H), 7.48 – 7.46 (m, 2H), 7.44 – 7.39 (m, 6H), 7.30 – 7.28 (m, 2H), 6.78 (d, $J = 9.0$ Hz, 1H), 2.24 (s, 3H).

¹³C NMR (150 MHz, CDCl₃) δ 173.1, 169.5, 143.6, 135.8, 134.3, 130.1, 129.9, 129.8, 129.3, 128.9, 128.8, 128.6, 126.3, 124.7, 111.0, 81.0, 20.9.

HRMS (ESI): exact mass calcd for C₂₂H₁₆ClNNaO₃⁺ (M+Na)⁺ requires m/z 400.0711, found m/z 400.0697.

(R)-6-Chloro-3-hydroxy-1,3-diphenylindolin-2-one (1l)



White solid (15.4 mg, 46% yield, 97% ee). m.p.: 198.9-201.2 °C. $R_f = 0.32$ (Pet/EtOAc, 5/1, v/v).

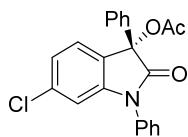
HPLC CHIRALCEL ODH, *n*-hexane/2-propanol = 90/10, flow rate = 1.0 mL/min, $\lambda = 256$ nm, retention time: 15.917 min, 22.748 min. $[\alpha]_D^{25} = +80.6$ ($c = 0.4$, CHCl₃).

¹H NMR (600 MHz, CDCl₃) δ 7.55 (t, $J = 7.8$ Hz, 2H), 7.47 – 7.41 (m, 5H), 7.38 – 7.33 (m, 3H), 7.25 (d, $J = 6.6$ Hz, 1H), 7.08 (dd, $J = 7.8, 1.8$ Hz, 1H), 6.87 (d, $J = 1.8$ Hz, 1H), 3.63 (br, 1H).

¹³C NMR (150 MHz, CDCl₃) δ 177.0, 144.7, 140.0, 135.8, 133.7, 130.1, 129.8, 128.0, 128.9, 128.8, 126.5, 126.4, 125.3, 110.8, 77.9.

HRMS (ESI): exact mass calcd for C₂₀H₁₄ClNNaO₂⁺ (M+Na)⁺ requires m/z 358.0605, found m/z 358.0604.

(S)-6-Chloro-2-oxo-1,3-diphenylindolin-3-yl acetate (3l)



White solid (18.4 mg, 49% yield, 92% ee). m.p.: 196.9-200.2 °C. $R_f = 0.48$ (Pet/EtOAc, 5/1, v/v).

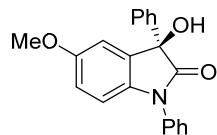
HPLC CHIRALCEL ODH, *n*-hexane/2-propanol = 90/10, flow rate = 1.0 mL/min, $\lambda = 254$ nm, retention time: 8.312 min, 10.654 min. $[\alpha]_D^{25} = +42.5$ ($c = 0.5$, CHCl₃).

¹H NMR (600 MHz, CDCl₃) δ 7.54 – 7.52 (m, 2H), 7.48 – 7.42 (m, 8H), 7.23 (d, $J = 7.8$ Hz, 1H), 7.12 (dd, $J = 7.8, 1.8$ Hz, 1H), 6.83 (d, $J = 1.8$ Hz, 1H), 2.22 (s, 3H).

¹³C NMR (150 MHz, CDCl₃) δ 173.4, 169.5, 146.3, 136.1, 135.9, 134.2, 130.0, 129.3, 128.9, 128.8, 127.0, 126.4, 125.5, 123.5, 110.6, 80.8, 20.9.

HRMS (ESI): exact mass calcd for C₂₂H₁₆ClNNaO₃⁺ (M+Na)⁺ requires m/z 400.0711, found m/z 400.0705.

(R)-3-Hydroxy-5-methoxy-1,3-diphenylindolin-2-one (1m)



White solid (15.6 mg, 47% yield, 83% ee). m.p.: 110.5.0-113.6 °C. $R_f = 0.13$ (Pet/EtOAc, 5/1, v/v).

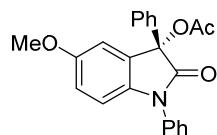
HPLC CHIRALCEL ODH, *n*-hexane/2-propanol = 90/10, flow rate = 1.0 mL/min, $\lambda = 256$ nm, retention time: 11.643 min, 19.335 min. $[\alpha]_D^{25} = +69.2$ ($c = 0.3$, CHCl₃).

¹H NMR (600 MHz, CDCl₃) δ 7.54 – 7.51 (m, 2H), 7.49 – 7.45 (m, 4H), 7.42 – 7.39 (m, 1H), 7.37 – 7.31 (m, 3H), 6.94 (d, $J = 2.4$ Hz, 1H), 6.84 – 6.79 (m, 2H), 3.75 (s, 3H), 3.72 (br, 1H).

¹³C NMR (150 MHz, CDCl₃) δ 176.9, 157.0, 140.5, 136.8, 134.4, 132.6, 129.8, 128.8, 128.5, 128.2, 126.3, 125.4, 115.0, 111.6, 110.9, 78.5, 55.9.

HRMS (ESI): exact mass calcd for C₂₁H₁₇NNaO₃⁺ (M+Na)⁺ requires m/z 354.1101, found m/z 354.1096.

(S)-5-Methoxy-2-oxo-1,3-diphenylindolin-3-yl acetate (3m)



White solid (16.5 mg, 44% yield, 83% ee). m.p.: 157.8-161.0 °C. $R_f = 0.28$ (Pet/EtOAc, 5/1, v/v).

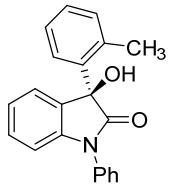
HPLC CHIRALCEL ODH, *n*-hexane/2-propanol = 90/10, flow rate = 1.0 mL/min, $\lambda = 254$ nm, retention time: 10.995 min, 12.090 min. $[\alpha]_D^{25} = +69.4$ ($c = 0.4$, CHCl₃).

¹H NMR (600 MHz, CDCl₃) δ 7.51 – 7.45 (m, 6H), 7.40 – 7.38 (m, 4H), 6.91 (d, $J = 2.4$ Hz, 1H), 6.86 – 6.79 (m, 2H), 3.78 (s, 3H), 2.22 (s, 3H).

¹³C NMR (150 MHz, CDCl₃) δ 173.3, 169.4, 156.6, 138.4, 136.5, 134.9, 129.7, 129.3, 129.1, 128.8, 128.2, 126.7, 126.4, 114.5, 111.3, 110.5, 81.6, 55.9, 21.0.

HRMS (ESI): exact mass calcd for C₂₁H₁₇NNaO₄⁺ (M+Na)⁺ requires m/z 380.1257, found m/z 380.1248.

(R)-3-Hydroxy-1-phenyl-3-(o-tolyl)indolin-2-one (1n)



White solid (11.1 mg, 35% yield, 93% ee). m.p.: 170.2–173.0 °C. $R_f = 0.25$ (Pet/EtOAc, 5/1, v/v).

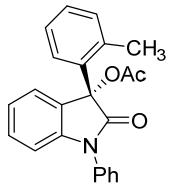
HPLC CHIRALCEL ODH, *n*-hexane/2-propanol = 90/10, flow rate = 1.0 mL/min, $\lambda = 256$ nm, retention time: 9.383 min, 11.168 min. $[\alpha]_D^{25} = +5.9$ ($c = 0.5$, CHCl_3).

$^1\text{H NMR}$ (600 MHz, CDCl_3) δ 8.01 (d, $J = 7.8$ Hz, 1H), 7.54 (t, $J = 7.8$ Hz, 2H), 7.48 – 7.42 (m, 3H), 7.31 (t, $J = 7.8$ Hz, 1H), 7.26 – 7.22 (m, 2H), 7.09 – 7.07 (m, 2H), 7.03 (t, $J = 7.8$ Hz, 1H), 6.88 (d, $J = 7.8$ Hz, 1H), 3.49 (br, 1H), 2.00 (s, 3H).

$^{13}\text{C NMR}$ (150 MHz, CDCl_3) δ 176.4, 144.2, 138.1, 134.5, 134.2, 131.6, 130.3, 129.9, 128.5, 128.4, 126.3, 126.2, 126.1, 125.4, 110.0, 77.7, 19.6.

HRMS (ESI): exact mass calcd for $\text{C}_{21}\text{H}_{17}\text{NNaO}_2^+$ ($\text{M}+\text{Na}$) $^+$ requires m/z 338.1151, found m/z 338.1159.

(S)-2-Oxo-1-phenyl-3-(o-tolyl)indolin-3-yl acetate (3n)



White solid (16.7 mg, 47% yield, 89% ee). m.p.: 147.5–151.3 °C. $R_f = 0.44$ (Pet/EtOAc, 5/1, v/v).

HPLC CHIRALCEL ODH, *n*-hexane/2-propanol = 90/10, flow rate = 1.0 mL/min, $\lambda = 256$ nm, retention time: 7.338 min, 8.273 min. $[\alpha]_D^{25} = +23.7$ ($c = 0.3$, CHCl_3).

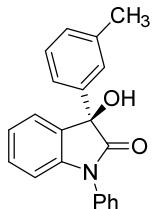
$^1\text{H NMR}$ (600 MHz, CDCl_3) δ 7.51 – 7.45 (m, 4H), 7.40 – 7.37 (m, 1H), 7.28 (t, $J = 7.8$ Hz, 1H), 7.23 – 7.19 (m, 4H), 7.14 – 7.08 (m, 2H), 6.80 (d, $J = 7.8$ Hz, 1H), 2.57 (s, 3H), 2.18 (s, 3H).

$^{13}\text{C NMR}$ (150 MHz, CDCl_3) δ 173.4, 168.9, 145.4, 137.8, 134.7, 133.1, 130.2, 129.7, 128.9, 128.4, 128.0, 127.4, 126.9, 126.0, 124.8, 123.6, 110.0, 82.9, 21.4, 21.0.

HRMS (ESI): exact mass calcd for $\text{C}_{23}\text{H}_{19}\text{NNaO}_3^+$ ($\text{M}+\text{Na}$) $^+$ requires m/z 380.1257, found m/z

380.1256.

(R)-3-Hydroxy-1-phenyl-3-(m-tolyl)indolin-2-one (1o)



White solid (15.5 mg, 49% yield, 83% ee). m.p.: 122.8–126.6 °C. $R_f = 0.24$ (Pet/EtOAc, 5/1, v/v).

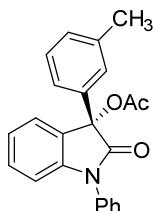
HPLC CHIRALCEL ODH, *n*-hexane/2-propanol = 90/10, flow rate = 1.0 mL/min, $\lambda = 256$ nm, retention time: 8.190 min, 10.218 min. $[\alpha]_D^{25} = +95.7$ ($c = 0.4$, CHCl₃).

¹H NMR (600 MHz, CDCl₃) δ 7.53 – 7.50 (m, 2H), 7.45 – 7.39 (m, 3H), 7.33 – 7.32 (m, 2H), 7.25 – 7.20 (m, 3H), 7.12 – 7.08 (m, 2H), 6.88 (d, $J = 7.8$ Hz, 1H), 3.83 (br, 1H), 2.33 (s, 3H).

¹³C NMR (150 MHz, CDCl₃) δ 177.1, 143.5, 140.4, 138.4, 131.6, 129.7, 129.6, 129.2, 128.3, 126.5, 126.0, 125.3, 124.0, 122.5, 110.0, 78.2, 21.7.

HRMS (ESI): exact mass calcd for C₂₁H₁₇NNaO₂⁺ (M+Na)⁺ requires m/z 338.1151, found m/z 338.1150.

(S)-2-Oxo-1-phenyl-3-(m-tolyl)indolin-3-yl acetate (3o)



White solid (17.1 mg, 48% yield, 87% ee). m.p.: 174.2–178.1 °C. $R_f = 0.47$ (Pet/EtOAc, 5/1, v/v).

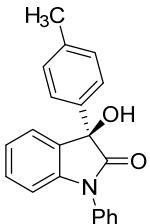
HPLC CHIRALCEL ODH, *n*-hexane/2-propanol = 90/10, flow rate = 1.0 mL/min, $\lambda = 256$ nm, retention time: 8.172 min, 9.900 min. $[\alpha]_D^{25} = +55.9$ ($c = 0.4$, CHCl₃).

¹H NMR (600 MHz, CDCl₃) δ 7.50 – 7.43 (m, 4H), 7.40 – 7.37 (m, 2H), 7.31 – 7.28 (m, 2H), 7.24 – 7.22 (m, 1H), 7.19 – 7.15 (m, 2H), 7.11 (t, $J = 7.8$ Hz, 1H), 6.83 (d, $J = 7.8$ Hz, 1H), 2.35 (s, 3H), 2.20 (s, 3H).

^{13}C NMR (150 MHz, CDCl_3) δ 173.7, 169.5, 145.0, 138.6, 136.4, 134.7, 130.0, 129.9, 129.7, 128.6, 128.4, 128.2, 127.1, 127.0, 124.5, 123.6, 123.5, 110.0, 81.4, 21.7, 21.0.

HRMS (ESI): exact mass calcd for $\text{C}_{23}\text{H}_{19}\text{NNaO}_3^+$ ($\text{M}+\text{Na}$) $^+$ requires m/z 380.1257, found m/z 380.1260.

(R)-3-Hydroxy-1-phenyl-3-(p-tolyl)indolin-2-one (1p)



White solid (14.7 mg, 47% yield, 75% ee). m.p.: 124.0–126.4 °C. $R_f = 0.24$ (Pet/EtOAc, 5/1, v/v).

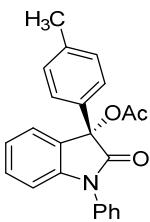
HPLC CHIRALCEL IA, *n*-hexane/2-propanol = 90/10, flow rate = 1.0 mL/min, $\lambda = 256$ nm, retention time: 20.473 min, 25.571 min. $[\alpha]_D^{25} = +85.3$ ($c = 0.3$, CHCl_3).

^1H NMR (600 MHz, CDCl_3) δ 7.51 (t, $J = 7.8$ Hz, 2H), 7.44 – 7.39 (m, 3H), 7.36 – 7.33 (m, 3H), 7.25 – 7.24 (m, 1H), 7.15 (d, $J = 7.8$ Hz, 2H), 7.09 (t, $J = 7.8$ Hz, 1H), 6.87 (d, $J = 7.8$ Hz, 1H), 3.65 (br, 1H), 2.33 (s, 3H).

^{13}C NMR (150 MHz, CDCl_3) δ 177.1, 148.5, 138.3, 137.6, 134.2, 131.6, 129.8, 129.7, 129.5, 128.4, 126.6, 125.4, 125.3, 124.0, 110.1, 78.1, 21.3.

HRMS (ESI): exact mass calcd for $\text{C}_{21}\text{H}_{17}\text{NNaO}_2^+$ ($\text{M}+\text{Na}$) $^+$ requires m/z 338.1151, found m/z 338.1142.

(S)-2-Oxo-1-phenyl-3-(p-tolyl)indolin-3-yl acetate (3p)



White solid (17.1 mg, 48% yield, 83% ee). m.p.: 164.2–166.1 °C. $R_f = 0.47$ (Pet/EtOAc, 5/1, v/v).

HPLC CHIRALCEL ODH, *n*-hexane/2-propanol = 90/10, flow rate = 1.0 mL/min, $\lambda = 256$ nm,

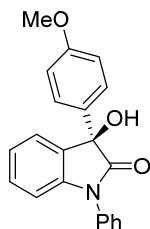
retention time: 8.221 min, 11.033 min. $[\alpha]_D^{25} = +46.8$ ($c = 0.5$, CHCl_3).

$^1\text{H NMR}$ (600 MHz, CDCl_3) δ 7.50 (t, $J = 7.8$ Hz, 2H), 7.46 – 7.44 (m, 2H), 7.41 – 7.37 (m, 3H), 7.32 – 7.30 (m, 2H), 7.18 (d, $J = 7.8$ Hz, 2H), 7.14 (t, $J = 7.8$ Hz, 1H), 6.84 (d, $J = 7.8$ Hz, 1H), 2.35 (s, 3H), 2.20 (s, 3H).

$^{13}\text{C NMR}$ (150 MHz, CDCl_3) δ 173.7, 169.5, 145.1, 139.1, 134.8, 133.5, 133.1, 129.7, 129.5, 128.3, 128.1, 127.0, 126.5, 124.5, 123.5, 110.0, 81.3, 21.3, 21.0.

HRMS (ESI): exact mass calcd for $\text{C}_{23}\text{H}_{19}\text{NNaO}_3^+$ ($\text{M}+\text{Na}$) $^+$ requires m/z 380.1257, found m/z 380.1258.

(R)-3-Hydroxy-3-(4-methoxyphenyl)-1-phenylindolin-2-one (1q)



White solid (15.0 mg, 45% yield, 69% ee). m.p.: 156.1–159.4 °C. $R_f = 0.12$ (Pet/EtOAc, 5/1, v/v).

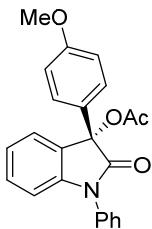
HPLC CHIRALCEL ODH, *n*-hexane/2-propanol = 90/10, flow rate = 1.0 mL/min, $\lambda = 256$ nm, retention time: 16.843 min, 22.111 min. $[\alpha]_D^{25} = +80.2$ ($c = 0.3$, CHCl_3).

$^1\text{H NMR}$ (600 MHz, CDCl_3) δ 7.46 (t, $J = 7.8$ Hz, 2H), 7.38 – 7.35 (m, 5H), 7.31 (d, $J = 7.8$ Hz, 1H), 7.21 (t, $J = 7.8$ Hz, 1H), 7.06 (t, $J = 7.8$ Hz, 1H), 6.83 – 6.81 (m, 3H), 4.07 (br, 1H), 3.73 (s, 3H).

$^{13}\text{C NMR}$ (150 MHz, CDCl_3) δ 177.2, 159.6, 143.4, 134.1, 132.5, 131.6, 129.7, 129.6, 128.3, 127.0, 126.5, 125.3, 124.0, 114.1, 110.0, 77.8, 55.3.

HRMS (ESI): exact mass calcd for $\text{C}_{21}\text{H}_{17}\text{NNaO}_3^+$ ($\text{M}+\text{Na}$) $^+$ requires m/z 354.1101, found m/z 354.1094.

(S)-3-(4-Methoxyphenyl)-2-oxo-1-phenylindolin-3-yl acetate (3q)



White solid (16.5 mg, 44% yield, 82% ee). m.p.: 134.3-138.2 °C. $R_f = 0.28$ (Pet/EtOAc, 5/1, v/v).

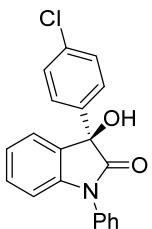
HPLC CHIRALCEL ODH, *n*-hexane/2-propanol = 90/10, flow rate = 1.0 mL/min, $\lambda = 256$ nm, retention time: 11.960 min, 17.981 min. $[\alpha]_D^{25} = +71.40$ ($c = 0.4$, CHCl₃).

¹H NMR (600 MHz, CDCl₃) δ 7.52 – 7.49 (m, 2H), 7.45 – 7.39 (m, 5H), 7.34 – 7.30 (m, 2H), 7.15 (t, $J = 6.6$ Hz, 1H), 6.92 – 6.89 (m, 2H), 6.84 (d, $J = 7.8$ Hz, 1H), 3.80 (s, 3H), 2.20 (s, 3H).

¹³C NMR (150 MHz, CDCl₃) δ 173.8, 169.6, 160.3, 145.0, 130.1, 129.7, 128.3, 128.2, 128.1, 127.9, 127.0, 124.5, 123.4, 114.1, 110.0, 81.0, 55.4, 21.0.

HRMS (ESI): exact mass calcd for C₂₃H₁₉NNaO₄⁺ (M+Na)⁺ requires m/z 396.1206, found m/z 396.1210.

(R)-3-(4-Chlorophenyl)-3-hydroxy-1-phenylindolin-2-one (1r)



White solid (9.6 mg, 29% yield, 88% ee). m.p.: 133.3-135.0 °C. $R_f = 0.21$ (Pet/EtOAc, 5/1, v/v).

HPLC CHIRALCEL ODH, *n*-hexane/2-propanol = 90/10, flow rate = 1.0 mL/min, $\lambda = 256$ nm, retention time: 7.855 min, 12.186 min. $[\alpha]_D^{25} = +84.9$ ($c = 0.3$, CHCl₃).

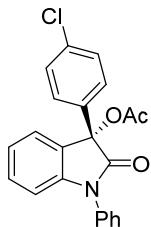
¹H NMR (600 MHz, CDCl₃) δ 7.53 (t, $J = 7.8$ Hz, 2H), 7.43 – 7.38 (m, 5H), 7.31 – 7.27 (m, 4H), 7.11 (t, $J = 7.8$ Hz, 1H), 6.89 (d, $J = 7.8$ Hz, 1H), 4.11 (br, 1H).

¹³C NMR (150 MHz, CDCl₃) δ 176.8, 143.4, 139.0, 134.4, 133.9, 131.2, 130.0, 129.8, 128.9, 128.5, 127.0, 126.5, 125.3, 124.3, 110.3, 77.8.

HRMS (ESI): exact mass calcd for C₂₀H₁₄ClNNaO₂⁺ (M+Na)⁺ requires m/z 358.0605, found m/z

358.0598.

(S)-3-(4-Chlorophenyl)-2-oxo-1-phenylindolin-3-yl acetate (3r)



White solid (16.4 mg, 43% yield, 75% ee). m.p.: 157.1–160.7 °C. $R_f = 0.41$ (Pet/EtOAc, 5/1, v/v).

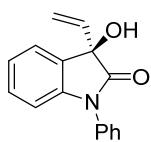
HPLC CHIRALCEL ODH, *n*-hexane/2-propanol = 90/10, flow rate = 1.0 mL/min, $\lambda = 256$ nm, retention time: 8.905 min, 11.168 min. $[\alpha]_D^{25} = +46.3$ ($c = 0.3$, CHCl_3).

$^1\text{H NMR}$ (600 MHz, CDCl_3) δ 7.51 (t, $J = 7.8$ Hz, 2H), 7.45 – 7.41 (m, 5H), 7.36 – 7.28 (m, 4H), 7.15 (t, $J = 7.8$ Hz, 1H), 6.85 (d, $J = 7.8$ Hz, 1H), 2.20 (s, 3H).

$^{13}\text{C NMR}$ (150 MHz, CDCl_3) δ 177.2, 159.6, 143.4, 134.1, 132.5, 131.6, 129.7, 129.6, 128.3, 127.0, 126.5, 125.3, 114.1, 110.0, 77.8, 55.3.

HRMS (ESI): exact mass calcd for $\text{C}_{22}\text{H}_{16}\text{ClNNaO}_3^+$ ($\text{M}+\text{Na}$) $^+$ requires m/z 354.1101, found m/z 354.1094.

(R)-3-Hydroxy-1-phenyl-3-vinylindolin-2-one (1s)



White solid (8.2 mg, 33% yield, 98% ee). m.p.: 116.5–119.8 °C. $R_f = 0.16$ (Pet/EtOAc, 5/1, v/v).

HPLC CHIRALCEL ID, *n*-hexane/2-propanol = 90/10, flow rate = 1.0 mL/min, $\lambda = 256$ nm, retention time: 16.466 min, 19.528 min. $[\alpha]_D^{25} = +50.4$ ($c = 0.4$, CHCl_3).

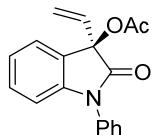
$^1\text{H NMR}$ (600 MHz, CDCl_3) δ 7.54 – 7.51 (m, 2H), 7.43 – 7.41 (m, 4H), 7.29 – 7.26 (m, 1H), 7.16 – 7.14 (m, 1H), 6.84 (d, $J = 7.8$ Hz, 1H), 6.14– 6.09 (m, 1H), 5.50 (d, $J = 17.4$ Hz, 1H), 5.38 (d, $J = 10.2$ Hz, 1H), 3.37 (br, 1H).

$^{13}\text{C NMR}$ (150 MHz, CDCl_3) δ 176.3, 143.5, 136.4, 134.1, 129.9, 129.8, 129.0, 128.4, 126.6,

125.2, 123.9, 117.2, 110.1, 77.4.

HRMS (ESI): exact mass calcd for $C_{16}H_{13}NNaO_2^+$ ($M+Na$)⁺ requires m/z 274.0838, found m/z 274.0838.

(R)-2-Oxo-1-phenyl-3-vinyllindolin-3-yl acetate (3s)



White solid (15.9 mg, 54% yield, 57% ee). m.p.: 100.6-103.3 °C. $R_f = 0.44$ (Pet/EtOAc, 5/1, v/v).

HPLC CHIRALCEL ODH, *n*-hexane/2-propanol = 90/10, flow rate = 1.0 mL/min, $\lambda = 256$ nm, retention time: 7.783 min, 9.143 min. $[\alpha]_D^{25} = +15.3$ ($c = 0.3$, CHCl₃).

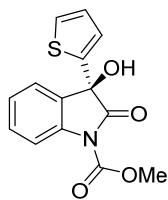
¹H NMR (600 MHz, CDCl₃) δ 7.52 – 7.50 (m, 2H), 7.44 – 7.39 (m, 3H), 7.29 – 7.25 (m, 2H), 7.10 (t, $J = 7.8$ Hz, 1H), 6.77 (d, $J = 7.8$ Hz, 1H), 6.12 (dd, $J = 17.4, 10.8$ Hz, 1H), 5.41 (d, $J = 10.8$ Hz, 1H), 5.36 (d, $J = 16.8$ Hz, 1H), 2.12 (s, 3H).

¹³C NMR (150 MHz, CDCl₃) δ 173.0, 169.2, 144.6, 134.6, 133.2, 130.1, 129.8, 128.4, 127.0, 126.2, 124.1, 123.3, 119.5, 110.0, 80.7, 20.9.

HRMS (ESI): exact mass calcd for $C_{18}H_{15}NNaO_3^+$ ($M+Na$)⁺ requires m/z 316.0944, found m/z 316.0947.

(R)-Methyl 3-hydroxy-2-oxo-3-(thiophen-2-yl)indoline-1-carboxylate (1t)

(Known compound, see: H. Mandai, R. Shiomoto, K. Fujii, K. Mitsudo and S. Suga, *Org. Lett.*, 2021, **23**, 1169.)



White solid (10.4 mg, 36% yield, 98% ee). m.p.: 116.2-120.0 °C. $R_f = 0.17$ (Pet/EtOAc, 5/1, v/v).

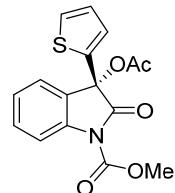
HPLC CHIRALCEL ODH, *n*-hexane/2-propanol = 90/10, flow rate = 1.0 mL/min, $\lambda = 256$ nm,

retention time: 14.312 min, 17.983 min. $[\alpha]_D^{25} = -31.2$ ($c = 0.7$, CHCl_3).

$^1\text{H NMR}$ (600 MHz, CDCl_3) δ 7.93 (d, $J = 8.4$ Hz, 1H), 7.54 (d, $J = 6.6$ Hz, 1H), 7.41 (t, $J = 7.8$ Hz, 1H), 7.31 (d, $J = 4.2$ Hz, 1H), 7.26 (t, $J = 7.8$ Hz, 1H), 6.89 (t, $J = 4.2$ Hz, 1H), 6.83 (d, $J = 1.8$ Hz, 1H), 4.10 (br, 1H), 3.95 (s, 1H).

HRMS (ESI): exact mass calcd for $\text{C}_{14}\text{H}_{11}\text{NSNaO}_4^+$ ($\text{M}+\text{Na}$) $^+$ requires m/z 312.0301, found m/z 312.0296.

(S)-Methyl 3-acetoxy-2-oxo-3-(thiophen-2-yl)indoline-1-carboxylate (3t)



White solid (13.3 mg, 40% yield, 89% ee). m.p.: 200.2-203.8 °C. $R_f = 0.43$ (Pet/EtOAc, 5/1, v/v).

HPLC CHIRALCEL ODH, *n*-hexane/2-propanol = 95/5, flow rate = 0.5 mL/min, $\lambda = 256$ nm, retention time: 12.005 min, 20.882 min. $[\alpha]_D^{25} = +128.7$ ($c = 0.4$, CHCl_3).

$^1\text{H NMR}$ (600 MHz, CDCl_3) δ 8.05 (d, $J = 7.8$ Hz, 1H), 7.47 (t, $J = 7.8$ Hz, 1H), 7.43 (d, $J = 7.2$ Hz, 1H), 7.40 (d, $J = 5.4$ Hz, 1H), 7.27 (t, $J = 7.2$ Hz, 1H), 6.93 (t, $J = 4.8$ Hz, 1H), 6.84 (d, $J = 3.6$ Hz, 1H), 3.97 (s, 3H), 2.13 (s, 3H).

$^{13}\text{C NMR}$ (150 MHz, CDCl_3) δ 170.4, 169.3, 151.4, 139.9, 137.9, 131.0, 128.8, 128.2, 126.8, 128.7, 125.3, 123.9, 115.7, 78.7, 54.1, 20.6.

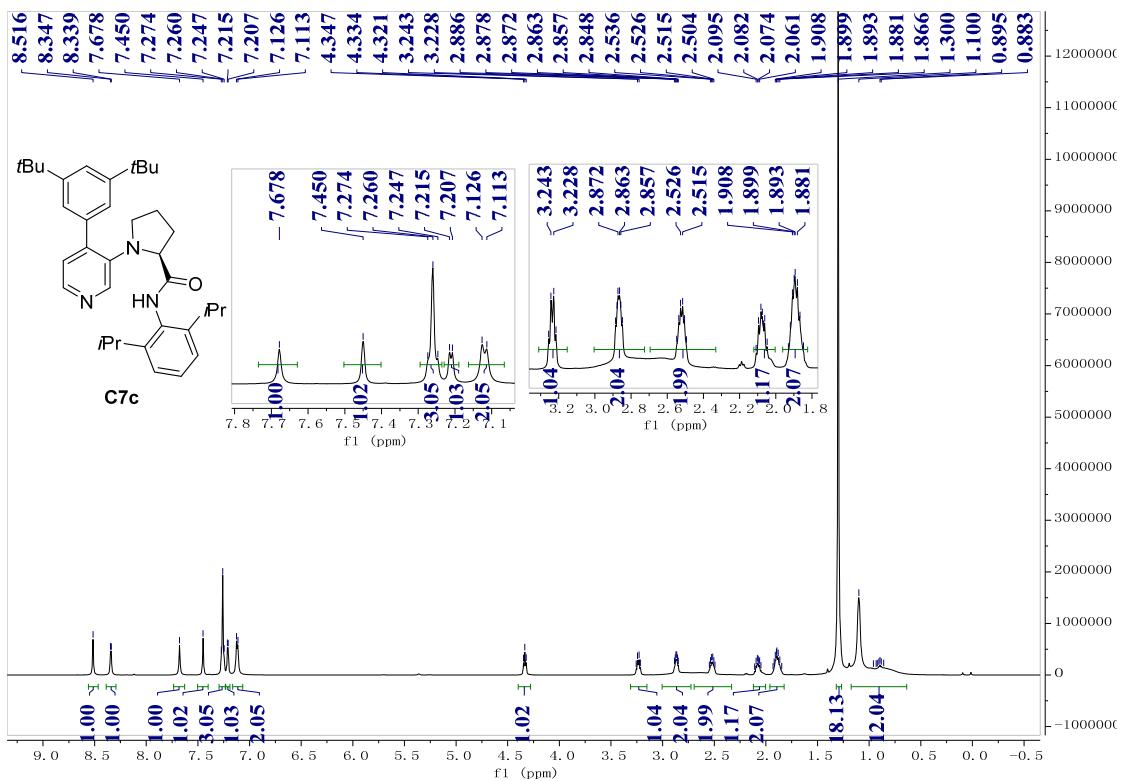
HRMS (ESI): exact mass calcd for $\text{C}_{16}\text{H}_{13}\text{NSNaO}_5^+$ ($\text{M}+\text{Na}$) $^+$ requires m/z 48.0842, found m/z 348.0843.

10. Reference

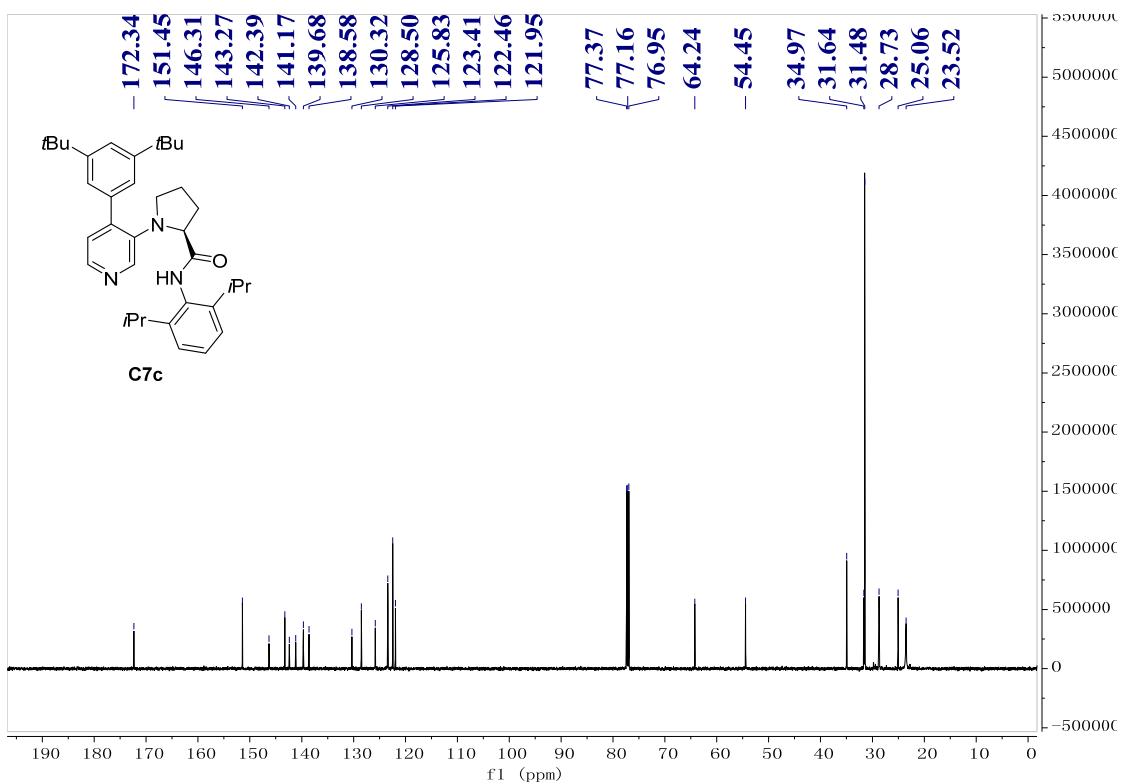
- (1) H. Mandai, R. Shiomoto, K. Fujii, K. Mitsudo and S. Suga, *Org. Lett.*, 2021, **23**, 1169.
- (2) M. D. Greenhalgh, S. M. Smith, D. M. Walden, J. E. Taylor, Z. Brice, E. R. T. Robinson, C. Fallan, D. B. Cordes, A. M. Z. Slawin, H. C. Richardson, M. A. Grove, P. H.-Y. Cheong and A. D. Smith, *Angew. Chem., Int. Ed.*, 2018, **57**, 3200.
- (3) M.-S. Xie, M. Shan, N. Li, Y.-G. Chen, X.-B. Wang, X. Cheng, Y. Tian, X.-X. Wu, Y. Deng, G.-R. Qu and H.-M. Guo, *ACS Catal.*, 2022, **12**, 877.
- (4) K. S. Kumar, R. Adepu, S. Sandra, D. Rambabu, R. Krishna, M. C. Reddy, R. Misra, M. Pal, *Bioorg. Med. Chem. Lett.*, **2012**, 22, 1146-1150.
- (5) H. B. Kagan and J.-C. Fiaud, *Top. Stereochem.*, 1988, **18**, 249.

11. Copies of NMR spectra

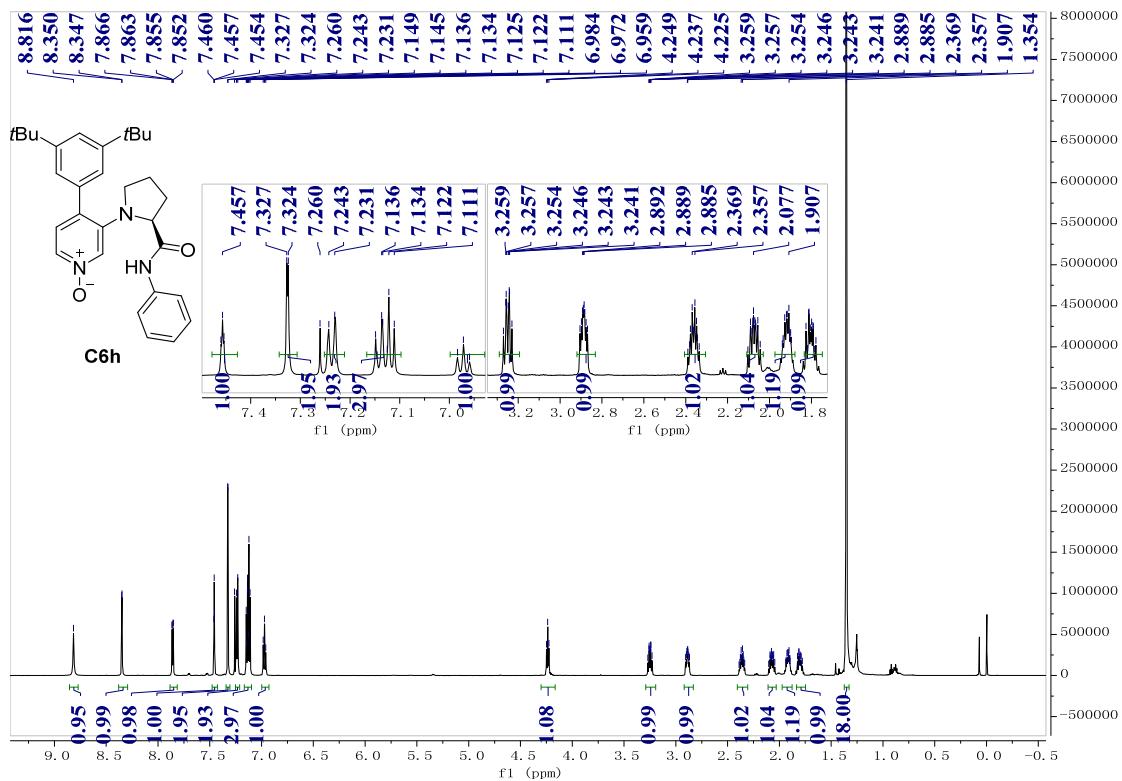
¹H NMR for C7c



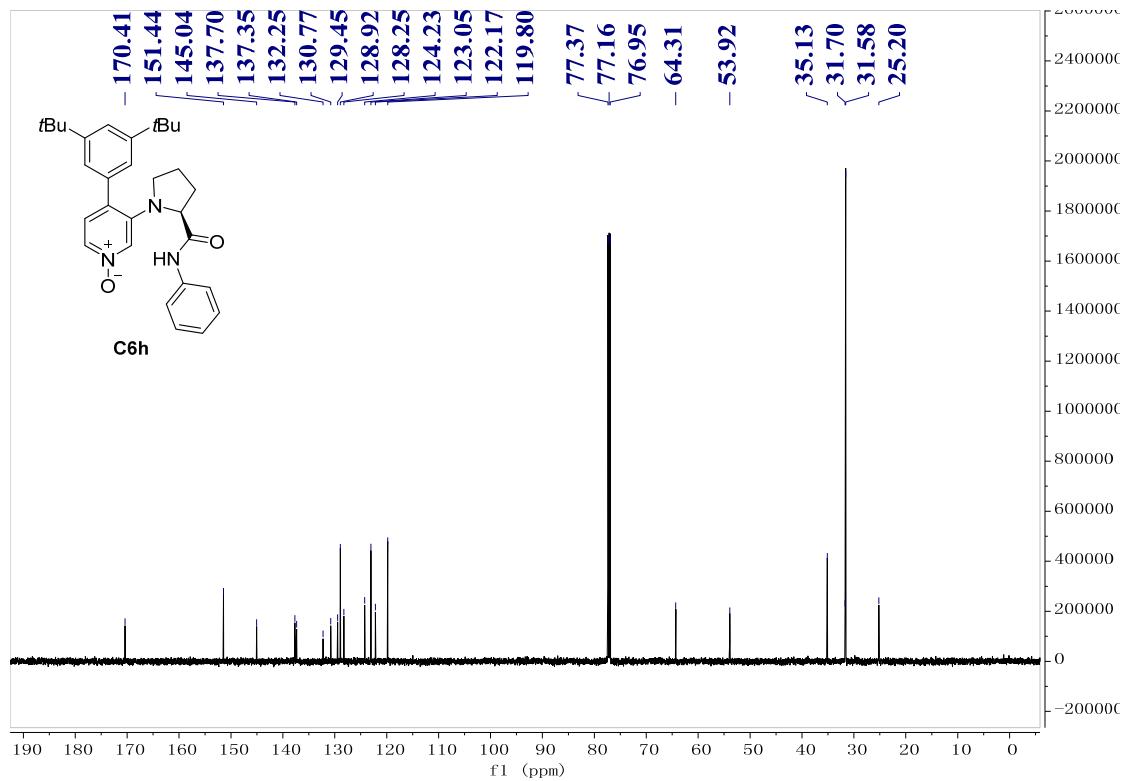
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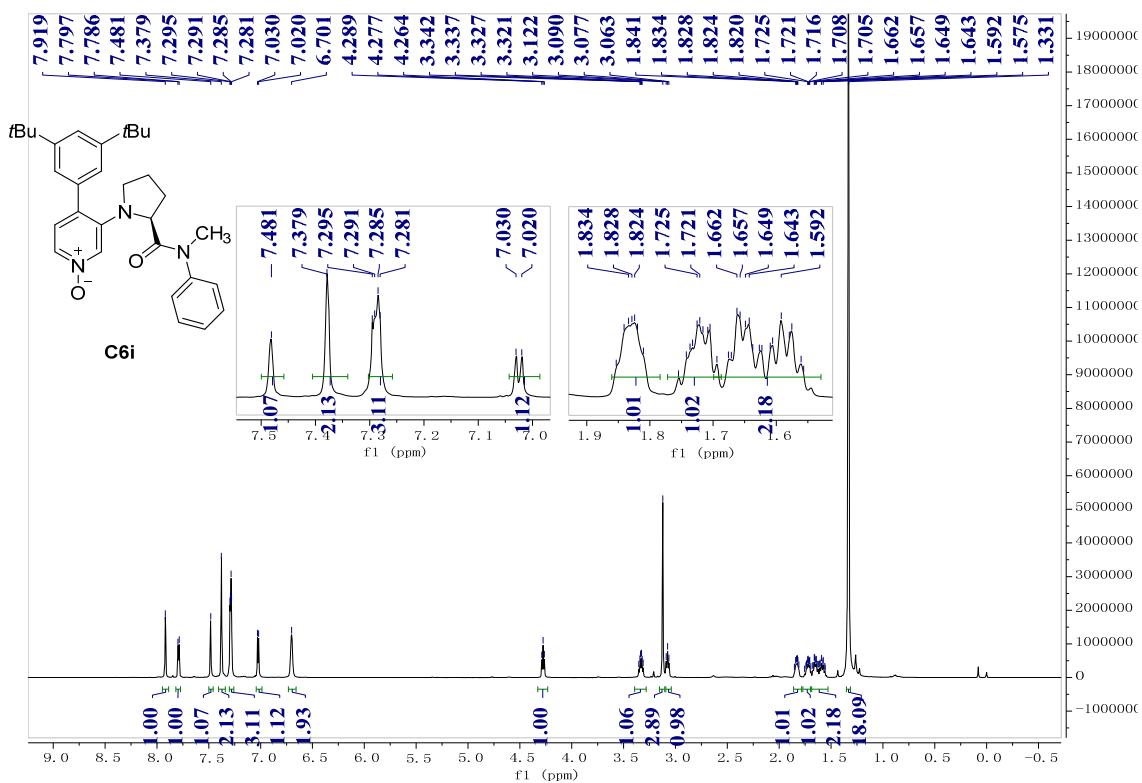
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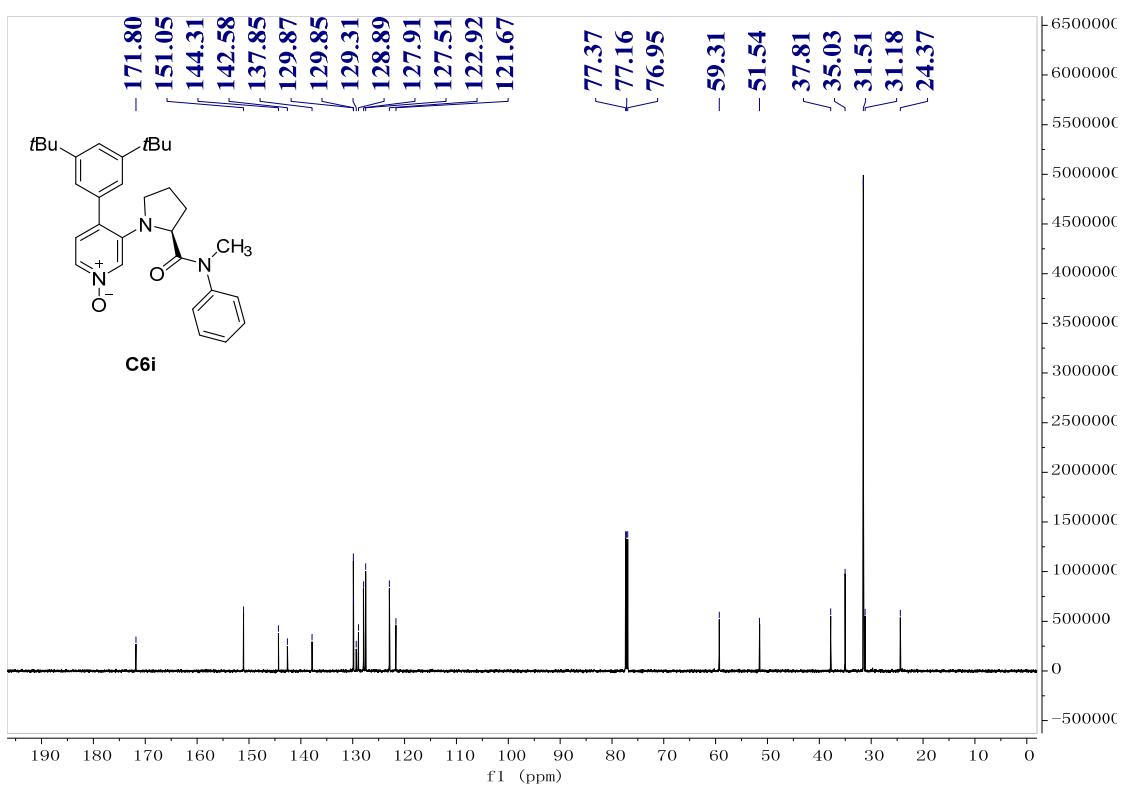
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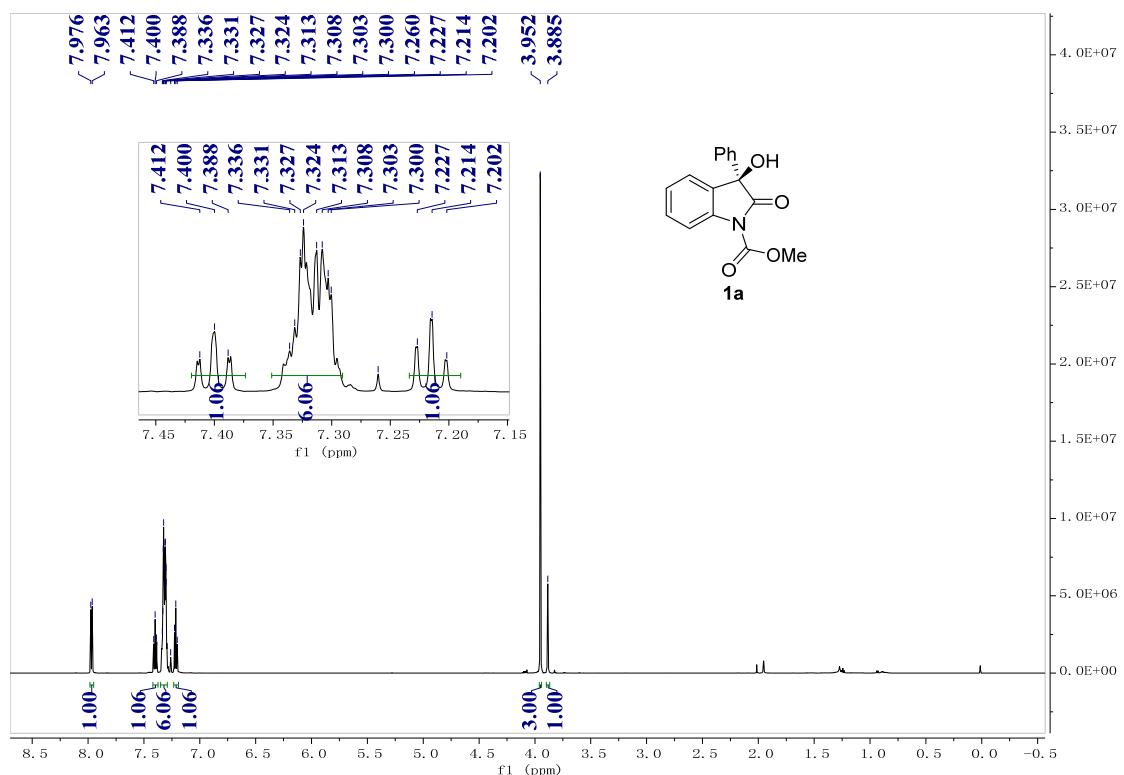
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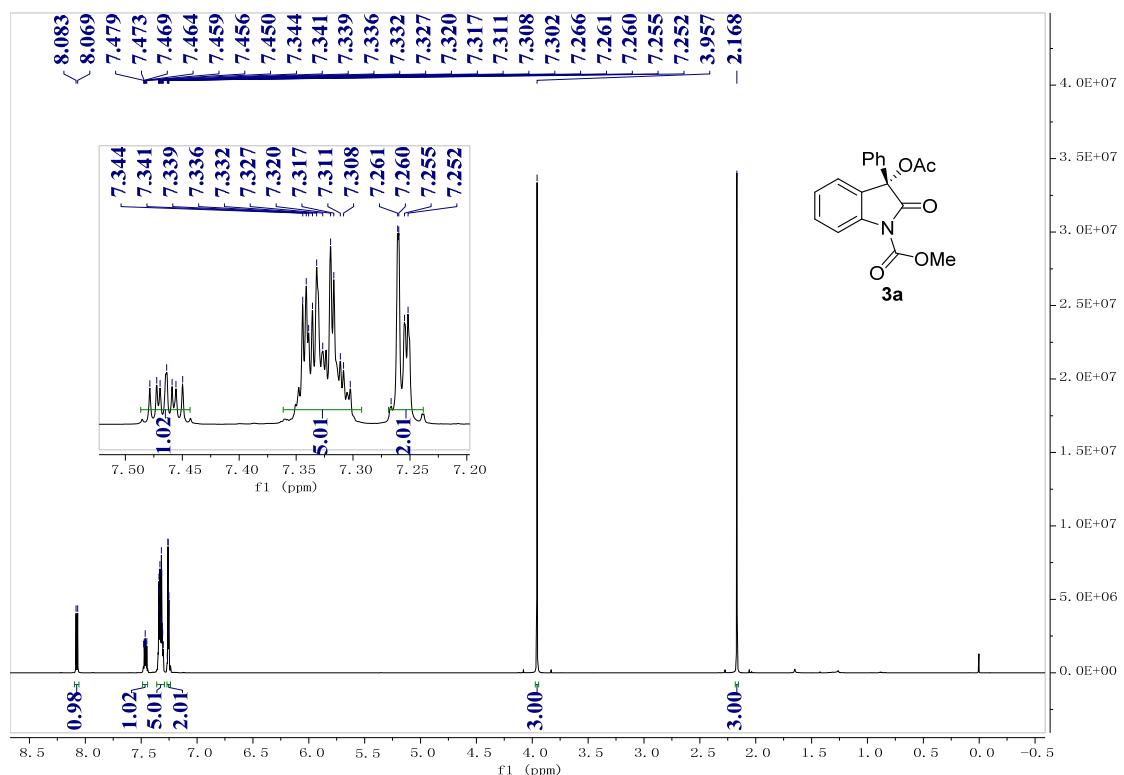
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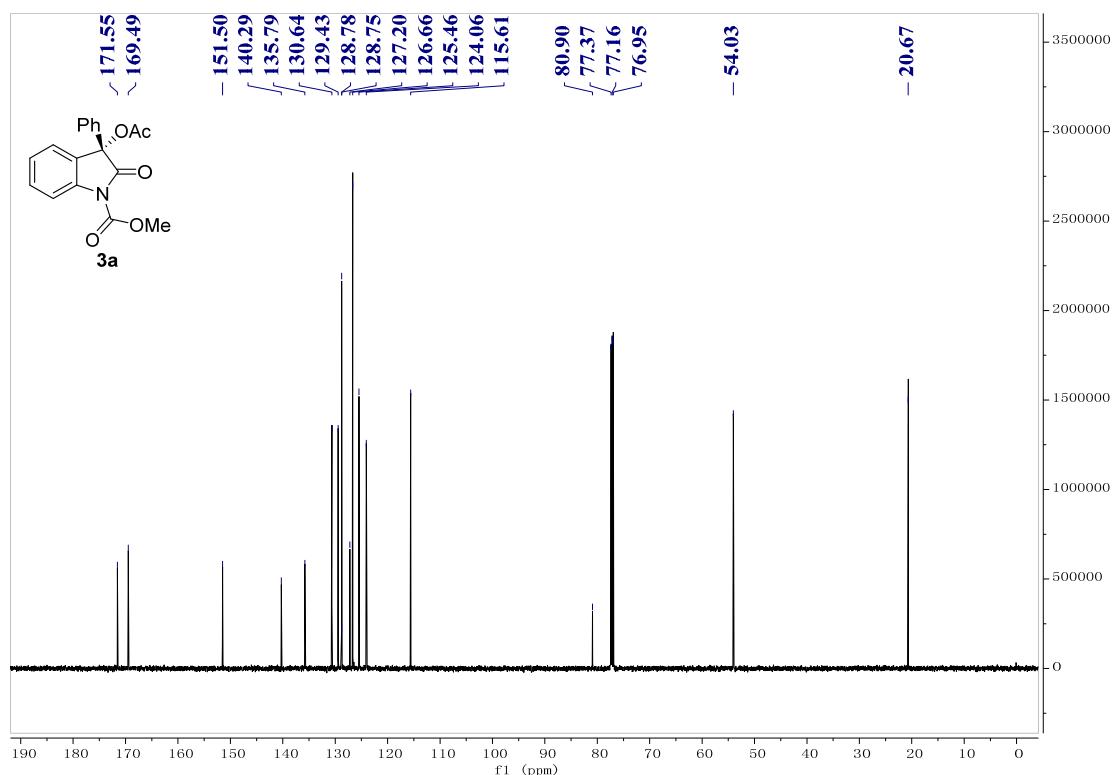
¹H NMR for 1a



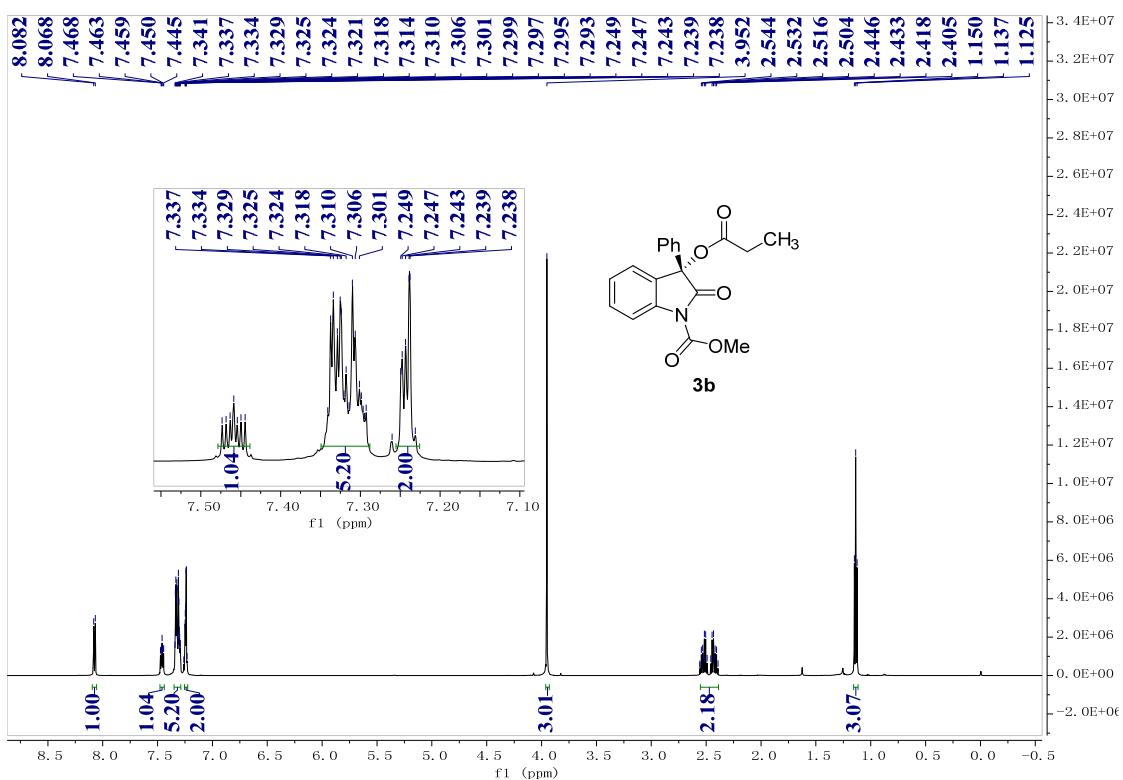
¹H NMR for 3a



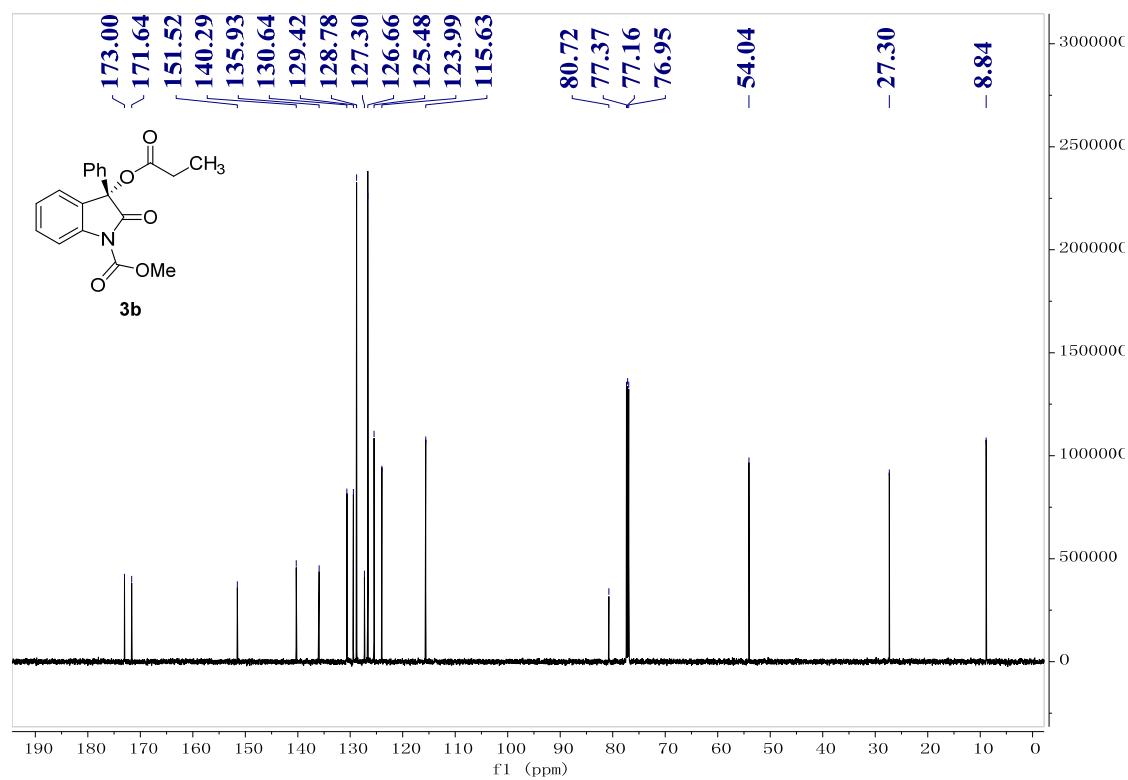
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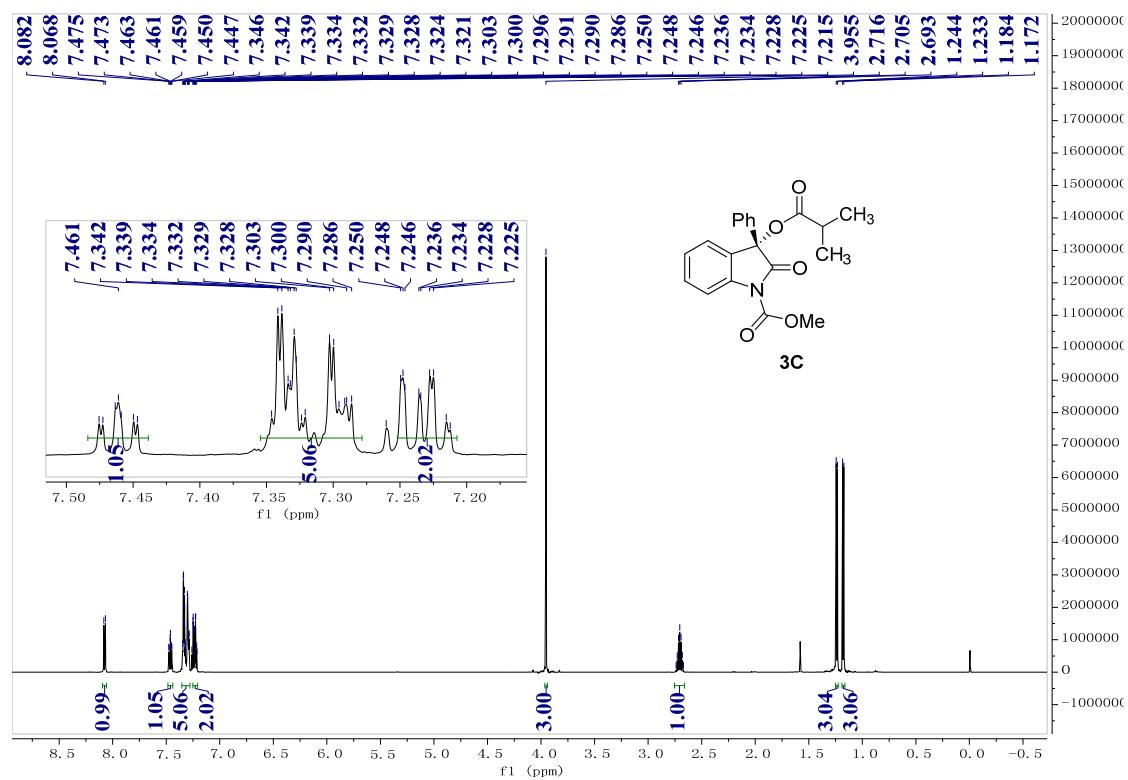
¹H NMR for 3b



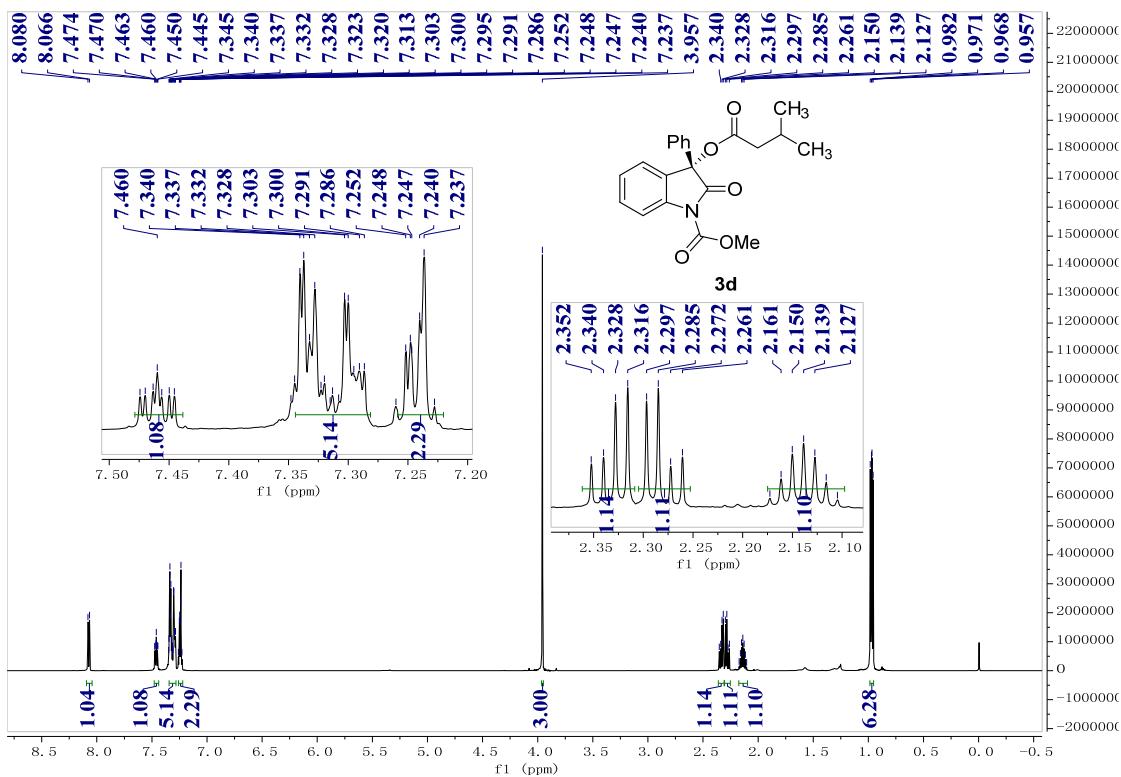
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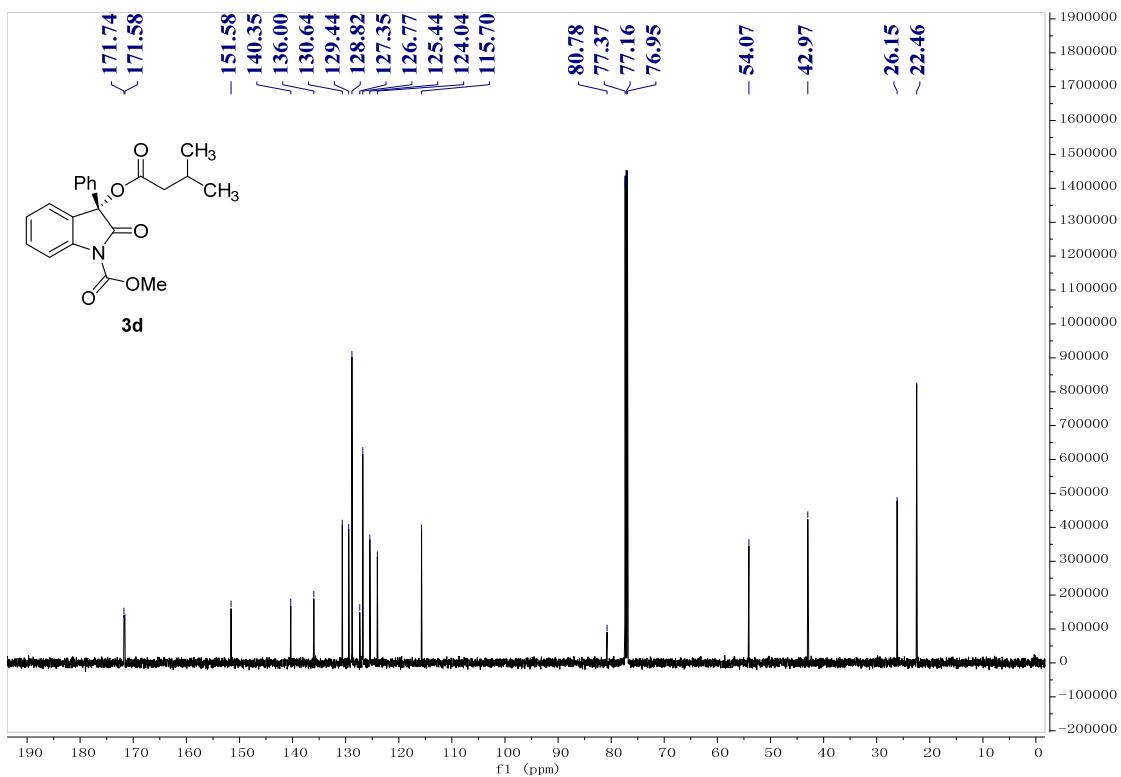
¹H NMR for 3c



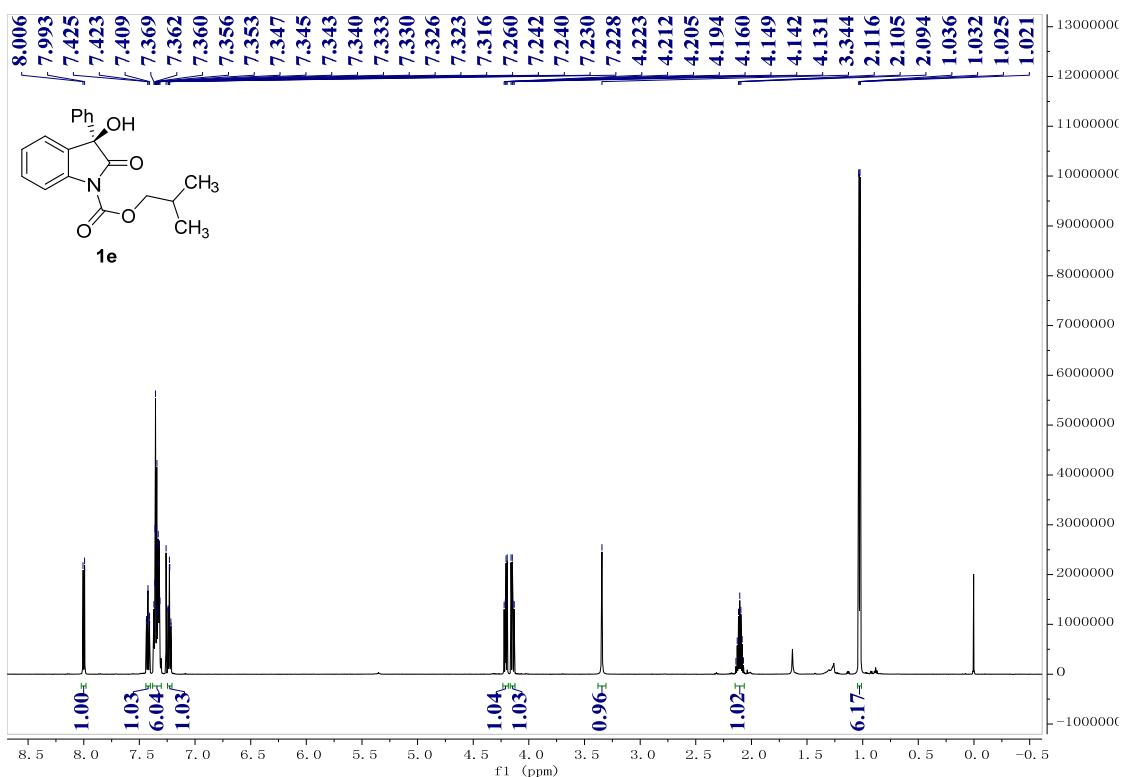
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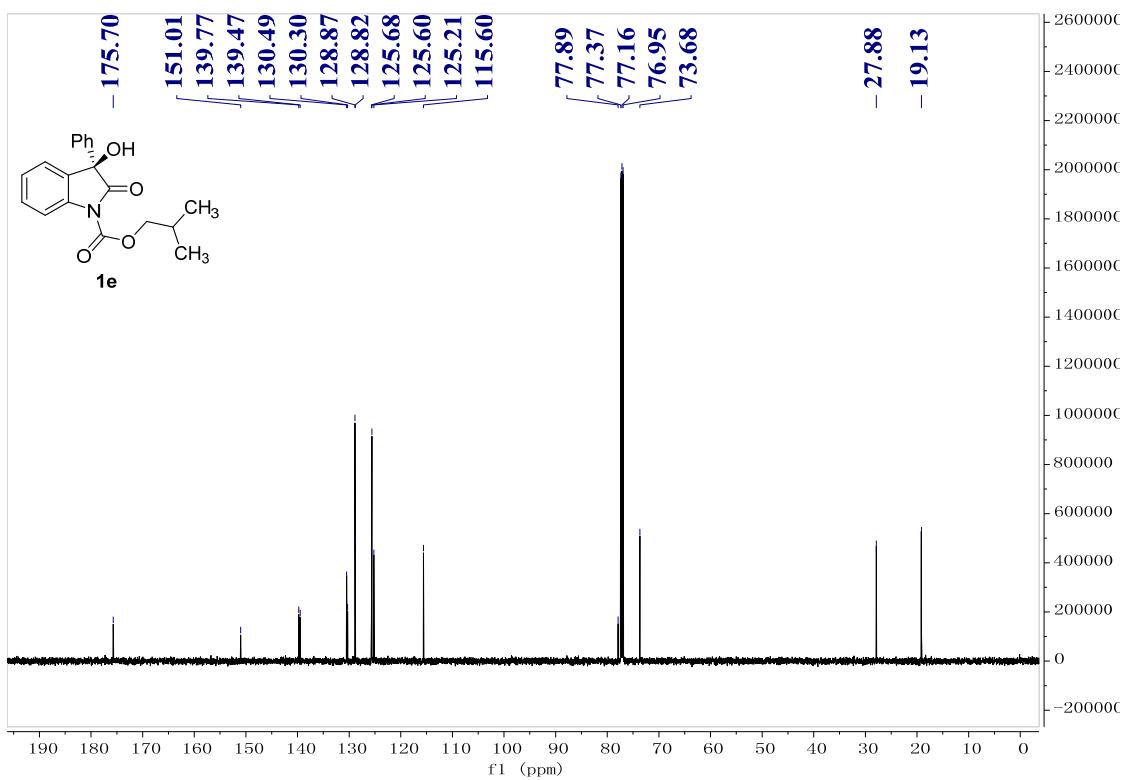
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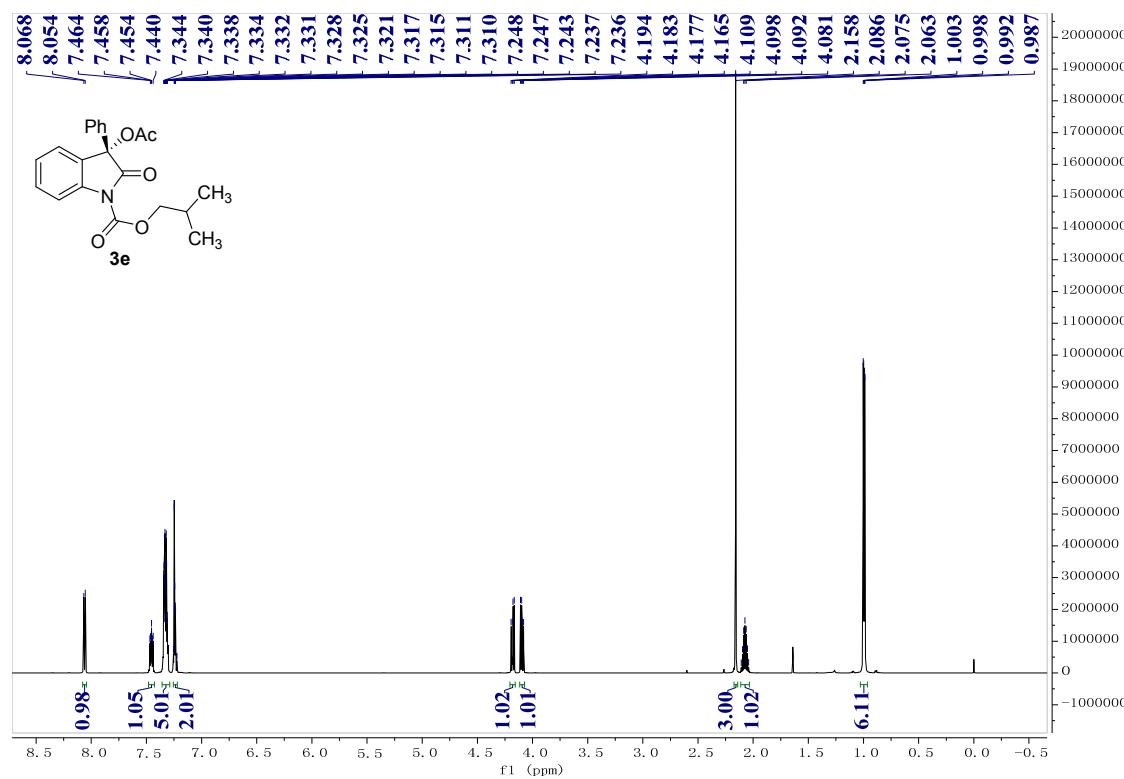
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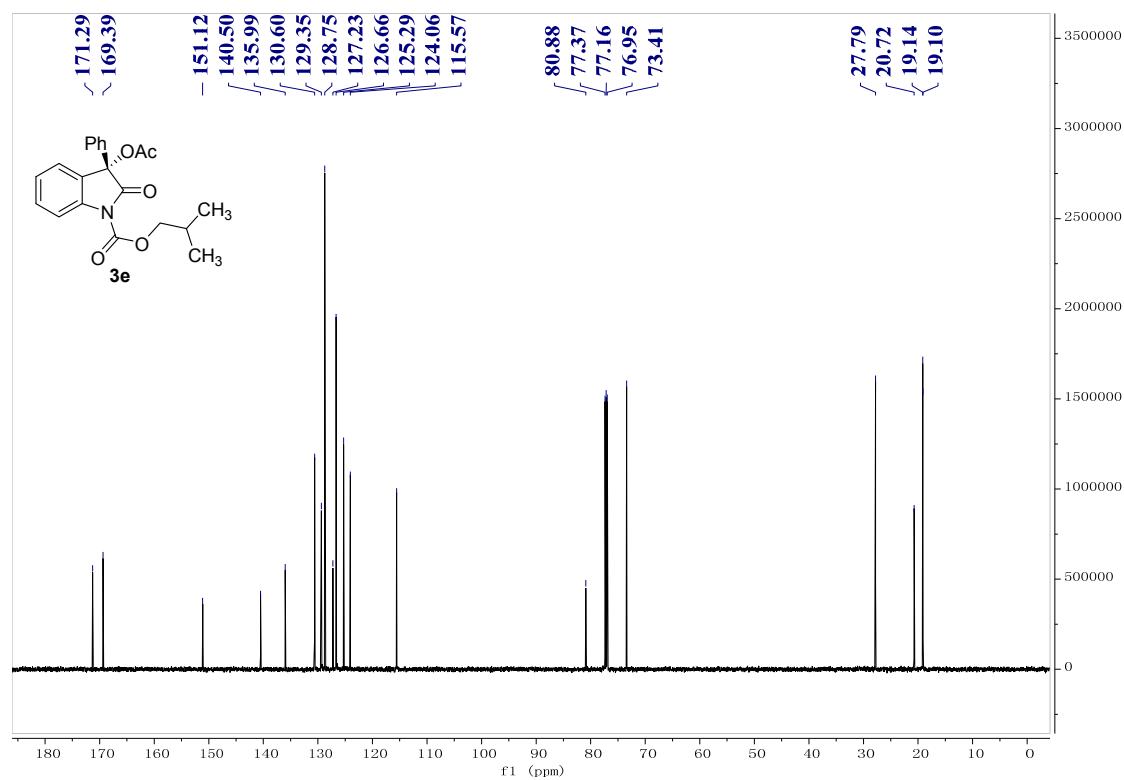
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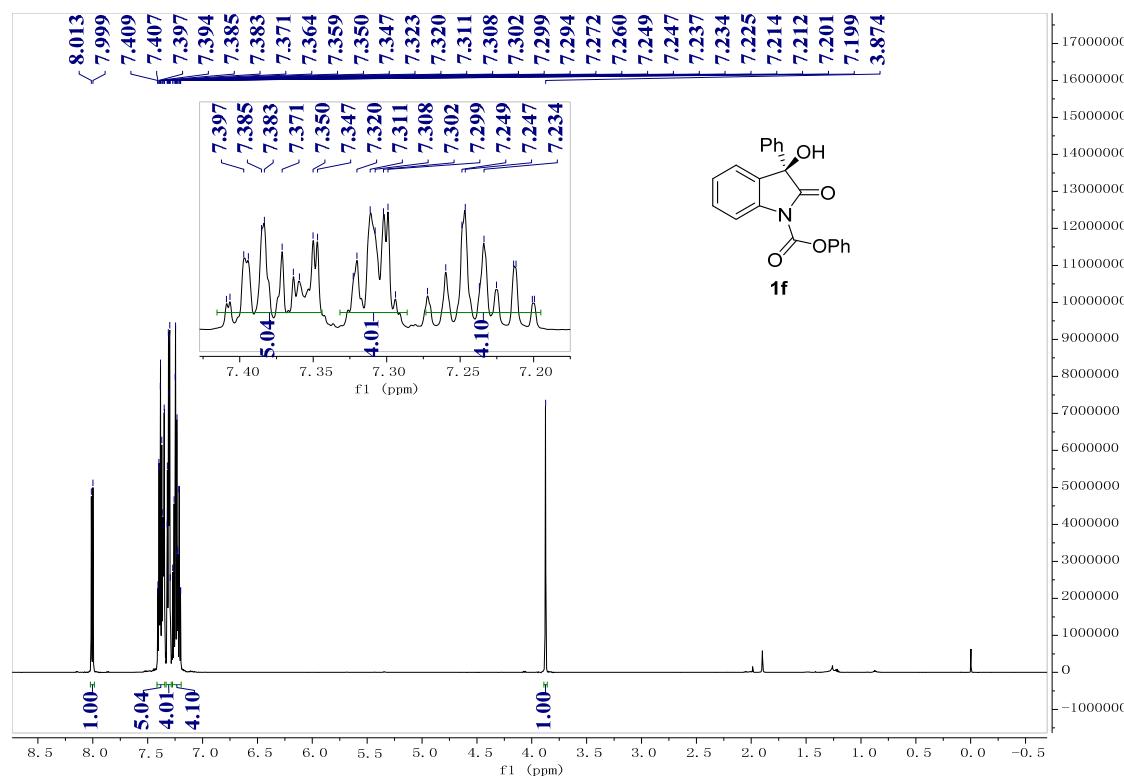
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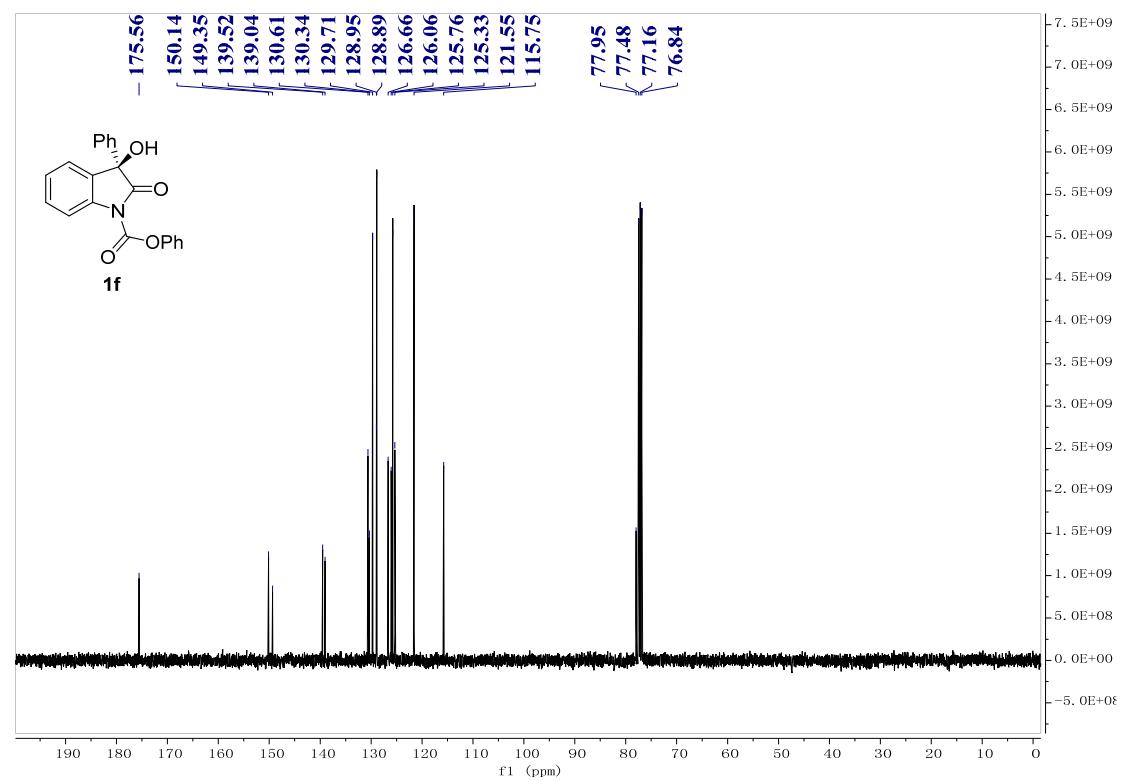
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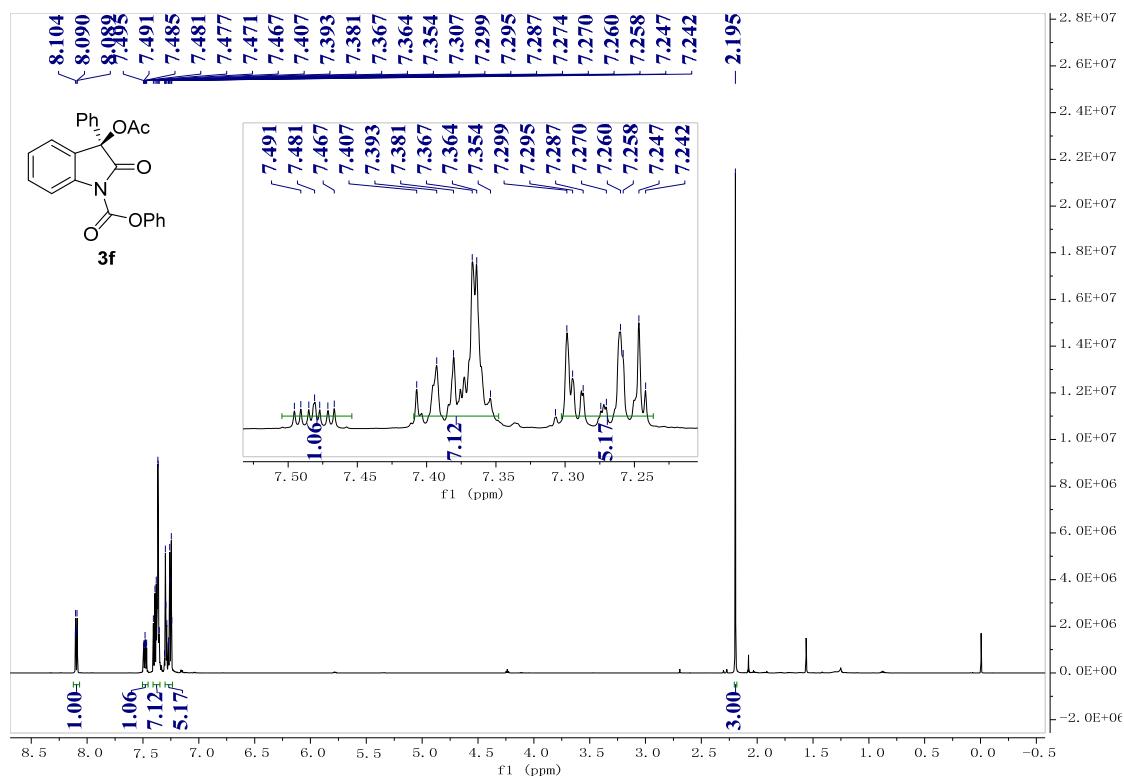
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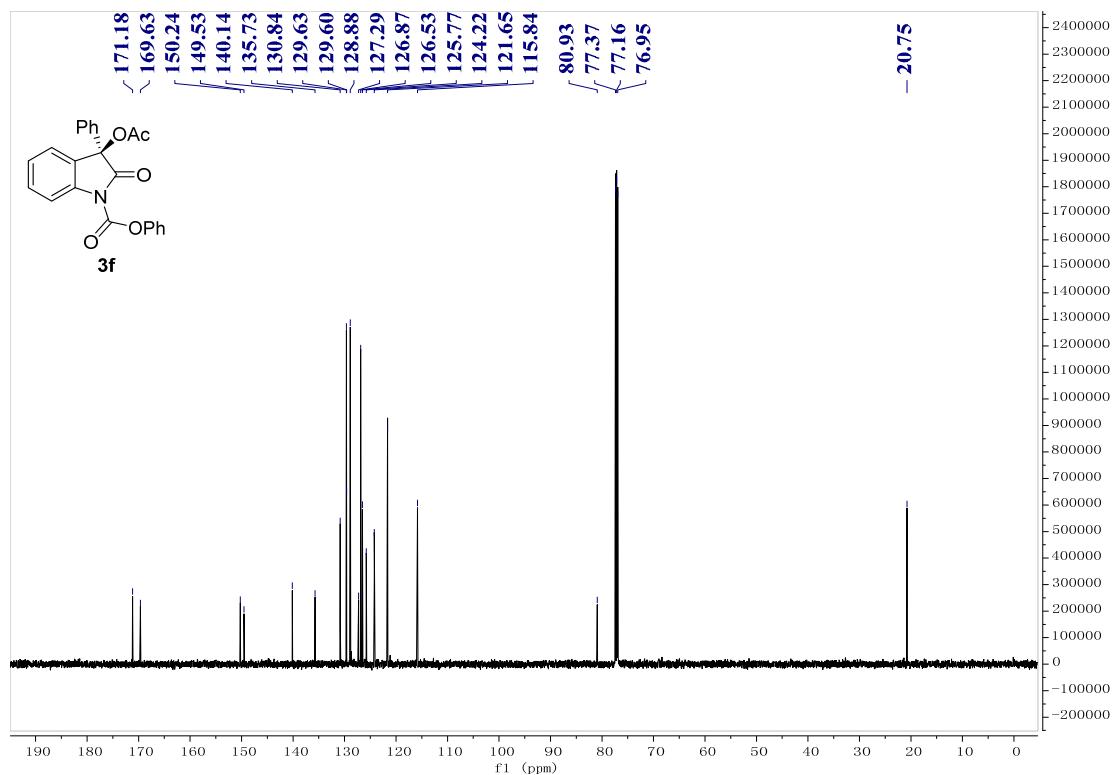
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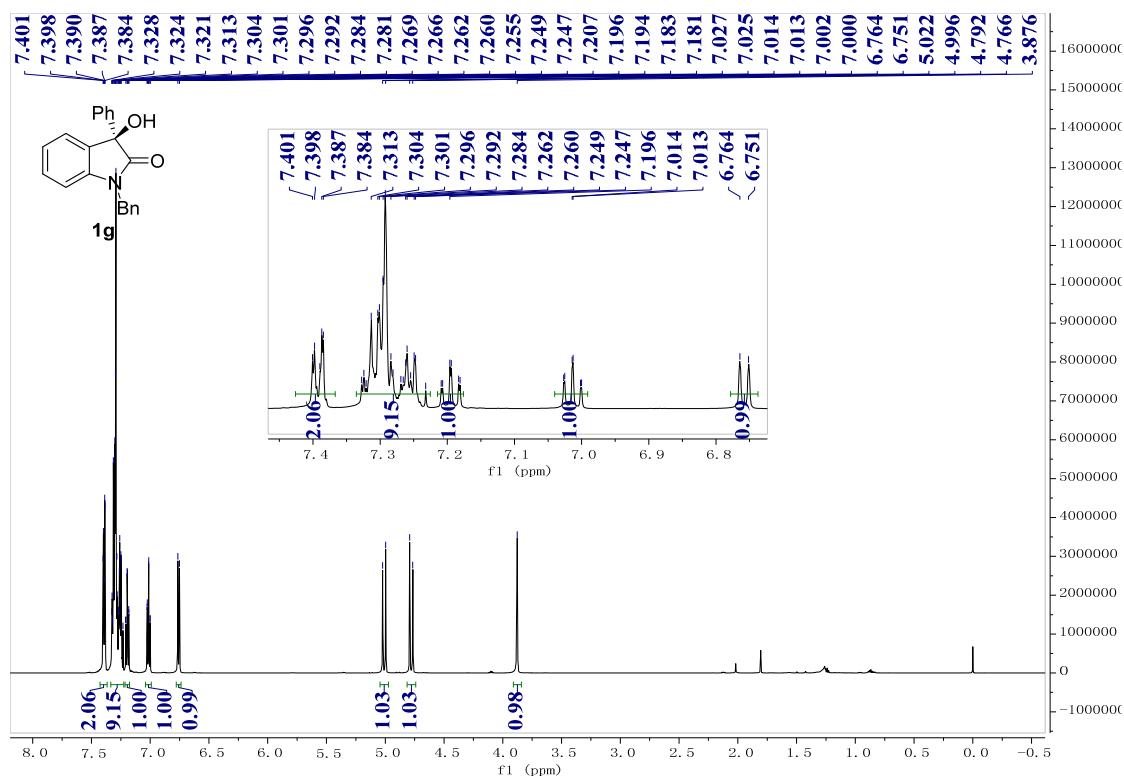
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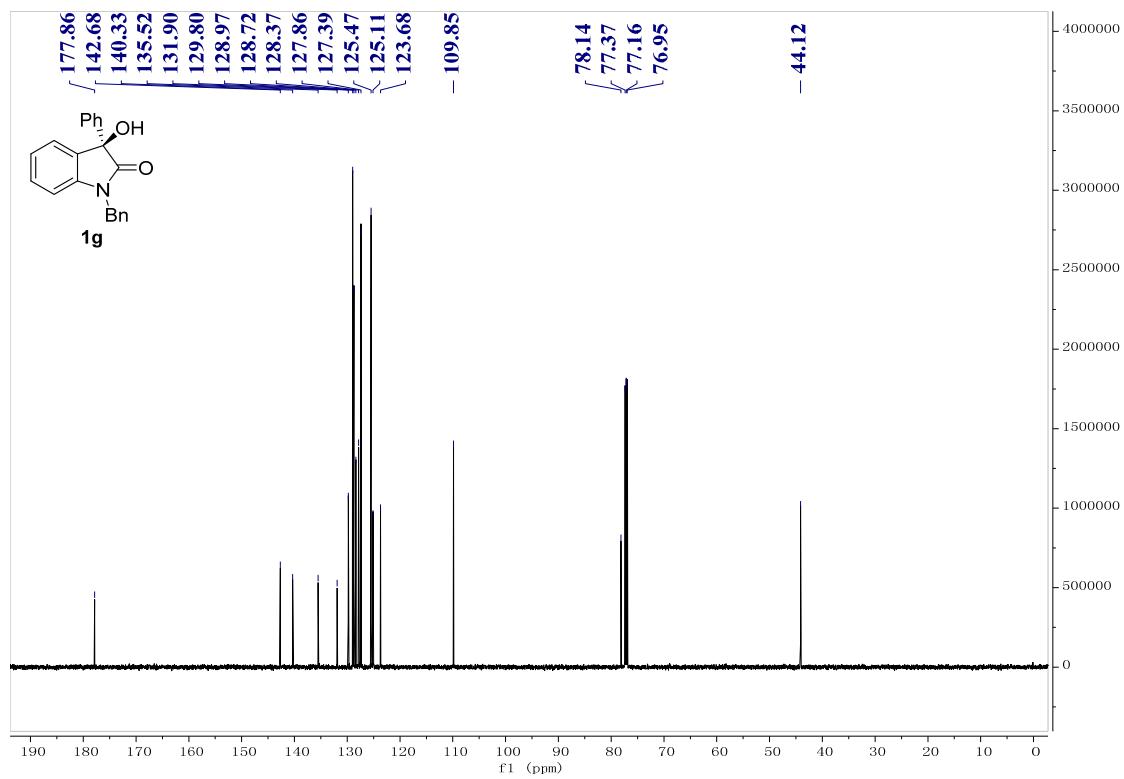
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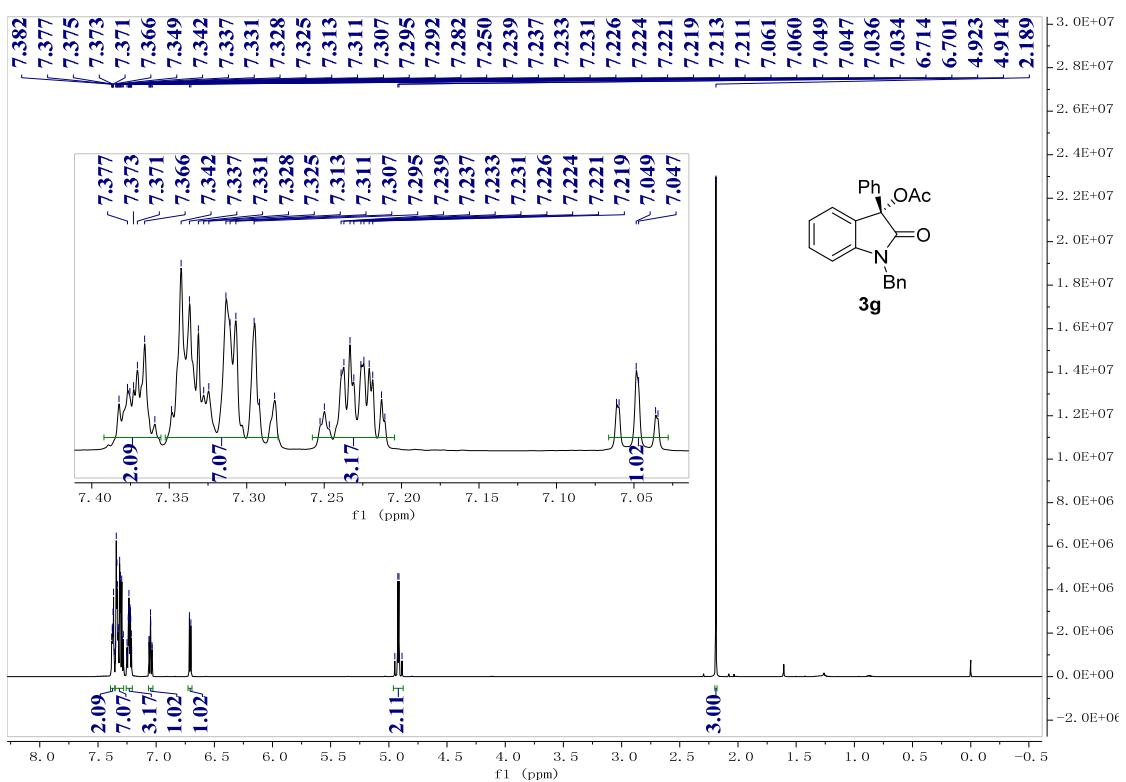
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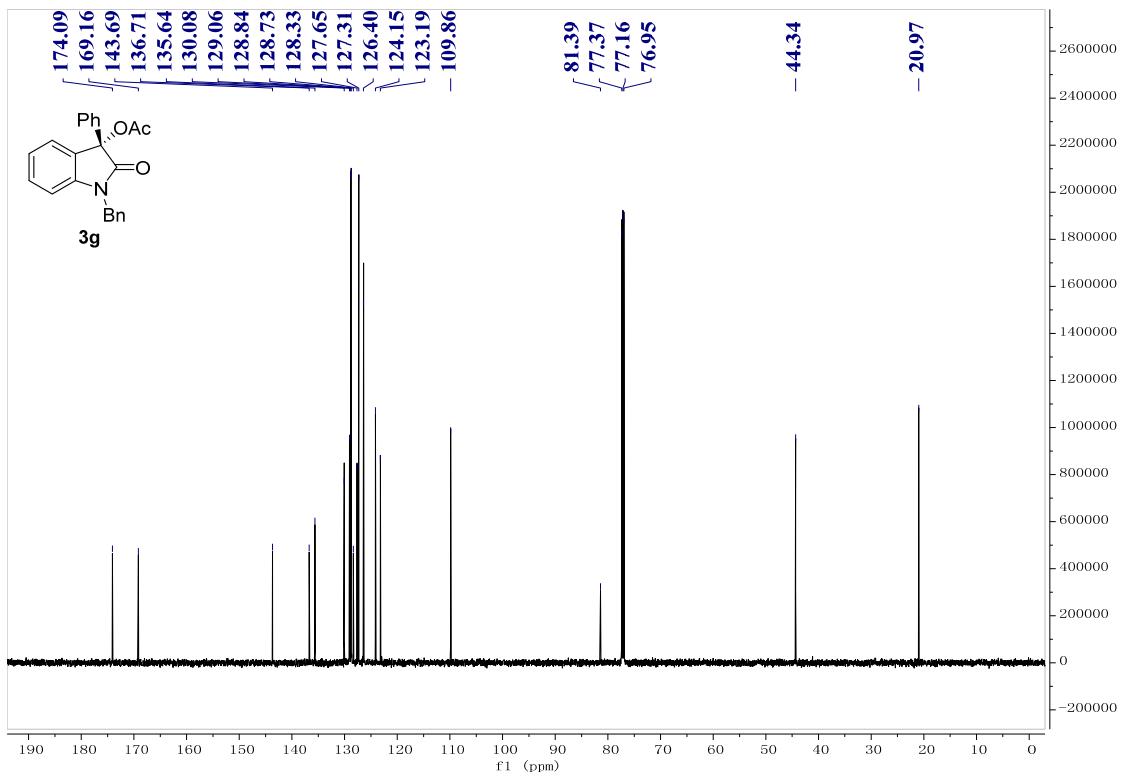
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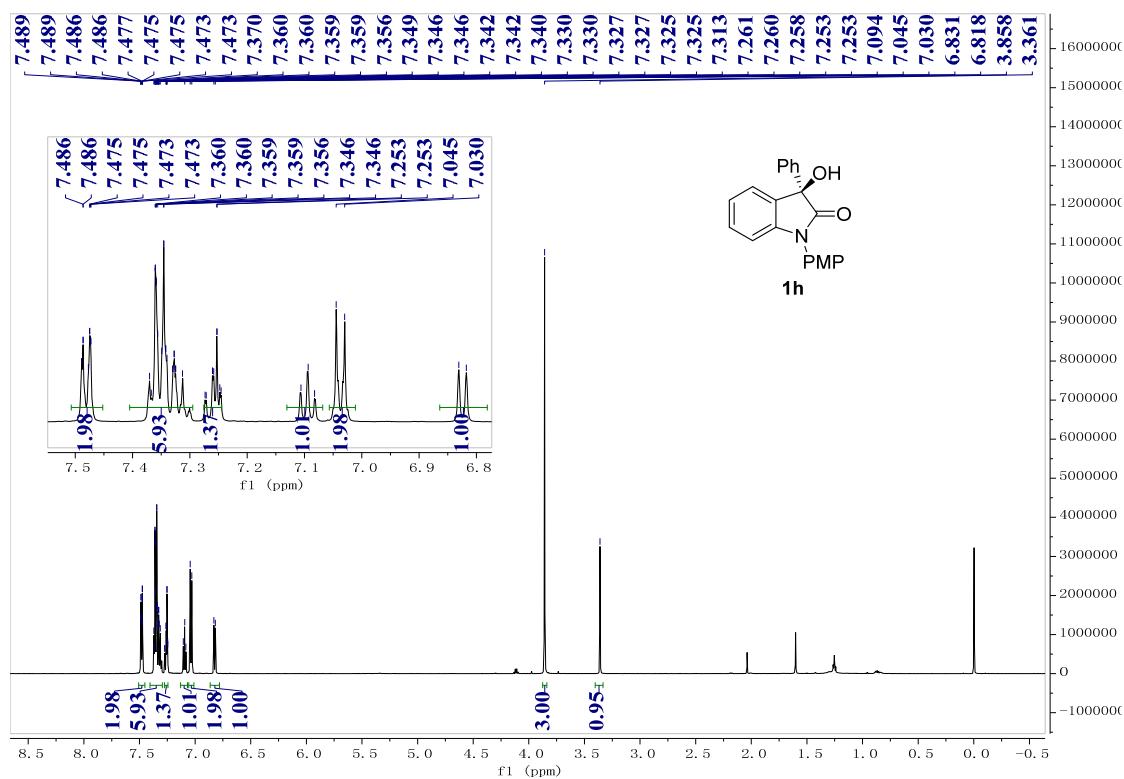
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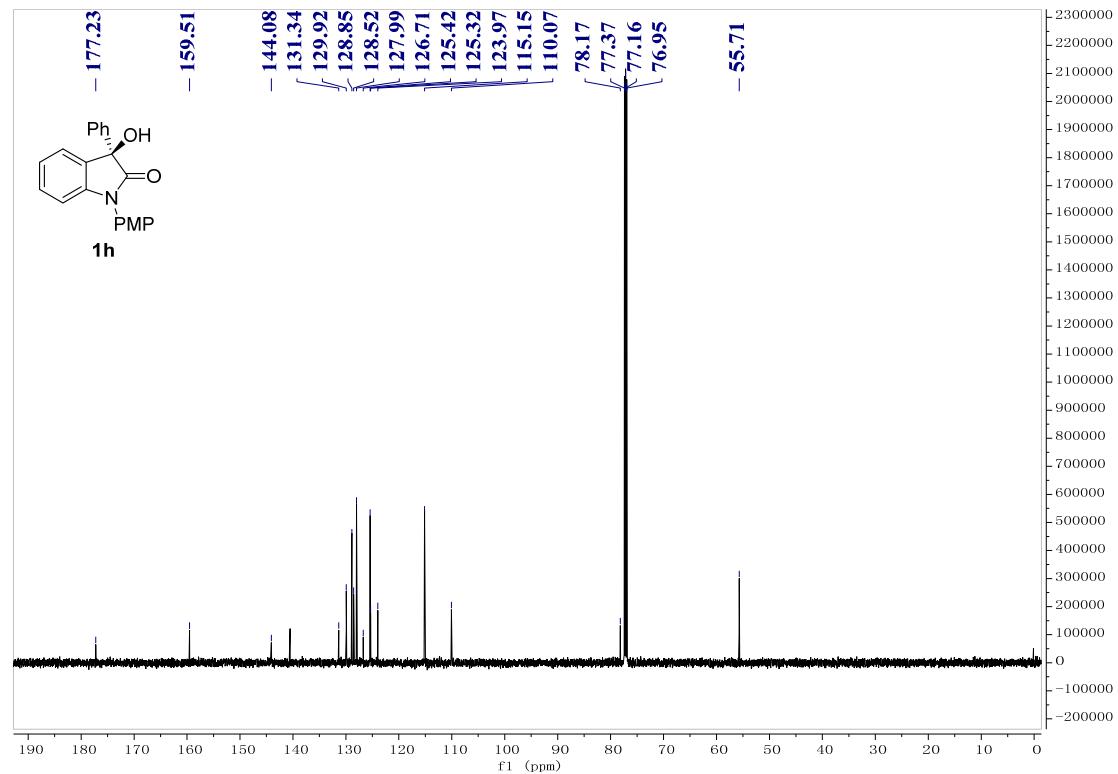
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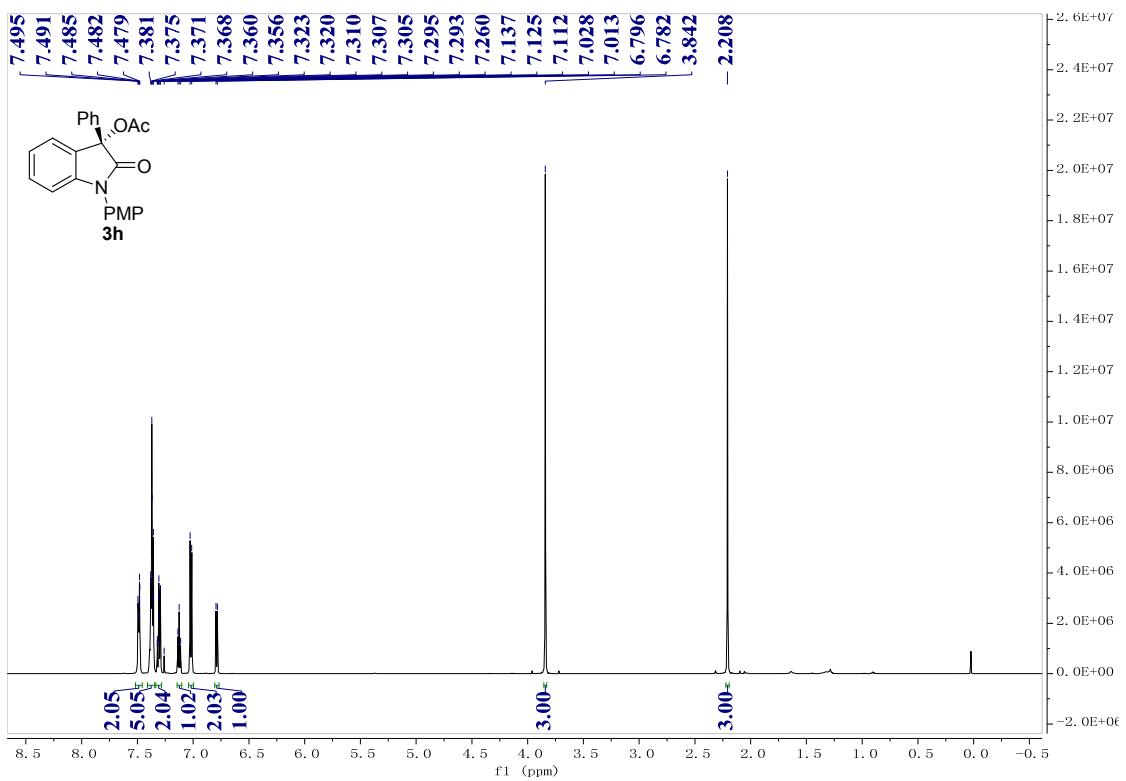
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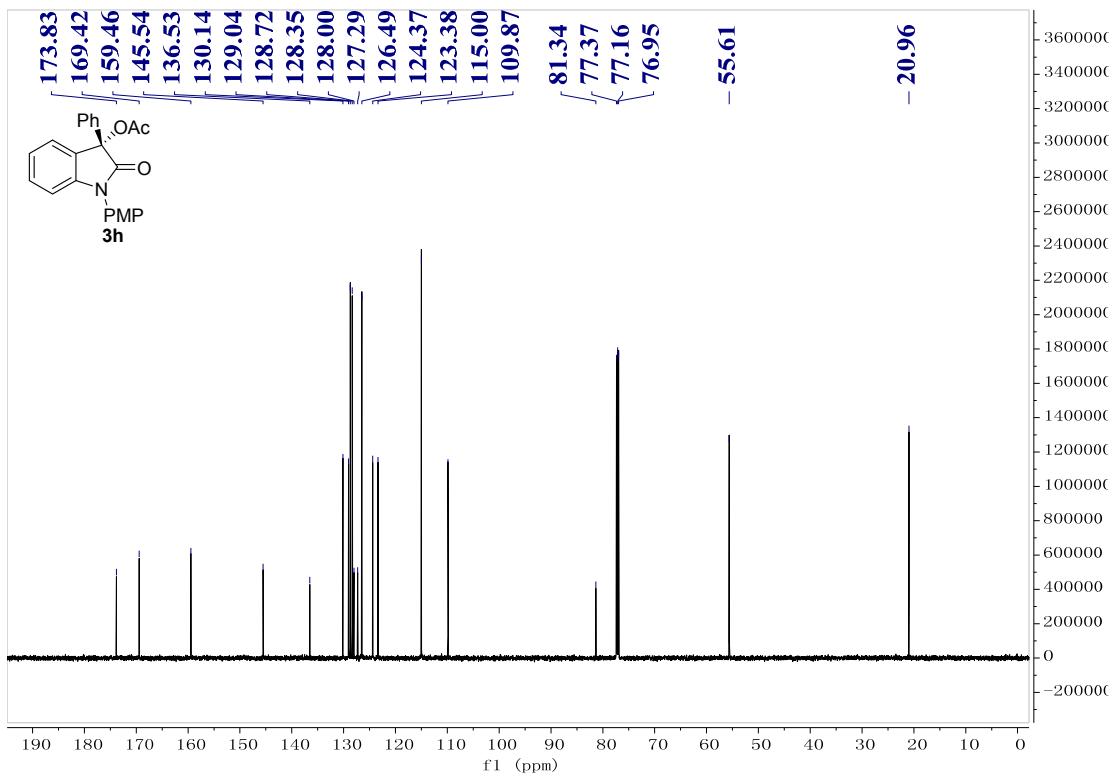
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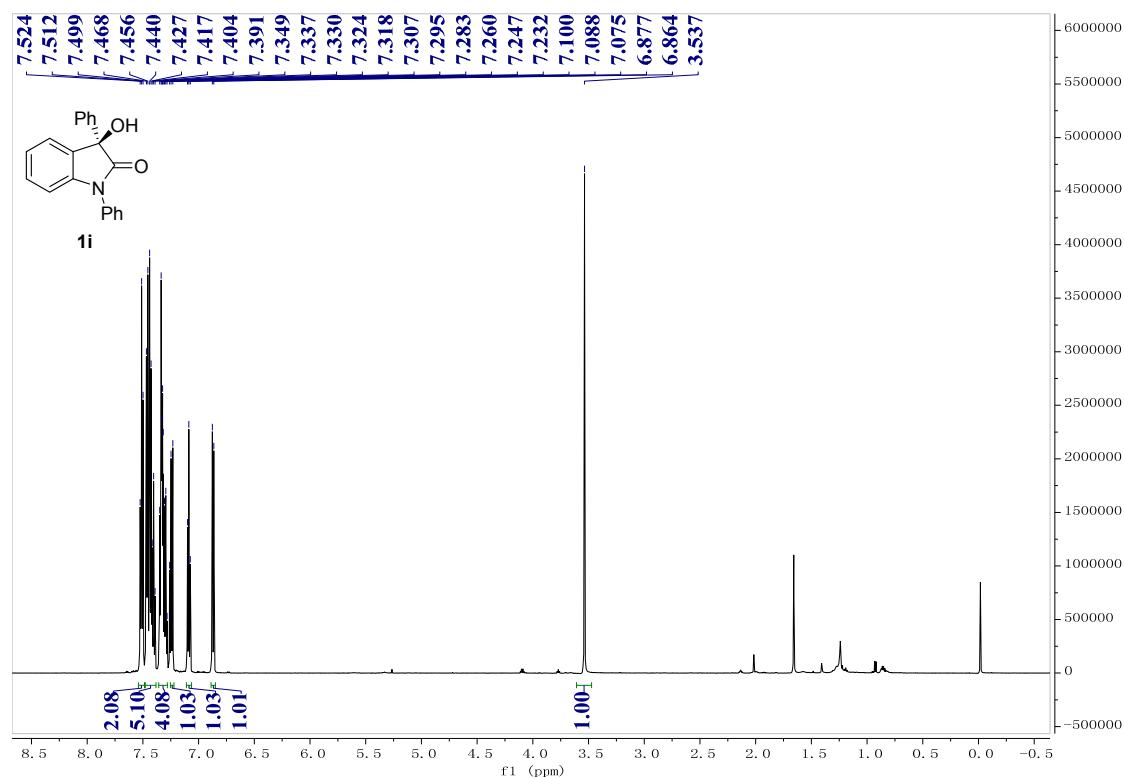
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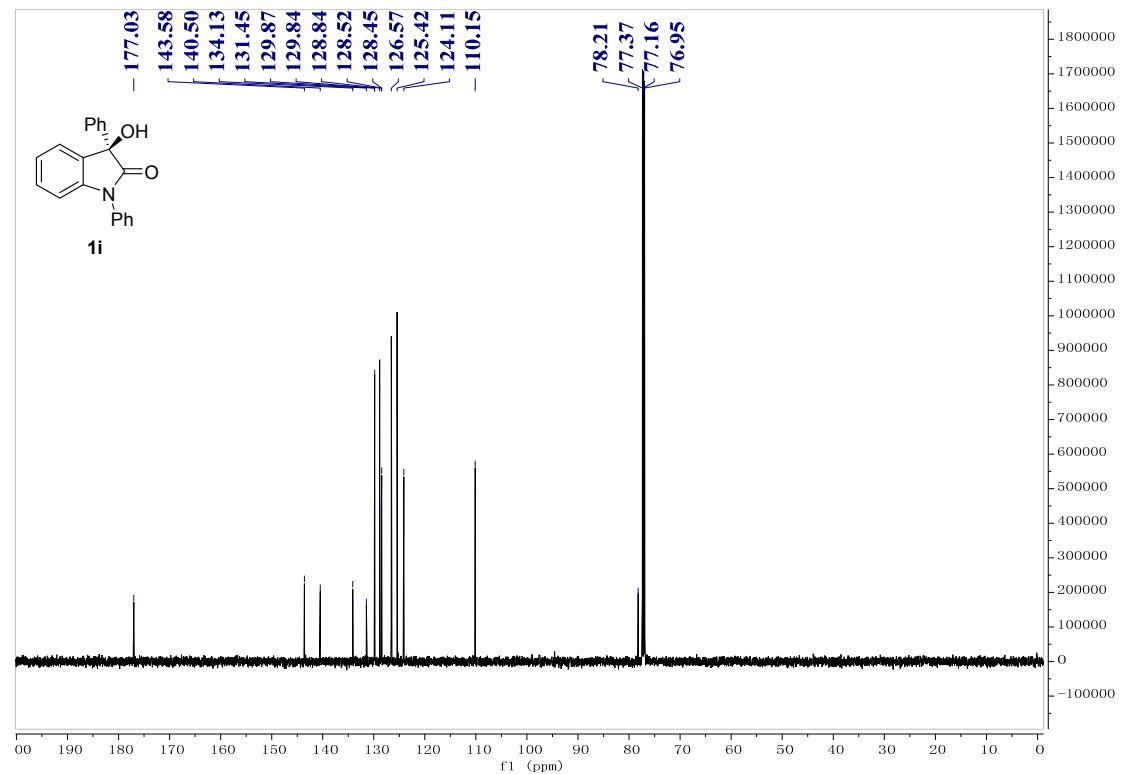
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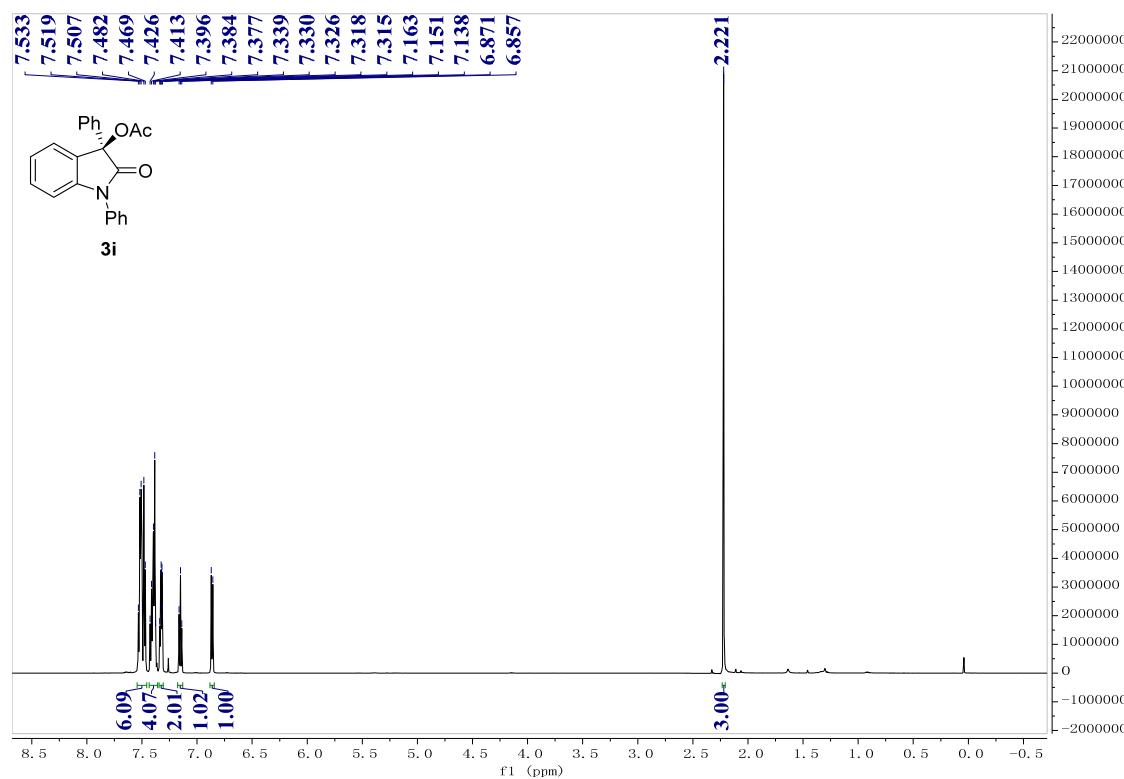
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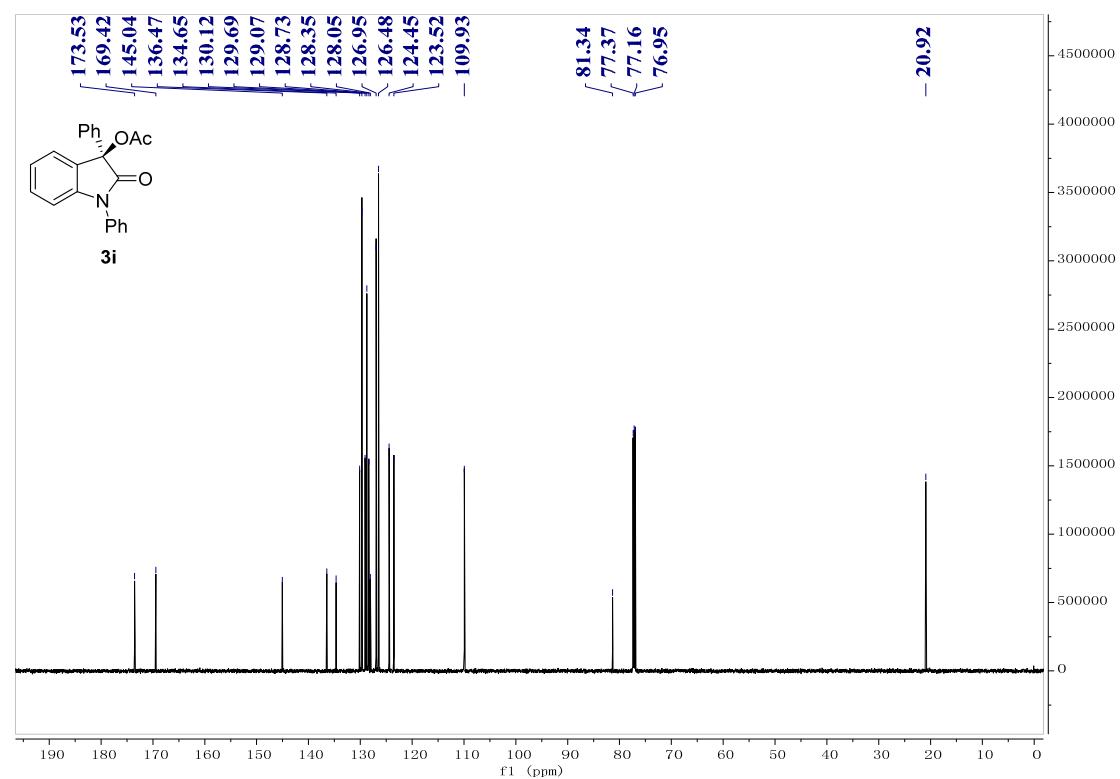
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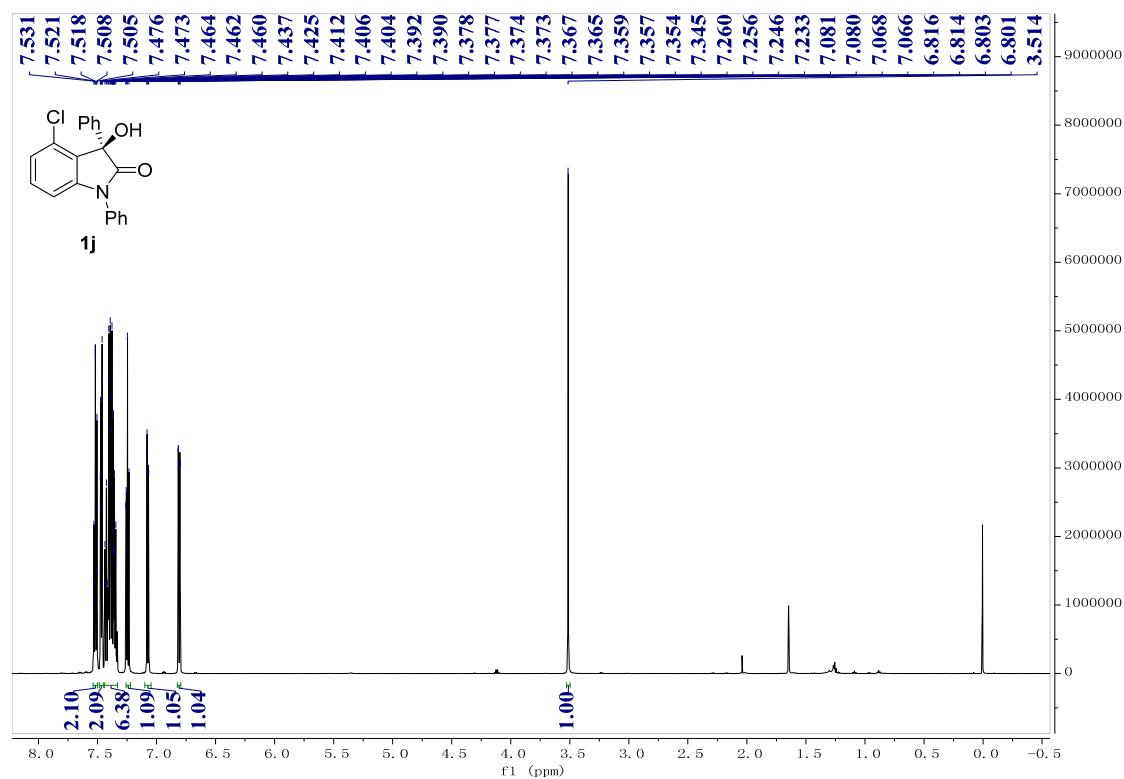
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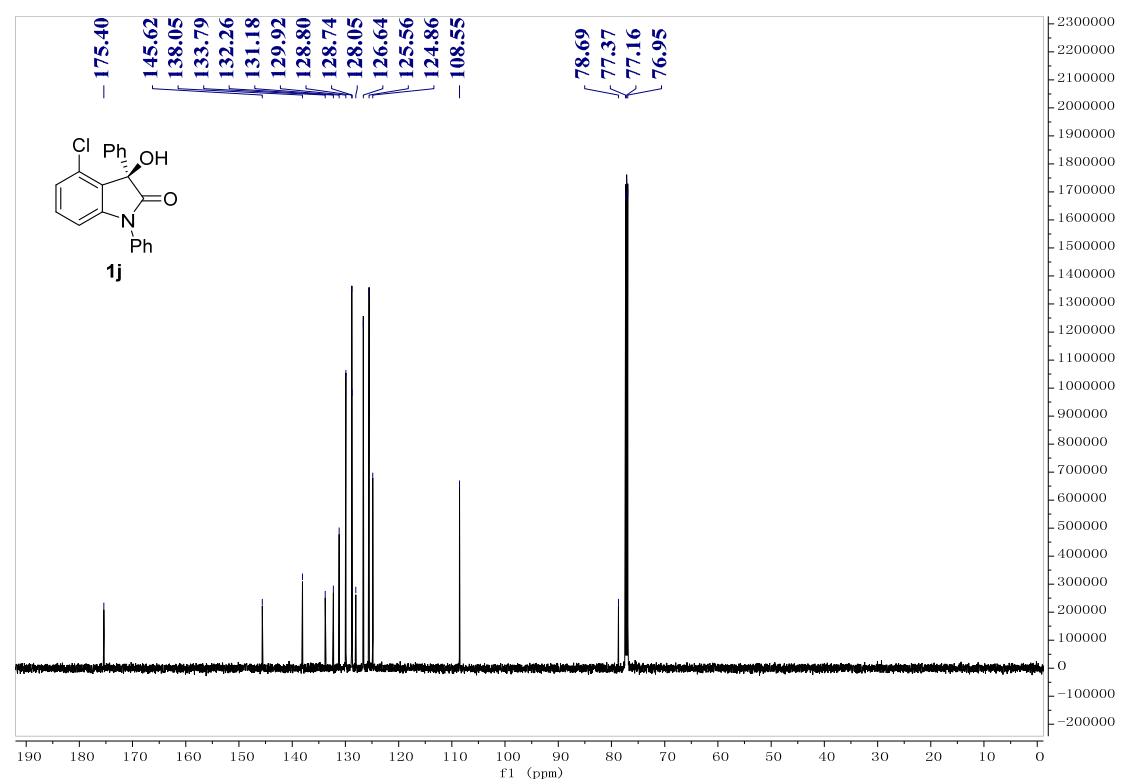
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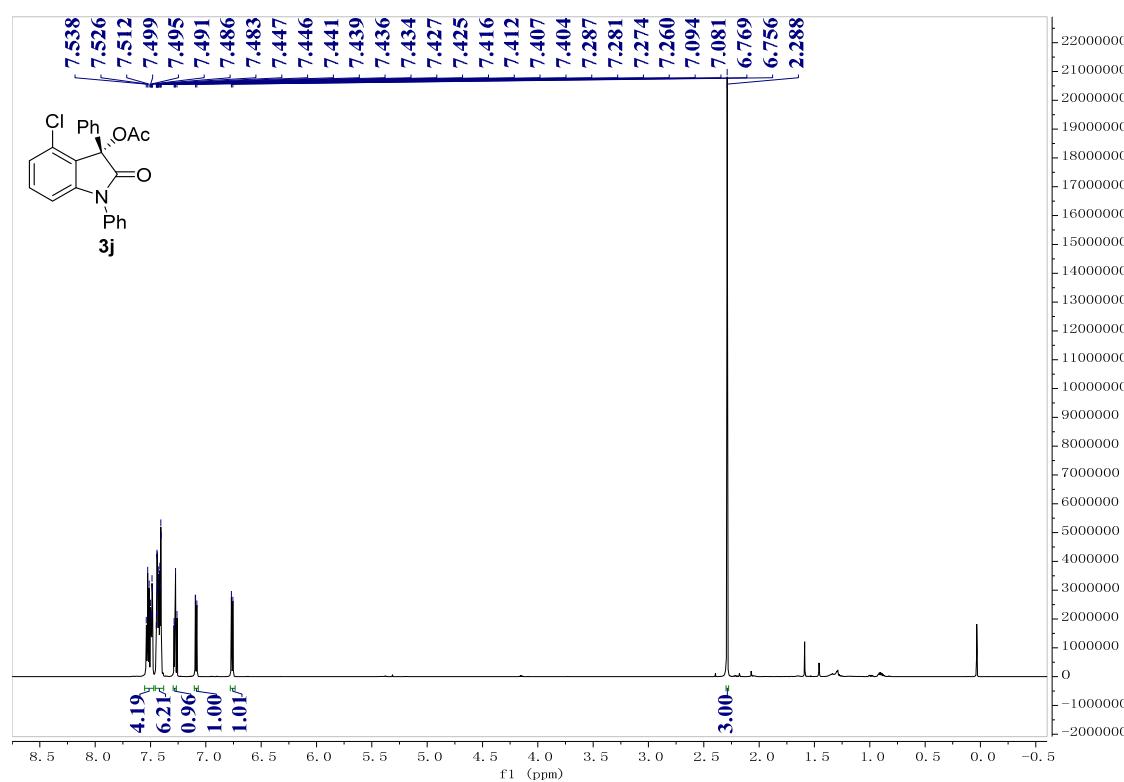
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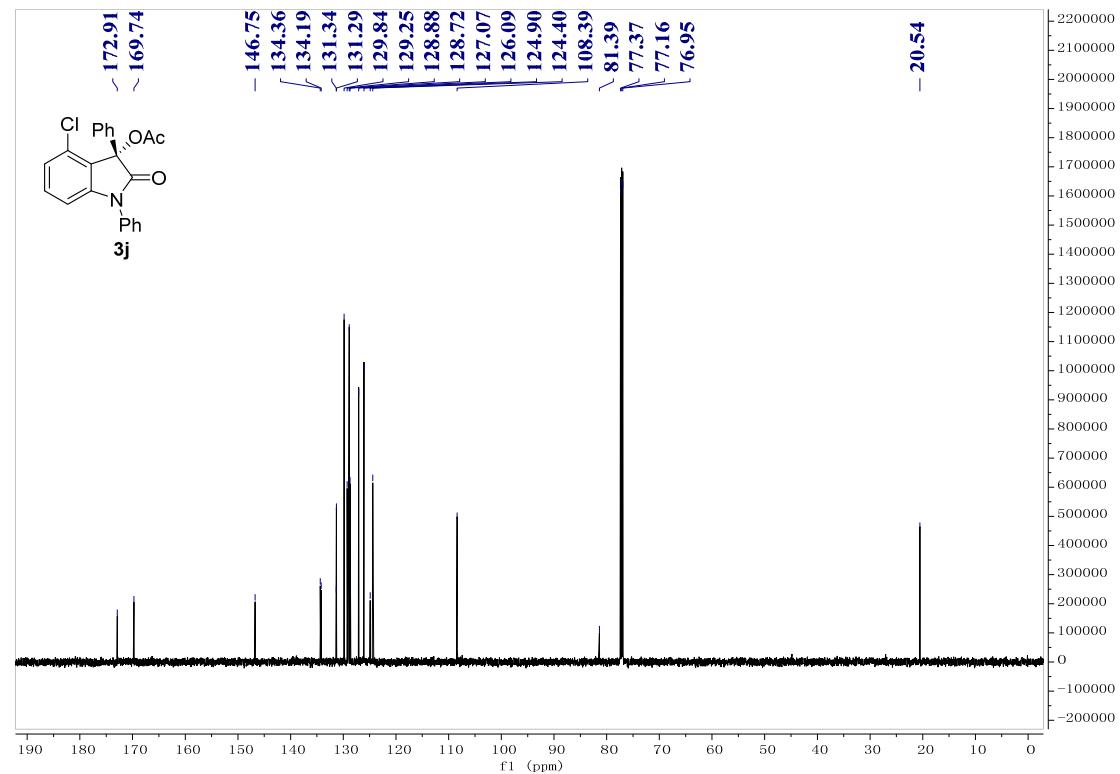
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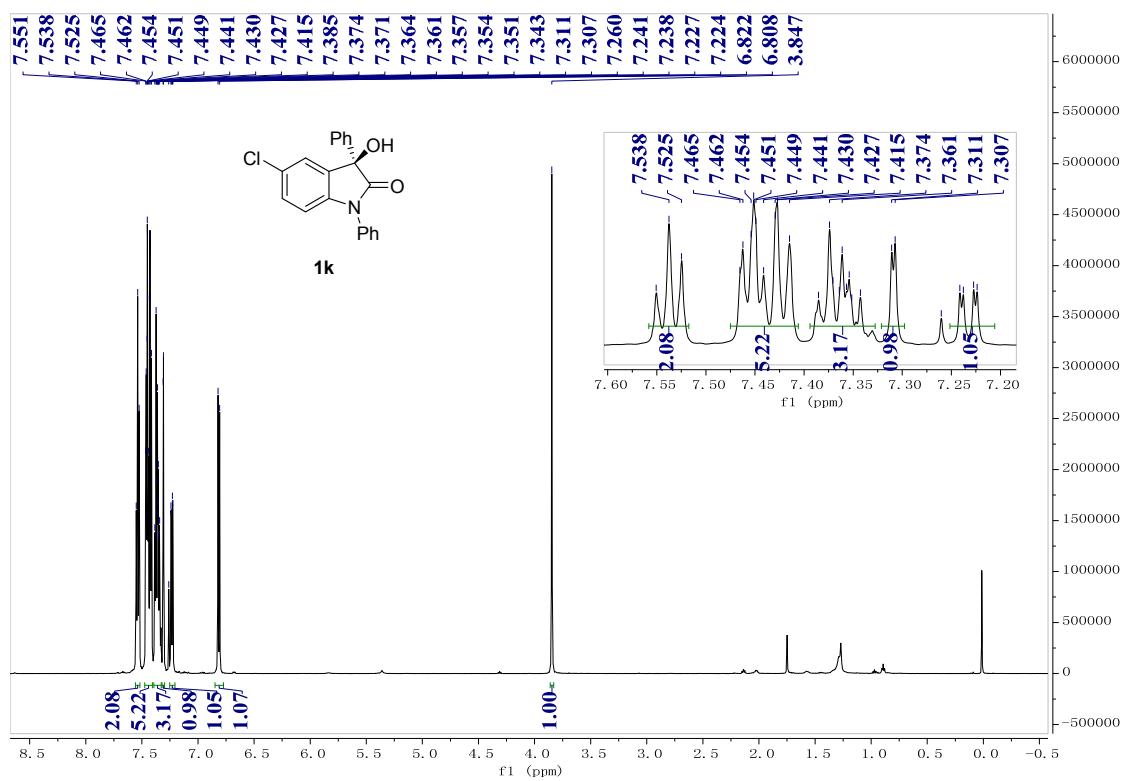
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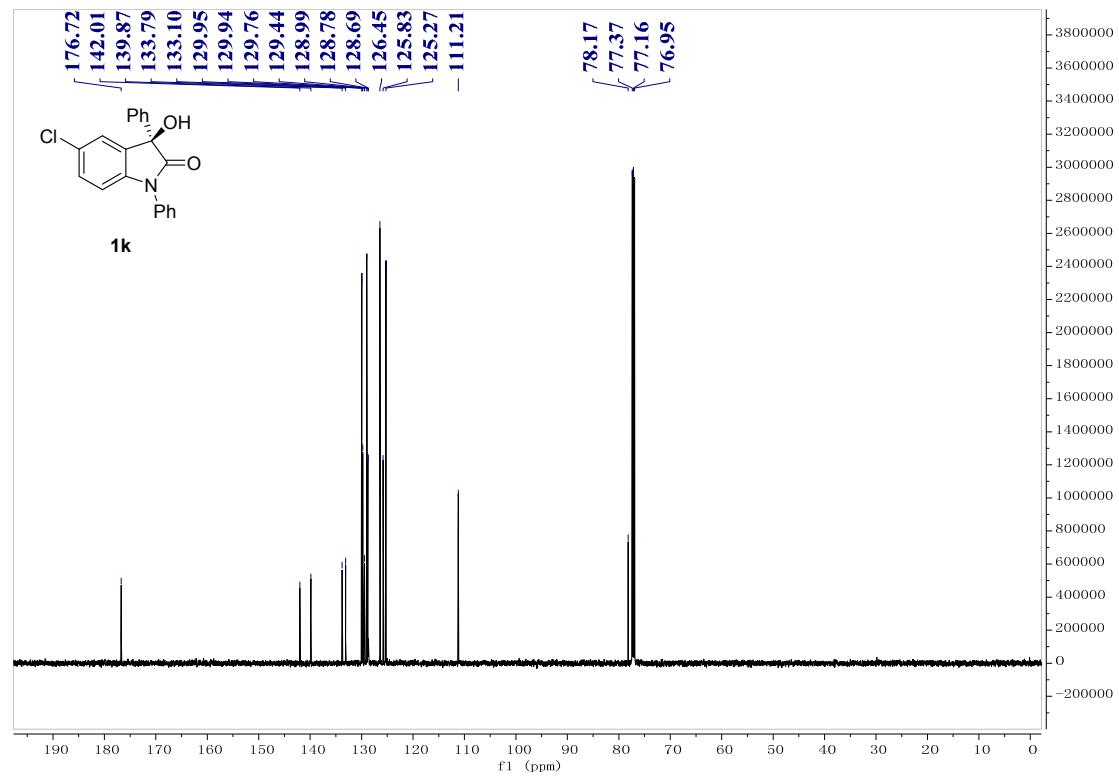
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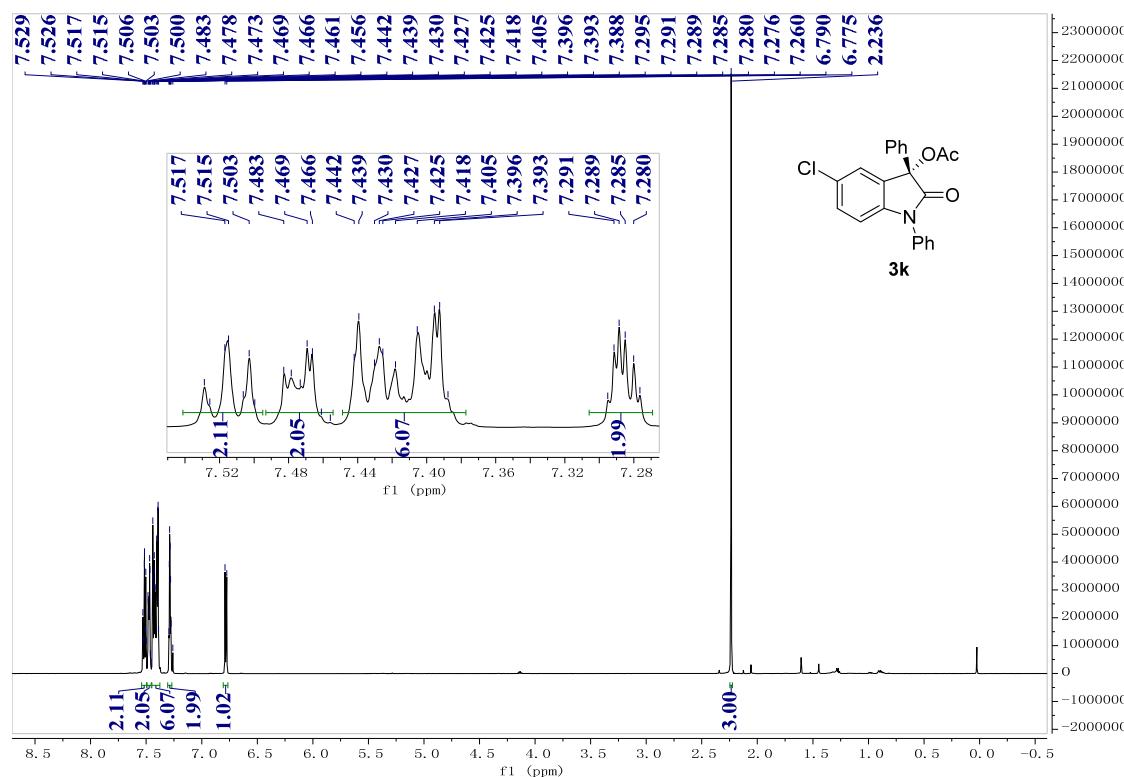
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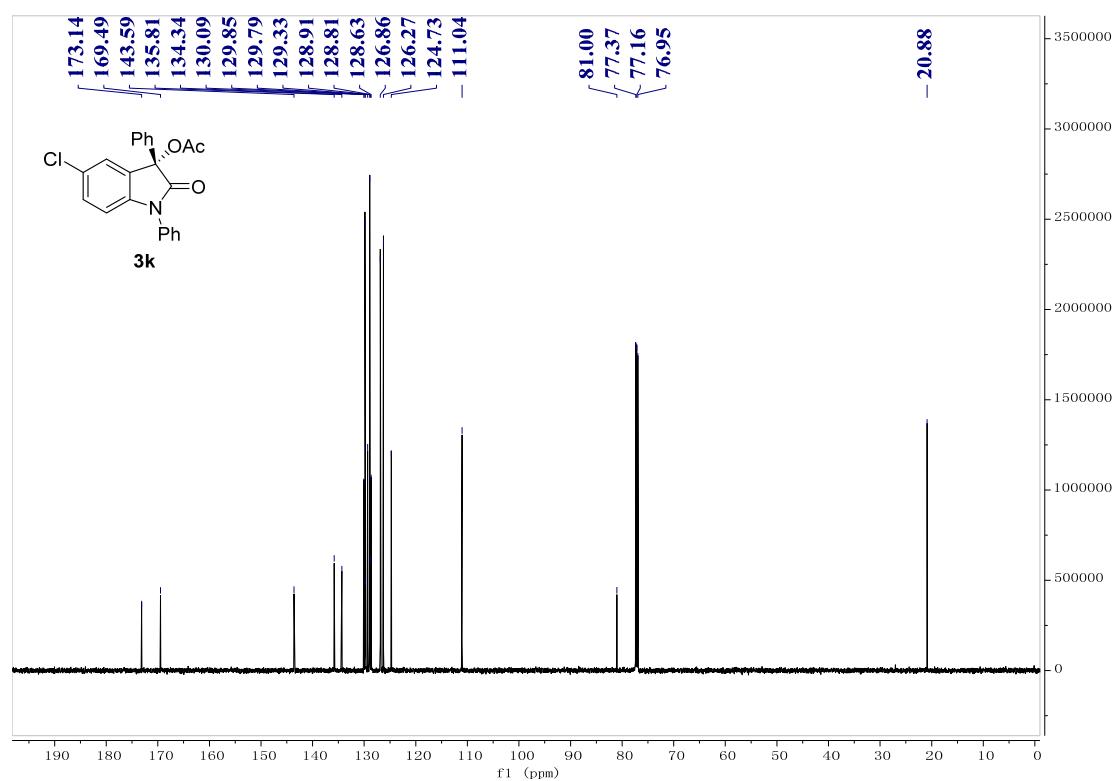
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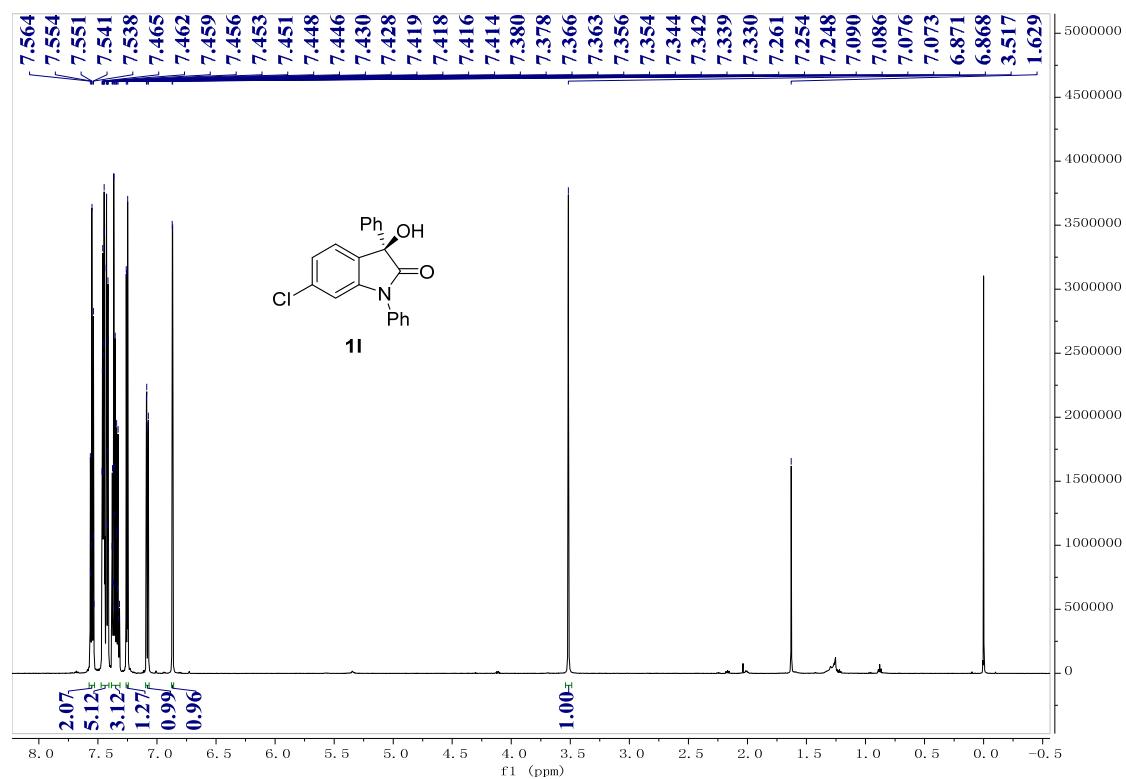
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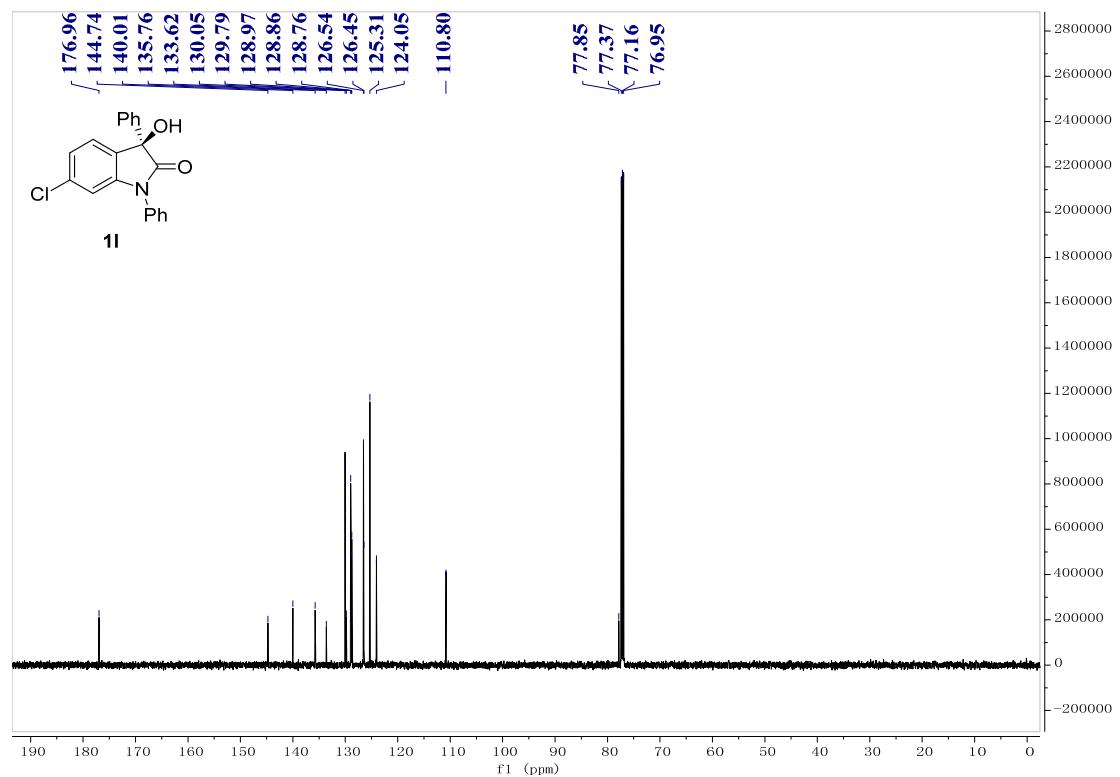
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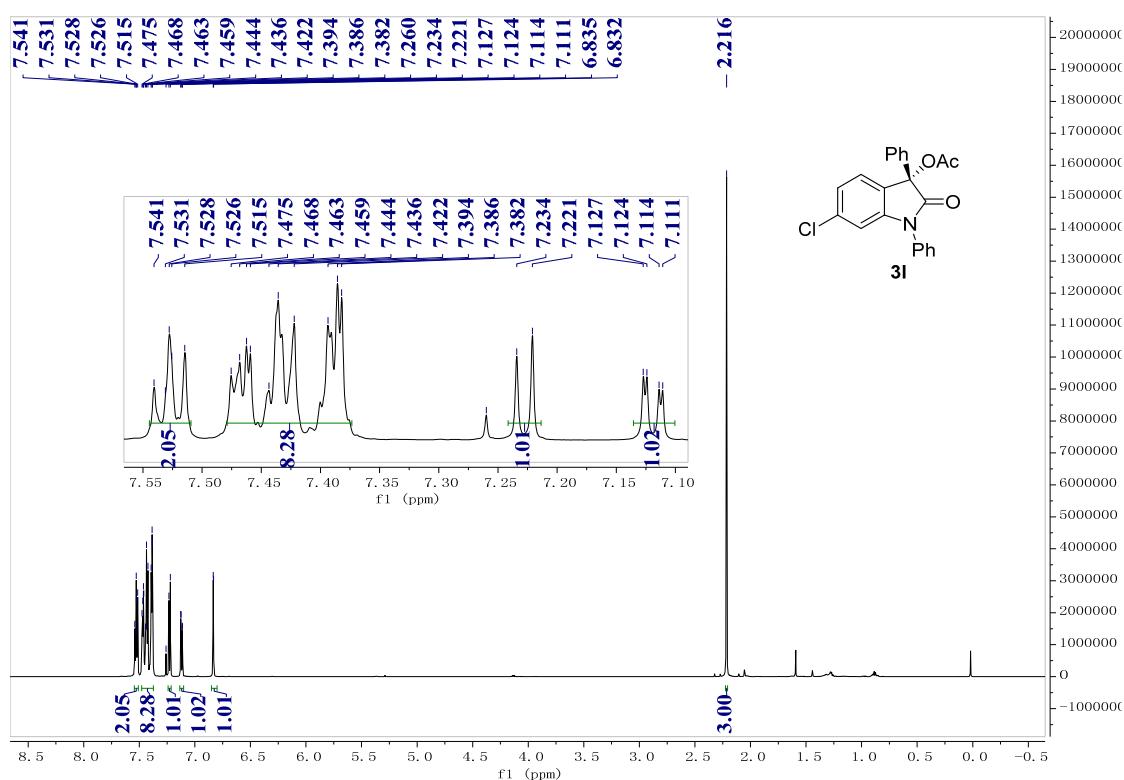
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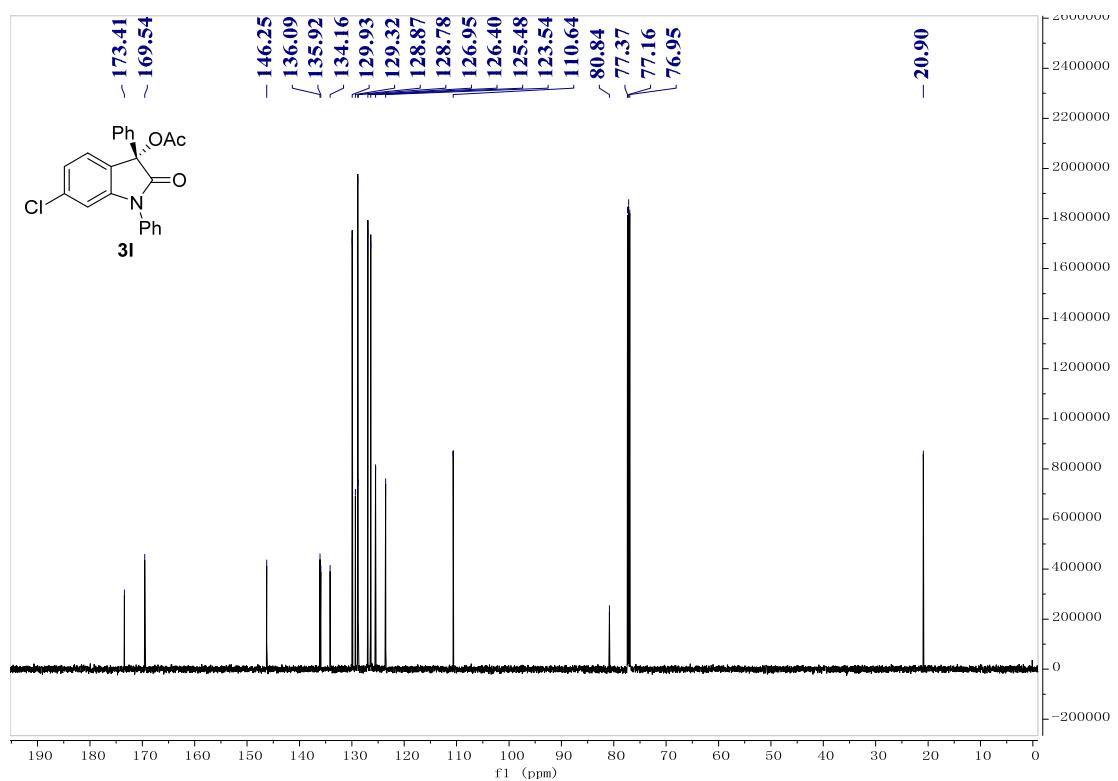
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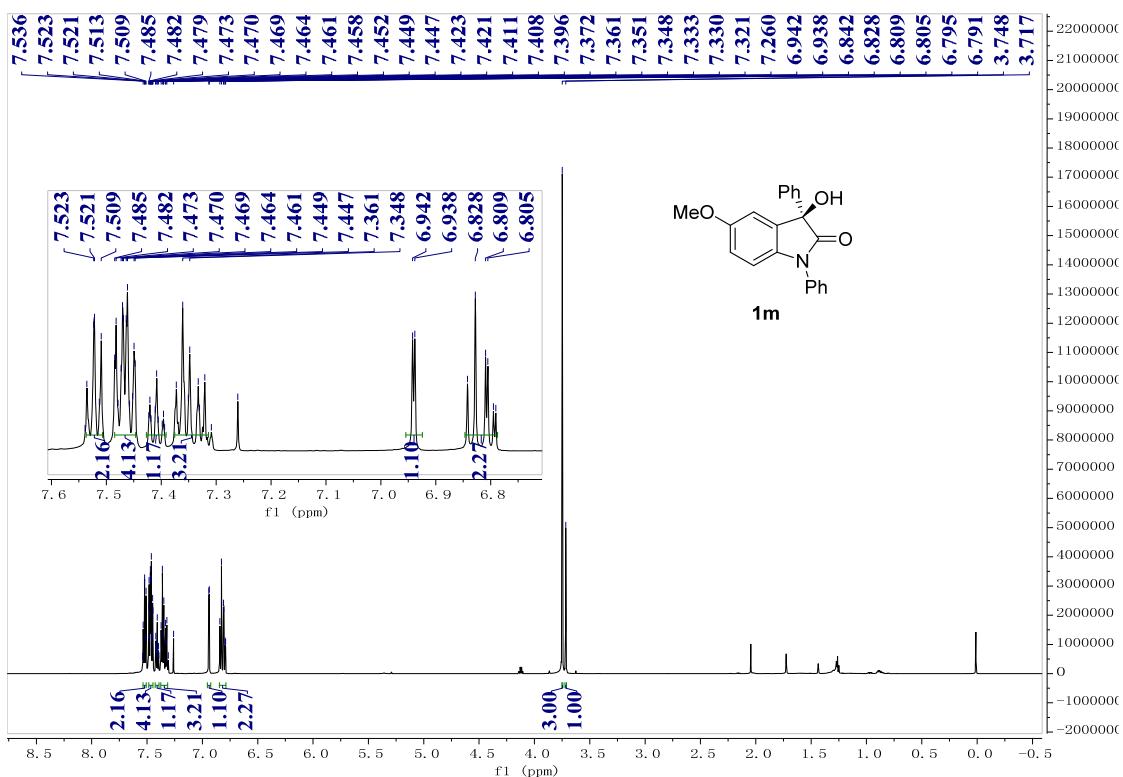
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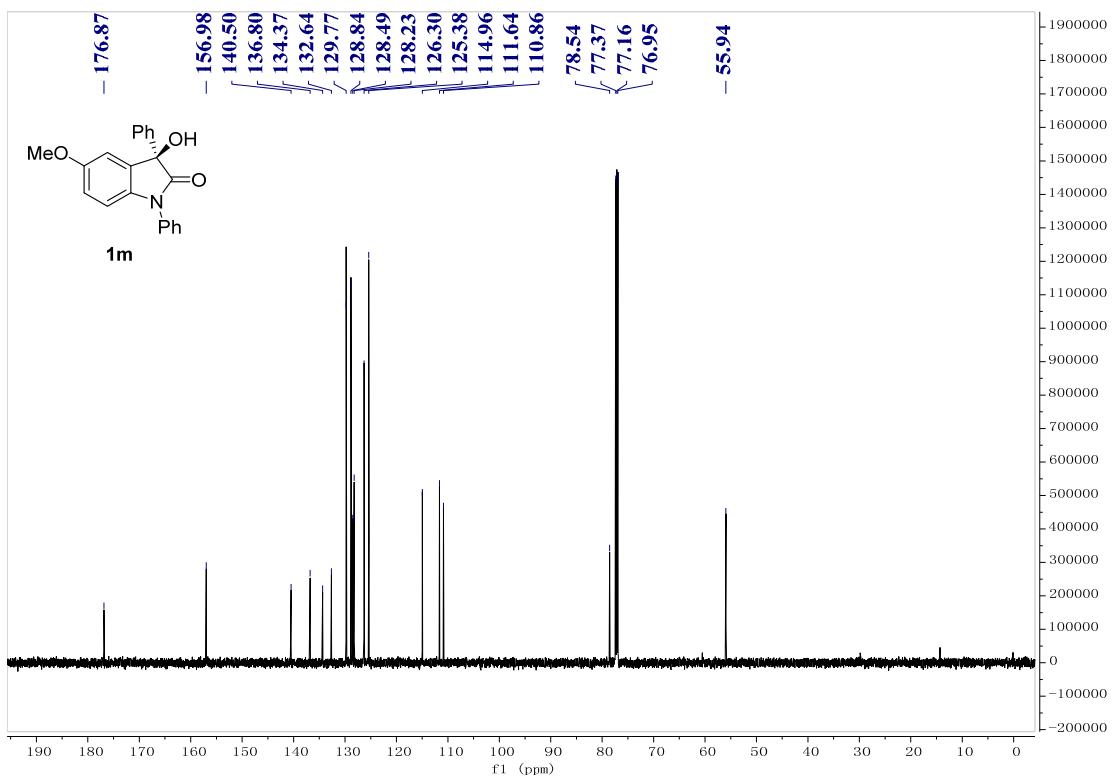
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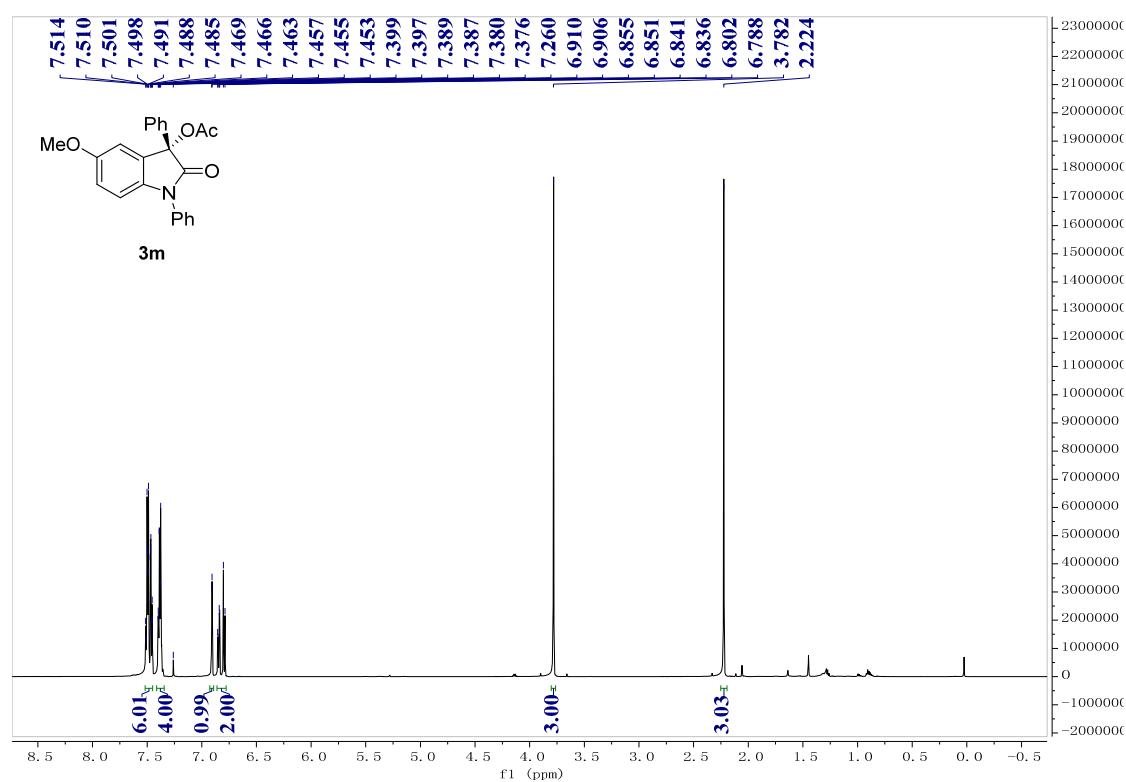
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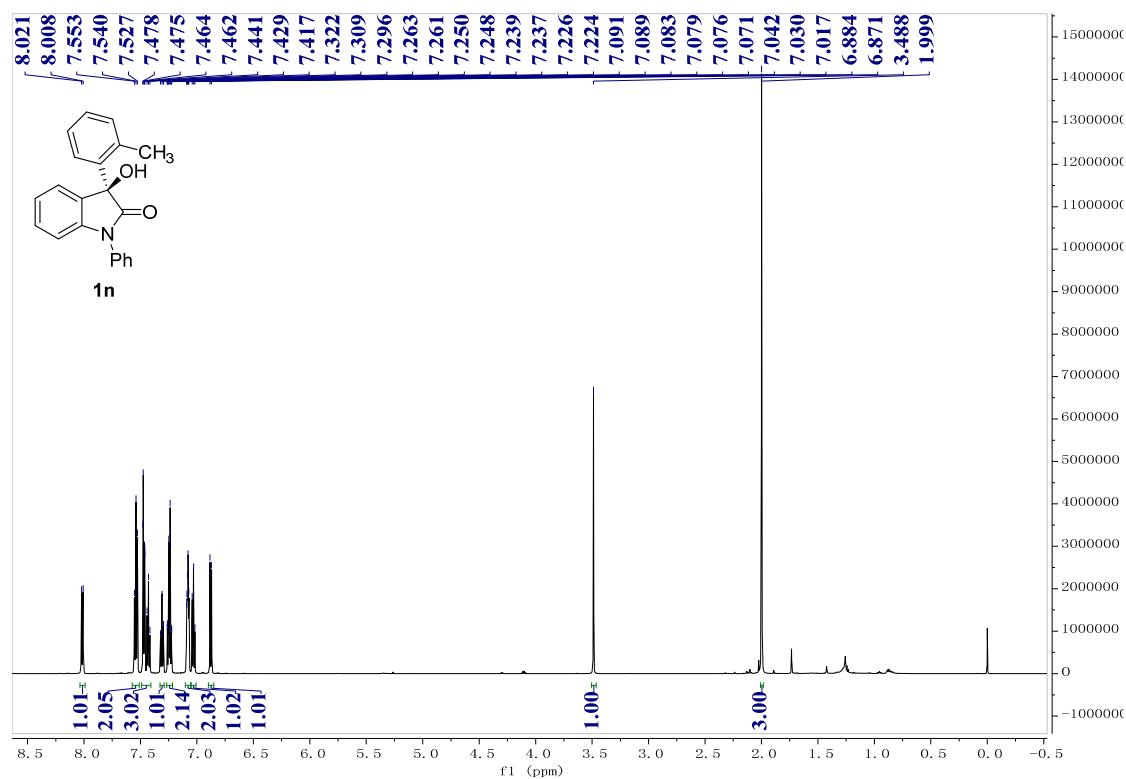
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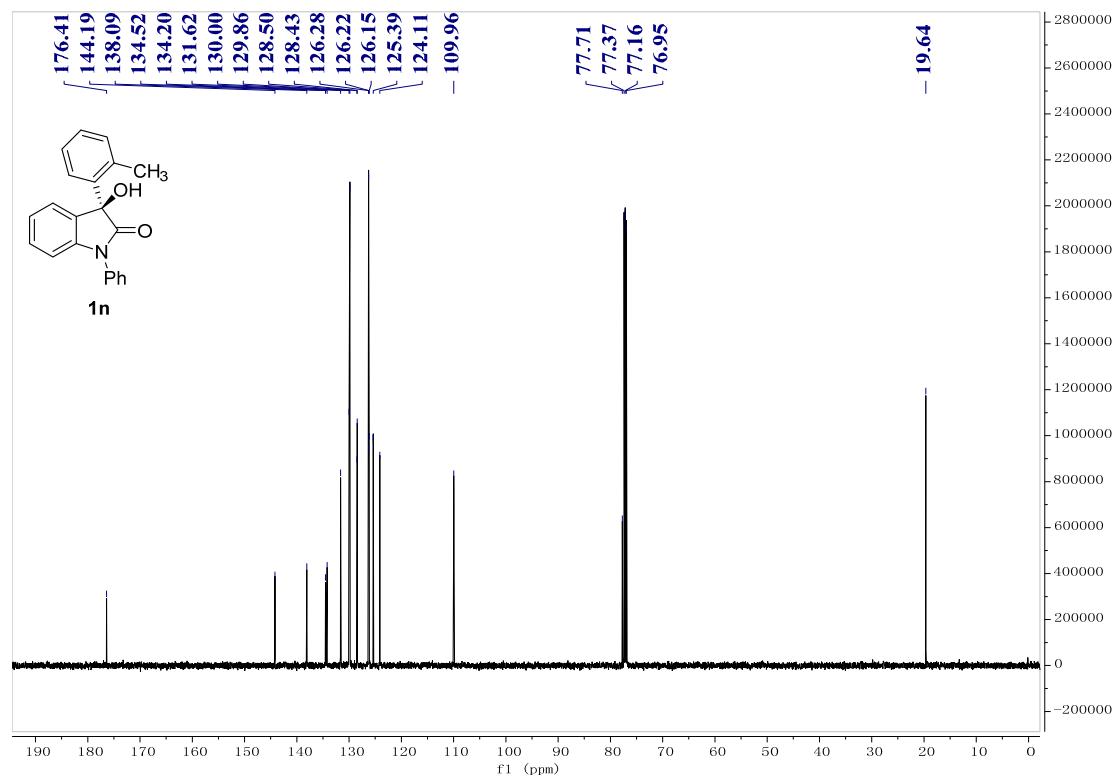
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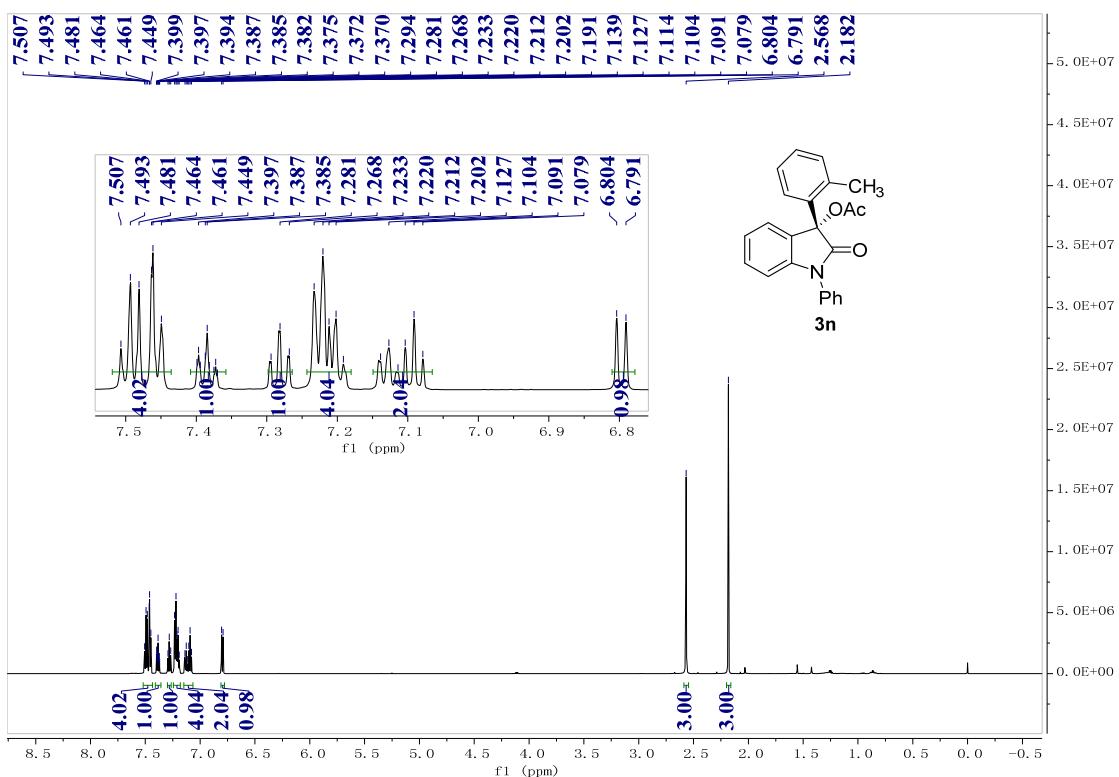
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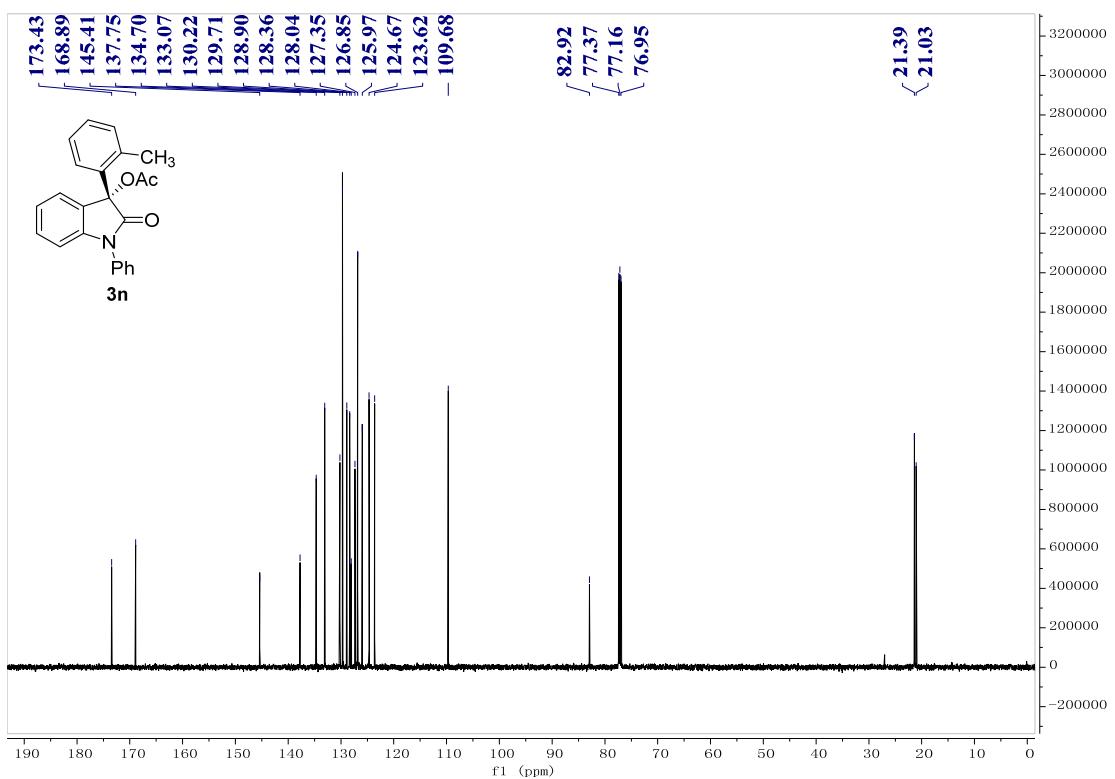
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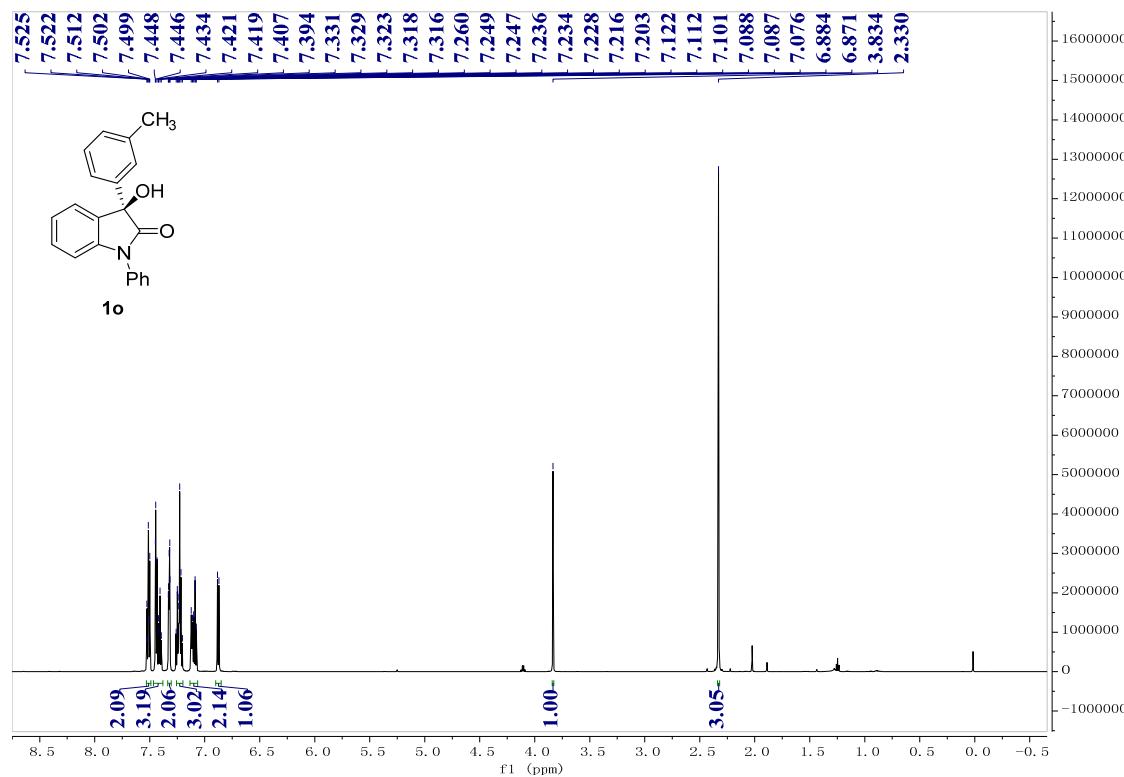
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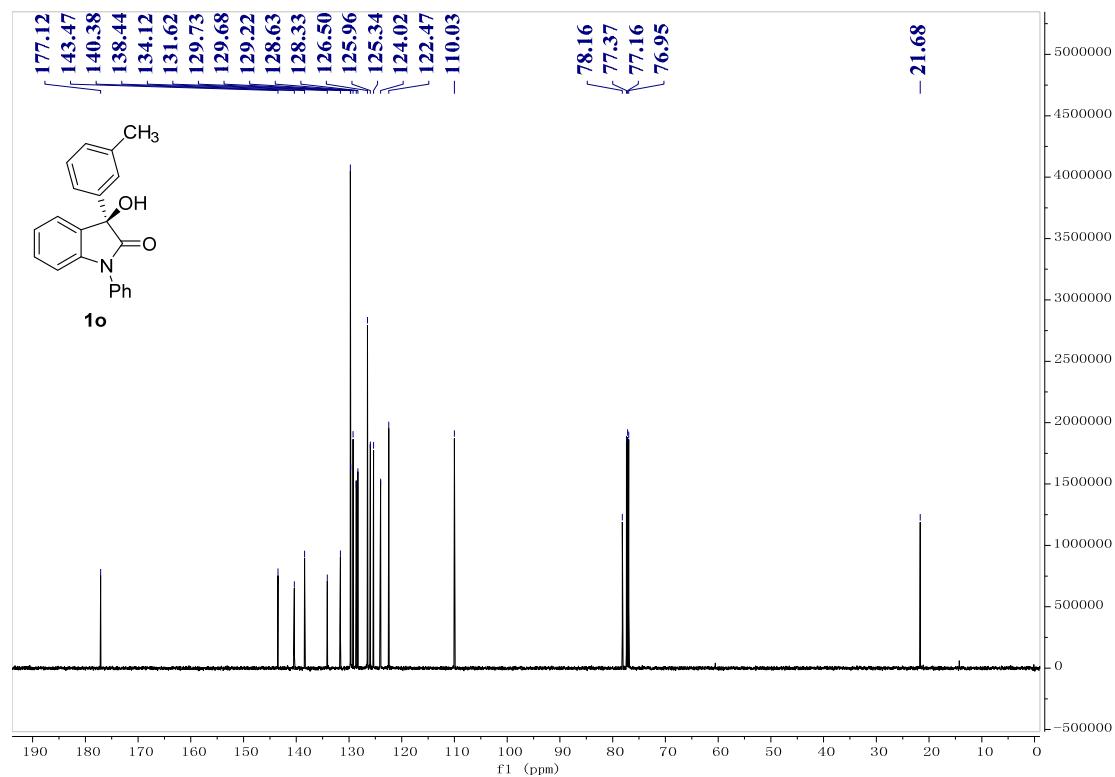
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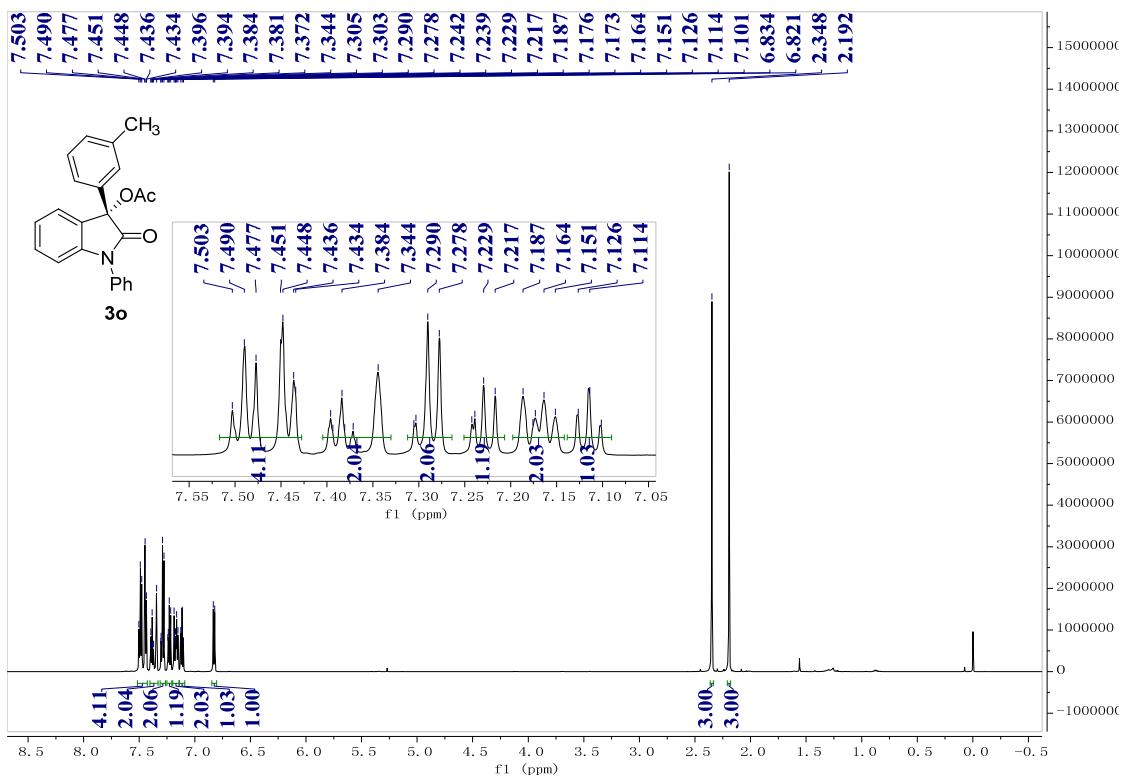
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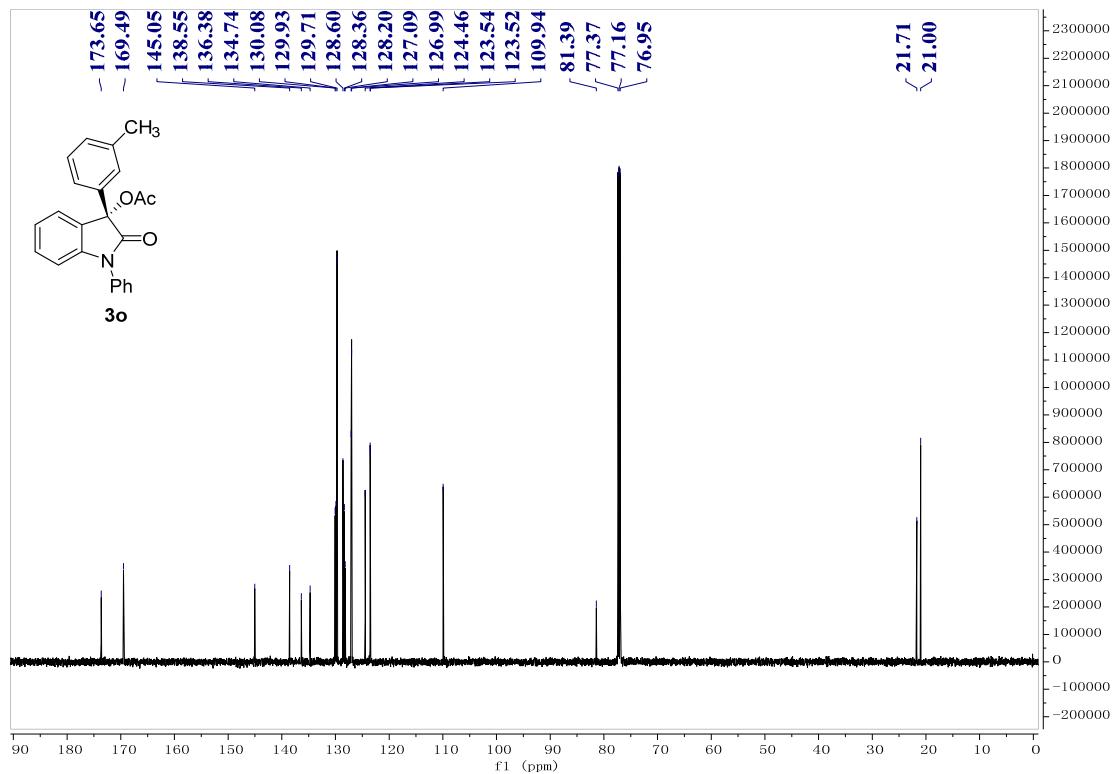
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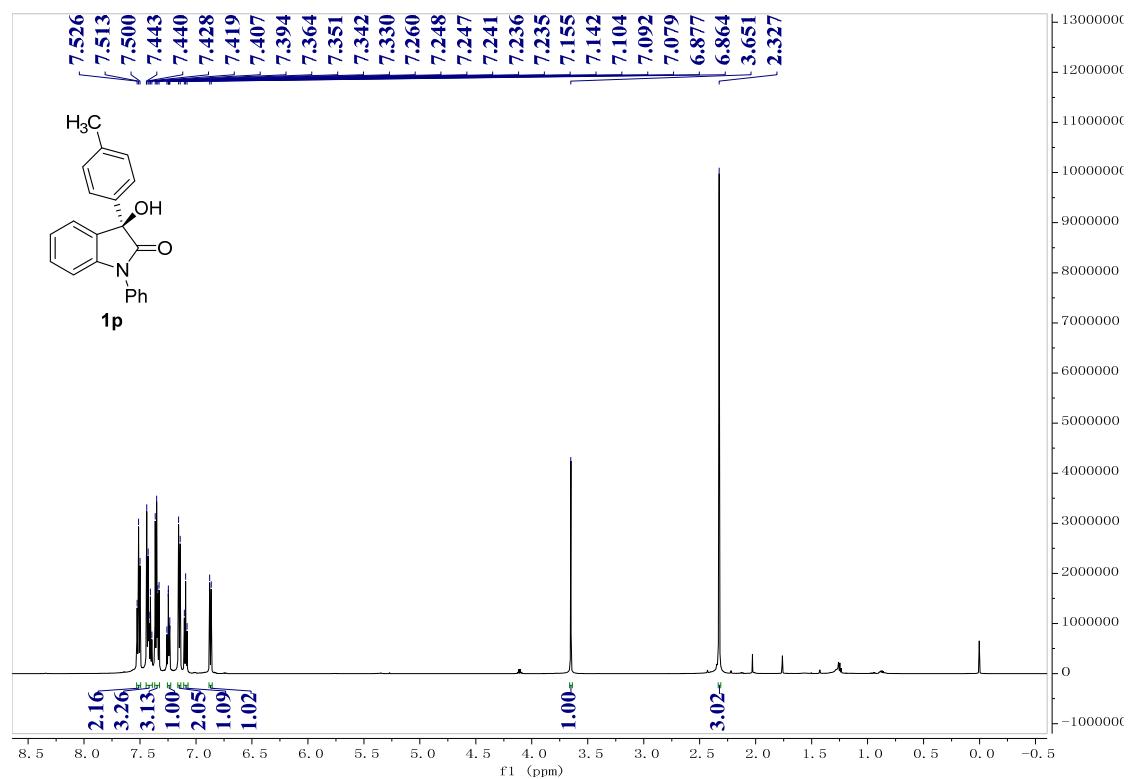
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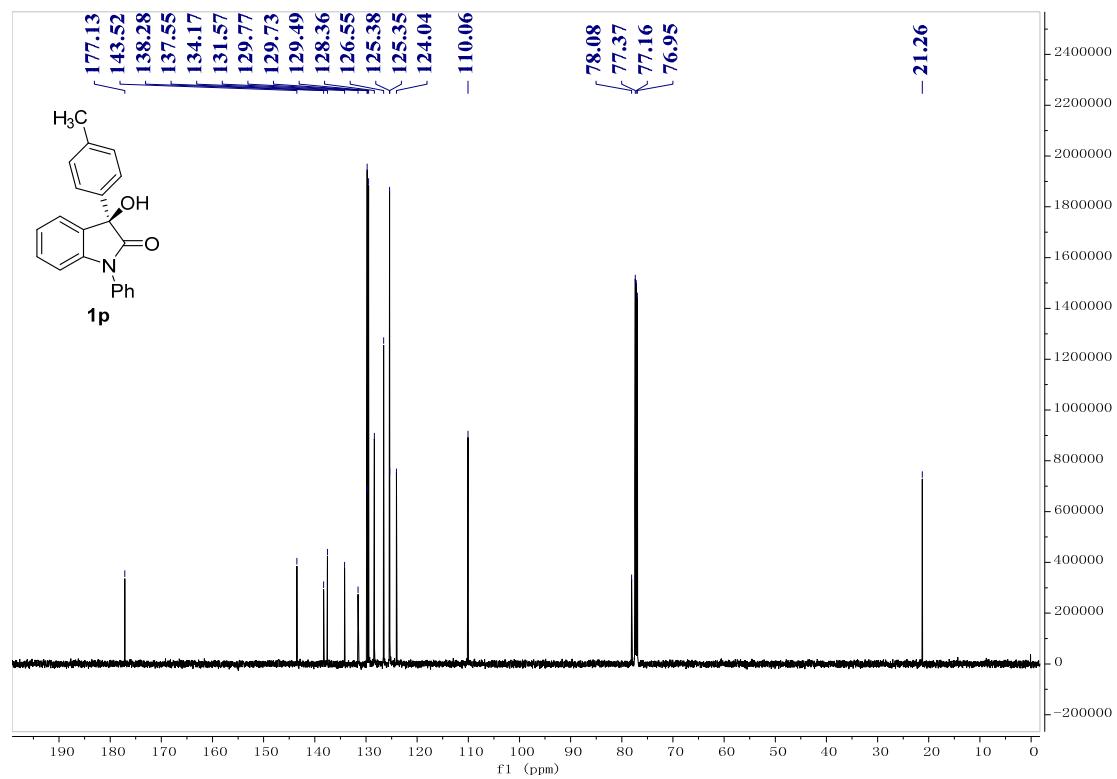
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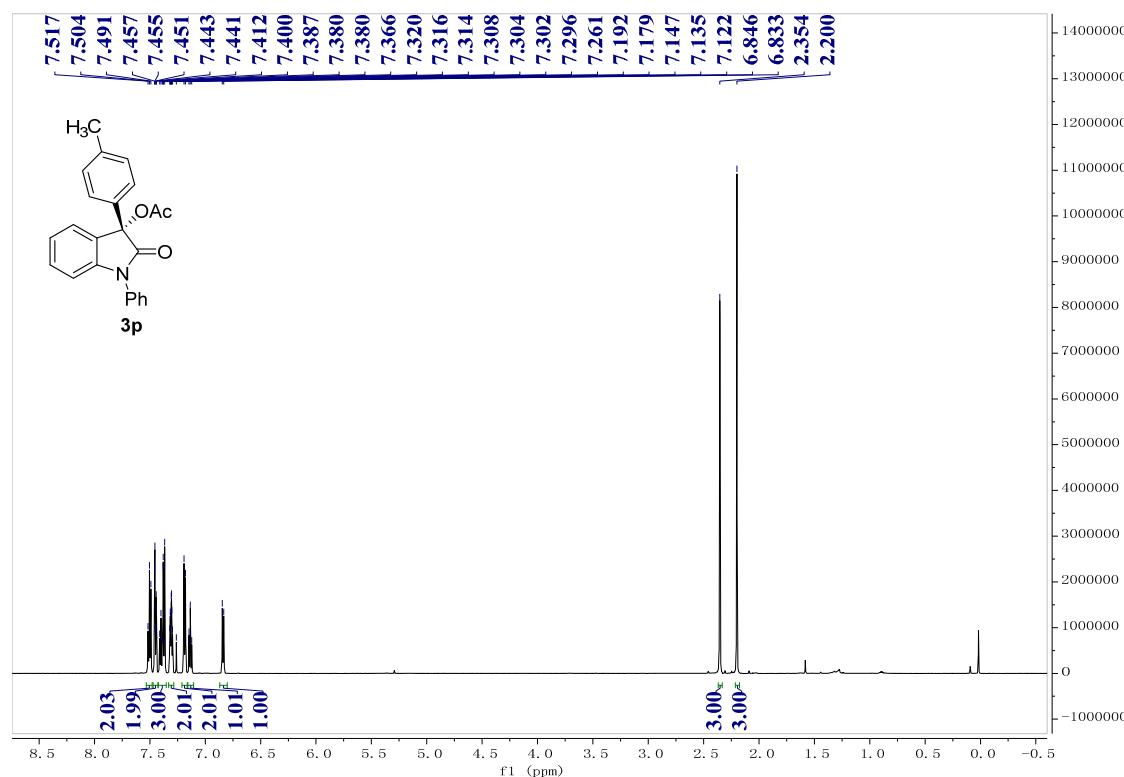
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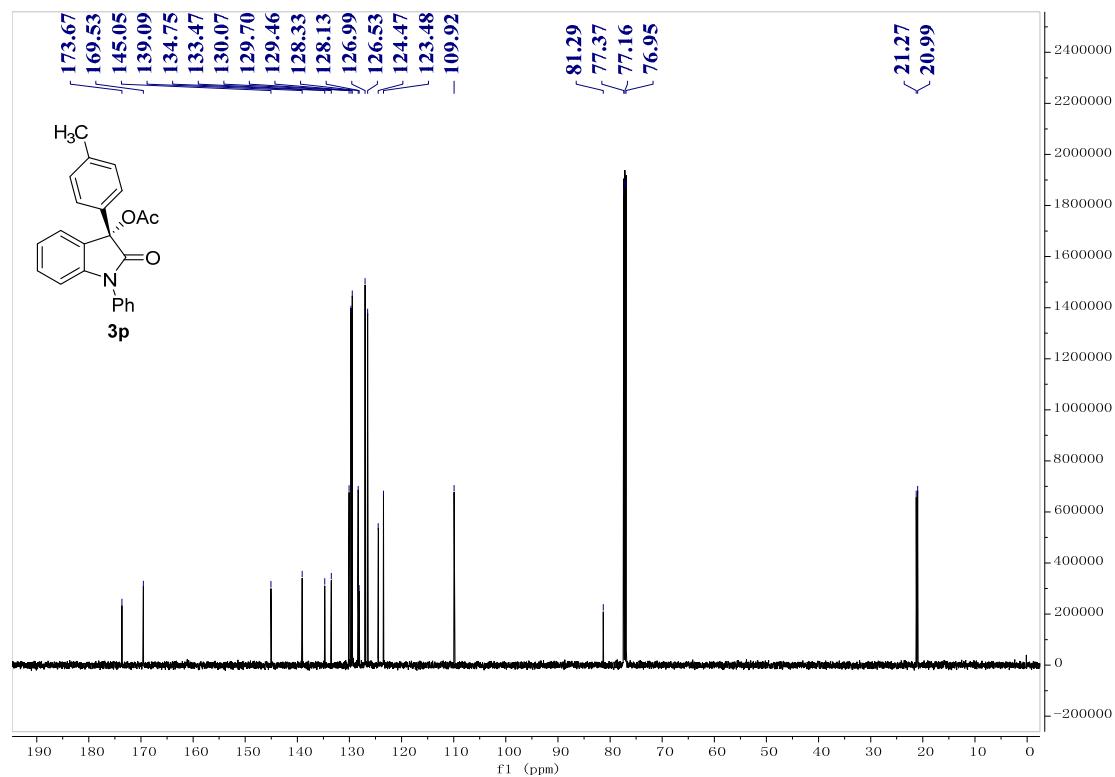
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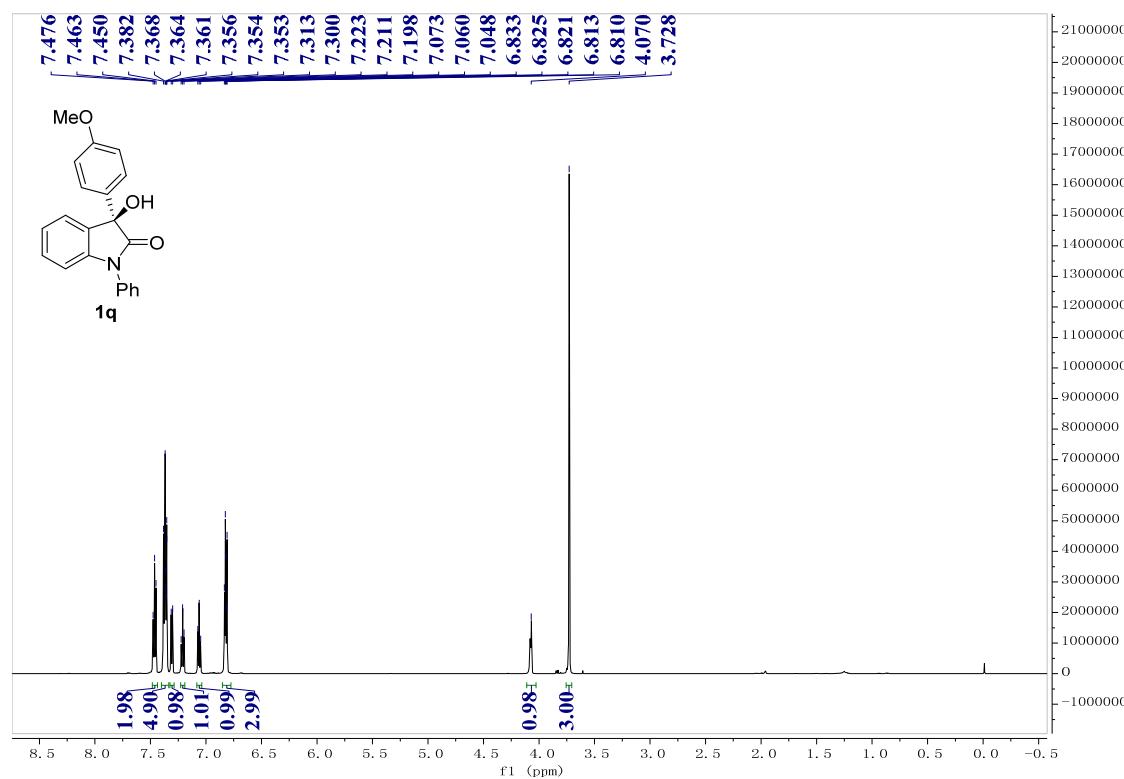
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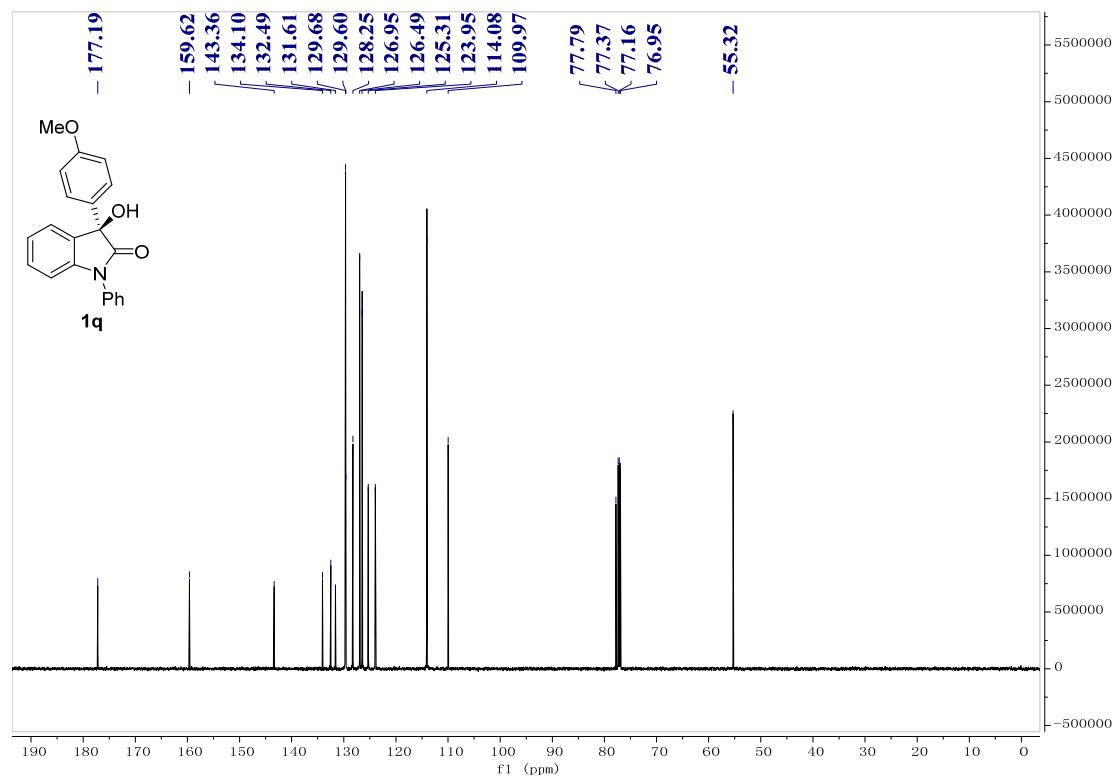
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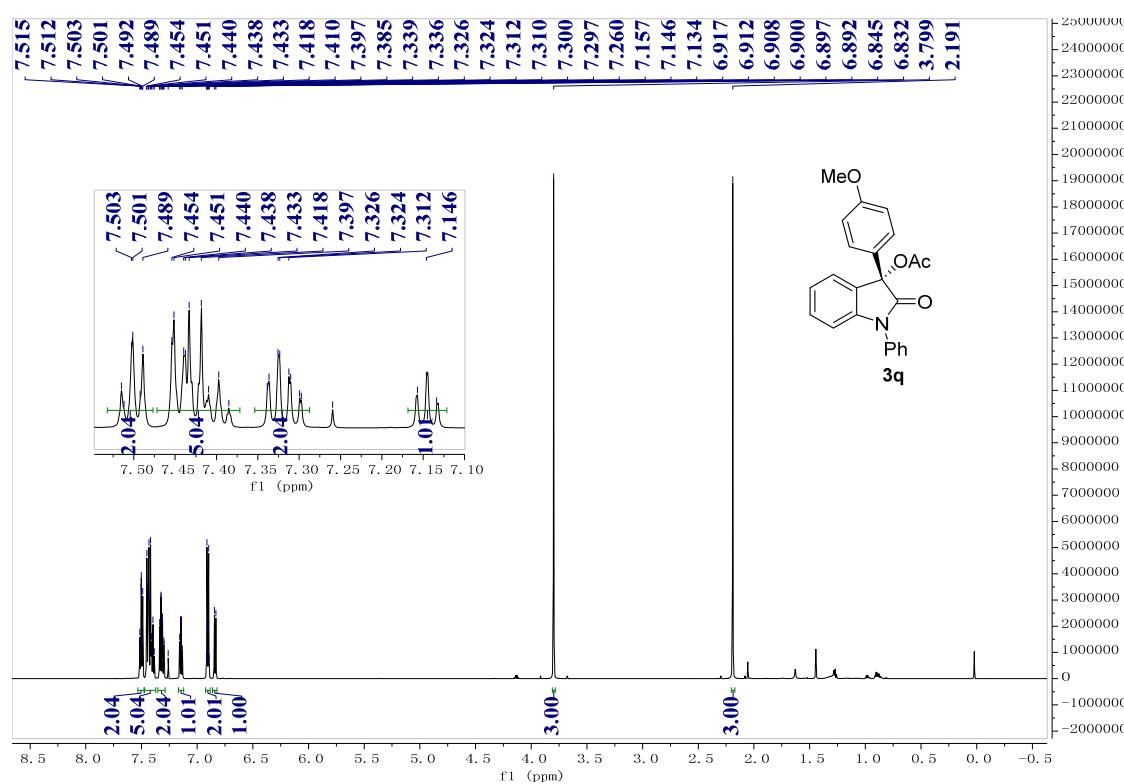
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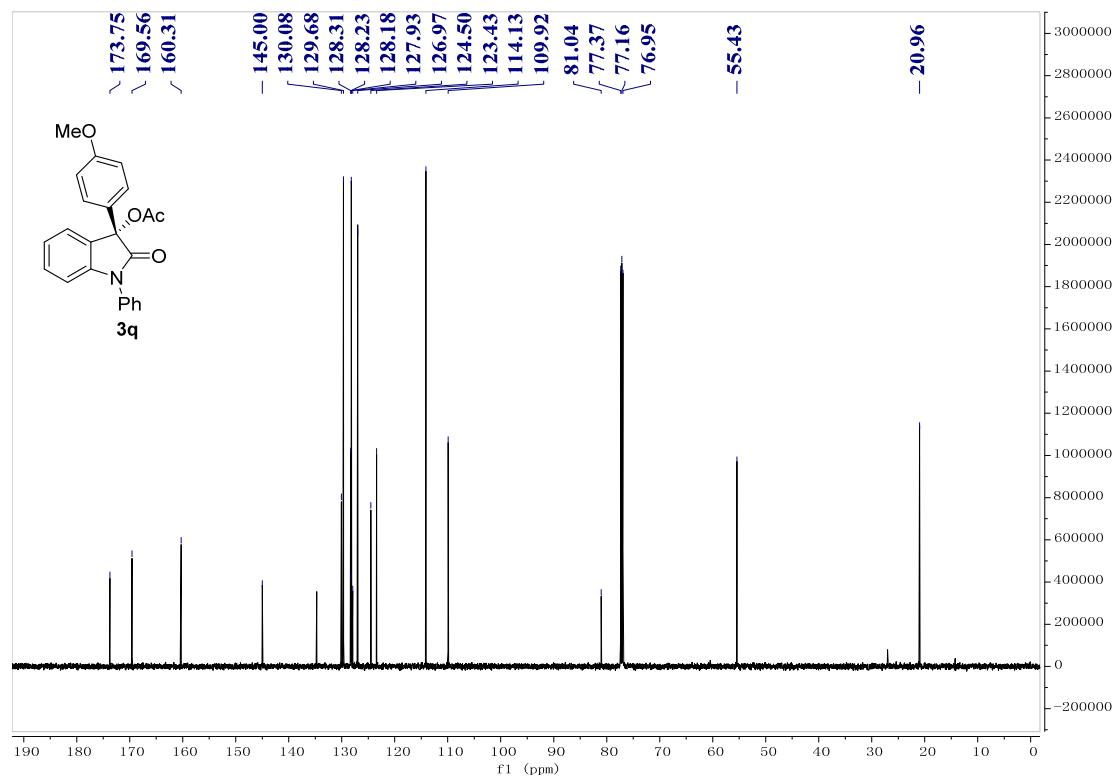
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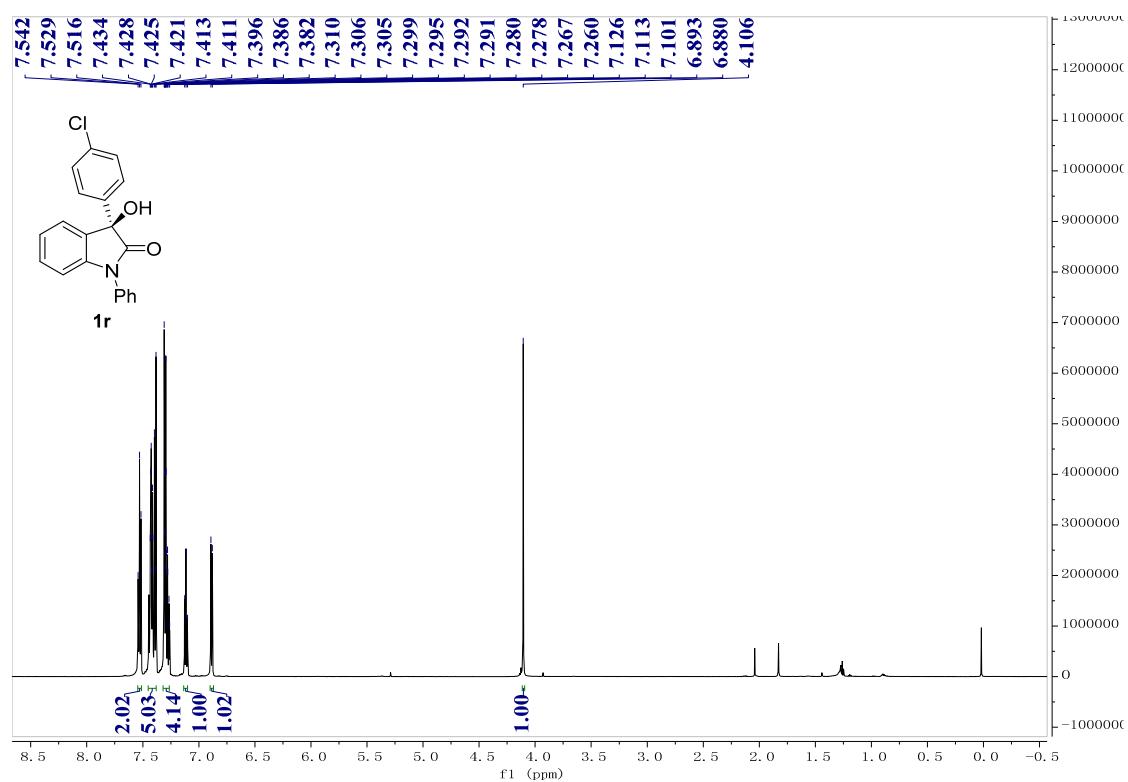
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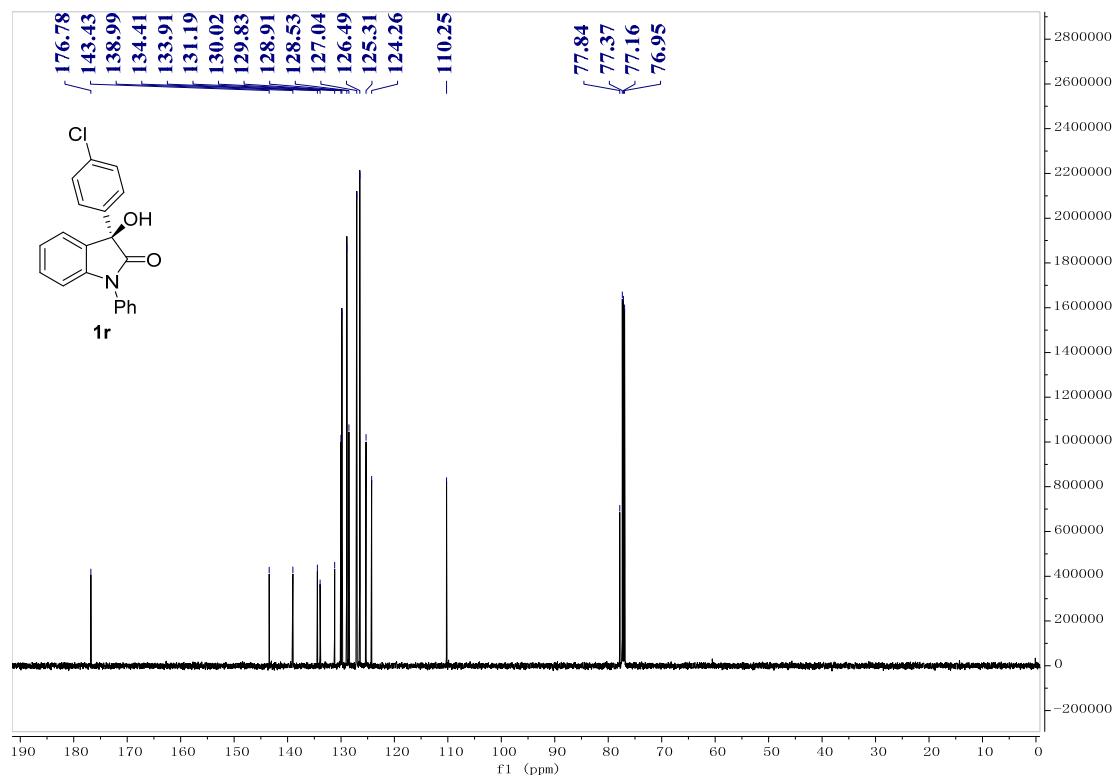
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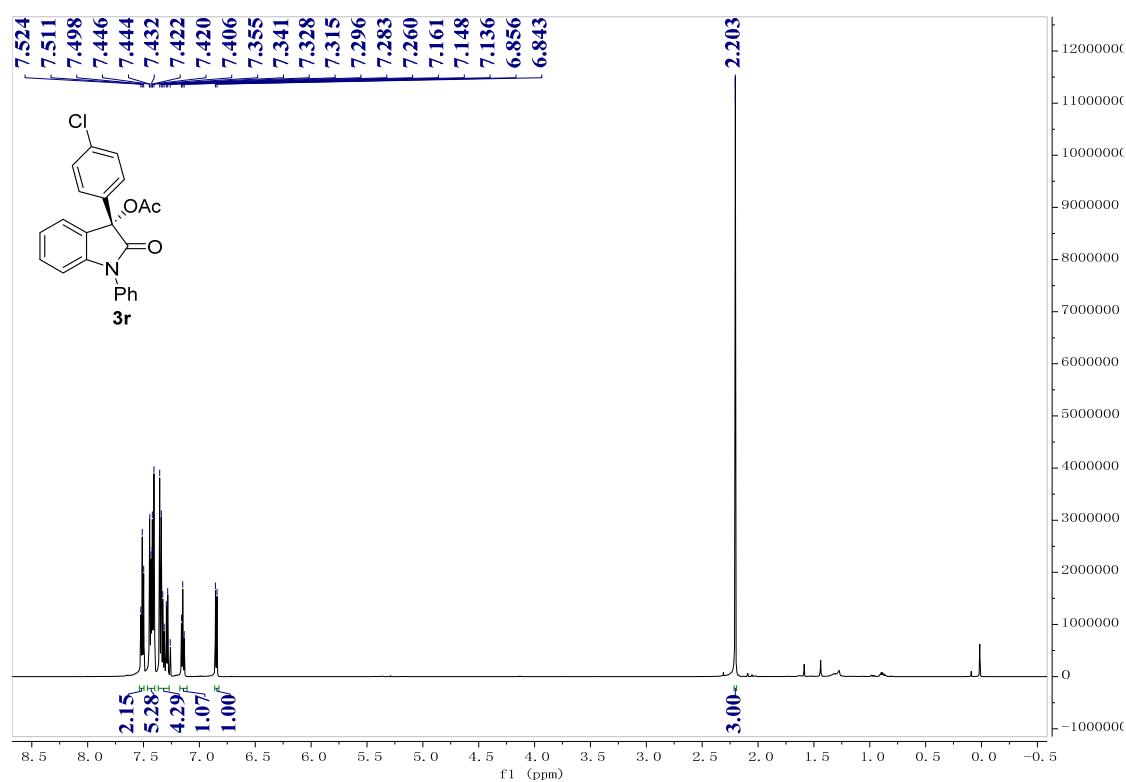
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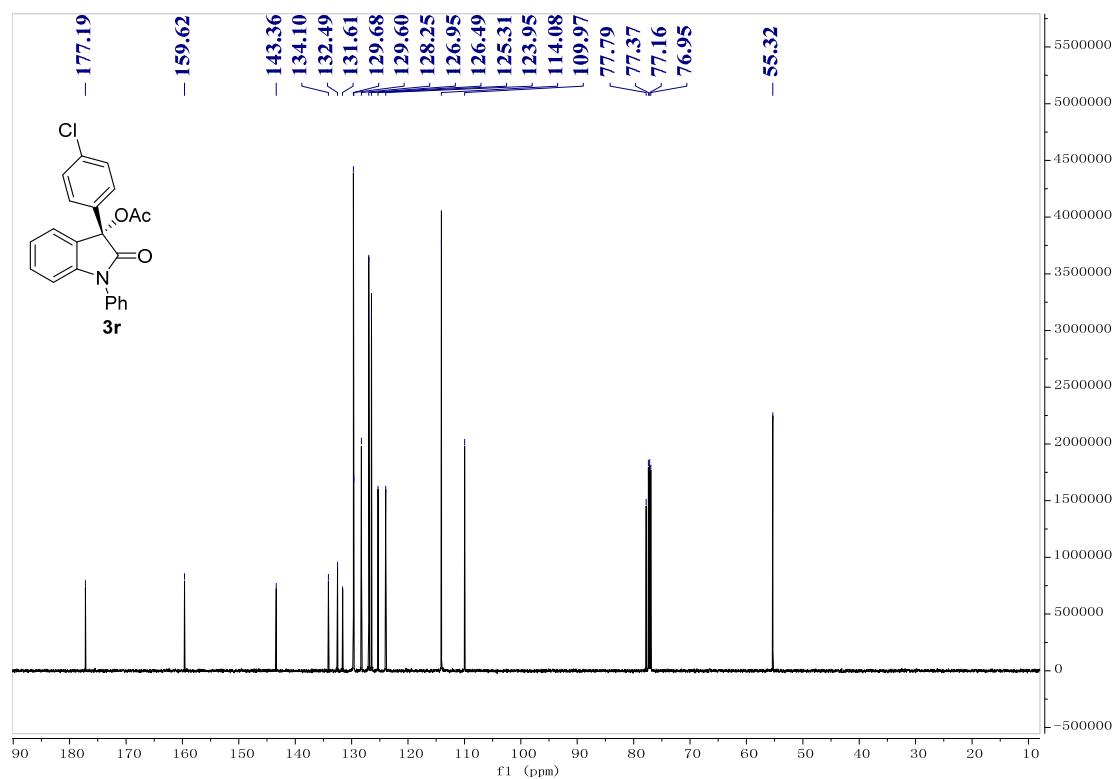
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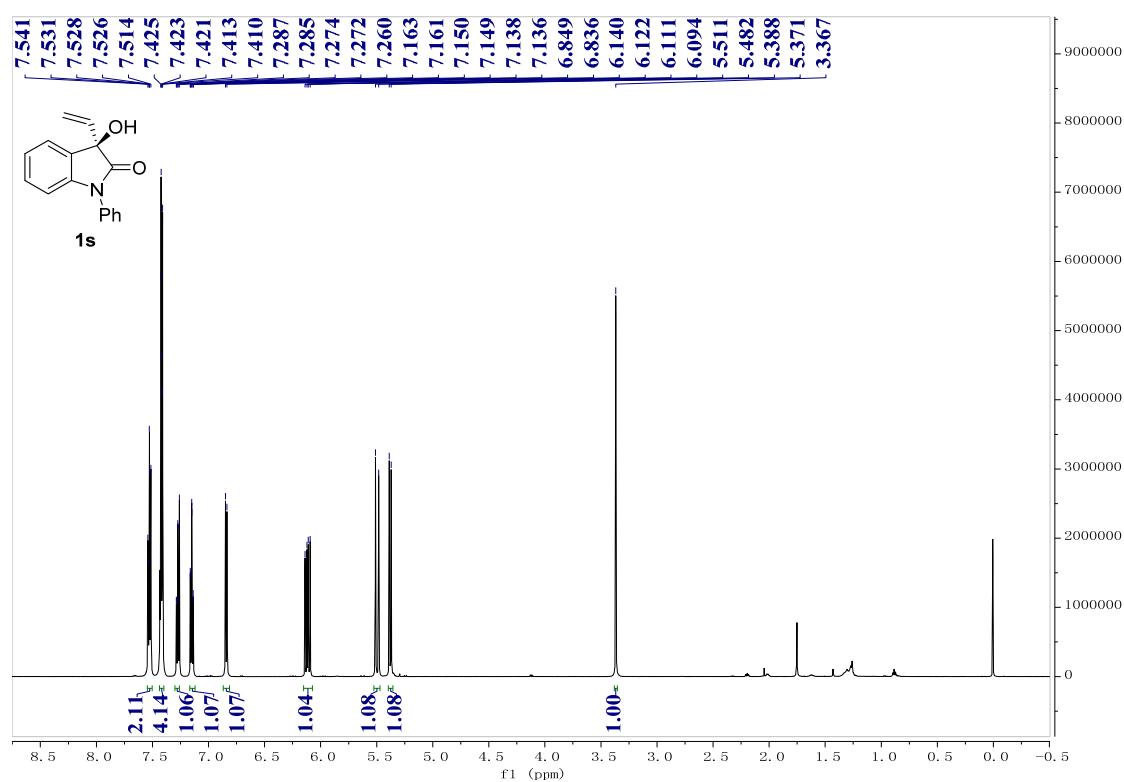
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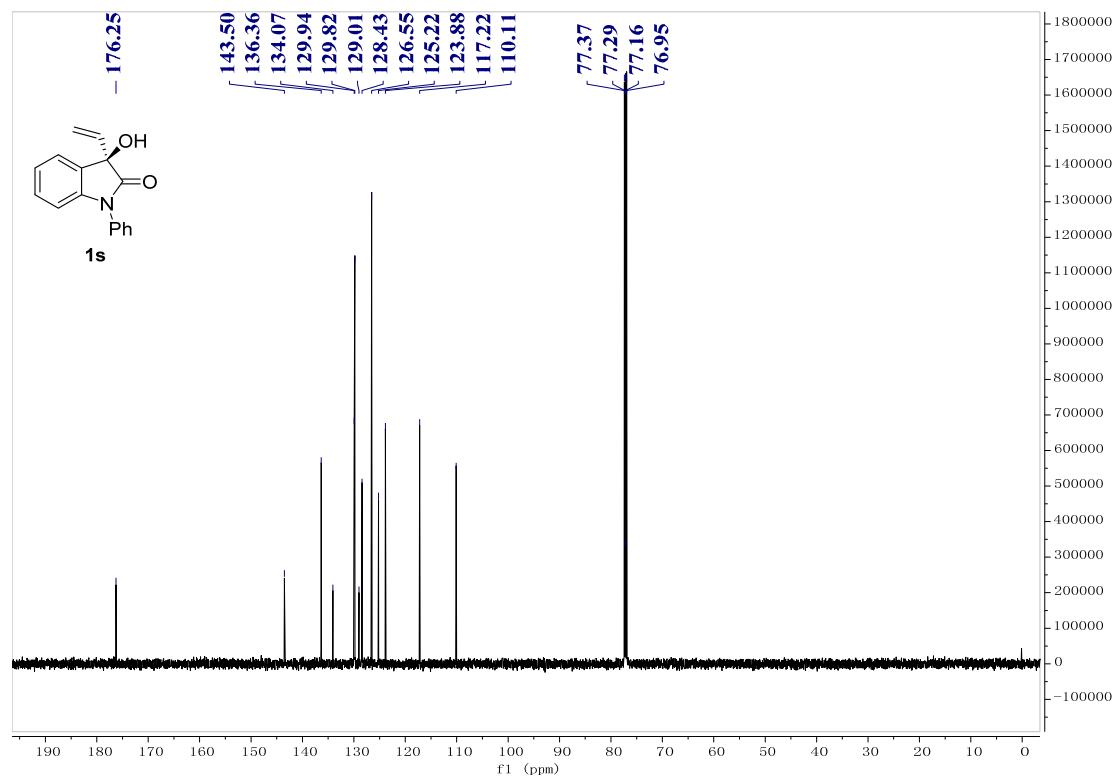
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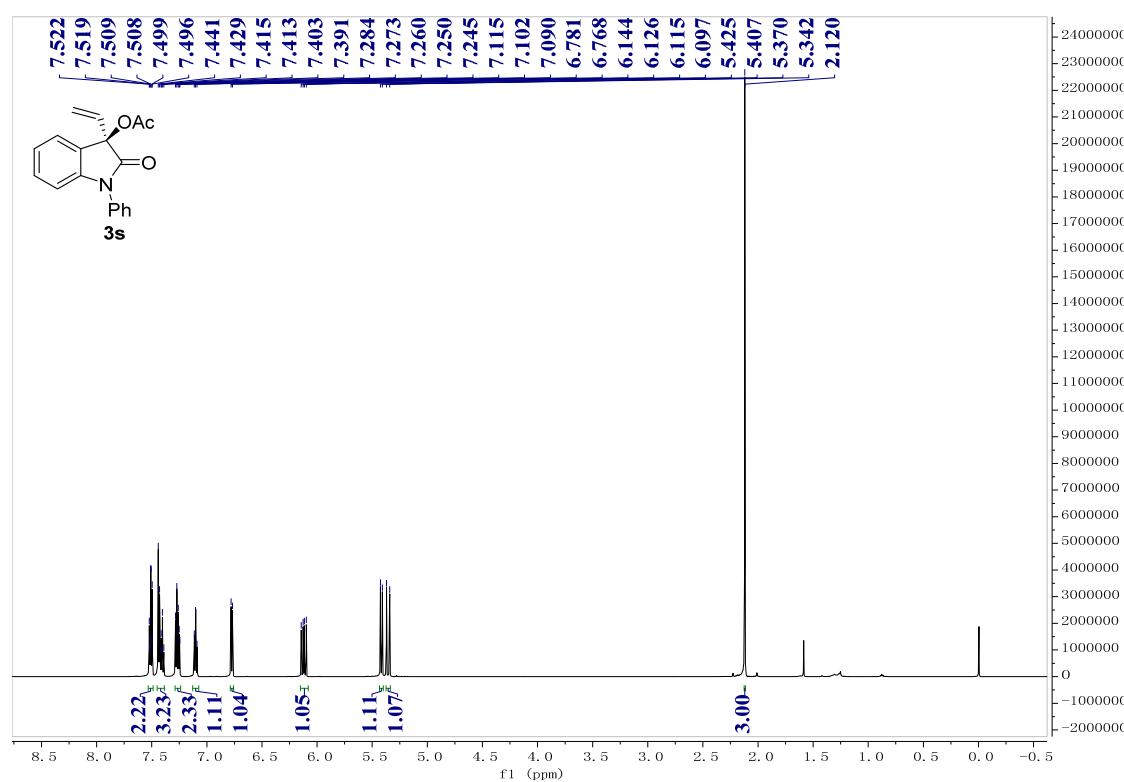
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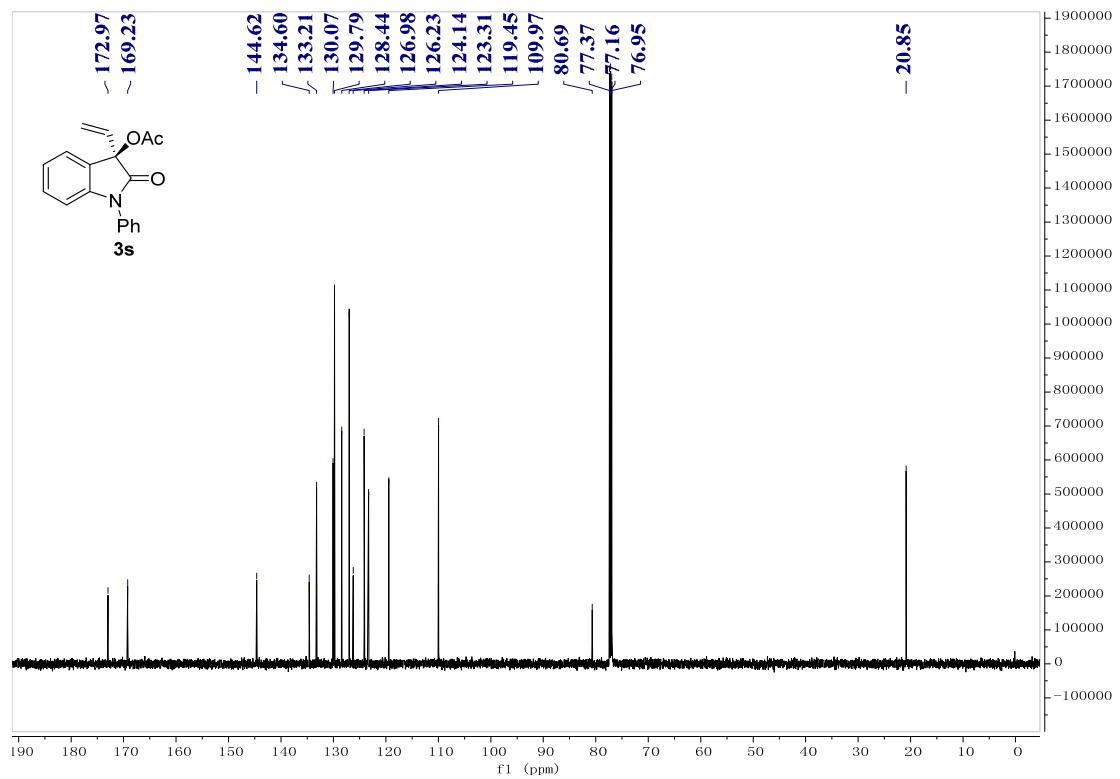
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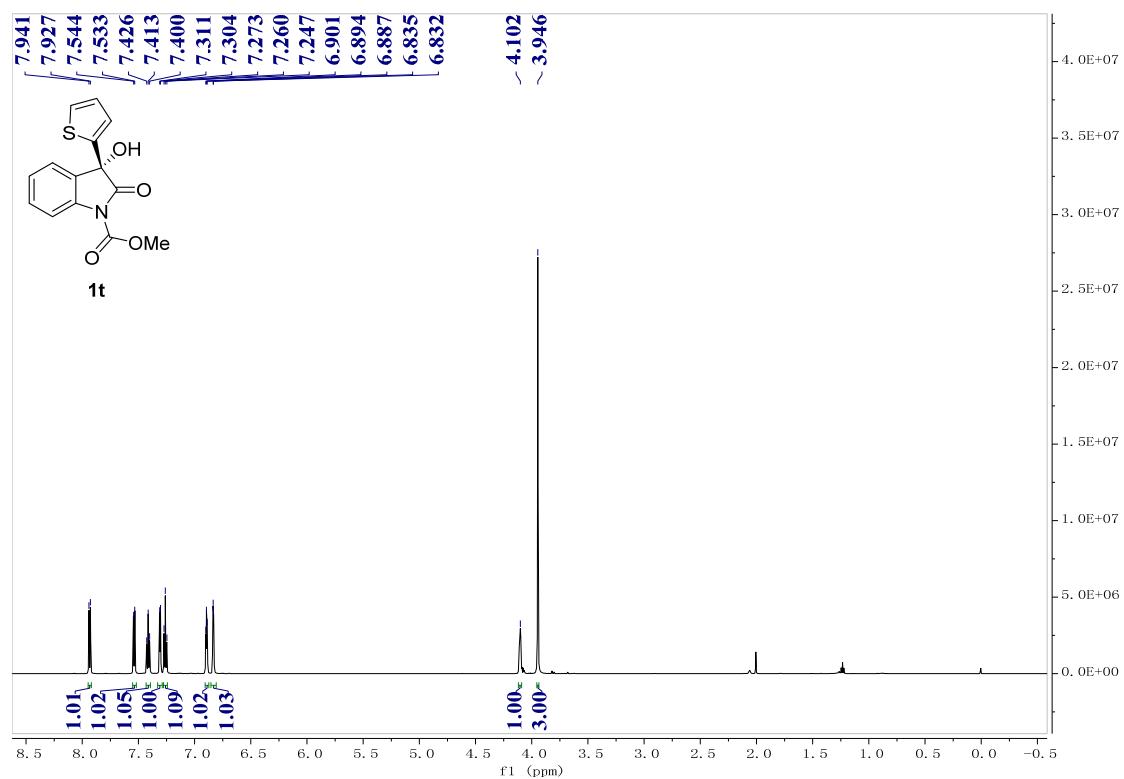
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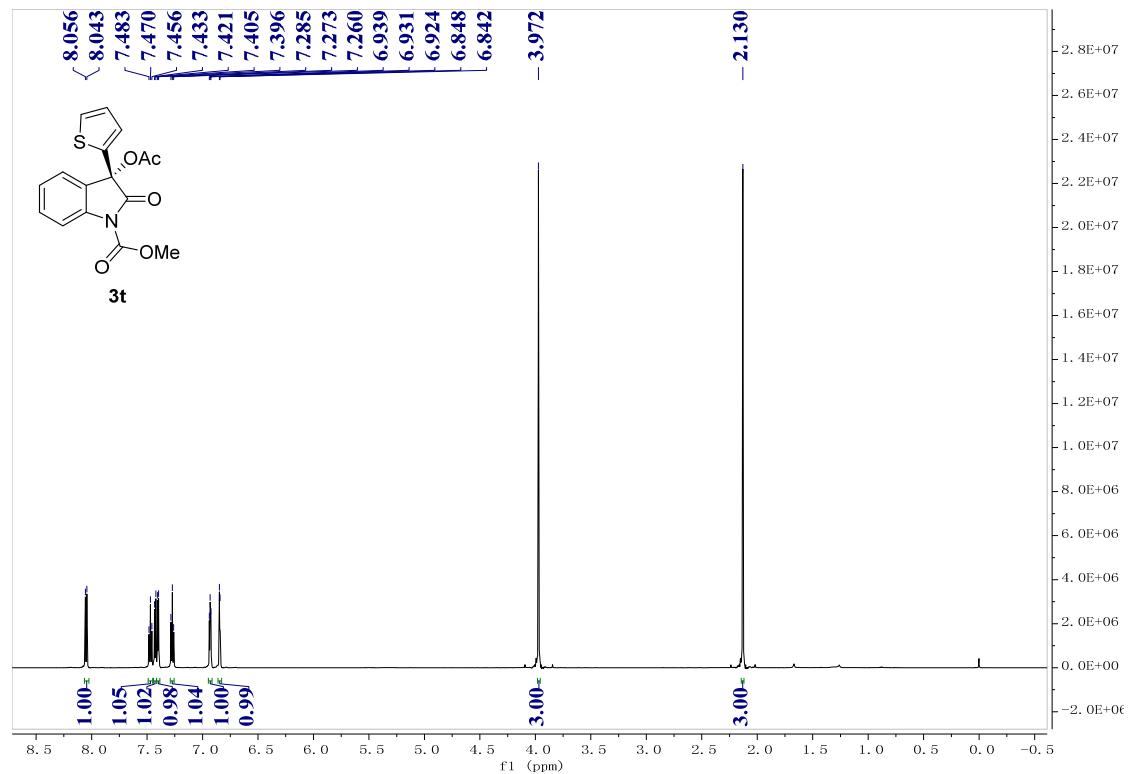
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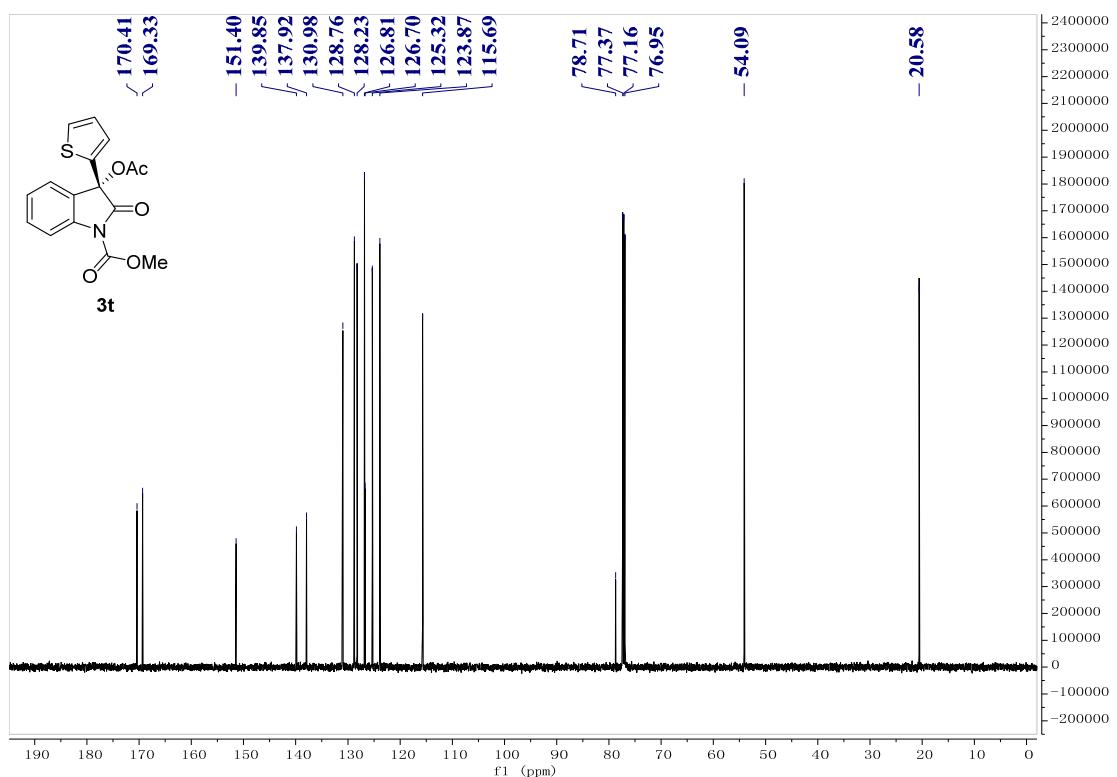
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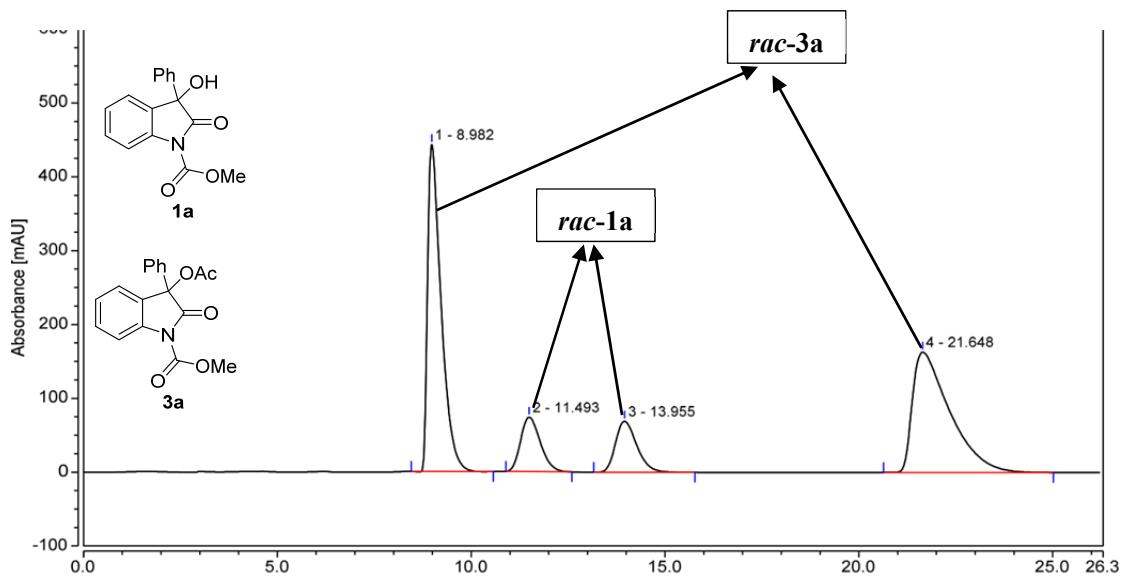
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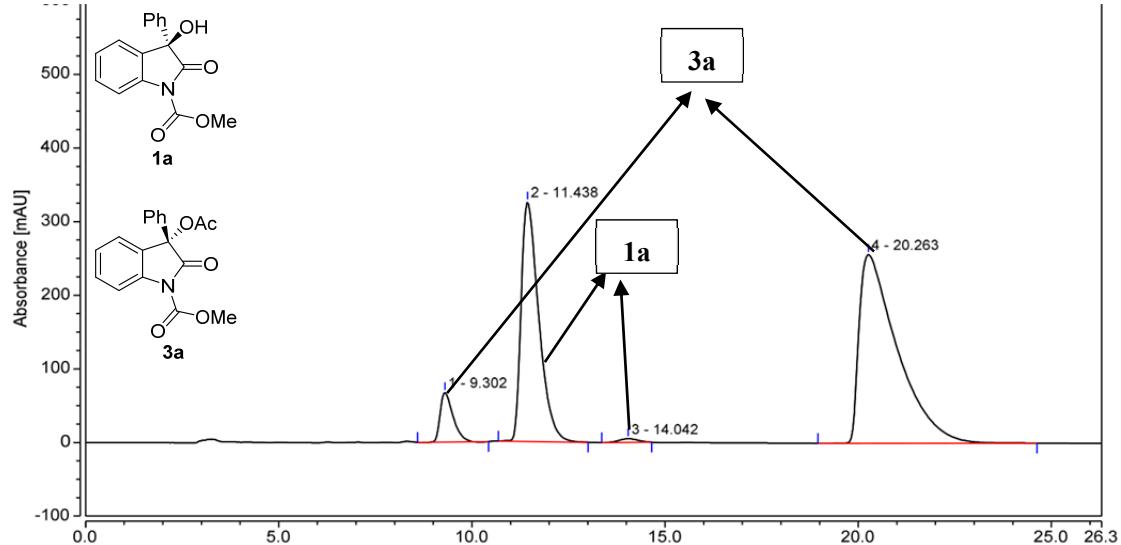
¹³C NMR for 3t

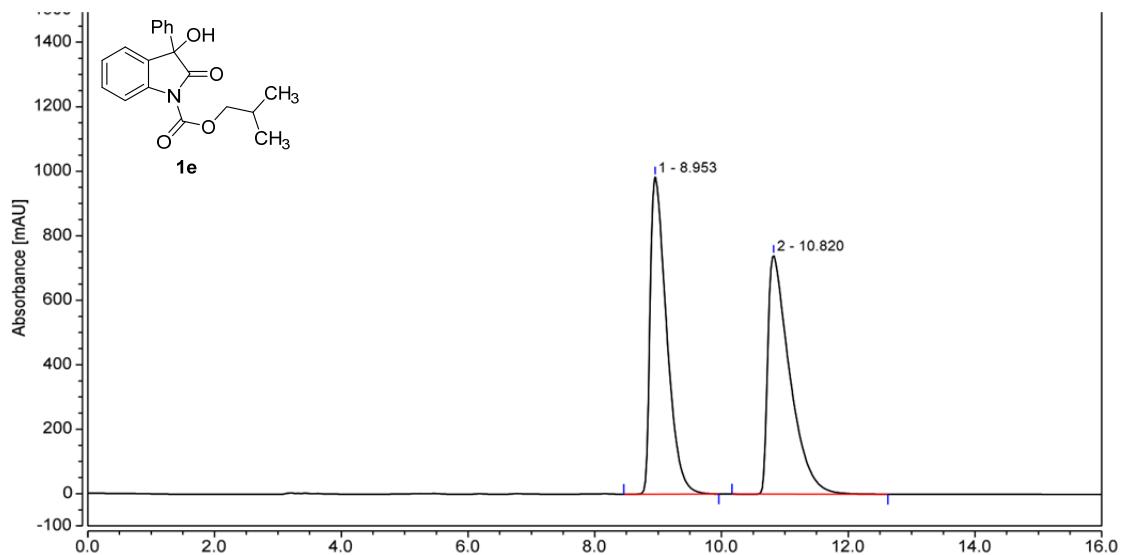


12. Copies of HPLC spectra

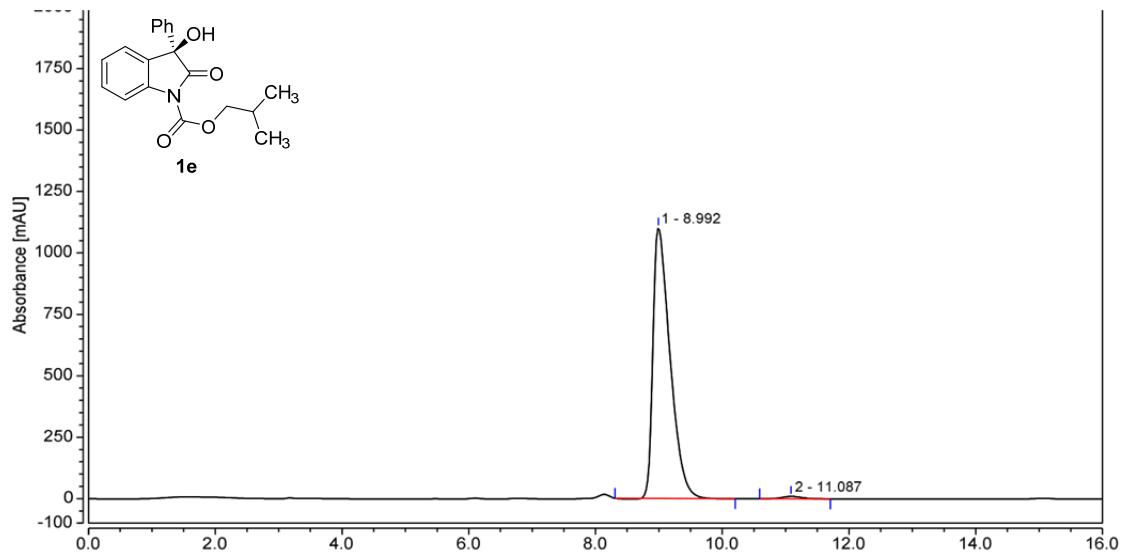


| Peak | Retention Time min | Area mAU*min | Height mAU | Area % | Height % |
|---------------|-----------------------|-----------------|----------------|---------------|---------------|
| 1 | 8.982 | 179.249 | 442.833 | 39.95 | 59.13 |
| 2 | 11.493 | 43.360 | 73.753 | 9.66 | 9.85 |
| 3 | 13.955 | 44.436 | 69.322 | 9.90 | 9.26 |
| 4 | 21.648 | 181.686 | 162.996 | 40.49 | 21.76 |
| Total: | | 448.731 | 748.904 | 100.00 | 100.00 |

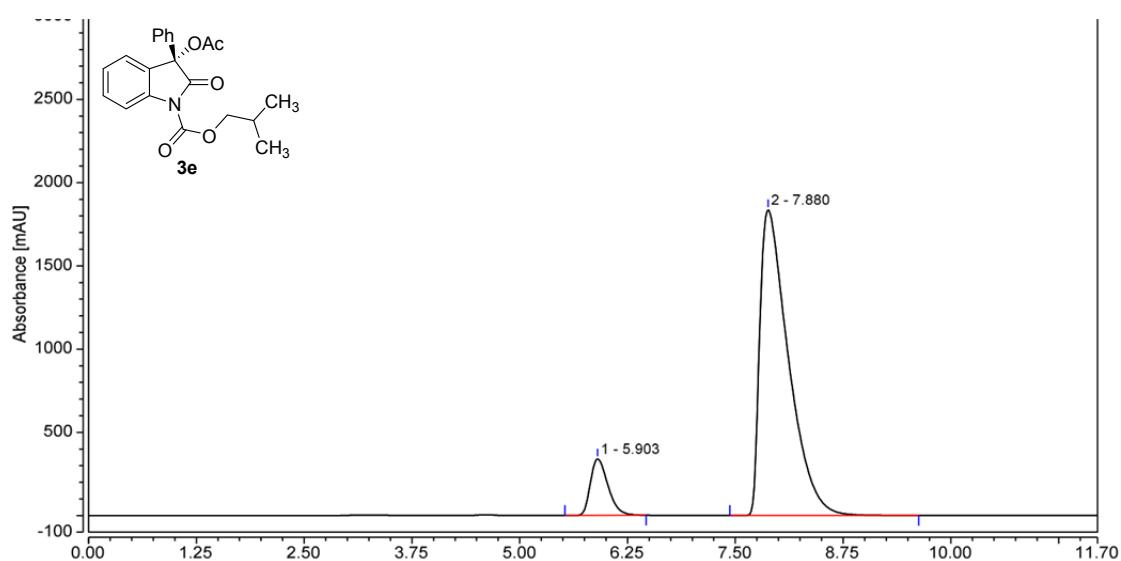
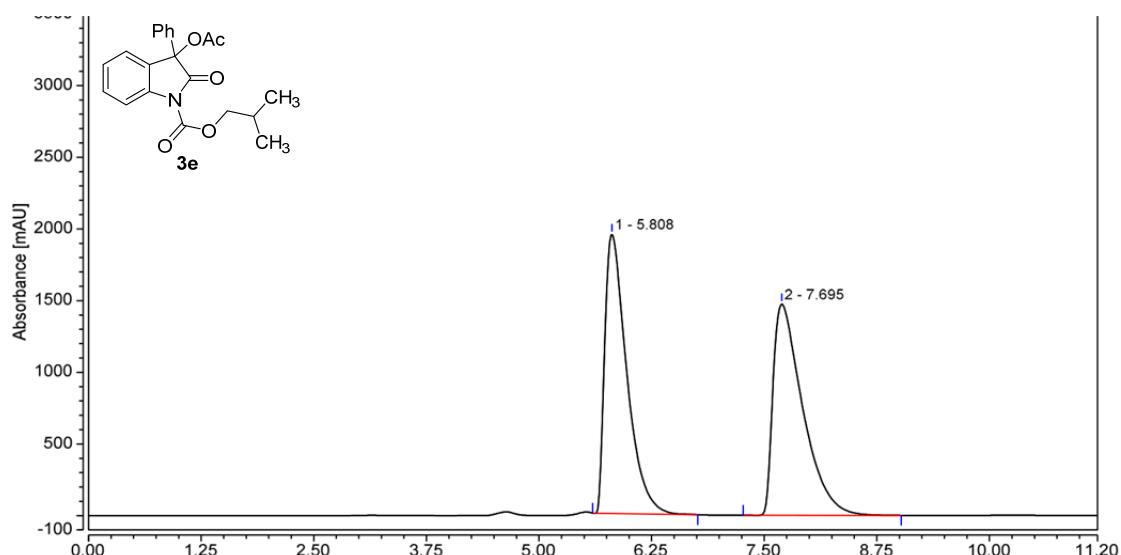


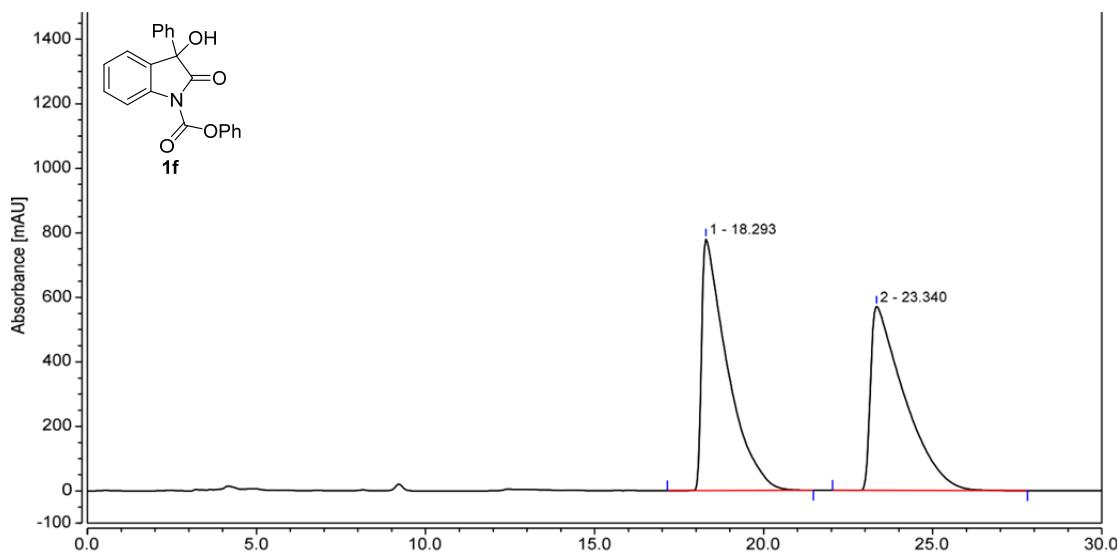


| Peak | Retention Time min | Area mAU*min | Height mAU | Area % | Height % |
|---------------|-----------------------|-----------------|-----------------|---------------|---------------|
| 1 | 8.953 | 296.429 | 983.672 | 49.97 | 57.05 |
| 2 | 10.820 | 296.827 | 740.481 | 50.03 | 42.95 |
| Total: | | 593.257 | 1724.153 | 100.00 | 100.00 |

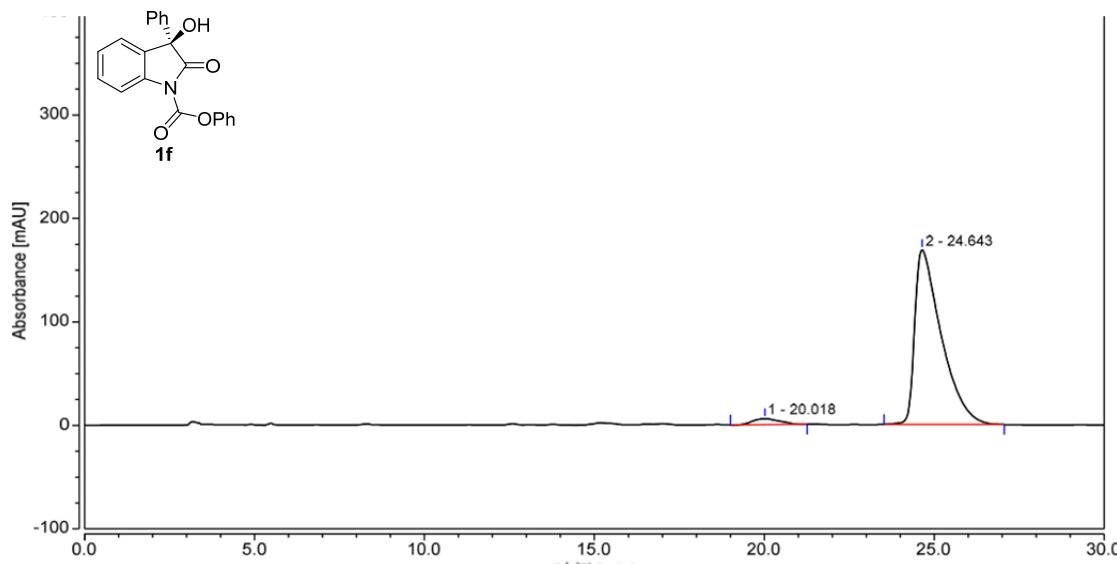


| Peak | Retention Time min | Area mAU*min | Height mAU | Area % | Height % |
|---------------|-----------------------|-----------------|-----------------|---------------|---------------|
| 1 | 8.992 | 343.786 | 1101.191 | 98.92 | 99.10 |
| 2 | 11.087 | 3.755 | 10.048 | 1.08 | 0.90 |
| Total: | | 347.541 | 1111.239 | 100.00 | 100.00 |

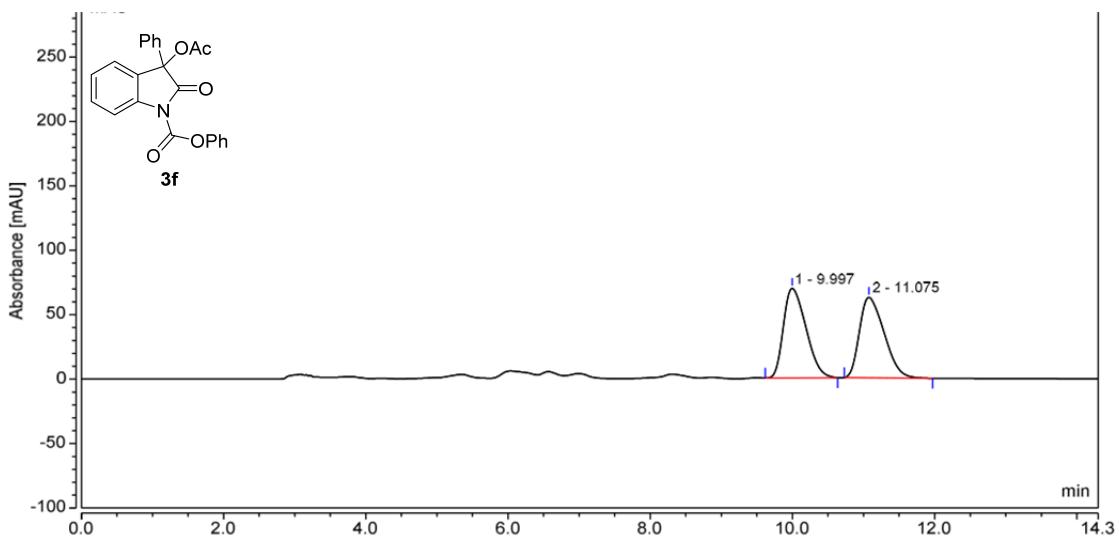




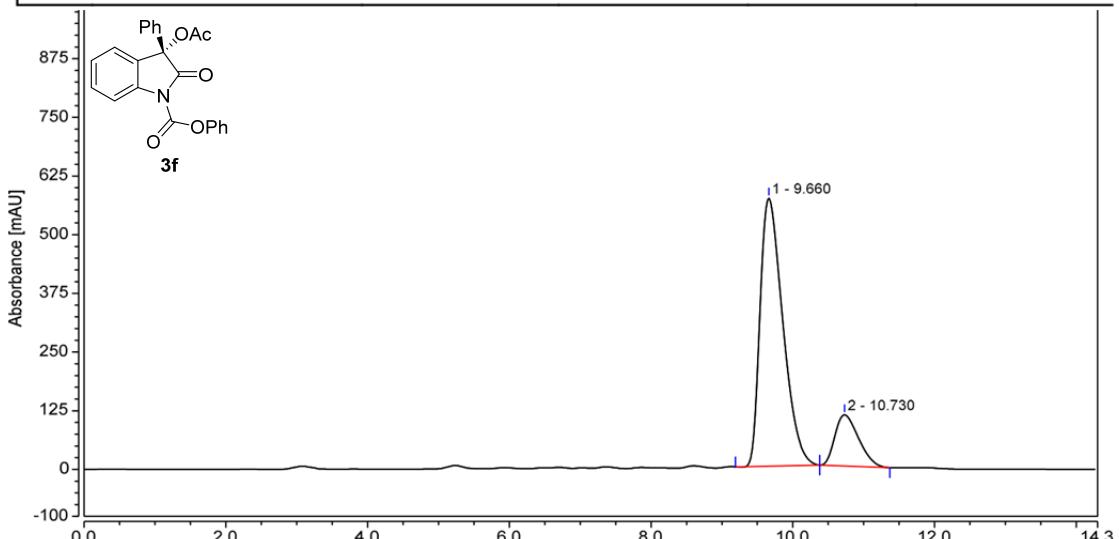
| Peak | Retention Time min | Area mAU*min | Height mAU | Area % | Height % |
|---------------|-----------------------|-----------------|-----------------|---------------|---------------|
| 1 | 18.293 | 687.033 | 779.896 | 50.94 | 57.76 |
| 2 | 23.340 | 661.615 | 570.361 | 49.06 | 42.24 |
| Total: | | 1348.648 | 1350.257 | 100.00 | 100.00 |



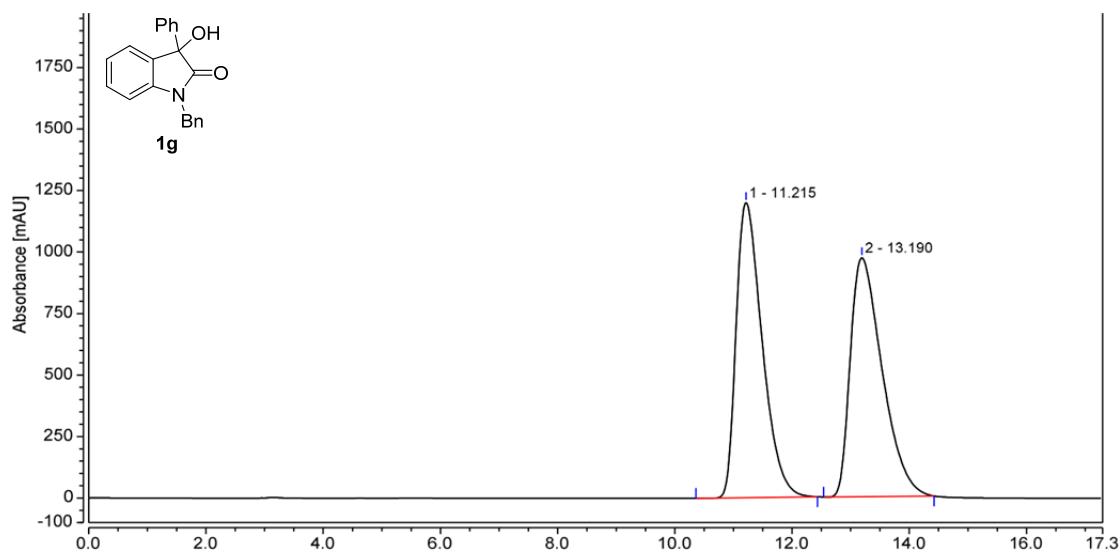
| Peak | Retention Time min | Area mAU*min | Height mAU | Area % | Height % |
|---------------|-----------------------|-----------------|----------------|---------------|---------------|
| 1 | 20.018 | 5.210 | 5.723 | 3.29 | 3.28 |
| 2 | 24.643 | 152.967 | 168.892 | 96.71 | 96.72 |
| Total: | | 158.177 | 174.615 | 100.00 | 100.00 |



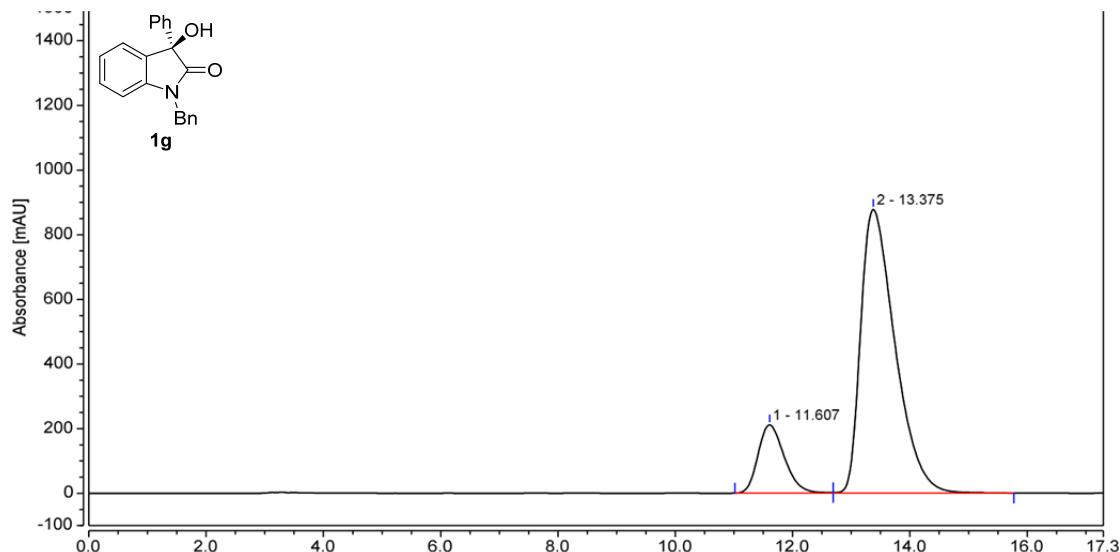
| Peak | Retention Time min | Area mAU*min | Height mAU | Area % | Height % |
|---------------|-----------------------|-----------------|----------------|---------------|---------------|
| 1 | 9.997 | 25.558 | 69.678 | 50.42 | 52.68 |
| 2 | 11.075 | 25.137 | 62.590 | 49.58 | 47.32 |
| Total: | | 50.695 | 132.267 | 100.00 | 100.00 |



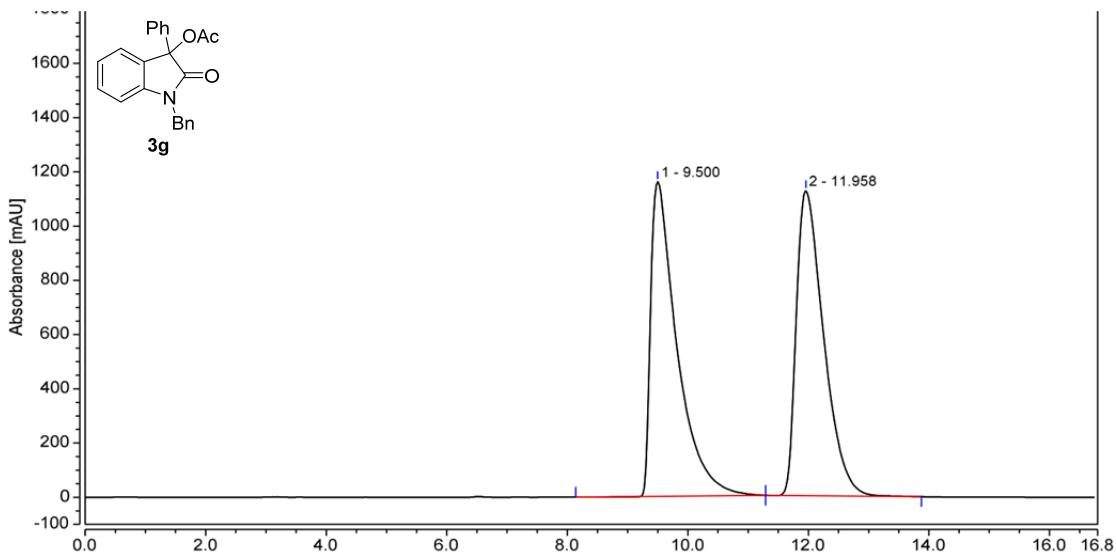
| Peak | Retention Time min | Area mAU*min | Height mAU | Area % | Height % |
|---------------|-----------------------|-----------------|----------------|---------------|---------------|
| 1 | 9.660 | 211.370 | 570.987 | 83.41 | 83.96 |
| 2 | 10.730 | 42.050 | 109.122 | 16.59 | 16.04 |
| Total: | | 253.420 | 680.108 | 100.00 | 100.00 |



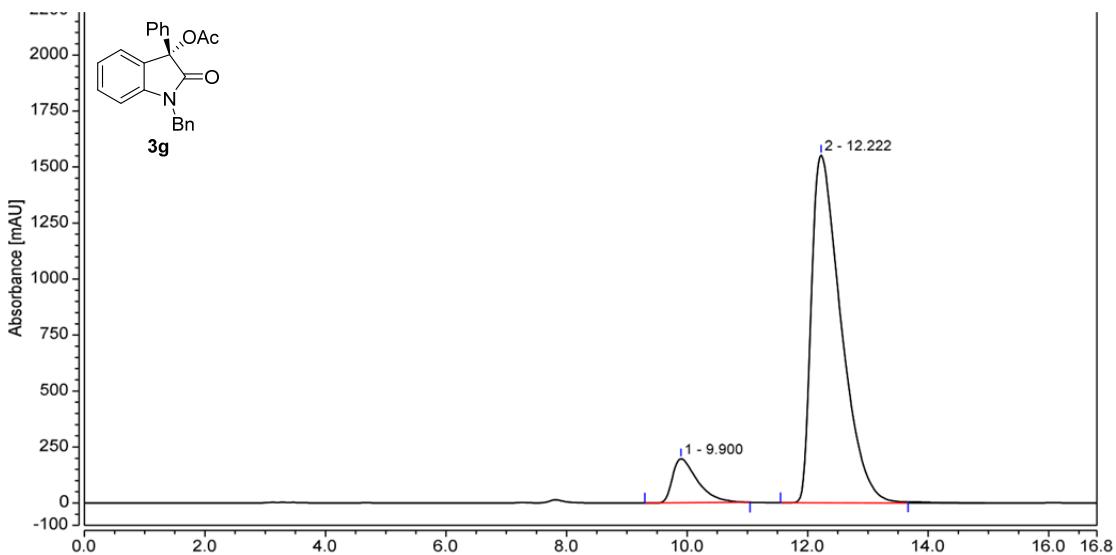
| Peak | Retention Time min | Area mAU*min | Height mAU | Area % | Height % |
|---------------|-----------------------|-----------------|-----------------|---------------|---------------|
| 1 | 11.215 | 617.849 | 1200.074 | 50.26 | 55.25 |
| 2 | 13.190 | 611.376 | 971.927 | 49.74 | 44.75 |
| Total: | | 1229.224 | 2172.001 | 100.00 | 100.00 |



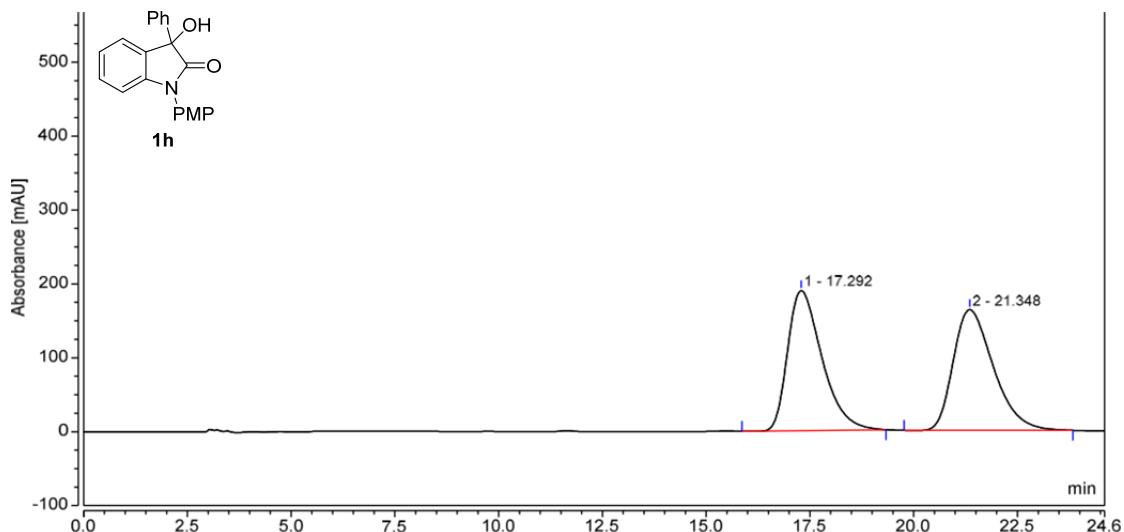
| Peak | Retention Time min | Area mAU*min | Height mAU | Area % | Height % |
|---------------|-----------------------|-----------------|-----------------|---------------|---------------|
| 1 | 11.607 | 109.626 | 211.150 | 15.57 | 19.39 |
| 2 | 13.375 | 594.595 | 877.820 | 84.43 | 80.61 |
| Total: | | 704.221 | 1088.970 | 100.00 | 100.00 |



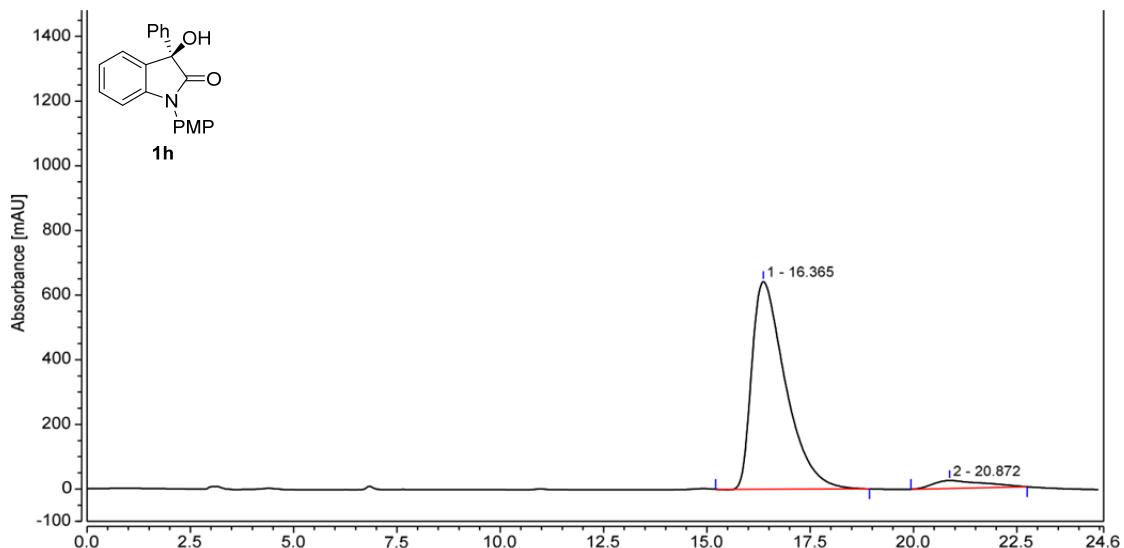
| Peak | Retention Time min | Area mAU*min | Height mAU | Area % | Height % |
|---------------|-----------------------|-----------------|-----------------|---------------|---------------|
| 1 | 9.500 | 585.020 | 1160.640 | 49.78 | 50.78 |
| 2 | 11.958 | 590.195 | 1124.835 | 50.22 | 49.22 |
| Total: | | 1175.215 | 2285.475 | 100.00 | 100.00 |



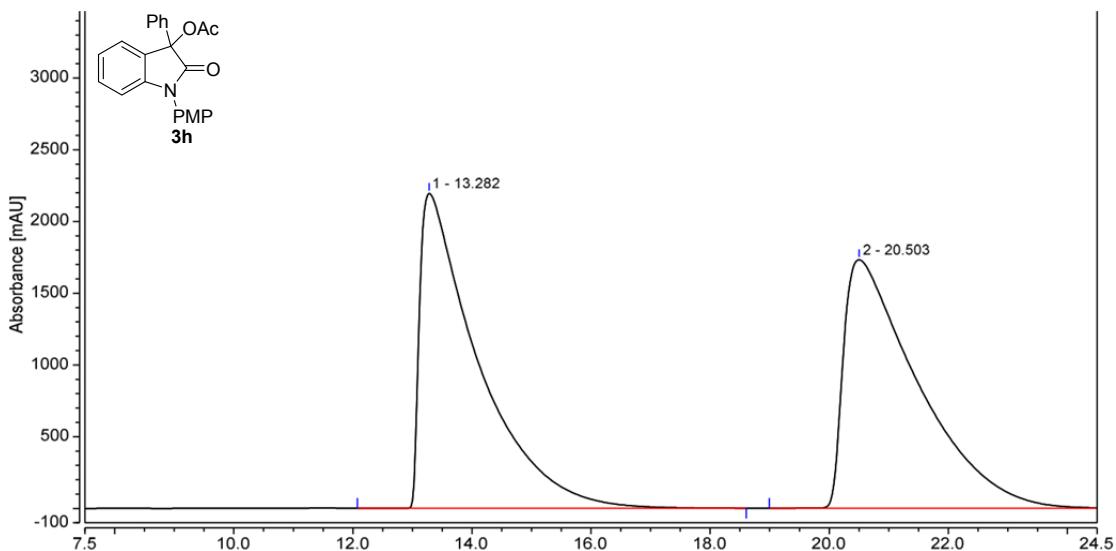
| Peak | Retention Time min | Area mAU*min | Height mAU | Area % | Height % |
|---------------|-----------------------|-----------------|-----------------|---------------|---------------|
| 1 | 9.900 | 94.648 | 196.486 | 9.70 | 11.24 |
| 2 | 12.222 | 881.278 | 1551.744 | 90.30 | 88.76 |
| Total: | | 975.926 | 1748.230 | 100.00 | 100.00 |



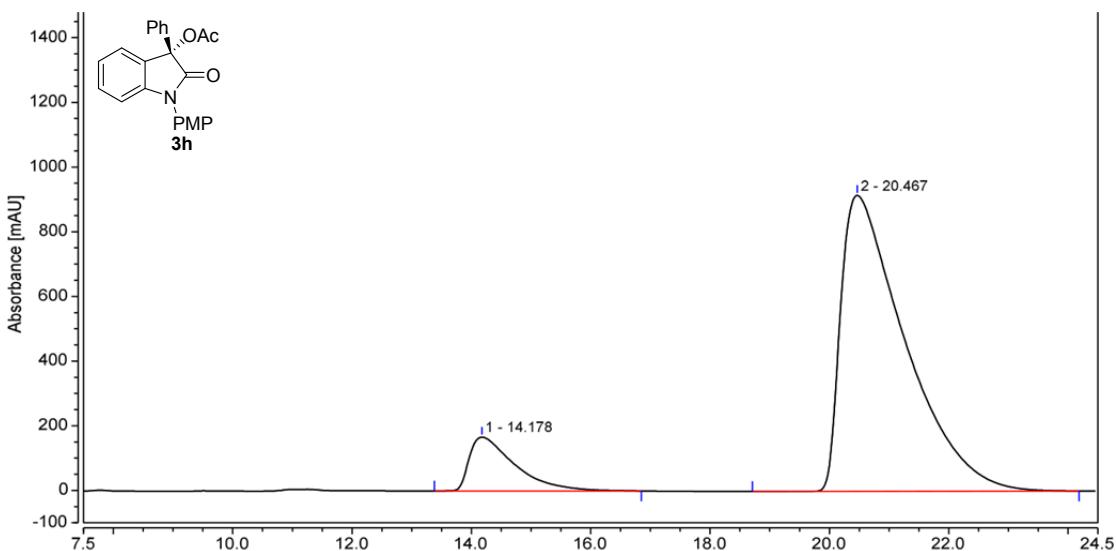
| Peak | Retention Time min | Area mAU*min | Height mAU | Area % | Height % |
|---------------|-----------------------|-----------------|----------------|---------------|---------------|
| 1 | 17.292 | 181.684 | 189.503 | 49.75 | 53.69 |
| 2 | 21.348 | 183.516 | 163.451 | 50.25 | 46.31 |
| Total: | | 365.200 | 352.954 | 100.00 | 100.00 |



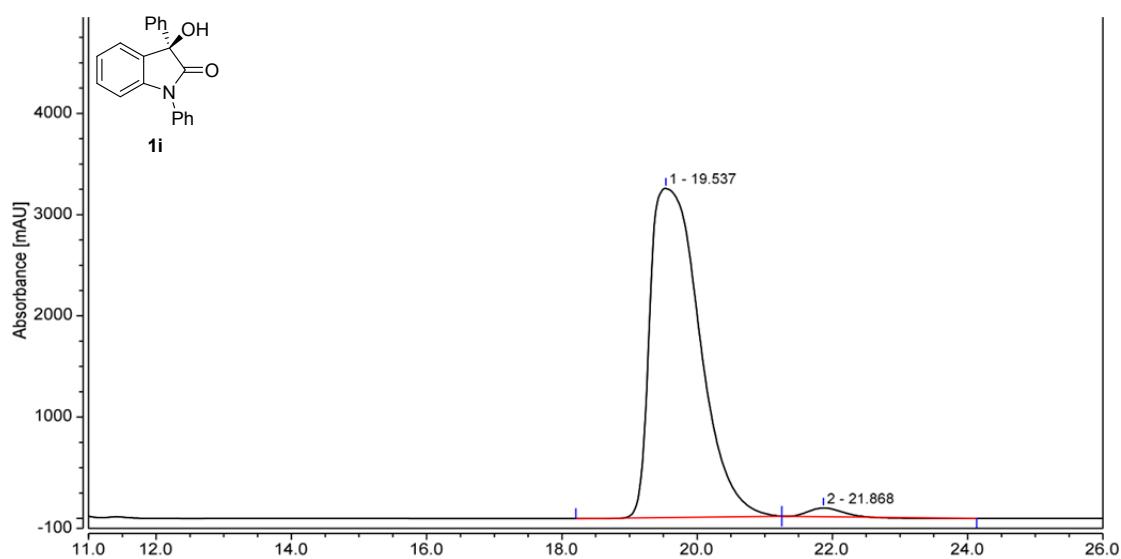
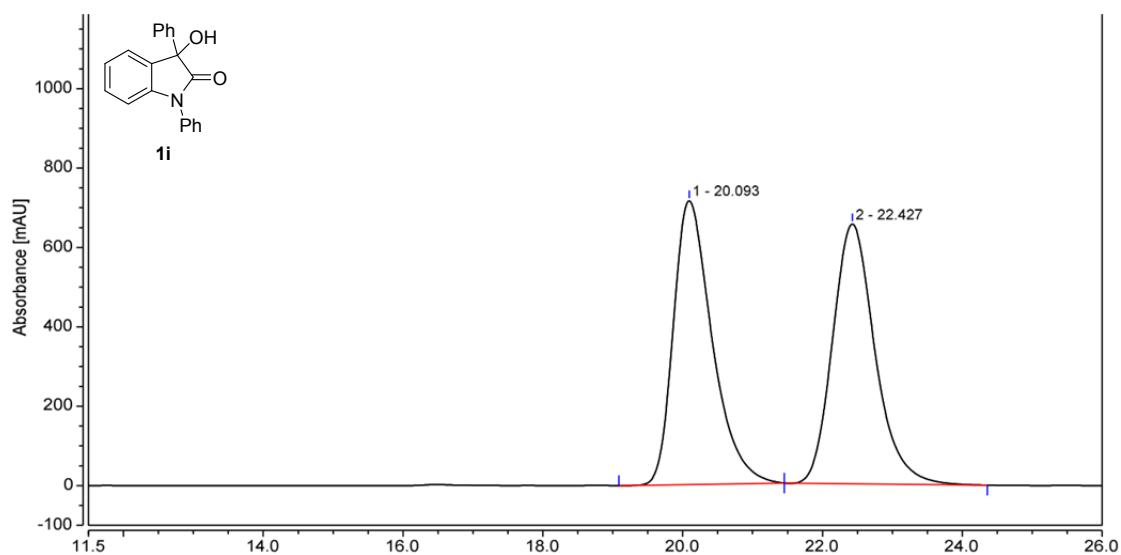
| Peak | Retention Time min | Area mAU*min | Height mAU | Area % | Height % |
|---------------|-----------------------|-----------------|----------------|---------------|---------------|
| 1 | 16.365 | 606.833 | 642.235 | 94.61 | 96.32 |
| 2 | 20.872 | 34.594 | 24.504 | 5.39 | 3.68 |
| Total: | | 641.428 | 666.738 | 100.00 | 100.00 |

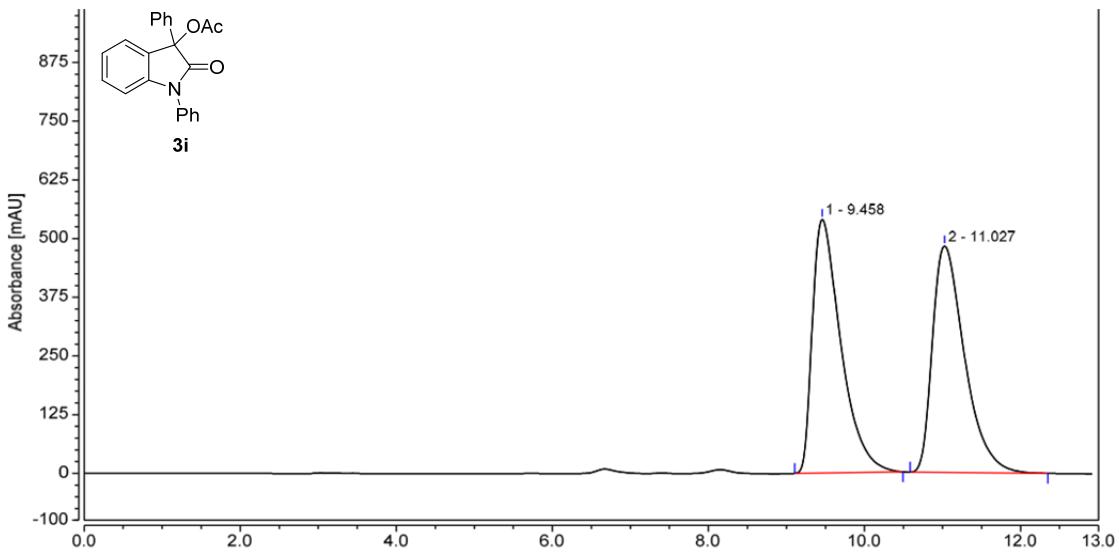


| Peak | Retention Time min | Area mAU·min | Height mAU | Area % | Height % |
|---------------|-----------------------|-----------------|-----------------|---------------|---------------|
| 1 | 13.282 | 2480.960 | 2196.143 | 49.82 | 55.90 |
| 2 | 20.503 | 2498.847 | 1732.723 | 50.18 | 44.10 |
| Total: | | 4979.808 | 3928.866 | 100.00 | 100.00 |

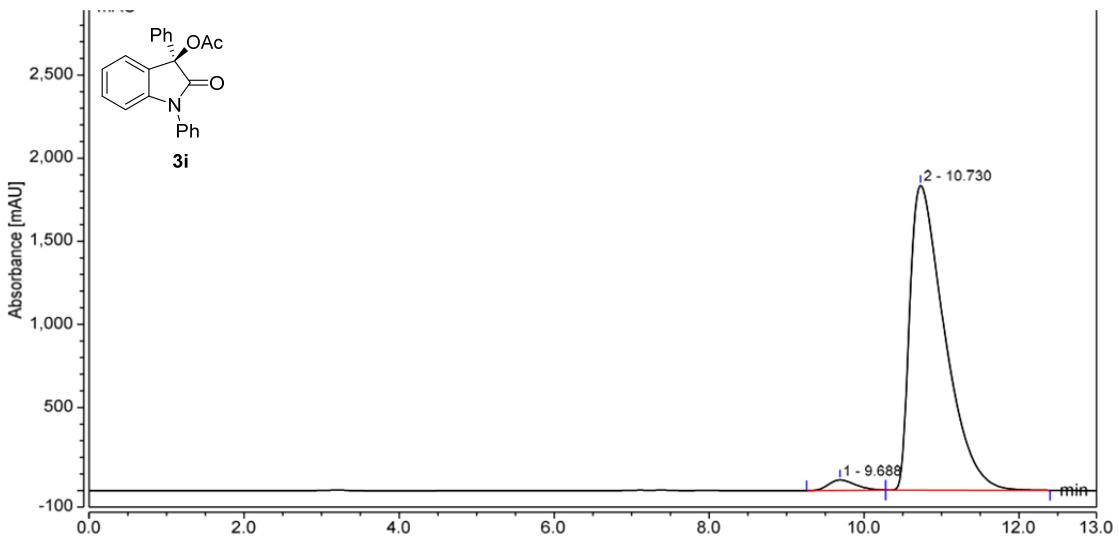


| Peak | Retention Time min | Area mAU·min | Height mAU | Area % | Height % |
|---------------|-----------------------|-----------------|-----------------|---------------|---------------|
| 1 | 14.178 | 147.339 | 166.540 | 11.45 | 15.40 |
| 2 | 20.467 | 1139.010 | 915.112 | 88.55 | 84.60 |
| Total: | | 1286.349 | 1081.652 | 100.00 | 100.00 |

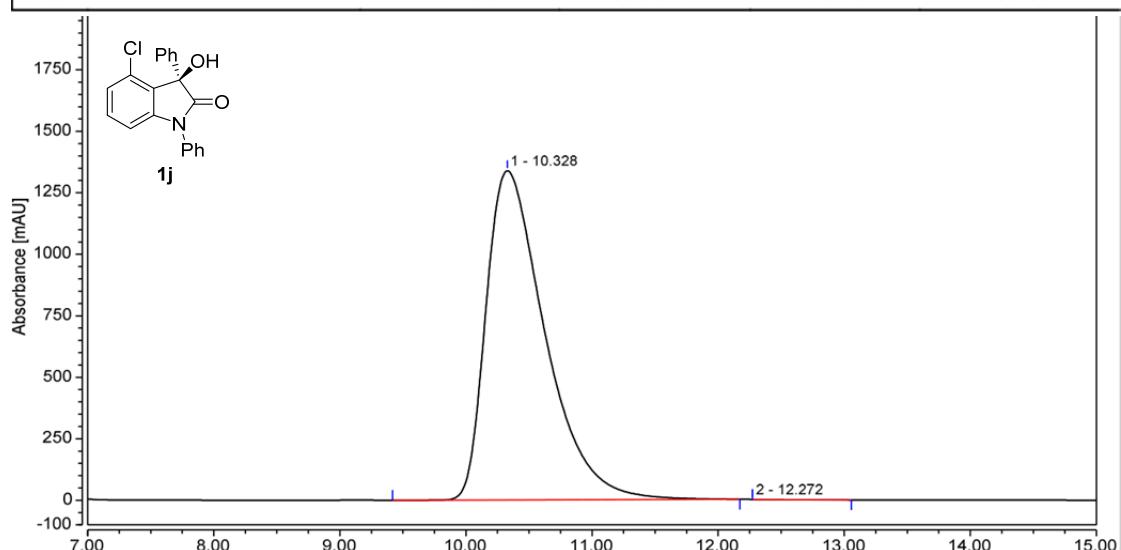
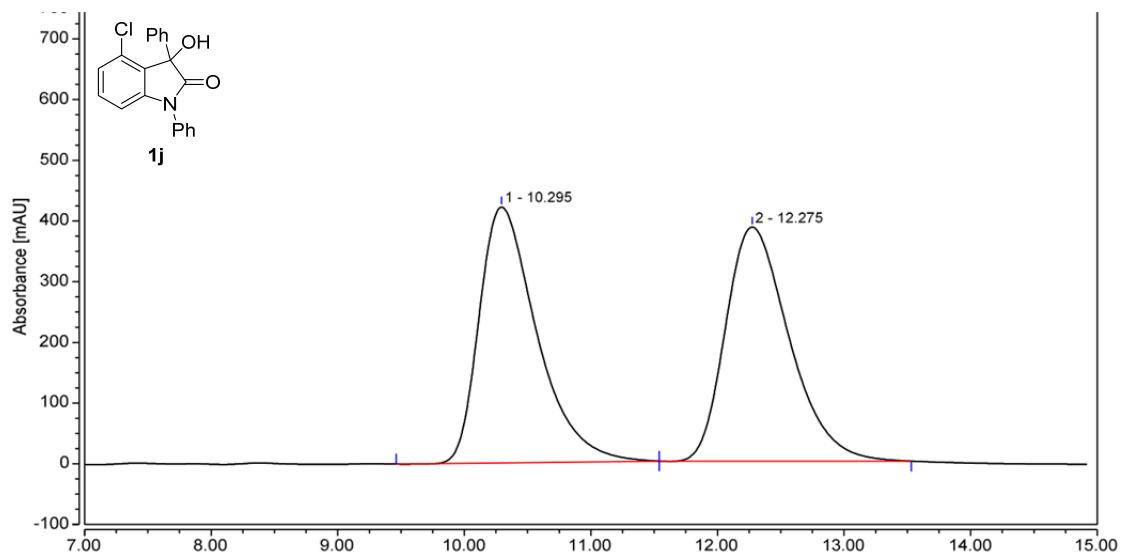


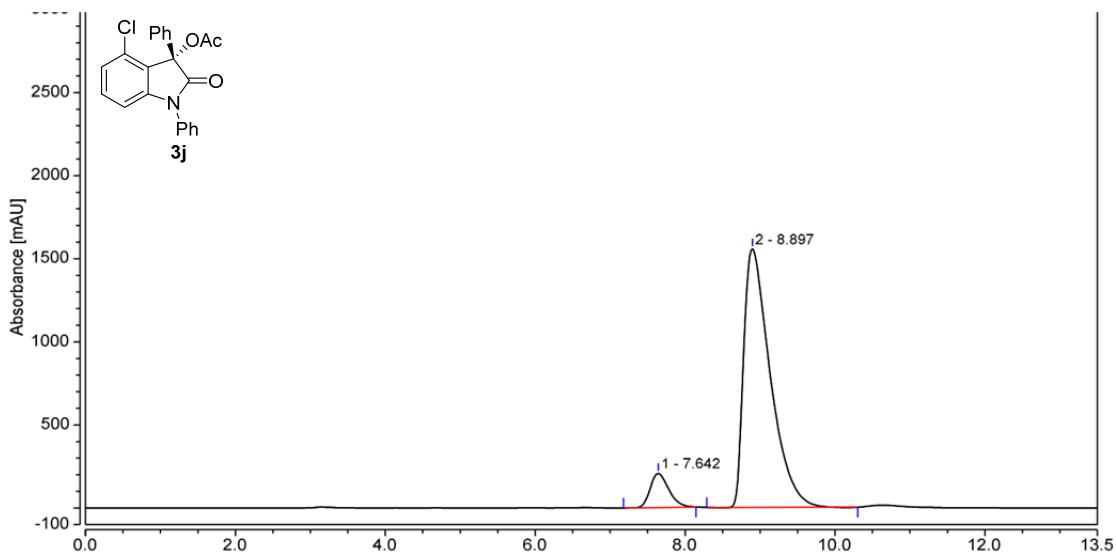
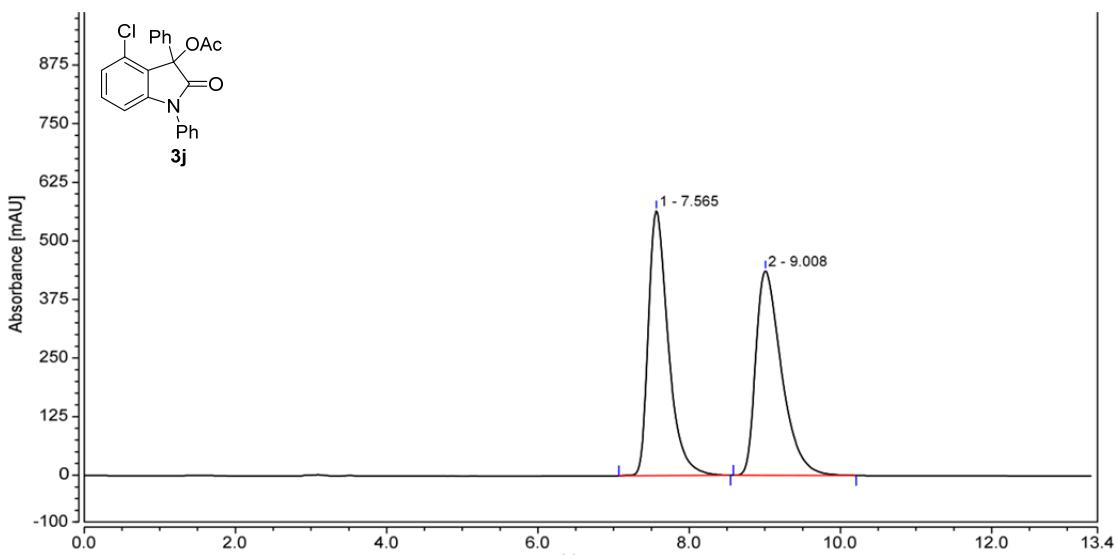


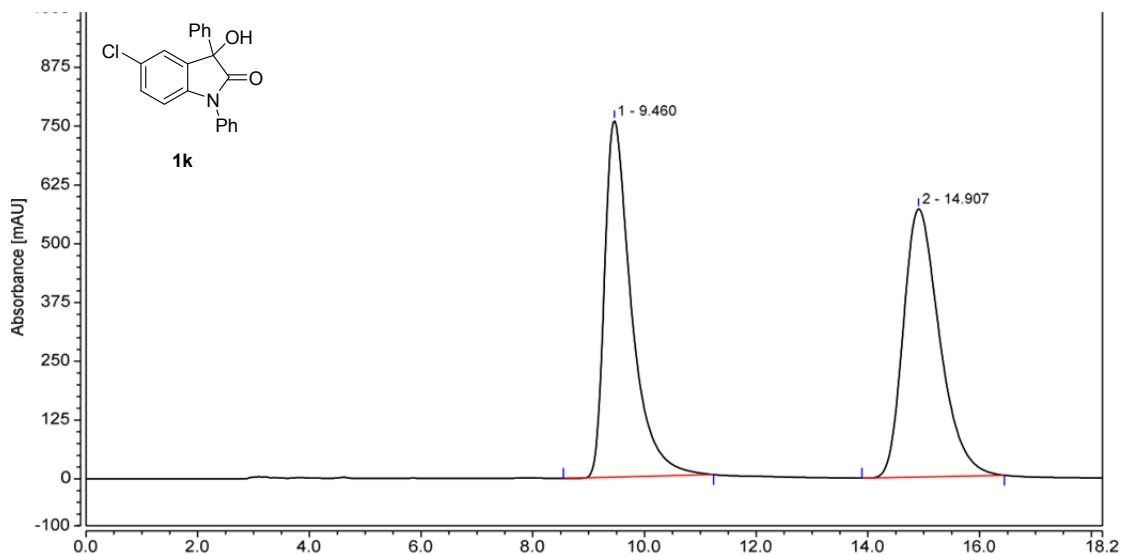
| Peak | Retention Time min | Area mAU*min | Height mAU | Area % | Height % |
|---------------|-----------------------|-----------------|-----------------|---------------|---------------|
| 1 | 9.458 | 228.468 | 540.519 | 49.85 | 52.83 |
| 2 | 11.027 | 229.859 | 482.641 | 50.15 | 47.17 |
| Total: | | 458.327 | 1023.159 | 100.00 | 100.00 |



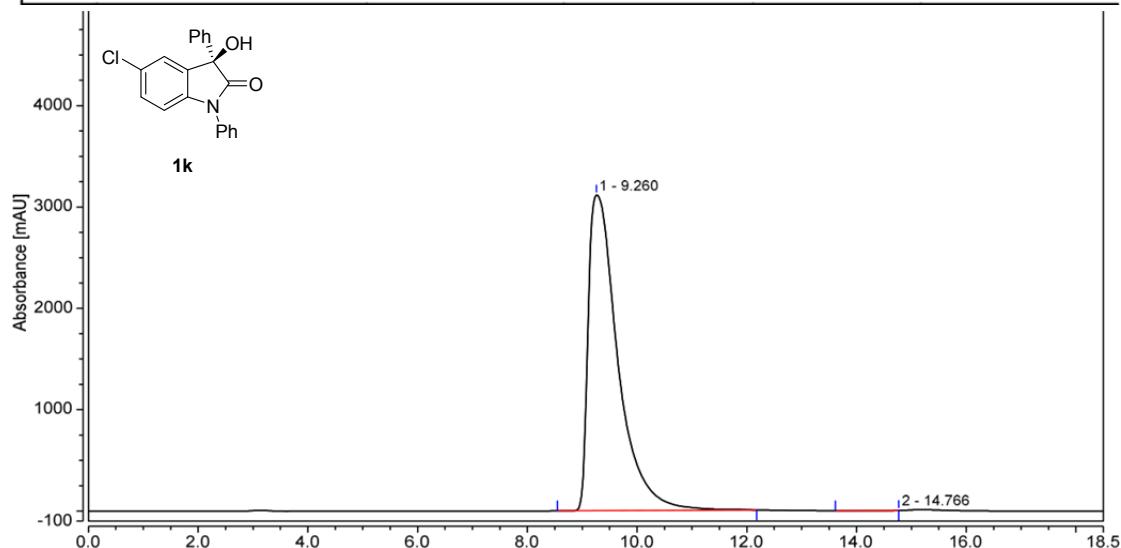
| Peak | Retention Time min | Area mAU*min | Height mAU | Area % | Height % |
|---------------|-----------------------|-----------------|-----------------|---------------|---------------|
| 1 | 9.688 | 25.080 | 62.982 | 2.57 | 3.32 |
| 2 | 10.730 | 952.170 | 1833.930 | 97.43 | 96.68 |
| Total: | | 977.250 | 1896.912 | 100.00 | 100.00 |



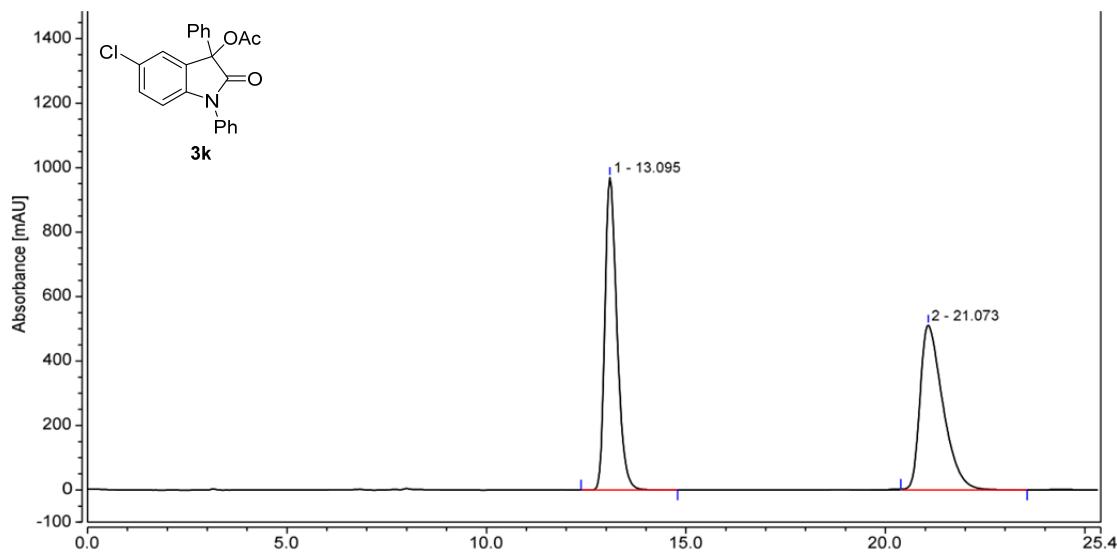




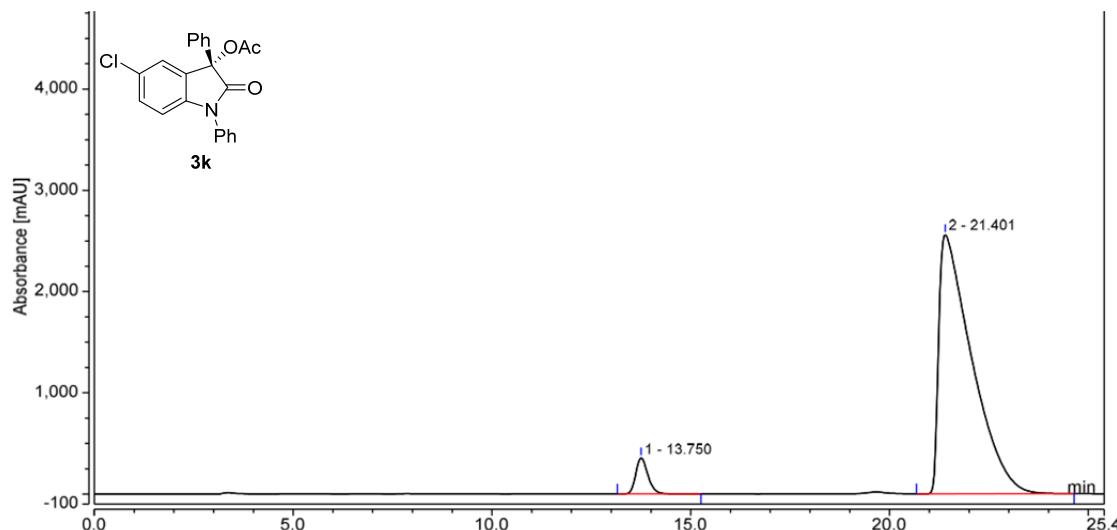
| Peak | Retention Time min | Area mAU*min | Height mAU | Area % | Height % |
|---------------|-----------------------|-----------------|-----------------|---------------|---------------|
| 1 | 9.460 | 421.957 | 758.342 | 49.62 | 57.07 |
| 2 | 14.907 | 428.341 | 570.402 | 50.38 | 42.93 |
| Total: | | 850.297 | 1328.744 | 100.00 | 100.00 |



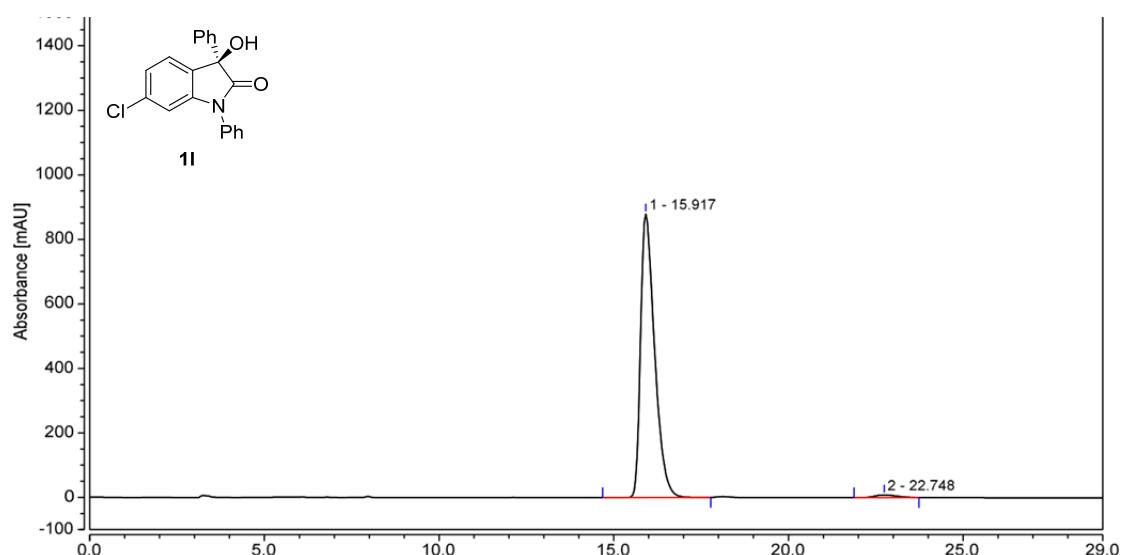
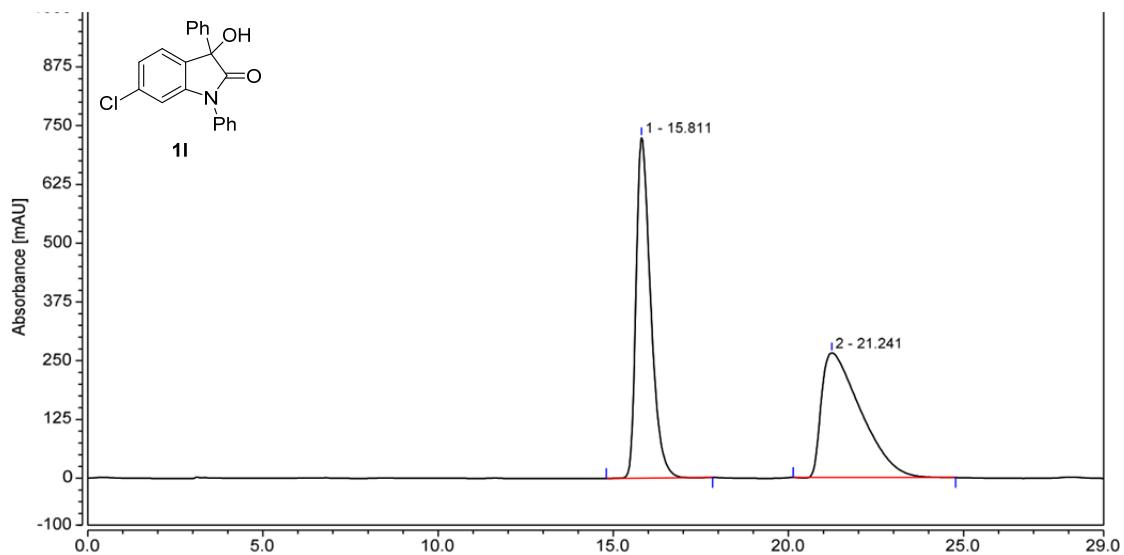
| Peak | Retention Time min | Area mAU*min | Height mAU | Area % | Height % |
|---------------|-----------------------|-----------------|-----------------|---------------|---------------|
| 1 | 9.260 | 1946.416 | 3115.453 | 99.91 | 100.00 |
| 2 | 14.766 | 1.741 | 0.000 | 0.09 | 0.00 |
| Total: | | 1948.157 | 3115.453 | 100.00 | 100.00 |

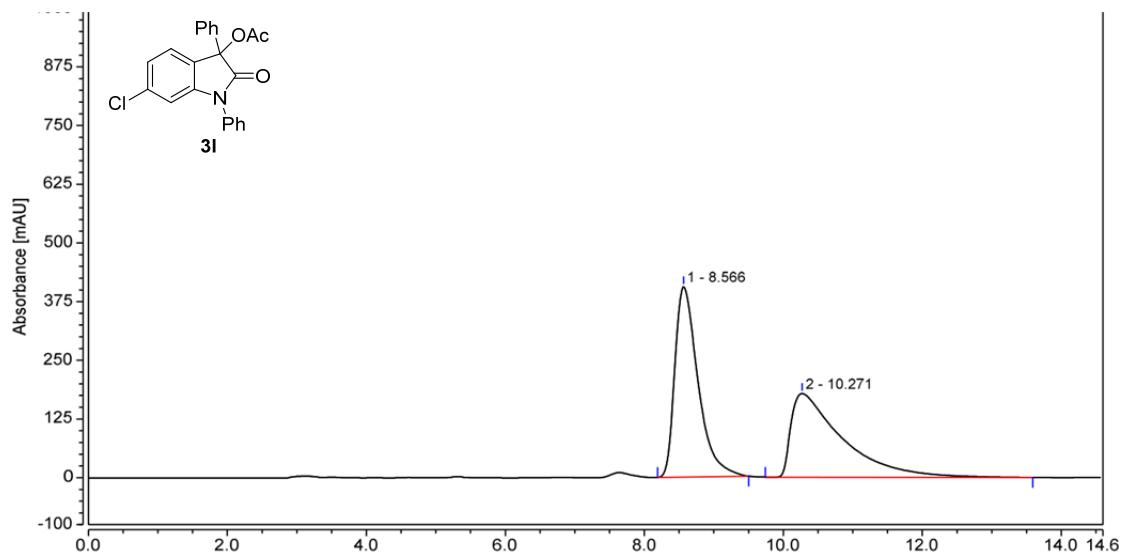


| Peak | Retention Time min | Area mAU*min | Height mAU | Area % | Height % |
|---------------|-----------------------|-----------------|-----------------|---------------|---------------|
| 1 | 13.095 | 340.235 | 969.987 | 49.92 | 65.46 |
| 2 | 21.073 | 341.284 | 511.740 | 50.08 | 34.54 |
| Total: | | 681.519 | 1481.727 | 100.00 | 100.00 |

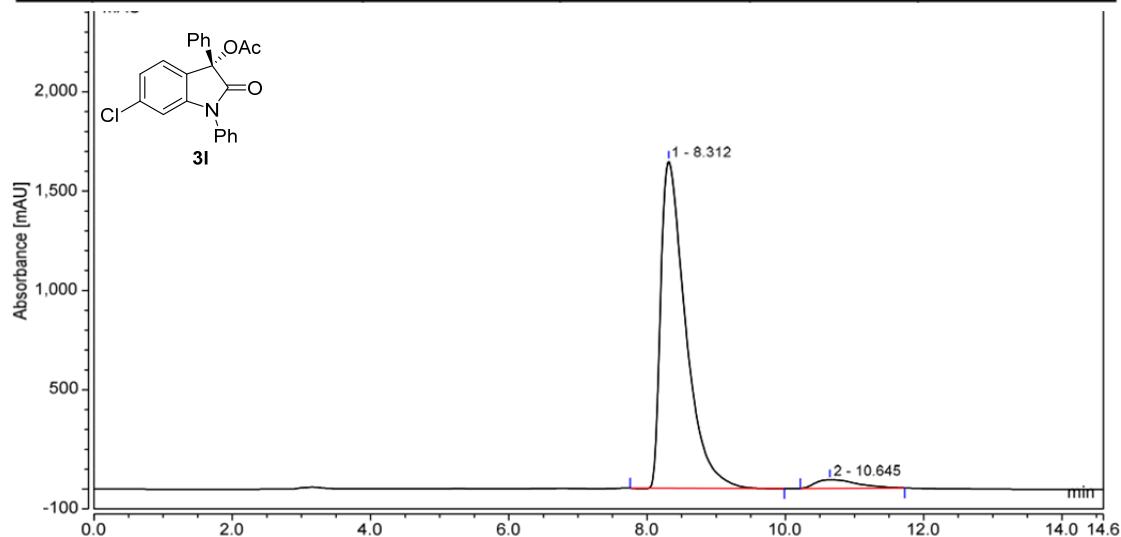


| Peak | Retention Time min | Area mAU*min | Height mAU | Area % | Height % |
|---------------|-----------------------|-----------------|-----------------|---------------|---------------|
| 1 | 13.750 | 126.641 | 356.108 | 4.89 | 12.21 |
| 2 | 21.401 | 2461.796 | 2560.402 | 95.11 | 87.79 |
| Total: | | 2588.437 | 2916.510 | 100.00 | 100.00 |

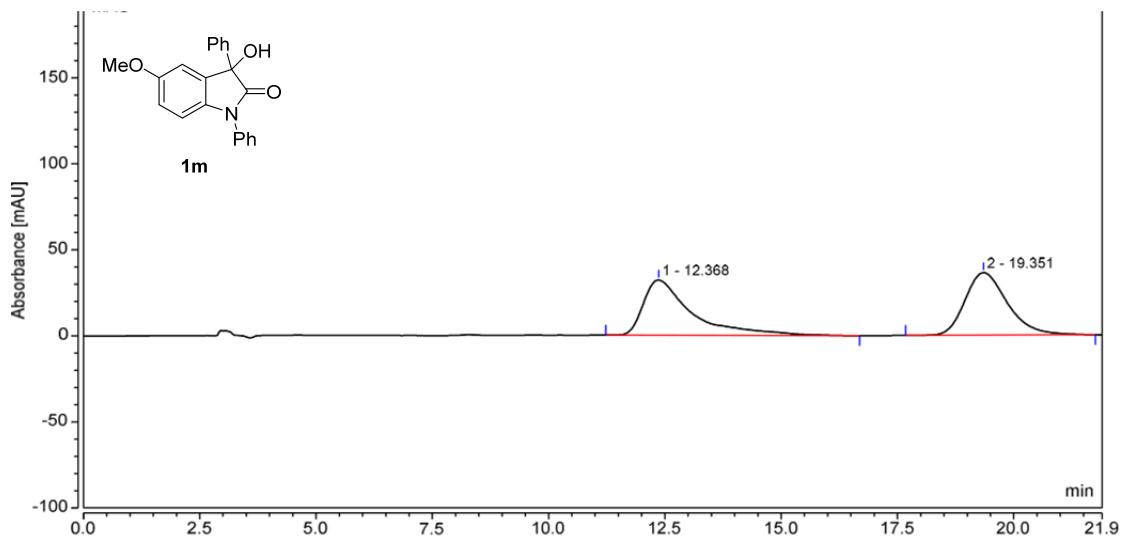




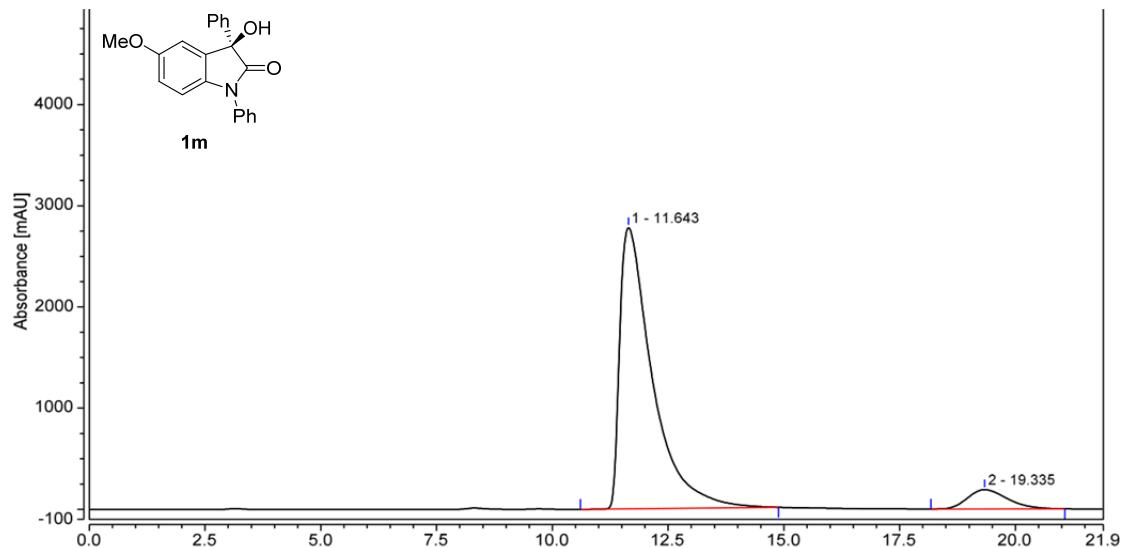
| Peak | Retention Time min | Area mAU*min | Height mAU | Area % | Height % |
|---------------|-----------------------|-----------------|----------------|---------------|---------------|
| 1 | 8.566 | 156.955 | 405.627 | 50.82 | 69.48 |
| 2 | 10.271 | 151.874 | 178.191 | 49.18 | 30.52 |
| Total: | | 308.829 | 583.818 | 100.00 | 100.00 |



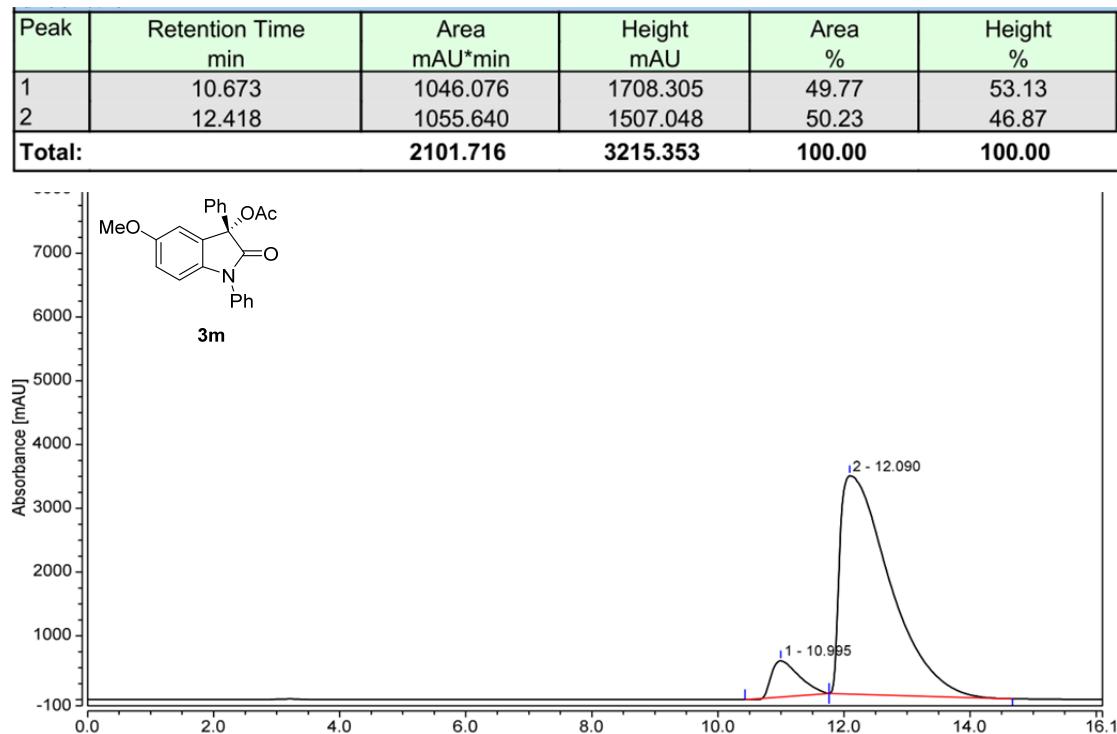
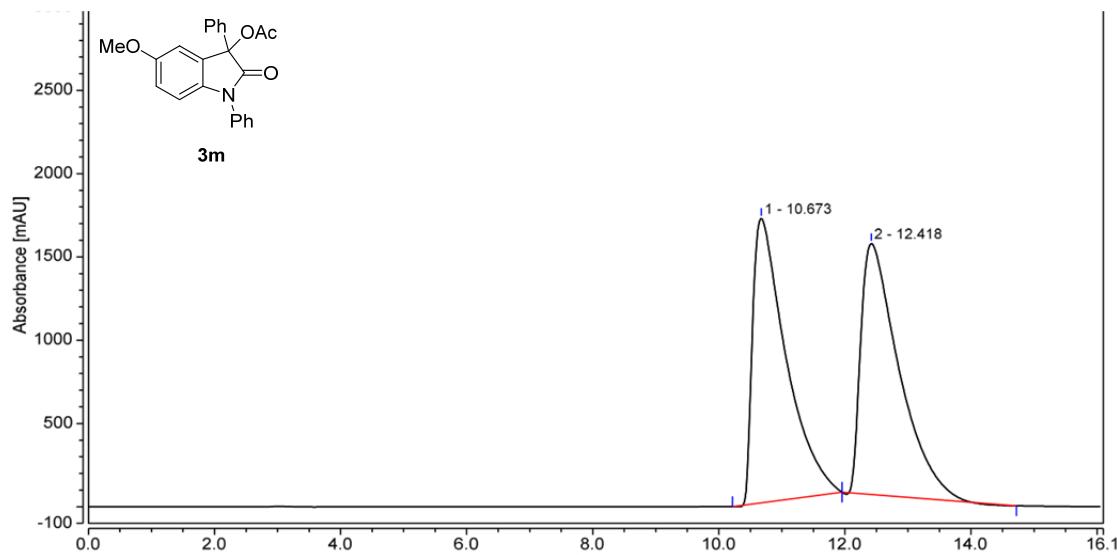
| Peak | Retention Time min | Area mAU*min | Height mAU | Area % | Height % |
|---------------|-----------------------|-----------------|-----------------|---------------|---------------|
| 1 | 8.312 | 685.666 | 1646.799 | 95.75 | 97.44 |
| 2 | 10.645 | 30.463 | 43.223 | 4.25 | 2.56 |
| Total: | | 716.129 | 1690.021 | 100.00 | 100.00 |

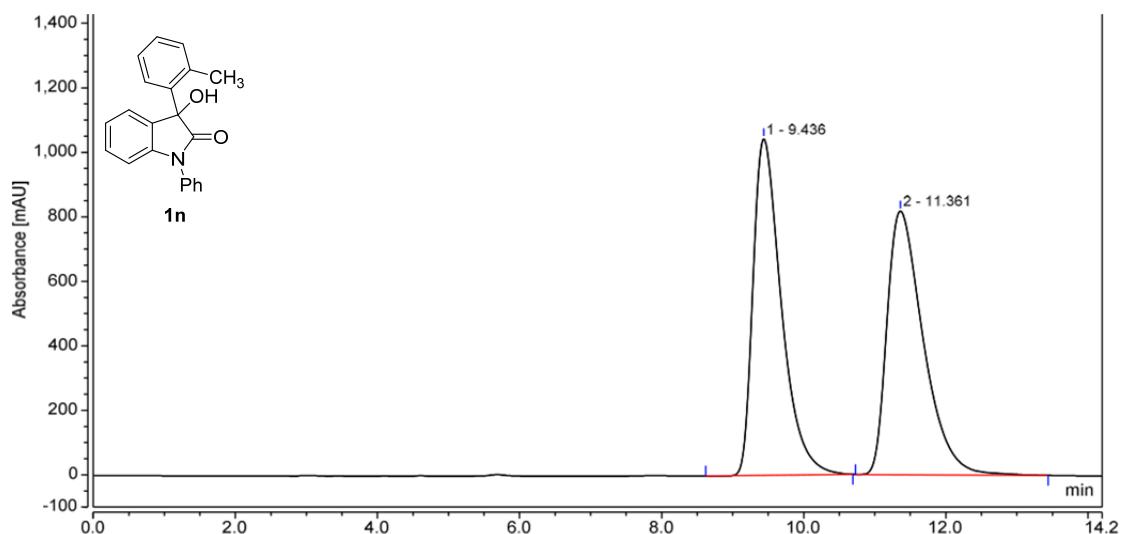


| Peak | Retention Time min | Area mAU*min | Height mAU | Area % | Height % |
|---------------|-----------------------|-----------------|---------------|---------------|---------------|
| 1 | 12.368 | 38.587 | 32.097 | 50.11 | 46.89 |
| 2 | 19.351 | 38.421 | 36.353 | 49.89 | 53.11 |
| Total: | | 77.008 | 68.450 | 100.00 | 100.00 |

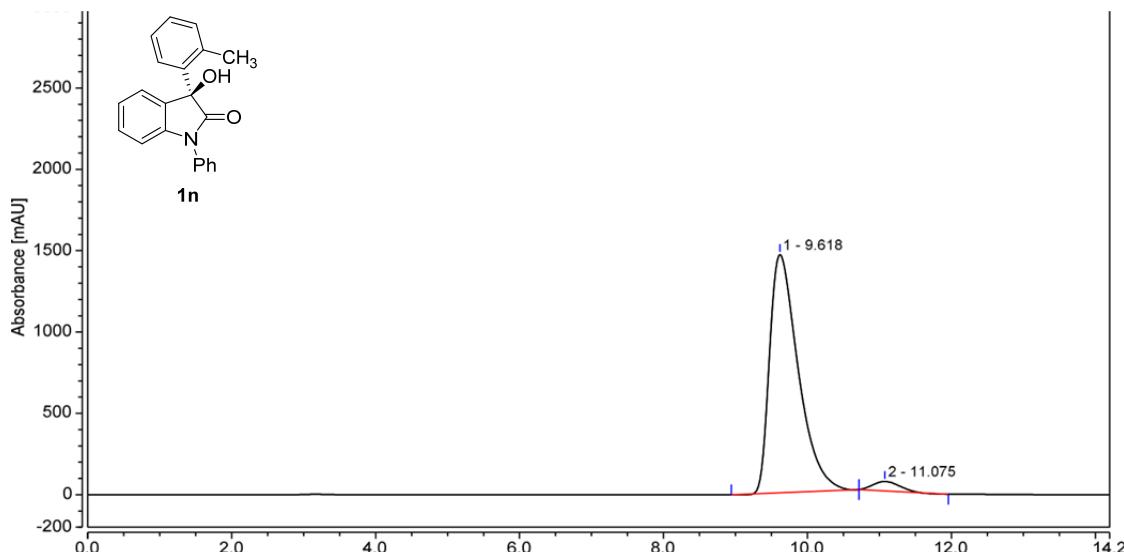


| Peak | Retention Time min | Area mAU*min | Height mAU | Area % | Height % |
|---------------|-----------------------|-----------------|-----------------|---------------|---------------|
| 1 | 11.643 | 2264.839 | 2779.093 | 92.23 | 93.59 |
| 2 | 19.335 | 190.734 | 190.376 | 7.77 | 6.41 |
| Total: | | 2455.572 | 2969.469 | 100.00 | 100.00 |

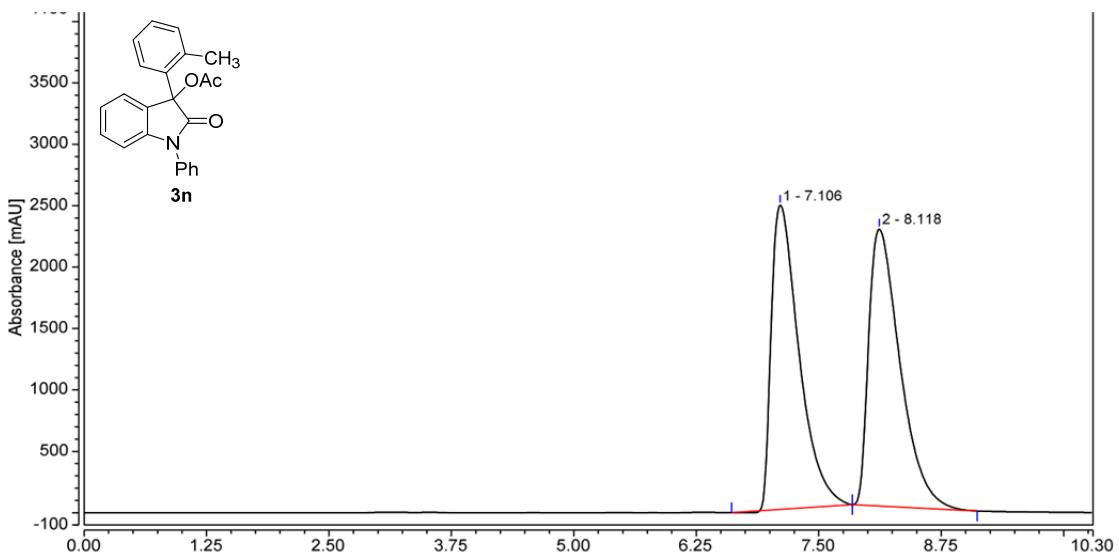




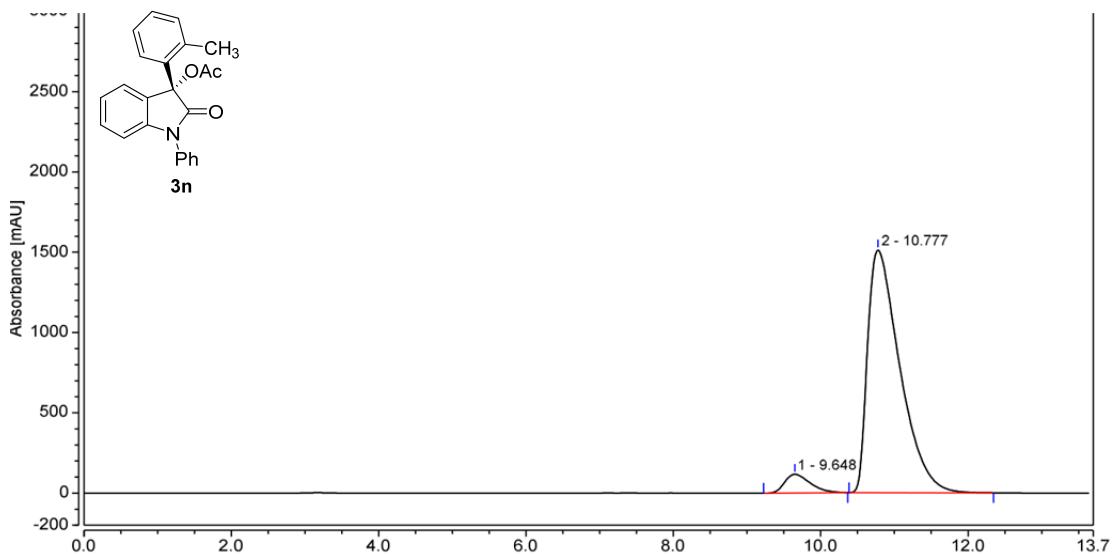
| Peak | Retention Time min | Area mAU*min | Height mAU | Area % | Height % |
|---------------|-----------------------|-----------------|-----------------|---------------|---------------|
| 1 | 9.436 | 481.013 | 1043.921 | 49.92 | 56.07 |
| 2 | 11.361 | 482.560 | 817.886 | 50.08 | 43.93 |
| Total: | | 963.573 | 1861.806 | 100.00 | 100.00 |



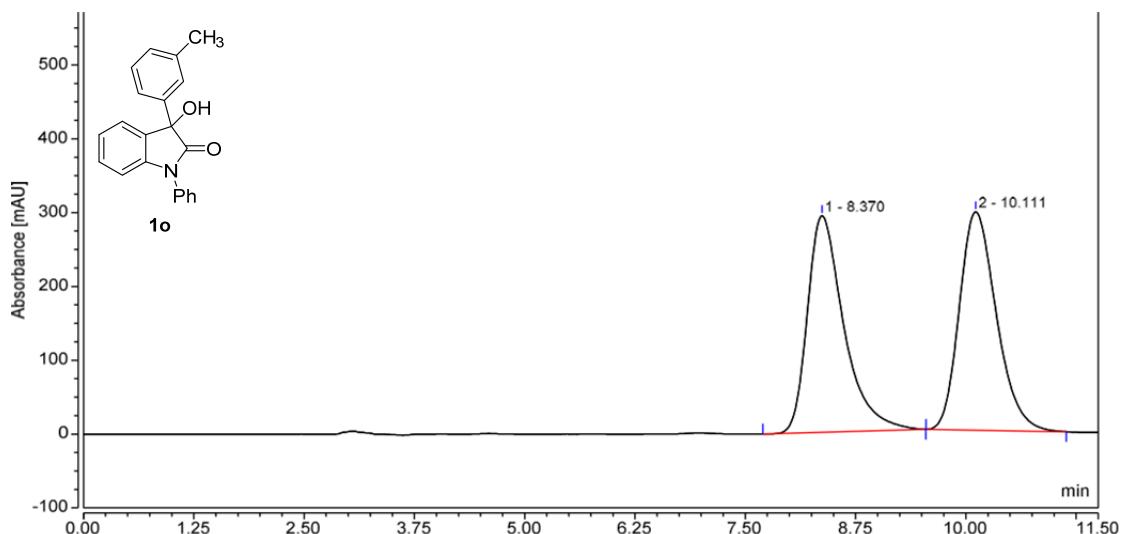
| Peak | Retention Time min | Area mAU*min | Height mAU | Area % | Height % |
|---------------|-----------------------|-----------------|-----------------|---------------|---------------|
| 1 | 9.618 | 675.626 | 1464.420 | 96.50 | 96.21 |
| 2 | 11.075 | 24.485 | 57.664 | 3.50 | 3.79 |
| Total: | | 700.110 | 1522.084 | 100.00 | 100.00 |



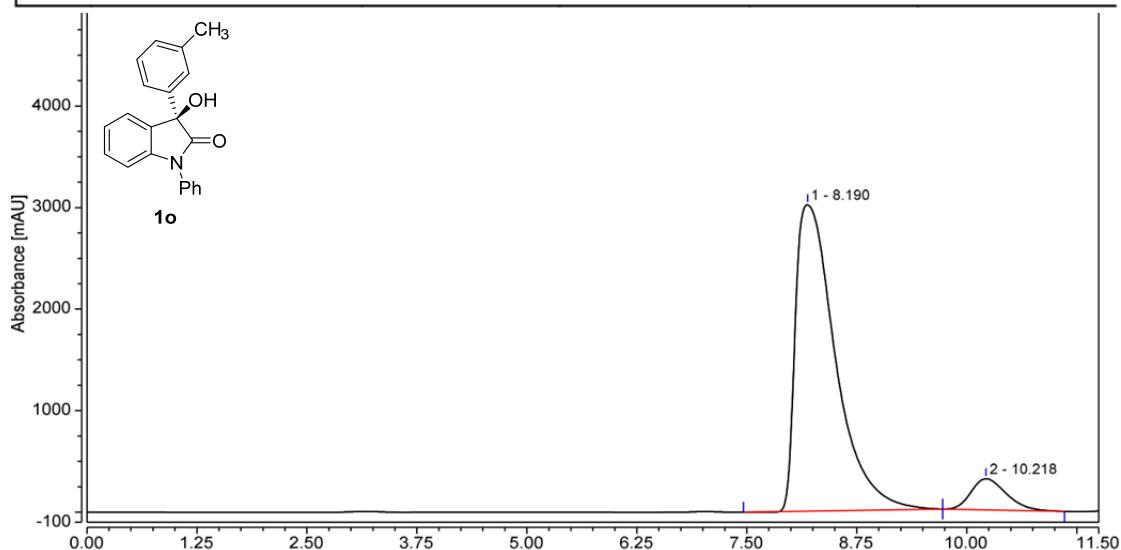
| Peak | Retention Time min | Area mAU*min | Height mAU | Area % | Height % |
|---------------|-----------------------|-----------------|-----------------|---------------|---------------|
| 1 | 7.106 | 811.778 | 2477.399 | 49.25 | 52.34 |
| 2 | 8.118 | 836.548 | 2256.315 | 50.75 | 47.66 |
| Total: | | 1648.326 | 4733.714 | 100.00 | 100.00 |



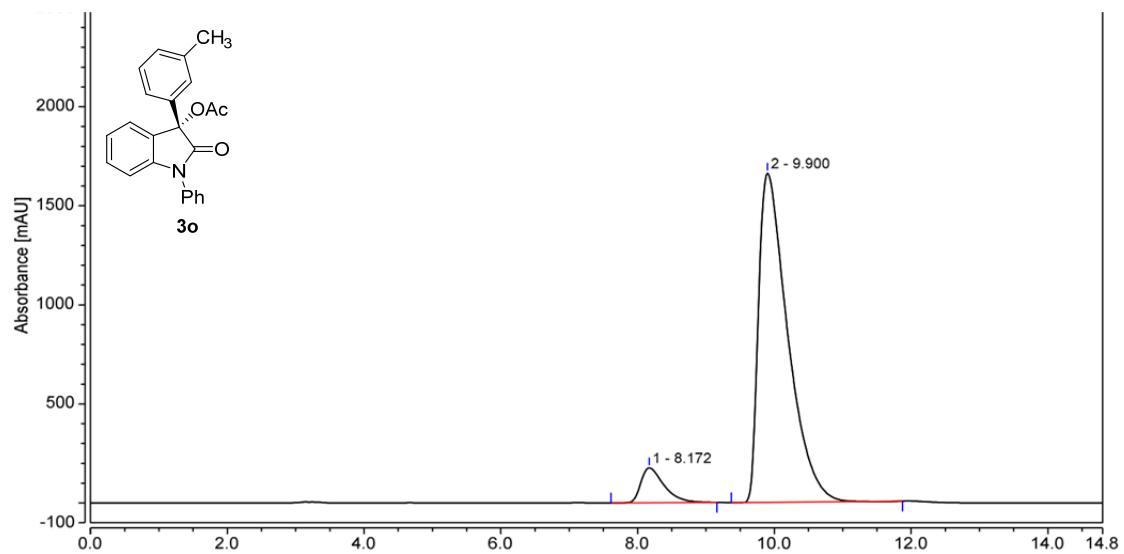
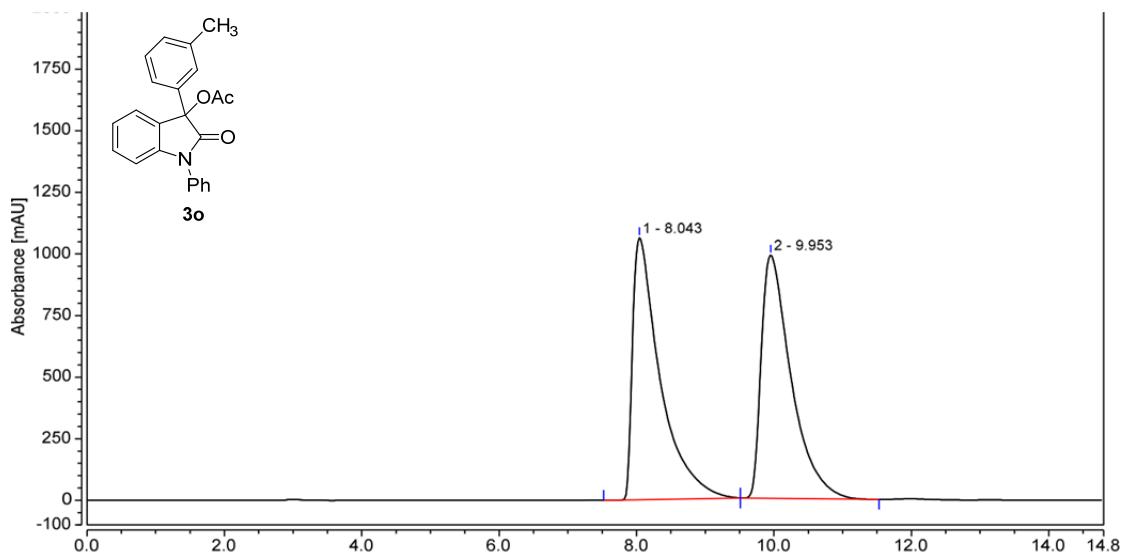
| Peak | Retention Time min | Area mAU*min | Height mAU | Area % | Height % |
|---------------|-----------------------|-----------------|-----------------|---------------|---------------|
| 1 | 9.648 | 47.066 | 116.723 | 5.79 | 7.17 |
| 2 | 10.777 | 765.358 | 1511.770 | 94.21 | 92.83 |
| Total: | | 812.425 | 1628.493 | 100.00 | 100.00 |

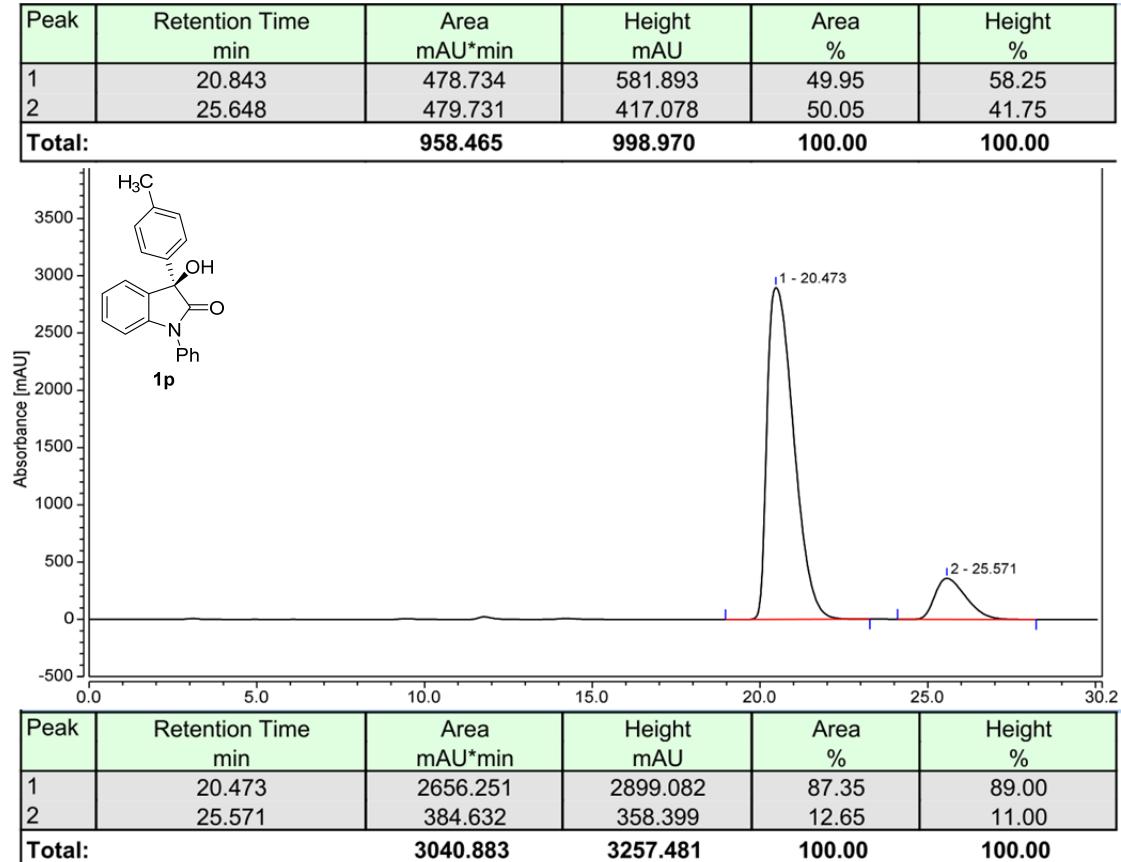
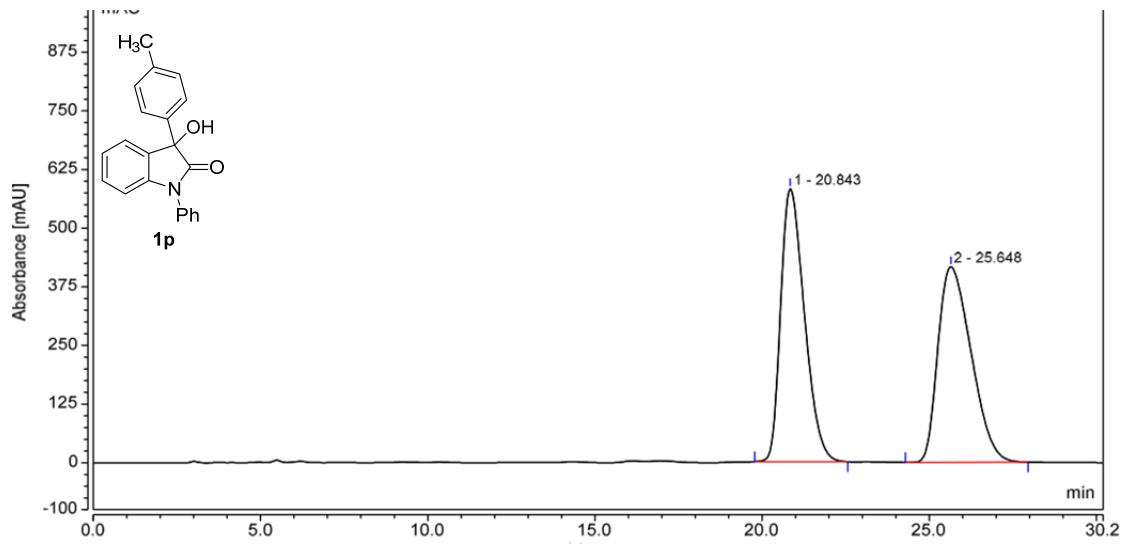


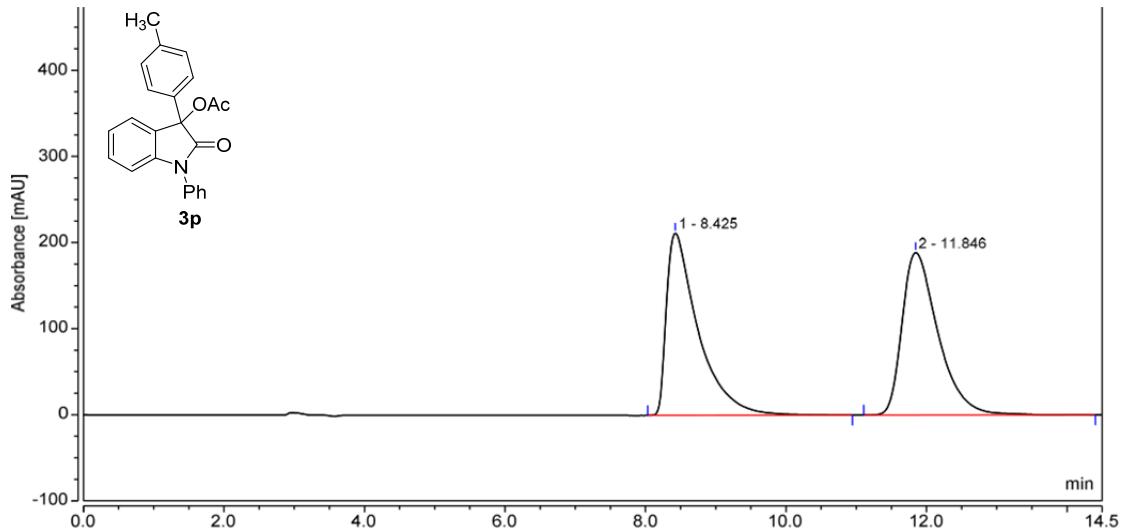
| Peak | Retention Time min | Area mAU*min | Height mAU | Area % | Height % |
|---------------|-----------------------|-----------------|----------------|---------------|---------------|
| 1 | 8.370 | 140.262 | 293.578 | 49.35 | 49.80 |
| 2 | 10.111 | 143.930 | 295.905 | 50.65 | 50.20 |
| Total: | | 284.191 | 589.483 | 100.00 | 100.00 |



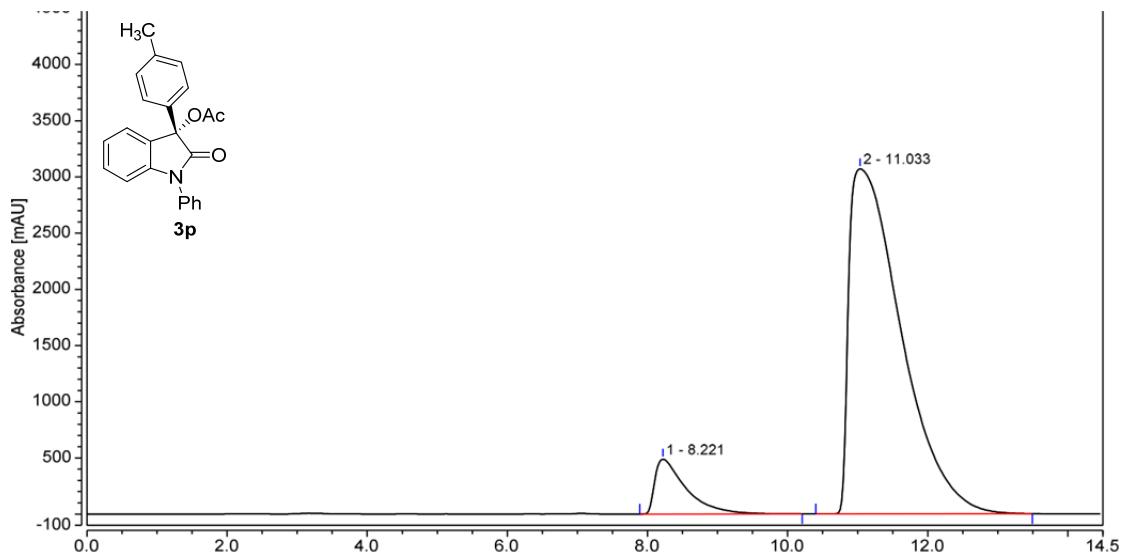
| Peak | Retention Time min | Area mAU*min | Height mAU | Area % | Height % |
|---------------|-----------------------|-----------------|-----------------|---------------|---------------|
| 1 | 8.190 | 1587.177 | 3020.418 | 91.74 | 90.78 |
| 2 | 10.218 | 142.861 | 306.935 | 8.26 | 9.22 |
| Total: | | 1730.038 | 3327.353 | 100.00 | 100.00 |



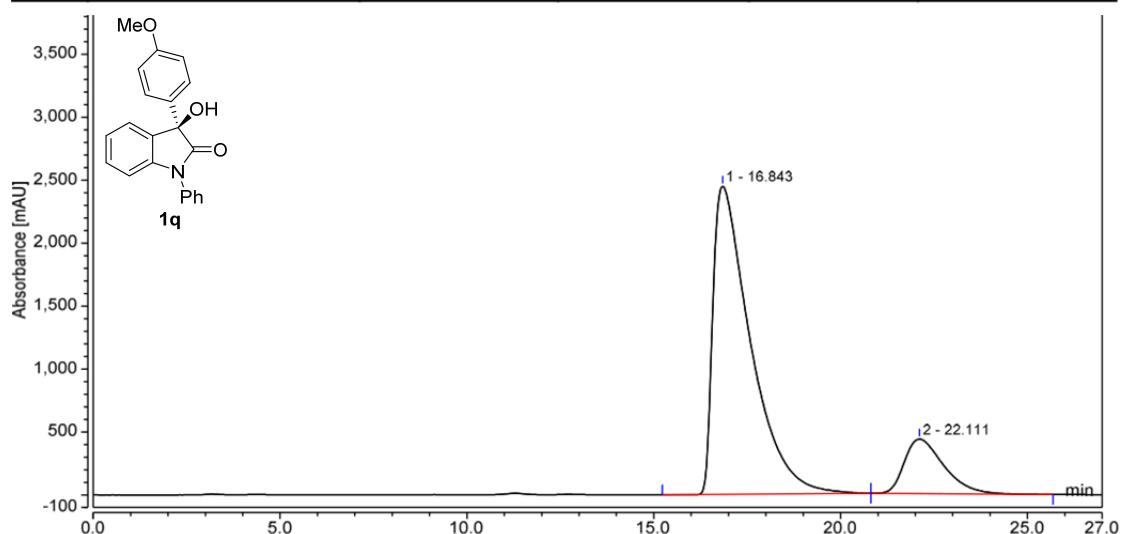
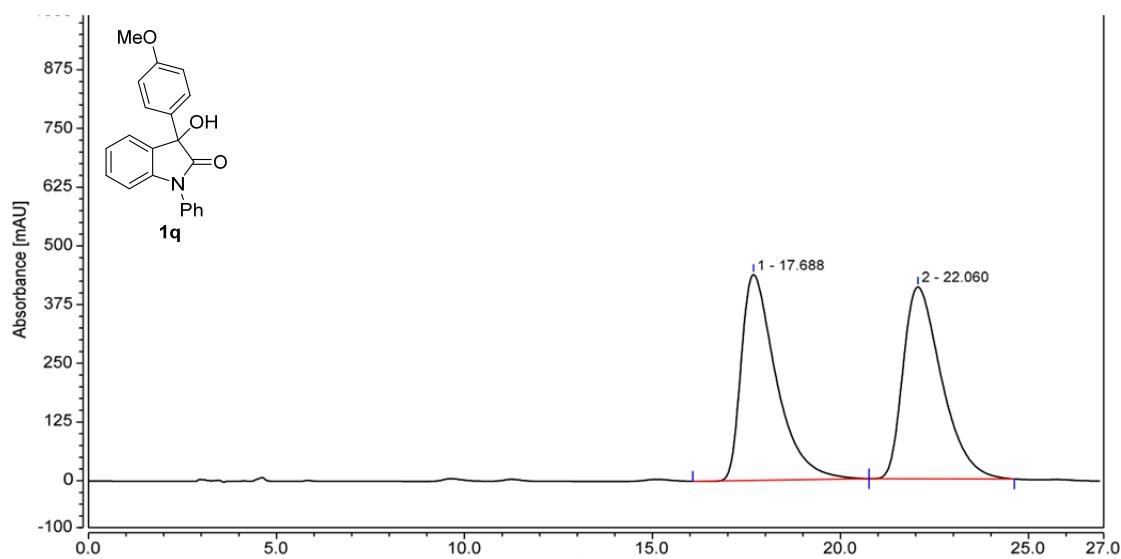


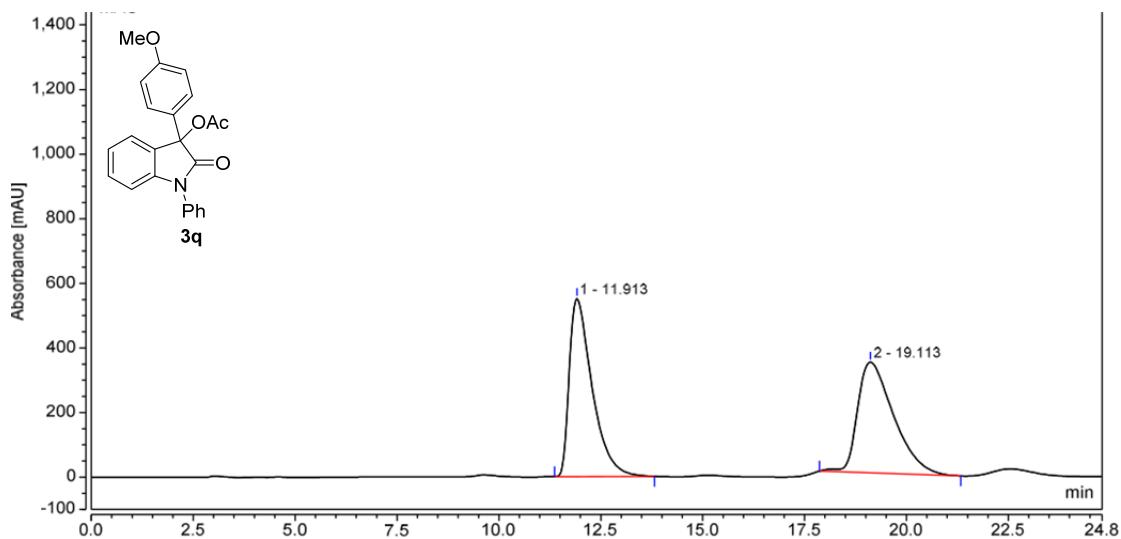


| Peak | Retention Time min | Area mAU*min | Height mAU | Area % | Height % |
|---------------|-----------------------|-----------------|----------------|---------------|---------------|
| 1 | 8.425 | 110.724 | 211.734 | 49.76 | 52.87 |
| 2 | 11.846 | 111.812 | 188.721 | 50.24 | 47.13 |
| Total: | | 222.536 | 400.454 | 100.00 | 100.00 |

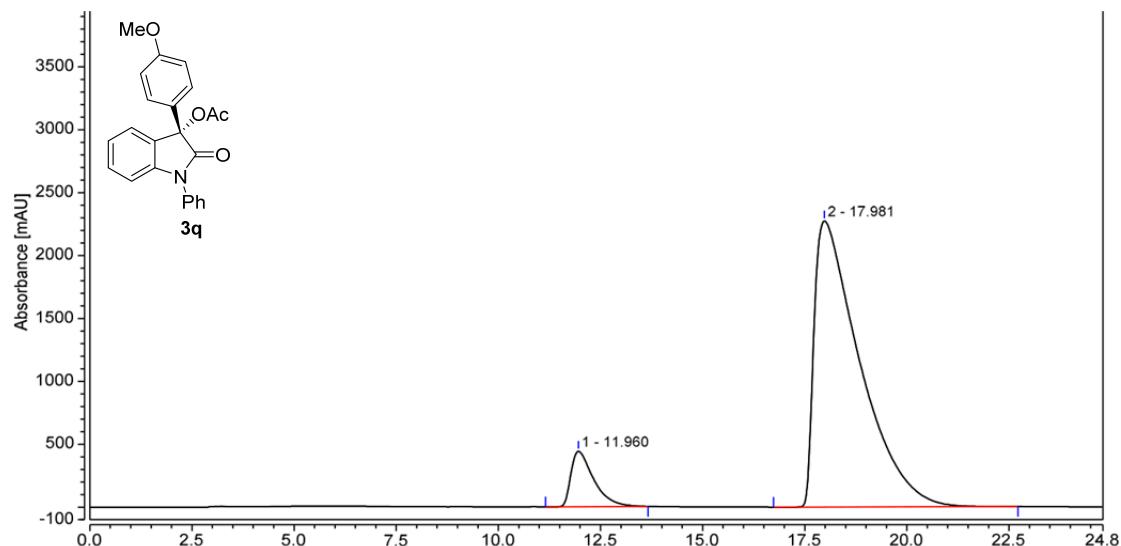


| Peak | Retention Time min | Area mAU*min | Height mAU | Area % | Height % |
|---------------|-----------------------|-----------------|-----------------|---------------|---------------|
| 1 | 8.221 | 251.319 | 488.373 | 8.66 | 13.72 |
| 2 | 11.033 | 2650.401 | 3071.029 | 91.34 | 86.28 |
| Total: | | 2901.720 | 3559.402 | 100.00 | 100.00 |

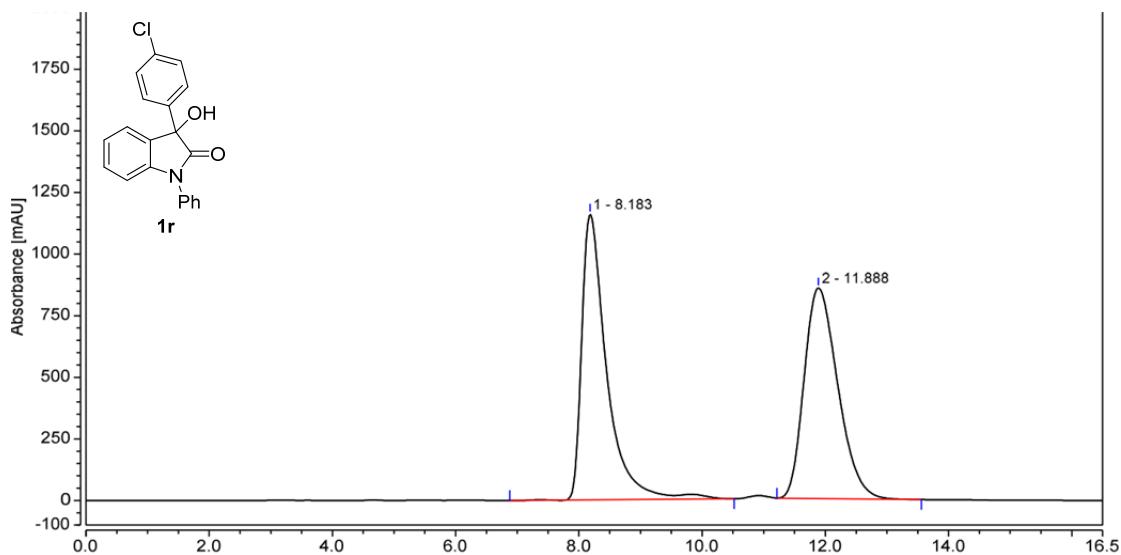




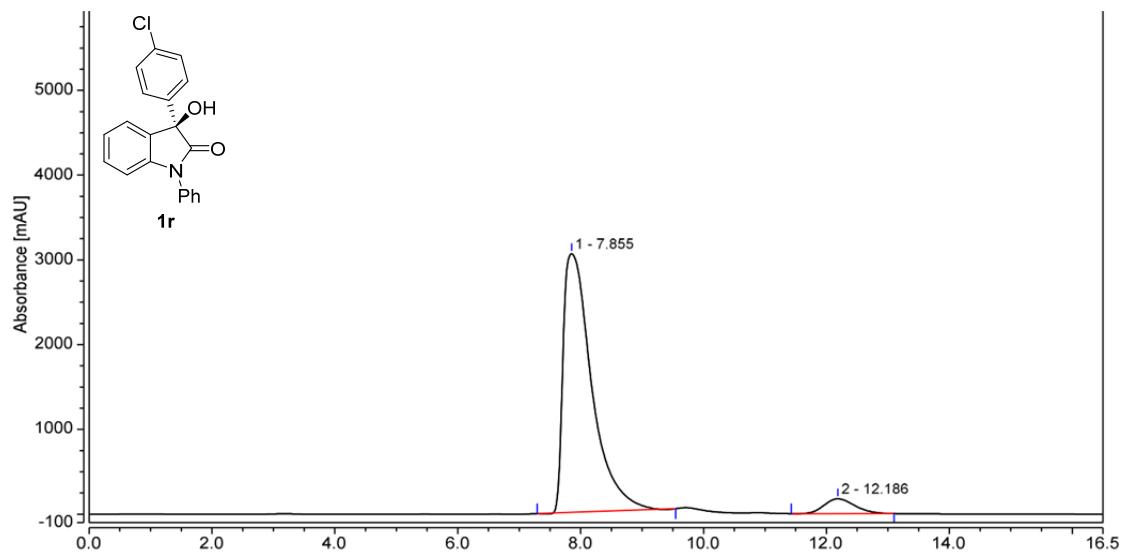
| Peak | Retention Time min | Area mAU*min | Height mAU | Area % | Height % |
|---------------|-----------------------|-----------------|----------------|---------------|---------------|
| 1 | 11.913 | 359.636 | 551.737 | 50.50 | 61.68 |
| 2 | 19.113 | 352.576 | 342.794 | 49.50 | 38.32 |
| Total: | | 712.211 | 894.531 | 100.00 | 100.00 |



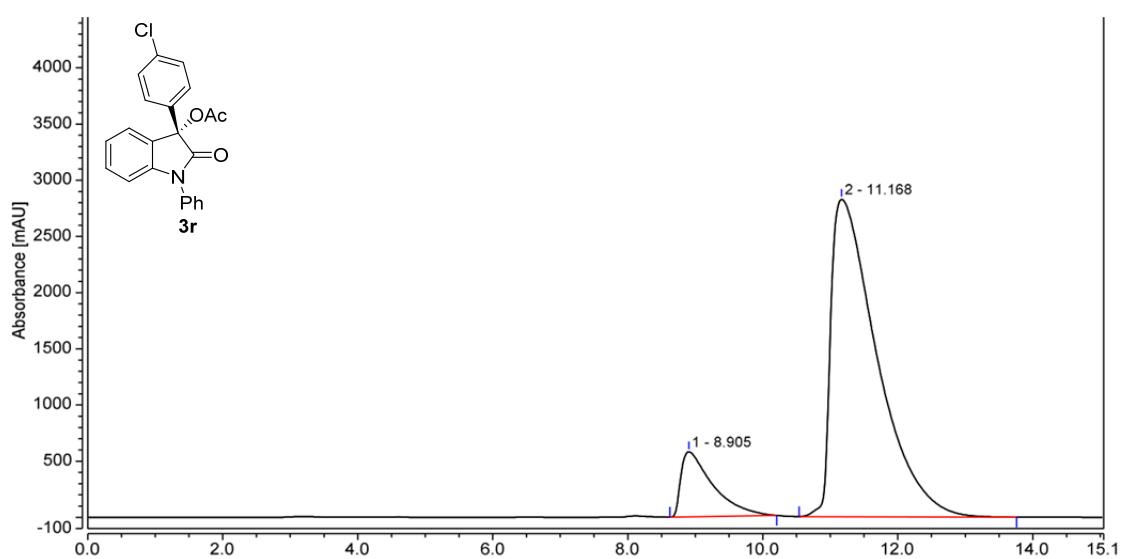
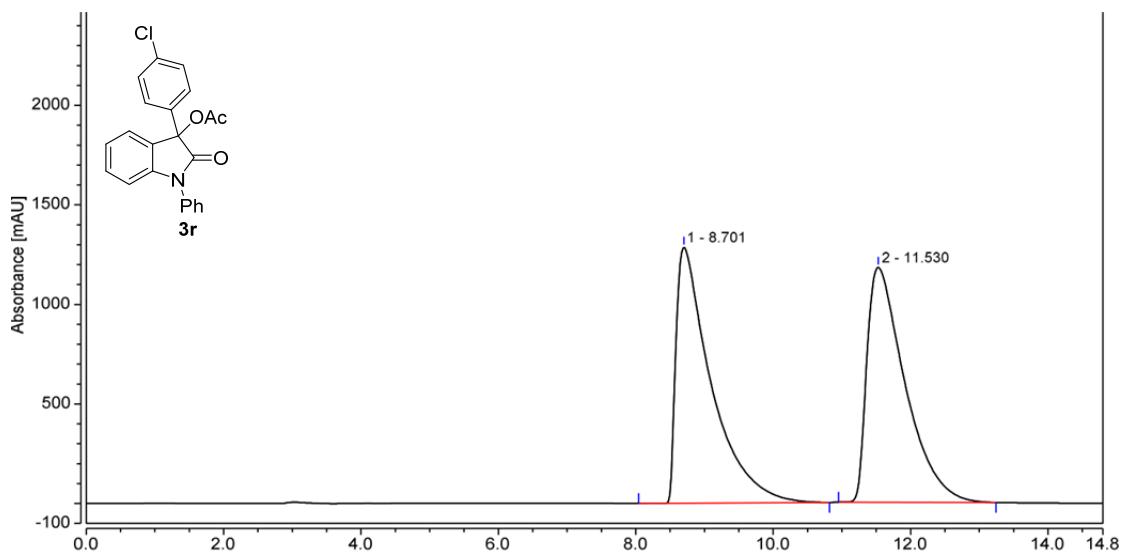
| Peak | Retention Time min | Area mAU*min | Height mAU | Area % | Height % |
|---------------|-----------------------|-----------------|-----------------|---------------|---------------|
| 1 | 11.960 | 284.455 | 441.398 | 8.82 | 16.25 |
| 2 | 17.981 | 2939.452 | 2274.628 | 91.18 | 83.75 |
| Total: | | 3223.907 | 2716.026 | 100.00 | 100.00 |

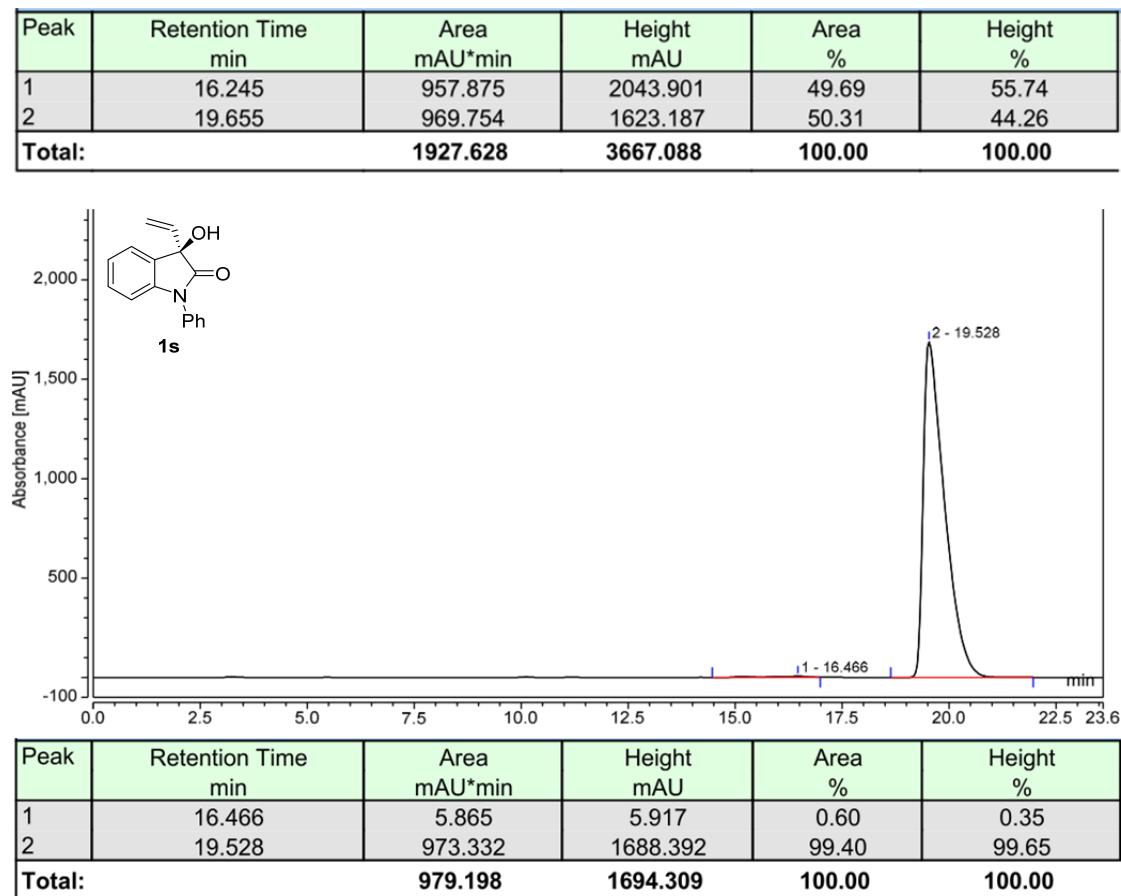
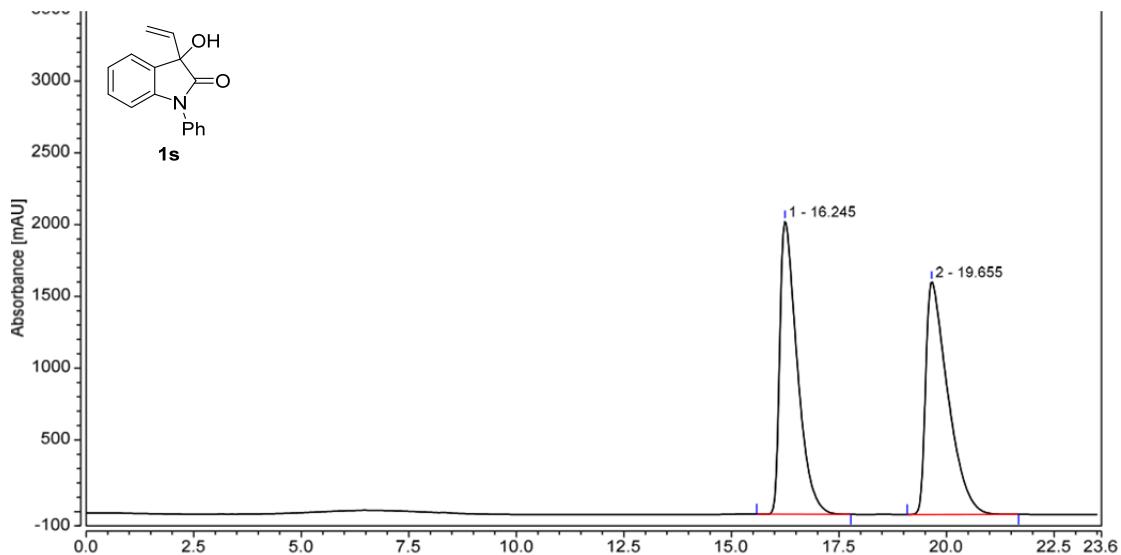


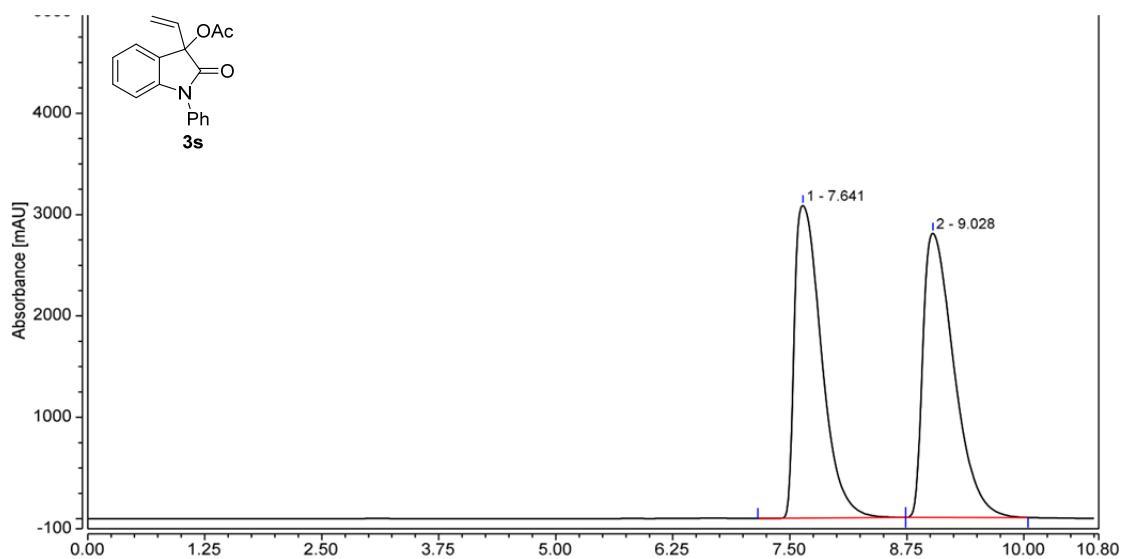
| Peak | Retention Time min | Area mAU*min | Height mAU | Area % | Height % |
|---------------|-----------------------|-----------------|-----------------|---------------|---------------|
| 1 | 8.183 | 545.332 | 1159.857 | 50.18 | 57.56 |
| 2 | 11.888 | 541.492 | 855.070 | 49.82 | 42.44 |
| Total: | | 1086.824 | 2014.927 | 100.00 | 100.00 |



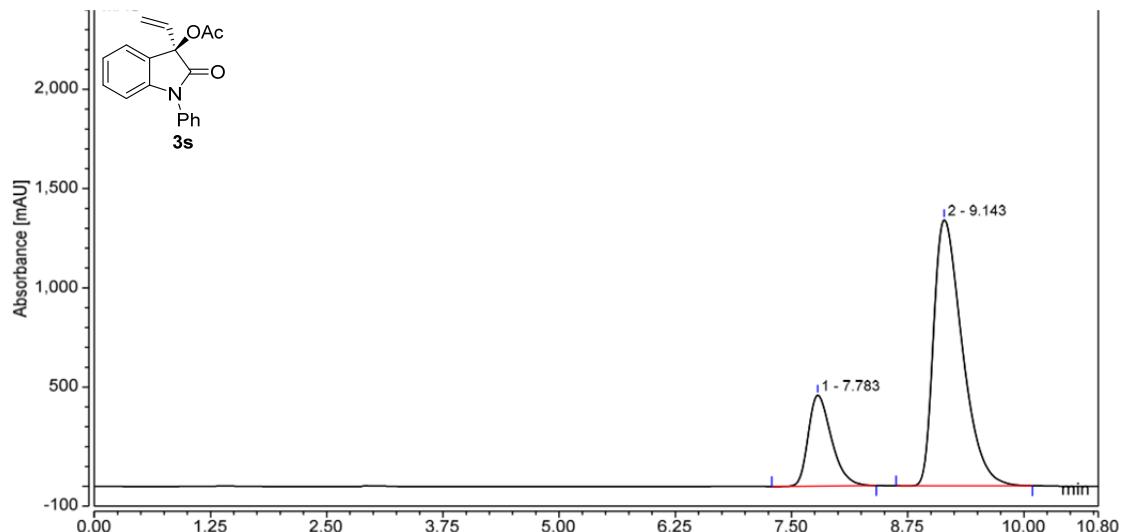
| Peak | Retention Time min | Area mAU*min | Height mAU | Area % | Height % |
|---------------|-----------------------|-----------------|-----------------|---------------|---------------|
| 1 | 7.855 | 1635.945 | 3053.711 | 94.15 | 94.57 |
| 2 | 12.186 | 101.632 | 175.416 | 5.85 | 5.43 |
| Total: | | 1737.577 | 3229.127 | 100.00 | 100.00 |



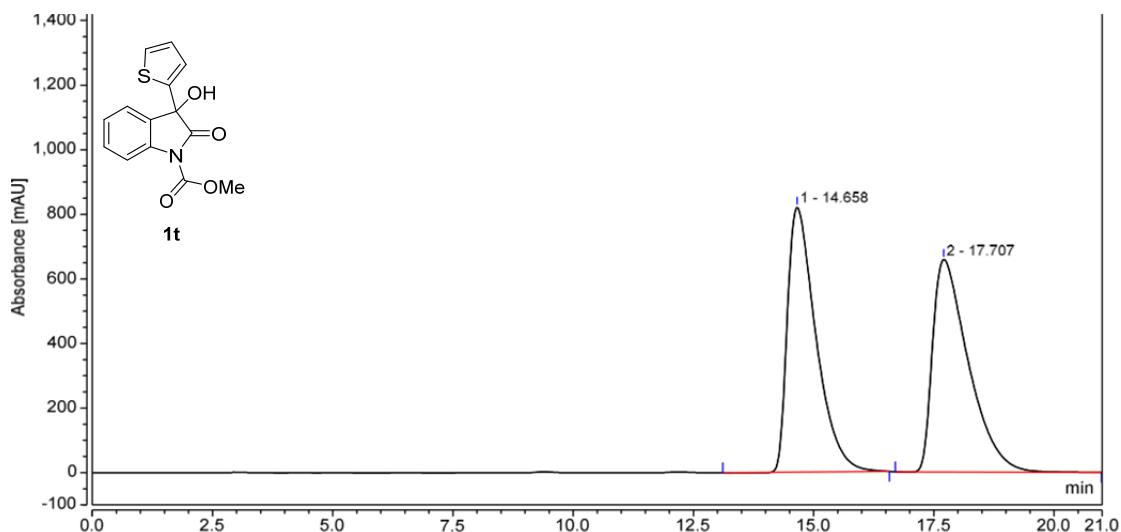




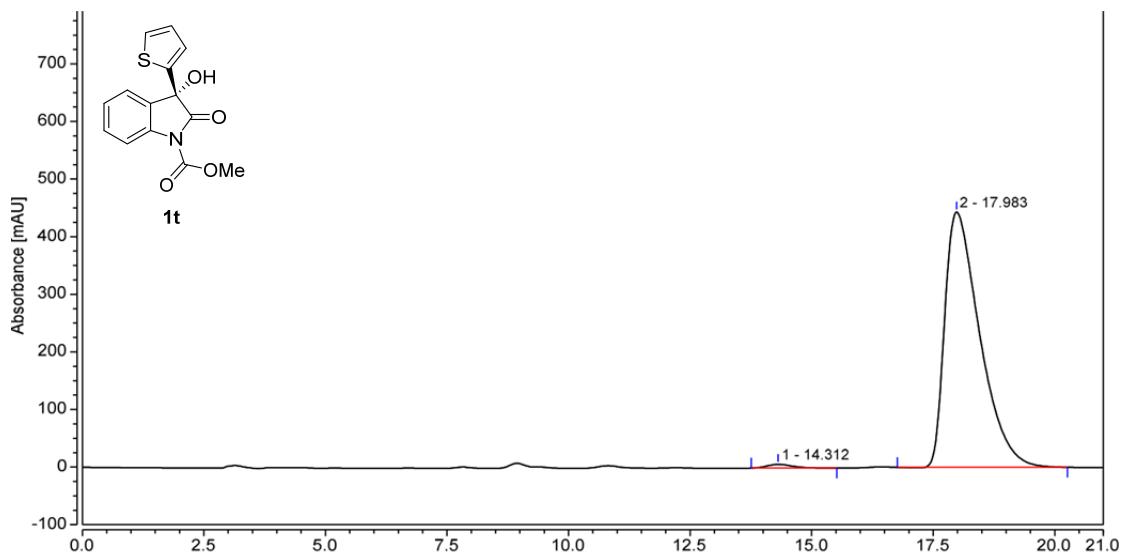
| Peak | Retention Time min | Area mAU*min | Height mAU | Area % | Height % |
|---------------|-----------------------|-----------------|-----------------|---------------|---------------|
| 1 | 7.641 | 1034.750 | 3084.036 | 48.99 | 52.37 |
| 2 | 9.028 | 1077.388 | 2805.315 | 51.01 | 47.63 |
| Total: | | 2112.139 | 5889.351 | 100.00 | 100.00 |



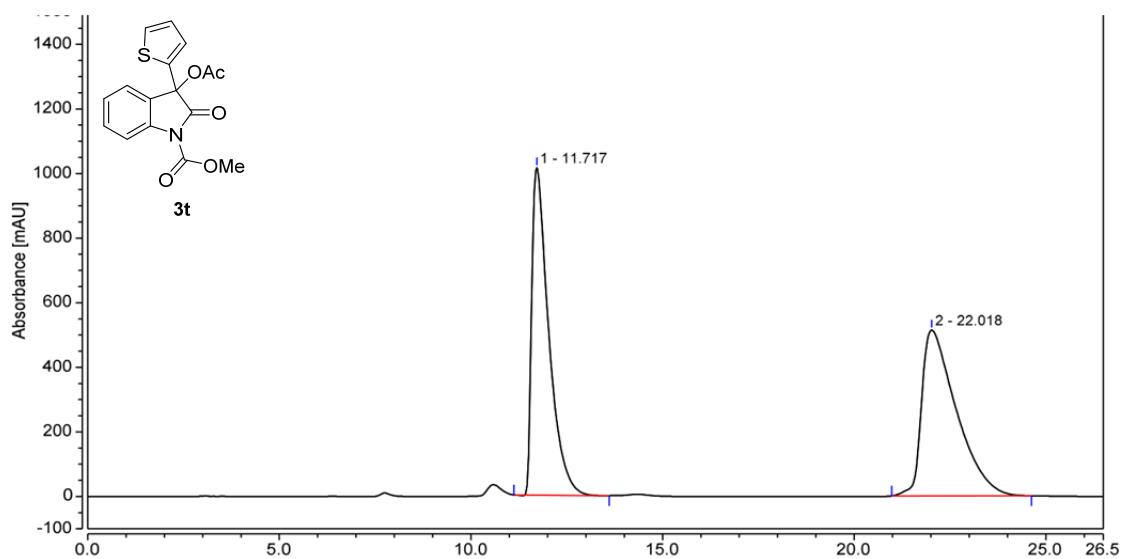
| Peak | Retention Time min | Area mAU*min | Height mAU | Area % | Height % |
|---------------|-----------------------|-----------------|-----------------|---------------|---------------|
| 1 | 7.783 | 132.984 | 458.036 | 21.77 | 25.46 |
| 2 | 9.143 | 477.837 | 1340.939 | 78.23 | 74.54 |
| Total: | | 610.821 | 1798.975 | 100.00 | 100.00 |



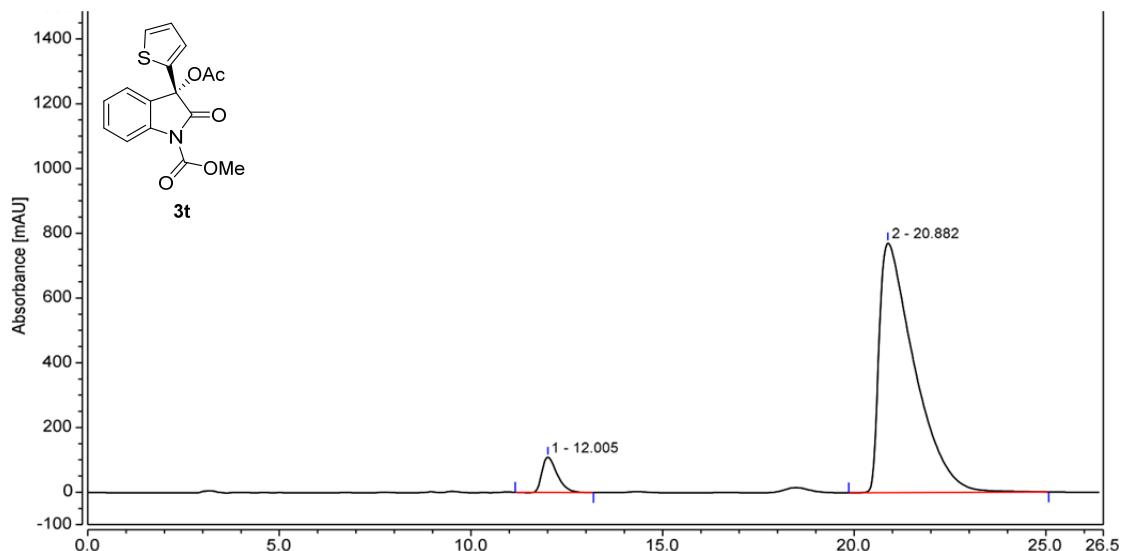
| Peak | Retention Time min | Area mAU*min | Height mAU | Area % | Height % |
|---------------|-----------------------|-----------------|-----------------|---------------|---------------|
| 1 | 14.658 | 564.468 | 820.239 | 49.85 | 55.49 |
| 2 | 17.707 | 567.781 | 657.926 | 50.15 | 44.51 |
| Total: | | 1132.249 | 1478.166 | 100.00 | 100.00 |



| Peak | Retention Time min | Area mAU*min | Height mAU | Area % | Height % |
|---------------|-----------------------|-----------------|----------------|---------------|---------------|
| 1 | 14.312 | 3.981 | 6.403 | 1.06 | 1.42 |
| 2 | 17.983 | 370.023 | 443.447 | 98.94 | 98.58 |
| Total: | | 374.004 | 449.849 | 100.00 | 100.00 |



| Peak | Retention Time min | Area mAU*min | Height mAU | Area % | Height % |
|---------------|-----------------------|-----------------|-----------------|---------------|---------------|
| 1 | 11.717 | 519.891 | 1013.821 | 49.06 | 66.36 |
| 2 | 22.018 | 539.891 | 513.915 | 50.94 | 33.64 |
| Total: | | 1059.781 | 1527.736 | 100.00 | 100.00 |



| Peak | Retention Time min | Area mAU*min | Height mAU | Area % | Height % |
|---------------|-----------------------|-----------------|----------------|---------------|---------------|
| 1 | 12.005 | 50.026 | 109.382 | 5.75 | 12.42 |
| 2 | 20.882 | 819.377 | 771.118 | 94.25 | 87.58 |
| Total: | | 869.403 | 880.501 | 100.00 | 100.00 |