

Supporting Information

Epiandrosterone-Derived Prolinamide as Efficient Asymmetric Catalyst for Michael Addition Reactions of Aldehydes to Nitroalkenes

Yongchao Wang, Shen Ji, Kun Wei* and Jun Lin*

*Key Laboratory of Medicinal Chemistry for Natural Resource (Yunnan University),
Ministry of Education, School of Chemical Science and Technology, Yunnan
University, Kunming 650091, PR China*

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1. General Information:

The NMR spectra were recorded on a Bruker DRX400 (^1H : 400 MHz, ^{13}C : 100 MHz) and DRX500 (^1H : 500 MHz, ^{13}C : 125 MHz) with TMS as the internal standard, chemical shifts (δ) are expressed in *ppm*, and *J* values are given in Hz, and deuterated CDCl_3 and was used as solvent. Highresolution mass spectrometry(HRMS) was recorded on a VG Auto Spec-3000 spectrometer. Optical rotations were measured on a JASCO DIP-370polarimeter. IR spectra were recorded on a FT-IR Thermo Nicolet Avatar 360 using KBr pellet. The mass spectroscopic data were obtained at the Agilent 1100 LC/MSD Trap LC-mass spectrometer. HPLC analysis was performed with a Shimadzu LC-10A instrument equipped with Daicel HPLC columns. Reagents and Materials were of the highest commercially available grade and used without further purification. Solvents were purified by standard procedures and distilled before use. The reactions were monitored by thin layer chromatography(TLC) using silica gel GF₂₅₄. Column chromatography was performed on silica gel (200–300 mesh). Compounds were visualized by UV and spraying with H_2SO_4 (10%) in ethanol and followed by heating.

2. Screening of non-chiral prolinamidecatalysts

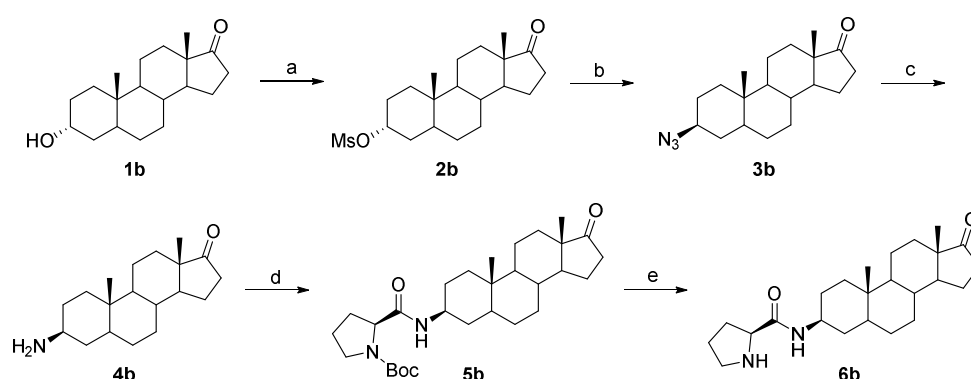
In order to evaluate the importance of the big chiral structure of epiandrosterone for the efficiency of the catalyst, as supplementary, several smaller non-chiral prolinamide derivatives has been tested in the model Michael reaction (Table 1). As shown in Table 1, although excellent yields were obtained, the diastereoselectivities and enantioselectivity were unsatisfactory. Significantly, when changed the steric hindrance of the catalysts from Cat.1 to Cat.4, it was observed that also led to the increasing of diastereoselectivities and enantioselectivities. The experimental results shown that the bulky epiandrosterone group is considered to be important to the high catalytic activity of the catalyzed reactions.

Table 1. Screening of non-chiral prolinamided catalysts:^a

Entry	Catalyst (mol%)	Time (h)	Yield ^b (%)	syn/anti ^c	ee(syn) ^d (%)
1	Cat.1	12	91	58:42	21
2	Cat.2	12	89	55:45	24
3	Cat.3	12	87	62:38	41
4	Cat.4	12	88	64:36	65

^aAll reactions were carried out using **12a** (3.0 mmol) and **13a** (1.0 mmol) in the presence of catalysts in solvent (1.0 mL).
^bYield of the isolated product. ^cDetermined by ¹H NMR analysis of the products. ^dDetermined by chiral HPLC, the absolute configuration was established by comparison with literature data.

3. Procedure for the synthesis of catalysts 6b



(3R,10S,13S)-10,13-dimethyl-17-oxohexadecahydro-1H-cyclopenta[a]phenanthrene-3-yl methanesulfonate (2b). The method for the synthesis of **2b** was similar to that of **2a**. **2b** is white solid, 92 % yield. $[\alpha]_D^{20} = -56.7$ (c 1.0, CDCl_3); IR (KBr) 510, 910, 964, 1276, 1450, 1748, 2897, 2972, 3488 cm^{-1} ; m.p. 157-150°C; HRMS (EI) calcd for $\text{C}_{20}\text{H}_{32}\text{O}_4\text{S}$ $[\text{M}+\text{Na}]^+$ 391.1913, found 391.1911. ¹H-NMR (500 MHz, CDCl_3) δ 4.99 (1H, m), 3.02 (3H, s), 2.48 (1H, dd, $J = 19, 8.8$ Hz), 2.08 (1H, dt, $J = 19, 9$ Hz), 2.13-2.05 (2H, m), 1.98-1.34 (10H, m), 1.31-1.22 (6H, m), 1.73 (1H, m), 1.07-1.02 (1H, m), 0.87 (3H, s), 0.83 (3H, s); ¹³C-NMR (125 MHz, CDCl_3) δ 221.6, 80., 0, 54.5, 51.8, 48.2, 39.8, 39.1, 36.2, 35.4, 34.3, 32.6, 31.9, 31.0, 28.2, 27.7, 22.1, 20.4, 14.2, 11.8.

(3S,10S,13S)-3-azido-10,13-dimethylhexadecahydro-17H-cyclopenta[a]phenanthrene-17-one (3b). The method for the synthesis of **3b** was similar to that of **3a**. **3b** is white solid, 94 % yield. $[\alpha]_D^{20} = -51.6$ (c 1.0, CDCl_3); IR (KBr) 787, 1021, 1143, 1298, 1749, 2093, 2945 cm^{-1} ; m.p. 114-116°C; HRMS (EI) calcd for $\text{C}_{19}\text{H}_{29}\text{N}_3\text{O}$ $[\text{M}+\text{Na}]^+$ 338.2202, found 338.2206. ¹H-NMR (500 MHz, CDCl_3) δ 3.30 (1H, m), 2.28 (1H, dd, $J = 19, 8.8$ Hz), 2.08 (1H, dd, $J = 19, 9.4$ Hz), 1.96-1.93 (3H, m), 1.84-1.47 (5H, m),

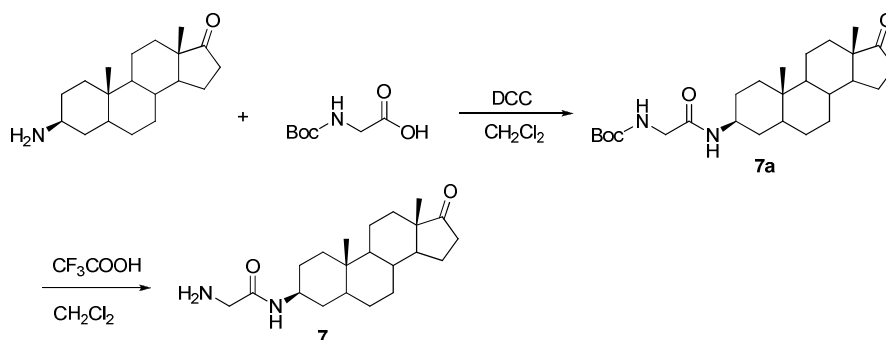
1.42-1.24 (7H, m), 1.19-1.00 (2H, m), 0.86 (3H, s), 0.84 (3H, s); ^{13}C -NMR (125 MHz, CDCl_3) δ 221.5, 60.8, 54.7, 51.8, 48.2, 45.6, 37.5, 36.2, 36.1, 35.4, 34.7, 31.9, 31.2, 28.7, 27.9, 22.2, 20.8, 14.2, 12.6.

(3S,10S,13S)-3-amino-10,13-dimethylhexadecahydro-17H-cyclopenta[a]phenanthren-17-one (4b). The method for the synthesis of **4b** was similar to that of **4a**. **4b** is white solid, 90 % yield. $[\alpha]_{\text{D}}^{20} = -96.8$ (c 1.0, CDCl_3); IR (KBr) 868, 1021, 1395, 1471, 1602, 1773, 2859, 3387 cm^{-1} ; m.p. 125-127°C; HRMS (EI) calcd for $\text{C}_{19}\text{H}_{31}\text{NO}$ $[\text{M}+\text{H}]^+$ 290.2478, found 290.2480. ^1H -NMR (500 MHz, CD_3OD) δ 3.42 (1H, m), 2.51 (1H, m), 2.38-2.32 (2H, m), 2.25 (1H, dd, $J = 19, 8.8$ Hz), 2.15 (1H, dt, $J = 19, 9$ Hz), 1.98 (3H, m), 1.97-1.93 (2H, m), 1.85-1.37 (22H, m), 1.25-0.71 (31H, m), 0.85 (3H, s), 0.82 (3H, s); ^{13}C -NMR (125 MHz, CD_3OD) δ 220.4, 54.8, 51.7, 51.4, 47.9, 45.9, 41.0, 38.1, 36.1, 35.4, 32.9, 32.2, 31.3, 28.9, 22.2, 20.8, 14.3, 12.9.

tert-butyl (2S)-2-(((3S,10S,13S)-10,13-dimethyl-17-oxohexadecahydro-1H-cyclopenta[a]phenanthren-3-yl)carbamoyl)pyrrolidine-1-carboxylate (5b). The method for the synthesis of **4b** was similar to that of **4a**. **4b** is white solid, 93 % yield. $[\alpha]_{\text{D}}^{20} = -15.2$ (c 1.0, CHCl_3); IR (KBr) 932, 1171, 1283, 1394, 1601, 1764, 2890, 2944, 3347 cm^{-1} ; HRMS (EI) calcd for $\text{C}_{29}\text{H}_{46}\text{N}_2\text{O}_4$ $[\text{M}+\text{Na}]^+$ 509.3385, found 509.3388. ^1H -NMR (500 MHz, CDCl_3) δ 4.15 (1H, m), 3.79-3.74 (2H, m), 3.46 (2H, m), 2.46-2.40 (1H, m), 2.10-2.03 (2H, m), 1.95-1.31 (20H, m), 1.29-0.96 (20H, m), 0.86 (3H, s), 0.82 (3H, s); ^{13}C -NMR (125 MHz, CDCl_3) δ 221.6, 172.5, 125.3, 80.9, 54.7, 51.8, 49.0, 48.8, 48.2, 47.5, 45.7, 42.9, 37.7, 36.2, 35.9, 35.7, 31.9, 31.2, 29.1, 28.8, 28.6, 22.5, 22.2, 20.8, 14.2, 12.6.

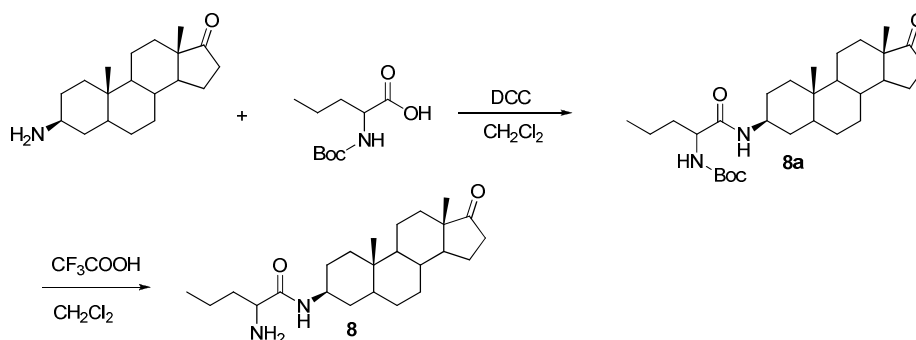
(2S)-N-((3S,10S,13S)-10,13-dimethyl-17-oxohexadecahydro-1H-cyclopenta[a]phenanthren-3-yl)pyrrolidine-2-carboxamide (6b). The method for the synthesis of **6b** was similar to that of **6a**. **6b** is white solid, 92 % yield. $[\alpha]_{\text{D}}^{20} = -43.0$ (c 1.0, CHCl_3); IR (KBr) 773, 959, 1247, 1262, 1427, 1538, 1848, 2831, 3001, 3364 cm^{-1} ; HRMS (EI) calcd $\text{C}_{24}\text{H}_{38}\text{N}_2\text{O}_2$, $[\text{M}+\text{H}]^+$ 387.3006, found for 387.3004. ^1H NMR (400 MHz, CDCl_3) δ 7.46 (1H, d, $J = 7.3$ Hz), 3.79-3.75 (3H, m), 3.70-3.68 (1H, m), 3.03-2.98 (2H, m), 2.46-2.41 (1H, m), 2.15-2.04 (3H, m), 1.96-1.30 (16H, m), 1.27-1.07 (22H, m), 0.88 (3H, s), 0.86 (3H, s); ^{13}C NMR (100 MHz, CDCl_3) δ 221.6, 174.6, 61.4, 54.8, 51.8, 48.8, 48.2, 47.7, 45.8, 42.9, 37.8, 36.3, 35.8, 35.5, 31.9, 31.2, 29.3, 29.1, 28.7, 26.5, 22.5, 22.2, 20.8, 14.2, 12.7.

4. Procedure for the synthesis of catalysts 7-10.



3α-*N*-(Boc-2-amino-acetyl)-5α-androstan-17-one (7a). The method for the synthesis of **7a** was similar to that of **5**. **7a** is white solid, 89% yield. $[\alpha]_D^{20} = +36.8$ (c 1.0, CHCl₃); IR (KBr) 1041, 1164, 1241, 1528, 1663, 1732, 2852, 2921, 3326 cm⁻¹; m.p. 91-94 °C; HRMS (EI) calcd for C₂₆H₄₂N₂O₄, $[M+Na]^+$ 469.3036, found 469.3031. ¹H NMR (500 MHz, CDCl₃): δ 6.71 (s, 1H), 5.06 (d, *J* = 8.1 Hz, 1H), 4.13-4.05 (m, 2H), 2.89-2.87 (d, *J* = 10.0 Hz, 1H), 3.65-3.62 (m, 1H), 2.98-2.94 (m, 1H), 2.88-2.82 (m, 1H), 2.08-2.06 (m, 1H), 2.05-1.85 (m, 7H), 2.49-2.44 (m, 1H), 2.09-2.04 (m, 1H), 1.94-1.91 (m, 1H), 1.82-1.49 (m, 10H), 1.41 (s, 9H), 1.38-1.25 (m, 6H), 1.38-1.22 (m, 6H), 0.95-0.93 (m, 3H), 0.87 (s, 3H), 0.83 (s, 3H); ¹³C NMR (100 MHz, CDCl₃): δ 221.7, 172.0, 156.3, 80.3, 60.8, 54.9, 53.6, 52.0, 48.8, 48.2, 45.0, 41.2, 36.9, 36.5, 36.2, 35.3, 33.5, 33.1, 32.0, 31.6, 31.1, 28.8, 28.5, 26.4, 25.2, 23.3, 22.5, 22.1, 21.4, 20.4, 14.6, 14.2, 11.8.

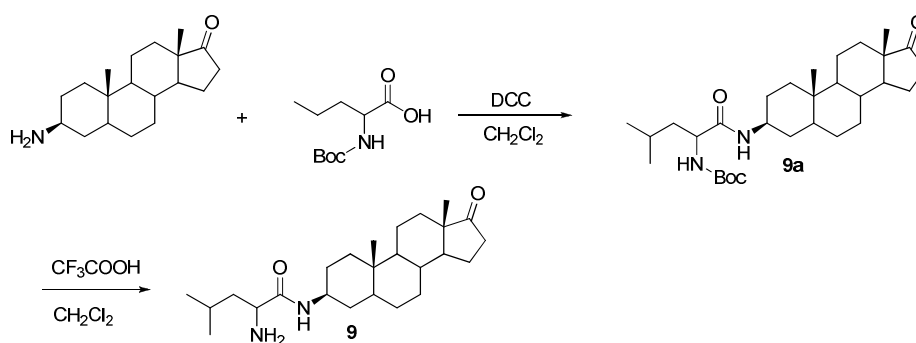
3α-*N*-(2-amino-acetyl)-5α-androstan-17-one (7). The method for the synthesis of **7** was similar to that of **6**. **7** is white solid, 93% yield. $[\alpha]_D^{20} = +69.8$ (c 1.0, CHCl₃); IR (KBr) 747, 1119, 1364, 1446, 1511, 1674, 1740, 2855, 2929, 3374 cm⁻¹; m.p. 88-90 °C; HRMS (EI) calcd for C₂₁H₃₄N₂O₂, $[M+H]^+$ 347.2693, found 347.2693. ¹H NMR (500 MHz, CDCl₃): δ 7.66 (d, *J* = 7.0 Hz, 1H), 4.10-4.09 (m, 1H), 3.38-3.36 (m, 1H), 2.47-2.41 (m, 1H), 2.08-1.48 (m, 22H), 1.38-1.20 (m, 12H), 1.08-0.77 (m, 16H); ¹³C NMR (100 MHz, CDCl₃): δ 221.8, 174.5, 55.0, 54.0, 51.9, 48.2, 44.5, 44.3, 41.5, 36.6, 36.2, 35.4, 33.7, 33.3, 31.9, 31.2, 28.6, 26.4, 25.3, 23.7, 22.5, 22.1, 21.8, 20.5, 14.2, 11.9.



3α-*N*-(Boc-2-amino-pentanoyl)-5α-androstan-17-one (8a). The method for the synthesis of **8a** was similar to that of **5**. **8a** is white solid, 86% yield. $[\alpha]_D^{20} = +50.2$ (c

1.0, CHCl₃); IR (KBr) 1052, 1168, 1241, 1588, 1674, 1792, 2842, 2971, 3332 cm⁻¹; m.p. 93-95 °C; HRMS (EI) calcd for C₂₉H₄₈N₂O₄, [M+Na]⁺ 511.3506, found 511.3503. ¹H NMR (500 MHz, CDCl₃): δ 6.66 (s, 1H), 5.17 (s, 1H), 4.12 (s, 1H), 4.00 (d, *J* = 6.0 Hz, 1H), 2.49-2.44 (m, 1H), 2.09-2.04 (m, 1H), 1.96-1.91 (m, 1H), 1.79-1.74 (m, 3H), 1.67-1.22 (m, 32H), 0.94-0.91 (m, 6H), 0.87 (s, 3H), 0.83 (s, 3H); ¹³C NMR (100 MHz, CDCl₃): δ 221.7, 171.7, 156.3, 80.3, 54.9, 51.9, 48.8, 48.2, 45.0, 41.2, 36.6, 36.2, 35.3, 34.8, 33.5, 33.1, 28.8, 28.2, 26.4, 22.5, 22.1, 20.4, 19.4, 14.2, 11.8.

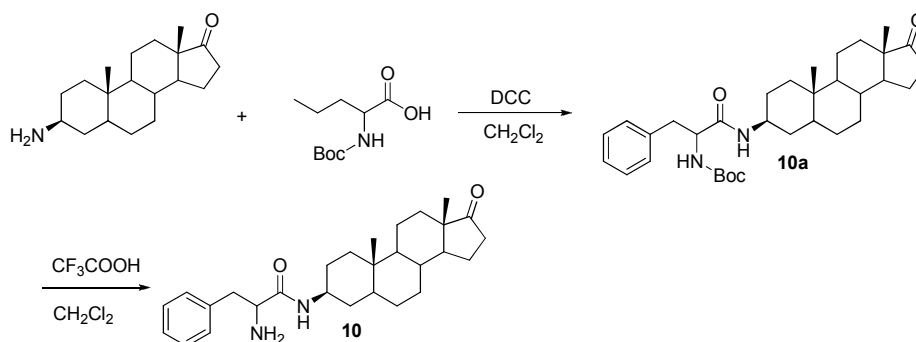
3α-*N*-(2-amino-pentanoyl)-5α-androstan-17-one (8). The method for the synthesis of **8** was similar to that of **6.8** is amorphous powder, 96% yield. [α]_D²⁰ = +50.8 (c 1.0, CHCl₃); IR (KBr) 976, 1123, 1319, 1376, 1446, 1519, 1675, 1740, 2852, 2925, 3354 cm⁻¹; HRMS (EI) calcd for C₂₄H₄₀N₂O₂, [M+H]⁺ 389.3162, found 389.3166. ¹H NMR (500 MHz, CDCl₃): δ 7.61 (d, *J* = 7.6 Hz, 1H), 3.99 (s, 1H), 3.24 (t, *J* = 7.8 Hz, 1H), 2.37-2.32 (m, 1H), 1.98-1.94 (m, 1H), 1.87-1.82 (m, 1H), 1.71-1.16 (m, 22H), 1.00-0.79 (m, 5H), 0.79 (s, 3H), 0.75 (m, 3H); ¹³C NMR (100 MHz, CDCl₃): δ 221.4, 174.5, 55.4, 54.9, 51.8, 48.7, 48.1, 46.2, 44.3, 41.3, 37.6, 37.0, 36.5, 35.3, 35.0, 33.6, 33.2, 31.9, 31.6, 31.3, 31.1, 28.5, 26.4, 23.5, 22.4, 22.0, 20.8, 19.5, 19.3, 17.2, 14.5, 14.1, 11.8.



3α-*N*-(Boc-2-amino-4-methylpentanoyl)-5α-androstan-17-one (9a). The method for the synthesis of **9a** was similar to that of **5.9a** is white solid, 87% yield. [α]_D²⁰ = +42.8 (c 1.0, CHCl₃); IR (KBr) 587, 645, 767, 1041, 1160, 1236, 1524, 1654, 1724, 2929, 3326 cm⁻¹; m.p. 111-114 °C; HRMS (EI) calcd for C₃₀H₅₀N₂O₄, [M+Na]⁺ 525.3684, found 525.3680. ¹H NMR (500 MHz, CDCl₃): δ 6.85 (s, 1H), 5.48 (s, 1H), 4.12 (s, 1H), 3.74 (t, *J* = 5.4 Hz, 2H), 2.48-2.45 (m, 1H), 2.11-2.04 (m, 1H), 1.94-1.91 (m, 1H), 1.82-1.51 (m, 8H), 1.48 (s, 9H), 1.41-1.18 (m, 8H), 1.08-0.96 (m, 1H), 0.87 (s, 3H), 0.83 (s, 3H), 0.77-0.73 (m, 1H); ¹³C NMR (100 MHz, CDCl₃): δ 221.8, 169.2, 156.9, 80.6, 54.9, 52.0, 48.2, 45.3, 45.1, 36.6, 36.2, 35.3, 33.4, 33.1, 31.9, 31.2, 28.8, 26.3, 22.1, 20.4, 14.2, 11.8.

3α-*N*-(2-amino-4-methylpentanoyl)-5α-androstan-17-one (9). The method for the synthesis of **9** was similar to that of **6.9** is amorphous powder, 88% yield. [α]_D²⁰ = +78.9 (c 1.0, CHCl₃); IR (KBr) 588, 669, 751, 1442, 1516, 1675, 1736, 2848, 2925, 3338 cm⁻¹; HRMS (EI) calcd for C₂₅H₄₂N₂O₂, [M+H]⁺ 403.3319, found 403.3316. ¹H NMR (500 MHz, CDCl₃): δ 8.02 (s, 1H), 7.66 (s, 1H), 4.15-4.04 (m, 1H), 3.80-3.77 (m,

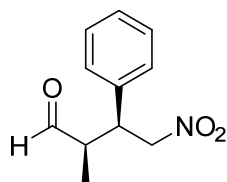
1H), 3.35 (s, 1H), 2.96-2.87 (m, 1H), 2.47-2.42 (m, 2H), 2.08-1.25 (m, 23H), 1.07-1.02 (m, 3H), 0.86 (s, 6H); ¹³C NMR (100 MHz, CDCl₃): δ 221.6, 171.9, 56.2, 55.8, 55.4, 55.0, 53.7, 53.4, 52.4, 51.9, 48.8, 48.2, 46.7, 46.3, 45.3, 44.4, 44.0, 41.4, 36.6, 36.2, 35.4, 34.9, 33.8, 33.4, 33.3, 32.2, 32.0, 31.6, 31.2, 28.6, 27.8, 26.5, 26.0, 23.6, 22.5, 22.1, 20.9, 20.5, 16.8, 14.2, 12.0.



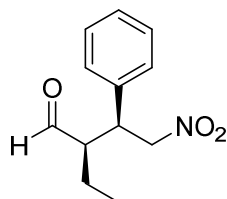
3α-N-(Boc-2-amino-3-phenylpropanoyl)-5α-androstan-17-one (10a). The method for the synthesis of **10a** was similar to that of **5.10a** is white solid, 85% yield. $[\alpha]_D^{20} = +50.4$ (c 1.0, CHCl₃); IR (KBr) 588, 645, 768, 1042, 1160, 1238, 1372, 1524, 1654, 1724, 2929, 3326 cm⁻¹; m.p. 172-174 °C; HRMS (EI) calcd for C₃₃H₄₈N₂O₄, $[M+Na]^+$ 559.3541, found 559.3542. ¹H NMR (500 MHz, CDCl₃): δ 7.33-7.25 (m, 5H), 5.95 (s, 1H), 5.30 (s, 1H), 4.29 (s, 1H), 4.03 (s, 1H), 3.17-3.12 (m, 1H), 3.00-2.96 (m, 1H), 2.49-2.43 (m, 1H), 2.12-2.06 (m, 1H), 1.98-1.93 (m, 1H), 1.82-1.77 (m, 2H), 1.64-1.14 (m, 23H), 0.95-0.92 (m, 2H), 0.86 (s, 3H), 0.77 (s, 3H), 0.76-0.60 (m, 1H); ¹³C NMR (100 MHz, CDCl₃): δ 221.6, 170.3, 156.2, 155.9, 137.6, 129.6, 129.4, 129.1, 127.3, 80.4, 56.5, 54.7, 52.0, 48.2, 45.2, 45.0, 41.1, 40.9, 39.4, 39.1, 36.4, 36.2, 35.3, 33.3, 33.1, 32.9, 31.9, 31.1, 30.1, 30.1, 28.8, 28.4, 26.2, 26.1, 22.1, 20.4, 14.2, 11.8.

3α-N-(2-amino-3-phenylpropanoyl)-5α-androstan-17-one (10). The method for the synthesis of **10** was similar to that of **6.10** is white solid, 95% yield. $[\alpha]_D^{20} = +43.8$ (c 1.0, CHCl₃); IR (KBr) 694, 751, 1319, 1446, 1511, 1671, 1732, 2848, 2929, 3346 cm⁻¹; m.p. 98-111 °C; HRMS (EI) calcd for C₂₈H₄₀N₂O₂, $[M+H]^+$ 437.3162, found 437.3164. ¹H NMR (500 MHz, CDCl₃): δ 7.34-7.16 (m, 5H), 4.14-4.13 (m, 1H), 3.63-3.60 (m, 1H), 3.27-3.20 (m, 1H), 2.89-2.73 (m, 1H), 2.48-2.43 (m, 1H), 2.11-1.23 (m, 29H), 1.07-0.63 (m, 16H), 0.95-0.92 (m, 2H), 0.86 (s, 3H), 0.77 (s, 3H), 0.76-0.60 (m, 1H); δ 221.6, 173.5, 138.4, 138.3, 130.5, 129.7, 129.1, 128.4, 128.3, 127.2, 126.7, 57.0, 56.8, 55.5, 54.9, 53.0, 52.5, 51.9, 48.2, 44.5, 44.3, 41.7, 41.5, 41.4, 40.9, 36.6, 36.2, 36.0, 35.4, 33.8, 33.6, 33.2, 32.2, 31.9, 31.6, 31.3, 31.1, 28.6, 26.5, 23.5, 22.1, 20.9, 20.5, 16.9, 14.2.

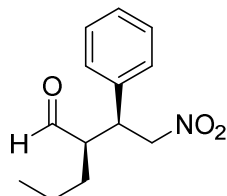
5. Characterization Data of Michael Adducts



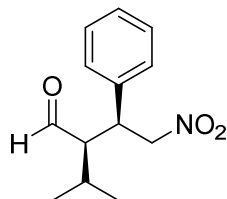
Pale yellow oil, 88% yield. ^1H NMR (400 MHz, CDCl_3): δ 9.63 (d, $J = 1.0$ Hz, 1H), 9.60 ((d, $J = 1.0$ Hz), 7.28-7.19 (m, 6H), 7.14-7.08 (m, 4H), 4.76-4.70 (m, 3H), 4.63-4.58 (m, 1H), 3.78-3.71 (m, 2H), 2.77-2.66 (m, 2H), 1.13 (d, $J = 7.2$ Hz, 2H), 0.92 (d, $J = 7.3$ Hz, 3H); ^{13}C NMR (100 MHz, CDCl_3): δ 201.3, 201.2, 135.9, 135.6, 128.1, 128.1, 127.1, 127.1, 77.1, 47.7, 47.4, 43.8, 43.0, 11.1, 10.7; HPLC (Chiralcel OD-H, Hexane: *i*-PrOH=90:10, flow rate: 1.0 mL/min, λ =254 nm), T_{major} =34.4, T_{minor} =25.6, 94% ee.



Pale yellow oil, 91% yield. ^1H NMR (400 MHz, CDCl_3): δ 9.71 (d, $J = 2.8$ Hz, 1H), 9.48 (d, $J = 2.8$ Hz), 7.36-7.27 (m, 4H), 7.18 (d, $J=7.2$, 2H), 4.82-4.70 (m, 2H), 4.65-4.60 (m, 1H), 3.85-3.76 (m, 1H), 2.71-2.65 (m, 1H), 1.73-1.64 (m, 1H), 1.54-1.00 (m, 1H), 0.97 (t, $J=7.2$ Hz, 1H), 0.82 (t, $J=7.2$ Hz, 3H); ^{13}C NMR (100 MHz, CDCl_3): δ 203.2, 203.1, 136.8, 136.3, 129.1, 128.2, 128.1, 128.0, 78.5, 77.9, 55.0, 54.9, 44.1, 42.7, 20.6, 20.4, 11.5, 10.7; HPLC (Chiralcel AD-H, Hexane: *i*-PrOH= 99: 1, flow rate: 0.8 mL/min, λ =254 nm), T_{major} =27.3, T_{minor} =32.7, 98% ee.

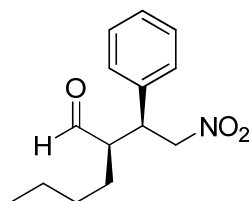


Pale yellow oil, 85% yield. ^1H NMR (400 MHz, CDCl_3): δ 9.71 (s, 1H), δ 9.70 (s), 7.36-7.26 (m, 4H), 7.17 (d, $J=7.2$, 3H), 4.73-4.62 (m, 3H), 3.81-3.75 (m, 2H), 2.74-2.67 (m, 1H), 1.62-0.94(m, 5H), 0.90 (t, $J=10.8$ Hz, 1H), 0.80 (t, $J=14.0$ Hz, 3H); ^{13}C NMR (100 MHz, CDCl_3): δ 203.2, 136.8, 129.1, 128.1, 128.0, 78.4, 53.8, 43.2, 29.5, 19.8, 13.9; HPLC (Chiralcel OD-H, Hexane: *i*-PrOH=96:4, flow rate: 1.0 mL/min, λ =254 nm), T_{major} =34.9, T_{minor} =28.0, 95% ee.

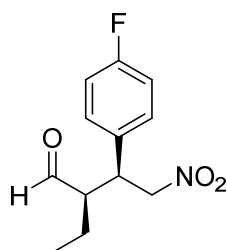


Pale yellow oil, 83% yield. ^1H NMR (400 MHz, CDCl_3): δ 9.92 (d, $J=2.0$ Hz, 1H), 9.47 (d, $J=4.4$ Hz), 7.36-7.27 (m, 3H), 7.19 (d, $J=7.2$, 2H), 4.69-4.65 (m, 1H), 4.60-4.54 (m, 1H), 3.93-3.87 (m, 1H), 2.80-2.75 (m, 1H), 1.74-1.67 (m, 1H), 1.09 (d,

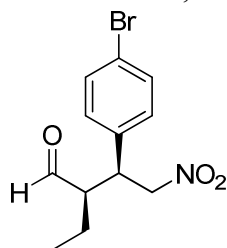
$J=7.2$ Hz, 3H), 0.87 (d, $J=7.2$ Hz, 3H); ^{13}C NMR (100 MHz, CDCl_3): δ 204.4, 137.1, 129.2, 128.1, 128.0, 79.0, 58.7, 41.9, 27.9, 21.7, 16.7; HPLC (Chiralcel AD-H, Hexane: i-PrOH= 97: 3, flow rate: 0.5 mL/min, $\lambda=254$ nm), $T_{\text{major}}=23.7$, $T_{\text{minor}}=28.1$, 99% ee.



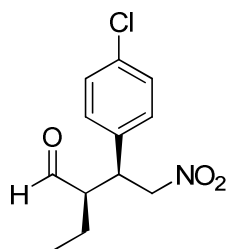
Pale yellow oil, 88% yield. ^1H NMR (400 MHz, CDCl_3): δ 9.70 (s, 1H), 9.47 (s), 7.36-7.27 (m, 3H), 7.17 (d, $J=7.2$, 2H), 4.73-4.61 (m, 2H), 3.81-3.75 (m, 1H), 2.73-2.67 (m, 1H), 1.53-1.28 (m, 9H), 1.21 (t, $J=10.4$ Hz, 1H), 1.17 (t, $J=17.2$ Hz, 3H); ^{13}C NMR (100 MHz, CDCl_3): δ 203.3, 136.8, 129.1, 128.1, 128.0, 78.4, 53.9, 43.1, 28.5, 27.0, 22.5, 13.6; HPLC (Chiralcel OD-H, Hexane: i-PrOH= 97: 3, flow rate: 1.0 mL/min, $\lambda=254$ nm), $T_{\text{major}}=35.7$, $T_{\text{minor}}=26.2$, 96% ee.



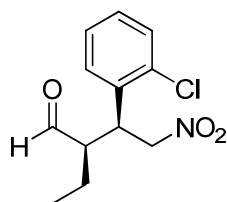
Pale yellow oil, 93% yield. ^1H NMR (400 MHz, CDCl_3): δ 9.72 (d, $J=2.4$ Hz), 9.49 (d, $J=2.8$ Hz, 1H), 7.19-7.15 (m, 2H), 7.07-6.99 (m, 2H), 4.82-4.70 (m, 2H), 3.84-3.79 (m, 2H), 2.61-2.55 (m, 1H), 1.78-1.57 (m, 3H), 1.00 (t, $J=15.2$ Hz, 3H), 0.84 (d, $J=15.2$ Hz, 1H); ^{13}C NMR (100 MHz, CDCl_3): δ 202.8, 163.6, 161.1, 132.1, 129.9, 116.2, 116.0, 78.0, 55.0, 43.3, 41.8, 20.6, 11.4; HPLC (Chiralcel AD-H, Hexane: i-PrOH= 99:1, flow rate: 1.0 mL/min, $\lambda=254$ nm), $T_{\text{major}}=25.0$, $T_{\text{minor}}=33.3$, 99% ee.



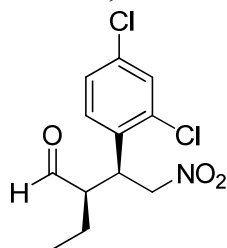
Pale yellow oil, 94% yield. ^1H NMR (400 MHz, CDCl_3): δ 9.72 (d, $J=2.4$ Hz, 1H), 9.49 (d, $J=2.0$ Hz), 7.50-7.45 (m, 3H), 7.08 (d, $J=2.4$, 3H), 4.78-4.70 (m, 2H), 4.62-4.57 (m, 1H), 3.80-3.74 (m, 2H), 2.70-2.64 (m, 1H), 1.72-1.46 (m, 3H), 0.98 (t, $J=14.8$ Hz, 2H), 0.84 (d, $J=14.8$ Hz, 3H); ^{13}C NMR (100 MHz, CDCl_3): δ 202.6, 135.9, 135.5, 132.3, 132.3, 130.0, 129.7, 122.3, 122.2, 78.2, 54.8, 54.7, 43.4, 42.1, 20.5, 20.3, 11.4, 10.5; HPLC (Chiralcel AD-H, Hexane: i-PrOH= 98.5:1.5, flow rate: 1.0 mL/min, $\lambda=254$ nm), $T_{\text{major}}=32.0$, $T_{\text{minor}}=50.4$, 98% ee.



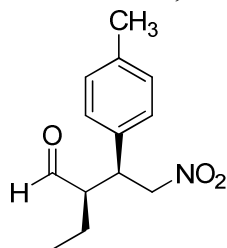
Pale yellow oil, 92% yield. ^1H NMR (400 MHz, CDCl_3): δ 9.71 (d, $J=2.4$ Hz, 1H), 9.49 (d, $J=2.4$ Hz), 7.32-7.15 (m, 2H), 7.13 (d, $J=8.4$, 2H), 4.78-4.70 (m, 1H), 4.63-4.57 (m, 1H), 3.82-3.76 (m, 1H), 2.70-2.64 (m, 1H), 1.00 (t, $J=14.4$ Hz), 0.95 (d, $J=15.2$ Hz, 3H); ^{13}C NMR (100 MHz, CDCl_3): δ 202.7, 135.4, 134.1, 130.2, 129.6, 129.4, 128.5, 78.3, 54.7, 42.0, 20.3, 10.5; HPLC (Chiralcel AD-H, Hexane: i-PrOH= 98.5:1.5, flow rate: 1.0 mL/min, $\lambda=254$ nm), $T_{\text{major}}=27.9$, $T_{\text{minor}}=42.0$, 97% ee.



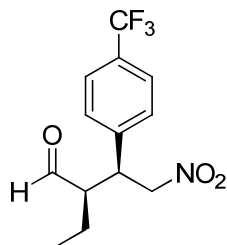
Pale yellow oil, 88% yield. ^1H NMR (400 MHz, CDCl_3): δ 9.73 (d, $J=2.0$ Hz, 1H), 9.56 (d, $J=2.8$ Hz), 7.42-7.28 (m, 1H), 7.26-7.20 (m, 4H), 4.89-4.76 (m, 2H), 4.72-4.67 (m, 1H), 4.38-4.33 (m, 1H), 2.95 (s, 1H), 1.78-1.70 (m, 1H), 1.65-1.50 (m, 2H), 0.97 (t, $J=15.2$ Hz, 1H), 0.87 (d, $J=15.2$ Hz, 3H); ^{13}C NMR (100 MHz, CDCl_3): δ 202.8, 202.3, 134.5, 134.4, 130.6, 129.3, 128.7, 127.5, 76.2, 54.5, 54.0, 39.2, 20.4, 19.8, 11.6, 10.7; HPLC (Chiralcel AD-H, Hexane: i-PrOH= 98.5:1.5, flow rate: 1.0 mL/min, $\lambda=254$ nm), $T_{\text{major}}=16.7$, $T_{\text{minor}}=18.7$, 96% ee.



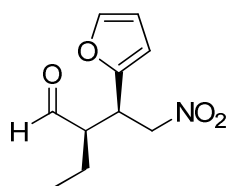
Pale yellow oil, 84% yield. ^1H NMR (400 MHz, CDCl_3): δ 9.72 (d, $J=2.0$ Hz, 1H), 9.56 (d, $J=2.8$ Hz), 7.44 (s, 1H), 7.27 (d, $J=2.0$ Hz, 1H), 7.25 (d, $J=2.0$ Hz, 1H), 4.88-4.82 (m, 1H), 4.70-4.66 (m, 1H), 4.38-4.27 (m, 1H), 2.30-2.80 (m, 1H), 1.62-1.55 (m, 2H), 1.53 (t, $J=14.8$ Hz, 1H), 0.99 (d, $J=14.8$ Hz, 3H); ^{13}C NMR (100 MHz, CDCl_3): δ 202.4, 201.9, 135.1, 134.5, 133.2, 130.4, 130.1, 129.6, 128.5, 127.8, 76.0, 54.3, 53.8, 38.7, 20.4, 19.9, 11.5, 10.6; HPLC (Chiralcel AD-H, Hexane: i-PrOH=99:1, flow rate: 1.0 mL/min, $\lambda=254$ nm), $T_{\text{major}}=19.2$, $T_{\text{minor}}=21.8$, 98% ee.



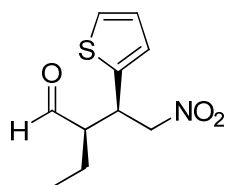
Pale yellow oil, 95% yield. ^1H NMR (400 MHz, CDCl_3): δ 9.71 (d, $J=2.4$ Hz, 1H), 9.47 (d, $J=3.2$ Hz), 7.15-7.12 (m, 2H), 7.06 (d, $J=8.0$ Hz, 2H), 4.78-4.38 (m, 1H), 4.60-4.57 (m, 1H), 3.78-3.72 (m, 1H), 2.68-2.62 (m, 1H), 2.31 (d, $J=6.0$ Hz, 3H), 1.51-1.47 (m, 2H), 0.98 (t, $J=14.8$ Hz, 1H), 0.83 (d, $J=14.8$ Hz, 3H); ^{13}C NMR (100 MHz, CDCl_3): δ 203.4, 203.3, 137.9, 133.6, 129.8, 128.1, 127.8, 78.7, 55.1, 55.0, 43.9, 42.4, 21.1, 20.7, 20.4, 11.5, 10.7; HPLC (Chiralcel OD-H, Hexane: i-PrOH= 92:8, flow rate: 0.5 mL/min, $\lambda=254$ nm), $T_{\text{major}}=39.8$, $T_{\text{minor}}=34.6$, 97% ee.



Pale yellow oil, 92% yield. ^1H NMR (400 MHz, CDCl_3): δ 9.72 (d, $J=2.0$ Hz, 1H), 9.51 (d, $J=2.4$ Hz), 7.63-7.51 (m, 3H), 7.48-7.35 (m, 2H), 4.83-4.75 (m, 1H), 4.69-4.63 (m, 1H), 3.92-3.86 (m, 1H), 2.77-2.70 (m, 1H), 1.58-1.44 (m, 2H), 1.01 (t, $J=14.8$ Hz, 1H), 0.84 (d, $J=14.8$ Hz, 3H); ^{13}C NMR (100 MHz, CDCl_3): δ 202.5, 141.1, 133.7, 130.6, 130.3, 128.8, 128.5, 126.1, 126.0, 125.2, 122.5, 78.1, 54.8, 54.5, 43.5, 42.3, 20.4, 20.3, 11.3, 10.5; HPLC (Chiralcel AS-H, Hexane: i-PrOH= 93:7, flow rate: 0.5 mL/min, $\lambda=254$ nm), $T_{\text{major}}=26.7$, $T_{\text{minor}}=29.2$, 99% ee.

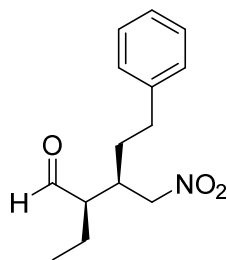


Pale yellow oil, 83% yield. ^1H NMR (400 MHz, CDCl_3): δ 9.71 (d, $J=1.6$ Hz, 1H), 9.60 (d, $J=2.4$ Hz, 1H), 7.36 (d, $J=1.2$ Hz, 2H), 7.36 (d, $J=0.4$ Hz, 2H), 7.35 (d, $J=0.8$ Hz, 2H), 4.74-4.65 (m, 4H), 4.04-3.97 (m, 2H), 2.77-2.75 (m, 1H), 2.56-2.53 (m, 1H), 1.75-1.73 (m, 1H), 1.63-1.55 (m, 4H), 1.00 (t, $J=14.8$ Hz, 2H), 0.90 (d, $J=14.8$ Hz, 3H); ^{13}C NMR (100 MHz, CDCl_3): δ 202.8, 202.3, 150.1, 149.7, 142.7, 110.5, 110.4, 109.0, 108.8, 76.0, 53.6, 53.4, 37.7, 36.6, 20.5, 20.0, 11.5, 10.9; HPLC (Chiralcel AS-H, Hexane: i-PrOH= 96:4, flow rate: 0.5 mL/min, $\lambda=254$ nm), $T_{\text{major}}=38.1$, $T_{\text{minor}}=34.3$, 93% ee.



Pale yellow oil, 89% yield. ^1H NMR (400 MHz, CDCl_3): δ 9.70 (d, $J=1.6$ Hz, 1H), 9.52 (d, $J=2.4$ Hz, 1H), 7.35-7.31 (m, 2H), 7.10 (d, $J=4.8$ Hz, 2H), 6.93 (d, $J=4.8$ Hz, 2H), 4.81-4.59 (m, 5H), 4.02-3.95 (m, 2H), 2.67-2.65 (m, 1H), 2.64-2.52 (m, 1H), 1.78-1.72 (m, 1H), 1.64-1.54 (m, 4H), 1.00 (t, $J=14.8$ Hz, 3H), 0.88 (t, $J=14.8$ Hz, 3H); ^{13}C NMR (100 MHz, CDCl_3): δ 203.3, 202.9, 137.2, 136.6, 127.0, 126.9, 126.1, 123.4, 123.3, 78.3, 77.9, 55.0, 54.6, 39.4, 38.2, 20.6, 20.3, 11.6, 10.9; HPLC

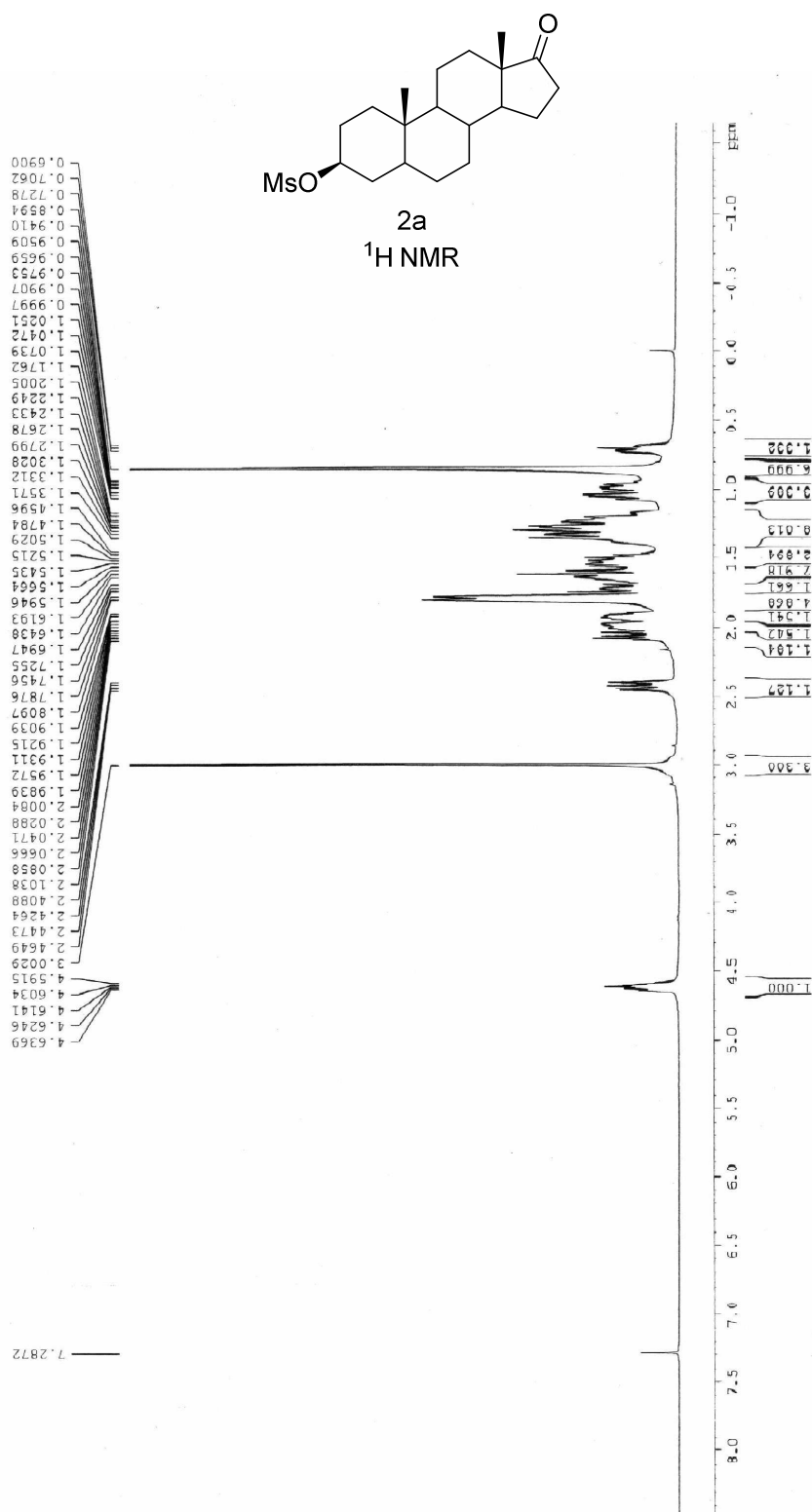
(Chiralcel AD-H, Hexane: i-PrOH= 98:2, flow rate: 0.7 mL/min, λ =254 nm),
 T_{major} =36.2, T_{minor} = 46.8, 97% ee.

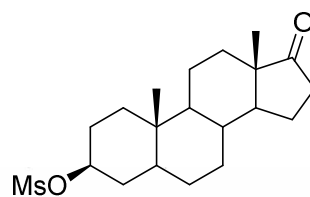


Pale yellow oil, 94% yield. ^1H NMR (400 MHz, CDCl_3): δ 9.71 (1H,s), 7.35-7.18 (1H,m), 4.58-4.49 (2H, m), 2.74-2.64 (3H,m), 2.51-2.47 (2H,m), 1.86-1.69 (3H, m), 1.61-1.54 (2H, m); ^{13}C NMR (100 MHz, CDCl_3): δ 203.4, 140.9, 129.1, 128.7, 126.8, 54.2, 36.6, 33.4, 31.4, 19.1, 12.3; HPLC (ChiralcelOD-H, Hexane: i-PrOH= 90:10, flow rate: 0.4 mL/min, λ =210 nm), T_{major} =37.4, T_{minor} = 40.1, 95% ee.

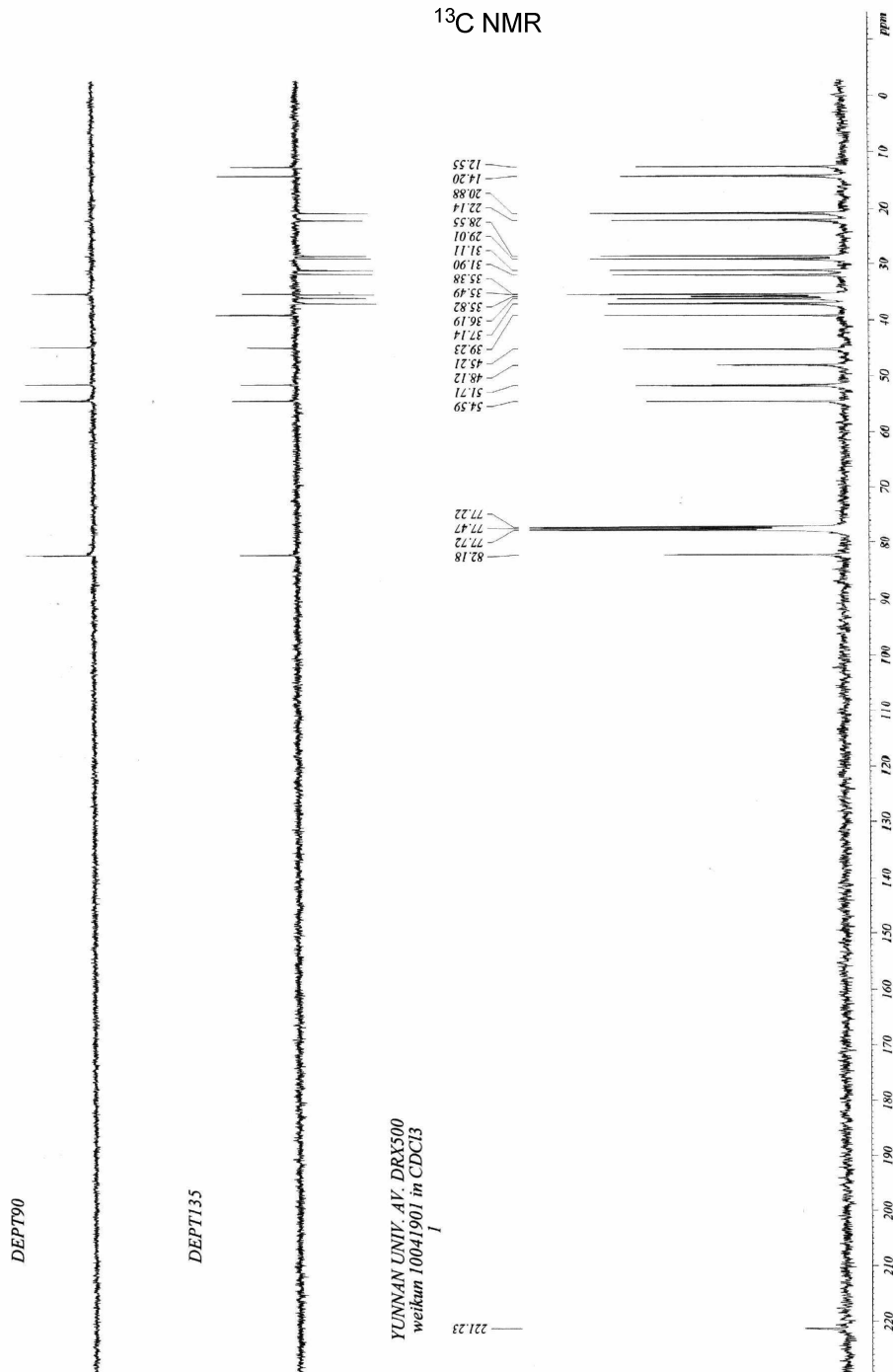
Spectra of Catalysts

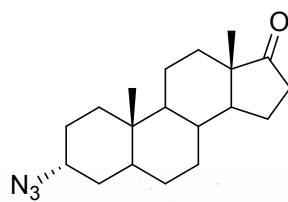
YUNNAN UNIV. AV. DRX500
weikun 10041901 in cdcl3



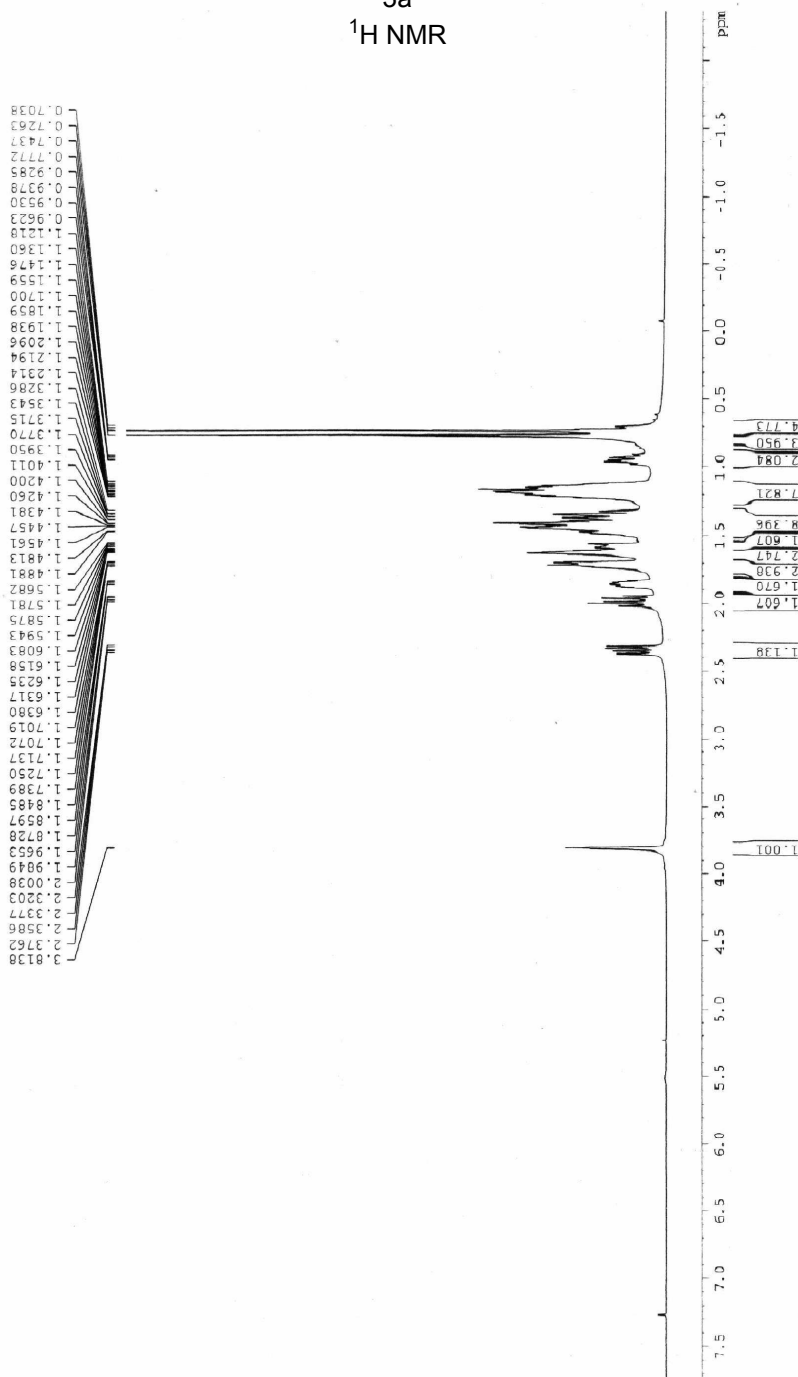


2a
 ^{13}C NMR

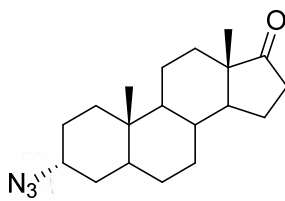




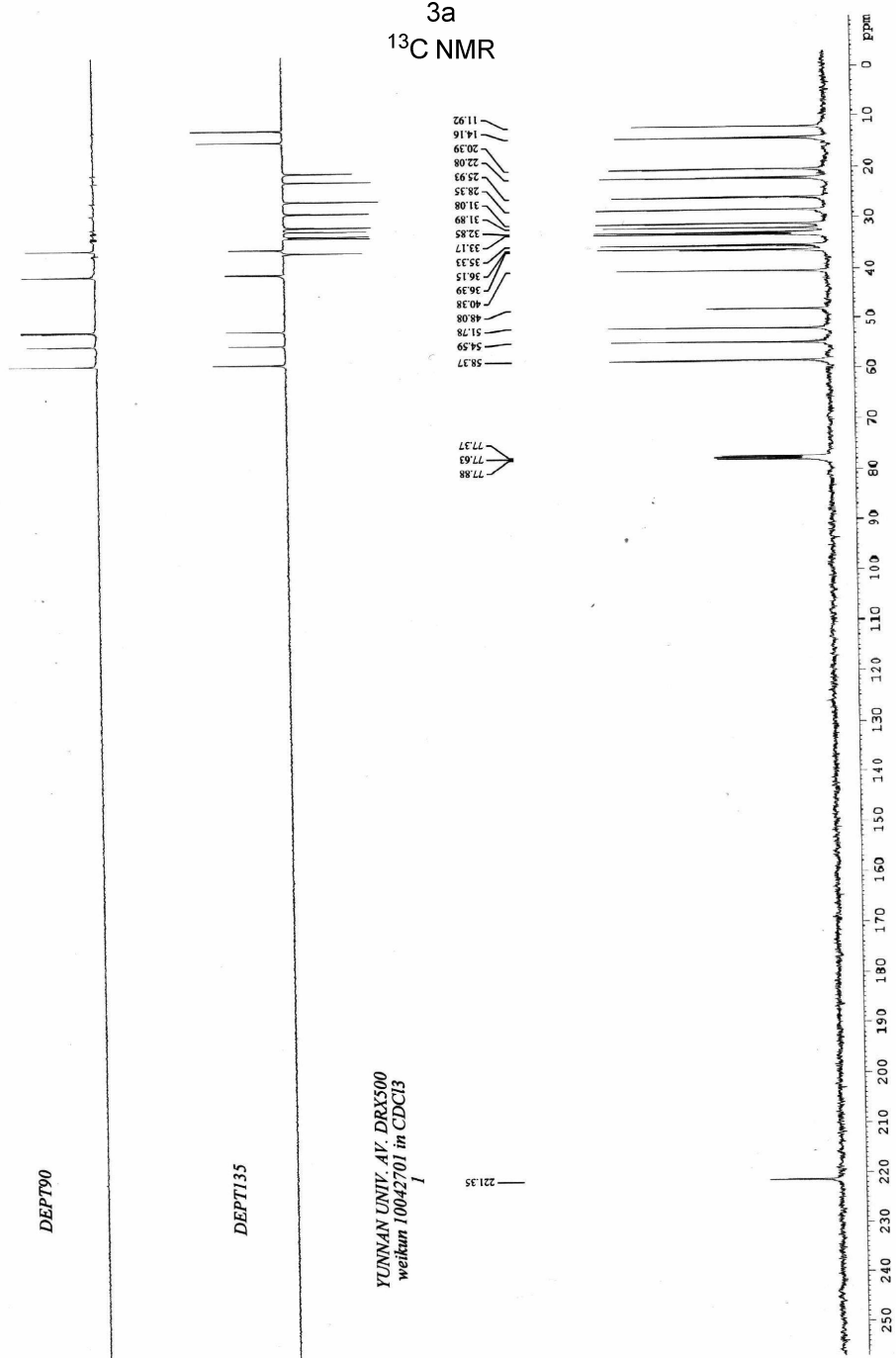
3a
¹H NMR

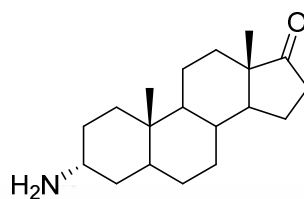


YUNNAN UNIV. AV. DRX500
weikun 10042701 in cdcl3

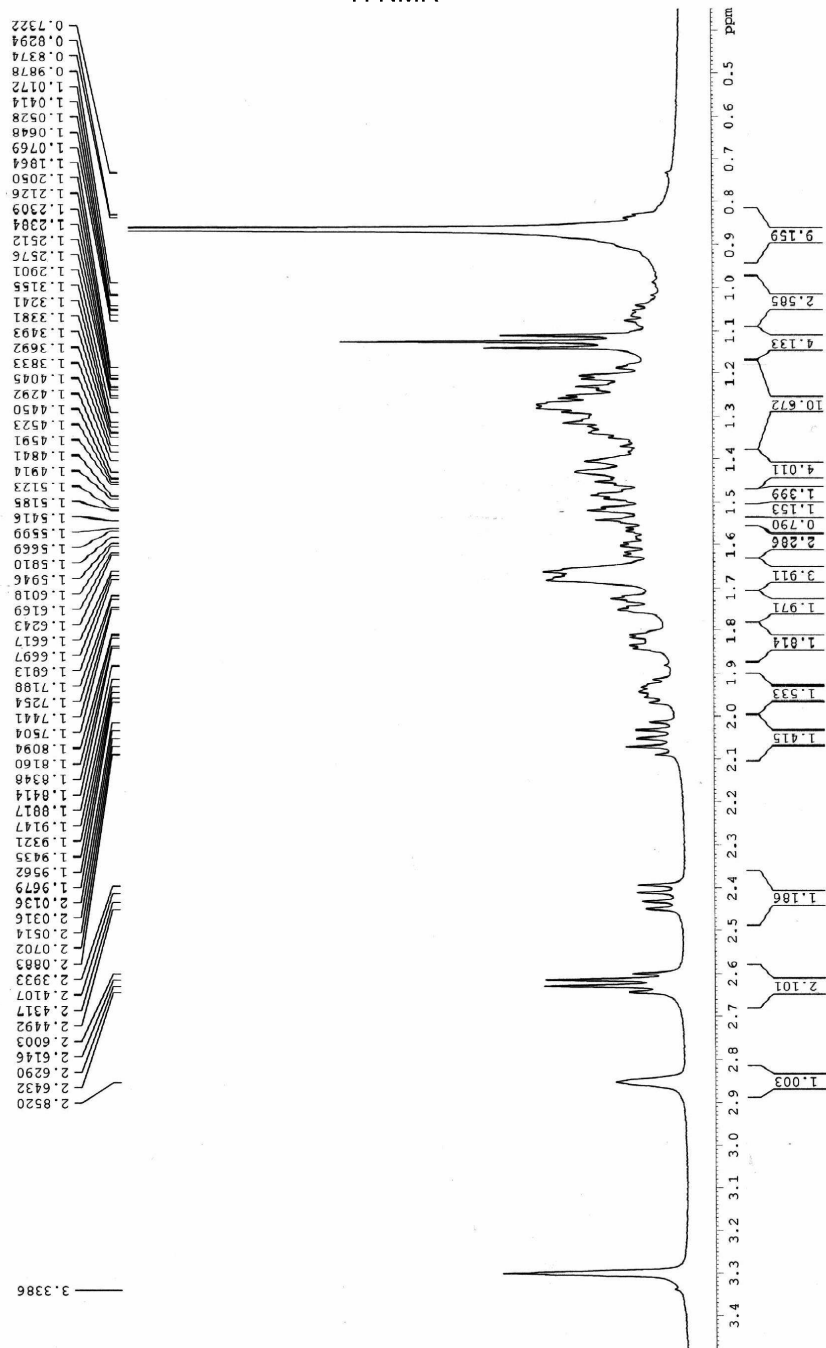


3a
¹³C NMR

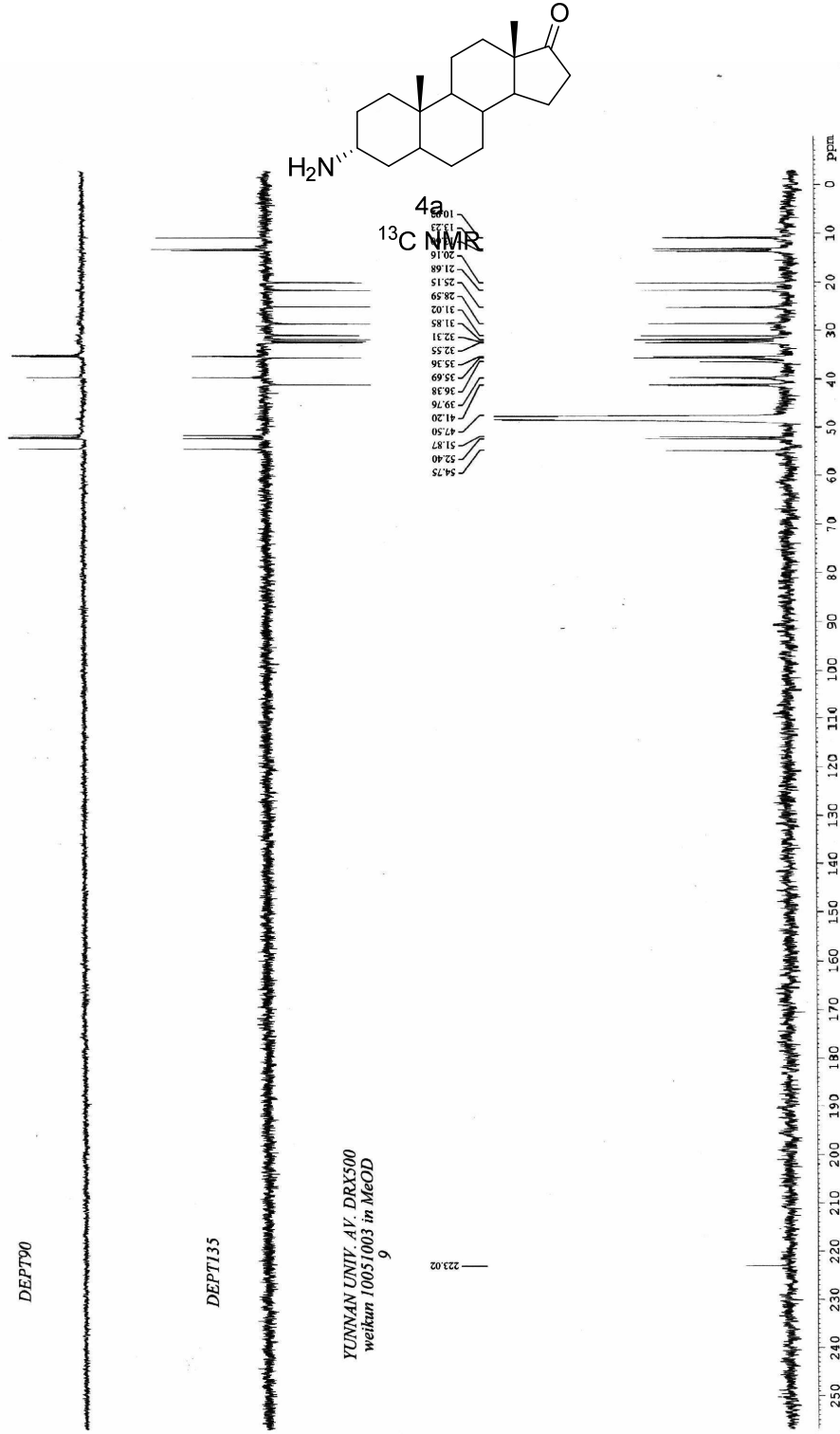
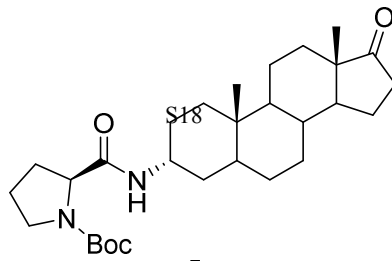


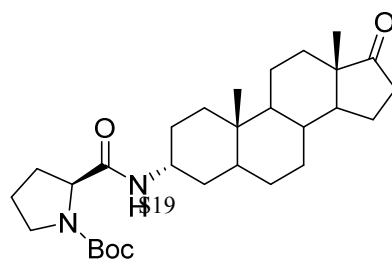
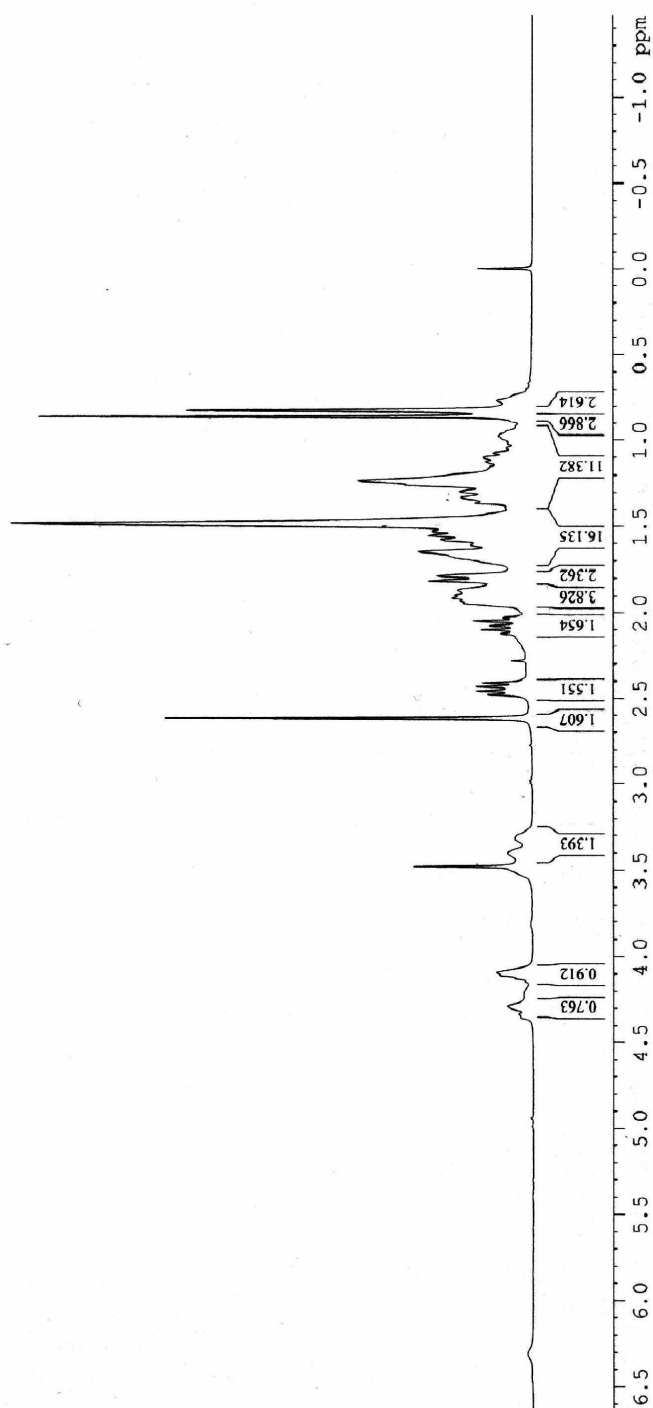


4a
¹H NMR

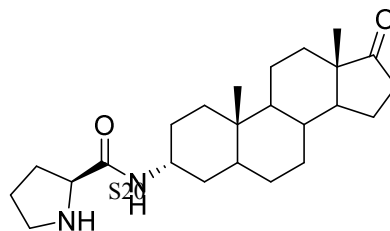


YUNNAN UNIV. AV. DRX500
weikun 10051003 in MeOD
9



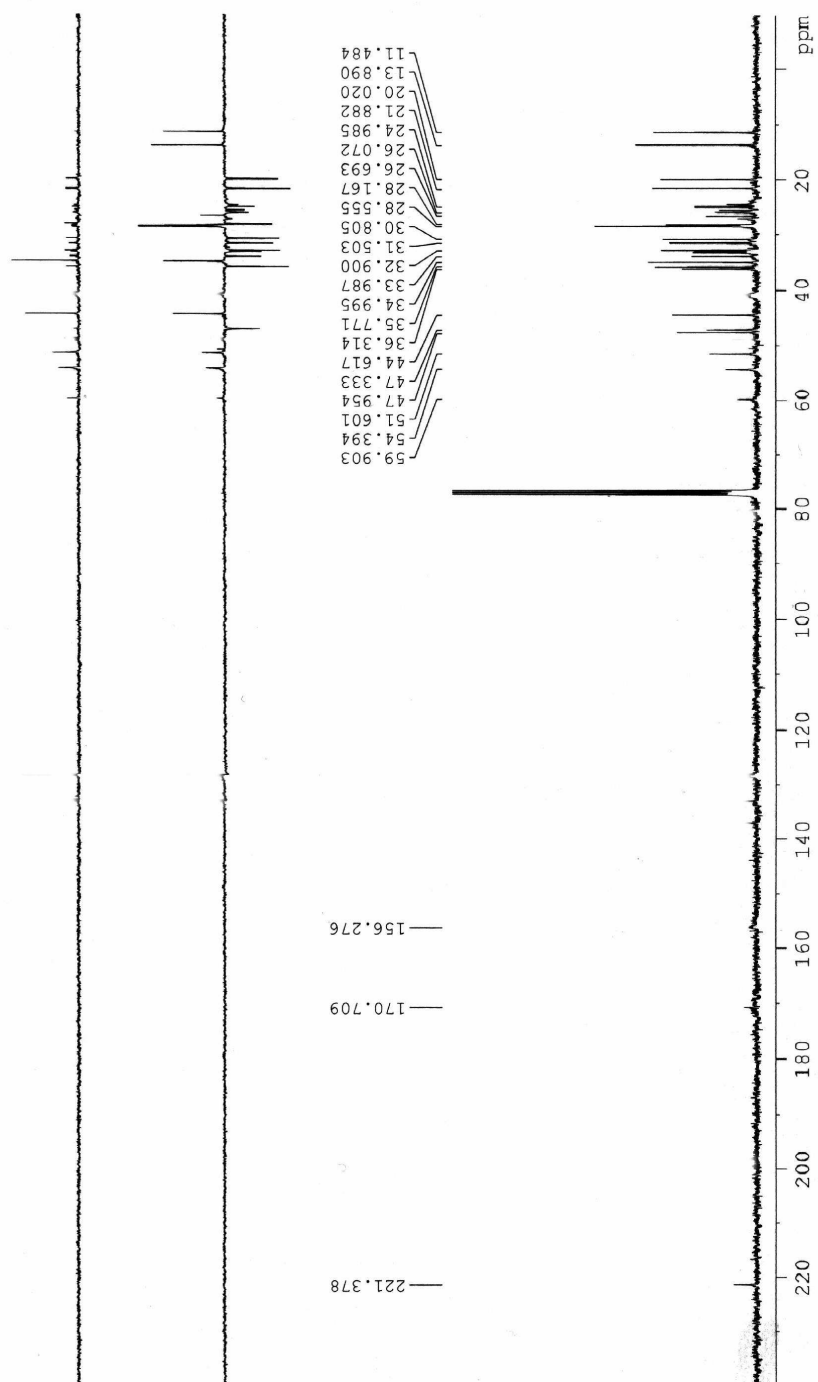


5a
¹³C NMR

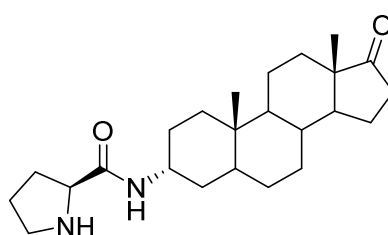
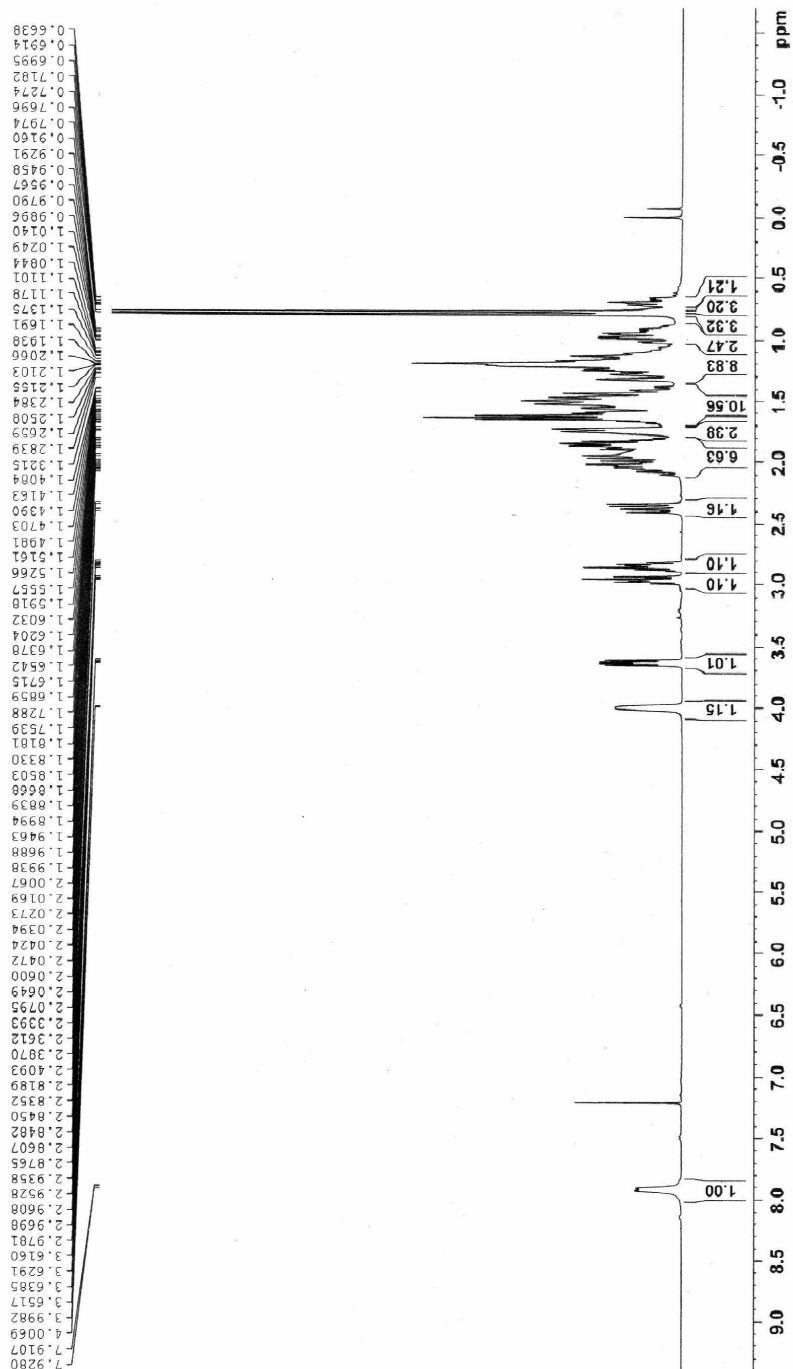


6a
 ^1H NMR

YUNNAN UNIVERSITY AVIII-400
CDCl₃

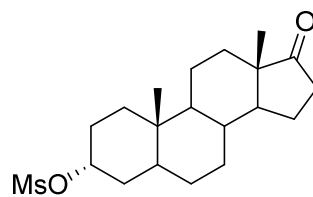


YUNNAN UNIVERSITY AVIII-400
wangyongchao F17 in CDCl3
478



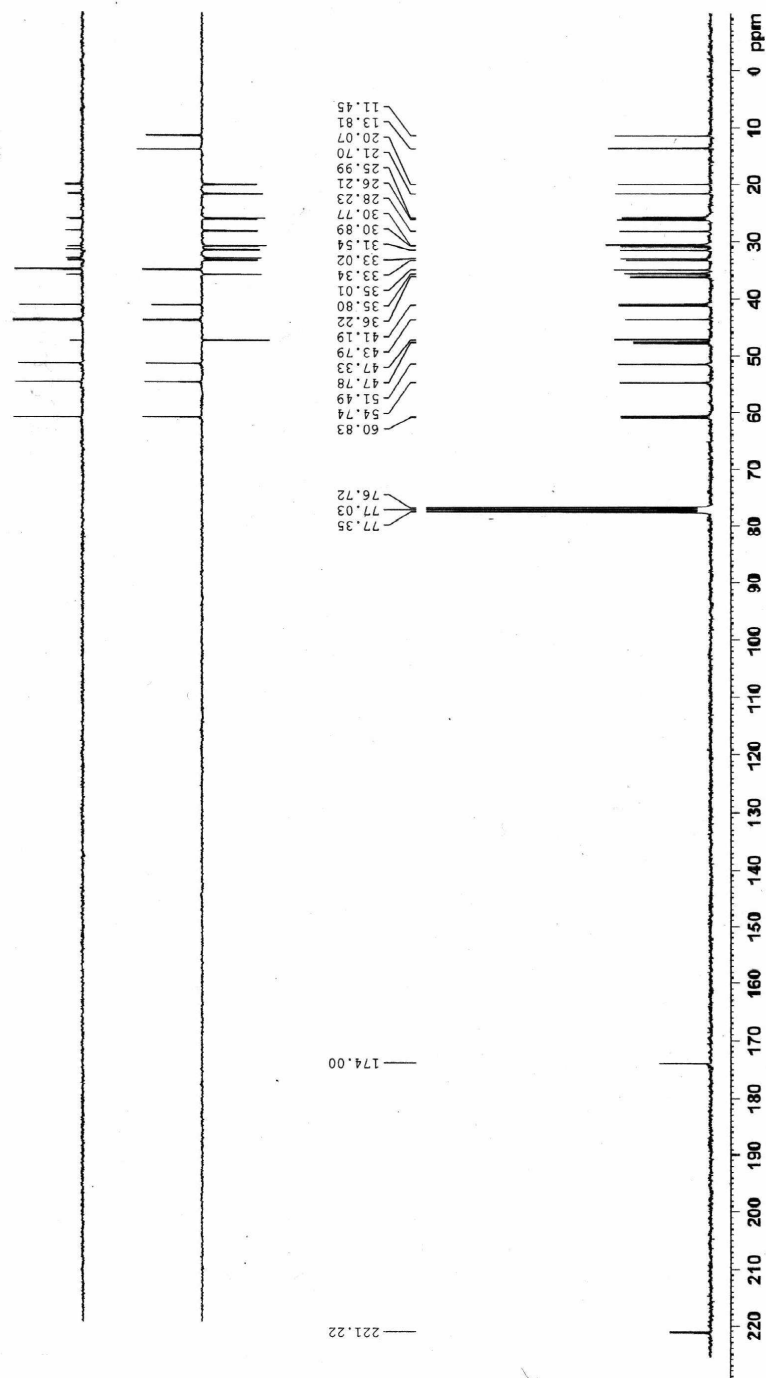
6a

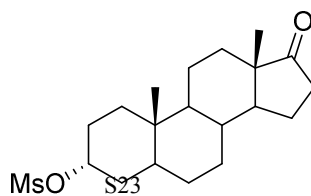
S21 ¹³C NMR



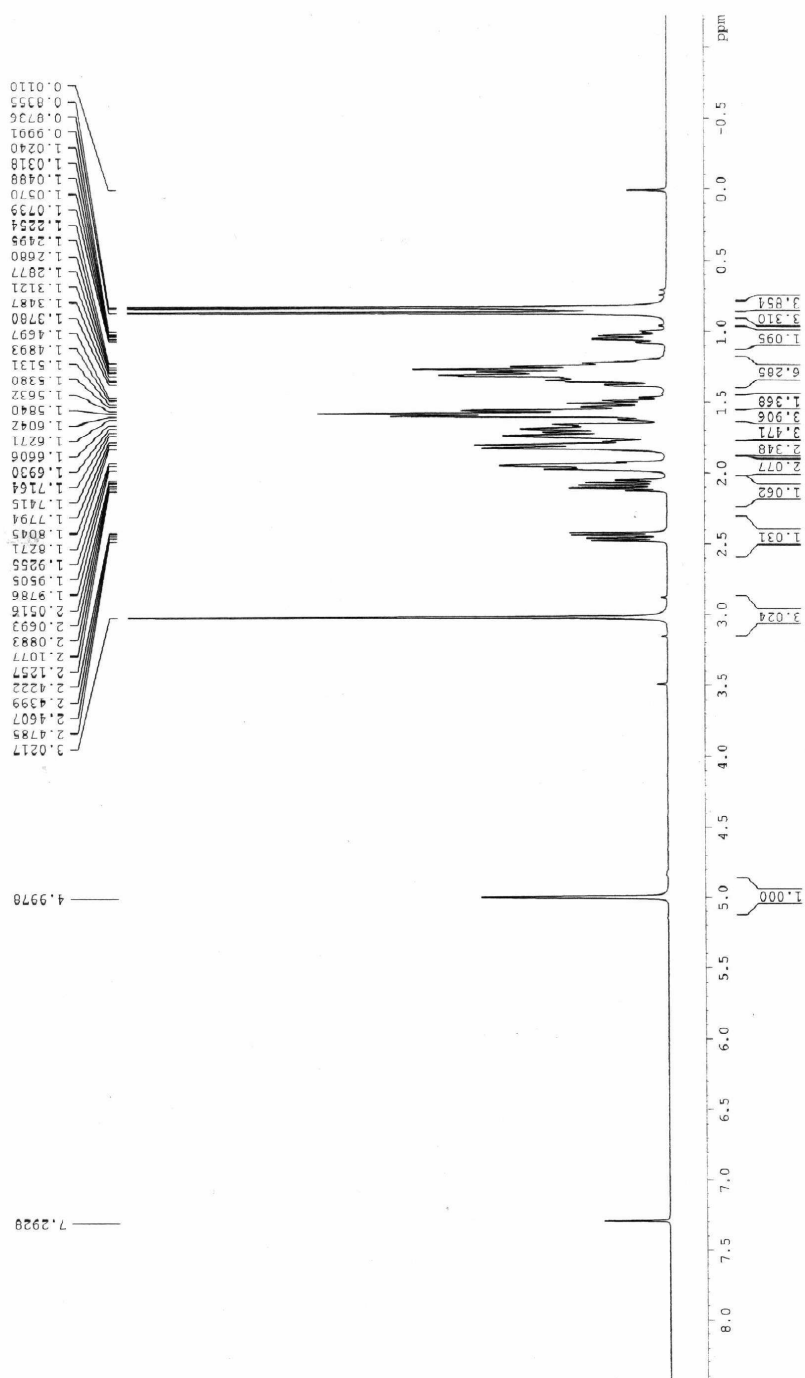
2b
¹H NMR

YUNNAN UNIVERSITY AVIII-400
 wangyongchao F17 in CDCl₃

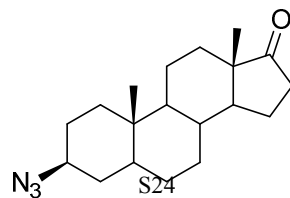




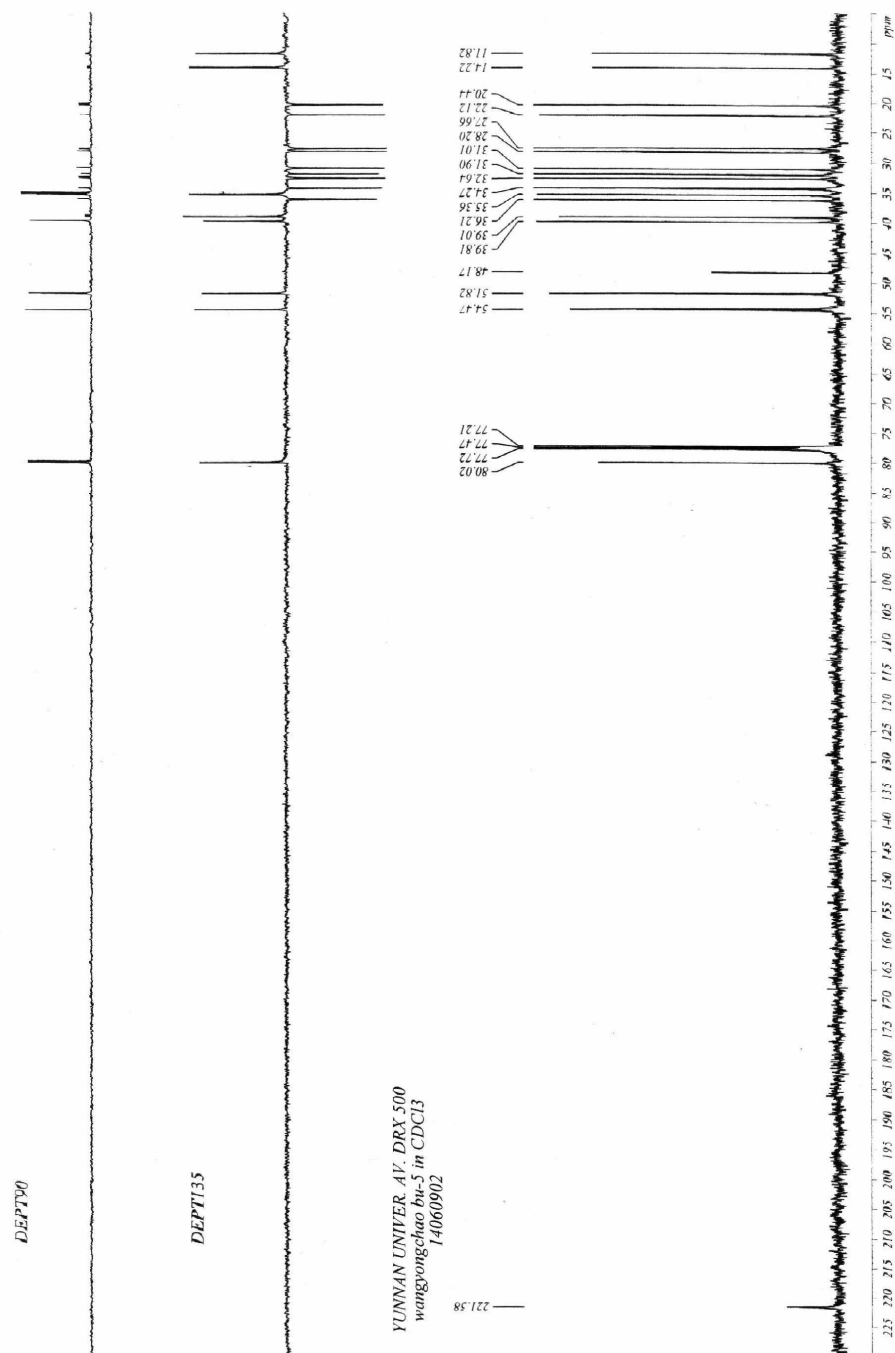
2b
¹³C-NMR

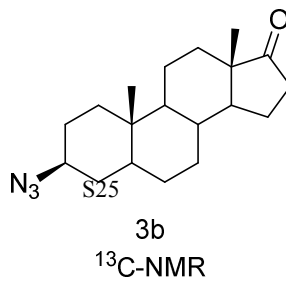


YUNNAN UNIVERSITY AV. DRX 500
 wangyongchao bu-5 in CDCl₃
 14060902

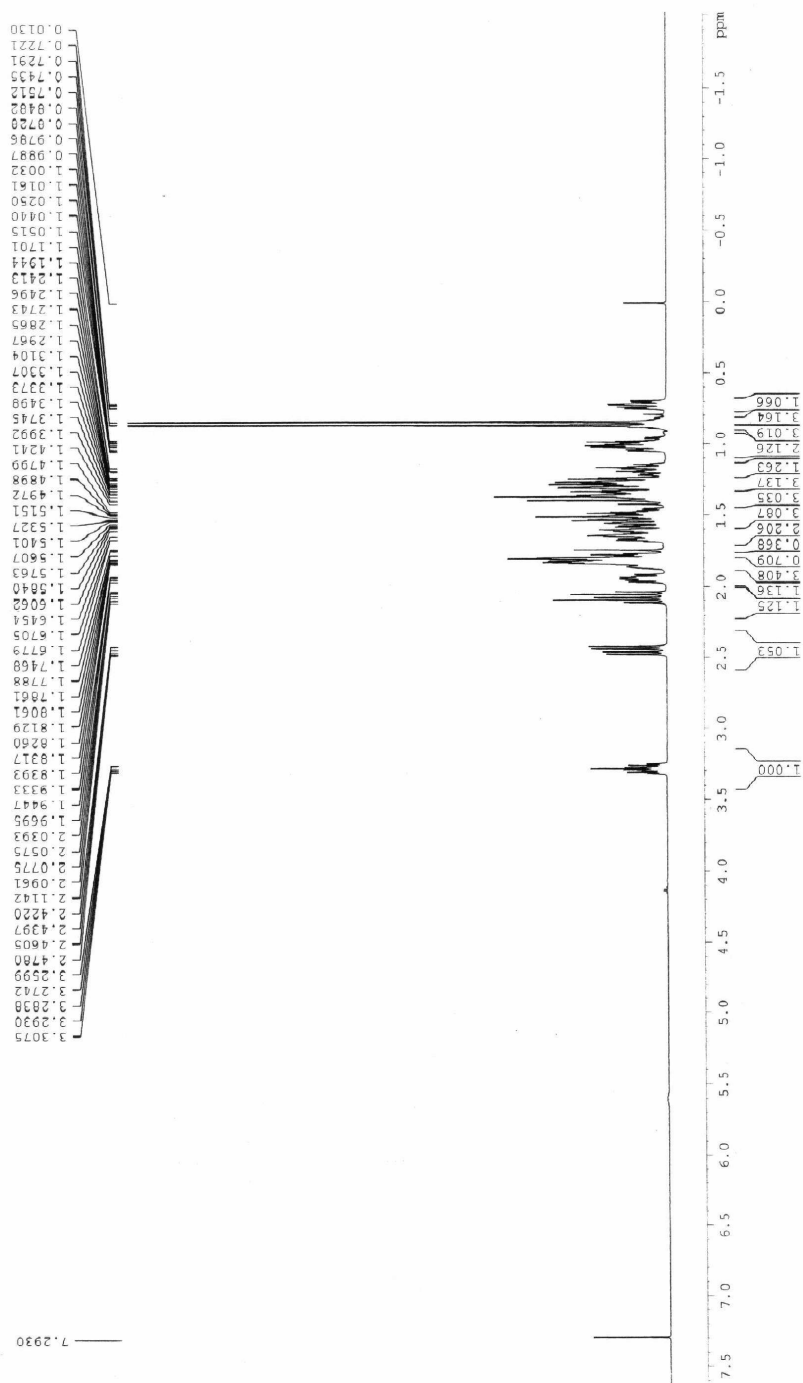


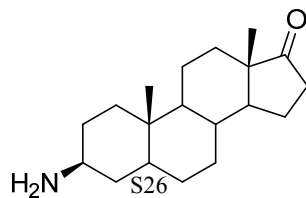
3b
¹H-NMR



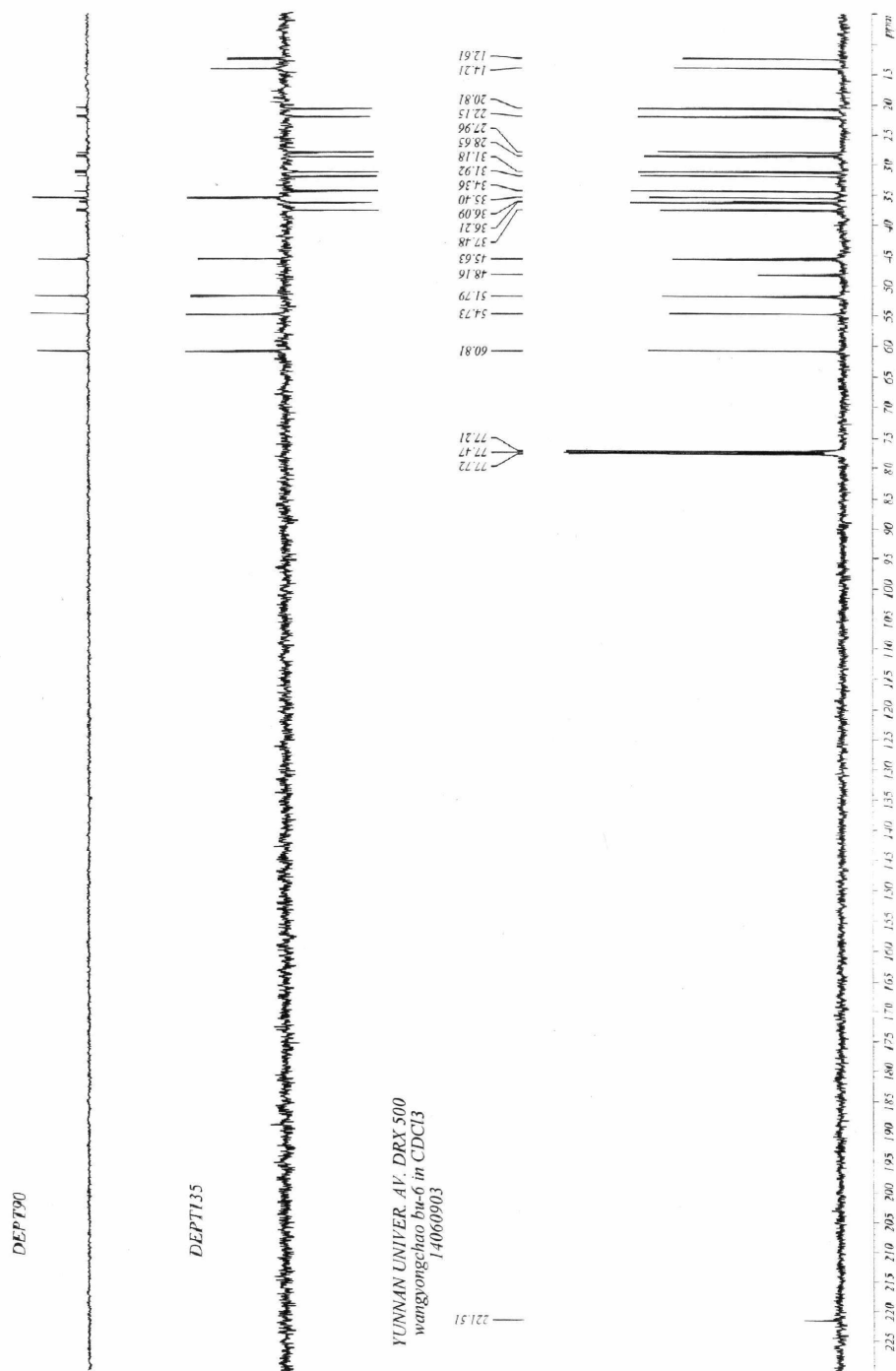


YUNNAN UNIVERSITY AV. DEX 500
 wangyongchao bu-6 in CDC13
 14060903

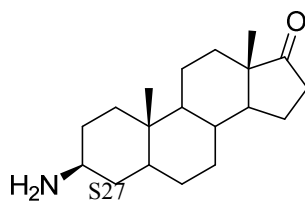
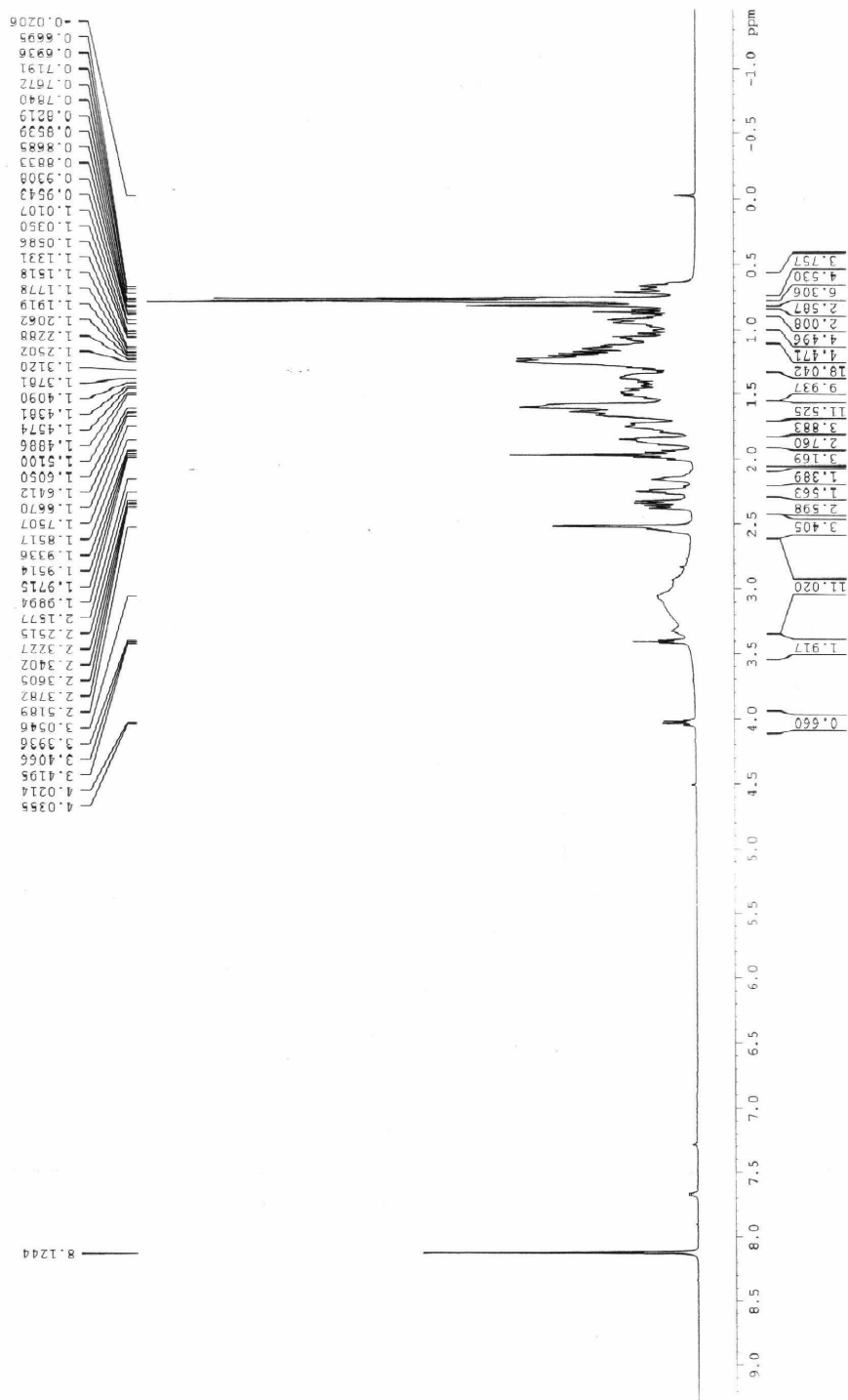




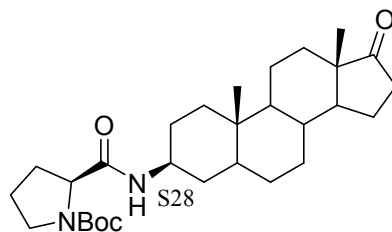
4b
¹H-NMR



YUNNAN UNIVERSITY AV. DRX 500
 wangyongchao bu-8 in DMSO-CDCl₃
 14061201



4b
¹³C-NMR

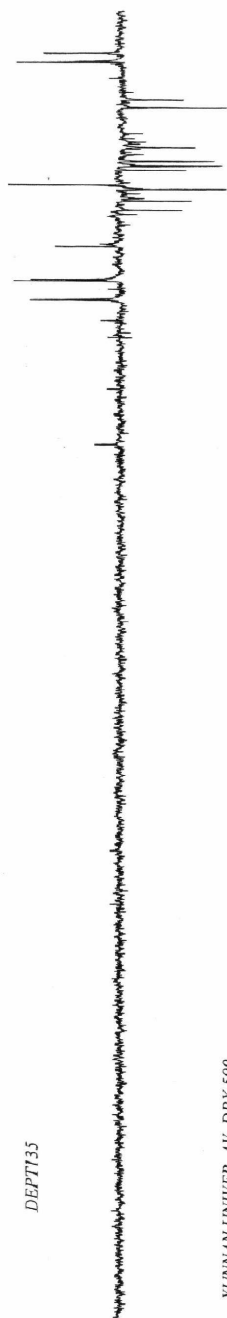


5b
¹H-NMR

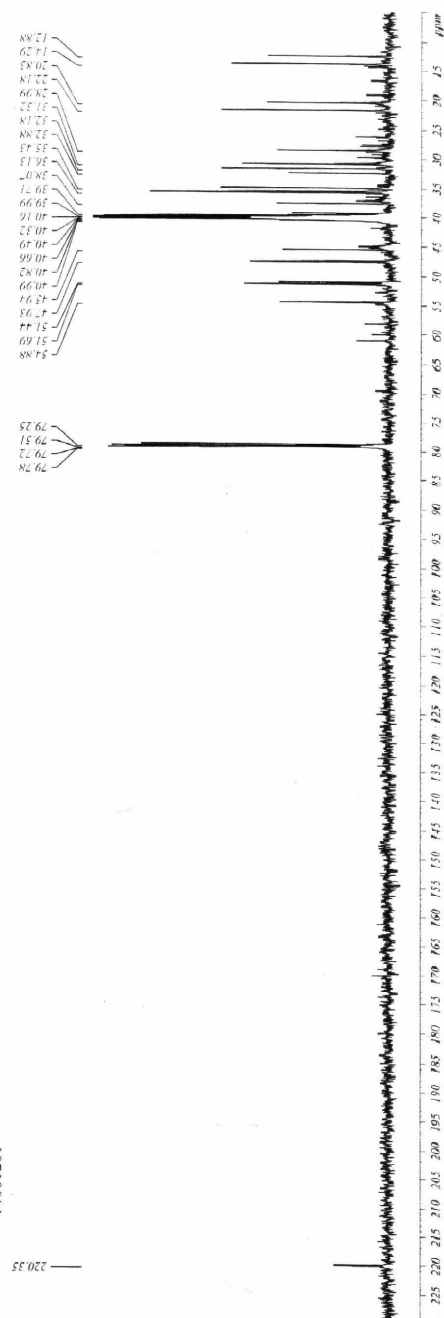
DEPT90

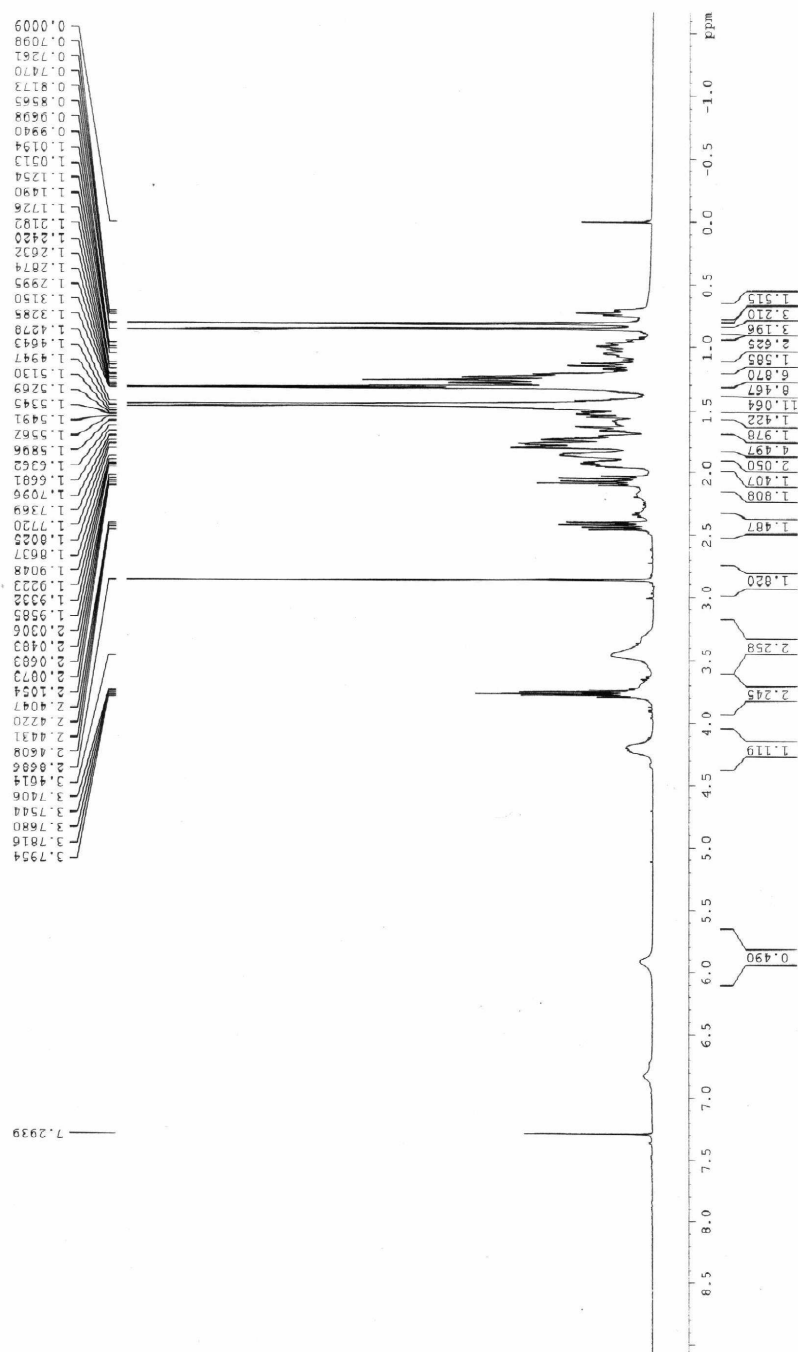


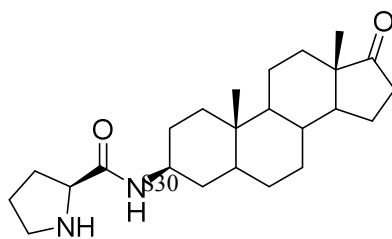
DEPT135



YUNNAN UNIVER. AV. DRX 500
wangyongchao hu-8 in DMSO+CDCl₃
14061201





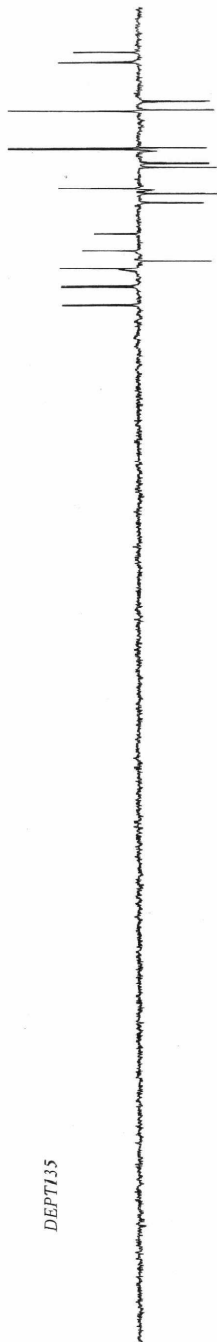


6b
¹H-NMR

DEPT90



DEPT135

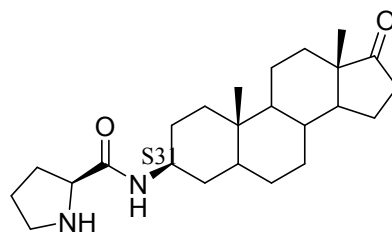


YUNNAN UNIVER. AV. DRX 500
wangyongchao bu-9 in CDCl3
14061202

221.64

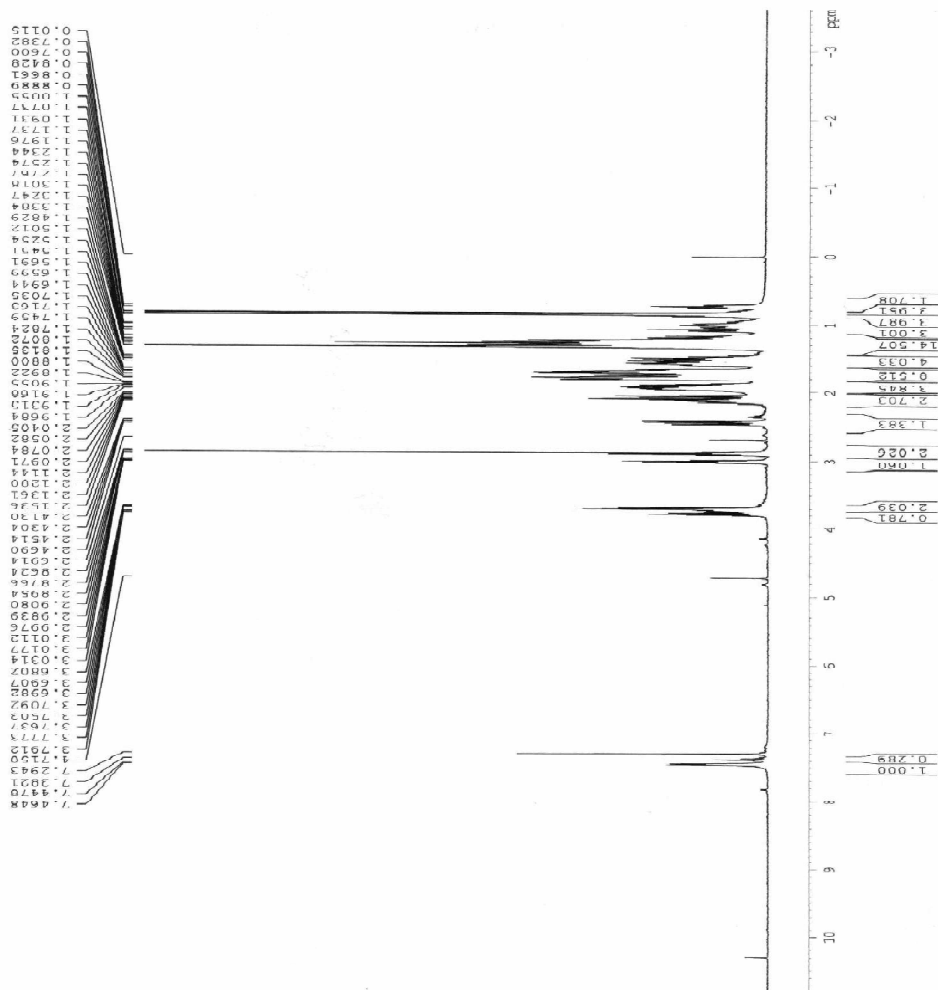
80.85
77.72
77.21
54.74
49.01
48.79
48.16
47.46
45.71
45.92
37.74
36.23
35.99
35.70
35.44
31.91
31.16
29.12
28.78
28.62
22.49
22.13
20.75
14.20
12.61





6b
¹³C-NMR

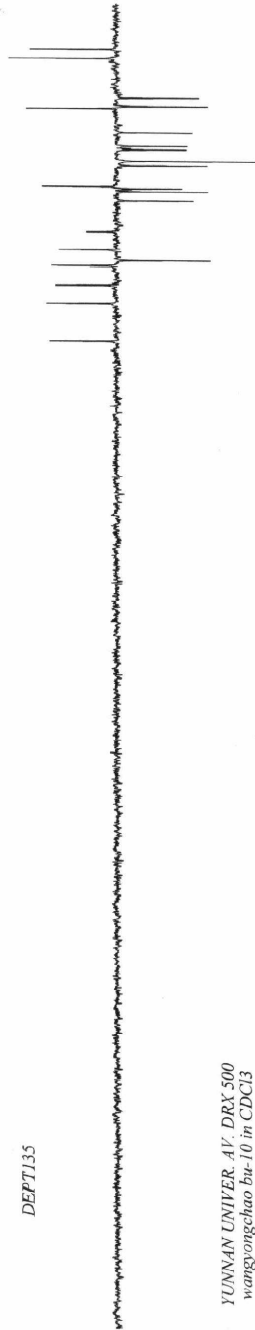
YUZHAN UNIVERSITY ET, DEK 500
 WANGYONGDAO BU-1G IN CDCl₃
 14061203



DEPT190



DEPT135



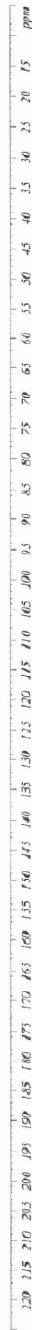
YUNNAN UNIVER. AV. DRX 500
wangyongchao bu-10 in CDC13
14061203

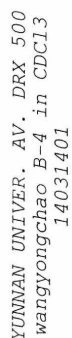
12.66
14.21
20.78
22.16
22.50
26.34
28.67
29.10
29.28
31.19
31.93
35.47
35.75
36.02
36.25
37.78
42.93
45.79
47.63
48.17
48.38
48.80
51.78
54.77
61.04

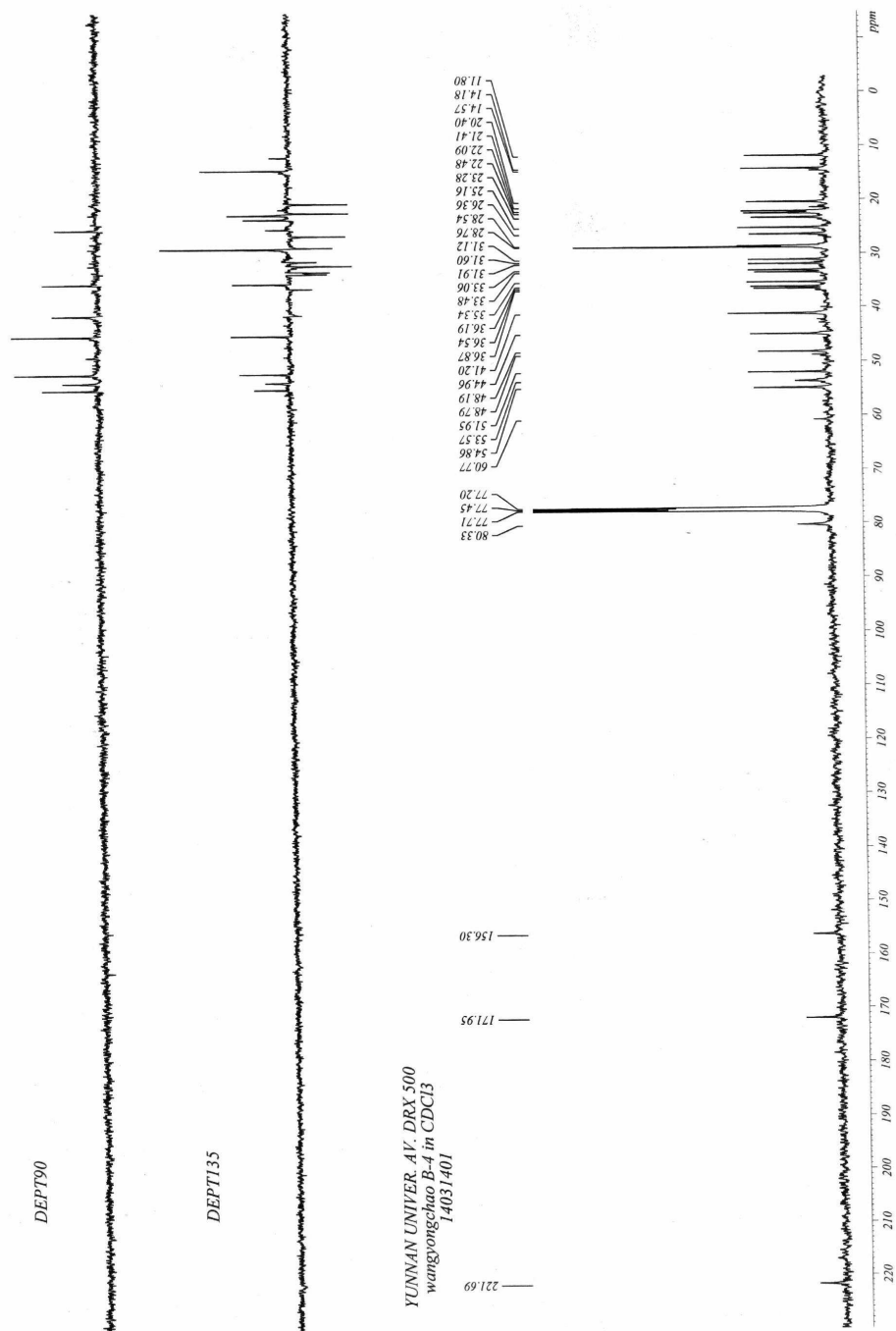
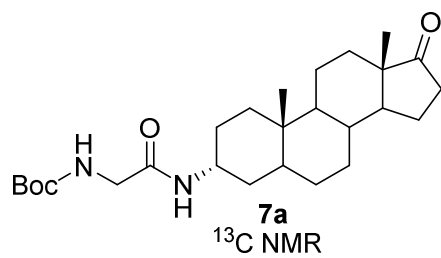
77.19
77.44
77.70

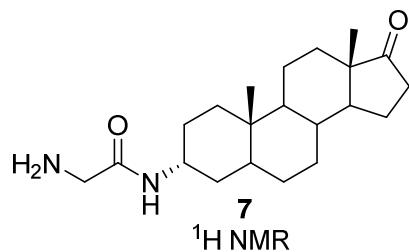
174.62

221.61

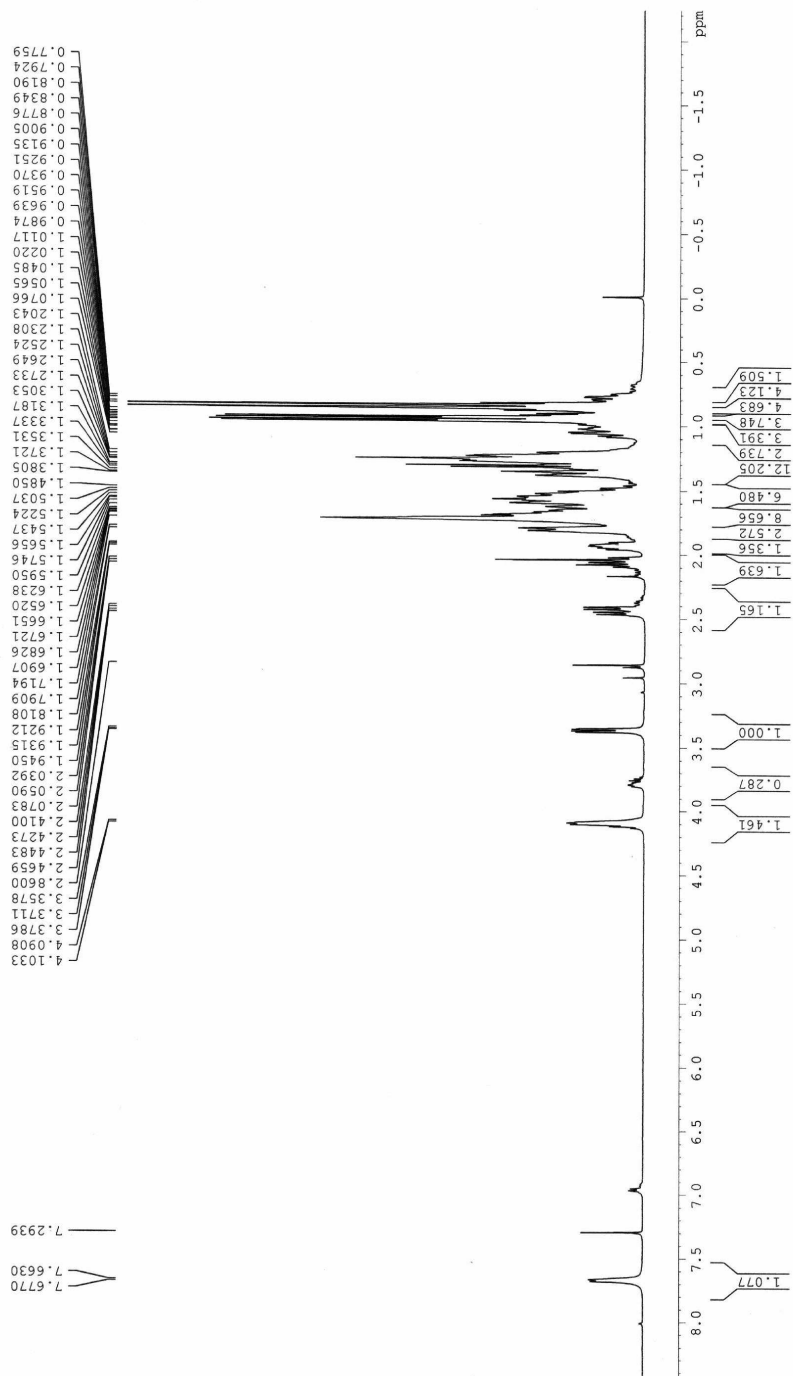


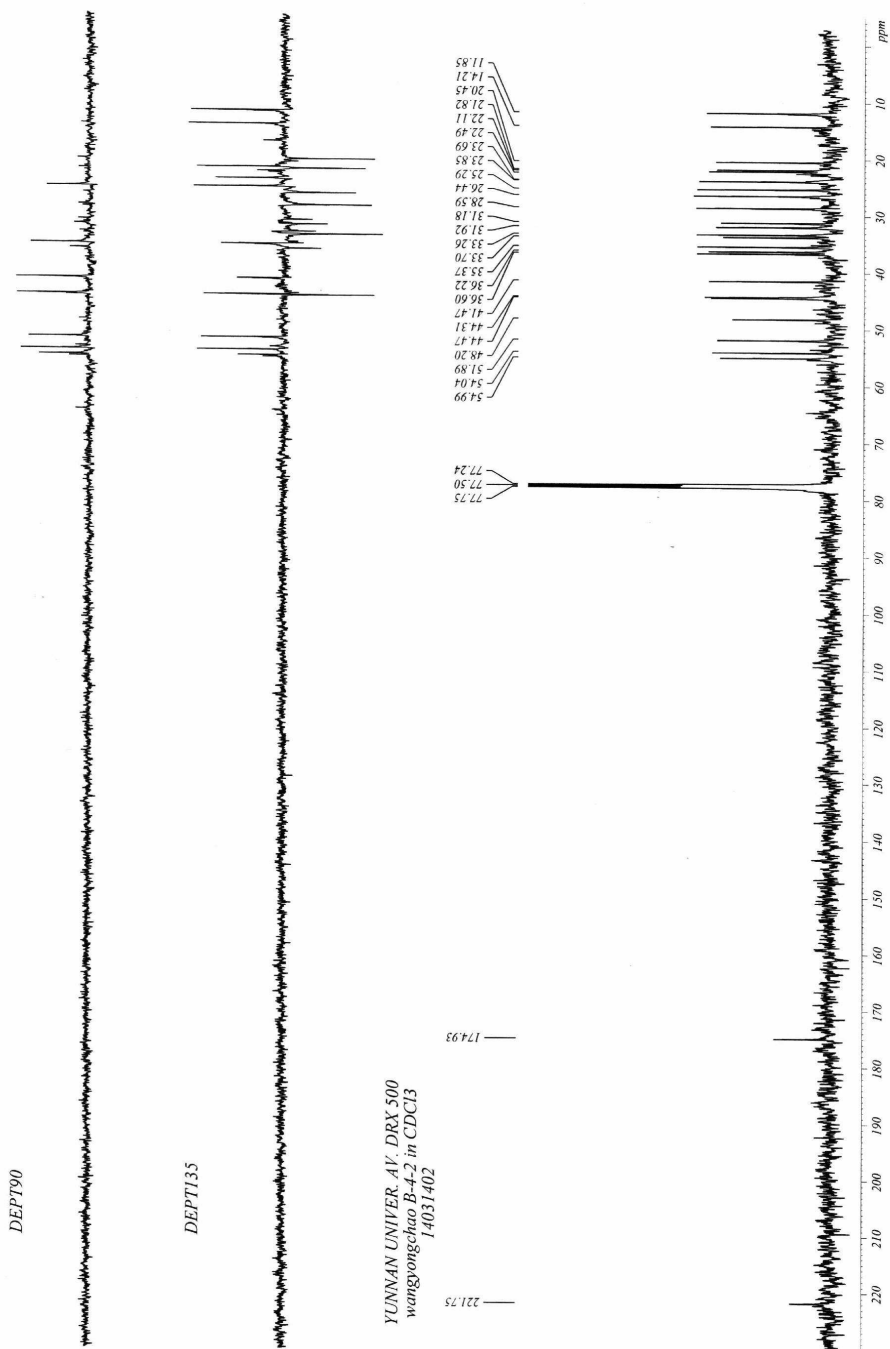
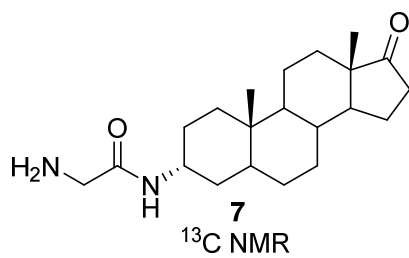


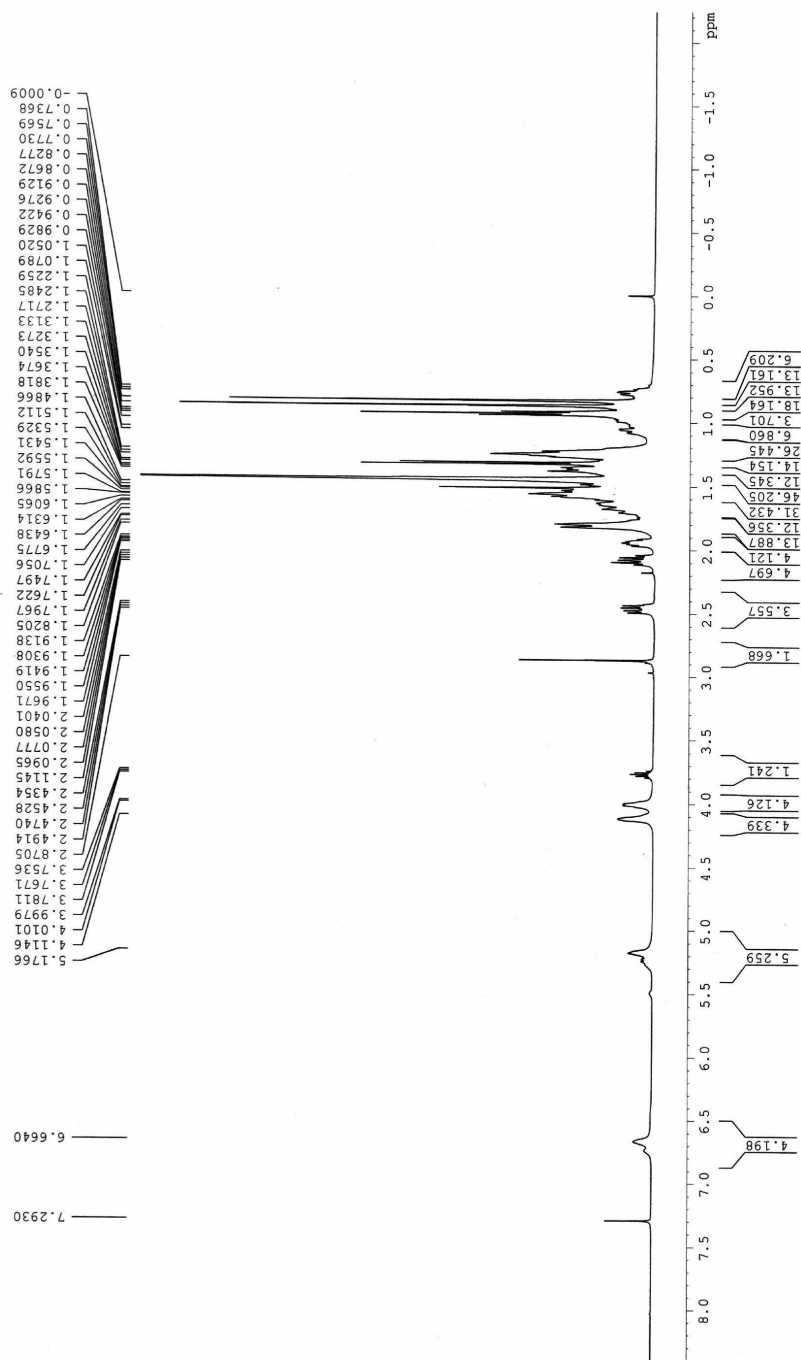
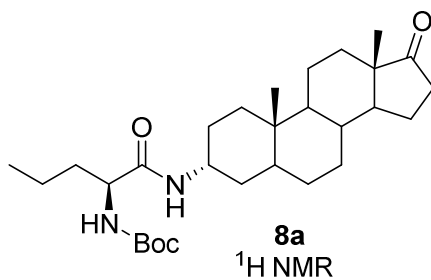




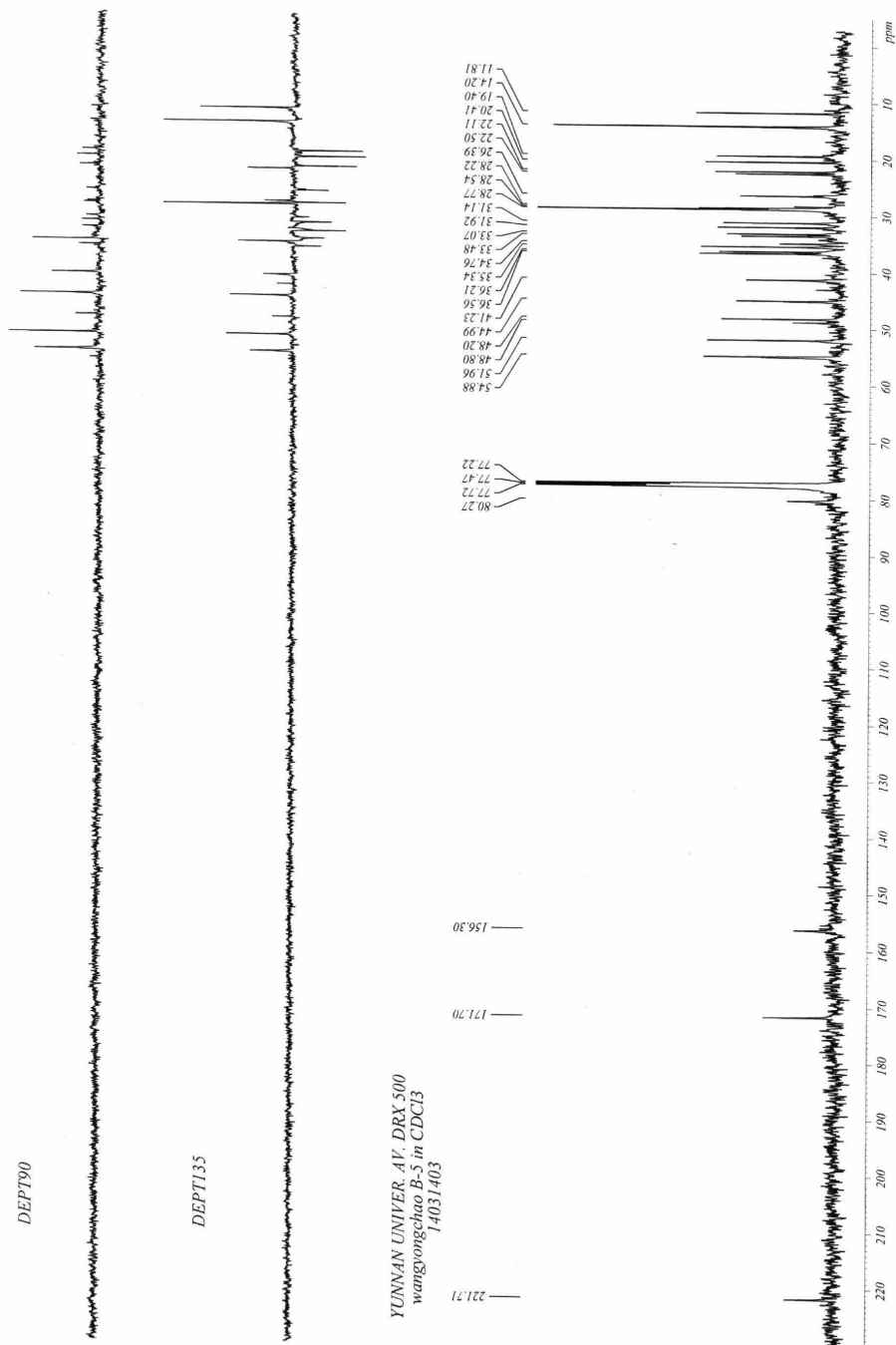
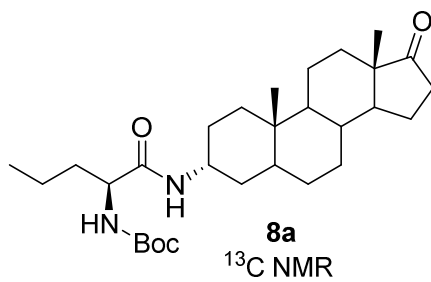
YUNNAN UNIVER. AV. DRX 500
 wangyongchao B-4-2 in CDCl₃
 14031402

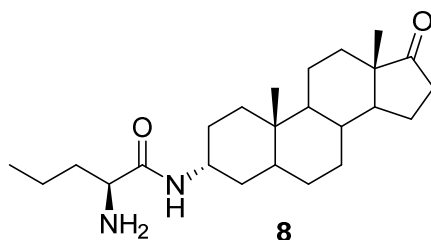




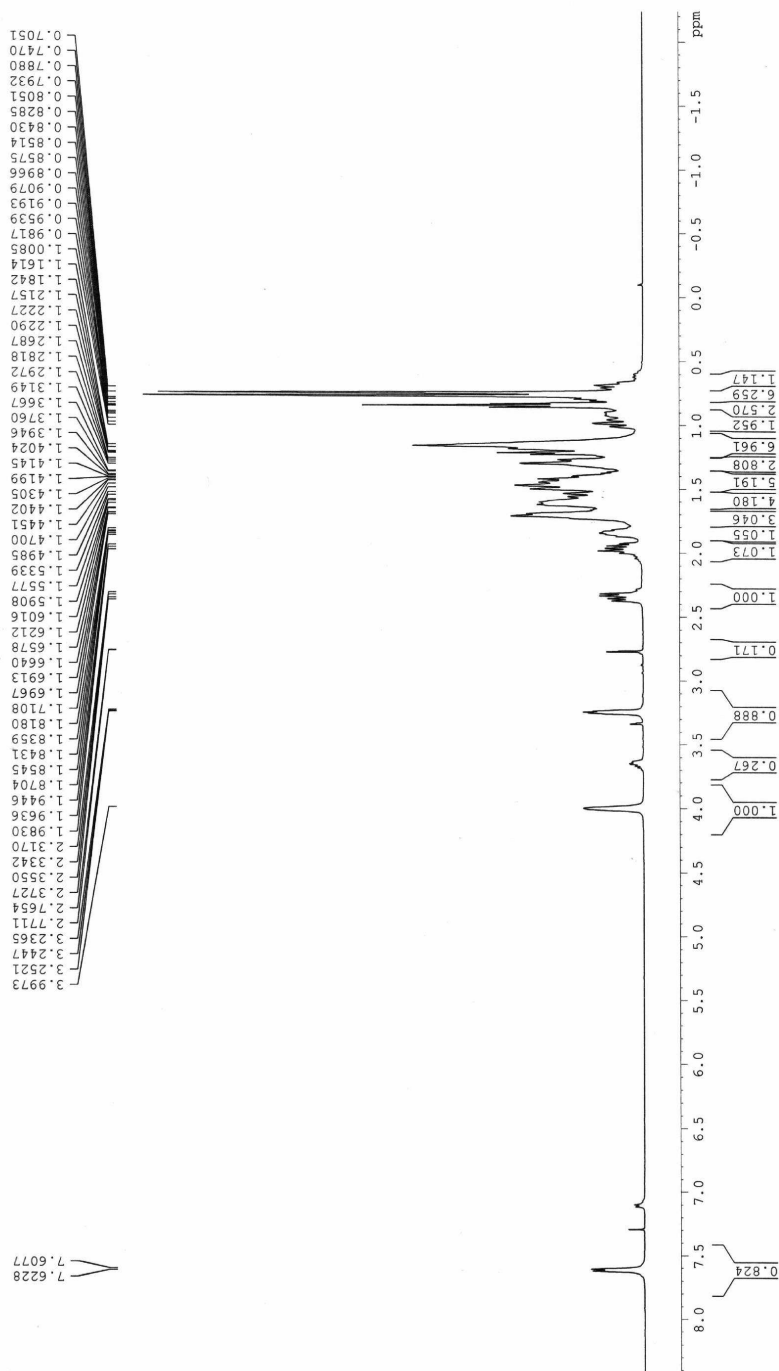


YUNNAN UNIVER. AV. DRX 500
 wangyongchao B-5 in CDCl₃
 14031403

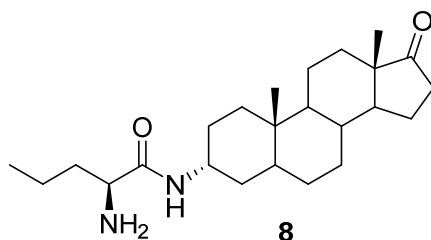




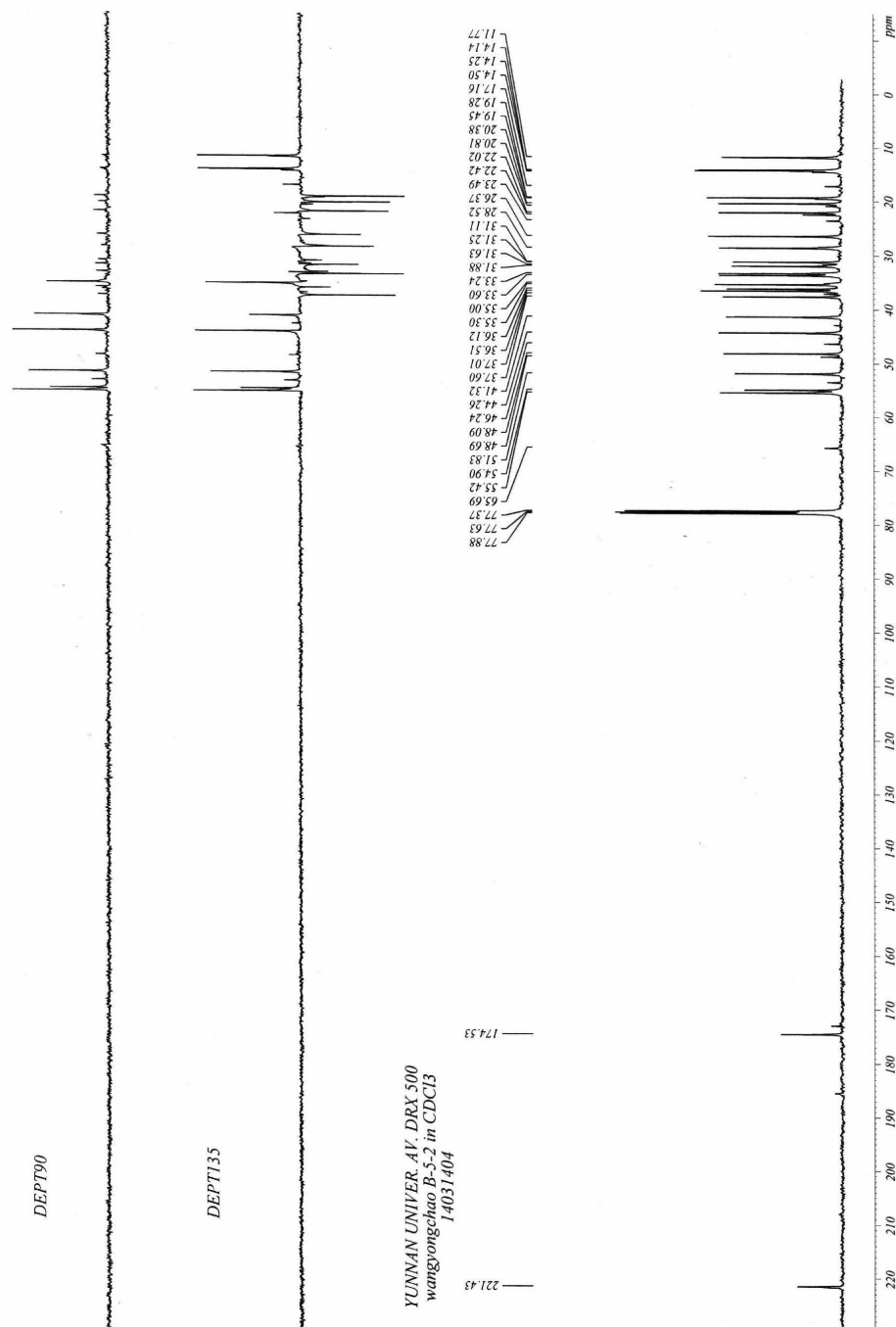
8
¹H NMR

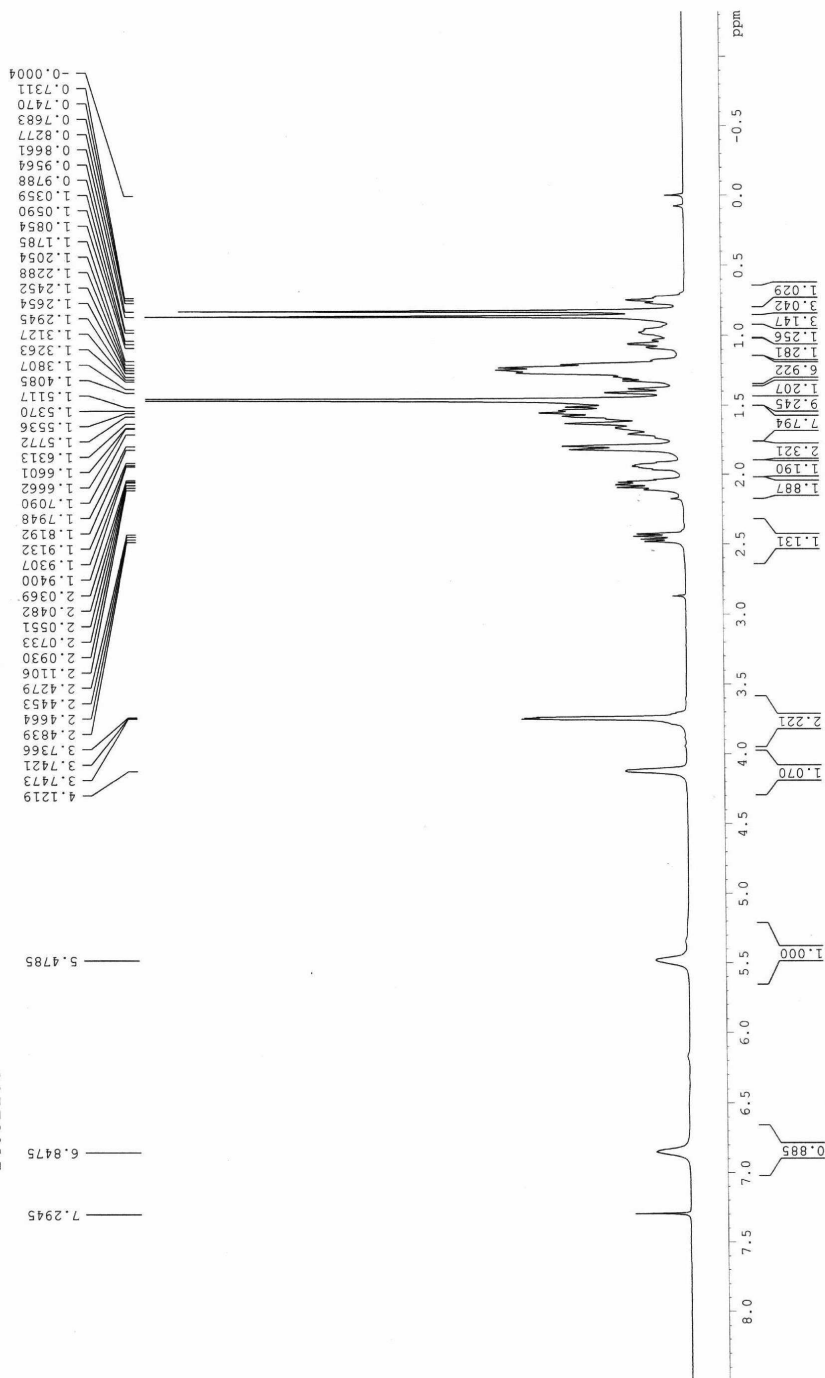
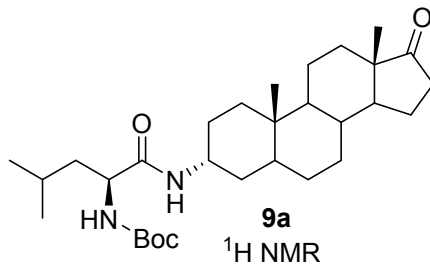


YUNNAN UNIVER. AV. DRX 500
wangyongchao B-5-2 in CDCl₃
14031404

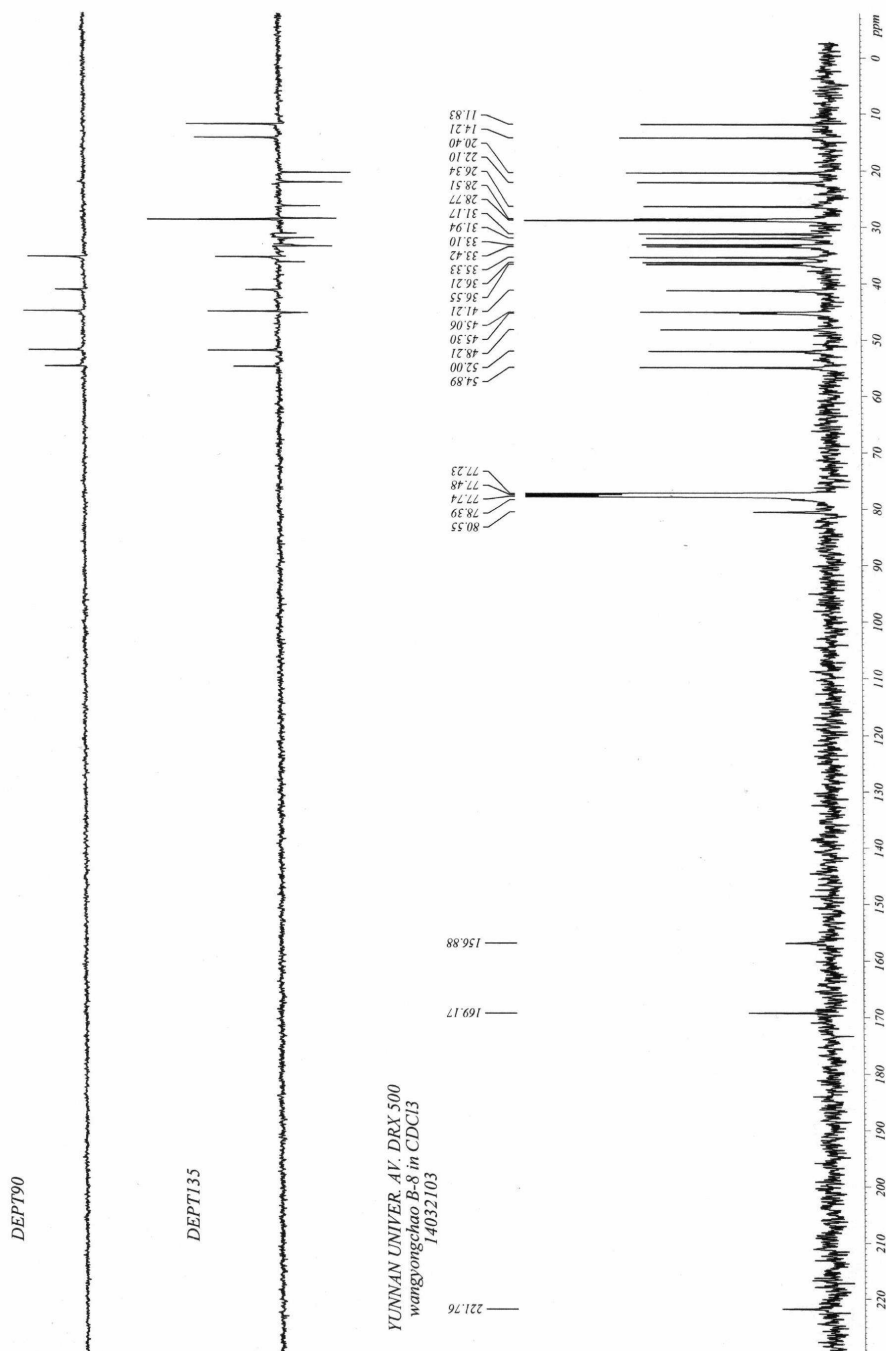
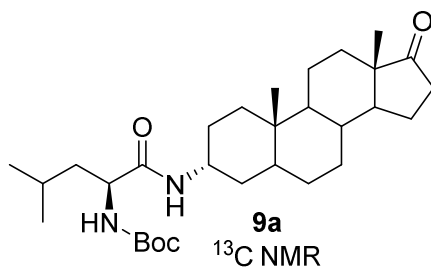


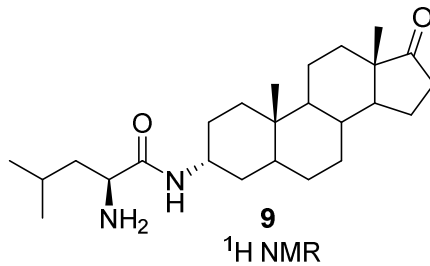
8
 ^{13}C NMR



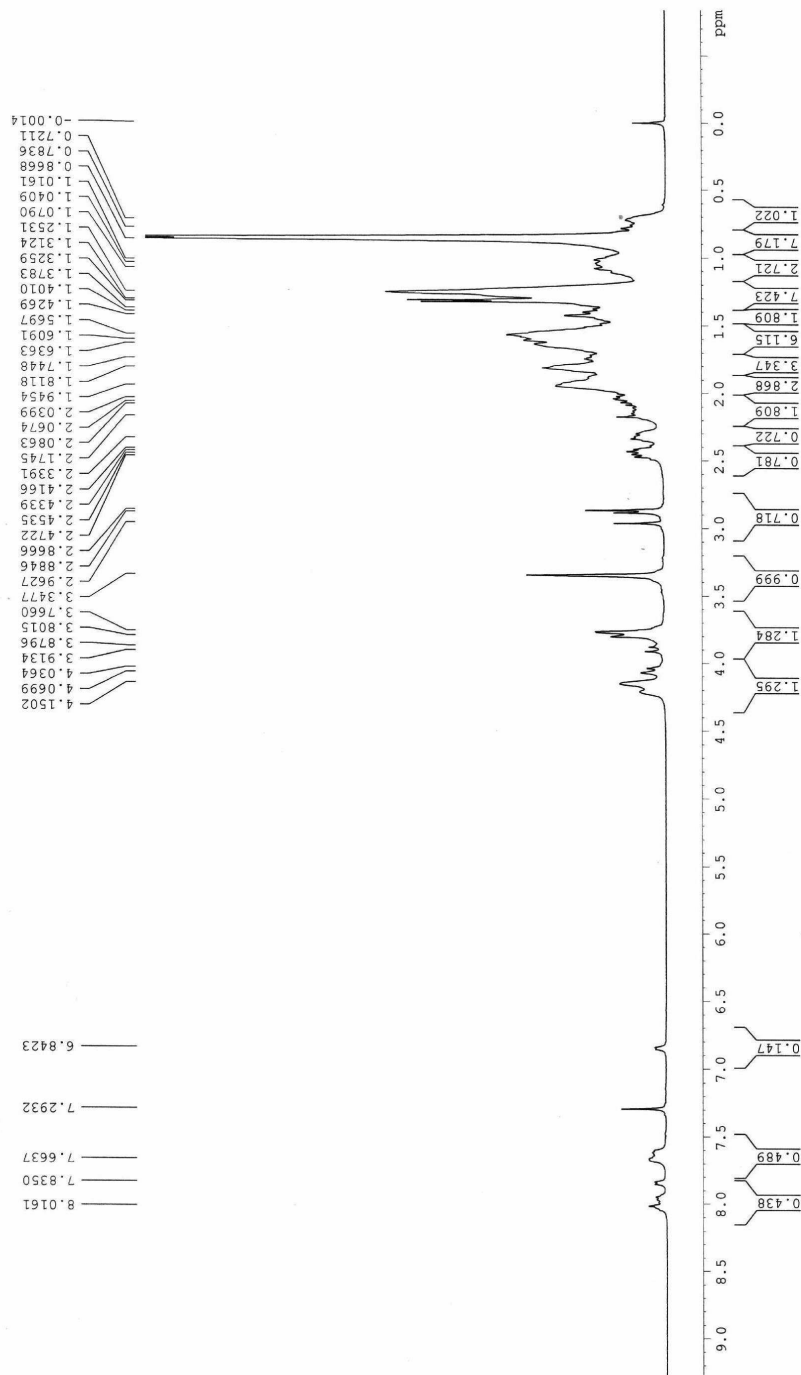


YUNNAN UNIVER. AV. DRX 500
 wangyongchao B-8 in CDCl3
 14032103

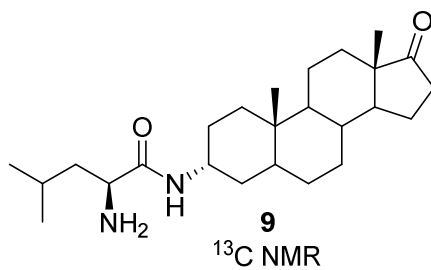




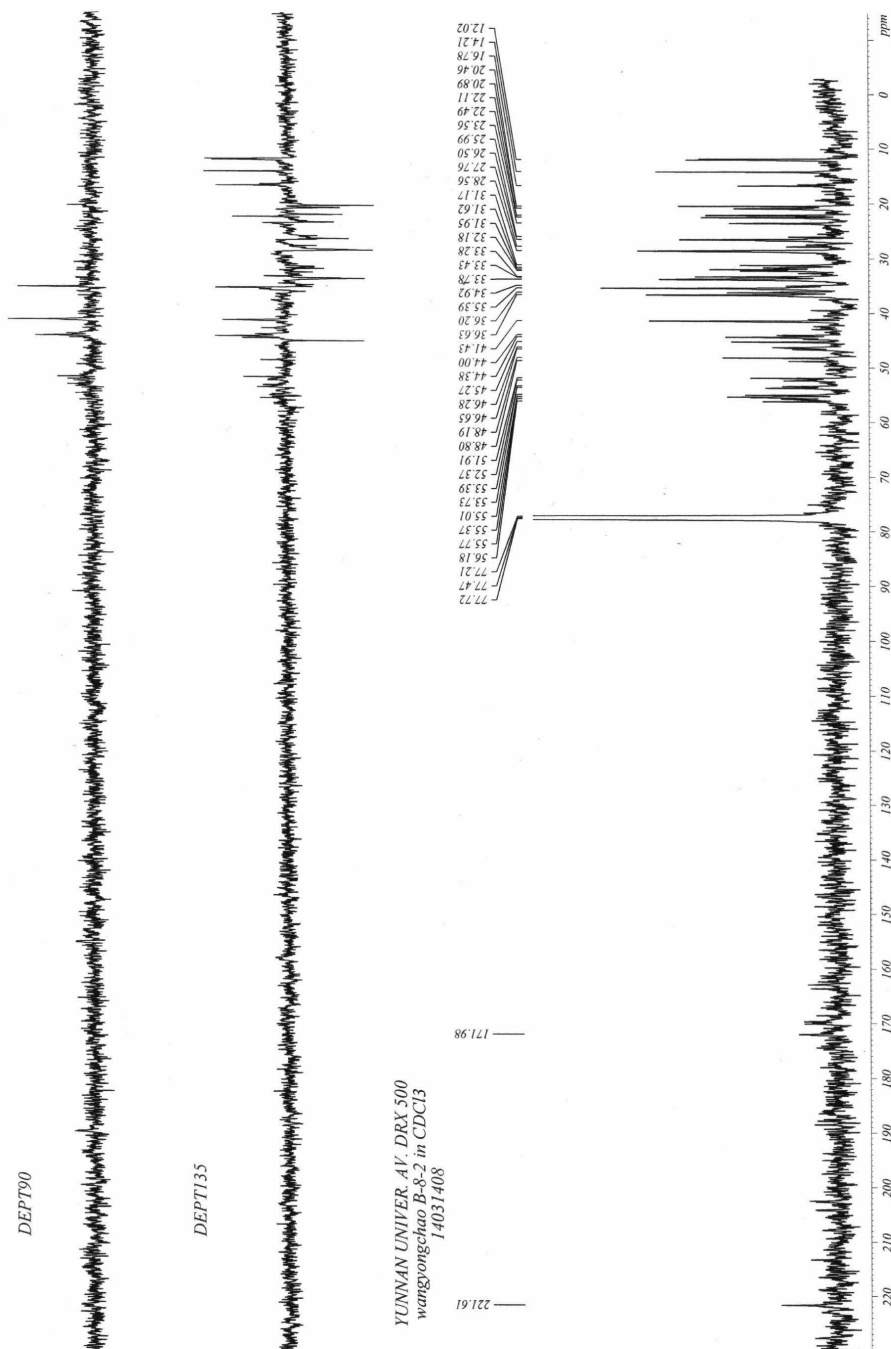
¹H NMR



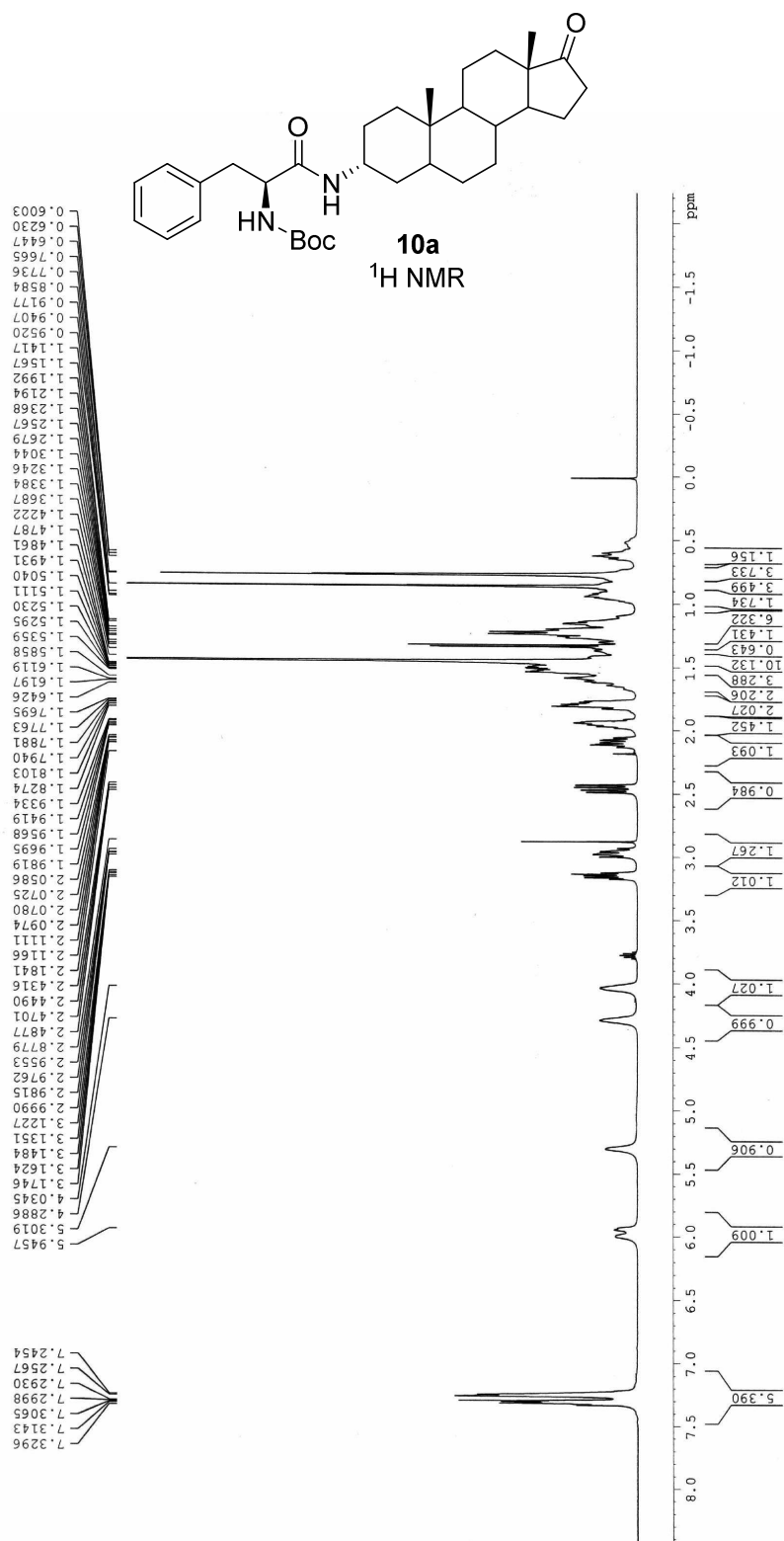
YUNNAN UNIVER. AV. DRX 500
wangyongchao B-8-2 in CDCl₃
14031408

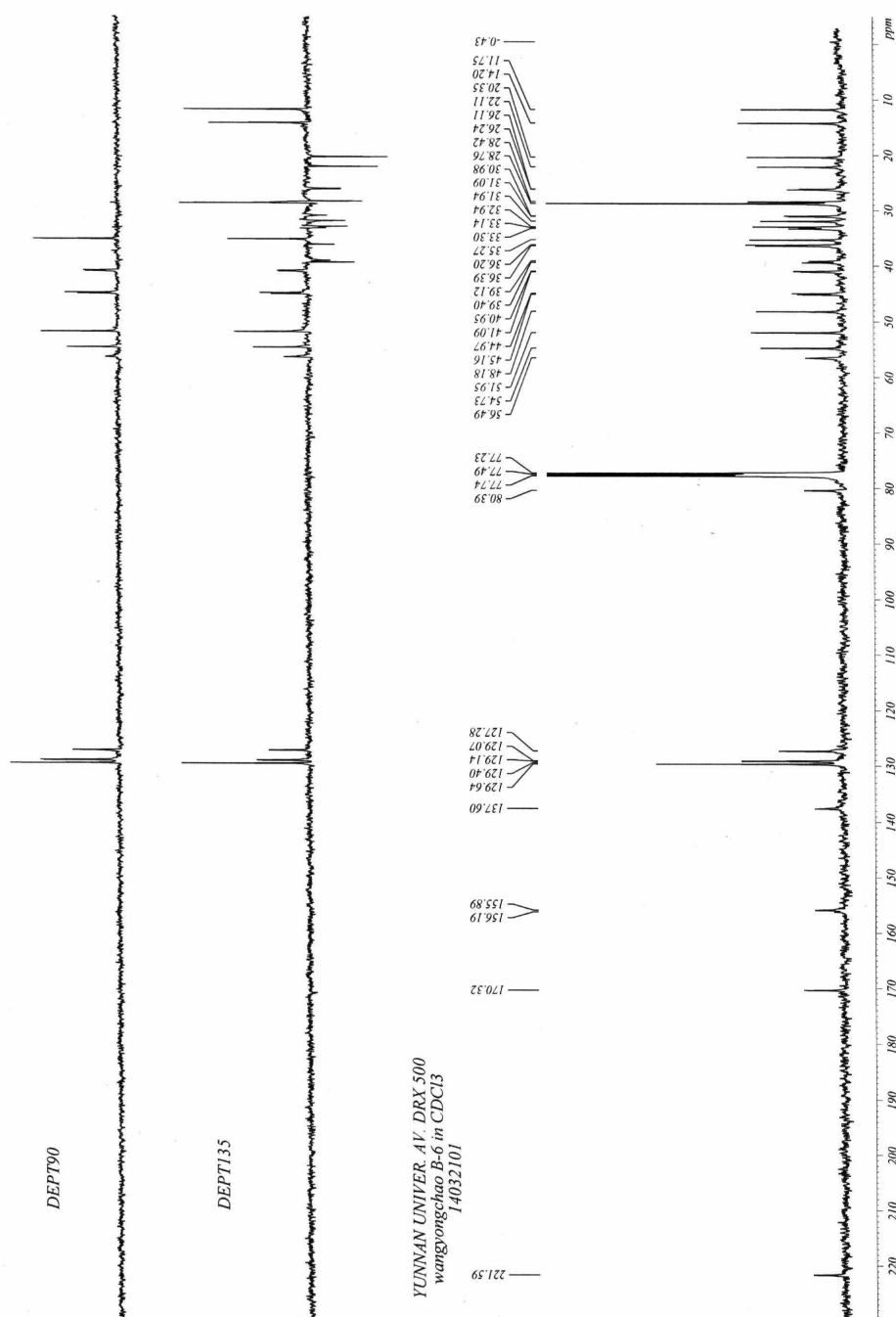
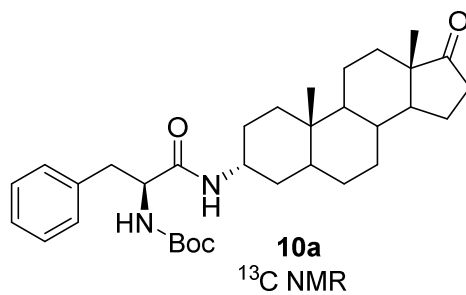


9
¹³C NMR

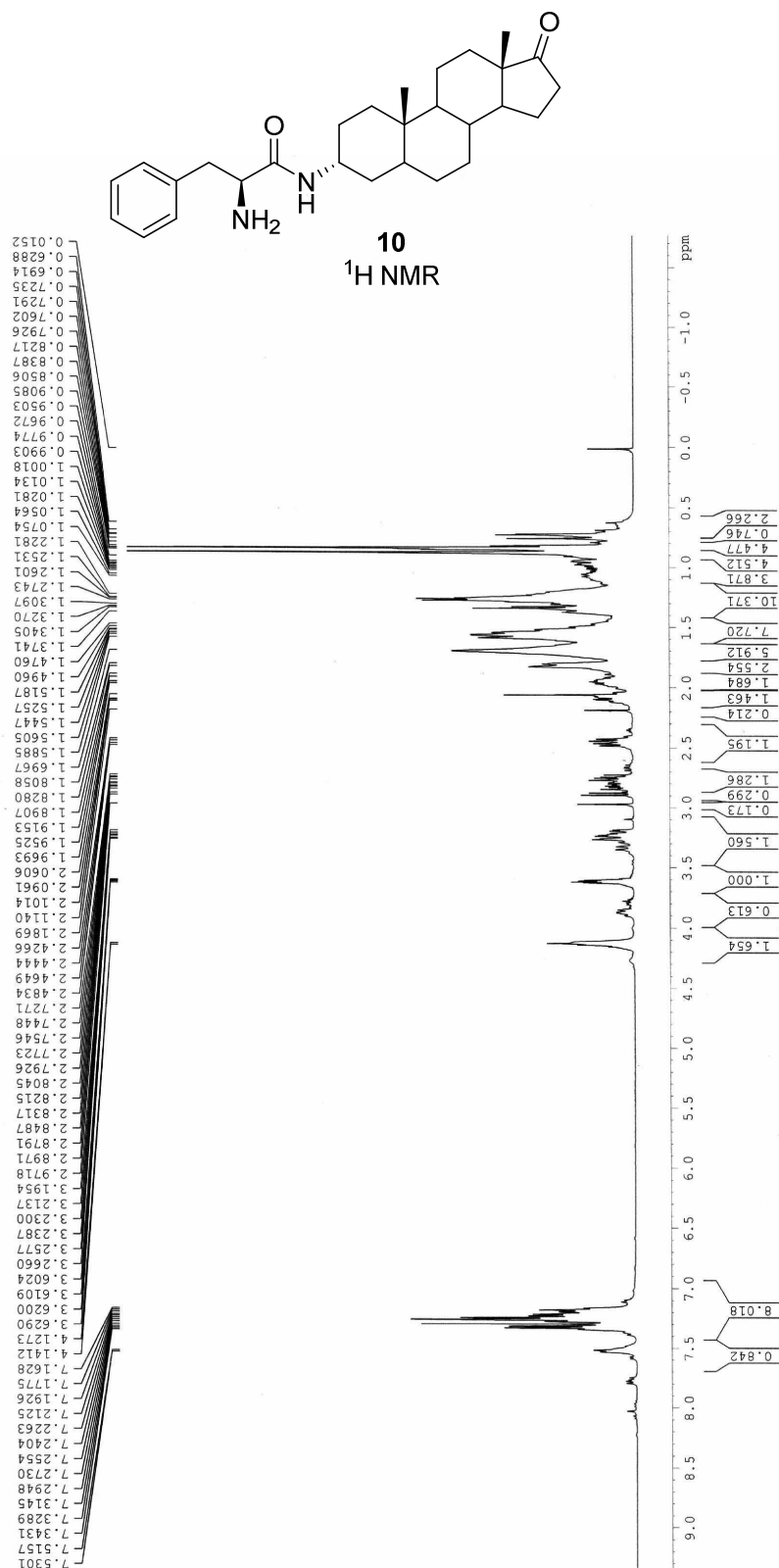


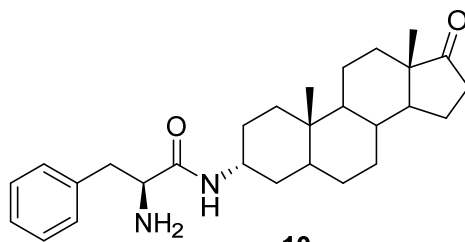
YUNNAN UNIVER. AV. DRX 500
wangyongchao B-6 in CDCl3
14031405



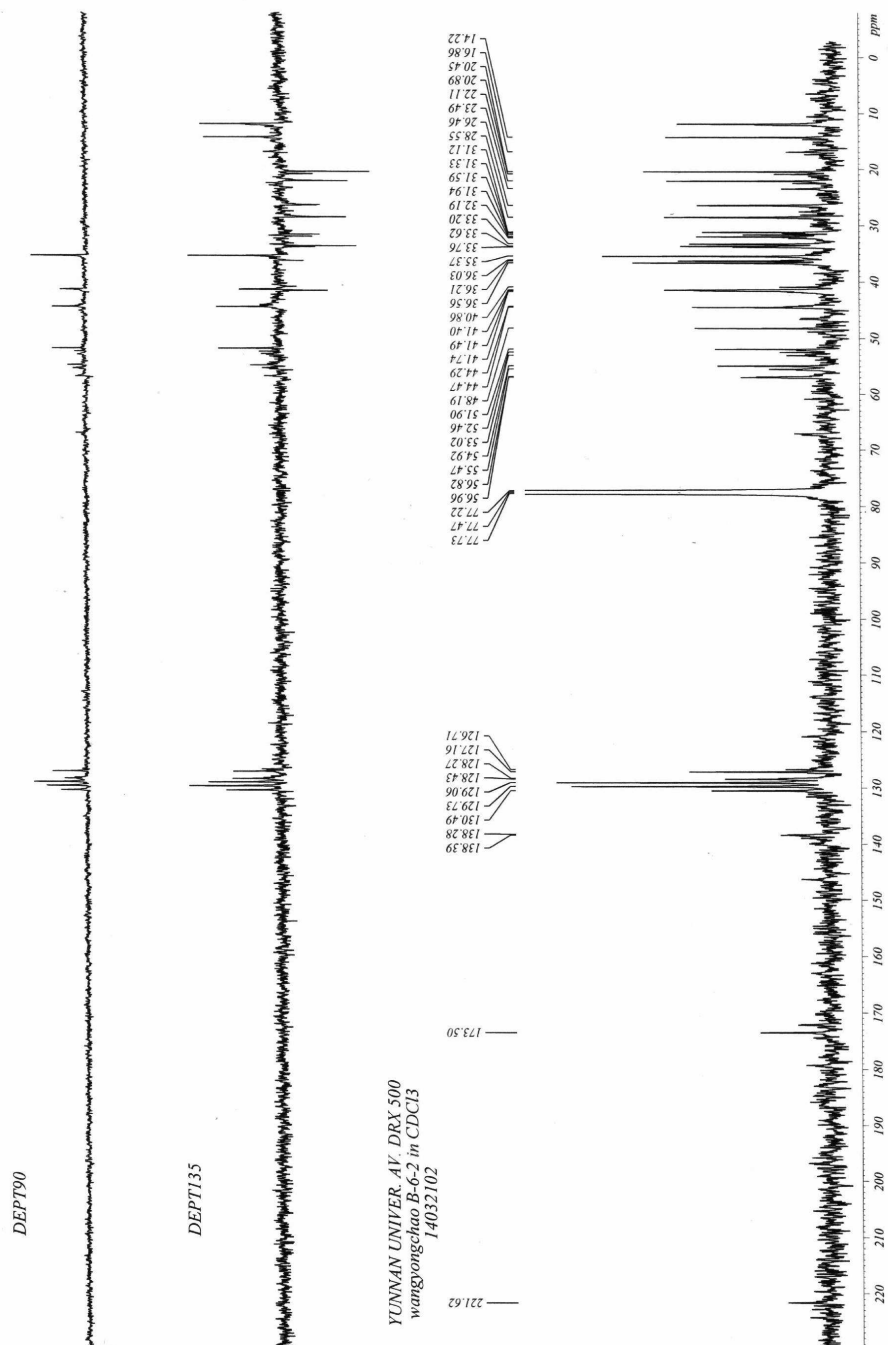


YUNNAN UNIVER. AV. DRX 500
wangyongchao B-6-2 in CDC13
14032102



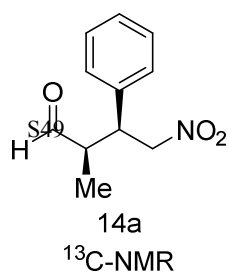
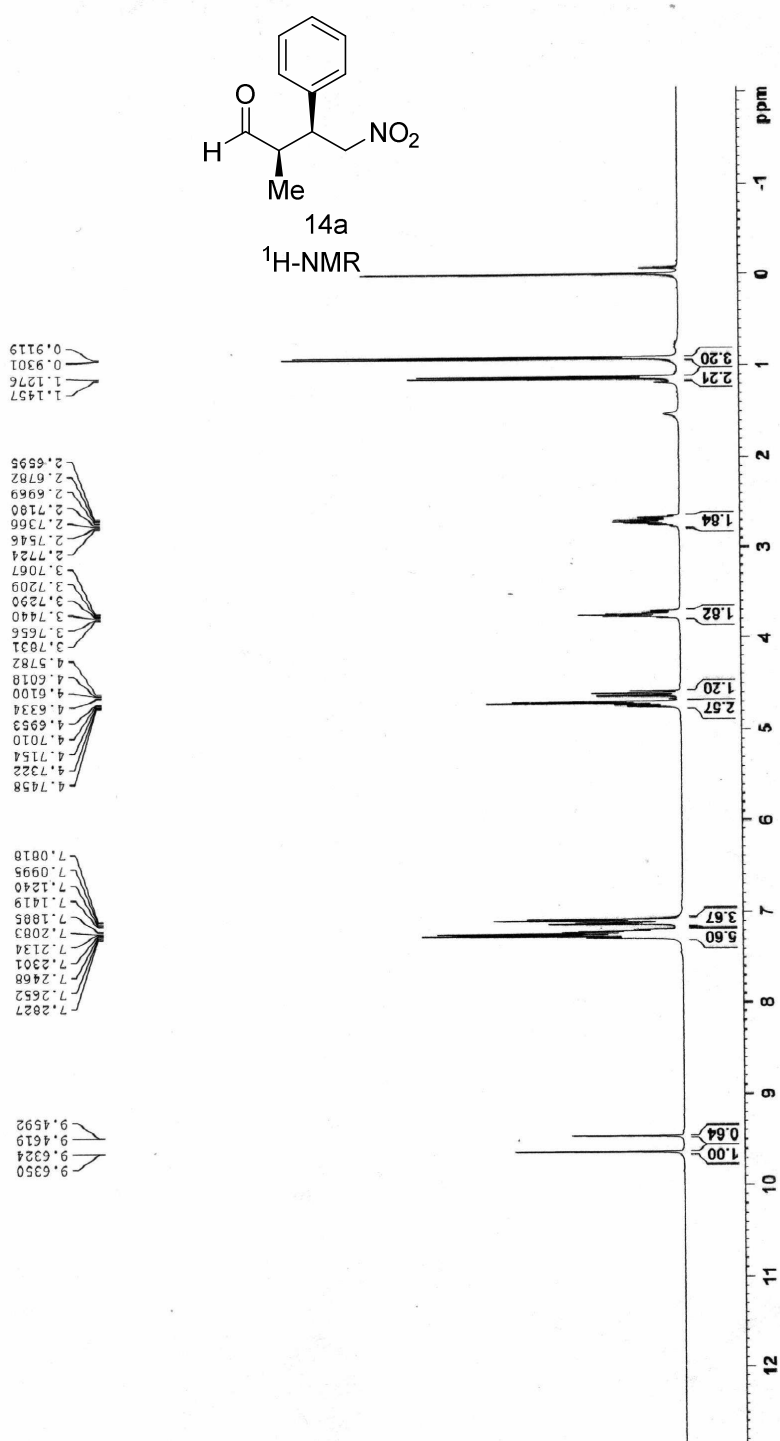


10
 ^{13}C NMR



Spectra of Michael Adducts

YUNNAN UNIVERSITY AVIII-400
wangyongchao F30-2 in CDCl3
450

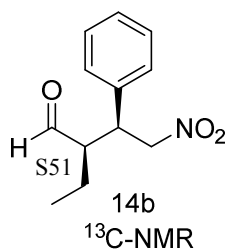
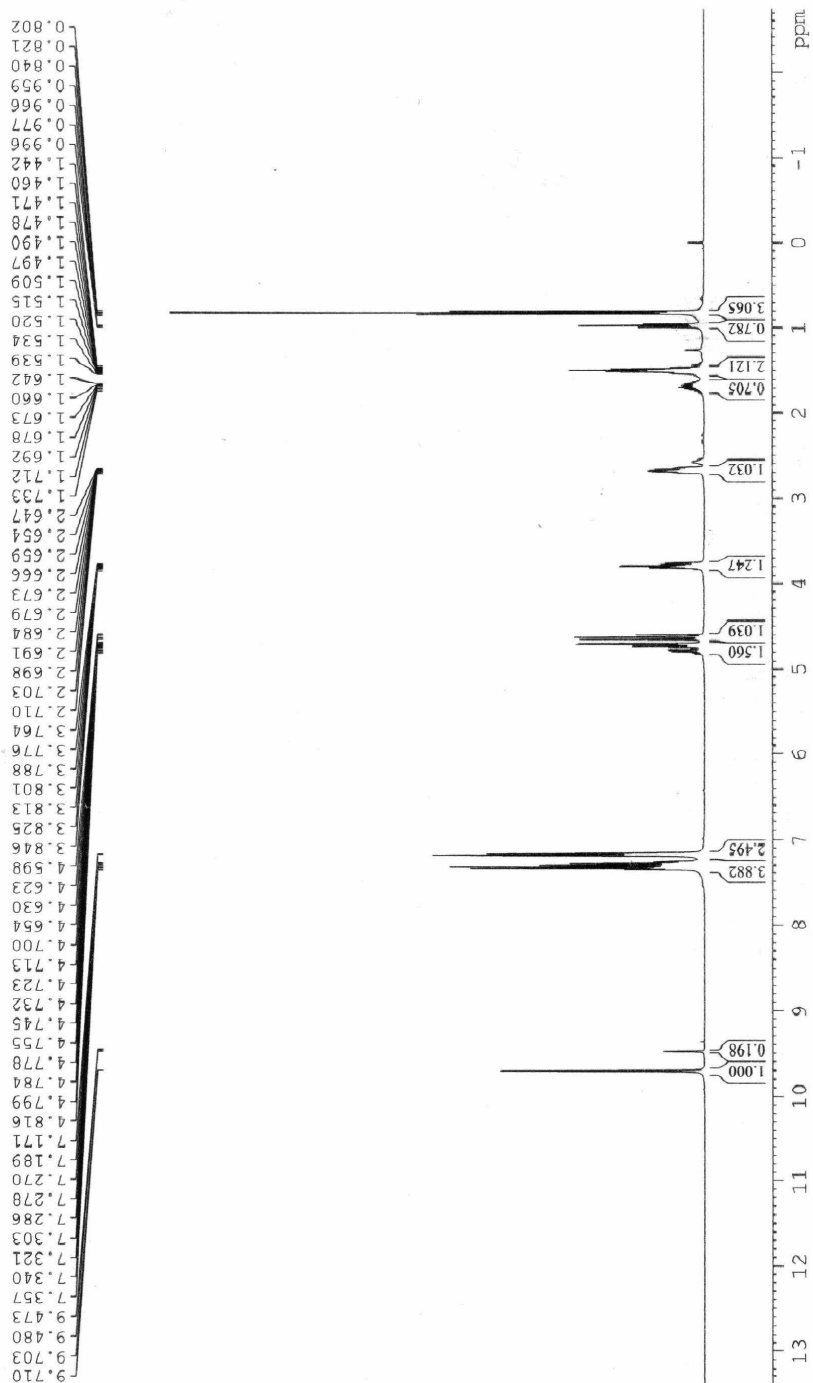


450

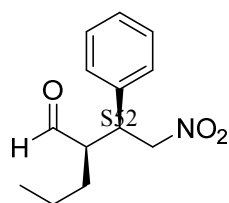
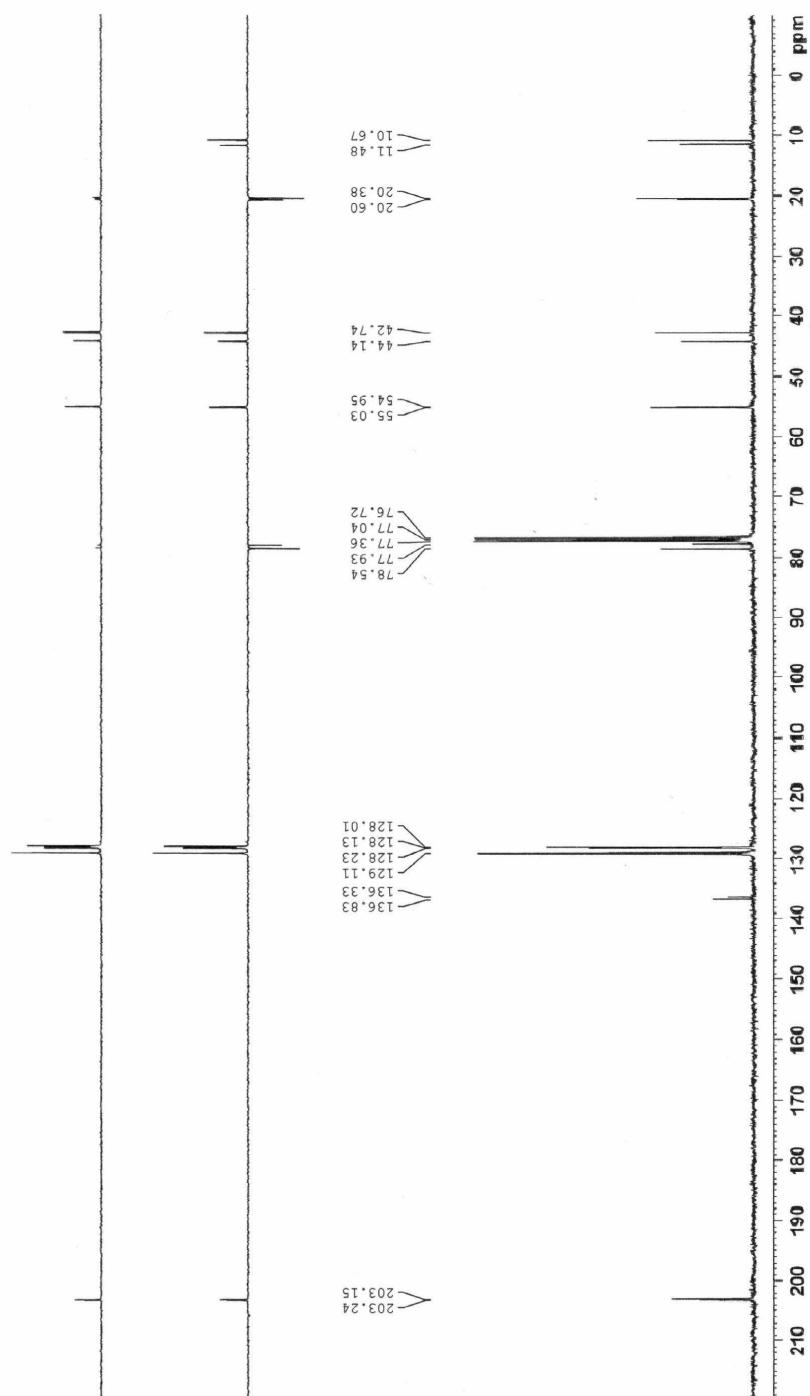


¹H NMR

YUNNAN UNIVERSITY AVIII-400
wangyongchao F60-3 in CDCl3
47



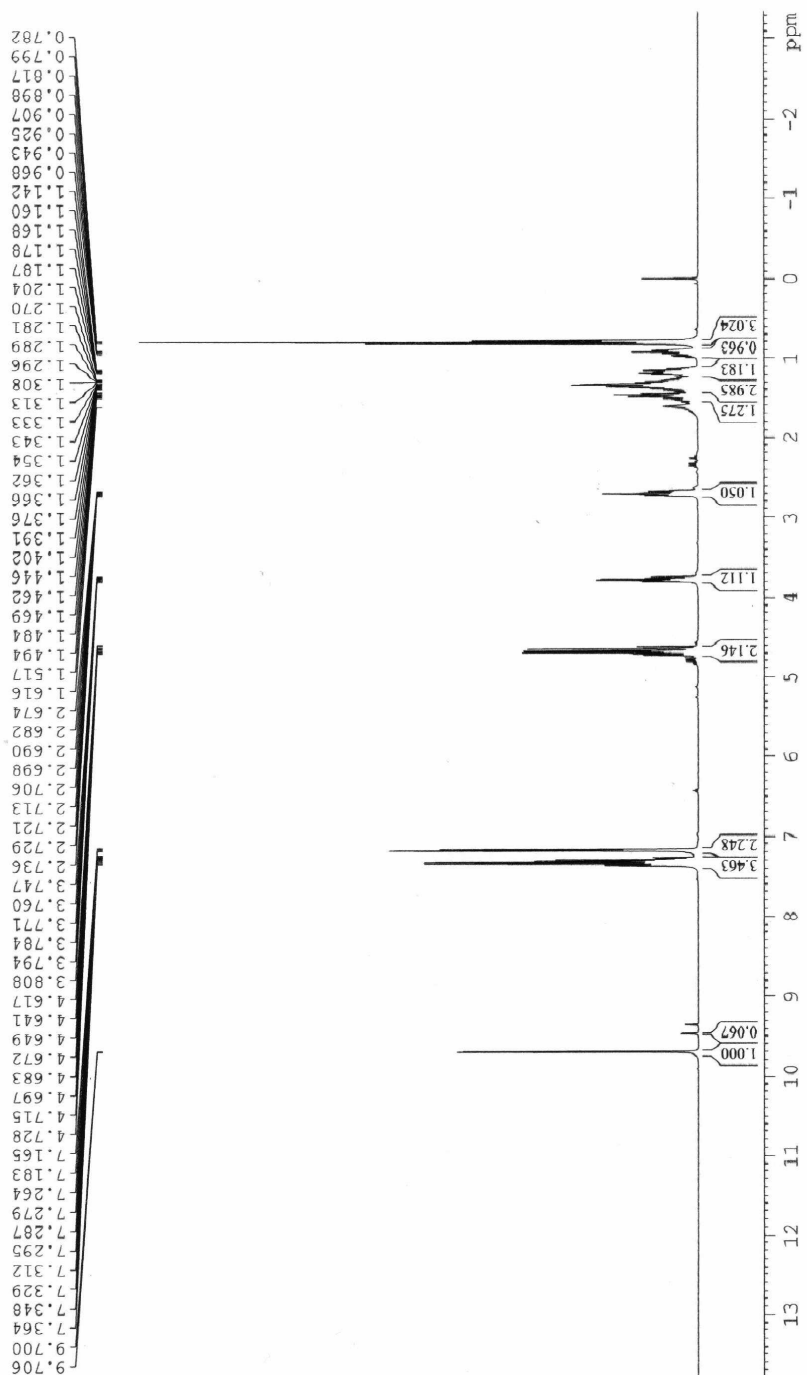
YUNNAN UNIVERSITY AVII-400
wangyongchao F60 in CDCl₃
555

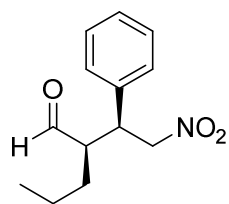


14c

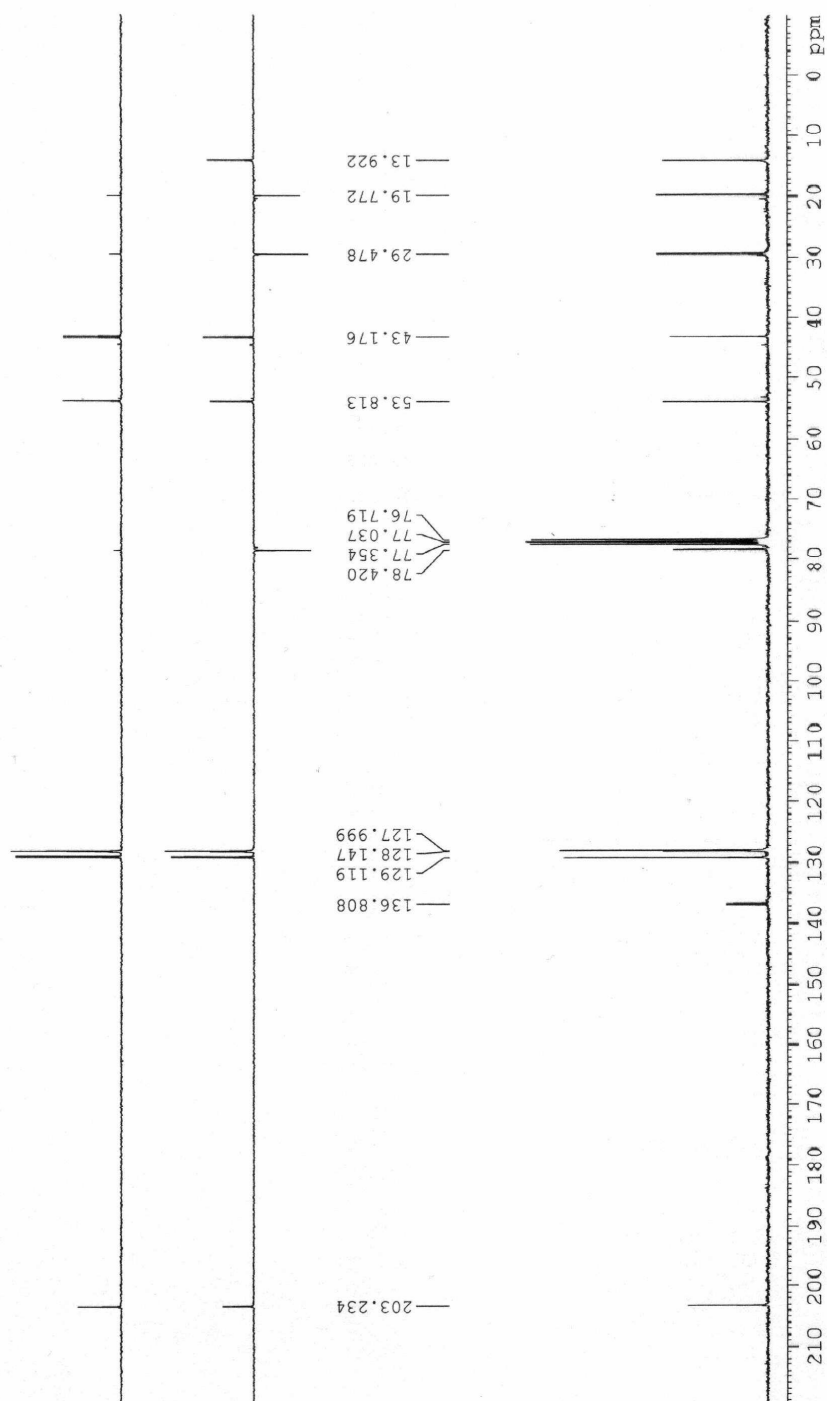
1H NMR

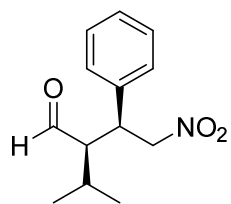
YUNNAN UNIVERSITY AVIII-400
 wangyongchao F61-3 in CDCl₃
 51



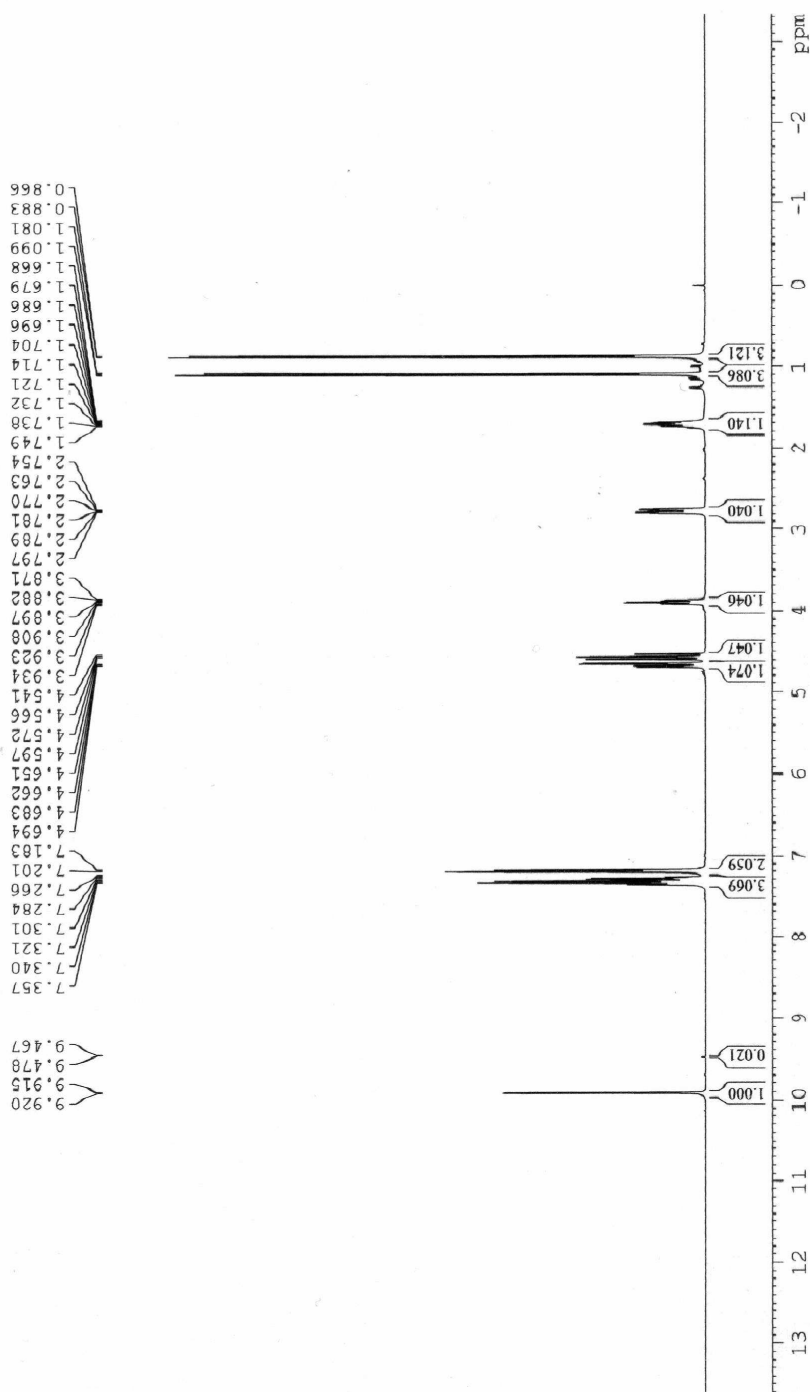


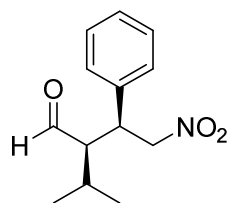
14c
¹³C-NMR





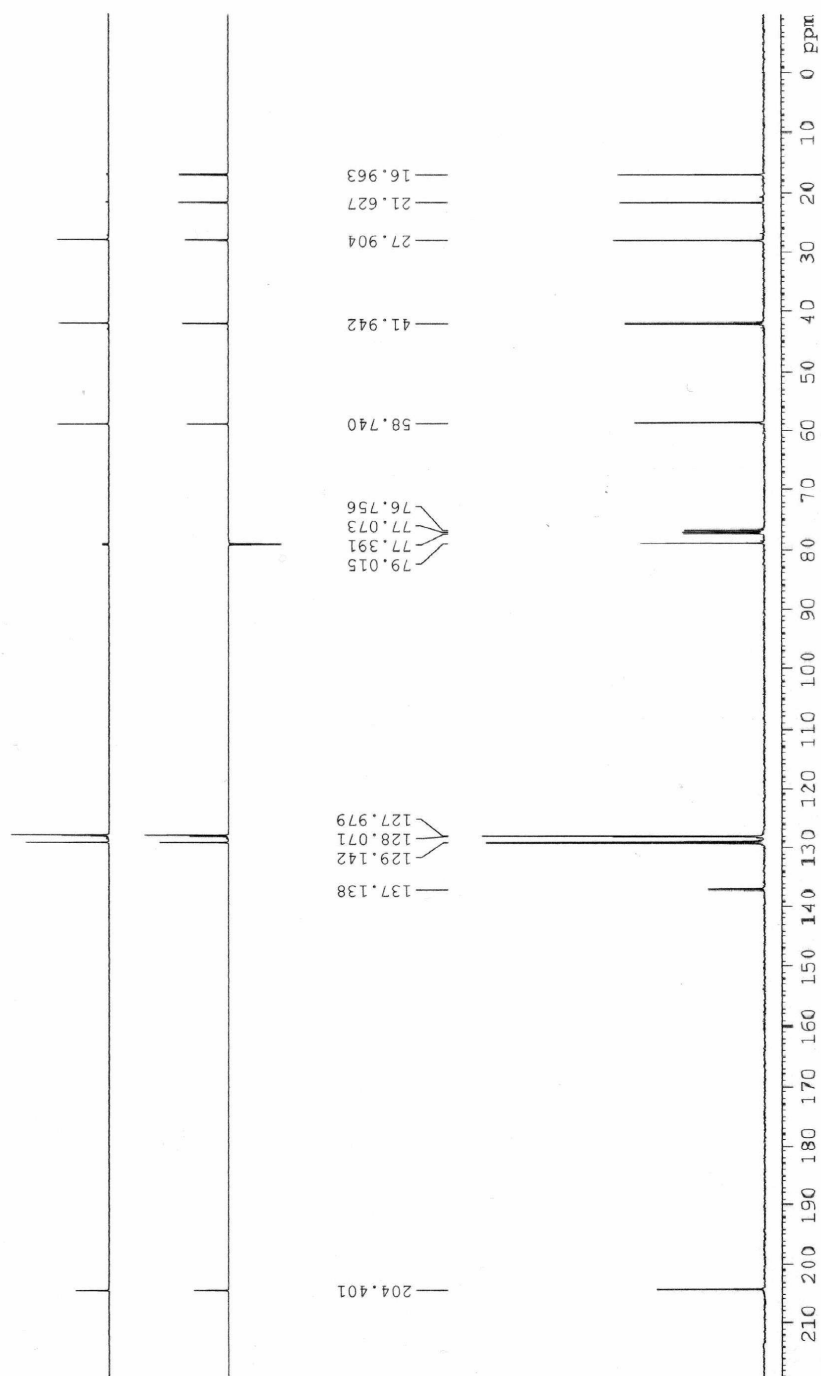
14d
¹H-NMR



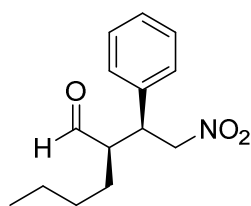


14d

¹³C-NMR

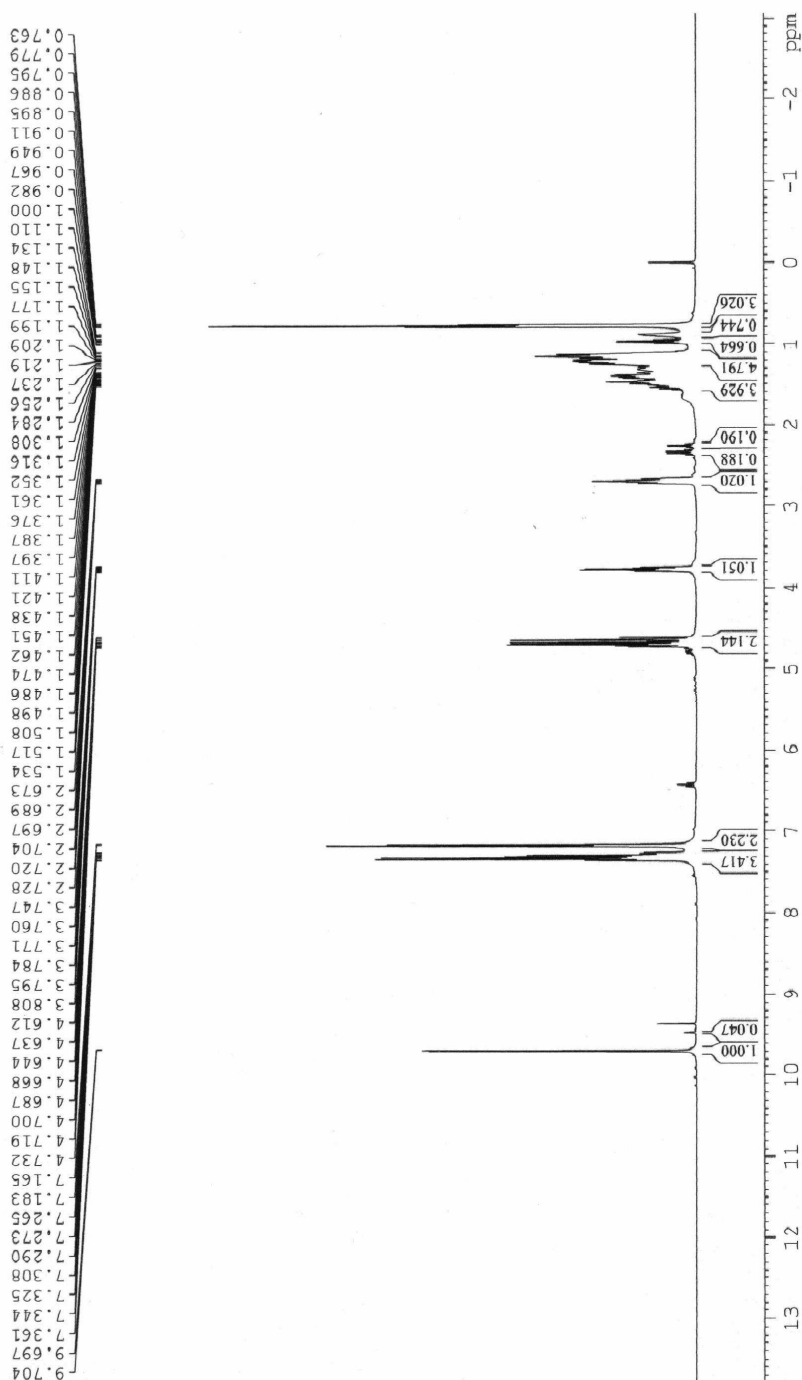


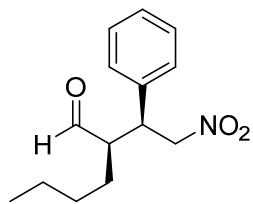
YUNNAN UNIVERSITY AVIII-400
wangyongchao F62-3 in CDCl₃
55



14e

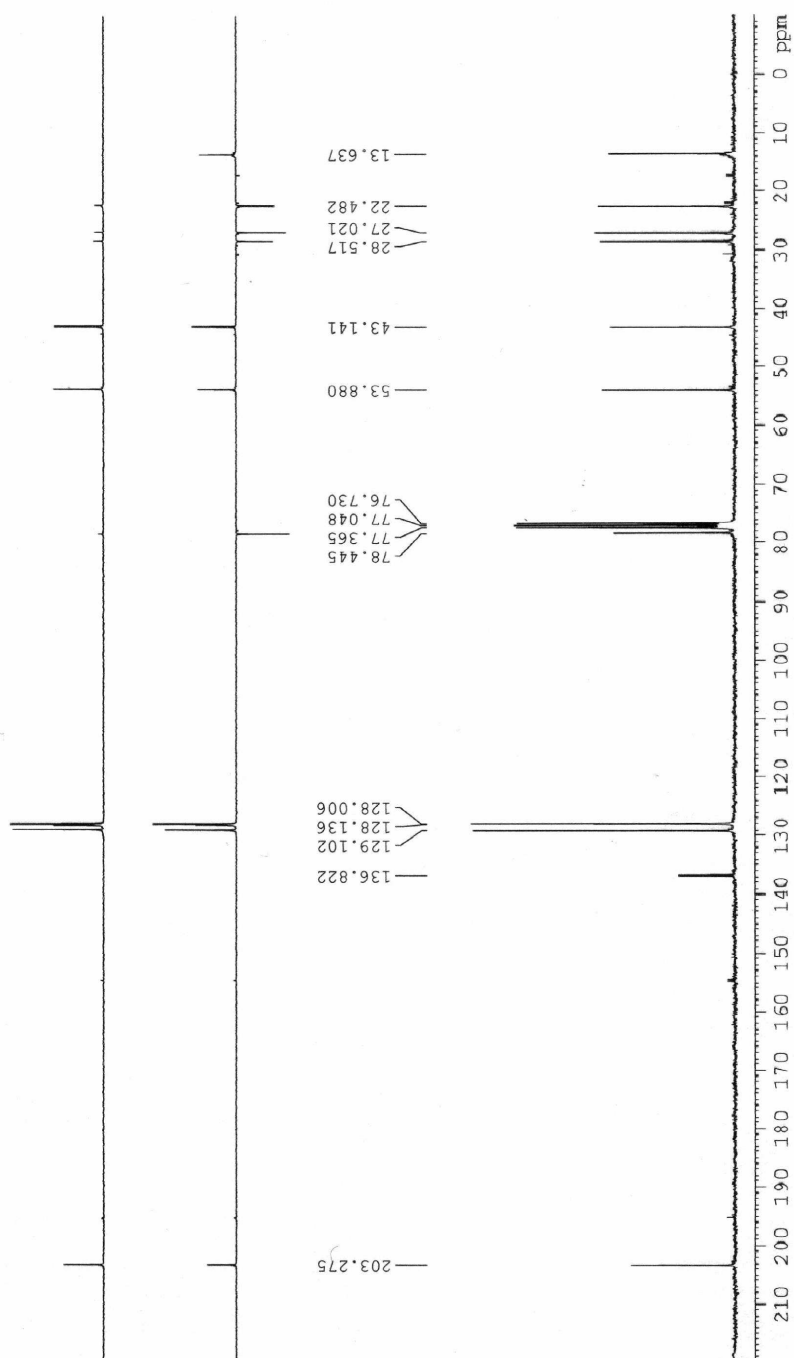
¹H-NMR



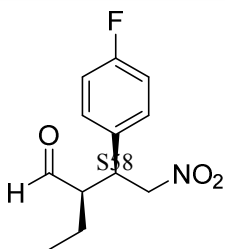


14e

^{13}C -NMR

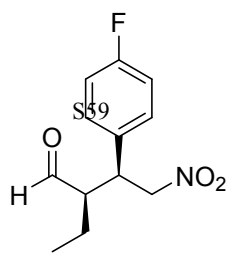


YUNNAN UNIVERSITY 2011-400
wangyongchao F63-3 in CDCl3
59

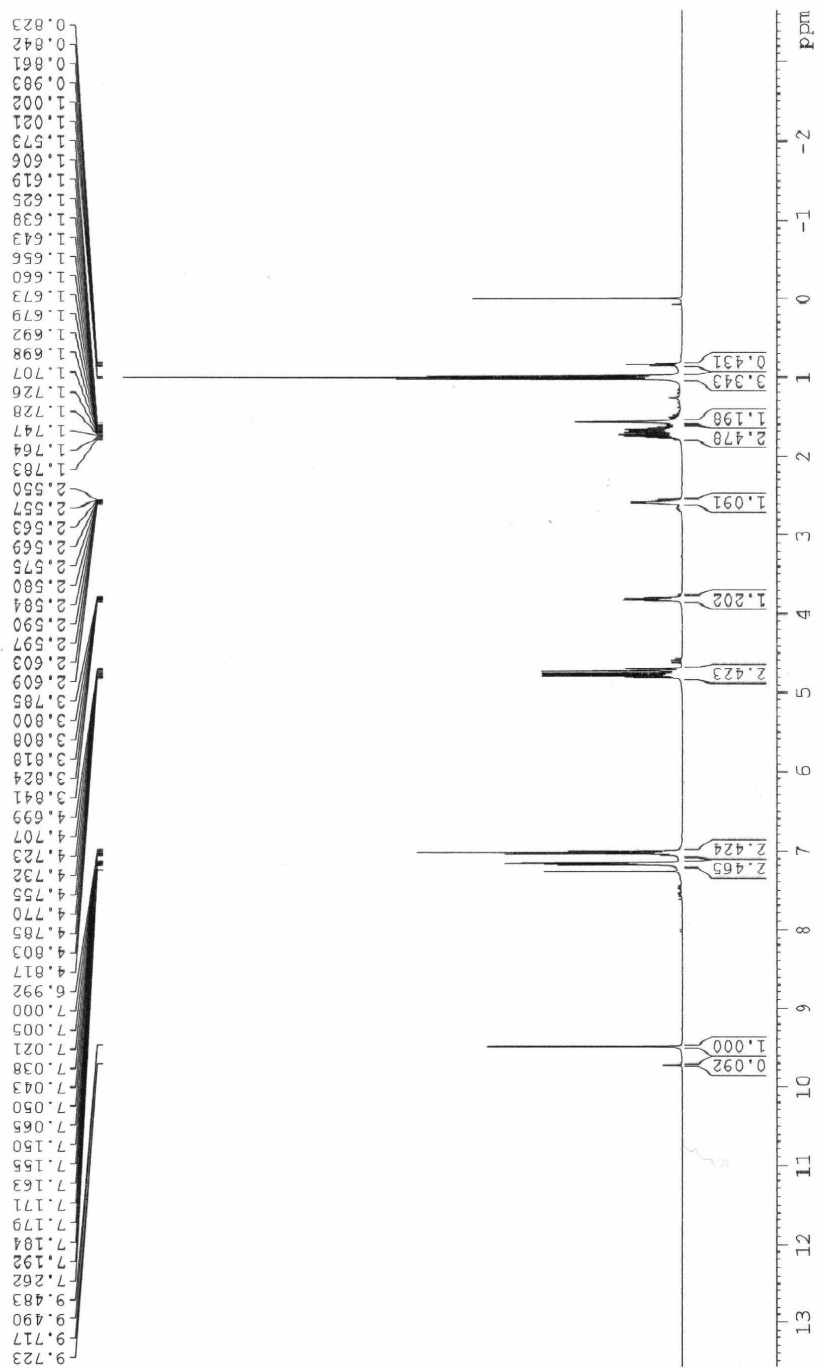


14f

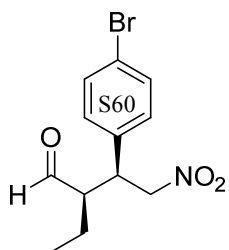
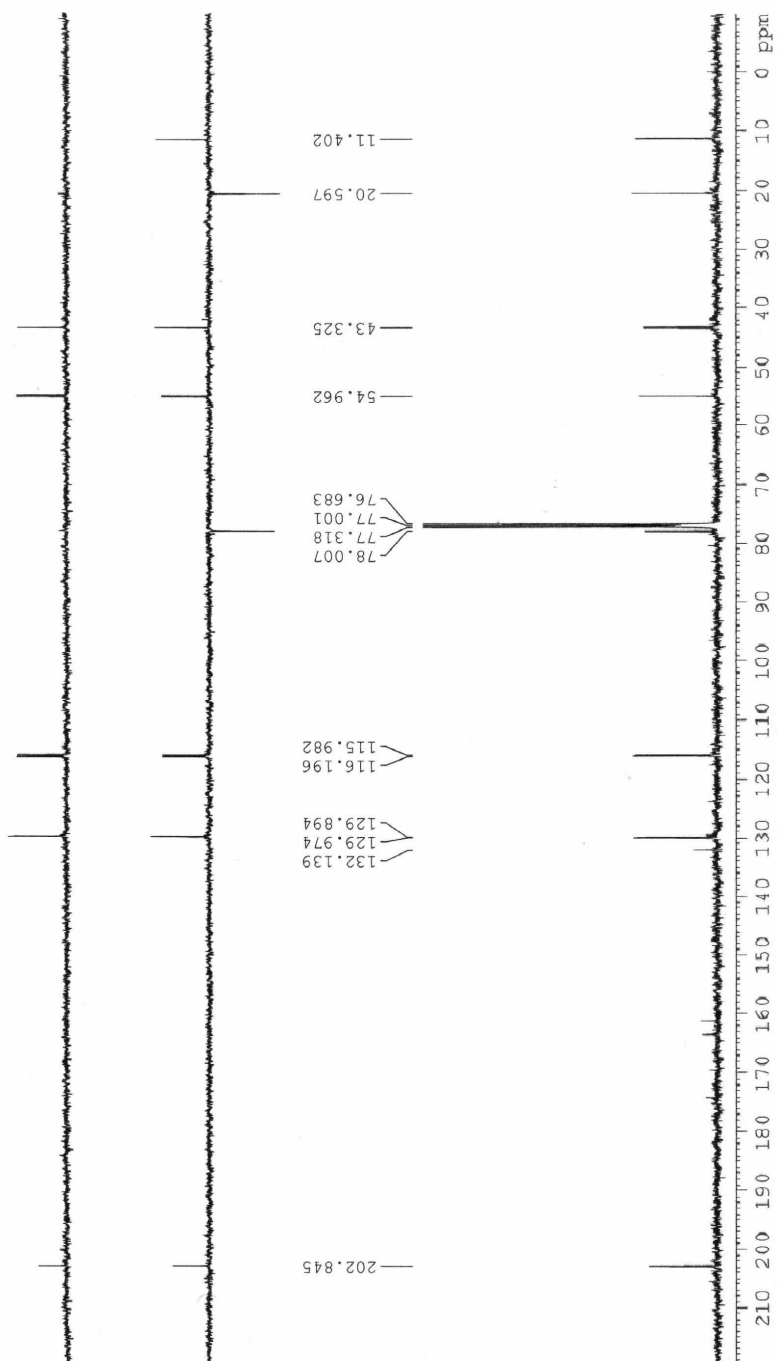
^{13}C -NMR

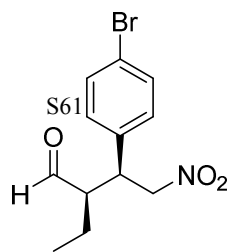


YUNNAN UNIVERSITY AYIII-400
wangyongchao E68 in CDCl3
591

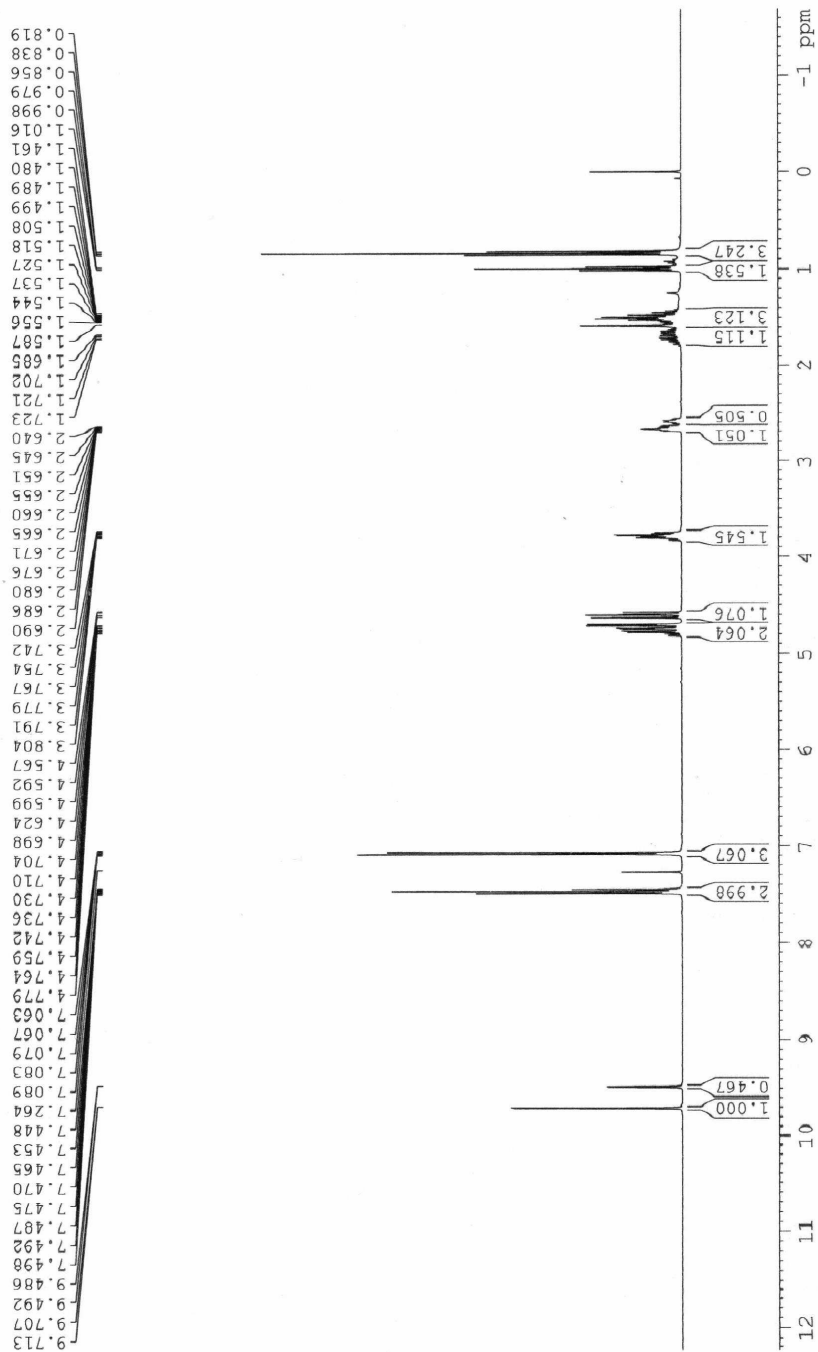


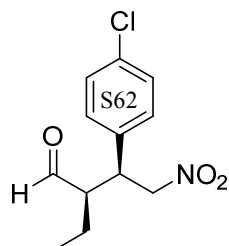
YUNNAN UNIVERSITY AVIII-400
 wangyongchao F68 in CDCl3
 591



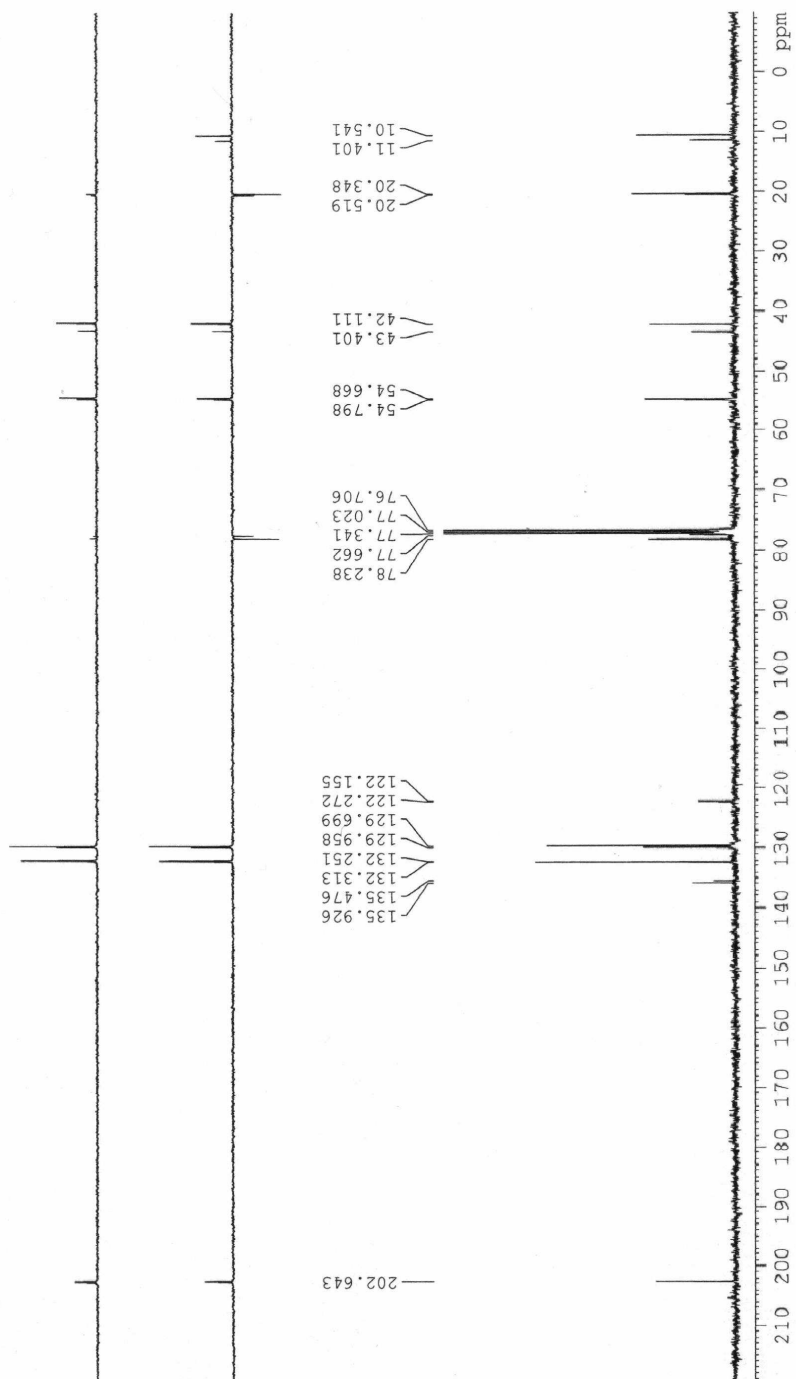


YUNNAN UNIVERSITY AVIII-400
wangyongchao F64 in CDCl3



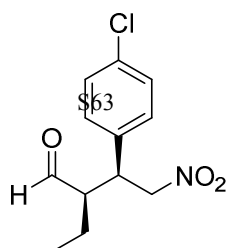
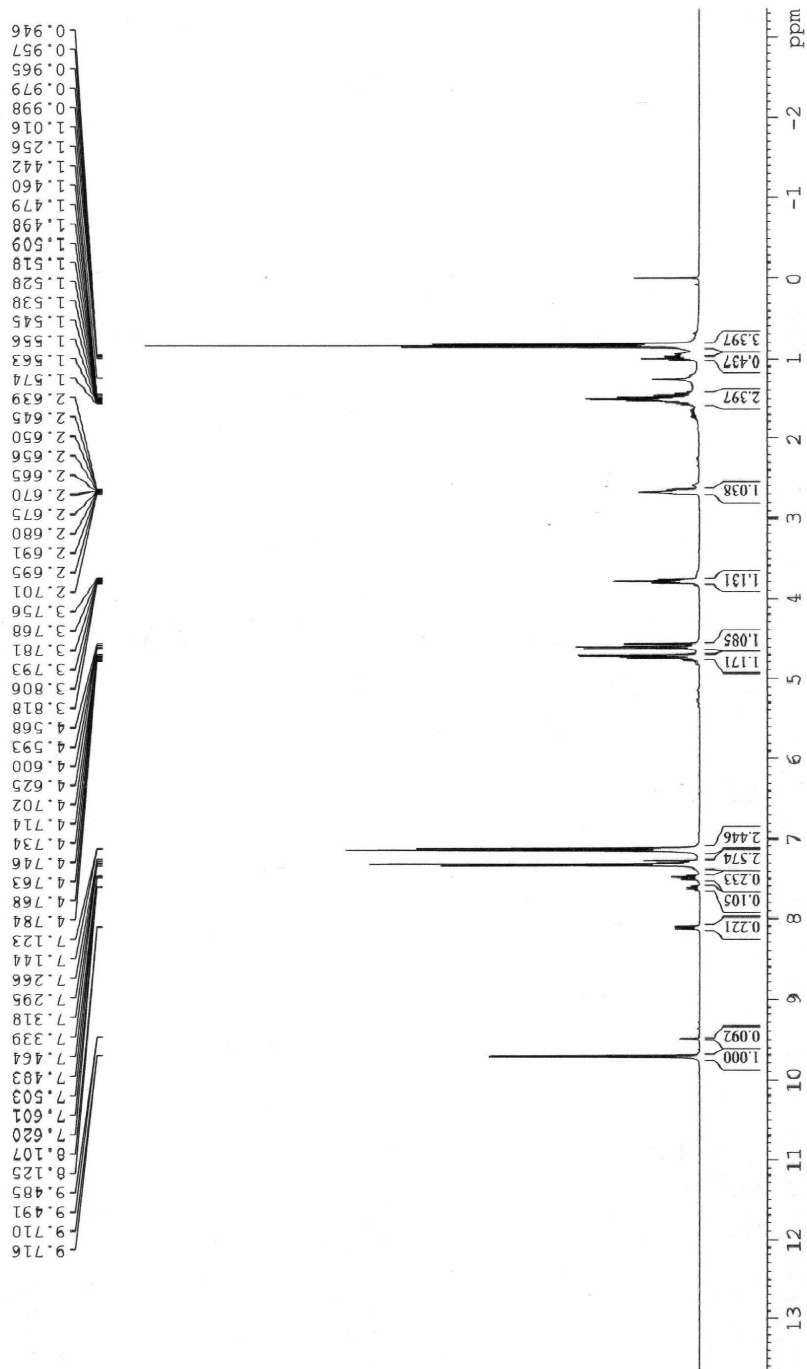


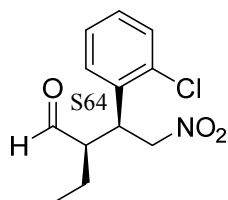
YUNNAN UNIVERSITY AVIII-400
wangyongchao F64 in CDCl₃
575



YUNNAN UNIVERSITY AVIII-400
wangyongchao F65-3 in CDCl3

27

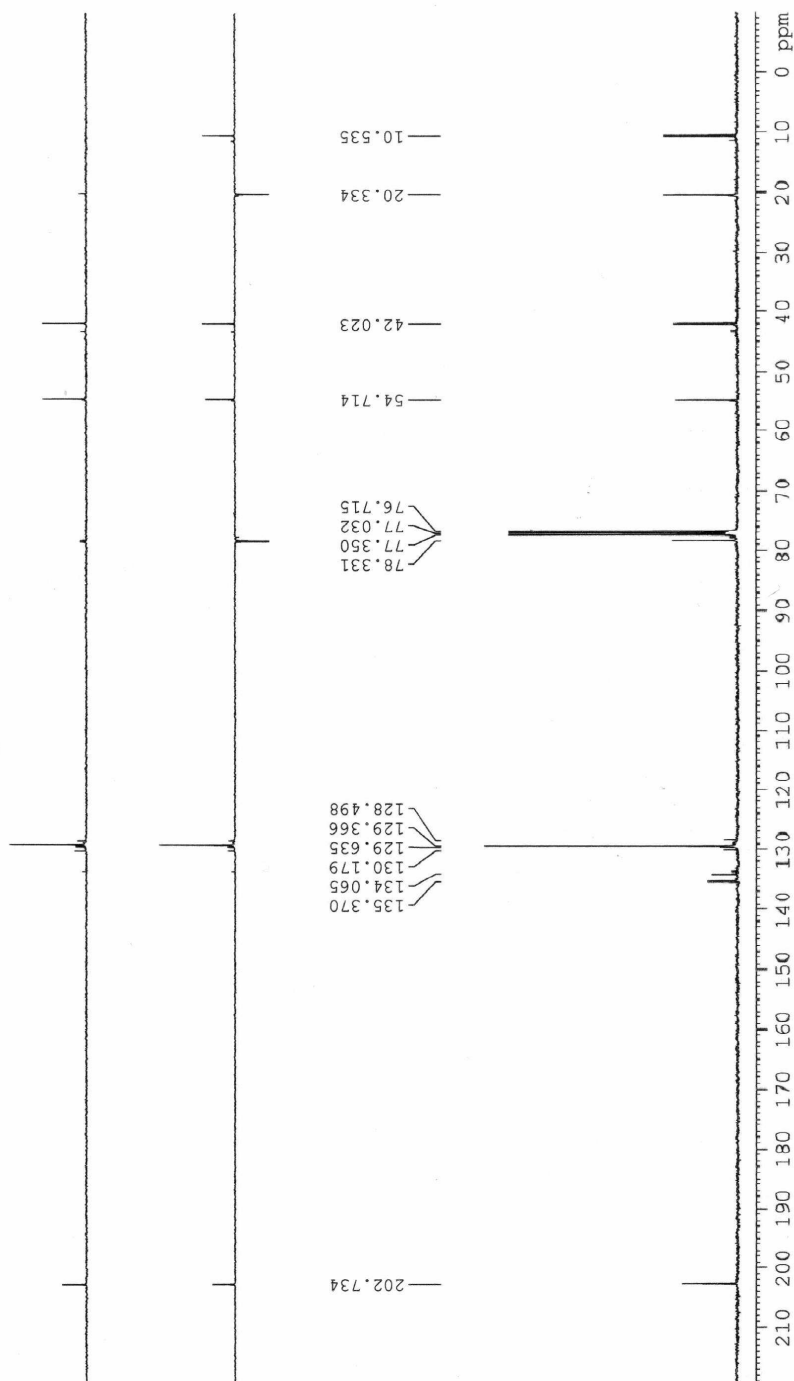




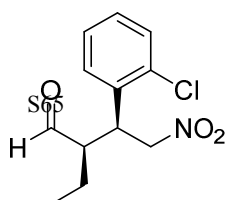
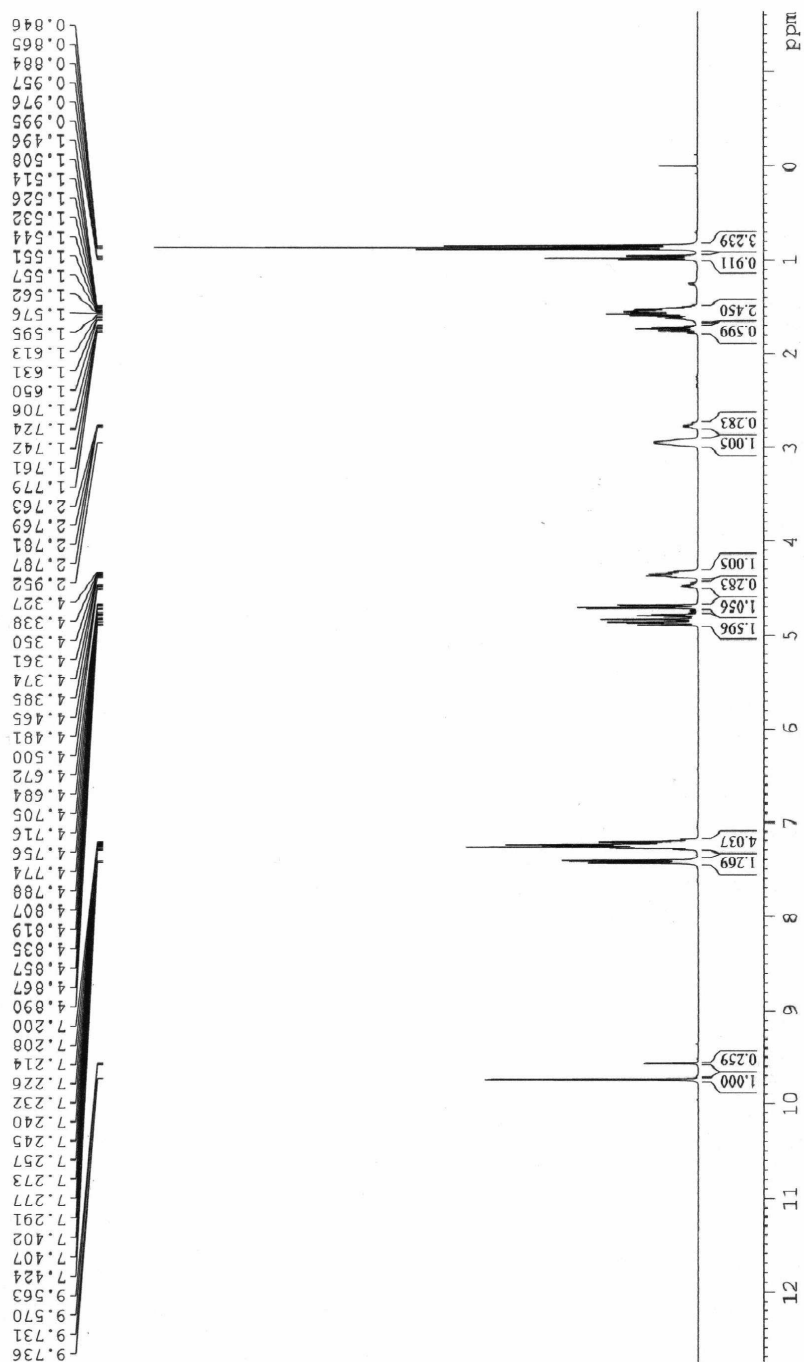
14i

YUNNAN UNIVERSITY AVIIL-400
wangyongchao E65-3 in CDCl₃

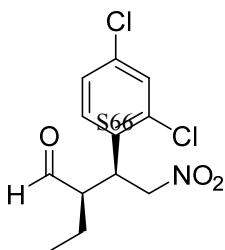
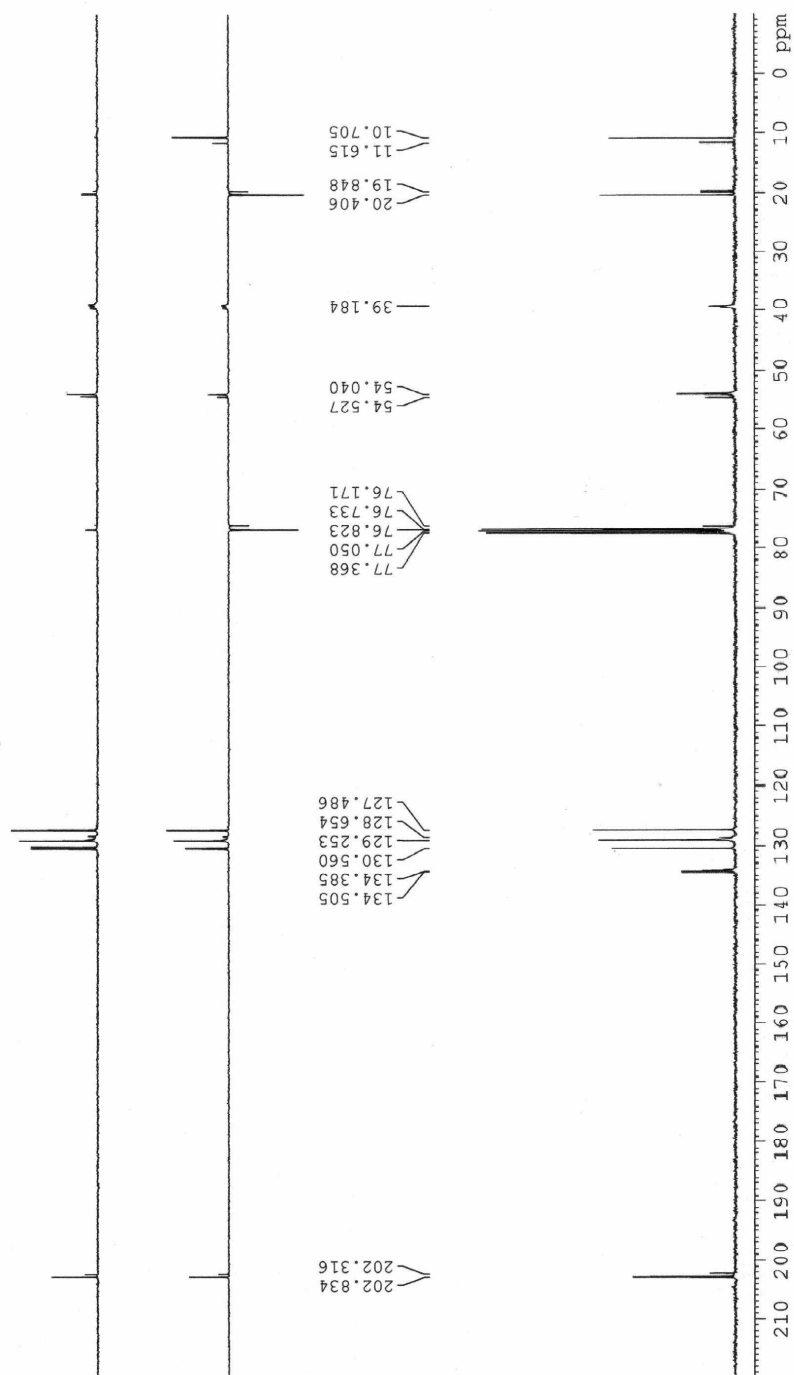
27

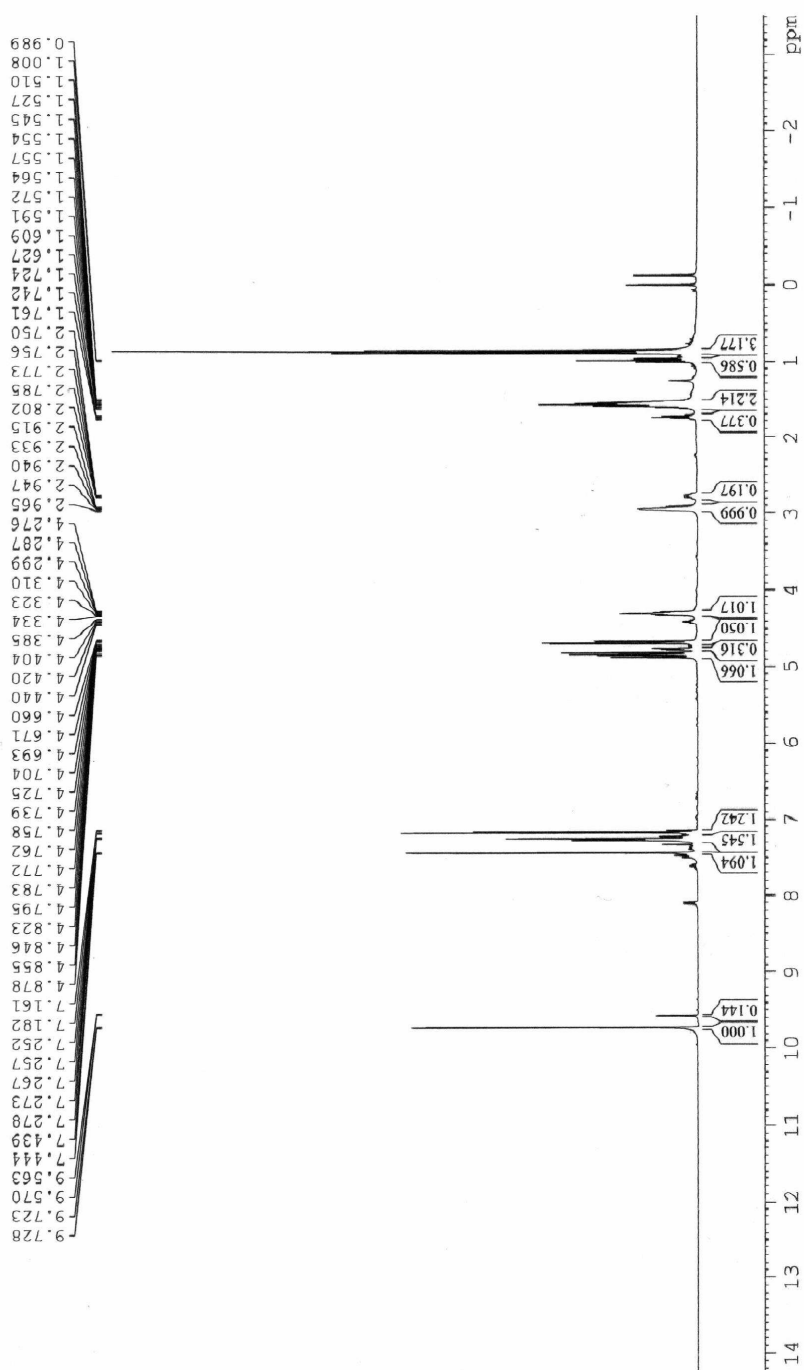
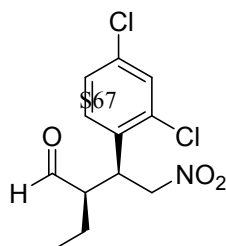


YUNNAN UNIVERSITY AVLIJ-400
wangyongchao F66-3 in CDCl₃
31

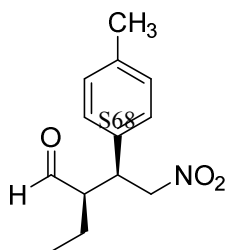


YUNNAN UNIVERSITY AVIII-400
wangyongchao F66-3 in CDCl₃
31

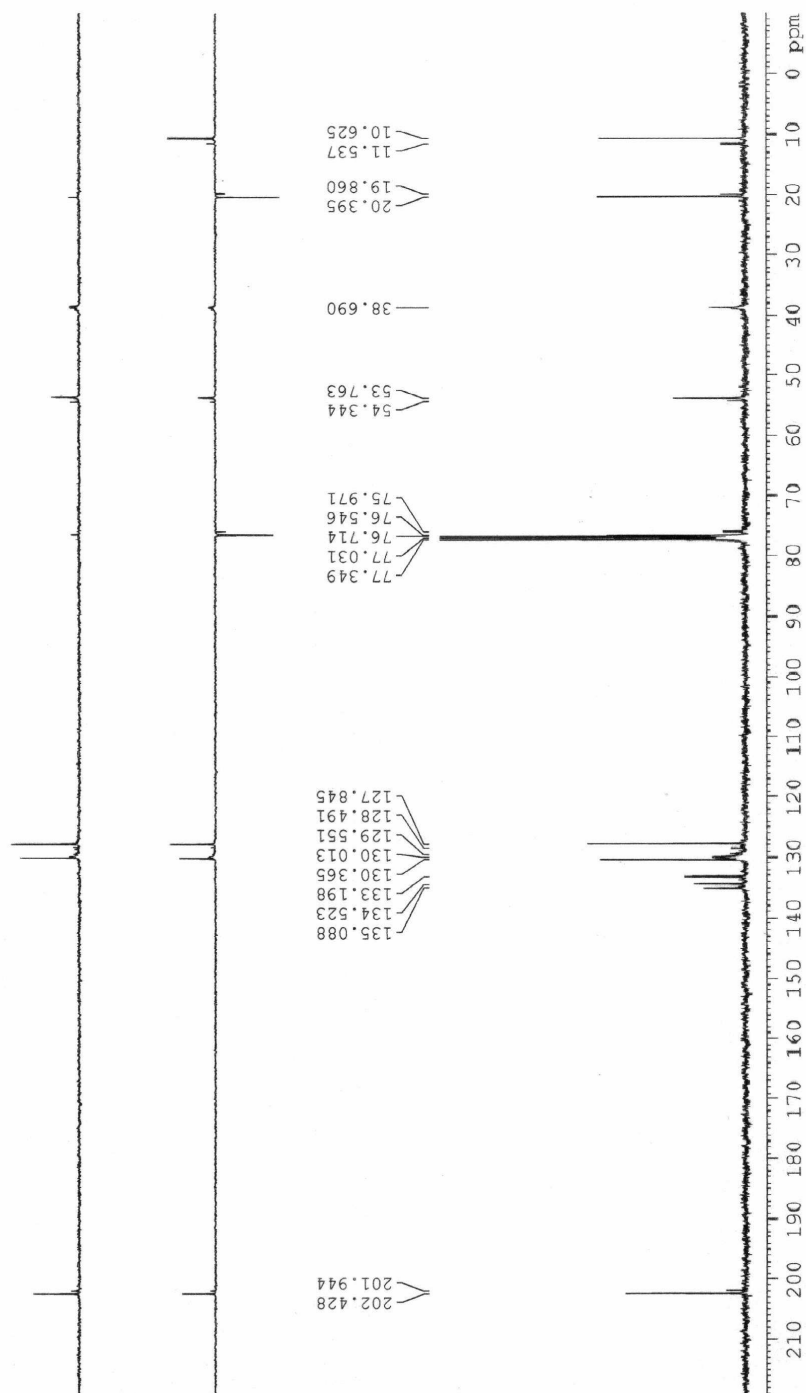




YUNNAN UNIVERSITY AVIII-400
wangyongchao F71-3 in CDCl3
67

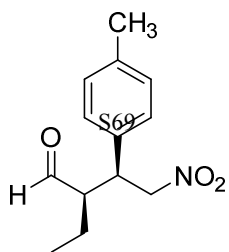
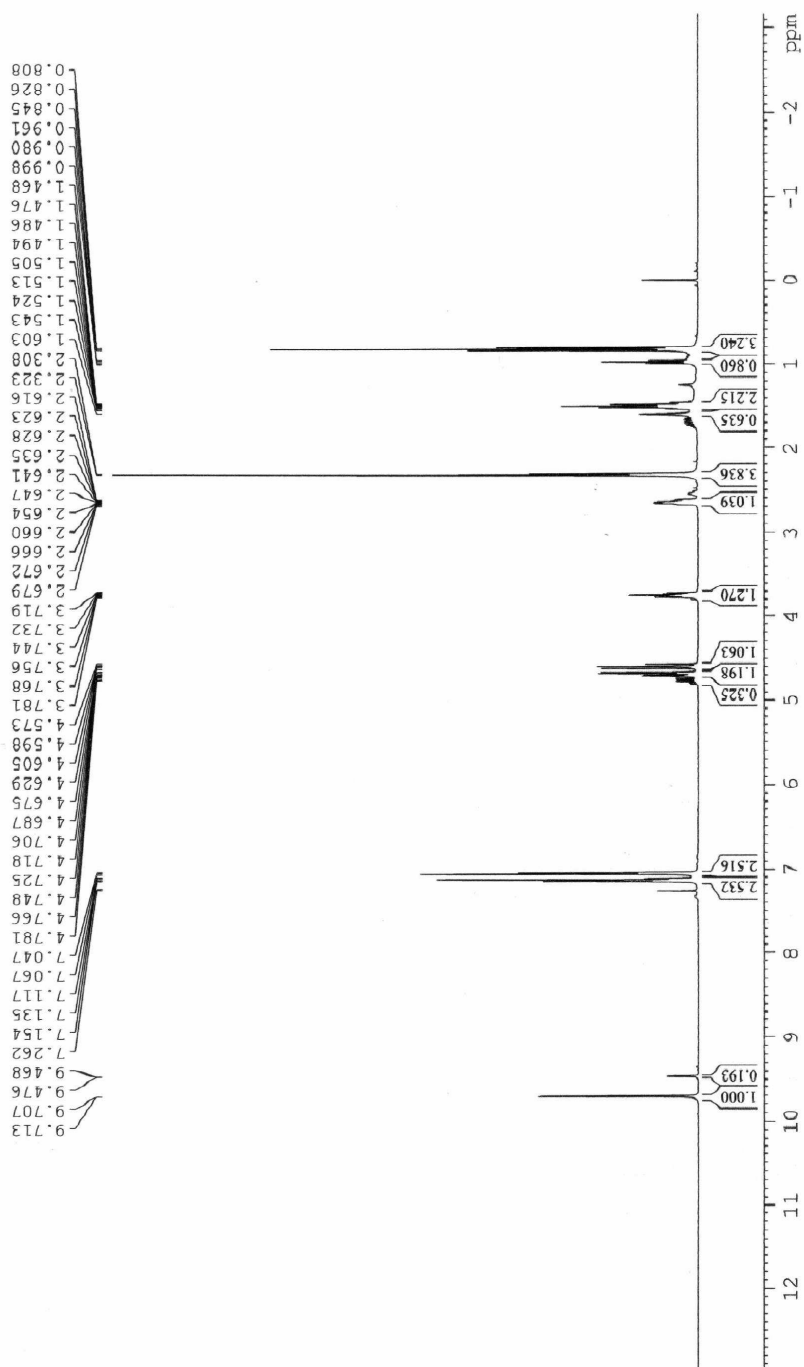


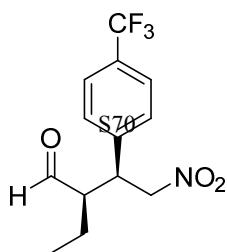
YUNNAN UNIVERSITY AVIII-400
wangyongchao F71-3 in CDCl₃
67



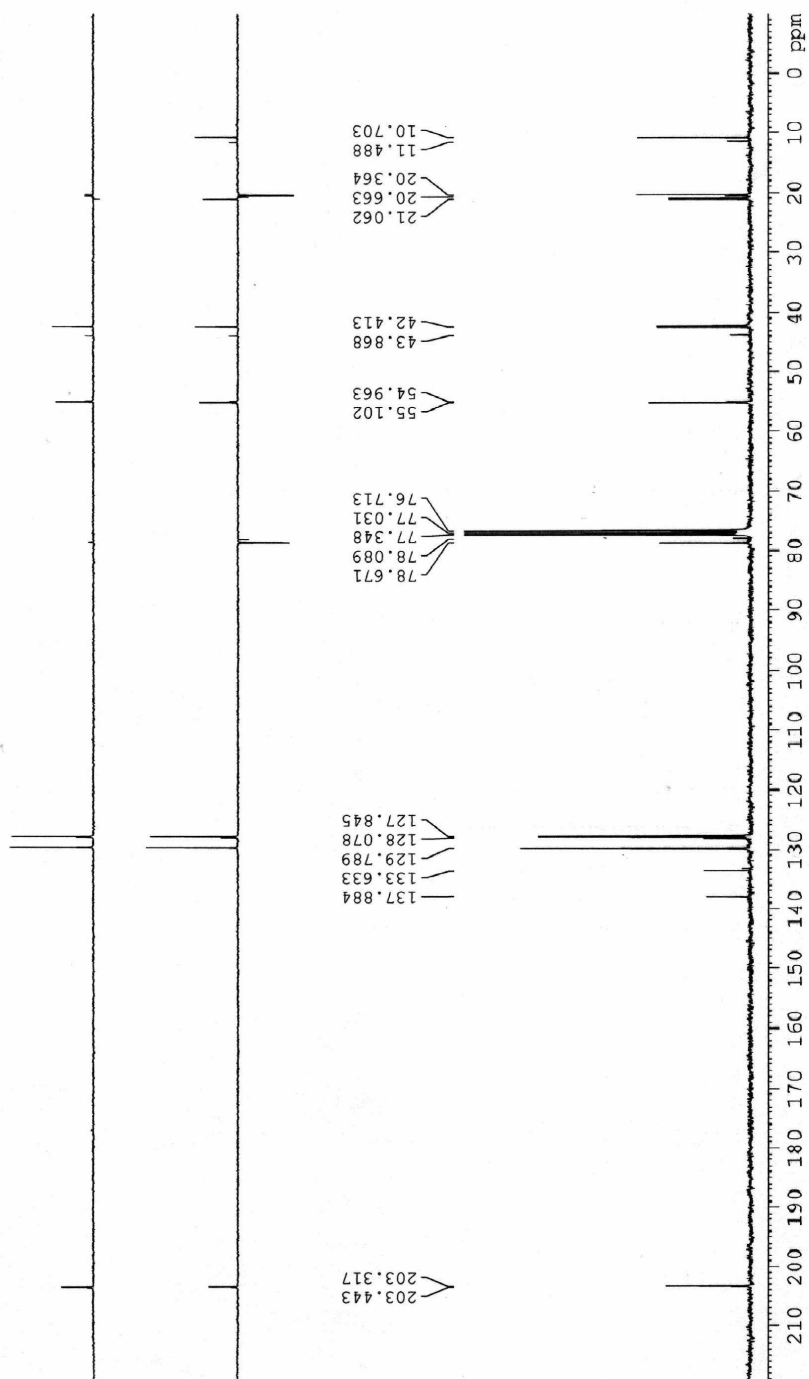
YUNNAN UNIVERSITY AVIII-400
wangyongchao F74-2 in CDCl3

8



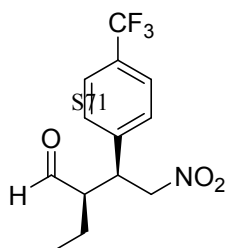
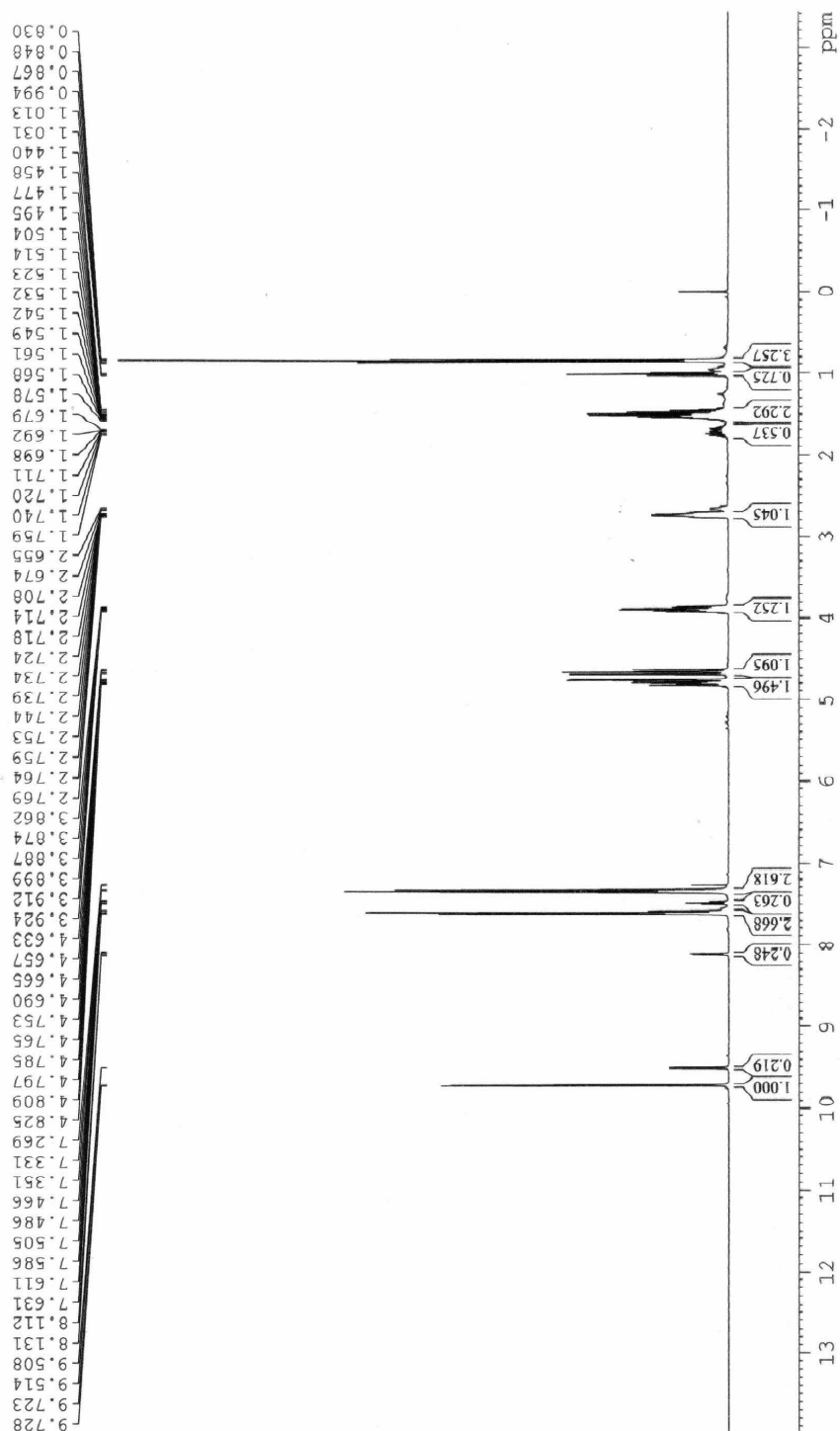


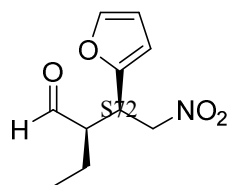
YUNNAN UNIVERSITY AVIII-400
wangyongchao F74-2 in CDCl₃



YUNNAN UNIVERSITY AVIII-400
wangyongchao F72-3 in CDCl₃

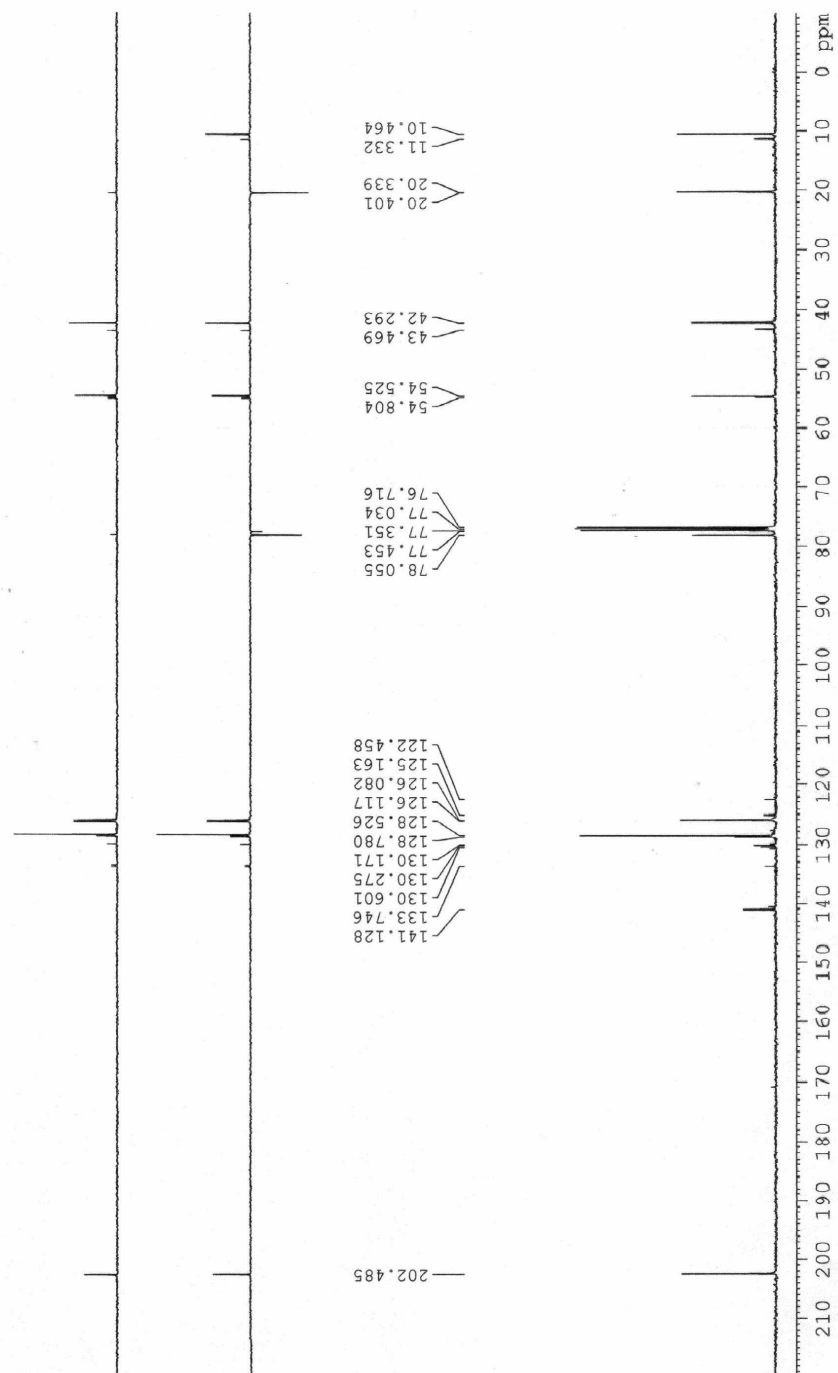
71



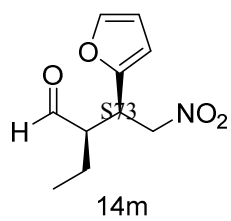
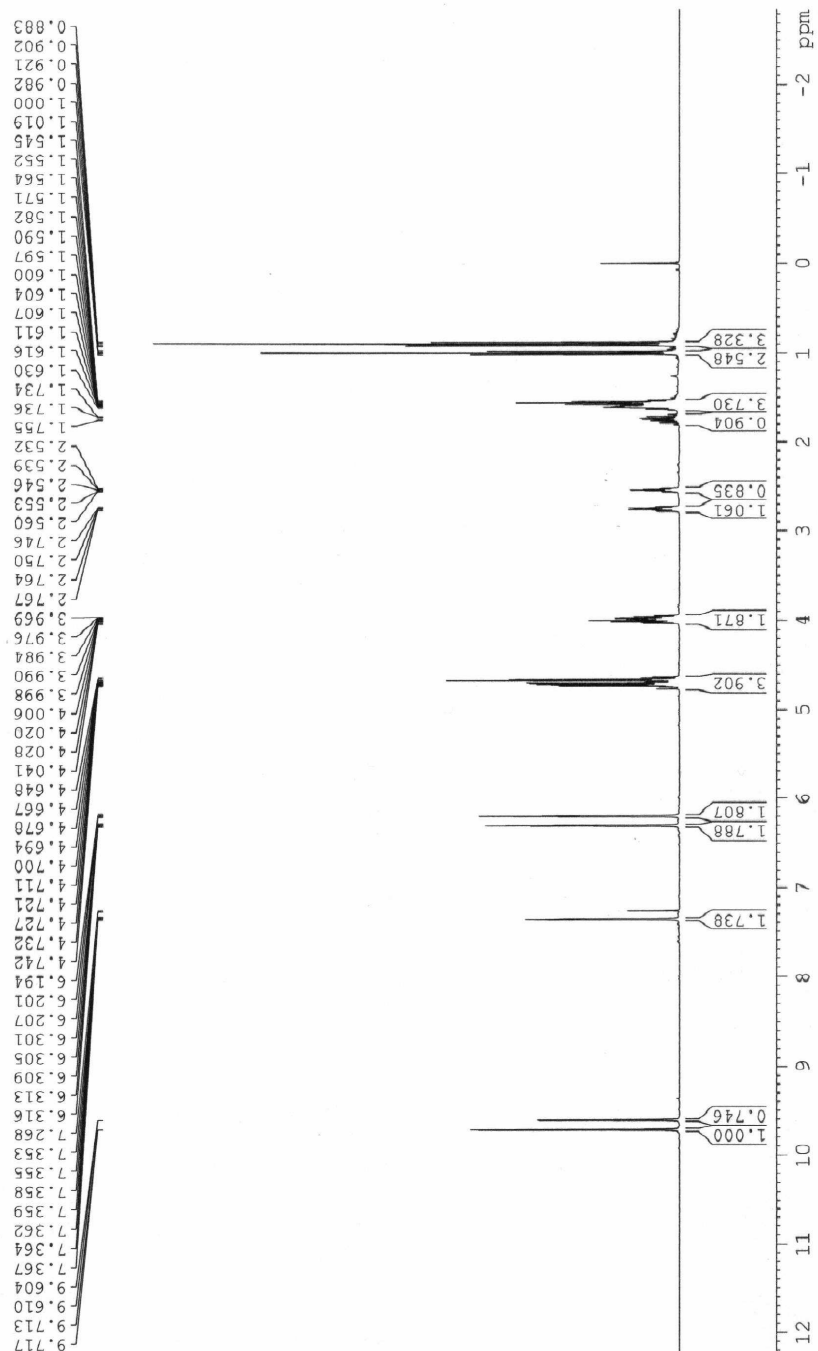


14m
1H-NMR

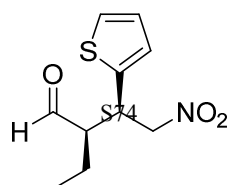
YUNNAN UNIVERSITY AVIII-400
wangyongchao F72-3 in CDCl₃
71



YUNNAN UNIVERSITY AVIII-400
wangyongchao F70 in CDCl3
599



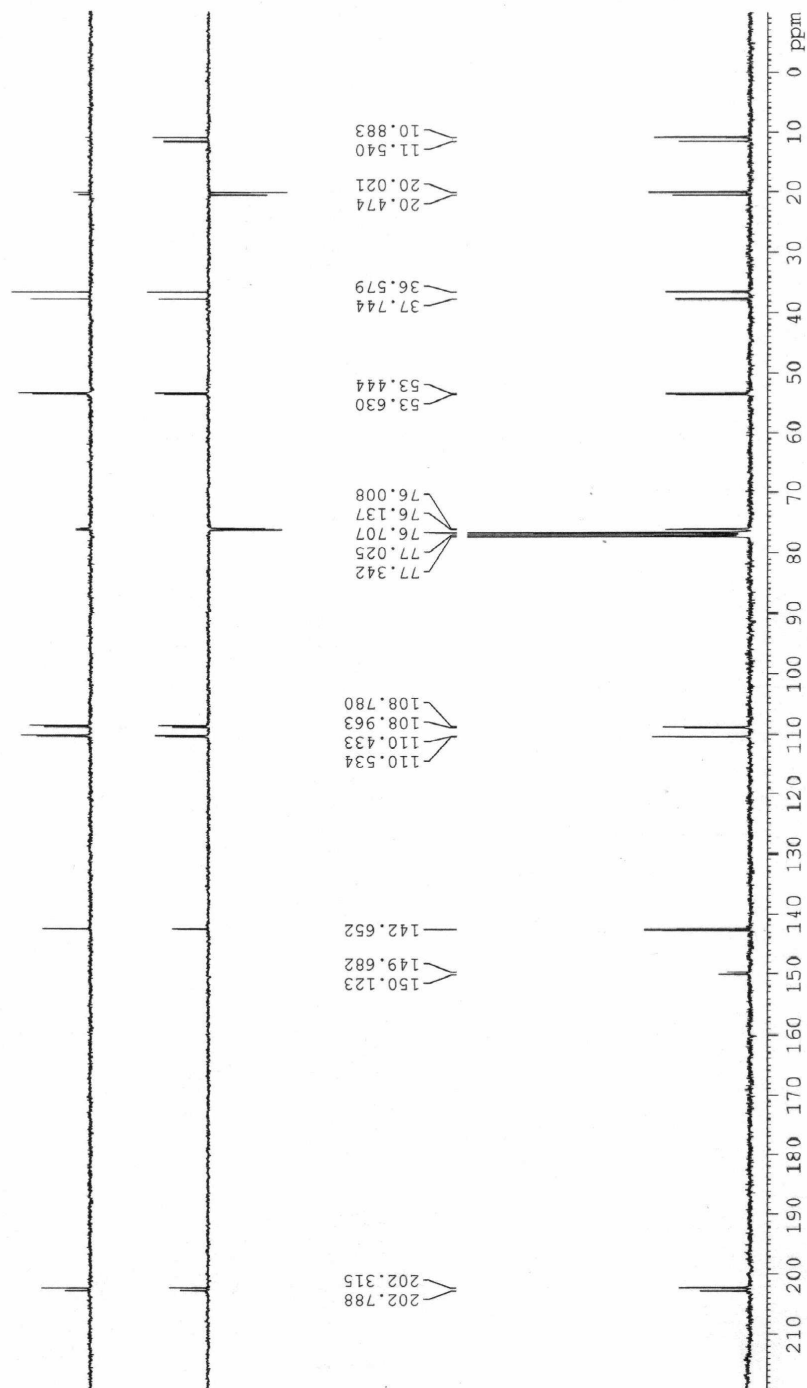
¹³C-NMR



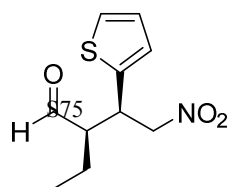
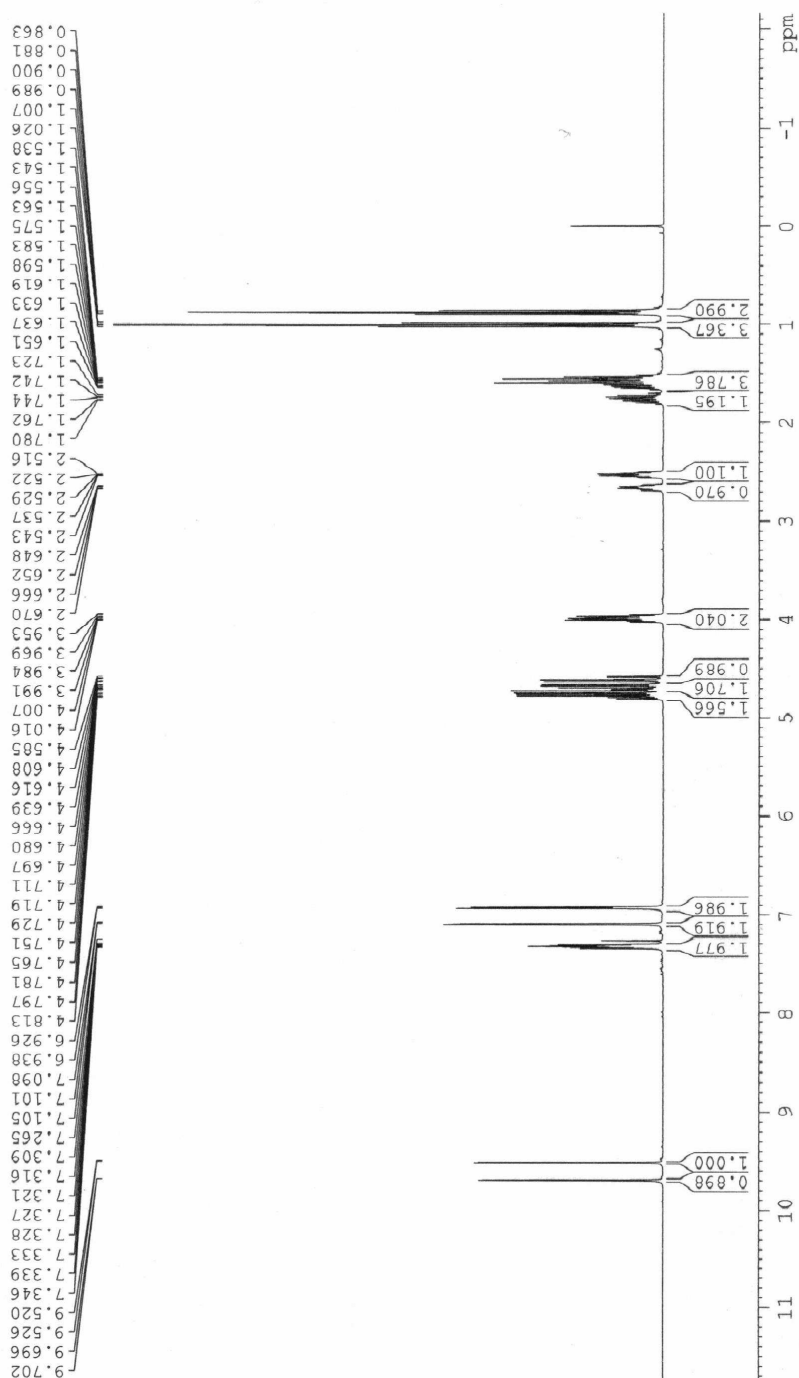
14n

¹H-NMR

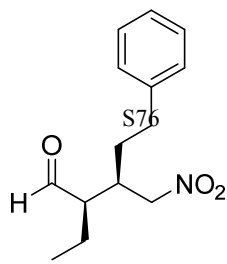
YUNNAN UNIVERSITY AVIII-400
wangyongchao F70 in CDCl₃
599



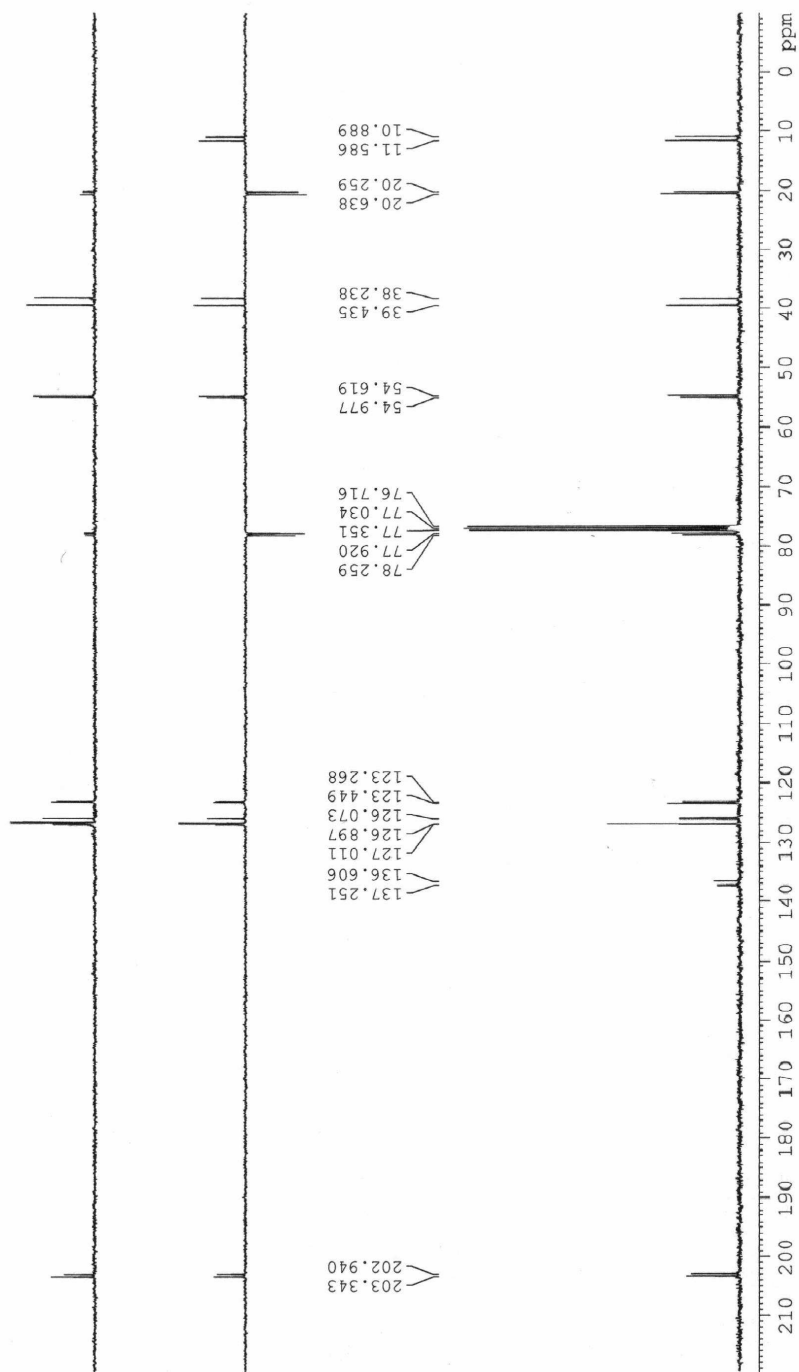
YUNNAN UNIVERSITY AVIII-400
wangyongchao F69 in CDCl3
595

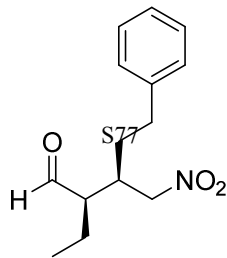


14n
13C-NMR

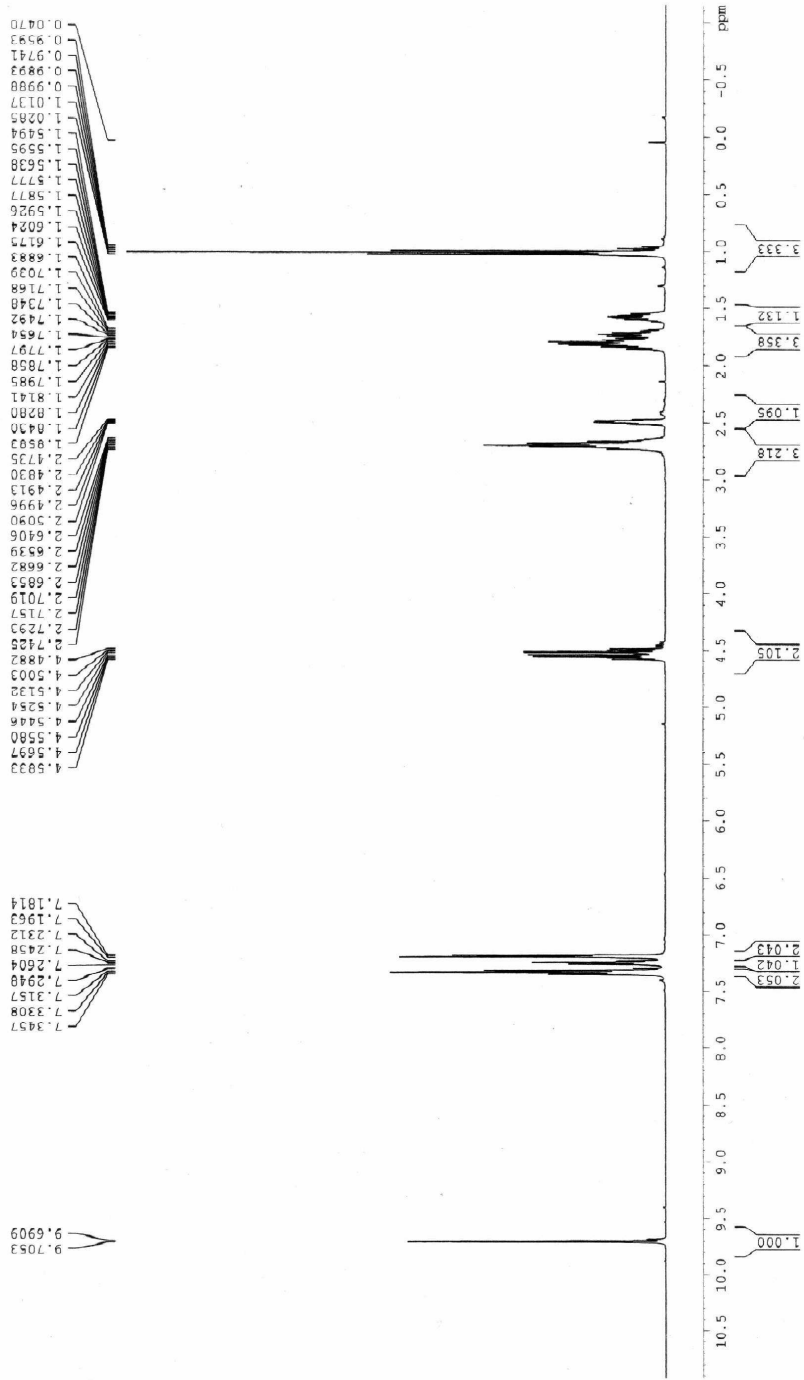


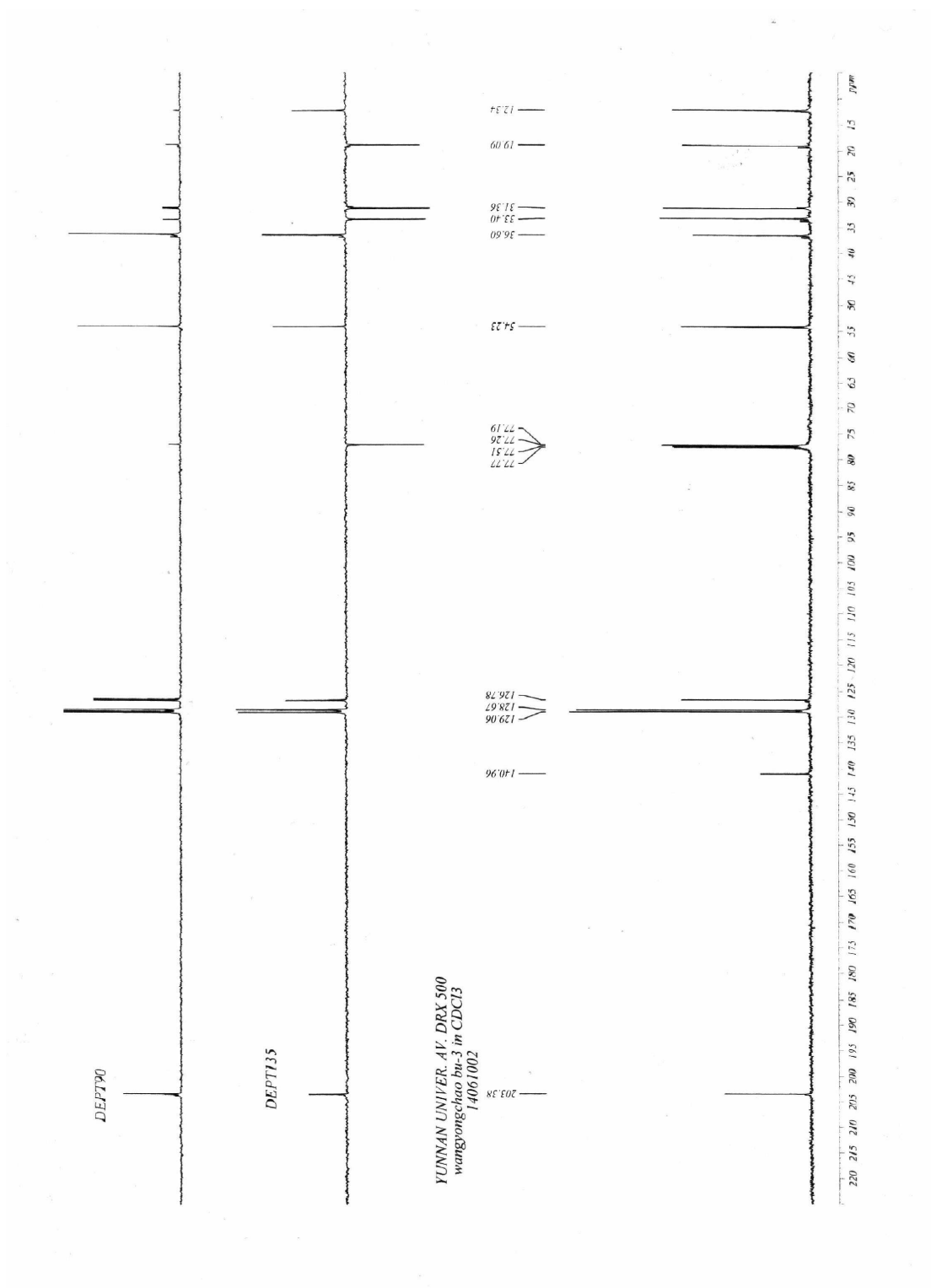
YUNNAN UNIVERSITY AVIII-400
 wangyongchao E69 in CDCl₃
 595





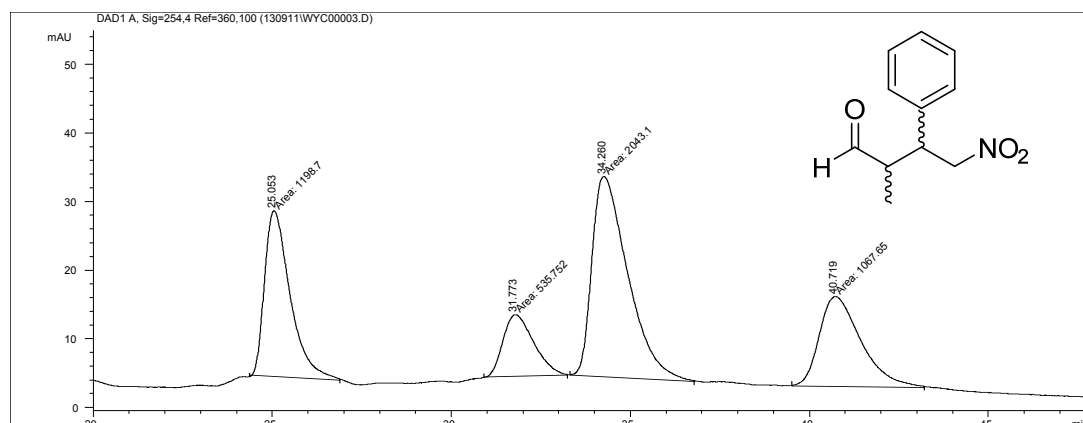
YUNNAN UNIVERSITY AV. DRX 500
wangyongchao bu-3 In CDCl₃
14061002





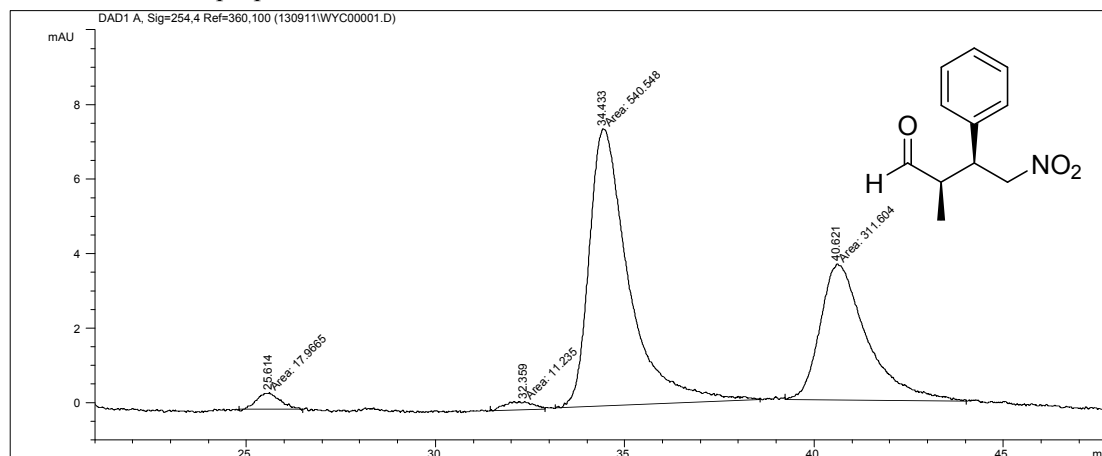
Spectra of chiralHPLC

14a: OD-H n-hexane:2-propanol=90:10 1.0 mL/min



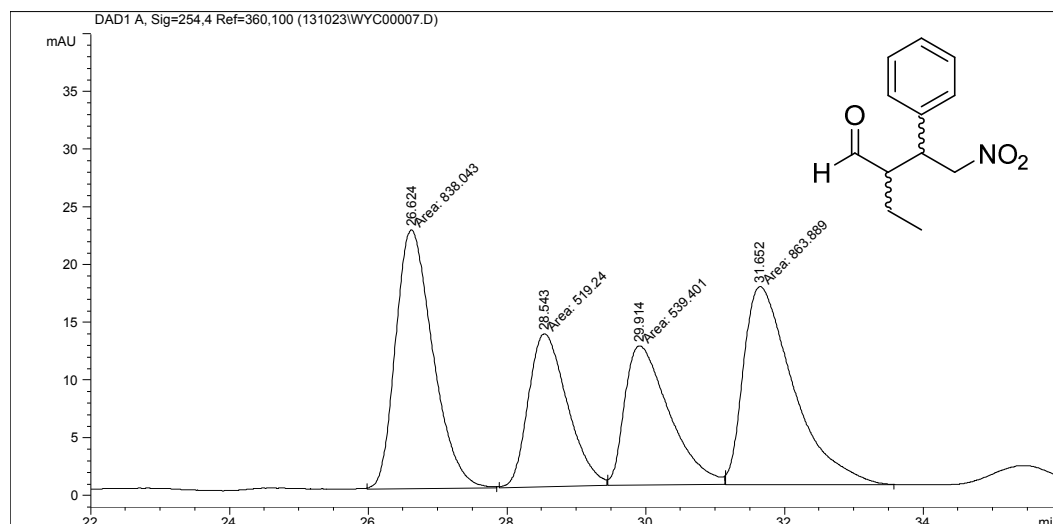
Peak	RetTime	Type	Width	Area	Height	Area
1	25.053	MM	0.8266	1198.7042	24.17069	24.7400
2	31.773	MM	0.9982	535.75201	8.94521	11.0574
3	34.260	MM	1.1657	2043.09766	29.21243	42.1674
4	40.719	MM	1.3525	1067.65210	13.15644	22.0352

OD-H n-hexane:2-propanol=90:10 1.0 mL/min ee=94%



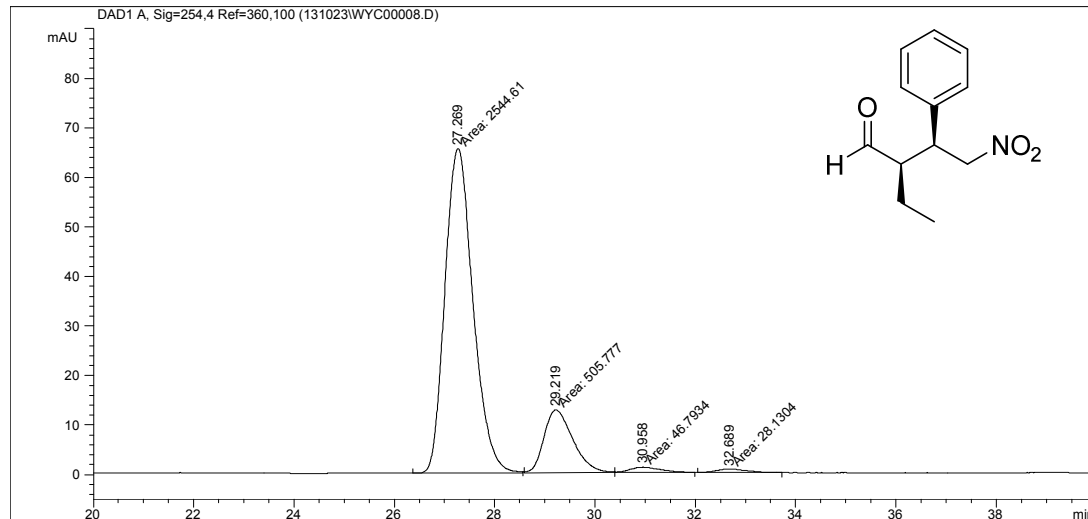
Peak	RetTime	Type	Width	Area	Height	Area
1	25.614	MM	0.6916	17.96647	4.32994	2.0385
2	32.359	MM	0.8468	11.23500	2.21128	1.2747
3	34.433	MM	1.2118	540.54779	7.43431	61.3315
4	40.621	MM	1.4245	311.60434	3.64568	35.3552

14b: AD-H n-hexane:2-propanol=99:1 0.8 mL/min



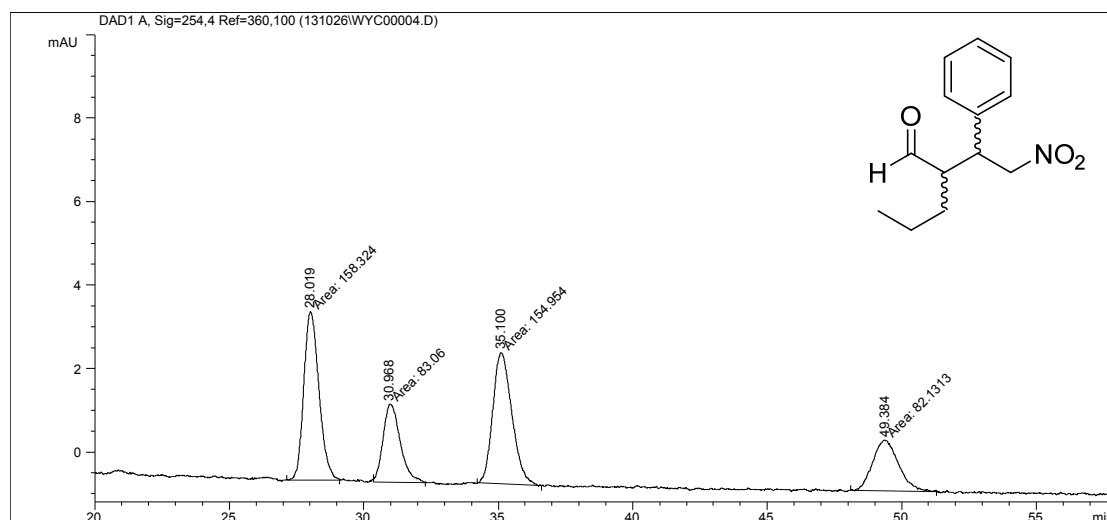
Peak	RetTime	Type	Width	Area	Height	Area
1	26.624	MM	0.6226	838.04266	22.43385	30.3576
2	28.543	MM	0.6525	519.24017	13.26336	18.8091
3	29.914	MM	0.7455	539.40118	12.05854	19.5395
4	31.652	MM	0.8387	863.88879	17.16640	31.2938

AD-H n-hexane:2-propanol=99:1 0.8 mL/min ee=98%

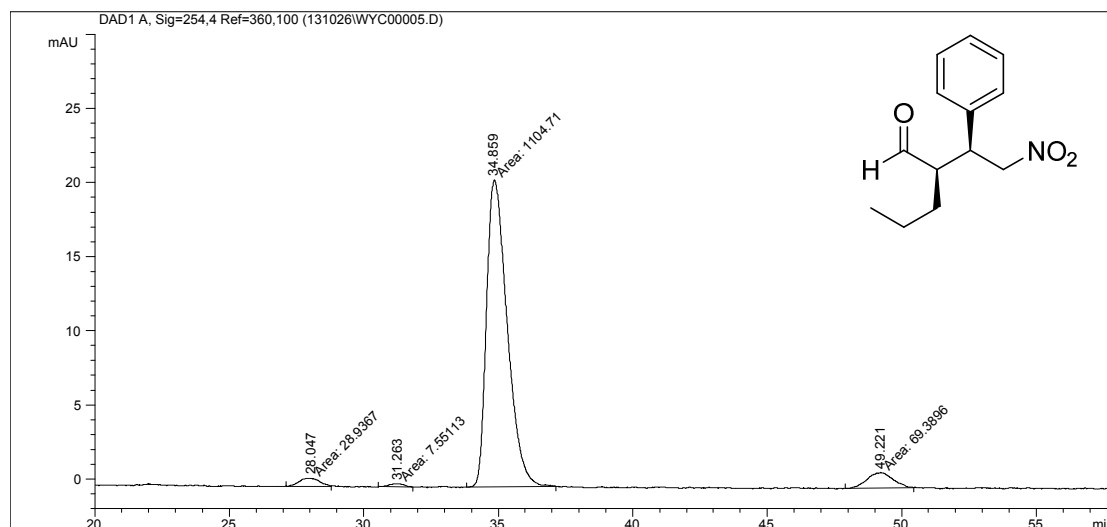


Peak	RetTime	Type	Width	Area	Height	Area
1	27.269	MM	0.6473	2544.60693	65.51886	81.4194
2	29.219	MM	0.6657	505.77750	12.66341	16.1833
3	30.958	MM	0.7146	46.79339	1.09133	1.4972
4	32.689	MM	0.7087	28.13035	6.61547e-1	0.9001

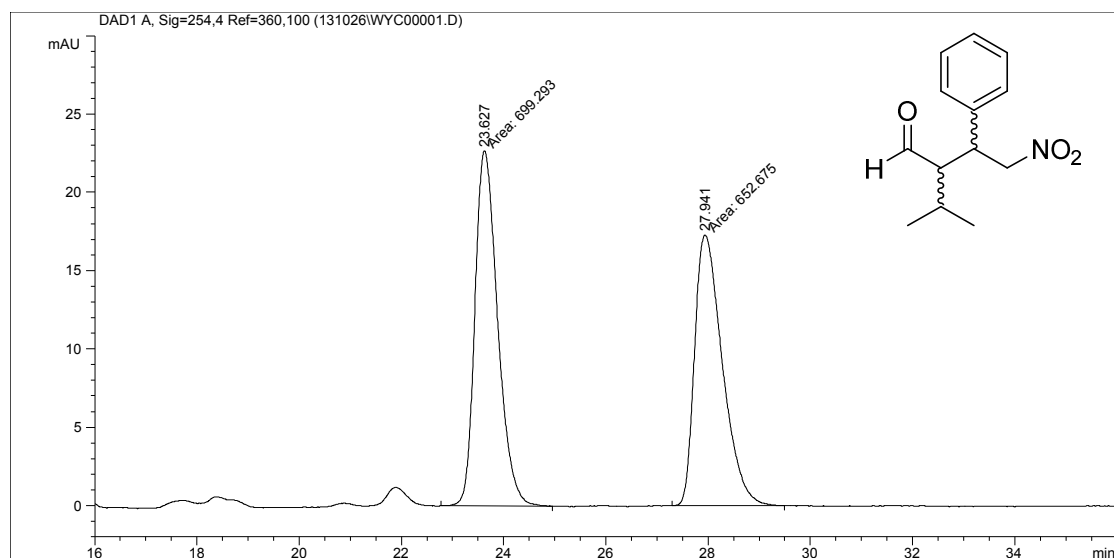
14c: OD-H n-hexane:2-propanol=96:4 1.0 mL/min



OD-H n-hexane:2-propanol=96:4 1.0 mL/min ee=95%

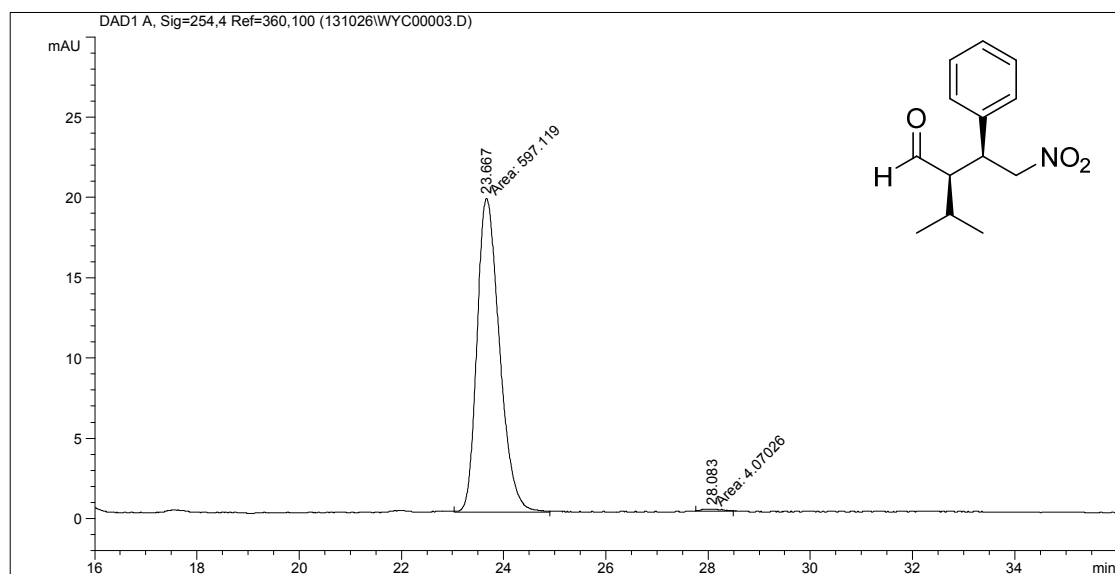


14d: AD-H n-hexane:2-propanol=97:3 0.5 mL/min



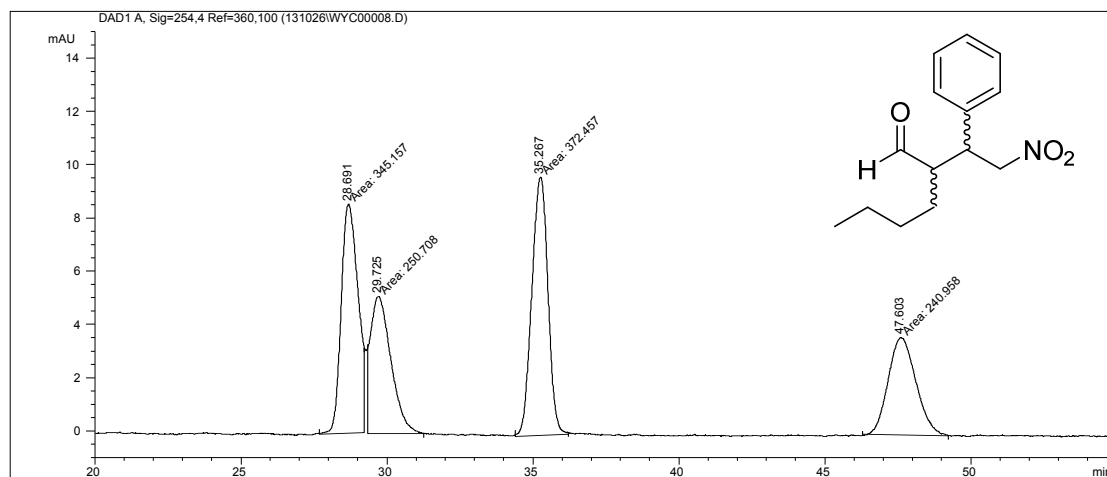
Peak	RetTime	Type	Width	Area	Height	Area
1	23.627	MM	0.5143	699.29346	22.66385	51.7241
2	27.941	MM	0.6288	652.67542	17.30001	48.2759

AD-H n-hexane:2-propanol=97:3 0.5 mL/min ee=99%



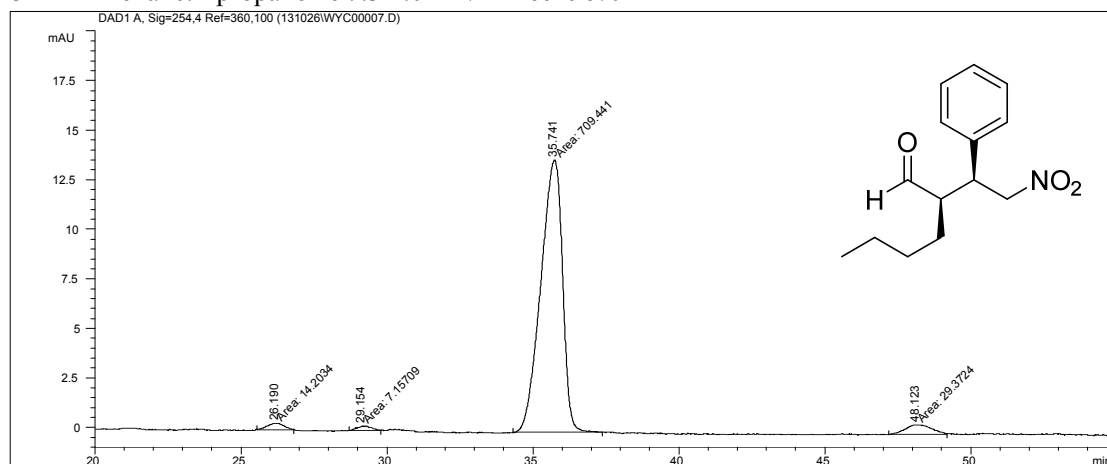
Peak	RetTime	Type	Width	Area	Height	Area
1	23.667	MM	0.5094	597.11914	19.53519	99.3230
2	28.083	MM	0.4521	4.07026	1.50051e-1	0.6770

14e: OD-H n-hexane:2-propanol=97:3 1.0 mL/min



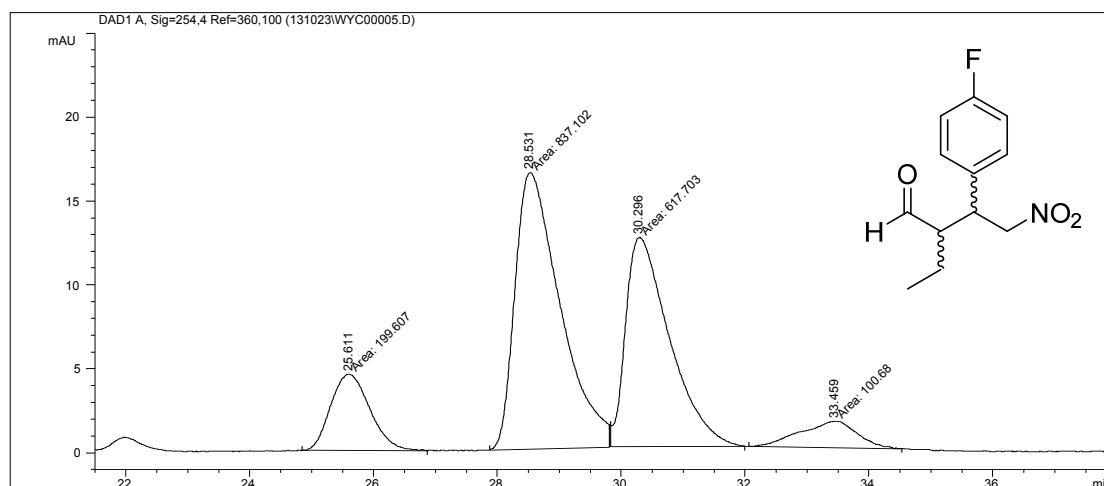
Peak	RetTime	Type	Width	Area	Height	Area
1	28.691	MM	0.6689	345.15674	8.60073	28.5424
2	29.725	MM	0.8116	250.70798	5.14862	20.7320
3	35.267	MM	0.6397	372.45657	9.70463	30.7999
4	47.603	MM	1.0966	240.95757	3.66232	19.9257

OD-H n-hexane:2-propanol=97:3 1.0 mL/min ee=96%

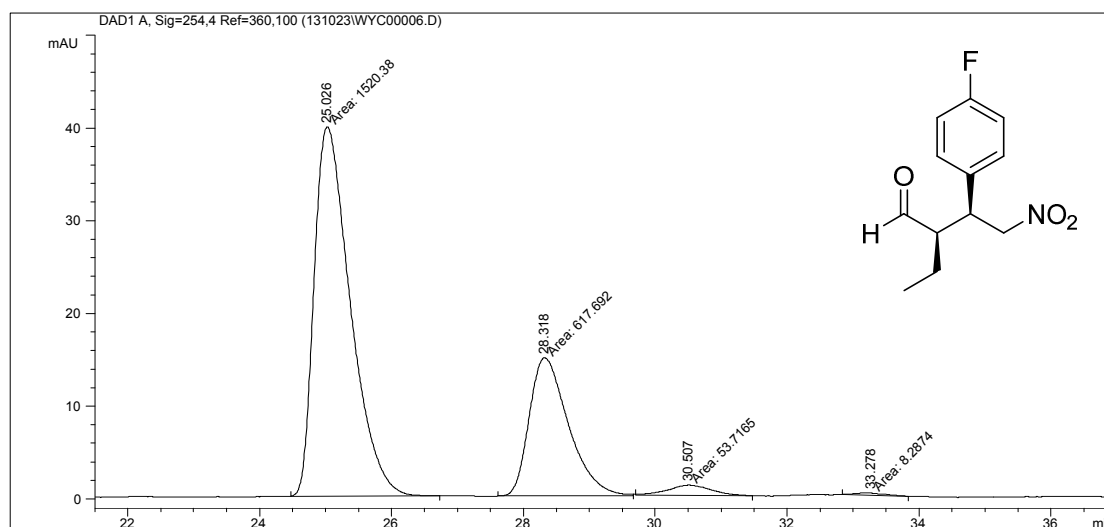


Peak	RetTime	Type	Width	Area	Height	Area
1	26.190	MM	0.6851	14.20342	3.45522	1.8684
2	29.154	MM	0.5448	7.15709	2.18970	0.9415
3	35.741	MM	0.8598	709.44061	13.75233	93.3261
4	48.123	MM	1.0290	29.37243	4.75746	3.8639

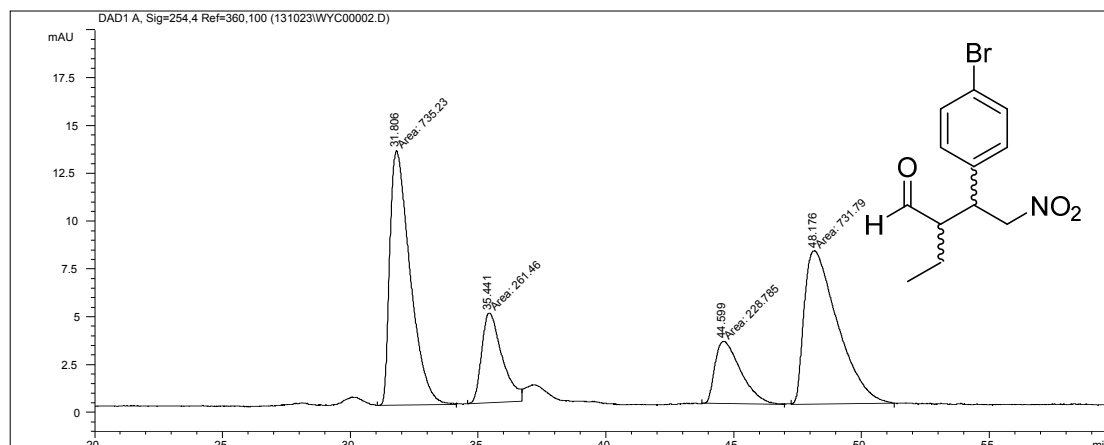
14f: AD-H n-hexane:2-propanol=99:1 1.0 mL/min



AD-H n-hexane:2-propanol=99:1 1.0 mL/min ee=99%

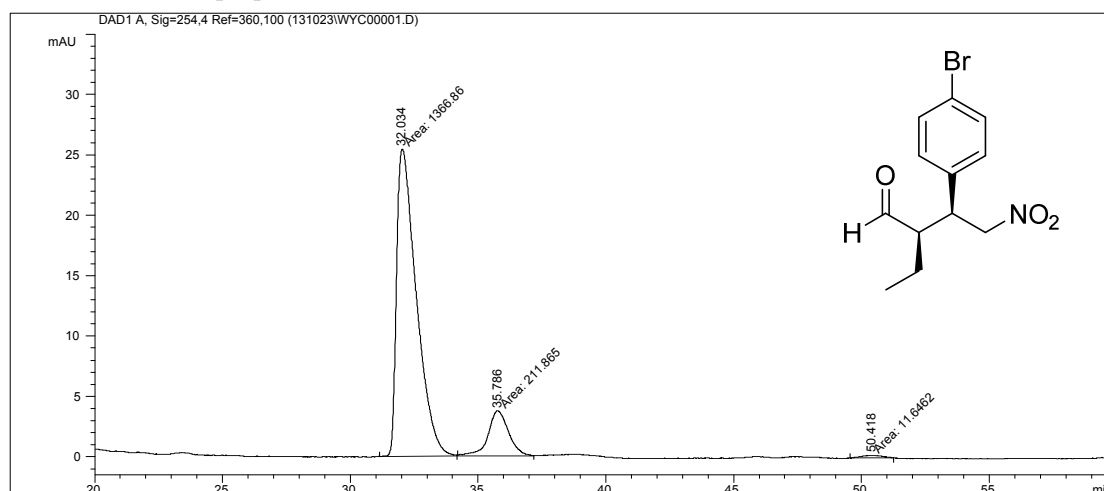


14g: AD-H n-hexane:2-propanol=98.5:1.5 1.0 mL/min



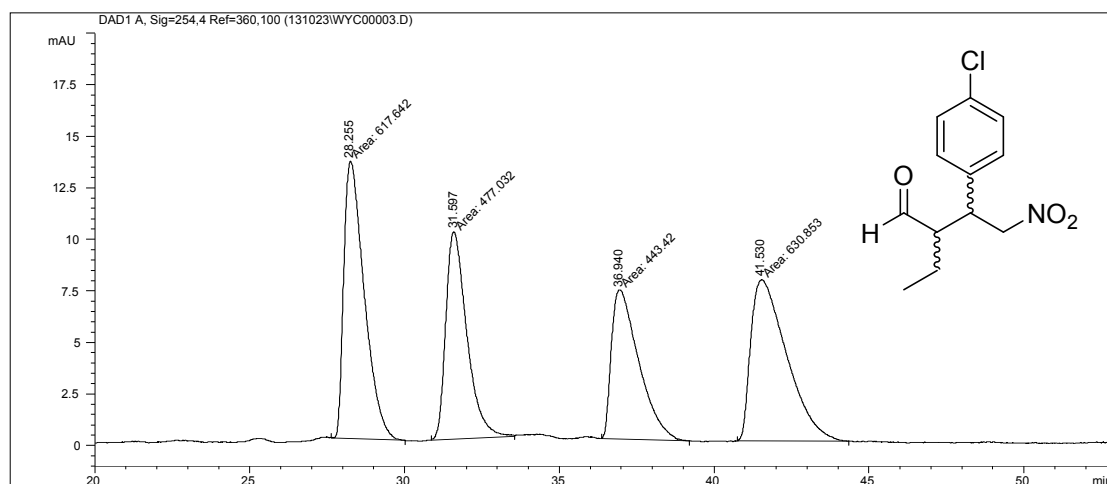
Peak	RetTime	Type	Width	Area	Height	Area
1	31.806	MM	0.9205	735.23010	13.31213	37.5642
2	35.441	MM	0.9287	261.46024	4.69229	13.3584
3	44.599	MM	1.1700	228.78531	3.25898	11.6890
4	48.176	MM	1.5213	731.78961	8.01691	37.3884

AD-H n-hexane:2-propanol=98.5:1.5 1.0 mL/min ee=98%



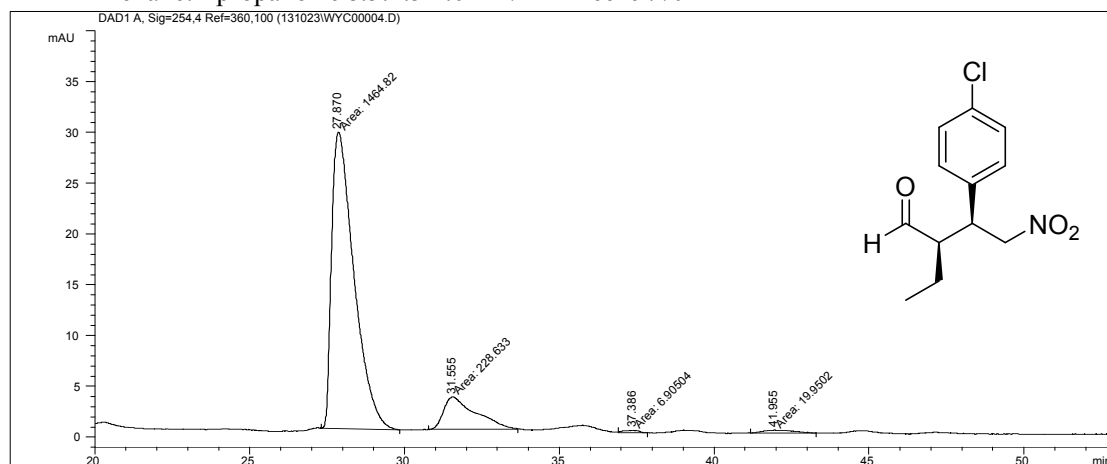
Peak	RetTime	Type	Width	Area	Height	Area
1	32.034	MM	0.8954	1366.86145	25.44221	85.9460
2	35.786	MM	0.9417	211.86499	3.74969	13.3217
3	50.418	MM	0.8921	11.64620	2.17569e-1	0.7323

14h: AD-H n-hexane:2-propanol=98.5:1.5 1.0 mL/min



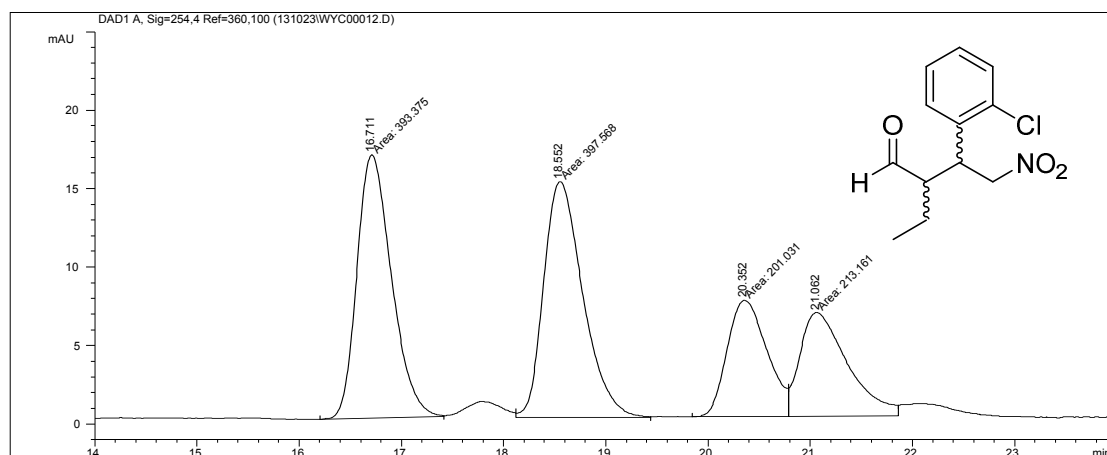
Peak	RetTime	Type	Width	Area	Height	Area
1	28.255	MM	0.7647	617.64178	13.46114	28.4766
2	31.597	MM	0.7902	477.03207	10.06172	21.9937
3	36.940	MM	1.0233	443.41980	7.22227	20.4440
4	41.530	MM	1.3439	630.85272	7.82346	29.0857

AD-H n-hexane:2-propanol=98.5:1.5 1.0 mL/min ee=97%



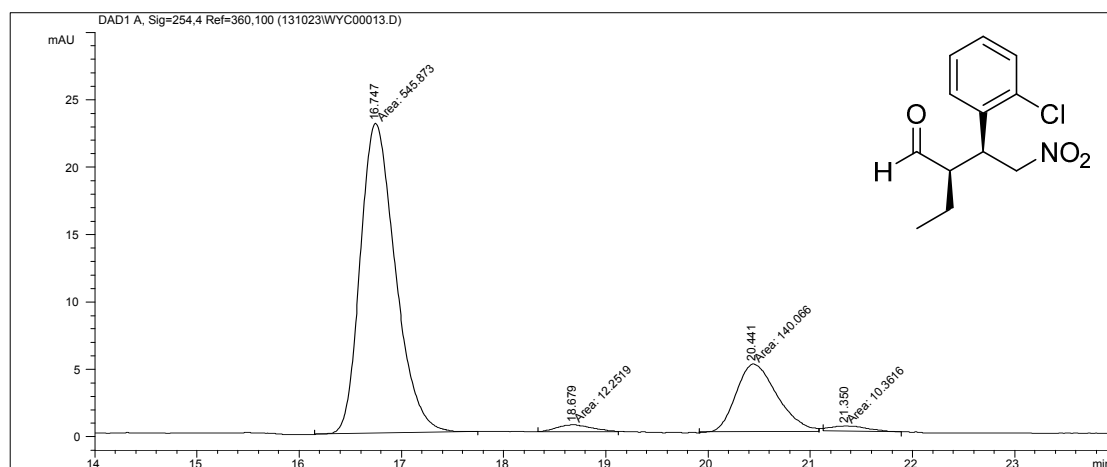
Peak	RetTime	Type	Width	Area	Height	Area
1	27.870	MM	0.8362	1464.81958	29.19622	85.1487
2	31.555	MM	1.1912	228.63293	3.19886	13.2902
3	37.386	MM	0.5867	6.90504	1.96170	0.4014
4	41.955	MM	1.1098	19.95020	2.99620	1.1597

14i: AD-H n-hexane:2-propanol=99:1 1.0 mL/min



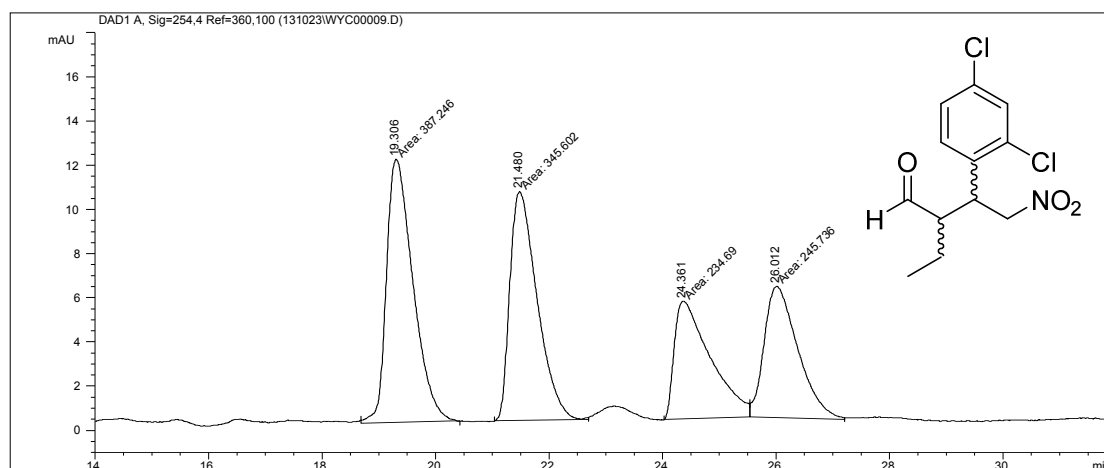
Peak	RetTime	Type	Width	Area	Height	Area
1	16.711	MM	0.3910	393.37469	16.76834	32.6416
2	18.552	MM	0.4415	397.56821	15.00797	32.9895
3	20.352	MM	0.4530	201.03058	7.39608	16.6812
4	21.062	MM	0.5374	213.16089	6.61054	17.6877

AD-H n-hexane:2-propanol=99:1 1.0 mL/min ee=96%

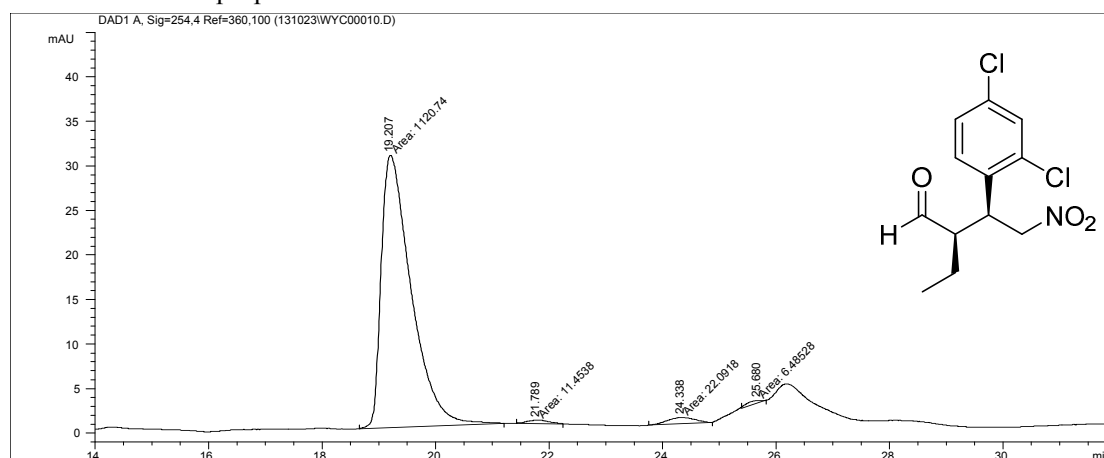


Peak	RetTime	Type	Width	Area	Height	Area
1	16.747	MM	0.3960	545.87335	22.97521	77.0406
2	18.679	MM	0.3943	12.25194	5.17894	1.7292
3	20.441	MM	0.4655	140.06561	5.01491	19.7679
4	21.350	MM	0.4213	10.36161	4.09883	1.4624

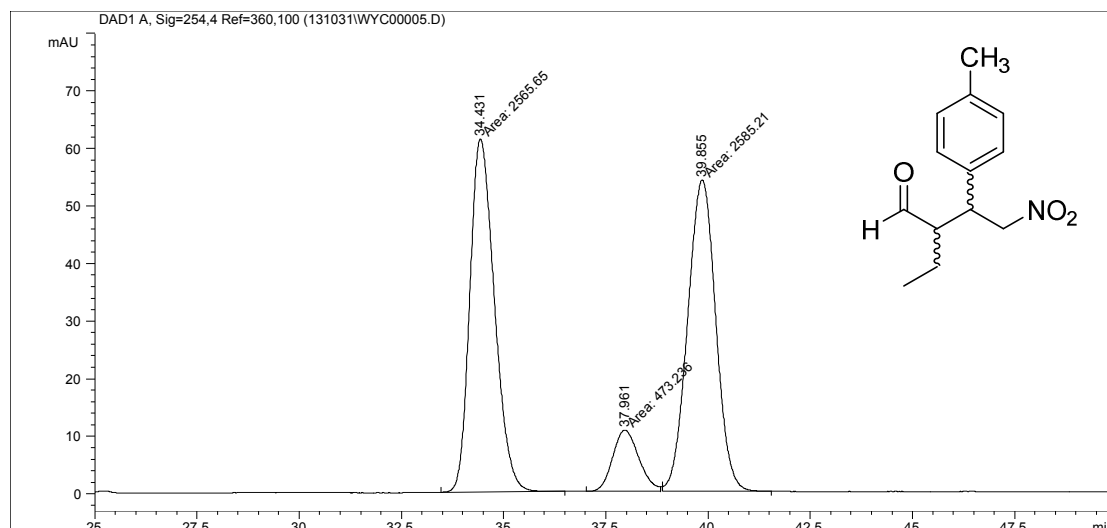
14j: AD-H n-hexane:2-propanol=99:1 1.0 mL/min



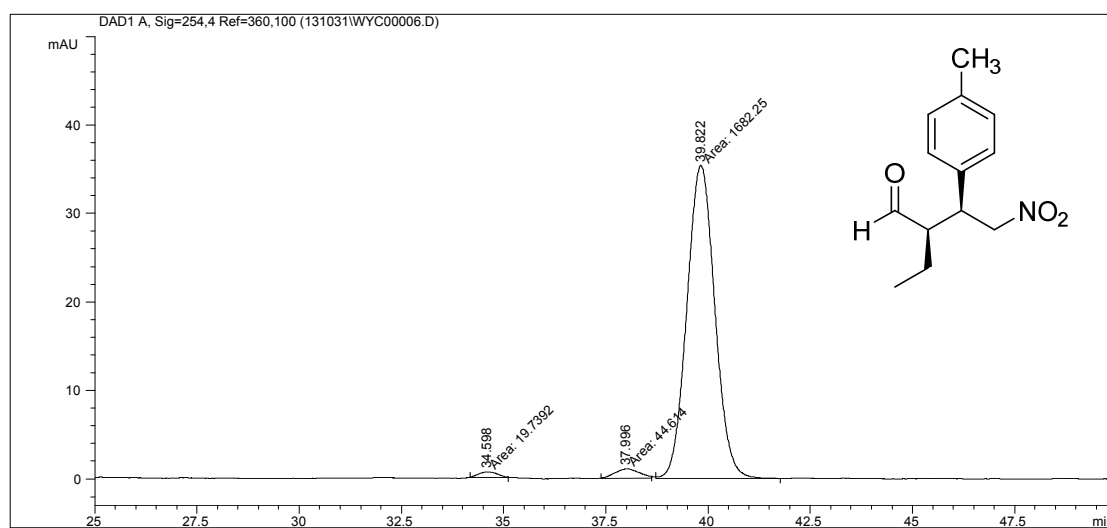
AD-H n-hexane:2-propanol=99:1 1.0 mL/min ee=98%



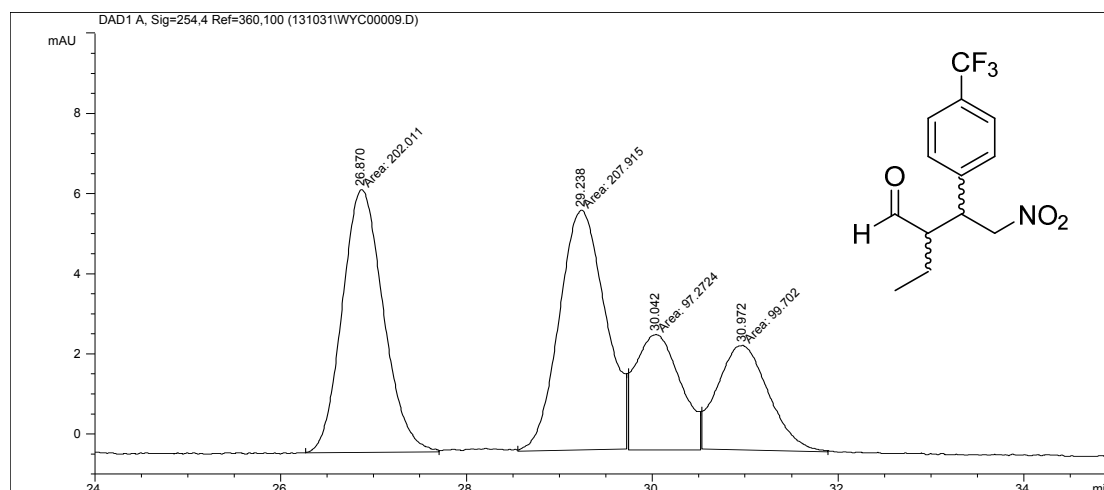
14k: OD-H n-hexane:2-propanol=92:8 0.5 mL/min



OD-H n-hexane:2-propanol=92:8 0.5 mL/min ee=98%

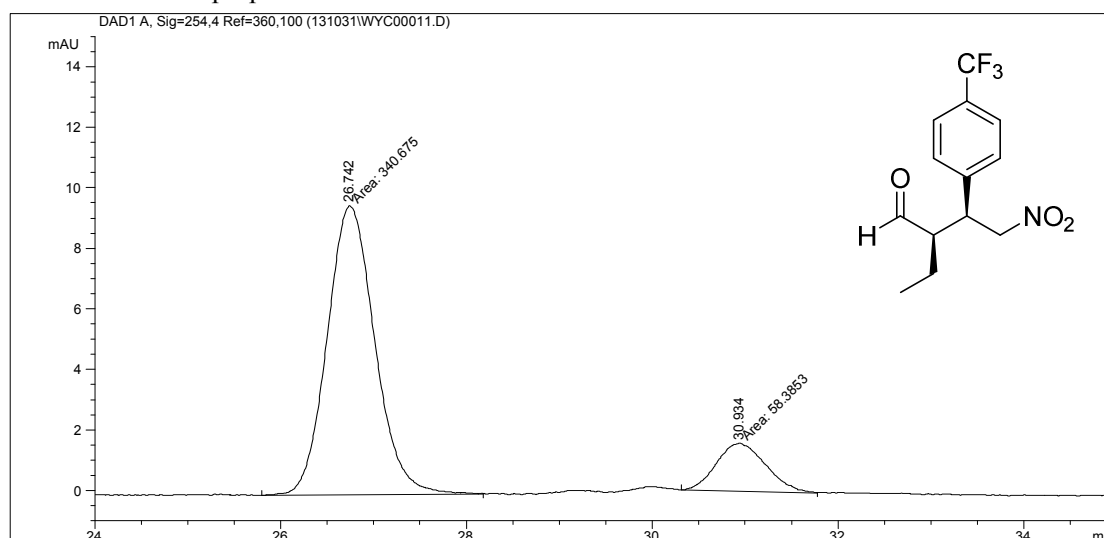


14l: AS-H n-hexane:2-propanol=93:7 0.5 mL/min



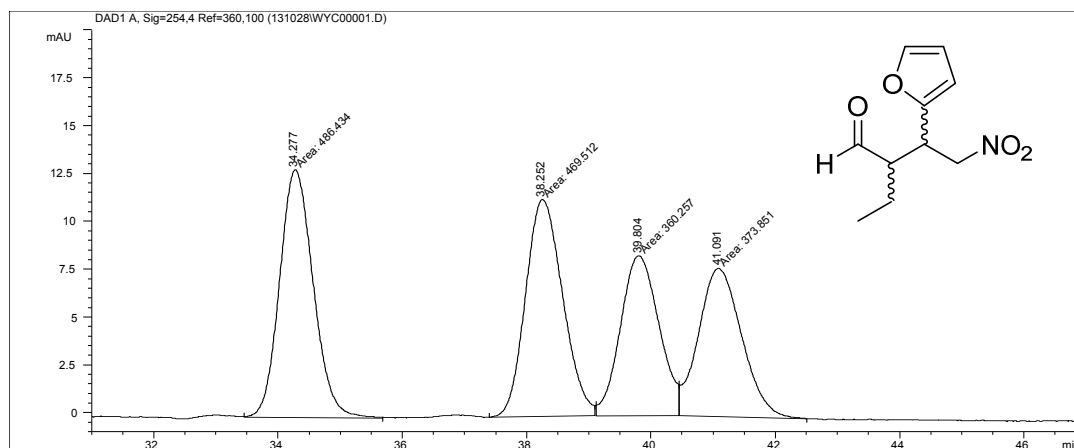
Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	26.870	MM	0.5132	202.01059	6.56055	33.2856
2	29.238	MM	0.5802	207.91518	5.97265	34.2585
3	30.042	MM	0.5641	97.27235	2.87403	16.0277
4	30.972	MM	0.6385	99.70204	2.60251	16.4281

AS-H n-hexane:2-propanol=93:7 0.5 mL/min ee=99%



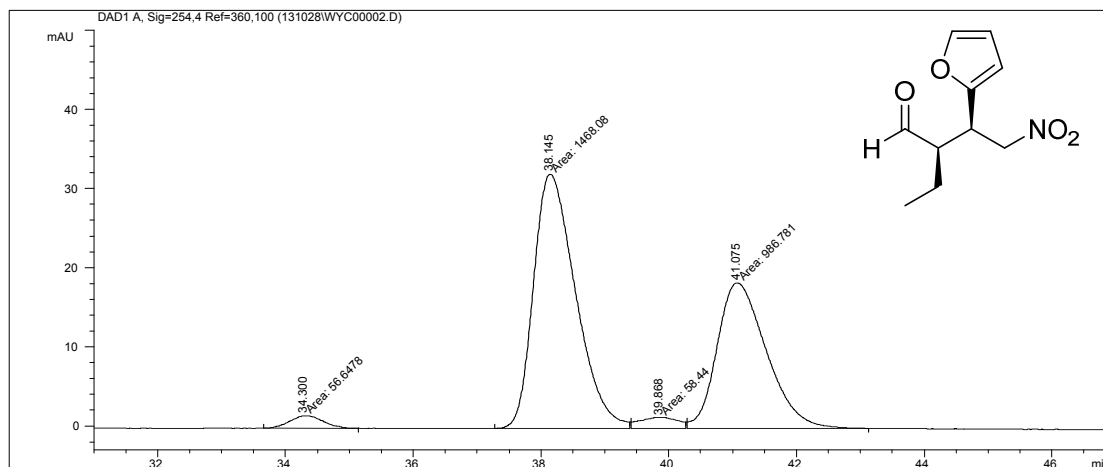
Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	26.742	MM	0.5947	340.67493	9.54781	85.3693
2	30.934	MM	0.6154	58.38535	1.58128	14.6307

14m: AS-H n-hexane:2-propanol=96:4 0.5 mL/min



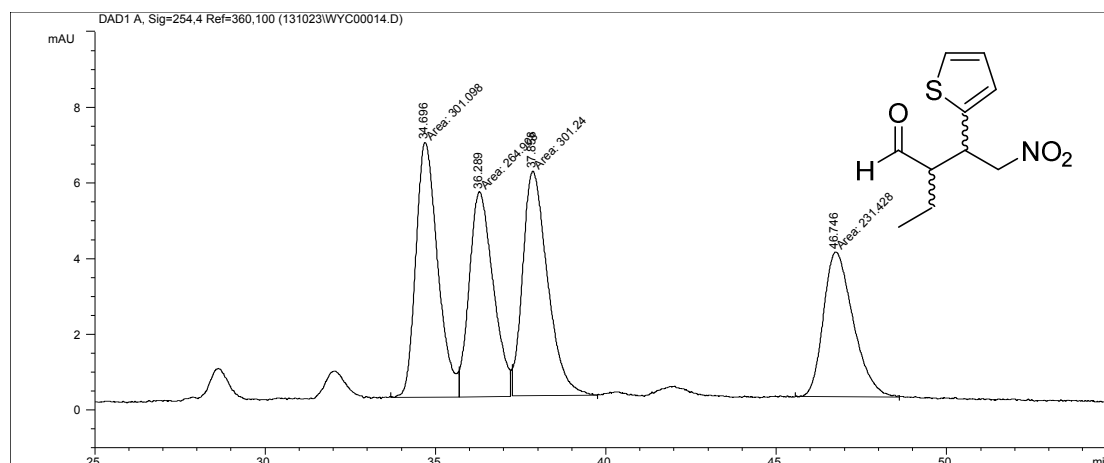
Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	34.277	MM	0.6267	486.43433	12.93736	28.7822
2	38.252	MM	0.6916	469.51236	11.31427	27.7809
3	39.804	MM	0.7187	360.25729	8.35455	21.3163
4	41.091	MM	0.8057	373.85095	7.73391	22.1206

AS-H n-hexane:2-propanol=96:4 0.5 mL/min ee=93%



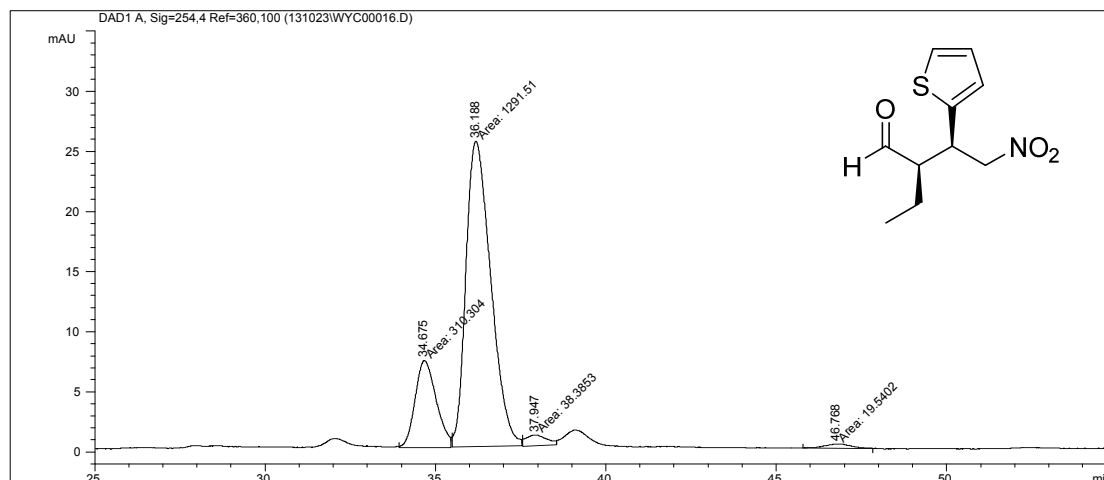
Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	34.300	MM	0.6009	56.64780	1.57118	2.2042
2	38.145	MM	0.7626	1468.08423	32.08387	57.1249
3	39.868	MM	0.6944	58.44001	1.40256	2.2740
4	41.075	MM	0.8940	986.78094	18.39577	38.3968

14n: AD-H n-hexane:2-propanol=98:2 0.7 mL/min



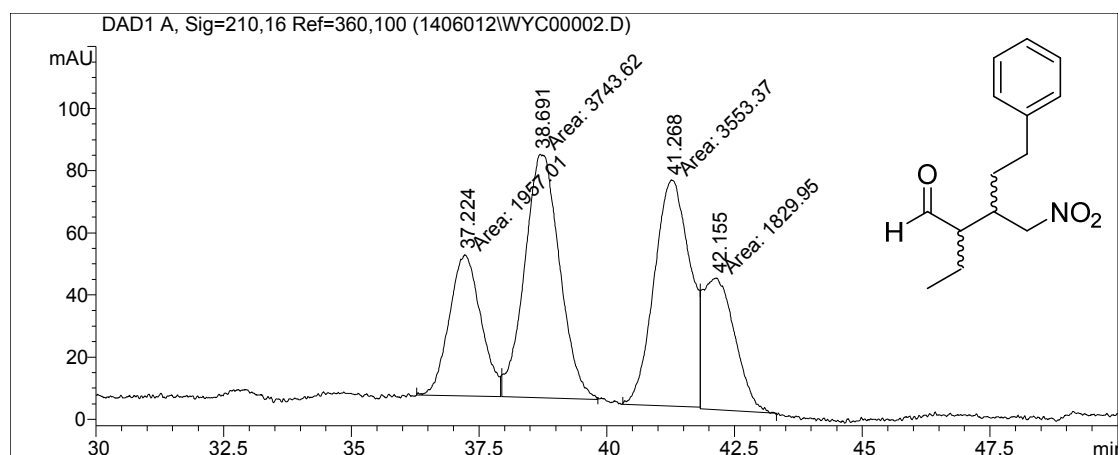
Peak	RetTime	Type	Width	Area	Height	Area
1	34.696	MM	0.7452	301.09787	6.73444	27.4056
2	36.289	MM	0.8161	264.90787	5.40991	24.1116
3	37.858	MM	0.8454	301.23978	5.93888	27.4185
4	46.746	MM	1.0105	231.42755	3.81700	21.0643

AD-H n-hexane:2-propanol=98:2 0.7 mL/min ee=97%



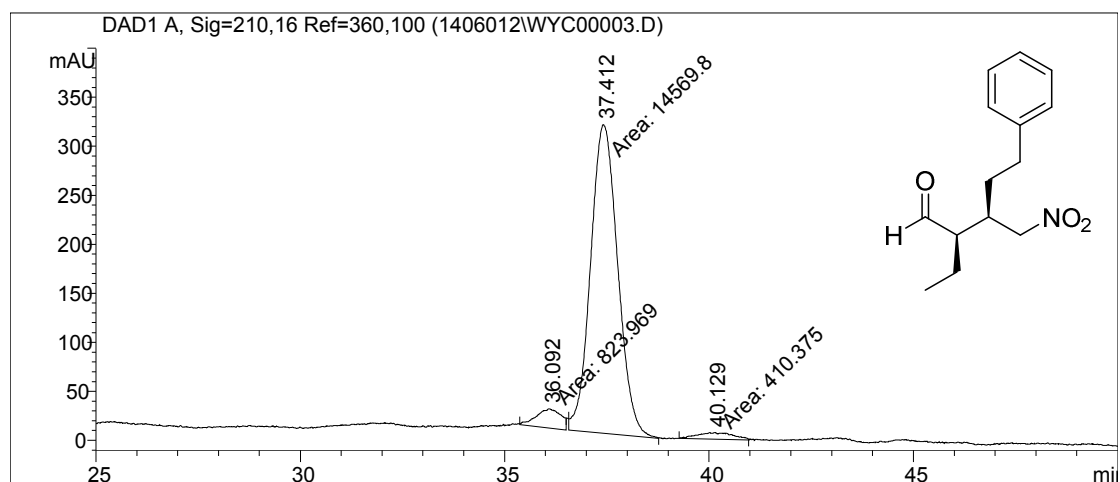
Peak	RetTime	Type	Width	Area	Height	Area
1	34.675	MM	0.7171	310.30368	7.21190	18.6960
2	36.187	MM	0.8485	1291.50806	25.36931	77.8140
3	37.947	MM	0.7115	38.38526	8.99133	2.3127
4	46.768	MM	0.9039	19.54017	3.60299	1.1773

14o: OD-H n-hexane:2-propanol=90:10 0.4 mL/min



Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	37.224MM	0.6989	1957.01	44.37	17.55	
2	38.691MM	0.7848	3743.62	34.41	34.42	
3	41.268	MM	0.8323	3553.37	33.88	33.88
4	42.155MM	0.6284	1829.95	39.77	14.14	

OD-H n-hexane:2-propanol=90:10 0.4 mL/min ee=95%



Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	36.092MM	0.6960	823.96	19.32	5.21	36
2	37.412MM	0.7710	14589.8	314.95	92.18	94
3	40.129MM	1.0101	410.37	2.59	6.66	7