

Supporting Information

Asymmetric Intermolecular Boron-Heck Type Reactions via Oxidative Palladium(II) Catalysis Using Chiral Tridentate NHC-Amidate-Alkoxide Ligands

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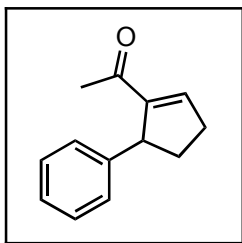
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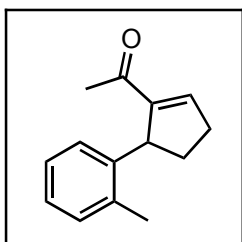
General Information. Prior to use, dichloromethane was distilled from calcium hydride. ^1H and ^{13}C NMR spectra were recorded on a 250 and 63 MHz or 400 and 100 MHz. Chemical shifts were reported in ppm relative to TMS for ^1H - and ^{13}C -NMR spectra and CD_3OD or CDCl_3 was used as the NMR solvent. Thin-layer chromatography (TLC) was performed using commercially prepared 60 mesh silica gel plates visualized with short-wavelength UV light (254 nm). Silica gel 60 (230-400 mesh) was used for column chromatography. The reported yields are isolated yields and are the average of two runs. Elemental analysis and high-resolution mass spectra (HRMS) HRMS data were obtained as specified. The enantiomeric excess was determined by HPLC and NMR analyses. HPLC analyses were conducted with an UV detector and a Chiralcel OD-H column, and NMR analyses were determined by using of Europium tris[3-(heptafluoro-propyl)-hydroxy-methylene]-(+)-camphorate].

Typical procedure Asymmetric Boron-Heck reaction between arylboronic acids and cyclic olefins:

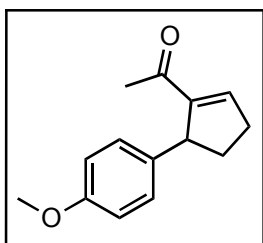
To an oven-dried round bottom flask equipped with a stir bar was added palladium catalyst (0.05 mmol) and DMF (3 ml). The resulting solution was allowed to stir for 10 minutes at room temperature. To the stirring solution was then added the arylboronic acid (1.0 mmol) and cyclic olefin (1.5 mmol) and the reaction flask was fitted with an oxygen balloon and stirred overnight at room temperature. After consumption of the starting (confirmed by TLC), the reaction solution was diluted with ethyl acetate (40 ml) and washed twice with water (2 x 20 ml), and once with brine (20 ml). The combined aqueous layers were then extracted once with dichloromethane (20 ml). All organic layers were then combined and anhydrous sodium sulfate added. The solution was filtered and the filtrate concentrated at reduced pressure. The crude product was then subjected to column chromatography using an eluent gradient (50:1 Hex/EA to 10:1 Hex/EA) to give the desired product.



1-(5-phenylcyclopent-1-enyl)ethanone (19). Following the typical procedure outlined above, the title compound was isolated as a colorless oil. ^1H NMR 250 MHz (CDCl_3): δ 1.85 ~ 1.97 (m, 1H), 2.24 (s, 3H), 2.43 ~ 2.64 (m, 2H), 2.67 ~ 2.84 (m, 1H), 4.14 ~ 4.22 (m, 1H), 6.92 ~ 6.95 (m, 1H), 7.11 ~ 7.19 (m, 3H), 7.22 ~ 7.29 (m, 2H); ^{13}C NMR, 63 MHz (CDCl_3): δ 27.2, 32.5, 33.9, 49.4, 126.1, 126.9, 128.4, 144.7, 145.0, 148.3, 195.9; Anal. calcd for $\text{C}_{13}\text{H}_{14}\text{O}$: C 83.83, H 7.58, found: C 83.59, H 7.71; HRMS-ESI (m/z) [$\text{M}+\text{H}^+$] calcd for $\text{C}_{13}\text{H}_{14}\text{O}$: 187.1117, found: 187.1126; NMR data for *ee* (after treating with europium tris[3-(heptafluoropropyl-hydroxyl-methylene)-(+)-camphorate]): δ 3.04 ppm (major) and 3.08 ppm (minor).

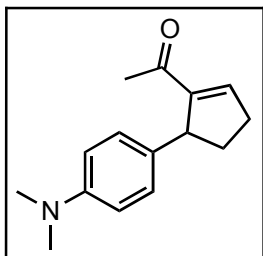


1-(5-*o*-tolylcyclopent-1-enyl)ethanone (20). Following the typical procedure outlined above, the title compound was isolated as a colorless oil. ^1H NMR, 400MHz (CDCl_3): δ 1.73 ~ 1.81 (m, 1H), 2.27 (s, 3H), 2.43 (s, 3H), 2.46 ~ 2.63 (m, 2H), 2.64 ~ 2.75 (m, 1H), 4.36 ~ 4.42 (m, 1H), 6.84 ~ 6.88 (m, 1H), 6.97 ~ 6.99 (m, 1H), 7.04 ~ 7.09 (m, 2H), 7.13 ~ 7.17 (m, 1H); ^{13}C NMR, 63MHz (CDCl_3): δ 19.7, 27.2, 32.2, 32.7, 45.2, 125.0, 125.9, 126.0, 130.3, 135.3, 143.0, 145.1, 148.3, 195.9; Anal. calcd for $\text{C}_{14}\text{H}_{16}\text{O}$: C 83.96, H 8.05, found: C 83.81, H 7.97; HRMS-ESI (m/z) [$\text{M}+\text{H}^+$] calcd for $\text{C}_{14}\text{H}_{16}\text{O}$: 201.1274, found: 201.1279; NMR data for *ee* (after treating with europium tris[3-(heptafluoropropyl-hydroxyl-methylene)-(+)-camphorate]): δ 2.97 ppm (major) and 3.04 ppm (minor).



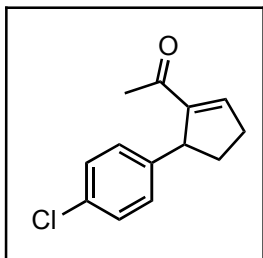
1-(5-(4-methoxyphenyl)cyclopent-1-enyl)ethanone (21). Following the typical procedure outlined above, the title compound was isolated as a pale yellow oil. ^1H NMR, 400 MHz (CDCl_3) δ 1.83 ~ 1.92 (m, 1H), 2.24 (s, 3H), 2.41 ~ 2.49 (m, 1H), 2.51 ~ 2.61 (m, 1H), 2.67 ~ 2.78 (m, 1H), 3.76 (s, 3H), 4.11 ~ 4.17 (m, 1H), 6.80 (d, 2H, J = 10.5 Hz), 6.90 (q, 1H, J = 6 Hz), 7.06 (d, 2H, J = 10.5 Hz); ^{13}C NMR, 100 MHz (CDCl_3) δ 27.3, 32.4, 33.9, 48.5, 55.1, 113.7, 127.8, 137.1, 144.5, 148.4, 157.8, 196.1; Anal. calcd for $\text{C}_{14}\text{H}_{16}\text{O}_2$: C 77.75, H 7.46, found: C 77.51, H 7.32; HRMS-

ESI (m/z) [M+H⁺] calcd for C₁₄H₁₆O₂: 217.1223, found: 217.1229; NMR data for *ee* (after treating with europium tris[3-(heptafluoropropyl-hydroxyl-methylene)-(+)-camphorate]): δ 3.06 ppm (major) and 3.15 ppm (minor).



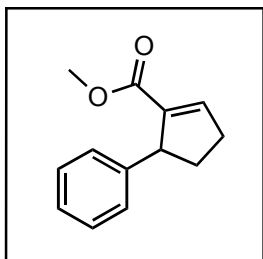
1-(5-(4-dimethylamino)phenyl)cyclopent-1-enyl)ethanone (22).

Following the typical procedure outlined above, the title compound was isolated as a light brown oil. ¹H NMR, 400 MHz (CDCl₃) δ 1.82 ~ 1.95 (m, 1H), 2.21 (s, 3H), 2.38 ~ 2.63 (m, 2H), 2.64 ~ 2.76 (m, 1H), 2.89 (s, 6H), 4.08 ~ 4.15 (m, 1H), 6.66 (d, 2H, *J* = 17 Hz), 6.86 ~ 6.90 (m, 1H), 7.02 (d, 2H, *J* = 18 Hz); ¹³C NMR, 100 MHz (CDCl₃) δ 27.4, 32.4, 34.0, 40.7, 48.4, 112.8, 127.5, 133.1, 144.0, 148.5, 149.1, 196.3; Anal. calcd for C₁₅H₁₉NO: C 78.56, H 8.35, N 6.11 found: C 78.11, H 8.19, N 5.97; HRMS-ESI (m/z) [M+H⁺] calcd for C₁₅H₁₉NO: 230.1539, found: 230.1546; NMR data for *ee* (after treating with europium tris[3-(heptafluoropropyl-hydroxyl-methylene)-(+)-camphorate]): δ 3.07 ppm (major) and 3.14 ppm (minor).



1-(5-(4-chlorophenyl)cyclopent-1-enyl)ethanone(23).

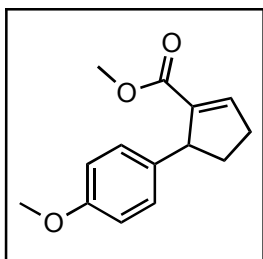
Following the typical procedure outlined above, the title compound was isolated as a colorless oil. ¹H NMR, 400MHz (CDCl₃) δ 1.81 ~ 1.90 (m, 1H), 2.25 (s, 3H), 2.41 ~ 2.53 (m, 1H), 2.55 ~ 2.65 (m, 1H), 2.68 ~ 2.79 (m, 1H), 4.12 ~ 4.18 (m, 1H), 6.92 ~ 6.95 (m, 1H), 7.07 (d, 2H, *J* = 10 Hz), 7.21 (d, 2H, *J* = 10.5 Hz); ¹³C NMR, 63 MHz (CDCl₃) δ 27.1, 32.5, 33.7, 48.8, 128.3, 128.5, 131.7, 143.6, 145.1, 148.0, 195.6; HRMS-ESI (m/z) [M+H⁺] calcd for C₁₃H₁₃ClO: 221.0728, found: 221.0734; NMR data for *ee* (after treating with europium tris[3-(heptafluoropropyl-hydroxyl-methylene)-(+)-camphorate]): δ 3.08 ppm (major) and 3.17 ppm (minor).



Methyl 5-phenylcyclopent-enecarboxylate (24).

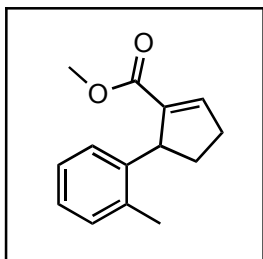
Following the typical procedure outlined above, the title compound was isolated as a colorless oil. ¹H NMR, 400 MHz (CDCl₃) δ 1.94 ~ 2.01 (m, 1H), 2.50 ~ 2.64 (m, 2H), 2.67 ~ 2.78 (m, 1H), 3.65 (s, 3H) 4.17 ~

4.20 (m, 1H), 7.02 ~ 7.05 (m, 1H), 7.19 ~ 7.25 (m, 3H), 7.29 ~ 7.35 (m, 2H); Anal. calcd for $C_{13}H_{14}O_2$: C 77.20, H 6.98, found: C 77.12, H 6.81; HRMS-ESI (m/z) $[M+H]^+$ calcd for $C_{13}H_{14}O_2$: 203.1067, found: 203.1073; HPLC (Daicel CHIRALCEL OD-H; 99:1 hexanes/isopropanol, detection wavelength = 200 nm, flow rate = 1.0 mL/min) t_r = 8.1 min (major) and 9.1 min (minor).



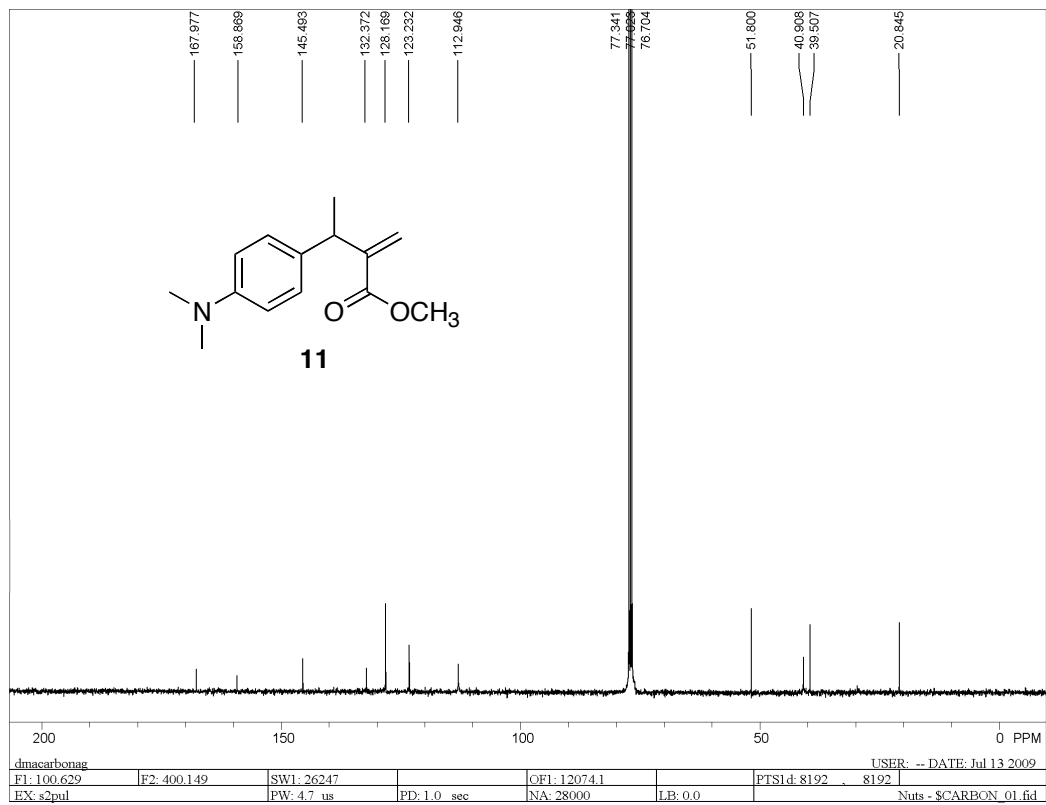
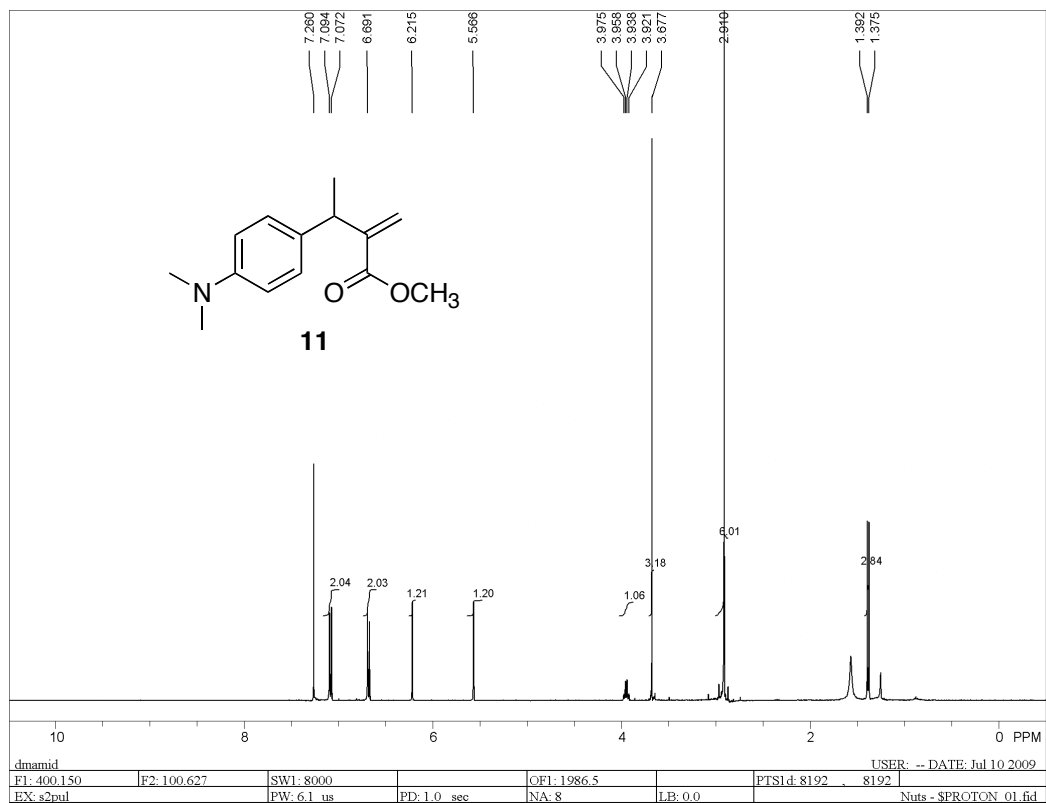
Methyl 5-(4-methoxyphenyl)cyclopent-1-enecarboxylate (25).

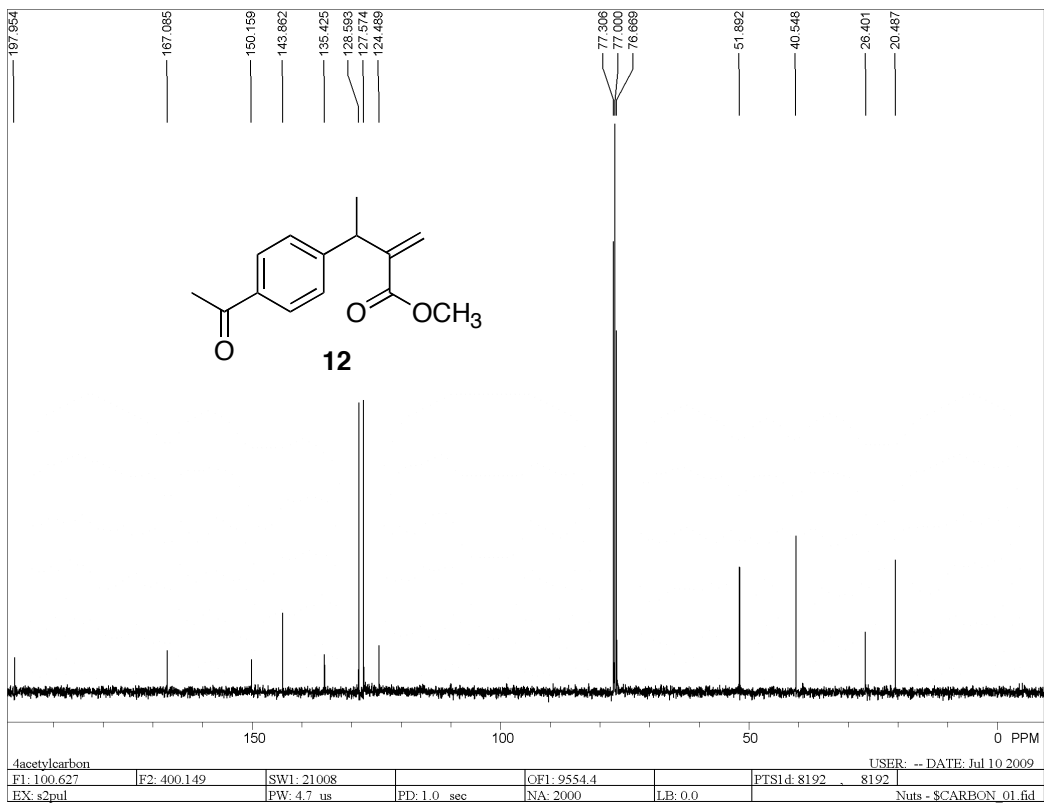
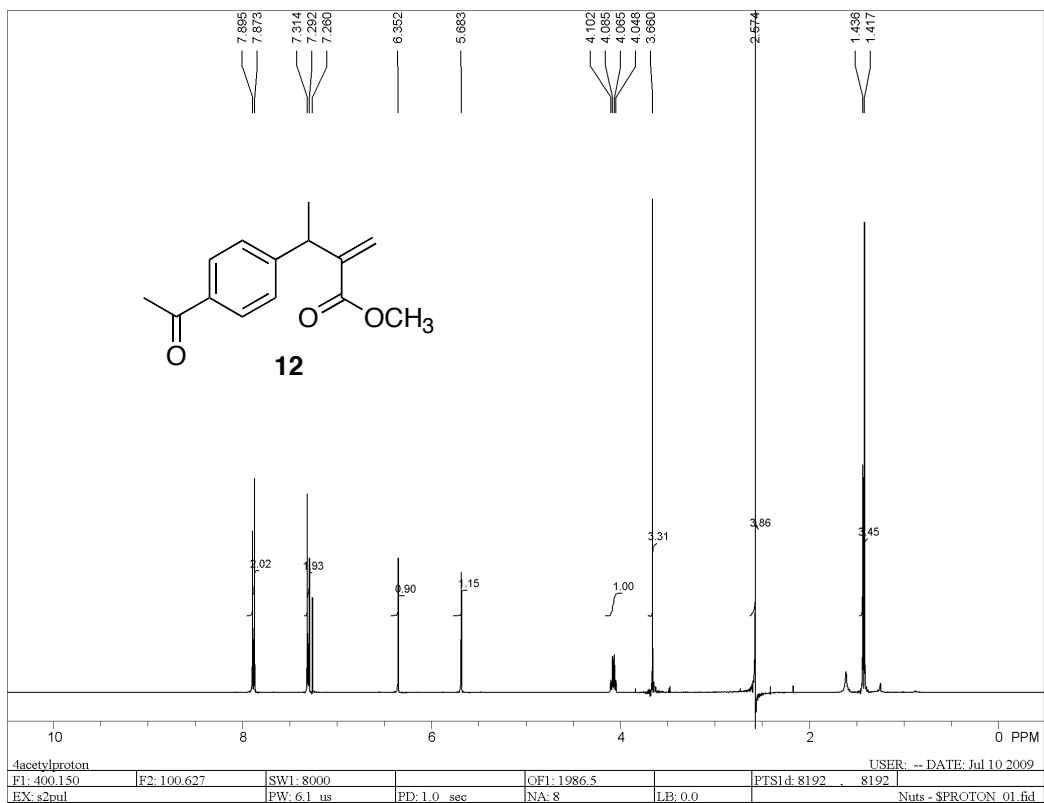
Following the typical procedure outlined above, the title compound was isolated as a pale yellow oil. 1H NMR, 400 MHz ($CDCl_3$) δ 1.85 ~ 1.93 (m, 1H), 2.44 ~ 2.56 (m, 2H), 2.61 ~ 2.73 (m, 1H), 3.61 (s, 3H), 3.77 (s, 3H), 4.08 ~ 4.12 (m, 1H), 6.82 (d, 2H, J = 11 Hz), 6.95 ~ 6.97 (m, 1H), 7.09 (d, 2H, J = 11 Hz); ^{13}C NMR, 63 MHz ($CDCl_3$) δ 32.0, 34.0, 49.2, 51.2, 55.1, 113.7, 127.8, 137.2, 139.3, 144.4, 157.9, 165.1; Anal. calcd for $C_{14}H_{16}O_3$: C 72.39, H 6.94, found: C 72.07, H 6.72; HRMS-ESI (m/z) $[M+H]^+$ calcd for $C_{14}H_{16}O_3$: 233.1172, found: 233.1179; HPLC (Daicel CHIRALCEL OD-H; 99:1 hexanes/isopropanol, detection wavelength = 200 nm, flow rate = 1.0 mL/min) t_r = 11.2 min (major) and 13.1 min (minor).

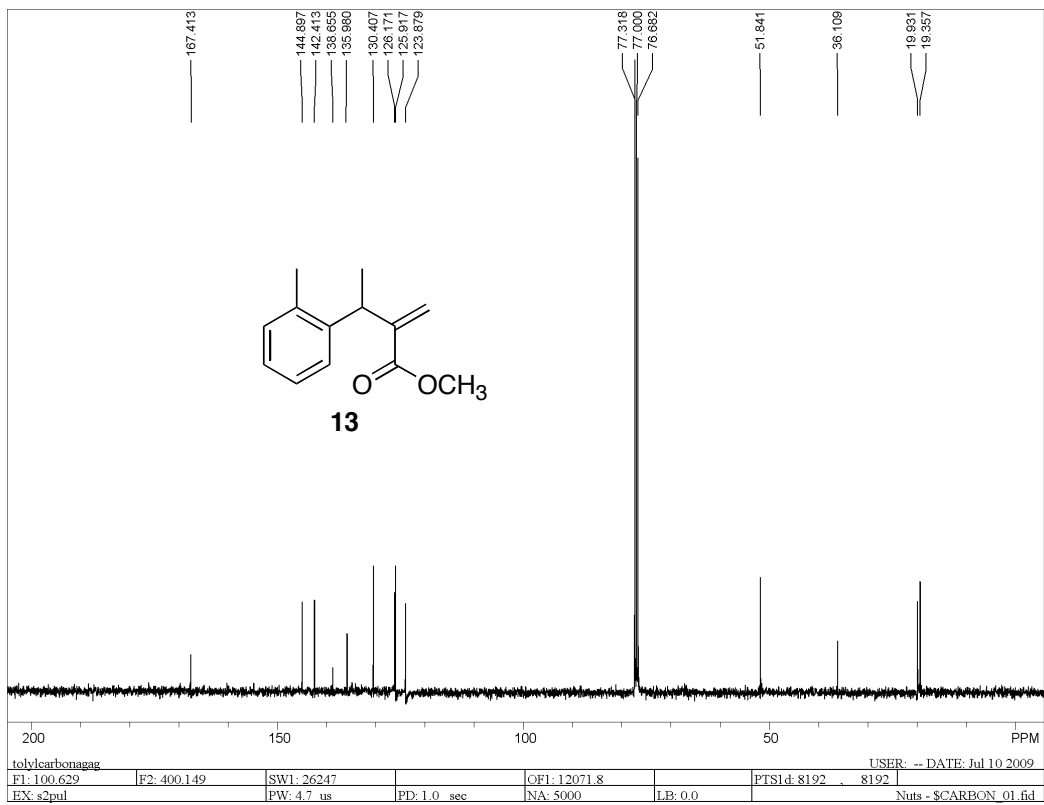
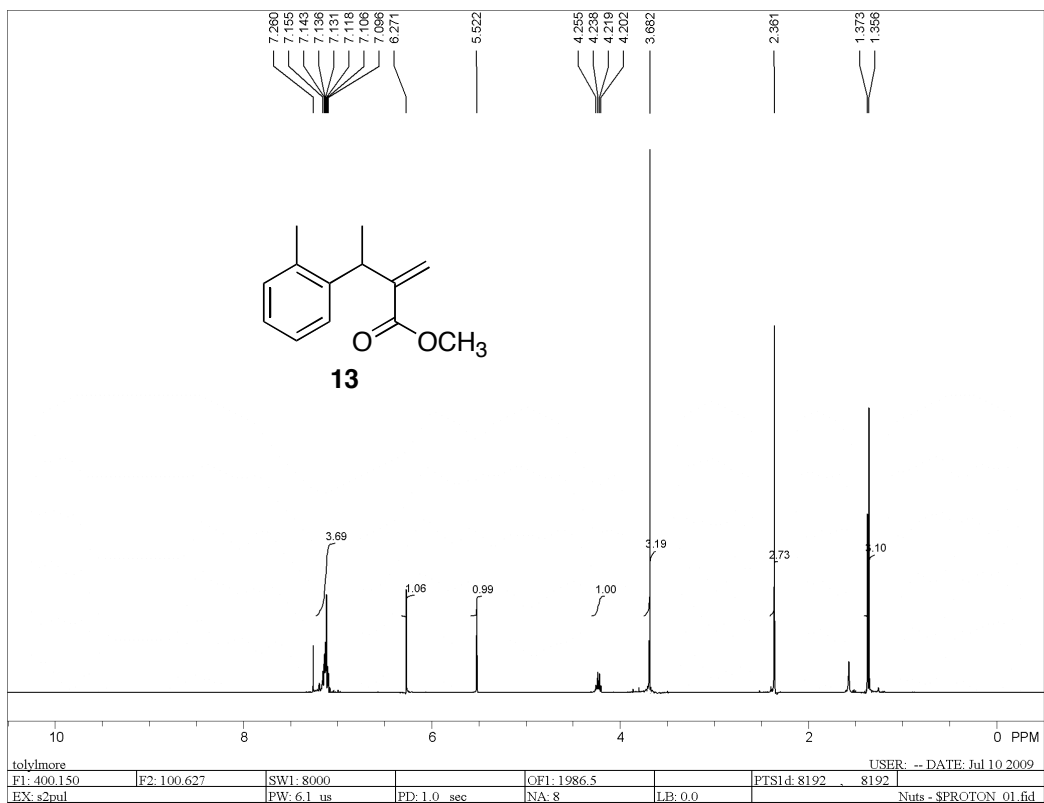


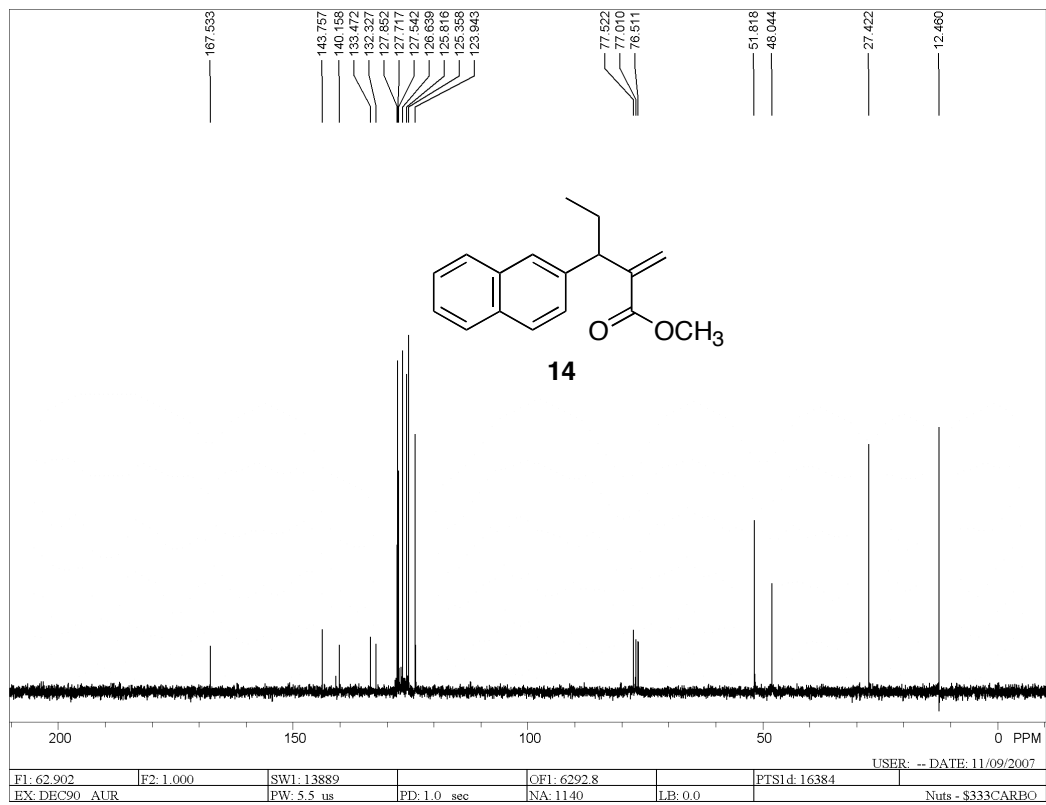
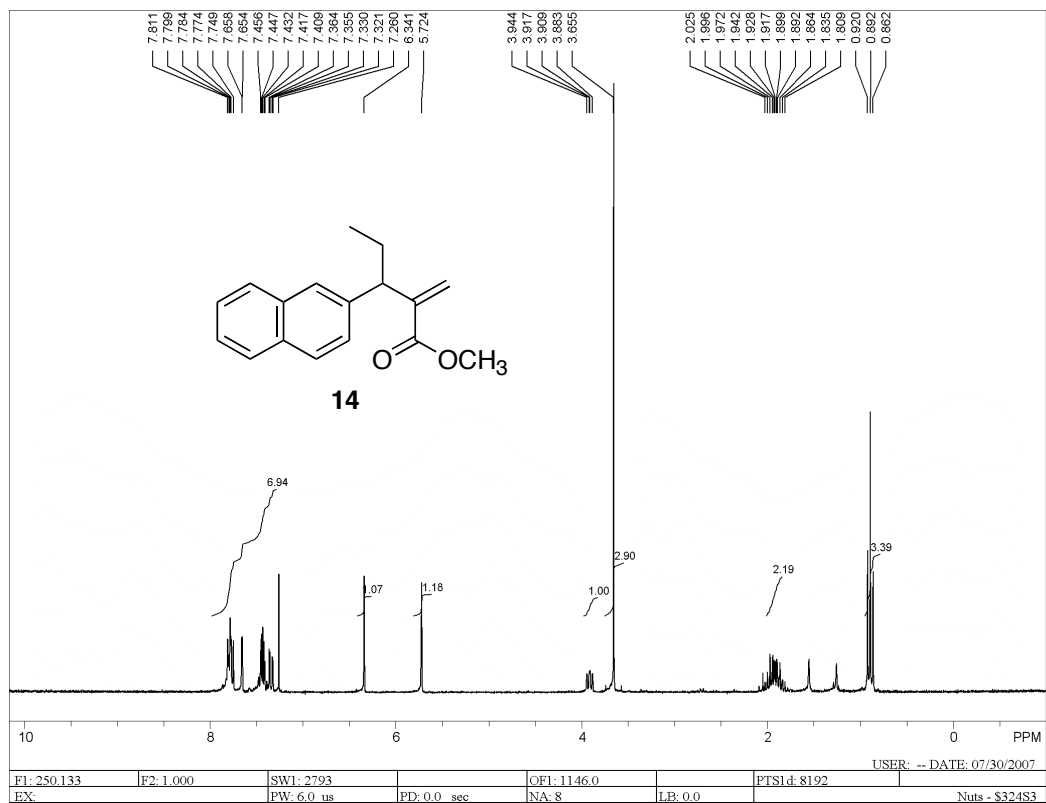
Methyl 5-o-tolylcyclopent-1-enecarboxylate (26).

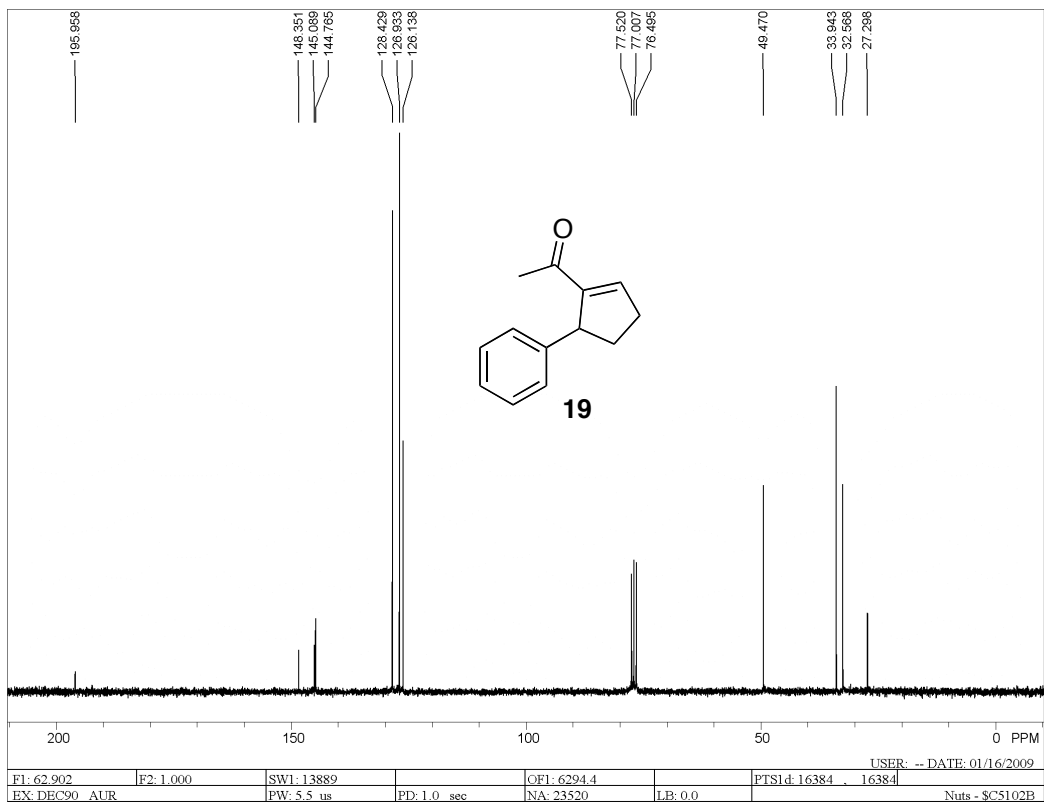
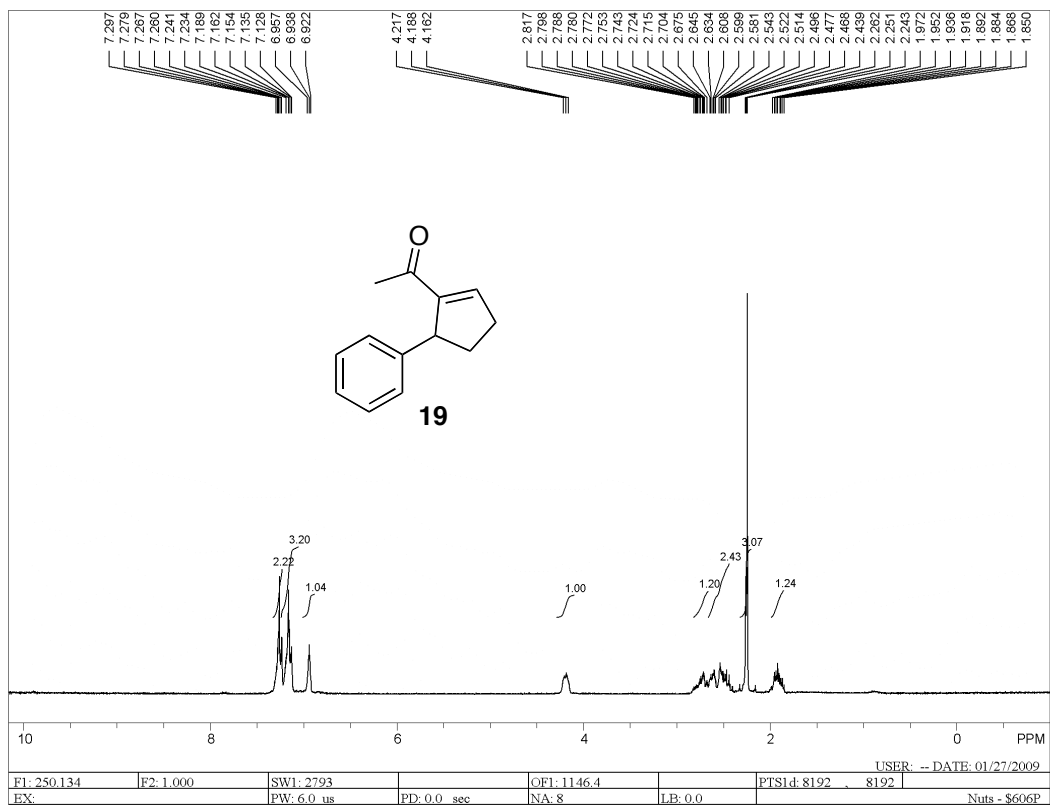
Following the typical procedure outlined above, the title compound was isolated as a colorless oil. 1H NMR, 400 MHz ($CDCl_3$) δ 1.76 ~ 1.82 (m, 1H), 2.41 (s, 3H), 2.50 ~ 2.69 (m, 3H), 3.61 (s, 3H) 4.35 ~ 4.40 (m, 1H), 6.94 ~ 6.97 (m, 1H), 7.03 ~ 7.06 (m, 1H), 7.08 ~ 7.12 (m, 2H), 7.14 ~ 7.17 (m, 1H); ^{13}C NMR, 63 MHz ($CDCl_3$) δ 19.7, 31.9, 32.9, 45.7, 51.3, 125.2, 125.9, 126.0, 130.2, 135.3, 139.0, 143.0, 145.1, 165.3; Anal. calcd for $C_{14}H_{16}O_2$: C 77.75, H 7.46, found: C 77.26, H 7.19; HRMS-ESI (m/z) $[M+H]^+$ calcd for $C_{14}H_{16}O_2$: 217.1223, found: 217.1230; HPLC (Daicel CHIRALCEL OD-H; 99:1 hexanes/isopropanol, detection wavelength = 200 nm, flow rate = 1.0 mL/min) t_r = 5.1 min (major) and 5.9 min (mior).

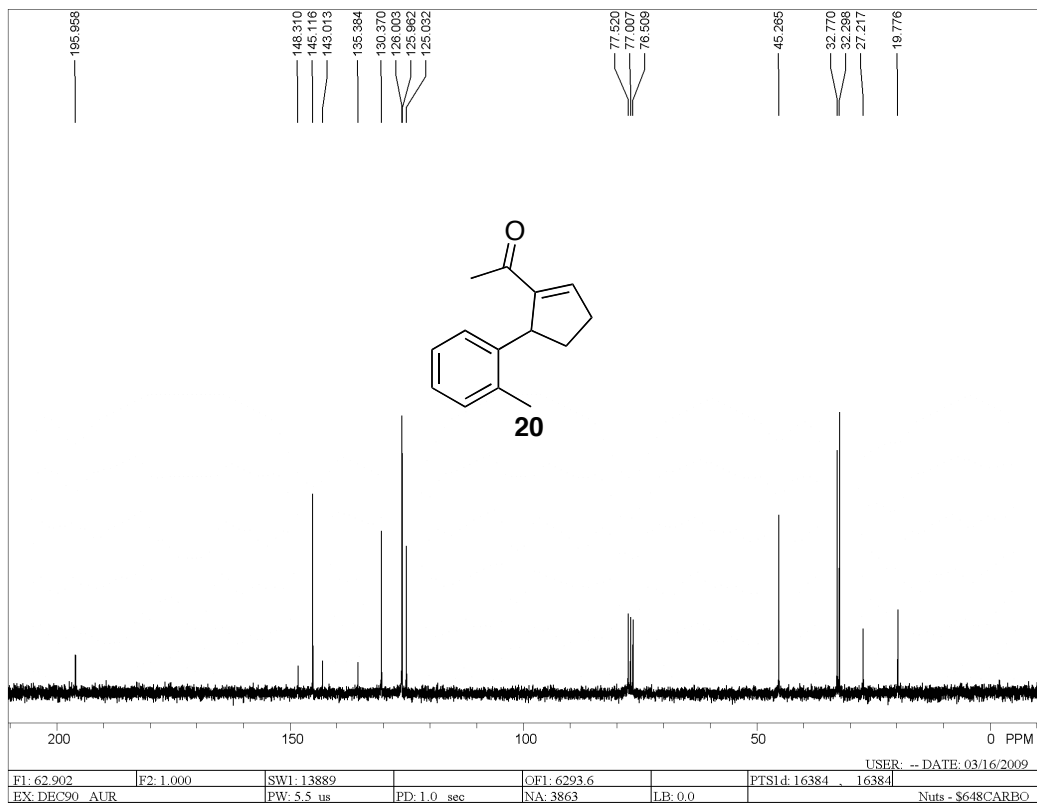
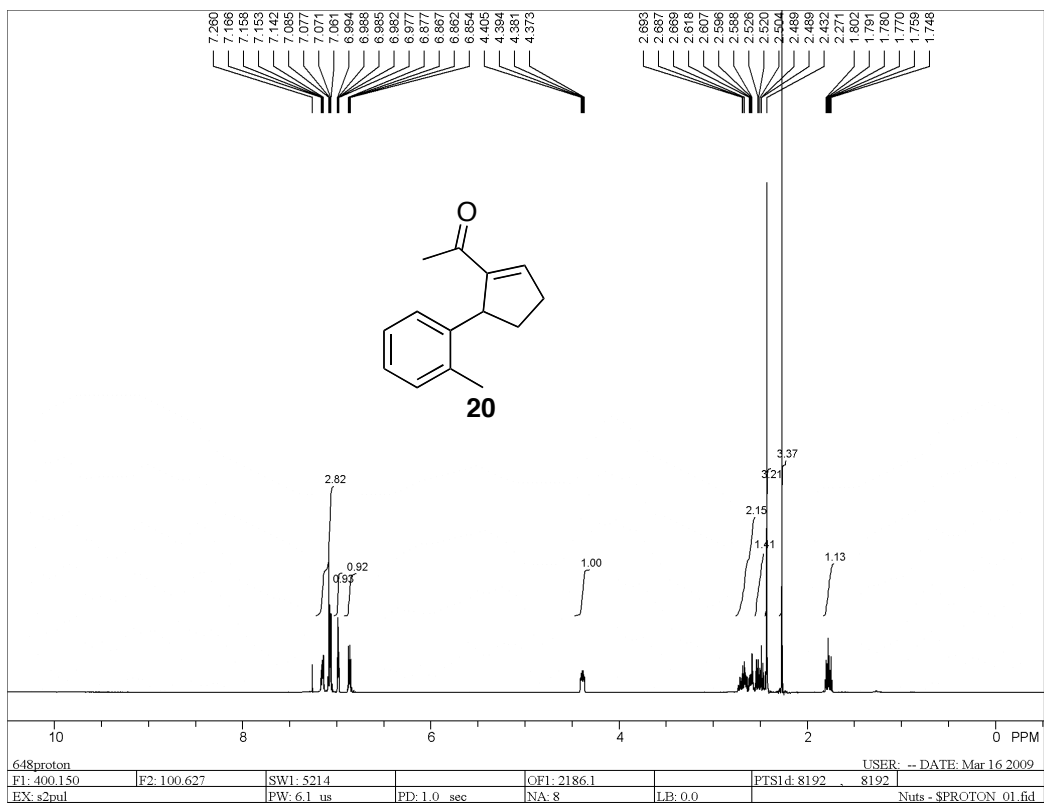


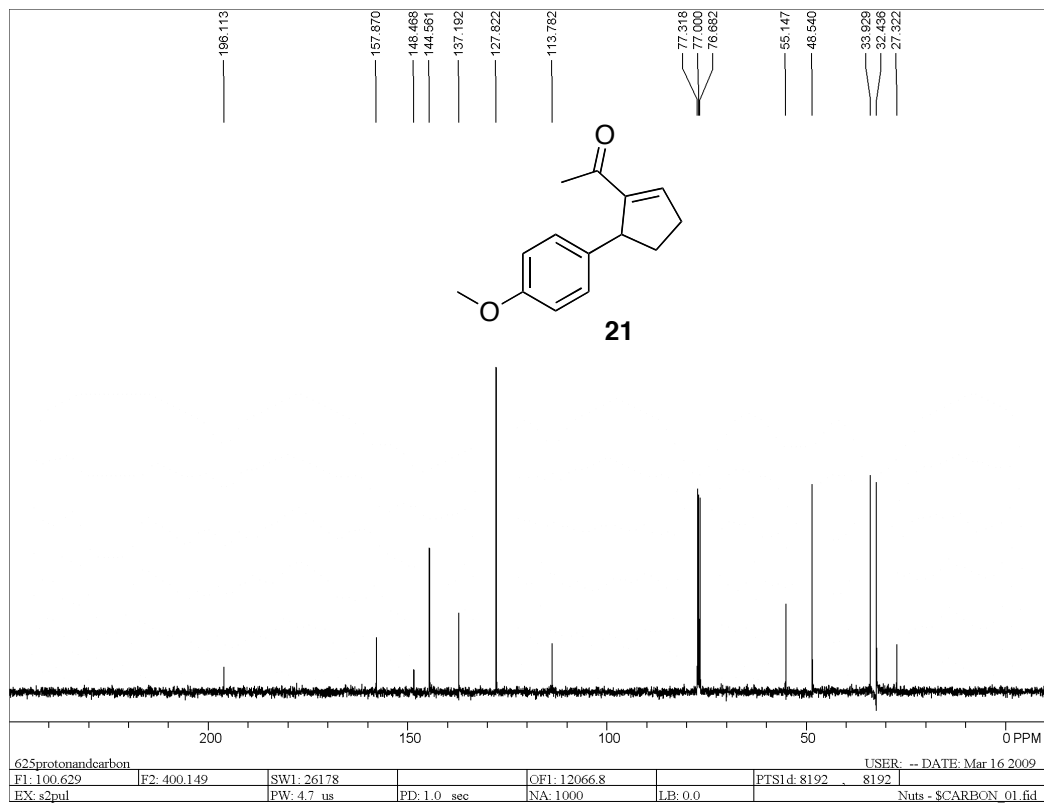
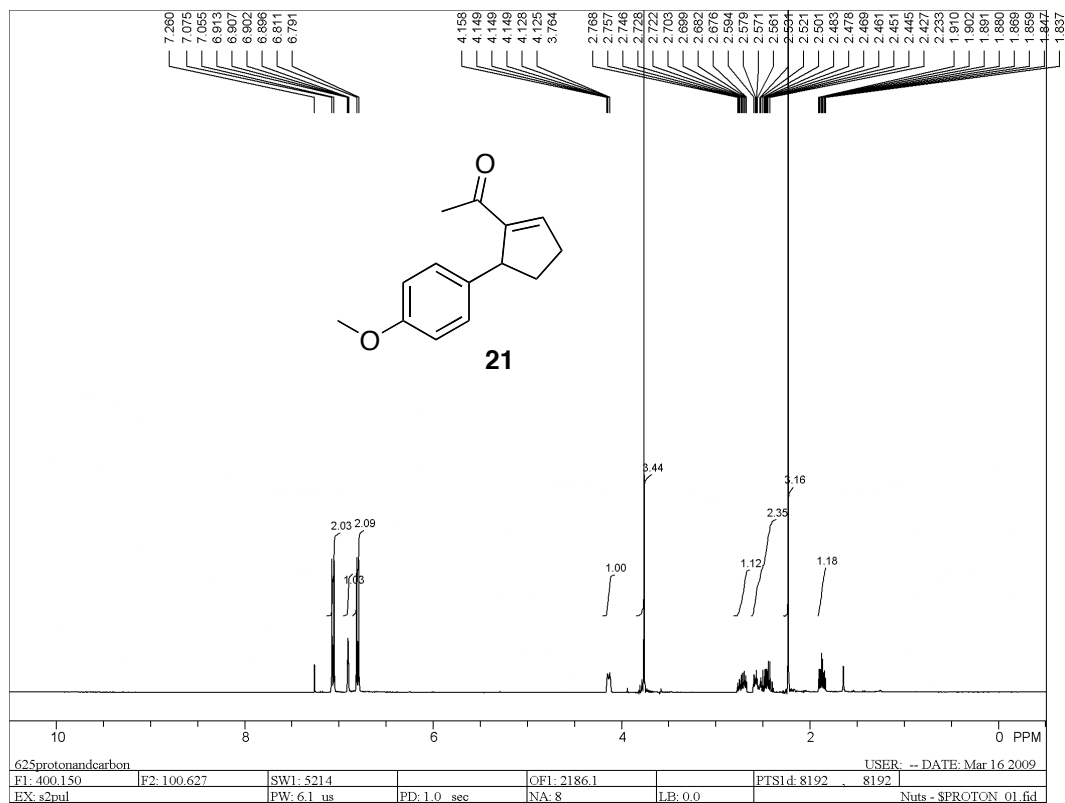


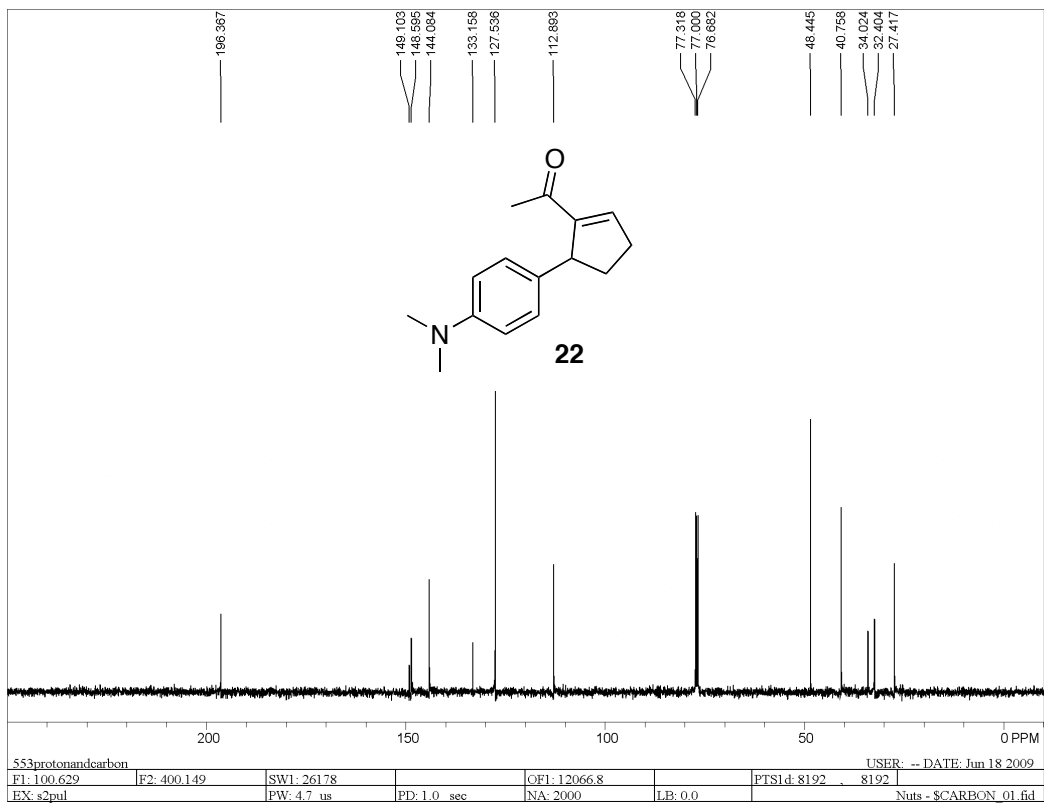
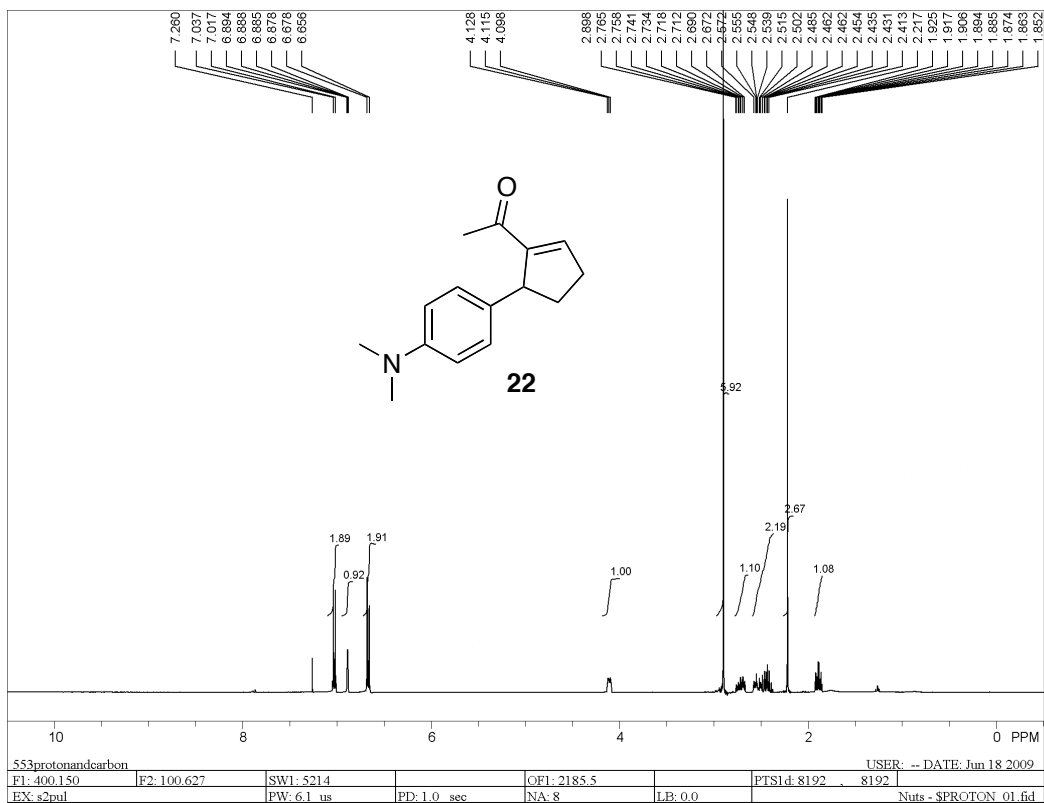


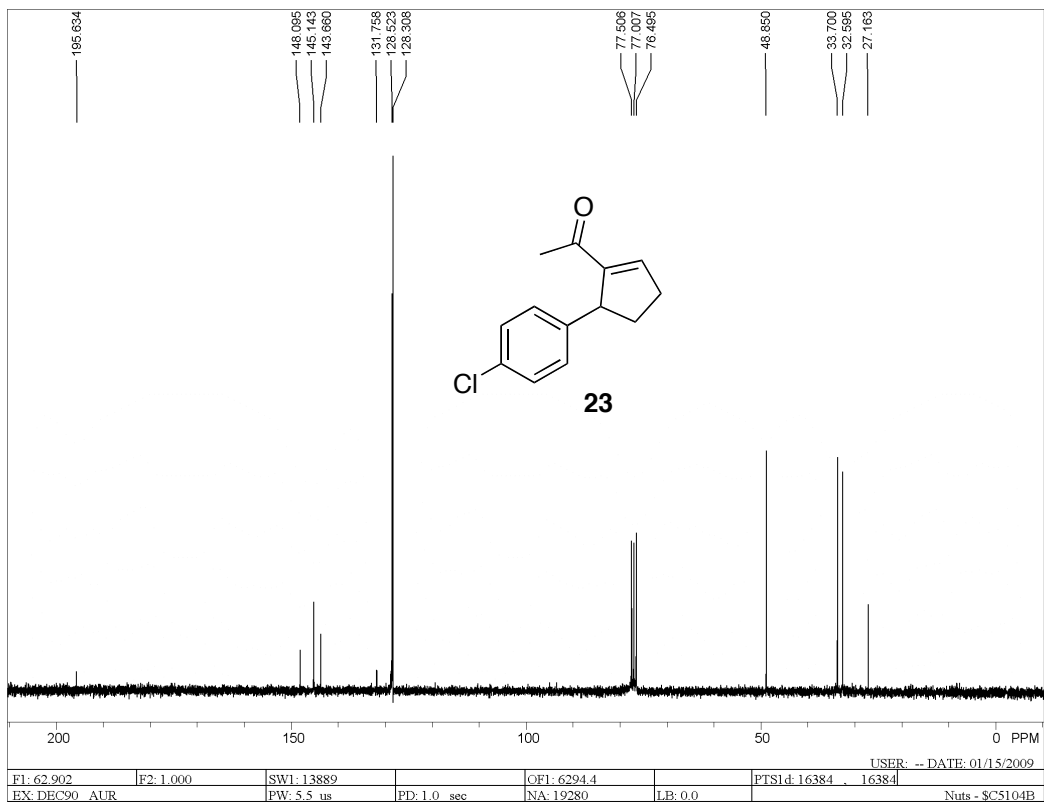
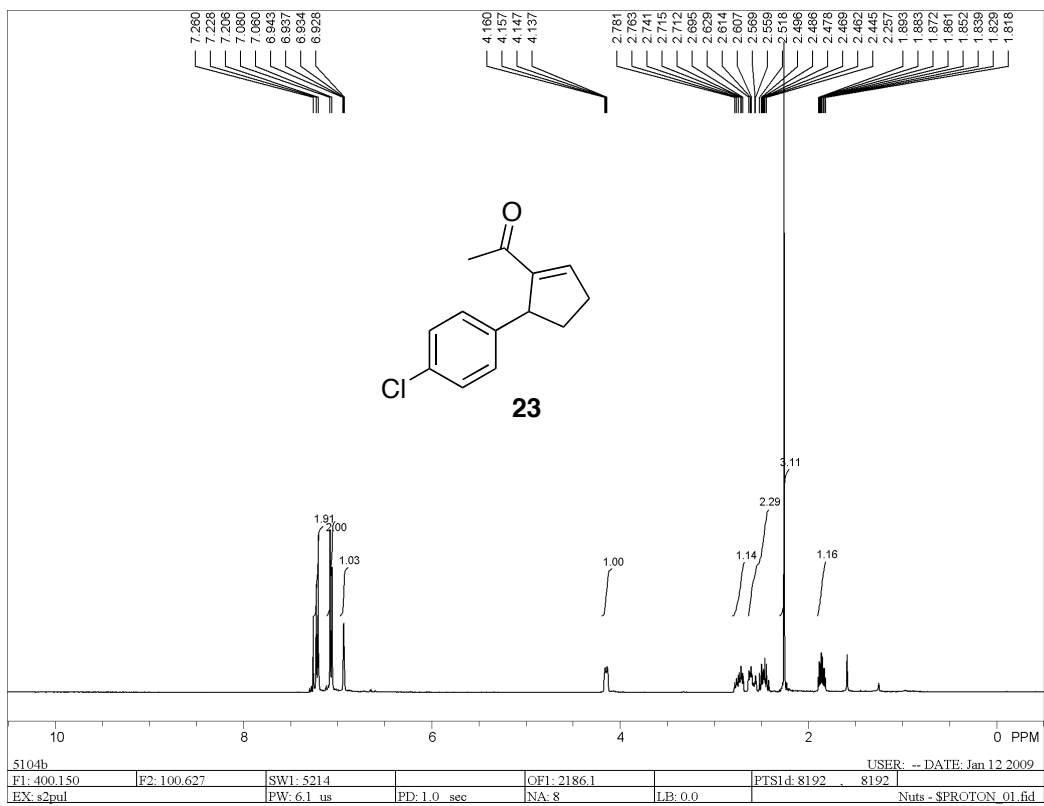


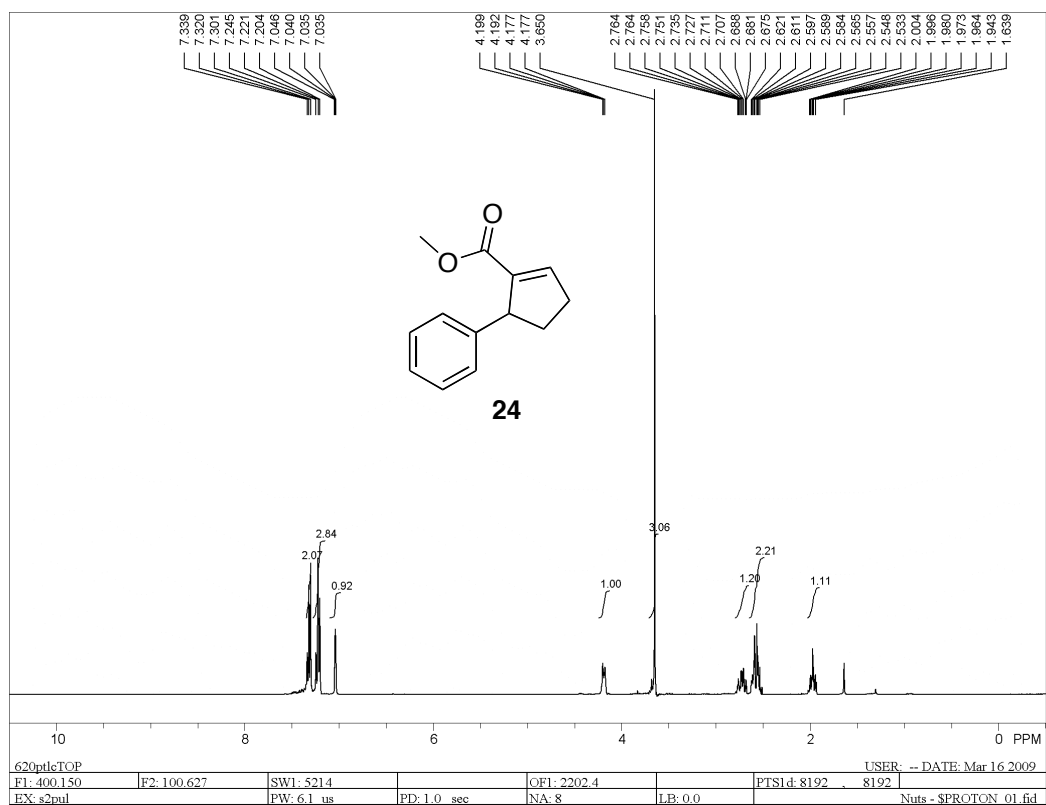


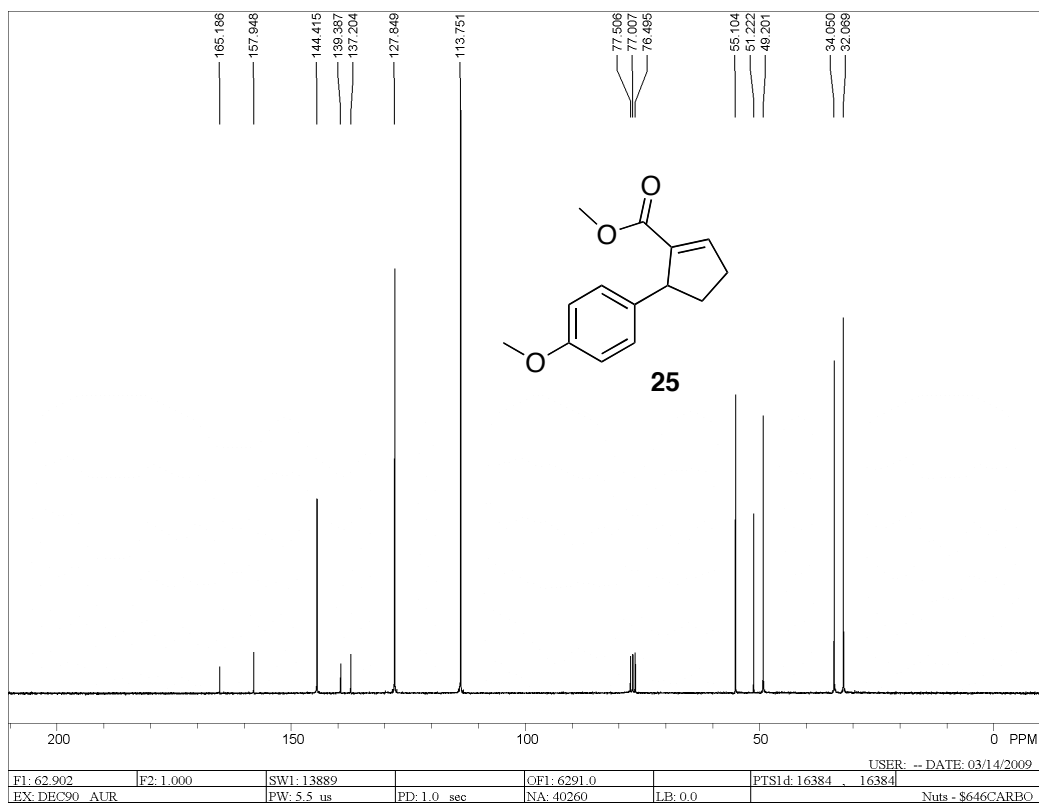


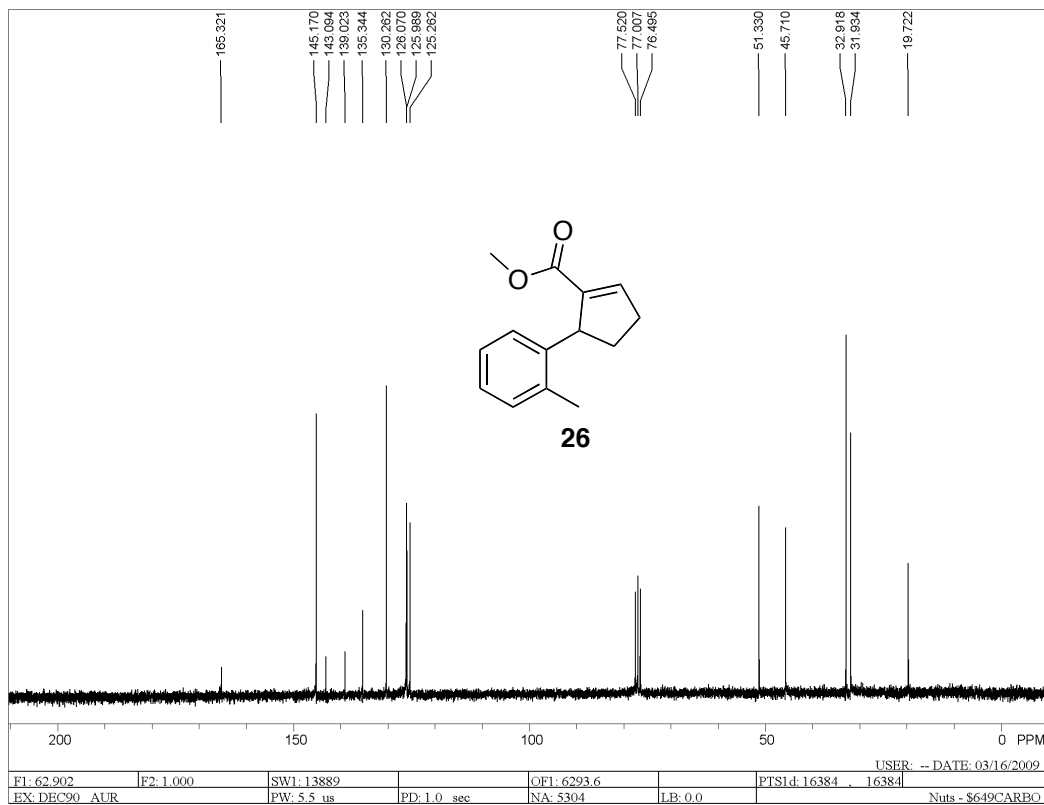
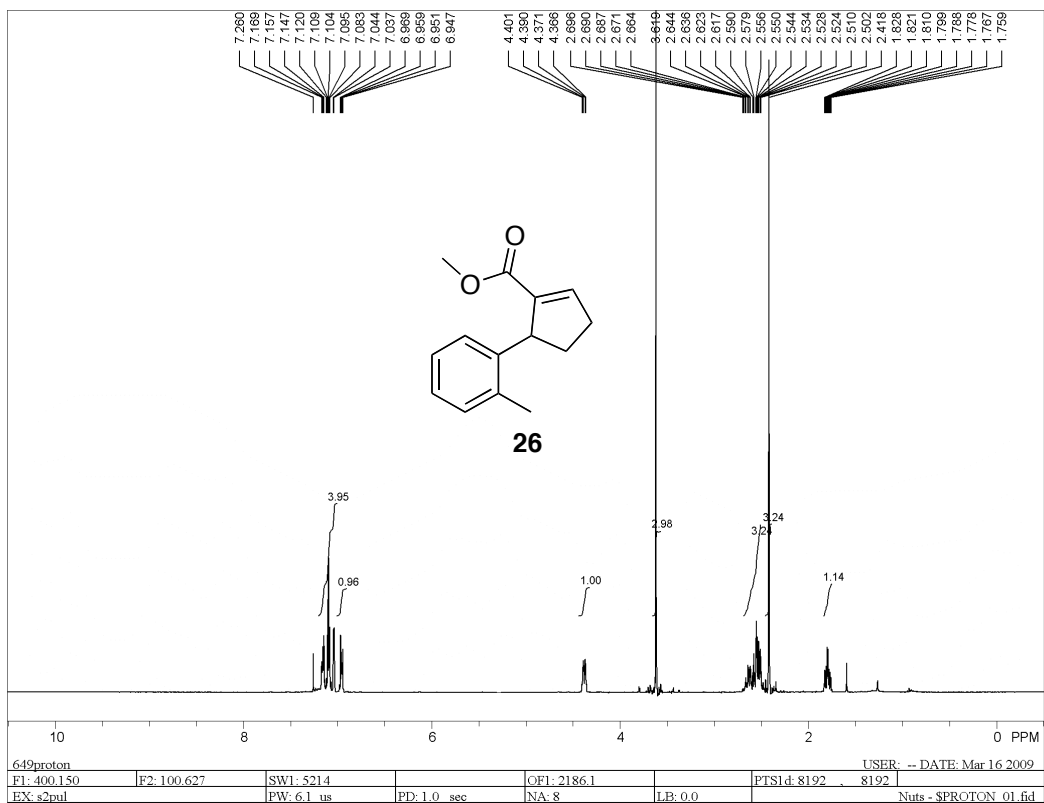






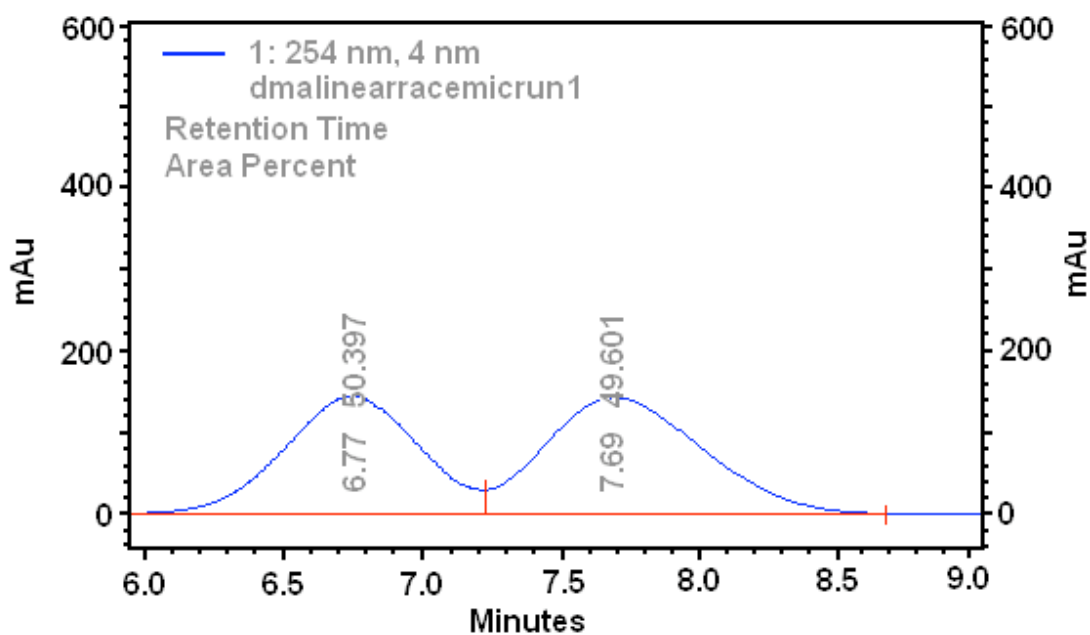
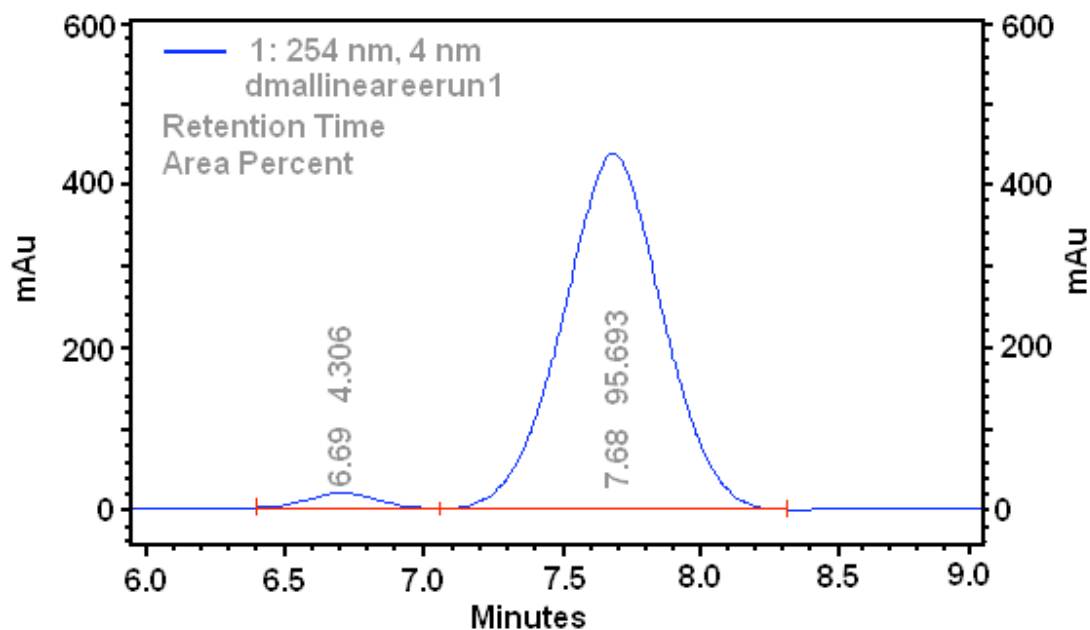




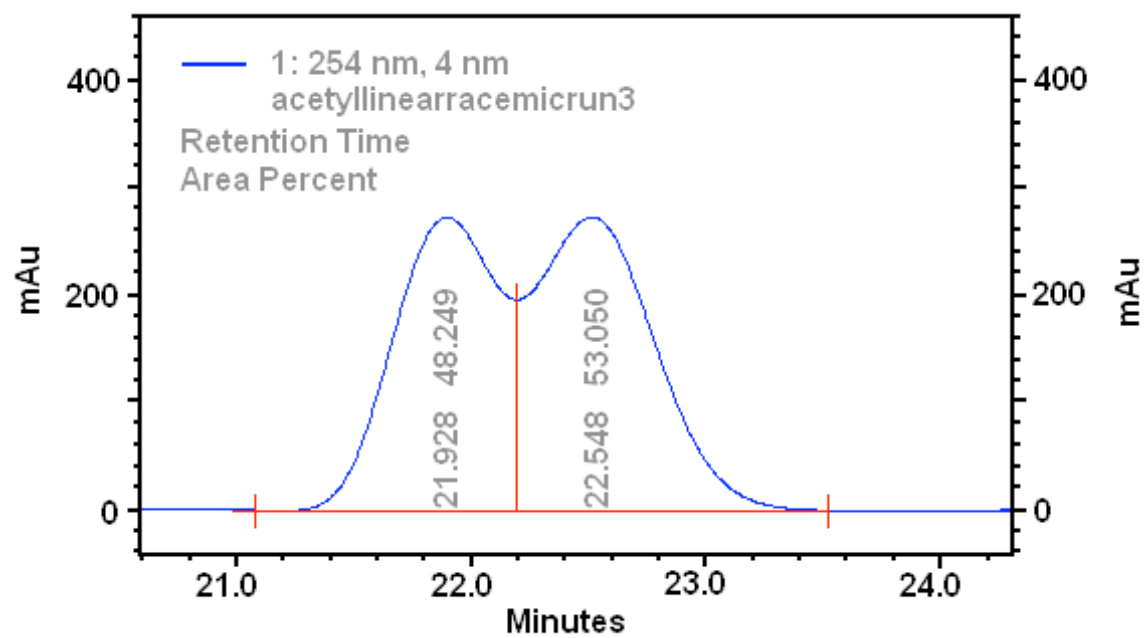
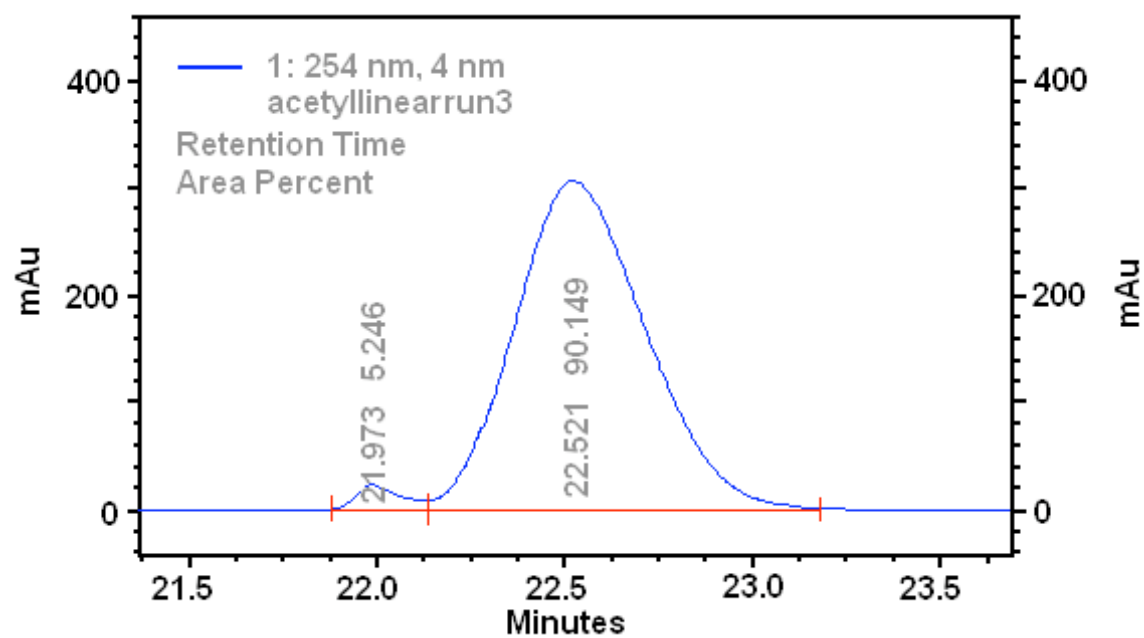


Enantioselectivities data

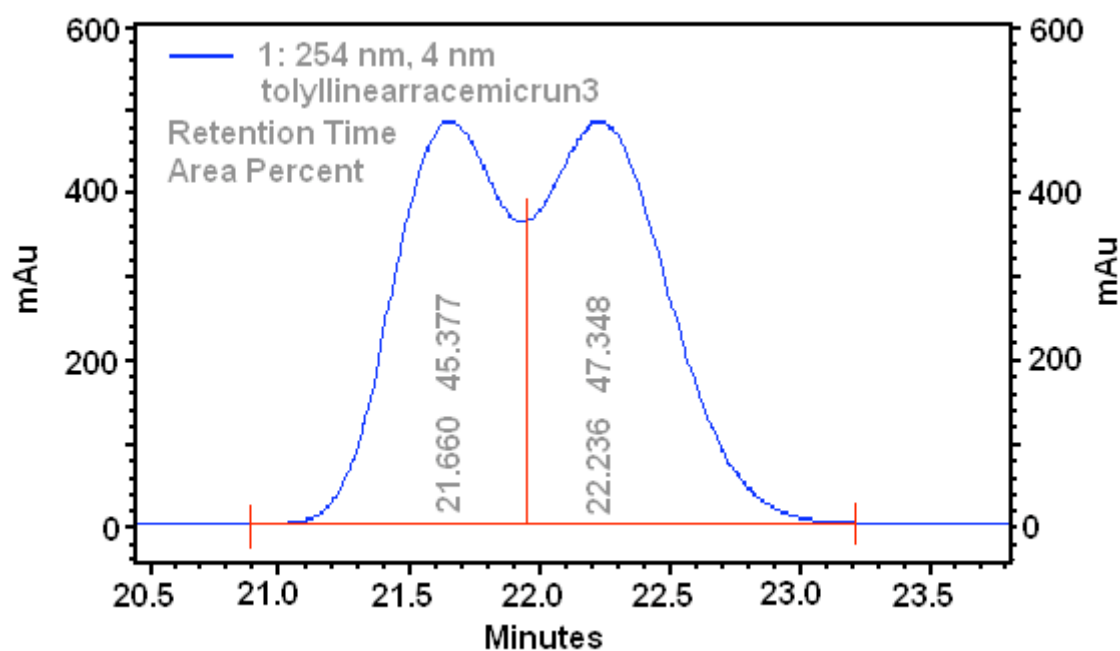
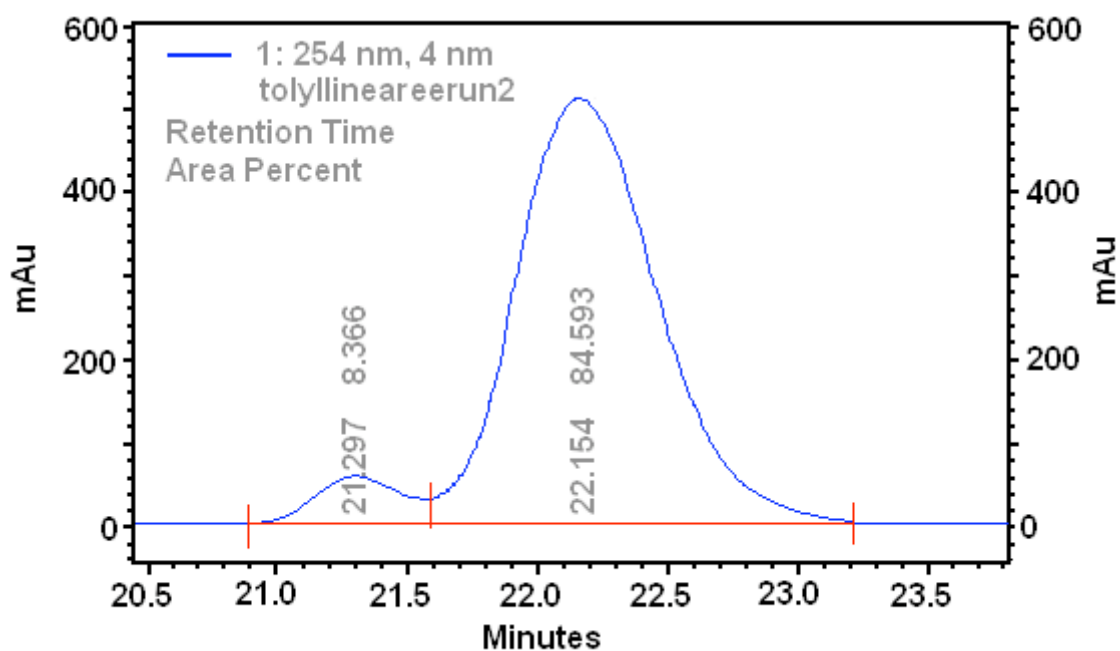
Compound 11



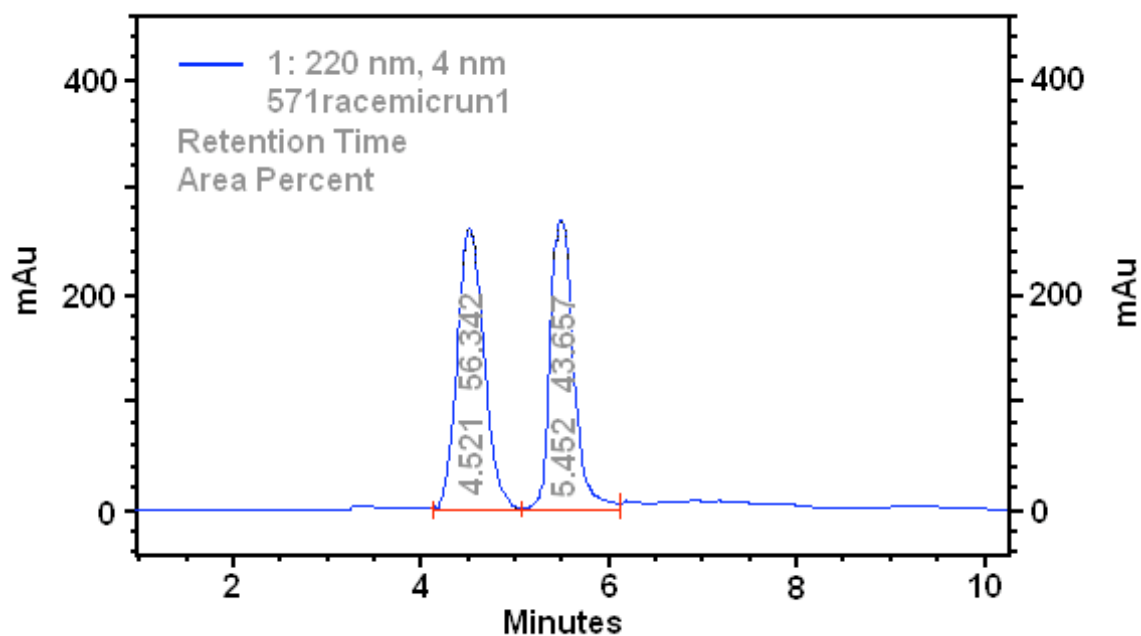
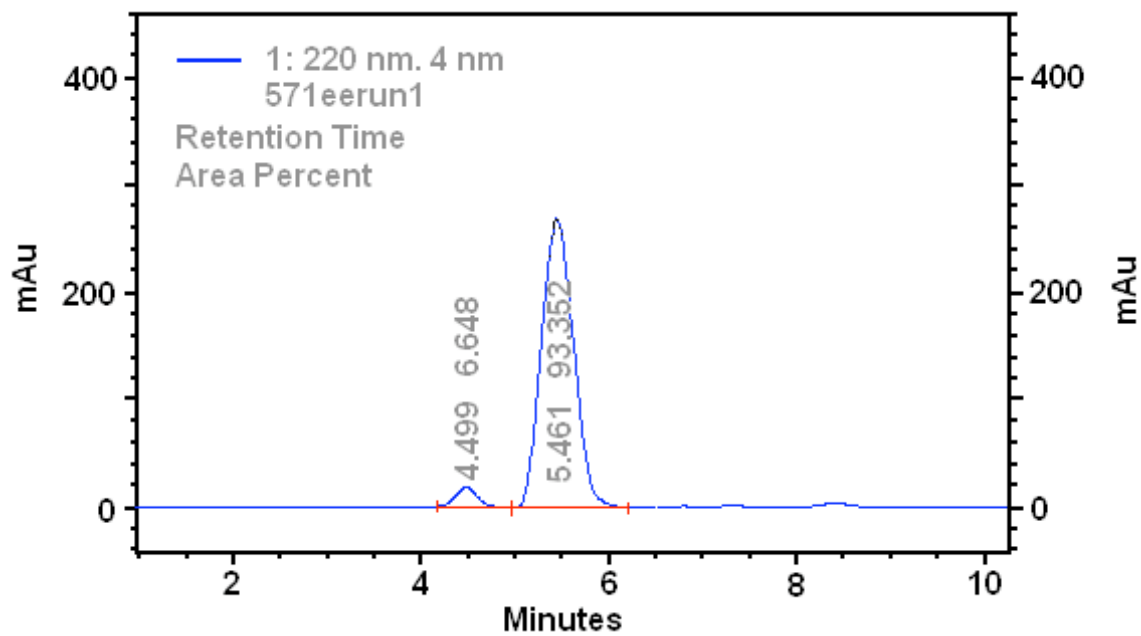
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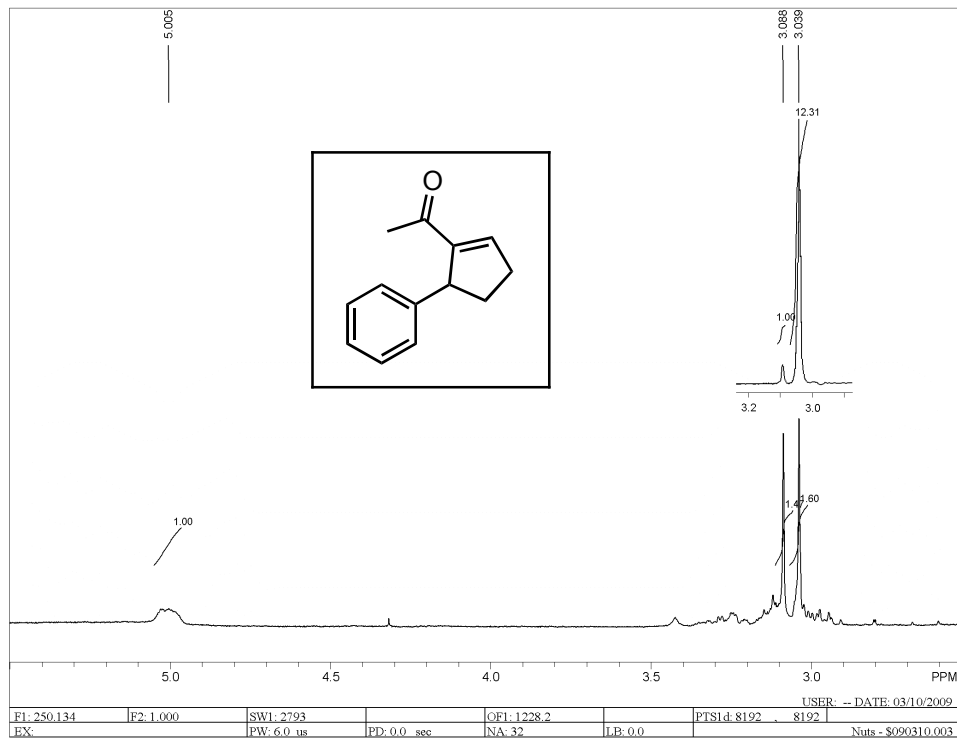
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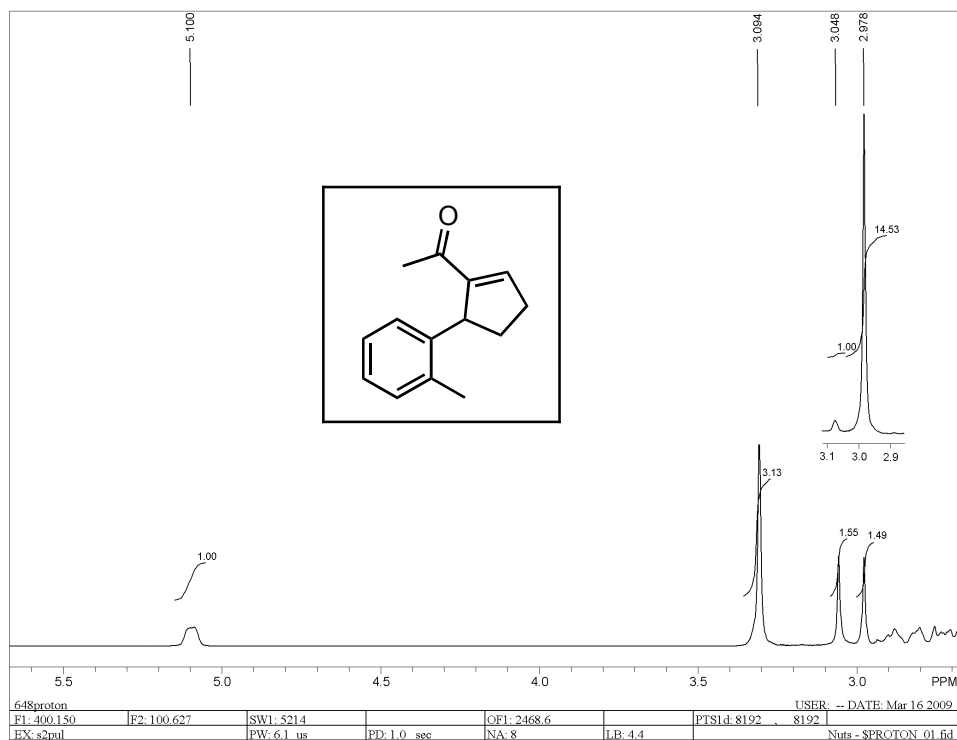
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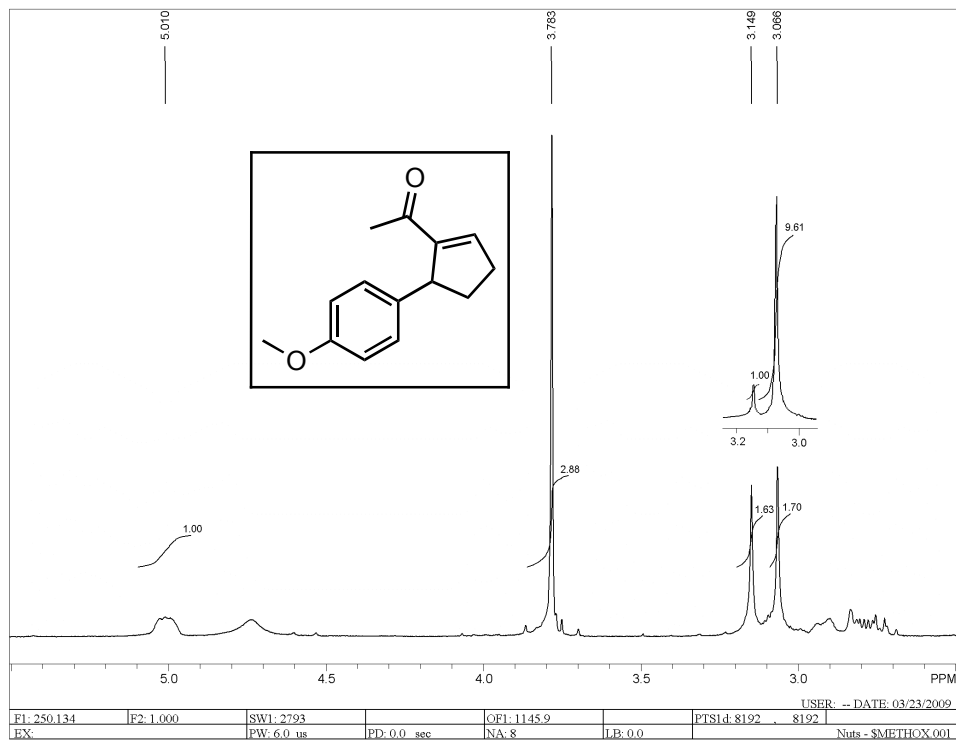
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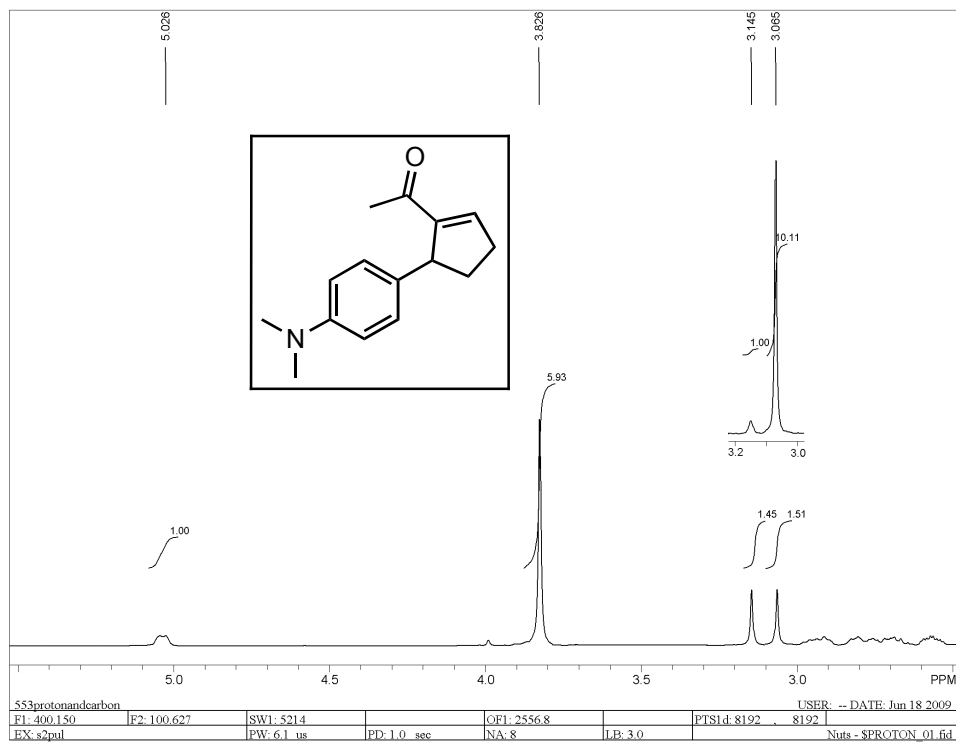
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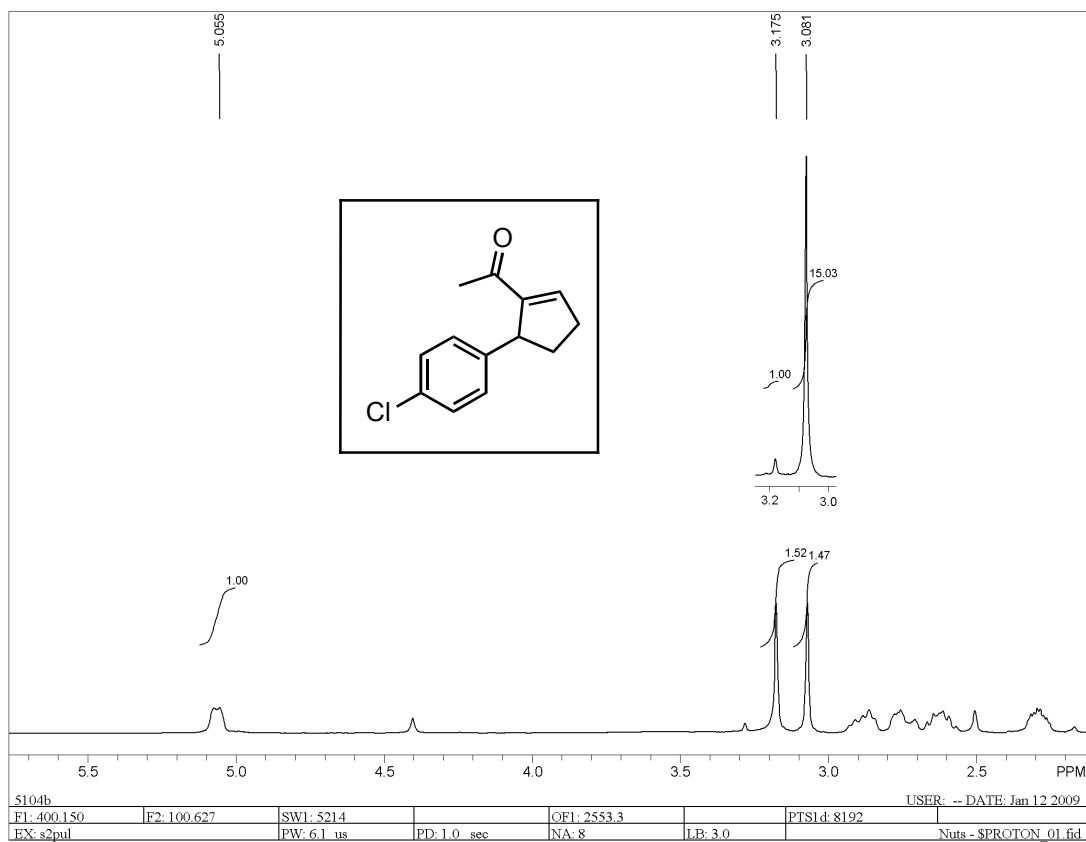
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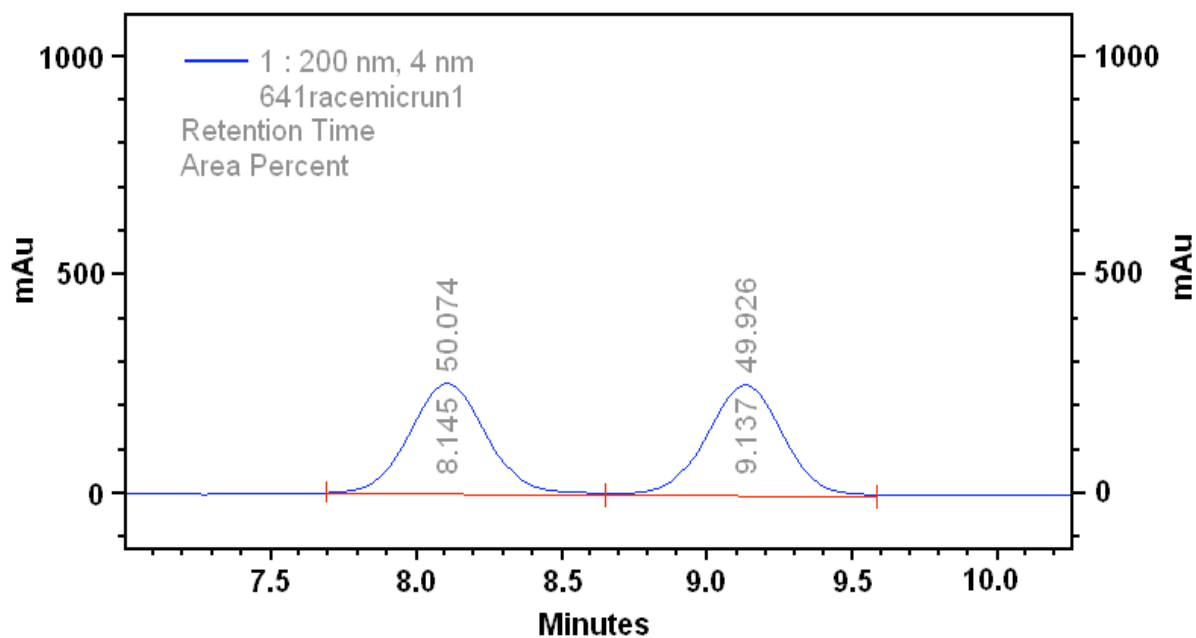
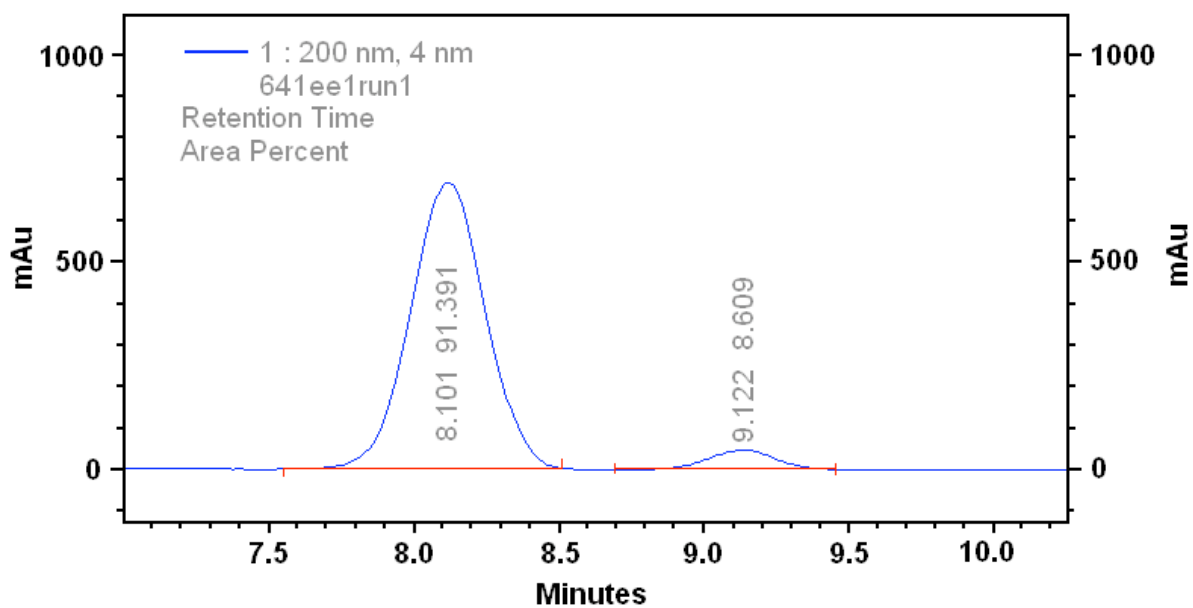
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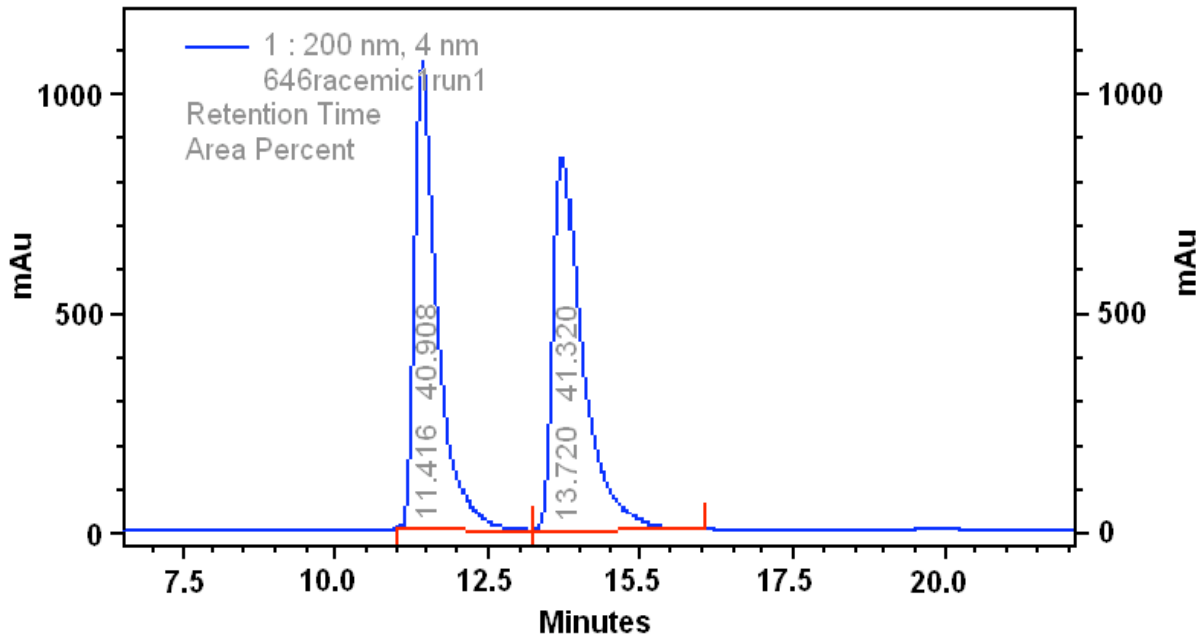
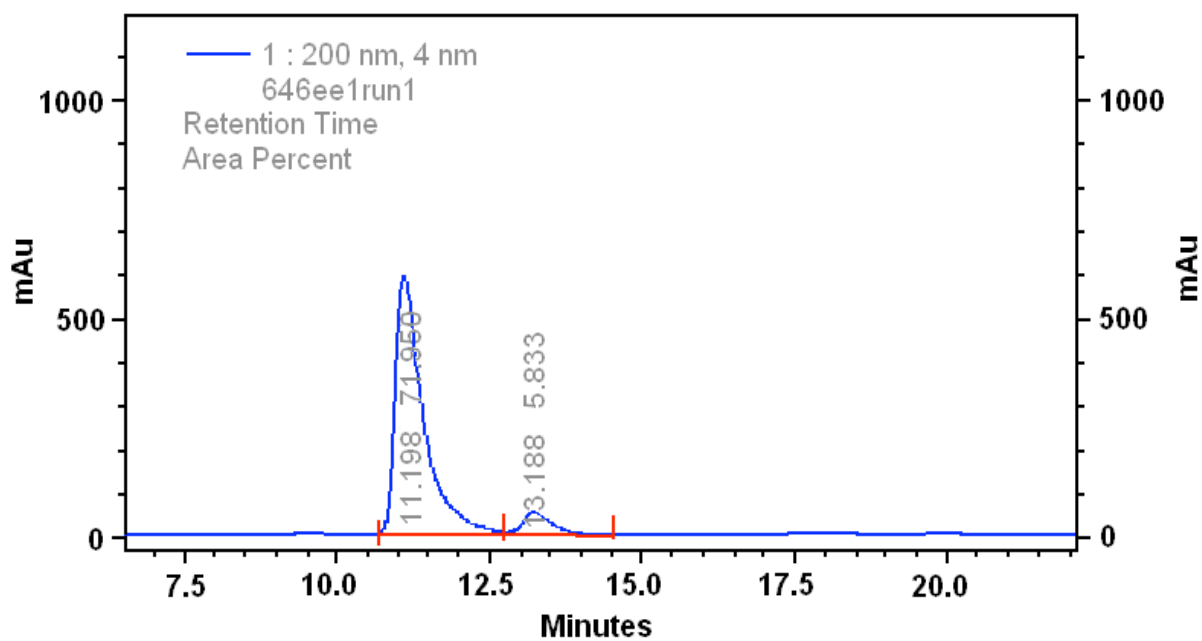
Compound 23



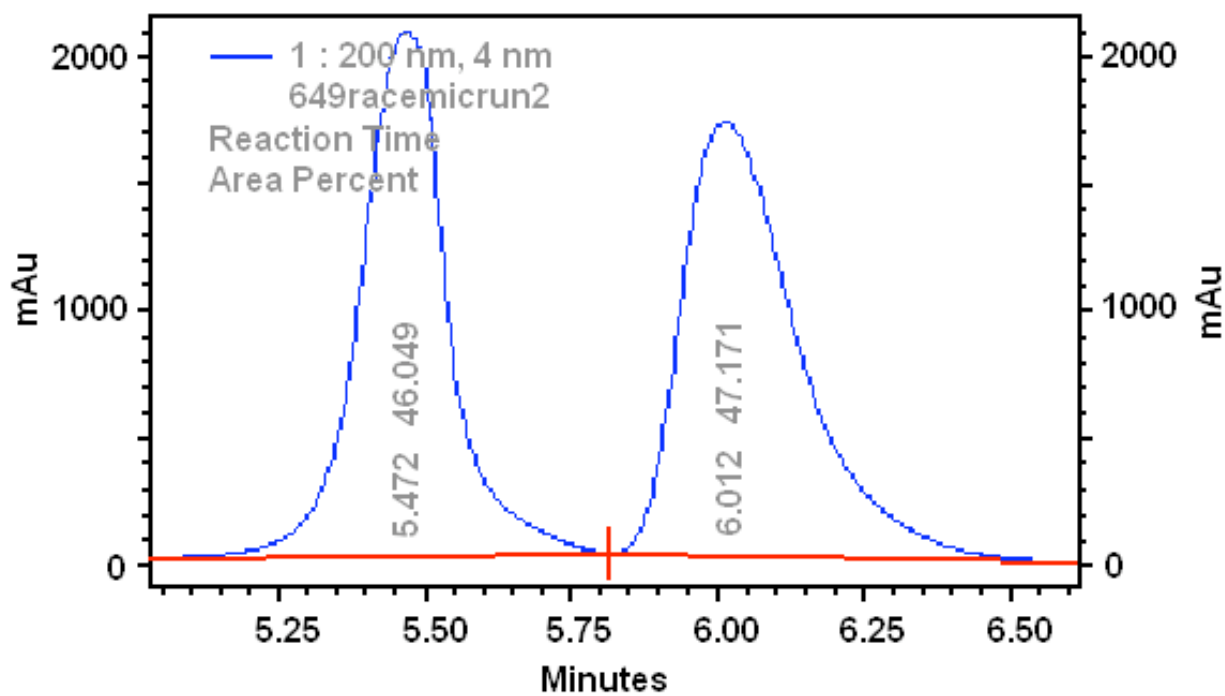
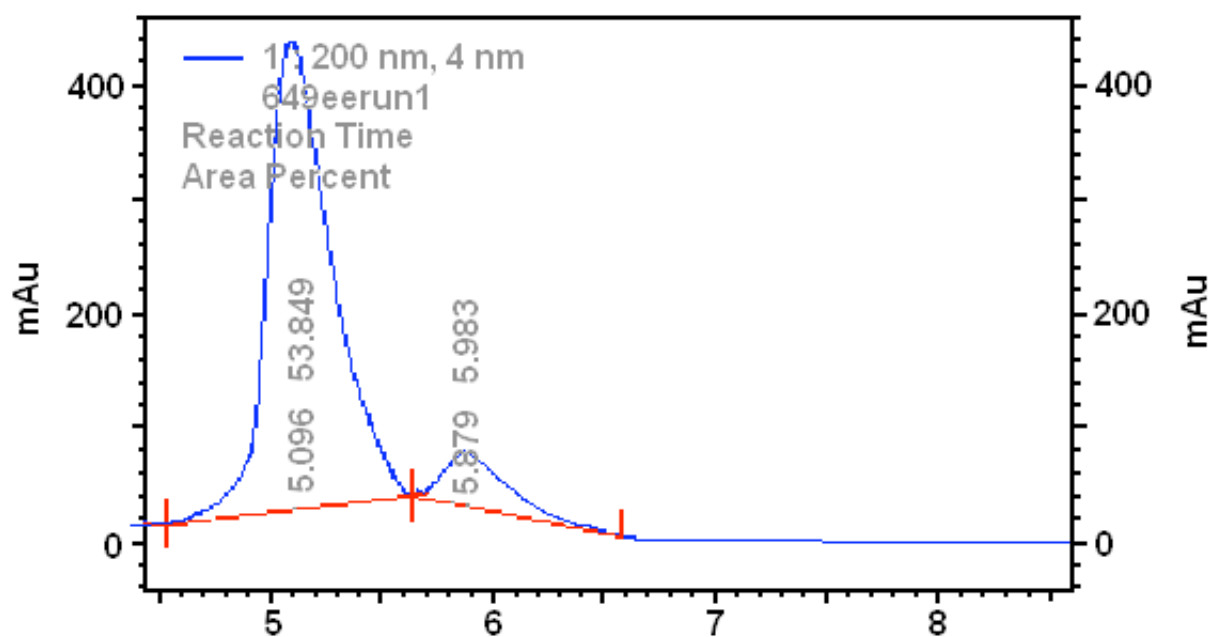
Compound 24



Compound 25



Compound 26



^1H -NMR analysis of phenyl-palladium complex 7 from 3a

