

Supporting Information

Highly Enantioselective Michael Addition of Cyclopentanone with Chalcones Via Novel Di-imine Mechanism

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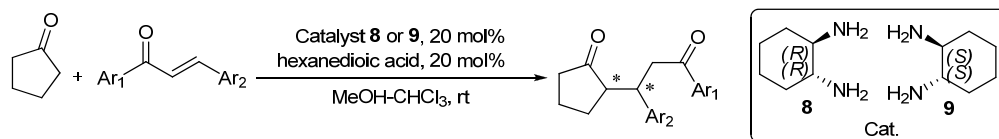
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General Information

Unless otherwise stated, all reagents were purchased from commercial suppliers and were used without further purification. Reactions were monitored by thin layer chromatography (TLC) on GF₂₅₄ silica gel plates. ¹H NMR spectra and ¹³C NMR spectra were recorded on a JEOL JNM-AL300 (300 MHz) spectrometer in needful D-reagents with tetramethylsilane (TMS) as an internal reference. Data for ¹H NMR are reported as follows: chemical shift (ppm), and multiplicity (s = singlet, d = doublet, t = triplet, dd = double of doublet, br = broad, m = multiplet), coupling constants (Hz) and integration; Data for ¹³C NMR are reported as ppm. Melting points were measured on an X₄-type micro-melting point apparatus and were uncorrected. HPLC analyses were performed using a Daicel ChiralPak AD or AS column purchased. Crystal structure determination of the Michael product **M-13b** was carried out on a Bruker Smart Apex-II CCD diffractometer. Optical rotations were measured on a AA-10R automatic polarimeter and are reported as follows: [α]_D²⁵ (c in g per 100 mL of solvent).

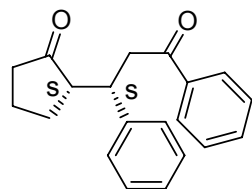
General procedure for the Michael reactions:



To a mixture of cyclopentanone (1.0 mmol), a chalcone (0.5 mmol) and chiral catalyst 1,2-diaminocyclohexane **8** or **9** (0.1 mmol) in 0.6 ml of CHCl₃ was added the acid additive (0.1 mmol of hexanedioic acid prepared in 0.6 ml of anhydrous CH₃OH). The resulting mixture was stirred under room temperature in dark for 6 days and then directly purified by silica gel chromatography, and fractions were collected and concentrated in vacuo to provide a solid or clear oil.

Scope of the Michael addition reaction:

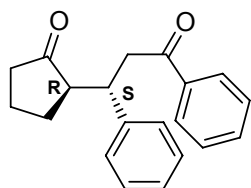
(S)-2-((S)-3-oxo-1,3-diphenylpropyl)cyclopentanone M-1: obtained in 69% yield;



colorless oil; ¹H NMR (300 MHz, CDCl₃): δ 7.97 (d, *J* = 7.2 Hz, 2H), 7.54 (tri, *J* = 7.2 Hz, 1H), 7.44 (tri, *J* = 7.2 Hz, 2H), 7.27-7.19 (m, 5H), 3.85-3.73 (m, 2H), 3.47 (dd, *J* = 10.2 Hz, 20.1 Hz, 1H), 2.50 (m, 1H), 2.24 (dd, *J* = 7.5 Hz, 18.3 Hz, 1H),

2.20-2.09 (m, 1H), 1.99-1.86 (m, 1H), 1.81-1.65 (m, 3H); HPLC (AD, hexane:*i*-PrOH 50:50, 1.0 mL/min): t_R 6.22 min (major enantiomer), 7.02 min (minor enantiomer); ee 98.5%; [α]_D²⁵ = +55 (*c* = 1.4, CHCl₃).

(R)-2-((S)-3-oxo-1,3-diphenylpropyl)cyclopentanone M-1: ¹H NMR (300 MHz,

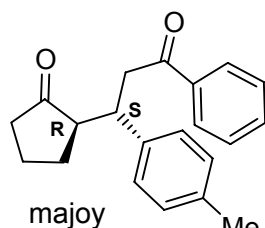
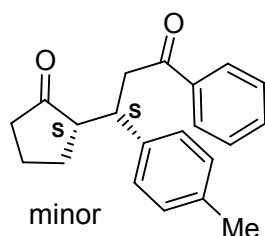


CDCl₃): δ 7.91 (d, *J* = 7.2 Hz, 2H), 7.53 (tri, *J* = 7.2 Hz, 1H), 7.42 (tri, *J* = 7.5 Hz, 2H), 7.29-7.17 (m, 5H), 3.87 (dd, *J* = 6.3 Hz, 16.5 Hz, 1H), 3.70 (dd, *J* = 7.5 Hz, 14.4 Hz, 1H), 3.36 (dd, *J* = 7.5 Hz, 16.8 Hz, 1H), 2.46 (dd, *J* = 8.7 Hz, 17.1 Hz, 1H),

2.27-2.21 (m, 1H), 2.06 (dd, *J* = 9.0 Hz, 18.6 Hz, 1H), 1.90-1.87 (m, 2H), 1.75-1.65

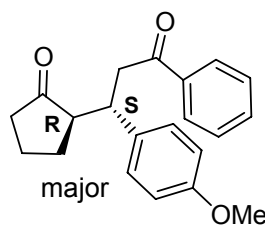
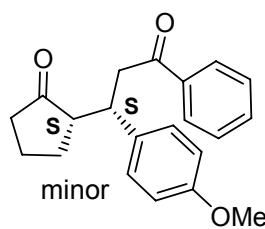
(m, 1H), 1.59-1.51 (m, 1H); HPLC (AD, hexane:*i*-PrOH 50:50, 1.0 mL/min): t_R 8.16 min (major enantiomer), 12.52 min (minor enantiomer); ee 97.4%; $[\alpha]_D^{25} = -46$ ($c = 1.2$, CHCl₃).

2-(3-Oxo-3-phenyl-1-*p*-tolylpropyl)cyclopentanone M-2: obtained in 73% yield;



white solid; m.p. 56-57°C; ¹H NMR (300 MHz, CDCl₃): δ 7.92 (d, $J = 8.4$ Hz, 2H), 7.53 (tri, $J = 7.5$ Hz, 1H), 7.42 (tri, $J = 7.5$ Hz, 2H), 7.11-7.08 (m, 4H), 3.84 (dd, $J = 6.0$ Hz, 16.5 Hz, 1H), 3.66 (dd, $J = 7.5$ Hz, 15.0 Hz, 1H), 3.33 (dd, $J = 7.5$ Hz, 16.5 Hz, 1H), 2.43 (dd, $J = 8.4$ Hz, 16.8 Hz, 1H), 2.29 (s, 3H), 2.29-2.20 (m, 1H), 2.13-2.01 (m, 1H), 1.89-1.87 (m, 2H), 1.74-1.67 (m, 1H), 1.58-1.52 (m, 1H); HPLC (AD, hexane:*i*-PrOH 50:50, 1.0 mL/min): dr 1:2; t_R 8.51 min (major enantiomer), 11.20 min (minor enantiomer); ee 98.3%; t_R 11.88 min (major enantiomer), 22.13 min (minor enantiomer); ee 97.2%; $[\alpha]_D^{25} = -23$ ($c = 1.2$, CHCl₃).

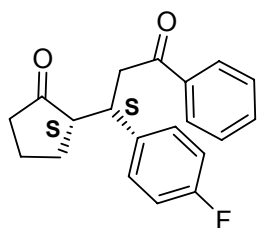
2-(1-(4-Methoxyphenyl)-3-oxo-3-phenylpropyl)cyclopentanone M-3: Obtained in



43% yield; colorless oil; ¹H NMR (300 MHz, CDCl₃): δ 7.98-7.89 (dd, $J = 7.2$ Hz, 15.6 Hz, 1.99H), 7.53-7.38 (m, 3.05H), 7.26-7.14 (m, 2.01H), 6.89-6.80 (m, 2.00H), 4.33 (dd, $J = 7.2$ Hz, 12.0 Hz, 0.61H), 4.03 (dd, $J = 4.8$ Hz, 16.8 Hz, 0.38H), 3.79 (s, 3.42H), 3.66 (dd, $J = 7.2$ Hz, 16.8 Hz, 0.63H), 3.47-3.38 (m, 1.02H), 2.68-2.55 (m, 1.00H), 2.29-2.20 (m, 1.42H), 2.09-1.93 (m, 1.79H), 1.88-1.60 (m, 3.08H), 1.53-1.44 (m, 0.45H); HPLC (AS, hexane:*i*-PrOH 80:20, 1.0 mL/min): dr 2:1; t_R 6.97 min (minor enantiomer), 12.45 min (major enantiomer); ee 95.8%; t_R 8.37 min (major enantiomer), 8.98 min (minor enantiomer); ee 97.8%; $[\alpha]_D^{25} = +27$ ($c = 1.1$, CHCl₃).

(S)-2-((S)-1-(4-fluorophenyl)-3-oxo-3-phenylpropyl)cyclopentanone M-4:

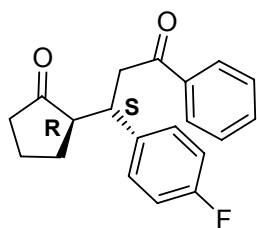
obtained in 83% yield; white solid; m.p. 82-83°C; ^1H NMR (300 MHz, CDCl_3): δ



7.96 (d, $J = 7.2$ Hz, 2H), 7.55 (tri, $J = 7.5$ Hz, 1H), 7.45 (tri, $J = 7.5$ Hz, 2H), 7.21 (dd, $J = 5.4$ Hz, 8.4 Hz, 2H), 6.95 (tri, $J = 8.4$ Hz, 2H), 3.82-3.73 (m, 2H), 3.47 (dd, $J = 9.6$ Hz, 19.2 Hz, 1H), 2.53-2.48 (m, 1H), 2.30-2.12 (m, 2H), 1.98-1.58 (m, 4H);

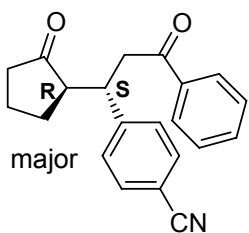
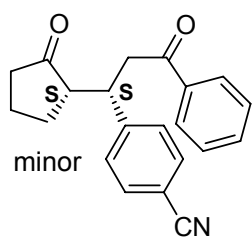
^{13}C NMR (75 MHz, CDCl_3): δ 220.5, 198.8, 163.2 (d, $^1J_{\text{C-F}} = 242.9$ Hz), 160.0, 137.9, 136.9, 133.1, 130.0, 129.9, 128.6, 128.1, 115.4, 115.1, 53.1, 41.1, 40.3, 39.7, 27.2, 20.5; HPLC (AD, hexane:*i*-PrOH 50:50, 1.0 mL/min): t_{R} 6.44 min (major enantiomer), 7.96 min (minor enantiomer); ee >99%; $[\alpha]_{\text{D}}^{25} = +27$ ($c = 0.5$, CHCl_3).

(R)-2-((S)-1-(4-fluorophenyl)-3-oxo-3-phenylpropyl)cyclopentanone M-4:



^1H NMR (300 MHz, CDCl_3): δ 7.91 (d, $J = 7.8$ Hz, 2H), 7.54 (tri, $J = 7.5$ Hz, 1H), 7.43 (tri, $J = 7.5$ Hz, 2H), 7.18 (dd, $J = 6.0$ Hz, 7.5 Hz, 2H), 6.95 (tri, $J = 8.4$ Hz, 2H), 3.85 (dd, $J = 6.0$ Hz, 17.1 Hz, 1H), 3.69 (dd, $J = 7.8$ Hz, 16.5 Hz, 1H), 3.34 (dd, $J =$

7.5 Hz, 16.8 Hz, 1H), 2.43 (dd, $J = 9.0$ Hz, 17.1 Hz, 1H), 2.27 (dd, $J = 7.5$ Hz, 18.3 Hz, 1H), 2.05 (dd, $J = 9.0$ Hz, 18.3 Hz, 1H), 1.90 (m, 2H), 1.76-1.69 (m, 1H), 1.57-1.51 (m, 2H); HPLC (AD, hexane:*i*-PrOH 50:50, 1.0 mL/min): t_{R} 8.55 min (major enantiomer), 10.67 min (minor enantiomer); ee 98.2%; $[\alpha]_{\text{D}}^{25} = -75$ ($c = 1.7$, CHCl_3).



4-(3-Oxo-1-(2-oxocyclopentyl)-3-phenylpropyl)benzonitrile

M-5: obtained in 92% yield; white solid; m.p. 100-102°C; ^1H NMR (300 MHz, CDCl_3): δ 7.90 (d, $J = 7.5$ Hz, 2.00H), 7.56 (tri, $J = 8.1$ Hz, 2.97H), 7.43 (m, 1.99H), 7.36 (m, 2.01H), 3.94 (dd, $J = 5.1$ Hz, 17.1 Hz, 0.80H), 3.83-3.72 (m, 1.07H), 3.67-3.54 (m, 0.34H), 3.39 (dd, $J = 8.4$ Hz, 17.1 Hz, 0.80H), 2.47 (dd, $J = 8.1$ Hz, 18.0 Hz, 0.99H), 2.36-2.28 (m, 1.03H), 2.10 (dd, $J = 9.0$ Hz, 18.9 Hz, 1.12H), 1.99-1.88 (m, 2.01H), 1.80-1.68 (m, 1.24H), 1.55-1.38 (m, 0.87H); HPLC (AD, hexane:*i*-PrOH 50:50, 1.0 mL/min): dr 3:1; t_{R}

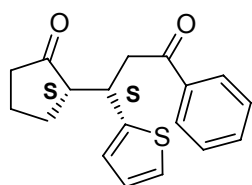
10.33 min (minor enantiomer), 24.40 min (major enantiomer); ee >99%; t_R 11.65 min (major enantiomer), 13.34 min (minor enantiomer); ee >99%; $[\alpha]_D^{25} = -32$ ($c = 1.0$, CHCl_3).

2-(1-(3-Chlorophenyl)-3-oxo-3-phenylpropyl)cyclopentanone M-6: obtained in 87% yield; colorless oil; ^1H NMR (300 MHz, CDCl_3): δ 7.94 (dd, $J = 7.2$ Hz, 14.1 Hz, 2.01H), 7.54 (dd, $J = 2.4$ Hz, 4.5 Hz, 1.00H), 7.52-7.41 (dd, $J = 5.1$ Hz, 7.8 Hz, 2.01H), 7.26-7.12 (m, 4.04H), 3.90 (dd, $J = 5.7$ Hz, 17.1 Hz, 0.55H), 3.76-3.69 (m, 1.34H), 3.49 (m, 0.40H), 3.34 (dd, $J = 7.8$ Hz, 17.1 Hz, 0.52H), 2.44 (m, 0.95H), 2.25 (m, 0.98H), 2.10 (m, 1.11H), 1.95-1.90 (m, 1.88H), 1.89-1.79 (m, 1.55H), 1.66 (m, 0.58H); ^{13}C NMR (75 MHz in CDCl_3): δ 219.8, 219.3, 198.4, 198.1, 144.7, 144.5, 136.8, 134.1, 133.1, 133.0, 129.6, 128.5, 128.2, 128.0, 127.9, 126.8, 126.7, 53.0, 52.6, 42.6, 40.5, 40.4, 40.4, 39.4, 38.7, 28.0, 27.0, 20.4, 20.1; HPLC (AD, hexane:*i*-PrOH 92:8, 1.0 mL/min): dr 2:3; t_R 12.09 min (minor enantiomer), 13.40 min (major enantiomer); ee 98.8%; t_R 18.24 min (minor enantiomer), 22.13 min (major enantiomer); ee 98.4%; $[\alpha]_D^{25} = +41$ ($c = 0.9$, CHCl_3).

2-(3-Oxo-3-phenyl-1-(3-(trifluoromethyl)phenyl)propyl)cyclopentanone M-7: Obtained in 73% yield; colorless oil; ^1H NMR (300 MHz, CDCl_3): δ 7.93 (dd, $J = 7.2$ Hz, 14.4 Hz, 1.90H), 7.58-7.37 (m, 6.92H), 3.99-3.73 (m, 1.95H), 3.54-3.33 (m, 0.98H), 2.48 (dd, $J = 8.4$ Hz, 18.3 Hz, 1.00H), 2.30-2.25 (m, 0.99H), 2.11 (dd, $J = 9.0$ Hz, 18.0 Hz, 1.06H), 2.00-1.89 (m, 2.07H), 1.80-1.67 (m, 1.43H), 1.54-1.41 (m, 0.77H); ^{13}C NMR (100 MHz, CDCl_3): δ 219.7, 219.2, 198.4, 198.1, 143.7, 143.4, 136.9, 136.8, 133.2, 133.1, 132.0, 131.9, 130.9, 130.5, 128.9, 128.9, 128.6, 128.6, 128.1, 128.0, 125.4, 125.2, 125.2, 124.8, 124.7, 124.7, 123.6, 123.6, 123.5, 122.7, 53.2, 52.6, 42.6, 40.7, 40.7, 40.6, 39.4, 38.7, 28.1, 27.1, 20.4,

20.2; HPLC (AD, hexane:*i*-PrOH 97:3, 1.0 mL/min): dr 1:2; t_R 15.68 min (minor enantiomer), 18.12 min (major enantiomer); ee >99%; t_R 20.50 min (major enantiomer), 29.89 min (minor enantiomer); ee >99%; $[\alpha]_D^{25} = +51$ ($c = 4.5$, CHCl₃).

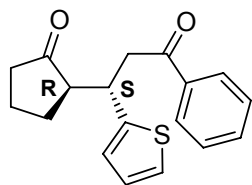
(S)-2-((S)-3-oxo-3-phenyl-1-(thiophen-2-yl)propyl)cyclopentanone M-8: Obtained



in 61 % yield; colorless oil; ¹H NMR (300 MHz, CDCl₃): δ 7.98 (d, $J = 7.8$ Hz, 2H), 7.55 (tri, $J = 7.5$ Hz, 1H), 7.45 (tri, $J = 7.5$ Hz, 2H), 7.11 (d, $J = 5.1$ Hz, 1H), 6.91-6.87 (m, 2H), 4.10 (dd, $J = 6.9$ Hz, 10.5 Hz, 1H), 3.84 (dd, $J = 6.9$ Hz, 17.4 Hz, 1H), 3.49

(dd, $J = 6.9$ Hz, 17.4 Hz, 1H), 2.56 (m, 1H), 2.27 (dd, $J = 7.5$ Hz, 18.0 Hz, 1H) overlapping with 2.23-2.17 (m, 1H), 2.06-1.65 (m, 4H); ¹³C NMR (100 MHz, CDCl₃): δ 220.3, 198.6, 145.2, 136.9, 133.1, 128.6, 128.2, 126.6, 125.5, 123.7, 52.9, 42.6, 39.7, 36.5, 27.4, 20.5; HPLC (AD, hexane:*i*-PrOH 50:50, 1.0 mL/min): t_R 6.97 min (major enantiomer), 7.42 min (minor enantiomer); ee 98.2%; $[\alpha]_D^{25} = +55$ ($c = 0.9$, CHCl₃).

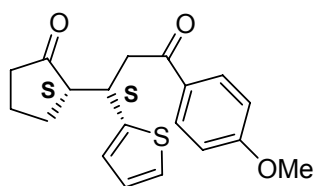
(R)-2-((S)-3-oxo-3-phenyl-1-(thiophen-2-yl)propyl)cyclopentanone M-8: ¹H NMR



(300 MHz, CDCl₃): δ 7.94 (d, $J = 6.9$ Hz, 2H), 7.55 (tri, $J = 7.5$ Hz, 1H), 7.44 (tri, $J = 7.5$ Hz, 2H), 7.11 (d, $J = 4.8$ Hz, 1H), 6.90-6.86 (m, 2H), 4.17 (dd, $J = 6.9$ Hz, 13.8 Hz, 1H), 3.68 (dd, $J = 6.9$ Hz, 16.8 Hz, 1H), 3.45 (dd, $J = 6.9$ Hz, 16.8 Hz, 1H),

2.47 (dd, $J = 7.8$ Hz, 18.6 Hz, 1H), 2.26 (dd, $J = 7.5$ Hz, 18.0 Hz, 1H), 2.08-1.84 (m, 3H), 1.79-1.61 (m, 2H); HPLC (AD, hexane:*i*-PrOH 50:50, 1.0 mL/min): t_R 8.59 min (major enantiomer), 13.27 min (minor enantiomer); ee 95%; $[\alpha]_D^{25} = -57$ ($c = 1.2$, CHCl₃).

(S)-2-((S)-3-(4-methoxyphenyl)-3-oxo-1-(thiophen-2-yl)propyl)cyclopentanone

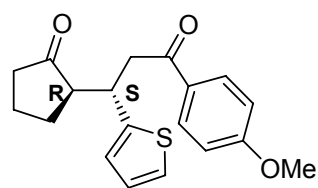


M-9: Obtained in 51% yield; colorless oil; ¹H NMR (300 MHz, CDCl₃): δ 7.98 (d, $J = 8.7$ Hz, 2H), 7.11 (d, $J = 4.8$ Hz, 1H), 6.94-6.88 (m, 4H), 4.08 (dd, $J = 6.9$ Hz, 10.5 Hz, 1H), 3.86 (s, 3H), 3.79 (dd, $J = 7.2$ Hz, 16.8 Hz, 1H), 3.42

(dd, $J = 6.9$ Hz, 16.8 Hz, 1H), 2.53 (m, 1H), 2.26 (dd, $J = 6.9$ Hz, 18.3 Hz, 1H), 2.20

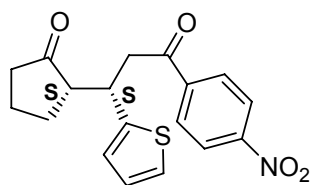
(dd, $J = 7.2$ Hz, 16.8 Hz, 1H), 1.97 (dd, $J = 8.4$ Hz, 18.0 Hz, 1H), 1.86-1.64 (m, 3H); ^{13}C NMR (75 MHz, CDCl_3): δ 220.3, 197.0, 163.5, 145.2, 130.5, 130.0, 126.6, 125.4, 123.6, 113.6, 55.4, 52.9, 42.1, 39.6, 36.6, 27.4, 20.4; HPLC (AD, hexane:*i*-PrOH 65:35, 1.0 mL/min): t_{R} 13.71 min (major enantiomer), 16.73 min (minor enantiomer); ee >98.8%; $[\alpha]_{\text{D}}^{25} = +41$ ($c = 0.9$, CHCl_3).

(R)-2-((S)-3-(4-methoxyphenyl)-3-oxo-1-(thiophen-2-yl)propyl)cyclopentanone



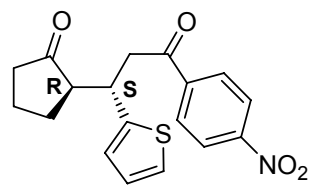
M-9: ^1H NMR (300 MHz, CDCl_3): δ 7.93 (d, $J = 9.0$ Hz, 2H), 7.11 (d, $J = 5.1$ Hz, 1H), 6.93-6.84 (m, 4H), 4.17 (dd, $J = 6.9$ Hz, 13.5 Hz, 1H), 3.86 (s, 3H), 3.58 (dd, $J = 7.2$ Hz, 16.8 Hz, 1H), 3.40 (dd, $J = 6.9$ Hz, 16.5 Hz, 1H), 2.47 (dd, $J = 7.8$ Hz, 18.0 Hz, 1H), 2.25 (dd, $J = 6.9$ Hz, 17.1 Hz, 1H), 2.07-1.84 (m, 3H), 1.78-1.64 (m, 2H); HPLC (AD, hexane:*i*-PrOH 65:35, 1.0 mL/min): t_{R} 19.32 min (major enantiomer), 32.24 min (minor enantiomer); ee >97.5%; $[\alpha]_{\text{D}}^{25} = -53$ ($c = 1.2$, CHCl_3).

(R)-2-((R)-3-(4-Nitrophenyl)-3-oxo-1-(thiophen-2-yl)propyl)cyclopentanone M-10:



Obtained in 29% yield; colorless oil; ^1H NMR (300 MHz, CDCl_3): δ 8.30 (d, $J = 8.1$ Hz, 2H), 8.12 (d, $J = 8.1$ Hz, 2H), 7.13 (d, $J = 5.4$ Hz, 1H), 6.89 (m, 2H), 4.08 (m, 1H), 3.86 (dd, $J = 6.6$ Hz, 17.4 Hz, 1H), 3.55 (dd, $J = 7.2$ Hz, 17.1 Hz, 1H), 2.56 (m, 1H), 2.34-2.21 (m, 2H), 2.08-1.95 (m, 1H), 1.86-1.76 (m, 3H); HPLC (AD, hexane:*i*-PrOH 60:40, 1.0 mL/min): t_{R} 14.85 min (major enantiomer), 16.06 min (minor enantiomer); ee 98%; $[\alpha]_{\text{D}}^{25} = +55$ ($c = 1.0$, CHCl_3).

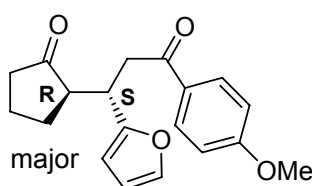
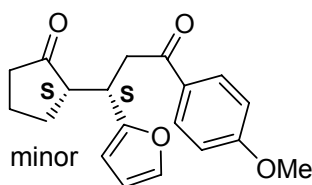
(R)-2-((S)-3-(4-Nitrophenyl)-3-oxo-1-(thiophen-2-yl)propyl)cyclopentanone M-10:



^1H NMR (300 MHz, CDCl_3): δ 8.30 (d, $J = 7.8$ Hz, 2H), 8.07 (d, $J = 8.1$ Hz, 2H), 7.14 (d, $J = 4.8$ Hz, 1H), 6.88 (m, 2H), 4.04 (m, 1H), 3.86 (dd, $J = 6.0$ Hz, 17.4 Hz, 1H), 3.43 (dd, $J = 7.2$ Hz, 16.8 Hz, 1H), 2.45 (dd, $J = 8.7$ Hz, 17.1 Hz, 1H), 2.33-2.27 (m, 1H), 2.17-1.94 (m, 3H), 1.79-1.58 (m, 2H); ^{13}C NMR (75 MHz, CDCl_3): δ 219.2, 196.6, 150.2, 145.2, 141.3, 129.0, 126.7, 125.3, 123.8, 53.3, 44.4,

38.8, 36.4, 27.7, 20.1; HPLC (AD, hexane:*i*-PrOH 60:40, 1.0 mL/min): t_R 23.38 min (major enantiomer), 32.97 min (minor enantiomer); ee >99%; $[\alpha]_D^{25} = -59$ ($c = 1.4$, CHCl₃).

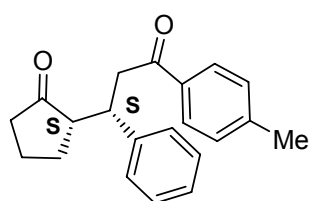
2-(1-(Furan-2-yl)-3-(4-methoxyphenyl)-3-oxopropyl)cyclopentanone M-11:



Obtained in 56% yield; colorless oil; ¹H NMR (300 MHz, CDCl₃): δ 7.95 (d, $J = 8.7$ Hz, 2.24H), 6.93 (d, $J = 8.7$ Hz, 2.65H), 6.23 (m, 1.03H), 6.04 (m, 1.00H), 3.96 (dd, $J = 6.9$ Hz, 13.5 Hz, 1.12H), 3.86 (s, 3.92H), 3.58 (dd, $J = 6.9$ Hz, 16.5 Hz, 0.59H), 3.44-3.36 (dd, $J = 3.0$ Hz, 6.9 Hz, 1.95H), 2.45 (dd, $J = 9.6$ Hz, 17.1 Hz, 1.37H), 2.28-2.16 (m, 1.82H), 2.11-1.99 (m, 2.25H), 1.89-1.54 (m, 4.85H); ¹³C NMR (75 MHz, CDCl₃): δ 220.1, 219.4, 197.1, 196.6,

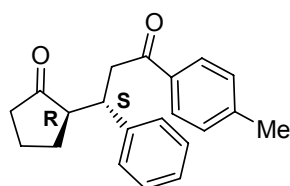
163.5, 155.7, 155.3, 141.3, 141.2, 130.4, 129.9, 129.6, 115.3, 113.7, 110.2, 110.1, 106.6, 106.4, 55.4, 51.8, 50.9, 39.8, 39.4, 39.2, 38.5, 35.0, 34.5, 27.5, 26.6, 20.5, 20.3; HPLC (AD, hexane:*i*-PrOH 60:40, 1.0 mL/min): dr 1:3; t_R 11.94 min (major enantiomer), 15.91 min (minor enantiomer); ee 98.2%; t_R 13.54 min (minor enantiomer), 18.76 min (major enantiomer); ee 97.1%; $[\alpha]_D^{25} = -28$ ($c = 0.9$, CHCl₃).

(S)-2-((S)-3-oxo-1-phenyl-3-p-tolylpropyl)cyclopentanone M-12: Obtained in 85%



yield; white solid; m.p. 80-81°C; ¹H NMR (300 MHz, CDCl₃): δ 7.87 (d, $J = 8.1$ Hz, 2H), 7.29-7.19 (m, 7H), 3.78 (m, 2H), 3.44 (dd, $J = 9.3$ Hz, 19.5 Hz, 1H), 2.52-2.49 (m, 1H), 2.39 (s, 3H), 2.24 (dd, $J = 6.0$ Hz, 18.0 Hz, 1H),

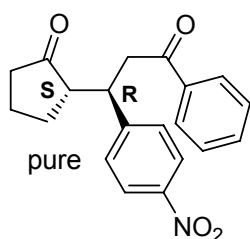
2.19-2.09 (m, 1H), 1.91 (dd, $J = 8.7$ Hz, 18.0 Hz, 1H), 1.83-1.61 (m, 3H); HPLC (AD, hexane:*i*-PrOH 60:40, 1.0 mL/min): t_R 8.96 min (major enantiomer), 11.87 min (minor enantiomer); ee >99%; $[\alpha]_D^{25} = +61$ ($c = 0.8$, CHCl₃).



(R)-2-((S)-3-oxo-1-phenyl-3-p-tolylpropyl)cyclopentanone M-12: ¹H NMR (300 MHz in CDCl₃): δ 7.81 (d, $J = 8.1$ Hz, 2H), 7.29-7.15 (m, 7H), 3.82 (dd, $J = 6.3$ Hz, 16.5 Hz, 1H),

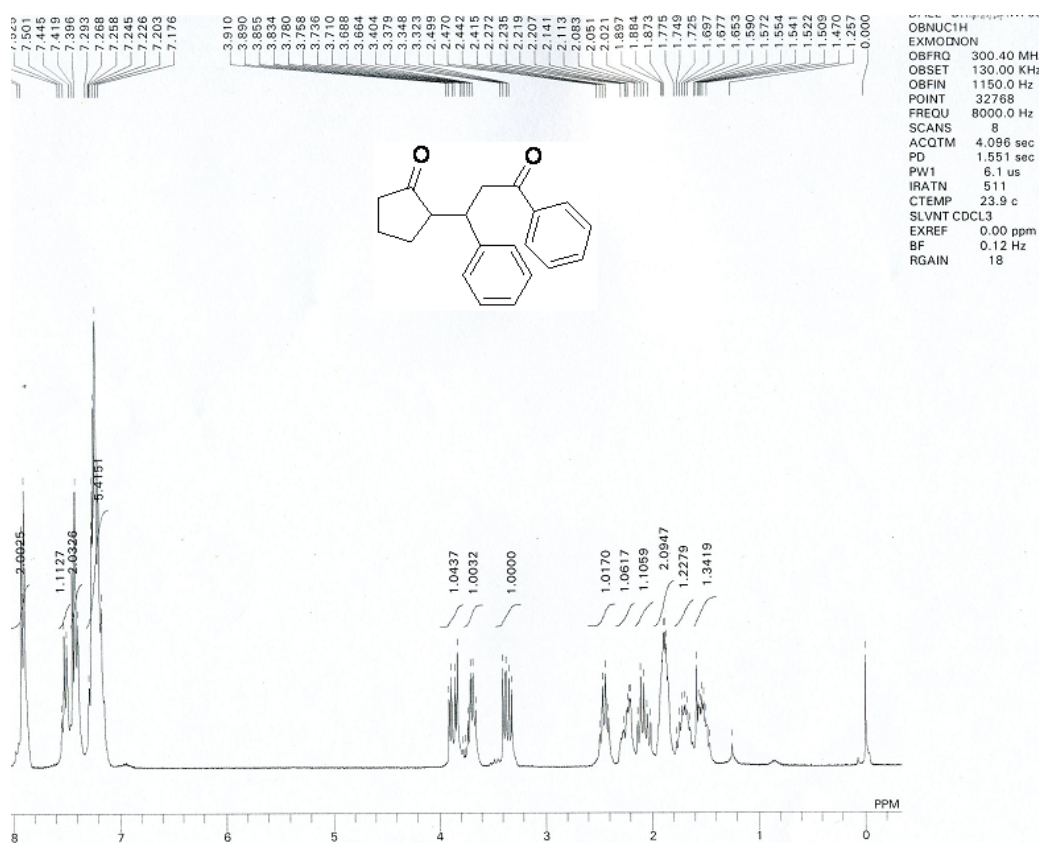
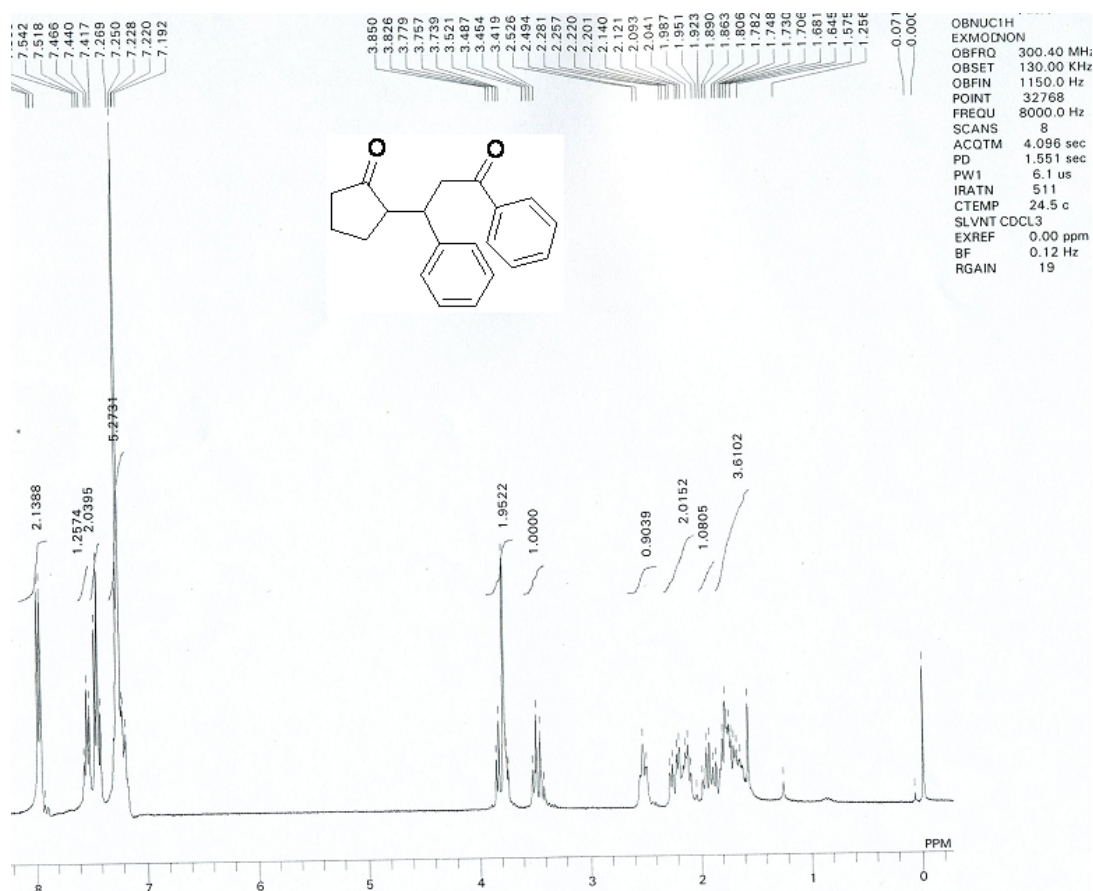
3.70 (dd, $J = 7.5$ Hz, 15.0 Hz, 1H), 3.35 (dd, $J = 7.5$ Hz, 16.5 Hz, 1H), 2.45 (dd, $J = 7.5$ Hz, 16.5 Hz, 1H), 2.39 (s, 3H), 2.29-2.19 (m, 1H), 2.04 (dd, $J = 9.0$ Hz, 18.0 Hz, 1H), 1.94-1.85 (m, 2H), 1.74-1.51 (m, 3H); HPLC (AD, hexane:*i*-PrOH 60:40, 1.0 mL/min): t_R 12.89 min (major enantiomer), 24.38 min (minor enantiomer); ee 97.4%; $[\alpha]_D^{25} = -57$ ($c = 1.2$, CHCl₃).

(S)-2-((R)-1-(4-nitrophenyl)-3-oxo-3-phenylpropyl)cyclopentanone M-13:

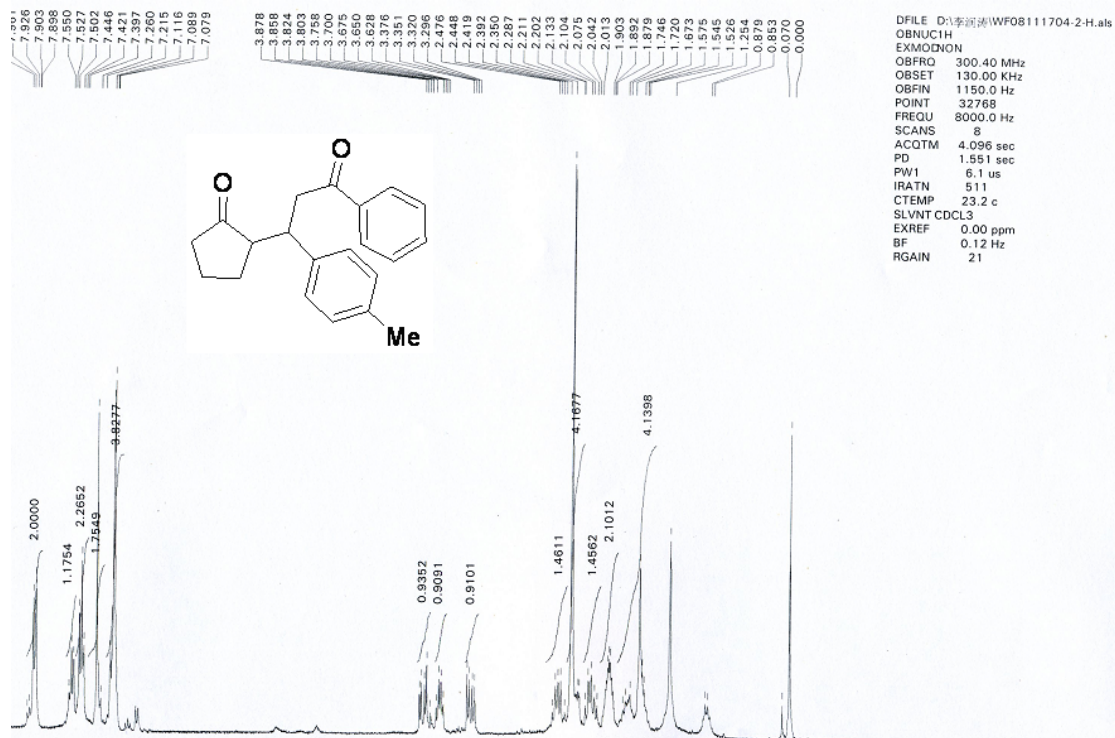


Obtained in 76% yield; light yellow crystal; m.p. 131-132°C; ¹H NMR (300 MHz, CDCl₃): δ 8.15 (d, $J = 8.4$ Hz, 2H), 7.92 (d, $J = 7.5$ Hz, 2H), 7.59-7.54 (m, 1H), 7.47-7.41 (m, 4H), 4.01 (dd, $J = 5.1$ Hz, 17.1 Hz, 1H), 3.80 (dd, $J = 4.8$ Hz, 8.4 Hz, 1H), 3.42 (dd, $J = 8.7$ Hz, 17.4 Hz, 1H), 2.50 (dd, $J = 8.7$ Hz, 18.3 Hz, 1H), 2.34 (dd, $J = 7.8$ Hz, 19.2 Hz, 1H), 2.12 (dd, $J = 8.4$ Hz, 18.6 Hz, 1H), 1.99-1.87 (m, 2H), 1.81-1.71 (m, 1H), 1.53-1.39 (m, 1H); ¹³C NMR (75 MHz, CDCl₃): δ 218.8, 197.7, 150.3, 146.7, 136.6, 133.3, 129.2, 128.6, 127.9, 123.7, 52.4, 42.4, 40.7, 38.7, 28.1, 20.2; HPLC (AS, hexane:*i*-PrOH 50:50, 1.0 mL/min): dr 3:2; t_R 10.02 min (major enantiomer), 11.53 min (minor enantiomer); ee >96.4%; t_R 11.65 min (major enantiomer), 13.34 min (minor enantiomer); ee >99%; $[\alpha]_D^{25} = +25$ ($c = 1.5$, CHCl₃); recrystallization: dr >99:1; ee >99.9%; $[\alpha]_D^{25} = +120$ ($c = 1.5$, CHCl₃).

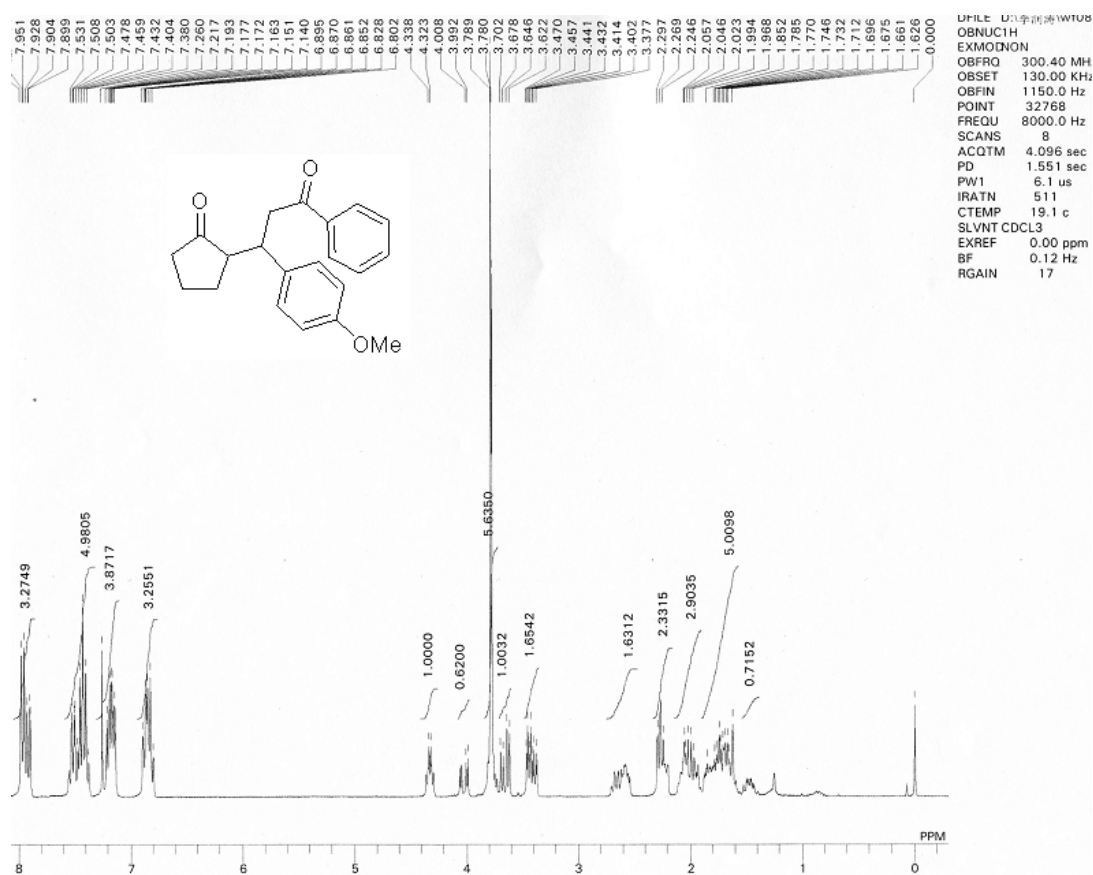
NMR Spectra for Michael Product M-1



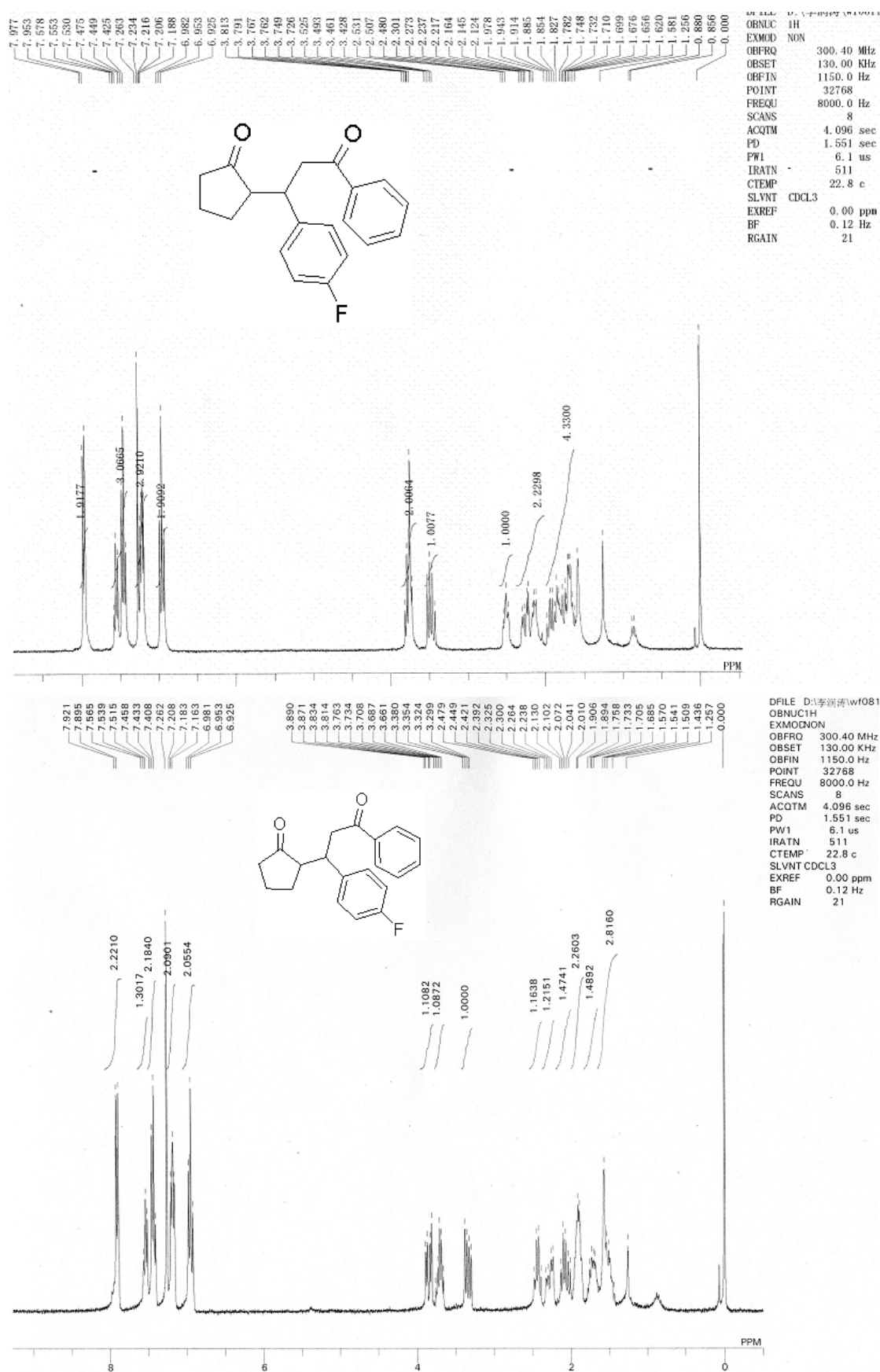
NMR Spectra for Michael Product M-2

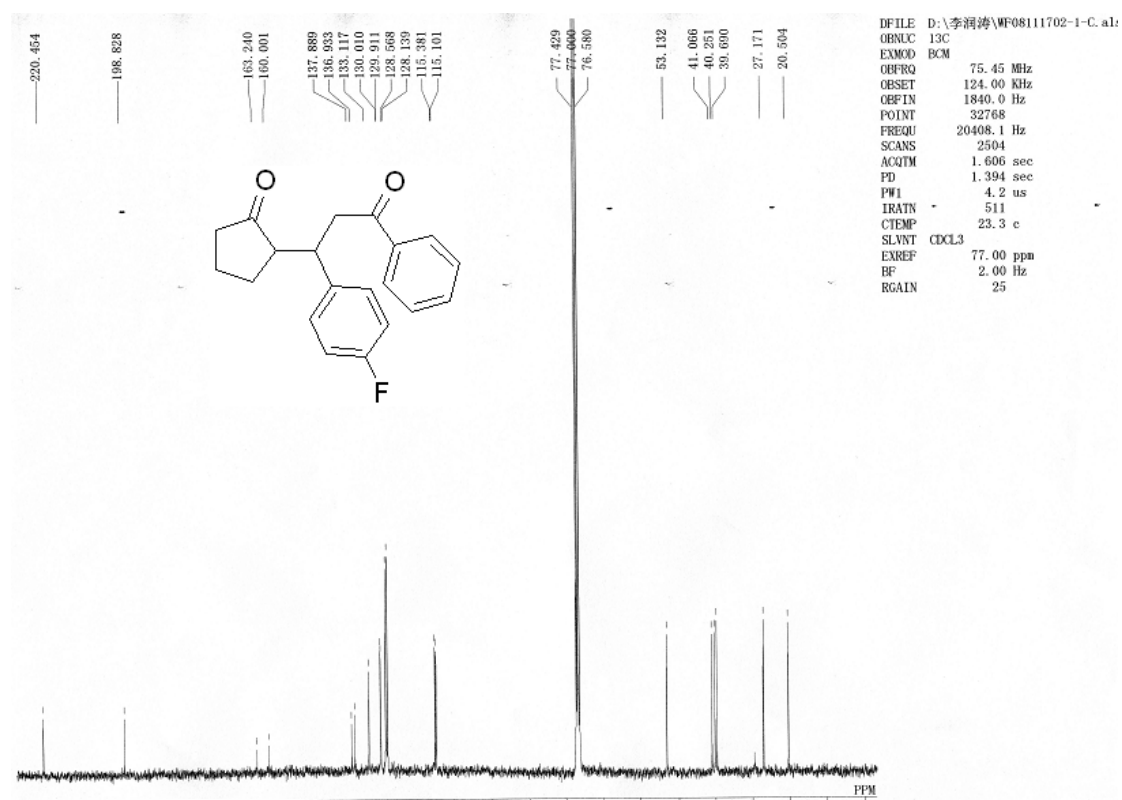


NMR Spectra for Michael Product M-3

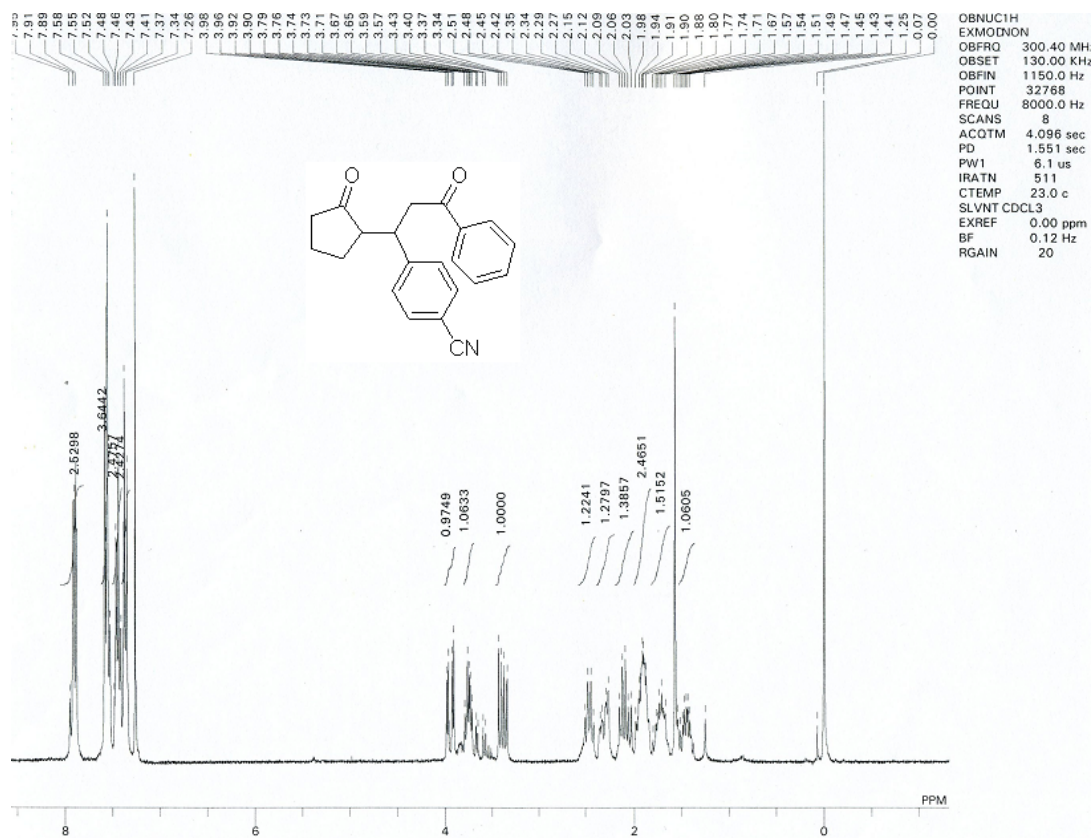


NMR Spectra for Michael Product M-4

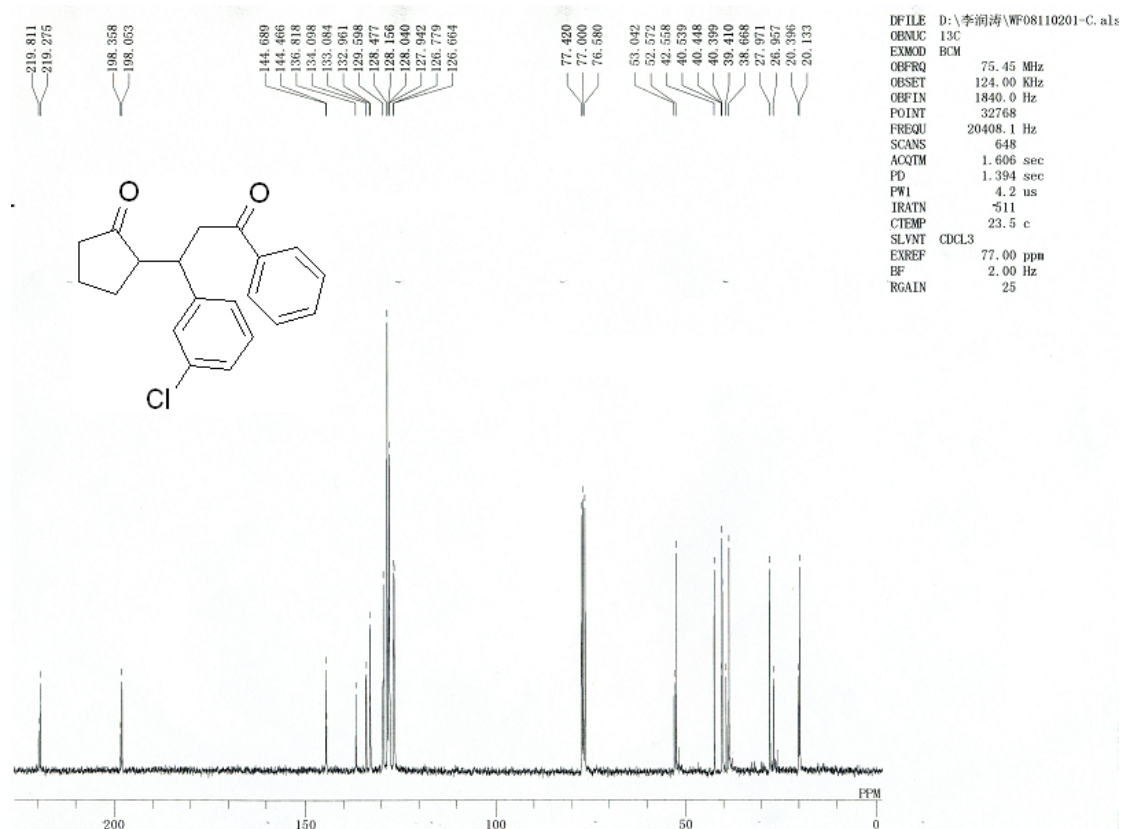
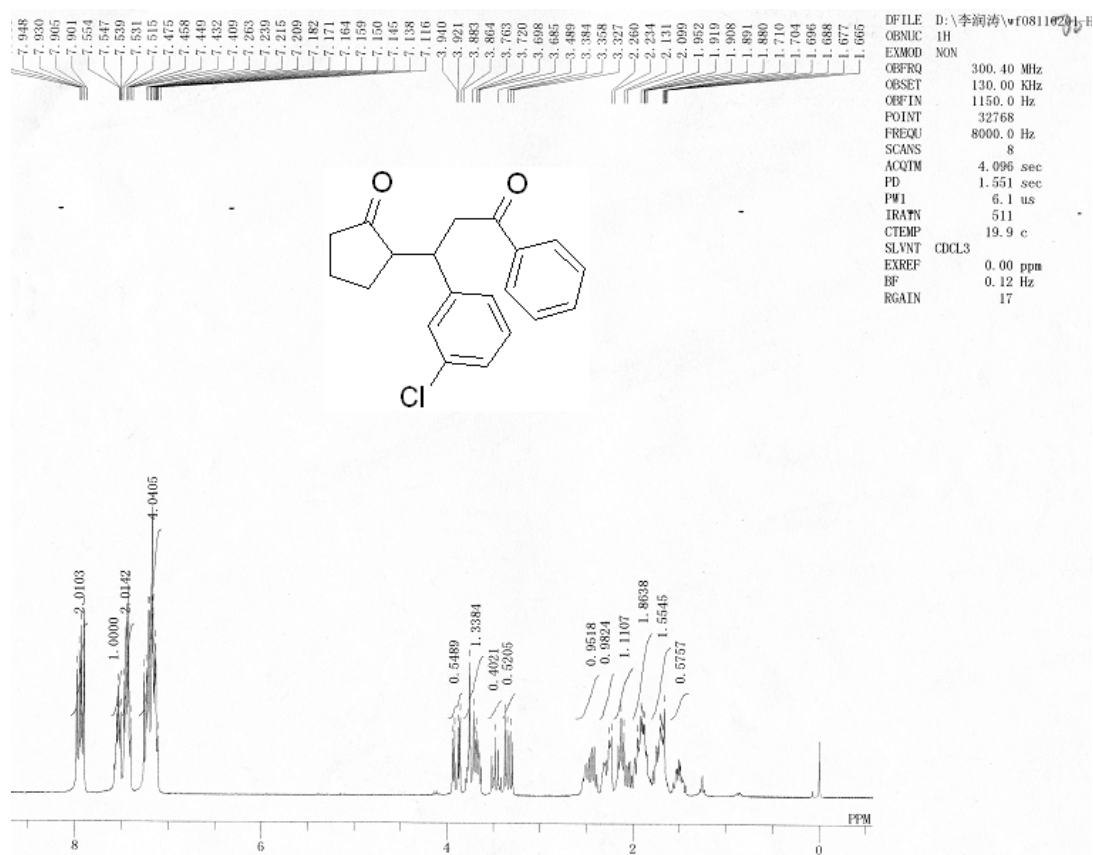




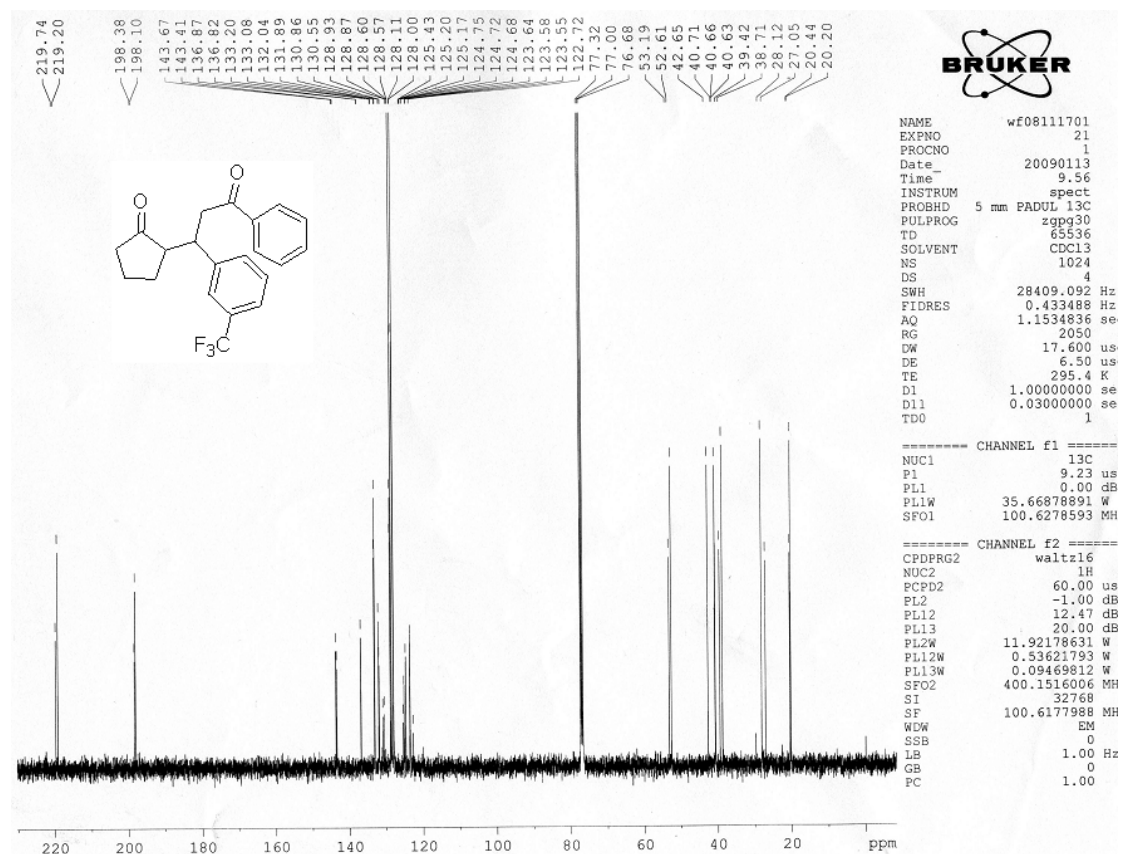
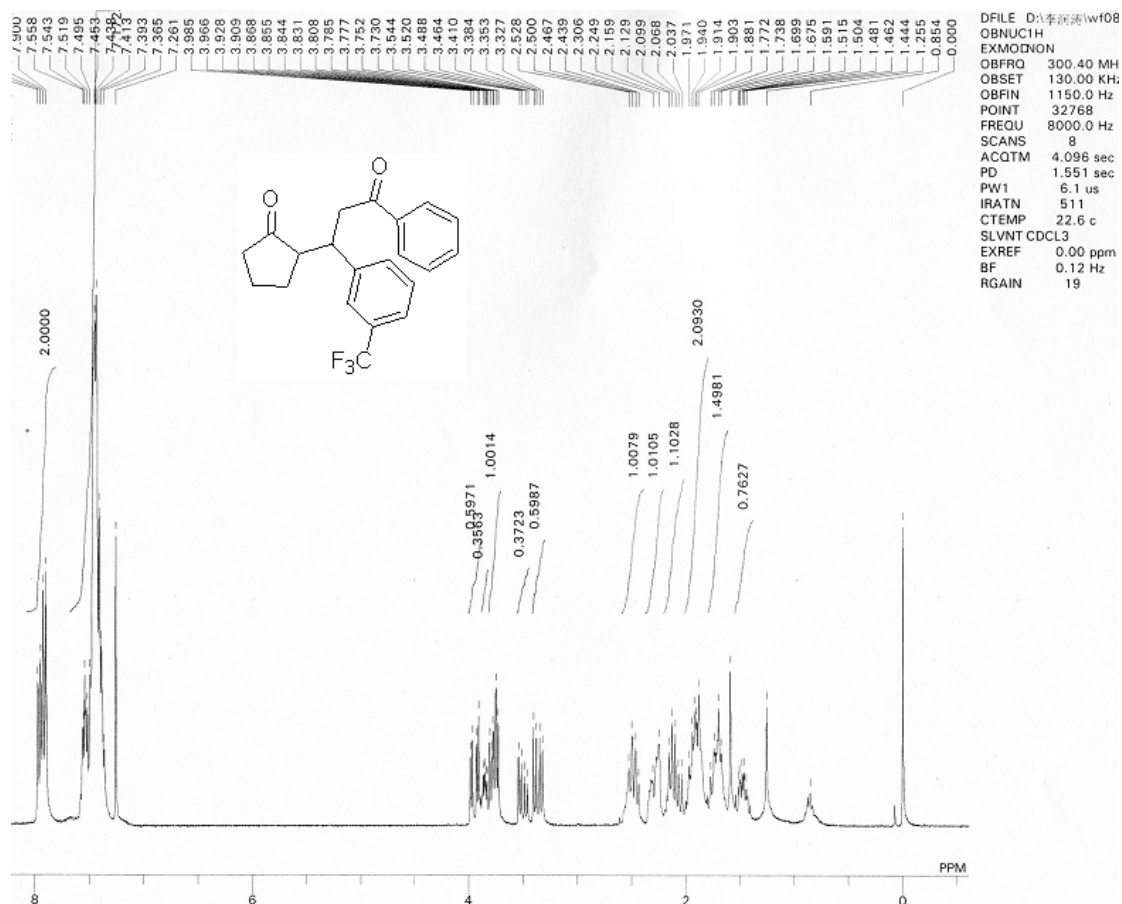
NMR Spectra for Michael Product M-5



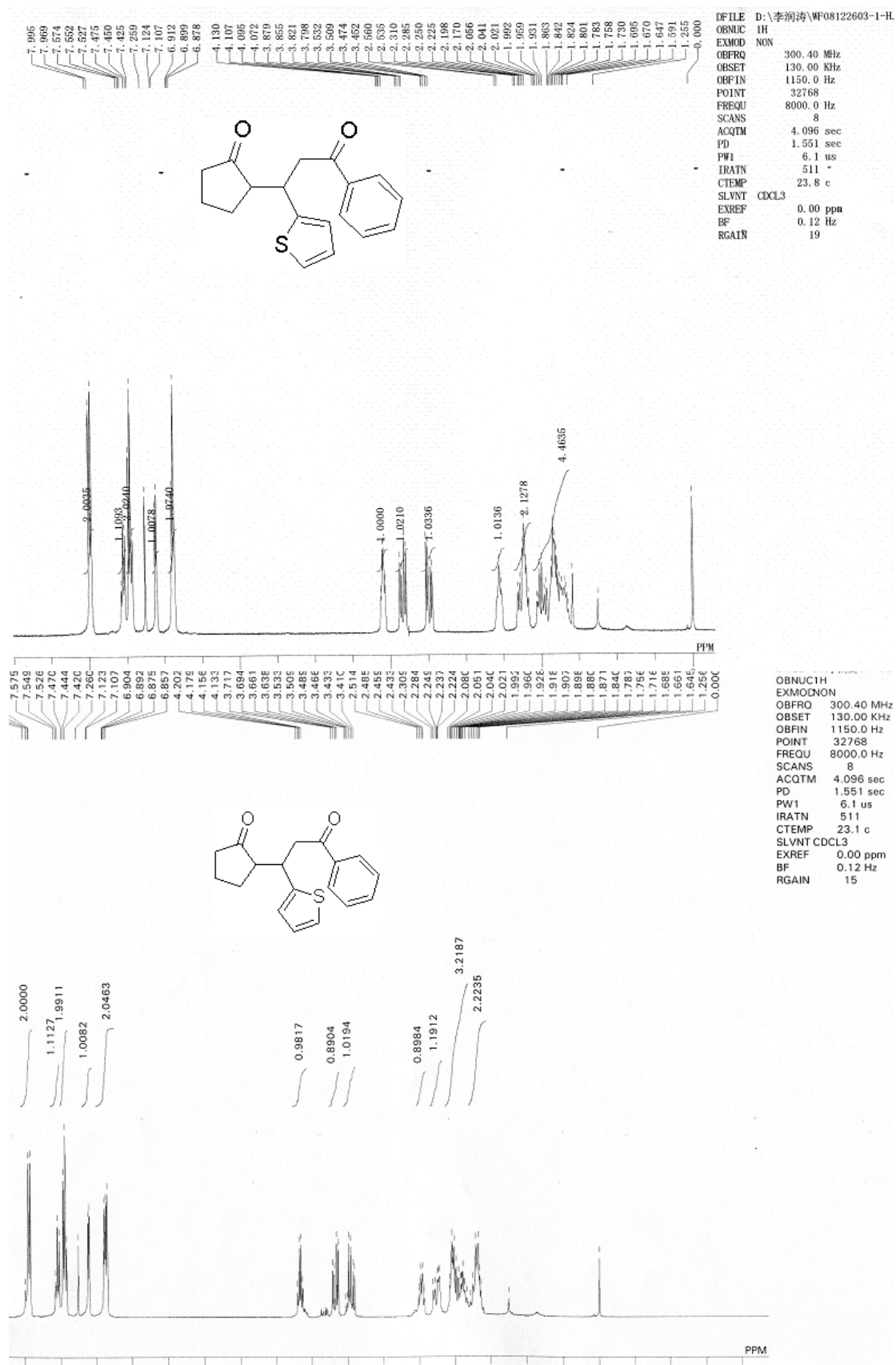
NMR Spectra for Michael Product M-6

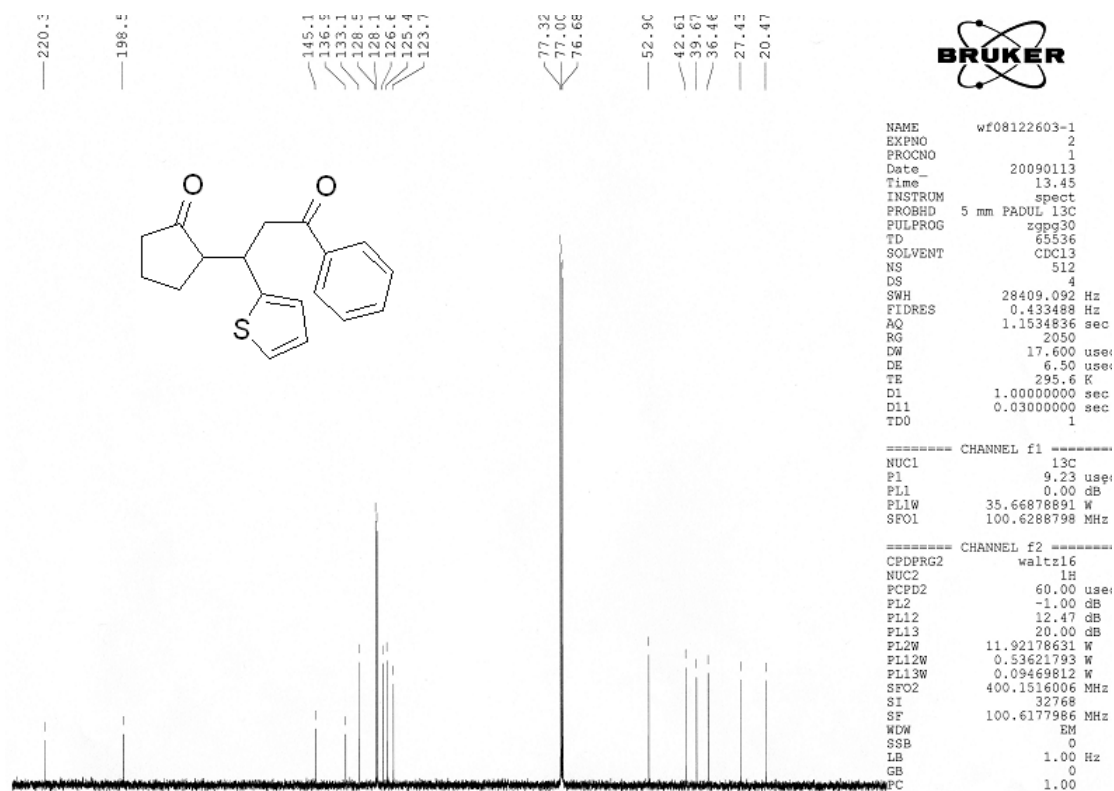


NMR Spectra for Michael Product M-7

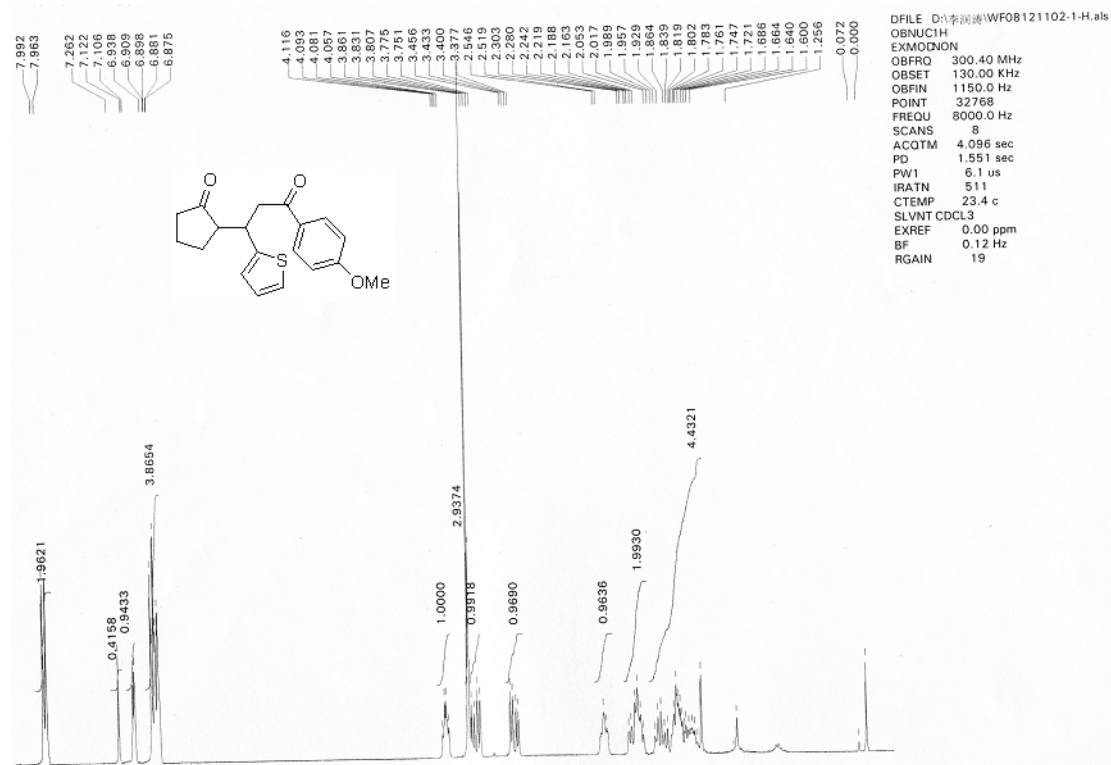


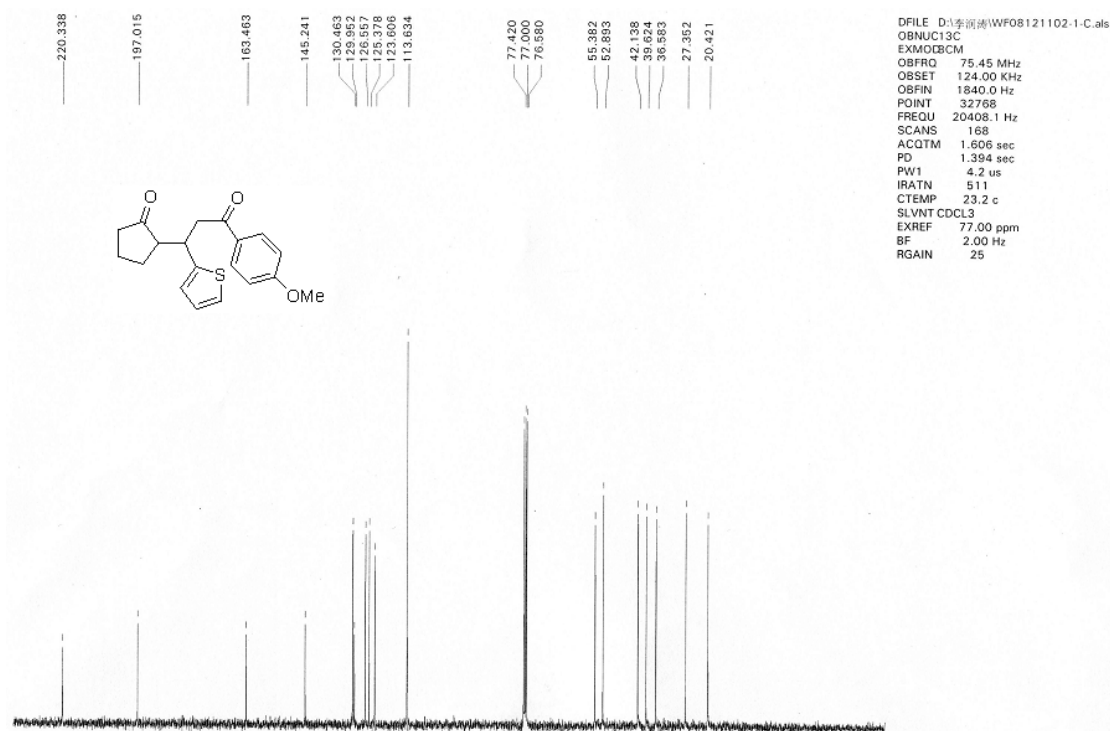
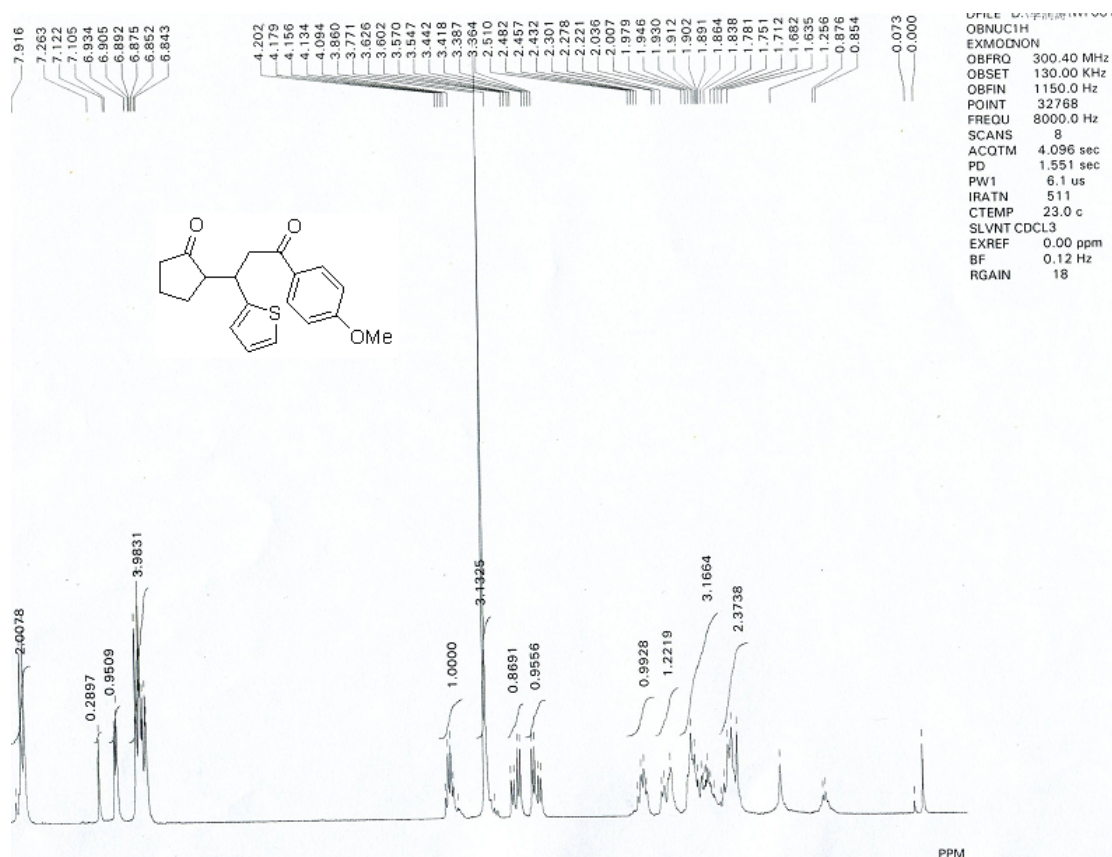
NMR Spectra for Michael Product M-8



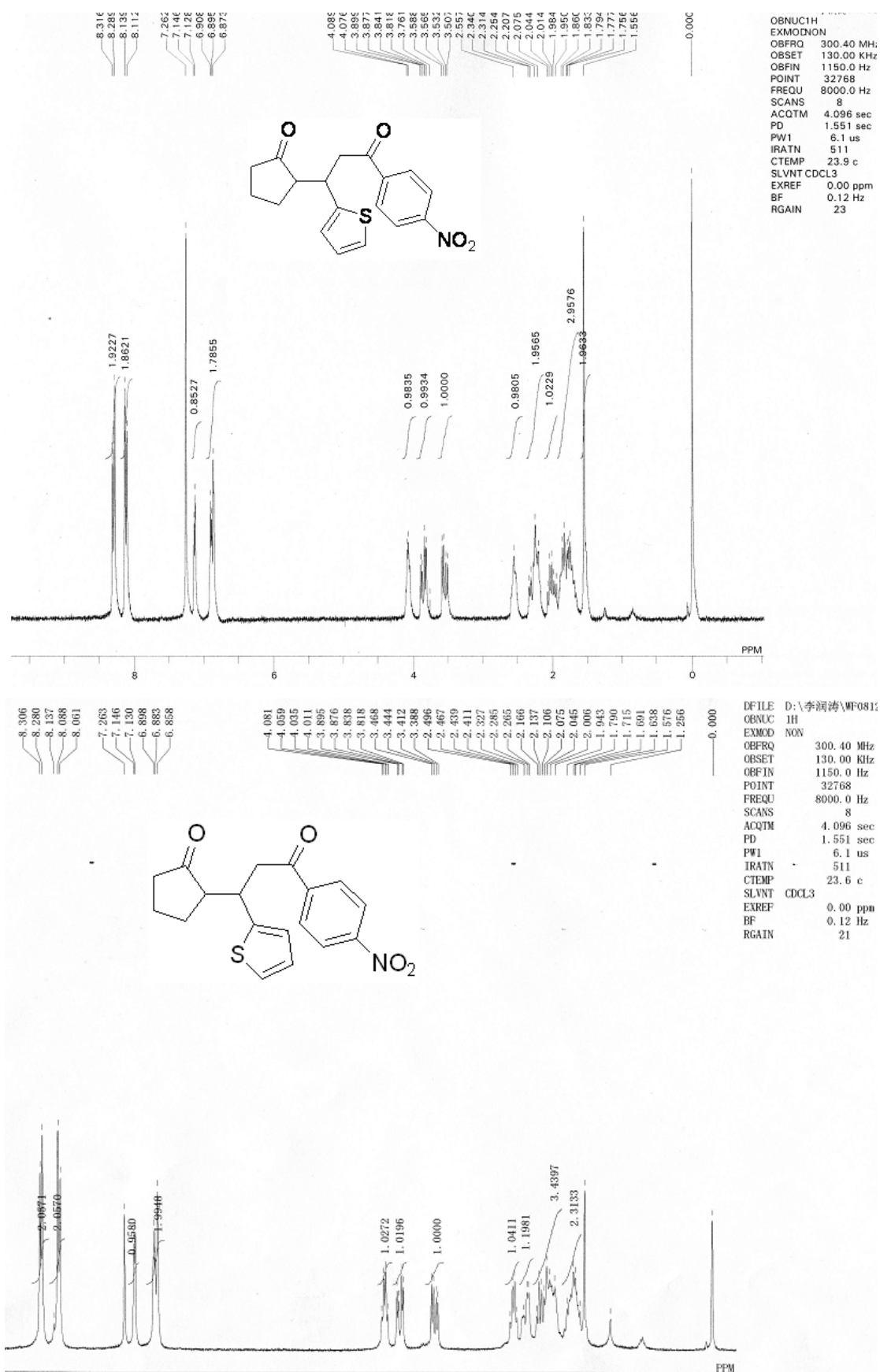


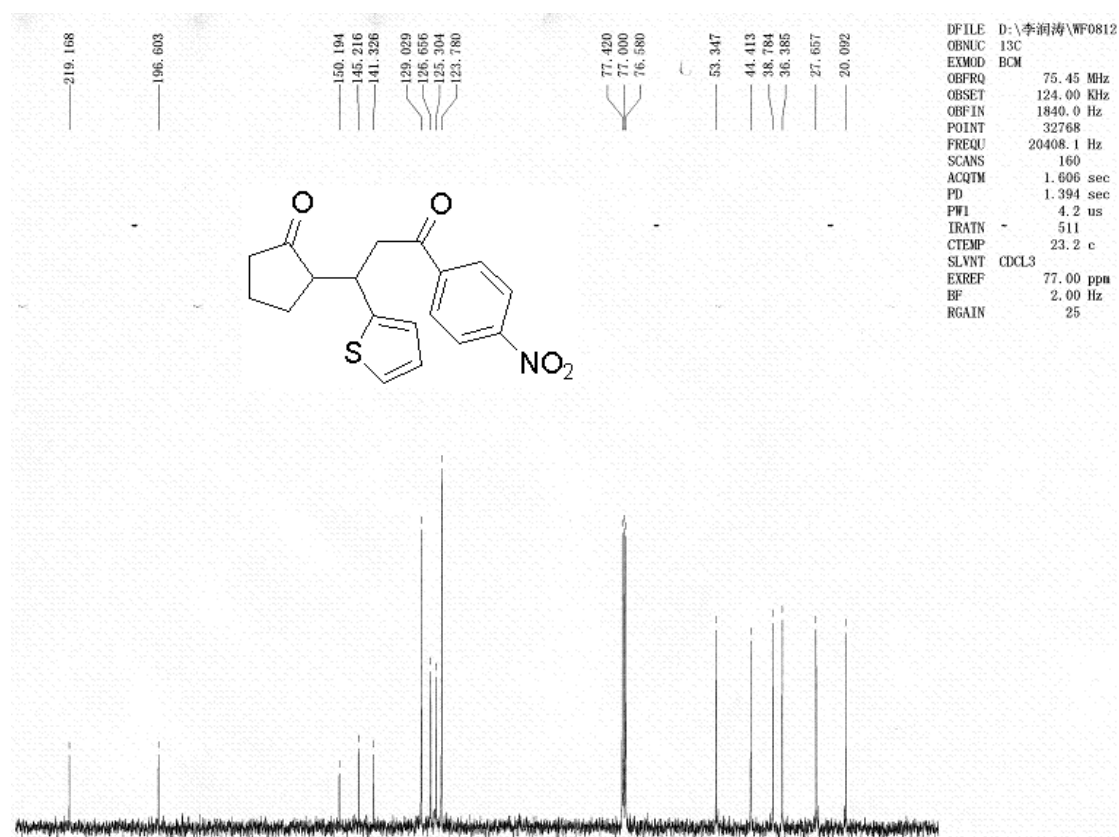
NMR Spectra for Michael Product M-9



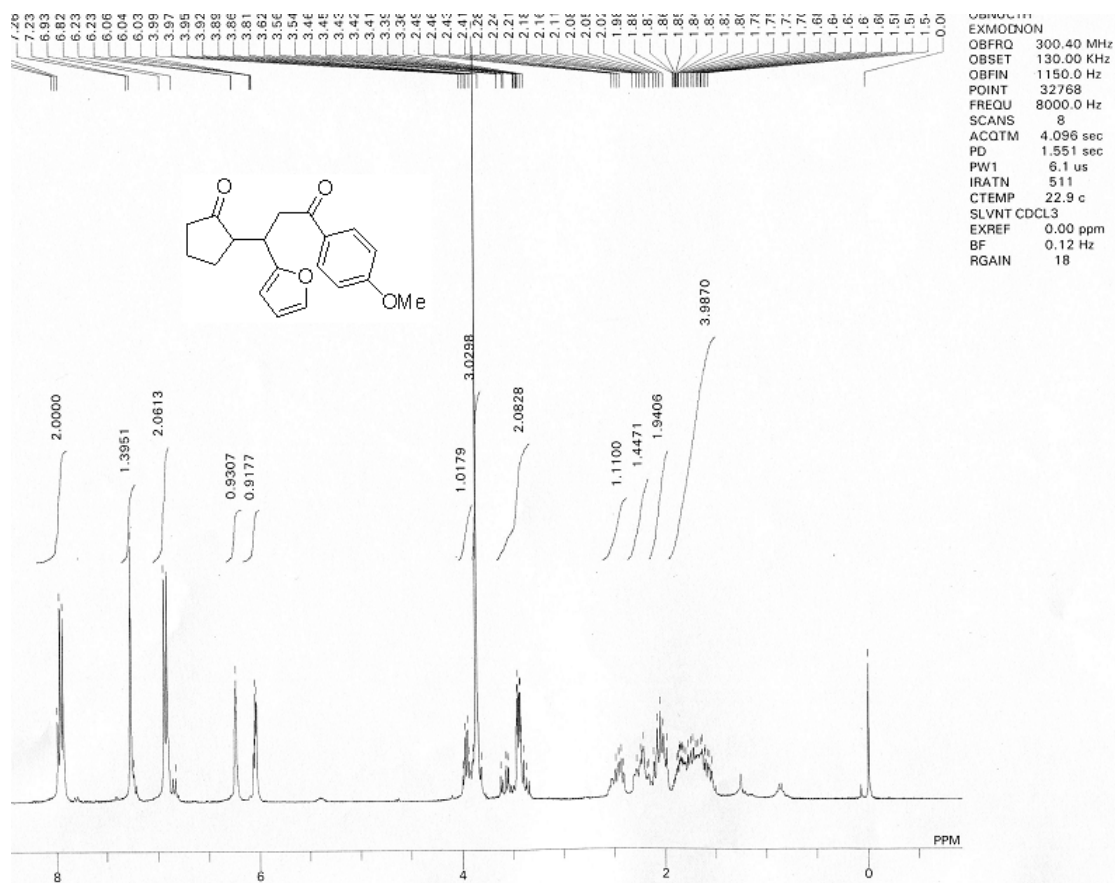


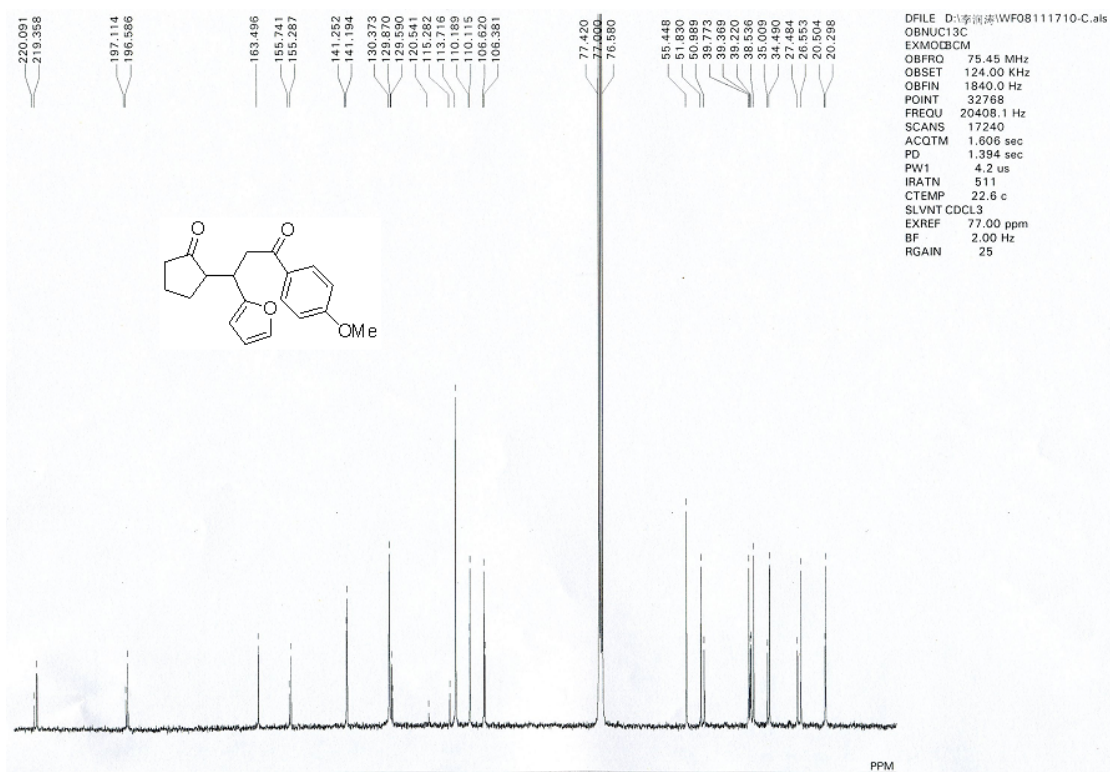
NMR Spectra for Michael Product M-10



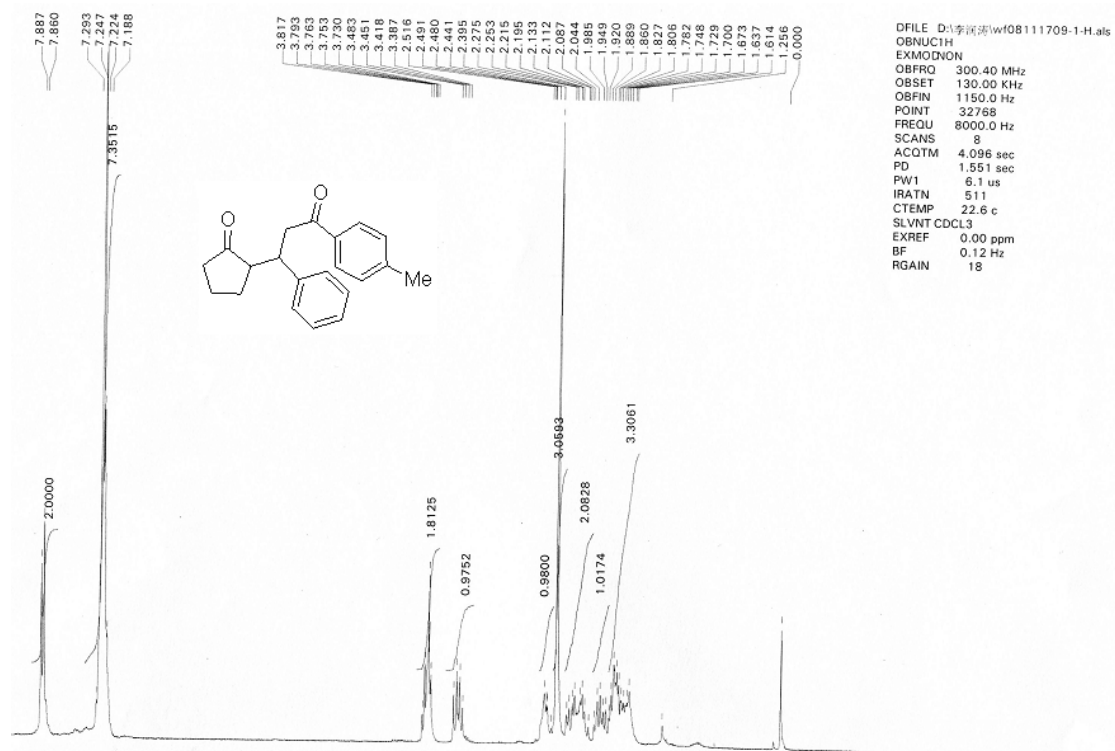


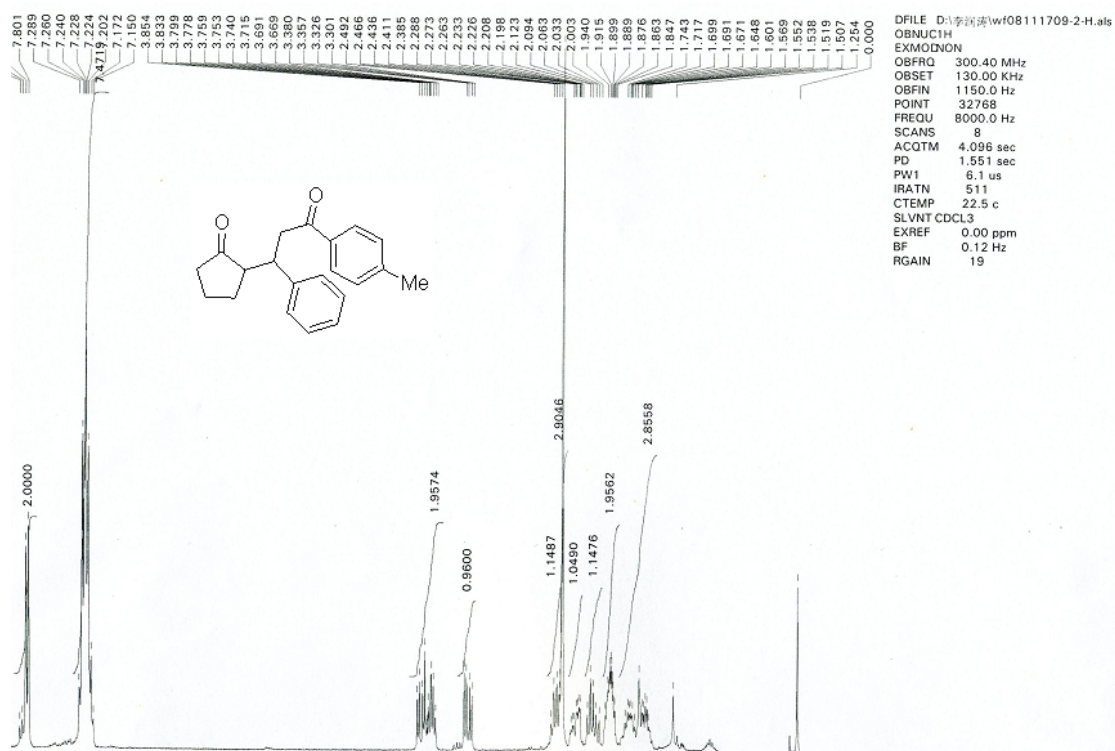
NMR Spectra for Michael Product M-11



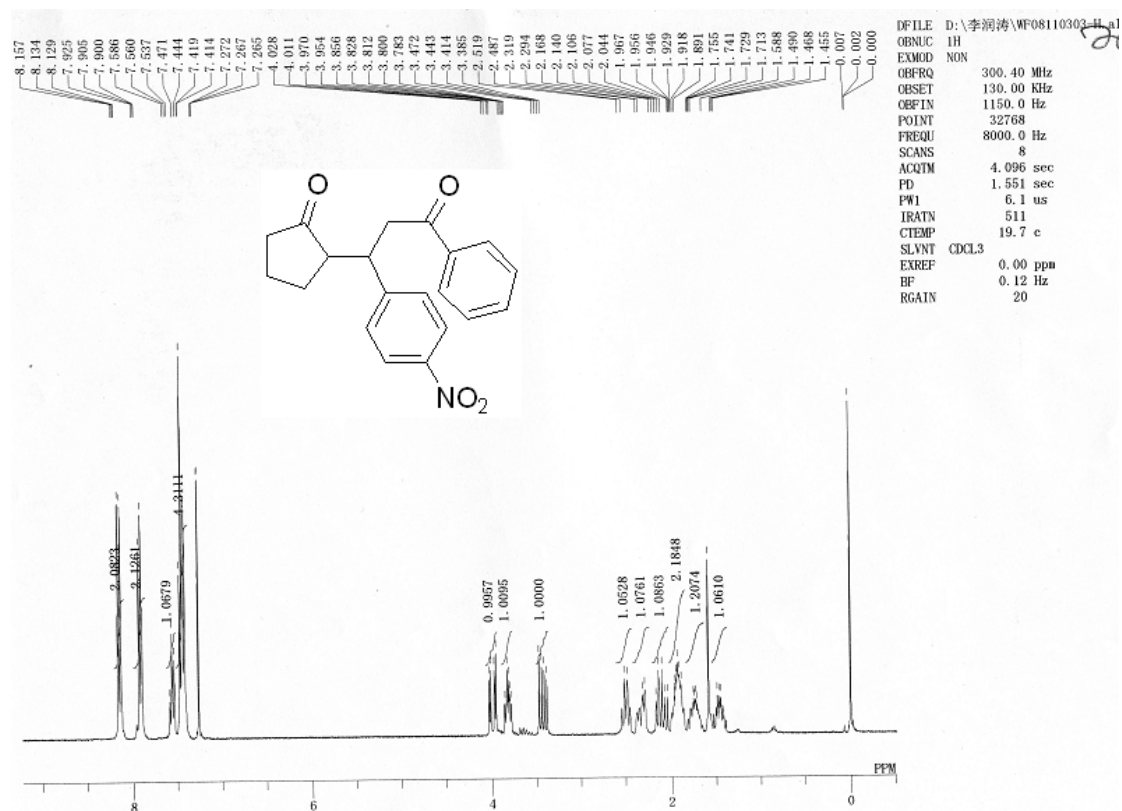


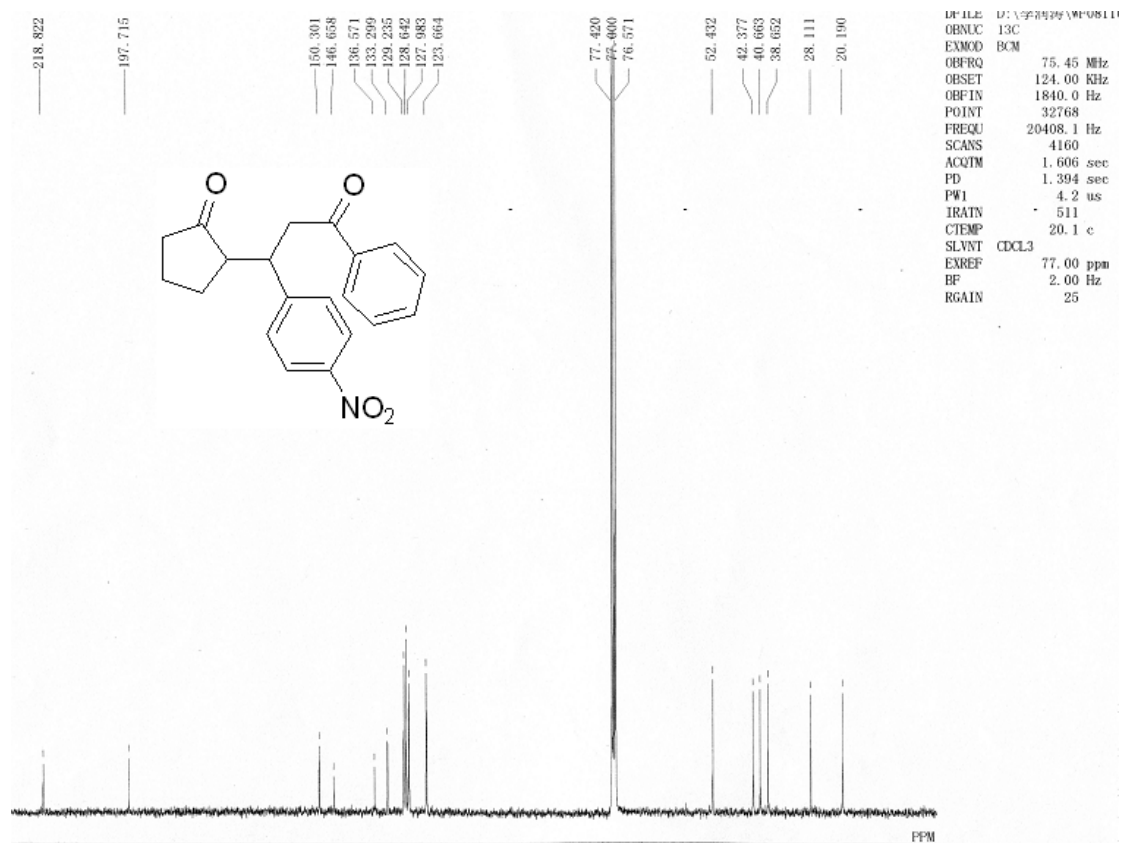
NMR Spectra for Michael Product M-12





NMR Spectra for Michael Product M-13

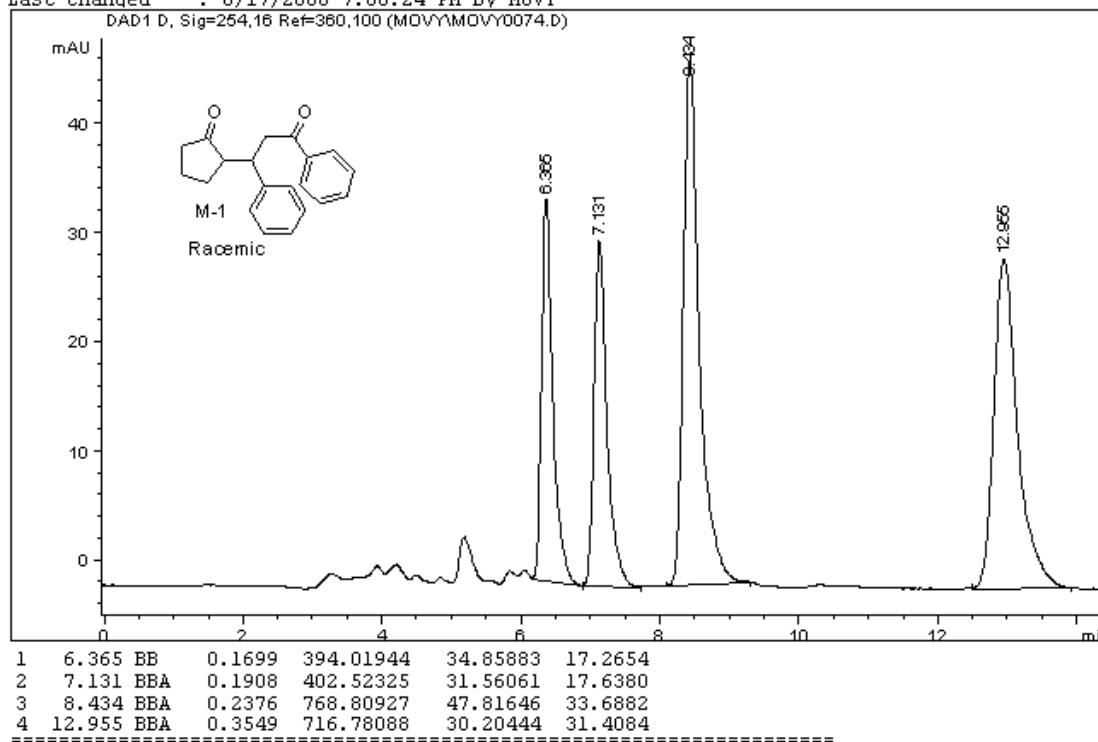




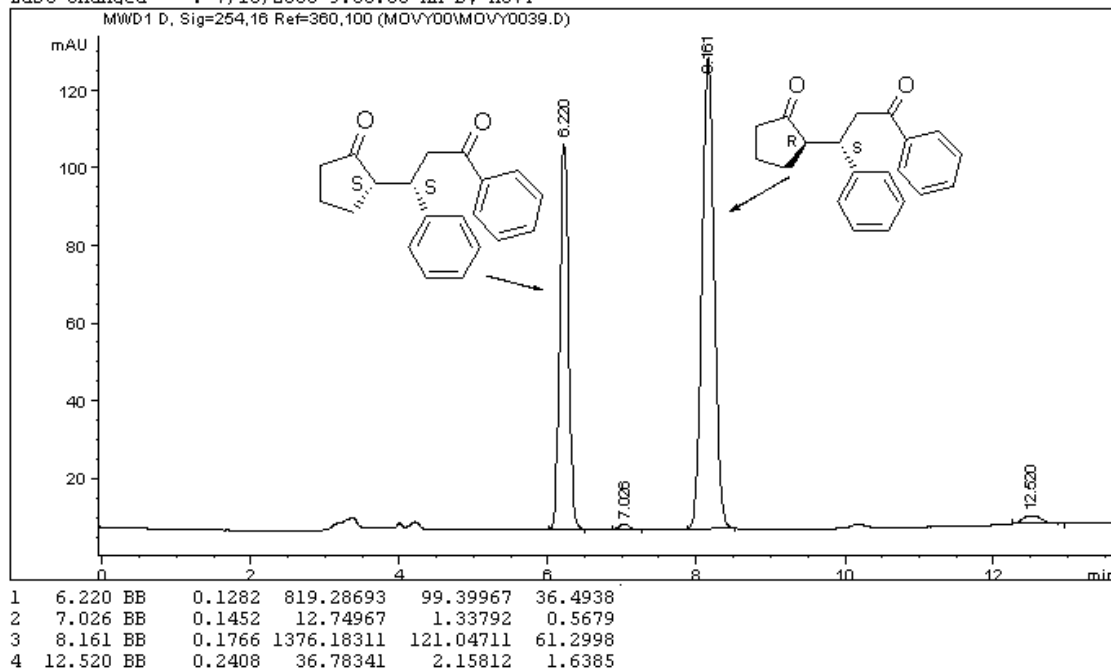
HPLC analysis for compounds M-1 to M-13

M-1

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Acq. Method : C:\HPCHEM\1\METHODS\YG.M
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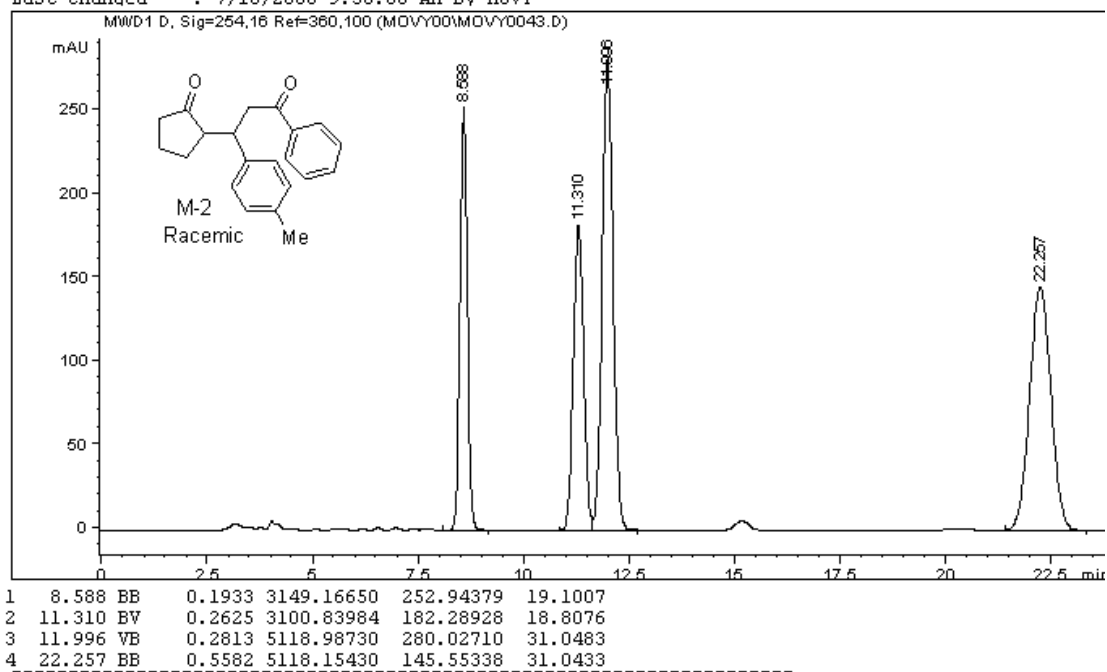


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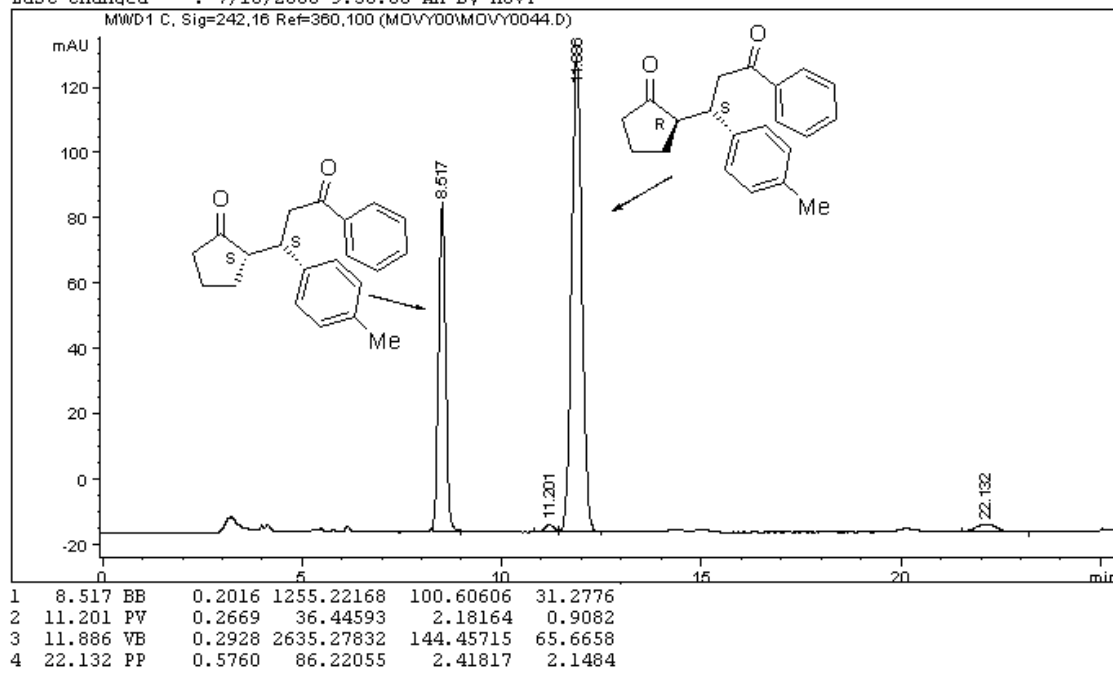


M-2

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Acq. Method : C:\HPCHEM\1\METHODS\LEIM.M
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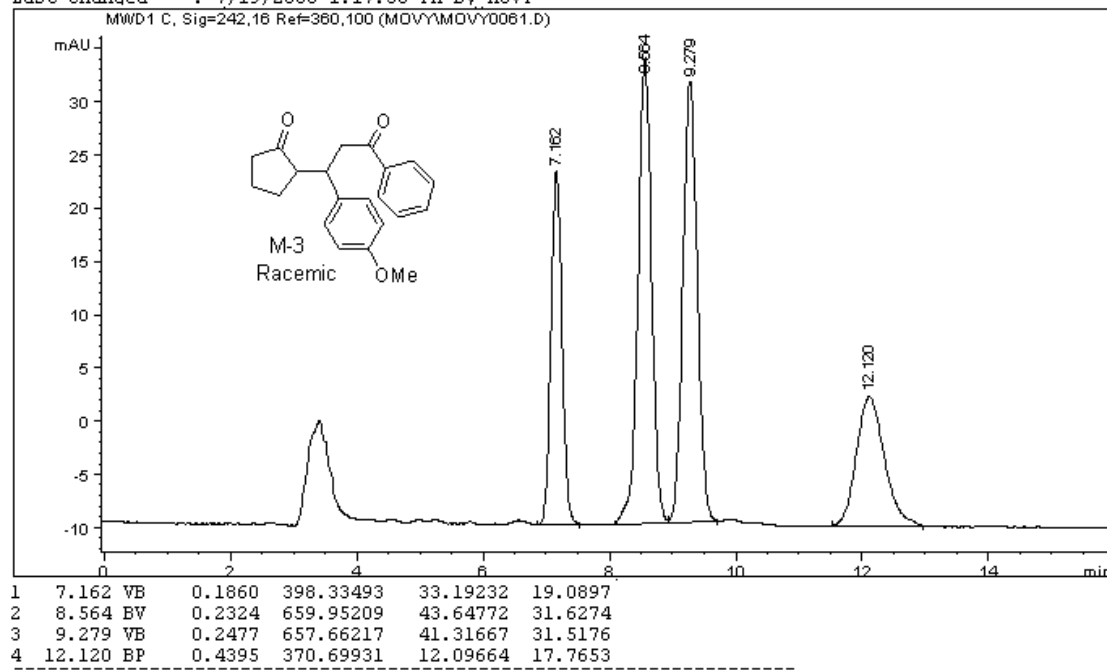


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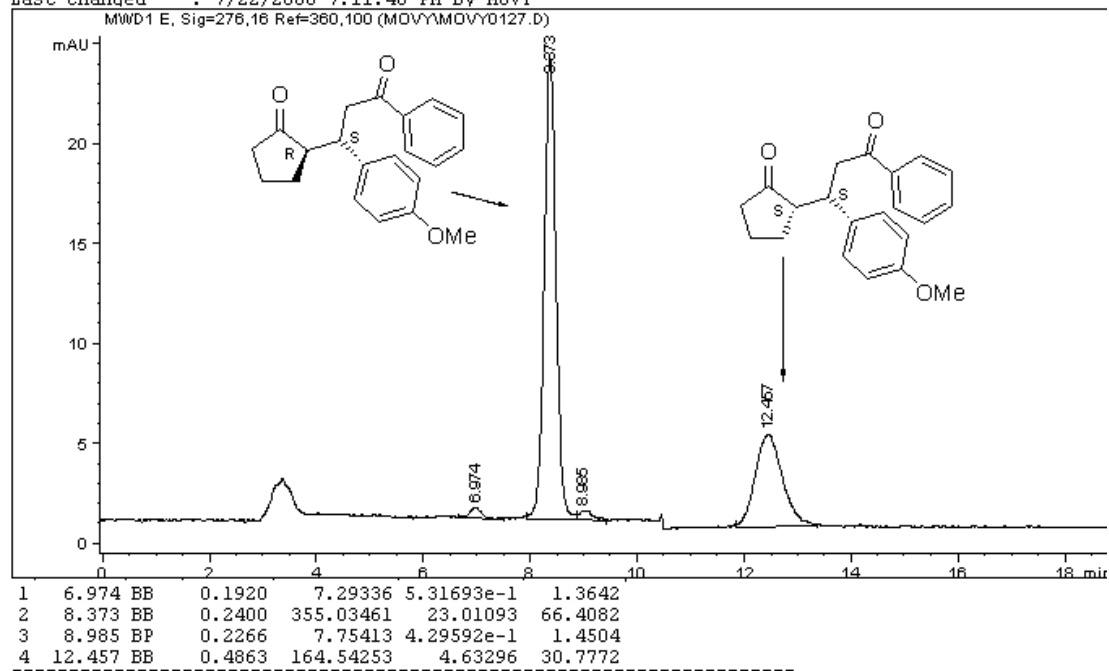


M-3

Injection Date : 7/19/2008 1:19:03 PM
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Acq. Method : C:\HPCHEM\1\METHODS\LEIM.M
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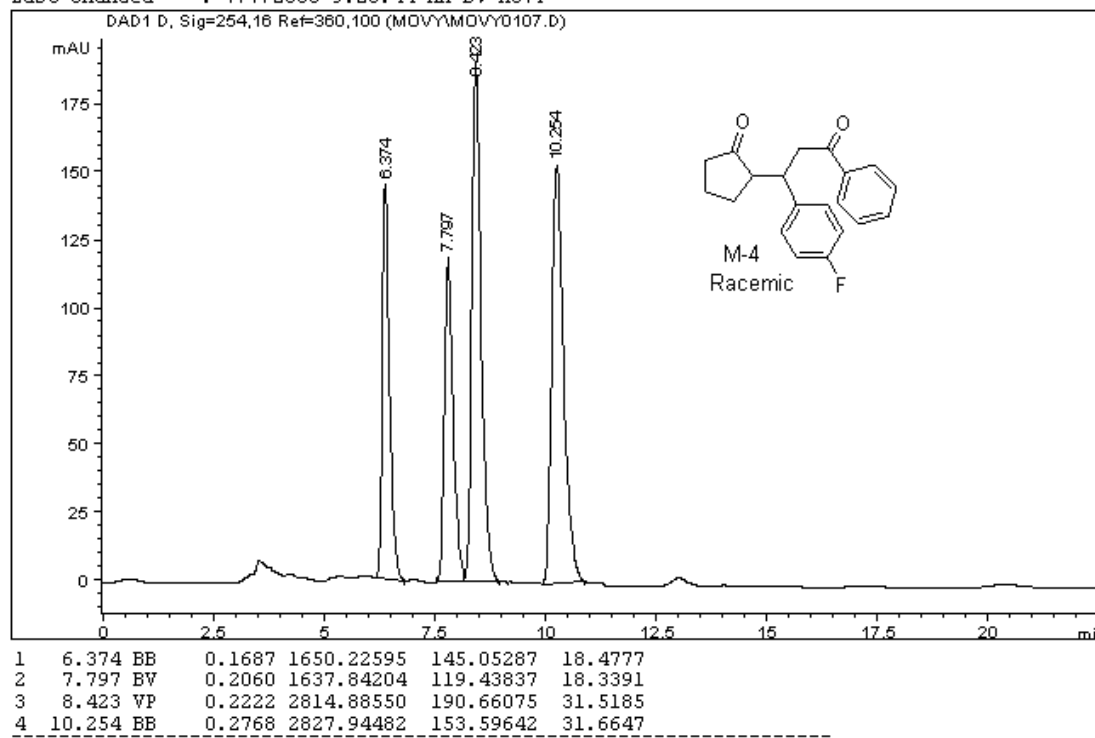


Injection Date : 7/22/2008 7:20:51 PM
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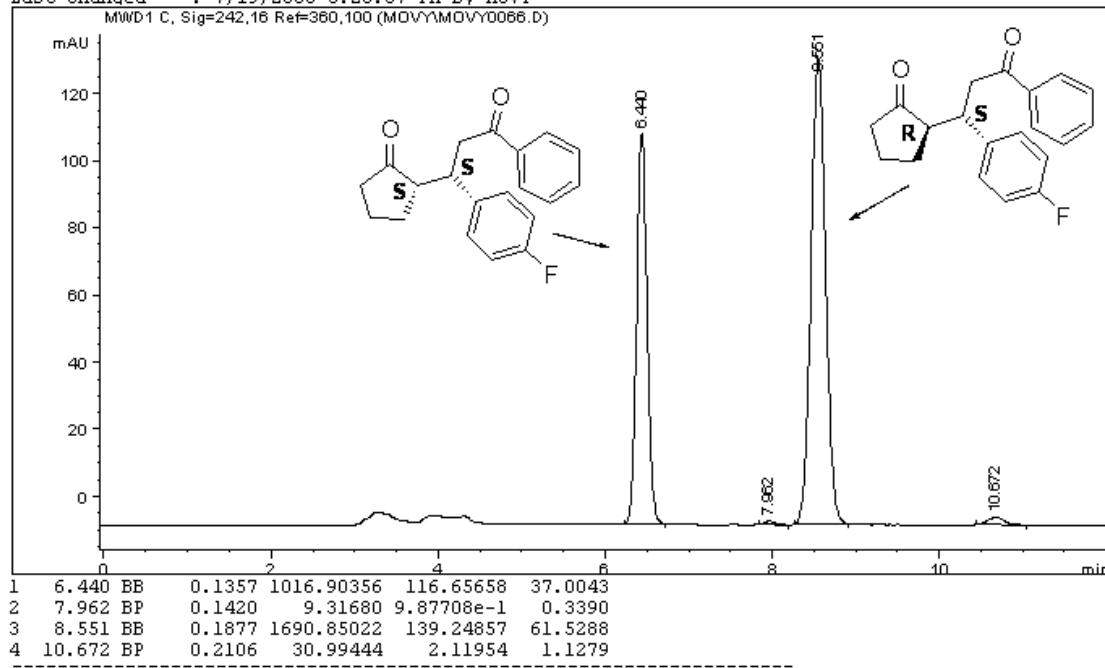
M-4

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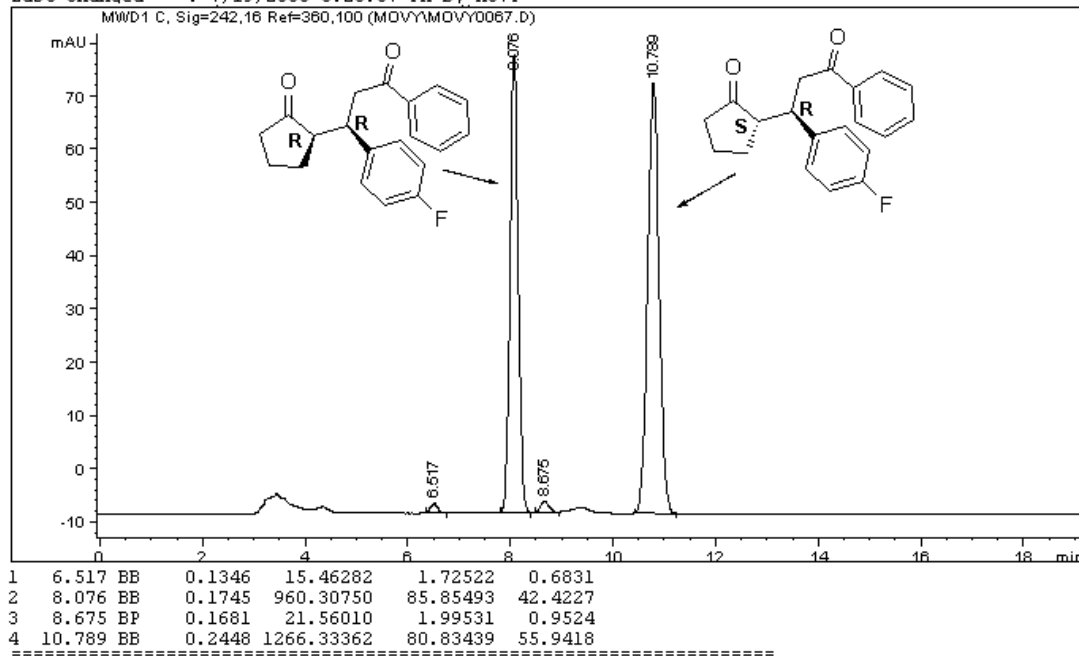
M-4a

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Sample Name : wf08071717
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Last changed : 7/19/2008 3:26:37 PM by MOVY

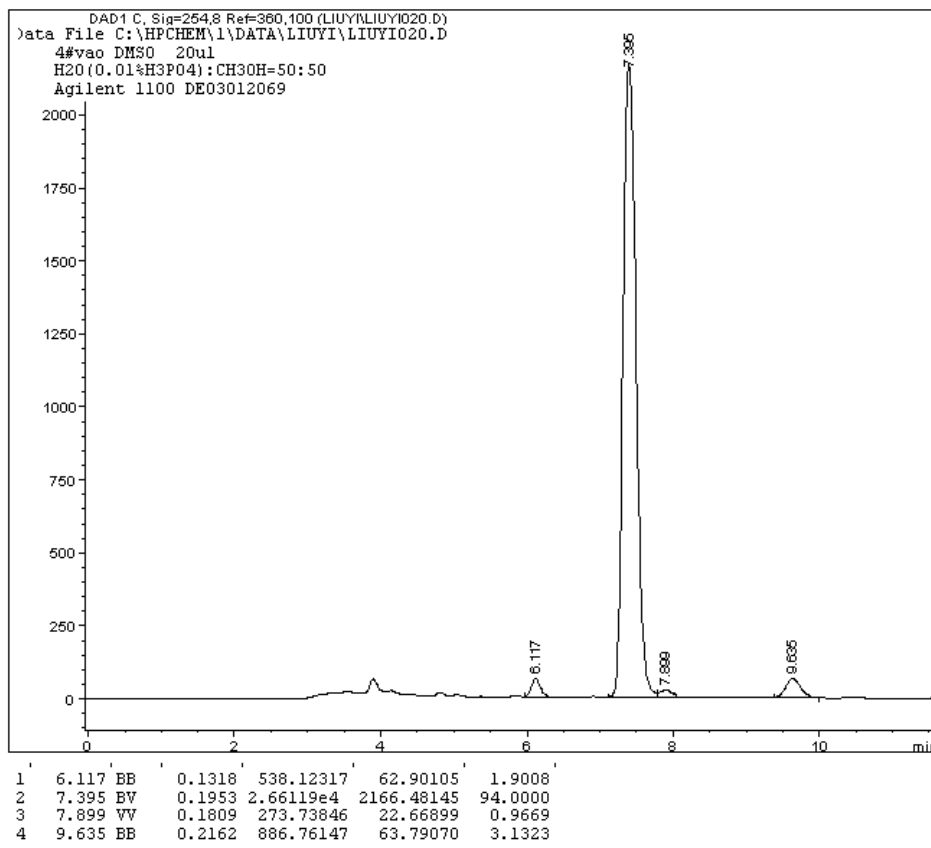


M-4b

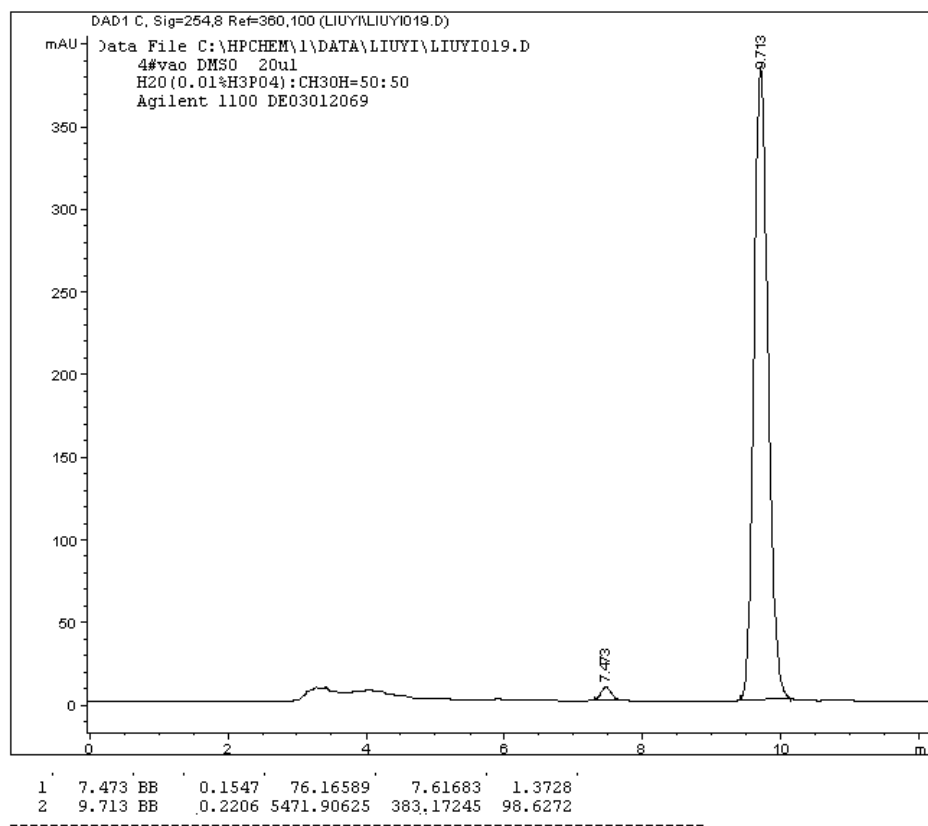
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M-4b1

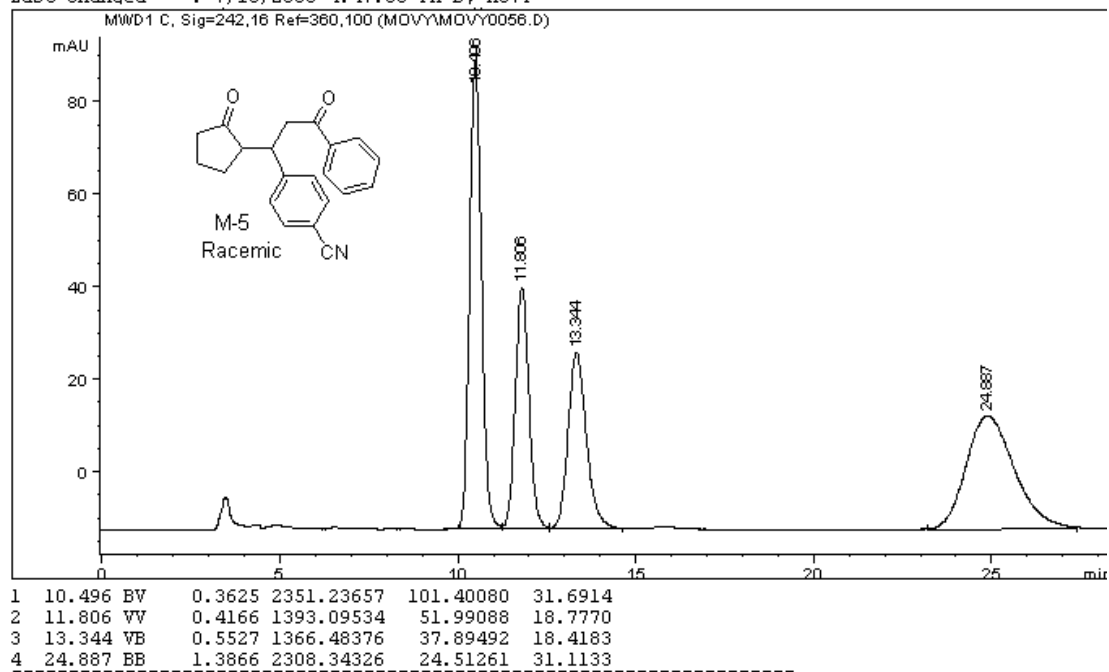


M-4b2

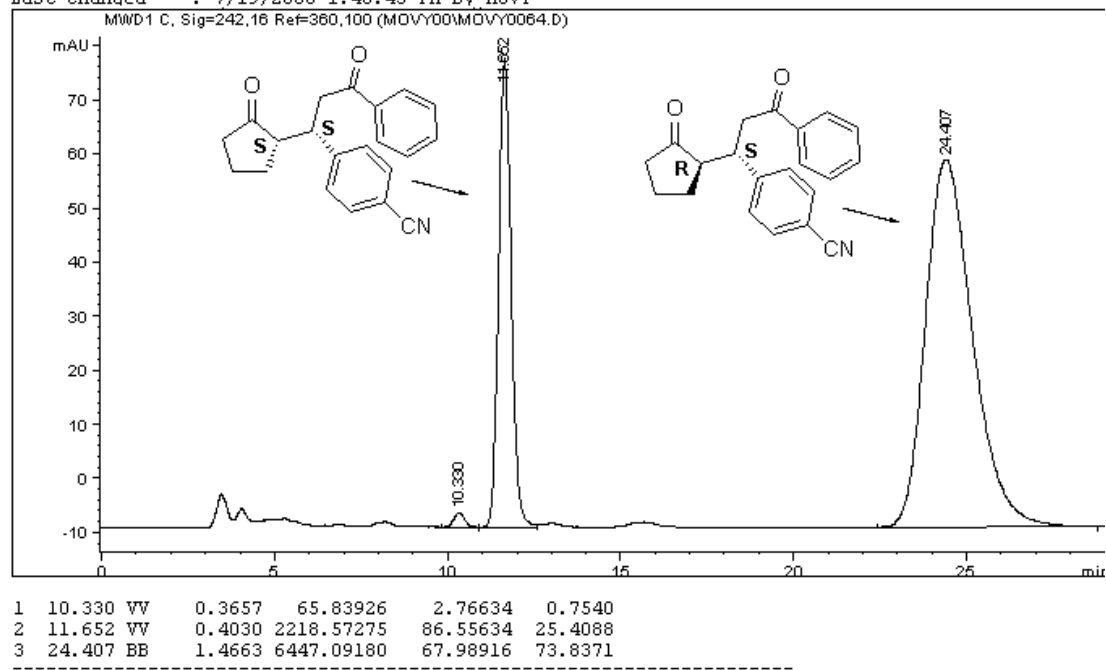


M-5

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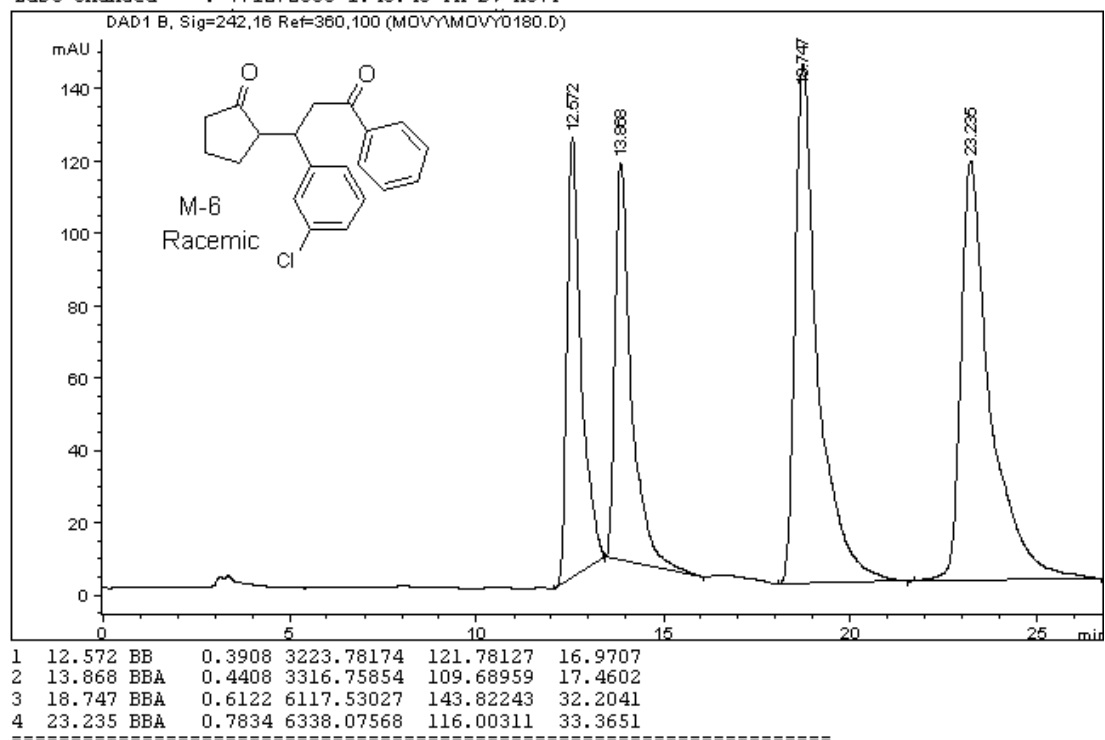


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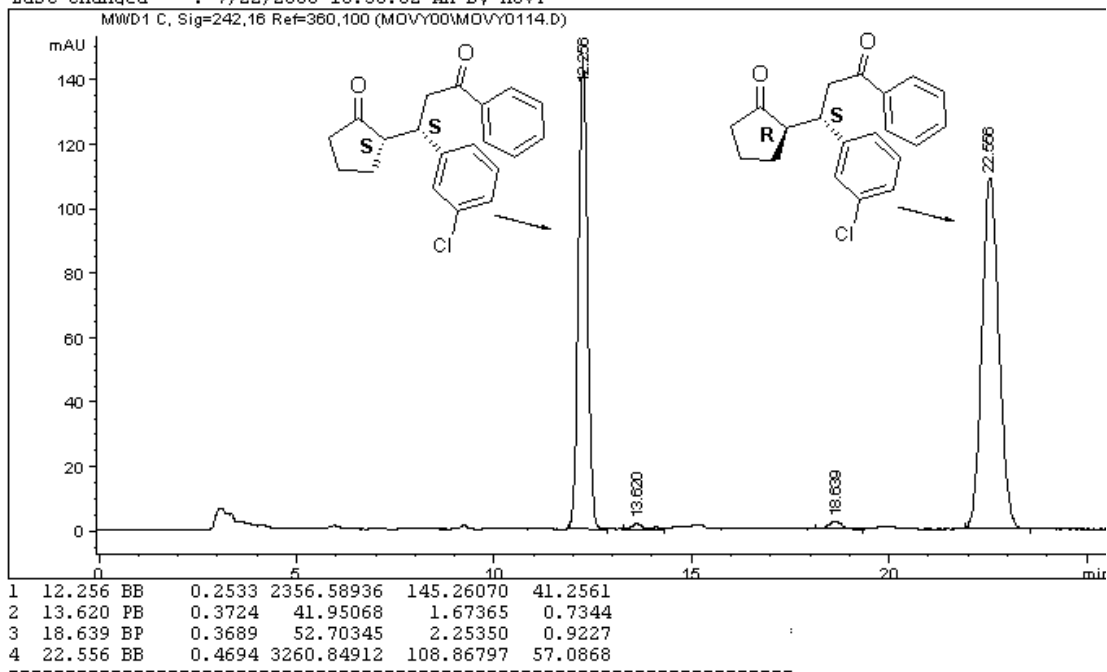
M-6

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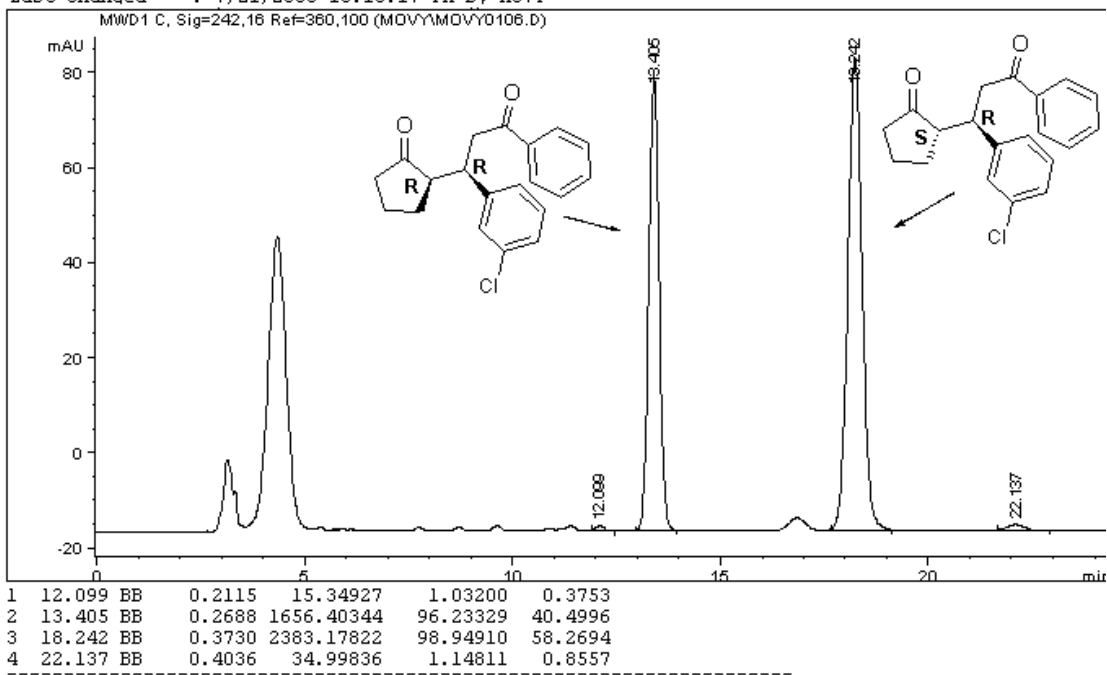
M-6a

Injection Date : 7/22/2008 12:07:35 PM
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Acq. Method : C:\HPCHEM\1\METHODS\LEIM.M
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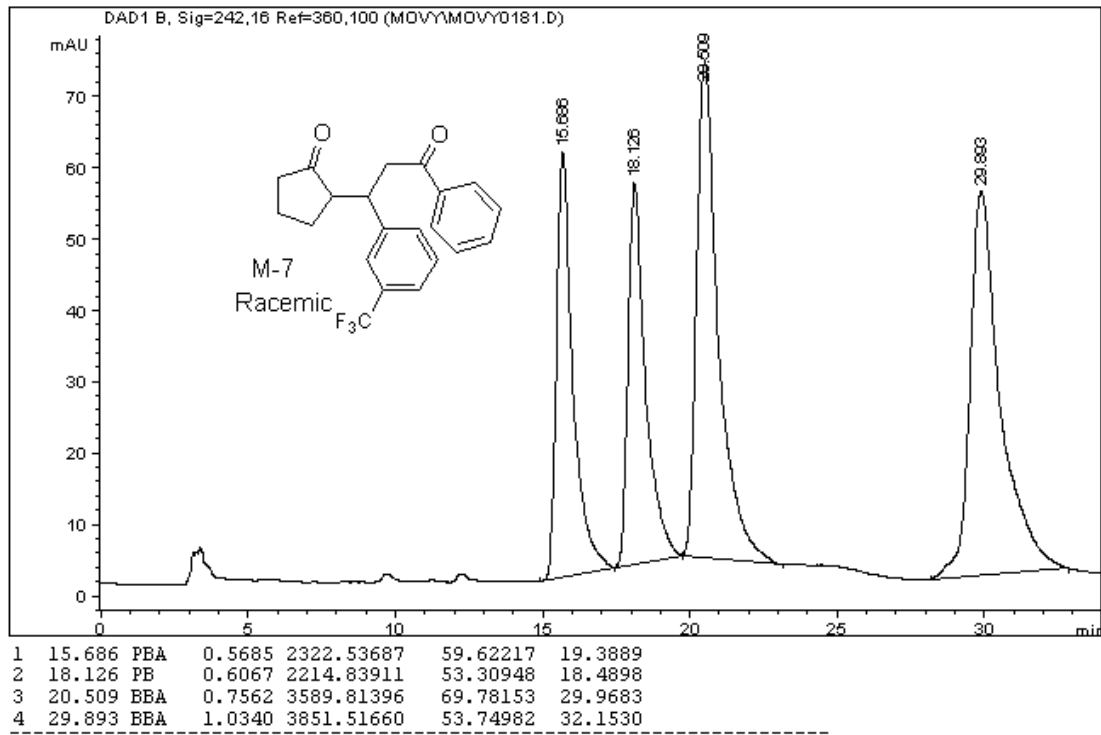
M-6b

Injection Date : 7/21/2008 10:47:18 PM
Sample Name : wf08072016
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Acq. Method : C:\HPCHEM\1\METHODS\LEIM.M
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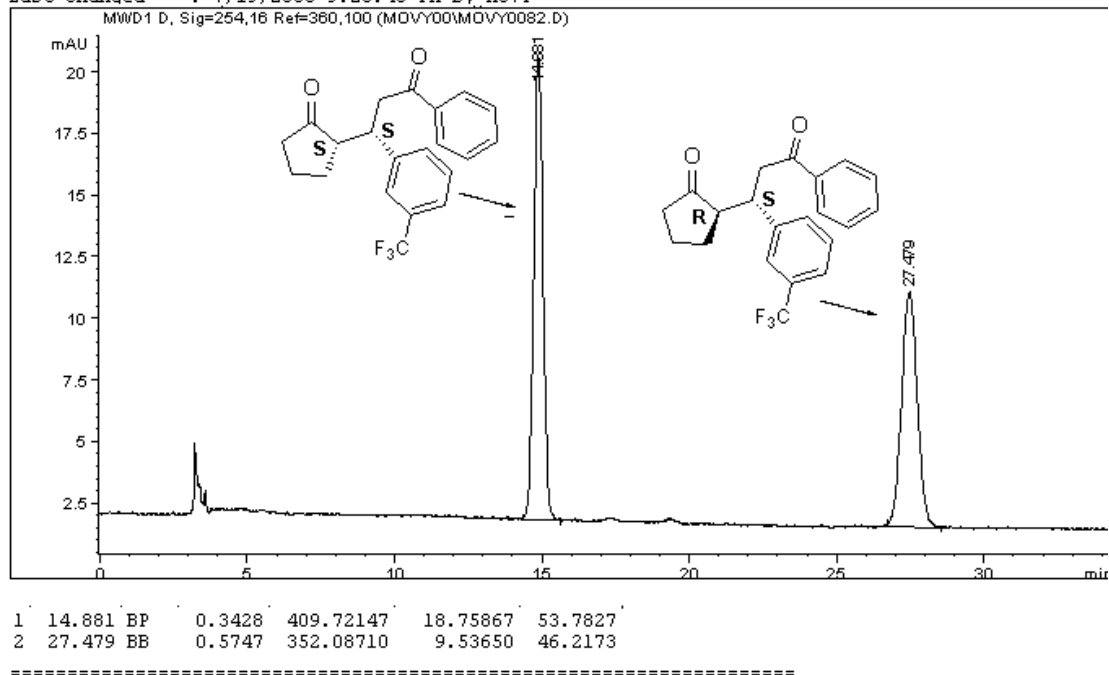
M-7

Injection Date : 7/12/2008 1:50:00 PM
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Acq. Method : C:\HPCHEM\1\METHODS\YG.M
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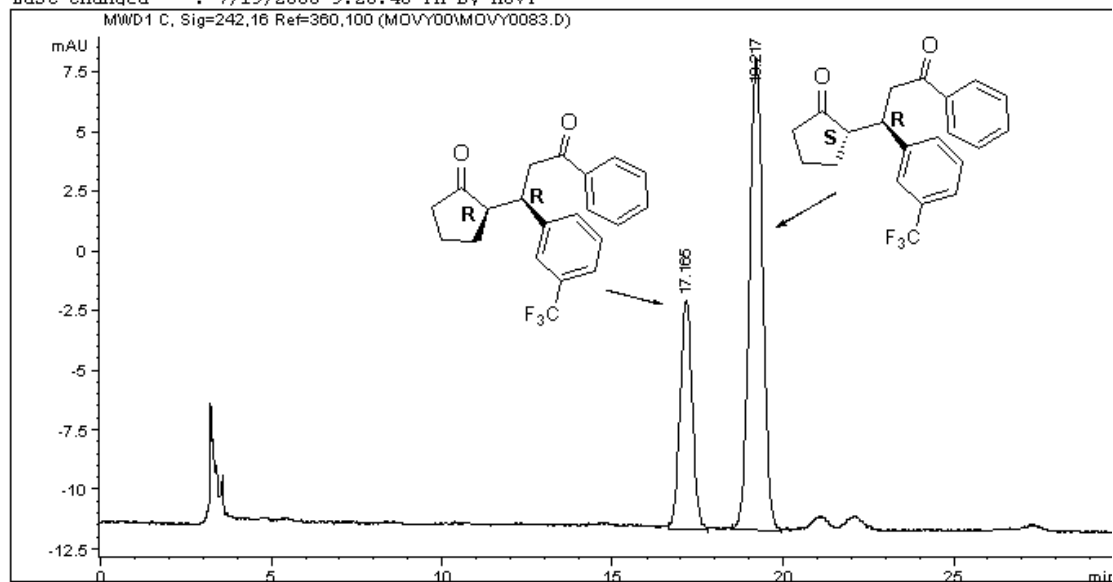
M-7a

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Last changed : 7/19/2008 9:26:48 PM by MOVY



M-7b

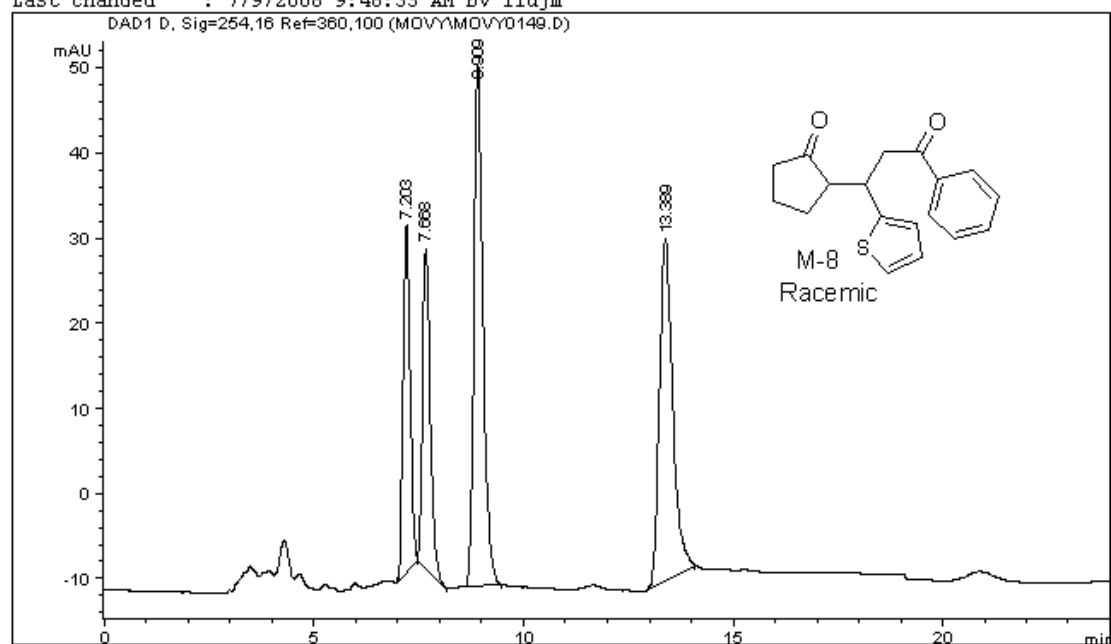
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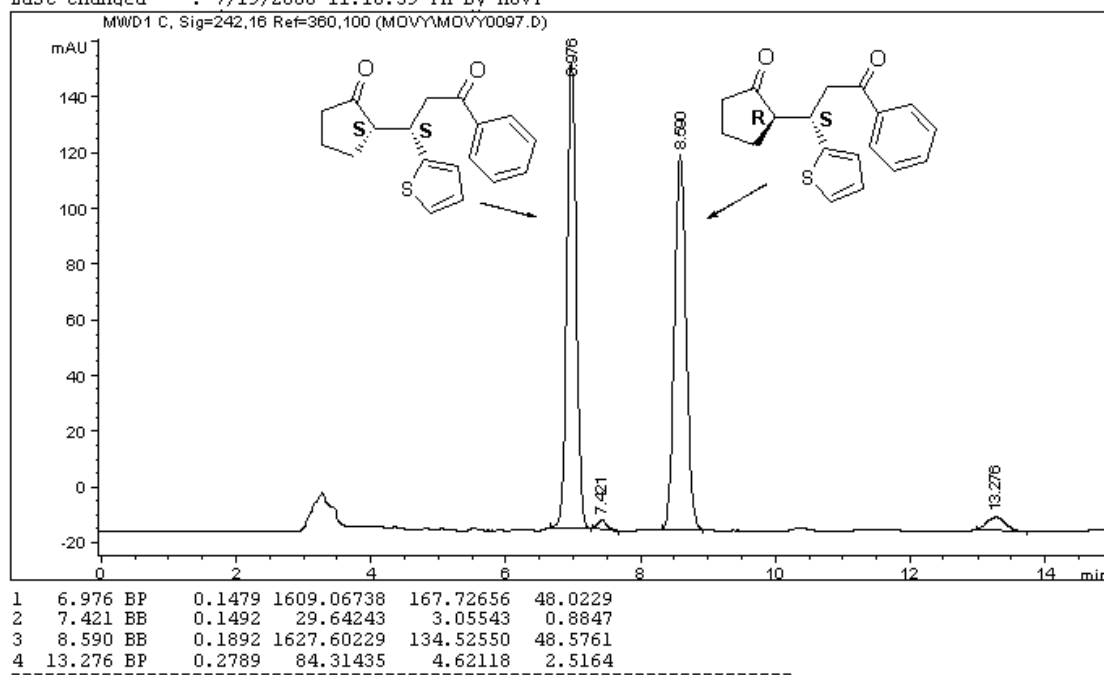
M-8

Injection Date : 7/9/2008 11:43:50 AM
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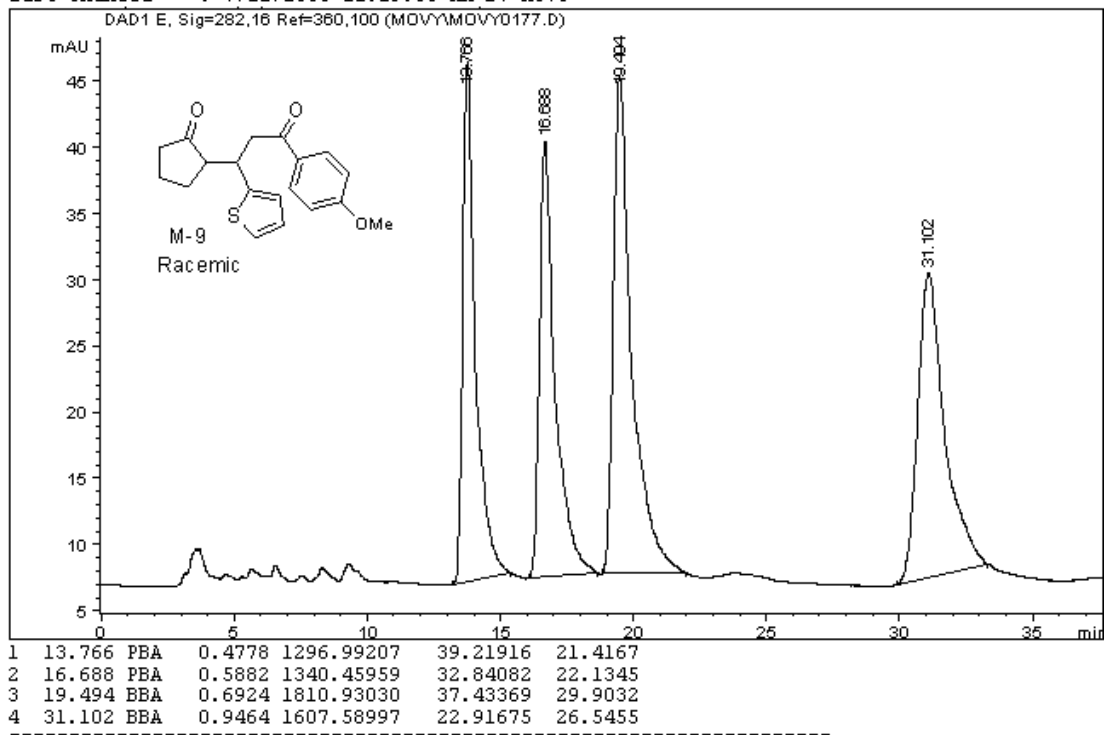
1	7.203	PB	0.1769	464.62149	40.79439	16.9335
2	7.668	BBA	0.1949	473.21408	37.57124	17.2467
3	8.909	BBA	0.2290	926.72363	61.07872	33.7753
4	13.389	PBA	0.3361	879.23499	40.04784	32.0445

Injection Date : 7/21/2008 7:27:58 PM
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Acq. Method : C:\HPCHEM\1\METHODS\LEIM.M
Last changed : 7/19/2008 11:16:59 PM by MOVY



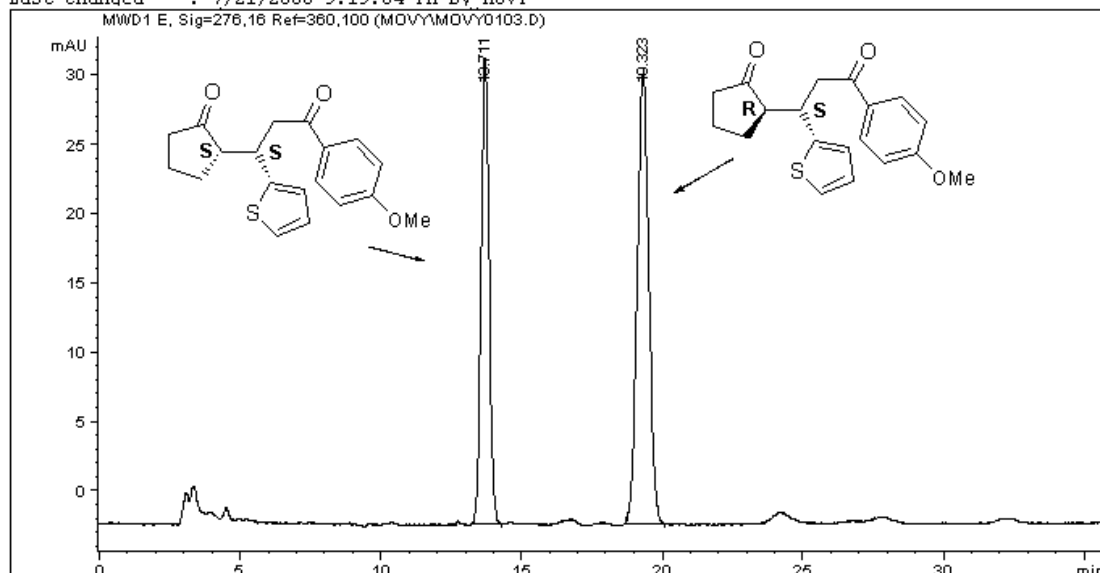
M-9

Injection Date : 7/12/2008 11:28:59 AM
Sample Name : wf08071116
Acq. Operator : MOVY
Acq. Method : C:\HPCHEM\1\METHODS\YG.M
Last changed : 7/12/2008 11:19:35 AM by MOVY



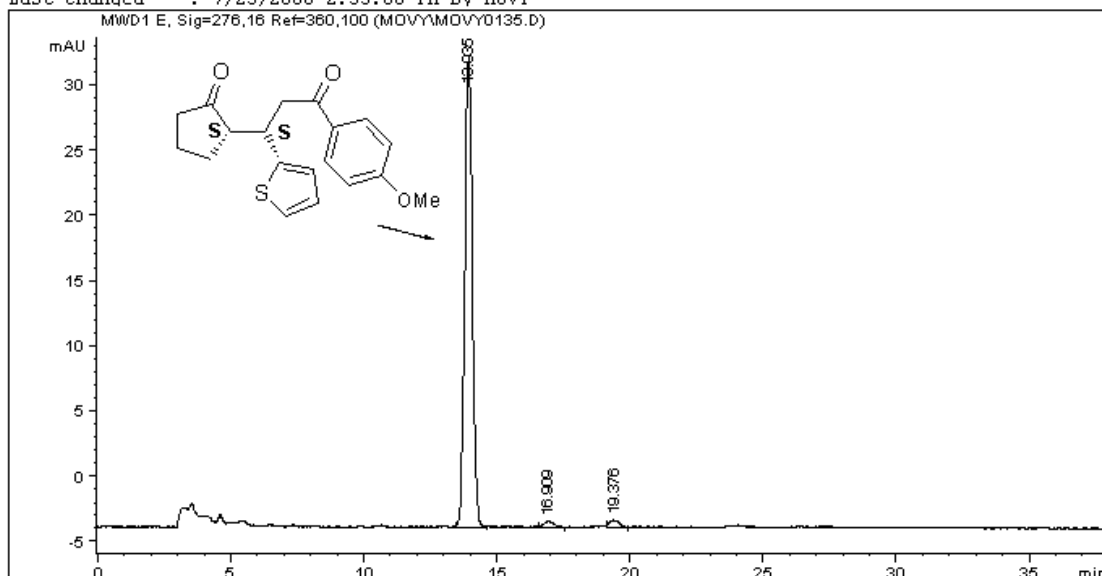
M-9a

Injection Date : 7/21/2008 9:30:02 PM
Sample Name : wf08072017
Acq. Operator : MOVY
Acq. Method : C:\HPCHEM\1\METHODS\LEIM.M
Last changed : 7/21/2008 9:19:04 PM by MOVY



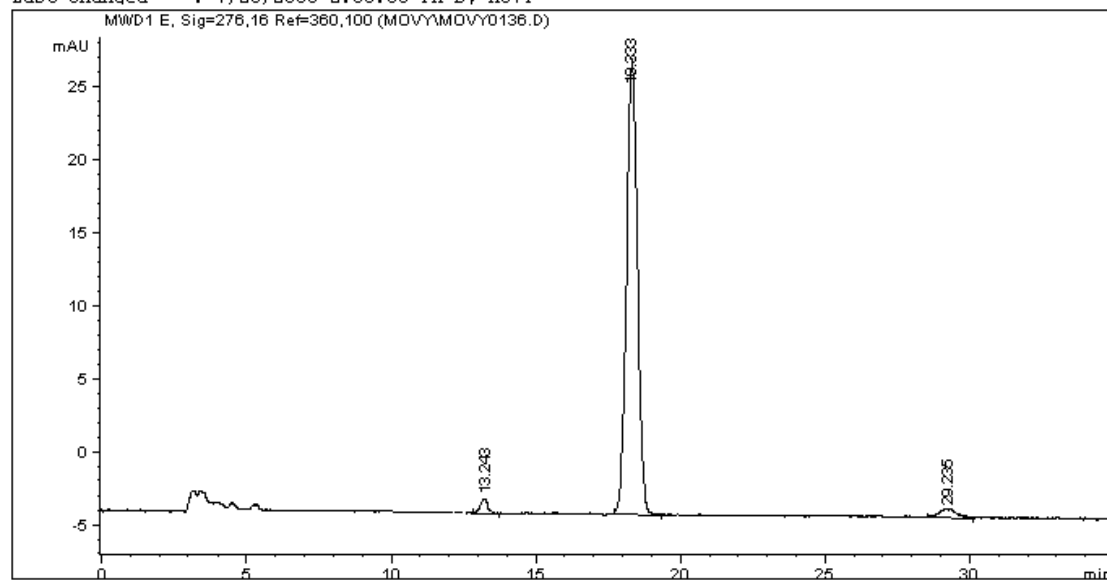
M-9a1

Injection Date : 7/23/2008 3:04:35 PM
Sample Name : wf08072017up
Acq. Operator : MOVY
Acq. Method : C:\HPCHEM\1\METHODS\LEIM.M
Last changed : 7/23/2008 2:53:08 PM by MOVY



M-9a2

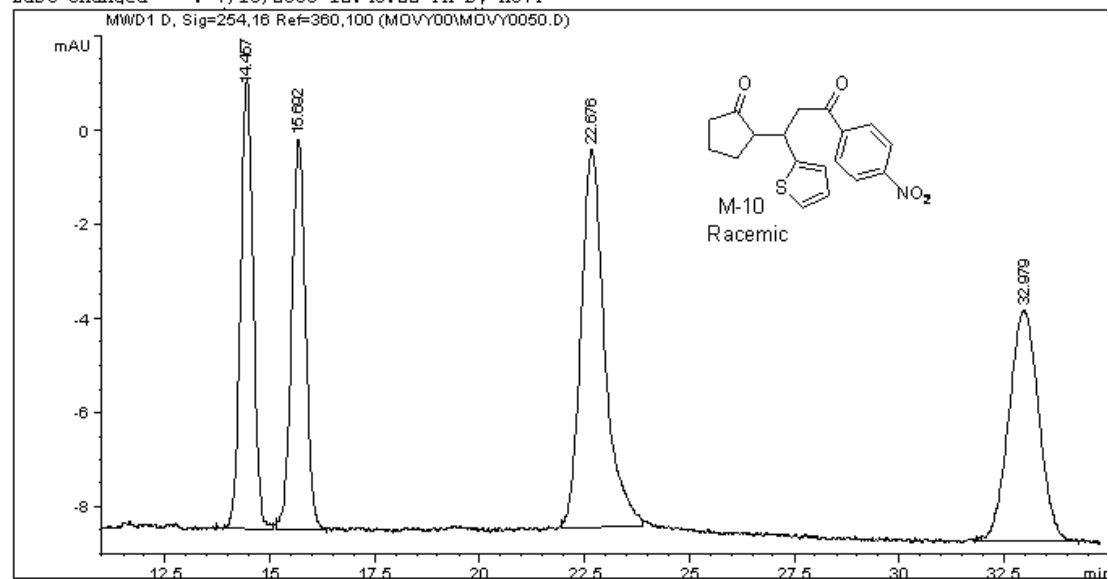
Injection Date : 7/23/2008 3:43:29 PM
Sample Name : wf08072017down
Acq. Operator : MOVY
Acq. Method : C:\HPCHEM\1\METHODS\LEIM.M
Last changed : 7/23/2008 2:53:08 PM by MOVY



1	13.243	BP	0.2608	17.87313	9.44178e-1	2.0545
2	18.333	BB	0.4178	826.43488	31.11989	95.0000
3	29.235	BP	0.5363	25.62372	5.70191e-1	2.9455

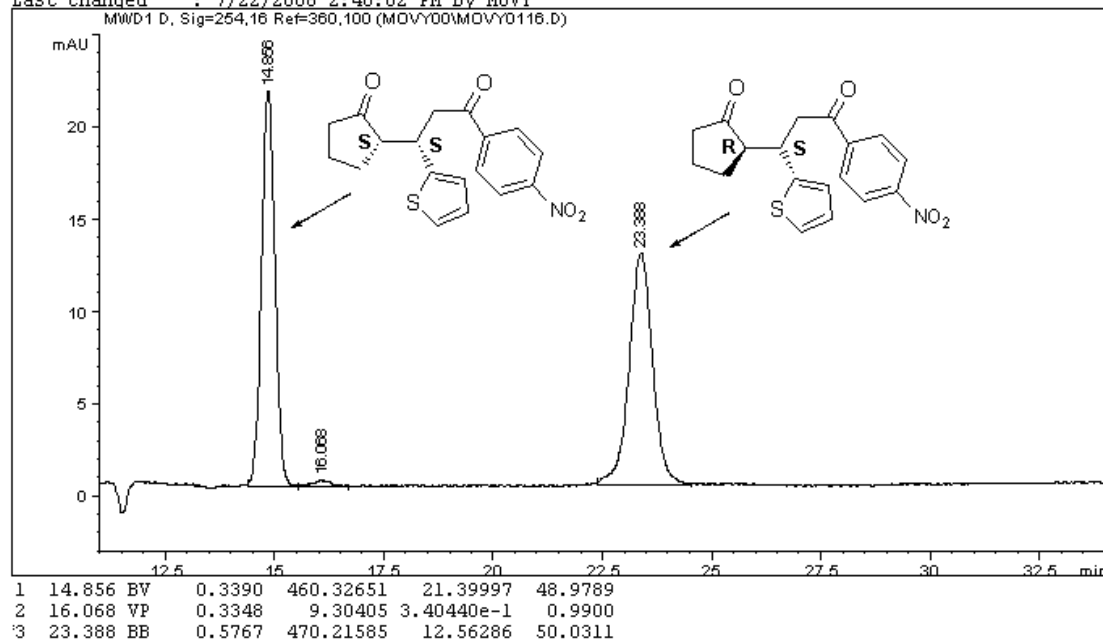
M-10

Injection Date : 7/18/2008 2:43:56 PM
Sample Name : wf08071805
Acq. Operator : MOVY
Acq. Method : C:\HPCHEM\1\METHODS\LEIM.M
Last changed : 7/18/2008 12:46:22 PM by MOVY



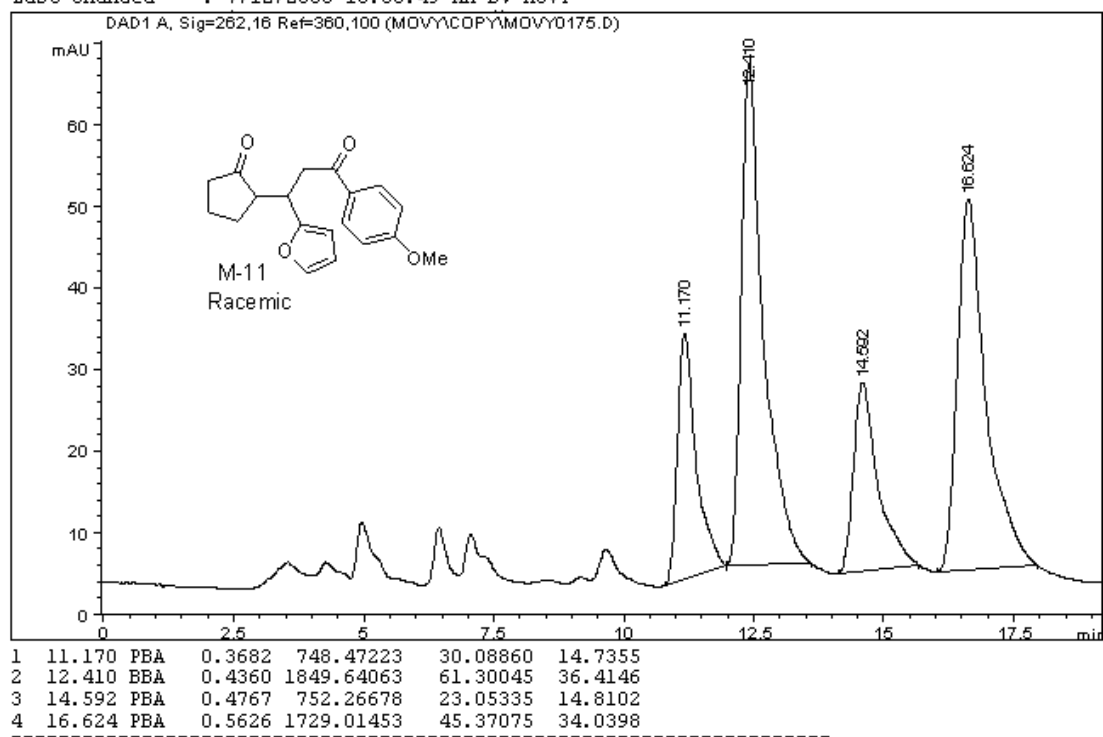
1	14.457	BB	0.3236	199.73701	9.56646	21.0242
2	15.692	BB	0.3574	191.21831	8.27995	20.1275
3	22.676	BB	0.5546	315.76495	8.03335	33.2372
4	32.979	BB	0.6493	243.31308	4.91734	25.6110

Injection Date : 7/22/2008 2:50:10 PM
Sample Name : wf08072029
Acq. Operator : MOVY
Acq. Method : C:\HPCHEM\1\METHODS\LEIM.M
Last changed : 7/22/2008 2:40:02 PM by MOVY



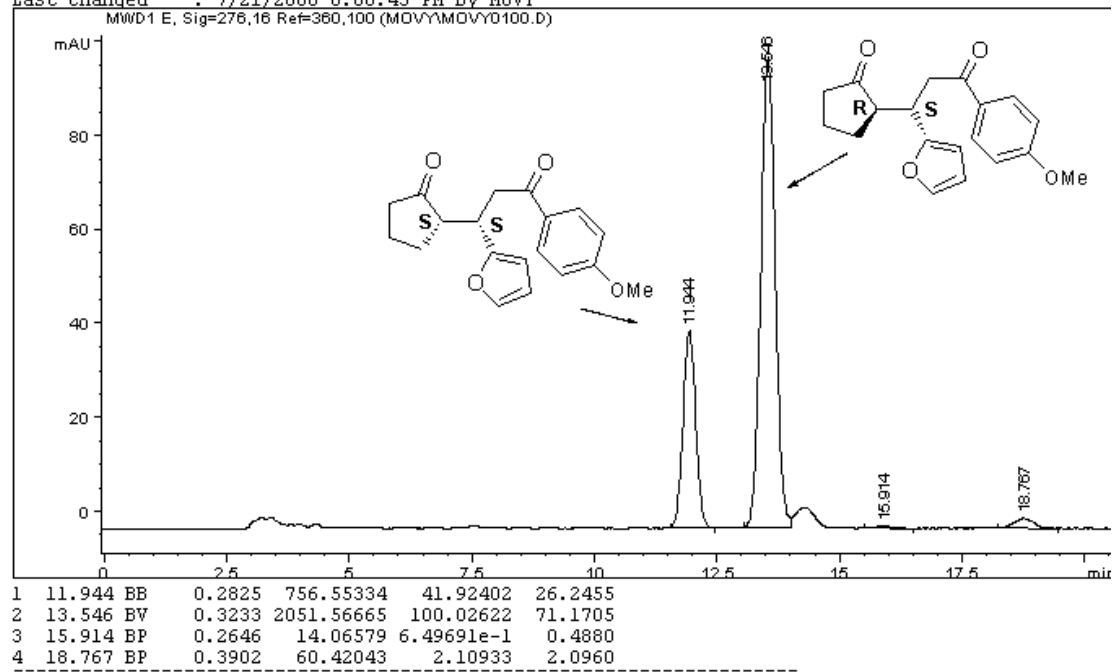
M-11

Injection Date : 7/12/2008 10:44:09 AM
Sample Name : wf08071121
Acq. Operator : MOVY
Acq. Method : C:\HPCHEM\1\METHODS\YG.M
Last changed : 7/12/2008 10:38:49 AM by MOVY



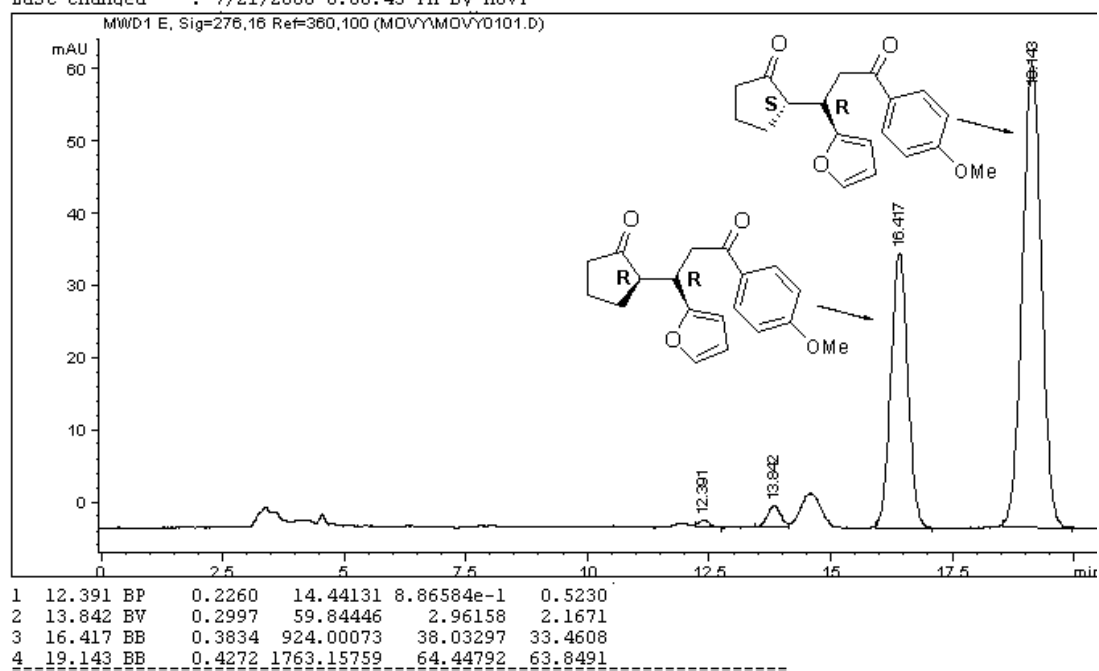
M-11a

Injection Date : 7/21/2008 8:17:48 PM
Sample Name : wf08072019
Acq. Operator : MOVY
Acq. Method : C:\HPCHEM\1\METHODS\LEIM.M
Last changed : 7/21/2008 8:08:43 PM by MOVY



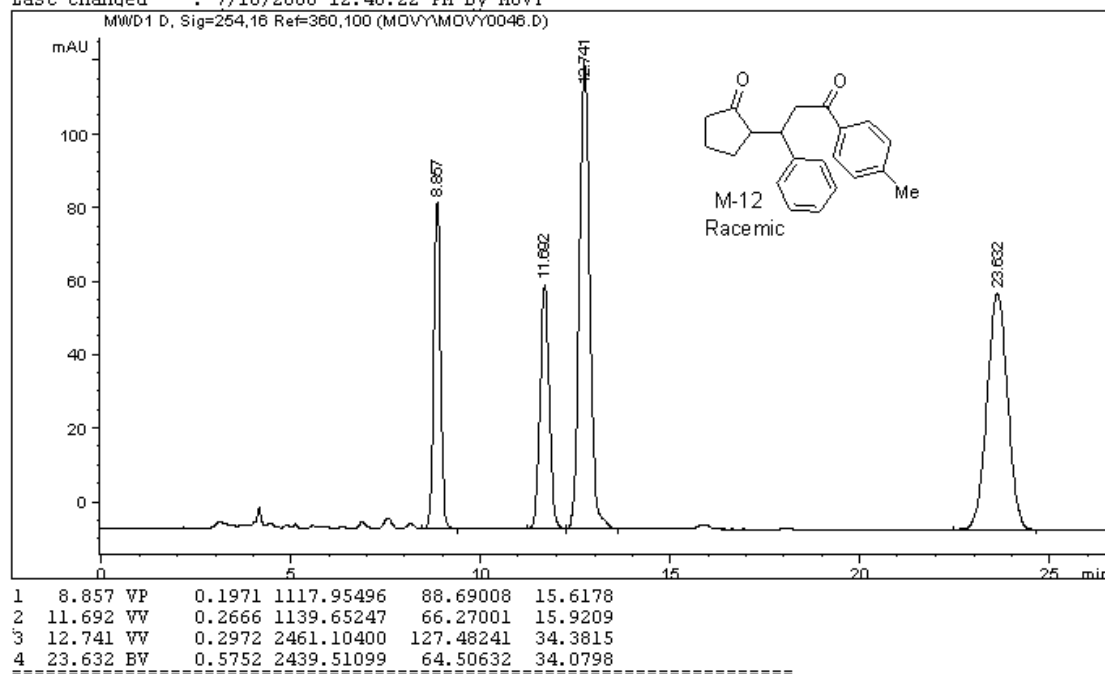
M-11b

Injection Date : 7/21/2008 8:38:49 PM
Sample Name : wf08072020
Acq. Operator : MOVY
Acq. Method : C:\HPCHEM\1\METHODS\LEIM.M
Last changed : 7/21/2008 8:08:43 PM by MOVY



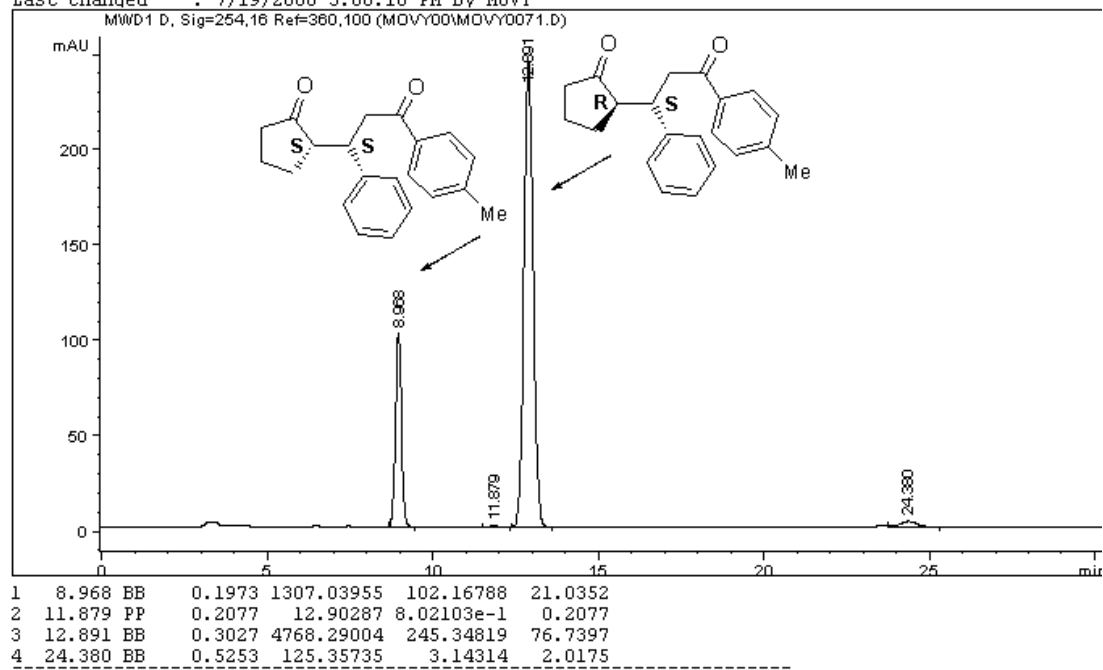
M-12

Injection Date : 7/18/2008 1:16:31 PM
Sample Name : wf08071217
Acq. Operator : MOVY
Acq. Method : C:\HPCHEM\1\METHODS\LEIM.M
Last changed : 7/18/2008 12:46:22 PM by MOVY



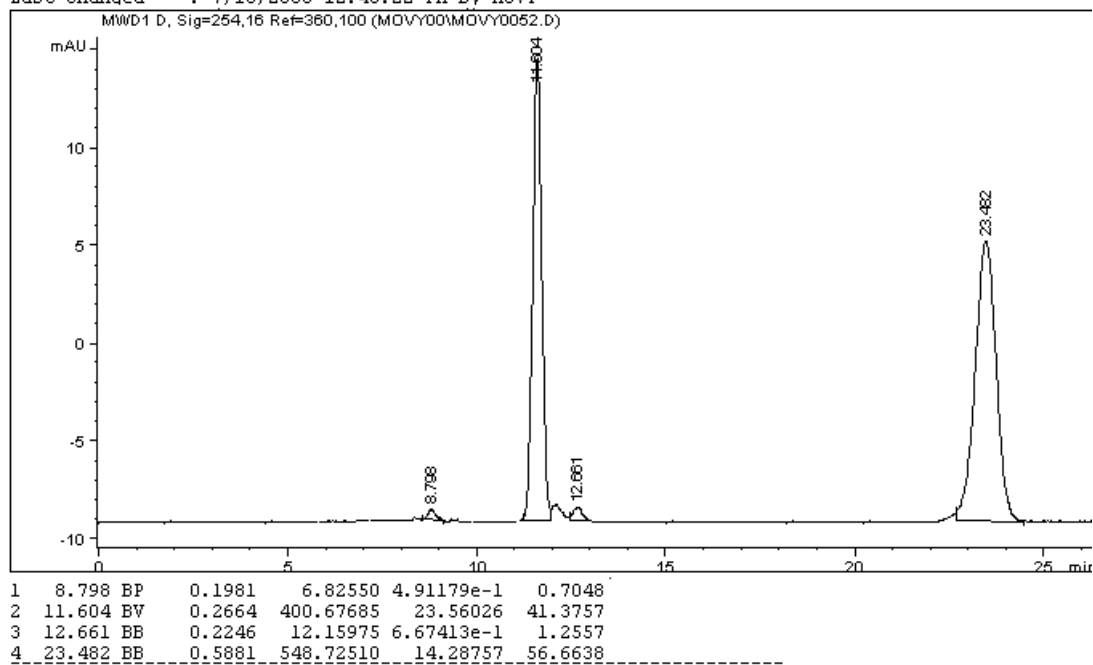
M-12a

Injection Date : 7/19/2008 5:18:45 PM
Sample Name : wf08071705
Acq. Operator : MOVY
Acq. Method : C:\HPCHEM\1\METHODS\LEIM.M
Last changed : 7/19/2008 5:06:10 PM by MOVY

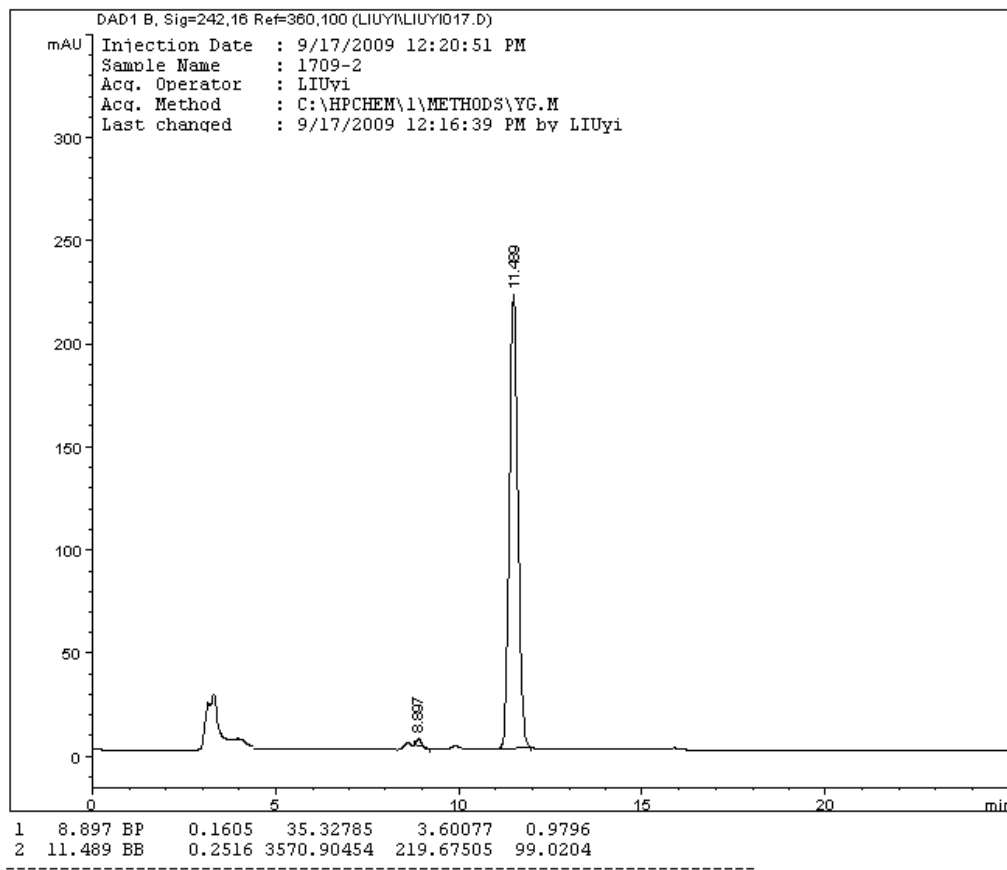


M-12b

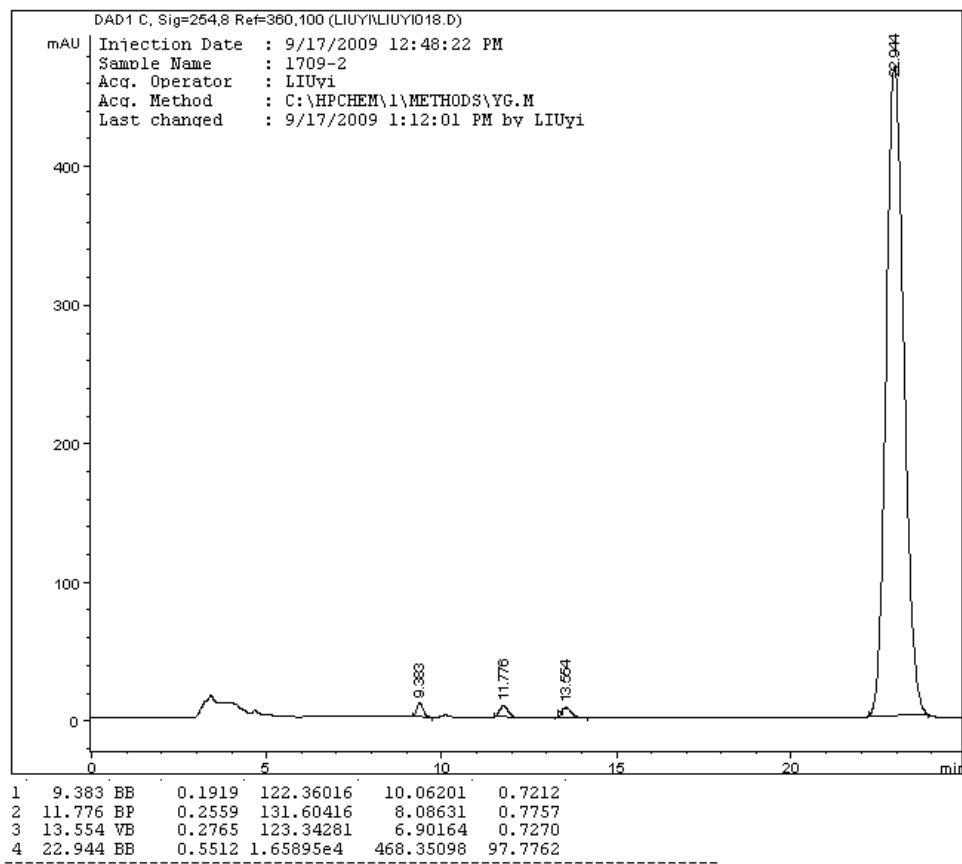
Injection Date : 7/18/2008 3:45:20 PM
Sample Name : wf08071723
Acq. Operator : MOVY
Acq. Method : C:\HPCHEM\1\METHODS\LEIM.M
Last changed : 7/18/2008 12:46:22 PM by MOVY



M-12b1

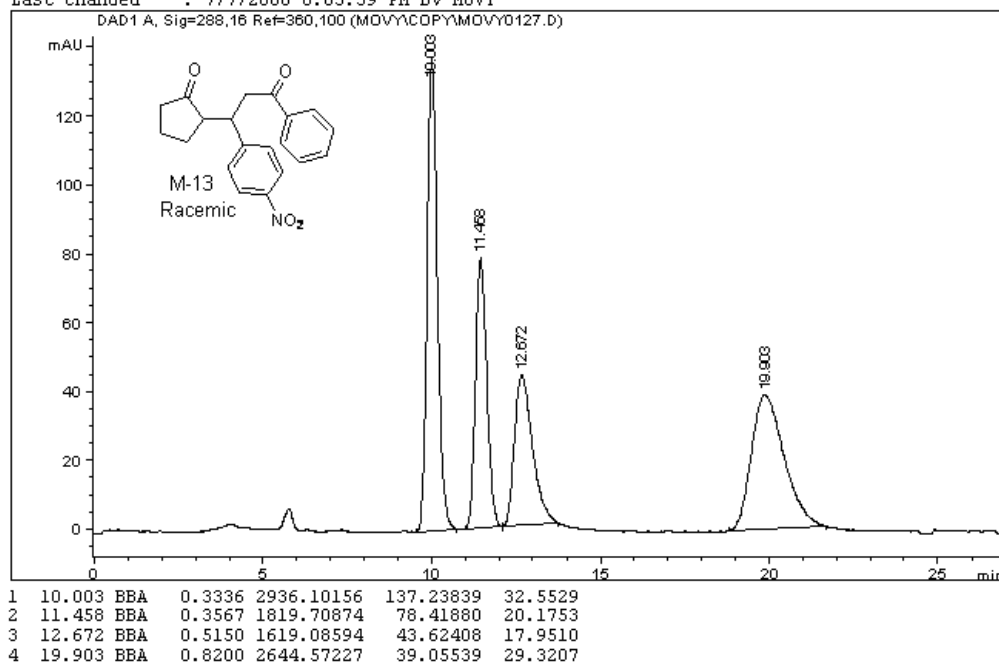


M-12b2



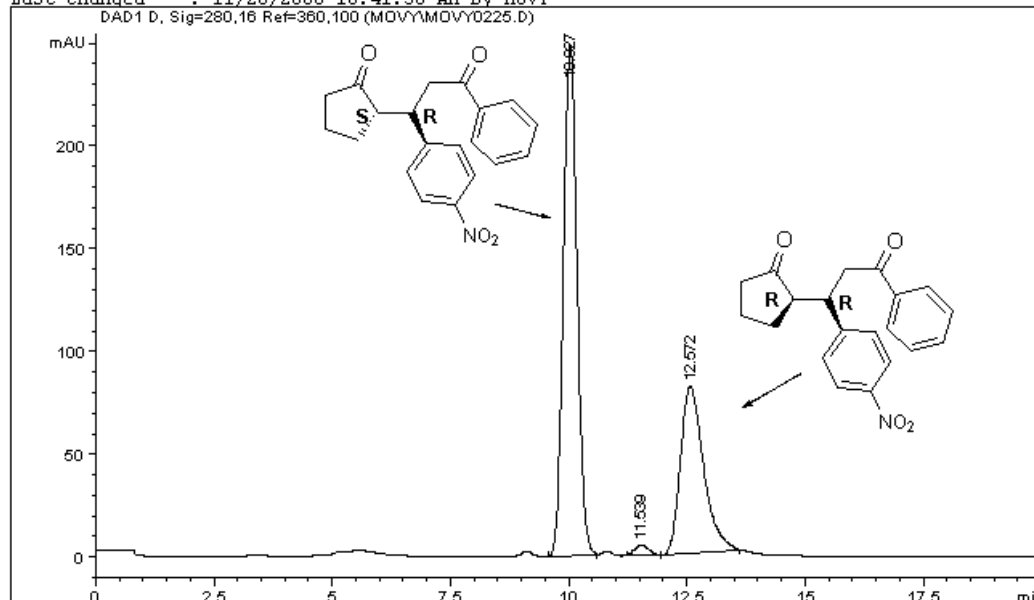
M-13

Injection Date : 7/7/2008 7:23:56 PM
Sample Name : wf08070603
Acq. Operator : MOVY
Acq. Method : C:\HPCHEM\1\METHODS\YG.M
Last changed : 7/7/2008 6:05:59 PM by MOVY



M-13b

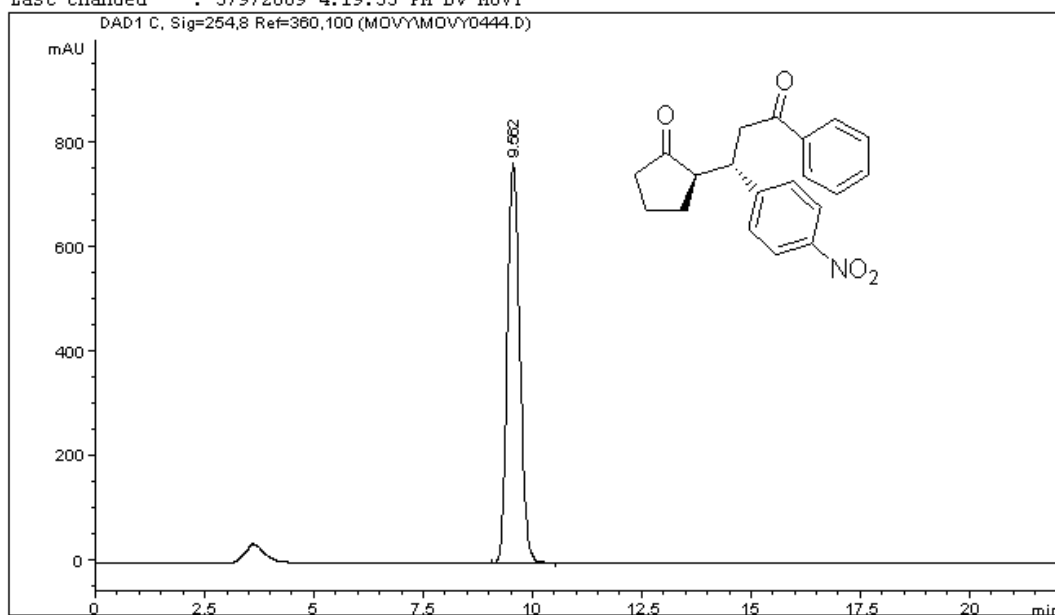
Injection Date : 11/20/2008 11:06:12 AM
Sample Name : wf08110303
Acq. Operator : MOVY
Acq. Method : C:\HPCHEM\1\METHODS\YG.M
Last changed : 11/20/2008 10:41:36 AM by MOVY
DAD1 D, Sig=280,16 Ref=360,100 (MOVY\MOVY0225.D)



1	10.027	BBA	0.3116	4986.48437	249.00954	63.6050
2	11.539	BB	0.3431	102.84580	4.73997	1.3118
3	12.572	BBA	0.5131	2750.43262	81.21510	35.0831

M-13b2

Injection Date : 3/9/2009 4:27:35 PM
Sample Name : wf08110303
Acq. Operator : MOVY
Acq. Method : C:\HPCHEM\1\METHODS\YG.M
Last changed : 3/9/2009 4:19:53 PM by MOVY
DAD1 C, Sig=254,8 Ref=360,100 (MOVY\MOVY0444.D)



1	9.562	BBA	0.3115	1.52304e4	767.51489	100.0000
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