

Supporting Information

Organocatalytic 1,6-hydrophosphination of *para*-quinone methides: enantioselective access to phosphorus-substituted quaternary carbon stereocenters

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Contents:

General remarks and materials	2
General Procedures.....	2
References:.....	5
Analysis data for products.....	6
Single Crystal X-ray Structure Determinations of Compound 3l (CCDC: 2019323)	20
¹H NMR, ¹³C NMR, ³¹P NMR, ¹⁹F NMR and HPLC spectra for products.....	22

General remarks and materials

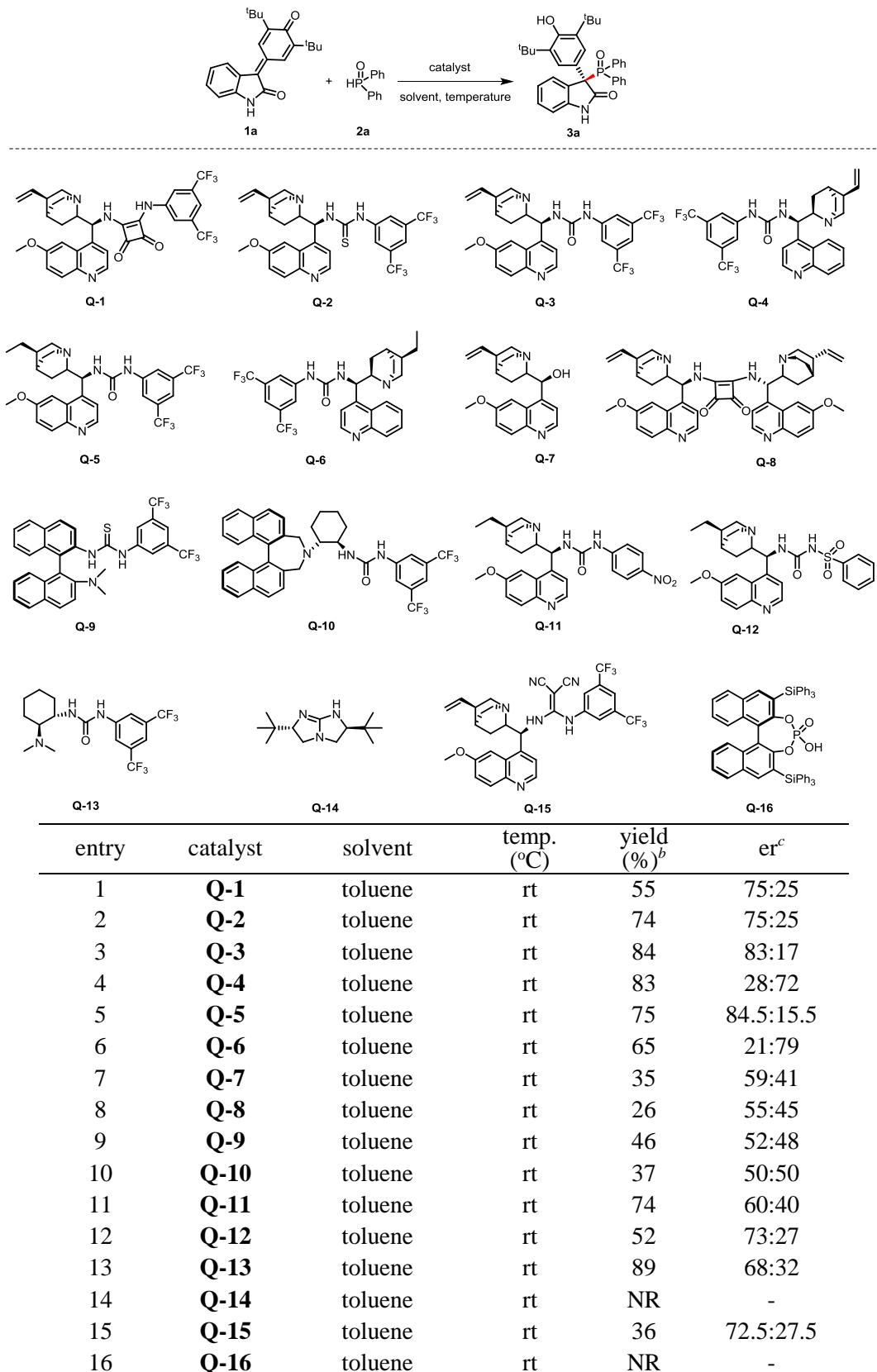
NMR spectra were recorded with a Bruker Avance III HD600 (500) spectrometer at 600 MHz or 500 MHz for ¹H NMR, 151 MHz or 126 MHz for ¹³C NMR, 243 MHz or 202 MHz for ³¹P NMR and 565 MHz or 471 MHz for ¹⁹F NMR. Tetramethylsilane (TMS) signals or residual solvent signals were used [TMS δ = 0.00 (¹H NMR), CDCl₃ δ = 77.00 (¹³C NMR), DMSO-d₆ δ = 2.50 (¹H NMR), 39.52 (¹³C NMR)] as internal standards. Data for ¹H NMR are reported in parts per million as follows: chemical shift, multiplicity (s = singlet, d = doublet, t = triplet, q = quartet, dd = double doublet, m = multiplet, hept = heptet). Data for ¹³C NMR, ³¹P NMR and ¹⁹F NMR are reported in terms of chemical shift in parts per million. HRMS (ESI) Mass spectra were recorded on Waters Xevo G2 Q-TOF MS with Acquity UPLC. Column chromatography was carried out on silica gel (particle size 300-400 mesh). HPLC analysis was performed on Shanghai Wufeng LC-P100 equipped with Daicel chiralpak IC, OD-H and AD-H. The racemic standards used in HPLC studies were prepared according to the general procedure by using DABCO. Unless stated otherwise, all the solvents and reagents were purchased from commercial suppliers and used without further purification. We used the commercial available powdered molecular sieves in the reaction. Molecular sieves were flame-dried under vacuum. Substrates **1** were synthesized according to the published procedures.¹ Substrates **2** were prepared according to the literature method.² Substrate **4** was prepared according to the literature method.³ Catalysts **Q-5** was prepared according to the literature method.⁴

General Procedures

General Procedure for Optimization of Reaction Conditions (Table 1 and Table S1):

The solvent was added to the mixture of **1a** (33.5 mg, 0.1 mmol), **2a** (40.4 mg, 0.2 mmol) and catalyst under the indicated temperature in Table 1. Upon completion (monitored by TLC), the mixture was purified by column chromatography on silica gel (petroleum ether/ethyl acetate = 2/1) to give the product **3a**.

Table S1. Optimization of the catalysts ^a

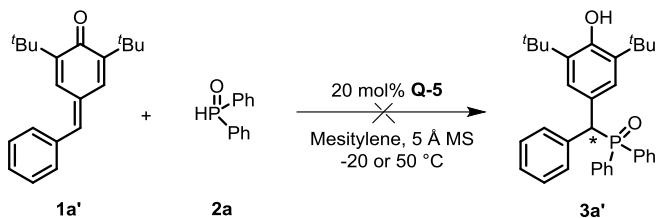


^aReaction conditions: **1a** (0.10 mmol), **2a** (0.20 mmol), catalyst (10 mol %), solvent (2 mL), 36 h. ^bIsolated yield. ^cDetermined by HPLC on a chiral stationary phase. NR = No Reaction.

General Procedure for asymmetric 1,6-hydrophosphination of *p*-QMs with H-phosphine oxides (Table 2, Table 3):

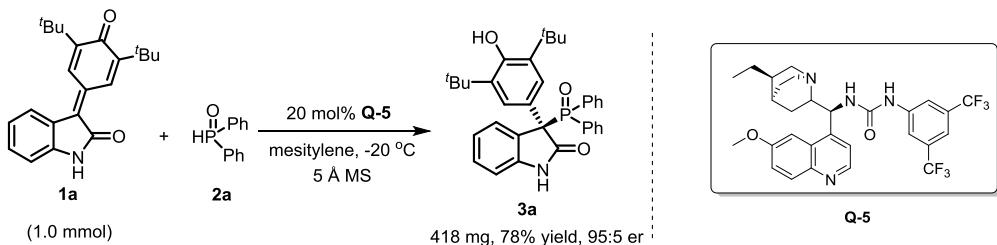
Mesitylene (4 mL) was added to the mixture of **1** (0.1 mmol), **2** (0.2 mmol), molecular sieves (50 mg, 5 Å) and catalyst **Q-5** (11.6 mg, 0.02 mmol) at -20 °C. Upon completion (monitored by TLC), the mixture was purified by column chromatography on silica gel (petroleum ether/ethyl acetate) to give the product.

General Procedure for asymmetric 1,6-hydrophosphination of *p*-QMs derived from aldehyde with H-phosphine oxide:



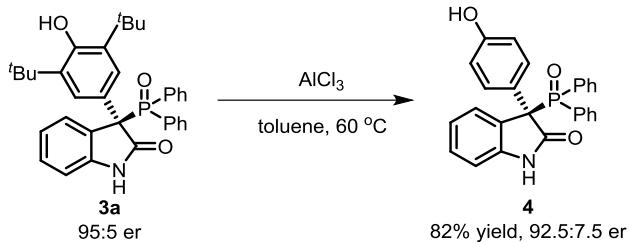
Mesitylene (4 mL) was added to the mixture of **1a'** (0.1 mmol), **2** (0.2 mmol), molecular sieves (50 mg, 5 Å) and catalyst **Q-5** (11.6 mg, 0.02 mmol) at -20 or 50 °C. The procedure was monitored by TLC. No desired product was found.

General procedure for scale-up reaction (Scheme 2a):



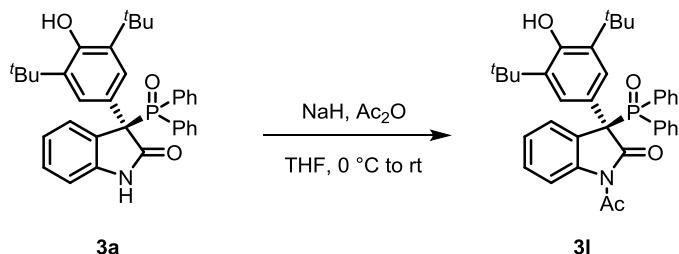
Mesitylene (40 mL) was added to the mixture of **1a** (335 mg, 1 mmol), **2a** (404 mg, 2 mmol), molecular sieves (500 mg, 5 Å) and catalyst **Q-5** (116 mg, 0.02 mmol) at -20 °C. The reaction was stirred at -20 °C for 72 h. Upon completion (monitored by TLC), the mixture was purified by column chromatography on silica gel (petroleum ether/ethyl acetate = 2/1) to give the product **3a** in 78% yield and 95:5 er. Then, the pure catalyst could be isolated and recovered in 89% yield (103.5 mg) by using CH₂Cl₂/MeOH/Et₃N 100:2:1 as eluent.

General procedure for the synthesis of compound 4 (Scheme 2b):



To a solution of **3a** (161.3 mg, 0.3 mmol) in toluene (3 mL) at rt was added AlCl_3 (20 equiv) in one portion. Then the mixture was stirred at 60 °C for 2 h. Upon completion (monitored by TLC), the mixture was cooled to room temperature and poured into 10 mL ice water. The mixture was extracted 3x with 10 mL ethyl acetate and the combined organic layers are dried over Na_2SO_4 , filtered, and concentrated *in vacuo*. And then the residue was purified by column chromatography on silica gel (petroleum ether/ethyl acetate = 1/2) to give the product **4** in 82% yield with 92.5:7.5 er.

General procedure for the synthesis of compound (*R*)-**3l**:

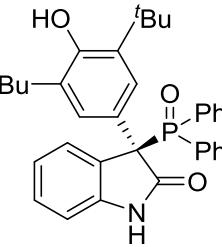


To a solution of **3a** (161.3 mg, 0.3 mmol) in 3 mL anhydrous THF was added NaH (21.6 mg, 0.9 mmol) at 0 °C. After the mixture was stirred at 0 °C for 0.5 h, Ac_2O (36.8 mg, 0.36 mmol) was added at the same temperature. Then the mixture was stirred at room temperature for 3 h. Upon completion (monitored by TLC), water (5 mL) was added. The mixture was extracted 3x with 10 mL ethyl acetate and the combined organic layers are dried over Na_2SO_4 , filtered, and concentrated *in vacuo*. And then the residue was purified by column chromatography on silica gel (petroleum ether/ethyl acetate = 5/1) to give the product **3l** in 66% yield with 93.5:6.5 er.

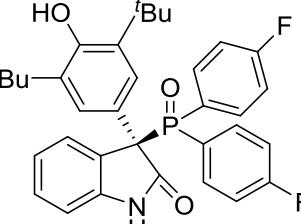
References:

1. H. Wang, K. Wang, Y. Man, X. Gao, L. Yang, Y. Ren, N. Li, B. Tang, G. Zhao, *Adv. Synth. Catal.* 2017, **359**, 3934.
2. C. A. Busacca, J. C. Lorenz, N. Grinberg, N. Haddad, M. Hrapchak, B. Latli, H. Lee, P. Sabilia, A. Saha, M. Sarvestani, S. Shen, R. Varsolona, X. Wei, C. H. Senanayake, *Org. Lett.* 2005, **7**, 4277.
3. Z. Feng, Z. Yuan, X. Zhao, Y. Huang, H. Yao, *Org. Chem. Front.* 2019, **6**, 3535.
4. M. S. Manna, S. Mukherjee, *J. Am. Chem. Soc.* 2015, **137**, 130.

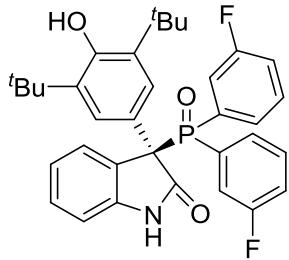
Analysis data for products



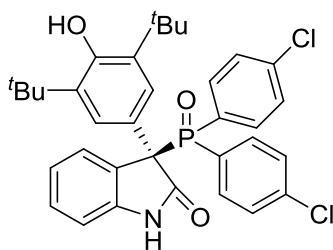
(*R*)-**3a**, white solid, 78% yield, 95:5 er; **1H NMR** (500 MHz, Chloroform-*d*) δ 8.34 (s, 1H), 7.87–7.78 (m, 2H), 7.57–7.46 (m, 6H), 7.39–7.33 (m, 3H), 7.23 (td, *J* = 7.8, 3.2 Hz, 2H), 7.18 (t, *J* = 7.7 Hz, 1H), 7.03 (t, *J* = 7.4 Hz, 1H), 6.68 (d, *J* = 7.7 Hz, 1H), 5.17 (s, 1H), 1.30 (s, 18H); **13C NMR** (126 MHz, Chloroform-*d*) δ 174.93, 153.37 (d, *J* = 2.5 Hz), 140.82 (d, *J* = 6.2 Hz), 135.30 (d, *J* = 1.7 Hz), 133.45 (d, *J* = 8.7 Hz), 132.27 (d, *J* = 9.0 Hz), 131.85 (d, *J* = 2.8 Hz), 131.79 (d, *J* = 2.7 Hz), 130.18 (d, *J* = 86.5 Hz), 129.39 (d, *J* = 88.6 Hz), 128.66 (d, *J* = 1.2 Hz), 128.63, 127.82 (d, *J* = 7.2 Hz), 127.73 (d, *J* = 7.0 Hz), 126.57 (d, *J* = 4.3 Hz), 125.62 (d, *J* = 4.8 Hz), 122.95 (d, *J* = 5.3 Hz), 122.08 (d, *J* = 2.0 Hz), 109.45, 62.03 (d, *J* = 56.5 Hz), 34.52, 30.11; **31P NMR** (202 MHz, CDCl₃) δ 28.80; **HRMS** (ESI) Calcd.for C₃₄H₃₆NO₃PNa (M+Na)⁺ 560.2325, Found: 560.2321; **HPLC** (Chiral IC, λ = 254 nm, hexane/2-propanol = 3/1, Flow rate = 0.6 mL/min), t_R = 7.915 min, 20.448 min.



(*R*)-**3b**, white solid, 81% yield, 96:4 er; **1H NMR** (500 MHz, Chloroform-*d*) δ 7.94 (ddd, *J* = 10.5, 8.7, 5.8 Hz, 2H), 7.70 (d, *J* = 9.3 Hz, 2H), 7.55 (d, *J* = 1.6 Hz, 2H), 7.47 (ddd, *J* = 10.7, 8.7, 5.7 Hz, 2H), 7.22 (t, *J* = 7.7 Hz, 1H), 7.12–7.03 (m, 3H), 6.94 (td, *J* = 8.7, 2.2 Hz, 2H), 6.69 (d, *J* = 7.8 Hz, 1H), 5.17 (s, 1H), 1.31 (s, 18H); **13C NMR** (126 MHz, Chloroform-*d*) δ 174.96, 166.05 (dd, *J* = 15.4, 3.2 Hz), 164.03 (dd, *J* = 15.4, 3.4 Hz), 153.43 (d, *J* = 2.3 Hz), 140.62 (d, *J* = 6.3 Hz), 135.94 (t, *J* = 9.4 Hz), 135.58 (d, *J* = 1.5 Hz), 134.69 (t, *J* = 9.5 Hz), 128.84 (d, *J* = 1.5 Hz), 128.56 (d, *J* = 2.6 Hz), 126.49 (d, *J* = 4.1 Hz), 126.00 (dd, *J* = 86.3, 3.0 Hz), 125.35 (d, *J* = 4.9 Hz), 125.19 (dd, *J* = 89.7, 3.5 Hz), 123.09 (d, *J* = 5.2 Hz), 122.34 (d, *J* = 1.6 Hz), 115.30 (dd, *J* = 13.4, 3.7 Hz), 115.13 (dd, *J* = 13.2, 3.7 Hz), 109.50, 62.18 (d, *J* = 58.1 Hz), 34.53, 30.11; **31P NMR** (202 MHz, CDCl₃) δ 28.15; **19F NMR** (471 MHz, Chloroform-*d*) δ -106.27 (d, *J* = 3.8 Hz), -106.51 (d, *J* = 4.6 Hz); **HRMS** (ESI) Calcd.for C₃₄H₃₄F₂NO₃PNa (M+Na)⁺ 596.2137, Found: 596.2137; **HPLC** (Chiral AD-H, λ = 254 nm, hexane/2-propanol = 3/1, Flow rate = 0.6 mL/min), t_R = 14.015 min, 19.598 min.

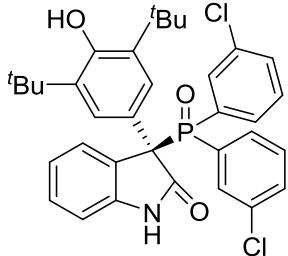


(R)-3c, white solid, 93% yield, 90:10 er; **1H NMR** (500 MHz, Chloroform-*d*) δ 7.81 (s, 1H), 7.74–7.60 (m, 3H), 7.56 (d, *J* = 1.8 Hz, 2H), 7.41–7.34 (m, 1H), 7.34–7.27 (m, 1H), 7.26–7.15 (m, 4H), 7.10 (t, *J* = 7.9 Hz, 2H), 6.72 (d, *J* = 7.8 Hz, 1H), 5.18 (s, 1H), 1.32 (s, 18H). **13C NMR** (126 MHz, Chloroform-*d* + DMSO-*d*₆) δ 174.30, 162.46 (t, *J* = 16.6 Hz), 160.49 (t, *J* = 16.8 Hz), 153.05 (d, *J* = 2.5 Hz), 141.41 (d, *J* = 6.5 Hz), 135.56, 132.42 (dd, *J* = 87.7, 5.4 Hz), 131.64 (dd, *J* = 91.4, 5.7 Hz), 129.44 (d, *J* = 7.5 Hz), 129.36, 129.27 (d, *J* = 7.4 Hz), 128.80 (dd, *J* = 8.3, 2.9 Hz), 128.55 (d, *J* = 1.5 Hz), 127.91 (d, *J* = 2.4 Hz), 127.49 (dd, *J* = 8.1, 2.9 Hz), 125.88 (d, *J* = 4.2 Hz), 124.98 (d, *J* = 5.0 Hz), 122.86 (d, *J* = 5.6 Hz), 121.51, 119.87 (dd, *J* = 23.4, 9.5 Hz), 118.68 (d, *J* = 21.3 Hz), 118.53 (dd, *J* = 22.8, 9.6 Hz), 109.46, 61.62 (d, *J* = 59.1 Hz), 34.21, 29.76; **³¹P NMR** (202 MHz, Chloroform-*d*) δ 26.85 (t, *J* = 5.7 Hz); **¹⁹F NMR** (471 MHz, Chloroform-*d*) δ -111.29 (d, *J* = 5.7 Hz), -111.51 (d, *J* = 5.9 Hz); **HRMS** (ESI) Calcd. for C₃₄H₃₄F₂NO₃PNa (M+Na)⁺ 596.2137, Found: 596.2138; **HPLC** (Chiral AD-H, λ = 254 nm, hexane/ethanol = 3/1, Flow rate = 0.6 mL/min), t_R = 7.357 min, 12.323 min.

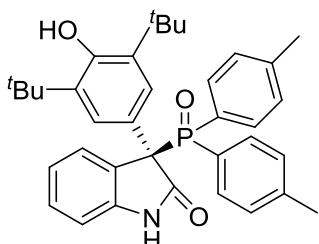


(R)-3d, white solid, 67% yield, 94:6 er; **1H NMR** (500 MHz, Chloroform-*d*) δ 9.03 (s, 1H), 7.80 (dd, *J* = 10.5, 8.6 Hz, 2H), 7.65 (d, *J* = 7.4 Hz, 1H), 7.55 (d, *J* = 1.0 Hz, 2H), 7.44 (dd, *J* = 10.6, 8.5 Hz, 2H), 7.35 (dd, *J* = 8.5, 2.2 Hz, 2H), 7.20 (dd, *J* = 8.5, 2.2 Hz, 2H), 7.17 (t, *J* = 7.7 Hz, 1H), 7.05 (t, *J* = 7.6 Hz, 1H), 6.65 (d, *J* = 7.7 Hz, 1H), 5.23 (s, 1H), 1.31 (s, 18H); **13C NMR** (126 MHz, Chloroform-*d*) δ 174.86, 153.49 (d, *J* = 2.5 Hz), 140.88 (d, *J* = 6.3 Hz), 138.78 (d, *J* = 3.5 Hz), 138.69 (d, *J* = 3.4 Hz), 135.59 (d, *J* = 1.8 Hz), 134.72 (d, *J* = 9.7 Hz), 133.52 (d, *J* = 9.8 Hz), 128.91 (d, *J* = 1.7 Hz), 128.47 (d, *J* = 3.0 Hz), 128.41 (d, *J* = 64.5 Hz), 128.28 (d, *J* = 2.0 Hz), 128.18 (d, *J* = 2.4 Hz), 127.61 (d, *J* = 68.4 Hz), 126.25 (d, *J* = 4.3 Hz), 125.39 (d, *J* = 4.9 Hz), 122.70 (d, *J* = 5.4 Hz), 122.28 (d, *J* = 1.9 Hz), 109.72, 61.92 (d, *J* = 58.5 Hz), 34.52, 30.07; **³¹P NMR** (202 MHz, CDCl₃) δ 27.99; **HRMS** (ESI) Calcd. for C₃₄H₃₄Cl₂NO₃PNa (M+Na)⁺ 628.1546,

Found: 628.1551; **HPLC** (Chiral AD-H, $\lambda = 254$ nm, hexane/ethanol = 3/1, Flow rate = 0.6 mL/min), t_R = 11.981 min, 18.073 min.

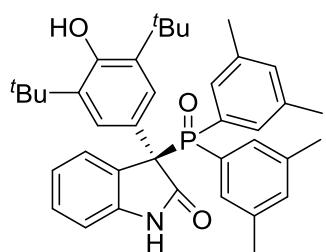


(R)-3e, white solid, 90% yield, 95:5 er; **¹H NMR** (500 MHz, Chloroform-*d*) δ 8.17 (s, 1H), 7.87 (d, $J = 11.3$ Hz, 1H), 7.79 (t, $J = 9.3$ Hz, 1H), 7.66 (d, $J = 7.5$ Hz, 1H), 7.57 (d, $J = 1.0$ Hz, 2H), 7.48–7.35 (m, 4H), 7.33 (td, $J = 7.9, 3.8$ Hz, 1H), 7.25–7.17 (m, 2H), 7.11 (t, $J = 7.6$ Hz, 1H), 6.74 (d, $J = 7.7$ Hz, 1H), 5.20 (s, 1H), 1.33 (s, 18H); **¹³C NMR** (126 MHz, Chloroform-*d*) δ 174.82, 153.60 (d, $J = 2.5$ Hz), 140.95 (d, $J = 6.4$ Hz), 135.71 (d, $J = 1.9$ Hz), 134.41, 134.28, 133.11 (d, $J = 9.7$ Hz), 132.21 (d, $J = 2.6$ Hz), 132.18 (d, $J = 2.6$ Hz), 132.04 (d, $J = 9.6$ Hz), 131.95 (d, $J = 78.4$ Hz), 131.43 (d, $J = 8.5$ Hz), 131.18 (d, $J = 81.5$ Hz), 130.06 (d, $J = 8.8$ Hz), 129.33 (d, $J = 9.5$ Hz), 129.23 (d, $J = 9.4$ Hz), 129.11 (d, $J = 1.7$ Hz), 128.40 (d, $J = 3.1$ Hz), 125.91 (d, $J = 4.3$ Hz), 125.39 (d, $J = 4.9$ Hz), 122.43, 122.38, 109.84, 61.94 (d, $J = 58.2$ Hz), 34.54, 30.09; **³¹P NMR** (202 MHz, CDCl₃) δ 26.87; **HRMS** (ESI) Calcd. for C₃₄H₃₄Cl₂NO₃PNa (M+Na)⁺ 628.1546, Found: 628.1537; **HPLC** (Chiral AD-H, $\lambda = 254$ nm, hexane/ethanol = 3/1, Flow rate = 0.6 mL/min), t_R = 7.040 min, 11.007 min.

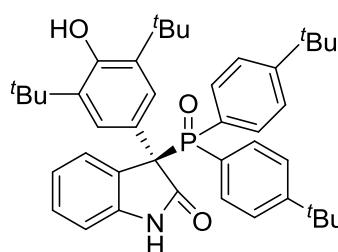


(R)-3f, white solid, 78% yield, 91:9 er; **¹H NMR** (500 MHz, Chloroform-*d*) δ 8.71 (s, 1H), 7.65 (dd, $J = 10.4, 8.3$ Hz, 2H), 7.55 (d, $J = 0.8$ Hz, 2H), 7.51 (d, $J = 7.3$ Hz, 1H), 7.41 (dd, $J = 10.8, 8.1$ Hz, 2H), 7.14 (t, $J = 7.6$ Hz, 3H), 7.05–6.97 (m, 3H), 6.66 (d, $J = 7.7$ Hz, 1H), 5.16 (s, 1H), 2.36 (s, 3H), 2.24 (s, 3H), 1.30 (s, 18H); **¹³C NMR** (126 MHz, Chloroform-*d*) δ 175.15, 153.24 (d, $J = 2.4$ Hz), 142.10 (d, $J = 2.7$ Hz), 142.04 (d, $J = 2.6$ Hz), 141.18 (d, $J = 5.9$ Hz), 135.08 (d, $J = 1.6$ Hz), 133.36 (d, $J = 9.0$ Hz), 132.30 (d, $J = 9.2$ Hz), 128.52 (d, $J = 2.1$ Hz), 128.48 (d, $J = 1.8$ Hz), 127.13 (d, $J = 95.2$ Hz), 126.78, 126.33 (d, $J = 94.5$ Hz), 125.68 (d, $J = 4.5$ Hz), 123.05 (d, $J = 5.1$ Hz), 121.77 (d, $J = 1.6$ Hz), 109.60, 61.87 (d, $J = 56.6$ Hz), 34.48, 30.08, 21.52, 21.43; **³¹P NMR** (202 MHz, CDCl₃) δ 29.32; **HRMS** (ESI) Calcd. for C₃₆H₄₀NO₃PNa (M+Na)⁺

588.2638, Found: 588.2645; **HPLC** (Chiral AD-H, $\lambda = 254$ nm, hexane/ethanol = 3/1, Flow rate = 0.6 mL/min), $t_R = 13.973$ min, 28.832 min.

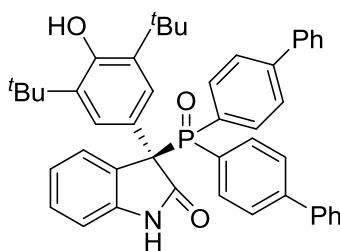


(*R*)-**3g**, white solid, 93% yield, 95:5 er; **¹H NMR** (500 MHz, Chloroform-*d*) δ 8.16 (s, 1H), 7.61 (d, $J = 1.6$ Hz, 2H), 7.39 (d, $J = 7.5$ Hz, 1H), 7.33 (d, $J = 11.2$ Hz, 2H), 7.20 (t, $J = 7.7$ Hz, 1H), 7.09 (s, 1H), 7.06–7.01 (m, 3H), 7.00 (s, 1H), 6.70 (d, $J = 7.7$ Hz, 1H), 5.16 (s, 1H), 2.25 (s, 6H), 2.15 (s, 6H), 1.32 (s, 18H); **¹³C NMR** (126 MHz, Chloroform-*d*) δ 174.88, 153.30 (d, $J = 2.4$ Hz), 141.42 (d, $J = 5.9$ Hz), 137.23 (d, $J = 9.2$ Hz), 137.13 (d, $J = 9.2$ Hz), 135.20 (d, $J = 1.7$ Hz), 133.48 (d, $J = 2.9$ Hz), 133.38 (d, $J = 2.9$ Hz), 130.99 (d, $J = 8.6$ Hz), 130.07 (d, $J = 97.4$ Hz), 130.02 (d, $J = 9.0$ Hz), 128.86 (d, $J = 98.4$ Hz), 128.64 (d, $J = 2.9$ Hz), 128.52 (d, $J = 1.8$ Hz), 126.53 (d, $J = 3.7$ Hz), 125.73 (d, $J = 4.5$ Hz), 123.18 (d, $J = 5.1$ Hz), 121.76 (d, $J = 1.4$ Hz), 109.46, 61.94 (d, $J = 55.4$ Hz), 34.49, 30.17, 21.27, 21.17; **³¹P NMR** (202 MHz, CDCl₃) δ 29.76; **HRMS** (ESI) Calcd.for C₃₈H₄₄NO₃PNa (M+Na)⁺ 616.2951, Found: 616.2953; **HPLC** (Chiral AD-H, $\lambda = 254$ nm, hexane/2-propanol = 3/1, Flow rate = 0.6 mL/min), $t_R = 6.632$ min, 10.982 min.

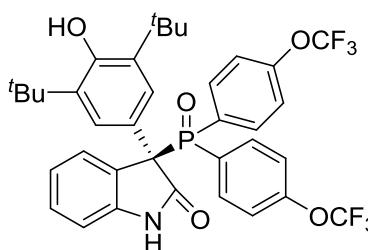


(*R*)-**3h**, white solid, 94% yield, 91:9 er; **¹H NMR** (500 MHz, Chloroform-*d*) δ 7.76 (s, 1H), 7.71 (dd, $J = 10.1, 8.6$ Hz, 2H), 7.52 (dd, $J = 10.8, 8.5$ Hz, 2H), 7.48 (d, $J = 1.0$ Hz, 2H), 7.44 (d, $J = 6.9$ Hz, 1H), 7.39 (dd, $J = 8.4, 2.8$ Hz, 2H), 7.28 (dd, $J = 8.4, 2.6$ Hz, 2H), 7.17 (t, $J = 7.7$ Hz, 1H), 7.01 (t, $J = 7.6$ Hz, 1H), 6.69 (d, $J = 7.7$ Hz, 1H), 5.14 (s, 1H), 1.31 (s, 9H), 1.27 (s, 18H), 1.25 (s, 9H); **¹³C NMR** (126 MHz, Chloroform-*d*) δ 174.84, 155.13 (d, $J = 2.8$ Hz), 154.96 (d, $J = 2.7$ Hz), 153.29 (d, $J = 2.7$ Hz), 141.11, 134.95 (d, $J = 2.0$ Hz), 133.37 (d, $J = 8.8$ Hz), 132.32 (d, $J = 9.2$ Hz), 128.65, 128.45 (d, $J = 1.7$ Hz), 127.14 (d, $J = 90.0$ Hz), 126.56 (d, $J = 4.0$ Hz), 126.33 (d, $J = 92.0$ Hz), 125.81 (d, $J = 4.6$ Hz), 124.80 (d, $J = 2.8$ Hz), 124.70 (d, $J = 2.9$ Hz), 122.66 (d, $J = 5.0$ Hz), 121.71, 109.46, 61.87 (d, $J = 56.5$ Hz), 34.91, 34.83, 34.50, 31.11, 31.01, 30.11; **³¹P NMR** (202 MHz, CDCl₃) δ 28.97; **HRMS** (ESI) Calcd.for C₄₂H₅₂NO₃PNa (M+Na)⁺

672.3577, Found: 672.3585; **HPLC** (Chiral IC, $\lambda = 254$ nm, hexane/ethanol = 5/1, Flow rate = 0.6 mL/min), $t_R = 7.240$ min, 21.123 min.

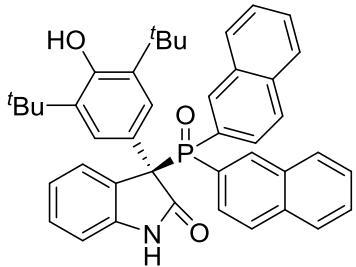


(R)-3i, white solid, 74% yield, 93:7 er; **¹H NMR** (500 MHz, Chloroform-*d*) δ 8.15 (s, 1H), 7.95 (dd, $J = 10.5, 8.4$ Hz, 2H), 7.70–7.55 (m, 9H), 7.52–7.42 (m, 6H), 7.42–7.37 (m, 3H), 7.34 (t, $J = 7.3$ Hz, 1H), 7.19 (t, $J = 7.7$ Hz, 1H), 7.07 (t, $J = 7.6$ Hz, 1H), 6.71 (d, $J = 7.7$ Hz, 1H), 5.16 (s, 1H), 1.30 (s, 18H); **¹³C NMR** (126 MHz, Chloroform-*d*) δ 175.18, 153.36 (d, $J = 2.5$ Hz), 144.49 (d, $J = 2.7$ Hz), 144.30 (d, $J = 2.8$ Hz), 141.52 (d, $J = 5.3$ Hz), 139.95, 139.66, 135.26 (d, $J = 1.4$ Hz), 133.87 (d, $J = 9.0$ Hz), 132.82 (d, $J = 9.1$ Hz), 128.85 (d, $J = 59.3$ Hz), 128.83, 128.73, 128.65, 128.45 (d, $J = 2.3$ Hz), 128.05 (d, $J = 62.7$ Hz), 128.00, 127.92, 127.19, 127.06, 126.47 (d, $J = 3.5$ Hz), 126.42, 126.37 (d, $J = 3.5$ Hz), 125.72 (d, $J = 4.5$ Hz), 122.76 (d, $J = 5.0$ Hz), 121.83, 109.94, 61.99 (d, $J = 57.4$ Hz), 34.49, 30.06; **³¹P NMR** (202 MHz, CDCl₃) δ 28.98; **HRMS** (ESI) Calcd.for C₄₆H₄₄NO₃PNa (M+Na)⁺ 712.2951, Found: 712.2950; **HPLC** (Chiral AD-H, $\lambda = 254$ nm, hexane/ethanol = 3/1, Flow rate = 0.6 mL/min), $t_R = 22.107$ min, 46.023 min.

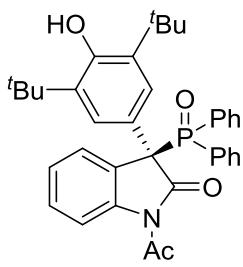


(R)-3j, white solid, 99% yield, 90.5:9.5 er; **¹H NMR** (500 MHz, Chloroform-*d*) δ 7.80 (s, 1H), 7.74–7.61 (m, 3H), 7.56 (d, $J = 1.8$ Hz, 2H), 7.41–7.34 (m, 1H), 7.34–7.28 (m, 1H), 7.26–7.15 (m, 4H), 7.10 (t, $J = 7.9$ Hz, 2H), 6.72 (d, $J = 7.8$ Hz, 1H), 5.18 (s, 1H), 1.32 (s, 18H); **¹³C NMR** (126 MHz, Chloroform-*d*) δ 174.76, 153.56 (d, $J = 2.5$ Hz), 152.06 (dd, $J = 3.6, 1.9$ Hz), 151.96 (dd, $J = 3.2, 1.6$ Hz), 140.69 (d, $J = 6.3$ Hz), 135.68 (d, $J = 1.8$ Hz), 135.47 (d, $J = 10.0$ Hz), 134.21 (d, $J = 10.0$ Hz), 129.01 (d, $J = 1.8$ Hz), 128.54 (d, $J = 2.9$ Hz), 128.41 (d, $J = 59.0$ Hz), 127.61 (d, $J = 62.4$ Hz), 126.12 (d, $J = 4.4$ Hz), 125.38, 125.34, 122.60 (d, $J = 5.4$ Hz), 122.41 (d, $J = 1.8$ Hz), 120.26 (q, $J = 259.2$ Hz), 120.18 (q, $J = 259.3$ Hz), 119.82 (d, $J = 25.3$ Hz), 109.63, 62.07 (d, $J = 58.7$ Hz), 34.51, 30.01; **³¹P NMR** (202 MHz, CDCl₃) δ 27.36; **¹⁹F NMR** (471 MHz, CDCl₃) δ -57.60, -57.63; **HRMS** (ESI) Calcd.for C₃₆H₃₄F₆NO₅PNa (M+Na)⁺ 728.1971,

Found: 728.1971; **HPLC** (Chiral AD-H, $\lambda = 254$ nm, hexane/ethanol = 3/1, Flow rate = 0.6 mL/min), t_R = 7.573 min, 10.248 min.

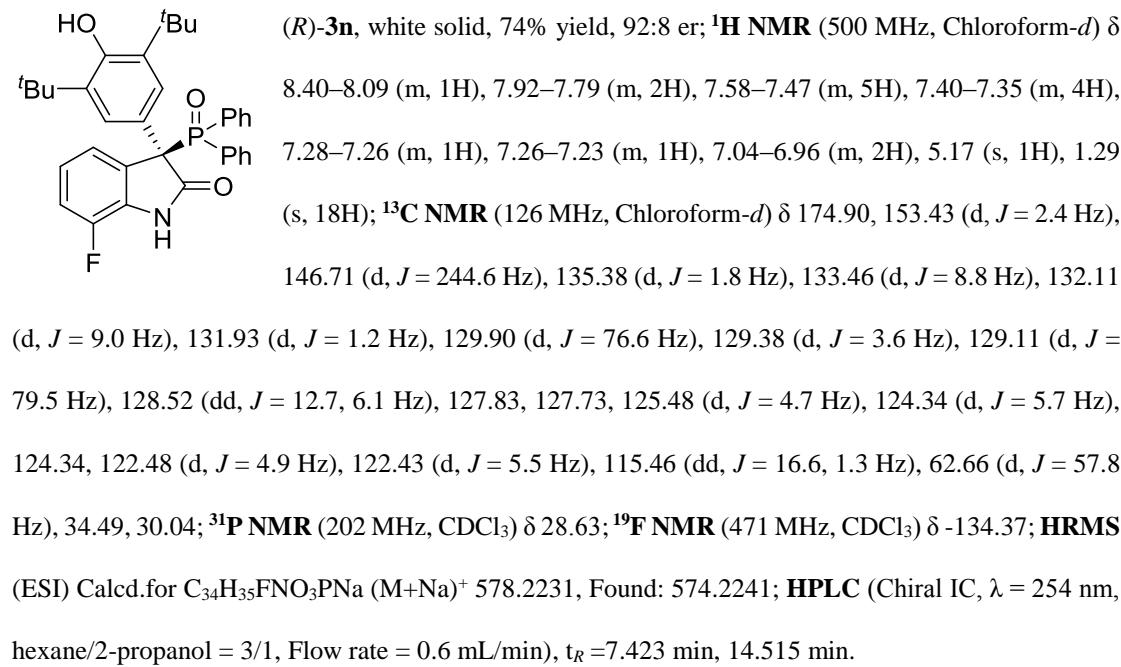
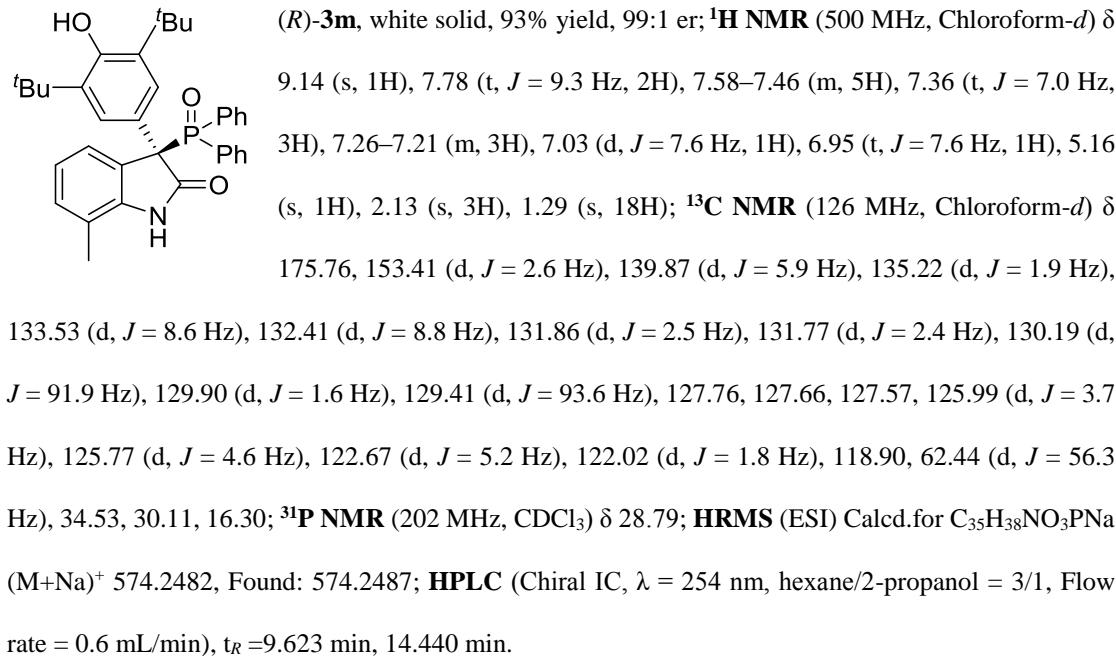


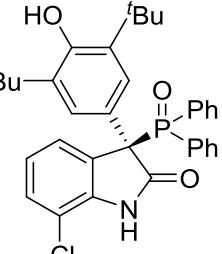
(*R*)-**3k**, white solid, 63% yield, 95:5 er; **¹H NMR** (500 MHz, Chloroform-*d*) δ 8.46 (d, $J = 13.2$ Hz, 1H), 8.18 (s, 1H), 8.13 (d, $J = 13.3$ Hz, 1H), 7.90–7.78 (m, 4H), 7.73 (d, $J = 8.2$ Hz, 1H), 7.70–7.55 (m, 7H), 7.50 (t, $J = 7.1$ Hz, 2H), 7.40 (t, $J = 7.4$ Hz, 1H), 7.16 (t, $J = 7.4$ Hz, 1H), 7.03 (t, $J = 7.5$ Hz, 1H), 6.63 (d, $J = 7.5$ Hz, 1H), 5.14 (s, 1H), 1.23 (s, 18H); **¹³C NMR** (126 MHz, Chloroform-*d*) δ 174.80, 153.41 (d, $J = 2.5$ Hz), 141.00 (d, $J = 6.2$ Hz), 136.04 (d, $J = 7.8$ Hz), 135.36 (d, $J = 1.8$ Hz), 134.76 (d, $J = 8.3$ Hz), 134.65 (d, $J = 2.4$ Hz), 134.55 (d, $J = 2.4$ Hz), 132.24 (d, $J = 13.2$ Hz), 132.06 (d, $J = 13.2$ Hz), 129.19, 129.13, 128.69 (d, $J = 1.8$ Hz), 128.64 (d, $J = 3.2$ Hz), 128.18, 128.07, 127.99 (d, $J = 9.9$ Hz), 127.55, 127.49, 127.52 (d, $J = 7.7$ Hz), 127.35 (d, $J = 11.8$ Hz), 127.23, 127.14 (d, $J = 2.5$ Hz), 126.73 (d, $J = 88.0$ Hz), 126.61 (d, $J = 4.1$ Hz), 126.47, 126.45, 125.70 (d, $J = 4.8$ Hz), 123.06 (d, $J = 5.2$ Hz), 122.12 (d, $J = 2.0$ Hz), 109.59, 62.08 (d, $J = 56.8$ Hz), 34.47, 30.05; **³¹P NMR** (202 MHz, CDCl₃) δ 29.61; **HRMS** (ESI) Calcd.for C₄₂H₄₀NO₃PNa (M+Na)⁺ 660.2638, Found: 660.2638; **HPLC** (Chiral AD-H, $\lambda = 254$ nm, hexane/ethanol = 3/1, Flow rate = 0.6 mL/min), t_R = 20.182 min, 65.065 min.



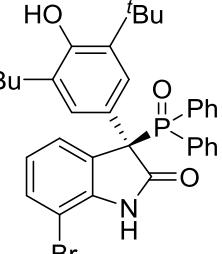
(*R*)-**3l**, white solid, 66% yield, 93.5:6.5 er; **¹H NMR** (500 MHz, Chloroform-*d*) δ 8.07 (d, $J = 8.2$ Hz, 1H), 7.78 (dd, $J = 10.8, 8.2$ Hz, 2H), 7.54–7.41 (m, 5H), 7.41–7.31 (m, 5H), 7.29–7.27 (m, 1H), 7.25 (d, $J = 3.4$ Hz, 1H), 7.22 (t, $J = 7.5$ Hz, 1H), 5.27 (s, 1H), 2.46 (s, 3H), 1.31 (s, 18H); **¹³C NMR** (126 MHz, Chloroform-*d*) δ 174.72, 170.32, 153.58 (d, $J = 1.9$ Hz), 140.00 (d, $J = 6.0$ Hz), 135.71, 133.33 (d, $J = 8.7$ Hz), 132.30 (d, $J = 2.8$ Hz), 132.14 (d, $J = 2.8$ Hz), 131.90 (d, $J = 9.1$ Hz), 129.78 (d, $J = 98.3$ Hz), 129.04 (d, $J = 2.1$ Hz), 128.69 (d, $J = 100.0$ Hz), 127.99 (d, $J = 3.5$ Hz), 127.89 (d, $J = 3.4$ Hz), 125.47 (d, $J = 4.9$ Hz), 125.00 (d, $J = 4.3$ Hz), 124.61 (d, $J = 2.2$ Hz), 123.27 (d, $J = 4.5$ Hz), 116.03 (d, $J = 0.6$ Hz), 62.62 (d, $J = 54.7$ Hz), 34.51, 30.07, 26.60; **³¹P NMR** (202 MHz, CDCl₃) δ

29.43; **HRMS** (ESI) Calcd.for $C_{36}H_{38}NO_4PNa$ ($M+Na$)⁺ 602.2431, Found: 602.2435; **HPLC** (Chiral IC, $\lambda = 254$ nm, hexane/2-propanol = 10/1, Flow rate = 0.8 mL/min), $t_R = 12.640$ min, 22.015 min.

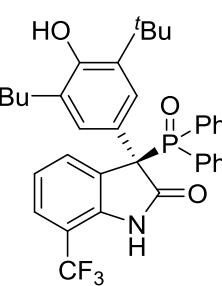


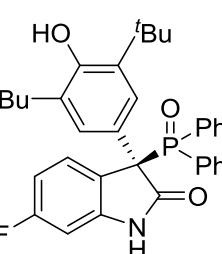


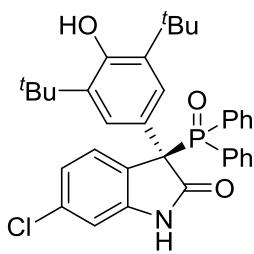
(R)-3o, white solid, 93% yield, 93.5:6.5 er; **¹H NMR** (500 MHz, Chloroform-*d*) δ 7.92–7.83 (m, 2H), 7.79 (s, 1H), 7.57–7.47 (m, 6H), 7.46–7.41 (m, 1H), 7.38 (td, *J* = 7.7, 3.4 Hz, 2H), 7.29 (td, *J* = 7.9, 3.3 Hz, 2H), 7.21 (dt, *J* = 8.2, 1.0 Hz, 1H), 7.03 (t, *J* = 7.9 Hz, 1H), 5.16 (s, 1H), 1.29 (s, 18H); **¹³C NMR** (126 MHz, Chloroform-*d*) δ 174.39, 153.49 (d, *J* = 2.4 Hz), 138.52 (d, *J* = 5.9 Hz), 135.45 (d, *J* = 1.8 Hz), 133.46 (d, *J* = 8.9 Hz), 132.14 (d, *J* = 9.0 Hz), 132.06 (d, *J* = 2.8 Hz), 131.99 (d, *J* = 2.8 Hz), 129.88 (d, *J* = 79.4 Hz), 129.10 (d, *J* = 82.4 Hz), 128.47 (d, *J* = 1.8 Hz), 128.15 (d, *J* = 4.1 Hz), 127.90 (d, *J* = 2.0 Hz), 127.80 (d, *J* = 2.3 Hz), 126.93 (d, *J* = 3.0 Hz), 125.44 (d, *J* = 4.8 Hz), 122.96 (d, *J* = 2.1 Hz), 122.47 (d, *J* = 5.2 Hz), 114.60, 63.34 (d, *J* = 55.4 Hz), 34.53, 30.08; **³¹P NMR** (243 MHz, CDCl₃) δ 28.67; **HRMS** (ESI) Calcd.for C₃₄H₃₅ClNO₃PNa (M+Na)⁺ 594.1935, Found: 594.1937; **HPLC** (Chiral IC, λ = 254 nm, hexane/2-propanol = 5/1, Flow rate = 0.6 mL/min), t_R = 12.665 min, 33.915 min.



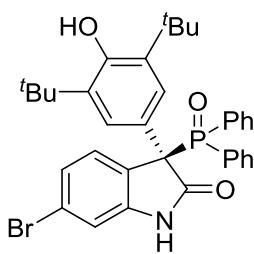
(R)-3p, white solid, 85% yield, 92:8 er; **¹H NMR** (600 MHz, Chloroform-*d*) δ 7.93–7.84 (m, 2H), 7.60–7.47 (m, 7H), 7.44 (t, *J* = 7.4 Hz, 1H), 7.38 (td, *J* = 7.6, 3.3 Hz, 2H), 7.34 (d, *J* = 8.1 Hz, 1H), 7.29 (td, *J* = 7.7, 3.0 Hz, 2H), 6.97 (t, *J* = 7.9 Hz, 1H), 5.16 (s, 1H), 1.30 (s, 18H); **¹³C NMR** (151 MHz, Chloroform-*d*) δ 173.84, 153.48 (d, *J* = 2.4 Hz), 139.89 (d, *J* = 5.6 Hz), 135.49, 133.45 (d, *J* = 8.9 Hz), 132.09 (d, *J* = 8.3 Hz), 132.09, 131.98 (d, *J* = 2.7 Hz), 131.23, 129.85 (d, *J* = 94.0 Hz), 129.19 (d, *J* = 97.3 Hz), 128.07 (d, *J* = 4.0 Hz), 127.91, 127.83, 127.55 (d, *J* = 3.1 Hz), 125.39 (d, *J* = 4.8 Hz), 123.40, 122.66 (d, *J* = 4.0 Hz), 102.26, 63.67 (d, *J* = 54.9 Hz), 34.53, 30.09; **³¹P NMR** (243 MHz, CDCl₃) δ 28.81; **HRMS** (ESI) Calcd.for C₃₄H₃₅BrNO₃PNa (M+Na)⁺ 638.1430, Found: 638.1425; **HPLC** (Chiral AD-H, λ = 254 nm, hexane/2-propanol = 3/1, Flow rate = 0.6 mL/min), t_R = 10.265 min, 12.373 min.


(R)-3q, white solid, 72% yield, 95:5 er; **¹H NMR** (600 MHz, Chloroform-*d*) δ 8.00–7.92 (m, 3H), 7.80 (s, 1H), 7.56–7.34 (m, 11H), 7.20 (t, *J* = 7.8 Hz, 1H), 5.16 (s, 1H), 1.30 (s, 18H); **¹³C NMR** (126 MHz, Chloroform-*d*) δ 174.95, 153.51 (d, *J* = 2.2 Hz), 137.84, 135.65 (d, *J* = 1.6 Hz), 133.44 (d, *J* = 9.1 Hz), 132.18, 132.14 (d, *J* = 2.9 Hz), 132.05 (d, *J* = 2.8 Hz), 131.81 (d, *J* = 8.9 Hz), 129.74 (d, *J* = 65.6 Hz), 128.95 (d, *J* = 69.5 Hz), 128.62, 128.59, 127.95 (d, *J* = 8.0 Hz), 127.85 (d, *J* = 7.7 Hz), 125.32 (d, *J* = 4.9 Hz), 123.64 (q, *J* = 272.2 Hz), 122.67 (d, *J* = 5.0 Hz), 122.05 (d, *J* = 2.0 Hz), 111.62 (q, *J* = 30.0 Hz), 61.82 (d, *J* = 54.3 Hz), 34.52, 30.06; **³¹P NMR** (243 MHz, CDCl₃) δ 28.84; **¹⁹F NMR** (471 MHz, CDCl₃) δ -61.01; **HRMS** (ESI) Calcd. for C₃₅H₃₅F₃BrNO₃PNa (M+Na)⁺ 628.2199, Found: 628.2189; **HPLC** (Chiral IC, λ = 254 nm, hexane/2-propanol = 5/1, Flow rate = 0.6 mL/min), t_R = 8.657 min, 10.782 min.

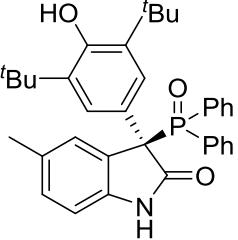

(R)-3r, white solid, 73% yield, 85.5:14.5 er; **¹H NMR** (600 MHz, Chloroform-*d*) δ 7.85 (dd, *J* = 11.2, 7.9 Hz, 2H), 7.76 (s, 1H), 7.56 (dd, *J* = 10.9, 8.1 Hz, 2H), 7.53–7.46 (m, 4H), 7.43 (t, *J* = 7.4 Hz, 1H), 7.39 (td, *J* = 7.5, 2.9 Hz, 2H), 7.29 (td, *J* = 7.7, 2.9 Hz, 2H), 6.74 (td, *J* = 9.0, 1.9 Hz, 1H), 6.43 (dd, *J* = 8.3, 1.7 Hz, 1H), 5.16 (s, 1H), 1.29 (s, 18H); **¹³C NMR** (126 MHz, Chloroform-*d*) δ 175.20, 163.09 (dd, *J* = 246.9, 2.1 Hz), 153.49 (d, *J* = 2.6 Hz), 142.78 (dd, *J* = 12.2, 6.1 Hz), 135.35 (d, *J* = 1.9 Hz), 133.34 (d, *J* = 8.6 Hz), 132.49 (d, *J* = 9.0 Hz), 132.05 (d, *J* = 2.7 Hz), 131.93 (d, *J* = 2.6 Hz), 129.90 (d, *J* = 73.7 Hz), 129.51 (d, *J* = 2.6 Hz), 129.12 (d, *J* = 75.8 Hz), 127.94 (d, *J* = 2.4 Hz), 127.84 (d, *J* = 2.4 Hz), 125.59 (d, *J* = 4.7 Hz), 122.49 (d, *J* = 4.6 Hz), 121.82 (dd, *J* = 3.6, 3.0 Hz), 108.36 (dd, *J* = 22.4, 2.0 Hz), 98.20 (d, *J* = 27.5 Hz), 61.61 (d, *J* = 56.9 Hz), 34.52, 30.07; **³¹P NMR** (202 MHz, CDCl₃) δ 29.39; **¹⁹F NMR** (471 MHz, CDCl₃) δ -111.39 (d, *J* = 3.5 Hz); **HRMS** (ESI) Calcd. for C₃₄H₃₅FNO₃PNa (M+Na)⁺ 578.2231, Found: 574.2231; **HPLC** (Chiral AD-H, λ = 254 nm, hexane/ethanol = 5/1, Flow rate = 0.6 mL/min), t_R = 12.765 min, 28.232 min.



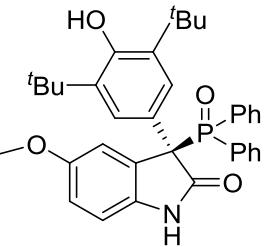
(*R*)-3s, white solid, 97% yield, 89.5:10.5 er; **1H NMR** (600 MHz, Chloroform-*d*) δ 8.01 (s, 1H), 7.83 (dd, *J* = 10.3, 8.4 Hz, 2H), 7.58 (dd, *J* = 10.7, 7.4 Hz, 2H), 7.51 (t, *J* = 7.4 Hz, 1H), 7.46 (d, *J* = 1.4 Hz, 2H), 7.45–7.36 (m, 4H), 7.30 (td, *J* = 7.7, 3.1 Hz, 2H), 7.01 (dd, *J* = 8.2, 1.7 Hz, 1H), 6.70 (d, *J* = 1.5 Hz, 1H), 5.17 (s, 1H), 1.29 (s, 18H); **13C NMR** (126 MHz, Chloroform-*d* + DMSO-*d*₆) δ 174.44, 152.88 (d, *J* = 2.3 Hz), 142.82 (d, *J* = 5.9 Hz), 135.34, 133.76 (d, *J* = 2.4 Hz), 132.81 (d, *J* = 8.7 Hz), 132.81 (d, *J* = 8.9 Hz), 131.41, 129.77 (d, *J* = 97.4 Hz), 129.33 (d, *J* = 100.1 Hz), 128.62 (d, *J* = 3.0 Hz), 127.38 (d, *J* = 5.1 Hz), 127.29 (d, *J* = 5.3 Hz), 124.87 (d, *J* = 4.8 Hz), 124.73 (d, *J* = 4.1 Hz), 122.50 (d, *J* = 5.1 Hz), 120.86 (d, *J* = 2.0 Hz), 109.70, 61.28 (d, *J* = 57.4 Hz), 34.06, 29.62; **31P NMR** (243 MHz, CDCl₃) δ 28.95; **HRMS** (ESI) Calcd. for C₃₄H₃₅ClNO₃PNa (M+Na)⁺ 594.1935, Found: 594.1926; **HPLC** (Chiral AD-H, λ = 254 nm, hexane/ethanol = 5/1, Flow rate = 0.6 mL/min), t_R = 14.077 min, 34.832 min.



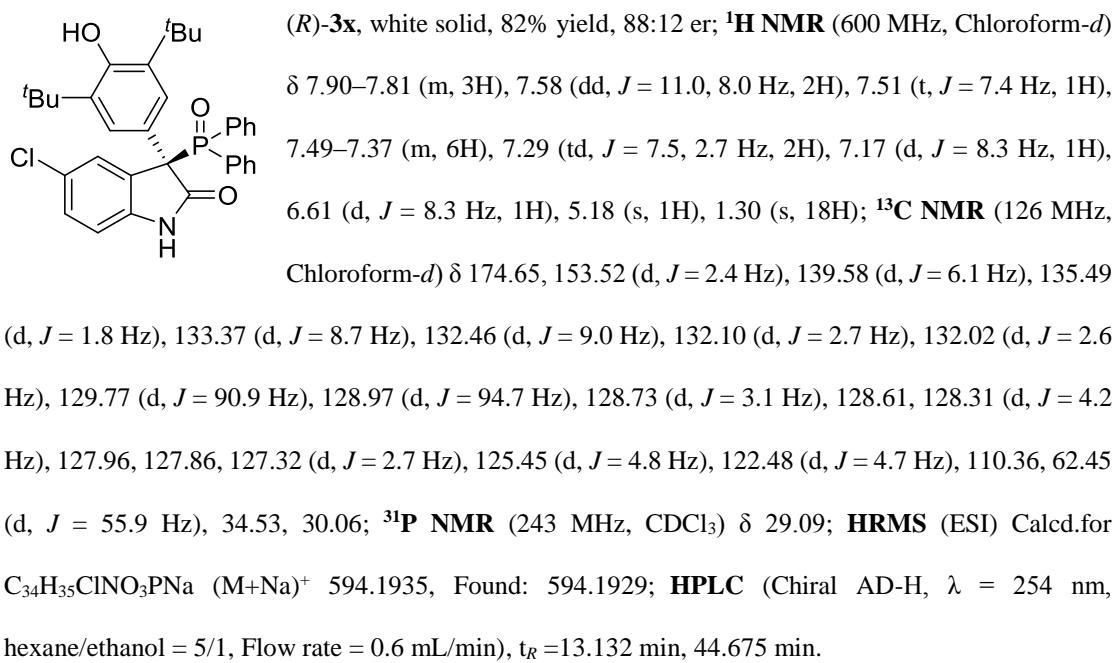
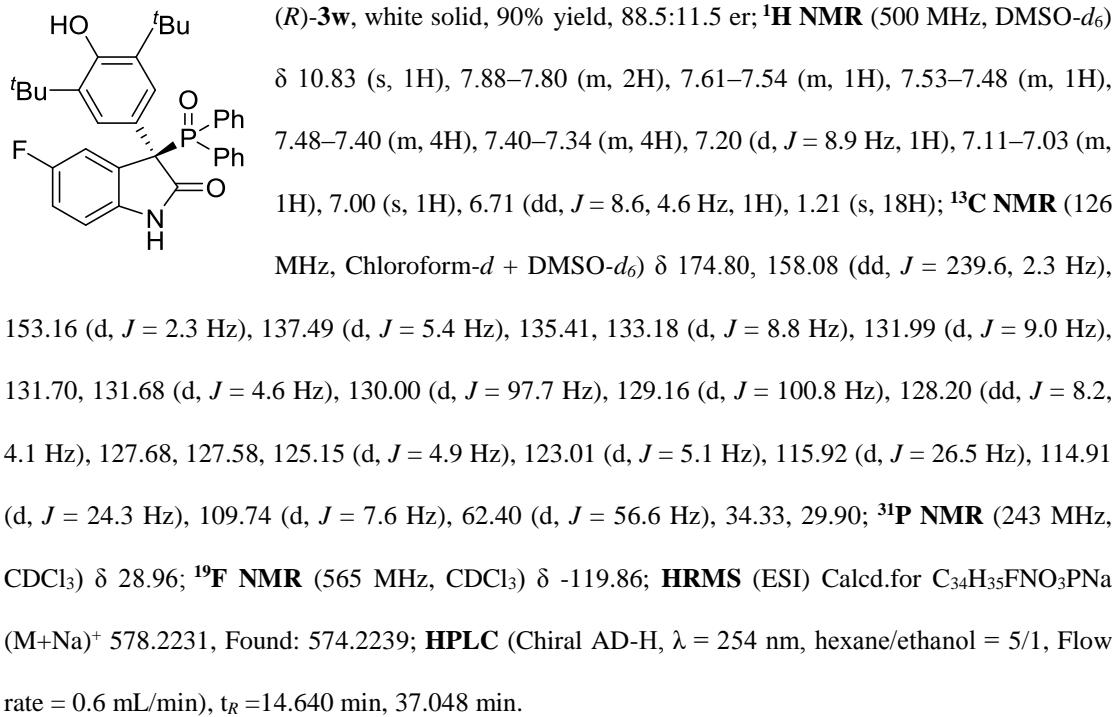
(*R*)-3t, white solid, 96% yield, 82.5:17.5 er; **1H NMR** (600 MHz, Chloroform-*d*) δ 7.92 (s, 1H), 7.83 (dd, *J* = 10.7, 8.2 Hz, 2H), 7.58 (dd, *J* = 11.0, 8.0 Hz, 2H), 7.51 (t, *J* = 7.3 Hz, 1H), 7.46 (s, 2H), 7.43 (t, *J* = 7.5 Hz, 1H), 7.39 (td, *J* = 7.7, 3.2 Hz, 2H), 7.35 (d, *J* = 7.9 Hz, 1H), 7.30 (td, *J* = 7.7, 3.1 Hz, 2H), 7.17 (dd, *J* = 8.1, 1.1 Hz, 1H), 6.86 (s, 1H), 5.17 (s, 1H), 1.29 (s, 18H); **13C NMR** (126 MHz, Chloroform-*d* + DMSO-*d*₆) δ 174.48, 153.00 (d, *J* = 1.8 Hz), 143.05 (d, *J* = 6.2 Hz), 135.32, 132.97 (d, *J* = 8.7 Hz), 131.84 (d, *J* = 8.9 Hz), 131.52 (d, *J* = 2.0 Hz), 129.91 (d, *J* = 97.4 Hz), 129.12, 129.10, 129.05 (d, *J* = 100.3 Hz), 127.51 (d, *J* = 6.1 Hz), 127.42 (d, *J* = 6.3 Hz), 125.45 (d, *J* = 4.0 Hz), 125.02 (d, *J* = 4.6 Hz), 123.96, 122.61 (d, *J* = 5.1 Hz), 121.94 (d, *J* = 1.8 Hz), 112.64, 61.53 (d, *J* = 57.3 Hz), 34.18, 29.76; **31P NMR** (202 MHz, CDCl₃) δ 29.00; **HRMS** (ESI) Calcd. for C₃₄H₃₅BrNO₃PNa (M+Na)⁺ 638.1430, Found: 638.1436; **HPLC** (Chiral AD-H, λ = 254 nm, hexane/ethanol = 3/1, Flow rate = 0.6 mL/min), t_R = 9.523 min, 19.832 min.

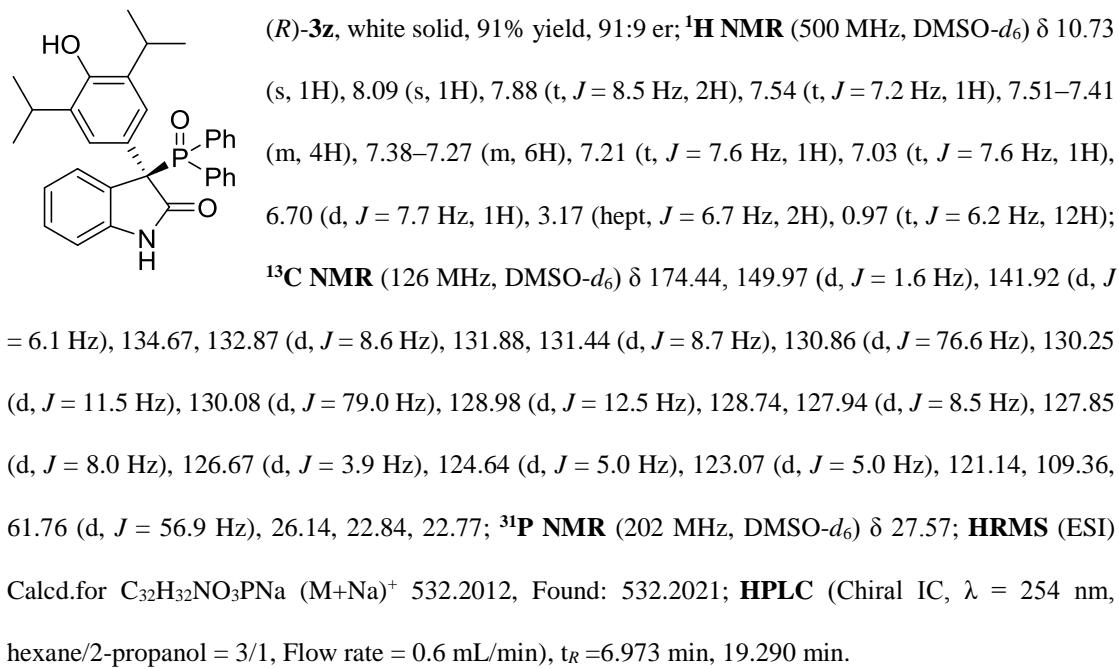
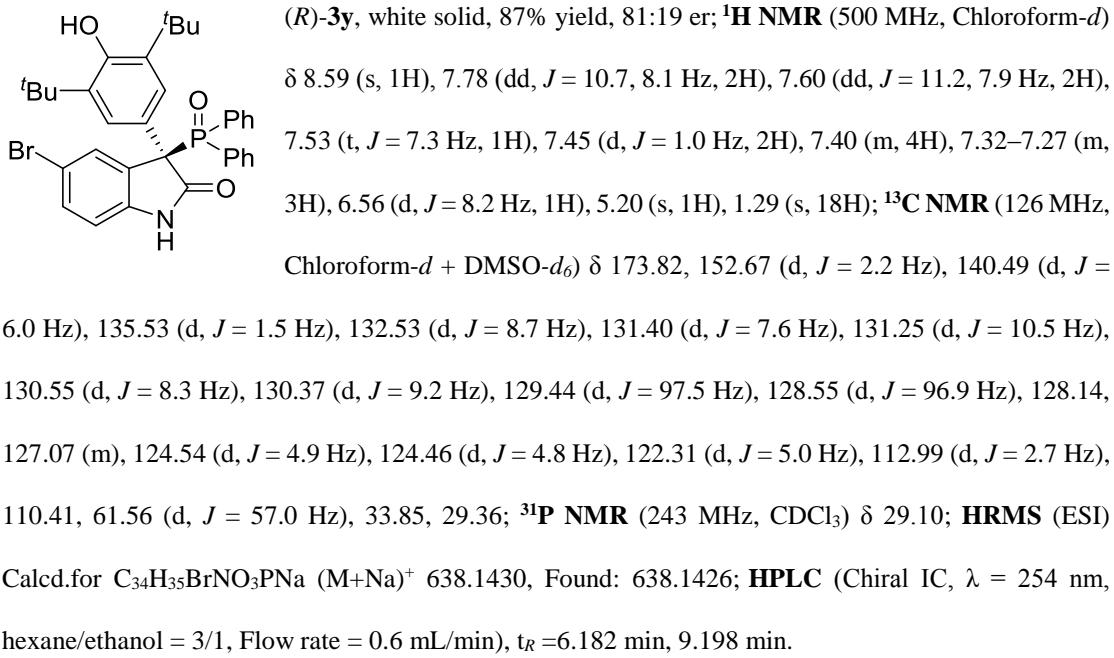


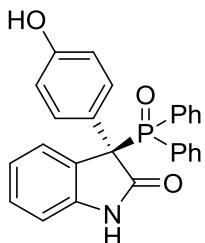
(R)-**3u**, white solid, 75% yield, 88:12 er; **¹H NMR** (600 MHz, Chloroform-*d*) δ 7.88 (t, *J* = 9.3 Hz, 2H), 7.57–7.45 (m, 6H), 7.42–7.34 (m, 4H), 7.26–7.23 (m, 2H), 7.01 (d, *J* = 7.8 Hz, 1H), 6.58 (d, *J* = 7.9 Hz, 1H), 5.13 (s, 1H), 2.31 (s, 3H), 1.30 (s, 18H); **¹³C NMR** (126 MHz, Chloroform-*d* + DMSO-*d*₆) δ 174.34, 152.63 (d, *J* = 2.2 Hz), 138.98 (d, *J* = 6.1 Hz), 135.14 (*J* = 1.5 Hz), 132.86 (d, *J* = 8.6 Hz), 131.63 (d, *J* = 8.9 Hz), 131.11, 130.16 (d, *J* = 97.5 Hz), 130.06 (d, *J* = 2.0 Hz), 129.17 (d, *J* = 99.7 Hz), 128.54 (d, *J* = 2.6 Hz), 128.37, 127.15, 127.05, 126.05 (d, *J* = 3.9 Hz), 124.98 (d, *J* = 4.8 Hz), 123.10 (d, *J* = 5.2 Hz), 108.76, 61.46 (d, *J* = 57.5 Hz), 34.00, 29.58, 20.75; **³¹P NMR** (243 MHz, CDCl₃) δ 28.85; **HRMS** (ESI) Calcd. for C₃₅H₃₈NO₃PNa (M+Na)⁺ 574.2482, Found: 574.2484; **HPLC** (Chiral IC, λ = 254 nm, hexane/ethanol = 5/1, Flow rate = 0.6 mL/min), t_R = 8.248 min, 23.748 min.



(R)-**3v**, white solid, 94% yield, 85:15 er; **¹H NMR** (500 MHz, Chloroform-*d*) δ 8.21 (s, 1H), 7.83 (dd, *J* = 10.7, 7.7 Hz, 2H), 7.61–7.52 (m, 4H), 7.49 (td, *J* = 7.5, 1.0 Hz, 1H), 7.38 (td, *J* = 7.7, 3.0 Hz, 3H), 7.24 (dd, *J* = 7.6, 3.1 Hz, 2H), 7.09 (s, 1H), 6.79–6.72 (m, 1H), 6.59 (d, *J* = 8.5 Hz, 1H), 5.17 (s, 1H), 3.70 (s, 3H), 1.30 (s, 18H); **¹³C NMR** (126 MHz, Chloroform-*d*) δ 175.07, 154.95 (d, *J* = 2.3 Hz), 153.37 (d, *J* = 2.5 Hz), 135.21 (d, *J* = 1.8 Hz), 134.80 (d, *J* = 6.2 Hz), 133.45 (d, *J* = 8.6 Hz), 132.34 (d, *J* = 9.0 Hz), 131.86 (d, *J* = 2.6 Hz), 131.77 (d, *J* = 2.6 Hz), 130.12 (d, *J* = 82.6 Hz), 129.34 (d, *J* = 84.2 Hz), 127.82 (d, *J* = 6.7 Hz), 127.73 (d, *J* = 6.7 Hz), 127.30 (d, *J* = 4.2 Hz), 125.65 (d, *J* = 4.7 Hz), 122.64 (d, *J* = 5.2 Hz), 115.34 (d, *J* = 1.7 Hz), 114.03 (d, *J* = 2.9 Hz), 110.22, 62.27 (d, *J* = 56.8 Hz), 55.67, 34.51, 30.10; **³¹P NMR** (243 MHz, CDCl₃) δ 28.78; **HRMS** (ESI) Calcd. for C₃₅H₃₈NO₄PNa (M+Na)⁺ 590.2431, Found: 590.2426; **HPLC** (Chiral IC, λ = 254 nm, hexane/ethanol = 3/1, Flow rate = 0.6 mL/min), t_R = 6.898 min, 14.348 min.

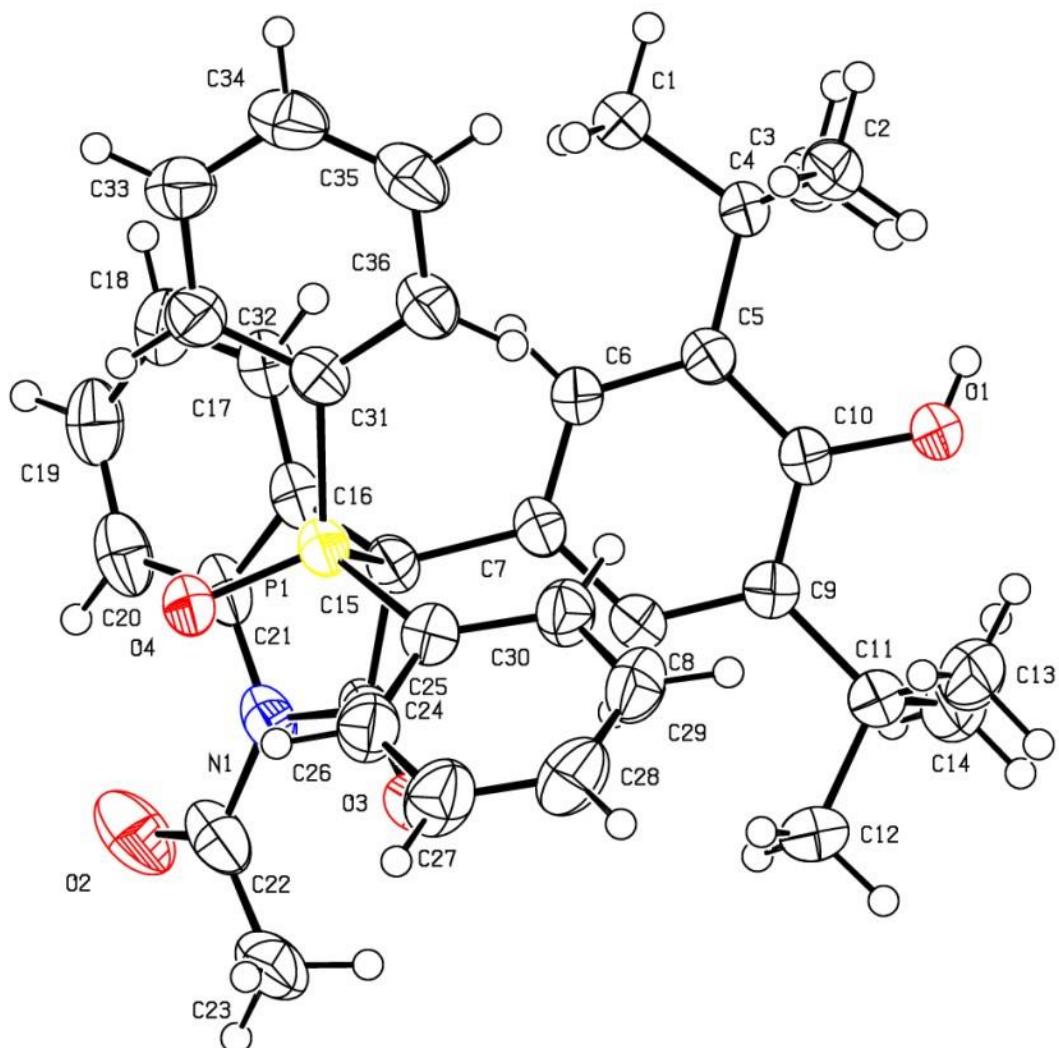






(*R*)-**4**, white solid, 82% yield, 92.5:7.5 er; **¹H NMR** (500 MHz, DMSO-*d*₆) δ 10.74 (s, 1H), 9.77 (s, 1H), 7.85–7.76 (m, 2H), 7.56–7.43 (m, 5H), 7.40 (td, *J* = 7.9, 3.2 Hz, 2H), 7.32–7.16 (m, 5H), 7.00 (t, *J* = 7.6, 0.7 Hz, 1H), 6.70–6.64 (m, 3H); **¹³C NMR** (126 MHz, DMSO-*d*₆) δ 174.96, 157.13, 142.04 (d, *J* = 6.0 Hz), 133.35 (d, *J* = 9.0 Hz), 132.93 (d, *J* = 1.7 Hz), 132.85 (d, *J* = 2.0 Hz), 131.92 (d, *J* = 8.9 Hz), 130.44 (d, *J* = 71.9 Hz), 129.65 (d, *J* = 73.8 Hz), 129.65 (d, *J* = 5.0 Hz), 129.55, 128.64 (d, *J* = 12.0 Hz), 128.52 (d, *J* = 11.8 Hz), 128.23 (d, *J* = 2.4 Hz), 127.18 (d, *J* = 3.8 Hz), 125.21 (d, *J* = 5.0 Hz), 122.26, 115.82, 110.08, 61.74 (d, *J* = 57.7 Hz); **³¹P NMR** (243 MHz, DMSO-*d*₆) δ 28.29; **HRMS** (ESI) Calcd. for C₂₆H₂₀NO₃PNa (M+Na)⁺ 448.1073, Found: 448.1072; **HPLC** (Chiral IC, λ = 254 nm, hexane/2-propanol = 3/1, Flow rate = 0.6 mL/min), t_R = 14.023 min, 16.482 min.

Single Crystal X-ray Structure Determinations of Compound (*R*)-3l (CCDC: 2019323)



Cell: $a=9.8737(2)$ $b=15.5010(3)$ $c=20.4589(4)$
 $\alpha=90$ $\beta=90$ $\gamma=90$

Temperature: 150 K

	Calculated	Reported
Volume	3131.28(11)	3131.28(11)
Space group	P 21 21 21	P 21 21 21
Hall group	P 2ac 2ab	P 2ac 2ab
Moiety formula	C36 H38 N O4 P	C36 H38 N O4 P
Sum formula	C36 H38 N O4 P	C36 H38 N O4 P
Mr	579.64	579.64
Dx,g cm ⁻³	1.230	1.230
Z	4	4

Mu (mm-1)	1.090	1.090
F000	1232.0	1232.0
F000'	1236.55	
h,k,lmax	12,19,25	12,19,25
Nref	6414[3606]	6348
Tmin,Tmax	0.761,0.858	0.064,0.174
Tmin'	0.761	

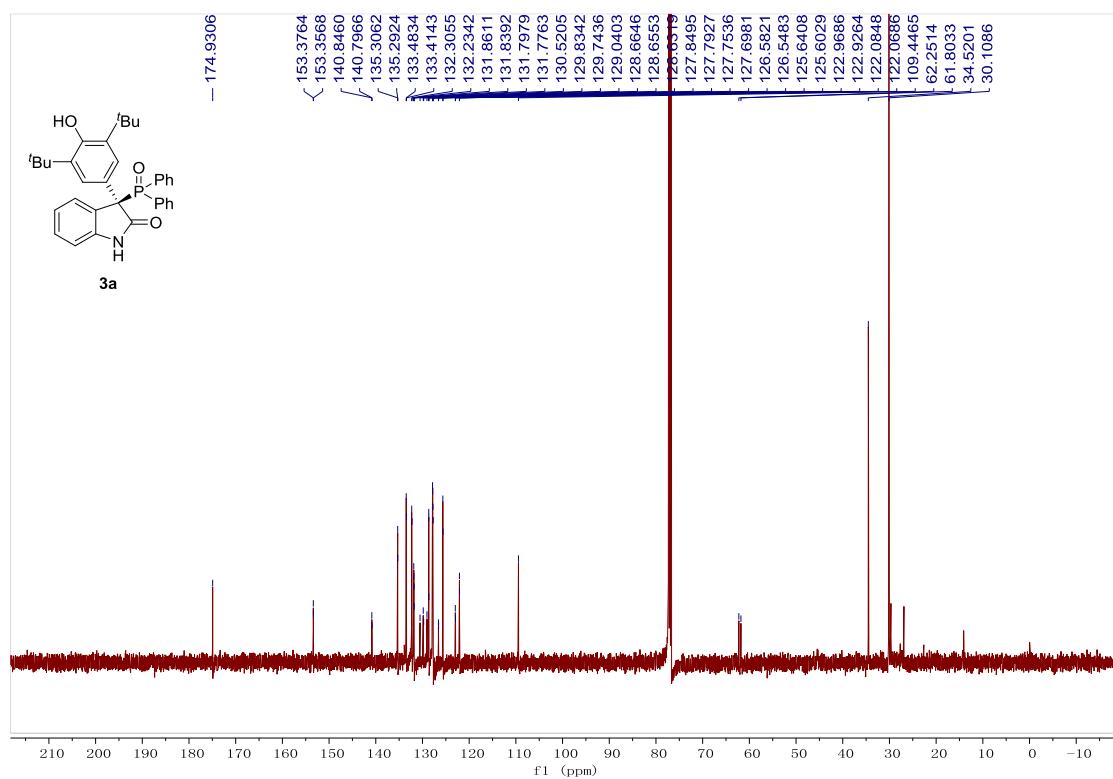
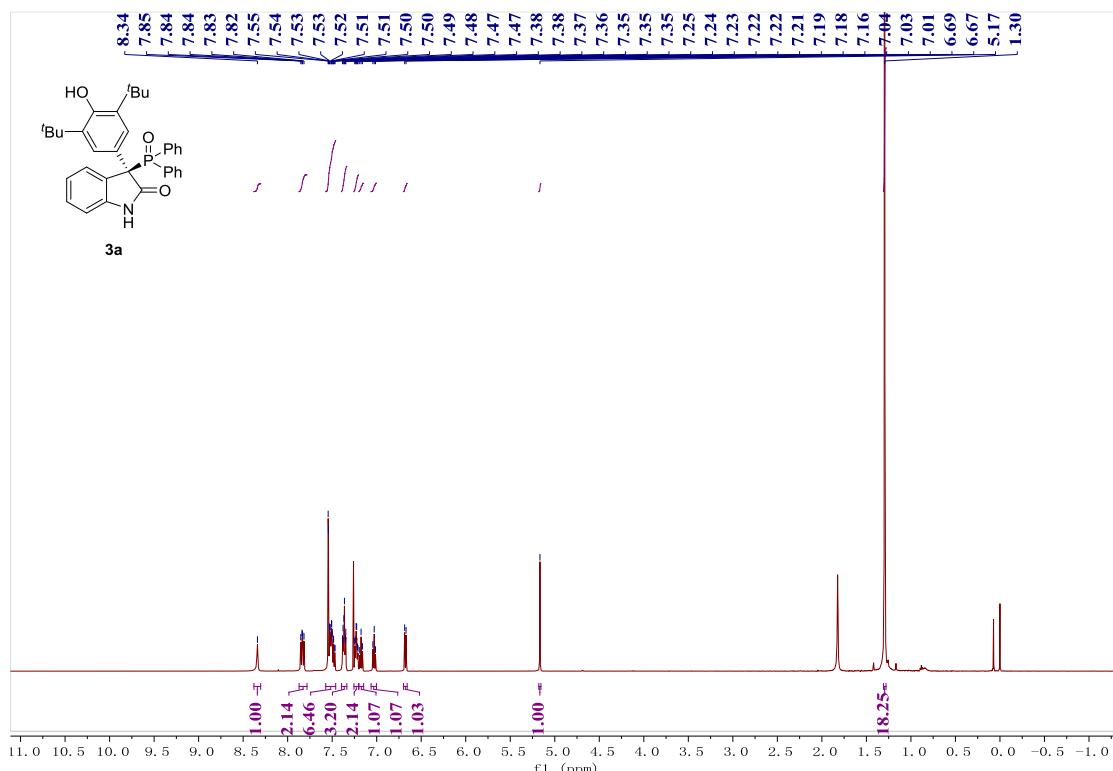
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SCAN

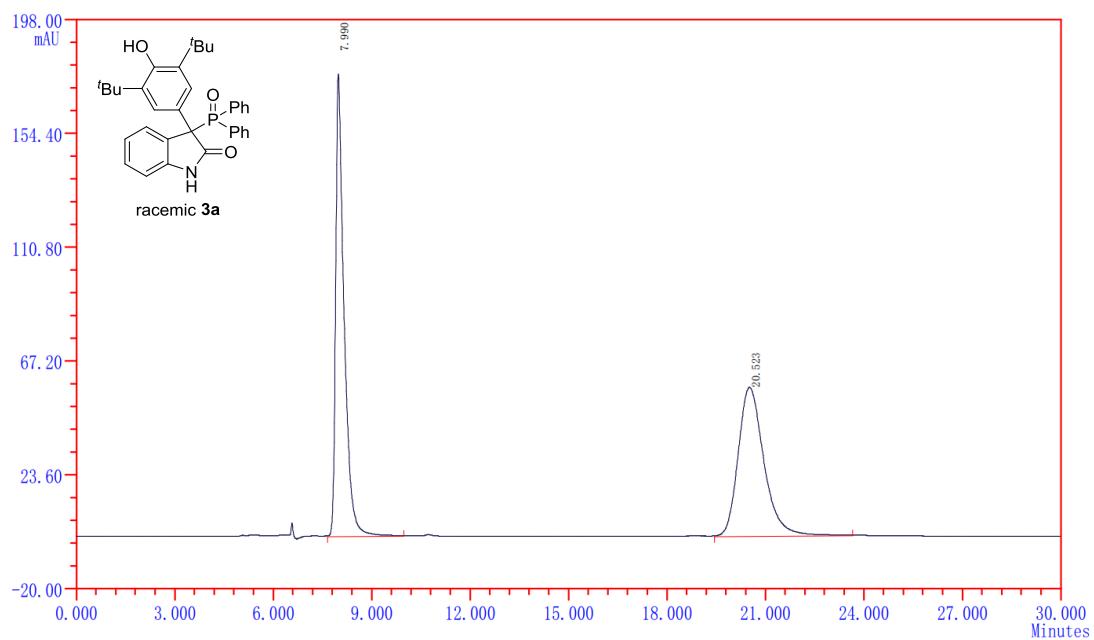
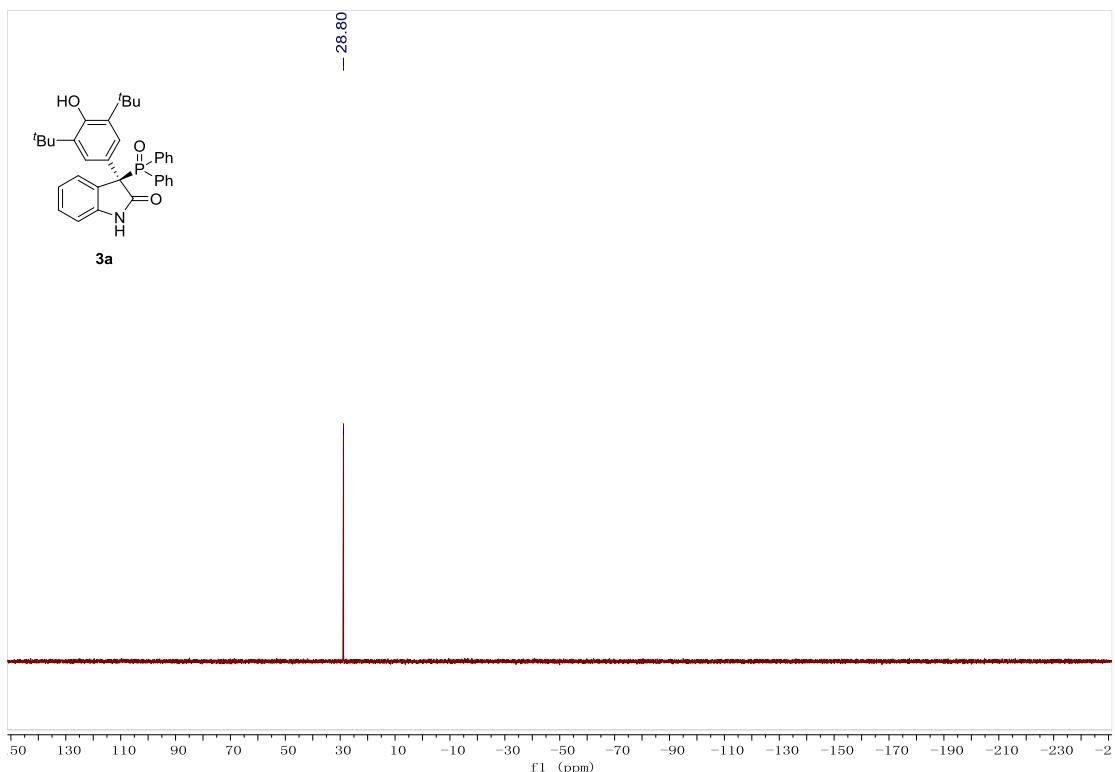
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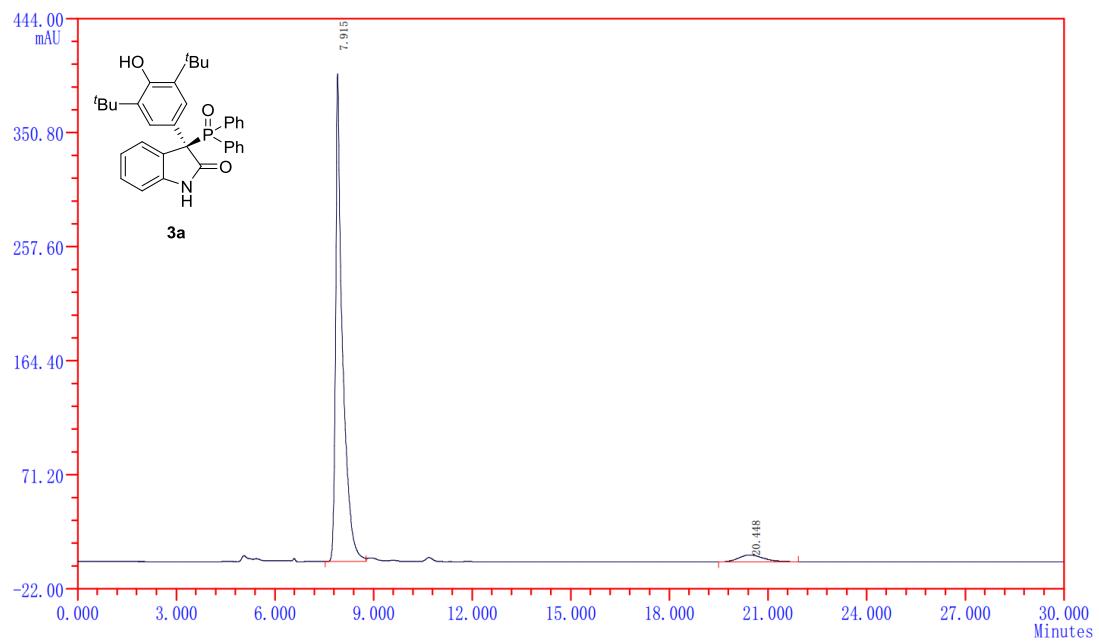
S = 1.050 Npar= 391

¹H NMR, ¹³C NMR, ³¹P NMR, ¹⁹F NMR and HPLC spectra for products

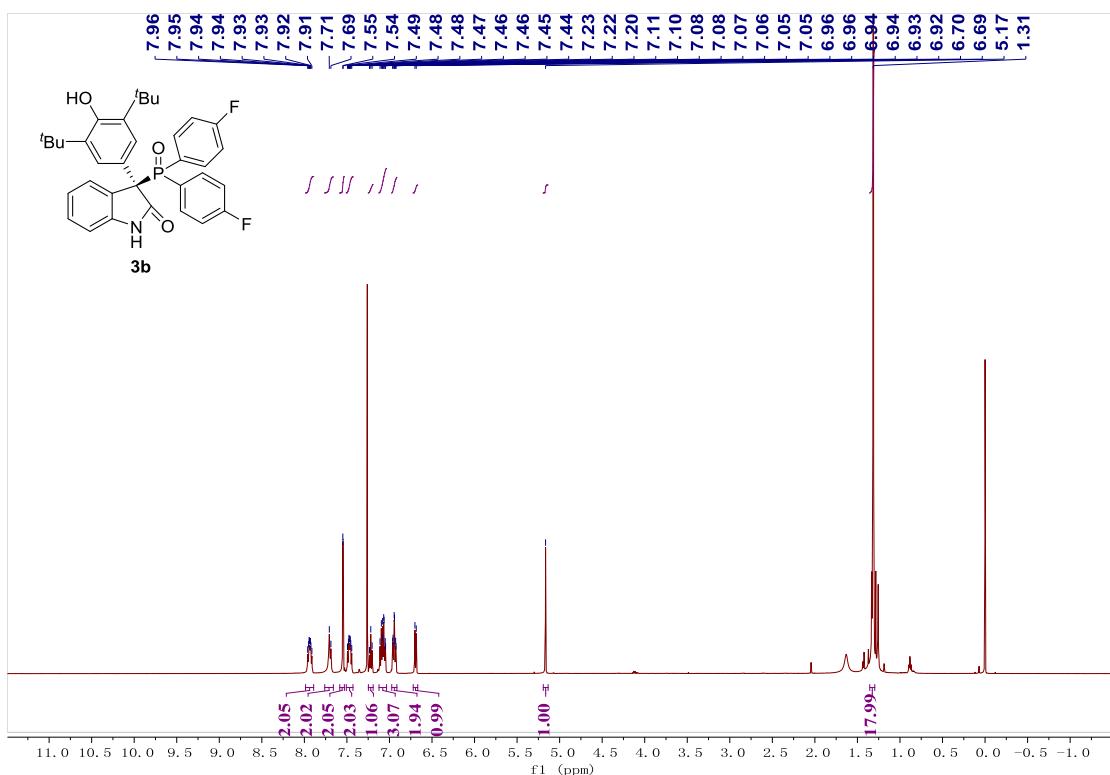


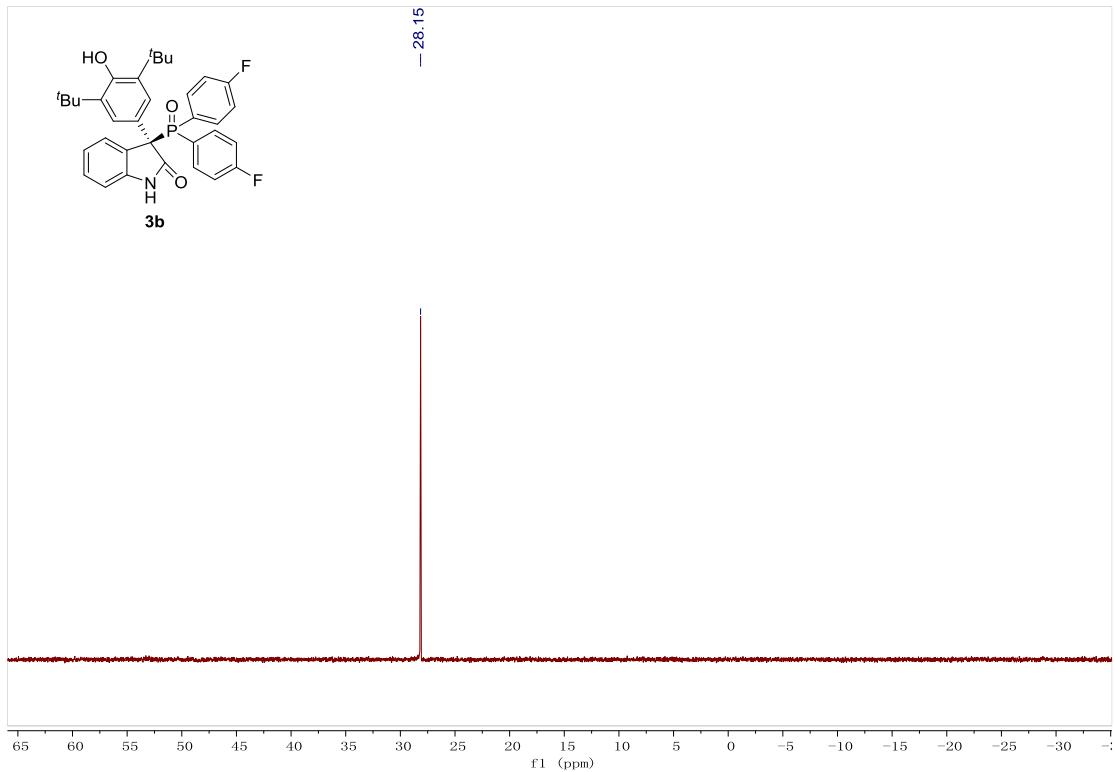
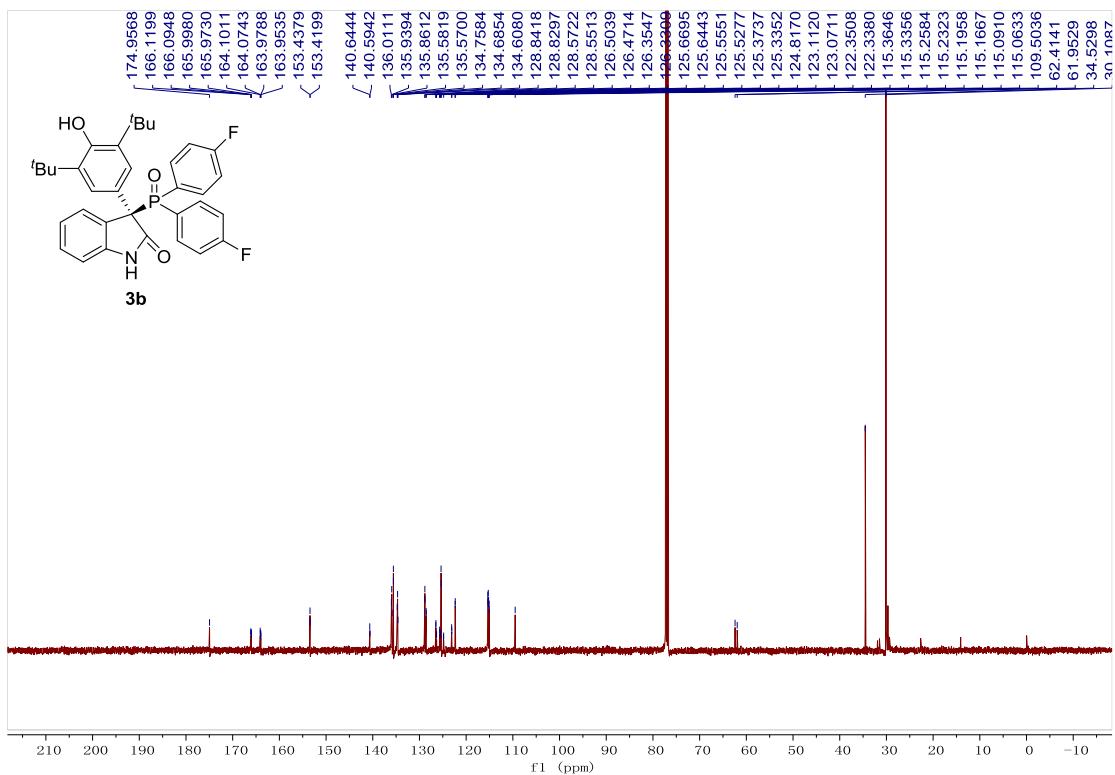


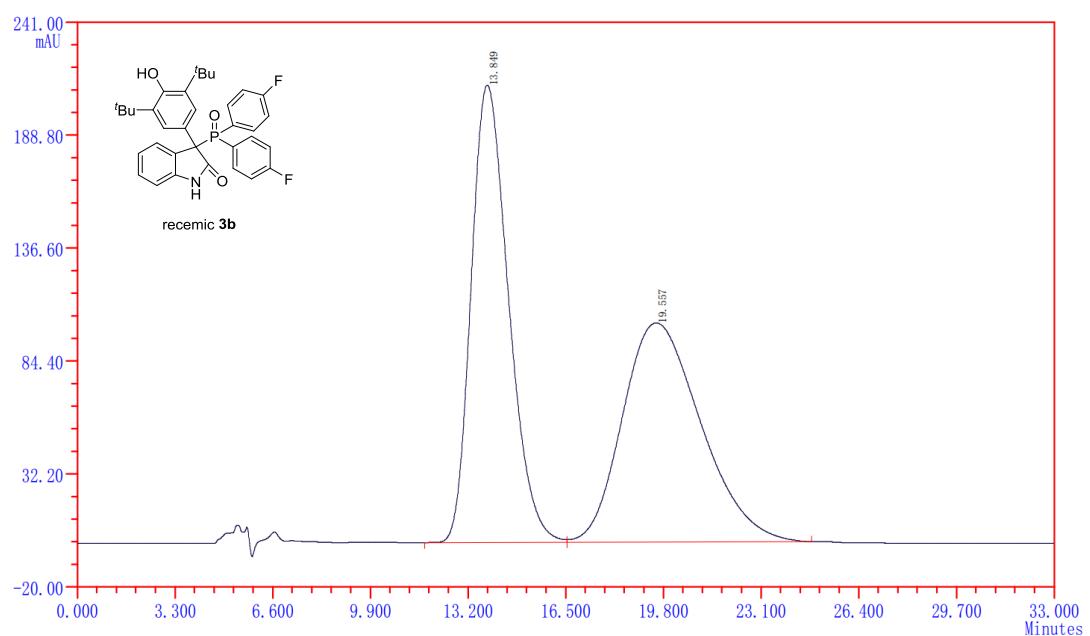
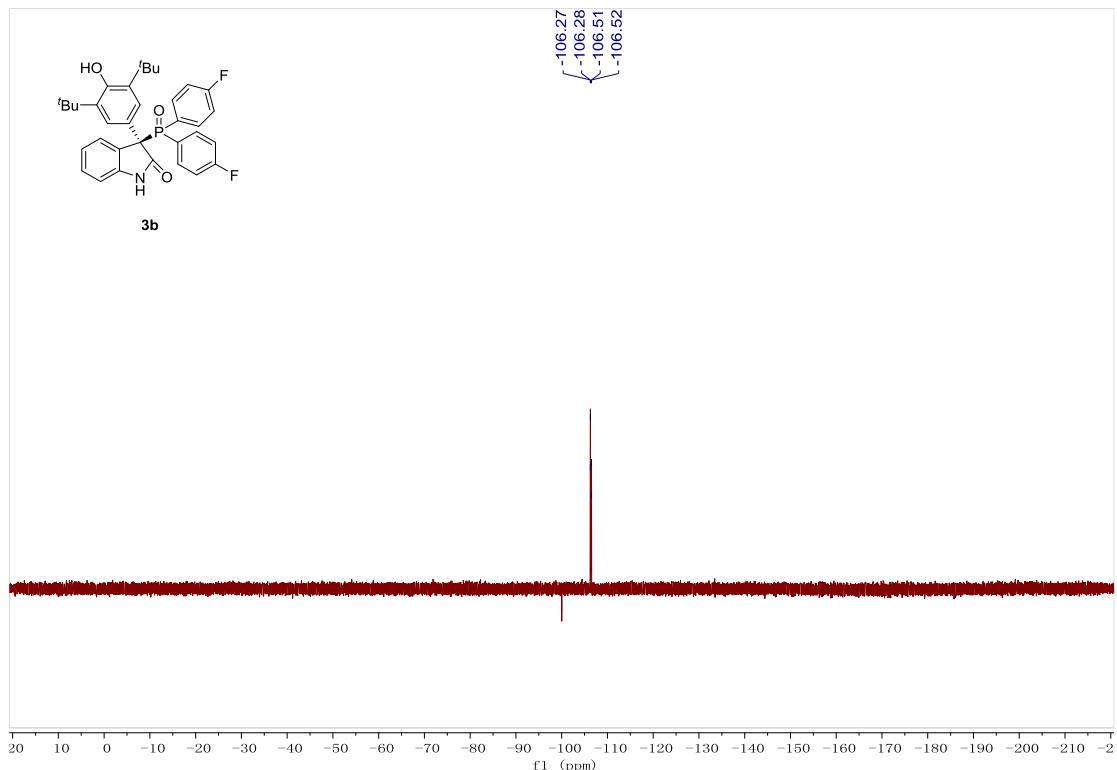
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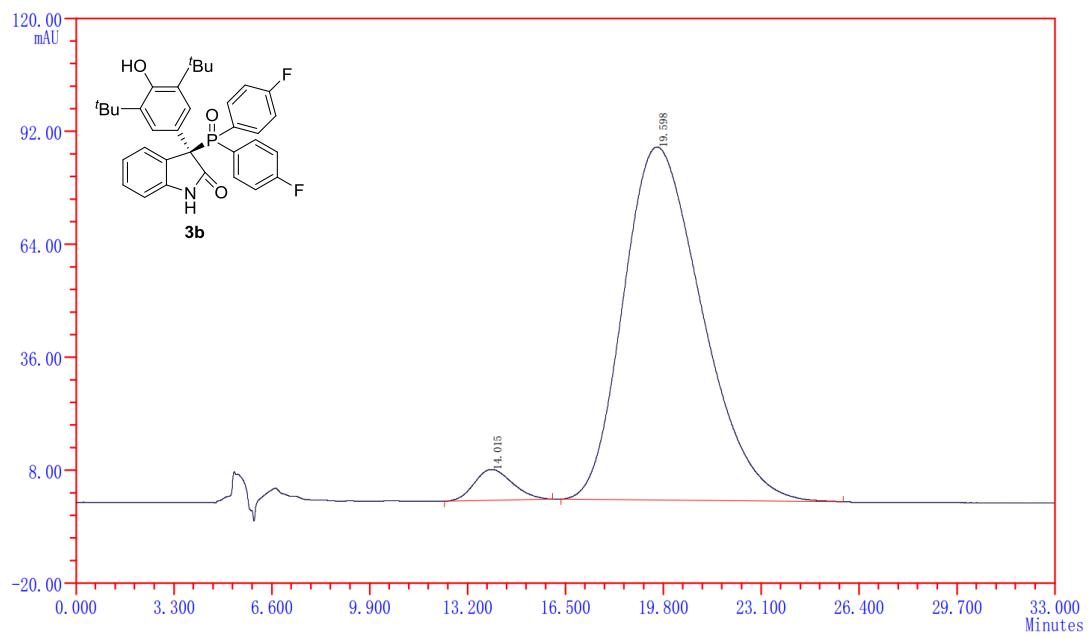


Peak #	RetTime [Min]	Height [mAu]	Area [mAu*s]	Area %
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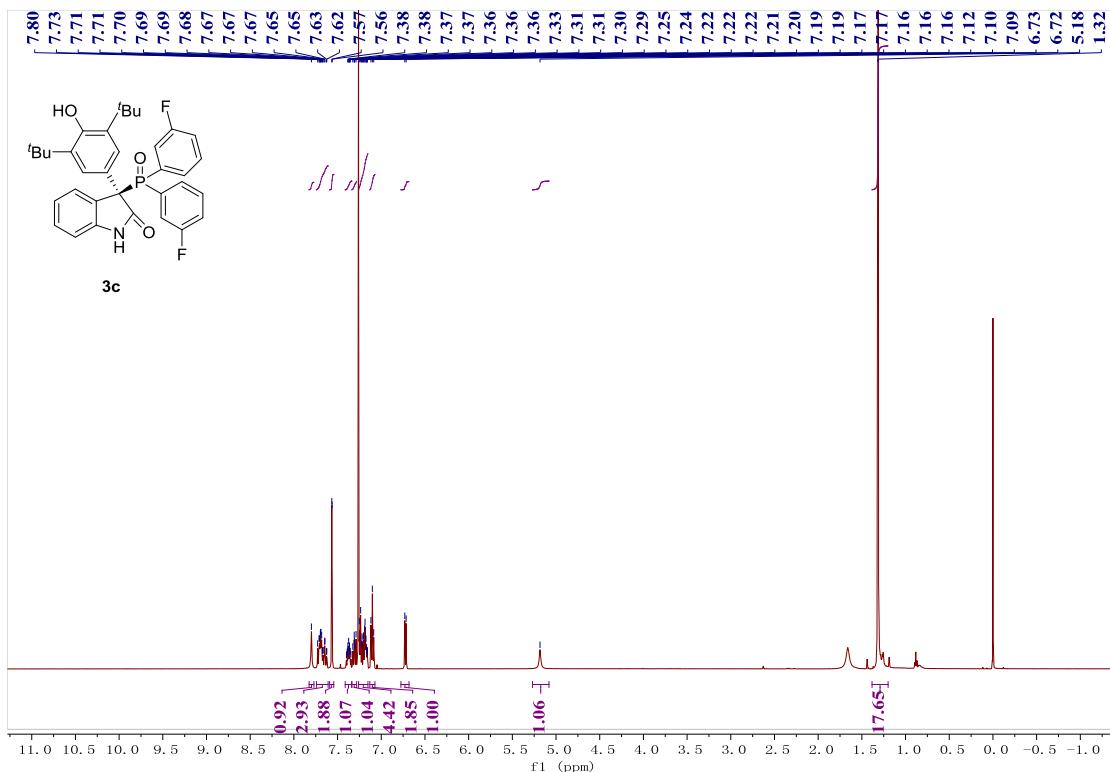


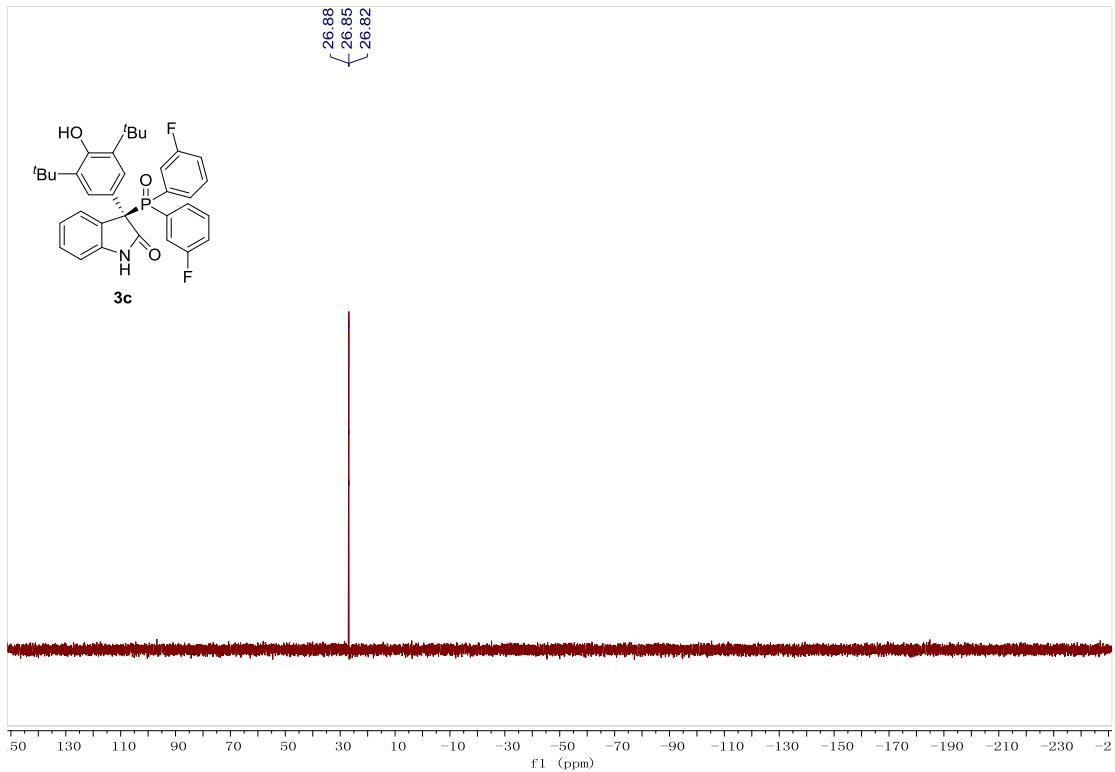
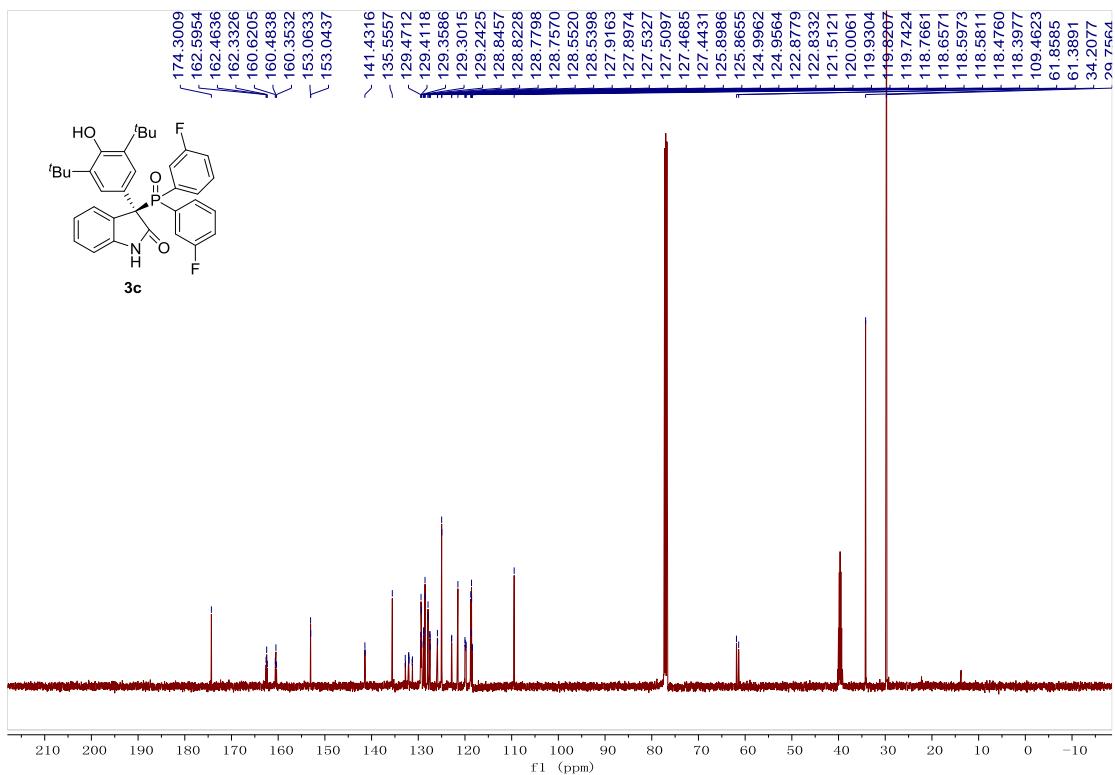


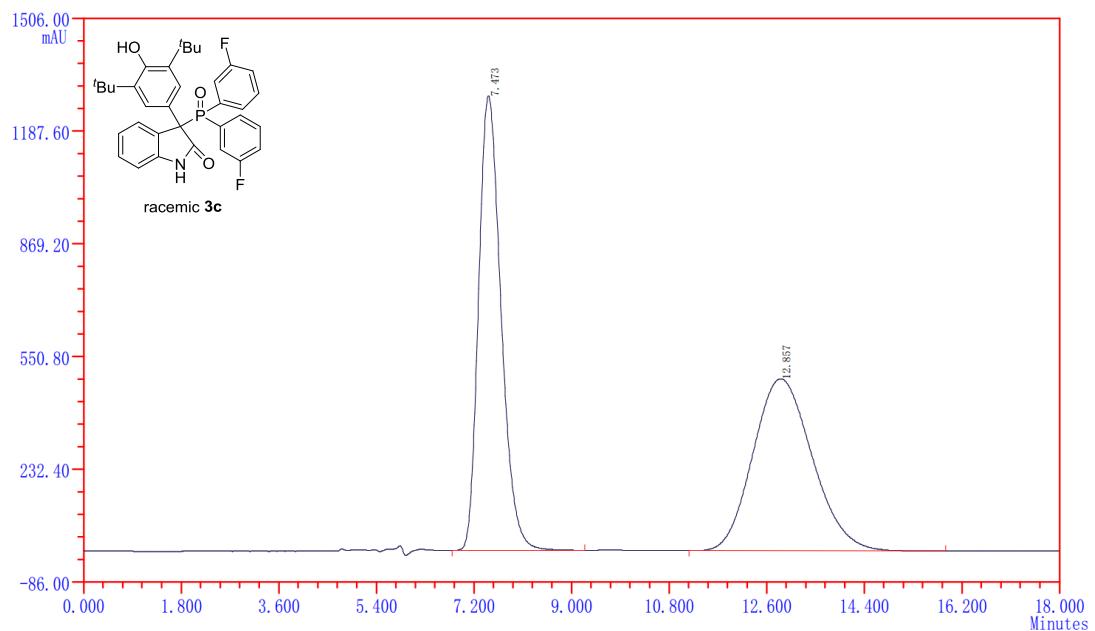
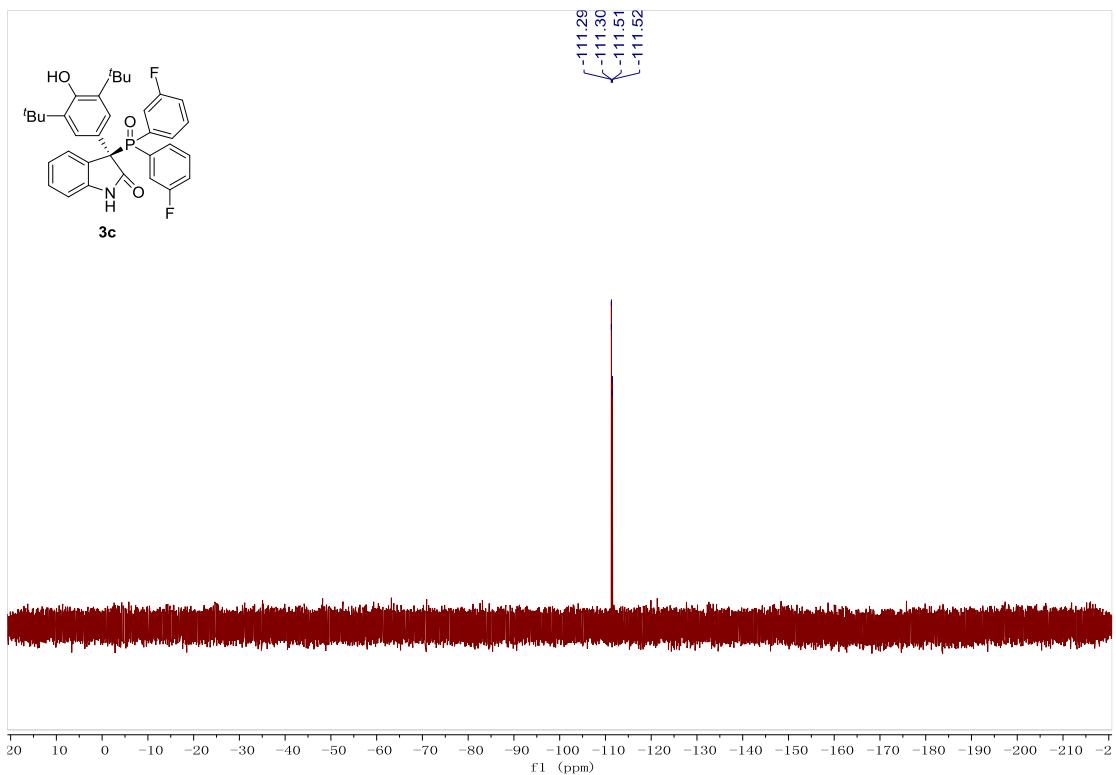




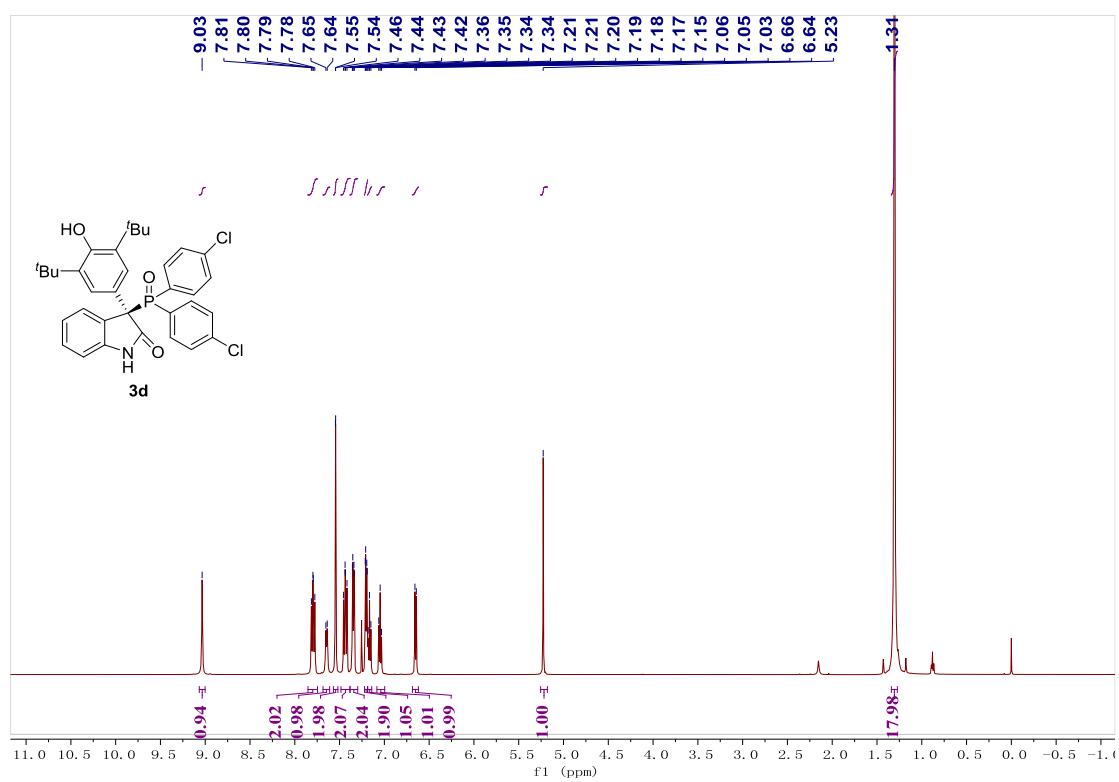
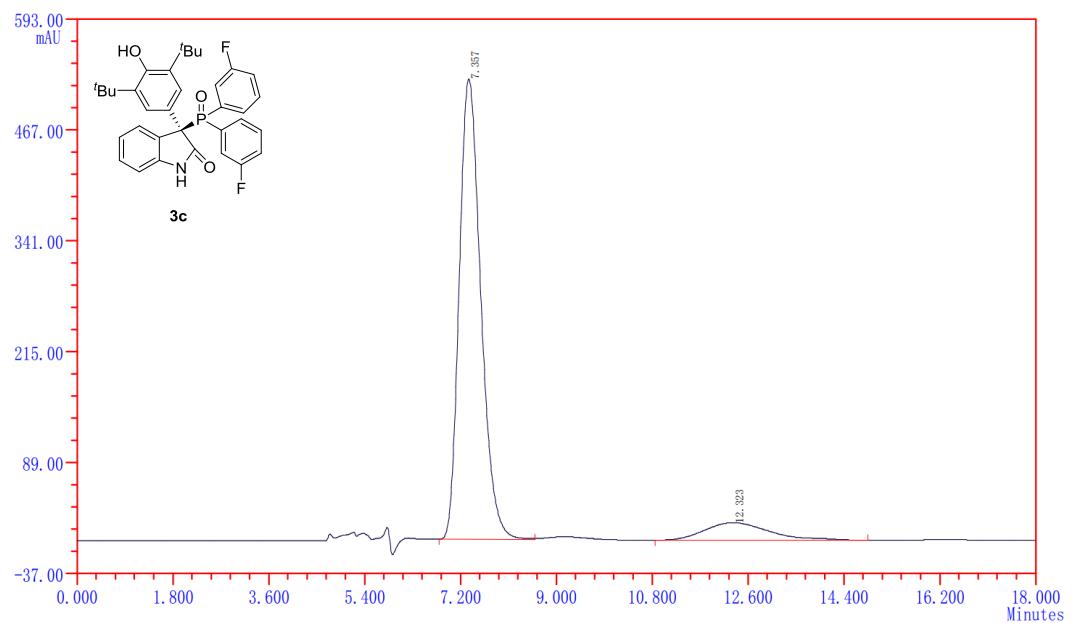
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2	19.598	87.49	16116.124	95.917
Total:		95.18	16802.133	100.0000

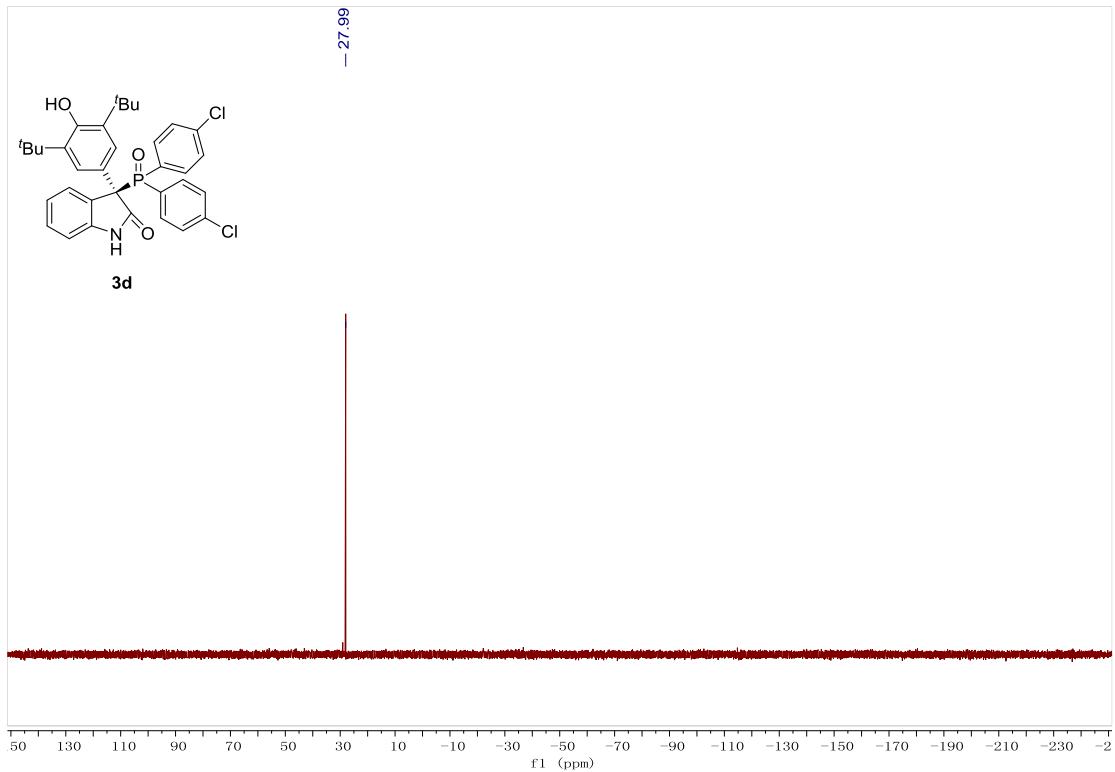
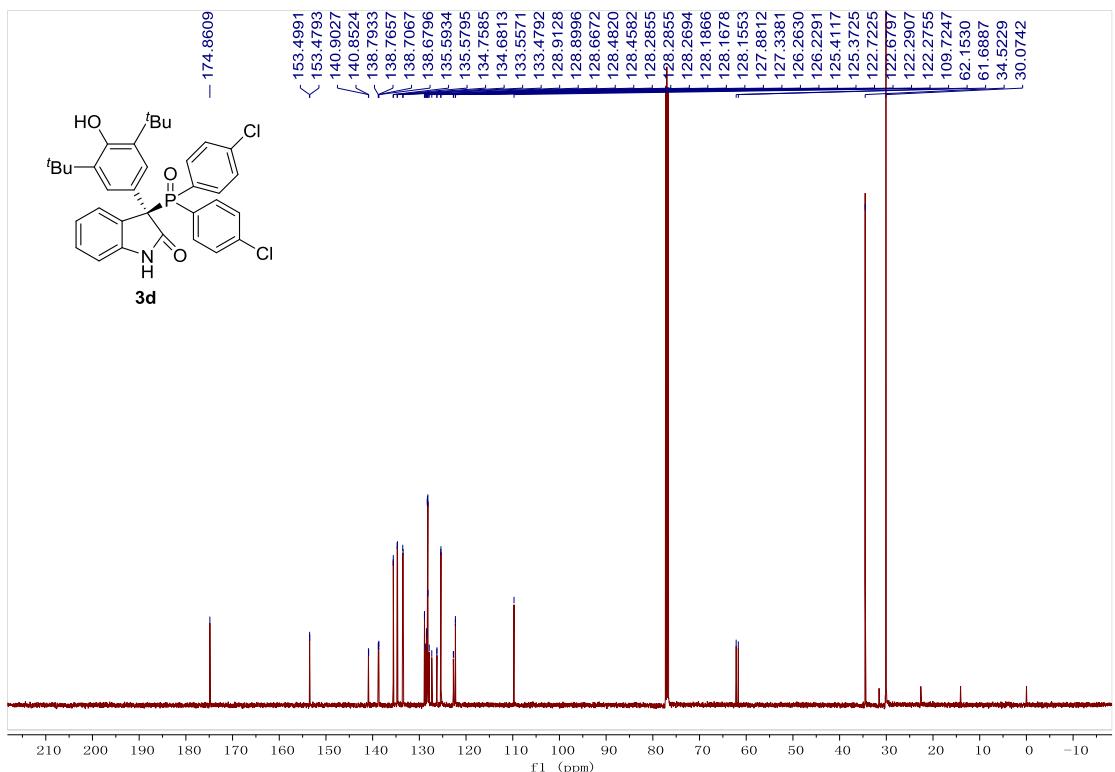


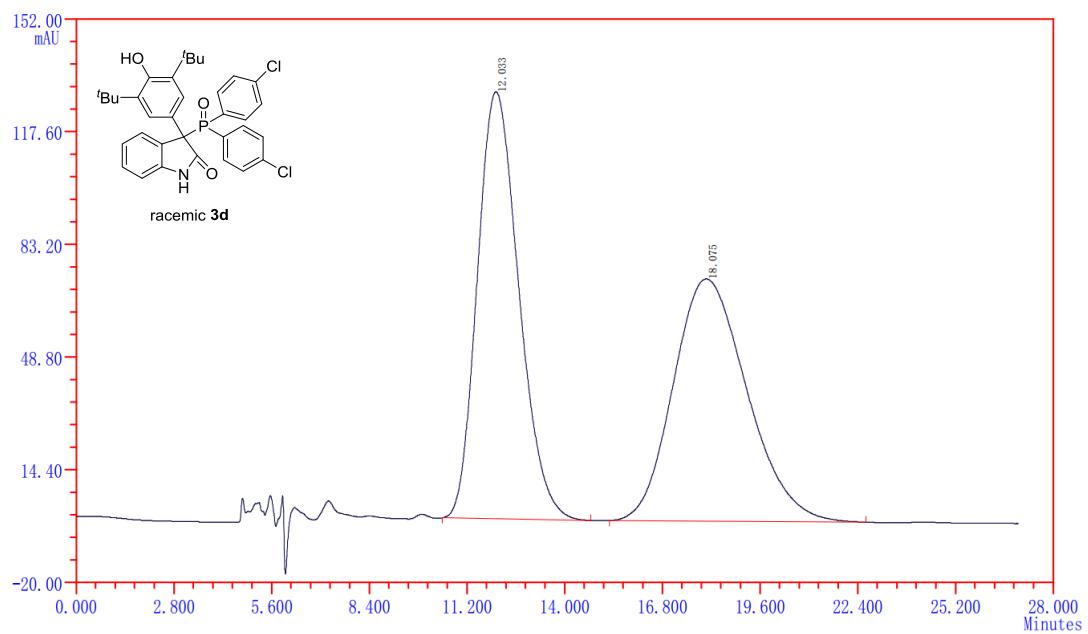




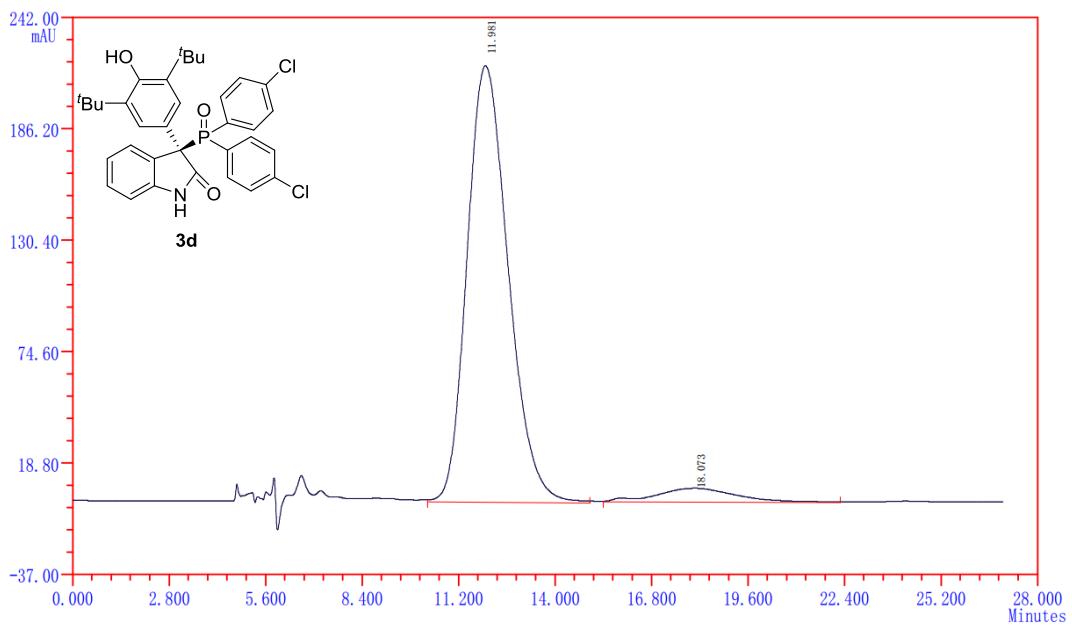
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2	12.857	485.83	36974.606	50.000
Total:		1769.99	73948.717	100.0000



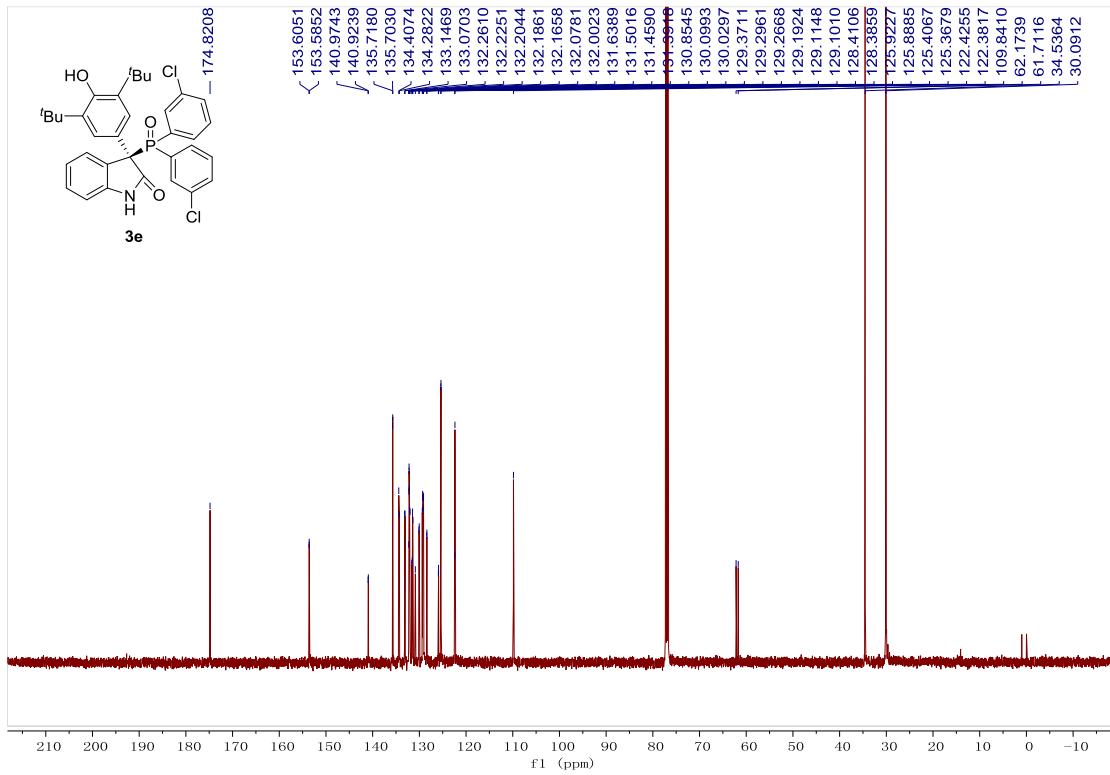
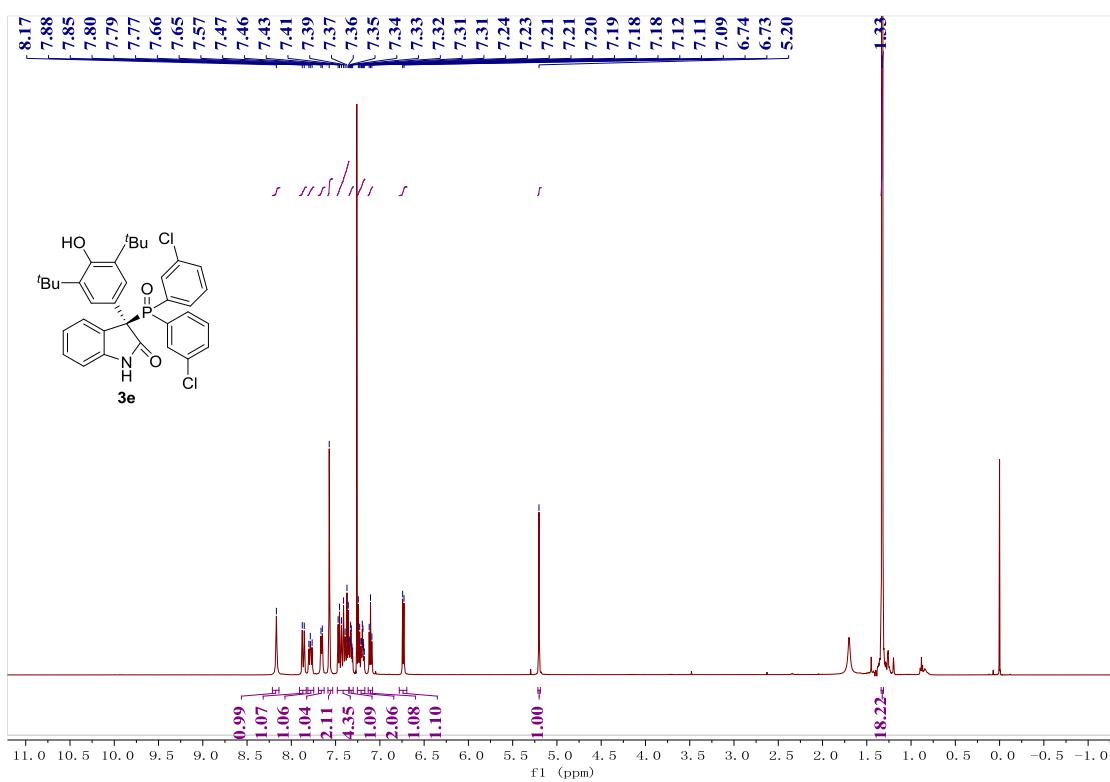


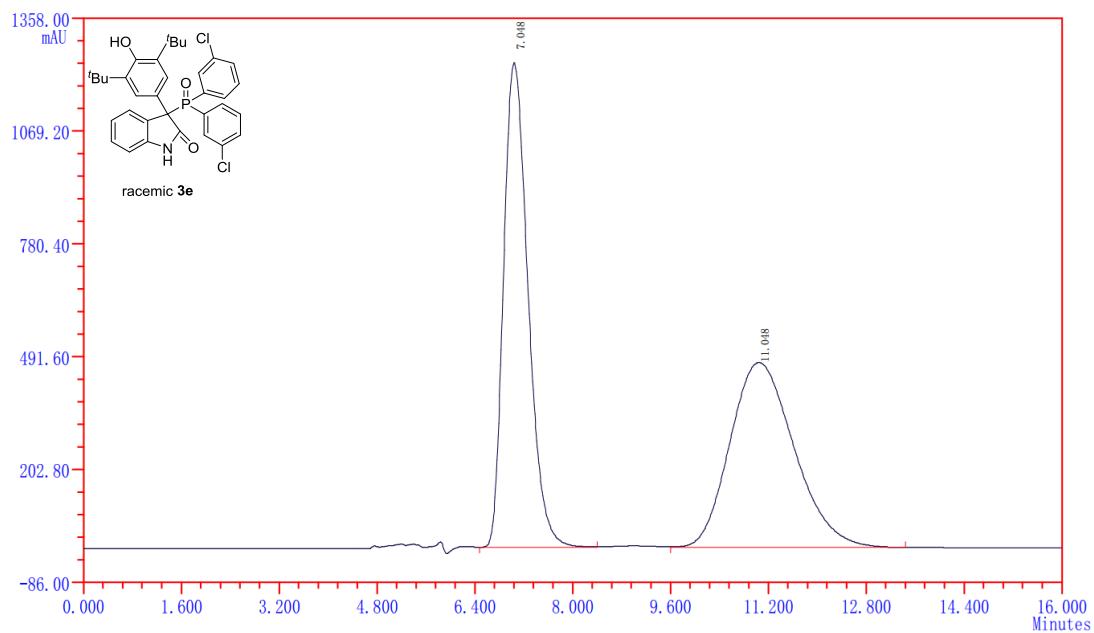
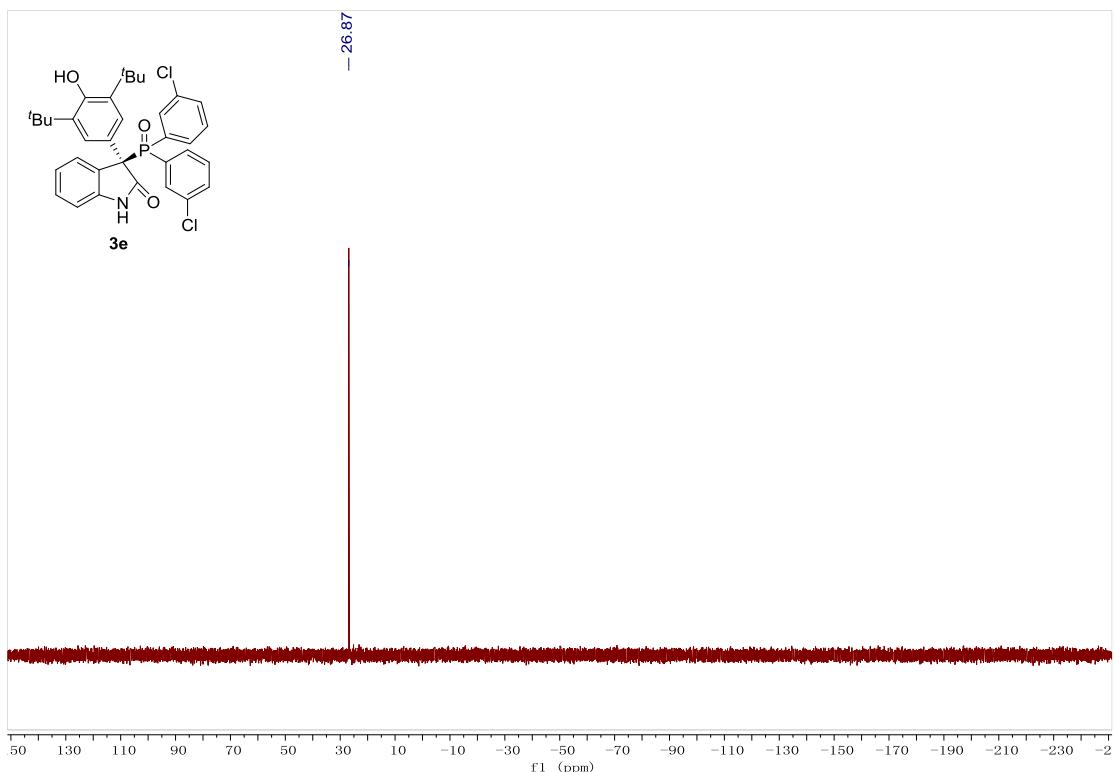


Peak #	RetTime [Min]	Height [mAu]	Area [mAu*s]	Area %
1	12.033	130.29	10764.277	49.827
2	18.075	73.93	10838.968	50.173
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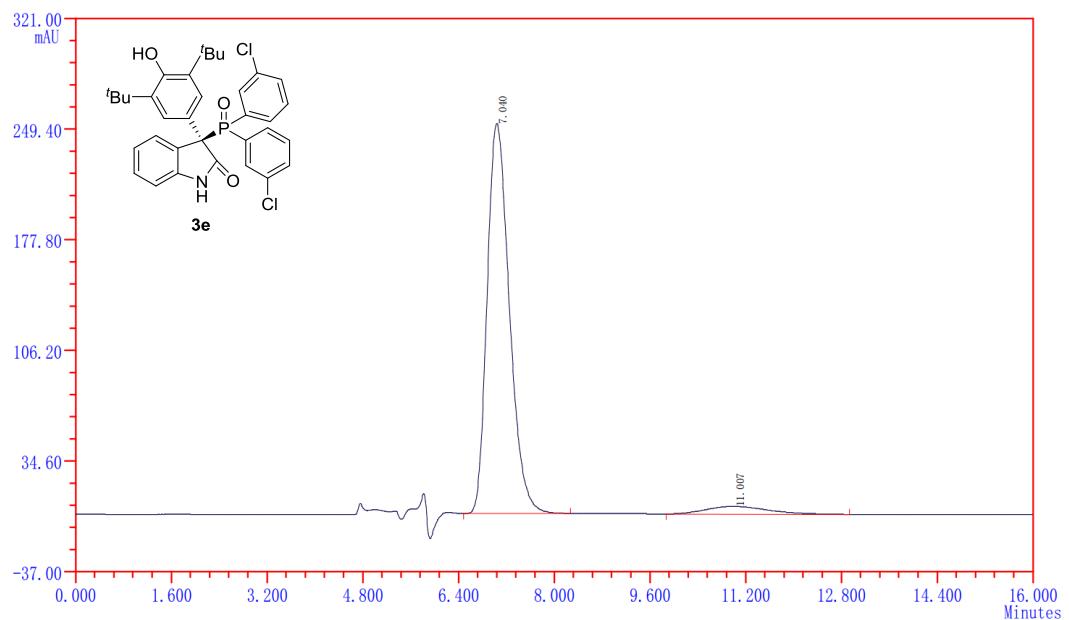


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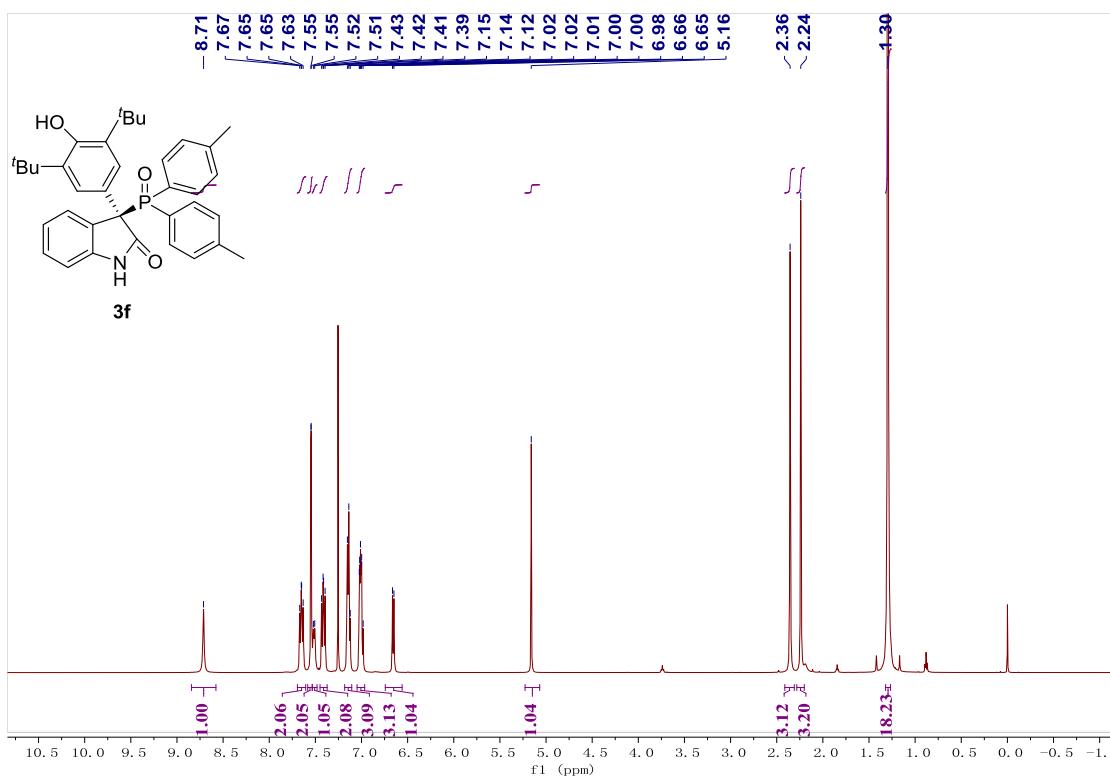


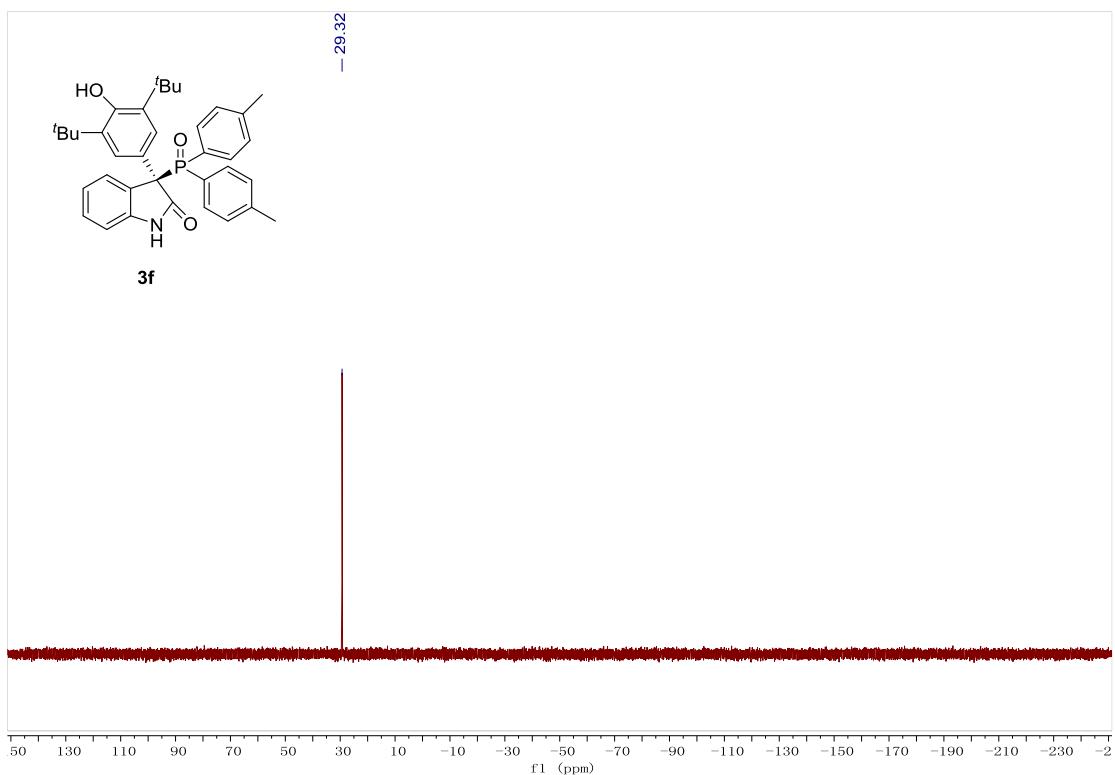
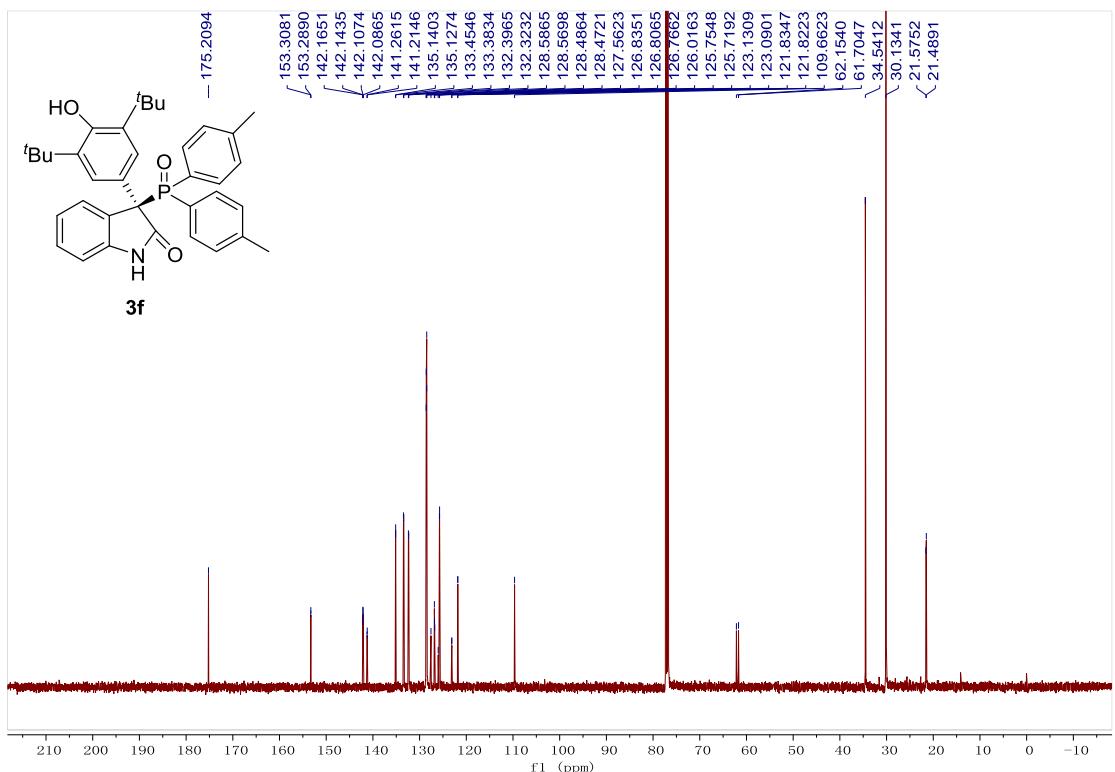


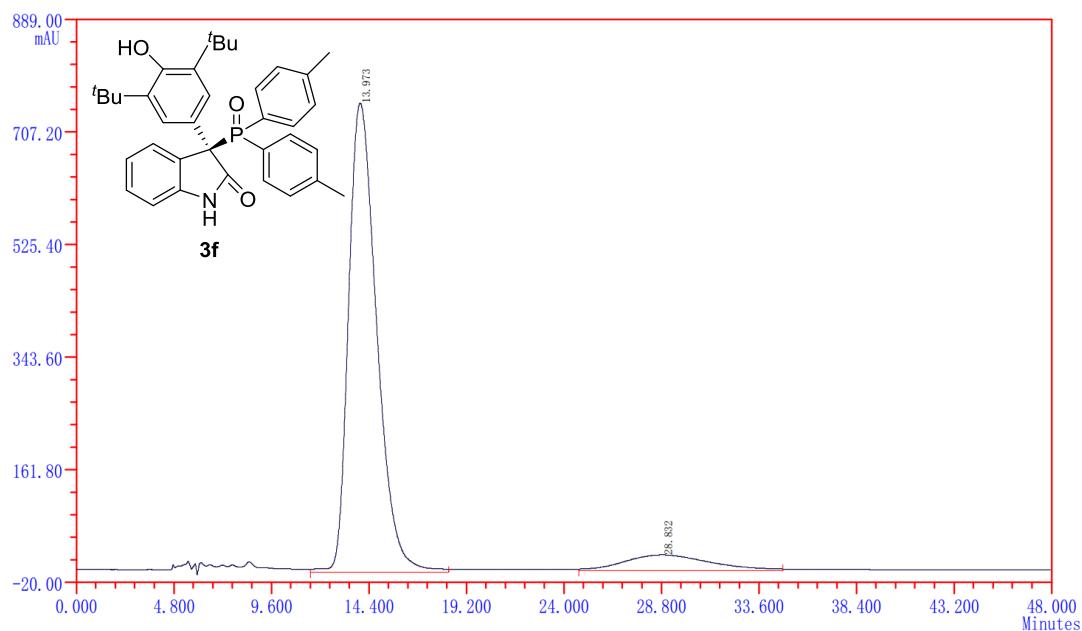
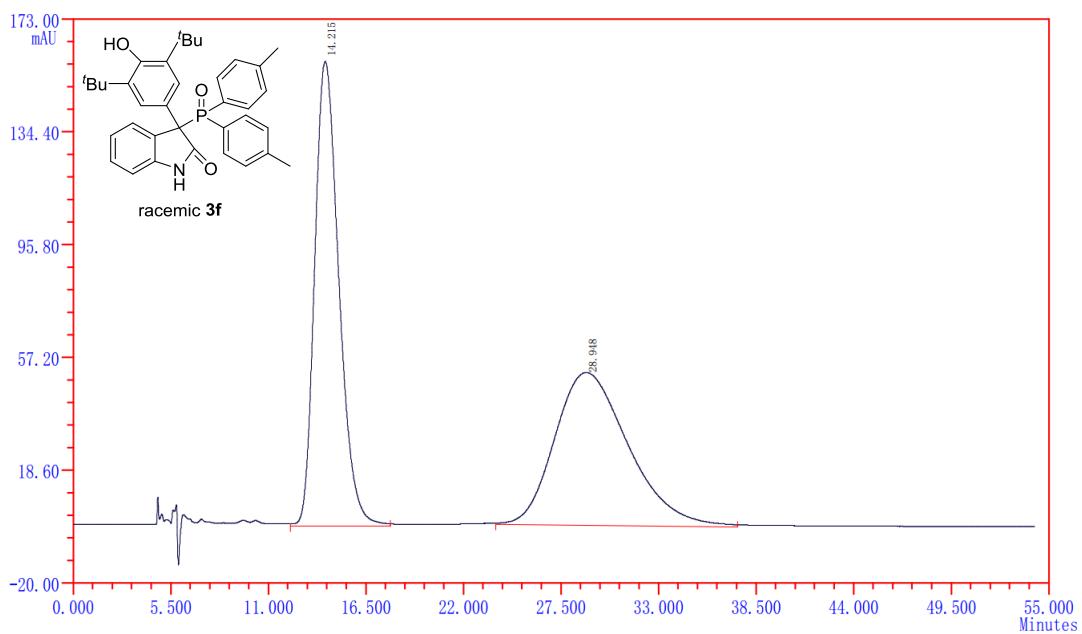
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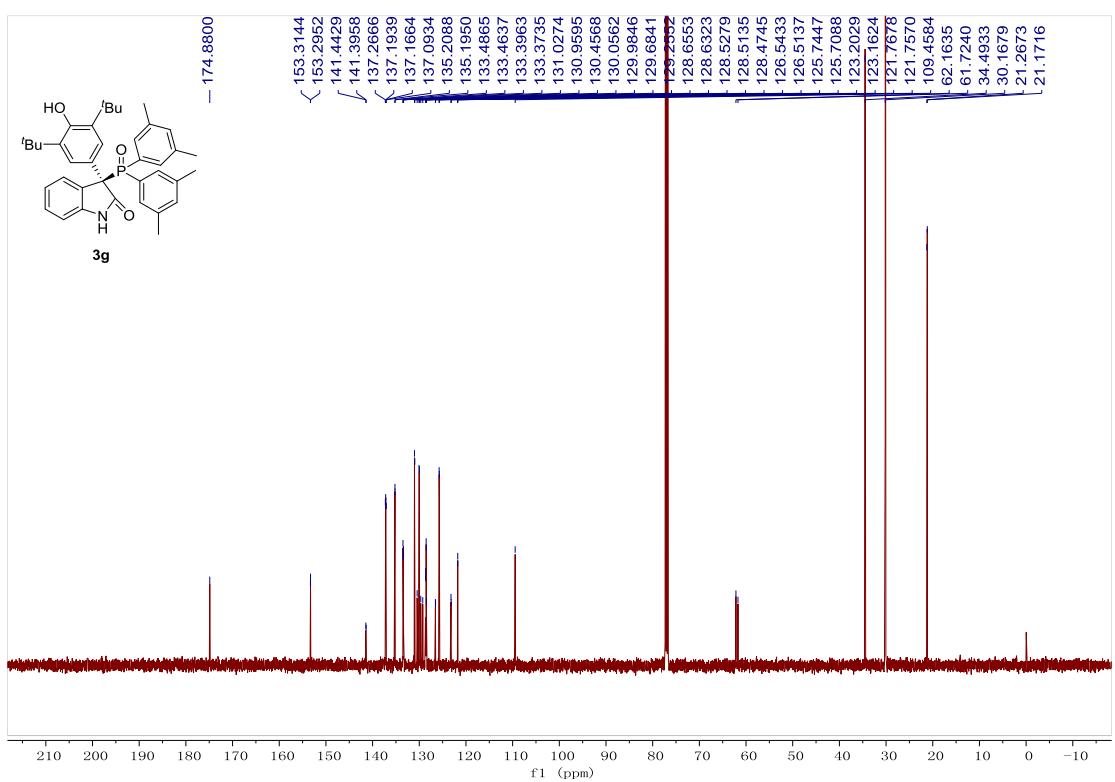
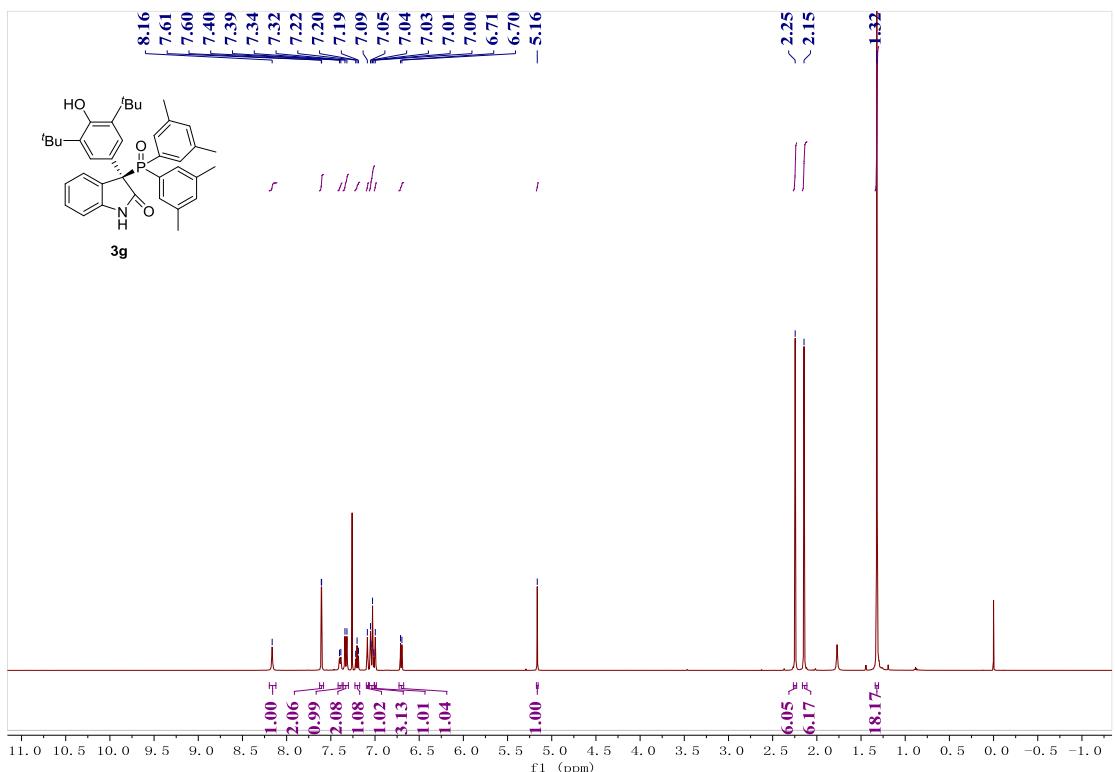


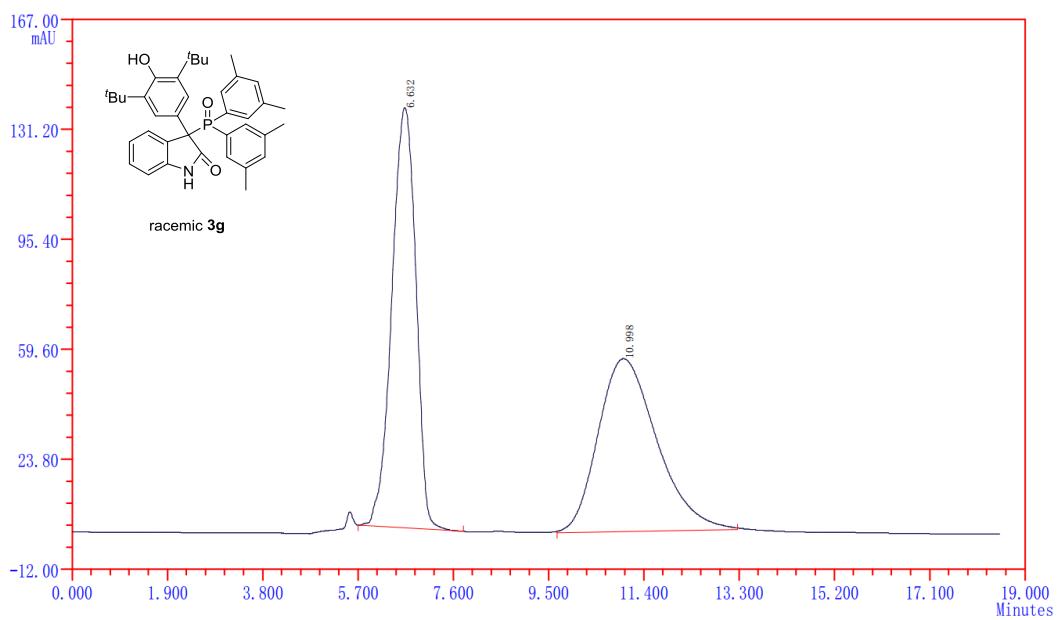
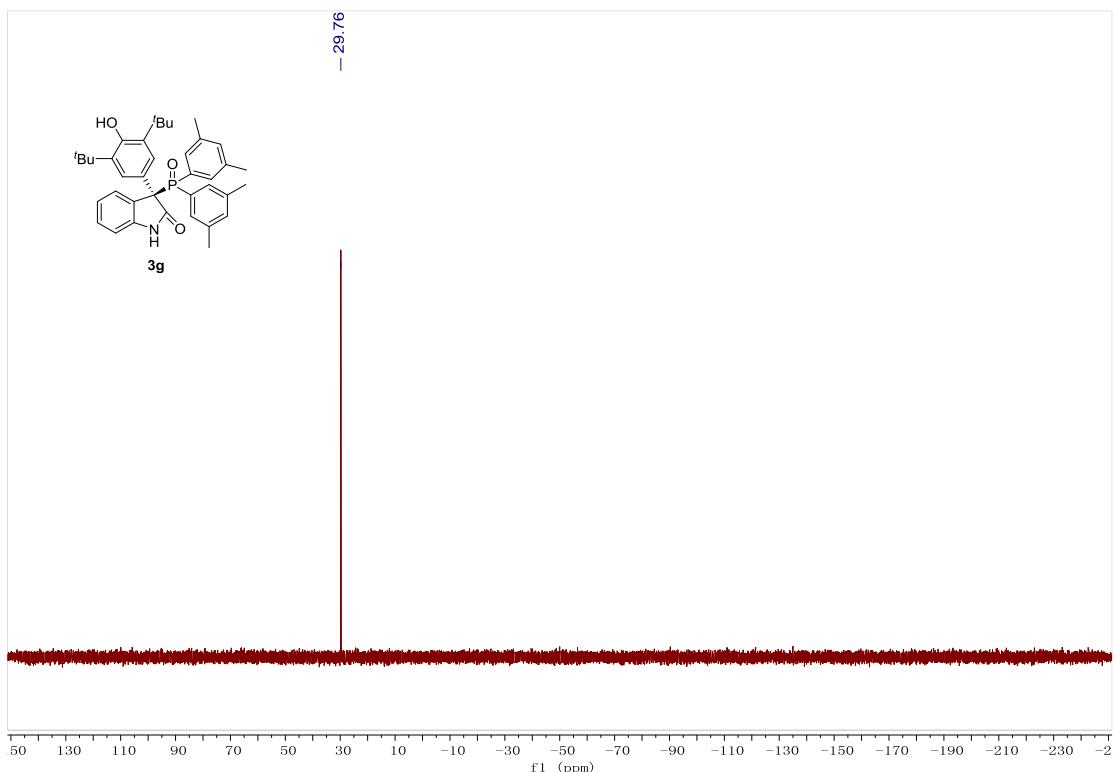
Peak #	RetTime [Min]	Height [mAU]	Area [mAU*s]	Area %
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Total:		257.54	6893.433	100.0000



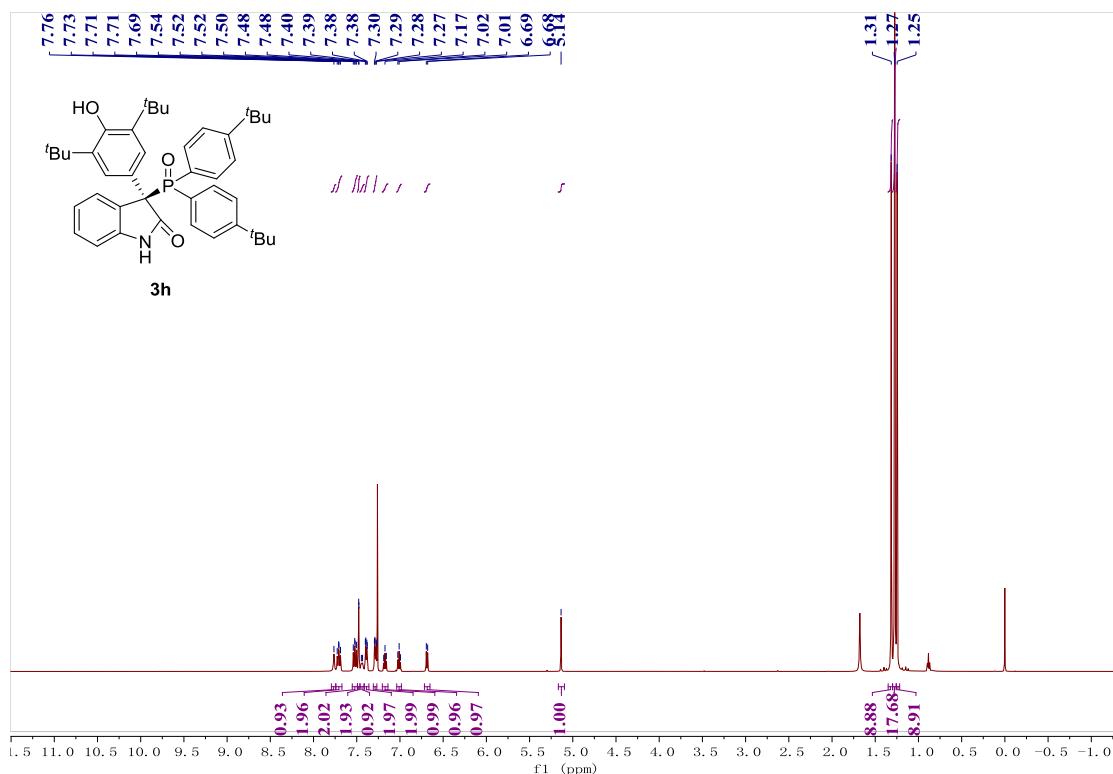
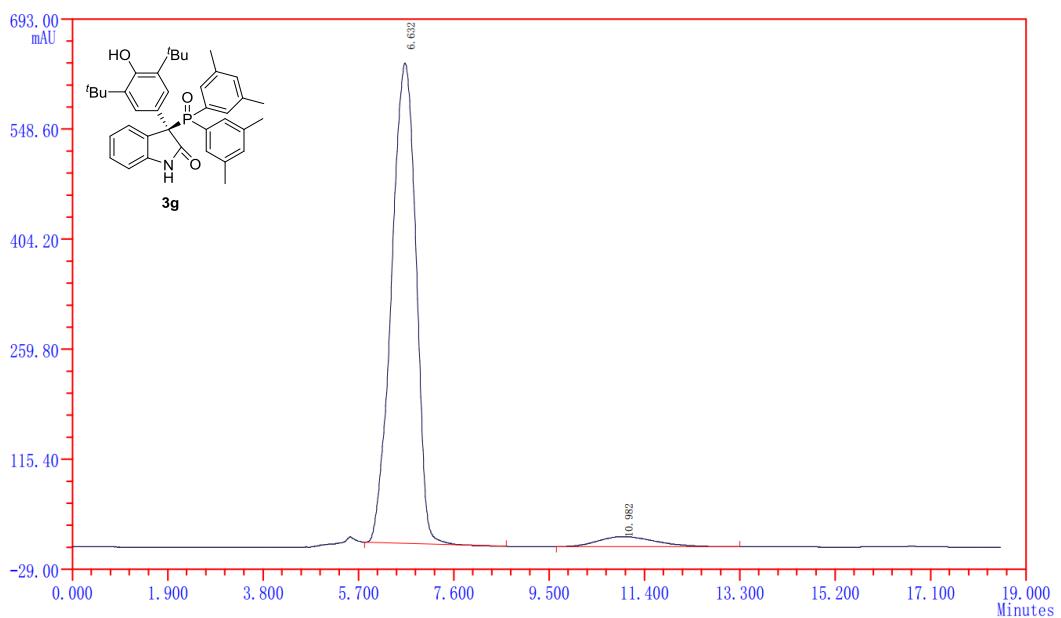


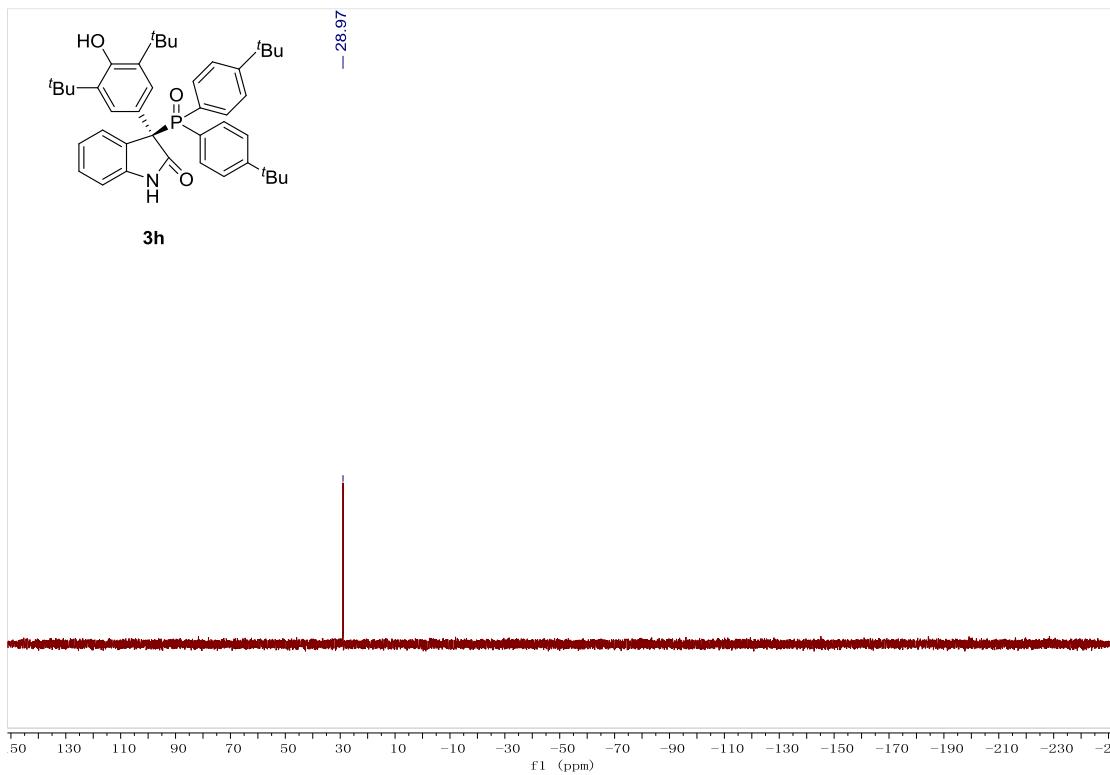
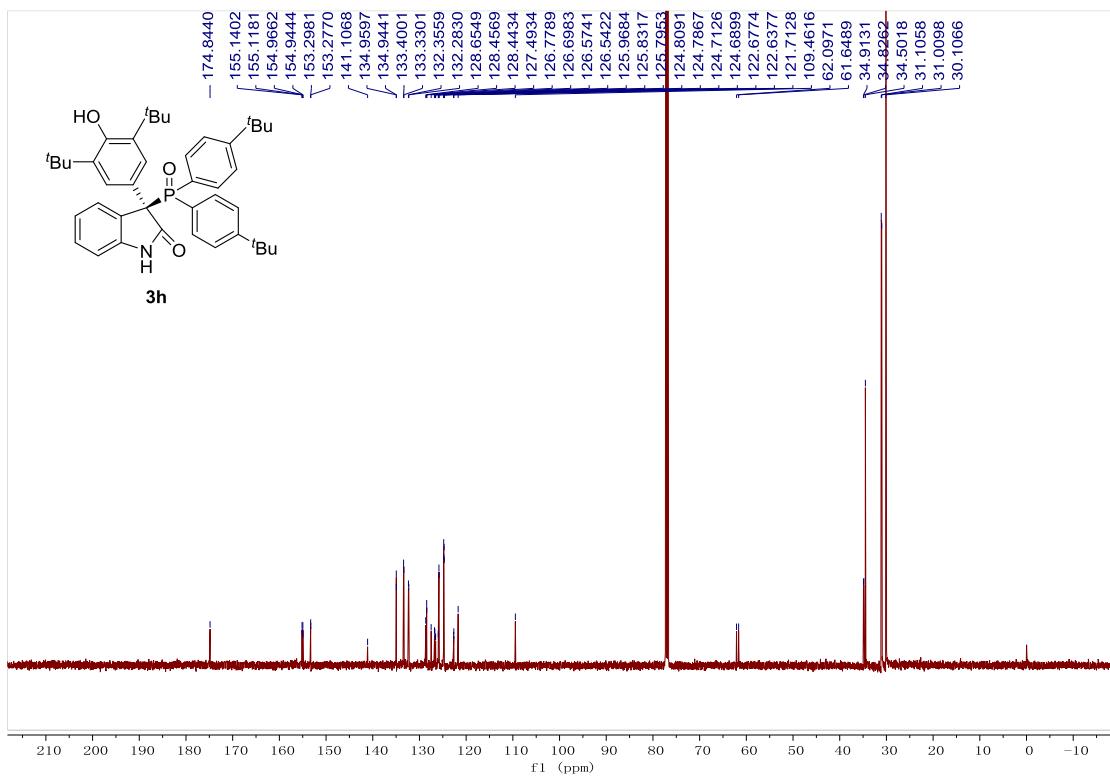


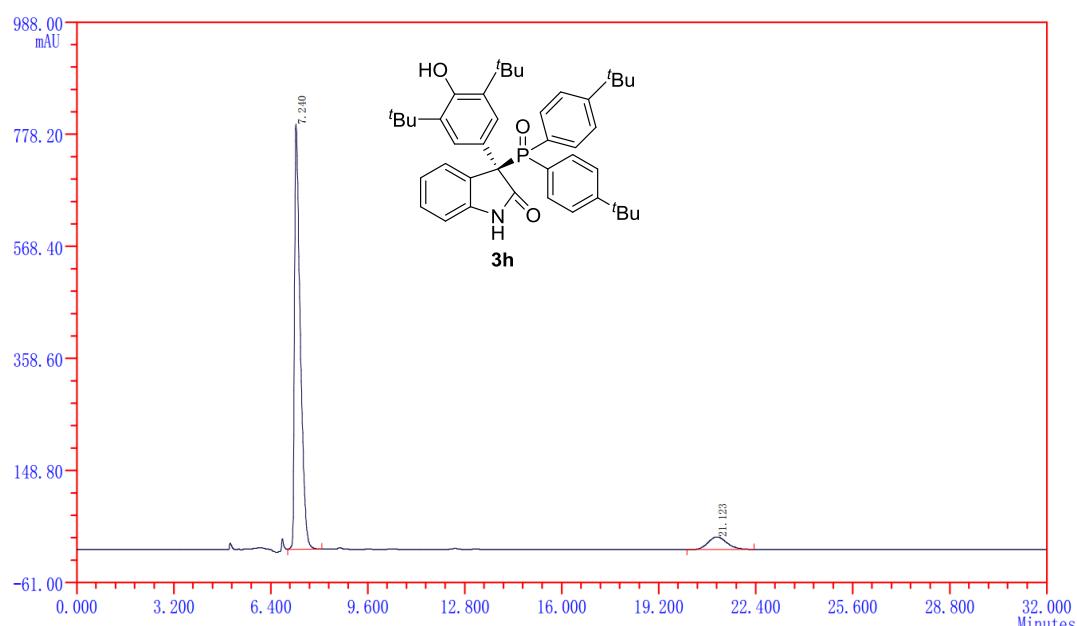
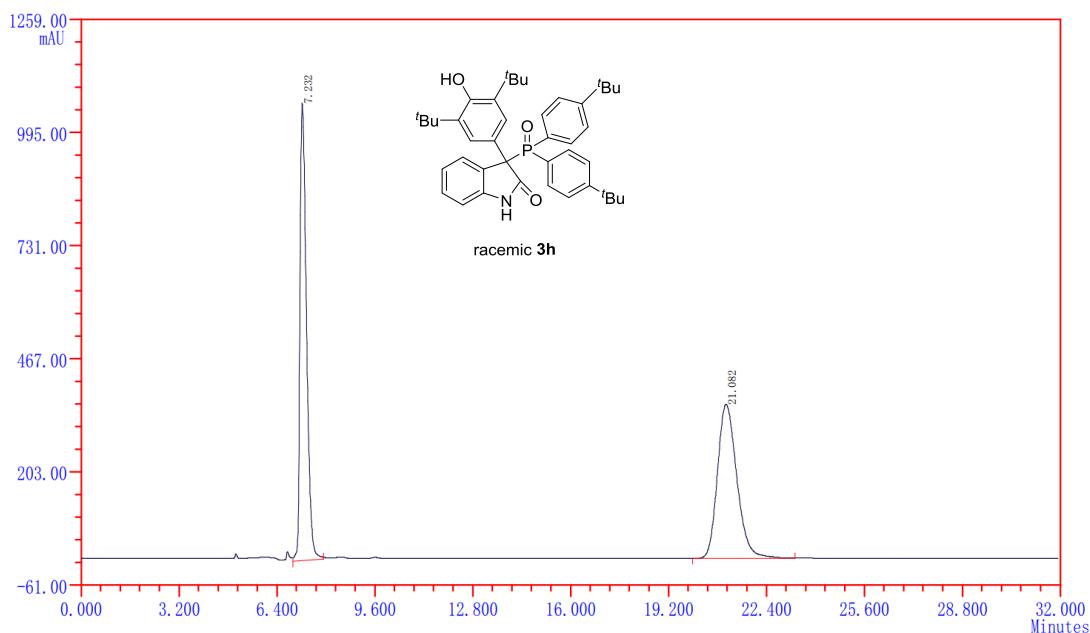


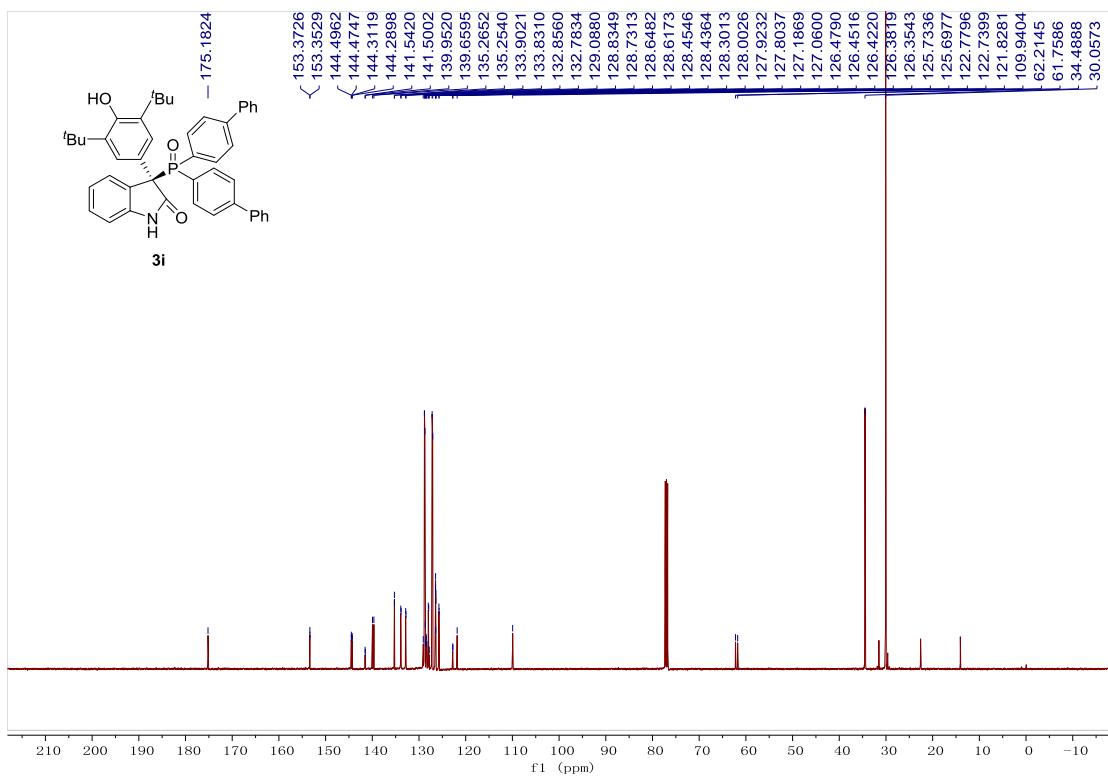
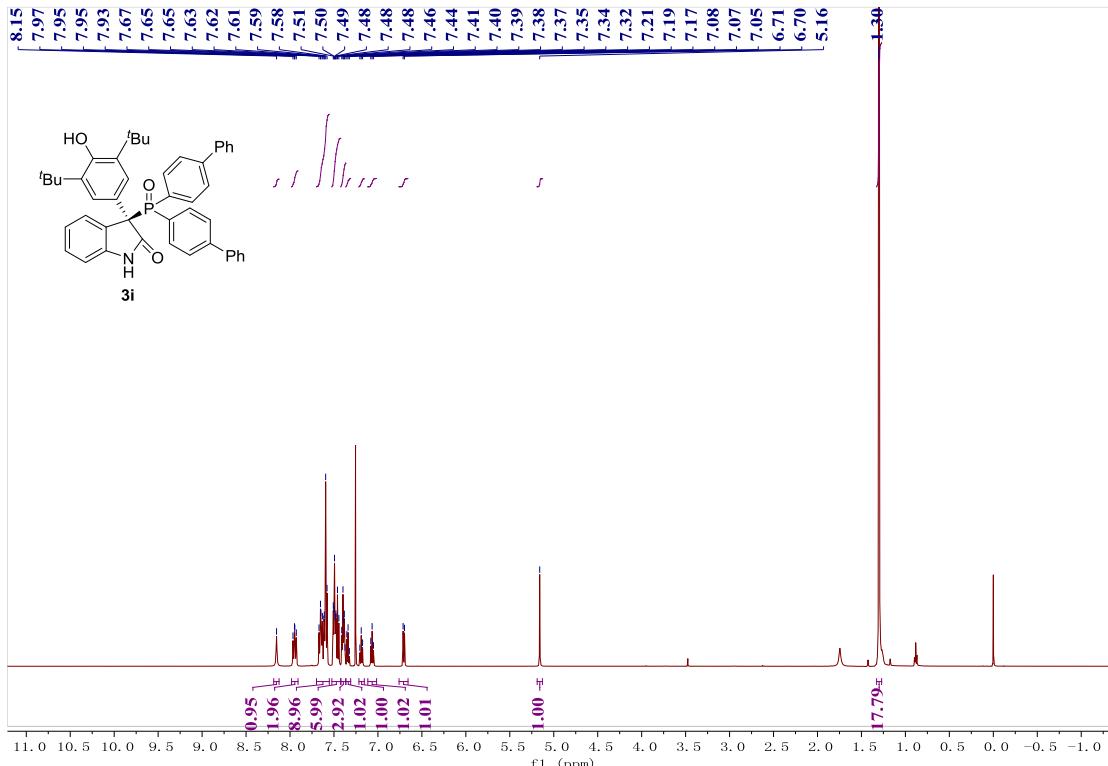


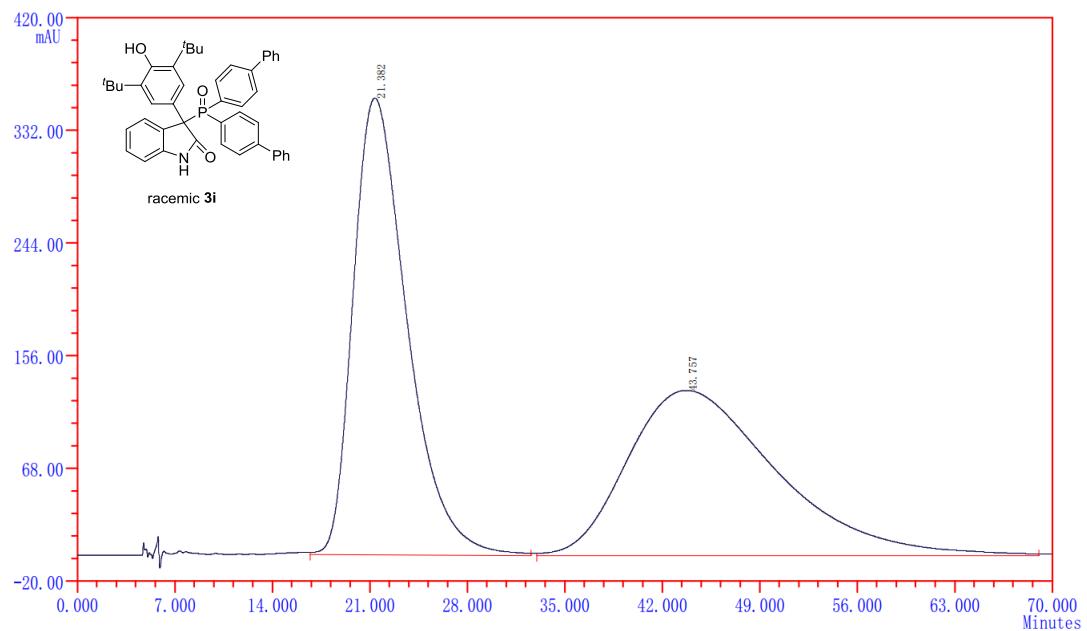
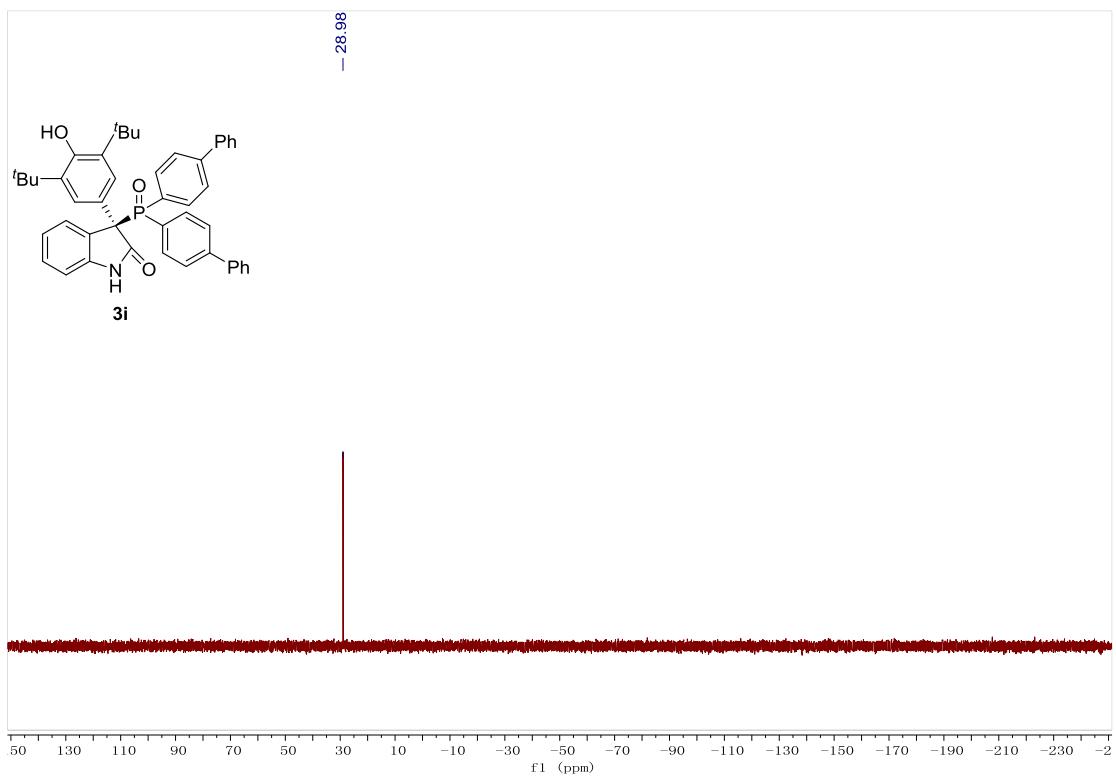
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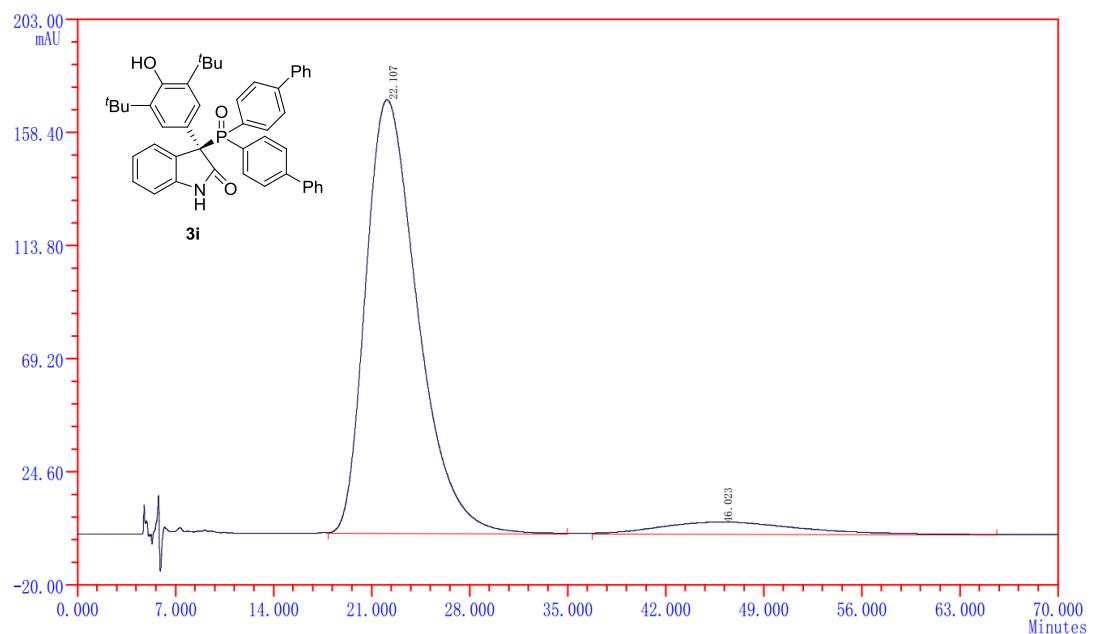




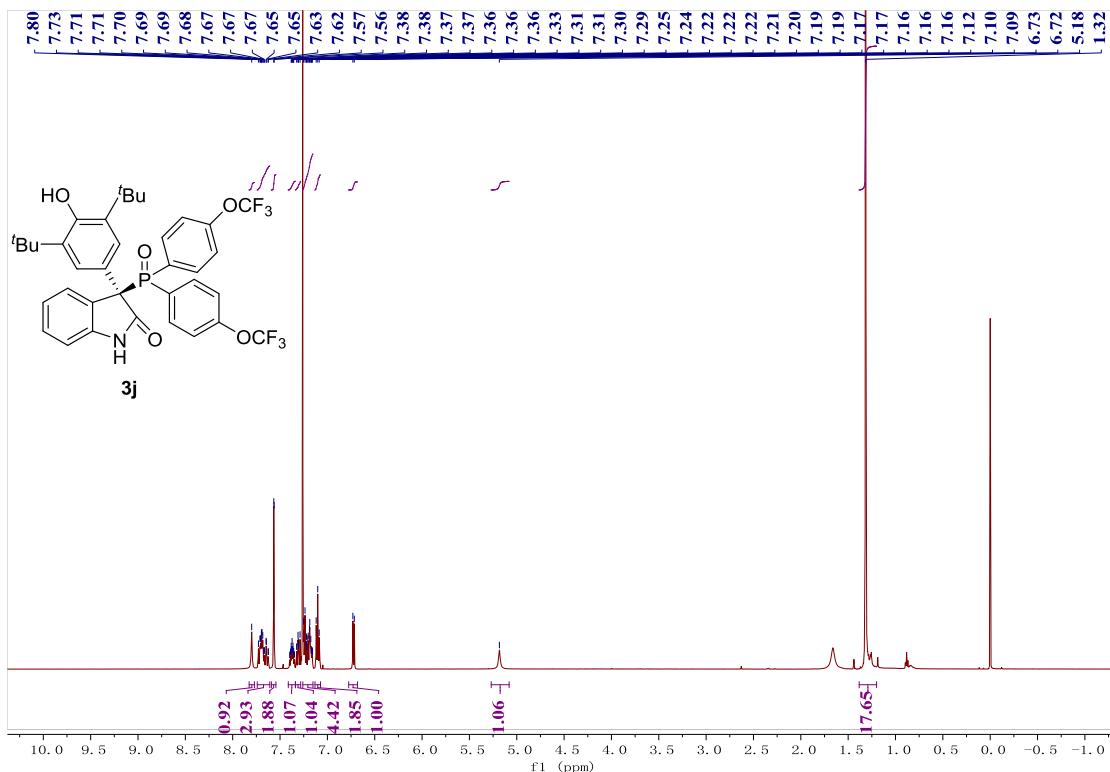


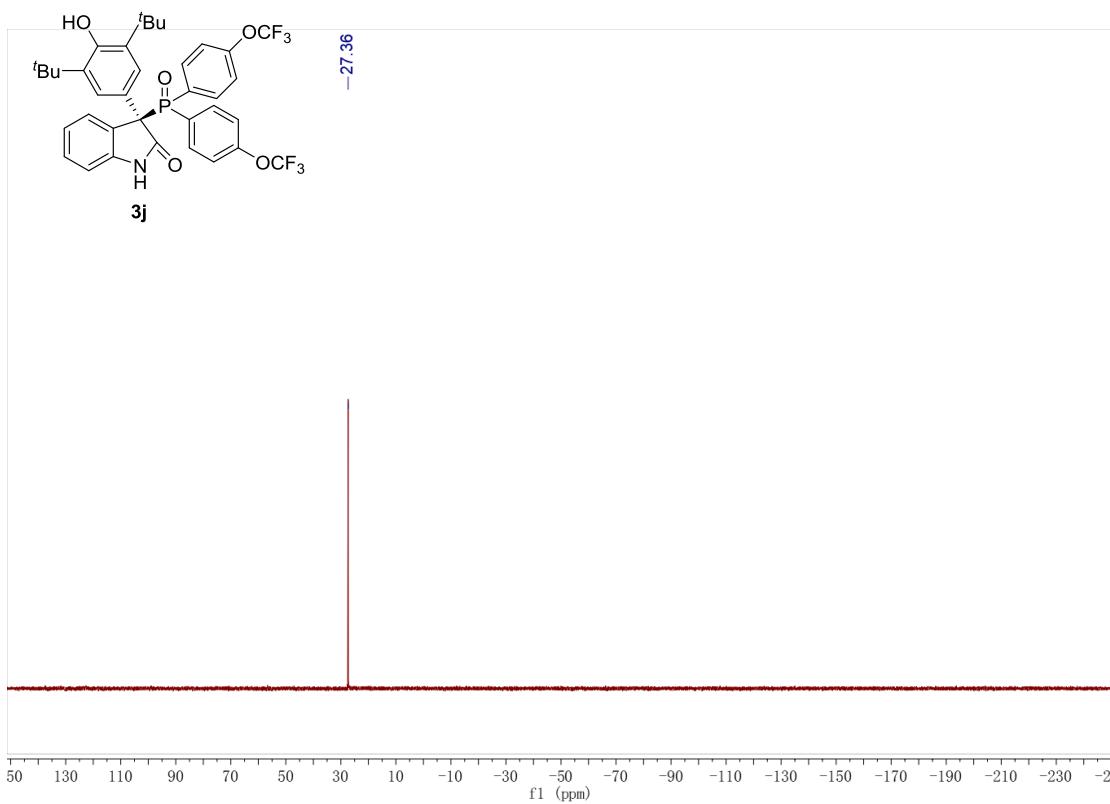
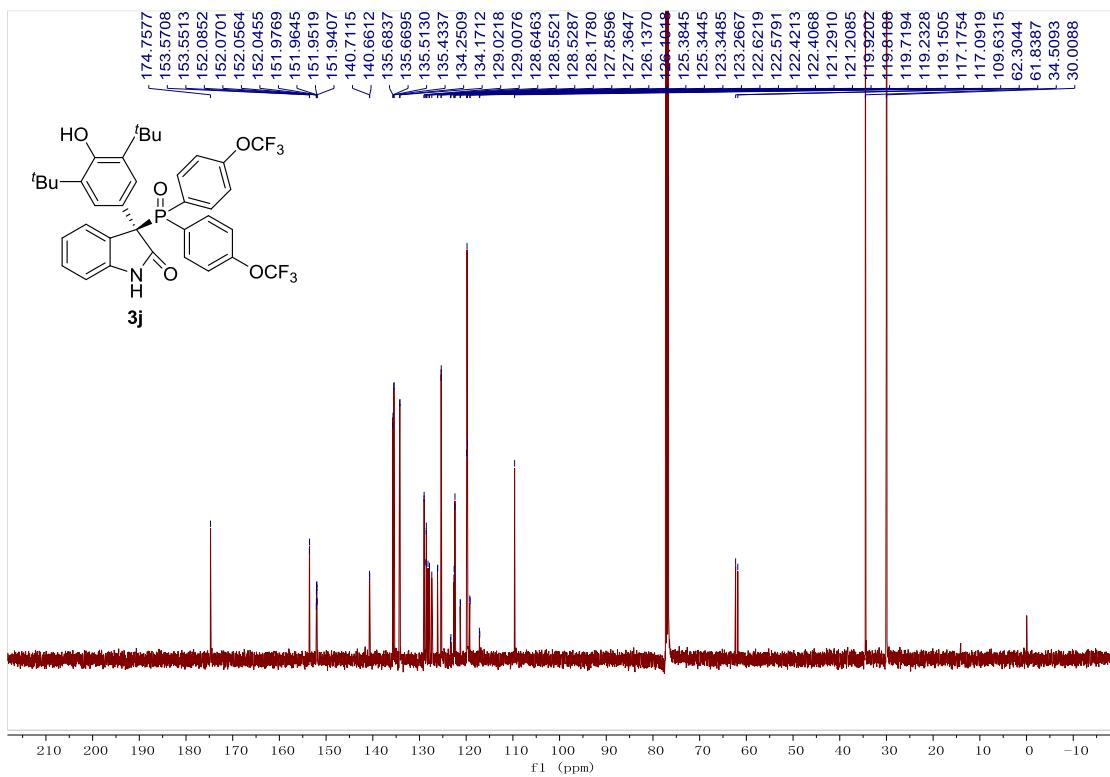


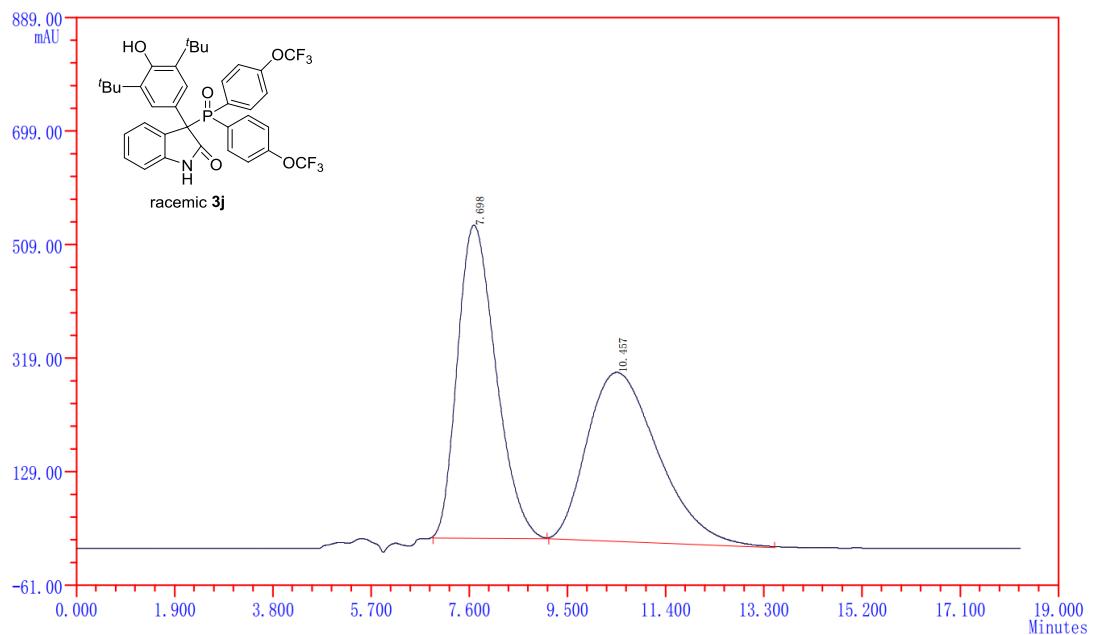
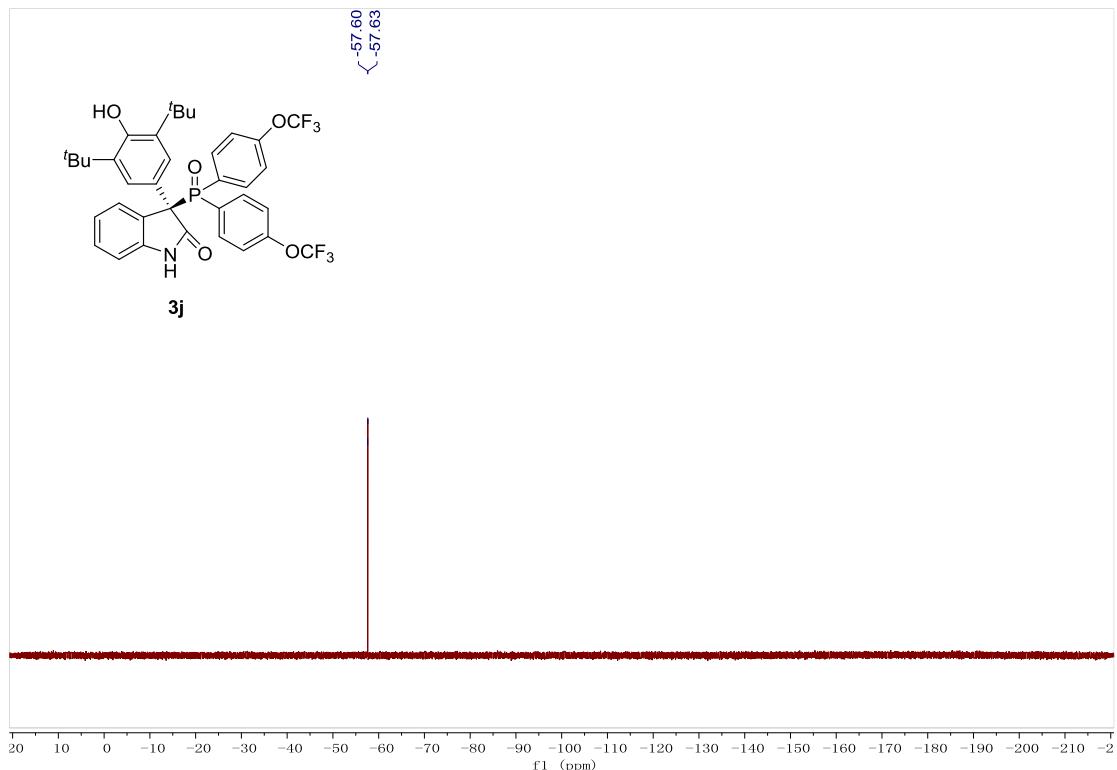
Peak	RetTime	Height	Area	Area
#	[Min]	[mAu]	[mAu*s]	%
1	21.382	356.81	96274.194	49.924
2	43.757	129.22	96569.196	50.076
Total:		387.78	192843.390	100.0000



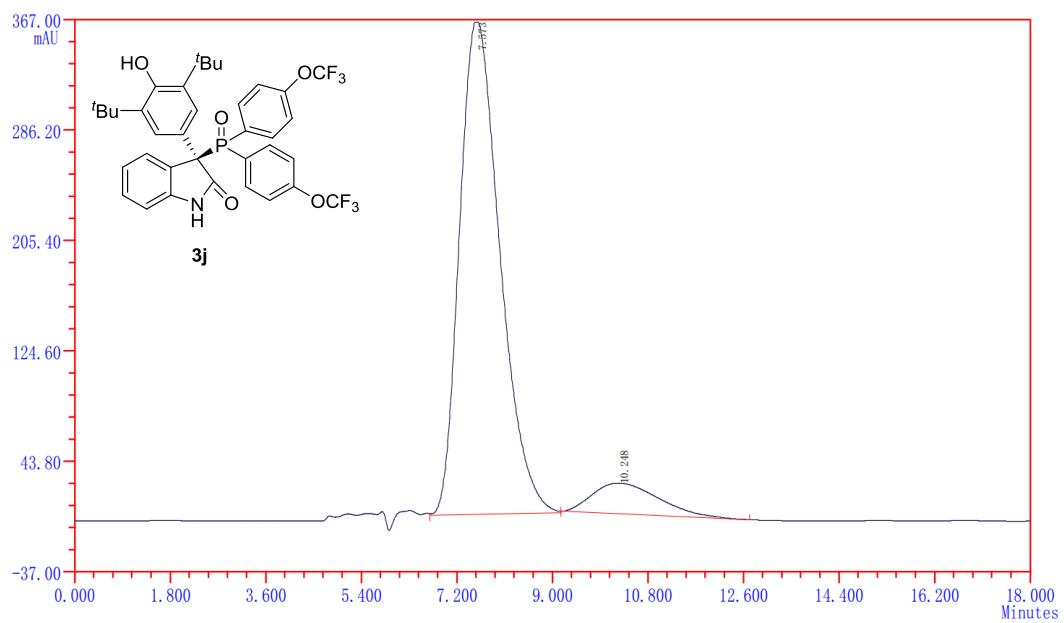
Peak #	RetTime [Min]	Height [mAu]	Area [mAu*s]	Area %
1	22.107	171.00	44075.641	92.714
2	46.023	4.86	3463.770	7.286
Total:		175.86	47539.411	100.0000



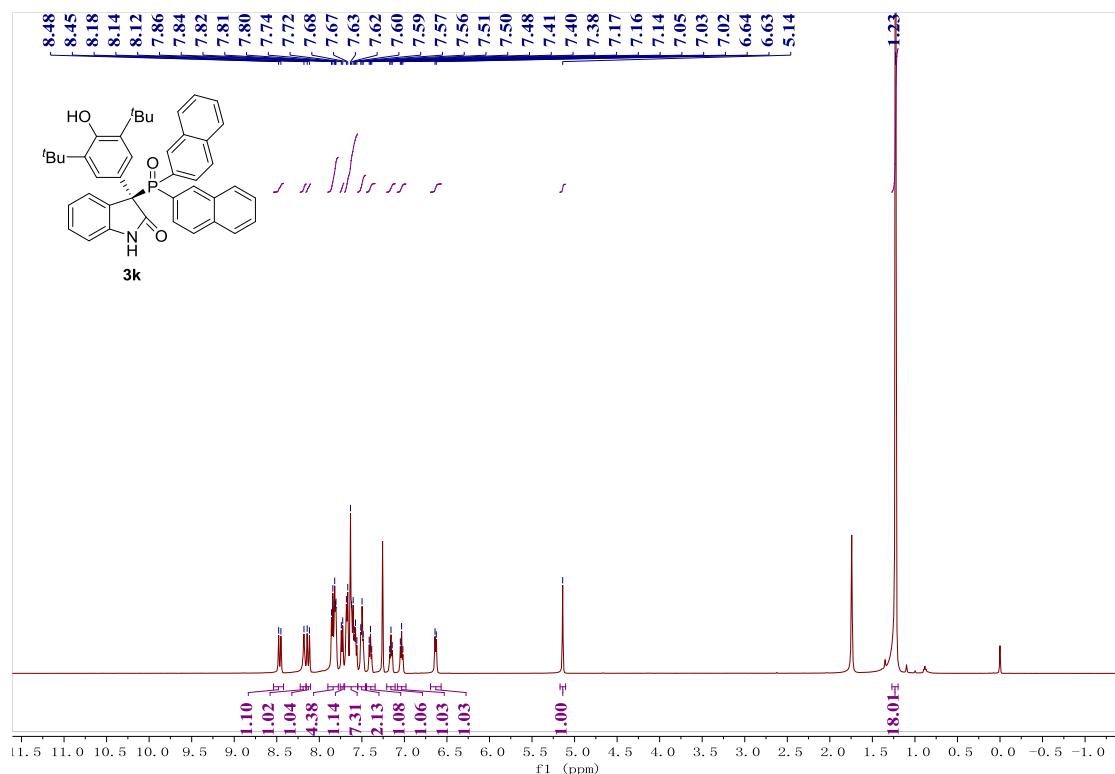


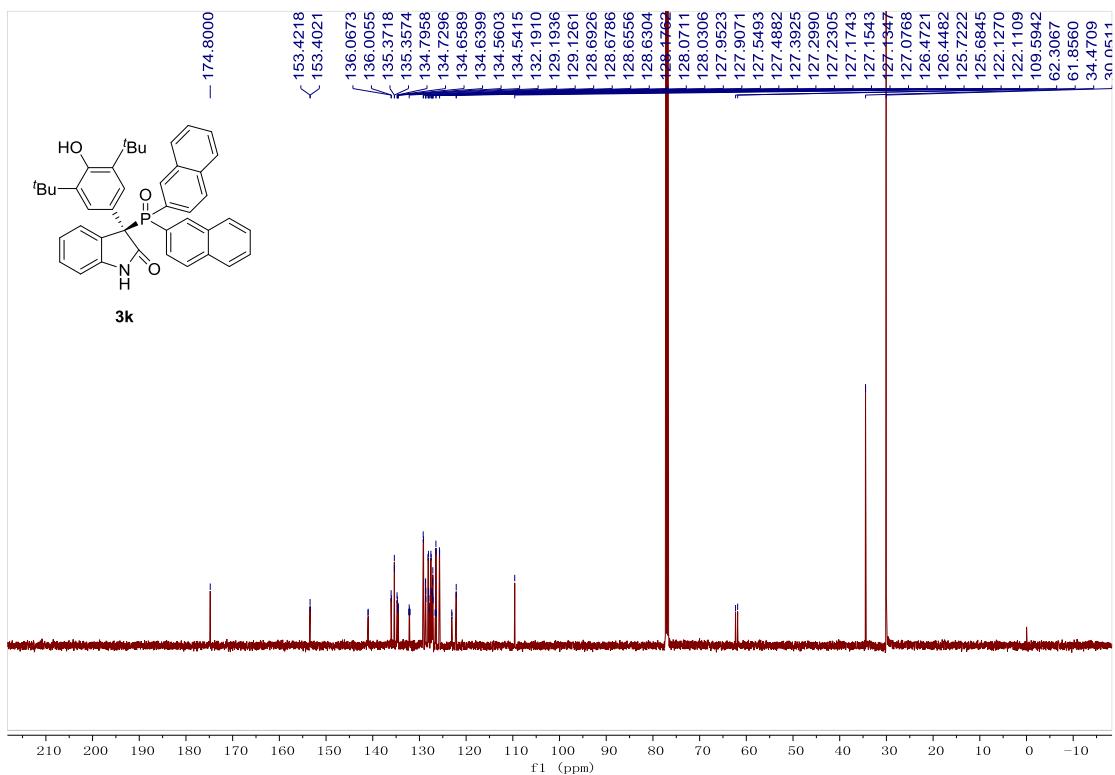


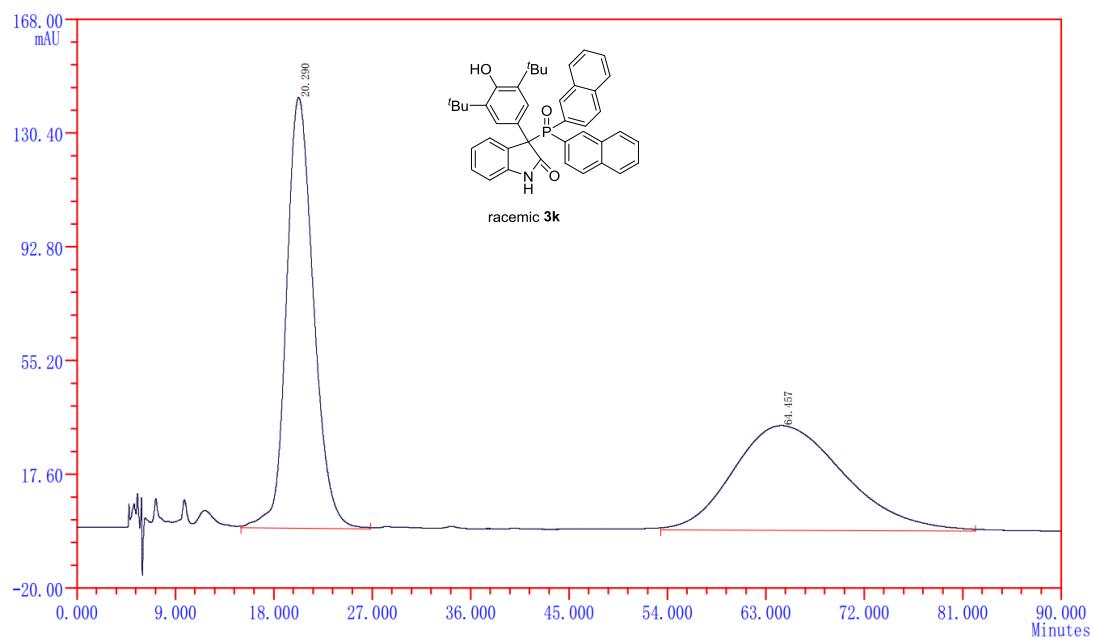
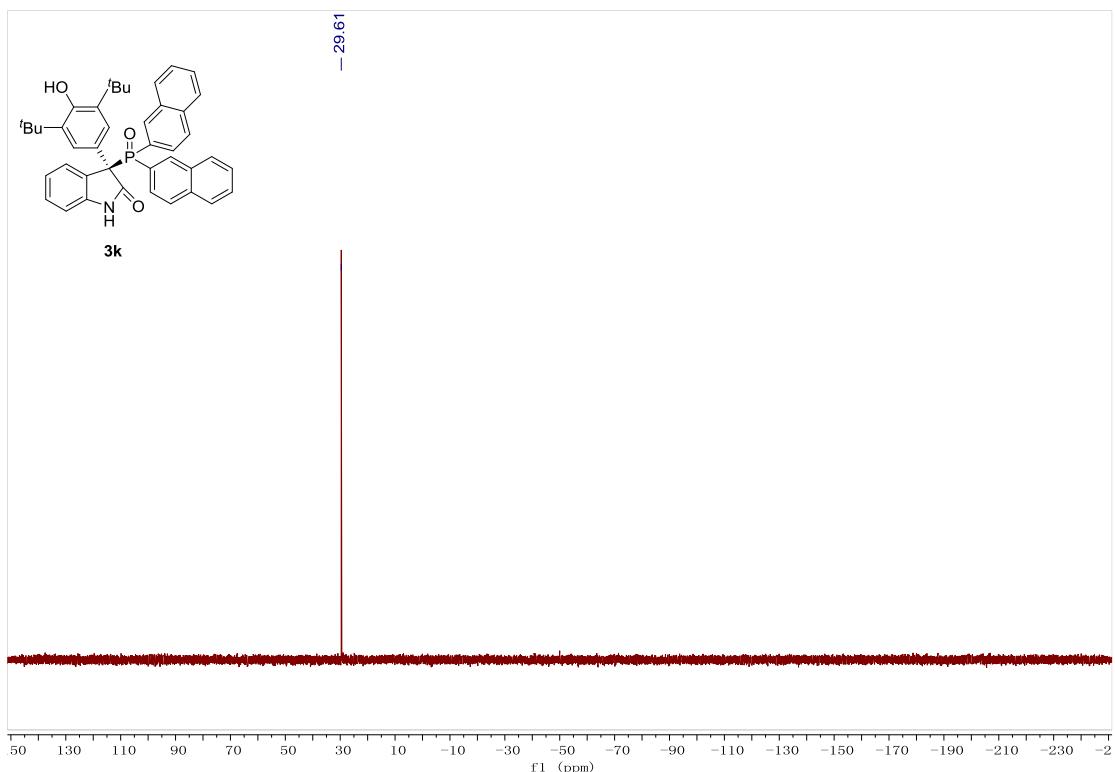
Peak #	RetTime [Min]	Height [mAu]	Area [mAu*s]	Area %
1	7.698	523.65	27121.834	50.008
2	10.457	282.84	27112.711	49.992
Total:		806.49	54234.545	100.0000



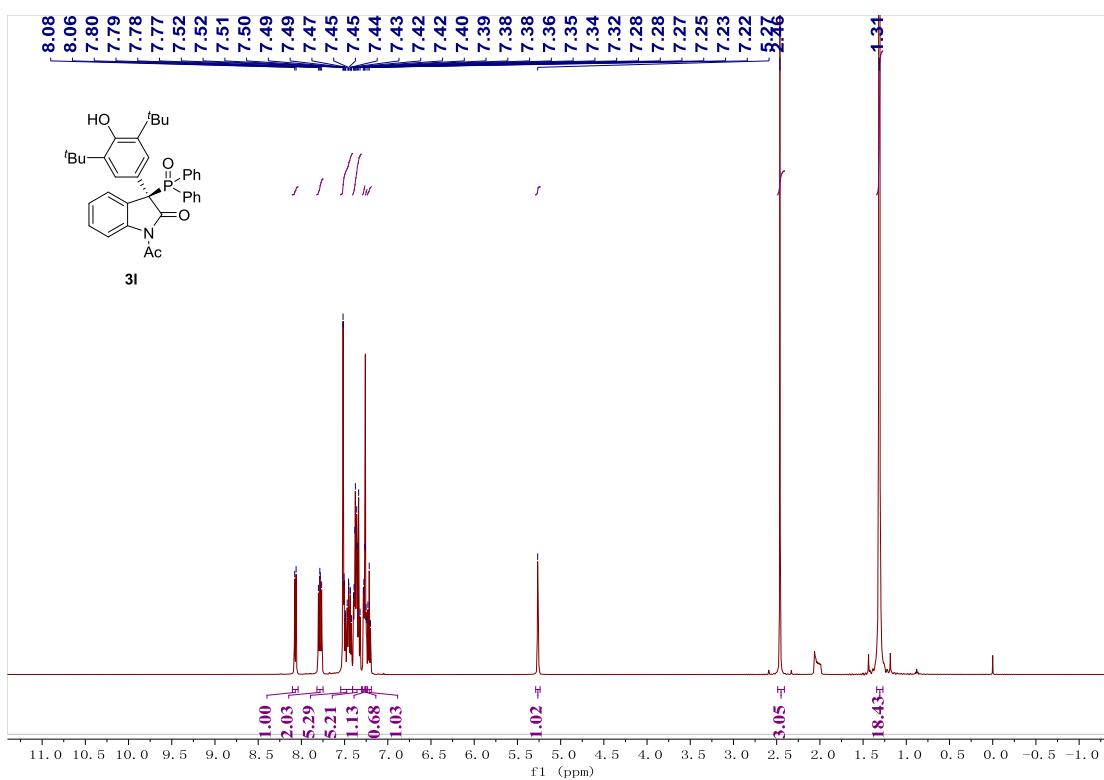
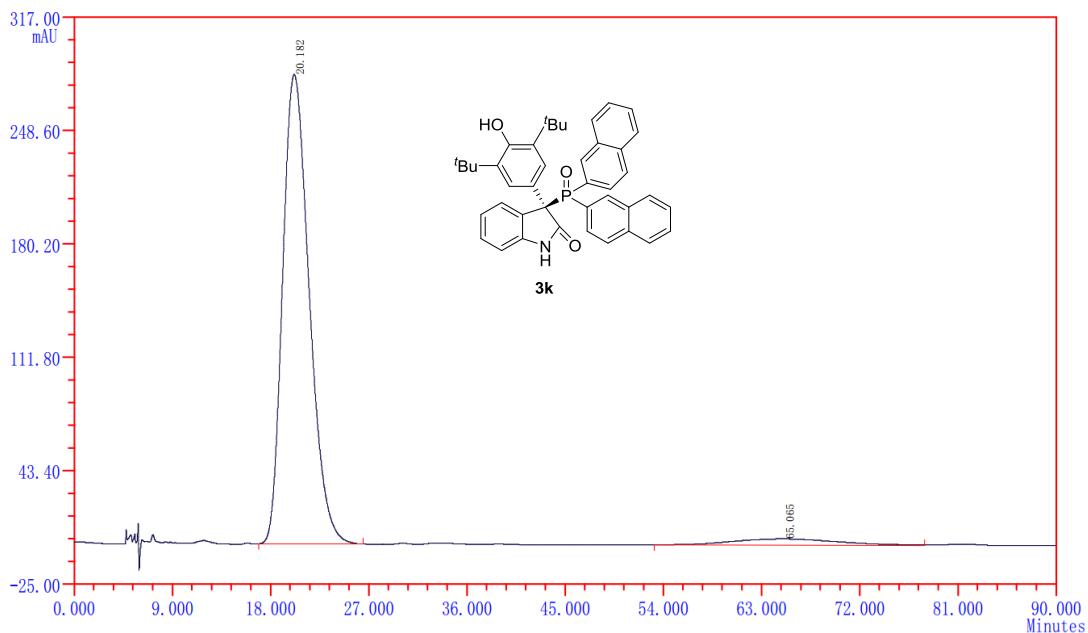
Peak #	RetTime [Min]	Height [mAu]	Area [mAu*s]	Area %
1	7.573	362.25	19099.044	90.670
2	10.248	22.46	1965.257	9.330
Total:		384.71	21064.301	100.0000

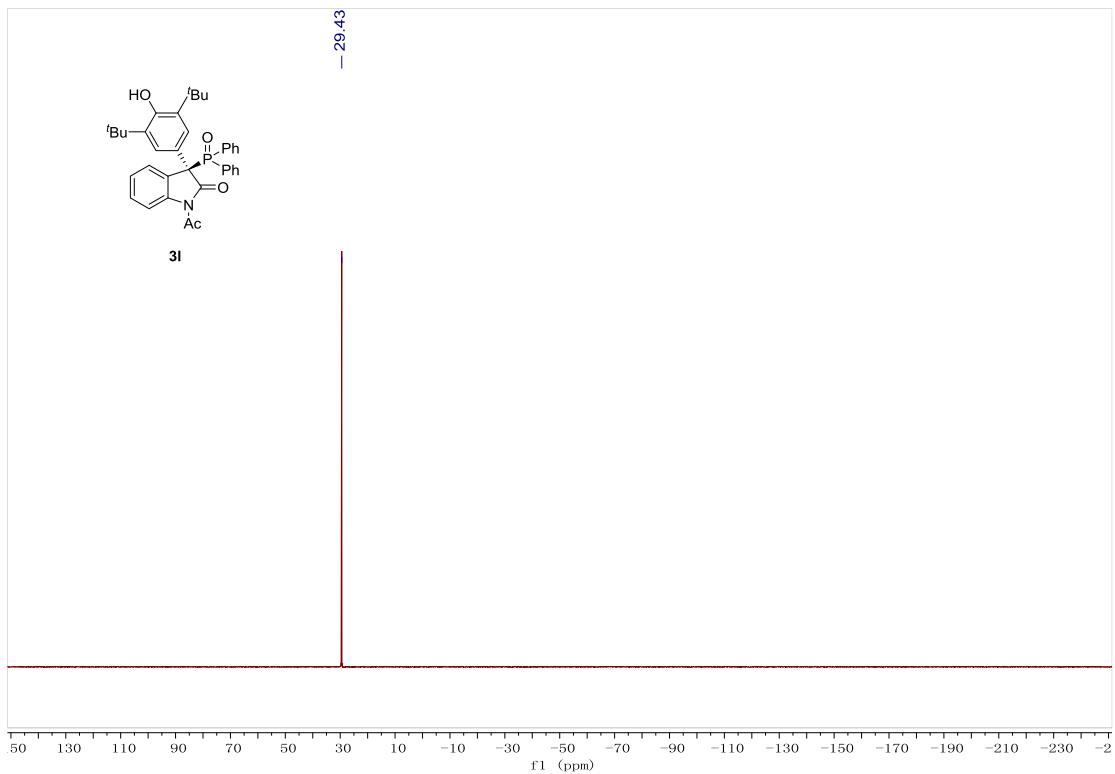
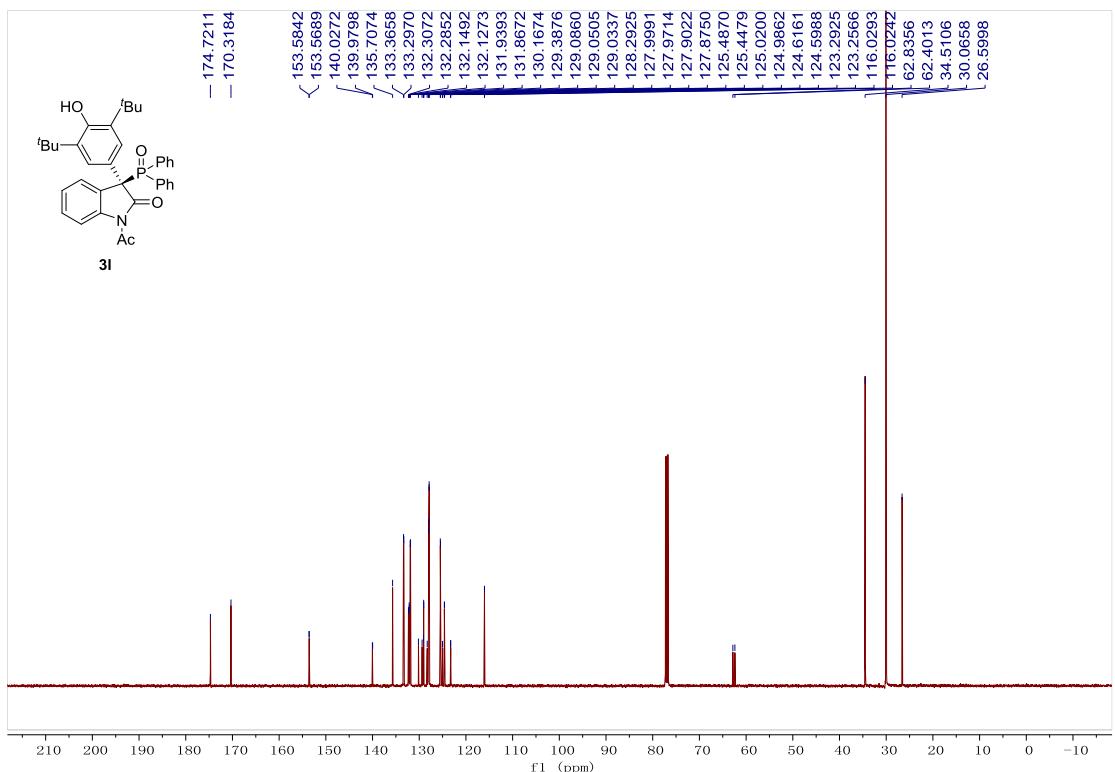


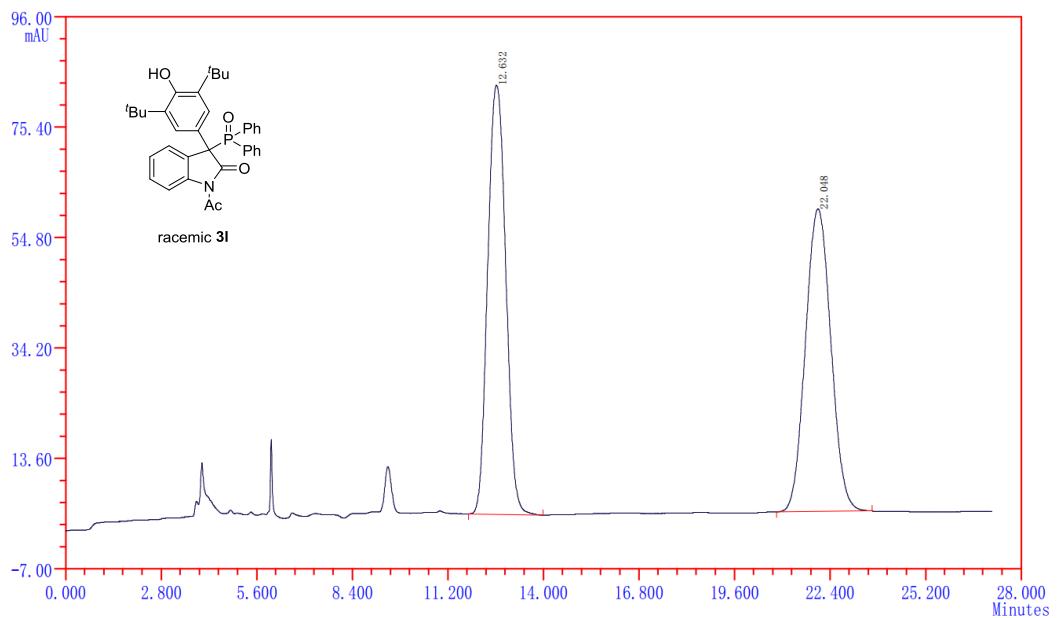




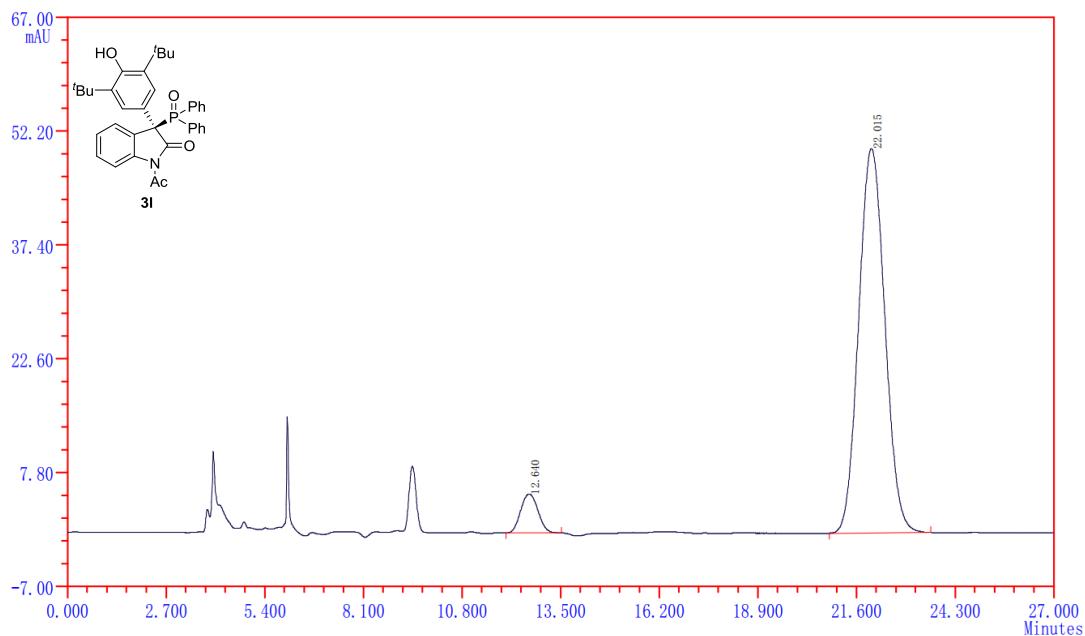
Peak #	RetTime [Min]	Height [mAu]	Area [mAu*s]	Area %
1	20.290	142.44	24619.352	50.119
2	64.457	34.66	24502.426	49.881
Total:		177.10	49121.778	100.0000



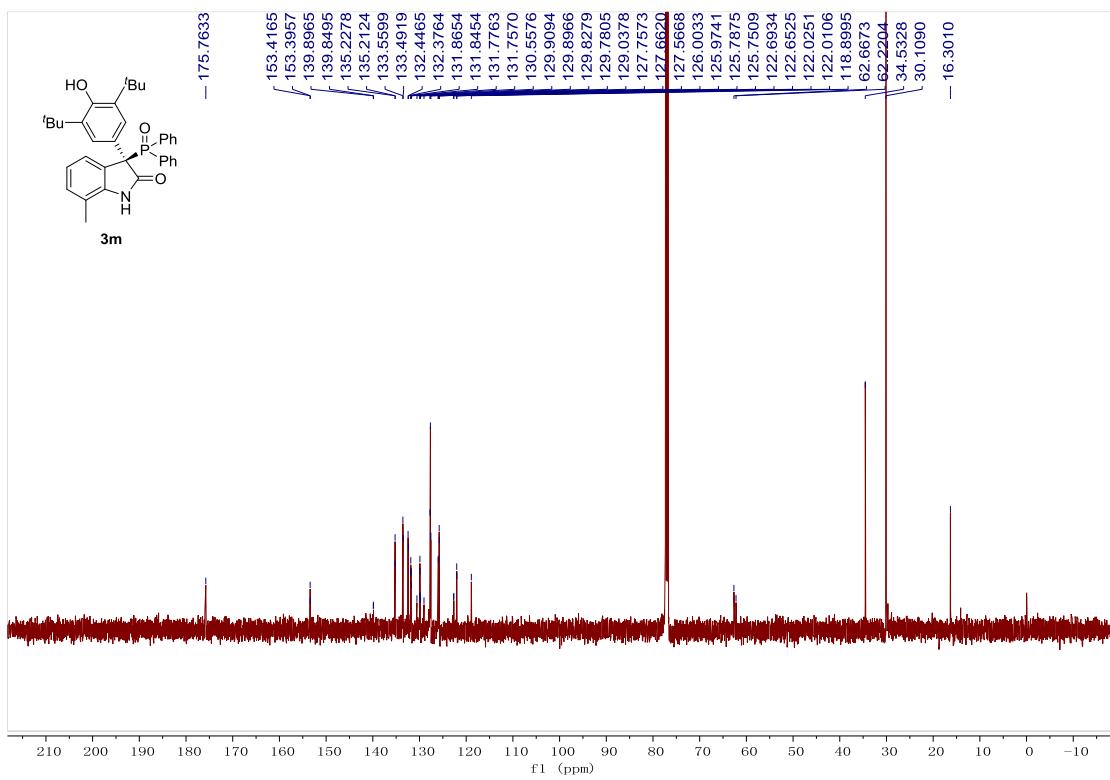
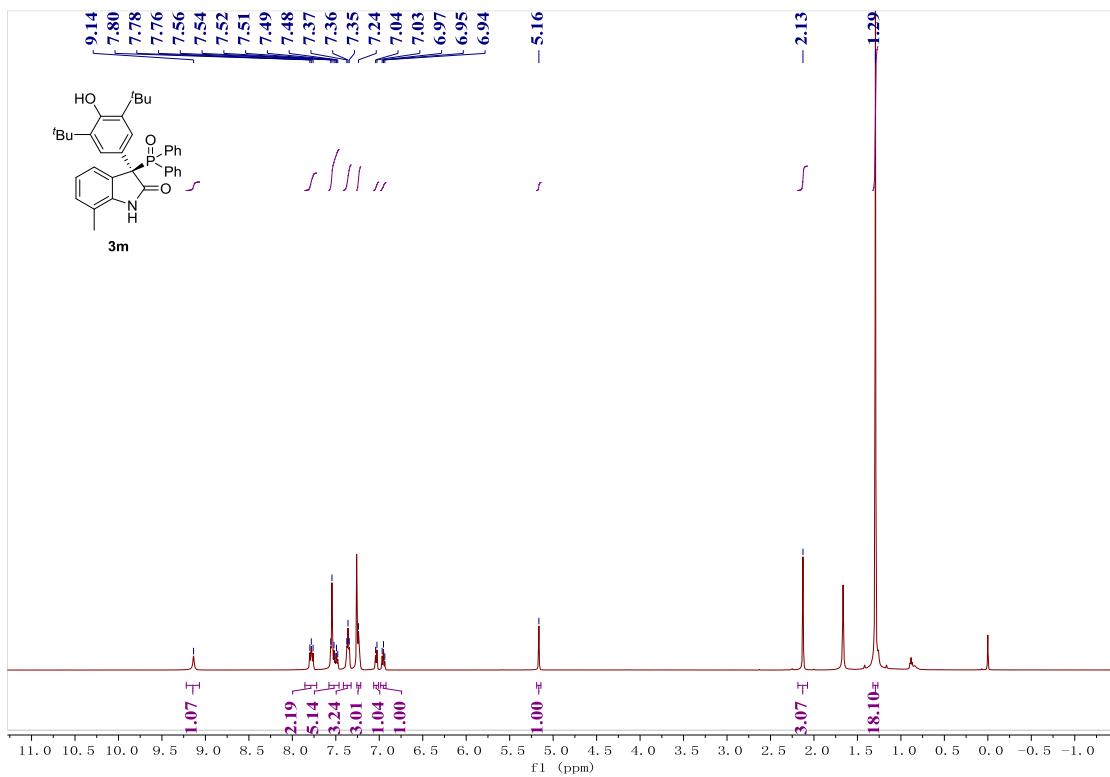


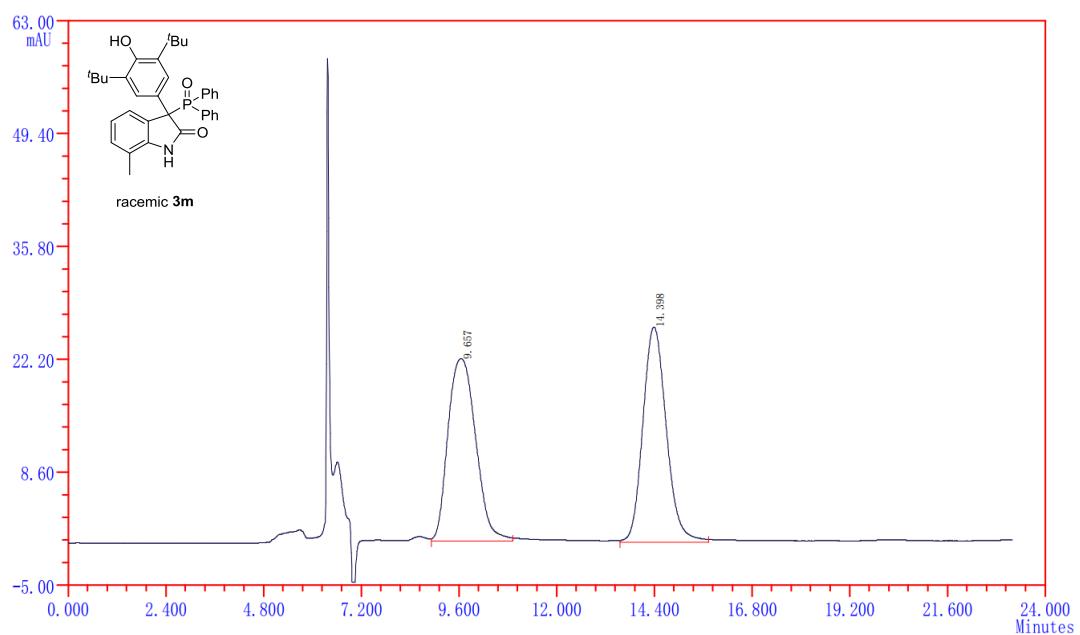
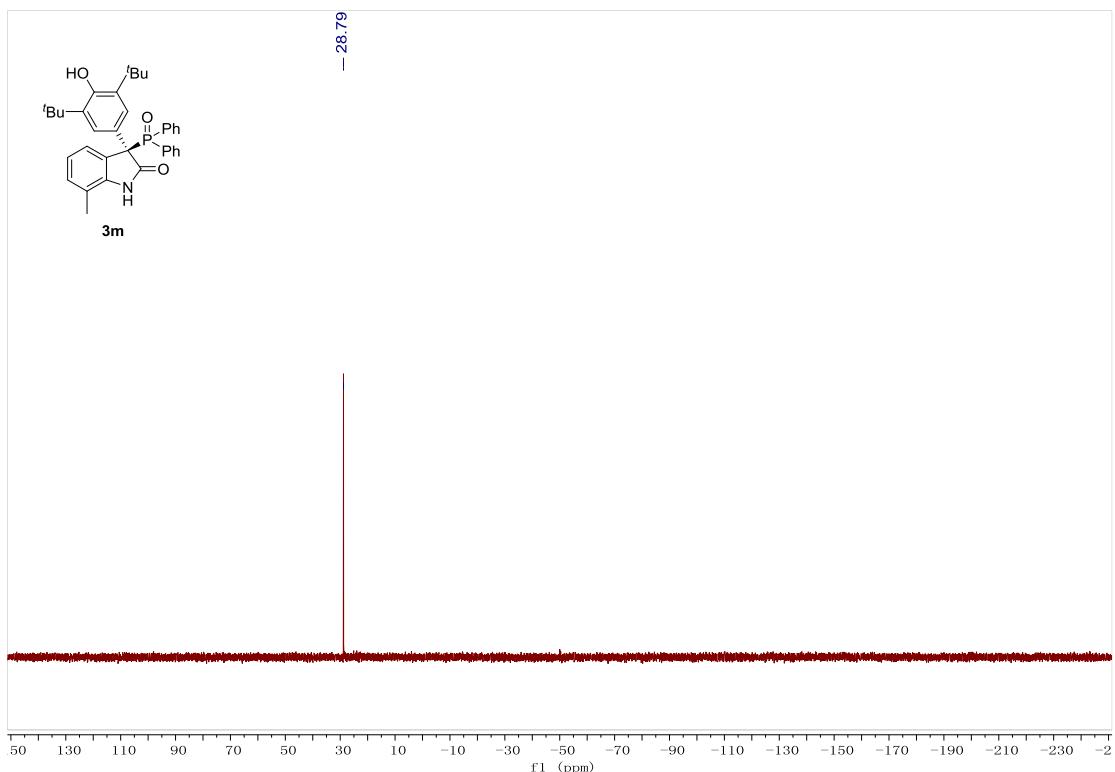


Peak #	RetTime [Min]	Height [mAu]	Area [mAu*s]	Area %
1	12.632	80.07	2940.826	50.087
2	22.048	56.48	2930.600	49.913
Total:		136.55	5871.426	100.0000

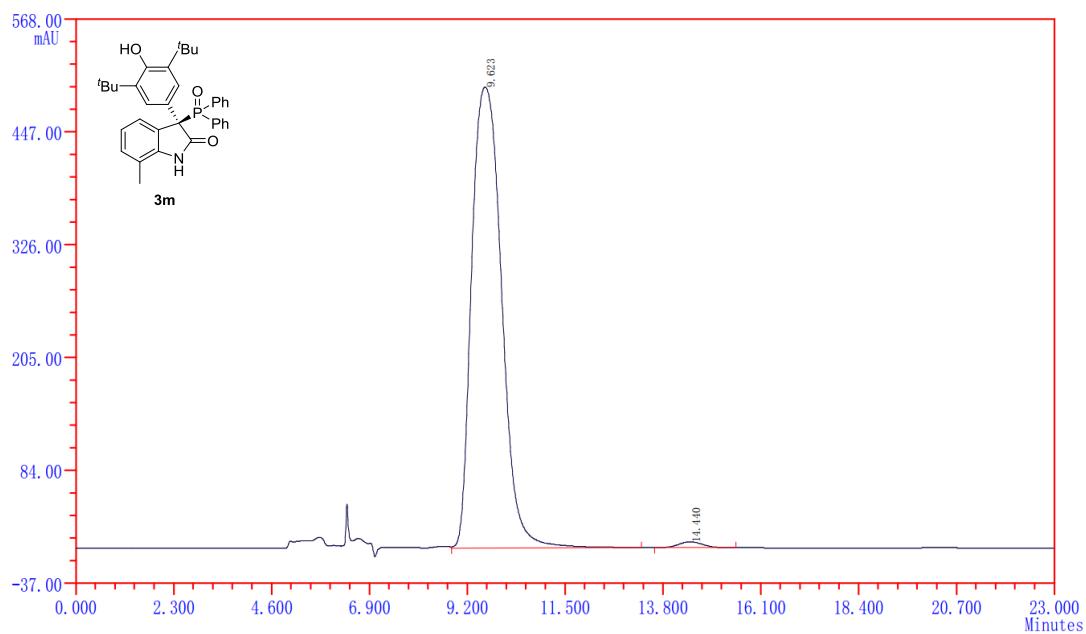


Peak #	RetTime [Min]	Height [mAu]	Area [mAu*s]	Area %
1	12.640	5.08	167.576	6.311
2	22.015	49.98	2487.613	93.689
Total:		55.06	2655.189	100.0000

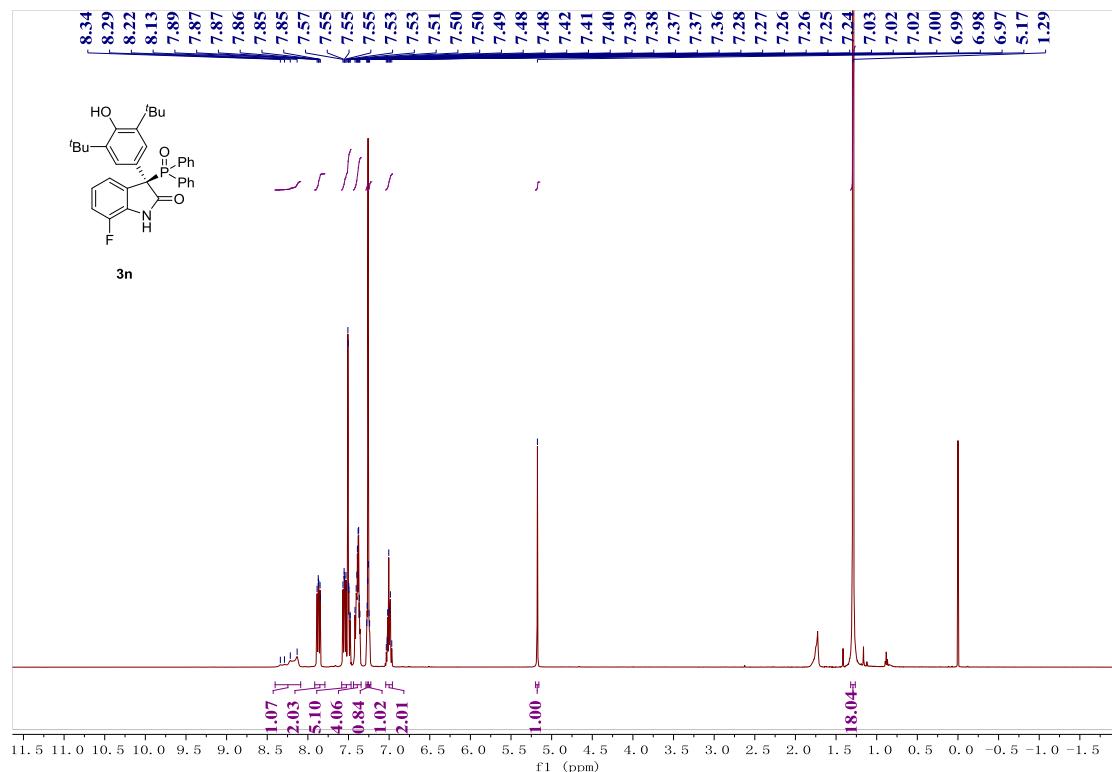


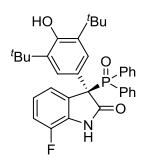
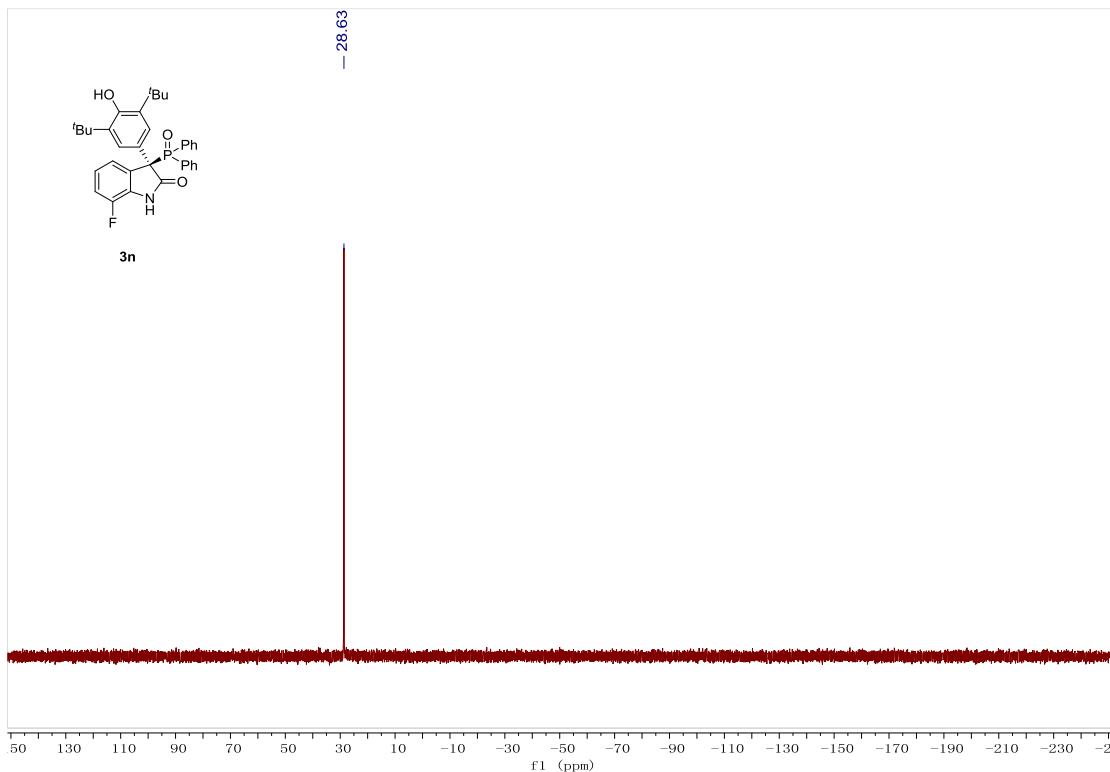
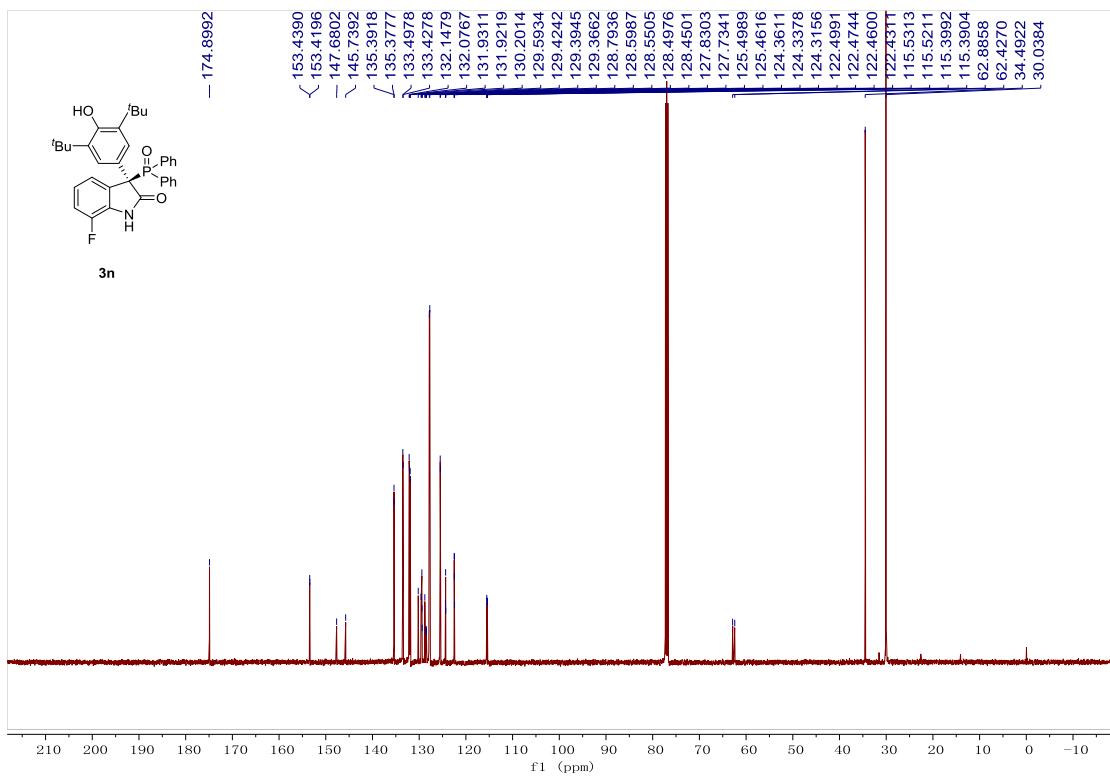


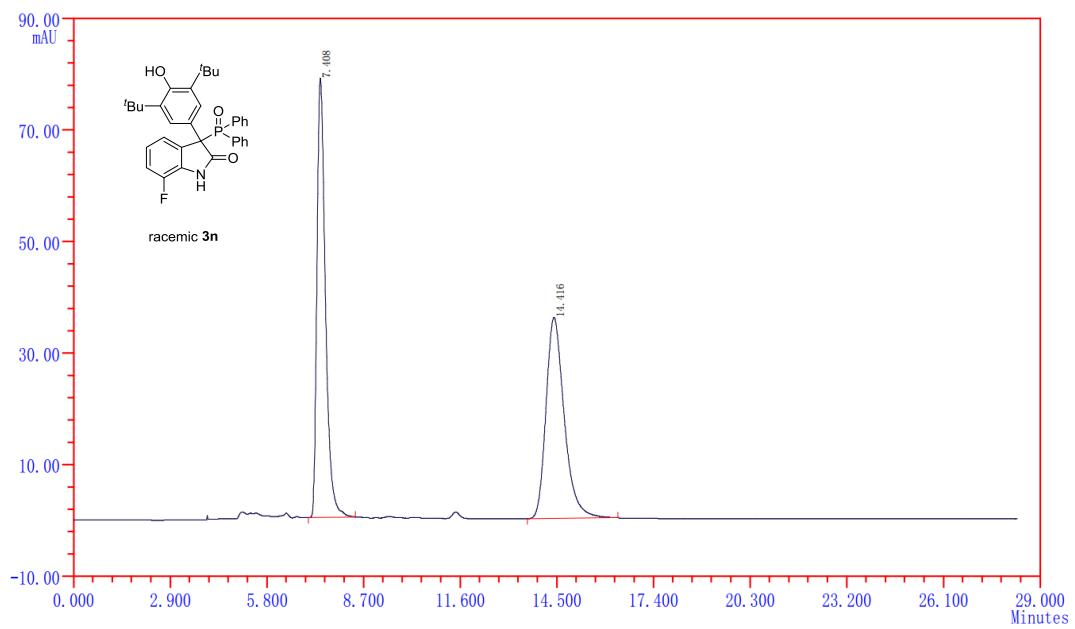
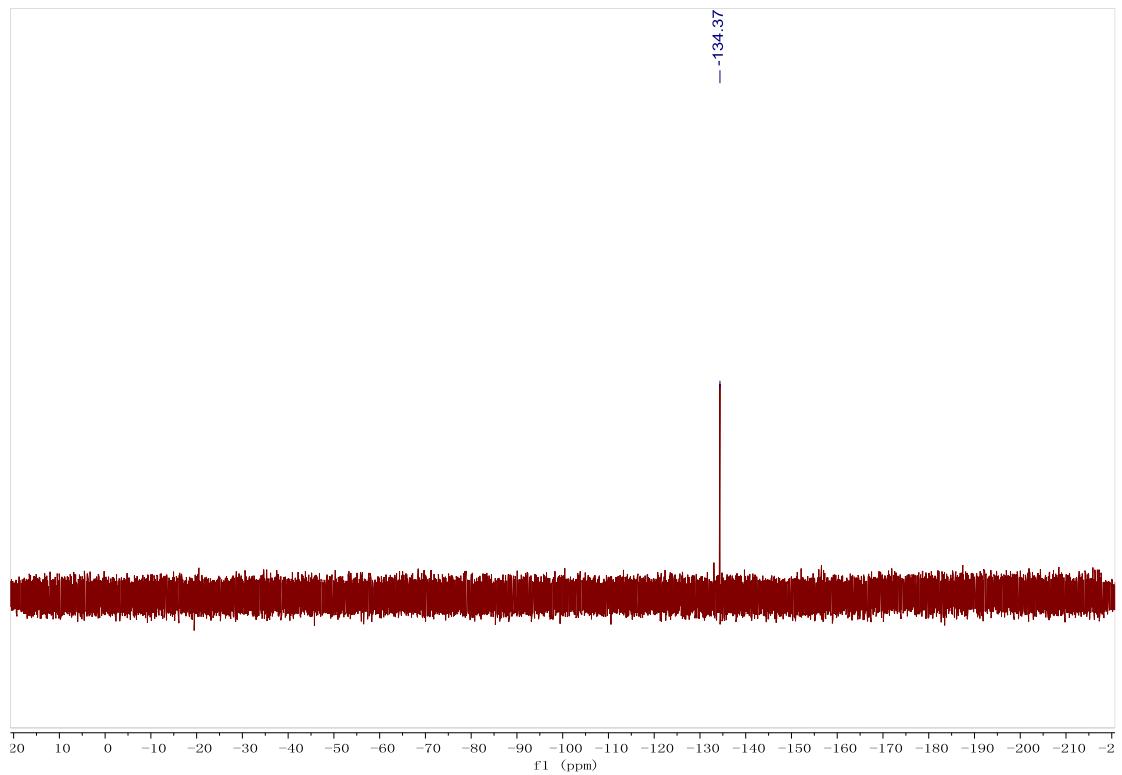
Peak #	RetTime [Min]	Height [mAu]	Area [mAu*s]	Area %
1	9.657	21.97	1041.091	49.905
2	14.398	25.95	1045.062	50.095
Total:		47.92	2086.153	100.0000



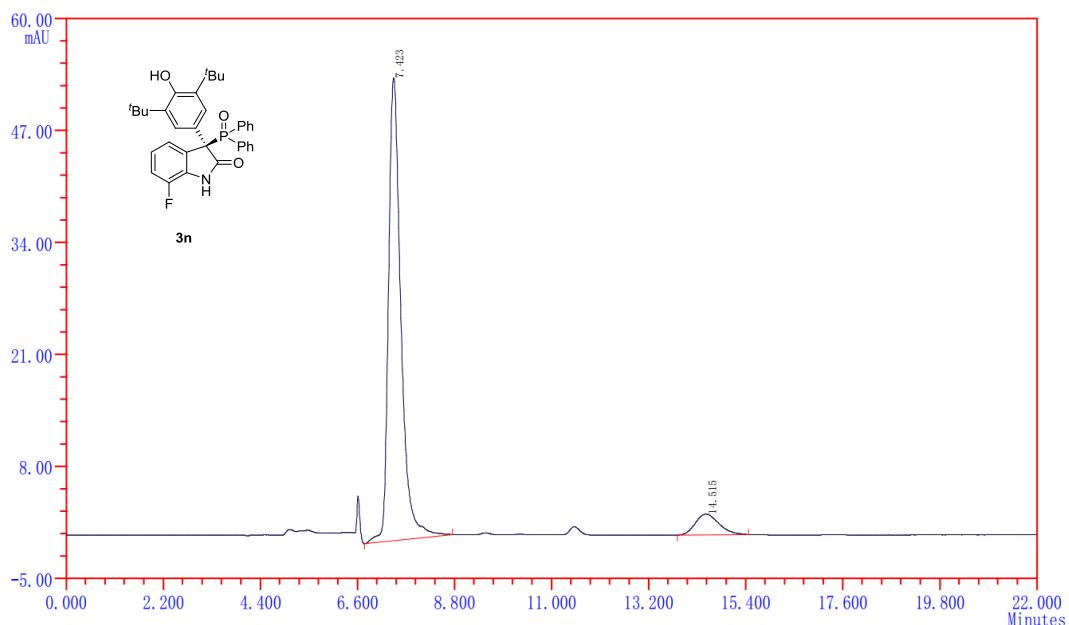
Peak #	RetTime [Min]	Height [mAu]	Area [mAu*s]	Area %
1	9.623	494.25	24128.201	98.973
2	14.440	6.34	250.376	1.027
Total:		500.59	24378.576	100.0000



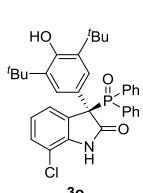
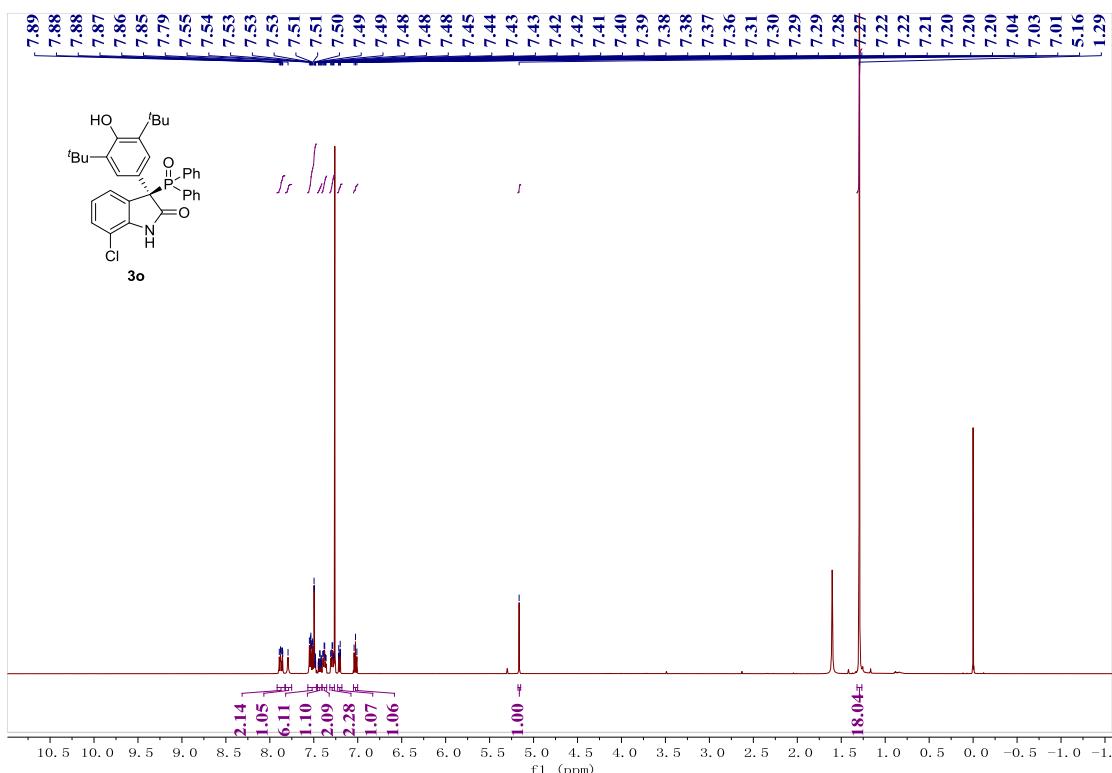


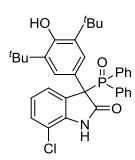
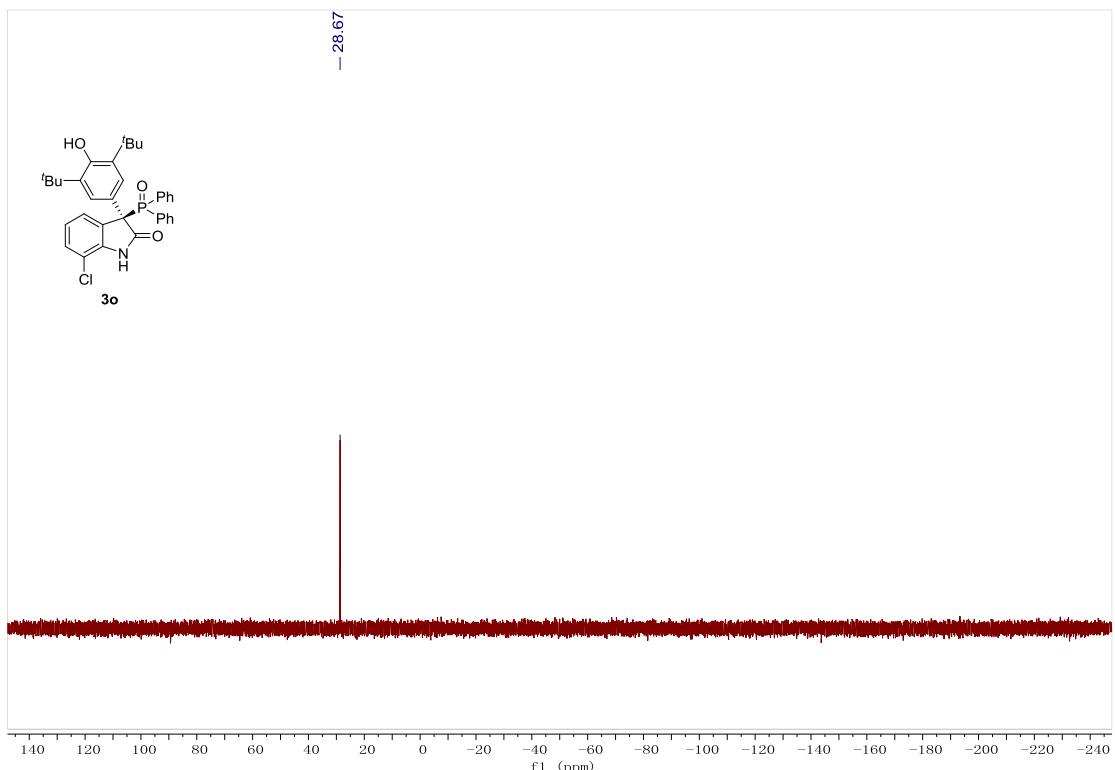
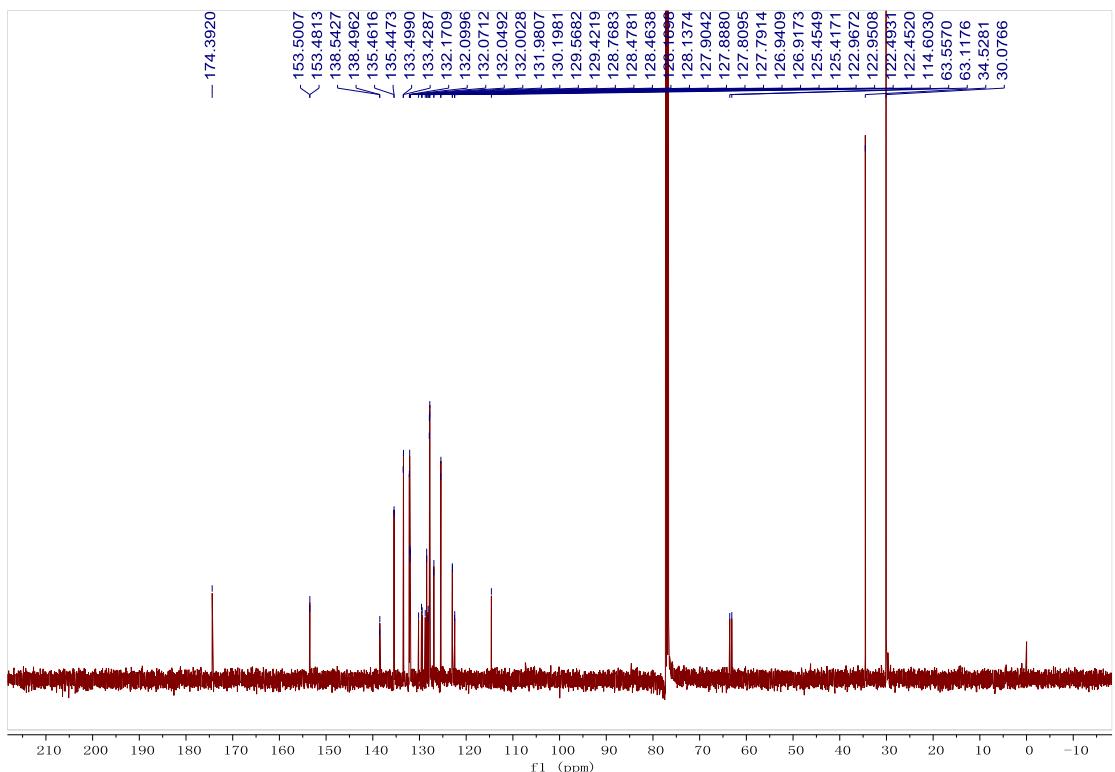


Peak #	RetTime [Min]	Height [mAu]	Area [mAu*s]	Area %
1	7.408	78.75	1393.744	50.152
2	14.416	36.04	1385.299	49.848
Total:		114.79	2779.043	100.0000

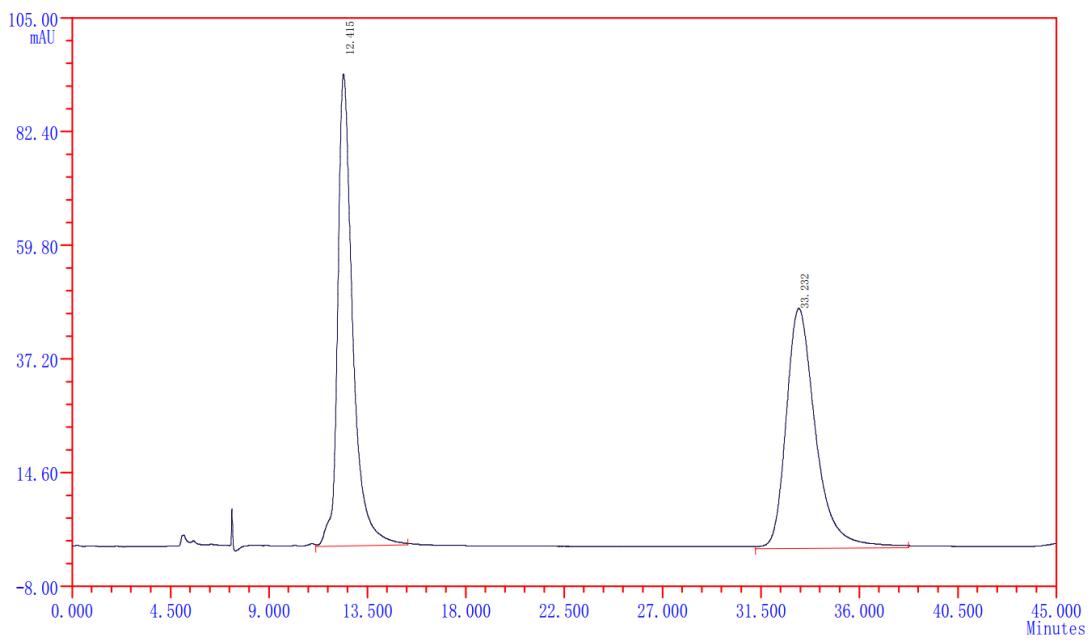


Peak #	RetTime [Min]	Height [mAu]	Area [mAu*s]	Area %
1	7.423	53.77	1053.744	92.140
2	14.515	2.41	89.885	7.860
Total:		56.18	1143.629	100.0000

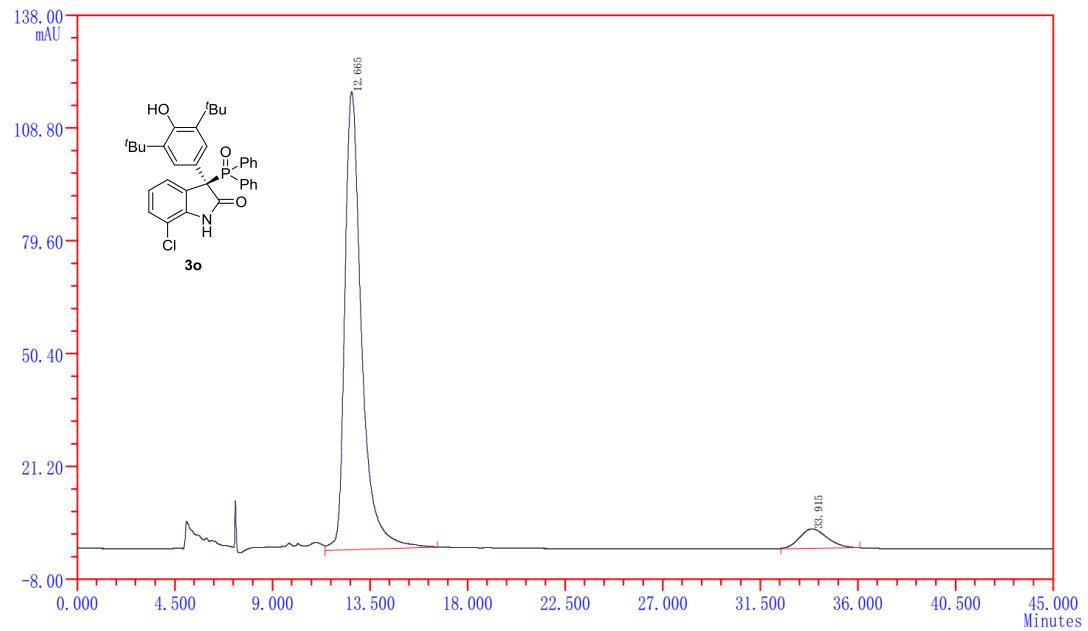




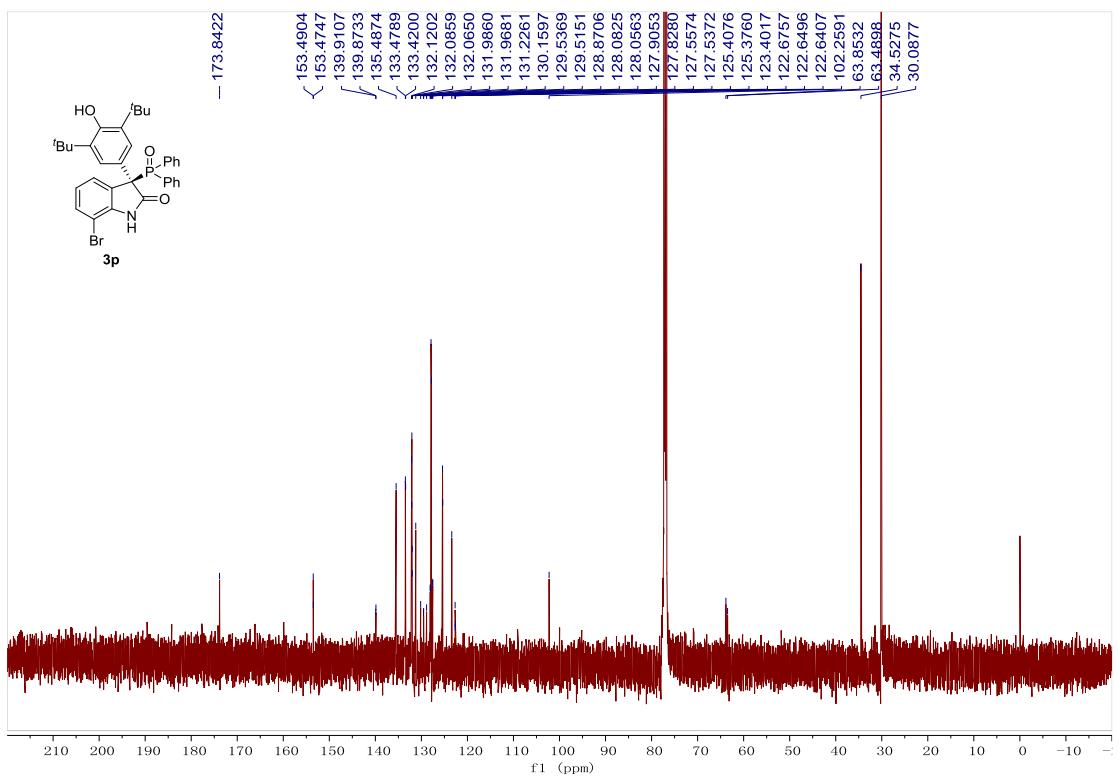
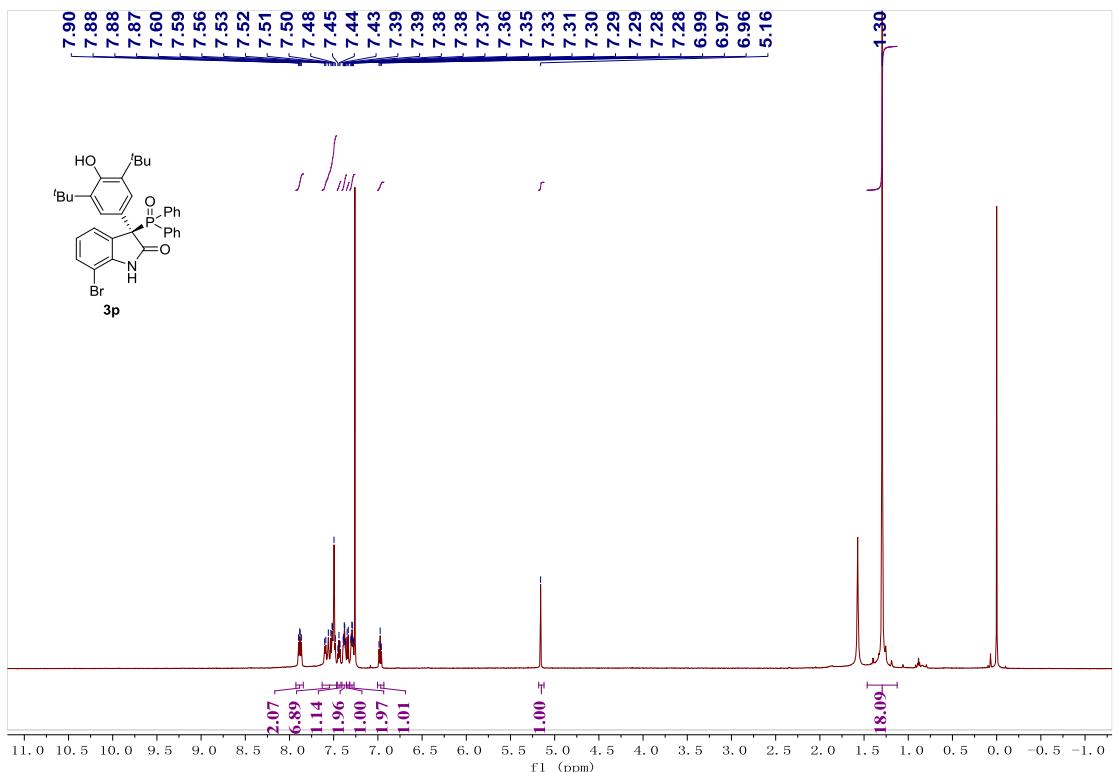
S60

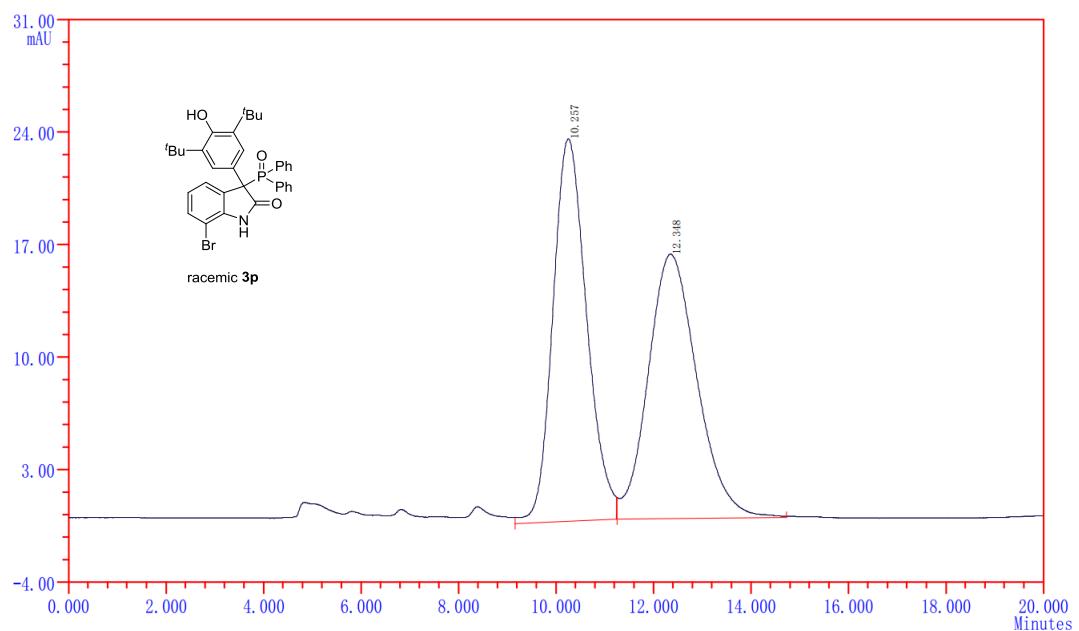
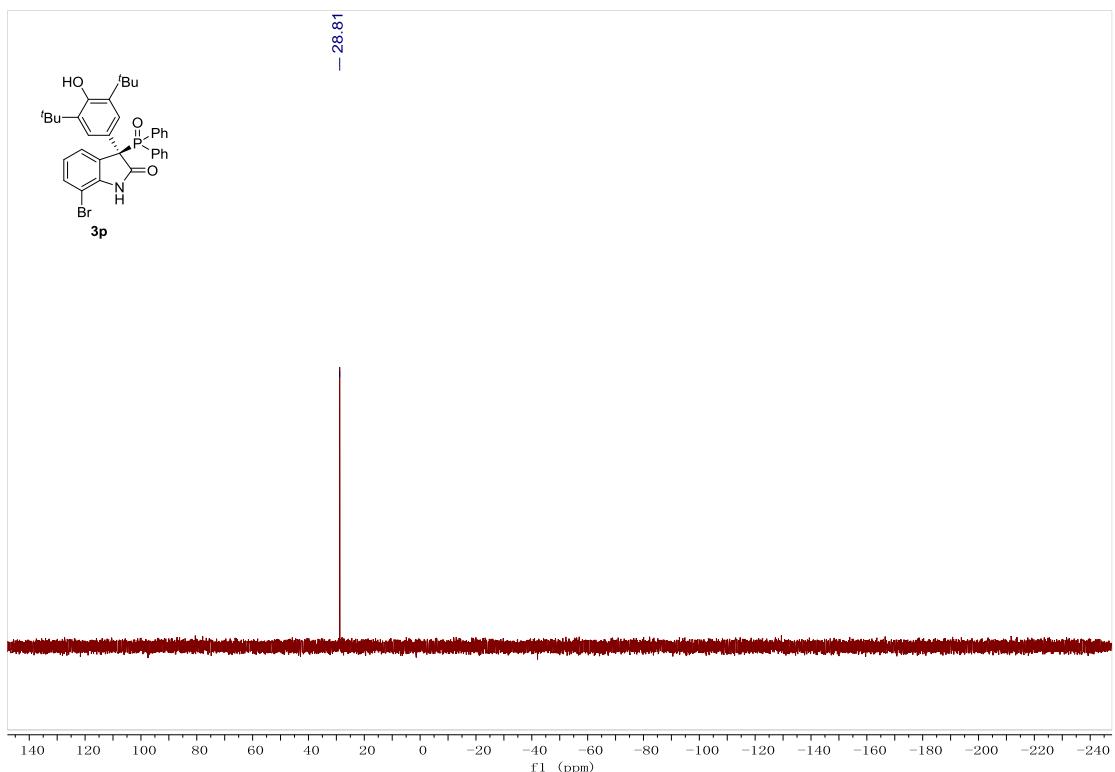


Peak #	RetTime [Min]	Height [mAu]	Area [mAu*s]	Area %
1	12.415	93.81	4482.293	49.966
2	33.232	47.72	4488.328	50.034
Total:		141.53	8970.621	100.0000

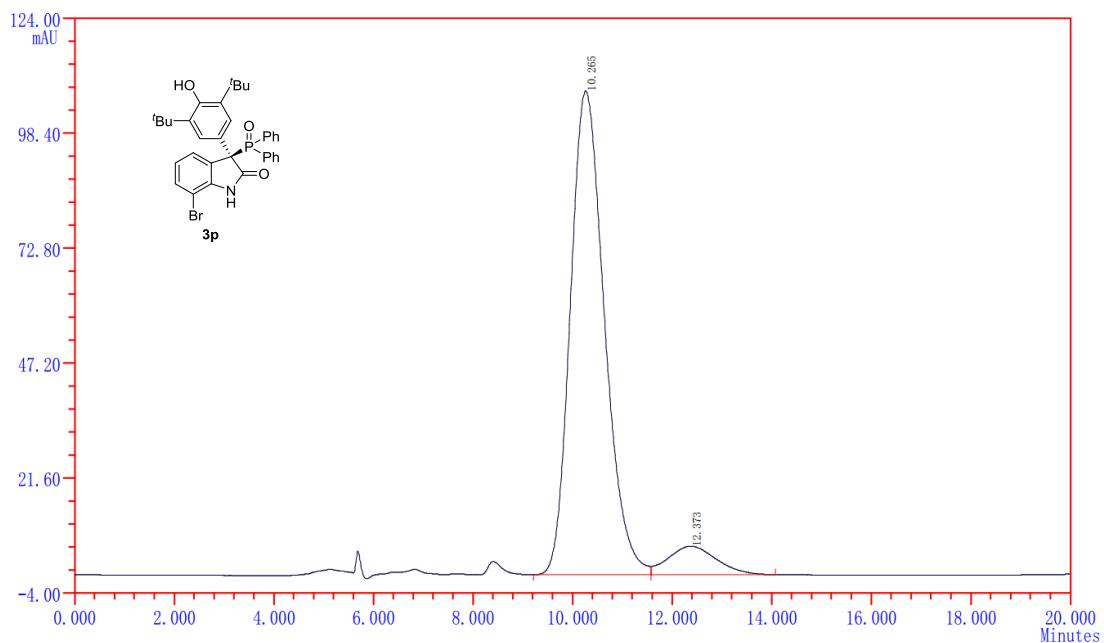


Peak #	RetTime [Min]	Height [mAu]	Area [mAu*s]	Area %
1	12.665	118.52	6386.209	93.560
2	33.915	4.98	439.591	6.440
Total:		123.50	6825.800	100.0000

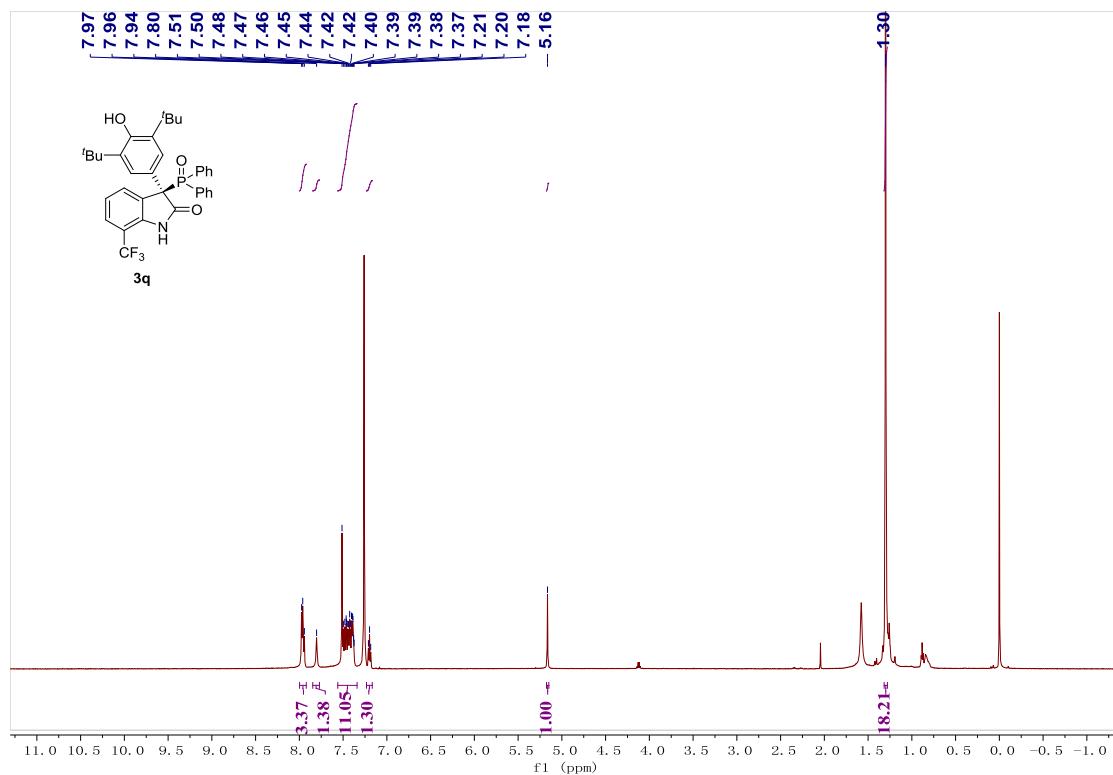


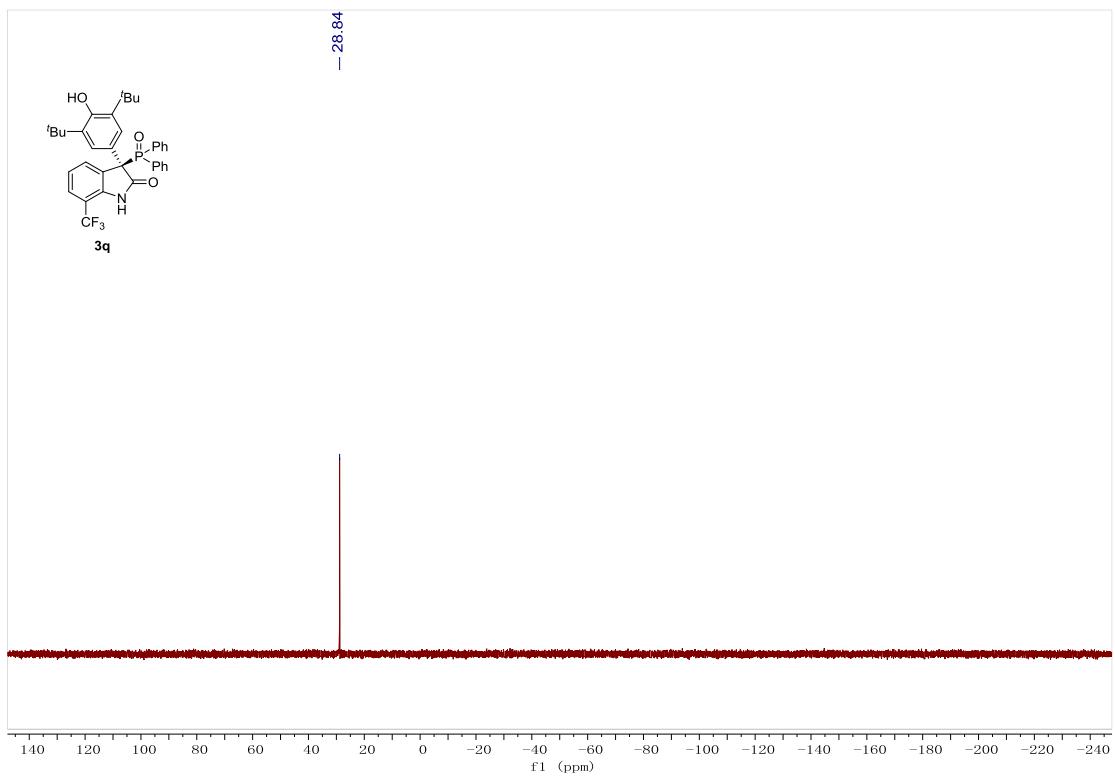
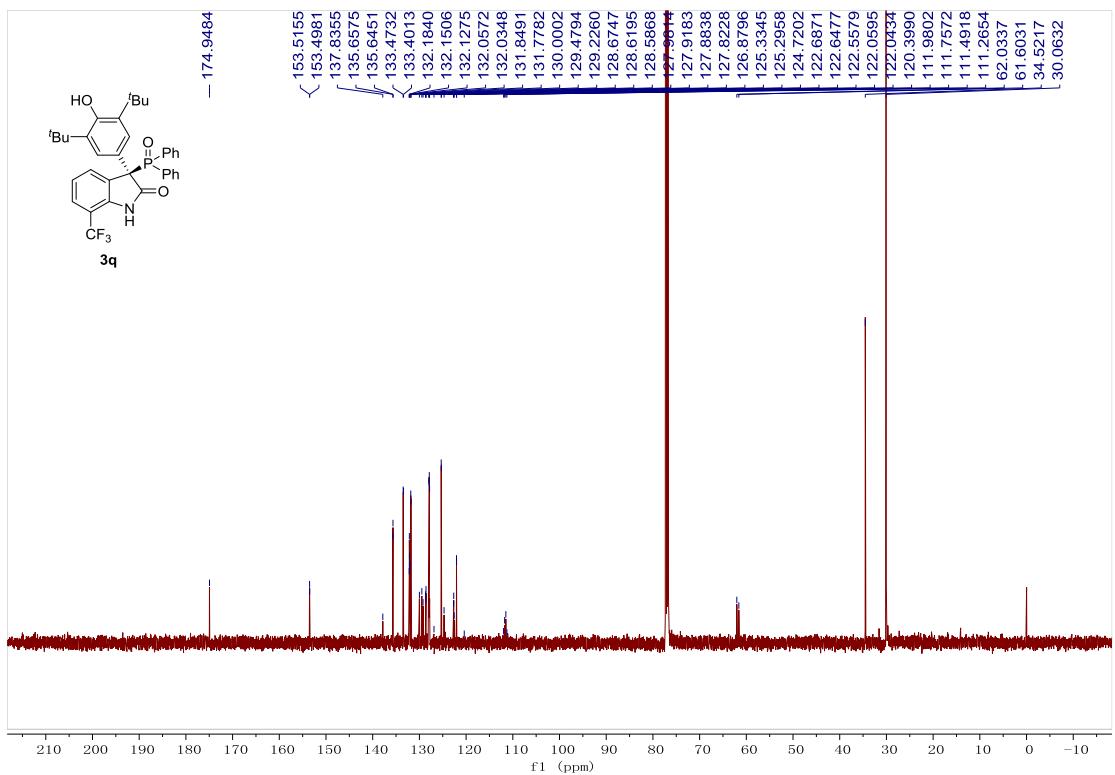


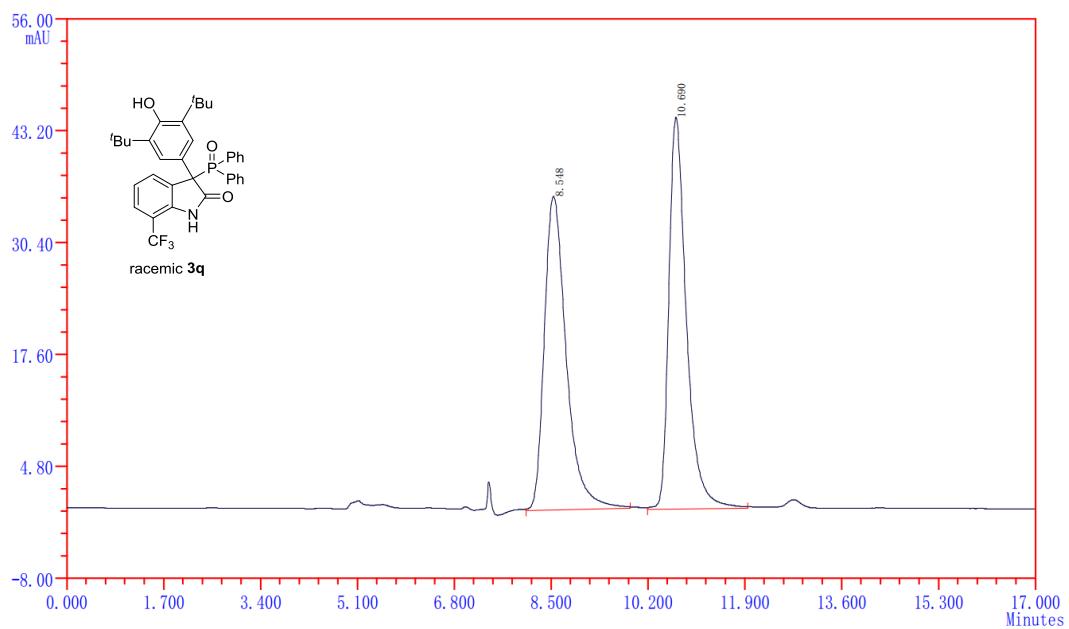
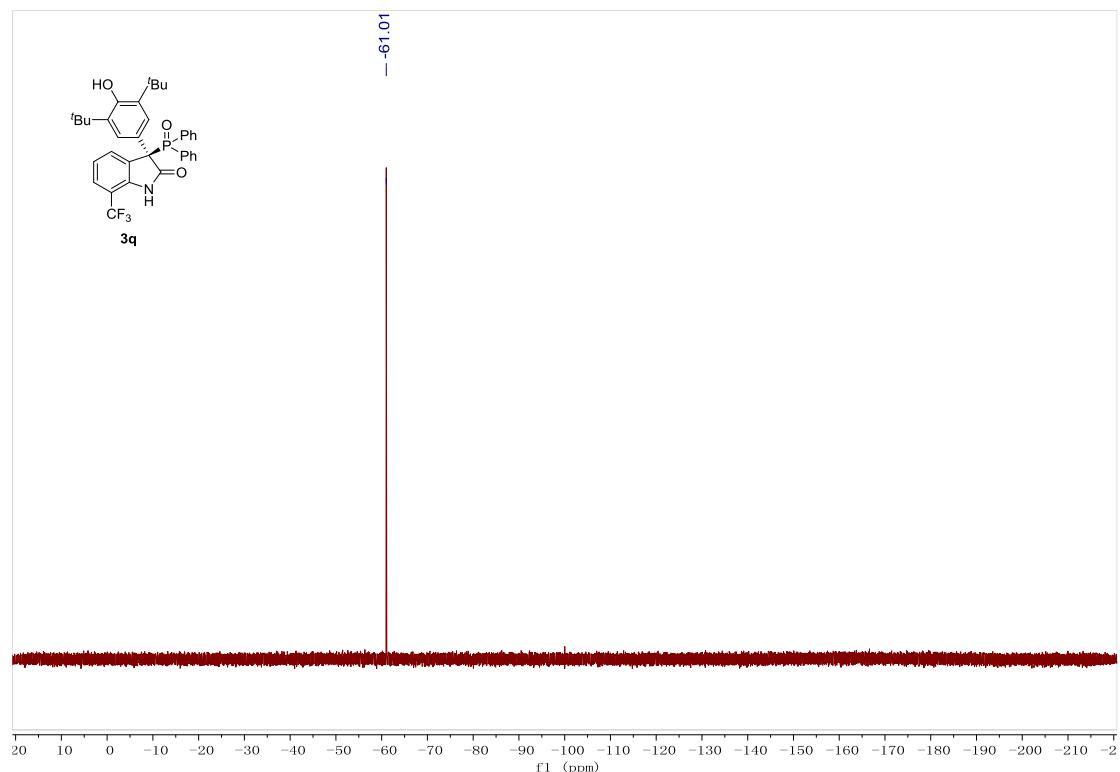
Peak #	RetTime [Min]	Height [mAu]	Area [mAu*s]	Area %
1	10.257	23.79	1145.604	49.959
2	12.348	16.44	1147.474	50.041
Total:		40.23	2293.079	100.0000



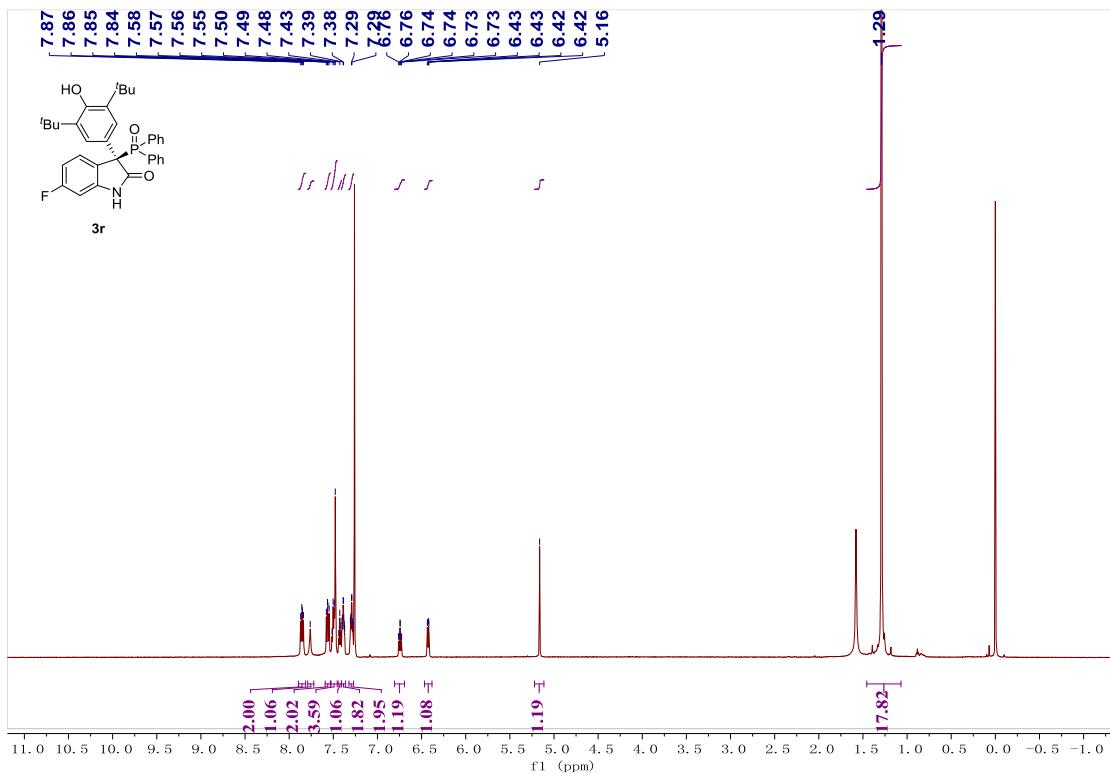
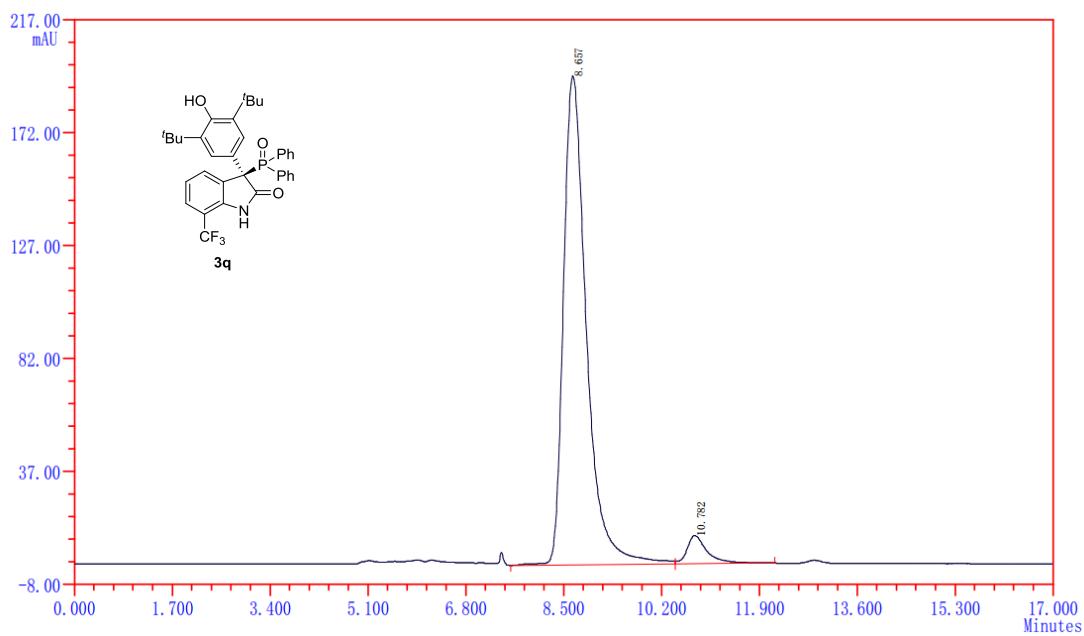
Peak #	RetTime [Min]	Height [mAu]	Area [mAu*s]	Area %
1	10.265	107.75	5119.707	92.261
2	12.373	6.34	429.453	7.739
Total:		114.09	5549.160	100.0000



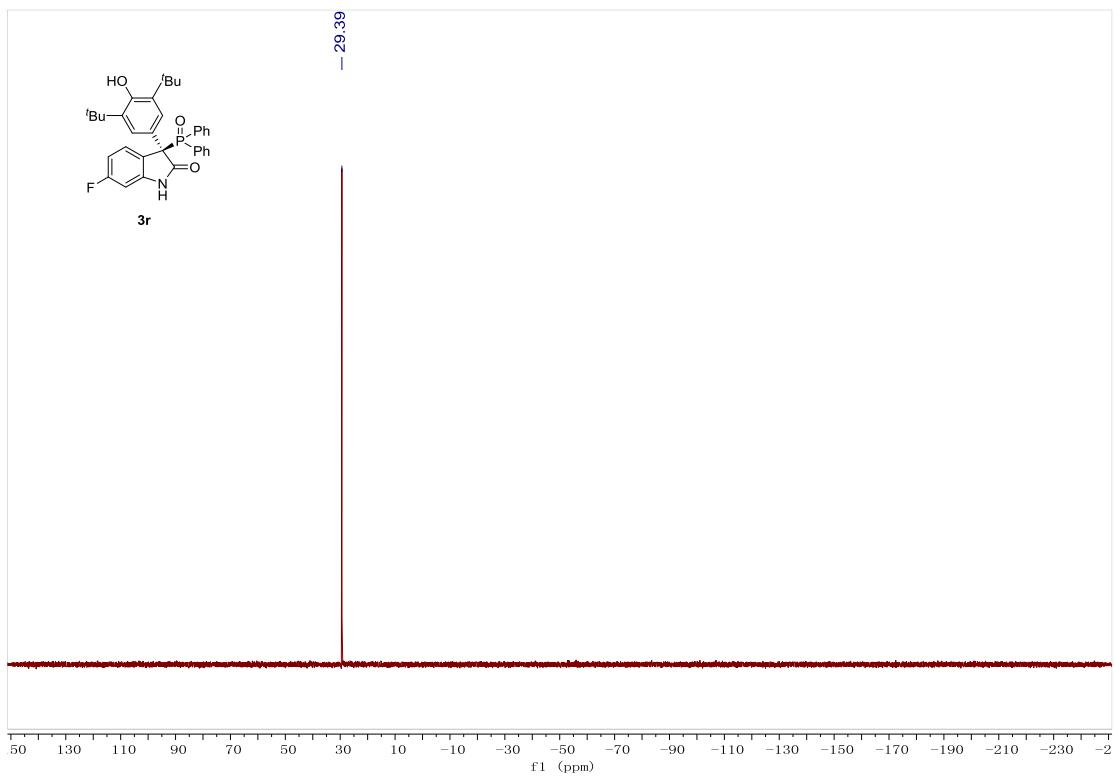
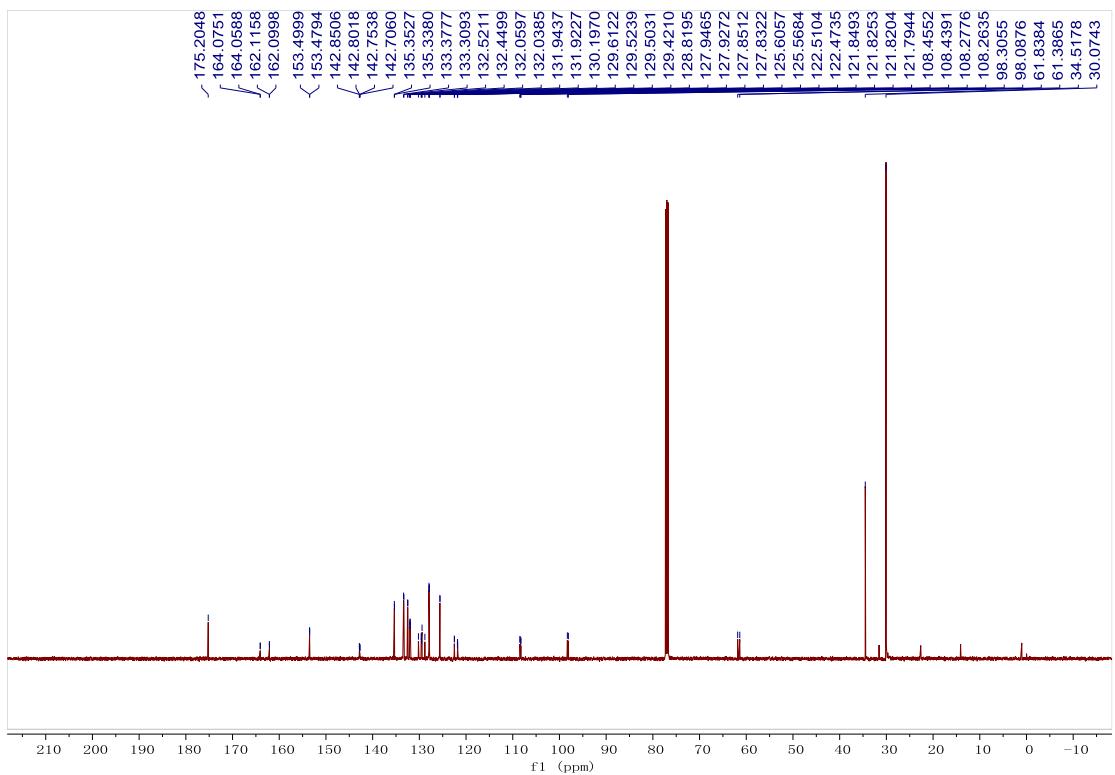


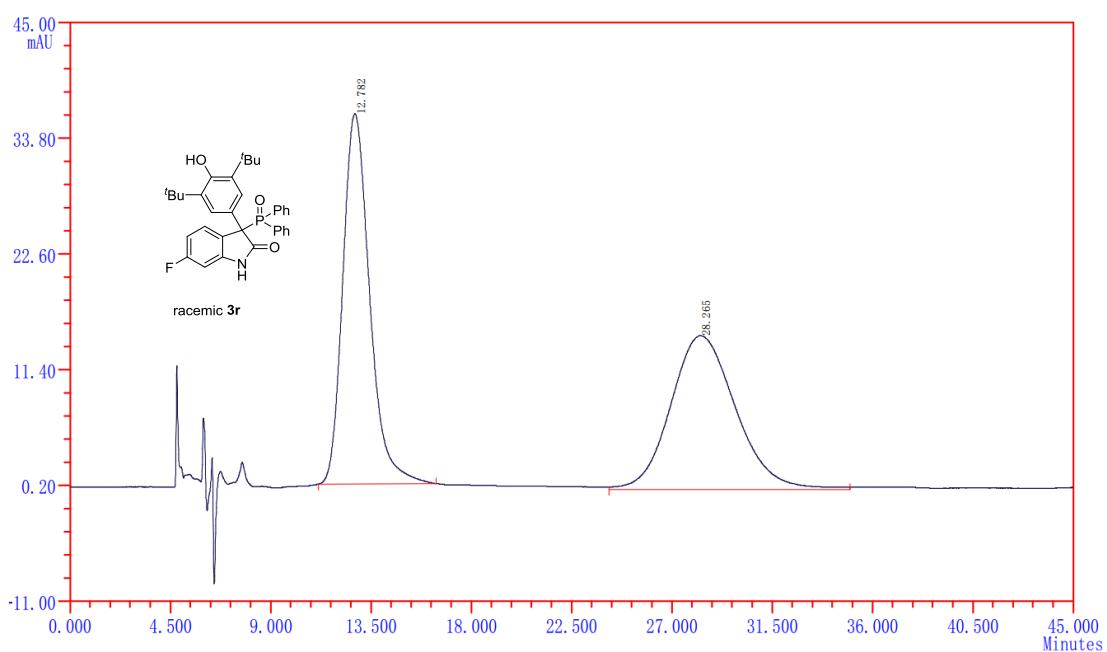
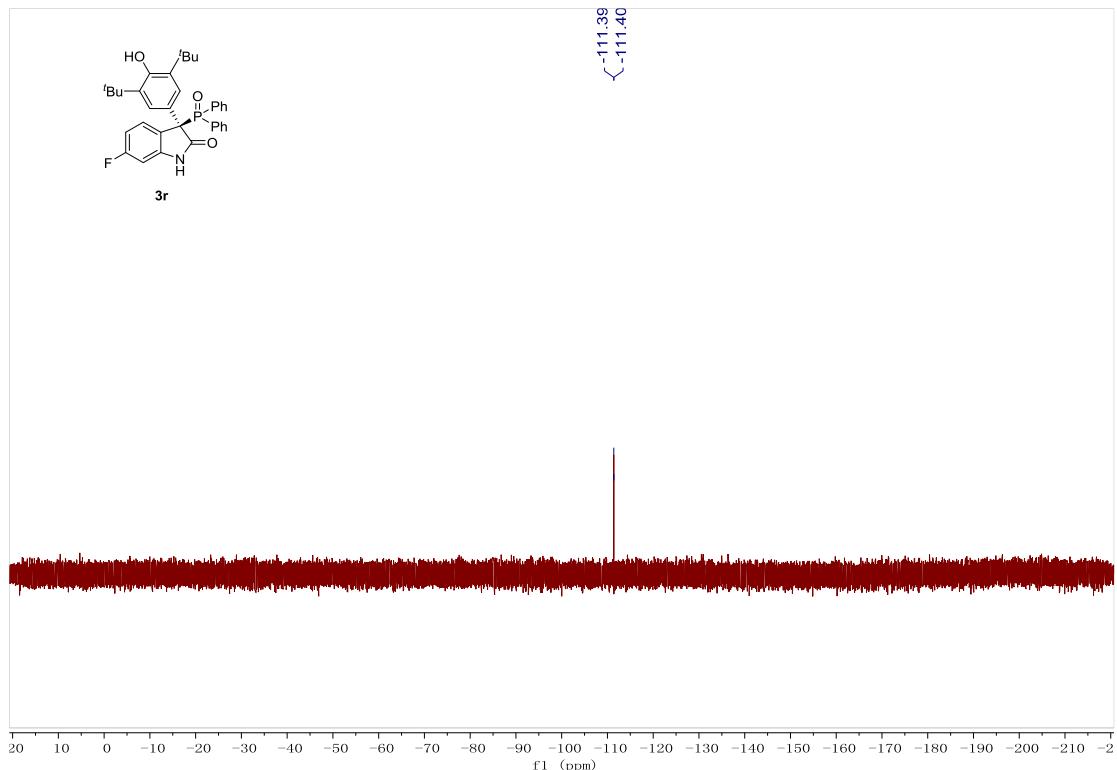


Peak #	RetTime [Min]	Height [mAu]	Area [mAu*s]	Area %
1	8.548	35.87	962.215	49.951
2	10.690	44.85	964.113	50.049
Total:		80.72	1926.328	100.0000

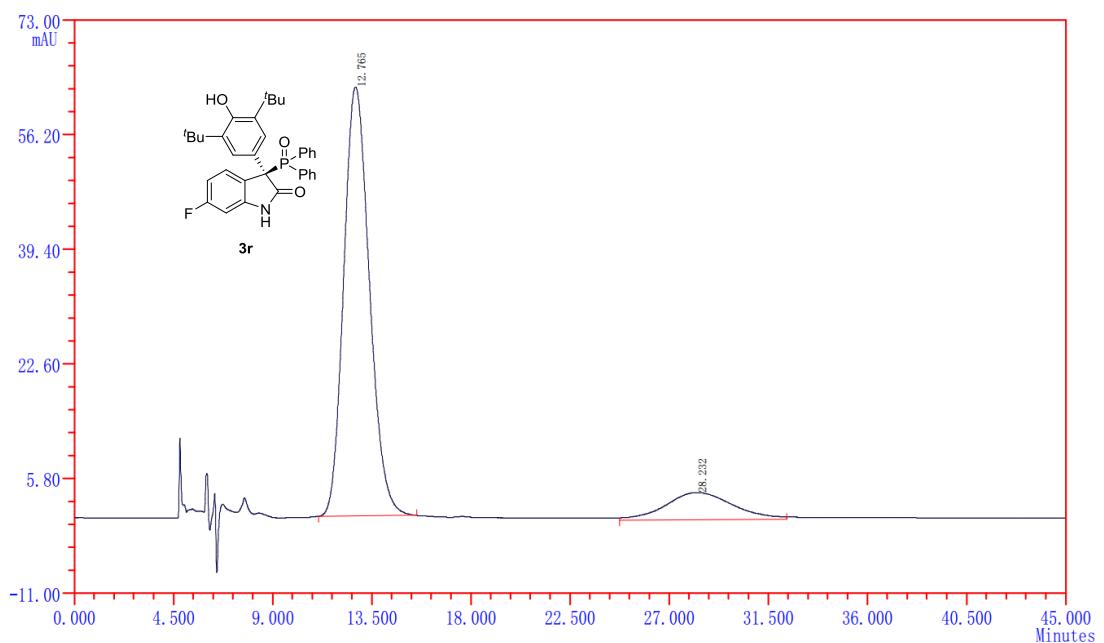


S67

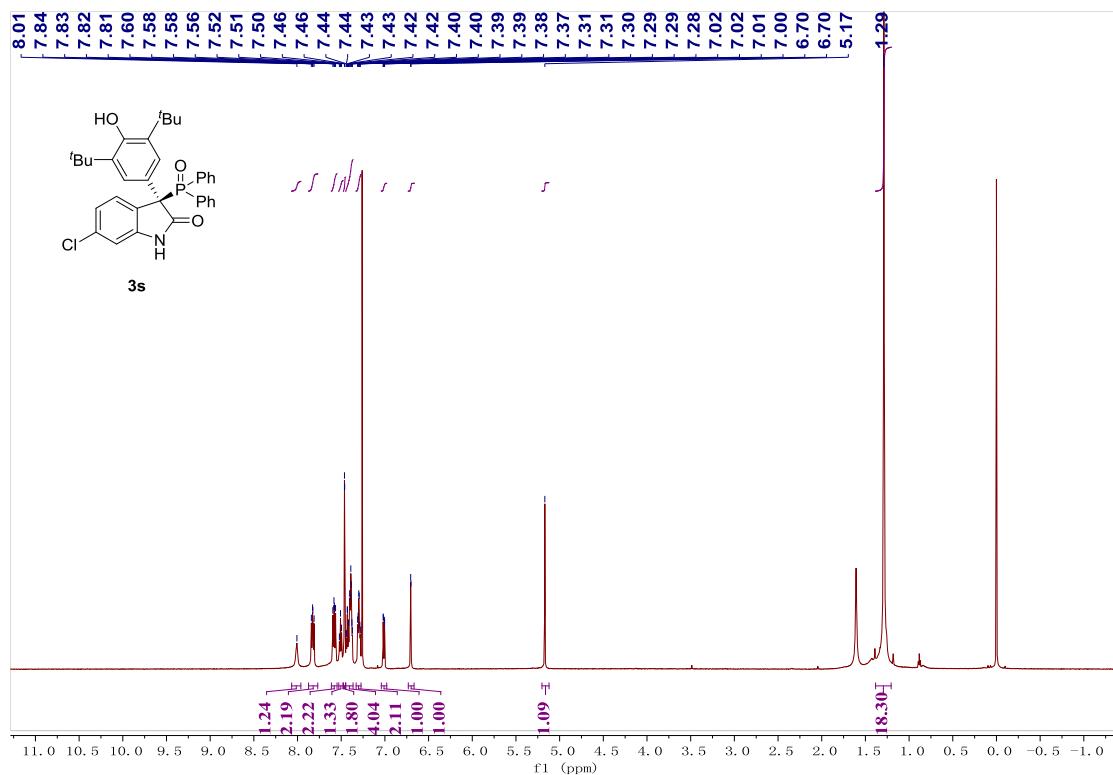


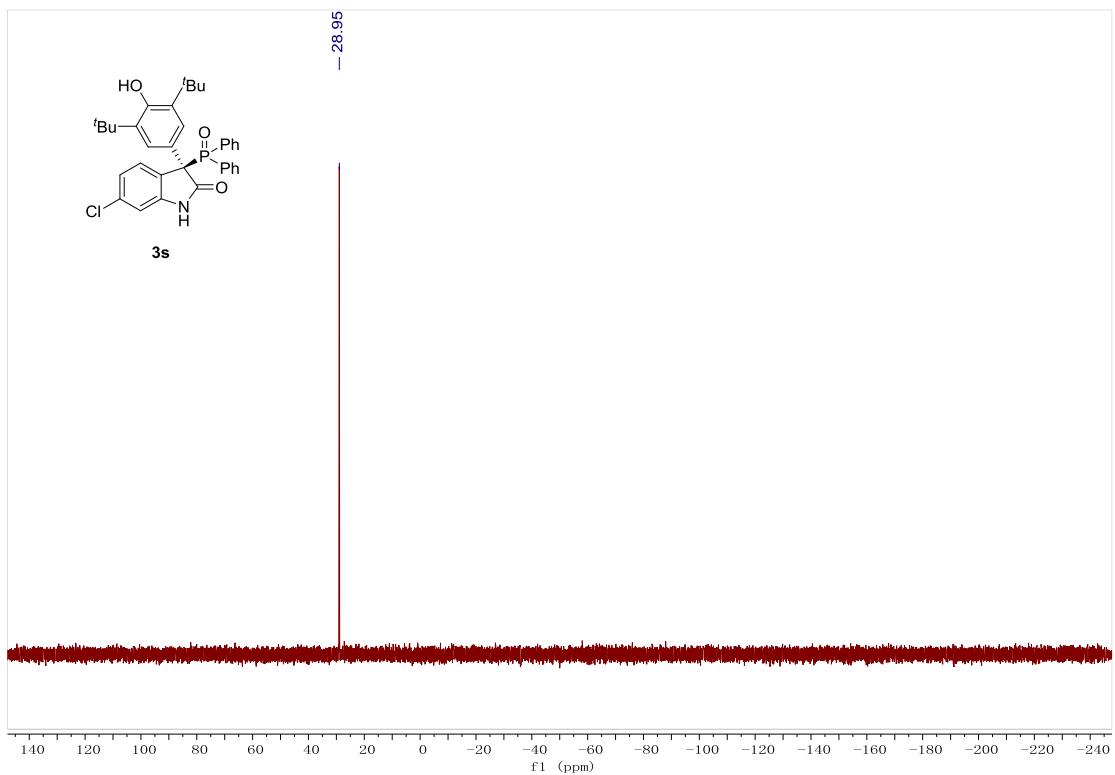
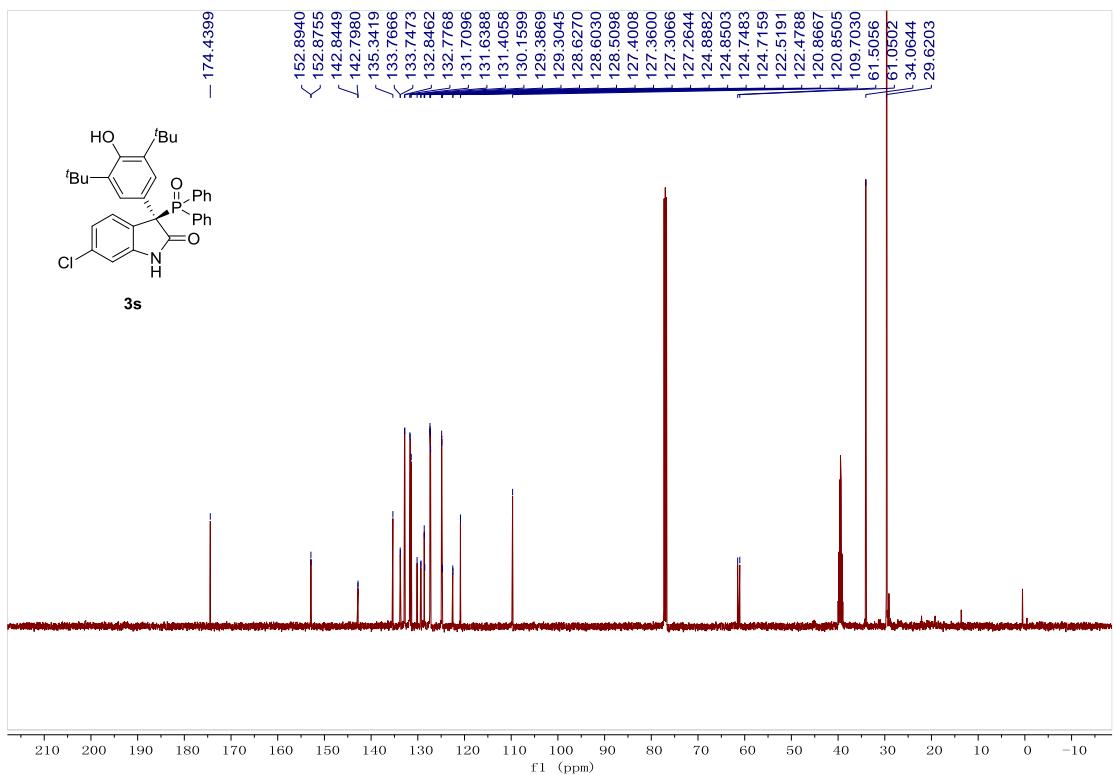


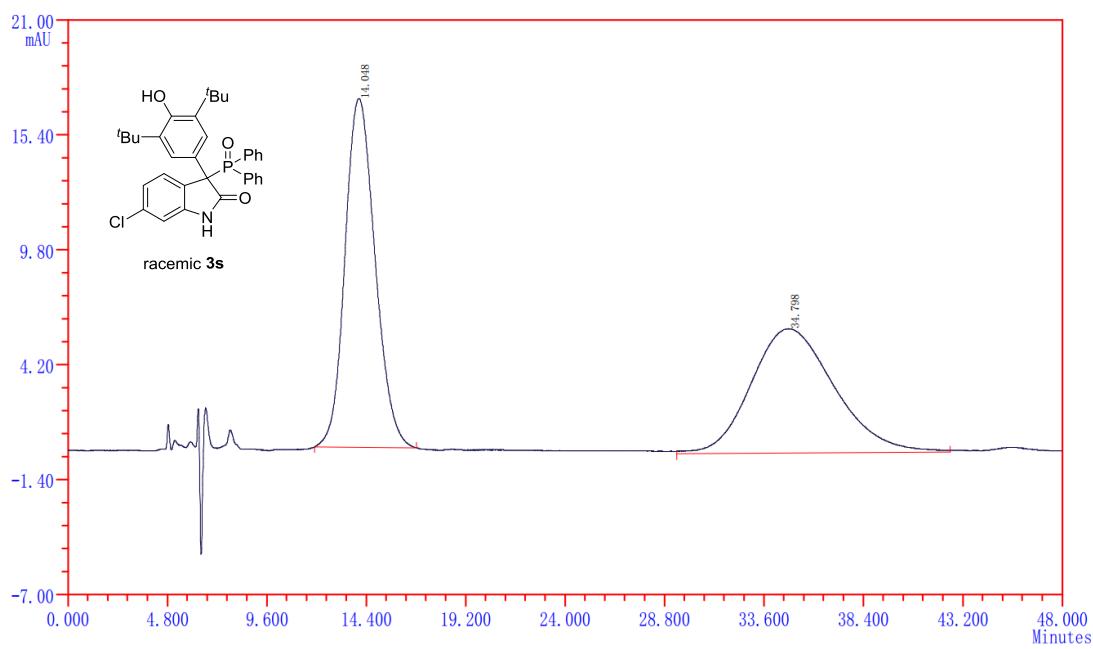
Peak #	RetTime [Min]	Height [mAu]	Area [mAu*s]	Area %
1	12.782	35.82	2998.913	49.903
2	28.265	14.86	3010.517	50.097
Total:		50.68	6009.429	100.0000



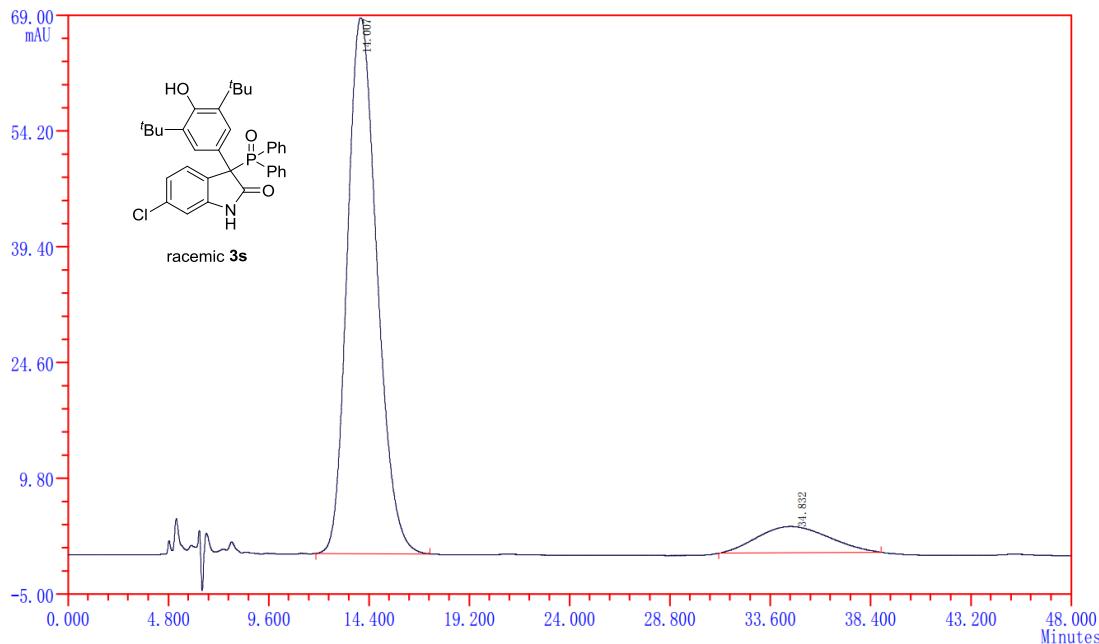
Peak #	RetTime [Min]	Height [mAu]	Area [mAu*s]	Area %
1	12.765	62.90	5106.763	85.519
2	28.232	4.01	864.753	14.481
Total:		66.91	5971.517	100.0000



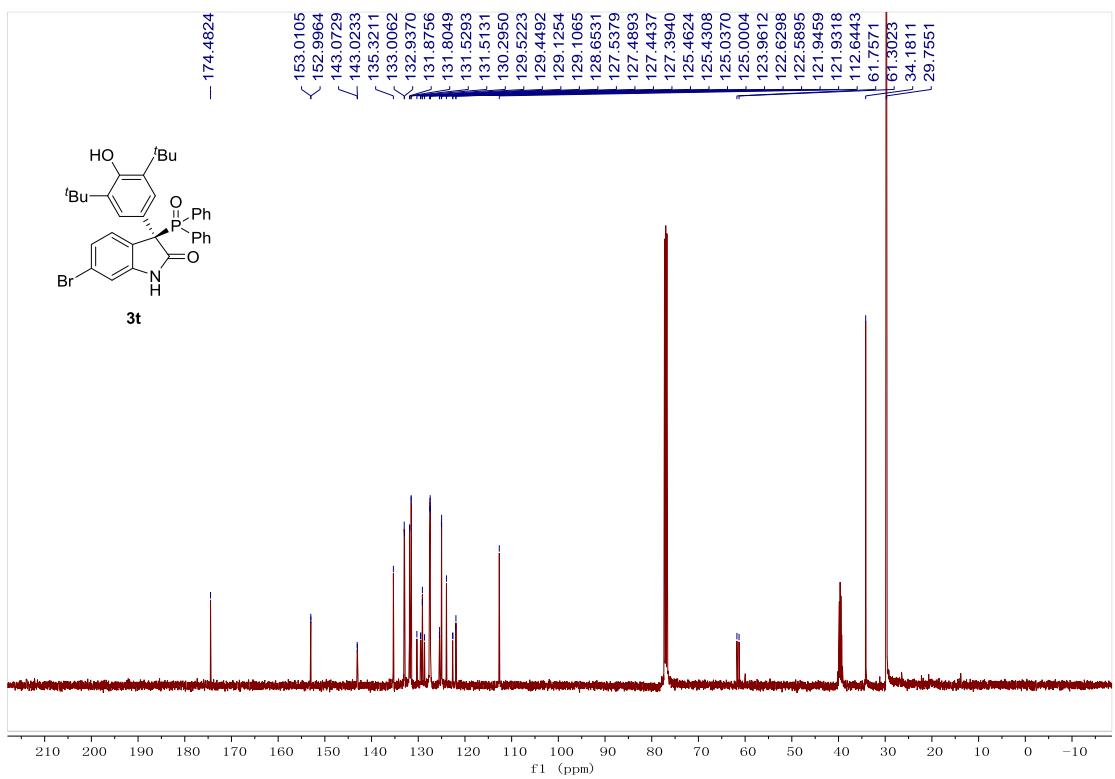
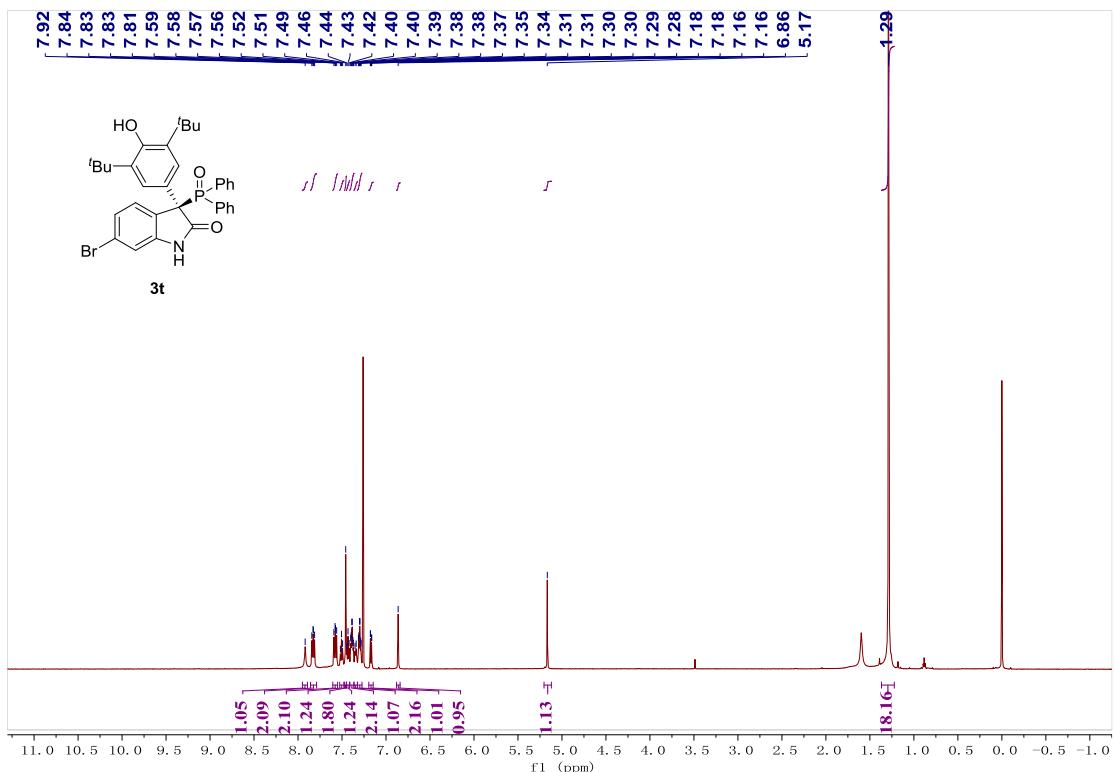


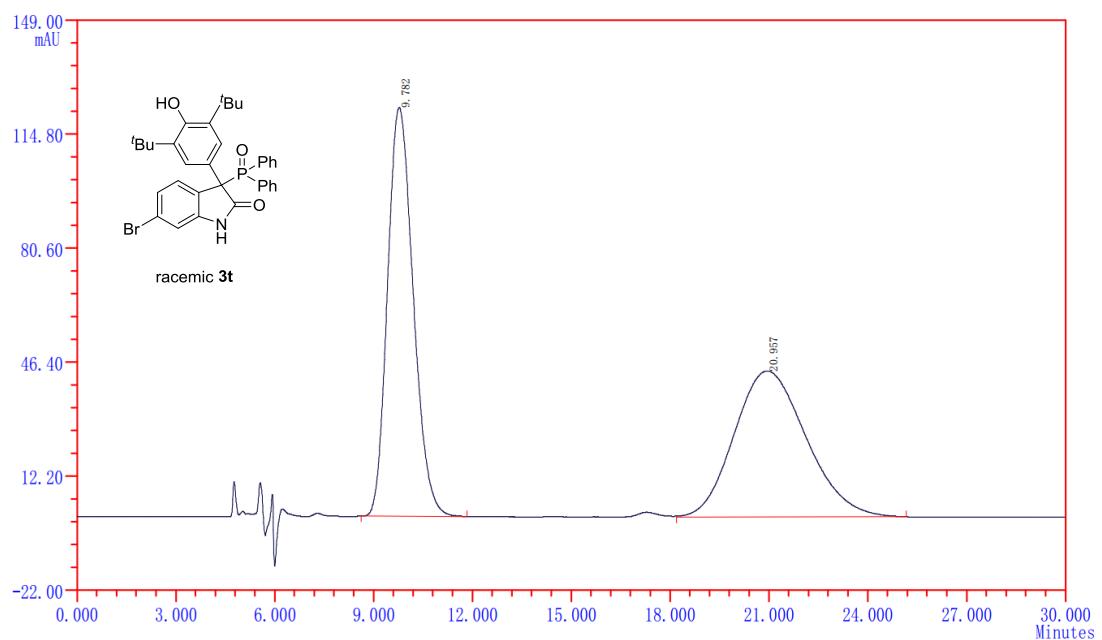
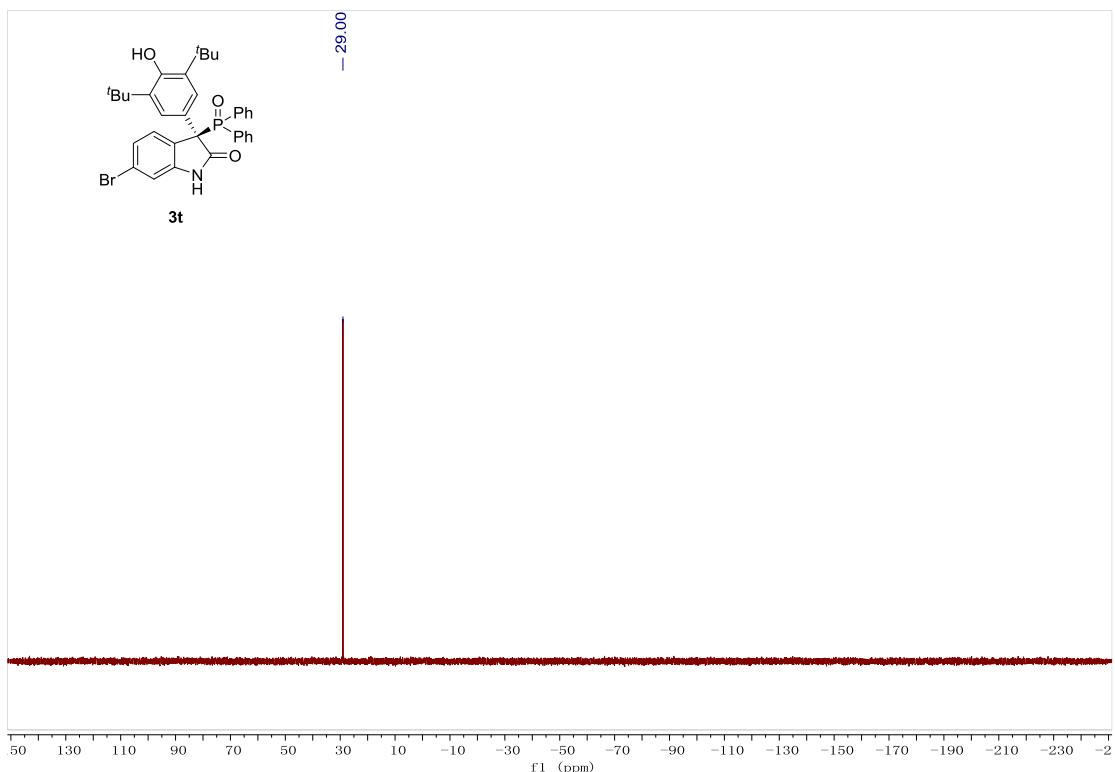


Peak #	RetTime [Min]	Height [mAu]	Area [mAu*s]	Area %
1	14.048	17.00	1714.971	50.191
2	34.798	6.06	1701.918	49.809
Total:		23.06	3416.889	100.0000

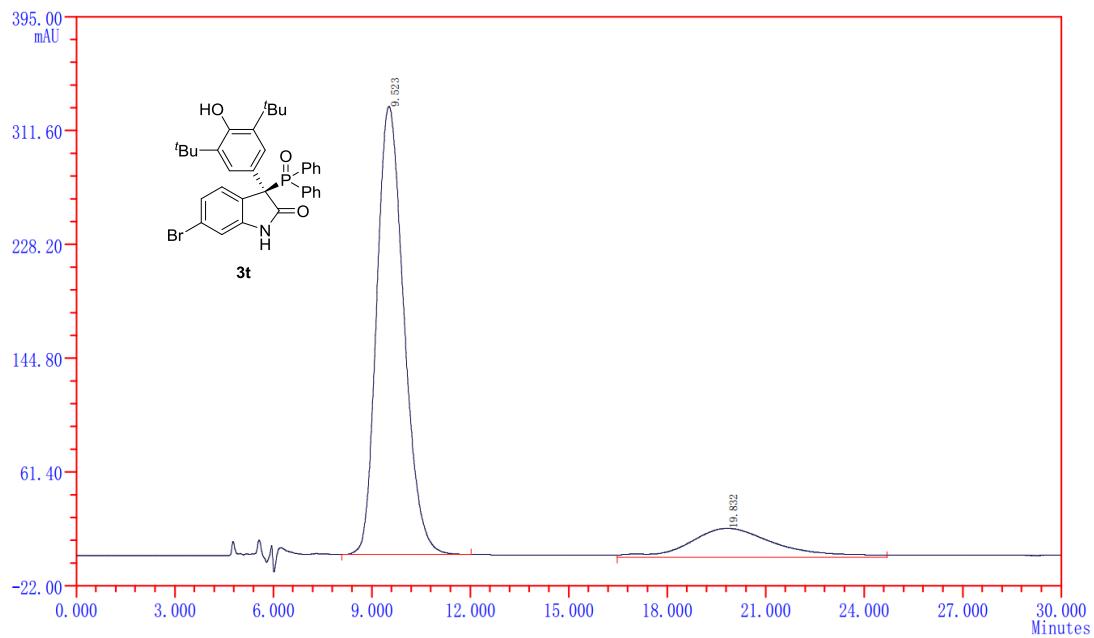


Peak #	RetTime [Min]	Height [mAu]	Area [mAu*s]	Area %
1	14.007	68.59	6770.425	89.404
2	34.832	3.36	802.411	10.596
Total:		71.95	7572.836	100.0000

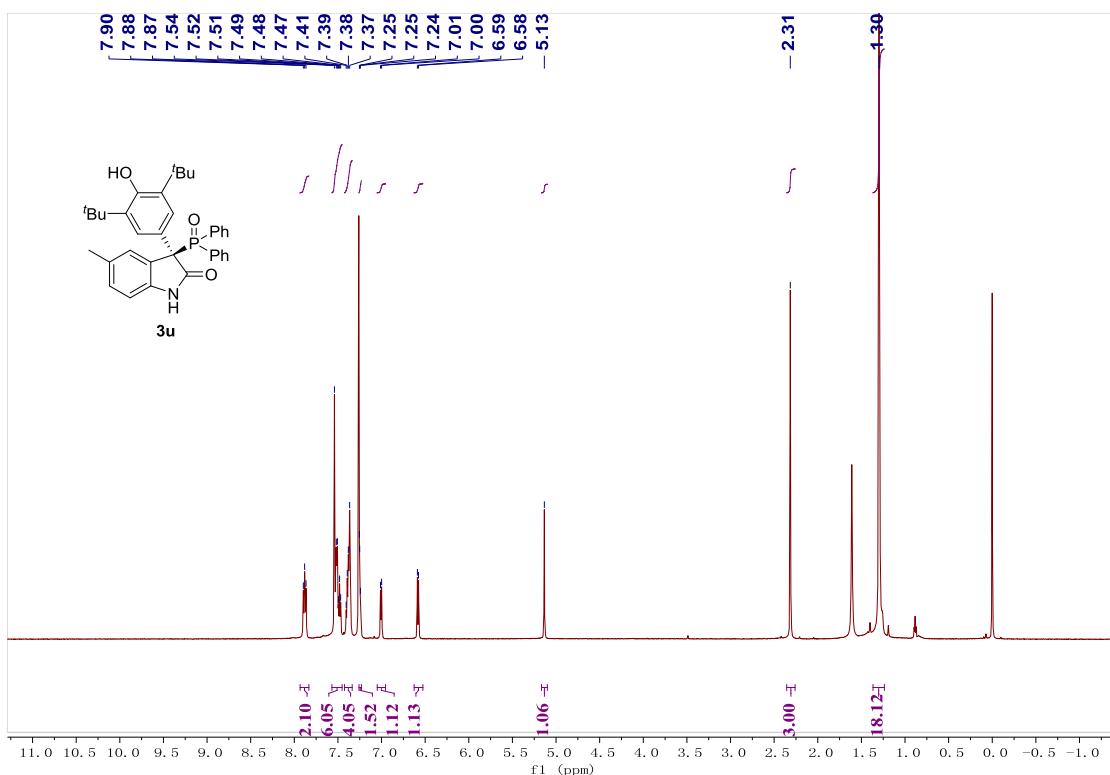


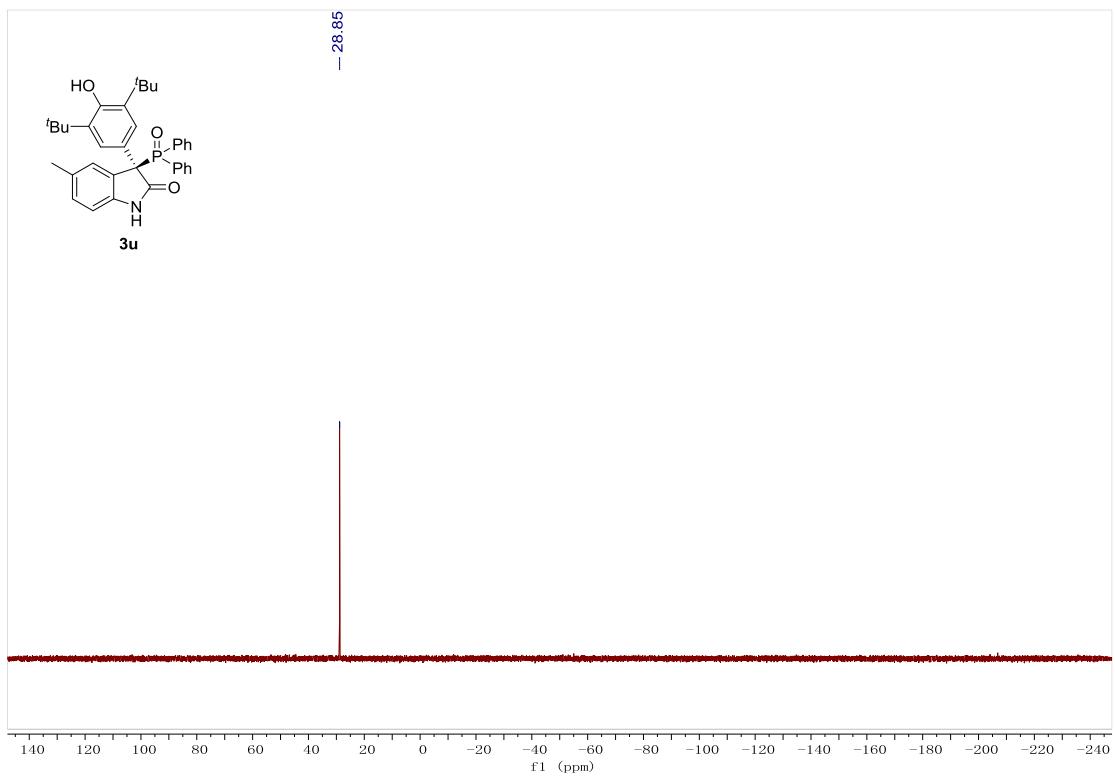
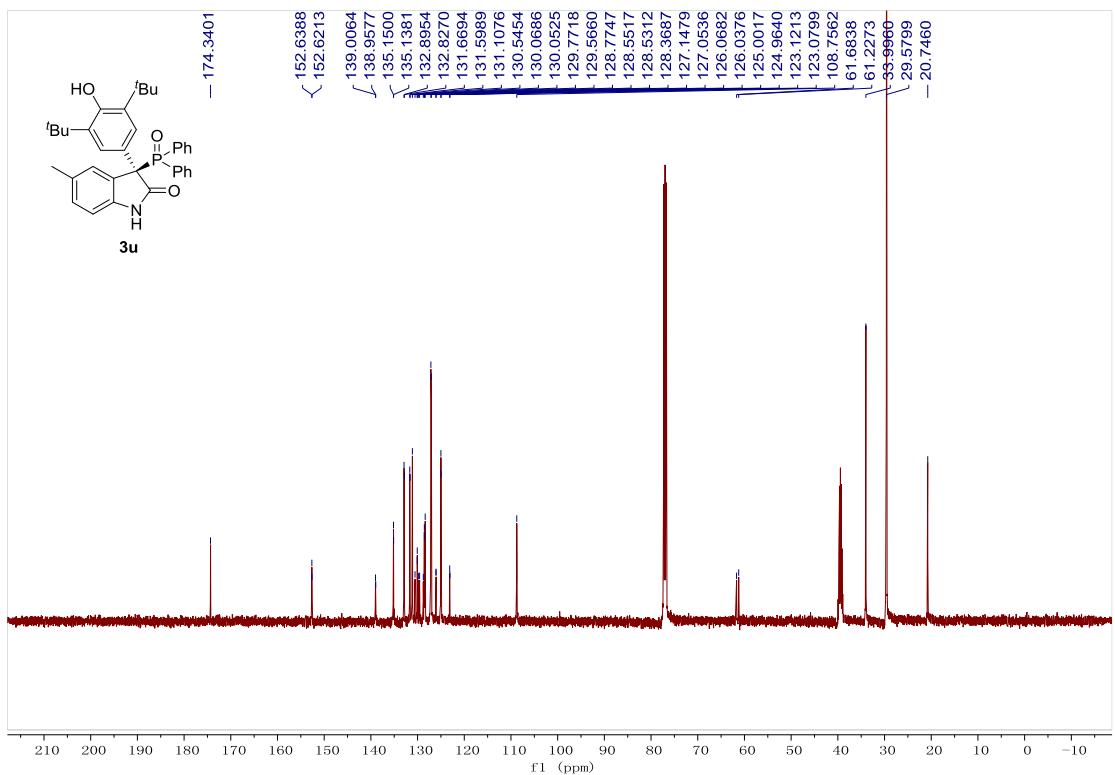


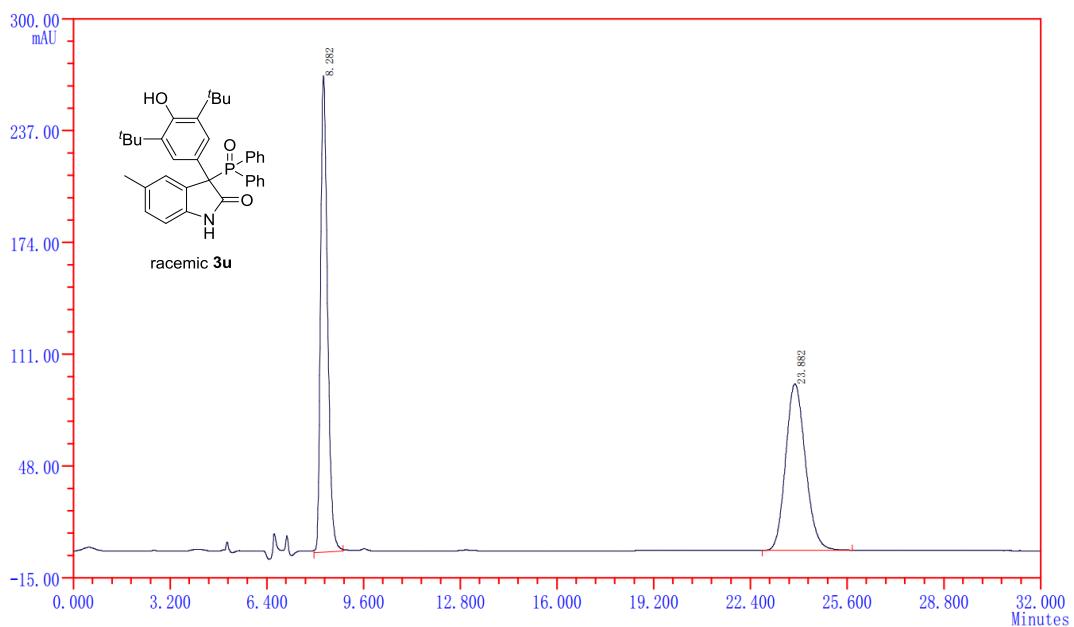
Peak #	RetTime [Min]	Height [mAu]	Area [mAu*s]	Area %
1	9.782	122.63	6652.943	50.050
2	20.957	43.75	6639.538	49.950
Total:		166.38	13292.481	100.0000



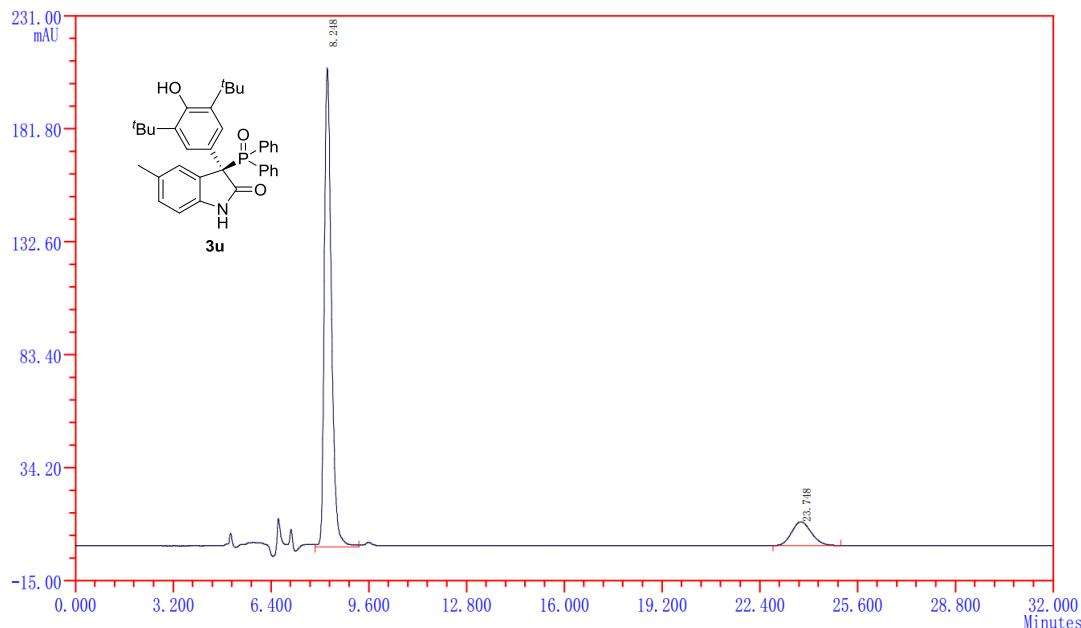
Peak	RetTime	Height	Area	Area
#	[Min]	[mAu]	[mAu*s]	%
1	9.523	328.39	18883.414	82.544
2	19.832	21.28	3993.449	17.456
Total:		349.67	22876.863	100.0000



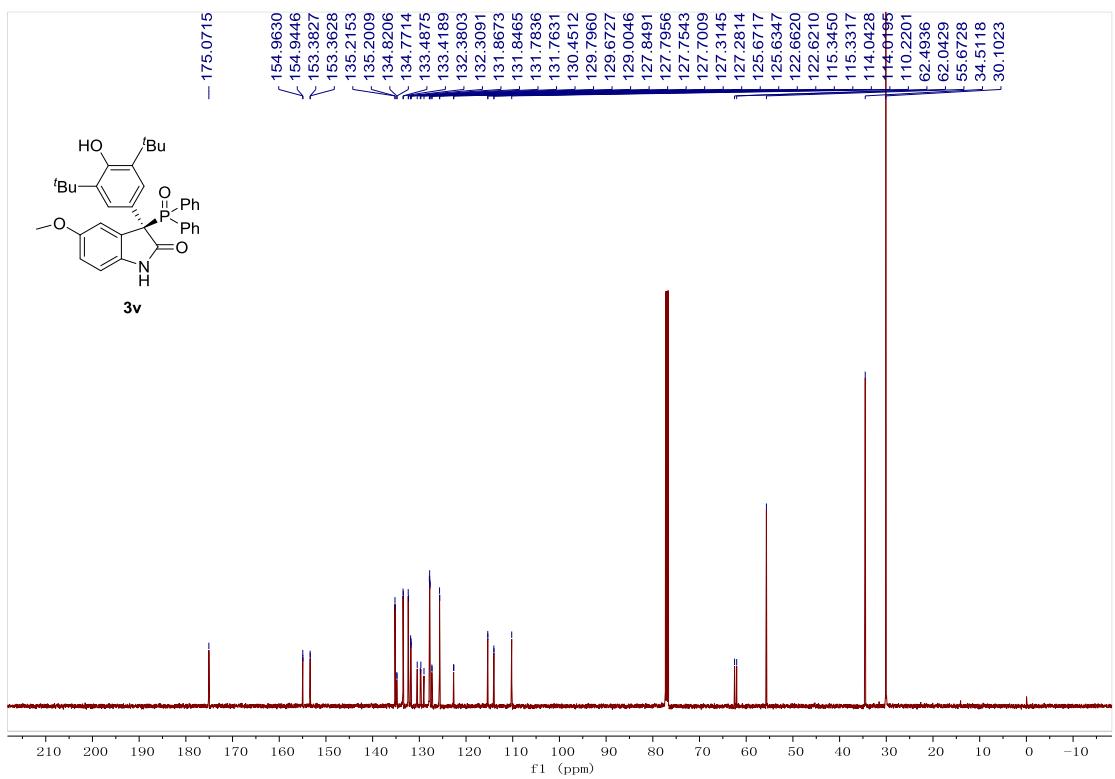
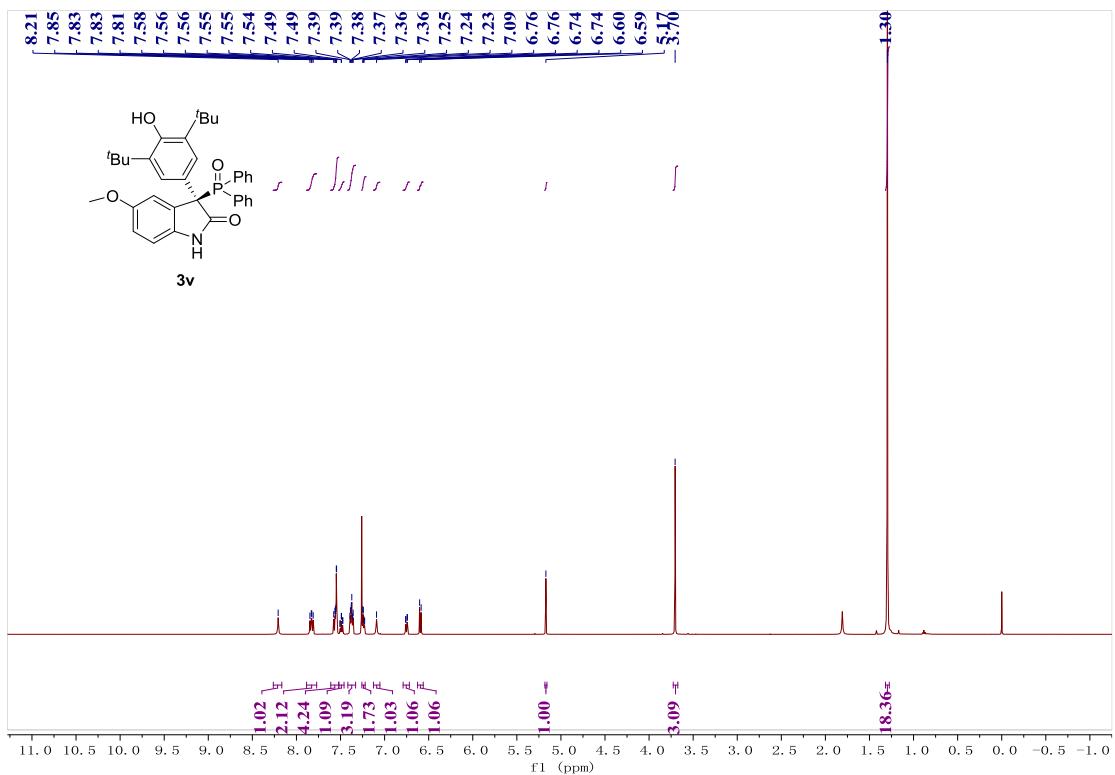


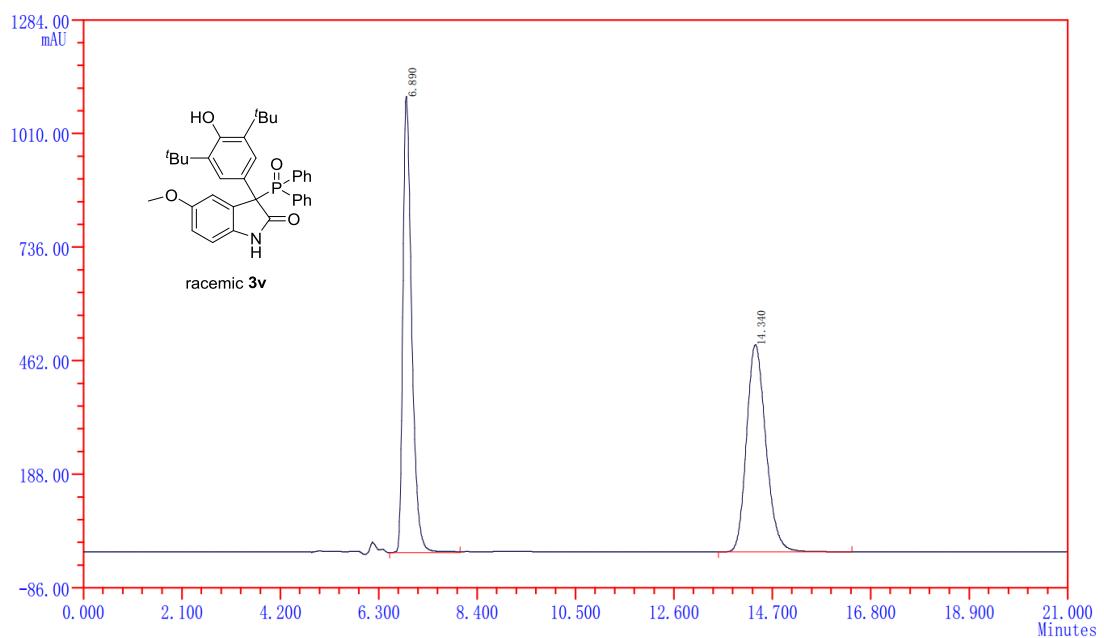
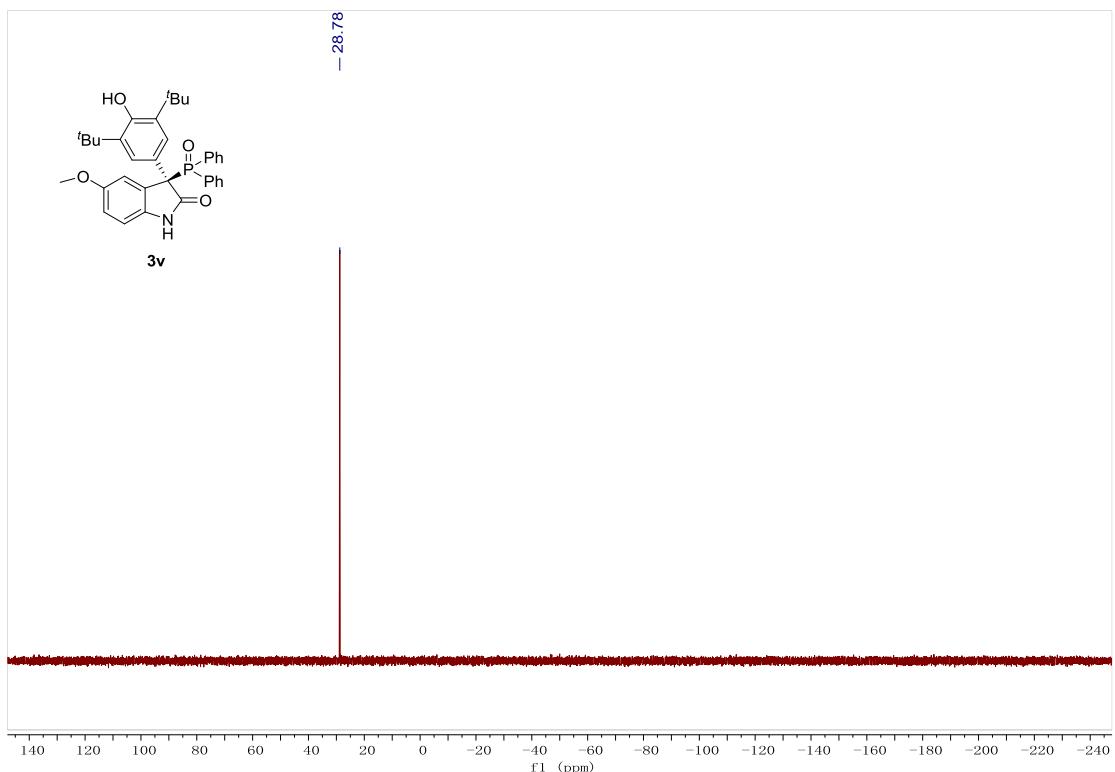


Peak #	RetTime [Min]	Height [mAu]	Area [mAu*s]	Area %
1	8.282	268.21	4320.289	50.176
2	23.882	93.87	4289.950	49.824
Total:		362.08	8610.238	100.0000

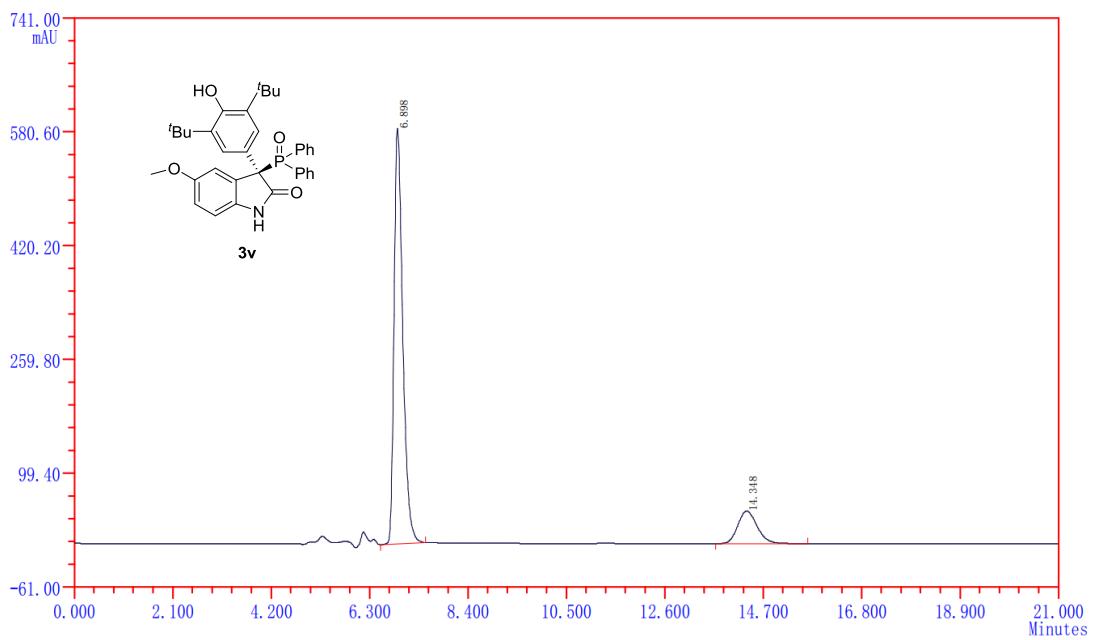


Peak #	RetTime [Min]	Height [mAu]	Area [mAu*s]	Area %
1	8.248	208.50	3371.057	87.761
2	23.748	10.40	470.105	12.239
Total:		362.08	3841.162	100.0000

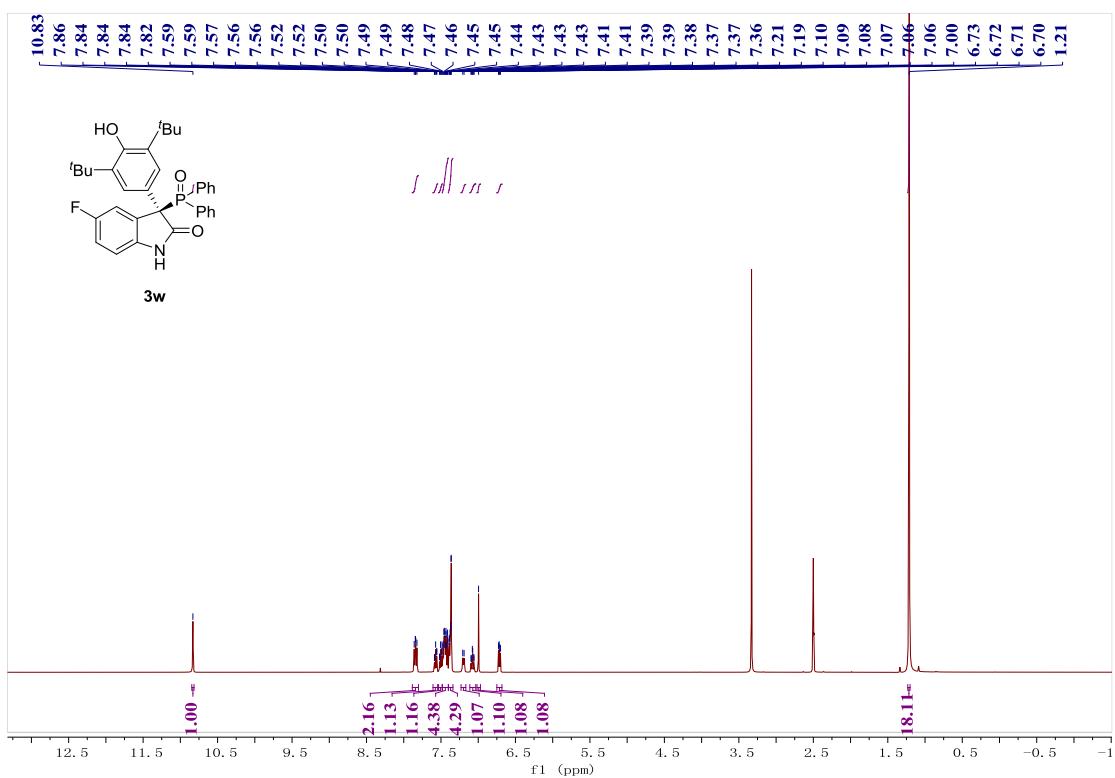


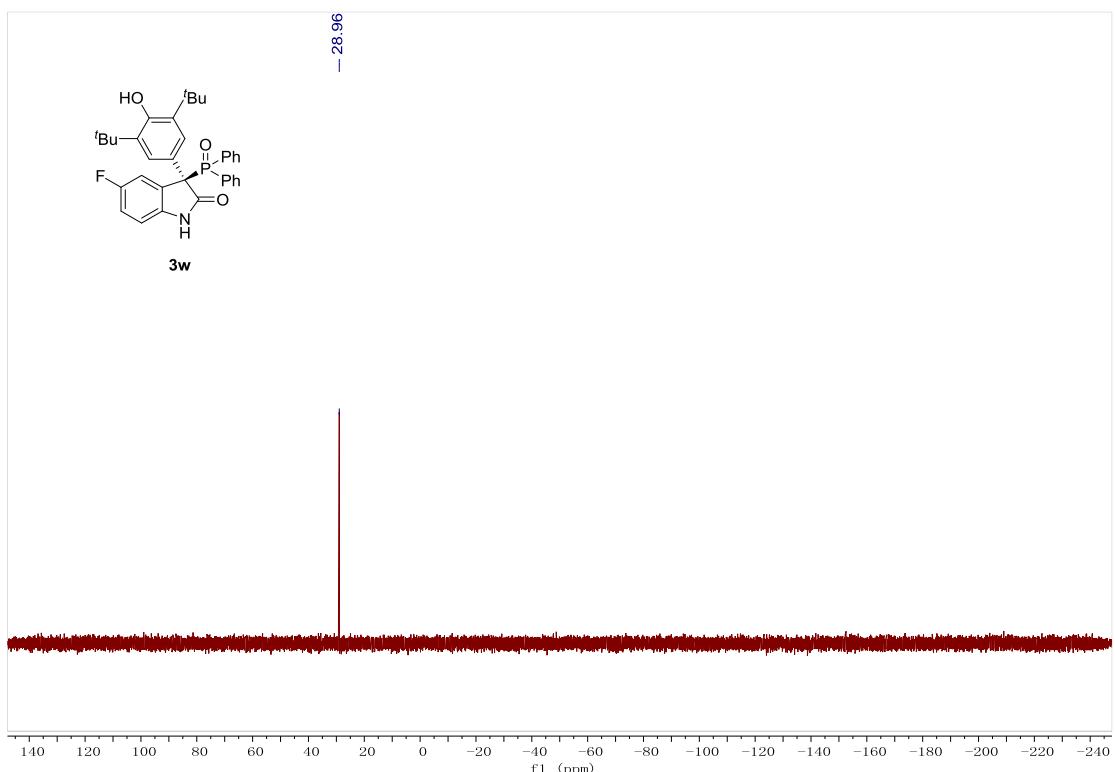
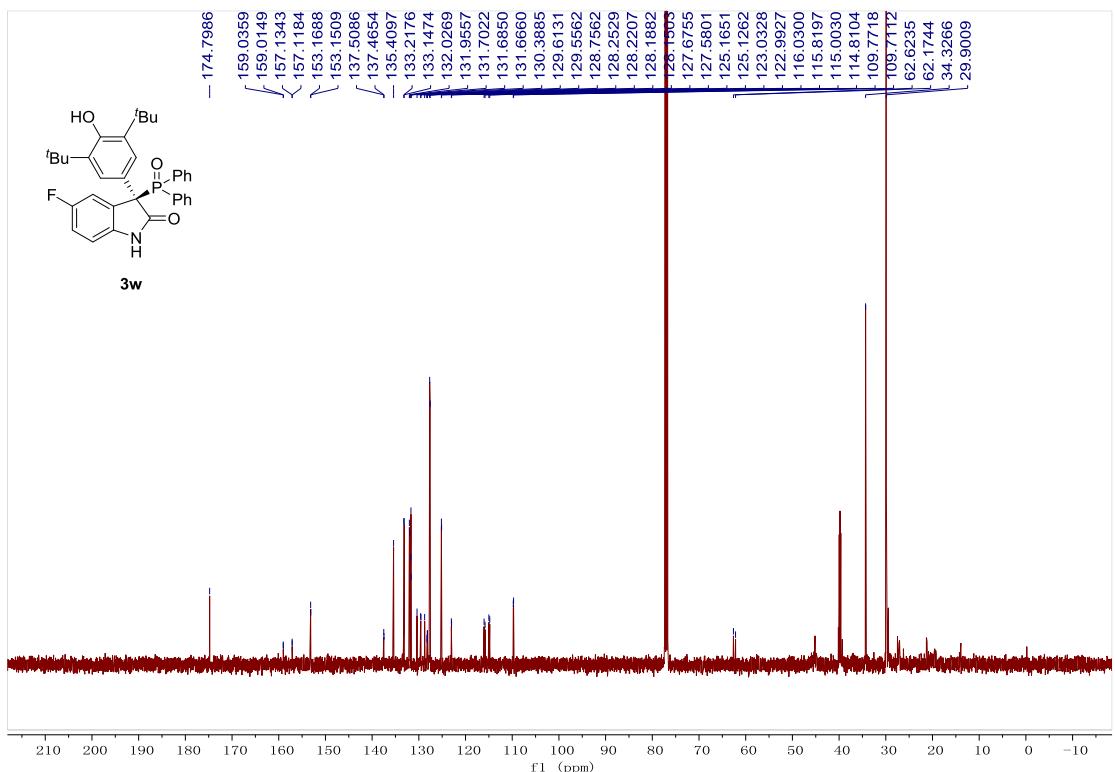


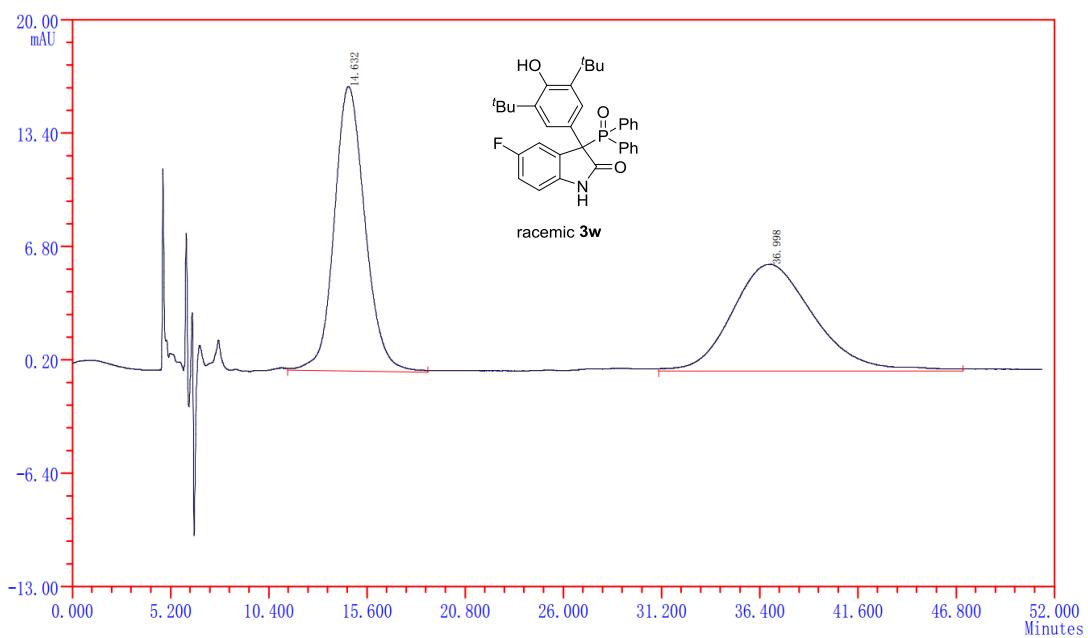
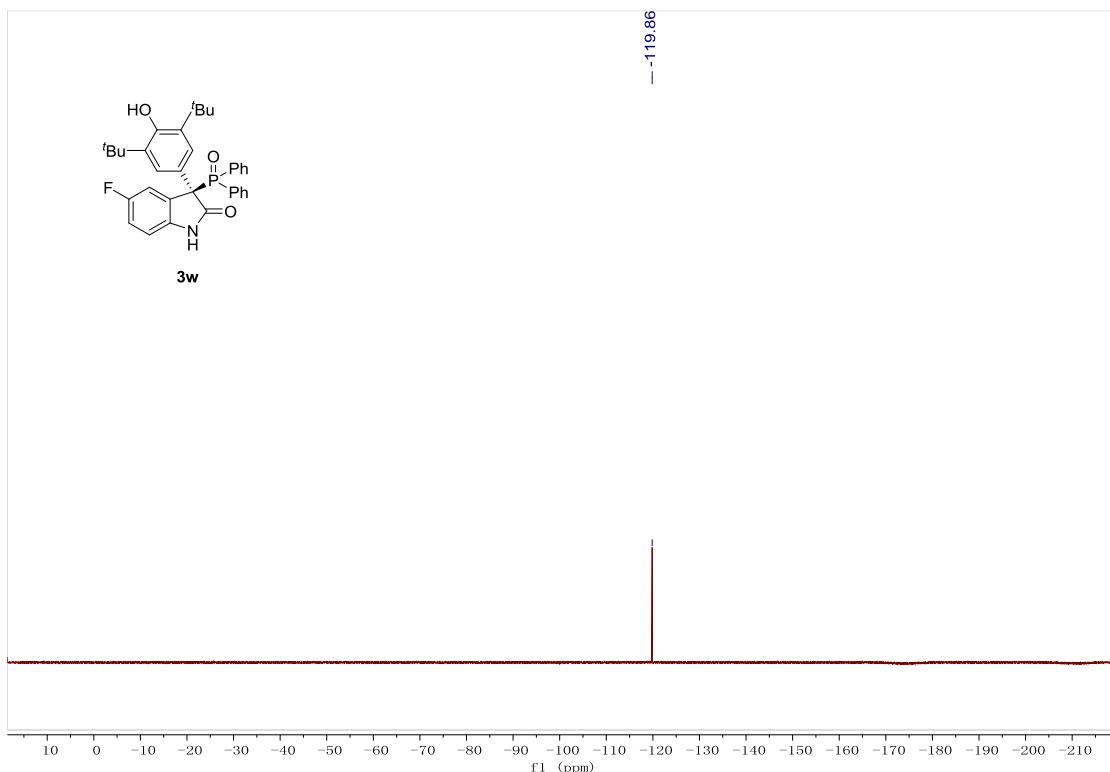
Peak #	RetTime [Min]	Height [mAu]	Area [mAu*s]	Area %
1	6.890	1100.23	14471.599	50.144
2	14.340	499.59	14388.358	49.856
Total:		1599.82	28859.957	100.0000



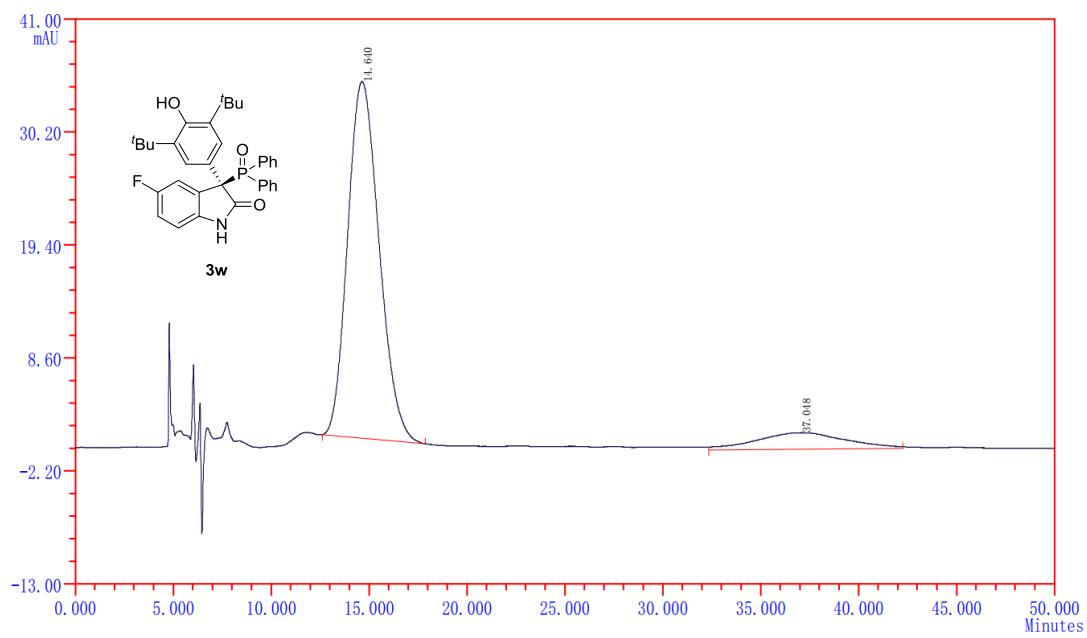
Peak	RetTime	Height	Area	Area
#	[Min]	[mAu]	[mAu*s]	%
1	6.898	586.25	7572.108	85.116
2	14.348	46.01	1324.138	14.884
Total:		632.26	8896.246	100.0000



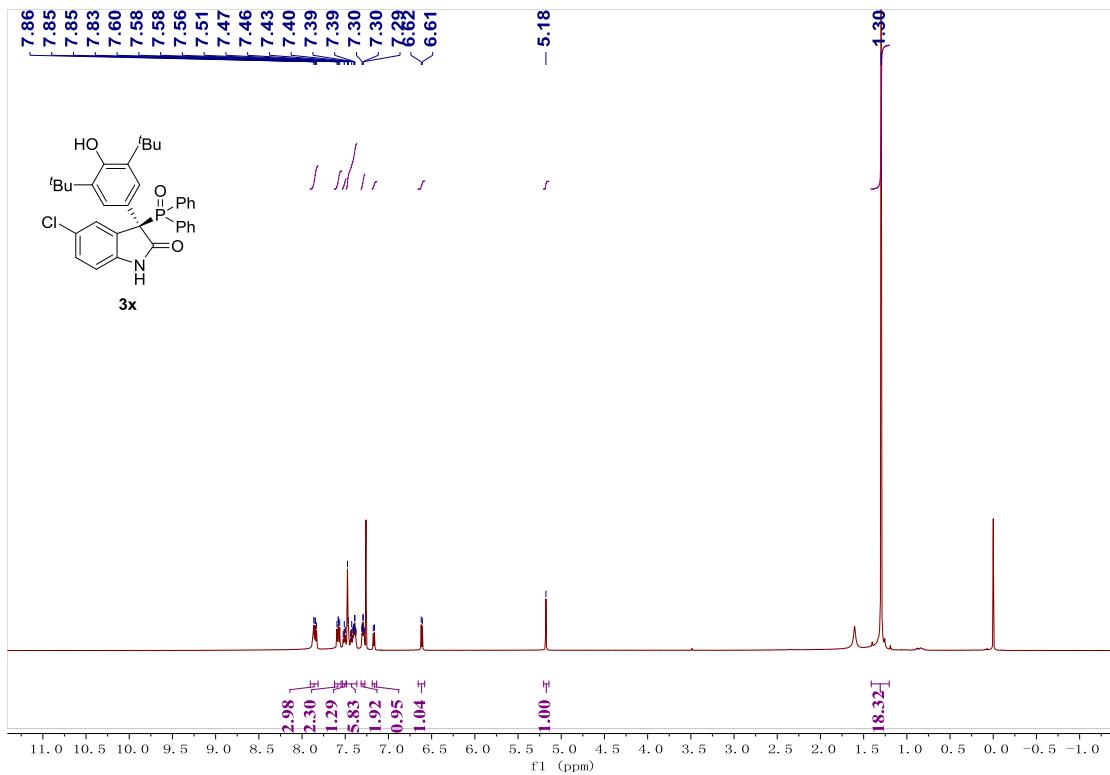


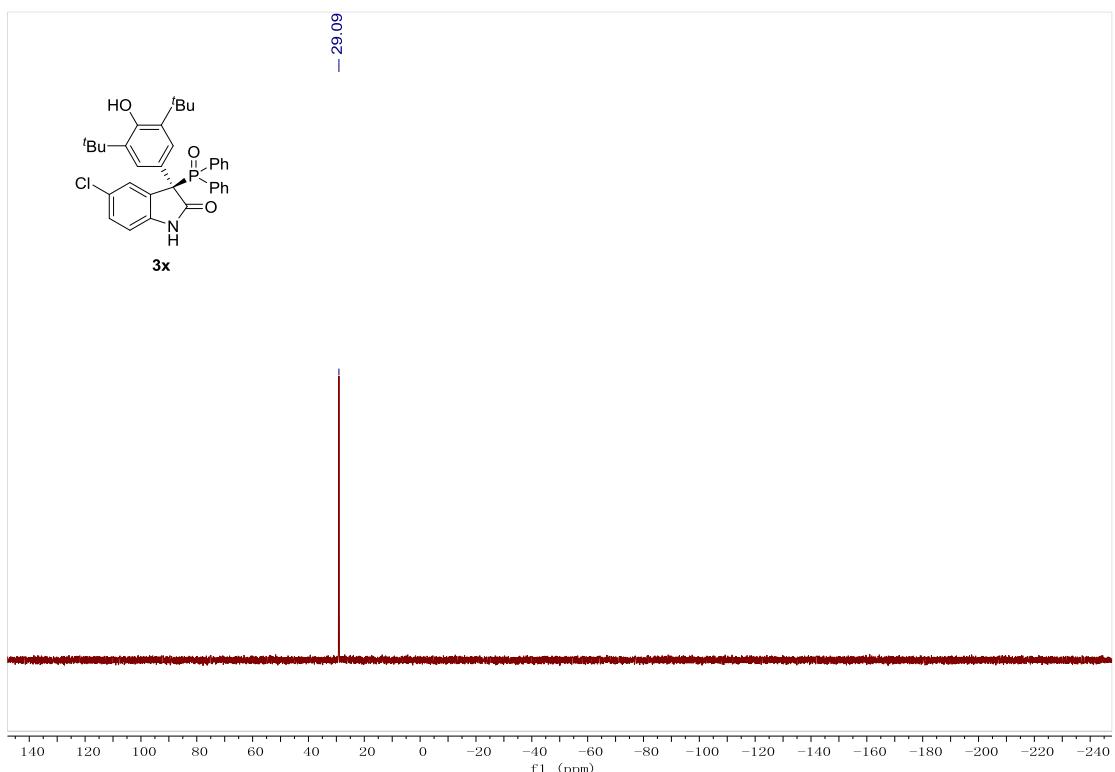
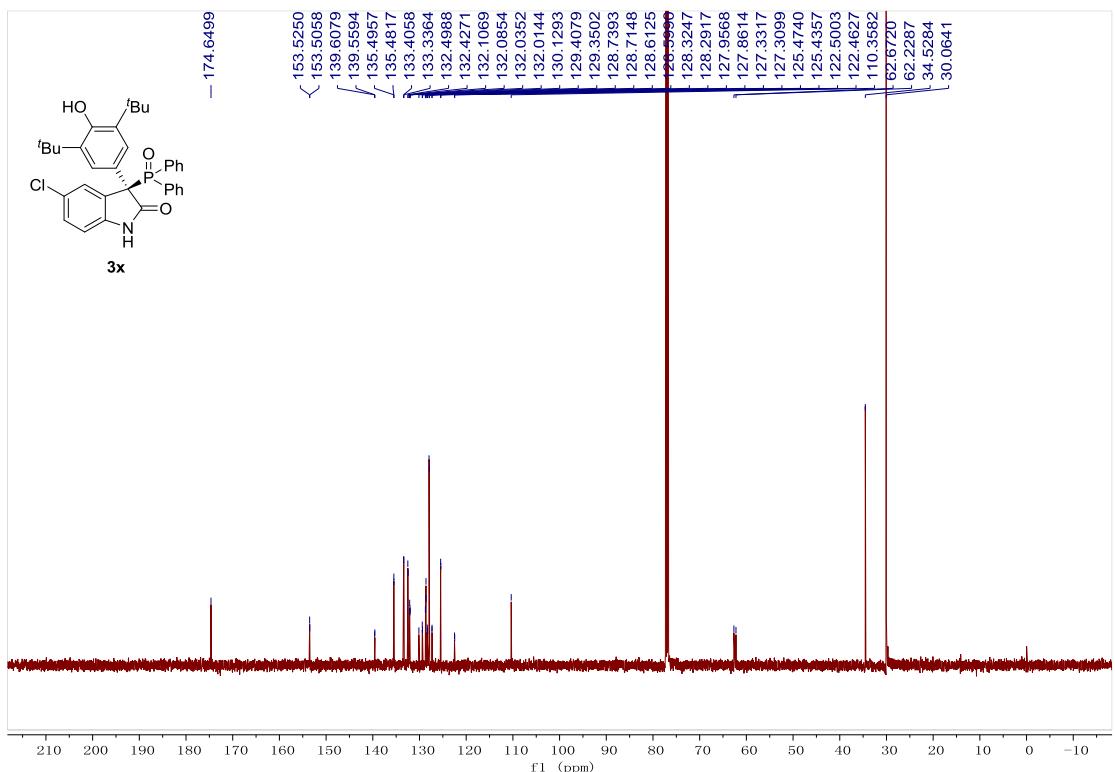


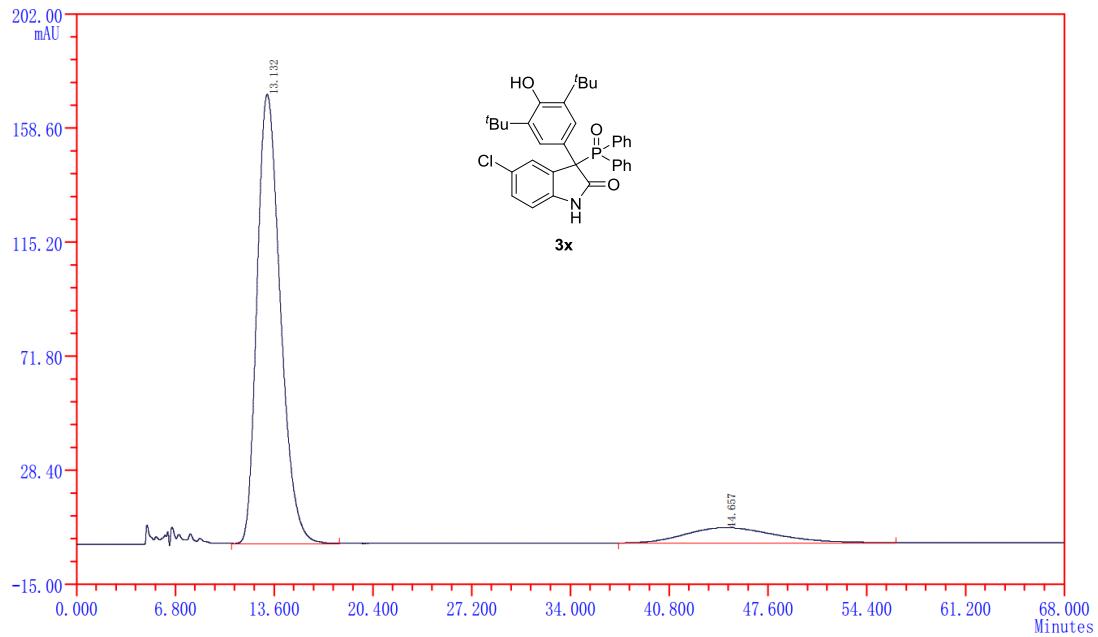
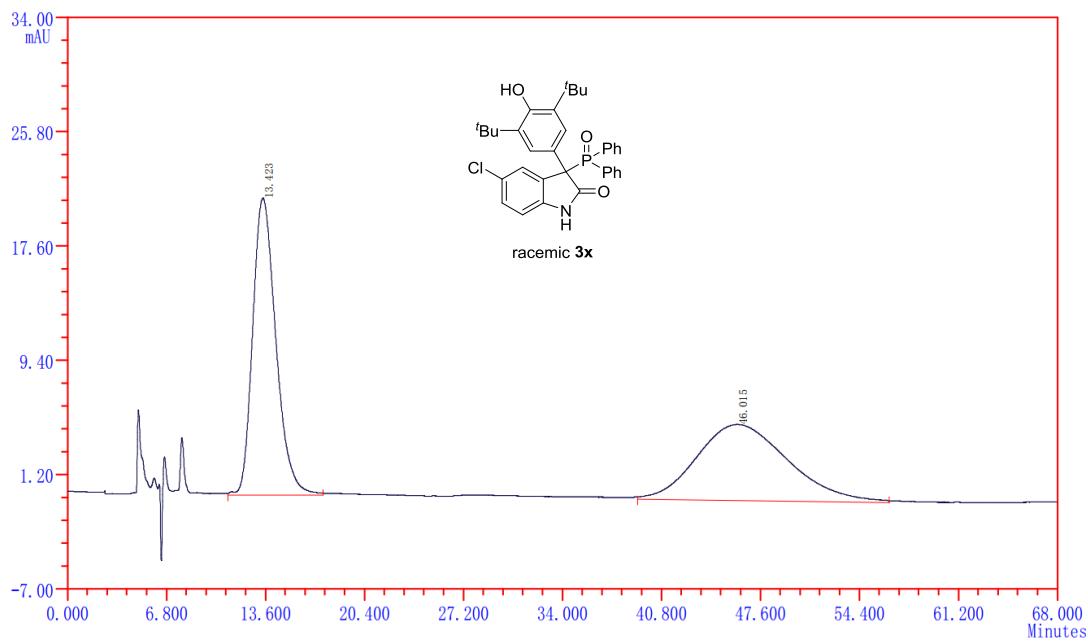
Peak #	RetTime [Min]	Height [mAu]	Area [mAu*s]	Area %
1	14.632	16.55	1871.109	49.939
2	36.998	6.21	1875.664	50.061
Total:		22.76	3746.772	100.0000

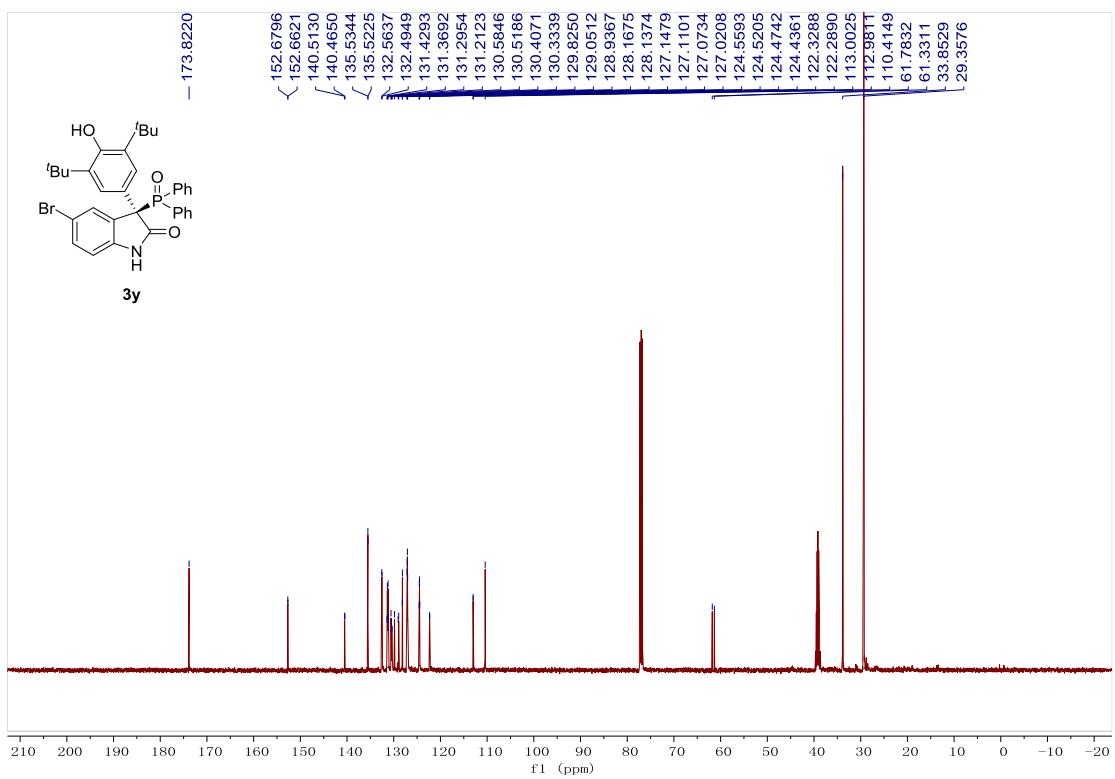
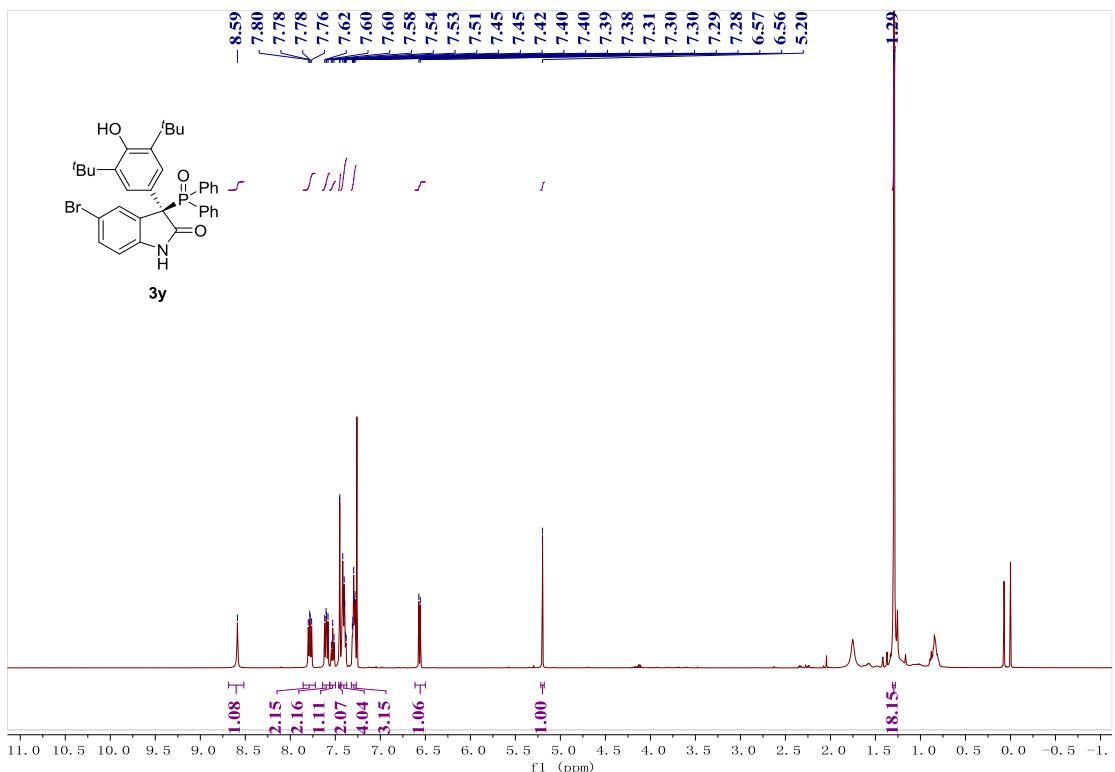


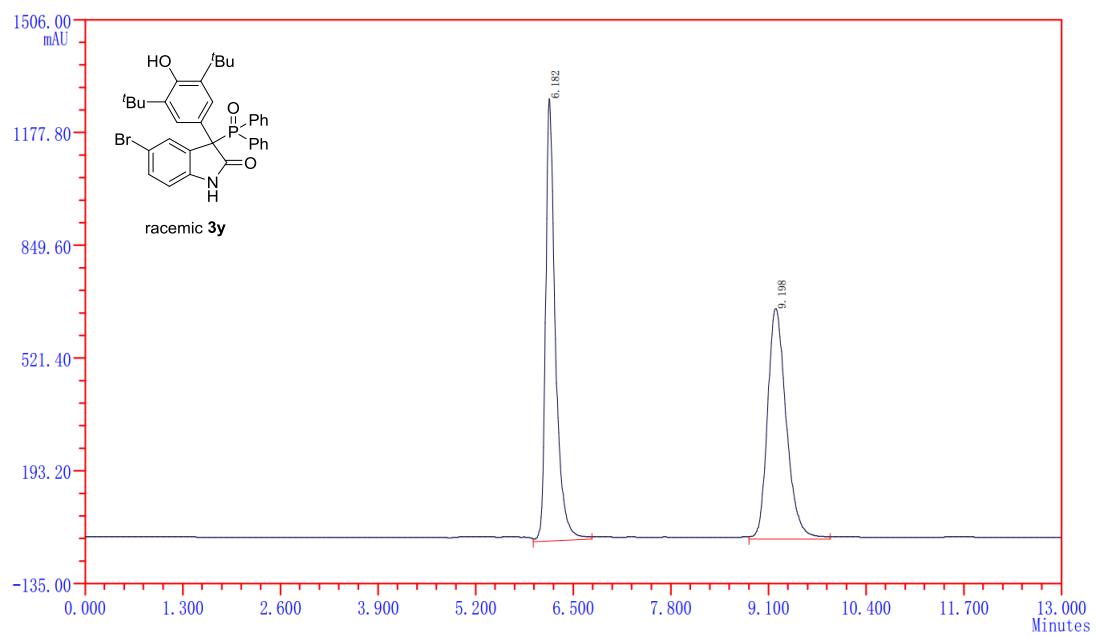
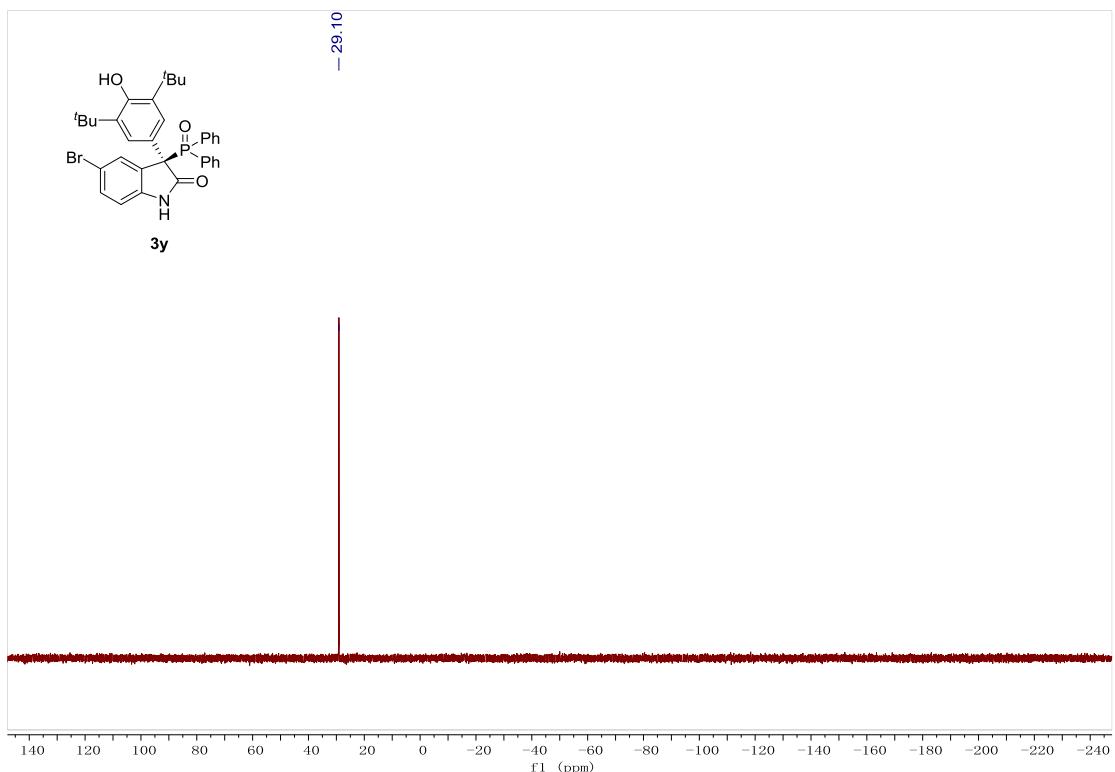
Peak	RetTime	Height	Area	Area
#	[Min]	[mAu]	[mAu*s]	%
1	14.640	34.08	3813.059	88.402
2	37.048	1.57	500.271	11.598
Total:		35.65	4313.329	100.0000



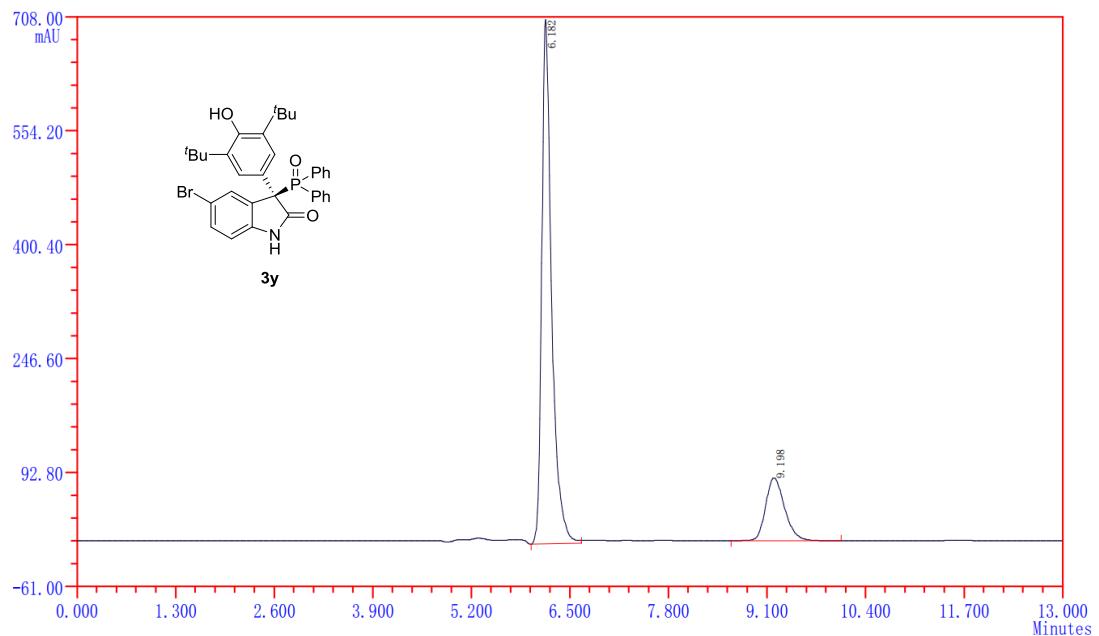




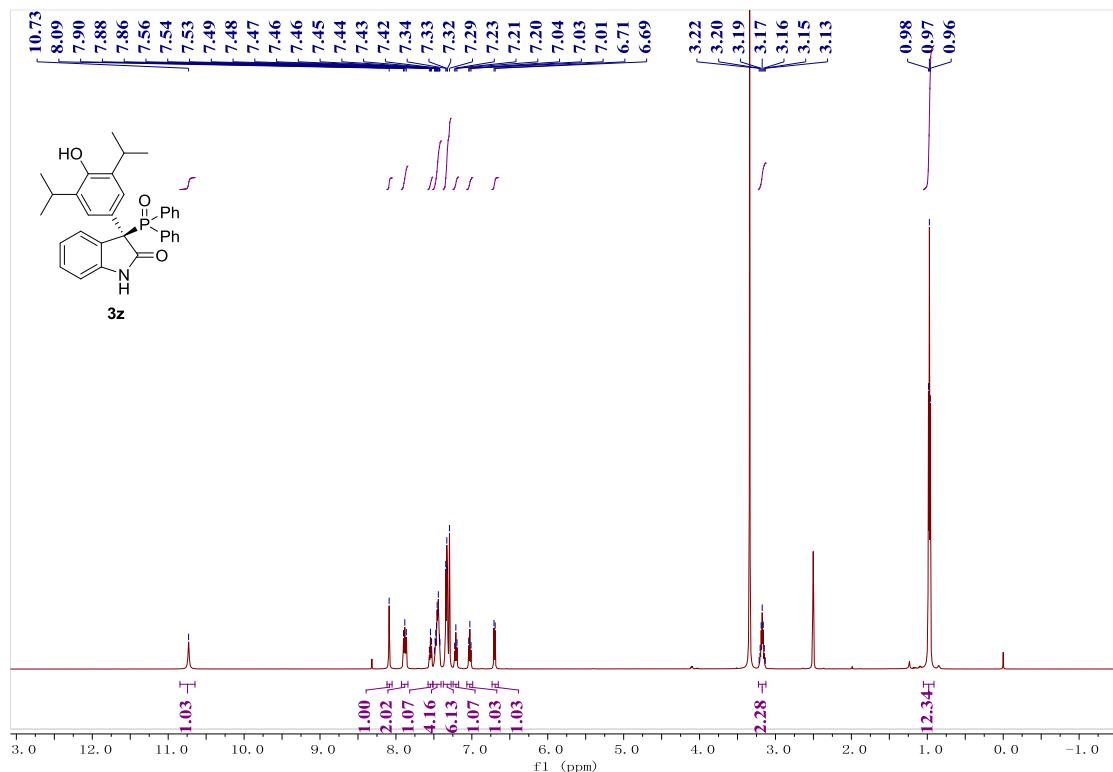


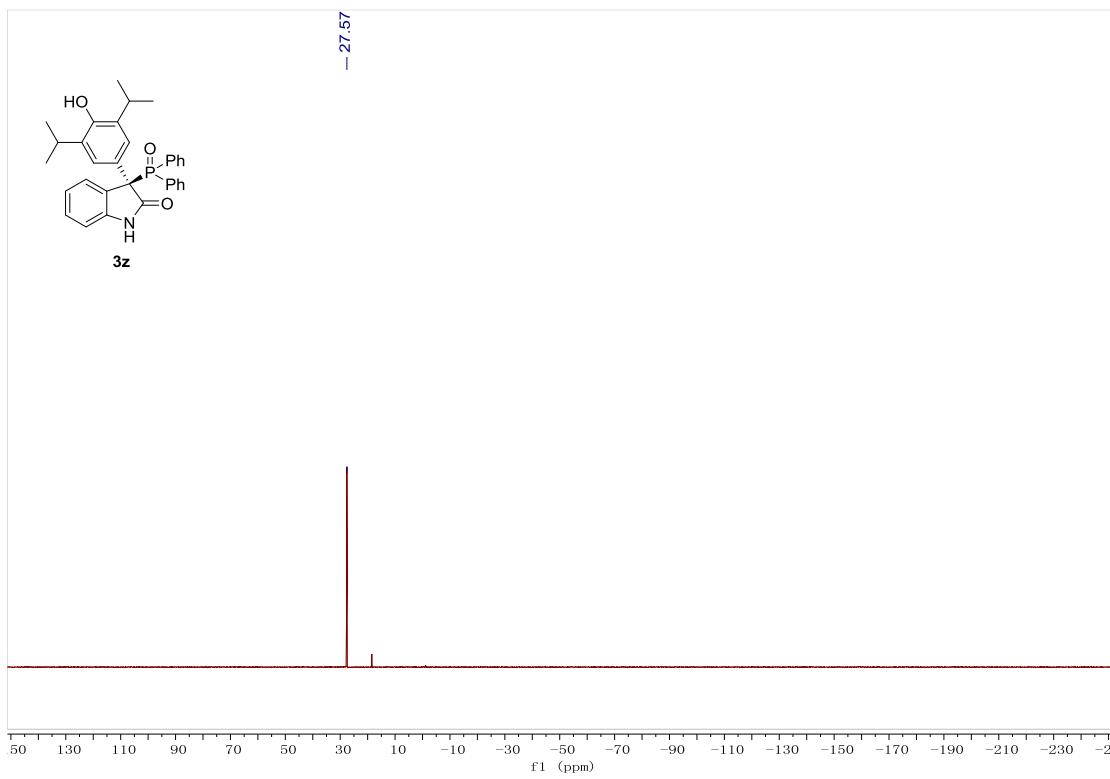
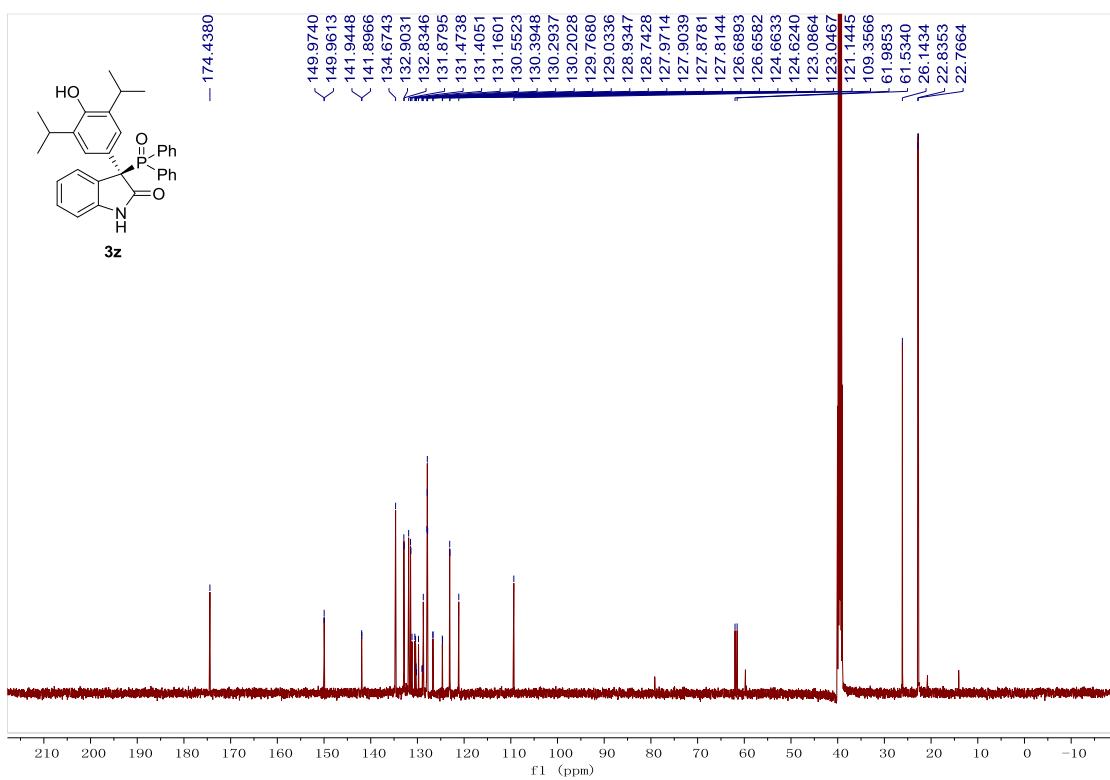


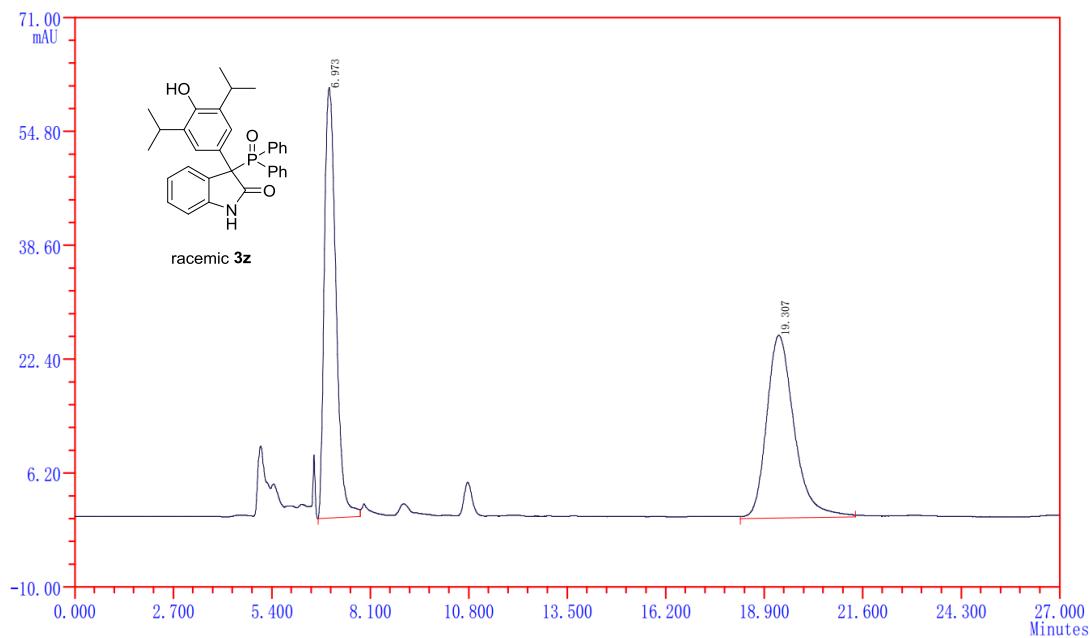
Peak #	RetTime [Min]	Height [mAu]	Area [mAu*s]	Area %
1	6.182	1287.10	11642.276	49.993
2	9.198	669.89	11645.343	50.007
Total:		1956.99	23287.618	100.0000



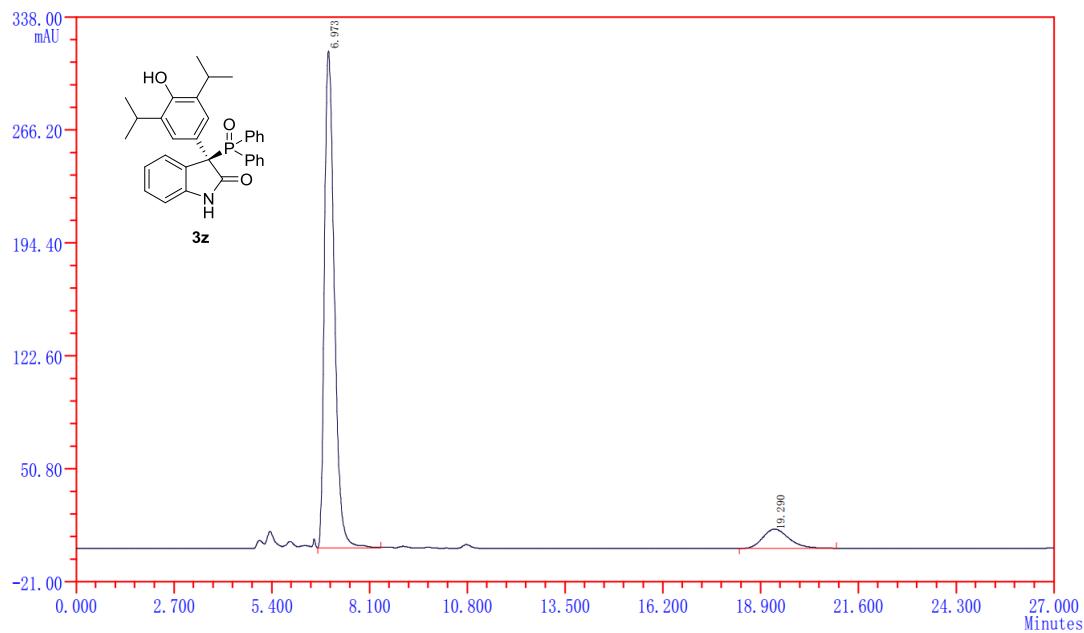
Peak	RetTime	Height	Area	Area
#	[Min]	[mAu]	[mAu*s]	%
1	6.182	710.37	6411.635	81.179
2	9.198	84.95	1486.527	18.821
Total:		795.32	7898.162	100.0000



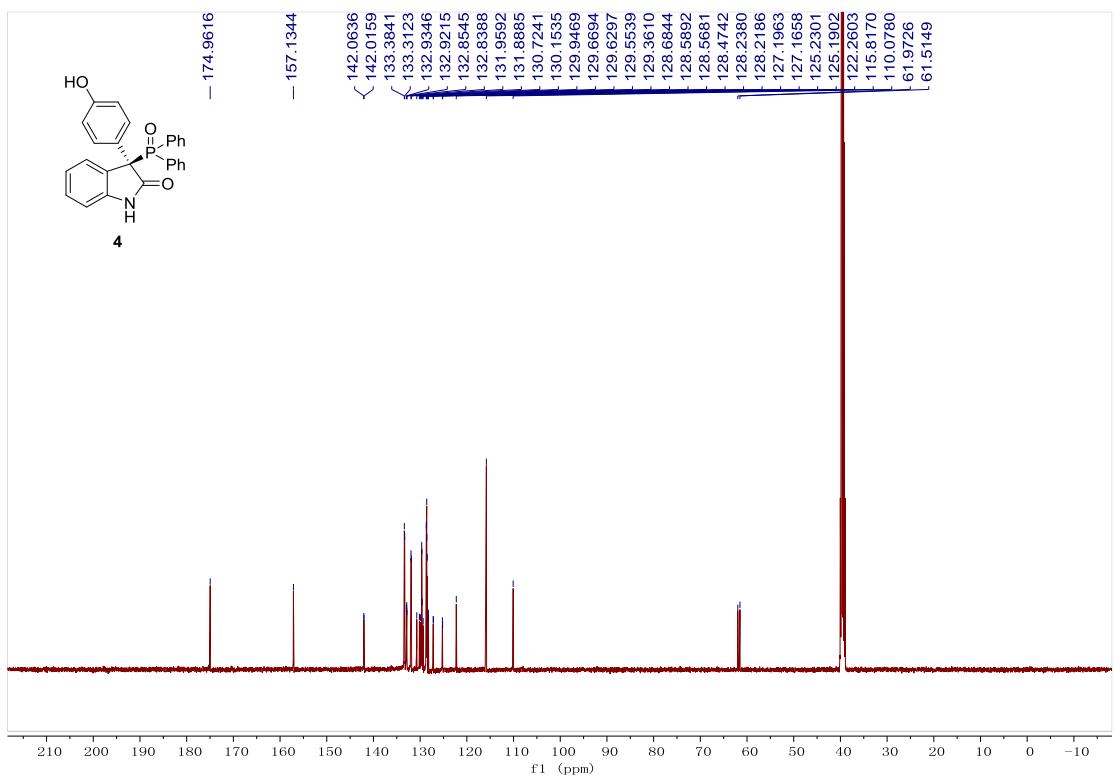
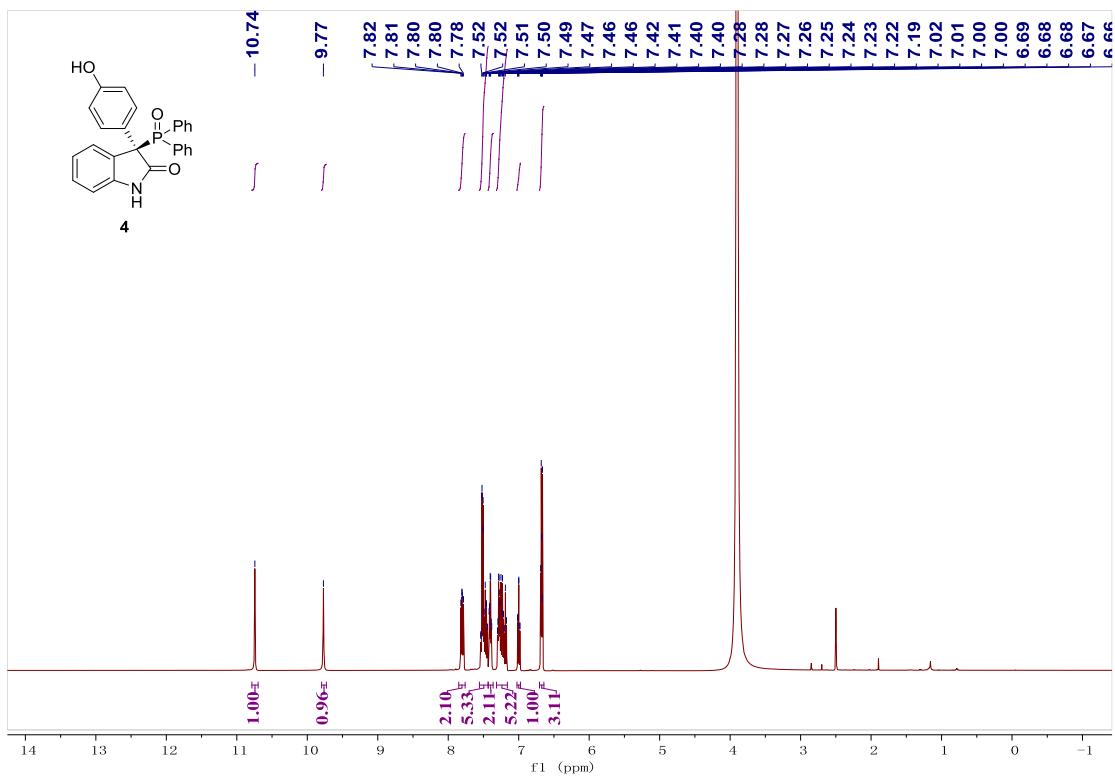


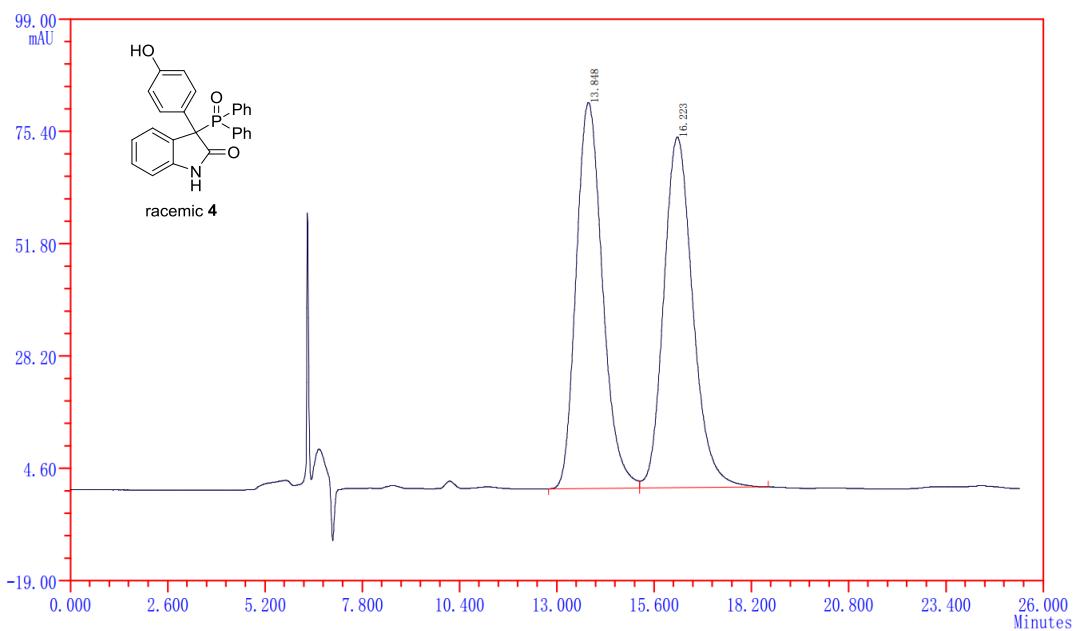
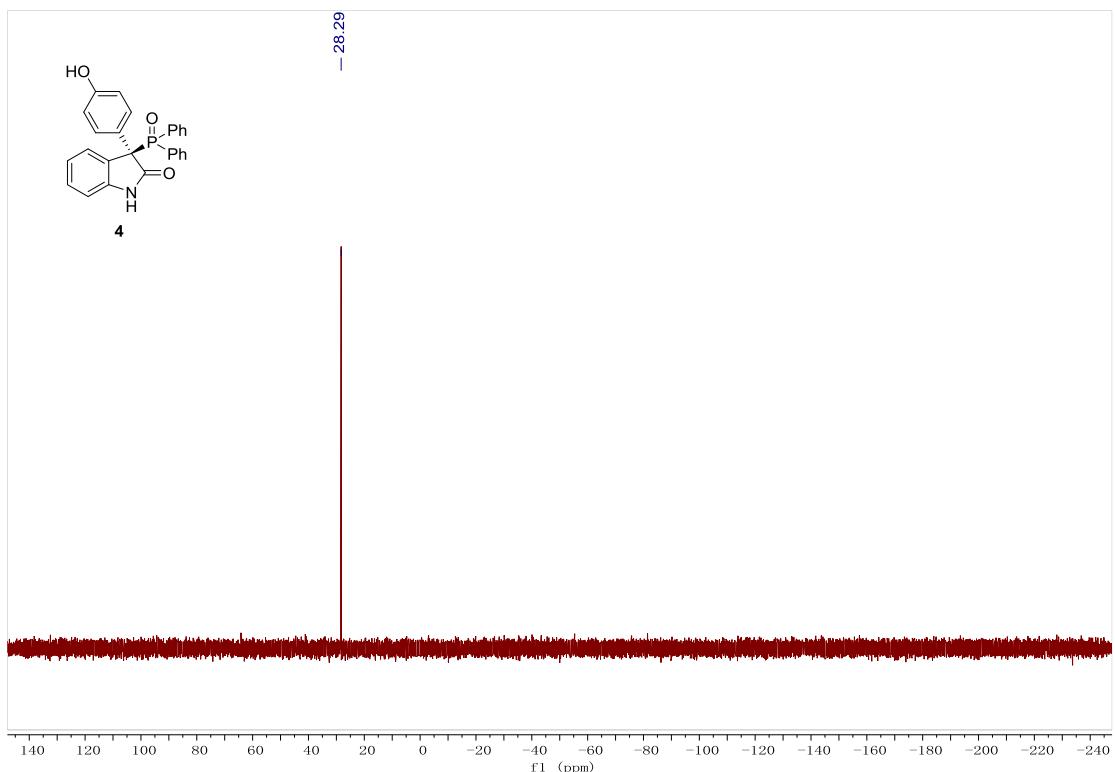


Peak #	RetTime [Min]	Height [mAu]	Area [mAu*s]	Area %
1	6.973	61.25	1358.339	49.876
2	19.307	25.96	1365.105	50.124
Total:		87.21	2723.444	100.0000

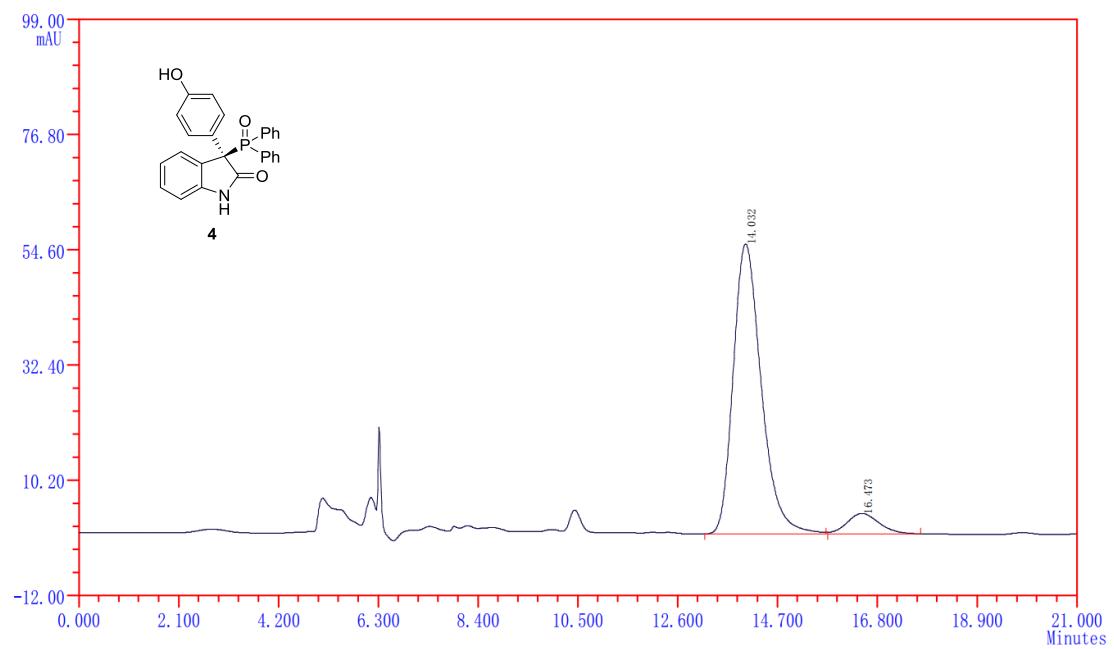


Peak #	RetTime [Min]	Height [mAu]	Area [mAu*s]	Area %
1	6.973	315.97	6010.459	90.754
2	19.290	12.21	612.331	9.246
Total:		328.18	6622.790	100.0000





Peak #	RetTime [Min]	Height [mAu]	Area [mAu*s]	Area %
1	13.848	81.12	3985.562	49.910
2	16.223	73.69	3999.863	50.090
Total:		328.18	7985.425	100.0000



Peak #	RetTime [Min]	Height [mAu]	Area [mAu*s]	Area %
1	14.032	55.84	2293.949	92.587
2	16.473	3.91	183.670	7.413
Total:		59.75	2477.619	100.0000