

Asymmetric [4 + 2] Annulations to Construct Norcamphor Scaffolds with 2-Cyclopentenone via Double Amine-Thiol Catalysis

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Supplementary Information

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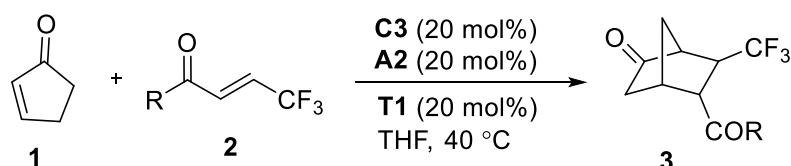
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1. General methods

NMR data were obtained for ^1H at 400 MHz or 600 MHz, and for ^{13}C at 100 MHz or 150 MHz. Chemical shifts were reported in ppm from tetramethylsilane with the solvent resonance as the internal standard in CDCl_3 solution. ESI-HRMS was recorded on a Waters SYNAPT G2. In each case, diastereomeric ratio was determined by $^1\text{H-NMR}$ and enantiomeric ratio was determined by HPLC analysis on a chiral column in comparison with authentic racemate, using a Daicel Chiraldak AD-H Column (250×4.6 mm) Chiraldak Column IB (250×4.6 mm) or Chiraldak ID Column (250×4.6 mm). UV detection was monitored at 254 nm. Optical rotation was measured in CHCl_3 solution at 25 °C. Column chromatography was performed on silica gel (200-300 mesh) eluting with ethyl acetate and petroleum ether. TLC was performed on glass-backed silica plates. UV light, I_2 , solution of potassium permanganate were used to visualize products or starting materials. All chemicals were used without purification as commercially available unless otherwise noted. Petroleum ether and ethyl acetate (EtOAc) were distilled. β -Trifluoromethyl enones **2**,¹ 3-olefinic oxindole **4**² and catalyst **C3**³ were prepared according to the literature procedures.

- (1) O. Marrec, J. Borrini, T. Billard and B. R. Langlois, *Synlett*, 2009, 1241.
- (2) (a) K. S. Halskov, T. K. Johansen, R. L. Davis, M. Steurer, F. Jensen and K. A. Jørgensen, *J. Am. Chem. Soc.*, 2012, **134**, 12943; (b) M. Sarangapani and V. J. Rao, *Synth. Commun.*, 2012, **42**, 3419; (c) Y. Liu, J. Xue, Z. Sun, D. Liu, Y. Xing and Y. Li, *Asian J. Org. Chem.*, 2016, **5**, 43; (d) H. J. Davis, M. E. Kavanagh, T. Balan, C. Abell and A. G. Coyne, *Bioorg. Med. Chem. Lett.*, 2016, **26**, 3735.
- (3) F. Yu, H. Hu, X. Gu and J. Ye, *Org. Lett.*, 2012, **14**, 2038.

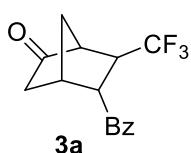
2. General procedure for [4 + 2] annulations of 2-cyclopentenone **1** and β -CF₃-substituted enones **2**



A solution of 2-cyclopentenone **1** (16.4 mg, 0.2 mmol), β -CF₃-substituted enones **2** (0.1 mmol), amine **C3** (4.0 mg, 0.02 mmol), benzoic acid **A2** (2.5 mg, 0.02 mmol) and 2-mercaptopbenzoic acid **T1** (3.1 mg, 0.02 mmol) in THF (1.0 mL) was stirred at 40 °C and the reaction was monitored by

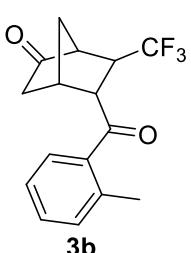
TLC. After completion, the product was obtained by flash chromatography on silica gel (EtOAc/petroleum ether = 1/40–1/10).

The racemates cannot be obtained by using the achiral primary amine catalysts, so two peaks of these enantiomers were assigned by HPLC analysis on a chiral column with the mixture of two enantiomers with the opposite configuration, which were produced by using chiral amine catalyst **C2** or **C3**, respectively.



(1*S*,4*S*,5*R*)-5-Benzoyl-6-(trifluoromethyl)bicyclo[2.2.1]heptan-2-one (3a):

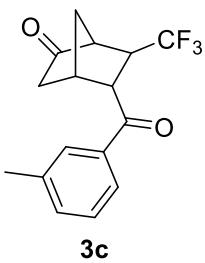
Following the general procedure, a solution of 2-cyclopentenone **1** (16.4 mg, 0.2 mmol), (*E*)-4,4,4-trifluoro-1-phenylbut-2-en-1-one **2a** (20.0 mg, 0.1 mmol), amine **C3** (4.0 mg, 0.02 mmol), benzoic acid **A2** (2.5 mg, 0.02 mmol) and 2-mercaptopbenzoic acid **T1** (3.1 mg, 0.02 mmol) in THF (1.0 mL) was stirred at 40 °C for 24 h. After completion, purification by flash chromatography on silica gel (EtOAc/petroleum ether = 1/25) to give product **3a**: 27.6 mg, as a light yellow oil, yield 98%; $[\alpha]_D^{20}$: −33.6 ($c = 0.24$ in CHCl₃); >19:1 dr, 95% ee, determined by HPLC analysis [Daicel Chiralpak ID, *n*-hexane/*i*-PrOH = 60/40, 1.0 mL/min, $\lambda = 254$ nm, t (minor) = 5.58 min, t (major) = 6.54 min]; ¹H NMR (400 MHz, CDCl₃) δ (ppm) 8.03 (d, $J = 7.6$ Hz, 2H), 7.64 (t, $J = 7.3$ Hz, 1H), 7.53 (t, $J = 7.6$ Hz, 2H), 4.11 (t, $J = 4.6$ Hz, 1H), 3.67–3.21 (m, 1H), 3.13 (s, 1H), 2.94 (s, 1H), 2.34 (d, $J = 10.4$ Hz, 1H), 2.13–1.74 (m, 3H); ¹³C NMR (100 MHz, CDCl₃) δ (ppm) 210.9, 196.1, 135.6, 134.0, 129.0, 128.5, 126.9 (q, $J = 276.7$ Hz), 51.2, 49.5, 41.4 (q, $J = 28.9$ Hz), 40.3, 38.9, 37.7; ESI-HRMS: calcd. for C₁₅H₁₃F₃O₂+Na⁺ 305.0758, found 305.0760.



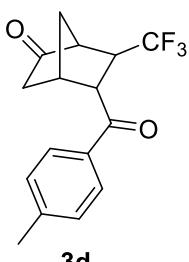
(1*S*,4*S*,5*R*)-5-(2-Methylbenzoyl)-6-(trifluoromethyl)bicyclo[2.2.1]heptan-2-one (3b):

Following the general procedure, a solution of 2-cyclopentenone **1** (16.4 mg, 0.2 mmol), (*E*)-4,4,4-trifluoro-1-(*o*-tolyl)but-2-en-1-one **2b** (21.4 mg, 0.1 mmol), amine **C3** (4.0 mg, 0.02 mmol), benzoic acid **A2** (2.5 mg, 0.02 mmol) and 2-mercaptopbenzoic acid **T1** (3.1 mg, 0.02 mmol) in THF (1.0 mL) was stirred at 40 °C for 24 h. After completion, purification by flash chromatography on silica gel (EtOAc/petroleum ether = 1/30) to give product **3b**: 27.2 mg, as a colorless oil, yield 92%; $[\alpha]_D^{20}$: −40.3 ($c = 0.24$ in CHCl₃); >19:1 dr, 94% ee, determined by HPLC analysis [Daicel Chiralpak ID, *n*-hexane/*i*-PrOH = 60/40, 1.0 mL/min, $\lambda = 254$ nm, t (minor) = 4.88 min, t (major) = 5.23 min]; ¹H NMR (600 MHz,

CDCl_3) δ (ppm) 7.71 (d, J = 7.7 Hz, 1H), 7.44 (t, J = 7.4 Hz, 1H), 7.36–7.28 (m, 2H), 4.01 (s, 1H), 3.39–3.30 (m, 1H), 3.02 (s, 1H), 2.93 (s, 1H), 2.49 (s, 3H), 2.27 (d, J = 10.2 Hz, 1H), 2.02–1.97 (m, 1H), 1.95–1.90 (m, 1H), 1.88–1.85 (m, 1H); ^{13}C NMR (100 MHz, CDCl_3) δ (ppm) 211.0, 199.8, 139.0, 136.4, 132.4, 132.1, 128.5, 126.9 (q, J = 278.2 Hz), 125.9, 51.8, 51.3, 41.4 (q, J = 29.0 Hz), 39.9, 38.9, 37.6, 21.3; ESI-HRMS: calcd. for $\text{C}_{16}\text{H}_{15}\text{F}_3\text{O}_2+\text{Na}^+$ 319.0916, found 319.0918.

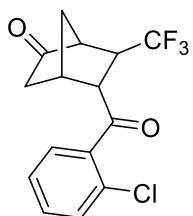


(1S,4S,5R)-5-(3-Methylbenzoyl)-6-(trifluoromethyl)bicyclo[2.2.1]heptan-2-one (3c): Following the general procedure, a solution of 2-cyclopentenone **1** (16.4 mg, 0.2 mmol), (*E*)-4,4,4-trifluoro-1-(*m*-tolyl)but-2-en-1-one **2c** (21.4 mg, 0.1 mmol), amine **C3** (4.0 mg, 0.02 mmol), benzoic acid **A2** (2.5 mg, 0.02 mmol) and 2-mercaptopbenzoic acid **T1** (3.1 mg, 0.02 mmol) in THF (1.0 mL) was stirred at 40 °C for 18 h. After completion, purification by flash chromatography on silica gel (EtOAc/petroleum ether = 1/30) to give product **3c**: 25.7 mg, as white solid, yield 87%; $[\alpha]_D^{20}$: -51.3 (c = 0.13 in CHCl_3); >19:1 dr, 92% ee, determined by HPLC analysis [Daicel Chiraldak ID, *n*-hexane/*i*-PrOH = 80/20, 1.0 mL/min, λ = 254 nm, t (minor) = 7.59 min, t (major) = 9.68 min]; ^1H NMR (600 MHz, CDCl_3) δ (ppm) 7.82 (s, 2H), 7.63–7.31 (m, 2H), 4.09 (s, 1H), 3.48–3.31 (m, 1H), 3.12 (s, 1H), 2.94 (s, 1H), 2.45 (s, 3H), 2.35 (d, J = 9.5 Hz, 1H), 1.99–1.85 (m, 3H); ^{13}C NMR (100 MHz, CDCl_3) δ (ppm) 211.0, 196.2, 138.9, 135.7, 134.7, 128.9, 128.8, 126.8 (q, J = 278.4 Hz), 125.7, 51.2, 49.5, 41.3 (q, J = 29.1 Hz), 40.3, 38.8, 37.6, 21.3; ESI-HRMS: calcd. for $\text{C}_{16}\text{H}_{15}\text{F}_3\text{O}_2+\text{Na}^+$ 319.0916, found 319.0916.



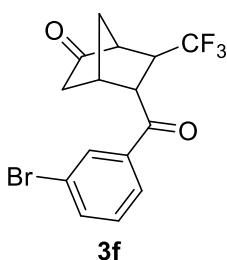
(1S,4S,5R)-5-(4-Methylbenzoyl)-6-(trifluoromethyl)bicyclo[2.2.1]heptan-2-one (3d): Following the general procedure, a solution of 2-cyclopentenone **1** (16.4 mg, 0.2 mmol), (*E*)-4,4,4-trifluoro-1-(*p*-tolyl)but-2-en-1-one **2d** (21.4 mg, 0.1 mmol), amine **C3** (4.0 mg, 0.02 mmol), benzoic acid **A2** (2.5 mg, 0.02 mmol) and 2-mercaptopbenzoic acid **T1** (3.1 mg, 0.02 mmol) in THF (1.0 mL) was stirred at 40 °C for 24 h. After completion, purification by flash chromatography on silica gel (EtOAc/petroleum ether = 1/25) to give product **3d**: 28.5 mg, as a white solid, yield 85%; $[\alpha]_D^{20}$: -45.3 (c = 0.26 in CHCl_3); >19:1 dr, 96% ee, determined by HPLC analysis [Daicel Chiraldak ID, *n*-hexane/*i*-PrOH = 60/40, 1.0 mL/min, λ = 254 nm, t (minor) = 5.59 min, t (major) = 6.26 min]; ^1H NMR (600 MHz,

CDCl_3) δ (ppm) 7.93 (d, J = 8.0 Hz, 2H), 7.32 (d, J = 8.0 Hz, 2H), 4.08 (t, J = 4.6 Hz, 1H), 3.47–3.34 (m, 1H), 3.11 (s, 1H), 2.93 (s, 1H), 2.44 (s, 3H), 2.33 (d, J = 9.5 Hz, 1H), 2.00–1.77 (m, 3H); ^{13}C NMR (100 MHz, CDCl_3) δ (ppm) 211.0, 195.6, 145.0, 133.2, 129.6, 128.6, 127.0 (q, J = 276.6 Hz) 51.3, 49.4, 41.3 (q, J = 28.9 Hz), 40.4, 38.9, 37.7, 21.7; ESI-HRMS: calcd. for $\text{C}_{16}\text{H}_{15}\text{F}_3\text{O}_2+\text{Na}^+$ 319.0916, found 319.0916.



(1*S*,4*S*,5*R*)-5-(2-Chlorobenzoyl)-6-(trifluoromethyl)bicyclo[2.2.1]heptan-2-one

(3e): Following the general procedure, a solution of 2-cyclopentenone **1** (16.4 mg, 0.2 mmol), (*E*)-1-(2-chlorophenyl)-4,4,4-trifluorobut-2-en-1-one **2e** (23.4 mg, 0.1 mmol), amine **C3** (4.0 mg, 0.02 mmol), benzoic acid **A2** (2.5 mg, 0.02 mmol) and 2-mercaptopbenzoic acid **T1** (3.1 mg, 0.02 mmol) in THF (1.0 mL) was stirred at 40 °C for 24 h. After completion, purification by flash chromatography on silica gel (EtOAc/petroleum ether = 1/25) to give product **3e**: 28.4 mg, as a white solid, yield 89%; $[\alpha]_D^{20}$: −38.9 (c = 0.29 in CHCl_3); >19:1 dr, 86% ee, determined by HPLC analysis [Daicel Chiraldak IB, *n*-hexane/*i*-PrOH = 90/10, 1.0 mL/min, λ = 254 nm, t (minor) = 6.52 min, t (major) = 7.13 min]; ^1H NMR (400 MHz, CDCl_3) δ (ppm) 7.54–7.30 (m, 4H), 4.11 (t, J = 4.8 Hz, 1H), 3.36–2.20 (m, 1H), 2.98 (s, 1H), 2.93 (s, 1H), 2.22 (d, J = 10.9 Hz, 1H), 2.05 (s, 2H), 1.86 (d, J = 10.9 Hz, 1H); ^{13}C NMR (150 MHz, CDCl_3) δ (ppm) 210.5, 199.1, 137.8, 132.1, 130.8, 130.7, 128.6, 126.9, 126.5 (q, J = 278.2 Hz), 53.1, 51.1, 41.1 (q, J = 29.3 Hz), 38.9, 38.8, 37.2; ESI-HRMS: calcd. for $\text{C}_{15}\text{H}_{12}\text{ClF}_3\text{O}_2+\text{Na}^+$ 339.0370 (^{35}Cl) and 341.0341 (^{37}Cl), found 339.0371, 341.0310.

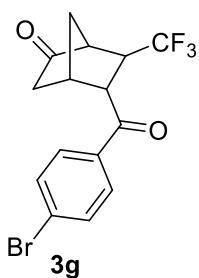


(1*S*,4*S*,5*R*)-5-(3-Bromobenzoyl)-6-(trifluoromethyl)bicyclo[2.2.1]heptan-2-one

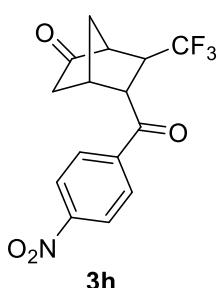
(3f): Following the general procedure, a solution of 2-cyclopentenone **1** (16.4 mg, 0.2 mmol), (*E*)-1-(3-bromophenyl)-4,4,4-trifluorobut-2-en-1-one **2f** (27.8 mg, 0.1 mmol), amine **C3** (4.0 mg, 0.02 mmol), benzoic acid **A2** (2.5 mg, 0.02 mmol) and 2-mercaptopbenzoic acid **T1** (3.1 mg, 0.02 mmol) in THF (1.0 mL)

was stirred at 40 °C for 36 h. After completion, purification by flash chromatography on silica gel (EtOAc/petroleum ether = 1/25) to give product **3f**: 25.2 mg, as a white solid, yield 70%; $[\alpha]_D^{20}$: −26.1 (c = 0.30 in CHCl_3); >19:1 dr, 93% ee, determined by HPLC analysis [Daicel Chiraldak ID, *n*-hexane/*i*-PrOH = 60/40, 1.0 mL/min, λ = 254 nm, t (minor) = 5.22 min, t (major) = 5.79 min]; ^1H

NMR (400 MHz, CDCl₃) δ (ppm) 8.14 (s, 1H), 7.95 (d, *J* = 7.8 Hz, 1H), 7.77 (d, *J* = 7.8 Hz, 1H), 7.42 (t, *J* = 7.8 Hz, 1H), 4.03 (t, *J* = 4.5 Hz, 1H), 3.46–3.28 (m, 1H), 3.12 (s, 1H), 2.95 (s, 1H), 2.35 (d, *J* = 10.6 Hz, 1H), 2.00 (dd, *J* = 18.5, 4.4 Hz, 1H), 1.92 (d, *J* = 10.6 Hz, 1H), 1.84 (dd, *J* = 18.5, 4.4 Hz, 1H); ¹³C NMR (100 MHz, CDCl₃) δ (ppm) 210.6, 195.0, 137.3, 136.8, 131.5, 130.6, 127.0, 126.7 (q, *J* = 278.3 Hz), 123.4, 51.2, 49.6, 41.5 (q, *J* = 28.7 Hz), 40.3, 38.8, 37.7; ESI-HRMS: calcd. for C₁₅H₁₂BrF₃O₂+Na⁺ 382.9865 (⁷⁹Br) and 384.9845 (⁸¹Br), found 382.9862, 384.9841.

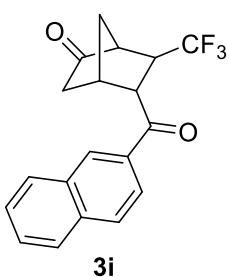


(1*S*,4*S*,5*R*)-5-(4-Bromobenzoyl)-6-(trifluoromethyl)bicyclo[2.2.1]heptan-2-one (3g): Following the general procedure, a solution of 2-cyclopentenone **1** (16.4 mg, 0.2 mmol), (*E*)-1-(4-bromophenyl)-4,4,4-trifluorobut-2-en-1-one **2g** (27.8 mg, 0.1 mmol), amine **C3** (4.0 mg, 0.02 mmol), benzoic acid **A2** (2.5 mg, 0.02 mmol) and 2-mercaptopbenzoic acid **T1** (3.1 mg, 0.02 mmol) in THF (1.0 mL) was stirred at 40 °C for 36 h. After completion, purification by flash chromatography on silica gel (EtOAc/petroleum ether = 1/25) to give product **3g**: 26.3 mg, as a colorless oil, yield 73%; [α]_D²⁰: −29.5 (*c* = 0.38 in CHCl₃); >19:1 dr, 87% ee, determined by HPLC analysis [Daicel Chiralpak ID, *n*-hexane/*i*-PrOH = 60/40, 1.0 mL/min, λ = 254 nm, t (minor) = 5.12 min, t (major) = 5.51 min]; ¹H NMR (600 MHz, CDCl₃) δ (ppm) 7.89 (d, *J* = 8.4 Hz, 2H), 7.67 (d, *J* = 8.4 Hz, 2H), 4.04 (t, *J* = 4.6 Hz, 1H), 3.43–3.34 (m, 1H), 3.10 (s, 1H), 2.94 (s, 1H), 2.34 (d, *J* = 9.3 Hz, 1H), 1.98 (dd, *J* = 18.5, 4.4 Hz, 1H), 1.92 (d, *J* = 11.0 Hz, 1H), 1.84 (dd, *J* = 18.5, 4.4 Hz, 1H); ¹³C NMR (150 MHz, CDCl₃) δ (ppm) 210.6, 195.2, 134.3, 132.4, 130.0, 129.4, 127.3 (q, *J* = 184.6 Hz), 51.2, 49.5, 41.5 (q, *J* = 29.2 Hz), 40.3, 38.8, 37.7; ESI-HRMS: calcd. for C₁₅H₁₂BrF₃O₂+Na⁺ 382.9865 (⁷⁹Br) and 384.9845 (⁸¹Br), found 382.9861, 384.9850.



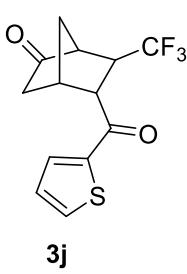
(1*S*,4*S*,5*R*)-5-(4-Nitrobenzoyl)-6-(trifluoromethyl)bicyclo[2.2.1]heptan-2-one (3h): Following the general procedure, a solution of 2-cyclopentenone **1** (16.4 mg, 0.2 mmol), (*E*)-4,4,4-trifluoro-1-(4-nitrophenyl)but-2-en-1-one **2h** (24.5 mg, 0.1 mmol), amine **C3** (4.0 mg, 0.02 mmol), benzoic acid **A2** (2.5 mg, 0.02 mmol) and 2-mercaptopbenzoic acid **T1** (3.1 mg, 0.02 mmol) in THF (1.0 mL) was stirred at 40 °C for 48 h. After completion, purification by flash chromatography on silica

gel (EtOAc/petroleum ether = 1/18) to give product **3h**: 21.5 mg, as a white solid, yield 65%; $[\alpha]_D^{20}$: -72.8 ($c = 0.42$ in CHCl₃); >19:1 dr, 89% ee, determined by HPLC analysis [Daicel Chiraldak ID, *n*-hexane/*i*-PrOH = 60/40, 1.0 mL/min, $\lambda = 254$ nm, t (minor) = 7.60 min, t (major) = 8.41 min]; ¹H NMR (400 MHz, CDCl₃) δ (ppm) 8.38 (d, $J = 8.7$ Hz, 2H), 8.19 (d, $J = 8.7$ Hz, 2H), 4.10 (t, $J = 4.4$ Hz, 1H), 3.50–3.29 (m, 1H), 3.13 (s, 1H), 2.98 (s, 1H), 2.37 (d, $J = 9.8$ Hz, 1H), 2.02 (dd, $J = 18.6$, 4.4 Hz, 1H), 1.96 (d, $J = 11.2$ Hz, 1H), 1.84 (dd, $J = 18.6$, 4.4 Hz, 1H); ¹³C NMR (150 MHz, CDCl₃) δ (ppm) 210.0, 195.1, 150.8, 140.0, 129.6, 126.6 (q, $J = 246.3$ Hz), 124.2, 51.1, 50.1, 41.7 (q, $J = 29.4$ Hz), 40.2, 38.7, 37.7; ESI-HRMS: calcd. for C₁₅H₁₂F₃NO₄+Na⁺ 350.0611, found 350.0613.



(1*S*,4*S*,5*R*)-5-(2-naphthoyl)-6-(trifluoromethyl)bicyclo[2.2.1]heptan-2-one

(3i): Following the general procedure, a solution of 2-cyclopentenone **1** (16.4 mg, 0.2 mmol), (*E*)-4,4,4-trifluoro-1-(naphthalen-2-yl)but-2-en-1-one **2i** (25.0 mg, 0.1 mmol), amine **C3** (4.0 mg, 0.02 mmol), benzoic acid **A2** (2.5 mg, 0.02 mmol) and 2-mercaptopbenzoic acid **T1** (3.1 mg, 0.02 mmol) in THF (1.0 mL) was stirred at 40 °C for 18 h. After completion, purification by flash chromatography on silica gel (EtOAc/petroleum ether = 1/25) to give product **3i**: 26.9 mg, as a colorless oil, yield 81%; $[\alpha]_D^{20}$: -10.0 ($c = 0.04$ in CHCl₃); >19:1 dr, 93% ee, determined by HPLC analysis [Daicel Chiraldak ID, *n*-hexane/*i*-PrOH = 60/40, 1.0 mL/min, $\lambda = 254$ nm, t (minor) = 5.62 min, t (major) = 6.55 min]; ¹H NMR (600 MHz, CDCl₃) δ (ppm) 8.55 (s, 1H), 8.06 (d, $J = 8.5$ Hz, 1H), 8.02 (d, $J = 8.1$ Hz, 1H), 7.95 (d, $J = 8.5$ Hz, 1H), 7.91 (d, $J = 8.1$ Hz, 1H), 7.65 (t, $J = 7.4$ Hz, 1H), 7.60 (t, $J = 7.4$ Hz, 1H), 4.27 (t, $J = 4.3$ Hz, 1H), 3.54–3.42 (m, 1H), 3.21 (s, 1H), 2.98 (s, 1H), 2.41 (d, $J = 10.1$ Hz, 1H), 2.08–1.83 (m, 3H); ¹³C NMR (150 MHz, CDCl₃) δ (ppm) 211.0, 196.1, 135.9, 133.0, 132.4, 130.3, 129.6, 129.1, 129.0, 127.9, 127.2, 126.9 (q, $J = 278.3$ Hz), 123.9, 51.3, 49.6, 41.5 (q, $J = 29.0$ Hz) 40.6, 38.9, 37.7; ESI-HRMS: calcd. for C₁₉H₁₅F₃O₂+H⁺ 333.1097, found 333.1094.

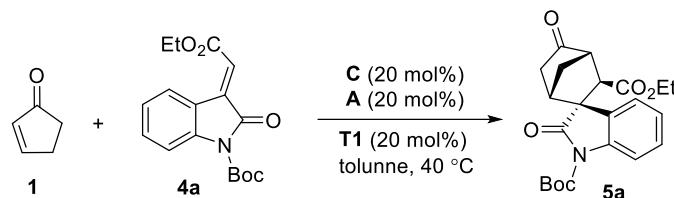


(1*S*,4*S*,5*R*)-5-(Thiophene-2-carbonyl)-6-(trifluoromethyl)bicyclo[2.2.1]heptan-2-one

(3j): Following the general procedure, a solution of 2-cyclopentenone **1** (16.4 mg, 0.2 mmol), (*E*)-4,4,4-trifluoro-1-(thiophen-2-yl)but-2-en-1-one **2j** (20.6 mg, 0.1 mmol), amine **C3** (4.0 mg, 0.02 mmol), benzoic acid **A2** (2.5 mg, 0.02 mmol) and 2-mercaptopbenzoic acid **T1** (3.1 mg, 0.02 mmol) in THF (1.0 mL) was stirred at 40

°C for 24 h. After completion, purification by flash chromatography on silica gel (EtOAc/petroleum ether = 1/20) to give product **3j**: 24.9 mg, as a colorless oil, yield 87%; $[\alpha]_D^{20}$: -7.0 ($c = 1.12$ in CHCl₃); >19:1 dr, 86% ee, determined by HPLC analysis [Daicel Chiralpak ID, *n*-hexane/*i*-PrOH = 60/40, 1.0 mL/min, $\lambda = 254$ nm, t (minor) = 5.87 min, t (major) = 8.90 min]; ¹H NMR (600 MHz, CDCl₃) δ (ppm) 7.86 (d, $J = 3.8$ Hz, 1H), 7.74 (d, $J = 4.9$ Hz, 1H), 7.21 (t, $J = 3.8$ Hz, 4.9 Hz, 1H), 3.94 (t, $J = 4.8$ Hz, 1H), 3.38–3.30 (m, 1H), 3.18 (s, 1H), 2.93 (s, 1H), 2.32 (d, $J = 11.0$ Hz, 1H), 2.02 (s, 2H), 1.92 (d, $J = 11.0$ Hz, 1H); ¹³C NMR (150 MHz, CDCl₃) δ (ppm) 210.8, 188.9, 142.8, 135.0, 132.7, 128.5, 126.8 (q, $J = 278.6$ Hz), 51.2, 50.5, 41.4 (q, $J = 29.2$ Hz), 41.1, 38.9, 37.7; ESI-HRMS: calcd. for C₁₃H₁₂F₃O₂S+Na⁺ 311.0324, found 311.0323.

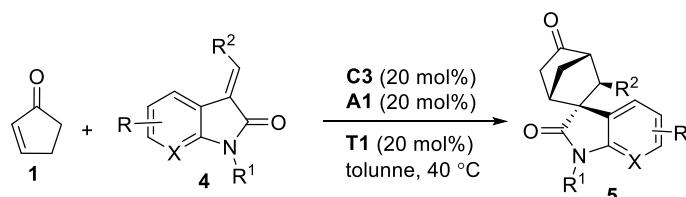
3. Screening conditions of asymmetric [4 + 2] annulation of 2-cyclopentenone **1** and 3-olefinic oxindole **4a**^a



Entry	Solvent	Thiol	Acid	Catalyst	yield(%) ^b	ee(%) ^c
1	toluene	T1	A1	C1	58	84
2	toluene	T1	A1	C2	80	78
3	toluene	T1	A1	C3	97	96
4	toluene	T1	A1	C4	57	79
5	toluene	T1	A1	C5	75	86
7	toluene	T1	A2	C3	93	94
8 ^d	toluene	/	A1	C3	39	93

^aUnless noted otherwise, reactions were performed with 2-cyclopentenone **1** (0.1 mmol), enone **2a** (0.05 mmol), amine **C** (20 mol%), acid **A** (20 mol%) and thiol **T** (20 mol%) in solvent (1.0 mL) at 40 °C for 24 h. ^bYield of isolated product. ^cDetermined by HPLC analysis on a chiral stationary phase.

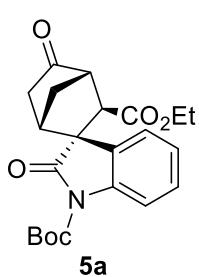
4. General procedure for [4 + 2] annulations of 2-cyclopentenone **1** and 3-olefinic oxindoles **4**



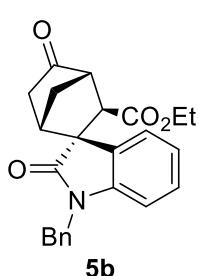
A solution of 3-olefinic oxindole **4** (0.1 mmol), 2-cyclopentenone **1** (16.4 mg, 0.2 mmol), amine **C3** (4.0 mg, 0.02 mmol), salicylic acid **A1** (2.7 mg, 0.02 mmol) and 2-mercaptopbenzoic acid **T1** (3.1 mg, 0.02 mmol) in toluene (1.0 mL) was stirred at 40 °C and the reaction was monitored by TLC.

After completion, the product was obtained by flash chromatography on silica gel (EtOAc/petroleum ether = 1/40–1/5).

The racemates cannot be obtained by using the achiral primary amine catalysts, so two peaks of these enantiomers were assigned by HPLC analysis on a chiral column with the mixture of two enantiomers with the opposite configuration, which were produced by using chiral amine catalyst **C2** or **C3**, respectively.

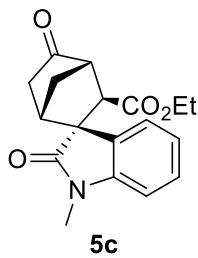


1'-(*tert*-Butyl) 3-ethyl (1*S*,2*R*,3*R*,4*S*)-2',5-dioxospiro[bicyclo[2.2.1]heptane-2,3'-indoline]-1',3-dicarboxylate (5a): Following the general procedure, a solution of 2-cyclopentenone **1** (16.4 mg, 0.2 mmol), *tert*-butyl(*E*)-3-(2-ethoxy-2-oxoethylidene)-2-oxoindoline-1-carboxylate **4a** (31.7 mg, 0.1 mmol), amine **C3** (4.0 mg, 0.02 mmol), salicylic acid **A1** (2.7 mg, 0.02 mmol) and 2-mercaptopbenzoic acid **T1** (3.1 mg, 0.02 mmol) in toluene (1.0 mL) was stirred at 40 °C for 24 h. After completion, purification by flash chromatography on silica gel (EtOAc/petroleum ether = 1/20) to give product **5a**: 38.7 mg, as a white solid, yield 97%; $[\alpha]_D^{20}$: +3.7 ($c = 0.56$ in CHCl₃); >19:1 dr, 96% ee, determined by HPLC analysis [Daicel Chiraldapak ID, *n*-hexane/*i*-PrOH = 60/40, 1.0 mL/min, $\lambda = 254$ nm, t (major) = 7.00 min, t (minor) = 9.35 min]; ¹H NMR (400 MHz, CDCl₃) δ (ppm) 7.91 (d, $J = 7.7$ Hz, 1H), 7.35 (t, $J = 7.7$ Hz, 1H), 7.29 (d, $J = 7.7$ Hz, 1H), 7.13 (t, $J = 7.7$ Hz, 1H), 3.82–3.69 (m, 1H), 3.69–3.57 (m, 1H), 3.27 (d, $J = 1.0$ Hz, 1H), 3.15 (s, 1H), 2.93 (dd, $J = 18.4, 4.7$ Hz, 1H), 2.81 (d, $J = 11.4$ Hz, 1H), 2.66 (d, $J = 2.0$ Hz, 1H), 2.07–1.93 (m, 2H), 1.66 (s, 9H), 0.67 (t, $J = 7.1$ Hz, 3H); ¹³C NMR (100 MHz, CDCl₃) δ (ppm) 213.3, 175.9, 169.6, 149.0, 139.2, 129.8, 128.9, 124.4, 123.1, 114.8, 84.9, 61.0, 56.2, 53.1, 52.3, 48.2, 40.0, 37.6, 28.1, 13.5; ESI-HRMS: calcd. for C₂₂H₂₅NO₆+Na⁺ 422.1574, found 422.1575.

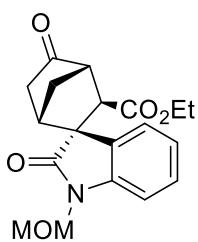


Ethyl (1*S*,2*R*,3*R*,4*S*)-1'-benzyl-2',5-dioxospiro[bicyclo[2.2.1]heptane-2,3'-indoline]-3-carboxylate (5b): Following the general procedure, a solution of ethyl (*E*)-2-(1-benzyl-2-oxoindolin-3-ylidene)acetate **4b** (30.7 mg, 0.1 mmol), 2-cyclopentenone **1** (16.4 mg, 0.2 mmol), amine **C3** (4.0 mg, 0.02 mmol), salicylic acid **A1** (2.7 mg, 0.02 mmol) and 2-mercaptopbenzoic acid **T1** (3.1 mg, 0.02 mmol)

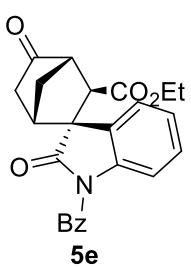
in toluene (1.0 mL) was stirred at 40 °C for 24 h. After completion, purification by flash chromatography on silica gel (EtOAc/petroleum ether = 1/12) to give product **5b**: 37.2 mg, as a white solid, yield 96%; $[\alpha]_D^{20}$: +17.2 ($c = 1.78$ in CHCl₃); >19:1 dr, 93% ee, determined by HPLC analysis [Daicel Chiralpak AD-H, *n*-hexane/*i*-PrOH = 80/20, 1.0 mL/min, $\lambda = 254$ nm, t (minor) = 9.12 min, t (major) = 16.34 min]; ¹H NMR (400 MHz, CDCl₃) δ (ppm) 7.33–7.23 (m, 6H), 7.18 (t, $J = 7.7$ Hz, 1H), 6.98 (t, $J = 7.7$ Hz, 1H), 6.72 (d, $J = 7.7$ Hz, 1H), 5.20 (d, $J = 15.8$ Hz, 1H), 4.76 (d, $J = 15.8$ Hz, 1H), 3.70–3.54 (m, 2H), 3.31 (s, 1H), 3.21 (dd, $J = 18.4, 4.6$ Hz, 1H), 3.17 (s, 1H), 2.82 (dd, $J = 14.8, 3.6$ Hz, 1H), 2.69 (s, 1H), 2.16–1.89 (m, 2H), 0.52 (t, $J = 7.1$ Hz, 3H); ¹³C NMR (100 MHz, CDCl₃) δ (ppm) 213.7, 177.4, 169.7, 142.3, 135.3, 130.9, 128.6, 128.5, 127.6, 126.9, 123.4, 122.4, 109.2, 60.7, 55.3, 53.0, 51.9, 47.0, 43.8, 39.3, 37.8, 13.2; ESI-HRMS: calcd. for C₂₄H₂₃NO₄+Na⁺ 412.1519, found 412.1526.



Ethyl (1*S*,2*R*,3*R*,4*S*)-1'-methyl-2',5-dioxospiro[bicyclo[2.2.1]heptane-2,3'-indoline]-3-carboxylate (5c): Following the general procedure, a solution of 2-cyclopentenone **1** (16.4 mg, 0.2 mmol), ethyl (*E*)-2-(1-methyl-2-oxoindolin-3-ylidene)acetate **4c** (23.1 mg, 0.1 mmol), amine **C3** (4.0 mg, 0.02 mmol), salicylic acid **A1** (2.7 mg, 0.02 mmol) and 2-mercaptopbenzoic acid **T1** (3.1 mg, 0.02 mmol) in toluene (1.0 mL) was stirred at 40 °C for 24 h. After completion, purification by flash chromatography on silica gel (EtOAc/petroleum ether = 1/12) to give product **5c**: 27.5 mg, as a white solid, yield 87%; $[\alpha]_D^{20}$: +70.8 ($c = 0.61$ in CHCl₃); >19:1 dr, 96% ee, determined by HPLC analysis [Daicel Chiralpak ID, *n*-hexane/*i*-PrOH = 80/20, 1.0 mL/min, $\lambda = 254$ nm, t (minor) = 40.08 min, t (major) = 44.59 min]; ¹H NMR (400 MHz, CDCl₃) δ (ppm) 7.32 (t, $J = 7.7$ Hz, 1H), 7.27 (d, $J = 7.7$ Hz, 1H), 7.03 (t, $J = 7.7$ Hz, 1H), 6.87 (d, $J = 7.7$ Hz, 1H), 3.77–3.44 (m, 2H), 3.26 (s, 3H), 3.20–3.12 (m, 3H), 2.80 (dd, $J = 10.9, 3.5$ Hz, 1H), 2.62 (s, 1H), 2.10–1.84 (m, 2H), 0.62 (t, $J = 7.1$ Hz, 3H); ¹³C NMR (150 MHz, CDCl₃) δ (ppm) 213.9, 177.2, 169.8, 143.4, 131.0, 128.7, 123.4, 122.5, 108.0, 60.7, 55.4, 53.1, 51.7, 47.0, 39.3, 37.8, 26.7, 13.4; ESI-HRMS: calcd. for C₁₈H₁₉NO₄+Na⁺ 336.1206, found 336.1213.

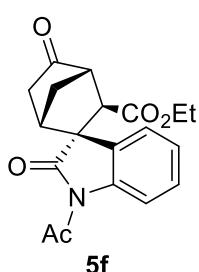


Ethyl (1*S*,2*R*,3*R*,4*S*)-1'-(methoxymethyl)-2',5-dioxospiro[bicyclo[2.2.1]heptane-2,3'-indoline]-3-carboxylate (5d): Following the general procedure, a solution of 2-cyclopentenone **1** (16.4 mg, 0.2 mmol), ethyl (*E*)-2-(1-methoxymethyl)-2-oxoindolin-3-ylidene)acetate **4d** (26.1 mg, 0.1 mmol), amine **C3** (4.0 mg, 0.02 mmol), salicylic acid **A1** (2.7 mg, 0.02 mmol) and 2-mercaptobenzoic acid **T1** (3.1 mg, 0.02 mmol) in toluene (1.0 mL) was stirred at 40 °C for 24 h. After completion, purification by flash chromatography on silica gel (EtOAc/petroleum ether = 1/12.5) to give product **5d**: 29.2 mg, as a white solid, yield 85%; $[\alpha]_D^{20}$: +10.5 ($c = 1.24$ in CHCl₃); >19:1 dr, 92% ee, determined by HPLC analysis [Daicel Chiralpak AD-H, *n*-hexane/*i*-PrOH = 90/10, 1.0 mL/min, $\lambda = 254$ nm, t (minor) = 15.36 min, t (major) = 16.03 min]; ¹H NMR (400 MHz, CDCl₃) δ (ppm) 7.34–7.25 (m, 2H), 7.05 (t, $J = 8.1$ Hz, 2H), 5.24 (d, $J = 11.0$ Hz, 1H), 5.13 (d, $J = 11.0$ Hz, 1H), 3.75–3.62 (m, 1H), 3.60–3.52 (m, 1H), 3.29 (s, 3H), 3.23 (s, 1H), 3.14 (s, 1H), 3.09 (dd, $J = 18.4, 4.6$ Hz, 1H), 2.81 (dd, $J = 10.8, 2.8$ Hz, 1H), 2.65 (s, 1H), 2.07–1.85 (m, 2H), 0.61 (t, $J = 7.1$ Hz, 3H); ¹³C NMR (100 MHz, CDCl₃) δ (ppm) 213.8, 178.2, 169.6, 141.4, 130.5, 128.9, 123.6, 123.1, 109.8, 71.3, 60.8, 56.0, 55.6, 53.0, 52.2, 47.2, 39.4, 37.8, 13.4; ESI-HRMS: calcd. for C₁₉H₂₁NO₅+Na⁺ 366.1312, found 366.1310.

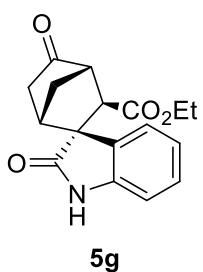


Ethyl (1*S*,2*R*,3*R*,4*S*)-1'-benzoyl-2',5-dioxospiro[bicyclo[2.2.1]heptane-2,3'-indoline]-3-carboxylate (5e): Following the general procedure, a solution of 2-cyclopentenone **1** (16.4 mg, 0.2 mmol), ethyl (*E*)-2-(1-benzoyl-2-oxoindolin-3-ylidene)acetate **4e** (32.1 mg, 0.1 mmol), amine **C3** (4.0 mg, 0.02 mmol), salicylic acid **A1** (2.7 mg, 0.02 mmol) and 2-mercaptobenzoic acid **T1** (3.1 mg, 0.02 mmol) in toluene (1.0 mL) was stirred at 40 °C for 24 h. After completion, purification by flash chromatography on silica gel (EtOAc/petroleum ether = 1/14) to give product **5e**: 31.7 mg, as a white solid, yield 79%; $[\alpha]_D^{20}$: -88.6 ($c = 0.37$ in CHCl₃); 89% ee, determined by HPLC analysis [Daicel Chiralpak AD-H, *n*-hexane/*i*-PrOH = 80/20, 1.0 mL/min, $\lambda = 254$ nm, t (major) = 12.58 min, t (minor) = 22.76 min]; ¹H NMR (400 MHz, CDCl₃) δ (ppm) 7.84 (d, $J = 8.0$ Hz, 1H), 7.70 (d, $J = 7.6$ Hz, 2H), 7.61 (t, $J = 7.6$ Hz, 1H), 7.48 (t, $J = 7.6$ Hz, 2H), 7.41–7.35 (m, 2H), 7.19 (t, $J = 7.6$ Hz, 1H), 3.82–3.73 (m, 1H), 3.68–3.60 (m, 1H), 3.25 (s, 1H), 3.16 (s, 1H), 2.93–2.76 (m, 3H), 2.07–2.00 (m, 2H), 0.71 (t, $J = 7.1$ Hz, 3H); ¹³C NMR (100 MHz, CDCl₃) δ (ppm) 212.8, 177.5, 169.3, 169.3, 139.6,

133.9, 133.3, 130.4, 129.3, 129.2, 128.5, 124.9, 123.5, 114.4, 61.2, 56.3, 52.8, 52.4, 48.0, 39.7, 37.8, 13.5; ESI-HRMS: calcd. for $C_{24}H_{21}NO_5 + Na^+$ 426.1312, found 426.1313.

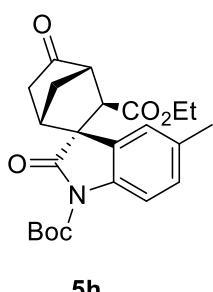


Ethyl (1*S*,2*R*,3*R*,4*S*)-1'-acetyl-2',5-dioxospiro[bicyclo[2.2.1]heptane-2,3'-indoline]-3-carboxylate (5f): Following the general procedure, a solution of 2-cyclopentenone **1** (16.4 mg, 0.2 mmol), ethyl (*E*)-2-(1-acetyl-2-oxoindolin-3-ylidene)acetate **4f** (25.9 mg, 0.1 mmol), amine **C3** (4.0 mg, 0.02 mmol), salicylic acid **A1** (2.7 mg, 0.02 mmol) and 2-mercaptopbenzoic acid **T1** (3.1 mg, 0.02 mmol) in toluene (1.0 mL) was stirred at 40 °C for 24 h. After completion, purification by flash chromatography on silica gel (EtOAc/petroleum ether = 1/18) to give product **5f**: 28.3 mg, as a white solid, yield 83%; $[\alpha]_D^{20}$: +16.7 ($c = 0.84$ in CHCl₃); 86% ee, determined by HPLC analysis [Daicel Chiralpak ID, *n*-hexane/*i*-PrOH = 70/30, 1.0 mL/min, $\lambda = 254$ nm, t (minor) = 10.50 min, t (major) = 14.37 min]; ¹H NMR (400 MHz, CDCl₃) δ (ppm) 8.31 (dd, $J = 8.2, 0.6$ Hz, 1H), 7.37 (td, $J = 7.7, 1.0$ Hz, 1H), 7.31 (dd, $J = 7.7, 1.0$ Hz, 1H), 7.18 (td, $J = 7.7, 1.0$ Hz, 1H), 3.90–3.48 (m, 2H), 3.26 (d, $J = 1.9$ Hz, 1H), 3.18 (s, 1H), 2.92–2.80 (m, 2H), 2.71 (s, 3H), 2.71–2.67 (m, 1H), 2.10–2.00 (m, 2H), 0.66 (t, $J = 7.2$ Hz, 3H); ¹³C NMR (100 MHz, CDCl₃) δ (ppm) 213.1, 178.5, 170.8, 169.3, 139.5, 130.0, 129.1, 125.2, 122.9, 116.4, 61.1, 56.3, 53.1, 52.7, 48.4, 40.1, 37.8, 27.0, 13.5; ESI-HRMS: calcd. for $C_{19}H_{19}NO_5 + Na^+$ 364.1155, found 364.1154.

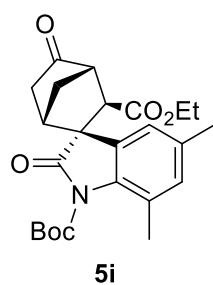


Ethyl (1*S*,2*R*,3*R*,4*S*)-2',5-dioxospiro[bicyclo[2.2.1]heptane-2,3'-indoline]-3-carboxylate (5g): Following the general procedure, a solution of 2-cyclopentenone **1** (16.4 mg, 0.2 mmol), ethyl (*E*)-2-(2-oxoindolin-3-ylidene)acetate **4g** (21.7 mg, 0.1 mmol), amine **C3** (4.0 mg, 0.02 mmol), salicylic acid **A1** (2.7 mg, 0.02 mmol) and 2-mercaptopbenzoic acid **T1** (3.1 mg, 0.02 mmol) in toluene (1.0 mL) was stirred at 40 °C for 24 h. After completion, purification by flash chromatography on silica gel (EtOAc/petroleum ether = 1/5) to give product **5g**: 26.3 mg, as a white solid, yield 88 %; $[\alpha]_D^{20}$: -3.3 ($c = 0.84$ in CHCl₃); 94% ee, determined by HPLC analysis [Daicel Chiralpak ID, *n*-hexane/*i*-PrOH = 70/30, 1.0 mL/min, $\lambda = 254$ nm, t (minor) = 9.03 min, t (major) = 10.56 min]; ¹H NMR (400 MHz, CDCl₃) δ (ppm) 8.57 (s, 1H), 7.37–7.20 (m, 2H), 7.01 (td, $J = 7.7, 1.0$ Hz, 1H), 6.95 (d, $J = 7.7$ Hz, 1H), 3.88–3.51 (m, 2H), 3.23 (s, 1H), 3.15 (s, 1H), 3.11 (d, $J = 4.7$

Hz, 1H), 2.80 (dd, J = 11.4, 4.6 Hz, 1H), 2.68 (d, J = 2.5 Hz, 1H), 2.10–1.87 (m, 2H), 0.66 (t, J = 7.1 Hz, 3H); ^{13}C NMR (100 MHz, CDCl_3) δ (ppm) 214.1, 179.5, 169.8, 140.5, 131.4, 128.8, 123.8, 122.5, 109.9, 60.8, 55.9, 53.2, 51.6, 47.2, 39.4, 37.8, 13.5; ESI-HRMS: calcd. for $\text{C}_{17}\text{H}_{17}\text{NO}_4+\text{Na}^+$ 322.1050, found 322.1052.

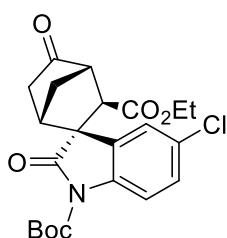


1'-(*tert*-Butyl) 3-ethyl (1*S*,2*R*,3*R*,4*S*)-5'-methyl-2',5-dioxospiro[bicyclo[2.2.1]heptane-2,3'-indoline]-1',3-dicarboxylate (5h): Following the general procedure, a solution of 2-cyclopentenone **1** (16.4 mg, 0.2 mmol), *tert*-butyl (*E*)-3-(2-ethoxy-2-oxoethylidene)-5-methyl-2-oxoindoline-1-carboxylate **4h** (33.1 mg, 0.1 mmol), amine **C3** (4.0 mg, 0.02 mmol), salicylic acid **A1** (2.7 mg, 0.02 mmol) and 2-mercaptopbenzoic acid **T1** (3.1 mg, 0.02 mmol) in toluene (1.0 mL) was stirred at 40 °C for 24 h. After completion, purification by flash chromatography on silica gel (EtOAc/petroleum ether = 1/18) to give product **5h**: 36.7 mg, as a white solid, yield 89%; $[\alpha]_D^{20}$: +119.0 (c = 0.09 in CHCl_3); >19:1 dr, 89% ee, determined by HPLC analysis [Daicel Chiralpak ID, *n*-hexane/*i*-PrOH = 70/30, 1.0 mL/min, λ = 254 nm, t (major) = 8.54 min, t (minor) = 10.94 min]; ^1H NMR (400 MHz, CDCl_3) δ (ppm) 7.76 (d, J = 8.3 Hz, 1H), 7.13 (d, J = 8.3 Hz, 1H), 7.07 (s, 1H), 3.76–3.64 (m, 2H), 3.25 (s, 1H), 3.14 (s, 1H), 2.91 (dd, J = 18.4, 4.6 Hz, 1H), 2.80 (d, J = 11.3 Hz, 1H), 2.63 (s, 1H), 2.32 (s, 3H), 2.08–1.91 (m, 2H), 1.64 (s, 9H), 0.67 (t, J = 7.1 Hz, 3H); ^{13}C NMR (100 MHz, CDCl_3) δ (ppm) 213.3, 176.0, 169.6, 149.1, 136.8, 133.9, 129.8, 129.2, 123.8, 114.6, 84.7, 60.9, 56.3, 53.1, 52.2, 48.2, 40.0, 37.7, 28.1, 21.1, 13.5; ESI-HRMS: calcd. for $\text{C}_{23}\text{H}_{27}\text{NO}_6+\text{Na}^+$ 436.1731, found 436.1737.



1'-(*tert*-Butyl) 3-ethyl (1*S*,2*R*,3*R*,4*S*)-5',7'-dimethyl-2',5-dioxospiro[bicycle[2.2.1]heptane-2,3'-indoline]-1',3-dicarboxylate (5i): Following the general procedure, a solution of 2-cyclopentenone **1** (16.4 mg, 0.2 mmol), *tert*-butyl (*E*)-3-(2-ethoxy-2-oxoethylidene)-5,7-dimethyl-2-oxoindoline-1-carboxylate **4i** (24.5 mg, 0.1 mmol), amine **C3** (4.0 mg, 0.02 mmol), salicylic acid **A1** (2.7 mg, 0.02 mmol) and 2-mercaptopbenzoic acid **T1** (3.1 mg, 0.02 mmol) in toluene (1.0 mL) was stirred at 40 °C for 24 h. After completion, purification by flash chromatography on silica gel (EtOAc/petroleum

ether = 1/20) to give product **5i**: 27.2 mg, as a white solid, yield 83%; $[\alpha]_D^{20}$: -19.3 ($c = 0.98$ in CHCl_3); 97% ee, determined by HPLC analysis [Daicel Chiralpak ID, *n*-hexane/*i*-PrOH = 70/30, 1.0 mL/min, $\lambda = 254$ nm, t (major) = 6.83 min, t (minor) = 8.25 min]; ^1H NMR (400 MHz, CDCl_3) δ (ppm) 6.95 (s, 1H), 6.92 (s, 1H), 3.82–3.52 (m, 2H), 3.25 (d, $J = 1.8$ Hz, 1H), 3.13 (s, 1H), 2.95 (dd, $J = 18.4, 4.8$ Hz, 1H), 2.79 (dd, $J = 11.4, 4.8$ Hz, 1H), 2.63 (d, $J = 2.4$ Hz, 1H), 2.29 (s, 3H), 2.20 (s, 3H), 2.03–1.92 (m, 2H), 1.63 (s, 9H), 0.67 (t, $J = 7.1$ Hz, 3H); ^{13}C NMR (100 MHz, CDCl_3) δ (ppm) 213.5, 177.3, 169.6, 149.2, 135.5, 133.7, 132.2, 131.3, 123.0, 121.4, 85.0, 60.9, 56.5, 52.9, 52.6, 47.8, 40.0, 37.7, 27.8, 21.0, 19.3, 13.3; ESI-HRMS: calcd. for $\text{C}_{24}\text{H}_{29}\text{NO}_6+\text{Na}^+$ 466.1626, found 466.1631.

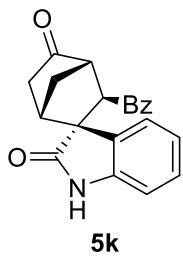


1'-(*tert*-Butyl) 3-ethyl (1*S*,2*R*,3*R*,4*S*)-5'-chloro-2',5-dioxospiro[bicycle[2.2.1]

heptane-2,3'-indoline]-1',3-dicarboxylate (5j): Following the general procedure, a solution of 2-cyclopentenone **1** (16.4 mg, 0.2 mmol), *tert*-butyl (*E*)-5-chloro-3-(2-ethoxy-2-oxoethylidene)-2-oxoindoline-1-carboxylate **4j** (35.1 mg, 0.1 mmol), amine **C3** (4.0 mg, 0.02 mmol), salicylic acid **A1** (2.7 mg, 0.02 mmol)

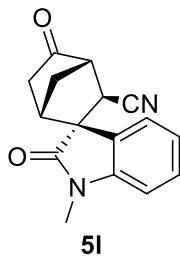
and 2-mercaptopbenzoic acid **T1** (3.1 mg, 0.02 mmol) in toluene (1.0 mL) was stirred at 40 °C for 24 h. After completion, purification by flash chromatography on silica gel (EtOAc/petroleum ether = 1/20) to give product **5j**: 34.5 mg, as a white solid, yield 80%; $[\alpha]_D^{20}$: +23.1 ($c = 1.37$ in CHCl_3); 92% ee, determined by HPLC analysis [Daicel Chiralpak ID, *n*-hexane/*i*-PrOH = 70/30, 1.0 mL/min, $\lambda = 254$ nm, t (major) = 7.60 min, t (minor) = 10.14 min]; ^1H NMR (400 MHz, CDCl_3) δ (ppm) 7.88 (d, $J = 8.7$ Hz, 1H), 7.32 (d, $J = 8.7$ Hz, 1H), 3.83–3.75 (m, 2H), 3.26 (s, 1H), 3.16 (s, 1H), 2.88 (dd, $J = 18.4, 4.6$ Hz, 1H), 2.72 (dd, $J = 11.3, 3.3$ Hz, 1H), 2.66 (s, 1H), 2.13–1.86 (m, 2H), 1.64 (s, 9H), 0.76 (t, $J = 7.1$ Hz, 3H); ^{13}C NMR (100 MHz, CDCl_3) δ (ppm) 212.8, 175.1, 169.2, 148.8, 137.7, 131.5, 129.9, 128.8, 123.4, 116.1, 85.3, 61.3, 56.2, 53.1, 52.3, 48.2, 40.0, 37.7, 28.1, 13.6; ESI-HRMS: calcd. for $\text{C}_{22}\text{H}_{24}\text{ClNO}_6+\text{Na}^+$ 456.1184 (^{35}Cl) and 458.1155 (^{37}Cl), found 456.1183, 458.1159.

(1*S*,2*R*,3*R*,4*S*)-3-Benzoylspiro[bicyclo[2.2.1]heptane-2,3'-indoline]-2',5-dione

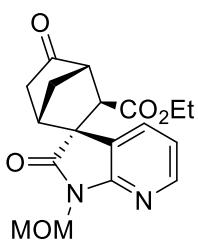


(5k): Following the general procedure, a solution of 2-cyclopentenone **1** (16.4 mg, 0.2 mmol), (*E*)-3-(2-oxo-2-phenylethylidene)indolin-2-one **4k** (24.9 mg, 0.1 mmol), amine **C3** (4.0 mg, 0.02 mmol), salicylic acid **A1** (2.7 mg, 0.02 mmol) and 2-mercaptopbenzoic acid **T1** (3.1 mg, 0.02 mmol) in toluene (1.0 mL) was stirred at 40

°C for 24 h. After completion, purification by flash chromatography on silica gel (EtOAc/petroleum ether = 1/5) to give product **5k**: 28.3 mg, as a white solid, yield 85%; $[\alpha]_D^{20}$: -30.8 ($c = 0.76$ in CHCl₃); 93% ee, determined by HPLC analysis [Daicel Chiralpak ID, *n*-hexane/*i*-PrOH = 70/30, 1.0 mL/min, $\lambda = 254$ nm, t (minor) = 9.69 min, t (major) = 13.10 min]; ¹H NMR (400 MHz, CDCl₃) δ (ppm) 8.46 (s, 1H), 7.44 (dd, $J = 8.3, 1.1$ Hz, 2H), 7.34–7.27 (m, 1H), 7.19–7.09 (m, 3H), 7.01 (td, $J = 7.7, 1.1$ Hz, 1H), 6.86 (td, $J = 7.7, 1.1$ Hz, 1H), 6.61 (d, $J = 7.7$ Hz, 1H), 4.12 (d, $J = 1.4$ Hz, 1H), 3.31 (s, 1H), 3.18 (dd, $J = 18.4, 4.7$ Hz, 1H), 2.87 (dd, $J = 11.4, 4.7$ Hz, 1H), 2.64 (d, $J = 2.4$ Hz, 1H), 2.14–1.99 (m, 2H); ¹³C NMR (100 MHz, CDCl₃) δ (ppm) 215.3, 196.5, 179.8, 139.7, 136.4, 133.0, 130.1, 128.5, 128.3, 127.7, 124.8, 122.6, 109.6, 56.3, 53.2, 52.8, 48.1, 39.9, 37.7; ESI-HRMS: calcd. for C₂₁H₁₇NO₃+Na⁺ 354.1101, found 354.1100.

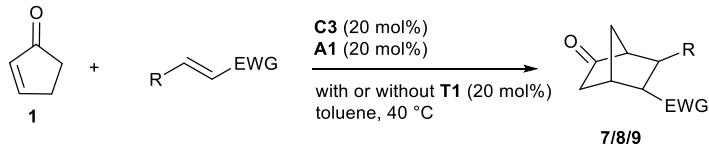


(1S,2R,3R,4S)-1'-Methyl-2',5-dioxospiro[bicyclo[2.2.1]heptane-2,3'-indoline]-3-carbonitrile (5l): Following the general procedure, a solution of 2-cyclopentenone **1** (16.4 mg, 0.2 mmol), (*E*)-2-(1-methyl-2-oxoindolin-3-ylidene)acetonitrile **4l** (18.4 mg, 0.1 mmol), amine **C3** (4.0 mg, 0.02 mmol), salicylic acid **A1** (2.7 mg, 0.02 mmol) and 2-mercaptopbenzoic acid **T1** (3.1 mg, 0.02 mmol) in toluene (1.0 mL) was stirred at 40 °C for 24 h. After completion, purification by flash chromatography on silica gel (EtOAc/petroleum ether = 1/5) to give product **5l**: 25.7 mg, as a white solid, yield 96%; $[\alpha]_D^{20}$: +185.1 ($c = 0.31$ in CHCl₃); 96% ee, determined by HPLC analysis [Daicel Chiralpak AD-H, *n*-hexane/*i*-PrOH = 80/20, 1.0 mL/min, $\lambda = 254$ nm, t (minor) = 15.12 min, t (major) = 20.18 min]; ¹H NMR (600 MHz, CDCl₃) δ (ppm) 7.59 (d, $J = 7.6$ Hz, 1H), 7.41 (t, $J = 7.6$ Hz, 1H), 7.19 (t, $J = 7.6$ Hz, 1H), 6.93 (d, $J = 7.6$ Hz, 1H), 3.35 (s, 1H), 3.25 (s, 3H), 3.17 (s, 1H), 3.03 (dd, $J = 18.5, 4.5$ Hz, 1H), 2.76 (dd, $J = 11.4, 2.4$ Hz, 1H), 2.71 (s, 1H), 2.12 (d, $J = 11.4$ Hz, 1H), 2.01 (dd, $J = 18.5, 4.5$ Hz, 1H); ¹³C NMR (100 MHz, CDCl₃) δ (ppm) 210.4, 176.0, 143.0, 129.6, 129.5, 124.8, 123.2, 117.3, 108.8, 55.5, 54.4, 48.1, 39.4, 38.4, 37.6, 26.8; ESI-HRMS: calcd. for C₁₆H₁₄N₂O₂+Na⁺ 289.0947, found 289.0948



Ethyl (1*S*,2*R*,3*R*,4*S*)-1'-(methoxymethyl)-2',5-dioxo-1',2'-dihydrospiro[bicycle[2.2.1]heptane-2,3'-pyrrolo[2,3-b]pyridine]-3-carboxylate (5m): Following the general procedure, a solution of 2-cyclopentenone **1** (16.4 mg, 0.2 mmol), ethyl (*E*)-2-(1-(methoxymethyl)-2-oxo-1,2-dihydro-3H-pyrrolo[2,3-b]pyridin-3-ylidene) acetate **4m** (27.8 mg, 0.1 mmol), amine **C3** (4.0 mg, 0.02 mmol), salicylic acid **A1** (2.7 mg, 0.02 mmol) and 2-mercaptopbenzoic acid **T1** (3.1 mg, 0.02 mmol) in toluene (1.0 mL) was stirred at 40 °C for 24 h. After completion, purification by flash chromatography on silica gel (EtOAc/petroleum ether = 1/5) to give product **5m**: 24.9 mg, as a white solid, yield 70%; $[\alpha]_D^{20}$: +3.3 (*c* = 0.71 in CHCl₃); 90% ee, determined by HPLC analysis [Daicel Chiralpak ID, *n*-hexane/*i*-PrOH = 70/30, 1.0 mL/min, λ = 254 nm, t (major) = 26.23 min, t (minor) = 35.09 min]; ¹H NMR (400 MHz, CDCl₃) δ (ppm) 8.28 (d, *J* = 5.2 Hz, 1H), 7.55 (d, *J* = 7.5 Hz, 1H), 7.00 (t, *J* = 7.5, 5.2 Hz, 1H), 5.29 (q, *J* = 10.4 Hz, 2H), 3.79–3.70 (m, 1H), 3.68–3.54 (m, 1H), 3.40 (s, 3H), 3.27 (s, 1H), 3.15 (s, 1H), 3.11 (dd, *J* = 18.6, 4.6 Hz, 1H), 2.68 (s, 2H), 2.16–1.89 (m, 2H), 0.70 (t, *J* = 7.1 Hz, 3H); ¹³C NMR (100 MHz, CDCl₃) δ (ppm) 212.9, 177.5, 169.4, 155.5, 147.9, 131.3, 124.9, 118.6, 70.2, 61.1, 57.1, 55.2, 52.9, 51.8, 47.1, 39.2, 37.8, 13.6; ESI-HRMS: calcd. for C₁₈H₂₀N₂O₅+Na⁺ 367.1264, found 367.1266.

5. More exploration of 2-cyclopentenone **1** with diverse activated alkenes



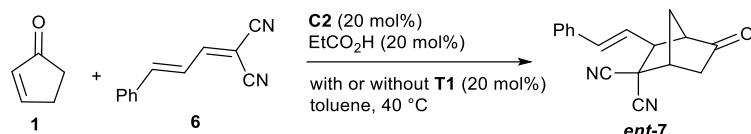
Condition A (with T1)

A solution of 2-cyclopentenone **1** (16.4 mg, 0.2 mmol), activated alkenes (0.1 mmol), amine **C3** (4.0 mg, 0.02 mmol), salicylic acid **A1** (2.7 mg, 0.02 mmol) and 2-mercaptopbenzoic acid **T1** (3.1 mg, 0.02 mmol) in toluene (1.0 mL) was stirred at 40 °C and the reaction was monitored by TLC. After completion, the product was obtained by flash chromatography on silica gel (EtOAc/petroleum ether = 1/40–1/10).

Condition B (without T1)

A solution of 2-cyclopentenone **1** (16.4 mg, 0.2 mmol), activated alkenes (0.1 mmol), amine **C3** (4.0 mg, 0.02 mmol) and salicylic acid **A1** (2.7 mg, 0.02 mmol) in toluene (1.0 mL) was stirred at 40

°C and the reaction was monitored by TLC. After completion, the product was obtained by flash chromatography on silica gel (EtOAc/petroleum ether = 1/40–1/10).



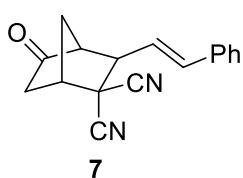
Reported catalytic conditions⁴

A solution of 2-cyclopentenone **1** (16.4 mg, 0.2 mmol), (*E*)-2-(3-phenylallylidene)malononitrile (0.1 mmol), amine **C2** (6.5 mg, 0.02 mmol) and propionic acid (1.5 mg, 0.02 mmol) in toluene (0.1 mL) was stirred at 40 °C and the reaction was monitored by TLC. After completion, the product was obtained by flash chromatography on silica gel (EtOAc/petroleum ether = 1/14).

Reported catalytic conditions by adding **T1**

A solution of 2-cyclopentenone **1** (16.4 mg, 0.2 mmol), activated alkenes (0.1 mmol), amine **C2** (6.5 mg, 0.02 mmol), propionic acid (1.5 mg, 0.02 mmol) and 2-mercaptopbenzoic acid **T1** (3.1 mg, 0.02 mmol) in toluene (0.1 mL) was stirred at 40 °C and the reaction was monitored by TLC. After completion, the product was obtained by flash chromatography on silica gel (EtOAc/petroleum ether = 1/14).

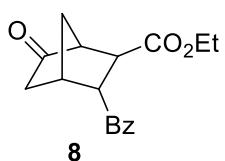
(4) R. Mose, M. E. Jensen, G. Preegel and K. A. Jørgensen, *Angew. Chem., Int. Ed.*, 2015, **54**, 13630.



(1*S*,4*S*)-5-oxo-3-((*E*)-styryl)bicyclo[2.2.1]heptane-2,2-dicarbonitrile (7):

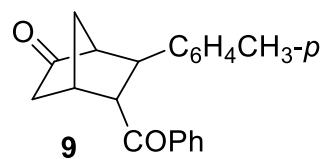
Following the general procedure, a solution of (*E*)-2-(3-phenylallylidene)malononitrile **6** (18.0 mg, 0.1 mmol), 2-cyclopentenone **1** (16.4 mg, 0.2 mmol), amine **C3** (4.0 mg, 0.02 mmol), salicylic acid **A1** (2.7 mg, 0.02 mmol) and 2-mercaptopbenzoic acid **T1** (3.1 mg, 0.02 mmol) in toluene (1.0 mL) was stirred at 40 °C for 24 h. After completion, purification by flash chromatography on silica gel (EtOAc/petroleum ether = 1/14) to give product **7**: 22.3 mg, as a white solid, yield 85%; $[\alpha]_D^{20}$: +55.4 ($c = 0.23$ in CHCl_3); 92% ee, determined by HPLC analysis [Daicel Chiralpak ID, *n*-hexane/*i*-PrOH = 80/20, 1.0 mL/min, $\lambda = 254$ nm, t (minor) = 10.52 min, t (major) = 11.23 min]; ^1H NMR (400 MHz, CDCl_3) δ (ppm) 7.42 (d, $J = 7.1$ Hz, 2H), 7.39–7.28 (m, 3H), 6.71 (d, $J = 15.5$ Hz, 1H), 6.13 (dd, $J = 15.5$, 9.4 Hz, 1H), 3.44 (d, $J = 3.3$ Hz, 1H), 3.23 (d, $J = 9.4$ Hz, 1H), 2.78 (s, 1H), 2.62 (dd, $J = 19.0$, 4.2 Hz, 1H), 2.50–2.35 (m, 2H), 2.15 (d, $J = 12.0$ Hz, 1H); ^{13}C NMR (100 MHz, CDCl_3) δ (ppm)

208.4, 136.6, 135.2, 128.9, 128.8, 127.0, 121.8, 115.0, 113.6, 55.1, 51.7, 47.1, 42.3, 40.4, 34.9; ESI-HRMS: calcd. for $C_{17}H_{14}N_2O+Na^+$ 285.0998, found 285.0996.



Ethyl (1*S*,3*R*,4*S*)-3-benzoyl-6-oxobicyclo[2.2.1]heptane-2-carboxylate (8):

Following the general procedure, a solution of ethyl (*E*)-4-oxo-4-phenylbut-2-enoate (20.4 mg, 0.1 mmol), 2-cyclopentenone **1** (16.4 mg, 0.2 mmol), amine **C3** (4.0 mg, 0.02 mmol), salicylic acid **A1** (2.7 mg, 0.02 mmol) and 2-mercaptopbenzoic acid **T1** (3.1 mg, 0.02 mmol) in toluene (1.0 mL) was stirred at 40 °C for 18 h. After completion, purification by flash chromatography on silica gel (EtOAc/petroleum ether = 1/18) to give product **8**: 22.6 mg, as a white solid, yield 89%; $[\alpha]_D^{20}$: -13.4 ($c = 1.84$ in CHCl₃); 96% ee, determined by HPLC analysis [Daicel Chiraldak ID, *n*-hexane/*i*-PrOH = 60/40, 1.0 mL/min, $\lambda = 254$ nm, t (minor) = 9.83 min, t (major) = 13.88 min]; ¹H NMR (400 MHz, CDCl₃) δ (ppm) 8.03 (d, $J = 7.6$ Hz, 2H), 7.61 (t, $J = 7.3$ Hz, 1H), 7.50 (t, $J = 7.6$ Hz, 2H), 4.42 (t, $J = 4.3$ Hz, 1H), 4.16 (q, $J = 7.0$ Hz, 2H), 3.49 (d, $J = 4.9$ Hz, 1H), 3.09 (s, 1H), 3.01 (s, 1H), 2.16 (d, $J = 10.2$ Hz, 1H), 1.95–1.77 (m, 3H), 1.25 (t, $J = 7.1$ Hz, 3H); ¹³C NMR (100 MHz, CDCl₃) δ (ppm) 212.8, 197.9, 173.0, 136.3, 133.6, 128.9, 128.5, 61.5, 54.5, 51.2, 42.7, 40.5, 39.4, 37.7, 14.2; ESI-HRMS: calcd. for $C_{17}H_{18}O_4+Na^+$ 309.1097, found 309.1100.

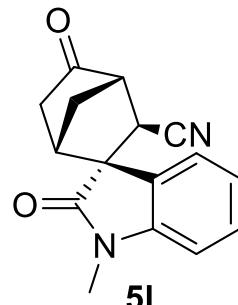
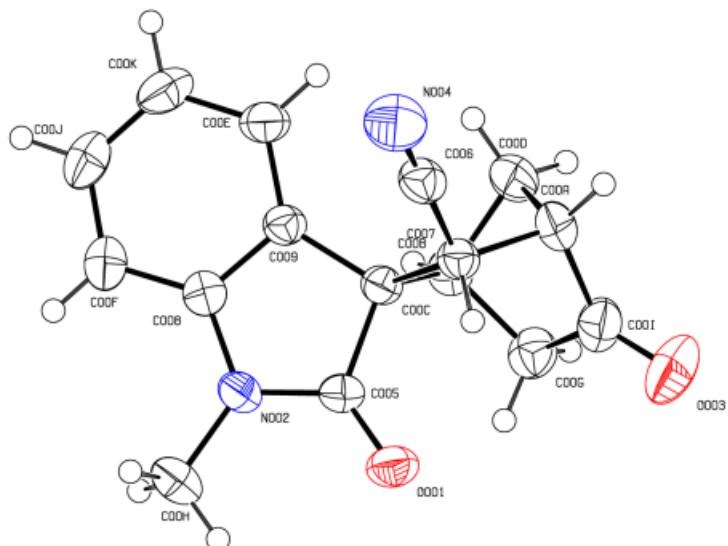


(1*S*,4*S*,5*R*)-5-(4-methylbenzoyl)-6-phenylbicyclo[2.2.1]heptan-2-one (9):

Following the general procedure, a solution of (*E*)-1-phenyl-3-(*p*-tolyl)prop-2-en-1-one (22.2 mg, 0.1 mmol), 2-cyclopentenone **1** (16.4 mg, 0.2 mmol), amine **C3** (4.0 mg, 0.02 mmol), salicylic acid **A1** (2.7 mg, 0.02 mmol) and 2-mercaptopbenzoic acid **T1** (3.1 mg, 0.02 mmol) in toluene (1.0 mL) was stirred at 40 °C for 24 h. After completion, purification by flash chromatography on silica gel (EtOAc/petroleum ether = 1/20) to give product **9**: 19.5 mg, as a colorless oil, yield 64%; $[\alpha]_D^{20}$: -67.7 ($c = 0.31$ in CHCl₃); 93% ee, determined by HPLC analysis [Daicel Chiraldak ID, *n*-hexane/*i*-PrOH = 70/30, 1.0 mL/min, $\lambda = 254$ nm, t (minor) = 5.31 min, t (major) = 5.82 min]; ¹H NMR (400 MHz, CDCl₃) δ (ppm) 7.98 (d, $J = 7.5$ Hz, 2H), 7.58 (t, $J = 7.5$ Hz, 1H), 7.47 (t, $J = 7.5$ Hz, 2H), 7.12 (s, 4H), 4.08 (t, $J = 4.8$ Hz, 1H), 3.92 (d, $J = 5.6$ Hz, 1H), 3.13 (s, 1H), 2.94 (s, 1H), 2.40 (d, $J = 10.5$ Hz, 1H), 2.31 (s, 3H), 2.02–1.88 (m, 3H); ¹³C NMR (150 MHz, CDCl₃) δ (ppm) 214.3, 198.8, 139.6, 136.7, 136.3, 133.4, 129.5, 128.8, 128.4, 126.7, 57.5, 56.4, 41.9, 41.2, 39.3, 38.0, 20.9; ESI-HRMS: calcd. for

$C_{21}H_{20}O_2 + Na^+$ 327.1356, found 327.1357.

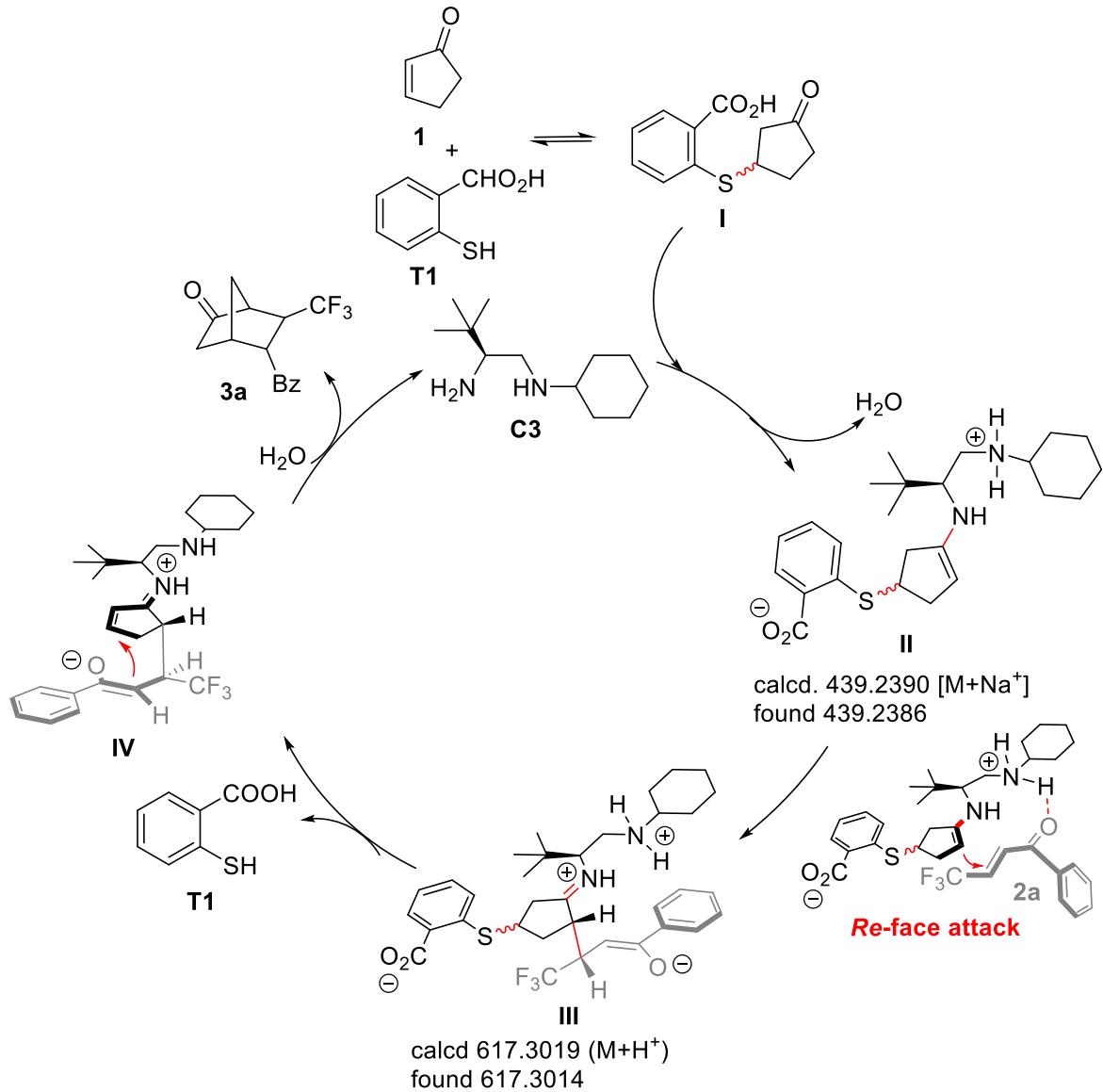
6. Crystal data and structural refinement for enantiopure **5l**

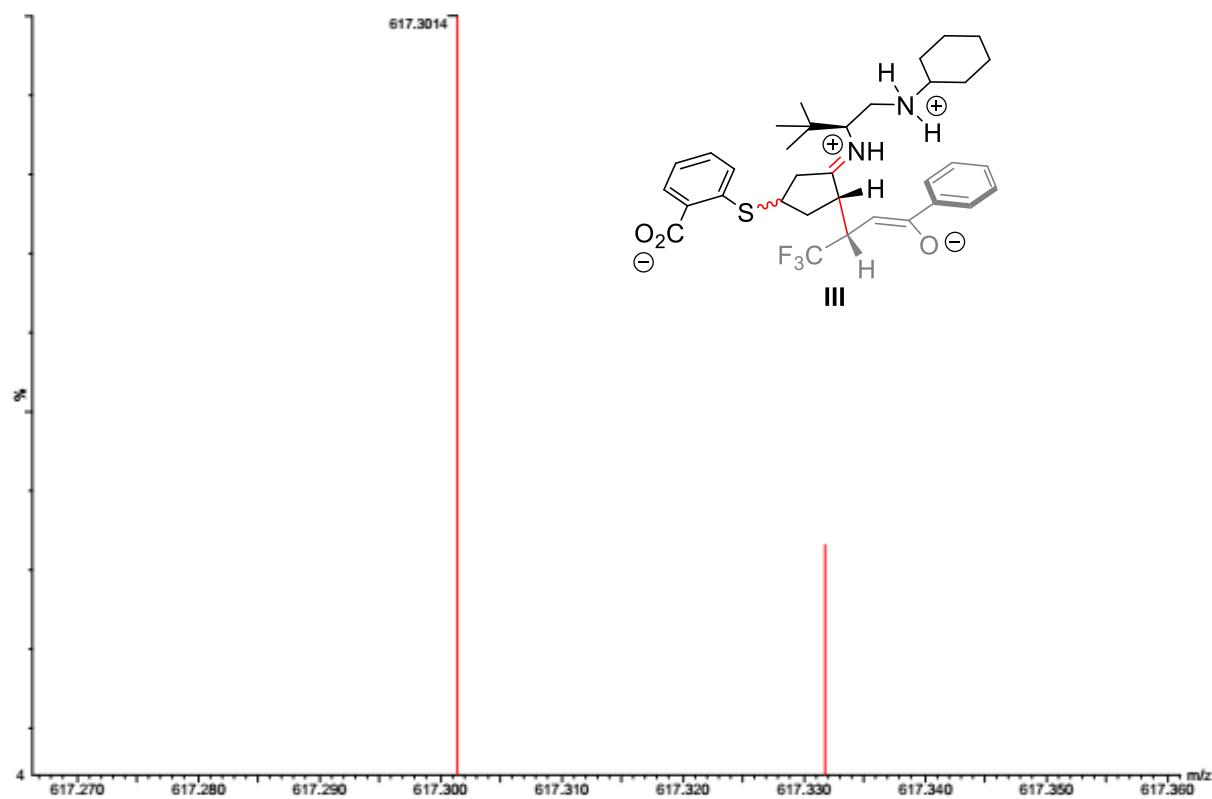
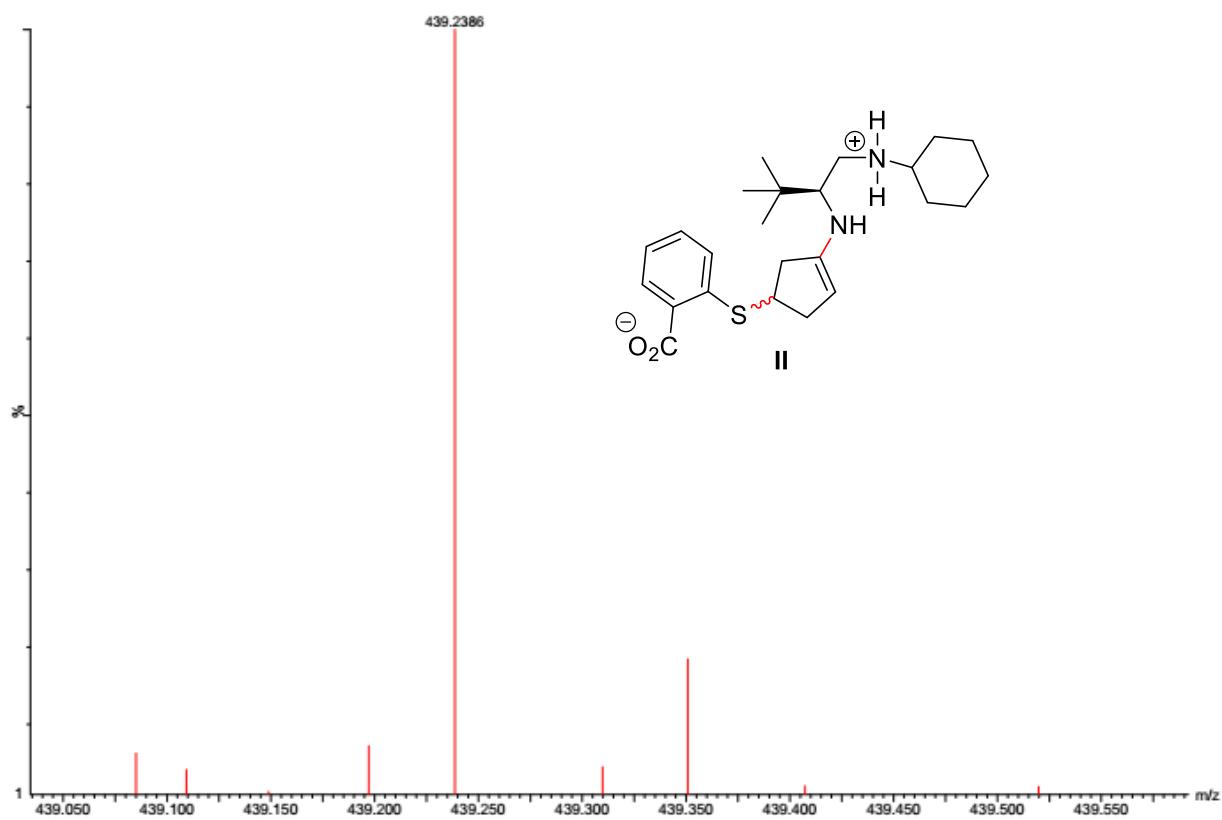


Identification code	5l
Empirical formula	$C_{16}H_{14}N_2O_2$
Formula weight	266.29
Temperature/K	293.47(10)
Crystal system	orthorhombic
Space group	P2 ₁ 2 ₁ 2 ₁
a/Å	7.7601(3)
b/Å	11.4659(4)
c/Å	14.7078(5)
$\alpha/^\circ$	90
$\beta/^\circ$	90
$\gamma/^\circ$	90
Volume/Å ³	1308.65(9)
Z	4
$\rho_{\text{calc}}/\text{g/cm}^3$	1.352
μ/mm^{-1}	0.734
F(000)	560.0
Crystal size/mm ³	0.7 × 0.6 × 0.5
Radiation	CuKα ($\lambda = 1.54184$)
2θ range for data collection/°	12.034 to 145.198
Index ranges	-6 ≤ h ≤ 9, -13 ≤ k ≤ 14, -17 ≤ l ≤ 17
Reflections collected	7223
Independent reflections	2539 [$R_{\text{int}} = 0.0179$, $R_{\text{sigma}} = 0.0158$]
Data/restraints/parameters	2539/0/182

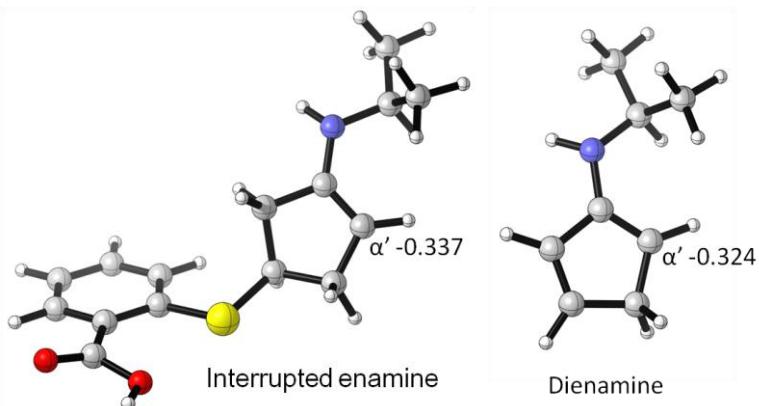
Goodness-of-fit on F ²	1.117
Final R indexes [I>=2σ (I)]	R ₁ = 0.0522, wR ₂ = 0.1269
Final R indexes [all data]	R ₁ = 0.0528, wR ₂ = 0.1280
Largest diff. peak/hole / e Å ⁻³	0.26/-0.49
Flack parameter	-0.06(10)

7. HRMS study of the key intermediates in [4 + 2] annulation reaction





8. DFT calculations of NPA charge of interrupted enamine and dienamine species



The structure and the NPA charge of interrupted enamine and dienamine species

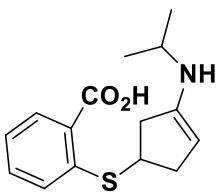
Computational method:

All calculations were carried out with the GAUSSIAN 09 packages.⁵ The recently developed M06-2x functional,⁶ together with 6-31+G(d) basis set, were used for optimizing the geometry of all the minima. All the optimized structures were confirmed by frequency calculations to be either minima using the same level of theory. The NPA charge was calculated using M06-2x functional², together with 6-311++G(2d,p) basis set. Structures were generated using GaussView 5.0.8 and CYLview.

(5) M. J. Frisch, G. W. Trucks, H. B. Schlegel, G. E. Scuseria, M. A. Robb, J. R. Cheeseman, G. Scalmani, V. Barone, B. Mennucci, G. A. Petersson, H. Nakatsuji, M. Caricato, X. Li, H. P. Hratchian, A. F. Izmaylov, J. Bloino, G. Zheng, J. L. Sonnenberg, M. Hada, M. Ehara, K. Toyota, R. Fukuda, J. Hasegawa, M. Ishida, T. Nakajima, Y. Honda, O. Kitao, H. Nakai, T. Vreven,, J. A. Montgomery Jr.; J. E. Peralta, F. Ogliaro, M. J. Bearpark, J. Heyd, E. N. Brothers, K. N. Kudin, V. N. Staroverov, R. Kobayashi, J. Normand, K. Raghavachari, A. P. Rendell, J. C. Burant, S. S. Iyengar, J. Tomasi, M. Cossi, N. Rega, N. J. Millam, M. Klene, J. E. Knox, J. B. Cross, V. Bakken, C. Adamo, J. Jaramillo, R. Gomperts, R. E. Stratmann, O. Yazyev, A. J. Austin, R. Cammi, C. Pomelli, J. W. Ochterski, R. L. Martin, K. Morokuma, V. G. Zakrzewski, G. A. Voth, P. Salvador, J. J. Dannenberg, S. Dapprich, A. D. Daniels, Ö. Farkas, J. B. Foresman, J. V. Ortiz, J. Cioslowski, D. J. Fox, Gaussian 09, Gaussian, Inc.: Wallingford, CT, USA, 2009.

(6) Y. Zhao, N. E. Schultz, D. G. Truhlar, Exchange-correlation functional with broad accuracy for metallic and nonmetallic compounds, kinetics, and noncovalent interactions. *J. Chem. Phys.* **123**, 161103 (2005). doi:10.1063/1.2126975

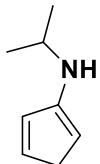
Interrupted enamine



Center Number	Atomic Number	Atomic Type	Coordinates (Angstroms)		
			X	Y	Z
1	6	0	-2.400250	-2.666033	0.723042
2	6	0	-1.654371	-1.502979	0.871586
3	6	0	-2.109669	-0.266097	0.388044
4	6	0	-3.374277	-0.242609	-0.245497
5	6	0	-4.106068	-1.426331	-0.400385
6	6	0	-3.633768	-2.639326	0.076680
7	1	0	-2.008724	-3.598866	1.119477
8	1	0	-0.702688	-1.566567	1.384040
9	1	0	-5.062817	-1.359152	-0.908703
10	1	0	-4.217456	-3.545622	-0.047706
11	6	0	-4.050609	0.968551	-0.794858
12	8	0	-4.988604	0.933736	-1.558826
13	8	0	-3.551310	2.129734	-0.339145
14	1	0	-4.059865	2.845137	-0.760144
15	16	0	-1.118919	1.203221	0.562686
16	6	0	0.532224	0.563117	0.977338
17	6	0	1.466101	1.767190	1.247370
18	6	0	1.242801	-0.249234	-0.120565
19	1	0	0.484606	-0.023056	1.900422
20	6	0	2.817470	1.222260	0.852661
21	1	0	1.404833	2.087392	2.292655
22	1	0	1.183676	2.632608	0.628686
23	6	0	2.695068	0.118758	0.091023
24	1	0	1.064050	-1.328218	-0.039416
25	1	0	0.913241	0.061541	-1.120910
26	1	0	3.745976	1.722074	1.104336
27	7	0	3.669876	-0.618441	-0.549449
28	1	0	3.426135	-1.588930	-0.707539
29	6	0	5.080151	-0.369488	-0.270718
30	1	0	5.191722	-0.142182	0.802836
31	6	0	5.579039	0.822074	-1.088214
32	1	0	5.565733	0.570510	-2.154229
33	1	0	4.942005	1.698401	-0.939813
34	1	0	6.603131	1.085483	-0.802395
35	6	0	5.881705	-1.625915	-0.590370

36	1	0	6.948174	-1.453108	-0.420102
37	1	0	5.570148	-2.469175	0.035825
38	1	0	5.747722	-1.902108	-1.643221

Dienamine

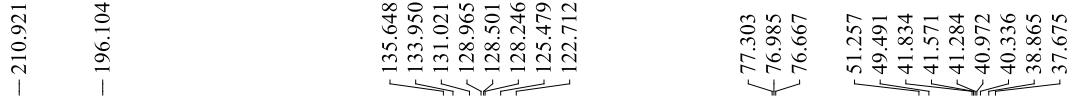
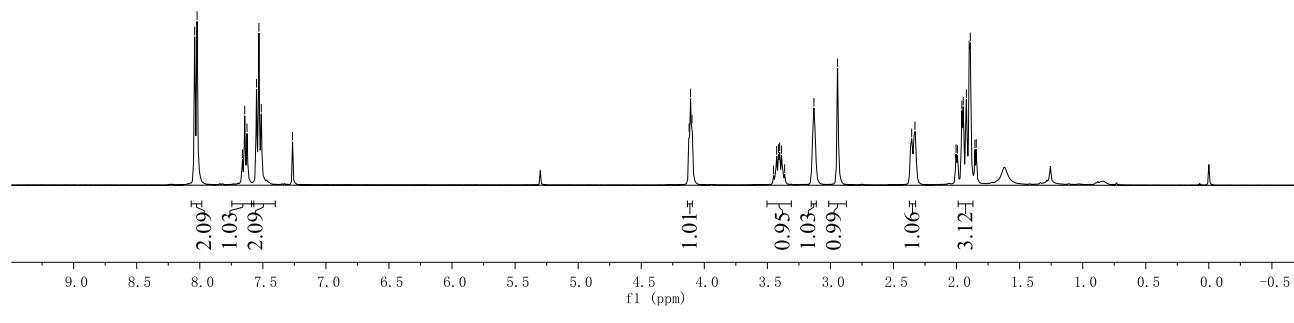


Center Number	Atomic Number	Atomic Type	Coordinates (Angstroms)		
			X	Y	Z
1	6	0	-2.890452	-0.501833	-0.130454
2	6	0	-2.581110	0.892172	0.342365
3	6	0	-1.743088	-1.159165	-0.362953
4	1	0	-3.893670	-0.890466	-0.262788
5	6	0	-1.077247	0.927881	0.357797
6	1	0	-3.016495	1.082521	1.333840
7	1	0	-3.015210	1.640464	-0.336710
8	6	0	-0.603412	-0.273657	-0.056292
9	1	0	-1.637072	-2.177051	-0.726402
10	1	0	-0.498184	1.794787	0.649140
11	7	0	0.703445	-0.698865	-0.237344
12	1	0	0.829964	-1.695289	-0.103976
13	6	0	1.797987	0.123268	0.265612
14	1	0	1.492588	0.573763	1.225510
15	6	0	2.116562	1.240950	-0.727783
16	1	0	2.523391	0.811656	-1.649789
17	1	0	1.217699	1.806606	-0.987831
18	1	0	2.853527	1.934044	-0.307502
19	6	0	3.018206	-0.758287	0.503346
20	1	0	3.866655	-0.156252	0.841452
21	1	0	2.819195	-1.521064	1.264379
22	1	0	3.308817	-1.259642	-0.427749

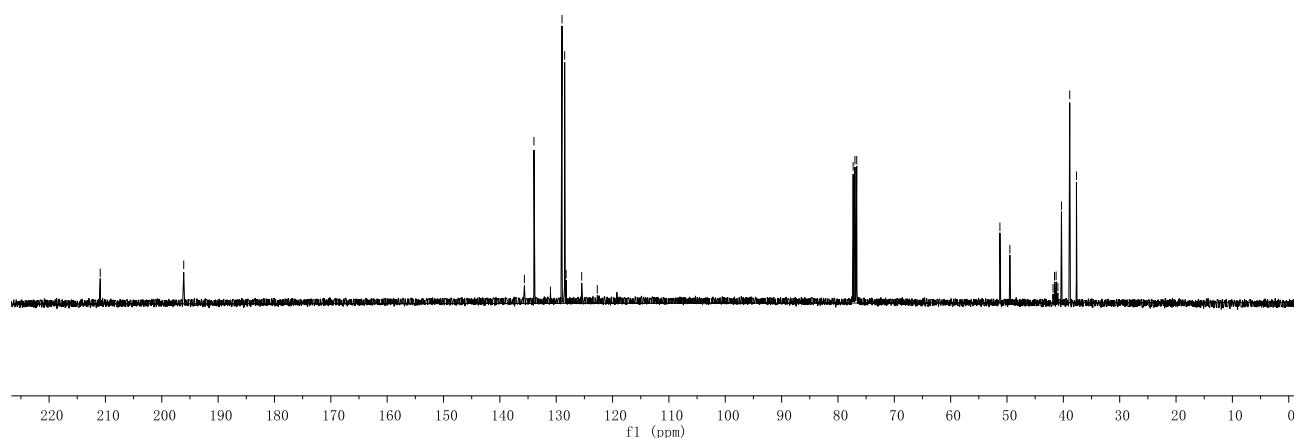
9. NMR spectra and HPLC chromatograms

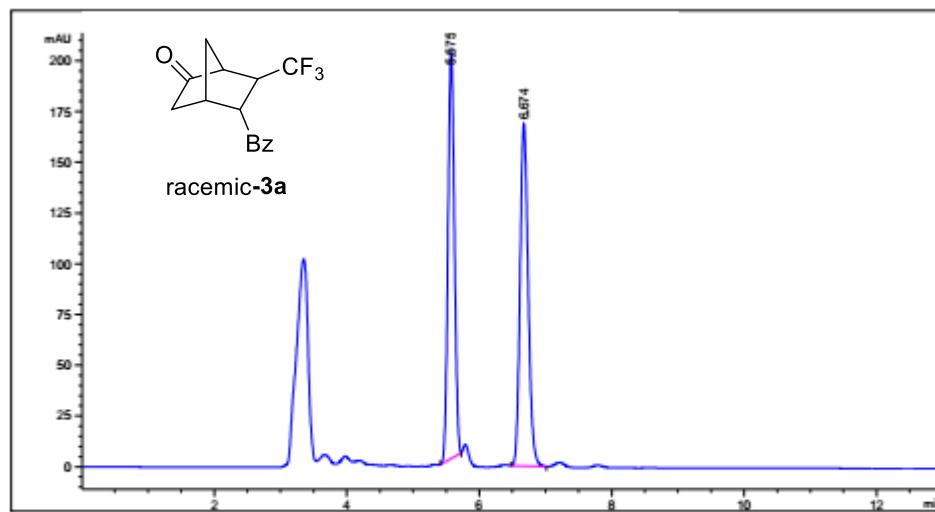


^1H NMR ($400 \text{ MHz}, \text{CDCl}_3$)

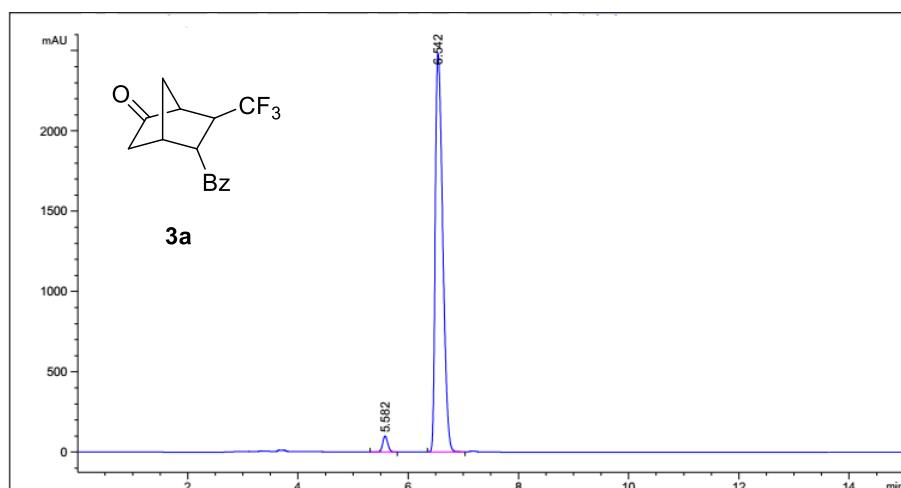


^{13}C NMR ($100 \text{ MHz}, \text{CDCl}_3$)

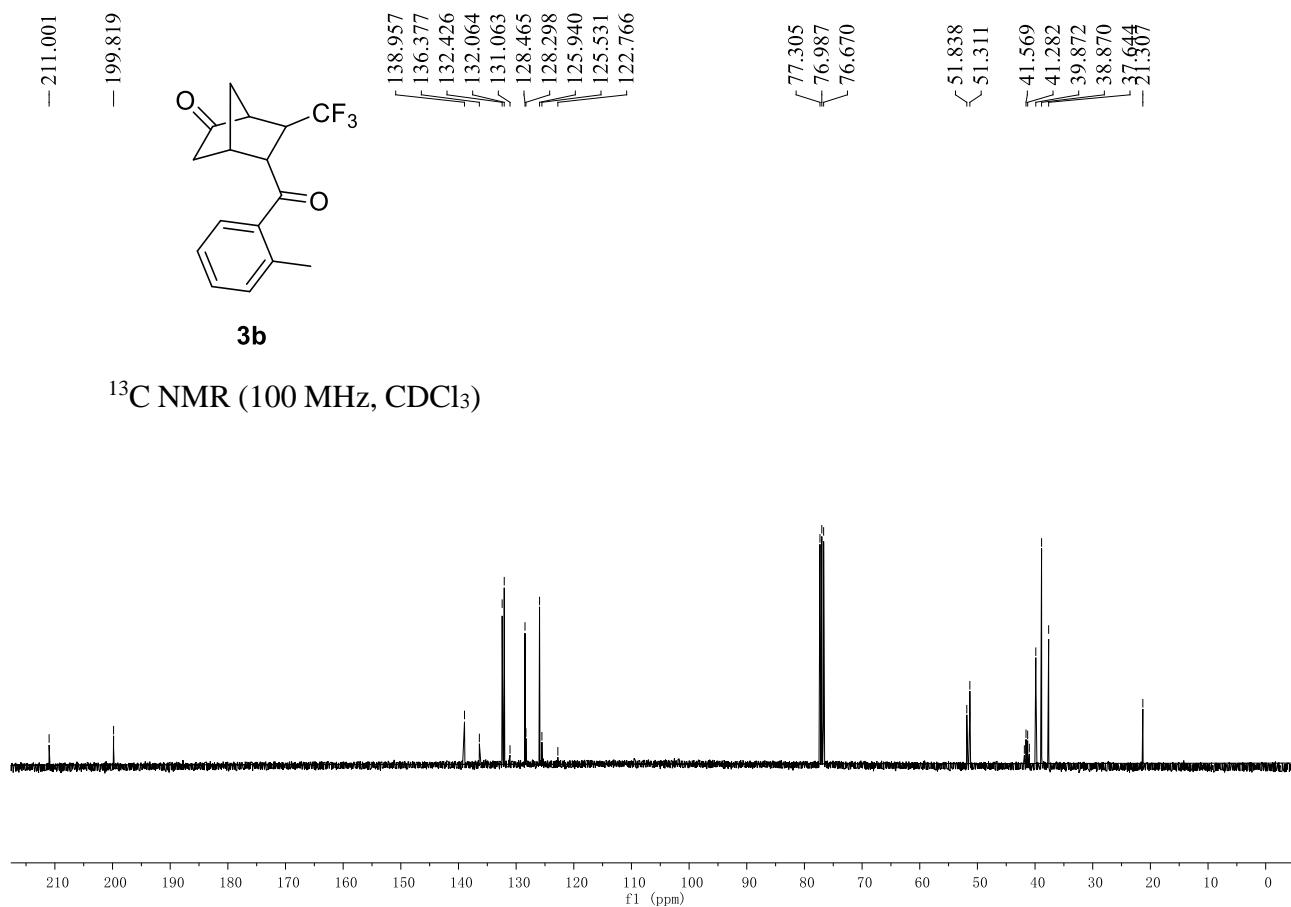
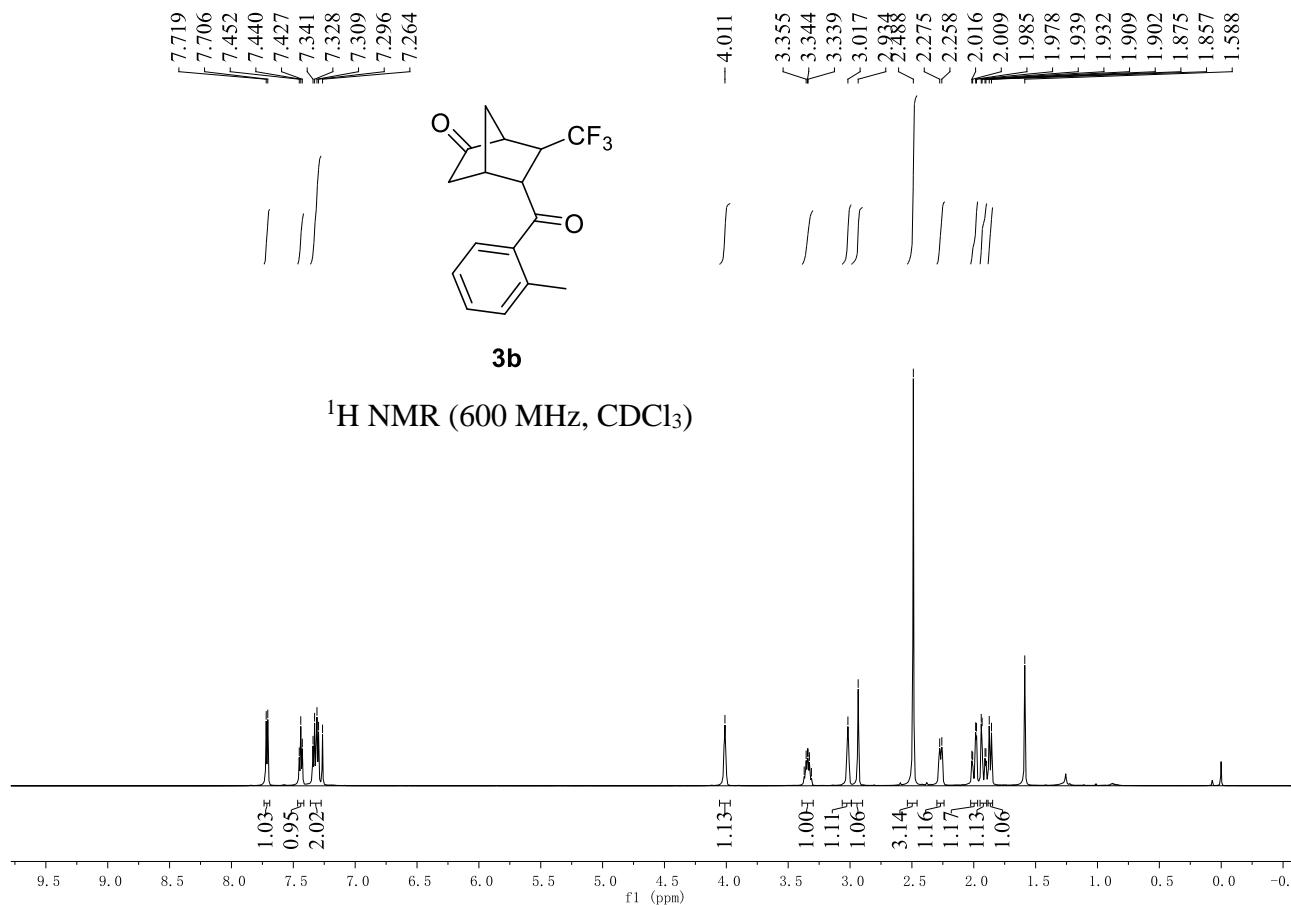


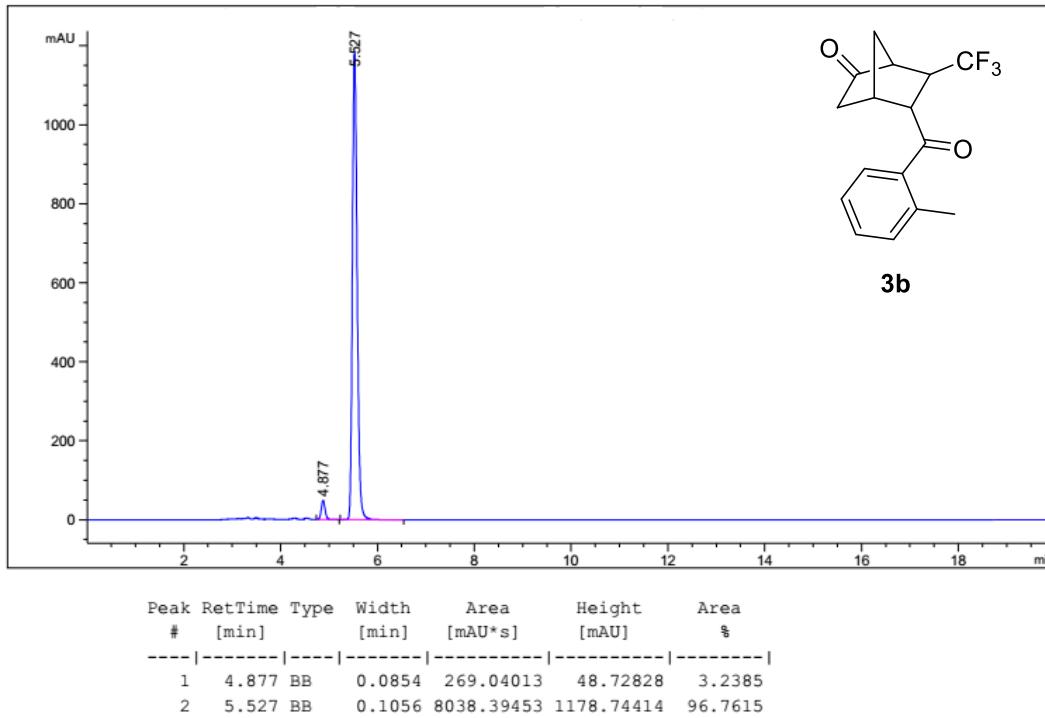
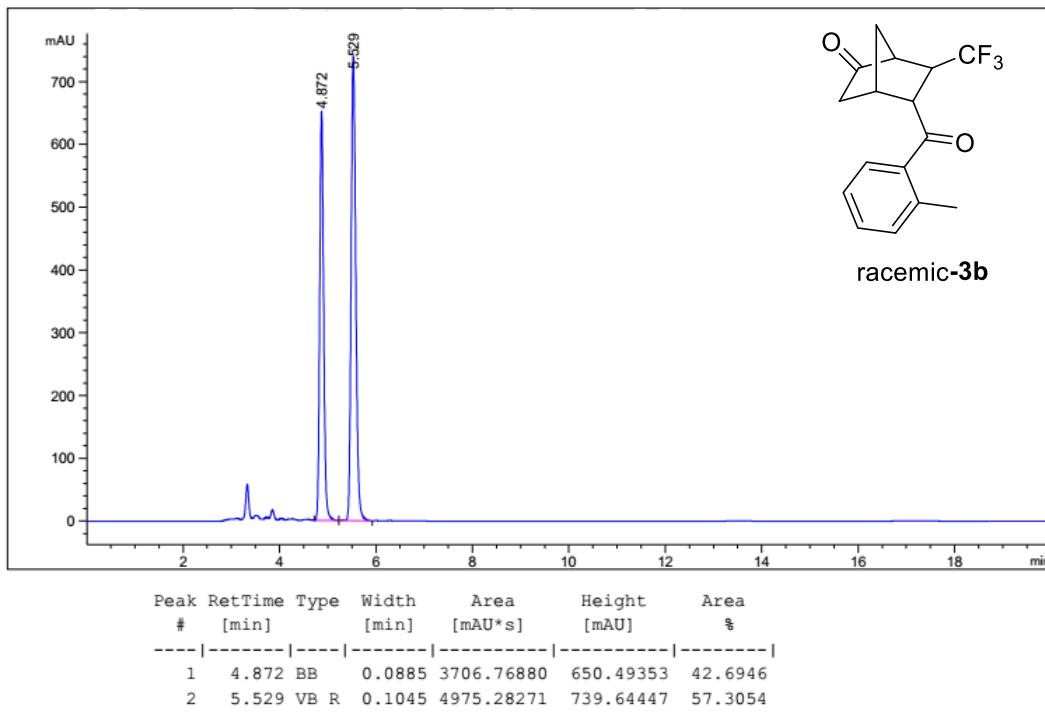


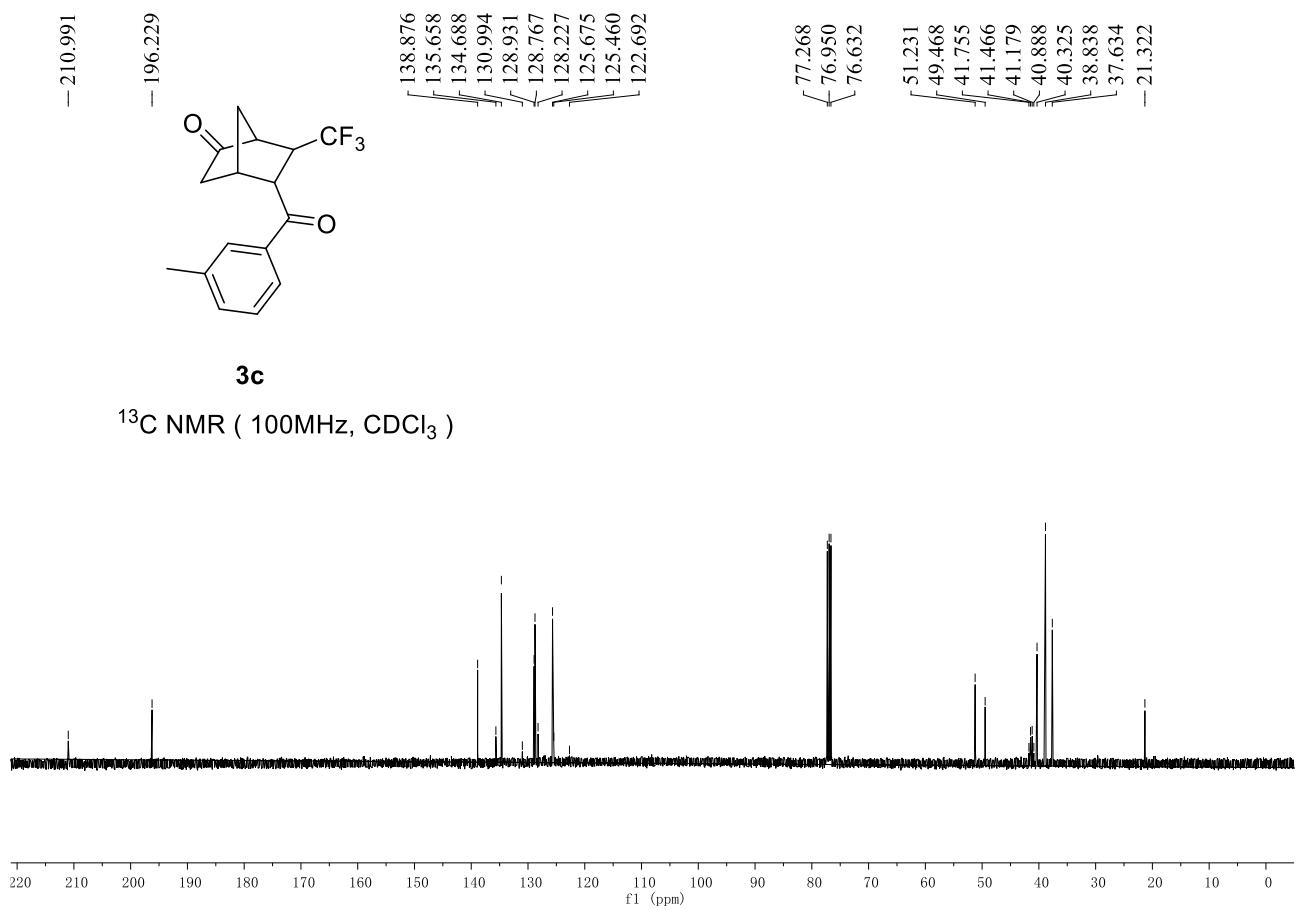
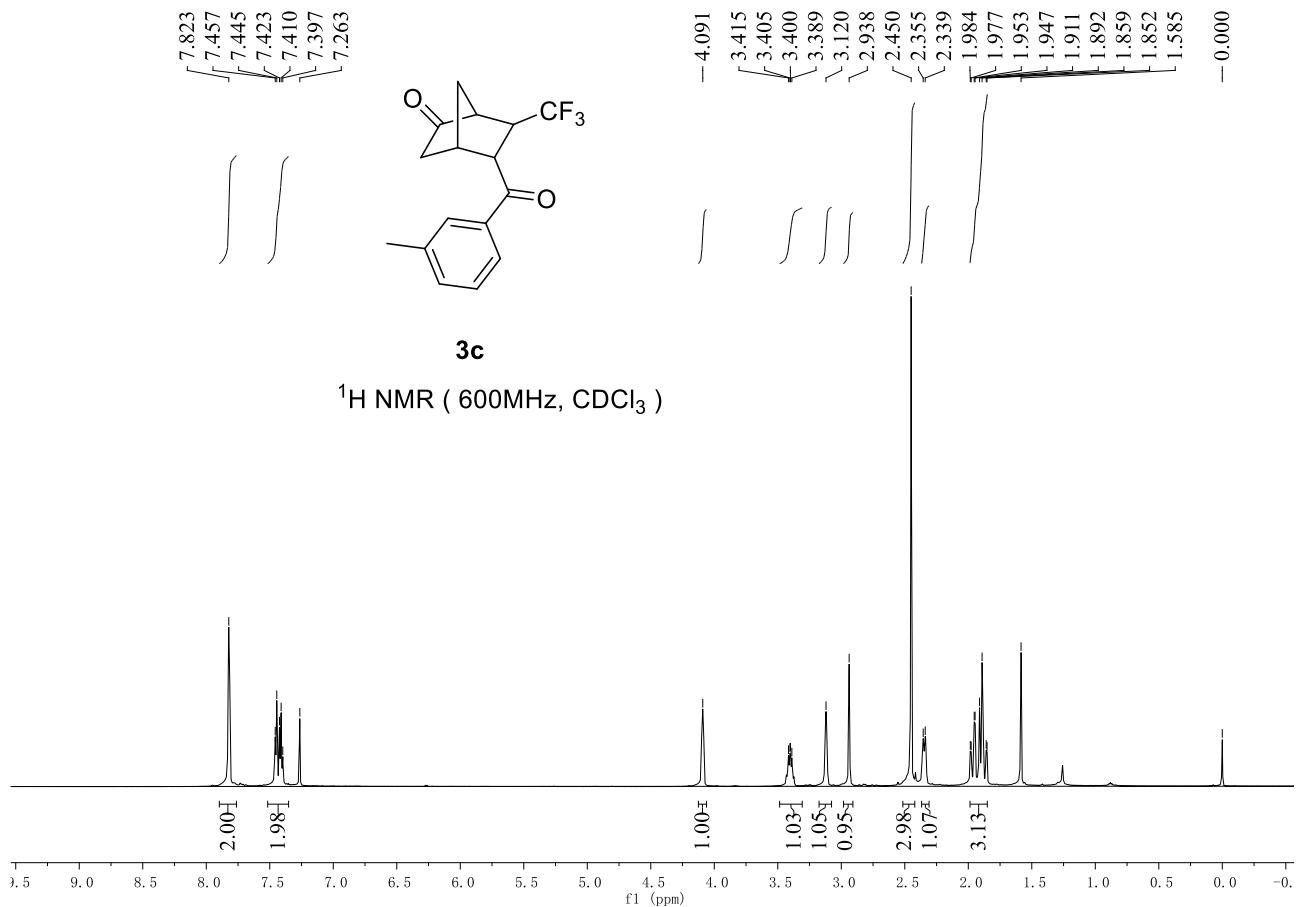
Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	5.575	BB	0.1056	1345.14038	199.55978	48.3667
2	6.674	BBA	0.1313	1435.98804	168.72050	51.6333

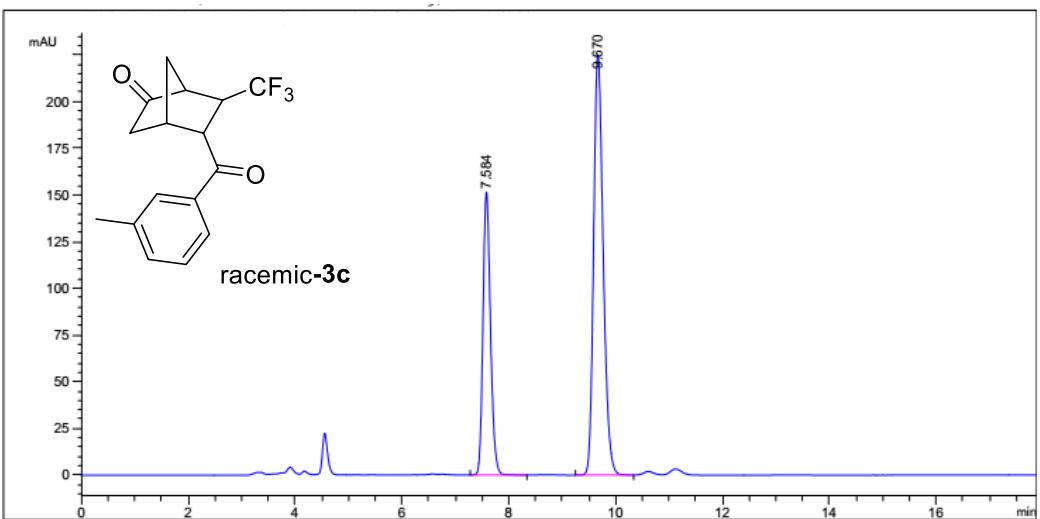


Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	5.582	BBA	0.0997	637.14618	99.51514	2.6608
2	6.542	BB	0.1497	2.33084e4	2478.99536	97.3392

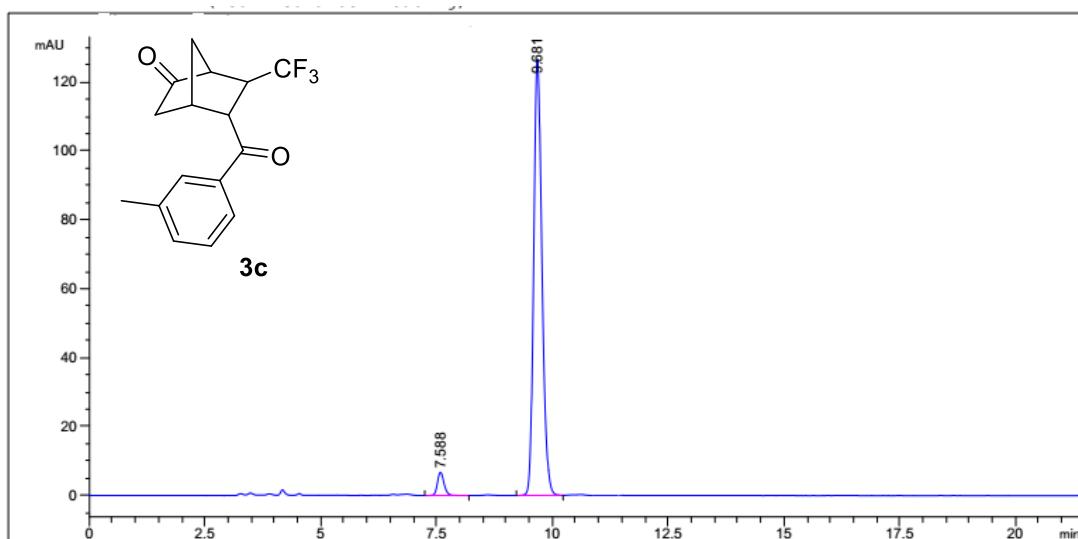




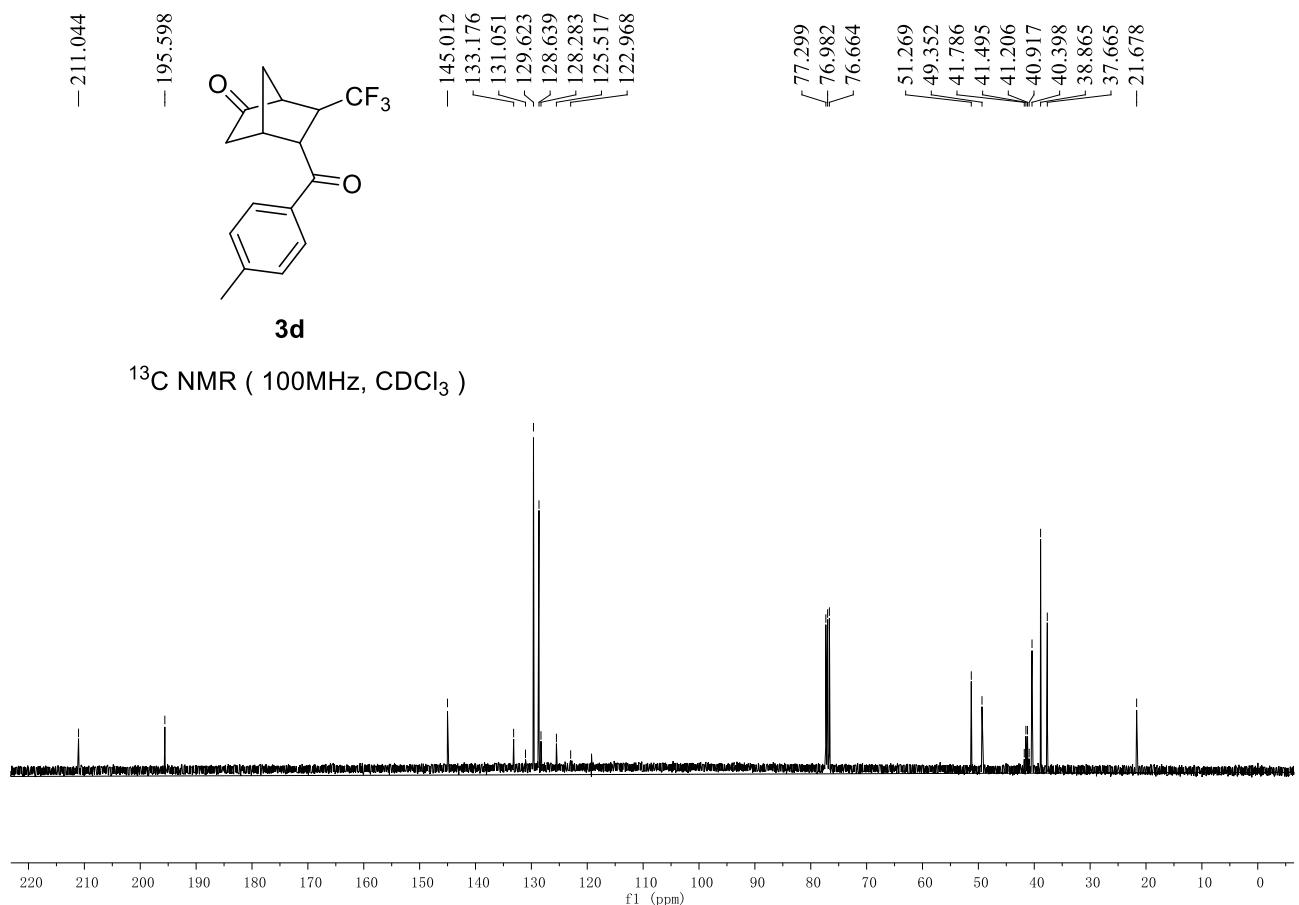
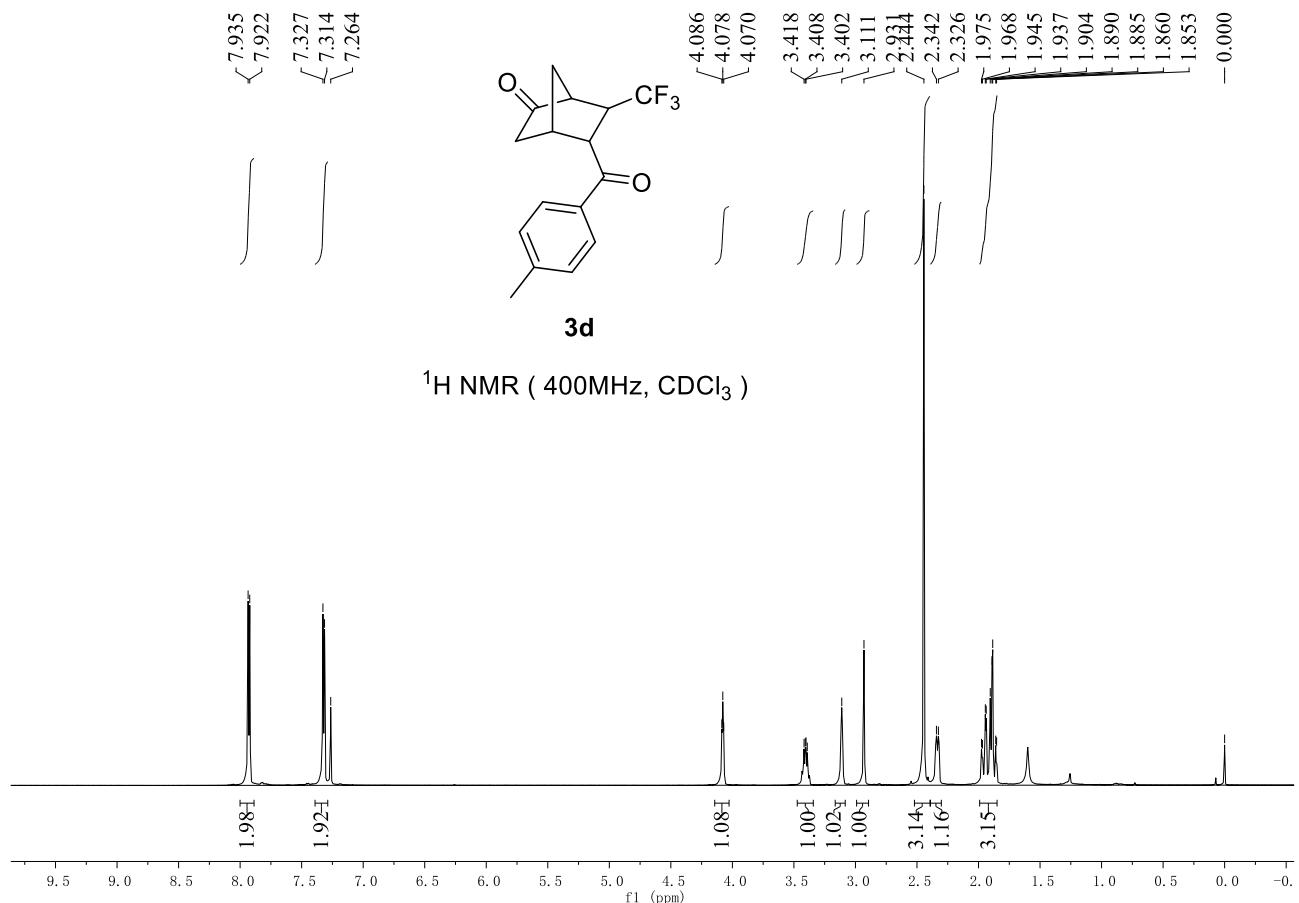


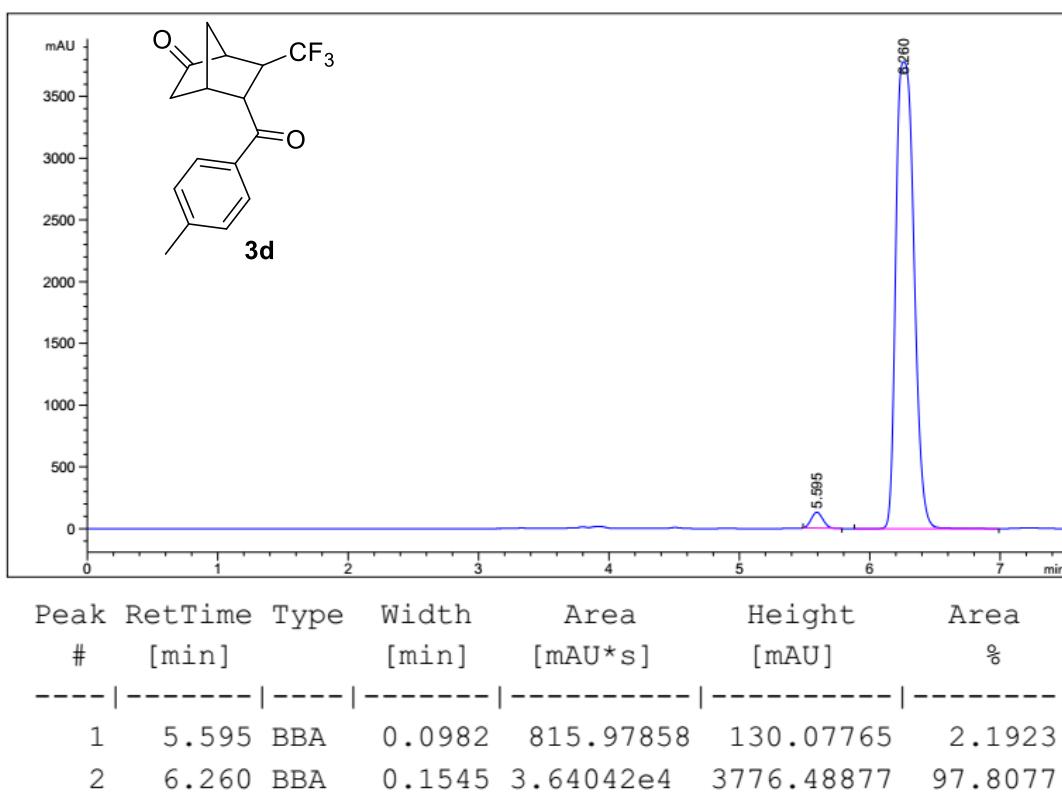
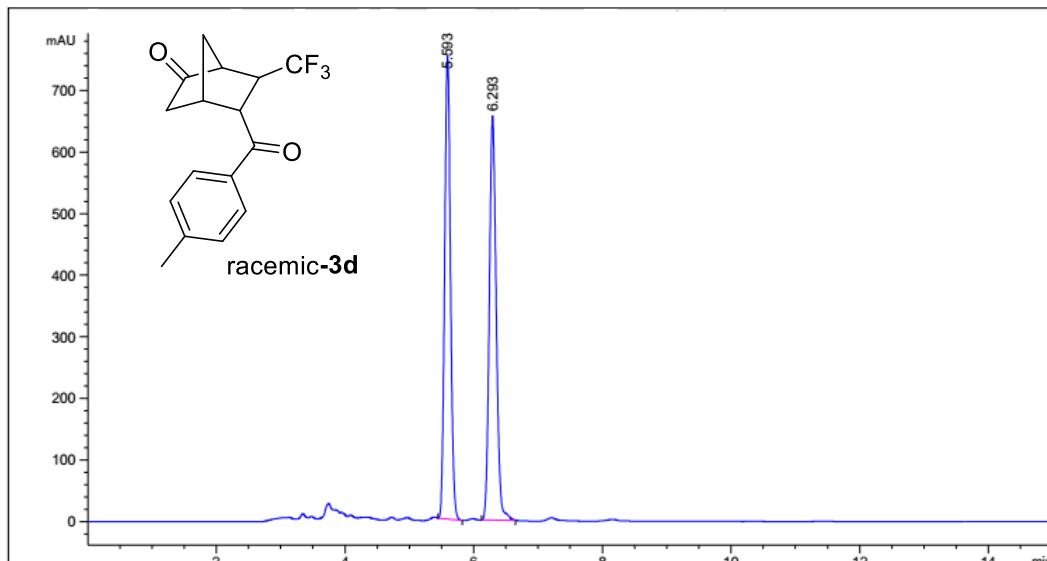


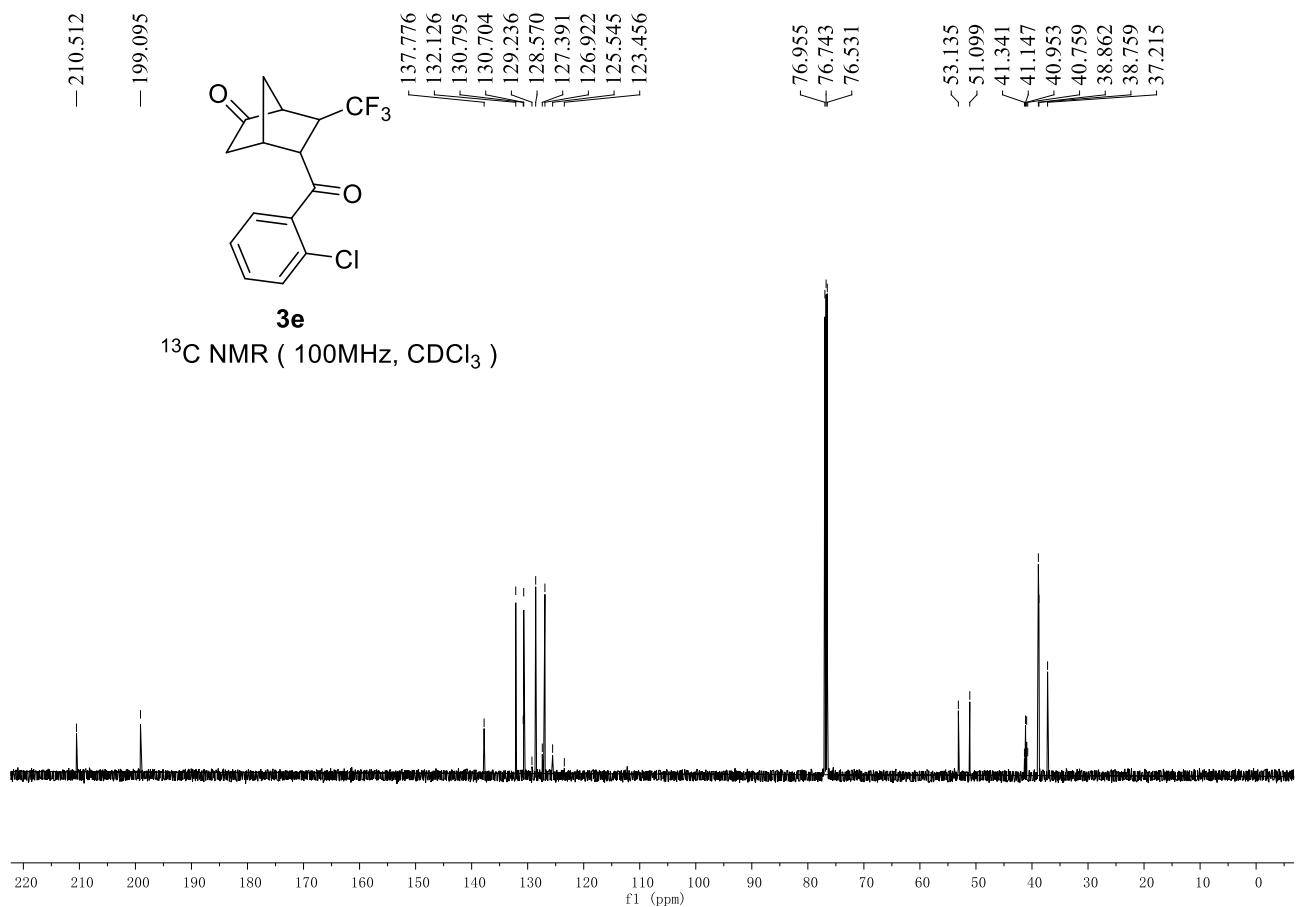
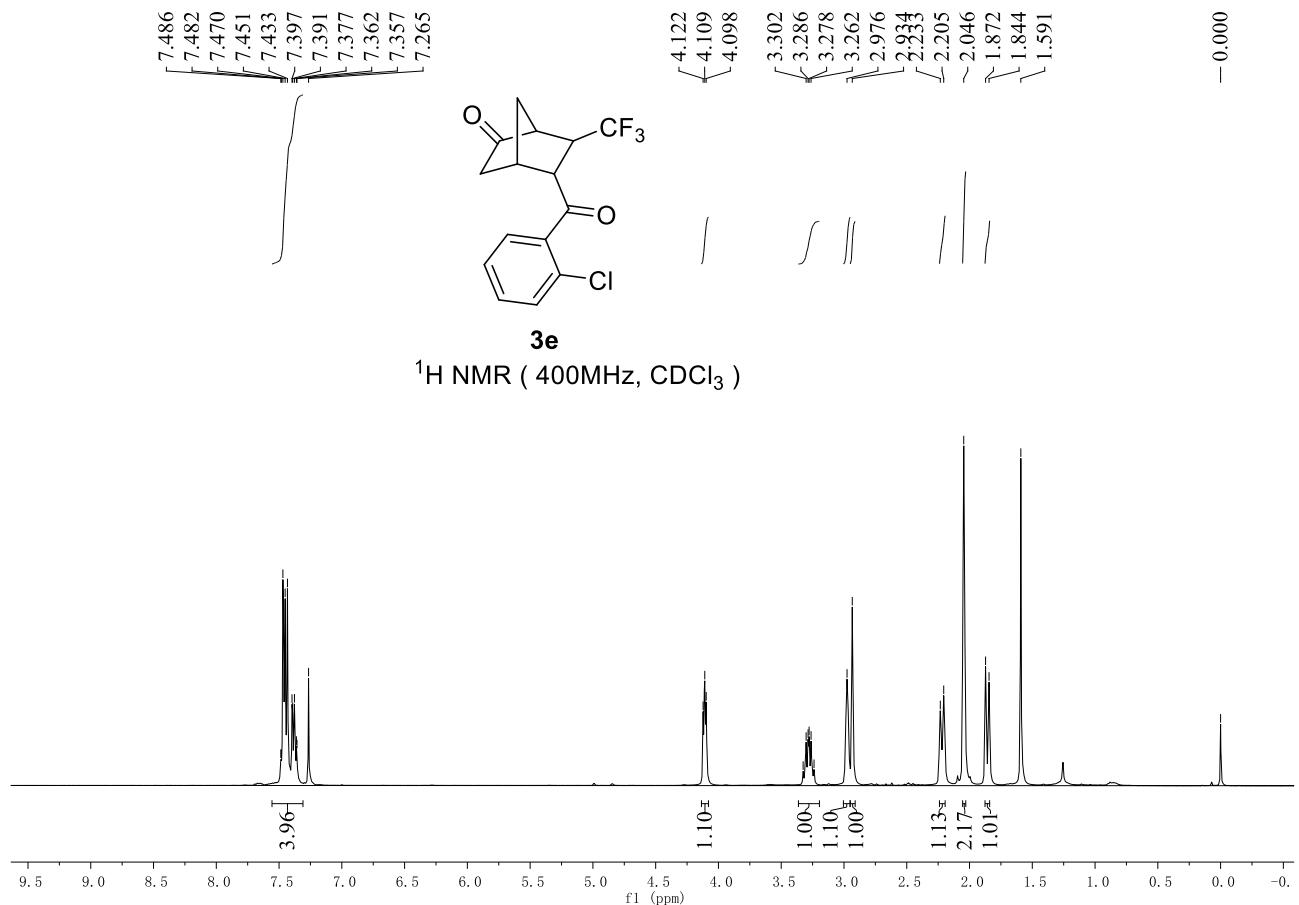
Peak #	RetTime [min]	Type	Width [min]	Area mAU	*s	Height [mAU]	Area %
1	7.584	BB	0.1487	1475.44214		151.33607	34.4736
2	9.670	BB	0.1919	2804.47949		225.19759	65.5264

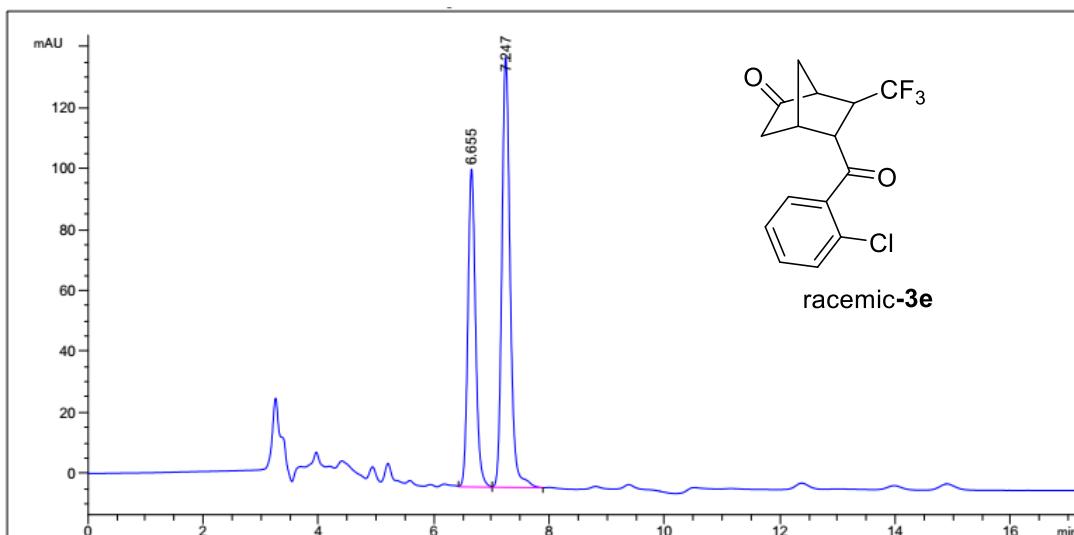


Peak #	RetTime [min]	Type	Width [min]	Area mAU	*s	Height [mAU]	Area %
1	7.588	BB	0.1515	66.47233		6.73677	4.0599
2	9.681	BB	0.1899	1570.82825		126.62000	95.9401

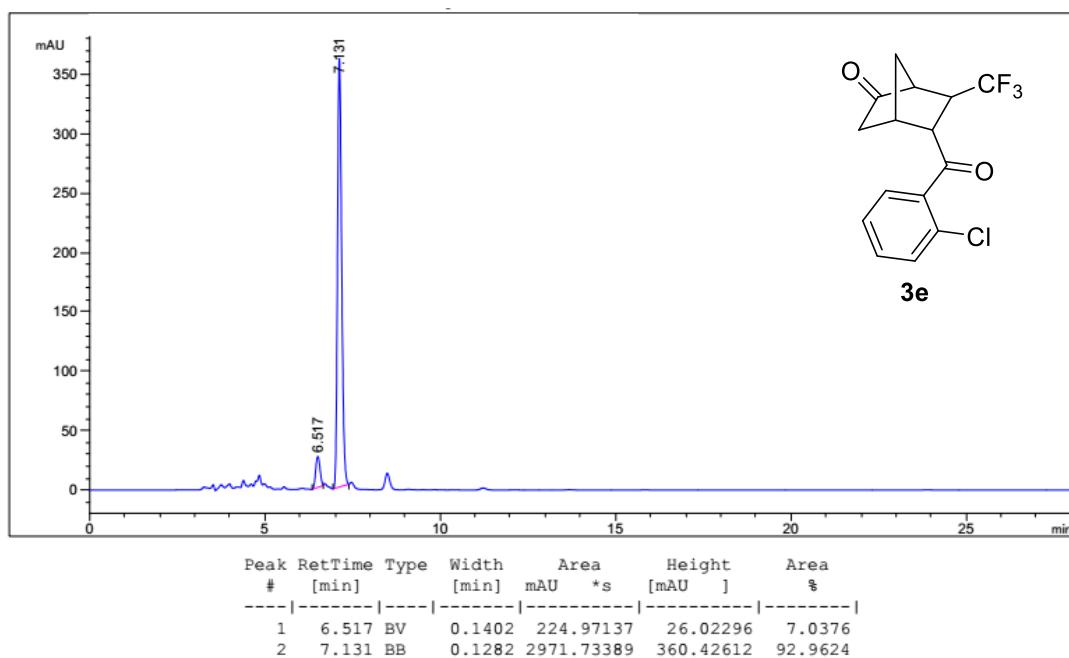




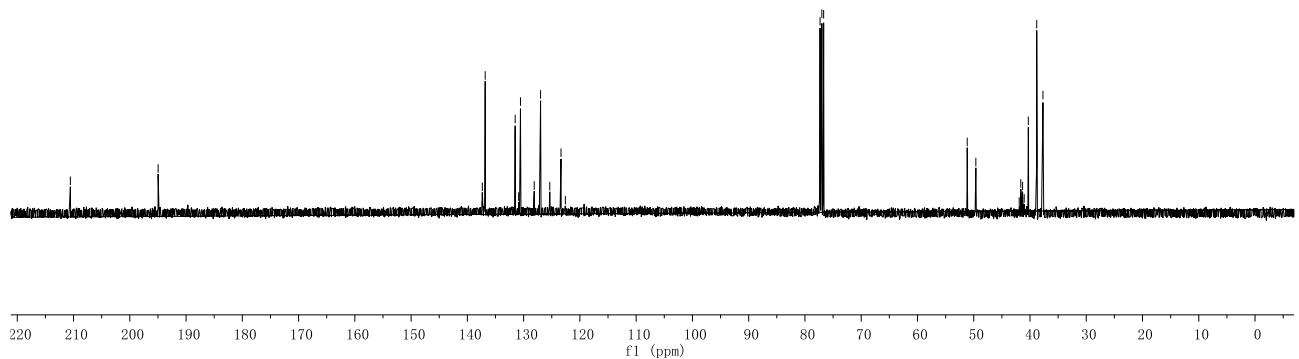
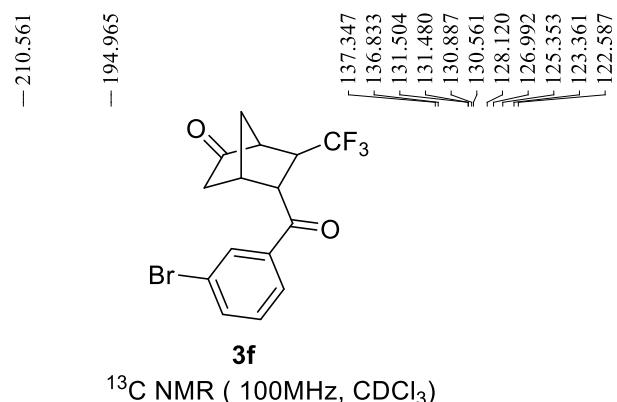
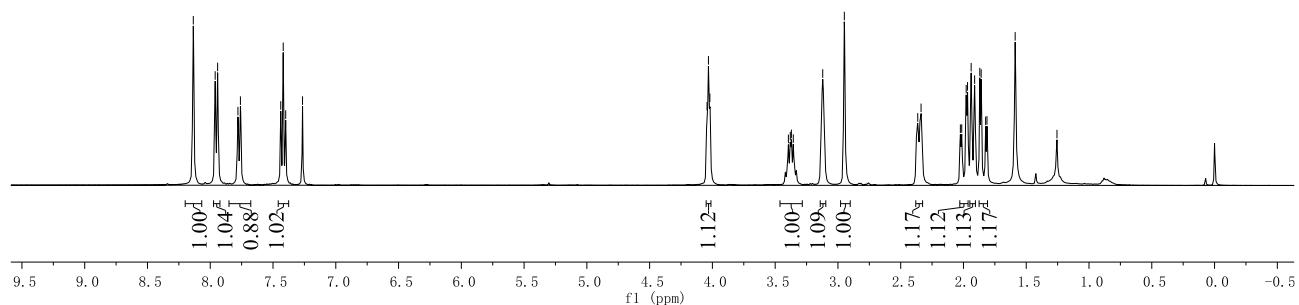
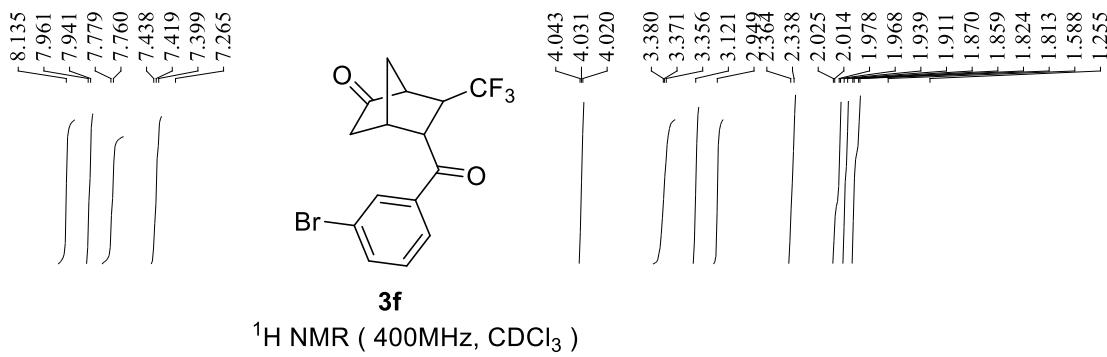


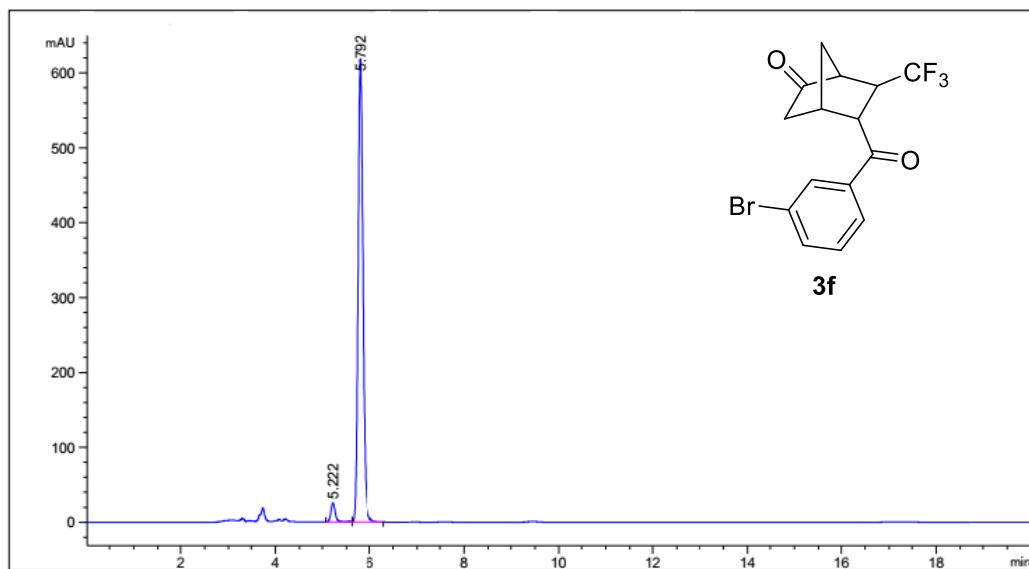
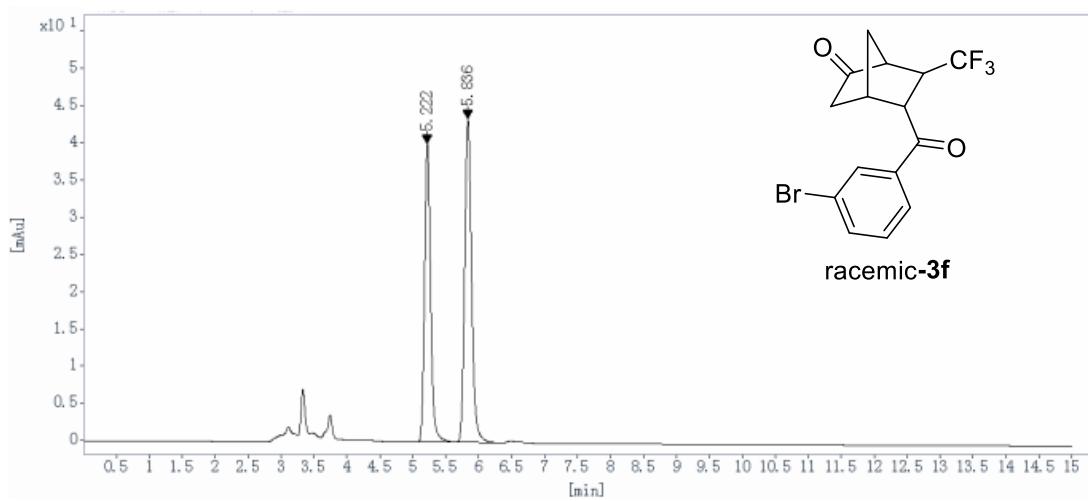


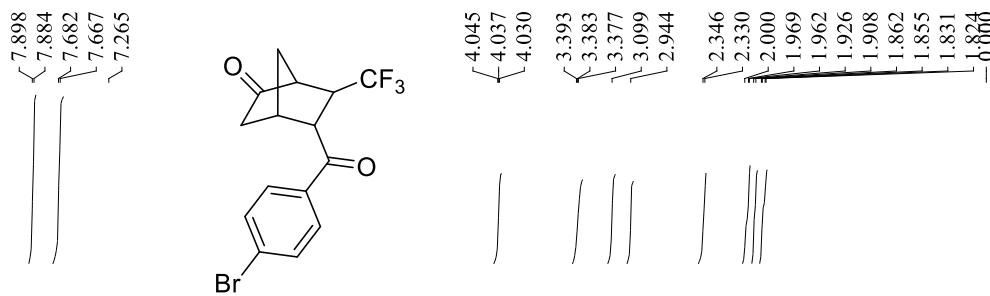
Peak #	RetTime [min]	Type	Width [min]	Area mAU	*s	Height [mAU]	Area %
1	6.655	VV	0.1408	959.40796		104.29235	40.6263
2	7.247	VBA	0.1523	1402.13672		141.10608	59.3737



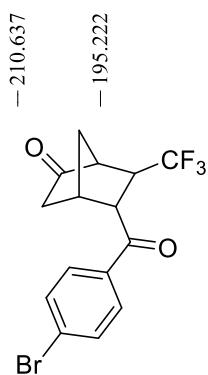
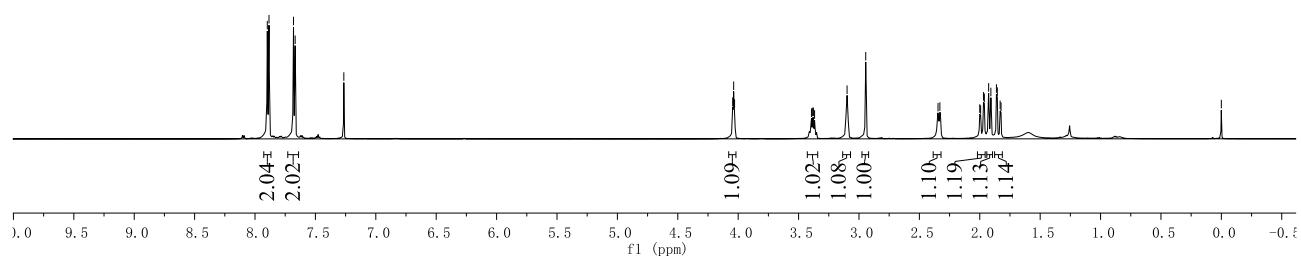
Peak #	RetTime [min]	Type	Width [min]	Area mAU	*s	Height [mAU]	Area %
1	6.517	BV	0.1402	224.97137		26.02296	7.0376
2	7.131	BB	0.1282	2971.73389		360.42612	92.9624



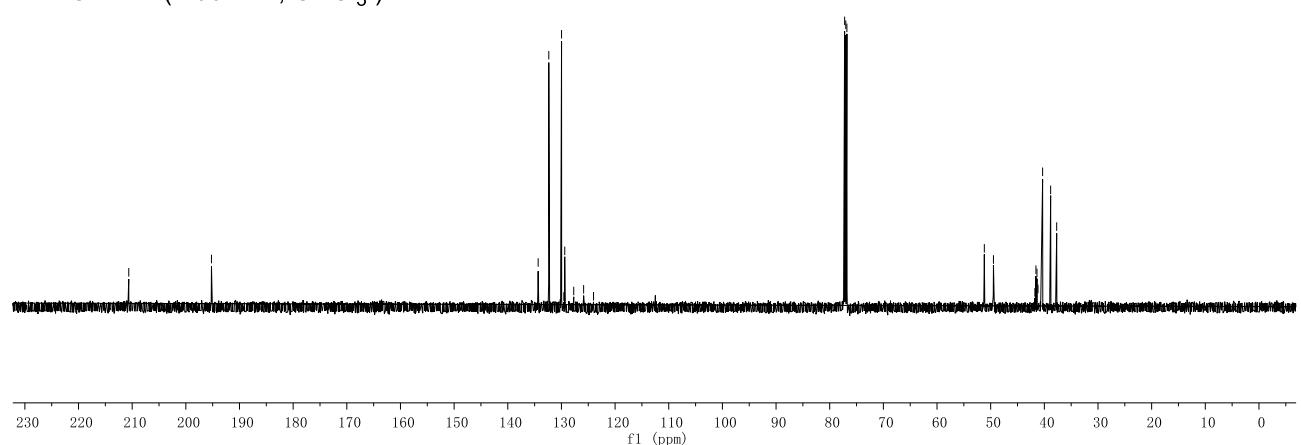


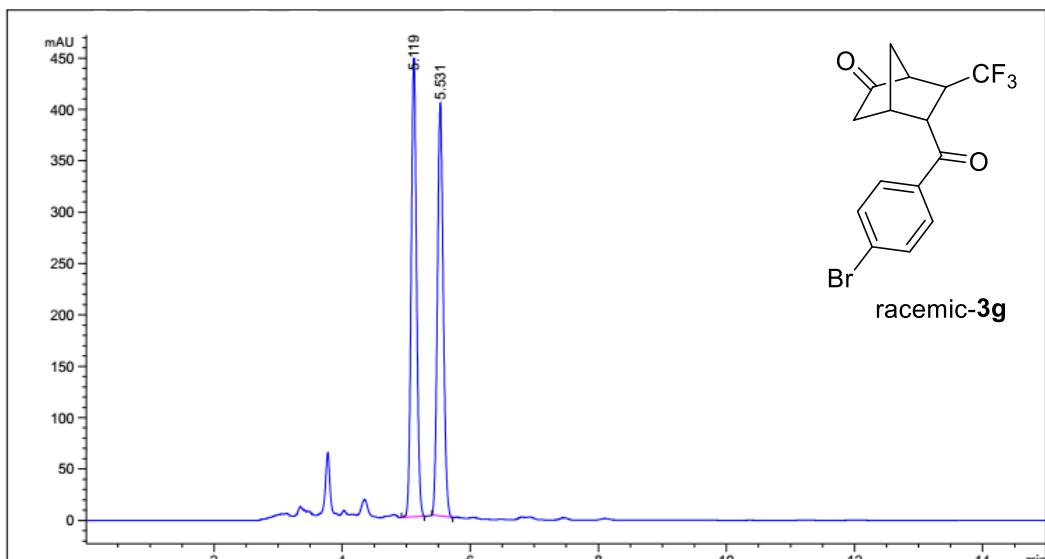


¹H NMR (400MHz, CDCl₃)

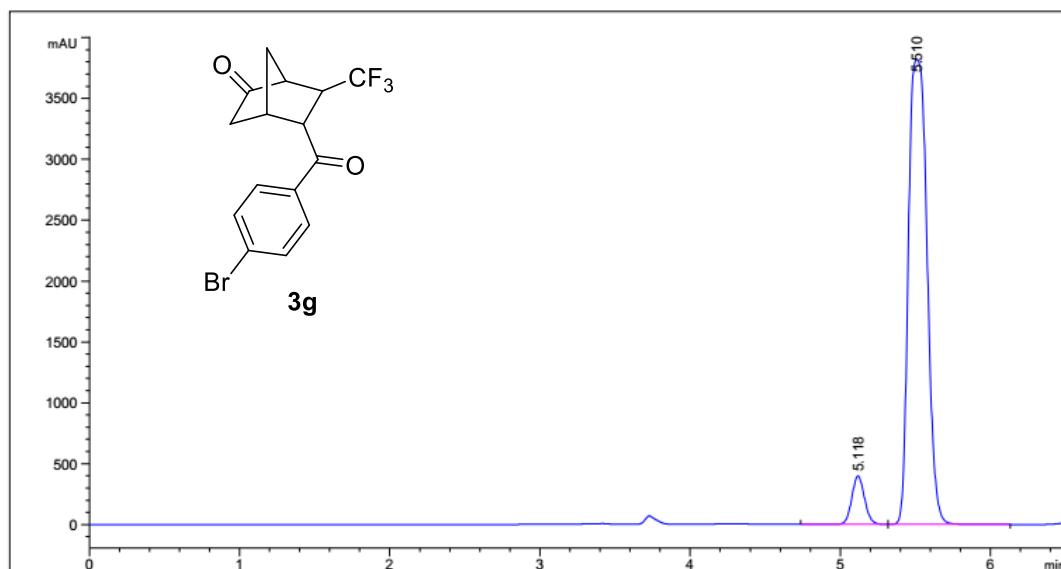


¹³C NMR (100MHz, CDCl₃)

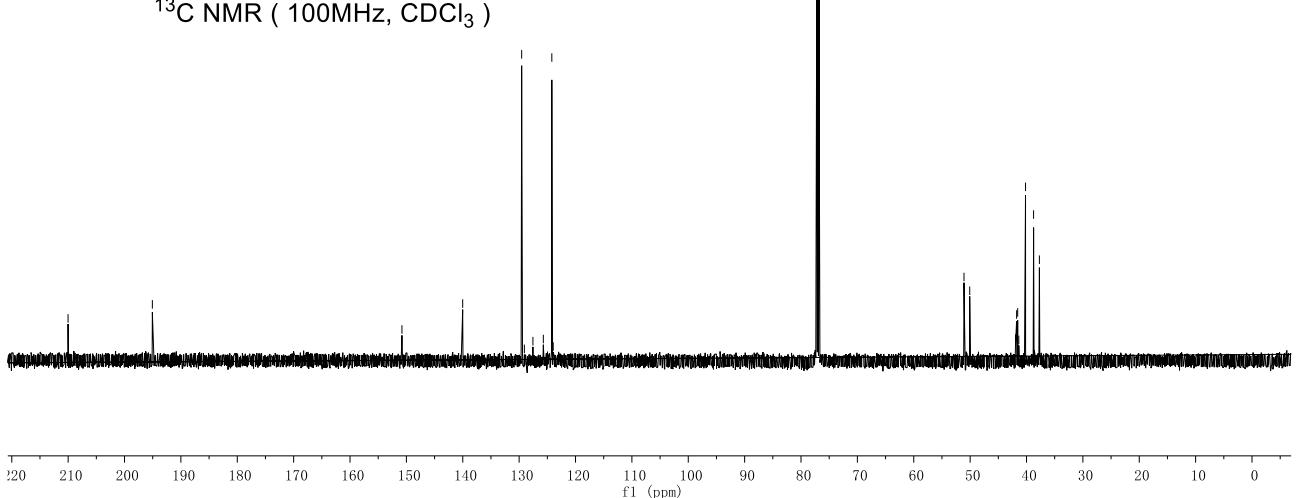
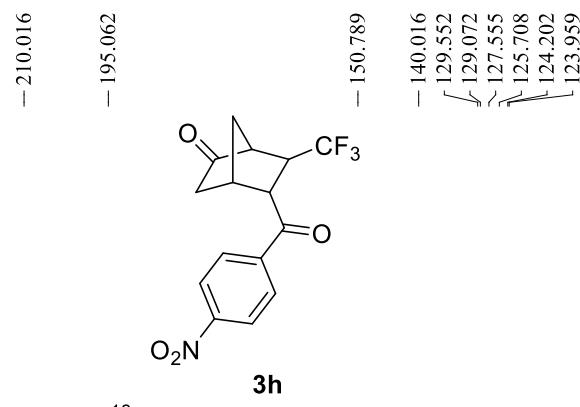
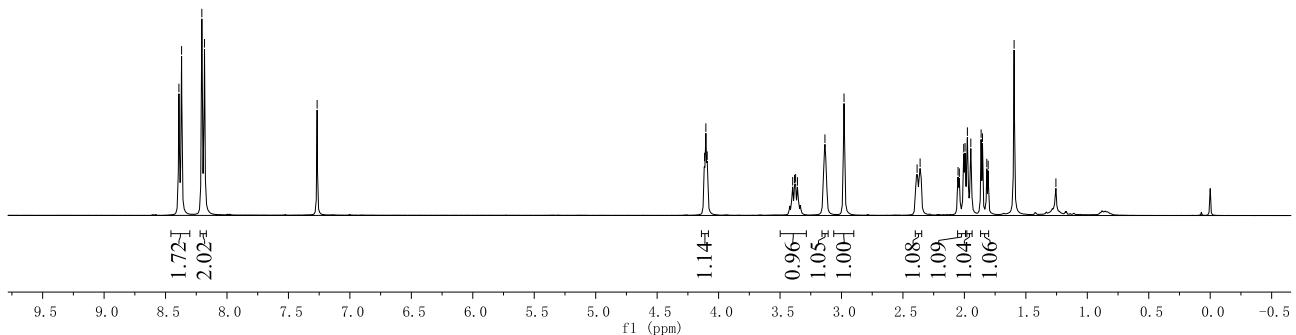
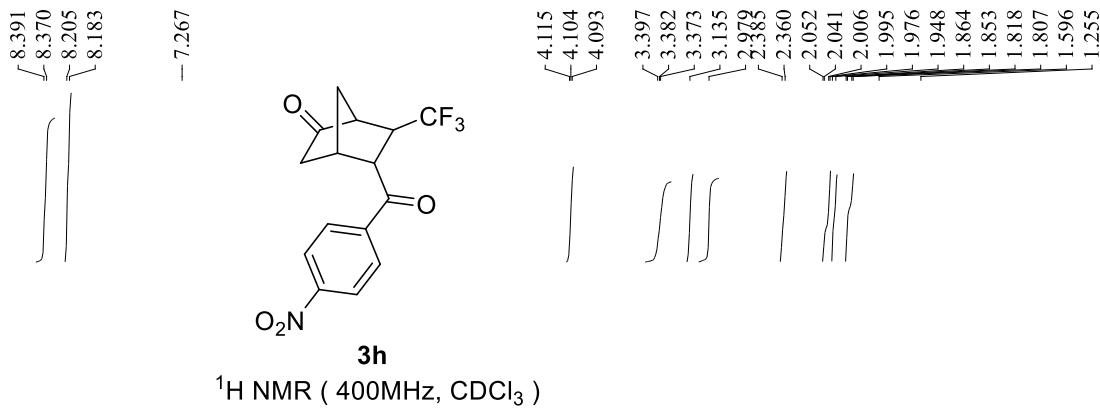


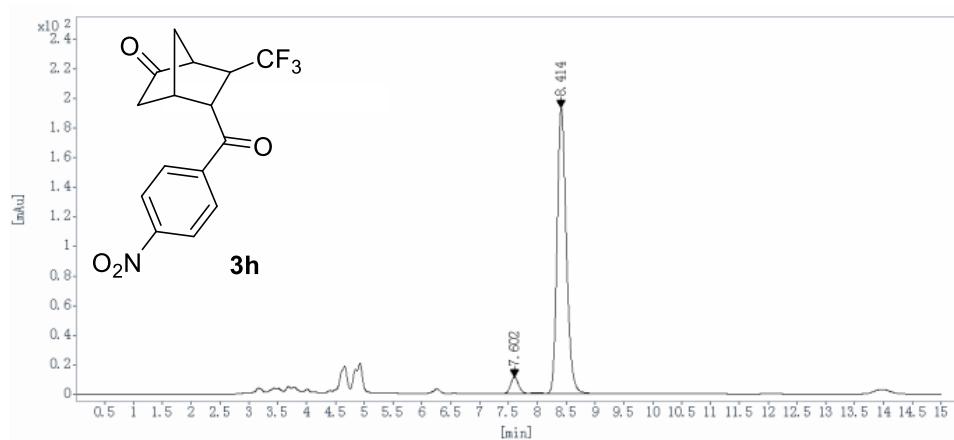
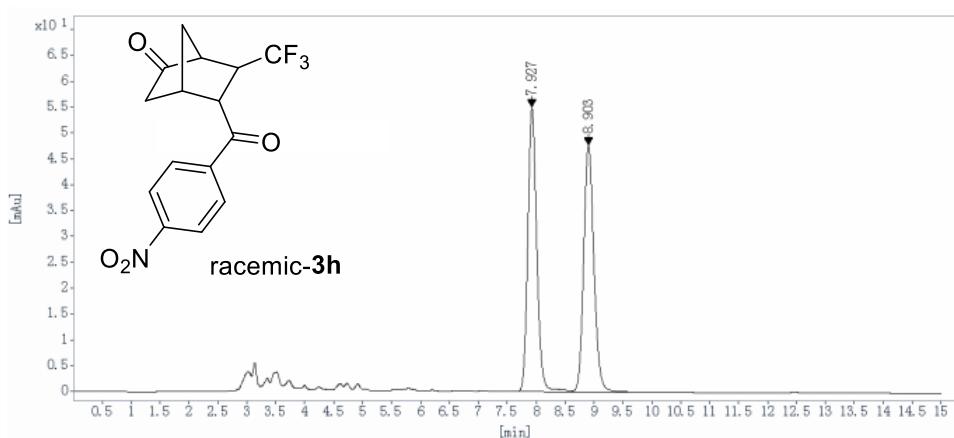


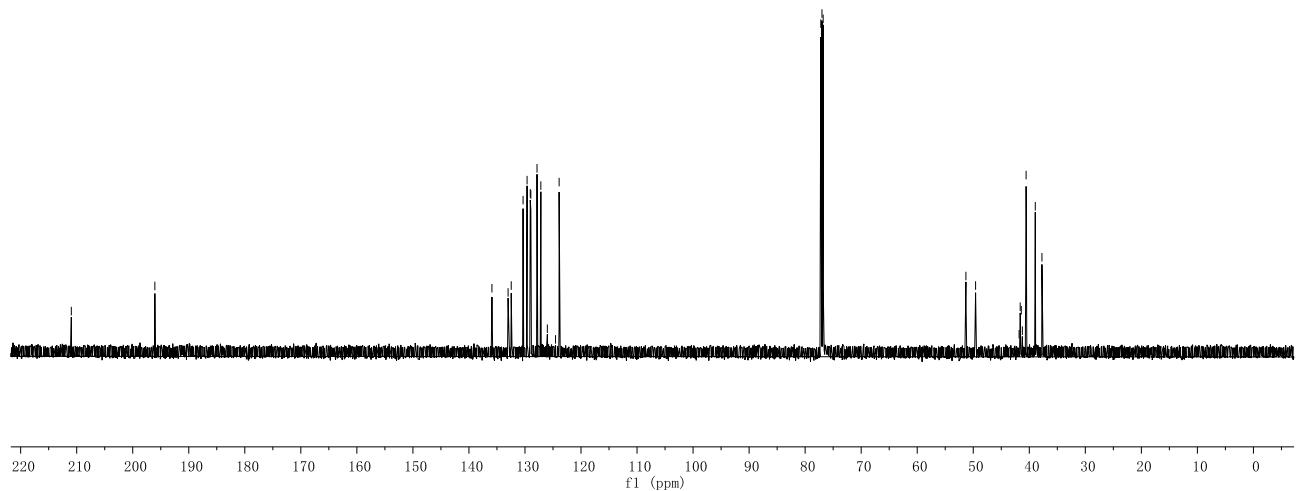
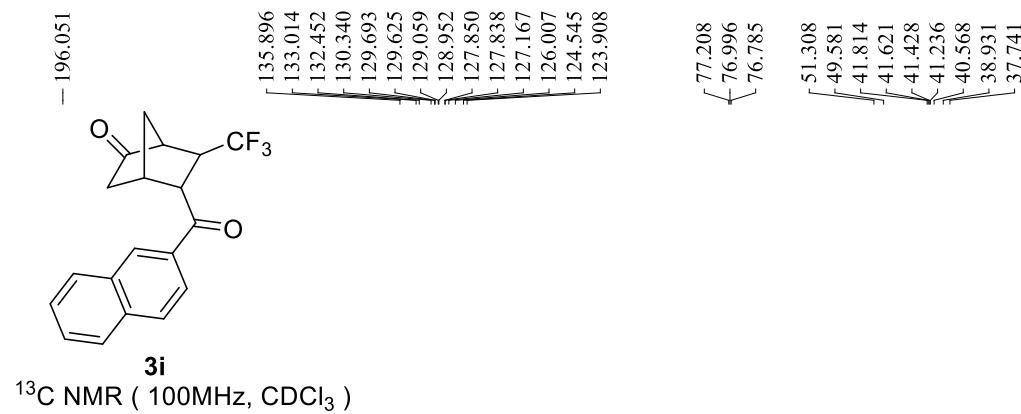
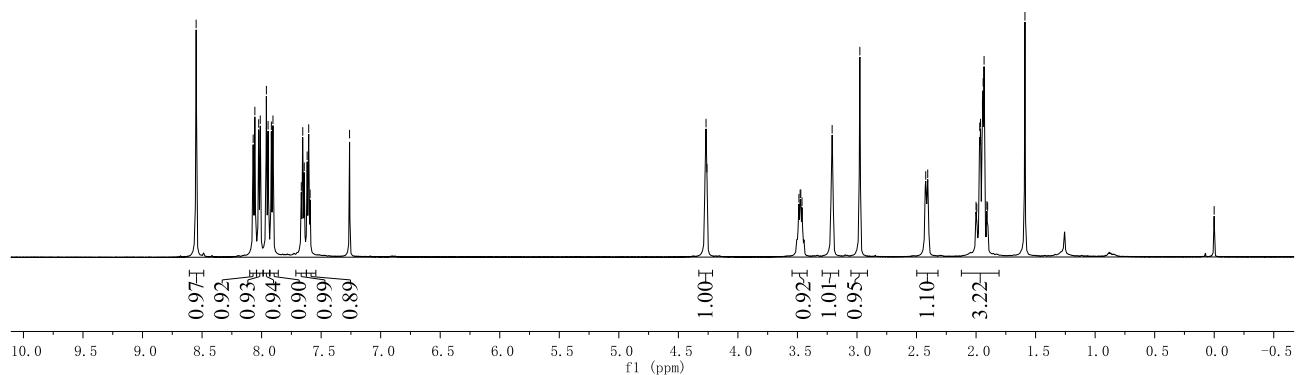
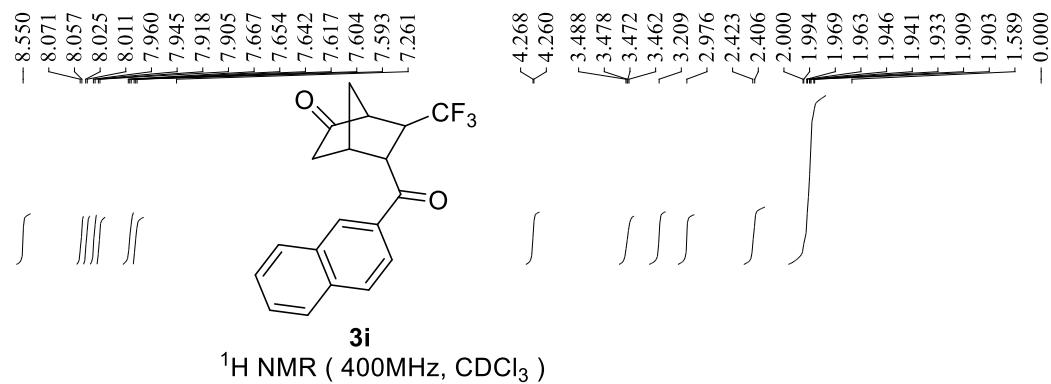
Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	5.119	BBA	0.0913	2616.83447	446.68286	50.4560
2	5.531	BB	0.0996	2569.53369	401.58118	49.5440

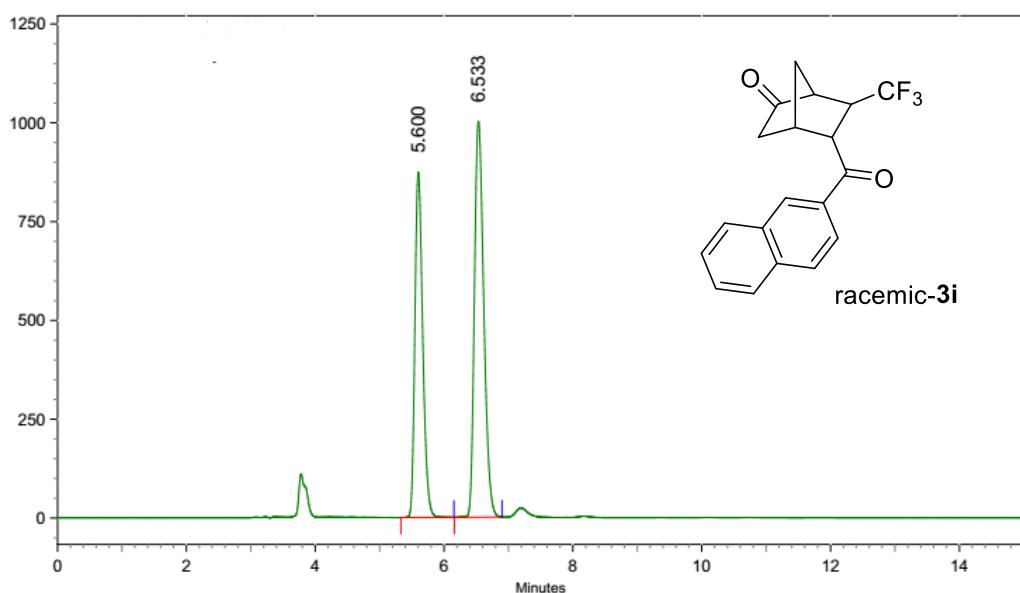


Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	5.118	BBA	0.0909	2305.58984	396.03934	6.6179
2	5.510	BBA	0.1375	3.25332e4	3815.08887	93.3821

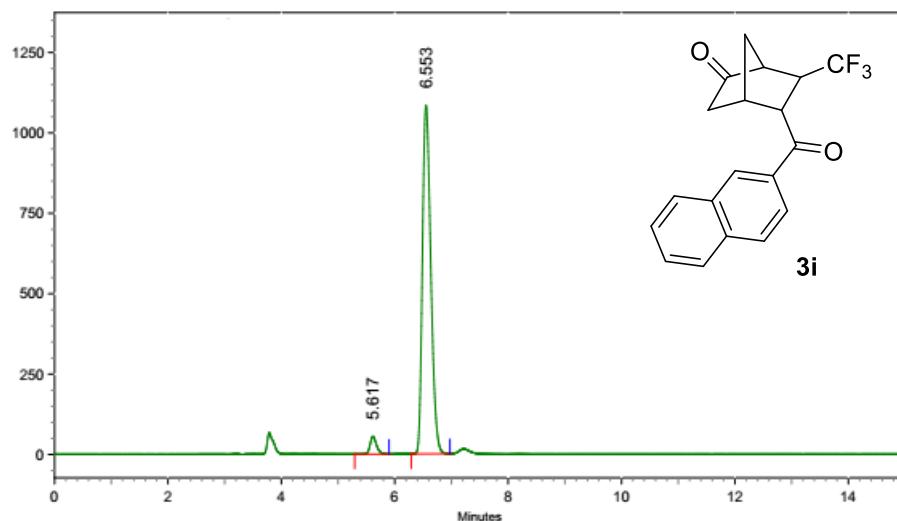




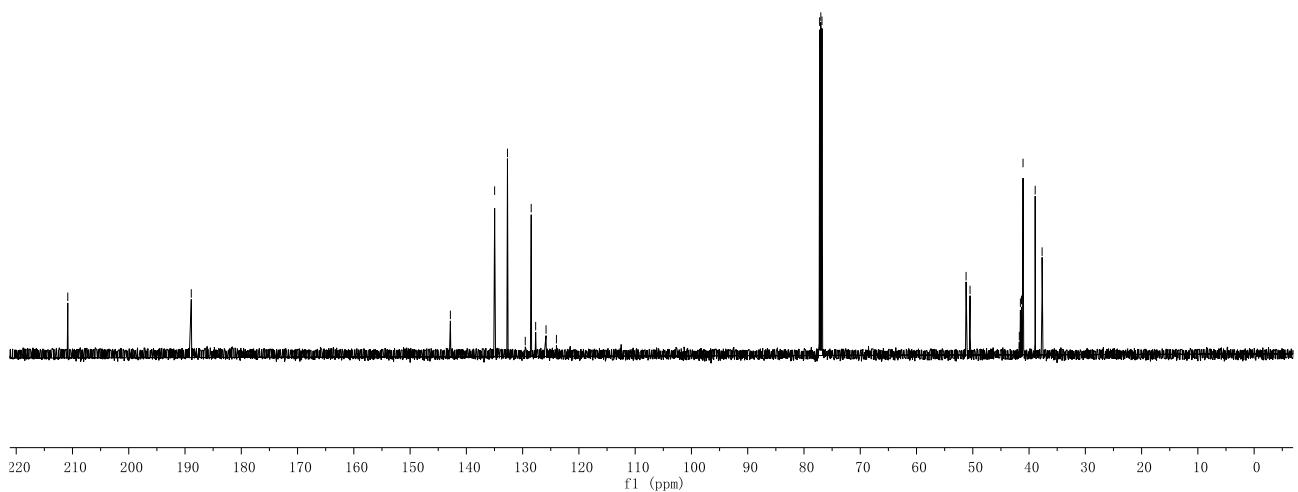
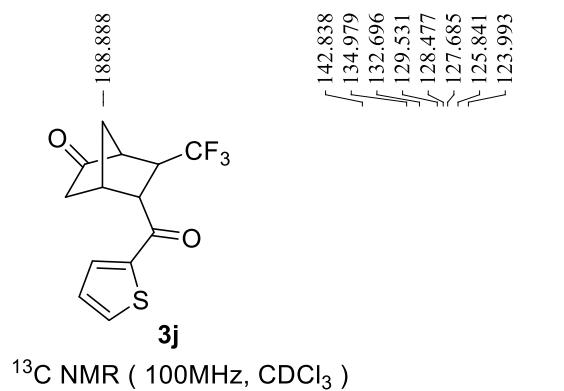
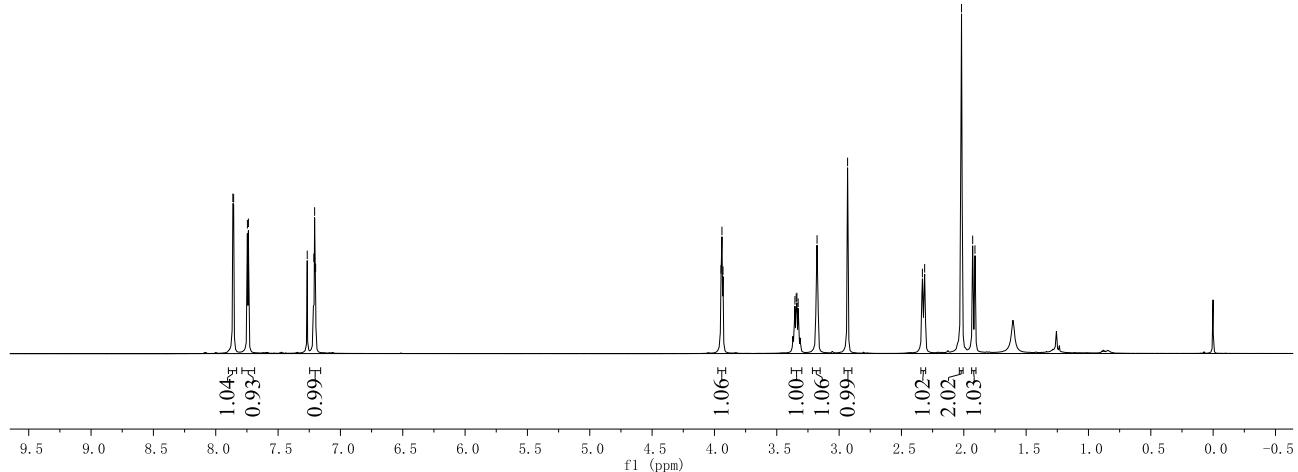
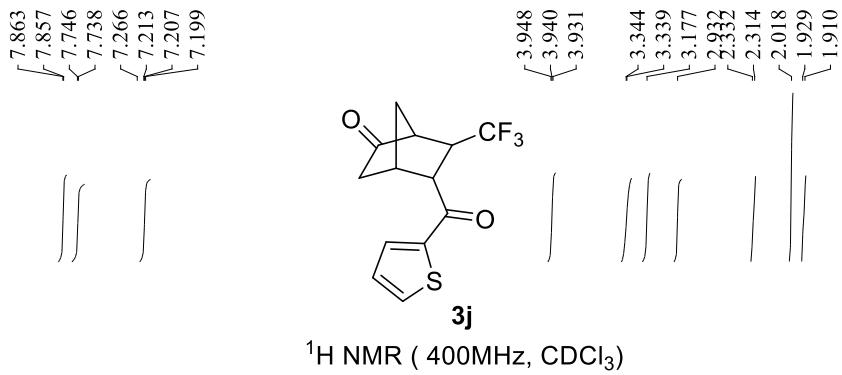


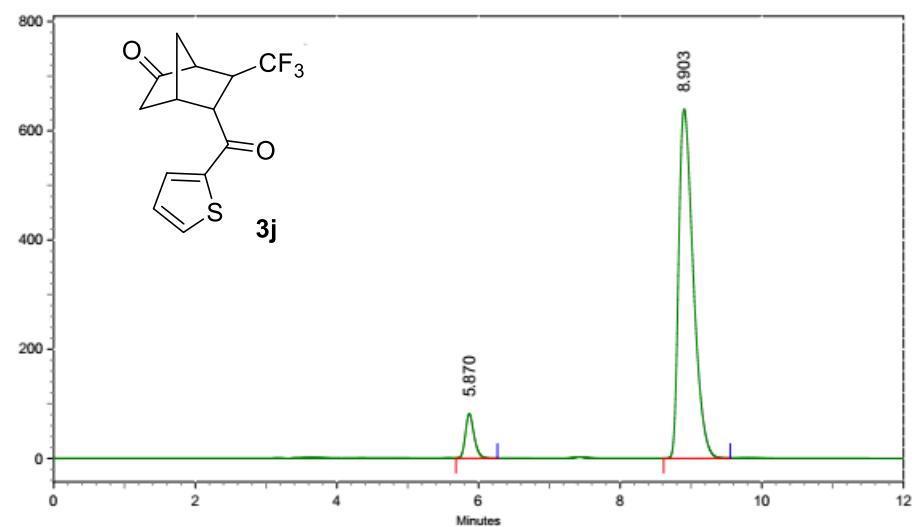
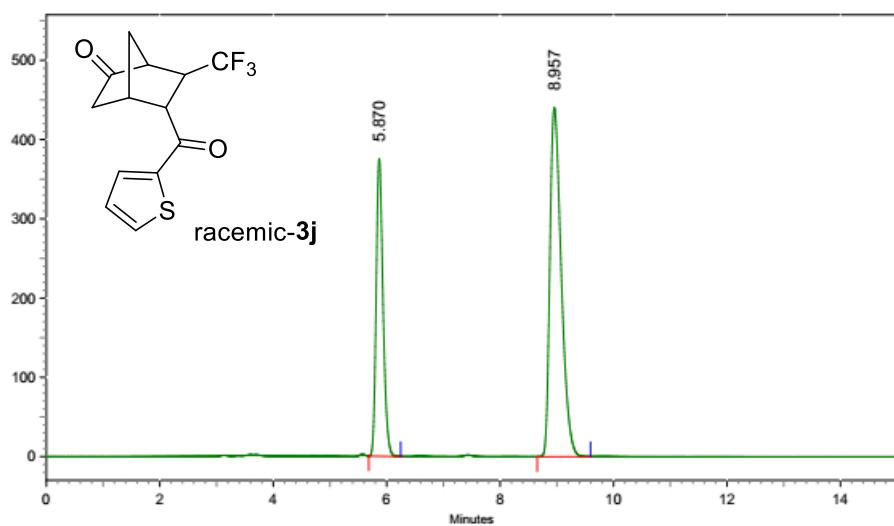


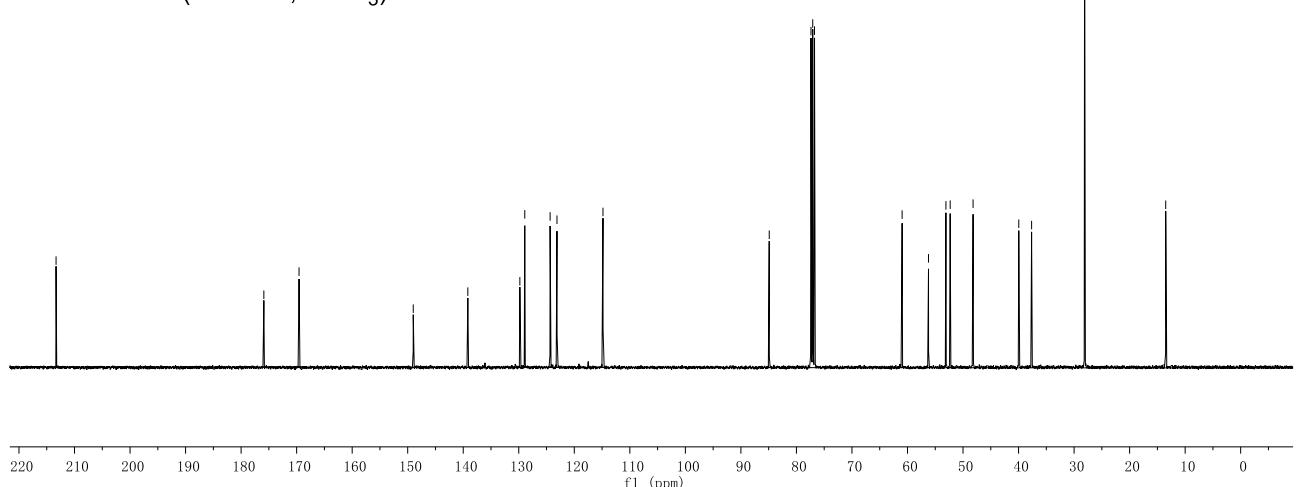
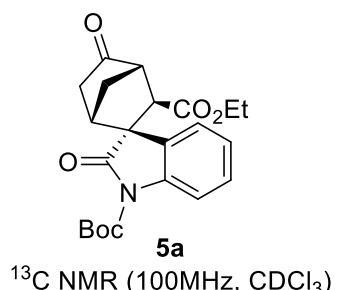
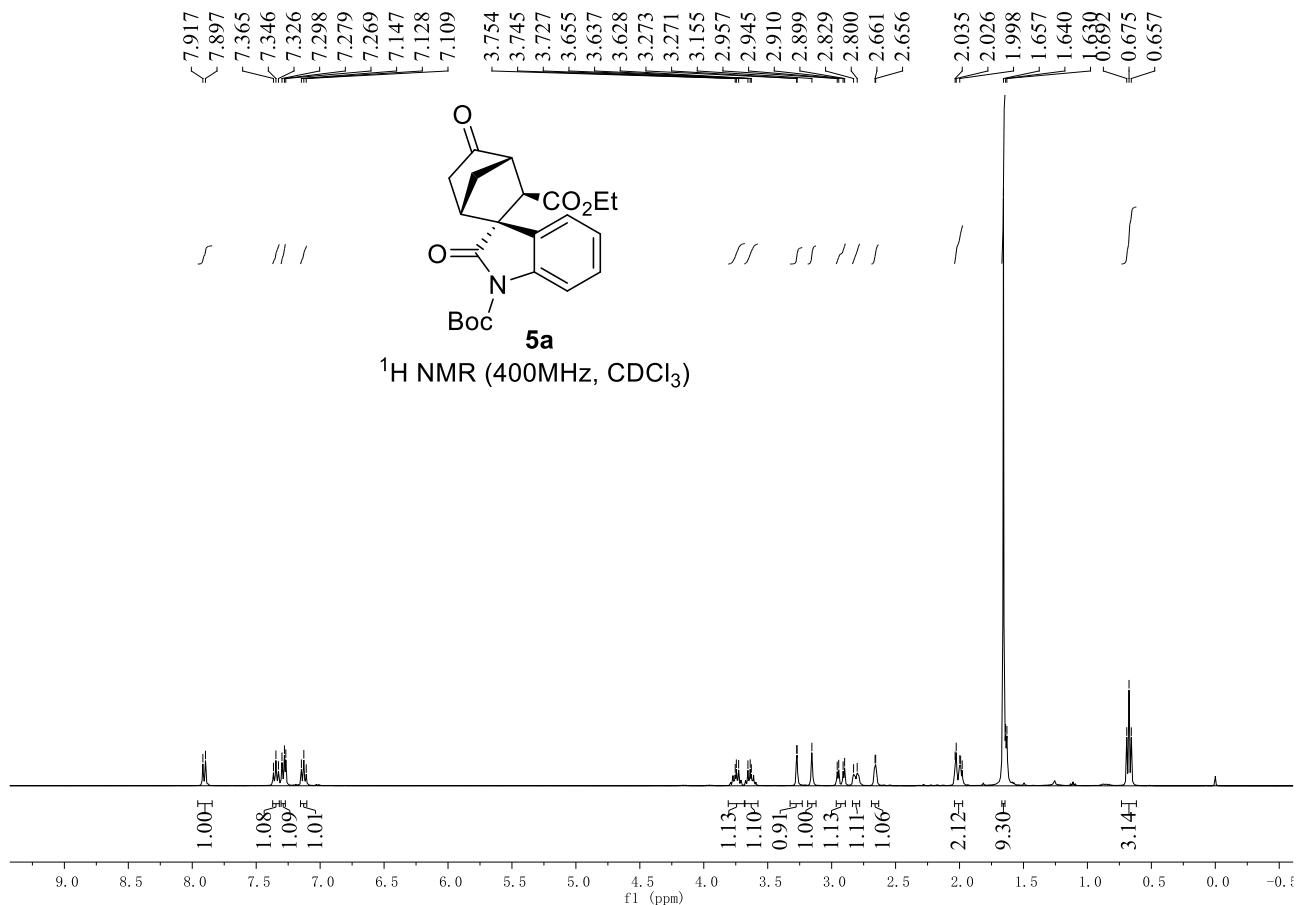
Peak No.	Ret Time	Width	Height	Area	Area [%]
1	5.600	0.823	14655913	123655853	42.2681
2	6.533	0.740	16796152	168895606	57.7319

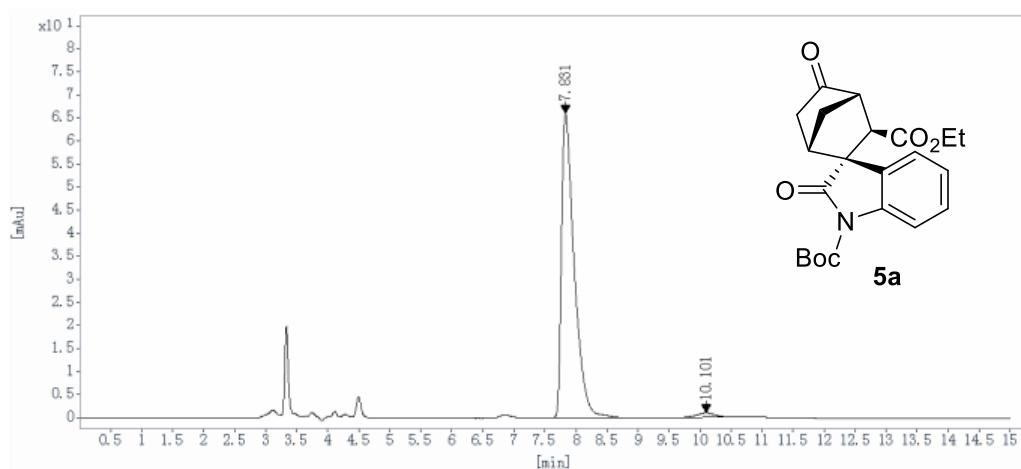
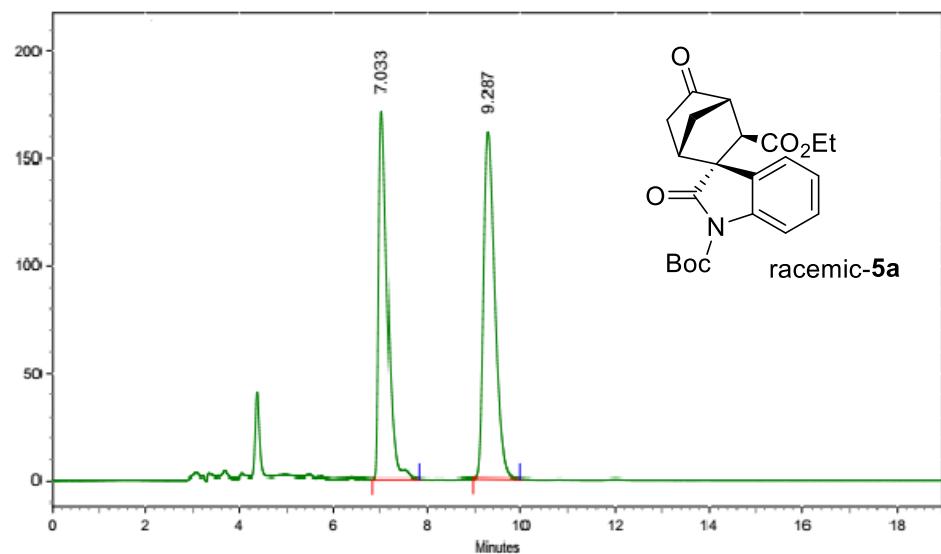


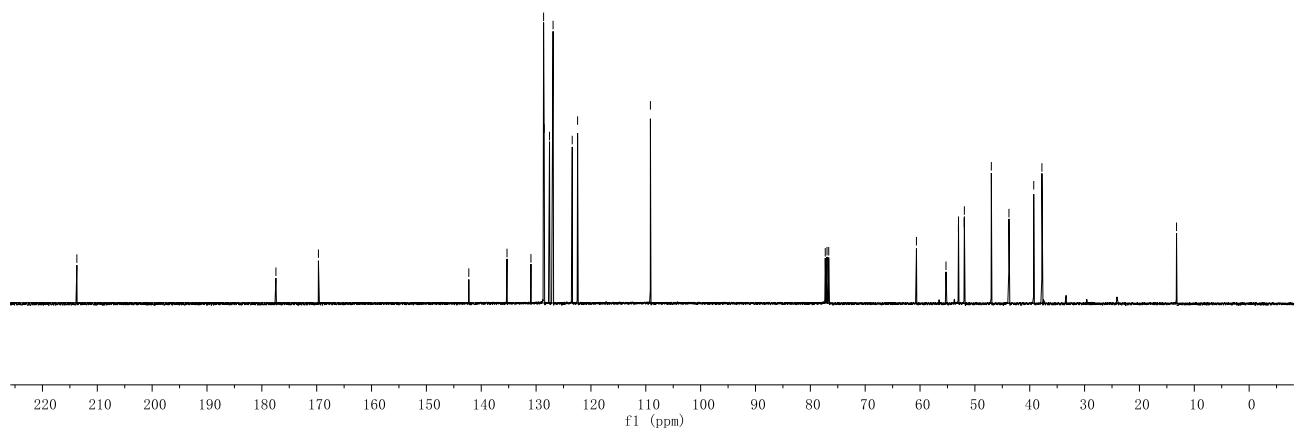
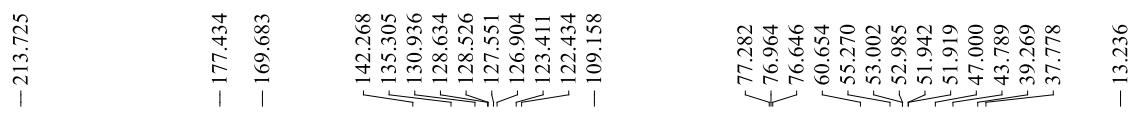
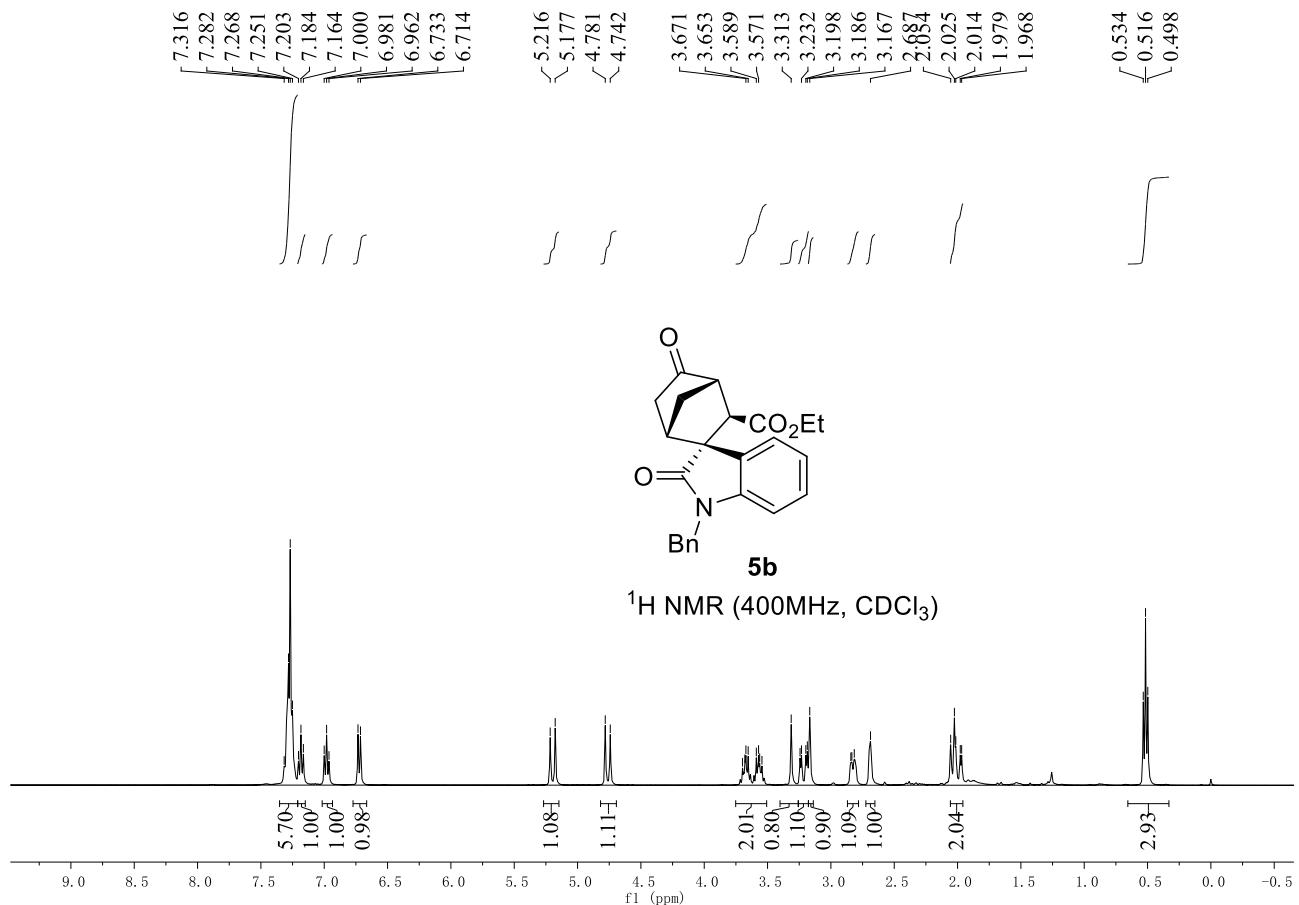
Peak No.	Ret Time	Width	Height	Area	Area [%]
1	5.617	0.607	924167	7221834	3.7347
2	6.553	0.683	18167039	186147648	96.2653

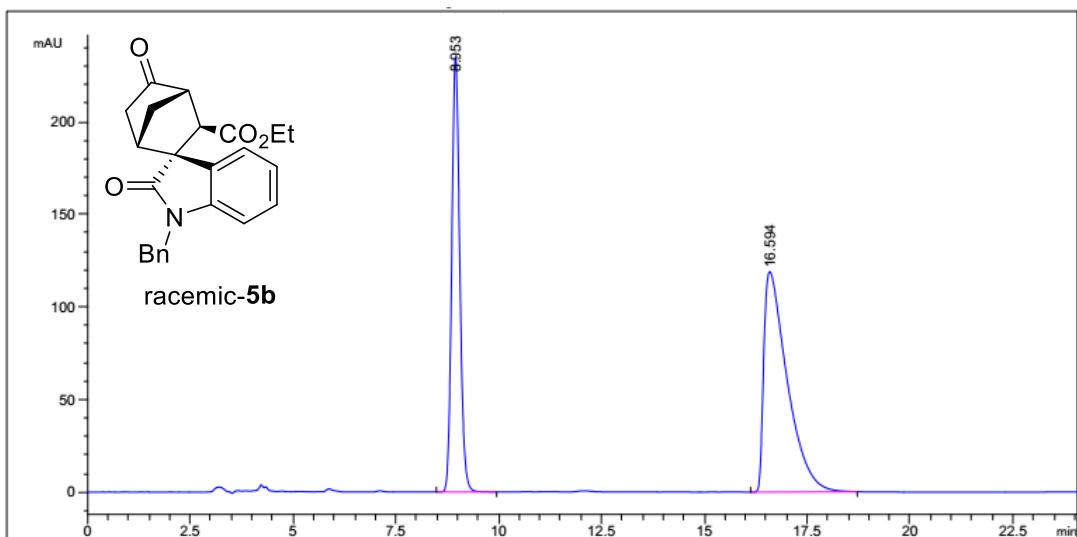




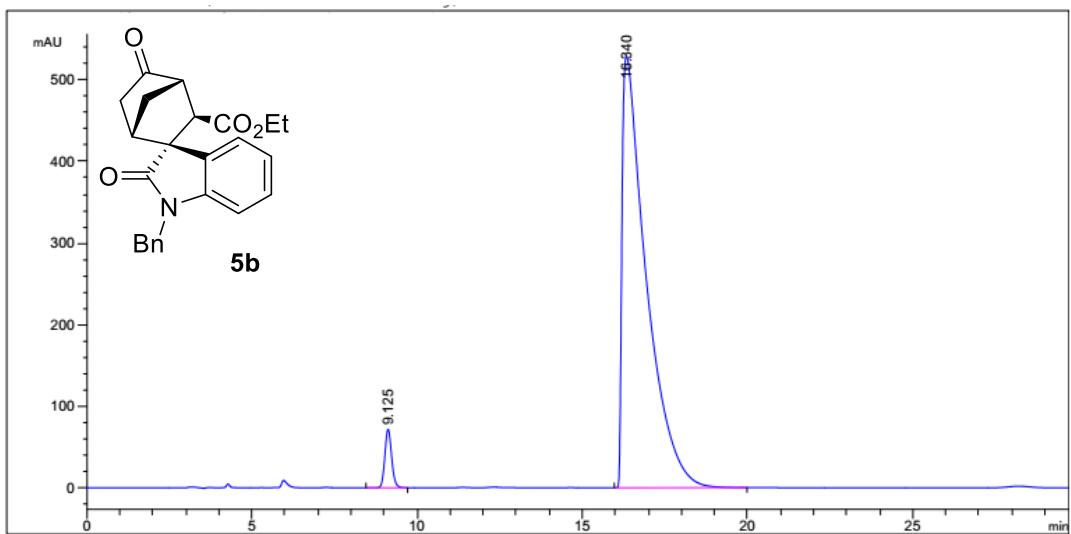




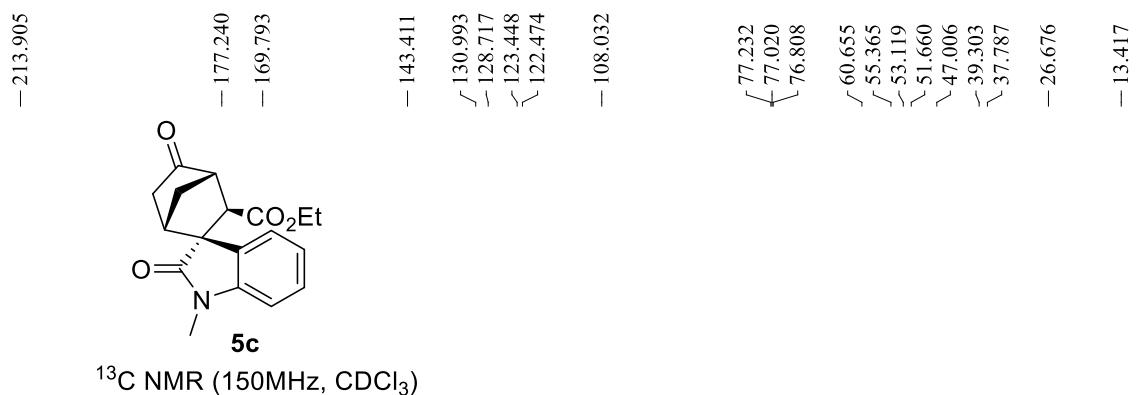
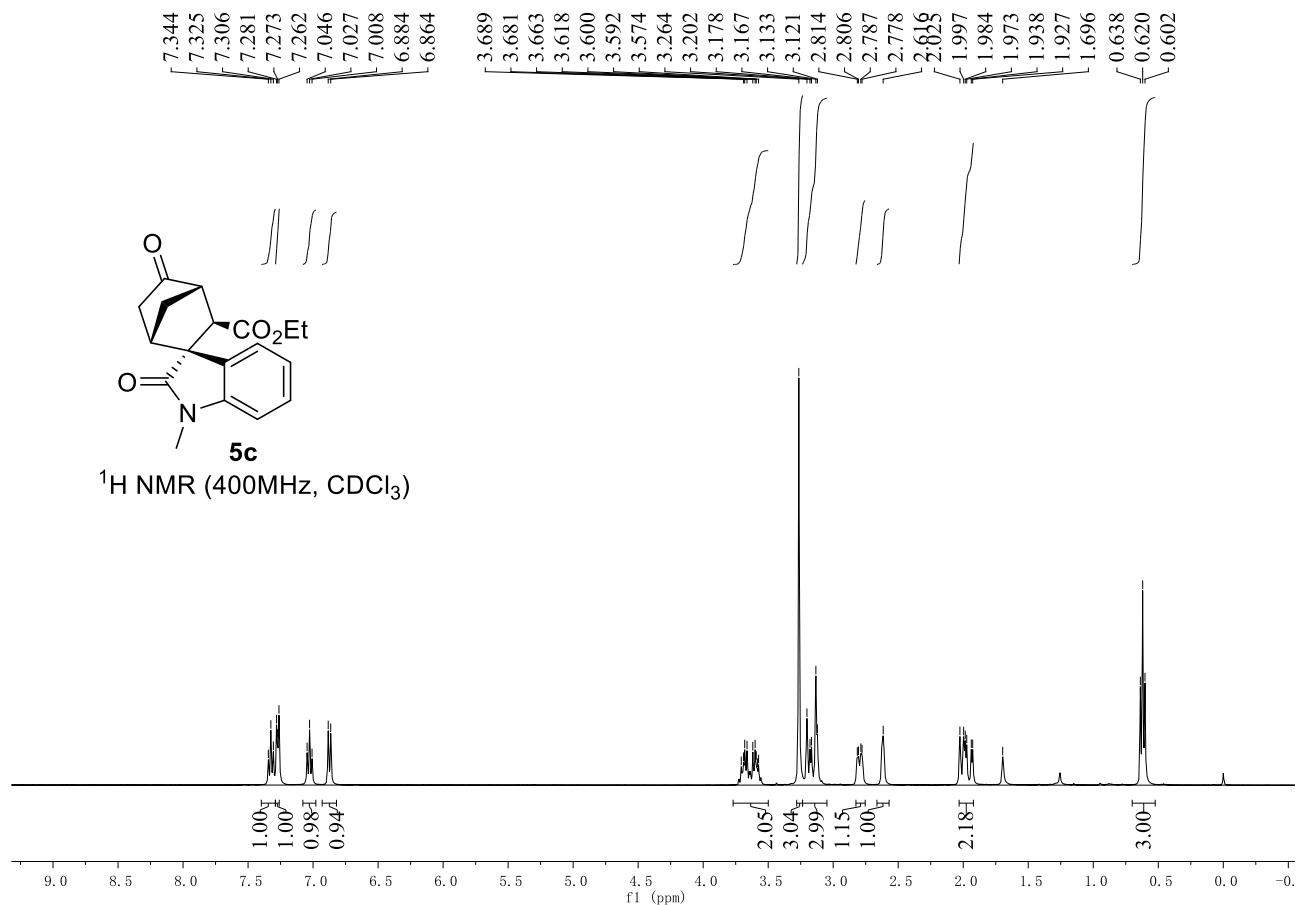


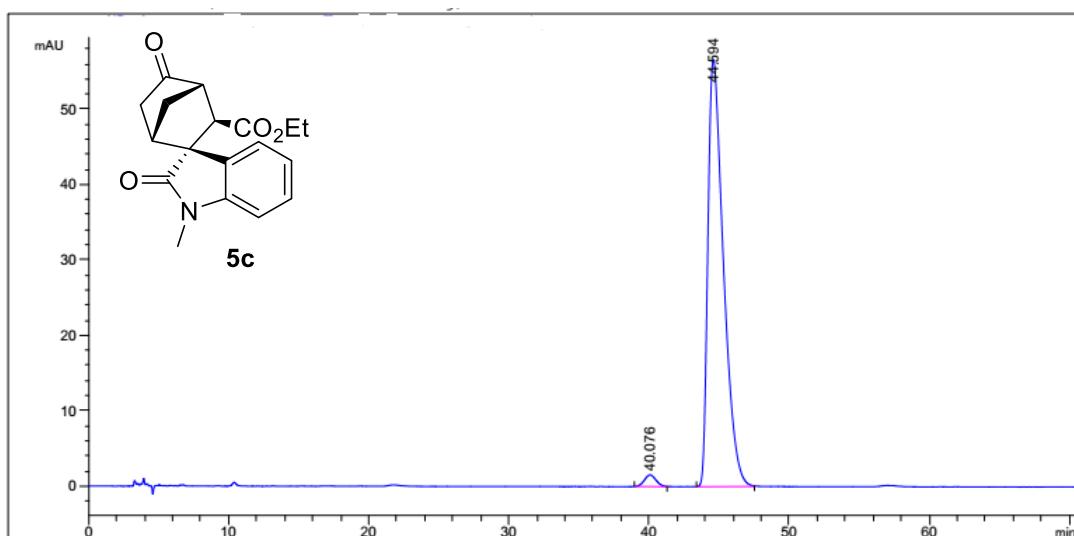
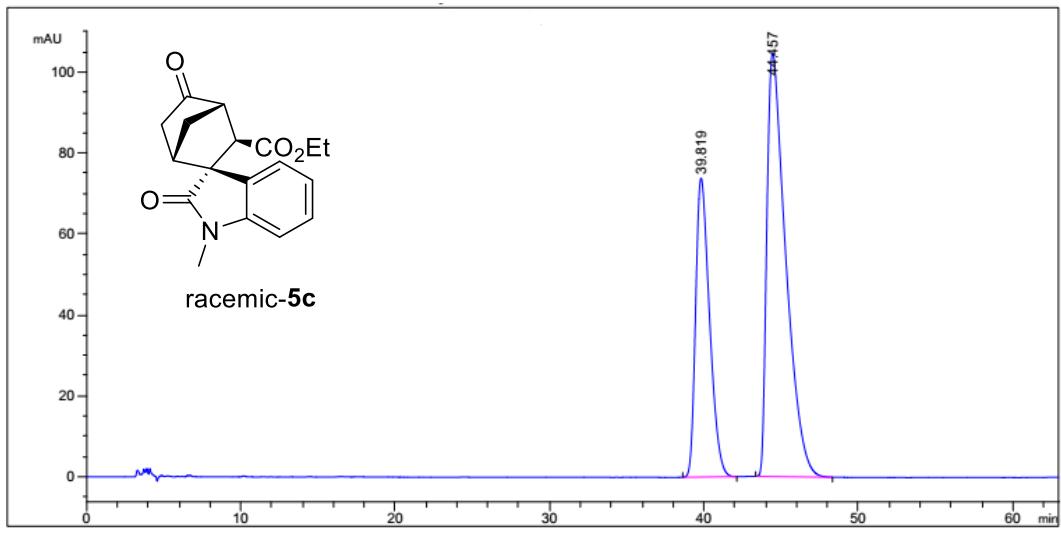


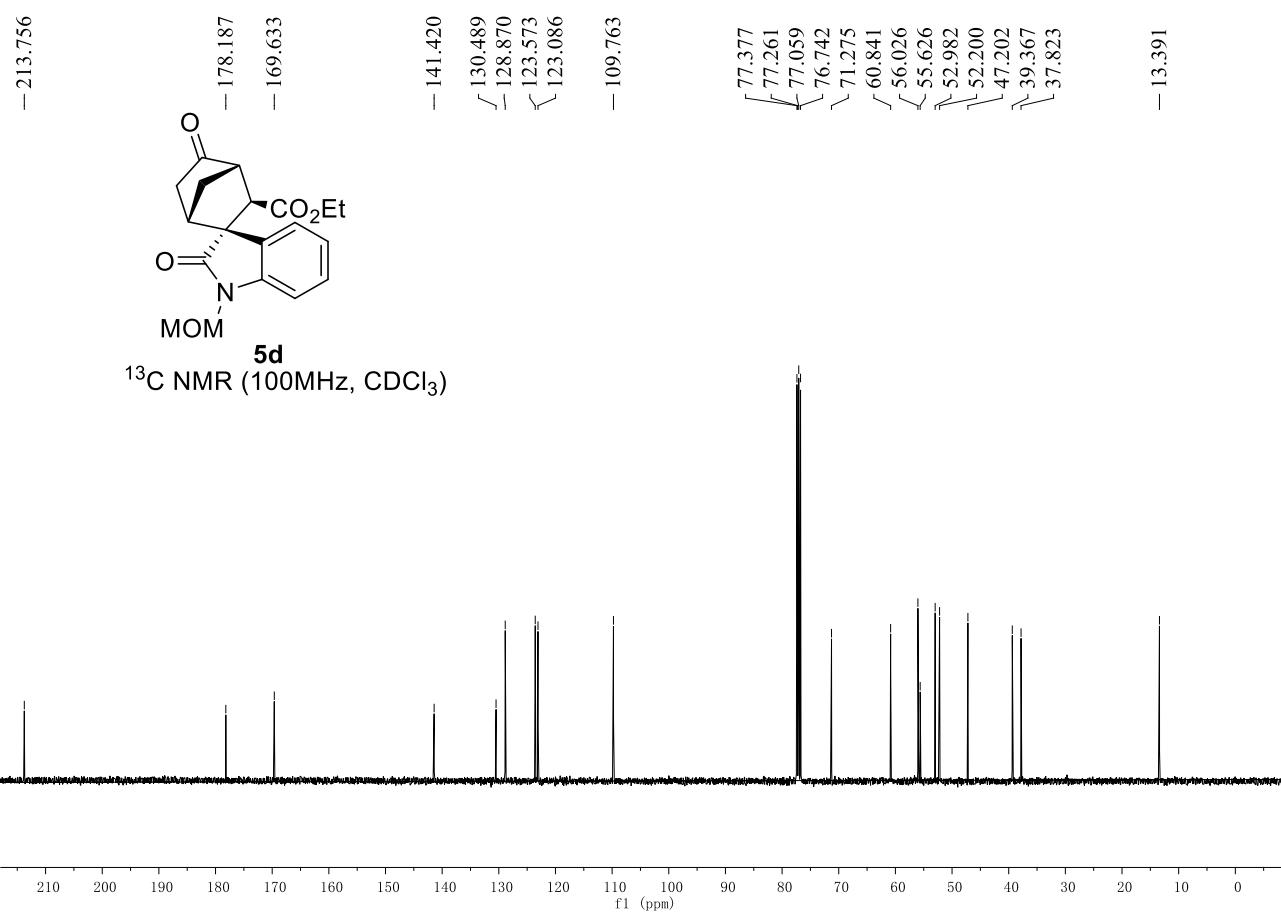
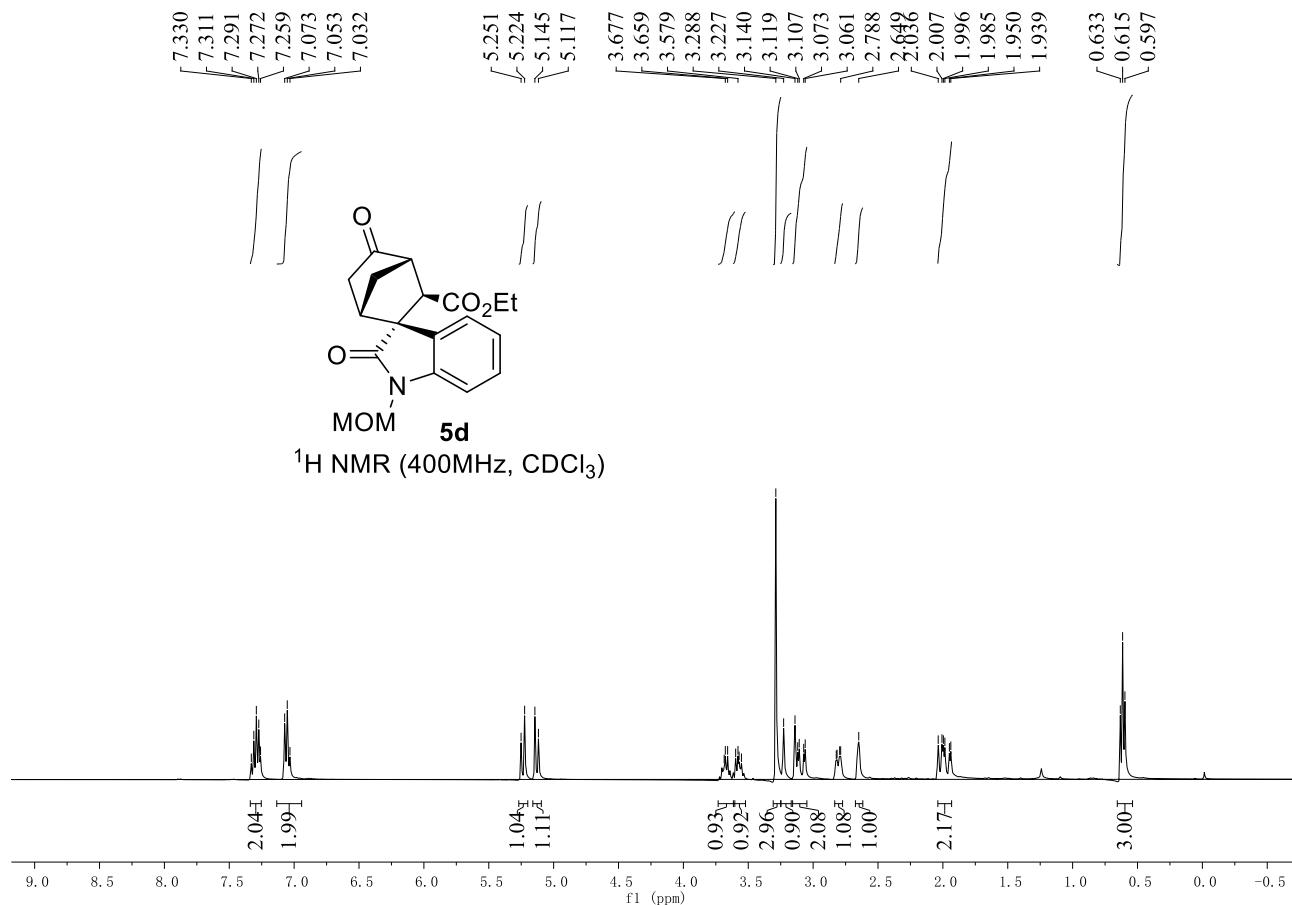
Peak #	RetTime [min]	Type	Width [min]	Area mAU	*s	Height [mAU]	Area %
1	8.953	BB	0.2094	3187.78662		234.79608	40.3718
2	16.594	BBA	0.5896	4708.29004		119.02106	59.6282

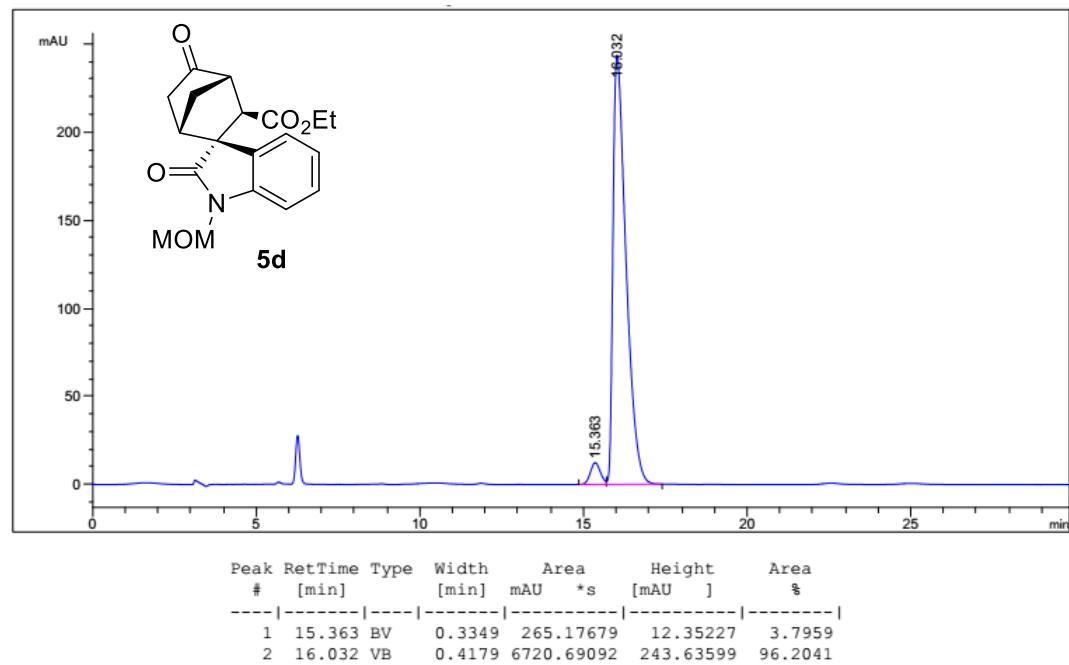
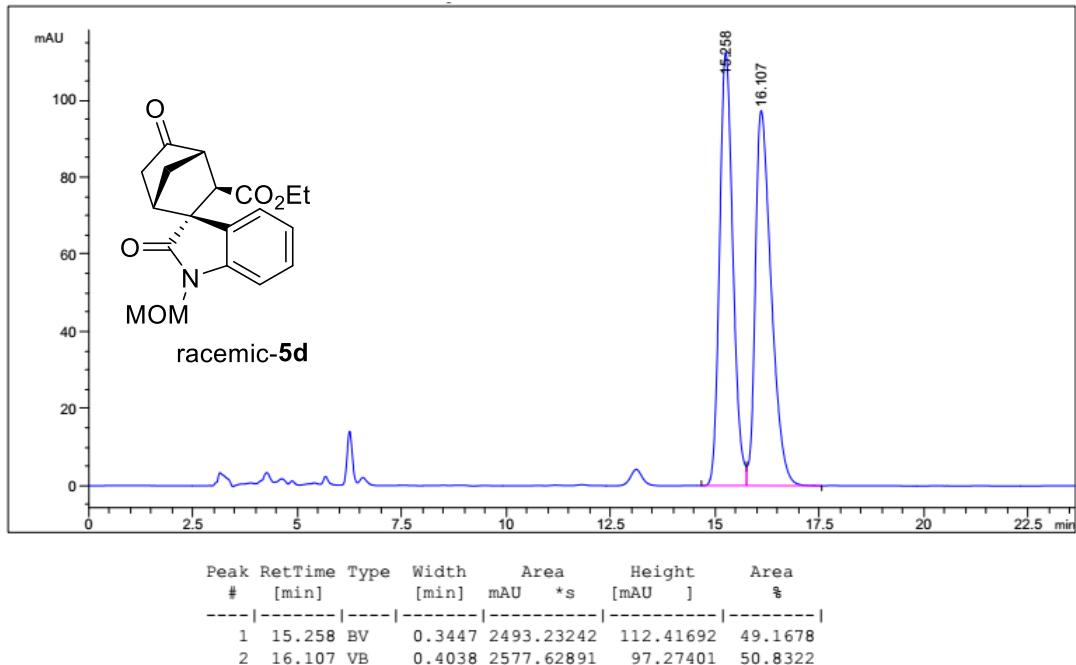


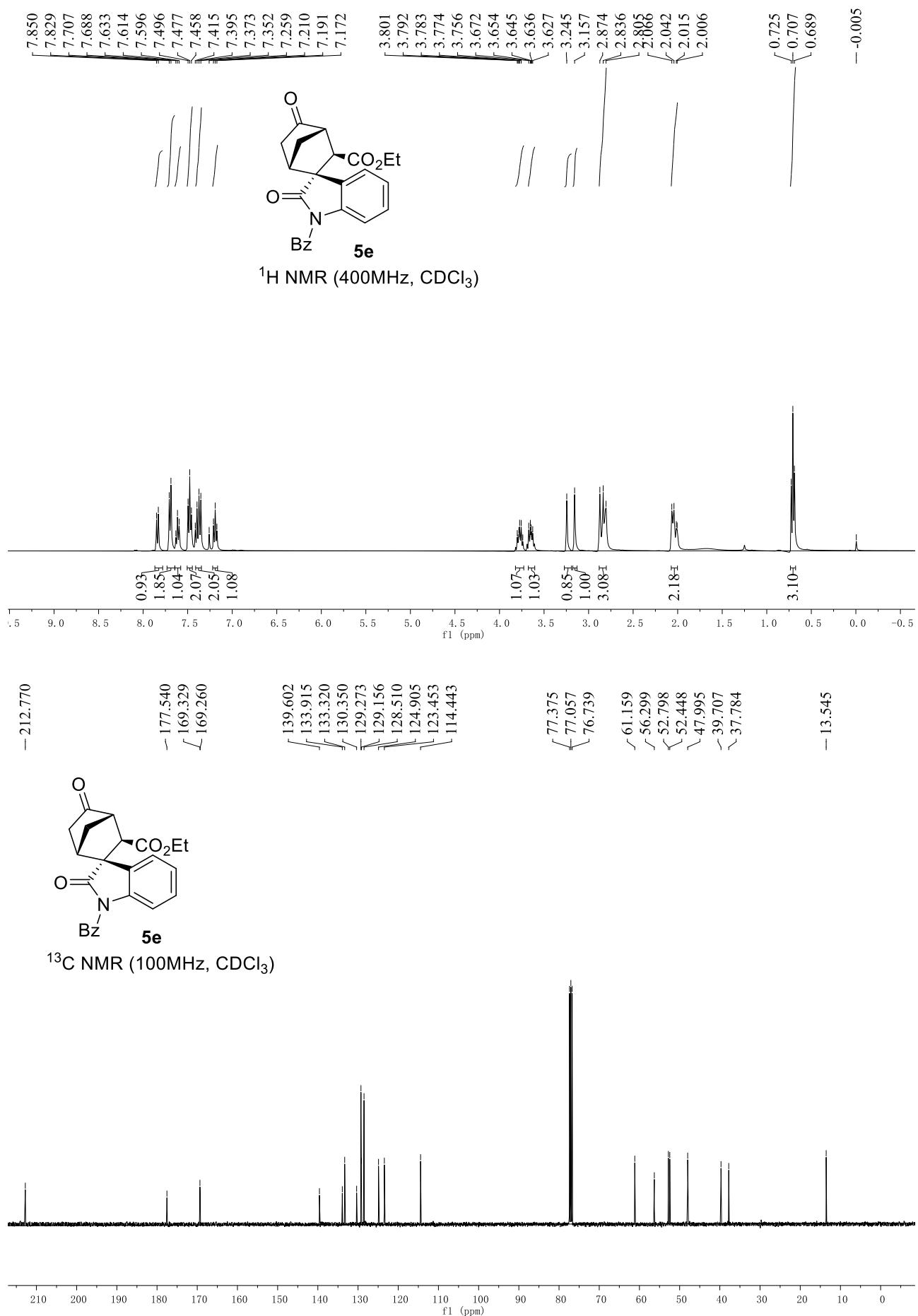
Peak #	RetTime [min]	Type	Width [min]	Area mAU	*s	Height [mAU]	Area %
1	9.125	BB	0.2199	1021.01642		71.72692	3.6671
2	16.340	BBA	0.7166	2.68216e4		529.10034	96.3329

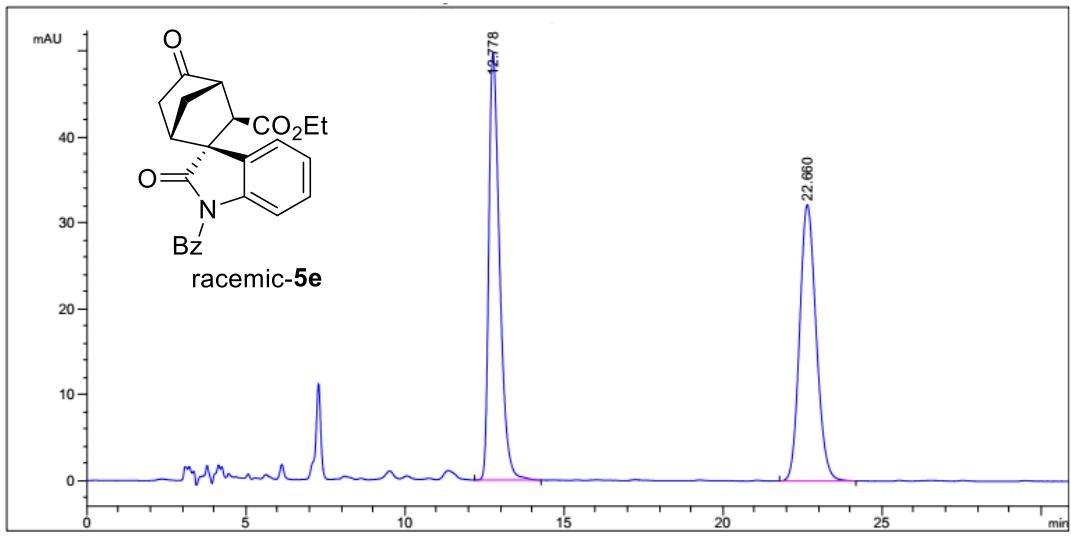




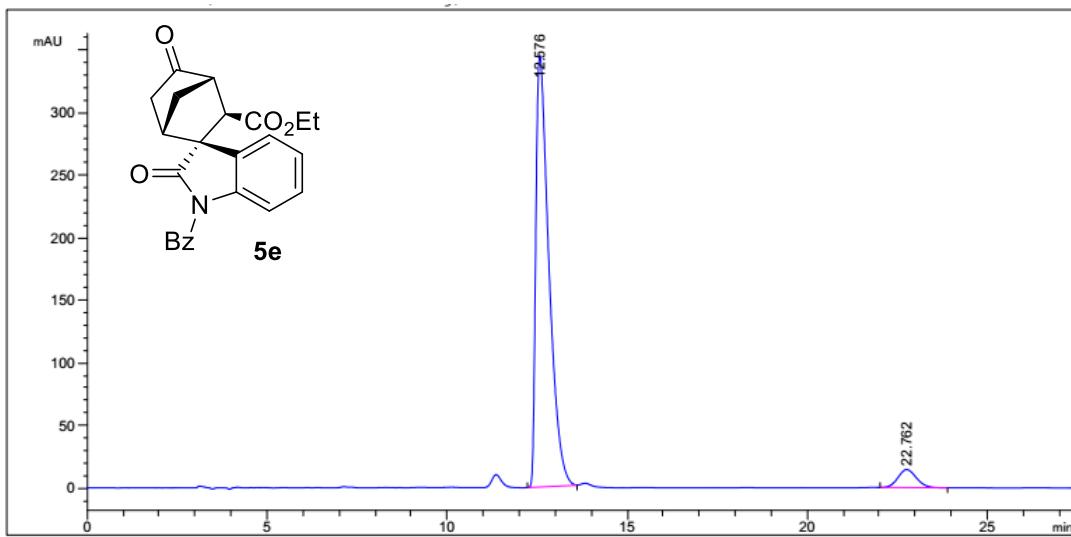




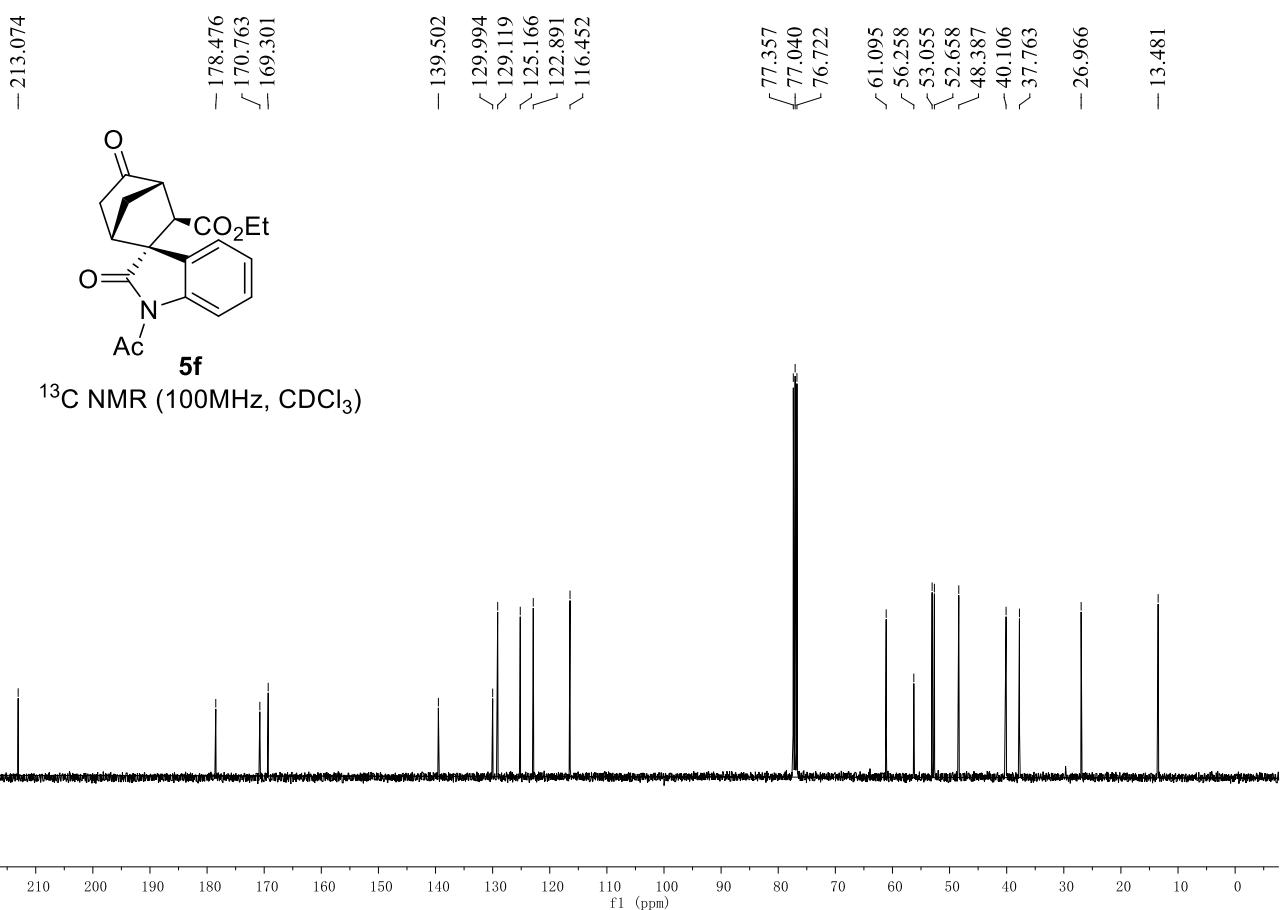
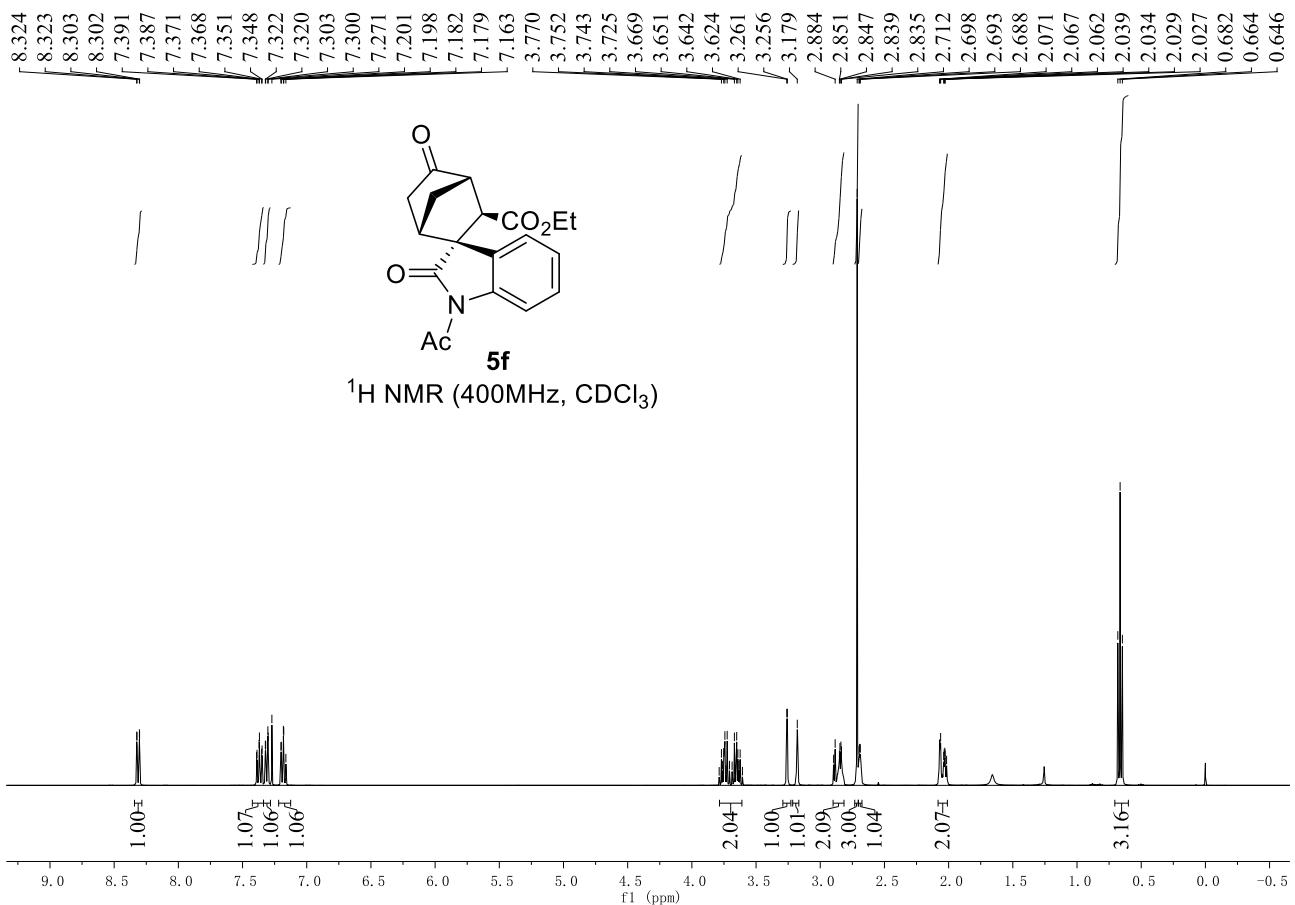


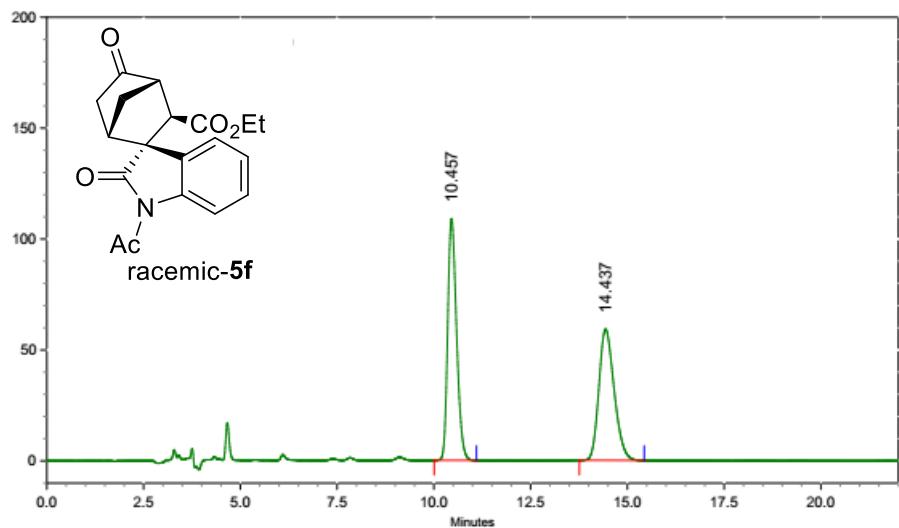


Peak #	RetTime [min]	Type	Width [min]	Area mAU	*s	Height [mAU]	Area %
1	12.778	BB	0.3614	1174.71741		49.75133	50.2782
2	22.660	BB	0.5582	1161.71936		32.16399	49.7218

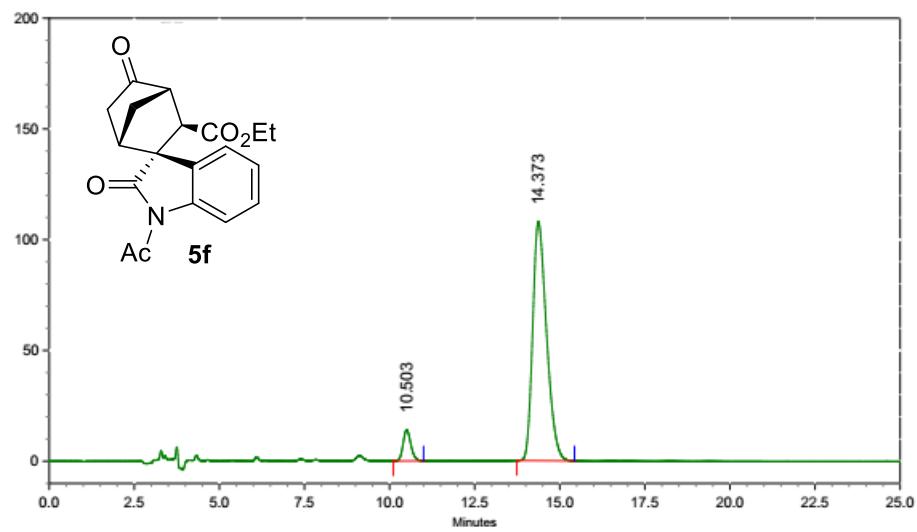


Peak #	RetTime [min]	Type	Width [min]	Area mAU	*s	Height [mAU]	Area %
1	12.576	BB	0.3797	8695.54883		345.24353	94.4017
2	22.762	BB	0.5551	515.67212		14.43615	5.5983

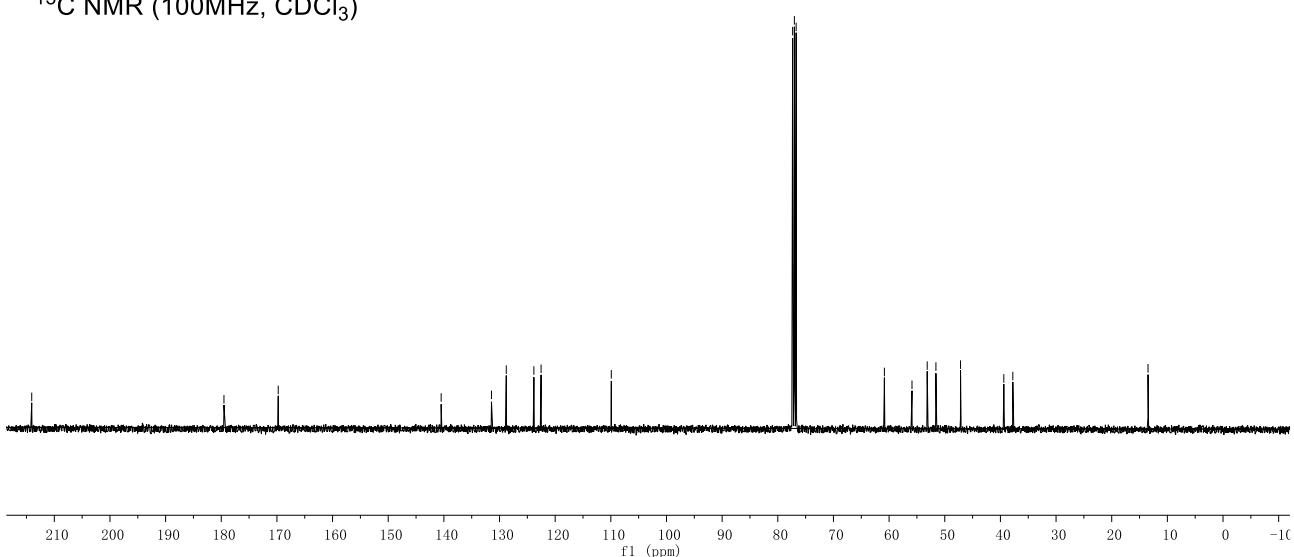
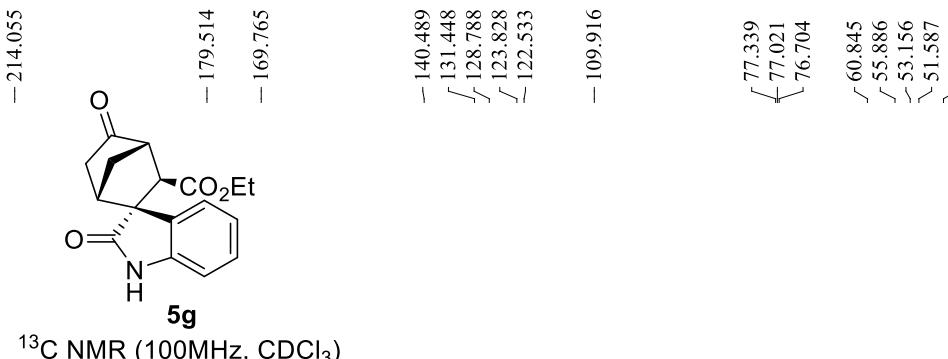
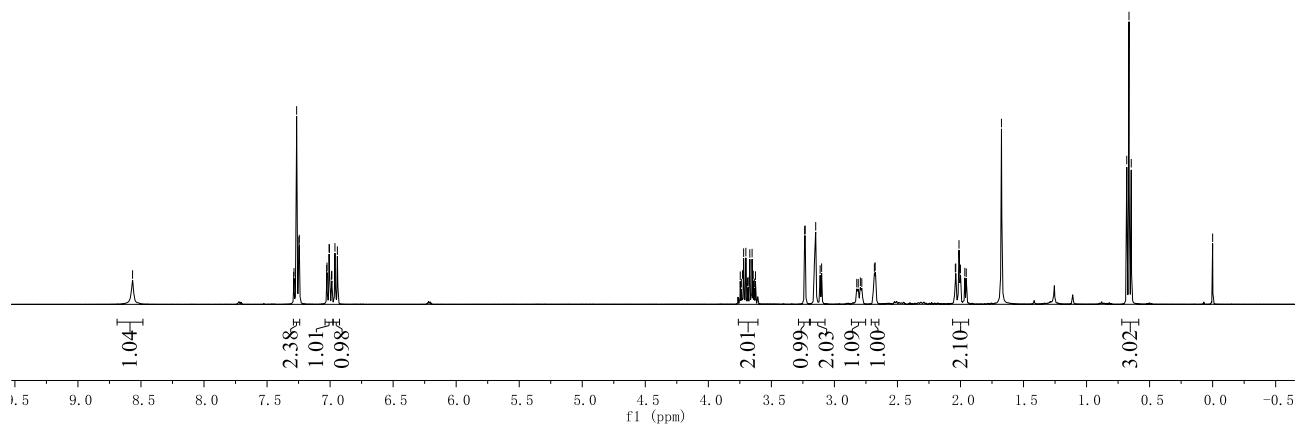
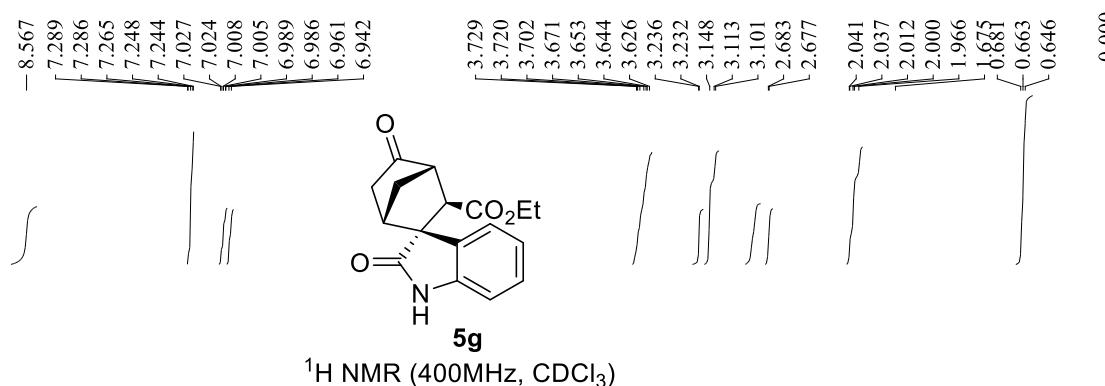


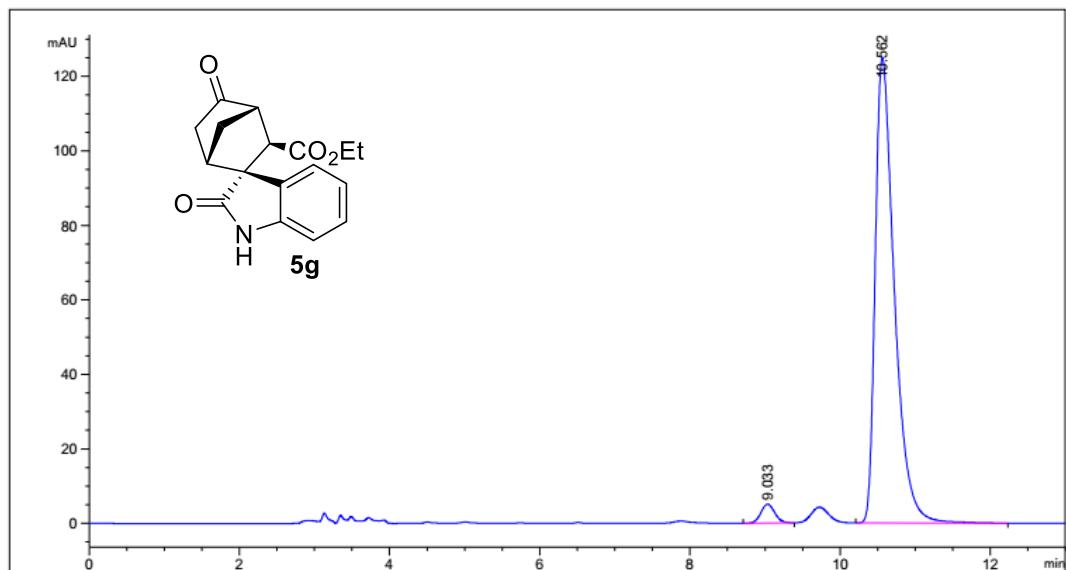
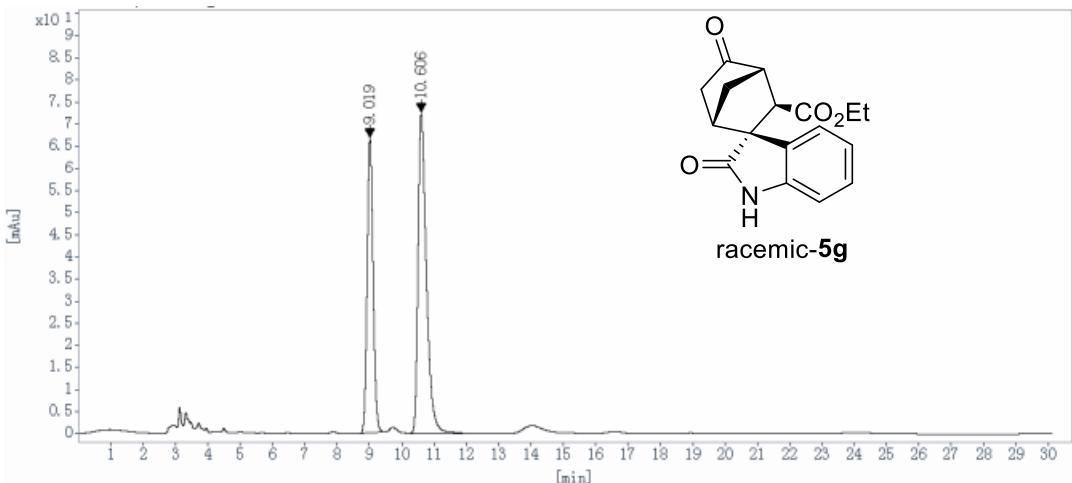


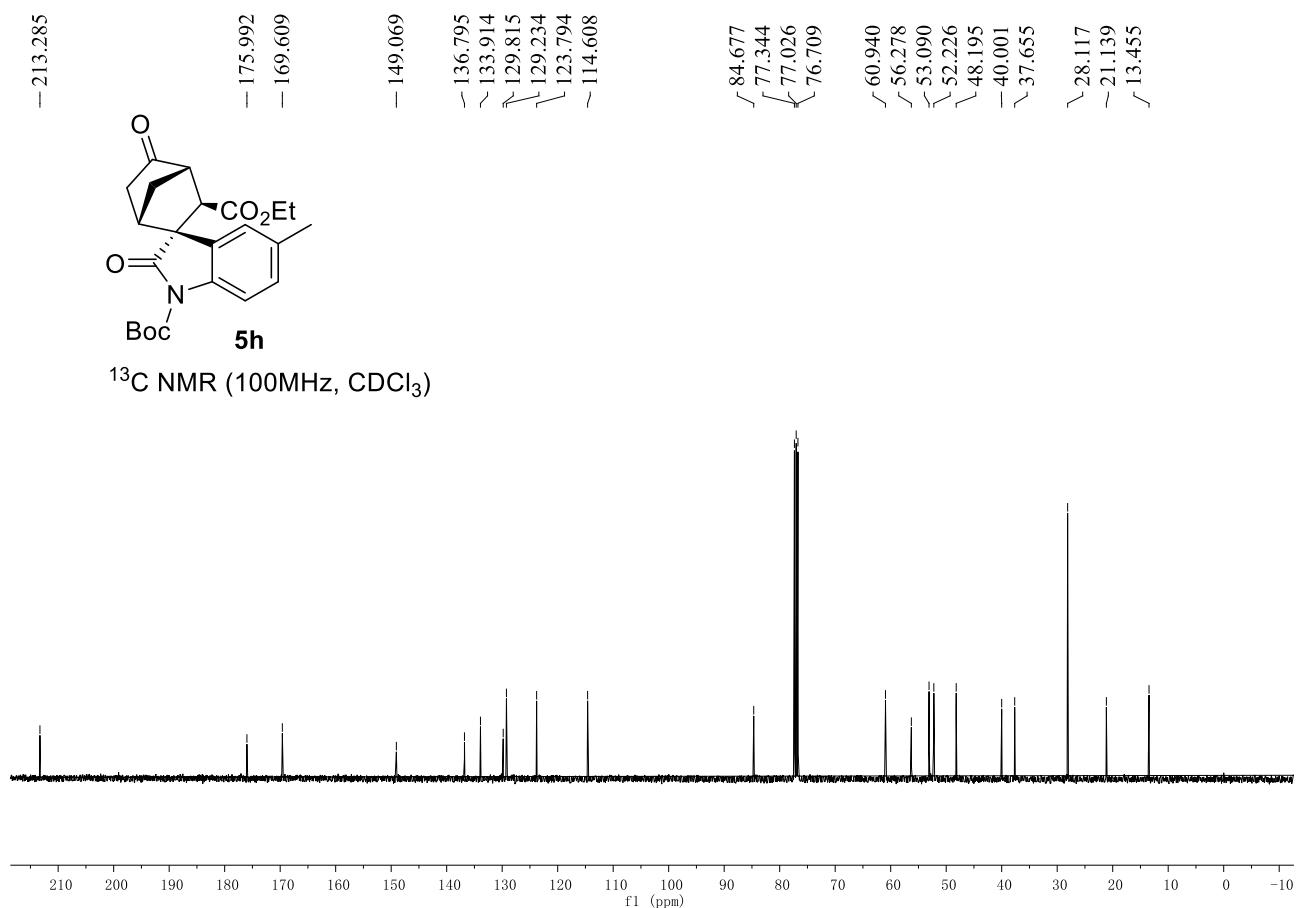
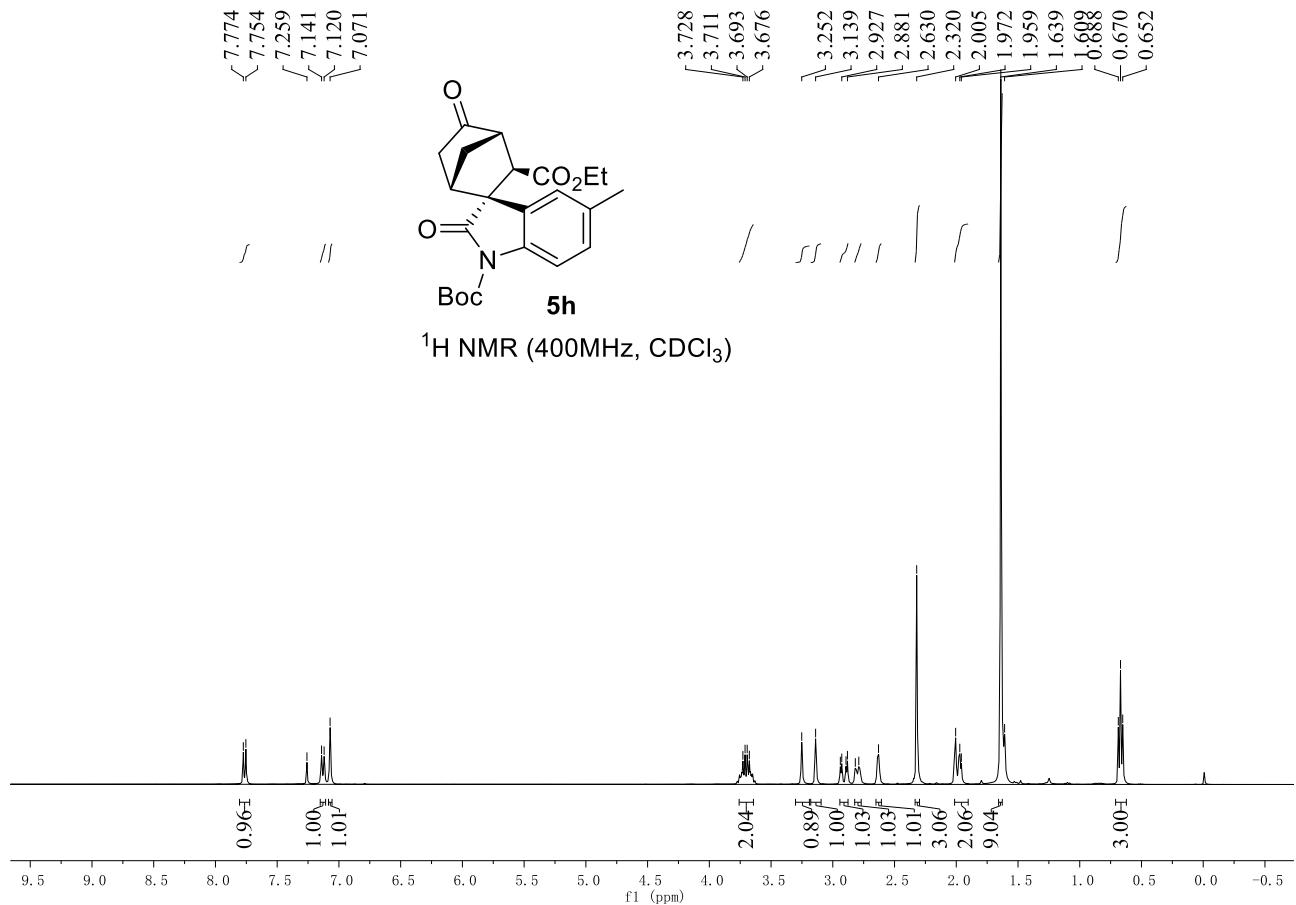
Peak No.	Ret Time	Width	Height	Area	Area [%]
1	10.457	1.093	1828333	29017106	51.6040
2	14.437	1.673	992293	27213228	48.3960

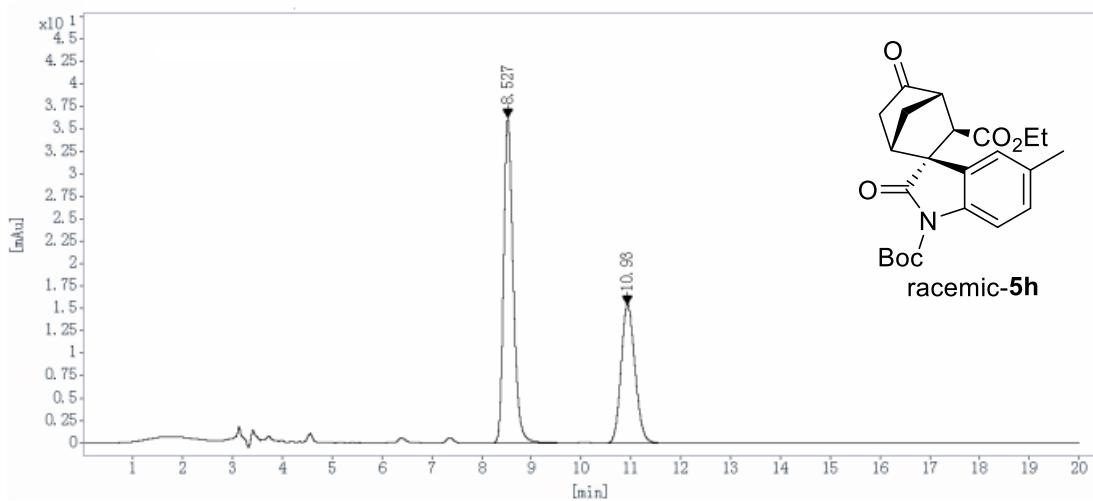


Peak No.	Ret Time	Width	Height	Area	Area [%]
1	10.503	0.893	235538	3730757	6.7869
2	14.373	1.693	1809481	51239537	93.2131

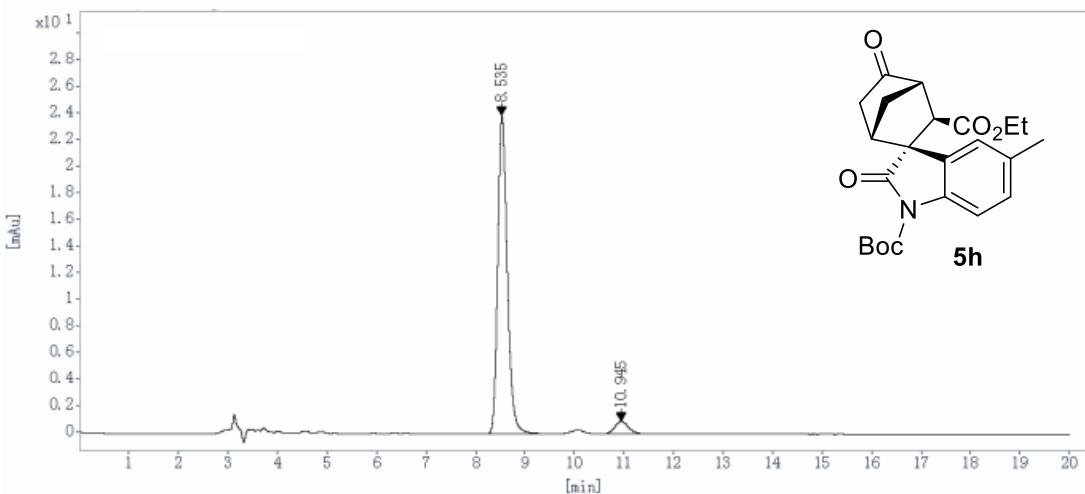




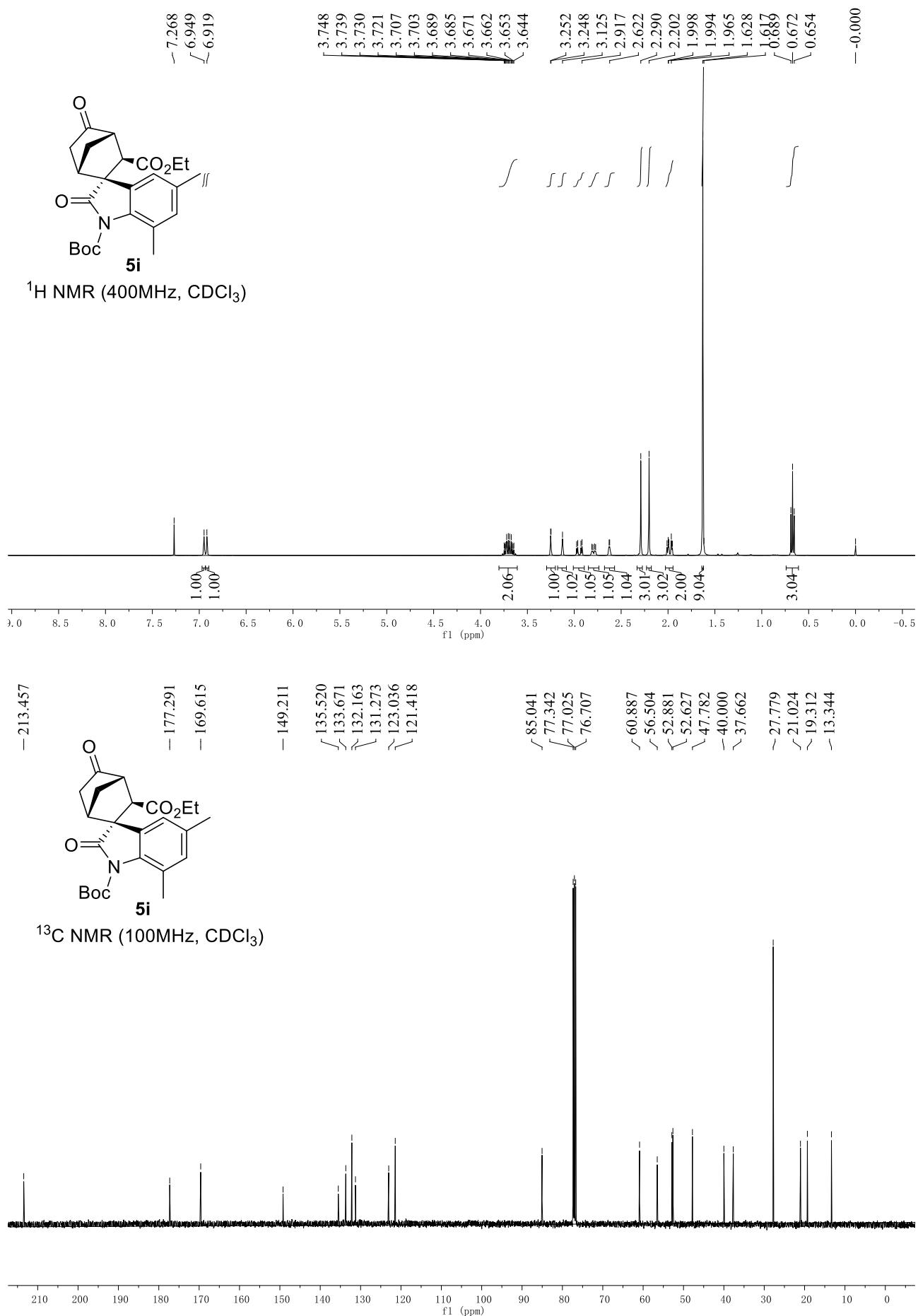


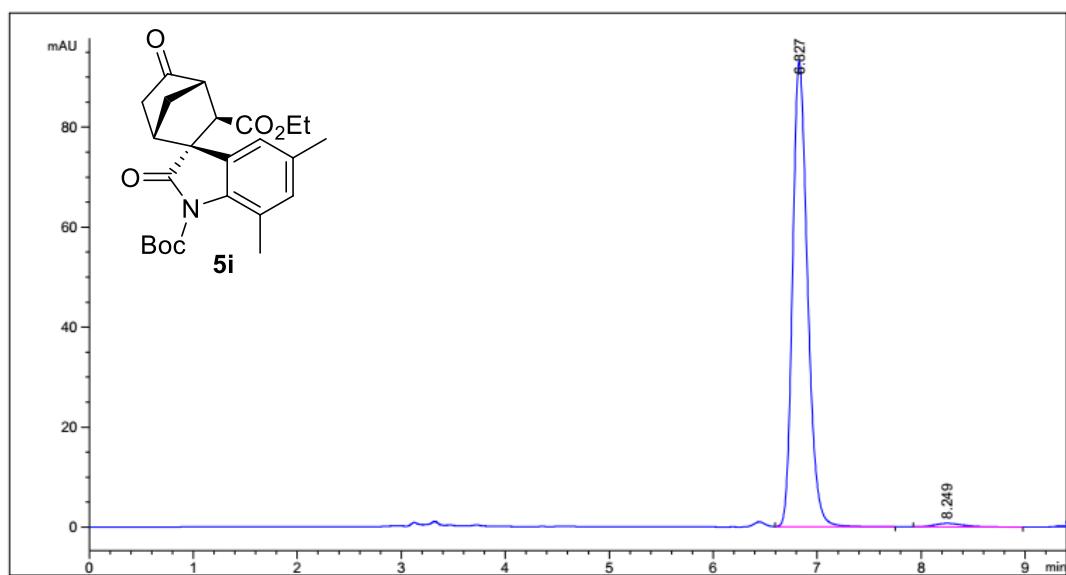
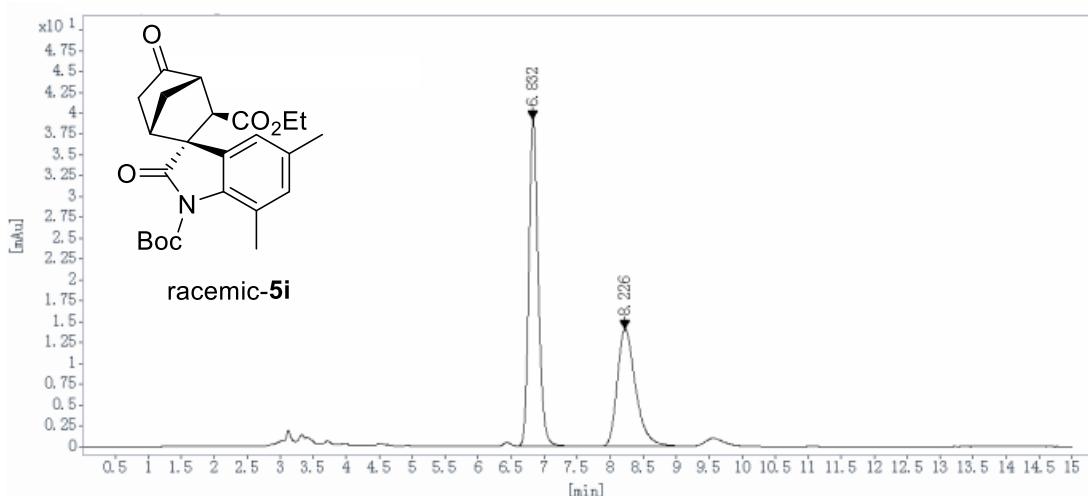


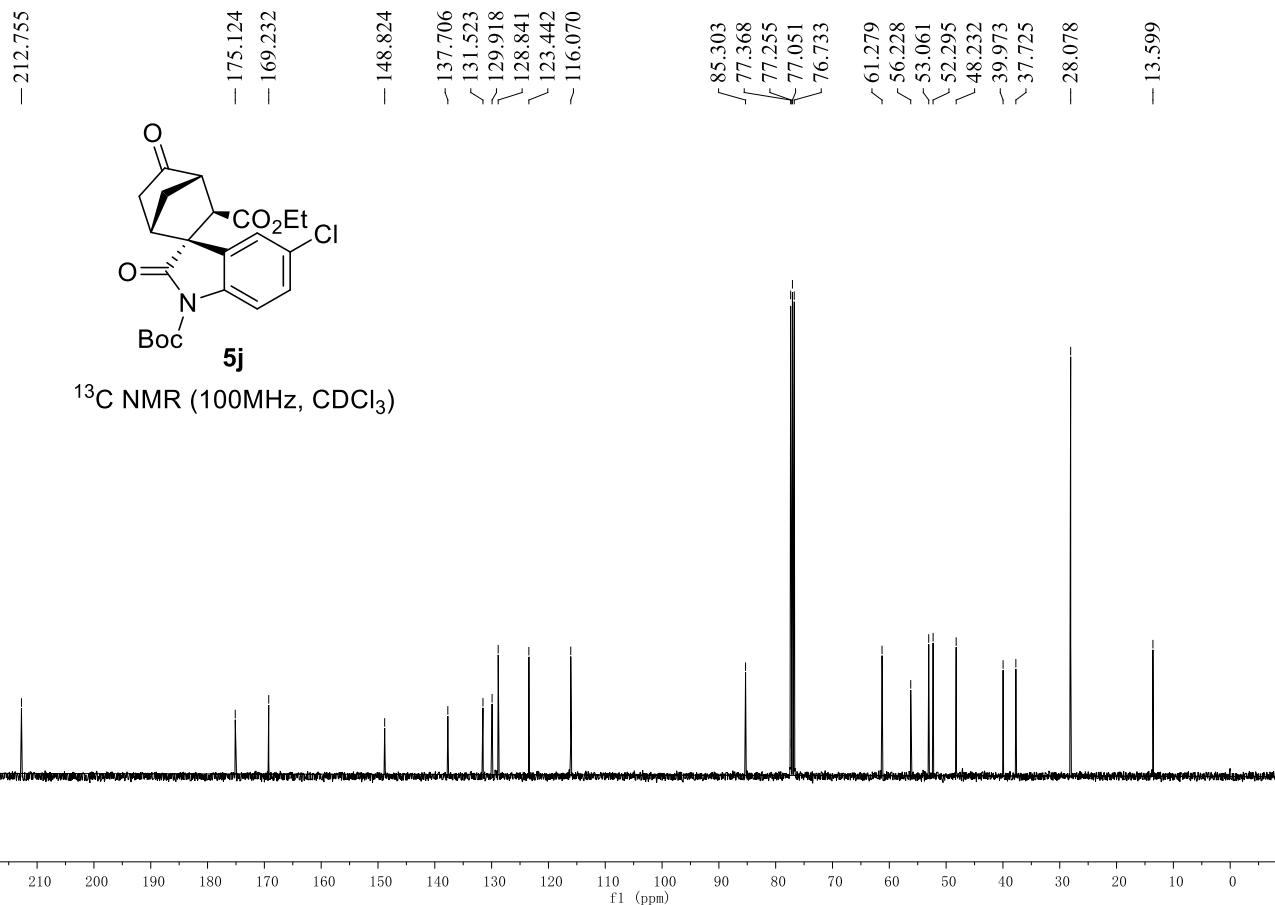
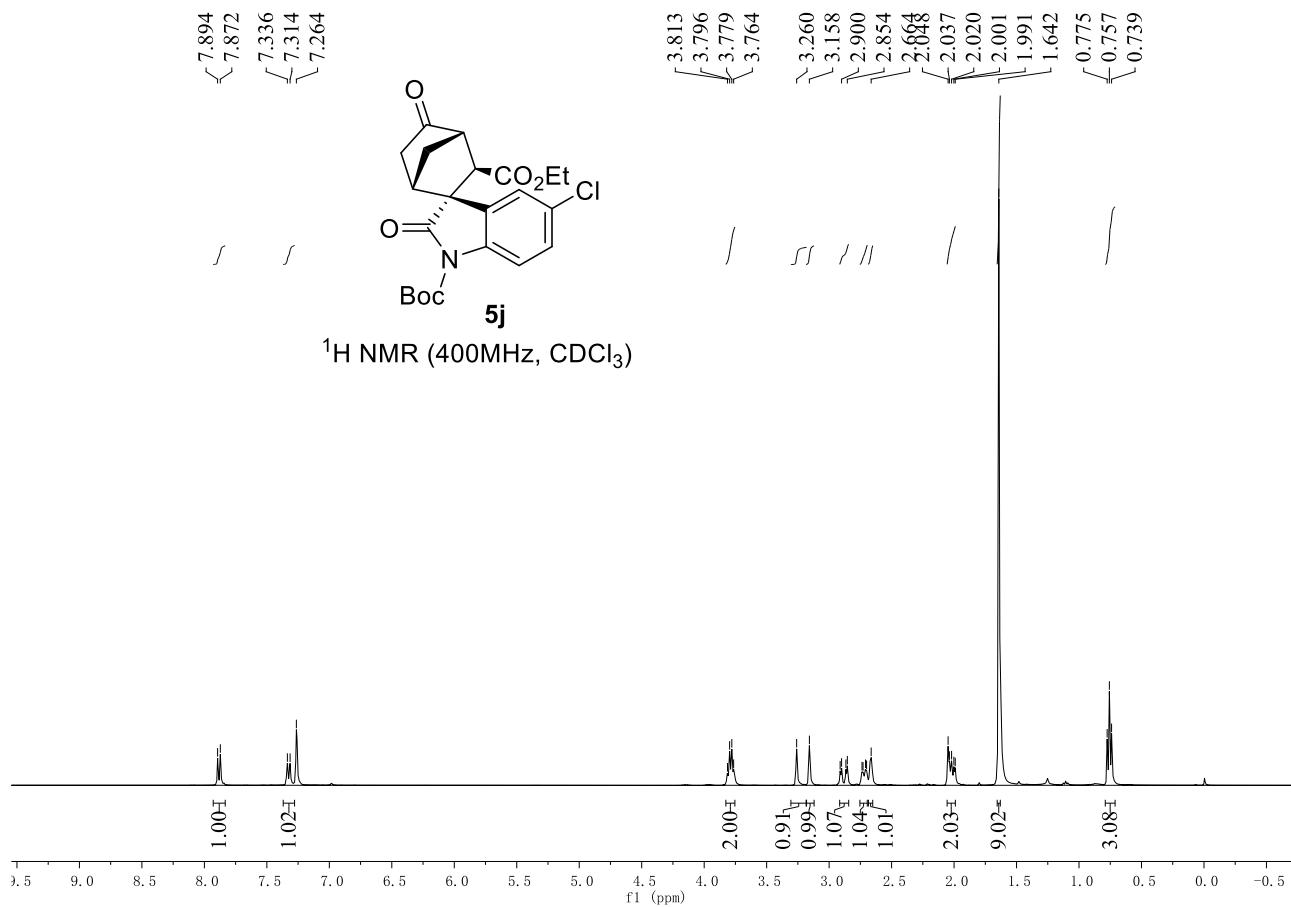
Ret Time [min]	Peak Type	Width [min]	Height [mAU]	Area [mAU*s]	Area [%]
8.527	BB	0.20	36.2378	483.5439	61.5707
10.930	BB	0.30	15.4897	301.8031	38.4293
Totals:			785.3470	100.0000	

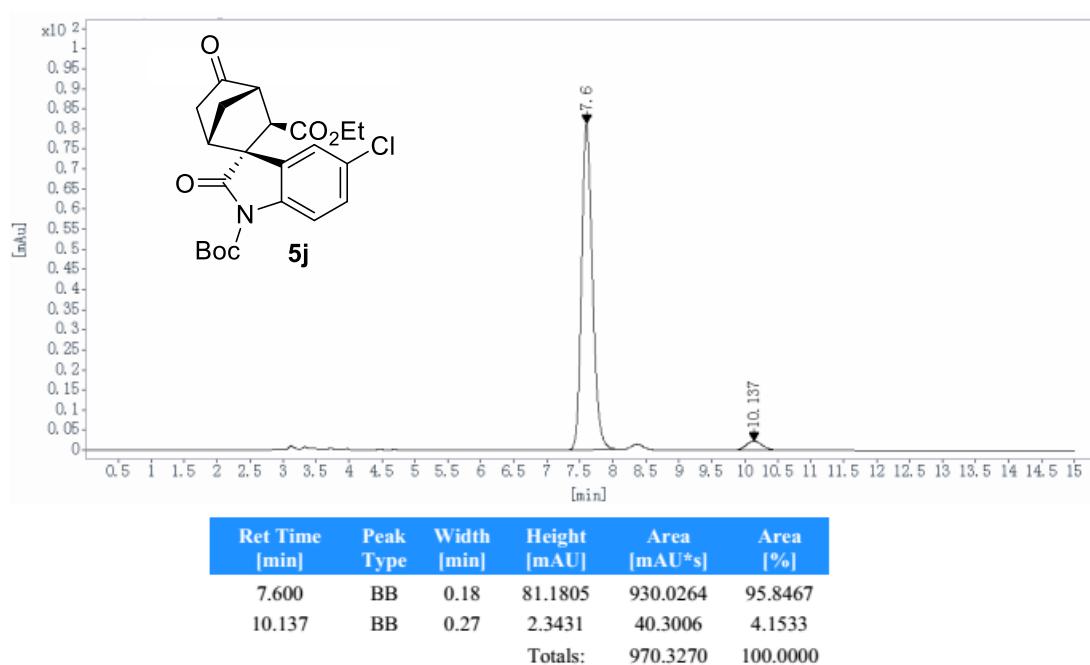
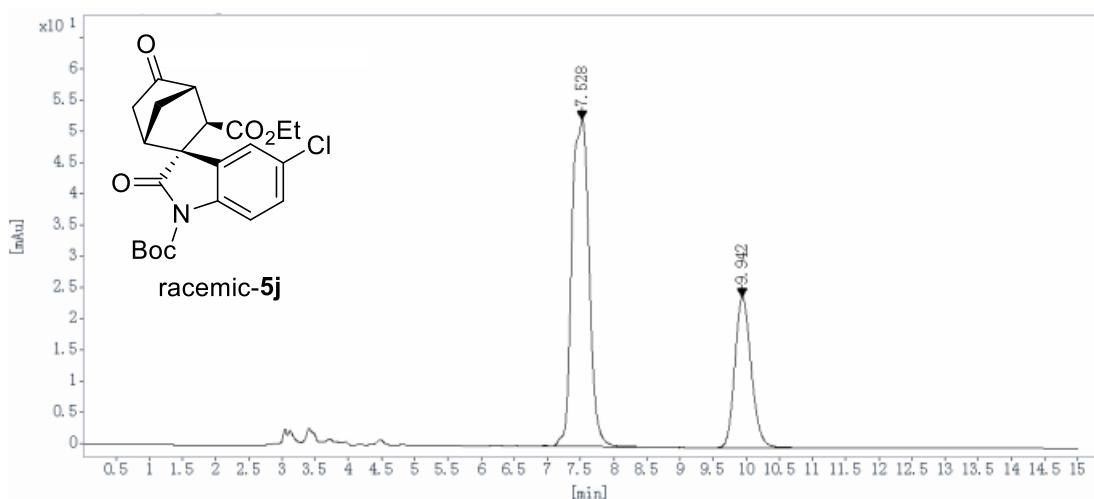


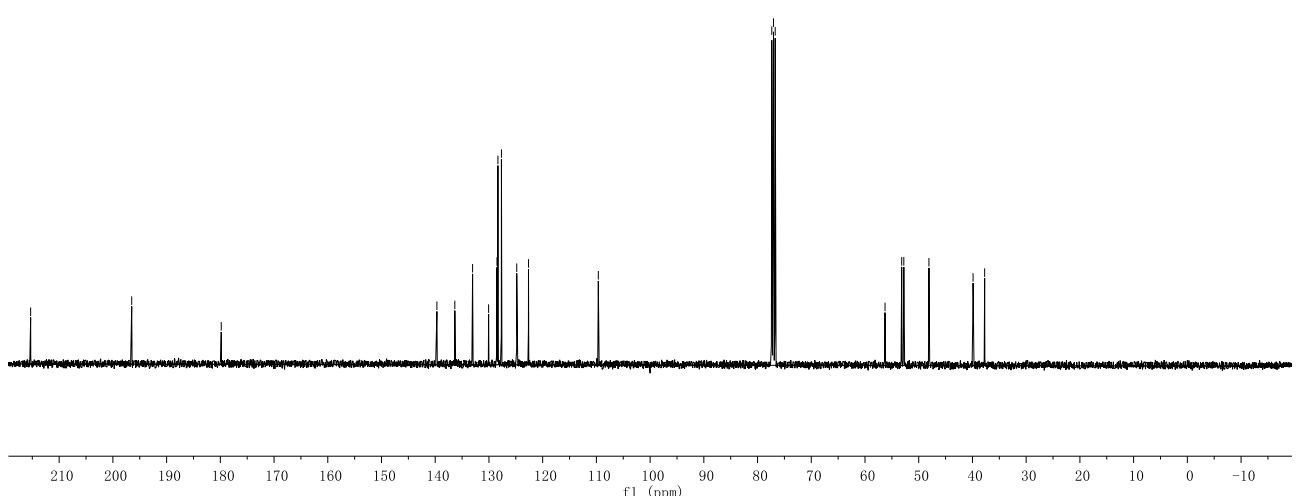
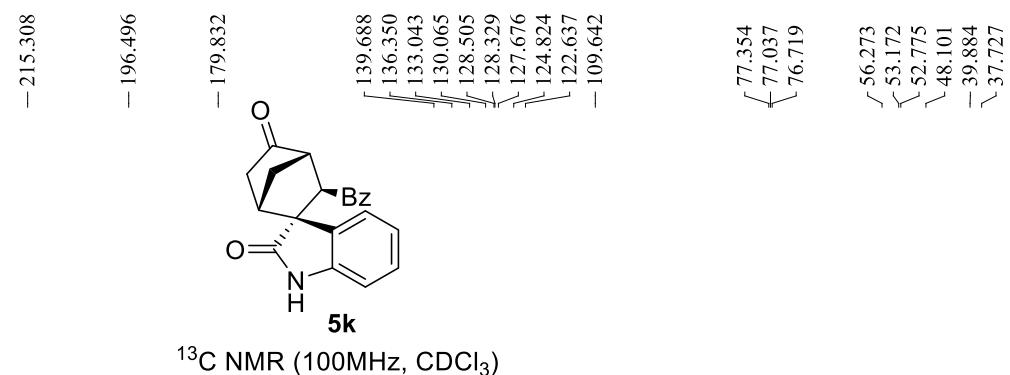
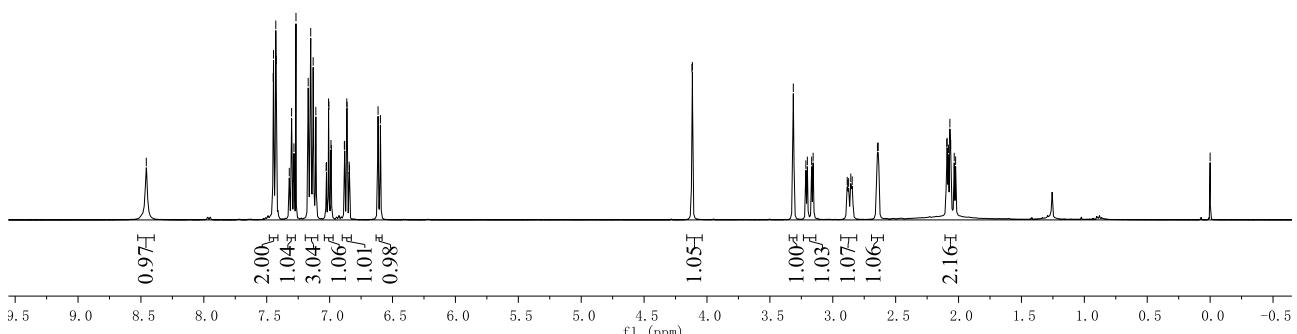
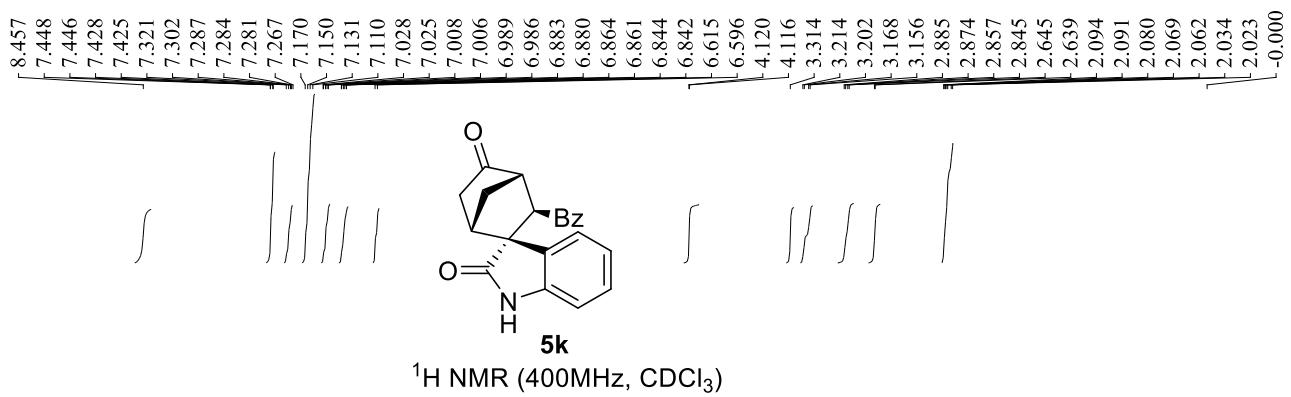
Ret Time [min]	Peak Type	Width [min]	Height [mAU]	Area [mAU*s]	Area [%]
8.535	BBA	0.20	23.9217	319.6052	94.6242
10.945	BB	0.29	0.9256	18.1574	5.3758
Totals:			337.7626	100.0000	

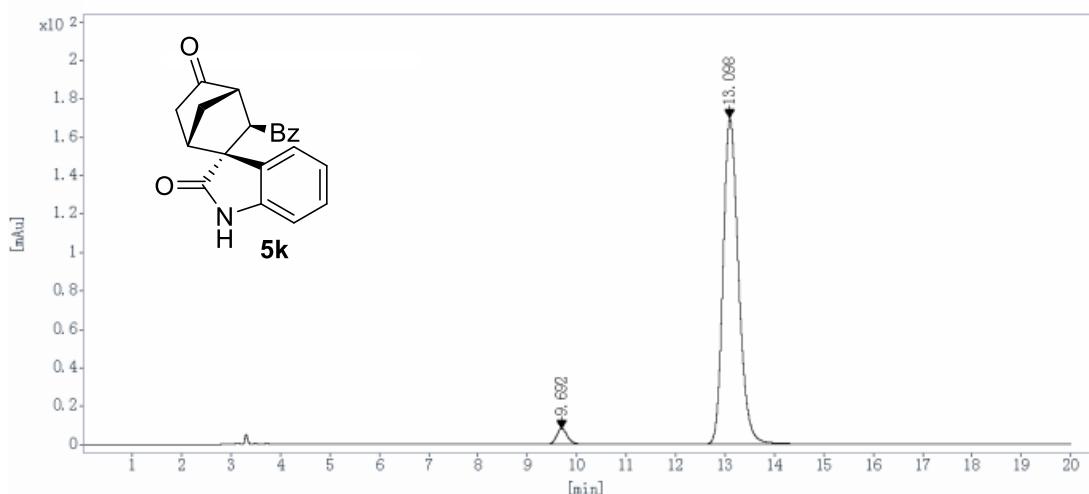
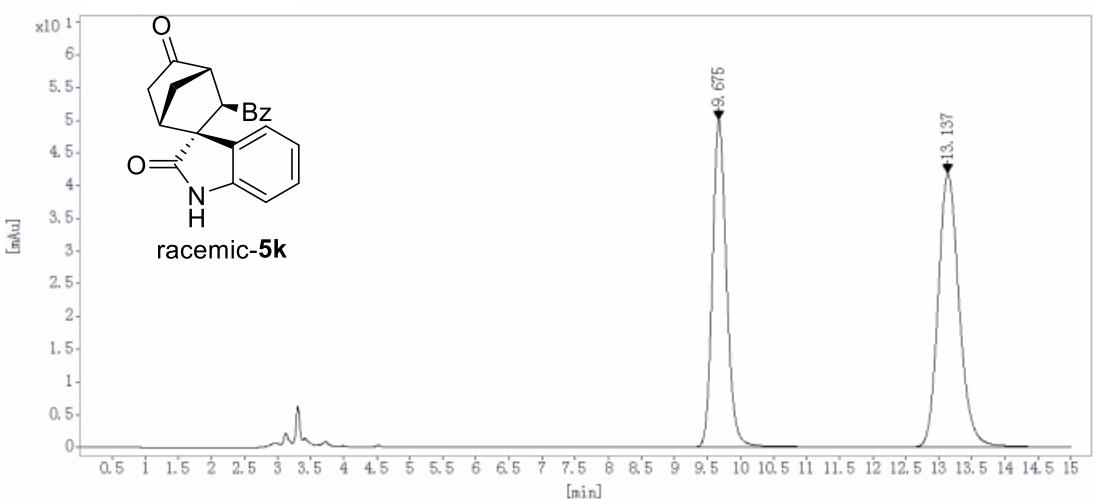


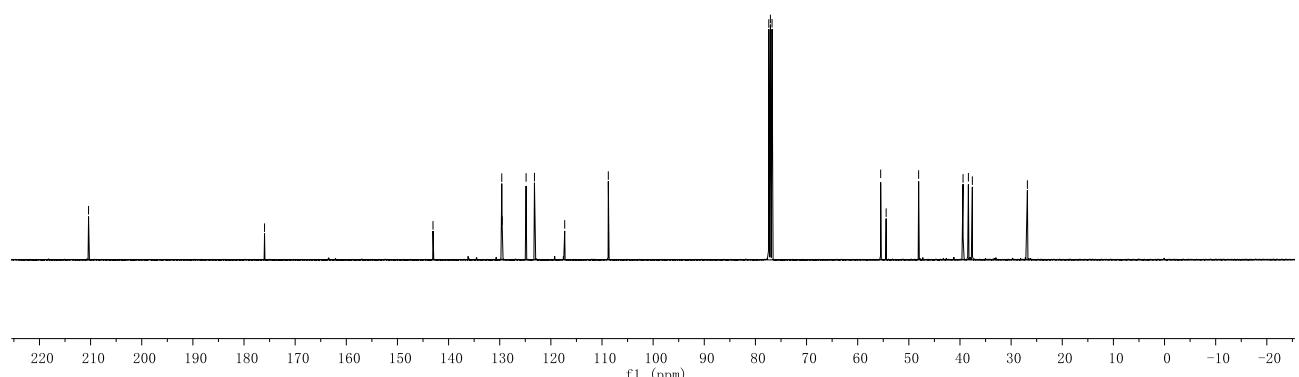
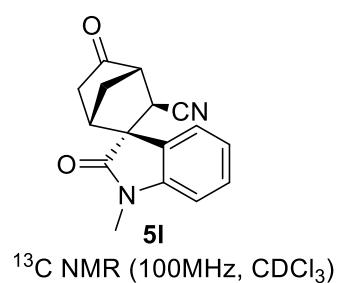
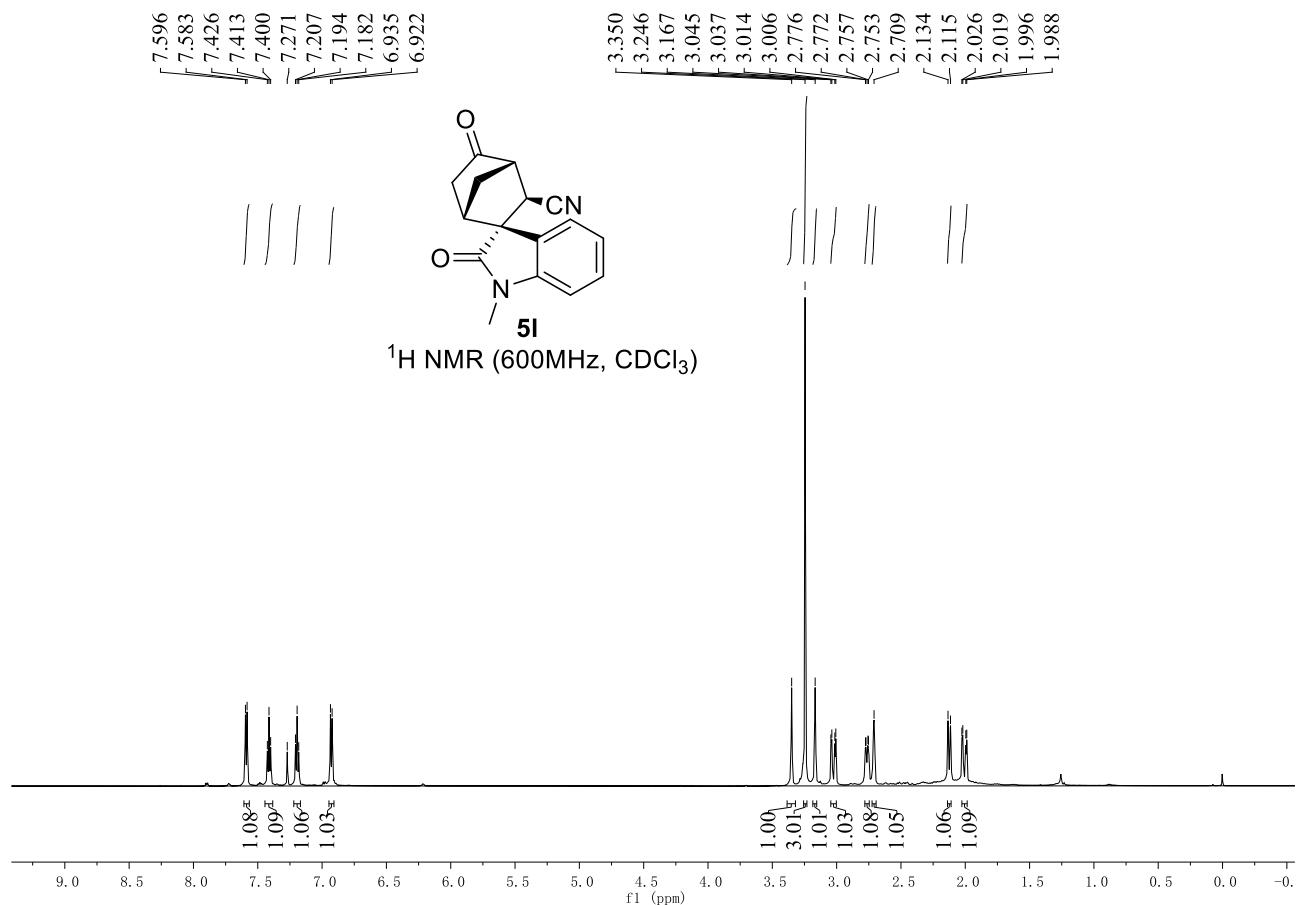


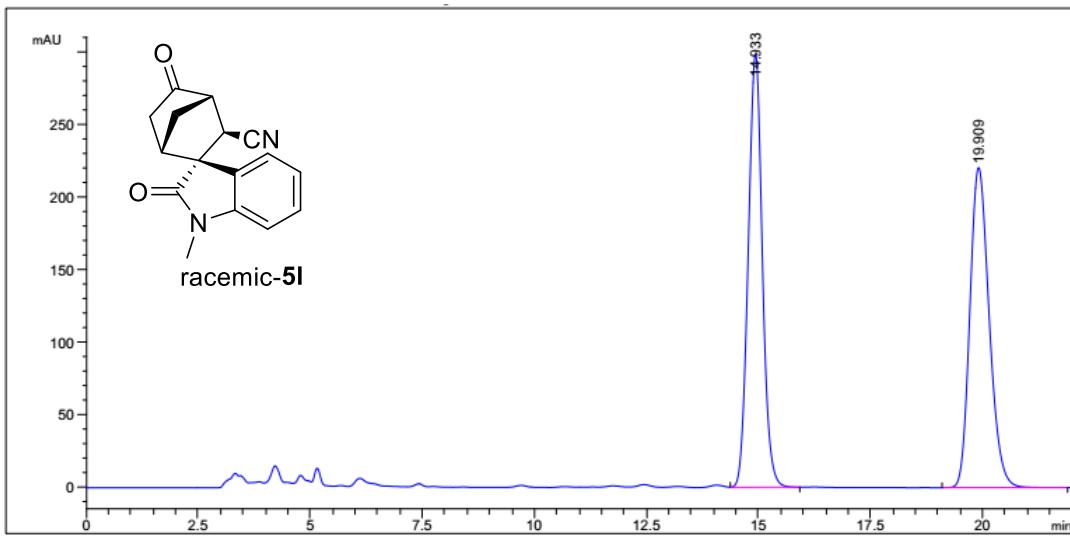




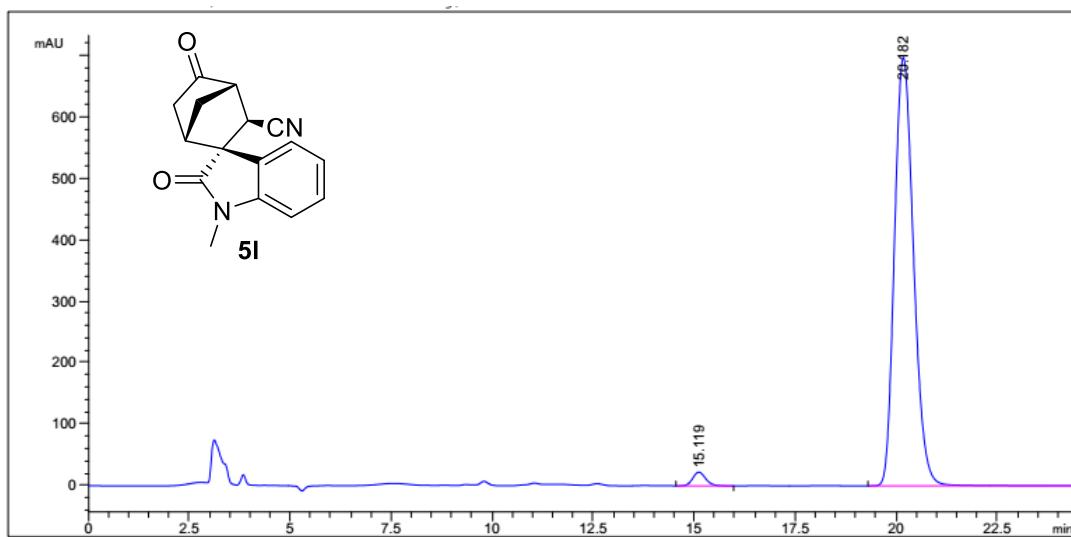




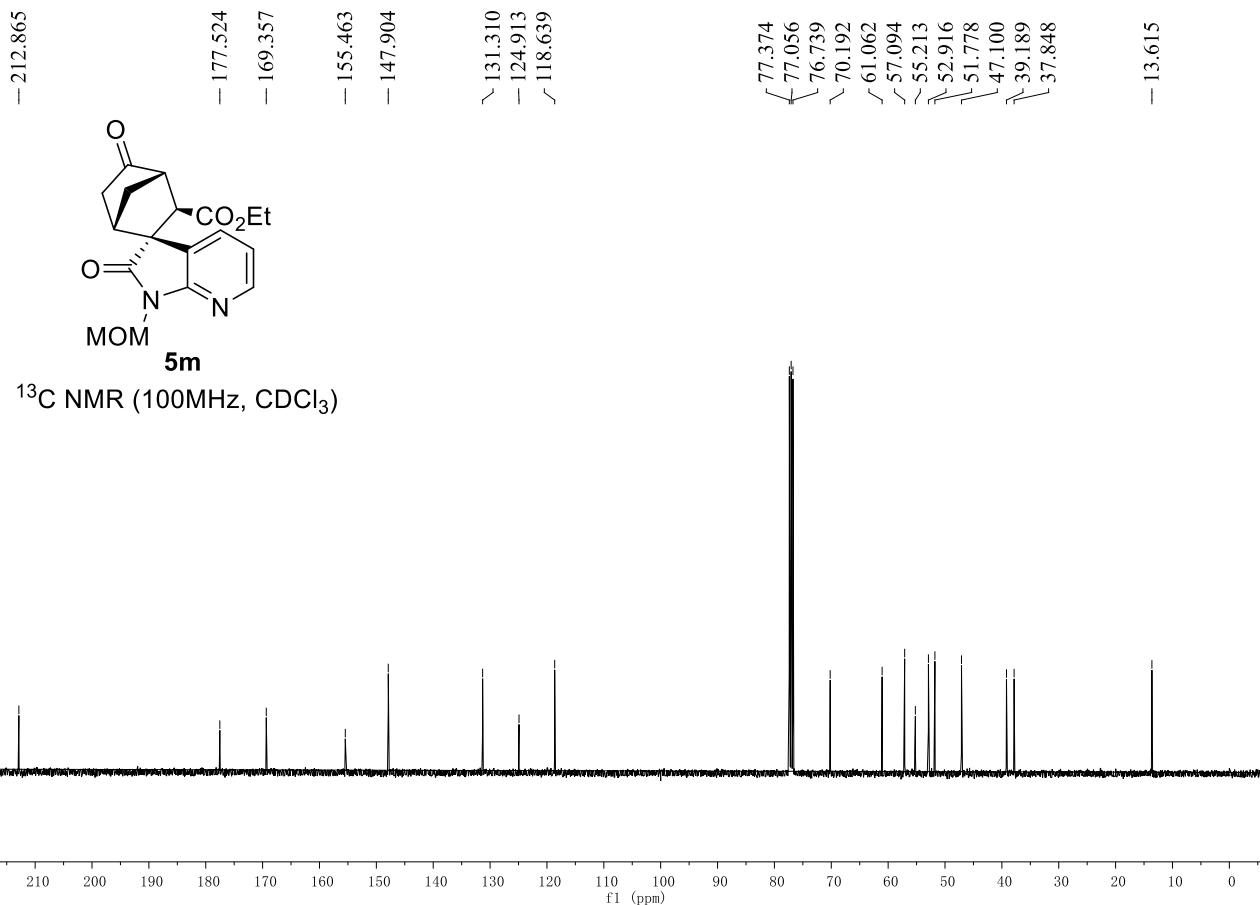
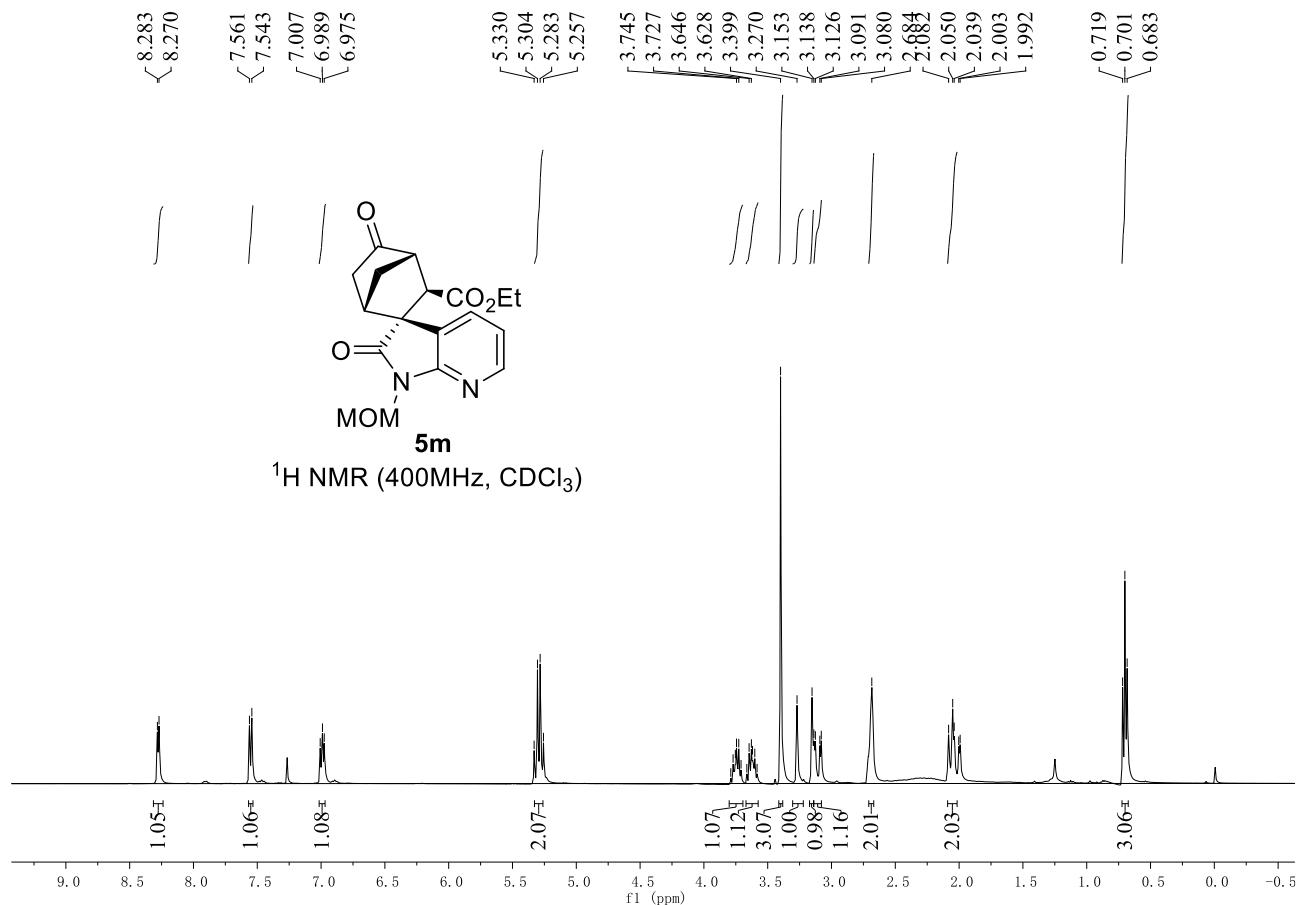


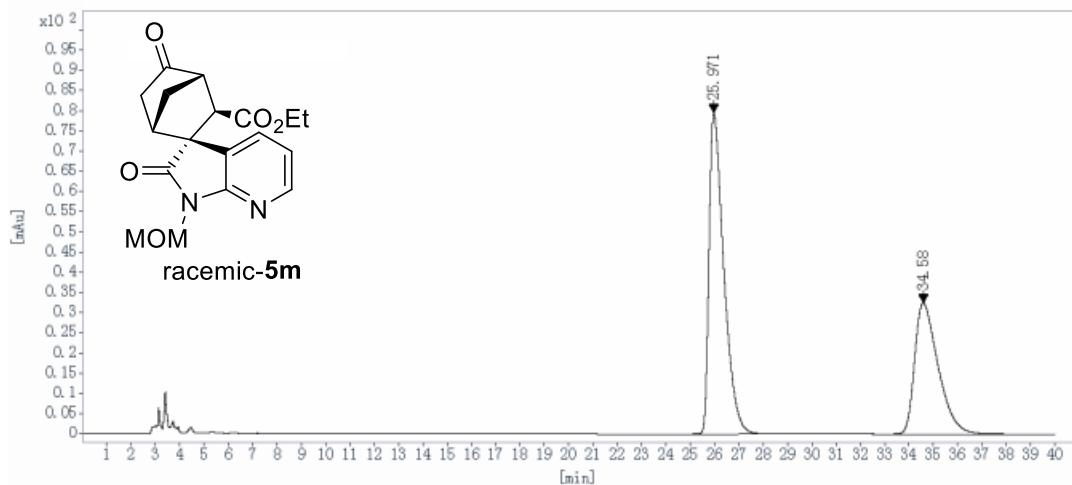


Peak #	RetTime [min]	Type	Width [min]	Area mAU	*s	Height [mAU]	Area %
1	14.933	VB	0.3368	6539.00049		298.80338	49.7906
2	19.909	BB	0.4621	6594.00635		220.73787	50.2094

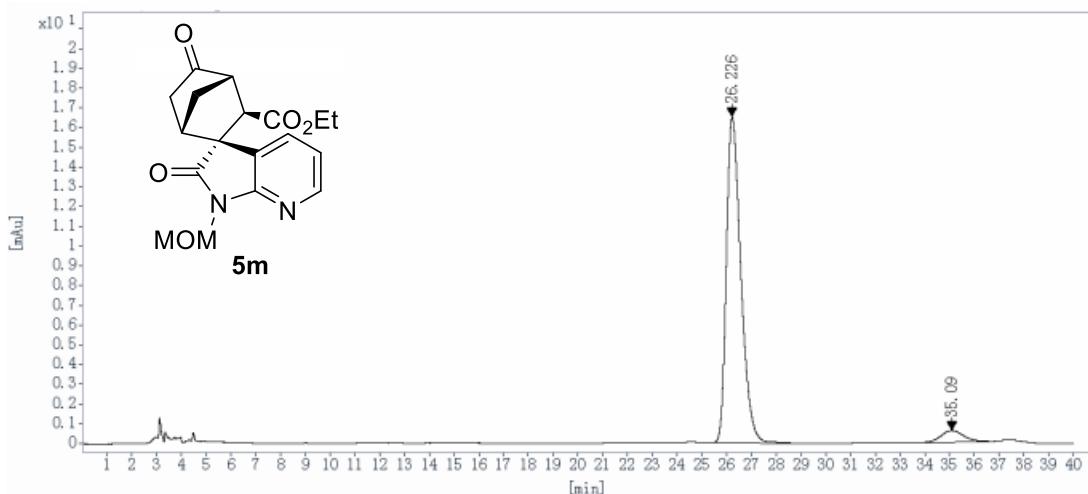


Peak #	RetTime [min]	Type	Width [min]	Area mAU	*s	Height [mAU]	Area %
1	15.119	BB	0.3551	496.39014		22.11240	2.1270
2	20.182	BBA	0.5239	2.28417e4		693.83154	97.8730

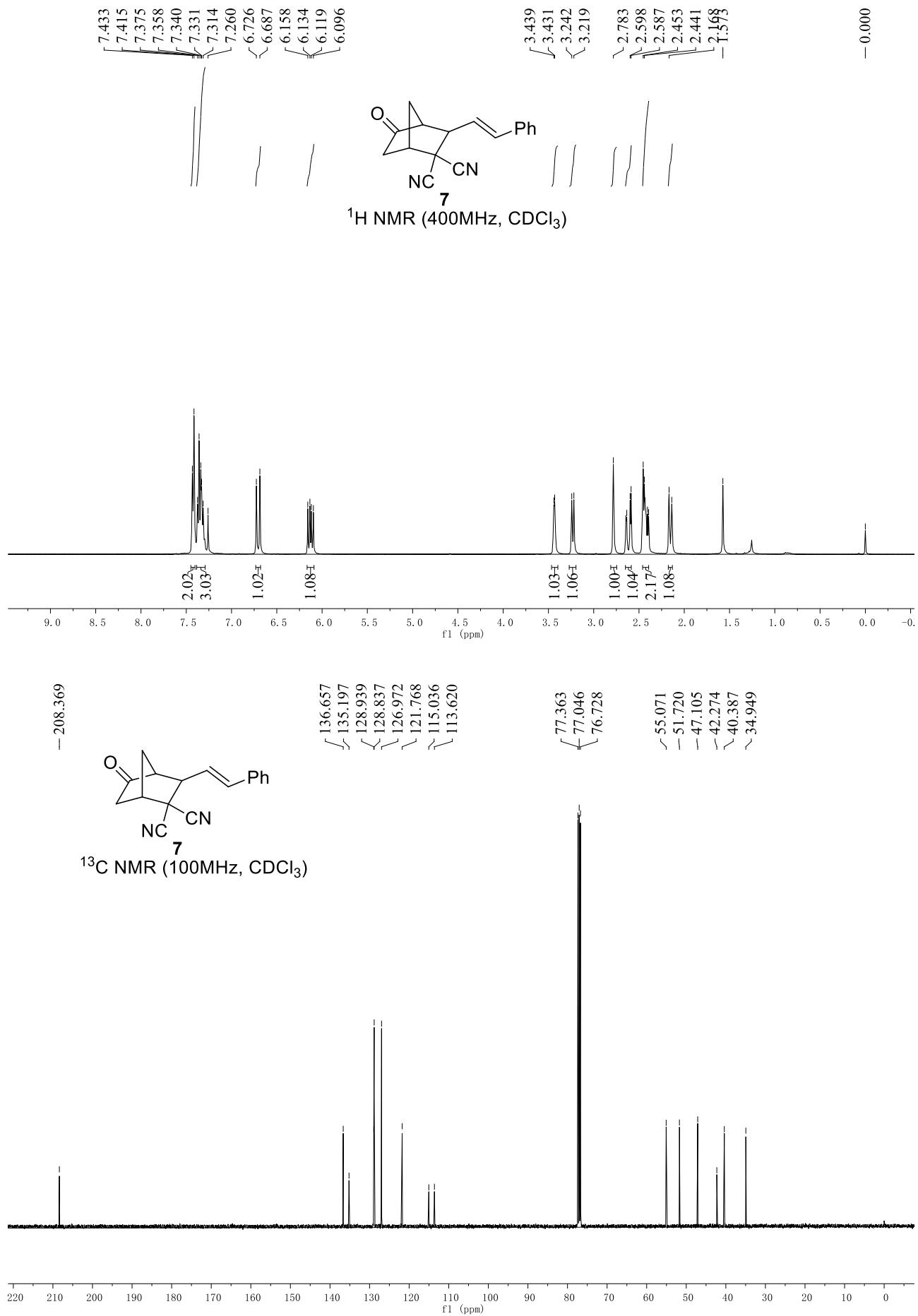


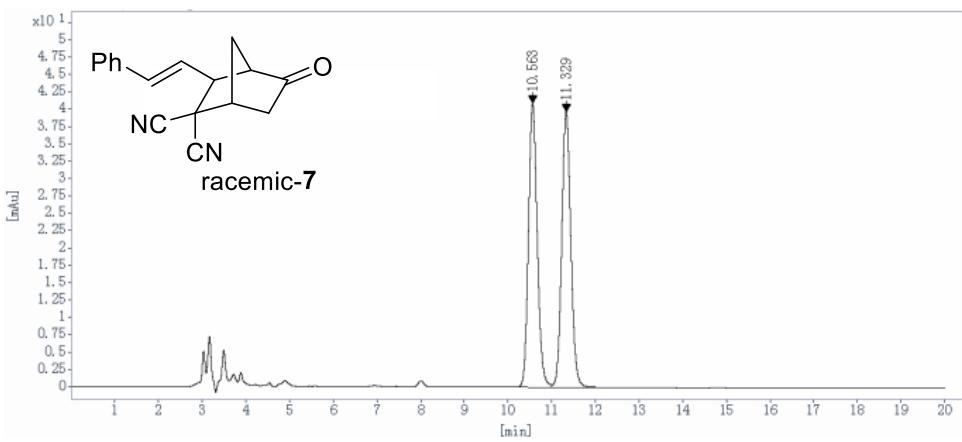


Ret Time [min]	Peak Type	Width [min]	Height [mAU]	Area [mAU*s]	Area [%]
25.971	BB	0.63	79.4465	3347.2537	60.5417
34.580	BB	1.01	32.5045	2181.5901	39.4583
Totals:			5528.8438	100.0000	

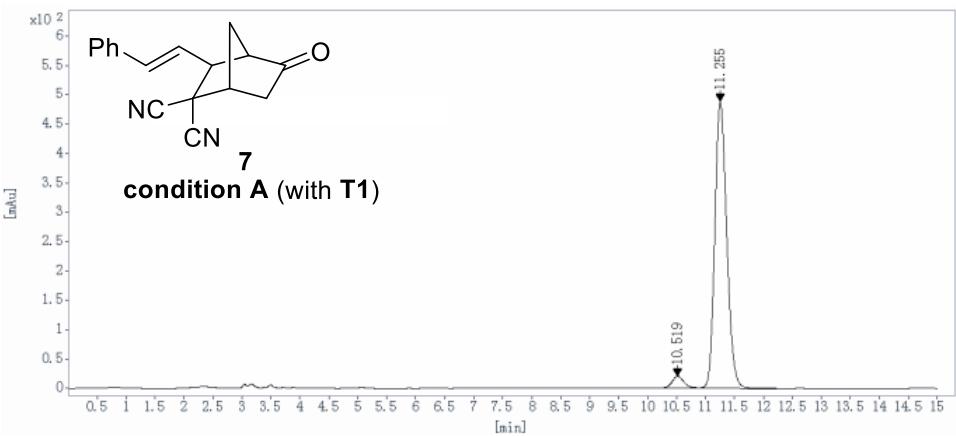


Ret Time [min]	Peak Type	Width [min]	Height [mAU]	Area [mAU*s]	Area [%]
26.226	BB	0.62	16.5212	672.7792	94.8929
35.090	BB	0.87	0.5763	36.2088	5.1071
Totals:			708.9879	100.0000	

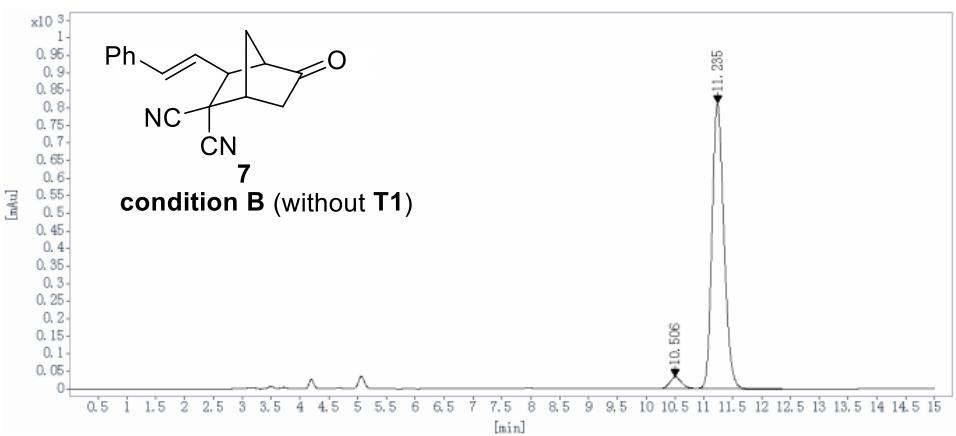




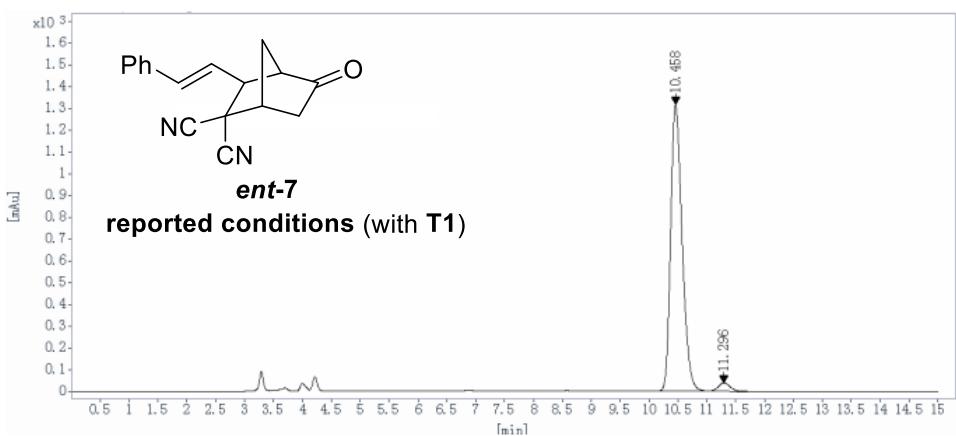
Ret Time [min]	Peak Type	Width [min]	Height [mAU]	Area [mAU*s]	Area [%]
10.563	BV	0.21	40.8915	569.9389	49.7528
11.329	VB	0.22	39.7118	575.6027	50.2472
Totals:			1145.5416	100.0000	



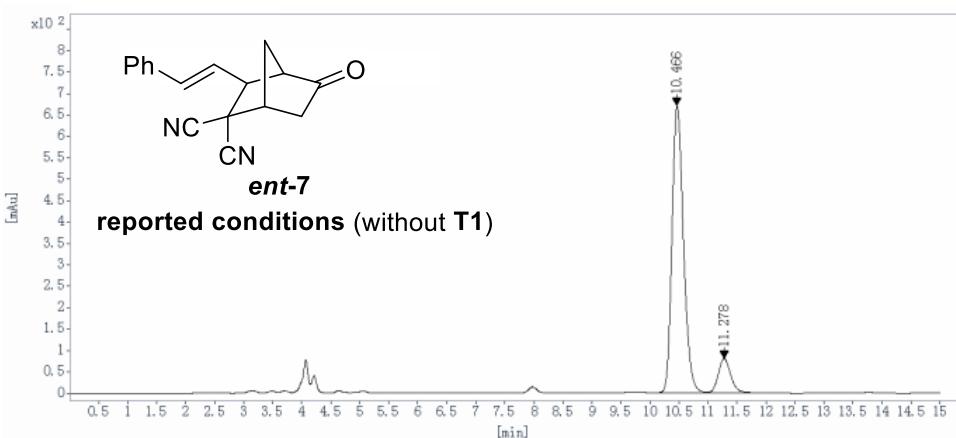
Ret Time [min]	Peak Type	Width [min]	Height [mAU]	Area [mAU*s]	Area [%]
10.519	BV	0.22	20.0539	283.2744	3.9280
11.255	VB	0.22	487.8672	6928.4829	96.0720
Totals:			7211.7573	100.0000	



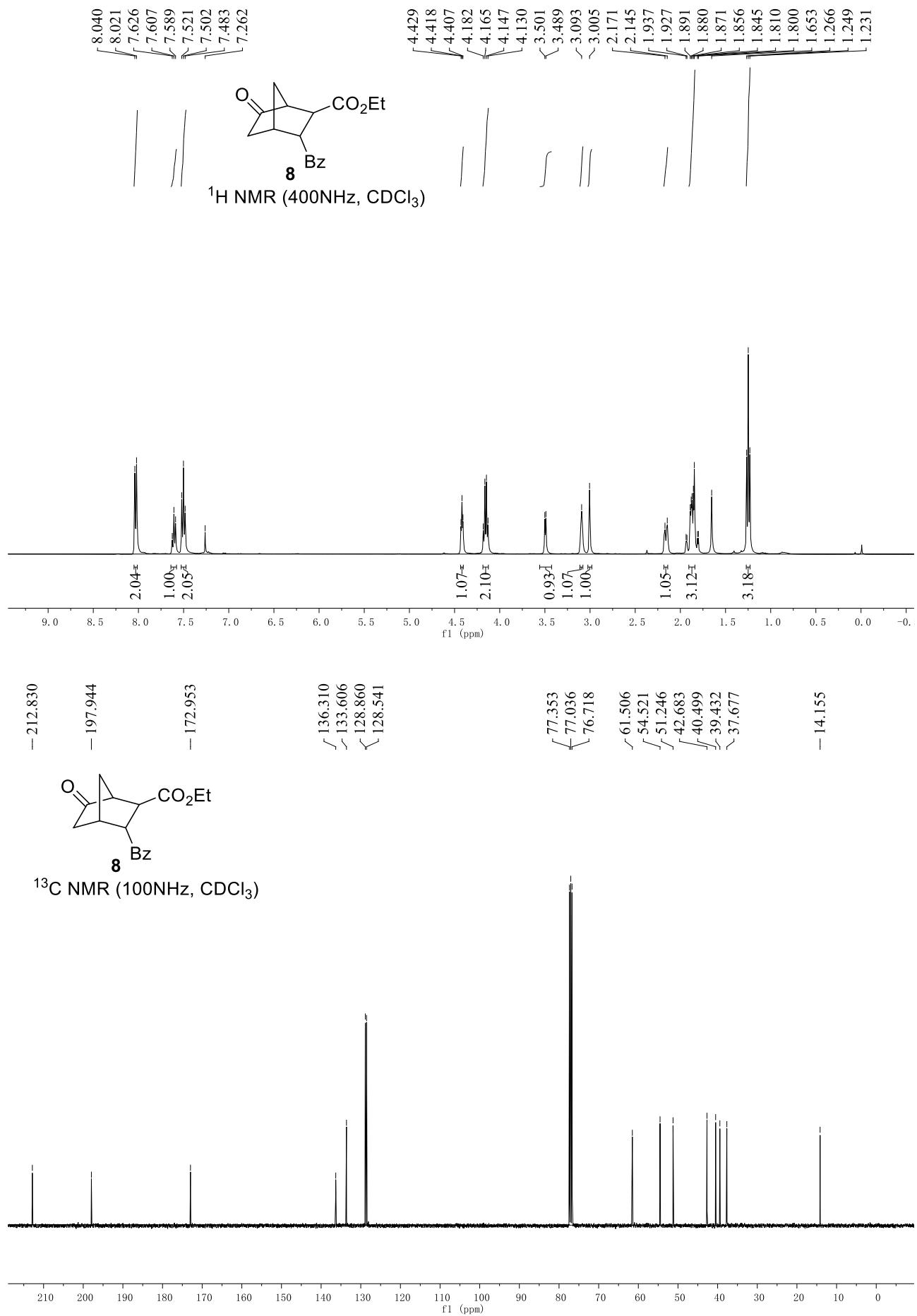
Ret Time [min]	Peak Type	Width [min]	Height [mAU]	Area [mAU*s]	Area [%]
10.506	BV	0.22	33.2222	473.8345	3.9218
11.235	VBA	0.22	811.3027	11608.3682	96.0782
Totals:			12082.2027	100.0000	

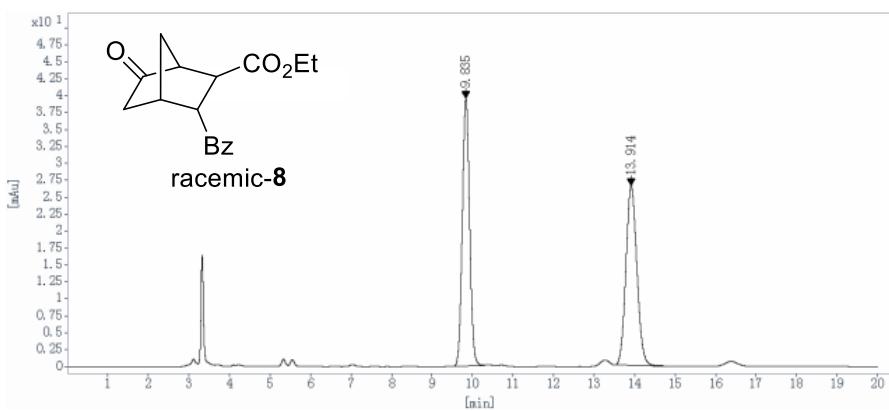


Ret Time [min]	Peak Type	Width [min]	Height [mAU]	Area [mAU*s]	Area [%]
10.458	BV	0.21	1314.5874	17988.1777	97.0229
11.296	VB	0.22	38.3837	551.9637	2.9771
Totals:			18540.1415	100.0000	

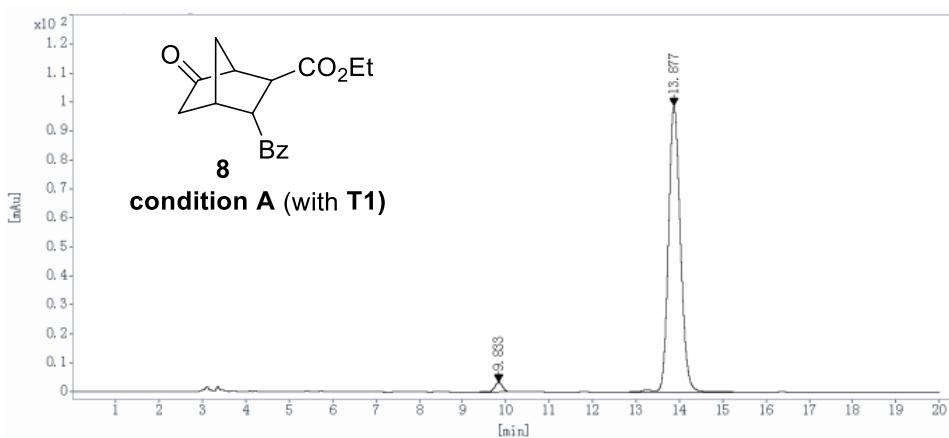


Ret Time [min]	Peak Type	Width [min]	Height [mAU]	Area [mAU*s]	Area [%]
10.466	BV	0.21	669.7605	9229.6680	88.3728
11.278	VB	0.23	80.3449	1214.3448	11.6272
Totals:			10444.0128	100.0000	

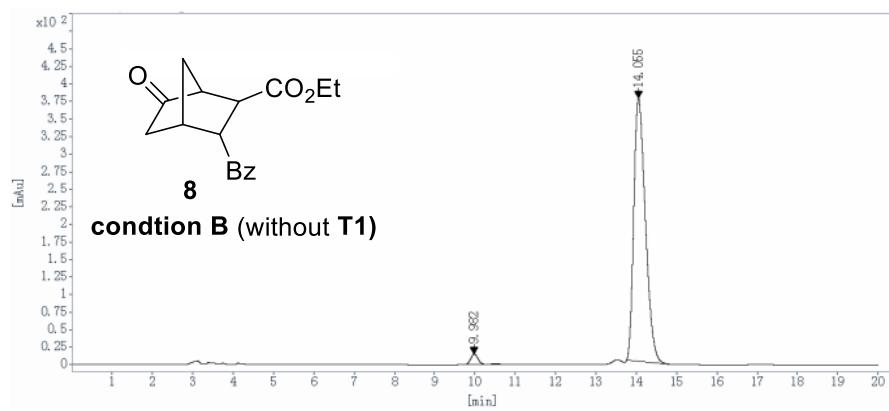




Ret Time [min]	Peak Type	Width [min]	Height [mAU]	Area [mAU*s]	Area [%]
9.835	BB	0.19	39.4440	489.9626	49.6021
13.914	BB	0.29	26.4938	497.8226	50.3979
Totals:					987.7852 100.0000



Ret Time [min]	Peak Type	Width [min]	Height [mAU]	Area [mAU*s]	Area [%]
9.833	BB	0.19	3.3774	42.5247	2.1989
13.877	VB R	0.30	98.6214	1891.4156	97.8011
Totals:					1933.9403 100.0000



Ret Time [min]	Peak Type	Width [min]	Height [mAU]	Area [mAU*s]	Area [%]
9.982	BV R	0.21	15.2291	211.8939	2.7517
14.055	BB	0.31	373.9328	7488.5815	97.2483
Totals:					7700.4754 100.0000

