Nickel-Catalyzed Enantioselective Cross-Couplings of Racemic Secondary Electrophiles that Bear an Oxygen Leaving Group

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Supporting Information

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I. General

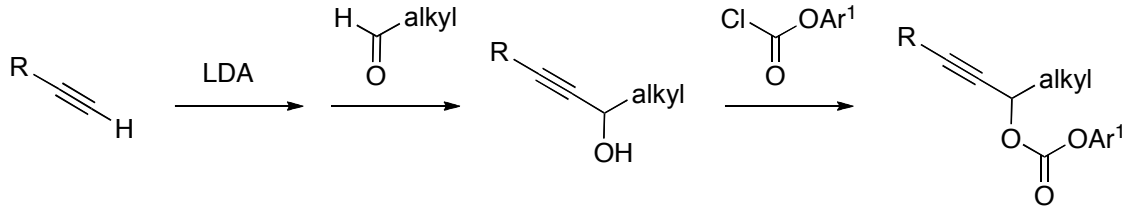
The following reagents were purchased and used as received: $NiCl_2(PCy_3)_2$ (Aldrich or Strem), ligand **L*** (Aldrich), 2,4,6-trimethoxybenzaldehyde (Acros, TCI, or Aldrich), phosgene (20% solution in toluene; Aldrich), ZnI_2 (Strem), PhMgBr (1.0 M solution in THF; Aldrich), *p*-TolMgBr (1.0 M solution in THF; Aldrich), 4-chloro-3-fluorophenylmagnesium bromide (1.0 M solution in THF; Aldrich), DME (anhydrous; Aldrich), THF (anhydrous; Aldrich).

Unless otherwise noted, reactions were conducted in oven-dried glassware under an inert atmosphere.

^{1}H and ^{13}C NMR data were collected on a Bruker Avance 400 spectrometer or a Bruker Avance 600 spectrometer at r.t. HPLC analyses were carried out on an Agilent 1100 series system with Daicel CHIRACEL® columns (internal diameter 4.6 mm, column length 250 mm, particle size 5 μm or 3 μm). GC analyses were carried out on an Agilent 6850 series system with a Chirasil Dex-CB column for chiral separation (length 25 m, internal diameter 0.25 mm) or an Agilent 6890N series system with an HP-5 column (length 30 m, internal diameter 0.32 mm).

II. Preparation of Materials

These procedures have not been optimized.



Ar^1 = 2,4,6-trimethoxyphenyl

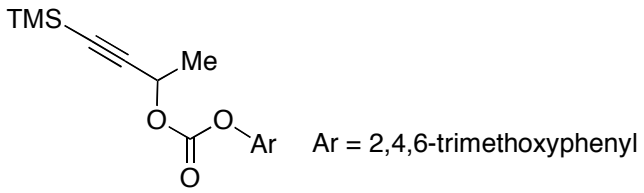
Representative procedure for the synthesis of propargylic alcohols: A solution of LDA (2.0 M in THF/heptane/ethylbenzene; 15 mL, 1.0 equiv) was added over one minute to a solution of TMS-acetylene (4.2 mL, 30 mmol) in THF (150 mL) at 0 °C. The resulting mixture was stirred at r.t. for 30 min, and then it was cooled to −78 °C. Valeraldehyde (4.2 mL, 40 mmol) was added dropwise over one minute. The reaction mixture was allowed to warm to r.t. overnight, and then the reaction was quenched by the addition of aqueous HCl (1 M; 10 mL). Next, saturated aqueous NaCl (30 mL) was added, and the layers were separated. The organic layer was washed with saturated aqueous $NaHCO_3$ (50 mL), dried over Na_2SO_4, and concentrated. Purification by flash chromatography afforded the propargylic alcohol as a pale-yellow liquid (4.6 g, 82%).

Representative procedure for the synthesis of propargylic carbonates:

1. Preparation of the chloroformate: A solution of 2,4,6-trimethoxyphenol[1] (4.4 g, 23 mmol) and triethylamine (4.4 mL, 31 mmol) in toluene (10 mL) was added to a solution of phosgene (20%; 60 mL, 118 mmol) in toluene (200 mL) at 0 °C. The mixture was stirred at 0 °C for 45 min, and then the excess phosgene was removed by purging the mixture with nitrogen or argon for 16 h (quenching the gas stream with KOH).

2. A solution of the propargylic alcohol (3.7 g, 20 mmol) and pyridine (2.5 mL, 30 mmol) in toluene (5 mL) was added to the 0 °C mixture containing the chloroformate. The resulting reaction mixture was allowed to warm to r.t. overnight. Next, saturated aqueous $NaHCO_3$ (50 mL) was added, and the organic layer was separated and concentrated. The residue was dissolved in ethyl acetate (25 mL), and the solution was washed with saturated aqueous $NaHCO_3$ (25 mL), water (25 mL), and brine (10 mL), and then dried over Na_2SO_4. The solvent was removed in vacuo. Flash chromatography of the residue afforded the propargylic carbonate as a colorless solid (4.2 g, 53%).

(1) Matsumoto, M.; Kobayashi, H.; Hotta, Y. *J. Org. Chem.* **1984**, *49*, 4740–4741.



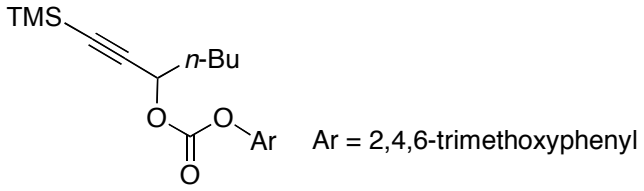
2,4,6-Trimethoxyphenyl (4-(trimethylsilyl)but-3-yn-2-yl) carbonate. The title compound was synthesized from TMS-acetylene and acetaldehyde, and it was purified by chromatography (0%→100% Et_2O/hexanes), which afforded a colorless solid.

^{1}H NMR (600 MHz, $CDCl_3$) δ 6.18 (s, 2H), 5.40 (q, J = 6.6 Hz, 1H), 3.83 (s, 6H), 3.81 (s, 3H), 1.62 (d, J = 6.7 Hz, 3H), 0.20 (s, 9H).

^{13}C NMR (150 MHz, $CDCl_3$) δ 158.6, 152.8, 152.7, 123.7, 102.7, 91.6, 90.8, 65.7, 56.3, 55.7, 21.5, 0.0.

FT-IR (neat) 2961, 2349, 1766, 1600, 1511, 1470, 1252, 1207, 1134, 1042, 929, 846 cm^{-1}.

MS (ESI) m/z (M+H$^+$) calcd for $C_{17}H_{25}O_6Si$: 353.1, found: 353.1.



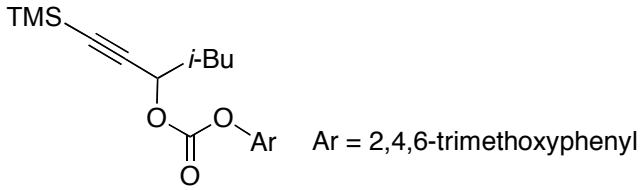
2,4,6-Trimethoxyphenyl (1-(trimethylsilyl)hept-1-yn-3-yl) carbonate. The title compound was synthesized from TMS-acetylene and valeraldehyde, and it was purified by chromatography (0%→100% Et_2O/hexanes), which afforded a colorless solid.

^{1}H NMR (600 MHz, $CDCl_3$) δ 6.18 (s, 2H), 5.33 (t, J = 6.6 Hz, 1H), 3.84 (s, 6H), 3.83 (s, 3H), 1.95–1.83 (m, 2H), 1.53–1.47 (m, 2H), 1.43–1.35 (m, 2H), 0.95 (t, J = 7.3 Hz, 3H), 0.20 (s, 9H).

^{13}C NMR (150 MHz, $CDCl_3$) δ 158.5, 152.9, 152.8, 123.8, 102.0, 91.6, 91.5, 69.5, 56.3, 55.7, 34.7, 27.1, 22.3, 14.1, 0.0.

FT-IR (neat) 2959, 2179, 1768, 1617, 1510, 1458, 1252, 1133, 1036, 951, 844, 761 cm^{-1}.

MS (ESI) m/z (M+H$^+$) calcd for $C_{20}H_{31}O_6Si$: 395.2, found: 395.2.



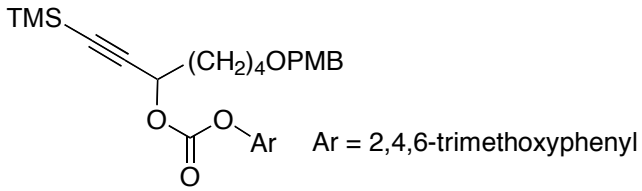
5-Methyl-1-(trimethylsilyl)hex-1-yn-3-yl (2,4,6-trimethoxyphenyl) carbonate. The title compound was synthesized from TMS-acetylene and isovaleraldehyde, and it was purified by chromatography (0%→100% Et_2O/hexanes), which afforded a colorless solid.

^{1}H NMR (600 MHz, $CDCl_3$) δ 6.16 (s, 2H), 5.35 (t, J = 8.3 Hz, 1H), 3.81 (s, 6H), 3.79 (s, 3H), 1.93–1.80 (m, 2H), 1.74–1.66 (m, 1H), 0.97 (app t, J = 7.1 Hz, 6H), 0.18 (s, 9H).

^{13}C NMR (150 MHz, $CDCl_3$) δ 158.0, 152.4, 152.3, 123.3, 101.7, 91.1, 91.0, 67.8, 55.8, 55.2, 43.3, 24.3, 22.0, −0.5.

FT-IR (neat) 2959, 1766, 1600, 1512, 1469, 1207, 1134, 1037, 845 cm^{-1}.

MS (ESI) m/z (M+H$^+$) calcd for $C_{20}H_{31}O_6Si$: 395.2, found: 395.2.



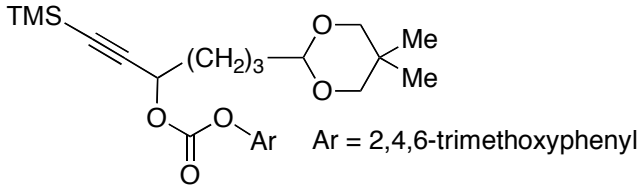
7-((4-Methoxybenzyl)oxy)-1-(trimethylsilyl)hept-1-yn-3-yl (2,4,6-trimethoxyphenyl) carbonate. The title compound was synthesized from TMS-acetylene and 5-(4-methoxybenzyloxy)pentanal, and it was purified by chromatography (0%→100% Et_2O/hexanes), which afforded a yellow oil.

^{1}H NMR (600 MHz, $CDCl_3$) δ 7.24 (d, J = 8.5 Hz, 2H), 6.86 (d, J = 8.5 Hz, 2H), 6.14 (s, 2H), 5.30 (t, J = 6.5 Hz, 1H), 4.42 (s, 2H), 3.76 (s, 9H), 3.74 (s, 3H), 3.45 (t, J = 6.2 Hz, 2H), 1.95–1.82 (m, 2H), 1.70–1.55 (m, 4H), 0.18 (s, 9H).

^{13}C NMR (150 MHz, $CDCl_3$) δ 159.3, 158.6, 152.9, 152.8, 130.8, 129.3, 123.7, 113.9, 101.9, 91.5, 72.7, 69.8, 69.8, 69.3, 56.3, 55.7, 55.4, 34.8, 29.4, 21.8, 0.0.

FT-IR (neat) 2956, 2844, 1767, 1616, 1512, 1458, 1251, 1156, 1035, 846 cm^{-1}.

MS (ESI) m/z (M+Na$^+$) calcd for $C_{28}H_{38}O_8SiNa$: 553.2, found: 553.2.



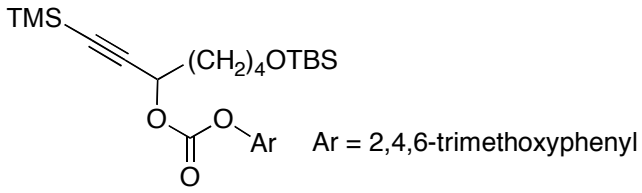
6-(5,5-Dimethyl-1,3-dioxan-2-yl)-1-(trimethylsilyl)hex-1-yn-3-yl (2,4,6-trimethoxyphenyl) carbonate. The title compound was synthesized from TMS-acetylene and 4-(5,5-dimethyl-1,3-dioxan-2-yl)butanal, and it was purified by chromatography (0%→100% Et_2O/hexanes), which afforded a colorless oil.

^{1}H NMR (600 MHz, $CDCl_3$) δ 6.13 (s, 2H), 5.27 (t, J = 6.5 Hz, 1H), 4.41 (t, J = 4.4 Hz, 1H), 3.78 (s, 6H), 3.76 (s, 3H), 3.57 (d, J = 10.5 Hz, 2H), 3.39 (d, J = 10.8 Hz, 2H), 1.95–1.81 (m, 2H), 1.70–1.58 (m, 4H), 1.17 (s, 3H), 0.70 (s, 3H), 0.16 (s, 9H).

^{13}C NMR (150 MHz, $CDCl_3$) δ 158.2, 152.6, 152.5, 123.5, 101.7, 101.5, 91.3, 77.0, 69.1, 69.0, 56.0, 55.4, 34.6, 34.1, 30.0, 22.9, 21.7, 19.3, −0.2.

FT-IR (neat) 2956, 2845, 2361, 1768, 1618, 1510, 1471, 1252, 1207, 1135, 845 cm^{-1}.

MS (ESI) m/z ($M+Na^+$) calcd for $C_{25}H_{38}O_8SiNa$: 517.2, found: 517.2.



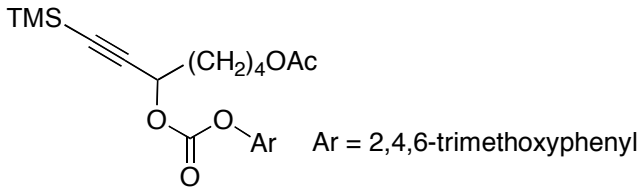
7-((*Tert*-butyldimethylsilyl)oxy)-1-(trimethylsilyl)hept-1-yn-3-yl (2,4,6-trimethoxyphenyl) carbonate. The title compound was synthesized from TMS-acetylene and 5-(*tert*-butyldimethylsilyloxy)pentanal,[2] and it was purified by chromatography (0%→100% Et_2O/hexanes), which afforded a yellow oil.

^1H NMR (600 MHz, $CDCl_3$) δ 6.13 (s, 2H), 5.28 (t, J = 6.6 Hz, 1H), 3.77 (s, 6H), 3.75 (s, 3H), 3.62 (t, J = 5.6 Hz, 2H), 1.91–1.83 (m, 2H), 1.58–1.52 (m, 4H), 0.88 (s, 9H), 0.16 (s, 9H), 0.04 (s, 6H).

^{13}C NMR (150 MHz, $CDCl_3$) δ 158.5, 152.9, 152.8, 123.7, 101.8, 91.6, 91.6, 69.4, 63.0, 56.3, 55.7, 34.7, 32.4, 26.1, 21.5, 18.5, 0.0, −5.0.

FT-IR (neat) 2956, 2858, 2361, 1768, 1617, 1510, 1472, 1252, 1207, 1134, 844 cm^{-1}.

MS (ESI) m/z ($M+Na^+$) calcd for $C_{26}H_{44}O_7Si_2Na$: 547.2, found: 547.2.



5-(((2,4,6-Trimethoxyphenoxy)carbonyl)oxy)-7-(trimethylsilyl)hept-6-yn-1-yl acetate. The title compound was synthesized from TMS-acetylene and 5-oxopentyl acetate,[3] and it was purified by chromatography (0%→100% Et_2O/hexanes), which afforded a yellow oil.

^1H NMR (600 MHz, $CDCl_3$) δ 6.14 (s, 2H), 5.32–5.25 (m, 1H), 4.09–4.00 (m, 2H), 3.80–3.73 (m, 9H), 2.04–2.00 (m, 3H), 1.92–1.82 (m, 2H), 1.72–1.62 (m, 2H), 1.62–1.52 (m, 2H), 0.17 (s, 9H).

^{13}C NMR (150 MHz, $CDCl_3$) δ 171.1, 158.6, 152.8, 152.8, 123.6, 101.6, 91.9, 91.6, 69.0, 64.3, 56.2, 55.6, 34.4, 28.2, 21.4, 21.0, −0.1.

FT-IR (neat) 2959, 1768, 1738, 1600, 1510, 1458, 1251, 1207, 1134, 845 cm^{-1}.

MS (ESI) m/z ($M+H^+$) calcd for $C_{22}H_{33}O_8Si$: 453.1, found: 453.1.

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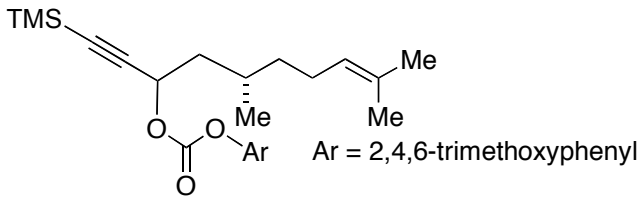
(2) Frankowski, K. J.; Golden, J. E.; Zeng, Y.; Lei, Y.; Aube, J. *J. Am. Chem. Soc.* **2008**, *130*, 6018–6024.

(3) Fryszkowska, A.; Ostaszewski, R. *J. Heterocyclic Chem.* **2008**, *45*, 765–772.

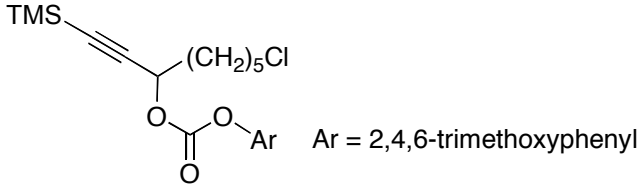


(5*S*)-5,9-Dimethyl-1-(trimethylsilyl)dec-8-en-1-yn-3-yl (2,4,6-trimethoxyphenyl) carbonate. The title compound was synthesized from TMS-acetylene and (*S*)-(−)-citronellal, and it was purified by chromatography (0%→100% Et_2O/hexanes), which afforded a colorless oil.

^{1}H NMR (600 MHz, $CDCl_3$, mixture of diastereoisomers) δ 6.15 (s, 2H), 5.41–5.32 (m, 1H), 5.13–5.07 (m, 1H), 3.80 (s, 6H), 3.78 (s, 3H), 2.08–1.92 (m, 2H), 1.80–1.70 (m, 1H), 1.68 (s, 3H), 1.60 (s, 3H), 1.45–1.14 (m, 4H), 0.98–0.86 (m, 3H), 0.17 (s, 9H).

^{13}C NMR (150 MHz, $CDCl_3$, mixture of diastereoisomers) δ 158.5, 152.8, 152.8, 132.6, 131.4, 131.0, 128.9, 124.6, 123.8, 102.3, 102.1, 91.6, 91.4, 68.5, 68.3, 68.1, 56.3, 55.7, 42.2, 41.8, 38.9, 37.1, 37.1, 30.5, 29.3, 29.1, 25.8, 25.5, 25.4, 23.9, 23.1, 19.5, 19.5, 17.8, 14.2, 11.1, 0.0.

MS (ESI) *m*/*z* ($M+H^+$) calcd for $C_{25}H_{39}O_6Si$: 463.2, found: 463.2.



8-Chloro-1-(trimethylsilyl)oct-1-yn-3-yl (2,4,6-trimethoxyphenyl) carbonate. The title compound was synthesized from TMS-acetylene and 6-chlorohexanal,[4] and it was purified by chromatography (0%→100% Et_2O/hexanes), which afforded a yellow oil.

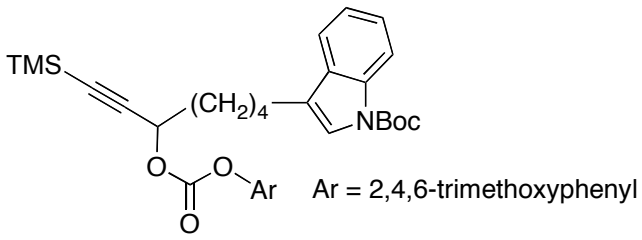
^{1}H NMR (600 MHz, $CDCl_3$) δ 6.15 (s, 2H), 5.30 (t, *J* = 6.4 Hz, 1H), 3.79 (s, 6H), 3.77 (s, 3H), 3.53 (t, *J* = 6.7 Hz, 2H), 1.89–1.84 (m, 2H), 1.82–1.75 (m, 2H), 1.56–1.46 (m, 4H), 0.17 (s, 9H).

^{13}C NMR (150 MHz, $CDCl_3$) δ 158.6, 152.9, 152.8, 123.7, 101.7, 91.8, 91.6, 69.2, 56.2, 55.7, 44.9, 34.7, 32.5, 26.4, 24.2, 0.0.

FT-IR (neat) 2957, 1768, 1600, 1510, 1458, 1251, 1207, 1134, 845 cm^{-1}.

MS (ESI) *m*/*z* ($M+Na^+$) calcd for $C_{21}H_{31}ClO_6SiNa$: 465.2, found: 465.2.

(4) Fox, R. J.; Lalic, G.; Bergman, R. G. *J. Am. Chem. Soc.* **2007**, *129*, 14144–14145.



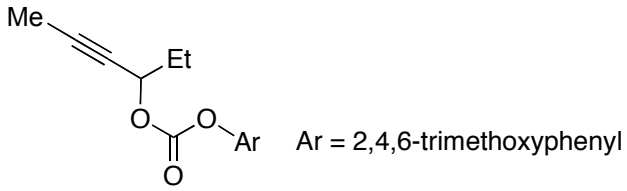
***Tert*-butyl 3-(5-(((2,4,6-trimethoxyphenoxy)carbonyl)oxy)-7-(trimethylsilyl)hept-6-yn-1-yl)-1*H*-indole-1-carboxylate.** The title compound was synthesized from TMS-acetylene and 3-(5-oxo-pentyl)-indole-1-carboxylic acid *tert*-butyl ester,[5] and it was purified by chromatography (0%→100% Et_2O/hexanes), which afforded a yellow oil.

^{1}H NMR (600 MHz, $CDCl_3$) δ 8.18 (br s, 1H), 7.56 (d, J = 7.7 Hz, 1H), 7.41 (br s, 1H), 7.34 (t, J = 7.7 Hz, 1H), 7.27 (t, J = 7.5 Hz, 1H), 6.20 (s, 2H), 5.38 (t, J = 6.5 Hz, 1H), 3.83 (s, 6H), 3.81 (s, 3H), 2.76 (t, J = 7.6 Hz, 2H), 2.05–1.92 (m, 2H), 1.87–1.80 (m, 2H), 1.71 (br s, 11H), 0.22 (s, 9H).

^{13}C NMR (150 MHz, $CDCl_3$) δ 158.2, 152.5, 152.4, 149.6, 135.4, 130.5, 124.0, 123.3, 122.0, 120.7, 118.8, 115.0, 101.5, 91.4, 91.2, 91.0, 83.0, 69.0, 65.6, 55.9, 55.3, 34.4, 28.5, 28.0, 24.6, −0.4.

FT-IR (neat) 2940, 1767, 1731, 1600, 1511, 1456, 1378, 1253, 1157, 1134, 846, 766 cm^{-1}.

MS (ESI) m/z (M+Na$^+$) calcd for $C_{33}H_{43}NO_8SiNa$: 632.2, found: 632.2.



Hex-4-yn-3-yl (2,4,6-trimethoxyphenyl) carbonate. The title compound was synthesized from 4-hexyn-3-ol, and it was purified by chromatography (0%→100% Et_2O/hexanes), which afforded a colorless oil.

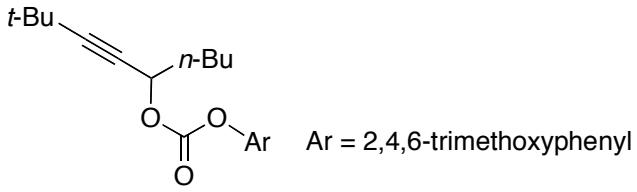
^{1}H NMR (600 MHz, $CDCl_3$) δ 6.08 (s, 2H), 5.18–5.13 (m, 1H), 3.71 (s, 6H), 3.68 (s, 3H), 1.80–1.78 (m, 5H), 0.99 (t, J = 7.4 Hz, 3H).

^{13}C NMR (150 MHz, $CDCl_3$) δ 158.5, 153.0, 152.8, 123.6, 91.4, 83.0, 75.9, 70.6, 56.1, 55.5, 28.5, 9.2, 3.5.

FT-IR (neat) 2973, 2362, 1768, 1617, 1508, 1457, 1206, 1132, 1035, 949, 812 cm^{-1}.

MS (ESI) m/z (M+H$^+$) calcd for $C_{16}H_{21}O_6$: 309.1, found: 309.1.

(5) Conrad, J. C.; Kong, J.; Laforteza, B. N.; MacMillan, D. W. C. *J. Am. Chem. Soc.* **2009**, *131*, 11640–11641.



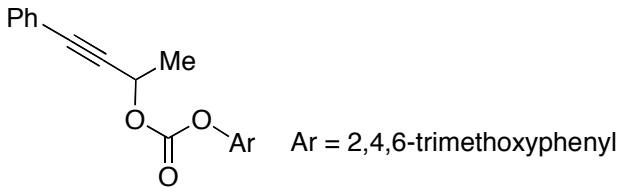
2,2-Dimethylnon-3-yn-5-yl (2,4,6-trimethoxyphenyl) carbonate. The title compound was synthesized from *tert*-butylacetylene and valeraldehyde, and it was purified by chromatography (0%→100% Et_2O/hexanes), which afforded a colorless solid.

^{1}H NMR (600 MHz, $CDCl_3$) δ 6.16 (s, 2H), 5.30 (t, *J* = 6.5 Hz, 1H), 3.80 (s, 6H), 3.77 (s, 3H), 1.91–1.78 (m, 2H), 1.53–1.44 (m, 2H), 1.43–1.32 (m, 2H), 1.23 (s, 9H), 0.94 (t, *J* = 7.3 Hz, 3H).

^{13}C NMR (100 MHz, $CDCl_3$) δ 158.5, 153.0, 152.8, 123.6, 95.4, 91.4, 75.5, 69.7, 56.2, 55.6, 35.0, 30.9, 27.5, 27.1, 22.3, 14.1.

FT-IR (neat) 2967, 2361, 2339, 1838, 1767, 1617, 1509, 1457, 1252, 1206, 1134, 1036, 950, 812 cm^{-1}.

MS (ESI) *m*/*z* ($M+H^+$) calcd for $C_{21}H_{31}O_6$: 379.2, found: 379.3.



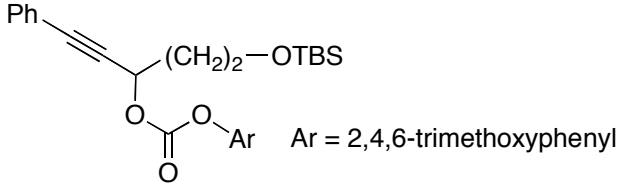
4-Phenylbut-3-yn-2-yl (2,4,6-trimethoxyphenyl) carbonate. The title compound was synthesized from phenylacetylene and acetaldehyde, and it was purified by chromatography (0%→100% Et_2O/hexanes), which afforded a colorless solid.

^{1}H NMR (600 MHz, $CDCl_3$) δ 7.49 (d, *J* = 6.2 Hz, 2H), 7.36–7.32 (m, 3H), 6.20 (s, 2H), 5.65 (q, *J* = 6.6 Hz, 1H), 3.84 (s, 6H), 3.82 (s, 3H), 1.74 (d, *J* = 6.7 Hz, 3H).

^{13}C NMR (150 MHz, $CDCl_3$) δ 158.6, 152.9, 152.8, 132.0, 128.8, 128.4, 123.8, 122.5, 91.6, 86.8, 85.7, 65.9, 56.3, 55.7, 21.6.

FT-IR (neat) 2941, 1765, 1600, 1510, 1457, 1250, 1206, 1132, 1088, 1034, 759 cm^{-1}.

MS (ESI) *m*/*z* ($M+H^+$) calcd for $C_{20}H_{21}O_6$: 357.1, found: 357.1.



5-((*Tert*-butyldimethylsilyl)oxy)-1-phenylpent-1-yn-3-yl (2,4,6-trimethoxyphenyl) carbonate. The title compound was synthesized from TMS-acetylene and 3-(*tert*-

butyldimethylsilyloxy)propanal,[6] and it was purified by chromatography (0%→100% Et_2O/hexanes), which afforded a yellow oil.

^1H NMR (600 MHz, $CDCl_3$) δ 7.49–7.46 (m, 2H), 7.35–7.31 (m, 3H), 6.18 (s, 2H), 5.75 (t, *J* = 6.9 Hz, 1H), 3.91 (t, *J* = 6.0 Hz, 2H), 3.80 (s, 6H), 3.78 (s, 3H), 2.34–2.26 (m, 1H), 2.21–2.14 (m, 1H), 0.95 (s, 9H), 0.13 (s, 6H).

^{13}C NMR (150 MHz, $CDCl_3$) δ 158.6, 152.8, 132.0, 131.9, 128.9, 128.4, 123.7, 122.4, 91.5, 86.6, 85.9, 66.9, 58.9, 56.3, 55.7, 38.1, 26.1, 18.4, −5.2.

FT-IR (neat) 2955, 2856, 2361, 1770, 1600, 1510, 1471, 1253, 1207, 1134, 835, 778 cm^{-1}.

MS (ESI) *m*/*z* ($M+H^+$) calcd for $C_{27}H_{37}O_7Si$: 501.2, found: 501.2.

III. Stereoconvergent Cross-Coupling Reactions

General procedure for the preparation of the organozinc reagents: A solution of the aryl bromide (10 mmol) in THF (10 mL) was prepared. A portion (2.0 mL) of this solution was added to magnesium powder (0.27 g, 12 mmol) in one portion. The suspension was vigorously stirred, and the temperature was monitored until it reached reflux (heating with a heat gun or cooling in a water bath, as required). The remaining aryl bromide solution was added to the reaction mixture over ~10 min, and stirring was continued at r.t. for 20 min. The suspension was filtered through an acrodisc, and then the solution was titrated using Knochel's method (~1.0 M).[7]

In a glovebox, a solution of the Grignard reagent (3.0 mL, 3.0 mmol) was added to a suspension of zinc iodide (1.0 g, 3.1 mmol) in THF (7.0 mL) in a 20-mL vial. The vial was capped and taken out of the glovebox, and the resulting suspension was stirred at r.t. for 30 min and then used directly in the cross-coupling reaction.

General cross-coupling procedure: DME (3.75 mL) was added to a 20-mL vial charged with the propargylic carbonate (0.75 mmol), (3*S*,8*R*)-pybox ligand **L*** (the enantiomer illustrated in eq 1; 39 mg, 0.098 mmol), and $NiCl_2(PCy_3)_2$ (53 mg, 0.076 mmol) under argon. The resulting suspension was cooled to 10 °C, and then the suspension that contained the organozinc reagent (3.75 mL, 1.5 mmol) was added in one portion. The reaction mixture was stirred vigorously at 10 °C for 20 h, during which the initially colorless suspension turned into a dark-red solution, from which a precipitate formed during the course of the reaction. The reaction was quenched by the addition of ethanol (0.75 mL). Next, the mixture was allowed to warm to r.t., diluted with diethyl ether/hexane (1:1; 5 mL), and filtered through a short plug of silica, eluting with diethyl ether/hexane (1:1; 20 mL). The solvent was removed in vacuo, and the residue was purified by reverse-phase flash chromatography (5→100% MeCN in water, Biotage 10-g SNAP cartridge).

A second run was performed with the (3*R*,8*S*) enantiomer of ligand **L***.

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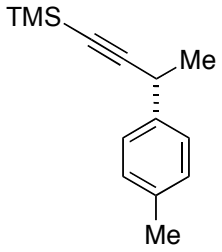
(6) Marshall, J. A.; Van Devender, E. A. *J. Org. Chem.* **2001**, *66*, 8037–8041.

(7) Krasovskiy, A.; Knochel, P. *Synthesis* **2006**, 890–891.



(*R*)-Trimethyl(3-(*p*-tolyl)but-1-yn-1-yl)silane (Table 2, entry 1). 2,4,6-Trimethoxyphenyl (4-(trimethylsilyl)but-3-yn-2-yl) carbonate (264 mg, 0.75 mmol) and *p*-tolylzinc iodide (0.30 M solution in THF; 3.75 mL, 1.13 mmol) were used. The product was obtained as a colorless oil. First run: 117 mg (72%, 92% ee). Second run (using (3*S*,8*R*)-**1**): 105 mg (65%, 94% ee).

The ee was determined by GC on a Chirasil Dex-CB column (75→160 °C @ 0.25 °C/min, then →170 °C @ 10 °C/min, hold 10 min; flow rate 1.0 mL/min) with t_r = 77.5 min (major), 78.6 min (minor).

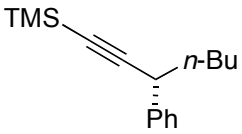
^{1}H NMR (600 MHz, $CDCl_3$) δ 7.32 (d, *J* = 7.9 Hz, 2H), 7.18 (d, *J* = 7.9 Hz, 2H), 3.80 (q, *J* = 7.1 Hz, 1H), 2.38 (s, 3H), 1.52 (d, *J* = 7.2 Hz, 3H), 0.23 (s, 9H).

^{13}C NMR (150 MHz, $CDCl_3$) δ 140.3, 136.3, 129.3, 126.9, 110.0, 86.1, 32.6, 24.8, 21.2, 0.4.

FT-IR (neat) 2961, 2166, 1513, 1250, 1095, 917, 843 cm^{-1}.

MS (ESI) *m*/*z* ($M-2H+H^+$) calcd for $C_{14}H_{19}Si$: 215.1, found: 215.1.

$[\alpha]^{23}_D$ = −6.1 (c 0.30, $CHCl_3$).



(*R*)-Trimethyl(3-phenylhept-1-yn-1-yl)silane (Table 2, entry 2). 2,4,6-Trimethoxyphenyl (1-(trimethylsilyl)hept-1-yn-3-yl) carbonate (200 mg, 0.50 mmol) and phenylzinc iodide (0.30 M solution in THF; 2.5 mL, 0.75 mmol) were used. The product was obtained as pale-yellow oil. First run: 97 mg (80%, 90% ee). Second run (0.75 mmol): 150 mg (82%, 90% ee).

The ee was determined by GC on a Chirasil Dex-CB column (100→130 °C @ 10 °C/min, hold 10 min, then →170 °C @ 9 °C/min, hold 5 min; flow rate 1.0 mL/min) with t_r = 13.2 min (minor), 13.3 min (major).

^{1}H NMR (600 MHz, $CDCl_3$) δ 7.37–7.31 (m, 4H), 7.26–7.22 (m, 1H), 3.66–3.63 (m, 1H), 1.79–1.68 (m, 2H), 1.49–1.25 (m, 4H), 0.90 (t, *J* = 7.2 Hz, 3H), 0.20 (s, 9H).

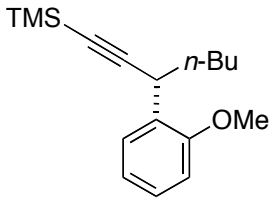
^{13}C NMR (150 MHz, $CDCl_3$) δ 142.1, 128.4, 127.4, 126.5, 108.6, 87.0, 38.8, 38.4, 29.4, 22.4, 14.0, 0.2.

FT-IR (neat) 2959, 2934, 2172, 1453, 1249, 843, 759, 698 cm^{-1}.

MS (ESI) *m*/*z* ($M+H^+$) calcd for $C_{16}H_{25}Si$: 245.2, found: 245.1.

$[\alpha]^{23}_D$ = −11 (c 0.50, $CHCl_3$, (*S*)-enantiomer).

The absolute configuration of the product was assigned by comparison with literature data.[8]



(*R*)-(3-(2-Methoxyphenyl)hept-1-yn-1-yl)trimethylsilane (Table 2, entry 3). 2,4,6-Trimethoxyphenyl (1-(trimethylsilyl)hept-1-yn-3-yl) carbonate (300 mg, 0.75 mmol) and *o*-methoxyphenylzinc iodide (0.30 M solution in THF; 3.75 mL, 1.13 mmol) were used. The product was obtained as pale-yellow oil. First run: 133 mg (65%, 92% ee). Second run: 134 mg (66%, 93% ee).

The ee was determined by HPLC on an OD-H column (hexanes, 0.9 mL/min) with t_r = 4.7 min (major), 5.0 min (minor).

^{1}H NMR (600 MHz, $CDCl_3$) δ 7.59 (dd, *J* = 7.5, 1.5 Hz, 1H), 7.25 (dt, *J* = 8.2, 1.6 Hz, 1H), 7.01 (t, *J* = 7.4 Hz, 1H), 6.88 (d, *J* = 8.1 Hz, 1H), 4.17 (dd, *J* = 8.7, 5.3 Hz, 1H), 3.86 (s, 3H), 1.80–1.72 (m, 1H), 1.70–1.62 (m, 1H), 1.54–1.31 (m, 4H), 0.95 (t, *J* = 7.3 Hz, 3H), 0.24 (s, 9H).

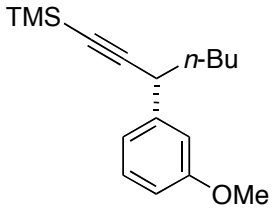
^{13}C NMR (150 MHz, $CDCl_3$) δ 156.3, 130.7, 128.7, 127.7, 120.7, 110.5, 109.5, 86.3, 55.5, 36.6, 32.1, 29.6, 22.5, 14.2, 0.5.

FT-IR (neat) 2958, 2169, 1601, 1493, 1465, 1246, 1051, 1032, 842 cm^{-1}.

MS (ESI) *m*/*z* ($M+Na^+$) calcd for $C_{17}H_{26}OSiNa$: 297.2, found: 297.2.

$[\alpha]^{23}_D$ = +20 (c 0.68, $CHCl_3$).

The absolute configuration of the product was assigned by comparison with literature data.[8]



(*R*)-(3-(3-Methoxyphenyl)hept-1-yn-1-yl)trimethylsilane (Table 2, entry 4). 2,4,6-Trimethoxyphenyl (1-(trimethylsilyl)hept-1-yn-3-yl) carbonate (300 mg, 0.75 mmol) and *m*-methoxyphenylzinc iodide (0.30 M solution in THF; 3.75 mL, 1.13 mmol) were used. The product was obtained as a yellow oil. First run: 147 mg (72%, 92% ee). Second run: 151 mg (74%, 91% ee).

The ee was determined by HPLC on an OD-H column (hexanes, 0.9 mL/min) with t_r = 7.0 min (minor), 8.8 min (major).

(8) Smith, S. W.; Fu, G. C. *J. Am. Chem. Soc*. **2008**, *130*, 12645–12647.

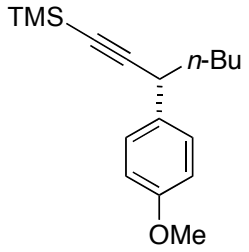
^{1}H NMR (600 MHz, $CDCl_3$) δ 7.76 (t, *J* = 7.9 Hz, 1H), 7.48 (s, 1H), 7.45 (d, *J* = 7.7 Hz, 1H), 7.30 (d, *J* = 8.2 Hz, 1H), 4.34 (s, 3H), 4.15 (t, *J* = 7.2 Hz, 1H), 2.30–2.22 (m, 2H), 2.02–1.80 (m, 4H), 1.43 (t, *J* = 7.3 Hz, 3H), 0.72 (s, 9H).

^{13}C NMR (150 MHz, $CDCl_3$) δ 159.3, 143.3, 128.9, 119.5, 112.8, 111.6, 108.2, 86.8, 54.8, 38.4, 37.9, 29.1, 22.0, 13.6, −0.1.

FT-IR (neat) 2958, 2860, 2171, 1601, 1487, 1466, 1437, 1250, 1153, 1046, 843 cm^{-1}.

MS (ESI) *m*/*z* ($M+Na^+$) calcd for $C_{17}H_{26}OSiNa$: 297.2, found: 297.2.

$[\alpha]^{23}_D$ = +16 (c 0.67, $CHCl_3$).



(*R*)-(3-(4-Methoxyphenyl)hept-1-yn-1-yl)trimethylsilane (Table 2, entry 5). 2,4,6-Trimethoxyphenyl (1-(trimethylsilyl)hept-1-yn-3-yl) carbonate (300 mg, 0.75 mmol) and *p*-methoxyphenylzinc iodide (0.30 M solution in THF; 3.75 mL, 1.13 mmol) were used. The product was obtained as a yellow oil. First run: 148 mg (73%, 89% ee). Second run: 159 mg (78%, 88% ee).

The ee was determined by HPLC on an OD-H column (hexanes, 0.9 mL/min) with t_r = 6.0 min (minor), 6.6 min (major).

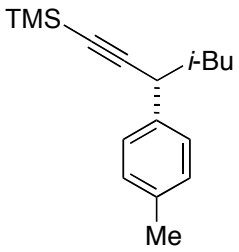
^{1}H NMR (600 MHz, $CDCl_3$) δ 7.24 (d, *J* = 8.3 Hz, 2H), 6.84 (d, *J* = 6.9 Hz, 2H), 3.79 (s, 3H), 3.57 (t, *J* = 6.4 Hz, 1H), 1.74–1.61 (m, 2H), 1.45–1.22 (m, 4H), 0.89–0.84 (m, 3H), 0.16 (s, 9H).

^{13}C NMR (150 MHz, $CDCl_3$) δ 157.9, 133.8, 128.0, 113.4, 108.6, 86.4, 54.9, 38.1, 37.5, 29.0, 22.0, 13.6, −0.1.

FT-IR (neat) 2958, 2361, 2171, 1512, 1249, 1176, 1039, 842 cm^{-1}.

MS (ESI) *m*/*z* ($M+H^+$) calcd for $C_{17}H_{27}OSi$: 275.2, found: 275.2.

$[\alpha]^{23}_D$ = +4.7 (c 0.48, $CHCl_3$).



(*R*)-Trimethyl(5-methyl-3-(*p*-tolyl)hex-1-yn-1-yl)silane (Table 2, entry 6). 5-Methyl-1-(trimethylsilyl)hex-1-yn-3-yl (2,4,6-trimethoxyphenyl) carbonate (300 mg, 0.75 mmol) and *p*-

tolylzinc iodide (0.30 M solution in THF; 3.75 mL, 1.13 mmol) were used. The product was obtained as a colorless oil. First run: 111 mg (58%, 94% ee). Second run: 108 mg (56%, 92% ee).

The ee was determined by GC on a Chirasil Dex-CB column (100→130 °C @ 10 °C/min, hold 10 min, then →170 °C @ 9 °C/min, hold 5 min; flow rate 1.0 mL/min) with t_r = 15.9 min (minor), 16.0 min (major).

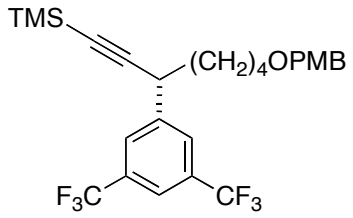
^{1}H NMR (600 MHz, $CDCl_3$) δ 7.26 (d, *J* = 8.9 Hz, 2H), 7.15 (d, *J* = 7.9 Hz, 2H), 3.67 (dd, *J* = 9.3, 6.5 Hz, 1H), 2.36 (s, 3H), 1.83–1.75 (m, 1H), 1.70 (ddd, *J* = 13.3, 9.4, 5.8 Hz, 1H), 1.52–1.46 (m, 1H), 0.97 (d, *J* = 2.7 Hz, 3H), 0.95 (d, *J* = 2.8 Hz, 3H), 0.20 (s, 9H).

^{13}C NMR (150 MHz, $CDCl_3$) δ 139.4, 136.0, 129.1, 127.3, 108.9, 86.5, 48.1, 36.4, 25.9, 22.9, 21.9, 20.9, 0.2.

FT-IR (neat) 2958, 2170, 1735, 1513, 1250, 842 cm^{-1}.

MS (ESI) *m*/*z* ($M+H^+$) calcd for $C_{17}H_{27}Si$: 259.2, found: 259.2.

$[\alpha]^{23}_D$ = +1.7 (c 0.63, $CHCl_3$).



(*R*)-(3-(3,5-Bis(trifluoromethyl)phenyl)-7-((4-methoxybenzyl)oxy)hept-1-yn-1-yl)trimethylsilane (Table 2, entry 7). 7-((4-Methoxybenzyl)oxy)-1-(trimethylsilyl)hept-1-yn-3-yl (2,4,6-trimethoxyphenyl) carbonate (398 mg, 0.75 mmol) and 3,5-*bis*(trifluoromethyl)phenylzinc iodide (0.30 M solution in THF; 3.75 mL, 1.13 mmol) were used. The product was obtained as a colorless oil. First run: 313 mg (81%, 84% ee). Second run: 342 mg (88%, 86% ee).

The ee was determined by HPLC on an OD-H column (1% IPA in hexanes, 0.9 mL/min) with t_r = 4.3 min (major), 4.7 min (minor).

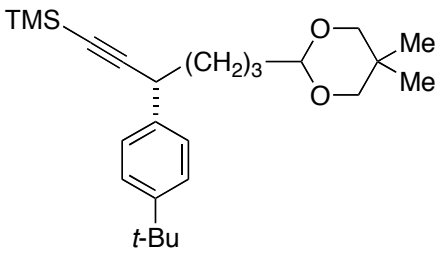
^{1}H NMR (600 MHz, $CDCl_3$) δ 7.85 (s, 2H), 7.79 (s, 1H), 7.28 (d, *J* = 8.7 Hz, 2H), 6.91 (d, *J* = 8.5 Hz, 2H), 4.46 (s, 2H), 3.83 (s, 3H), 3.82–3.77 (m, 1H), 3.48 (t, *J* = 6.4 Hz, 2H), 1.83–1.74 (m, 2H), 1.73–1.48 (m, 4H), 0.23 (s, 9H).

^{13}C NMR (150 MHz, $CDCl_3$) δ 159.3, 144.7, 131.9 (q, $^2J_{CF}$ = 33 Hz), 130.7, 129.4, 127.9, 123.6 (q, $^1J_{CF}$ = 273 Hz), 121.0, 113.9, 106.1, 89.7, 72.7, 69.8, 55.4, 38.7, 38.3, 29.4, 24.2, 0.1.

FT-IR (neat) 2955, 2859, 2174, 1616, 1514, 1376, 1280, 1251, 1173, 1137, 845 cm^{-1}.

MS (ESI) *m*/*z* ($M-2H+Na^+$) calcd for $C_{26}H_{28}F_6O_2SiNa$: 537.2, found: 537.3.

$[\alpha]^{23}_D$ = +12 (c 0.55, $CHCl_3$).



(*R*)-(3-(4-(*Tert*-butyl)phenyl)-6-(5,5-dimethyl-1,3-dioxan-2-yl)hex-1-yn-1-yl)trimethylsilane (Table 2, entry 8). 6-(5,5-Dimethyl-1,3-dioxan-2-yl)-1-(trimethylsilyl)hex-1-yn-3-yl (2,4,6-trimethoxyphenyl) carbonate (371 mg, 0.75 mmol) and *p-tert*-butylphenylzinc iodide (0.30 M solution in THF; 3.75 mL, 1.13 mmol) were used. The product was obtained as a colorless oil. First run: 264 mg (88%, 91% ee). Second run: 259 mg (86%, 92% ee).

The ee was determined by HPLC on an OD-H column (0.3% IPA in hexanes, 0.9 mL/min) with t_r = 8.7 min (minor), 10.9 min (major).

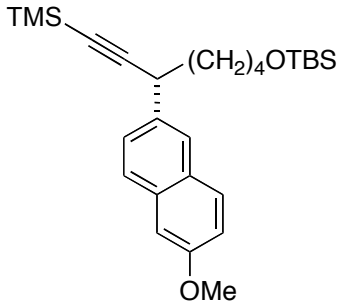
^{1}H NMR (600 MHz, $CDCl_3$) δ 7.35 (d, *J* = 8.2 Hz, 2H), 7.30–7.27 (m, 2H), 4.43 (t, *J* = 4.7 Hz, 1H), 3.66–3.60 (m, 3H), 3.44 (d, *J* = 11.0 Hz, 2H), 1.81–1.74 (m, 2H), 1.72–1.61 (m, 3H), 1.59–1.51 (m, 1H), 1.34 (s, 9H), 1.21 (s, 3H), 0.74 (s, 3H), 0.21 (s, 9H).

^{13}C NMR (150 MHz, $CDCl_3$) δ 149.5, 138.9, 127.2, 125.4, 108.7, 102.3, 87.2, 38.7, 38.4, 34.7, 34.6, 31.5, 30.3, 23.1, 22.1, 22.0, 0.4.

FT-IR (neat) 2957, 2868, 2171, 1508, 1463, 1394, 1363, 1249, 1134, 843 cm^{-1}.

MS (ESI) *m*/*z* ($M+H^+$) calcd for $C_{25}H_{41}O_2Si$: 401.2, found: 401.2.

$[\alpha]^{23}_D$ = +10 (c 0.51, $CHCl_3$).



(*R*)-*Tert*-butyl((5-(6-methoxynaphthalen-2-yl)-7-(trimethylsilyl)hept-6-yn-1-yl)oxy)dimethylsilane (Table 2, entry 9). 7-((*Tert*-butyldimethylsilyl)oxy)-1-(trimethylsilyl)hept-1-yn-3-yl (2,4,6-trimethoxyphenyl) carbonate (393 mg, 0.75 mmol) and 6-methoxynaphthylzinc iodide (0.30 M solution in THF; 3.75 mL, 1.13 mmol) were used. The product was obtained as a colorless oil. First run: 324 mg (95%, 88% ee). Second run: 317 mg (93%, 94% ee).

The ee was determined by HPLC on an IB column (hexanes, 0.9 mL/min) with t_r = 18.8 min (major), 20.4 min (minor).

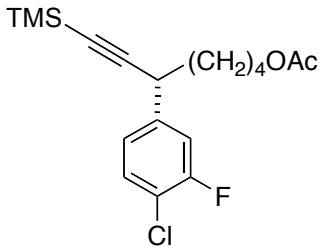
^{1}H NMR (600 MHz, $CDCl_3$) δ 7.77–7.73 (m, 3H), 7.49 (d, *J* = 8.5 Hz, 1H), 7.19 (d, *J* = 8.8 Hz, 1H), 7.15 (s, 1H), 3.95 (s, 3H), 3.83 (t, *J* = 7.2 Hz, 1H), 3.64 (t, *J* = 6.1 Hz, 2H), 1.92–1.82 (m, 2H), 1.62–1.45 (m, 3H), 1.35–1.26 (m, 1H), 0.93 (s, 9H), 0.26 (s, 6H), 0.09 (s, 9H).

^{13}C NMR (150 MHz, $CDCl_3$) δ 157.6, 137.2, 133.7, 129.4, 129.1, 127.1, 126.5, 126.0, 119.0, 108.8, 105.8, 87.4, 63.3, 55.4, 38.9, 38.5, 32.7, 26.2, 23.9, 18.5, 0.4, −5.0.

FT-IR (neat) 2955, 2361, 2170, 1607, 1507, 1390, 1250, 1105, 1035, 841, 775 cm^{-1}.

MS (ESI) *m*/*z* ($M+H^+$) calcd for $C_{27}H_{43}O_2Si_2$: 455.3, found: 455.3.

$[\alpha]^{23}_D$ = −8.6 (c 0.51, $CHCl_3$).



(*R*)-5-(4-Chloro-3-fluorophenyl)-7-(trimethylsilyl)hept-6-yn-1-yl acetate (Table 2, entry 10). 5-(((2,4,6-Trimethoxyphenoxy)carbonyl)oxy)-7-(trimethylsilyl)hept-6-yn-1-yl acetate (340 mg, 0.75 mmol) and 4-chloro-3-fluorophenylzinc iodide (0.30 M solution in THF; 3.75 mL, 1.13 mmol) were used. The product was obtained as a colorless oil. First run: 204 mg (77%, 87% ee). Second run: 226 mg (85%, 85% ee).

The ee was determined by HPLC on an OD-H column (hexanes, 0.9 mL/min) with t_r = 25.8 min (major), 29.2 min (minor).

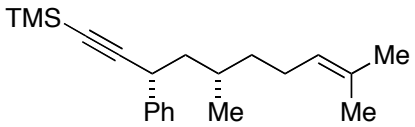
^{1}H NMR (600 MHz, $CDCl_3$) δ 7.32 (t, *J* = 7.8 Hz, 1H), 7.15 (d, *J* = 10.1 Hz, 1H), 7.04 (d, *J* = 8.3 Hz, 1H), 4.04 (t, *J* = 6.7 Hz, 2H), 3.62 (t, *J* = 7.2 Hz, 1H), 2.03 (s, 3H), 1.75–1.57 (m, 4H), 1.54–1.36 (m, 2H), 0.18 (s, 9H).

^{13}C NMR (150 MHz, $CDCl_3$) δ 171.4, 158.2 (d, $^1J_{CF}$ = 250 Hz), 142.8 (d, $^3J_{CF}$ = 6 Hz), 130.6, 124.0, 119.3 (d, $^2J_{CF}$ = 17 Hz), 115.9 (d, $^2J_{CF}$ = 22 Hz), 106.7, 88.6, 64.4, 38.1, 37.9, 28.3, 23.7, 21.2, 0.3.

FT-IR (neat) 2957, 2351, 2172, 1740, 1487, 1424, 1249, 1062, 843, 760 cm^{-1}.

MS (ESI) *m*/*z* ($M-Ac+H+H^+$) calcd for $C_{16}H_{23}ClFOSi$: 313.1, found: 313.1.

$[\alpha]^{23}_D$ = +10 (c 0.55, $CHCl_3$).



((3*R*,5*S*)-5,9-Dimethyl-3-phenyldec-8-en-1-yn-1-yl)trimethylsilane (Table 2, entry 11). (5*S*)-5,9-Dimethyl-1-(trimethylsilyl)dec-8-en-1-yn-3-yl (2,4,6-trimethoxyphenyl) carbonate (349 mg, 0.75 mmol) and phenylzinc iodide (0.30 M solution in THF; 3.75 mL, 1.13 mmol) were used. The product was obtained as a colorless oil. First run: 190 mg (81%, 90% de). Second run: 177 mg (76%, 88% de).

The de was determined by GC on an HP-5 column (120 °C for 1 min, then 120→280 °C @ 10 °C/min, hold 2 min; flow rate 1.0 mL/min) with t_r = 9.3 min (minor), 9.4 min (major).

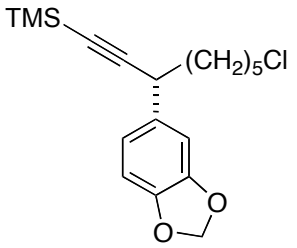
^{1}H NMR (600 MHz, $CDCl_3$) δ 7.28–7.21 (m, 3H), 7.18–7.11 (m, 2H), 5.04–5.00 (m, 1H), 3.64–3.60 (m, 1H), 1.93–1.87 (m, 1H), 1.70–1.64 (m, 1H), 1.60 (s, 3H), 1.52 (s, 3H), 1.37–1.20 (m, 3H), 1.16–1.09 (m, 1H), 0.88 (d, J = 6.5 Hz, 3H), 0.86–0.79 (m, 1H), 0.09 (s, 9H).

^{13}C NMR (150 MHz, $CDCl_3$) δ 142.7, 131.4, 128.6, 127.5, 126.7, 124.9, 108.5, 87.3, 46.7, 37.5, 36.9, 30.6, 26.0, 25.5, 19.3, 17.9, 0.4.

FT-IR (neat) 2961, 2927, 2361, 2171, 1466, 1250, 842 cm^{-1}.

MS (ESI) m/z (M+H$^+$) calcd for $C_{21}H_{33}Si$: 313.2, found: 313.2.

$[\alpha]^{23}_D$ = +6.7 (c 0.60, $CHCl_3$).



(*R*)-(3-(Benzo[d][1,3]dioxol-5-yl)-8-chlorooct-1-yn-1-yl)trimethylsilane (Table 2, entry 12). 8-Chloro-1-(trimethylsilyl)oct-1-yn-3-yl (2,4,6-trimethoxyphenyl) carbonate (332 mg, 0.75 mmol) and 3,4-methylenedioxophenylzinc iodide (0.30 M solution in THF; 3.75 mL, 1.13 mmol) were used. The product was obtained as a colorless oil. First run: 157 mg (65%, 83% ee). Second run: 157 mg (65%, 85% ee).

The ee was determined by HPLC on an OD-H column (hexanes, 0.9 mL/min) with t_r = 19.1 min (major), 23.7 min (minor).

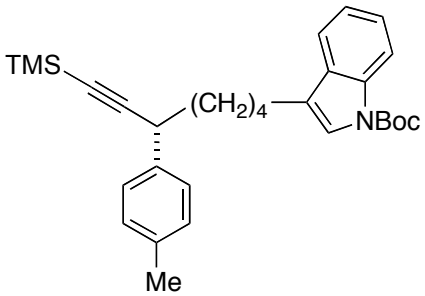
^{1}H NMR (600 MHz, $CDCl_3$) δ 6.89 (s, 1H), 6.82–6.75 (m, 2H), 5.97 (s, 2H), 3.60 (t, J = 7.1 Hz, 1H), 3.57–3.52 (m, 2H), 1.83–1.76 (m, 2H), 1.76–1.68 (m, 2H), 1.53–1.40 (m, 4H), 0.21 (s, 9H).

^{13}C NMR (150 MHz, $CDCl_3$) δ 147.8, 146.4, 135.8, 120.6, 108.4, 108.2, 108.1, 101.1, 87.4, 45.2, 38.7, 38.5, 32.6, 26.6, 26.5, 0.4.

FT-IR (neat) 2940, 2170, 1504, 1486, 1442, 1249, 1041, 938, 843 cm^{-1}.

MS (ESI) m/z (M+H$^+$) calcd for $C_{18}H_{26}ClO_2Si$: 337.1, found: 337.1.

$[\alpha]^{23}_D$ = +9.0 (c 0.60, $CHCl_3$).



(*R*)-*Tert*-butyl 3-(5-(*p*-tolyl)-7-(trimethylsilyl)hept-6-yn-1-yl)-1*H*-indole-1-carboxylate (Table 2, entry 13). *Tert*-butyl 3-(5-(((2,4,6-trimethoxyphenoxy)carbonyl)oxy)-7-

(trimethylsilyl)hept-6-yn-1-yl)-1*H*-indole-1-carboxylate (457 mg, 0.75 mmol) and *p*-tolylzinc iodide (0.30 M solution in THF; 3.75 mL, 1.13 mmol) were used. The product was obtained as a colorless oil. First run: 262 mg (74%, 90% ee). Second run: 247 mg (70%, 89% ee).

The ee of the deprotected product (i.e., the free indole) was determined by HPLC using an IB column (5% IPA in hexanes, 0.9 mL/min) with t_r = 26.1 min (minor), 29.5 min (major).

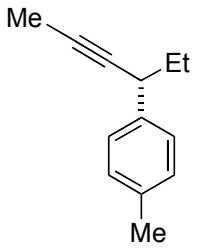
^{1}H NMR (600 MHz, $CDCl_3$) δ 8.19 (s, 1H), 7.57 (d, *J* = 7.7 Hz, 1H), 7.41 (s, 1H), 7.37 (t, *J* = 7.4 Hz, 1H), 7.31–7.27 (m, 3H), 7.19 (d, *J* = 7.9 Hz, 2H), 3.69 (t, *J* = 7.2 Hz, 1H), 2.74 (t, *J* = 7.6 Hz, 2H), 2.40 (s, 3H), 1.87–1.75 (m, 4H), 1.74 (s, 9H), 1.68–1.56 (m, 2H), 0.24 (s, 9H).

^{13}C NMR (150 MHz, $CDCl_3$) δ 150.0, 139.1, 136.3, 131.0, 129.3, 127.5, 124.3, 122.4, 121.4, 119.2, 115.4, 108.9, 100.2, 87.2, 83.4, 38.7, 38.5, 29.1, 28.4, 27.4, 25.0, 21.2, 0.4.

FT-IR (neat) 2932, 2857, 2361, 2171, 1733, 1455, 1379, 1251, 1160, 1092, 843, 745 cm^{-1}.

MS (ESI) *m*/*z* (M−Boc+H+H^+) calcd for $C_{25}H_{32}NSi$: 374.2, found: 374.2.

$[\alpha]^{23}_D$ = +5.7 (c 0.78, $CHCl_3$).



(*R*)-1-(Hex-4-yn-3-yl)-4-methylbenzene (eq 4). Hex-4-yn-3-yl (2,4,6-trimethoxyphenyl) carbonate (231 mg, 0.75 mmol) and *p*-tolylzinc iodide (0.30 M solution in THF; 3.75 mL, 1.13 mmol) were used. The product was obtained as a colorless oil. First run: 90 mg (70%, 78% ee). Second run: 96 mg (74%, 78% ee).

The ee was determined by GC on a Chirasil Dex-CB column (90→110 °C @ 0.4 °C/min, then →140 °C @ 15 °C/min, hold 6 min; flow rate 1.0 mL/min) with t_r = 31.4 min (minor), 34.0 min (major).

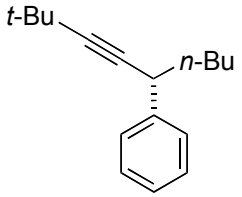
^{1}H NMR (600 MHz, $CDCl_3$) δ 7.27 (d, *J* = 8.0 Hz, 2H), 7.17 (d, *J* = 7.9 Hz, 2H), 3.53–3.48 (m, 1H), 2.37 (s, 3H), 1.90 (s, 3H), 1.80–1.71 (m, 2H), 1.01 (t, *J* = 7.4 Hz, 3H).

^{13}C NMR (150 MHz, $CDCl_3$) δ 139.9, 136.2, 129.2, 127.5, 81.2, 78.3, 39.2, 31.9, 21.3, 12.2, 3.9.

FT-IR (neat) 2967, 2927, 2361, 1513, 1457, 807 cm^{-1}.

MS (ESI) *m*/*z* (M+H^+) calcd for $C_{13}H_{17}$: 173.1, found: 173.1.

$[\alpha]^{23}_D$ = +6.0 (c 0.50, $CHCl_3$).



(*R*)-(2,2-Dimethylnon-3-yn-5-yl)benzene (eq 5). 2,2-Dimethylnon-3-yn-5-yl (2,4,6-trimethoxyphenyl) carbonate (142 mg, 0.375 mmol) and phenylzinc iodide (0.30 M solution in THF; 1.88 mL, 0.56 mmol) were used. The product was obtained as a yellow oil. First run: 54 mg (64%, 84% ee). Second run: 51 mg (60%, 81% ee).

The ee was determined by GC on a Chirasil Dex-CB column (100→130 °C @ 10 °C/min, hold 10 min, then →170 °C @ 9 °C/min, hold 5 min; flow rate 1.0 mL/min) with t_r = 11.4 min (minor), 11.6 min (major).

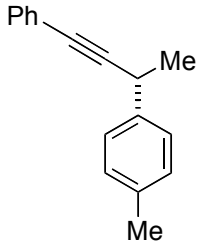
^{1}H NMR (600 MHz, $CDCl_3$) δ 7.36 (d, *J* = 7.2 Hz, 2H), 7.31 (t, *J* = 7.7 Hz, 2H), 7.22 (t, *J* = 7.3 Hz, 1H), 3.59 (dd, *J* = 8.2, 6.1 Hz, 1H), 1.73–1.62 (m, 2H), 1.46–1.28 (m, 4H), 1.26 (s, 9H), 0.90 (t, *J* = 7.2 Hz, 3H).

^{13}C NMR (150 MHz, $CDCl_3$) δ 143.3, 128.2, 127.4, 126.3, 91.9, 80.0, 39.0, 37.7, 31.4, 29.5, 27.5, 22.4, 14.0.

FT-IR (neat) 2929, 2361, 1494, 1452 cm^{-1}.

MS (ESI) *m*/*z* ($M+H^+$) calcd for $C_{17}H_{25}$: 229.2, found: 229.2.

$[\alpha]^{23}_D$ = +8.6 (c 1.0, $CHCl_3$).



(*R*)-1-Methyl-4-(4-phenylbut-3-yn-2-yl)benzene (eq 6). 4-Phenylbut-3-yn-2-yl (2,4,6-trimethoxyphenyl) carbonate (270 mg, 0.75 mmol) and *p*-tolylzinc iodide (0.30 M solution in THF; 3.75 mL, 1.13 mmol) were used. The product was obtained as a colorless oil. First run: 162 mg (98%, 88% ee). Second run: 152 mg (92%, 88% ee).

The ee was determined by HPLC on an OD-H column (hexanes, 0.9 mL/min) with t_r = 13.8 min (minor), 22.2 min (major).

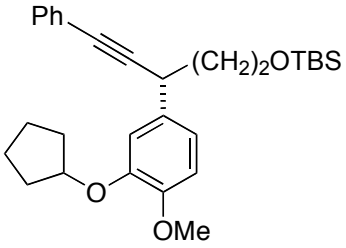
^{1}H NMR (600 MHz, $CDCl_3$) δ 7.58–7.56 (m, 2H), 7.47 (d, *J* = 8.0 Hz, 2H), 7.39 (t, *J* = 5.8 Hz, 3H), 7.28 (d, *J* = 7.9 Hz, 2H), 4.07 (q, *J* = 7.1 Hz, 1H), 2.46 (s, 3H), 1.70 (d, *J* = 7.2 Hz, 3H).

^{13}C NMR (150 MHz, $CDCl_3$) δ 140.6, 136.4, 131.9, 129.5, 128.4, 127.9, 127.1, 124.1, 93.1, 82.5, 32.3, 24.8, 21.3.

FT-IR (neat) 2975, 2928, 2361, 1598, 1513, 1490, 1303, 1070, 816, 756, 691 cm^{-1}.

MS (ESI) *m*/*z* ($M+H^+$) calcd for $C_{17}H_{17}$: 221.1, found: 221.1.

$[\alpha]^{23}_D$ = −2.8 (c 0.55, $CHCl_3$).



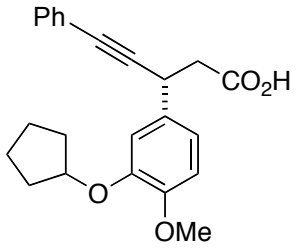
(*R*)-*Tert*-butyl((3-(3-(cyclopentyloxy)-4-methoxyphenyl)-5-phenylpent-4-yn-1-yl)oxy)dimethylsilane (eq 7). 5-((*Tert*-butyldimethylsilyl)oxy)-1-phenylpent-1-yn-3-yl (2,4,6-trimethoxyphenyl) carbonate (325 mg, 0.75 mmol) and 3-cyclopentyloxy-4-methoxyphenylzinc iodide (0.30 M solution in THF; 3.75 mL, 1.13 mmol) were used.[9] The product, a colorless oil that included the corresponding allene (3:1 alkyne:allene), was used directly in the subsequent steps. First run: 273 mg (79%, 92% ee). Second run: 269 mg (78%, 92% ee). Third run (4.0 mmol): 1.34 g (73%, 90% ee).

The ee of the desilylated product was determined by HPLC on an IB column (3% IPA in hexanes, 0.9 mL/min) with t_r = 35.8 min (major), 38.1 min (minor).

^{1}H NMR (600 MHz, $CDCl_3$) δ 7.47 (dd, *J* = 7.4, 2.0 Hz, 2H), 7.35–7.31 (m, 3H), 7.03 (d, *J* = 1.9 Hz, 1H), 6.99 (dd, *J* = 8.2, 1.9 Hz, 1H), 6.87 (d, *J* = 8.2 Hz, 1H), 4.86–4.82 (m, 1H), 4.04 (t, *J* = 7.5 Hz, 1H), 3.92–3.88 (m, 1H), 3.88 (s, 3H), 3.78–3.73 (m, 1H), 2.04 (dd, *J* = 13.0, 6.7 Hz, 2H), 2.01–1.82 (m, 6H), 1.68–1.59 (m, 2H), 0.97 (s, 9H), 0.14 (s, 3H), 0.12 (s, 3H).

^{13}C NMR (100 MHz, $CDCl_3$, mixture with allene) δ 205.8, 149.0, 147.8, 134.5, 131.7, 128.6, 128.4, 127.9, 127.2, 124.0, 121.1, 119.7, 114.8, 112.2, 109.7, 91.9, 91.0, 83.3, 80.6, 80.5, 60.8, 56.3, 41.8, 34.2, 33.0, 33.0, 26.2, 24.3, 24.2, 18.5, −4.9.

MS (ESI) *m*/*z* ($M+H^+$) calcd for $C_{29}H_{41}O_3Si$: 465.3, found: 465.3.



(*R*)-3-(3-(Cyclopentyloxy)-4-methoxyphenyl)-5-phenylpent-4-ynoic acid (eq 7). HCl (2.0 M solution in diethyl ether; 4.0 mL, 8.0 mmol) was added to a solution of (*R*)-*tert*-butyl((3-(3-(cyclopentyloxy)-4-methoxyphenyl)-5-phenylpent-4-yn-1-yl)oxy)dimethylsilane (485 mg of a 3:1 alkyne:allene mixture, corresponding to 364 mg (0.78 mmol) of the alkyne) in dichloromethane (50 mL) at 0 °C. The reaction mixture was allowed to warm to r.t. and stirred for 2.5 h. Next, the reaction was quenched by the addition of saturated aqueous $NaHCO_3$ (20 mL). The layers were separated, and the organic layer was extracted with dichloromethane (3 × 20 mL). The combined organic layers were dried (Na_2SO_4), and the solvent was removed in vacuo.

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(9) Meyers, A. I.; Snyder, L. *J. Org. Chem.* **1993**, *58*, 36–42.

TPAP (30 mg, 0.085 mmol) was added to a solution of the unpurified alcohol and *N*-methylmorpholine-*N*-oxide (1.12 g, 8.0 mmol) in acetonitrile (2 mL) in a water bath.[10] The reaction mixture was stirred for 3 h, and then it was quenched by the addition of methanol (0.5 mL). The volatiles were removed in vacuo, and the residue was purified by flash chromatography (1→4% MeOH with 1% AcOH in dichloromethane), which afforded the title compound as a yellow oil (244 mg, 86%).

^{1}H NMR (600 MHz, $CDCl_3$) δ 11.50–10.81 (m, 1H), 7.44 (s, 2H), 7.29 (s, 3H), 7.04 (s, 1H), 7.01 (s, 1H), 6.85–6.80 (m, 1H), 4.81 (s, 1H), 4.34 (s, 1H), 3.84 (s, 3H), 3.03–2.73 (m, 2H), 2.15–1.68 (m, 6H), 1.68–1.55 (m, 2H).

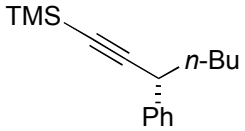
^{13}C NMR (150 MHz, $CDCl_3$) δ 177.5, 149.1, 147.8, 133.1, 131.8, 128.4, 123.5, 119.5, 114.3, 112.1, 90.4, 83.6, 80.5, 56.2, 44.2, 34.5, 33.0, 32.9, 24.3.

FT-IR (neat) 2960, 2361, 2339, 1717, 1514, 1260, 1136, 1029, 911, 758, 733, 692 cm^{-1}.

MS (ESI) *m*/*z* ($M+H^+$) calcd for $C_{23}H_{25}O_4$: 365.1, found: 365.1.

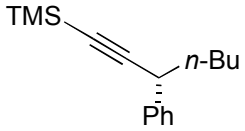
$[\alpha]^{23}_D = -3.5$ (c 0.75, $CHCl_3$).

The ee value (90%) was determined by HPLC analysis of the desilylated primary alcohol (see the preceding experimental procedure).



(*R*)-Trimethyl(3-phenylhept-1-yn-1-yl)silane (eq 8). (3-Bromohept-1-yn-1-yl)trimethylsilane (188 mg, 0.75 mmol) and phenylzinc iodide (0.30 M solution in THF; 3.75 mL, 1.13 mmol) were used. The product was obtained as pale-yellow oil. First run: 132 mg (72%, 90% ee). Second run: 135 mg (74%, 88% ee).

The ee was determined by GC on a Chirasil Dex-CB column (100→130 °C @ 10 °C/min, hold 10 min, then →170 °C @ 9 °C/min, hold 5 min; flow rate 1.0 mL/min) with t_r = 12.9 min (minor), 13.0 min (major).



(*R*)-Trimethyl(3-phenylhept-1-yn-1-yl)silane (eq 9). (3-Chlorohept-1-yn-1-yl)trimethylsilane (152 mg, 0.75 mmol) and phenylzinc iodide (0.30 M solution in THF; 3.75 mL, 1.13 mmol) were used. The product was obtained as pale-yellow oil. First run: 132 mg (72%, 90% ee). Second run: 153 mg (84%, 90% ee).

The ee was determined by GC on a Chirasil Dex-CB column (100→130 °C @ 10 °C/min, hold 10 min, then →170 °C @ 9 °C/min, hold 5 min; flow rate 1.0 mL/min) with t_r = 12.9 min (minor), 13.0 min (major).

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(10) Schmidt, A.-K. C.; Stark, C. B. W. *Org. Lett.* **2011**, *13*, 4164–4167.

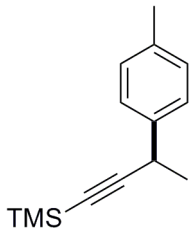

Table 2, entry 1


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PROCNO                     1

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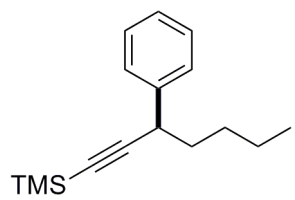
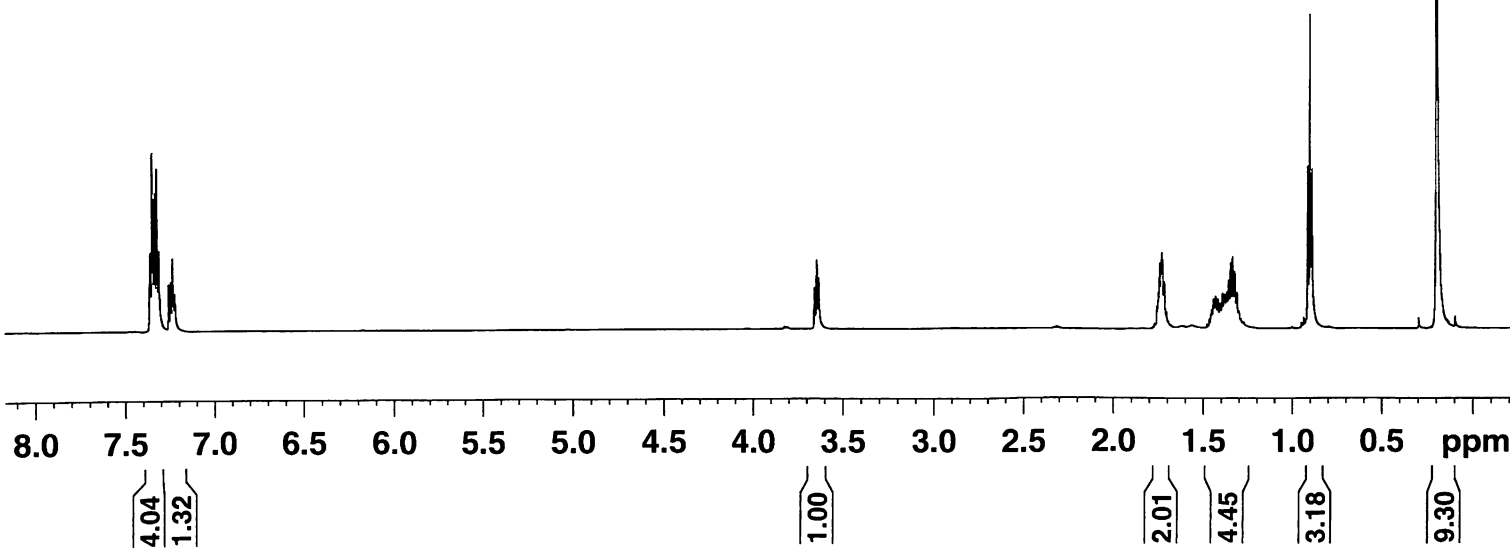


Table 2, entry 2

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PROCNO                    1

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D1              1.00000000 sec
TD0                       1

======== CHANNEL f1 ========
NUC1                    1H
P1                  11.00 usec
PL1                  4.00 dB
SFO1          600.1337060 MHz

F2 - Processing parameters
SI                    65536
SF            600.1300171 MHz
WDW                      EM
SSB                       0
LB                   0.30 Hz
GB                        0
PC                     1.00
```

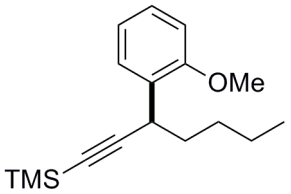


Table 2, entry 3


```
Current Data Parameters
NAME                  ao336b
EXPNO                      2
PROCNO                     1

F2 - Acquisition Parameters
Date_              20110806
Time                  13.19
INSTRUM               spect
PROBHD    5 mm CPTXI 1H-
PULPROG                zg30
TD                    65536
SOLVENT               CDCl3
NS                       16
DS                        2
SWH              12376.237 Hz
FIDRES            0.188846 Hz
AQ                2.6477449 sec
RG                     20.2
DW                  40.400 usec
DE                   6.00 usec
TE                  303.1 K
D1              1.00000000 sec
TD0                       1

======== CHANNEL f1 ========
NUC1                      1H
P1                  11.00 usec
PL1                  4.00 dB
SFO1          600.1337060 MHz

F2 - Processing parameters
SI                        65536
SF              600.1300000 MHz
WDW                         EM
SSB                          0
LB                    0.30 Hz
GB                           0
PC                        1.00
```

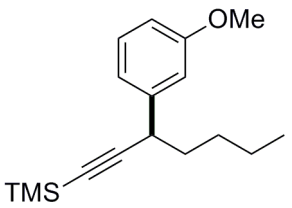


Table 2, entry 4


```
Current Data Parameters
NAME                  ao355b
EXPNO                      1
PROCNO                     1

F2 - Acquisition Parameters
Date_              20110507
Time                  13.58
INSTRUM               spect
PROBHD    5 mm CPTXI 1H-
PULPROG                zg30
TD                    65536
SOLVENT               CDCl3
NS                        9
DS                        2
SWH              12376.237 Hz
FIDRES            0.188846 Hz
AQ                2.6477449 sec
RG                     14.3
DW                   40.400 usec
DE                    6.00 usec
TE                   303.3 K
D1               1.00000000 sec
TD0                       1

======== CHANNEL f1 ========
NUC1                      1H
P1                     11.00 usec
PL1                     4.00 dB
SFO1           600.1337060 MHz

F2 - Processing parameters
SI                    65536
SF             600.1297102 MHz
WDW                      EM
SSB                       0
LB                     0.30 Hz
GB                        0
PC                     1.00
```

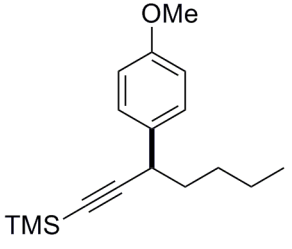


Table 2, entry 5


```
Current Data Parameters
NAME                  ao356a
EXPNO                      1
PROCNO                     1

F2 - Acquisition Parameters
Date_              20110506
Time                   9.06
INSTRUM               spect
PROBHD    5 mm CPTXI 1H-
PULPROG                zg30
TD                    65536
SOLVENT               CDCl3
NS                       10
DS                        2
SWH               12376.237 Hz
FIDRES             0.188846 Hz
AQ                 2.6477449 sec
RG                      20.2
DW                    40.400 usec
DE                     6.00 usec
TE                    302.9 K
D1              1.00000000 sec
TD0                        1

======== CHANNEL f1 ========
NUC1                      1H
P1                     11.00 usec
PL1                     4.00 dB
SFO1           600.1337060 MHz

F2 - Processing parameters
SI                     65536
SF             600.1297102 MHz
WDW                       EM
SSB                        0
LB                      0.30 Hz
GB                         0
PC                      1.00
```

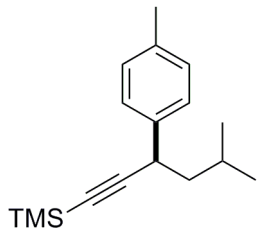


Table 2, entry 6


```
Current Data Parameters
NAME                  ao361b1
EXPNO                       1
PROCNO                      1

F2 - Acquisition Parameters
Date_              20110930
Time                  11.01
INSTRUM               spect
PROBHD    5 mm BBO BB-1H
PULPROG                zg30
TD                    65536
SOLVENT               CDCl3
NS                       16
DS                        2
SWH              12376.237 Hz
FIDRES            0.188846 Hz
AQ                2.6477449 sec
RG                    406.4
DW                  40.400 usec
DE                   6.00 usec
TE                   293.0 K
D1              1.00000000 sec
TD0                       1

======== CHANNEL f1 ========
NUC1                     1H
P1                    11.00 usec
PL1                    4.00 dB
SFO1          600.1337060 MHz

F2 - Processing parameters
SI                    65536
SF            600.1300000 MHz
WDW                      EM
SSB                       0
LB                     0.30 Hz
GB                        0
PC                     1.00
```

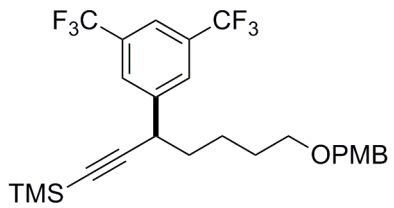


Table 2, entry 7


```
Current Data Parameters
NAME                  ao385a
EXPNO                      1
PROCNO                     1

F2 - Acquisition Parameters
Date_              20110526
Time                  17.08
INSTRUM               spect
PROBHD    5 mm CPTXI 1H-
PULPROG                zg30
TD                    65536
SOLVENT               CDCl3
NS                       16
DS                        2
SWH              12376.237 Hz
FIDRES            0.188846 Hz
AQ                2.6477449 sec
RG                       18
DW                  40.400 usec
DE                   6.00 usec
TE                  293.2 K
D1               1.00000000 sec
TD0                       1

======== CHANNEL f1 ========
NUC1                     1H
P1                  11.00 usec
PL1                  4.00 dB
SFO1          600.1337060 MHz

F2 - Processing parameters
SI                    65536
SF            600.1300008 MHz
WDW                      EM
SSB                       0
LB                   0.30 Hz
GB                        0
PC                     1.00
```

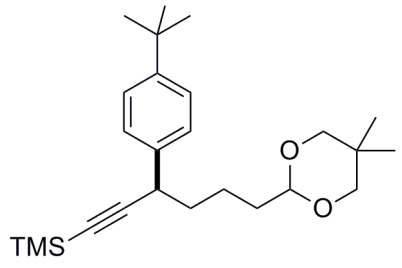


Table 2, entry 8


```
Current Data Parameters
NAME          ao408B.R1
EXPNO                 1
PROCNO                1

F2 - Acquisition Parameters
Date_          20110723
Time              11.34
INSTRUM           spect
PROBHD   5 mm CPTXI 1H-
PULPROG           zg30
TD               65536
SOLVENT          CDCl3
NS                  16
DS                   2
SWH          12376.237 Hz
FIDRES        0.188846 Hz
AQ            2.6477449 sec
RG                20.2
DW              40.400 usec
DE               6.00 usec
TE              303.1 K
D1          1.00000000 sec
TD0                  1

======== CHANNEL f1 ========
NUC1                1H
P1             11.00 usec
PL1             4.00 dB
SFO1       600.1337060 MHz

F2 - Processing parameters
SI                65536
SF         600.1300000 MHz
WDW                  EM
SSB                   0
LB             0.30 Hz
GB                    0
PC                 1.00
```

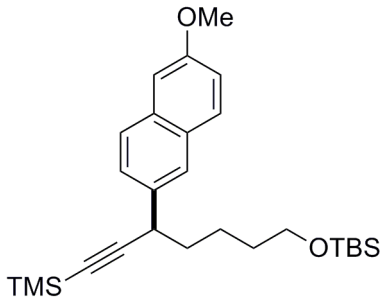


Table 2, entry 9


```
Current Data Parameters
NAME                  ao394a
EXPNO                      1
PROCNO                     1

F2 - Acquisition Parameters
Date_              20110527
Time                  18.23
INSTRUM               spect
PROBHD   5 mm CPTXI 1H-
PULPROG                zg30
TD                    65536
SOLVENT               CDCl3
NS                       16
DS                        2
SWH              12376.237 Hz
FIDRES            0.188846 Hz
AQ                2.6477449 sec
RG                      7.1
DW                   40.400 usec
DE                    6.00 usec
TE                   298.2 K
D1              1.00000000 sec
TD0                       1

======== CHANNEL f1 ========
NUC1                     1H
P1                   11.00 usec
PL1                   4.00 dB
SFO1          600.1337060 MHz

F2 - Processing parameters
SI                    65536
SF            600.1300031 MHz
WDW                      EM
SSB                       0
LB                    0.30 Hz
GB                        0
PC                    1.00
```

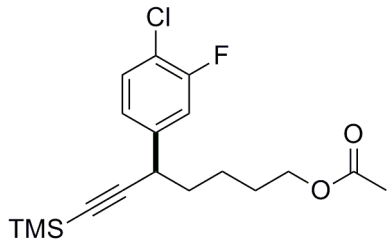


Table 2, entry 10


```
Current Data Parameters
NAME                  ao383.2
EXPNO                       1
PROCNO                      1

F2 - Acquisition Parameters
Date_              20110930
Time                  11.15
INSTRUM               spect
PROBHD   5 mm BBO BB-1H
PULPROG                zg30
TD                    65536
SOLVENT               CDCl3
NS                       16
DS                        2
SWH              12376.237 Hz
FIDRES            0.188846 Hz
AQ                2.6477449 sec
RG                    228.1
DW                   40.400 usec
DE                    6.00 usec
TE                   293.0 K
D1              1.00000000 sec
TD0                       1

======== CHANNEL f1 ========
NUC1                      1H
P1                    11.00 usec
PL1                    4.00 dB
SFO1          600.1337060 MHz

F2 - Processing parameters
SI                    65536
SF            600.1300000 MHz
WDW                      EM
SSB                       0
LB                     0.30 Hz
GB                        0
PC                     1.00
```

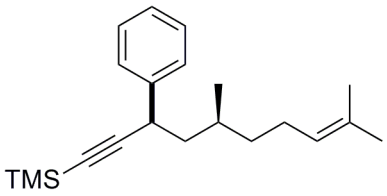


Table 2, entry 11

BRUKER

```
Current Data Parameters
NAME                  ao360a
EXPNO                      5
PROCNO                     1

F2 - Acquisition Parameters
Date_              20120102
Time                  15.18
INSTRUM               spect
PROBHD    5 mm BBO BB-1H
PULPROG                zg30
TD                    65536
SOLVENT               CDCl3
NS                       16
DS                        0
SWH              12376.237 Hz
FIDRES            0.188846 Hz
AQ                2.6477449 sec
RG                    645.1
DW                   40.400 usec
DE                    6.00 usec
TE                   287.7 K
D1              1.00000000 sec
TD0                       1

======== CHANNEL f1 ========
NUC1                     1H
P1                   11.00 usec
PL1                   4.00 dB
SFO1          600.1337060 MHz

F2 - Processing parameters
SI                    65536
SF            600.1300171 MHz
WDW                      EM
SSB                       0
LB                    0.30 Hz
GB                        0
PC                    1.00
```

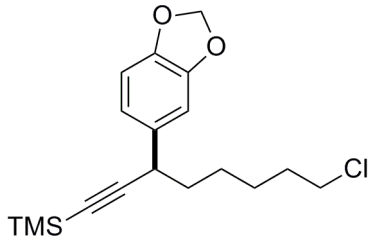


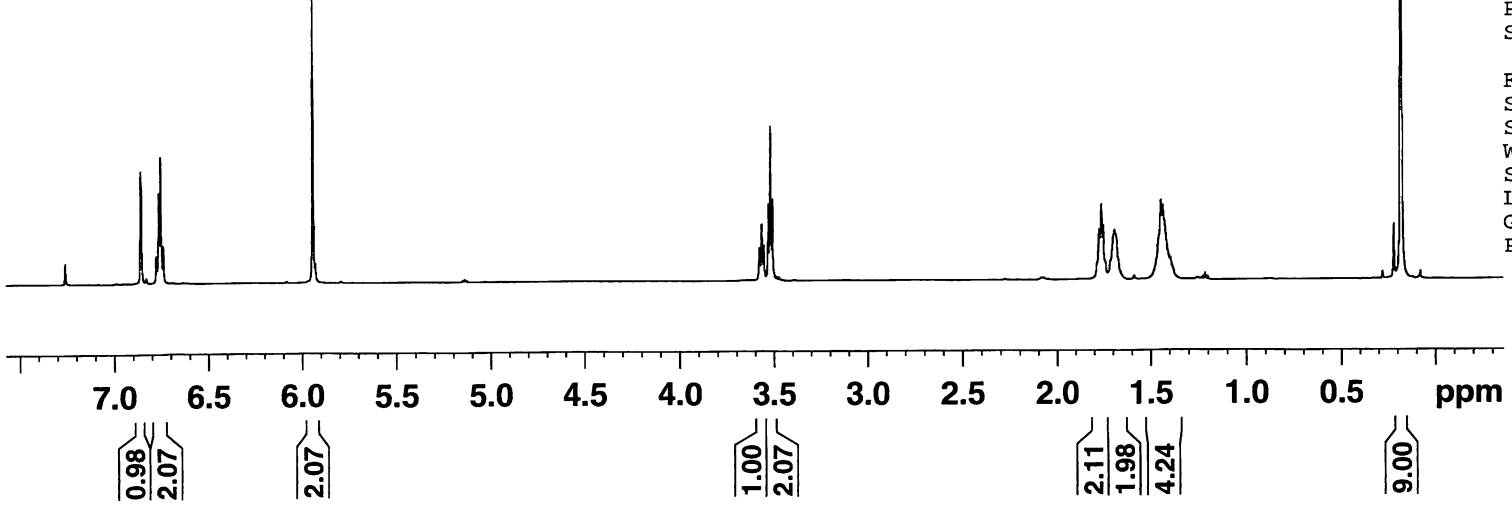
Table 2, entry 12


```
Current Data Parameters
NAME                  ao401a
EXPNO                      5
PROCNO                     1

F2 - Acquisition Parameters
Date_              20120102
Time                  15.21
INSTRUM               spect
PROBHD    5 mm BBO BB-1H
PULPROG                zg30
TD                    65536
SOLVENT               CDCl3
NS                       16
DS                        0
SWH              12376.237 Hz
FIDRES            0.188846 Hz
AQ                2.6477449 sec
RG                    645.1
DW                   40.400 usec
DE                    6.00 usec
TE                   287.8 K
D1             1.00000000 sec
TD0                       1

======== CHANNEL f1 ========
NUC1                     1H
P1                   11.00 usec
PL1                   4.00 dB
SFO1          600.1337060 MHz

F2 - Processing parameters
SI                    65536
SF            600.1300171 MHz
WDW                      EM
SSB                       0
LB                    0.30 Hz
GB                        0
PC                    1.00
```



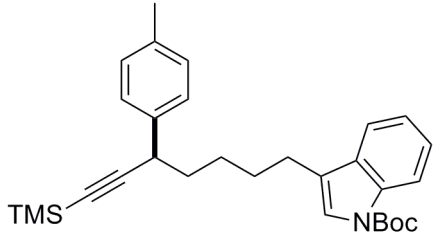


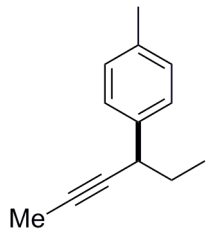
Table 2, entry 13


```
Current Data Parameters
NAME                 ao436A
EXPNO                     3
PROCNO                    1

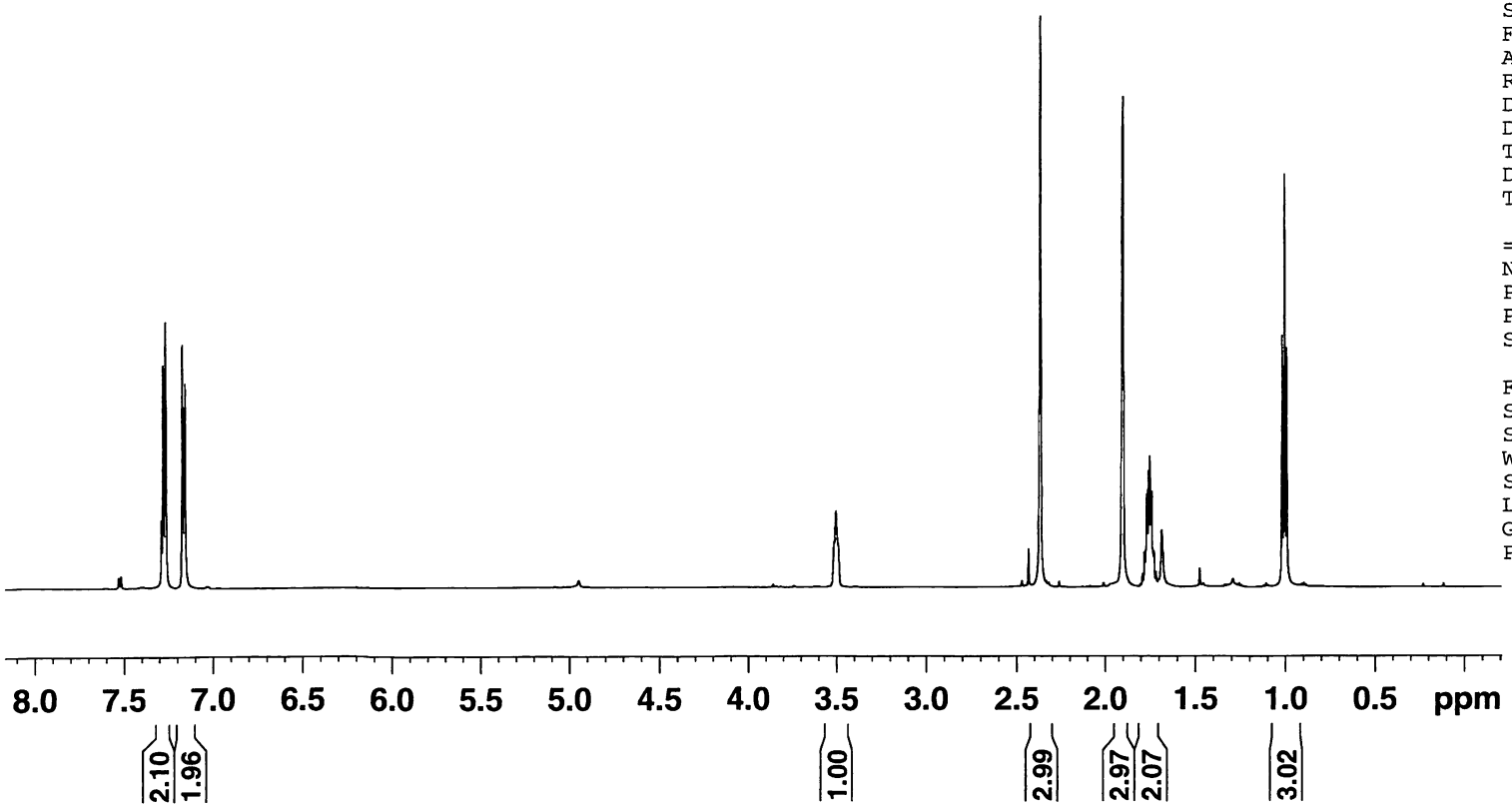
F2 - Acquisition Parameters
Date_             20110630
Time                 16.03
INSTRUM              spect
PROBHD    5 mm CPTXI 1H-
PULPROG               zg30
TD                   65536
SOLVENT              CDCl3
NS                      12
DS                       2
SWH              12376.237 Hz
FIDRES            0.188846 Hz
AQ                2.6477449 sec
RG                    11.3
DW                  40.400 usec
DE                   6.00 usec
TE                  303.2 K
D1               1.00000000 sec
TD0                       1

======== CHANNEL f1 ========
NUC1                     1H
P1                   11.00 usec
PL1                   4.00 dB
SFO1          600.1337060 MHz

F2 - Processing parameters
SI                    65536
SF            600.1300000 MHz
WDW                      EM
SSB                       0
LB                   0.30 Hz
GB                        0
PC                    1.00
```



Equation 4

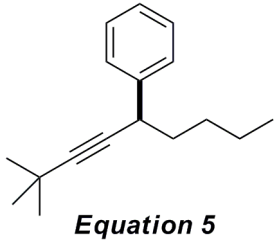



```
Current Data Parameters
NAME                 ao334b
EXPNO                     4
PROCNO                    1

F2 - Acquisition Parameters
Date_             20110523
Time                 17.44
INSTRUM              spect
PROBHD    5 mm CPTXI 1H-
PULPROG              zg30
TD                  65536
SOLVENT             CDCl3
NS                     16
DS                      2
SWH              12376.237 Hz
FIDRES               0.188846 Hz
AQ                2.6477449 sec
RG                     16
DW                  40.400 usec
DE                   6.00 usec
TE                  283.0 K
D1              1.00000000 sec
TD0                     1

======== CHANNEL f1 ========
NUC1                   1H
P1                  11.00 usec
PL1                  4.00 dB
SFO1          600.1337060 MHz

F2 - Processing parameters
SI                  65536
SF            600.1300000 MHz
WDW                    EM
SSB                     0
LB                   0.30 Hz
GB                      0
PC                   1.00
```



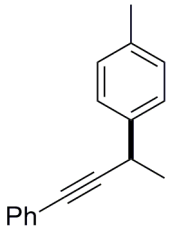
Equation 5


```
Current Data Parameters
NAME                  ao512B
EXPNO                      1
PROCNO                     1

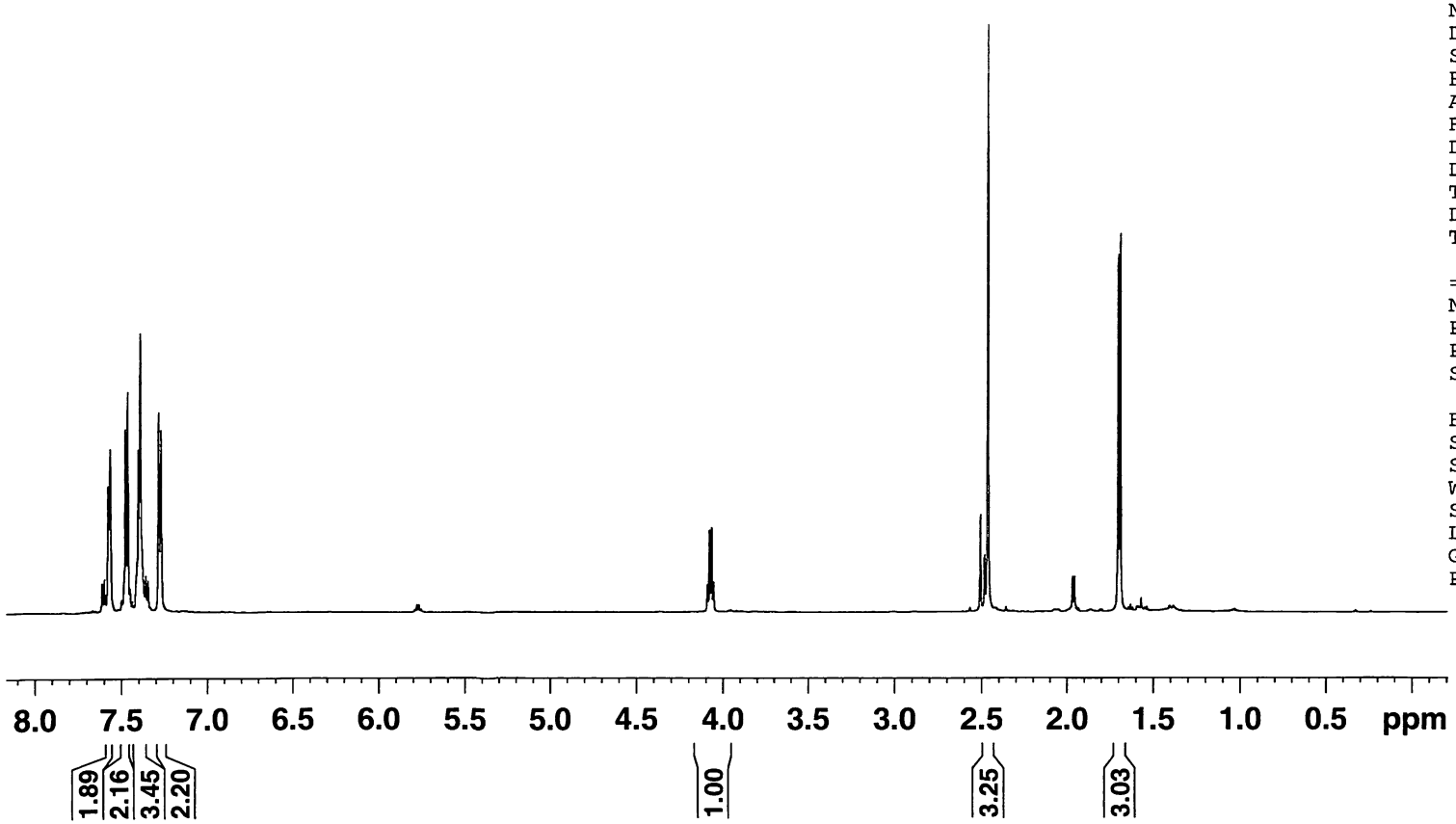
F2 - Acquisition Parameters
Date_              20111128
Time                  17.50
INSTRUM               spect
PROBHD    5 mm BBO BB-1H
PULPROG                zg30
TD                    65536
SOLVENT               CDCl3
NS                       10
DS                        2
SWH              12376.237 Hz
FIDRES            0.188846 Hz
AQ                2.6477449 sec
RG                    406.4
DW                  40.400 usec
DE                   6.00 usec
TE                   293.0 K
D1              1.00000000 sec
TD0                        1

======== CHANNEL f1 ========
NUC1                      1H
P1                    11.00 usec
PL1                    4.00 dB
SFO1          600.1337060 MHz

F2 - Processing parameters
SI                        65536
SF            600.1300171 MHz
WDW                          EM
SSB                           0
LB                     0.30 Hz
GB                            0
PC                         1.00
```



Equation 6

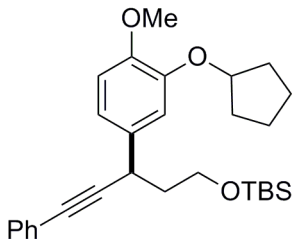



```
Current Data Parameters
NAME                  ao320.1
EXPNO                       1
PROCNO                      1

F2 - Acquisition Parameters
Date_                20110314
Time                    14.36
INSTRUM                 spect
PROBHD   5 mm CPTXI 1H-
PULPROG                 zg30
TD                     65536
SOLVENT                CDCl3
NS                        12
DS                         2
SWH                12376.237 Hz
FIDRES              0.188846 Hz
AQ                  2.6477449 sec
RG                        7.1
DW                     40.400 usec
DE                      6.00 usec
TE                     300.0 K
D1                 1.00000000 sec
TD0                        1

======== CHANNEL f1 ========
NUC1                      1H
P1                     11.00 usec
PL1                     4.00 dB
SFO1            600.1337060 MHz

F2 - Processing parameters
SI                     65536
SF              600.1300000 MHz
WDW                       EM
SSB                        0
LB                      0.30 Hz
GB                         0
PC                      1.00
```



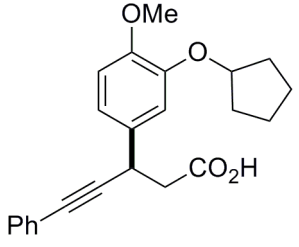
Equation 7


```
Current Data Parameters
NAME                  ao439a2
EXPNO                       1
PROCNO                      1

F2 - Acquisition Parameters
Date_              20110930
Time                  11.09
INSTRUM               spect
PROBHD    5 mm BBO BB-1H
PULPROG               zg30
TD                    65536
SOLVENT               CDCl3
NS                       16
DS                        2
SWH              12376.237 Hz
FIDRES            0.188846 Hz
AQ                2.6477449 sec
RG                    101.6
DW                   40.400 usec
DE                    6.00 usec
TE                   293.0 K
D1             1.00000000 sec
TD0                       1

======== CHANNEL f1 ========
NUC1                     1H
P1                   11.00 usec
PL1                   4.00 dB
SFO1          600.1337060 MHz

F2 - Processing parameters
SI                    65536
SF            600.1300000 MHz
WDW                      EM
SSB                       0
LB                    0.30 Hz
GB                        0
PC                    1.00
```



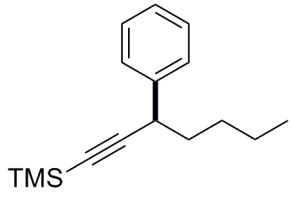
Equation 7


```
Current Data Parameters
NAME         ao462ptlcF1
EXPNO                  1
PROCNO                 1

F2 - Acquisition Parameters
Date_           20110824
Time               15.52
INSTRUM            spect
PROBHD   5 mm CPTXI 1H-
PULPROG            zg30
TD                65536
SOLVENT           CDCl3
NS                   16
DS                    2
SWH           12376.237 Hz
FIDRES         0.188846 Hz
AQ             2.6477449 sec
RG                35.9
DW               40.400 usec
DE                6.00 usec
TE               293.2 K
D1            1.00000000 sec
TD0                   1

======== CHANNEL f1 ========
NUC1                  1H
P1                11.00 usec
PL1                4.00 dB
SFO1         600.1337060 MHz

F2 - Processing parameters
SI                65536
SF           600.1300177 MHz
WDW                  EM
SSB                   0
LB                0.30 Hz
GB                    0
PC                 1.00
```



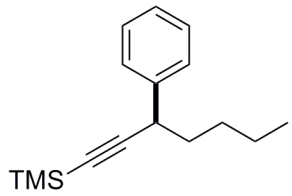
Equation 8


```
Current Data Parameters
NAME                 ao531A
EXPNO                     1
PROCNO                    1

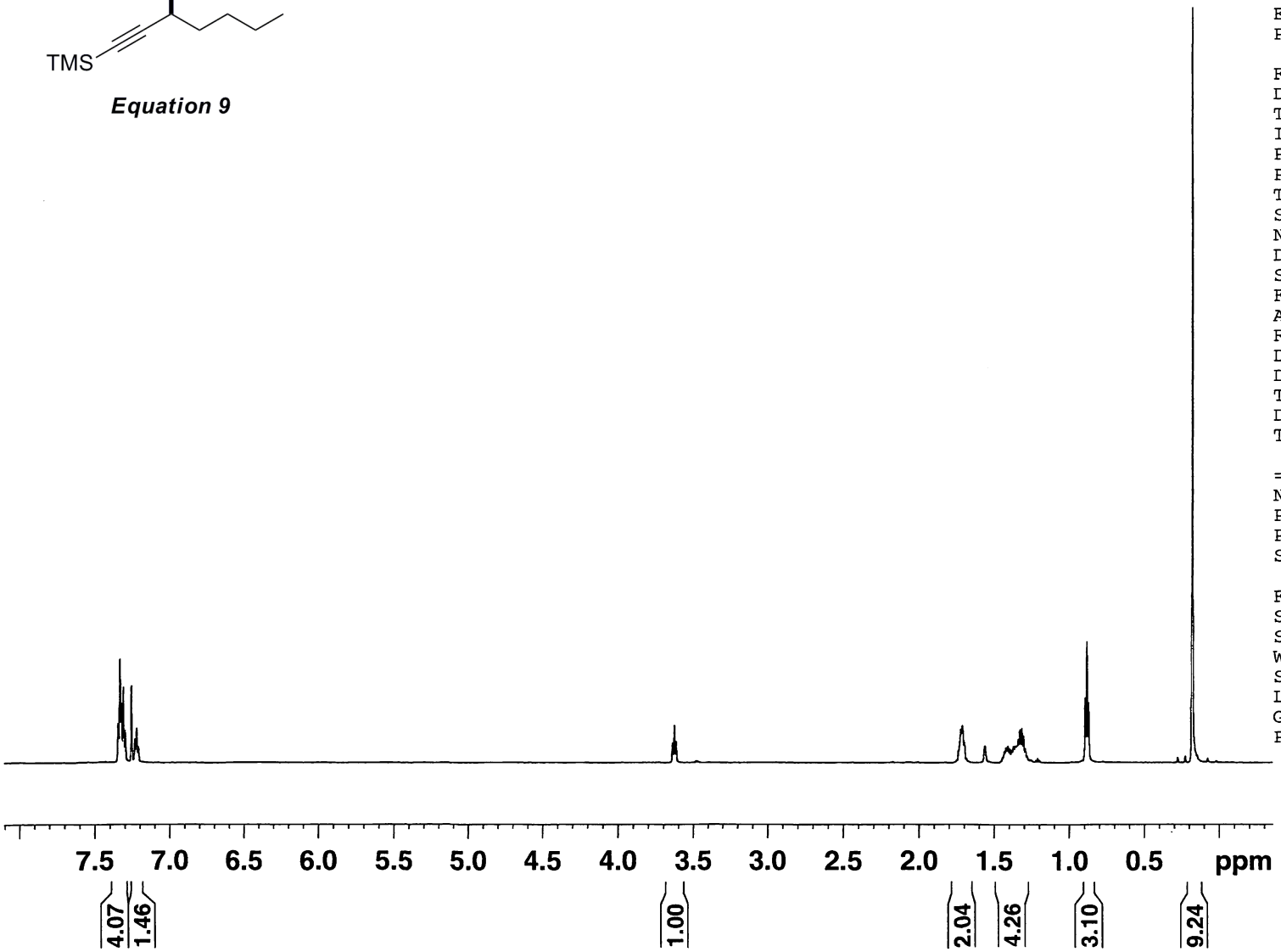
F2 - Acquisition Parameters
Date_              20111211
Time                 17.41
INSTRUM              spect
PROBHD    5 mm BBO BB-1H
PULPROG               zg30
TD                   65536
SOLVENT              CDCl3
NS                       8
DS                       0
SWH              12376.237 Hz
FIDRES            0.188846 Hz
AQ                2.6477449 sec
RG                   645.1
DW                  40.400 usec
DE                   6.00 usec
TE                  286.9 K
D1              1.00000000 sec
TD0                      1

======== CHANNEL f1 ========
NUC1                    1H
P1                  11.00 usec
PL1                  4.00 dB
SFO1          600.1337060 MHz

F2 - Processing parameters
SI                   65536
SF            600.1300171 MHz
WDW                     EM
SSB                      0
LB                  0.30 Hz
GB                       0
PC                    1.00
```



Equation 9




```
Current Data Parameters
NAME                  ao532A
EXPNO                      1
PROCNO                     1

F2 - Acquisition Parameters
Date_              20111211
Time                  17.45
INSTRUM               spect
PROBHD   5 mm BBO BB-1H
PULPROG                zg30
TD                    65536
SOLVENT               CDCl3
NS                        8
DS                        0
SWH              12376.237 Hz
FIDRES            0.188846 Hz
AQ                2.6477449 sec
RG                    645.1
DW                  40.400 usec
DE                   6.00 usec
TE                   287.0 K
D1              1.00000000 sec
TD0                       1

======== CHANNEL f1 ========
NUC1                     1H
P1                   11.00 usec
PL1                   4.00 dB
SFO1          600.1337060 MHz

F2 - Processing parameters
SI                    65536
SF            600.1300171 MHz
WDW                      EM
SSB                       0
LB                   0.30 Hz
GB                        0
PC                    1.00
```

Data File C:\HPCHEM\3\DATA\AJO\AOTR2D.D

```
==========================================================================
Injection Date  : 3/13/2011 3:15:52 AM          Seq. Line :   8
Sample Name     :                                Location : Vial 5
Acq. Operator   : AJO                               Inj :   1
Acq. Instrument : Instrument 3                  Inj Volume : 1 µl
Different Inj Volume from Sequence !     Actual Inj Volume : 5 µl
Acq. Method     : C:\HPCHEM\3\METHODS\AJO75180.M
Last changed    : 3/12/2011 6:09:42 PM by AJO
Analysis Method : C:\HPCHEM\3\METHODS\RL80180.M
Last changed    : 10/10/2011 9:43:53 AM by HD
                  (modified after loading)
```

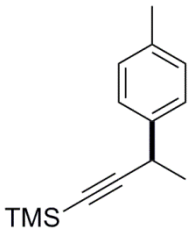
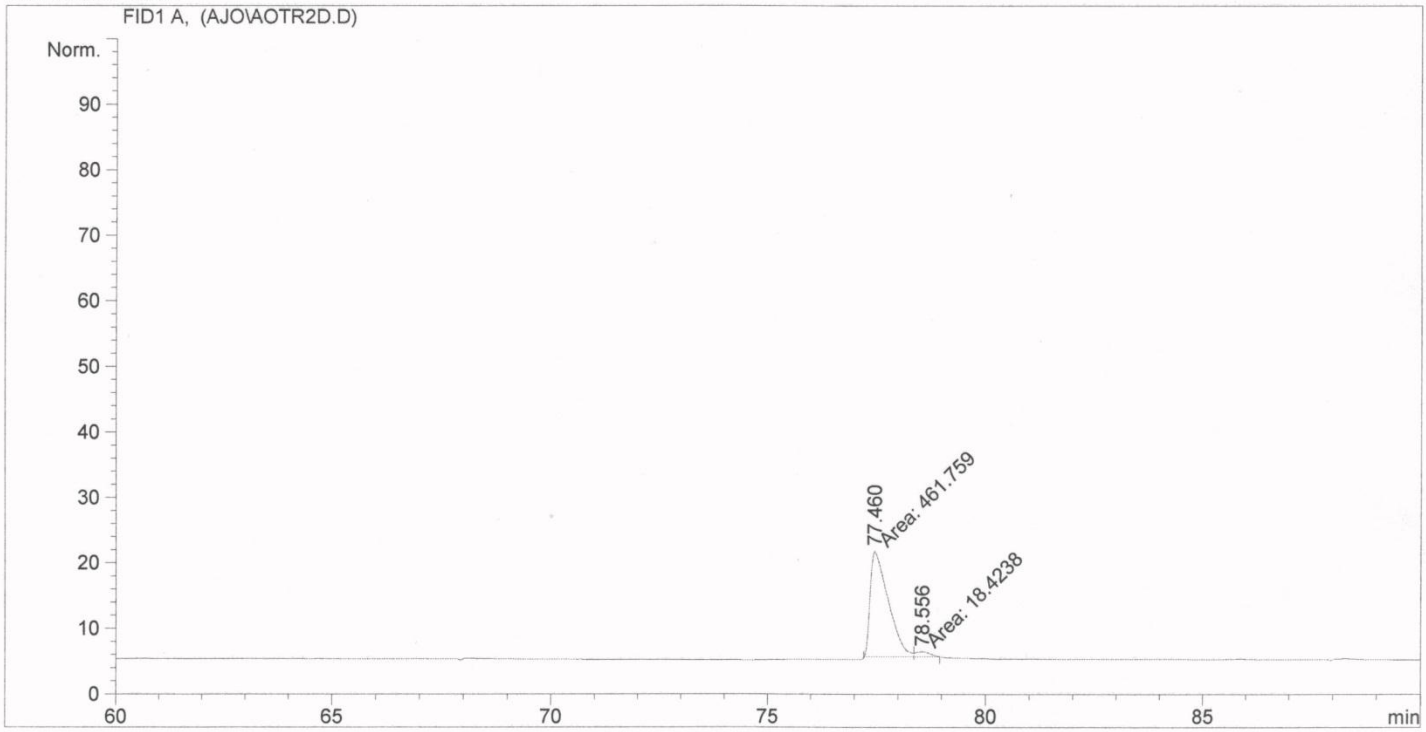


Table 2, entry 1 with (3S,8R)

Initial test




```
==========================================================================
                        Area Percent Report
==========================================================================

Sorted By             :      Signal
Multiplier            :      1.0000
Dilution              :      1.0000
Use Multiplier & Dilution Factor with ISTDs


Signal 1: FID1 A,

Peak RetTime Type  Width     Area      Height     Area
  #   [min]        [min]   [pA*s]      [pA]       %
----|-------|----|-------|----------|----------|--------|
   1  77.460 MF    0.4775  461.75916   16.11809 96.16317
   2  78.556 FM    0.3845   18.42380 7.98504e-1  3.83683

Totals :                   480.18296   16.91659

 Results obtained with enhanced integrator!
==========================================================================
                        *** End of Report ***
```

Data File C:\HPCHEM\3\DATA\HD\AO478B.D

```
==========================================================================
Injection Date  : 10/15/2011 2:57:39 PM          Seq. Line :  18
Sample Name     :                                 Location : Vial 4
Acq. Operator   : HD                                  Inj :   1
Acq. Instrument : Instrument 3                   Inj Volume : 1 µl
Different Inj Volume from Sequence !     Actual Inj Volume : 5 µl
Acq. Method     : C:\HPCHEM\3\METHODS\AJO75180.M
Last changed    : 3/12/2011 6:09:42 PM by AJO
Analysis Method : C:\HPCHEM\3\METHODS\SN100150.M
Last changed    : 1/25/2012 10:45:54 AM by SN
                  (modified after loading)
Initial test
==========================================================================
```

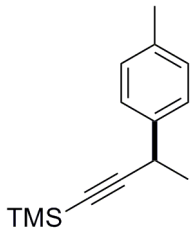
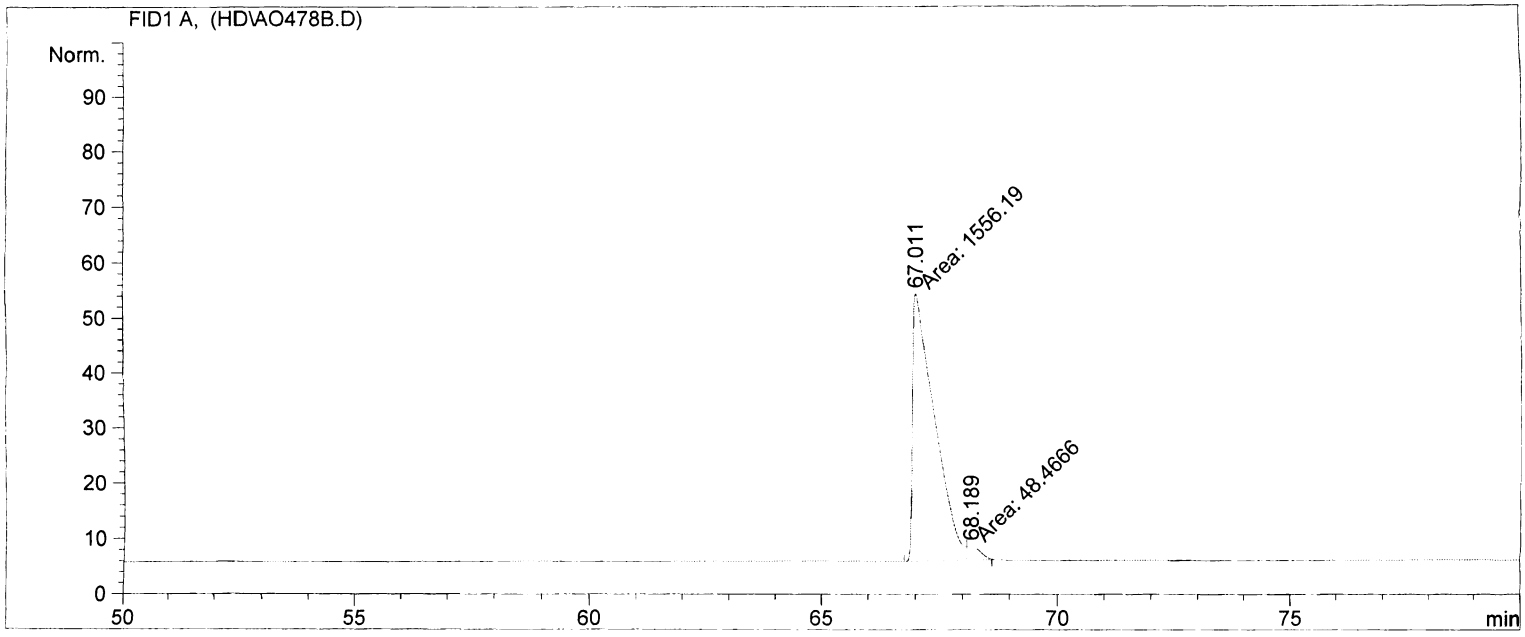


Table 2, entry 1 with (3S,8R)




```
==========================================================================
                        Area Percent Report
==========================================================================

Sorted By             :      Signal
Multiplier            :      1.0000
Dilution              :      1.0000
Use Multiplier & Dilution Factor with ISTDs


Signal 1: FID1 A,

Peak RetTime Type  Width     Area      Height     Area
  #   [min]        [min]   [pA*s]      [pA]        %
----|-------|----|-------|----------|----------|--------|
   1  67.011 MF    0.5358 1556.18994   48.40761 96.97963
   2  68.189 FM    0.3314   48.46662    2.43725  3.02037

Totals :                  1604.65656   50.84486

 Results obtained with enhanced integrator!
==========================================================================
                        *** End of Report ***
```

Data File C:\HPCHEM\3\DATA\AJO\AO299.D

Injection Date : 2/23/2011 1:19:55 PM
Sample Name :
Acq. Operator : AJO
Acq. Instrument : Instrument 3
Different Inj Volume from Sequence ! Actual Inj Volume : 5 µl
Acq. Method : C:\HPCHEM\3\METHODS\AJO100.M
Last changed : 10/13/2010 9:09:31 AM by AJO
Analysis Method : C:\HPCHEM\3\METHODS\AJO65VS2.M
Last changed : 2/23/2011 1:41:08 PM by AJO
(modified after loading)

Seq. Line : 1
Location : Vial 8
Inj : 1
Inj Volume : 1 µl

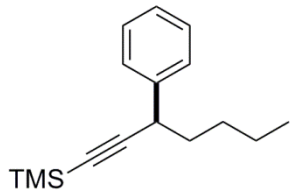
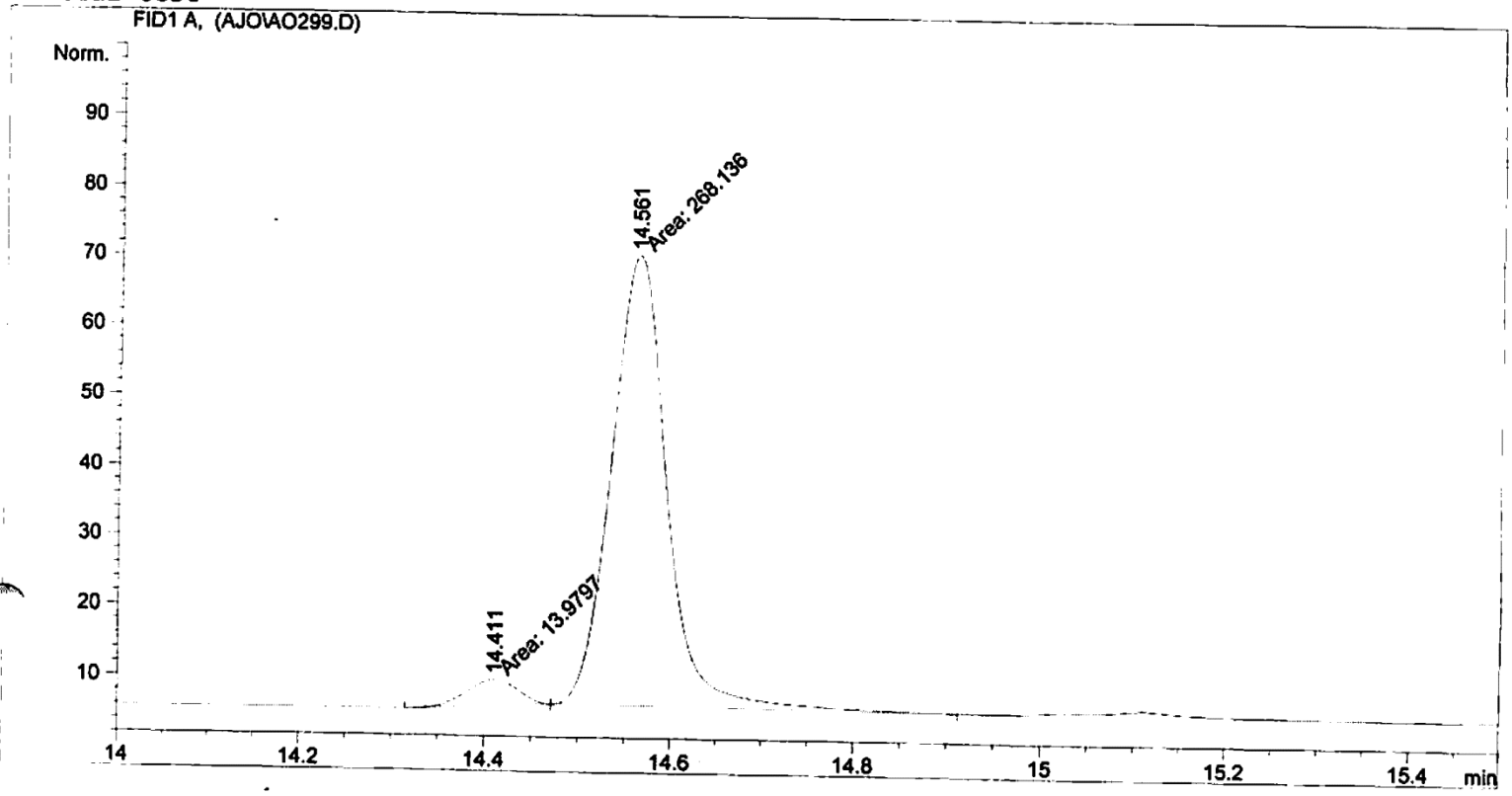


Table 2, entry 2 with (3S,8R)

Initial test



Area Percent Report

Sorted By : Signal
Multiplier : 1.0000
Dilution : 1.0000
Use Multiplier & Dilution Factor with ISTDs

Signal 1: FID1 A,

Peak #	RetTime [min]	Type	Width [min]	Area [pA*s]	Height [pA]	Area %
1	14.411	MM	0.0634	13.97968	3.67282	4.95529
2	14.561	MM	0.0696	268.13626	64.24078	95.04471
Totals :				282.11594	67.91359	

Results obtained with enhanced integrator!

*** End of Report ***

Data File C:\HPCHEM\3\DATA\AJO\AO477.D

```
==========================================================================
Injection Date  : 10/4/2011 5:56:56 PM          Seq. Line :   1
Sample Name     :                               Location : Vial 3
Acq. Operator   : AJO                              Inj :   1
Acq. Instrument : Instrument 3                 Inj Volume : 1 µl
Different Inj Volume from Sequence !     Actual Inj Volume : 5 µl
Acq. Method     : C:\HPCHEM\3\METHODS\AJO100.M
Last changed    : 10/13/2010 9:09:31 AM by AJO
Analysis Method : C:\HPCHEM\3\METHODS\RL100180.M
Last changed    : 10/17/2011 10:09:23 AM by HD
                  (modified after loading)
```

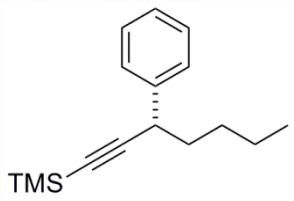
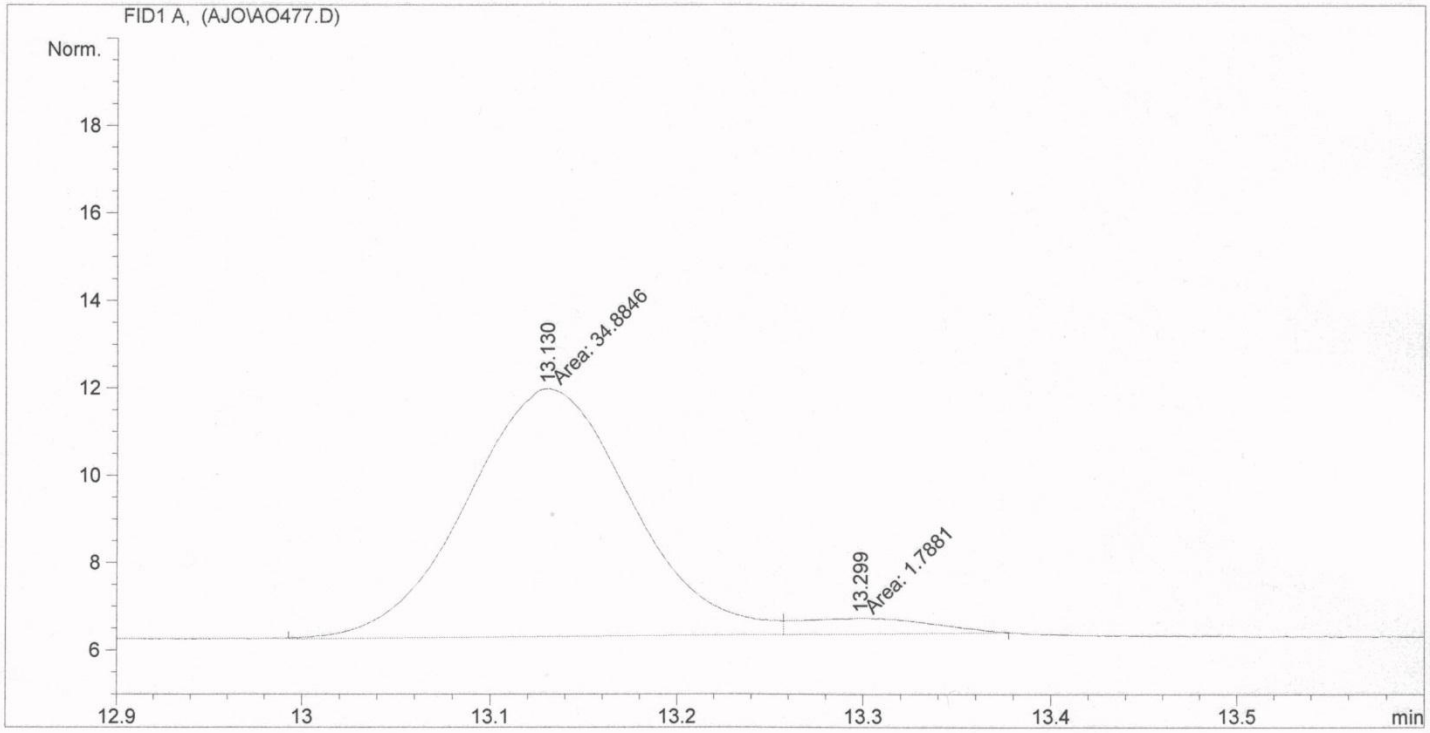


Table 2, entry 2 with (3R,8S)

Initial test




```
==========================================================================
                        Area Percent Report
==========================================================================

Sorted By             :      Signal
Multiplier            :      1.0000
Dilution              :      1.0000
Use Multiplier & Dilution Factor with ISTDs


Signal 1: FID1 A,

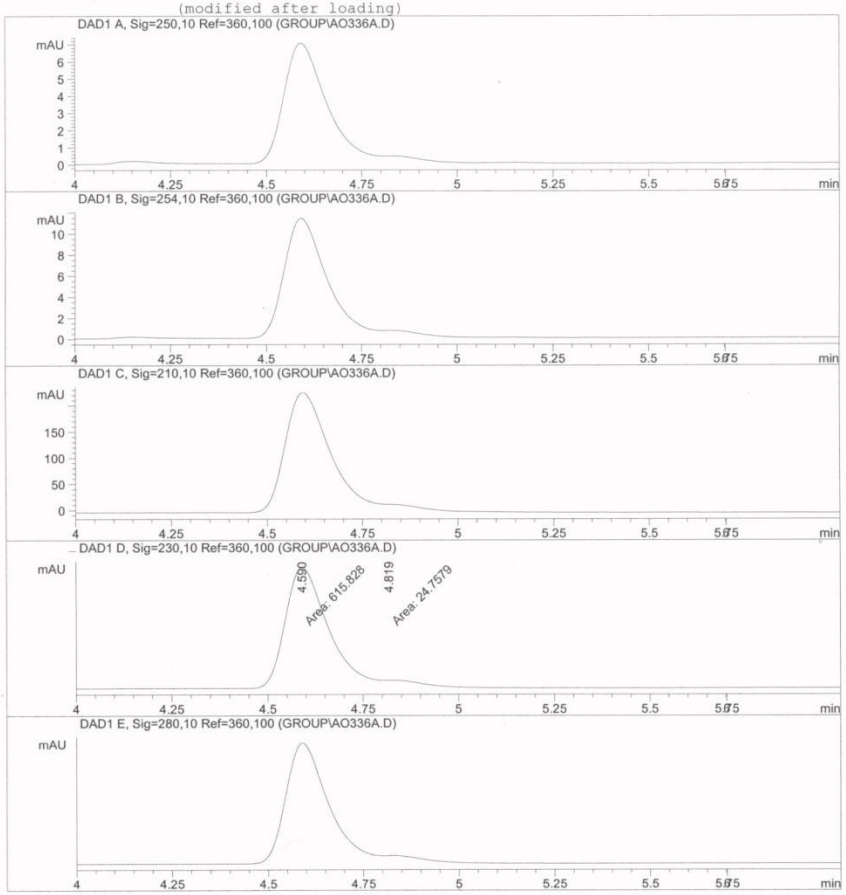
Peak RetTime Type  Width     Area      Height     Area
  #   [min]        [min]   [pA*s]      [pA]       %
----|-------|----|-------|----------|----------|--------|
   1  13.130 MF    0.1025   34.88464    5.67405 95.12416
   2  13.299 FM    0.0819    1.78810 3.63884e-1  4.87584

Totals :                    36.67274    6.03793

 Results obtained with enhanced integrator!
==========================================================================
                          *** End of Report ***
```

Data File C:\HPCHEM\1\DATA\GROUP\AO336A.D Sample Name: AO336A

```
Injection Date  : 4/28/2011 5:47:40 PM          Seq. Line :   5
Sample Name     : AO336A                        Location : Vial 61
Acq. Operator   : NB                               Inj :   1
Acq. Instrument : Instrument 1                  Inj Volume : 15 µl
Different Inj Volume from Sequence !     Actual Inj Volume : 3 µl
Acq. Method     : C:\HPCHEM\1\METHODS\OD-00-30.M
Last changed    : 4/7/2011 2:46:23 AM by CC
Analysis Method : C:\HPCHEM\1\METHODS\YL-AD04.M
Last changed    : 10/11/2011 3:02:56 PM by NB
                  (modified after loading)
```



Data File C:\HPCHEM\1\DATA\GROUP\AO336A.D Sample Name: AO336A

Area Percent Report

```
Sorted By             :      Signal
Multiplier            :      1.0000
Dilution              :      1.0000
Use Multiplier & Dilution Factor with ISTDs


Signal 1: DAD1 A, Sig=250,10 Ref=360,100


Signal 2: DAD1 B, Sig=254,10 Ref=360,100


Signal 3: DAD1 C, Sig=210,10 Ref=360,100


Signal 4: DAD1 D, Sig=230,10 Ref=360,100

Peak RetTime Type  Width     Area      Height     Area
  #   [min]        [min]   [mAU*s]     [mAU]       %
----|-------|----|-------|----------|----------|--------|
   1   4.590 MF    0.1323  615.82849   77.56291  96.1351
   2   4.819 FM    0.0881   24.75788    4.68484   3.8649

Totals :                   640.58638   82.24775

 Results obtained with enhanced integrator!

Signal 5: DAD1 E, Sig=280,10 Ref=360,100
```

*** End of Report ***

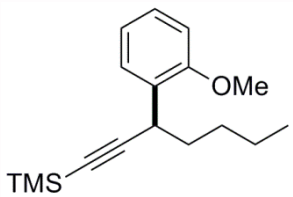
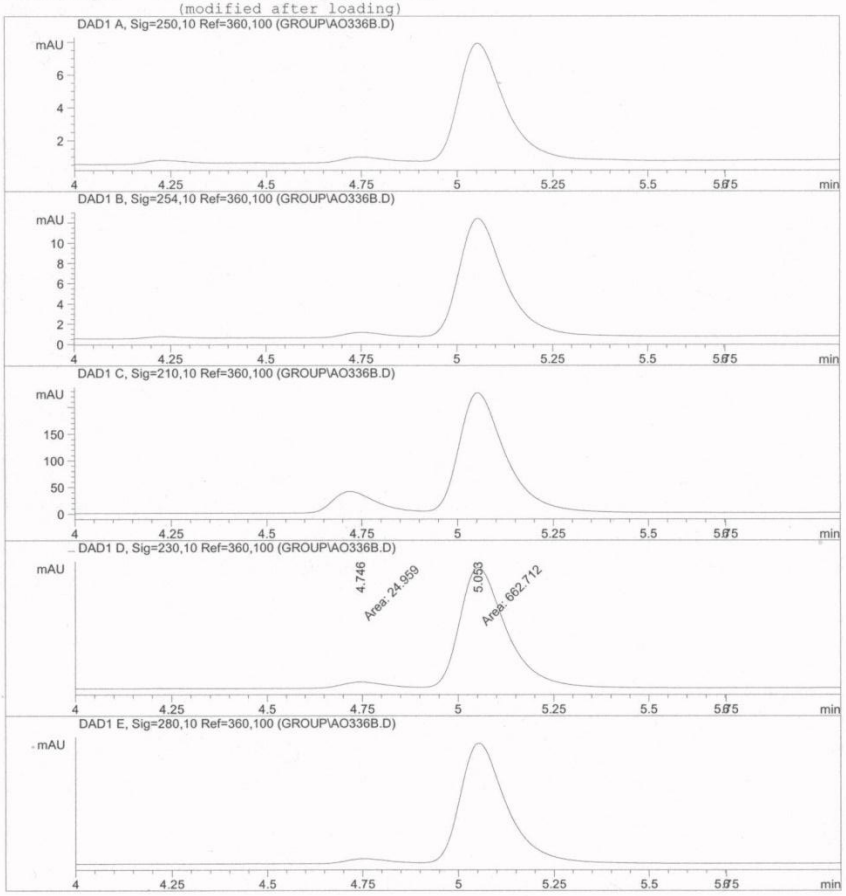


Table 2, entry 3 with (3S,8R)

Data File C:\HPCHEM\1\DATA\GROUP\AO336B.D Sample Name: AO336E

```
Injection Date  : 4/28/2011 6:18:59 PM          Seq. Line :   6
Sample Name     : AO336B                        Location : Vial 62
Acq. Operator   : NB                               Inj :   1
Acq. Instrument : Instrument 1                 Inj Volume : 15 µl
Different Inj Volume from Sequence !     Actual Inj Volume : 3 µl
Acq. Method     : C:\HPCHEM\1\METHODS\OD-00-30.M
Last changed    : 4/7/2011 2:46:23 AM by CC
Analysis Method : C:\HPCHEM\1\METHODS\YL-AD04.M
Last changed    : 10/11/2011 3:01:29 PM by NB
                  (modified after loading)
```



Data File C:\HPCHEM\1\DATA\GROUP\AO336B.D Sample Name: AO336E

Area Percent Report

```
Sorted By             :      Signal
Multiplier            :      1.0000
Dilution              :      1.0000
Use Multiplier & Dilution Factor with ISTDs


Signal 1: DAD1 A, Sig=250,10 Ref=360,100


Signal 2: DAD1 B, Sig=254,10 Ref=360,100


Signal 3: DAD1 C, Sig=210,10 Ref=360,100


Signal 4: DAD1 D, Sig=230,10 Ref=360,100

Peak RetTime Type  Width     Area      Height     Area
  #   [min]        [min]   [mAU*s]     [mAU]       %
----|-------|----|-------|----------|----------|--------|
   1   4.746 MF    0.1184   24.95901   3.51419   3.6295
   2   5.053 FM    0.1395  662.71222  79.20329  96.3705

Totals :                   687.67123  82.71748

 Results obtained with enhanced integrator!

Signal 5: DAD1 E, Sig=280,10 Ref=360,100
```

*** End of Report ***

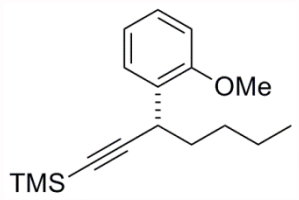
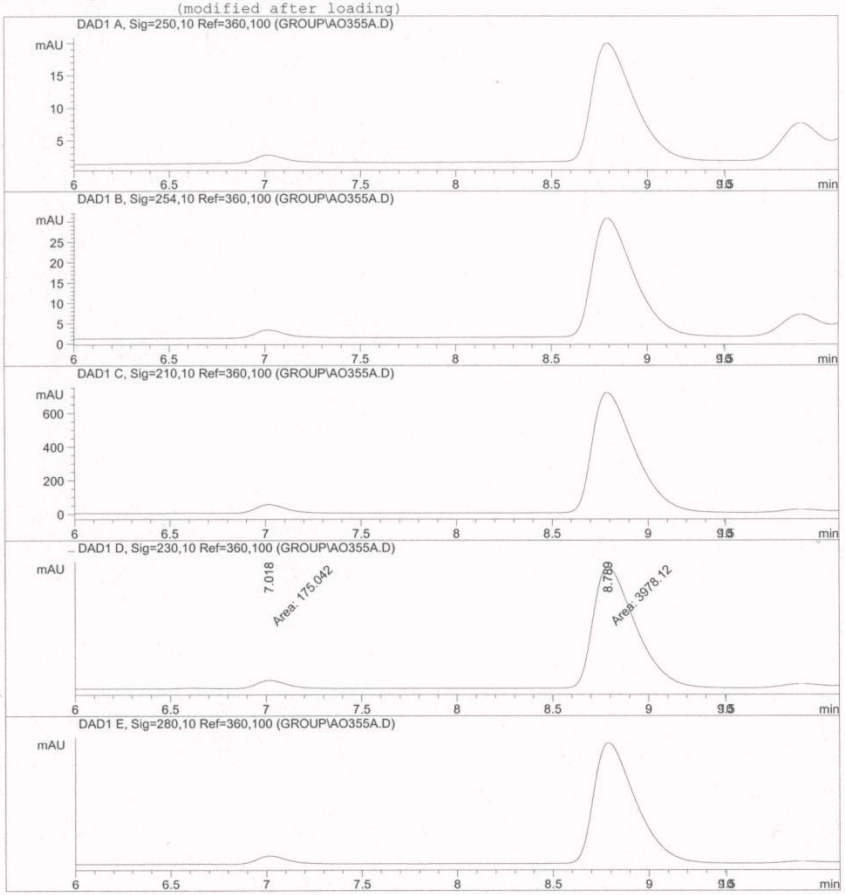


Table 2, entry 3 with (3R,8S)

Data File C:\HPCHEM\1\DATA\GROUP\AO355A.D Sample Name: AO355A

Injection Date : 4/28/2011 6:34:46 PM Seq. Line : 1
Sample Name : AO355A Location : Vial 63
Acq. Operator : NB Inj : 1
Acq. Instrument : Instrument 1 Inj Volume : 15 µl
Different Inj Volume from Sequence ! Actual Inj Volume : 3 µl
Acq. Method : C:\HPCHEM\1\METHODS\OD-00-30.M
Last changed : 4/7/2011 2:46:23 AM by CC
Analysis Method : C:\HPCHEM\1\METHODS\YL-AD04.M
Last changed : 10/11/2011 3:04:57 PM by NB
(modified after loading)



Data File C:\HPCHEM\1\DATA\GROUP\AO355A.D Sample Name: AO355A

Area Percent Report

Sorted By : Signal
Multiplier : 1.0000
Dilution : 1.0000
Use Multiplier & Dilution Factor with ISTDs

Signal 1: DAD1 A, Sig=250,10 Ref=360,100

Signal 2: DAD1 B, Sig=254,10 Ref=360,100

Signal 3: DAD1 C, Sig=210,10 Ref=360,100

Signal 4: DAD1 D, Sig=230,10 Ref=360,100

Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	7.018	MM	0.1722	175.04150	16.94658	4.2147
2	8.789	MM	0.2557	3978.12183	259.32043	95.7853

Totals : 4153.16333 276.26702

Results obtained with enhanced integrator!

Signal 5: DAD1 E, Sig=280,10 Ref=360,100

*** End of Report ***

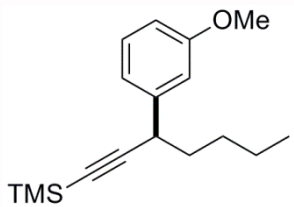
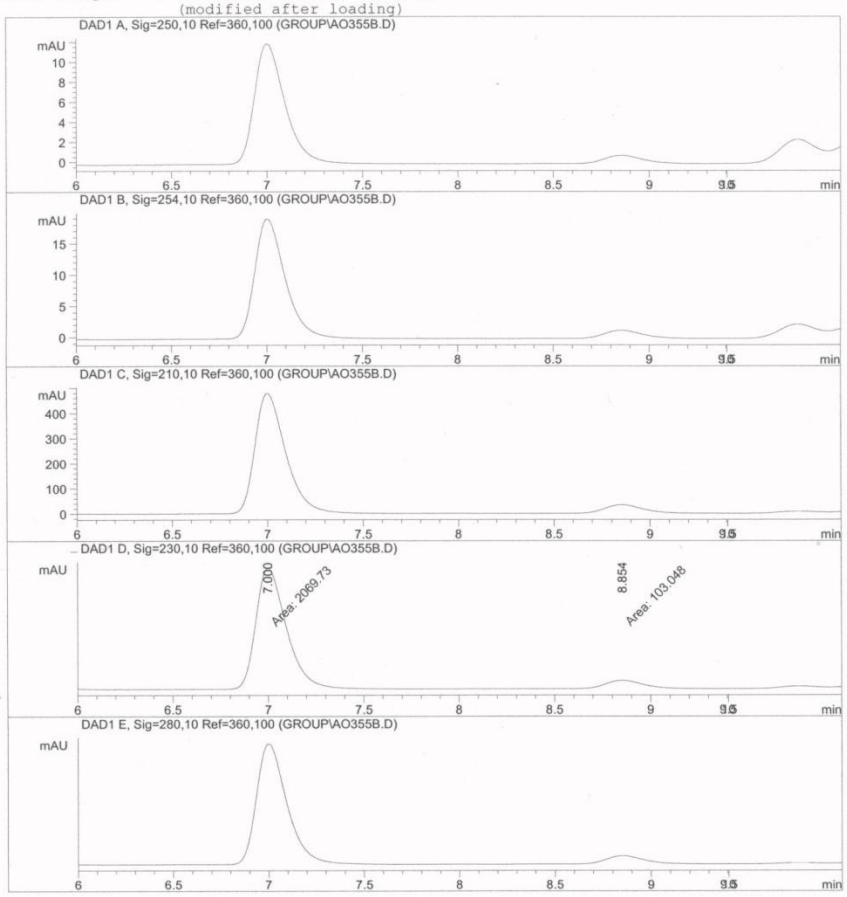


Table 2, entry 4 with (3S,8R)

Data File C:\HPCHEM\1\DATA\GROUP\AO355B.D Sample Name: AO355E

```
Injection Date  : 4/28/2011 7:06:02 PM          Seq. Line :   2
Sample Name     : AO355B                       Location : Vial 64
Acq. Operator   : NB                              Inj :   1
Acq. Instrument : Instrument 1                 Inj Volume : 15 µl
Different Inj Volume from Sequence !     Actual Inj Volume : 3 µl
Acq. Method     : C:\HPCHEM\1\METHODS\OD-00-30.M
Last changed    : 4/7/2011 2:46:23 AM by CC
Analysis Method : C:\HPCHEM\1\METHODS\YL-AD04.M
Last changed    : 10/11/2011 3:04:57 PM by NB
                  (modified after loading)
```



Data File C:\HPCHEM\1\DATA\GROUP\AO355B.D Sample Name: AO355E

Area Percent Report

```
Sorted By             :      Signal
Multiplier            :      1.0000
Dilution              :      1.0000
Use Multiplier & Dilution Factor with ISTDs


Signal 1: DAD1 A, Sig=250,10 Ref=360,100


Signal 2: DAD1 B, Sig=254,10 Ref=360,100


Signal 3: DAD1 C, Sig=210,10 Ref=360,100


Signal 4: DAD1 D, Sig=230,10 Ref=360,100

Peak RetTime Type  Width     Area      Height     Area
  #   [min]        [min]   [mAU*s]     [mAU]       %
----|-------|----|-------|----------|----------|--------|
   1   7.000 MM    0.1972 2069.72974  174.89160  95.2573
   2   8.854 MM    0.1802  103.04781    9.53217   4.7427

Totals :                  2172.77755  184.42378

 Results obtained with enhanced integrator!

Signal 5: DAD1 E, Sig=280,10 Ref=360,100
```

*** End of Report ***

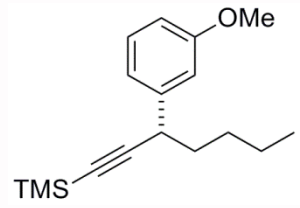
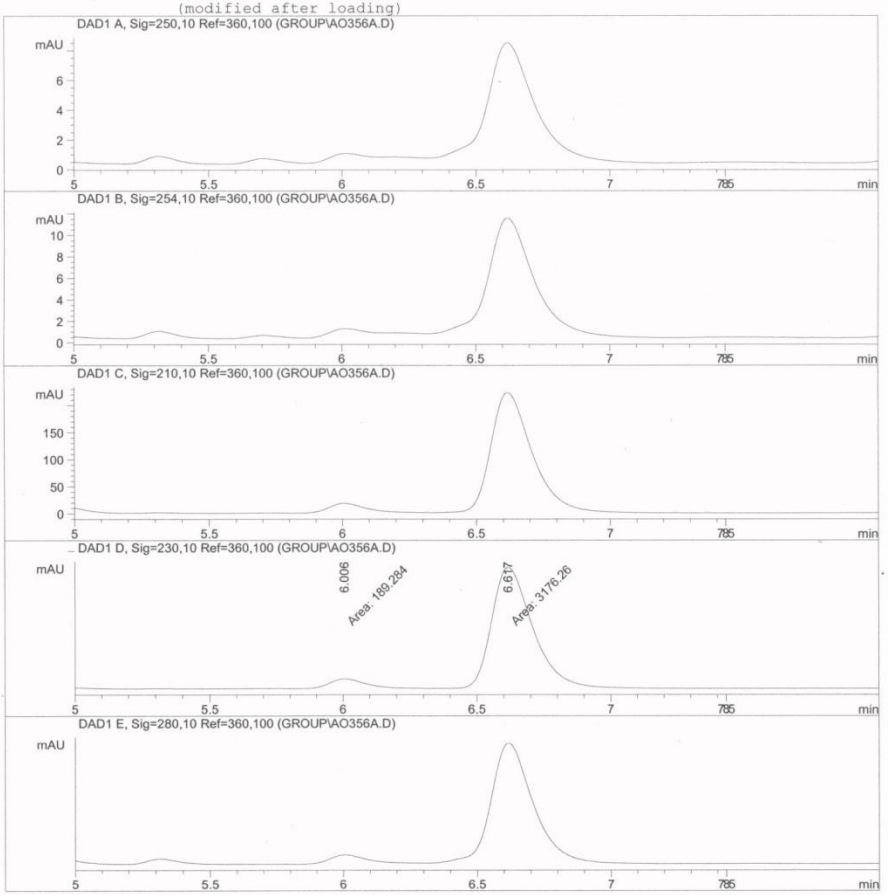


Table 2, entry 4 with (3R,8S)

Data File C:\HPCHEM\1\DATA\GROUP\AO356A.D Sample Name: AO356A

Injection Date : 4/28/2011 7:37:17 PM Seq. Line : 3
Sample Name : AO356A Location : Vial 65
Acq. Operator : NB Inj : 1
Acq. Instrument : Instrument 1 Inj Volume : 15 µl
Different Inj Volume from Sequence ! Actual Inj Volume : 3 µl
Acq. Method : C:\HPCHEM\1\METHODS\OD-00-30.M
Last changed : 4/7/2011 2:46:23 AM by CC
Analysis Method : C:\HPCHEM\1\METHODS\YL-AD03.M
Last changed : 10/10/2011 10:20:49 AM by NB
(modified after loading)



Area Percent Report

Sorted By : Signal
Multiplier : 1.0000
Dilution : 1.0000
Use Multiplier & Dilution Factor with ISTDs

Signal 1: DAD1 A, Sig=250,10 Ref=360,100

Signal 2: DAD1 B, Sig=254,10 Ref=360,100

Signal 3: DAD1 C, Sig=210,10 Ref=360,100

Signal 4: DAD1 D, Sig=230,10 Ref=360,100

Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	6.006	FM	0.1427	189.28445	22.10045	5.6242
2	6.617	MM	0.1792	3176.26147	295.39551	94.3758
Totals :				3365.54593	317.49596	

Results obtained with enhanced integrator!

Signal 5: DAD1 E, Sig=280,10 Ref=360,100

*** End of Report ***

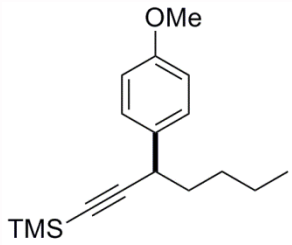
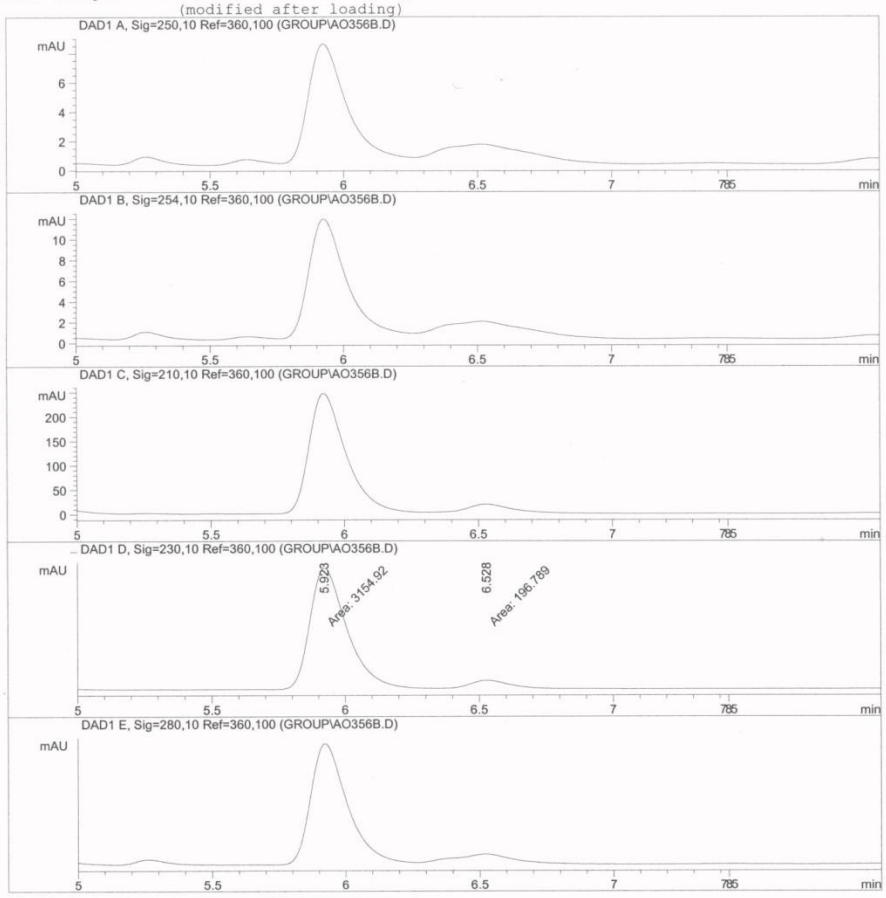


Table 2, entry 5 with (3S,8R)

Data File C:\HPCHEM\1\DATA\GROUP\AO356B.D Sample Name: AO356E

```
Injection Date  : 4/28/2011 8:08:33 PM          Seq. Line :   4
Sample Name     : AO356B                        Location : Vial 66
Acq. Operator   : NB                              Inj :   1
Acq. Instrument : Instrument 1                  Inj Volume : 15 µl
Different Inj Volume from Sequence !     Actual Inj Volume : 3 µl
Acq. Method     : C:\HPCHEM\1\METHODS\OD-00-30.M
Last changed    : 4/7/2011 2:46:23 AM by CC
Analysis Method : C:\HPCHEM\1\METHODS\YL-AD03.M
Last changed    : 10/10/2011 10:19:18 AM by NB
                  (modified after loading)
```



Data File C:\HPCHEM\1\DATA\GROUP\AO356B.D Sample Name: AO356E

Area Percent Report

```
Sorted By             :      Signal
Multiplier            :      1.0000
Dilution              :      1.0000
Use Multiplier & Dilution Factor with ISTDs


Signal 1: DAD1 A, Sig=250,10 Ref=360,100


Signal 2: DAD1 B, Sig=254,10 Ref=360,100


Signal 3: DAD1 C, Sig=210,10 Ref=360,100


Signal 4: DAD1 D, Sig=230,10 Ref=360,100

Peak RetTime Type  Width     Area      Height     Area
  #   [min]        [min]   [mAU*s]     [mAU]       %
----|-------|----|-------|----------|----------|--------|
   1   5.923 MM    0.1605 3154.92480  327.60562  94.1287
   2   6.528 MM    0.1555  196.78894   21.09148   5.8713

Totals :                  3351.71375  348.69711

 Results obtained with enhanced integrator!

Signal 5: DAD1 E, Sig=280,10 Ref=360,100
```

*** End of Report ***

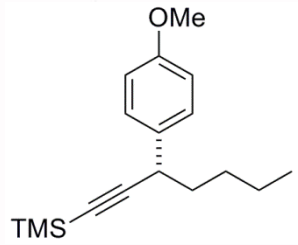


Table 2, entry 5 with (3R,8S)

Data File C:\HPCHEM\3\DATA\AJO\AO361A.D

```
Injection Date  : 5/5/2011 12:37:45 PM          Seq. Line :   1
Sample Name     :                               Location : Vial 7
Acq. Operator   : AJO                              Inj :   1
Acq. Instrument : Instrument 3                 Inj Volume : 1 µl
Different Inj Volume from Sequence !     Actual Inj Volume : 3 µl
Acq. Method     : C:\HPCHEM\3\METHODS\AJO100.M
Last changed    : 10/13/2010 9:09:31 AM by AJO
Analysis Method : C:\HPCHEM\3\METHODS\RL80180.M
Last changed    : 10/10/2011 9:50:23 AM by HD
                  (modified after loading)
```

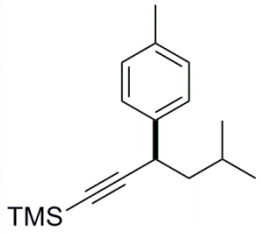
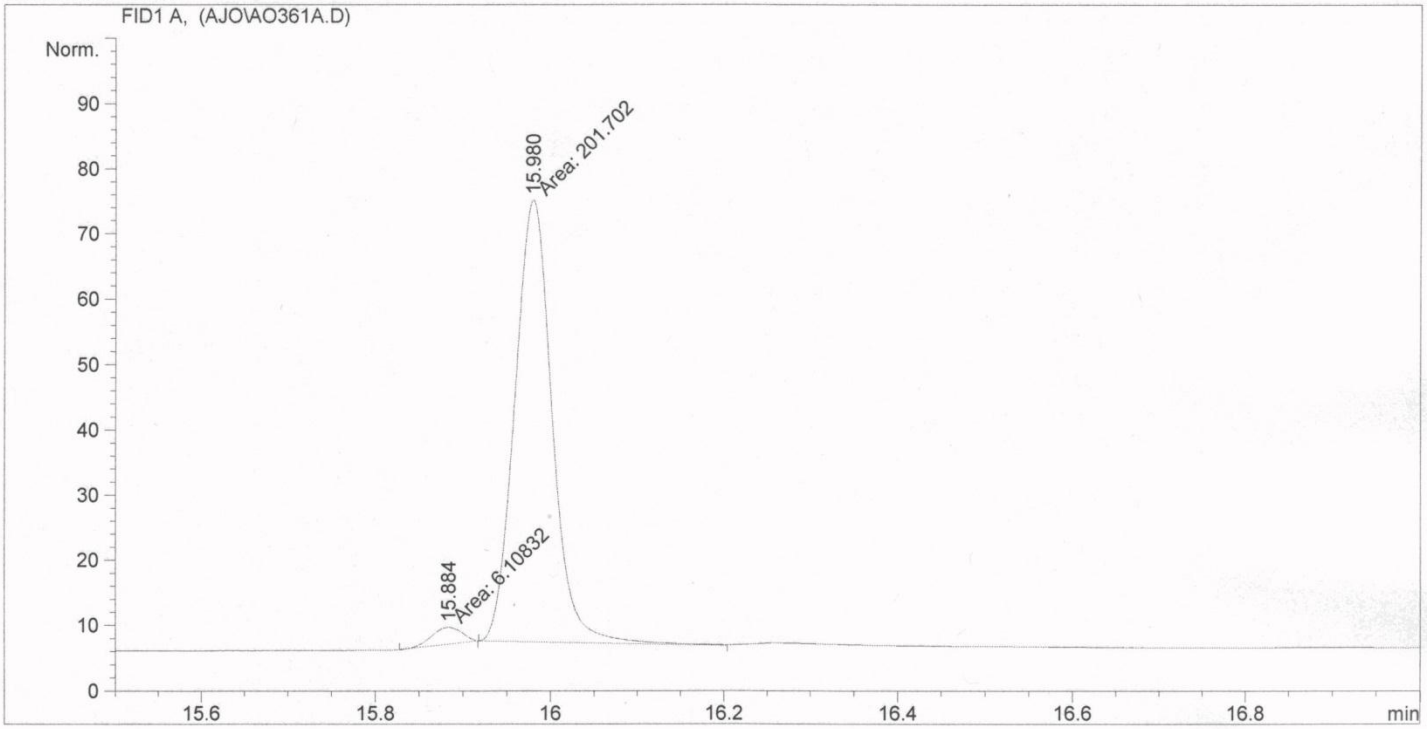


Table 2, entry 6 with (3S,8R)

Initial test




```
=====================================================================
                        Area Percent Report
=====================================================================

Sorted By             :      Signal
Multiplier            :      1.0000
Dilution              :      1.0000
Use Multiplier & Dilution Factor with ISTDs


Signal 1: FID1 A,

Peak RetTime Type  Width     Area      Height     Area
  #   [min]        [min]   [pA*s]      [pA]        %
----|-------|----|-------|----------|----------|--------|
   1  15.884 MM    0.0396    6.10832    2.56914  2.93937
   2  15.980 MM    0.0496  201.70221   67.73990 97.06063

Totals :                   207.81053   70.30904

 Results obtained with enhanced integrator!
=====================================================================
                        *** End of Report ***
```

Data File C:\HPCHEM\3\DATA\AJO\AO361B.D

```
==========================================================================
Injection Date  : 5/5/2011 1:03:41 PM          Seq. Line :   2
Sample Name     :                               Location : Vial 8
Acq. Operator   : AJO                              Inj :   1
Acq. Instrument : Instrument 3                 Inj Volume : 1 µl
Different Inj Volume from Sequence !     Actual Inj Volume : 3 µl
Acq. Method     : C:\HPCHEM\3\METHODS\AJO100.M
Last changed    : 10/13/2010 9:09:31 AM by AJO
Analysis Method : C:\HPCHEM\3\METHODS\RL80180.M
Last changed    : 10/10/2011 9:54:41 AM by HD
                  (modified after loading)
```

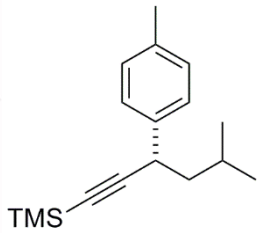
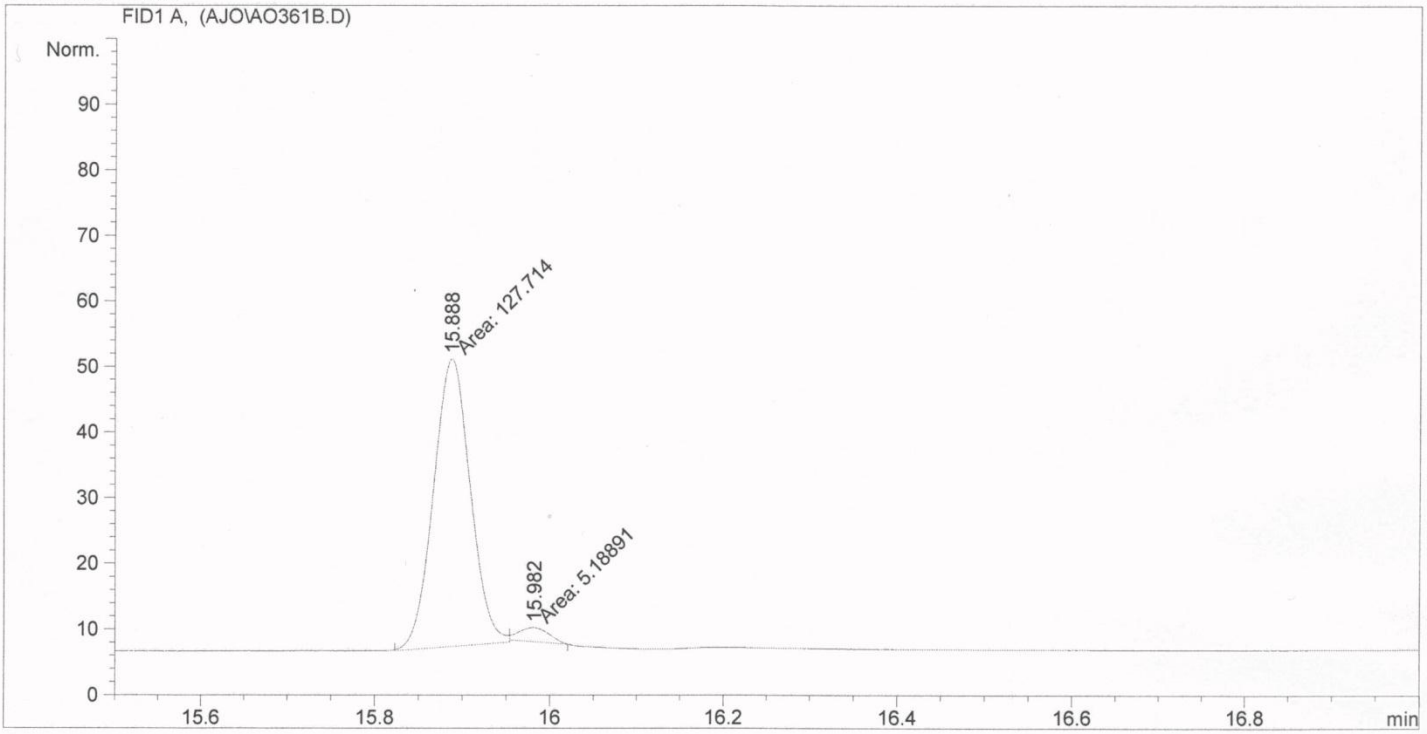


Table 2, entry 6 with (3R,8S)

Initial test




```
==========================================================================
                        Area Percent Report
==========================================================================

Sorted By             :      Signal
Multiplier            :      1.0000
Dilution              :      1.0000
Use Multiplier & Dilution Factor with ISTDs


Signal 1: FID1 A,

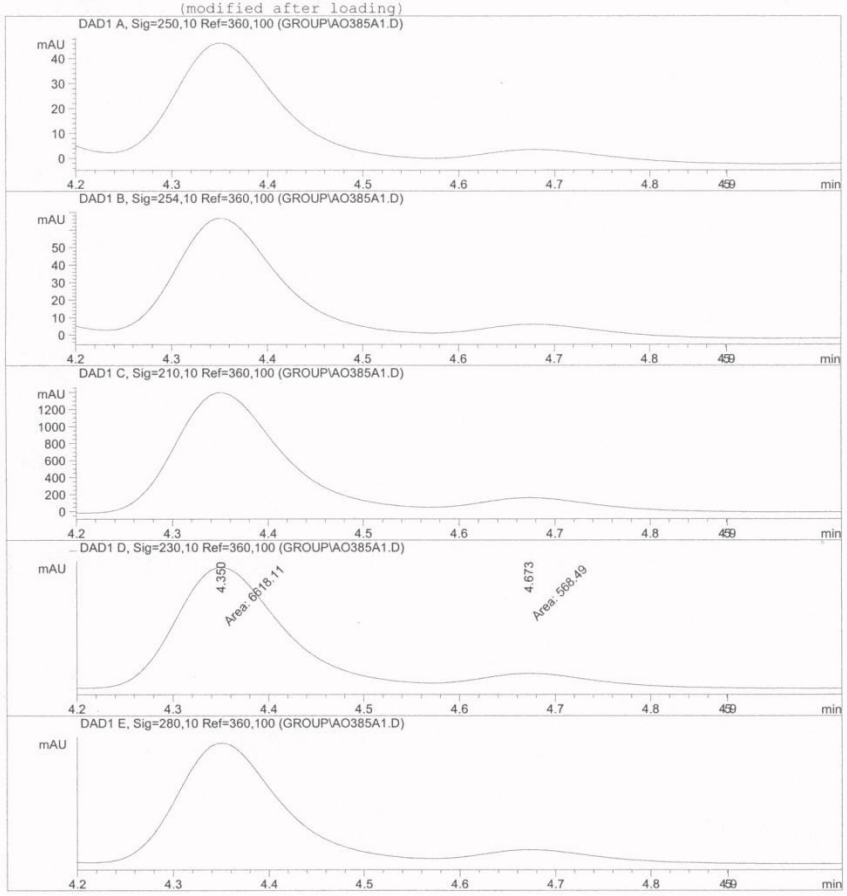
Peak RetTime Type  Width     Area      Height     Area
  #   [min]        [min]   [pA*s]      [pA]       %
----|-------|----|-------|----------|----------|--------|
   1  15.888 MM    0.0486  127.71436   43.83421 96.09572
   2  15.982 MM    0.0399    5.18891    2.16550  3.90428

Totals :                   132.90327   45.99971

 Results obtained with enhanced integrator!
==========================================================================
                        *** End of Report ***
```

Data File C:\HPCHEM\1\DATA\GROUP\AO385A1.D

```
Injection Date  : 5/27/2011 6:47:08 PM          Seq. Line :   1
Sample Name     :                               Location : Vial 12
Acq. Operator   : NB                               Inj :   1
Acq. Instrument : Instrument 1                 Inj Volume : 15 µl
Different Inj Volume from Sequence !     Actual Inj Volume : 3 µl
Acq. Method     : C:\HPCHEM\1\METHODS\OD-01-15.M
Last changed    : 4/20/2011 5:28:41 PM by CC
Analysis Method : C:\HPCHEM\1\METHODS\YL-AD04.M
Last changed    : 10/11/2011 3:28:25 PM by NB
                  (modified after loading)
```



Data File C:\HPCHEM\1\DATA\GROUP\AO385A1.D

Area Percent Report

```
Sorted By             :      Signal
Multiplier            :      1.0000
Dilution              :      1.0000
Use Multiplier & Dilution Factor with ISTDs


Signal 1: DAD1 A, Sig=250,10 Ref=360,100


Signal 2: DAD1 B, Sig=254,10 Ref=360,100


Signal 3: DAD1 C, Sig=210,10 Ref=360,100


Signal 4: DAD1 D, Sig=230,10 Ref=360,100

Peak RetTime Type  Width     Area      Height     Area
  #   [min]        [min]   [mAU*s]     [mAU]       %
----|-------|----|-------|----------|----------|--------|
   1   4.350 MM    0.1253 6618.11182  880.47015  92.0896
   2   4.673 MM    0.1172  568.49048   80.87708   7.9104

Totals :                  7186.60229  961.34724

 Results obtained with enhanced integrator!

Signal 5: DAD1 E, Sig=280,10 Ref=360,100
```

*** End of Report ***

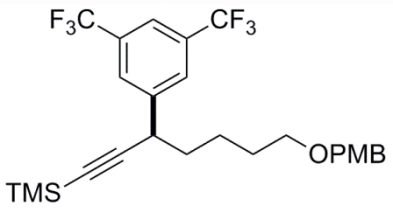
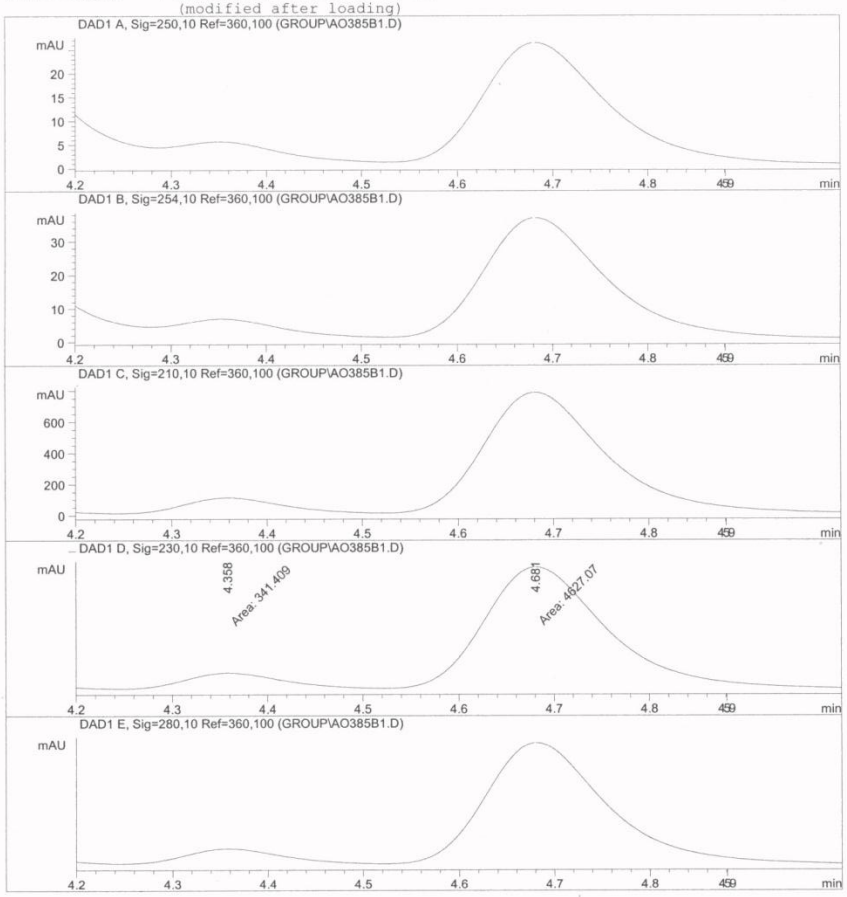


Table 2, entry 7
with (3S,8R)

Data File C:\HPCHEM\1\DATA\GROUP\AO385B1.D

```
Injection Date  : 5/27/2011 7:03:24 PM          Seq. Line :   2
Sample Name     :                               Location : Vial 13
Acq. Operator   : NB                               Inj :   1
Acq. Instrument : Instrument 1                 Inj Volume : 15 µl
Different Inj Volume from Sequence !     Actual Inj Volume : 3 µl
Acq. Method     : C:\HPCHEM\1\METHODS\OD-01-15.M
Last changed    : 4/20/2011 5:28:41 PM by CC
Analysis Method : C:\HPCHEM\1\METHODS\YL-AD04.M
Last changed    : 10/11/2011 3:26:33 PM by NB
                  (modified after loading)
```



Data File C:\HPCHEM\1\DATA\GROUP\AO385B1.D

Area Percent Report

```
Sorted By             :      Signal
Multiplier            :      1.0000
Dilution              :      1.0000
Use Multiplier & Dilution Factor with ISTDs


Signal 1: DAD1 A, Sig=250,10 Ref=360,100


Signal 2: DAD1 B, Sig=254,10 Ref=360,100


Signal 3: DAD1 C, Sig=210,10 Ref=360,100


Signal 4: DAD1 D, Sig=230,10 Ref=360,100

Peak RetTime Type  Width     Area      Height     Area
  #   [min]        [min]   [mAU*s]     [mAU]       %
----|-------|----|-------|----------|----------|--------|
   1   4.358 MM    0.1017  341.40915   55.92992   6.8715
   2   4.681 MM    0.1534 4627.07080  502.83765  93.1285

Totals :                  4968.47995  558.76757

 Results obtained with enhanced integrator!

Signal 5: DAD1 E, Sig=280,10 Ref=360,100
```

*** End of Report ***

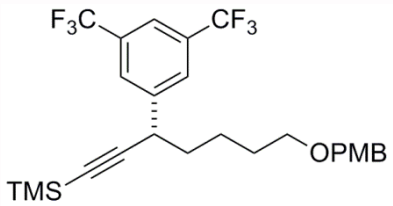
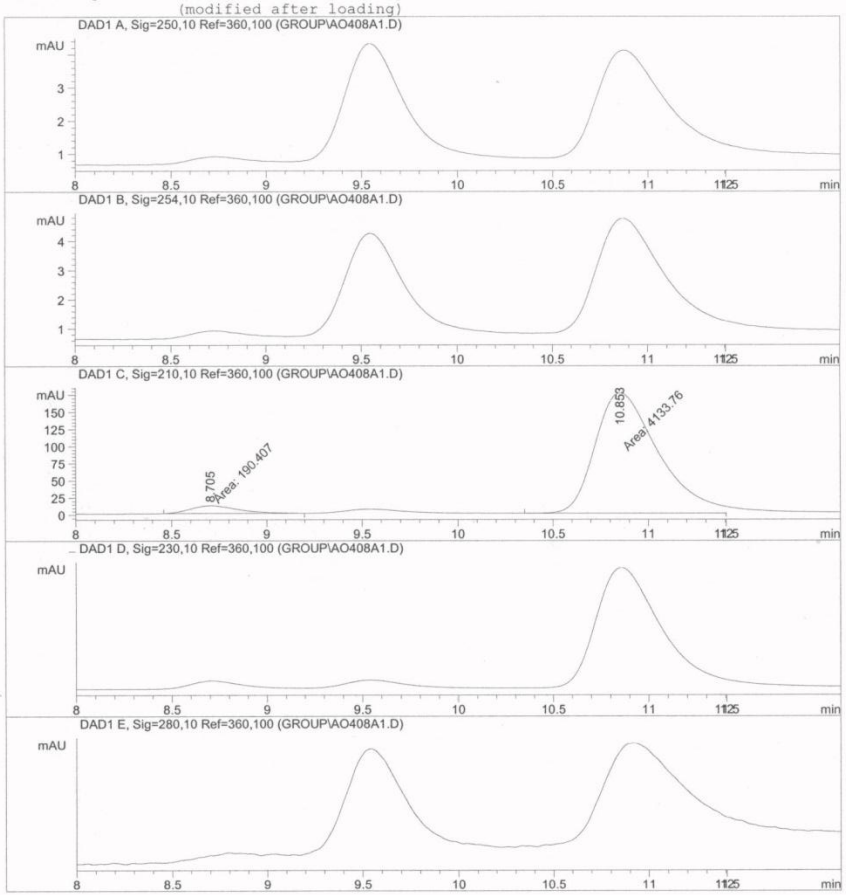


Table 2, entry 7 with (3R,8S)

Data File C:\HPCHEM\1\DATA\GROUP\AO408A1.D

```
Injection Date  : 6/8/2011 1:07:17 AM            Seq. Line :  38
Sample Name     :                                 Location : Vial 15
Acq. Operator   : NB                                 Inj :  1
Acq. Instrument : Instrument 1                 Inj Volume : 1 µl
Different Inj Volume from Sequence !     Actual Inj Volume : 2 µl
Acq. Method     : C:\HPCHEM\1\METHODS\OD-00360.M
Last changed    : 5/28/2011 2:14:00 PM by NB
Analysis Method : C:\HPCHEM\1\METHODS\YL-AD04.M
Last changed    : 10/11/2011 3:09:30 PM by NB
                  (modified after loading)
```



Data File C:\HPCHEM\1\DATA\GROUP\AO408A1.D

Area Percent Report

```
Sorted By             :      Signal
Multiplier            :      1.0000
Dilution              :      1.0000
Use Multiplier & Dilution Factor with ISTDs


Signal 1: DAD1 A, Sig=250,10 Ref=360,100


Signal 2: DAD1 B, Sig=254,10 Ref=360,100


Signal 3: DAD1 C, Sig=210,10 Ref=360,100

Peak RetTime Type  Width     Area      Height     Area
  #   [min]       [min]   [mAU*s]     [mAU]       %
----|-------|----|-------|----------|----------|--------|
   1   8.705 MM    0.2860  190.40735   11.09406   4.4033
   2  10.853 MM    0.3925 4133.76270  175.54211  95.5967

Totals :                  4324.17004  186.63617

 Results obtained with enhanced integrator!

Signal 4: DAD1 D, Sig=230,10 Ref=360,100


Signal 5: DAD1 E, Sig=280,10 Ref=360,100
```

*** End of Report ***

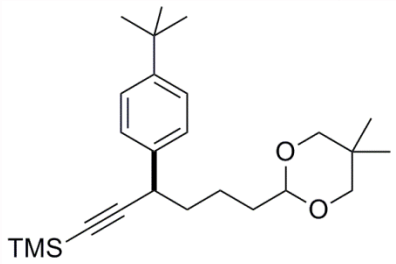
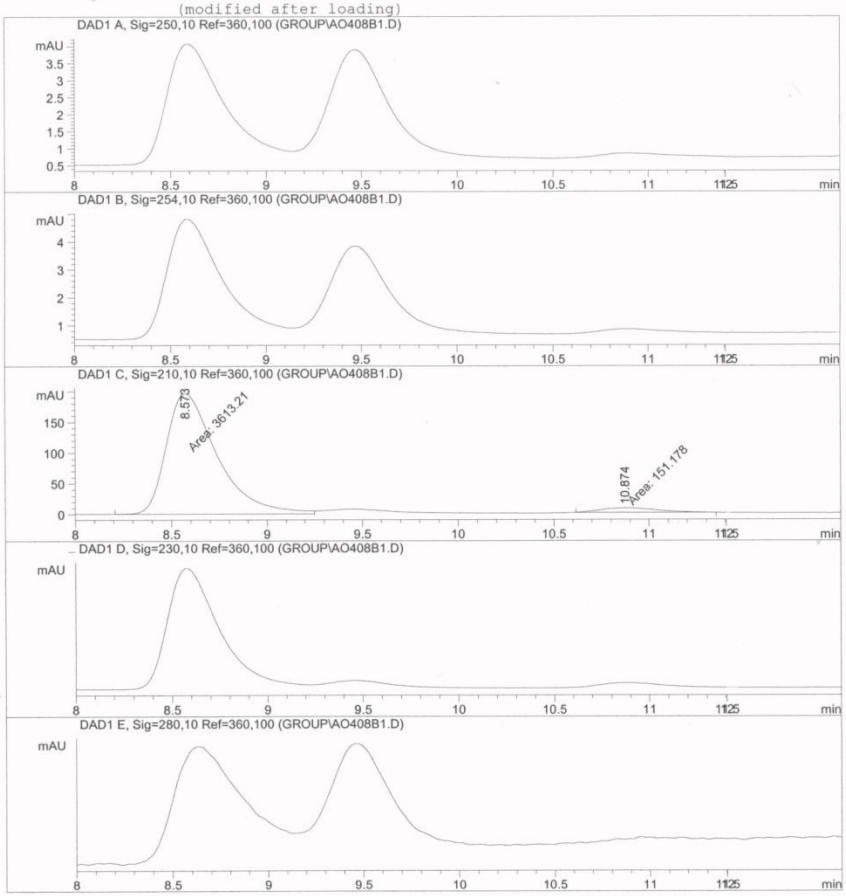


Table 2, entry 8 with (3S,8R)

Data File C:\HPCHEM\1\DATA\GROUP\AO408B1.D

```
Injection Date  : 6/8/2011 2:08:31 AM            Seq. Line :  39
Sample Name     :                                 Location : Vial 16
Acq. Operator   : NB                                 Inj :   1
Acq. Instrument : Instrument 1                 Inj Volume : 1 µl
Different Inj Volume from Sequence !     Actual Inj Volume : 2 µl
Acq. Method     : C:\HPCHEM\1\METHODS\OD-00360.M
Last changed    : 5/28/2011 2:14:00 PM by NB
Analysis Method : C:\HPCHEM\1\METHODS\YL-AD04.M
Last changed    : 10/11/2011 3:11:18 PM by NB
                  (modified after loading)
```



Data File C:\HPCHEM\1\DATA\GROUP\AO408B1.D

```
                          Area Percent Report

Sorted By             :      Signal
Multiplier            :      1.0000
Dilution              :      1.0000
Use Multiplier & Dilution Factor with ISTDs


Signal 1: DAD1 A, Sig=250,10 Ref=360,100


Signal 2: DAD1 B, Sig=254,10 Ref=360,100


Signal 3: DAD1 C, Sig=210,10 Ref=360,100

Peak RetTime Type  Width     Area      Height     Area
  #   [min]       [min]   [mAU*s]     [mAU]       %
----|-------|----|-------|----------|----------|--------|
   1   8.573 MF    0.3074 3613.20874  195.92921  95.9840
   2  10.874 MM    0.3393  151.17828    7.42600   4.0160

Totals :                  3764.38702  203.35521

 Results obtained with enhanced integrator!

Signal 4: DAD1 D, Sig=230,10 Ref=360,100


Signal 5: DAD1 E, Sig=280,10 Ref=360,100

                          *** End of Report ***
```

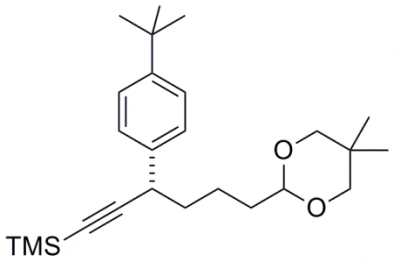
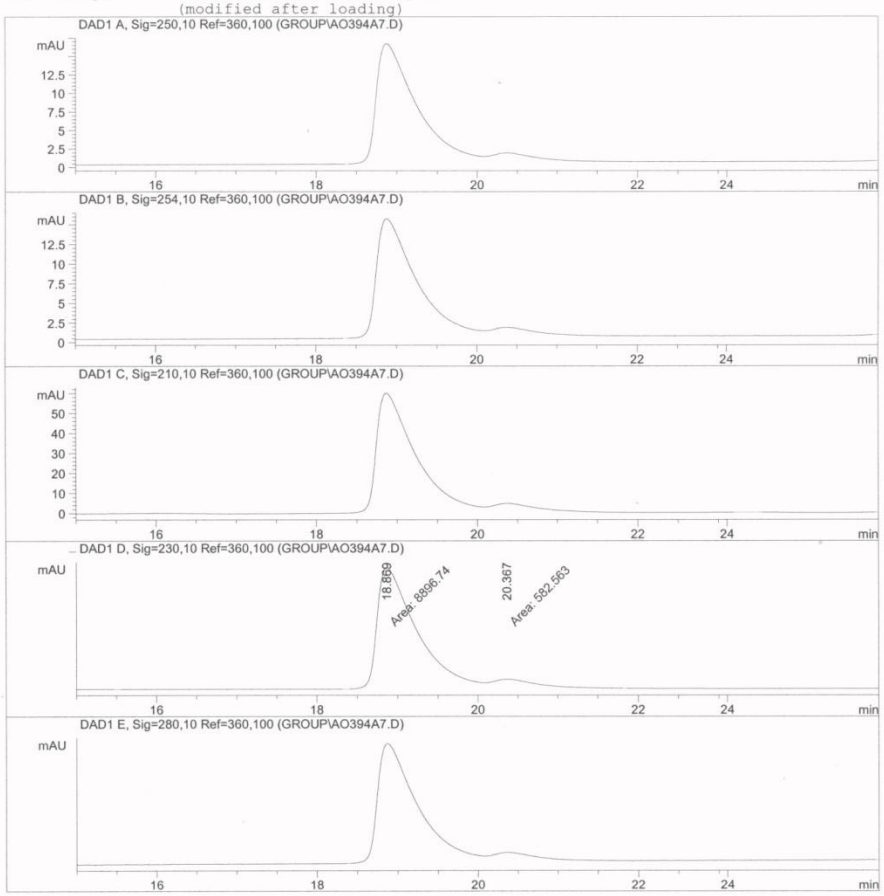


Table 2, entry 8 with (3R,8S)

Data File C:\HPCHEM\1\DATA\GROUP\AO394A7.D

```
Injection Date  : 5/29/2011 8:37:38 AM          Seq. Line :  33
Sample Name     :                               Location : Vial 92
Acq. Operator   : NB                               Inj :   1
Acq. Instrument : Instrument 1                 Inj Volume : 15 µl
Different Inj Volume from Sequence !     Actual Inj Volume : 1 µl
Acq. Method     : C:\HPCHEM\1\METHODS\IB-00-60.M
Last changed    : 4/7/2011 8:01:54 PM by CC
Analysis Method : C:\HPCHEM\1\METHODS\OJ-02-20.M
Last changed    : 10/11/2011 10:00:59 AM by NB
                  (modified after loading)
```



Data File C:\HPCHEM\1\DATA\GROUP\AO394A7.D

Area Percent Report

```
Sorted By             :      Signal
Multiplier            :      1.0000
Dilution              :      1.0000
Use Multiplier & Dilution Factor with ISTDs


Signal 1: DAD1 A, Sig=250,10 Ref=360,100


Signal 2: DAD1 B, Sig=254,10 Ref=360,100


Signal 3: DAD1 C, Sig=210,10 Ref=360,100


Signal 4: DAD1 D, Sig=230,10 Ref=360,100

Peak RetTime Type  Width     Area      Height     Area
  #   [min]        [min]   [mAU*s]     [mAU]       %
----|-------|----|-------|----------|----------|--------|
   1  18.869 MM    0.5689 8896.73828  260.66391  93.8544
   2  20.367 MM    0.5559  582.56335   17.46569   6.1456

Totals :                  9479.30164  278.12960

 Results obtained with enhanced integrator!

Signal 5: DAD1 E, Sig=280,10 Ref=360,100
```

*** End of Report ***

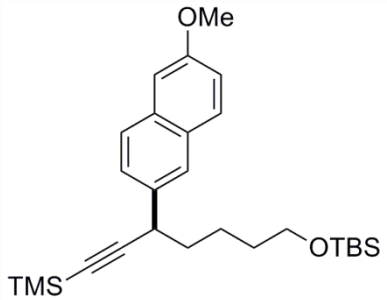
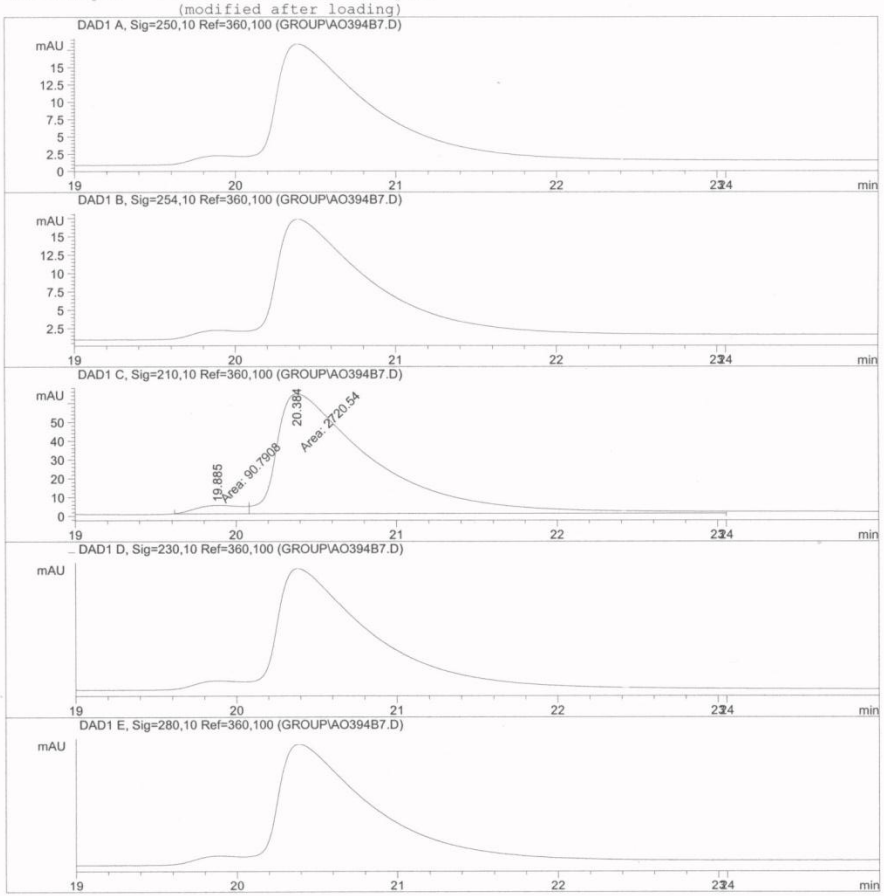


Table 2, entry 9 with (3S,8R)

Data File C:\HPCHEM\1\DATA\GROUP\AO394B7.D

```
Injection Date  : 5/29/2011 9:38:52 AM          Seq. Line :  34
Sample Name     :                               Location : Vial 93
Acq. Operator   : NB                               Inj :   1
Acq. Instrument : Instrument 1                 Inj Volume : 15 µl
Different Inj Volume from Sequence !     Actual Inj Volume : 1 µl
Acq. Method     : C:\HPCHEM\1\METHODS\IB-00-60.M
Last changed    : 4/7/2011 8:01:54 PM by CC
Analysis Method : C:\HPCHEM\1\METHODS\OJ-02-20.M
Last changed    : 10/11/2011 9:55:51 AM by NB
                  (modified after loading)
```



Data File C:\HPCHEM\1\DATA\GROUP\AO394B7.D

Area Percent Report

```
Sorted By             :      Signal
Multiplier            :      1.0000
Dilution              :      1.0000
Use Multiplier & Dilution Factor with ISTDs


Signal 1: DAD1 A, Sig=250,10 Ref=360,100


Signal 2: DAD1 B, Sig=254,10 Ref=360,100


Signal 3: DAD1 C, Sig=210,10 Ref=360,100

Peak RetTime Type  Width     Area      Height     Area
  #   [min]       [min]   [mAU*s]     [mAU]       %
----|-------|----|-------|----------|----------|--------|
   1  19.885 MF    0.3421   90.79084    4.42354   3.2295
   2  20.384 FM    0.7119 2720.53564   63.69624  96.7705

Totals :                  2811.32648   68.11978

 Results obtained with enhanced integrator!

Signal 4: DAD1 D, Sig=230,10 Ref=360,100


Signal 5: DAD1 E, Sig=280,10 Ref=360,100
```

*** End of Report ***

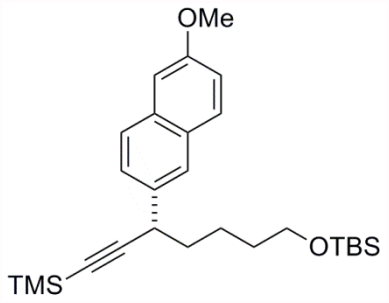
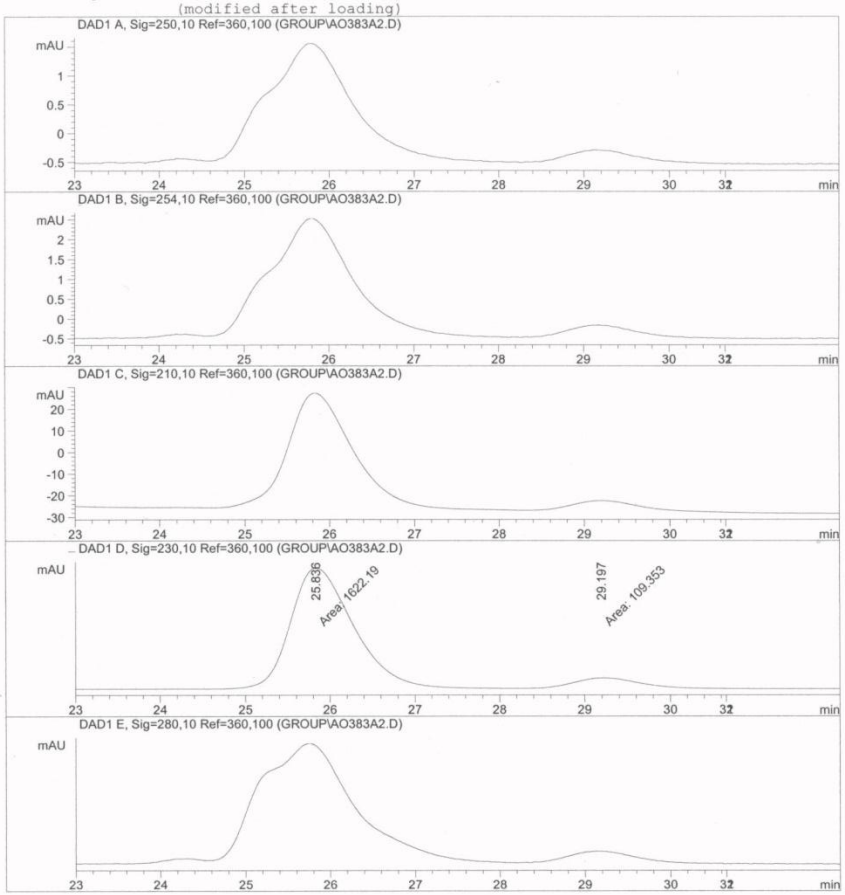


Table 2, entry 9
with (3R,8S)

Data File C:\HPCHEM\1\DATA\GROUP\AO383A2.D

```
Injection Date  : 5/24/2011 3:24:42 PM          Seq. Line :   2
Sample Name     :                               Location : Vial 1
Acq. Operator   : NB                               Inj :   1
Acq. Instrument : Instrument 1                 Inj Volume : 15 µl
Different Inj Volume from Sequence !     Actual Inj Volume : 1 µl
Acq. Method     : C:\HPCHEM\1\METHODS\OD-00-40.M
Last changed    : 6/3/2005 8:24:08 PM by GROUP
Analysis Method : C:\HPCHEM\1\METHODS\YL-AD04.M
Last changed    : 10/11/2011 3:17:27 PM by NB
                  (modified after loading)
```



Data File C:\HPCHEM\1\DATA\GROUP\AO383A2.D

Area Percent Report

```
Sorted By             :      Signal
Multiplier            :      1.0000
Dilution              :      1.0000
Use Multiplier & Dilution Factor with ISTDs


Signal 1: DAD1 A, Sig=250,10 Ref=360,100


Signal 2: DAD1 B, Sig=254,10 Ref=360,100


Signal 3: DAD1 C, Sig=210,10 Ref=360,100


Signal 4: DAD1 D, Sig=230,10 Ref=360,100

Peak RetTime Type  Width     Area      Height     Area
  #   [min]        [min]   [mAU*s]     [mAU]       %
----|-------|----|-------|----------|----------|--------|
   1  25.836 MM    0.8808 1622.18762   30.69631  93.6847
   2  29.197 MM    0.7686  109.35281    2.37139   6.3153

Totals :                  1731.54043   33.06769

 Results obtained with enhanced integrator!

Signal 5: DAD1 E, Sig=280,10 Ref=360,100
```

*** End of Report ***

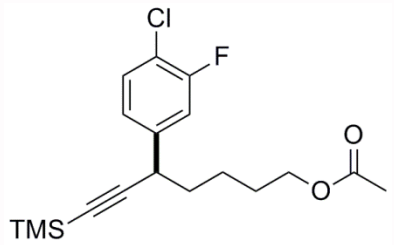
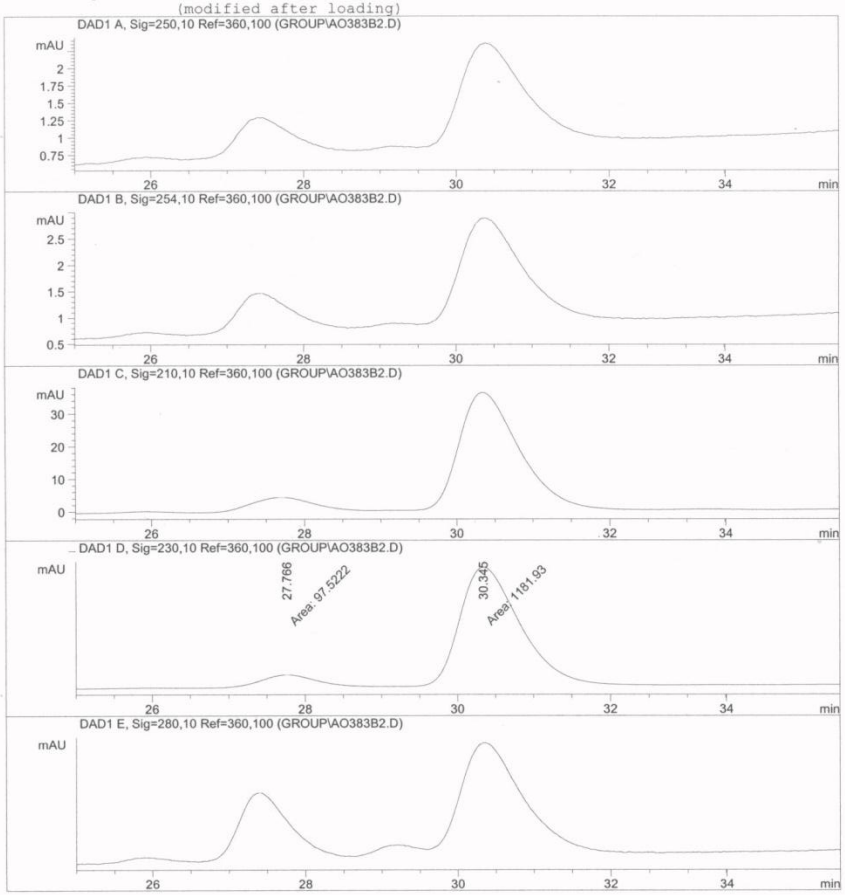


Table 2, entry 10 with (3S,8R)

Data File C:\HPCHEM\1\DATA\GROUP\AO383B2.D

```
Injection Date  : 5/24/2011 4:05:54 PM          Seq. Line :   3
Sample Name     :                               Location : Vial 2
Acq. Operator   : NB                              Inj :   1
Acq. Instrument : Instrument 1                Inj Volume : 15 µl
Different Inj Volume from Sequence !     Actual Inj Volume : 1 µl
Acq. Method     : C:\HPCHEM\1\METHODS\OD-00-40.M
Last changed    : 6/3/2005 8:24:08 PM by GROUP
Analysis Method : C:\HPCHEM\1\METHODS\YL-AD04.M
Last changed    : 10/11/2011 3:21:24 PM by NB
                  (modified after loading)
```



Data File C:\HPCHEM\1\DATA\GROUP\AO383B2.D

Area Percent Report

```
Sorted By             :      Signal
Multiplier            :      1.0000
Dilution              :      1.0000
Use Multiplier & Dilution Factor with ISTDs


Signal 1: DAD1 A, Sig=250,10 Ref=360,100


Signal 2: DAD1 B, Sig=254,10 Ref=360,100


Signal 3: DAD1 C, Sig=210,10 Ref=360,100


Signal 4: DAD1 D, Sig=230,10 Ref=360,100

Peak RetTime Type  Width     Area      Height     Area
  #   [min]       [min]   [mAU*s]     [mAU]       %
----|-------|----|-------|----------|----------|--------|
   1  27.766 MM    0.7914   97.52222    2.05370   7.6222
   2  30.345 MM    0.9437 1181.93335   20.87317  92.3778

Totals :                  1279.45557   22.92687

 Results obtained with enhanced integrator!

Signal 5: DAD1 E, Sig=280,10 Ref=360,100
```

*** End of Report ***

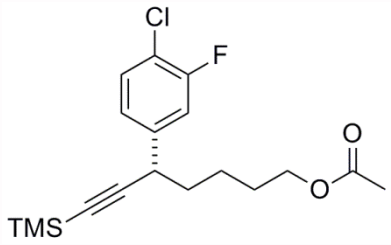


Table 2, entry 10 with (3R,8S)

Data File D:\HPCHEM\2\DATA\AJO\AO360A2.D

```
Injection Date  : 5/3/2011 4:51:37 PM          Seq. Line :   3
Sample Name     :                              Location : Vial 9
Acq. Operator   : AJO                             Inj :   1
                                               Inj Volume : 1 µl

Acq. Method     : D:\HPCHEM\2\METHODS\100280B.M
Last changed    : 12/18/2010 1:41:19 PM by AJO
Analysis Method : D:\HPCHEM\2\METHODS\100310L.M
Last changed    : 10/10/2011 9:37:30 AM by YL
                  (modified after loading)
```

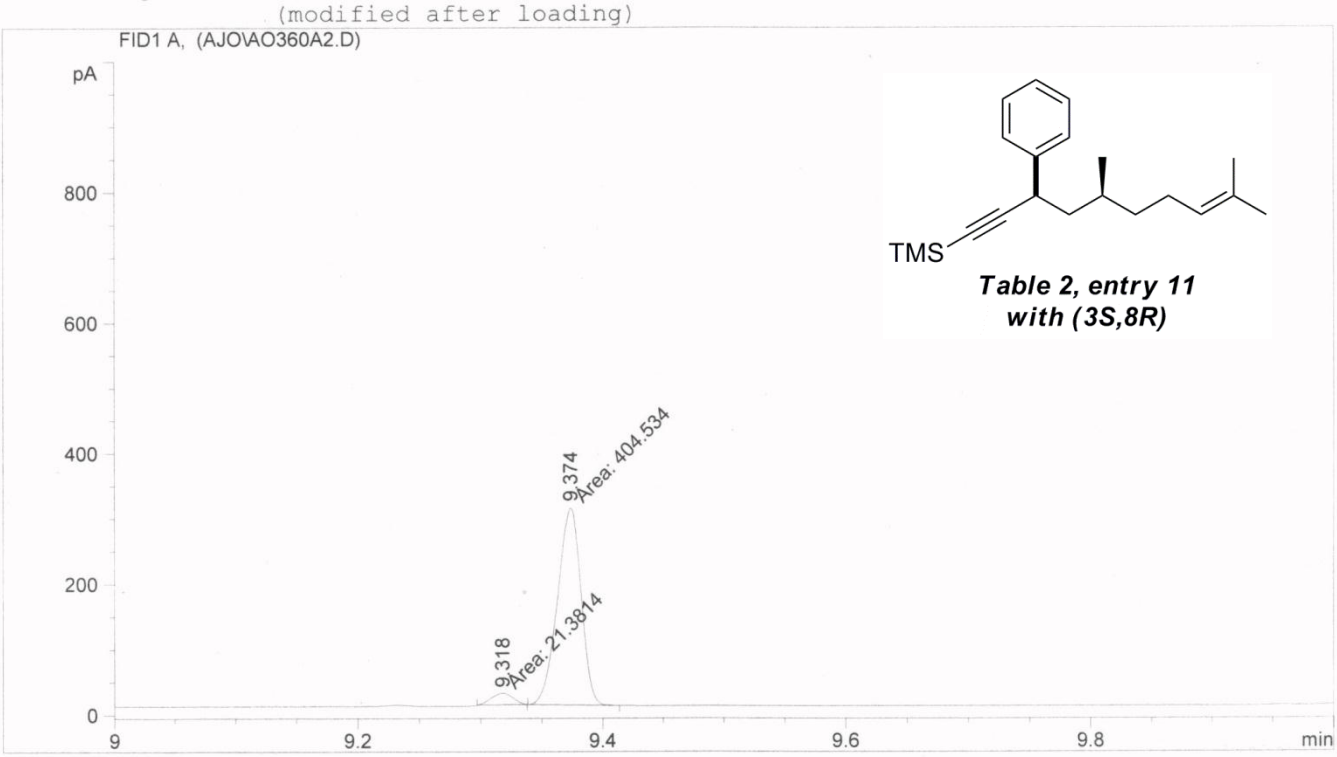


Table 2, entry 11 with (3S,8R)

```
                          Area Percent Report

Sorted By             :      Signal
Multiplier            :      1.0000
Dilution              :      1.0000
Use Multiplier & Dilution Factor with ISTDs


Signal 1: FID1 A,

Peak RetTime Type  Width     Area      Height     Area
  #   [min]        [min]   [pA*s]      [pA]       %
----|-------|----|-------|----------|----------|--------|
   1   9.318 MM    0.0205   21.38142   17.41595  5.02011
   2   9.374 MM    0.0223  404.53354  301.80872 94.97989

Totals :                   425.91496  319.22466

 Results obtained with enhanced integrator!

                        *** End of Report ***
```

Data File D:\HPCHEM\2\DATA\AJO\AO360B2.D

```
Injection Date  : 5/3/2011 5:14:30 PM          Seq. Line :   4
Sample Name     :                              Location : Vial 10
Acq. Operator   : AJO                             Inj :   1
                                               Inj Volume : 1 µl

Acq. Method     : D:\HPCHEM\2\METHODS\100280B.M
Last changed    : 12/18/2010 1:41:19 PM by AJO
Analysis Method : D:\HPCHEM\2\METHODS\100310L.M
Last changed    : 10/10/2011 9:38:23 AM by YL
                  (modified after loading)
```

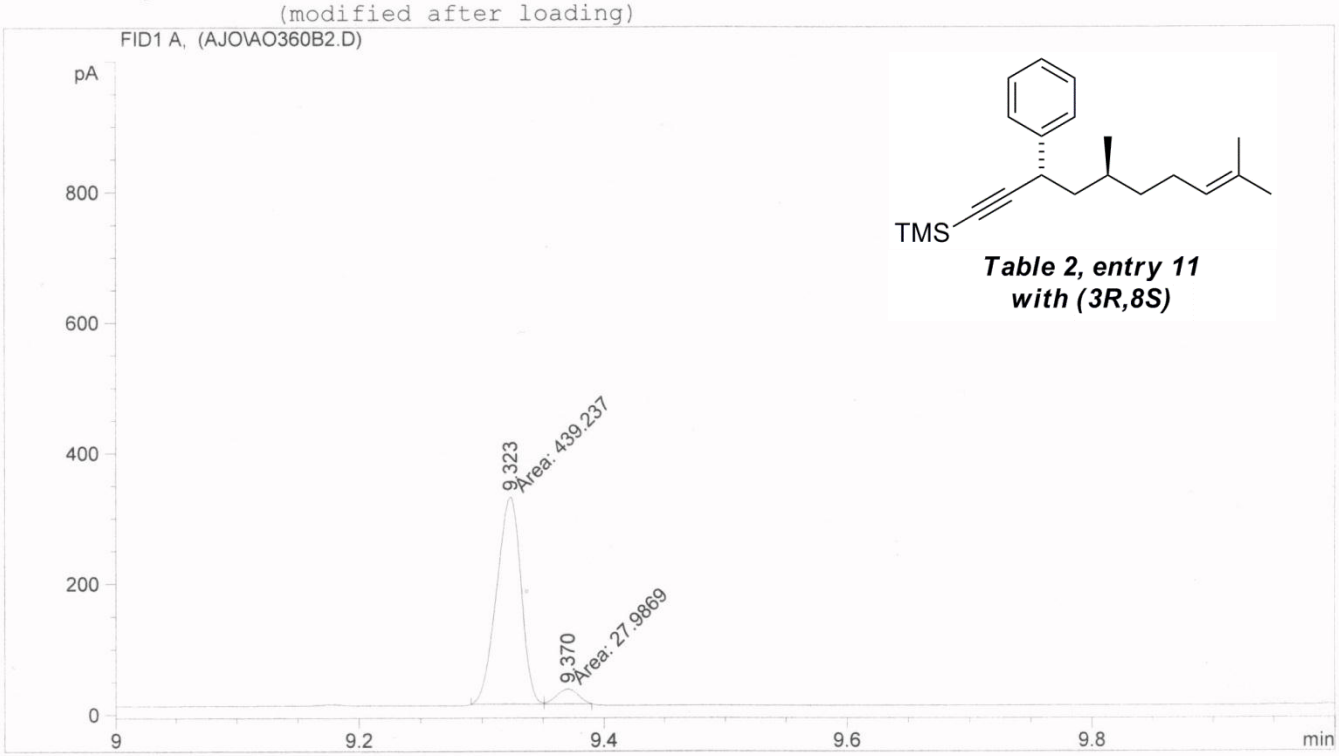


Table 2, entry 11 with (3R,8S)

```
                          Area Percent Report

Sorted By             :      Signal
Multiplier            :      1.0000
Dilution              :      1.0000
Use Multiplier & Dilution Factor with ISTDs


Signal 1: FID1 A,

Peak RetTime Type  Width     Area      Height     Area
  #   [min]        [min]   [pA*s]      [pA]       %
----|-------|----|-------|----------|----------|--------|
   1   9.323 MF    0.0231  439.23700  316.74741 94.00995
   2   9.370 FM    0.0204   27.98693   22.82645  5.99005

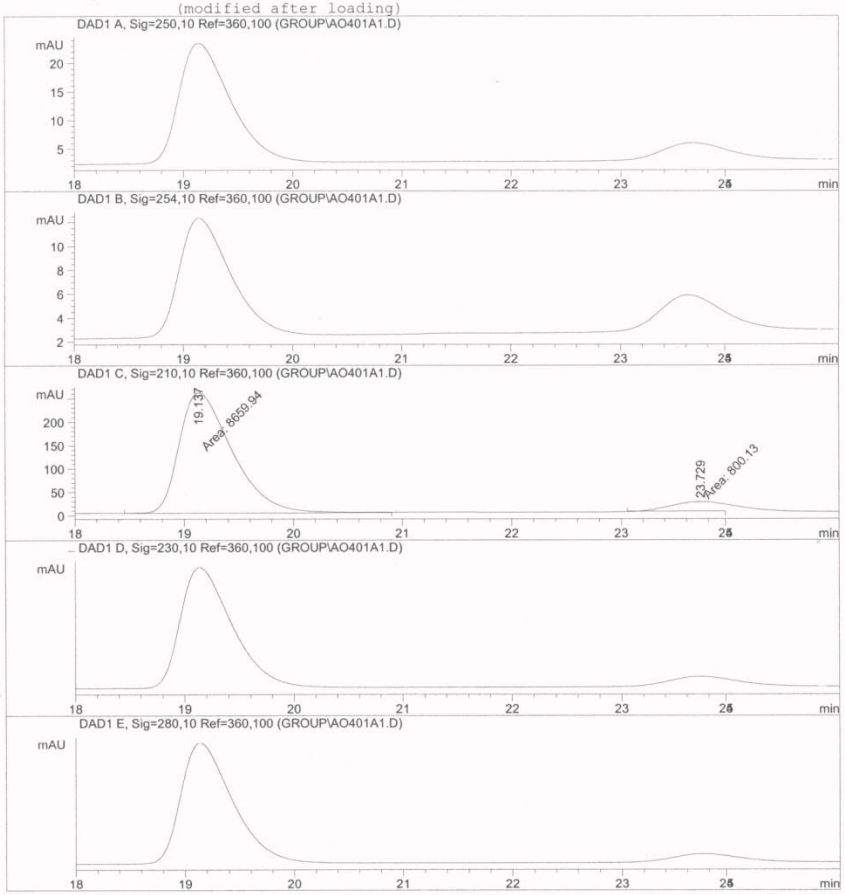
Totals :                   467.22393  339.57385

 Results obtained with enhanced integrator!

                          *** End of Report ***
```

Data File C:\HPCHEM\1\DATA\GROUP\AO401A1.D

```
Injection Date  : 6/7/2011 9:40:42 PM          Seq. Line :  33
Sample Name     :                              Location : Vial 12
Acq. Operator   : NB                              Inj :  1
Acq. Instrument : Instrument 1                 Inj Volume : 15 µl
Different Inj Volume from Sequence !     Actual Inj Volume : 2 µl
Acq. Method     : C:\HPCHEM\1\METHODS\OD-00-50.M
Last changed    : 4/17/2009 9:17:30 PM by GROUP
Analysis Method : C:\HPCHEM\1\METHODS\YL-AD04.M
Last changed    : 10/11/2011 3:14:51 PM by NB
                  (modified after loading)
```



Data File C:\HPCHEM\1\DATA\GROUP\AO401A1.D

```
                          Area Percent Report

Sorted By             :      Signal
Multiplier            :      1.0000
Dilution              :      1.0000
Use Multiplier & Dilution Factor with ISTDs


Signal 1: DAD1 A, Sig=250,10 Ref=360,100


Signal 2: DAD1 B, Sig=254,10 Ref=360,100


Signal 3: DAD1 C, Sig=210,10 Ref=360,100

Peak RetTime Type  Width     Area      Height     Area
  #   [min]       [min]   [mAU*s]     [mAU]       %
----|-------|----|-------|----------|----------|--------|
   1  19.137 MM    0.5615 8659.93848  257.07010  91.5420
   2  23.729 MM    0.6642  800.12970   20.07790   8.4580

Totals :                  9460.06818  277.14800

 Results obtained with enhanced integrator!

Signal 4: DAD1 D, Sig=230,10 Ref=360,100


Signal 5: DAD1 E, Sig=280,10 Ref=360,100

                          *** End of Report ***
```

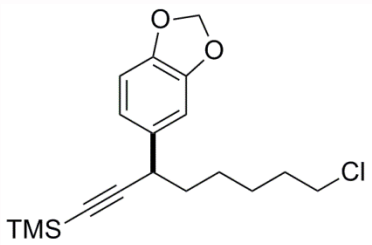
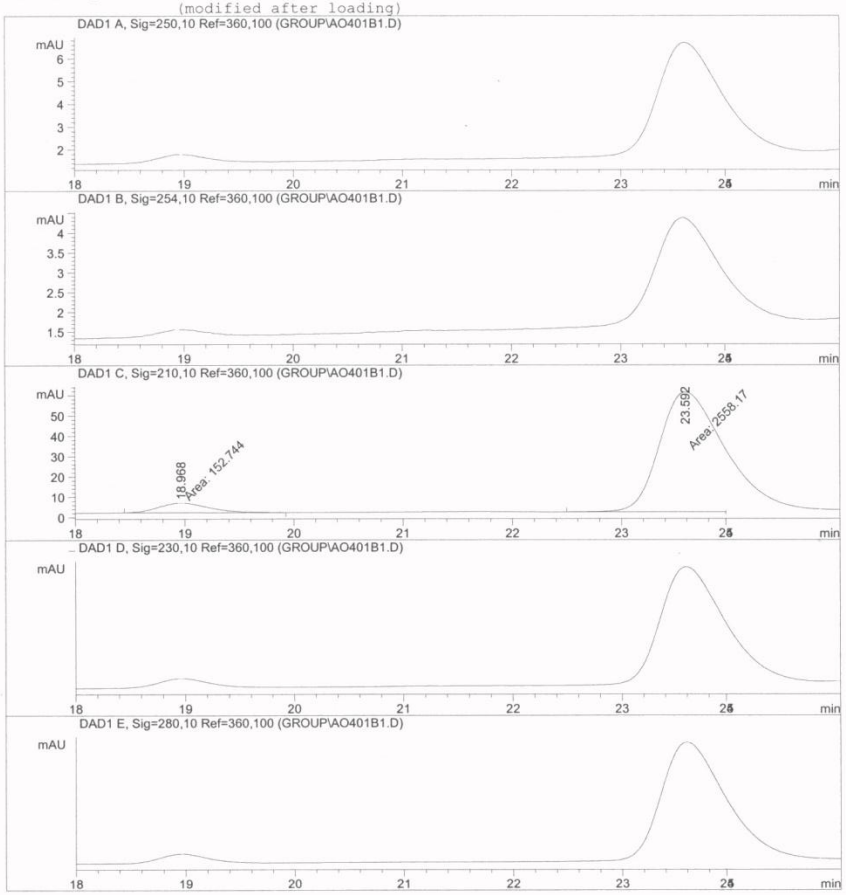


Table 2, entry 12 with (3S,8R)

Data File C:\HPCHEM\1\DATA\GROUP\AO401B1.D

```
Injection Date  : 6/7/2011 10:31:53 PM          Seq. Line :  34
Sample Name     :                               Location : Vial 13
Acq. Operator   : NB                               Inj :  1
Acq. Instrument : Instrument 1                 Inj Volume : 15 µl
Different Inj Volume from Sequence !     Actual Inj Volume : 2 µl
Acq. Method     : C:\HPCHEM\1\METHODS\OD-00-50.M
Last changed    : 4/17/2009 9:17:30 PM by GROUP
Analysis Method : C:\HPCHEM\1\METHODS\YL-AD04.M
Last changed    : 10/11/2011 3:12:59 PM by NB
                  (modified after loading)
```



Data File C:\HPCHEM\1\DATA\GROUP\AO401B1.D

```
                          Area Percent Report

Sorted By             :      Signal
Multiplier            :      1.0000
Dilution              :      1.0000
Use Multiplier & Dilution Factor with ISTDs


Signal 1: DAD1 A, Sig=250,10 Ref=360,100


Signal 2: DAD1 B, Sig=254,10 Ref=360,100


Signal 3: DAD1 C, Sig=210,10 Ref=360,100

Peak RetTime Type  Width     Area      Height     Area
  #   [min]        [min]   [mAU*s]     [mAU]       %
----|-------|----|-------|----------|----------|--------|
   1  18.968 MM    0.5335  152.74353    4.77174   5.6344
   2  23.592 MM    0.7236 2558.17041   58.92229  94.3656

Totals :                  2710.91394   63.69403

 Results obtained with enhanced integrator!

Signal 4: DAD1 D, Sig=230,10 Ref=360,100


Signal 5: DAD1 E, Sig=280,10 Ref=360,100

                          *** End of Report ***
```

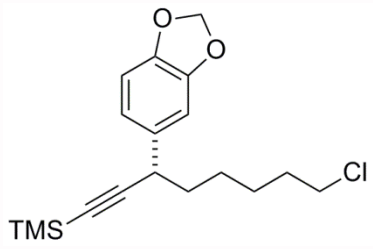
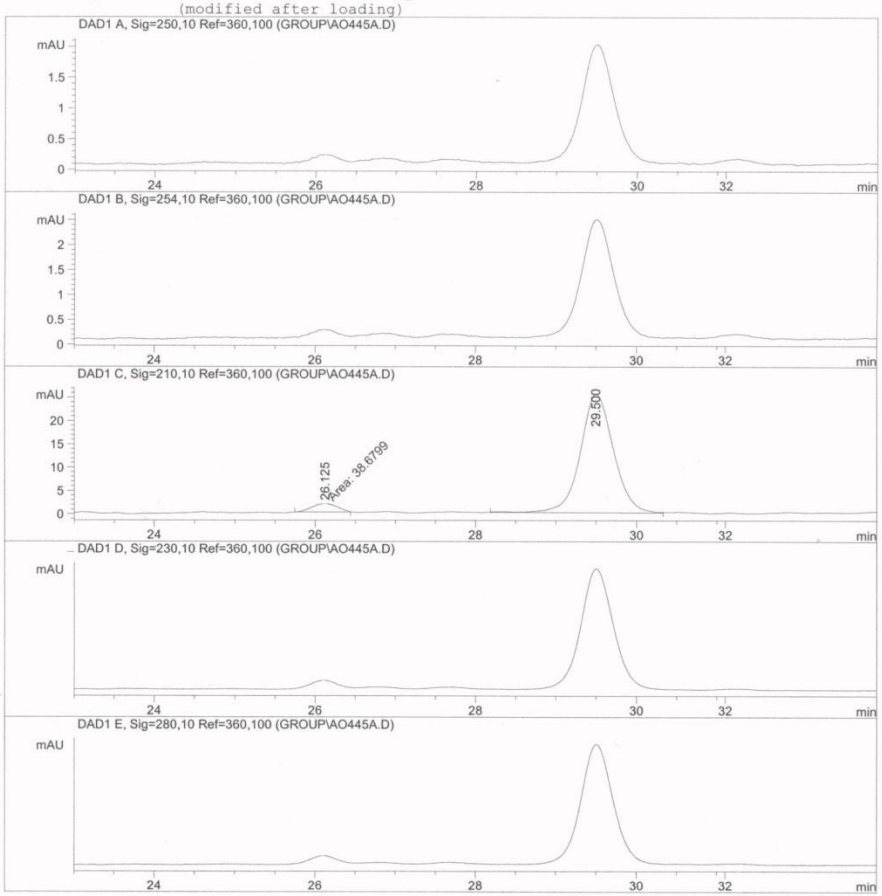


Table 2, entry 12 with (3R,8S)

Data File C:\HPCHEM\1\DATA\GROUP\AO445A.D

Injection Date	: 7/21/2011 5:04:40 PM	Seq. Line	: 72
Sample Name	:	Location	: Vial 93
Acq. Operator	: NB	Inj	: 1
Acq. Instrument	: Instrument 1	Inj Volume	: 15 µl
Different Inj Volume from Sequence !		Actual Inj Volume	: 2 µl
Acq. Method	: C:\HPCHEM\1\METHODS\IB-05-60.M		
Last changed	: 6/4/2011 9:40:33 AM by NB		
Analysis Method	: C:\HPCHEM\1\METHODS\YL-AD03.M		
Last changed	: 10/10/2011 10:09:06 AM by NB		
	(modified after loading)		



Data File C:\HPCHEM\1\DATA\GROUP\AO445A.D

Area Percent Report

Sorted By : Signal
Multiplier : 1.0000
Dilution : 1.0000
Use Multiplier & Dilution Factor with ISTDs

Signal 1: DAD1 A, Sig=250,10 Ref=360,100

Signal 2: DAD1 B, Sig=254,10 Ref=360,100

Signal 3: DAD1 C, Sig=210,10 Ref=360,100

Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	26.125	MM	0.3624	38.67986	1.77895	5.0488
2	29.500	BB	0.4376	727.43829	25.44360	94.9512
Totals :				766.11815	27.22255	

Results obtained with enhanced integrator!

Signal 4: DAD1 D, Sig=230,10 Ref=360,100

Signal 5: DAD1 E, Sig=280,10 Ref=360,100

*** End of Report ***

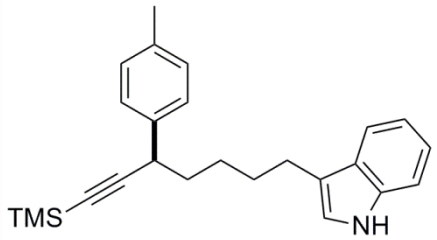
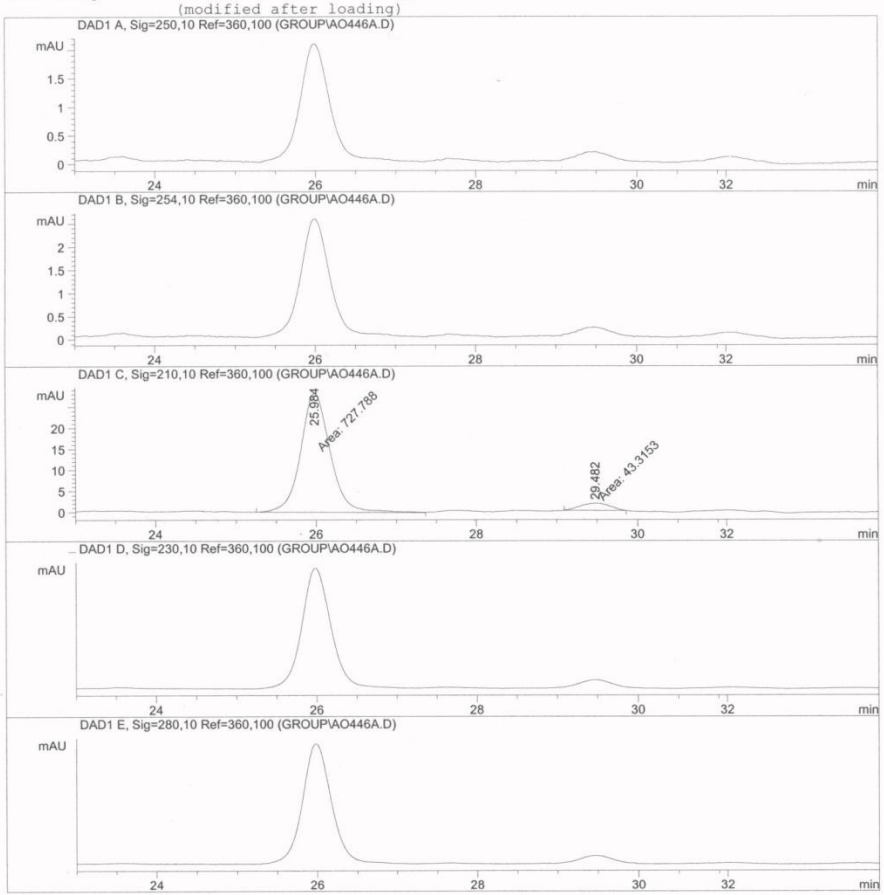


Table 2, entry 13 with (3S,8R)

Data File C:\HPCHEM\1\DATA\GROUP\AO446A.D

```
Injection Date  : 7/21/2011 6:05:58 PM          Seq. Line :  73
Sample Name     :                               Location : Vial 94
Acq. Operator   : NB                               Inj :  1
Acq. Instrument : Instrument 1                 Inj Volume : 15 µl
Different Inj Volume from Sequence !     Actual Inj Volume : 2 µl
Acq. Method     : C:\HPCHEM\1\METHODS\IB-05-60.M
Last changed    : 6/4/2011 9:40:33 AM by NB
Analysis Method : C:\HPCHEM\1\METHODS\YL-AD03.M
Last changed    : 10/10/2011 10:09:06 AM by NB
                  (modified after loading)
```



Data File C:\HPCHEM\1\DATA\GROUP\AO446A.D

Area Percent Report

```
Sorted By             :      Signal
Multiplier            :      1.0000
Dilution              :      1.0000
Use Multiplier & Dilution Factor with ISTDs


Signal 1: DAD1 A, Sig=250,10 Ref=360,100


Signal 2: DAD1 B, Sig=254,10 Ref=360,100


Signal 3: DAD1 C, Sig=210,10 Ref=360,100

Peak RetTime Type  Width     Area      Height     Area
  #   [min]       [min]   [mAU*s]     [mAU]       %
----|-------|----|-------|----------|----------|--------|
   1  25.984 MM    0.4292  727.78833   28.26185  94.3827
   2  29.482 MM    0.4212   43.31525    1.71412   5.6173

Totals :                   771.10358   29.97597

 Results obtained with enhanced integrator!

Signal 4: DAD1 D, Sig=230,10 Ref=360,100


Signal 5: DAD1 E, Sig=280,10 Ref=360,100
```

*** End of Report ***

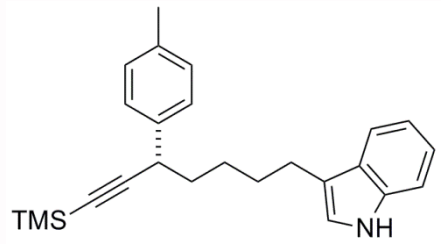
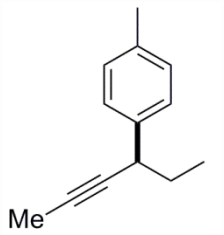


Table 2, entry 13 with (3R,8S)

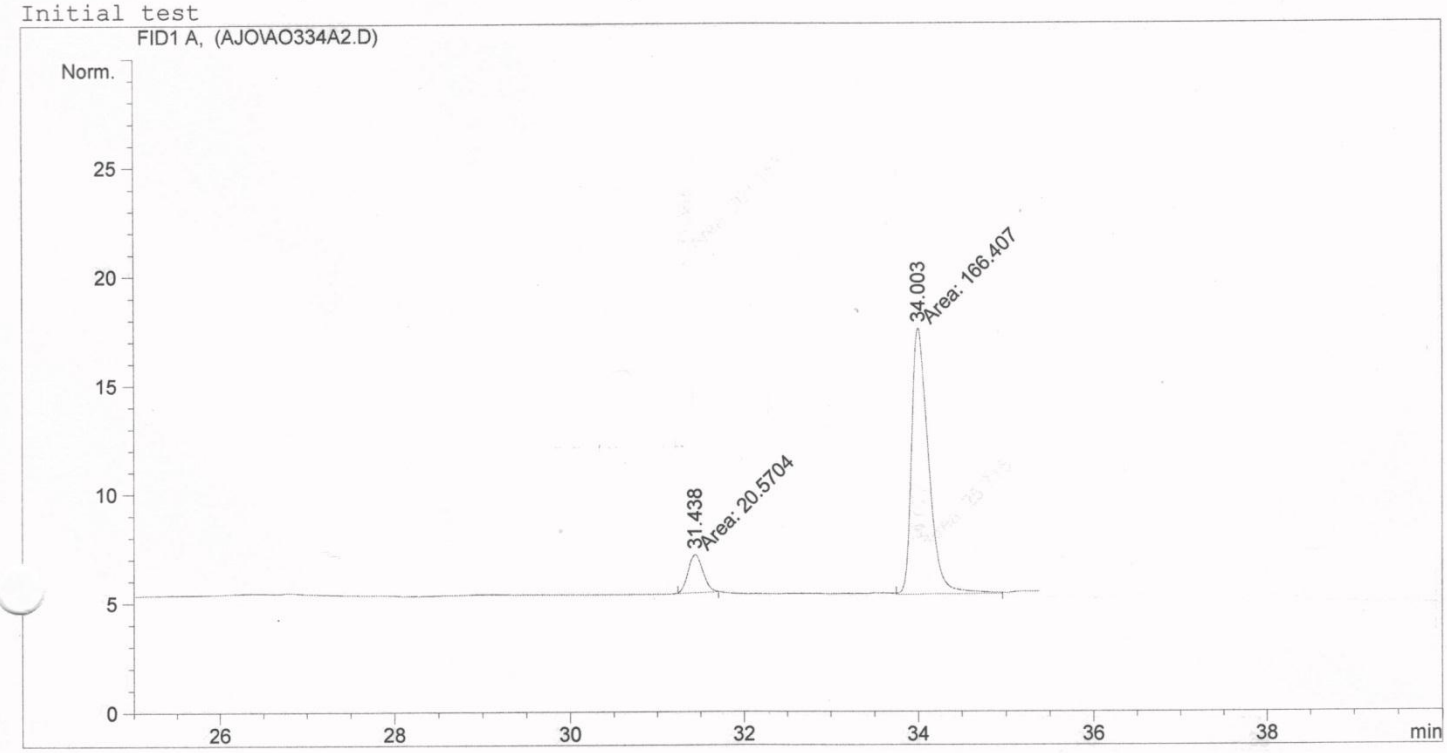
Data File C:\HPCHEM\3\DATA\AJO\AO334A2.D

```
==========================================================================
Injection Date  : 4/7/2011 6:46:31 PM          Seq. Line :   1
Sample Name     :                               Location : Vial 3
Acq. Operator   : AJO                              Inj :   1
Acq. Instrument : Instrument 3                 Inj Volume : 1 µl
Different Inj Volume from Sequence !     Actual Inj Volume : 3 µl
Acq. Method     : C:\HPCHEM\3\METHODS\JSSS33B.M
Last changed    : 4/7/2011 4:43:53 PM by JTB
Analysis Method : C:\HPCHEM\3\METHODS\JC100200.M
Last changed    : 4/7/2011 7:22:21 PM by JTB
                  (modified after loading)
```



Equation 4 with (3S,8R)

Initial test




```
==========================================================================
                        Area Percent Report
==========================================================================

Sorted By             :      Signal
Multiplier            :      1.0000
Dilution              :      1.0000
Use Multiplier & Dilution Factor with ISTDs

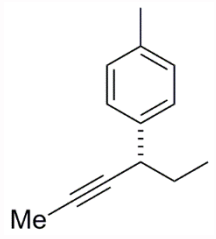

Signal 1: FID1 A,

Peak RetTime Type  Width     Area      Height     Area
  #   [min]        [min]   [pA*s]      [pA]        %
----|-------|----|-------|----------|----------|--------|
   1  31.438 MM    0.1971   20.57044    1.73922 11.00156
   2  34.003 MM    0.2269  166.40704   12.22372 88.99844

Totals :                   186.97748   13.96295

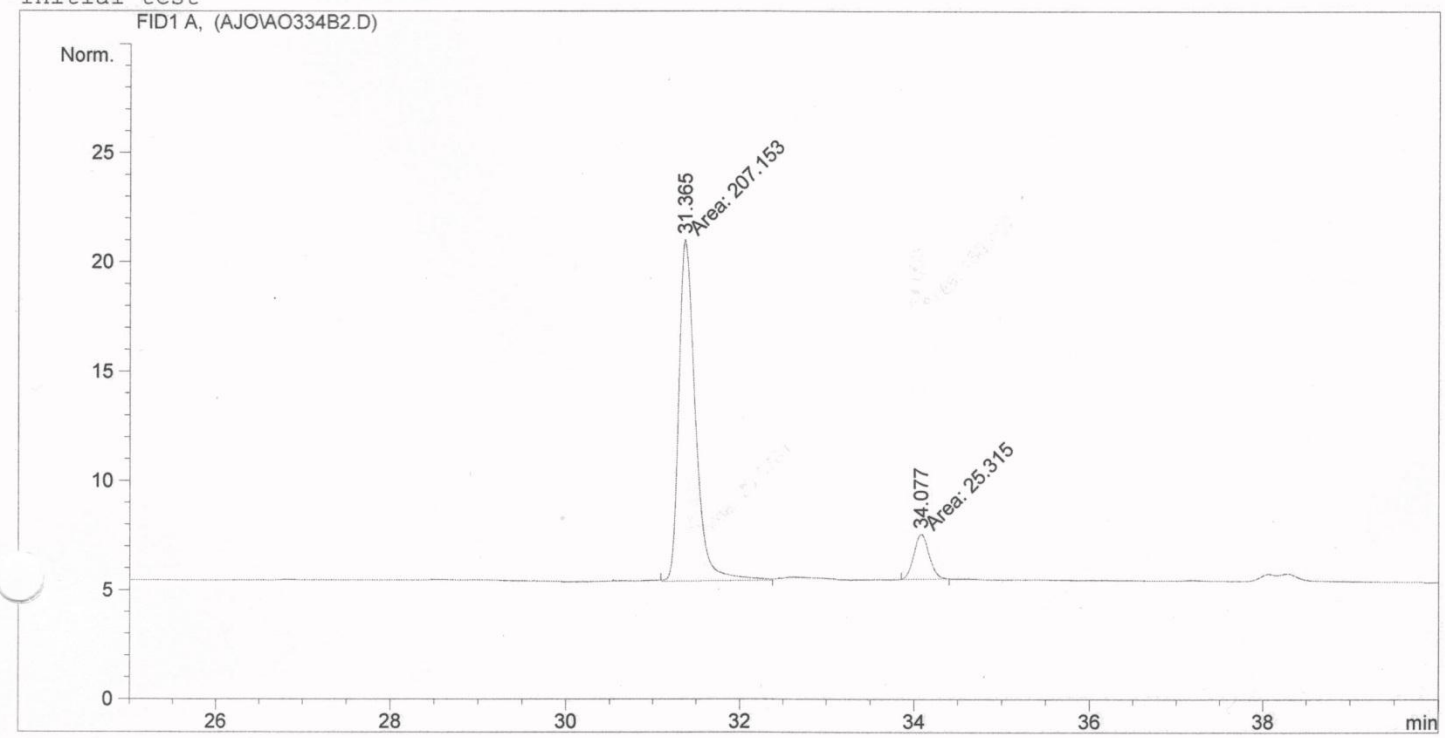
Results obtained with enhanced integrator!
==========================================================================
                        *** End of Report ***
```

ile C:\HPCHEM\3\DATA\AJO\AO334B2.D



Equation 4 with (3R,8S)

```
Injection Date  : 4/7/2011 5:51:29 PM          Seq. Line :   4
Sample Name     :                              Location : Vial 4
Acq. Operator   : AJO                             Inj :   1
Acq. Instrument : Instrument 3                 Inj Volume : 1 µl
Different Inj Volume from Sequence !     Actual Inj Volume : 3 µl
Acq. Method     : C:\HPCHEM\3\METHODS\JSSS33B.M
Last changed    : 4/7/2011 4:43:53 PM by JTB
Analysis Method : C:\HPCHEM\3\METHODS\JC100200.M
Last changed    : 4/7/2011 6:44:54 PM by JTB
                  (modified after loading)
Initial test
```




```
                          Area Percent Report

Sorted By             :      Signal
Multiplier            :      1.0000
Dilution              :      1.0000
Use Multiplier & Dilution Factor with ISTDs


Signal 1: FID1 A,

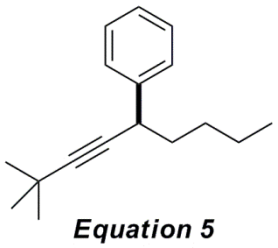
Peak RetTime Type  Width     Area      Height     Area
  #   [min]        [min]   [pA*s]      [pA]       %
----|-------|----|-------|----------|----------|--------|
   1  31.365 MM    0.2212  207.15323   15.60810 89.11034
   2  34.077 MM    0.2055   25.31501    2.05351 10.88966

Totals :                   232.46824   17.66161

 Results obtained with enhanced integrator!
                        *** End of Report ***
```

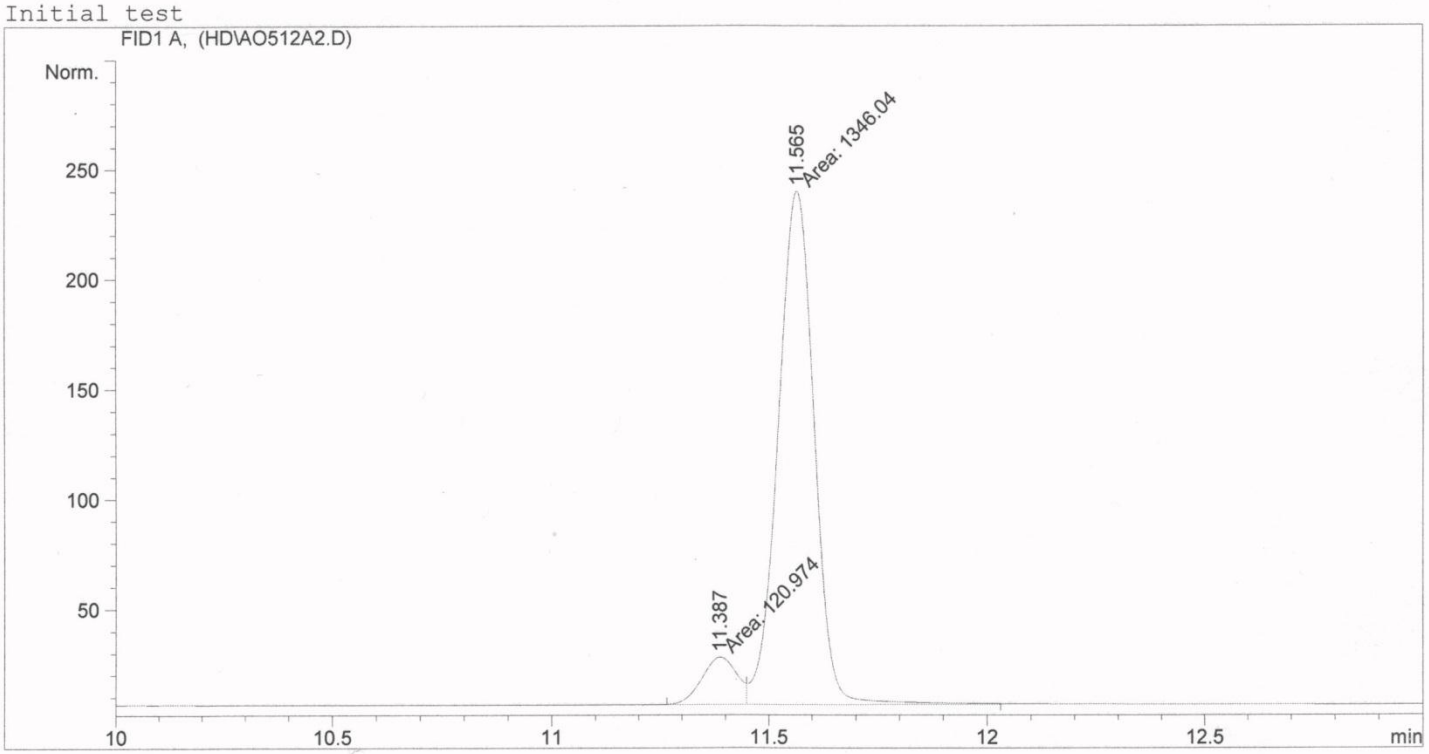
Data File C:\HPCHEM\3\DATA\HD\AO512A2.D

```
Injection Date  : 11/29/2011 12:59:25 PM        Seq. Line :   1
Sample Name     :                               Location : Vial 3
Acq. Operator   : JC                               Inj :   1
Acq. Instrument : Instrument 3                 Inj Volume : 1 µl
Different Inj Volume from Sequence !     Actual Inj Volume : 5 µl
Acq. Method     : C:\HPCHEM\3\METHODS\AJO100B.M
Last changed    : 12/18/2010 6:48:36 PM by NV
Analysis Method : C:\HPCHEM\3\METHODS\AJO100D.M
Last changed    : 11/29/2011 1:43:01 PM by JC
                  (modified after loading)
```



Equation 5 with (3S,8R)

Initial test



Area Percent Report

```
Sorted By             :      Signal
Multiplier            :      1.0000
Dilution              :      1.0000
Use Multiplier & Dilution Factor with ISTDs


Signal 1: FID1 A,

Peak RetTime Type  Width     Area      Height     Area
  #   [min]        [min]   [pA*s]      [pA]       %
----|-------|----|-------|----------|----------|--------|
   1  11.387 MF    0.0939  120.97383   21.47045  8.24628
   2  11.565 FM    0.0962 1346.03687  233.19830 91.75372

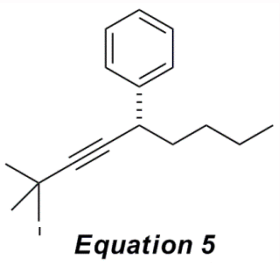
Totals :                  1467.01070  254.66875

 Results obtained with enhanced integrator!
```

*** End of Report ***

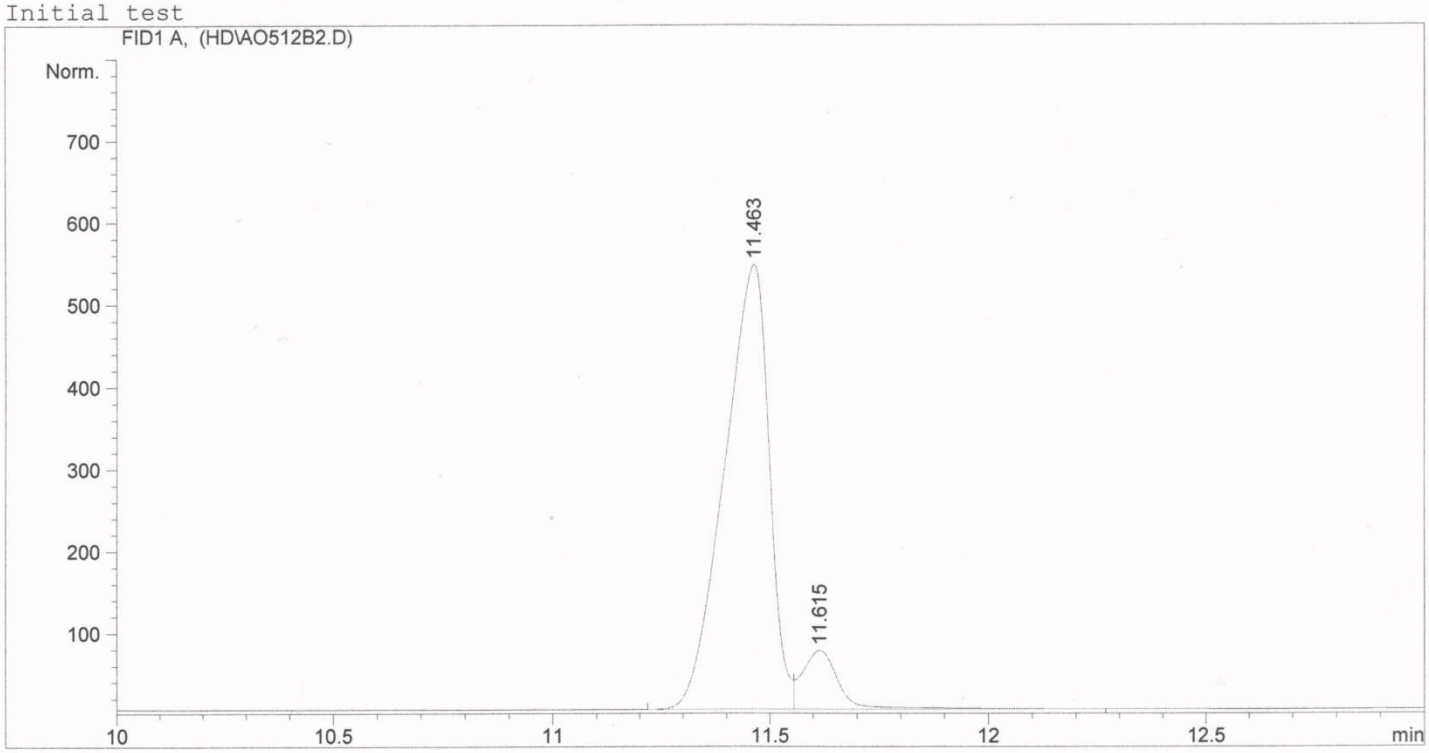
84

Data File C:\HPCHEM\3\DATA\HD\AO512B2.D



Equation 5 with (3R,8S)

```
Injection Date  : 11/29/2011 1:29:42 PM          Seq. Line :   1
Sample Name     :                                 Location : Vial 6
Acq. Operator   : JC                                  Inj :   1
Acq. Instrument : Instrument 3                  Inj Volume : 1 µl
Different Inj Volume from Sequence !     Actual Inj Volume : 5 µl
Acq. Method     : C:\HPCHEM\3\METHODS\AJO100D.M
Last changed    : 11/29/2011 1:27:59 PM by JC
Analysis Method : C:\HPCHEM\3\METHODS\AJO100D.M
Last changed    : 11/29/2011 1:45:13 PM by JC
                  (modified after loading)
Initial test
```




```
                          Area Percent Report

Sorted By             :      Signal
Multiplier            :      1.0000
Dilution              :      1.0000
Use Multiplier & Dilution Factor with ISTDs


Signal 1: FID1 A,

Peak RetTime Type  Width     Area      Height     Area
  #   [min]        [min]   [pA*s]      [pA]       %
----|-------|----|-------|----------|----------|--------|
   1  11.463 PV    0.1057 3884.07568  541.16205 90.29608
   2  11.615 VB    0.0868  417.41281   71.83868  9.70392

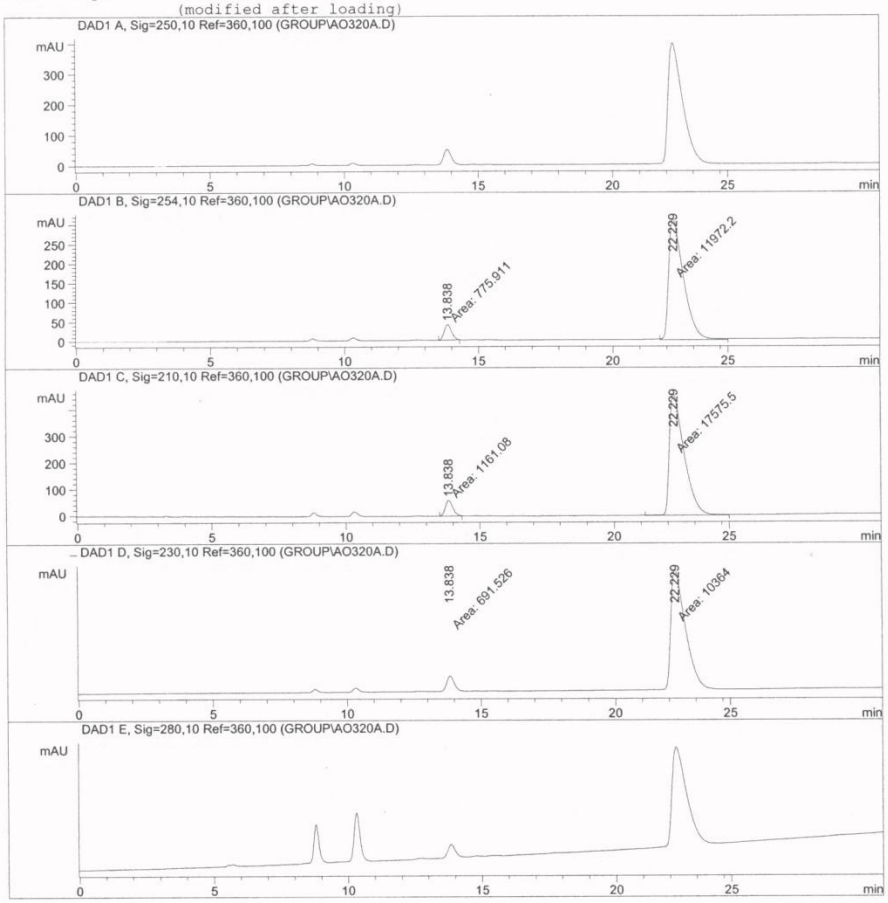
Totals :                  4301.48849  613.00072

 Results obtained with enhanced integrator!
                          *** End of Report ***
```

81

Data File C:\HPCHEM\1\DATA\GROUP\AO320A.D

```
Injection Date  : 4/7/2011 3:50:21 AM          Seq. Line :   3
Sample Name     :                               Location : Vial 96
Acq. Operator   : CC                              Inj :   1
Acq. Instrument : Instrument 1                Inj Volume : 15 µl
Different Inj Volume from Sequence !     Actual Inj Volume : 3 µl
Acq. Method     : C:\HPCHEM\1\METHODS\OD-00-30.M
Last changed    : 4/7/2011 2:46:23 AM by CC
Analysis Method : C:\HPCHEM\1\METHODS\AS-10-20.M
Last changed    : 4/7/2011 8:18:43 AM by CC
                  (modified after loading)
```



Data File C:\HPCHEM\1\DATA\GROUP\AO320A.D

Area Percent Report

```
Sorted By             :      Signal
Multiplier            :      1.0000
Dilution              :      1.0000
Use Multiplier & Dilution Factor with ISTDs
```

Signal 1: DAD1 A, Sig=250,10 Ref=360,100

Signal 2: DAD1 B, Sig=254,10 Ref=360,100

Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	13.838	MM	0.3212	775.91058	40.26458	6.0865
2	22.229	MM	0.6418	1.19722e4	310.92383	93.9135
Totals :				1.27481e4	351.18841	

Results obtained with enhanced integrator!

Signal 3: DAD1 C, Sig=210,10 Ref=360,100

Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	13.838	MM	0.3258	1161.07666	59.39996	6.1969
2	22.229	MM	0.6424	1.75755e4	455.98447	93.8031
Totals :				1.87365e4	515.38443	

Results obtained with enhanced integrator!

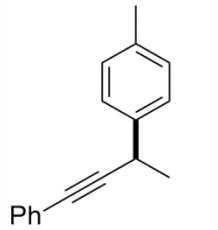
Signal 4: DAD1 D, Sig=230,10 Ref=360,100

Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	13.838	MM	0.3296	691.52570	34.96553	6.2550
2	22.229	MM	0.6332	1.03640e4	272.78244	93.7450
Totals :				1.10555e4	307.74797	

Results obtained with enhanced integrator!

Signal 5: DAD1 E, Sig=280,10 Ref=360,100

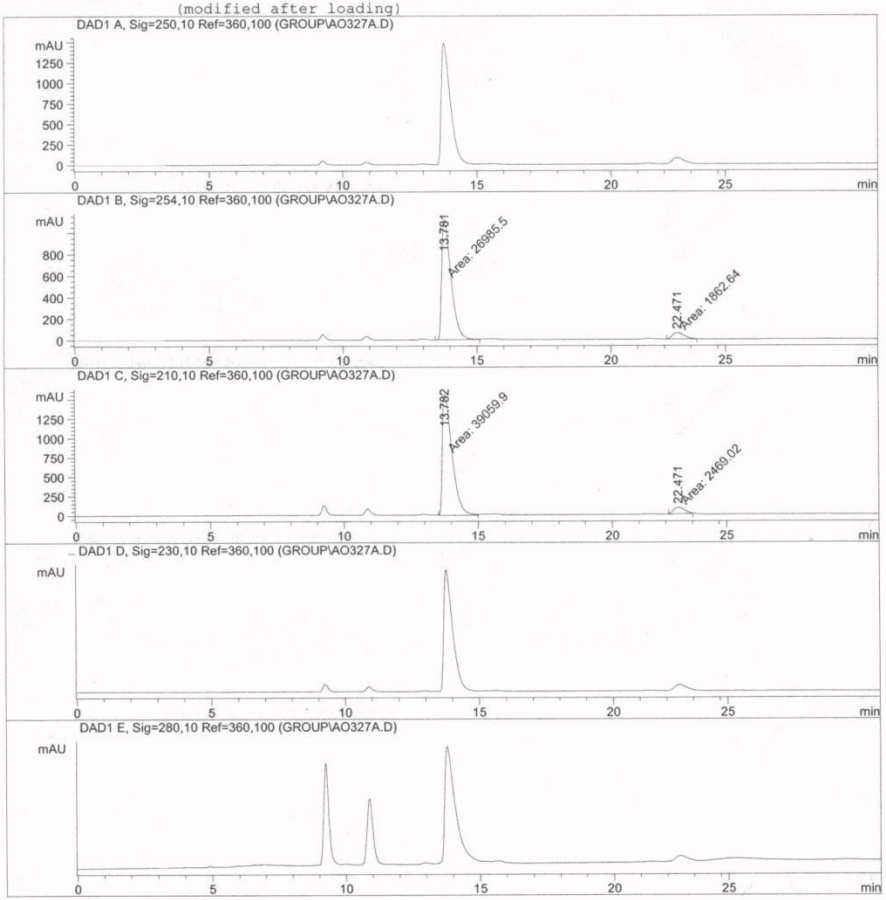
*** End of Report ***



Equation 6 with (3S,8R)

Data File C:\HPCHEM\1\DATA\GROUP\AO327A.D

Injection Date	: 4/7/2011 4:52:49 AM	Seq. Line	: 5
Sample Name	:	Location	: Vial 98
Acq. Operator	: CC	Inj	: 1
Acq. Instrument	: Instrument 1	Inj Volume	: 15 µl
Different Inj Volume from Sequence !		Actual Inj Volume	: 3 µl
Acq. Method	: C:\HPCHEM\1\METHODS\OD-00-30.M		
Last changed	: 4/7/2011 2:46:23 AM by CC		
Analysis Method	: C:\HPCHEM\1\METHODS\AS-10-20.M		
Last changed	: 4/7/2011 8:18:43 AM by CC		
	(modified after loading)		



Data File C:\HPCHEM\1\DATA\GROUP\AO327A.D

Area Percent Report

Sorted By	:	Signal	
Multiplier	:	1.0000	
Dilution	:	1.0000	

Use Multiplier & Dilution Factor with ISTDs

Signal 1: DAD1 A, Sig=250,10 Ref=360,100

Signal 2: DAD1 B, Sig=254,10 Ref=360,100

Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	13.781	MM	0.4006	2.69855e4	1122.78381	93.5433
2	22.471	MM	0.5112	1862.64185	60.72767	6.4567
Totals :				2.88481e4	1183.51148	

Results obtained with enhanced integrator!

Signal 3: DAD1 C, Sig=210,10 Ref=360,100

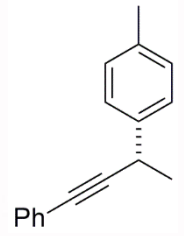
Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	13.782	MM	0.4167	3.90599e4	1562.44849	94.0547
2	22.471	MM	0.4748	2469.01538	86.66386	5.9453
Totals :				4.15289e4	1649.11234	

Results obtained with enhanced integrator!

Signal 4: DAD1 D, Sig=230,10 Ref=360,100

Signal 5: DAD1 E, Sig=280,10 Ref=360,100

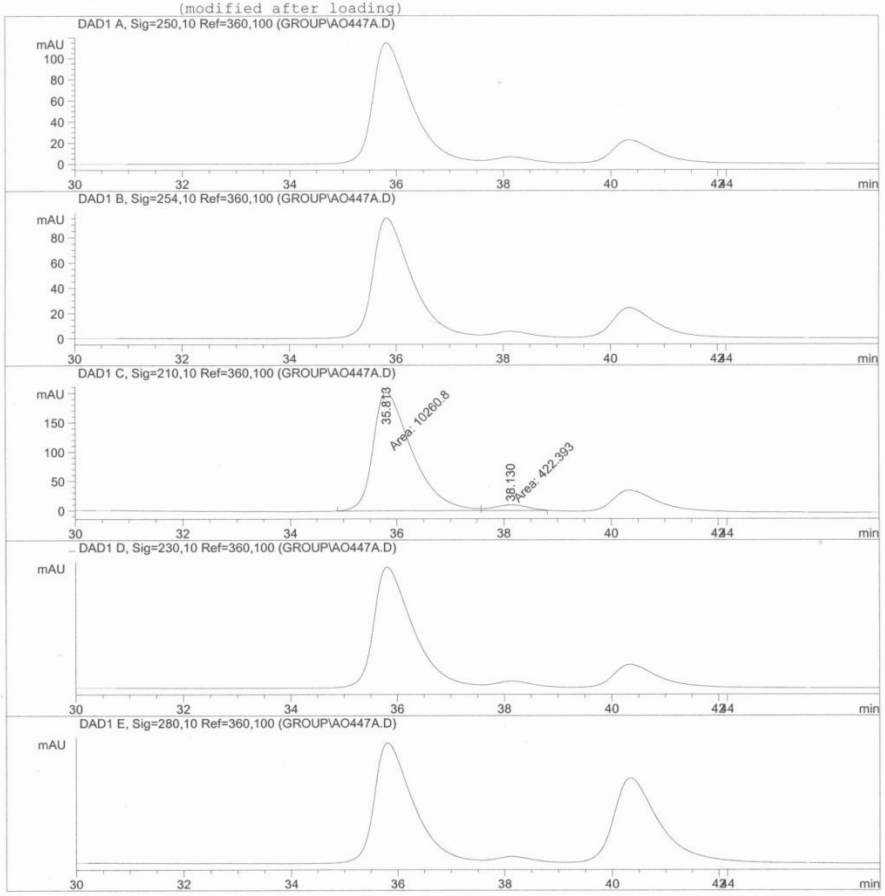
*** End of Report ***



Equation 6 with (3R,8S)

Data File C:\HPCHEM\1\DATA\GROUP\AO447A.D

```
Injection Date  : 7/21/2011 10:32:35 PM          Seq. Line :  78
Sample Name     :                                 Location : Vial 95
Acq. Operator   : NB                                 Inj :   1
Acq. Instrument : Instrument 1                  Inj Volume : 15 µl
Different Inj Volume from Sequence !     Actual Inj Volume : 2 µl
Acq. Method     : C:\HPCHEM\1\METHODS\IB-03-60.M
Last changed    : 4/7/2011 8:06:41 PM by CC
Analysis Method : C:\HPCHEM\1\METHODS\YL-AD03.M
Last changed    : 10/10/2011 10:15:56 AM by NB
                  (modified after loading)
```



Data File C:\HPCHEM\1\DATA\GROUP\AO447A.D

Area Percent Report

```
Sorted By             :      Signal
Multiplier            :      1.0000
Dilution              :      1.0000
Use Multiplier & Dilution Factor with ISTDs


Signal 1: DAD1 A, Sig=250,10 Ref=360,100


Signal 2: DAD1 B, Sig=254,10 Ref=360,100


Signal 3: DAD1 C, Sig=210,10 Ref=360,100

Peak RetTime Type  Width     Area      Height     Area
  #   [min]       [min]   [mAU*s]     [mAU]       %
----|-------|----|-------|----------|----------|--------|
   1  35.813 MF    0.8466 1.02608e4   201.99796  96.0462
   2  38.130 FM    0.7286  422.39297    9.66245   3.9538

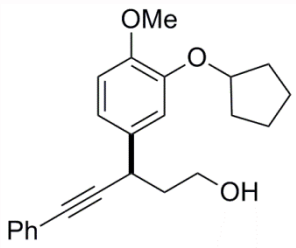
Totals :                  1.06832e4   211.66041

 Results obtained with enhanced integrator!

Signal 4: DAD1 D, Sig=230,10 Ref=360,100


Signal 5: DAD1 E, Sig=280,10 Ref=360,100
```

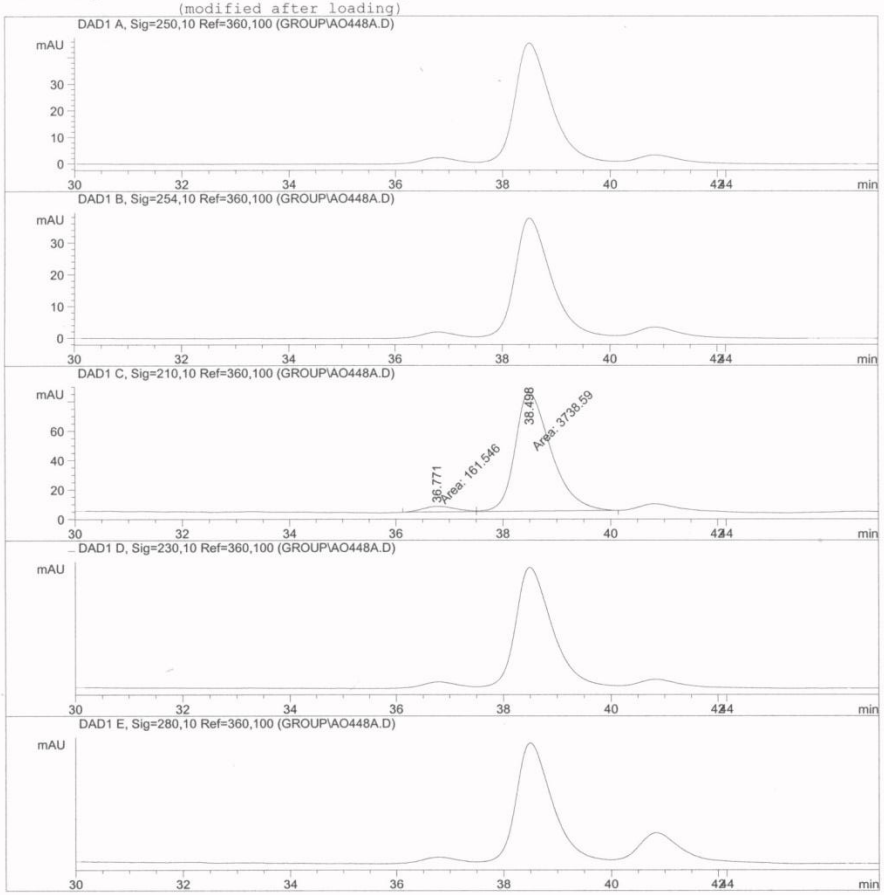
*** End of Report ***



Equation 7 with (3S,8R)

Data File C:\HPCHEM\1\DATA\GROUP\AO448A.D

```
Injection Date  : 7/21/2011 11:33:47 PM          Seq. Line :  79
Sample Name     :                                Location : Vial 96
Acq. Operator   : NB                                Inj :  1
Acq. Instrument : Instrument 1                  Inj Volume : 15 µl
Different Inj Volume from Sequence !     Actual Inj Volume : 2 µl
Acq. Method     : C:\HPCHEM\1\METHODS\IB-03-60.M
Last changed    : 4/7/2011 8:06:41 PM by CC
Analysis Method : C:\HPCHEM\1\METHODS\YL-AD03.M
Last changed    : 10/10/2011 10:16:35 AM by NB
                  (modified after loading)
```



Data File C:\HPCHEM\1\DATA\GROUP\AO448A.D

Area Percent Report

```
Sorted By             :      Signal
Multiplier            :      1.0000
Dilution              :      1.0000
Use Multiplier & Dilution Factor with ISTDs


Signal 1: DAD1 A, Sig=250,10 Ref=360,100


Signal 2: DAD1 B, Sig=254,10 Ref=360,100


Signal 3: DAD1 C, Sig=210,10 Ref=360,100

Peak RetTime Type  Width     Area      Height     Area
  #   [min]        [min]   [mAU*s]     [mAU]       %
----|-------|----|-------|----------|----------|--------|
   1  36.771 MF    0.7140  161.54572    3.77105   4.1420
   2  38.498 FM    0.7727 3738.59351   80.63858  95.8580

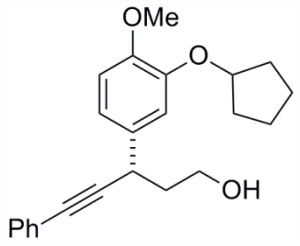
Totals :                  3900.13922   84.40964

 Results obtained with enhanced integrator!

Signal 4: DAD1 D, Sig=230,10 Ref=360,100


Signal 5: DAD1 E, Sig=280,10 Ref=360,100
```

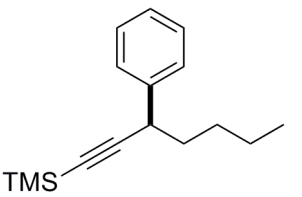
*** End of Report ***



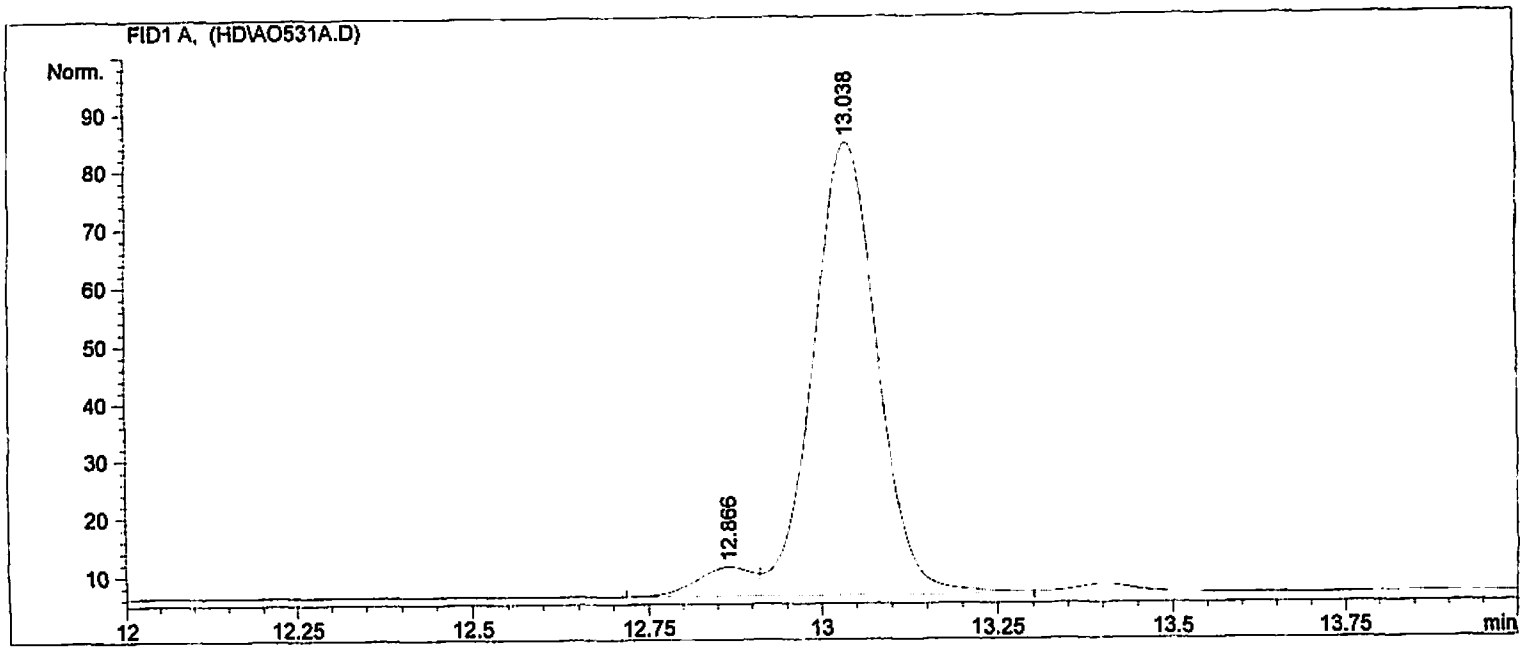
Equation 7 with (3R,8S)

Data File C:\HPCHEM\3\DATA\HD\AO531A.D

```
Injection Date  : 12/11/2011 3:42:42 PM          Seq. Line :  11
Sample Name     :                                 Location : Vial 1
Acq. Operator   : hd                                 Inj :   1
Acq. Instrument : Instrument 3                  Inj Volume : 1 µl
Different Inj Volume from Sequence !     Actual Inj Volume : 5 µl
Acq. Method     : C:\HPCHEM\3\METHODS\AJO100.M
Last changed    : 10/13/2010 9:09:31 AM by AJO
Analysis Method : C:\HPCHEM\3\METHODS\CJC18.M
Last changed    : 1/22/2012 2:18:26 PM by HD
                  (modified after loading)
Initial test
```



Equation 8 with (3S,8R)



Area Percent Report

```
Sorted By             :      Signal
Multiplier            :      1.0000
Dilution              :      1.0000
Use Multiplier & Dilution Factor with ISTDs


Signal 1: FID1 A,

Peak RetTime Type  Width     Area      Height     Area
  #   [min]        [min]   [pA*s]      [pA]        %
----|-------|----|-------|----------|----------|--------|
   1  12.866 PV    0.0850   27.32010    4.90110  5.19883
   2  13.038 VV    0.0985  498.18481   77.99696 94.80117

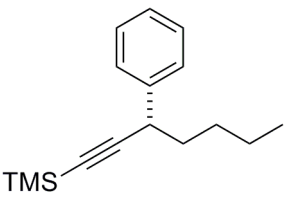
Totals :                   525.50491   82.89806

 Results obtained with enhanced integrator!
```

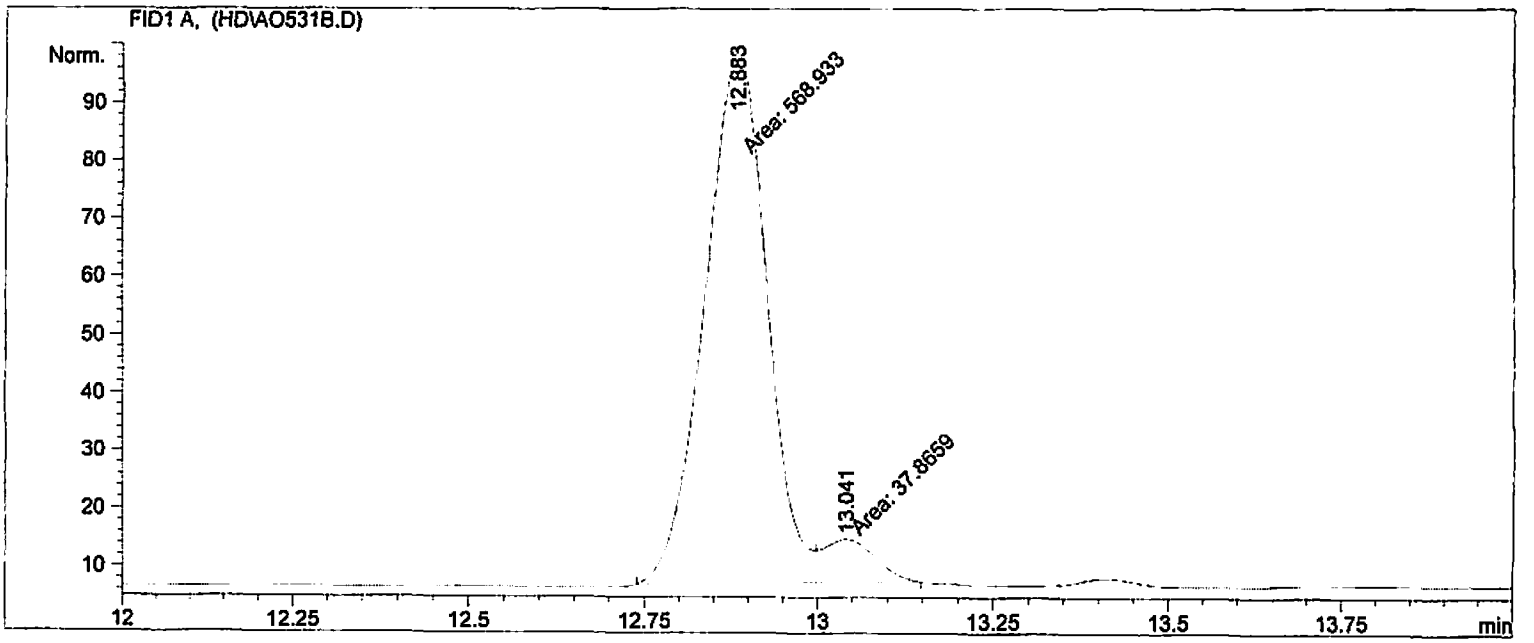
*** End of Report ***

Data File C:\HPCHEM\3\DATA\HD\AO531B.D

```
Injection Date  : 12/11/2011 4:08:47 PM          Seq. Line :  12
Sample Name     :                                Location : Vial 2
Acq. Operator   : hd                                 Inj :   1
Acq. Instrument : Instrument 3                  Inj Volume : 1 µl
Different Inj Volume from Sequence !     Actual Inj Volume : 5 µl
Acq. Method     : C:\HPCHEM\3\METHODS\AJO100.M
Last changed    : 10/13/2010 9:09:31 AM by AJO
Analysis Method : C:\HPCHEM\3\METHODS\CJC18.M
Last changed    : 1/22/2012 2:19:19 PM by HD
                  (modified after loading)
Initial test
```



Equation 8 with (3R,8S)



Area Percent Report

```
Sorted By             :      Signal
Multiplier            :      1.0000
Dilution              :      1.0000
Use Multiplier & Dilution Factor with ISTDs


Signal 1: FID1 A,

Peak RetTime Type  Width     Area      Height     Area
  #   [min]        [min]   [pA*s]      [pA]        %
----|-------|----|-------|----------|----------|--------|
   1  12.883 MF    0.1037  568.93274   91.43867 93.75972
   2  13.041 FM    0.0858   37.86594    7.35501  6.24028

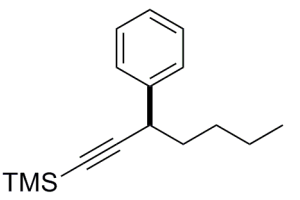
Totals :                   606.79868   98.79369

 Results obtained with enhanced integrator!
```

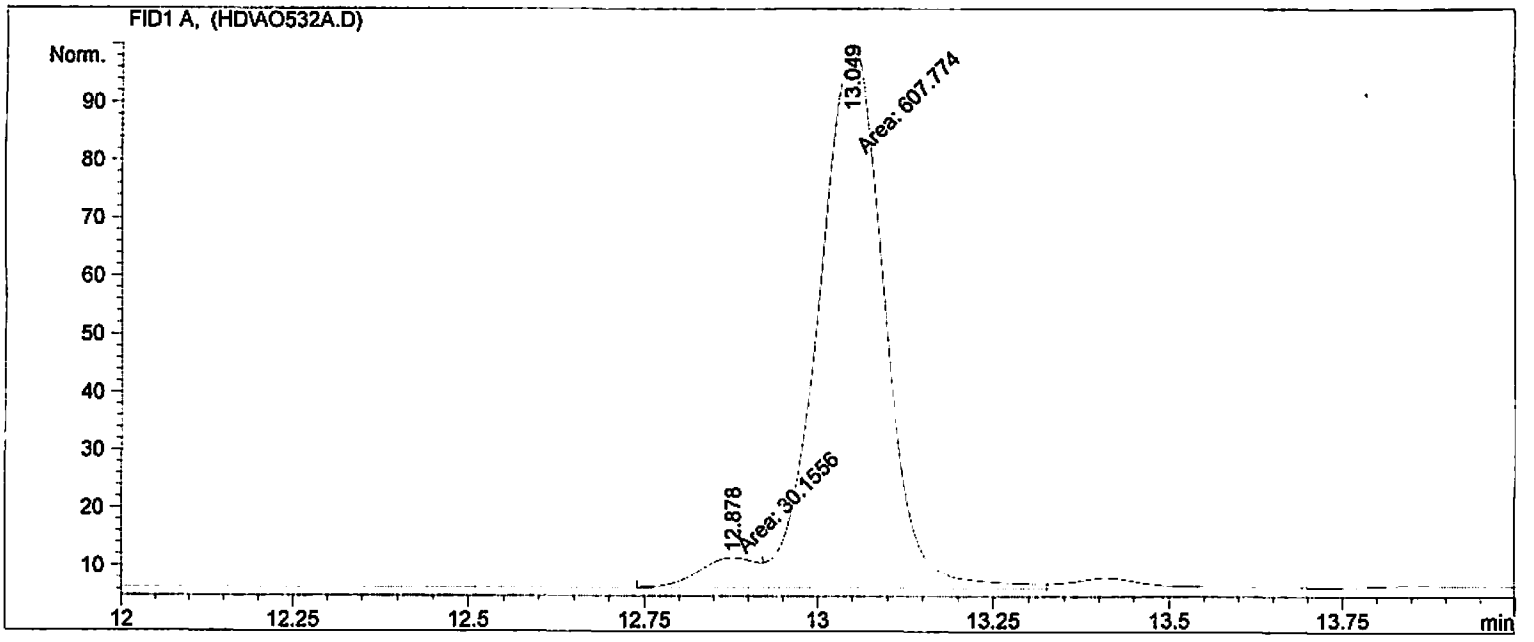
*** End of Report ***

Data File C:\HPCHEM\3\DATA\HD\AO532A.D

```
==========================================================================
Injection Date  : 12/11/2011 4:34:56 PM          Seq. Line :  13
Sample Name     :                                 Location : Vial 3
Acq. Operator   : hd                                 Inj :   1
Acq. Instrument : Instrument 3                   Inj Volume : 1 µl
Different Inj Volume from Sequence !     Actual Inj Volume : 5 µl
Acq. Method     : C:\HPCHEM\3\METHODS\AJO100.M
Last changed    : 10/13/2010 9:09:31 AM by AJO
Analysis Method : C:\HPCHEM\3\METHODS\CJC18.M
Last changed    : 1/22/2012 2:21:35 PM by HD
                  (modified after loading)
Initial test
==========================================================================
```



Equation 9 with (3S,8R)




```
==========================================================================
                        Area Percent Report
==========================================================================

Sorted By             :      Signal
Multiplier            :      1.0000
Dilution              :      1.0000
Use Multiplier & Dilution Factor with ISTDs


Signal 1: FID1 A,

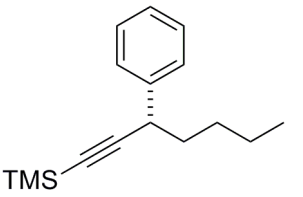
Peak RetTime Type  Width     Area      Height     Area
  #   [min]        [min]   [pA*s]      [pA]       %
----|-------|----|-------|----------|----------|--------|
   1  12.878 MF    0.0974   30.15556    5.15921  4.72710
   2  13.049 FM    0.1080  607.77362   93.80832 95.27290

Totals :                   637.92918   98.96753

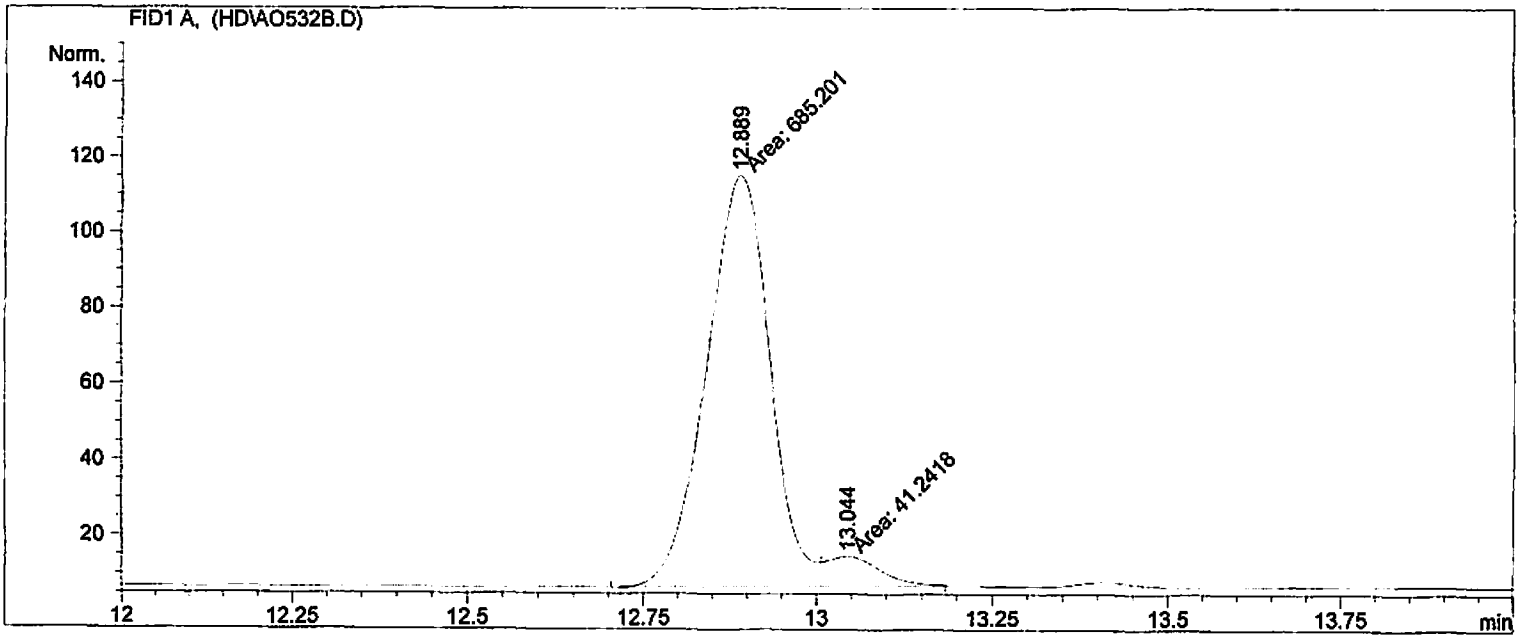
 Results obtained with enhanced integrator!
==========================================================================
                        *** End of Report ***
```

Data File C:\HPCHEM\3\DATA\HD\AO532B.D

```
Injection Date  : 12/11/2011 5:01:01 PM          Seq. Line :  14
Sample Name     :                                Location : Vial 4
Acq. Operator   : hd                                Inj :   1
Acq. Instrument : Instrument 3                  Inj Volume : 1 µl
Different Inj Volume from Sequence !     Actual Inj Volume : 5 µl
Acq. Method     : C:\HPCHEM\3\METHODS\AJO100.M
Last changed    : 10/13/2010 9:09:31 AM by AJO
Analysis Method : C:\HPCHEM\3\METHODS\CJC18.M
Last changed    : 1/22/2012 2:23:52 PM by HD
                  (modified after loading)
Initial test
```



Equation 9 with (3R,8S)



Area Percent Report

```
Sorted By             :      Signal
Multiplier            :      1.0000
Dilution              :      1.0000
Use Multiplier & Dilution Factor with ISTDs
```

Signal 1: FID1 A,

Peak #	RetTime [min]	Type	Width [min]	Area [pA*s]	Height [pA]	Area %
1	12.889	MF	0.1053	685.20050	108.47028	94.32277
2	13.044	FM	0.0895	41.24178	7.68089	5.67723
Totals :				726.44228	116.15118	

Results obtained with enhanced integrator!

*** End of Report ***