

Supporting Information:

Enantioselective Rearrangement of Indolyl Carbonates Catalyzed by Chiral DMAP-*N*-oxides

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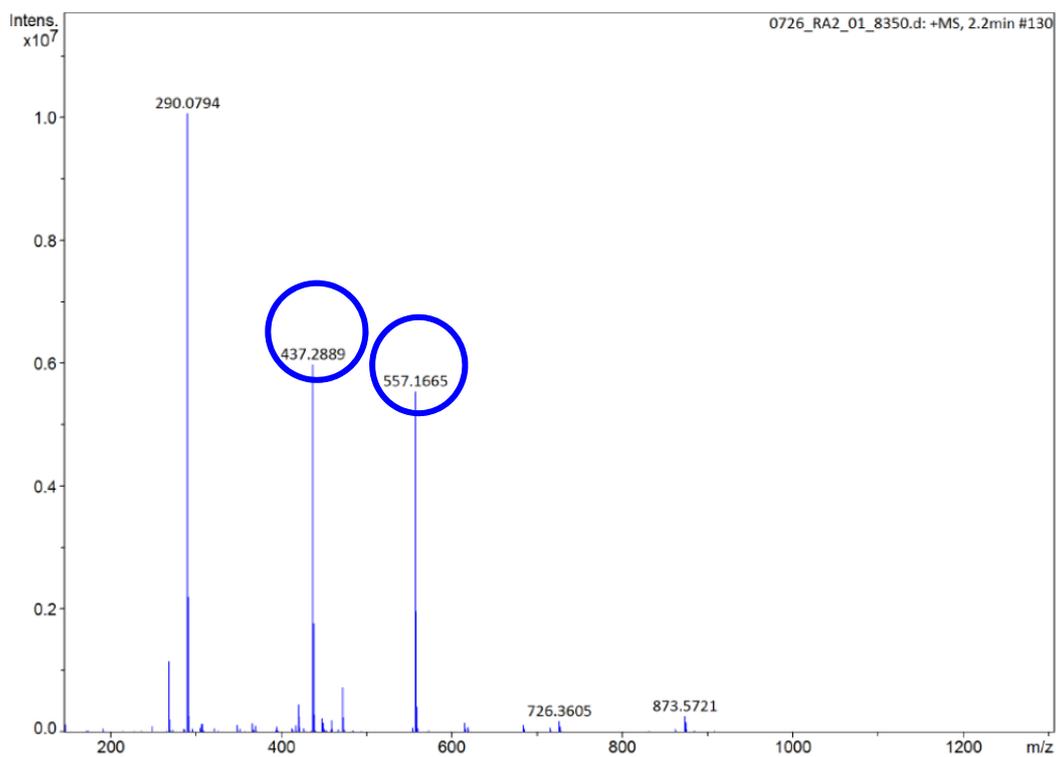
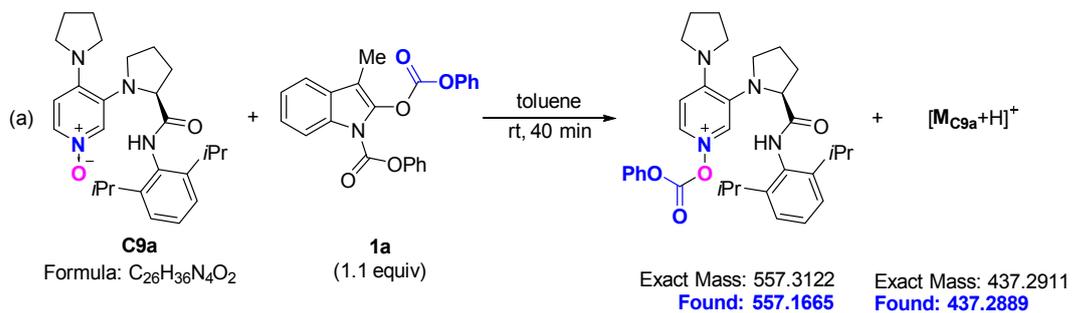
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1. General information

¹H NMR spectra were recorded on Bruker Avance III HD 600 or Avance 400 MHz spectrometer. Chemical shifts are recorded in ppm relative to tetramethylsilane and with the solvent resonance as the internal standard. Data are reported as follows: chemical shift, multiplicity (s = singlet, d = doublet; t = triplet; q = quartet; sext = sextet; br = broad, m = multiplet), coupling constants (Hz), integration. ¹³C NMR data were collected on Bruker Avance III HD 150 or Avance 100 MHz spectrometer. Chemical shifts are reported in ppm from the tetramethylsilane with the solvent resonance as internal standard. Enantiomer excesses were determined by chiral HPLC analysis on Chiralcel ADH/ODH/IE in comparison with the authentic racemates. Chiral HPLC analysis recorded on Thermo scientific Dionex Ultimate 3000 and Agilent Technologies 1260 Infinity. Optical rotations were reported as follows: $[\alpha]_D^{25}$ (c: g/100 mL, in solvent). Optical rotations recorded on Autopol Automatic Polarimeter. HRMS was recorded on an ABI/Sciex QStar Mass Spectrometer (ESI). Toluene and THF were freshly distilled from sodium under nitrogen prior to use. CH₂Cl₂ was distilled from CaH₂ under nitrogen prior to use. Other solvents used for work-up and purification purposes were purchased in technical grade quality and distilled by rotary evaporator before use. The chiral DMAP-*N*-oxides **C9a-C9f** and catalyst **C10a** were synthesized by the same procedure in the literature.¹

2. HRMS experiments



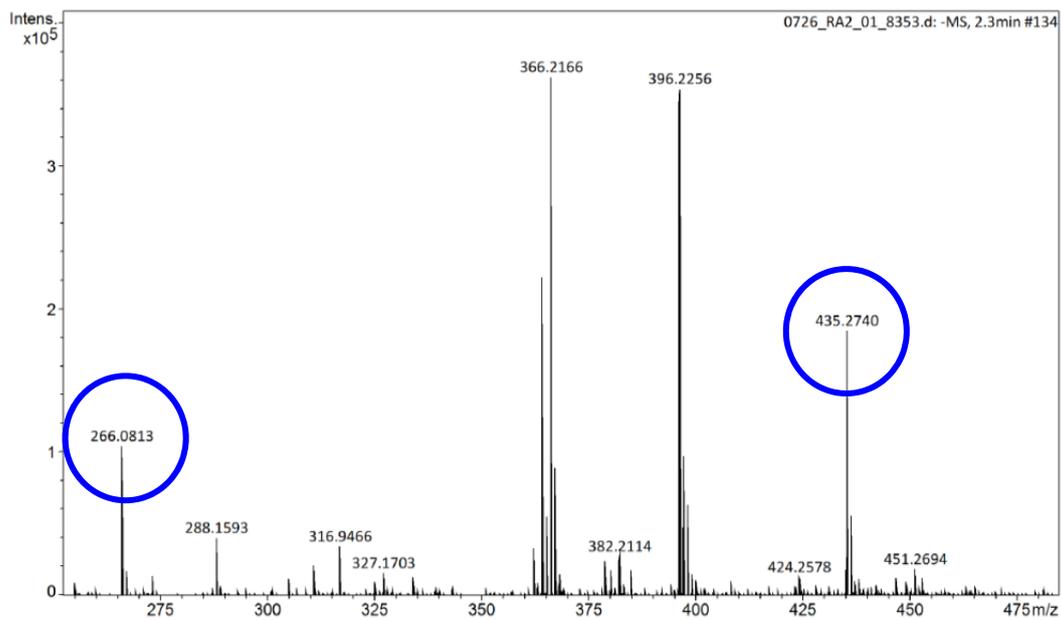
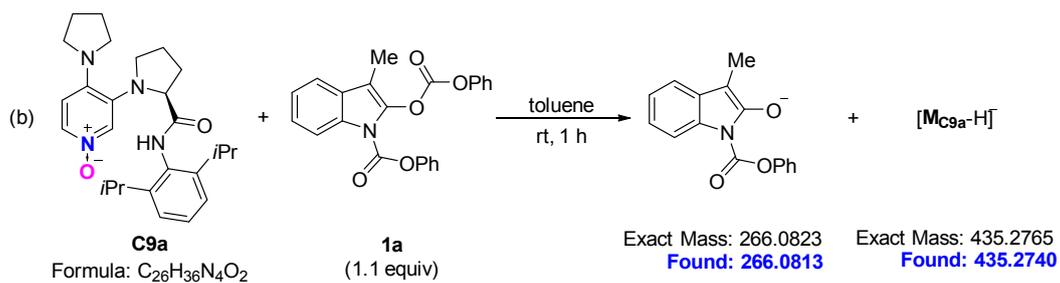
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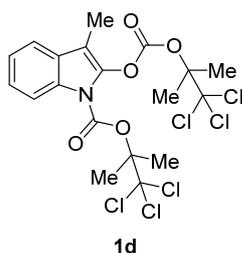
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3. Substrates Synthesis

Indolyl carbonates **1a-1t** were prepared according to literature precedents.²⁻⁴ Among these substrates, indolyl carbonates **1d**, **1k**, **1o**, **1r**, and **1t** were new compounds and their characterization data were listed as follows.

1,1,1-Trichloro-2-methylpropan-2-yl 3-methyl-2-(((1,1,1-trichloro-2-methylpropan-2-yl)oxy)carbonyloxy)-1H-indole-1-carboxylate (**1d**)



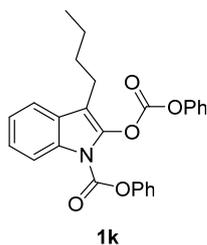
A colorless solid. m.p.: 160.4-161.2 °C.

¹H NMR (400 MHz, CDCl₃) δ 8.20 (d, *J* = 8.0 Hz, 1H), 7.49-7.42 (m, 1H), 7.35-7.30 (m, 1H), 7.30-7.24 (m, 1H), 2.18 (s, 3H), 2.10 (s, 6H), 2.02 (s, 6H).

¹³C NMR (100 MHz, CDCl₃) δ 149.2, 148.1, 138.3, 131.5, 127.9, 124.7, 123.5, 118.9, 115.9, 105.6, 105.5, 105.1, 92.4, 91.8, 21.9, 21.1, 7.0.

HRMS: exact mass calcd for C₁₉H₁₉Cl₆NO₅Na⁺ (M+Na)⁺ requires *m/z* 573.9287, found *m/z* 573.9284.

Phenyl 3-butyl-2-((phenoxy)carbonyloxy)-1H-indole-1-carboxylate (**1k**)



A colorless solid. m.p.: 115.0-115.8 °C.

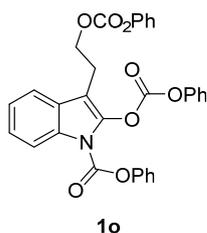
¹H NMR (400 MHz, CDCl₃) δ 8.18 (d, *J* = 8.0 Hz, 1H), 7.62-7.54 (m, 1H), 7.51-7.42 (m, 2H), 7.40-7.28 (m, 7H), 7.25-7.21 (m, 1H), 7.11 (d, *J* = 8.0 Hz, 2H), 2.75 (d, *J* = 7.6 Hz, 2H), 1.77-1.65 (m, 2H), 1.45 (sext, *J* = 7.6 Hz, 2H), 0.98 (t, *J* = 7.6 Hz, 3H).

^{13}C NMR (100 MHz, CDCl_3) δ 151.4, 151.1, 150.1, 148.8, 137.2, 132.5, 129.9, 129.7, 127.8, 126.8, 126.7, 125.2, 123.8, 121.8, 120.9, 119.5, 115.8, 111.0, 31.2, 22.7, 22.3, 14.0.

HRMS: exact mass calcd for $\text{C}_{26}\text{H}_{23}\text{NO}_5\text{Na}^+$ ($\text{M}+\text{Na}$) $^+$ requires m/z 452.1468, found m/z 452.1475.

Phenyl 2-((phenoxy-carbonyl)oxy)-3-(2-((phenoxy-carbonyl)oxy)ethyl)-1*H*-indole

-1-carboxylate (**1o**)



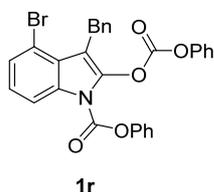
A colorless solid. m.p.: 146.2-147.6 °C.

^1H NMR (600 MHz, CDCl_3) δ 8.20 (d, $J = 8.4$ Hz, 1H), 7.64 (d, $J = 7.8$ Hz, 1H), 7.51-7.45 (m, 2H), 7.43-7.39 (m, 1H), 7.38-7.33 (m, 4H), 7.33-7.28 (m, 4H), 7.25-7.20 (m, 2H), 7.18-7.07 (m, 4H), 4.54 (t, $J = 7.2$ Hz, 2H), 3.23 (t, $J = 7.2$ Hz, 2H).

^{13}C NMR (100 MHz, CDCl_3) δ 153.9, 151.3, 151.2, 151.0, 150.0, 148.6, 138.5, 132.5, 129.9, 129.7, 129.6, 127.2, 126.9, 126.7, 126.2, 125.6, 124.2, 121.7, 121.3, 120.9, 119.2, 115.9, 106.1, 66.9, 22.5.

HRMS: exact mass calcd for $\text{C}_{31}\text{H}_{23}\text{NO}_8\text{Na}^+$ ($\text{M}+\text{Na}$) $^+$ requires m/z 560.1316, found m/z 560.1317.

Phenyl 3-benzyl-4-bromo-2-((phenoxy-carbonyl)oxy)-1*H*-indole-1-carboxylate (**1r**)



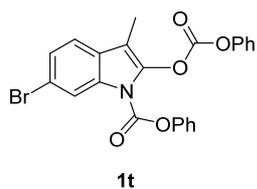
A colorless solid. m.p.: 174.2-176.3 °C.

^1H NMR (400 MHz, CDCl_3) δ 8.25 (d, $J = 8.4$ Hz, 1H), 7.49-7.44 (m, 3H), 7.37-7.29 (m, 9H), 7.24-7.19 (m, 3H), 6.96 (d, $J = 8.0$ Hz, 2H), 4.44 (s, 2H).

^{13}C NMR (100 MHz, CDCl_3) δ 150.92, 150.88, 149.4, 148.3, 139.7, 139.6, 134.0, 130.0, 129.7, 129.0, 128.59, 128.56, 127.1, 126.8, 126.3, 126.1, 125.7, 121.6, 120.8, 115.0, 114.6, 109.7, 28.9.

HRMS: exact mass calcd for $\text{C}_{29}\text{H}_{20}\text{BrNO}_5\text{Na}^+$ ($\text{M}+\text{Na}$) $^+$ requires m/z 564.0417, found m/z 564.0415

Phenyl 6-bromo-3-methyl-2-((phenoxy-carbonyl)oxy)-1H-indole-1-carboxylate (1t)



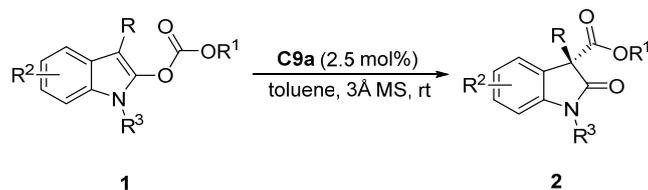
A colorless solid. m.p.: 157.1-161.3 °C.

^1H NMR (400 MHz, CDCl_3) δ 8.35 (s, 1H), 7.50-7.45 (m, 3H), 7.40-7.29 (m, 6H), 7.26-7.23 (m, 1H), 7.11 (d, $J = 8.0$ Hz, 2H), 2.26 (s, 3H).

^{13}C NMR (100 MHz, CDCl_3) δ 151.2, 151.0, 150.0, 148.5, 137.5, 132.9, 129.9, 129.8, 127.2, 127.1, 127.0, 126.8, 121.7, 120.9, 120.5, 118.9, 118.8, 106.4, 7.2.

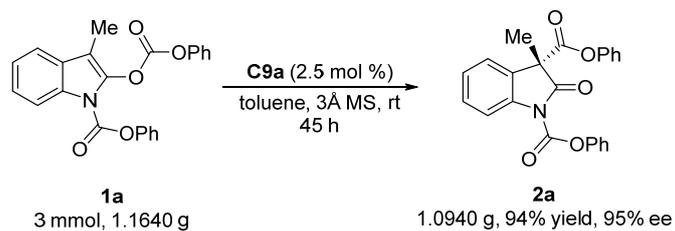
HRMS: exact mass calcd for $\text{C}_{23}\text{H}_{16}\text{BrNO}_5\text{Na}^+$ ($\text{M}+\text{Na}$) $^+$ requires m/z 488.0104, found m/z 488.0094

4. Typical procedure for the rearrangement of indolyl carbonates



In a test tube, indolyl carbonate **1** (0.05 mmol), catalyst **C9a** (0.6 mg, 2.5 mol%), and 3Å MS (40 mg) were added subsequently. Then, the tube was filled with N₂ gas. After that, toluene (0.5 mL) was added and the reaction was stirred at rt until reactant **1** was consumed (determined by TLC). Then, the reaction was quenched with iodomethane (0.05 mL). Subsequently, the crude mixture was purified by flash column chromatography on silica gel (gradient elution: i) pure petroleum ii) petroleum: CH₂Cl₂ = 1:10) to give the desired rearrangement product **2**.

5. Gram-scale synthesis of **2a**



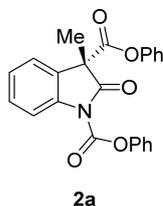
In a 50 mL round bottom flask equipped with a magnetic stir bar, indolyl carbonate **1a** (1.1640 g, 3 mmol), catalyst **C9a** (33 mg, 2.5 mol %), and 3Å MS (2.4000 g) were added subsequently. Then, the round bottom flask was filled with N₂ gas. After that, toluene (30 mL) was added and the reaction was stirred at rt until reactant **1a** was consumed (45 h). Then, the reaction was quenched with iodomethane (3.0 mL). Subsequently, the crude mixture was extracted with EtOAc/H₂O, dried over Na₂SO₄ and concentrated *in vacuo*. Subsequently, the crude product was purified by flash column chromatography on silica gel (gradient elution: i) pure petroleum ii) petroleum: CH₂Cl₂ = 1:10) to give the desired rearrangement product **2a** in 1.0940 g.

6. References

- (1) M.-S. Xie, Y.-F. Zhang, M. Shan, X.-X. Wu, G.-R. Qu and H.-M. Guo, *Angew. Chem., Int. Ed.*, 2019, **58**, 2839.
- (2) H. Mandai, T. Fujiwara, K. Noda, K. Fujii, K. Mitsudo, T. Korenaga and S. Suga, *Org. Lett.*, 2015, **17**, 4436;
- (3) H. Mandai, K. Fujii, H. Yasuhara, K. Abe, K. Mitsudo, T. Korenaga and S. Suga, *Nat. Commun.*, 2016, **7**, 11297.
- (4) S. A. Shaw, P. Aleman, J. Christy, J. W. Kampf, P. Va and E. Vedejs, *J. Am. Chem. Soc.*, 2006, **128**, 925.

7. The analytical and spectral characterization data for the oxindoles

(*S*)-Diphenyl-3-methyl-2-oxindoline-1,3-dicarboxylate (**2a**)



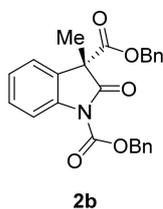
A pale yellow oil; 18.9 mg, 98% yield, 94% ee.

HPLC CHIRALCEL IE, *n*-hexane/2-propanol = 80/20, flow rate = 0.8 mL/min, λ = 256 nm, retention time: 11.370 min (minor), 12.302 min (major).

$[\alpha]_D^{27} = +97.5$ ($c = 0.46$, CHCl_3). The absolute configuration of compound (*S*)-**2a** was assigned by comparison with the (*S*)-enantiomer reported in the literature.³

¹H NMR (600 MHz, CDCl_3) δ 8.05 (d, $J = 8.4$ Hz, 1H), 7.50-7.40 (m, 4H), 7.38-7.28 (m, 6H), 7.22 (t, $J = 7.2$ Hz, 1H), 6.98 (d, $J = 7.8$ Hz, 2H), 1.90 (s, 3H).

(*S*)-Dibenzyl-3-methyl-2-oxindoline-1,3-dicarboxylate (**2b**)



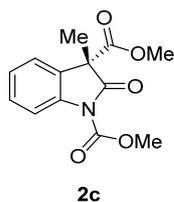
A colorless oil; 19.0 mg, 92% yield, 91% ee.

HPLC CHIRALCEL IE, *n*-hexane/2-propanol = 80/20, flow rate = 0.8 mL/min, λ = 256 nm, retention time: 26.345 min (major), 31.578 min (minor).

$[\alpha]_D^{27} = 79.8$ ($c = 0.19$, CHCl_3). The absolute configuration of compound (*S*)-**2b** was assigned by comparison with the (*S*)-enantiomer reported in the literature.²

¹H NMR (400 MHz, CDCl_3) δ 7.93 (d, $J = 8.4$ Hz, 1H), 7.56-7.47 (m, 2H), 7.42-7.31 (m, 4H), 7.26-7.20 (m, 4H), 7.19-7.13 (m, 1H), 7.12-7.06 (m, 2H), 5.46 (s, 2H), 5.11 (s, 2H), 1.74 (s, 3H).

(S)-Dimethyl-3-methyl-2-oxoindoline-1,3-dicarboxylate (2c)



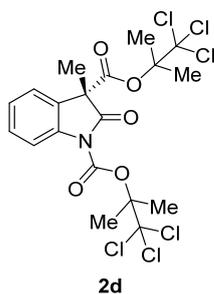
A colorless oil; 11.2 mg, 87% yield, 93% ee.

HPLC CHIRALCEL IE, *n*-hexane/2-propanol = 95/5, flow rate = 0.8 mL/min, λ = 256 nm, retention time: 21.517 min (minor), 22.097 min (major).

$[\alpha]_D^{27} = +74.3$ ($c = 0.14$, CHCl_3). The absolute configuration of compound (*S*)-**2c** was assigned by comparison with the (*S*)-enantiomer reported in the literature.³

¹H NMR (400 MHz, CDCl_3) δ 7.96 (d, $J = 8.0$ Hz, 1H), 7.41-7.35 (m, 1H), 7.30-7.26 (m, 1H), 7.23-7.17 (m, 1H), 4.04 (s, 3H), 3.67 (s, 3H), 1.73 (s, 3H).

(S)-Bis(1,1,1-trichloro-2-methylpropan-2-yl)-3-methyl-2-oxoindoline-1,3-dicarboxylate (2d)



A colorless solid; 24.3 mg, 88% yield, 91% ee.

HPLC CHIRALCEL IE, *n*-hexane/2-propanol = 80/20, flow rate = 0.8 mL/min, λ = 256 nm, retention time: 5.543 min (major), 6.099 min (minor).

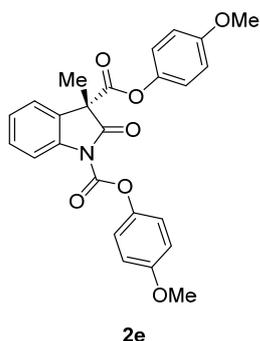
$[\alpha]_D^{27} = +85.6$ ($c = 0.75$, CHCl_3). The absolute configuration of the product (*S*)-**2d** was assigned by analogy.

¹H NMR (400 MHz, CDCl_3) δ 8.01 (d, $J = 8.0$ Hz, 1H), 7.39-7.32 (m, 1H), 7.28-7.24 (m, 1H), 7.22-7.16 (m, 1H), 2.10 (s, 3H), 2.09 (s, 3H), 1.85 (s, 3H), 1.72 (s, 3H), 1.64 (s, 3H).

¹³C NMR (100 MHz, CDCl_3) δ 172.4, 166.4, 148.0, 139.5, 129.6, 128.5, 125.3, 122.5, 116.1, 105.4, 105.3, 92.1, 90.2, 56.7, 21.79, 21.78, 21.3, 20.7, 18.8.

HRMS: exact mass calcd for $\text{C}_{19}\text{H}_{19}\text{Cl}_6\text{NO}_5\text{Na}^+$ ($\text{M}+\text{Na}$)⁺ requires m/z 573.9287, found m/z 573.9287.

(*S*)-Bis(4-methoxyphenyl)-3-methyl-2-oxoindoline-1,3-dicarboxylate (2e)



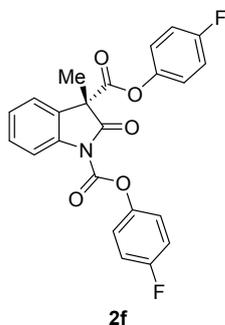
A colorless solid; 19.0 mg, 86% yield, 96% ee.

HPLC CHIRALCEL ADH, *n*-hexane/2-propanol = 90/10, flow rate = 1.0 mL/min, λ = 256 nm, retention time: 34.812 min (minor), 52.155 min (major).

$[\alpha]_D^{27} = +85.7$ ($c = 0.62$, CHCl_3). The absolute configuration of compound (*S*)-**2e** was assigned by comparison with the (*S*)-enantiomer reported in the literature.³

¹H NMR (400 MHz, CDCl_3) δ 8.04 (d, $J = 8.0$ Hz, 1H), 7.47-7.38 (m, 2H), 7.32-7.27 (m, 1H), 7.25-7.20 (m, 2H), 6.98-6.91 (m, 2H), 6.90-6.80 (m, 4H), 3.83 (s, 3H), 3.77 (s, 3H), 1.88 (s, 3H).

(*S*)-Bis(4-fluorophenyl)-3-methyl-2-oxoindoline-1,3-dicarboxylate (2f)



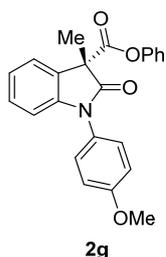
A colorless oil; 19.8 mg, 94% yield, 93% ee.

HPLC CHIRALCEL IE, *n*-hexane/2-propanol = 80/20, flow rate = 0.8 mL/min, λ = 256 nm, retention time: 9.338min (minor), 10.020 min (major).

$[\alpha]_D^{27} = 95.4$ ($c = 0.23$, CHCl_3). The absolute configuration of compound (*S*)-**2f** was assigned by comparison with the (*S*)-enantiomer reported in the literature.³

¹H NMR (400 MHz, CDCl_3) δ 8.04 (d, $J = 8.4$ Hz, 1H), 7.50-7.39 (m, 2H), 7.34-7.27 (m, 3H), 7.18-7.09 (m, 2H), 7.06-6.98 (m, 2H), 6.97-6.90 (m, 2H), 1.89 (s, 3H).

(S)-Phenyl -1-(4-methoxyphenyl)-3-methyl-2-oxindoline-3-carboxylate (2g)



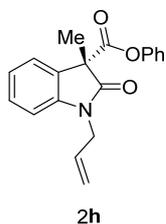
A colorless oil; 18.3 mg, 98% yield, 88% ee.

HPLC CHIRALCEL IE, *n*-hexane/2-propanol = 80/20, flow rate = 0.8 mL/min, λ = 256 nm, retention time: 41.653 min (major), 50.765 min (minor).

$[\alpha]_D^{27} = -175$ ($c = 0.504$, CHCl_3). The absolute configuration of compound (*S*)-**2g** was assigned by analogy.

$^1\text{H NMR}$ (400 MHz, CDCl_3) δ 7.43-7.27 (m, 6H), 7.20 (t, $J = 7.6$ Hz, 1H), 7.15 (t, $J = 7.6$ Hz, 1H), 7.08-7.02 (m, 2H), 7.02-6.96 (m, 2H), 6.82 (d, $J = 8.0$ Hz, 1H), 3.87 (s, 3H), 1.88 (s, 3H).

(S)-Phenyl -1-allyl-3-methyl-2-oxindoline-3-carboxylate (2h)



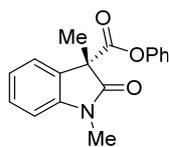
A colorless oil; 14.5 mg, 95% yield, 81% ee.

HPLC CHIRALCEL ADH, *n*-hexane/2-propanol = 90/10, flow rate = 1.0 mL/min, λ = 256 nm, retention time: 9.665 min (minor), 12.630 min (major).

$[\alpha]_D^{27} = 66.48$ ($c = 0.307$, CHCl_3). The absolute configuration of compound (*S*)-**2h** was assigned by analogy.

$^1\text{H NMR}$ (400 MHz, CDCl_3) δ 7.37-7.29 (m, 4H), 7.19 (t, $J = 7.6$ Hz, 1H), 7.12 (t, $J = 7.6$ Hz, 1H), 6.95 (d, $J = 8.4$ Hz, 2H), 6.89 (d, $J = 8.0$ Hz, 1H), 5.91-5.82 (m, 1H), 5.28-5.19 (m, 2H), 4.54-4.45 (m, 1H), 4.40-4.28 (m, 1H), 1.79 (s, 3H).

(S)-Phenyl-1,3-dimethyl-2-oxindoline-3-carboxylate (2i)



2i

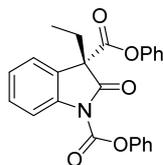
A colorless oil; 12.8 mg, 91% yield, 50% ee.

HPLC CHIRALCEL OD(H), *n*-hexane/2-propanol = 90/10, flow rate = 0.6 mL/min, λ = 256 nm, retention time: 13.400 min (minor), 15.830 min (major).

$[\alpha]_D^{27}$ = 30.9 (*c* = 0.204, CHCl₃). The absolute configuration of compound (*S*)-**2i** was assigned by analogy.

¹H NMR (400 MHz, CDCl₃) δ 7.39-7.35 (m, 2H), 7.33-7.27 (m, 2H), 7.20-7.17 (m, 1H), 7.13 (t, *J* = 7.6 Hz, 1H), 6.96-6.90 (m, 3H), 3.30 (s, 3H), 1.78 (s, 3H).

(S)-Diphenyl-3-ethyl-2-oxindoline-1,3-dicarboxylate (2j)



2j

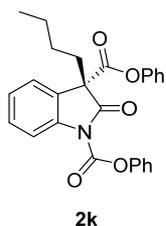
A colorless solid; 18.4 mg, 92% yield, 96% ee.

HPLC CHIRALCEL ADH, *n*-hexane/2-propanol = 90/10, flow rate = 1.0 mL/min, λ = 256 nm, retention time: 12.400 min (minor), 14.880 min (major).

$[\alpha]_D^{27}$ = +90.0 (*c* = 0.32, CHCl₃). The absolute configuration of compound (*S*)-**2j** was assigned by comparison with the (*S*)-enantiomer reported in the literature.³

¹H NMR (400 MHz, CDCl₃) δ 8.05 (d, *J* = 8.0 Hz, 1H), 7.49-7.39 (m, 4H), 7.38-7.28 (m, 6H), 7.25-7.18 (m, 1H), 7.02-6.95 (m, 2H), 2.56 (dq, *J* = 14.0, 7.2 Hz, 1H), 2.42 (dq, *J* = 14.0, 7.2 Hz, 1H), 0.86 (t, *J* = 7.2 Hz, 3H).

(S)-Diphenyl-3-butyl-2-oxoindoline-1,3-dicarboxylate (2k)



A colorless solid; 19.4 mg, 92% yield, 96% ee.

HPLC CHIRALCEL ADH, *n*-hexane/2-propanol = 80/20, flow rate = 0.8 mL/min, λ = 256 nm, retention time: 19.597 min (major), 22.448 min (minor).

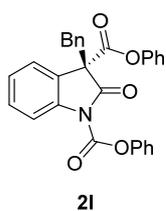
$[\alpha]_D^{27} = +31.4$ ($c = 0.78$, CHCl_3). The absolute configuration of the product (*S*)-**2h** was assigned by analogy.

¹H NMR (400 MHz, CDCl_3) δ 8.05 (d, $J = 8.0$ Hz, 1H), 7.48-7.40 (m, 4H), 7.36-7.28 (m, 6H), 7.25-7.19 (m, 1H), 7.01-6.95 (m, 2H), 2.54-2.44 (m, 1H), 2.42-2.32 (m, 1H), 1.39-1.29 (m, 2H), 1.27-1.20 (m, 1H), 1.12-1.00 (m 1H), 0.86 (t, $J = 7.2$ Hz, 3H).

¹³C NMR (150 MHz, CDCl_3) δ 171.9, 167.5, 150.4, 150.2, 149.4, 139.9, 129.9, 129.8, 129.6, 127.0, 126.7, 126.5, 125.8, 123.3, 121.7, 121.3, 115.9, 60.4, 34.8, 25.9, 22.8, 13.9.

HRMS: exact mass calcd for $\text{C}_{26}\text{H}_{23}\text{NO}_5\text{Na}^+$ ($\text{M}+\text{Na}$)⁺ requires m/z 452.1468, found m/z 452.1472.

(S)-Diphenyl-3-benzyl-2-oxoindoline-1,3-dicarboxylate (2l)



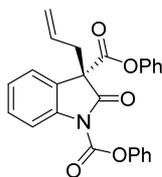
A colorless solid; 22.6 mg, 98% yield, 92% ee.

HPLC CHIRALCEL IE, *n*-hexane/2-propanol = 80/20, flow rate = 0.8 mL/min, λ = 256 nm, retention time: 8.145 min (major), 9.283 min (minor).

$[\alpha]_D^{27} = +33.1$ ($c = 0.24$, CHCl_3). The absolute configuration of compound (*S*)-**2i** was assigned by comparison with the (*S*)-enantiomer reported in the literature.³

¹H NMR (400 MHz, CDCl₃) δ 7.78 (d, *J* = 7.6 Hz, 1H), 7.52 (dd, *J* = 7.6, 1.6 Hz, 1H), 7.45-7.08 (m, 13H), 7.06-7.00 (m, 2H), 6.96-6.90 (m, 2H), 3.78 (d, *J* = 13.2 Hz, 1H), 3.68 (d, *J* = 13.2 Hz, 1H).

(*S*)-Diphenyl-3-allyl-2-oxoindoline-1,3-dicarboxylate (2m)



2m

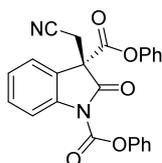
A colorless solid; 18.3 mg, 89% yield, 84% ee.

HPLC CHIRALCEL IE, *n*-hexane/2-propanol = 50/50, flow rate = 1.0 mL/min, λ = 256 nm, retention time: 6.277min (minor), 6.767 min (major).

[α]_D²⁷ = +77.5 (c = 0.60, CHCl₃). The absolute configuration of compound (*S*)-**2j** was assigned by comparison with the (*S*)-enantiomer reported in the literature.³

¹H NMR (600 MHz, CDCl₃) δ 8.03 (d, *J* = 8.4 Hz, 1H), 7.50-7.40 (m, 4H), 7.38-7.27 (m, 6H), 7.23 (t, *J* = 7.2 Hz, 1H), 6.99 (d, *J* = 7.8 Hz, 2H), 5.58-5.47 (m, 1H), 5.18 (d, *J* = 16.8 Hz, 1H), 5.09 (d, *J* = 10.2 Hz, 1H), 3.18 (d, *J* = 7.2 Hz, 2H).

(*S*)-Diphenyl-3-(cyanomethyl)-2-oxoindoline-1,3-dicarboxylate (2n)



2n

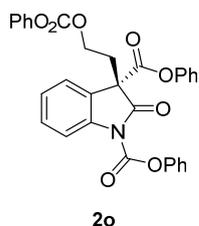
A pale yellow solid; 20.0 mg, 98% yield, 85% ee.

HPLC CHIRALCEL IE, *n*-hexane/2-propanol = 80/20, flow rate = 0.8 mL/min, λ = 256 nm, retention time: 20.940 min (minor), 28.458 min (major).

[α]_D²⁷ = +70.4 (c = 0.12, CHCl₃). The absolute configuration of compound (*S*)-**2k** was assigned by comparison with the (*S*)-enantiomer reported in the literature.³

$^1\text{H NMR}$ (400 MHz, CDCl_3) δ 8.17-8.08 (m, 1H), 7.60-7.52 (m, 2H), 7.50-7.43 (m, 2H), 7.42-7.30 (m, 6H), 7.28-7.23 (m, 1H), 7.03-6.93 (m, 2H), 3.51 (d, $J = 16.8$ Hz, 1H), 3.31 (d, $J = 16.8$ Hz, 1H).

(S)-Diphenyl-2-oxo-3-(2-((phenoxy-carbonyl)oxy)ethyl)indoline-1,3-dicarboxylate (2o)



A colorless oil; 25.2 mg, 94 % yield, 95% ee.

HPLC CHIRALCEL IE, *n*-hexane/2-propanol = 80/20, flow rate = 0.8 mL/min, $\lambda = 256$ nm, retention time: 24.280 min (minor), 28.282 min (major).

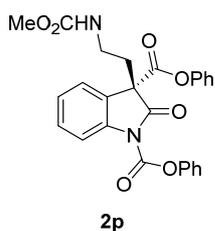
$[\alpha]_{\text{D}}^{27} = +46.0$ ($c = 0.57$, CHCl_3). The absolute configuration of the product (*S*)-**2i** was assigned by analogy.

$^1\text{H NMR}$ (400 MHz, CDCl_3) δ 8.14 (d, $J = 8.0$ Hz, 1H), 7.55-7.47 (m, 1H), 7.46-7.41 (m, 1H), 7.38-7.28 (m, 7H), 7.25-7.17 (m, 5H), 7.15-7.08 (m, 2H), 7.02-6.95 (m, 2H), 4.45 (ddd, $J = 9.2, 5.6, 3.6$ Hz, 1H), 4.01 (td, $J = 10.8, 4.4$ Hz, 1H), 3.15 (ddd, $J = 15.2, 10.8, 6.0$ Hz, 1H), 2.85 (dt, $J = 14.8, 4.0$ Hz, 1H).

$^{13}\text{C NMR}$ (100 MHz, CDCl_3) δ 171.7, 167.1, 153.2, 151.0, 150.3, 150.2, 149.6, 140.3, 130.6, 129.64, 129.61, 129.59, 126.68, 126.58, 126.3, 125.9, 125.1, 123.4, 121.6, 121.2, 116.5, 64.1, 58.5, 33.0.

HRMS: exact mass calcd for $\text{C}_{31}\text{H}_{23}\text{NO}_8\text{Na}^+$ ($\text{M}+\text{Na}$) $^+$ requires m/z 560.1316, found m/z 560.1299.

(S)-Diphenyl-3-(2-((methoxy-carbonyl)amino)ethyl)-2-oxoindoline-1,3-dicarboxylate (2p)



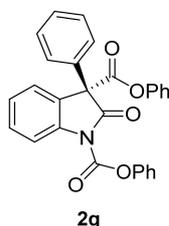
A colorless oil; 22.8 mg, 96% yield, 88% ee.

HPLC CHIRALCEL IE, *n*-hexane/2-propanol = 80/20, flow rate = 0.8 mL/min, λ = 256 nm, retention time: 42.518 min (major), 49.835 min (minor).

$[\alpha]_D^{27} = +73.5$ ($c = 0.55$, CHCl_3). The absolute configuration of compound (*S*)-**2m** was assigned by comparison with the (*S*)-enantiomer reported in the literature.³

¹H NMR (400 MHz, CDCl_3) δ 8.05 (d, $J = 8.4$ Hz, 1H), 7.50-7.40 (m, 4H), 7.37-7.28 (m, 6H), 7.22 (t, $J = 7.6$ Hz, 1H), 7.01-6.92 (m, 2H), 4.75 (br, 1H), 3.58 (s, 3H), 3.36-3.12 (m, 2H), 2.81 (dt, $J = 14.4, 7.6$ Hz, 1H), 2.68-2.53 (m, 1H).

(*S*)-Diphenyl-2-oxo-3-phenylindoline-1,3-dicarboxylate (**2q**)



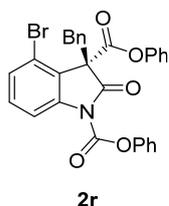
A colorless solid; 22.0 mg, 98% yield, 92% ee.

HPLC CHIRALCEL ADH, *n*-hexane/2-propanol = 90/10, flow rate = 1.0 mL/min, λ = 256 nm, retention time: 15.922 min (minor), 23.277 min (major).

$[\alpha]_D^{27} = +70.3$ ($c = 0.64$, CHCl_3). The absolute configuration of compound (*S*)-**2n** was assigned by comparison with the (*S*)-enantiomer reported in the literature.²

¹H NMR (400 MHz, CDCl_3) δ 8.16 (d, $J = 8.0$ Hz, 1H), 7.65 (dd, $J = 7.6, 1.2$ Hz, 1H), 7.56 (td, $J = 7.6, 1.2$ Hz, 1H), 7.48-7.20 (m, 14H), 7.11-7.00 (m, 2H).

(*S*)-Diphenyl-3-benzyl-4-bromo-2-oxoindoline-1,3-dicarboxylate (**2r**)



A colorless oil; 23.5 mg, 87 % yield, 92% ee.

HPLC CHIRALCEL IE, *n*-hexane/2-propanol = 80/20, flow rate = 0.8 mL/min, λ = 256 nm, retention time: 12.035 min (minor), 15.068 min (major).

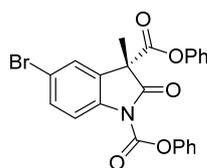
$[\alpha]_D^{27} = -765$ ($c = 0.200$, CHCl_3). The absolute configuration of the product (*S*)-**2r** was assigned by analogy.

$^1\text{H NMR}$ (400 MHz, CDCl_3) δ 7.69 (d, $J = 8.4$ Hz, 1H), 7.49-7.35 (m, 5H), 7.31 (t, $J = 7.6$ Hz, 1H), 7.28-7.23 (m, 1H), 7.23-7.16 (m, 3H), 7.16-7.06 (m, 5H), 6.95 (d, $J = 7.2$ Hz, 2H), 4.06 (d, $J = 13.6$ Hz, 1H), 3.80 (d, $J = 13.2$ Hz, 1H).

$^{13}\text{C NMR}$ (100 MHz, CDCl_3) δ 170.5, 165.6, 150.5, 150.0, 148.5, 141.6, 133.5, 131.1, 129.8, 129.74, 129.65, 129.1, 128.2, 127.6, 126.8, 126.6, 126.3, 121.6, 121.5, 118.9, 114.5, 63.6, 38.3.

HRMS: exact mass calcd for $\text{C}_{29}\text{H}_{20}\text{BrNO}_5\text{Na}^+$ ($\text{M}+\text{Na}$) $^+$ requires m/z 564.0417, found m/z 564.0417

(*S*)-Diphenyl-5-bromo-3-methyl-2-oxindoline-1,3-dicarboxylate (**2s**)



2s

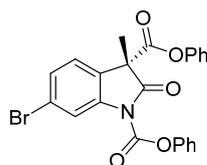
A colorless solid; 22.8 mg, 98% yield, 92% ee.

HPLC CHIRALCEL IE, *n*-hexane/2-propanol = 80/20, flow rate = 0.8 mL/min, $\lambda = 256$ nm, retention time: 9.515 min (minor), 10.178 min (major).

$[\alpha]_D^{27} = +6.5$ ($c = 0.42$, CHCl_3). The absolute configuration of compound (*S*)-**2o** was assigned by comparison with the (*S*)-enantiomer reported in the literature.²

$^1\text{H NMR}$ (400 MHz, CDCl_3) δ 7.96 (d, $J = 8.8$ Hz, 1H), 7.60-7.54 (m, 2H), 7.49-7.41 (m, 2H), 7.39-7.21 (m, 6H), 7.04-6.98 (m, 2H), 1.90 (s, 3H).

(*S*)-Diphenyl-6-bromo-3-methyl-2-oxindoline-1,3-dicarboxylate (**2t**)



2t

A colorless oil; 21.6 mg, 93 % yield, 93% ee.

HPLC CHIRALCEL IE, *n*-hexane/2-propanol = 80/20, flow rate = 0.8 mL/min, λ = 256 nm, retention time: 9.253 min (minor), 10.567 min (major).

$[\alpha]_D^{27} = -162.62$ ($c = 0.610$, CHCl_3). The absolute configuration of the product (*S*)-**2t** was assigned by analogy.

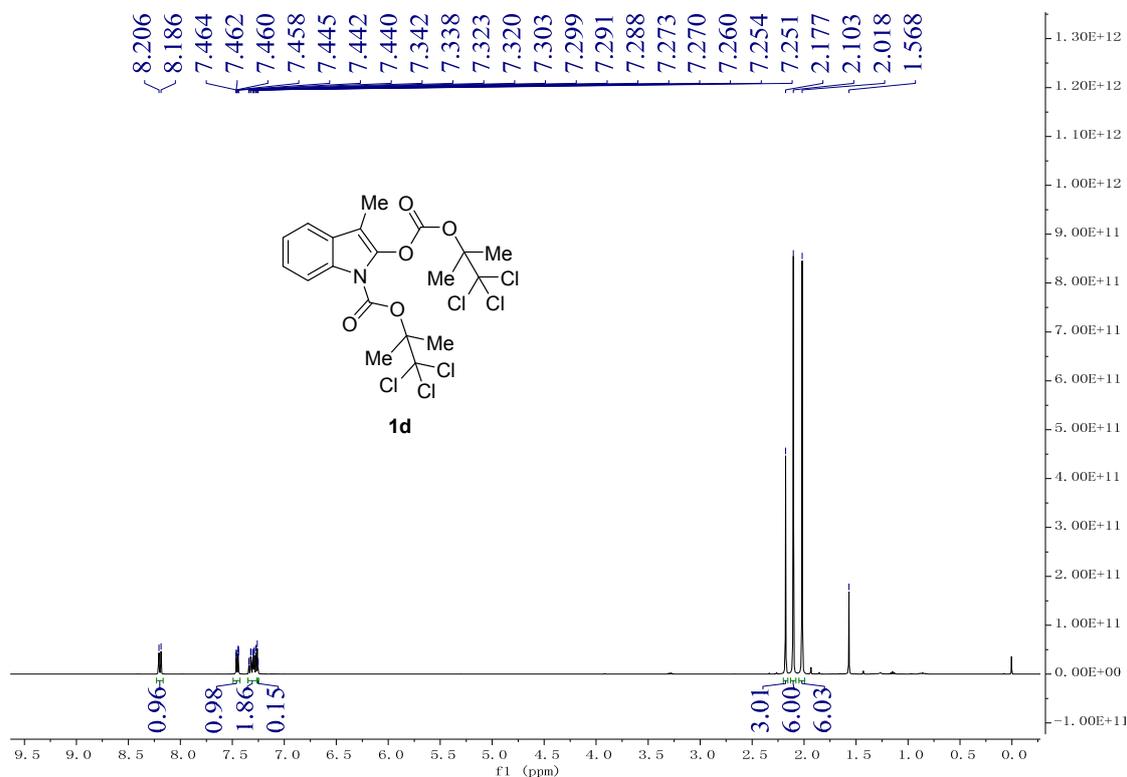
¹H NMR (400 MHz, CDCl_3) δ 8.28 (s, 1H), 7.50-7.42 (m, 3H), 7.39-7.28 (m, 6H), 7.26-7.21 (m, 1H), 6.98 (d, $J = 8.4$ Hz, 2H), 1.89 (s, 3H).

¹³C NMR (100 MHz, CDCl_3) δ 171.9, 167.2, 150.3, 150.1, 149.3, 140.2, 129.8, 129.7, 128.9, 127.6, 126.9, 126.7, 124.3, 123.7, 121.5, 121.2, 119.6, 55.8, 20.9.

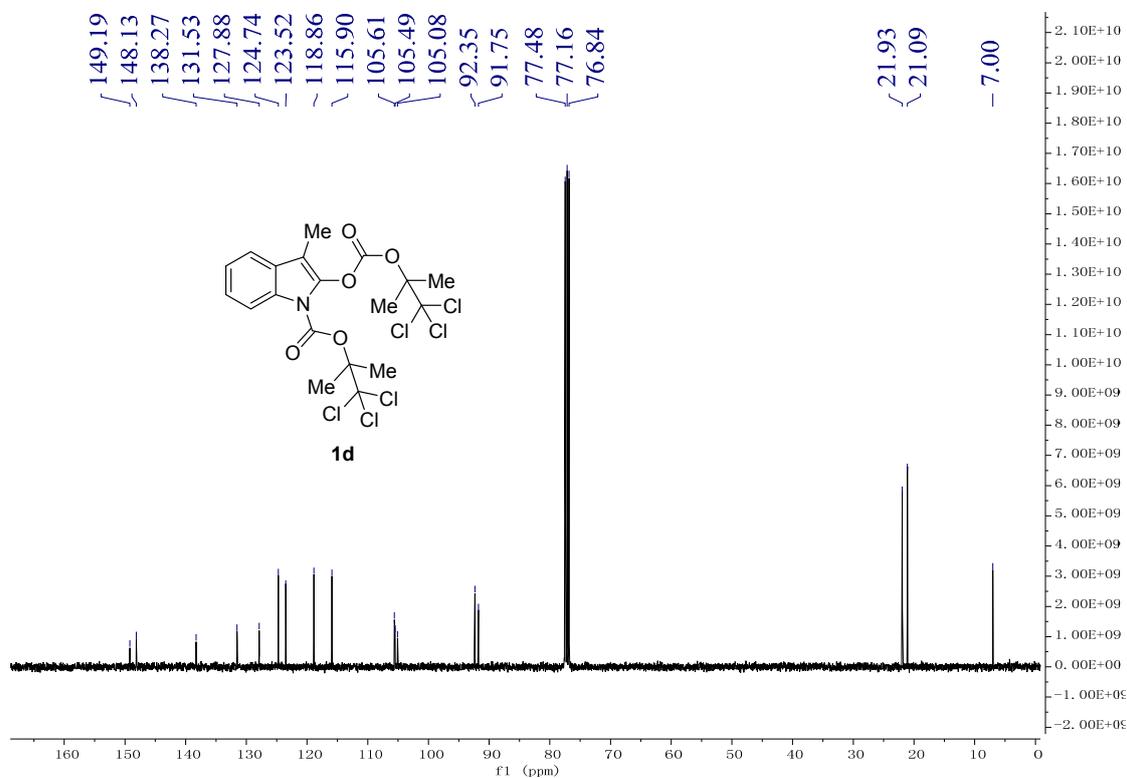
HRMS: exact mass calcd for $\text{C}_{23}\text{H}_{16}\text{BrNO}_5\text{Na}^+$ ($\text{M}+\text{Na}$)⁺ requires m/z 488.0104, found m/z 488.0103.

8. Copies of NMR spectra

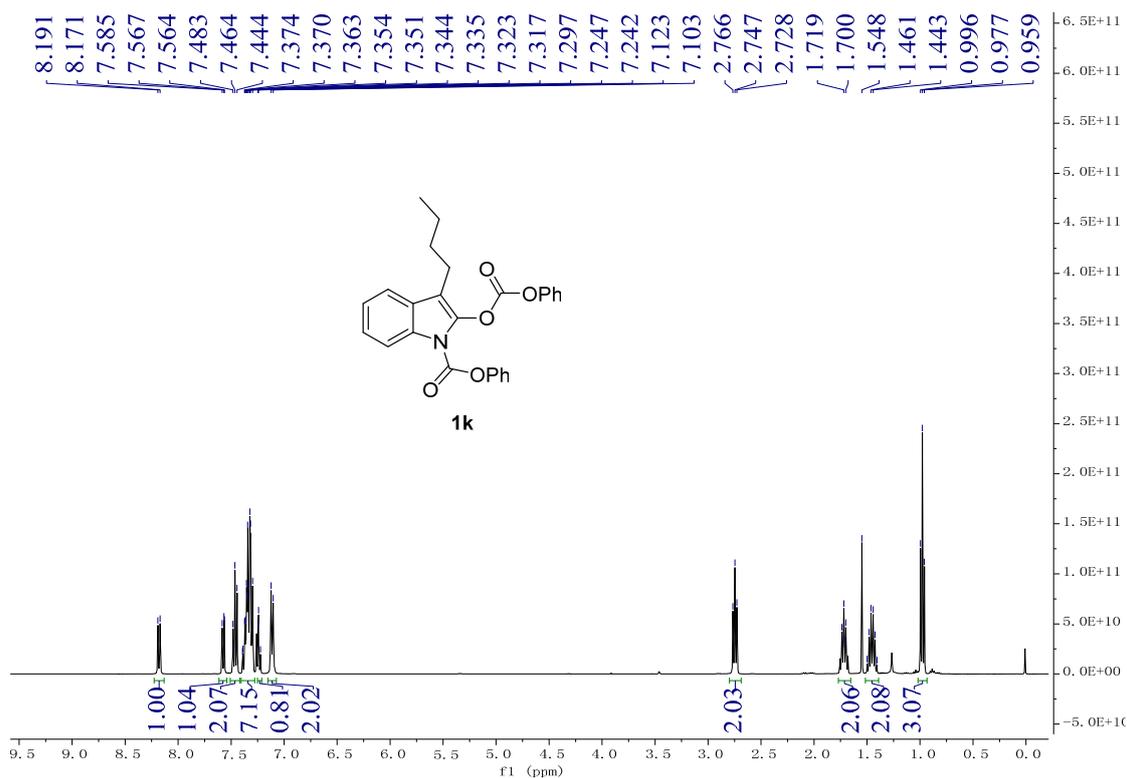
^1H NMR of 1d



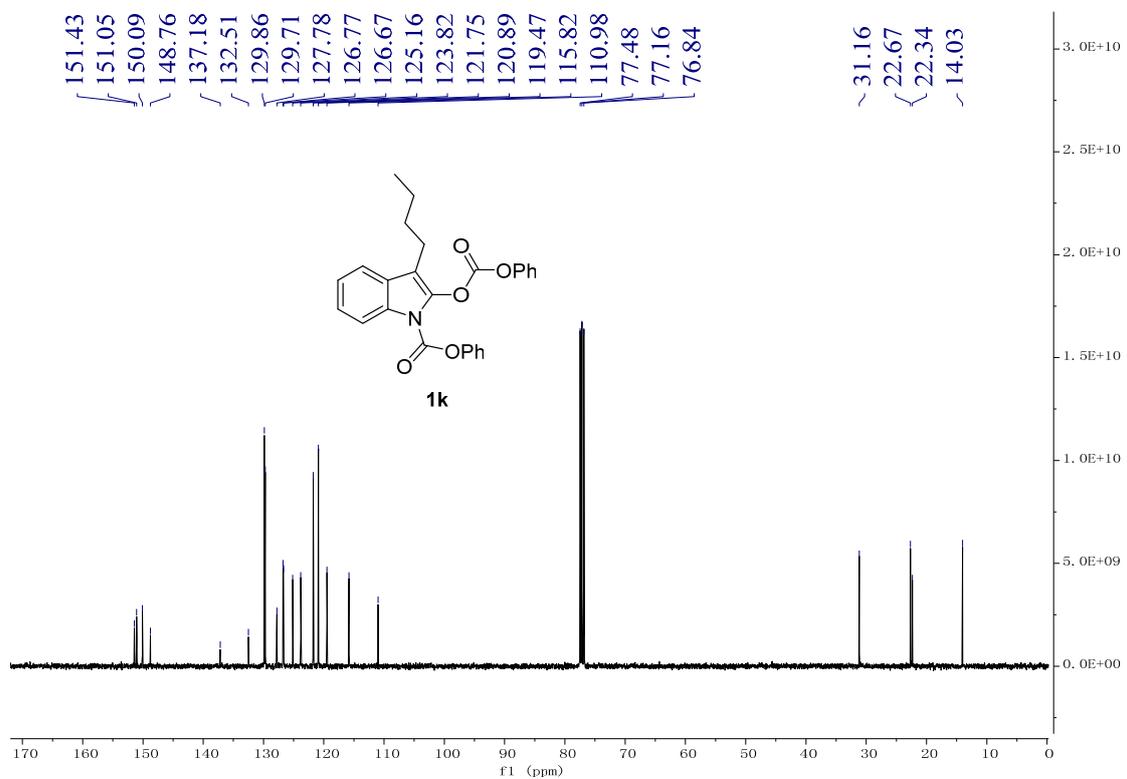
^{13}C NMR of 1d



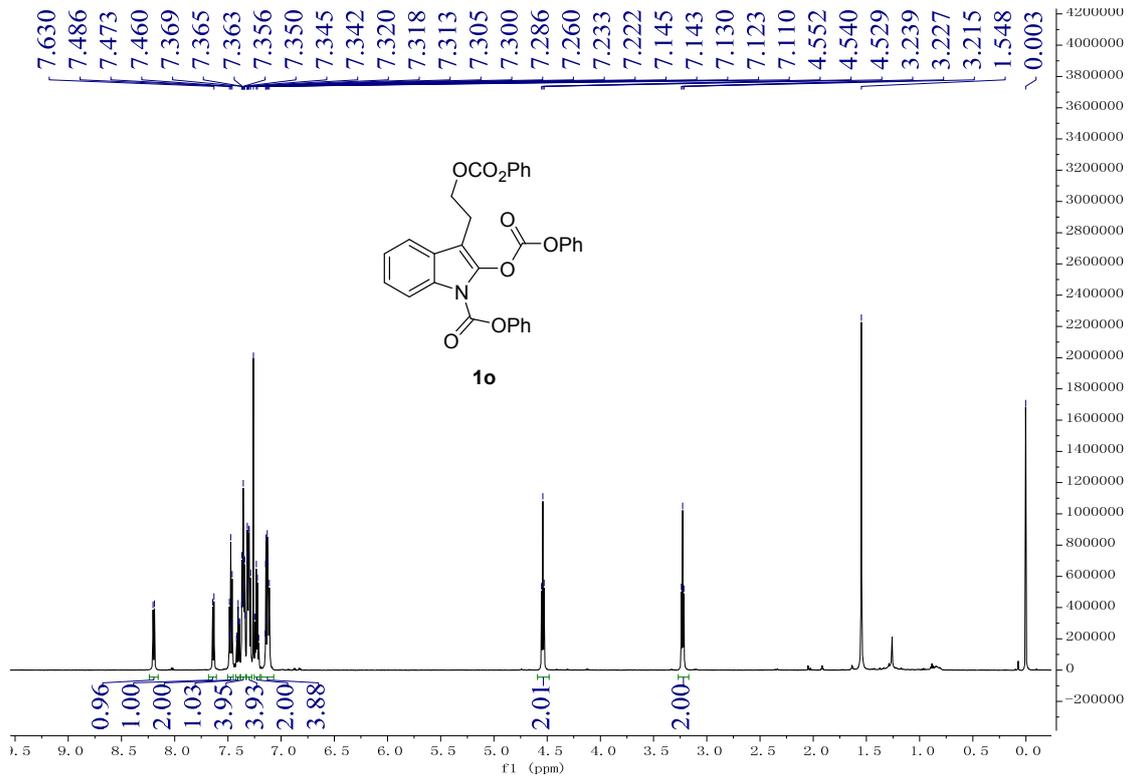
¹H NMR of 1h



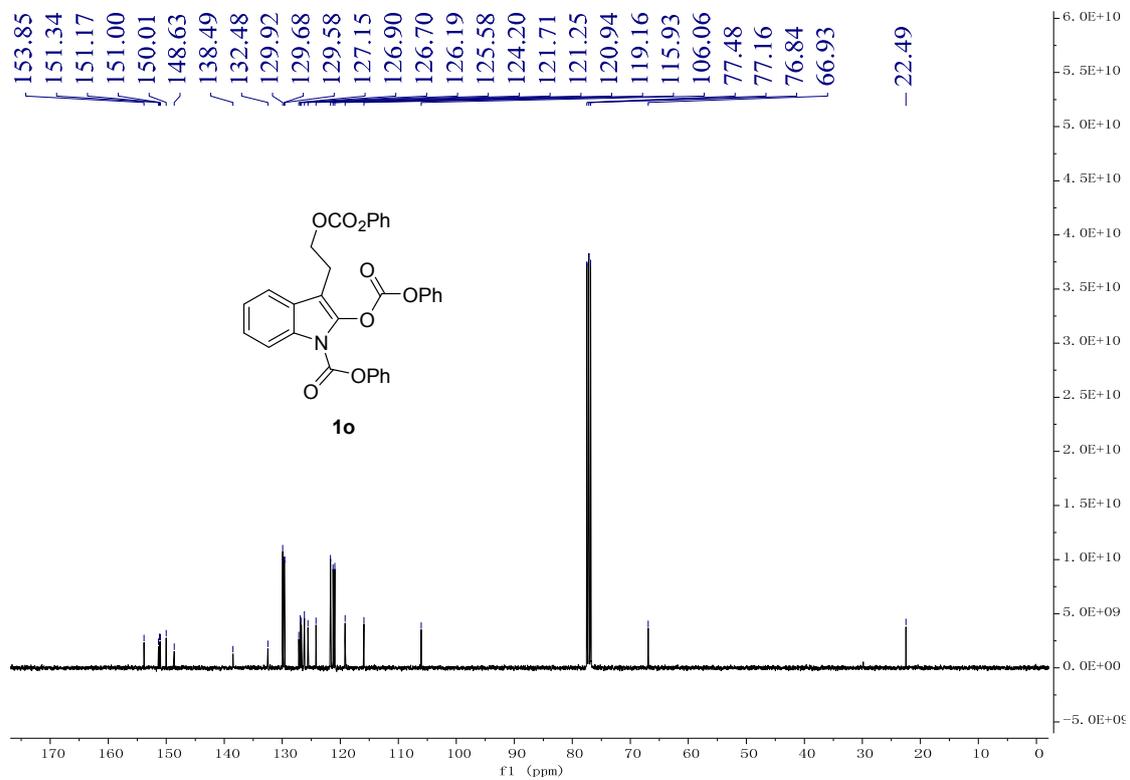
¹³C NMR of 1h



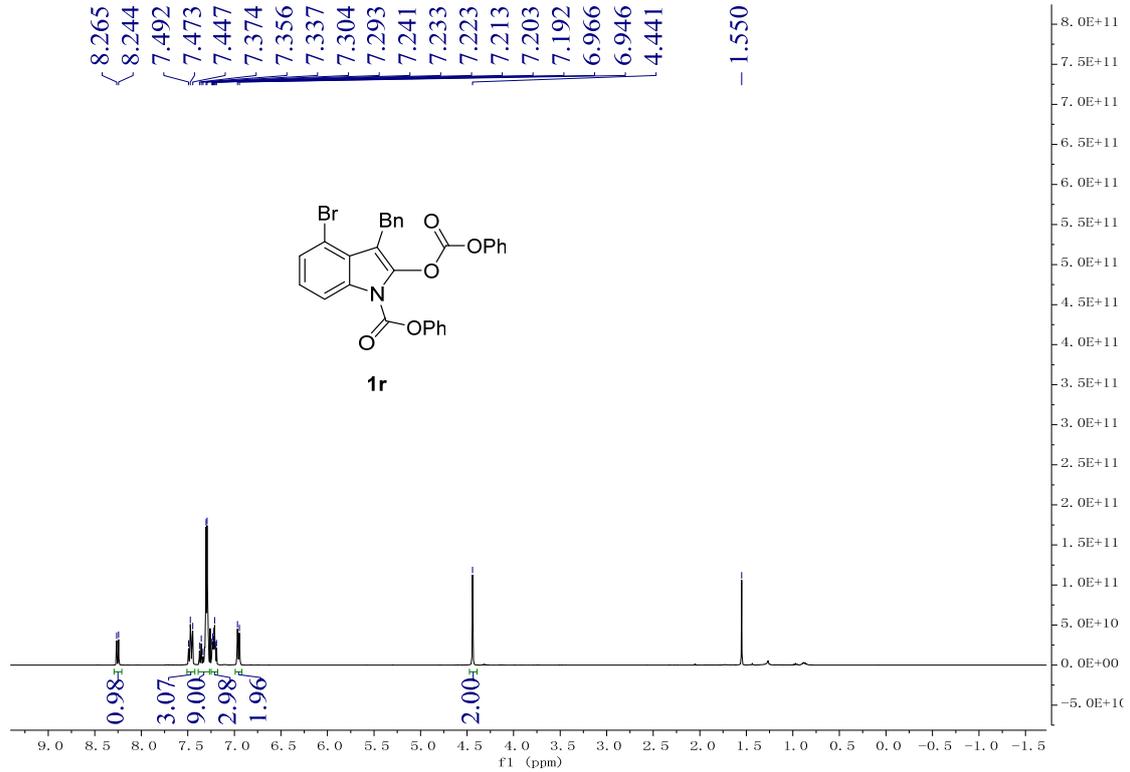
¹H NMR of 1l



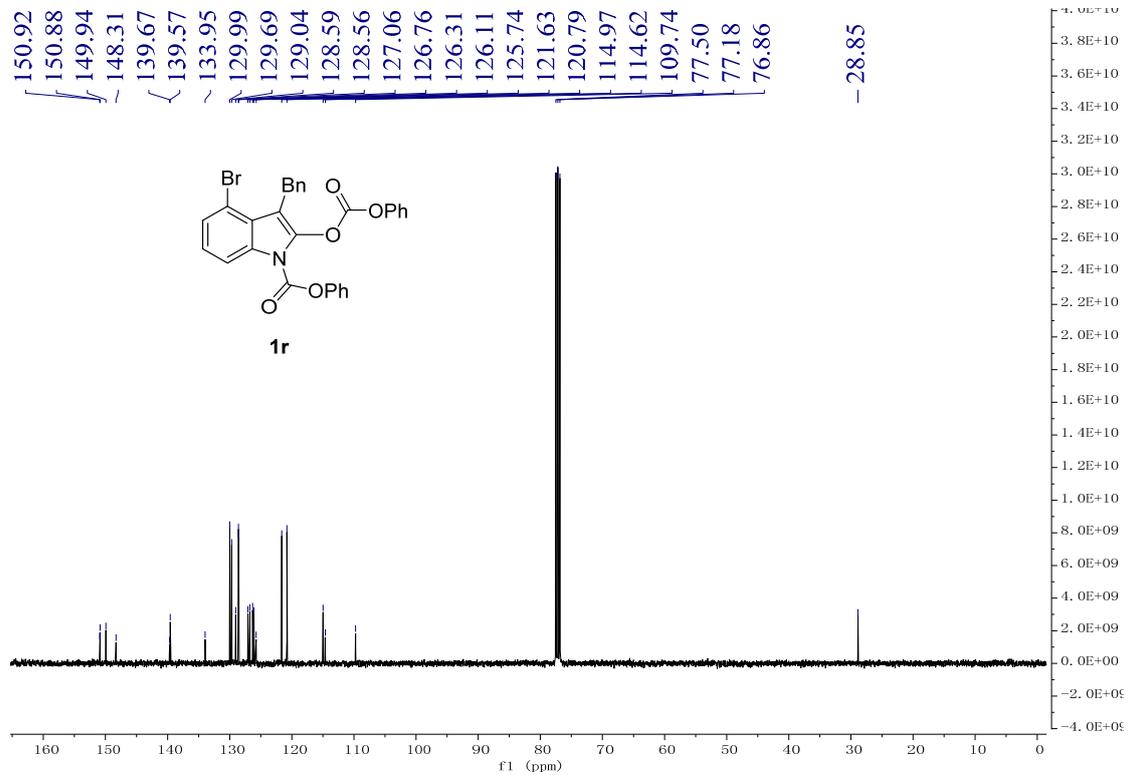
¹³C NMR of 1l



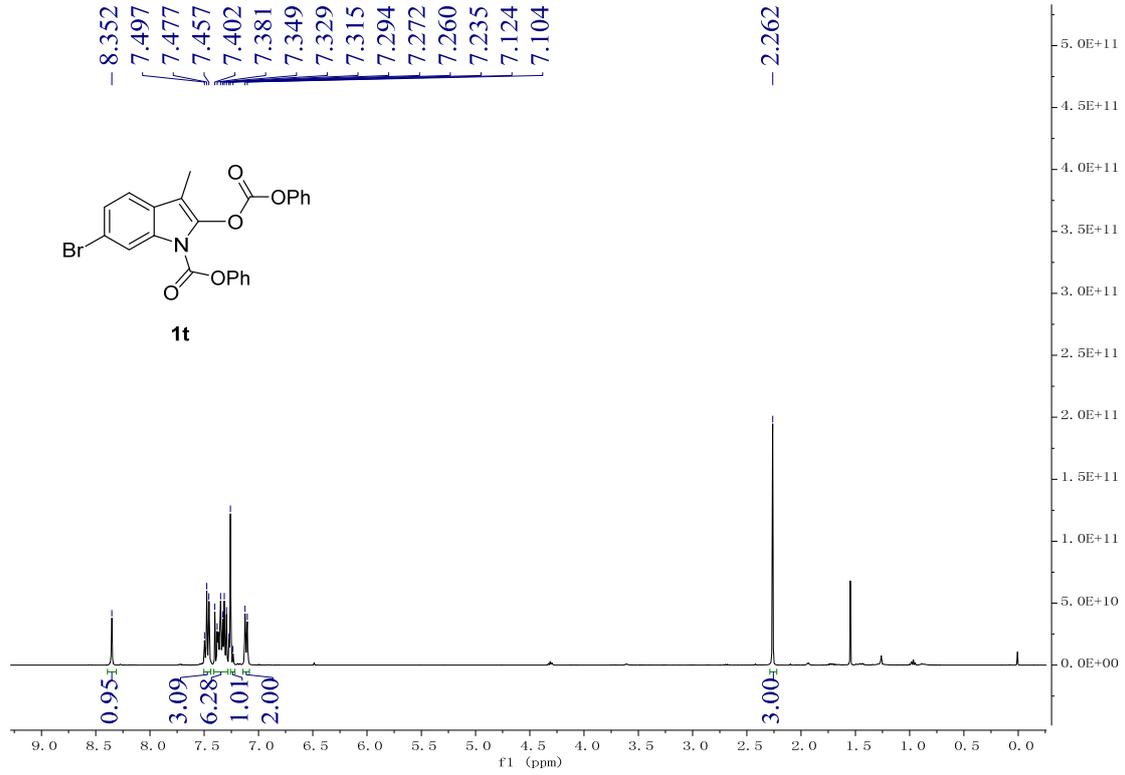
¹H NMR of 1r



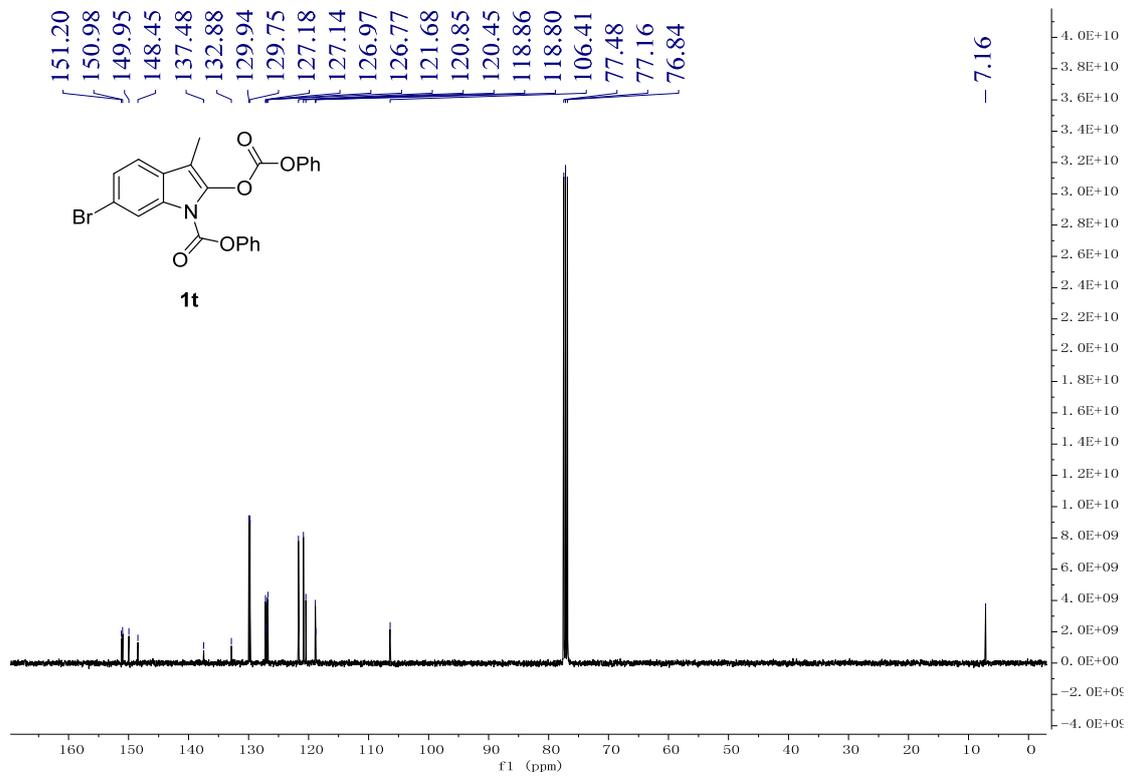
¹³C NMR of 1r



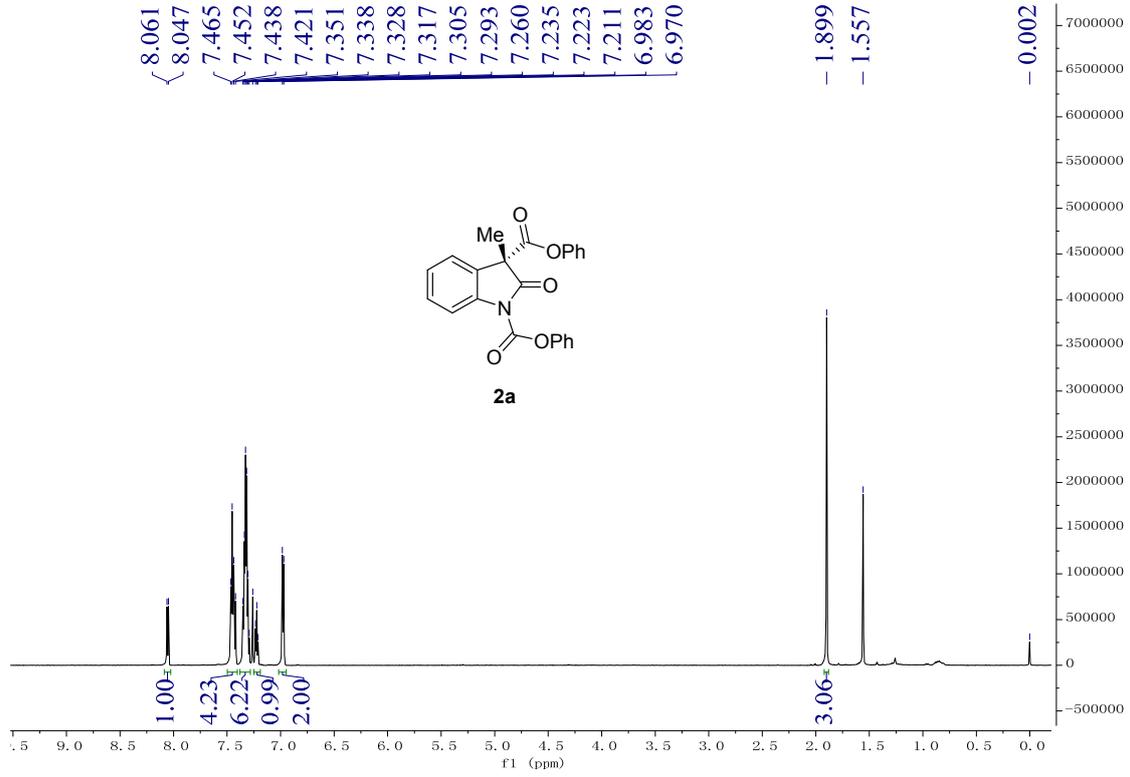
¹H NMR of 1t



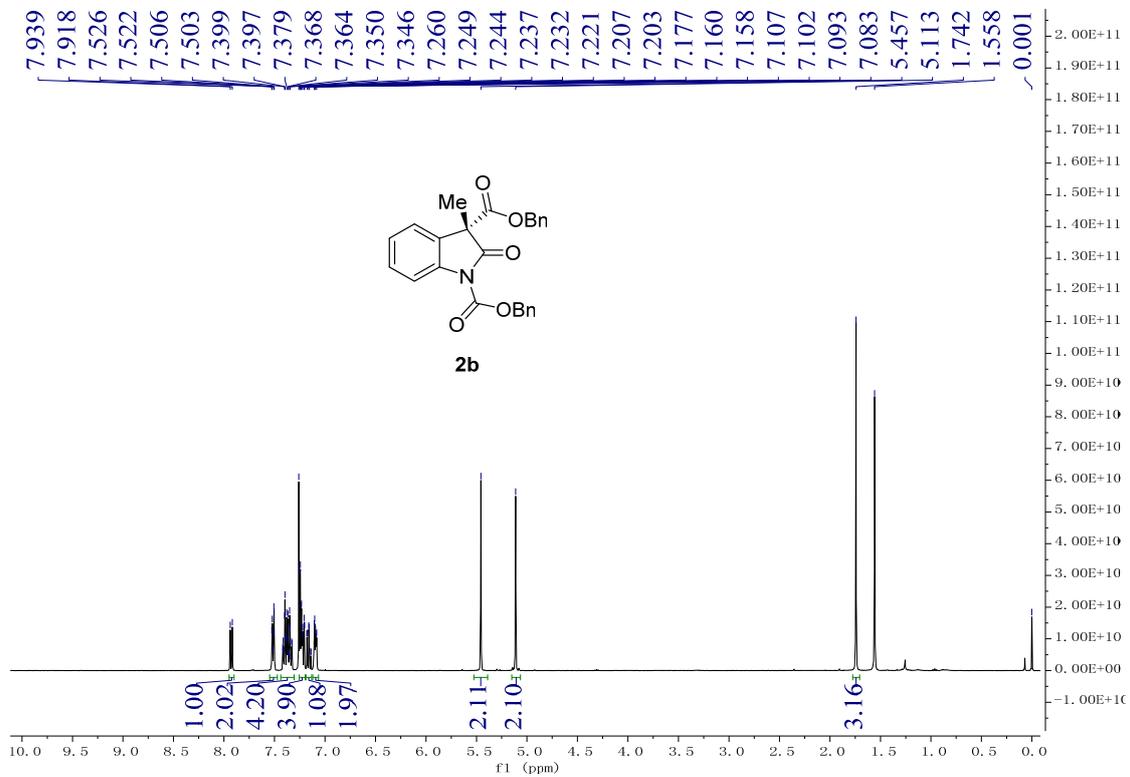
¹³C NMR of 1t



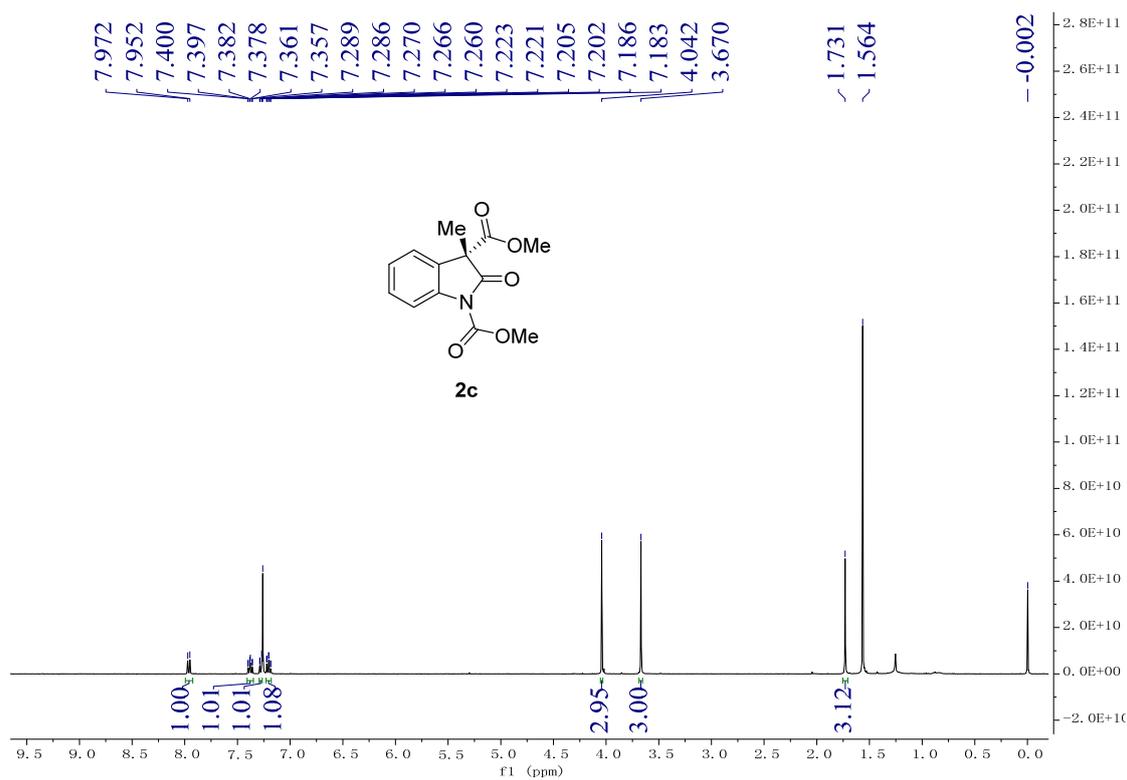
¹H NMR of 2a



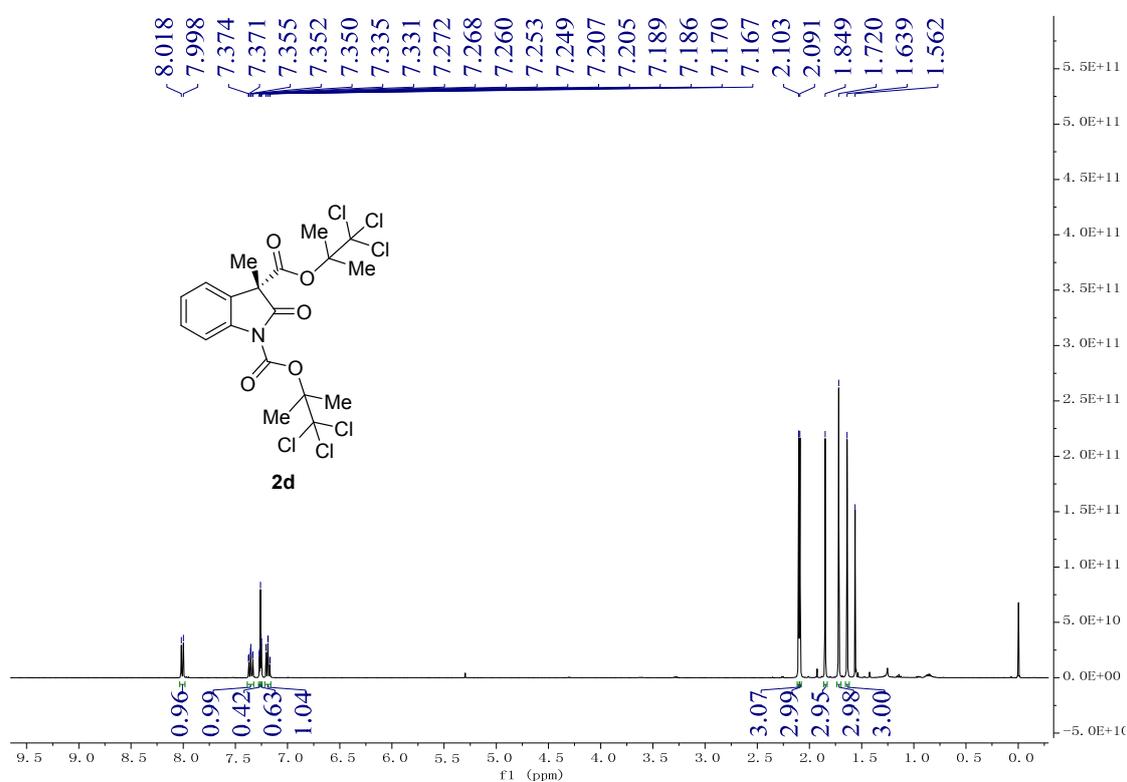
¹H NMR of 2b



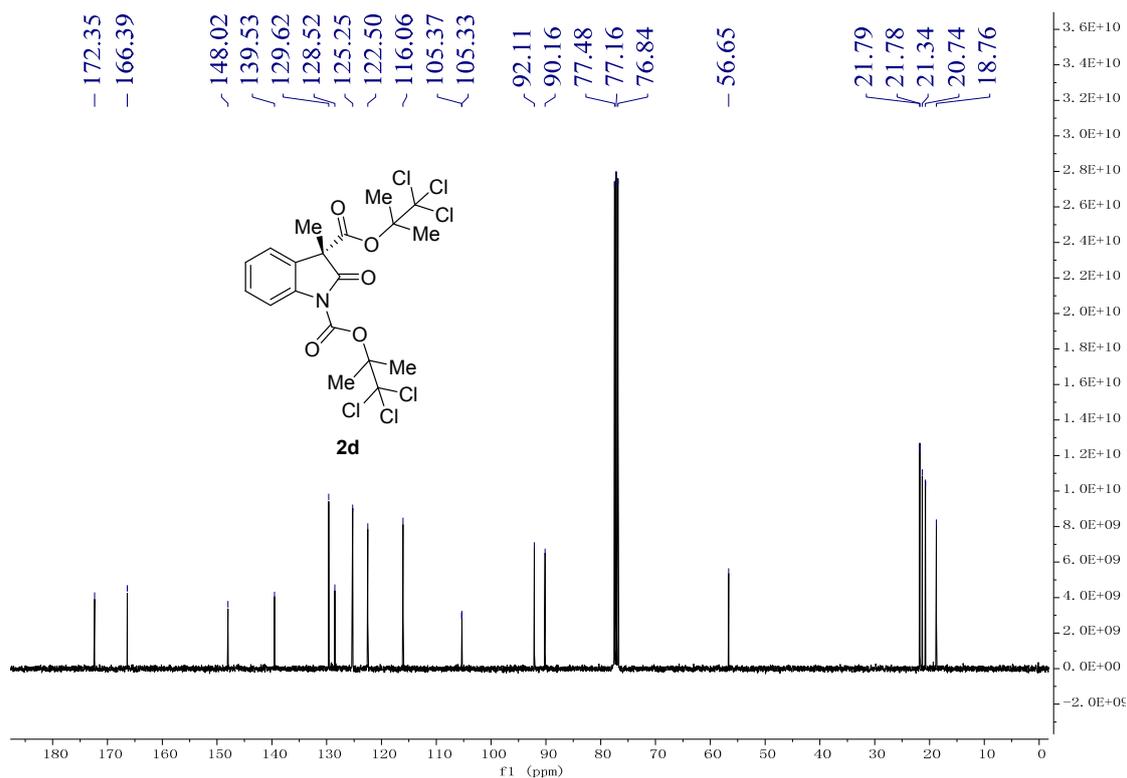
¹H NMR of 2c



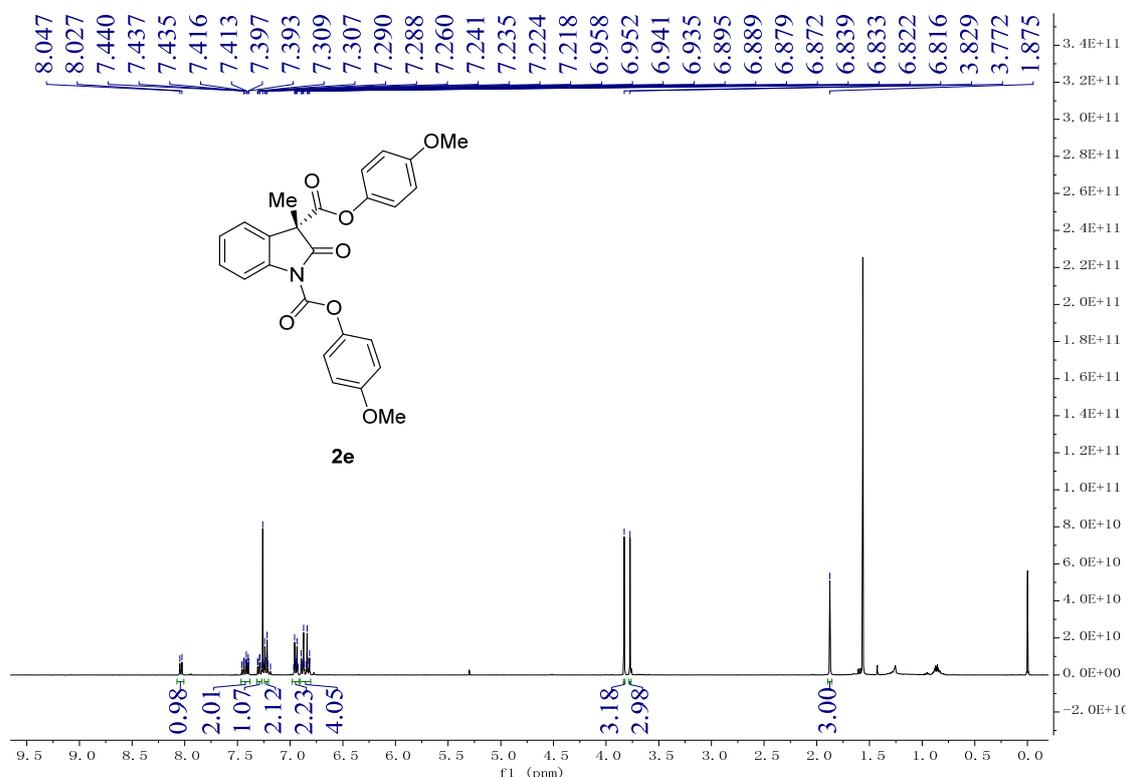
¹H NMR of 2d



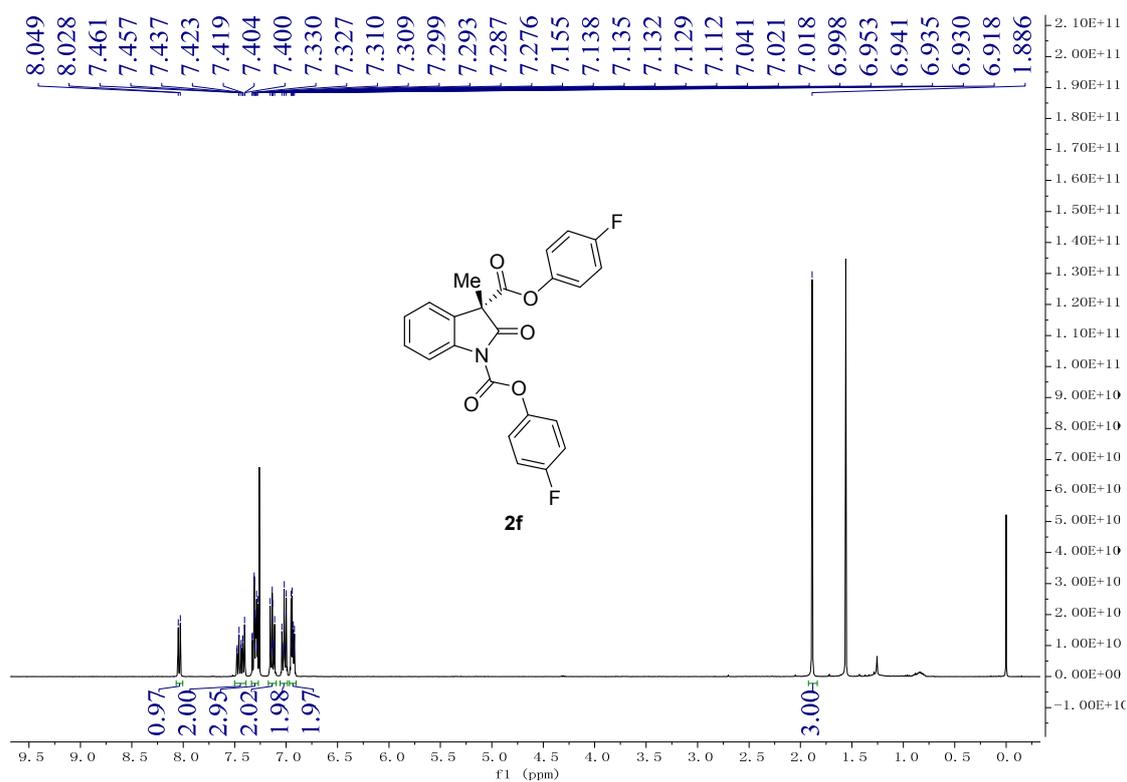
¹³C NMR of 2d



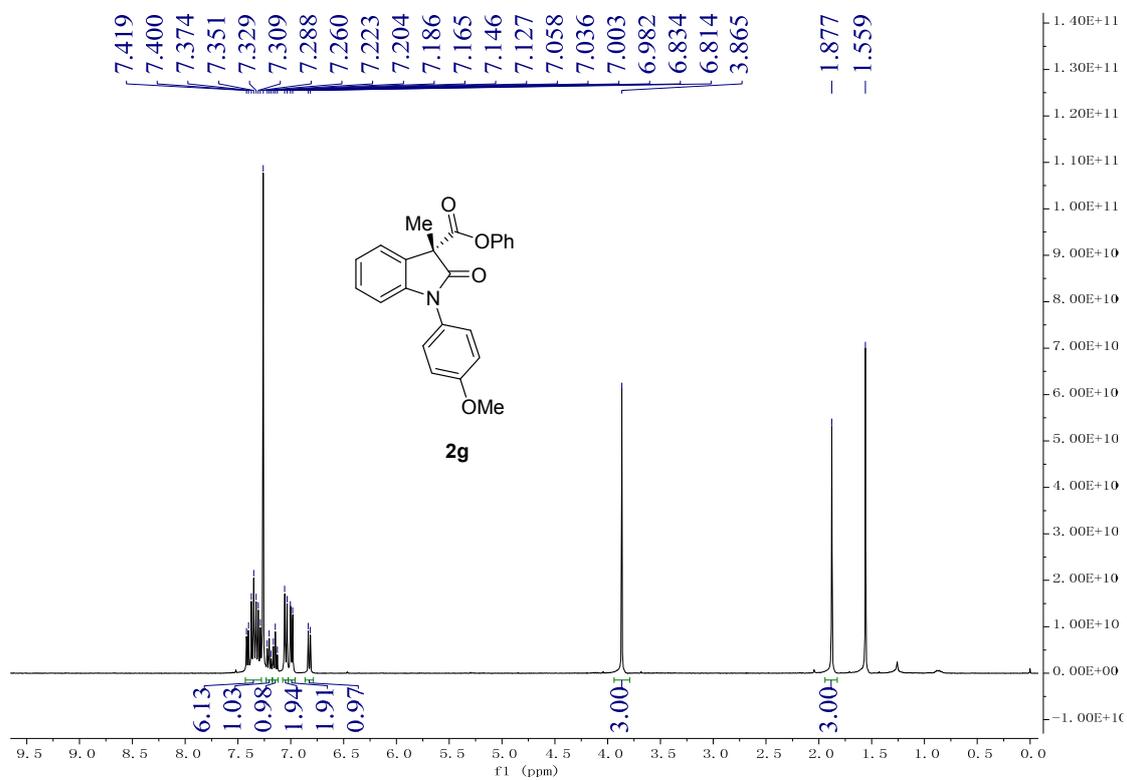
¹H NMR of 2e



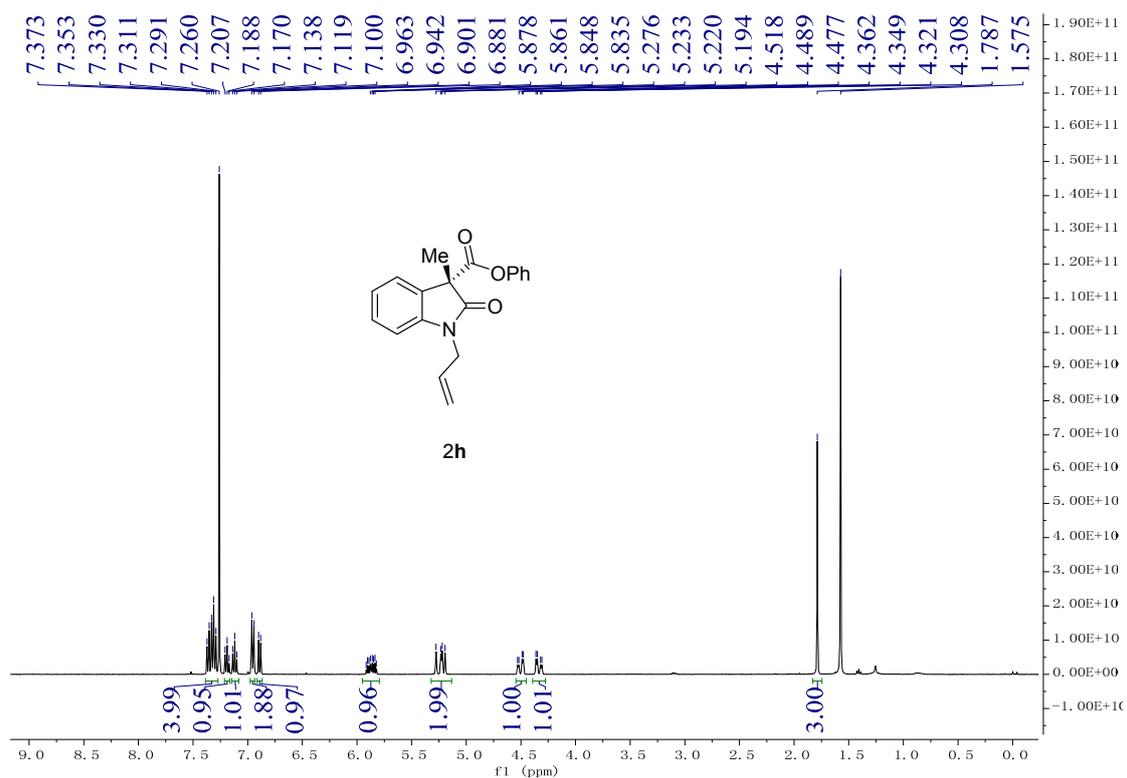
¹H NMR of 2f



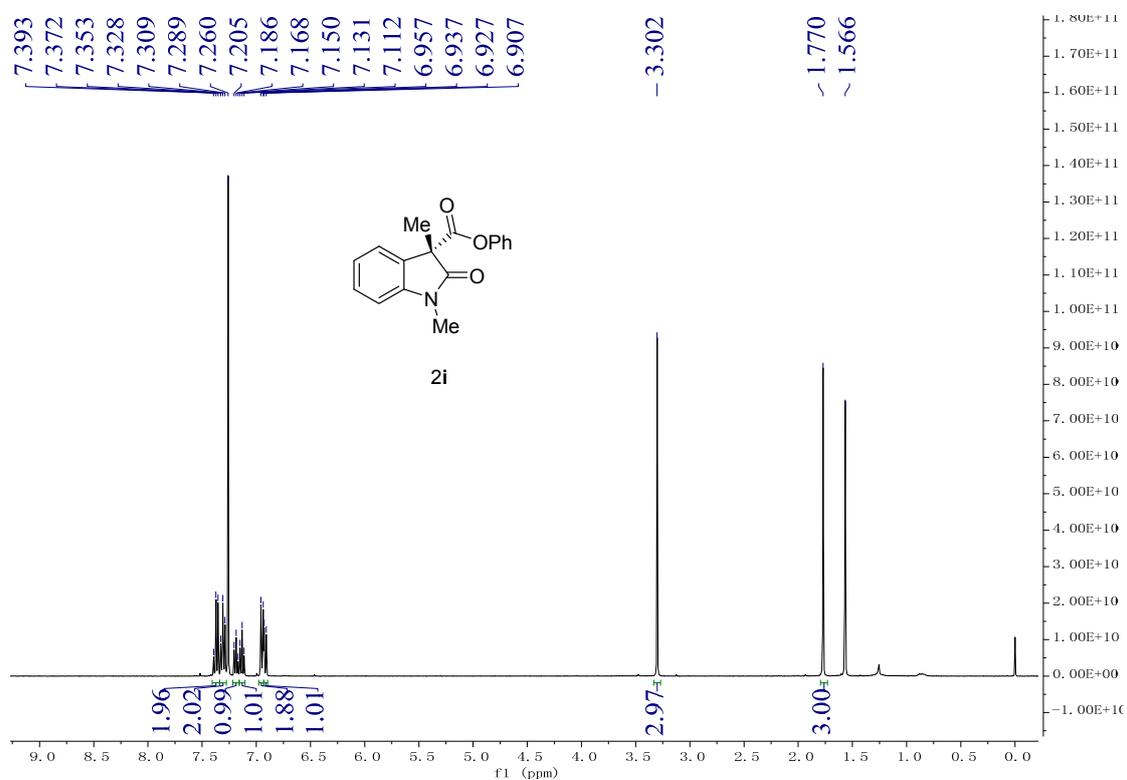
¹H NMR of 2g



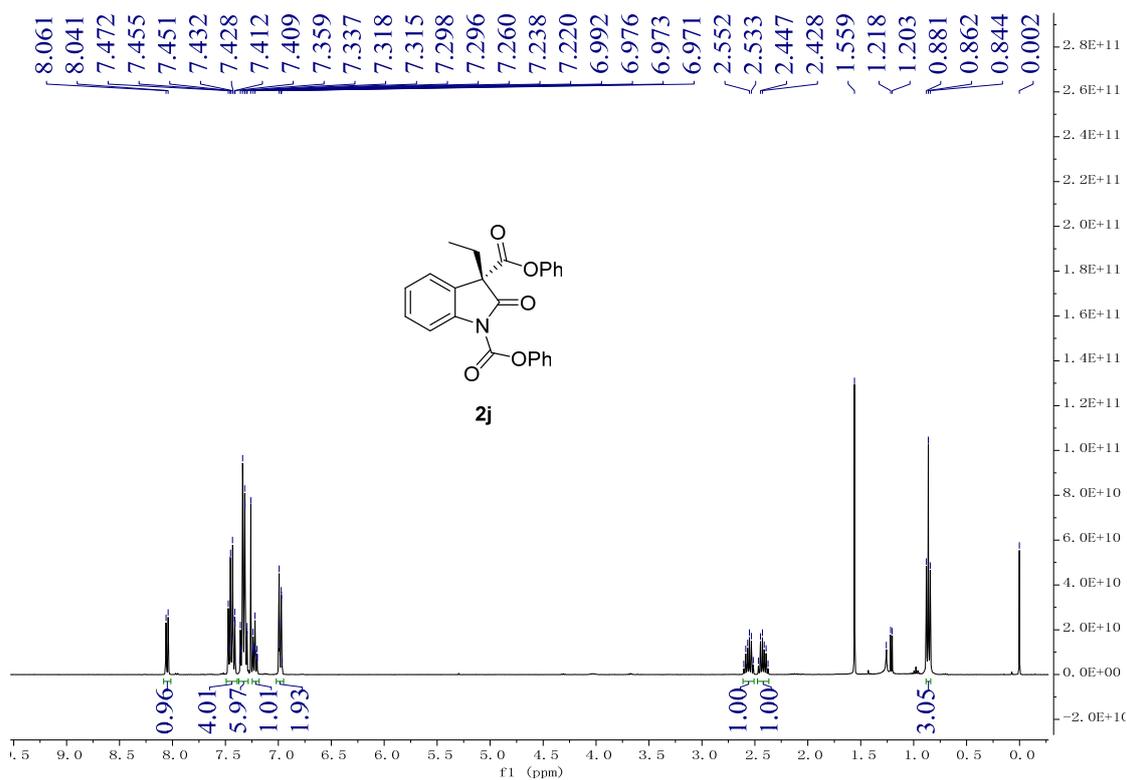
¹H NMR of 2h



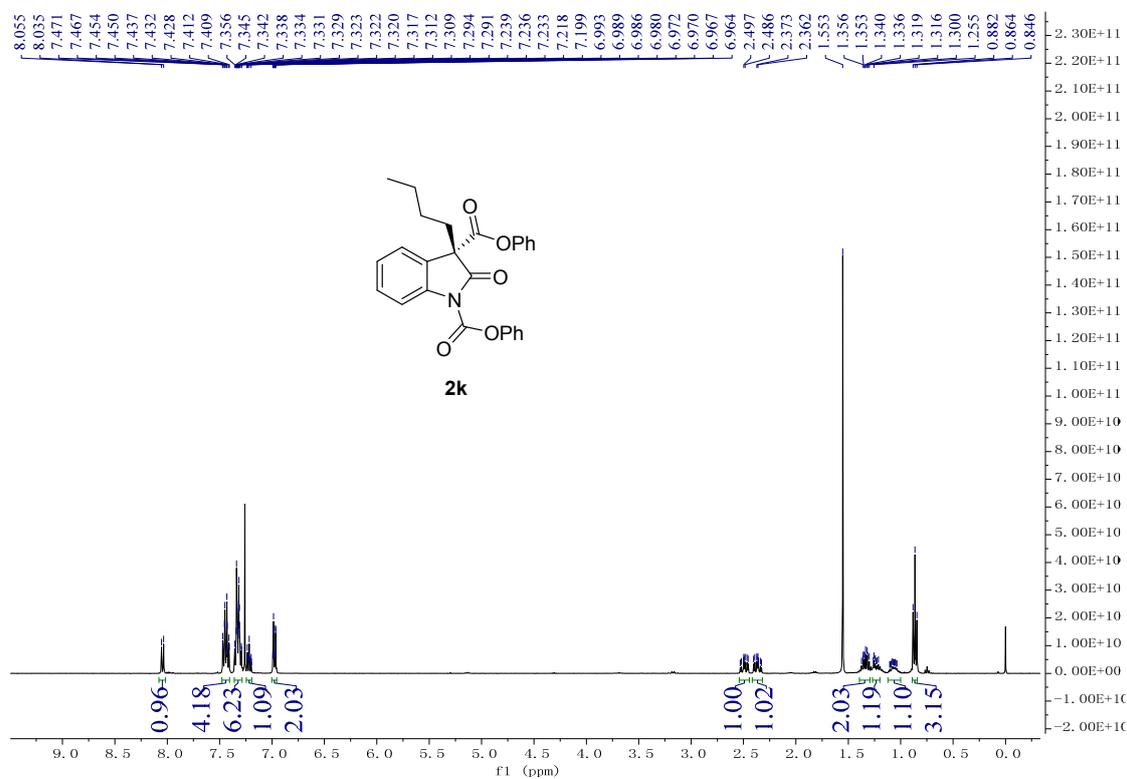
¹H NMR of 2i



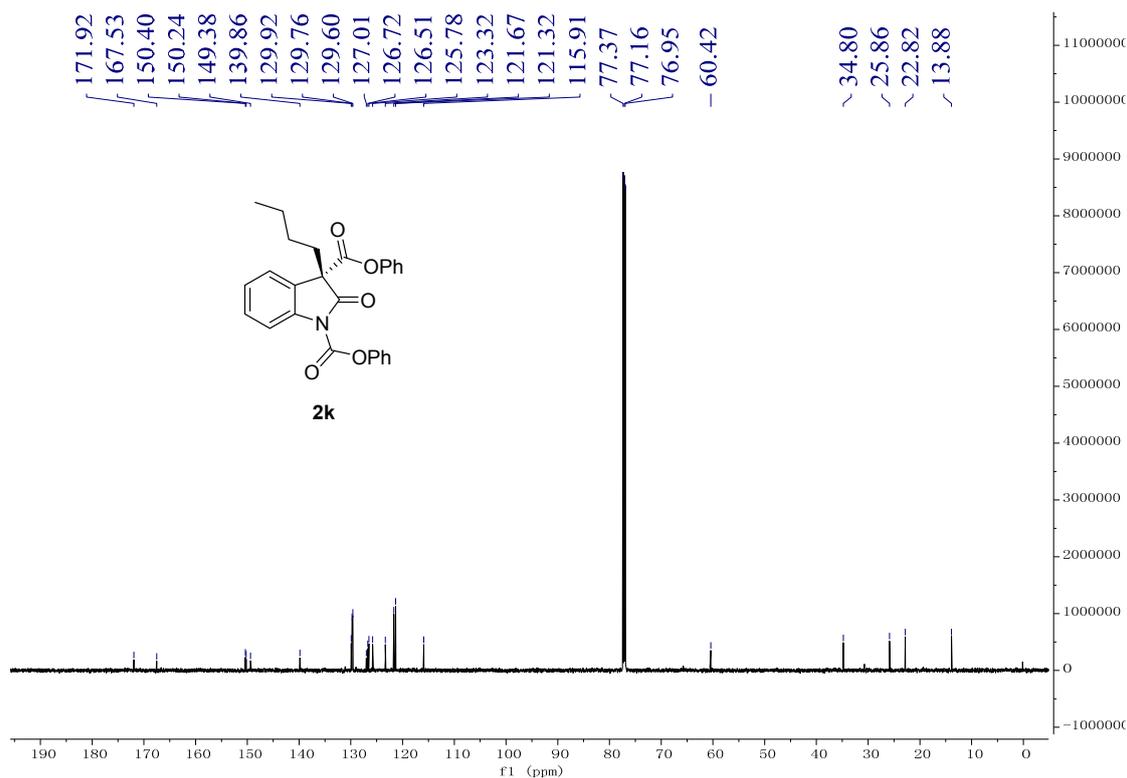
¹H NMR of 2j



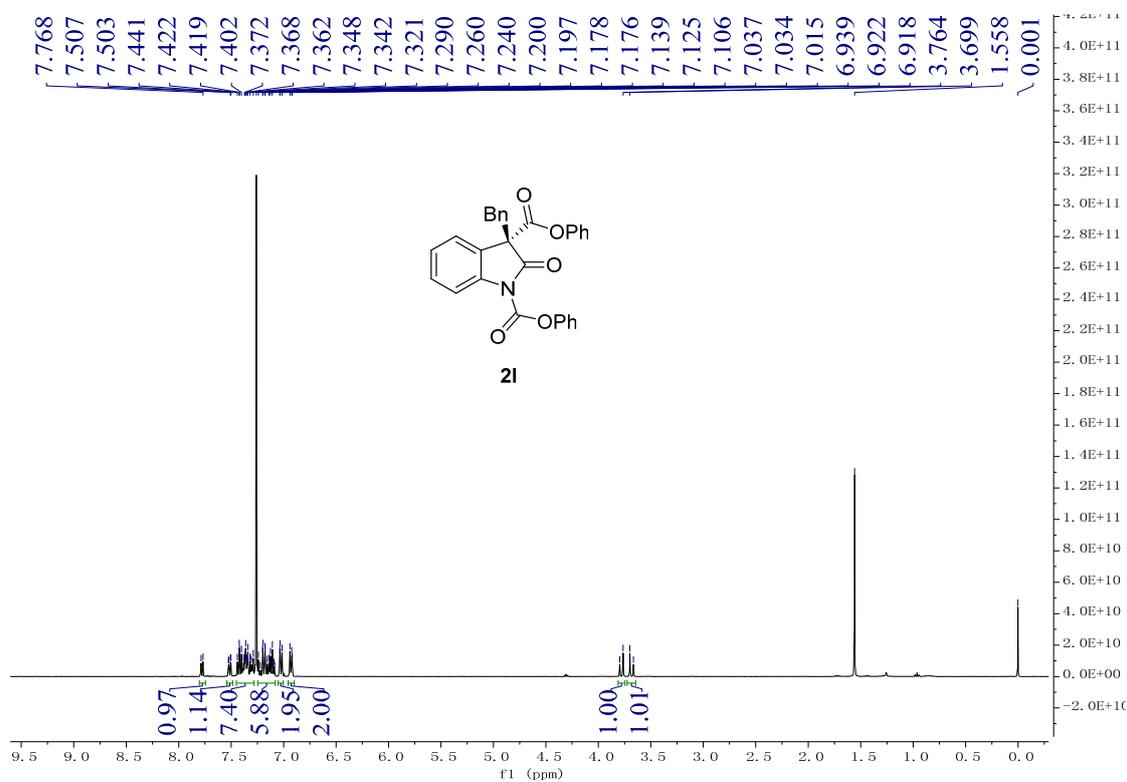
¹H NMR of 2k



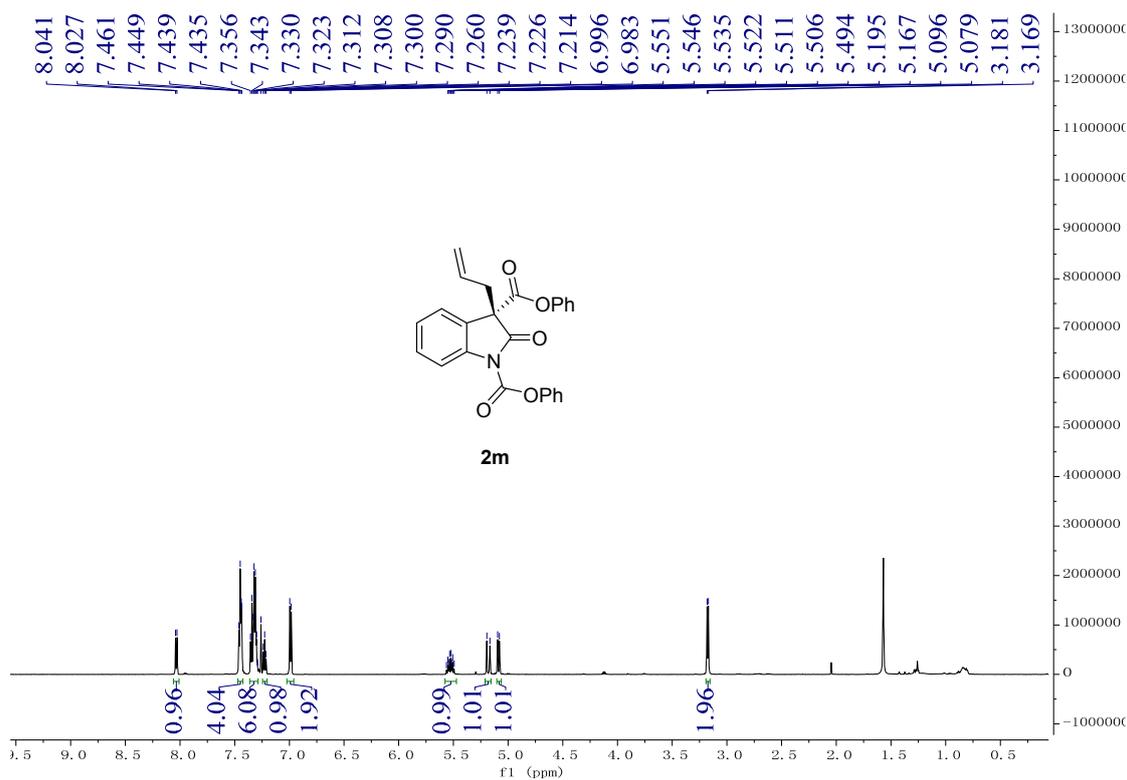
¹³C NMR of 2k



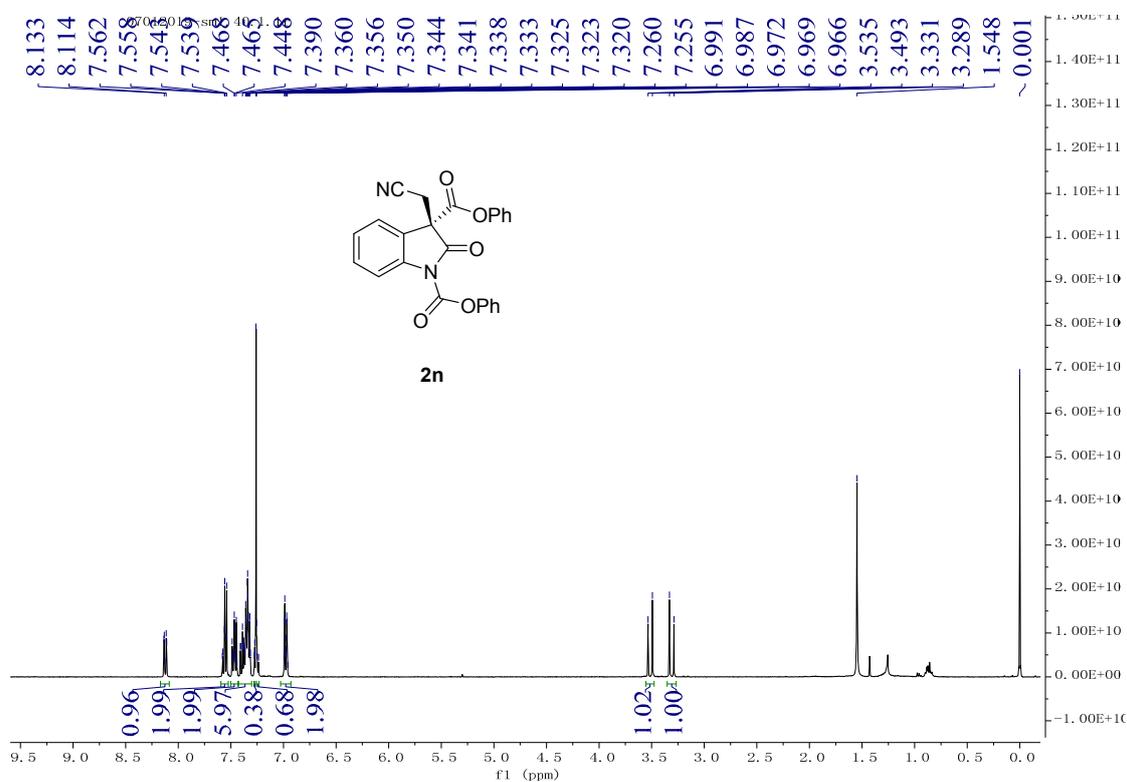
¹H NMR of 2l



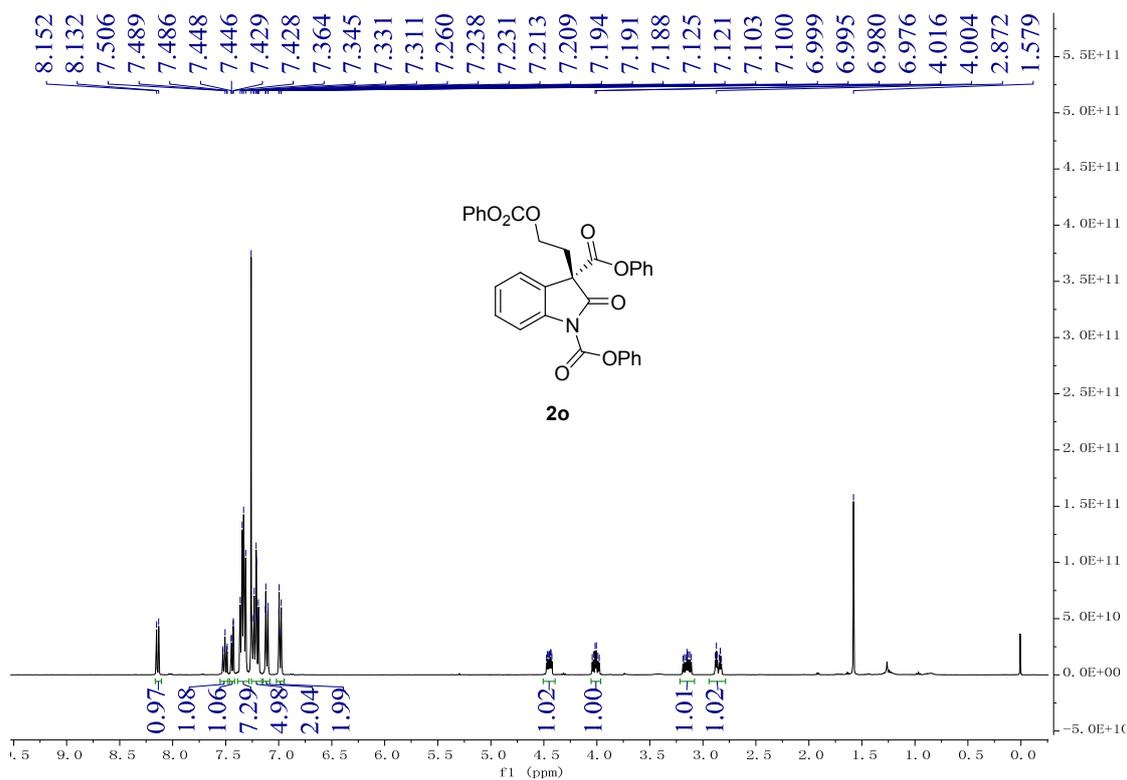
¹H NMR of 2m



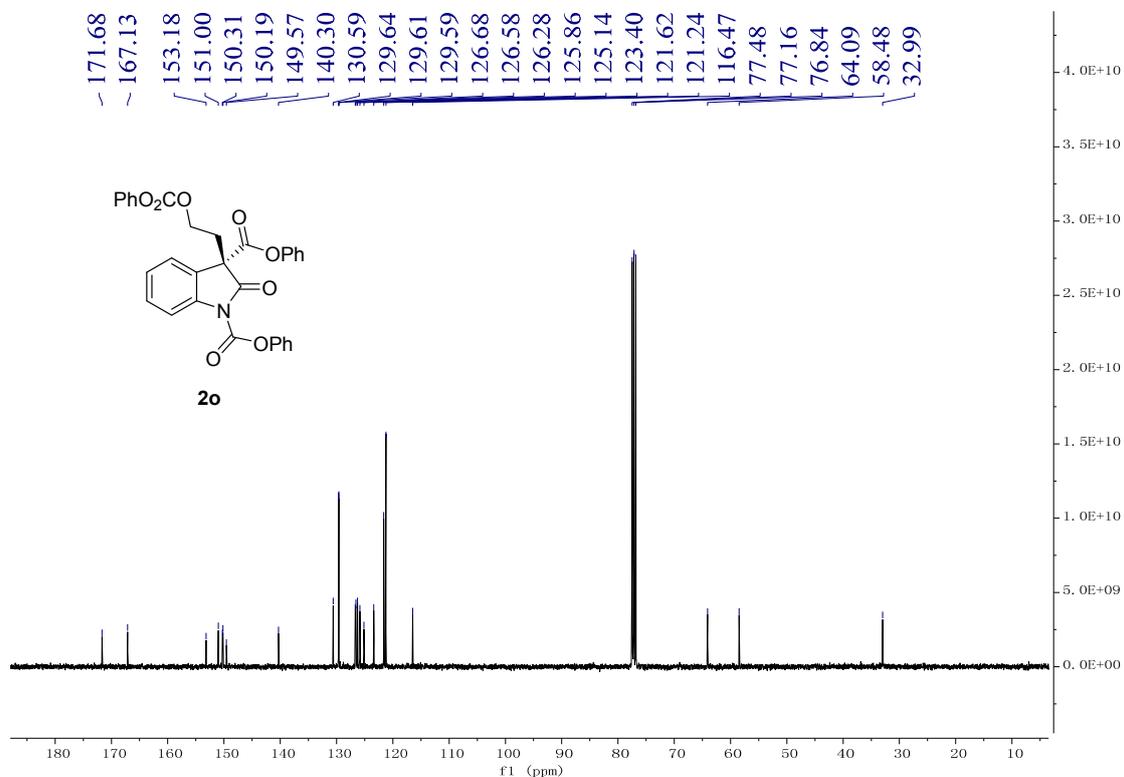
¹H NMR of 2n



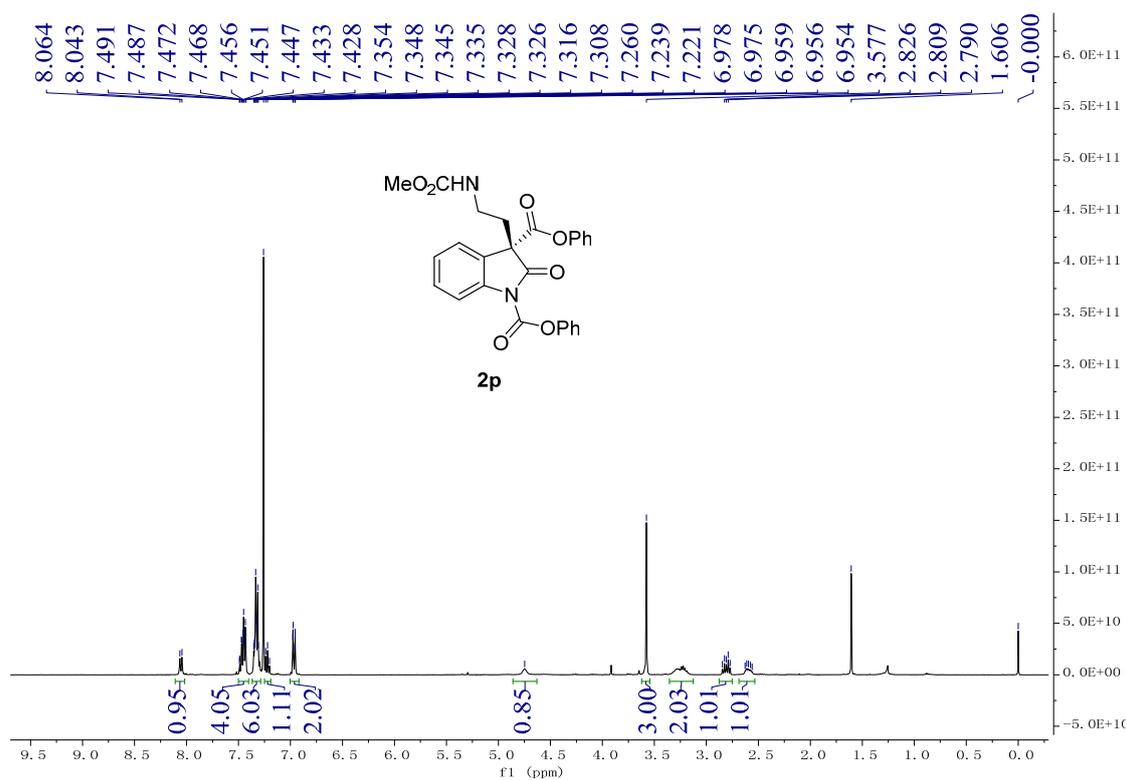
¹H NMR of 2o



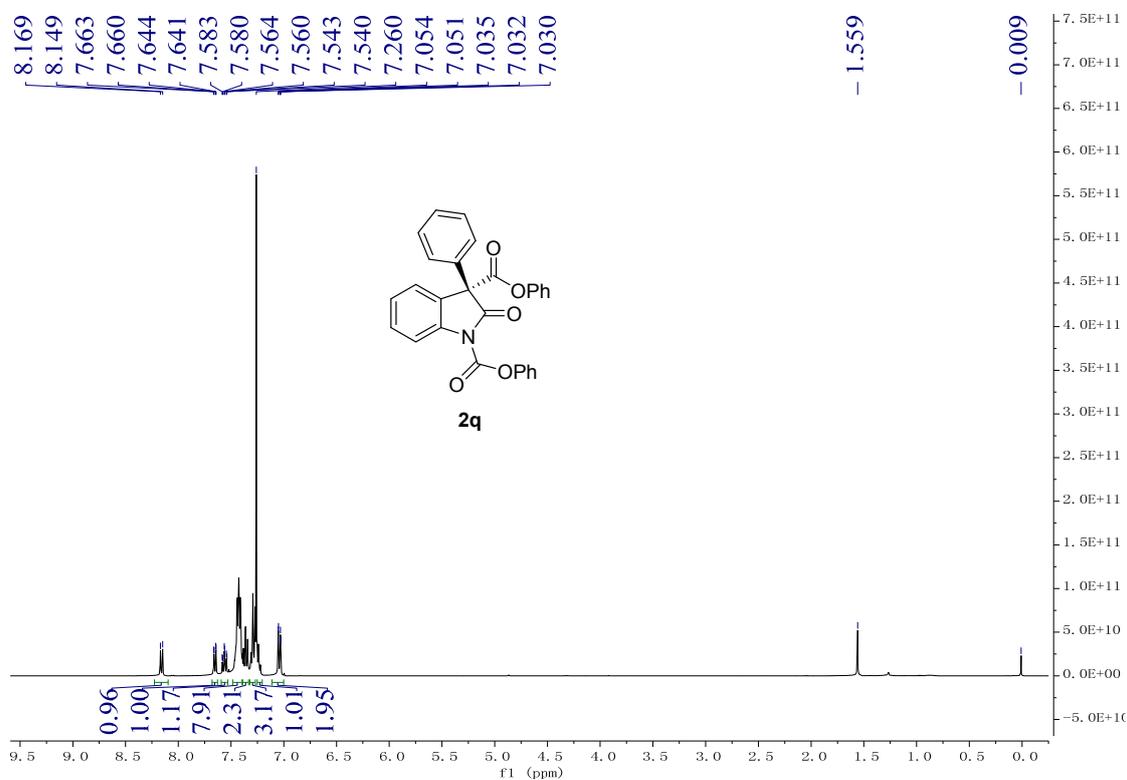
¹³C NMR of 2o



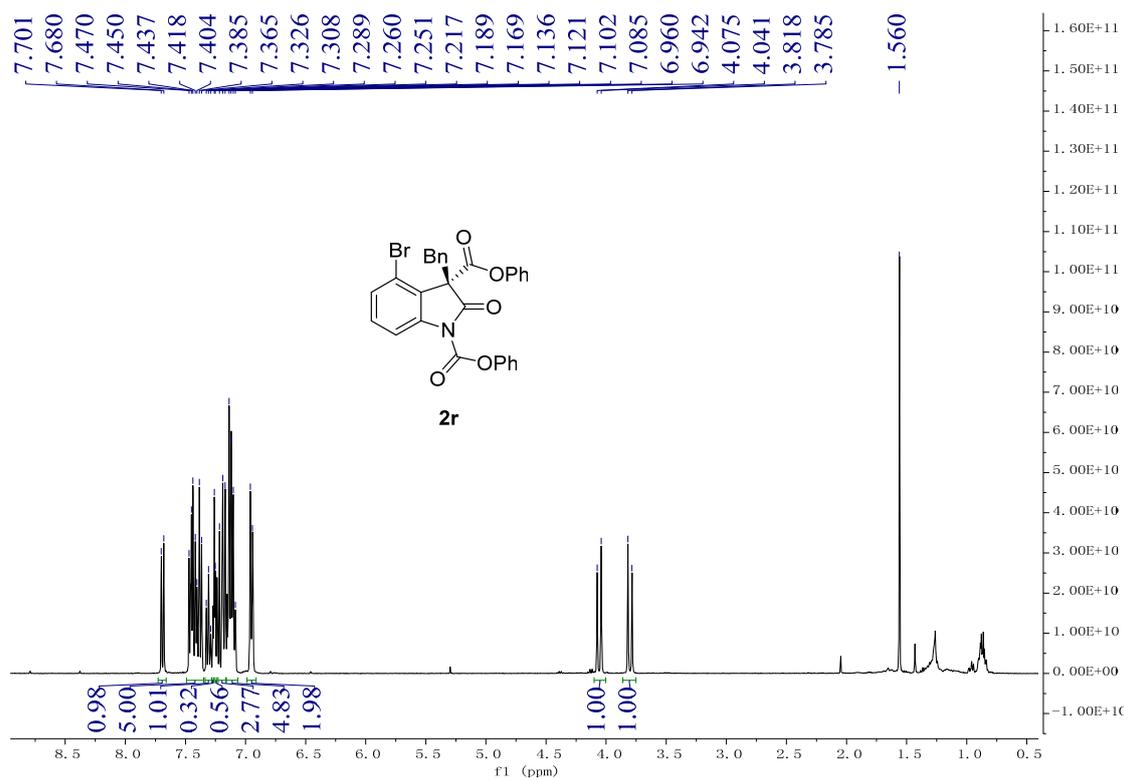
¹H NMR of 2p



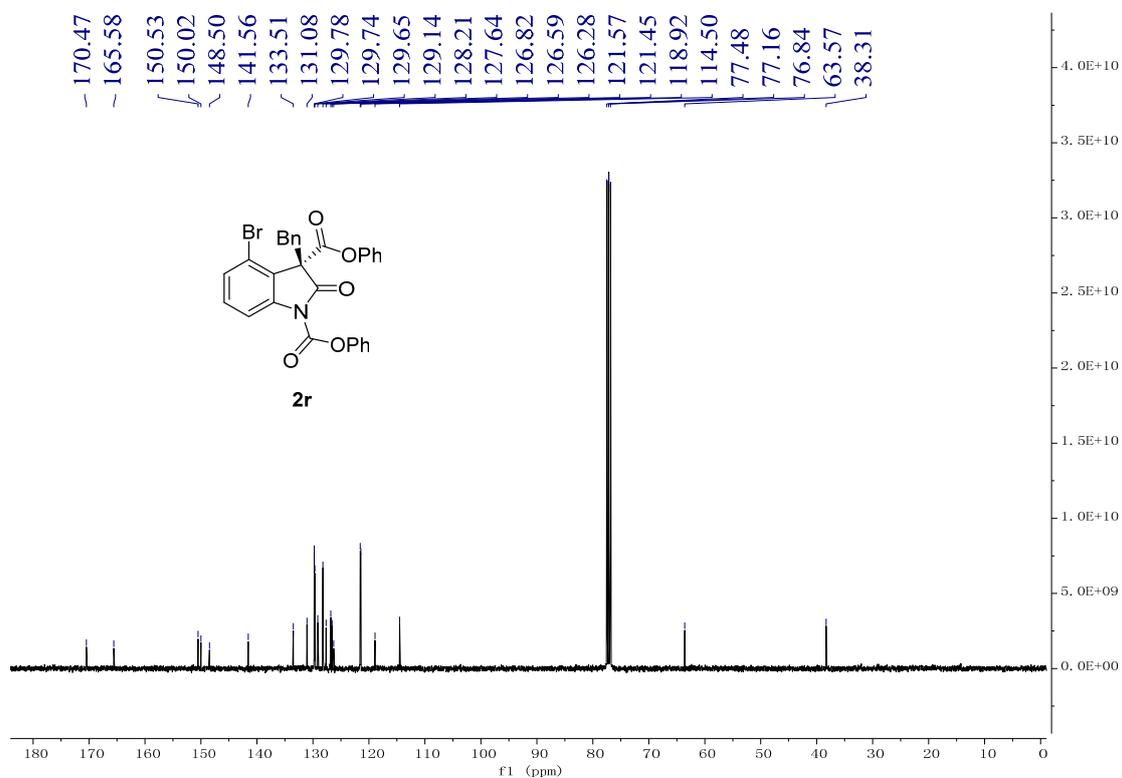
¹H NMR of 2q



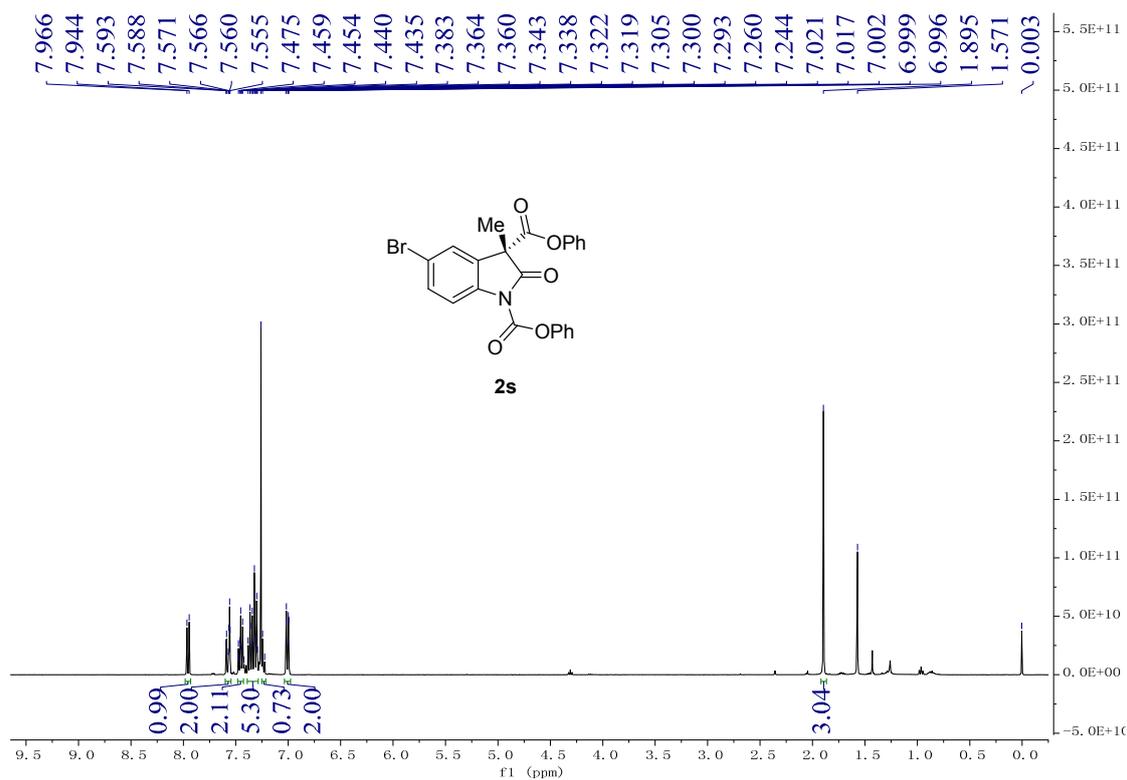
¹H NMR of 2r



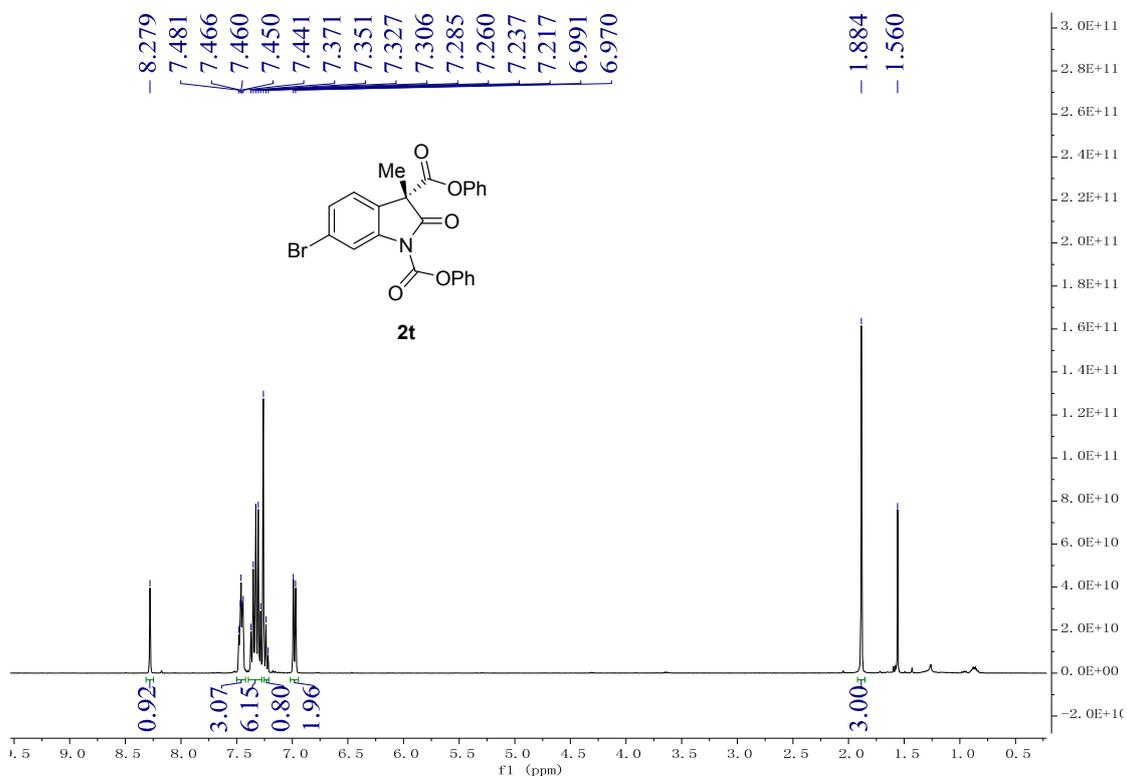
¹³C NMR of 2r



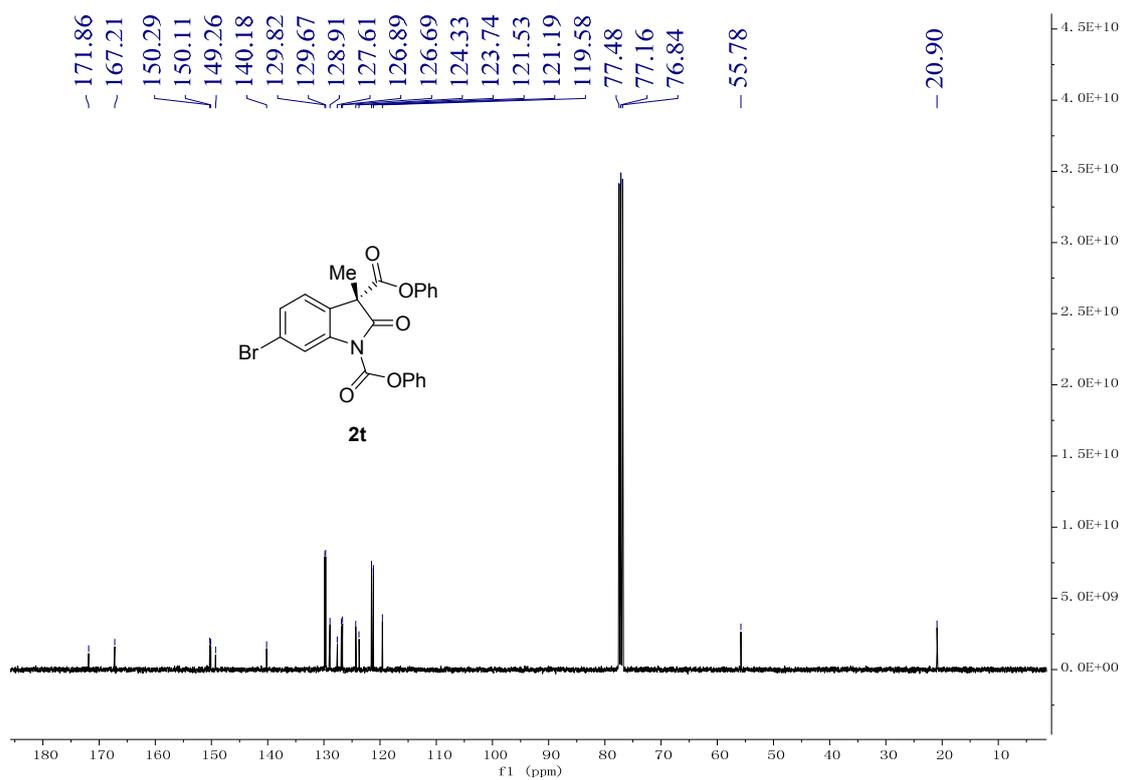
¹H NMR of 2s



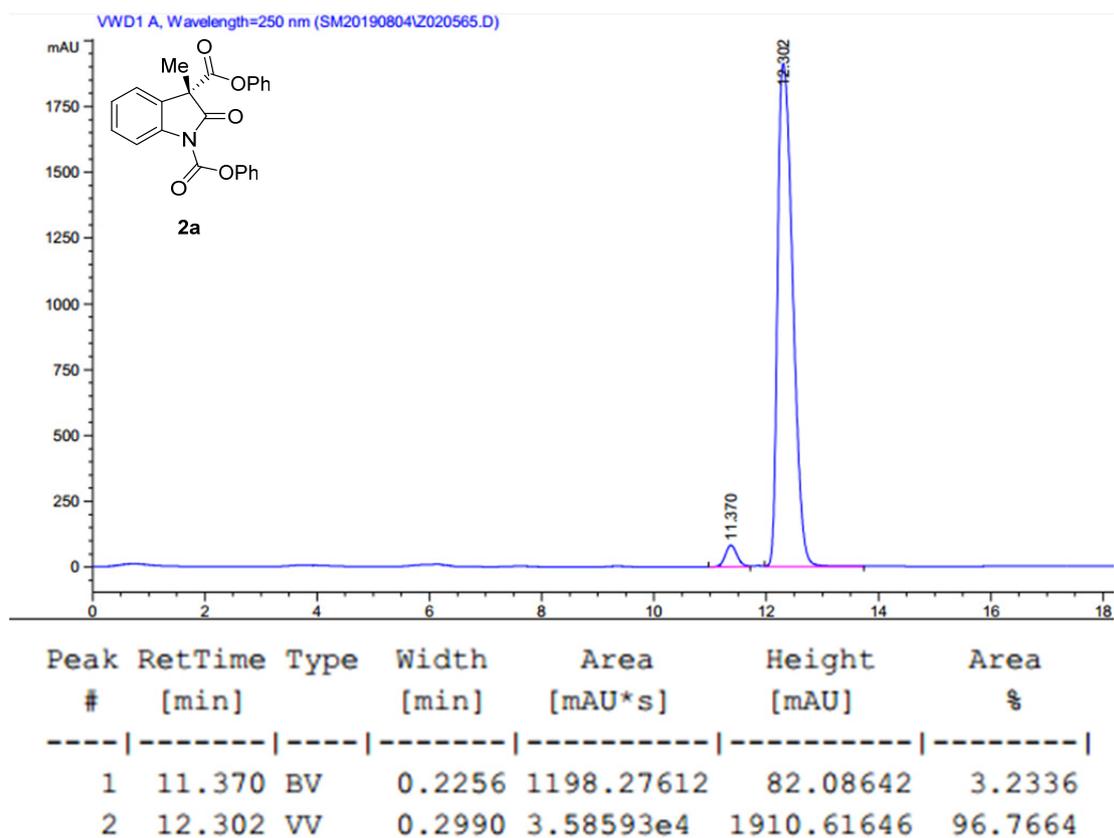
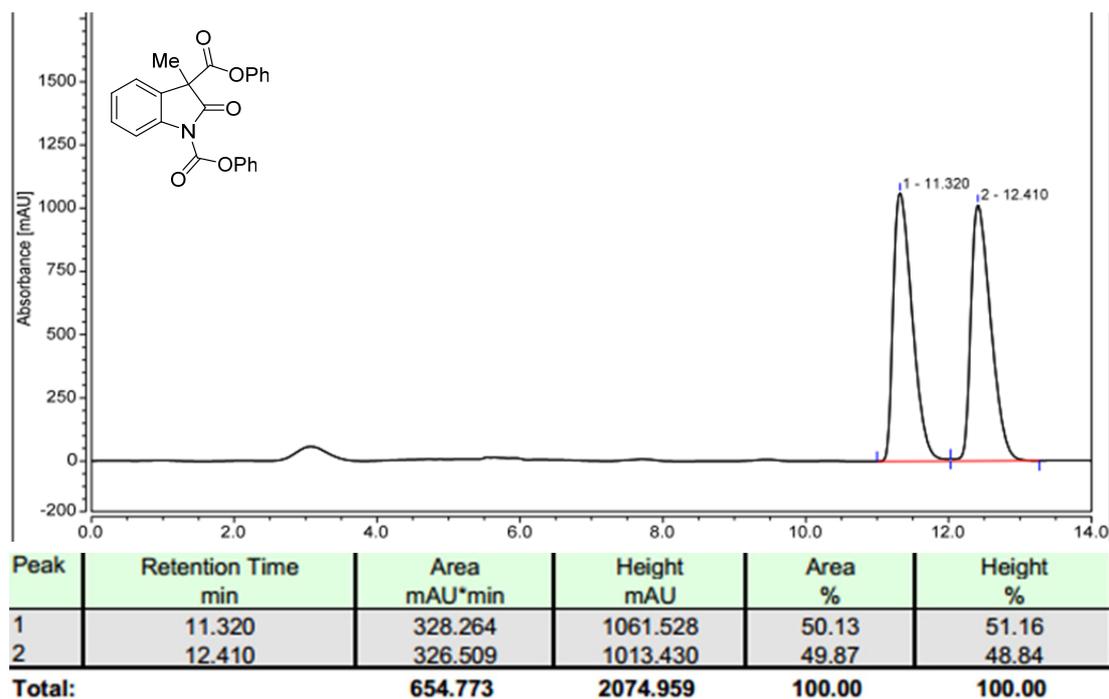
¹H NMR of 2t

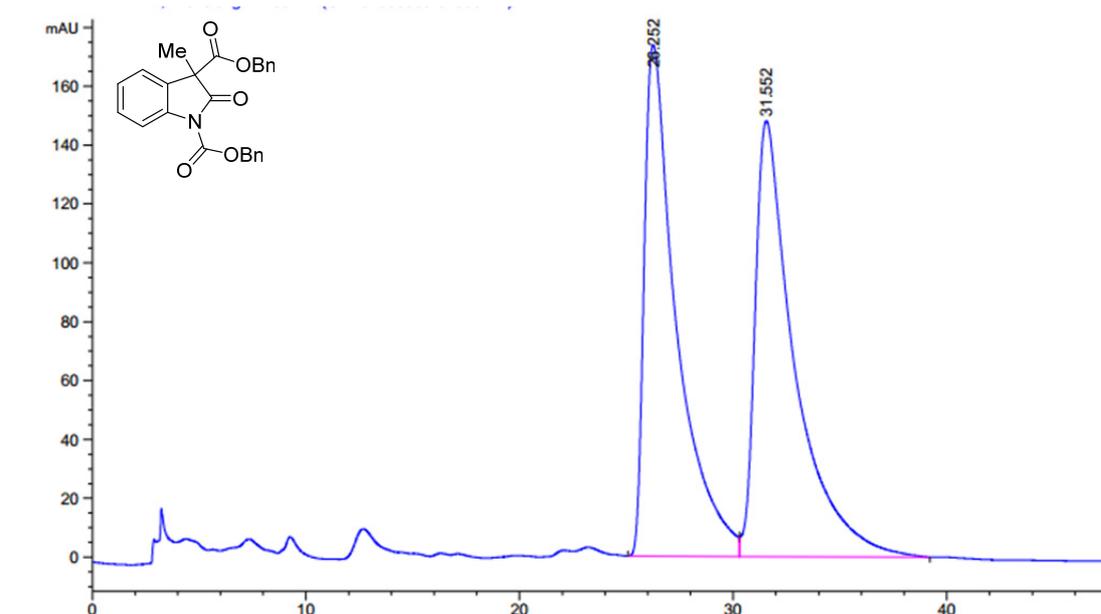


¹³C NMR of 2t

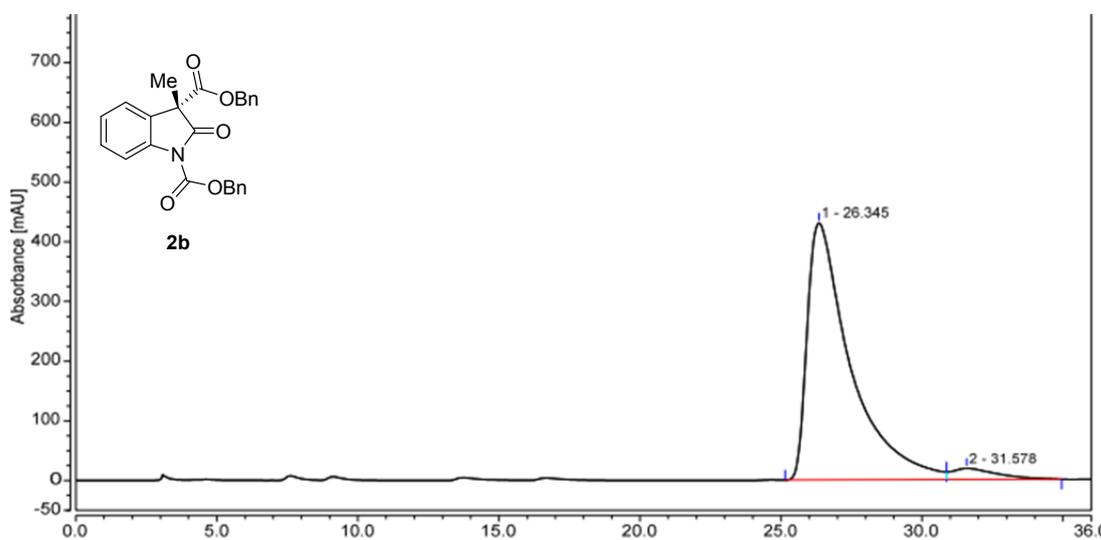


9. Copies of HPLC Spectra



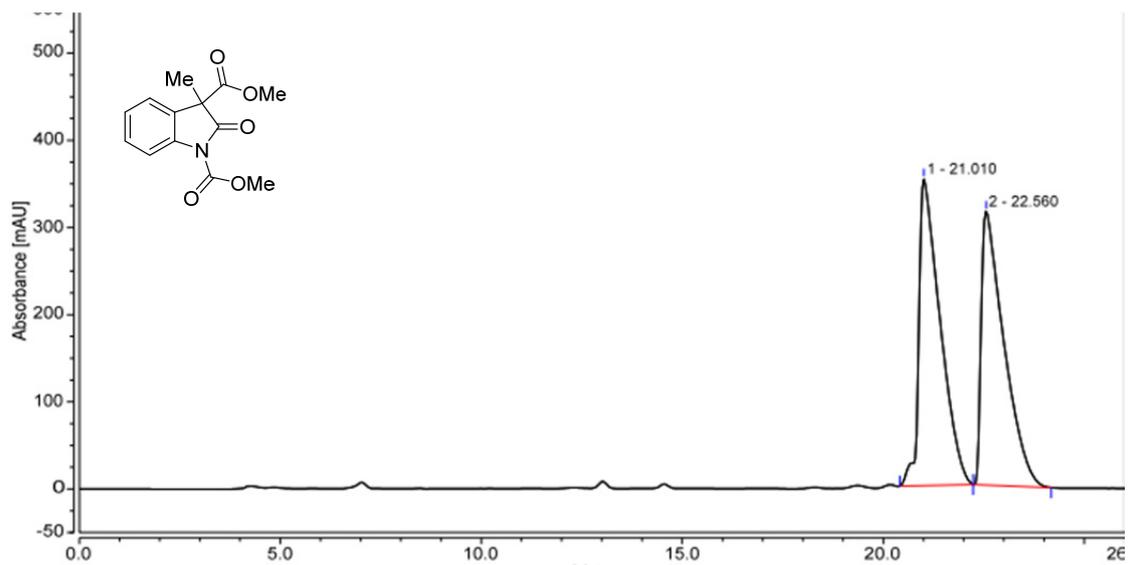


Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	26.252	BV	1.4950	1.82735e4	173.74110	49.0803
2	31.552	VB	1.7662	1.89584e4	148.05878	50.9197

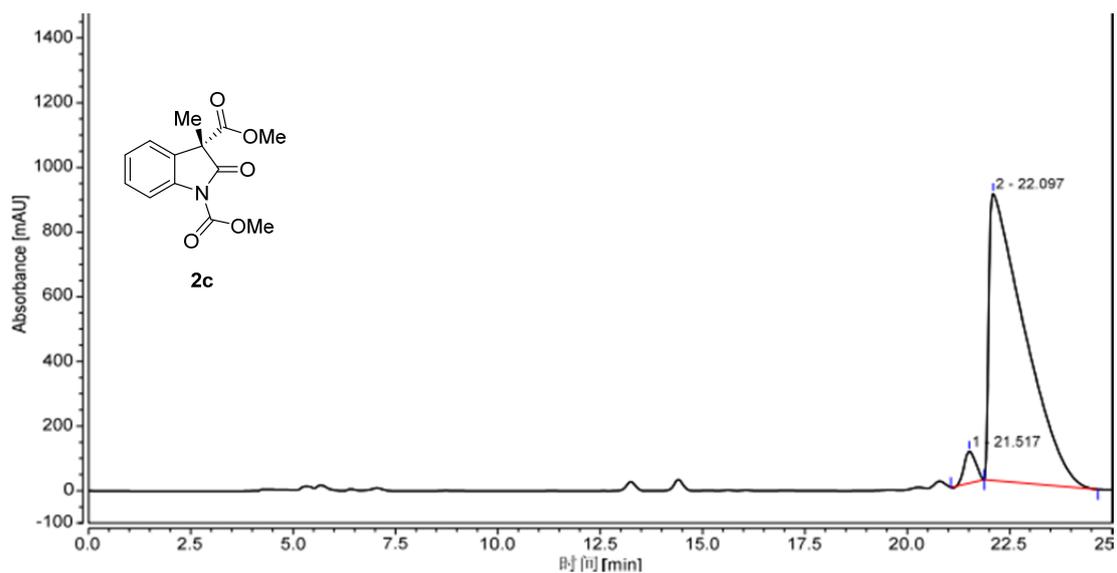


积分结果

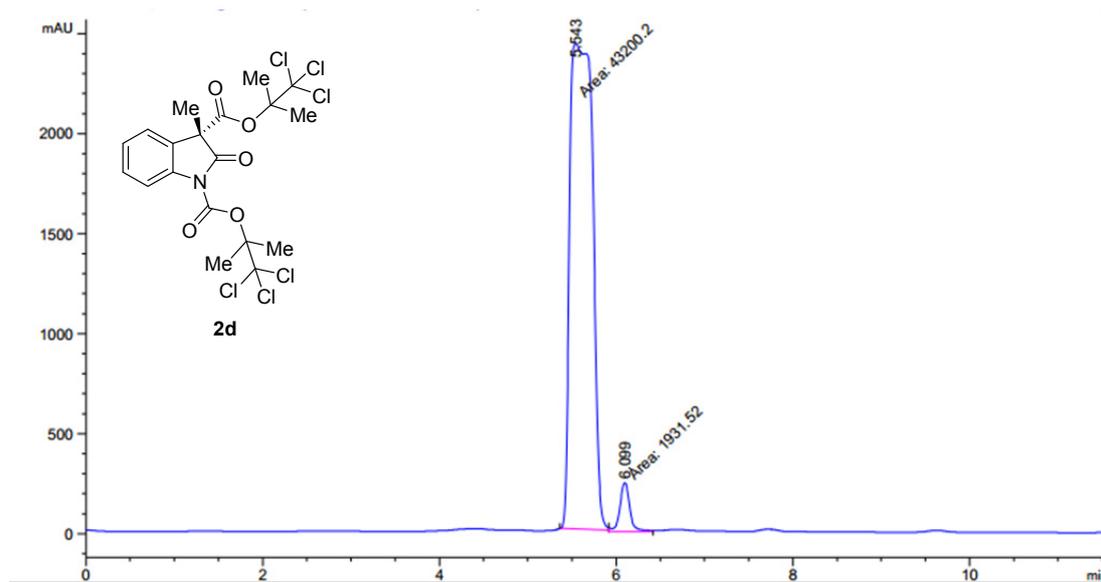
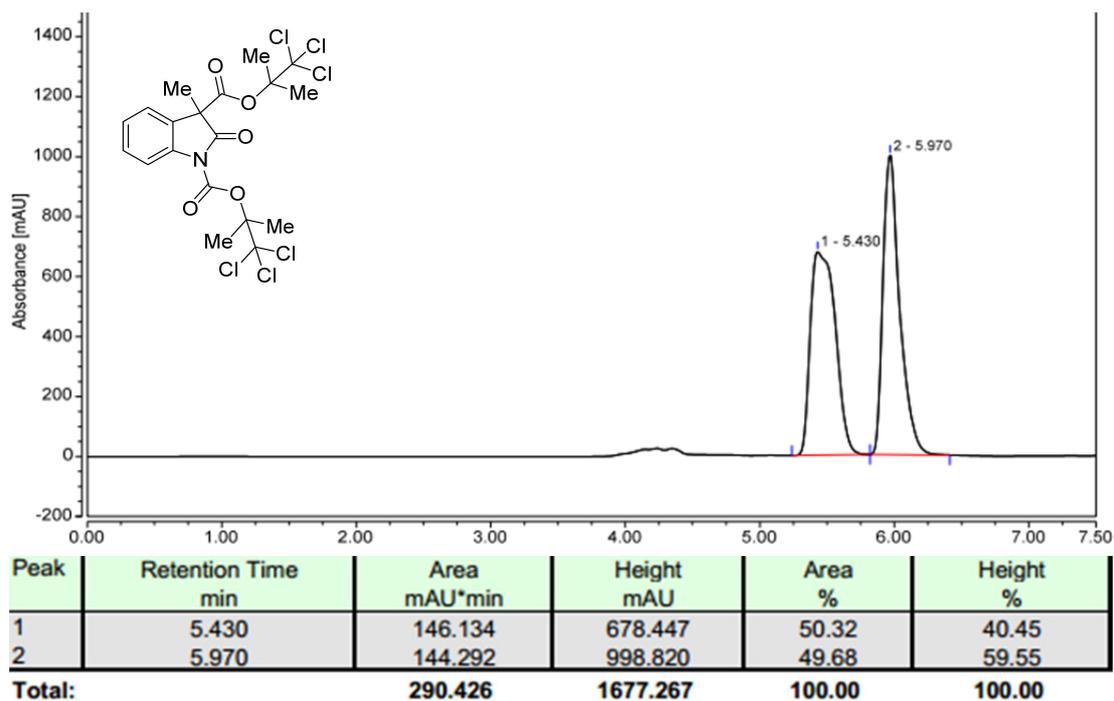
Peak	Retention Time min	Area mAU*min	Height mAU	Area %	Height %
1	26.345	764.464	430.290	95.66	95.84
2	31.578	34.712	18.664	4.34	4.16
Total:		799.176	448.954	100.00	100.00

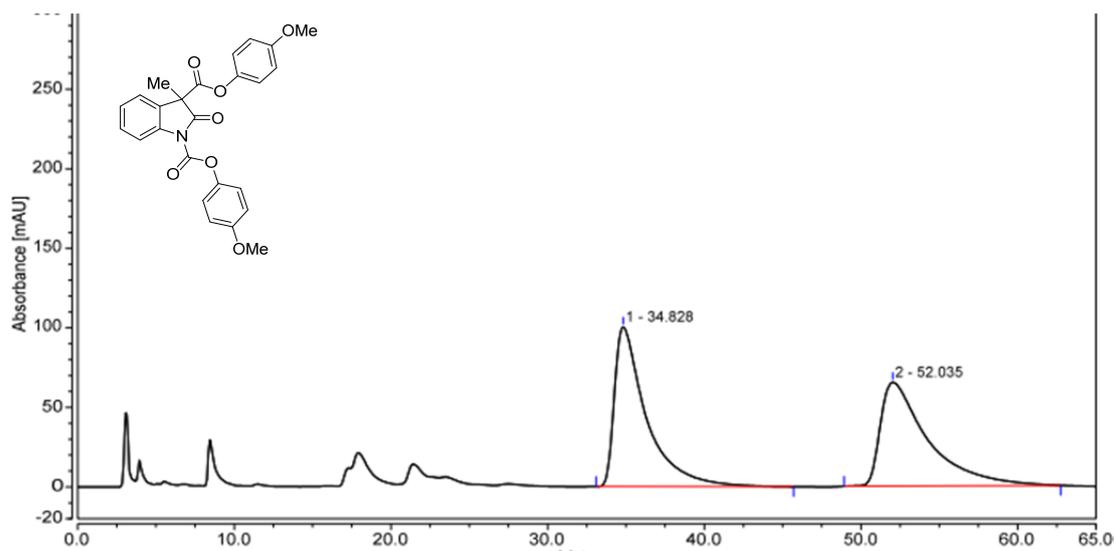


Peak	Retention Time min	Area mAU*min	Height mAU	Area %	Height %
1	21.010	216.097	351.820	51.24	52.84
2	22.560	205.602	314.056	48.76	47.16
Total:		421.700	665.875	100.00	100.00

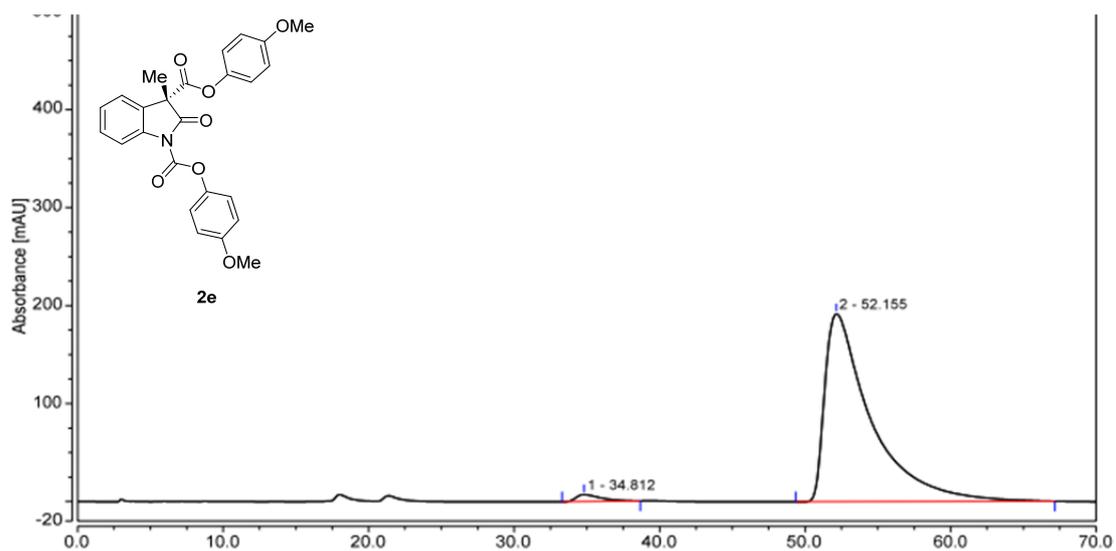


Peak	Retention Time min	Area mAU*min	Height mAU	Area %	Height %
1	21.517	32.069	98.238	3.47	9.97
2	22.097	892.689	887.431	96.53	90.03
Total:		924.758	985.669	100.00	100.00

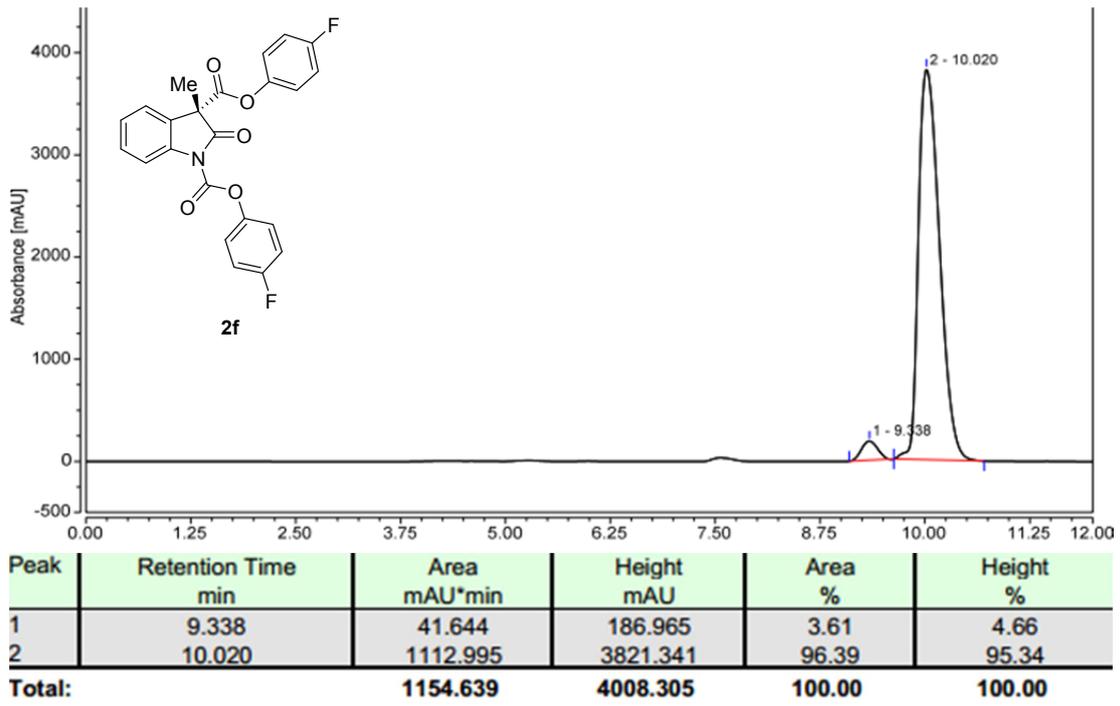
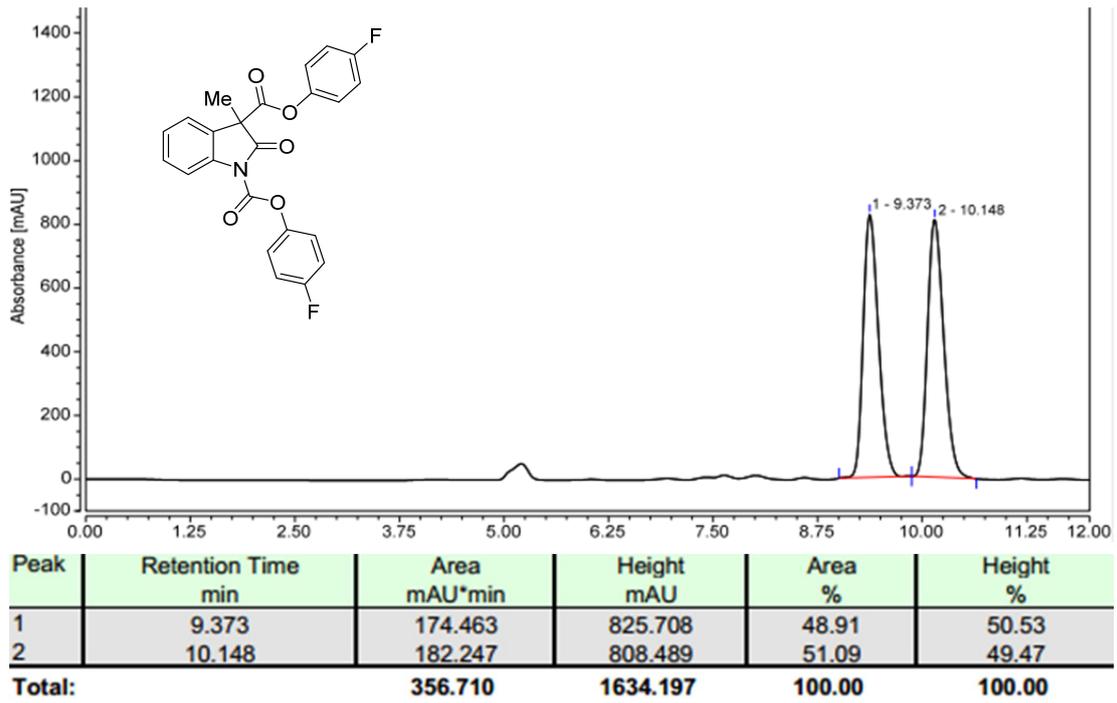


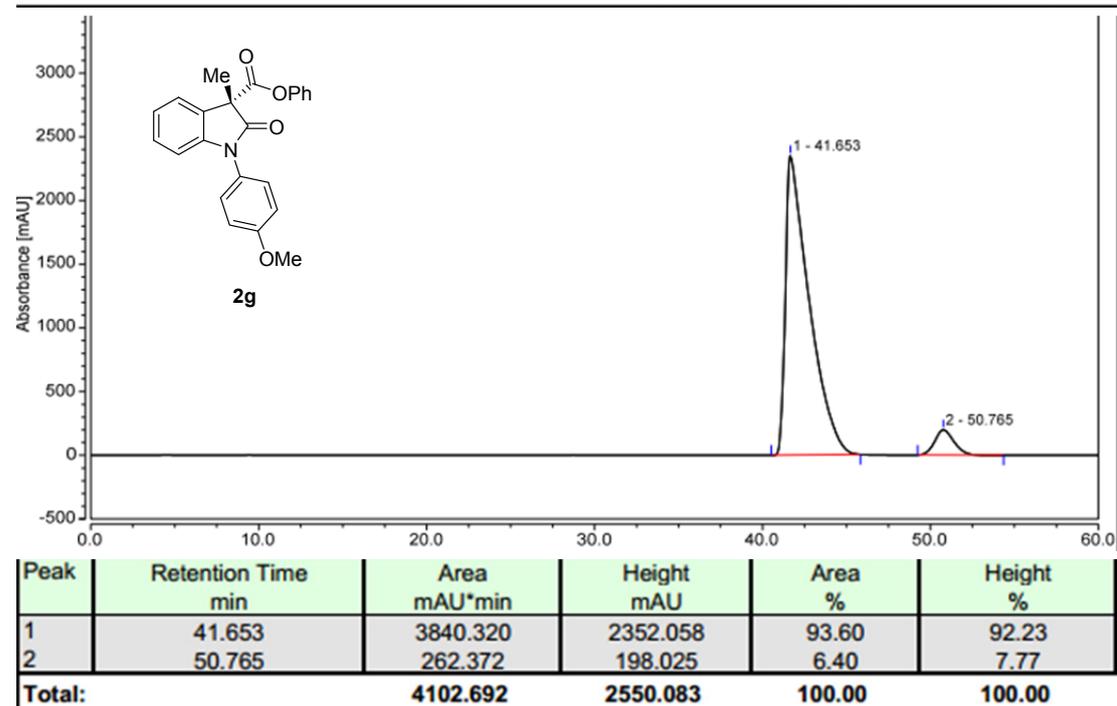
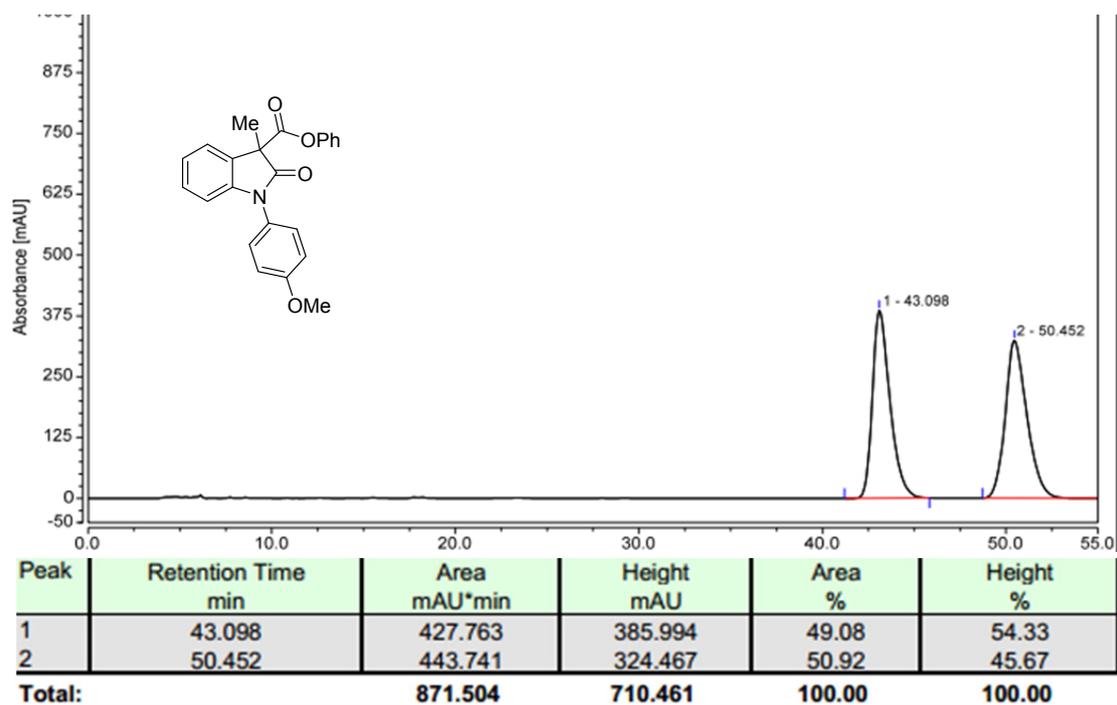


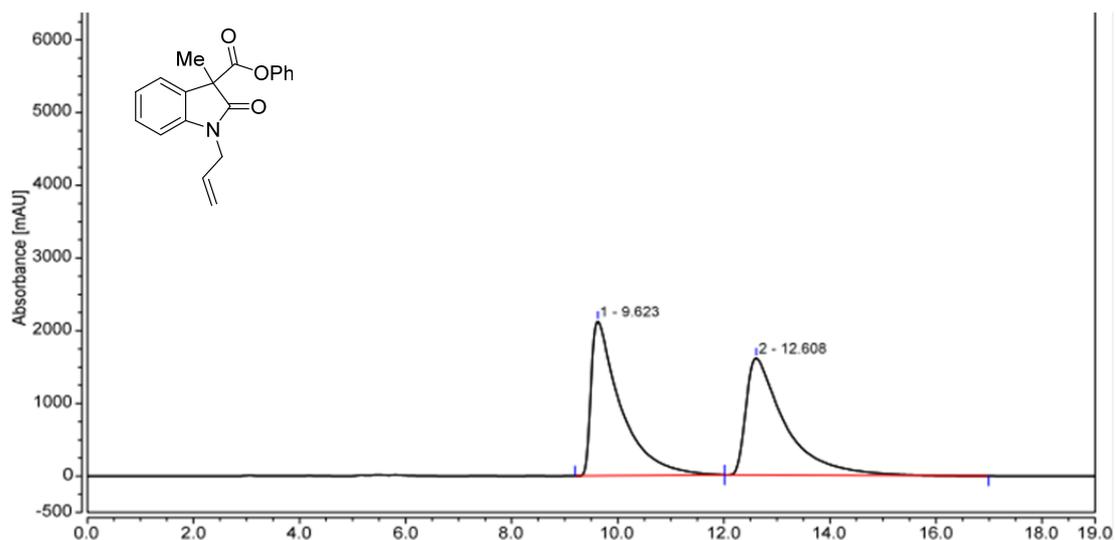
Peak	Retention Time min	Area mAU*min	Height mAU	Area %	Height %
1	34.828	236.943	100.299	50.94	60.62
2	52.035	228.205	65.160	49.06	39.38
Total:		465.148	165.459	100.00	100.00



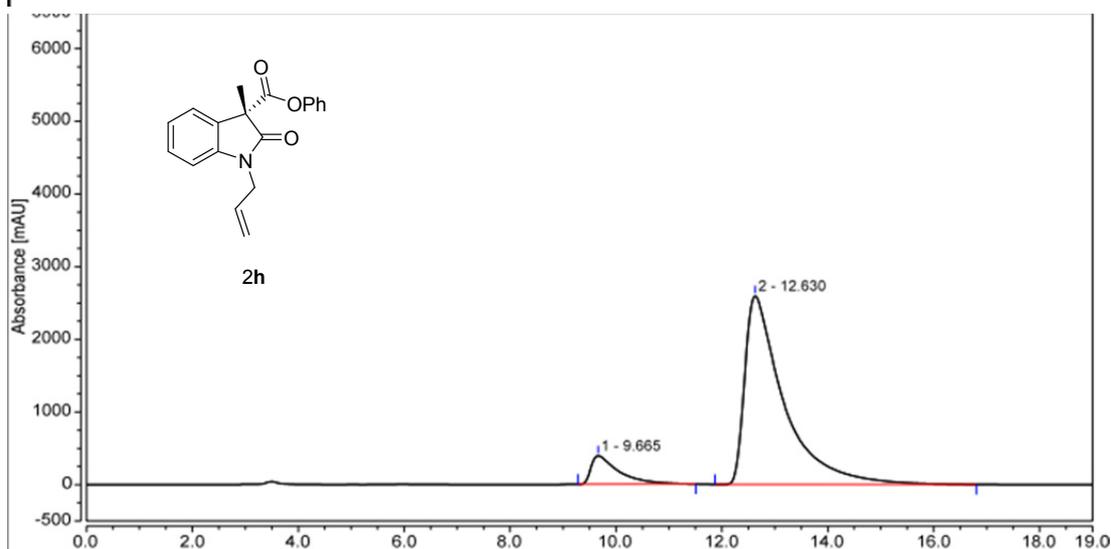
Peak	Retention Time min	Area mAU*min	Height mAU	Area %	Height %
1	34.812	13.681	6.987	1.90	3.51
2	52.155	706.138	191.832	98.10	96.49
Total:		719.818	198.819	100.00	100.00



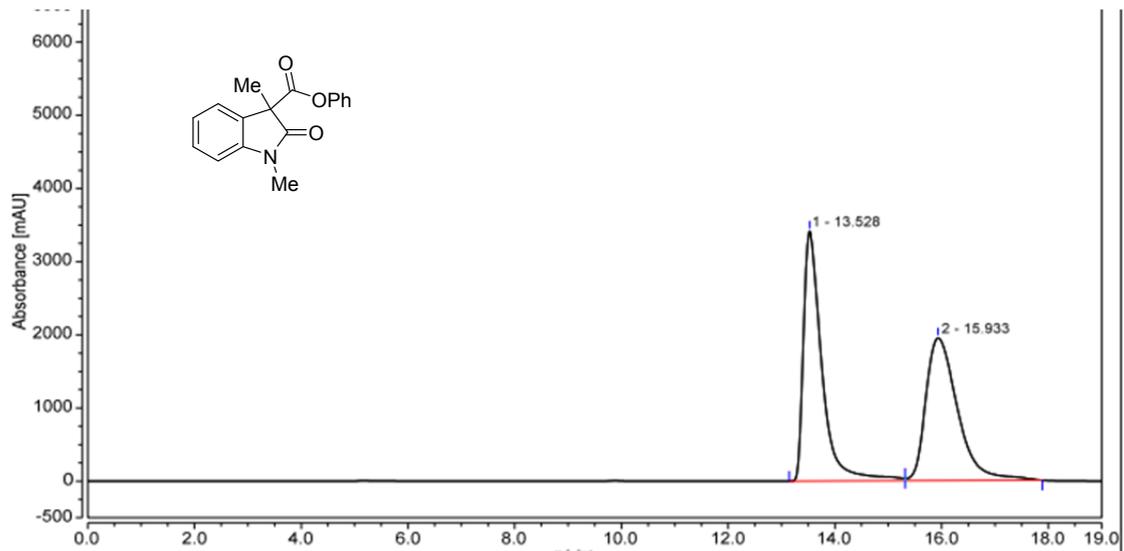




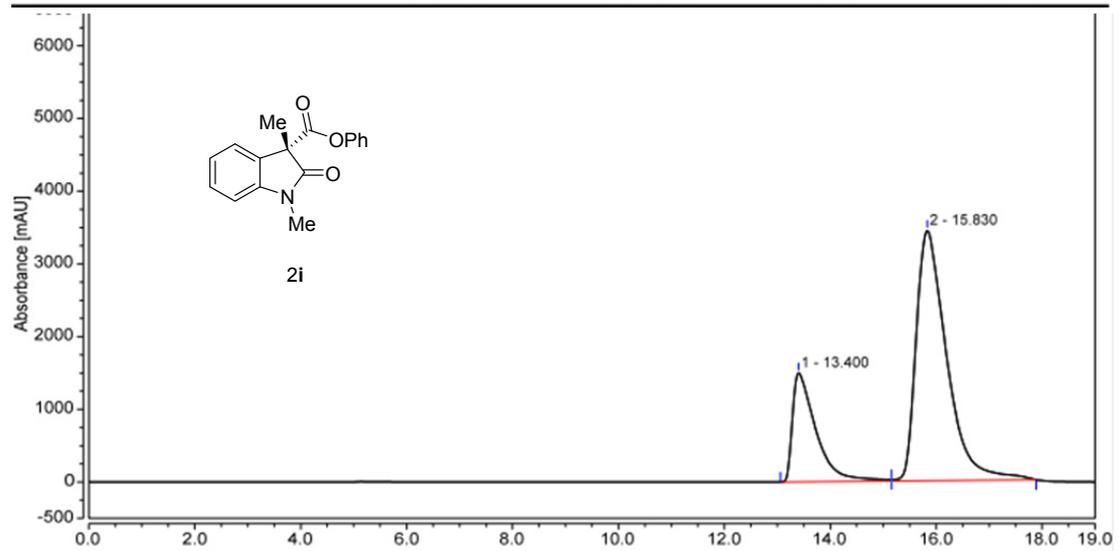
Peak	Retention Time min	Area mAU*min	Height mAU	Area %	Height %
1	9.623	1377.298	2125.891	50.08	56.93
2	12.608	1373.030	1608.531	49.92	43.07
Total:		2750.328	3734.422	100.00	100.00



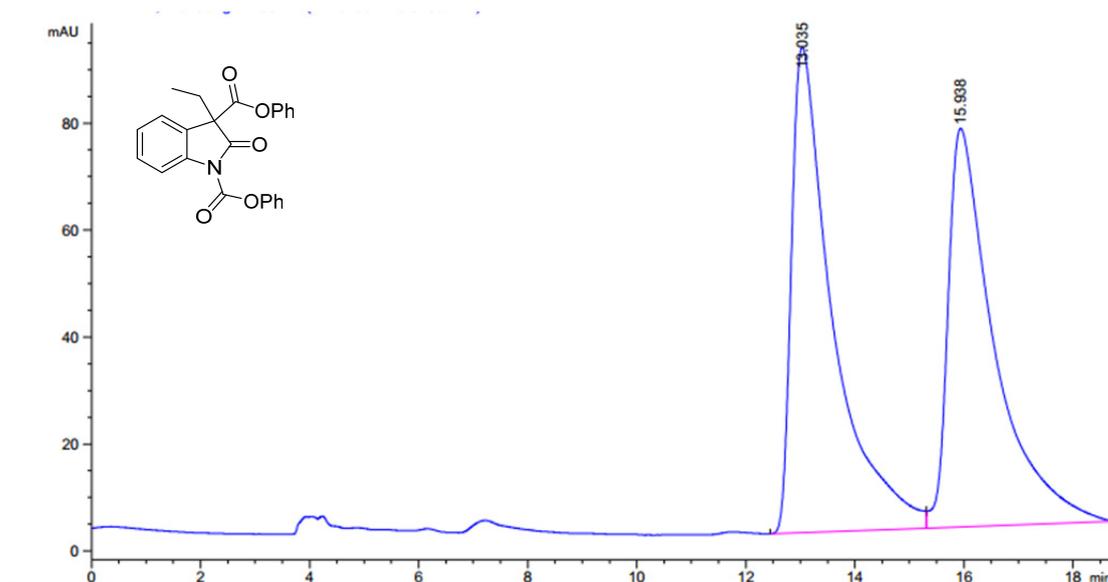
Peak	Retention Time min	Area mAU*min	Height mAU	Area %	Height %
1	9.665	237.790	391.848	9.68	13.12
2	12.630	2219.912	2594.100	90.32	86.88
Total:		2457.702	2985.948	100.00	100.00



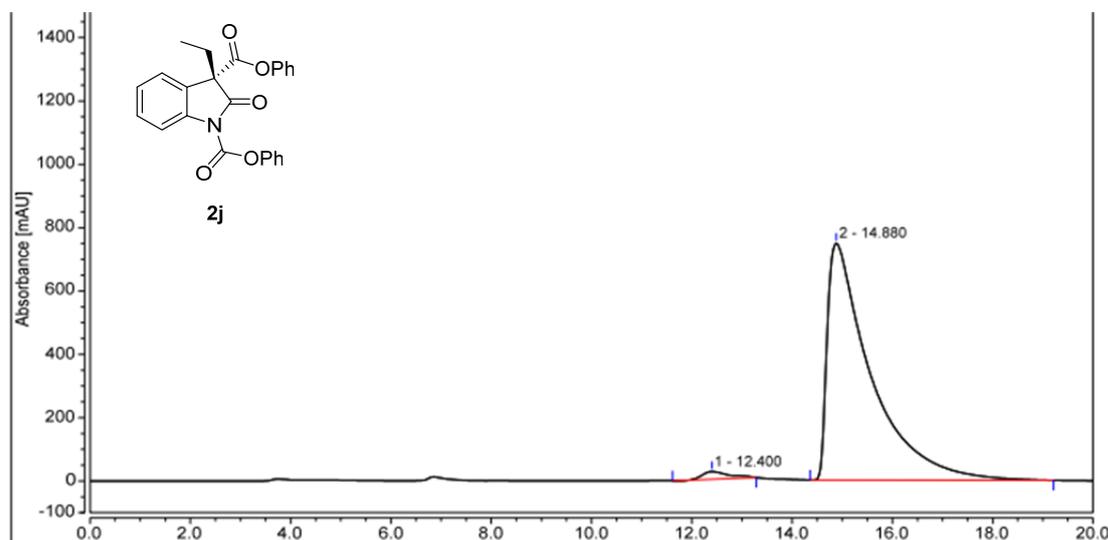
Peak	Retention Time min	Area mAU*min	Height mAU	Area %	Height %
1	13.528	1365.006	3416.573	50.39	63.66
2	15.933	1344.098	1950.698	49.61	36.34
Total:		2709.104	5367.272	100.00	100.00



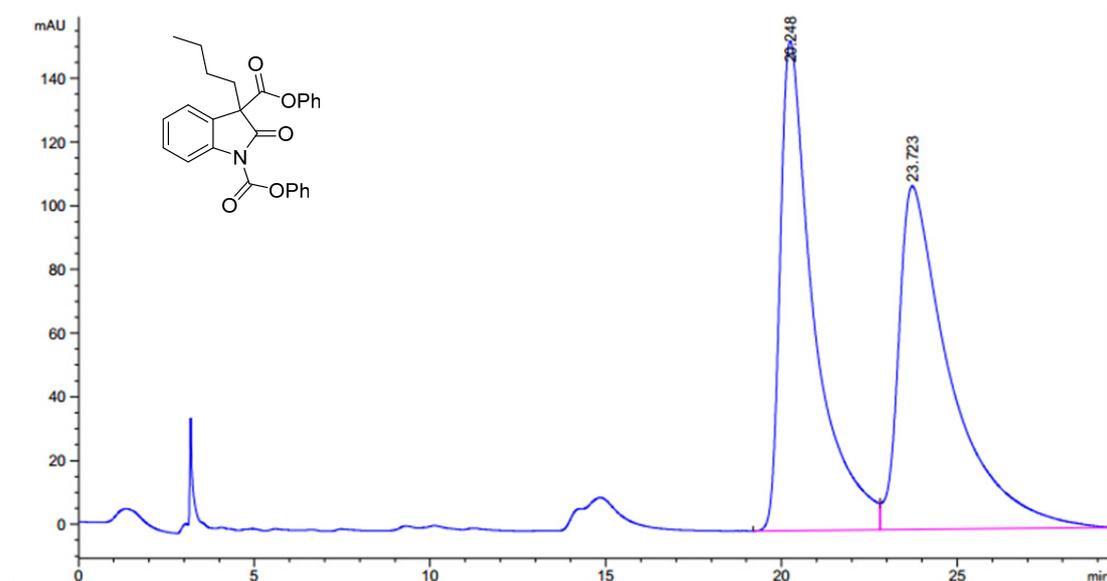
Peak	Retention Time min	Area mAU*min	Height mAU	Area %	Height %
1	13.400	765.240	1499.833	25.01	30.33
2	15.830	2293.962	3445.686	74.99	69.67
Total:		3059.202	4945.518	100.00	100.00



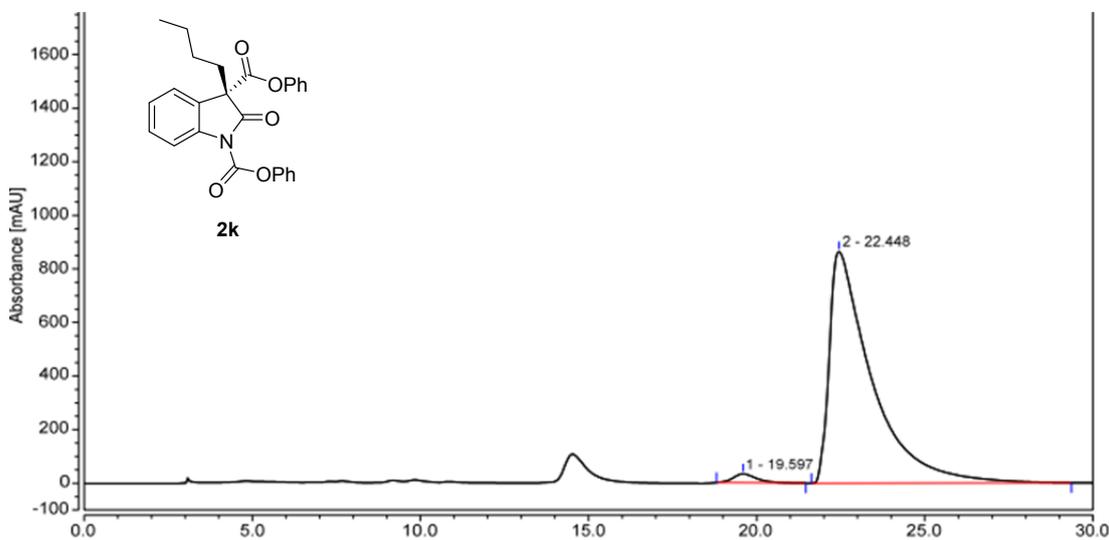
Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	13.035	BV	0.7421	4765.00977	90.76213	52.0541
2	15.938	VBA	0.8327	4388.94775	74.52774	47.9459



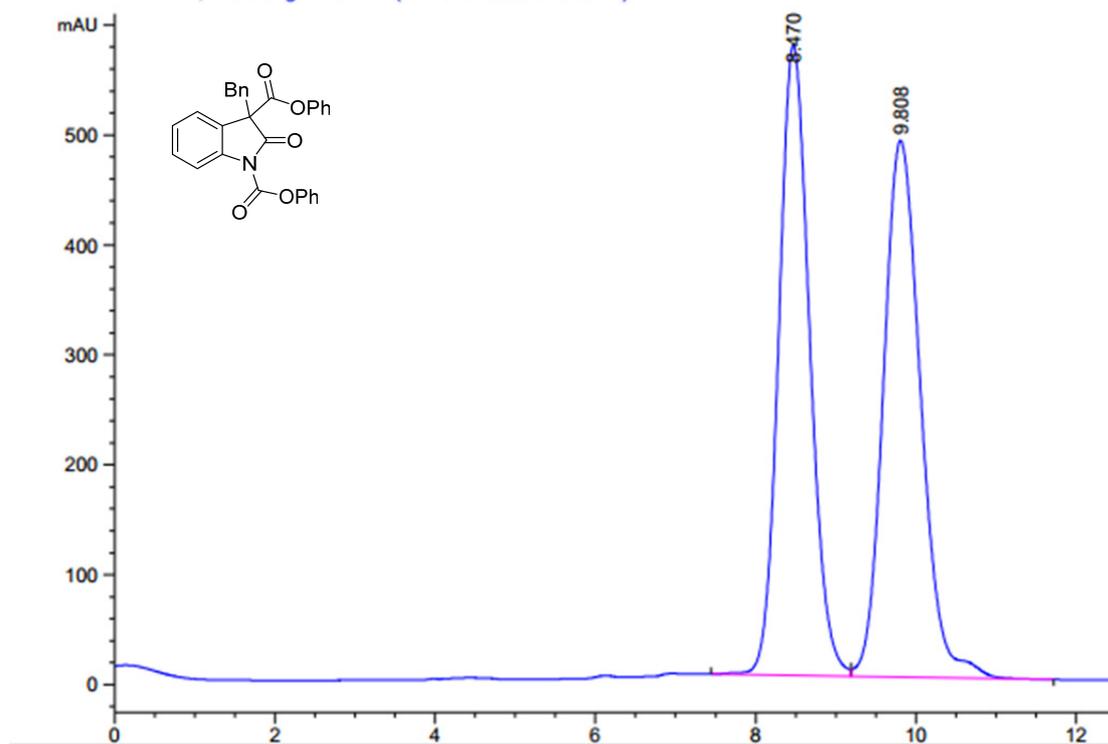
Peak	Retention Time min	Area mAU*min	Height mAU	Area %	Height %
1	12.400	14.386	24.019	1.88	3.11
2	14.880	750.424	748.314	98.12	96.89
Total:		764.810	772.334	100.00	100.00



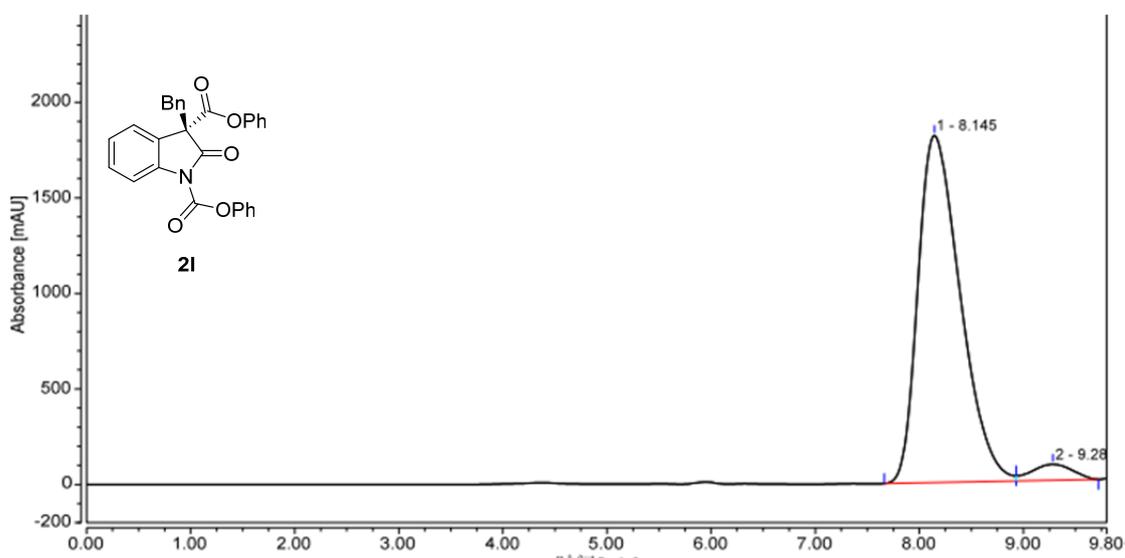
Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	20.248	BV	0.9685	1.03027e4	153.67387	48.4500
2	23.723	VBA	1.4008	1.09619e4	107.76720	51.5500



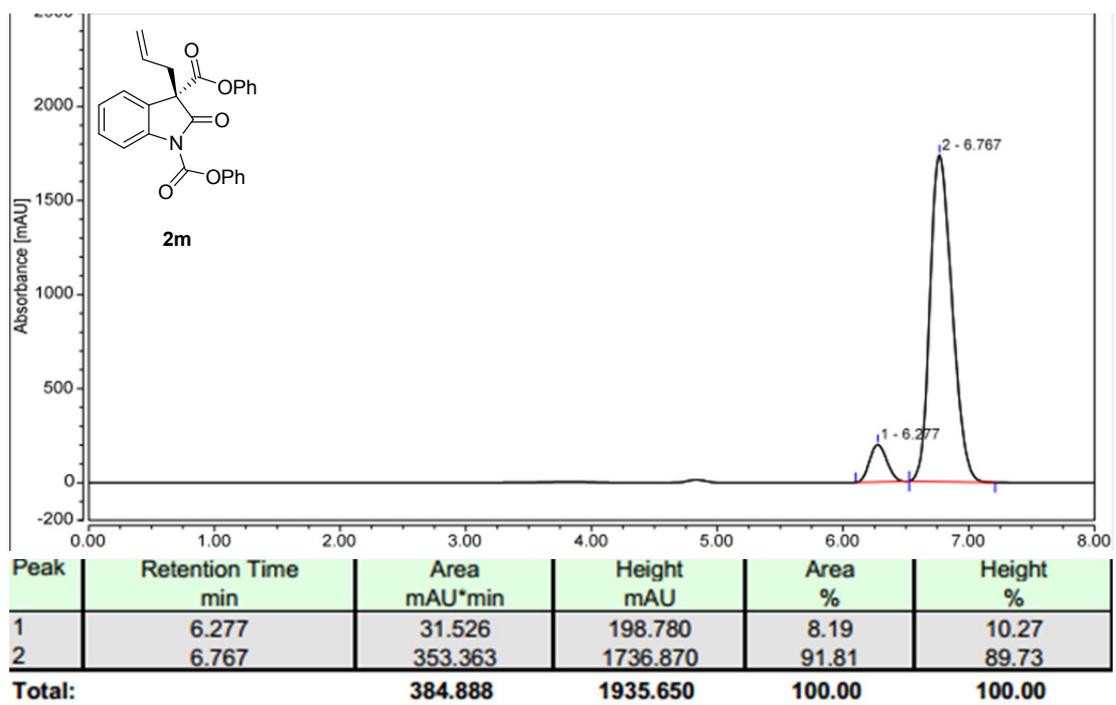
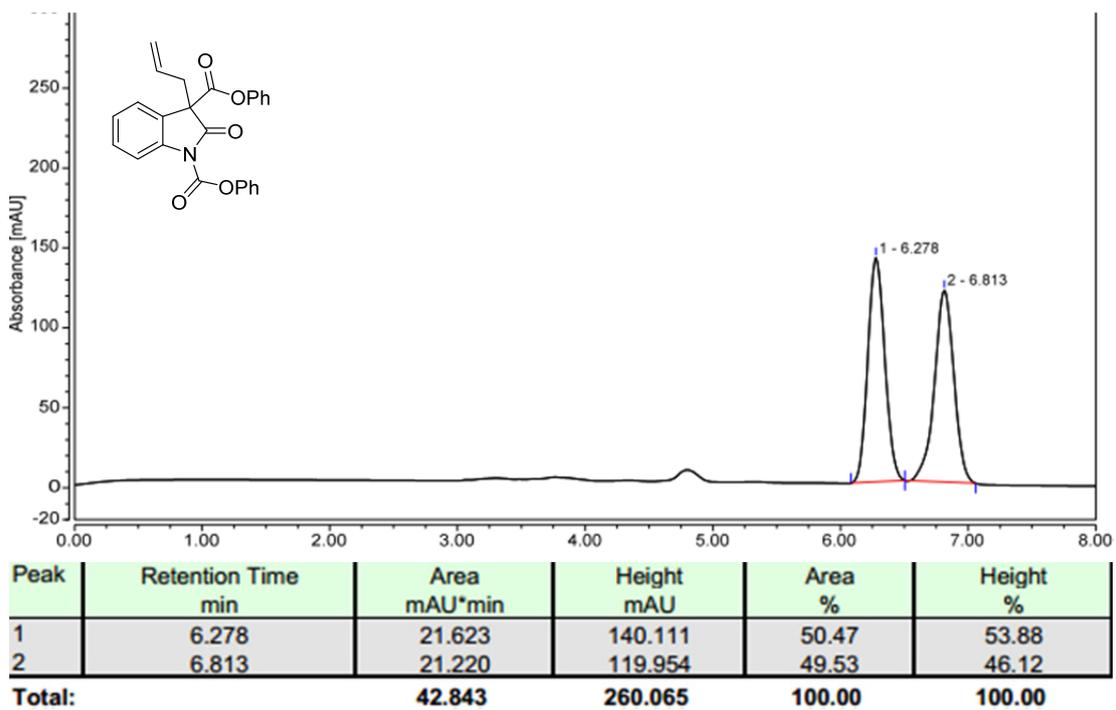
Peak	Retention Time min	Area mAU*min	Height mAU	Area %	Height %
1	19.597	26.681	33.102	2.07	3.69
2	22.448	1261.620	864.320	97.93	96.31
Total:		1288.301	897.421	100.00	100.00

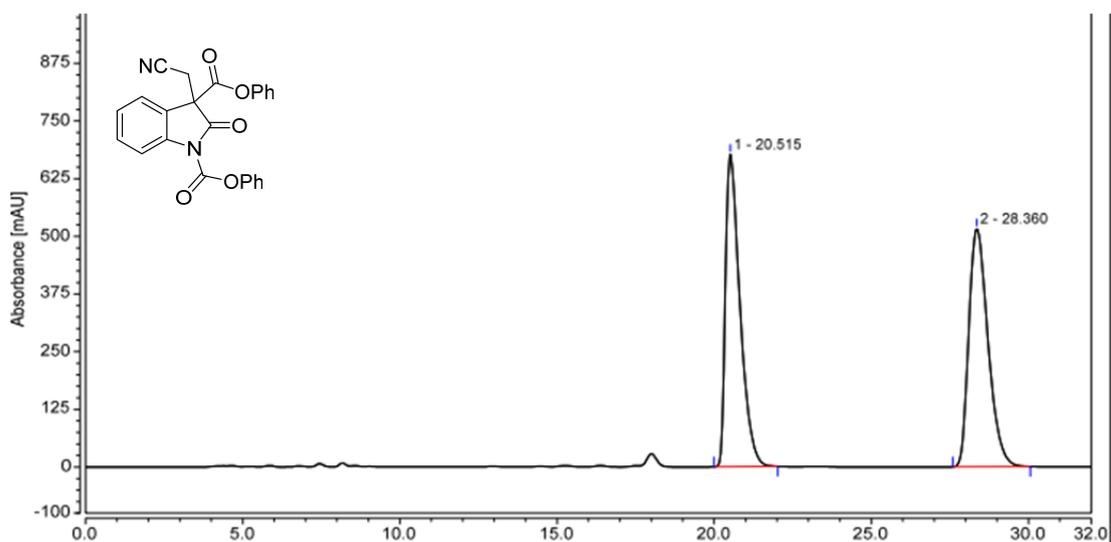


Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	8.470	BV	0.4133	1.53731e4	573.24371	49.3676
2	9.808	VB	0.5020	1.57670e4	488.19241	50.6324

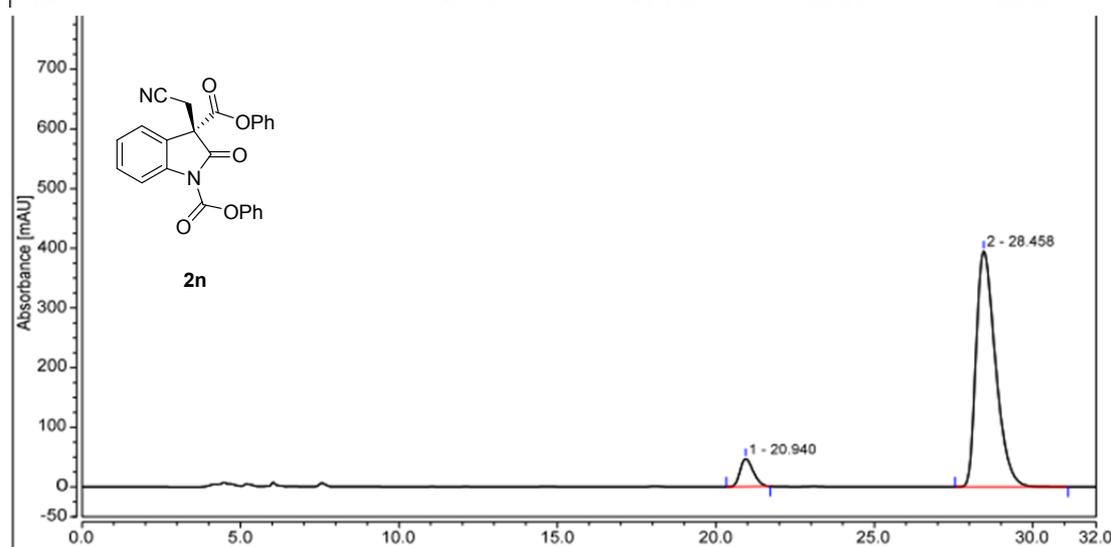


Peak	Retention Time min	Area mAU*min	Height mAU	Area %	Height %
1	8.145	855.160	1816.486	95.77	95.62
2	9.283	37.765	83.221	4.23	4.38
Total:		892.925	1899.707	100.00	100.00

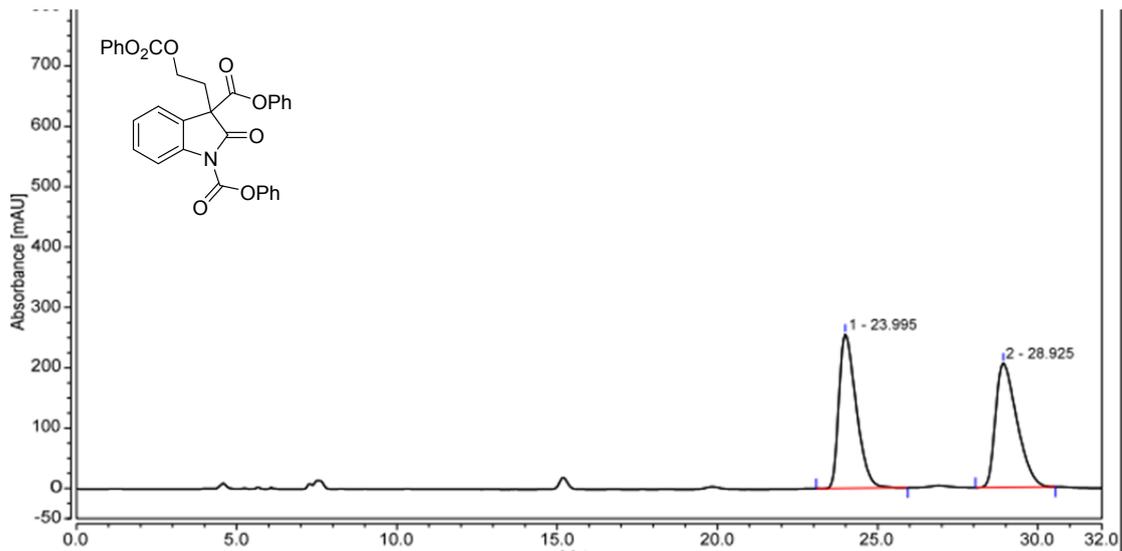




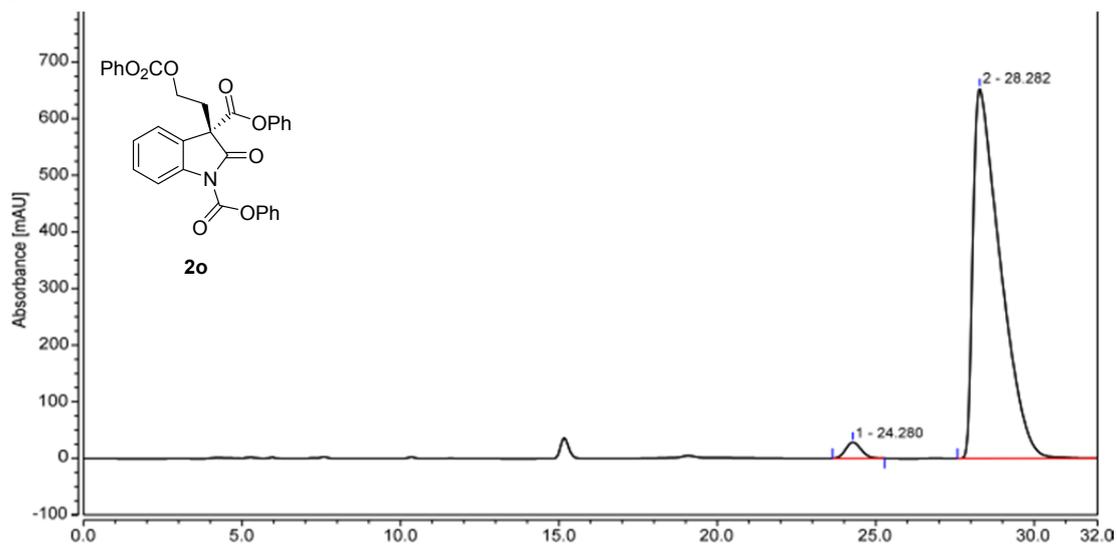
Peak	Retention Time min	Area mAU*min	Height mAU	Area %	Height %
1	20.515	362.912	677.262	49.80	56.76
2	28.360	365.829	516.044	50.20	43.24
Total:		728.740	1193.306	100.00	100.00



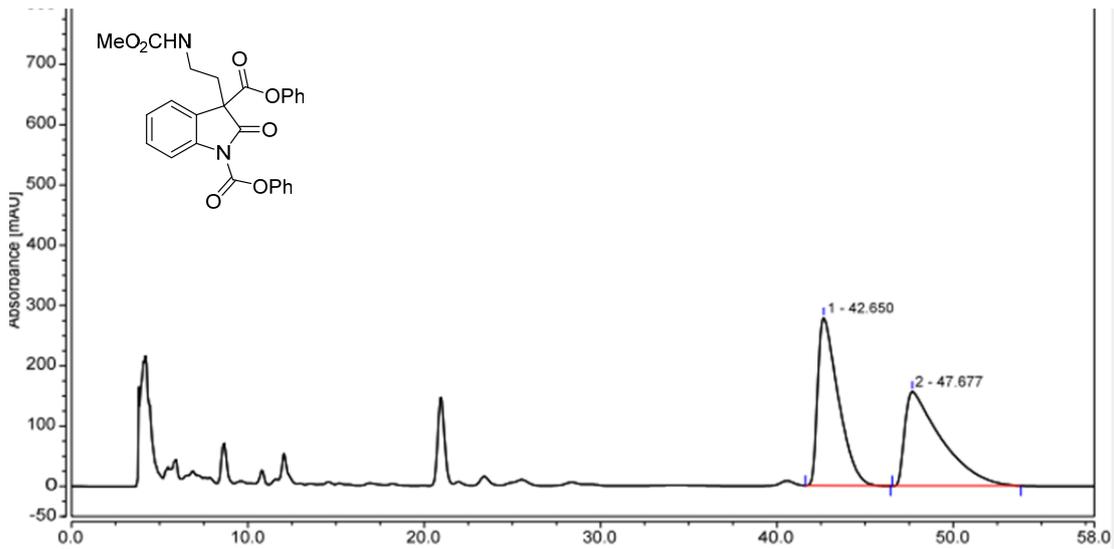
Peak	Retention Time min	Area mAU*min	Height mAU	Area %	Height %
1	20.940	22.672	46.878	7.48	10.60
2	28.458	280.621	395.303	92.52	89.40
Total:		303.293	442.181	100.00	100.00



Peak	Retention Time min	Area mAU*min	Height mAU	Area %	Height %
1	23.995	160.739	255.285	50.16	55.39
2	28.925	159.690	205.567	49.84	44.61
Total:		320.429	460.852	100.00	100.00

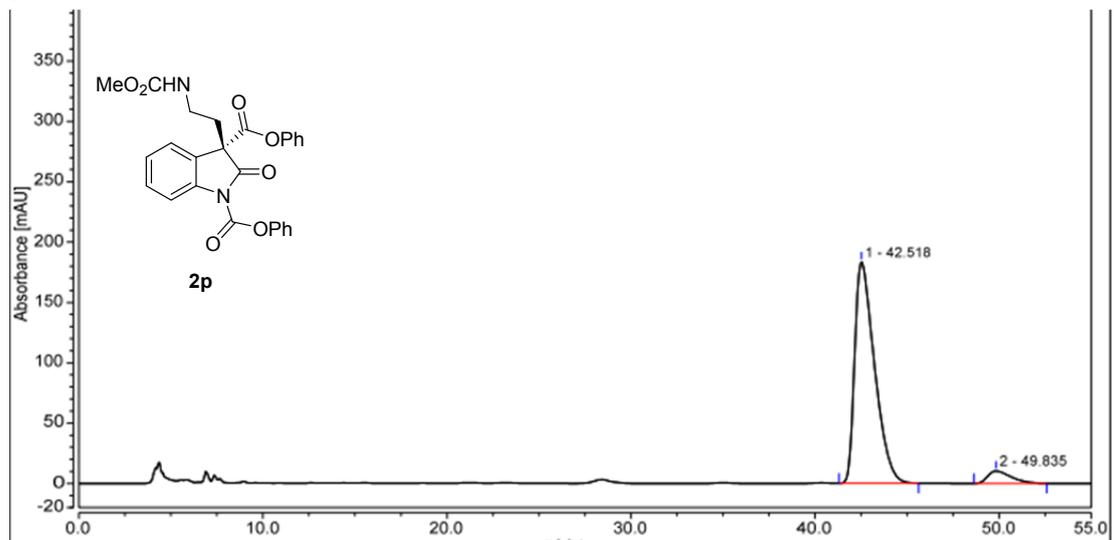


Peak	Retention Time min	Area mAU*min	Height mAU	Area %	Height %
1	24.280	16.161	28.359	2.42	4.16
2	28.282	652.395	653.434	97.58	95.84
Total:		668.556	681.792	100.00	100.00



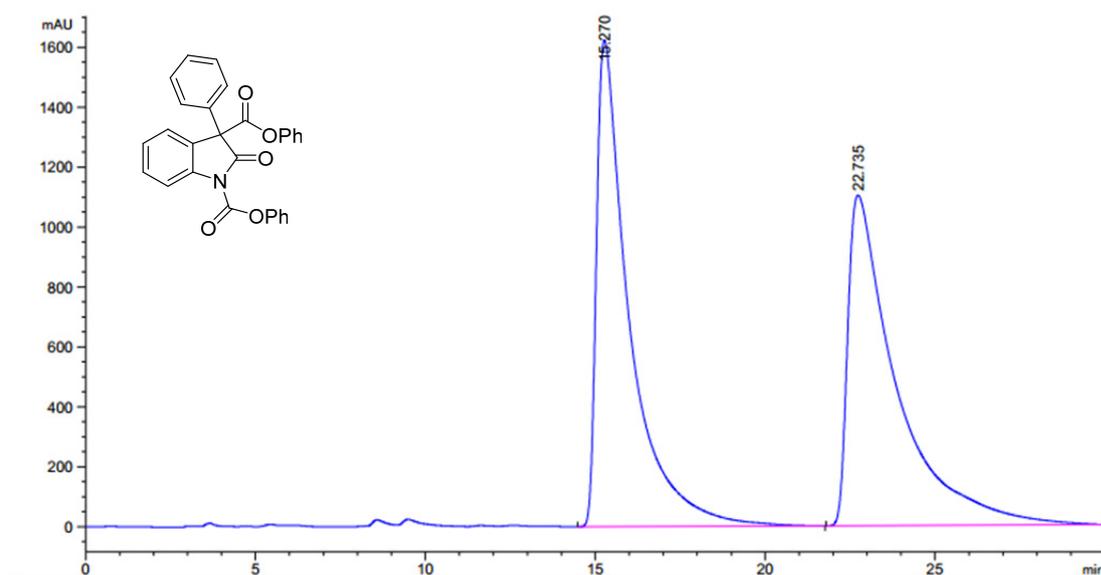
Peak	Retention Time min	Area mAU*min	Height mAU	Area %	Height %
1	42.650	378.572	278.578	50.21	64.01
2	47.677	375.420	156.636	49.79	35.99

Total: 753.992 435.213 100.00 100.00

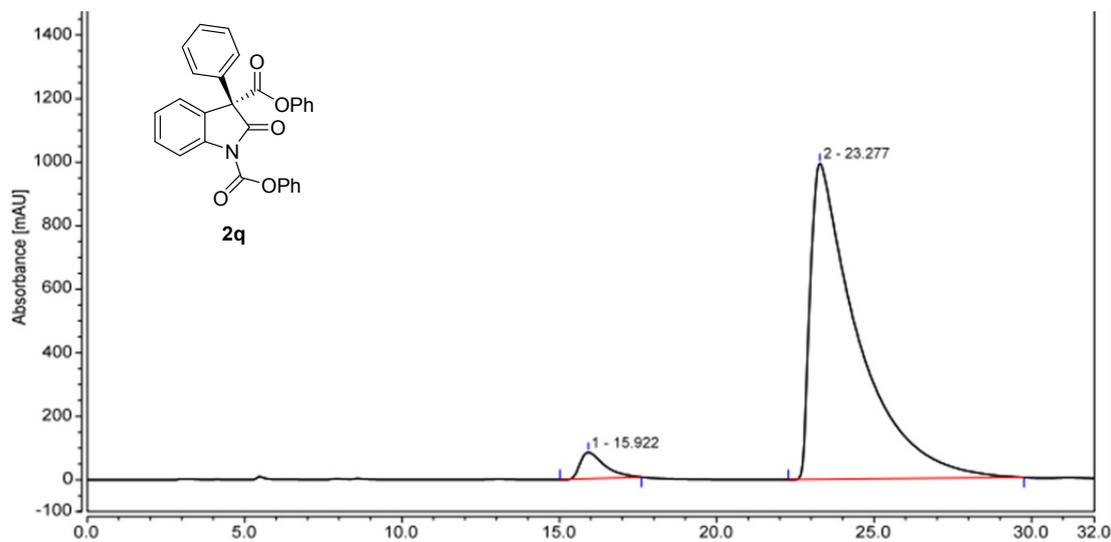


Peak	Retention Time min	Area mAU*min	Height mAU	Area %	Height %
1	42.518	229.389	183.516	93.80	94.70
2	49.835	15.152	10.277	6.20	5.30

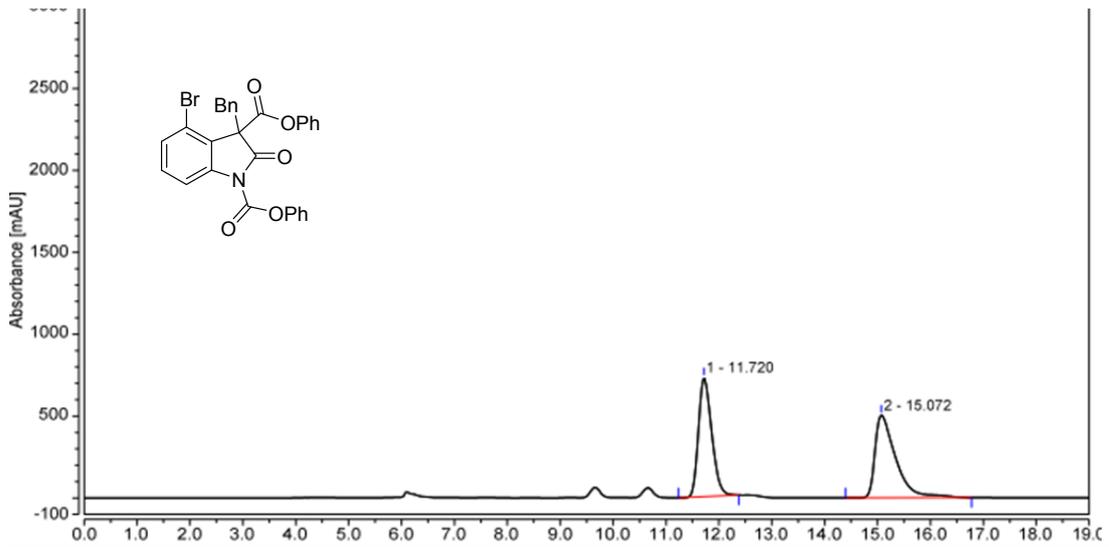
Total: 244.541 193.793 100.00 100.00



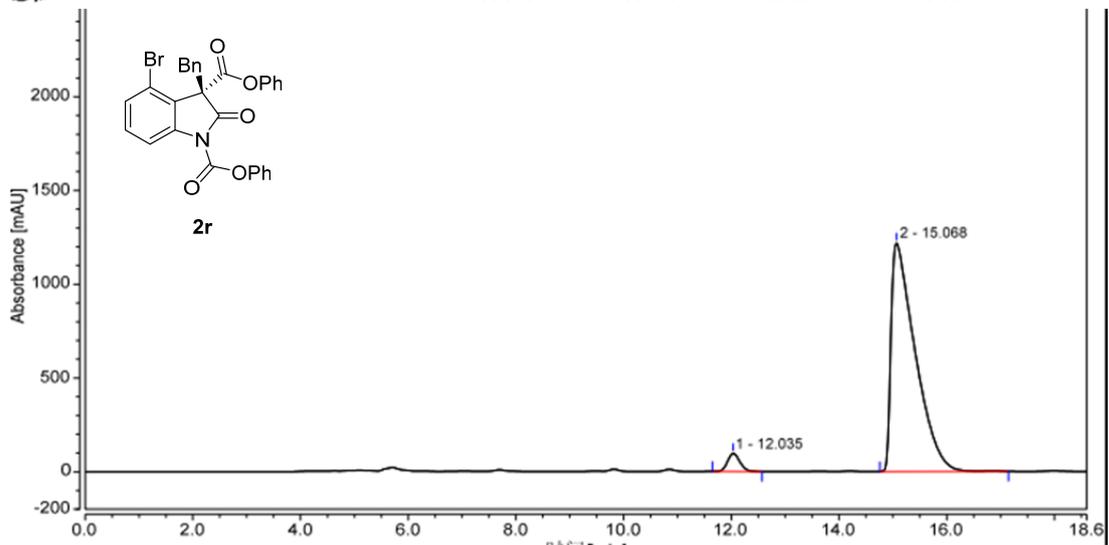
Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	15.270	BB	0.9386	1.08993e5	1624.32153	49.9349
2	22.735	BBA	1.3687	1.09277e5	1104.15698	50.0651



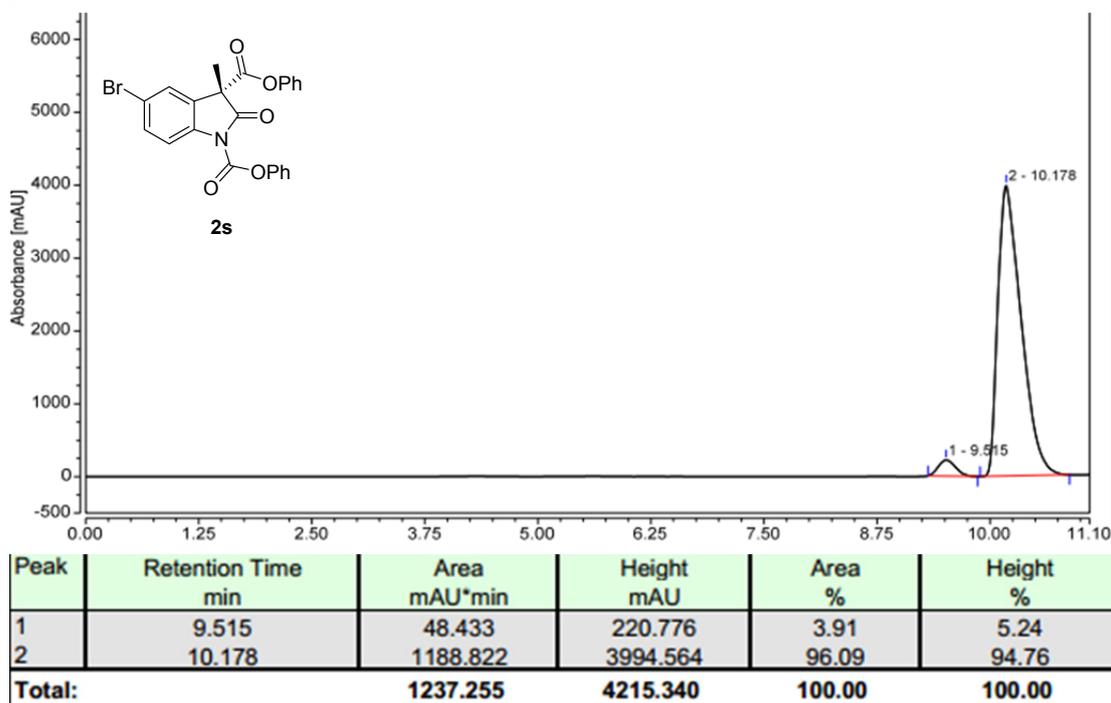
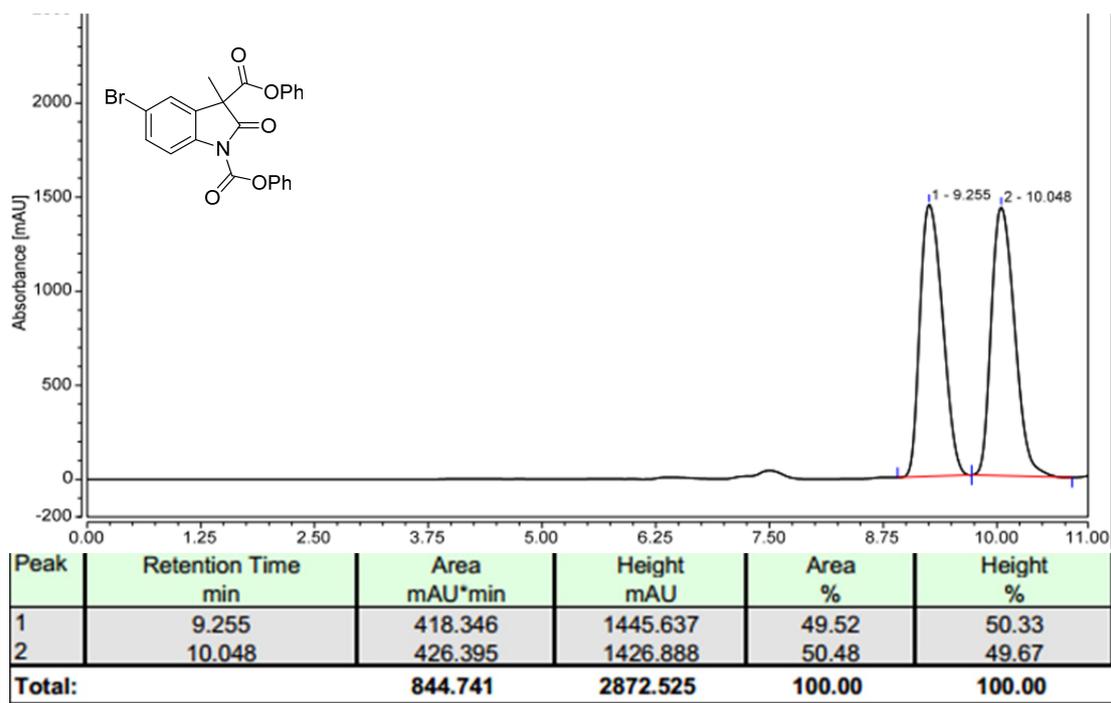
Peak	Retention Time min	Area mAU*min	Height mAU	Area %	Height %
1	15.922	74.524	82.762	4.11	7.69
2	23.277	1740.773	994.022	95.89	92.31
Total:		1815.297	1076.784	100.00	100.00

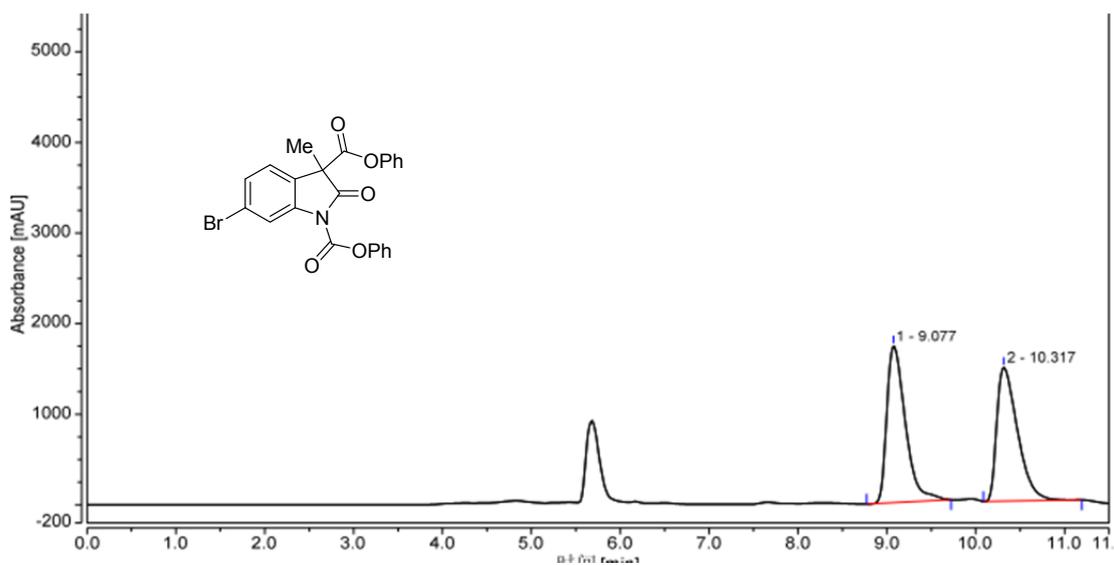


序号	峰名称	保留时间 min	峰面积 mAU*min	峰高 mAU	相对峰面积 %	相对峰高 %	样品量 n.a.
1		11.720	210.955	725.774	48.06	59.00	n.a.
2		15.072	227.991	504.369	51.94	41.00	n.a.
总和:			438.946	1230.143	100.00	100.00	

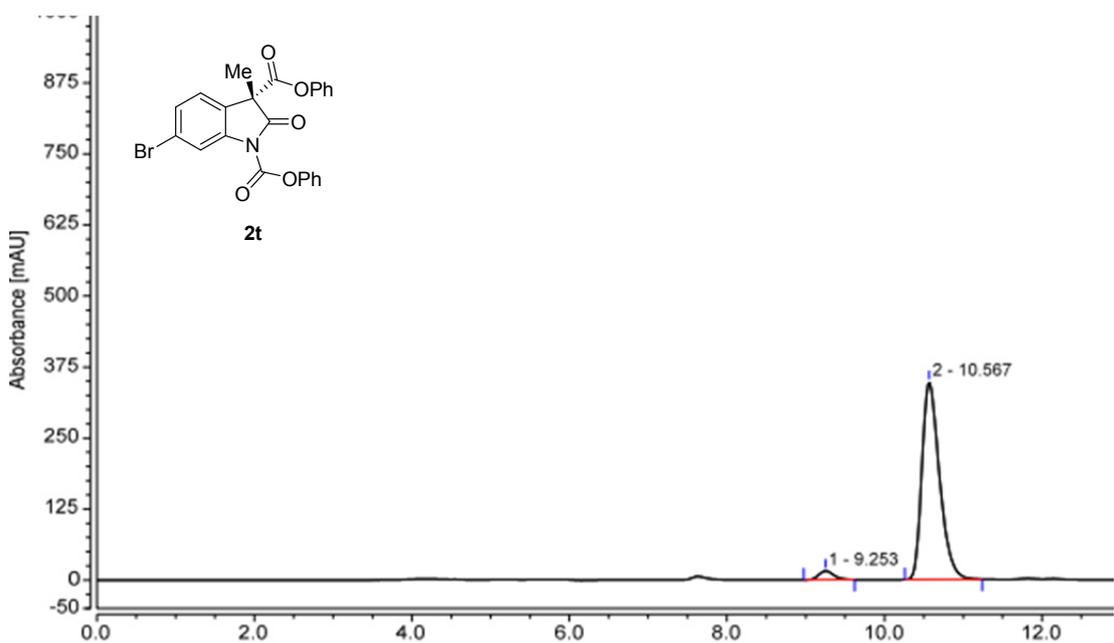


Peak	Retention Time min	Area mAU*min	Height mAU	Area %	Height %
1	12.035	25.112	95.701	3.81	7.28
2	15.068	633.850	1219.397	96.19	92.72
Total:		658.962	1315.097	100.00	100.00

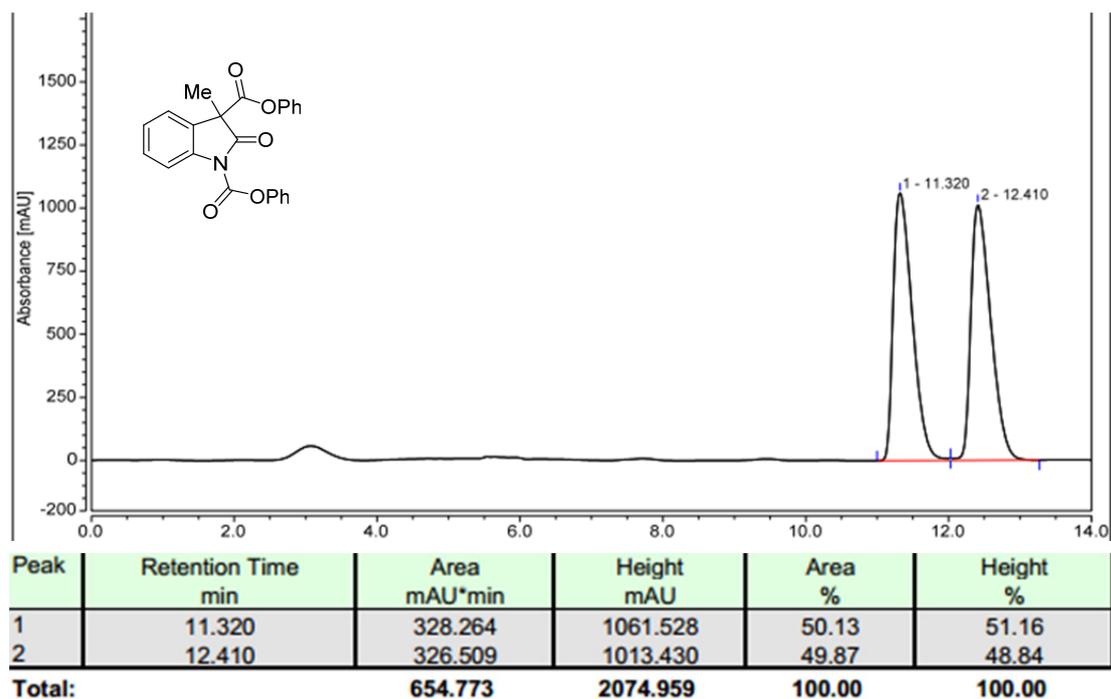




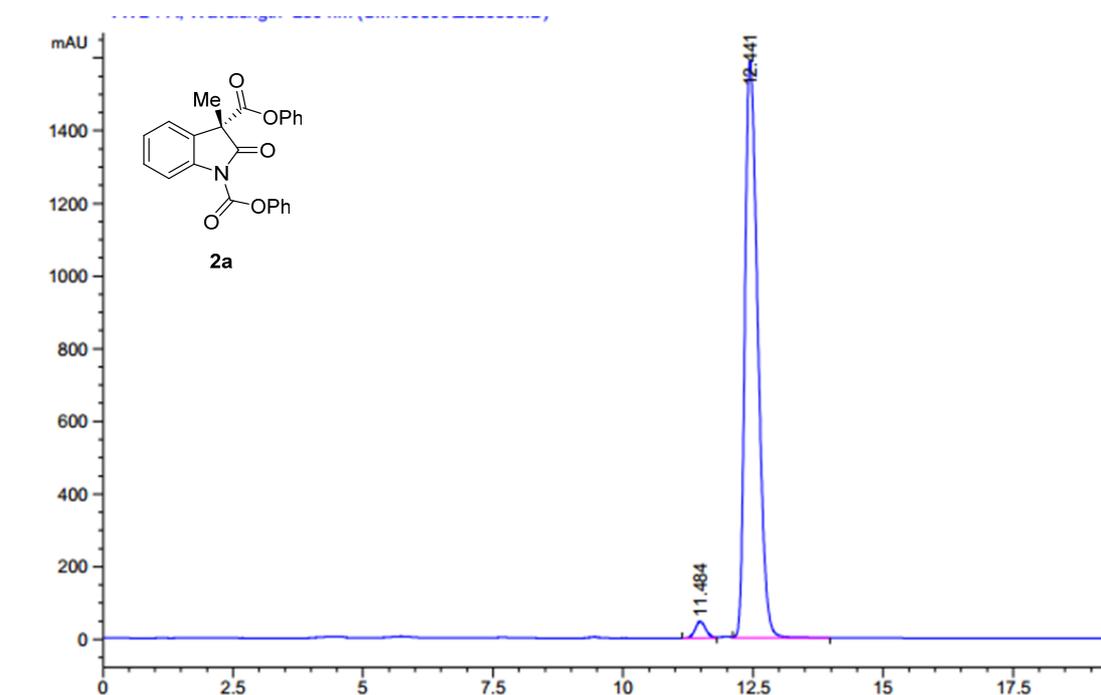
序号	峰名称	保留时间 min	峰面积 mAU*min	峰高 mAU	相对峰面积 %	相对峰高 %	样品量 n.a.
1		9.077	419.719	1730.363	51.22	53.96	n.a.
2		10.317	399.648	1476.297	48.78	46.04	n.a.
总和:			819.367	3206.659	100.00	100.00	



Peak	Retention Time min	Area mAU*min	Height mAU	Area %	Height %
1	9.253	3.456	15.539	3.69	4.28
2	10.567	90.085	347.116	96.31	95.72
Total:		93.541	362.655	100.00	100.00



3 mmol scale



Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	11.484	BV	0.2190	649.43195	45.88321	2.3239
2	12.441	VB	0.2705	2.72960e4	1587.22070	97.6761