

Supporting Information

Organocatalyzed Asymmetric Aldol Reaction of Methyl Ketones and α,β -Unsaturated Trifluoromethyl Ketones

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General:

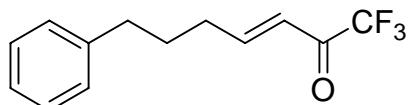
Melting points were uncorrected. ^1H NMR spectra were recorded in CDCl_3 on a Bruker AM-300 spectrometer (300 MHz) with TMS as internal standard. ^{19}F NMR spectra were taken on a Bruker AM-300 (282 MHz) spectrometer using CFCl_3 as external standard. ^{13}C NMR spectra were taken on a Bruker AM-400 (100 MHz) spectrometer. IR spectra were obtained with a Nicolet AV-360 spectrophotometer. Mass spectra was obtained on a Finnigan GC-MS 4021 spectrometer.

Unless otherwise mentioned, solvents and reagents were purchased from commercial sources and used as received. Acetone was distilled from potassium carbonate. The known unsaturated ketones **1a-b**^[1a], **1c**^[1b], **1d-f**^[1a], **1g**^[1c], **1h**^[1d], **1i**^[1c] and **1k**^[1a] were prepared according to literature. Proline derivatives **5**^[2a], **7**^[2b], **8**^[2a], **9**^[2c], **10**^[2c], **11**^[2d] were prepared using known procedures.

Preparation of unsaturated ketone **1j**

A solution of Grignard reagent from 3-phenylpropyl bromide (4.378 g, 22 mmol) and magnesium turnings (0.583 g, 24 mmol) in anhydrous diethyl ether (45 mL) was added dropwise to the solution of 4-dimethylamino-1,1,1-trifluoro-3-buten-2-one (3.340 g, 20 mmol) in anhydrous ether (25 mL) at 0 °C under nitrogen. The mixture was slowly warmed to room temperature and further stirred for 2 h. Then the mixture was poured into cold saturated NH_4Cl solution. The ethereal layer was separated and the aqueous layer was extracted with ether (2 X 50 mL). The combined ether phase was washed with brine, dried over Na_2SO_4 and the solvent was removed in vacuo. The crude product was purified by column chromatography (silica gel, petroleum ether / ethyl acetate = 9:1) to afford the title compound **1j** (3.443 g, 71%).

(E)-1,1,1-trifluoro-7-phenylhept-3-en-2-one (**1j**)



Colorless oil. ^1H NMR (300 MHz, CDCl_3): δ 7.35~7.16 (m, 6 H), 6.40 (d, J = 15.6 Hz, 1 H), 2.67 (t, J = 7.5 Hz, 2 H), 2.38~2.35 (m, 2 H), 1.90~1.83 (m, 2 H); ^{19}F NMR (282 MHz, CDCl_3) δ -77.5 (s, 3 F); ^{13}C NMR (100 Hz, CDCl_3) δ 29.1, 32.6, 35.2, 116.3 (q, J = 289.3 Hz), 121.6, 126.1, 128.4, 128.5, 141.1, 156.1, 179.7 (q, J = 34.7 Hz); IR (film): 2939, 1627, 1205, 1148 cm^{-1} ; MS (70 ev): m/z (%): 242 (0.66) [M^+], 91(100); Anal. calcd. for $\text{C}_{13}\text{H}_{13}\text{F}_3\text{O}$: C: 64.46; H: 5.41. Found: C: 64.37; H: 5.40.

General procedure for the preparation of racemic compound 3

Unsaturated ketone **1** (1 mmol) was added to a solution of *D/L*-proline (23 mg, 0.2 mmol) and trifluoroacetic acid (23 mg, 0.2 mmol) in acetone (5 mL). The reaction mixture was stirred overnight at room temperature. After removal of the solvent, the crude reaction product was directly charged on the chromatography column and purified on silica gel.

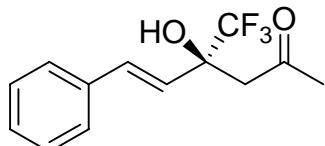
Typical procedure for the asymmetric aldol reaction of unsaturated ketone **1 and acetone**

Unsaturated ketone **1** (0.4 mmol) was added to a solution of N-sulfonyl amide **10** (15 mg, 0.04 mmol) and trifluoroacetic acid (4.6 mg, 0.04 mmol) in acetone (2 mL) at 0 °C. The reaction mixture was stirred for the time indicated in Table 2. After removal of the solvent, the crude reaction product was directly charged on the chromatography column and purified on silica gel.

Procedure for the determination of the ratio of **3a/**2a****

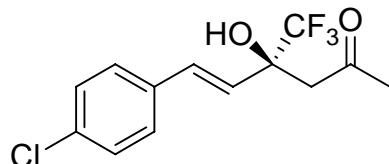
After the reaction was completed, the reaction mixture was directly analyzed by ^{19}F NMR to determine the ratio of **3a** and **2a**.

(S,E)-4-hydroxy-6-phenyl-4-(trifluoromethyl)hex-5-en-2-one (**3a**)



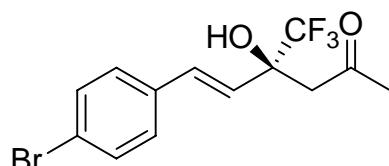
Colorless oil. $[\alpha]_D^{20} = -56.5$ ($c = 0.40$ in chloroform); ^1H NMR (300 MHz, CDCl_3): δ 7.43~6.98 (m, 5 H), 6.95 (d, $J = 15.9$ Hz, 1 H), 6.14 (d, $J = 15.9$ Hz, 1 H), 5.37 (s, 1 H), 3.04, 2.90 (AB, $J_{AB} = 17.1$ Hz, 2 H), 2.27 (s, 3 H); ^{19}F NMR (282 MHz, CDCl_3) δ -81.4 (s, 3 F); ^{13}C NMR (100 Hz, CDCl_3) δ 32.1, 44.6, 75.2 (q, $J = 28.7$ Hz), 124.2, 124.6 (q, $J = 283.0$ Hz), 126.9, 128.5, 128.7, 133.8, 135.5, 208.8. IR (film): 3410, 1708, 1171 cm^{-1} ; MS (70 ev): m/z (%): 258 (10.50) [M^+], 131(100); Anal. calcd. for $\text{C}_{13}\text{H}_{13}\text{F}_3\text{O}_2$: C: 60.46; H: 5.07. Found: C: 60.30; H: 4.93. The chiral HPLC analytical data: chiralpak AD-H column, detected at 254 nm, eluent: *n*-hexane/*iso*-propanol = 90/10, retention times: tr(minor) = 9.0 min, tr(major) = 9.7 min.

(S,E)-6-(4-chlorophenyl)-4-hydroxy-4-(trifluoromethyl)hex-5-en-2-one (3b)



White solid. Mp: 75~76 °C; $[\alpha]_D^{20} = -73.0$ ($c = 0.40$ in chloroform); ^1H NMR (300 MHz, CDCl_3): δ 7.34~7.28 (m, 4 H), 6.90 (d, $J = 15.9$ Hz, 1 H), 6.10 (d, $J = 15.9$ Hz, 1 H), 3.06, 2.87 (AB, $J_{AB} = 16.8$ Hz, 2 H), 2.26 (s, 3 H); ^{19}F NMR (282 MHz, CDCl_3) δ -80.9 (s, 3 F); ^{13}C NMR (100 Hz, CDCl_3) δ 32.0, 44.6, 75.2 (q, $J = 29.0$ Hz), 124.5 (q, $J = 283.3$ Hz), 124.9, 128.1, 128.8, 132.7, 134.0, 134.2, 208.7; IR (film): 3340, 1717, 1194, 1168 cm^{-1} ; MS (70 ev): m/z (%): 292 (7.46) [M^+], 43(100); Anal. calcd. for $\text{C}_{13}\text{H}_{12}\text{ClF}_3\text{O}_2$: C: 53.35; H: 4.13. Found: C: 53.30; H: 4.10. The chiral HPLC analytical data: chiralpak AD-H column, detected at 214 nm, eluent: *n*-hexane/*iso*-propanol = 90/10, retention times: tr(minor) = 19.1 min, tr (major) = 25.8 min.

(S,E)-6-(4-bromophenyl)-4-hydroxy-4-(trifluoromethyl)hex-5-en-2-one (3c)³



White solid. Mp: 63~64 °C; $[\alpha]_D^{20} = -66.5$ ($c = 0.40$ in chloroform); ^1H NMR (300 MHz, CDCl_3): δ 7.47~7.45 (m, 2 H), 7.28~7.25 (m, 2 H), 6.89 (d, $J = 15.9$ Hz, 1 H), 6.12 (d, $J = 15.9$ Hz, 1 H), 5.37 (s, 1 H), 3.04, 2.87 (AB, $J_{AB} = 16.8$ Hz, 2 H), 2.26 (s, 3 H); ^{19}F NMR (282 MHz, CDCl_3) δ -80.9 (s, 3 F);

¹³C NMR (100 Hz, CDCl₃) δ 32.0, 44.5, 75.1 (q, *J* = 29.0 Hz), 122.4, 124.5 (q, *J* = 283.0 Hz), 125.0, 128.4, 131.8, 132.7, 134.4, 208.7. IR (film): 3452, 1718, 1191, 1133 cm⁻¹; MS (70 ev): *m/z* (%): 336 (4.21) [M⁺], 43 (100); Anal. calcd. for C₁₃H₁₂BrF₃O₂: C: 46.31; H: 3.59. Found: C: 46.42; H: 3.65. The chiral HPLC analytical data: chiralpak AD-H column, detected at 254 nm, eluent: *n*-hexane/*iso*-propanol = 90/10, retention times: tr(minor) = 9.7 min, tr (major) = 13.4 min.

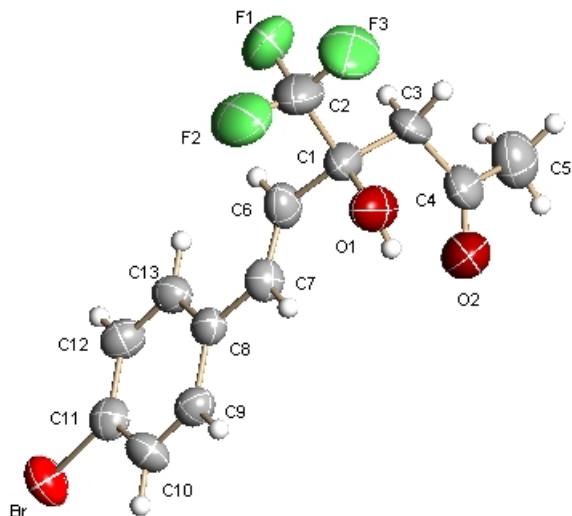
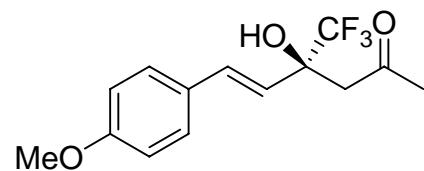


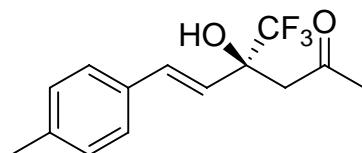
Figure The X-ray single crystal structure of **3c**

(*S,E*)-4-hydroxy-6-(4-methoxyphenyl)-4-(trifluoromethyl)hex-5-en-2-one (**3d**)



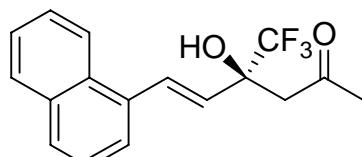
Colorless oil. $[\alpha]_D^{20} = -53.1$ ($c = 0.94$ in chloroform); ^1H NMR (300 MHz, CDCl_3): δ 7.38 (d, $J = 7.8$ Hz, 2 H), 6.89~6.84 (m, 3 H), 5.99 (d, $J = 16.2$ Hz, 1 H), 5.27 (s, 1 H), 3.81 (s, 3 H), 3.02, 2.88 (AB, $J_{AB} = 17.1$ Hz, 2 H), 2.26 (s, 3 H); ^{19}F NMR (282 MHz, CDCl_3) δ -81.1 (s, 3 F); ^{13}C NMR (100 Hz, CDCl_3) δ 32.0, 44.7, 55.2, 75.1 (q, $J = 28.7$ Hz), 114.1, 121.9, 124.6 (q, $J = 283.2$ Hz), 128.1, 128.2, 133.1, 159.9, 208.8. IR (film): 3414, 1708, 1680, 1251, 1176 cm^{-1} ; MS (70 ev): m/z (%): 288 (16.56) [M^+], 161 (100); Anal. calcd. for $\text{C}_{14}\text{H}_{15}\text{F}_3\text{O}_3$: C: 58.33; H: 5.24. Found: C: 58.21; H: 5.42. The chiral HPLC analytical data: chiralpak AD-H column, detected at 214 nm, eluent: *n*-hexane/*iso*-propanol = 90/10, retention times: tr(minor) = 23.0 min, tr (major) = 30.6 min.

(S,E)-4-hydroxy-6-p-tolyl-4-(trifluoromethyl)hex-5-en-2-one (3e)



White solid. Mp 73~74 °C; $[\alpha]_D^{20} = -61.2$ ($c = 0.50$ in chloroform); ^1H NMR (300 MHz, CDCl_3): δ 7.29 (d, $J = 8.1$ Hz, 2 H), 7.14 (d, $J = 7.8$ Hz, 2 H), 6.90 (d, $J = 16.2$ Hz, 1 H), 6.07 (d, $J = 15.6$ Hz, 1 H), 5.32 (s, 1 H), 3.02, 2.88 (AB, $J_{AB} = 16.8$ Hz, 2 H), 2.34 (s, 3 H), 2.25 (s, 3 H); ^{19}F NMR (282 MHz, CDCl_3) δ -81.0 (s, 3 F); ^{13}C NMR (100 Hz, CDCl_3) δ 21.1, 32.0, 44.6, 75.2 (q, $J = 28.7$ Hz), 123.2, 124.6 (q, $J = 282.6$ Hz), 126.8, 129.3, 132.7, 133.6, 138.4, 208.8. IR (film): 3451, 1722, 1184, 1133 cm^{-1} ; MS (70 ev): m/z (%): 272 (12.55) [M^+], 145 (100); Anal. calcd. for $\text{C}_{14}\text{H}_{15}\text{F}_3\text{O}_2$: C: 61.76; H: 5.55. Found: C: 61.73; H: 5.56. The chiral HPLC analytical data: chiralpak AD-H column, detected at 254 nm, eluent: *n*-hexane/*iso*-propanol = 90/10, retention times: tr(minor) = 8.8 min, tr (major) = 11.1 min.

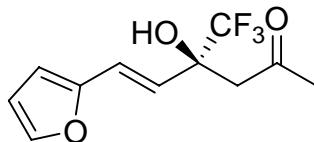
(S,E)-4-hydroxy-6-(naphthalen-1-yl)-4-(trifluoromethyl)hex-5-en-2-one (3f)



White solid. Mp: 91~92 °C; $[\alpha]_D^{20} = -11.2$ ($c = 0.44$ in chloroform); ^1H NMR (300 MHz, CDCl_3): δ 8.06 (d, $J = 7.8$ Hz, 1 H), 7.87~7.70 (m, 3 H), 7.55~7.44 (m, 4 H), 6.14 (d, $J = 15.3$ Hz, 1 H), 5.42 (s, 1 H), 3.09, 2.96 (AB, $J_{AB} = 17.1$ Hz, 2 H), 2.28 (s, 3 H); ^{19}F NMR (282 MHz, CDCl_3) δ -80.9 (s, 3 F); ^{13}C NMR (100 Hz, CDCl_3) δ 31.8, 44.6, 75.3 (q, $J = 28.9$ Hz), 123.6, 124.1, 124.6 (q, $J = 282.8$ Hz),

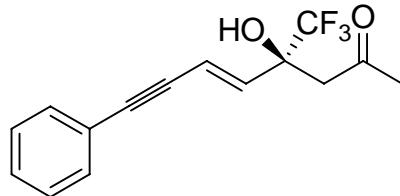
125.4, 125.9, 126.3, 127.5, 128.4, 128.6, 128.9, 131.1, 131.5, 133.4, 133.5, 208.8. IR (film): 3453, 1714, 1189, 1171, 1132 cm^{-1} ; MS (70 ev): m/z (%): 308 (20.91) [M^+], 181 (100); Anal. calcd. for $\text{C}_{17}\text{H}_{15}\text{F}_3\text{O}_2$: C: 66.23; H: 4.90. Found: C: 66.19; H: 4.92. The chiral HPLC analytical data: chiralpak OJ column, detected at 214 nm, eluent: *n*-hexane/*iso*-propanol = 98/2, retention times: tr(minor) = 47.8 min, tr (major) = 56.8 min.

(*S,E*)-6-(furan-2-yl)-4-hydroxy-4-(trifluoromethyl)hex-5-en-2-one (3g**)**



Colorless oil. $[\alpha]_D^{20} = -65.4$ ($c = 0.45$ in chloroform); ^1H NMR (300 MHz, CDCl_3): δ 7.36 (s, 1 H), 6.76(d, $J = 16.2$ Hz, 1 H), 6.40~6.37 (m, 1 H), 6.34 (s, 1 H), 6.06 (d, $J = 15.3$ Hz, 1 H), 5.30 (s, 1 H), 3.01, 2.85 (AB, $J_{AB} = 16.5$ Hz, 2 H), 2.26(s, 3 H); ^{19}F NMR (282 MHz, CDCl_3) δ -81.0 (s, 3 F); ^{13}C NMR (100 Hz, CDCl_3) δ 32.1, 44.6, 75.0 (q, $J = 29.1$ Hz), 110.2, 111.6, 122.0, 111.5, 124.5 (q, $J = 282.4$ Hz), 142.7, 151.4, 208.9; IR (film): 3418, 1709, 1172 cm^{-1} ; MS (70 ev): m/z (%): 248 (14.62) [M^+], 121 (100); Anal. calcd. for $\text{C}_{11}\text{H}_{11}\text{F}_3\text{O}_3$: C: 53.23; H: 4.47. Found: C: 52.94; H: 4.42. The chiral HPLC analytical data: chiralpak OD column, detected at 230 nm, eluent: *n*-hexane/*iso*-propanol = 97/3, retention times: tr(minor) = 8.3 min, tr (major) = 10.7 min.

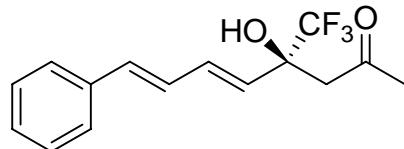
(*S,E*)-4-hydroxy-8-phenyl-4-(trifluoromethyl)oct-5-en-7-yn-2-one (3h**)**



Colorless oil. $[\alpha]_D^{20} = -62.2$ ($c = 0.73$ in chloroform); ^1H NMR (300 MHz, CDCl_3): δ 7.46~7.42 (m, 2 H), 7.33~7.31 (m, 3 H), 6.33 (d, $J = 16.2$ Hz, 1 H), 6.12 (d, $J = 15.6$ Hz, 1 H), 5.36 (s, 1 H), 2.99, 2.81 (AB, $J_{AB} = 16.8$ Hz, 2 H), 2.27 (s, 3 H); ^{19}F NMR (282 MHz, CDCl_3) δ -80.8 (s, 3 F); ^{13}C NMR (100 Hz, CDCl_3) δ 31.8, 44.0, 75.0 (q, $J = 29.6$ Hz), 86.2, 92.7, 114.8, 122.7, 124.2 (q, $J = 284.6$ Hz), 128.3, 128.6, 131.5, 136.6, 208.6; IR (film): 3410, 1708, 1172 cm^{-1} ; MS (70 ev): m/z (%): 282 (3.73) [M^+], 43 (100); Anal. calcd. for $\text{C}_{15}\text{H}_{13}\text{F}_3\text{O}_2$: C: 63.83; H: 4.64. Found: C: 63.73; H: 4.43. The chiral HPLC

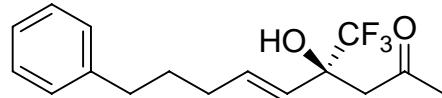
analytical data: chiralpak OD column, detected at 214 nm, eluent: *n*-hexane/*iso*-propanol = 90/10, retention times: tr(minor) = 12.7 min, tr (major) = 14.0 min.

(*S,5E,7E*)-4-hydroxy-8-phenyl-4-(trifluoromethyl)octa-5,7-dien-2-one (3i**)**



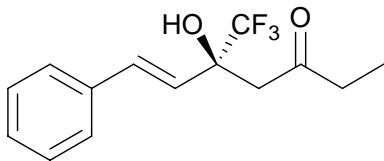
Colorless oil. $[\alpha]_D^{20} = -38.4$ ($c = 0.48$ in chloroform); ^1H NMR (300 MHz, CDCl_3): δ 7.41~7.24 (m, 5 H), 6.78~6.62 (m, 3 H), 5.73 (d, $J = 14.7$ Hz, 1 H), 5.20 (s, 1 H), 2.98, 2.84 (AB, $J_{AB} = 16.8$ Hz, 2 H), 2.26 (s, 3 H); ^{19}F NMR (282 MHz, CDCl_3) δ -81.0 (s, 3 F); ^{13}C NMR (100 Hz, CDCl_3) δ 31.9, 44.6, 75.0 (q, $J = 29.0$ Hz), 124.5 (q, $J = 283.0$ Hz), 126.6, 126.9, 127.7, 128.0, 128.6, 134.0, 135.2, 136.7, 208.7; IR (film): 3408, 1708, 1179 cm^{-1} ; MS (70 ev): m/z (%): 284 (7.51) [M^+], 43 (100); Anal. calcd. for $\text{C}_{15}\text{H}_{15}\text{F}_3\text{O}_2$: C: 63.38; H: 5.32. Found: C: 63.42; H: 5.26. The chiral HPLC analytical data: chiralpak AD-H column, detected at 254 nm, eluent: *n*-hexane/*iso*-propanol = 90/10, retention times: tr(minor) = 11.4 min, tr (major) = 13.4 min.

(*S,E*)-4-hydroxy-9-phenyl-4-(trifluoromethyl)non-5-en-2-one (3j**)**



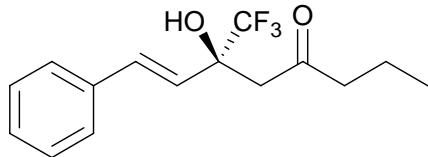
Colorless oil. $[\alpha]_D^{20} = -6.5$ ($c = 0.43$ in chloroform); ^1H NMR (300 MHz, CDCl_3): δ 7.30~7.25 (m, 2 H), 7.20~7.15 (m, 3 H), 6.08~5.98 (m, 1 H), 5.45 (d, $J = 15.9$ Hz, 1 H), 5.03 (s, 1 H), 2.91, 2.79 (AB, $J_{AB} = 16.8$ Hz, 2 H), 2.59 (t, $J = 7.5$ Hz, 2 H), 2.23 (s, 3 H), 2.14~2.09 (m, 2 H), 1.75~1.70 (m, 2 H); ^{19}F NMR (282 MHz, CDCl_3) δ -81.5 (s, 3 F); ^{13}C NMR (100 Hz, CDCl_3) δ 30.4, 31.5, 32.0, 35.1, 44.6, 74.7 (q, $J = 29.1$ Hz), 124.6 (q, $J = 280.2$ Hz), 125.8, 128.3, 128.4, 135.2, 142.0, 208.7; IR (film): 3419, 1708, 1169 cm^{-1} ; MS (70ev): m/z (%): 282 (2.87) [$\text{M}^+ \text{-H}_2\text{O}$], 104 (100); Anal. calcd. for $\text{C}_{16}\text{H}_{19}\text{F}_3\text{O}_2$: C: 63.99; H: 6.38. Found: C: 63.95; H: 6.35. The chiral HPLC analytical data: chiralpak OD column, detected at 214 nm, eluent: *n*-hexane/*iso*-propanol = 100/1, retention times: tr(minor) = 30.8 min, tr (major) = 35.8 min.

(*S,E*)-5-hydroxy-7-phenyl-5-(trifluoromethyl)hept-6-en-3-one (3m**)**



Colorless oil. $[\alpha]_D^{20} = -73.5$ ($c = 0.62$ in chloroform); ^1H NMR (300 MHz, CDCl₃): δ 7.42~7.26 (m, 5 H), 6.94 (d, $J = 15.9$ Hz, 1 H), 6.13 (d, $J = 15.9$ Hz, 1 H), 5.51 (s, 1 H), 3.00, 2.84 (AB, $J_{AB} = 16.5$ Hz, 2 H), 2.56~2.51 (m, 2 H), 1.06 (t, $J = 7.2$ Hz, 3 H); ^{19}F NMR (282 MHz, CDCl₃) δ -80.9 (s, 3 F); ^{13}C NMR (125 Hz, CDCl₃) δ 7.1, 29.7, 38.2, 43.5, 75.3 (q, $J = 29.1$ Hz), 124.3, 124.6 (q, $J = 283.9$ Hz), 126.9, 128.4, 128.7, 133.8, 135.6, 211.7; IR (film): 3397, 1705, 1174 cm⁻¹; MS (70 ev): m/z (%): 272 (4.10) [M⁺], 57 (100); Anal. calcd. for C₁₄H₁₅F₃O₂: C: 61.76; H: 5.55. Found: C: 61.73; H: 5.59. The chiral HPLC analytical data: chiralpak AD-H column, detected at 254 nm, eluent: *n*-hexane/*iso*-propanol = 90/10, retention times: tr(minor) = 7.7 min, tr(major) = 8.8 min.

(*S,E*)-6-hydroxy-8-phenyl-6-(trifluoromethyl)oct-7-en-4-one (**3n**)



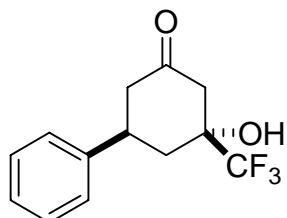
White solid. Mp: 47~48 °C; $[\alpha]_D^{20} = -61.9$ ($c = 0.40$ in chloroform); ^1H NMR (300 MHz, CDCl₃): δ 7.41~7.28 (m, 5 H), 6.94 (d, $J = 16.2$ Hz, 1 H), 6.13 (d, $J = 16.2$ Hz, 1 H), 5.52 (s, 1 H), 2.99, 2.84 (AB, $J_{AB} = 16.5$ Hz, 2 H), 2.51~2.45 (m, 2 H), 1.64~1.57 (m, 2 H), 0.90 (t, $J = 7.2$ Hz, 3 H); ^{19}F NMR (282 MHz, CDCl₃) δ -80.9 (s, 3 F); ^{13}C NMR (125 Hz, CDCl₃) δ 13.4, 16.6, 43.7, 46.8, 75.3 (q, $J = 29.0$ Hz), 124.3, 124.6, (q, $J = 283.8$ Hz), 126.9, 128.4, 128.6, 133.7, 135.6, 211.3; IR (film): 3355, 1686, 1146 cm⁻¹; MS (70 ev): m/z (%): 286 (3.85) [M⁺], 43 (100); Anal. calcd. for C₁₅H₁₇F₃O₂: C: 62.93; H: 5.99. Found: C: 63.16; H: 5.95. The chiral HPLC analytical data: chiralpak AD-H column, detected at 254 nm, eluent: *n*-hexane/*iso*-propanol = 90/10, retention times: tr(minor) = 8.1 min, tr(major) = 9.6 min.

Typical procedure for the domino Michael-aldol reaction of unsaturated ketone **1a** and acetone

Unsaturated ketone **1a** (200 mg, 1 mmol) and pyrrolidine (14 mg, 0.2 mmol) were added to acetone (5 mL). The reaction mixture was stirred for 6 h at room temperature. After removal of the solvent, the

crude reaction product was directly charged on the chromatography column and purified on silica gel (petroleum ether / ethyl acetate = 5:1) to afford the title compound **2a** (186 mg, 72%).

3-hydroxy-5-phenyl-3-(trifluoromethyl)cyclohexanone (2a**)³**



White solid. Mp: 140~141 °C; ¹H NMR (300 MHz, CDCl₃): δ 7.39~7.25 (m, 5 H), 3.49 (tt, *J*₁ = 12.9 Hz, *J*₂ = 3.9 Hz, 1 H), 2.81~2.44 (m, 5 H), 2.30~2.04 (m, 2 H); ¹⁹F NMR (282 MHz, CDCl₃) δ -84.1 (s, 3 F); ¹³C NMR (75 Hz, CD₃COCD₃) δ 36.2, 37.6, 45.0, 47.3, 75.1 (q, *J* = 28.6 Hz), 125.8 (q, *J* = 283.4 Hz), 126.9, 127.0, 128.8, 143.5, 205.0; IR (film): 3290, 1720, 1192, 1170 cm⁻¹; MS (70 ev): *m/z* (%): 258 (37.65) [M⁺], 104 (100); Anal. calcd. for C₁₃H₁₃F₃O₂: C: 60.46; H: 5.07. Found: C: 60.73; H: 5.28.

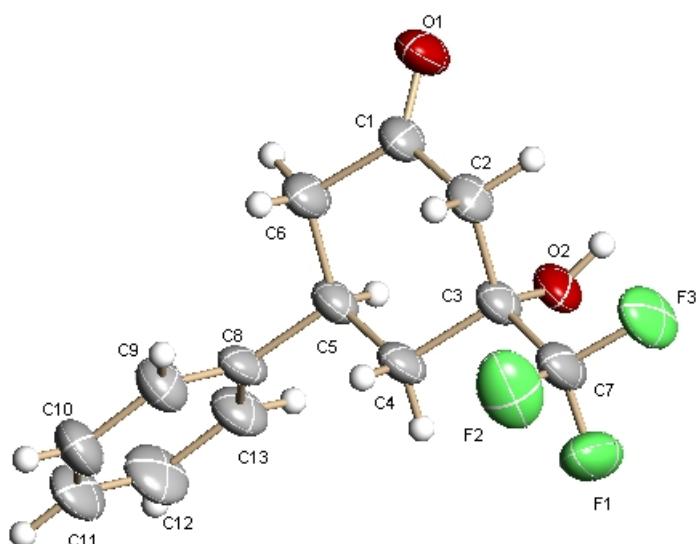
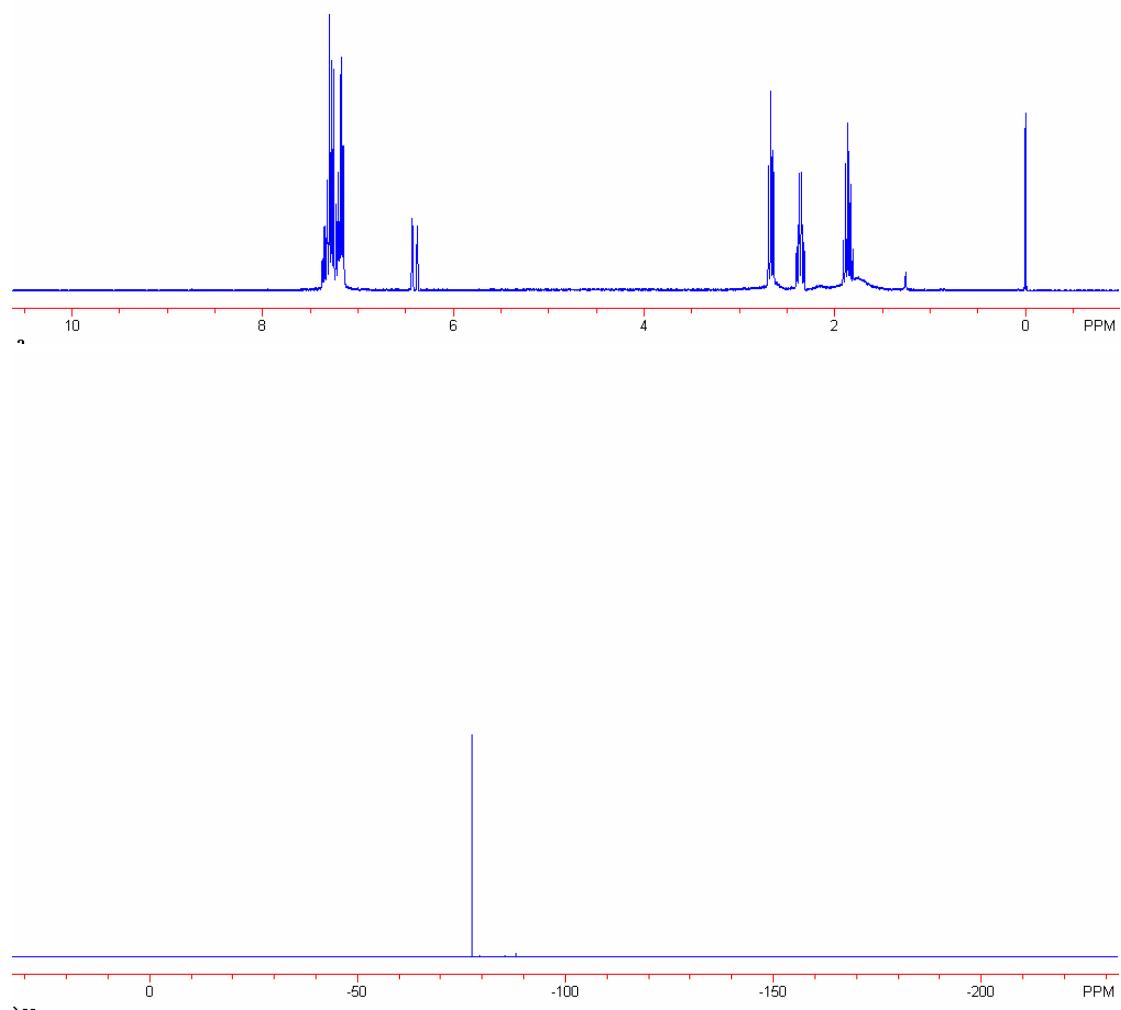
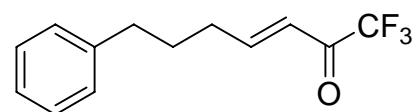
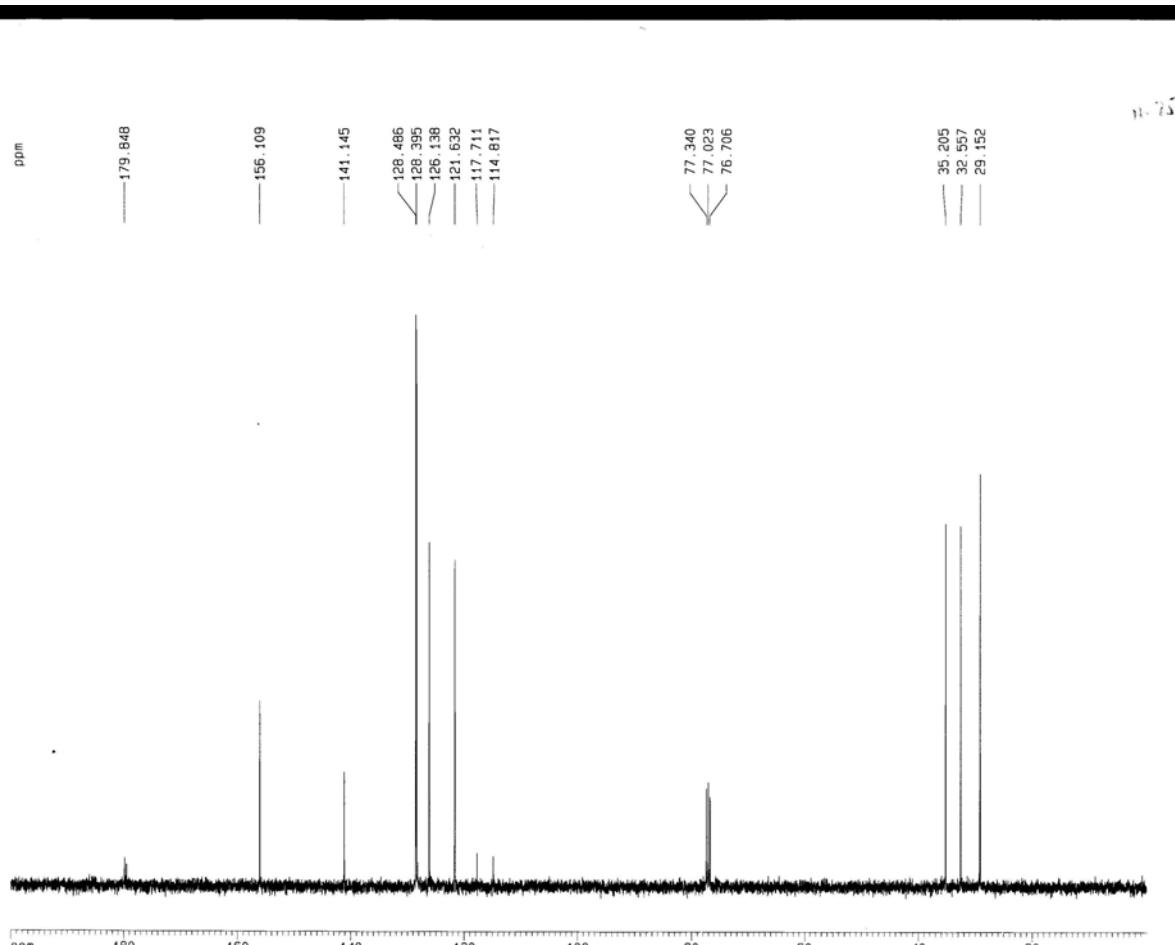


Figure The X-ray single crystal structure of **2a**

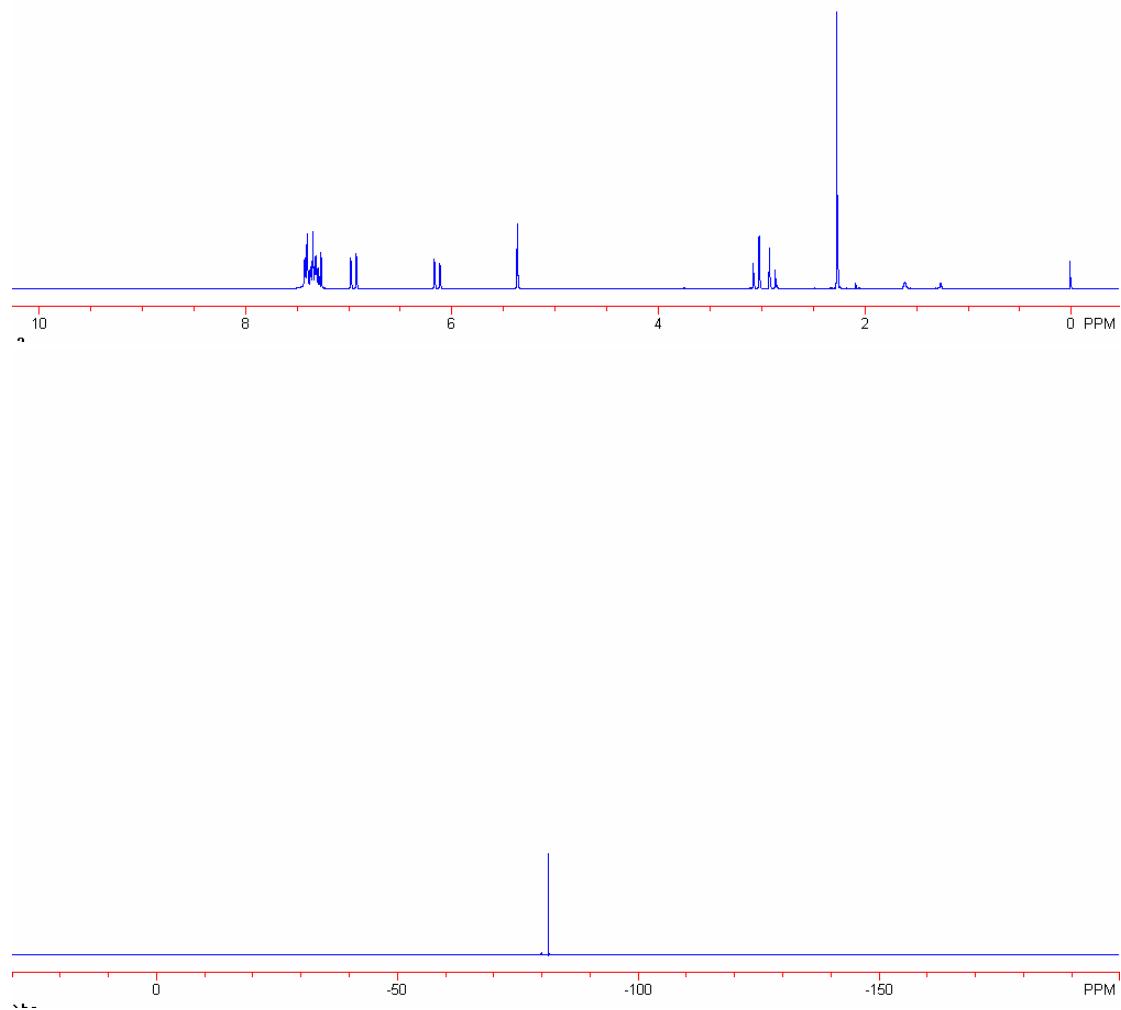
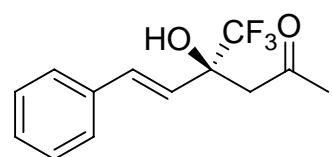
¹H NMR and ¹⁹ F NMR spectra of new compounds and HPLC spectra

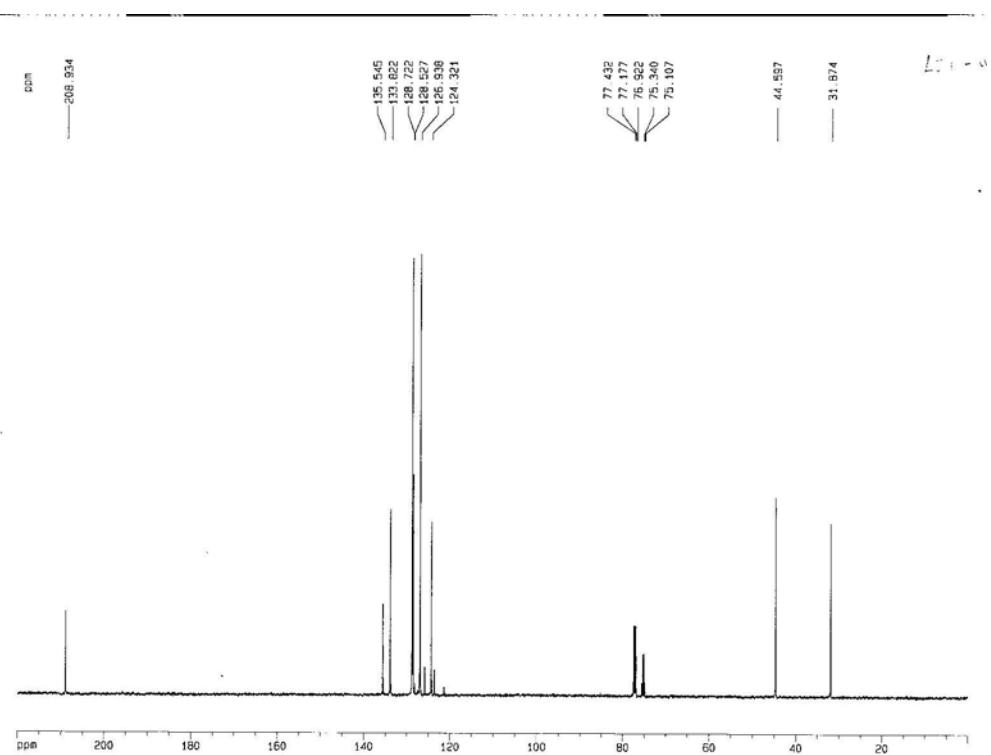
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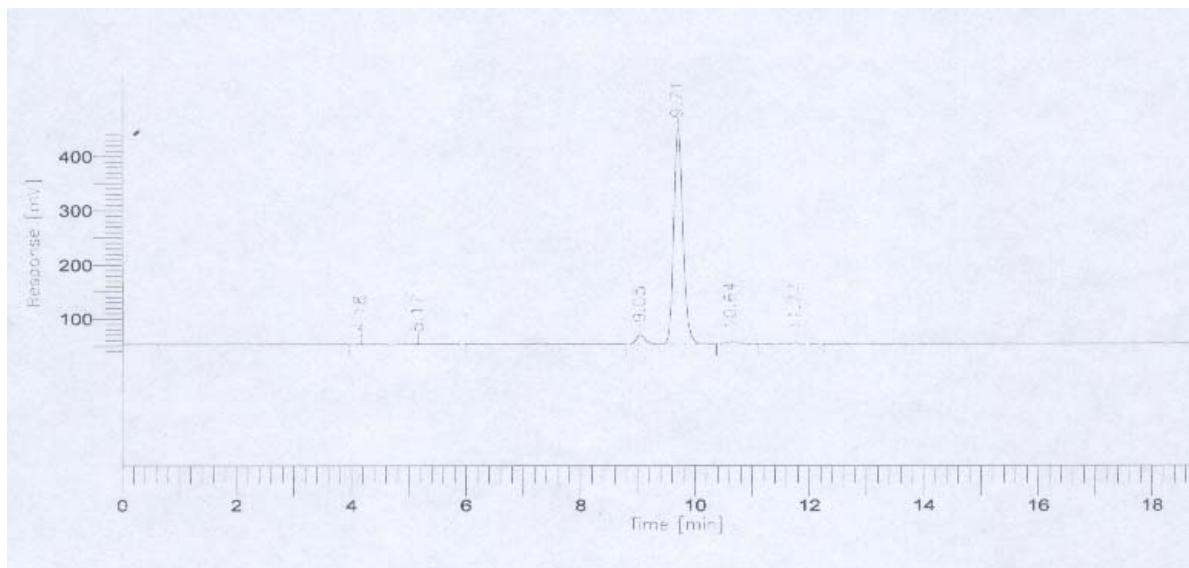
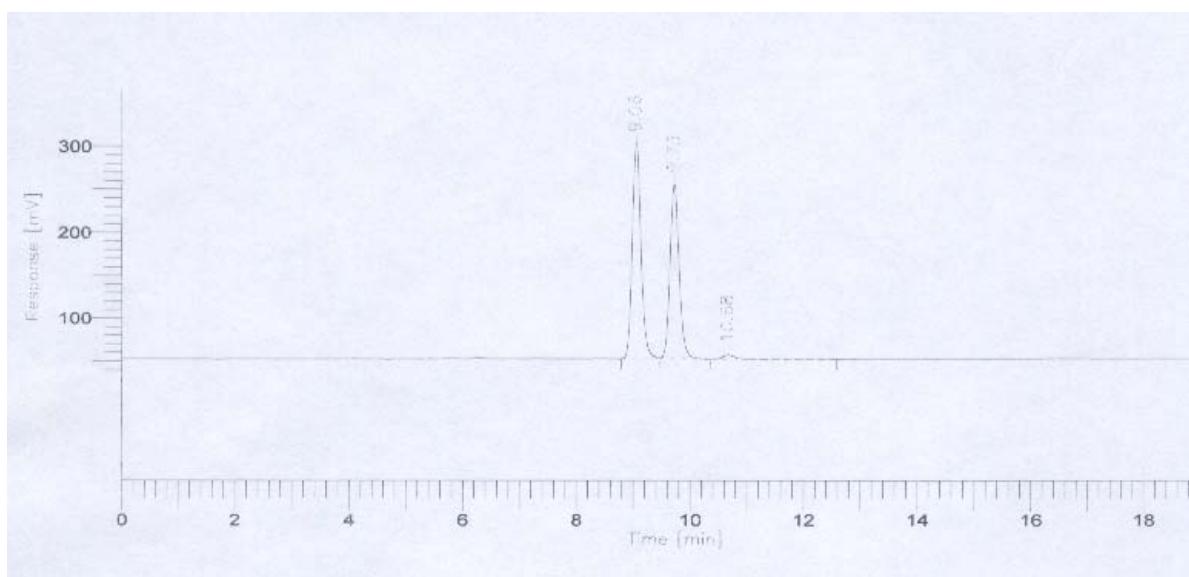


3a

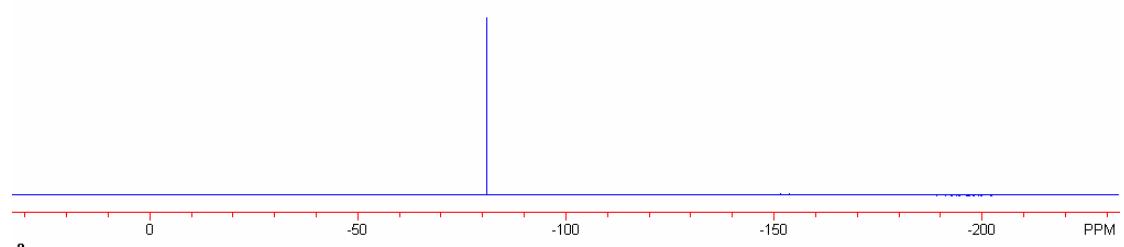
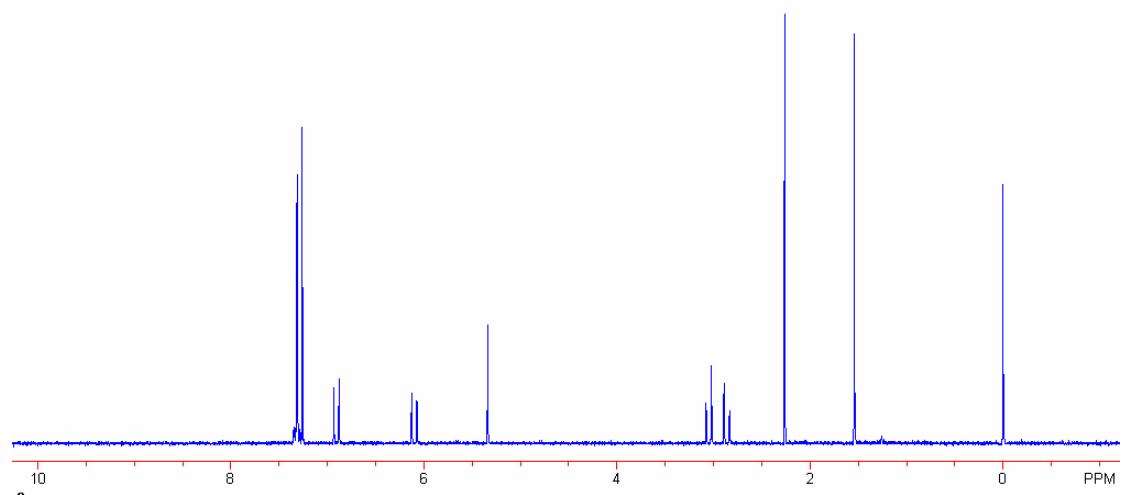
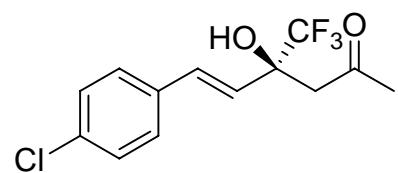


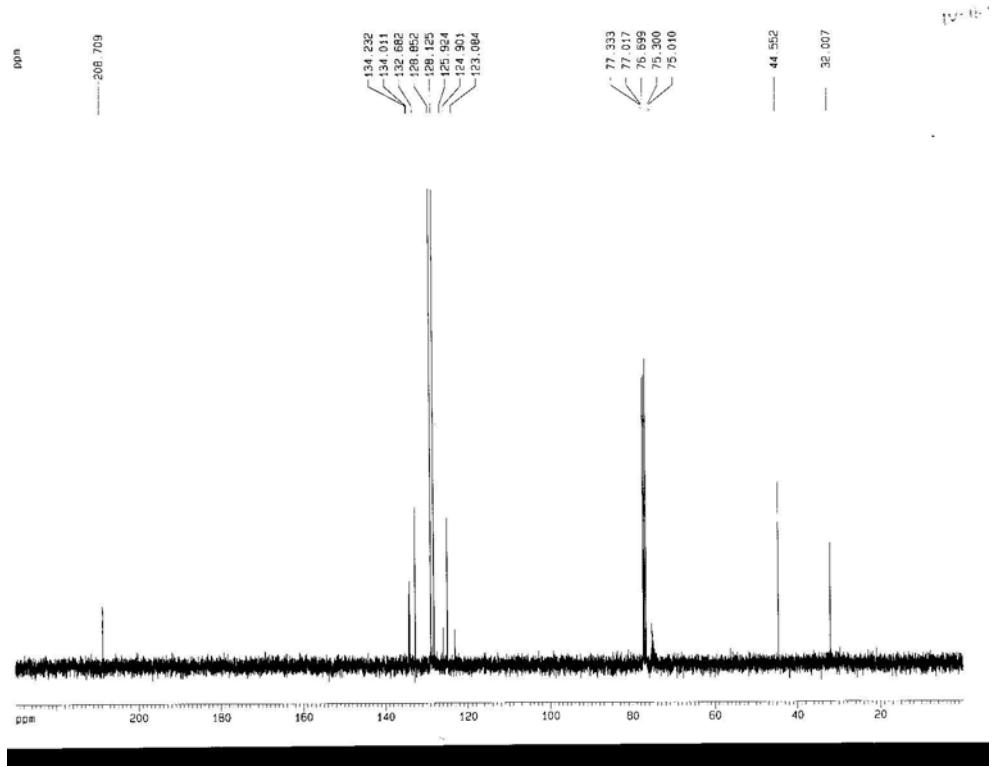


3a (HPLC)

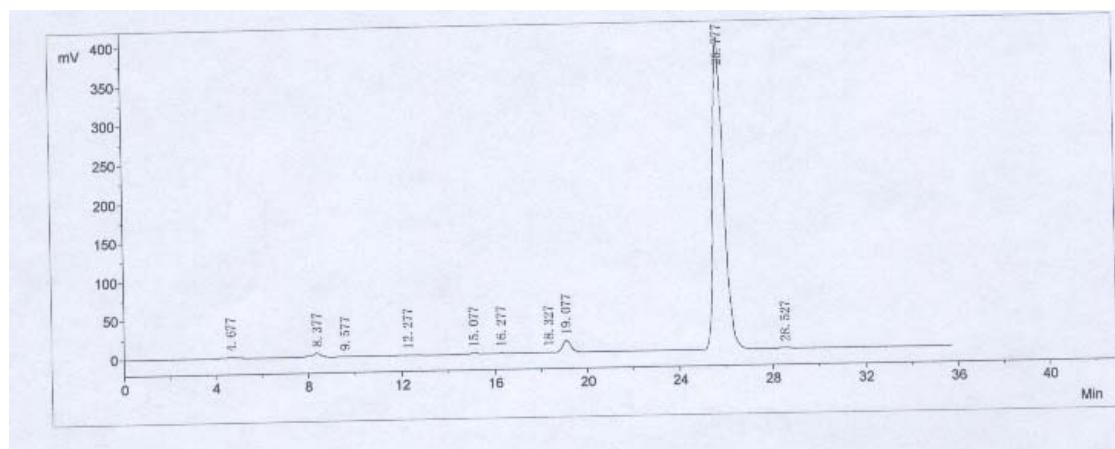
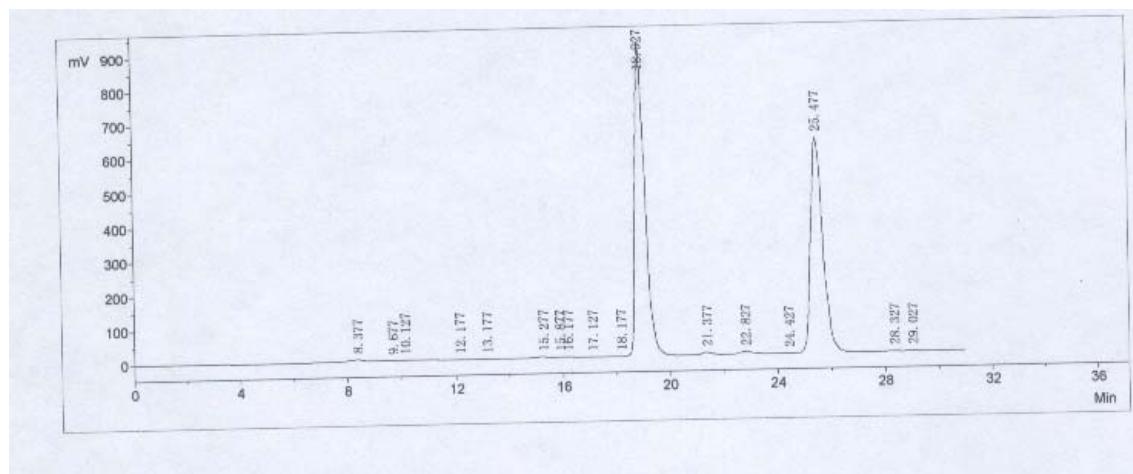


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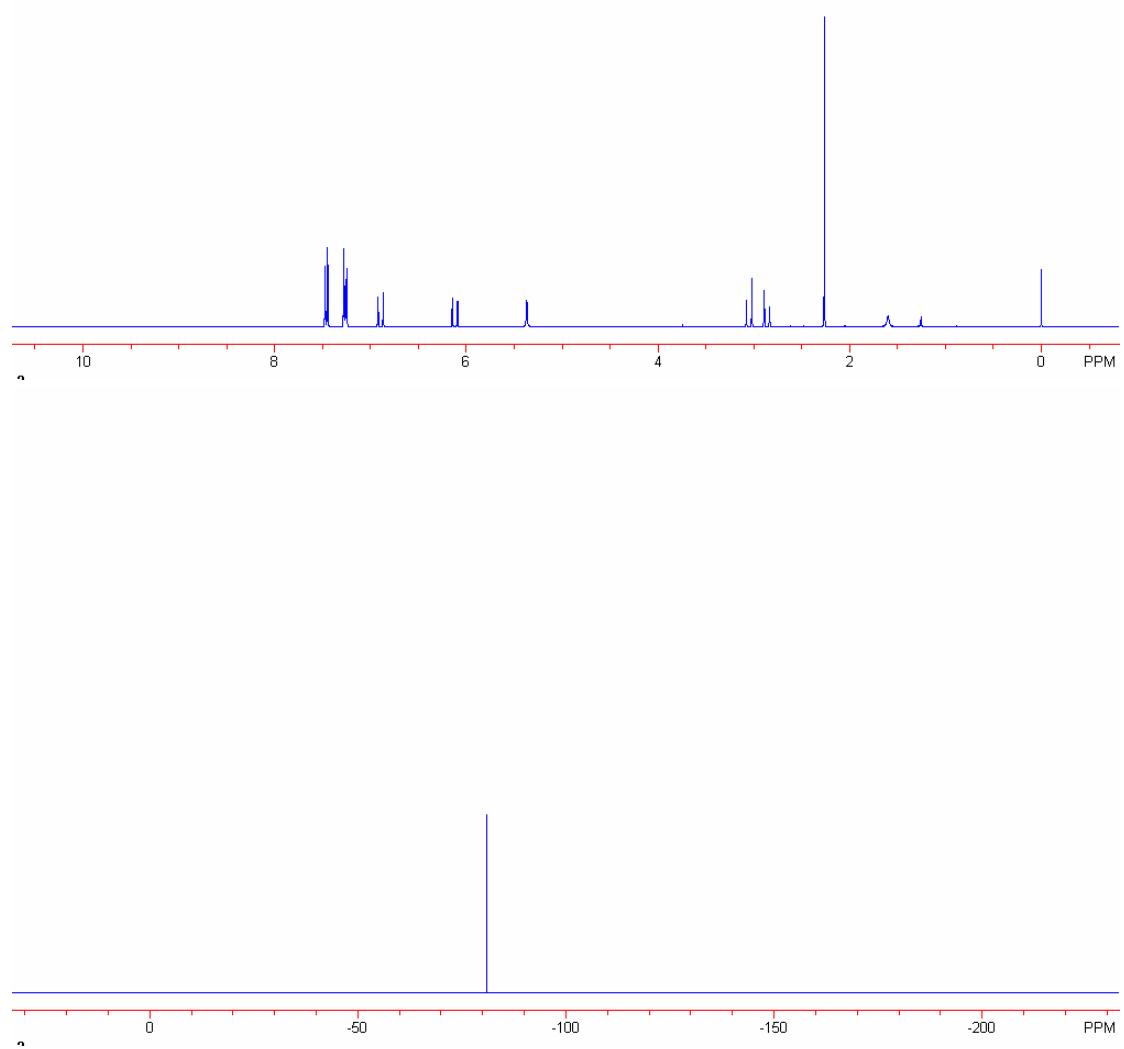
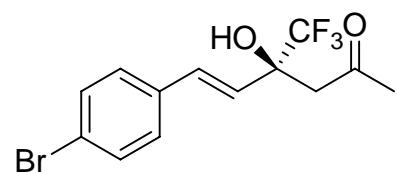


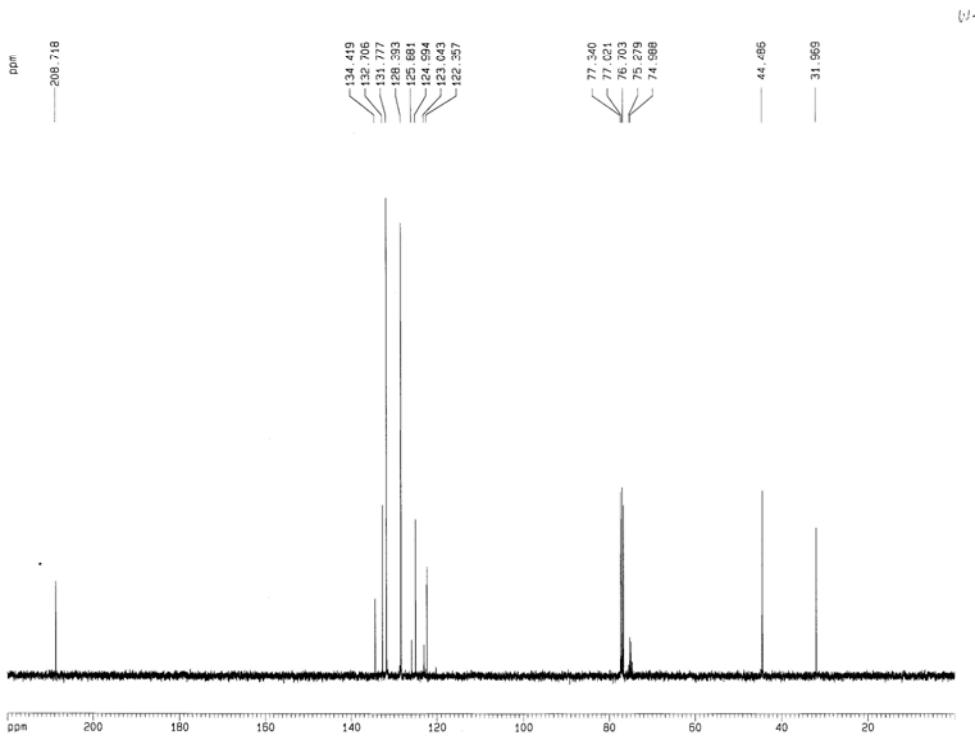


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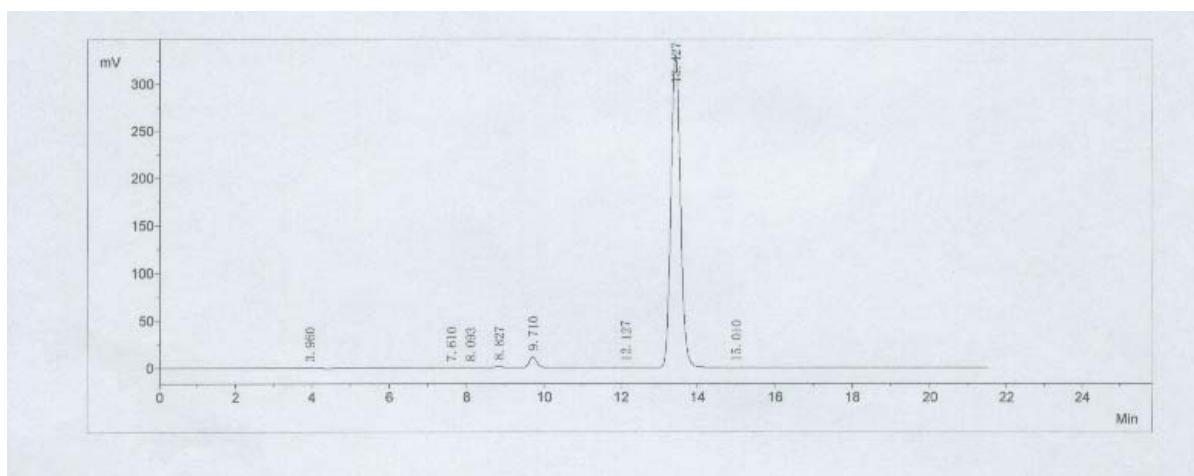
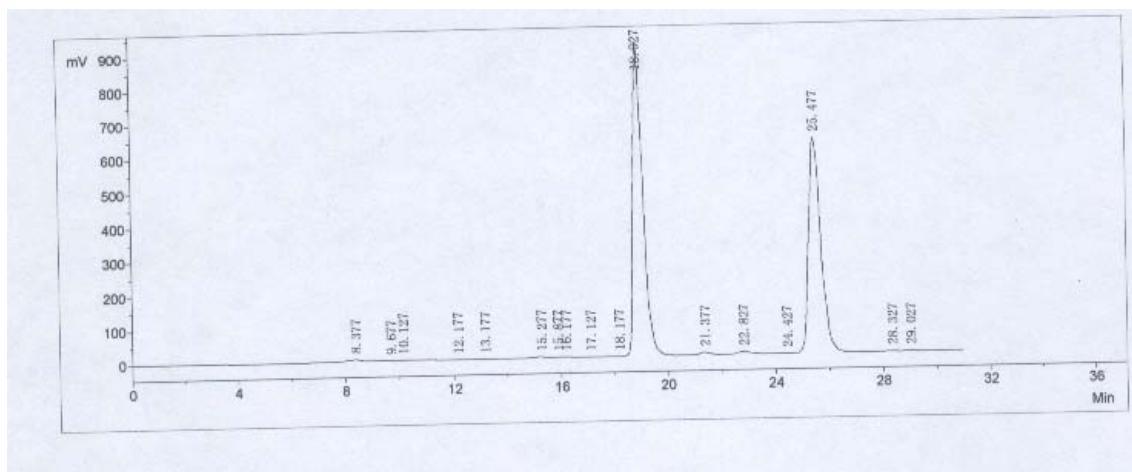


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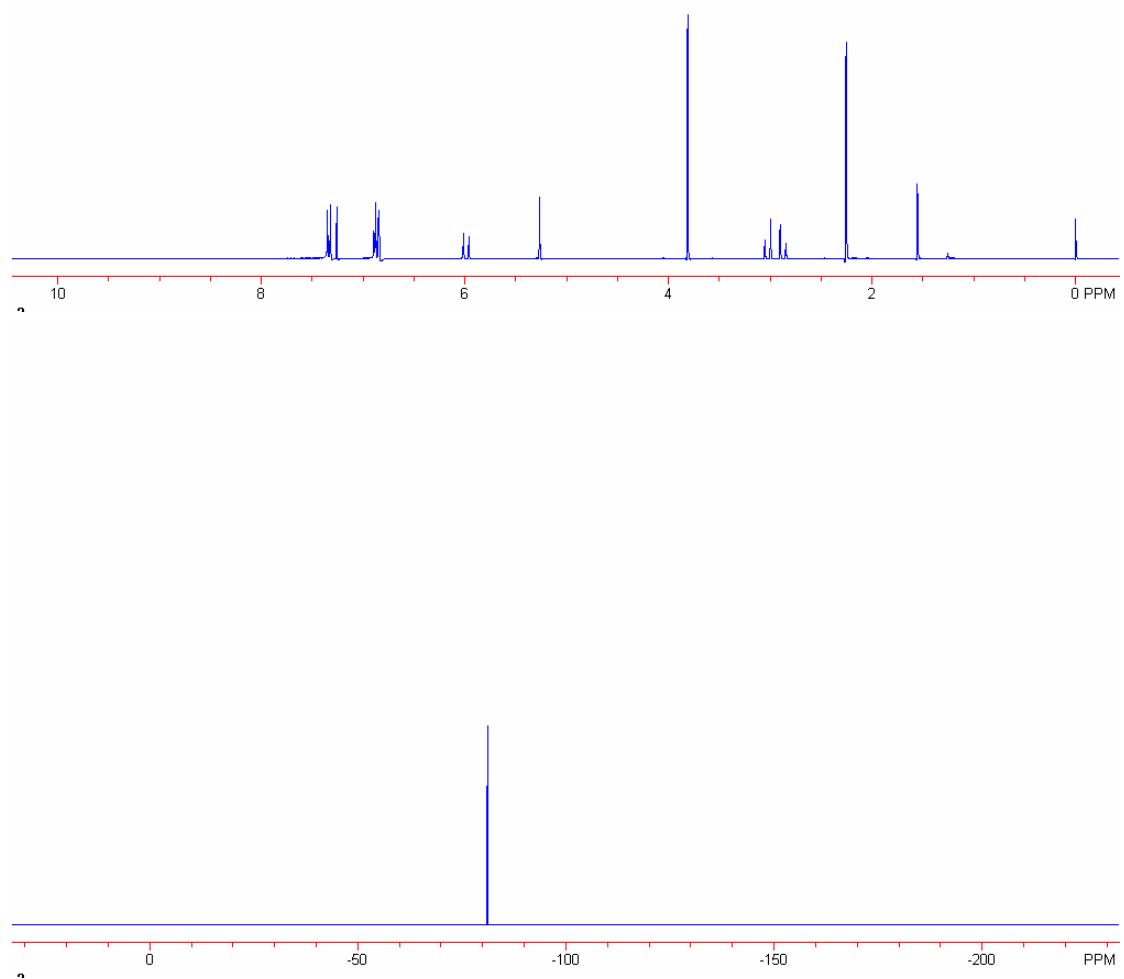
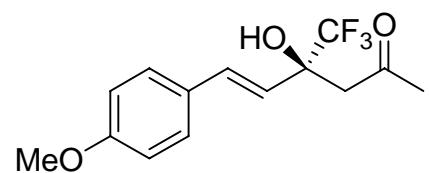


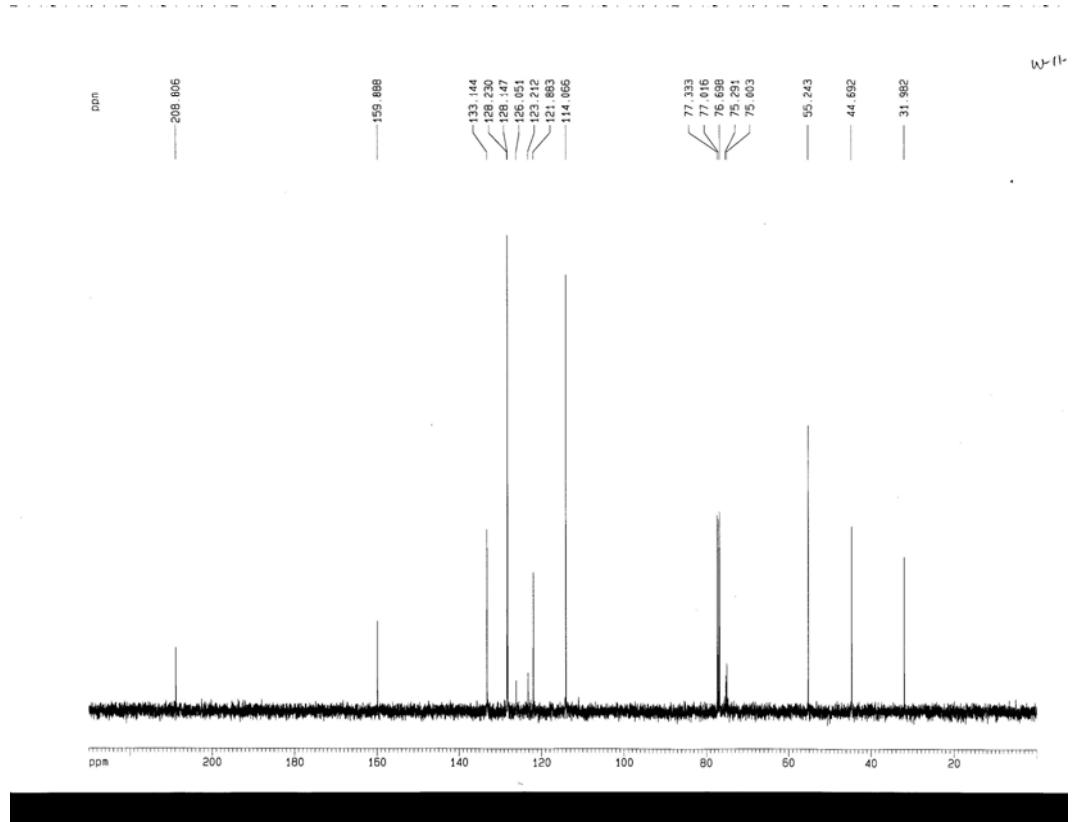


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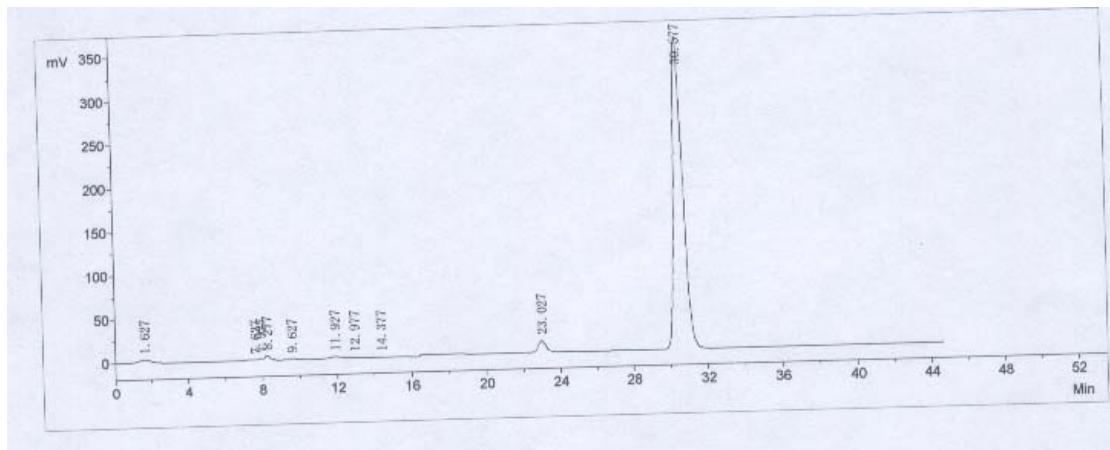
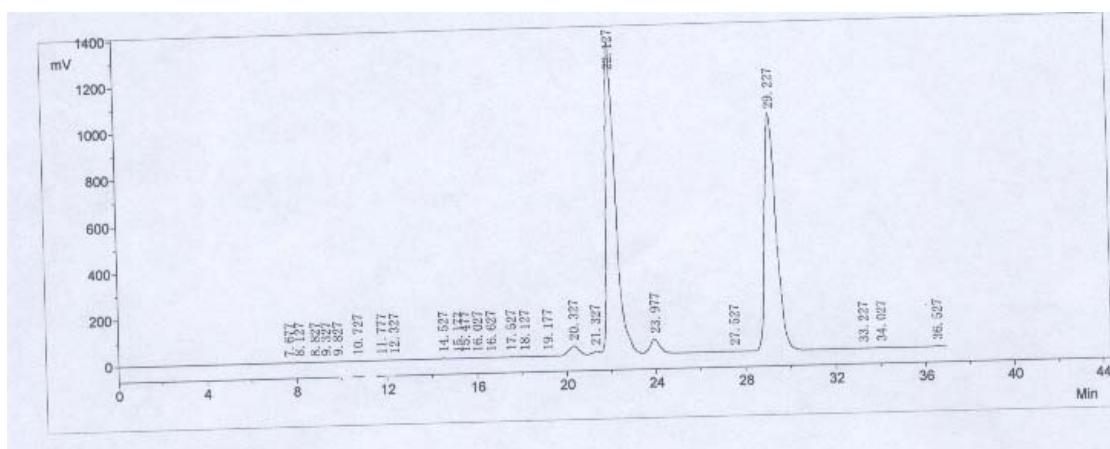


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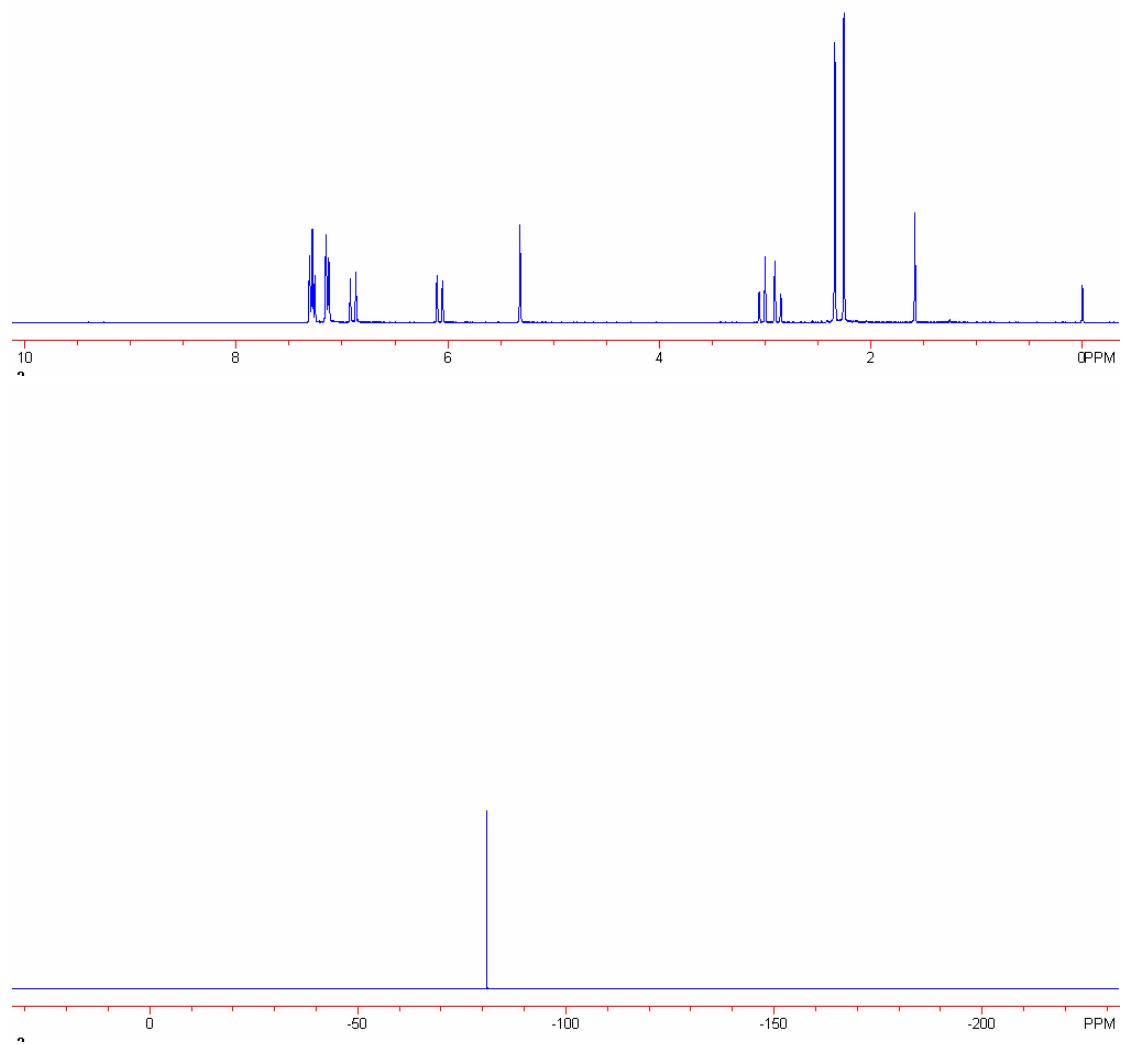
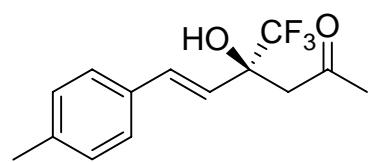


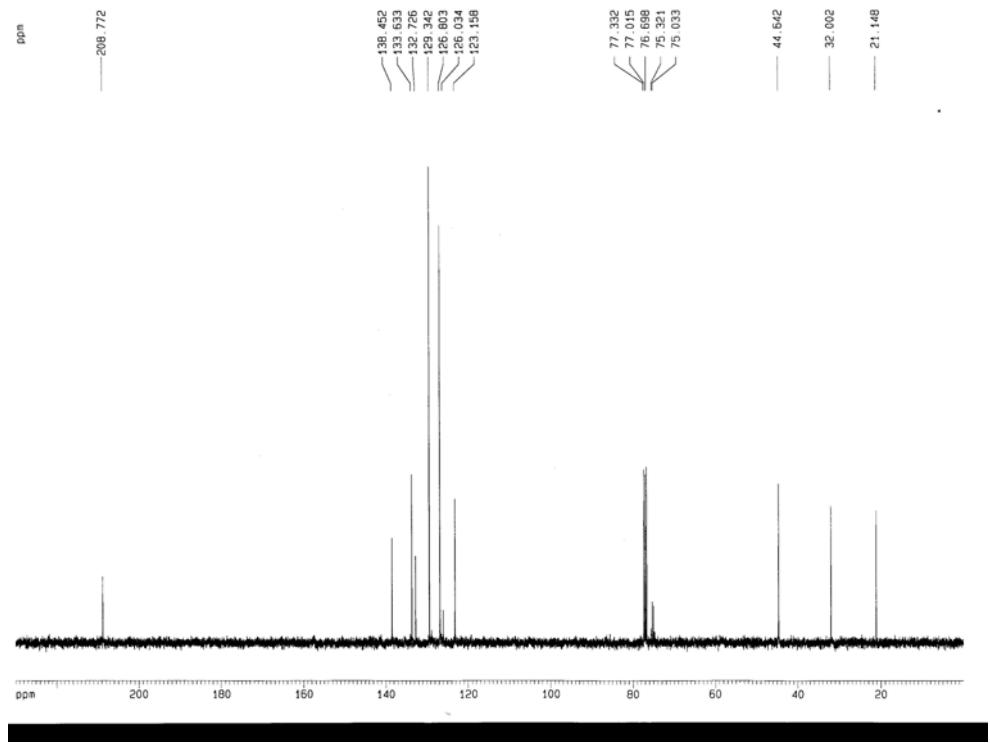


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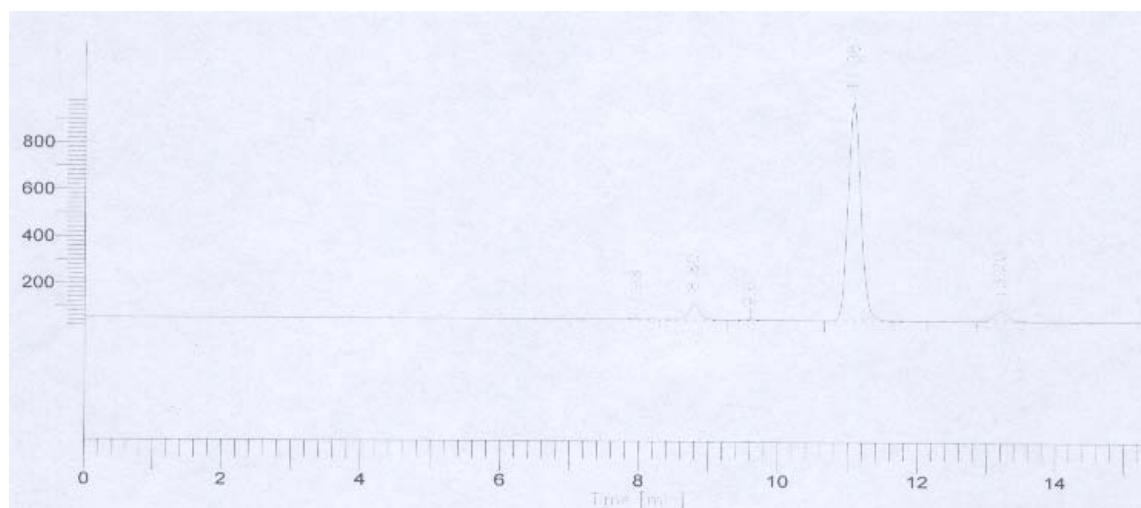
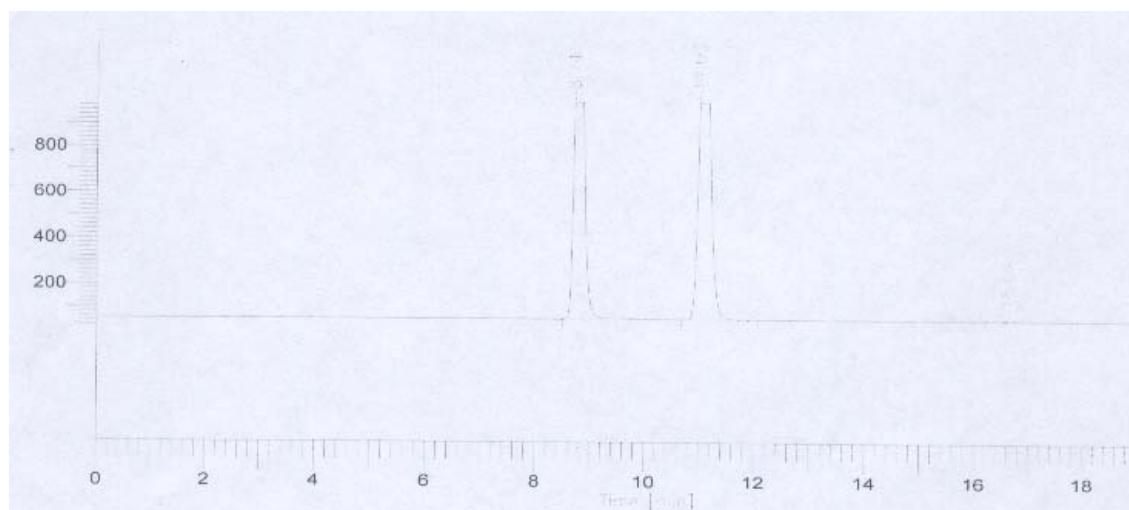


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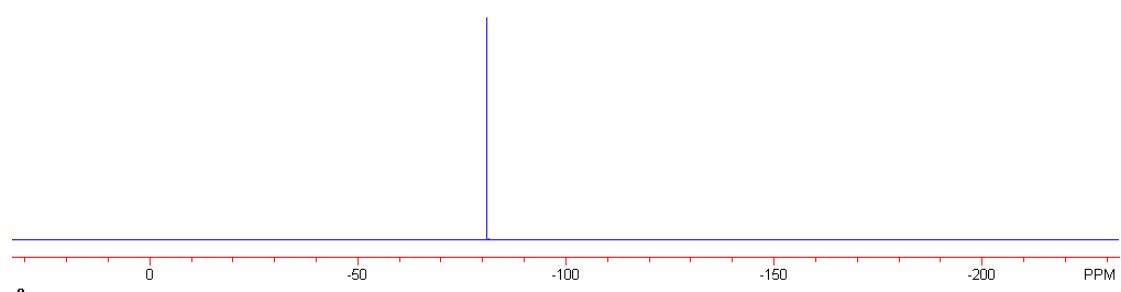
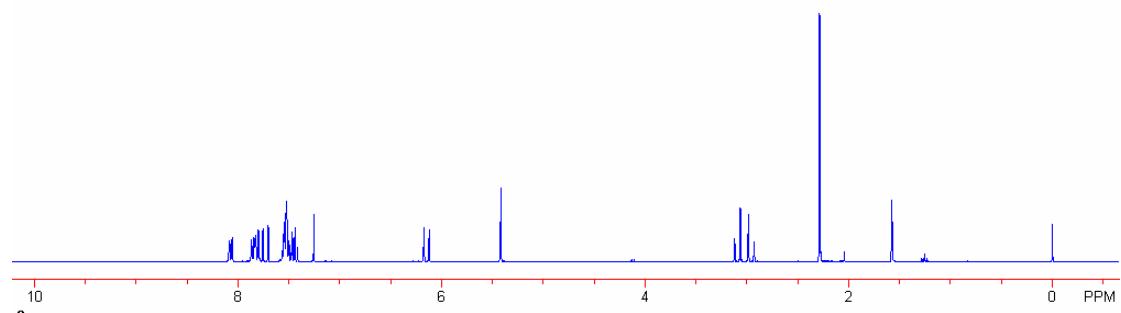
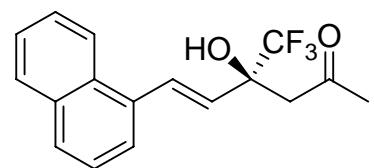


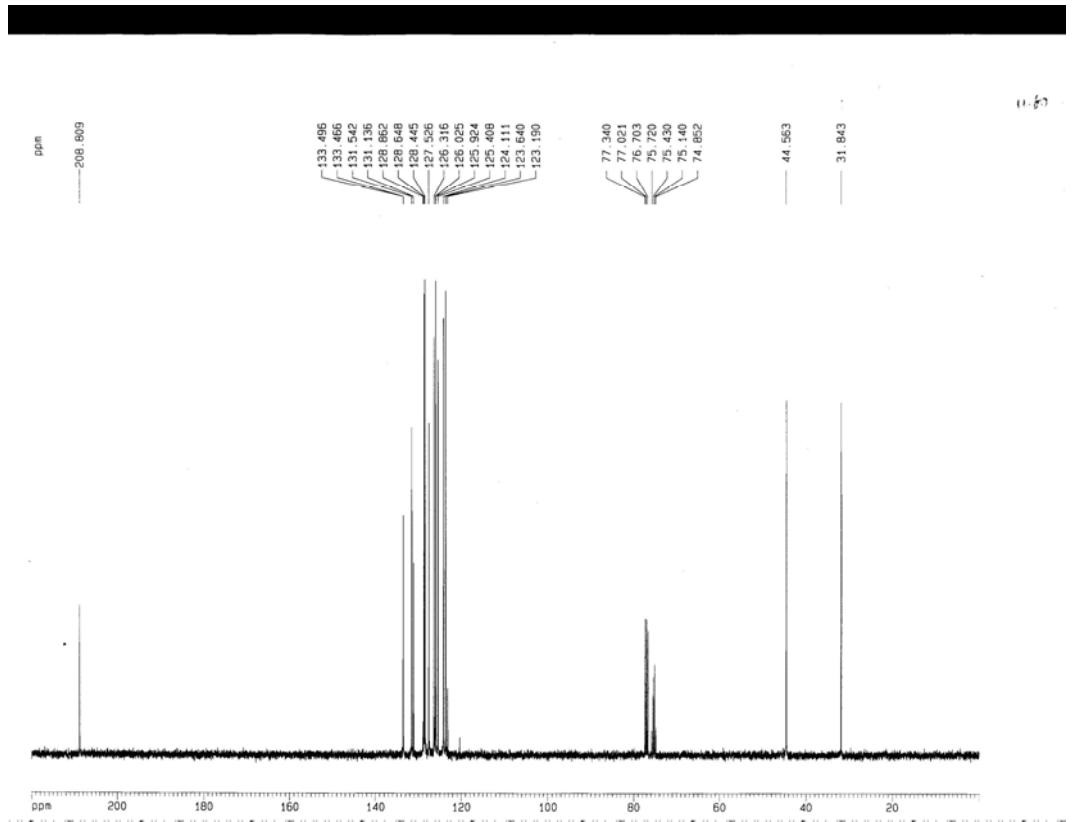


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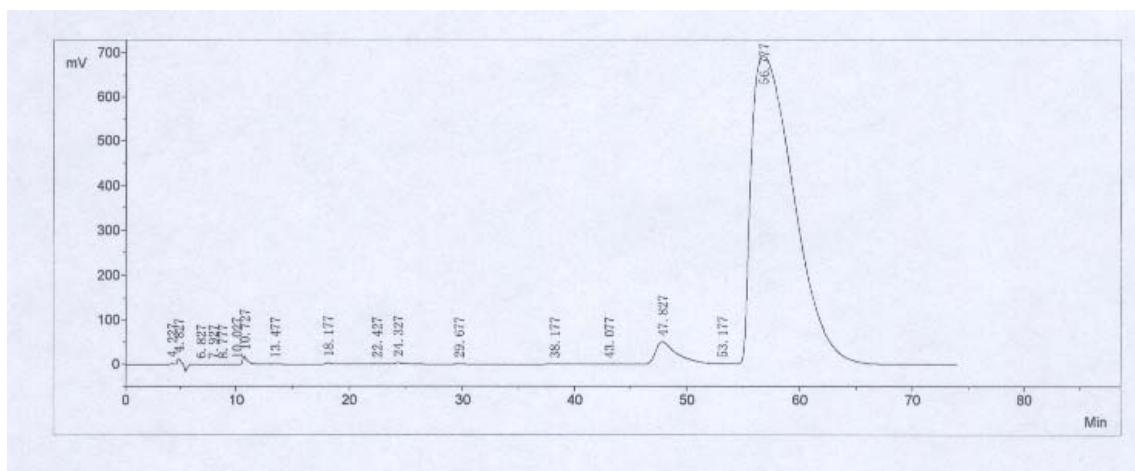
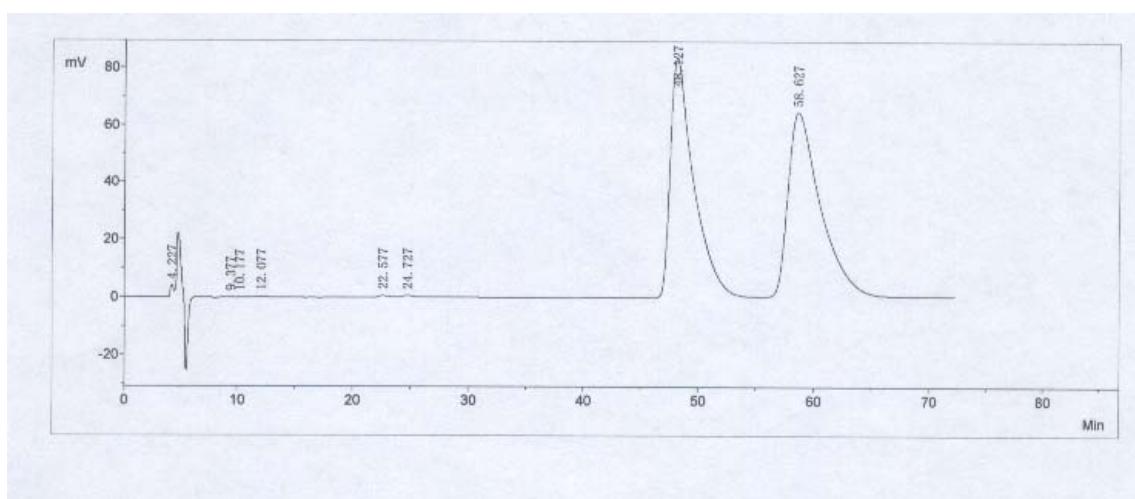


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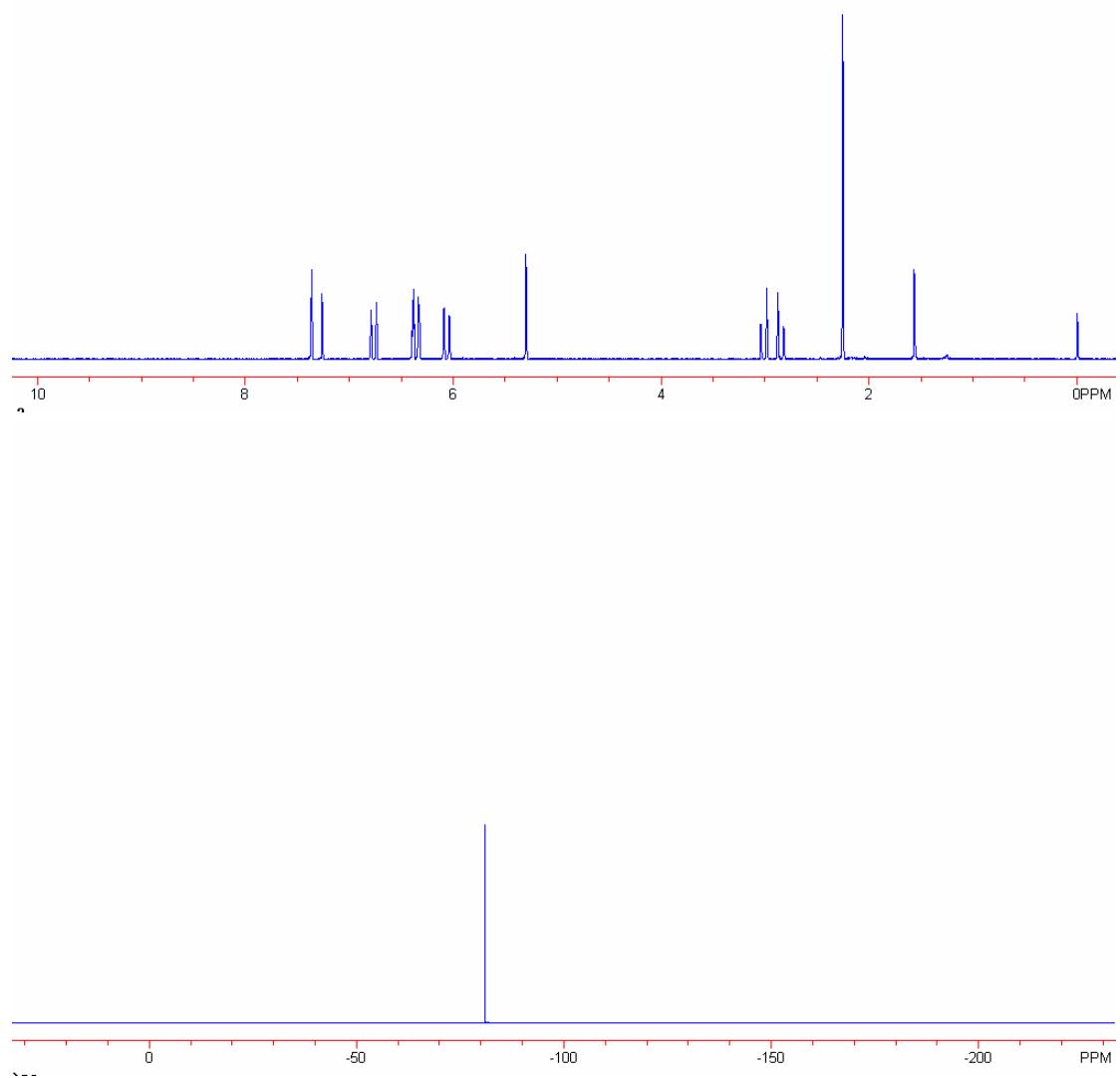
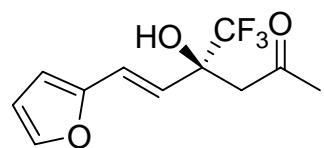


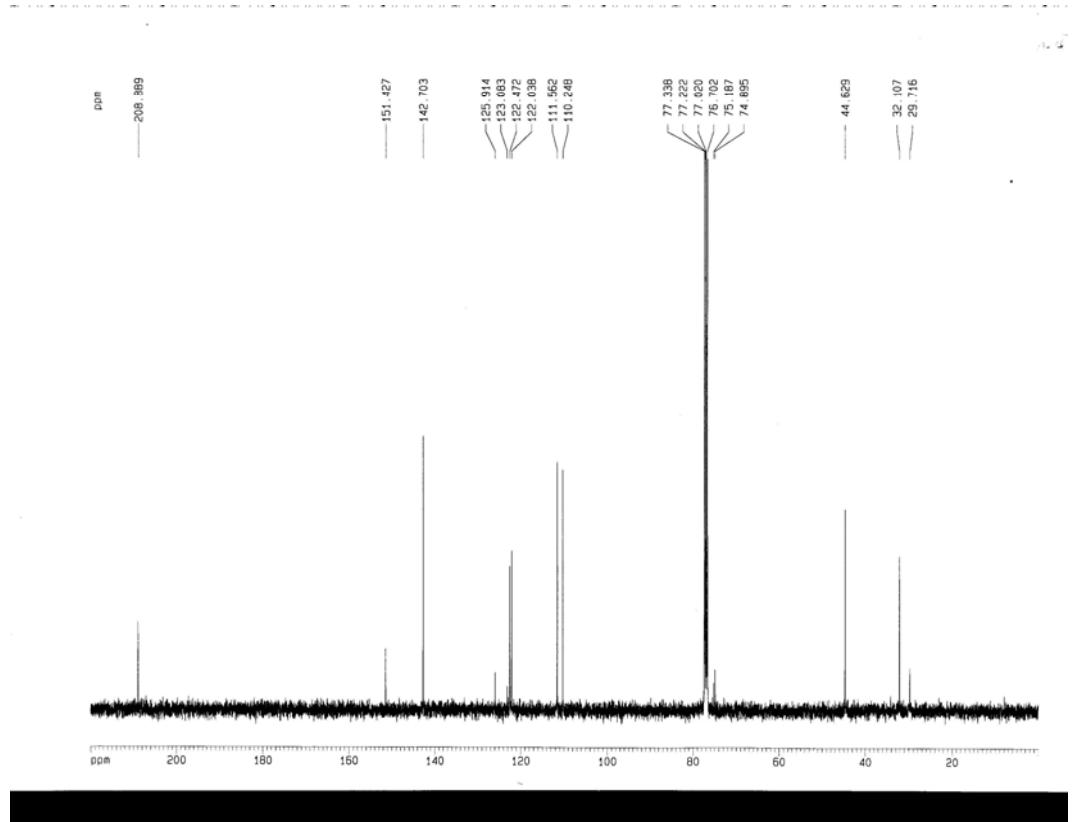


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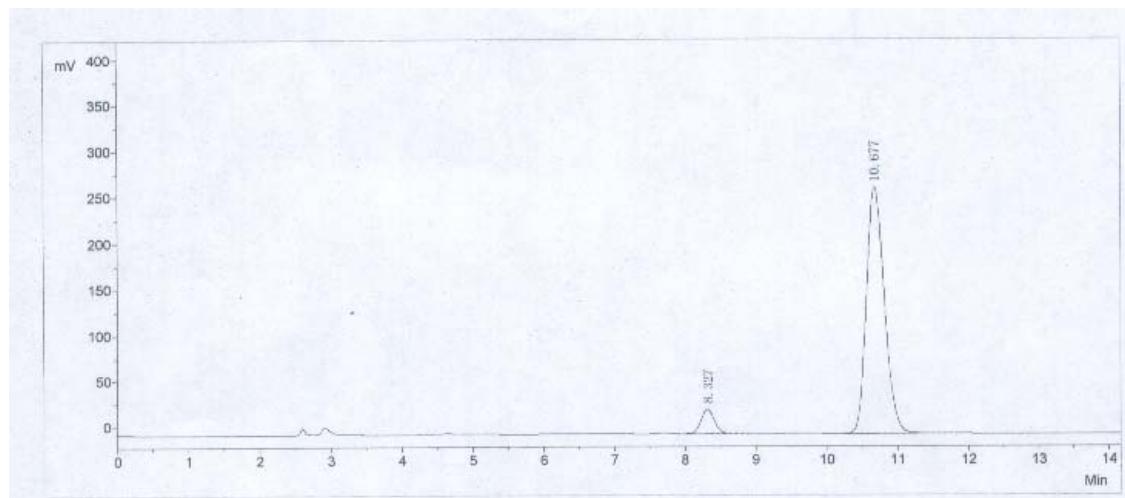
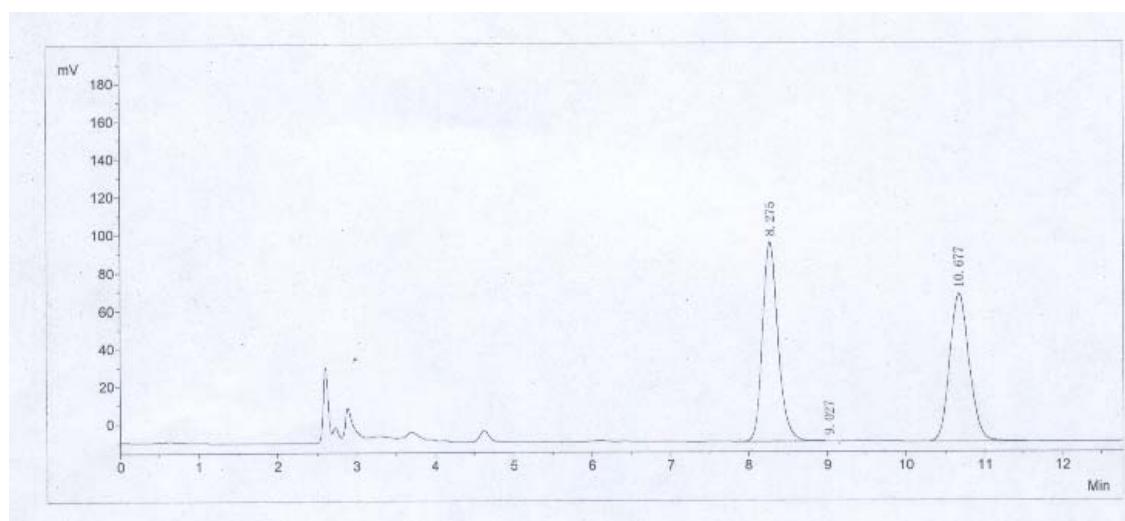


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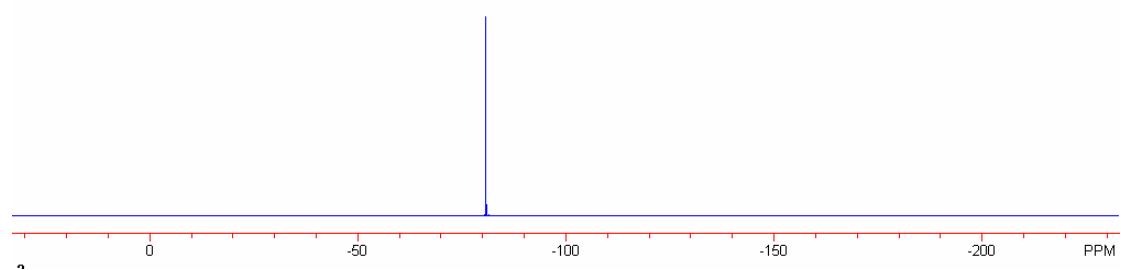
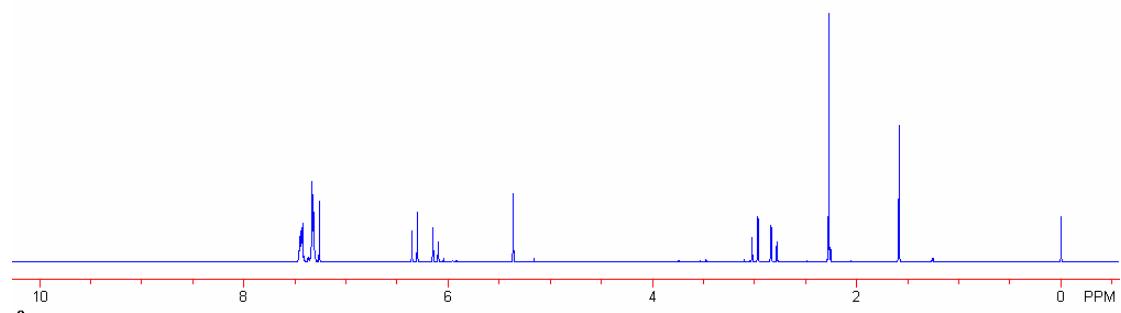
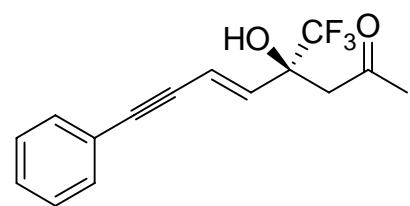


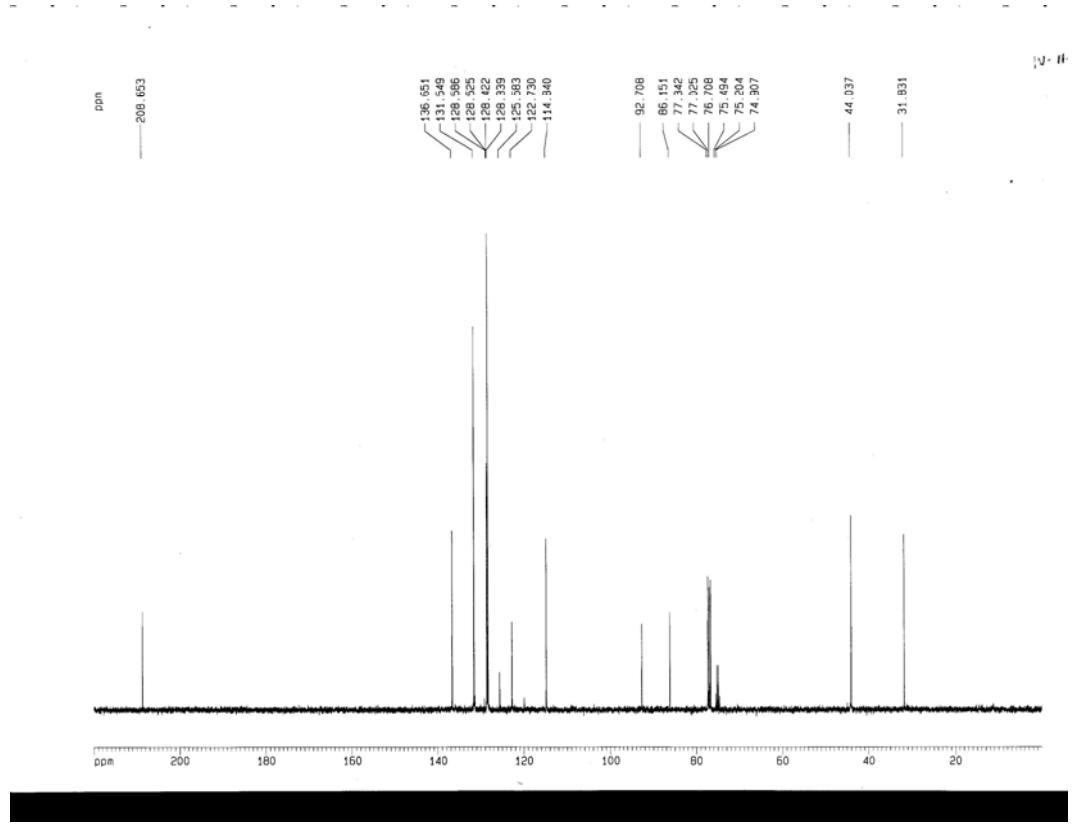


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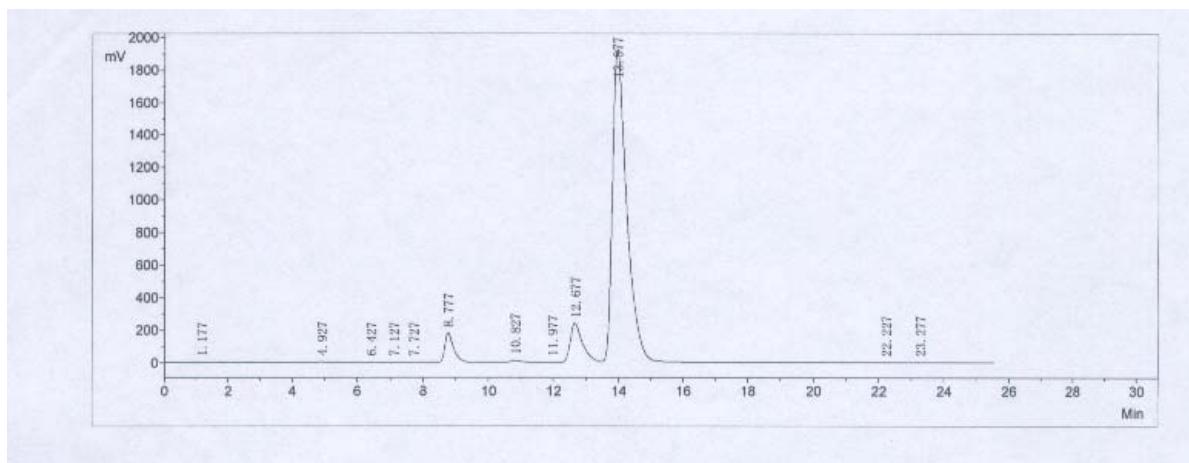
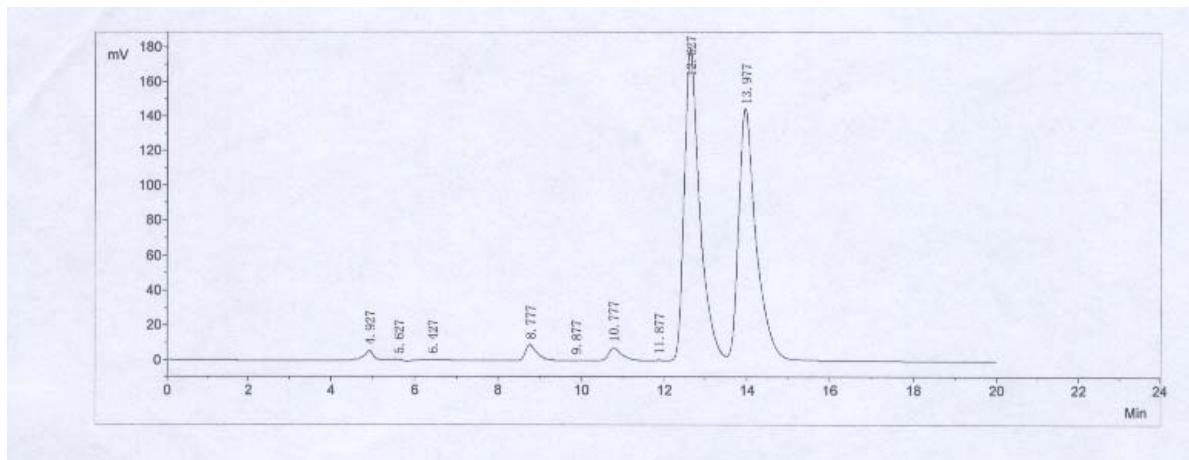


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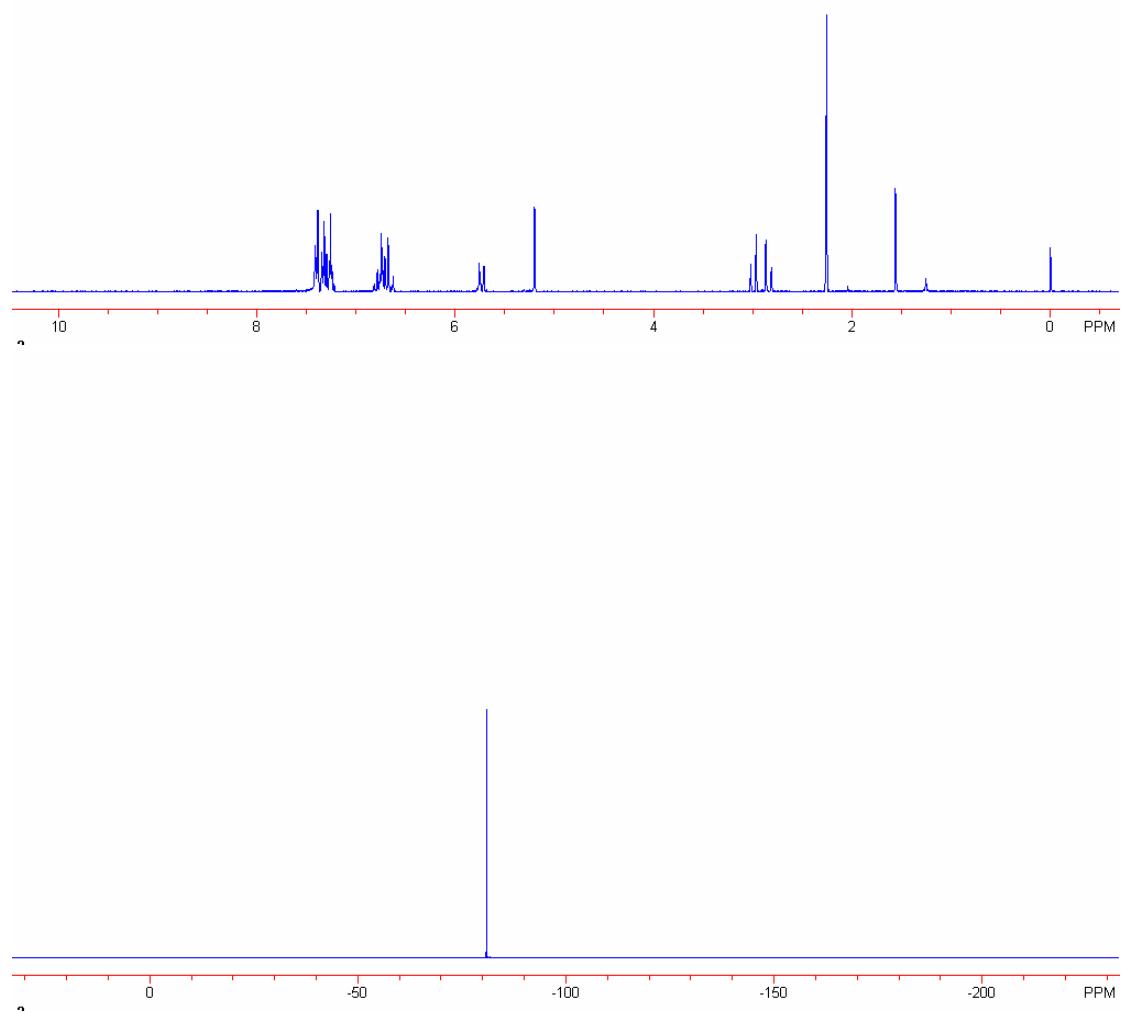
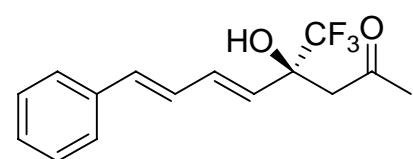


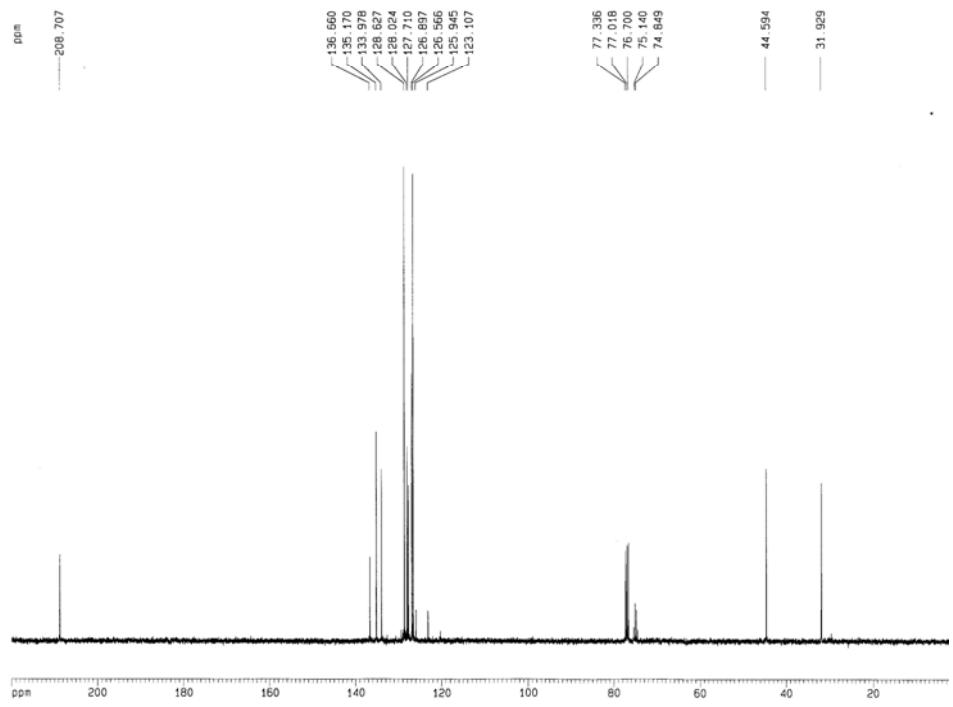


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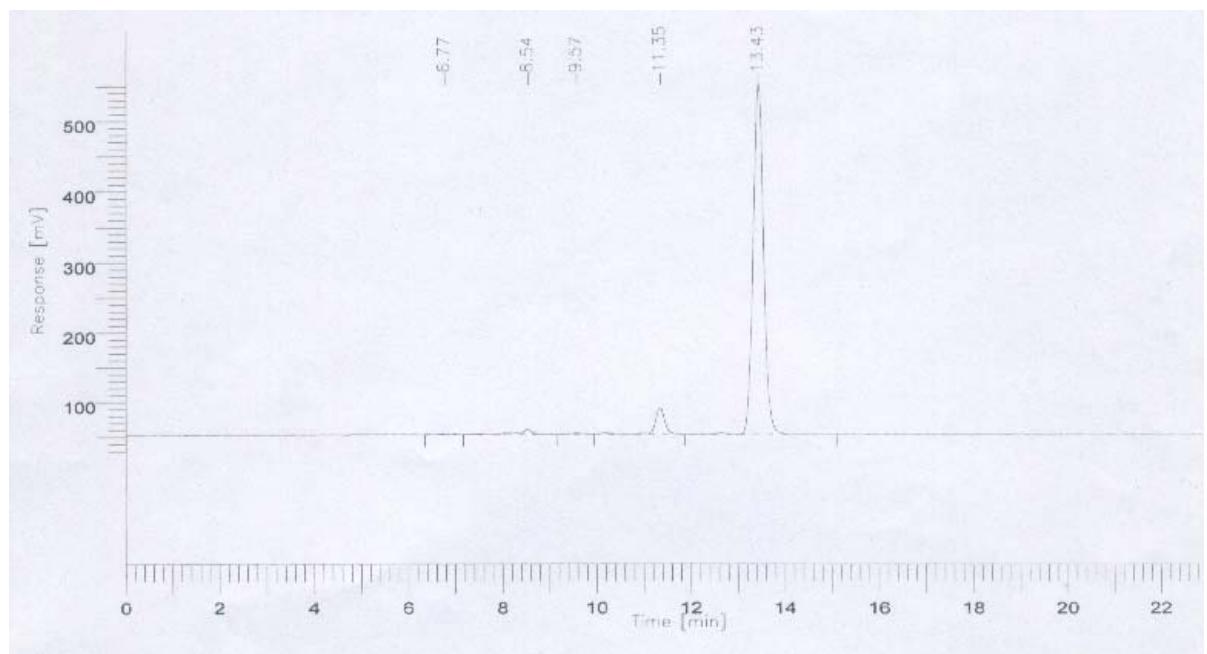
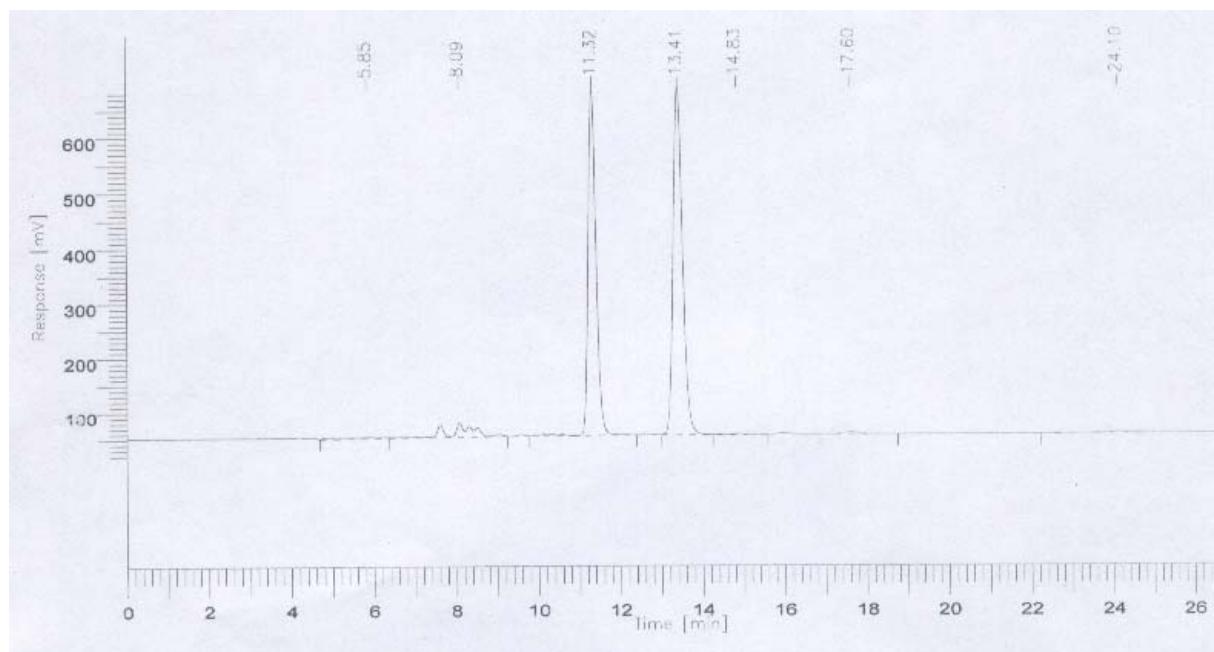


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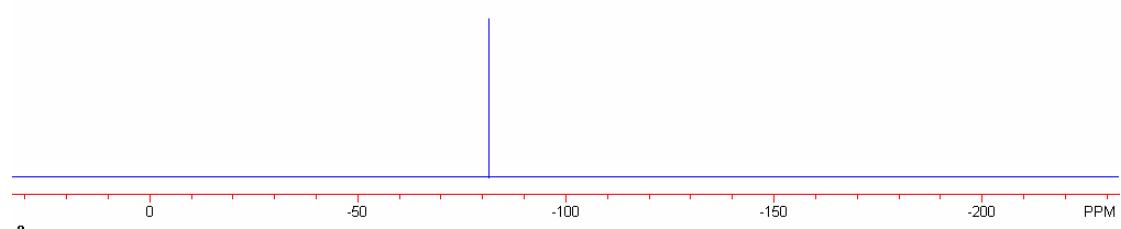
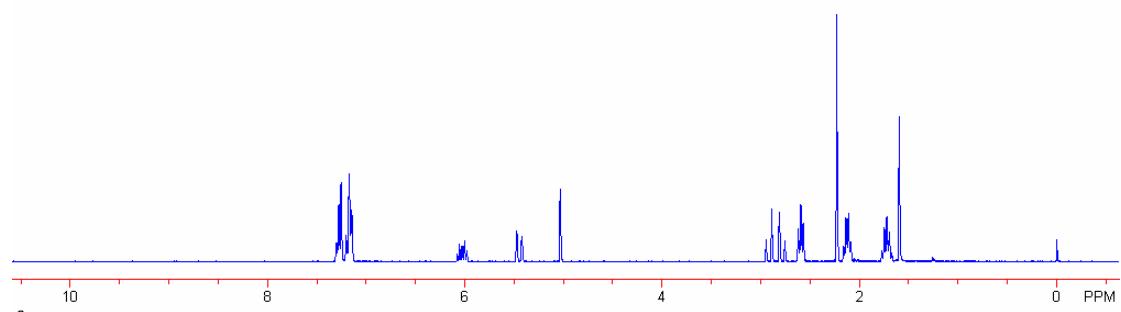
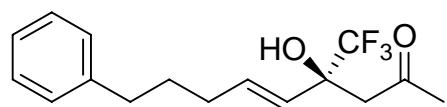


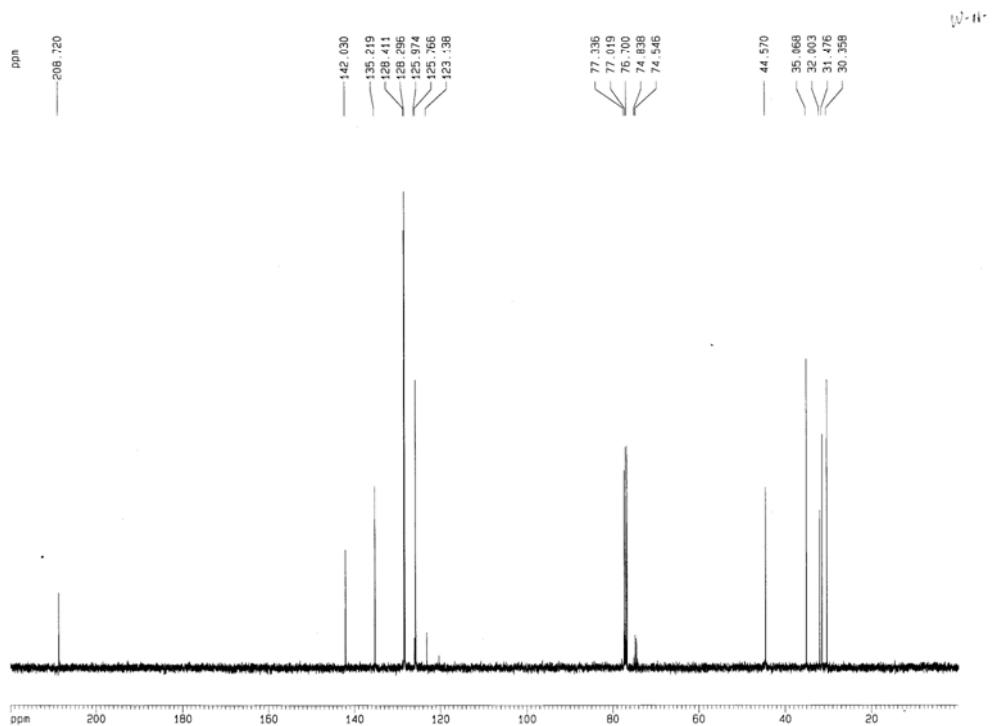


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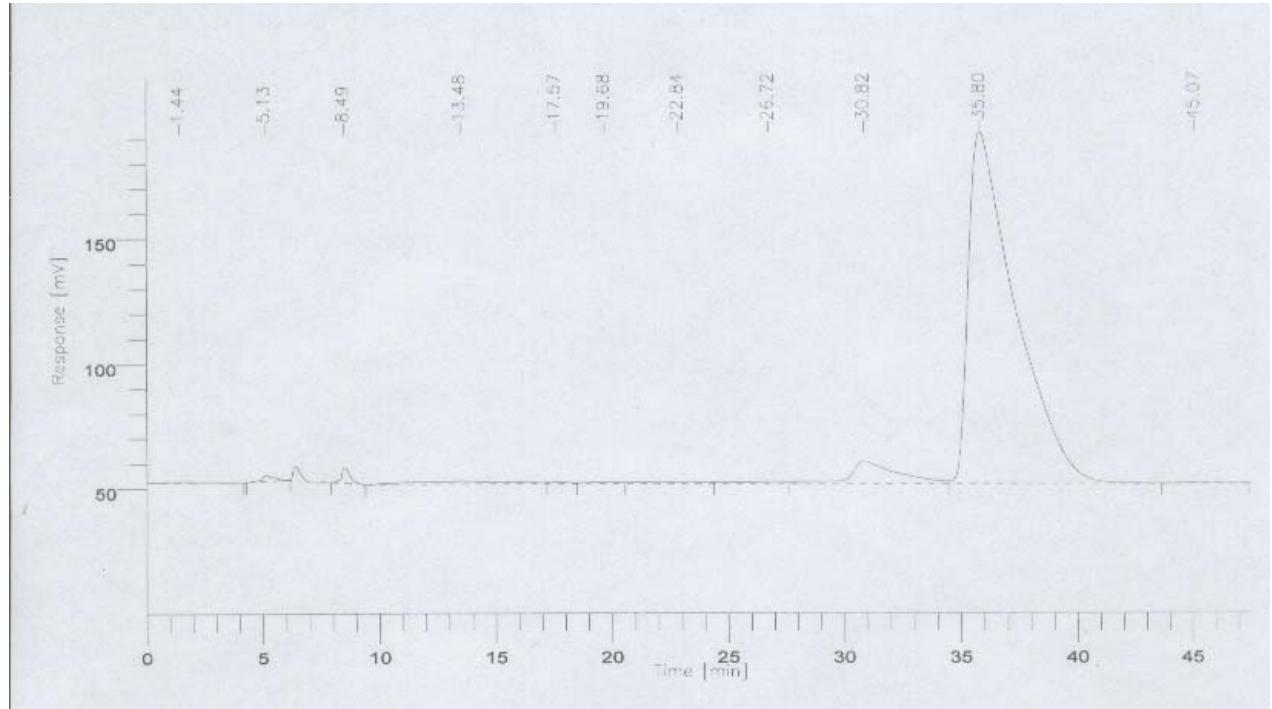
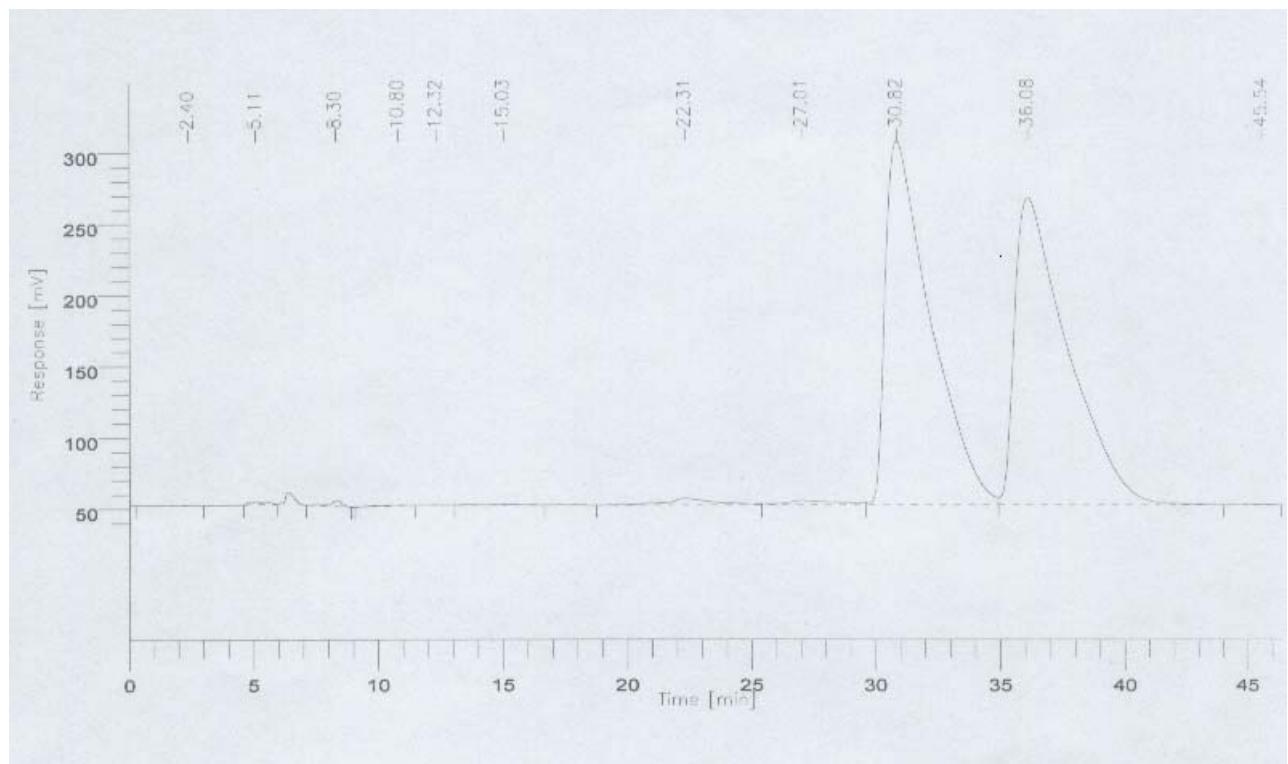


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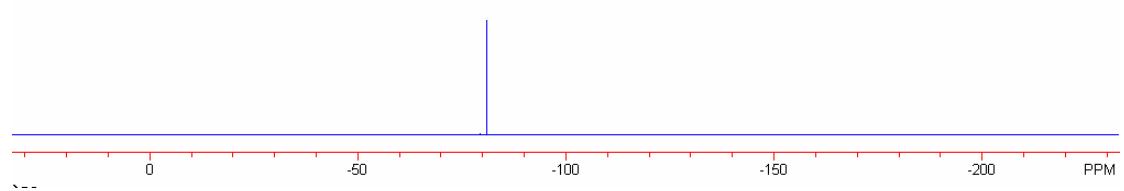
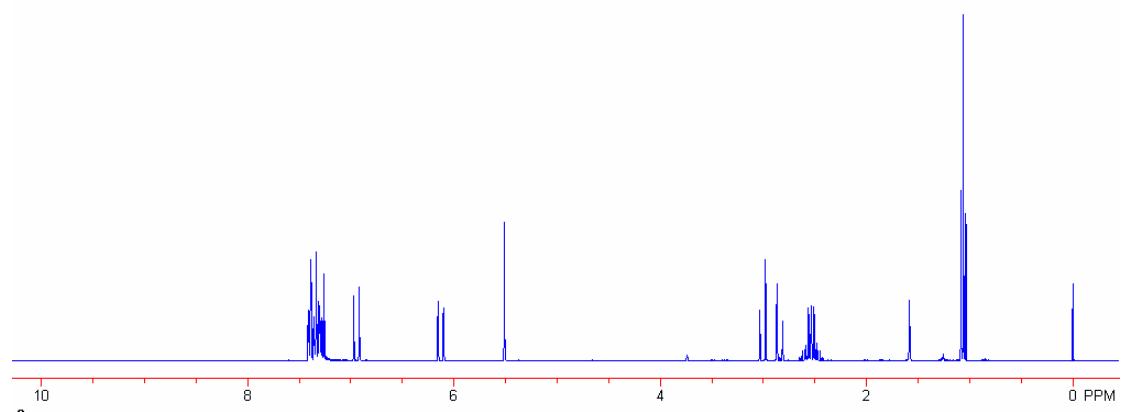
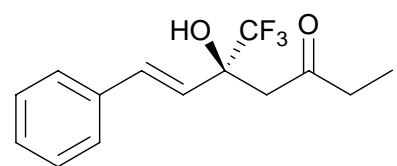


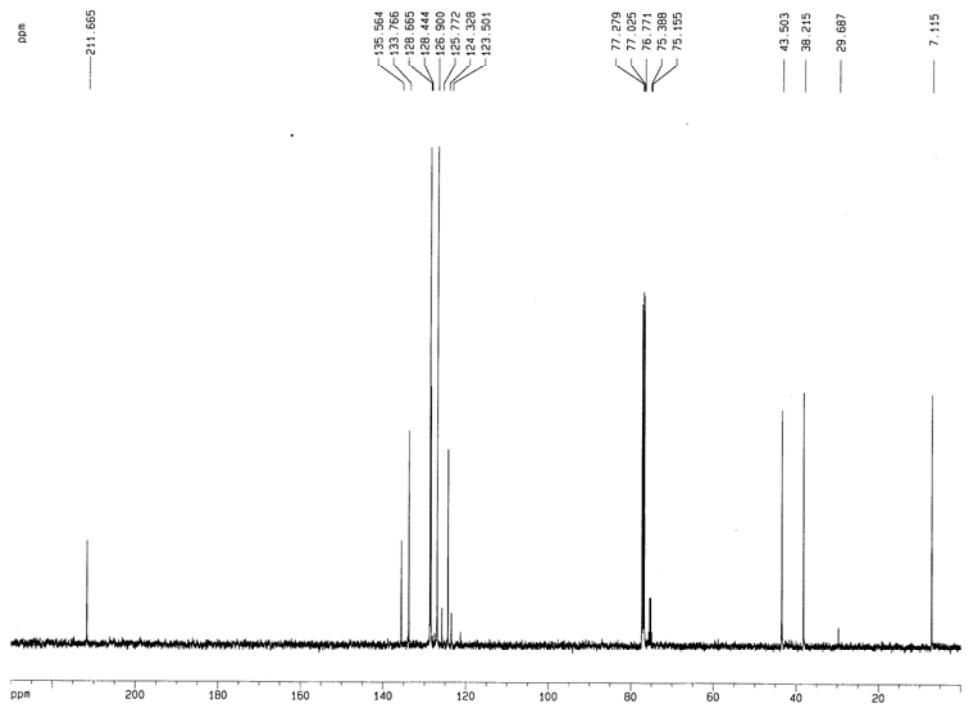


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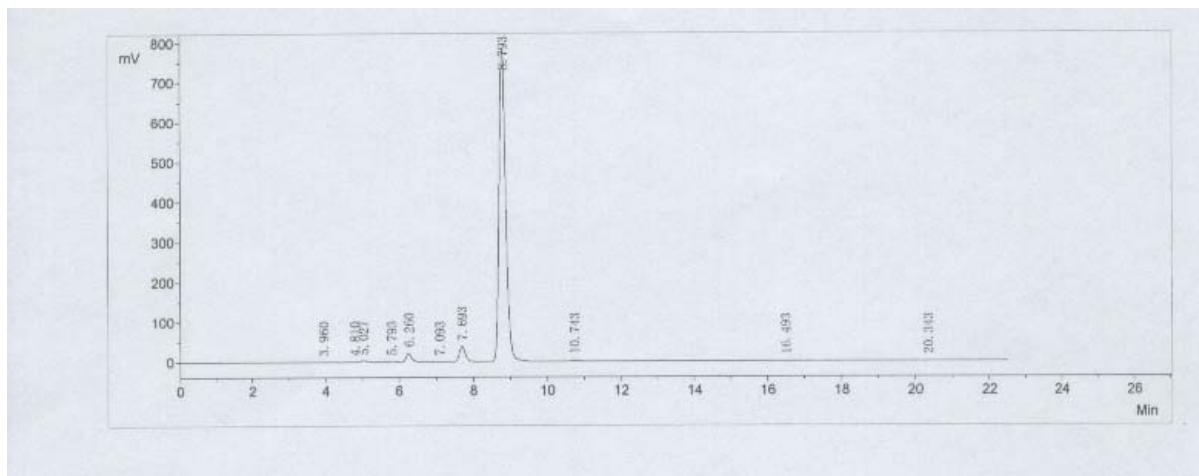
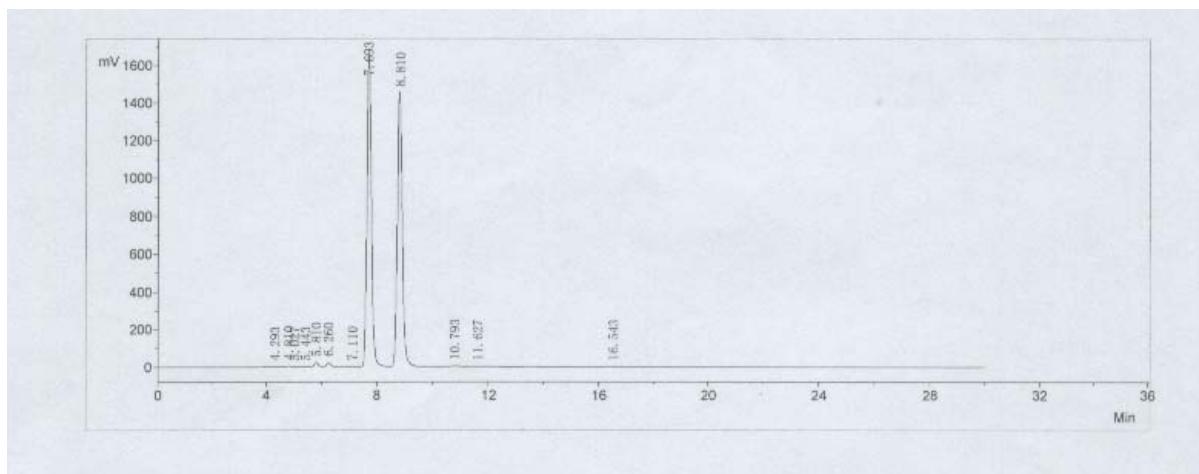


3m

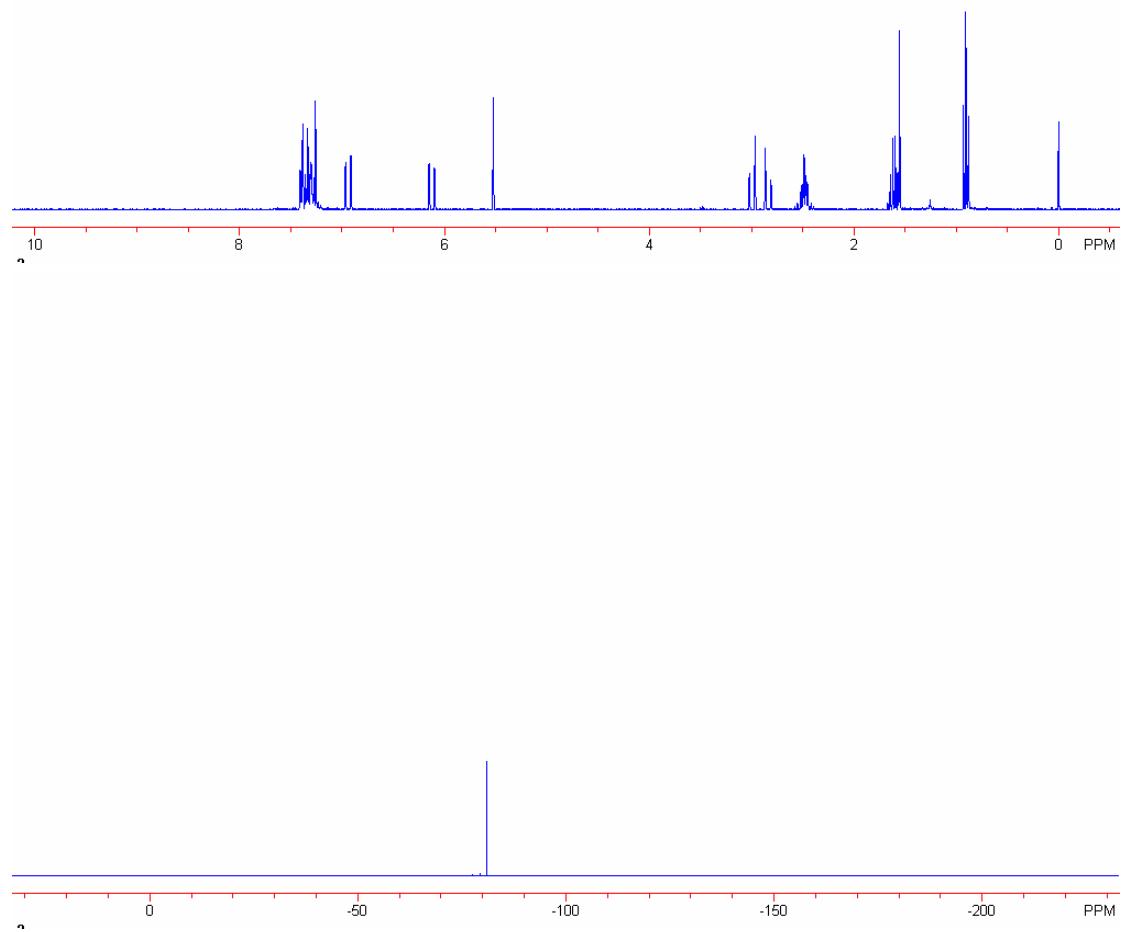
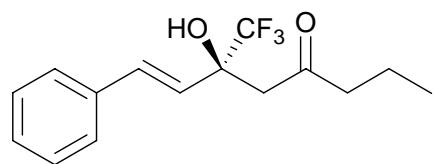


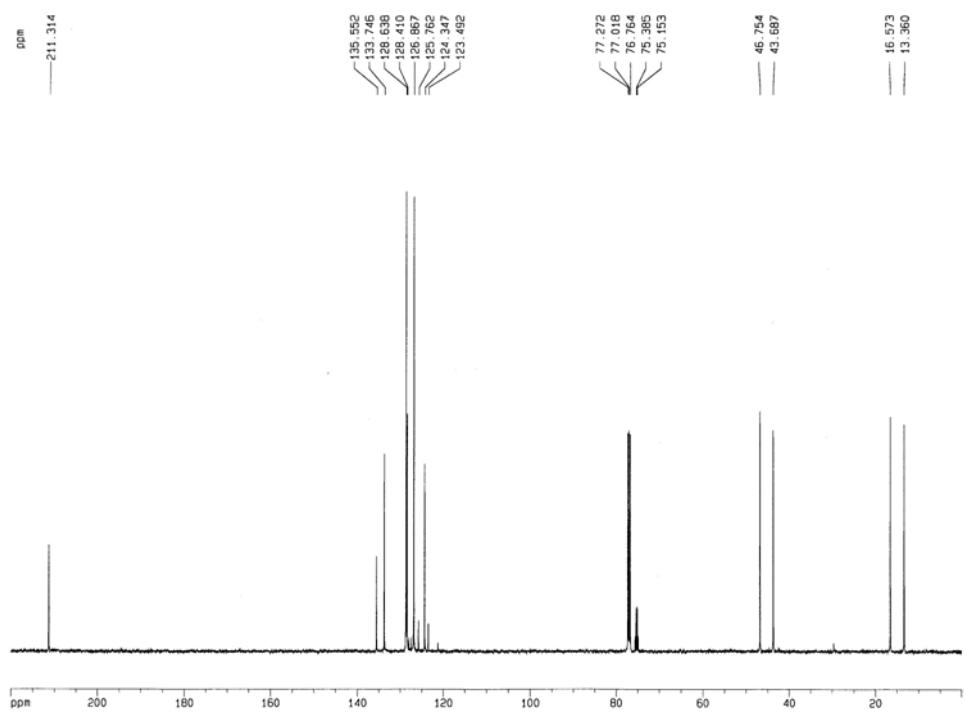


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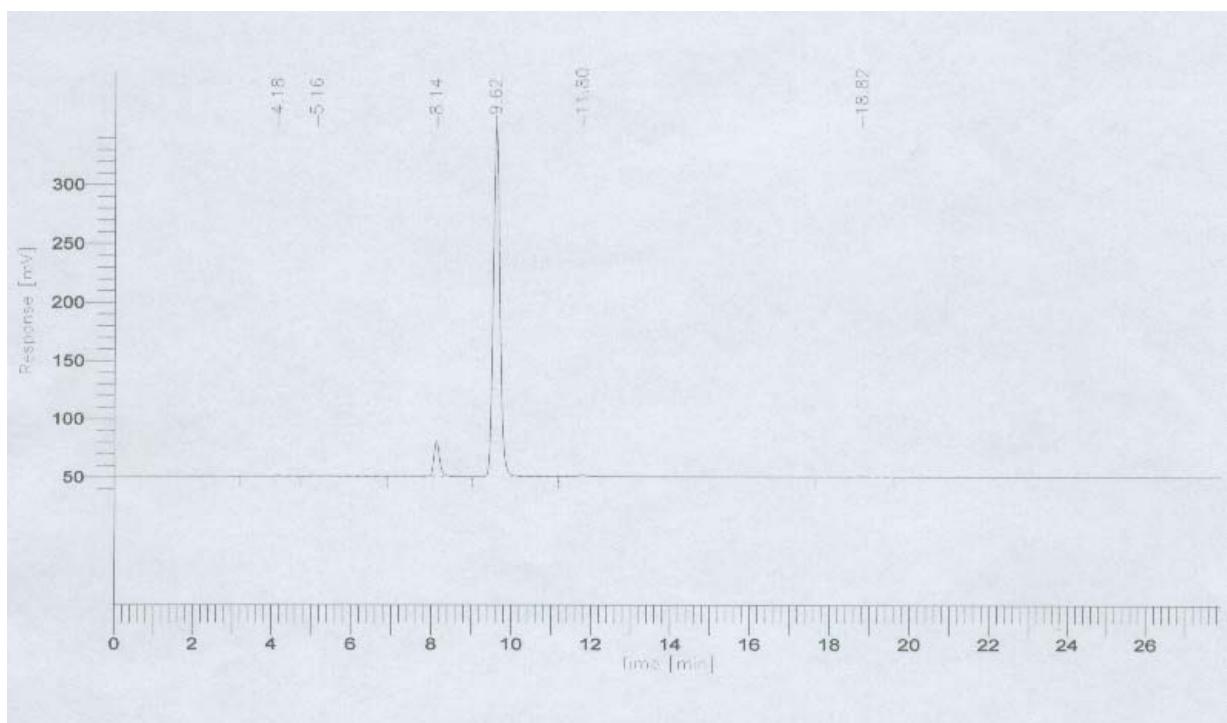
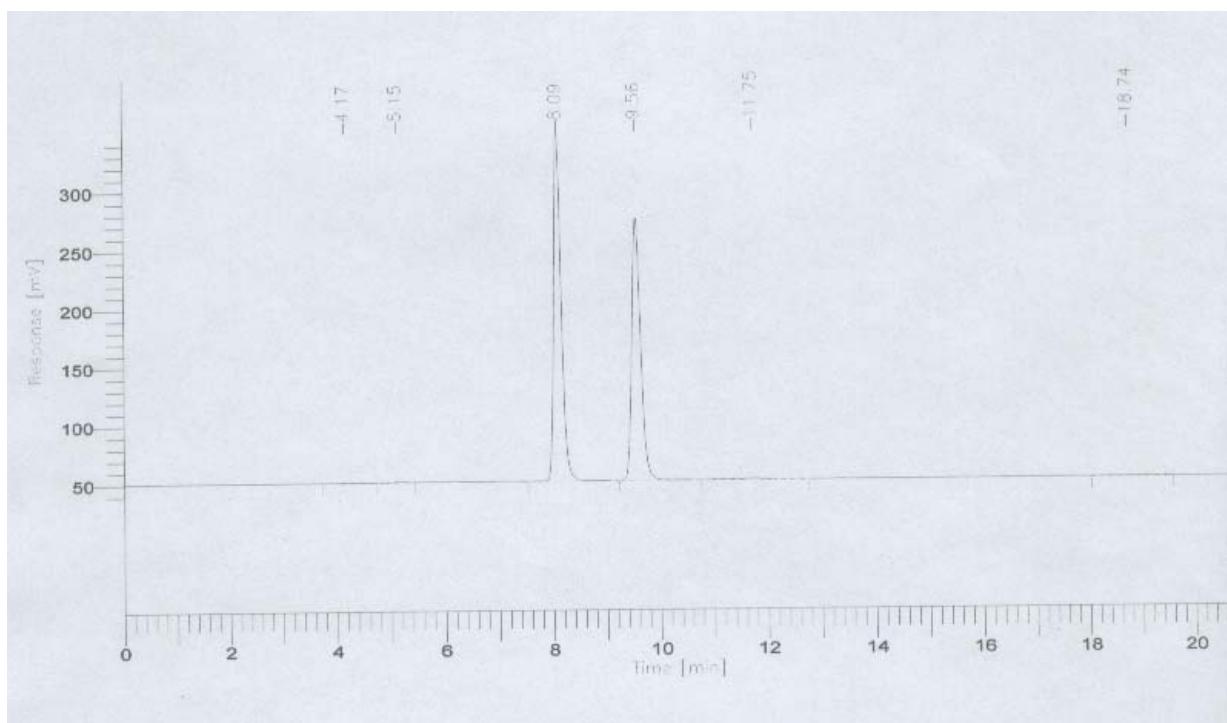


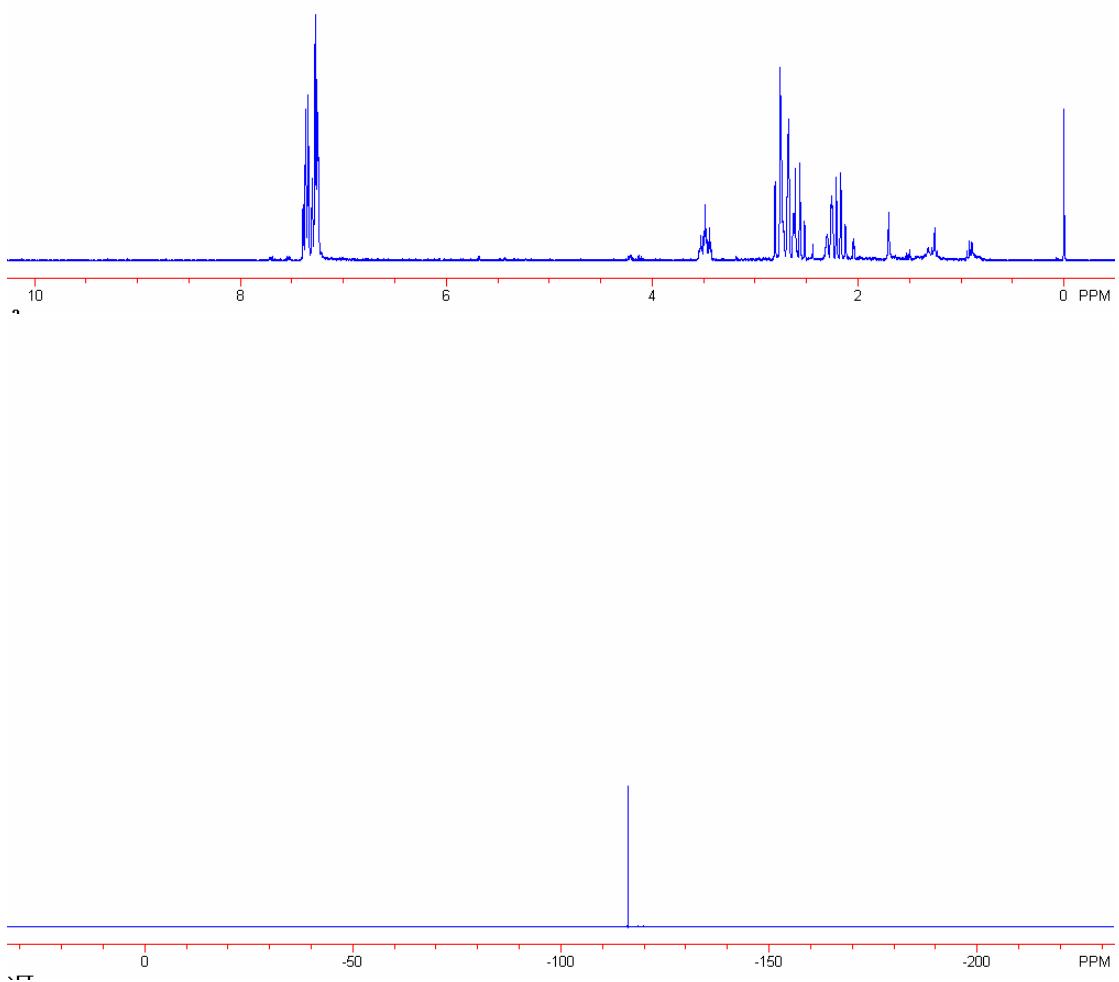
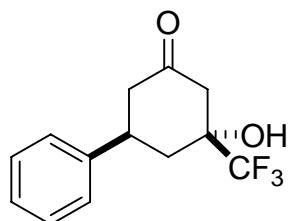
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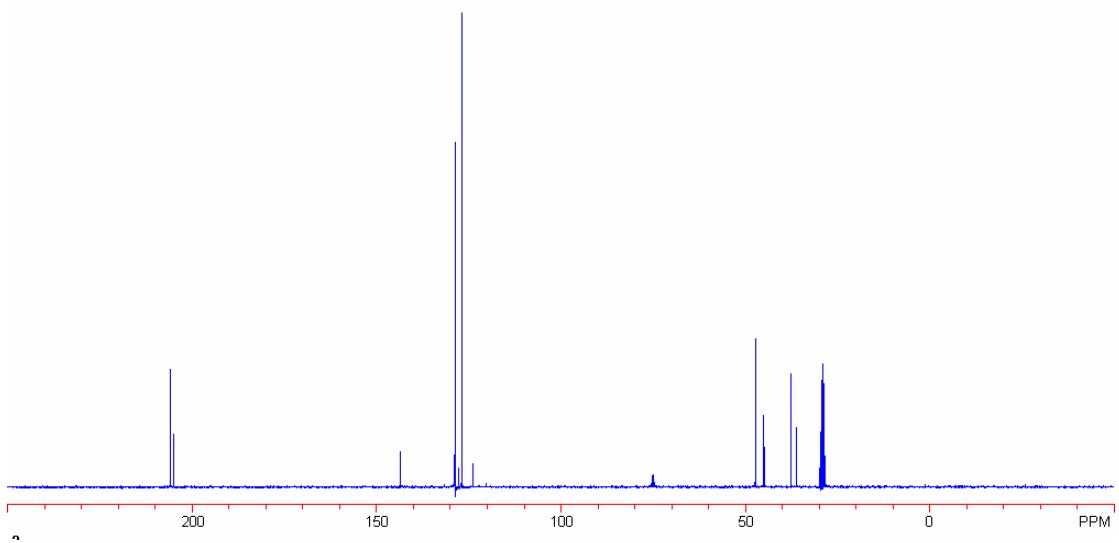




3n (HPLC)







Reference

- [1] (a) Andrew, R. J.; Mellor, J. M. *Tetrahedron* **2000**, *56*, 7261~7266. (b) Nenajdenko, V. G.; Smolko, K. I.; Balenkova, E. S. *Tetrahedron: Asymmetry* **2001**, *12*, 1259~1266. (c) Mead, D.; Loh, R.; Asato, A. E.; Liu, R. S. H. *Tetrahedron Lett.* **1985**, *26*, 2873~2876. (d) Martins, M. A. P.; Emmerich, D. J.; Pereira, C. M. P.; Cunico, W.; Rossato, M.; Zanatta, N.; Bonacorso, H. G. *Tetrahedron Lett.* **2004**, *45*, 4935~4938.
- [2] (a) Cobb, A. J. A.; Shaw, D. M.; Longbottom, D. A.; Gold, J. B.; Ley, S. V. *Org. Biomol. Chem.* **2005**, *3*, 84~96. (b) Tang, Z.; Yang, Z. H.; Hua, X. H.; Cun, L. F.; Mi, A. Q.; Yao, Y. Z.; Gong, L. Z. *J. Am. Chem. Soc.* **2005**, *127*, 9285~9289. (c) Berkessel, A.; Koch, B.; Lex, J. *Adv. Synth. Catal.* **2004**, *346*, 1141~1146. (d) Wang, W.; Mei, Y.; Li, H.; Wang, J. *Org. Lett.* **2005**, *7*, 601~604.
- [3] CCDC-619907 (**2a**) and CCDC-619908 (**3c**) contain the supplementary crystallographic data for this paper. These data can be obtained free of charge via www.ccdc.cam.ac.uk/conts/retrieving.html (or from the Cambridge Crystallographic Data Center, 12, Union Road, Cambridge CB21EZ, UK; Fax; (+44) 1223-336-033; or deposit@ccdc.cam.ac.uk).