An Asymmetric Dehydrogenative Diels–Alder Reaction for the Synthesis of Chiral Tetrahydrocarbazole Derivatives

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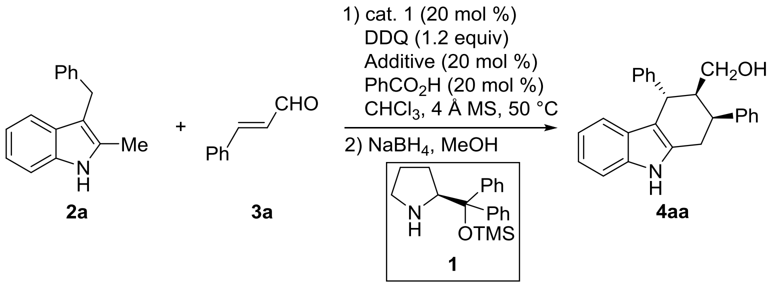
1. General Data

NMR spectra were recorded on Aglient-600 MHz or Brucker-400 MHz spectrometer. Mass spectra were recorded on a Thermo LTQ Orbitrap XL (ESI+) or a P-SIMS-Gly of Brucker DaltonicsInc (EI+). HPLC analysis was performed on waters 2489、2487 and Agilent 1200 (UV detection monitored at 254nm). Chiralpak OD-H, AD-H, columns were purchased from Daicel Chemical Industries, LTD. Optical rotations were measured on Perkin Elmer Model 343 Polarimeter. UV detection was monitored at 220 nm. 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. All chemicals were used without purification as commercially available unless otherwise noted. Indole substrates were prepared according to the literature procedures[1,2]. Cinnamic aldehyde substrates were prepared according to the literature procedures[3]. α,α-Diarylprolinol ethers were synthesized according to the literature procedures[4].

[1] L.-L. Cao, D.-S. Wang, G.-F. Jiang, Y.-G. Zhou, *Tetrahedron Lett.* **2011**, *52*, 2837-2839.
[2] S. L. Zhang, Z. L. Yu, *Org. Biomol. Chem.* **2016**, *14*, 10511-10515.
[3] A. Schmidt, G. Hilt, *Org. Lett.* **2013**, *15*, 2708-2711.
[4] M. Marigo, T. C. Wabnitz, D. Fielenbach, K. A. Jorgensen, *Angew. Chem. Int. Ed.* **2005**, *44*, 794-797.

2. Screening of palladium species and oxophilic Lewis acids

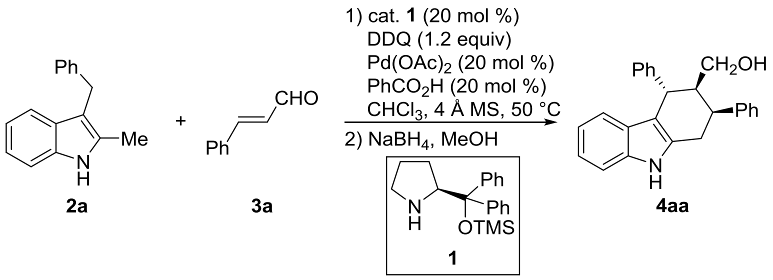


entry	additive	yield(%)	dr	ee
1	$Pd(OAc)_2$	70	>10:1	98
2	$PdCl_2$	11	>10:1	ND
3	$Pd(PPh_3)_4$	51	>10:1	93
4	$Pd(acac)_2$	60	>10:1	99
5	$Pd_2(dba)_3$	57	>10:1	80
6	SingaCyCle(TM)-A1	18	>10:1	96
7	$AlCl_3$	33	>10:1	98
8	$BF_3·Et_2O$	trace		

Reaction conditions: **2a** (0.15 mmol), **3a** (0.3 mmol), benzoic acid (0.03 mmol), catalyst **1** (0.03 mmol), **Additive** (0.03 mmol)**,** DDQ (0.18 mmol), 4 Å MS (50 mg) in $CHCl_3$ (1.0 mL) under N_2 at 50 °C for 72 h.

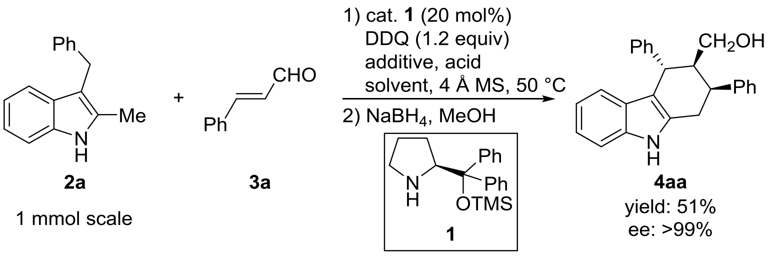
Several palladium species were screened. $Pd(OAc)_2$ performed better than other species (entry 1 vs entries 2-6). $AlCl_3$ could improve the diastereoselectivity to >10:1 and maintian the enantioselectivity, however the yield decreased to 33%. When $BF_3·Et_2O$ was added to the reaction system, there is no obvious product and the starting material **2a** decomposed.

3. General procedure for the asymmetric synthesis of tetrahydrocarbazoles



3-Benzyl-2-methyl-1H-indole **2a** (33 mg, 0.15 mmol), DDQ (41 mg, 0.18 mmol), $PhCO_2H$ (3.7 mg, 0.03 mmol), $Pd(OAc)_2$ (7.3 mg, 0.03 mmol), 4 Å (50 mg) and catalyst **1** (9.8 mg, 0.03 mmol) were added in an oven-dried Schlenk tube. The tube was then sealed, evacuated, and backfilled with nitrogen using standard Schlenk technique. $CHCl_3$ (1 mL) and Cinnamic aldehyde (40 mg, 0.3 mmol), were sequentially added by syringe at ambient temperature. The resulting mixture was heated to 50 °C (oil bath) for 72 hours. Solvents were evaporated under reduced pressure. The residue was directed purified by column chromatography on silica gel (petroleum ether/EtOAc = 30/1 to 20/1) to afford crude aldehyde compound. The D-A product was dissolved in MeOH, then $NaBH_4$ (1.2 equiv.) was added. After the reaction was completed (monitored by TLC), the solvent was evaporated and the residue was purified by column chromatography on silica gel (petroleum ether/EtOAc=8/1 to 5/1) to afford separable pure product **4aa**.

4. 1 mmol-scale reaction of 2a with 3a

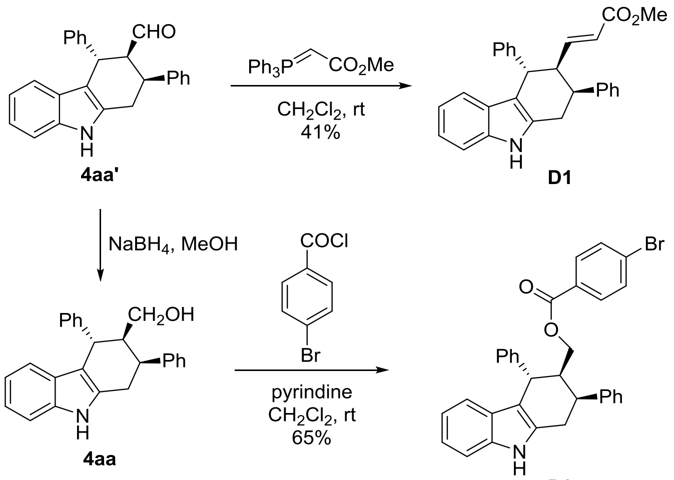


A 1 mmol scale reaction of **2a** with **3a** was performed smoothly to give the product in slightly decreased yield (51%) and excellent enatioselectivity (>99% ee).

3-Benzyl-2-methyl-1H-indole **2a** (221 mg, 1.0 mmol), DDQ (272 mg, 1.2 mmol), $PhCO_2H$ (22.4 mg, 0.2 mmol), $Pd(OAc)_2$ (44.8 mg, 0.2 mmol), 4 Å (350 mg) and catalyst **1** (65 mg, 0.2 mmol) were added in an oven-dried Schlenk tube. The tube was then sealed, evacuated, and backfilled with nitrogen using standard Schlenk technique. $CHCl_3$ (7 mL) and Cinnamic aldehyde (264 mg, 2.0 mmol), were sequentially added by syringe at ambient temperature. The resulting mixture was heated to 50 °C (oil bath) for 72 hours. Solvents were evaporated under reduced pressure. The residue was directed purified by column chromatography on silica gel (petroleum ether/EtOAc = 30/1 to 20/1) to afford crude aldehyde compound. The D-A product was dissolved in MeOH, then $NaBH_4$ (1.2 equiv.) was added. After the reaction was completed (monitored by TLC), the solvent was evaporated and the residue was purified by column chromatography on silica gel (petroleum ether/EtOAc=8/1 to 5/1) to afford separable pure product **4aa**.

5. Product derivatization

Diversity-oriented derivatization of the cycloaddition products was conducted. A Wittig reaction of unstable **4aa'** with methyl (triphenylphosphoranylidene) acetate gave the E-selective unsaturated ester **D1**. In the presence of 4-bromobenzoyl chloride and pyridine, esterification of **4aa** afforded the **D2** in 65% yield (Scheme 4).

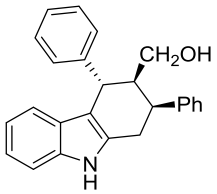


(2R,3R,4R)-2,4-diphenyl-2,3,4,9-tetrahydro-1H-carbazole-3-carbaldehyde (**4aa'**) (52 mg, 0.15 mmol) was dissolved in CH_2Cl_2 (1 mL), then $Ph_3P=CHCO_2Me$ (100 mg, 2.0 equiv) was added. After the reaction was completed (monitored by TLC), the solvent was evaporated and the residue was purified by column chromatography on silica gel to afford separable pure product **D1** (25 mg, 41% yield).

((2R,3R,4R)-2,4-diphenyl-2,3,4,9-tetrahydro-1H-carbazol-3-yl)methanol (**4aa**) (67 mg, 0.2 mmol), pyridine (79 mg, 5.0 equiv) and DMAP (2.4 mg, 0.1 equiv) was dissolved in toluene, then 4-bromobenzoyl chloride (131.4 mg, 3.0 equiv) was added. The reaction was stirred at 50 °C After the reaction was completed (monitored by TLC), the mixture was cooled to room temperature and extracted with dichloromethane. Then, the combined organic layer was dried by anhydrous sodium sulfate. After concentration under vacuum, the crude product was purified by flash chromatography on silica gel to afford the product **D2** (70 mg, 41% yield).

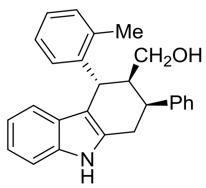
6. Characterization Data for the Products

((2S,3S,4S)-2,4-diphenyl-2,3,4,9-tetrahydro-1H-carbazol-3-yl)methanol (4aa)



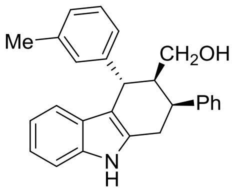
4aa (39 mg) was obtained as a white semisolid in 74% yield after flash chromatography and the enantiomeric excess was determined to be 99% by HPLC analysis on Chiralpak AD-H column (20% 2-propanol/n-hexane, 1 mL/min), UV 254 nm, t (major) = 10.52 min, t (minor) = 15.54 min; $[\alpha]_D^{20}$ = +12.0 (c 0.05, $CHCl_3$); ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.91 (s, 1H), 7.34 – 7.17 (m, 9H), 7.16 – 7.06 (m, 3H), 6.88 (m, 1H), 6.81 (d, *J* = 7.8 Hz, 1H), 4.12 (d, *J* = 4.4 Hz, 1H), 3.62 (dd, *J* = 3.2 Hz, 1H), 3.54 (dd, *J* = 10.5, 6.8 Hz, 1H), 3.47 (dd, *J* = 10.4, 6.8 Hz, 1H), 3.23 (dd, *J* = 16.5, 5.9 Hz, 1H), 3.08 (dd, *J* = 16.5, 6.8 Hz, 1H), 2.46 – 2.37 (m, 1H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 144.46, 142.54, 136.44, 134.25, 128.76, 128.48, 128.37, 128.12, 127.43, 126.64, 126.33, 121.29, 119.29, 119.21, 111.21, 110.51, 61.69, 50.89, 39.97, 37.94, 26.65. HRMS (ESI) m/z $(M+H)^+$ calculated for $C_{25}H_{24}NO$: 354.1858, observed: 354.1858.

((2S,3S,4S)-2-phenyl-4-(o-tolyl)-2,3,4,9-tetrahydro-1H-carbazol-3-yl)methanol (4ba)



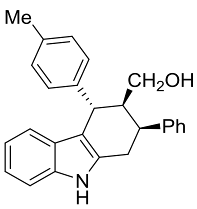
4ba (36 mg) was obtained as a white semisolid in 66% yield after flash chromatography and the enantiomeric excess was determined to be 94% by HPLC analysis on Chiralpak AD-H column (15% 2-propanol/n-hexane, 1 mL/min), UV 254 nm, t (major) = 23.17 min, t (minor) = 9.83 min; $[\alpha]_D^{20}$ = +4.3 (c 0.054, $CHCl_3$); ^{1}H NMR (600 MHz, $CDCl_3$) δ 7.93 (s, 1H), 7.33 (d, *J* = 8.1 Hz, 1H), 7.28-7.24 (m, 2H), 7.22-7.20 (m, 4H), 7.11 (m, 3H), 7.04 (t, *J* = 7.4 Hz, 1H), 6.88 (t, *J* = 7.5 Hz, 1H), 6.77 (d, *J* = 7.9 Hz, 1H), 4.51 (d, *J* = 5.2 Hz, 1H), 3.66 (q, *J* = 6.2 Hz, 1H), 3.56 (dd, *J* = 11.5, 5.4 Hz, 1H), 3.46 (dd, *J* = 11.5, 6.3 Hz, 1H), 3.27 (dd, *J* = 16.8, 5.8 Hz, 1H), 3.09 (dd, *J* = 16.9, 5.8 Hz, 1H), 2.65 – 2.57 (m, 1H), 2.40 (s, 3H). ^{13}C NMR (151 MHz, $CDCl_3$) δ 146.90, 142.46, 138.87, 136.30, 133.40, 132.36, 131.26, 130.11, 129.69, 129.15, 129.03, 128.45, 123.85, 122.23, 121.70, 114.47, 113.11, 66.10, 49.47, 42.15, 37.85, 22.37. HRMS (ESI) m/z $(M+H)^+$ calculated for $C_{26}H_{26}NO$: 368.2009, observed: 368.2007.

((2S,3S,4S)-2-phenyl-4-(m-tolyl)-2,3,4,9-tetrahydro-1H-carbazol-3-yl)methanol (4ca)



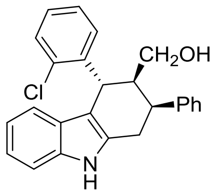
4ca (39 mg) was obtained as a white semisolid in 72% yield after flash chromatography and the enantiomeric excess was determined to be 98% by HPLC analysis on Chiralpak OD-H column (15% 2-propanol/n-hexane, 1 mL/min), UV 254 nm, t (major) = 10.54min, t (minor) = 18.43 min; $[\alpha]_D^{20}$ = +13.9 (c 0.122, $CHCl_3$); ^{1}H NMR (600 MHz, $CDCl_3$) δ 7.93 (s, 1H), 7.34 (d, *J* = 8.1 Hz, 1H), 7.27 – 7.21 (m, 3H), 7.15 (t, *J* = 7.3 Hz, 3H), 7.10 (t, *J* = 7.5 Hz, 1H), 7.04 (d, *J* = 9.6 Hz, 2H), 6.98 (d, *J* = 7.5 Hz, 1H), 6.89 (t, *J* = 7.4 Hz, 1H), 6.84 (d, *J* = 7.2 Hz, 1H), 4.08 (brs, 1H), 3.65-3.63 (m, 1H), 3.56-3.53 (m, 1H), 3.51 – 3.46 (m, 1H), 3.28 (dd, *J* = 16.4, 5.6 Hz, 1H), 3.11 (dd, *J* = 16.4, 6.6 Hz, 1H), 2.47 – 2.38 (m, 1H), 2.29 (s, 3H). ^{13}C NMR (151 MHz, $CDCl_3$) δ 147.01, 145.19, 140.46, 139.05, 136.80, 132.06, 131.09, 130.83, 130.77, 130.12, 129.77, 129.25, 128.49, 123.85, 121.93, 121.88, 113.10, 64.45, 53.41, 42.61, 40.60, 32.40, 24.21. HRMS (ESI) m/z $(M+H)^+$ calculated for $C_{26}H_{26}NO$: 368.2009, observed: 368.2012.

((2S,3S,4S)-2-phenyl-4-(p-tolyl)-2,3,4,9-tetrahydro-1H-carbazol-3-yl)methanol (4da)



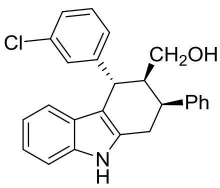
4da (37 mg) was obtained as a white semisolid in 67% yield after flash chromatography and the enantiomeric excess was determined to be 91% by HPLC analysis on Chiralpak OD-H column (15% 2-propanol/n-hexane, 1 mL/min), UV 254 nm, t (major) = 12.39 min, t (minor) = 17.52 min; $[\alpha]_D^{20}$ = +12.5 (c 0.08, $CHCl_3$); ^{1}H NMR (600 MHz, $CDCl_3$) δ 7.92 (s, 1H), 7.33 (d, *J* = 8.1 Hz, 1H), 7.28 – 7.19 (m, 3H), 7.16 (d, *J* = 7.2 Hz, 2H), 7.12 – 7.06 (m, 5H), 6.90 (t, *J* = 7.4 Hz, 1H), 6.85 (d, *J* = 7.6 Hz, 1H), 4.10 (brs, 1H), 3.63-3.62 (m, 1H), 3.57 (dd, J = 10.7, 6.7 Hz, 1H), 3.49 (dd, J = 10.6, 6.7 Hz, 1H), 3.26 (dd, *J* = 16.4, 5.6 Hz, 1H), 3.11 (dd, *J* = 16.4, 6.8 Hz, 1H), 2.41-2.37 (m, 1H), 2.33 (s, 3H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 142.60, 141.31, 136.42, 135.71, 134.15, 129.06, 128.58, 128.43, 128.11, 127.49, 126.58, 121.24, 119.26, 119.25, 110.45, 61.82, 50.91, 39.58, 37.99, 21.11. HRMS (ESI) m/z $(M+H)^+$ calculated for $C_{26}H_{26}NO$: 368.2009, observed: 368.2004.

((2S,3S,4R)-4-(2-chlorophenyl)-2-phenyl-2,3,4,9-tetrahydro-1H-carbazol-3-yl)methanol (4ea)



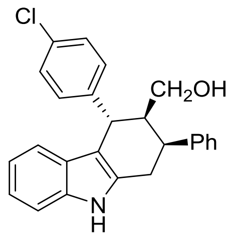
4ea (41 mg) was obtained as a white solid in 71% yield after flash chromatography and the enantiomeric excess was determined to be more than 99% by HPLC analysis on Chiralpak OD-H column (15% 2-propanol/n-hexane, 1 mL/min), UV 254 nm, t (major) = 27.14 min, t (minor) = 16.42 min; $[\alpha]_D^{20}$ = +5.71 (c 0.07, $CHCl_3$); ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.89 (s, 1H), 7.44-7.42 (m, 1H), 7.34 – 7.28 (m, 3H), 7.28 – 7.22 (m, 3H), 7.21 – 7.06 (m, 4H), 6.94 (m, 2H), 5.02 (d, *J* = 5.5 Hz, 1H), 3.56-3.55 (m, 1H), 3.48 -3.46(m, 1H), 3.31 (dd, *J* = 11.9, 6.5 Hz, 1H), 3.25 (d, *J* = 5.8 Hz, 1H), 3.13 (dd, *J* = 16.8, 8.1 Hz, 1H), 2.77 m, 1H). ^{13}C NMR (151 MHz, $CDCl_3$) δ 146.46, 142.19, 138.88, 136.55, 136.47, 134.22, 132.35, 131.37, 130.44, 130.32, 129.40, 129.37, 129.31, 124.12, 121.99, 121.61, 114.29, 113.11, 65.79, 49.18, 41.81, 38.50. HRMS (ESI) m/z $(M+H)^+$ calculated for $C_{25}H_{23}ClNO$: 388.1463, observed: 388.1465.

((2S,3S,4S)-4-(3-chlorophenyl)-2-phenyl-2,3,4,9-tetrahydro-1H-carbazol-3-yl)methanol (4fa)



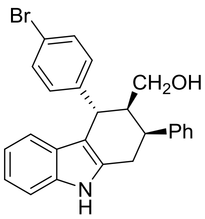
4fa (39 mg) was obtained as a white semisolid in 68% yield after flash chromatography and the enantiomeric excess was determined to be 99% by HPLC analysis on Chiralpak OD-H column (15% 2-propanol/n-hexane, 1 mL/min), UV 254 nm, t (major) = 11.52min, t (minor) = 22.46 min; $[\alpha]_D^{20}$ = +13.0 (c 0.10, $CHCl_3$); ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.93 (s, 1H), 7.33 (d, *J* = 8.1 Hz, 1H), 7.30 – 7.16 (m, 6H), 7.13-7.10 (m, 4H), 6.97 – 6.79 (m, 2H), 4.17 (brs, 1H), 3.59-3.57 (m, 1H), 3.56 – 3.44 (m, 2H), 3.21 (dd, *J* = 16.4, 5.8 Hz, 1H), 3.08 (dd, *J* = 16.5, 7.4 Hz, 1H), 2.44 – 2.30 (m, 1H). ^{13}C NMR (151 MHz, $CDCl_3$) δ 149.53, 144.88, 139.06, 137.03, 136.83, 132.26, 131.35, 131.16, 130.65, 129.85, 129.63, 129.36, 129.24, 124.10, 122.09, 121.62, 113.23, 63.89, 53.52, 42.31, 40.35, 32.39. HRMS (ESI) m/z $(M+H)^+$ calculated for $C_{25}H_{23}ClNO$: 388.1463, observed: 388.1461.

((2S,3S,4S)-4-(4-chlorophenyl)-2-phenyl-2,3,4,9-tetrahydro-1H-carbazol-3-yl)methanol (4ga)



4ga (42 mg) was obtained as a white semisolid in 73% yield after flash chromatography and the enantiomeric excess was determined to be 99% by HPLC analysis on Chiralpak OD-H column (15% 2-propanol/n-hexane, 1 mL/min), UV 254 nm, t (major) = 12.73 min, t (minor) = 24.99 min; $[\alpha]_D^{20}$ = +14.9 (c 0.134, $CHCl_3$); ^{1}H NMR (600 MHz, $CDCl_3$) δ 7.97 (s, 1H), 7.35 (d, *J* = 8.1 Hz, 1H), 7.31 – 7.20 (m, 5H), 7.17 – 7.12 (m, 5H), 6.94 (t, *J* = 7.4 Hz, 1H), 6.86 (d, *J* = 6.9 Hz, 1H), 4.18 (brs, 1H), 3.59-3.58 (m, 1H), 3.55-3.53 (m, 1H), 3.52 – 3.47 (m, 1H), 3.23 (dd, *J* = 16.2, 5.1 Hz, 1H), 3.11 (dd, *J* = 16.4, 7.3 Hz, 1H), 2.40 – 2.31 (m, 1H). ^{13}C NMR (151 MHz, $CDCl_3$) δ 145.76, 144.98, 139.09, 136.98, 134.57, 132.69, 131.16, 131.12, 130.64, 129.89, 129.35, 124.10, 122.08, 121.65, 113.22, 63.96, 53.66, 41.96, 40.47. HRMS (ESI) m/z $(M+H)^+$ calculated for $C_{25}H_{23}ClNO$: 388.1463, observed: 388.1465.

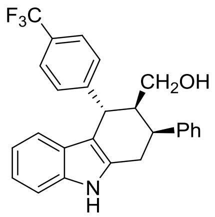
((2S,3S,4S)-4-(4-bromophenyl)-2-phenyl-2,3,4,9-tetrahydro-1H-carbazol-3-yl)methanol (4ha)



4ha (37 mg) was obtained as a white solid in 57% yield after flash chromatography and the enantiomeric excess was determined to be 94% by HPLC analysis on Chiralpak OD-H column (15% 2-propanol/n-hexane, 1 mL/min), UV 254 nm, t (major) = 14.08 min, t (minor) = 26.22 min; $[\alpha]_D^{20}$ = +23.0 (c 0.018, $CHCl_3$); ^{1}H NMR (600 MHz, $CDCl_3$) δ 7.94 (s, 1H), 7.40 (d, *J* = 8.3 Hz, 2H), 7.34 (d, *J* = 8.1 Hz, 1H), 7.27-7.25 (m, 2H), 7.22-7.20 (m, 1H), 7.13-7.12 (m, 3H), 7.09 (d, *J* = 8.3 Hz, 2H), 6.93 (t, *J* = 7.4 Hz, 1H), 6.86 -6.84(m, 1H), 4.17 (brs, 1H), 3.62 – 3.53 (m, 2H), 3.50-3.48 (m, 1H), 3.22 (dd, *J* = 16.5, 5.7 Hz, 1H), 3.11 (dd, *J* = 16.4, 7.4 Hz, 1H), 2.39 – 2.34 (m, 1H).

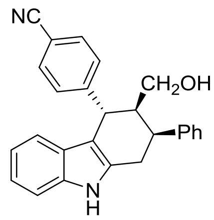
^{13}C NMR (151 MHz, $CDCl_3$) δ 146.29, 144.94, 139.08, 136.97, 134.06, 133.10, 131.15, 130.62, 129.86, 129.34, 124.11, 122.68, 122.09, 121.64, 113.20, 63.94, 53.62, 42.01, 40.46. HRMS (ESI) m/z $(M+H)^+$ calculated for $C_{25}H_{23}BrNO$: 432.0958, observed: 432.0960.

((2S,3S,4S)-2-phenyl-4-(4-(trifluoromethyl)phenyl)-2,3,4,9-tetrahydro-1H-carbazol-3-yl)methanol (4ia)



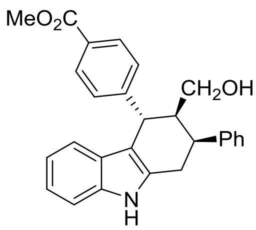
4ia (35 mg) was obtained as a white semisolid in 56% yield after flash chromatography and the enantiomeric excess was determined to be 99% by HPLC analysis on Chiralpak OD-H column (15% 2-propanol/n-hexane, 1 mL/min), UV 254 nm, t (major) = 10.63 min, t (minor) = 20.92 min; $[\alpha]_D^{20}$ = -11.5 (c 0.104, $CHCl_3$); ^1H NMR (600 MHz, $CDCl_3$) δ 7.98 (s, 1H), 7.54 (d, *J* = 8.1 Hz, 2H), 7.35 (dd, *J* = 13.9, 8.1 Hz, 3H), 7.31 – 7.21 (m,3H), 7.14 (m, 3H), 6.94 (t, *J* = 7.5 Hz, 1H), 6.84-6.81 (m, 1H), 4.31 (brs, 1H), 3.63 – 3.48 (m, 3H), 3.24 (dd, *J* = 16.4, 5.7 Hz, 1H), 3.13 (dd, *J* = 16.4, 7.6 Hz, 1H), 2.41-2.39 (m, 1H). ^{13}C NMR (151 MHz, $CDCl_3$) δ 151.50, 144.80, 139.07, 137.10, 131.65, 131.20, 130.60, 129.77, 129.42, 127.95 (q, *J* = 7.5, 3.8 Hz), 126.11, 124.20, 122.15, 121.51, 113.28, 63.76, 53.60, 42.34, 40.40, 32.38. HRMS (ESI) m/z $(M+H)^+$ calculated for $C_{26}H_{23}F_3NO$: 422.1726, observed: 422.1723.

4-((2S,3S,4S)-3-(hydroxymethyl)-2-phenyl-2,3,4,9-tetrahydro-1H-carbazol-4-yl)benzonitrile (4ja)



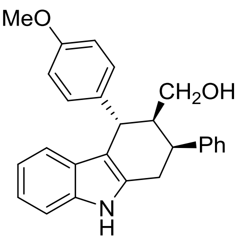
4ja (34 mg) was obtained as a white semisolid in 60% yield after flash chromatography and the enantiomeric excess was determined to be 99% by HPLC analysis on Chiralpak OD-H column (15% 2-propanol/n-hexane, 1 mL/min), UV 254 nm, t (major) = 18.15 min, t (minor) = 37.80 min; $[\alpha]_D^{20}$ = -28.3 (c 0.06, $CHCl_3$); ^1H NMR (400 MHz, $CDCl_3$) δ 7.98 (s, 1H), 7.49 (d, *J* = 8.1 Hz, 2H), 7.27-7.24 (m, 2H), 7.22 – 7.13 (m, 4H), 7.06-7.00 (m, 3H), 6.86 (t, *J* = 7.4 Hz, 1H), 6.73 (d, *J* = 7.8 Hz, 1H), 4.25 (brs, 1H), 3.45 (d, *J* = 6.3 Hz, 3H), 3.15 (dd, *J* = 16.5, 5.7 Hz, 1H), 3.05 (dd, *J* = 16.4, 7.9 Hz, 1H), 2.30 -2.28(m, 1H). ^{13}C NMR (151 MHz, $CDCl_3$) δ 153.23, 144.62, 139.09, 137.19, 134.86, 132.15, 131.23, 130.50, 129.64, 129.47, 124.33, 122.25, 121.73, 121.30, 113.34, 112.81, 63.60, 53.60, 42.64, 40.47, 34.26, 32.31. HRMS (ESI) m/z $(M+H)^+$ calculated for $C_{26}H_{23}N_2O$: 379.1805, observed: 379.1807.

methyl4-((2S,3S,4S)-3-(hydroxymethyl)-2-phenyl-2,3,4,9-tetrahydro-1H-carbazol -4-yl)benzoate (4ka)



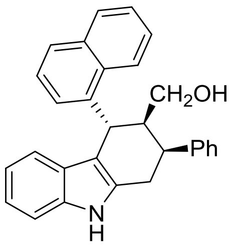
4ka (34 mg) was obtained as a white semisolid in 56% yield after flash chromatography and the enantiomeric excess was determined to be 98% by HPLC analysis on Chiralpak OD-H column (15% 2-propanol/n-hexane, 1 mL/min), UV 254 nm, t (major) = 18.83 min, t (minor) = 31.19 min; $[\alpha]_D^{20}$ = +15.2 (c 0.021, $CHCl_3$); ^{1}H NMR (600 MHz, $CDCl_3$) δ 7.97 (s, 1H), 7.87 (d, *J* = 8.2 Hz, 2H), 7.27 (d, *J* = 8.1 Hz, 1H), 7.20 (d, *J* = 8.1 Hz, 2H), 7.18 – 7.11 (m, 3H), 7.07 – 6.99 (m, 3H), 6.85 – 6.77 (m, 1H), 6.72-6.70 (m, 1H), 4.16 (brs, 1H), 3.82 (s, 3H), 3.51 -3.49(m, 1H), 3.45-3.42 (m, 1H), 3.42 – 3.38 (m, 1H), 3.14 (dd, *J* = 16.2, 4.9 Hz, 1H), 3.02 (dd, *J* = 16.4, 7.3 Hz, 1H), 2.36 – 2.26 (m, 1H).^{13}C NMR (151 MHz, $CDCl_3$) δ 169.94, 152.96, 144.86, 139.05, 137.08, 132.38, 131.46, 131.16, 130.88, 130.67, 129.81, 129.37, 124.09, 122.06, 121.56, 113.27, 63.84, 54.75, 53.48, 42.56, 40.45. HRMS (ESI) m/z $(M+H)^+$ calculated for $C_{27}H_{26}NO_3$: 412.1907, observed: 412.1904.

((2S,3S,4S)-4-(4-methoxyphenyl)-2-phenyl-2,3,4,9-tetrahydro-1H-carbazol-3-yl) methanol (4la)



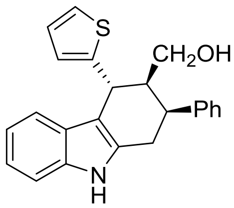
4la (30 mg) was obtained as a white semisolid in 53% yield after flash chromatography and the enantiomeric excess was determined to be more than 99% by HPLC analysis on Chiralpak OD-H column (15% 2-propanol/n-hexane, 1 mL/min), UV 254 nm, t (major) = 19.73 min, t (minor) = 26.52 min; $[\alpha]_D^{20}$ = +2.9 (c 0.138, $CHCl_3$); ^{1}H NMR (600 MHz, $CDCl_3$) δ 7.93 (s, 1H), 7.33 (d, *J* = 8.1 Hz, 1H), 7.28 – 7.20 (m, 3H), 7.16 (d, *J* = 7.0 Hz, 2H), 7.14 – 7.08 (m, 3H), 6.90 (t, *J* = 7.4 Hz, 1H), 6.86-6.84 (m, 1H), 6.82 (d, *J* = 8.7 Hz, 2H), 4.08 (brs, 1H), 3.79 (s, 3H), 3.65-3.62 (m, 1H), 3.57 (dd, *J* = 10.7, 6.6 Hz, 1H), 3.48-3.35 (m, 1H), 3.26 (dd, J = 16.3, 5.7 Hz, 1H), 3.10 (dd, J = 16.4, 6.7 Hz, 1H), 2.39-2.37 (m, 1H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 158.03, 142.60, 136.43, 134.12, 129.61, 128.45, 128.11, 127.46, 126.60, 121.25, 119.28, 119.27, 113.71, 110.47, 61.81, 55.23, 50.96, 39.13, 38.01. HRMS (ESI) m/z $(M+H)^+$ calculated for $C_{26}H_{26}NO_2$: 384.1958, observed: 384.1960.

((2S,3S,4S)-4-(naphthalen-1-yl)-2-phenyl-2,3,4,9-tetrahydro-1H-carbazol-3-yl)methanol (4ma)



4ma (23 mg) was obtained as a white solid in 38% yield after flash chromatography and the enantiomeric excess was determined to be 98% by HPLC analysis on Chiralpak OD-H column (15% 2-propanol/n-hexane, 1 mL/min), UV 254 nm, t (major) = 31.72 min, t (minor) = 25.21 min; $[\alpha]_D^{20}$ = -33.0 (c 0.1, $CHCl_3$); ^{1}H NMR (600 MHz, $CDCl_3$) δ 8.20 (d, J = 7.7 Hz, 1H), 7.93-7.90 (m, 2H), 7.81 – 7.70 (m, 1H), 7.57 – 7.47 (m, 2H), 7.37 – 7.29 (m, 5H), 7.27-7.24 (m, 3H), 7.08 (t, J = 7.5 Hz, 1H), 6.81 (t, J = 7.5 Hz, 1H), 6.74 (d, J = 7.9 Hz, 1H), 5.23 (d, J = 5.1 Hz, 1H), 3.70-3.68 (m, 1H), 3.43 (q, J = 11.5, 6.0 Hz, 1H), 3.33 (dd, J = 16.9, 5.8 Hz, 1H), 3.20 (dd, J = 11.4, 6.8 Hz, 1H), 3.15 (dd, J = 16.9, 6.1 Hz, 1H), 2.85 – 2.79 (m, 1H). ^{13}C NMR (151 MHz, $CDCl_3$) δ 146.89, 140.07, 138.99, 136.72, 134.71, 131.77, 131.33, 130.20, 130.12, 129.81, 129.67, 129.24, 128.84, 128.12, 127.82, 125.73, 123.90, 122.35, 121.70, 114.47, 113.09, 65.74, 49.89, 41.76, 36.63. HRMS (ESI) m/z $(M+H)^+$ calculated for $C_{29}H_{26}NO$: 404.2009, observed: 404.2006.

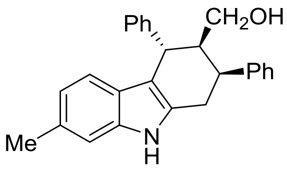
((2S,3S,4R)-2-phenyl-4-(thiophen-2-yl)-2,3,4,9-tetrahydro-1H-carbazol-3-yl)methanol (4na)



4na (27 mg) was obtained as a white semisolid in 51% yield after flash chromatography and the enantiomeric excess was determined to be 99% by HPLC analysis on Chiralpak OD-H column (15% 2-propanol/n-hexane, 1 mL/min), UV 254 nm, t (major) = 15.37 min, t (minor) = 27.38 min; $[\alpha]_D^{20}$ = -70 (c 0.066, $CHCl_3$); ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.90 (s, 1H), 7.36 – 7.06 (m, 9H), 6.99 (t, J = 7.4 Hz, 1H), 6.95 – 6.88 (m, 1H), 6.84-6.80 (m, 1H), 4.57 (d, J = 3.5 Hz, 1H), 3.69-3.66 (m, 1H), 3.63 –

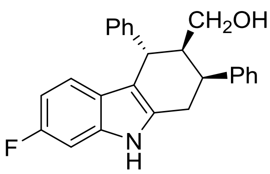
3.47 (m, 2H), 3.20 – 3.01 (m, 2H), 2.53 (s, 1H). ^{13}C NMR (151 MHz, $CDCl_3$) δ 152.03, 145.03, 138.89, 136.31, 131.16, 130.57, 130.09, 129.31, 129.16, 127.97, 126.36, 124.12, 122.16, 121.55, 113.23, 63.78, 54.40, 40.54, 38.11. HRMS (ESI) m/z $(M+H)^+$ calculated for $C_{23}H_{22}NOS$: 360.1428, observed: 360.1422.

((2S,3S,4S)-7-methyl-2,4-diphenyl-2,3,4,9-tetrahydro-1H-carbazol-3-yl)methanol (4oa)



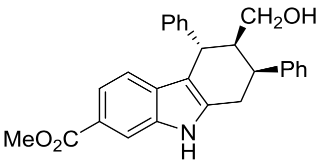
4oa (26 mg) was obtained as a white semisolid in 48% yield after flash chromatography and the enantiomeric excess was determined to be 94% by HPLC analysis on Chiralpak AD-H column (20% 2-propanol/n-hexane, 1 mL/min), UV 254 nm, t (major) = 16.03 min, t (minor) = 27.46 min; $[\alpha]_D^{20}$ = +8.3 (c 0.036, $CHCl_3$); ^{1}H NMR (600 MHz, DMSO) δ 10.74 (s, 1H), 7.24-7.22 (m, 4H), 7.16-7.15 (m, 2H), 7.11 (d, *J* = 7.3 Hz, 2H), 7.09 – 7.05 (m, 3H), 6.56 (s, 2H), 4.53 (t, *J* = 5.0 Hz, 1H), 3.44 (d, 1H), 3.34 (s, 3H), 3.23-3.22 (m, 2H), 3.11 – 3.00 (m, 2H), 2.20 (d, J = 3.2 Hz, 1H).^{13}C NMR (151 MHz, DMSO) δ 148.73, 146.05, 140.01, 137.34, 132.14, 131.40, 131.23, 131.15, 130.91, 129.21, 128.92, 128.09, 122.78, 120.77, 113.85, 82.29, 61.58, 39.89, 24.48. HRMS (ESI) m/z $(M+H)^+$ calculated for $C_{26}H_{26}NO$: 368.2011, observed: 368.2013.

((2S,3S,4S)-7-fluoro-2,4-diphenyl-2,3,4,9-tetrahydro-1H-carbazol-3-yl)methanol (4pa)



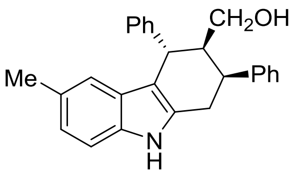
4pa (30 mg) was obtained as a white semisolid in 54% yield after flash chromatography and the enantiomeric excess was determined to be more than 99% by HPLC analysis on Chiralpak AD-H column (20% 2-propanol/n-hexane, 1 mL/min), UV 254 nm, t (major) = 10.46 min, t (minor) = 14.20 min; $[\alpha]_D^{20}$ = +8.0 (c 0.05, $CHCl_3$); ^{1}H NMR (600 MHz, $CDCl_3$) δ 7.94 (s, 1H), 7.31 – 7.21 (m, 6H), 7.19 (d, *J* = 7.4 Hz, 2H), 7.14 (d, *J* = 7.3 Hz, 2H), 7.01-7.00 (m, 1H), 6.69 -6.67(m, 1H), 6.65-6.63 (m, 1H), 4.11 (brs, 1H), 3.63-3.61 (m, 1H), 3.56-3.54 (m, 1H), 3.49-3.47 (m, 1H), 3.24 (dd, *J* = 16.2, 5.3 Hz, 1H), 3.08 (dd, *J* = 16.4, 6.7 Hz, 1H), 2.45 – 2.37 (m, 1H). ^{13}C NMR (151 MHz, $CDCl_3$) δ 162.92, 161.35, 146.86, 145.04, 137.06, 131.32, 131.08 (d, *J* = 12.2 Hz), 130.70, 129.31, 129.07, 126.58, 122.32 (d, *J* = 9.9 Hz), 110.40, 110.24, 99.86, 99.68, 64.26, 53.43, 42.50, 40.52. HRMS (ESI) m/z $(M+H)^+$ calculated for $C_{25}H_{23}FNO$: 372.1758, observed: 372.1760.

methyl(2S,3S,4S)-3-(hydroxymethyl)-2,4-diphenyl-2,3,4,9-tetrahydro-1H-carbazole-7-carboxylate (4qa)



4qa (37 mg) was obtained as a white solid in 61% yield after flash chromatography and the enantiomeric excess was determined to be 96% by HPLC analysis on Chiralpak AD-H column (20% 2-propanol/n-hexane, 1 mL/min), UV 254 nm, t (major) = 13.58 min, t (minor) = 24.55 min; $[\alpha]_D^{20}$ = -23.6 (c 0.072, $CHCl_3$); ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.37 (s, 1H), 8.10 (s, 1H), 7.58 (d, *J* = 8.4 Hz, 1H), 7.31 – 7.21 (m, 6H), 7.17-7.16 (m, 2H), 7.15 – 7.09 (m, 2H), 6.81 (d, *J* = 8.3 Hz, 1H), 4.15 (d, *J* = 5.1 Hz, 1H), 3.90 (s, 3H), 3.65 (d, *J* = 3.0 Hz, 1H), 3.52-3.50 (m, 2H), 3.28 (dd, *J* = 16.7, 5.6 Hz, 1H), 3.13 (dd, *J* = 16.7, 6.8 Hz, 1H), 2.48 – 2.37 (m, 1H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 167.33, 142.98, 141.10, 137.15, 134.70, 130.07, 127.60, 127.46, 127.40, 126.98, 125.68, 125.44, 121.72, 119.49, 117.57, 111.72, 110.86, 60.42, 50.90, 49.70, 38.69, 36.66. HRMS (ESI) m/z $(M+H)^+$ calculated for $C_{27}H_{26}NO_3$: 412.1907, observed: 412.1909.

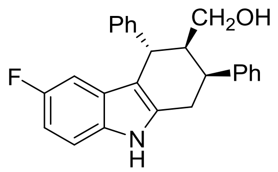
((2S,3S,4S)-6-methyl-2,4-diphenyl-2,3,4,9-tetrahydro-1H-carbazol-3-yl)methanol (4ra)



4ra (31 mg) was obtained as a white solid in 57% yield after flash chromatography and the enantiomeric excess was determined to be 99% by HPLC analysis on Chiralpak OD-H column (15% 2-propanol/n-hexane, 1 mL/min), UV 254 nm, t (major) = 12.89 min, t (minor) = 10.56 min; $[\alpha]_D^{20}$ = -12.3 (c 0.106, $CHCl_3$); ^{1}H NMR (600 MHz, $CDCl_3$) δ 7.82 (s, 1H), 7.31-7.30 (m, 2H), 7.27-7.25 (m, 3H), 7.23-7.22 (m, 4H), 7.15 (d, *J* = 7.3 Hz, 2H), 6.95 (d, *J* = 8.0 Hz, 1H), 6.69 (s, 1H), 4.20 (brs, 1H), 3.60-3.58 (m, 1H), 3.56-3.54 (m, 1H), 3.54 – 3.49 (m, 1H), 3.20 (dd, *J*

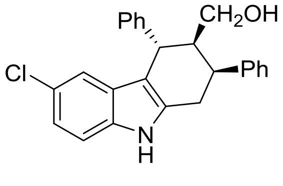
= 15.8, 4.7 Hz, 1H), 3.09 (dd, *J* = 16.3, 7.6 Hz, 1H), 2.43 (m, 1H), 2.28 (s, 3H). ^{13}C NMR (151 MHz, $CDCl_3$) δ 147.28, 145.29, 137.41, 137.04, 131.35, 131.14, 131.08, 130.97, 130.66, 130.40, 129.20, 128.86, 125.45, 121.53, 112.81, 64.26, 53.85, 42.63, 40.40, 24.07. HRMS (ESI) m/z $(M+H)^+$ calculated for $C_{26}H_{26}NO$: 368.2011, observed: 368.2014.

((2S,3S,4S)-6-fluoro-2,4-diphenyl-2,3,4,9-tetrahydro-1H-carbazol-3-yl)methanol (4sa)



4sa (29 mg) was obtained as a white solid in 53% yield after flash chromatography and the enantiomeric excess was determined to be 99% by HPLC analysis on Chiralpak AD-H column (15% 2-propanol/n-hexane, 1 mL/min), UV 254 nm, t (major) = 10.90 min, t (minor) = 21.44 min; $[\alpha]_D^{20}$ = -60.0 (c 0.02, $CHCl_3$); ^1H NMR (600 MHz, $CDCl_3$) δ 7.97 (s, 1H), 7.30-7.28 (t, *J* = 7.4 Hz, 2H), 7.27 – 7.22 (m, 5H), 7.18 (d, *J* = 7.5 Hz, 2H), 7.12 (d, *J* = 7.4 Hz, 2H), 7.05 (m, 1H), 6.80 (s, 1H), 4.12 (brs, 1H), 3.63-3.62 (m, 1H), 3.57-3.54 (m, 1H), 3.52 – 3.47 (m, 1H), 3.23 (dd, *J* = 16.4, 5.3 Hz, 1H), 3.10 (dd, *J* = 16.5, 7.1 Hz, 1H), 2.41 (m, 1H). ^{13}C NMR (151 MHz, $CDCl_3$) δ 146.59, 144.91, 138.44, 137.42, 131.24, 131.22, 131.13, 131.12, 130.62, 129.33, 129.17, 127.64, 124.17, 121.25, 114.04, 64.16, 53.55, 42.44, 40.36. HRMS (ESI) m/z $(M+H)^+$ calculated for $C_{25}H_{23}FNO$: 372.1758, observed: 372.1757.

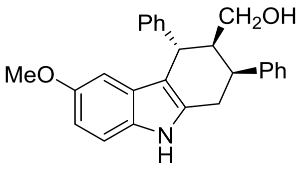
((2S,3S,4S)-6-chloro-2,4-diphenyl-2,3,4,9-tetrahydro-1H-carbazol-3-yl)methanol (4ta)



4ta (37 mg) was obtained as a white solid in 64% yield after flash chromatography and the enantiomeric excess was determined to be 97% by HPLC analysis on Chiralpak AD-H column (15% 2-propanol/n-hexane, 1 mL/min), UV 254 nm, t (major) = 11.85 min, t (minor) = 17.84 min; $[\alpha]_D^{20}$ = +4.05 (c 0.074, $CHCl_3$); ^1H NMR (600 MHz, $CDCl_3$) δ 7.94 (s, 1H), 7.30-7.28 (m, 2H), 7.27 – 7.21 (m, 5H), 7.20-7.18 (m, 2H), 7.14 (d, *J* = 7.1 Hz, 2H), 6.84-6.83 (m, 1H), 6.45 (d, *J* = 9.3 Hz, 1H), 4.08 (brs, 1H), 3.66-3.64(m, 1H), 3.56-3.55 (m, 1H), 3.50-3.48 (m, 1H), 3.25 (dd, *J* = 16.5, 5.5 Hz, 1H), 3.09 (dd,

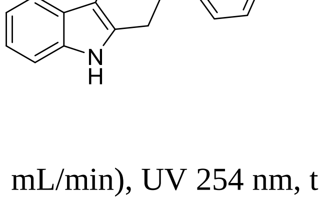
J = 16.5, 6.6 Hz, 1H), 2.46 – 2.38 (m, 1H). ^{13}C NMR (151 MHz, $CDCl_3$) δ 160.96, 159.41, 146.56, 144.97, 138.81, 135.51, 131.28, 131.13, 131.11, 130.70, 129.33, 129.17, 113.55, 113.49, 112.00, 111.83, 107.03, 106.87, 64.27, 53.40, 42.53, 40.54. HRMS (ESI) m/z $(M+H)^+$ calculated for $C_{25}H_{23}ClNO$: 388.1463, observed: 388.1462.

((2S,3S,4S)-6-methoxy-2,4-diphenyl-2,3,4,9-tetrahydro-1H-carbazol-3-yl)methan ol (4ua)



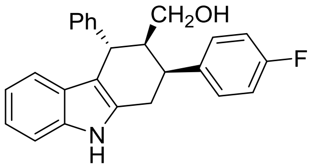
4ua (37 mg) was obtained as a white semisolid in 65% yield after flash chromatography and the enantiomeric excess was determined to be more than 99% by HPLC analysis on Chiralpak AD-H column (20% 2-propanol/n-hexane, 1 mL/min), UV 254 nm, t (major) = 14.63 min, t (minor) = 21.21 min; $[\alpha]_D^{20}$ = -15.0 (c 0.02, $CHCl_3$); ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.83 (s, 1H), 7.30 – 7.25 (m, 3H), 7.25 – 7.19 (m, 6H), 7.18 – 7.13 (m, 2H), 6.75 (dd, J = 8.7, 2.4 Hz, 1H), 6.25 (s, 1H), 4.08 (d, J = 5.8 Hz, 1H), 3.68 – 3.60 (m, 1H), 3.57 (s, 3H), 3.56-3.54 (m, 1H), 3.49 (dd, J = 10.6, 6.9 Hz, 1H), 3.25 (dd, J = 16.5, 5.9 Hz, 1H), 3.08 (dd, J = 16.5, 6.7 Hz, 1H), 2.44 (m, 1H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 153.65, 144.26, 142.52, 135.05, 131.45, 128.79, 128.46, 128.37, 128.13, 127.92, 126.63, 126.32, 111.04, 110.80, 101.52, 61.72, 55.63, 50.75, 39.97, 37.94. HRMS (ESI) m/z $(M+H)^+$ calculated for $C_{26}H_{26}NO_2$: 384.1958, observed: 384.1956.

((2S,3S,4S)-4-phenyl-2-(p-tolyl)-2,3,4,9-tetrahydro-1H-carbazol-3-yl)methanol (4ab)



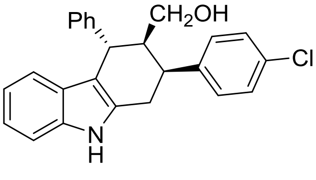
4ab (30 mg) was obtained as a white solid in 54% yield after flash chromatography and the enantiomeric excess was determined to be more than 99% by HPLC analysis on Chiralpak OD-H column (15% 2-propanol/n-hexane, 1 mL/min), UV 254 nm, t (major) = 10.03 min, t (minor) = 21.42 min; $[\alpha]_D^{20}$ = +28.0 (c 0.082, $CHCl_3$); ^{1}H NMR (600 MHz, $CDCl_3$) δ 7.91 (s, 1H), 7.33 (d, J = 8.1 Hz, 1H), 7.31 – 7.25 (m, 3H), 7.23-7.22(m, 3H), 7.10-7.08 (m, 1H), 7.05-7.02 (m, 3H), 6.89 (t, J = 7.4 Hz, 1H), 6.82-6.80 (m,, 1H), 4.14 (brs, 1H), 3.62-3.60 (m, 1H), 3.57-3.54 (m, 1H), 3.52-3.50 (m, 1H), 3.26 (dd, *J* = 16.4, 5.5 Hz, 1H), 3.09 (dd, *J* = 16.4, 6.7 Hz, 1H), 2.43 – 2.38 (m, 1H), 2.31 (s, 3H). ^{13}C NMR (151 MHz, $CDCl_3$) δ 147.13, 142.09, 139.07, 138.80, 136.92, 131.78, 131.38, 130.96, 130.60, 130.10, 128.91, 123.87, 121.89, 121.85, 113.08, 64.50, 53.52, 42.65, 40.33, 23.64. HRMS (ESI) m/z $(M+H)^+$ calculated for $C_{26}H_{26}NO$: 368.2009, observed: 368.2010.

((2S,3S,4S)-2-(4-fluorophenyl)-4-phenyl-2,3,4,9-tetrahydro-1H-carbazol-3-yl)methanol (4ac)



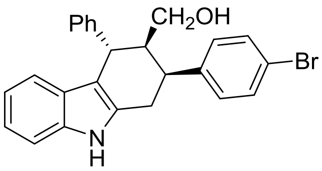
4ac (26 mg) was obtained as a white semisolid in 47% yield after flash chromatography and the enantiomeric excess was determined to be 98% by HPLC analysis on Chiralpak OD-H column (15% 2-propanol/n-hexane, 1 mL/min), UV 254 nm, t (major) = 10.73 min, t (minor) = 21.47 min; $[\alpha]_D^{20}$ = +32.5 (c 0.04, $CHCl_3$); ^{1}H NMR (600 MHz, $CDCl_3$) δ 7.93 (s, 1H), 7.33 (d, *J* = 8.1 Hz, 1H), 7.28-7.25 (m, 3H), 7.24 (d, *J* = 6.9 Hz, 1H), 7.20 (d, *J* = 7.6 Hz, 2H), 7.11 (m, 3H), 6.93 (t, *J* = 8.4 Hz, 2H), 6.88 (t, *J* = 7.5 Hz, 1H), 6.78 (d, *J* = 7.4 Hz, 1H), 4.04 (brs, 1H), 3.66-3.64 (m, 1H), 3.56-3.53 (m, *J* = 10.5, 6.4 Hz, 1H), 3.46 – 3.37 (m, 1H), 3.29 (dd, *J* = 16.2, 5.2 Hz, 1H), 3.07 (dd, *J* = 16.4, 6.0 Hz, 1H), 2.40-2.38 (m, 1H). ^{13}C NMR (101 MHz, CDCl3) δ 162.83, 160.40, 144.22, 138.02 (d, J = 3.3 Hz), 136.44, 133.95, 129.63 (d, J = 7.6 Hz), 128.75, 128.41, 127.31, 126.43, 121.36, 119.30 (d, J = 8.5 Hz), 115.26, 115.05, 110.53, 61.60, 50.61, 39.97, 37.24, 29.74. HRMS (ESI) m/z $(M+H)^+$ calculated for $C_{25}H_{23}FNO$: 372.1763, observed: 372.1764.

((2S,3S,4S)-2-(4-chlorophenyl)-4-phenyl-2,3,4,9-tetrahydro-1H-carbazol-3-yl)methanol (4ad)



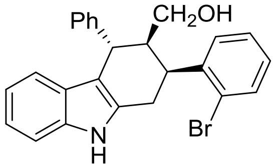
4ad (27 mg) was obtained as a white semisolid in 48% yield after flash chromatography and the enantiomeric excess was determined to be 99% by HPLC analysis on Chiralpak OD-H column (15% 2-propanol/n-hexane, 1 mL/min), UV 254 nm, t (major) = 12.73 min, t (minor) = 24.99 min; $[\alpha]_D^{20}$ = +19.3 (c 0.088, $CHCl_3$); ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.94 (s, 1H), 7.34 (d, *J* = 8.1 Hz, 1H), 7.29 – 7.25 (m, 3H), 7.20-7.18 (m, 4H), 7.10 (t, *J* = 8.2 Hz, 3H), 6.88 (t, *J* = 7.5 Hz, 1H), 6.77 (d, *J* = 7.7 Hz, 1H), 4.01 (brs, 1H), 3.67-3.65 (m, 1H), 3.57-3.54 (m, 1H), 3.46 – 3.37 (m, 1H), 3.30 (dd, *J* = 16.6, 5.7 Hz, 1H), 3.06 (dd, *J* = 16.4, 5.9 Hz, 1H), 2.41 (m, 1H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 143.08, 139.79, 135.37, 132.77, 131.24, 128.53, 127.66, 127.42, 127.36, 126.21, 125.39, 120.31, 118.28, 118.19, 109.48, 60.46, 49.44, 38.89, 36.28. HRMS (ESI) m/z $(M+H)^+$ calculated for $C_{25}H_{23}ClNO$: 388.1465, observed: 388.1467.

((2S,3S,4S)-2-(4-bromophenyl)-4-phenyl-2,3,4,9-tetrahydro-1H-carbazol-3-yl)methanol (4ae)



4ae (26 mg) was obtained as a white semisolid in 41% yield after flash chromatography and the enantiomeric excess was determined to be more than 99% by HPLC analysis on Chiralpak OD-H column (15% 2-propanol/n-hexane, 1 mL/min), UV 254 nm, t (major) = 11.54 min, t (minor) = 26.02 min; $[\alpha]_D^{20}$ = +30.9 (c 0.084, $CHCl_3$); ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.85 (s, 1H), 7.28-7.24 (m, 2H), 7.21 – 7.14 (m, 4H), 7.12 – 7.09 (m, 2H), 7.06 – 6.99 (m, 1H), 6.95 (d, *J* = 8.4 Hz, 2H), 6.79 (t, *J* = 7.4 Hz, 1H), 6.67 (d, *J* = 7.7 Hz, 1H), 3.91 (brs, 1H), 3.57-3.55 (m, 1H), 3.47-3.45 (m, 1H), 3.33-3.31 (m, 1H), 3.21 (dd, *J* = 16.4, 5.8 Hz, 1H), 2.97 (dd, *J* = 16.4, 5.8 Hz, 1H), 2.32 (m, 1H). ^{13}C NMR (75 MHz, $CDCl_3$) δ 144.10, 141.39, 136.45, 133.74, 131.44, 129.97, 128.71, 128.41, 127.28, 126.44, 121.39, 120.41, 119.35, 119.26, 110.49, 61.57, 50.45, 39.98, 37.46. HRMS (ESI) m/z $(M+H)^+$ calculated for $C_{25}H_{23}BrNO$: 432.0958, observed: 432.0954.

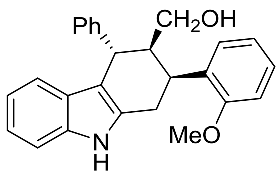
((2S,3S,4S)-2-(2-bromophenyl)-4-phenyl-2,3,4,9-tetrahydro-1H-carbazol-3-yl)methanol (4af)



4af (29 mg) was obtained as a white solid in 45% yield after flash chromatography and the enantiomeric excess was determined to be more than 99% by HPLC analysis on Chiralpak OD-H column (15% 2-propanol/n-hexane, 1 mL/min), UV 254 nm, t (major) = 19.50 min, t (minor) = 32.71 min; $[\alpha]_D^{20}$ = -47.3 (c 0.074, $CHCl_3$); ^{1}H NMR

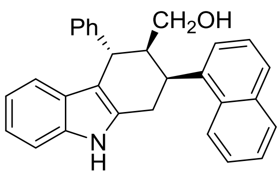
(600 MHz, $CDCl_3$) δ 7.95 (s, 1H), 7.50 (d, *J* = 7.9 Hz, 1H), 7.35 (d, *J* = 8.1 Hz, 1H), 7.28 – 7.24 (m, 4H), 7.22-7.20(m, 3H), 7.17 – 7.10 (m, 2H), 7.08-7.06 (m, 1H), 6.97 (t, *J* = 7.5 Hz, 1H), 4.55 (brs, 1H), 3.93 – 3.86 (m, 1H), 3.67 – 3.59 (m, 2H), 3.20-3.17 (m, 1H), 2.96 (dd, *J* = 16.0, 5.1 Hz, 1H), 2.44-2.41 (m, 1H). ^{13}C NMR (151 MHz, $CDCl_3$) δ 147.04, 144.08, 139.13, 136.73, 136.26, 131.54, 131.14, 130.74, 130.26, 129.92, 128.77, 127.90, 124.18, 122.08, 121.71, 113.17, 112.44, 63.91, 51.55, 42.67, 39.57. HRMS (ESI) m/z $(M+H)^+$ calculated for $C_{25}H_{23}BrNO$: 432.0958, observed: 432.0955.

((2S,3S,4S)-2-(2-methoxyphenyl)-4-phenyl-2,3,4,9-tetrahydro-1H-carbazol-3-yl) methanol (4ag)



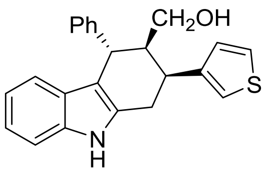
4ag (38 mg) was obtained as a white semisolid in 66% yield after flash chromatography and the enantiomeric excess was determined to be more than 99% by HPLC analysis on Chiralpak OD-H column (15% 2-propanol/n-hexane, 1 mL/min), UV 254 nm, t (major) = 14.93 min, t (minor) = 26.23 min; $[\alpha]_D^{20}$ = +11.63 (c 0.086, $CHCl_3$); ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.94 (s, 1H), 7.32 (d, *J* = 8.1 Hz, 1H), 7.30 – 7.17 (m, 6H), 7.12 – 7.04 (m, 2H), 6.89-6.87 (m, 1H), 6.86 – 6.79 (m, 2H), 6.68 (d, *J* = 7.6 Hz, 1H), 4.12 (brs, 1H), 3.88 – 3.80 (m, 1H), 3.75 (s, 3H), 3.43 (dd, *J* = 11.5, 5.5 Hz, 1H), 3.37 – 3.21 (m, 2H), 3.03 (dd, *J* = 16.6, 4.4 Hz, 1H), 2.51 (m, 1H). ^{13}C NMR (75 MHz, $CDCl_3$) δ 156.78, 144.03, 136.37, 134.41, 130.76, 128.93, 128.18, 127.93, 127.68, 127.38, 126.23, 121.51, 121.12, 119.36, 119.19, 110.45, 110.41, 62.31, 55.67, 49.26, 39.99, 29.71. HRMS (ESI) m/z $(M+H)^+$ calculated for $C_{26}H_{26}NO$: 368.2009, observed: 368.2006.

((2S,3S,4S)-2-(naphthalen-1-yl)-4-phenyl-2,3,4,9-tetrahydro-1H-carbazol-3-yl)methanol (4ah)



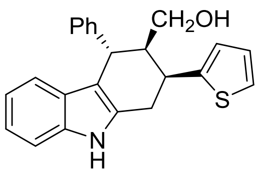
4ah (34 mg) was obtained as a white semisolid in 57% yield after flash chromatography and the enantiomeric excess was determined to be 96% by HPLC analysis on Chiralpak AD-H column (20% 2-propanol/n-hexane, 1 mL/min), UV 254 nm, t (major) = 9.98 min, t (minor) = 7.09 min; $[\alpha]_D^{20}$ = -186.4 (c 0.066, $CHCl_3$); ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.98 (s, 1H), 7.79 (d, *J* = 8.1 Hz, 1H), 7.72 (d, *J* = 8.0 Hz, 1H), 7.45 – 7.26 (m, 8H), 7.24-7.22(m, 2H), 7.18-7.16 (m, 1H), 7.03 (t, *J* = 7.6 Hz, 2H), 6.75 (d, *J* = 8.6 Hz, 1H), 4.71 (s, 1H), 4.22 (d, *J* = 10.9 Hz, 1H), 3.65-3.64 (m, 2H), 3.37-3.35 (m, 1H), 2.93 (d, *J* = 15.5 Hz, 1H), 2.50-2.48 (s, 1H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 144.92, 138.35, 136.50, 134.95, 134.06, 131.59, 128.87, 128.83, 128.38, 127.83, 127.37, 126.34, 126.02, 125.46, 124.99, 123.52, 123.07, 121.58, 119.51, 118.92, 110.60, 109.21, 61.28, 50.69, 40.00, 32.69, 24.29. HRMS (ESI) m/z $(M+H)^+$ calculated for $C_{29}H_{26}NO$: 404.2009, observed: 404.2007.

((2S,3S,4S)-4-phenyl-2-(thiophen-3-yl)-2,3,4,9-tetrahydro-1H-carbazol-3-yl)methanol (4ai)



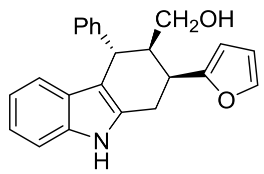
4ai (27 mg) was obtained as a white semisolid in 51% yield after flash chromatography and the enantiomeric excess was determined to be more than 99% by HPLC analysis on Chiralpak AD-H column (20% 2-propanol/n-hexane, 1 mL/min), UV 254 nm, t (major) = 10.98 min, t (minor) = 12.06 min; $[\alpha]_D^{20}$ = +15.8 (c 0.076, $CHCl_3$); ^{1}H NMR (600 MHz, $CDCl_3$) δ 7.91 (s, 1H), 7.32 (d, *J* = 8.1 Hz, 1H), 7.30 – 7.24 (m, 2H), 7.24 – 7.18 (m, 4H), 7.10 (t, *J* = 7.5 Hz, 1H), 6.95-6.93 (m, 1H), 6.89-6.87 (m, 1H), 6.87 – 6.85 (m, 1H), 6.80 (d, *J* = 7.7 Hz, 1H), 4.04 (brs, 1H), 3.78 -3.76(m, 1H), 3.58-3.56 (m, 1H), 3.49-3.47 (m, 1H), 3.32 (dd, *J* = 16.3, 5.7 Hz, 1H), 3.01 (dd, *J* = 16.3, 5.8 Hz, 1H), 2.46 – 2.39 (m, 1H). ^{13}C NMR (151 MHz, $CDCl_3$) δ 147.01, 145.70, 139.08, 136.47, 131.40, 131.00, 130.85, 129.97, 129.00, 127.92, 123.93, 123.62, 121.94, 121.86, 113.12, 64.87, 52.77, 42.87, 36.92. HRMS (ESI) m/z $(M+H)^+$ calculated for $C_{23}H_{22}NOS$: 360.1417, observed: 360.1415.

((2S,3R,4S)-4-phenyl-2-(thiophen-2-yl)-2,3,4,9-tetrahydro-1H-carbazol-3-yl)methanol (4aj)



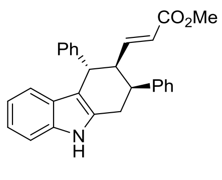
4aj (24 mg) was obtained as a white solid in 45% yield after flash chromatography and the enantiomeric excess was determined to be 95% by HPLC analysis on Chiralpak OD-H column (15% 2-propanol/n-hexane, 1 mL/min), UV 254 nm, t (major) = 12.58 min, t (minor) = 17.25 min; $[\alpha]_D^{20}$ = +50.0 (c 0.034, $CHCl_3$); ^1H NMR (600 MHz, $CDCl_3$) δ 7.89 (s, 1H), 7.32 (d, *J* = 8.1 Hz, 1H), 7.27-7.24 (m, 2H), 7.22-7.20 (m, 3H), 7.09 -7.06(m, 2H), 6.94 – 6.90 (m, 1H), 6.89 – 6.84 (m, 2H), 6.79 (d, *J* = 7.5 Hz, 1H), 4.05 (d, *J* = 26.9 Hz, 2H), 3.63-3.62 (m, 1H), 3.58 – 3.51 (m, 1H), 3.41 (dd, *J* = 16.1, 5.1 Hz, 1H), 3.03 (dd, *J* = 16.1, 4.7 Hz, 1H), 2.44-2.42 (m, 1H). ^{13}C NMR (151 MHz, $CDCl_3$) δ 146.83, 139.23, 135.72, 131.44, 131.03, 129.89, 129.07, 129.00, 127.85, 126.34, 124.04, 121.97, 121.95, 113.13, 64.79, 53.04, 42.93, 37.66. HRMS (ESI) m/z $(M+H)^+$ calculated for $C_{23}H_{22}NOS$: 360.1417, observed: 360.1415.

((2S,3R,4S)-2-(furan-2-yl)-4-phenyl-2,3,4,9-tetrahydro-1H-carbazol-3-yl)methanol (4ak)



4ak (32 mg) was obtained as a white semisolid in 62% yield after flash chromatography and the enantiomeric excess was determined to be 95% by HPLC analysis on Chiralpak OD-H column (15% 2-propanol/n-hexane, 1 mL/min), UV 254 nm, t (major) = 13.69 min, t (minor) = 21.54 min; $[\alpha]_D^{20}$ = +7.14 (c 0.084, $CHCl_3$); ^1H NMR (400 MHz, $CDCl_3$) δ 7.84 (s, 1H), 7.32 – 7.09 (m, 7H), 7.06 – 6.97 (m, 1H), 6.87 – 6.71 (m, 2H), 6.20 (q, *J* = 3.1, 1.9 Hz, 1H), 5.86 (d, *J* = 3.2 Hz, 1H), 4.09 (d, *J* = 5.3 Hz, 1H), 3.62-3.60 (m, 1H), 3.54 (d, *J* = 6.8 Hz, 2H), 3.20 (dd, *J* = 16.4, 5.5 Hz, 1H), 2.95 (dd, *J* = 16.3, 7.1 Hz, 1H), 2.46-2.42(m, 1H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 156.67, 144.26, 141.01, 136.37, 133.11, 128.67, 128.35, 127.41, 126.35, 121.35, 119.32, 119.12, 110.47, 110.30, 105.67, 62.51, 49.01, 40.09, 32.53. HRMS (ESI) m/z $(M+H)^+$ calculated for $C_{23}H_{22}NO_2$: 344.1645, observed: 344.1641.

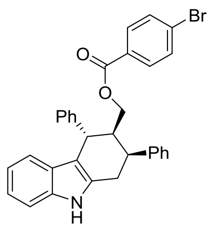
methyl(E)-3-((2S,3S,4S)-2,4-diphenyl-2,3,4,9-tetrahydro-1H-carbazol-3-yl)acrylate (D1)



D1 (25 mg) was obtained as a white solid in 41% yield after flash chromatography and the enantiomeric excess was determined to be 99% by HPLC analysis on Chiralpak AD-H column (15% 2-propanol/n-hexane, 1 mL/min), UV 254 nm, t (major) = 6.53 min, t (minor) = 5.40

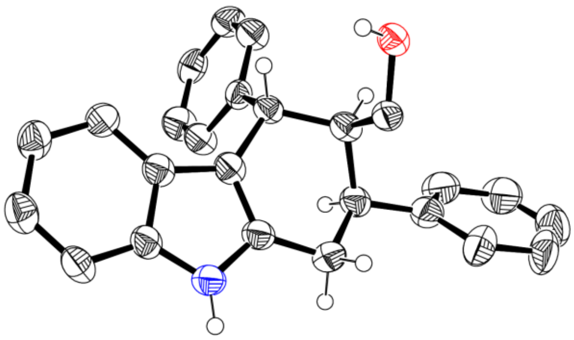
min; $[\alpha]_D^{20}$ = +41.38 (c 0.058, $CHCl_3$); ^{1}H NMR (600 MHz, $CDCl_3$) δ 7.99 (s, 1H), 7.36 (d, *J* = 8.1 Hz, 1H), 7.30 – 7.20 (m, 6H), 7.15 (dd, *J* = 15.4, 7.4 Hz, 3H), 7.04 (d, *J* = 7.2 Hz, 3H), 6.97 (dd, *J* = 15.8, 8.6 Hz, 2H), 5.62 (d, *J* = 15.7 Hz, 1H), 4.32 (brs, 1H), 3.65 (s, 3H), 3.48-3.46 (m, 1H), 3.19 (dd, *J* = 16.2, 10.4 Hz, 1H), 3.11 (dd, *J* = 16.2, 4.7 Hz, 1H), 3.02-3.00 (m, 1H). ^{13}C NMR (151 MHz, $CDCl_3$) δ 169.39, 151.09, 146.29, 144.53, 139.11, 136.88, 131.15, 131.01, 131.00, 130.58, 129.99, 129.37, 129.14, 125.55, 124.23, 122.11, 121.51, 113.20, 55.05, 54.09, 45.78, 32.37. HRMS (ESI) m/z $(M+H)^+$ calculated for $C_{28}H_{26}NO_2$: 407.1885, observed: 407.1882.

((2S,3S,4S)-2,4-diphenyl-2,3,4,9-tetrahydro-1H-carbazol-3-yl)methyl 4-bromobenzoate (D2)



D2 (70 mg) was obtained as a white semisolid in 65% yield after flash chromatography and the enantiomeric excess was determined to be 96% by HPLC analysis on Chiralpak AD-H column (15% 2-propanol/n-hexane, 1 mL/min), UV 254 nm, t (major) = 9.16 min, t (minor) = 10.89 min; $[\alpha]_D^{20}$ = +11.76 (c 0.068, $CHCl_3$); ^{1}H NMR (600 MHz, cdcl$_3$) δ 8.00 (s, 1H), 7.69-7.67 (m, 2H), 7.57 – 7.50 (m, 2H), 7.35 (d, *J* = 8.1 Hz, 1H), 7.30 (t, *J* = 7.1 Hz, 2H), 7.28 – 7.17 (m, 6H), 7.13 (d, *J* = 6.9 Hz, 3H), 6.91 (dd, *J* = 14.9, 7.8 Hz, 2H), 4.32 – 4.25 (m, 2H), 4.23 – 4.17 (m, 1H), 3.64 (brs, 1H), 3.31 (d, *J* = 14.5 Hz, 1H), 3.20 (dd, *J* = 16.1, 7.7 Hz, 1H), 2.79-2.76 (m, 1H). ^{13}C NMR (151 MHz, $CDCl_3$) δ 168.31, 146.50, 144.66, 139.13, 136.54, 134.27, 133.66, 131.67, 131.26, 131.21, 131.13, 130.64, 130.48, 130.00, 129.37, 129.19, 124.13, 122.04, 121.73, 113.17, 67.44, 50.20, 43.24, 32.36. HRMS (ESI) m/z $(M+H)^+$ calculated for $C_{32}H_{27}BrNO_2$: 536.1212, observed: 536.1225.

7. X-ray Single Crystal Data for 4aa



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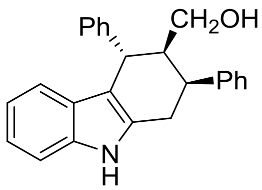


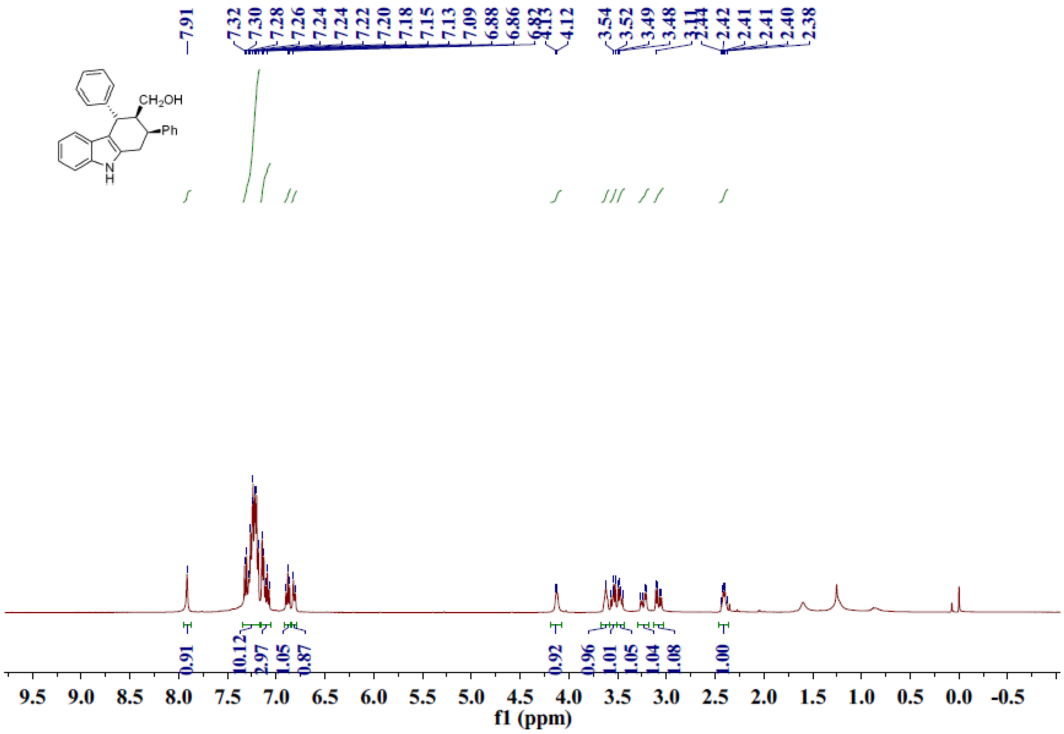
4aa

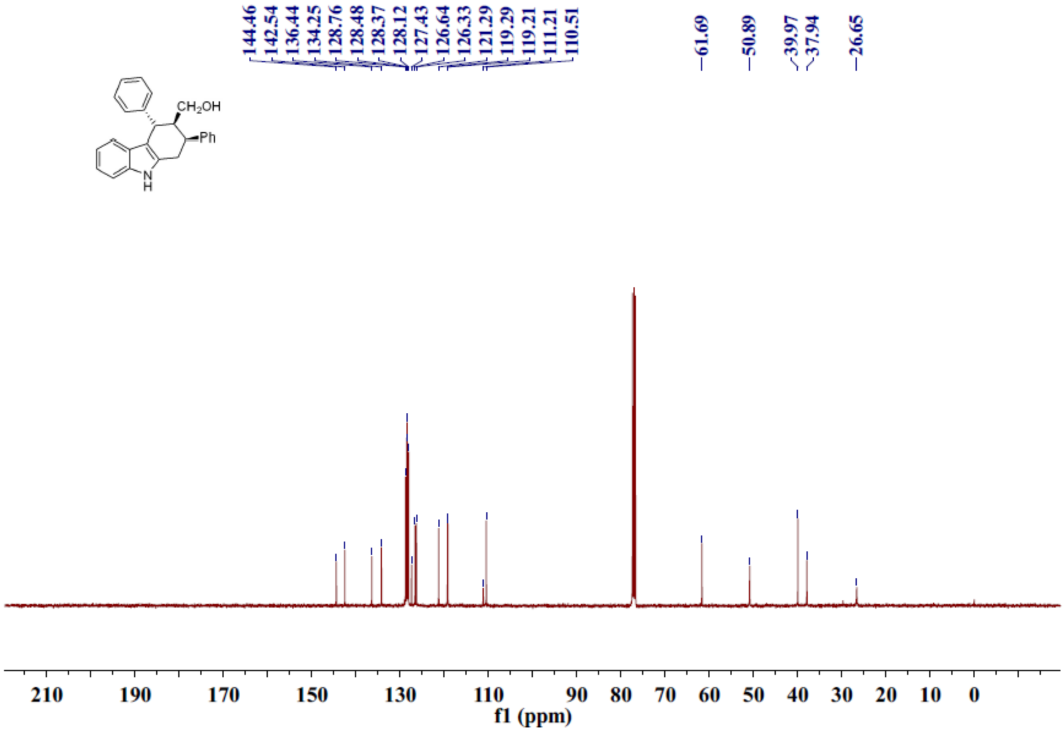
Identification code	cu_dm16449_0m	
Empirical formula	C27 H27 N O2	
Formula weight	397.50	
Temperature	130 K	
Wavelength	1.54178 Å	
Crystal system	Orthorhombic	
Space group	P 21 21 21	
Unit cell dimensions	a = 14.0799(3) Å	α= 90°.
	b = 14.3773(3) Å	β= 90°.
	c = 44.2794(10) Å	γ = 90°.
Volume	8963.5(3) $Å^3$	
Z	16	
Density (calculated)	1.178 Mg/m^3	
Absorption coefficient	0.576 mm^{-1}	
F(000)	3392	
Crystal size	0.12 x 0.1 x 0.03 mm^3	
Theta range for data collection	1.995 to 66.658°.	
Index ranges	-16<=h<=16, -17<=k<=9, -52<=l<=52	
Reflections collected	41784	
Independent reflections	15250 [R(int) = 0.1282]	
Completeness to theta = 66.658°	99.5 %	
Absorption correction	Semi-empirical from equivalents	
Max. and min. transmission	0.7528 and 0.5466	
Refinement method	Full-matrix least-squares on F^2	
Data / restraints / parameters	15250 / 0 / 1090	
Goodness-of-fit on F^2	1.004	
Final R indices [I>2sigma(I)]	R1 = 0.0696, wR2 = 0.1718	
R indices (all data)	R1 = 0.0979, wR2 = 0.1947	

Absolute structure parameter	0.3(3)
Extinction coefficient	0.00110(13)
Largest diff. peak and hole	0.284 and -0.259 e.$Å^{-3}$

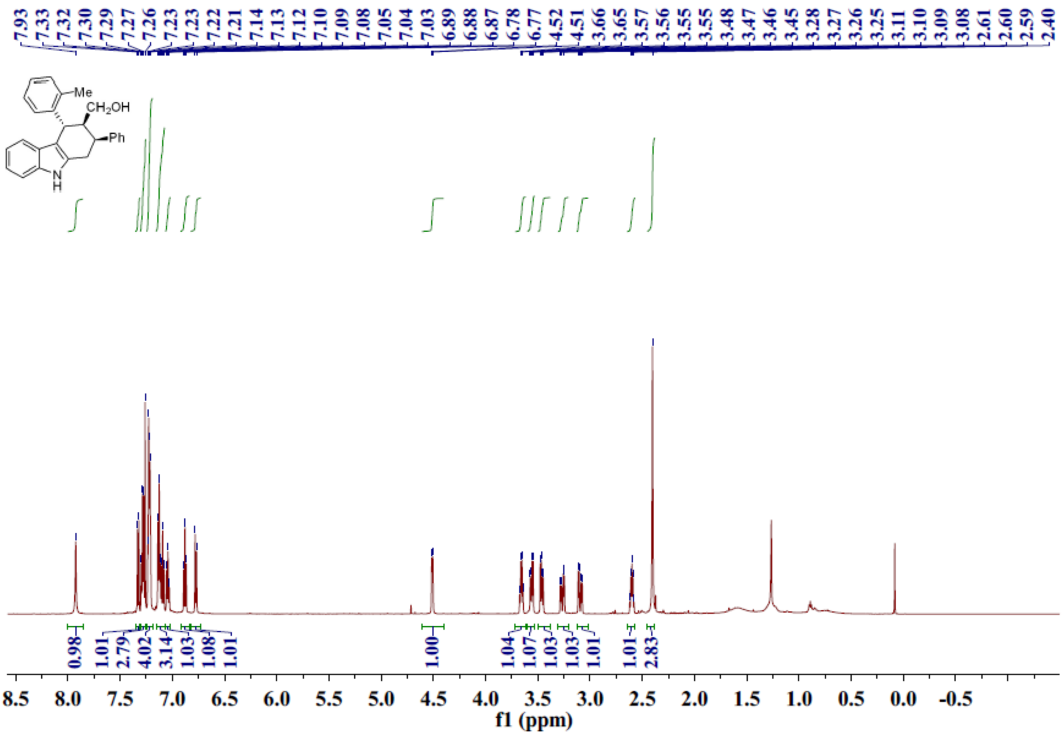
8. ^{1}H NMR and ^{13}C NMR Spectra for the Product

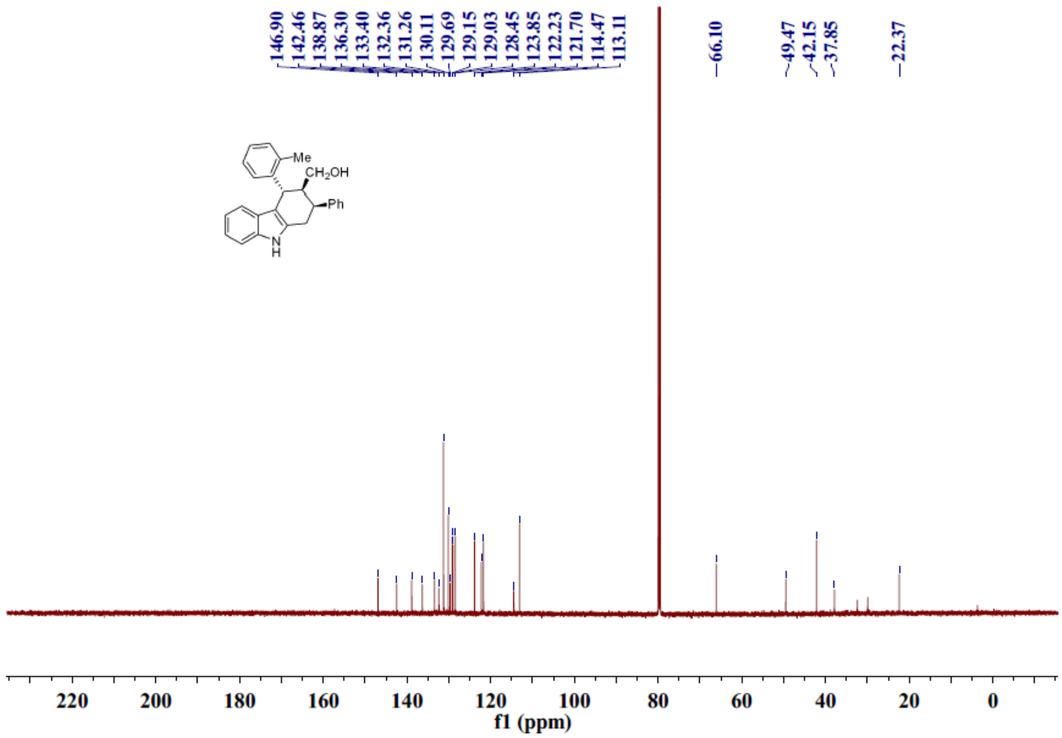
(2,4-diphenyl-2,3,4,9-tetrahydro-1H-carbazol-3-yl)methanol (4aa)



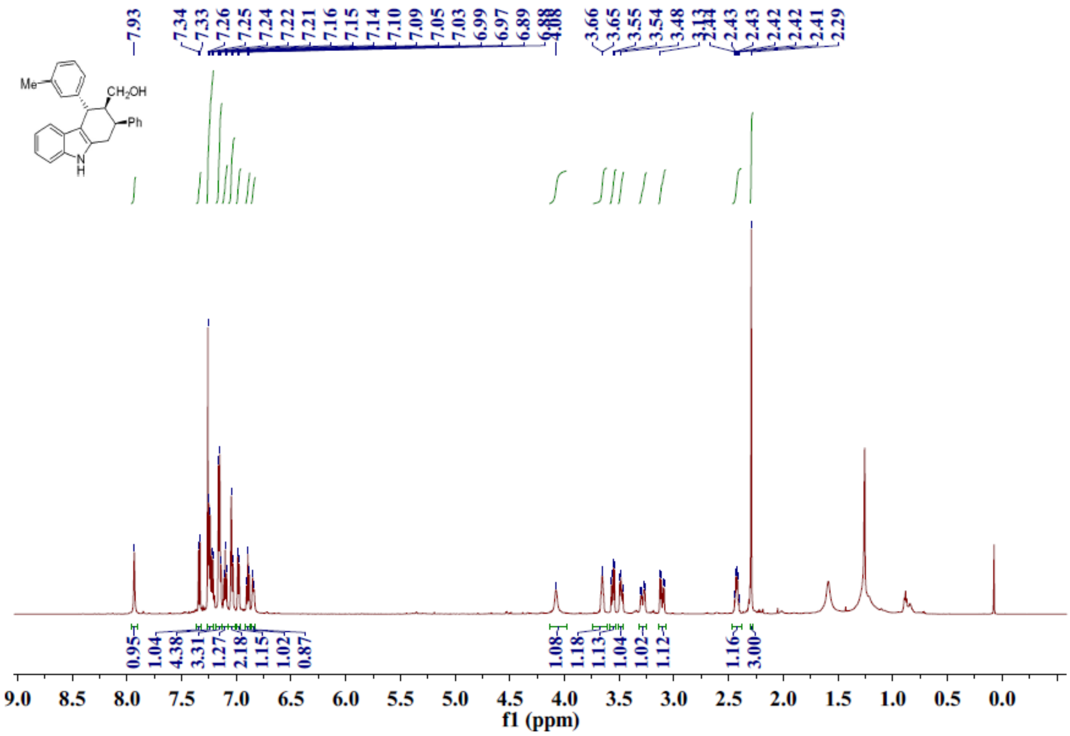


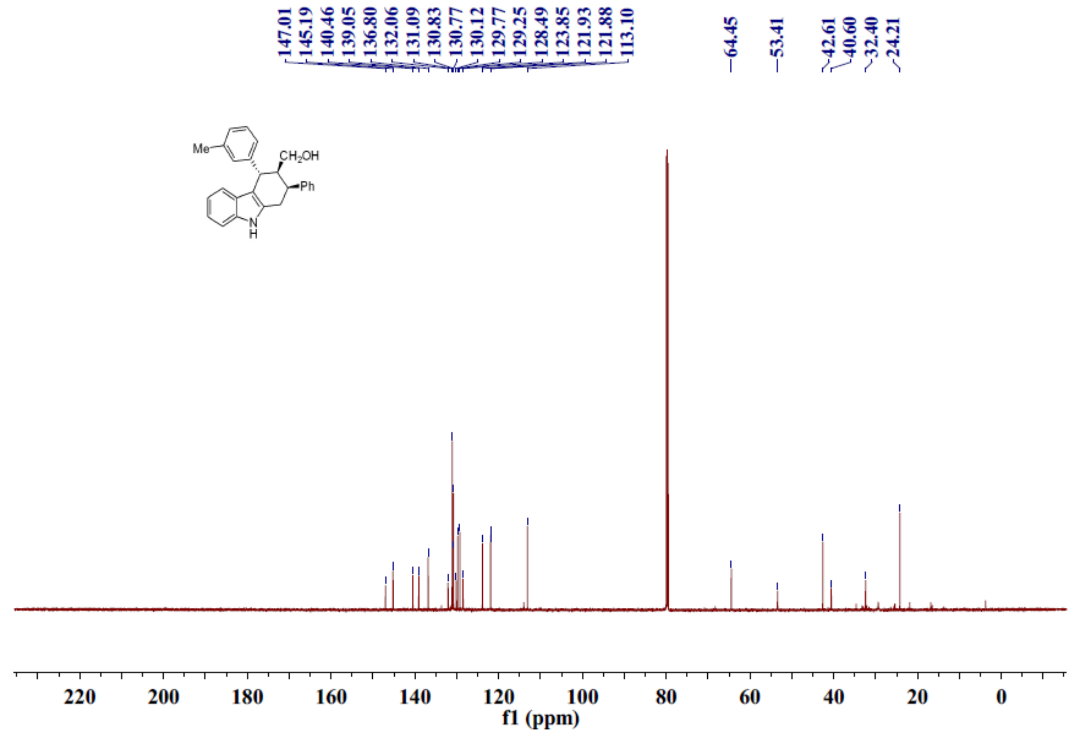
(2-phenyl-4-(o-tolyl)-2,3,4,9-tetrahydro-1H-carbazol-3-yl)methanol (4ba)



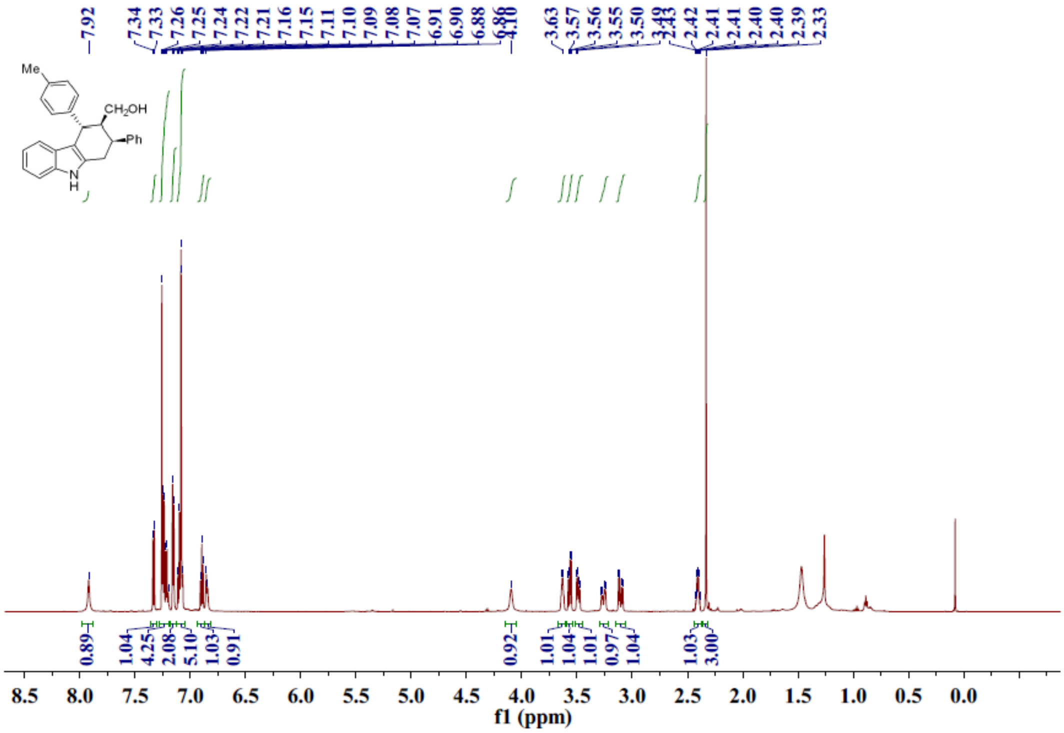


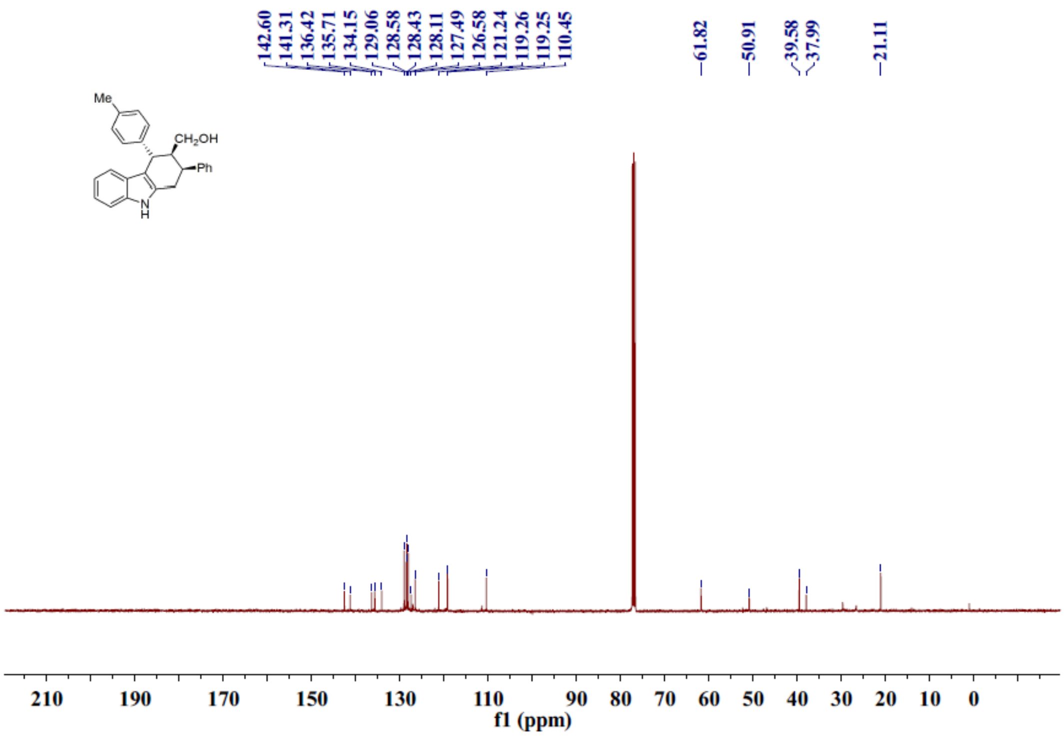
(2-phenyl-4-(m-tolyl)-2,3,4,9-tetrahydro-1H-carbazol-3-yl)methanol (4ca)



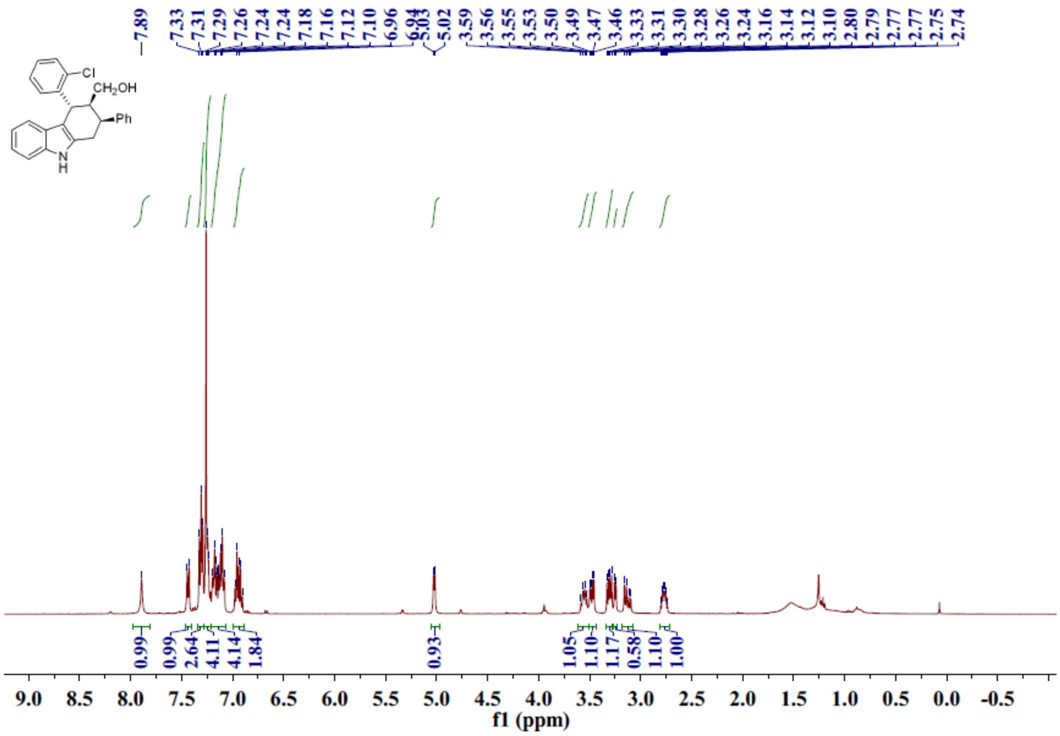


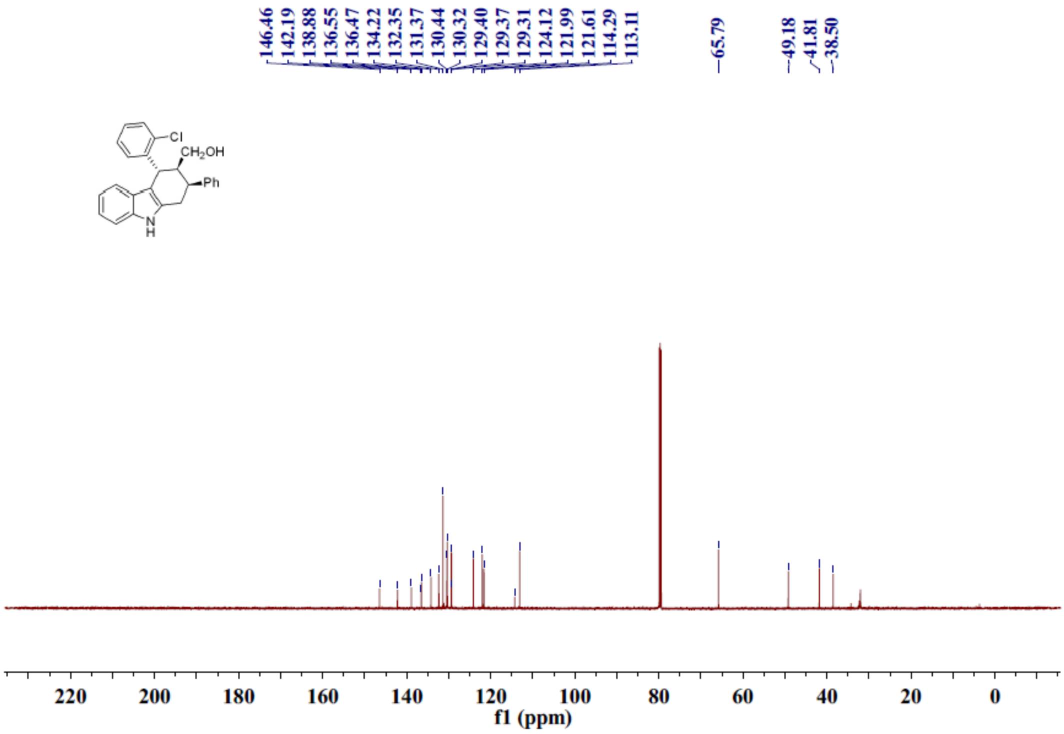
(2-phenyl-4-(p-tolyl)-2,3,4,9-tetrahydro-1H-carbazol-3-yl)methanol (4da)



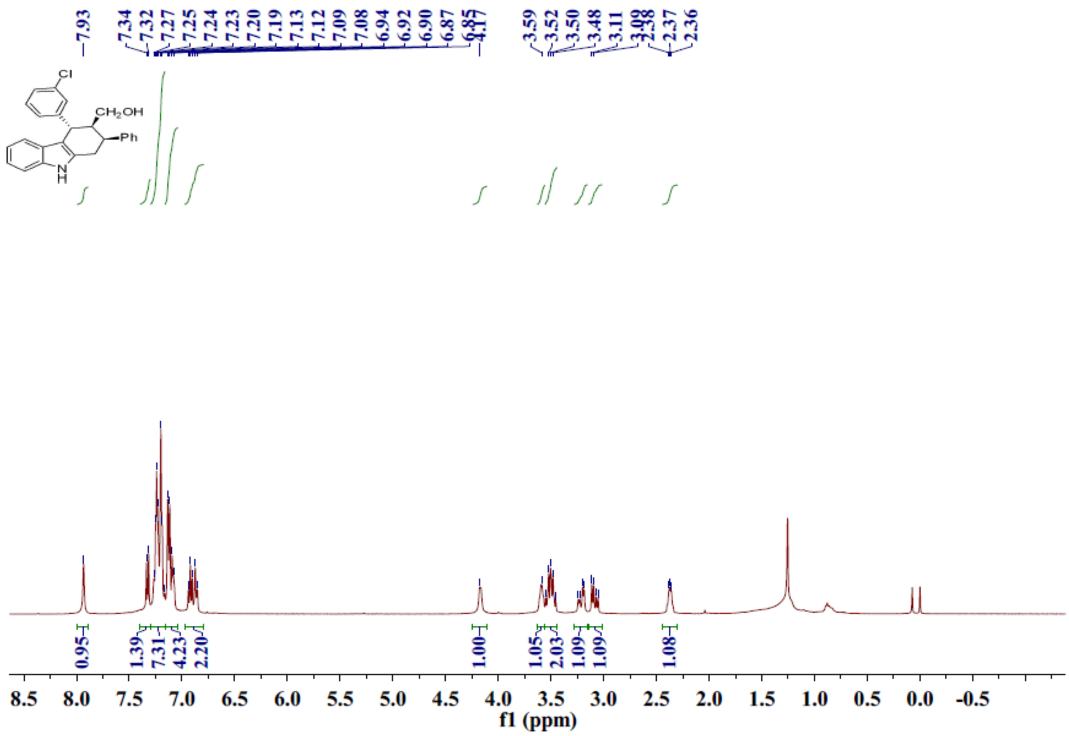


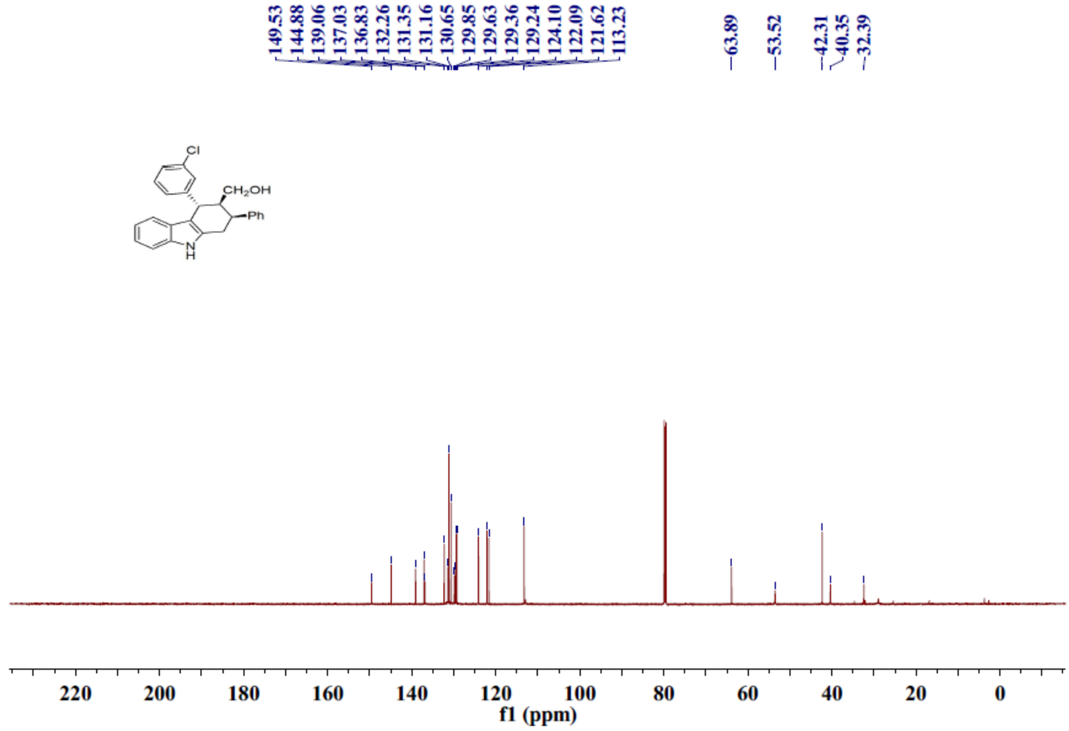
(4-(2-chlorophenyl)-2-phenyl-2,3,4,9-tetrahydro-1H-carbazol-3-yl)methanol (4ea)



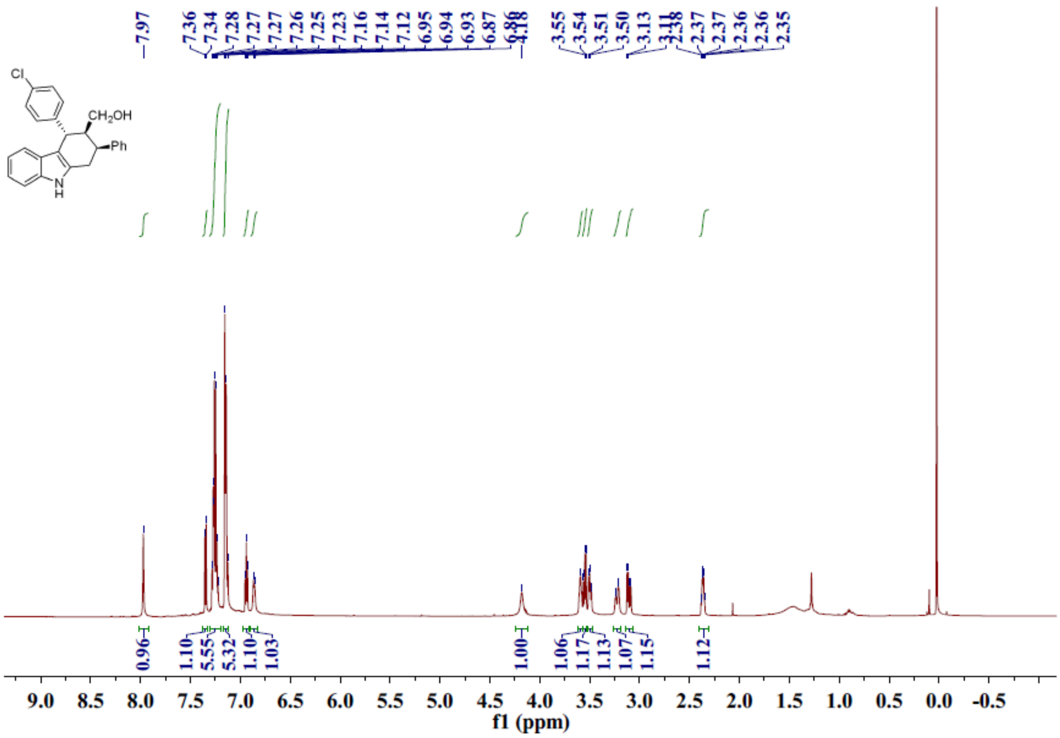


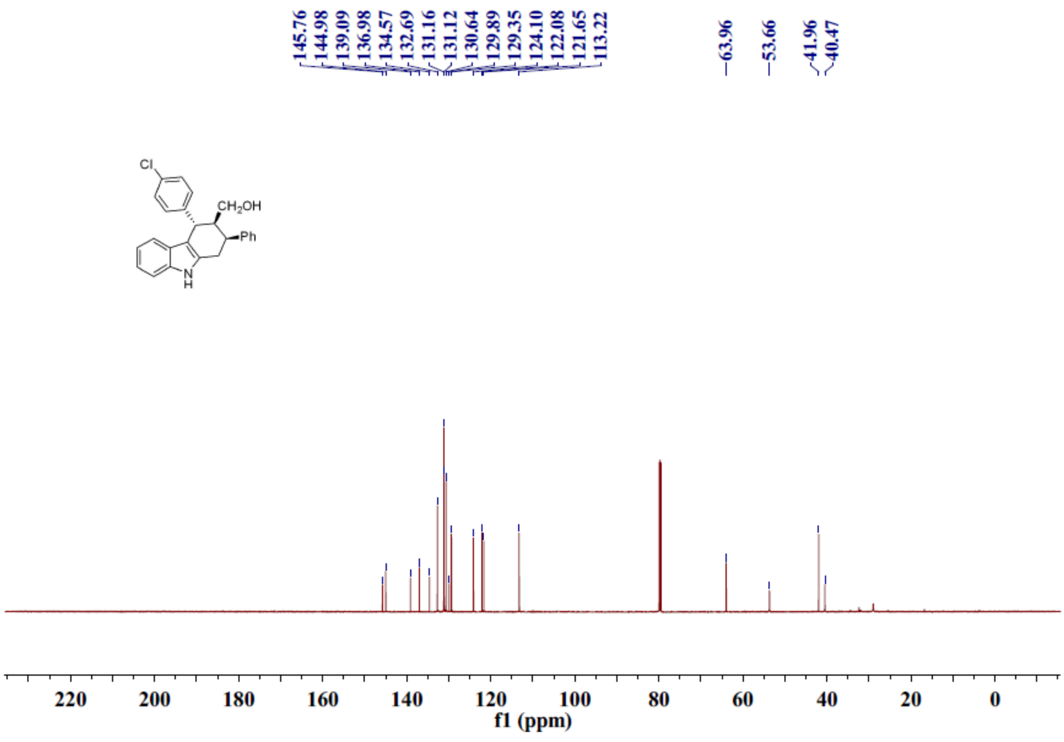
(4-(3-chlorophenyl)-2-phenyl-2,3,4,9-tetrahydro-1H-carbazol-3-yl)methanol (4fa)



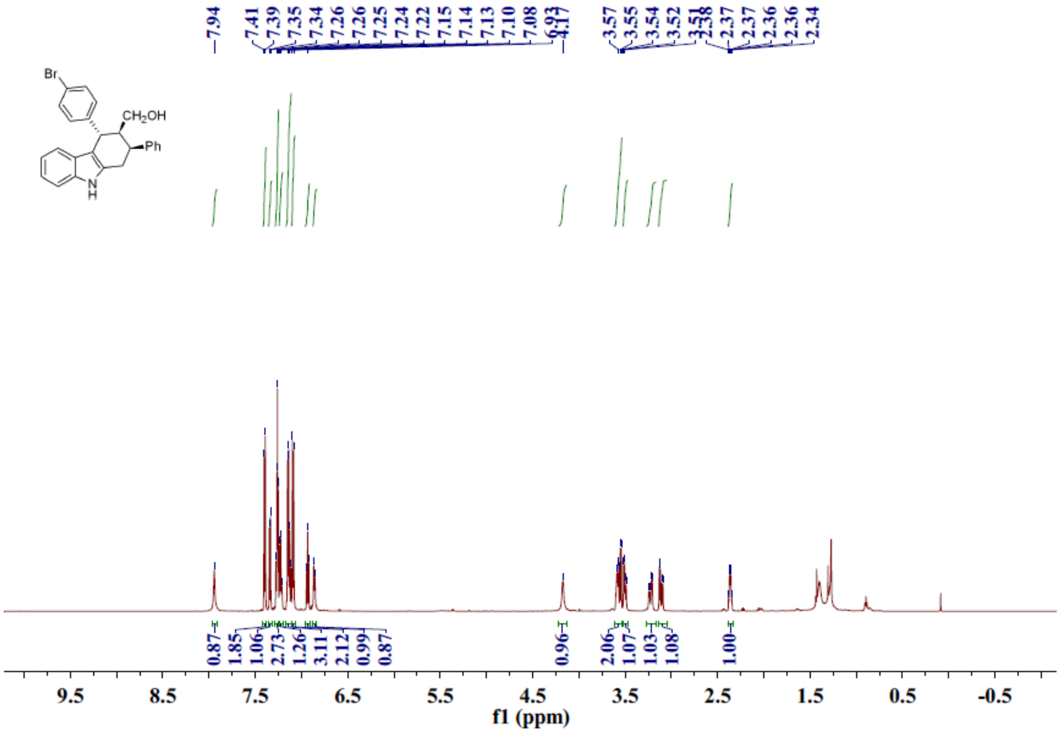


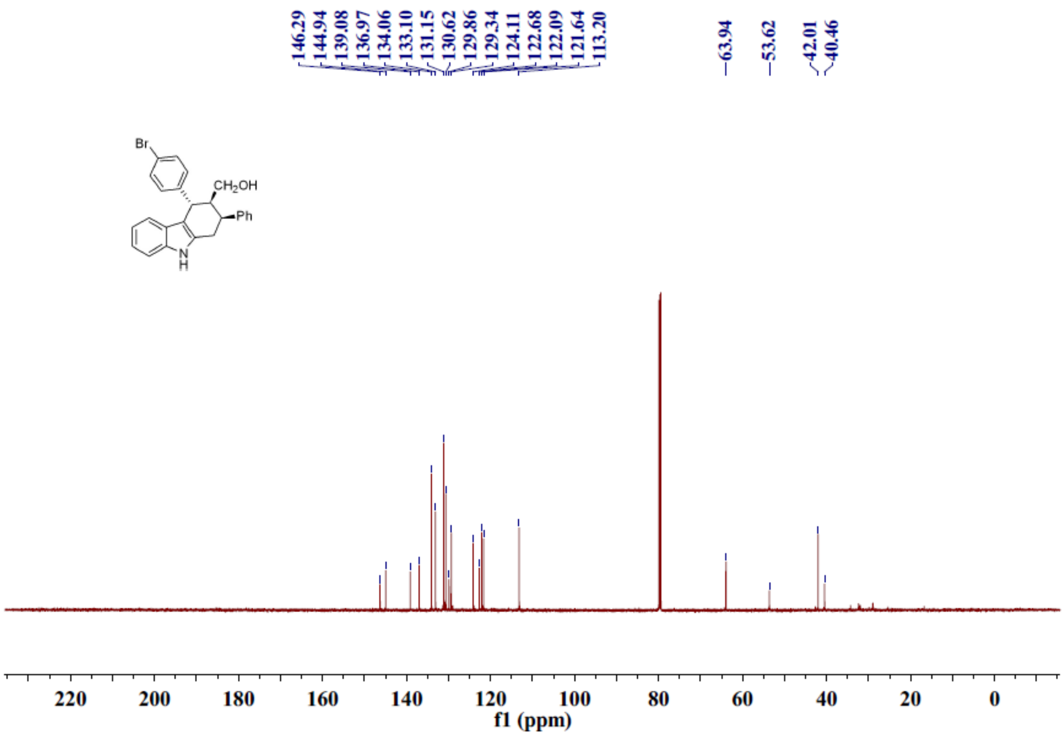
(4-(4-chlorophenyl)-2-phenyl-2,3,4,9-tetrahydro-1H-carbazol-3-yl)methanol (4ga)



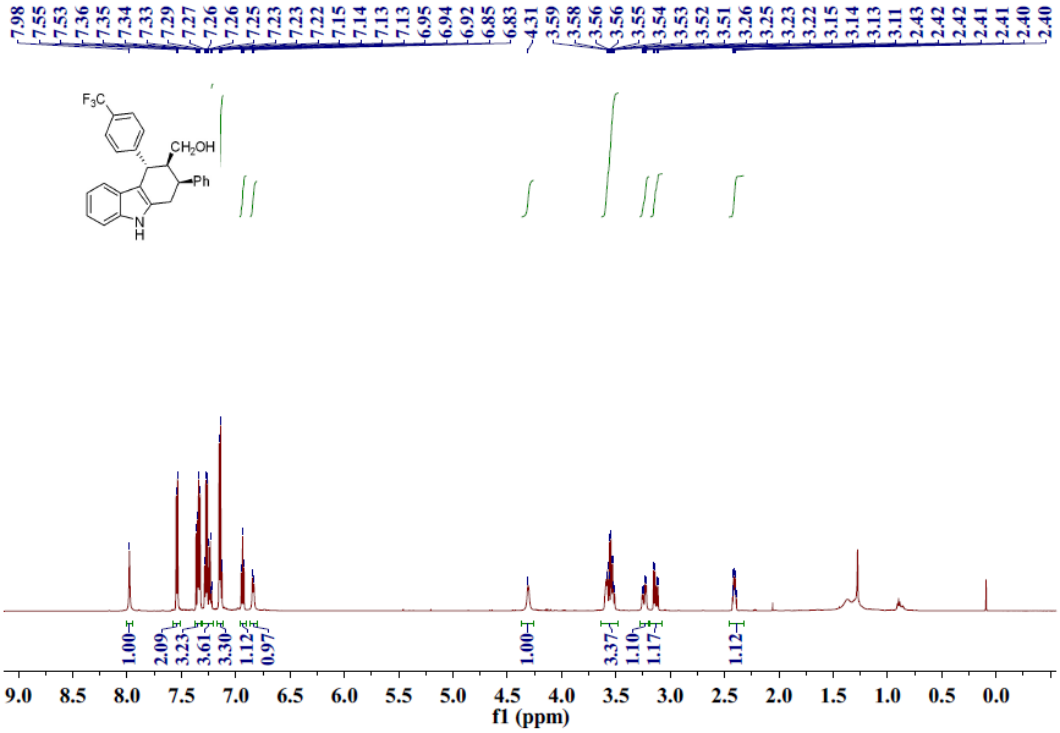


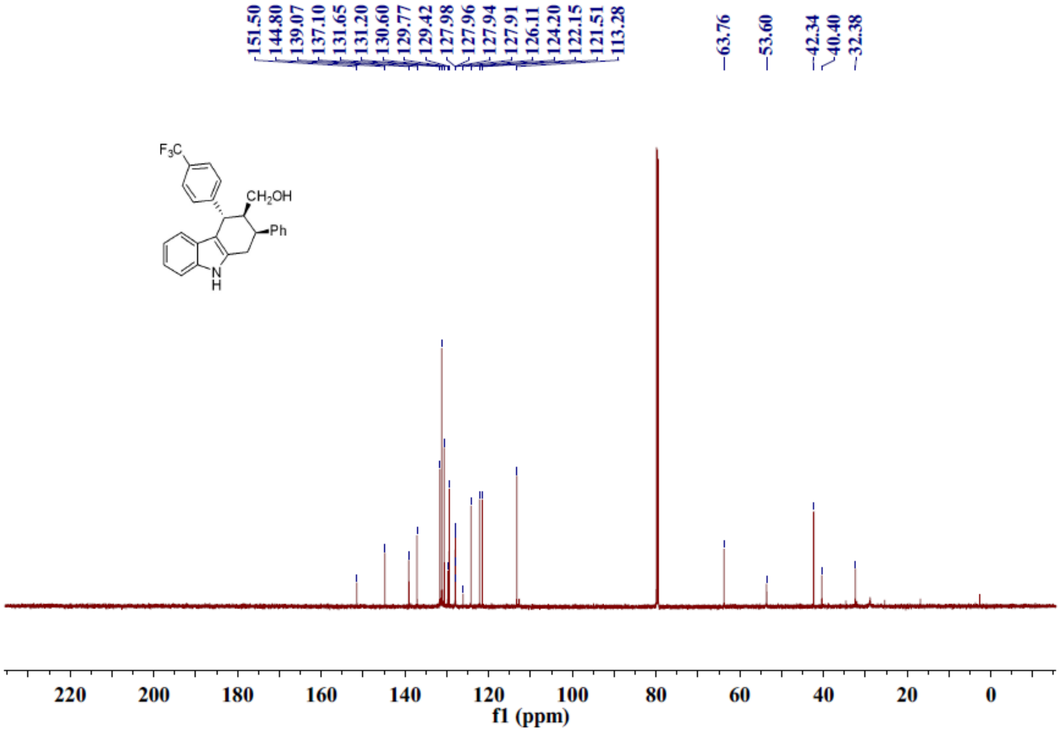
(4-(4-bromophenyl)-2-phenyl-2,3,4,9-tetrahydro-1H-carbazol-3-yl)methanol (4ha)



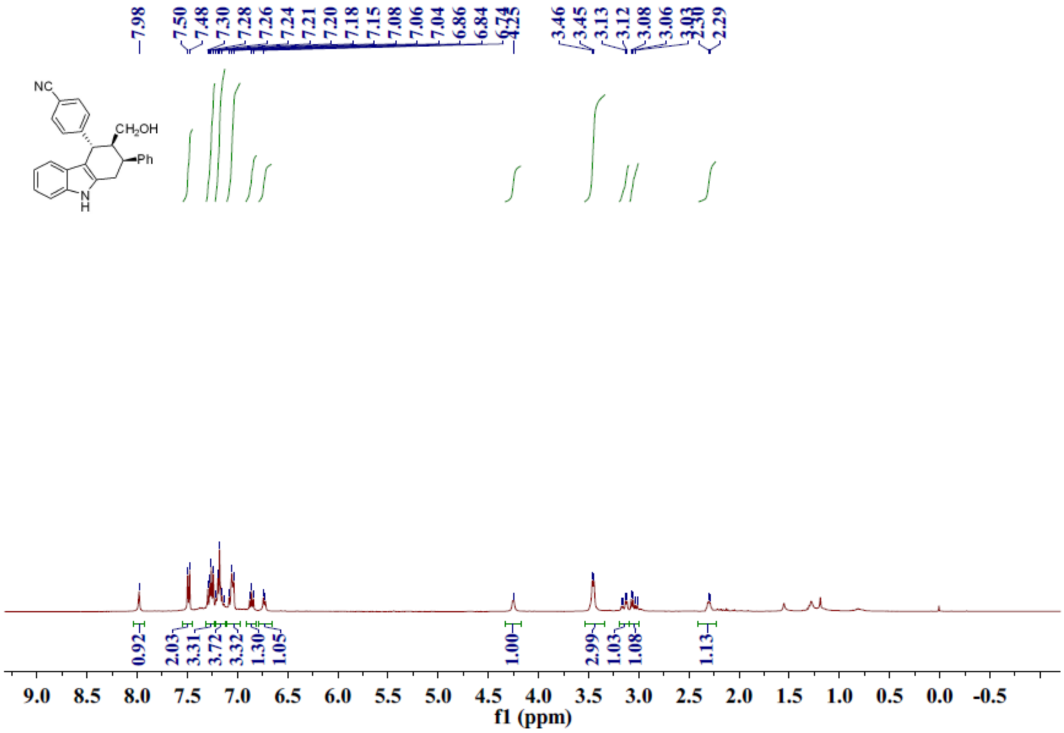


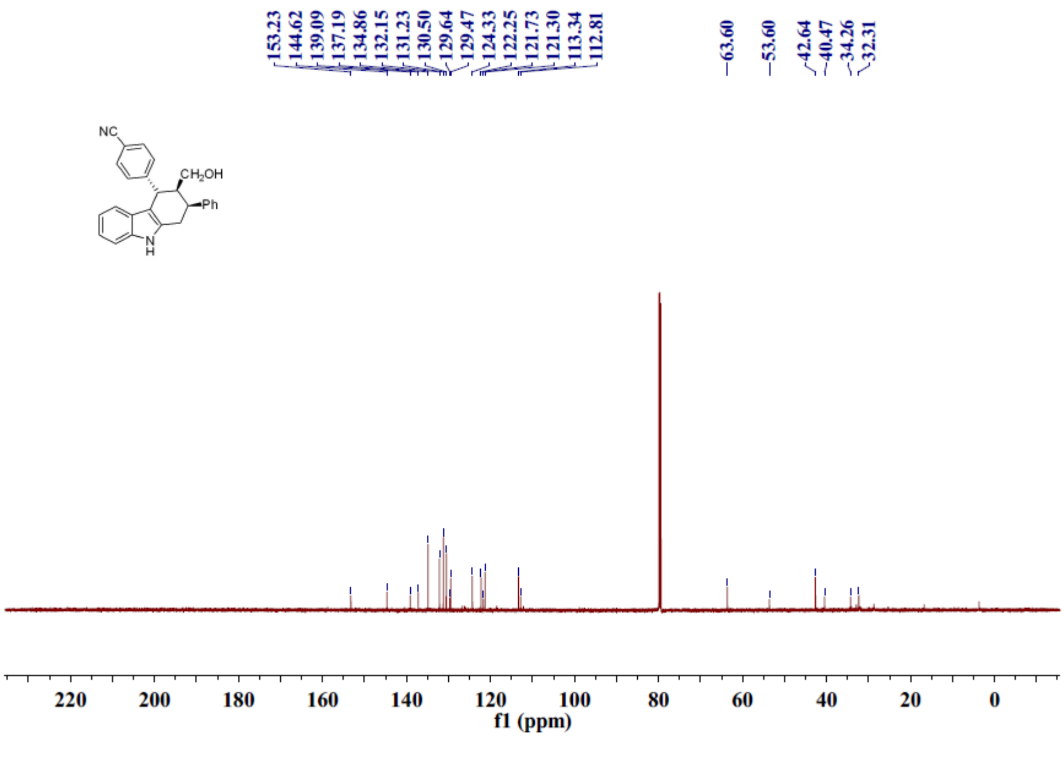
(2-phenyl-4-(4-(trifluoromethyl)phenyl)-2,3,4,9-tetrahydro-1H-carbazol-3-yl)methanol (4ia)



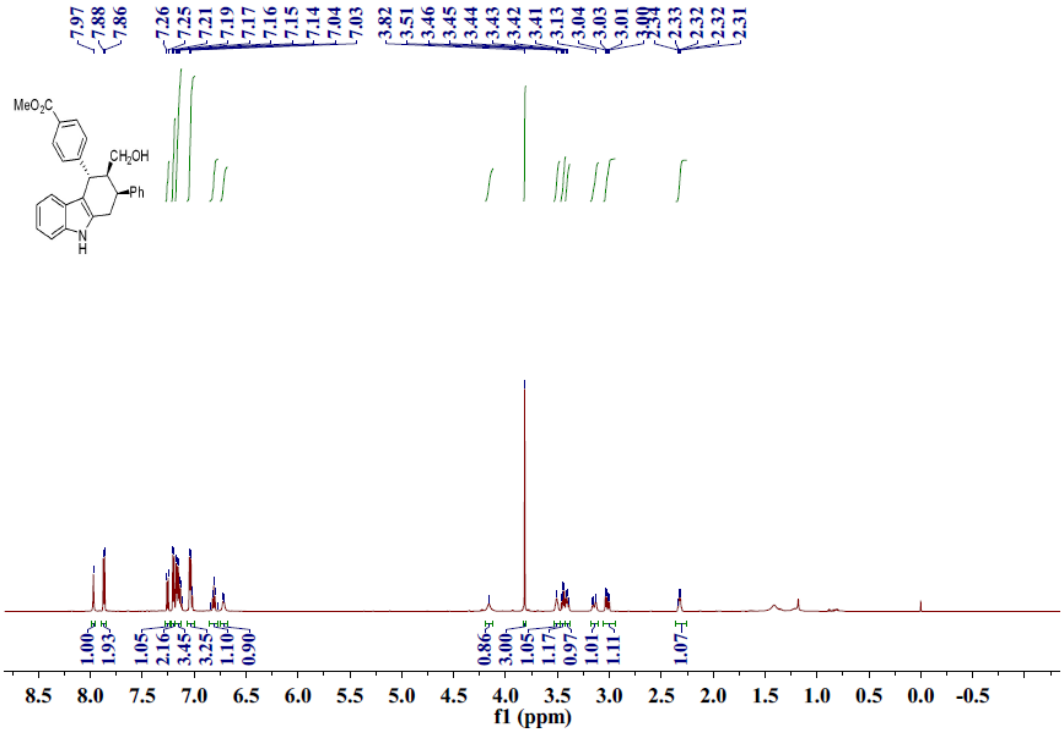


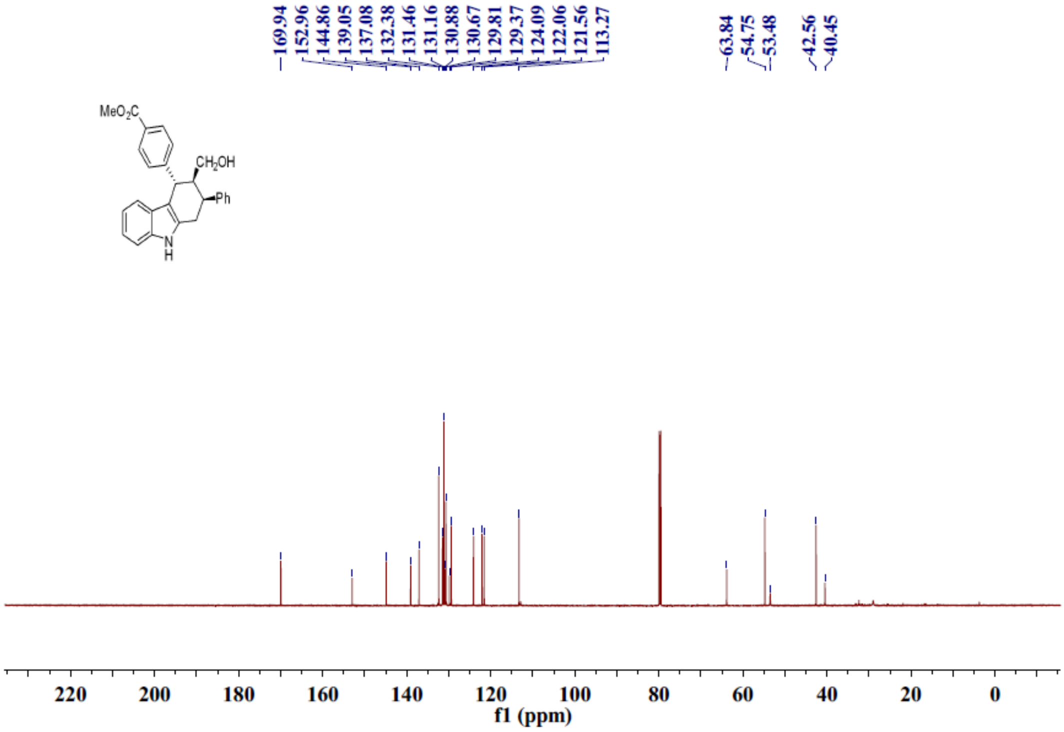
4-3-(hydroxymethyl)-2-phenyl-2,3,4,9-tetrahydro-1H-carbazol-4-yl)benzonitrile (4ja)



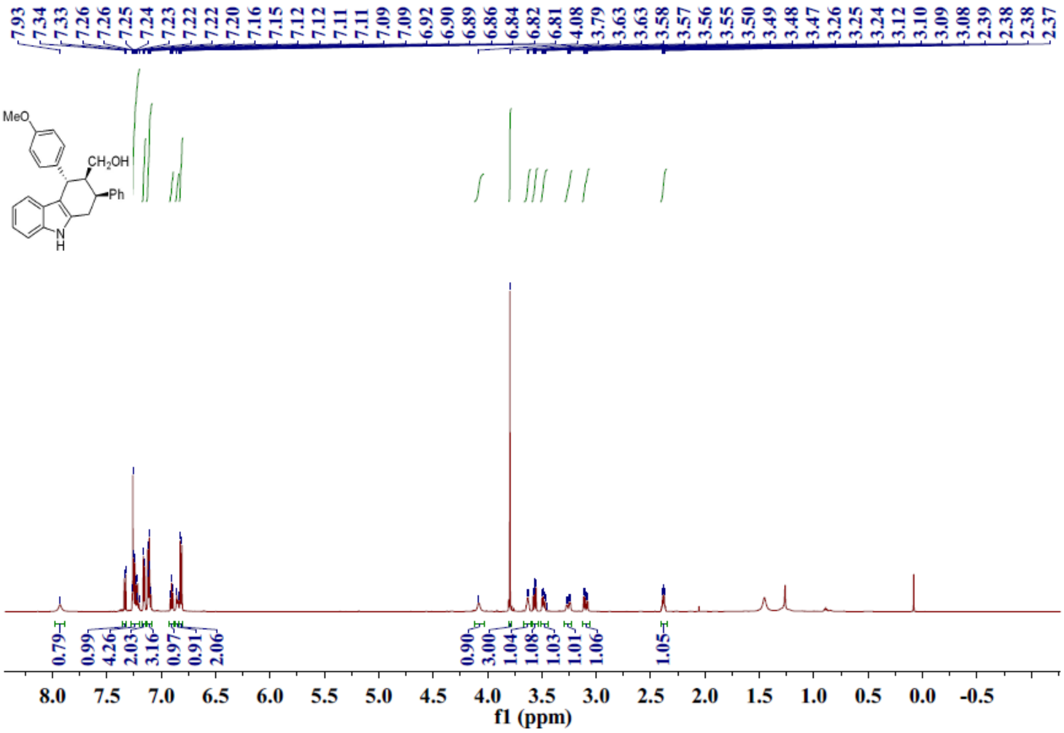


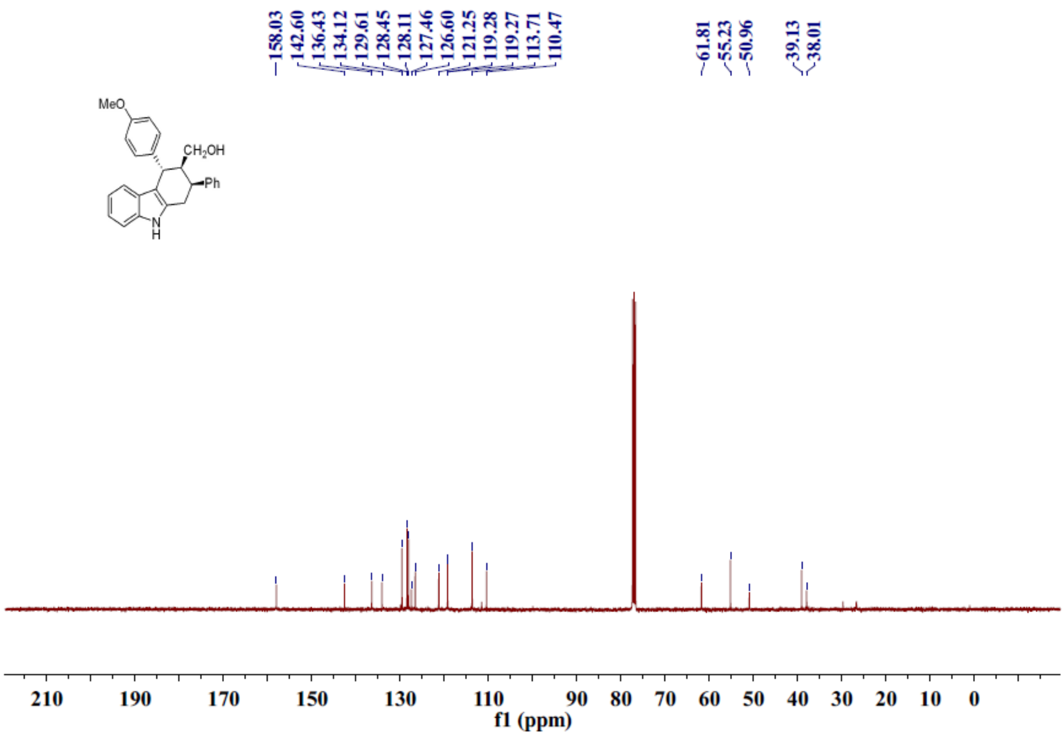
methyl4-(3-(hydroxymethyl)-2-phenyl-2,3,4,9-tetrahydro-1H-carbazol-4-yl)benzoate (4ka)



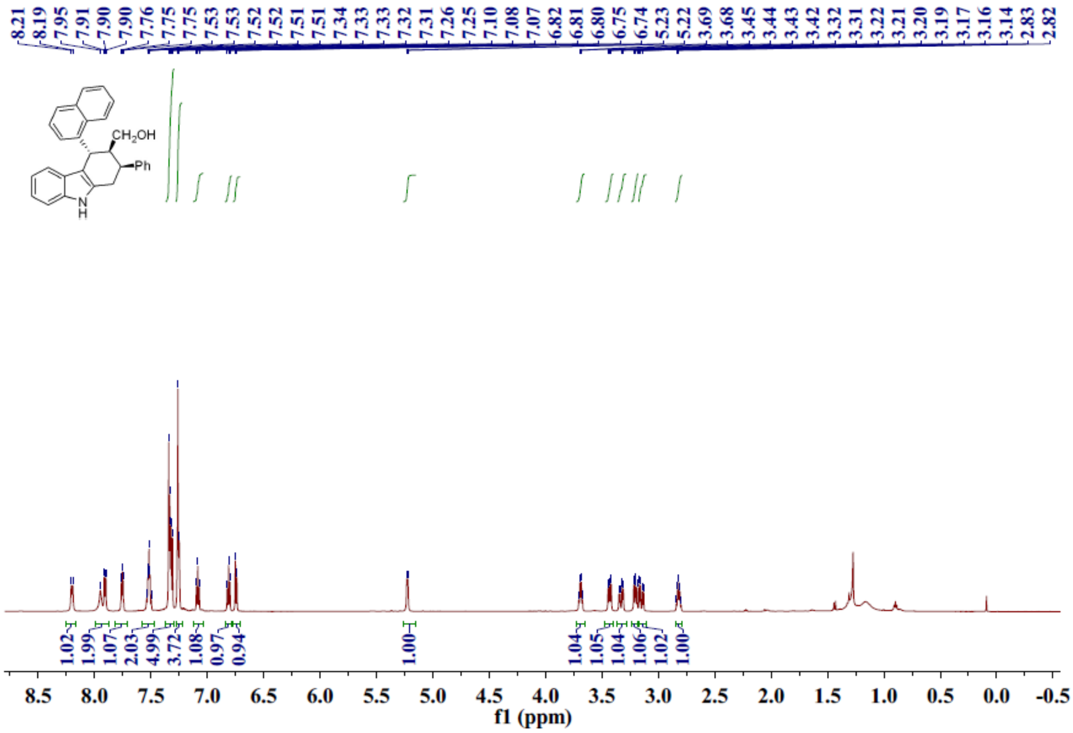


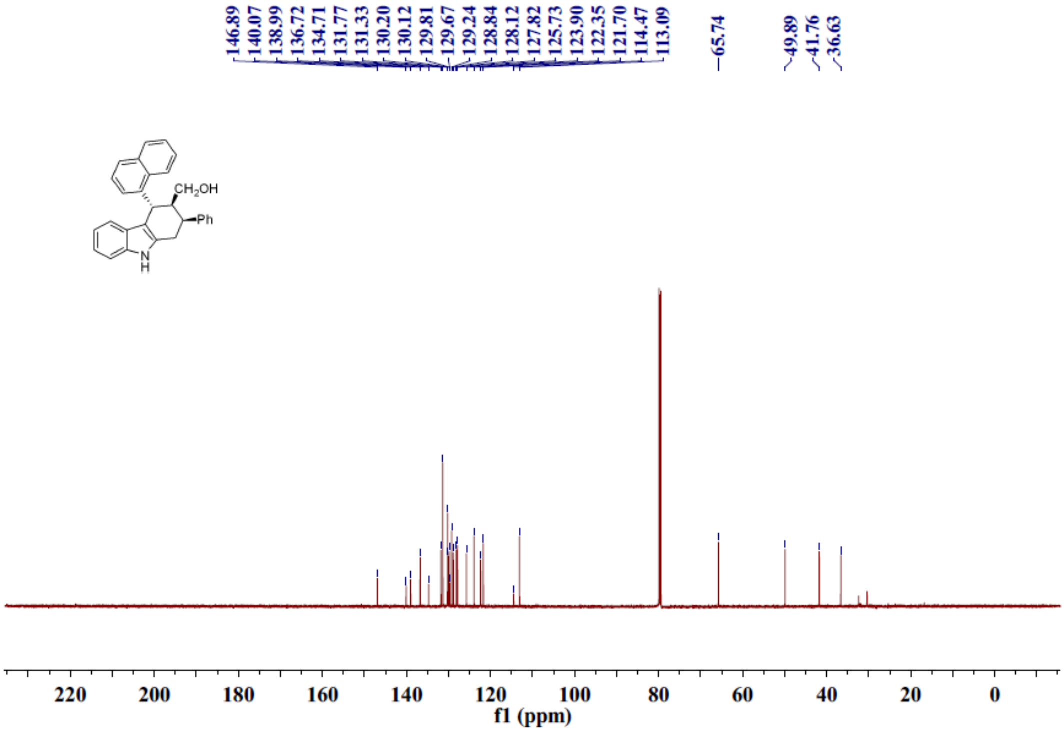
(4-(4-methoxyphenyl)-2-phenyl-2,3,4,9-tetrahydro-1H-carbazol-3-yl)methanol (4la)



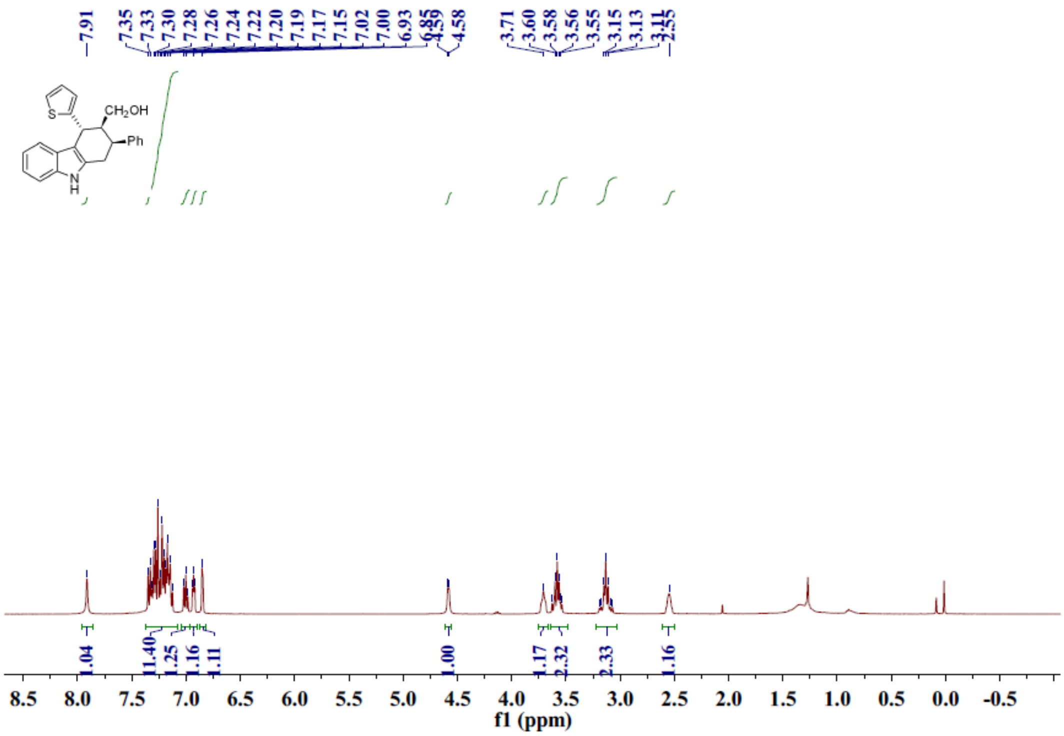


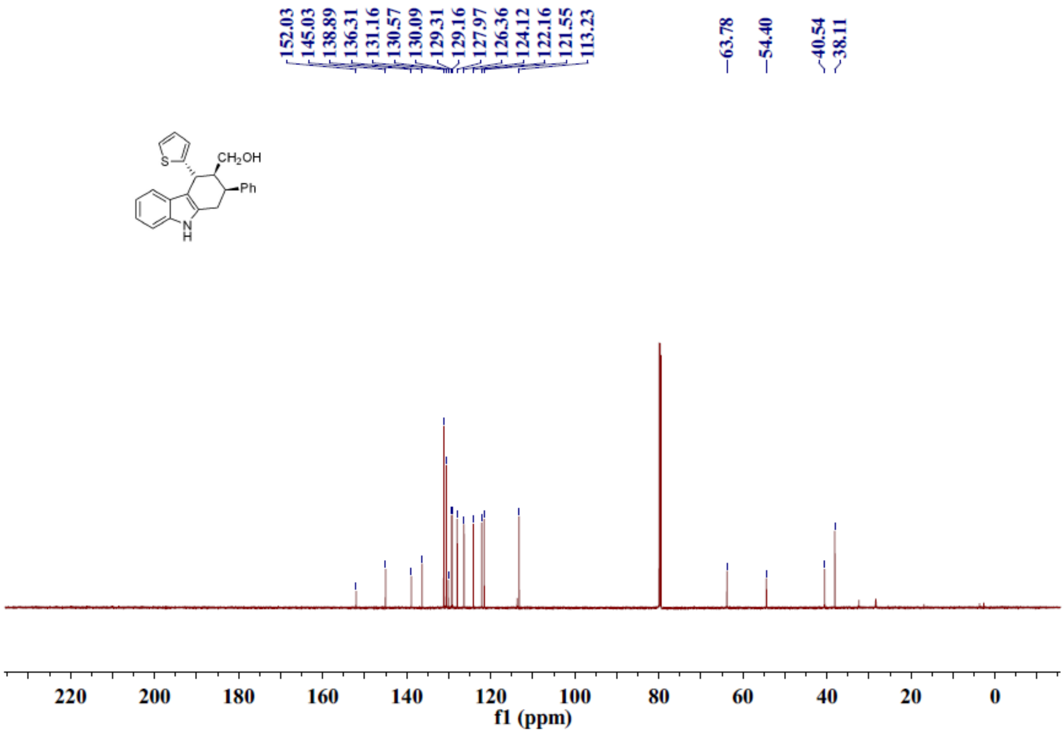
(4-(naphthalen-1-yl)-2-phenyl-2,3,4,9-tetrahydro-1H-carbazol-3-yl)methanol (4ma)



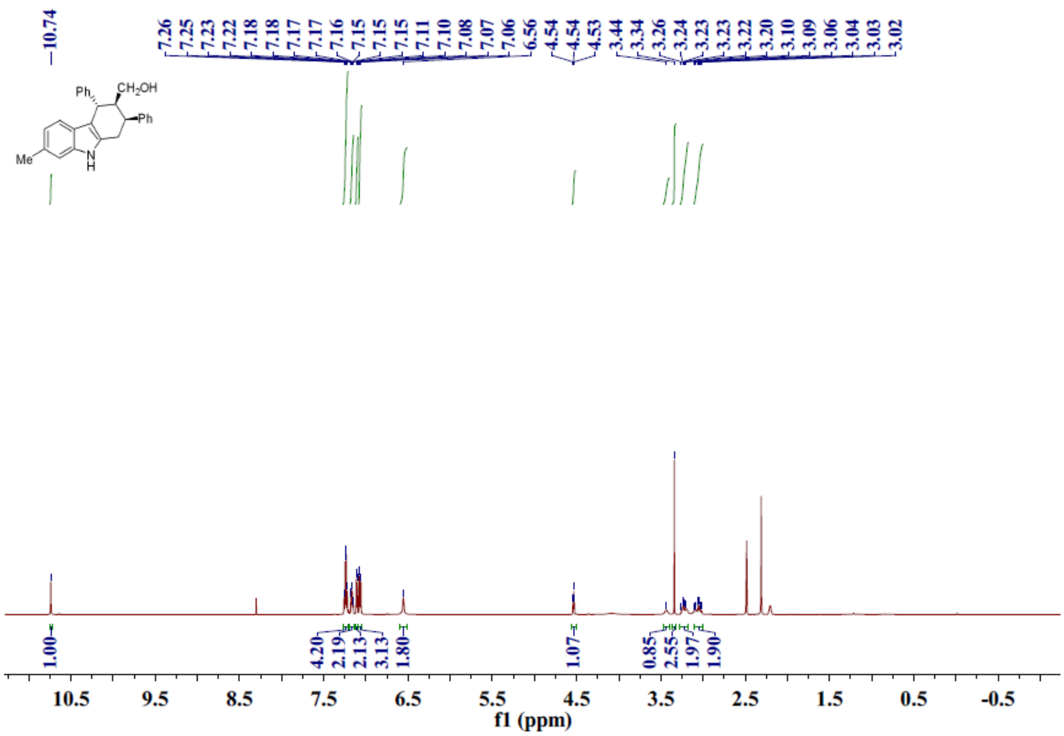


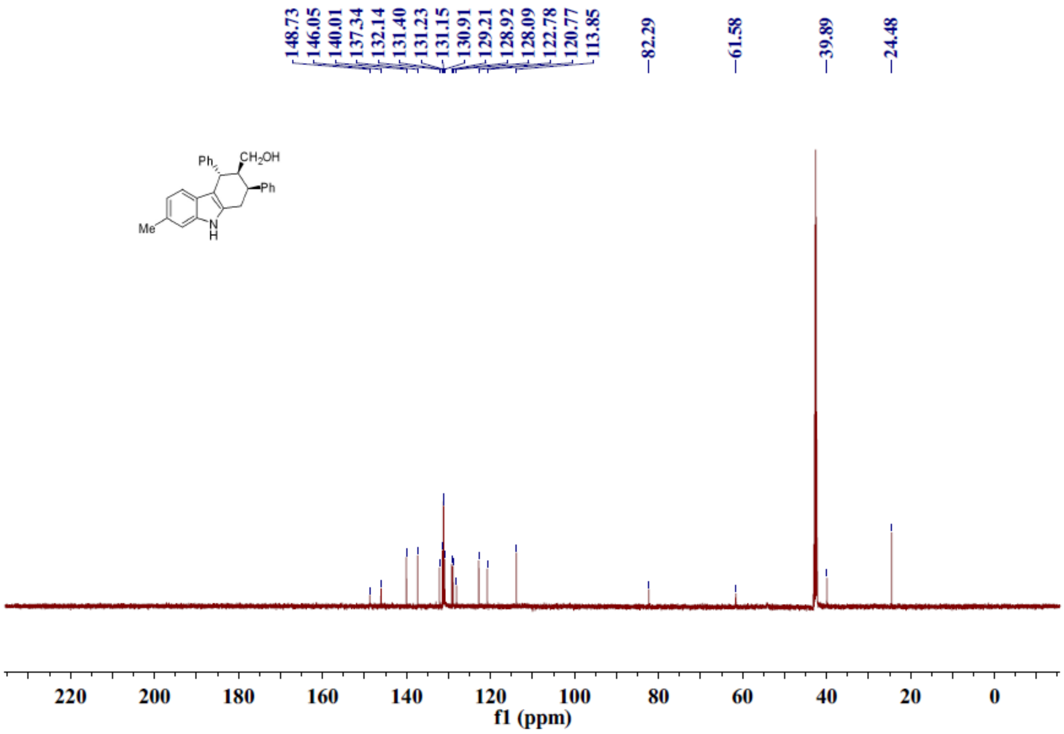
(2-phenyl-4-(thiophen-2-yl)-2,3,4,9-tetrahydro-1H-carbazol-3-yl)methanol (4na)



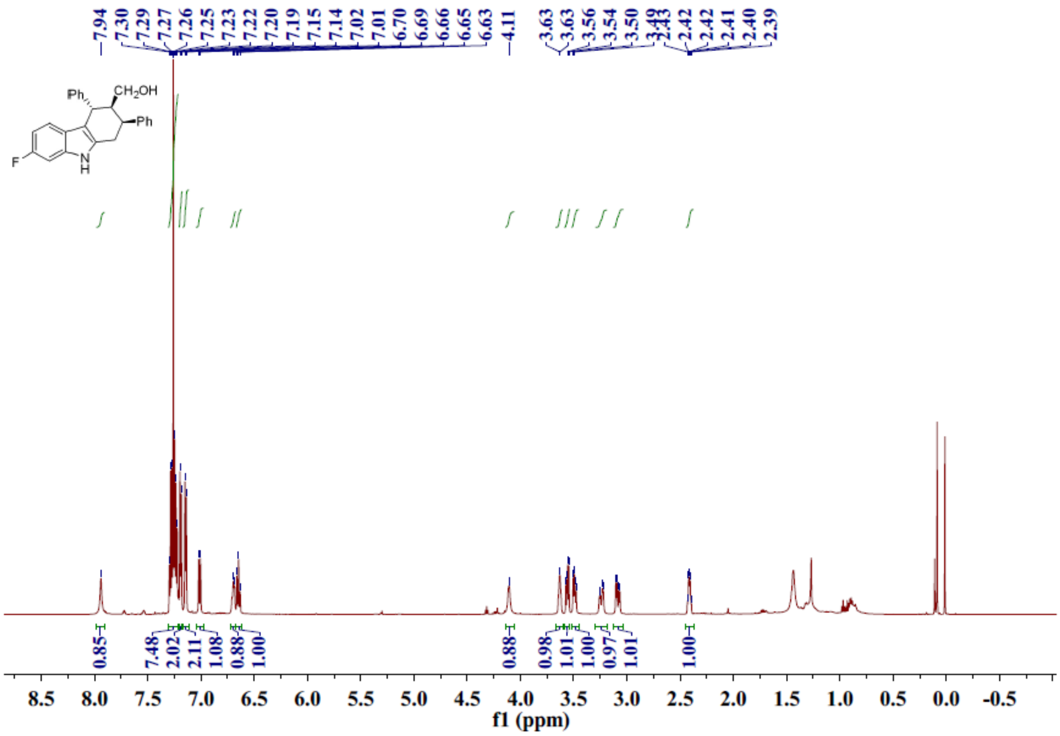


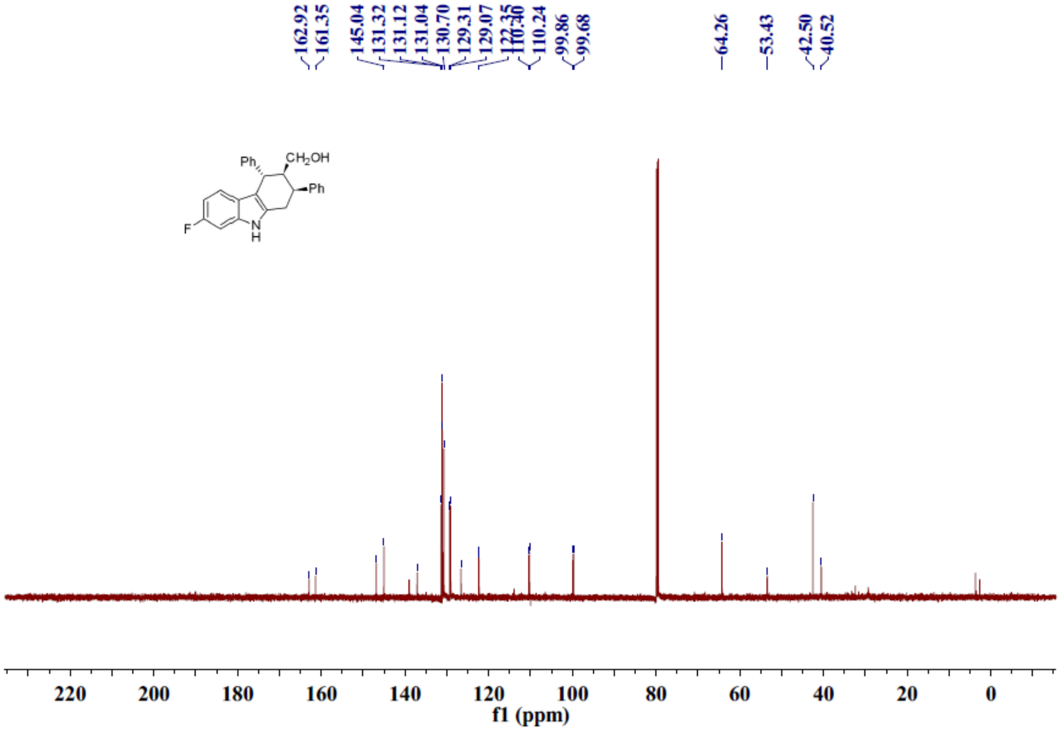
(7-methyl-2,4-diphenyl-2,3,4,9-tetrahydro-1H-carbazol-3-yl)methanol (4oa)



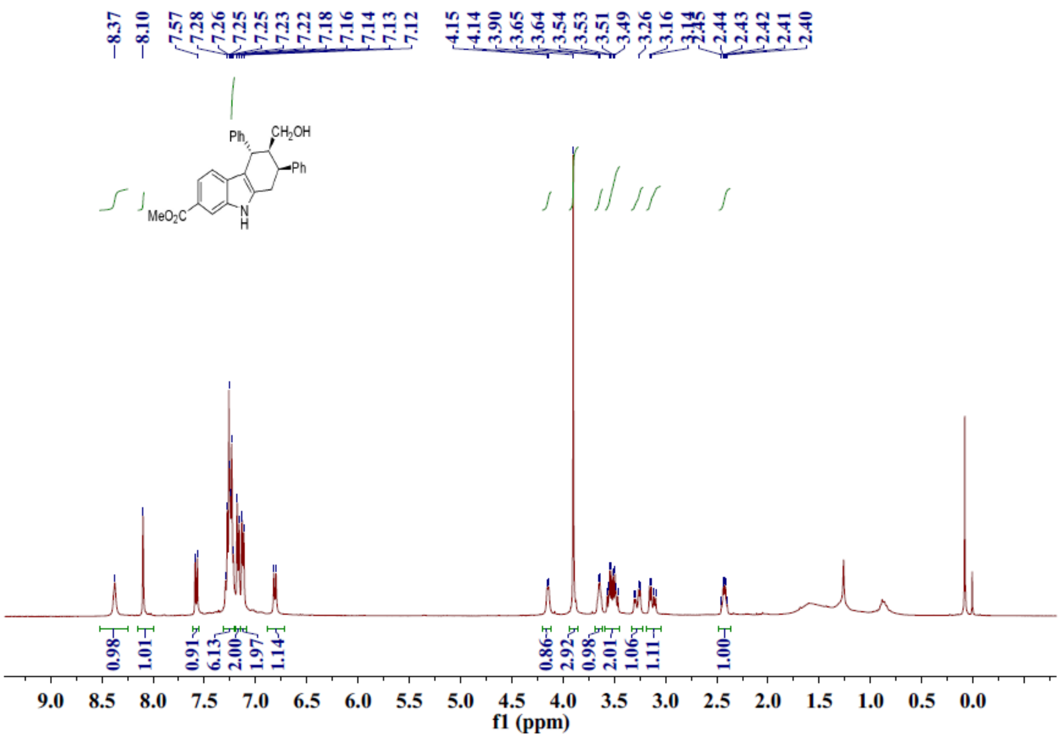


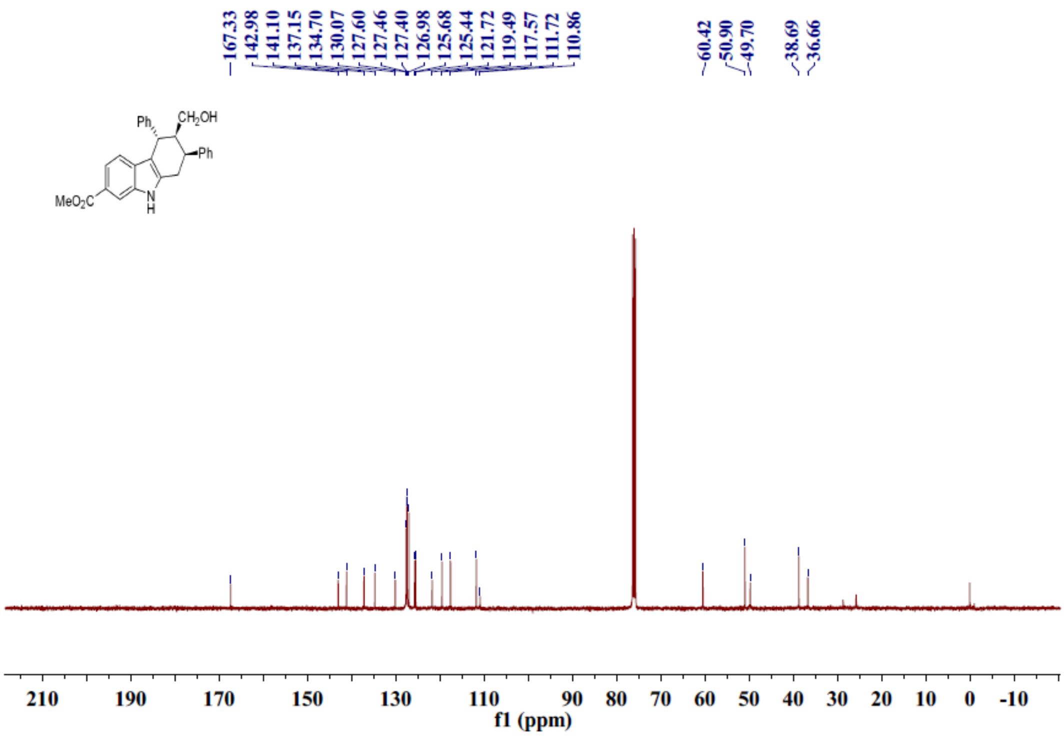
(7-fluoro-2,4-diphenyl-2,3,4,9-tetrahydro-1H-carbazol-3-yl)methanol (4pa)



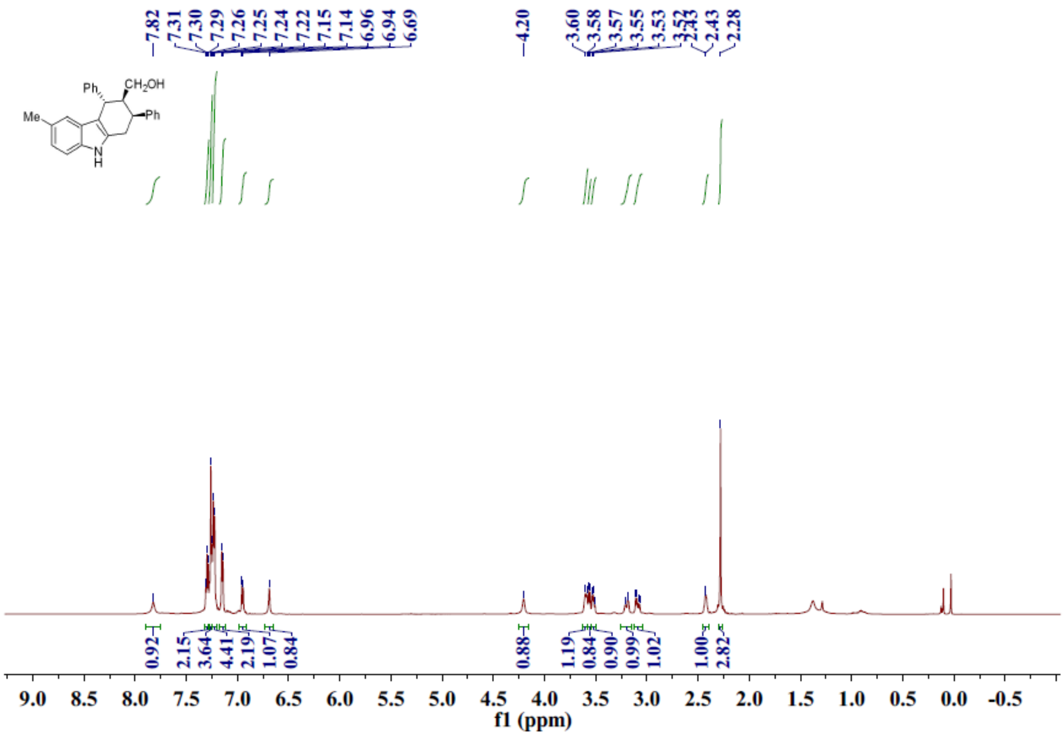


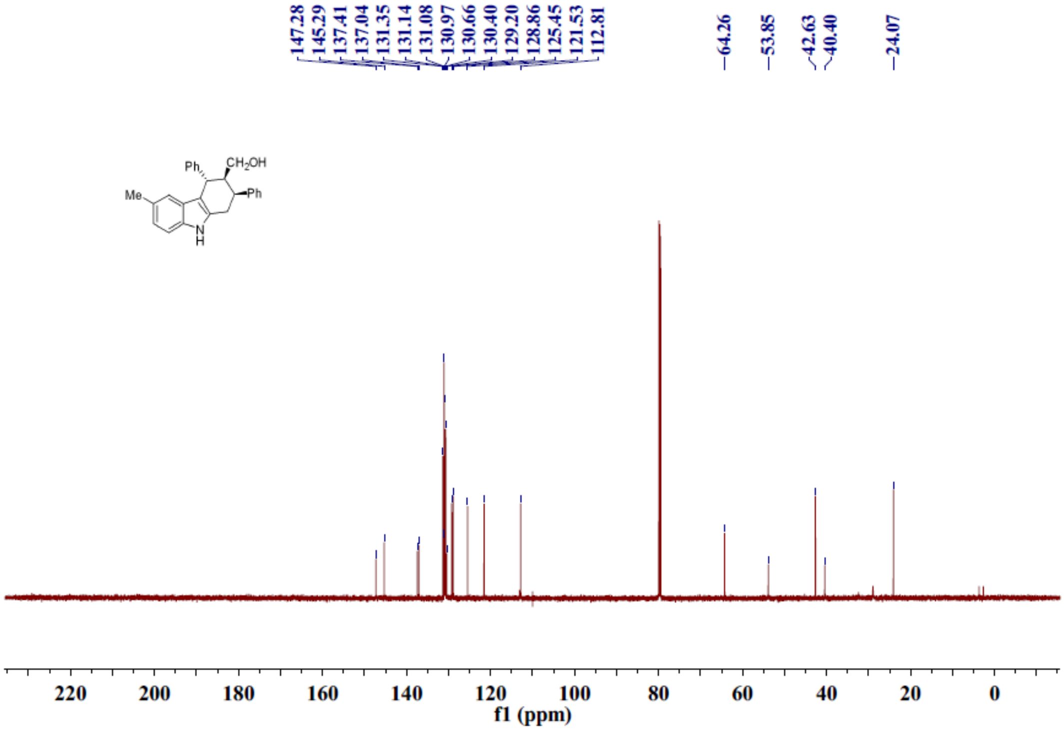
methyl-3-(hydroxymethyl)-2,4-diphenyl-2,3,4,9-tetrahydro-1H-carbazole-7-carboxylate (4qa)



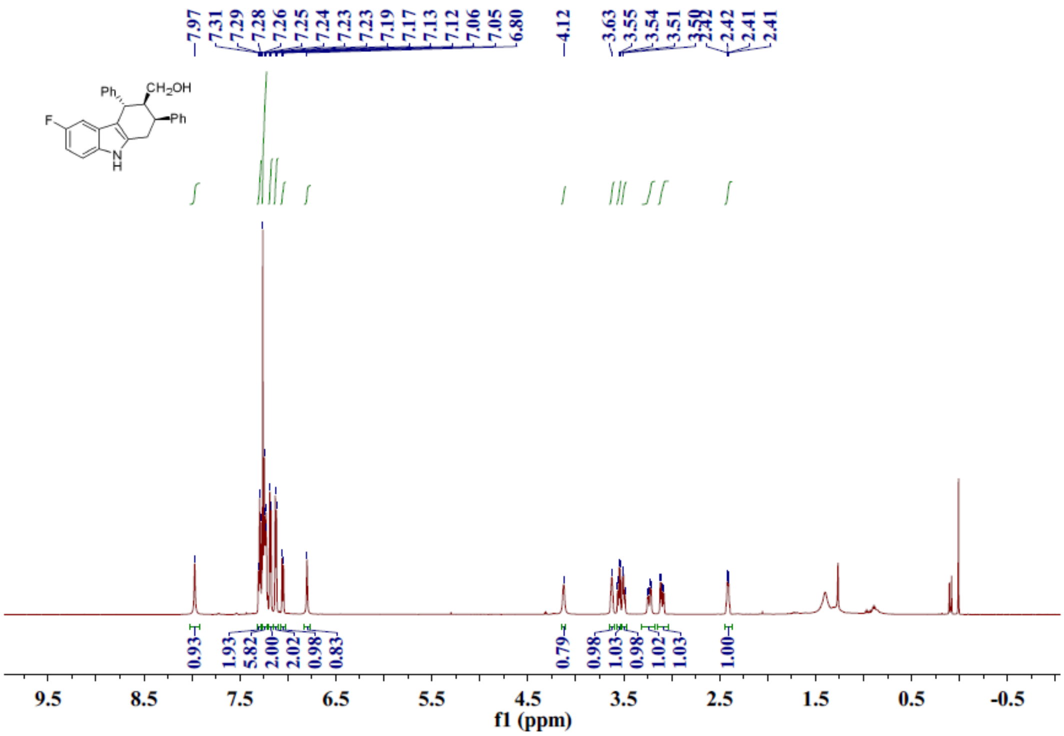


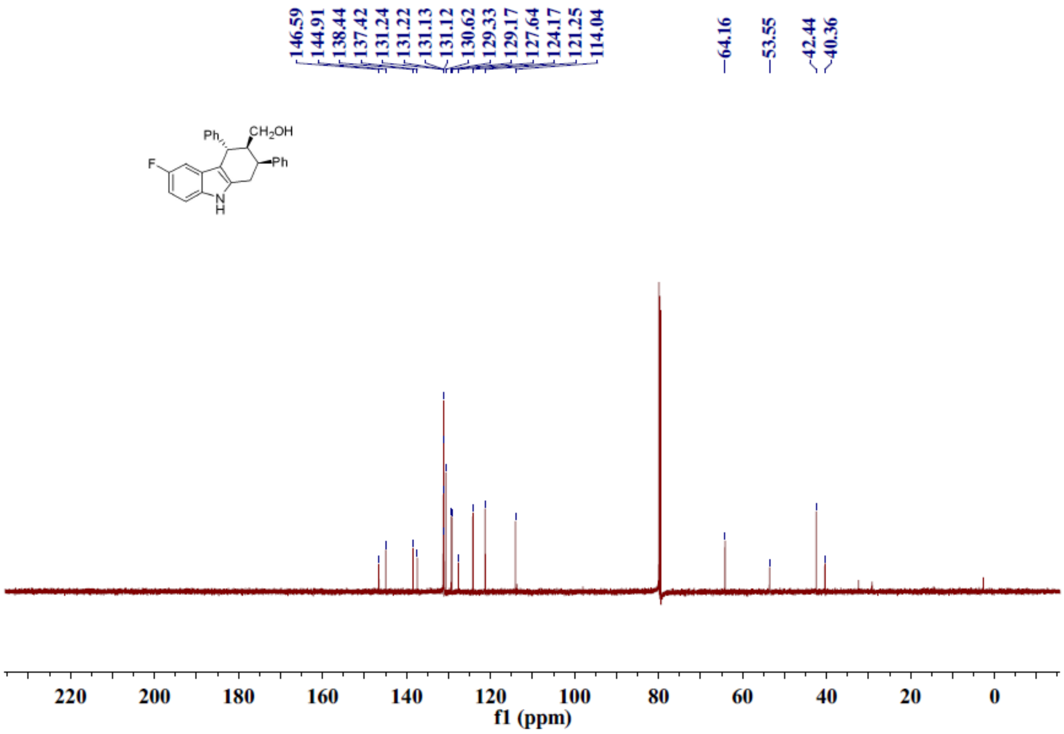
(6-methyl-2,4-diphenyl-2,3,4,9-tetrahydro-1H-carbazol-3-yl)methanol (4ra)



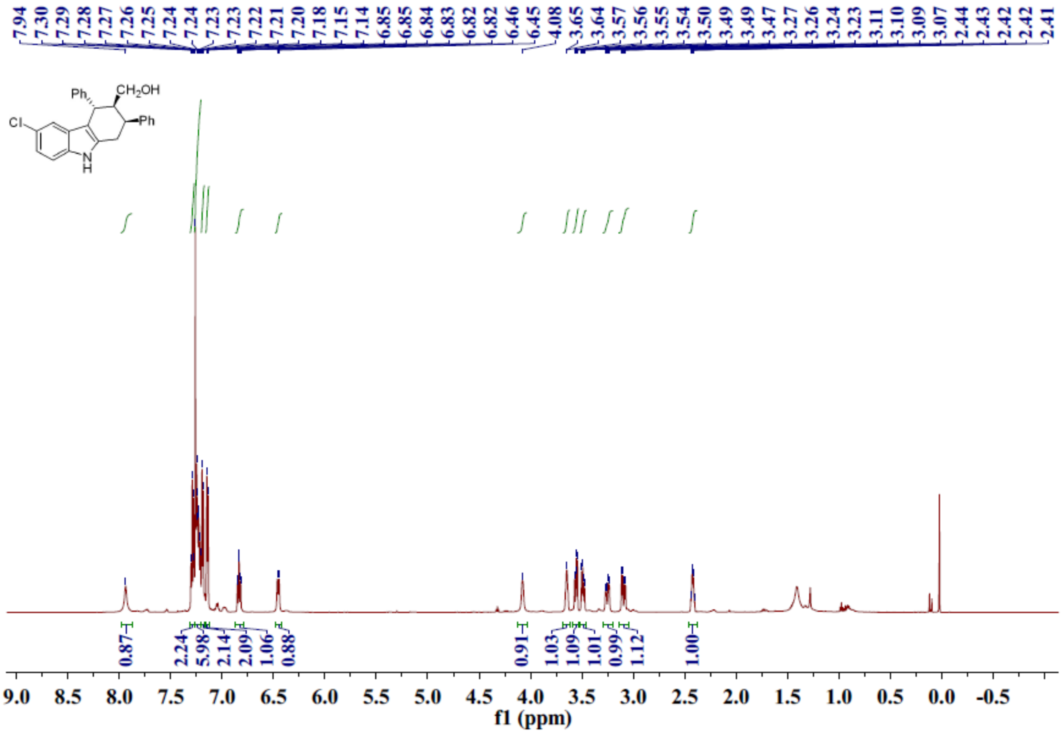


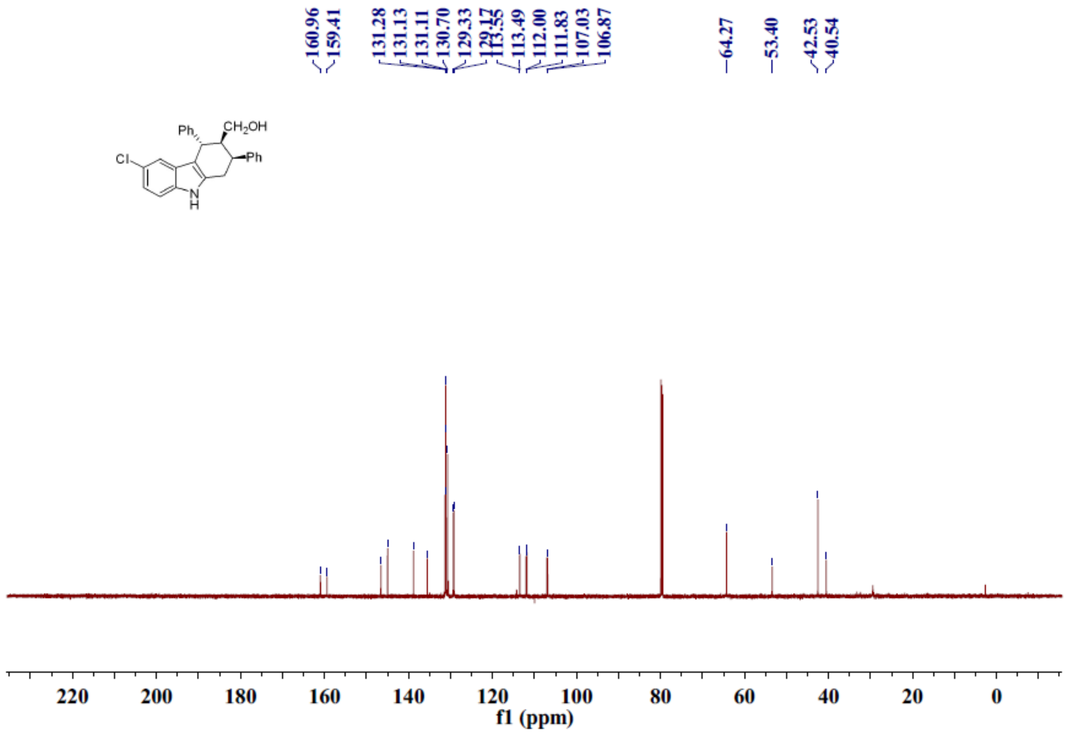
(6-fluoro-2,4-diphenyl-2,3,4,9-tetrahydro-1H-carbazol-3-yl)methanol (4sa)



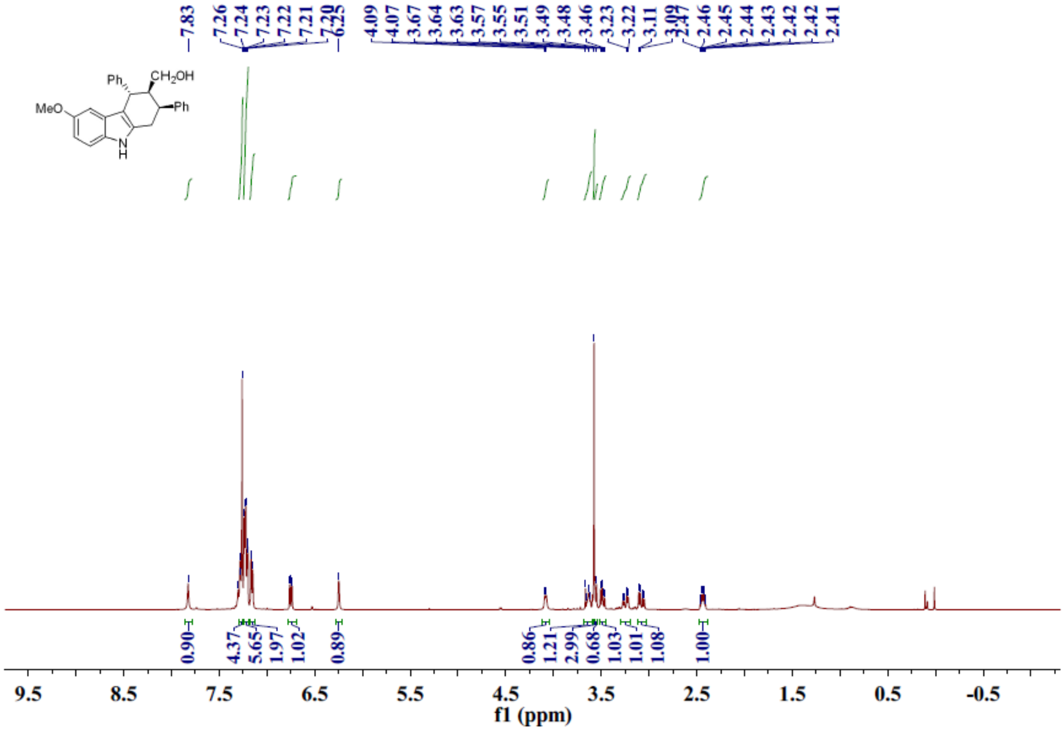


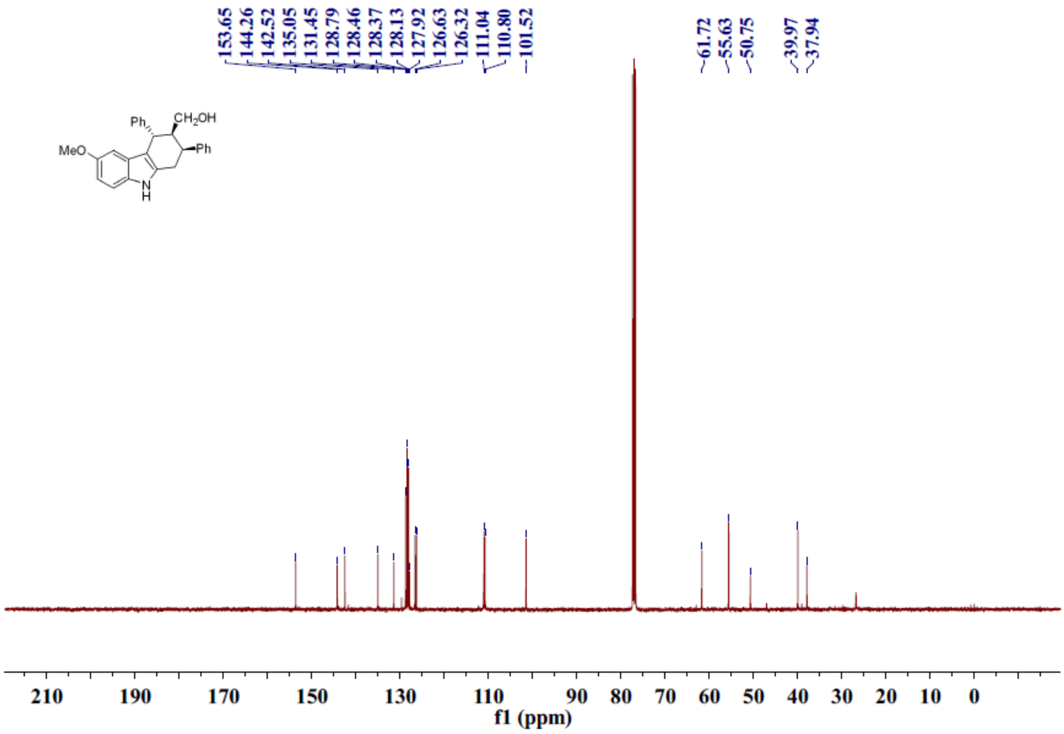
(6-chloro-2,4-diphenyl-2,3,4,9-tetrahydro-1H-carbazol-3-yl)methanol (4ta)



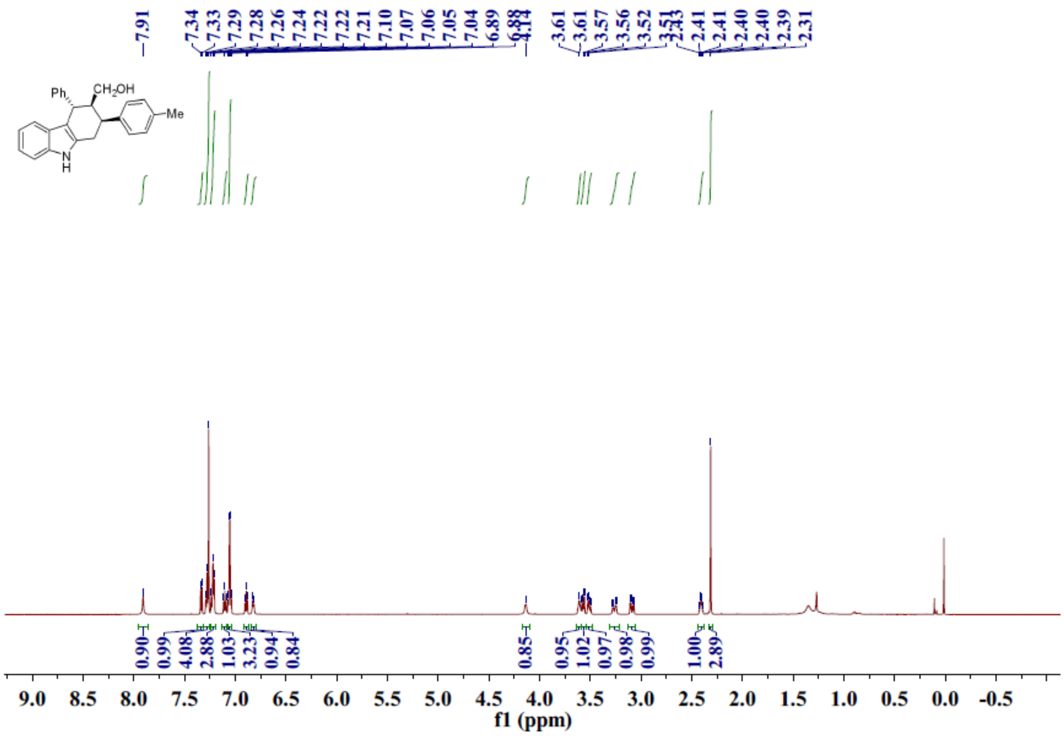


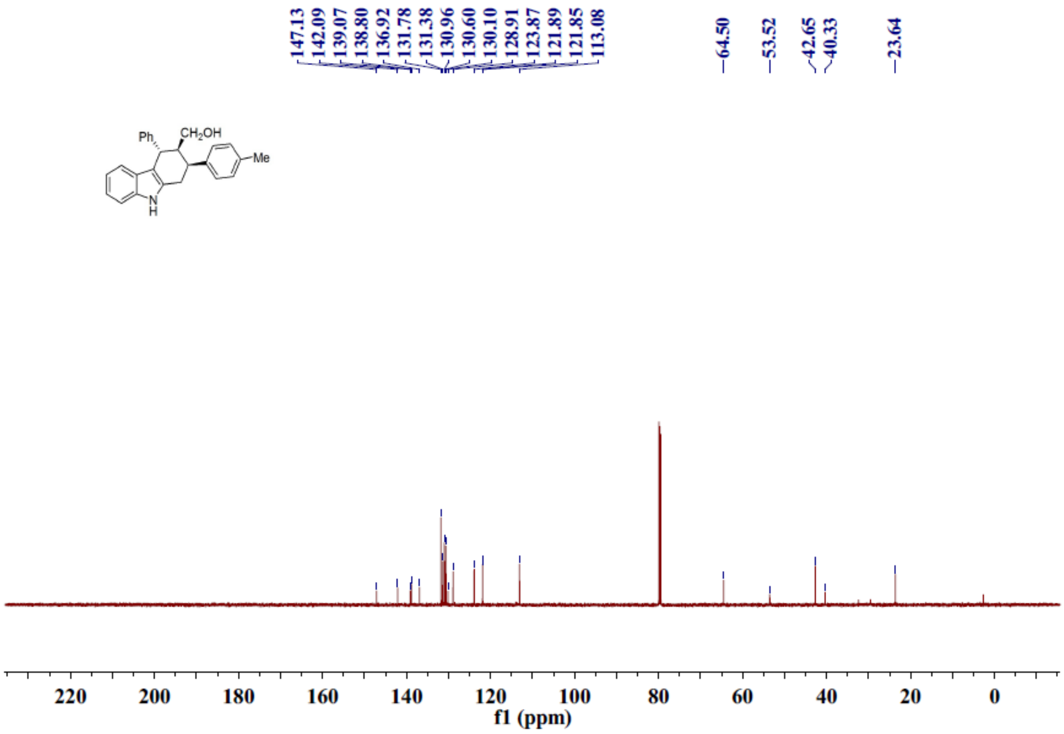
(6-methoxy-2,4-diphenyl-2,3,4,9-tetrahydro-1H-carbazol-3-yl)methanol (4ua)



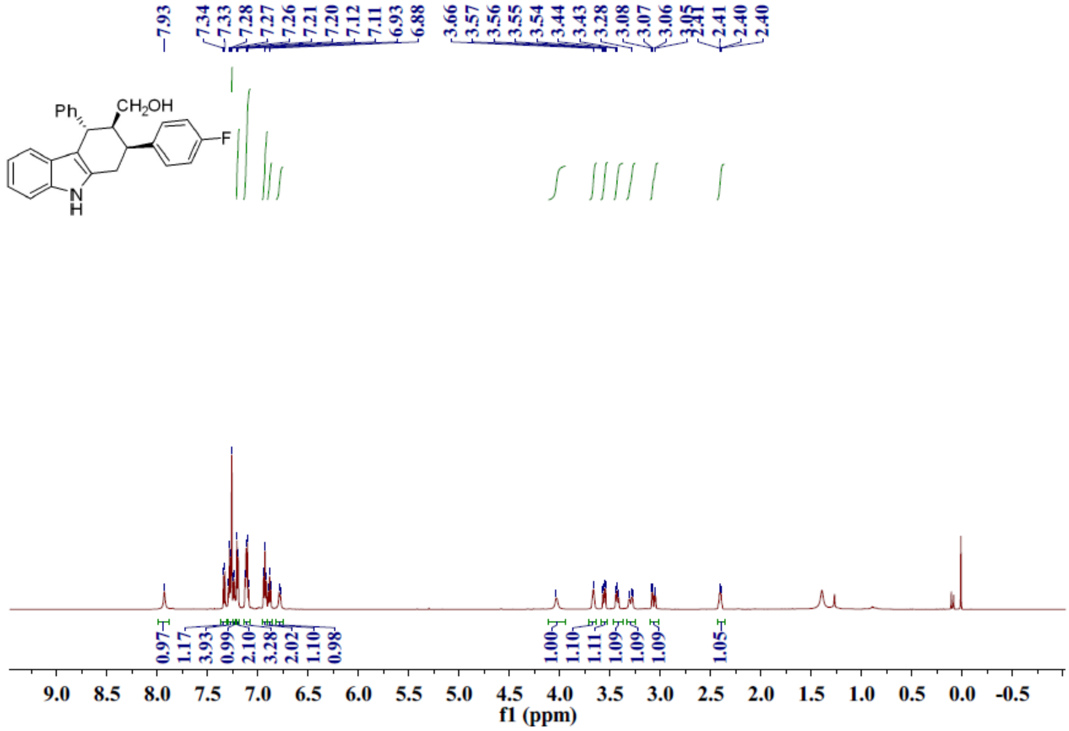


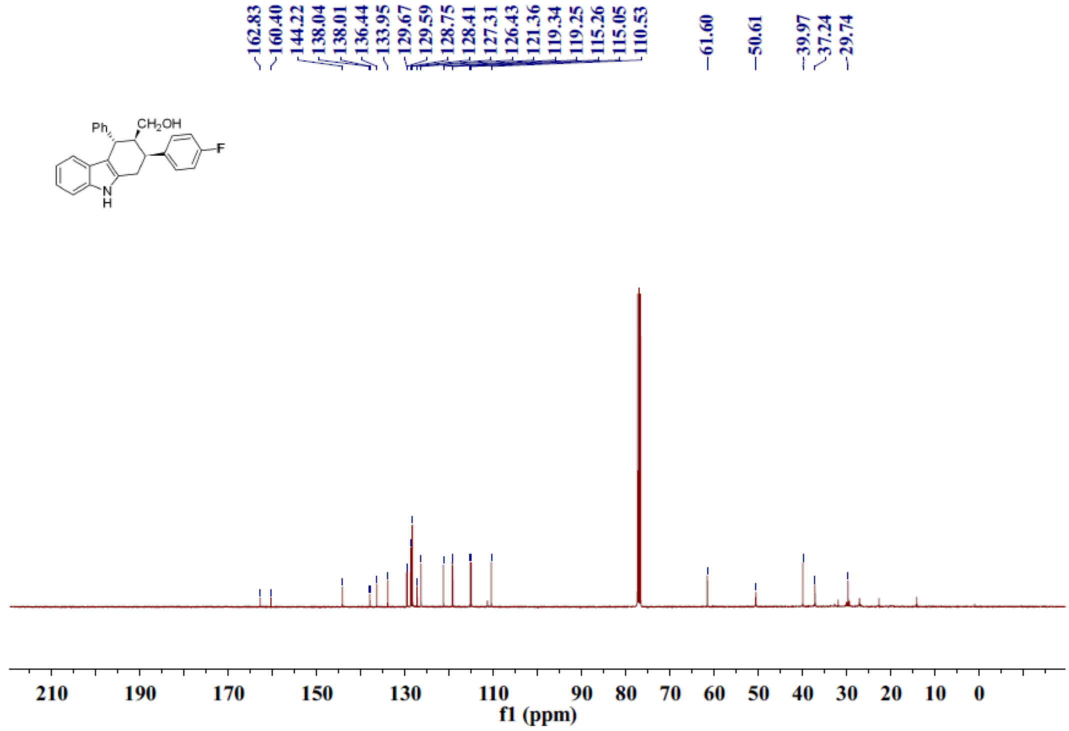
(4-phenyl-2-(p-tolyl)-2,3,4,9-tetrahydro-1H-carbazol-3-yl)methanol (4ab)



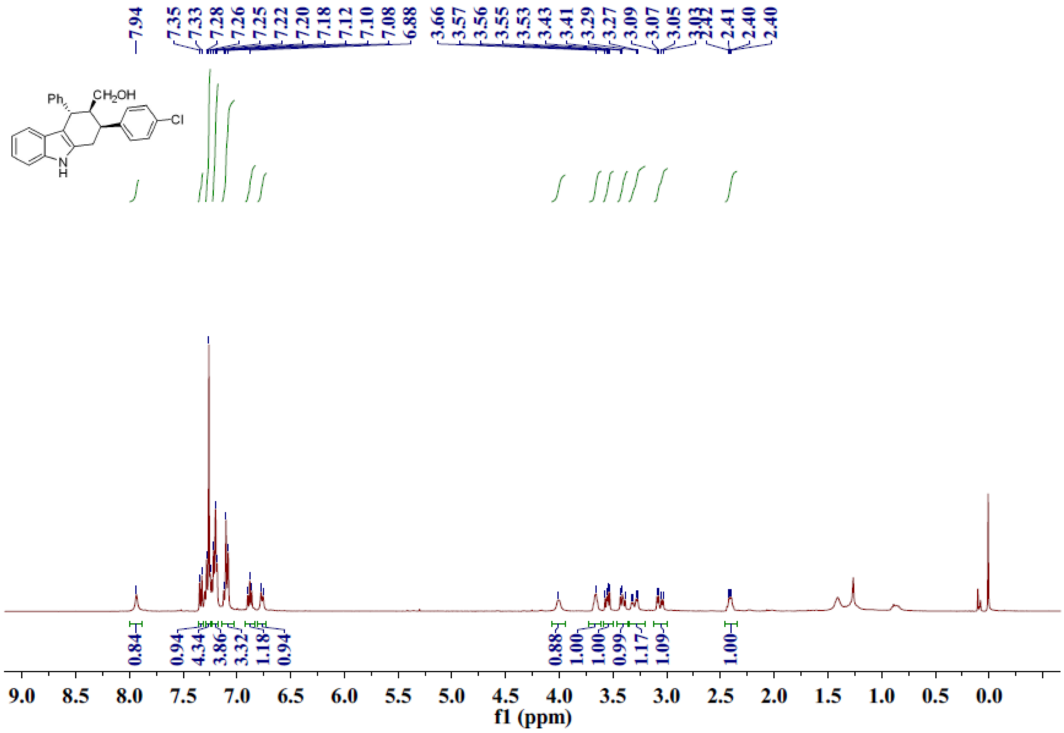


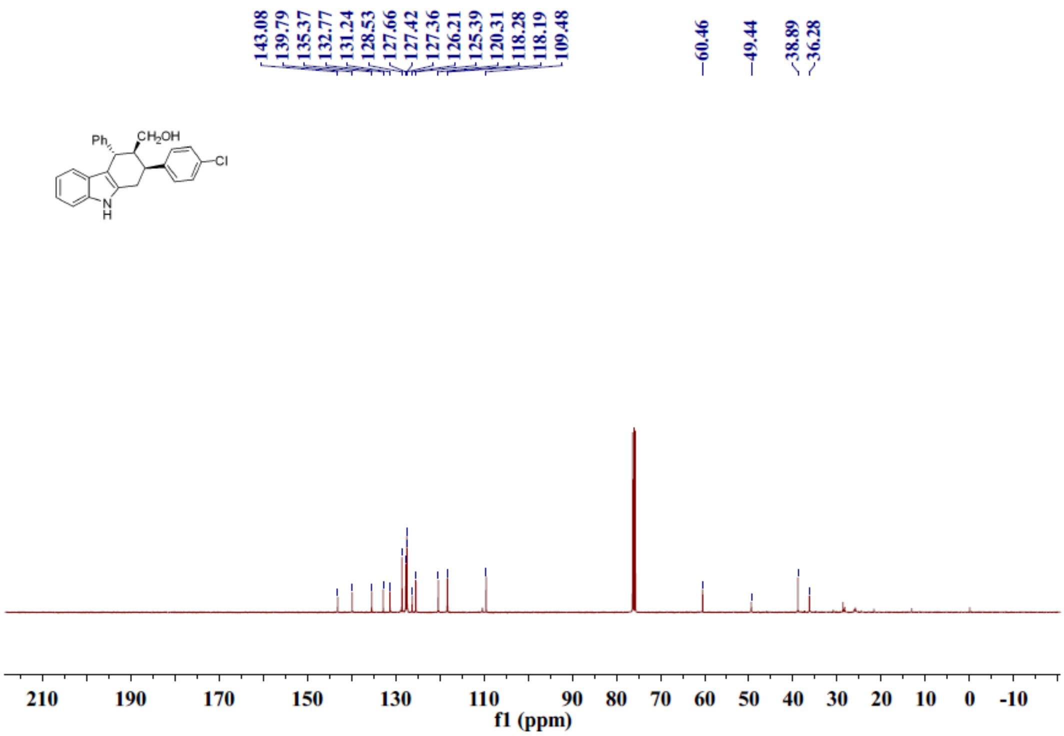
(2-(4-fluorophenyl)-4-phenyl-2,3,4,9-tetrahydro-1H-carbazol-3-yl)methanol (4ac)



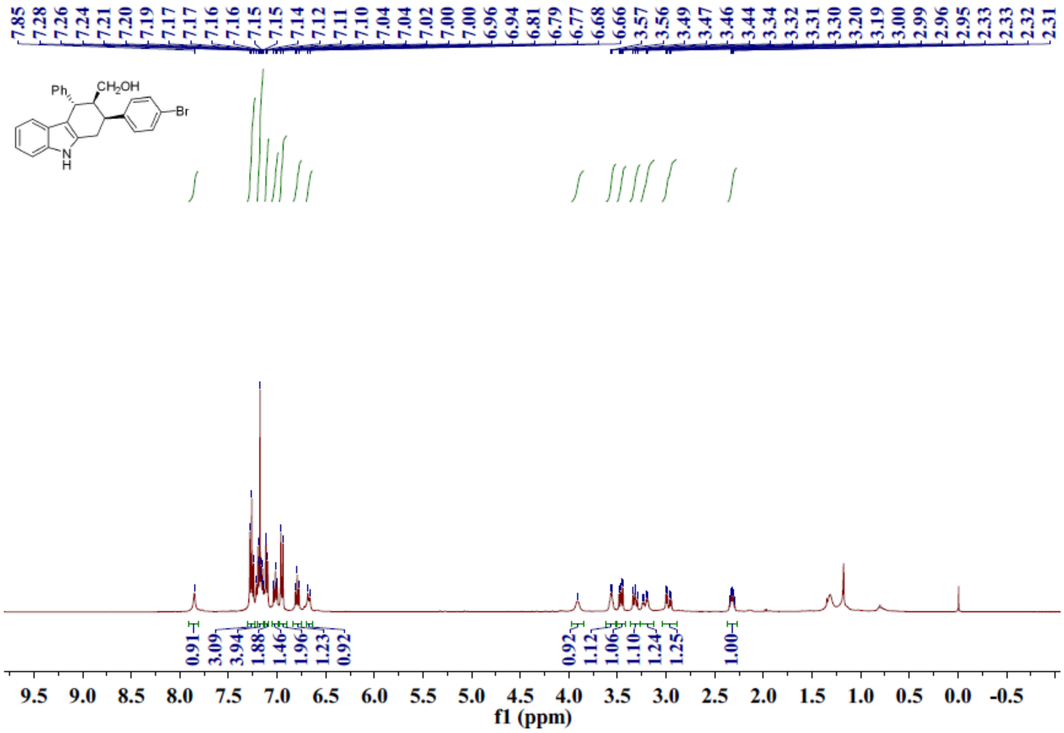


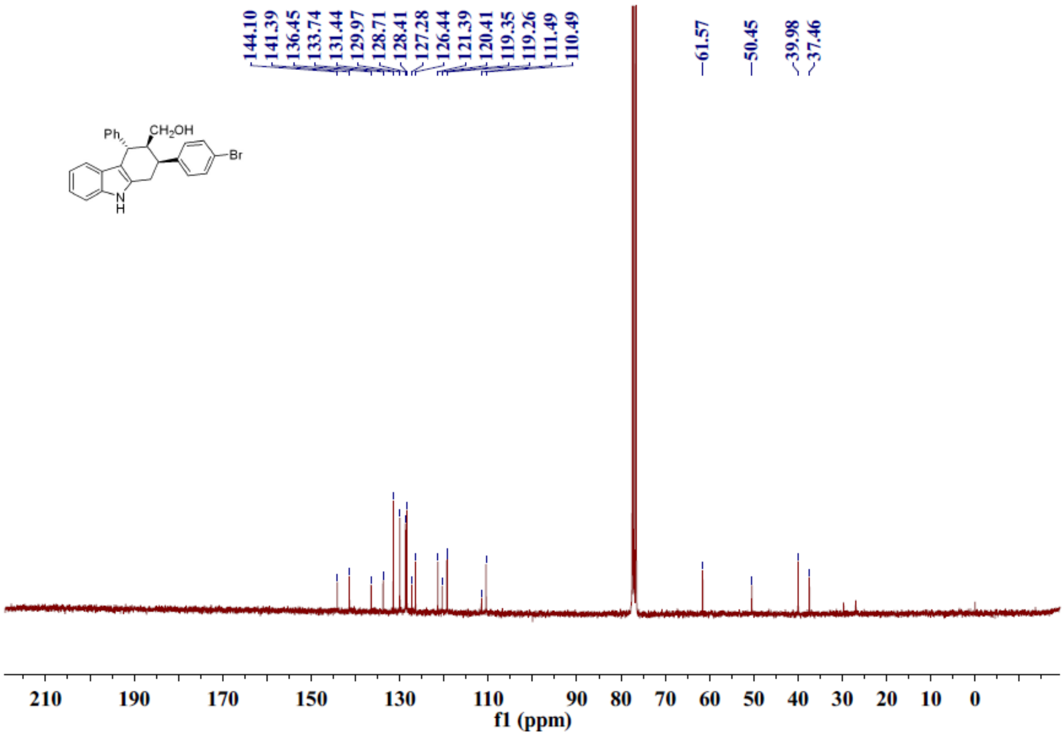
(2-(4-chlorophenyl)-4-phenyl-2,3,4,9-tetrahydro-1H-carbazol-3-yl)methanol (4ad)



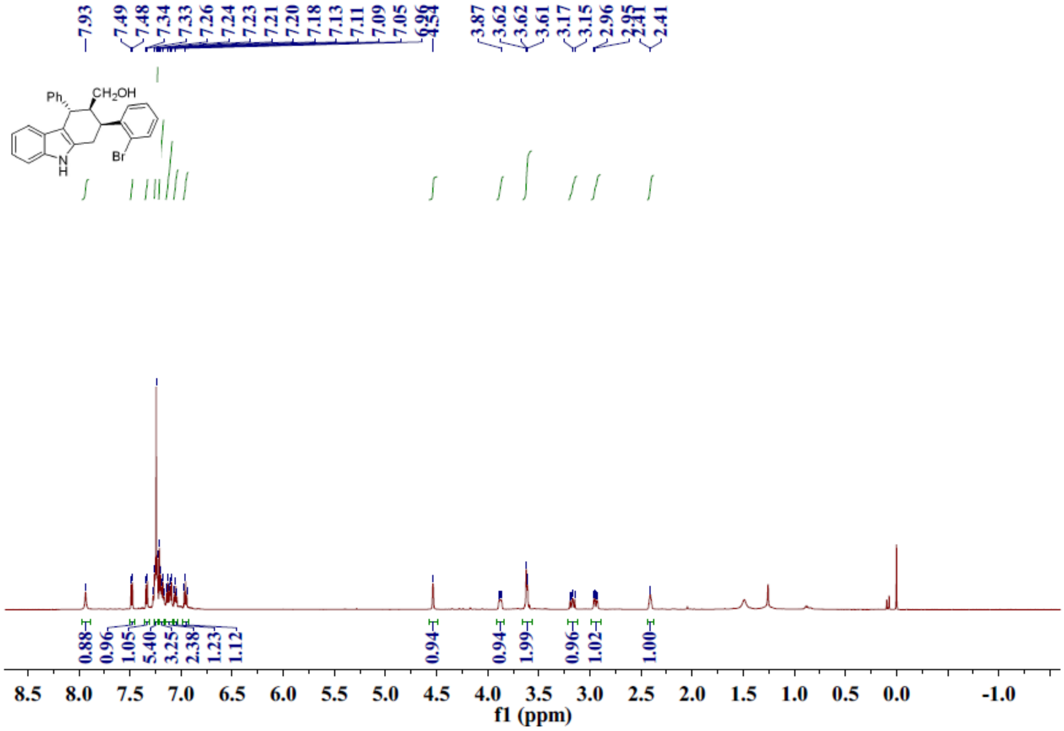


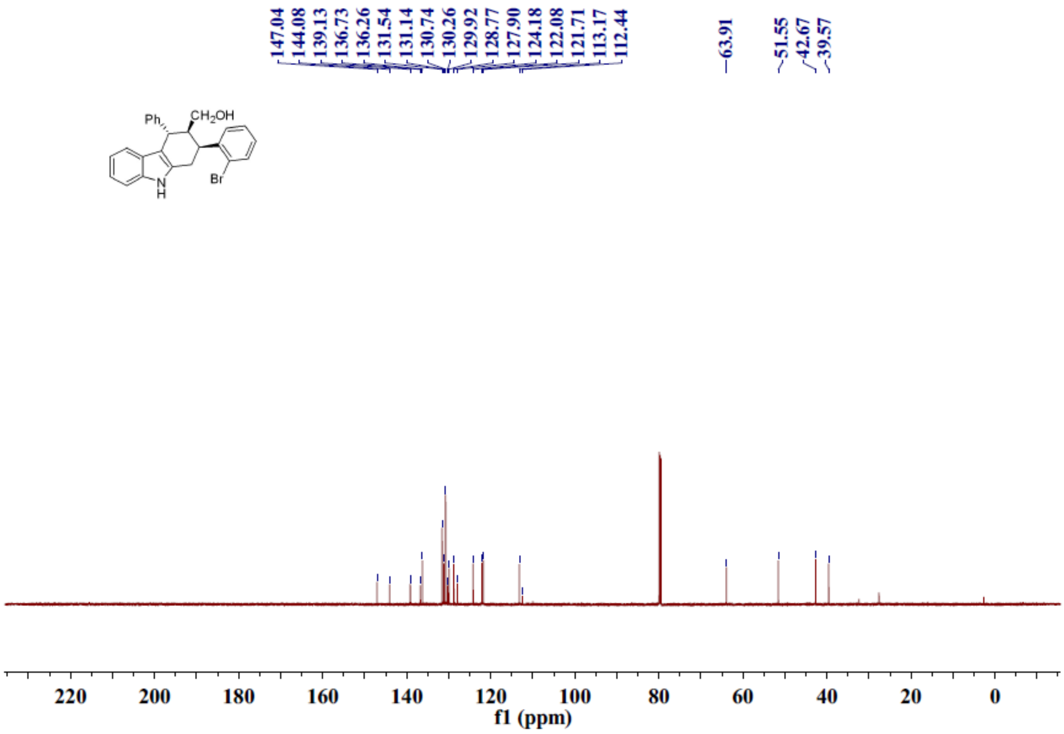
(2-(4-bromophenyl)-4-phenyl-2,3,4,9-tetrahydro-1H-carbazol-3-yl)methanol (4ae)



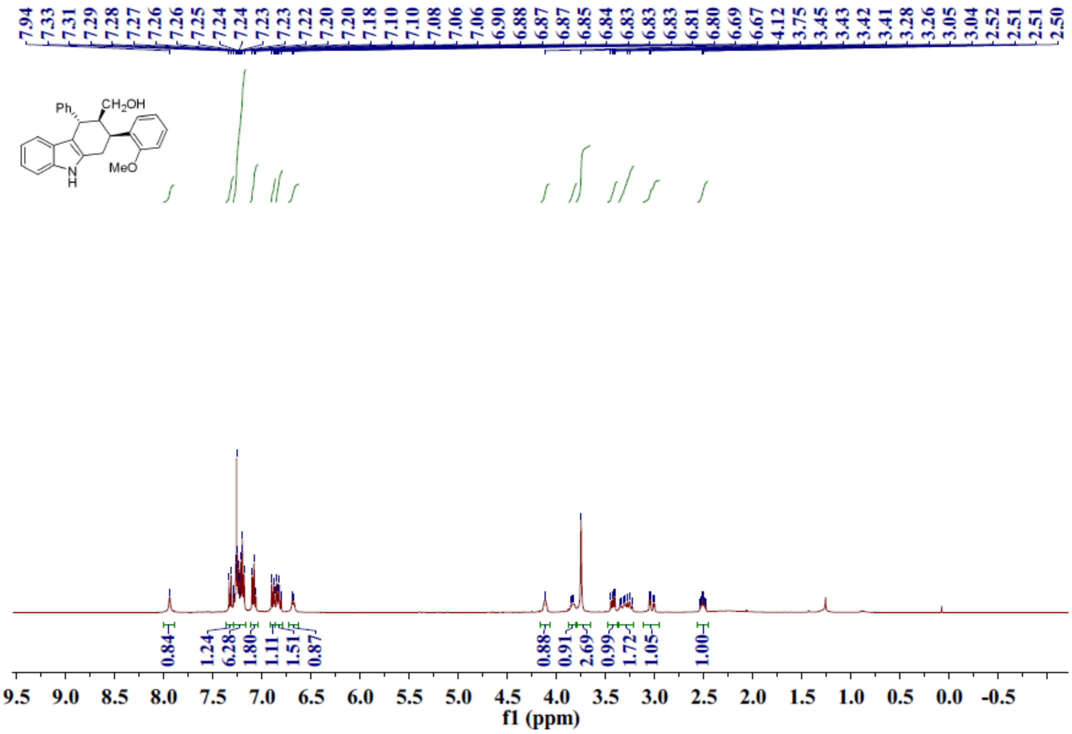


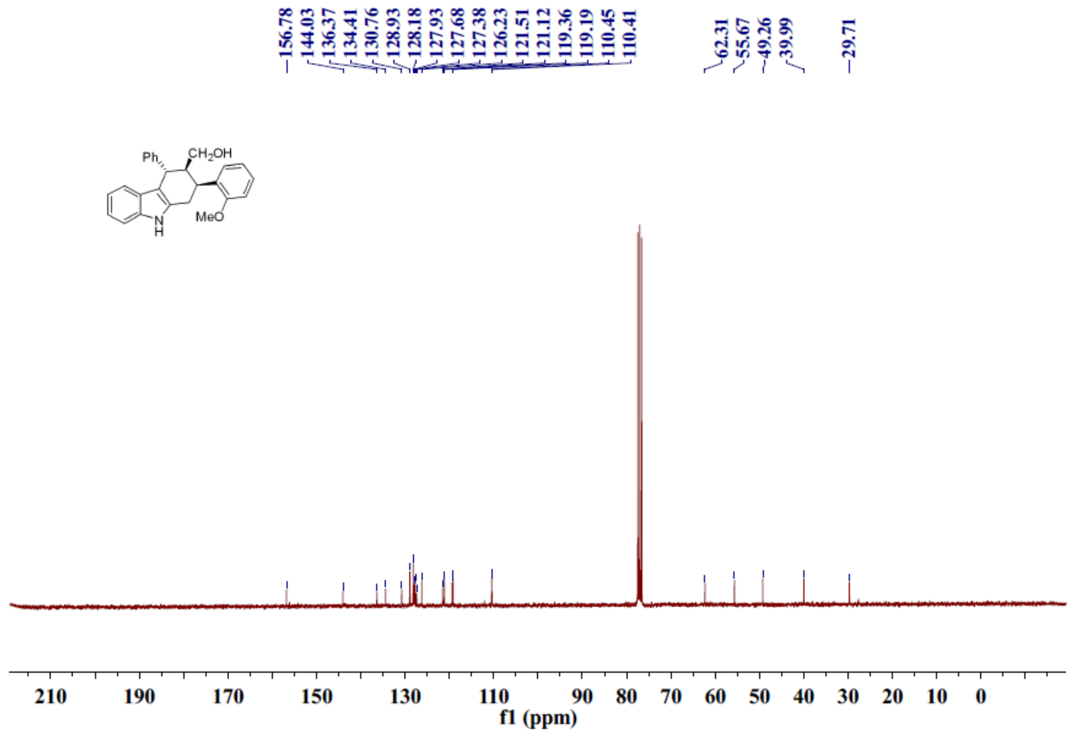
(2-(2-bromophenyl)-4-phenyl-2,3,4,9-tetrahydro-1H-carbazol-3-yl)methanol (4af)



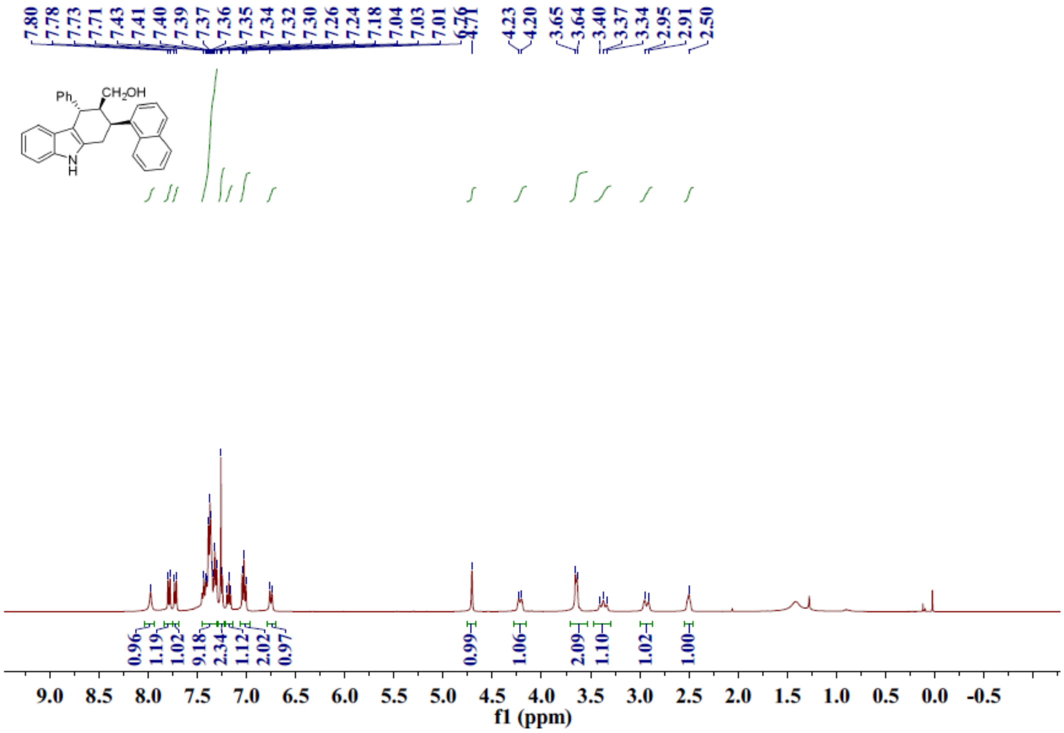


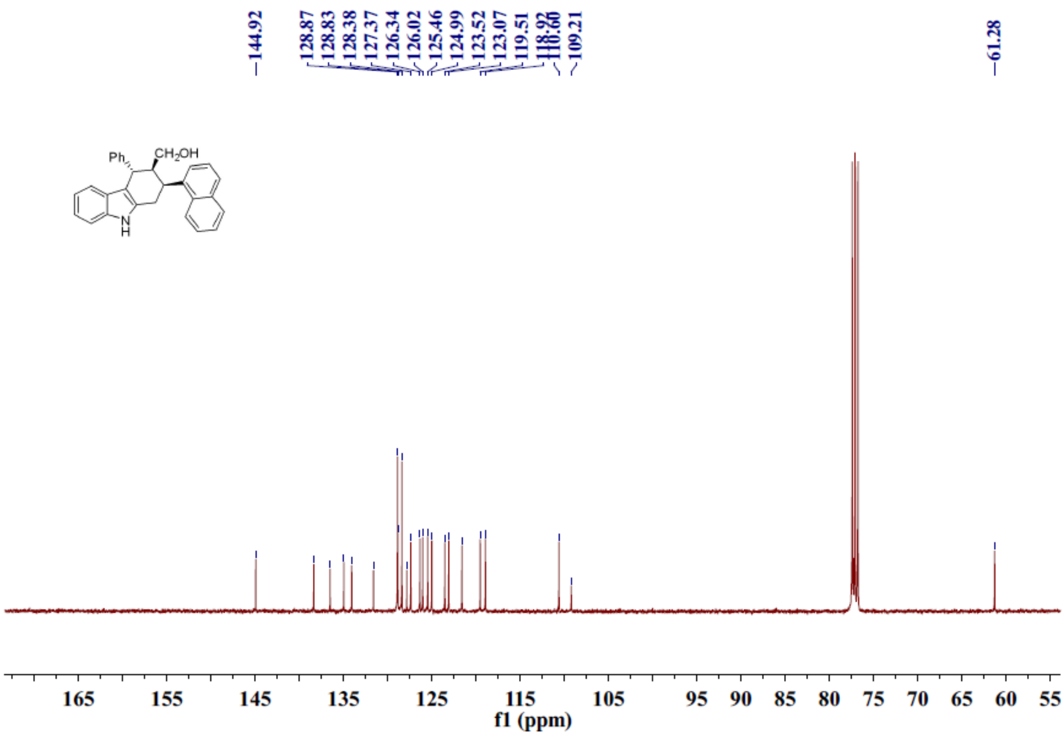
(4-phenyl-2-(o-tolyl)-2,3,4,9-tetrahydro-1H-carbazol-3-yl)methanol (4ag)



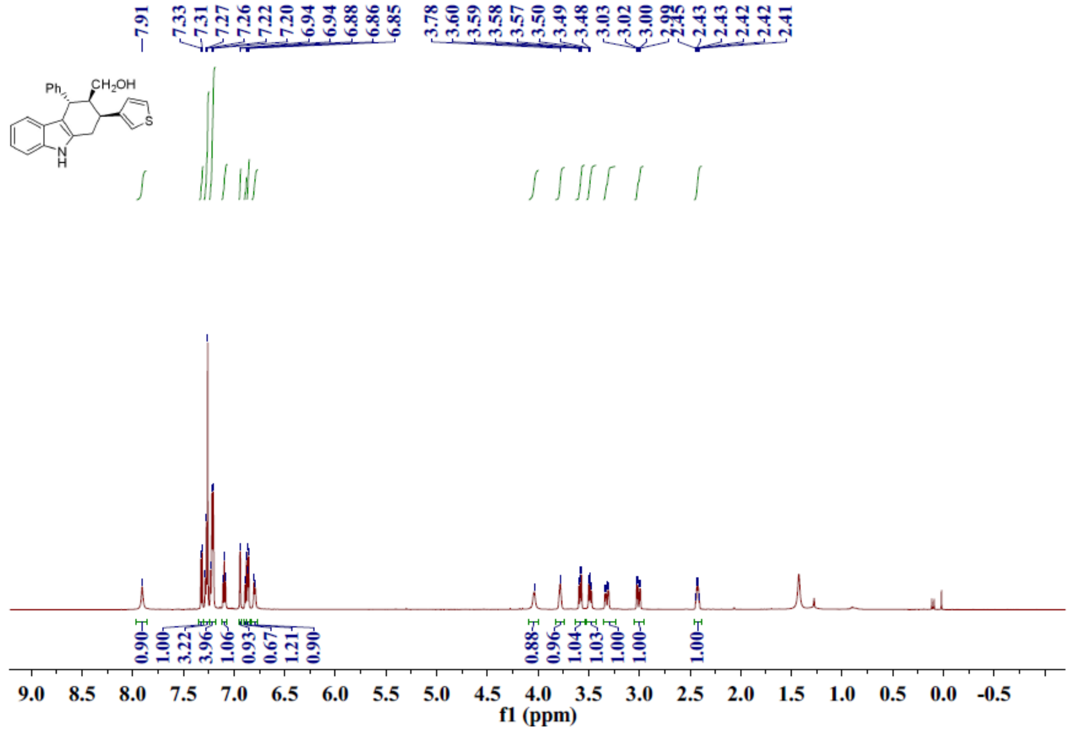


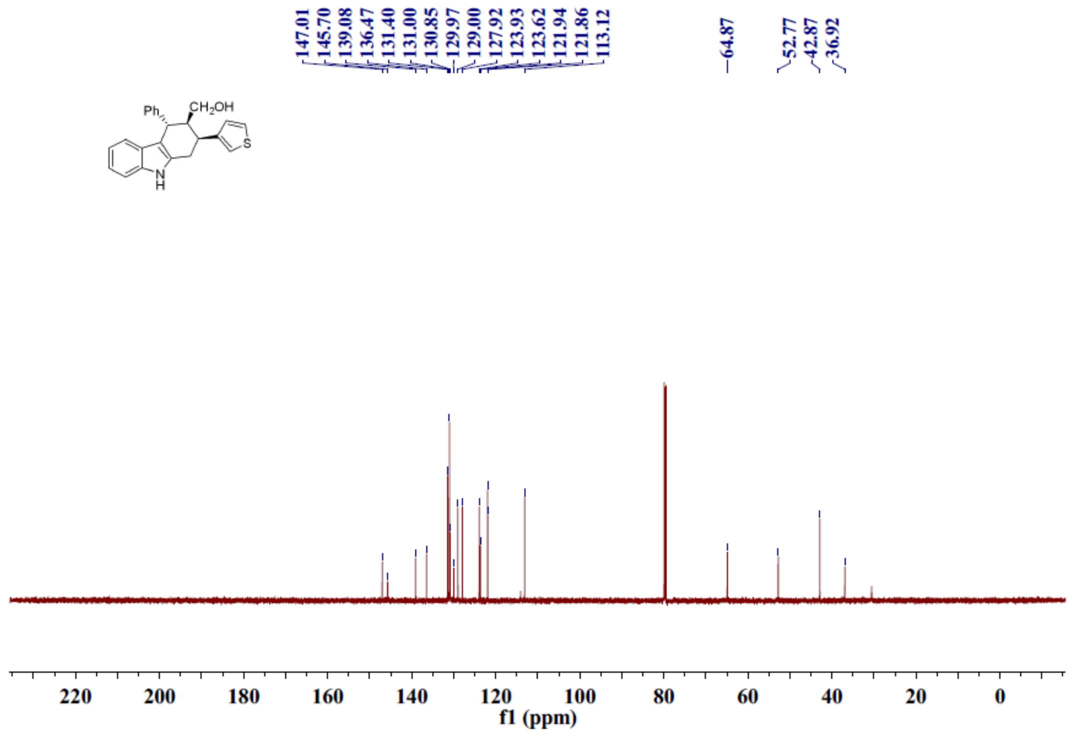
(2-(naphthalen-1-yl)-4-phenyl-2,3,4,9-tetrahydro-1H-carbazol-3-yl)methanol (4ah)



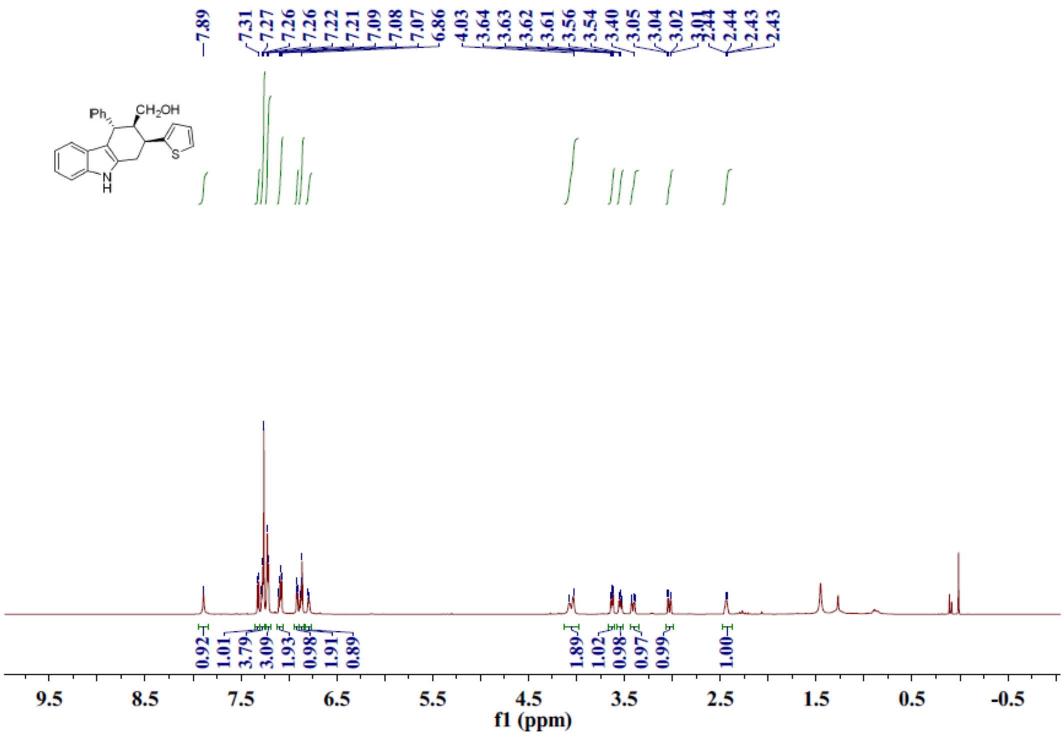


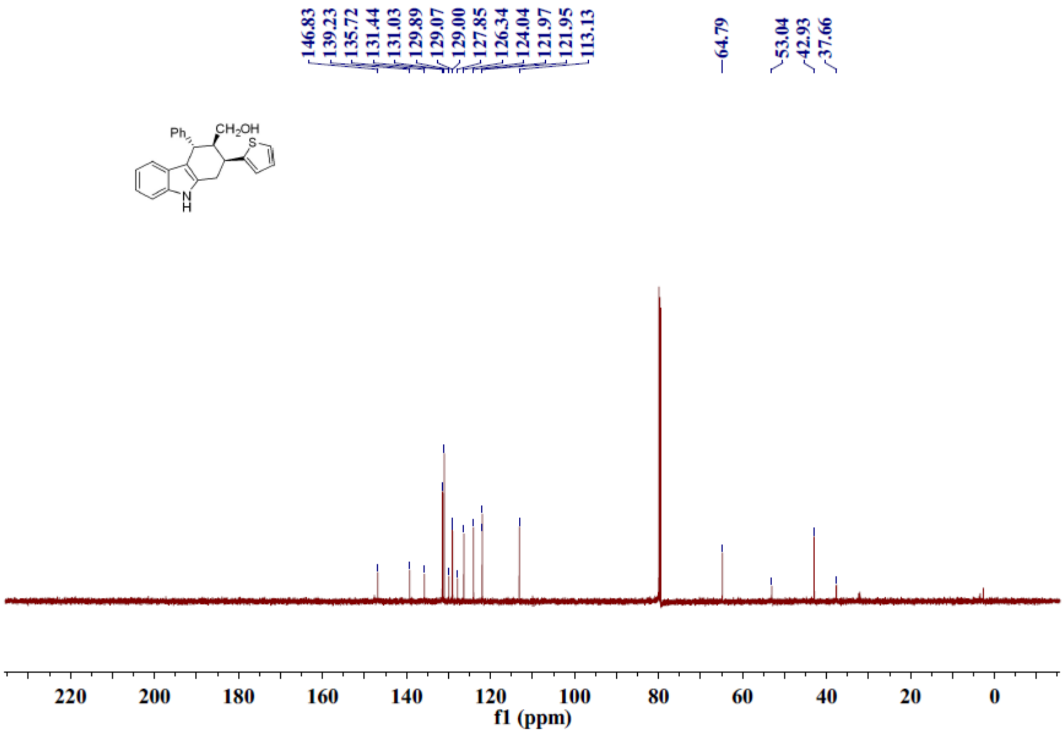
(4-phenyl-2-(thiophen-3-yl)-2,3,4,9-tetrahydro-1H-carbazol-3-yl)methanol (4ai)



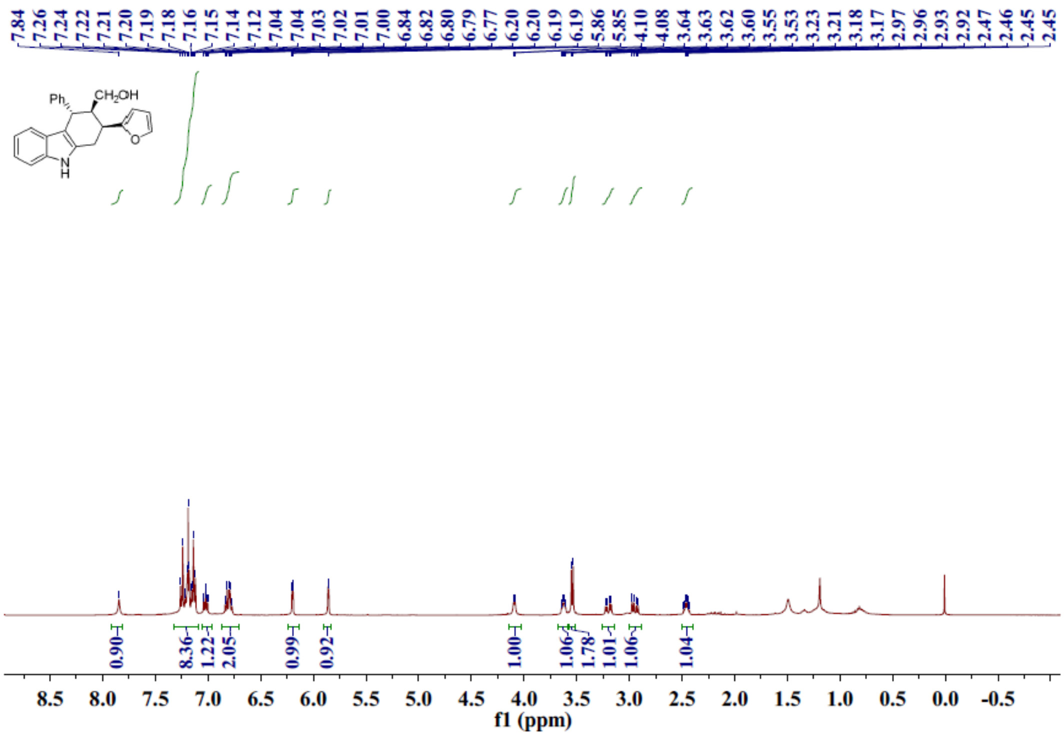


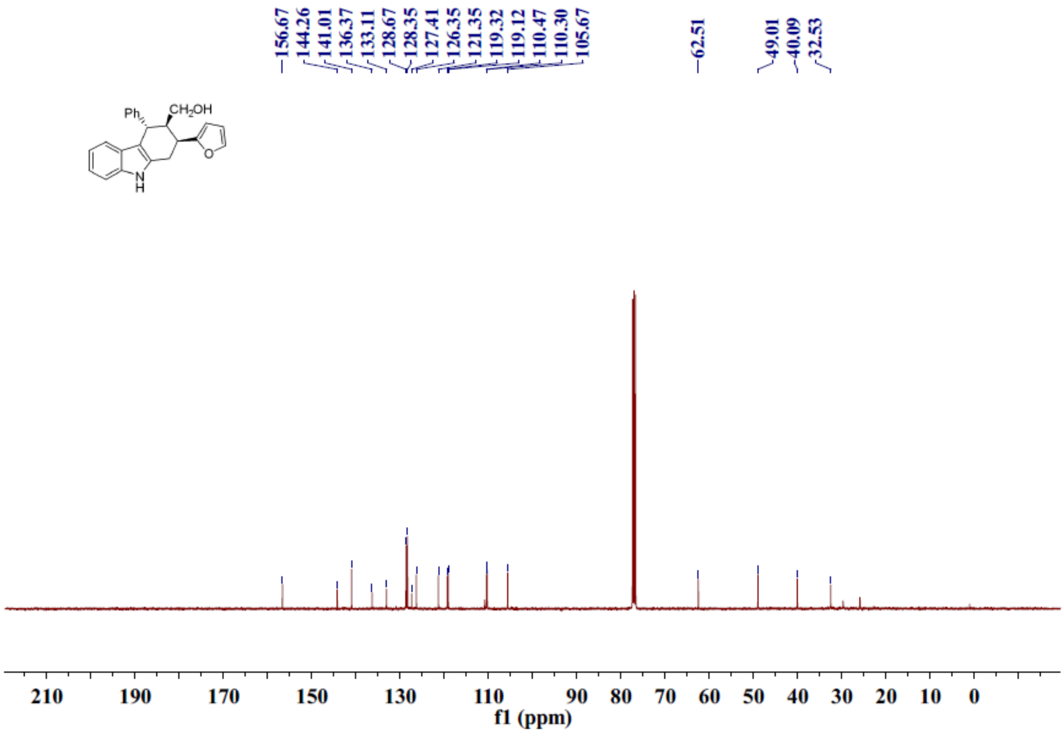
(4-phenyl-2-(thiophen-2-yl)-2,3,4,9-tetrahydro-1H-carbazol-3-yl)methanol (4aj)



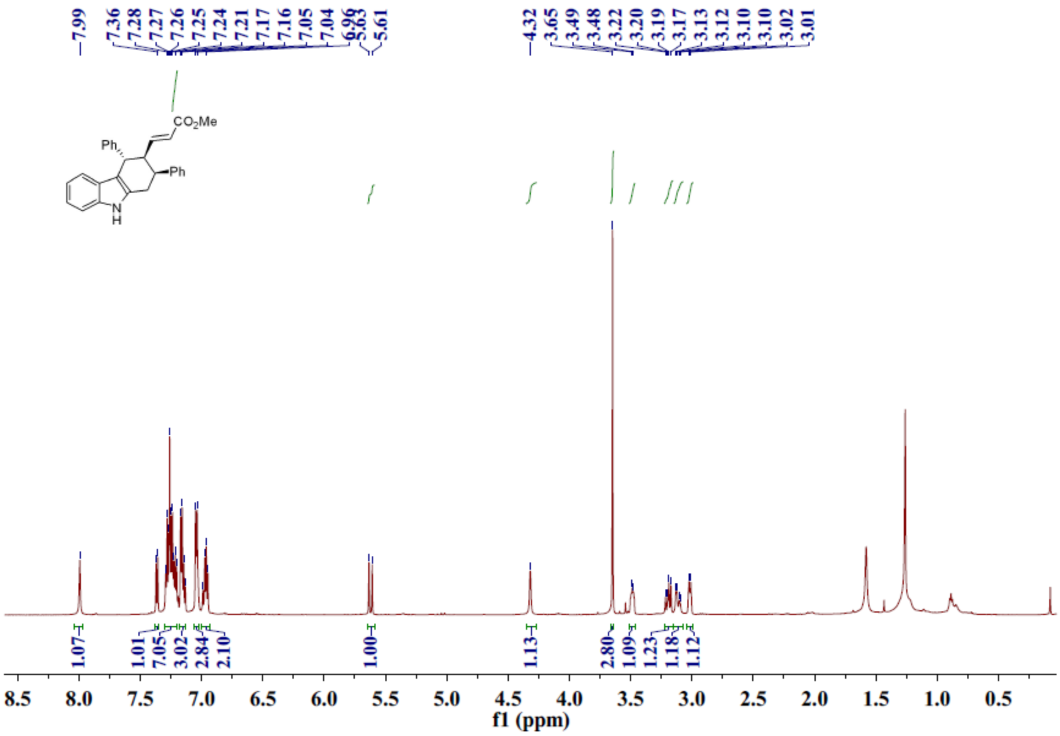


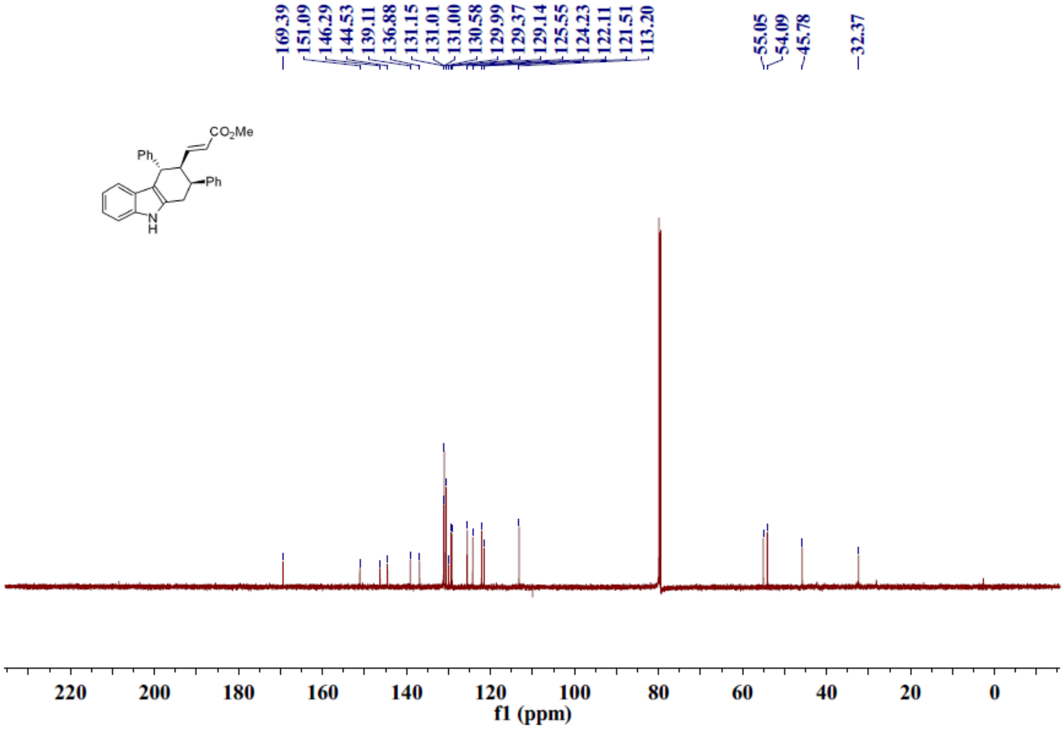
(2-(furan-2-yl)-4-phenyl-2,3,4,9-tetrahydro-1H-carbazol-3-yl)methanol (4ak)



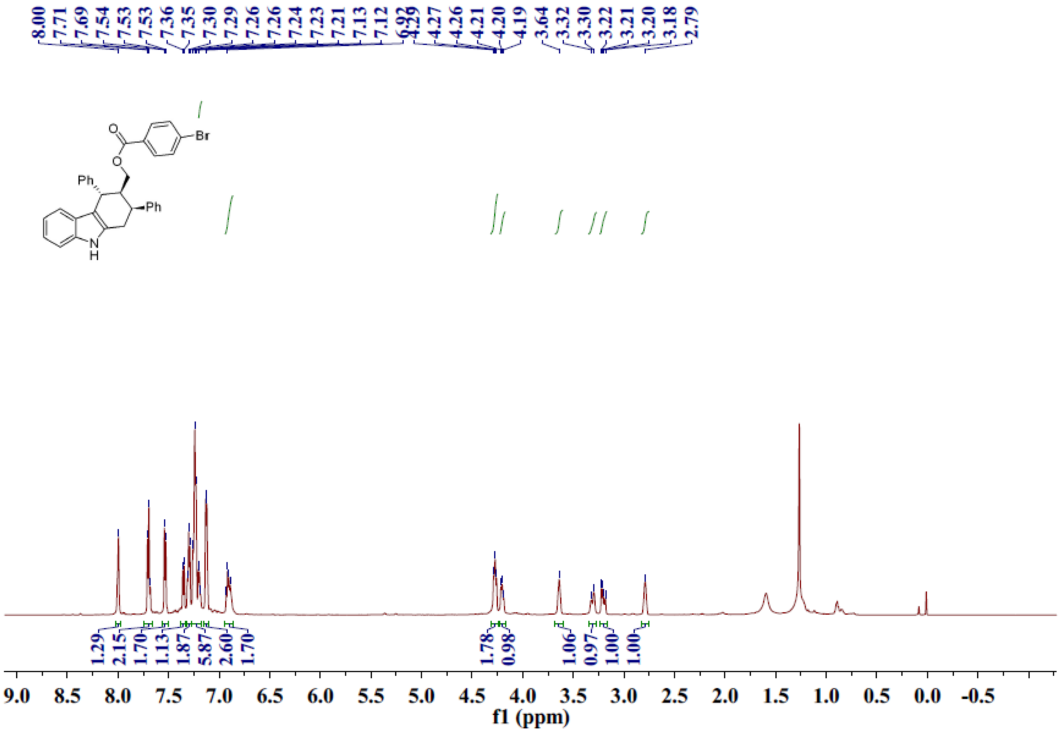


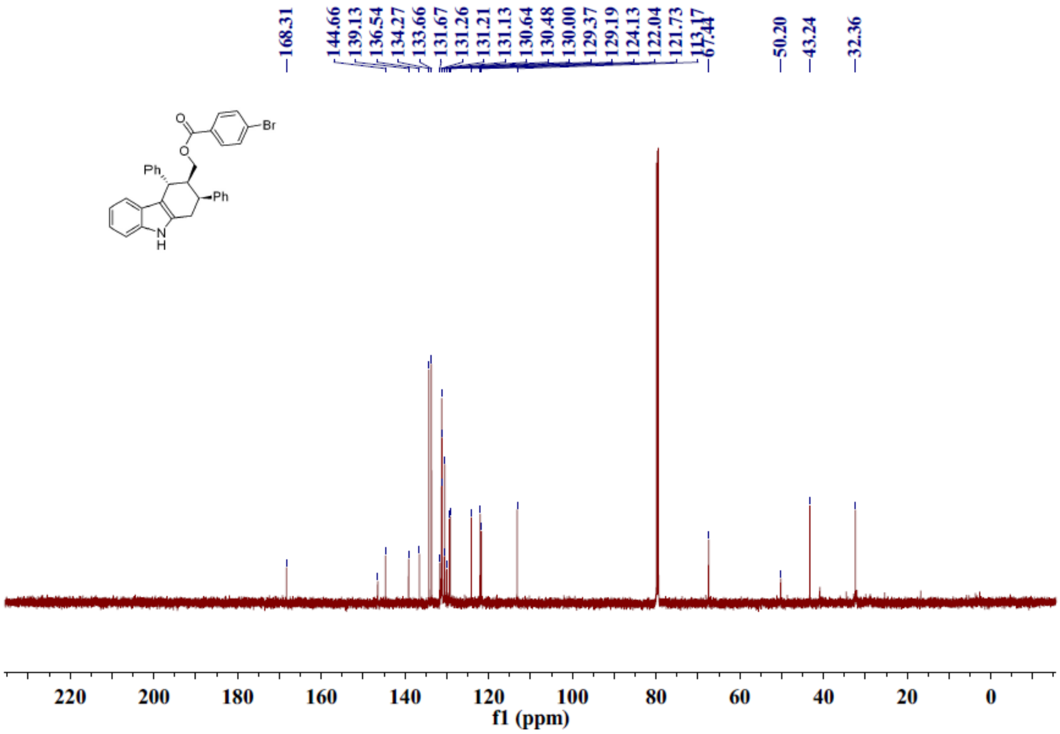
methyl(E)-3-(2,4-diphenyl-2,3,4,9-tetrahydro-1H-carbazol-3-yl)acrylate (D1)





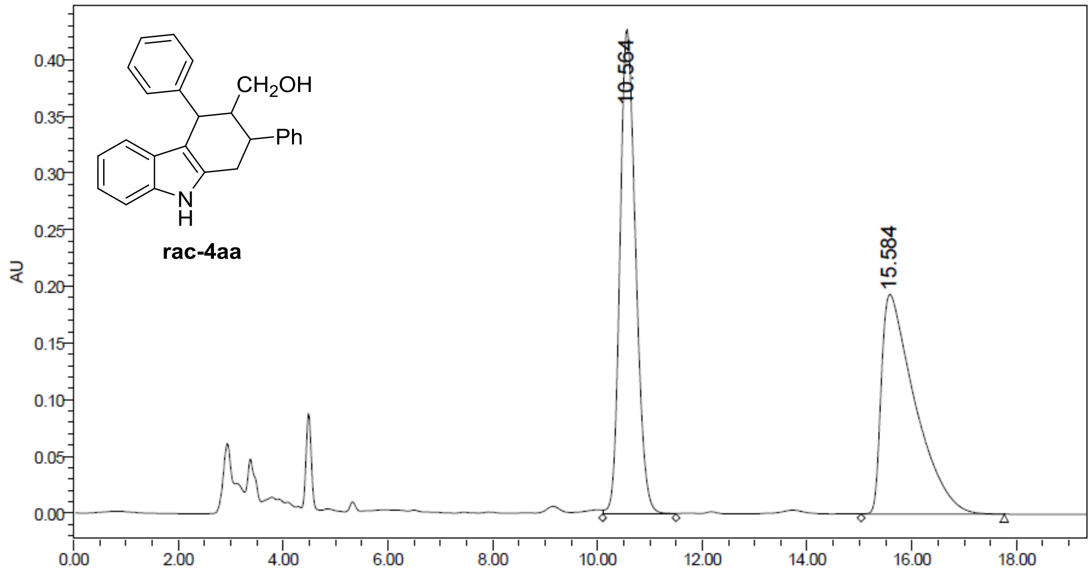
(2,4-diphenyl-2,3,4,9-tetrahydro-1H-carbazol-3-yl)methyl 4-bromobenzoate (D2)



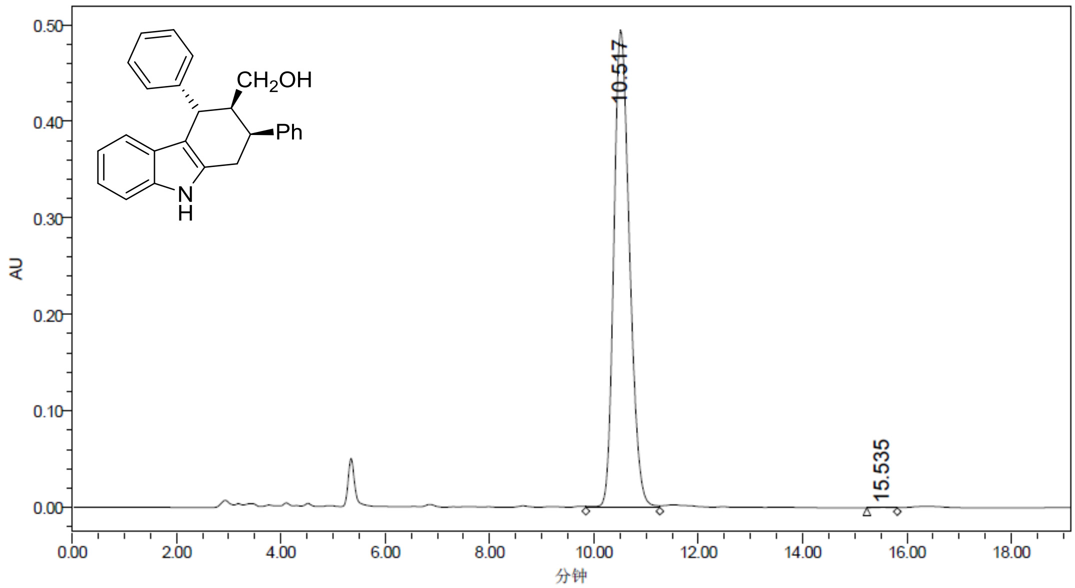


9. HPLC Analysis for Pruduct.

((2S,3S,4S)-2,4-diphenyl-2,3,4,9-tetrahydro-1H-carbazol-3-yl)methanol (4aa)

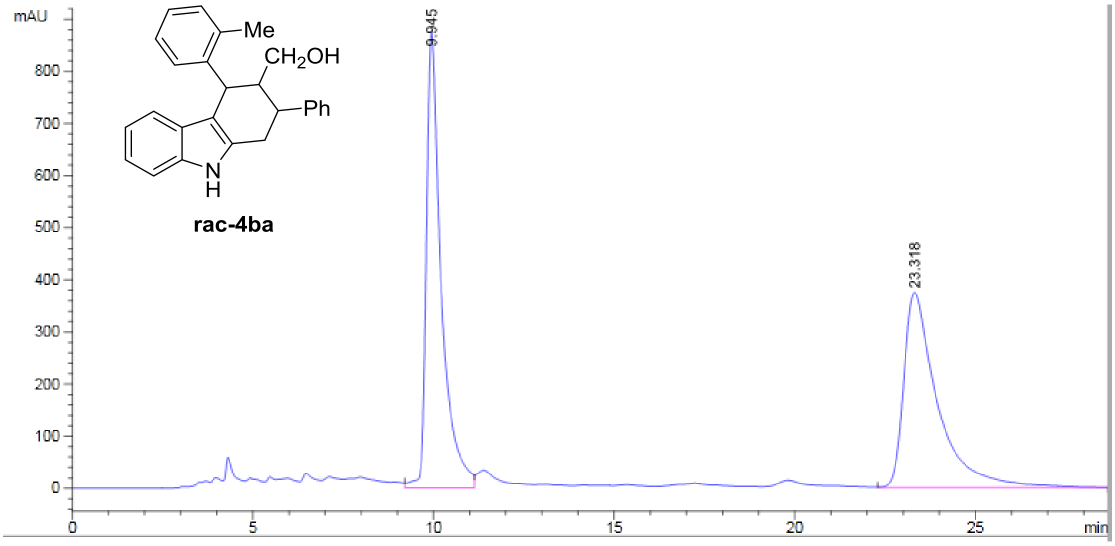


	RT (min)	Peak Type	Area (礦*sec)	% Area	Height (礦)	% Height	Integration Type	Points Across Peak	Start Time (min)	End Time (min)
1	10.564	未知	8872180	50.66	427186	68.80	VV	84	10.100	11.500
2	15.584	未知	8639950	49.34	193719	31.20	VB	164	15.033	17.767

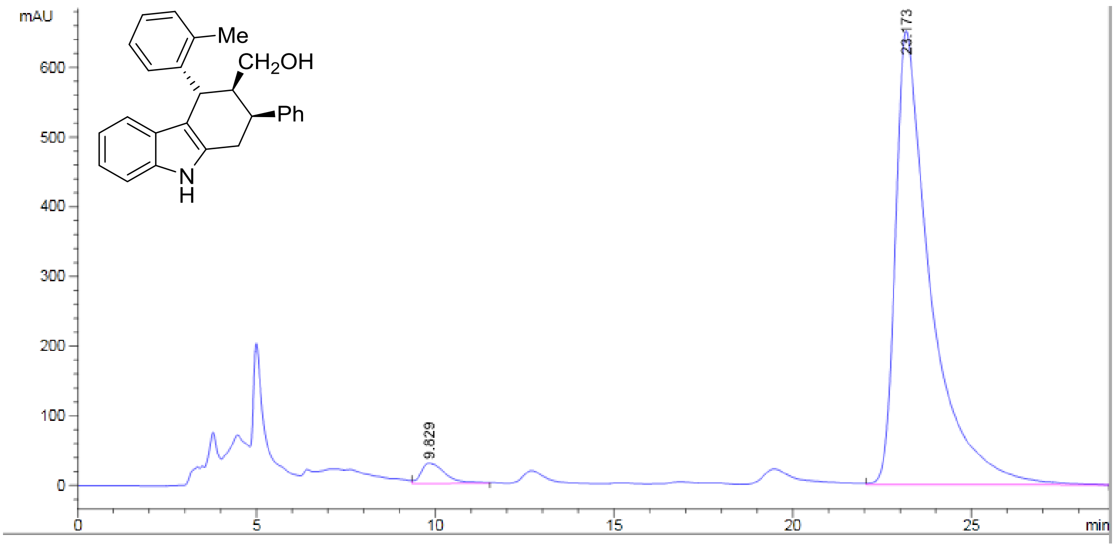


	RT (min)	Peak Type	Area (礦*sec)	% Area	Height (礦)	% Height	Integration Type	Points Across Peak	Start Time (min)	End Time (min)
1	10.517	未知	10353779	99.93	494511	99.92	VV	85	9.850	11.267
2	15.535	未知	7247	0.07	393	0.08	BV	35	15.233	15.817

((2S,3S,4S)-2-phenyl-4-(o-tolyl)-2,3,4,9-tetrahydro-1H-carbazol-3-yl)methanol (4ba)

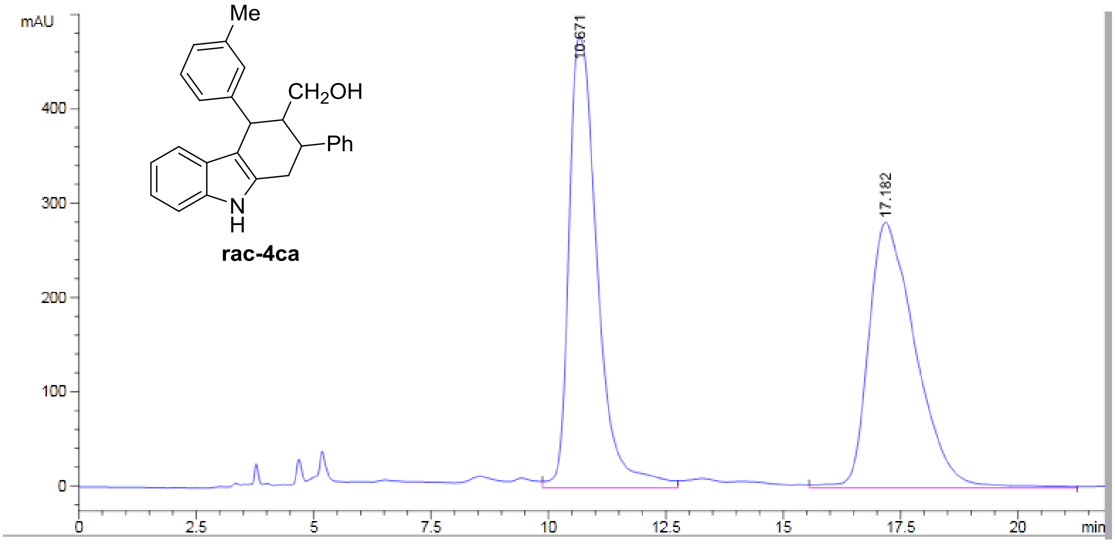


Peak #	RetTime [min]	Type	Width [min]	Area mAU *s	Height [mAU]	Area %
1	9.945	VV	0.4165	2.51449e4	875.72925	50.8046
2	23.318	VB	0.9162	2.43484e4	374.27045	49.1954

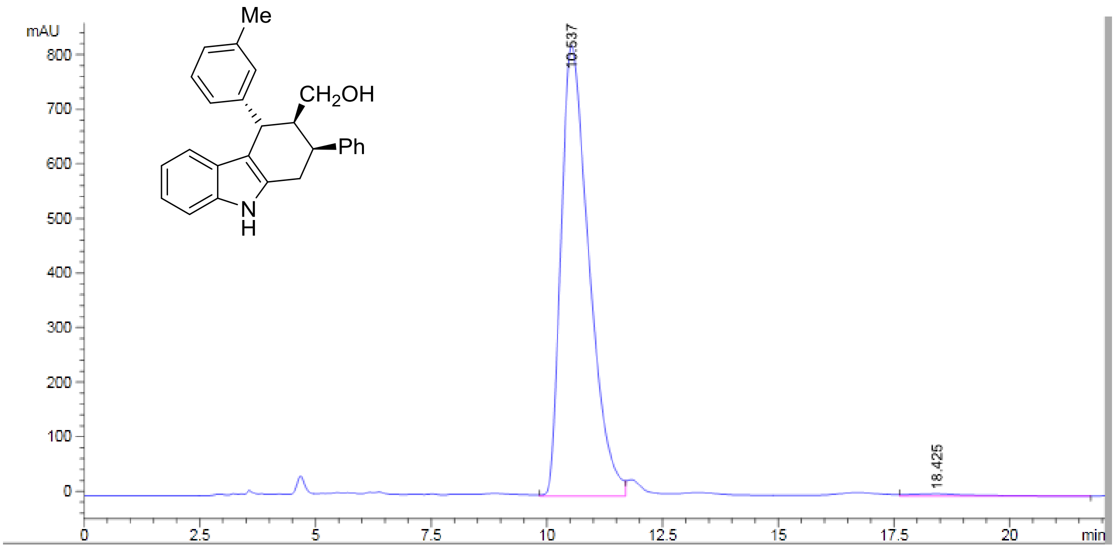


Peak #	RetTime [min]	Type	Width [min]	Area mAU *s	Height [mAU]	Area %
1	9.829	VB	0.7362	1385.51404	29.09309	3.0289
2	23.173	BB	0.9470	4.43576e4	650.48523	96.9711

((2S,3S,4S)-2-phenyl-4-(m-tolyl)-2,3,4,9-tetrahydro-1H-carbazol-3-yl)methanol (4ca)

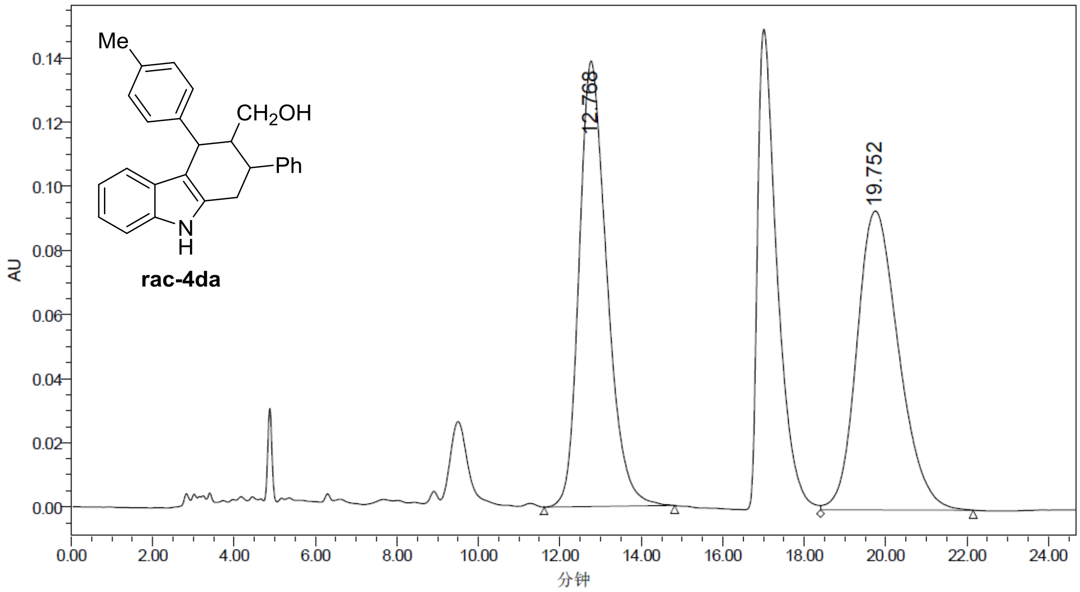


Peak #	RetTime [min]	Type	Width [min]	Area mAU *s	Height [mAU]	Area %
1	10.671	VV	0.6422	2.01426e4	478.80597	50.6996
2	17.182	VB	0.9744	1.95867e4	281.65613	49.3004

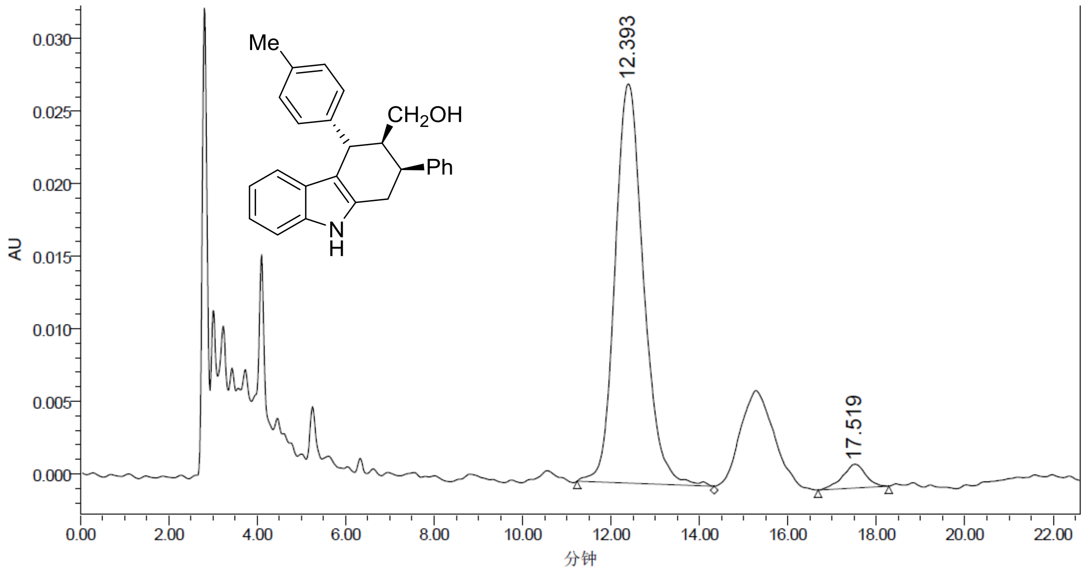


Peak #	RetTime [min]	Type	Width [min]	Area mAU *s	Height [mAU]	Area %
1	10.537	VV	0.6180	3.46335e4	824.82776	99.0563
2	18.425	VV	1.2407	329.95337	3.86443	0.9437

((2S,3S,4S)-2-phenyl-4-(p-tolyl)-2,3,4,9-tetrahydro-1H-carbazol-3-yl)methanol (4da)

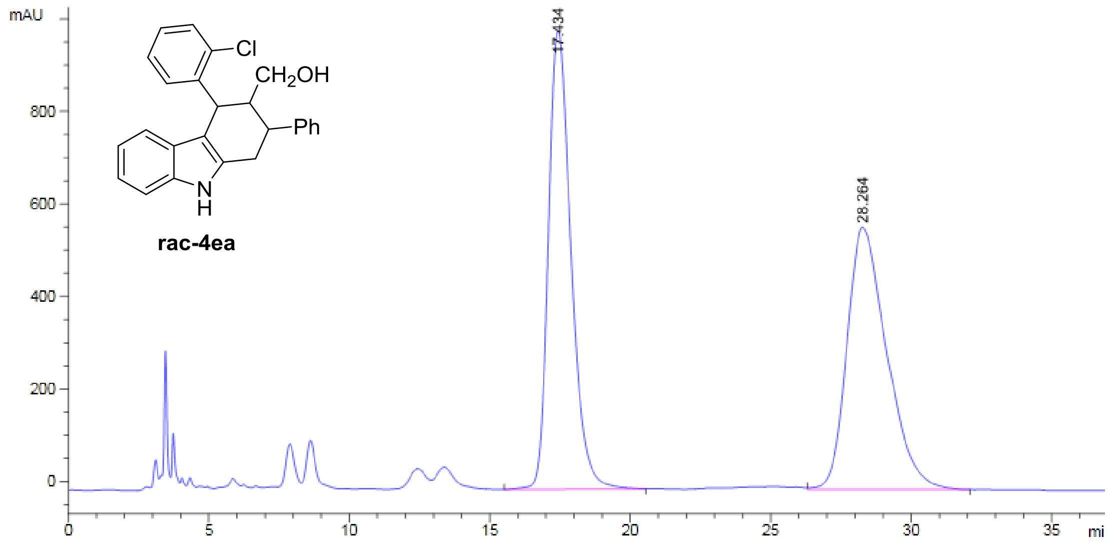


	RT (min)	Peak Type	Area (礦*sec)	% Area	Height (礦)	% Height	Integration Type	Points Across Peak	Start Time (min)	End Time (min)
1	12.768	未知	6576967	49.68	139008	59.84	BB	192	11.617	14.817
2	19.752	未知	6660789	50.32	93272	40.16	VB	225	18.400	22.150

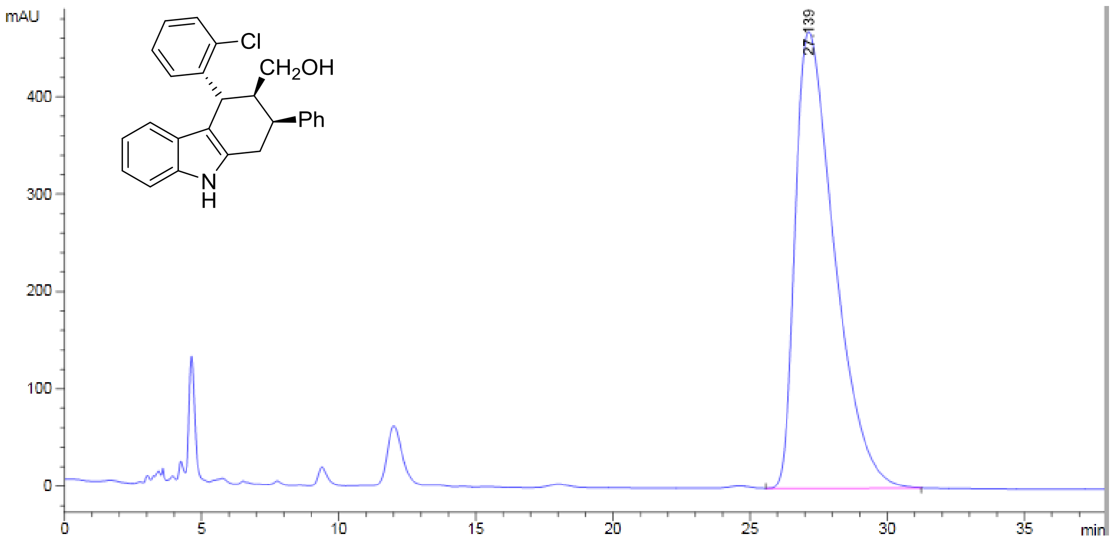


	RT (min)	Peak Type	Area (礦*sec)	% Area	Height (礦)	% Height	Integration Type	Points Across Peak	Start Time (min)	End Time (min)
1	12.393	未知	1231655	95.38	27506	94.40	BV	186	11.233	14.333
2	17.519	未知	59650	4.62	1633	5.60	BB	96	16.683	18.283

((2S,3S,4R)-4-(3-chlorophenyl)-2-phenyl-2,3,4,9-tetrahydro-1H-carbazol-3-yl)methanol (4ea)

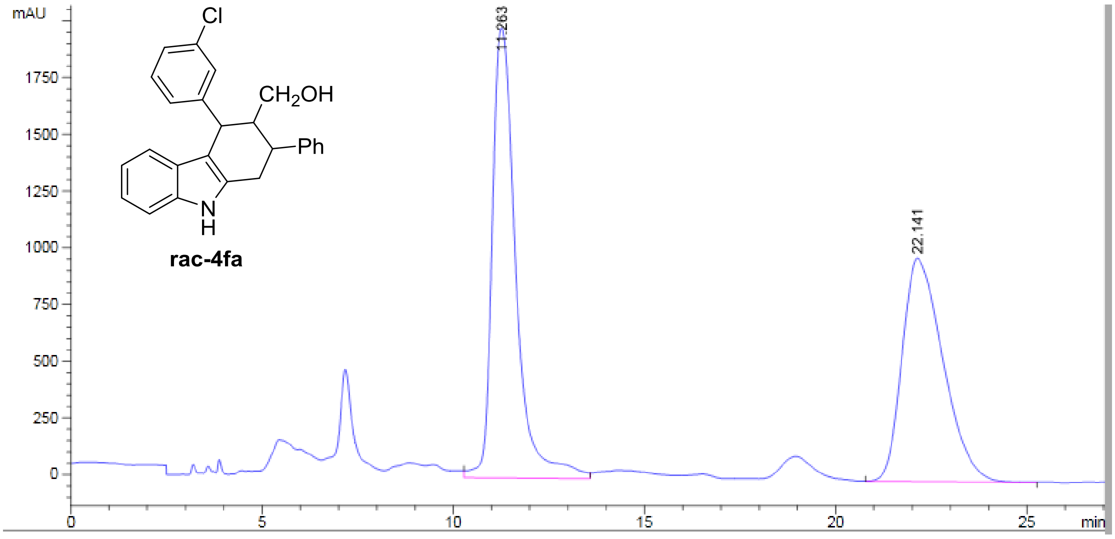


Peak #	RetTime [min]	Type	Width [min]	Area mAU *s	Height [mAU]	Area %
1	17.434	BB	0.8560	5.54830e4	992.53687	49.9150
2	28.264	VB	1.4581	5.56719e4	566.52032	50.0850

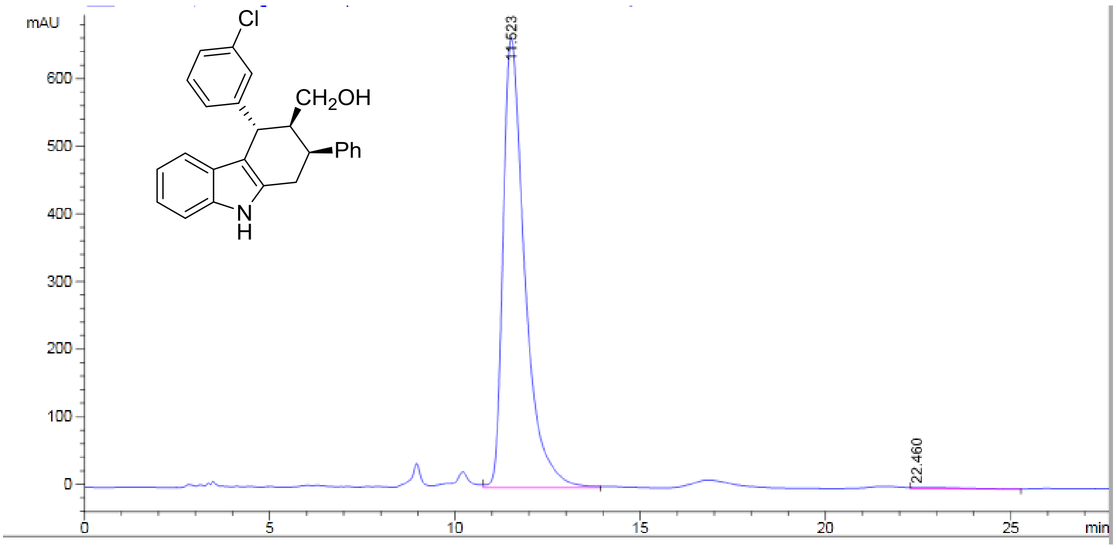


Peak #	RetTime [min]	Type	Width [min]	Area mAU *s	Height [mAU]	Area %
1	27.139	VB	1.5138	4.66994e4	469.09204	100.0000

((2S,3S,4S)-4-(3-chlorophenyl)-2-phenyl-2,3,4,9-tetrahydro-1H-carbazol-3-yl)methanol (4fa)

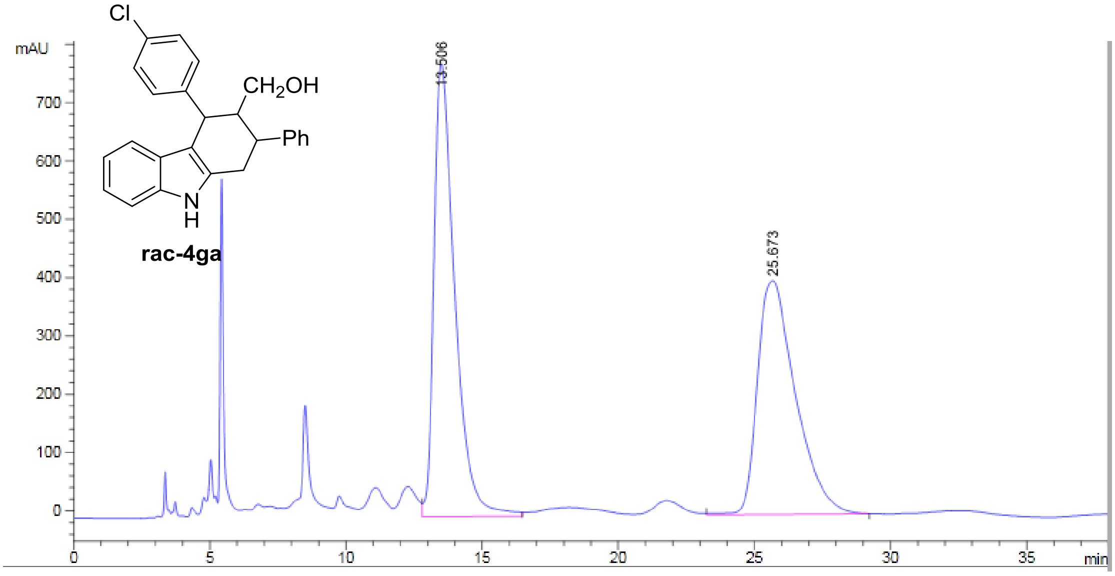


Peak #	RetTime [min]	Type	Width [min]	Area mAU *s	Height [mAU]	Area %
1	11.263	VV	0.6596	8.53343e4	1981.90417	53.7880
2	22.141	VB	1.1485	7.33151e4	984.38831	46.2120

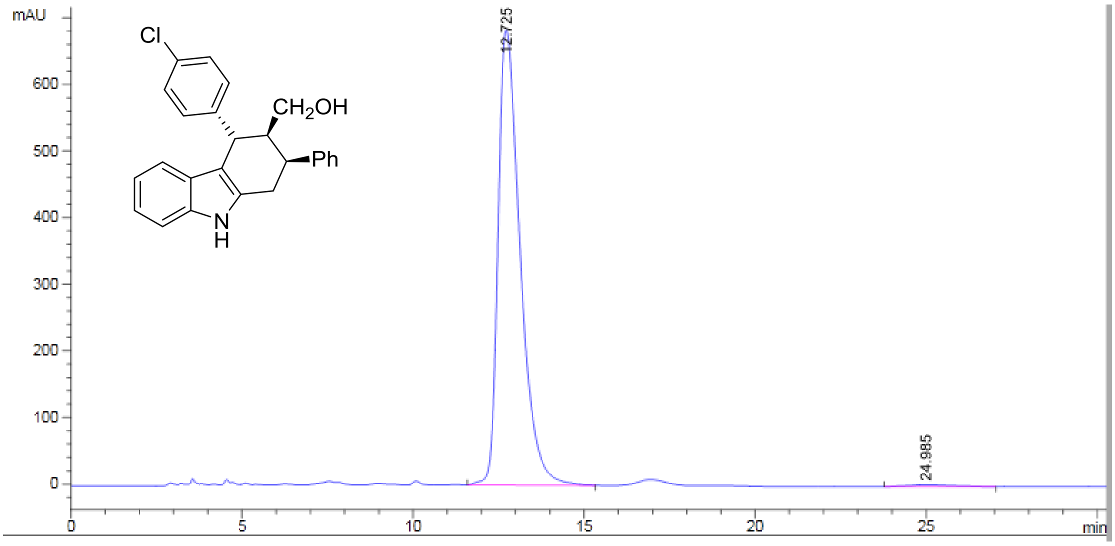


Peak #	RetTime [min]	Type	Width [min]	Area mAU *s	Height [mAU]	Area %
1	11.523	VB	0.6146	2.70730e4	665.16290	99.4292
2	22.460	VV	1.0545	155.42934	1.80959	0.5708

((2S,3S,4S)-4-(4-chlorophenyl)-2-phenyl-2,3,4,9-tetrahydro-1H-carbazol-3-yl)methanol (4ga)

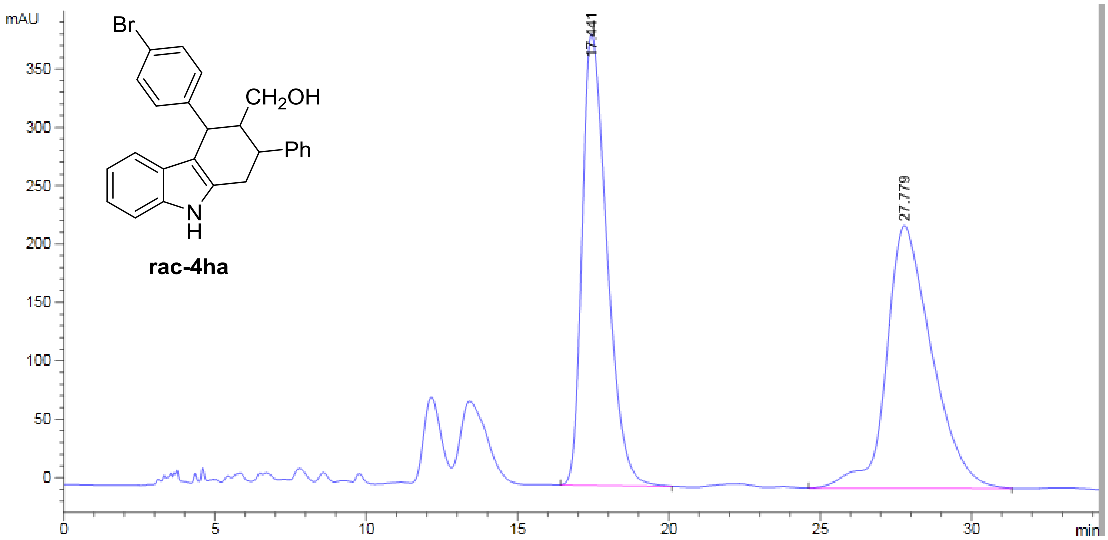


Peak #	RetTime [min]	Type	Width [min]	Area mAU *s	Height [mAU]	Area %
1	13.506	VB	0.7809	4.13111e4	776.43036	51.5142
2	25.673	VB	1.4087	3.88825e4	400.70239	48.4858

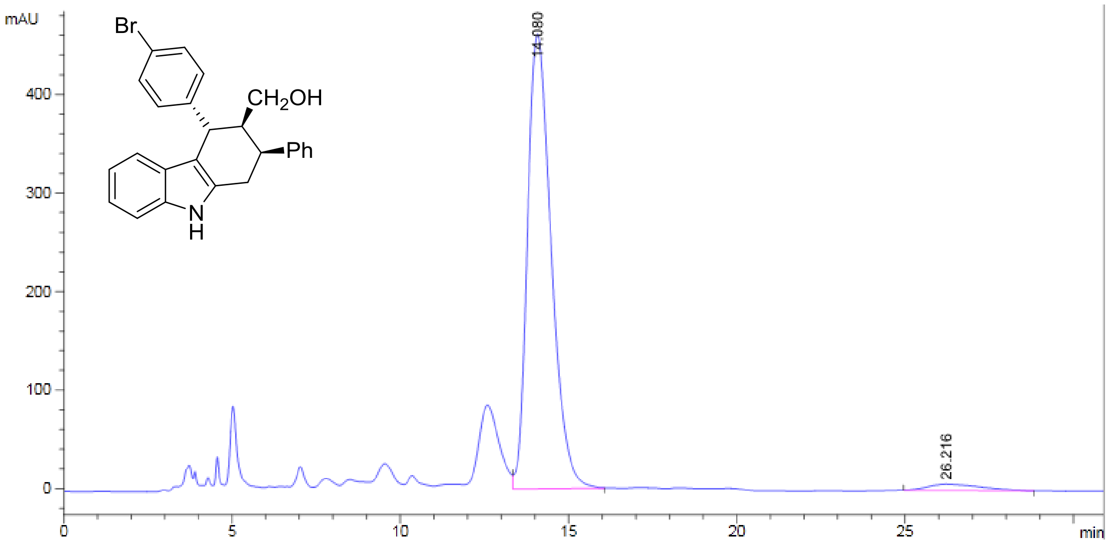


Peak #	RetTime [min]	Type	Width [min]	Area mAU *s	Height [mAU]	Area %
1	12.725	BB	0.6869	3.06708e4	683.06854	99.1650
2	24.985	BB	1.0973	258.26514	2.86776	0.8350

((2S,3S,4S)-4-(4-bromophenyl)-2-phenyl-2,3,4,9-tetrahydro-1H-carbazol-3-yl)methanol (4ha)

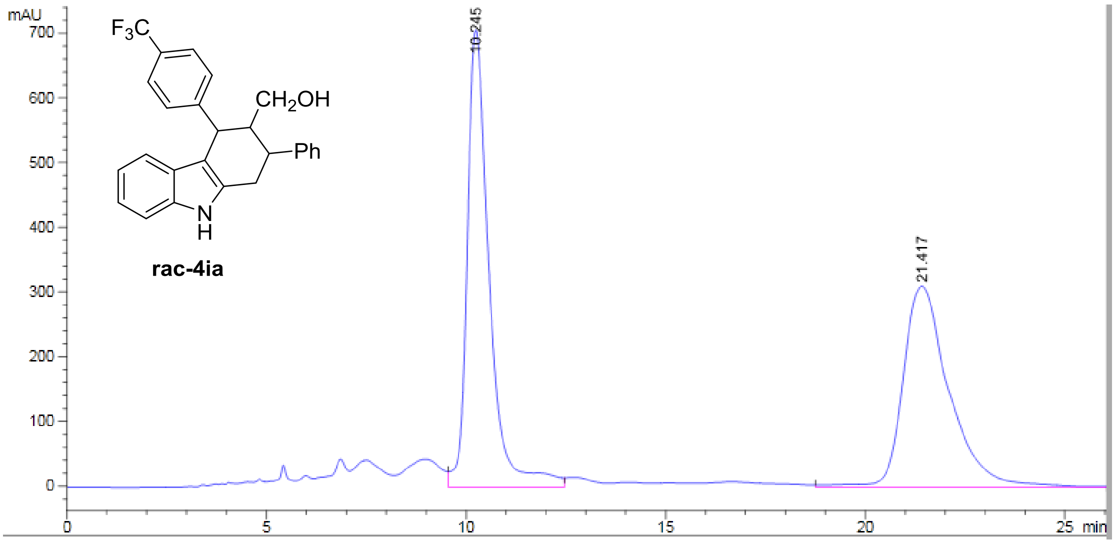


Peak #	RetTime [min]	Type	Width [min]	Area mAU *s	Height [mAU]	Area %
1	17.441	BB	0.8549	2.20532e4	386.56491	48.5472
2	27.779	VB	1.4953	2.33732e4	224.83096	51.4528

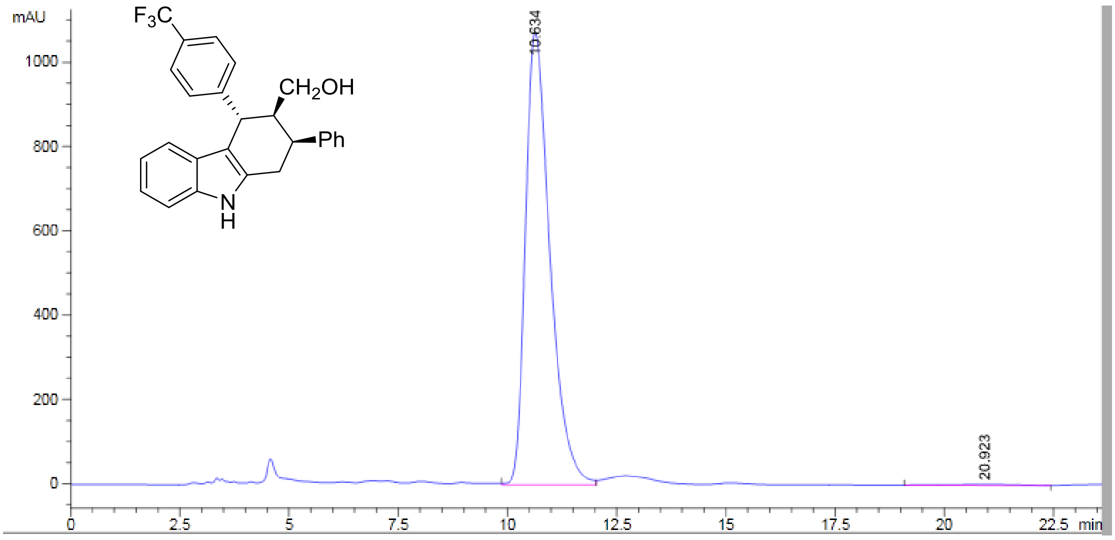


Peak #	RetTime [min]	Type	Width [min]	Area mAU *s	Height [mAU]	Area %
1	14.080	VB	0.7358	2.26383e4	461.11267	96.9638
2	26.216	BB	1.3728	708.87012	6.50753	3.0362

((2S,3S,4S)-2-phenyl-4-(4-(trifluoromethyl)phenyl)-2,3,4,9-tetrahydro-1H-carbazol-3-yl)methanol (4ia)

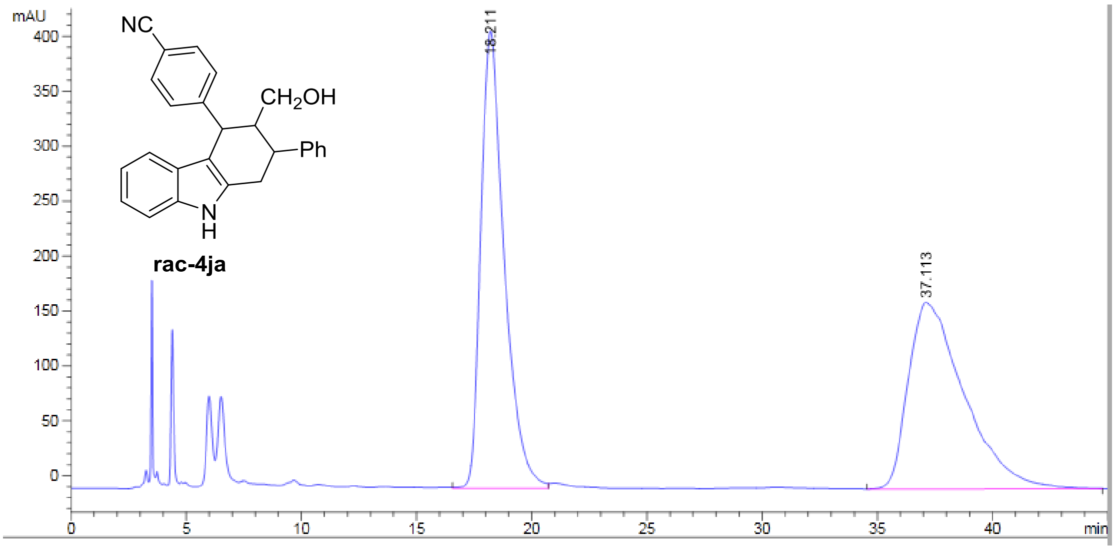


Peak #	RetTime [min]	Type	Width [min]	Area mAU *s	Height [mAU]	Area %
1	10.245	VV	0.5701	2.71268e4	706.82684	51.9806
2	21.417	VBA	1.1863	2.50596e4	310.46713	48.0194

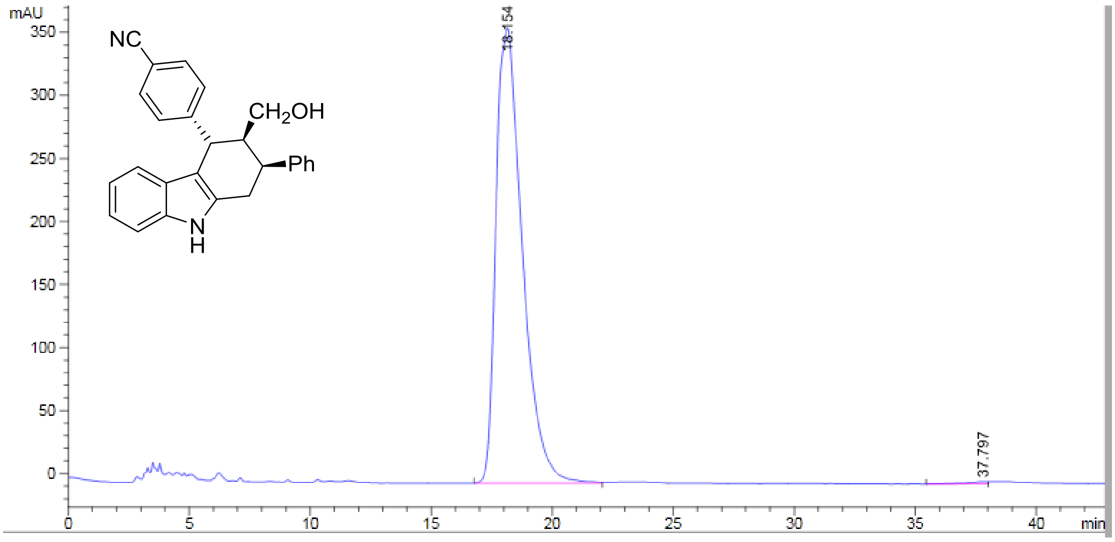


Peak #	RetTime [min]	Type	Width [min]	Area mAU *s	Height [mAU]	Area %
1	10.634	VV	0.6071	4.19518e4	1074.14185	99.4971
2	20.923	BV	1.1969	212.06166	2.58225	0.5029

4-((2S,3S,4S)-3-(hydroxymethyl)-2-phenyl-2,3,4,9-tetrahydro-1H-carbazol-4-yl)benzonitrile (4ja)

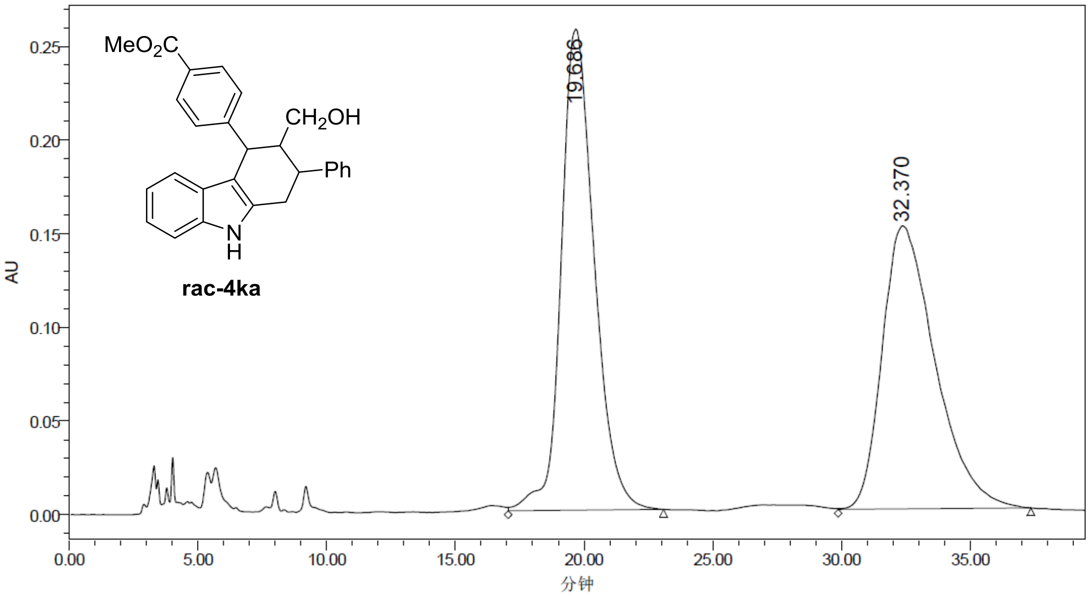


Peak #	RetTime [min]	Type	Width [min]	Area mAU *s	Height [mAU]	Area %
1	18.211	BV	1.0590	2.94721e4	416.22723	50.7173
2	37.113	VB	2.1930	2.86384e4	169.95695	49.2827

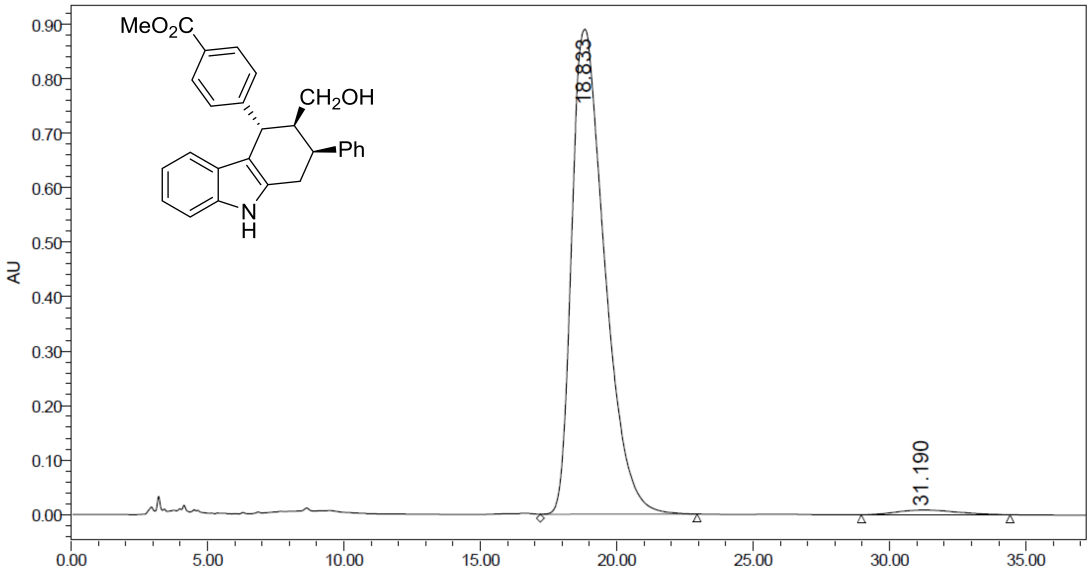


Peak #	RetTime [min]	Type	Width [min]	Area mAU *s	Height [mAU]	Area %
1	18.154	BB	0.9888	2.73665e4	361.19360	99.6016
2	37.797	BV	0.8236	109.47755	1.74858	0.3984

methyl4-((2S,3S,4S)-3-(hydroxymethyl)-2-phenyl-2,3,4,9-tetrahydro-1H-carbazol -4-yl)benzoate (4ka)

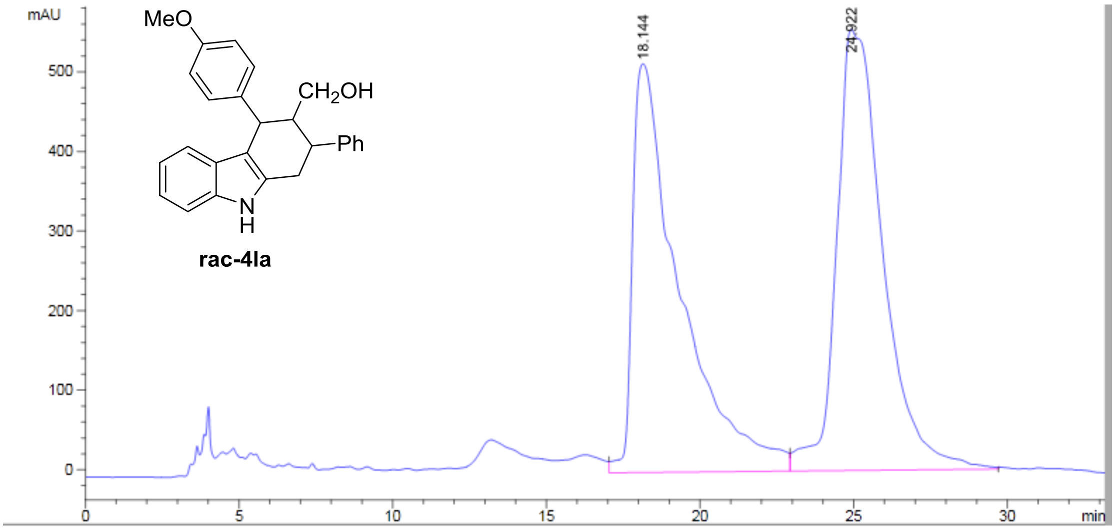


	RT (min)	Peak Type	Area (磺*sec)	% Area	Height (磺)	% Height	Integration Type	Points Across Peak	Start Time (min)	End Time (min)
1	19.686	未知	22920350	51.45	256603	62.94	VB	362	17.050	23.083
2	32.370	未知	21628533	48.55	151085	37.06	VB	449	29.867	37.350

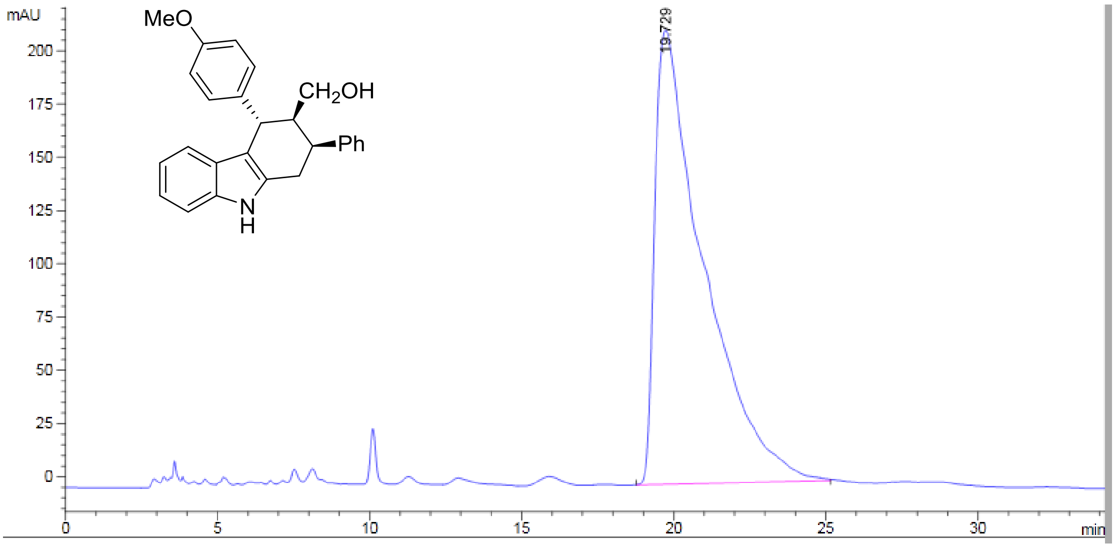


	RT (min)	Peak Type	Area (磺*sec)	% Area	Height (磺)	% Height	Integration Type	Points Across Peak	Start Time (min)	End Time (min)
1	18.833	未知	74614538	98.25	890503	99.01	VB	345	17.200	22.950
2	31.190	未知	1327692	1.75	8896	0.99	BB	327	28.967	34.417

((2S,3S,4S)-4-(4-methoxyphenyl)-2-phenyl-2,3,4,9-tetrahydro-1H-carbazol-3-yl) methanol (4la)

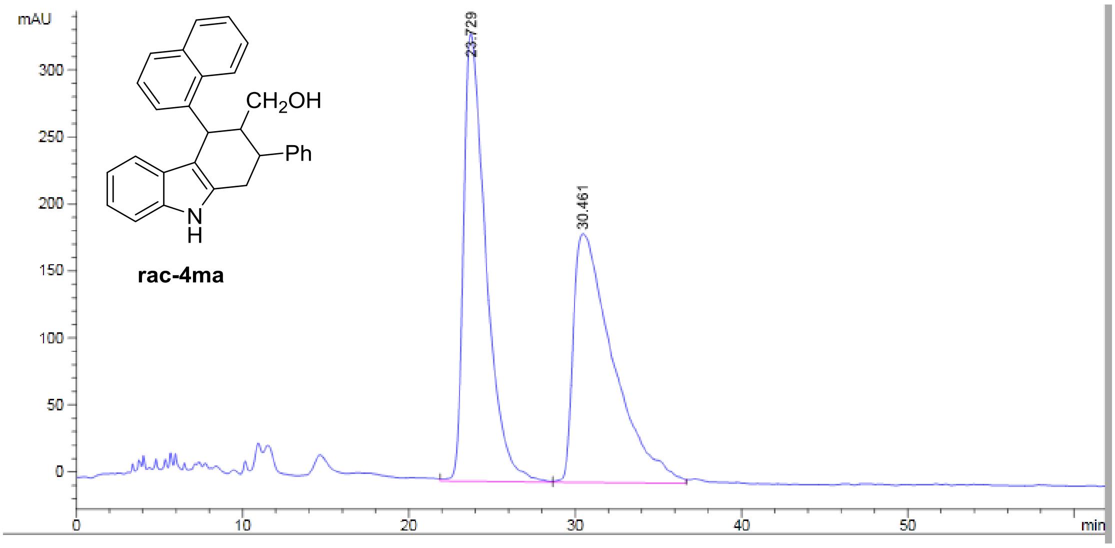


Peak #	RetTime [min]	Type	Width [min]	Area mAU *s	Height [mAU]	Area %
1	18.144	VV	1.5262	5.48632e4	513.42957	48.4543
2	24.922	VB	1.3304	5.83634e4	554.27417	51.5457

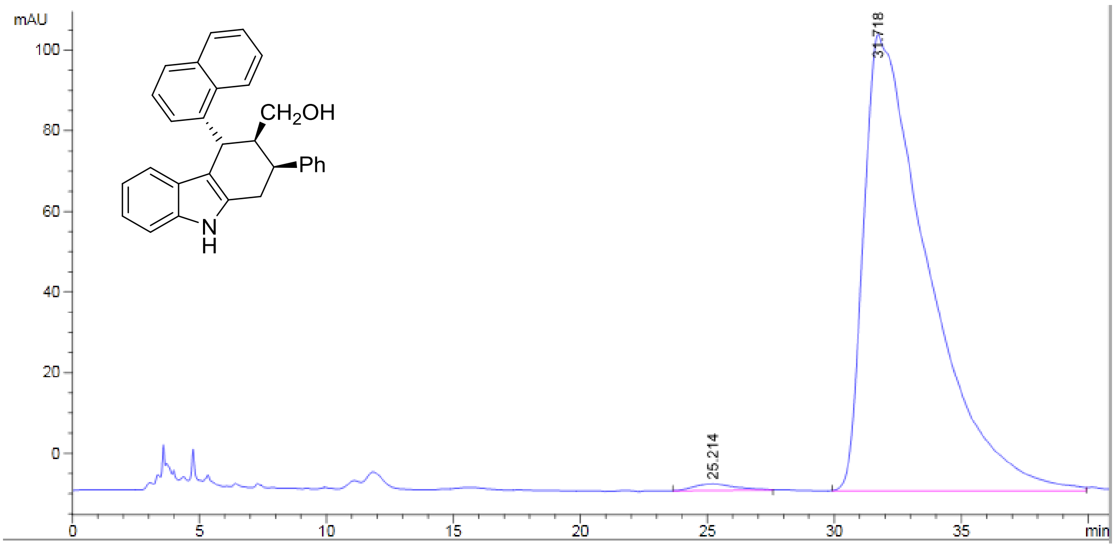


Peak #	RetTime [min]	Type	Width [min]	Area mAU *s	Height [mAU]	Area %
1	19.729	BB	1.5361	2.37728e4	213.31628	100.0000

((2S,3S,4S)-4-(naphthalen-1-yl)-2-phenyl-2,3,4,9-tetrahydro-1H-carbazol-3-yl)methanol (4ma)

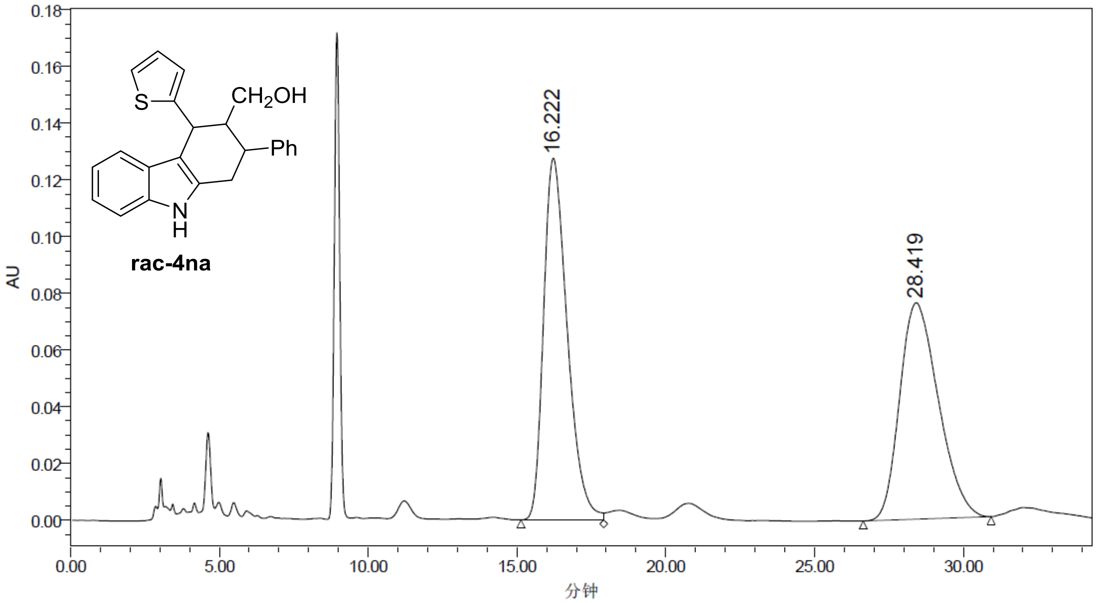


Peak #	RetTime [min]	Type	Width [min]	Area mAU *s	Height [mAU]	Area %
1	23.729	VB	1.2919	3.14092e4	334.10483	50.4209
2	30.461	BV	2.2633	3.08848e4	185.45058	49.5791

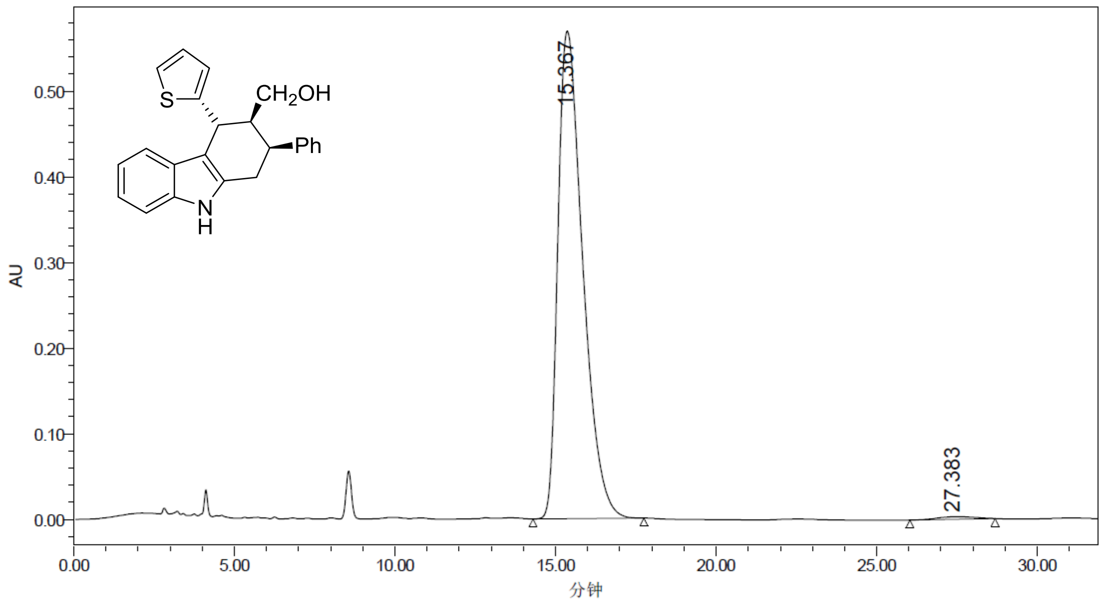


Peak #	RetTime [min]	Type	Width [min]	Area mAU *s	Height [mAU]	Area %
1	25.214	BB	1.3308	178.08234	1.65539	0.8854
2	31.718	BV	2.2005	1.99359e4	113.18633	99.1146

((2S,3S,4R)-2-phenyl-4-(thiophen-2-yl)-2,3,4,9-tetrahydro-1H-carbazol-3-yl)methanol (4na)

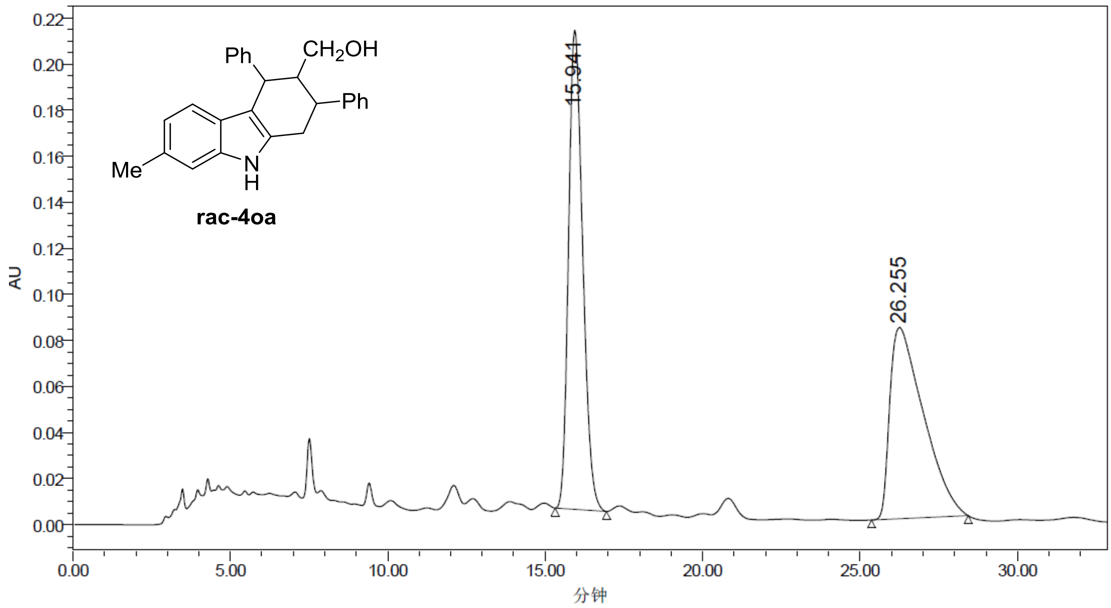


	RT (min)	Peak Type	Area (礦*sec)	% Area	Height (礦)	% Height	Integration Type	Points Across Peak	Start Time (min)	End Time (min)
1	16.222	未知	7054358	50.54	127498	62.55	BV	167	15.133	17.917
2	28.419	未知	6902675	49.46	76329	37.45	BB	258	26.633	30.933

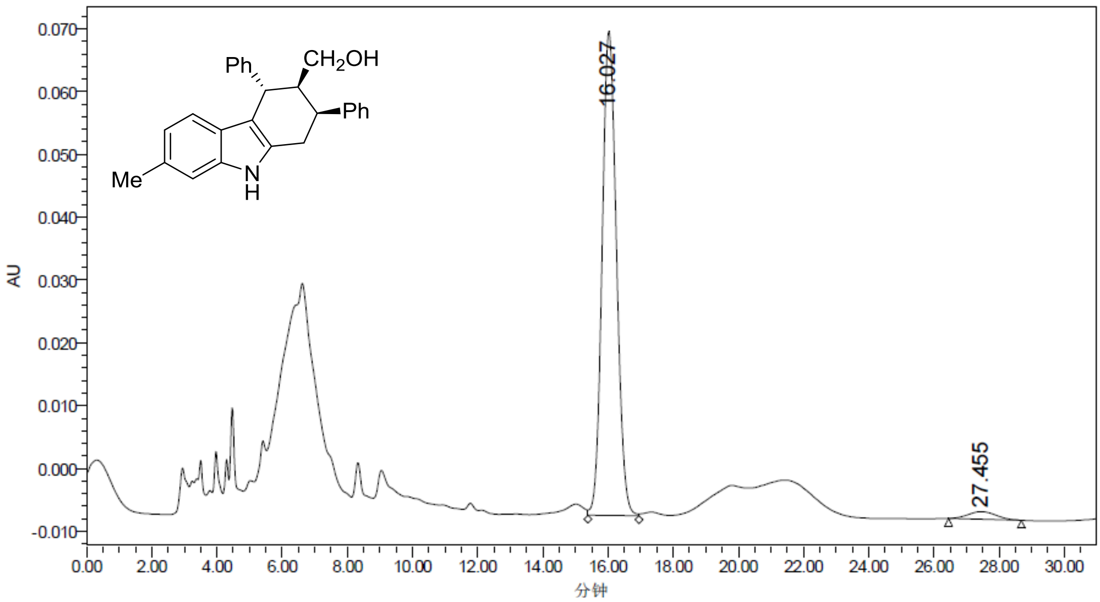


	RT (min)	Peak Type	Area (礦*sec)	% Area	Height (礦)	% Height	Integration Type	Peak Codes	Points Across Peak	Start Time (min)
1	15.367	未知	30612170	99.20	569362	99.44	BB		207	14.300
2	27.383	未知	245993	0.80	3199	0.56	BB	I08	159	26.033

((2S,3S,4S)-7-methyl-2,4-diphenyl-2,3,4,9-tetrahydro-1H-carbazol-3-yl)methanol (4oa)

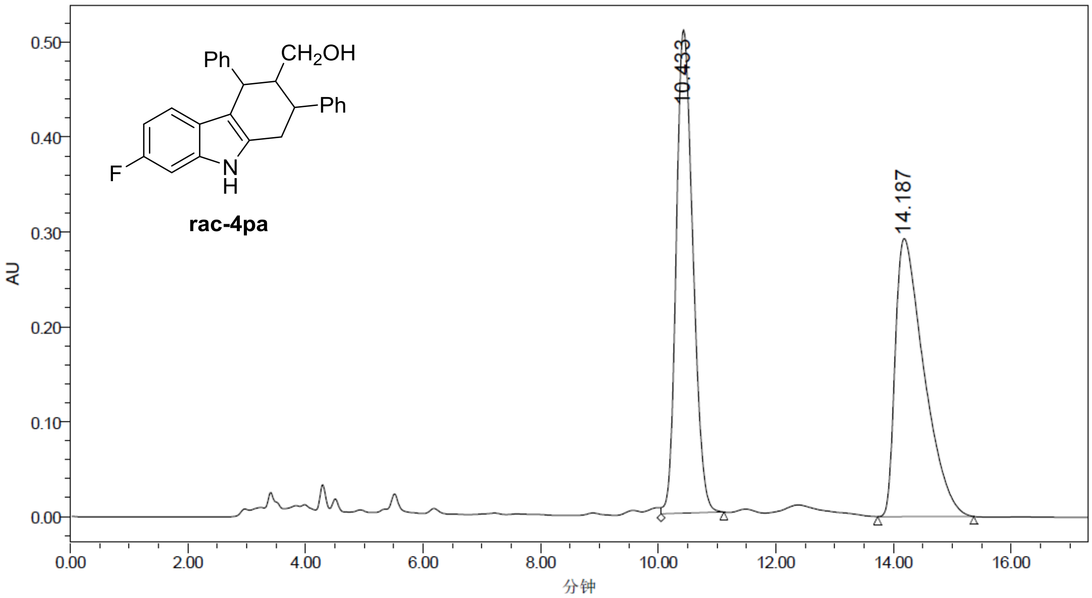


	RT (min)	Peak Type	Area (礦*sec)	% Area	Height (礦)	% Height	Integration Type	Points Across Peak	Start Time (min)	End Time (min)
1	15.941	未知	6489833	51.24	208075	71.48	BB	98	15.317	16.950
2	26.255	未知	6175419	48.76	83024	28.52	BB	184	25.367	28.433

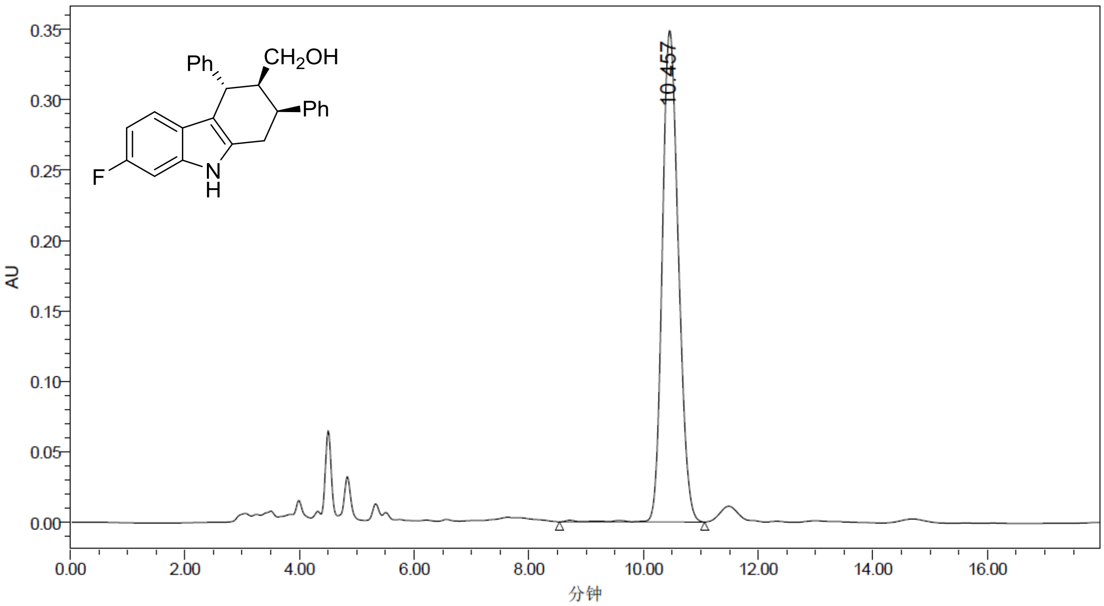


	RT (min)	Peak Type	Area (礦*sec)	% Area	Height (礦)	% Height	Integration Type	Points Across Peak	Start Time (min)	End Time (min)
1	16.027	未知	2354214	97.02	77099	98.43	VV	94	15.383	16.950
2	27.455	未知	72222	2.98	1228	1.57	BB	134	26.450	28.683

((2S,3S,4S)-7-fluoro-2,4-diphenyl-2,3,4,9-tetrahydro-1H-carbazol-3-yl)methanol (4pa)

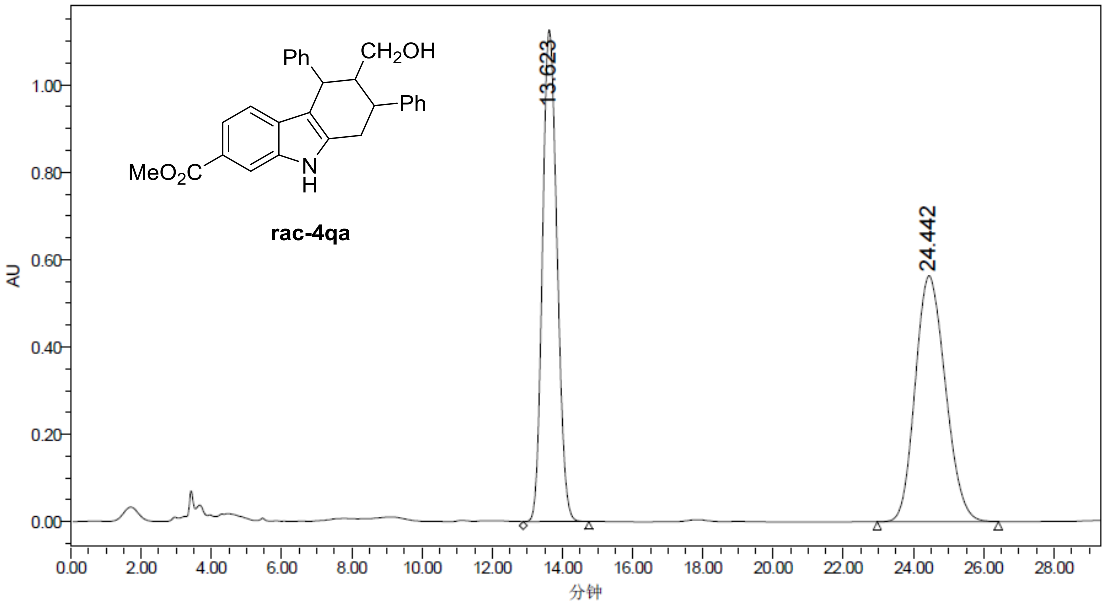


	RT (min)	Peak Type	Area (礦*sec)	% Area	Height (礦)	% Height	Integration Type	Points Across Peak	Start Time (min)	End Time (min)
1	10.433	未知	10035823	50.20	509541	63.49	VB	64	10.050	11.117
2	14.187	未知	9954085	49.80	293028	36.51	BB	98	13.733	15.367

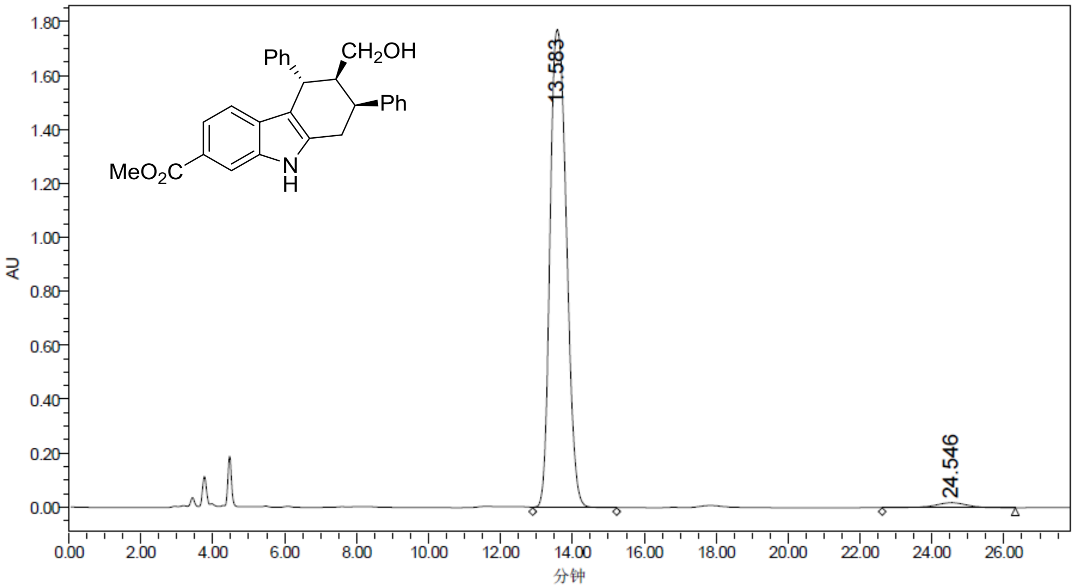


	RT (min)	Peak Type	Area (礦*sec)	% Area	Height (礦)	% Height	Integration Type	Points Across Peak	Start Time (min)	End Time (min)
1	10.457	未知	6840837	100.00	349546	100.00	BB	152	8.533	11.067

methyl(2S,3S,4S)-3-(hydroxymethyl)-2,4-diphenyl-2,3,4,9-tetrahydro-1H-carbazole-7-carboxylate (4qa)

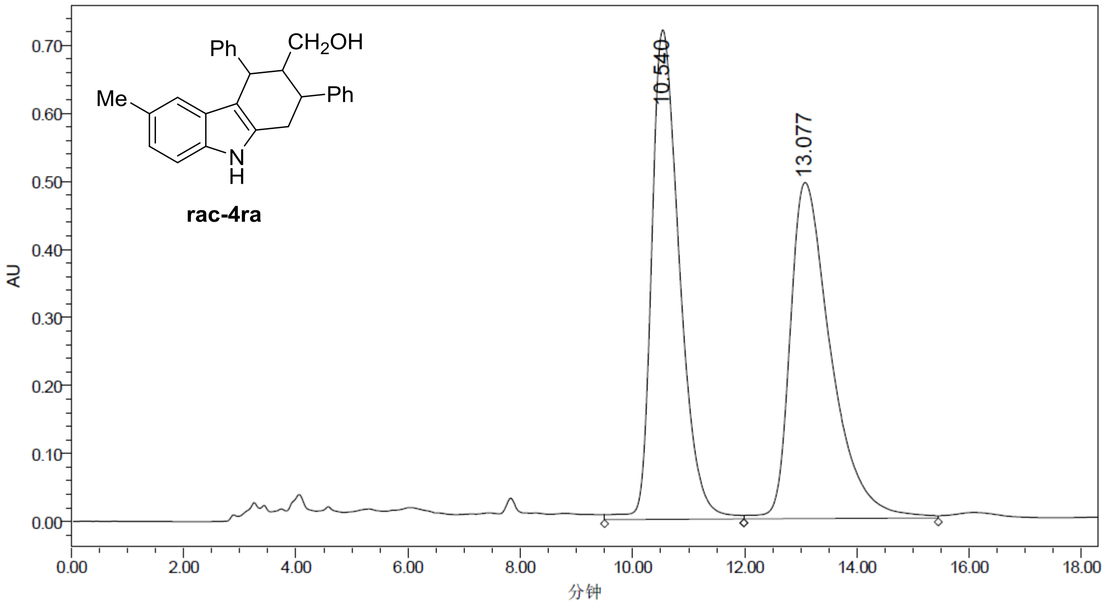


	RT (min)	Peak Type	Area (礦*sec)	% Area	Height (礦)	% Height	Integration Type	Points Across Peak	Start Time (min)	End Time (min)
1	13.623	未知	32460214	49.10	1125889	66.65	VB	112	12.883	14.750
2	24.442	未知	33646577	50.90	563400	33.35	BB	207	22.967	26.417

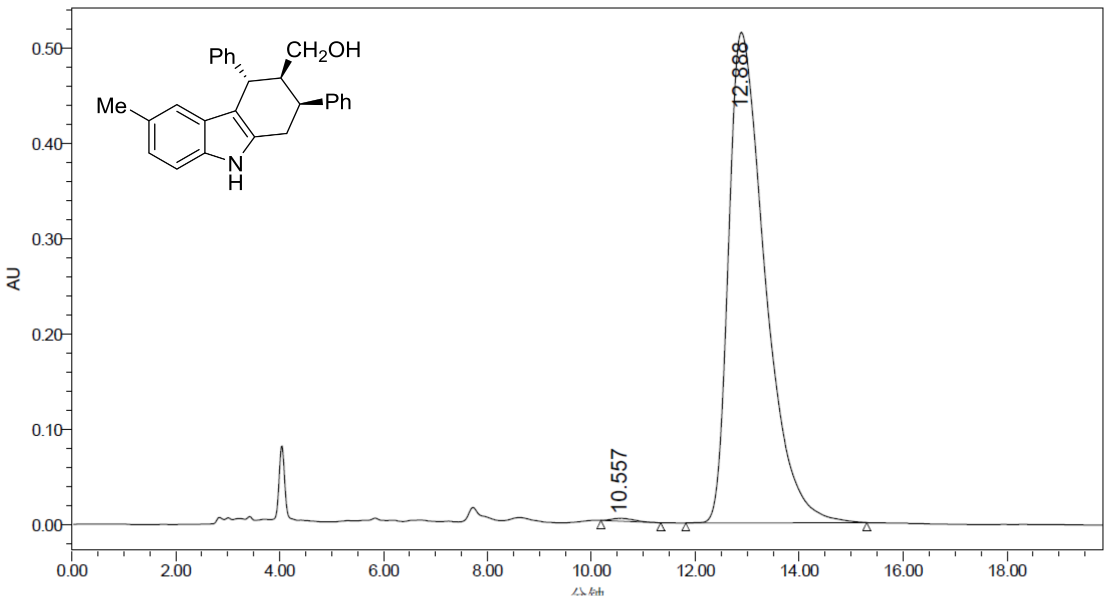


	RT (min)	Peak Type	Area (礦*sec)	% Area	Height (礦)	% Height	Integration Type	Points Across Peak	Start Time (min)	End Time (min)
1	13.583	未知	56227930	97.95	1773515	98.97	VV	140	12.900	15.233
2	24.546	未知	1175830	2.05	18509	1.03	VB	222	22.617	26.317

((2S,3S,4S)-6-methyl-2,4-diphenyl-2,3,4,9-tetrahydro-1H-carbazol-3-yl)methanol (4ra)

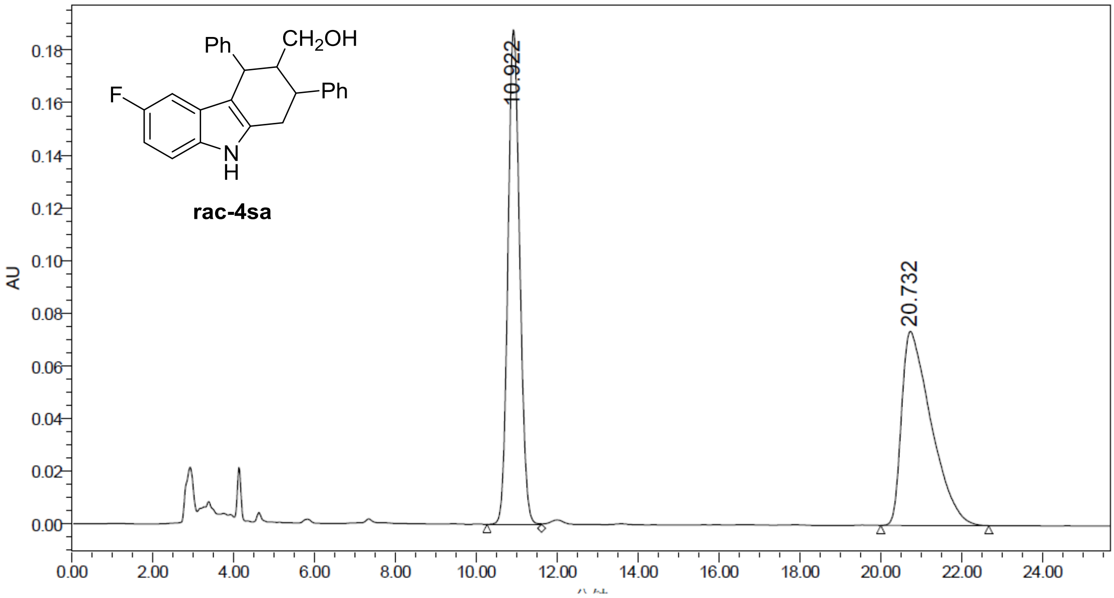


	RT (min)	Peak Type	Area (礦*sec)	% Area	Height (礦)	% Height	Integration Type	Points Across Peak	Start Time (min)	End Time (min)
1	10.540	未知	24853195	49.86	719959	59.30	VV	149	9.500	11.983
2	13.077	未知	24992539	50.14	494233	40.70	VV	208	11.983	15.450

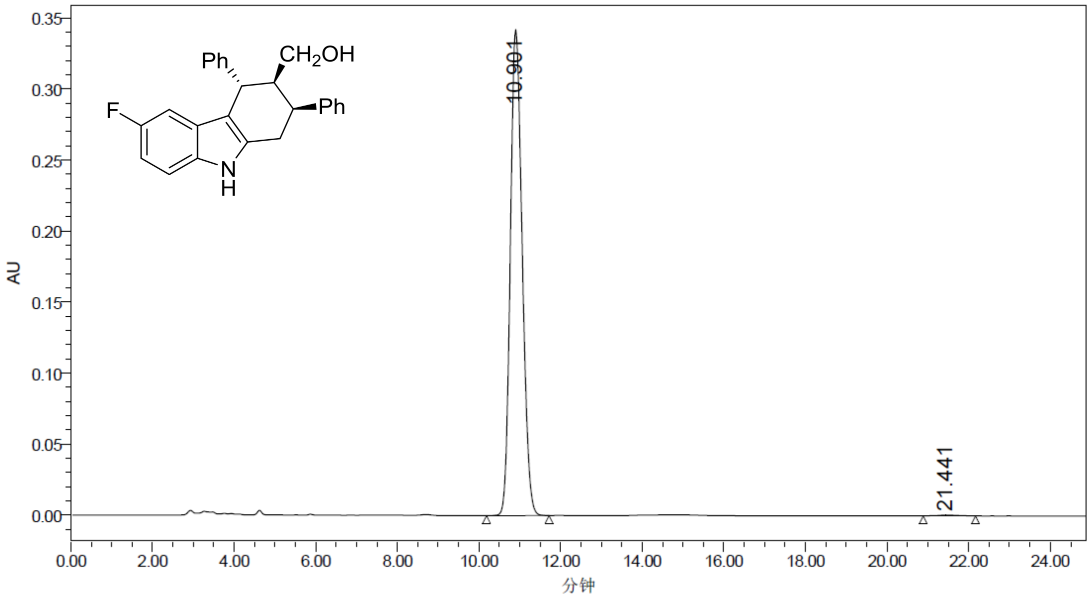


	RT (min)	Peak Type	Area (礦*sec)	% Area	Height (礦)	% Height	Integration Type	Points Across Peak	Start Time (min)	End Time (min)
1	10.557	未知	91410	0.36	2997	0.58	BB	69	10.183	11.333
2	12.888	未知	24994303	99.64	514852	99.42	BB	209	11.817	15.300

((2S,3S,4S)-6-fluoro-2,4-diphenyl-2,3,4,9-tetrahydro-1H-carbazol-3-yl)methanol (4sa)

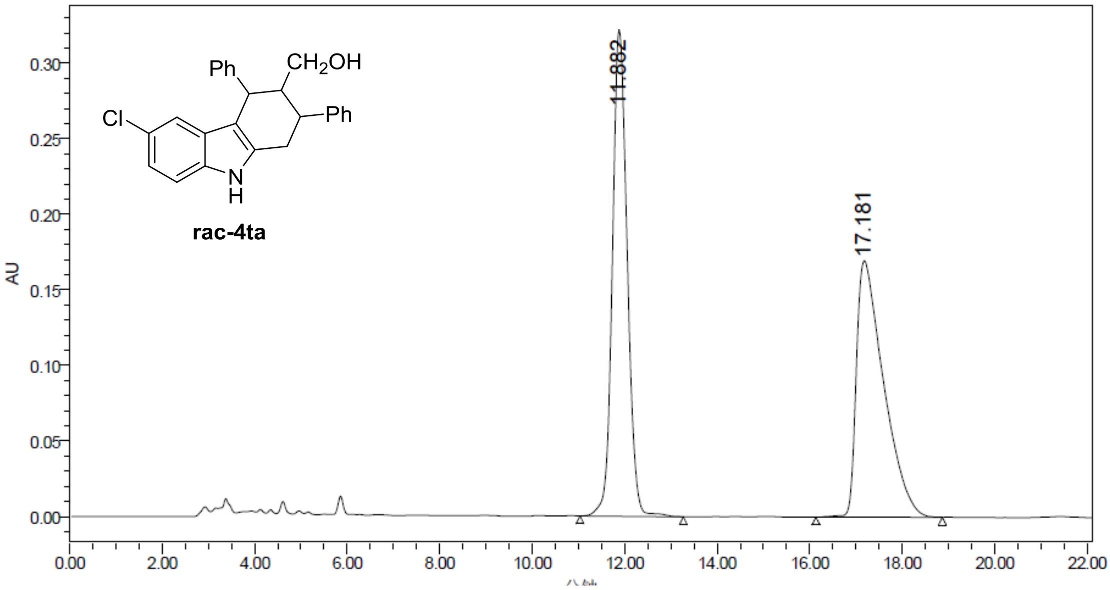


	RT (min)	Peak Type	Area (礦*sec)	% Area	Height (礦)	% Height	Integration Type	Points Across Peak	Start Time (min)	End Time (min)
1	10.922	未知	3801925	50.40	188071	71.83	BV	81	10.267	11.617
2	20.732	未知	3740857	49.60	73749	28.17	BB	160	20.000	22.667

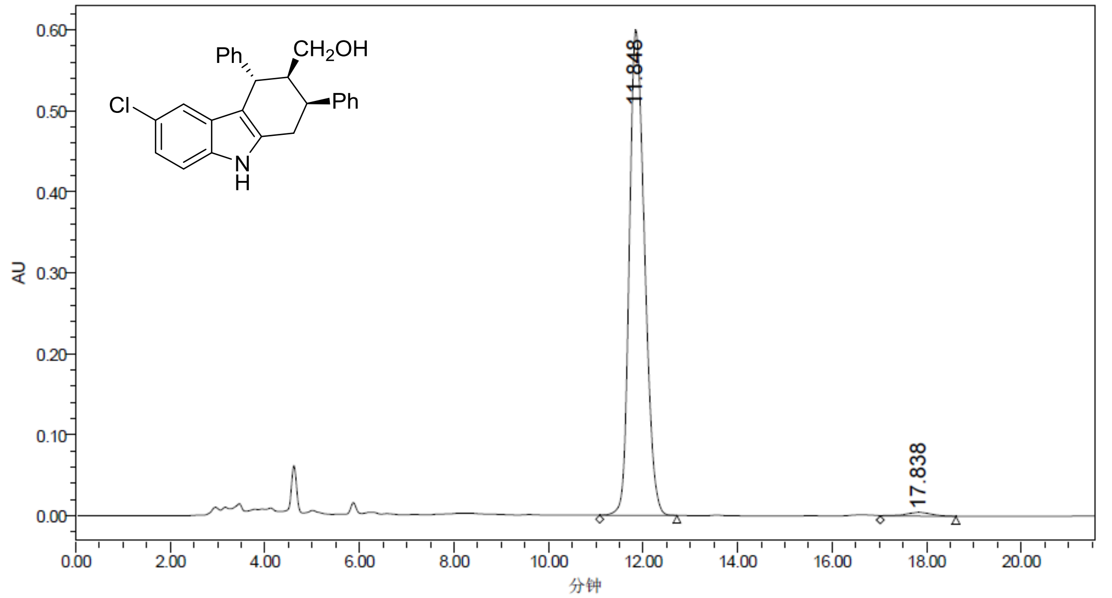


	RT (min)	Peak Type	Area (礦*sec)	% Area	Height (礦)	% Height	Integration Type	Points Across Peak	Start Time (min)	End Time (min)
1	10.901	未知	6884624	99.69	342136	99.84	BB	92	10.183	11.717
2	21.441	未知	21295	0.31	546	0.16	BB	77	20.883	22.167

((2S,3S,4S)-6-chloro-2,4-diphenyl-2,3,4,9-tetrahydro-1H-carbazol-3-yl)methanol (4ta)

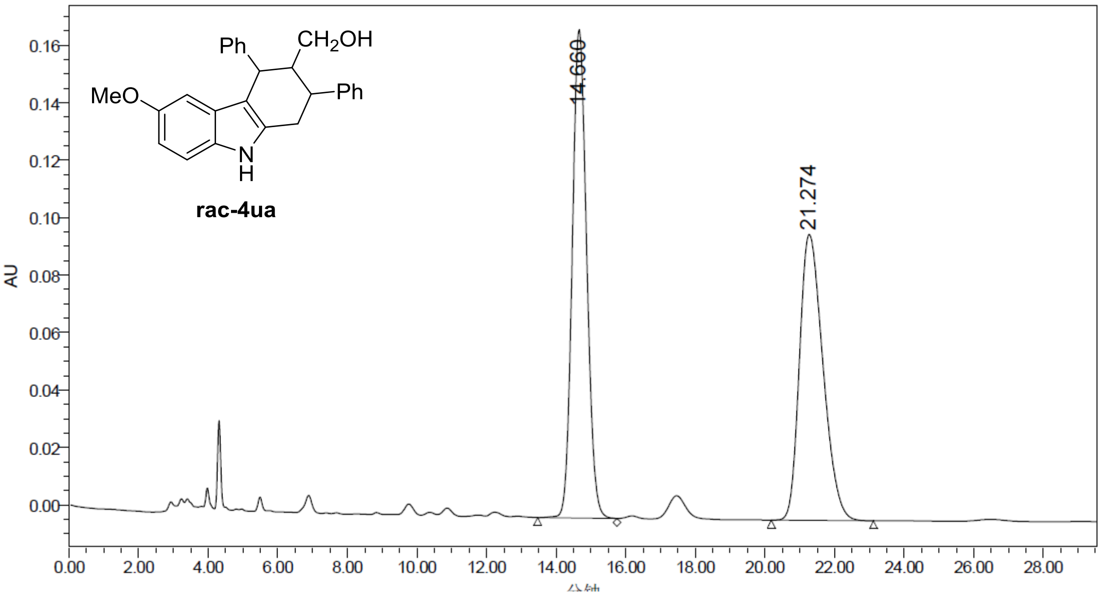


	RT (min)	Peak Type	Area (礦*sec)	% Area	Height (礦)	% Height	Integration Type	Points Across Peak	Start Time (min)	End Time (min)
1	11.882	未知	7166182	50.81	321919	65.48	BB	134	11.033	13.267
2	17.181	未知	6938805	49.19	169739	34.52	BB	164	16.133	18.867

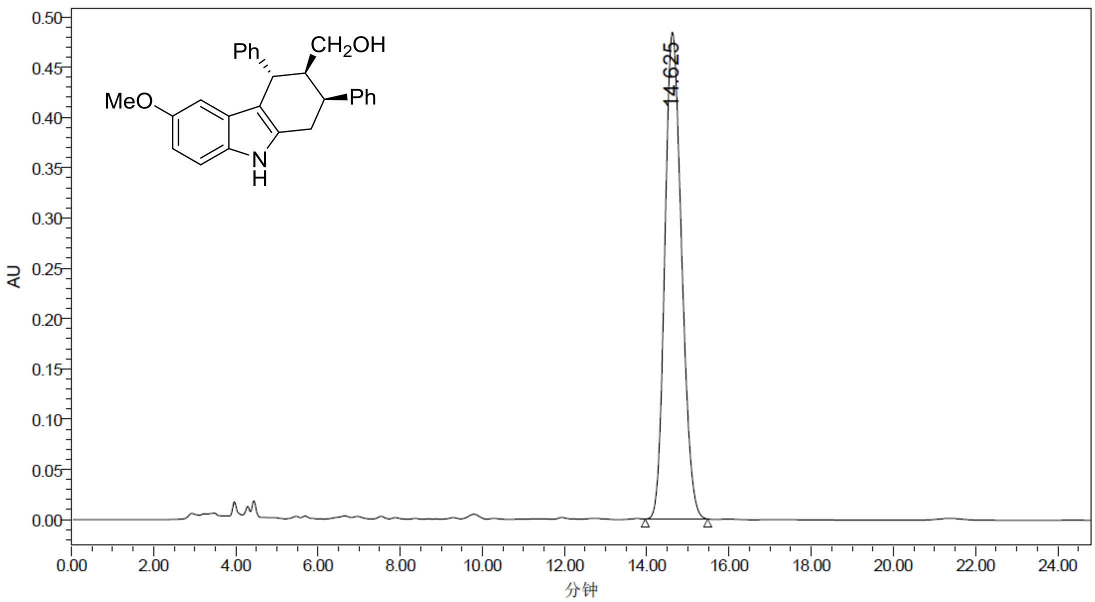


	RT (min)	Peak Type	Area (礦*sec)	% Area	Height (礦)	% Height	Integration Type	Points Across Peak	Start Time (min)	End Time (min)
1	11.848	未知	13441502	98.70	599443	99.25	VB	98	11.083	12.717
2	17.838	未知	177480	1.30	4503	0.75	VB	96	17.017	18.617

((2S,3S,4S)-6-methoxy-2,4-diphenyl-2,3,4,9-tetrahydro-1H-carbazol-3-yl)methanol (4ua)

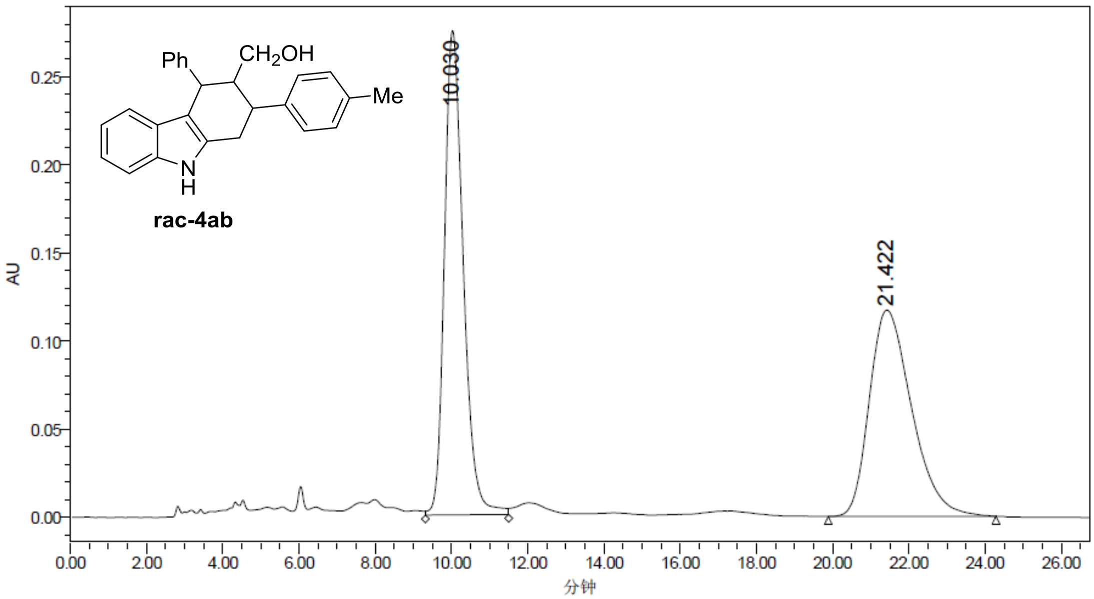


	RT (min)	Peak Type	Area (礦*sec)	% Area	Height (礦)	% Height	Integration Type	Points Across Peak	Start Time (min)	End Time (min)
1	14.660	未知	4893446	51.17	170025	63.08	BV	137	13.467	15.750
2	21.274	未知	4670441	48.83	99527	36.92	BB	176	20.183	23.117

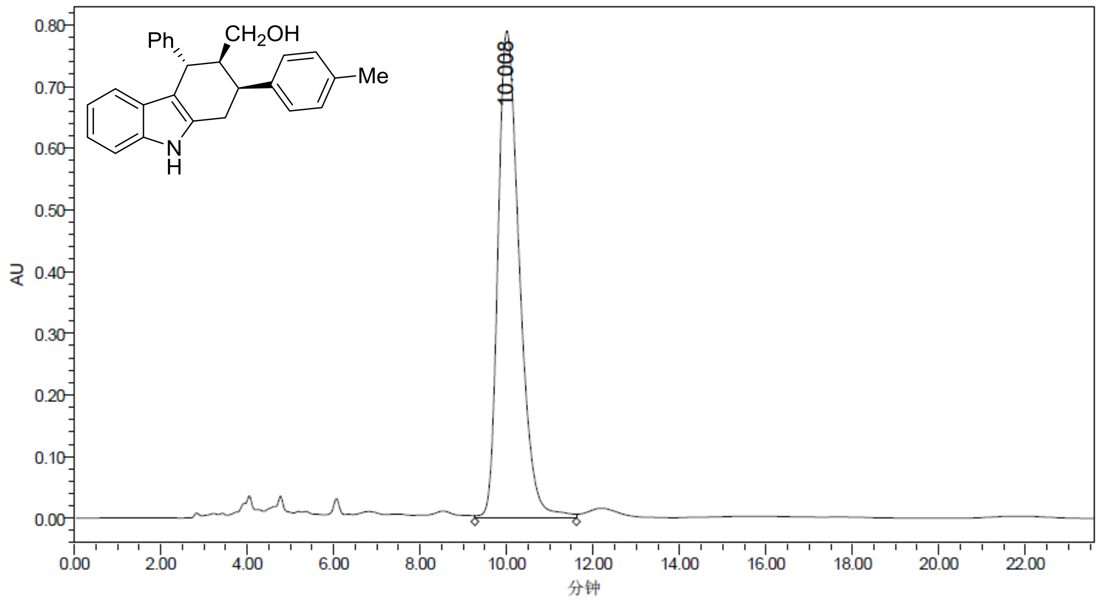


	RT (min)	Peak Type	Area (礦*sec)	% Area	Height (礦)	% Height	Integration Type	Points Across Peak	Start Time (min)	End Time (min)
1	14.625	未知	13759342	100.00	484095	100.00	BB	91	13.967	15.483

((2S,3S,4S)-4-phenyl-2-(p-tolyl)-2,3,4,9-tetrahydro-1H-carbazol-3-yl)methanol (4ab)

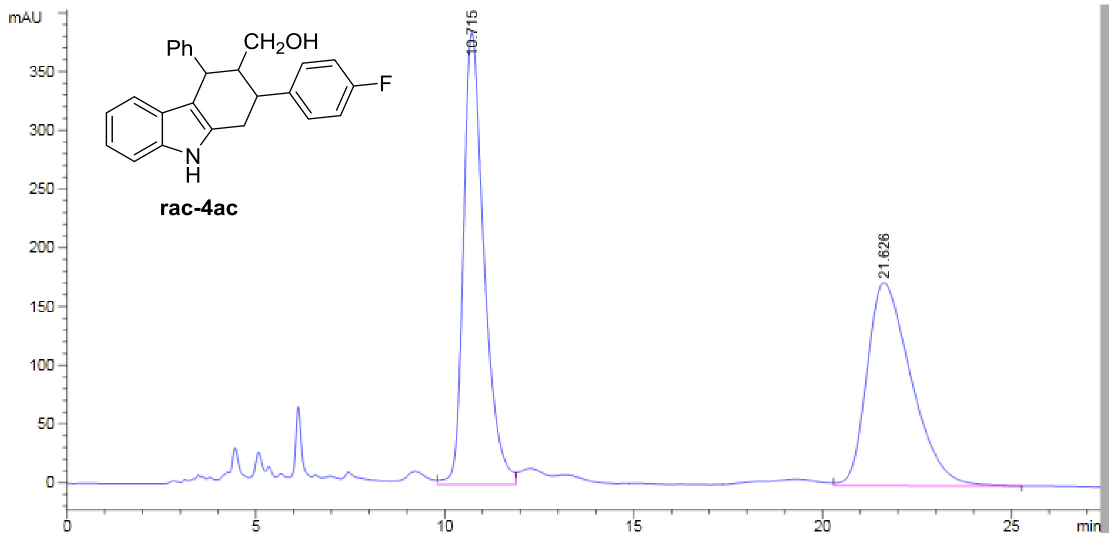


	RT (min)	Peak Type	Area (磺*sec)	% Area	Height (磺)	% Height	Integration Type	Points Across Peak	Start Time (min)	End Time (min)
1	10.030	未知	9450240	51.10	274897	70.11	VV	131	9.317	11.500
2	21.422	未知	9044378	48.90	117208	29.89	BB	264	19.883	24.283

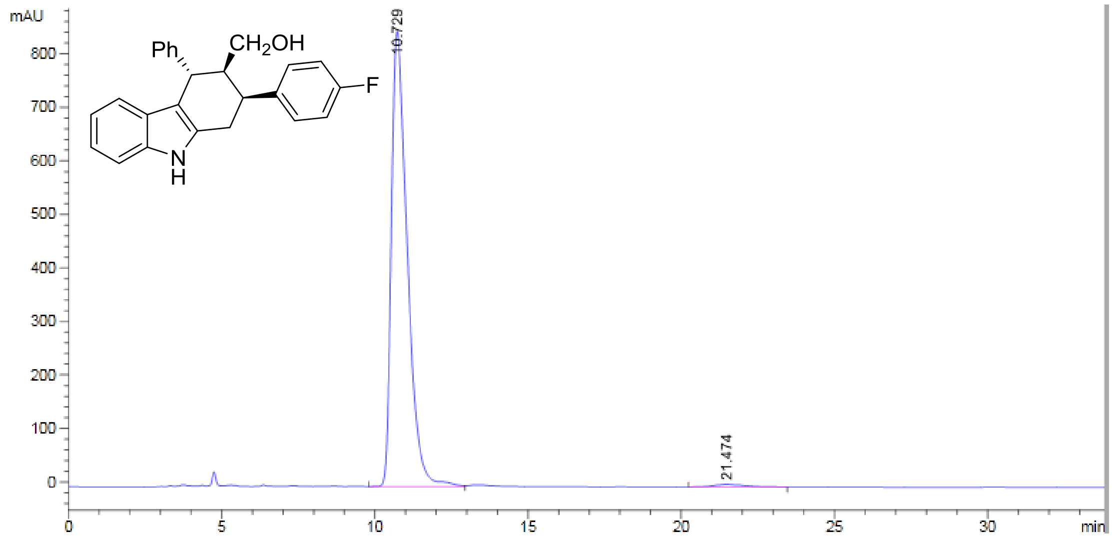


	RT (min)	Peak Type	Area (磺*sec)	% Area	Height (磺)	% Height	Integration Type	Points Across Peak	Start Time (min)	End Time (min)
1	10.008	未知	27138878	100.00	789499	100.00	VV	141	9.267	11.617

((2S,3S,4S)-2-(4-fluorophenyl)-4-phenyl-2,3,4,9-tetrahydro-1H-carbazol-3-yl)methanol (4ac)

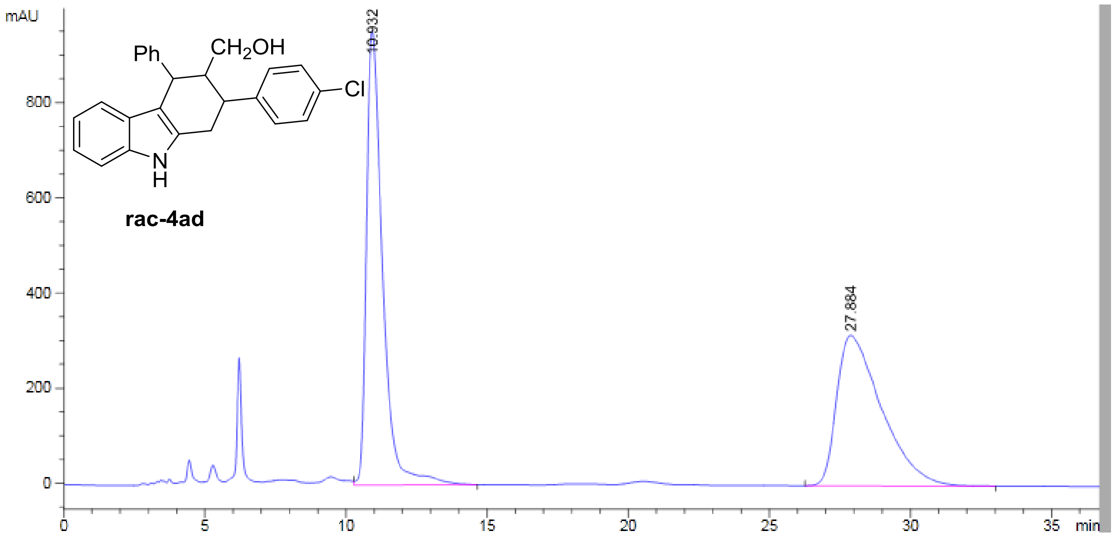


Peak #	RetTime [min]	Type	Width [min]	Area mAU *s	Height [mAU]	Area %
1	10.715	VV	0.5687	1.46289e4	384.87903	51.0383
2	21.626	VB	1.2369	1.40337e4	172.59236	48.9617

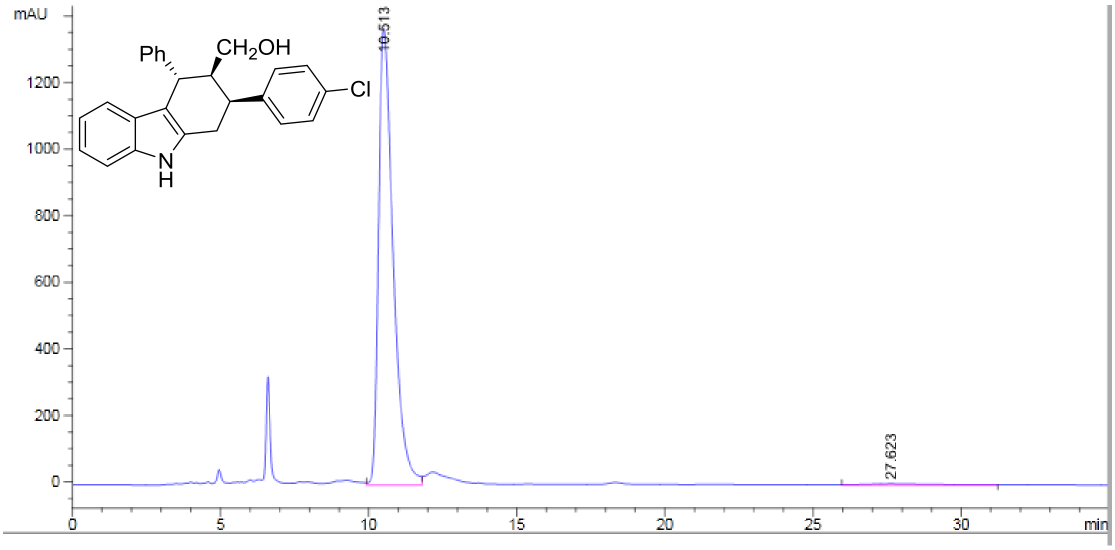


Peak #	RetTime [min]	Type	Width [min]	Area mAU *s	Height [mAU]	Area %
1	10.729	VV	0.5290	3.07476e4	851.52509	98.7780
2	21.474	BB	1.0437	380.38828	5.03948	1.2220

((2S,3S,4S)-2-(4-chlorophenyl)-4-phenyl-2,3,4,9-tetrahydro-1H-carbazol-3-yl)methanol (4ad)

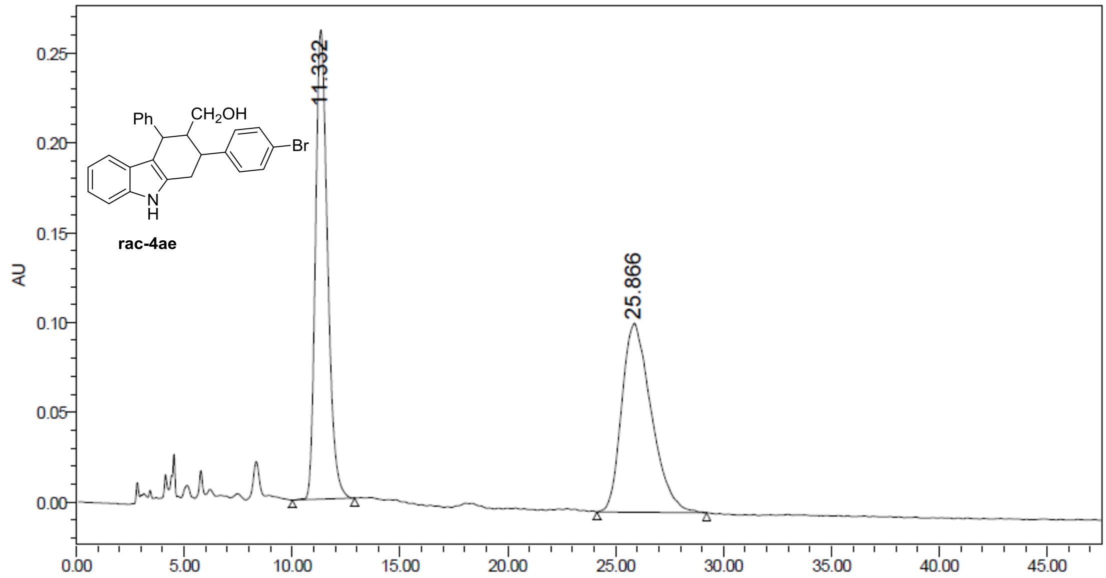


Peak #	RetTime [min]	Type	Width [min]	Area mAU *s	Height [mAU]	Area %
1	10.932	VB	0.6034	3.79065e4	953.77881	52.0585
2	27.884	BB	1.6071	3.49086e4	315.79773	47.9415

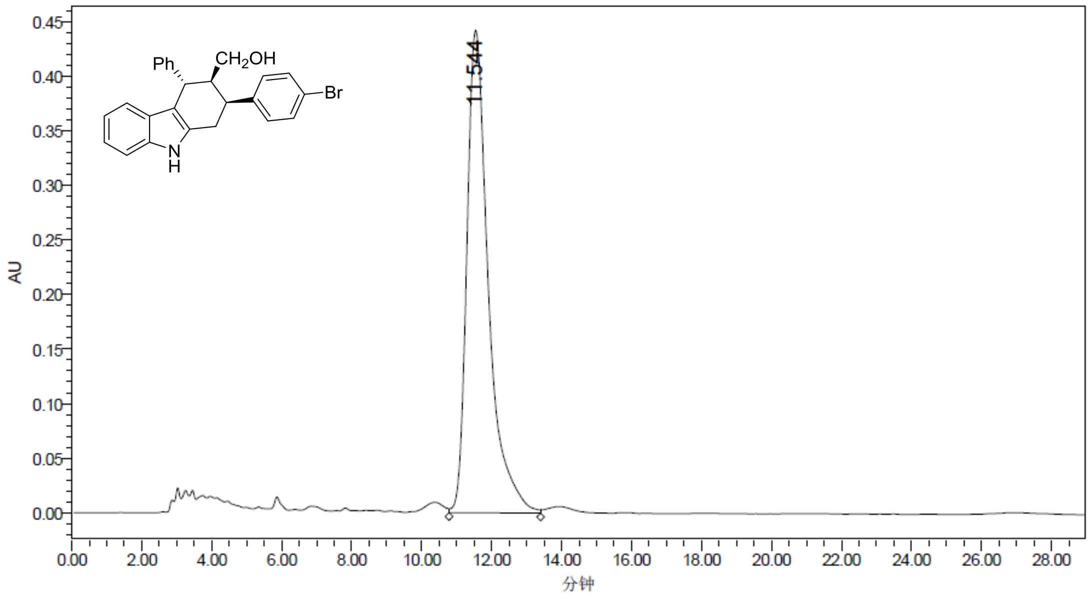


Peak #	RetTime [min]	Type	Width [min]	Area mAU *s	Height [mAU]	Area %
1	10.513	VV	0.5171	4.70328e4	1369.62402	99.0190
2	27.623	BV	1.8724	465.96320	3.61105	0.9810

((2S,3S,4S)-2-(4-bromophenyl)-4-phenyl-2,3,4,9-tetrahydro-1H-carbazol-3-yl)methanol (4ae)

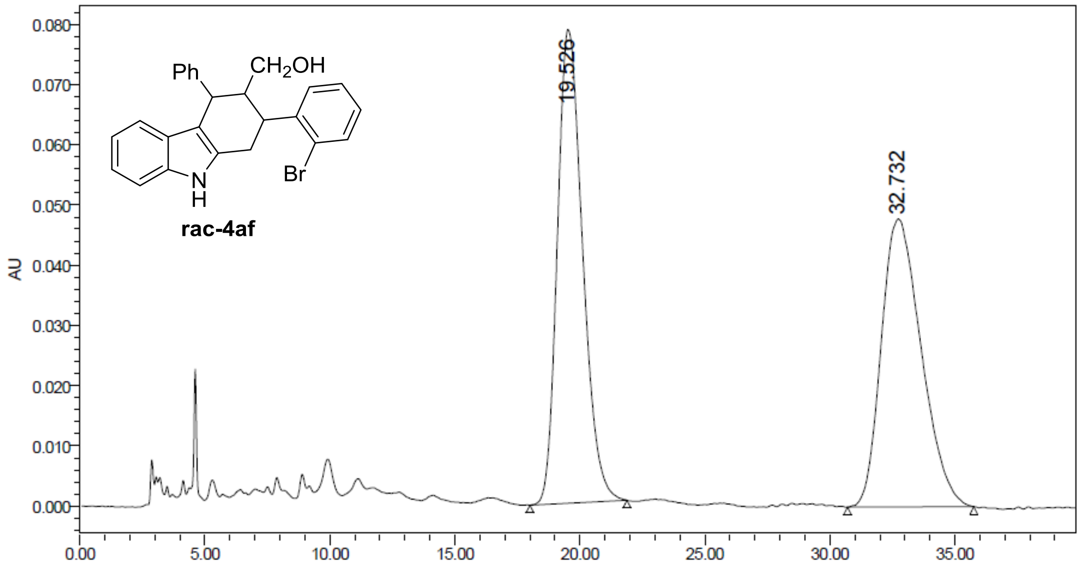


	RT (min)	Peak Type	Area (礦*sec)	% Area	Height (礦)	% Height	Integration Type	Points Across Peak	Start Time (min)	End Time (min)
1	11.332	未知	10175629	50.34	261227	71.29	BB	173	10.017	12.900
2	25.866	未知	10038398	49.66	105219	28.71	BB	305	24.133	29.217

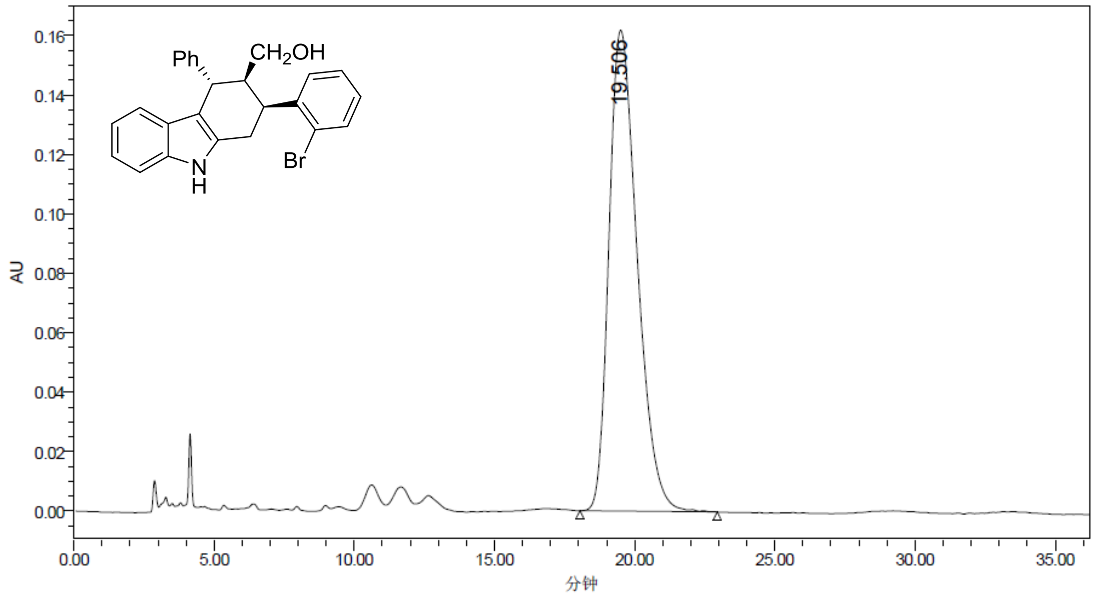


	RT (min)	Peak Type	Area (礦*sec)	% Area	Height (礦)	% Height	Integration Type	Points Across Peak	Start Time (min)	End Time (min)
1	11.544	未知	18847596	100.00	441664	100.00	VV	157	10.783	13.400

((2S,3S,4S)-2-(2-bromophenyl)-4-phenyl-2,3,4,9-tetrahydro-1H-carbazol-3-yl)methanol (4af)

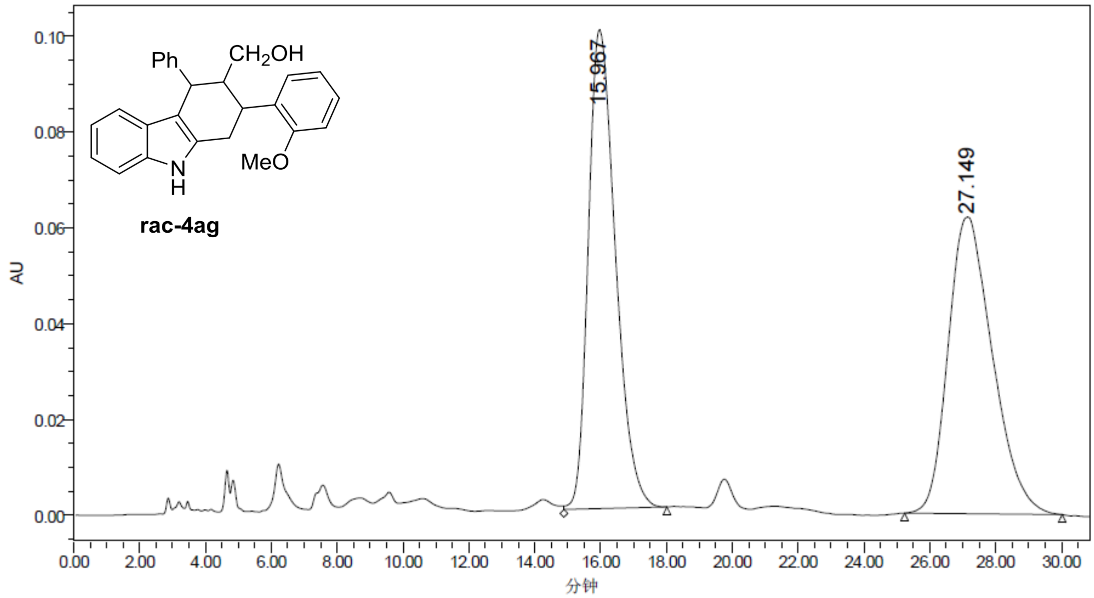


	RT (min)	Peak Type	Area (礦*sec)	% Area	Height (礦)	% Height	Integration Type	Points Across Peak	Start Time (min)	End Time (min)
1	19.526	未知	5523144	50.96	78665	62.20	BB	233	18.000	21.883
2	32.732	未知	5315962	49.04	47811	37.80	BB	303	30.700	35.750

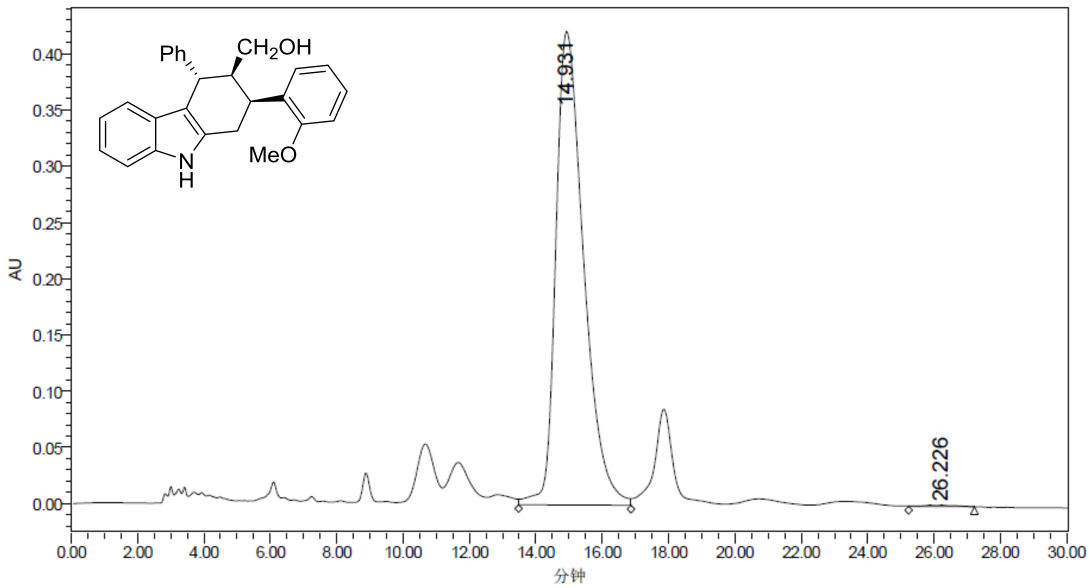


	RT (min)	Peak Type	Area (礦*sec)	% Area	Height (礦)	% Height	Integration Type	Points Across Peak	Start Time (min)	End Time (min)
1	19.506	未知	11353268	100.00	161831	100.00	BB	294	18.050	22.950

((2S,3S,4S)-2-(2-methoxyphenyl)-4-phenyl-2,3,4,9-tetrahydro-1H-carbazol-3-yl) methanol (4ag)

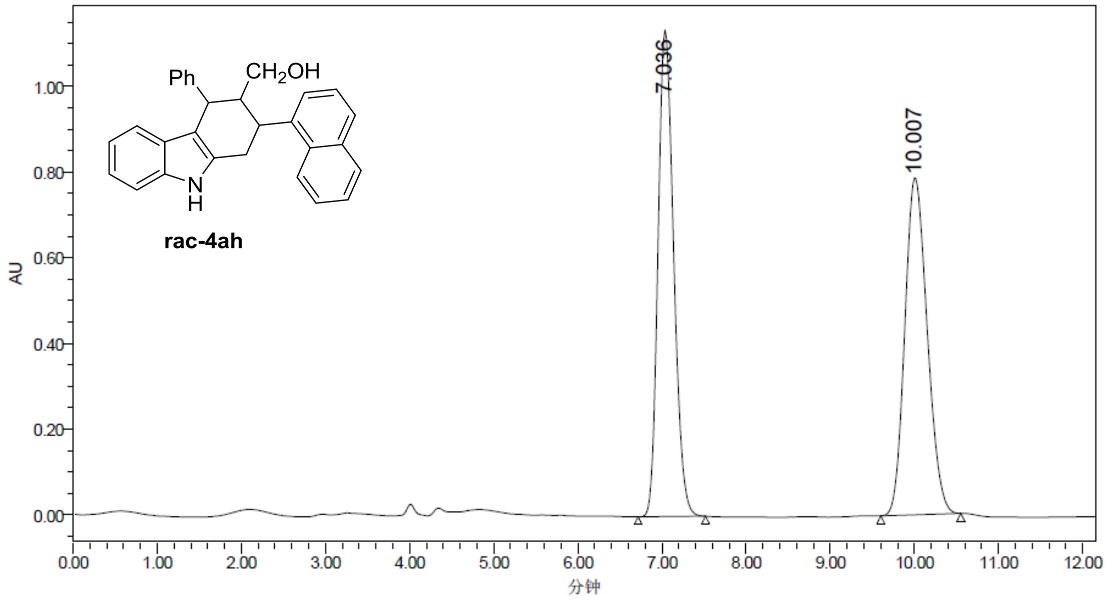


	RT (min)	Peak Type	Area (磺*sec)	% Area	Height (磺)	% Height	Integration Type	Points Across Peak	Start Time (min)	End Time (min)
1	15.967	未知	5738745	49.74	100015	61.77	VB	188	14.883	18.017
2	27.149	未知	5798001	50.26	61904	38.23	BB	287	25.233	30.017

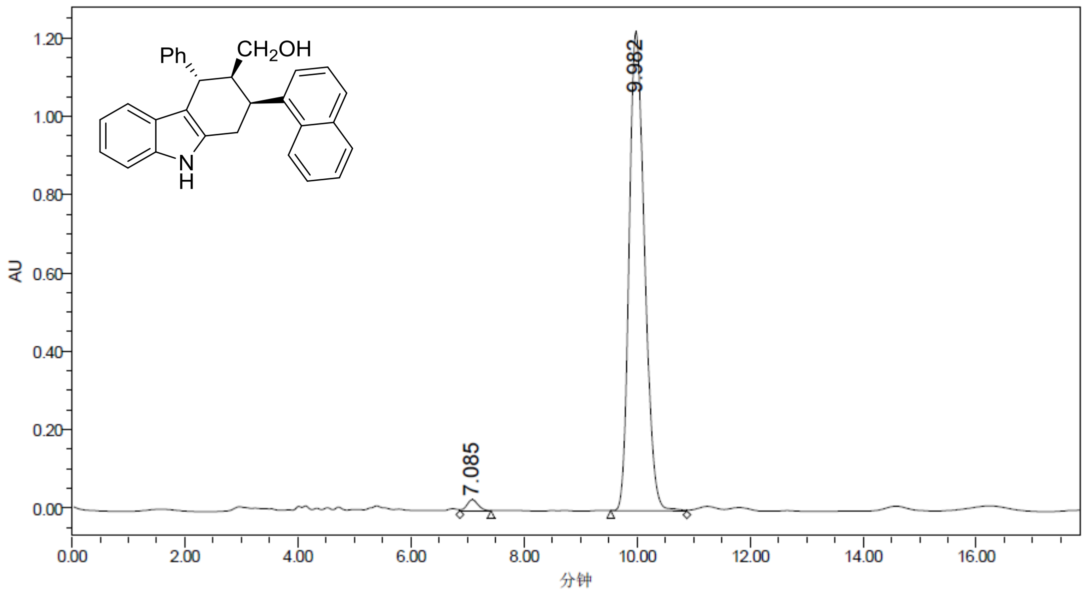


	RT (min)	Peak Type	Area (磺*sec)	% Area	Height (磺)	% Height	Integration Type	Points Across Peak	Start Time (min)	End Time (min)
1	14.931	未知	24610269	99.65	420912	99.72	VV	203	13.483	16.867
2	26.226	未知	86757	0.35	1192	0.28	VB	119	25.233	27.217

((2S,3S,4S)-2-(naphthalen-1-yl)-4-phenyl-2,3,4,9-tetrahydro-1H-carbazol-3-yl)methanol (4ah)

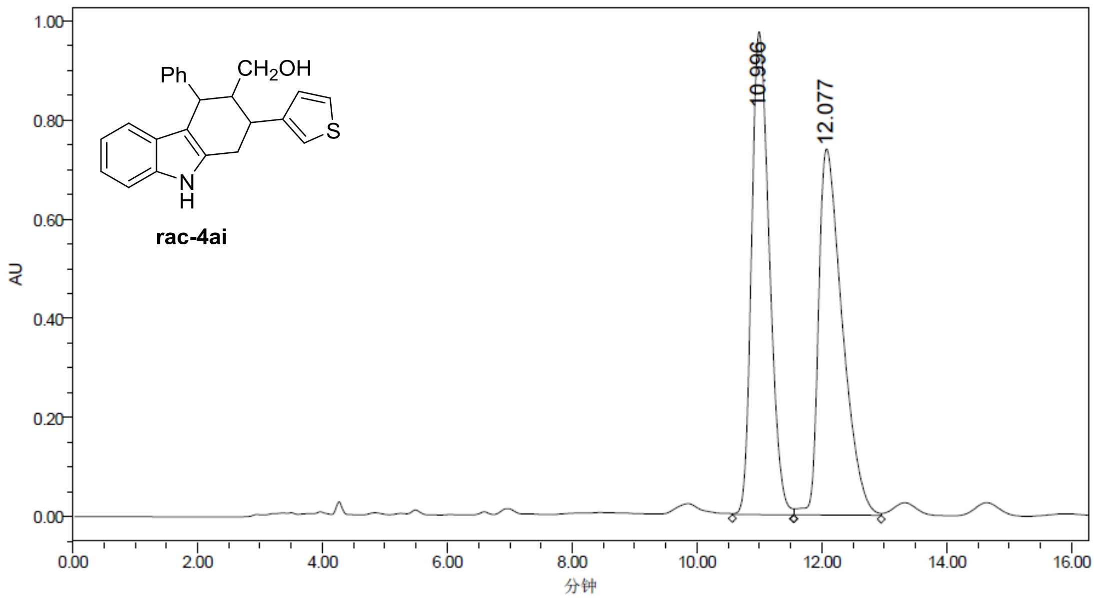


	RT (min)	Peak Type	Area (礦*sec)	% Area	Height (礦)	% Height	Integration Type	Points Across Peak	Start Time (min)	End Time (min)
1	7.036	未知	14674588	50.17	1136433	59.05	BB	48	6.717	7.517
2	10.007	未知	14575432	49.83	788173	40.95	BB	57	9.600	10.550

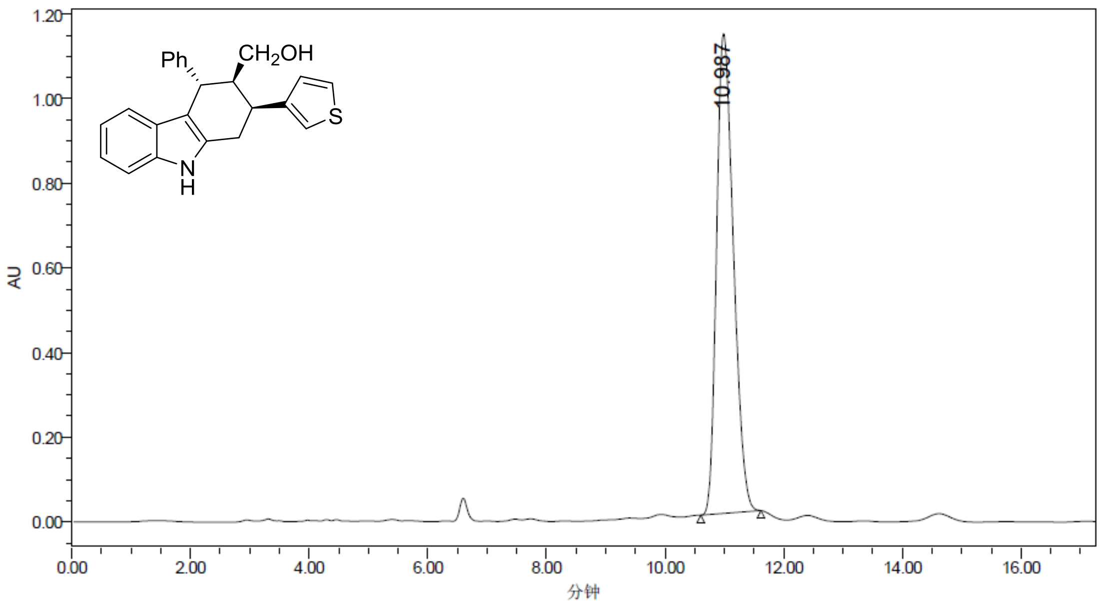


	RT (min)	Peak Type	Area (礦*sec)	% Area	Height (礦)	% Height	Integration Type	Points Across Peak	Start Time (min)	End Time (min)
1	7.085	未知	375904	1.60	28058	2.24	VB	33	6.867	7.417
2	9.982	未知	23178136	98.40	1224486	97.76	BV	81	9.533	10.883

((2S,3S,4S)-4-phenyl-2-(thiophen-3-yl)-2,3,4,9-tetrahydro-1H-carbazol-3-yl)methanol (4ai)

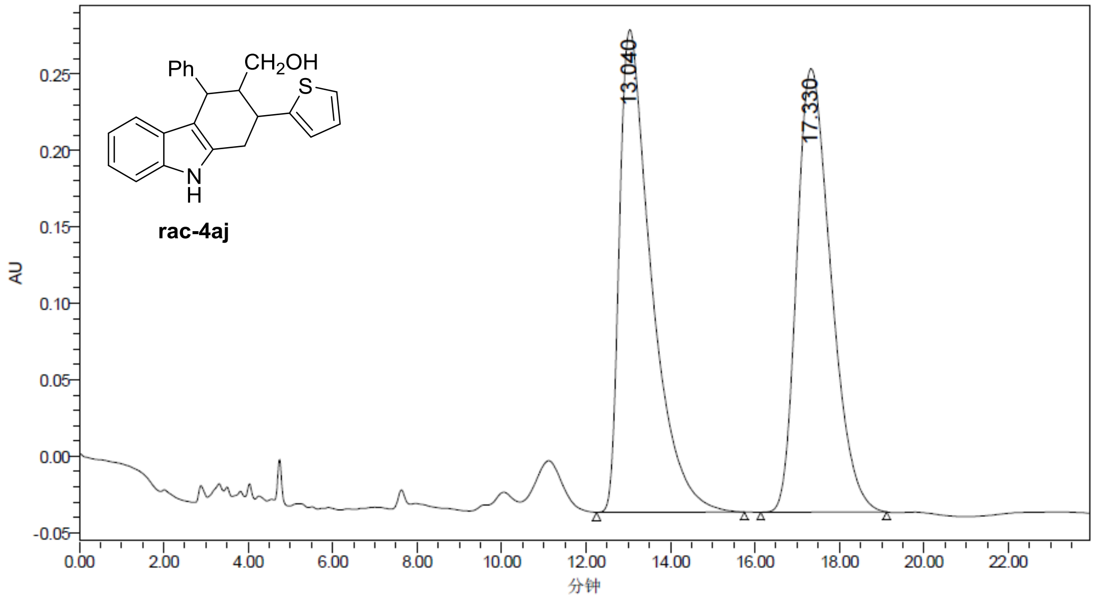


	RT (min)	Peak Type	Area (礦*sec)	% Area	Height (礦)	% Height	Integration Type	Points Across Peak	Start Time (min)	End Time (min)
1	10.996	未知	19214650	49.58	974011	56.86	VV	59	10.567	11.550
2	12.077	未知	19542497	50.42	738840	43.14	VV	84	11.550	12.950

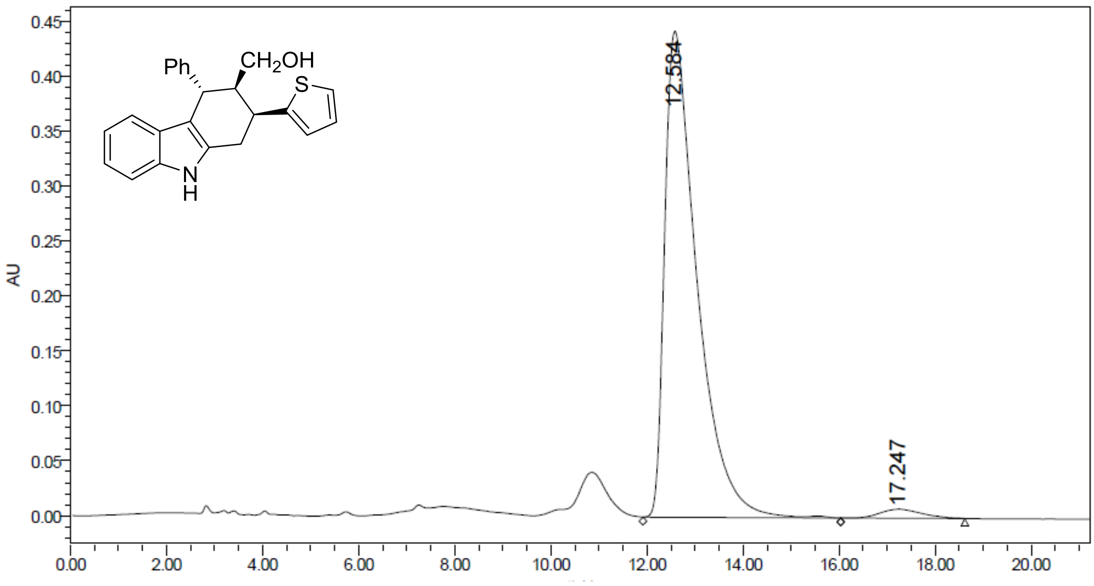


	RT (min)	Peak Type	Area (礦*sec)	% Area	Height (礦)	% Height	Integration Type	Points Across Peak	Start Time (min)	End Time (min)
1	10.987	未知	22426811	100.00	1134957	100.00	BB	61	10.600	11.617

((2S,3R,4S)-4-phenyl-2-(thiophen-2-yl)-2,3,4,9-tetrahydro-1H-carbazol-3-yl)methanol (4aj)

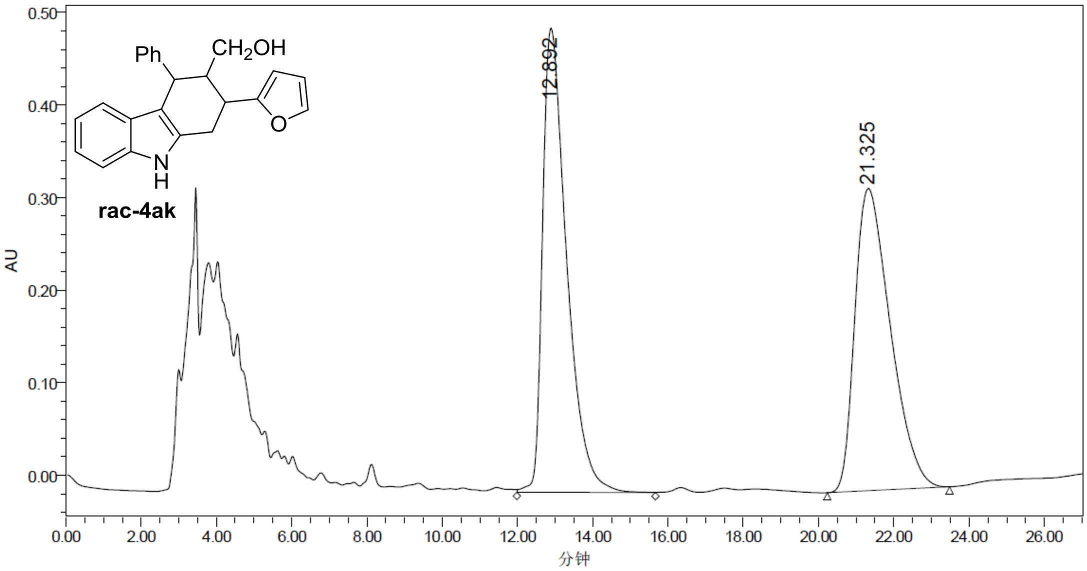


	RT (min)	Peak Type	Area (礦*sec)	% Area	Height (礦)	% Height	Integration Type	Points Across Peak	Start Time (min)	End Time (min)
1	13.040	未知	16548907	50.38	315566	52.12	BB	210	12.250	15.750
2	17.330	未知	16298871	49.62	289917	47.88	BB	179	16.133	19.117

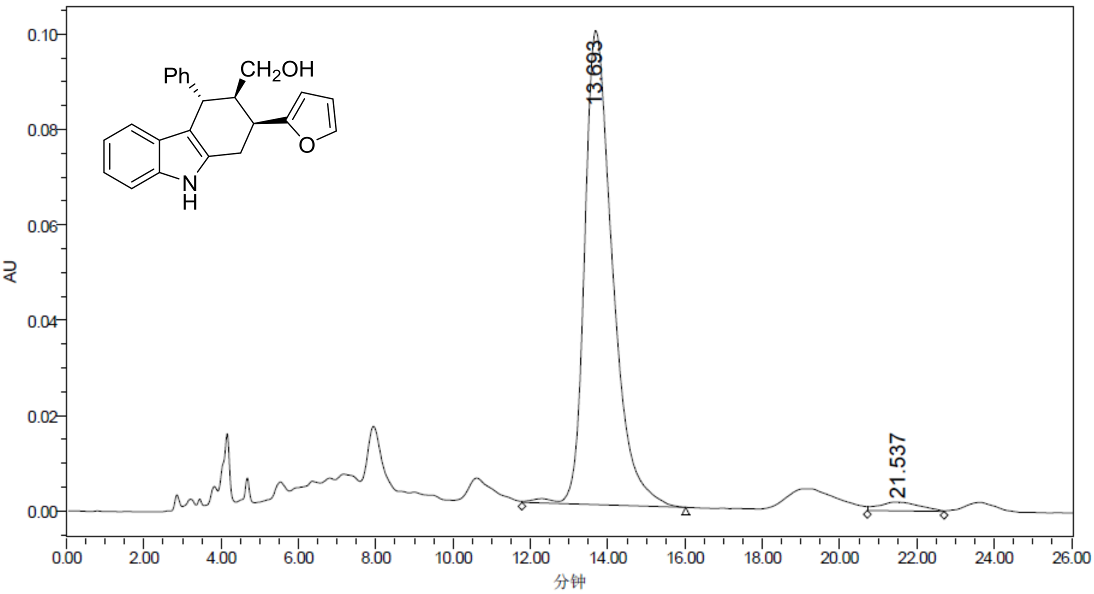


	RT (min)	Peak Type	Area (礦*sec)	% Area	Height (礦)	% Height	Integration Type	Points Across Peak	Start Time (min)	End Time (min)
1	12.584	未知	20719213	97.68	442216	98.18	VV	247	11.917	16.033
2	17.247	未知	492540	2.32	8183	1.82	VB	155	16.033	18.617

((2S,3R,4S)-2-(furan-2-yl)-4-phenyl-2,3,4,9-tetrahydro-1H-carbazol-3-yl)methanol (4ak)

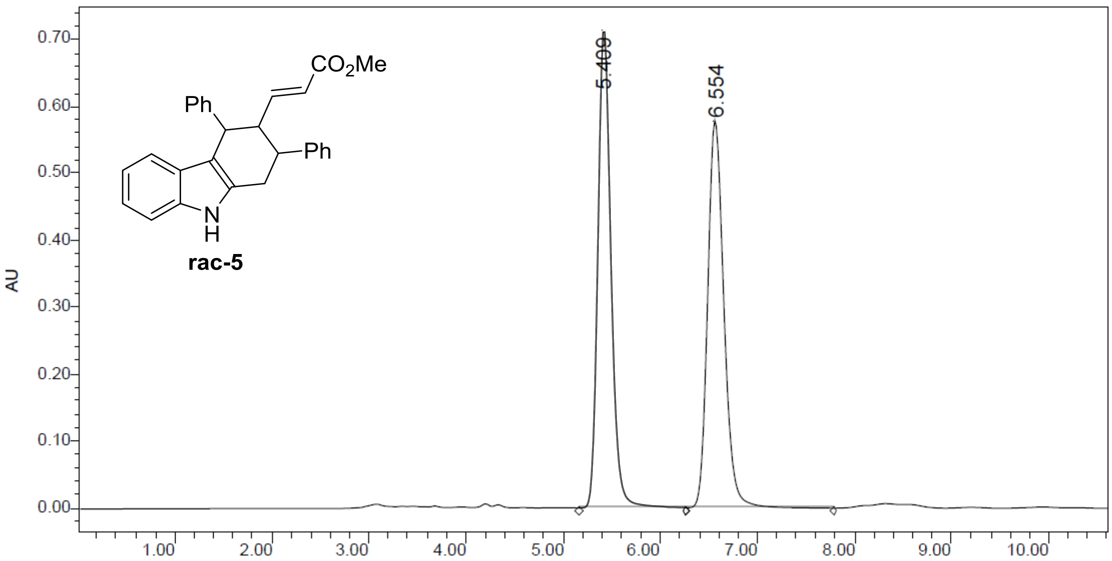


	RT (min)	Area (礦*sec)	% Area	Height (礦)	% Height
1	12.892	22300860	51.01	501315	60.55
2	21.325	21419911	48.99	326610	39.45

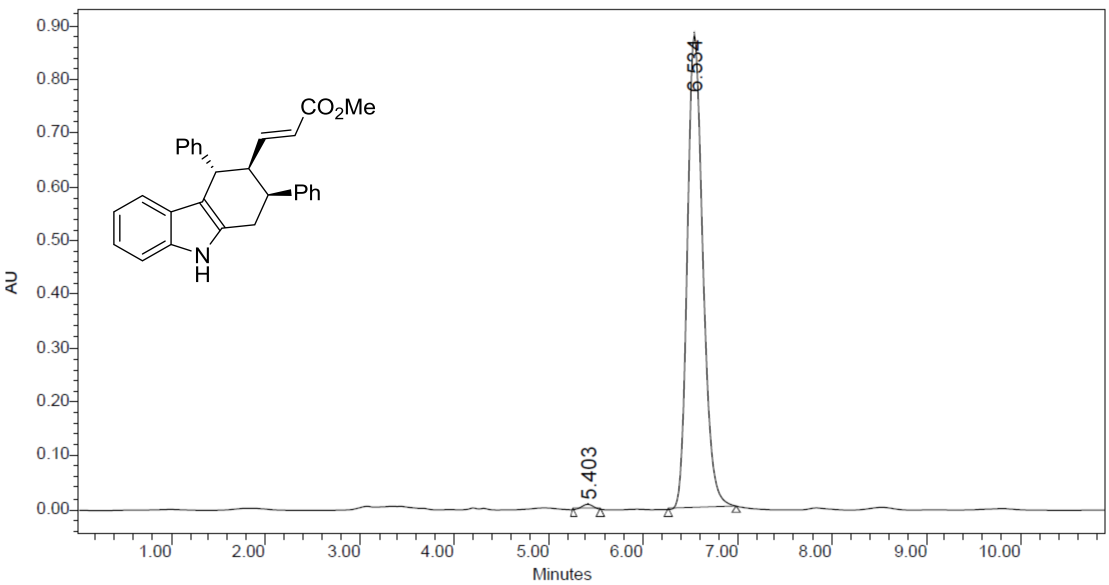


	RT (min)	Peak Type	Area (礦*sec)	% Area	Height (礦)	% Height	Integration Type	Points Across Peak	Start Time (min)	End Time (min)
1	13.693	未知	4996193	97.39	99401	98.23	VB	254	11.783	16.017
2	21.537	未知	133882	2.61	1789	1.77	VV	119	20.717	22.700

methyl(E)-3-((2S,3S,4S)-2,4-diphenyl-2,3,4,9-tetrahydro-1H-carbazol-3-yl)acrylate

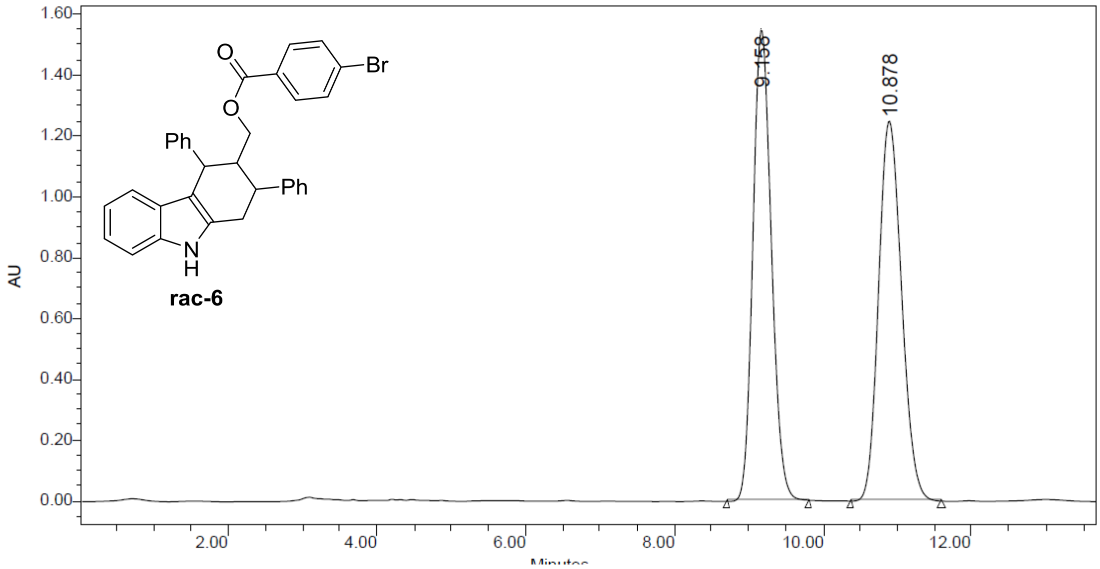


	RT (min)	Area (□V*sec)	% Area	Height (□V)	% Height
1	5.409	6812378	49.96	716606	55.23
2	6.554	6823805	50.04	580776	44.77

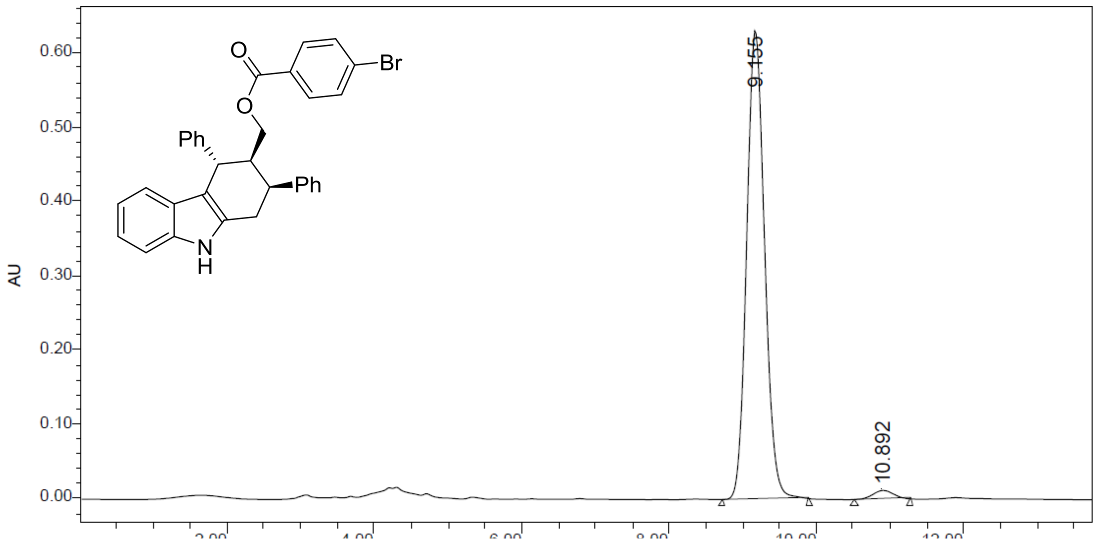


	RT (min)	Area (□V*sec)	% Area	Height (□V)	% Height
1	5.403	78732	0.77	9596	1.08
2	6.534	10096897	99.23	880773	98.92

((2S,3S,4S)-2,4-diphenyl-2,3,4,9-tetrahydro-1H-carbazol-3-yl)methyl 4-bromobenzoate



	RT (min)	Area (µV*sec)	% Area	Height (µV)	% Height
1	9.158	26724331	49.84	1550733	55.36
2	10.878	26896648	50.16	1250452	44.64



	RT (min)	Area (µV*sec)	% Area	Height (µV)	% Height
1	9.155	10645660	97.89	631264	98.18
2	10.892	229882	2.11	11732	1.82