Supplementary Materials: Chitosan Aerogel Catalyzed Asymmetric Aldol Reaction in Water: Highly Enantioselective Construction of 3-Substituted-3-hydroxy-2-oxindoles

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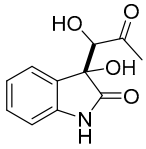
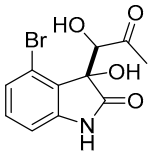
Characterization Data of All Compounds

3-Hydroxy-3-(1-hydroxy-2-oxopropyl)indolin-2-one ***3a***



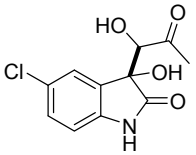
White solid, yield 92%, mp 144–146 °C. ^{1}H NMR (400 MHz, DMSO) δ 10.22 (s, 1H), 7.39 (d, *J* = 7.3 Hz, 1H), 7.19 (t, *J* = 7.6 Hz, 1H), 6.93 (t, *J* = 7.5 Hz, 1H), 6.74 (d, *J* = 7.7 Hz, 1H), 6.27 (s, 1H), 5.76 (d, *J* = 4.6 Hz, 1H), 4.24 (d, *J* = 4.6 Hz, 1H), 2.01 (s, 3H). ^{13}C NMR (101 MHz, DMSO) δ 208.94, 176.86, 142.45, 129.90, 128.91, 124.70, 121.20, 109.40, 79.81, 76.33, 27.27. HRMS (*m*/*z*): calcd. for 244.0580 ([M+Na]$^{+}$), obsd. 244.0587. The ee was determined by chiral HPLC analysis using a ChiralCel AD-H column (*n*-hexane:*i*-PrOH = 85:15): major diastereoisomer: t_{maj} = 25.3 min, t_{min} = 49.3 min, 71% ee; minor diastereoisomer: t_{maj} = 114.8 min, t_{min} = 22.3 min, 82% ee, λ = 254 nm.

4-Bromo-3-hydroxy-3-(1-hydroxy-2-oxopropyl)indolin-2-one ***3b***



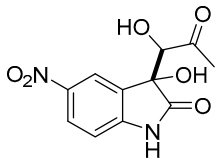
White solid, yield 94%, mp 140–142 °C. ^{1}H NMR (400 MHz, DMSO) δ 10.49 (s, 1H), 7.12 (t, *J* = 7.9 Hz, 1H), 7.04 (d, *J* = 8.0 Hz, 1H), 6.75 (d, *J* = 7.5 Hz, 1H), 6.48 (s, 1H), 5.21 (d, *J* = 5.7 Hz, 1H), 4.45 (d, *J* = 5.7 Hz, 1H), 2.33 (s, 3H). ^{13}C NMR (101 MHz, DMSO) δ 208.04, 177.12, 145.33, 131.10, 127.13, 125.57, 119.12, 108.87, 78.90, 78.37, 29.42. HRMS (*m*/*z*): calcd. for 321.9691 ([M+Na]$^{+}$), obsd. 321.9685. The ee was determined by chiral HPLC analysis using a ChiralCel AD-H column (*n*-hexane:*i*-PrOH = 85:15): major diastereoisomer: t_{maj} = 63.8 min, t_{min} = 23.1 min, 36% ee; minor diastereoisomer: t_{maj} = 35.9 min, t_{min} = 75.8 min, 84% ee, λ = 254 nm.

5-Chloro-3-hydroxy-3-(1-hydroxy-2-oxopropyl)indolin-2-one ***3c***



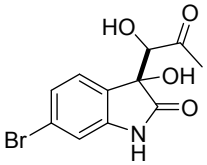
White solid, yield 93%, mp 152–154 °C. ^{1}H NMR (400 MHz, DMSO) δ 10.36 (s, 1H), 7.39 (d, *J* = 2.2 Hz, 1H), 7.25 (dd, *J* = 8.3, 2.2 Hz, 1H), 6.76 (d, *J* = 8.3 Hz, 1H), 6.42 (s, 1H), 5.89 (d, *J* = 5.0 Hz, 1H), 4.28 (d, *J* = 5.0 Hz, 1H), 2.06 (s, 3H). ^{13}C NMR (101 MHz, DMSO) δ 209.20, 176.98, 142.05, 132.70, 129.35, 125.65, 125.35, 111.26, 80.11, 76.95, 27.98. HRMS (*m*/*z*): calcd. for 278.0191 ([M+Na]$^{+}$), obsd. 278.0193. The ee could not be clearly identified by chiral HPLC analysis.

3-Hydroxy-3-(1-hydroxy-2-oxopropyl)-5-nitroindolin-2-one ***3d***



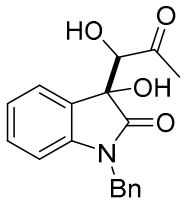
Yellow solid, yield 96%, mp 179–181 °C. ^{1}H NMR (400 MHz, DMSO) δ 8.21 (d, *J* = 9.1 Hz, 1H), 7.75 (s, 1H), 6.99 (d, *J* = 8.6 Hz, 1H), 6.77 (s, 1H), 5.40 (d, *J* = 6.3 Hz, 1H), 4.47 (d, *J* = 6.3 Hz, 1H), 2.40 (s, 3H).^{13}C NMR (101 MHz, DMSO) δ 208.12, 178.12, 149.87, 141.60, 129.41, 126.76, 120.48, 109.71, 77.45, 76.64, 29.75. HRMS (*m*/*z*): calcd. for 289.0431 ([M+Na]$^{+}$), obsd. 289.0439. The ee was determined by chiral HPLC analysis using a ChiralCel AD-H column (*n*-hexane:*i*-PrOH = 85:15): major diastereoisomer: t_{maj} = 111.6 min, t_{min} = 51.5 min, 92% ee, λ = 254 nm.

6-Bromo-3-hydroxy-3-(1-hydroxy-2-oxopropyl)indolin-2-one ***3e***



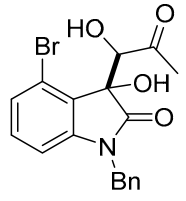
White solid, yield 93%, mp 164–166 °C. ^{1}H NMR (400 MHz, DMSO) δ 10.37 (s, 1H), 7.33 (d, *J* = 7.6 Hz, 1H), 7.13 (d, *J* = 7.8 Hz, 1H), 6.84 (d, *J* = 7.7 Hz, 1H), 6.55 (s, 1H), 5.08 (d, *J* = 5.1 Hz, 1H), 4.41 (d, *J* = 5.1 Hz, 1H), 2.05 (s, 3H).^{13}C NMR (101 MHz, DMSO) δ 209.42, 208.58, 178.04, 177.14, 145.46, 144.86, 129.98, 128.18, 127.13, 124.34, 124.13, 122.49, 122.25, 112.70, 112.59, 80.13, 78.42, 77.22, 76.53, 29.85, 27.96. HRMS (*m*/*z*): calcd. for 299.9866 ([M+H]$^{+}$), obsd. 299.9850. The ee was determined by chiral HPLC analysis using a ChiralCel AD-H column (*n*-hexane:*i*-PrOH = 85:15): major diastereoisomer: t_{maj} = 28.2 min, t_{min} = 16.6 min, 66% ee; minor diastereoisomer: t_{maj} = 107.5 min, t_{min} = 41.2 min, 77% ee, λ = 254 nm.

1-Benzyl-3-hydroxy-3-(1-hydroxy-2-oxopropyl)indolin-2-one ***3f***



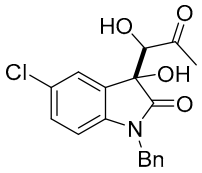
White solid, yield 95%, mp 119–121 °C. ^{1}H NMR (400 MHz, DMSO) δ 7.38 (d, *J* = 7.2 Hz, 2H), 7.31 (t, *J* = 7.2 Hz, 2H), 7.28–7.23 (m, 1H), 7.20 (t, *J* = 7.4 Hz, 1H), 6.96 (q, *J* = 7.1 Hz, 2H), 6.74 (d, *J* = 7.7 Hz, 1H), 6.69 (s, 1H), 5.18 (d, *J* = 5.2 Hz, 1H), 4.99 (d, *J* = 16.1 Hz, 1H), 4.77 (d, *J* = 16.1 Hz, 1H), 4.55 (d, *J* = 5.0 Hz, 1H), 2.43 (s, 3H). ^{13}CNMR (101 MHz, DMSO) δ 208.61, 176.78, 144.19, 136.51, 129.86, 128.91, 128.31, 127.66, 127.55, 125.07, 122.31, 109.43, 78.74, 77.37, 43.00, 29.81. HRMS (*m*/*z*): calcd. for 334.1050 ([M+Na]$^{+}$), obsd. 334.1191. The ee was determined by chiral HPLC analysis using a ChiralCel AD-H column (*n*-hexane:*i*-PrOH = 85:15): major diastereoisomer: t_{maj} = 63.6 min, t_{min} = 42.2 min, 72% ee; minor diastereoisomer: t_{maj} = 71.9 min, t_{min} = 78.4 min, 90% ee, λ = 254 nm.

1-Benzyl-4-bromo-3-hydroxy-3-(1-hydroxy-2-oxopropyl)indolin-2-one ***3g***



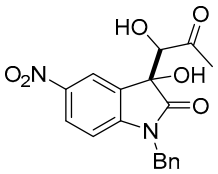
White solid, yield 92%, mp 120–122 °C. ^{1}H NMR (400 MHz, DMSO) δ 7.37–7.28 (m, 4H), 7.26 (dd, J = 5.9, 2.7 Hz, 1H), 7.20–7.10 (m, 2H), 6.74 (dd, *J* = 7.4, 1.2 Hz, 1H), 6.70 (s, 1H), 5.22 (d, *J* = 4.3 Hz, 1H), 4.89–4.82 (m, 2H), 4.81 (s, 1H), 2.43 (s, 3H).^{13}CNMR (101 MHz, DMSO) δ 207.89, 174.81, 145.38, 135.50, 130.95, 128.47, 128.32, 127.28, 127.03, 126.33, 118.39, 108.40, 79.12, 76.11, 42.54, 28.50. HRMS (*m*/*z*): calcd. for 412.0155 ([M+Na]$^{+}$), obsd. 412.0178. The ee was determined by chiral HPLC analysis using a ChiralCel AD-H column (*n*-hexane:*i*-PrOH = 85:15): major diastereoisomer: t_{maj} = 72.5 min, t_{min} = 51.1 min, 74% ee; minor diastereoisomer: t_{maj} = 77.9 min, t_{min} = 84.0 min, 94% ee, λ = 254 nm.

1-Benzyl-5-chloro-3-hydroxy-3-(1-hydroxy-2-oxopropyl)indolin-2-one ***3h***



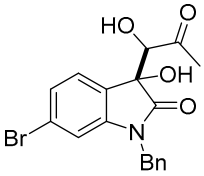
White solid, yield 91%, mp 100–102 °C.^{1}H NMR (400 MHz, DMSO) δ 7.36 (d, *J* = 1.6 Hz, 1H), 7.35–7.33 (m, 2H), 7.31 (d, *J* = 1.7 Hz, 1H), 7.30 (d, *J* = 2.1 Hz, 1H), 7.27 (d, *J* = 2.1 Hz, 1H), 6.97 (d, *J* = 2.2 Hz, 1H), 6.82 (s, 1H), 6.76 (d, *J* = 8.4 Hz, 1H), 5.40 (d, *J* = 5.8 Hz, 1H), 4.97 (s, 1H), 4.80 (s, 1H), 4.55 (d, *J* = 5.8 Hz, 1H), 2.41 (s, 3H).^{13}C NMR (101 MHz, DMSO) δ 208.55, 176.47, 143.06, 136.14, 130.47, 128.96, 128.80, 127.76, 127.50, 126.61, 126.44, 126.07, 125.27, 110.94, 78.33, 77.37, 43.07, 30.10. HRMS (*m*/*z*): calcd. for 368.0660 ([M+Na]$^{+}$), obsd. 368.0668. The ee was determined by chiral HPLC analysis using a ChiralCel AD-H column (*n*-hexane:*i*-PrOH = 85:15): major diastereoisomer: t_{maj} = 72.0 min, t_{min} = 27.3 min, 73% ee; minor diastereoisomer: t_{maj} = 52.5 min, t_{min} = 89.3 min, 47% ee, λ = 254 nm.

1-Benzyl-3-hydroxy-3-(1-hydroxy-2-oxopropyl)-5-nitroindolin-2-one ***3i***



Faint yellow solid, yield 92%, mp 154–156 °C. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.37 (t, 3H), 7.31 (s, 2H), 6.97 (t, *J* = 8.8 Hz, 1H), 6.89 (d, *J* = 7.5 Hz, 1H), 6.63 (dd, *J* = 8.3, 3.4 Hz, 1H), 5.17 (d, *J* = 15.9 Hz, 1H), 4.75 (d, *J* = 7.2 Hz, 1H), 4.70 (d, *J* = 15.8 Hz, 1H), 4.07 (d, *J* = 39.3 Hz, 1H), 3.65 (d, *J* = 7.1 Hz, 1H), 1.66 (s, 3H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 207.16, 176.07, 157.93, 139.69, 134.57, 128.93, 127.90, 127.10, 117.01, 116.78, 112.88, 112.63, 110.62, 110.54, 79.07, 44.20, 29.00, 0.01. HRMS (*m*/*z*): calcd. for 379.0901 ([M+Na]$^{+}$), obsd. 379.0907. The ee was determined by chiral HPLC analysis using a ChiralCel AD-H column (*n*-hexane:*i*-PrOH = 85:15): major diastereoisomer: t_{maj} = 95.4 min, t_{min} = 114.8 min, 94% ee; minor diastereoisomer: t_{maj} = 48.1 min, t_{min} = 70.4 min, 25% ee, λ = 254 nm.

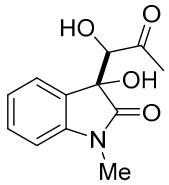
1-Benzyl-6-bromo-3-hydroxy-3-(1-hydroxy-2-oxopropyl)indolin-2-one ***3j***



White solid, yield 96%, mp 136–138 °C. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.33 (t, *J* = 6.4 Hz, 2H), 7.28 (d, *J* = 7.5 Hz, 1H), 7.23 (t, 1H), 7.12 (d, *J* = 7.9 Hz, 1H), 6.95 (s, 1H), 6.88 (d, *J* = 7.9 Hz, 1H), 6.75 (s, 1H), 5.30 (d, *J* = 5.6 Hz, 1H), 4.97 (d, *J* = 16.1 Hz, 1H), 4.77 (d, *J* = 16.1 Hz, 1H), 4.51 (d, *J* = 5.6 Hz, 1H), 4.38 (t, *J* = 5.6 Hz, 1H), 2.37 (s, 3H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 213.16, 181.55, 150.60, 140.90, 133.72, 132.51, 132.39, 132.25, 131.63, 129.69, 127.46, 117.14, 83.19, 81.88, 77.71, 68.27, 47.68, 34.68.

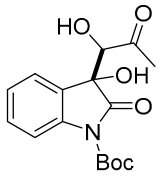
HRMS (*m*/*z*): calcd. for 412.0155 ([M+Na]$^+$), obsd. 412.0163. The ee was determined by chiral HPLC analysis using a ChiralCel AD-H column (*n*-hexane:*i*-PrOH = 85:15): major diastereoisomer: t_{maj}= 65.7 min, t_{min} = 26.5 min, 34% ee; minor diastereoisomer: t_{maj} = 43.0 min, t_{min} = 76.4 min,91% ee, λ = 254 nm.

3-Hydroxy-3-(1-hydroxy-2-oxopropyl)-1-methylindolin-2-one ***3k***



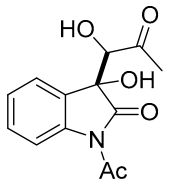
White solid, yield 93%, mp 140–142 °C. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.46 (d, *J* = 7.3 Hz, 1H), 7.36 (t, *J* = 7.7 Hz, 1H), 7.10 (t, *J* = 7.6 Hz, 1H), 6.83 (d, *J* = 7.8 Hz, 1H), 4.52 (d, *J* = 3.4 Hz, 1H), 3.98 (s, 1H), 3.91 (d, *J* = 3.3 Hz, 1H), 3.18 (s, 3H), 2.22 (s, 3H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 207.70, 175.21, 143.86, 130.56, 127.29, 124.47, 123.45, 108.78, 79.74, 78.93, 27.35, 26.35. HRMS (*m*/*z*): calcd. for 257.0737 ([M+Na]$^+$), obsd. 257.0738. The ee was determined by chiral HPLC analysis using a ChiralCel AD-H column (*n*-hexane:*i*-PrOH = 85:15): major diastereoisomer: t_{maj} = 31.2 min, t_{min} = 27.7 min, 77% ee; minor diastereoisomer: t_{maj} = 35.2 min, t_{min} = 44.3 min, 85% ee, λ = 254 nm.

Tert-butyl 3-hydroxy-3-(1-hydroxy-2-oxopropyl)-2-oxoindoline-1-carboxylate ***3l***



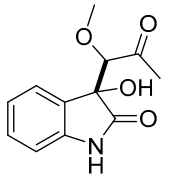
White solid, yield 92%, mp 128–130 °C. ^{1}H NMR (400 MHz, DMSO) δ 7.72 (d, *J* = 8.2 Hz, 1H), 7.55 (d, *J* = 7.3 Hz, 1H), 7.36 (t, *J* = 7.8 Hz, 1H), 7.18 (t, *J* = 7.4 Hz, 1H), 6.61 (s, 1H), 6.16 (d, *J* = 4.4 Hz, 1H), 4.38 (d, *J* = 4.0 Hz, 1H), 2.03 (s, 3H), 1.57 (s, 9H). ^{13}C NMR (101 MHz, DMSO) δ 209.84, 174.25, 149.15, 140.18, 129.92, 129.27, 125.35, 124.68, 114.75, 83.95, 80.85, 76.03, 28.14, 27.85. HRMS (*m*/*z*): calcd. for 344.1105 ([M+Na]$^+$), obsd. 344.1108. The ee could not be clearly identified by chiral HPLC analysis.

1-Acetyl-3-hydroxy-3-(1-hydroxy-2-oxopropyl)indolin-2-one ***3m***



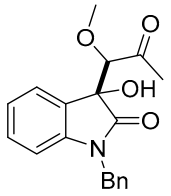
White solid, yield 97%, mp 122–124 °C. ^{1}H NMR (400 MHz, DMSO) δ 8.07 (s, 1H), 7.61 (s, 1H), 7.38 (d, *J* = 6.0 Hz, 1H), 7.24 (d, *J* = 6.3 Hz, 1H), 6.70 (s, 1H), 6.33 (s, 1H), 4.42 (s, 1H), 2.58 (s, 3H), 1.99 (s, 3H). ^{13}C NMR (101 MHz, DMSO) δ 210.37, 177.14, 170.66, 140.53, 129.97, 129.35, 125.49, 125.39, 115.91, 81.29, 76.33, 27.71, 26.49. HRMS (*m*/*z*): calcd. for 286.0686 ([M+Na]$^+$), obsd. 286.0690. The ee could not be clearly identified by chiral HPLC analysis.

3-Hydroxy-3-(1-methoxy-2-oxopropyl)indolin-2-one ***3n***



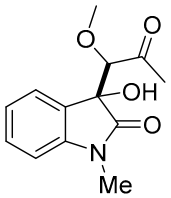
White solid, yield 92%, mp 150–152 °C. ^{1}H NMR (400 MHz, DMSO) δ 10.23 (s, 1H), 7.38 (d, *J* = 7.2 Hz, 1H), 7.20 (t, *J* = 7.5 Hz, 1H), 6.94 (t, *J* = 7.3 Hz, 1H), 6.75 (d, *J* = 7.6 Hz, 1H), 6.29 (s, 1H), 3.39 (s, 3H), 1.97 (s, 3H). ^{13}C NMR (101 MHz, DMSO) δ 207.95, 176.70, 142.93, 130.28, 129.85, 125.30, 121.81, 109.90, 90.07, 76.97, 60.65, 27.94. HRMS (*m*/*z*): calcd. for 258. 0737 ([M+Na]$^{+}$), obsd.258.0742.The ee was determined by chiral HPLC analysis using a ChiralCel AD-H column (*n*-hexane:*i*-PrOH = 90:10): major diastereoisomer: t_{maj} = 71.3 min, t_{min} = 89.3 min, 87% ee; minor diastereoisomer: t_{maj} = 60.8 min, t_{min} = 54.1 min, 91% ee, λ = 254 nm.

1-Benzyl-3-hydroxy-3-(1-methoxy-2-oxopropyl)indolin-2-one ***3o***



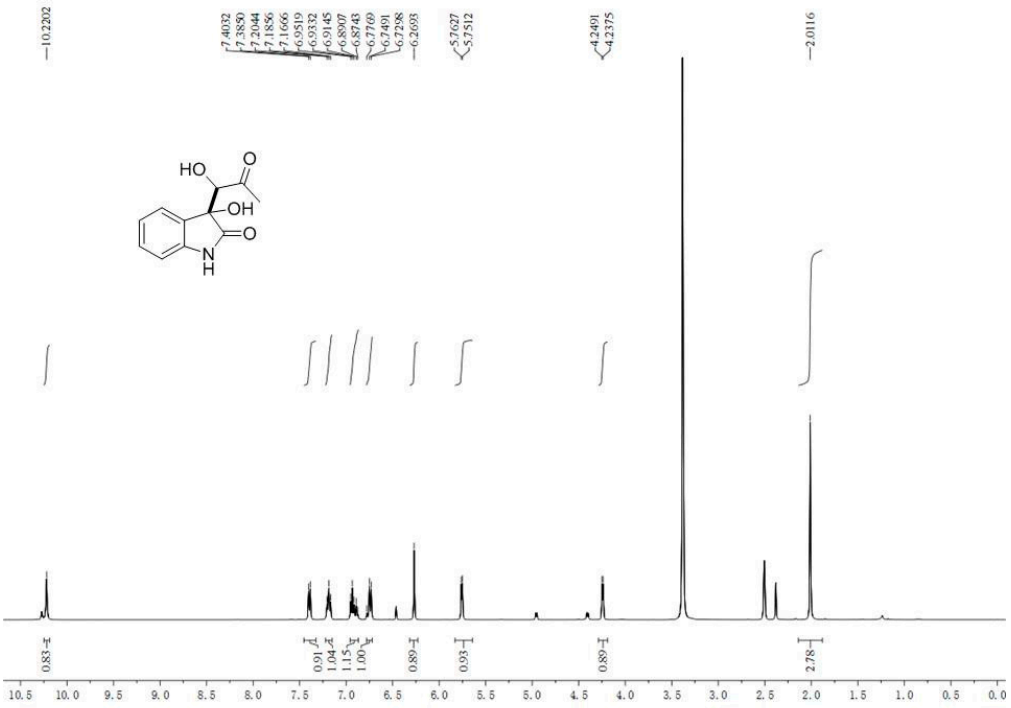
White solid, yield 90%, mp 156–158 °C. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.30 (s, 1H), 7.22 (t, *J* = 7.8 Hz, 1H), 7.13 (d, *J* = 7.4 Hz, 1H), 7.01 (t, *J* = 7.5 Hz, 1H), 6.69 (d, *J* = 7.8 Hz, 1H), 5.17 (d, *J* = 15.9 Hz, 1H), 5.17 (d, *J* = 15.9 Hz, 1H), 4.66 (t, *J* = 11.7 Hz, 1H), 4.29 (s, 1H), 4.18 (s, 1H), 3.42 (s, 1H), 2.35 (s, 1H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 212.14, 174.93, 143.68, 135.18, 130.31, 128.77, 127.63, 127.08, 127.02, 124.29, 123.11, 109.71, 99.99, 87.35, 60.29, 43.84, 29.02. HRMS (*m*/*z*): calcd. for 326.1394 ([M+H]$^{+}$), obsd. 326.1387. The ee was determined by chiral HPLC analysis using a ChiralCel AD-H column (*n*-hexane:*i*-PrOH = 90:10): major diastereoisomer: t_{maj} = 68.4 min, t_{min} = 50.1 min, 94% ee; minor diastereoisomer: t_{maj} = 85.4 min, t_{min} = 93.8 min, 54% ee, λ = 254 nm.

3-Hydroxy-3-(1-methoxy-2-oxopropyl)-1-methylindolin-2-one ***3p***

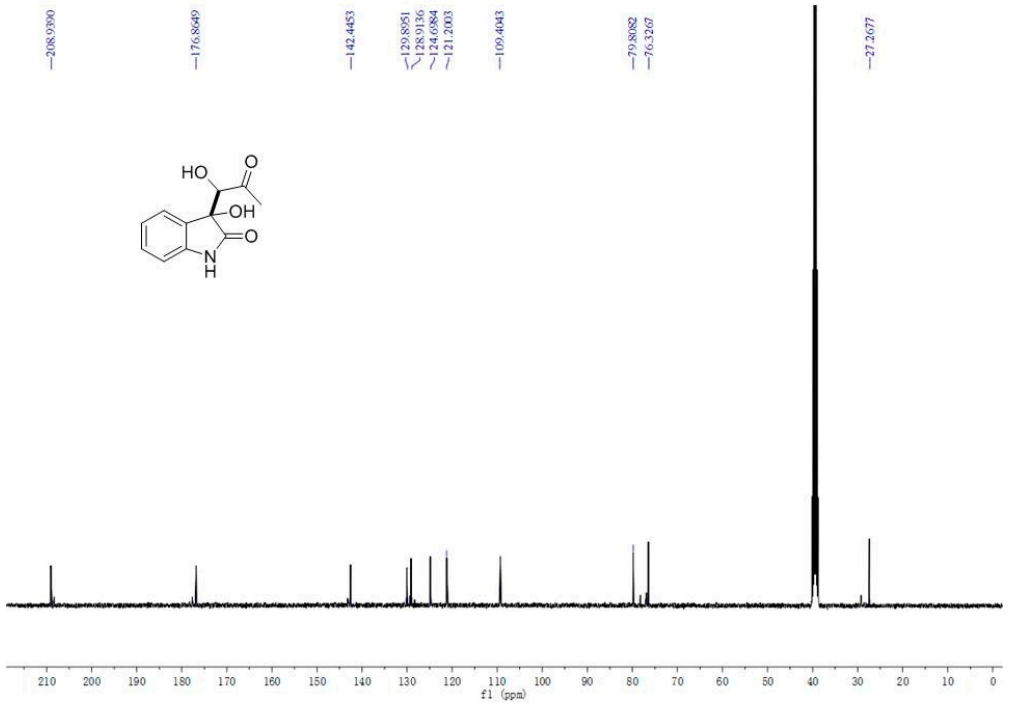


White solid, yield 89%, mp 113–115 °C. ^{1}H NMR (400 MHz, DMSO) δ 7.42 (d, *J* = 7.3 Hz, 1H), 7.31 (t, *J* = 7.7 Hz, 1H), 7.03 (t, *J* = 7.4 Hz, 1H), 6.94 (d, *J* = 7.8 Hz, 1H), 6.38 (s, 1H), 4.01 (s, 1H), 3.41 (s, 3H), 3.06 (s, 3H), 1.96 (s, 3H). ^{13}C NMR (101 MHz, DMSO) δ 207.43, 174.52, 143.85, 129.50, 129.06, 124.39, 122.02, 108.28, 89.49, 76.19, 60.28, 27.47, 25.80. HRMS (*m*/*z*): calcd. For 272.0899 ([M+Na]$^{+}$), obsd. 272.0897. The ee was determined by chiral HPLC analysis using a ChiralCel AD-H column (*n*-hexane:*i*-PrOH = 90:10): major diastereoisomer: t_{maj} = 41.1 min, t_{min} = 48.8 min,87% ee; minor diastereoisomer: t_{maj} = 32.4 min, t_{min} = 36.2 min, 91% ee, λ = 254 nm.

Compound 3a



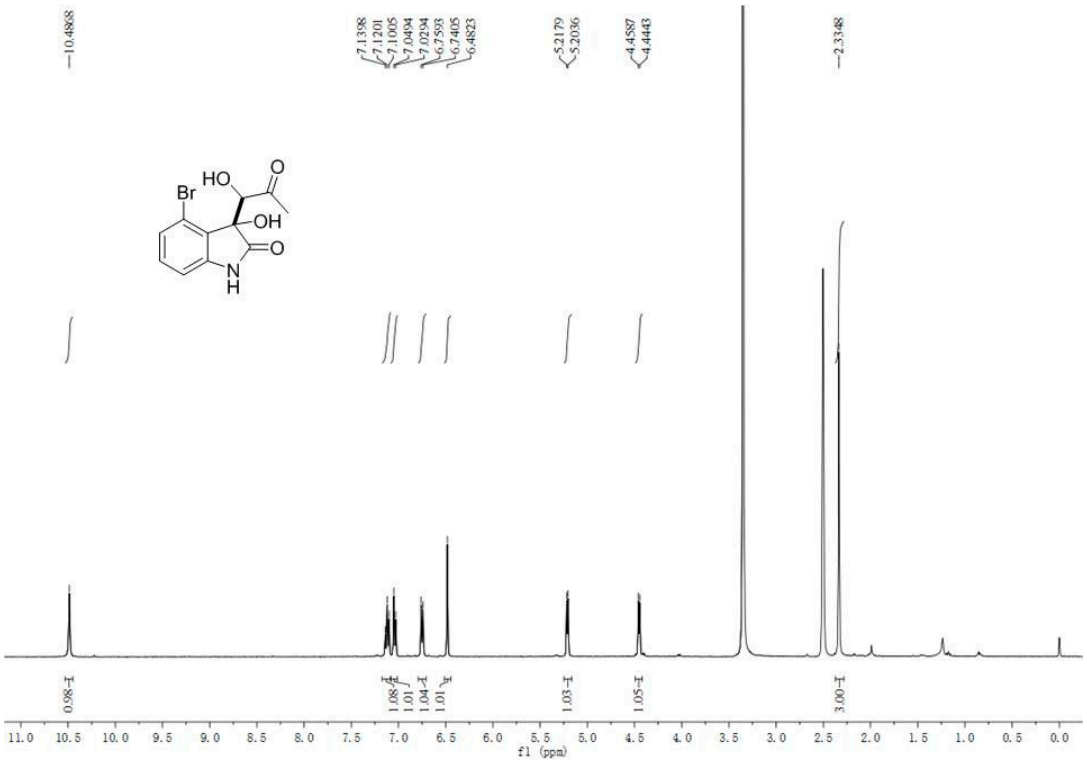
(**a**)



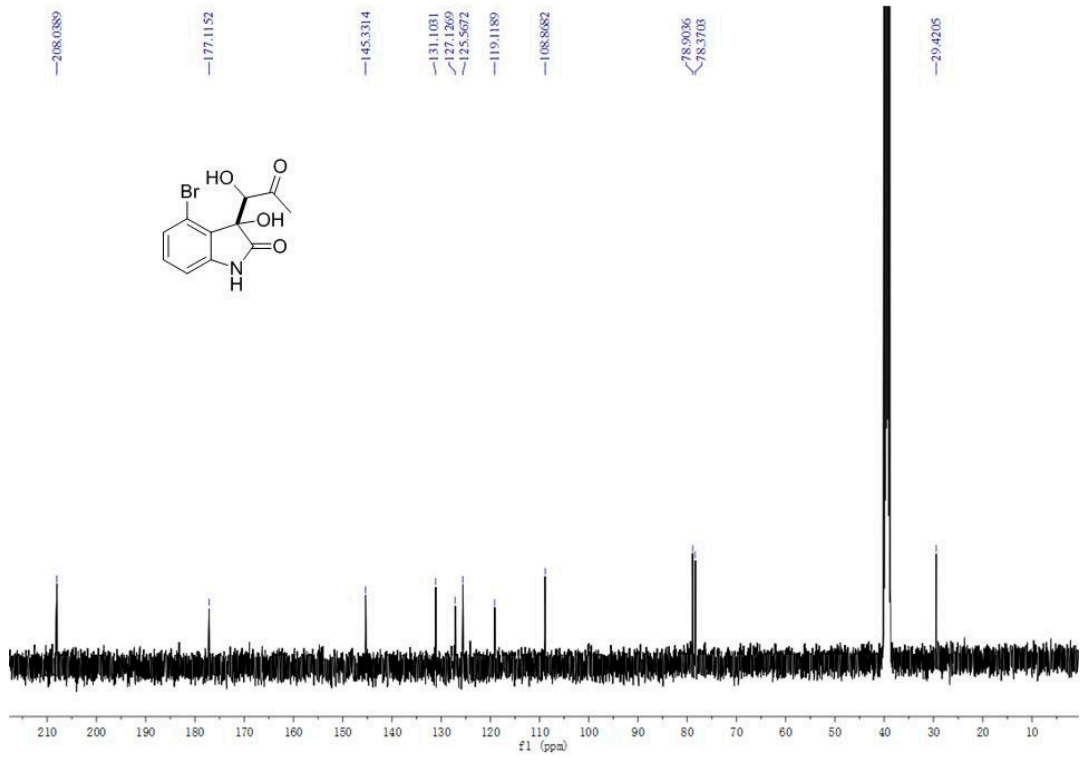
(**b**)

Figure S1. (**a**) ^{1}H NMR and (**b**) ^{13}C NMR of compound **3a**.

Compound 3b



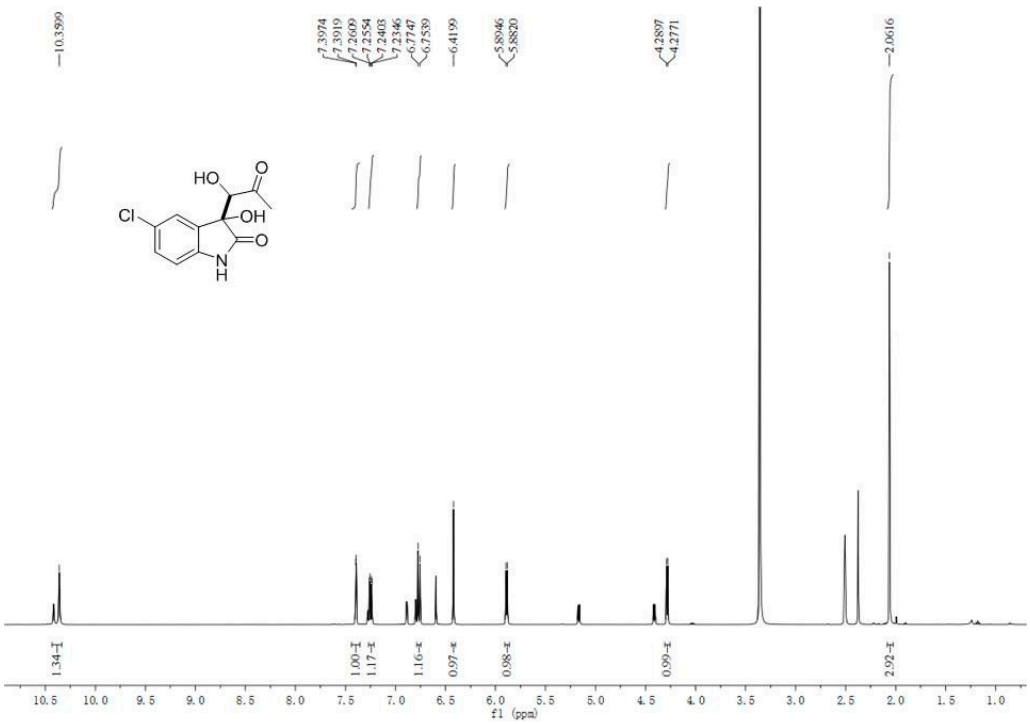
(**a**)



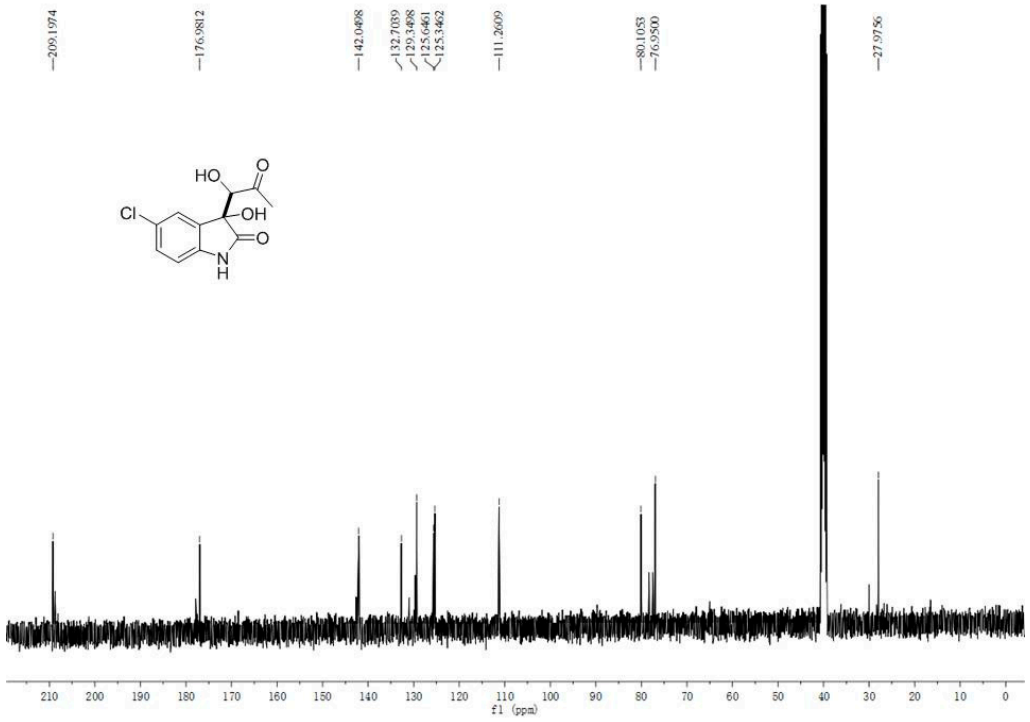
(**b**)

Figure S2. (**a**) ^{1}H NMR and (**b**) ^{13}C NMR of compound **3b**.

Compound 3c



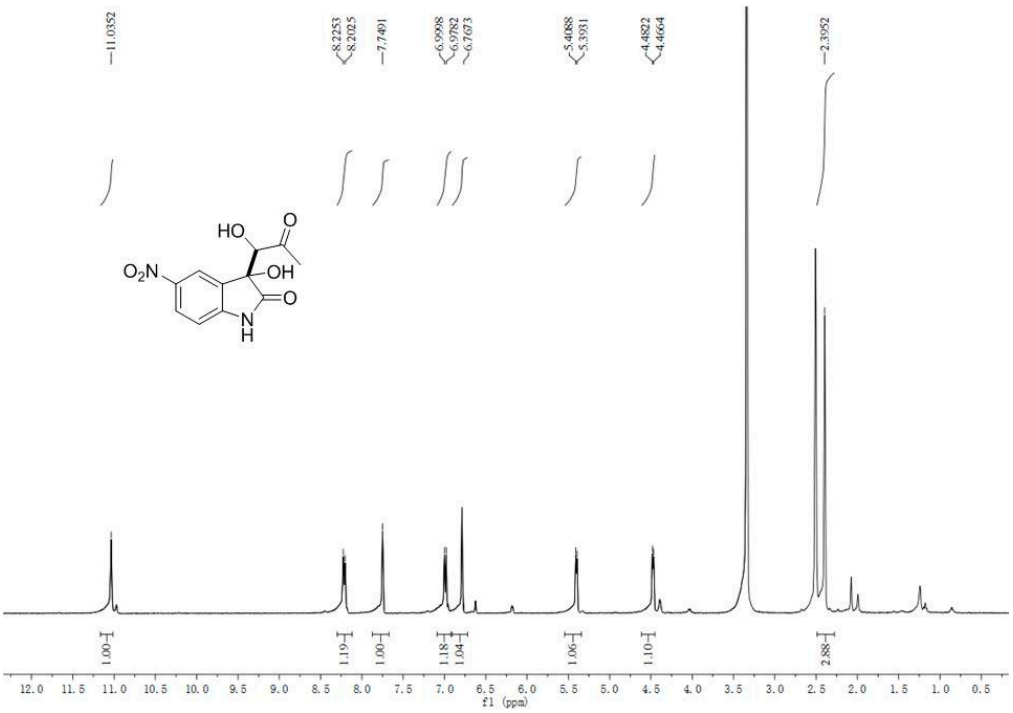
(**a**)



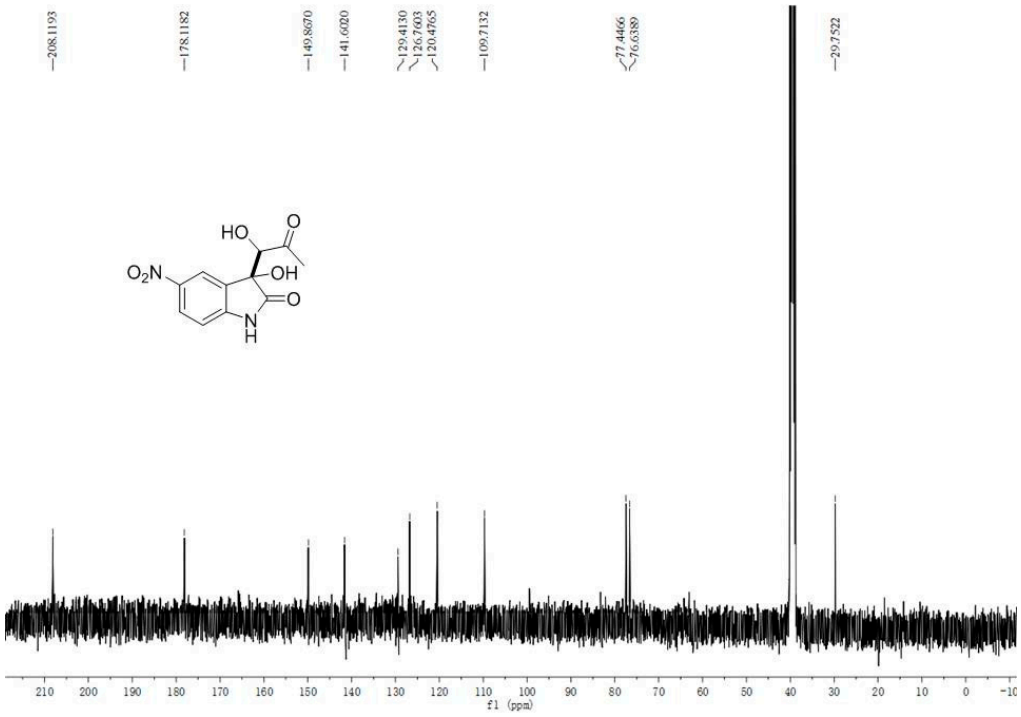
(**b**)

Figure S3. (**a**) ^{1}H NMR and (**b**) ^{13}C NMR of compound **3c**.

Compound 3d



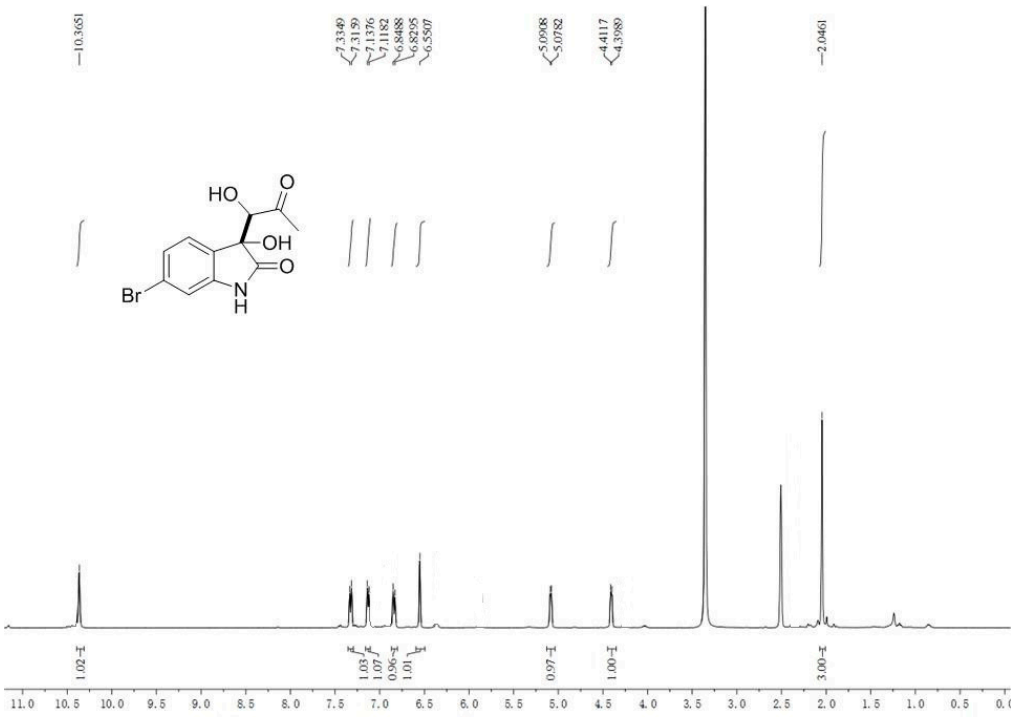
(**a**)



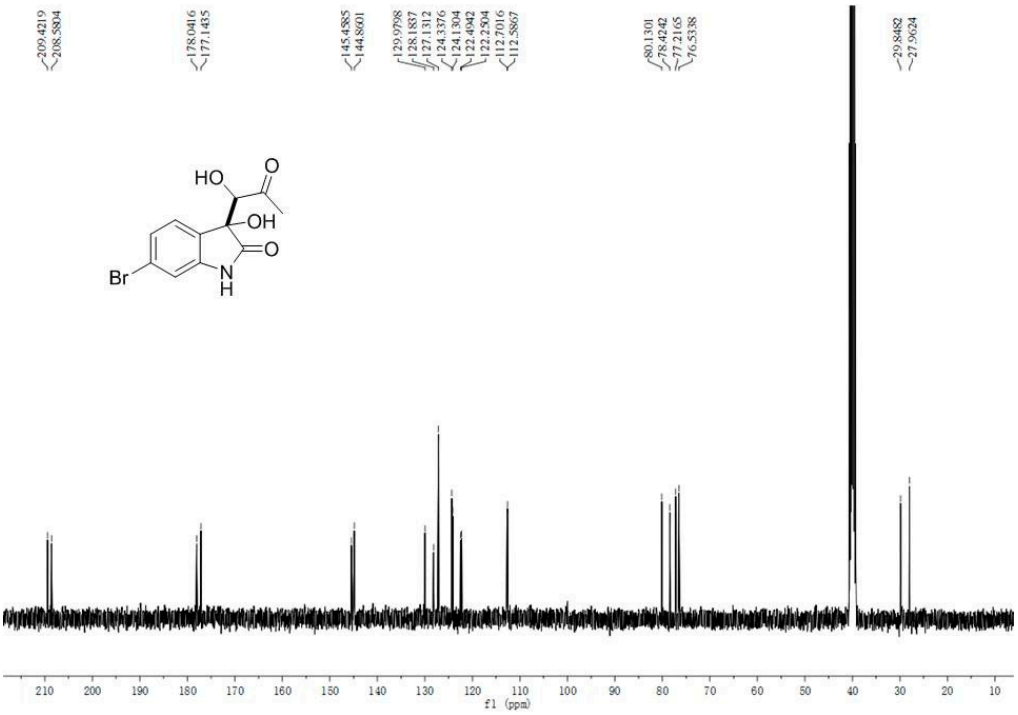
(**b**)

Figure S4. (**a**) ^{1}H NMR and (**b**) ^{13}C NMR of compound **3d.**

Compound 3e



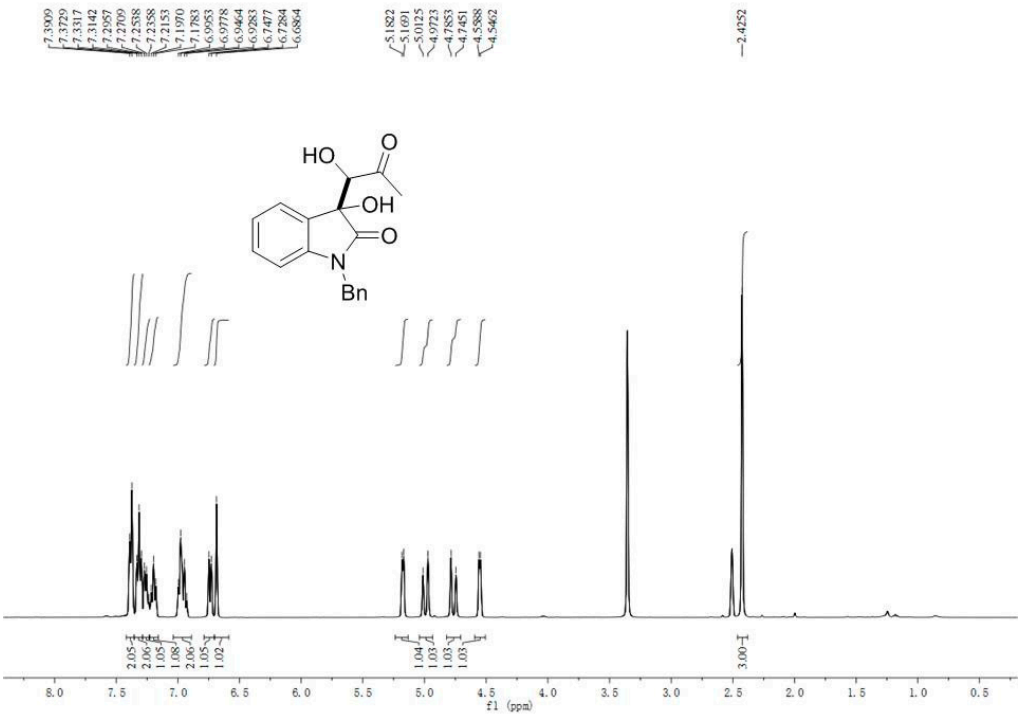
(**a**)



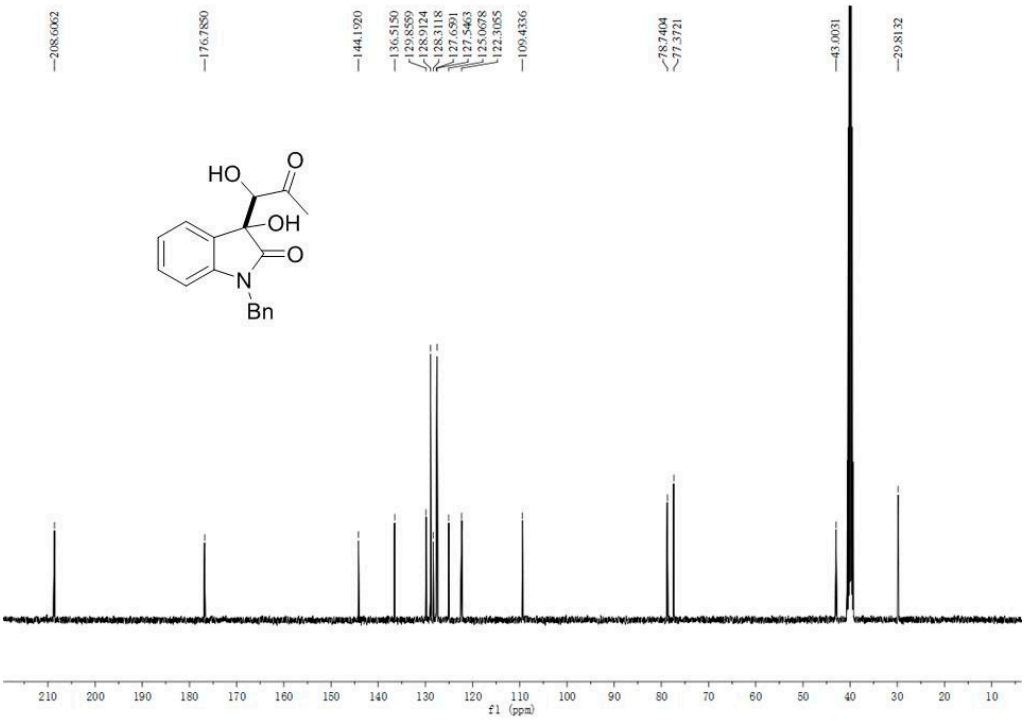
(**b**)

Figure S5. (**a**) ^{1}H NMR and (**b**) ^{13}C NMR of compound **3e**.

Compound 3f



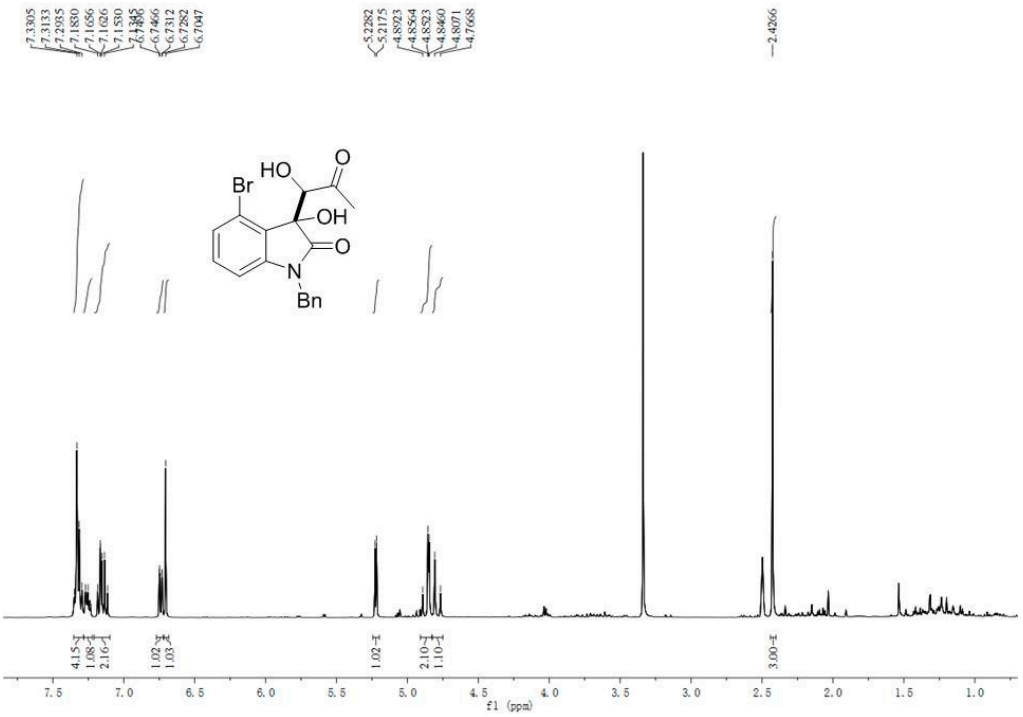
(**a**)



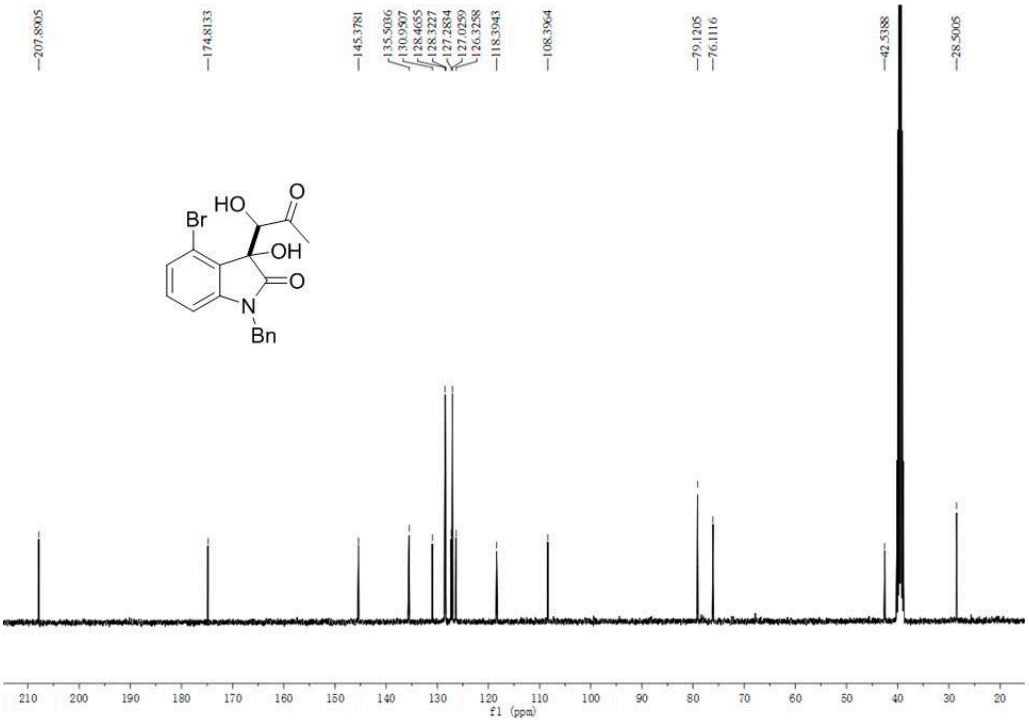
(**b**)

Figure S6. (**a**) ^{1}H NMR and (**b**) ^{13}C NMR of compound **3f**.

Compound 3g



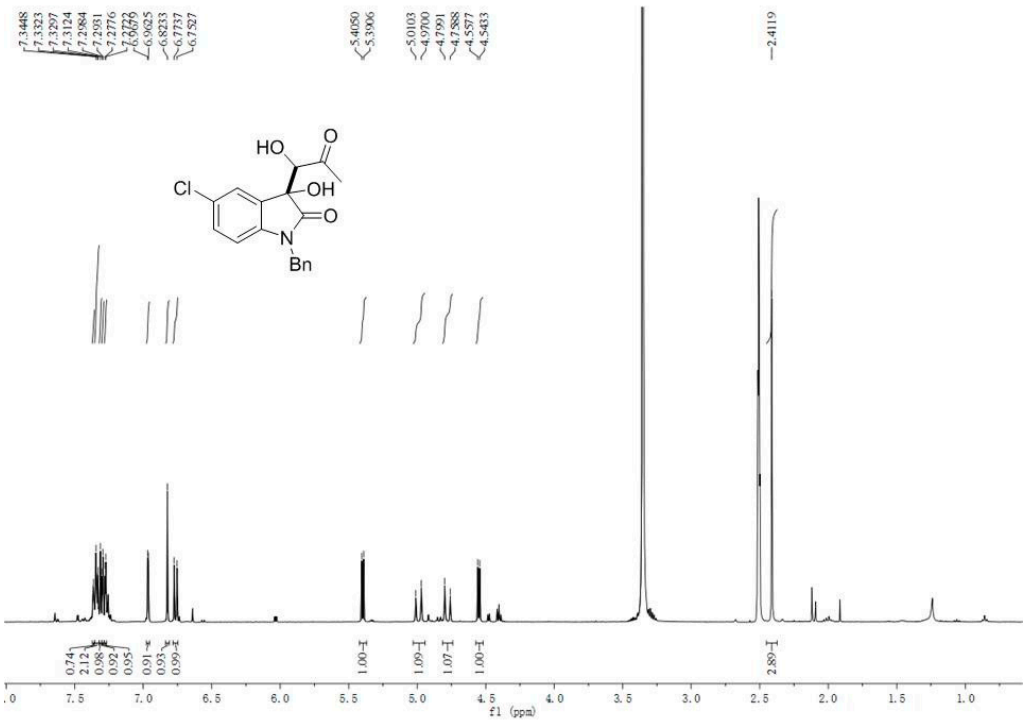
(**a**)



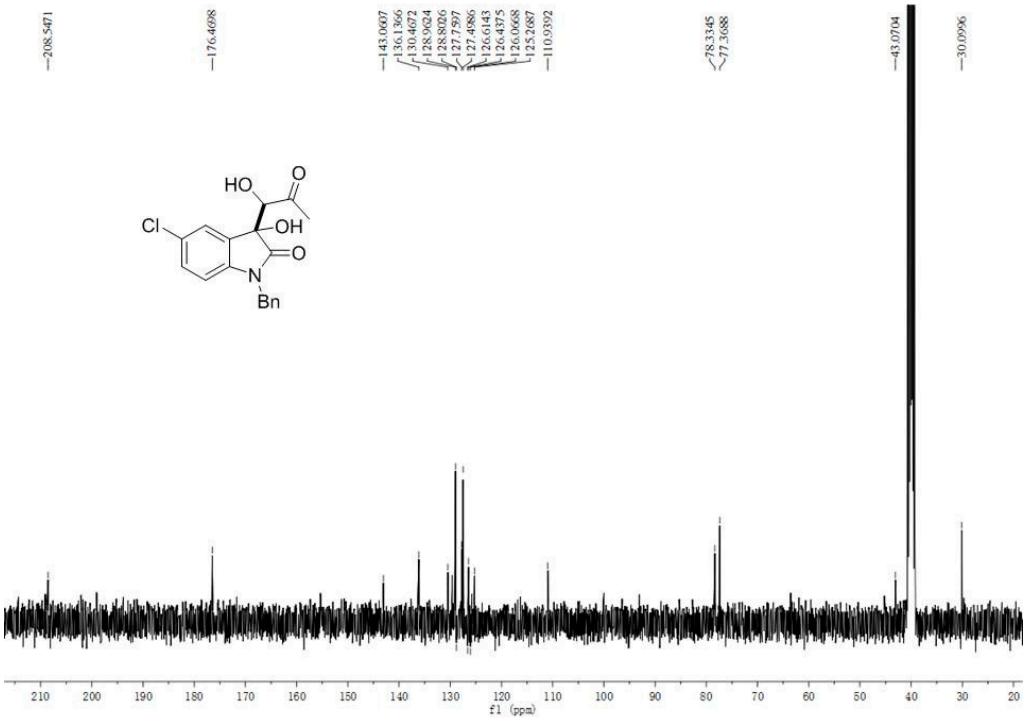
(**b**)

Figure S7. (**a**) ^{1}H NMR and (**b**) ^{13}C NMR of compound **3g**.

Compound 3h



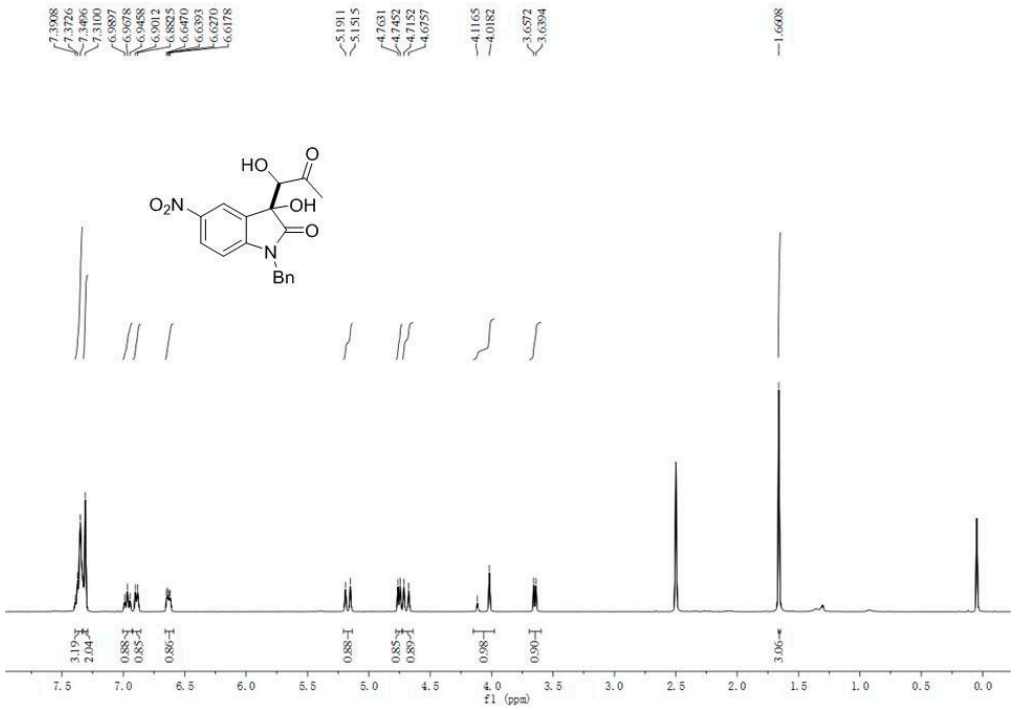
(**a**)



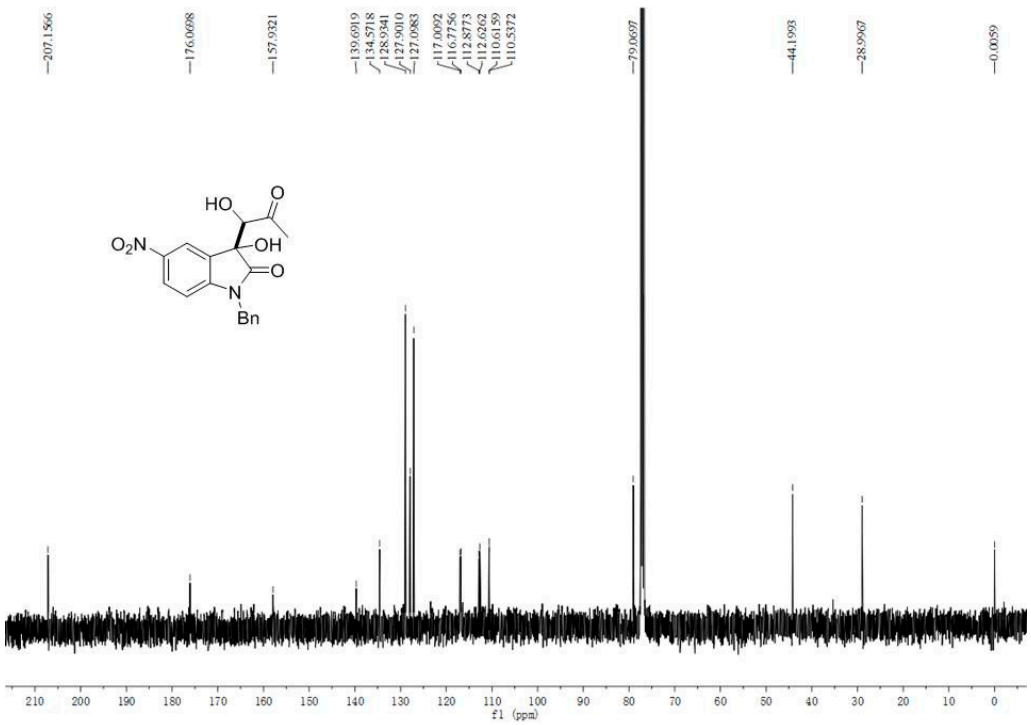
(**b**)

Figure S8. (**a**) ^{1}H NMR and (**b**) ^{13}C NMR of compound **3h**.

Compound 3i



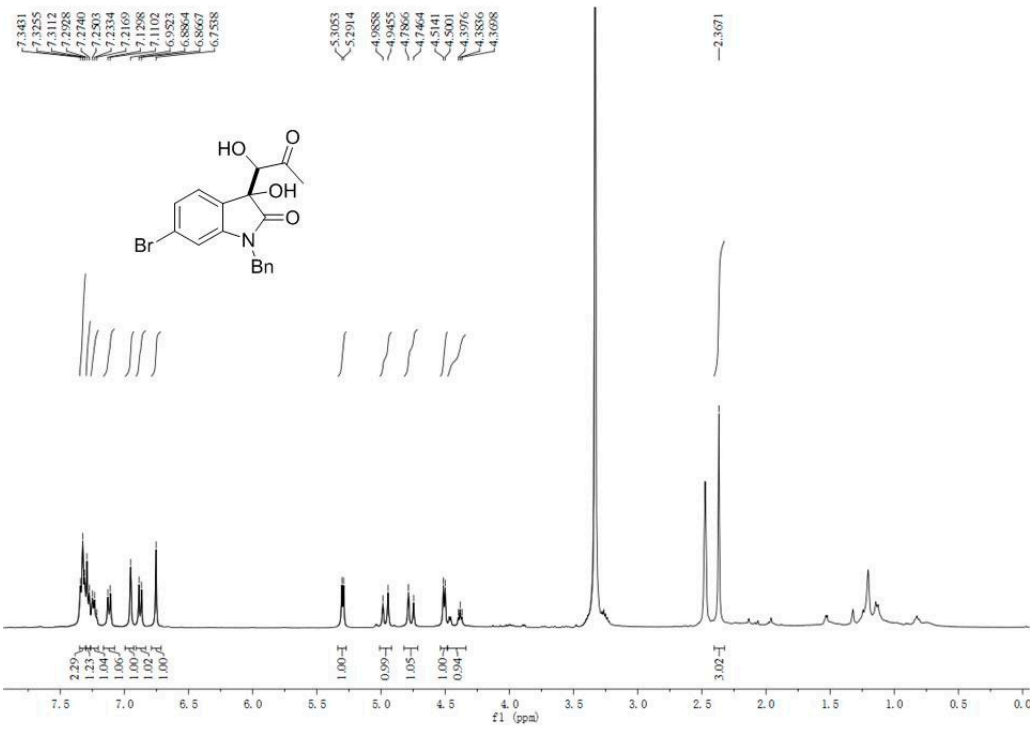
(**a**)



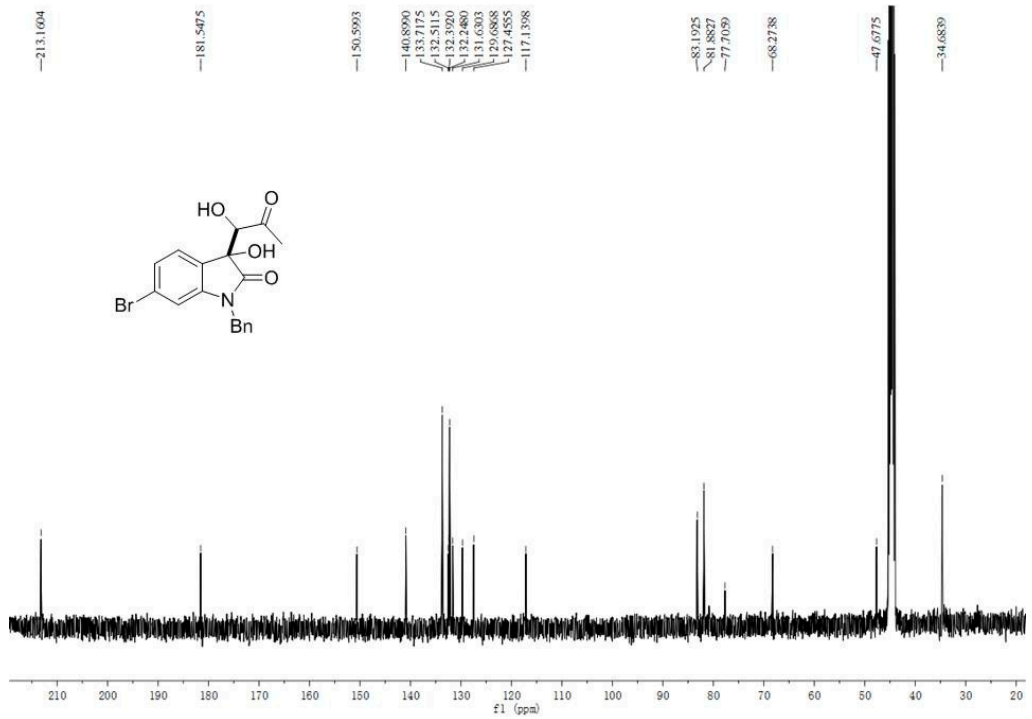
(**b**)

Figure S9. (**a**) ^{1}H NMR and (**b**) ^{13}C NMR of compound **3i**.

Compound 3j



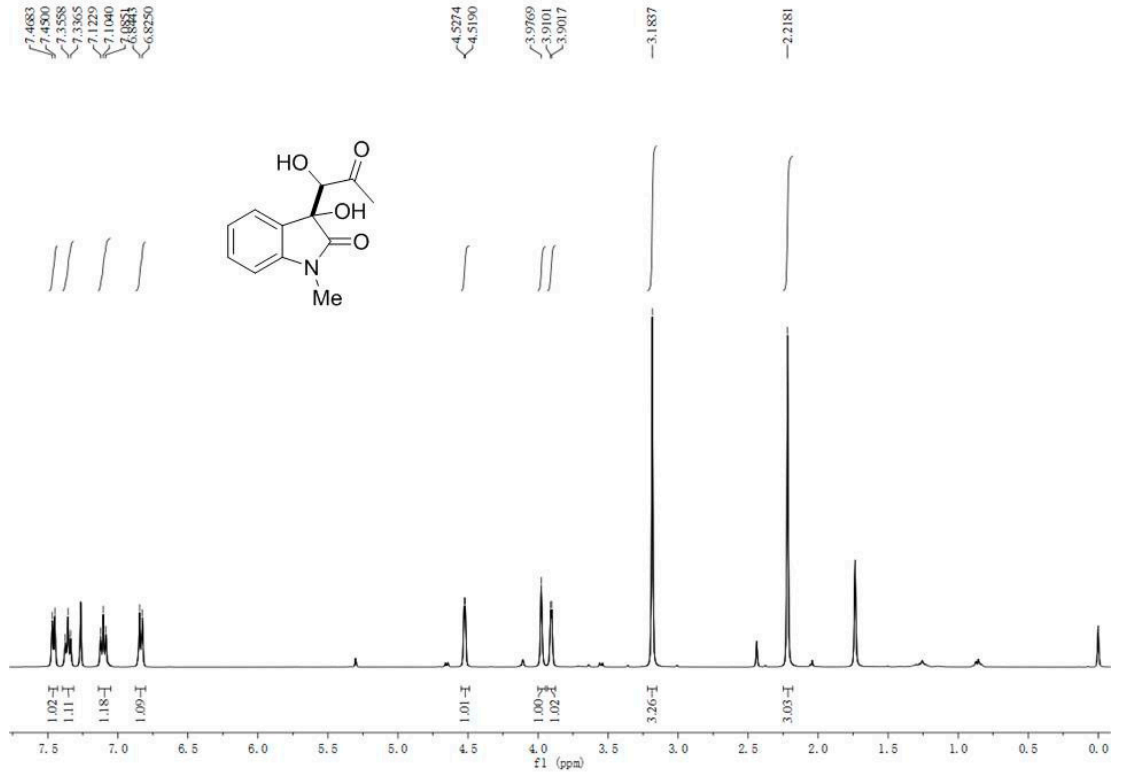
(**a**)



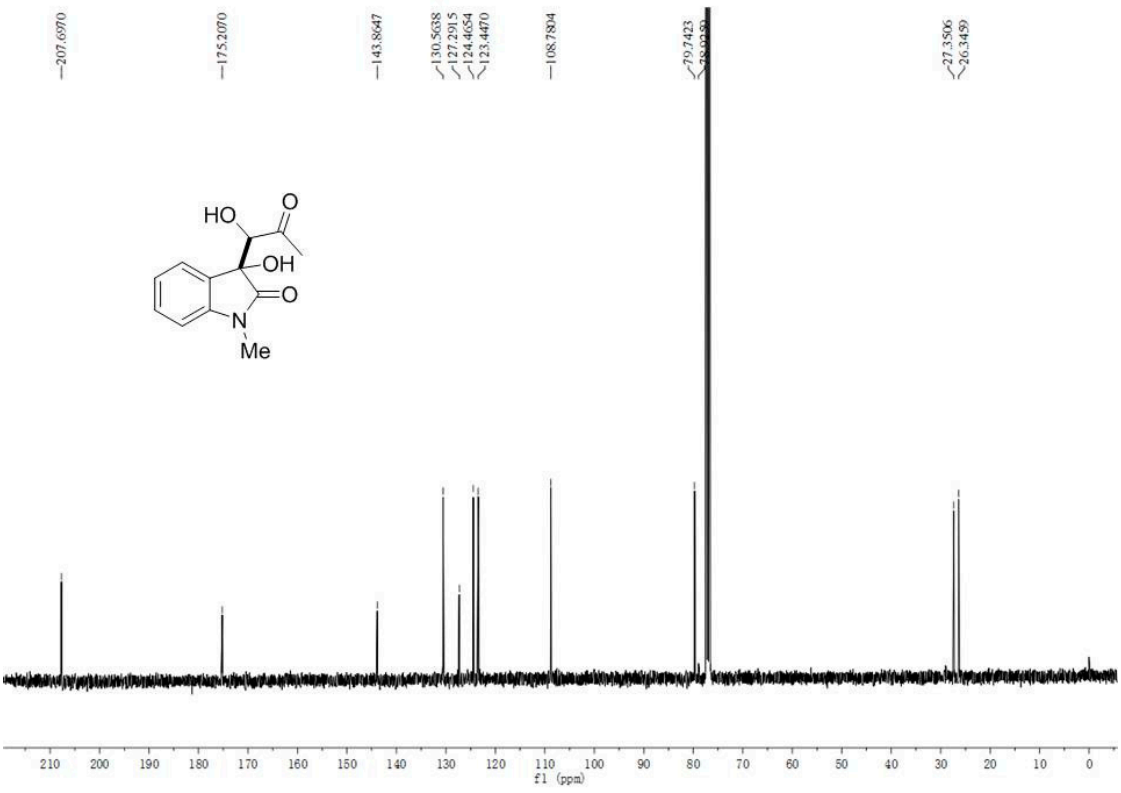
(**b**)

Figure S10. (**a**) ^{1}H NMR and (**b**) ^{13}C NMR of compound **3j**.

Compound 3k



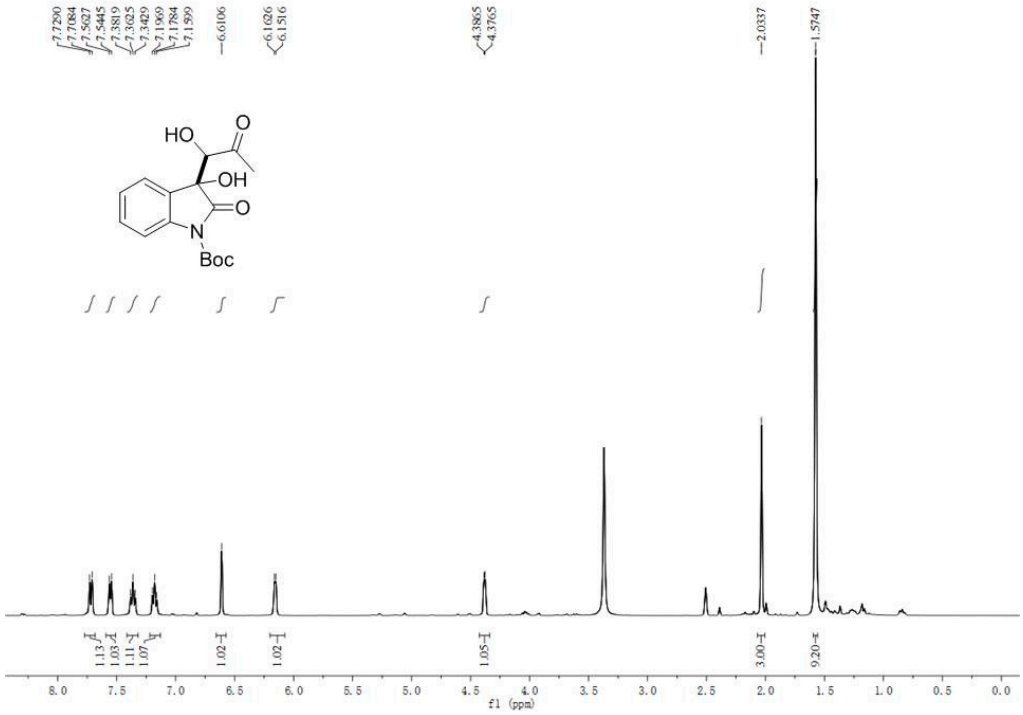
(**a**)



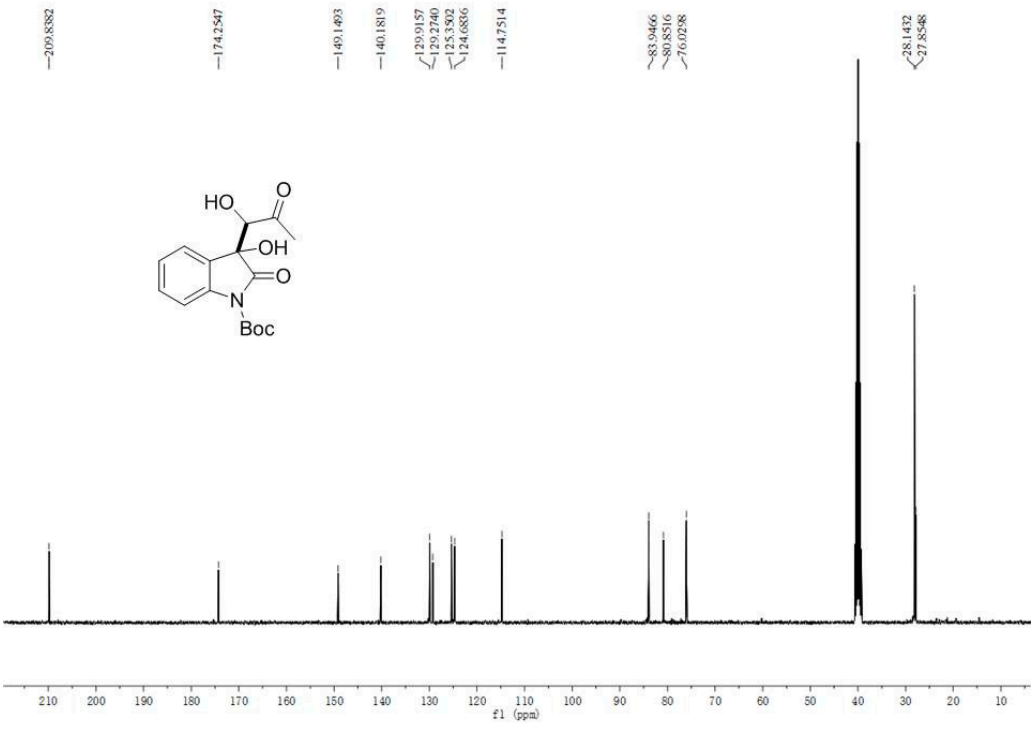
(**b**)

Figure S11. (**a**) ^{1}H NMR and (**b**) ^{13}C NMR of compound **3k**.

Compound 3l



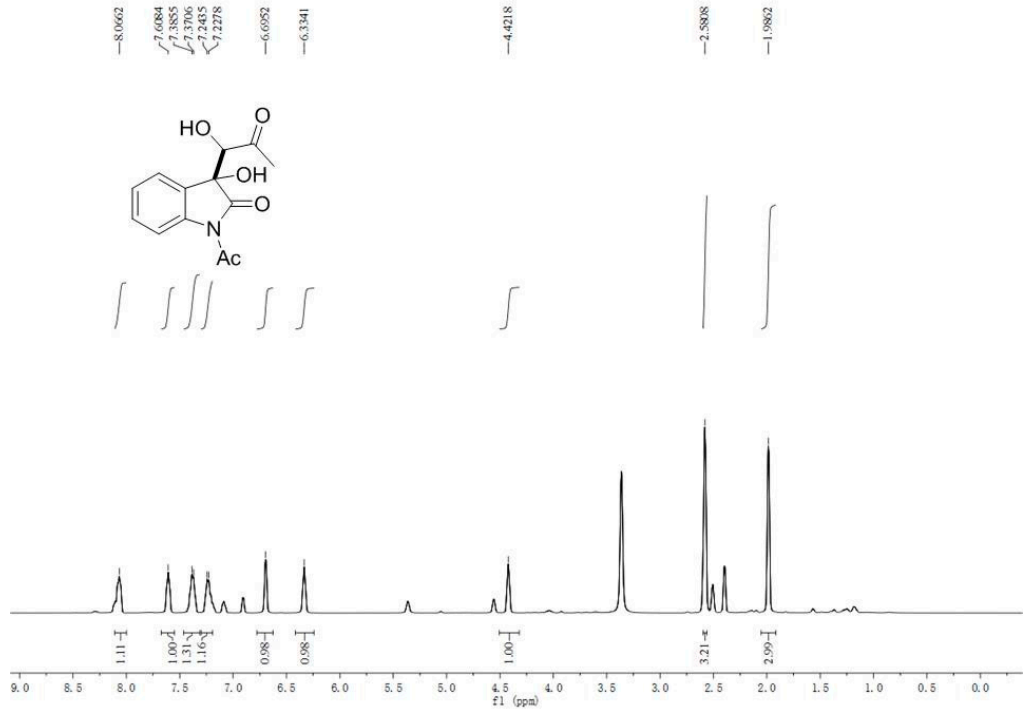
(**a**)



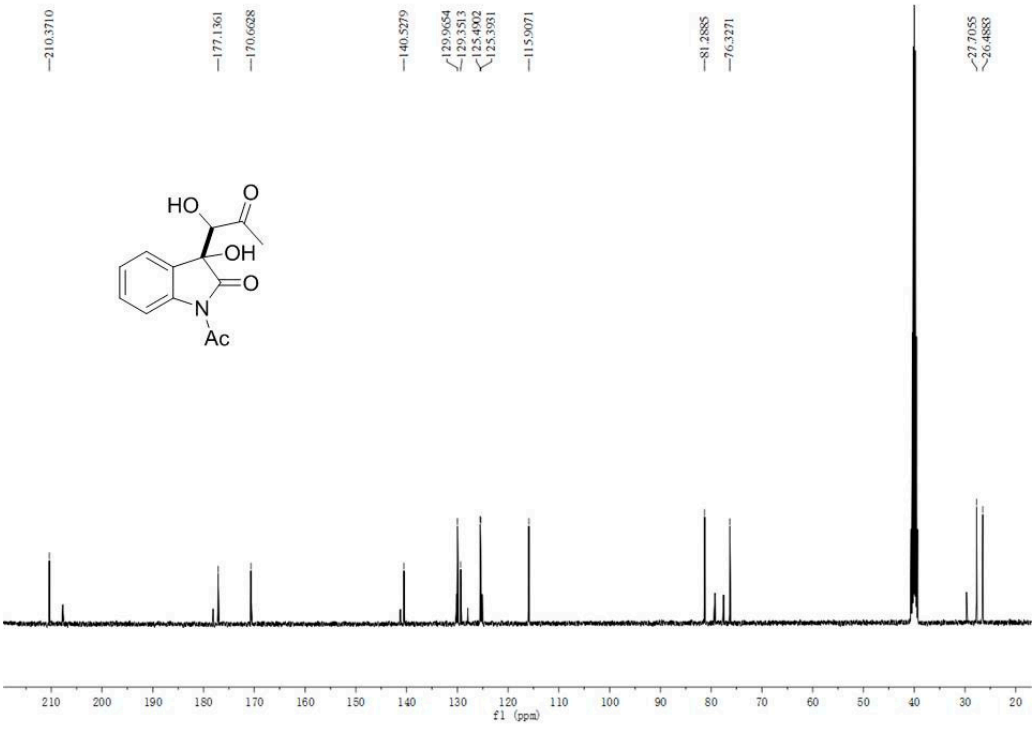
(**b**)

Figure S12. (**a**) ^{1}H NMR and (**b**) ^{13}C NMR of compound **3l**.

Compound 3m



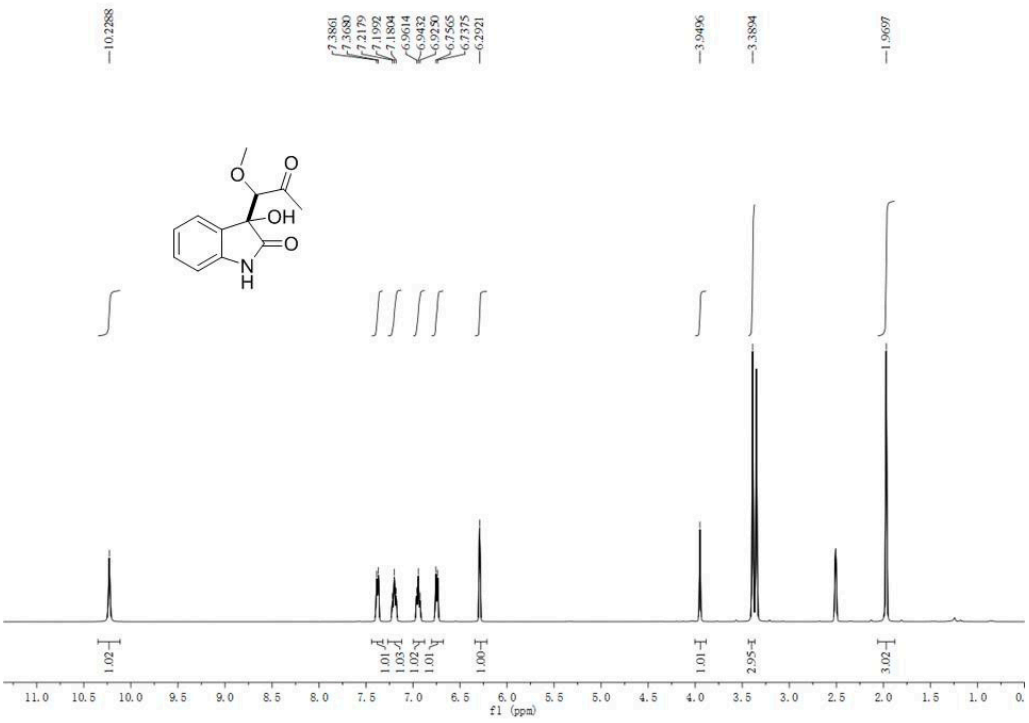
(**a**)



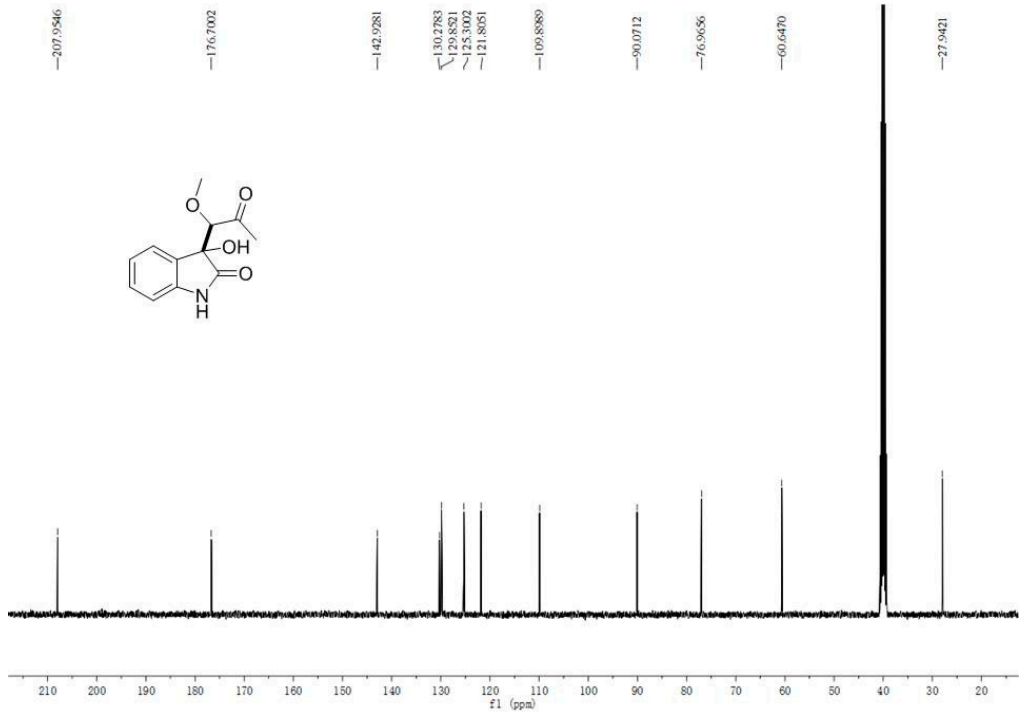
(**b**)

Figure S13. (**a**) ^{1}H NMR and (**b**) ^{13}C NMR of compound **3m**.

Compound 3n



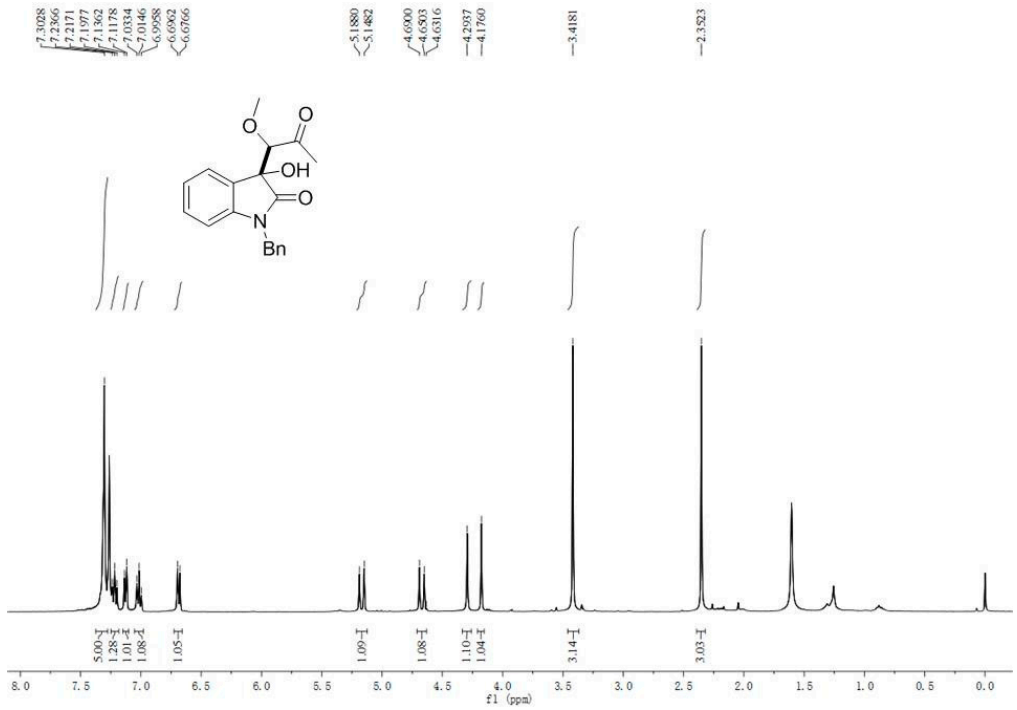
(**a**)



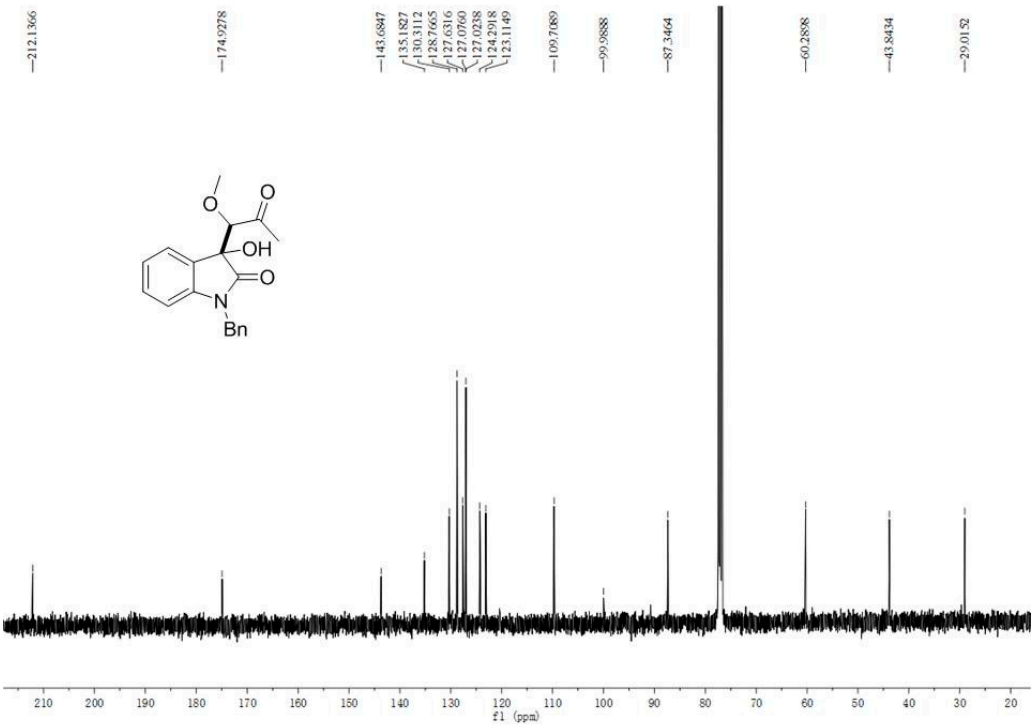
(**b**)

Figure S14. (**a**) ^{1}H NMR and (**b**) ^{13}C NMR of compound **3n**.

Compound 3o



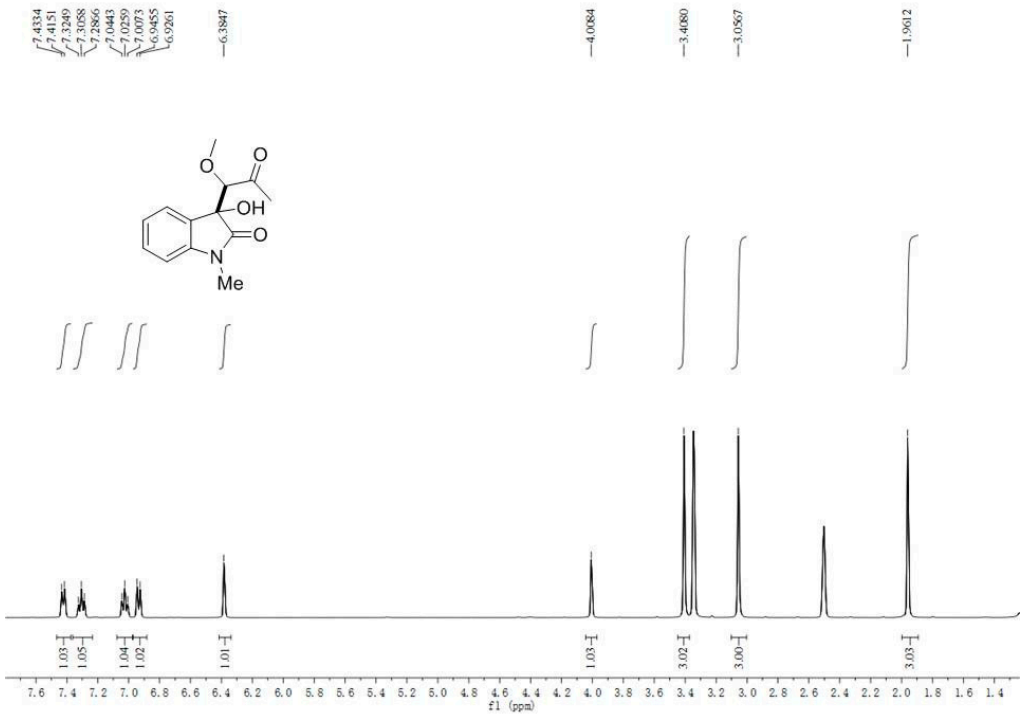
(**a**)



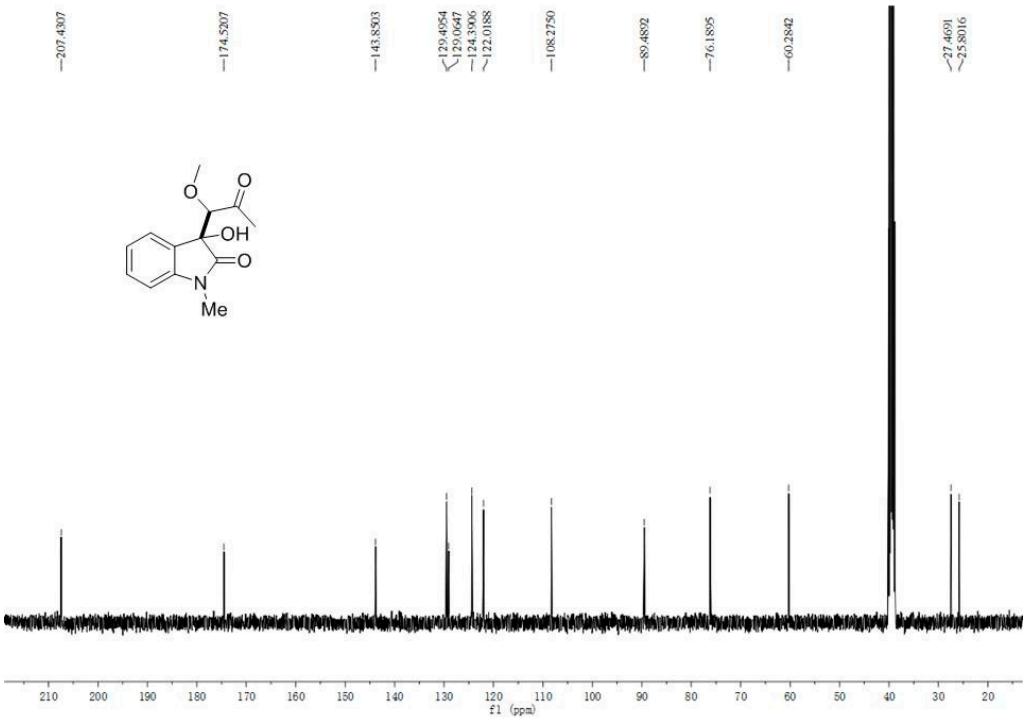
(**b**)

Figure S15. (**a**) ^{1}H NMR and (**b**) ^{13}C NMR of compound **3o**.

Compound 3p



(**a**)

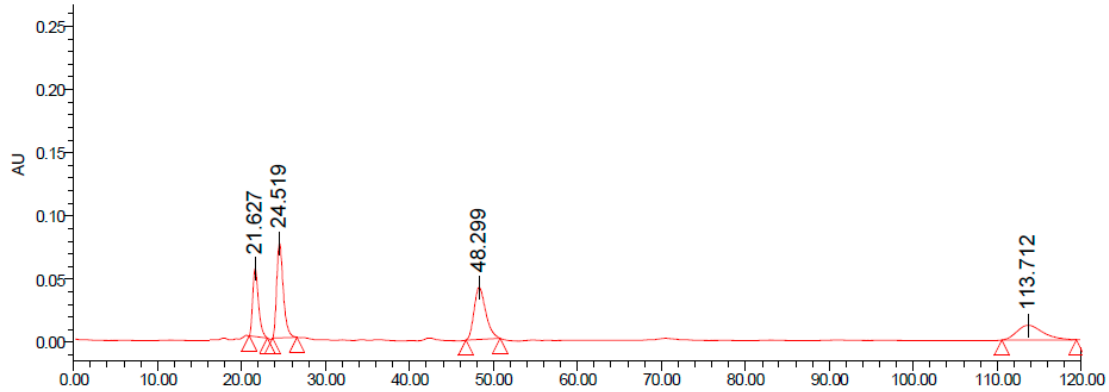


(**b**)

Figure S16. (**a**) ^{1}H NMR and (**b**) ^{13}C NMR of compound **3p**.

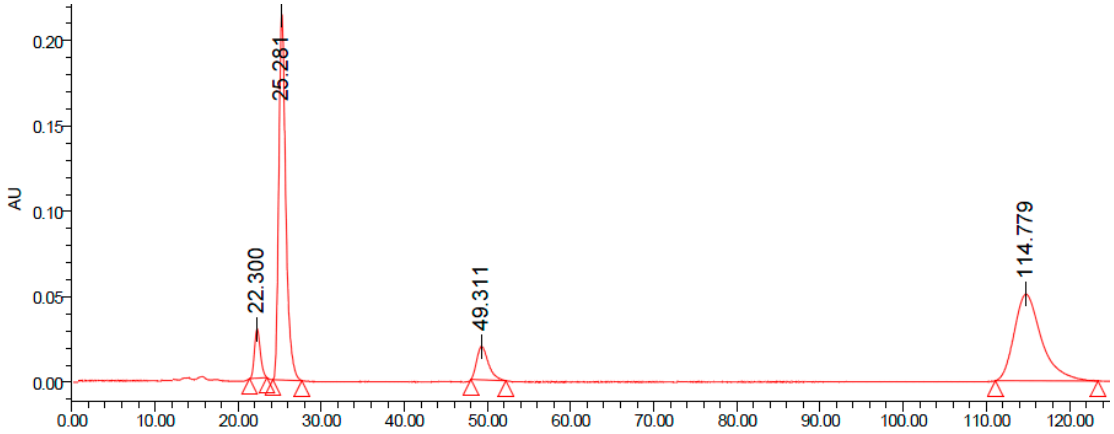
HPLC Analysis

Compound 3a (racemate)



	Ret. Time	Area	Area %	Height
1	21.627	2574703	19.58	53778
2	24.519	4091703	31.11	75039
3	48.299	3971742	30.20	41240
4	113.712	2514296	19.12	11672

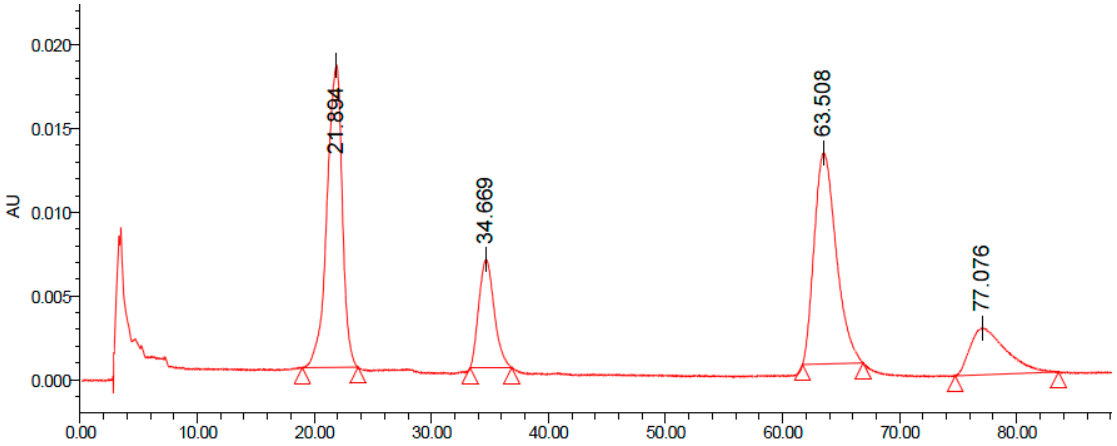
Compound 3a



	Ret. Time	Area	Area %	Height
1	22.300	1423940	5.19	28837
2	25.281	12511349	45.64	213961
3	49.311	1902702	6.94	19554
4	114.779	11577032	42.23	50700

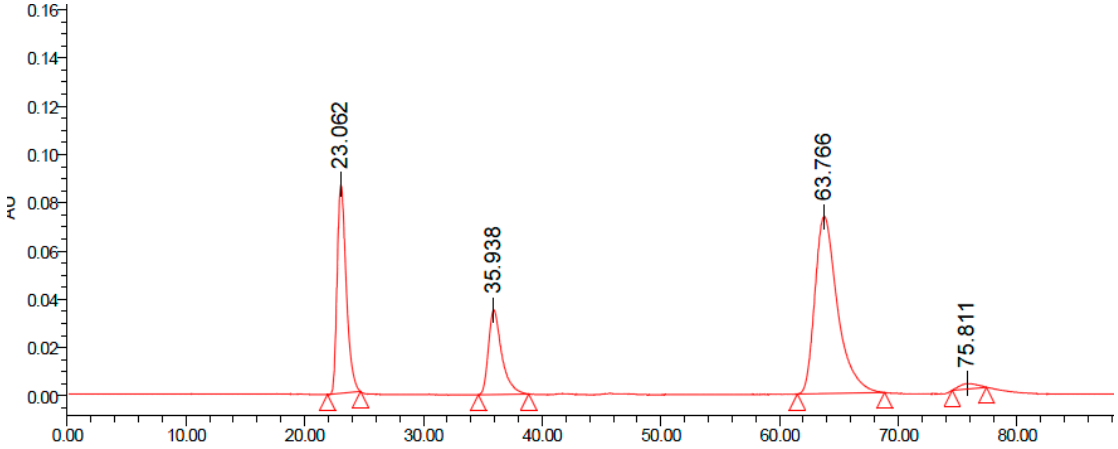
Figure S17. HPLC analysis of compound **3a**.

Compound 3b (racemate)



	Ret. Time	Area	Area %	Height
1	21.894	1630518	36.60	18056
2	34.669	588492	13.21	6451
3	63.508	1648458	37.00	12612
4	77.076	587266	13.18	2785

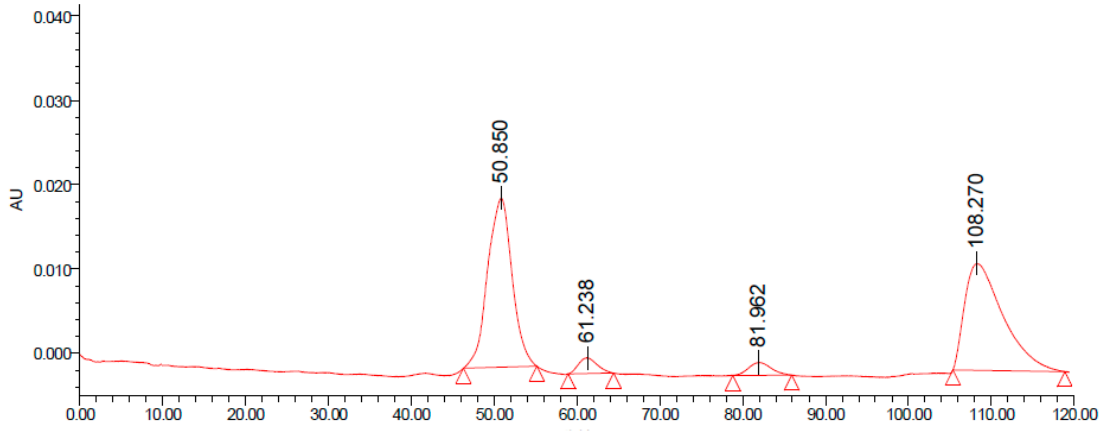
Compound 3b



	Ret. Time	Area	Area %	Height
1	23.062	4574949	26.49	86453
2	35.938	2729398	15.81	35038
3	63.766	9734256	56.37	73446
4	75.811	229486	1.33	2237

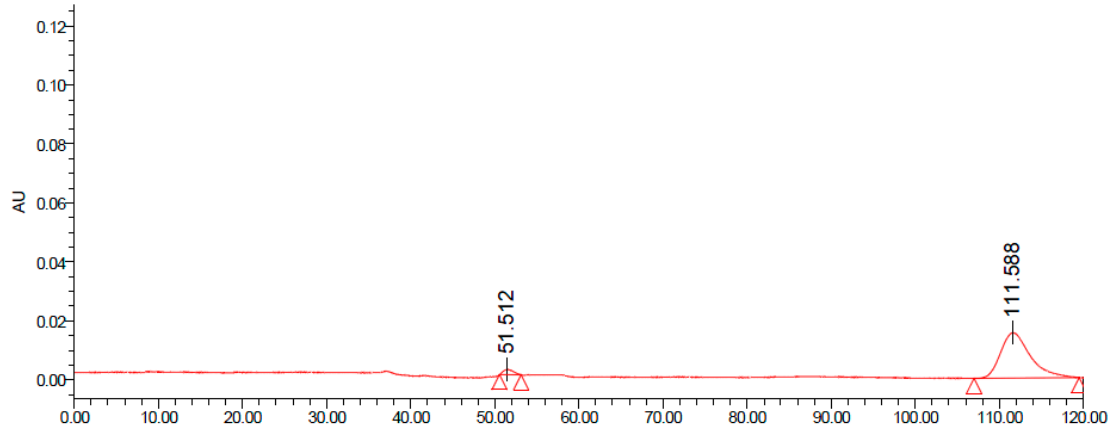
Figure S18. HPLC analysis of compound **3b**.

Compound 3d(racemate)



	Ret. Time	Area	Area %	Height
1	50.850	4120201	46.87	20070
2	61.238	291322	3.31	1868
3	81.962	290028	3.30	1549
4	108.270	4089697	46.52	12663

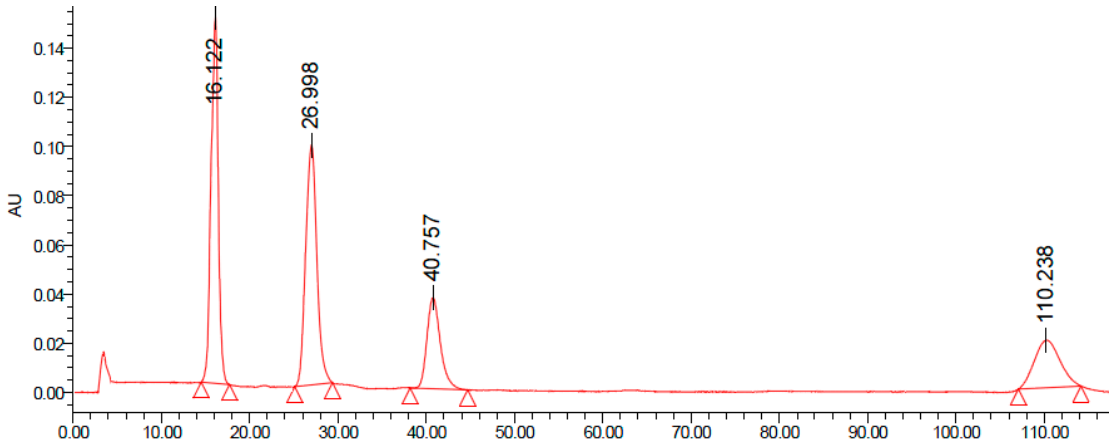
Compound 3d



	Ret. Time	Area	Area %	Height
1	51.512	152854	3.89	1773
2	111.588	3772464	96.11	15369

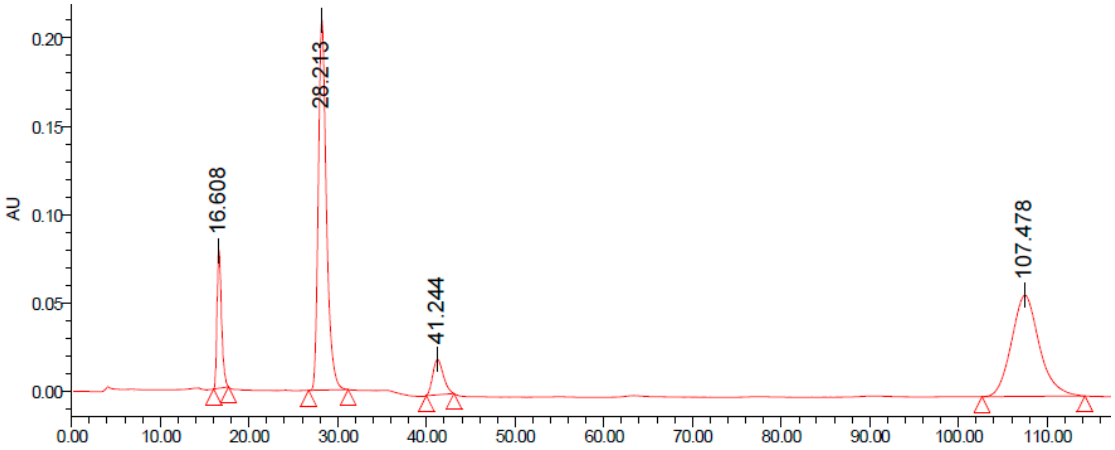
Figure S19. HPLC analysis of compound **3d**.

Compound 3e (racemate)



	Ret. Time	Area	Area %	Height
1	16.122	8494380	34.11	149142
2	26.998	8611687	34.58	97424
3	40.757	3899042	15.66	37092
4	110.238	3900717	15.66	19323

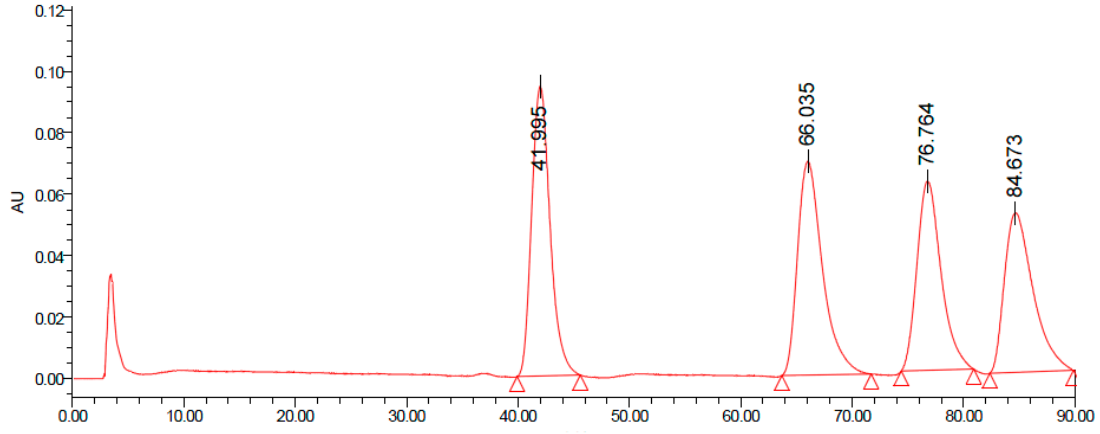
Compound 3e



	Ret. Time	Area	Area %	Height
1	16.608	2761807	9.14	77958
2	28.213	13363839	44.22	209393
3	41.244	1653048	5.47	19991
4	107.478	12445786	41.18	57172

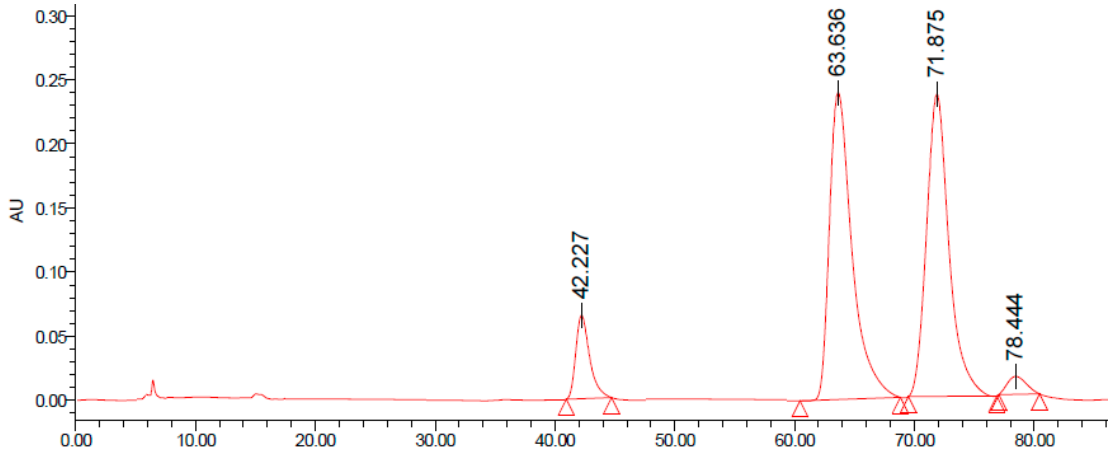
Figure S20. HPLC analysis of compound **3e**.

Compound 3f (racemate)



	Ret. Time	Area	Area %	Height
1	41.995	10825617	26.95	94179
2	66.035	10815666	26.93	69498
3	76.764	9263953	23.06	61476
4	84.673	9261296	23.06	51806

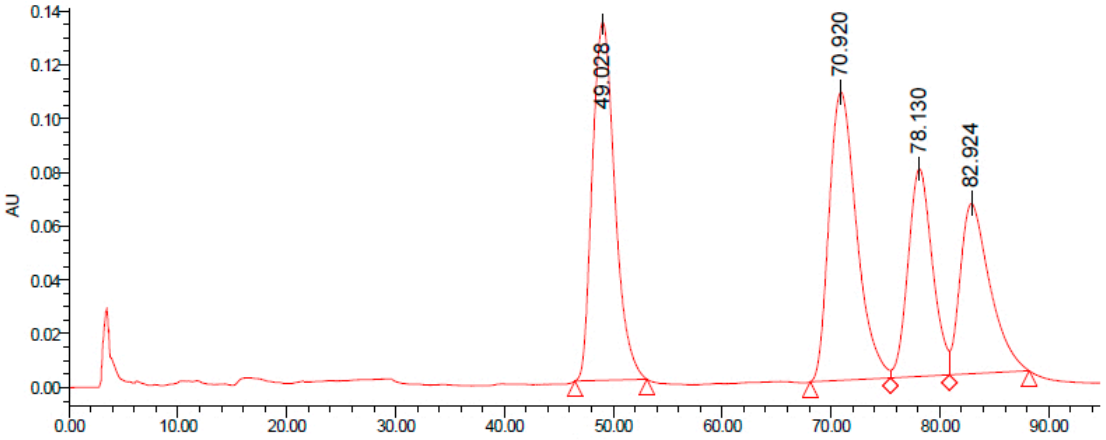
Compound 3f



	Ret. Time	Area	Area %	Height
1	42.227	5202974	7.54	64997
2	63.636	31467205	45.63	239199
3	71.875	30753578	44.59	235472
4	78.444	1543266	2.24	13915

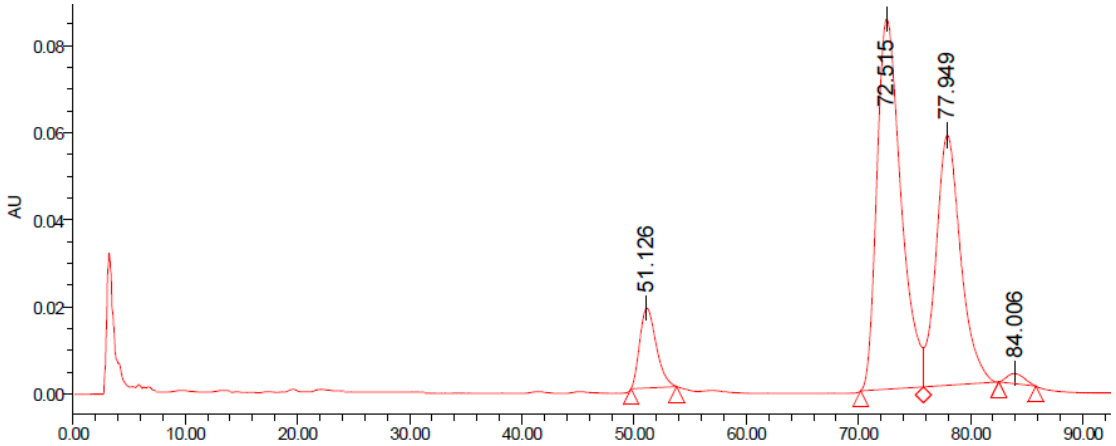
Figure S21. HPLC analysis of compound **3**f.

Compound 3g (racemate)



	Ret. Time	Area	Area %	Height
1	49.028	19085126	30.77	133069
2	70.920	18907400	30.48	107050
3	78.130	11991768	19.33	77101
4	82.924	12050711	19.43	63243

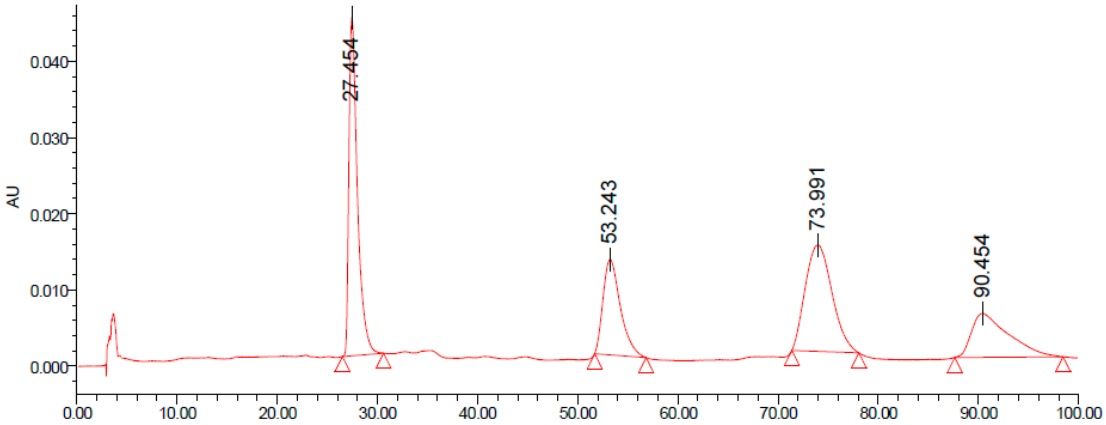
Compound 3g



	Ret. Time	Area	Area %	Height
1	51.126	1863758	7.88	18330
2	72.515	12713894	53.79	85006
3	77.949	8808075	37.26	57360
4	84.006	251272	1.06	2335

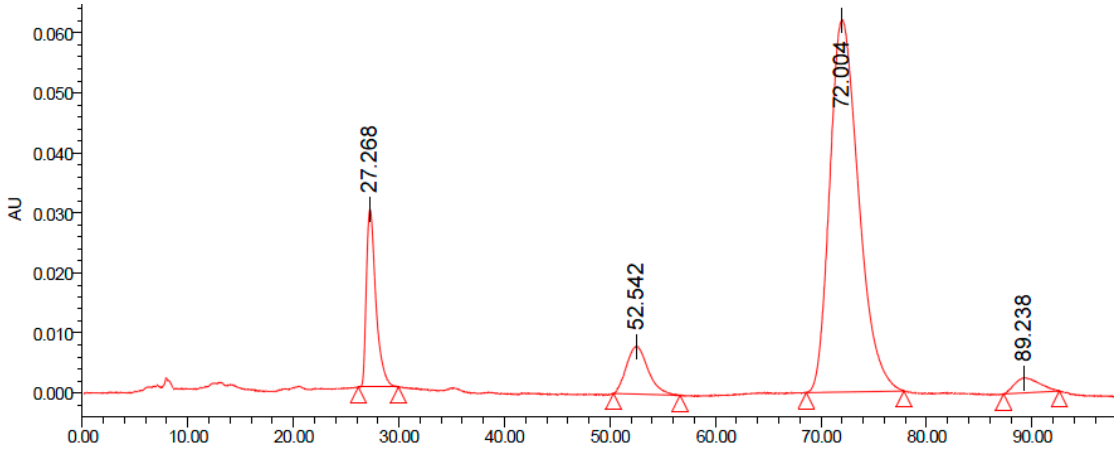
Figure S22. HPLC analysis of compound **3g**.

Compound 3h (racemate)



	Ret. Time	Area	Area %	Height
1	27.454	2622660	31.95	44402
2	53.243	1510491	18.40	12559
3	73.991	2595541	31.62	13933
4	90.454	1479809	18.03	5778

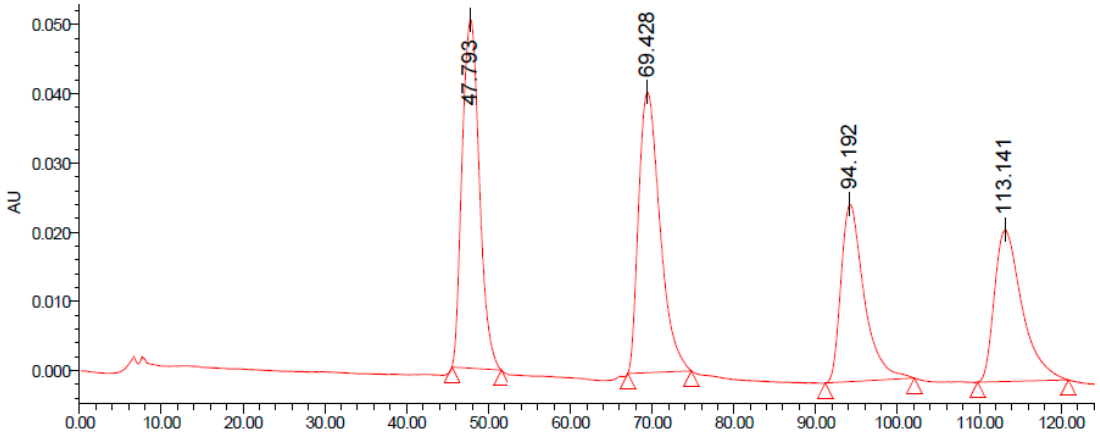
Compound 3h



	Ret. Time	Area	Area %	Height
1	27.268	1854323	12.18	29658
2	52.542	1137354	7.47	7937
3	72.004	11817340	77.64	61975
4	89.238	410935	2.70	2480

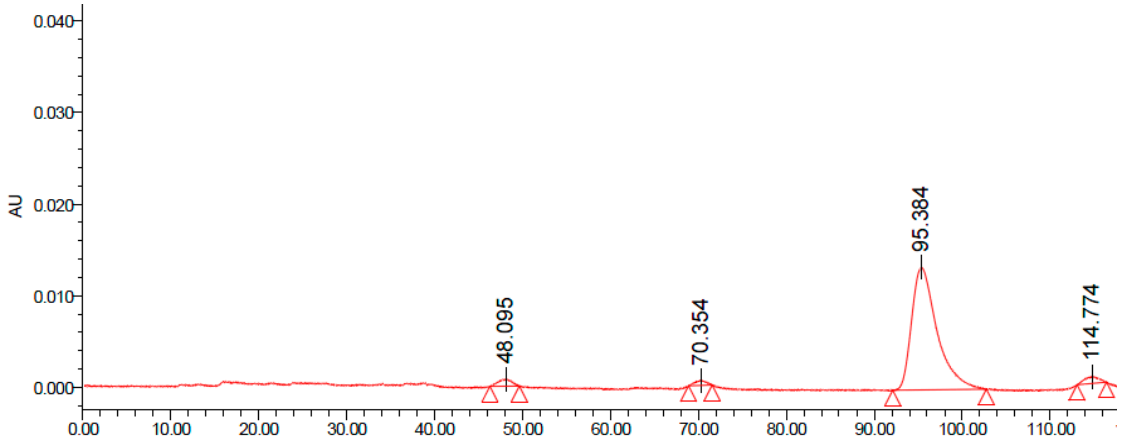
Figure S23. HPLC analysis of compound **3h**.

Compound 3i (racemate)



	Ret. Time	Area	Area %	Height
1	47.793	7342981	29.46	50422
2	69.428	7377598	29.60	40532
3	94.192	5059229	20.30	25620
4	113.141	5141651	20.63	21895

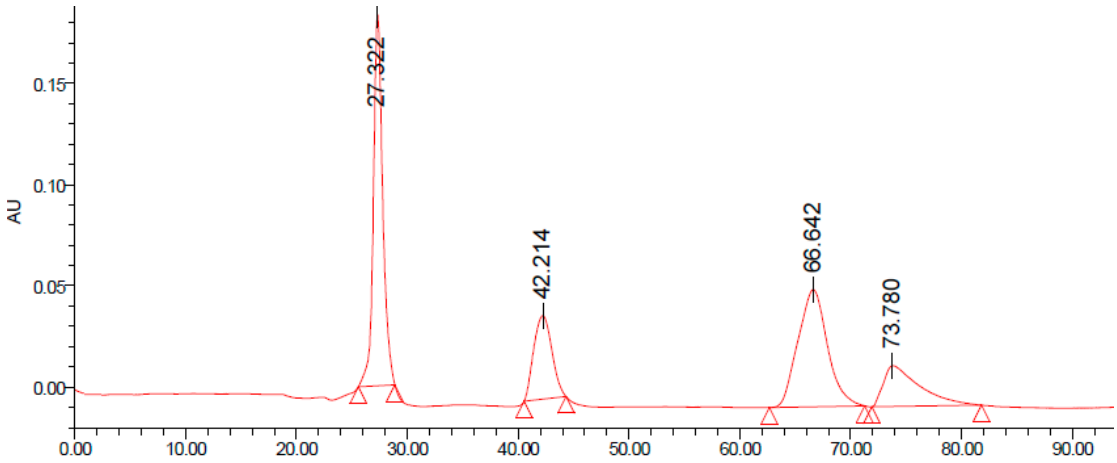
Compound 3i



	Ret. Time	Area	Area %	Height
1	48.095	80290	2.78	736
2	70.354	48685	1.68	507
3	95.384	2675444	92.49	13360
4	114.774	88295	3.05	743

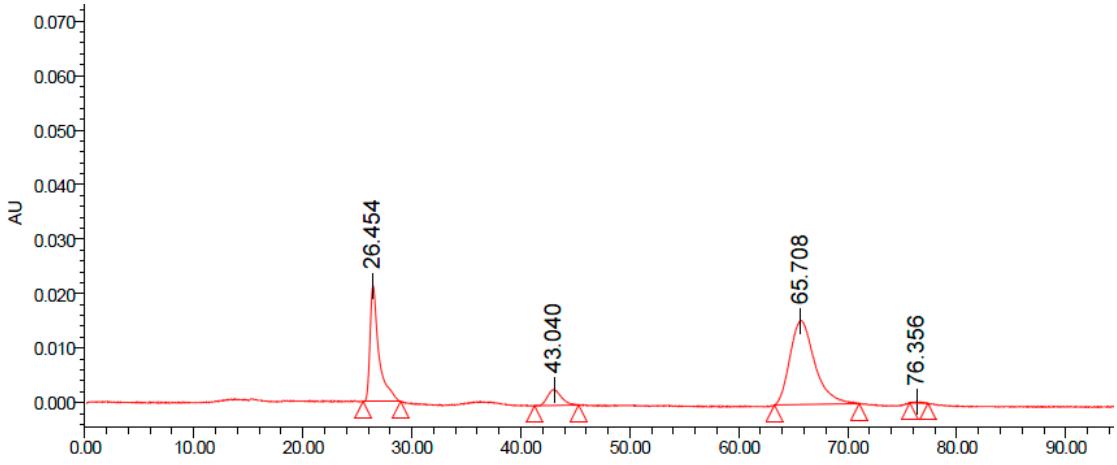
Figure S24. HPLC analysis of compound **3i**.

Compound 3j (racemate)



	Ret. Time	Area	Area %	Height
1	27.322	10715317	34.93	183115
2	42.214	4688836	15.28	41254
3	66.642	10691772	34.85	57835
4	73.780	4581627	14.93	20182

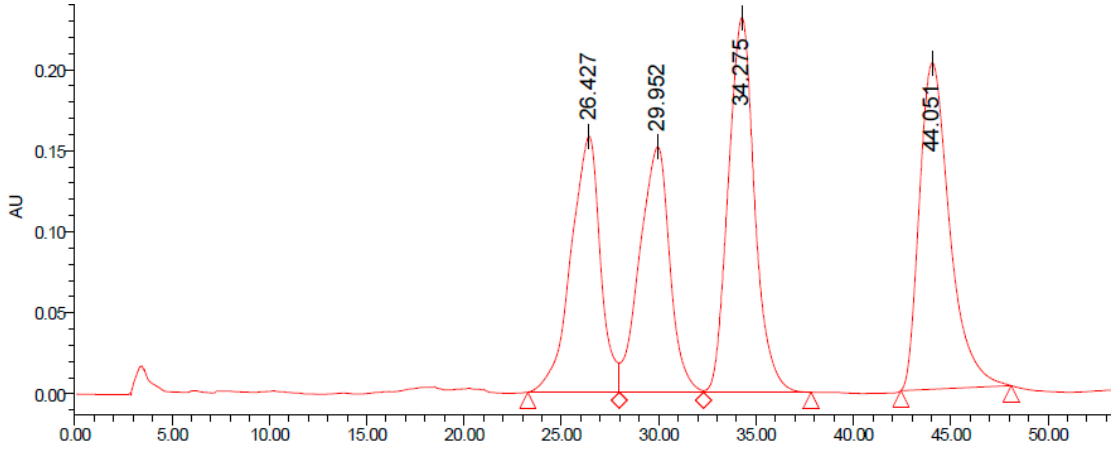
Compound 3j



	Ret. Time	Area	Area %	Height
1	26.454	1189809	30.56	21265
2	43.040	256113	6.58	2898
3	65.708	2436013	62.56	15370
4	76.356	11885	0.31	215

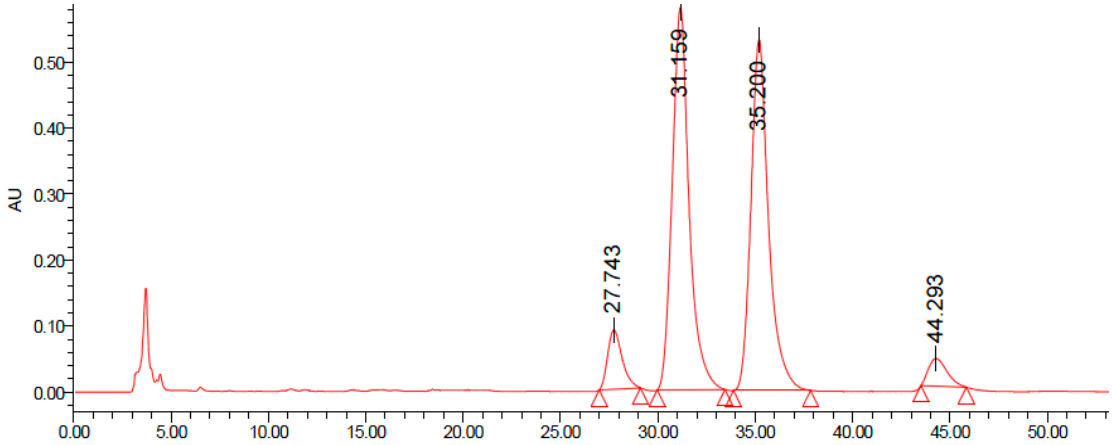
Figure S25. HPLC analysis of compound **3j**.

Compound 3k (racemate)



	Ret. Time	Area	Area %	Height
1	26.427	16580543	21.69	157903
2	29.952	16310003	21.34	151332
3	34.275	21786570	28.50	231237
4	44.051	21754794	28.46	201443

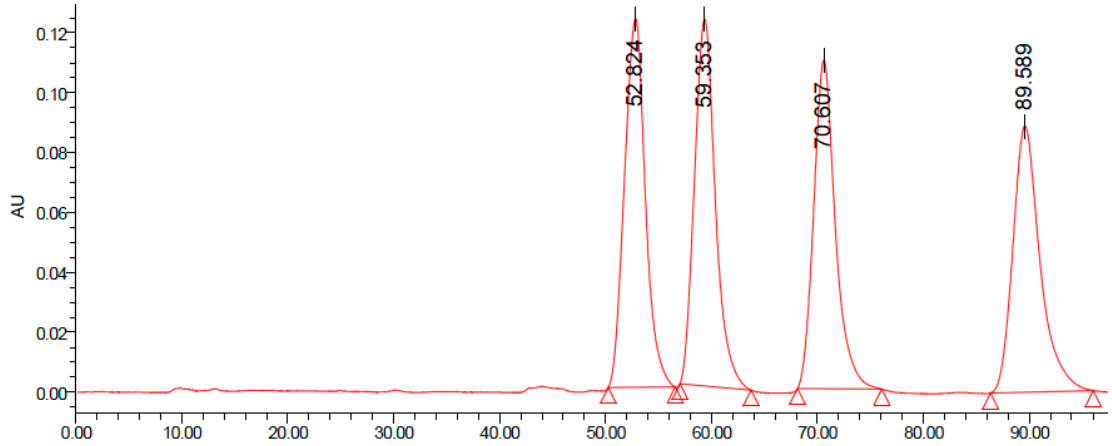
Compound 3k



	Ret. Time	Area	Area %	Height
1	27.743	4636137	6.12	89840
2	31.159	34854142	46.02	579477
3	35.200	33449369	44.17	531981
4	44.293	2793318	3.69	41880

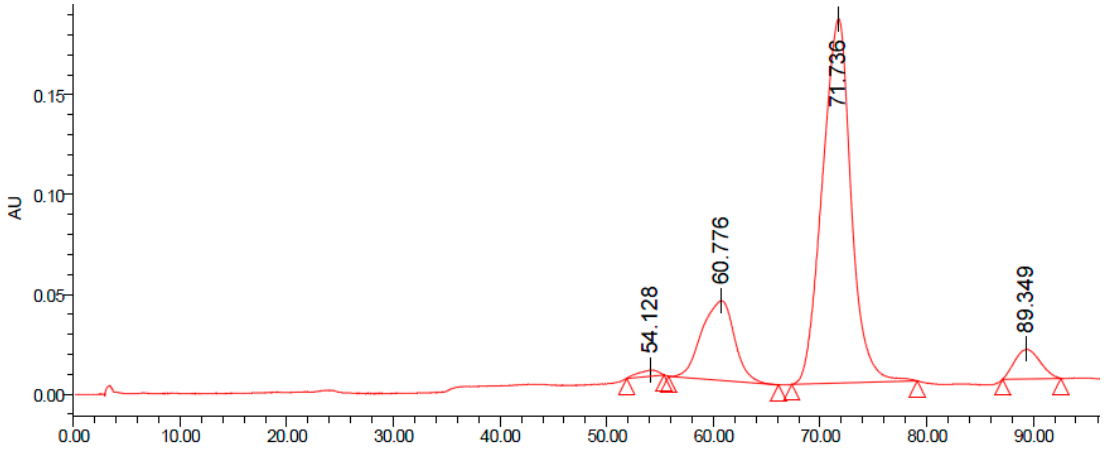
Figure S26. HPLC analysis of compound **3k**.

Compound 3n (racemate)



	Ret. Time	Area	Area %	Height
1	52.824	16830548	25.89	123155
2	59.353	16741456	25.75	122464
3	70.607	15611242	24.01	109716
4	89.589	15825348	24.34	88785

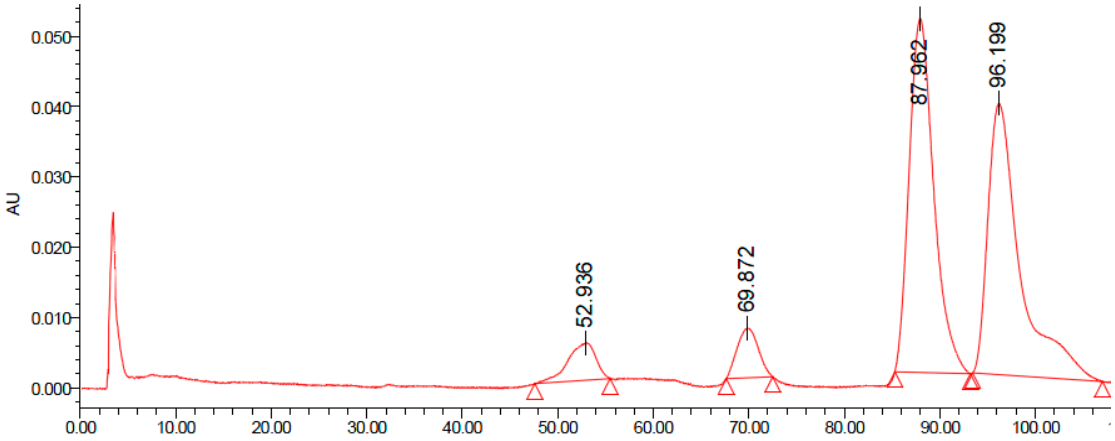
Compound 3n



	Ret. Time	Area	Area %	Height
1	54.128	392130	0.86	3005
2	60.776	8447986	18.55	39909
3	71.736	34267830	75.22	182414
4	89.349	2445939	5.37	14827

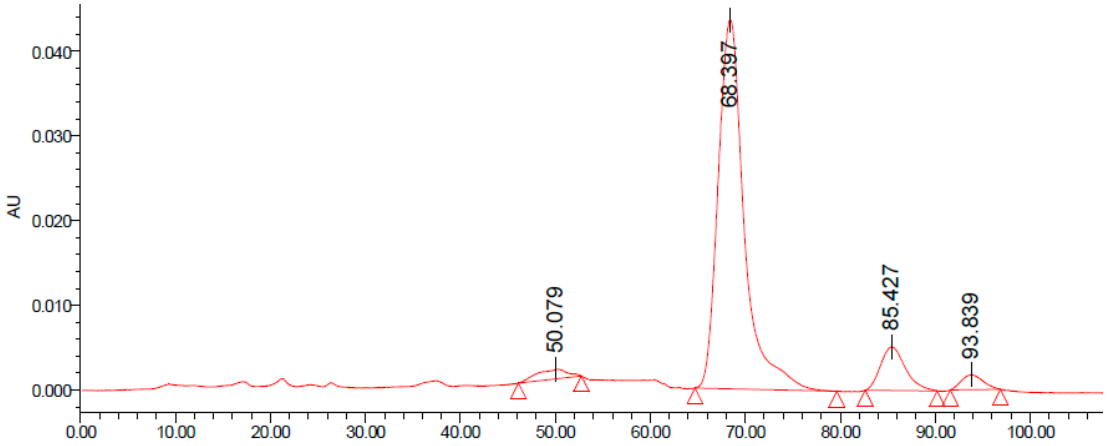
Figure S27. HPLC analysis of compound **3n**.

Compound 3o (racemate)



	Ret. Time	Area	Area %	Height
1	52.936	1079000	5.33	5264
2	69.872	1083486	5.35	7046
3	87.962	9045193	44.65	50333
4	96.199	9051105	44.68	38576

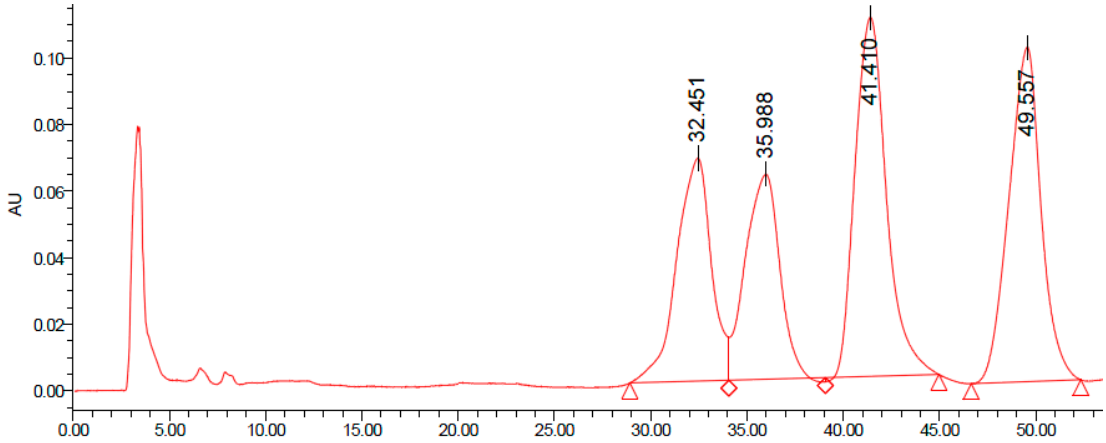
Compound 3o



	Ret. Time	Area	Area %	Height
1	50.079	261467	2.66	111(
2	68.397	8353573	85.00	43526
3	85.427	934197	9.51	5148
4	93.839	278160	2.83	1763

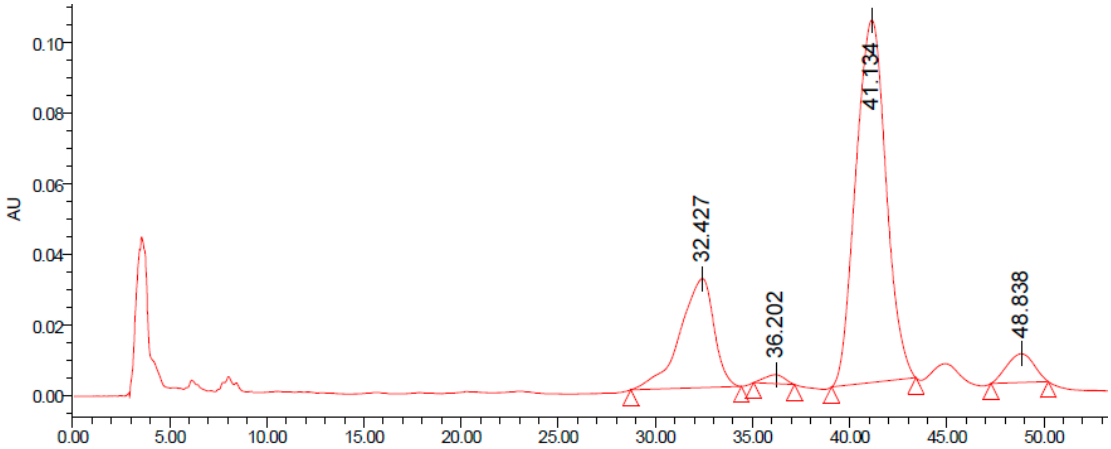
Figure S28. HPLC analysis of compound **3o**.

Compound 3p (racemate)



	Ret. Time	Area	Area %	Height
1	32.451	8395407	20.99	66983
2	35.988	7688292	19.22	61529
3	41.410	12252009	30.63	107863
4	49.557	11666667	29.16	100481

Compound 3p



	Ret. Time	Area	Area %	Height
1	32.427	3741394	23.62	30901
2	36.202	177277	1.12	2518
3	41.134	1113431(	70.31	102689
4	48.838	784100	4.95	8150

Figure S29. HPLC analysis of compound **3p**.